Supporting Information

Asymmetric Synthesis of 2,3-Disubstituted Indolines via an Organocatalytic Intramolecular Michael Addition

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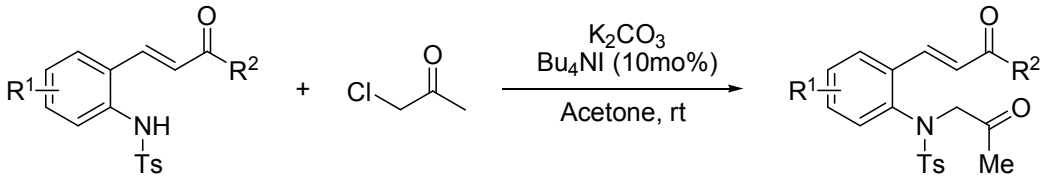
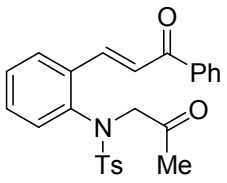
General Information. Organic solvents were distilled prior to use. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Developed chromatograms were visualized by fluorescence quenching and anisaldehyde stain.

^{1}H and ^{13}C NMR spectra were recorded (400 MHz for ^{1}H and 100 MHz for ^{13}C) and were internally referenced to residual protio solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. Optical rotations were recorded on a Jasco P-1010 polarimeter (WI lamp, 589 nm). IR spectra were recorded on ALPHA FT-IR spectrometer, and reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectrometry data was recorded on a JEOL JMS-700 MStation mass spectrometer. Enantiomeric excesses were determined on a HPLC instrument using Chiralpak columns as noted.

Typical Procedure for 2-(2-Oxoalkyltosylamino)phenyl α,β-Unsaturated Ketones

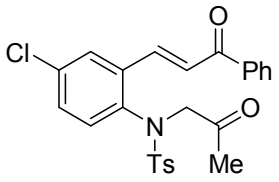


To a solution of 2-(tosylamino)phenyl α,β-unsaturated ketone (1.0 mmol) in acetone (10 mL) were added α-chloroacetone (1.5 mmol), K_2CO_3 (1.3 mmol) and Bu_4NI (0.1 mmol) at room temperature. The resulting mixture was stirred at constant temperature until complete consumption of 2-(tosylamino)phenyl α,β-unsaturated ketone was observed as determined by TLC. The resulting mixture was filtered under celite. The filtrate was purified by flash column chromatography with EtOAc/hexanes as the eluent to afford product.



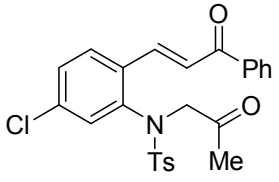
1a

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-phenylprop-2-en-1-one (1a) 368 mg, 85%; white solid; m.p. 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.92 (m, 2H), 7.85–7.72 (m, 2H), 7.65–7.46 (m, 5H), 7.41–7.24 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.43 (brs, 2H), 2.26 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 190.7, 144.2, 140.1, 139.4, 137.8, 135.1, 134.9, 132.9, 131.1, 130.9, 129.6, 129.2, 128.7, 128.7, 127.9, 127.3, 124.4, 61.4, 27.1, 21.4; IR (film) 2955, 2819, 2853, 1735, 1660, 1598, 1492, 1328, 1268, 1154, 1121, 1099, 1050 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{23}NO_4S$: 433.1348 Found: 433.1347.



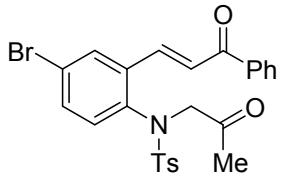
1b

(*E*)-3-(2-(2-Oxopropyltosylamino)-5-chlorophenyl)-1-phenylprop-2-en-1-one (1b) 224 mg, 48%, white solid; m.p. 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.73–7.59 (m, 3H), 7.58–7.44 (m, 4H), 7.36–7.25 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 4.50 (brs, 1H), 4.24 (brs, 1H), 2.24 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 189.9, 144.3, 138.4, 137.6, 137.5, 136.9, 135.2, 135.0, 133.1, 132.9, 130.7, 129.7, 128.7, 128.7, 127.9, 127.1, 125.2, 61.1, 27.0, 21.4; IR (film) 3133, 2968, 2923, 1735, 1657, 1602, 1567, 1463, 1345, 1280, 1157, 1089, 1044 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0972.



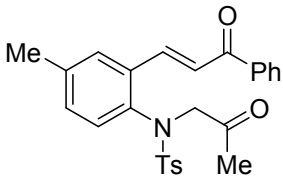
1c

(*E*)-3-(2-(2-Oxopropyltosylamino)-4-chlorophenyl)-1-phenylprop-2-en-1-one (1c) 266 mg, 57%, white solid; m.p. 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.71 (t, *J* = 11.2 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 13.7, 7.8 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.31–7.18 (m, 4H), 4.36 (brs, 2H), 2.26 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 190.3, 144.5, 140.2, 138.8, 137.6, 136.1, 134.7, 133.8, 133.0, 131.5, 129.8, 129.6, 128.7 (two peaks overlapping), 128.2, 127.9, 124.6, 61.1, 27.0, 21.5; IR (film) 3065, 2956, 2922, 1713, 1656, 1588, 1481, 1403, 1353, 1266, 1217, 1162, 1054 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0965.



1d

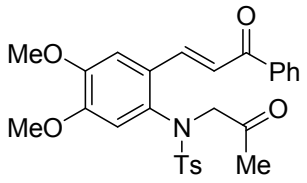
(*E*)-3-(2-(2-Oxopropyltosylamino)-5-bromophenyl)-1-phenylprop-2-en-1-one (1d) 408 mg, 83%, white solid; m.p. 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.97 (m, 2H), 7.85 (d, *J* = 2.3 Hz, 1H), 7.71–7.58 (m, 2H), 7.5 –7.44 (m, 5H), 7.32–7.24 (m, 1H), 7.19 (dd, *J* = 8.3, 1.5 Hz, 3H), 4.47 (brs, 1H), 4.26 (brs, 1H), 2.24 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 189.9, 144.3, 138.3, 138.2, 137.5, 137.2, 135.0, 133.7, 133.1, 133.1, 130.1, 129.7, 128.7 (two peaks overlapping), 127.9, 125.2, 123.3, 61.1, 27.0, 21.4; IR (film) 3050, 2920, 2845, 1739, 1663, 1602, 1474, 1346, 1311, 1265, 1215, 1159, 1100 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}BrNO_4S$: 511.0453 Found: 511.0450.



1e

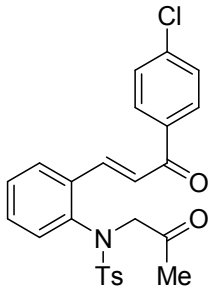
(*E*)-3-(2-(2-Oxopropyltosylamino)-5-methylphenyl)-1-phenylprop-2-en-1-one (1e) 438 mg, 98%, white solid; m.p. 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 15.9 Hz, 1H), 7.54 (ddd, *J* = 25.0, 15.7, 7.3 Hz, 6H), 7.19 (ddd, *J* = 24.0, 14.7, 8.5 Hz, 5H), 4.45 (brs, 1H), 4.21 (brs, 1H), 2.38 (s, 3H), 2.25 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 190.7, 144.0, 140.2, 139.2, 137.8, 136.9, 135.0, 134.6, 132.1, 131.8, 130.9, 129.6, 128.7, 128.6, 128.0, 127.7, 124.2,

61.5, 27.1, 21.4, 21.3; IR (film) 2956, 2920, 2853, 1732, 1662, 1598, 1492, 1414, 1328, 1267, 1215, 1123, 1051 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_4S$: 447.1504 Found 447.1514.



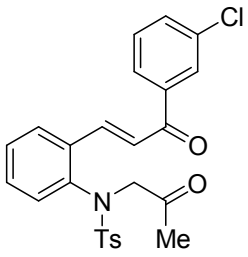
1f

(*E*)-3-(2-(2-Oxopropyltosylamino)-4,5-dimethoxyphenyl)-1-phenylprop-2-en-1-one (1f) 330 mg, 67%, white solid; m.p. 176-178 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99–7.94 (m, 2H), 7.72–7.43 (m, 6H), 7.14 (dd, *J* = 19.2, 6.2 Hz, 4H), 6.83 (s, 1H), 4.64 (brs, 1H), 4.17 (brs, 1H), 3.95 (s, 3H), 3.76 (s, 3H), 2.23 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 190.8, 151.0, 149.4, 144.0, 139.8, 138.0, 135.3, 133.0, 132.7, 129.5, 128.7, 128.5, 128.0, 127.2, 122.5, 114.4, 108.0, 61.7, 56.1, 56.0, 27.0, 21.4; IR (film) 2967, 2927, 1736, 1660, 1597, 1463, 1395, 1344, 1305, 1204, 1167, 1120, 1089 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{27}H_{27}NO_6S$: 493.1559 Found 493.1567.



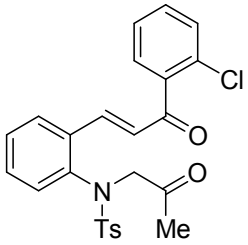
1g

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(4-chlorophenyl)prop-2-en-1-one (1g) 182 mg, 39%, white solid; m.p. 146-147 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dt, *J* = 21.8, 7.5 Hz, 3H), 7.77 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 4H), 7.42–7.31 (m, 2H), 7.23 (dd, *J* = 18.0, 12.0 Hz, 3H), 7.13 (dd, *J* = 7.8, 1.3 Hz, 1H), 4.36 (brs, 2H), 2.30 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 189.8, 144.2, 140.8, 139.5, 139.2, 136.1, 135.2, 134.8, 131.0, 130.6, 130.3, 129.6, 129.2, 128.9, 128.0, 127.4, 124.1, 61.3, 27.1, 21.5; IR (film) 3068, 2968, 2921, 1735, 1650, 1594, 1516, 1482, 1413, 1348, 1231, 1157, 1058 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found 467.0972.



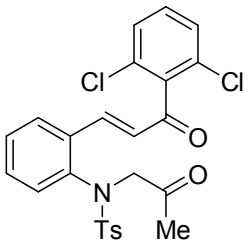
1h

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(3-chlorophenyl)prop-2-en-1-one (1h) 149 mg, 32%, white solid; m.p. 67-71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.83 (m, 3H), 7.77 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.52–7.32 (m, 5H), 7.25–7.16 (m, 4H), 4.41 (brs, 2H), 2.30 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 189.7, 144.2, 141.1, 139.5, 139.4, 135.0, 134.9, 132.7, 131.2, 131.0, 123.0, 129.6, 129.2, 128.8, 128.0, 127.4, 127.0, 124.1, 61.3, 27.1, 21.5; IR (film) 3068, 2968, 2921, 1735, 1650, 1594, 1482, 1413, 1349, 1231, 1157, 1090, 1058 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found 467.0972.



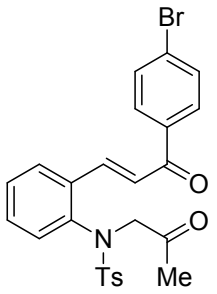
1i

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(2-chlorophenyl)prop-2-en-1-one (1i) 201 mg, 43%, white solid; m.p. 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.66 (d, *J* = 16.3 Hz, 1H), 7.55–7.35 (m, 7H), 7.32 (td, *J* = 7.7, 1.6 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.05 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.99 (d, *J* = 16.3 Hz, 1H), 4.23 (brs, 2H), 2.39 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 194.2, 144.2, 142.4, 139.6, 138.5, 134.7, 134.4, 131.5, 131.2, 130.3, 129.6 (two peaks overlapping), 129.2, 128.2, 128.0 (two peaks overlapping), 127.4, 126.9, 61.5, 27.1, 21.6; IR (film) 2969, 2923, 1735, 1657, 1602, 1567, 1463, 1394, 1345, 1157, 1089, 1044 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found 467.0971.



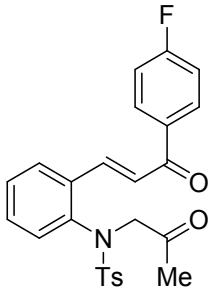
1j

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(2,6-dichlorophenyl)prop-2-en-1-one (1j) 396 mg, 79%, hite solid; m.p. 200-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.57 (d, *J* = 16.5 Hz, 1H), 7.48 – 7.28 (m, 7H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.01 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.89 (d, *J* = 16.5 Hz, 1H), 4.12 (d, *J* = 21.3 Hz, 2H), 2.42 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 193.2, 144.2, 143.9, 139.7, 137.5, 134.4, 134.2, 131.9, 131.5, 130.8, 130.0, 129.6, 129.1, 128.2, 128.1, 127.8, 127.6, 61.5, 27.0, 21.7; IR (film) 2956, 1734, 1640, 1595, 1561, 1432, 1345, 1295, 1278, 1162, 1120, 1089, 1046 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{21}Cl_2NO_4S$: 501.0568 Found 501.0569.



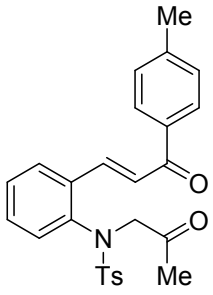
1k

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(4-bromophenyl)prop-2-en-1-one (1k) 332 mg, 65%, white solid; m.p. 78-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.91–7.84 (m, 2H), 7.77 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.69–7.62 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.43–7.28 (m, 2H), 7.29–7.18 (m, 3H), 7.13 (dd, *J* = 7.8, 1.3 Hz, 1H), 4.36 (brs, 2H), 2.30 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 190.0, 144.2, 140.9, 139.5, 136.5, 135.2, 134.8, 131.9, 131.0, 130.6, 130.4, 129.6, 129.2, 128.0, 127.9, 127.4, 124.1, 61.3, 27.1, 21.5; IR (film) 3068, 2968, 2921, 1736, 1648, 1593, 1520, 1480, 1348, 1231, 1156, 1058 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}BrNO_4S$: 511.0453 Found 511.0462.



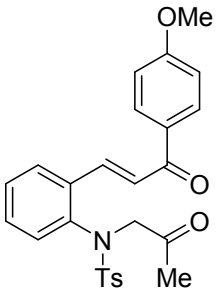
1l

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(4-fluorophenyl)prop-2-en-1-one (1l) 185 mg, 41%, white solid; m.p. 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.02 (m, 2H), 7.90 (d, J = 16.0 Hz, 1H), 7.77 (dd, J = 7.7, 1.5 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.43–7.31 (m, 2H), 7.29–7.13 (m, 6H), 4.37 (brs, 2H), 2.30 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 189.5, 165.6 (d, J^1 = 254.4 Hz), 144.2, 140.5, 139.4, 135.2, 134.9, 134.1 (d, J^4 = 2.9 Hz), 131.5 (d, J^3 = 9.2 Hz), 130.9, 130.7, 129.6, 129.2, 128.0, 127.4, 124.3, 115.8 (d, J^2 = 21.8 Hz), 61.3, 27.1, 21.5; IR (film) 3068, 2969, 2922, 1735, 1650, 1594, 1482, 1413, 1348, 1231, 1157, 1119, 1058 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}FNO_4S$: 451.1254 Found 451.1243.



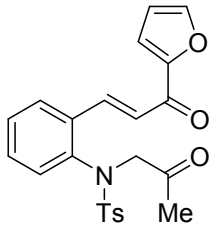
1m

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(4-methylphenyl)prop-2-en-1-one (1m) 237 mg, 53%, white solid; m.p. 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 2H), 7.80–7.70 (m, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.42–7.26 (m, 6H), 7.18 (d, J = 8.0 Hz, 2H), 4.38 (brs, 2H), 2.44 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 190.0, 144.1, 143.7, 139.3, 139.3, 135.2, 135.1, 135.1, 131.4, 130.8, 129.6, 129.4, 129.2, 128.9, 127.9, 127.3, 124.0, 61.4, 27.1, 21.7, 21.4; IR (film) 2958, 2920, 1741, 1661, 1595, 1481, 1331, 1275, 1182, 1158, 1117 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_4S$: 447.1504 Found 447.1498.



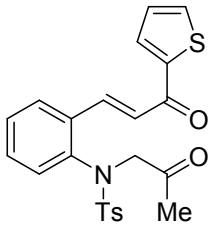
1n

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (1n) 354 mg, 76 %, white solid; m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.96 (m, 2H), 7.81–7.70 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.42–7.23 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.03–6.95 (m, 2H), 4.46 (brs, 1H), 4.26 (brs, 1H), 3.88 (s, 3H), 2.24 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 188.7, 163.5, 144.1, 139.2, 138.9, 135.2, 135.1, 131.3, 131.0, 130.7, 129.6, 129.2, 127.9 (two peaks overlapping), 127.3, 124.3, 113.9, 61.4, 55.6, 27.1, 21.4; IR (film) 3068, 2968, 2922, 1735, 1650, 1594, 1482, 1423, 1347, 1231, 1157, 1058 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_5S$: 463.1453 Found 463.1451.



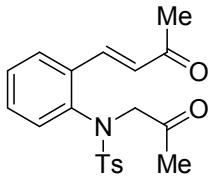
1o

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(furan-2-yl)prop-2-en-1-one (1o) 177 mg, 42%, white solid; m.p. 71-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 16.0 Hz, 1H), 7.76–7.69 (m, 1H), 7.66 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.54–7.46 (m, 2H), 7.42–7.29 (m, 4H), 7.19 (dd, *J* = 12.0, 6.5 Hz, 3H), 6.61 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.54 (brs, 1H), 4.26 (brs, 1H), 2.28 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 177.7, 153.3, 146.6, 144.2, 139.3, 138.8, 135.1, 134.9, 131.6, 131.0, 129.6, 129.2, 127.9, 127.4, 123.8, 117.9, 112.6, 61.4, 27.1, 21.4; IR (film) 3132, 2969, 2923, 1735, 1657, 1602, 1567, 1463, 1394, 1345, 1157, 1120, 1089, 1044 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{21}NO_5S$: 423.1140 Found 423.1188.



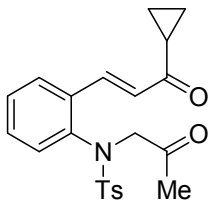
1p

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-(thien-2-yl)prop-2-en-1-one (1p) 311 mg, 71%, white solid; m.p. 70-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.79 (d, *J* = 15.8 Hz, 1H), 7.76–7.67 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.35 (dqd, *J* = 7.8, 7.0, 1.9 Hz, 3H), 7.23–7.16 (m, 4H), 4.51 (brs, 1H), 4.28 (brs, 1H), 2.25 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 181.9, 145.1, 144.2, 139.3, 138.9, 135.1, 134.9, 134.0, 132.2, 131.6, 131.0, 129.7, 129.2, 128.4, 127.9, 127.4, 124.0, 61.4, 27.1, 21.4; IR (film) 3097, 2962, 2922, 1735, 1649, 1594, 1481, 1413, 1348, 1231, 1157, 1089, 1058 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{21}NO_4S_2$: 439.0912 Found 439.0892.



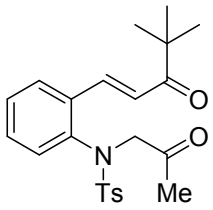
3a

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)but-3-en-2-one (3a) 252 mg, 68%, white solid; m.p. 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 16.6 Hz, 1H), 7.67 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.29 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.51 (d, *J* = 16.6 Hz, 1H), 4.50 (brs, 1H), 4.27 (brs, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 199.3, 144.4, 140.0, 139.4, 135.4, 134.9, 130.9, 130.2, 129.6, 129.3, 129.2, 128.1, 127.2, 61.3, 27.1, 26.4, 21.6; IR (film) 3068, 2968, 2921, 1735, 1650, 1594, 1516, 1482, 1413, 1348, 1157, 1090, 1058 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{20}H_{21}NO_4S$: 371.1191 Found 371.1176.



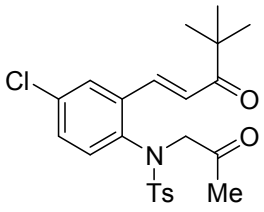
3b

(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-1-cyclopropylprop-2-en-1-one (3b) 254 mg, 64%, white solid; m.p. 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.5 Hz, 1H), 7.67 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.34 (dtd, *J* = 16.9, 7.4, 1.3 Hz, 2H), 7.25 (t, *J* = 10.2 Hz, 2H), 7.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.61 (d, *J* = 16.5 Hz, 1H), 4.38 (brs, 2H), 2.48–2.37 (m, 3H), 2.35 (td, *J* = 7.9, 4.0 Hz, 1H), 2.18 (s, 3H), 1.12 (brs, 2H), 0.99 (dd, *J* = 7.7, 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 200.3, 144.2, 139.3, 137.9, 135.4, 135.0, 130.8 (two peaks overlapping), 129.6, 129.2, 129.0, 128.0, 127.1, 61.4, 27.1, 21.6, 18.0, 11.4; IR (film) 3066, 2968, 2922, 1735, 1666, 1604, 1463, 1394, 1346, 1168, 1119, 1089, 1042 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{22}H_{23}NO_4S$: 397.1348 Found 397.1333.



3c

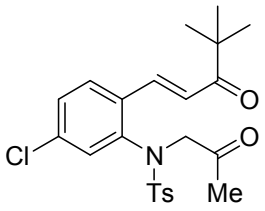
(*E*)-3-(2-(2-Oxopropyltosylamino)phenyl)-4,4-dimethylpent-1en-3-one (3c) 335 mg, 81%, white solid; m.p. 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.61 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.33 (ddt, *J* = 9.0, 7.2, 3.7 Hz, 2H), 7.31–7.20 (m, 3H), 7.02 (d, *J* = 15.7 Hz, 1H), 4.39 (brs, 2H), 2.39 (s, 3H), 2.20 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 202.7, 144.0, 139.3, 137.7, 135.3, 134.8, 131.5, 130.6, 129.6, 129.0, 128.0, 127.2, 122.7, 61.4, 43.2, 27.1, 26.2, 21.6; IR (film) 2967, 2926, 1736, 1659, 1598, 1570, 1463, 1394, 1347, 1204, 1158, 1120, 1089 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{27}NO_4S$: 413.1661 Found 413.1634.



3d

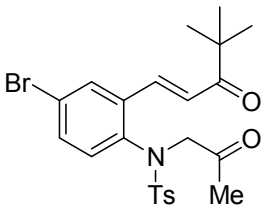
(*E*)-3-(2-(2-Oxopropyltosylamino)-5-chlorophenyl)-4,4-dimethylpent-1en-3-one (3d) 139 mg, 31%, white solid; m.p. 62-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.56–7.49 (m, 3H), 7.28 (d, *J* = 1.3 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 15.7 Hz, 1H), 4.48 (brs, 2H), 2.40 (s, 3H), 2.17 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 202.2, 144.1, 137.6, 136.5, 136.3, 135.2, 135.0, 133.2,

130.4, 129.7, 127.9, 127.0, 123.7, 61.2, 43.3, 27.0, 26.2, 21.6; IR (film) 2966, 2929, 2869, 1735, 1684, 1607, 1476, 1350, 1306, 1159, 1074, 1007 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{26}ClNO_4S$: 447.1271 Found 447.1277.



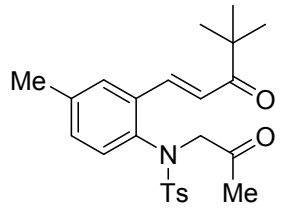
3e

(*E*)-3-(2-(2-Oxopropyltosylamino)-4-chlorophenyl)-4,4-dimethylpent-1en-3-one (3e) 268 mg, 60%, white solid; m.p. 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.50 (m, 4H), 7.35–7.27 (m, 4H), 6.99 (d, *J* = 15.7 Hz, 1H), 4.34 (brs, 2H), 2.41 (s, 3H), 2.18 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 202.0, 144.3, 140.1, 136.6, 135.8, 135.0, 133.4, 131.8, 129.7, 129.4, 128.1, 127.9, 122.9, 61.1, 43.3, 27.1, 26.2, 21.7; IR (film) 2954, 2924, 2870, 1713, 1678, 1598, 1477, 1357, 1217, 1078, 1010 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{26}ClNO_4S$: 447.1271 Found 447.1288.



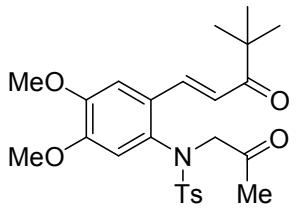
3f

(*E*)-3-(2-(2-Oxopropyltosylamino)-5-bromophenyl)-4,4-dimethylpent-1en-3-one (3f) 157 mg, 32%, white solid; m.p. 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.3 Hz, 1H), 7.52 (dd, *J* = 12.0, 8.0 Hz, 3H), 7.43 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 15.7 Hz, 1H), 4.37 (brs, 2H), 2.40 (s, 3H), 2.16 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 202.2, 144.2, 138.1, 136.8, 136.2, 135.2, 133.4, 133.4, 130.0, 129.7, 127.9, 123.7, 123.1, 61.1, 43.3, 27.0, 26.2, 21.7; IR (film) 2965, 2929, 2869, 1736, 1684, 1606, 1475, 1350, 1159, 1123, 1073, 1006 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{26}BrNO_4S$: 491.0766 Found 491.0758.



3g

(*E*)-3-(2-(2-Oxopropyltosylamino)-5-methylphenyl)-4,4-dimethylpent-1en-3-one (3g) 149 mg, 35%, white solid; m.p. 65-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.7 Hz, 1H), 7.56–7.49 (m, 2H), 7.45 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18–7.10 (m, 2H), 6.99 (d, *J* = 15.7 Hz, 1H), 4.50 (s, 1H), 4.15 (brs, 1H), 2.39 (brs, 3H), 2.37 (s, 3H), 2.19 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 202.9, 143.9, 139.0, 137.8, 136.8, 135.3, 134.3, 131.5, 131.1, 129.5, 128.0, 127.6, 122.4, 61.5, 43.2, 27.2, 26.3, 21.6, 21.2; IR (film) 2966, 2927, 2869, 1736, 1682, 1600, 1490, 1349, 1159, 1077, 1053 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{24}H_{29}NO_4S$: 427.1817 Found 427.1816.

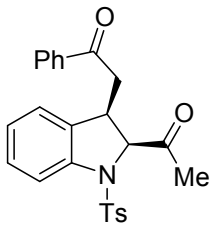


3h

(*E*)-3-(2-(2-Oxopropyltosylamino)-4,5-dimethoxyphenyl)-4,4-dimethylpent-1en-3-one (3h) 383 mg, 81%, white solid; m.p. 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 15.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 1H), 6.88 (s, 1H), 6.84 (d, *J* = 15.6 Hz, 1H), 4.70 (brs, 1H), 4.03 (brs, 1H), 3.93 (s, 3H), 3.76 (s, 3H), 2.38 (s, 3H), 2.18 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 202.8, 150.7, 149.2, 143.8, 137.4, 135.7, 133.0, 129.5, 128.0, 126.8, 120.3, 114.8, 108.0, 61.8, 56.1, 56.0, 43.1, 27.0, 26.4, 21.6; IR (film) 2953, 2930, 2864, 1732, 1672, 1587, 1509, 1443, 1337, 1288, 1211, 1158, 1082, 1010 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{31}NO_6S$: 473.1872 Found 473.1876.

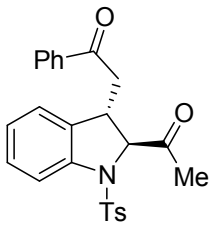
General Procedure for the Catalytic Asymmetric Intramolecular Michael Addition

An amber 2-dram vial equipped with a magnetic stir bar, containing catalyst **IIId** (3 mg, 0.01 mmol), 2-nitrobenzoic acid (3 mg, 0.02 mmol), and 2-(2-oxoalkyltosylamino)phenyl α,β-unsaturated ketone **1** or **3** (0.10 mmol) was charged with EtOAc (0.5 mL) at 0 °C. The resulting mixture was stirred at constant temperature until complete consumption of 2-(2-oxoalkyltosylamino)phenyl α,β-unsaturated ketone **1** or **3** was observed as determined by TLC. The resulting mixture was added water and extracted with EtOAc. The combined organic layer were washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude residue was purified by flash column chromatography with EtOAc/hexanes as the eluent to afford the desired 2,3-disubstituted indoline compound **2** or **4**.



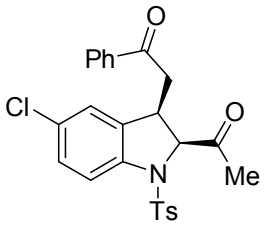
***cis*-2a**

2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-phenylethanone (*cis*-2a) 42 mg, 97%, white solid; m.p. 70-71 °C; $[\alpha]_D^{23}$ = 29.1 (*c* = 0.35, $CHCl_3$); 98% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.79 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.22–7.11 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 3.83 (dd, *J* = 15.2, 9.0 Hz, 1H), 3.35 (dd, *J* = 18.3, 8.4 Hz, 1H), 3.16 (dd, *J* = 18.3, 5.9 Hz, 1H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 196.8, 143.6, 140.1, 135.3, 133.5, 133.3, 132.5, 128.9, 127.7, 127.7, 127.0, 126.1, 124.1, 122.6, 115.7, 69.4, 37.8, 37.6, 28.1, 20.6; IR (film) 2922, 2852, 1716, 1683, 1596, 1459, 1352, 1219, 1165, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{23}NO_4S$: 433.1348 Found: 433.1362; Chiralpak IA column and IA guard column (155% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 23.4 min and *major*-isomer t_r = 31.5 min.



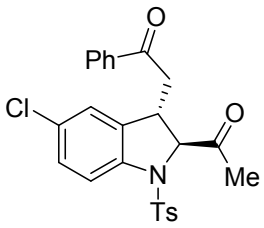
***trans*-2a**

2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-phenylethanone (*trans*-2a) 42 mg, 97%, white solid; m.p. 167-169 °C; $[\alpha]_D^{23}$ = 121.1 (*c* = 0.38, $CHCl_3$); 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.60–7.54 (m, 2H), 7.54–7.46 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.27–7.20 (m, 1H), 7.00 (ddd, *J* = 8.3, 6.8, 2.1 Hz, 4H), 4.31 (d, *J* = 3.0 Hz, 1H), 3.86 (ddd, *J* = 8.6, 5.7, 2.9 Hz, 1H), 2.65 (dd, *J* = 18.3, 5.7 Hz, 1H), 2.43 (s, 3H), 2.21 (s, 3H), 1.95 (dd, *J* = 18.3, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 195.8, 143.5, 139.7, 135.0, 133.2, 133.1, 132.5, 128.9, 127.8, 127.6, 126.8, 126.3, 124.3, 124.0, 116.1, 72.5, 43.4, 37.8, 26.0, 20.5; IR (film) 2922, 2852, 1716, 1683, 1596, 1459, 1351, 1217, 1165, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{23}NO_4S$: 433.1348 Found: 433.1355; Chiralpak IA column and IA guard column (15% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 18.7 min and *major*-isomer t_r = 27.7 min.



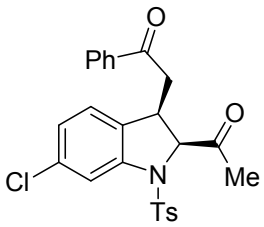
***cis*-2b**

2-((2*S*,3*R*)-2-Acetyl-5-chloro-1-tosylindolin-3-yl)-1-phenylethanone (*cis*-2b) 45 mg, 96%, white solid; m.p. 196-198 °C; $[\alpha]_D^{25}$ = 85.0 (*c* = 0.92, $CHCl_3$); 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.74–7.54 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.26 (dd, *J* = 10.2, 6.1 Hz, 3H), 6.95 (s, 1H), 4.98 (d, *J* = 10.0 Hz, 1H), 3.80 (dd, *J* = 14.9, 8.9 Hz, 1H), 3.45 (dd, *J* = 18.4, 8.5 Hz, 1H), 3.23 (dd, *J* = 18.4, 5.7 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 197.6, 144.9, 139.9, 136.6, 136.1, 134.3, 133.7, 130.6, 130.1, 128.8, 128.7, 128.0, 127.2, 124.1, 117.9, 70.4, 38.7, 38.4, 29.1, 21.7; IR (film) 2960, 2923, 2852, 1720, 1681, 1596, 1448, 1357, 1219, 1165, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0978; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 37.3 min and *minor*-isomer t_r = 43.4 min.



***trans*-2b**

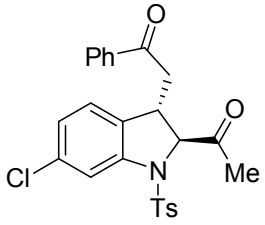
2-((2*S*,3*S*)-2-Acetyl-5-chloro-1-tosylindolin-3-yl)-1-phenylethanone (*trans*-2b) 45 mg, 96%, white solid; m.p. 143-145 °C; $[\alpha]_D^{25}$ = 148.7 (*c* = 0.69, $CHCl_3$); 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 1H), 7.66–7.51 (m, 5H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.29–7.23 (m, 1H), 7.09 (dd, *J* = 8.1, 5.0 Hz, 3H), 4.40 (d, *J* = 2.8 Hz, 1H), 3.92 (ddd, *J* = 8.4, 5.7, 2.7 Hz, 1H), 2.69 (dd, *J* = 18.4, 5.7 Hz, 1H), 2.51 (s, 3H), 2.29 (s, 3H), 1.99 (dd, *J* = 18.4, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 196.5, 144.9, 139.5, 136.29, 135.8, 133.9, 133.7, 130.7, 130.1, 128.9, 128.7, 127.9, 127.4, 125.3, 118.2, 73.6, 44.2, 38. 6, 27.1, 21.6; IR (film) 2963, 2923, 2852, 1733, 1682, 1596, 1468, 1355, 1213, 1163, 1087 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0969; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 23.3 min and *major*-isomer t_r = 37.7 min.



***cis*-2c**

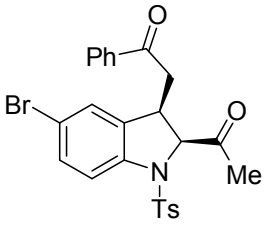
2-((2*S*,3*R*)-2-Acetyl-6-chloro-1-tosylindolin-3-yl)-1-phenylethanone (*cis*-2c) 41 mg, 88%, white solid; m.p. 150-151 °C; $[\alpha]_D^{25}$ = 108.0 (*c* = 0.86, $CHCl_3$); 99% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.86 (m, 2H), 7.70 (dd, *J* = 13.2, 5.1 Hz, 3H), 7.63–7.53 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31–7.25 (m, 2H), 7.02 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.89 (dd, *J* = 8.1, 1.0 Hz, 1H), 4.95 (d, *J* = 10.2 Hz, 1H), 3.88 (dt, *J* = 8.7, 6.8 Hz, 1H), 3.40 (dd, *J* = 18.4, 8.1 Hz, 1H), 3.21 (dd, *J* = 18.4, 6.0 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 197.6, 145.0, 142.4, 136.2, 134.4, 134.3, 133.7, 132.8, 130.1, 128.8, 128.0, 127.2, 125.1, 124.5, 116.8, 70.7, 38.6, 38.4, 29.1, 21.7; IR (film) 2969, 2923, 1721, 1683, 1597, 1474, 1418, 1355, 1263, 1215, 1169, 1089, 1071 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958

Found: 467.0943; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 15.6 min and *minor*-isomer t_r = 23.0 min.



***trans*-2c**

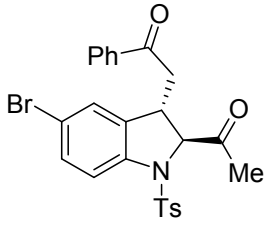
2-((2*S*,3*S*)-2-Acetyl-6-chloro-1-tosylindolin-3-yl)-1-phenylethanone (*trans*-2c) 41 mg, 88%, white solid; m.p. 68-70 °C; $[\alpha]_D^{25}$ = 111.2 (*c* = 0.81, $CHCl_3$); 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 1.1 Hz, 1H), 7.67–7.55 (m, 5H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.06–6.97 (m, 2H), 4.39 (d, *J* = 3.0 Hz, 1H), 3.88 (ddd, *J* = 8.6, 5.9, 2.9 Hz, 1H), 2.68 (dd, *J* = 18.3, 5.9 Hz, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 2.09 (dd, *J* = 18.3, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 196.6, 144.9, 142.0, 135.9, 134.6, 134.0, 133.7, 132.7, 130.1, 128.7, 127.9, 127.4, 125.9, 125.4, 117.2, 73.9, 44.3, 38.5, 27.0, 21.6; IR (film) 2923, 2853, 1720, 1683, 1596, 1474, 1449, 1418, 1356, 1215, 1164, 1089 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0977; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 12.1 min and *major*-isomer t_r = 18.1 min.



***cis*-2d**

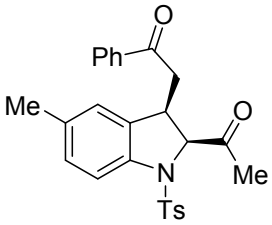
2-((2*S*,3*R*)-2-Acetyl-5-bromo-1-tosylindolin-3-yl)-1-phenylethanone (*cis*-2d) 50 mg, 97%, white solid; m.p. 210-212 °C; $[\alpha]_D^{25}$ = 98.8 (*c* = 0.26, $CHCl_3$); 99% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.88 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 7.9, 6.1 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.27 (d, *J* = 5.6 Hz, 2H), 7.10 (s, 1H), 4.97 (d, *J* = 10.0 Hz, 1H), 3.83 (dt, *J* = 15.4, 7.7 Hz, 1H), 3.45 (dd, *J* = 18.4, 8.5 Hz, 1H), 3.23 (dd, *J* = 18.4, 5.7 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 197.6, 144.9, 140.4, 136.9, 136.1, 134.2, 133.7, 131.6, 130.1, 128.8, 128.0, 127.1, 126.9, 118.2, 118.1, 70.3, 38.6, 38.4, 29.1, 21.6; IR (film) 3067, 2968, 2920, 1734, 1718, 1651, 1595, 1449, 1414, 1351, 1219, 1158, 1090, 1059 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}BrNO_4S$: 511.0453

Found: 511.0457; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 27.8 min and *major*-isomer t_r = 31.1 min.



***trans*-2d**

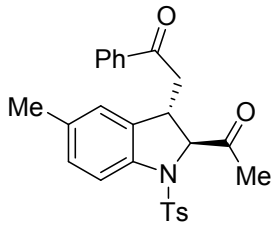
2-((2*S*,3*S*)-2-Acetyl-5-bromo-1-tosylindolin-3-yl)-1-phenylethanone (*trans*-2d) 50 mg, 97%, white solid; m.p. 76-78 °C; $[\alpha]_D^{25}$ = 111.2 (*c* = 0.81, $CHCl_3$); 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.57 (m, 4H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.49–7.37 (m, 3H), 7.23 (d, *J* = 1.5 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.39 (d, *J* = 2.8 Hz, 1H), 3.91 (ddd, *J* = 8.5, 5.6, 2.8 Hz, 1H), 2.70 (dd, *J* = 18.4, 5.7 Hz, 1H), 2.51 (s, 3H), 2.29 (s, 3H), 1.99 (dd, *J* = 18.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 196.5, 144.9, 140.0, 136.6, 135.8, 133.9, 133.7, 131.8, 130.1, 128.7, 128.2, 127.9, 127.3, 118.6, 118.2, 73.5, 44.2, 38.5, 27.1, 21.6; IR (film) 3088, 2969, 2921, 1734, 1718, 1651, 1595, 1517, 1481, 1414, 1350, 1231, 1158, 1119, 1059 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}BrNO_4S$: 511.0453 Found: 511.0439; Chiralpak IA column and IA guard column (15% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 15.8 min and *major*-isomer t_r = 19.1 min.



***cis*-2e**

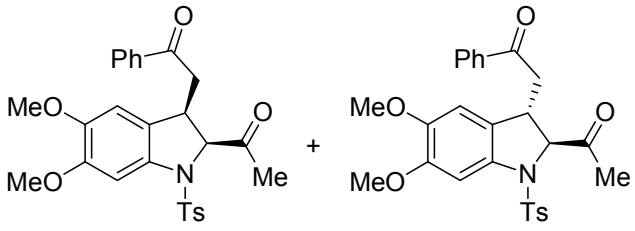
2-((2*S*,3*R*)-2-Acetyl-5-methyl-1-tosylindolin-3-yl)-1-phenylethanone (*cis*-2e) 41 mg, 91%, white solid; m.p. 143-144 °C; $[\alpha]_D^{25}$ = 64.3 (*c* = 0.87, $CHCl_3$); 99% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.62–7.54 (m, 2H), 7.45 (dd, *J* = 10.7, 4.7 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.76 (s, 1H), 4.92 (d, *J* = 10.0 Hz, 1H), 3.80 (dd, *J* = 15.1, 9.0 Hz, 1H), 3.40 (dd, *J* = 18.4, 8.5 Hz, 1H), 3.21 (dd, *J* = 18.4, 5.8 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 197.9, 144.5, 138.7, 136.4, 135.1, 134.7, 134.5, 133.5, 129.9, 129.2, 128.7, 128.0, 127.2, 124.2, 116.8, 70.7, 38.7, 38.6, 29.1, 21.6, 21.1; IR (film) 2970, 2923, 1719, 1684,

1597, 1474, 1418, 1355, 1214, 1165, 1090, 1071 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_4S$: 447.1504 Found: 447.1497; Chiralpak IA column and IA guard column (30% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 14.7 min and *minor*-isomer t_r = 17.3 min.



***trans*-2e**

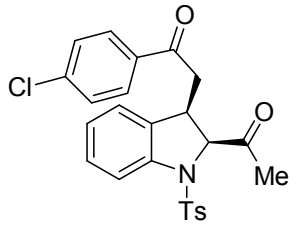
2-((2*S*,3*S*)-2-Acetyl-5-methyl-1-tosylindolin-3-yl)-1-phenylethanone (*trans*-2e) 41 mg, 91%, white solid; m.p. 116-118 °C; $[\alpha]_D^{25}$ = 129.1 (*c* = 0.50, $CHCl_3$); 92% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68–7.60 (m, 3H), 7.60–7.53 (m, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 6.0 Hz, 3H), 6.88 (s, 1H), 4.36 (d, *J* = 2.8 Hz, 1H), 3.89 (ddd, *J* = 8.5, 5.7, 2.8 Hz, 1H), 2.69 (dd, *J* = 18.3, 5.8 Hz, 1H), 2.49 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H), 1.96 (dd, *J* = 18.3, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 196.9, 144.4, 138.3, 136.1, 135.2, 134.5, 134.1, 133.5, 129.9, 129.5, 128.6, 127.9, 127.4, 125.5, 117.0, 73.7, 44.5, 38.8, 27.0, 21.6, 21.1; IR (film) 2970, 2921, 1719, 1682, 1597, 1487, 1449, 1351, 1227, 1162, 1090, 1070 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_4S$: 447.1504 Found: 447.1496; Chiralpak IA column and IA guard column (30% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 11.6 min and *major*-isomer t_r = 18.8 min.



***cis*-2f** ***trans*-2f**

2-(2-Acetyl-5,6-dimethoxy-1-tosylindolin-3-yl)-1-phenylethanone (2f) 31 mg, 62%, 95% ee for *cis* isomer; 97% ee for *trans* isomer; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.86 (m, 1H), 7.64–7.50 (m, 4H), 7.49–7.35 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 1.16H, *cis* isomer), 7.10 (d, *J* = 8.0 Hz, 0.84H, *trans* isomer), 6.62 (s, 0.84H, *trans* isomer), 6.48 (s, 0.58H, *cis* isomer), 4.89 (d, *J* = 9.8 Hz, 0.58H, *cis* isomer), 4.34 (d, *J* = 2.3 Hz, 0.42H, *trans* isomer), 3.97 (s, 3H), 3.87 (dd, *J* = 5.7, 2.0 Hz, 0.42H, *trans* isomer), 3.78 (s, 1.26H,

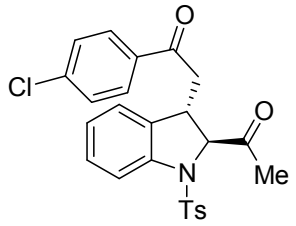
trans isomer), 3.78 (s, 1.74H, *cis* isomer), 3.71 (dd, *J* = 15.4, 8.7 Hz, 0.58H, *cis* isomer), 3.38 (dd, *J* = 18.1, 8.3 Hz, 0.58H, *cis* isomer), 3.16 (dd, *J* = 18.1, 6.2 Hz, 0.58H, *cis* isomer), 2.52 (dd, *J* = 18.2, 6.4 Hz, 0.42H, *trans* isomer), 2.39 (s, 1.26H, *trans* isomer), 2.39 (s, 1.74H, *cis* isomer), 2.35 (s, 1.74H, *cis* isomer), 2.30 (s, 0.1.26H, *trans* isomer), 1.86 (dd, *J* = 18.2, 8.2 Hz, 0.42H, *trans* isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1 (*cis* isomer), 205.7 (*trans* isomer), 198.1 (*cis* isomer), 197.1 (*trans* isomer), 149.6 (*trans* isomer), 149.3 (*cis* isomer), 147.4 (*trans* isomer), 147.2 (*cis* isomer), 144.6 (*cis* isomer), 144.5 (*trans* isomer), 136.4 (*cis* isomer), 136.1 (*trans* isomer), 134.2 (*cis* isomer), 134.0 (*cis* isomer), 133.9 (*trans* isomer), 133.7 (*trans* isomer), 133.6 (*cis* isomer), 133.5 (*trans* isomer), 129.9 (*trans* isomer), 128.8 (*cis* isomer), 128.6 (*trans* isomer), 128.0 (*cis* isomer), 127.8 (*trans* isomer), 127.5 (*trans* isomer), 127.3 (*cis* isomer), 126.1 (*cis* isomer), 125.9 (*trans* isomer), 107.6 (*trans* isomer), 106.6 (*cis* isomer), 102.0 (*cis* isomer), 101.9 (*trans* isomer), 74.0 (*trans* isomer), 70.9 (*cis* isomer), 56.4 (*cis* isomer), 56.4 (*trans* isomer), 56.2 (*cis* isomer), 56.2 (*trans* isomer), 44.6 (*trans* isomer), 38.8 (*trans* isomer), 38.8 (*cis* isomer), 38.7 (*cis* isomer), 29.1 (*cis* isomer), 27.2 (*trans* isomer), 21.7 (*cis* isomer), 21.6 (*trans* isomer); IR (film) 2959, 2923, 2853, 1719, 1682, 1596, 1495, 1448, 1356, 1306, 1214, 1164, 1089 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{27}H_{27}NO_6S$: 493.1559 Found: 493.1551; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major-cis*-isomer t_r = 28.6 min, *minor-trans*-isomer t_r = 32.9 min, *major-trans*-isomer t_r = 54.0 min and *minor-cis*-isomer t_r = 66.3 min.



***cis*-2g**

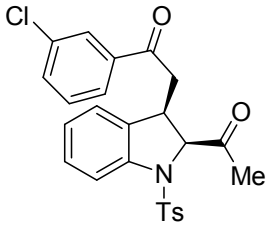
2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-chlorophenyl)ethanone (*cis*-2g) 40 mg, 86%, white solid; m.p. 130-132 °C; $[\alpha]_D^{24}$ = 18.2 (*c* = 0.23, $CHCl_3$); 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.80 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.48–7.39 (m, 2H), 7.33–7.20 (m, 3H), 7.11–7.02 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 3.87 (td, *J* = 9.2, 5.7 Hz, 1H), 3.38 (dd, *J* = 18.3, 8.7 Hz, 1H), 3.18 (dd, *J* = 18.3, 5.6 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 196.7, 144.6, 141.1, 140.0, 134.7, 134.6, 134.2, 129.9, 129.4, 129.1, 128.8, 127.2, 125.2, 123.5, 116.9, 70.3, 38.8, 38.6, 29.2, 21.6; IR (film) 2958, 2922, 2852, 1717, 1684, 1588, 1478, 1400, 1349, 1290, 1218, 1160. 1088, 1062 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0950;

Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 40.9 min and *minor*-isomer t_r = 53.3 min.



***trans*-2g**

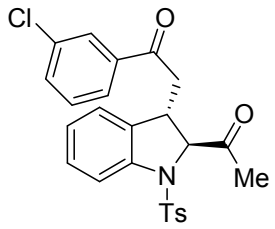
2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-chlorophenyl)ethanone (*trans*-2g) 40 mg, 86%, white solid; m.p. 190-112 °C; $[\alpha]_D^{25}$ = 90.9 (*c* = 0.47, $CHCl_3$); 75% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.62–7.52 (m, 4H), 7.44–7.37 (m, 2H), 7.30 (ddd, *J* = 8.4, 4.8, 2.7 Hz, 1H), 7.16–7.04 (m, 4H), 4.36 (d, *J* = 3.0 Hz, 1H), 3.92 (ddd, *J* = 8.6, 5.7, 3.0 Hz, 1H), 2.70 (dd, *J* = 18.2, 5.7 Hz, 1H), 2.49 (s, 3H), 2.31 (s, 3H), 2.03 (dd, *J* = 18.2, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 195.6, 144.5, 140.7, 140.0, 134.4, 134.2, 134.0, 129.9, 129.3, 128.9, 128.9, 127.4, 125.3, 124.9, 117.1, 73.5, 44.4, 38.8, 26.9, 21.6; IR (film) 2961, 2921, 2852, 1716, 1682, 1590, 1459, 1401, 1353, 1210, 1166, 1091, 1062 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0985; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 16.8 min and *major*-isomer t_r = 34.8 min.



***cis*-2h**

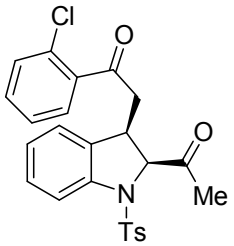
2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(3-chlorophenyl)ethanone (*cis*-2h) 43 mg, 93%, colorless gum; $[\alpha]_D^{25}$ = 23.3 (*c* = 0.54, $CHCl_3$); 92% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 1.8 Hz, 1H), 7.83–7.76 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.54 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.32–7.22 (m, 3H), 7.07 (td, *J* = 7.5, 0.8 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 3.85 (td, *J* = 9.3, 5.6 Hz, 1H), 3.39 (dd, *J* = 18.4, 8.8 Hz, 1H), 3.19 (dd, *J* = 18.4, 5.5 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 196.6, 144.6, 141.1, 137.9, 135.1,

134.5, 134.1, 133.4, 130.1, 129.9, 128.8, 128.1, 127.2, 126.1, 125.2, 123.5, 116.9, 70.3, 38.8, 38.7, 29.2, 21.6; IR (film) 2956, 2921, 2851, 1686, 1596, 1456, 1421, 1353, 1215, 1164, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0974; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 17.7 min and *minor*-isomer t_r = 21.3 min.



***trans*-2h**

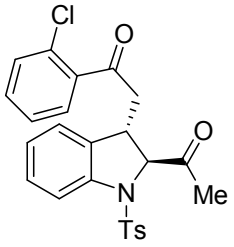
2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(3-chlorophenyl)ethanone (*trans*-2h) 43 mg, 93%, white solid; m.p. 137-139 °C; $[\alpha]_D^{25}$ = 84.1 (*c* = 0.57, $CHCl_3$); 90% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 3.5 Hz, 1H), 7.58–7.53 (m, 5H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (ddd, *J* = 12.2, 9.0, 8.4 Hz, 1H), 7.10 (dd, *J* = 12.5, 5.2 Hz, 3H), 4.37 (d, *J* = 2.9 Hz, 1H), 3.93 (ddd, *J* = 8.5, 5.7, 2.9 Hz, 1H), 2.68 (dd, *J* = 18.4, 5.7 Hz, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 2.02 (dd, *J* = 18.4, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 195.6, 144.8, 140.7, 137.5, 134.9, 134.1, 134.0, 133.5, 130.0, 129.9, 128.9, 128.0, 127.4, 125.9, 125.4, 125.0, 117.2, 73.5, 44.5, 38.7, 27.0, 21.6; IR (film) 2959, 2920, 2850, 1716, 1688, 1570, 1476, 1411, 1353, 1207, 1167, 1091 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0978; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 12.6 min and *major*-isomer t_r = 16.5 min.



***cis*-2i**

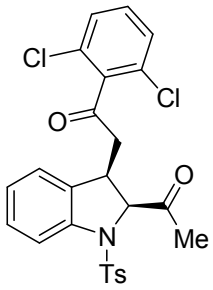
2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(2-chlorophenyl)ethanone (*cis*-2i) 45 mg, 96%, white solid; m.p. 57-59 °C; $[\alpha]_D^{22}$ = 73.8 (*c* = 0.45, $CHCl_3$); 94% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.44–7.37 (m, 2H), 7.38–7.32 (m, 1H), 7.31–7.21

(m, 3H), 7.07 (dd, *J* = 7.4, 7.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 4.90 (d, *J* = 10.1 Hz, 1H), 3.88 (dd, *J* = 15.4, 9.0 Hz, 1H), 3.39–3.21 (m, 2H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 200.4, 144.7, 141.1, 138.3, 134.5, 134.0, 132.2, 130.9, 130.7, 130.0, 129.5, 128.8, 127.2, 127.1, 125.2, 123.6, 116.9, 70.4, 42.8, 39.0, 29.1, 21.6; IR (film) 2921, 2851, 1711, 1591, 1477, 1433, 1352, 1165, 1090, 1062 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0967; Chiralpak IA column and IA guard column (30% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 13.5 min and *minor*-isomer t_r = 29.1 min.



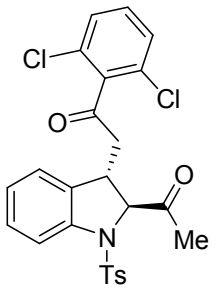
***trans*-2i**

2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(2-chlorophenyl)ethanone (*trans*-2i) 45 mg, 96%, white solid; m.p. 120-122 °C; $[\alpha]_D^{22}$ = 99.7 (*c* = 0.36, $CHCl_3$); 92% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.46–7.38 (m, 2H), 7.37–7.27 (m, 3H), 7.09 (ddd, *J* = 15.6, 10.7, 4.3 Hz, 4H), 4.31 (d, *J* = 3.2 Hz, 1H), 3.93 (ddd, *J* = 8.7, 5.8, 3.1 Hz, 1H), 2.75 (dd, *J* = 18.0, 5.8 Hz, 1H), 2.48 (s, 3H), 2.23 (s, 3H), 2.08 (dd, *J* = 18.0, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 199.6, 144.7, 140.8, 138.2, 133.9, 133.8, 132.3, 131.2, 130.7, 129.8, 129.3, 128.9, 127.3, 127.1, 125.3, 125.0, 117.0, 73.5, 48.5, 39.3, 26.9, 21.5; IR (film) 2921, 2851, 1711, 1591, 1476, 1432, 1352, 1165, 1089, 1033 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}ClNO_4S$: 467.0958 Found: 467.0974; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 18.5 min and *major*-isomer t_r = 28.2 min.



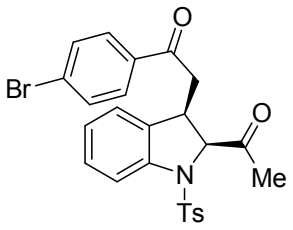
***cis*-2j**

2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(2,6-dichlorophenyl)ethanone (*cis*-2j) 42 mg, 83%, colorless gum; $[\alpha]_D^{26}$ = 38.3 (*c* = 0.36, $CHCl_3$); 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.30 (dq, *J* = 9.4, 4.8 Hz, 4H), 7.26–7.22 (m, 2H), 7.08 (dt, *J* = 13.9, 7.5 Hz, 2H), 4.92 (d, *J* = 10.2 Hz, 1H), 3.88 (dd, *J* = 16.4, 7.1 Hz, 1H), 3.34 (dd, *J* = 19.6, 5.9 Hz, 1H), 3.10 (dd, *J* = 19.6, 7.5 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 200.3, 144.7, 141.0, 138.6, 134.5, 133.9, 131.0, 130.5, 130.0, 128.8, 128.3, 127.2, 125.3, 124.5, 116.5, 70.3, 43.7, 37.8, 28.7, 21.6; IR (film) 2923, 2853, 1716, 1597, 1583, 1561, 1459, 1429, 1355, 1166, 1103, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{21}Cl_2NO_4S$: 501.0568 Found: 501.0538; Chiralpak OD column and OD guard column (1% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 40.2 min and *major*-isomer t_r = 44.6 min.



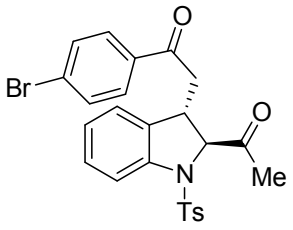
***trans*-2j**

2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(2-dichlorophenyl)ethanone (*trans*-2j) 42 mg, 83%, white solid; m.p. 165-167 °C; $[\alpha]_D^{27}$ = 103.7 (*c* = 1.04, $CHCl_3$); 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.32–7.27 (m, 4H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.06 (td, *J* = 7.5, 0.9 Hz, 1H), 4.35 (d, *J* = 3.4 Hz, 1H), 4.00 (td, *J* = 6.7, 3.3 Hz, 1H), 2.48 (s, 3H), 2.34 (d, *J* = 6.8 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 199.1, 144.6, 140.8, 138.5, 134.0, 133.33, 130.9, 130.3, 129.8, 128.9, 128.2, 127.4, 125.7, 125.2, 116.5, 73.8, 49.1, 38.4, 26.9, 21.4; IR (film) 2921, 2851, 1710, 1596, 1560, 1459, 1429, 1393, 1350, 1221, 1166, 1090, 1069 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{21}Cl_2NO_4S$: 501.0568 Found: 501.0540; Chiralpak IB column and IB guard column (2% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 19.6 min and *major*-isomer t_r = 21.4 min.



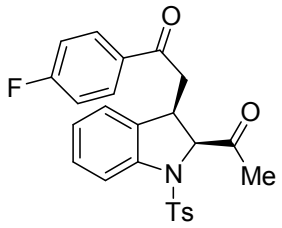
***cis*-2k**

2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-bromophenyl)ethanone (*cis*-2k) 42 mg, 82%, white solid; m.p. 68-70 °C; $[\alpha]_D^{23}$ = 20.1 (*c* = 0.28, $CHCl_3$); 98% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.31–7.21 (m, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 3.86 (dt, *J* = 15.1, 7.6 Hz, 1H), 3.38 (dd, *J* = 18.3, 8.7 Hz, 1H), 3.17 (dd, *J* = 18.3, 5.6 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 196.9, 144.6, 141.1, 135.1, 134.5, 134.2, 132.0, 129.9 (two peaks overlapping), 129.5, 128.8, 127.1, 125.2, 123.5, 116.9, 70.3, 38.8, 38.5, 29.2, 21.6; IR (film) 2921, 2851, 1711, 1591, 1477, 1444, 1353, 1165, 1090, 1062 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}BrNO_4S$: 511.0453 Found: 511.0445; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 35.7 min and *minor*-isomer t_r = 49.9 min.



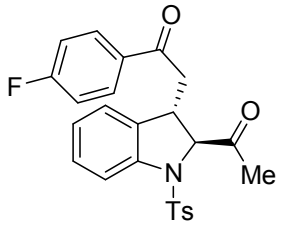
***trans*-2k**

2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-bromophenyl)ethanone (*trans*-2k) 42 mg, 82%, white solid; m.p. 184-186 °C; $[\alpha]_D^{24}$ = 107.5 (*c* = 0.39, $CHCl_3$); 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.60–7.54 (m, 4H), 7.52–7.47 (m, 2H), 7.34–7.28 (m, 1H), 7.14–7.05 (m, 4H), 4.36 (d, *J* = 3.0 Hz, 1H), 3.92 (ddd, *J* = 8.6, 5.7, 3.0 Hz, 1H), 2.69 (dd, *J* = 18.2, 5.7 Hz, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 2.01 (dd, *J* = 18.3, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 195.8, 144.5, 140.7, 134.7, 134.2, 134.0, 131.9, 129.9, 129.3, 128.9, 128.8, 127.4, 125.3, 124.9, 117.1, 73.5, 44.3, 38.8, 26.9, 21.6; IR (film) 2921, 2851, 1712, 1591, 1477, 1433, 1352, 1165, 1090, 1062 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}BrNO_4S$: 511.0453 Found: 511.0479; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 24.3 min and *major*-isomer t_r = 45.5 min.



***cis*-2l**

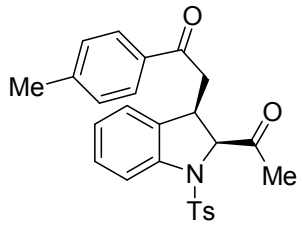
2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-fluorophenyl)ethanone (*cis*-2l) 43 mg, 95%, white solid; m.p. 72-74 °C; $[\alpha]_D^{20}$ = 37.5 (*c* = 0.37, $CHCl_3$); 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (ddd, *J* = 6.9, 5.2, 2.5 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.32–7.26 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17–7.09 (m, 2H), 7.06 (td, *J* = 7.5, 0.8 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 3.88 (td, *J* = 9.2, 5.8 Hz, 1H), 3.39 (dd, *J* = 18.3, 8.6 Hz, 1H), 3.19 (dd, *J* = 18.3, 5.7 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 196.2, 166.0 (d, J^1 = 255.5 Hz), 144.6, 141.1, 134.5, 134.2, 132.8 (d, J^4 = 3.0 Hz), 130.7 (d, J^3 = 9.4 Hz), 129.9, 128.7, 127.2, 125.2, 123.5, 116.8, 115.9 (d, J^2 = 21.9 Hz), 70.3, 38.8, 38.5, 29.2, 21.6; IR (film) 2970, 2921, 2851, 1716, 1682, 1596, 1459, 1352, 1229, 1157, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}FNO_4S$: 451.1254 Found: 451.1267; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 28.1 min and *minor*-isomer t_r = 31.3 min.



***trans*-2l**

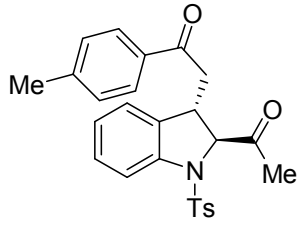
2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-fluorophenyl)ethanone (*trans*-2l) 43 mg, 95%, white solid; m.p. 175-177 °C; $[\alpha]_D^{20}$ = 98.0 (*c* = 0.38, $CHCl_3$); 86% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.72–7.64 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.34–7.28 (m, 1H), 7.16–7.03 (m, 6H), 4.37 (d, *J* = 3.1 Hz, 1H), 3.93 (ddd, *J* = 8.6, 5.7, 3.1 Hz, 1H), 2.73 (d, *J* = 5.8 Hz, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 2.04 (dd, *J* = 18.2, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 195.2, 165.9 (d, J^1 = 255.8 Hz), 144.5, 140.7, 134.2, 134.0, 132.5 (d, J^4 = 3.1 Hz), 130.6 (d, J^3 = 9.4 Hz), 129.9, 128.9, 127.4, 125.3, 125.0, 117.1, 115.8 (d, J^2 = 21.9 Hz), 73.6, 44.3, 38.9, 27.0, 21.6; IR (film) 2958, 2920, 2851, 1716, 1672, 1569,

1466, 1352, 1237, 1164, 1089, 1019 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{22}FNO_4S$: 451.1254 Found: 451.1266; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 15.6 min and *major*-isomer t_r = 30.0 min.



***cis*-2m**

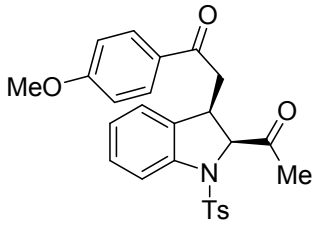
2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-methylphenyl)ethanone (*cis*-2m) 38 mg, 85%, colorless gum; $[\alpha]_D^{20}$ = 21.4 (*c* = 0.45, $CHCl_3$); 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.30–7.21 (m, 5H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 3.90 (dd, *J* = 15.5, 8.7 Hz, 1H), 3.38 (dd, *J* = 18.2, 8.3 Hz, 1H), 3.20 (dd, *J* = 18.2, 6.0 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 197.4, 144.6, 144.4, 141.1, 134.3, 134.4, 133.9, 129.9, 129.4, 128.6, 128.1, 127.2, 125.1, 123.7, 116.7, 70.5, 38.8, 38.5, 29.1, 21.7, 21.6; IR (film) 2957, 2920, 2851, 1716, 1678, 1605, 1459, 1353, 1225, 1166, 1119, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_4S$: 447.1504 Found: 447.1520; Chiralpak IA column and IA guard column (7% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 48.3 min and *minor*-isomer t_r = 66.2 min.



***trans*-2m**

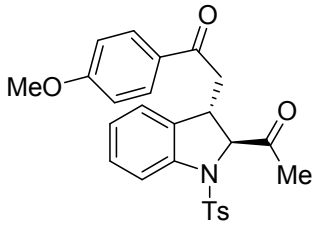
2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-methylphenyl)ethanone (*trans*-2m) 38 mg, 85%, white solid; m.p. 154-156 °C; $[\alpha]_D^{24}$ = 107.5 (*c* = 0.34, $CHCl_3$); 84% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 13.2, 8.2 Hz, 4H), 7.29 (dd, *J* = 10.9, 4.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13–7.02 (m, 4H), 4.38 (d, *J* = 3.0 Hz, 1H), 3.92 (ddd, *J* = 8.6, 5.7, 3.0 Hz, 1H), 2.75–2.64 (m, 1H), 2.50 (s, 3H), 2.42 (s, 3H), 2.30 (s, 3H), 2.02 (dd, *J* = 18.2, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4,

196.5, 144.5, 144.4, 140.7, 134.3, 134.1, 133.6, 129.9, 129.2, 128.7, 128.0, 127.3, 125.2, 125.0, 117.1, 73.6, 44.3, 38.9, 27.0, 21.7, 21.6; IR (film) 2958, 2922, 2852, 1717, 1678, 1605, 1459, 1353, 1291, 1226, 1157, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_4S$: 447.1504 Found: 447.1533; Chiralpak IA column and IA guard column (20% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 14.9 min and *major*-isomer t_r = 31.6 min.



***cis*-2n**

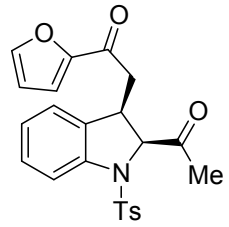
2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-methoxyphenyl)ethanone (*cis*-2n) 42 mg, 91%, white solid; m.p. 118-120 °C; $[\alpha]_D^{20}$ = 17.1 (*c* = 0.33, $CHCl_3$); 96% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93–7.86 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.25 (dd, *J* = 17.1, 8.2 Hz, 3H), 7.04 (td, *J* = 7.5, 0.8 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.95–6.89 (m, 2H), 4.94 (d, *J* = 10.1 Hz, 1H), 3.96–3.88 (m, 1H), 3.87 (s, 3H), 3.35 (dd, *J* = 18.1, 8.2 Hz, 1H), 3.18 (dd, *J* = 18.1, 6.0 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 196.2, 163.8, 144.6, 141.1, 134.6, 134.5, 130.3, 129.9, 129.5, 128.6, 127.2, 125.1, 123.7, 116.6, 113.9, 70.5, 55.5, 38.8, 38.3, 29.1, 21.6; IR (film) 2959, 2919, 2850, 1716, 1656, 1598, 1572, 1479, 1421, 1354, 1259, 1226, 1166, 1090, 1026 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_5S$: 463.1453 Found: 463.1458; Chiralpak IA column and IA guard column (7% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 23.2 min and *minor*-isomer t_r = 26.7 min.



***trans*-2n**

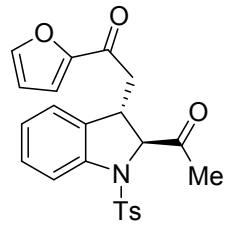
2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(4-methoxyphenyl)ethanone (*trans*-2n) 42 mg, 91%, white solid; m.p. 118-119 °C; $[\alpha]_D^{20}$ = 124.2 (*c* = 0.34, $CHCl_3$); 89% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.65–7.59 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.32–7.27 (m, 1H), 7.07 (ddd, *J* = 12.0, 8.3,

4.5 Hz, 4H), 6.92–6.86 (m, 2H), 4.39 (d, J = 3.1 Hz, 1H), 3.95–3.89 (m, 1H), 3.87 (d, J = 5.5 Hz, 3H), 2.69 (dd, J = 18.0, 5.7 Hz, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 2.02 (dd, J = 18.0, 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 195.3, 163.7, 144.5, 140.7, 134.3, 134.2, 130.2, 129.9, 129.2, 128.7, 127.4, 125.2, 125.0, 117.0, 113.1, 73.6, 55.6, 44.1, 39.0, 26.9, 21.6; IR (film) 2958, 2920, 2851, 1718, 1674, 1598, 1463, 1351, 1307, 1260, 1215, 1166, 1090, 1031 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{25}NO_5S$: 463.1453 Found: 463.1431; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 14.4 min and *major*-isomer t_r = 24.2 min.



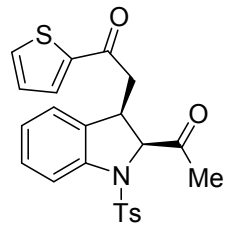
***cis*-2o**

2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(furan-2-yl)ethanone (*cis*-2o) 39 mg, 92%, colorless gum; $[\alpha]_D^{20}$ = 29.4 (c = 0.31, $CHCl_3$); 92% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 1.0 Hz, 1H), 7.24 (ddd, J = 19.9, 11.5, 5.6 Hz, 4H), 7.05 (td, J = 7.5, 0.8 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.54 (dd, J = 3.6, 1.7 Hz, 1H), 4.88 (d, J = 10.1 Hz, 1H), 3.85 (dd, J = 16.3, 8.3 Hz, 1H), 3.25 (dd, J = 18.2, 8.3 Hz, 1H), 3.12 (dd, J = 18.2, 6.3 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 186.7, 152.2, 146.6, 144.6, 141.0, 134.4, 134.2, 129.9, 128.7, 127.6, 125.1, 123.7, 117.4, 116.7, 112.5, 70.4, 38.2, 38.1, 29.0, 21.6; IR (film) 2958, 2919, 2851, 1716, 1672, 1569, 1466, 1352, 1237, 1164, 1089, 1019 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{21}NO_5S$: 423.1140 Found: 423.1164; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 12.4 min and *minor*-isomer t_r = 16.9 min.



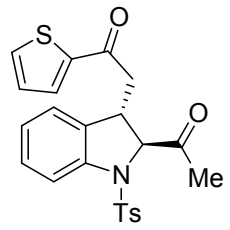
***trans*-2o**

2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(furan-2-yl)ethanone (*trans*-2o) 39 mg, 92%, white solid; m.p. 123-125 °C; $[\alpha]_D^{22}$ = 110.2 (*c* = 0.31, $CHCl_3$); 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.53 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.31–7.27 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10–7.02 (m, 2H), 7.00 (d, *J* = 3.3 Hz, 1H), 6.53 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.40 (d, *J* = 3.3 Hz, 1H), 3.92–3.84 (m, 1H), 2.62 (dd, *J* = 17.7, 6.2 Hz, 1H), 2.47 (s, 3H), 2.34 (s, 3H), 2.02 (dd, *J* = 17.7, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 186.0, 152.1, 146.5, 144.6, 140.7, 134.0, 133.7, 129.8, 128.8, 127.4, 125.2, 125.0, 117.2, 116.8, 112.4, 73.5, 44.0, 38.7, 26.8, 21.6; IR (film) 2958, 2920, 2851, 1716, 1672, 1569, 1466, 1352, 1237, 1164, 1089, 1019 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{21}NO_5S$: 423.1140 Found: 423.1124; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 14.0 min and *major*-isomer t_r = 18.8 min.



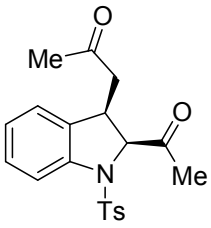
***cis*-2p**

2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)-1-(thiophen-2-yl)ethanone (*cis*-2p) 38 mg, 86%, colorless gum; $[\alpha]_D^{20}$ = 49.1 (*c* = 0.22, $CHCl_3$); 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.68–7.60 (m, 4H), 7.30–7.26 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.05 (td, *J* = 7.5, 0.8 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 4.91 (d, *J* = 10.1 Hz, 1H), 3.86 (dd, *J* = 15.7, 8.8 Hz, 1H), 3.34 (dd, *J* = 17.9, 8.3 Hz, 1H), 3.18 (dd, *J* = 17.9, 6.1 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 190.5, 144.7, 143.4, 141.1, 134.5, 134.2, 134.1, 132.3, 129.9, 128.7, 128.3, 127.2, 125.2, 123.6, 116.8, 70.3, 39.1, 38.7, 29.1, 21.6; IR (film) 2957, 2921, 2851, 1714, 1656, 1596, 1478, 1414, 1351, 1233, 1164, 1089, 1056 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{21}NO_4S_2$: 439.0912 Found: 439.0912; Chiralpak IB column and IB guard column (15% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 17.2 min and *minor*-isomer t_r = 22.2 min.



***trans*-2p**

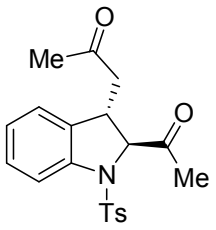
2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-(thiophen-2-yl)ethanone (*trans*-2p) 38 mg, 86%, white solid; m.p. 165-167 °C; $[\alpha]_D^{19}$ = 144.6 (*c* = 0.48, $CHCl_3$); 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.28 (ddd, *J* = 6.1, 4.8, 1.6 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.12–7.03 (m, 3H), 4.41 (d, *J* = 3.1 Hz, 1H), 3.95–3.86 (m, 1H), 2.64 (dd, *J* = 17.6, 6.1 Hz, 1H), 2.48 (s, 3H), 2.32 (s, 3H), 2.09 (dd, *J* = 17.6, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 189.7, 144.6, 143.3, 140.7, 134.2 (two peaks overlapping), 133.8, 131.9, 129.9, 128.9, 128.0, 127.4, 125.3, 125.1, 116.9, 73.5, 44.8, 39.1, 26.9, 21.6; IR (film) 2955, 2922, 2852, 1726, 1657, 1474, 1416, 1353, 1251, 1213, 1164, 1067, 1055 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{21}NO_4S_2$: 439.0912 Found: 439.0902; Chiralpak IA column and IA guard column (10% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 31.2 min and *major*-isomer t_r = 42.5 min.



***cis*-4a**

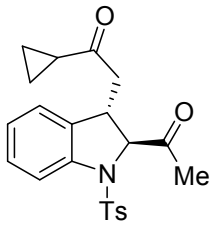
2-((2*S*,3*R*)-2-Acetyl-1-tosylindolin-3-yl)propan-2-one (*cis*-4a) 24 mg, 65%, white solid; m.p. 150-153 °C; $[\alpha]_D^{25}$ = 53.9 (*c* = 0.32, $CHCl_3$); 87% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.24 (dd, *J* = 15.0, 7.7 Hz, 3H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 4.78 (d, *J* = 10.2 Hz, 1H), 3.69 (dt, *J* = 15.6, 7.8 Hz, 1H), 2.79 (dd, *J* = 18.4, 8.7 Hz, 1H), 2.69 (dd, *J* = 18.4, 5.8 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 206.3, 144.6, 141.0, 134.5, 134.1, 129.9, 128.7, 127.1, 125.1, 123.4, 116.7, 70.3, 43.1, 38.6, 30.2, 29.1, 21.6; IR (film) 2960, 2923, 2851, 1721, 1706, 1595, 1477, 1459, 1356, 1234, 1115, 1086, 1057 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{20}H_{21}NO_4S$: 371.1191 Found: 371.1186; Chiralpak AD-H column and AD-H guard

column (15% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 21.0 min and *minor*-isomer t_r = 34.5 min.



***trans*-4a**

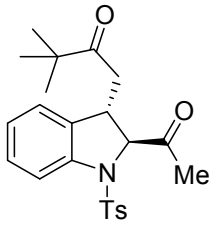
1-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)propan-2-one (*trans*-4a) 24 mg, 65%, colorless gum; $[\alpha]_D^{25}$ = 184.8 (*c* = 0.25, $CHCl_3$); 82% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.28–7.23 (m, 3H), 7.09–6.99 (m, 2H), 4.20 (d, *J* = 3.8 Hz, 1H), 3.76–3.69 (m, 1H), 2.45 (s, 3H), 2.40 (s, 3H), 2.19 (dd, *J* = 18.0, 6.2 Hz, 1H), 1.96 (s, 3H), 1.74 (dd, *J* = 18.0, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 205.5, 144.7, 140.7, 133.9, 133.6, 129.8, 128.8, 127.6, 125.1, 124.8, 116.6, 73.6, 48.9, 38.8, 29.8, 26.7, 21.6; IR (film) 2923, 2854, 1714, 1596, 1477, 1461, 1233, 1163, 1090 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{20}H_{21}NO_4S$: 371.1191 Found: 371.1203; Chiralpak AD-H column and AD-H guard column (7% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *major*-isomer t_r = 49.4 min and *minor*-isomer t_r = 61.6 min.



***trans*-4b**

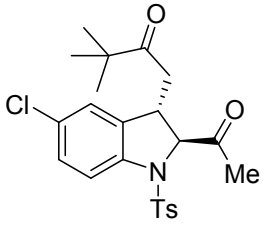
2-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-1-cyclopropylethanone (*trans*-4b) 37 mg, 93%, colorless gum; $[\alpha]_D^{23}$ = 88.9 (*c* = 0.42, $CHCl_3$); 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.31–7.23 (m, 3H), 7.04 (q, *J* = 7.4 Hz, 2H), 4.23 (d, *J* = 3.6 Hz, 1H), 3.78–3.70 (m, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.35 (dd, *J* = 17.8, 6.0 Hz, 1H), 1.81 (dd, *J* = 17.8, 8.4 Hz, 1H), 1.64–1.54 (m, 1H), 1.02–0.94 (m, 2H), 0.86 (dt, *J* = 4.2, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 205.7, 144.6, 140.7, 134.0, 133.8, 129.9, 128.7, 127.5, 125.1, 124.8, 116.6, 73.6, 48.6, 38.9, 26.7, 21.6, 20.6, 11.2, 11.1; IR (film) 2970, 2922, 2852, 1719, 1696, 1596, 1475, 1389, 1353, 1165, 1089, 1052, 1018 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{22}H_{23}NO_4S$: 397.1348 Found: 397.1319; Chiralpak IA column and IA guard

column (35% *i*-PrOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 15.9 min and *major*-isomer t_r = 19.2 min.



***trans*-4c**

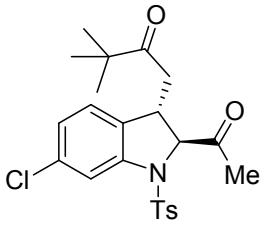
1-((2*S*,3*S*)-2-Acetyl-1-tosylindolin-3-yl)-3,3-dimethylbutan-2-one (*trans*-4c) 40 mg, 98%, colorless gum; $[\alpha]_D^{23}$ = 150.6 (*c* = 0.42, $CHCl_3$); 98% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.31–7.22 (m, 3H), 7.02 (ddd, *J* = 12.2, 9.5, 3.8 Hz, 2H), 4.18 (d, *J* = 3.5 Hz, 1H), 3.76 (td, *J* = 7.0, 3.5 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.12 (dd, *J* = 18.0, 7.2 Hz, 1H), 1.95 (dd, *J* = 18.0, 6.8 Hz, 1H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 206.0, 144.7, 140.7, 134.1, 134.1, 129.9, 128.8, 127.5, 125.1 (two peaks overlapping), 116.6, 74.0, 43.8, 43.0, 39.1, 26.7, 26.0, 21.6; IR (film) 2969, 2926, 1718, 1701, 1597, 1476, 1460, 1353, 1166, 1089, 1054 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{27}NO_4S$: 413.1661 Found: 413.1656; Chiralpak IA column and IA guard column (5% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 15.1 min and *major*-isomer t_r = 19.3 min.



***trans*-4d**

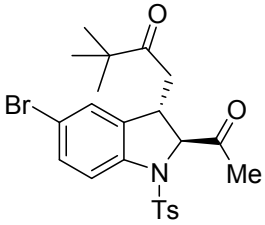
1-((2*S*,3*S*)-2-Acetyl-5-chloro-1-tosylindolin-3-yl)-3,3-dimethylbutan-2-one (*trans*-4d) 43 mg, 97%, colorless gum; $[\alpha]_D^{26}$ = 98.9 (*c* = 1.1, $CHCl_3$); 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.30–7.23 (m, 3H), 6.99 (d, *J* = 1.8 Hz, 1H), 4.19 (d, *J* = 3.3 Hz, 1H), 3.73 (td, *J* = 7.0, 3.3 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 2.09 (dd, *J* = 18.1, 7.1 Hz, 1H), 1.91 (dd, *J* = 18.1, 7.0 Hz, 1H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 205.5, 145.0, 139.4, 136.1, 133.9, 130.5, 130.0, 128.9, 127.5, 125.4, 117.7, 74.0, 43.8, 42.7, 38.9, 26.8, 26.0, 21.6; IR (film) 2968, 2930, 2872, 1720, 1703, 1597, 1469, 1400, 1164, 1113, 1088, 1054 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$

$C_{23}H_{26}ClNO_4S$: 447.1271 Found: 447.1263; Chiralpak IA column and IA guard column (3% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 20.5 min and *major*-isomer t_r = 23.9 min.



***trans*-4e**

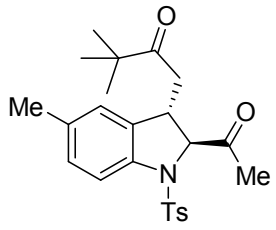
1-((2*S*,3*S*)-2-Acetyl-6-chloro-1-tosylindolin-3-yl)-3,3-dimethylbutan-2-one (*trans*-4e) 35 mg, 78%, colorless gum; $[\alpha]_D^{26}$ = 201.2 (*c* = 1.2, $CHCl_3$); 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.00 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 4.18 (d, *J* = 3.4 Hz, 1H), 3.70 (td, *J* = 6.9, 3.4 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.07 (dd, *J* = 18.1, 7.4 Hz, 1H), 1.99 (dd, *J* = 18.1, 6.7 Hz, 1H), 0.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 205.1, 145.1, 141.9, 134.5, 134.0, 132.5, 130.1, 127.5, 126.0, 125.2, 116.7, 74.3, 43.8, 42.9, 38.8, 26.7, 26.0, 21.6; IR (film) 2962, 2928, 2870, 1710, 1694, 1596, 1415, 1354, 1302, 1189, 1171, 1085, 1030 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{26}ClNO_4S$: 447.1271 Found: 447.1249; Chiralpak IA column and IA guard column (13% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 10.5 min and *major*-isomer t_r = 14.8 min.



***trans*-4f**

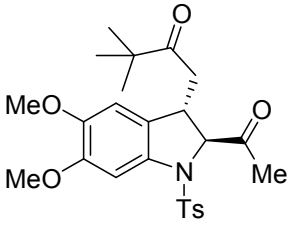
1-((2*S*,3*S*)-2-Acetyl-5-bromo-1-tosylindolin-3-yl)-3,3-dimethylbutan-2-one (*trans*-4f) 45 mg, 92%, white solid; m.p. 64-66 °C; $[\alpha]_D^{26}$ = 106.2 (*c* = 1.3, $CHCl_3$); 98% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.5, 2.9 Hz, 3H), 7.39 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 1.3 Hz, 1H), 4.18 (d, *J* = 3.4 Hz, 1H), 3.72 (td, *J* = 6.9, 3.3 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 2.11 (dd, *J* = 18.1, 7.0 Hz, 1H), 1.91 (dd, *J* = 18.1, 7.1 Hz, 1H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 205.4, 145.0, 140.0, 136.4, 133.9, 131.8, 130.0, 128.3, 127.5, 118.0, 118.0, 74.0, 43.8, 42.8, 38.9, 26.8, 26.0, 21.6; IR

(film) 2967, 2871, 1720, 1702, 1596, 1467, 1354, 1163, 1111, 1088, 1054 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{23}H_{26}BrNO_4S$: 491.0766 Found: 491.0787; Chiralpak IA column and IA guard column (3% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 21.5 min and *major*-isomer t_r = 24.6 min.



***trans*-4g**

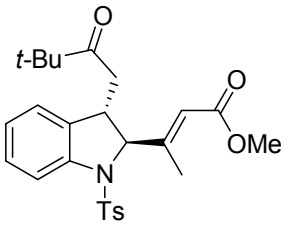
1-((2*S*,3*S*)-2-Acetyl-5-methyl-1-tosylindolin-3-yl)-3,3-dimethylbutan-2-one (*trans*-4g) 42 mg, 98%, colorless gum; $[\alpha]_D^{26}$ = 58.0 (*c* = 0.44, $CHCl_3$); 99% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.2, 5.3 Hz, 3H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.07 (dd, *J* = 8.2, 0.6 Hz, 1H), 6.79 (s, 1H), 4.15 (d, *J* = 3.4 Hz, 1H), 3.71 (td, *J* = 7.0, 3.3 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H), 2.10 (dd, *J* = 18.0, 7.1 Hz, 1H), 1.87 (dd, *J* = 18.0, 6.9 Hz, 1H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.8, 206.2, 144.5, 138.3, 135.0, 134.3, 134.1, 129.9, 129.4, 127.5, 125.6, 116.5, 74.2, 43.8, 43.0, 39.1, 26.8, 26.0, 21.6, 21.0; IR (film) 2965, 2927, 2869, 1720, 1703, 1597, 1486, 1353, 1211, 1164, 1088, 1054 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{24}H_{29}NO_4S$: 427.1817 Found: 427.1807; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 12.1 min and *major*-isomer t_r = 14.8 min.



***trans*-4h**

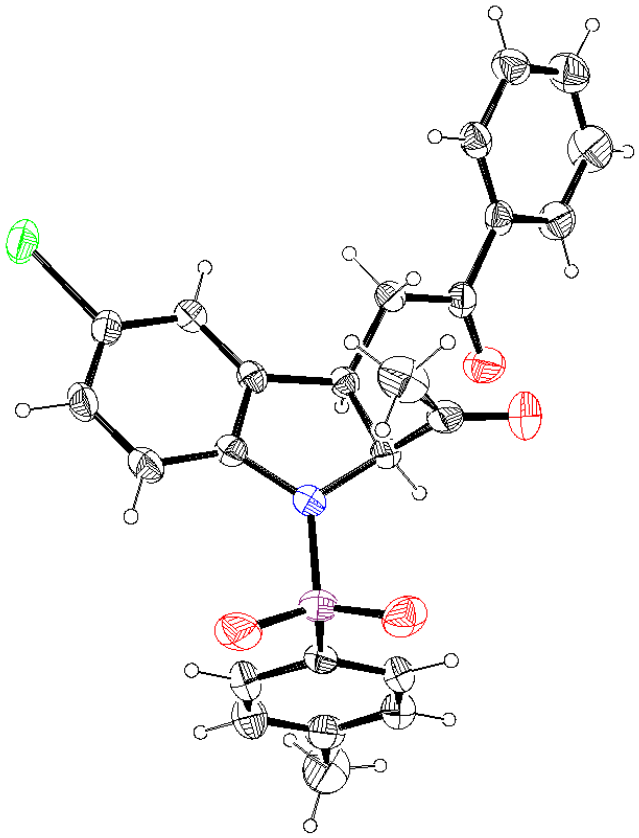
1-((2*S*,3*S*)-2-Acetyl-5,6-dimethoxy-1-tosylindolin-3-yl)-3,3-dimethylbutan-2-one (*trans*-4h) 40 mg, 85%, White solid; m.p. 66-68 °C; $[\alpha]_D^{26}$ = 207.4 (*c* = 0.98, $CHCl_3$); 99% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.38 (s, 1H), 7.2 (d, *J* = 8.3 Hz, 2H), 6.52 (s, 1H), 4.11 (d, *J* = 2.7 Hz, 1H), 3.97 (s, 3H), 3.76 (d, *J* = 10.8 Hz, 3H), 3.75–3.69 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 1.84 (dd, *J* = 17.9, 6.1 Hz, 1H), 1.78 (dd, *J* = 17.9, 8.3 Hz, 1H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.9, 206.6, 149.5, 147.2, 144.7, 133.8, 133.6, 129.9, 127.6, 126.0, 107.8, 101.4, 74.4, 56.3, 56.1, 43.8, 43.5, 39.1, 27.0, 25.9,

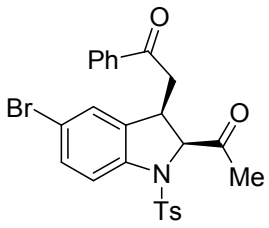
21.6; IR (film) 2963, 2932, 2869, 1720, 1701, 1597, 1499, 1464, 1415, 1351, 1263, 1215, 1161, 1089, 996 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{25}H_{31}NO_6S$: 473.1872 Found: 473.1850; Chiralpak IA column and IA guard column (10% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 16.7 min and *major*-isomer t_r = 22.4 min.



Synthesis of compound 5. To a solution of compound *trans*-**4c** (21 mg, 0.05 mmol) in toluene (0.3 mL) was added methyl (triphenylphosphoranylidene)acetate (25 mg, 0.08 mmol). The solution was stirred at 90 °C for 18 h. Then, the resulting mixture was concentrated in vacuo and purified by flash column chromatography with 15% EtOAc/hexanes as eluent to afford desired product **5** as an white solid (11 mg, 45%); m.p. 193-195 °C; $[\alpha]_D^{26}$ = +62.5 (*c* = 0.36, $CHCl_3$); 98% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.29–7.23 (m, 4H), 7.05–6.94 (m, 2H), 5.96 (s, 1H), 4.18 (s, 1H), 3.67 (s, 3H), 3.41 (dd, *J* = 7.0, 4.9 Hz, 1H), 2.38 (s, 3H), 2.13 (d, *J* = 1.1 Hz, 3H), 2.09–1.90 (m, 2H), 0.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 166.8, 155.3, 144.3, 141.3, 135.2, 134.2, 129.8, 128.8, 127.2, 125.2, 124.8, 116.3, 116.2, 73.4, 51.0, 44.2, 43.8, 42.0, 25.9, 21.5, 14.9; IR (neat) 2961, 2910, 2850, 1714, 1655, 1474, 1348, 1324, 1259, 1214, 1169, 1145, 1087, 1052, 1032, 998 cm^{-1}; HRMS (EI) m/z calcd for $[M]^+$ $C_{26}H_{31}NO_5S$: 469.1923 Found: 469.1904; Chiralpak IA column and IA guard column (1% EtOH:hexanes, 1.0 mL/min flow, λ = 254 nm); *minor*-isomer t_r = 51.8 min and *major*-isomer t_r = 57.4 min.

Crystallography Data for Compound *cis*-2d



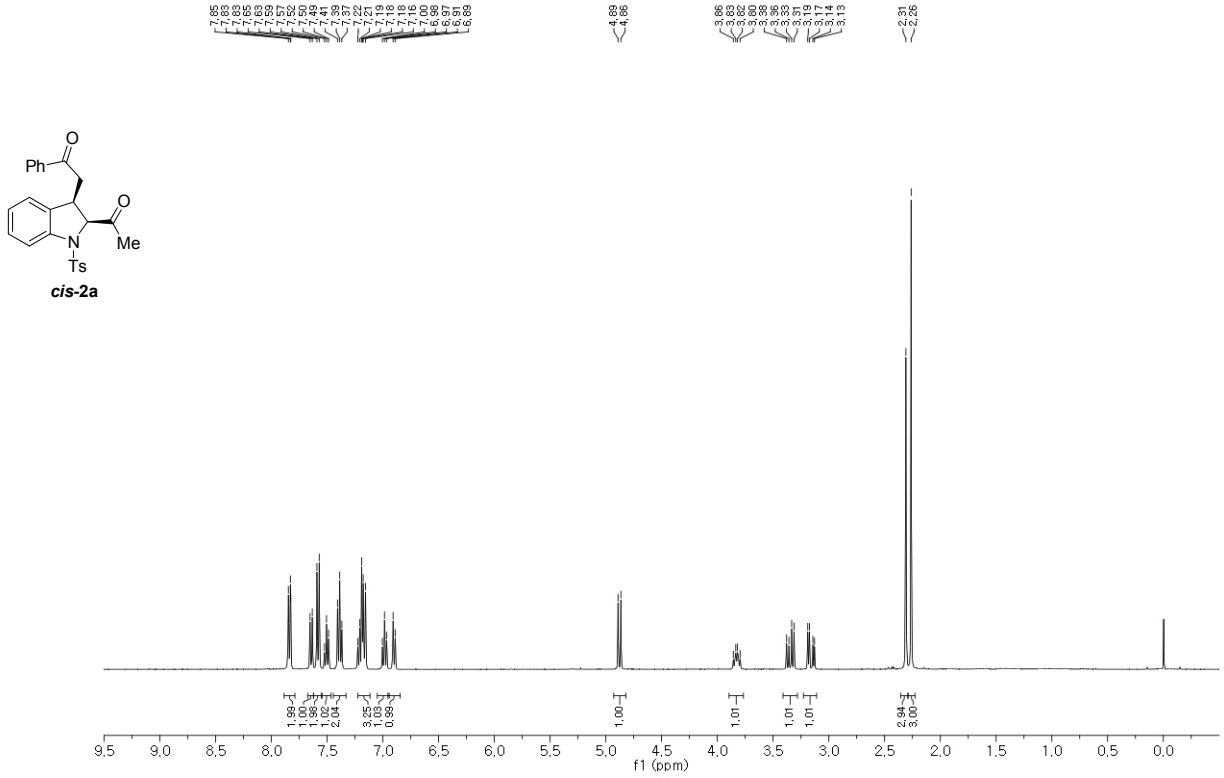


***cis*-2d**

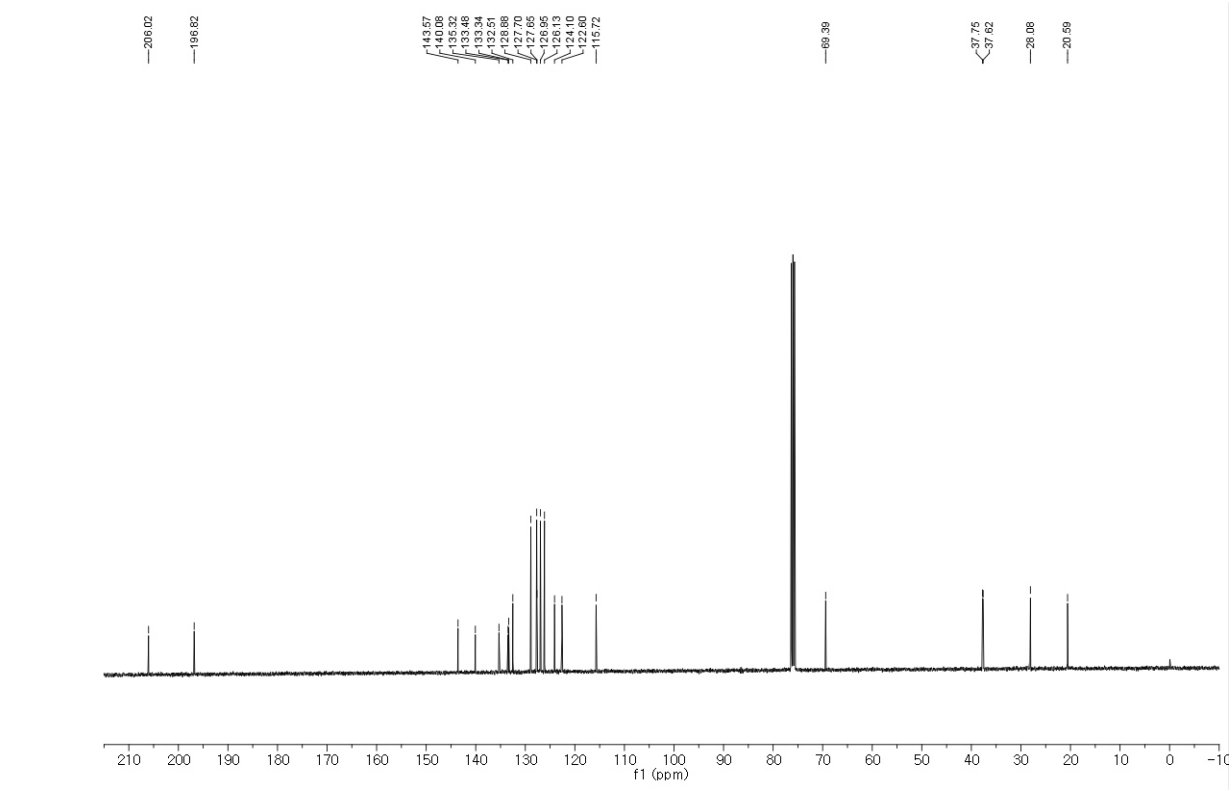
Identification code	SGK0603	
Empirical formula	C_{25} H_{22} Br N O_4 S	
Formula weight	512.41	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.3185(9) Å	= 90°.
	b = 14.6660(11) Å	= 90°.
	c = 14.8630(14) Å	= 90°.
Volume	2249.2(3) $Å^3$	
Z	4	
Density (calculated)	1.513 Mg/m^3	
Absorption coefficient	1.953 mm^{-1}	

F(000)	1048
Crystal size	0.19 x 0.16 x 0.10 mm^3
Theta range for data collection	2.40 to 28.32°.
Index ranges	-13<=h<=13, -19<=k<=19, -19<=l<=19
Reflections collected	92751
Independent reflections	5584 [R(int) = 0.0706]
Completeness to theta = 28.32°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8286 and 0.7079
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5584 / 0 / 291
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0565
R indices (all data)	R1 = 0.0415, wR2 = 0.0604
Absolute structure parameter	0.002(5)
Largest diff. peak and hole	0.489 and -0.393 $e.Å^{-3}$

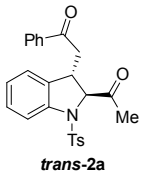
^{1}H NMR (400 MHz) in $CDCl_3$



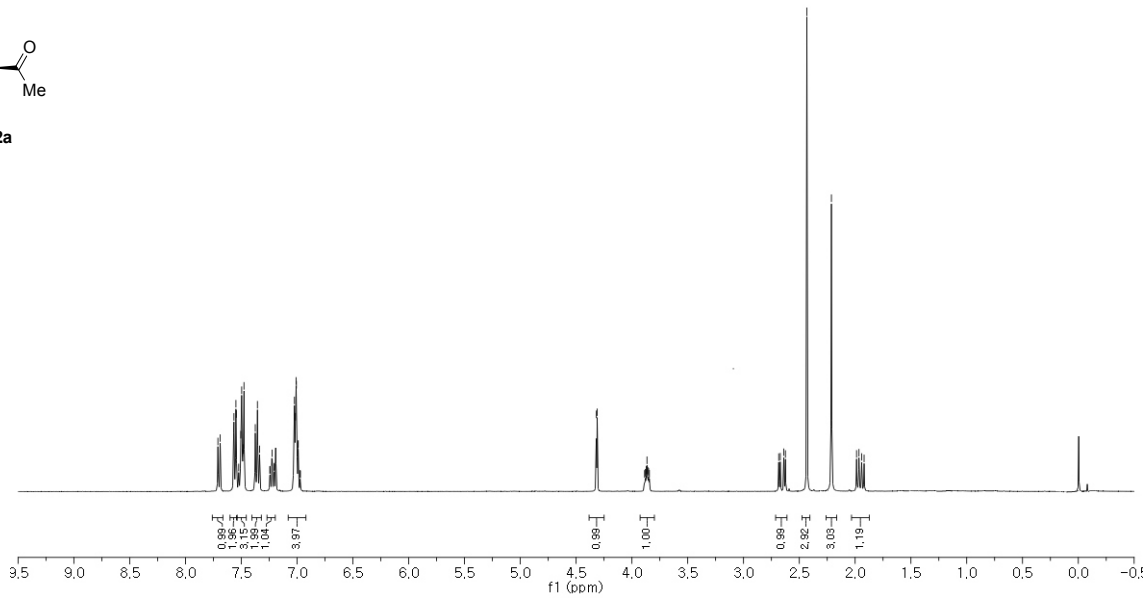
^{13}C NMR (100 MHz) in $CDCl_3$



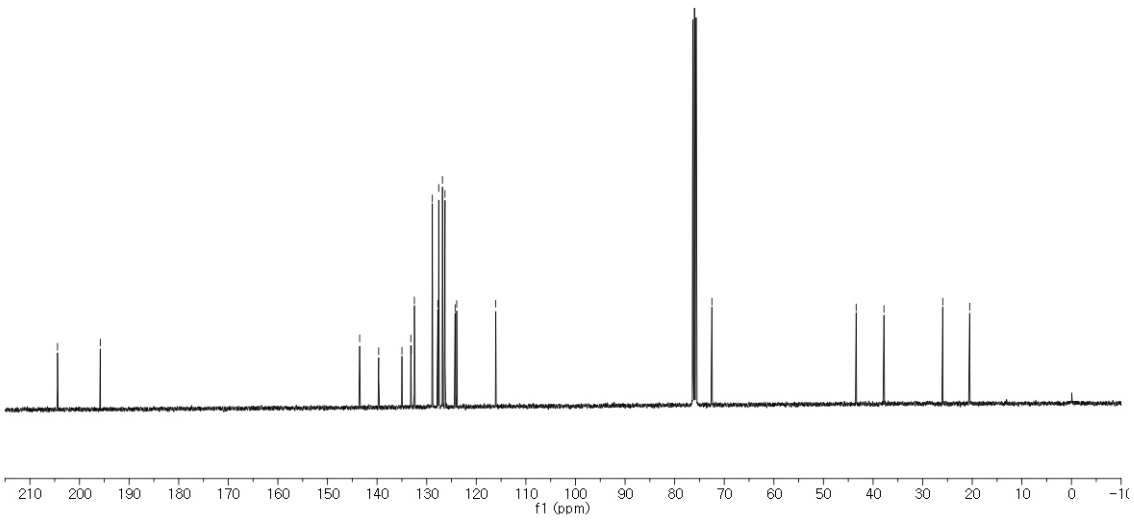
^{1}H NMR (400 MHz) in $CDCl_3$



***trans*-2a**

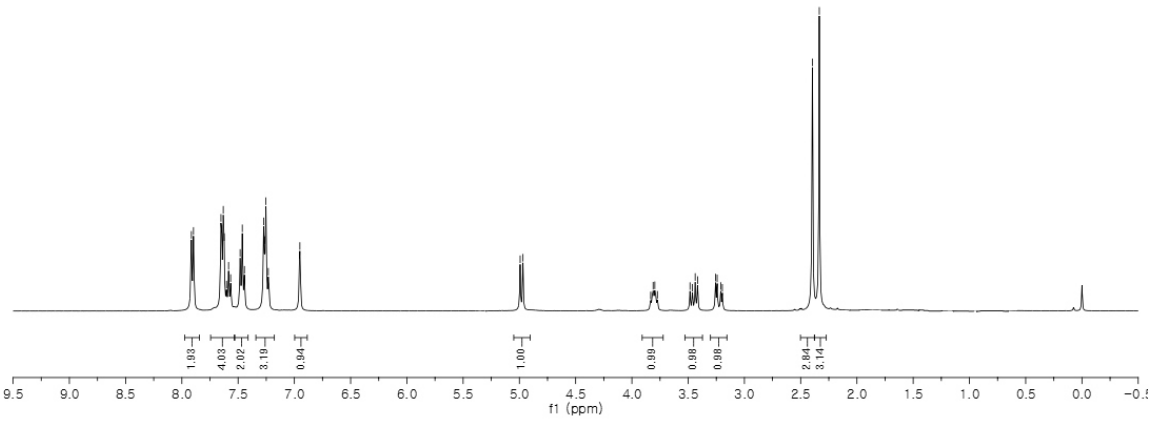


^{13}C NMR (100 MHz) in $CDCl_3$

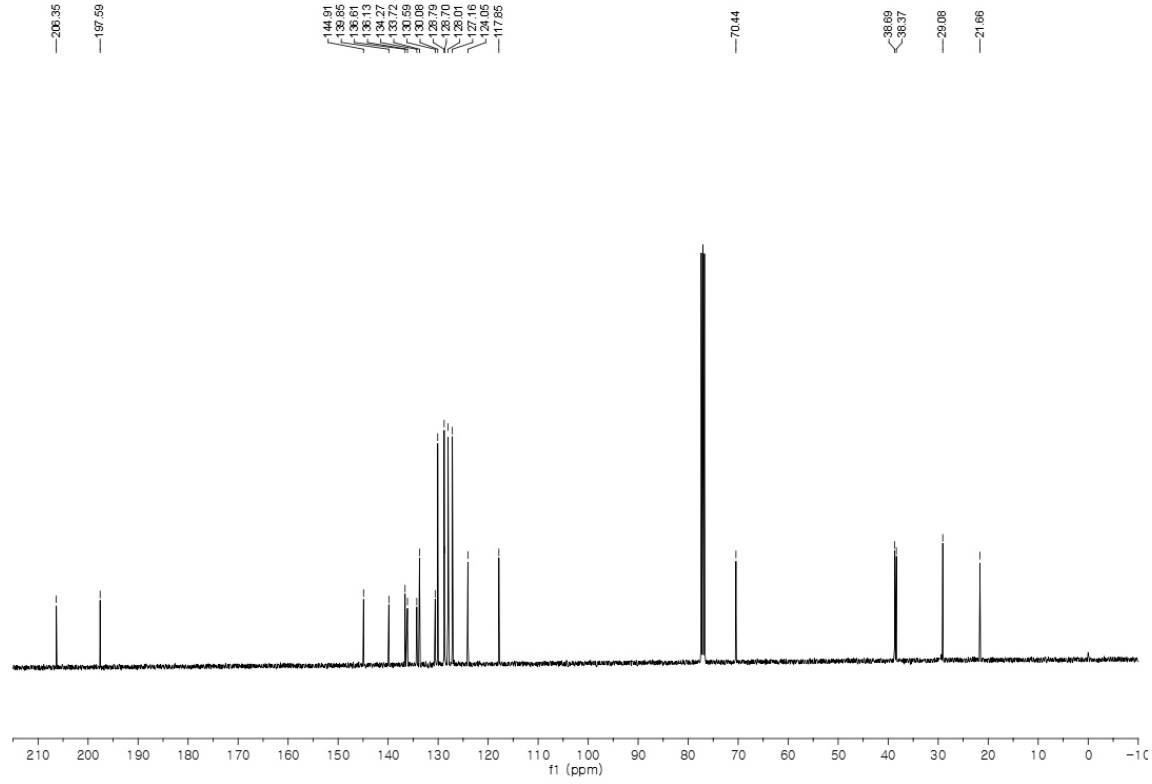


^{1}H NMR (400 MHz) in $CDCl_3$

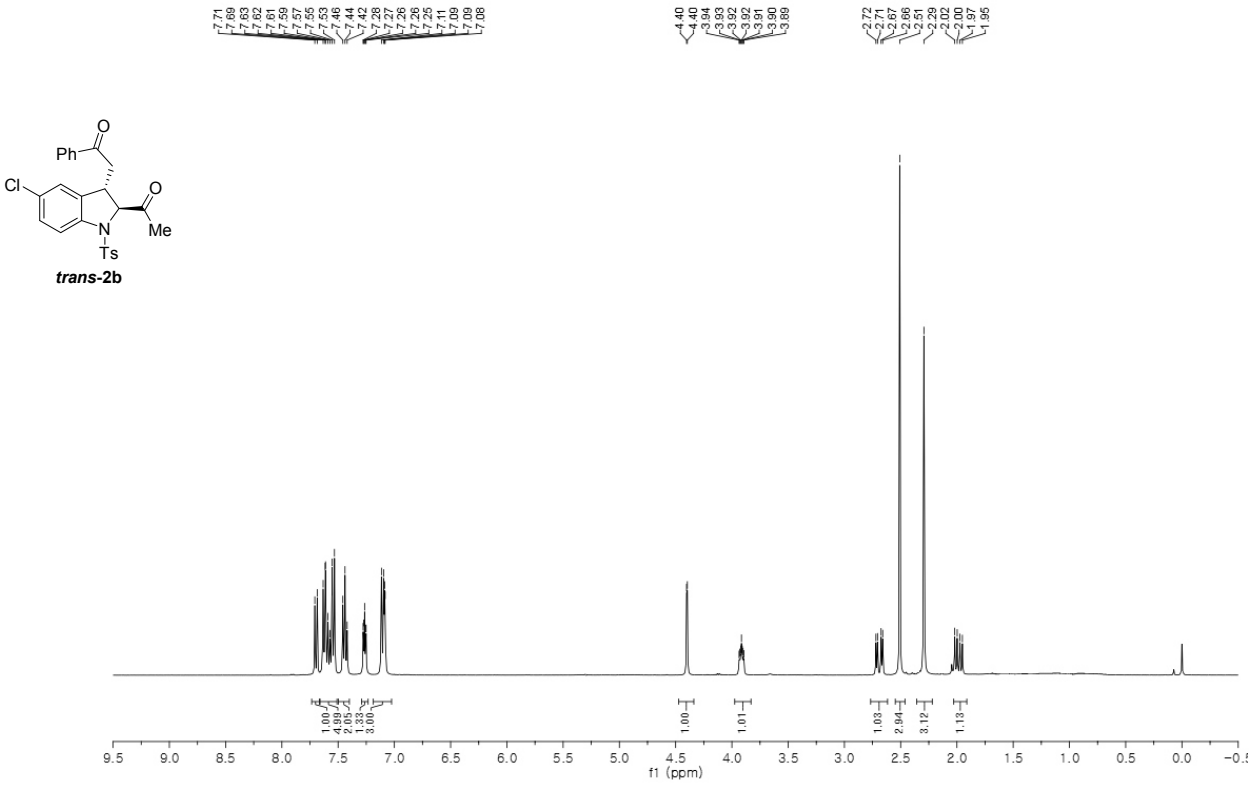
***cis*-2b**



^{13}C NMR (100 MHz) in $CDCl_3$

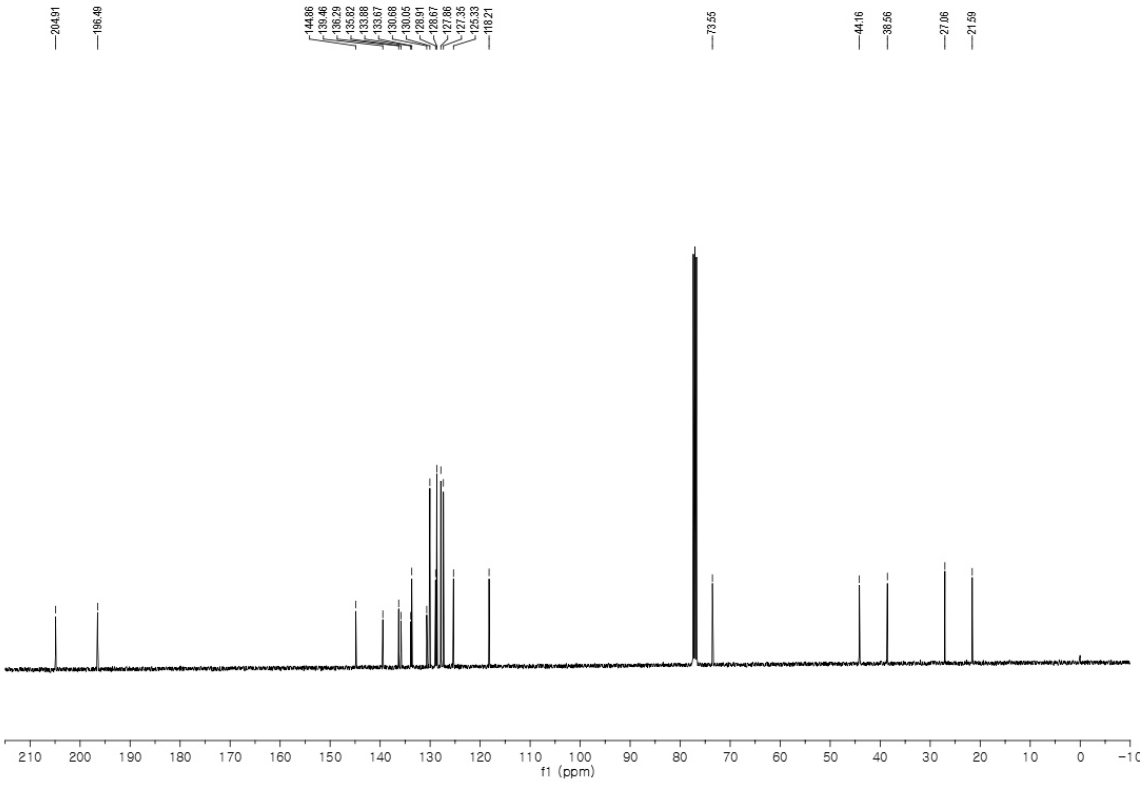


^{1}H NMR (400 MHz) in $CDCl_3$

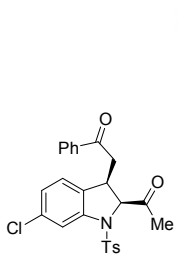


***trans*-2b**

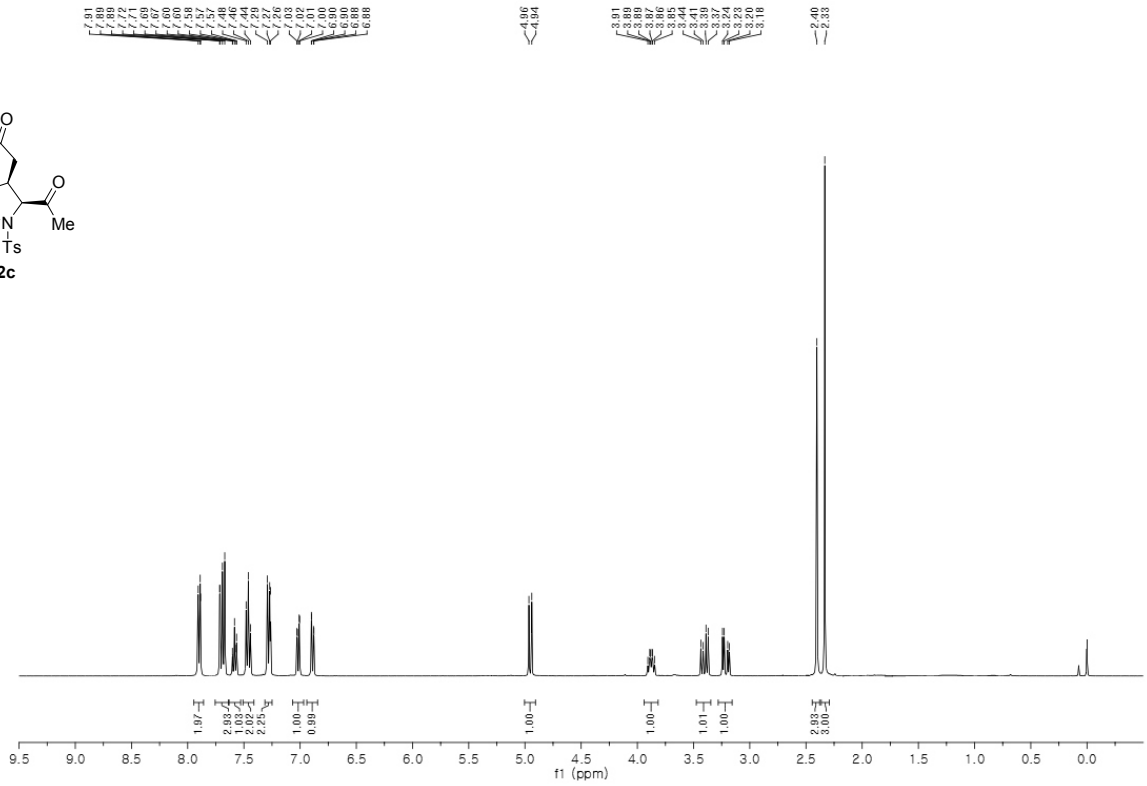
^{13}C NMR (100 MHz) in $CDCl_3$



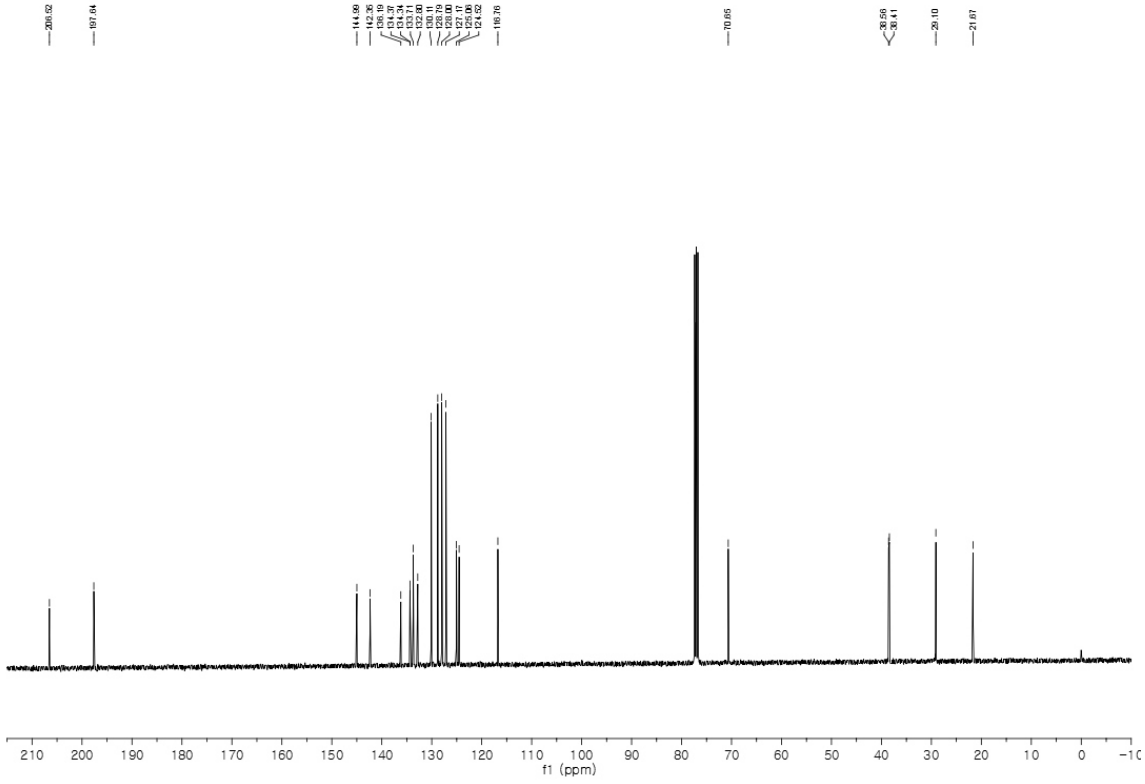
^{1}H NMR (400 MHz) in $CDCl_3$



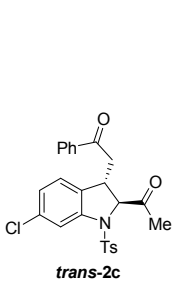
***cis*-2c**



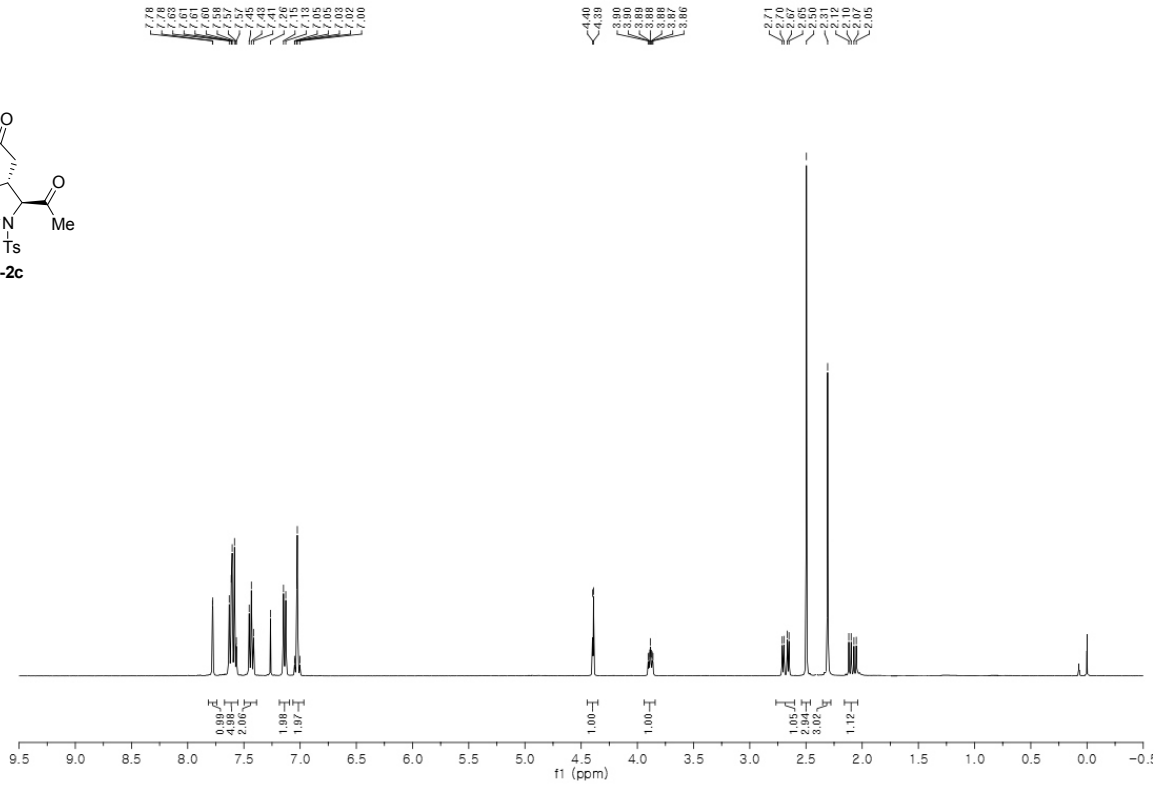
^{13}C NMR (100 MHz) in $CDCl_3$



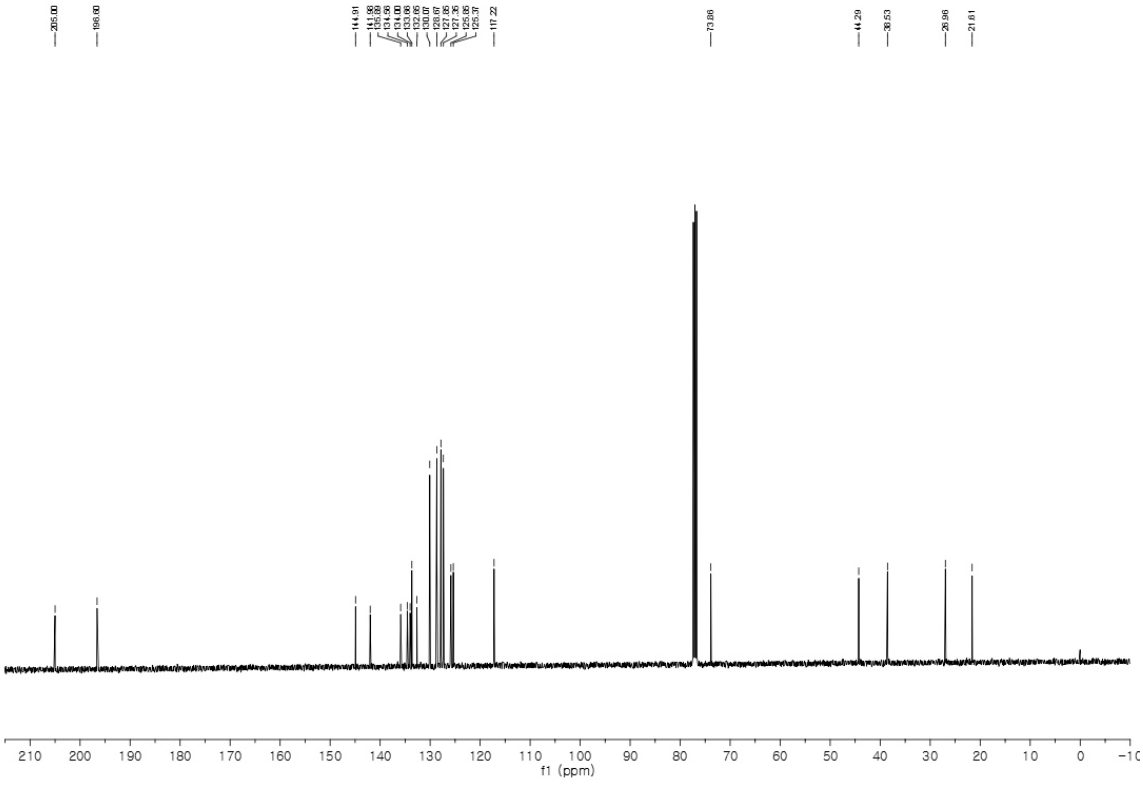
^{1}H NMR (400 MHz) in $CDCl_3$



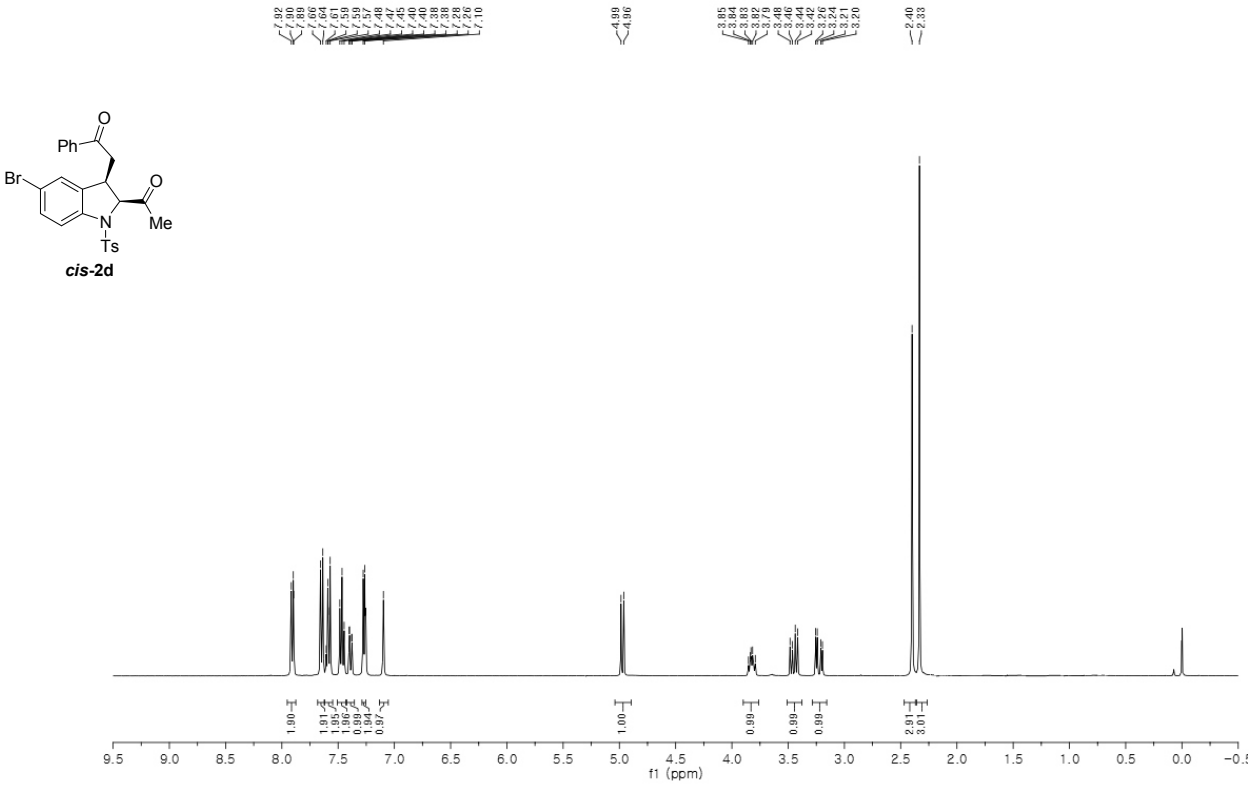
***trans*-2c**



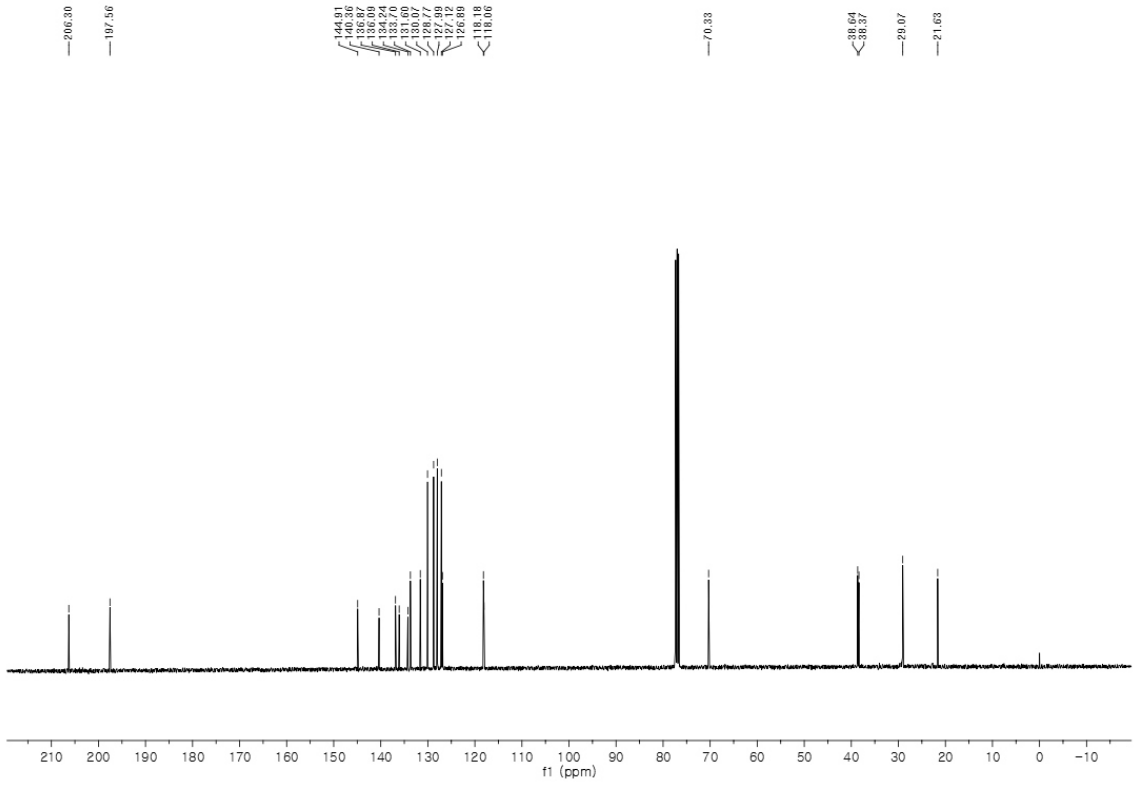
^{13}C NMR (100 MHz) in $CDCl_3$



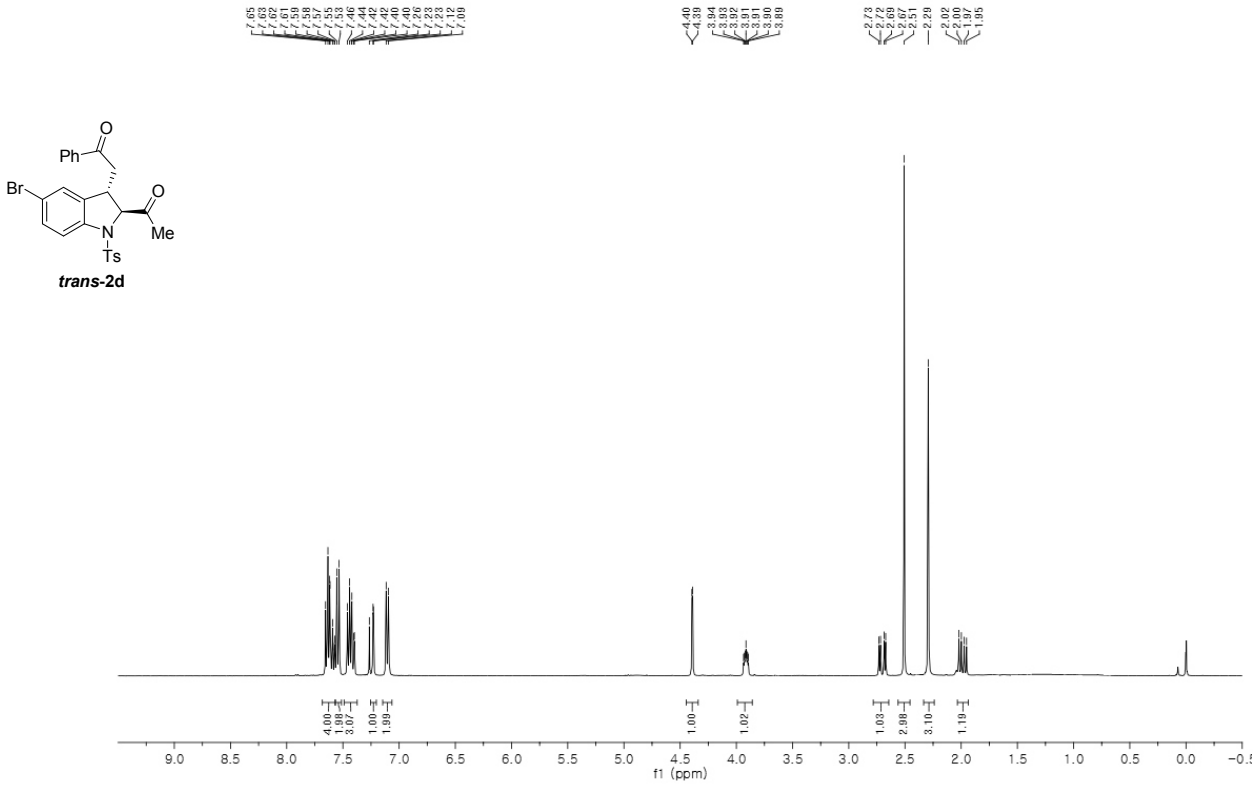
^{1}H NMR (400 MHz) in $CDCl_3$



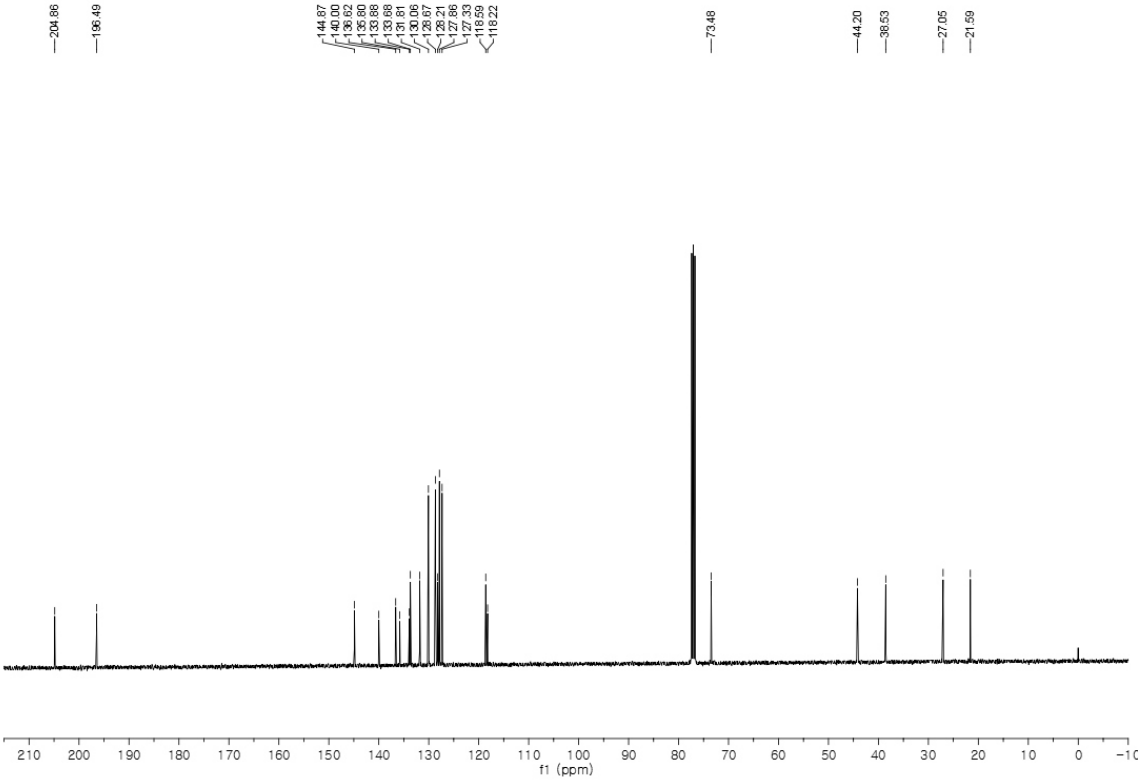
^{13}C NMR (100 MHz) in $CDCl_3$



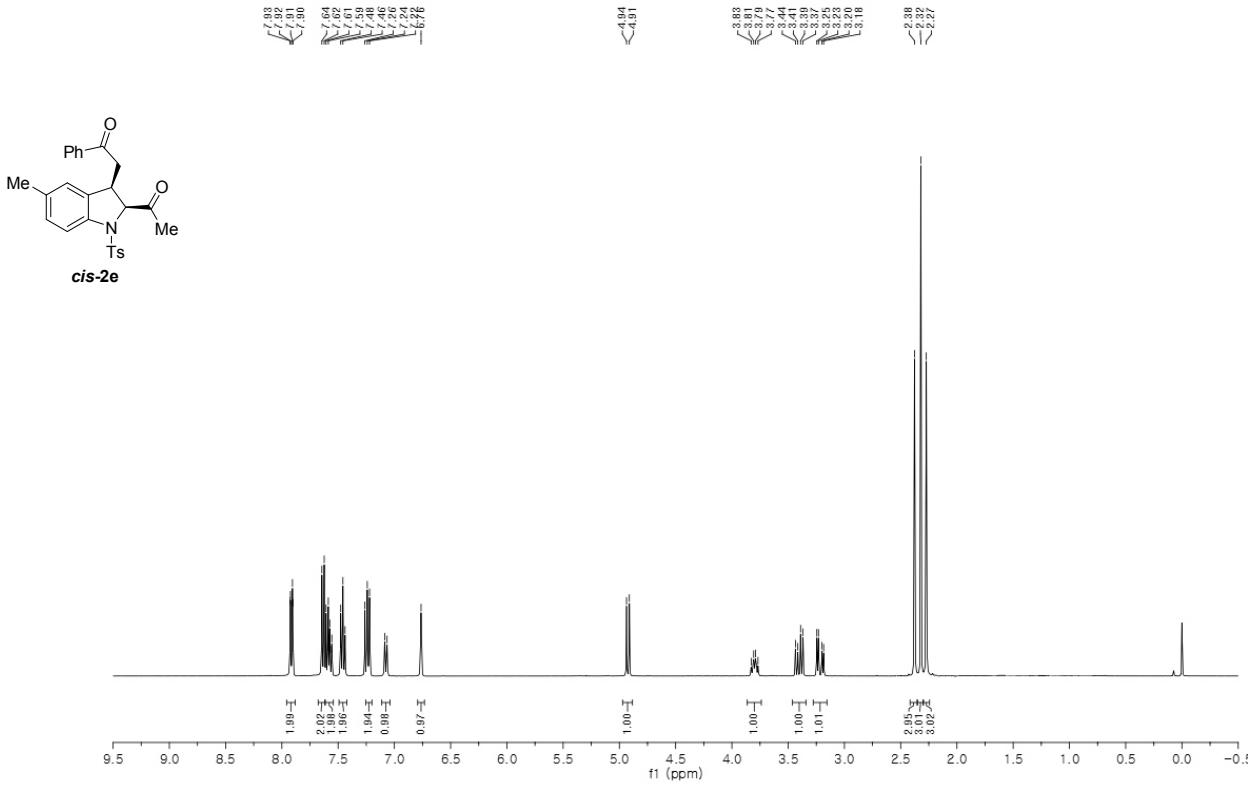
^{1}H NMR (400 MHz) in $CDCl_3$



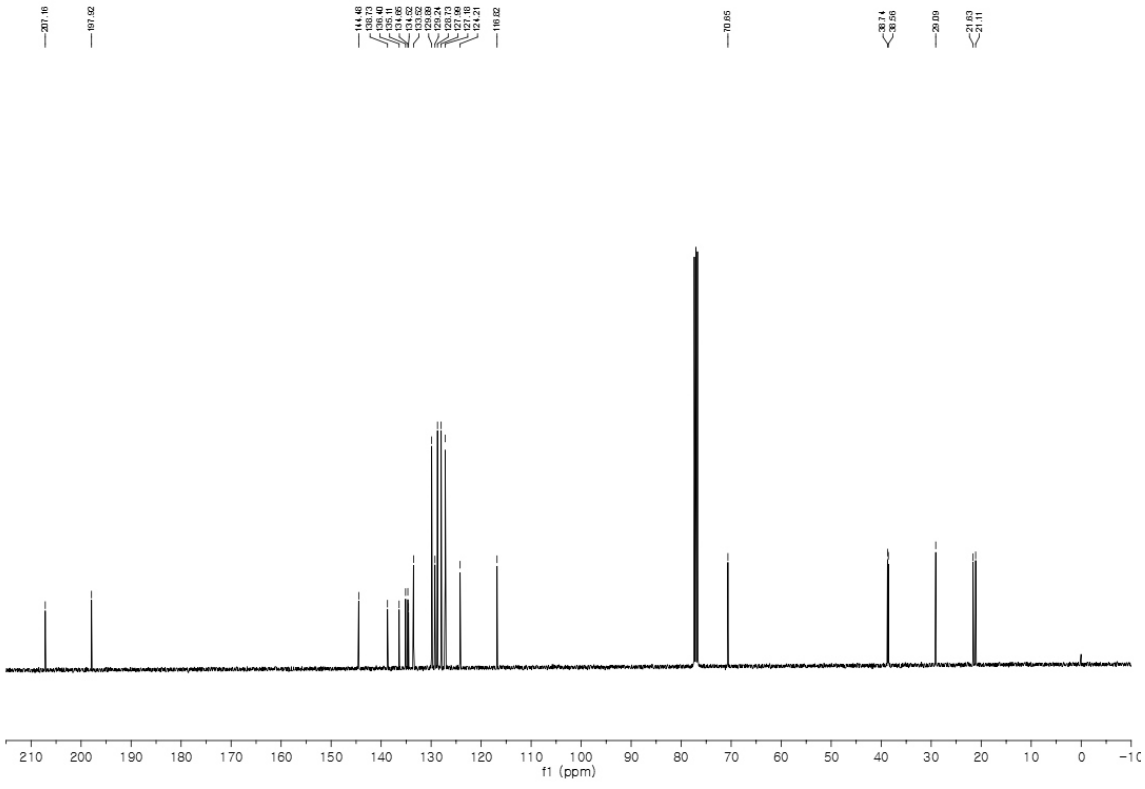
^{13}C NMR (100 MHz) in $CDCl_3$



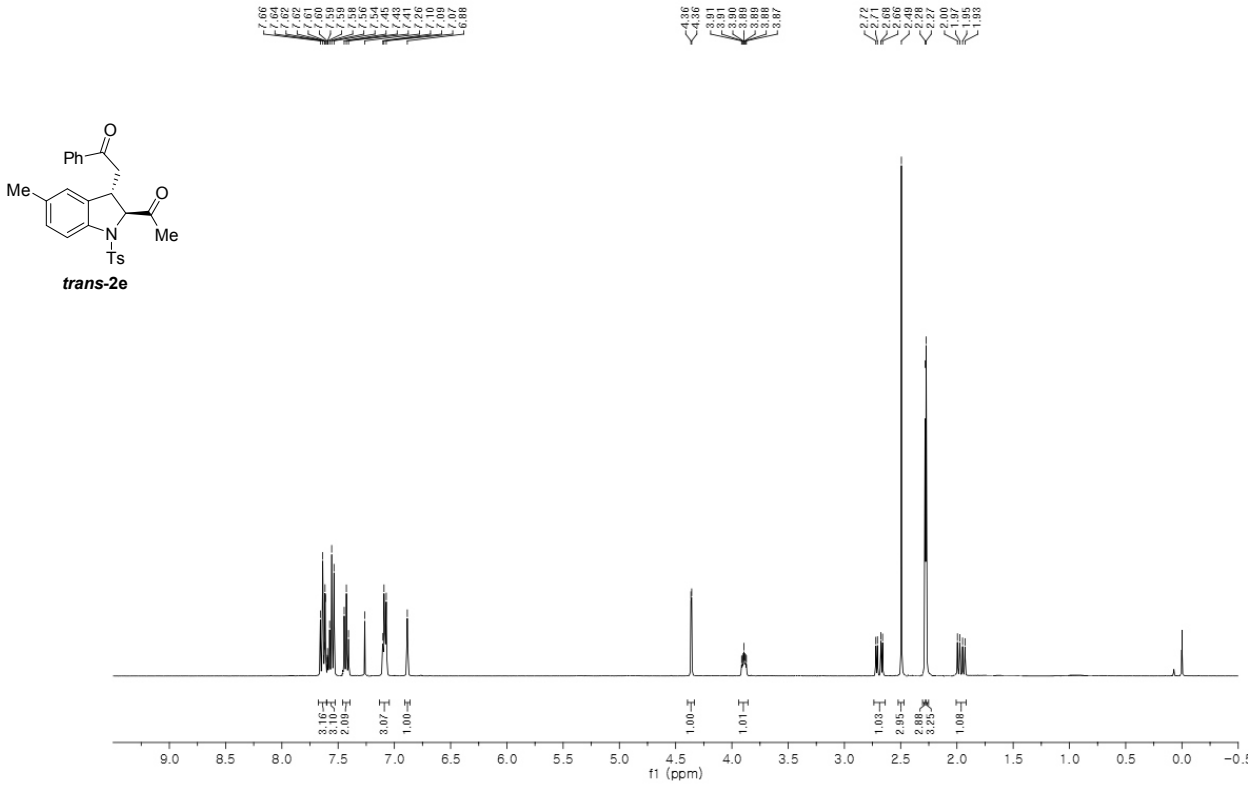
^{1}H NMR (400 MHz) in $CDCl_3$



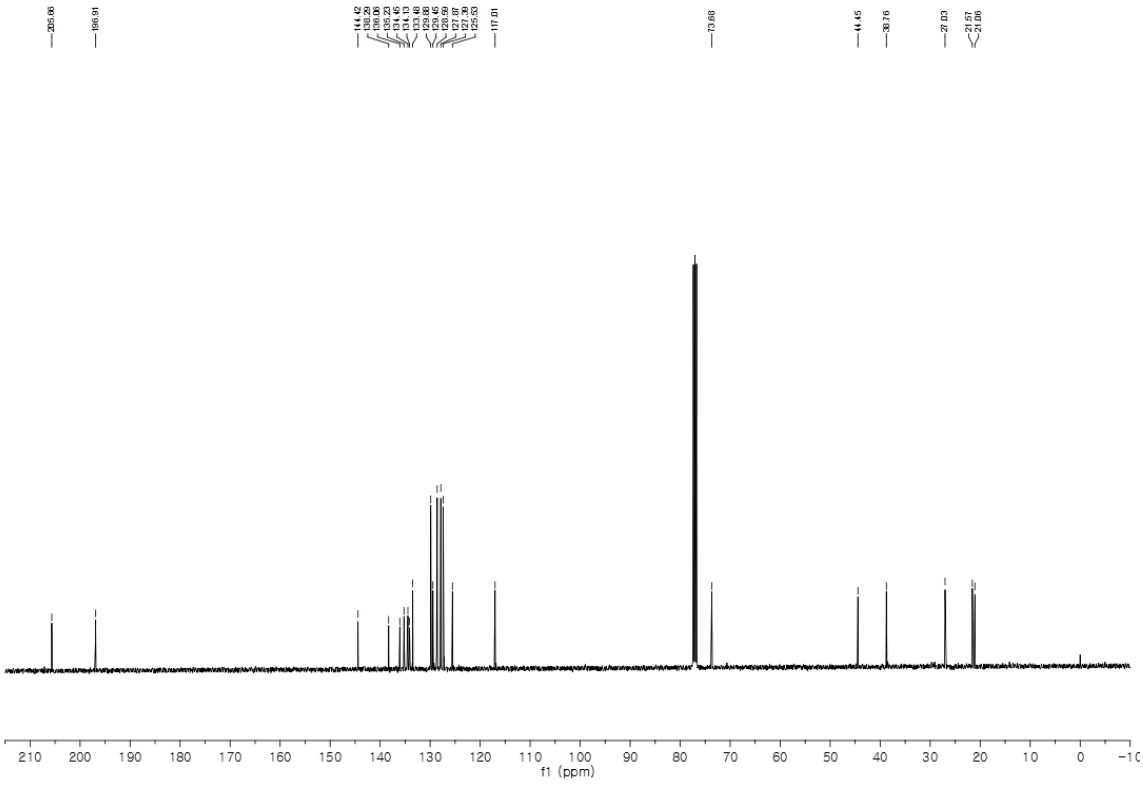
^{13}C NMR (100 MHz) in $CDCl_3$



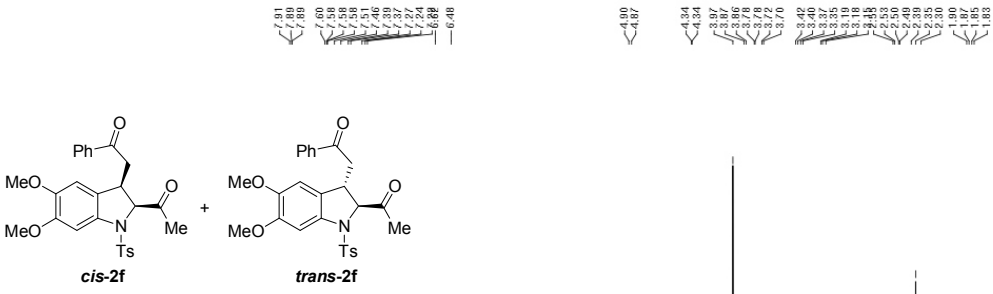
^{1}H NMR (400 MHz) in $CDCl_3$



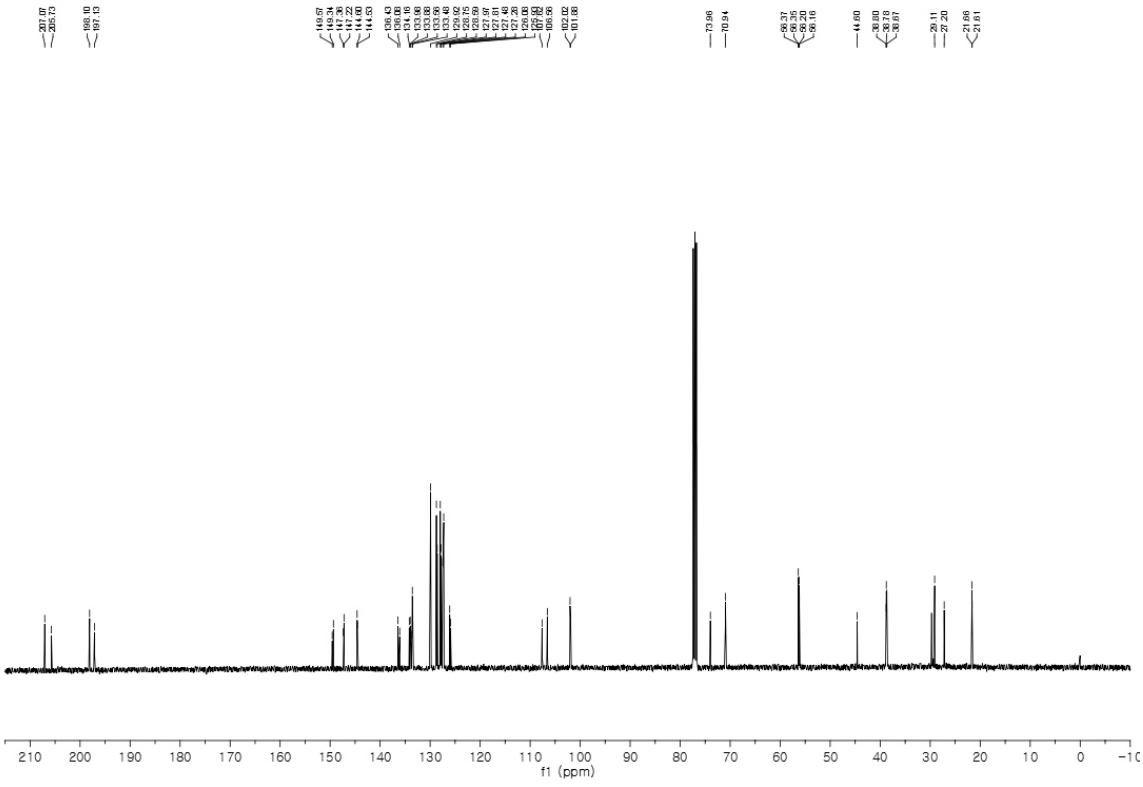
^{13}C NMR (100 MHz) in $CDCl_3$



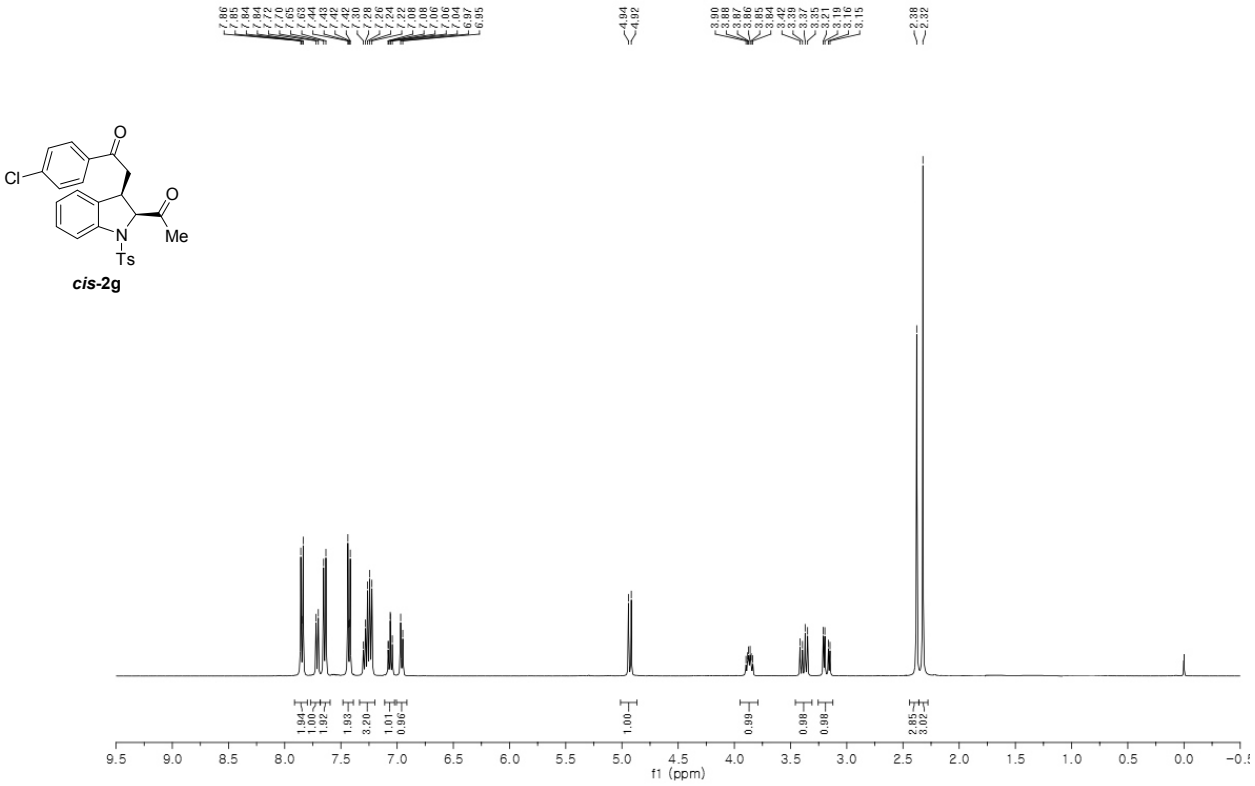
^{1}H NMR (400 MHz) in $CDCl_3$



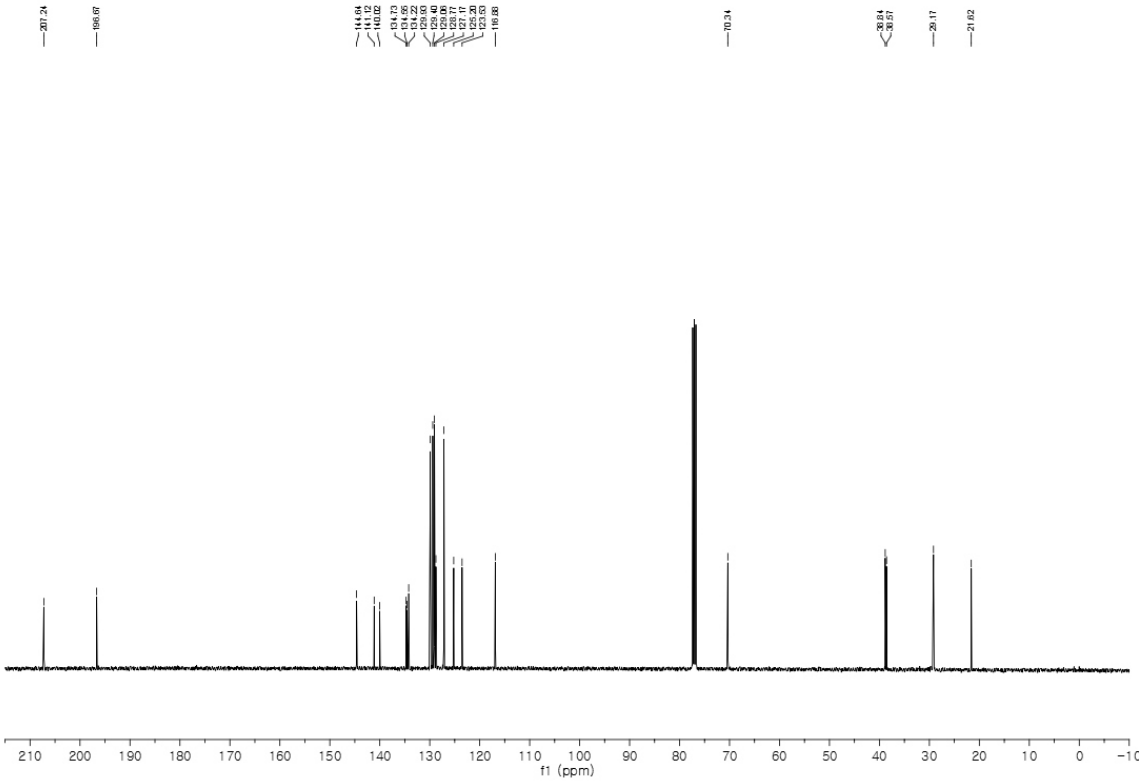
^{13}C NMR (100 MHz) in $CDCl_3$



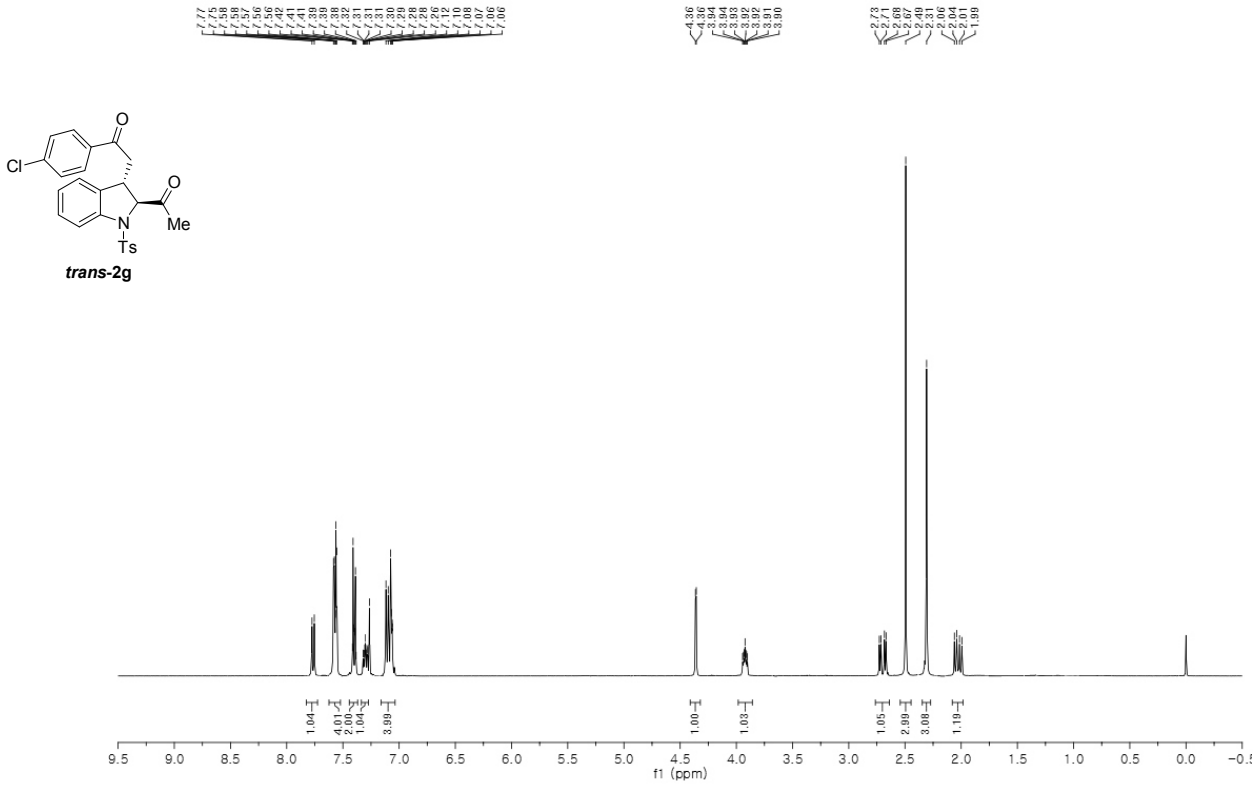
^{1}H NMR (400 MHz) in $CDCl_3$



^{13}C NMR (100 MHz) in $CDCl_3$

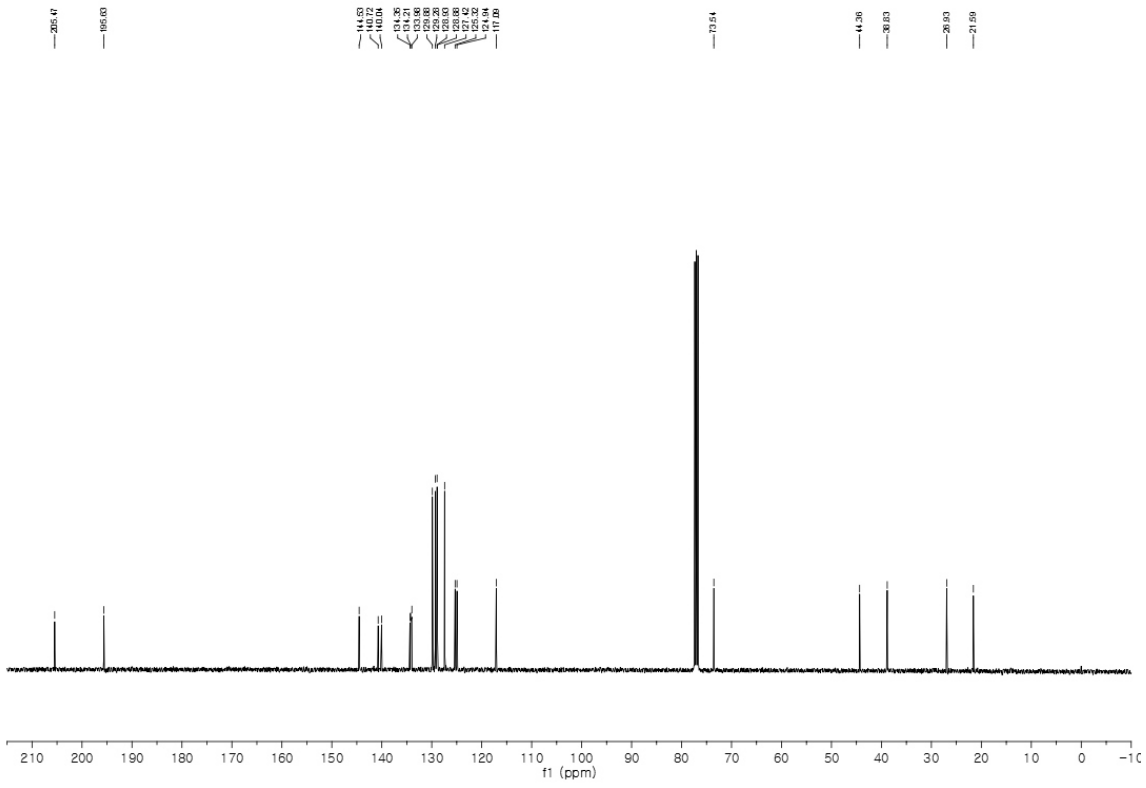


^{1}H NMR (400 MHz) in $CDCl_3$

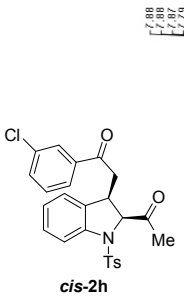


***trans*-2g**

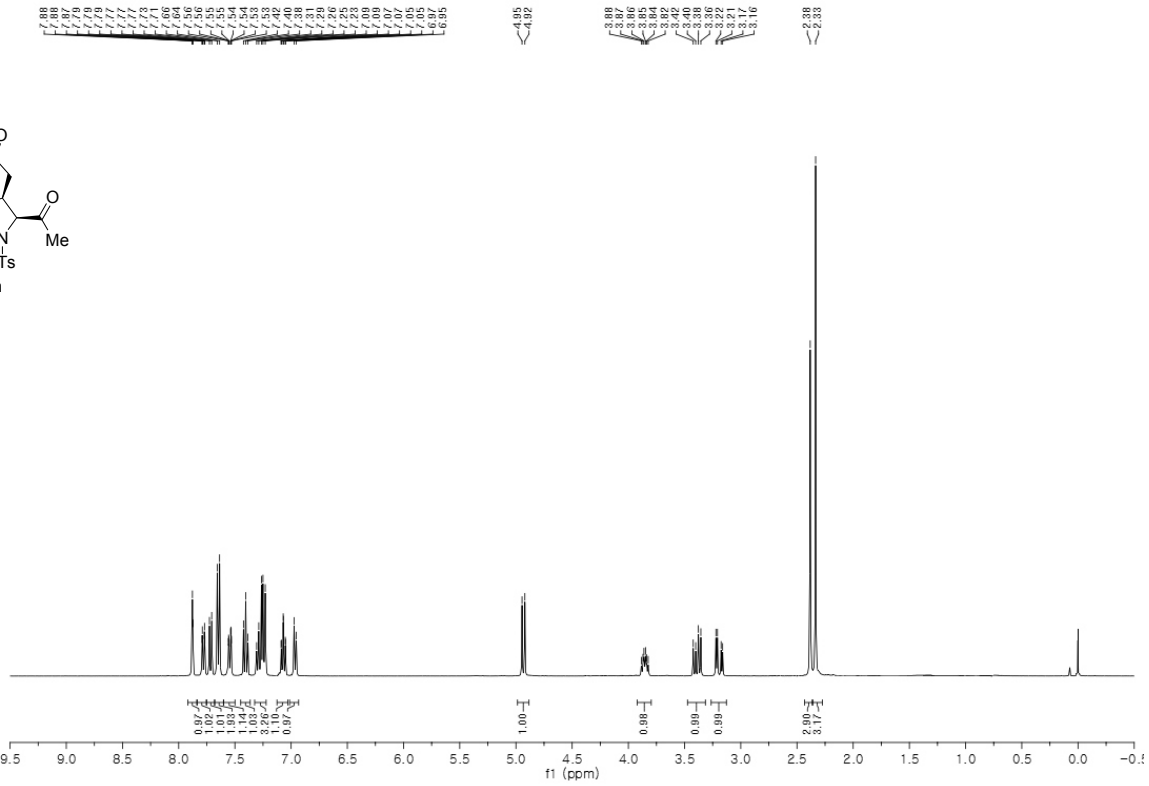
^{13}C NMR (100 MHz) in $CDCl_3$



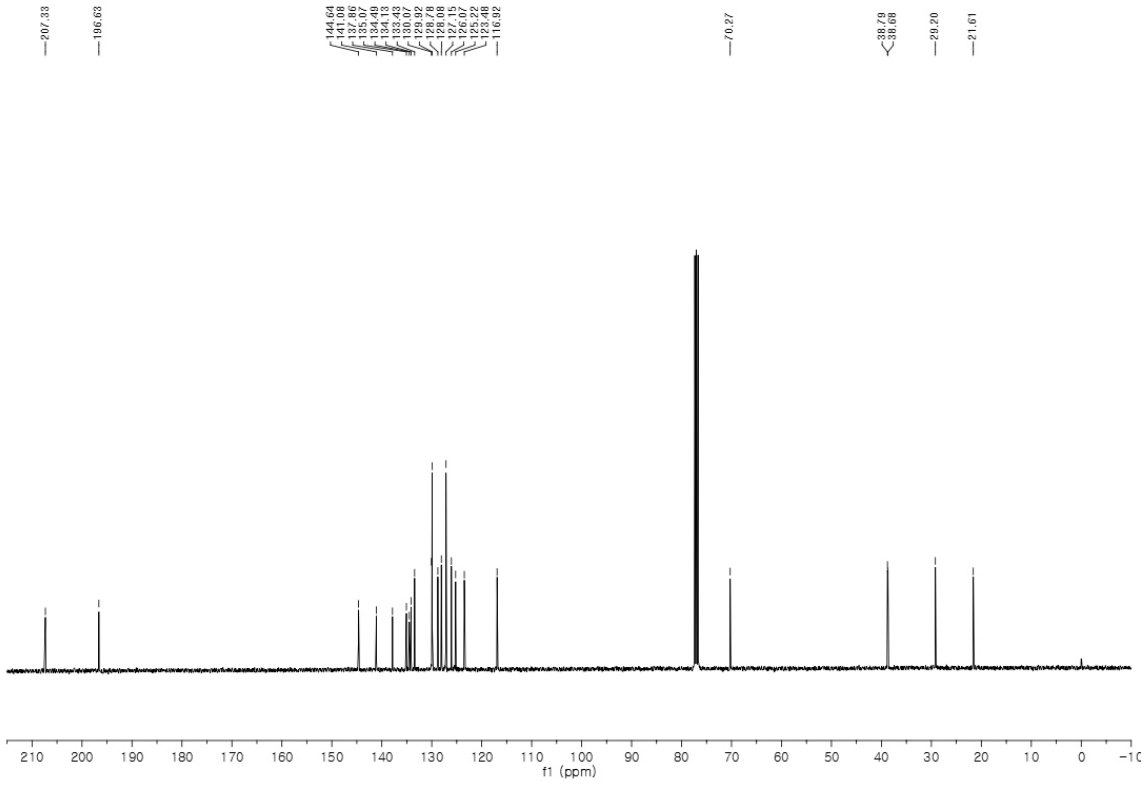
^{1}H NMR (400 MHz) in $CDCl_3$



***cis*-2h**



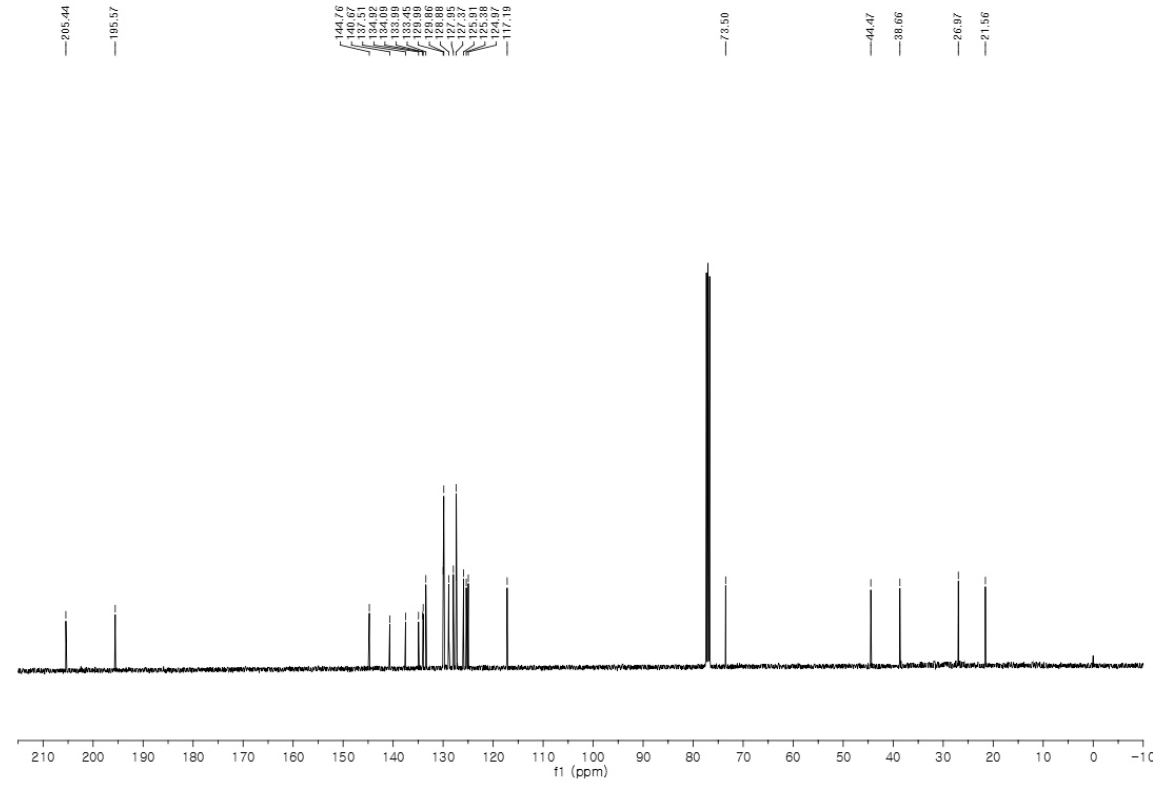
^{13}C NMR (100 MHz) in $CDCl_3$



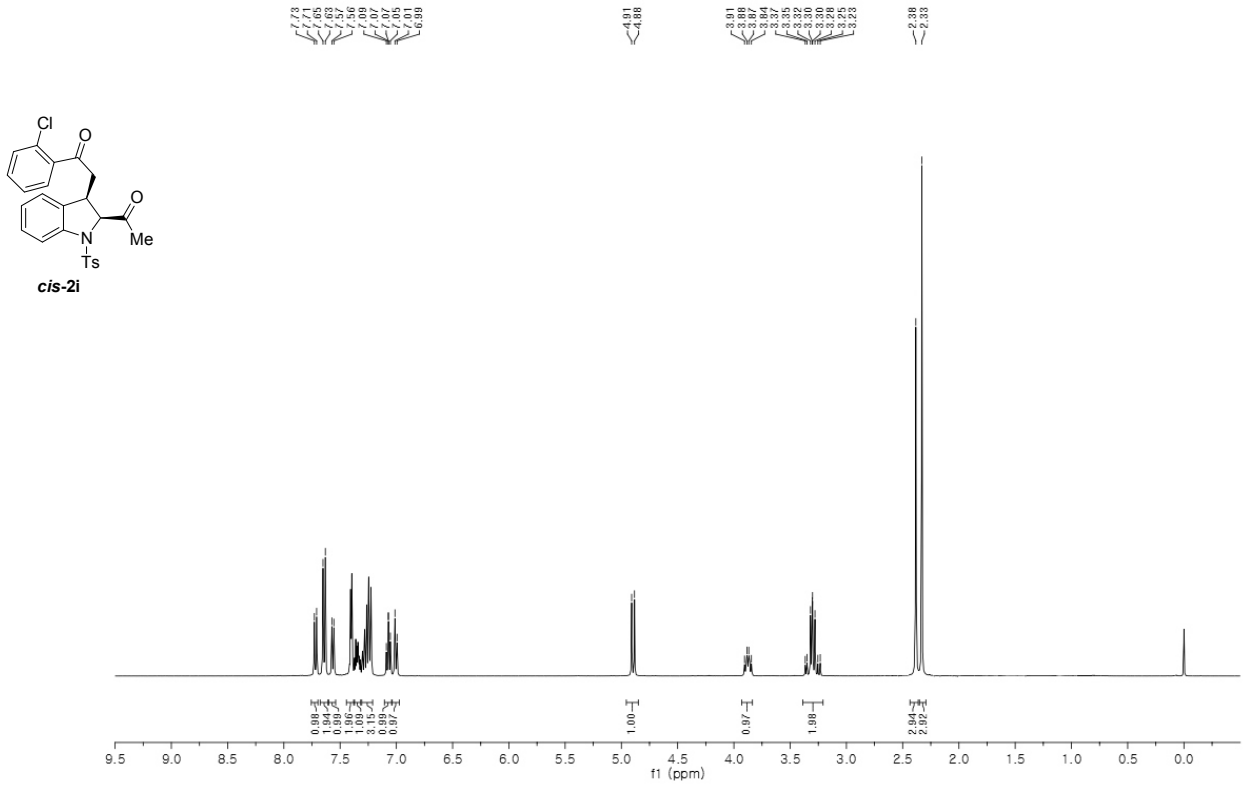
^{1}H NMR (400 MHz) in $CDCl_3$

***trans*-2h**

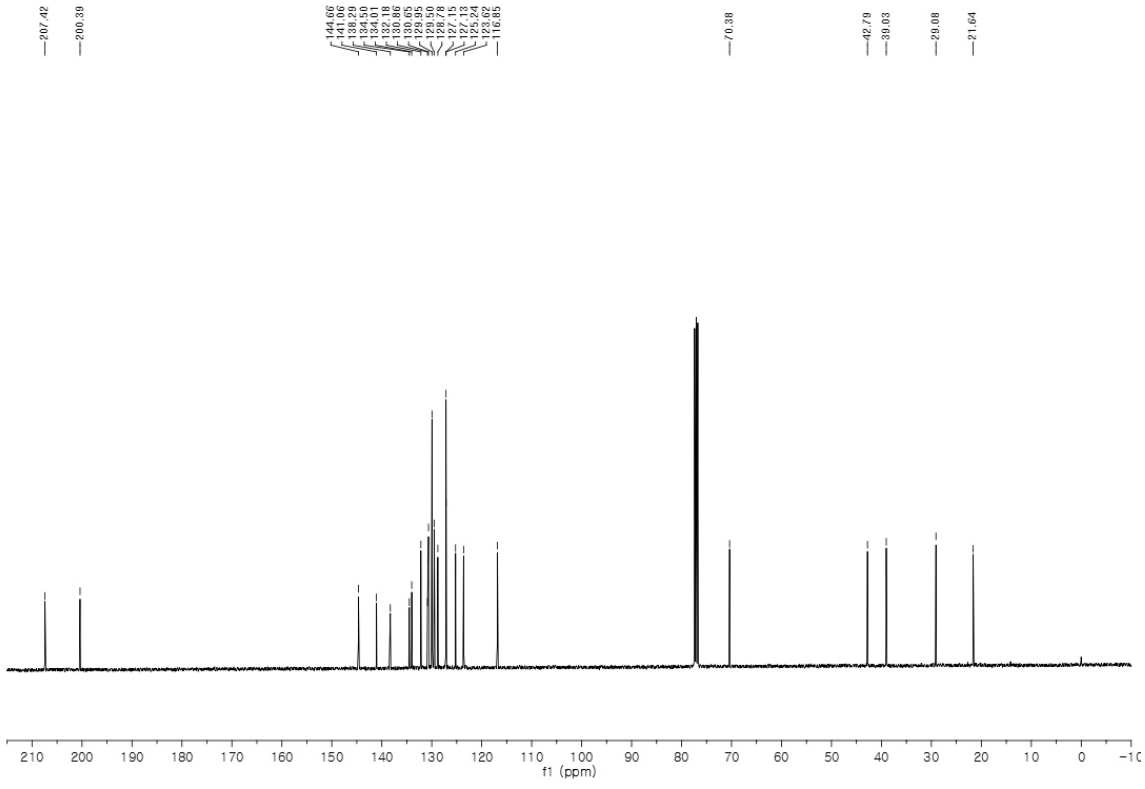
^{13}C NMR (100 MHz) in $CDCl_3$



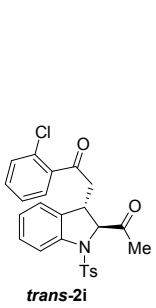
^{1}H NMR (400 MHz) in $CDCl_3$



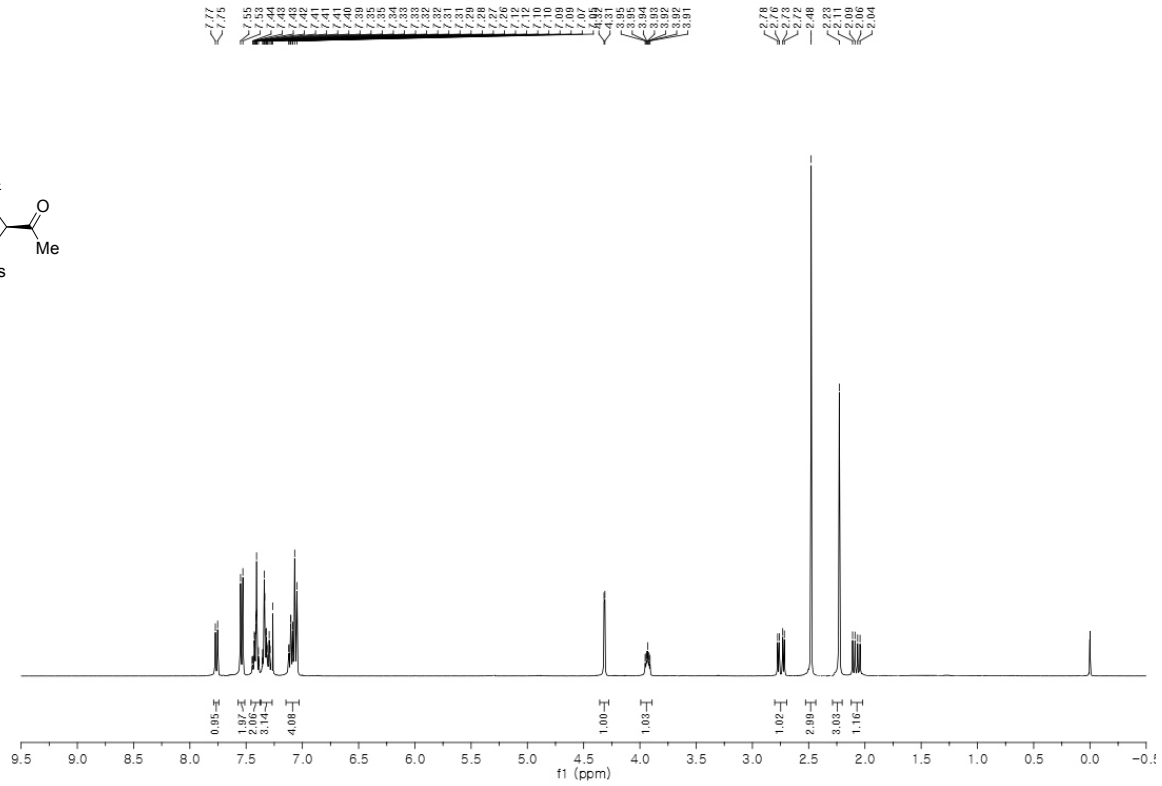
^{13}C NMR (100 MHz) in $CDCl_3$



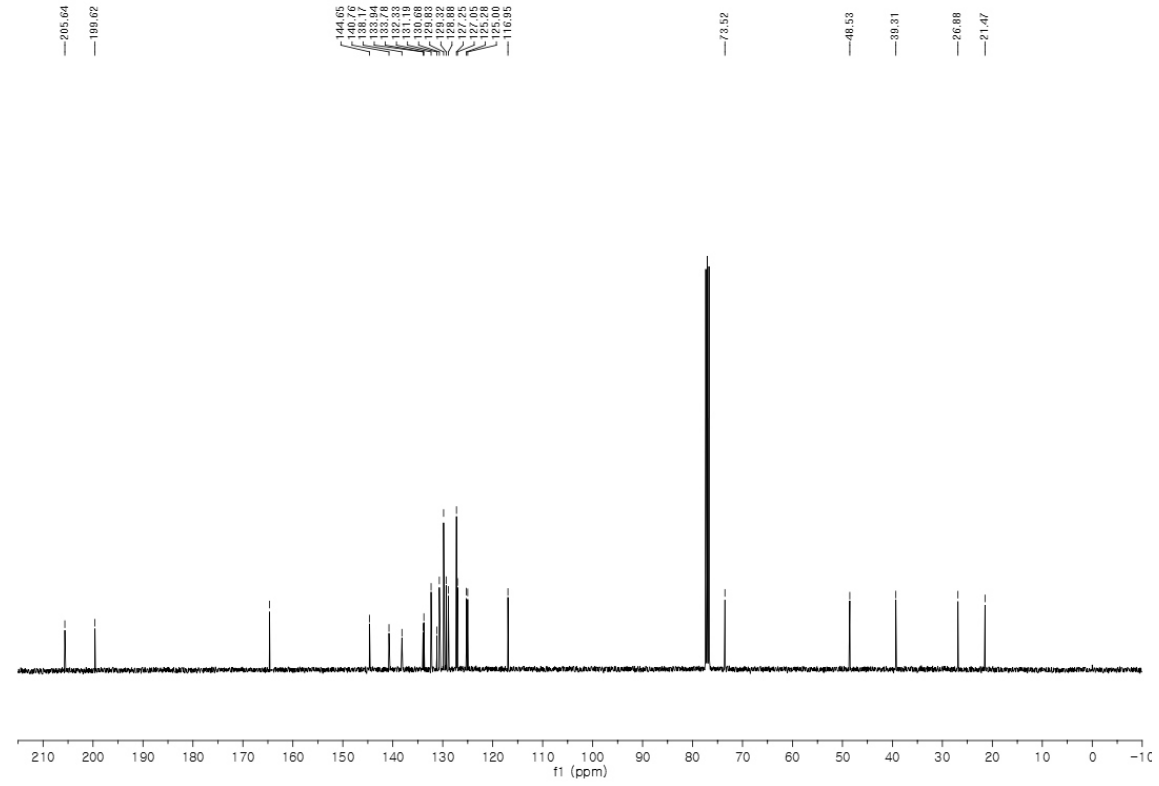
^{1}H NMR (400 MHz) in $CDCl_3$



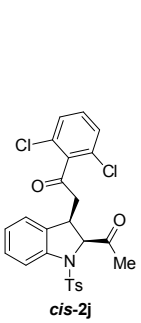
***trans*-2i**



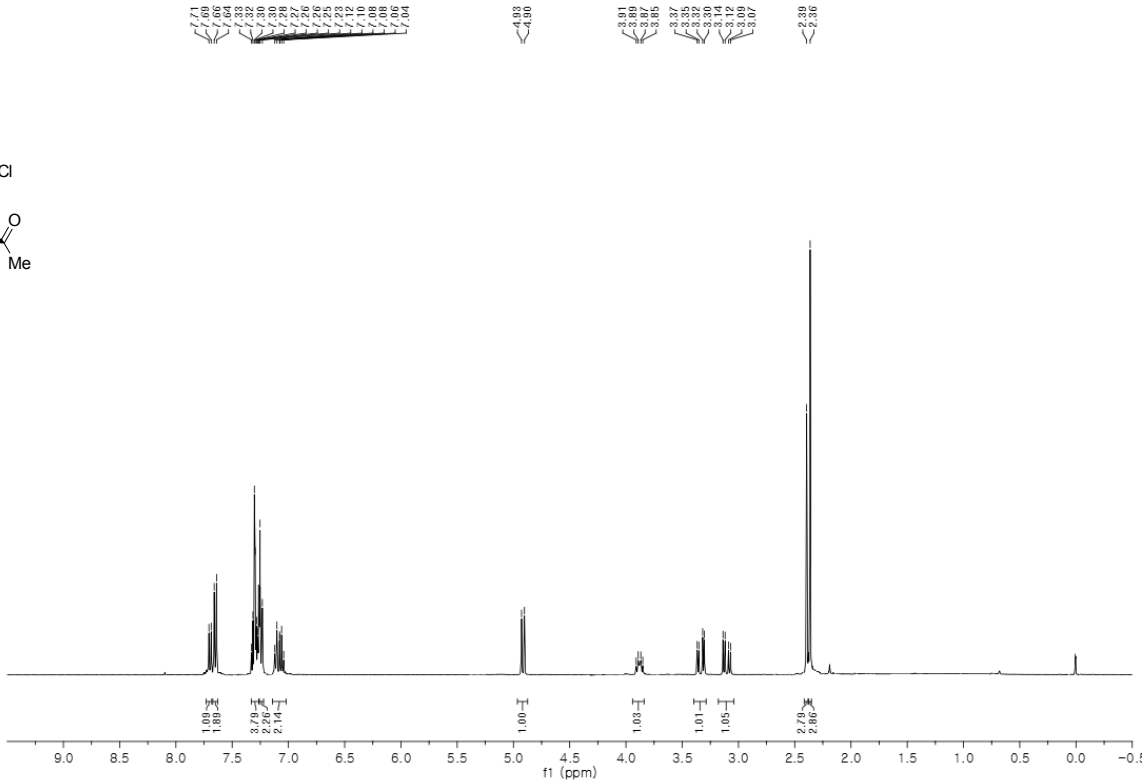
^{13}C NMR (100 MHz) in $CDCl_3$



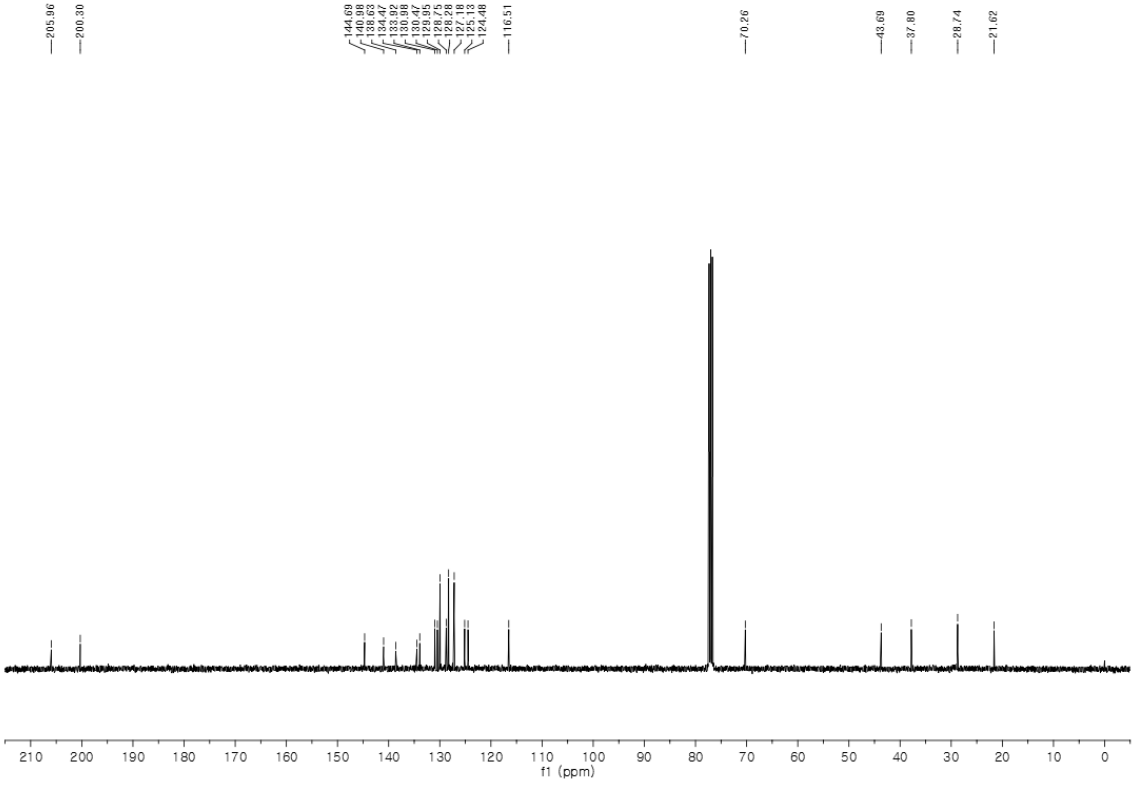
^{1}H NMR (400 MHz) in $CDCl_3$



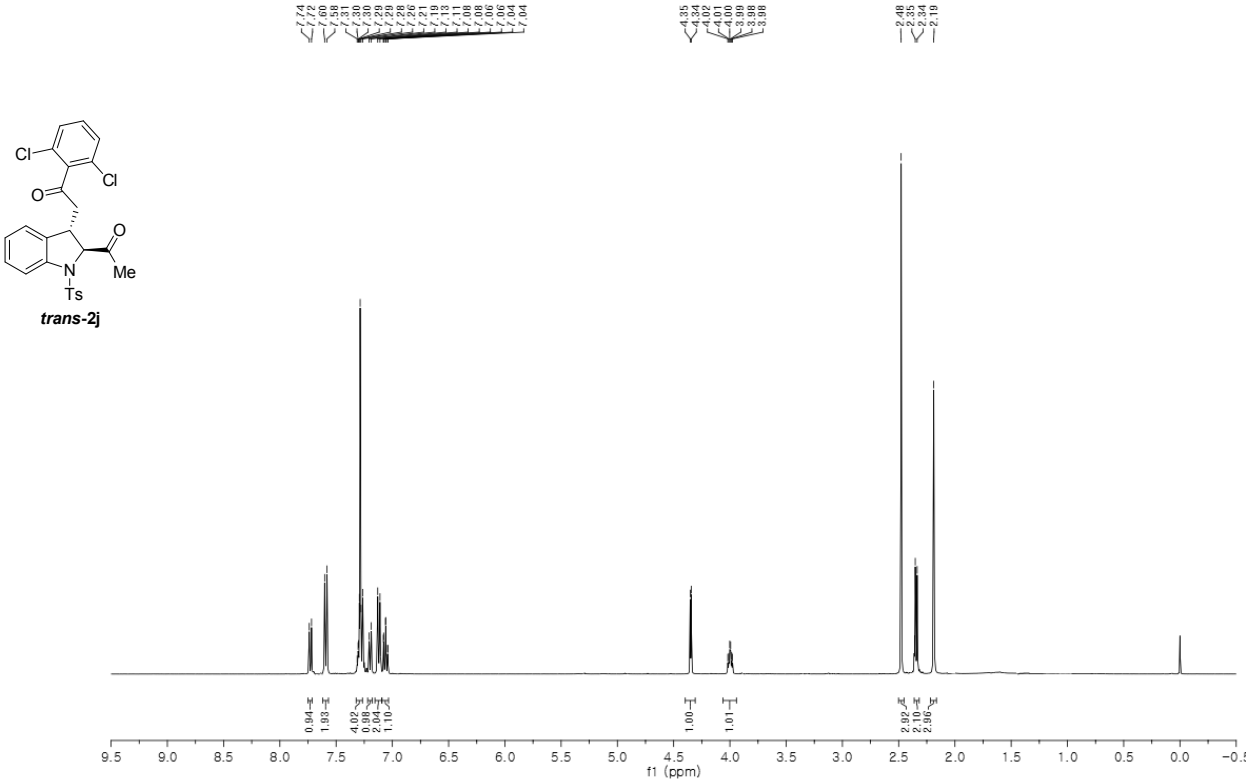
***cis*-2j**



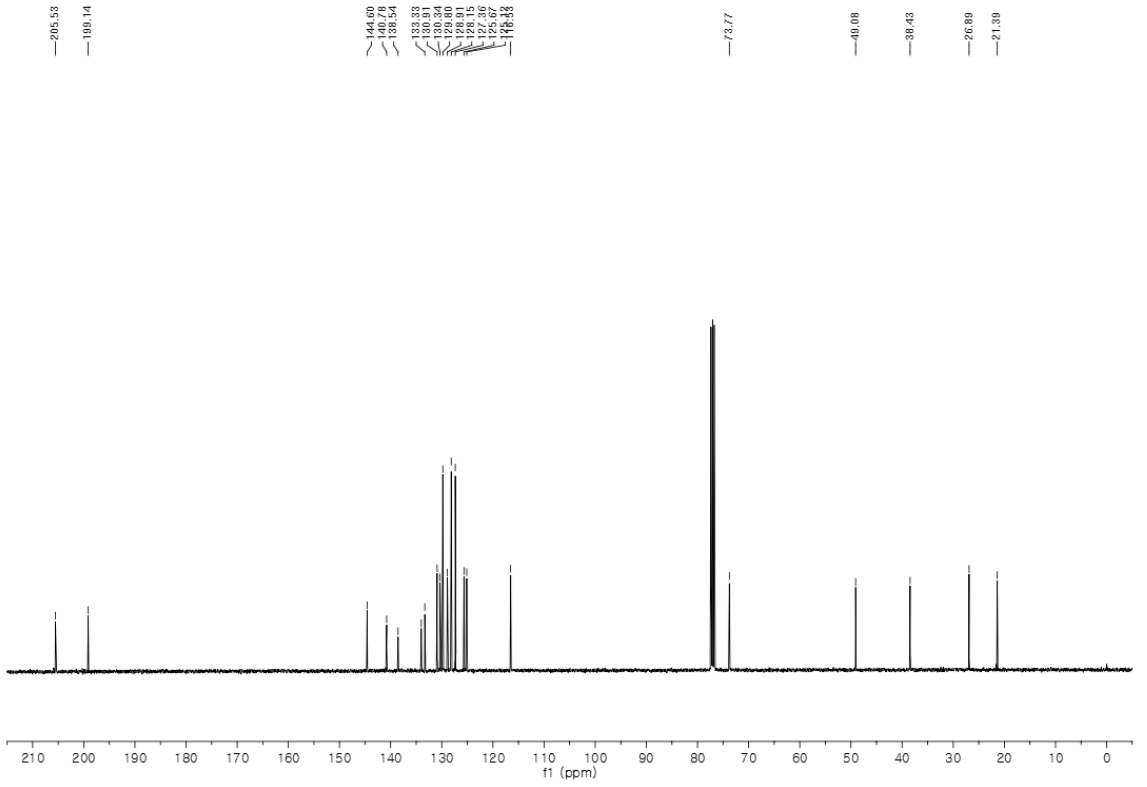
^{13}C NMR (100 MHz) in $CDCl_3$



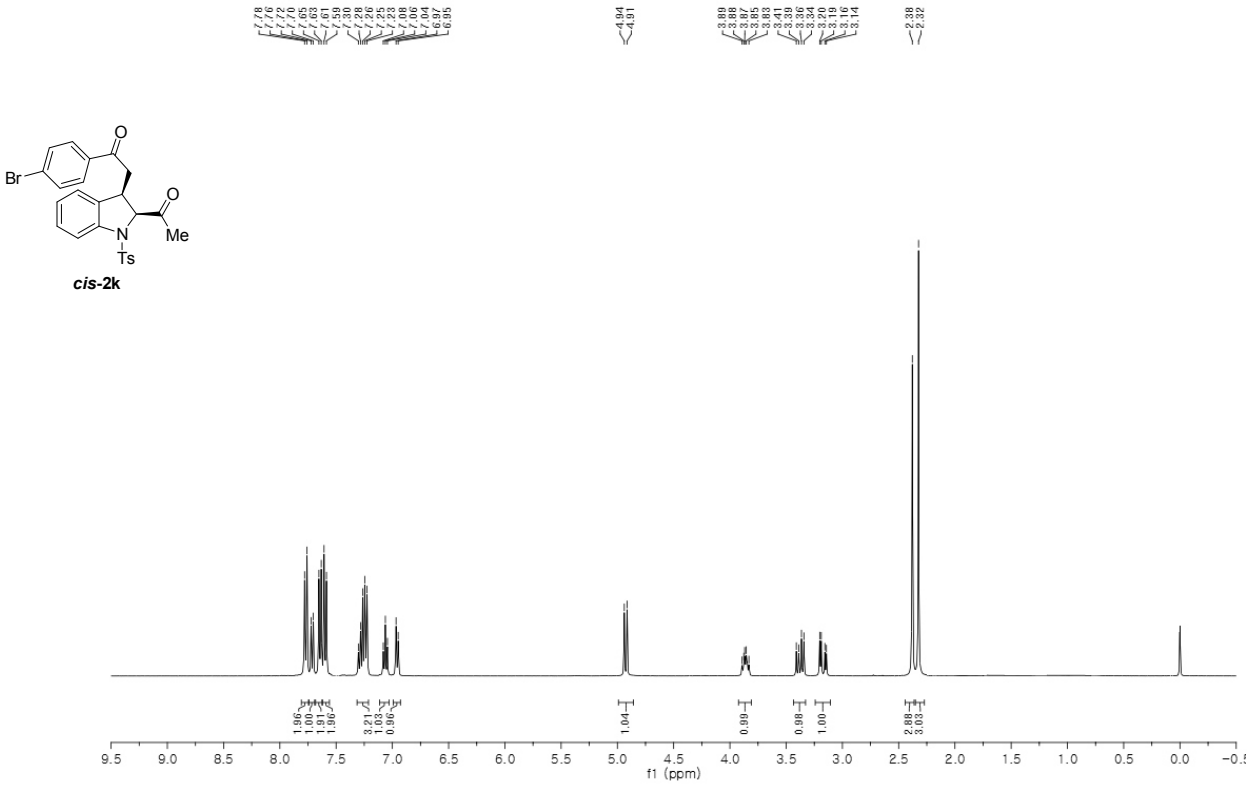
^{1}H NMR (400 MHz) in $CDCl_3$



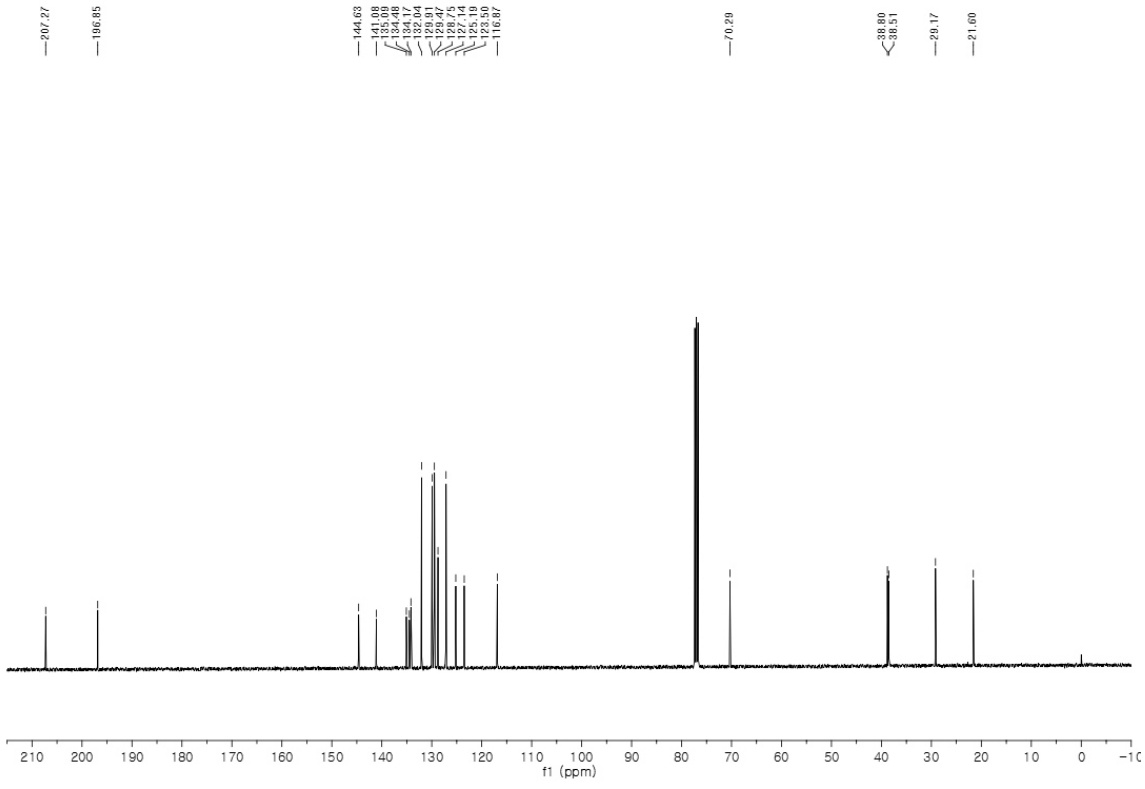
^{13}C NMR (100 MHz) in $CDCl_3$



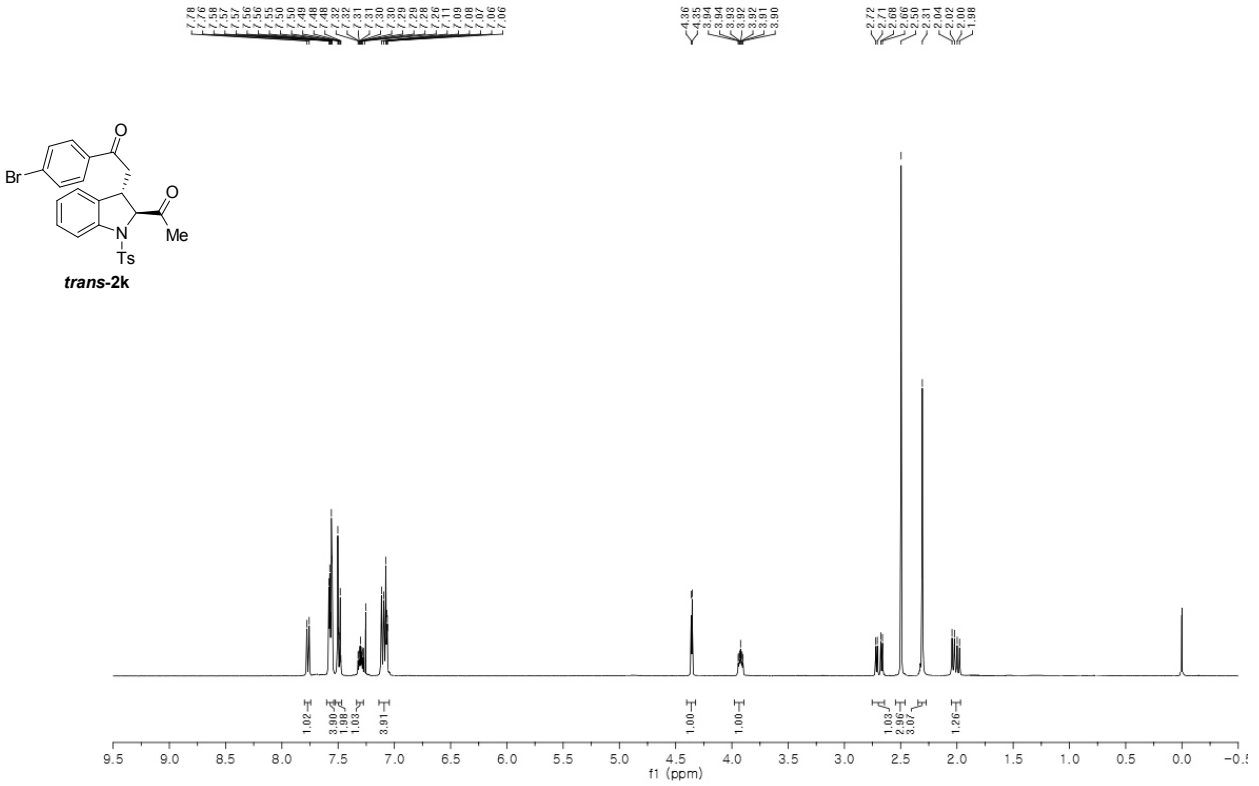
^{1}H NMR (400 MHz) in $CDCl_3$



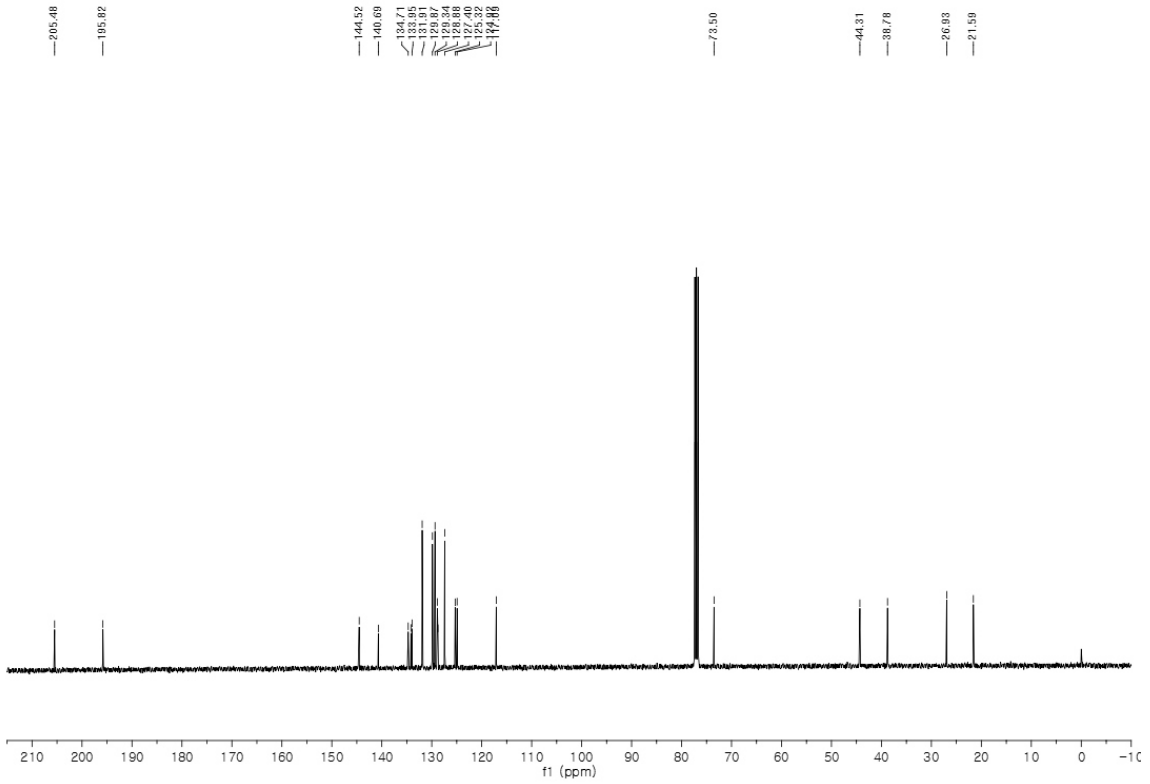
^{13}C NMR (100 MHz) in $CDCl_3$



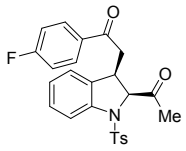
^{1}H NMR (400 MHz) in $CDCl_3$



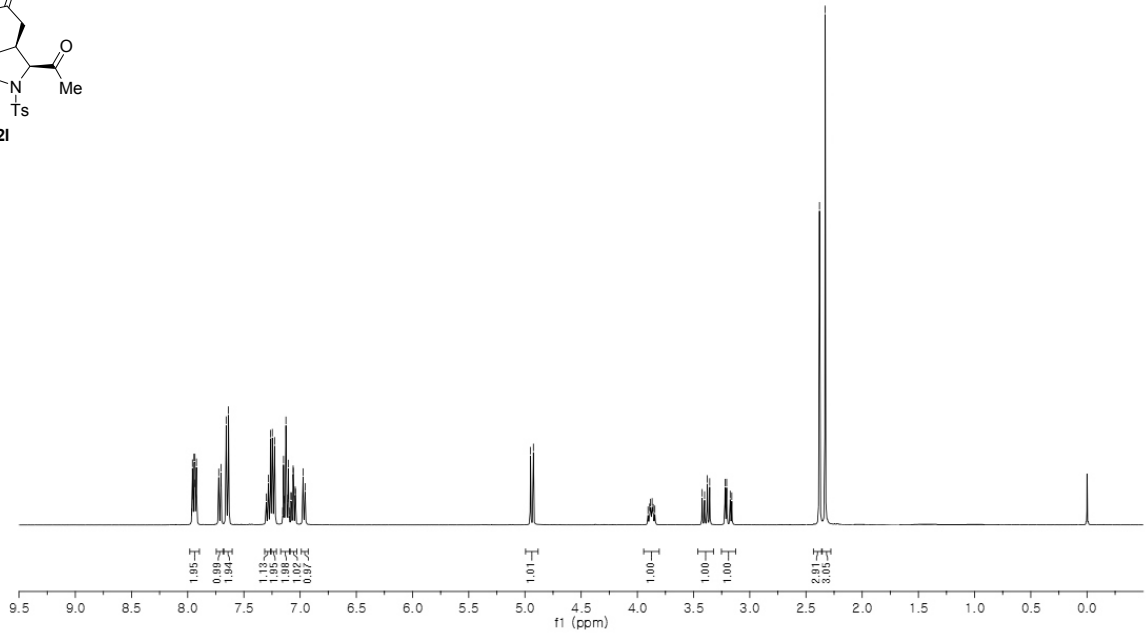
^{13}C NMR (100 MHz) in $CDCl_3$



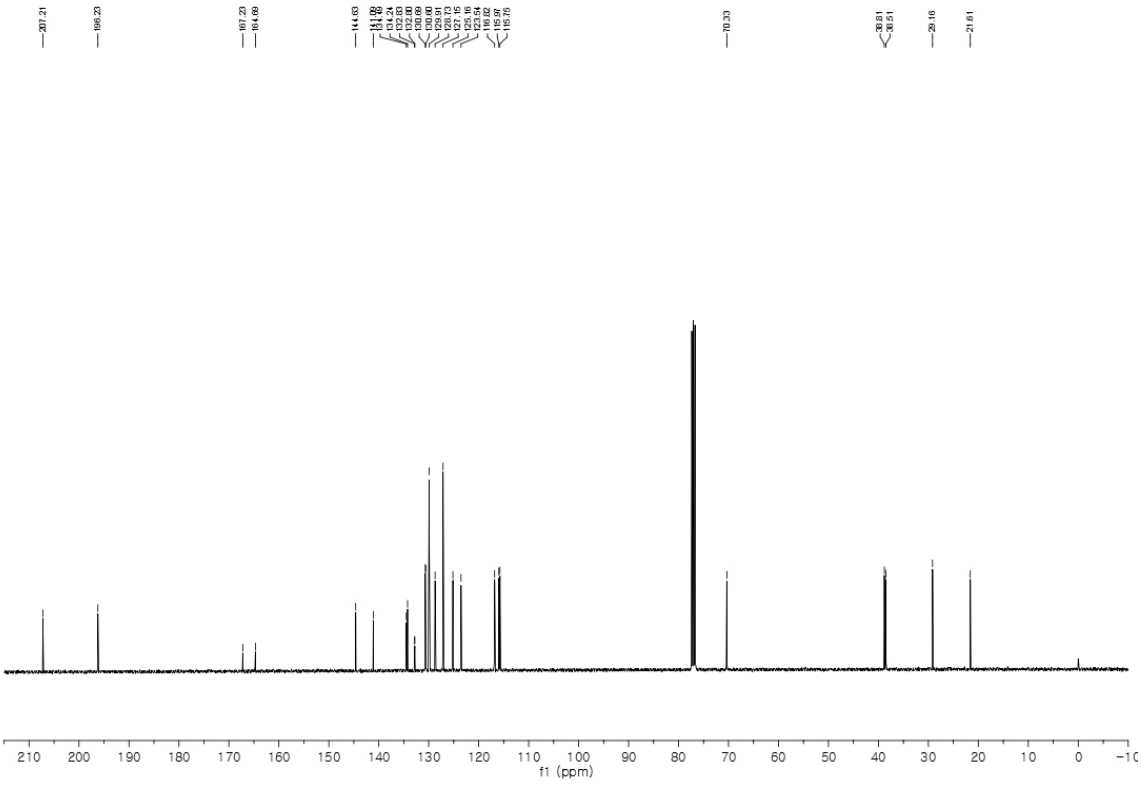
^{1}H NMR (400 MHz) in $CDCl_3$



***cis*-2l**

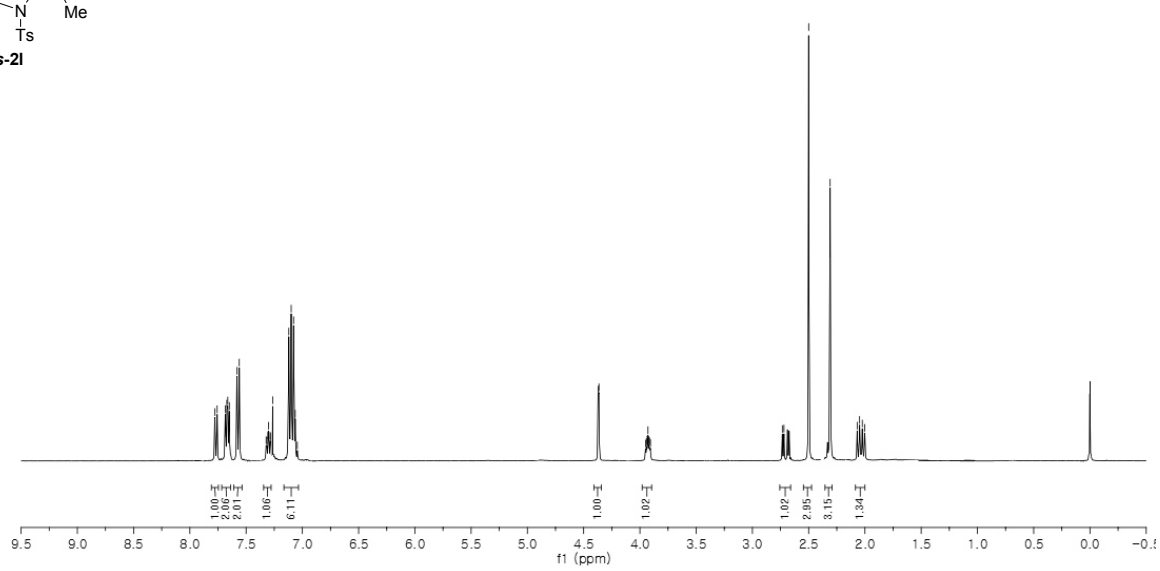


^{13}C NMR (100 MHz) in $CDCl_3$

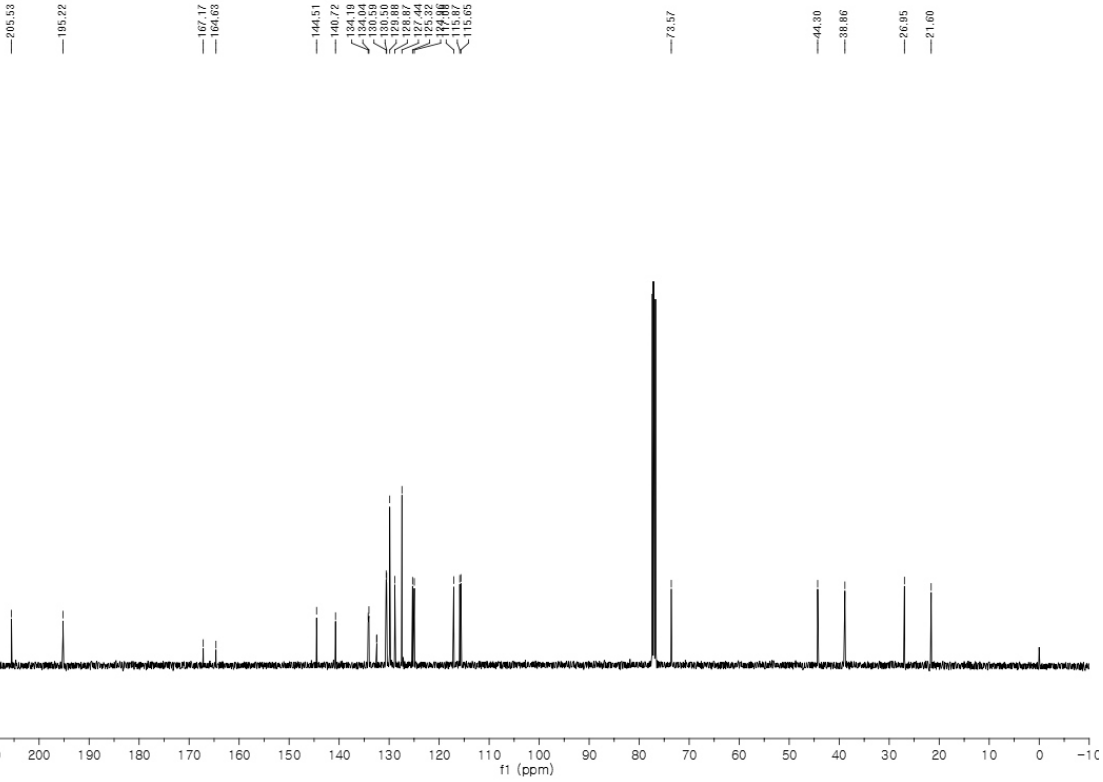


^{1}H NMR (400 MHz) in $CDCl_3$

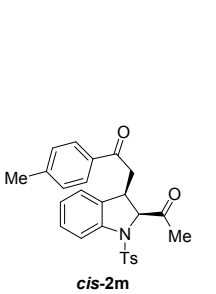
***trans*-2l**



^{13}C NMR (100 MHz) in $CDCl_3$

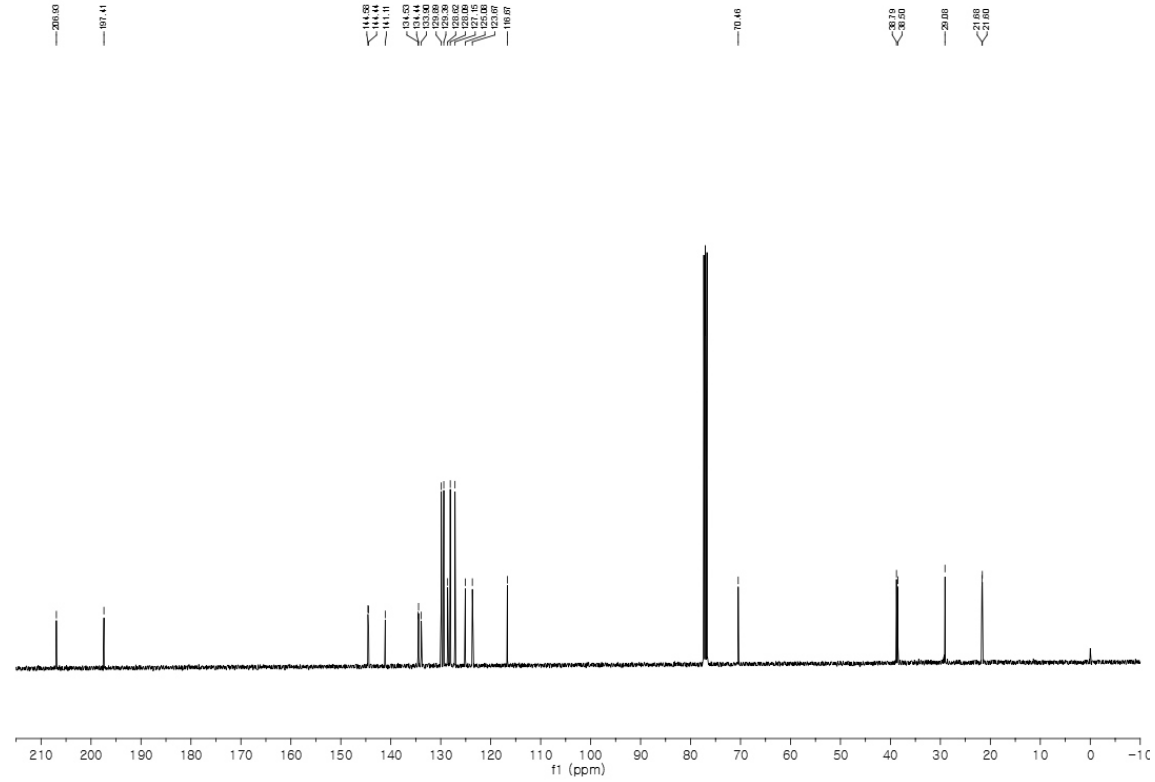


^{1}H NMR (400 MHz) in $CDCl_3$

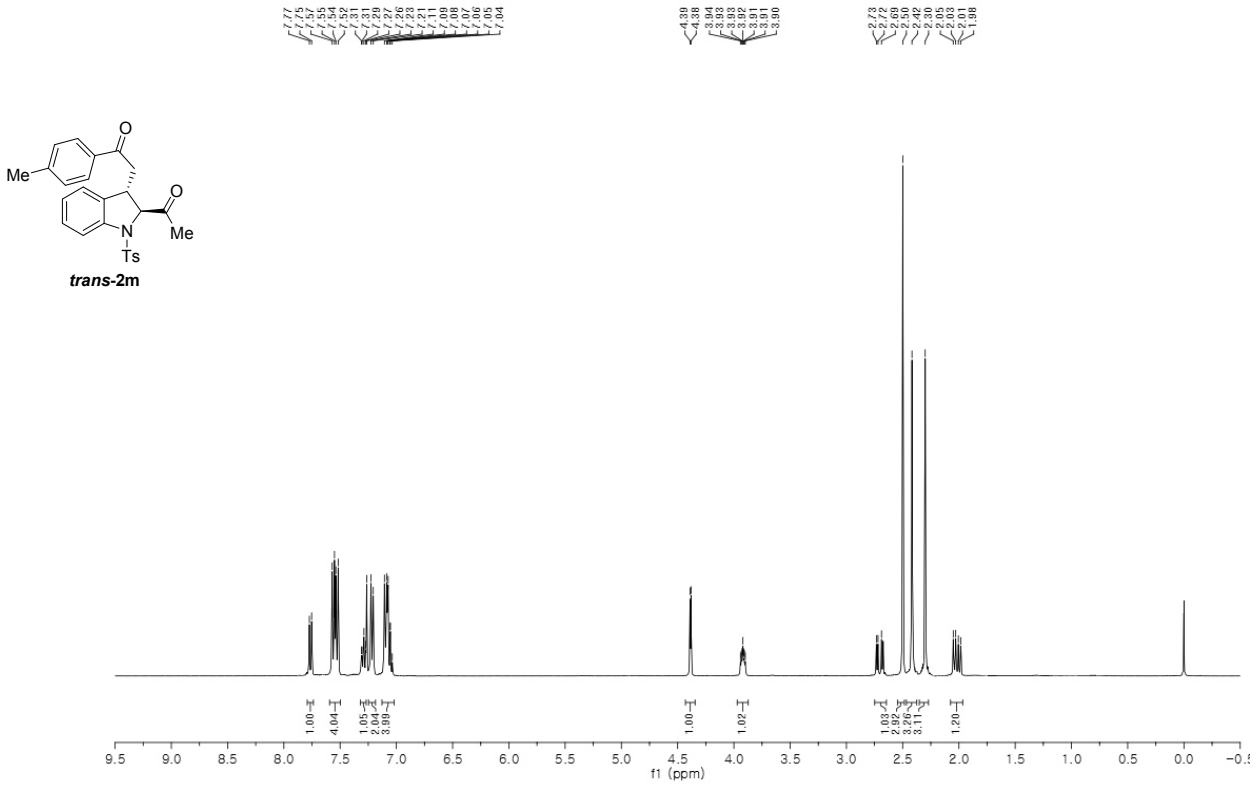


***cis*-2m**

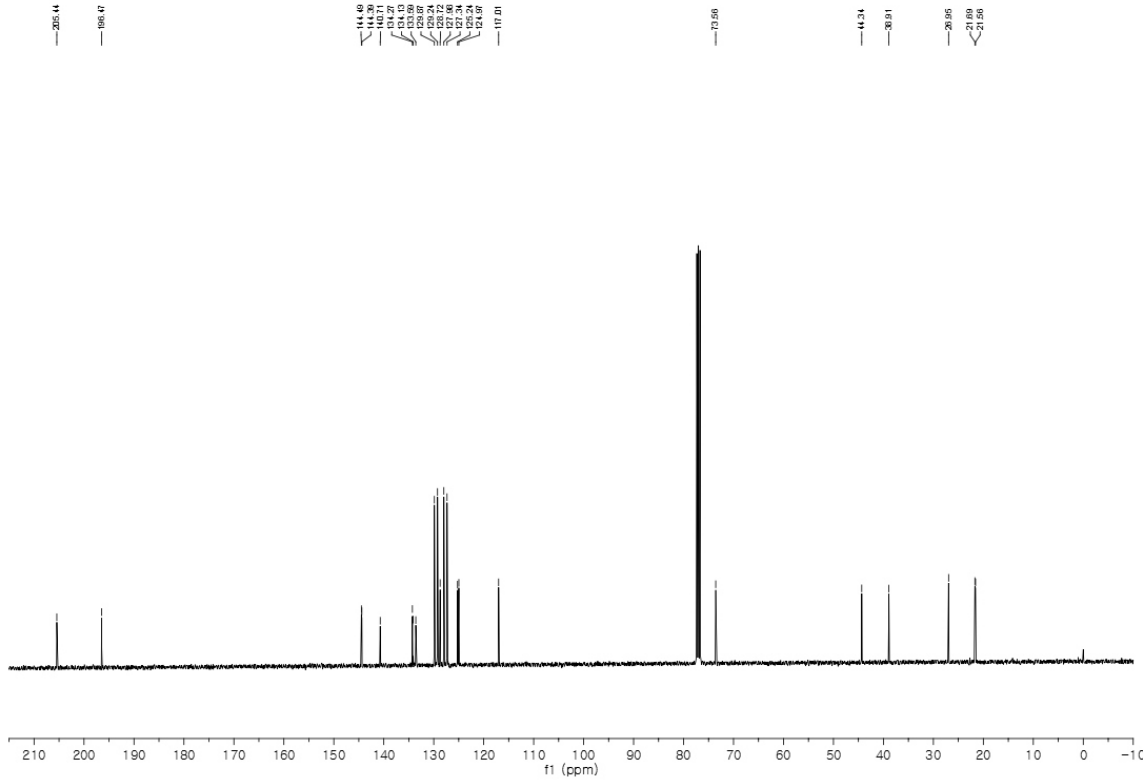
^{13}C NMR (100 MHz) in $CDCl_3$



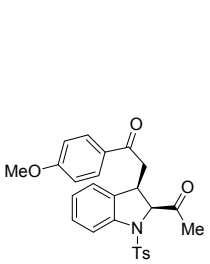
^{1}H NMR (400 MHz) in $CDCl_3$



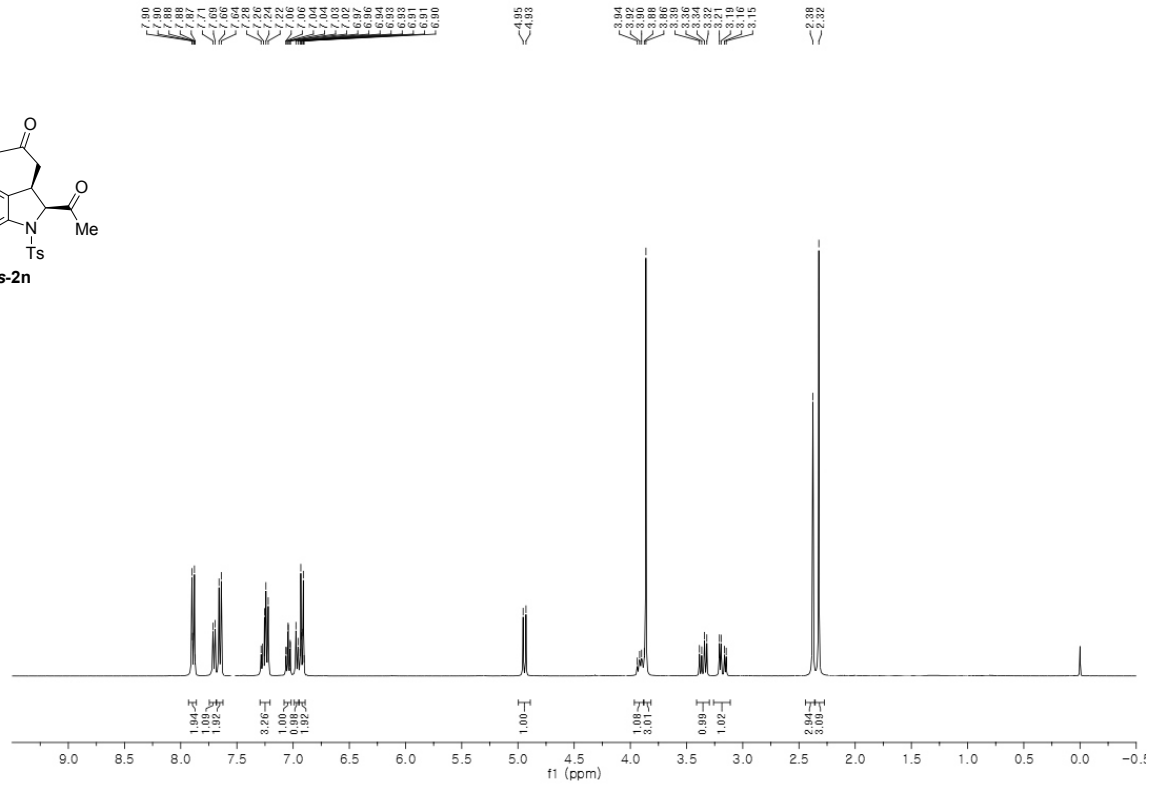
^{13}C NMR (100 MHz) in $CDCl_3$



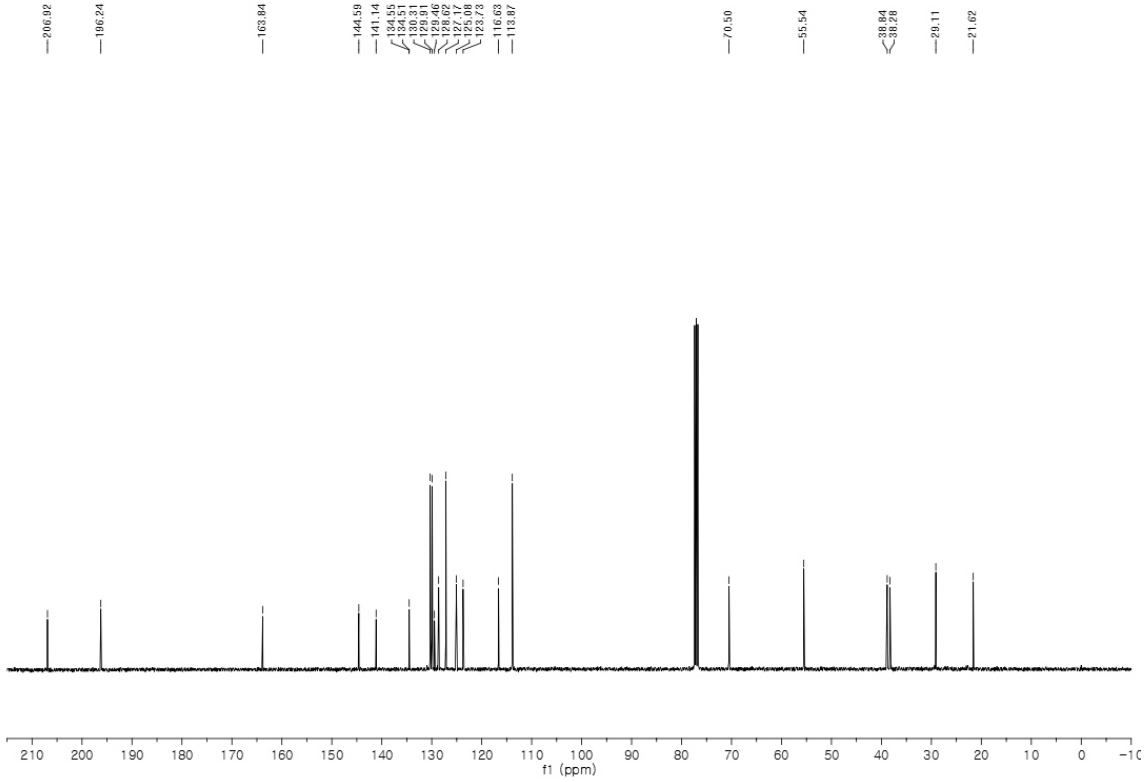
^{1}H NMR (400 MHz) in $CDCl_3$



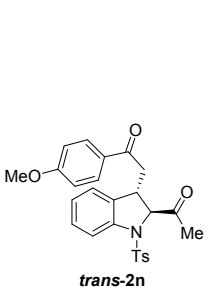
***cis*-2n**



^{13}C NMR (100 MHz) in $CDCl_3$

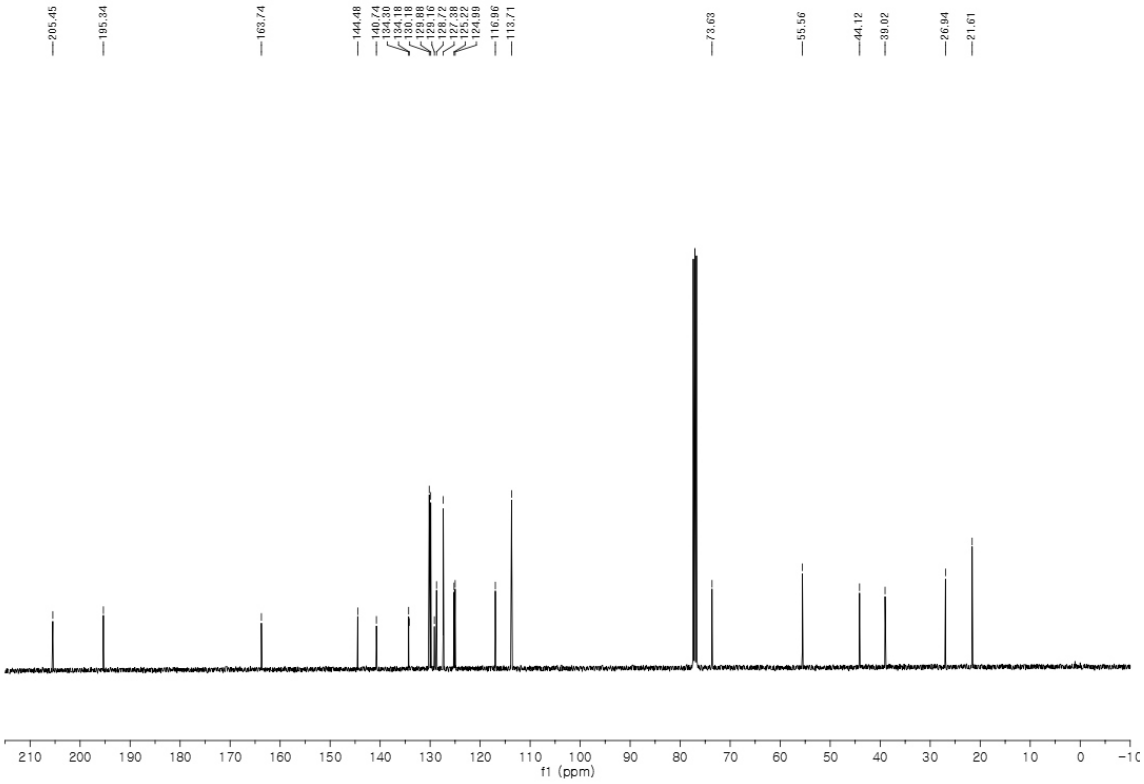


^{1}H NMR (400 MHz) in $CDCl_3$

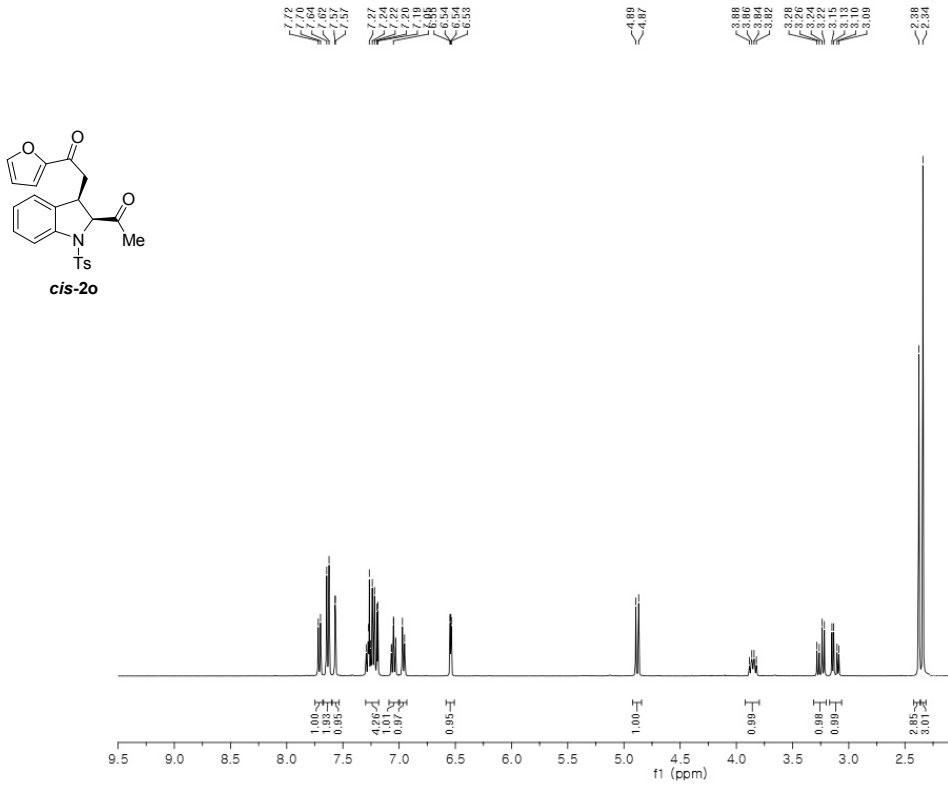


***trans*-2n**

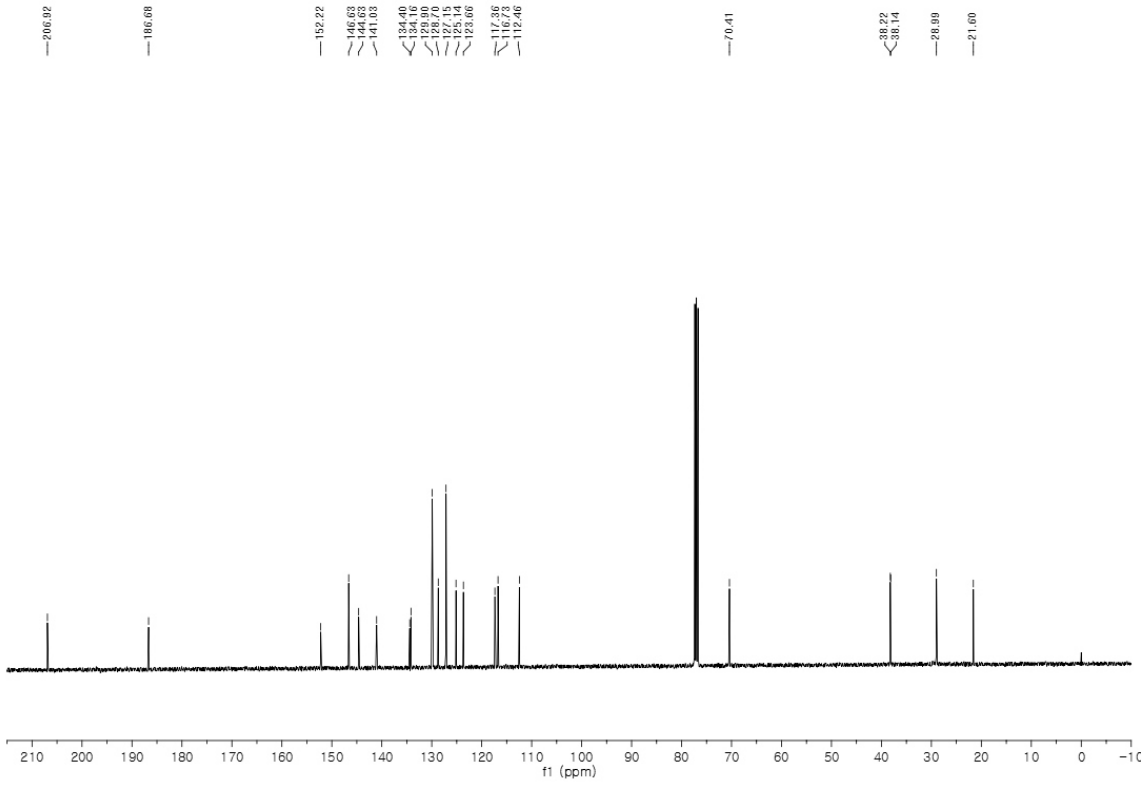
^{13}C NMR (100 MHz) in $CDCl_3$



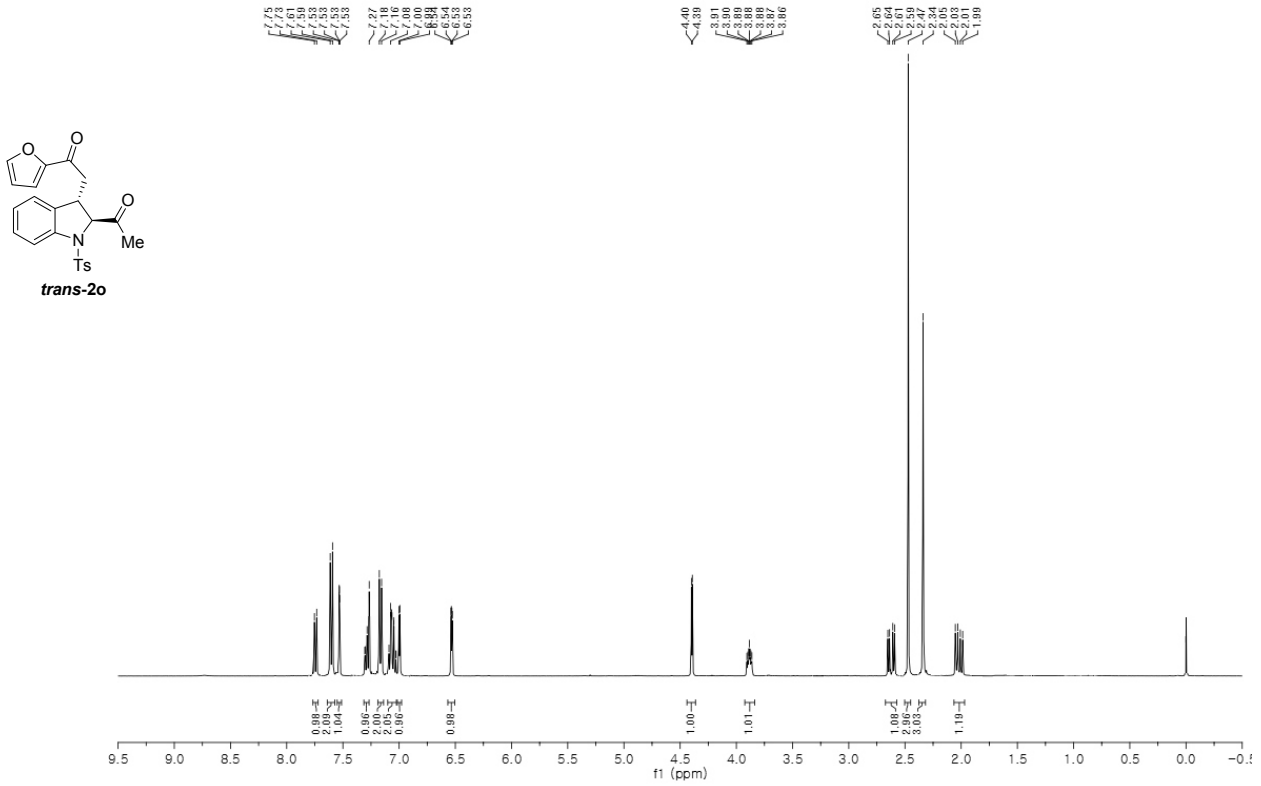
^{1}H NMR (400 MHz) in $CDCl_3$



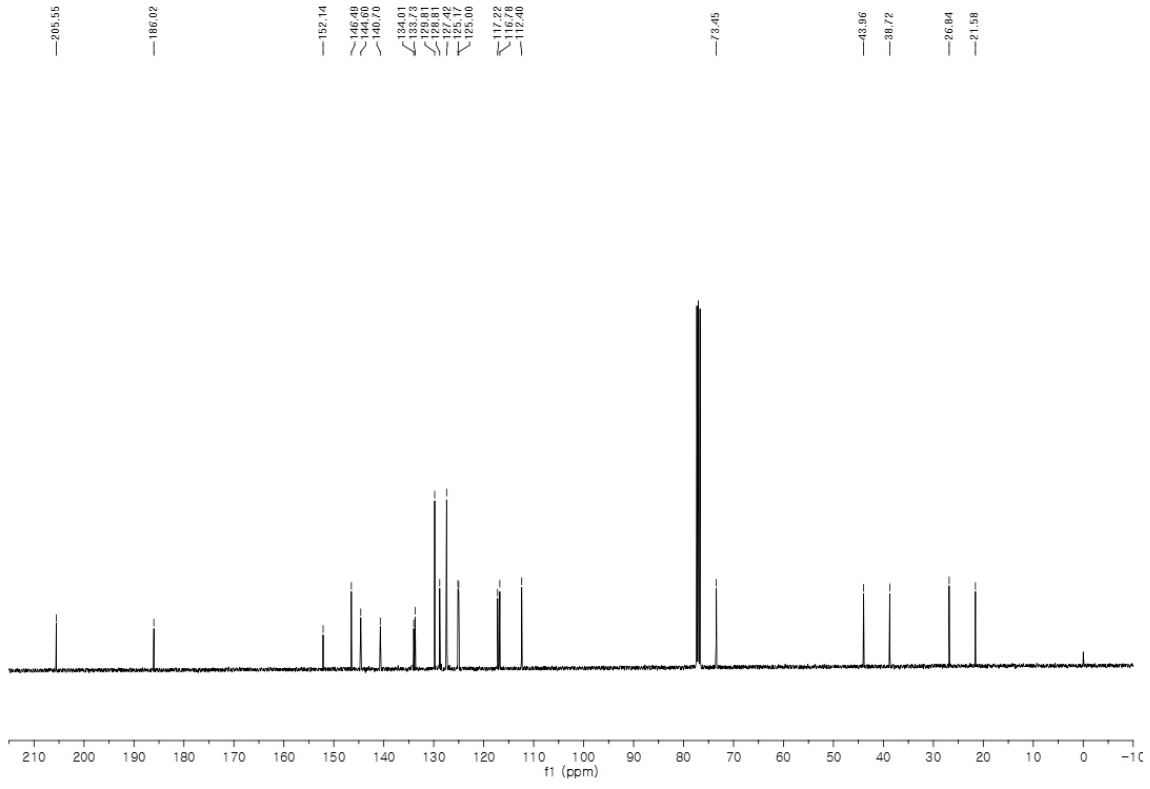
^{13}C NMR (100 MHz) in $CDCl_3$



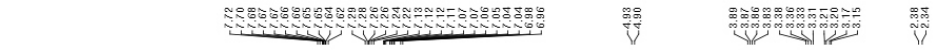
^{1}H NMR (400 MHz) in $CDCl_3$

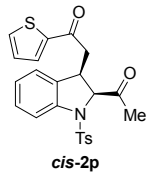


^{13}C NMR (100 MHz) in $CDCl_3$

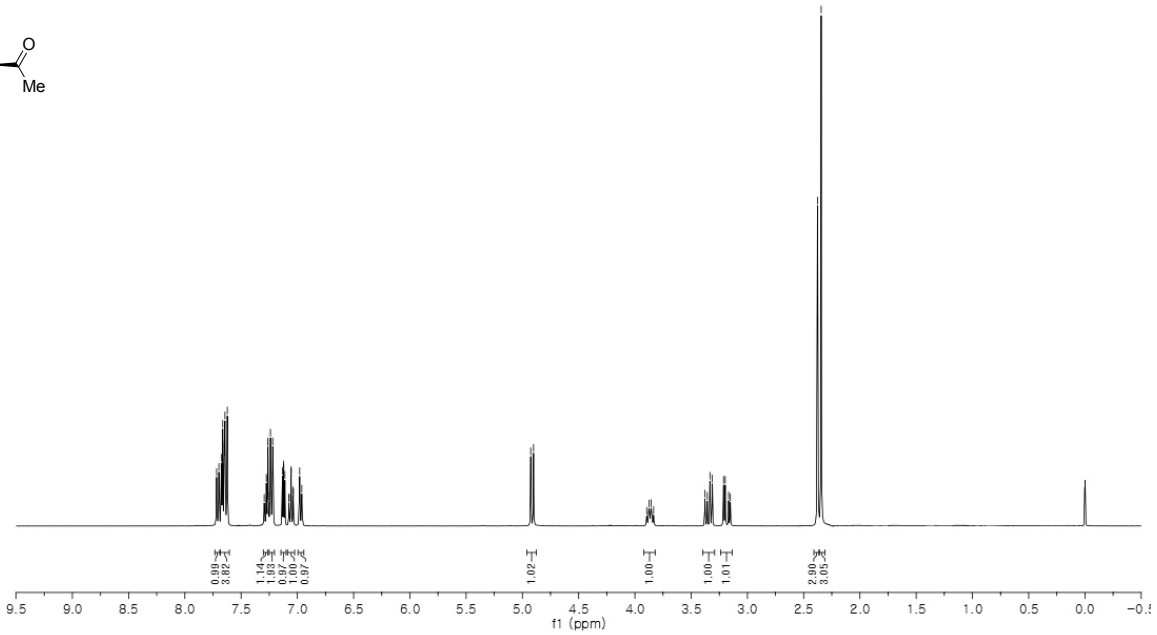


^{1}H NMR (400 MHz) in $CDCl_3$

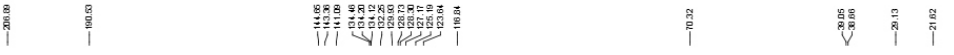


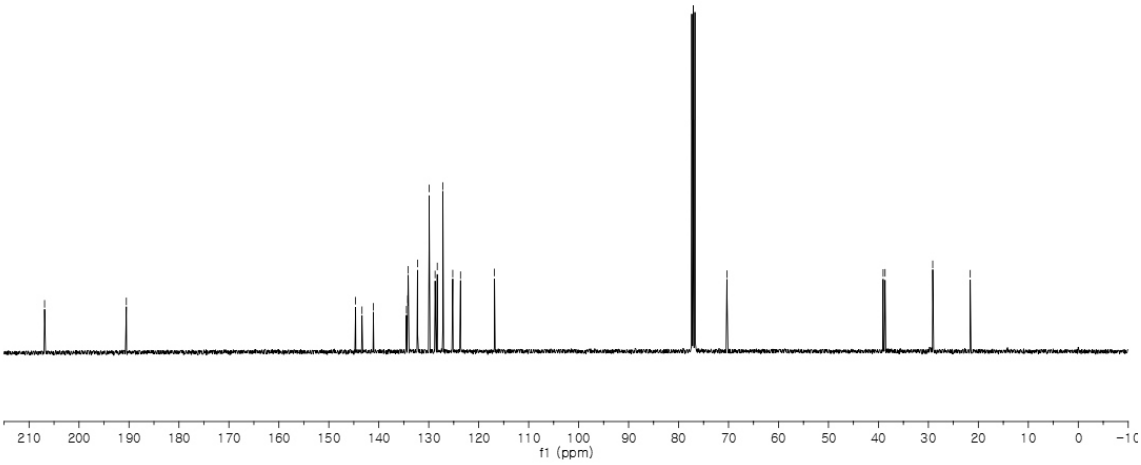


***cis*-2p**

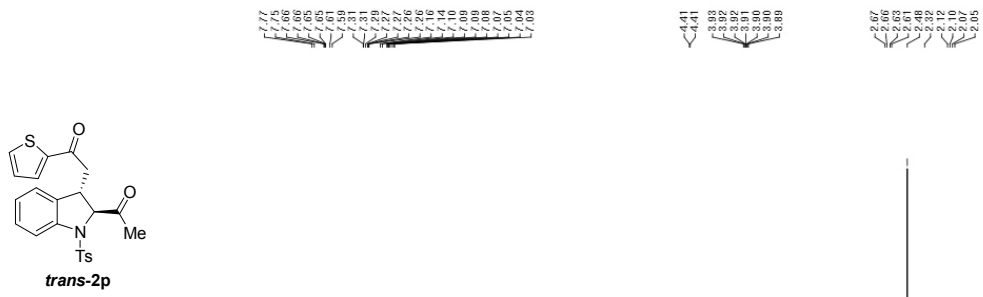


^{13}C NMR (100 MHz) in $CDCl_3$

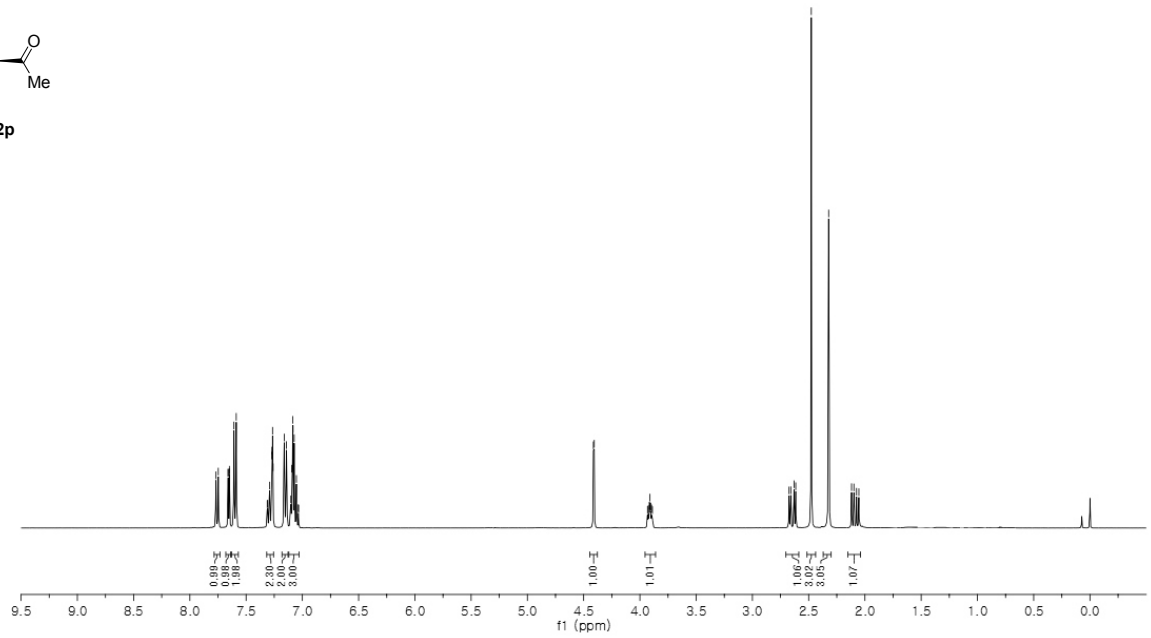




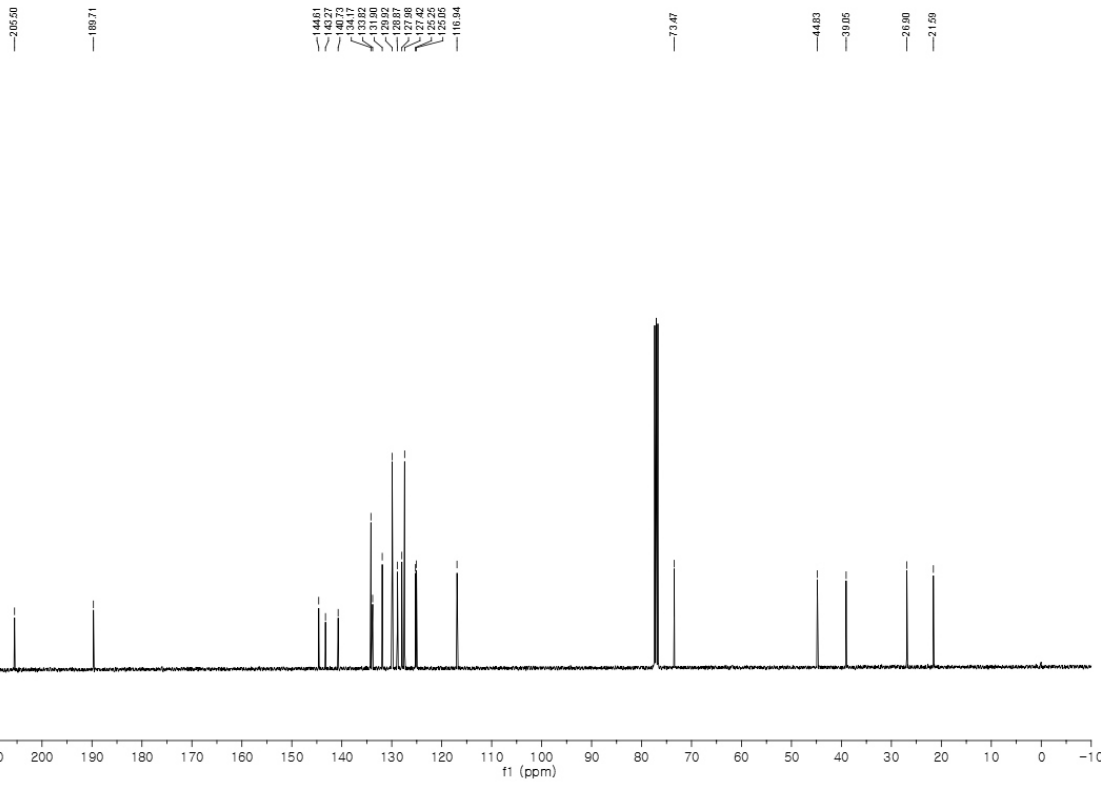
^{1}H NMR (400 MHz) in $CDCl_3$



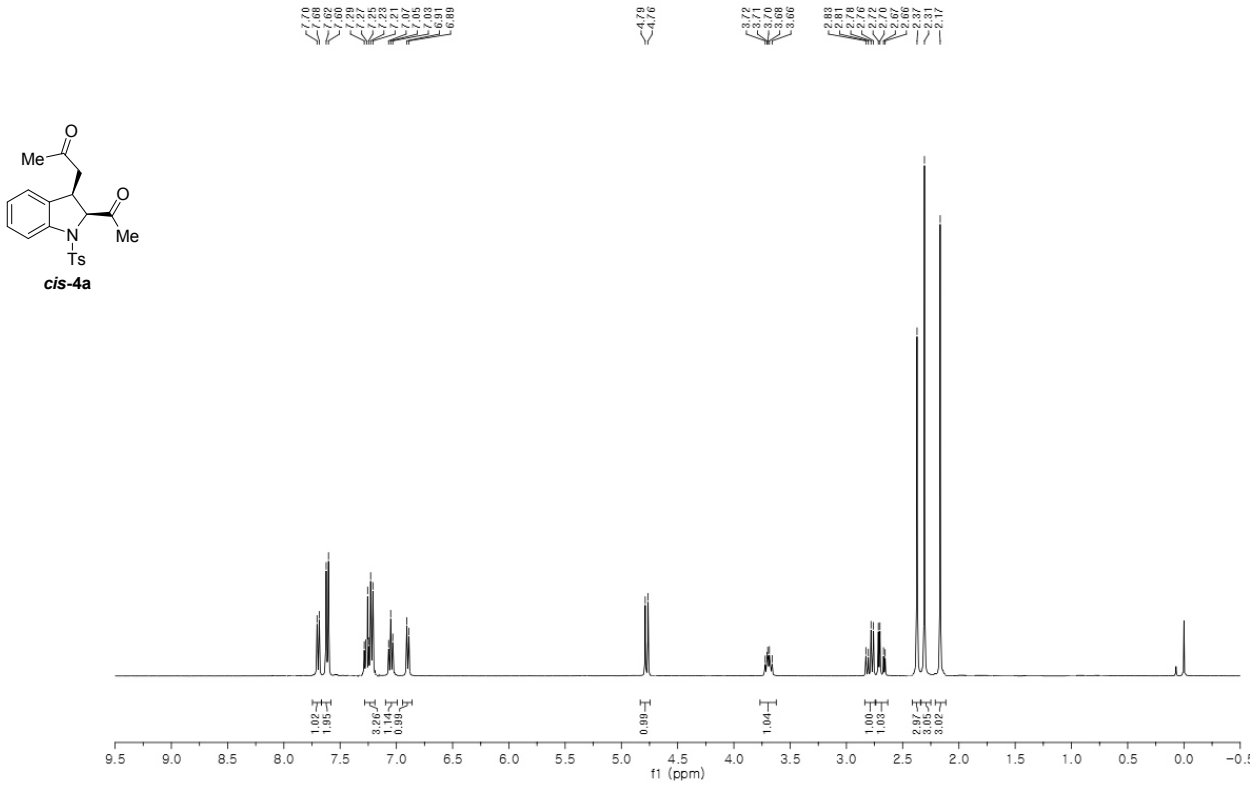
***trans*-2p**



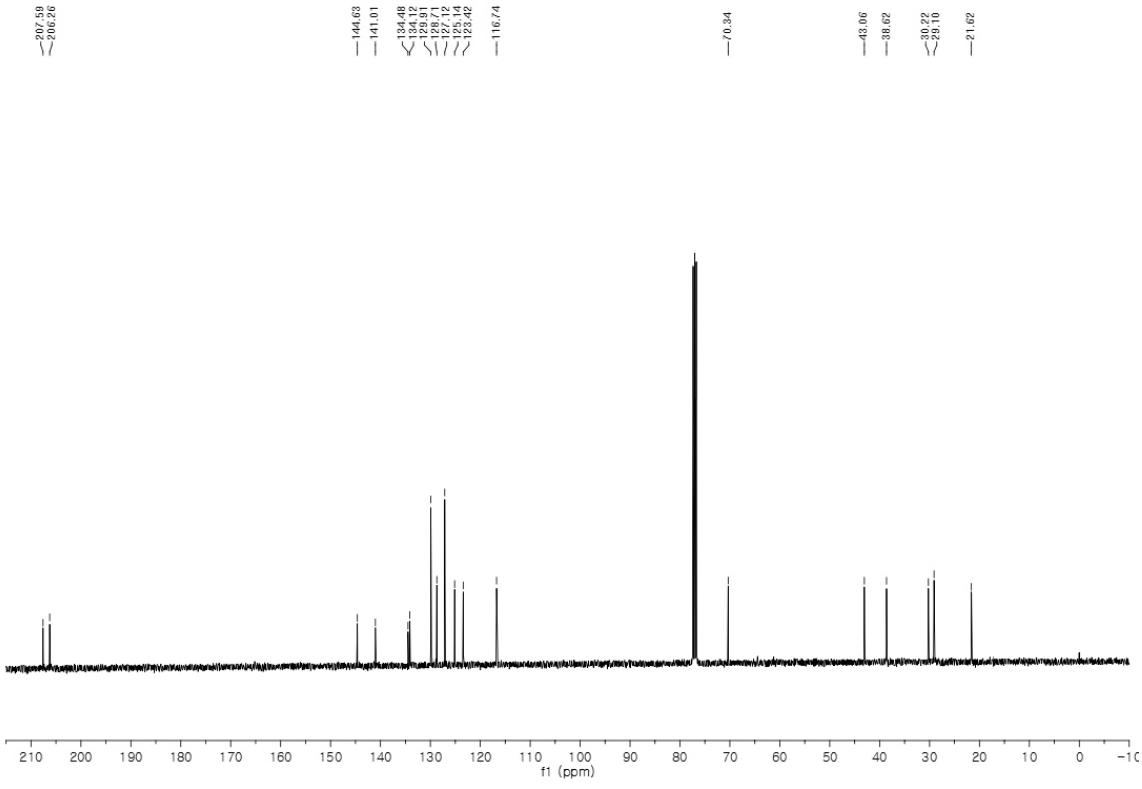
^{13}C NMR (100 MHz) in $CDCl_3$



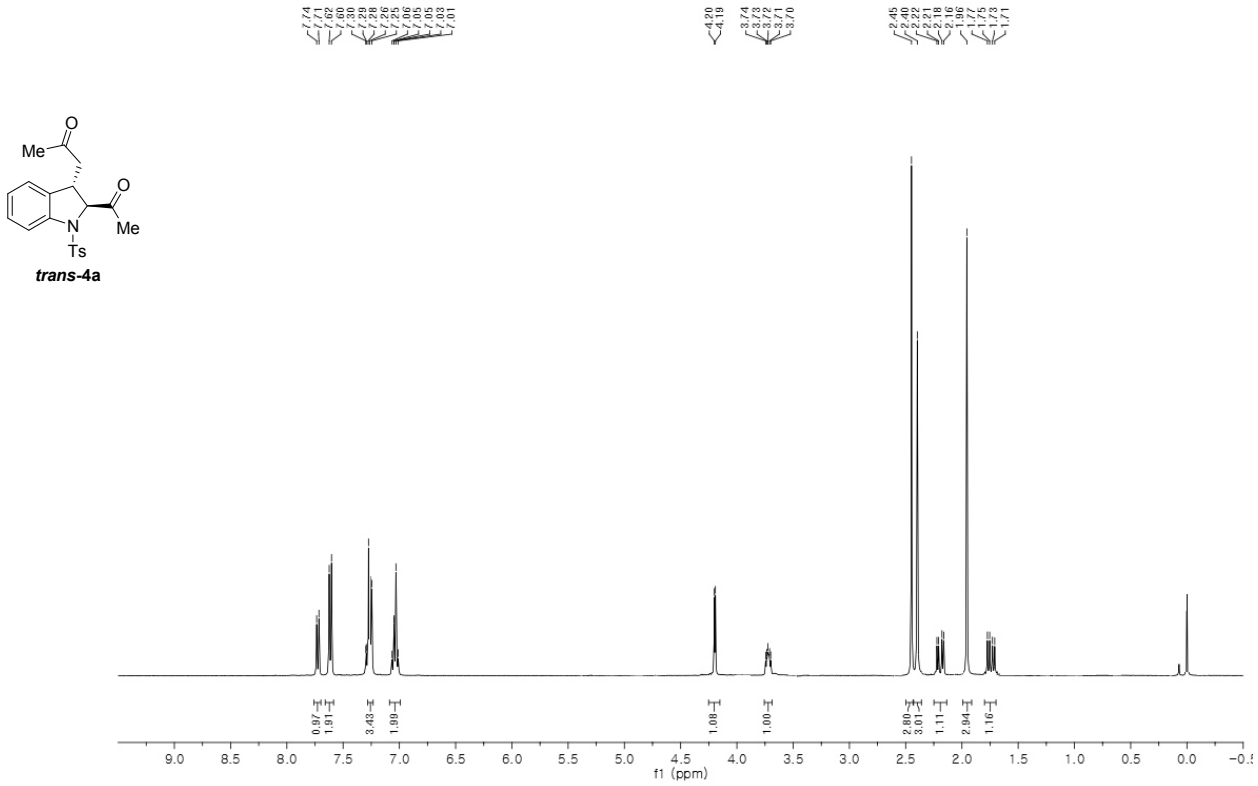
^{1}H NMR (400 MHz) in $CDCl_3$



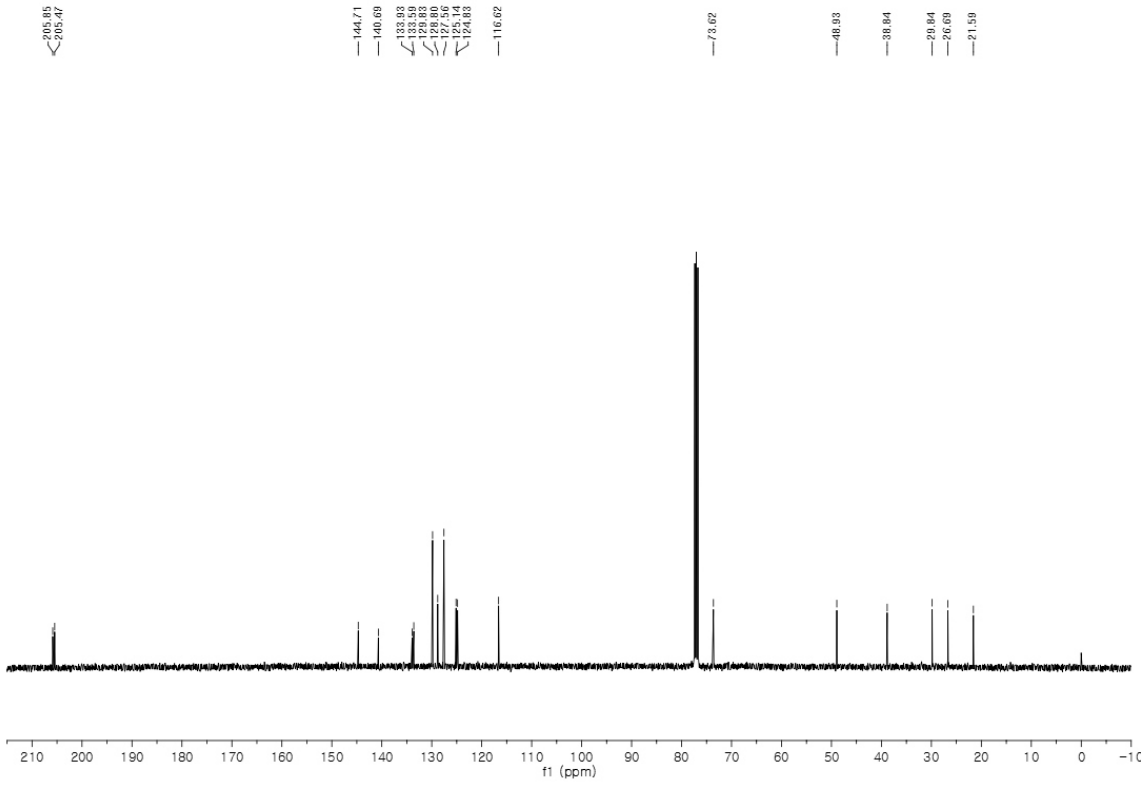
^{13}C NMR (100 MHz) in $CDCl_3$



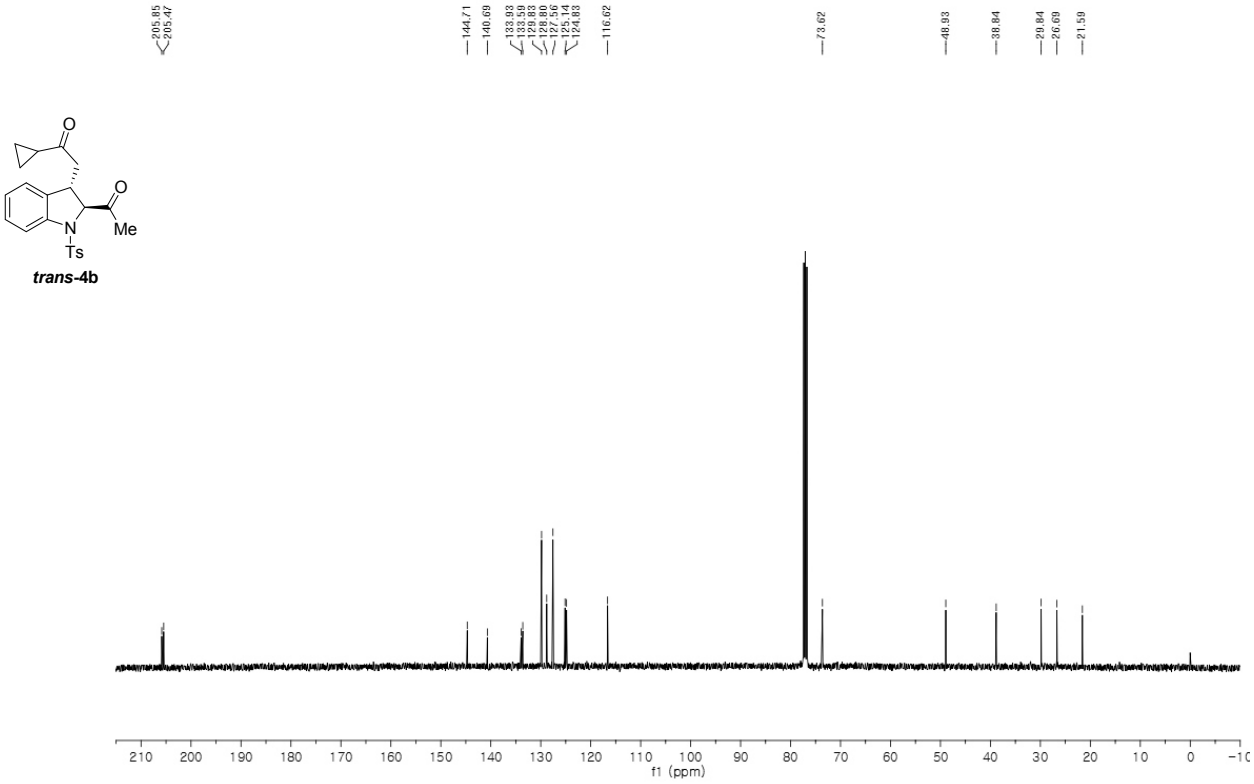
^{1}H NMR (400 MHz) in $CDCl_3$



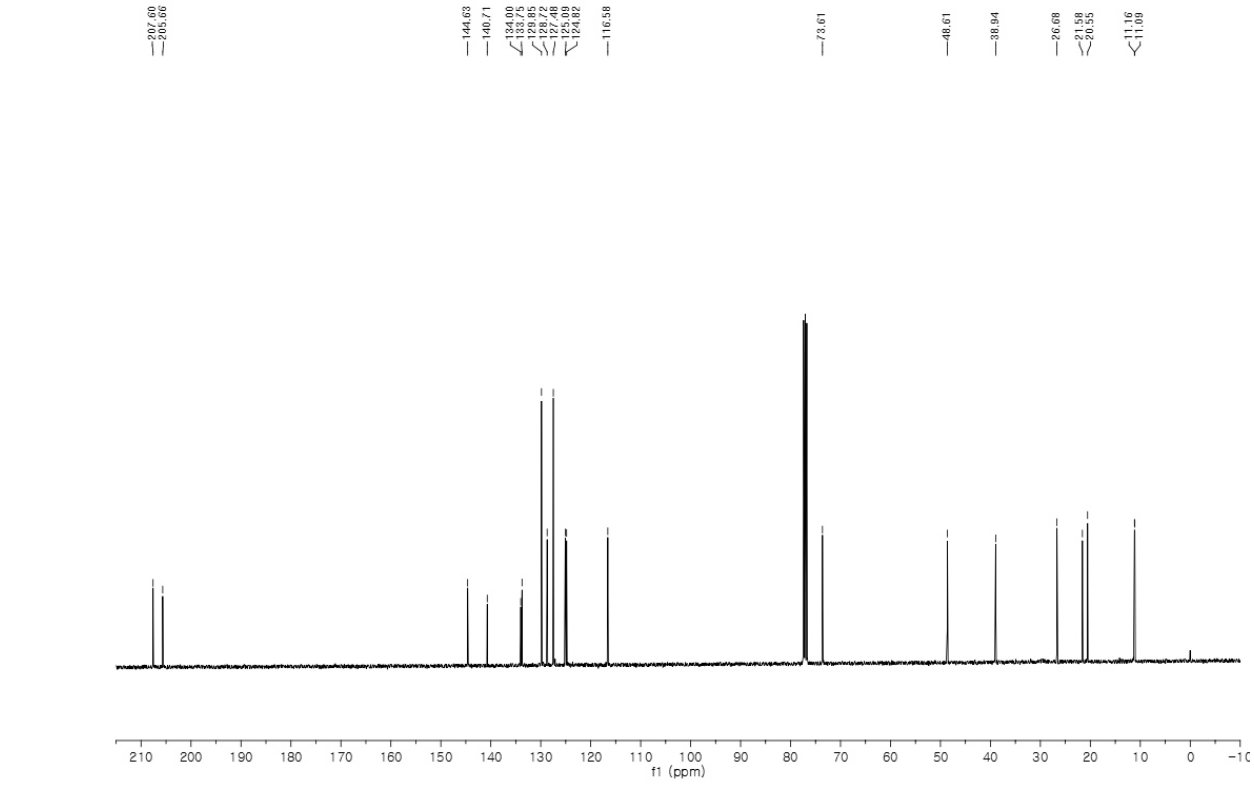
^{13}C NMR (100 MHz) in $CDCl_3$



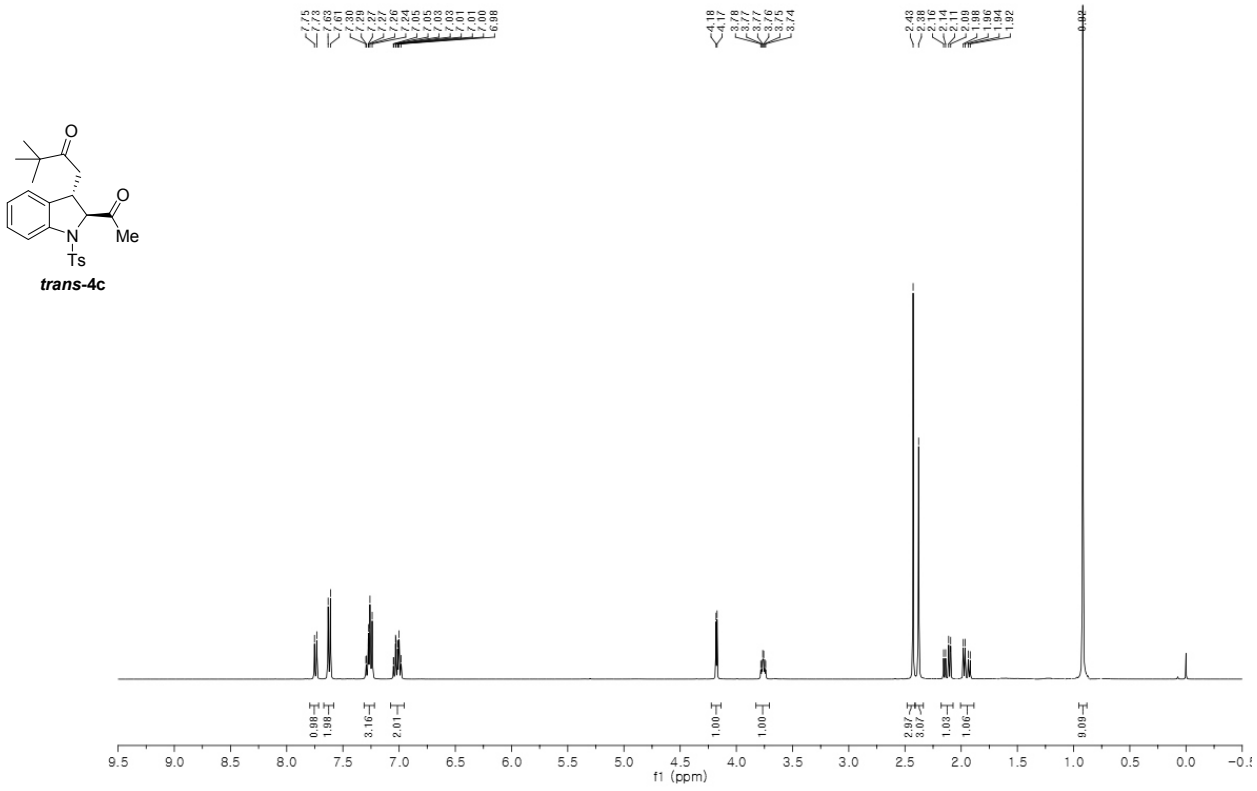
^{1}H NMR (400 MHz) in $CDCl_3$



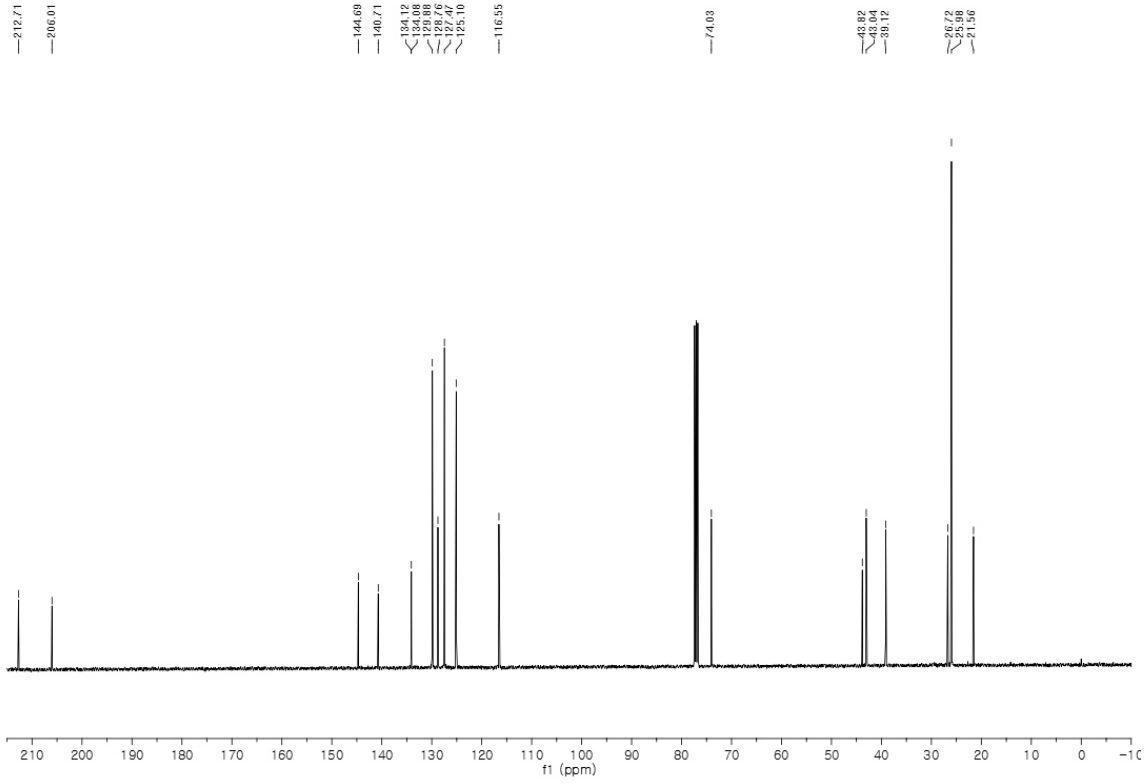
^{13}C NMR (100 MHz) in $CDCl_3$



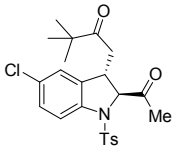
^{1}H NMR (400 MHz) in $CDCl_3$



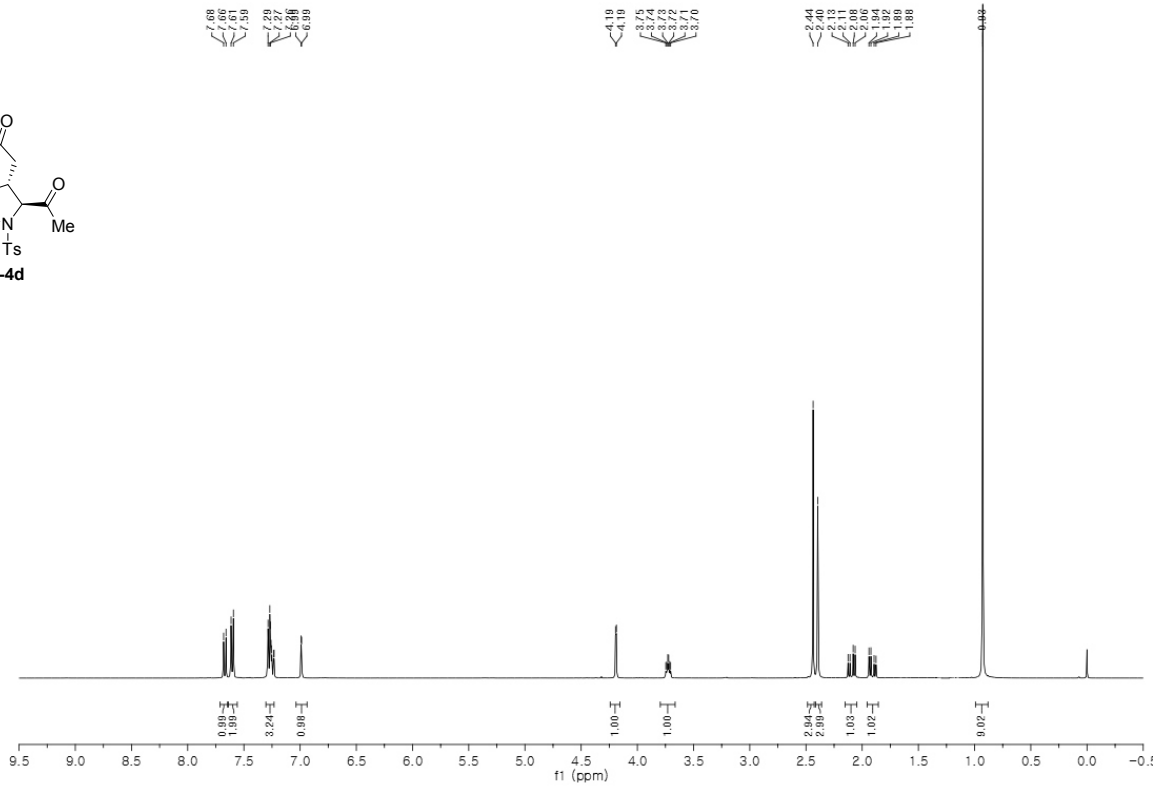
^{13}C NMR (100 MHz) in $CDCl_3$



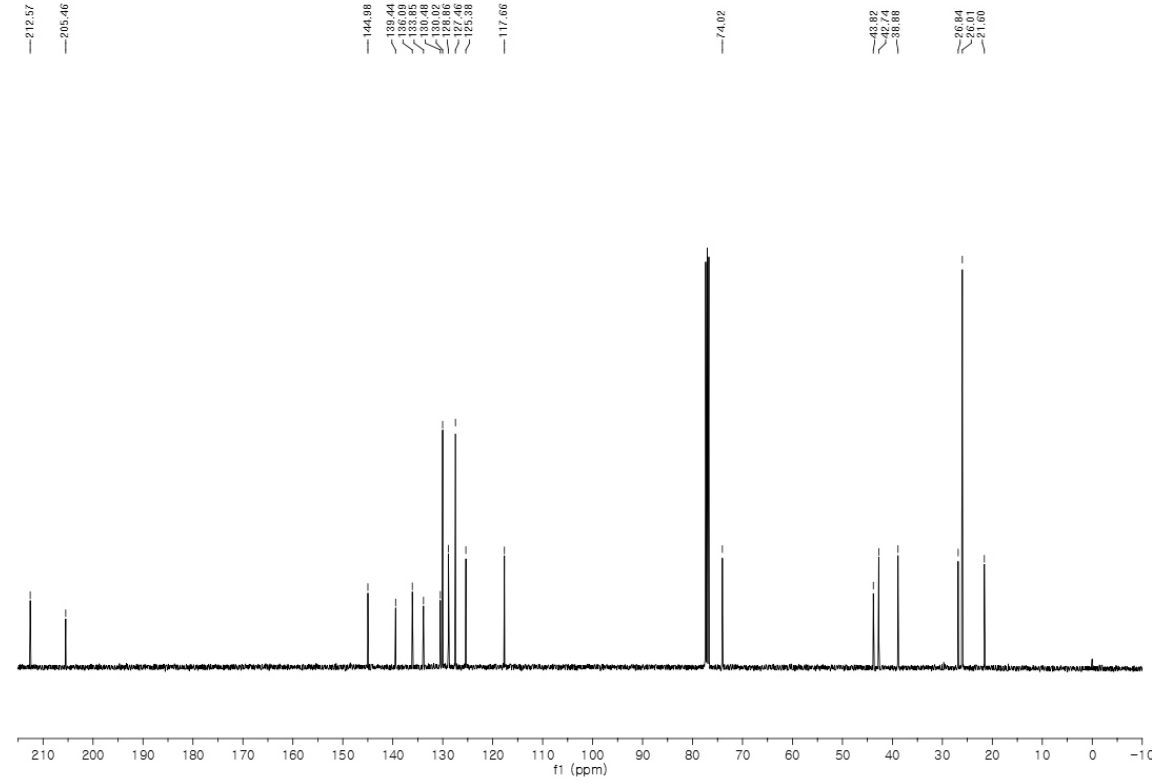
^{1}H NMR (400 MHz) in $CDCl_3$



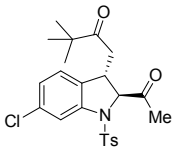
***trans*-4d**



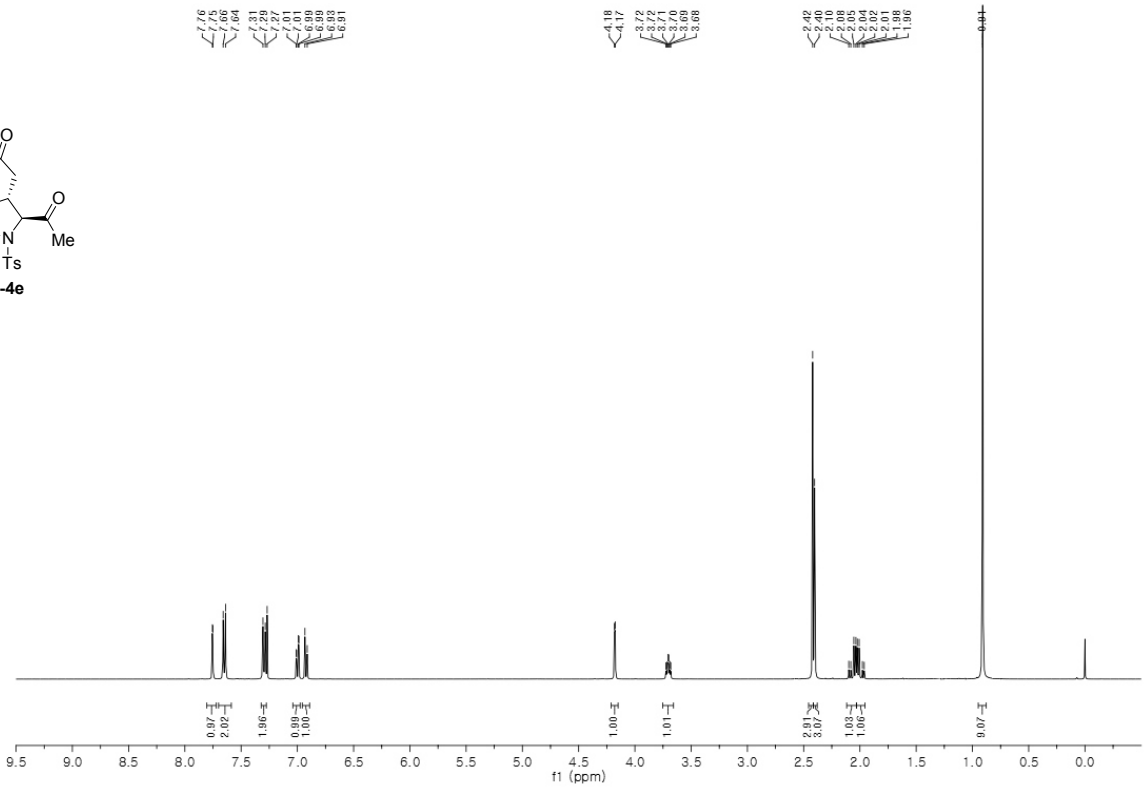
^{13}C NMR (100 MHz) in $CDCl_3$



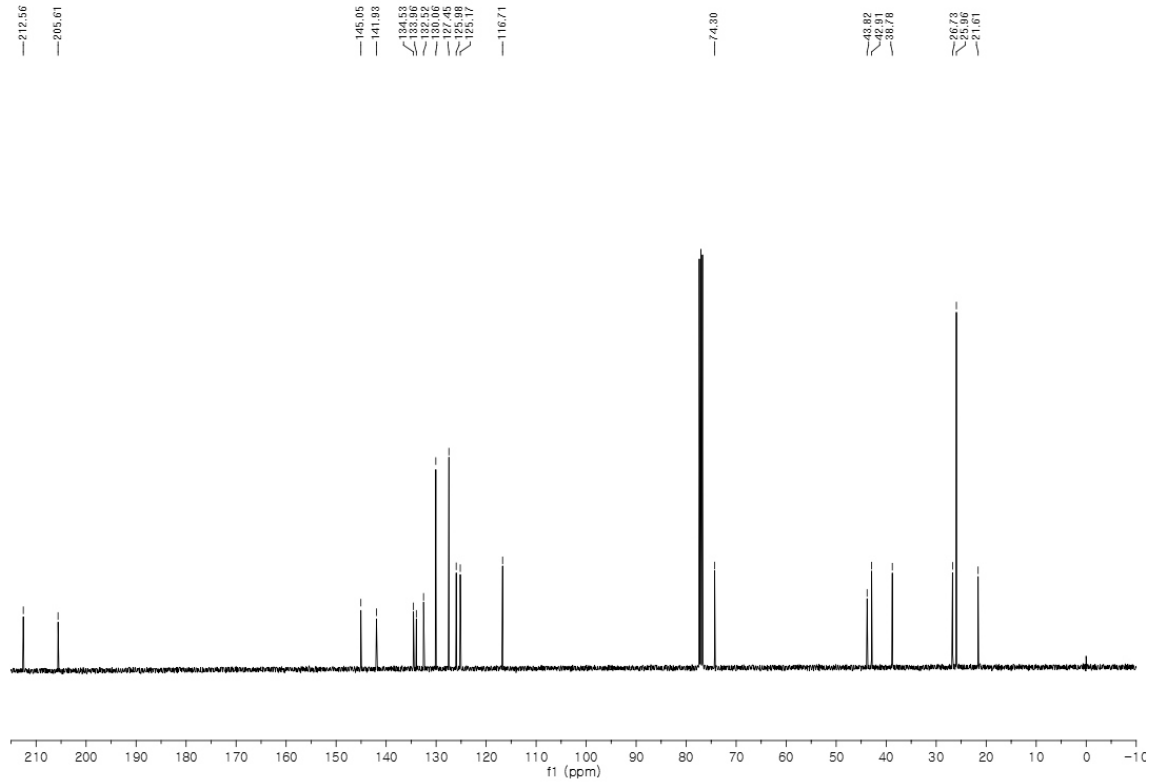
^{1}H NMR (400 MHz) in $CDCl_3$



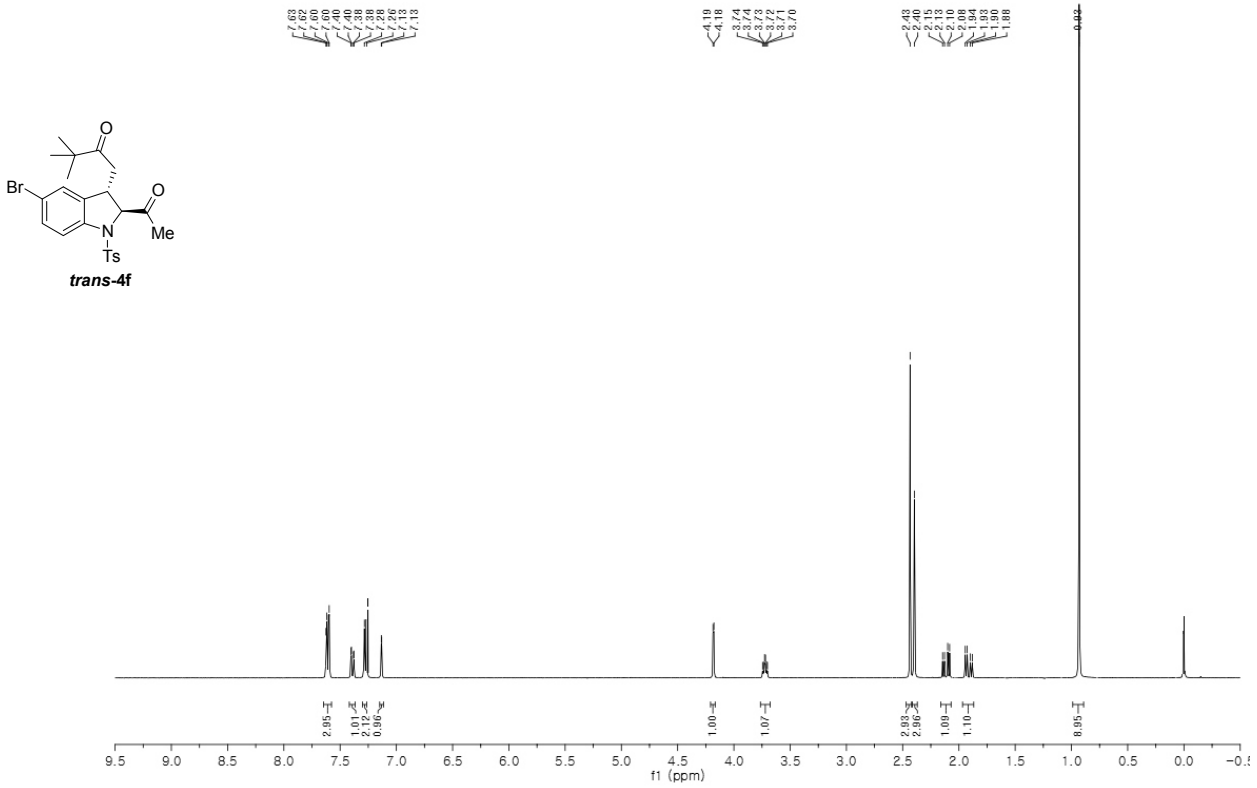
***trans*-4e**



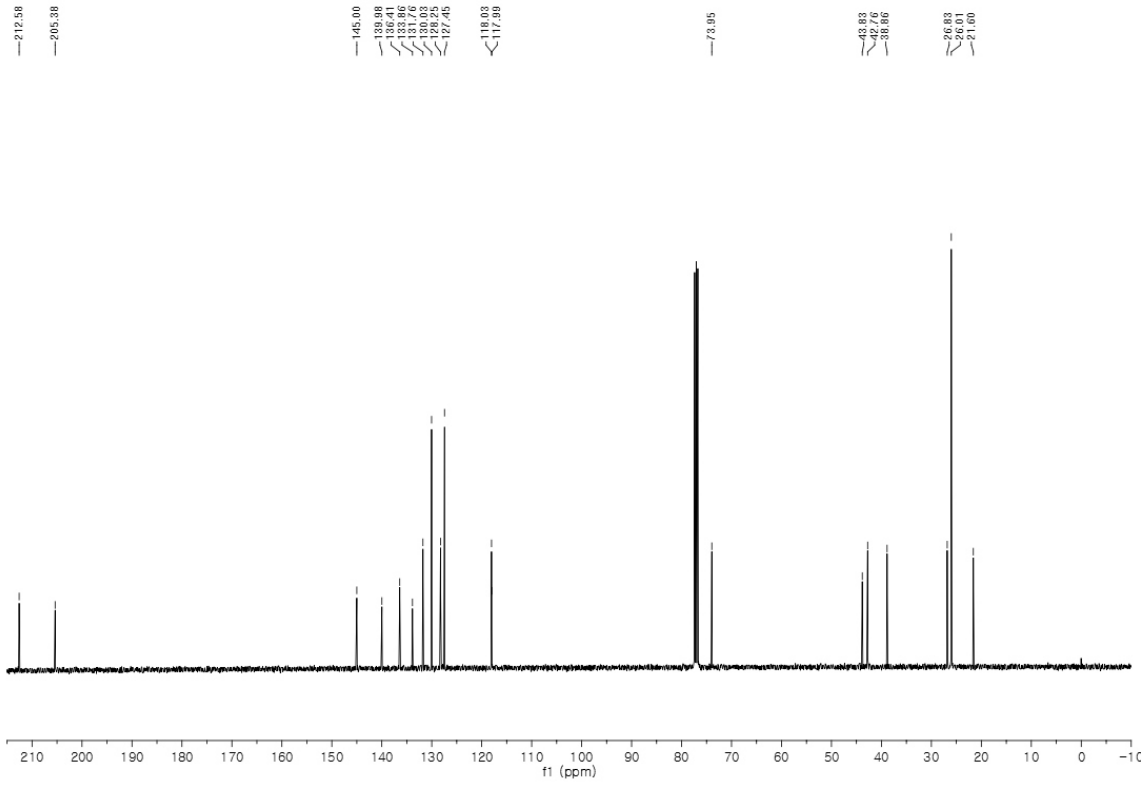
^{13}C NMR (100 MHz) in $CDCl_3$



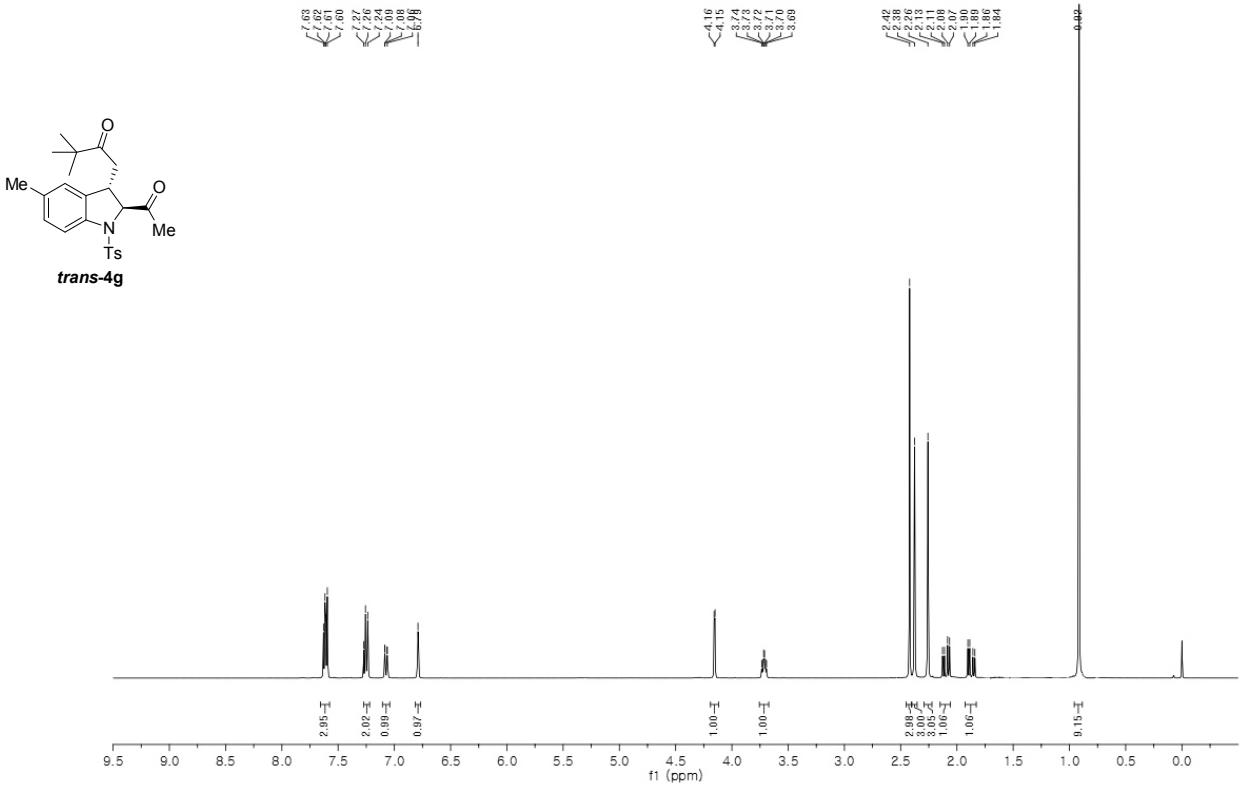
^{1}H NMR (400 MHz) in $CDCl_3$



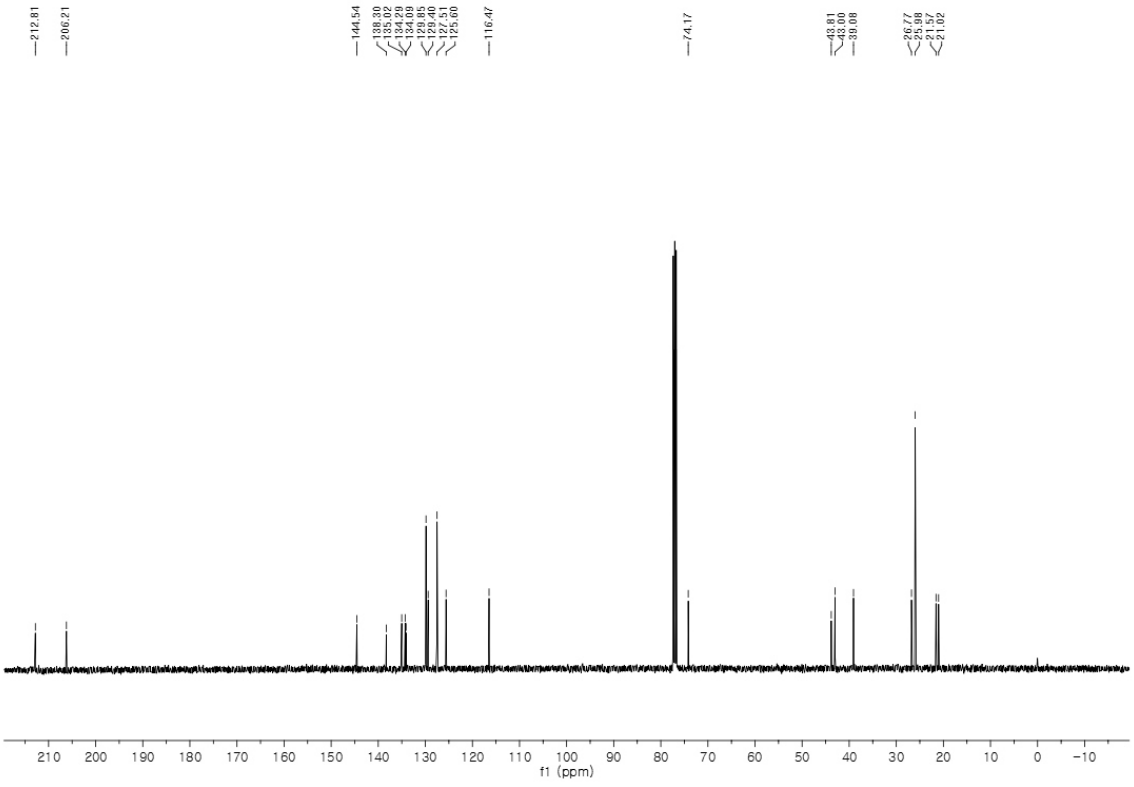
^{13}C NMR (100 MHz) in $CDCl_3$



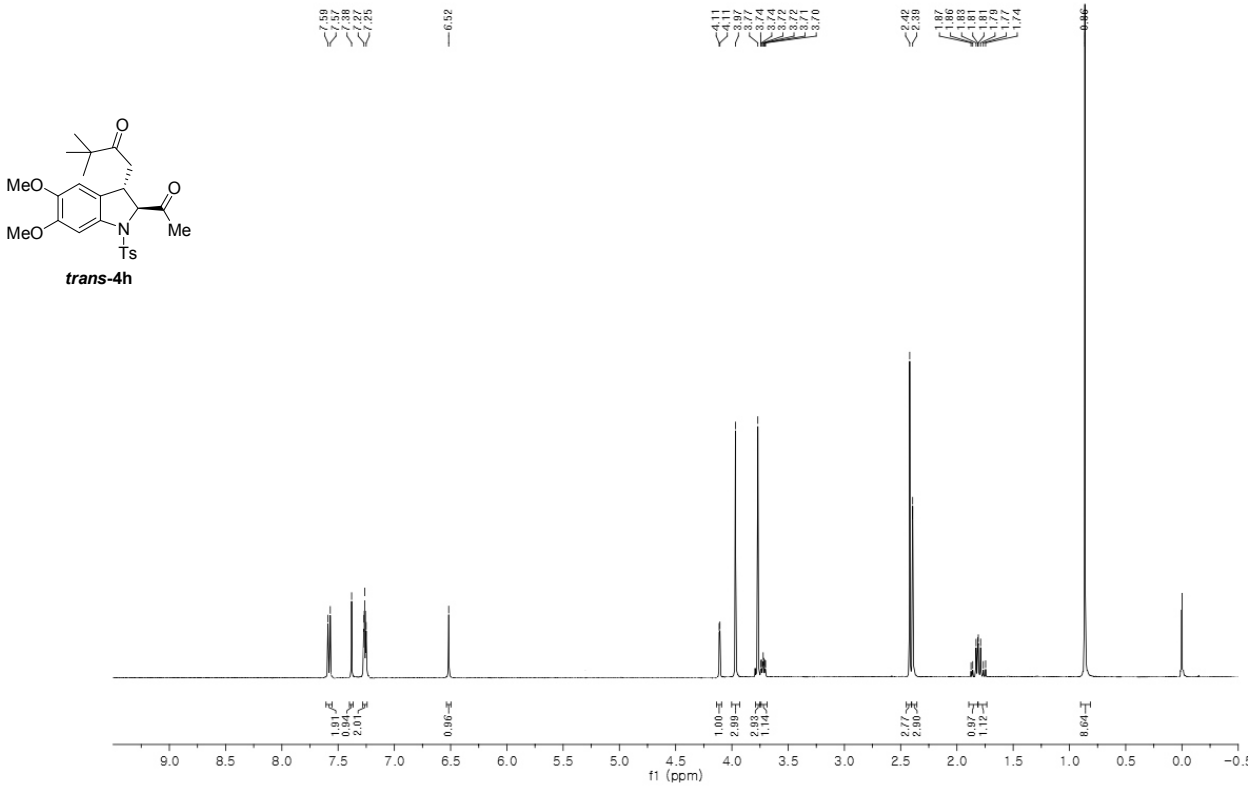
^{1}H NMR (400 MHz) in $CDCl_3$



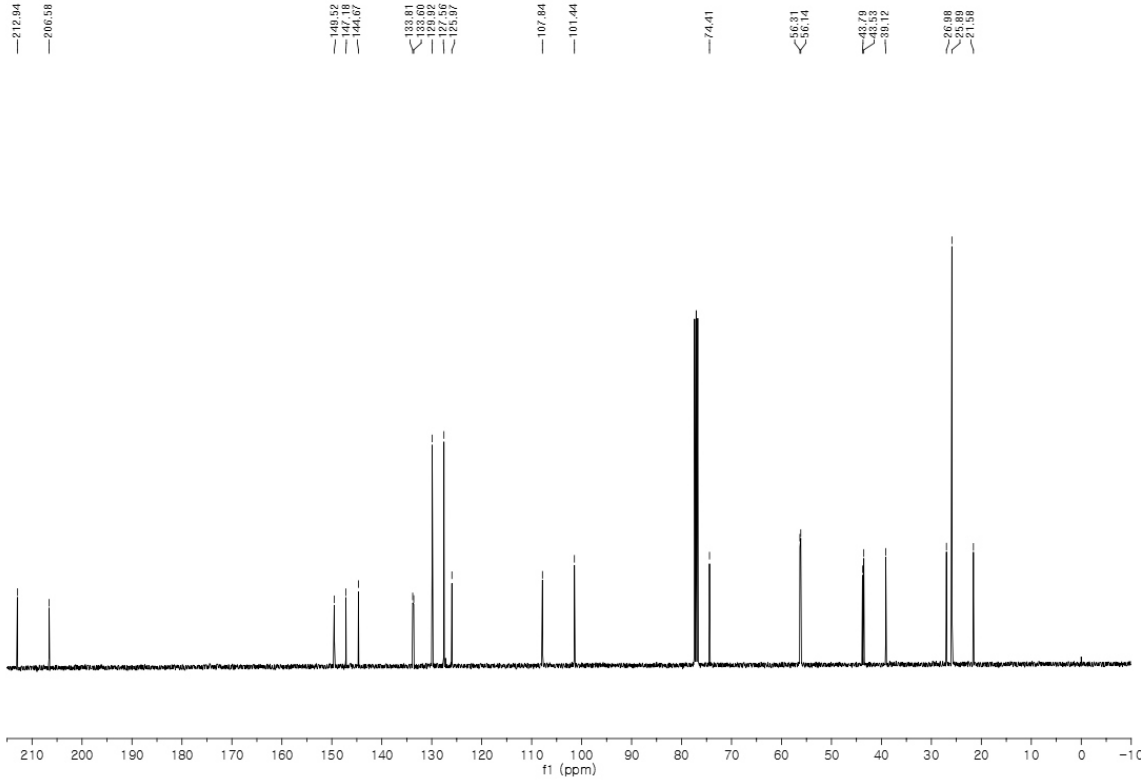
^{13}C NMR (100 MHz) in $CDCl_3$



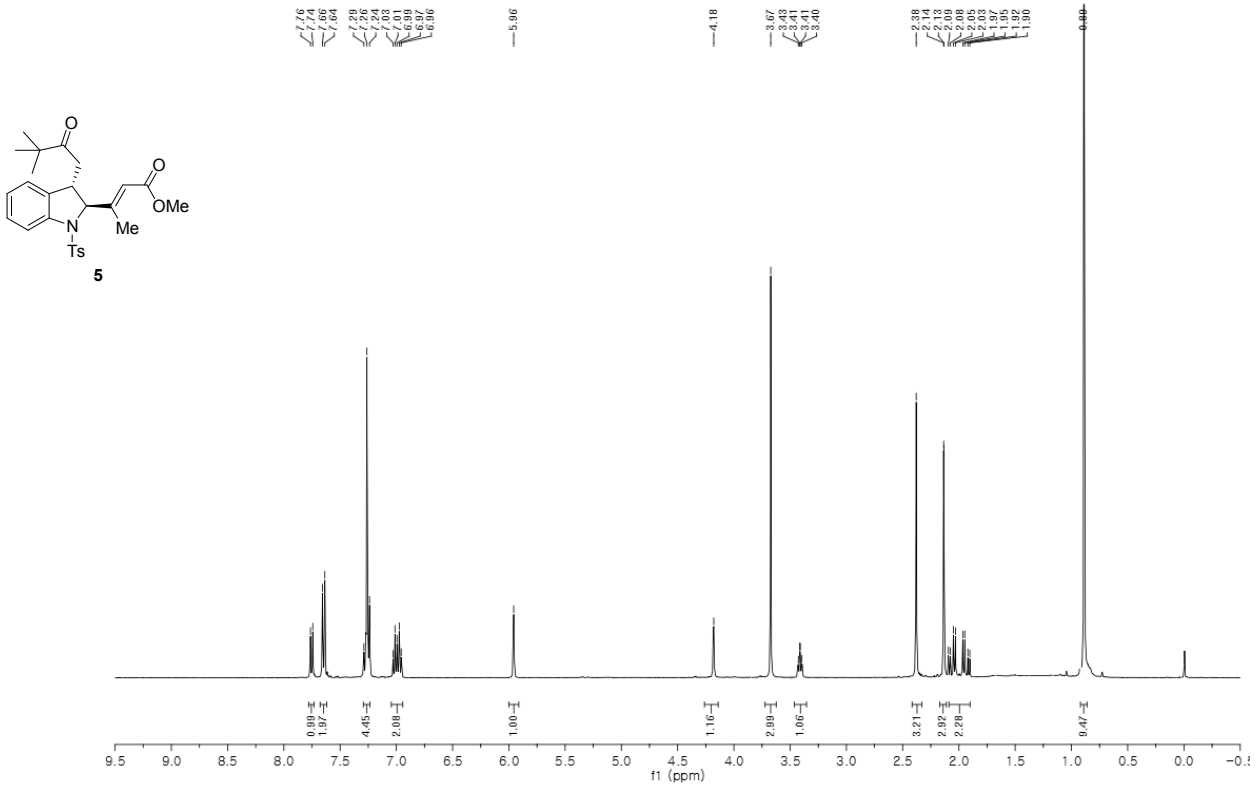
^{1}H NMR (400 MHz) in $CDCl_3$



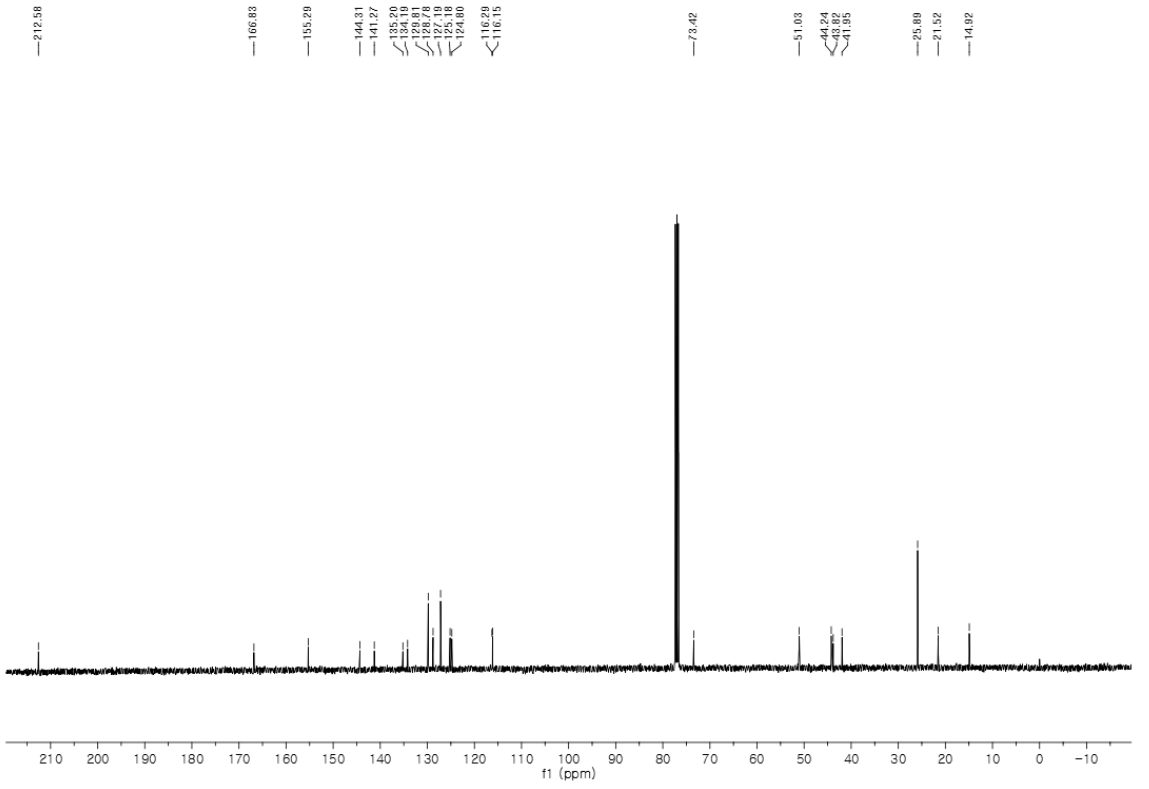
^{13}C NMR (100 MHz) in $CDCl_3$



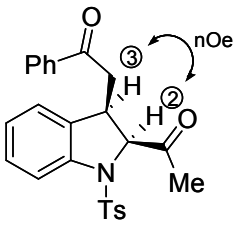
^{1}H NMR (400 MHz) in $CDCl_3$



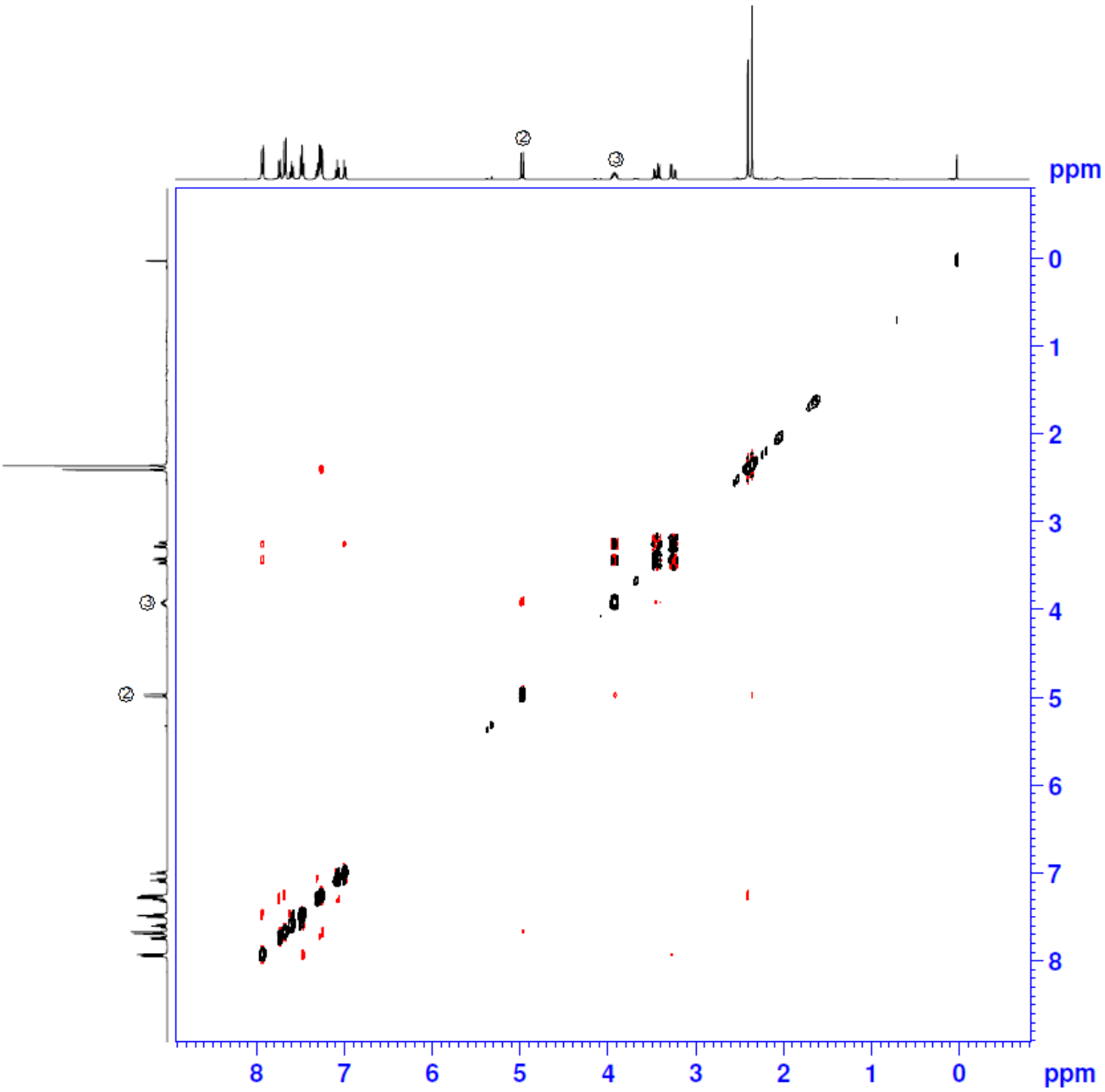
^{13}C NMR (100 MHz) in $CDCl_3$



NOESY



***cis*-2a**



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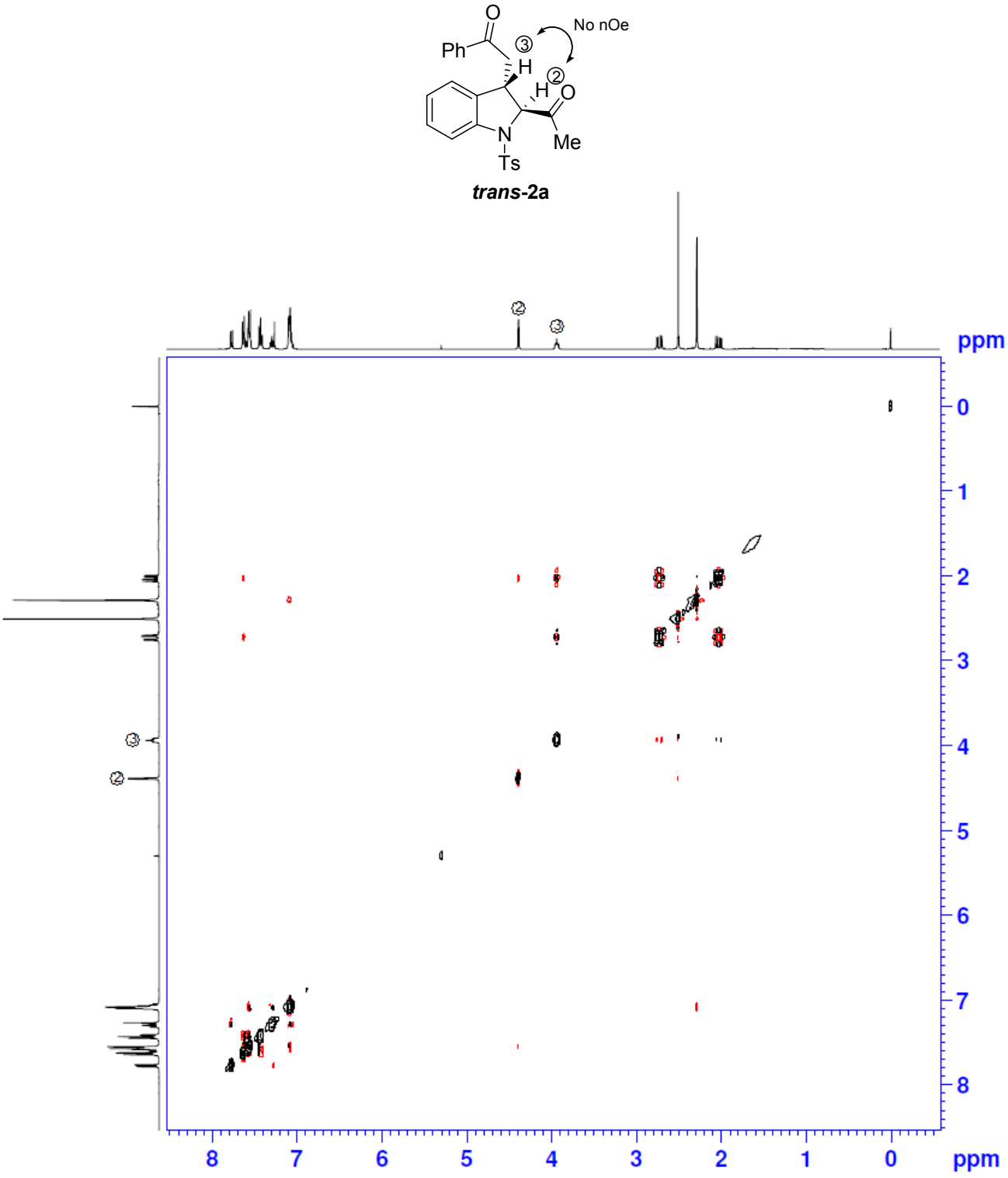
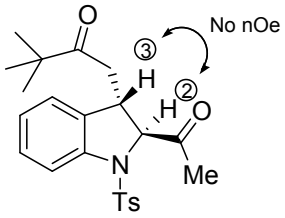
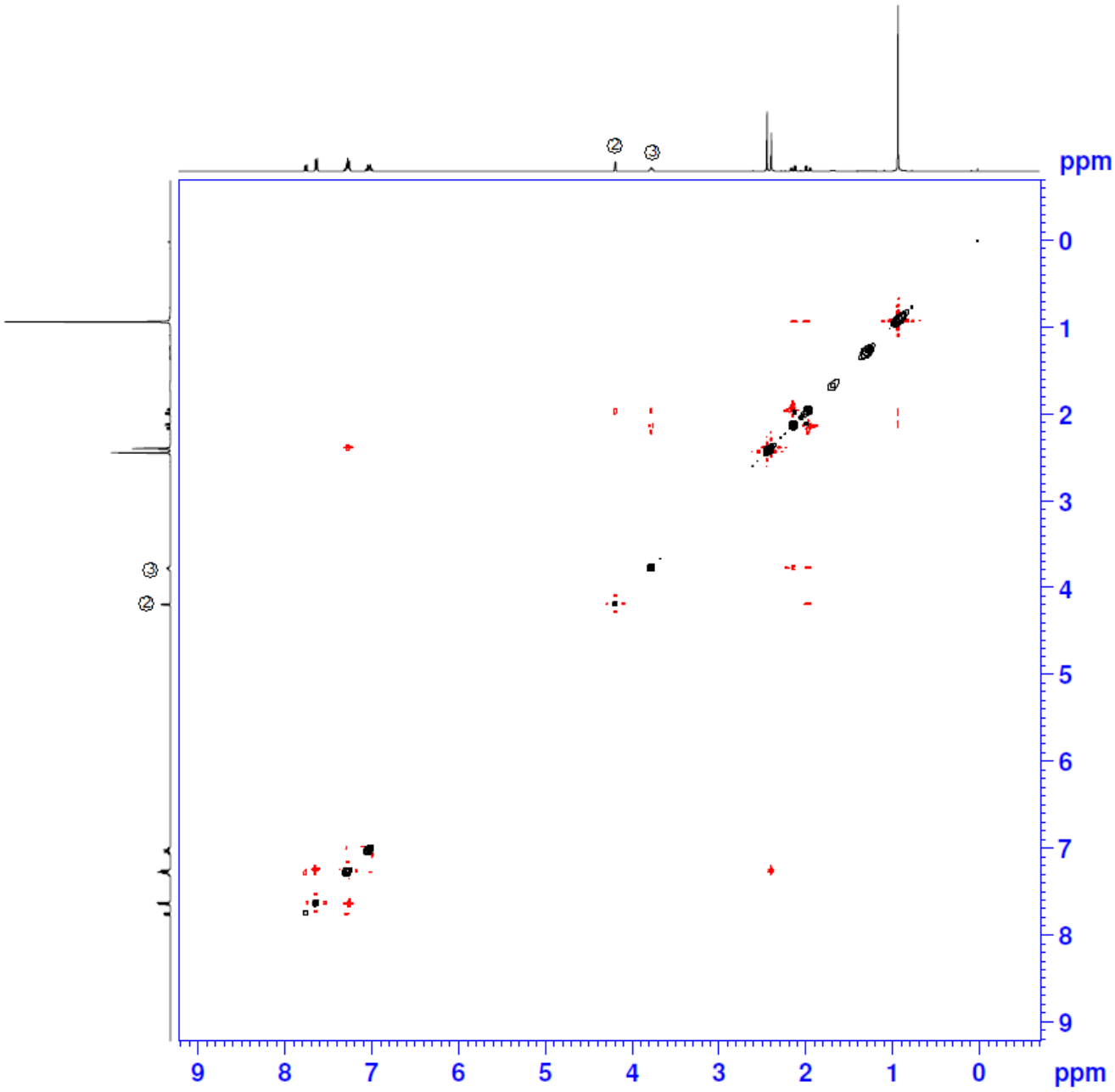

O
Ph
③
H
②
H
O
No nOe
N
Ts
Me
***trans*-2a**
②
③
ppm
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
ppm

NOESY

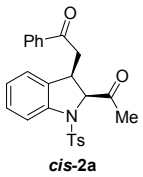


***trans*-4c**

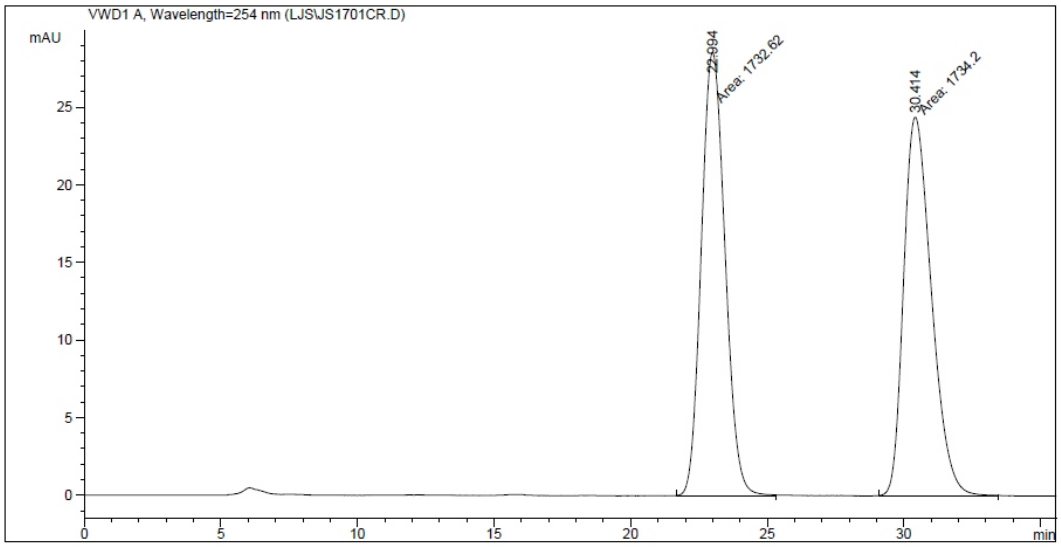


HPLC analysis

racemic



***cis*-2a**

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=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  22.994 MM    1.0094 1732.61792   28.60897  49.9771
   2  30.414 MM    1.1828 1734.20288   24.43619  50.0229
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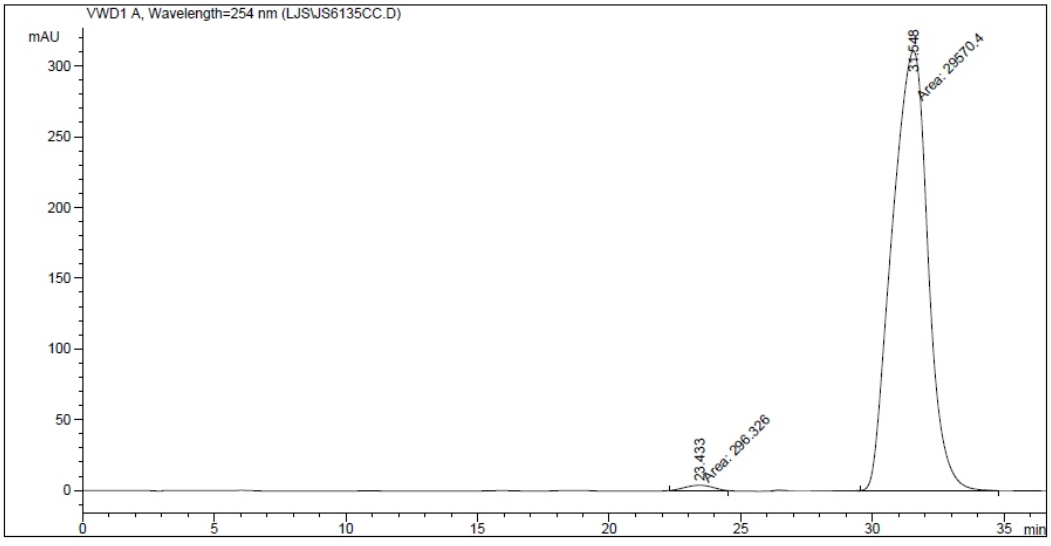
chiral

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                      Area Percent Report
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Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  23.433 MM    1.2631  296.32605    3.91012   0.9922
   2  31.548 MM    1.5827 2.95704e4   311.40012  99.0078
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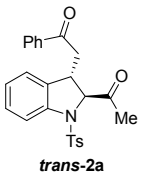
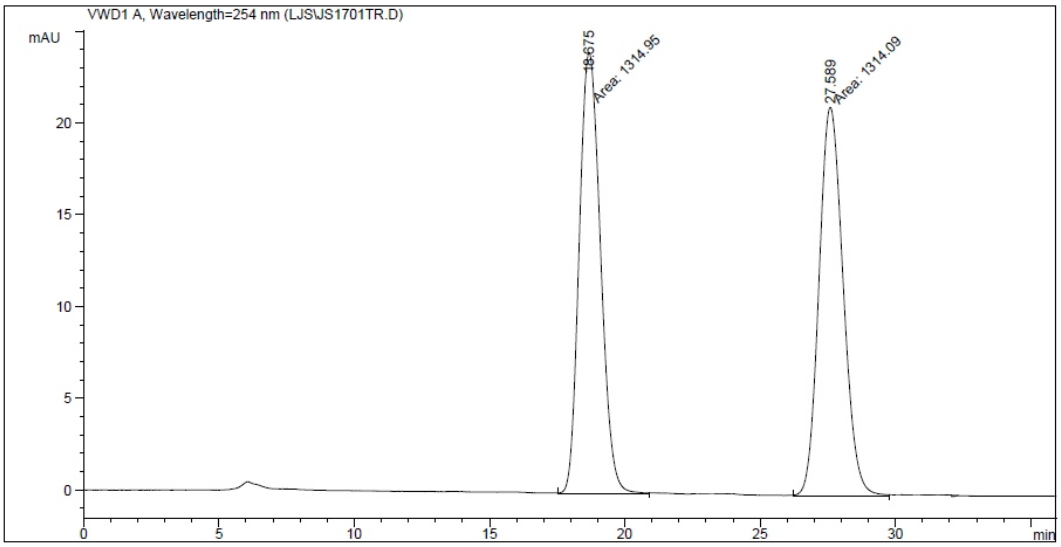
HPLC analysis

racemic



***trans*-2a**

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                      Area Percent Report
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Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.675 MM    0.9112 1314.95056   24.05093  50.0163
   2  27.589 MM    1.0346 1314.09436   21.16842  49.9837
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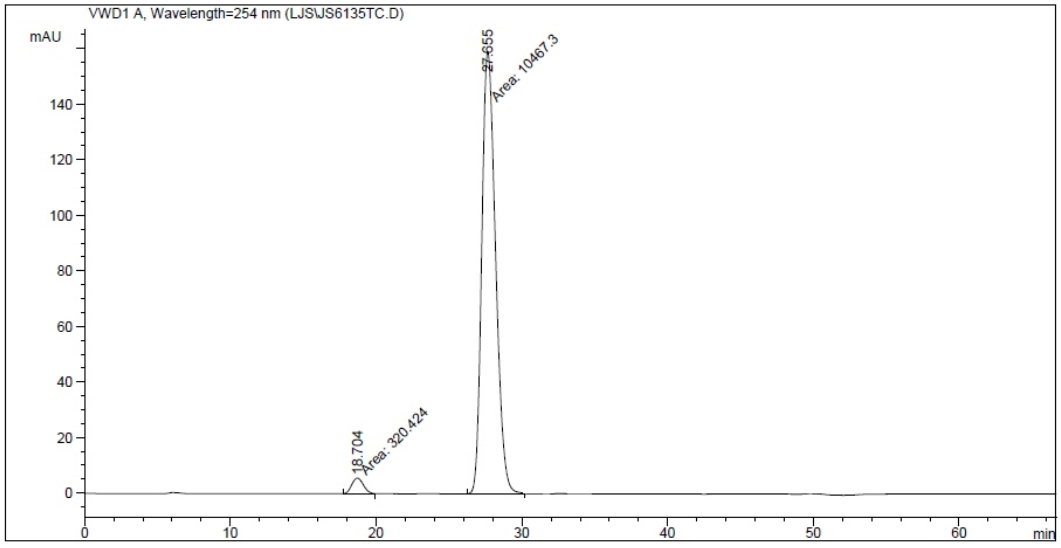
chiral

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                      Area Percent Report
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Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.704 MM    0.9381  320.42389    5.69291   2.9703
   2  27.655 MM    1.0948 1.04673e4   159.35616  97.0297
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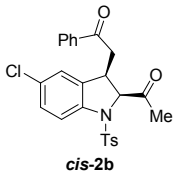
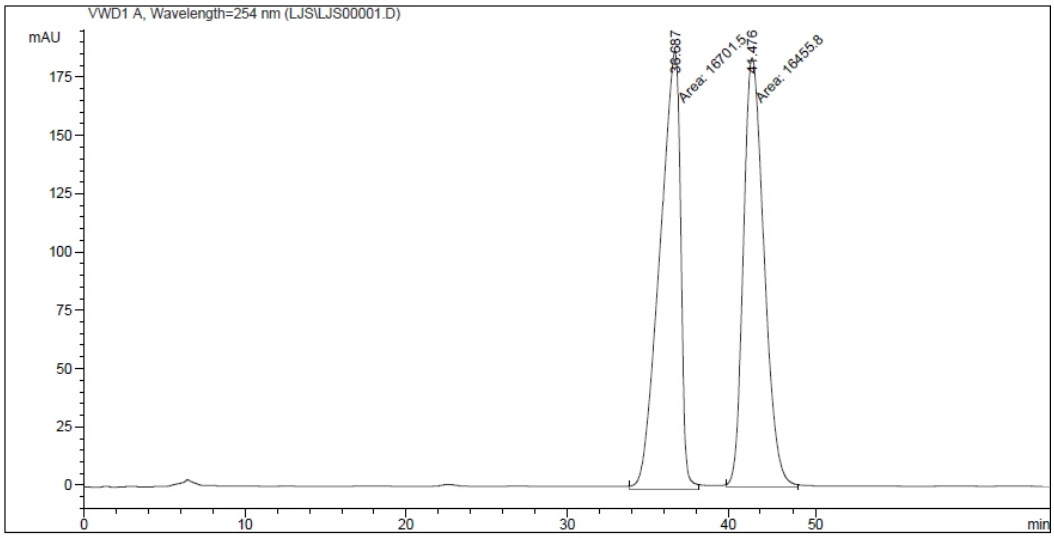
HPLC analysis

racemic



***cis*-2b**

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                      Area Percent Report
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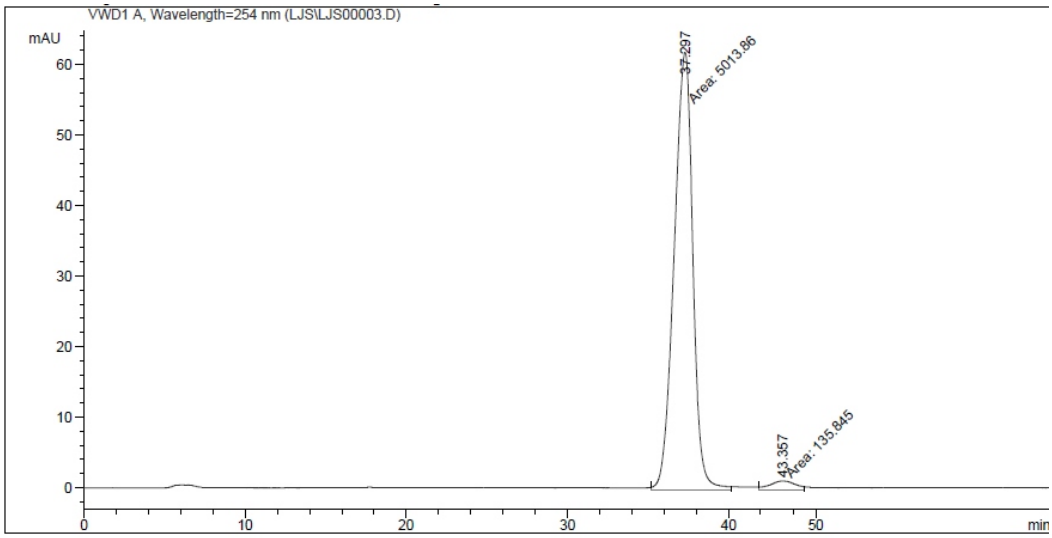
Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  36.687 MM    1.4833 1.67015e4   187.65604  50.3706
   2  41.476 MM    1.4906 1.64558e4   183.99289  49.6294
```

chiral

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                      Area Percent Report
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Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  37.297 MM    1.3484 5013.86084   61.97408  97.3621
   2  43.357 MM    1.8231  135.84497    1.24186   2.6379
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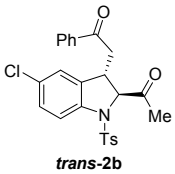
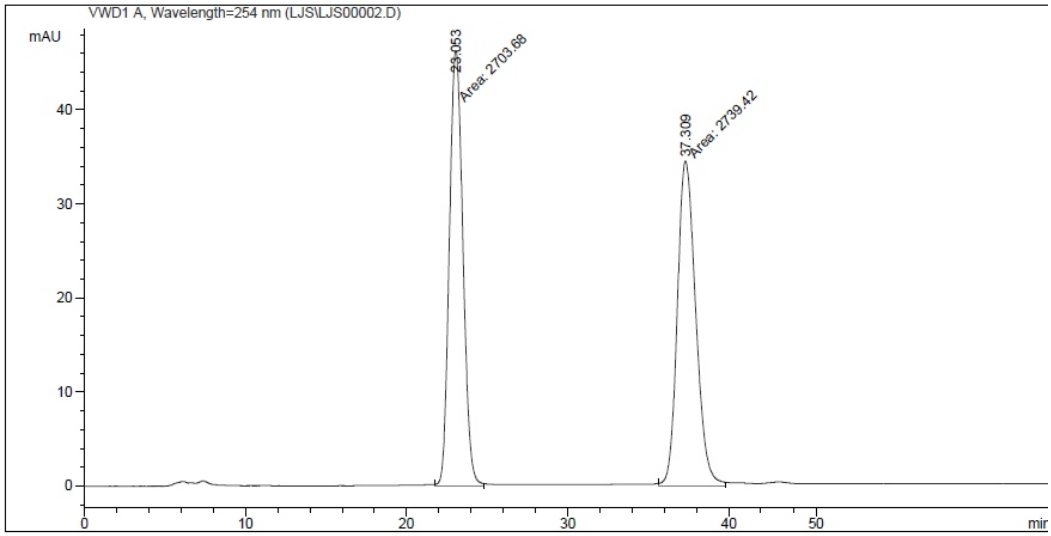
HPLC analysis

racemic



***trans*-2b**

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                      Area Percent Report
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Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  23.053 MM    0.9737 2703.68262   46.27657  49.6717
   2  37.309 MM    1.3211 2739.41870   34.55961  50.3283
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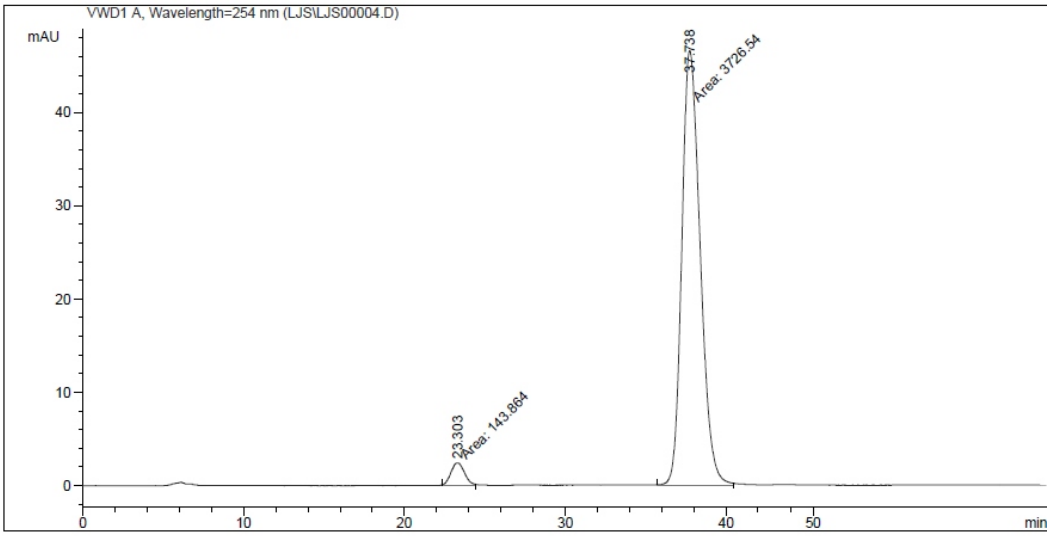
chiral

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                      Area Percent Report
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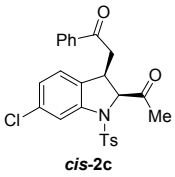
Signal 1: VWD1 A, Wavelength=254 nm

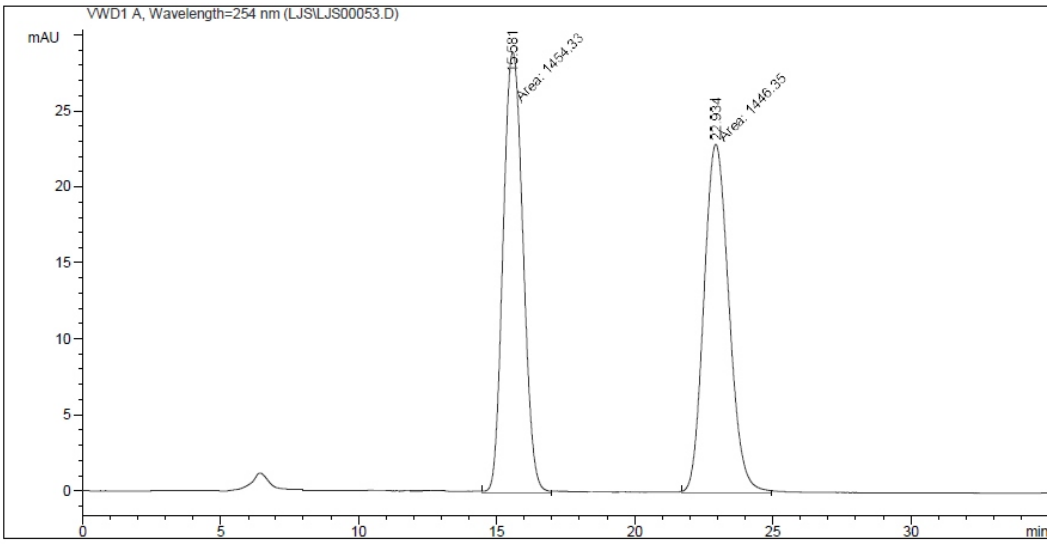
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  23.303 MM    0.9841  143.86441    2.43650   3.7170
   2  37.738 MM    1.3325 3726.54272   46.61250  96.2830
```

HPLC analysis

racemic



***cis*-2c**

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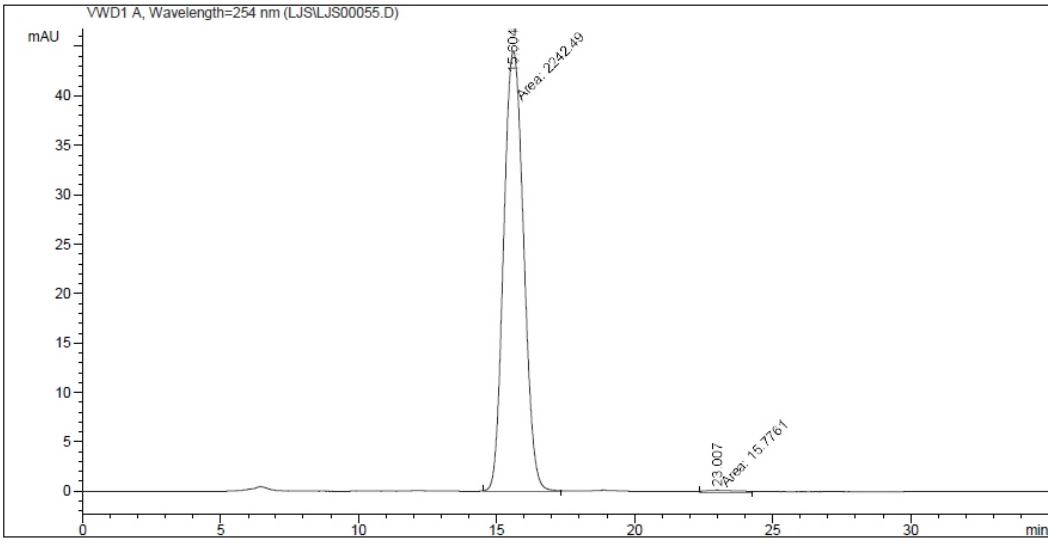
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.581 MM    0.8353 1454.32971   29.01744  50.1376
   2  22.934 MM    1.0509 1446.34851   22.93833  49.8624
```

chiral

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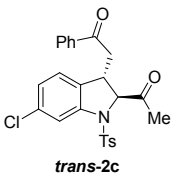
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

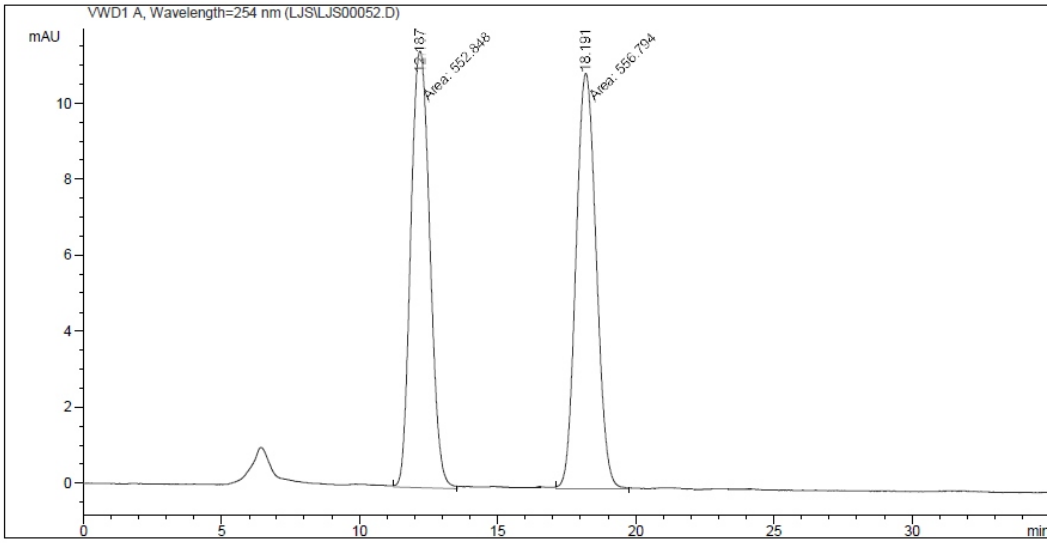
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.604 MM    0.8384 2242.49072   44.58118  99.3014
   2  23.007 MM    1.3967   15.77606 1.88258e-1   0.6986
```

HPLC analysis

racemic



***trans*-2c**

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=====================================================================
                      Area Percent Report
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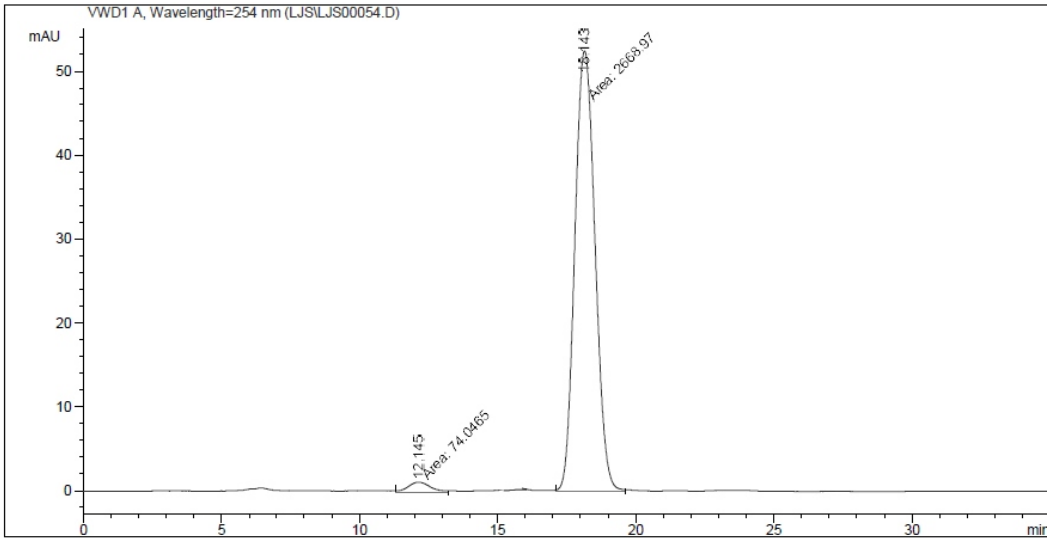
Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.187 MM    0.8011  552.84784   11.50142  49.8222
   2  18.191 MM    0.8482  556.79425   10.94055  50.1778
```

chiral



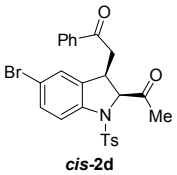

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

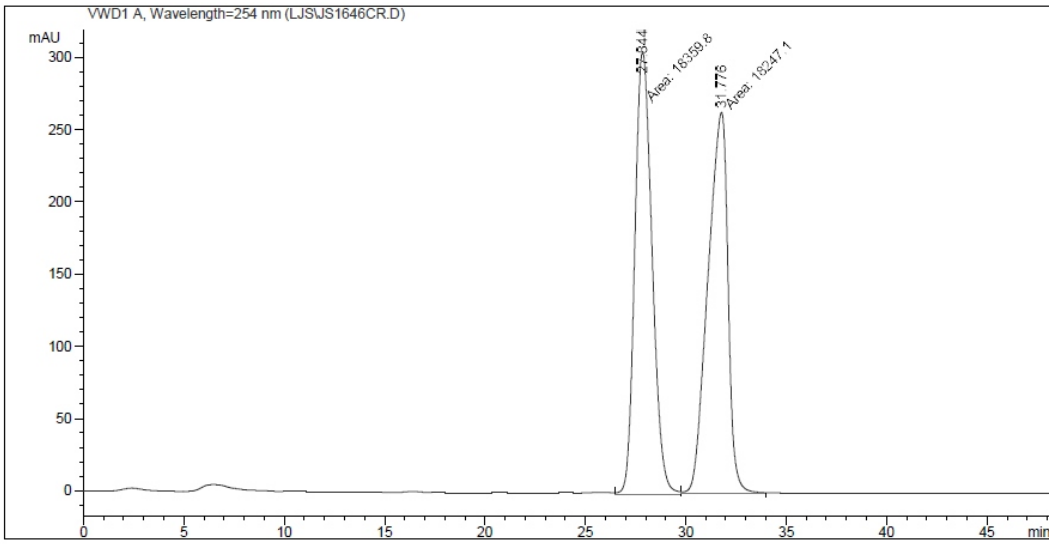
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.145 MM    0.9962   74.04646    1.23884   2.6995
   2  18.143 MM    0.8465 2668.97388   52.54628  97.3005
```

HPLC analysis

racemic



***cis*-2d**

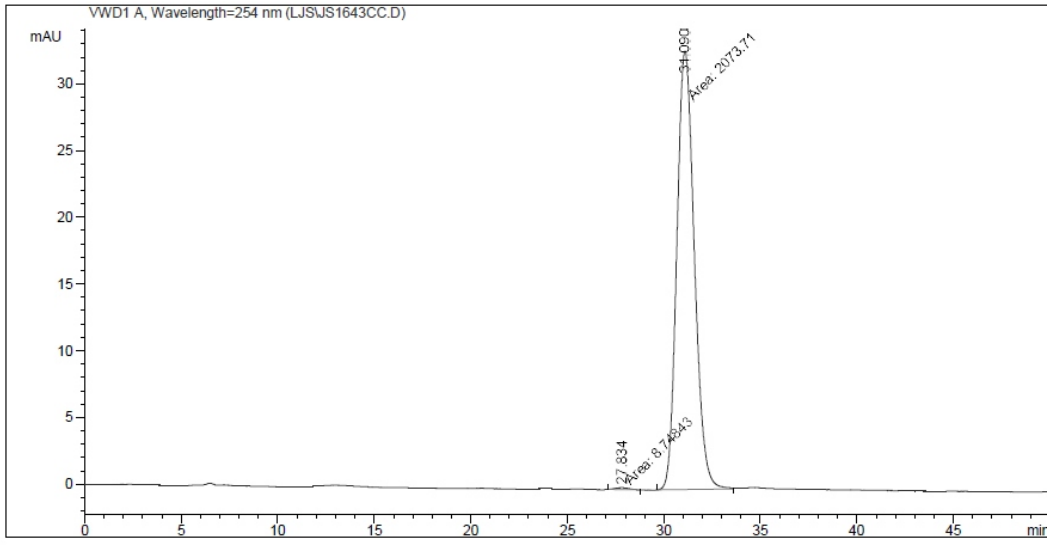



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.844 MM    0.9992 1.83598e4   306.24304  50.1540
   2  31.776 MM    1.1541 1.82471e4   263.50684  49.8460
```

chiral



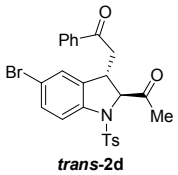

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

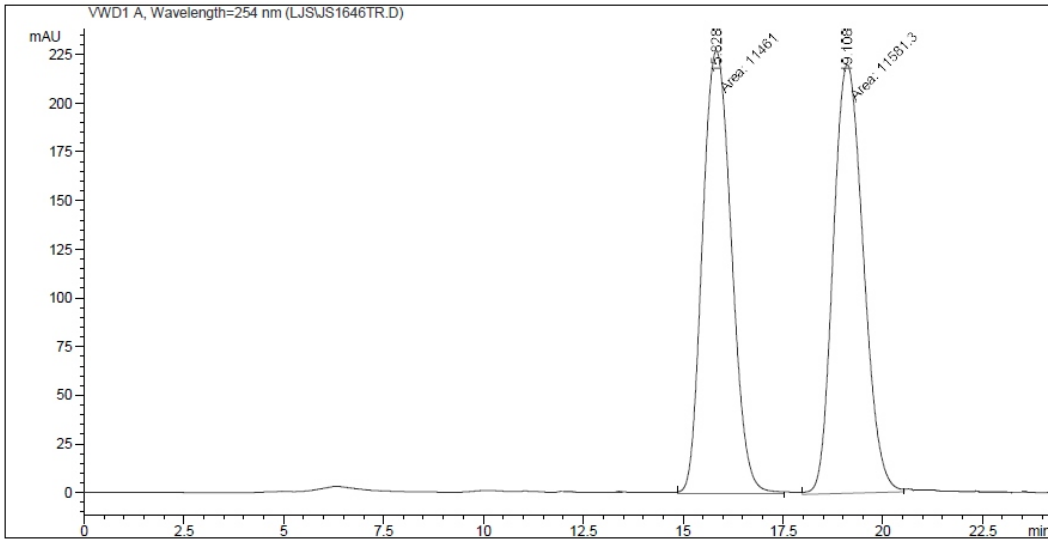
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.834 MM    0.9458    8.74843 1.54163e-1   0.4201
   2  31.090 MM    1.0516 2073.71167   32.86654  99.5799
```

HPLC analysis

racemic



***trans*-2d**

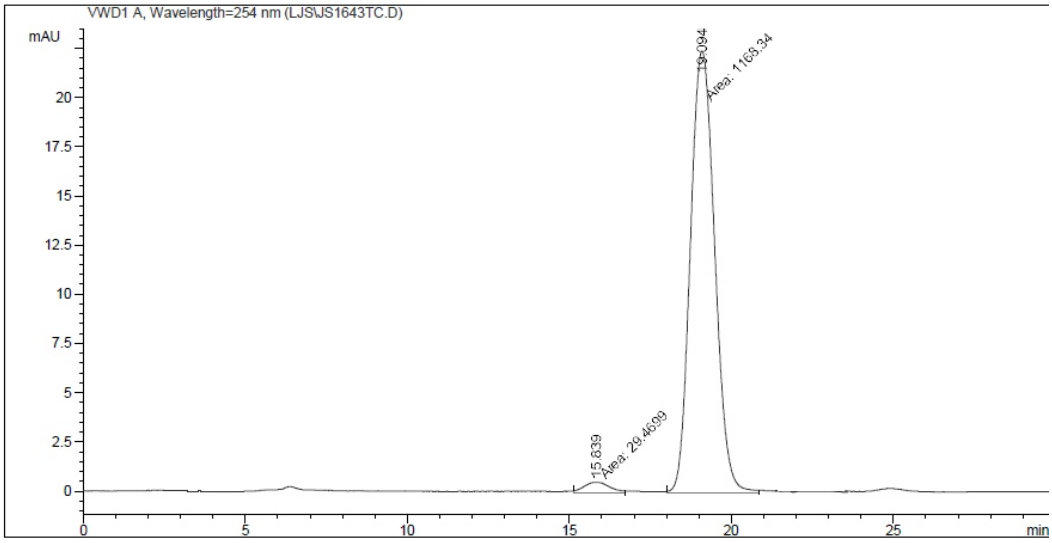



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.828 MM    0.8406 1.14610e4   227.24185  49.7390
   2  19.108 MM    0.8759 1.15813e4   220.37016  50.2610
```

chiral



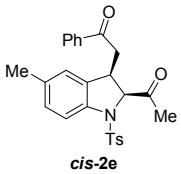

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

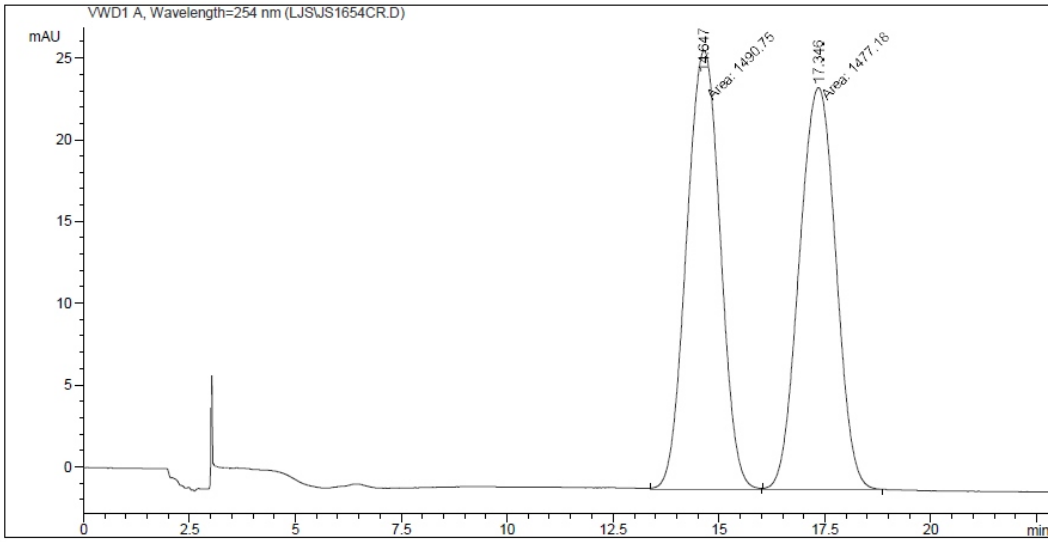
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.839 MM    0.9170   29.46995 5.35614e-1   2.4603
   2  19.094 MM    0.8670 1168.34363   22.45969  97.5397
```

HPLC analysis

racemic



***cis*-2e**

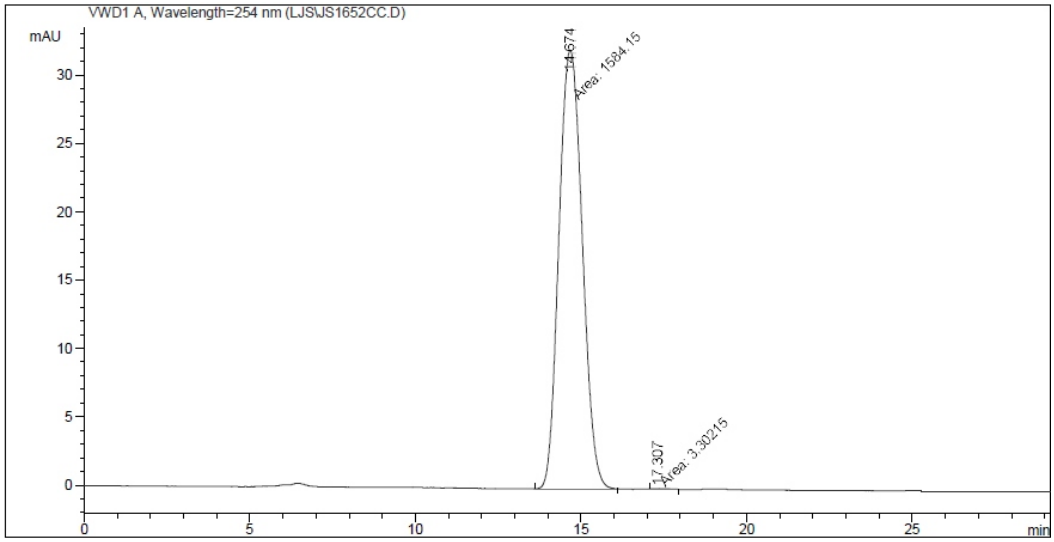



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.647 MM    0.9252 1490.74963   26.85409  50.2287
   2  17.346 MM    1.0011 1477.17700   24.59181  49.7713
```

chiral



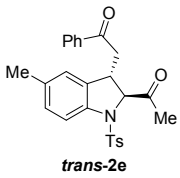

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

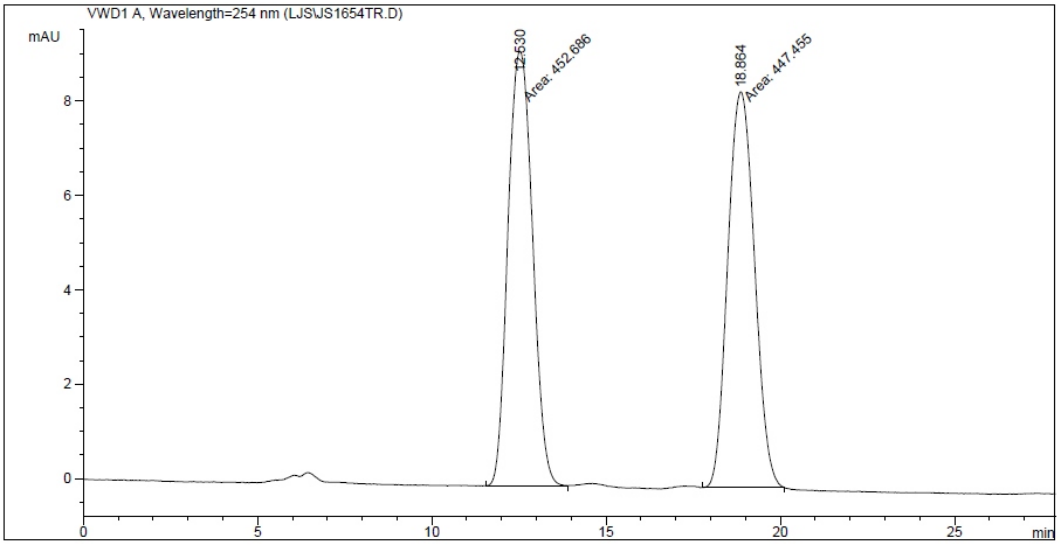
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.674 MM    0.8214 1584.14783   32.14402  99.7920
   2  17.307 MM    0.6551    3.30215 8.40094e-2   0.2080
```

HPLC analysis

racemic



***trans*-2e**

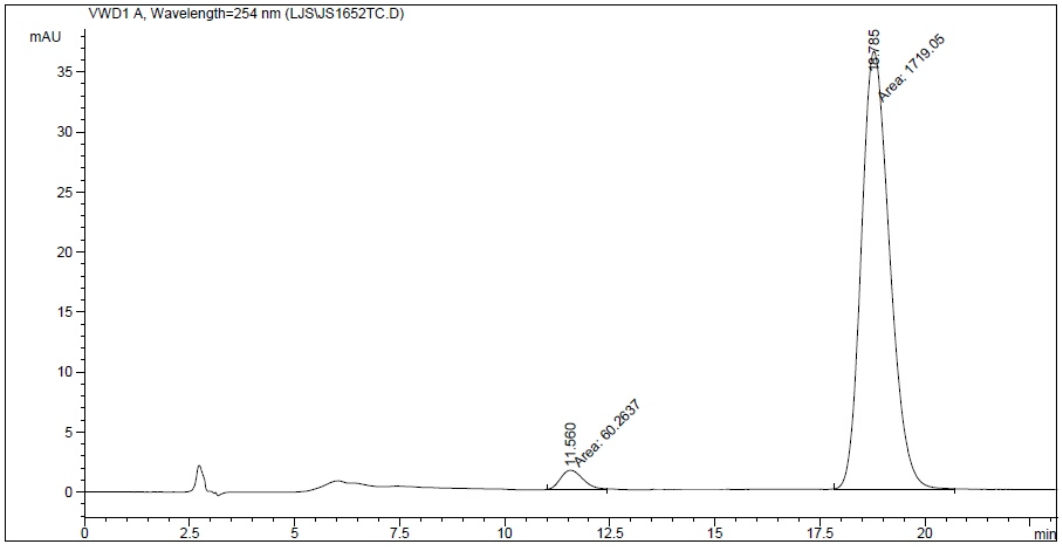



```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.530 MM    0.8190  452.68591    9.21261  50.2906
   2  18.864 MM    0.8890  447.45514    8.38864  49.7094
```

chiral



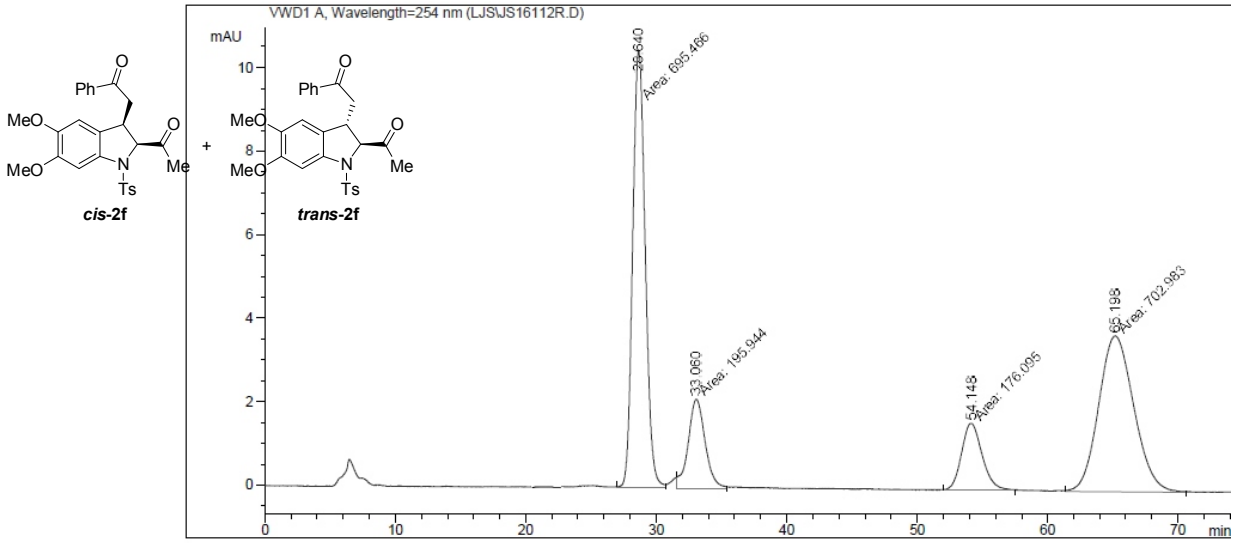

```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.560 MM    0.6228   60.26366    1.61258   3.3869
   2  18.785 MM    0.7846 1719.05444   36.51610  96.6131
```

HPLC analysis

racemic

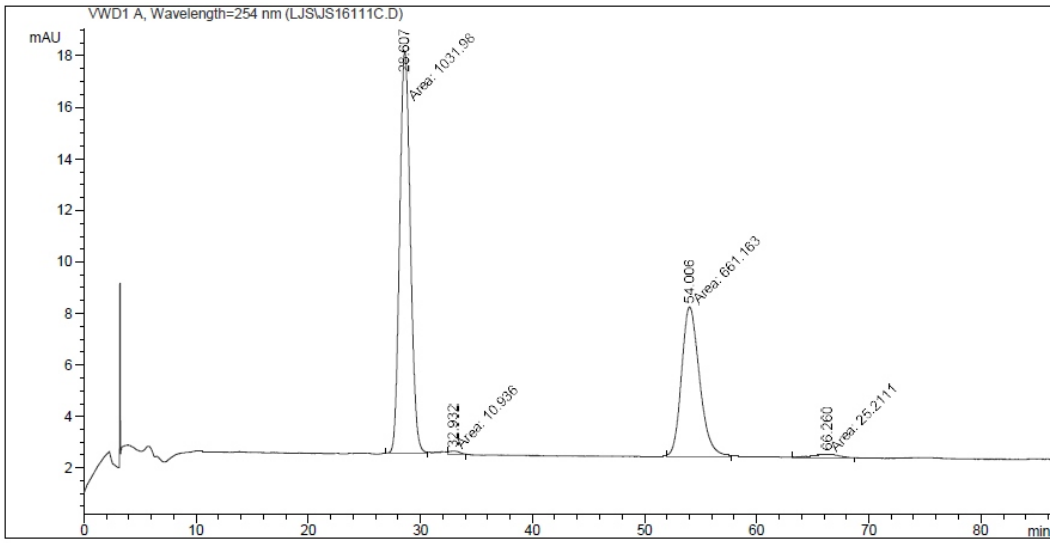



```
=====================================================================
                    Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  28.640 MM    1.1088  695.46631   10.45417  39.2810
   2  33.060 MM    1.5188  195.94395    2.15025  11.0672
   3  54.148 MM    1.8319  176.09546    1.60214   9.9461
   4  65.198 MM    3.1337  702.98309    3.73886  39.7056
```

chiral



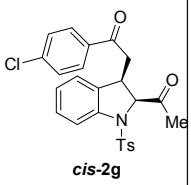

```
=====================================================================
                    Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

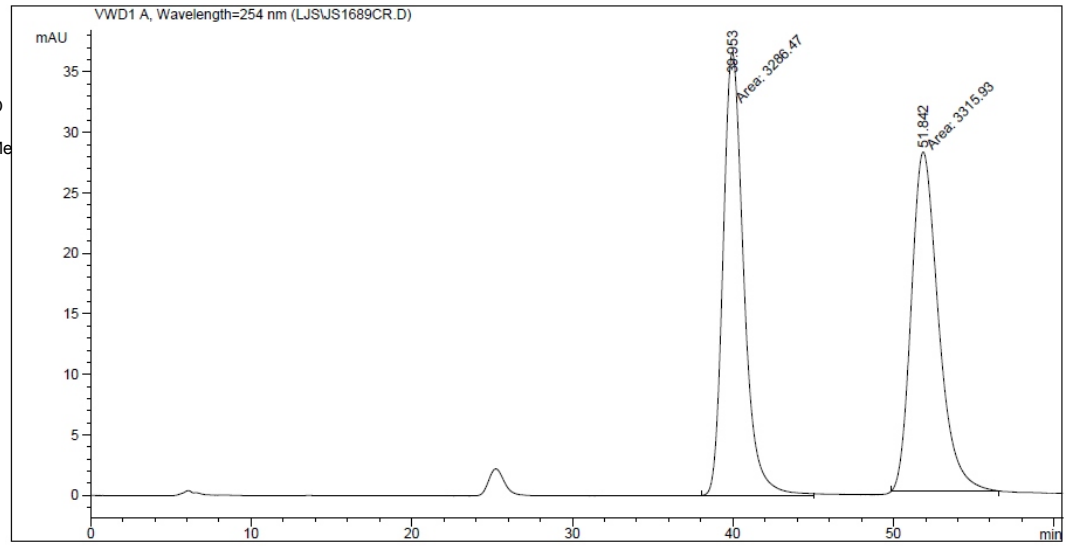
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  28.607 MM    1.1032 1031.98376   15.59039  59.6766
   2  32.932 MM    1.2104   10.93600 1.50578e-1   0.6324
   3  54.006 MM    1.8872  661.16327    5.83916  38.2331
   4  66.260 MM    3.0640   25.21112 1.37135e-1   1.4579
```

HPLC analysis

racemic



***cis*-2g**

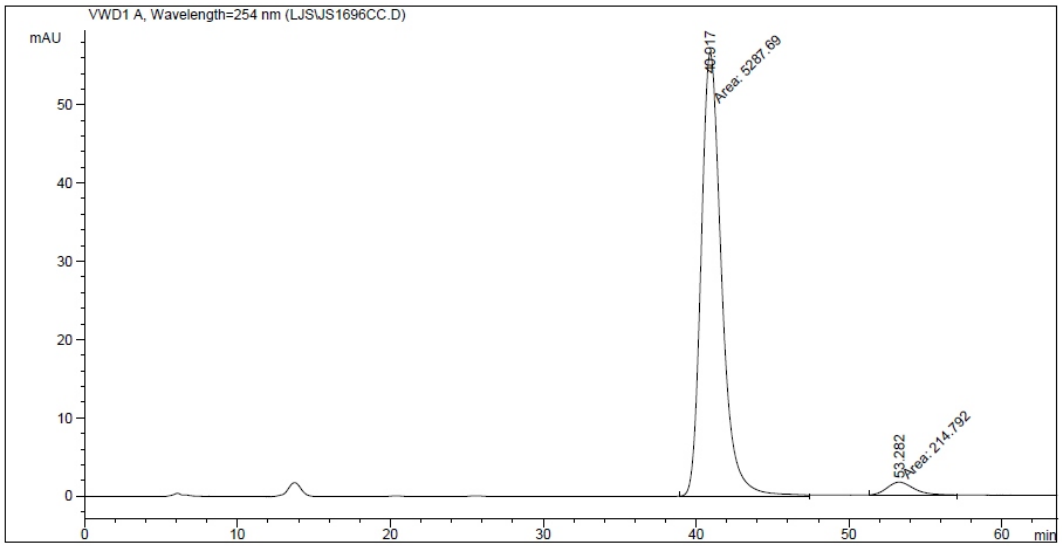



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  39.953 MM    1.4943 3286.46509   36.65532  49.7769
   2  51.842 MM    1.9688 3315.93018   28.07064  50.2231
```

chiral



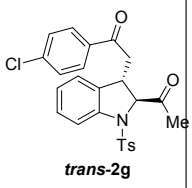

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

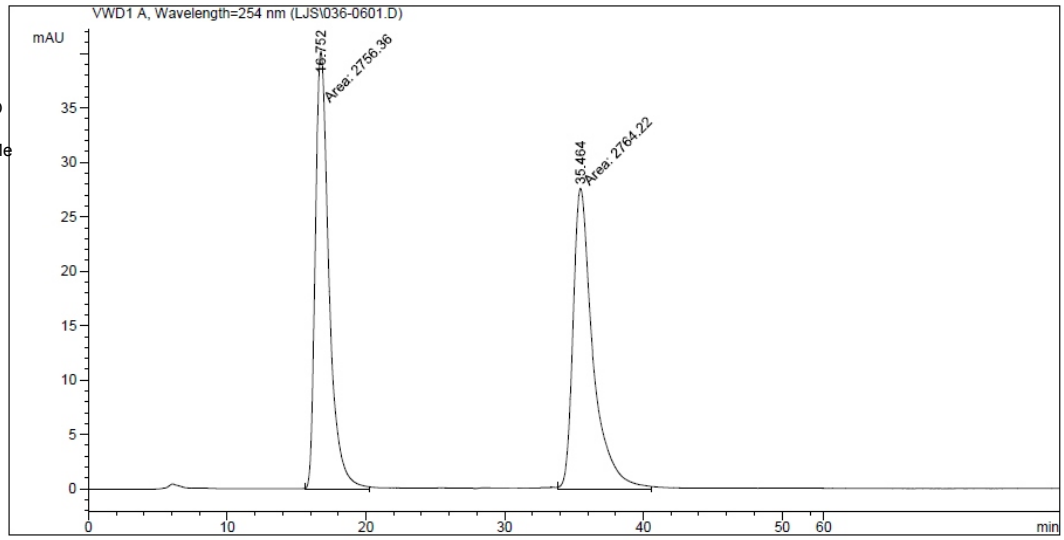
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  40.917 MM    1.5548 5287.68896   56.68187  96.0965
   2  53.282 MM    2.1206  214.79192    1.68816   3.9035
```

HPLC analysis

racemic



***trans*-2g**

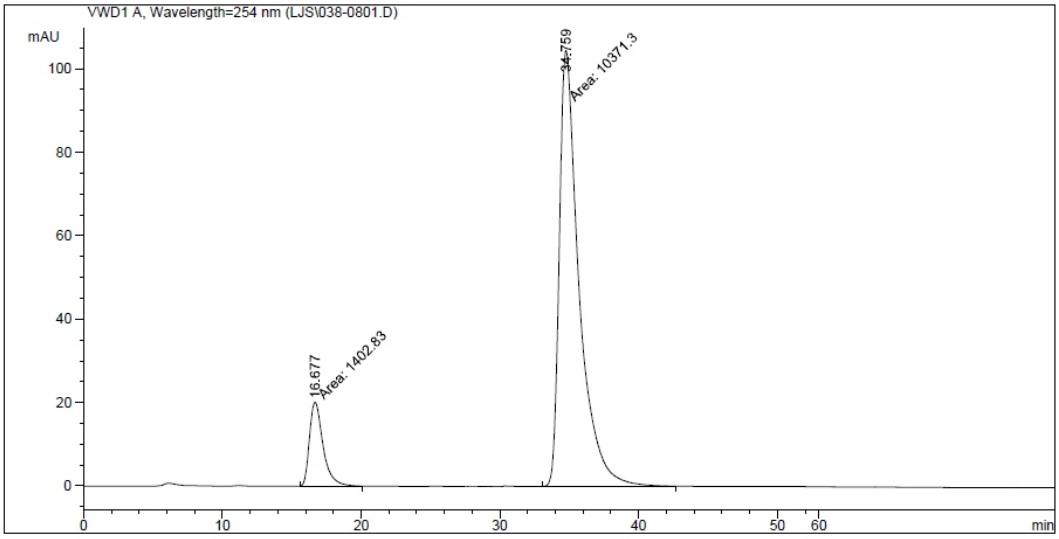



```
==================================================================
                      Area Percent Report
==================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.752 MM    1.1431 2756.35986   40.18931  49.9288
   2  35.464 MM    1.6674 2764.22241   27.63067  50.0712
```

chiral



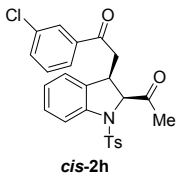

```
==================================================================
                      Area Percent Report
==================================================================

Signal 1: VWD1 A, Wavelength=254 nm

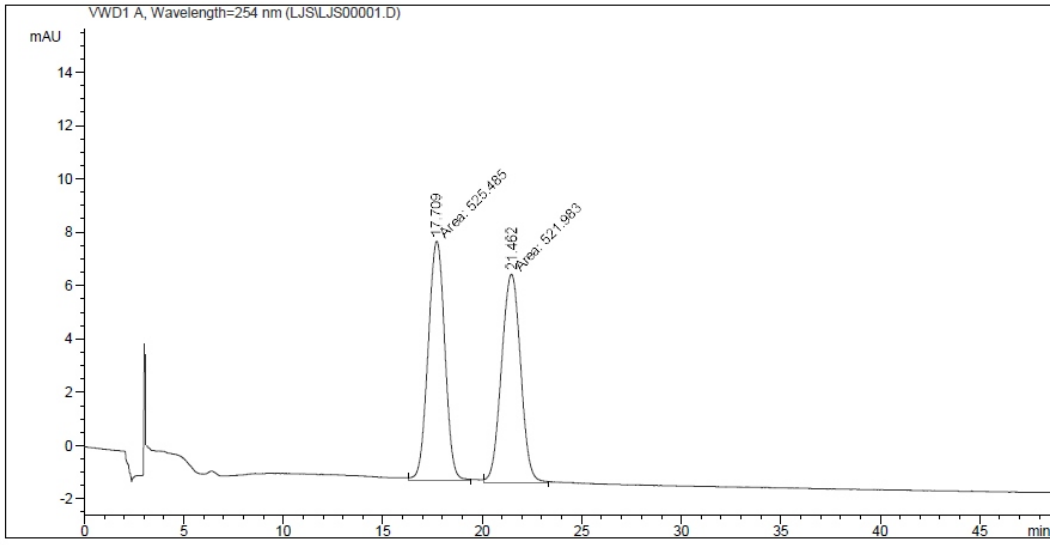
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.677 MM    1.1558 1402.83337   20.22908  11.9146
   2  34.759 MM    1.6543 1.03713e4   104.48775  88.0854
```

HPLC analysis

racemic



***cis*-2h**

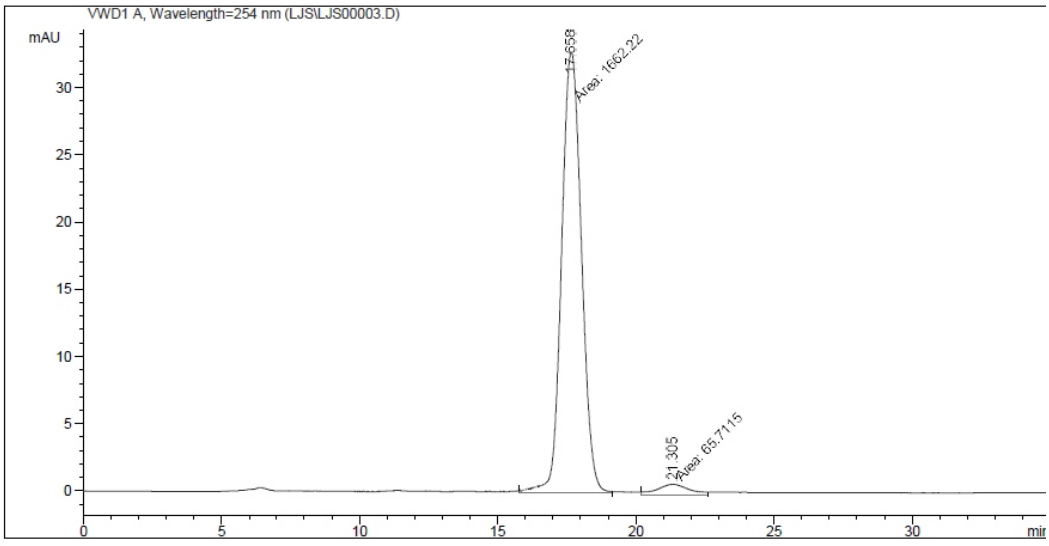



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  17.709 MM    0.9755  525.48486    8.97781  50.1671
   2  21.462 MM    1.1136  521.98340    7.81232  49.8329
```

chiral



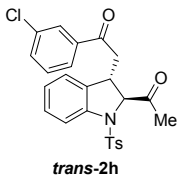

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

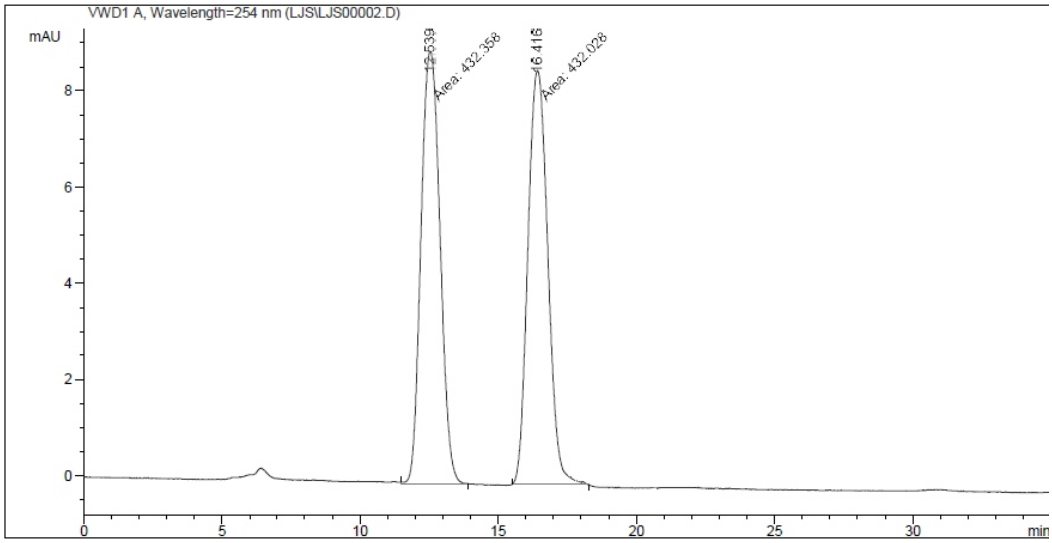
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  17.658 MM    0.8441 1662.22302   32.81898  96.1971
   2  21.305 MM    1.3906   65.71154 7.87590e-1   3.8029
```

HPLC analysis

racemic



***trans*-2h**

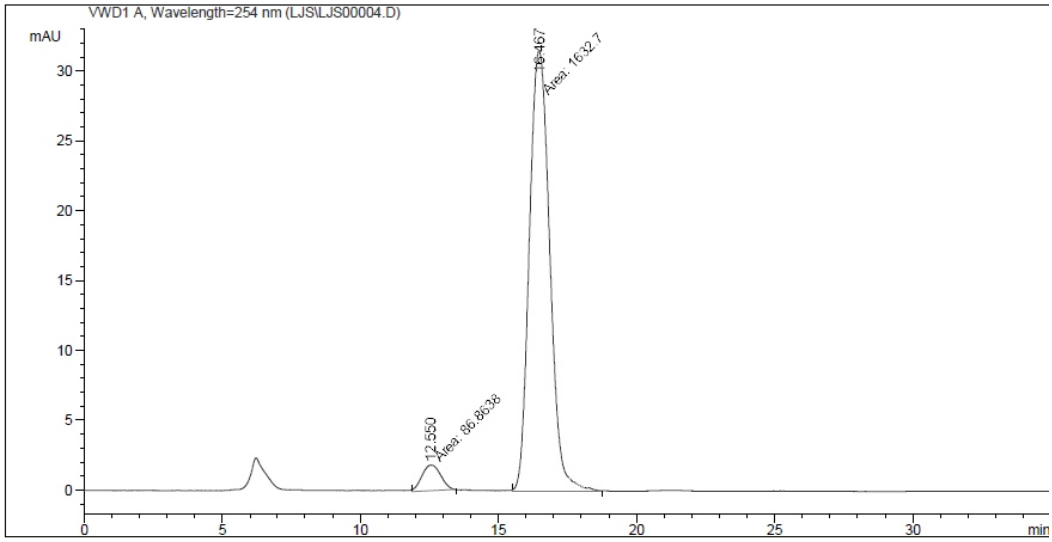



```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.539 MM    0.7998  432.35782    9.01013  50.0191
   2  16.416 MM    0.8369  432.02808    8.60383  49.9809
```

chiral

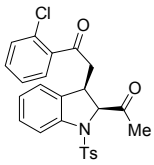



```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

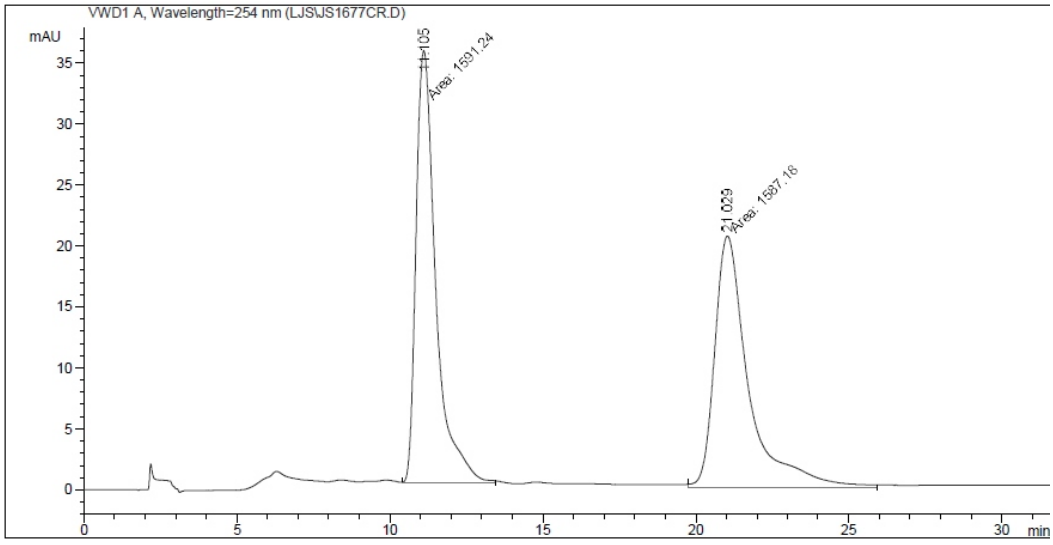
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.550 MM    0.7899   86.86384    1.83284   5.0515
   2  16.467 MM    0.8620 1632.70105   31.56742  94.9485
```

HPLC analysis



***cis*-2i**

racemic

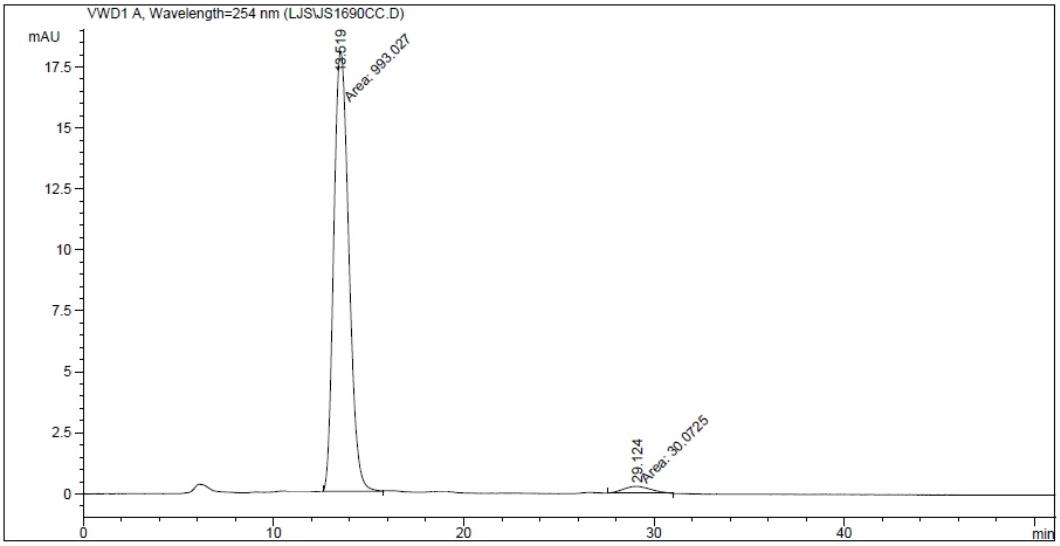



```
================================================================================
                              Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.105 MM    0.7483 1591.24402   35.44194  50.0639
   2  21.029 MM    1.2834 1587.18201   20.61097  49.9361
```

chiral



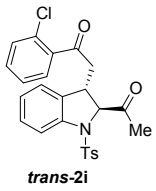

```
================================================================================
                              Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

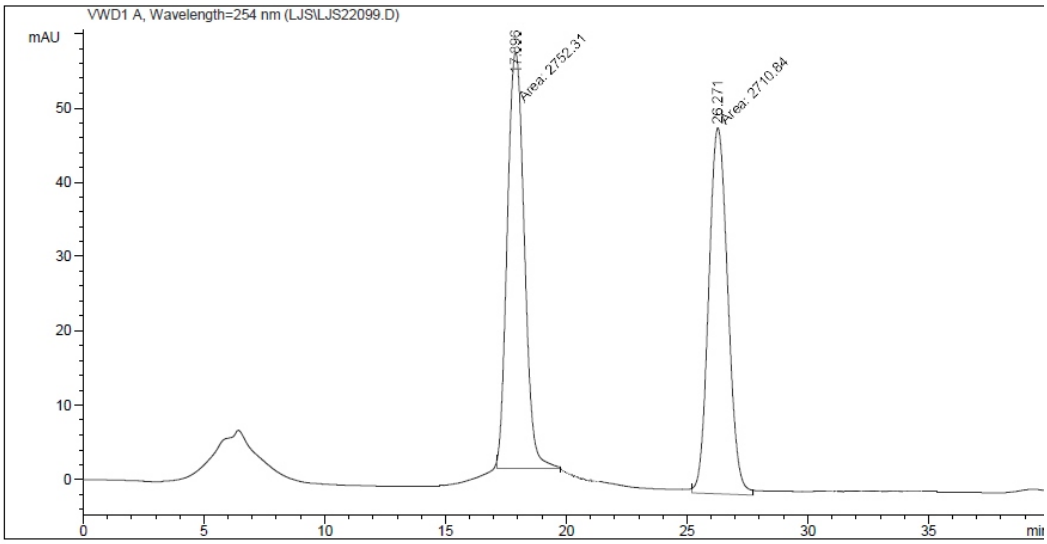
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.519 MM    0.9175  993.02686   18.03777  97.0606
   2  29.124 MM    1.7366   30.07250 2.88623e-1   2.9394
```

HPLC analysis

racemic



***trans*-2i**

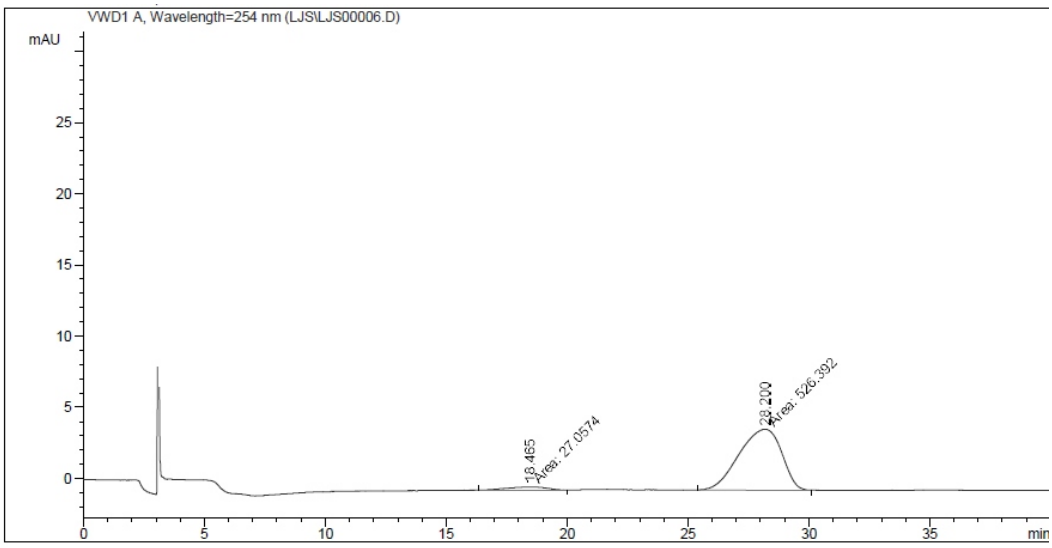



```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  17.896 MM    0.8181 2752.31494   56.07085  50.3796
   2  26.271 MM    0.9172 2710.84326   49.25792  49.6204
```

chiral



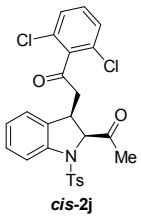

```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

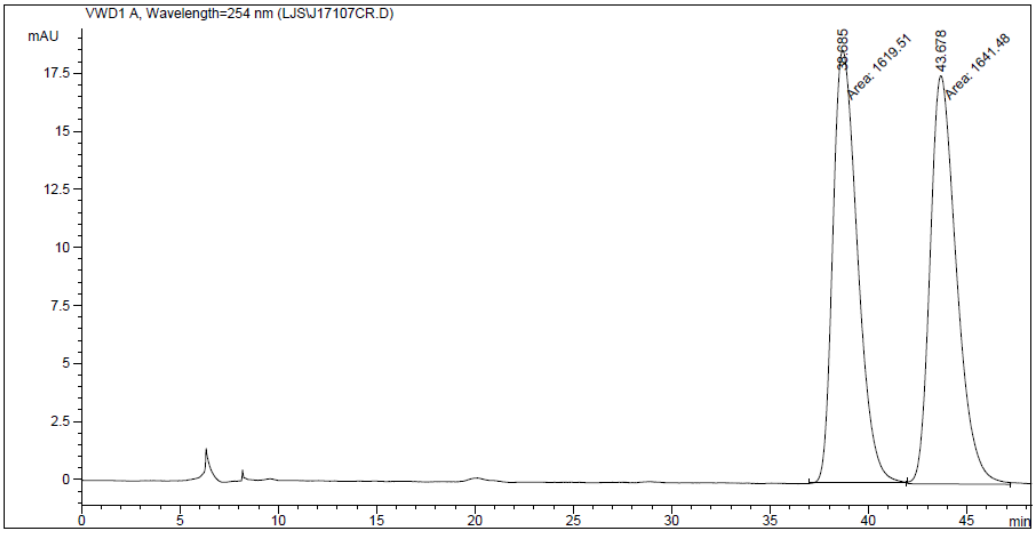
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  18.465 MM    1.9047   27.05741 2.36765e-1   4.8889
   2  28.200 MM    2.0483  526.39203    4.28317  95.1111
```

HPLC analysis

racemic



***cis*-2j**

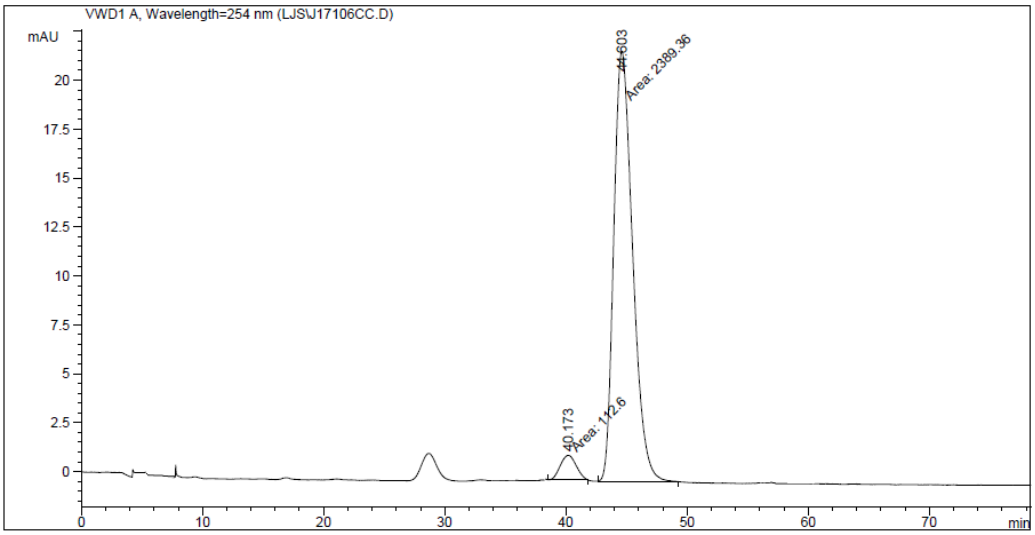



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  38.685 MM    1.4487 1619.51343   18.63186  49.6633
   2  43.678 MM    1.5564 1641.47607   17.57793  50.3367
```

chiral



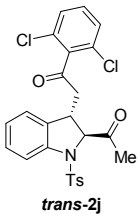

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

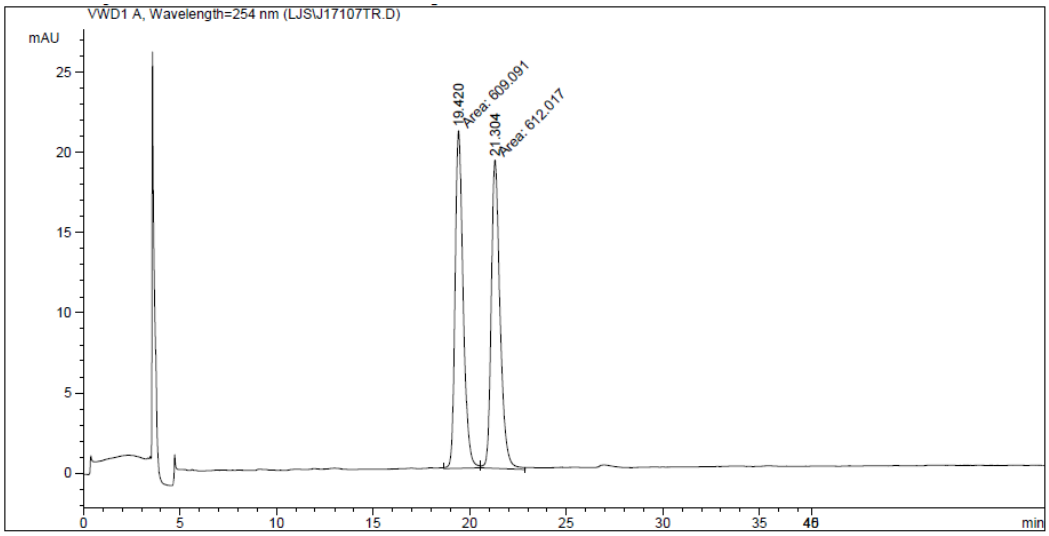
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  40.173 MM    1.5050  112.59995    1.24699   4.5005
   2  44.603 MM    1.8084 2389.36377   22.02059  95.4995
```

HPLC analysis

racemic



***trans*-2j**

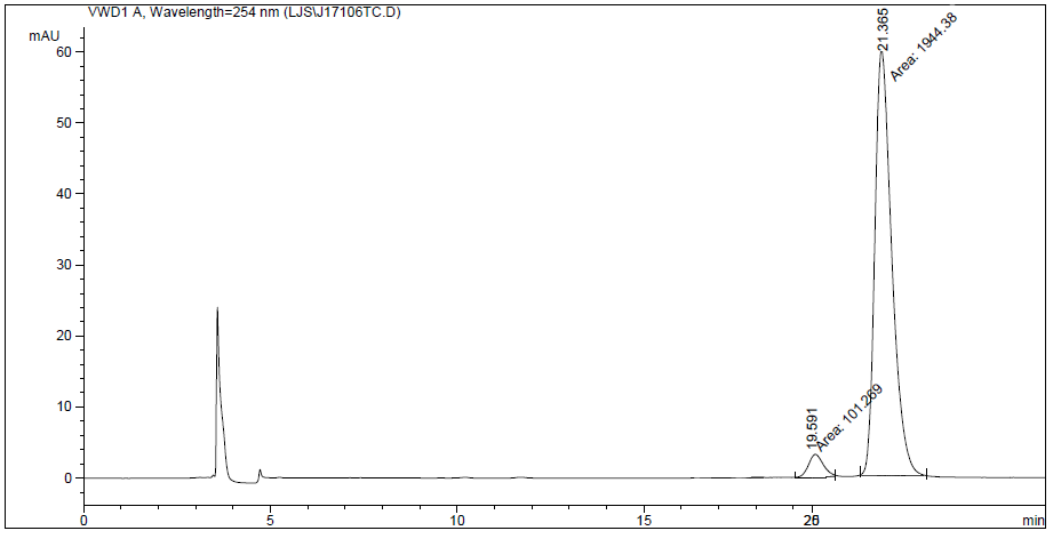



```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  19.420 MM    0.4825  609.09131   21.04026  49.8802
   2  21.304 MM    0.5310  612.01733   19.20907  50.1198
```

chiral



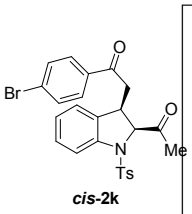

```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

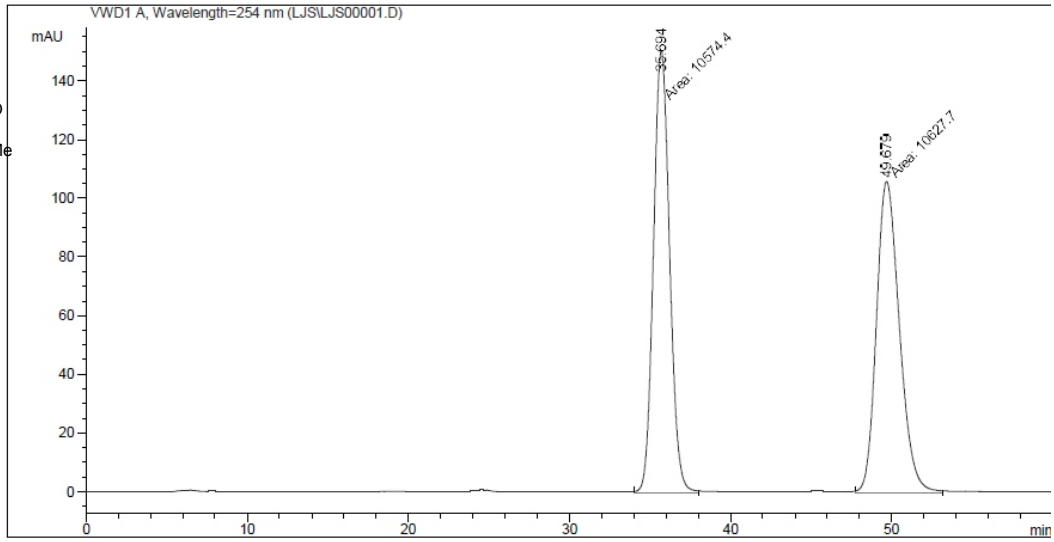
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  19.591 MM    0.5106  101.26903    3.30544   4.9505
   2  21.365 MM    0.5376 1944.37720   60.28051  95.0495
```

HPLC analysis

racemic



***cis*-2k**

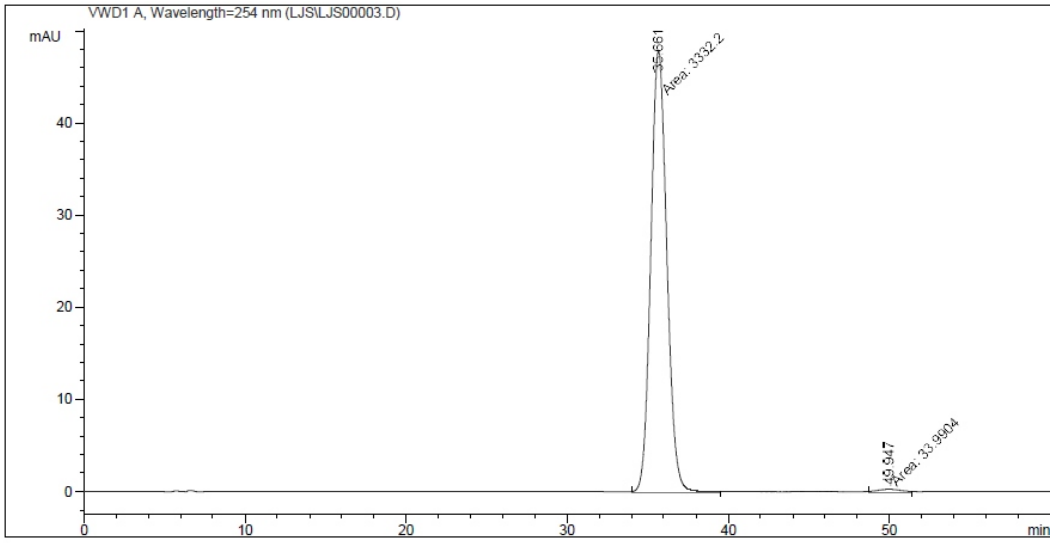



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  35.694 MM    1.1673 1.05744e4   150.98483  49.8743
   2  49.679 MM    1.6642 1.06277e4   106.43457  50.1257
```

chiral



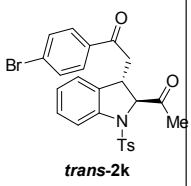

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

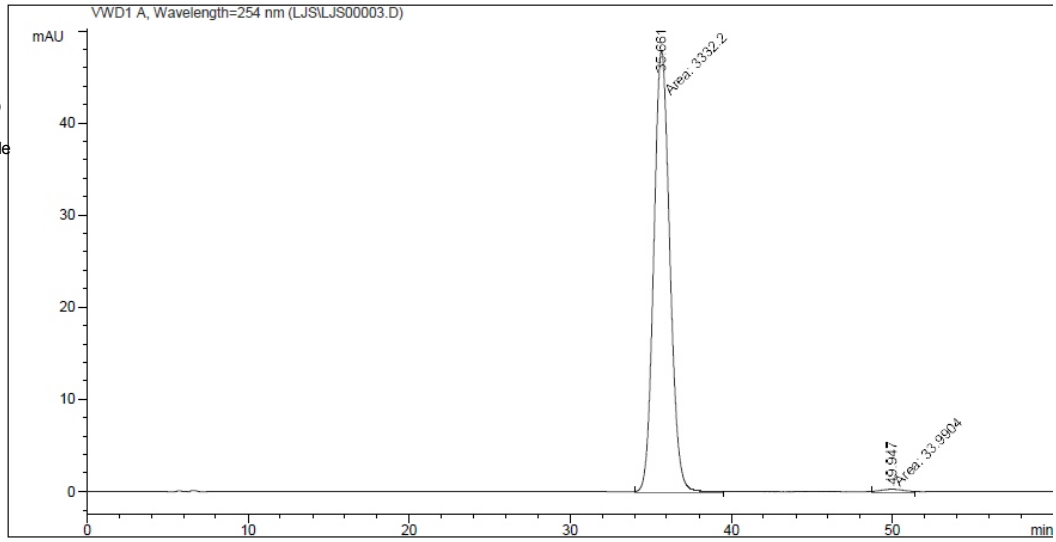
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  35.661 MM    1.1593 3332.19775   47.90477  98.9902
   2  49.947 MM    1.7489   33.99036 3.23924e-1   1.0098
```

HPLC analysis

racemic



***trans*-2k**

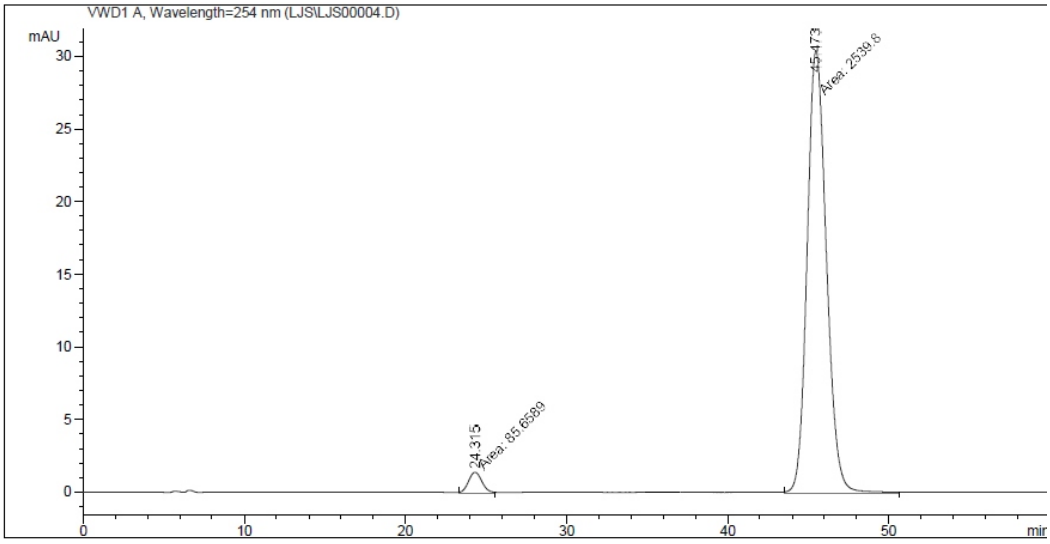



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  35.661 MM    1.1593 3332.19775   47.90477  98.9902
   2  49.947 MM    1.7489   33.99036 3.23924e-1   1.0098
```

chiral



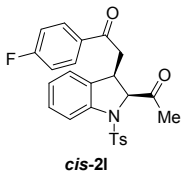

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

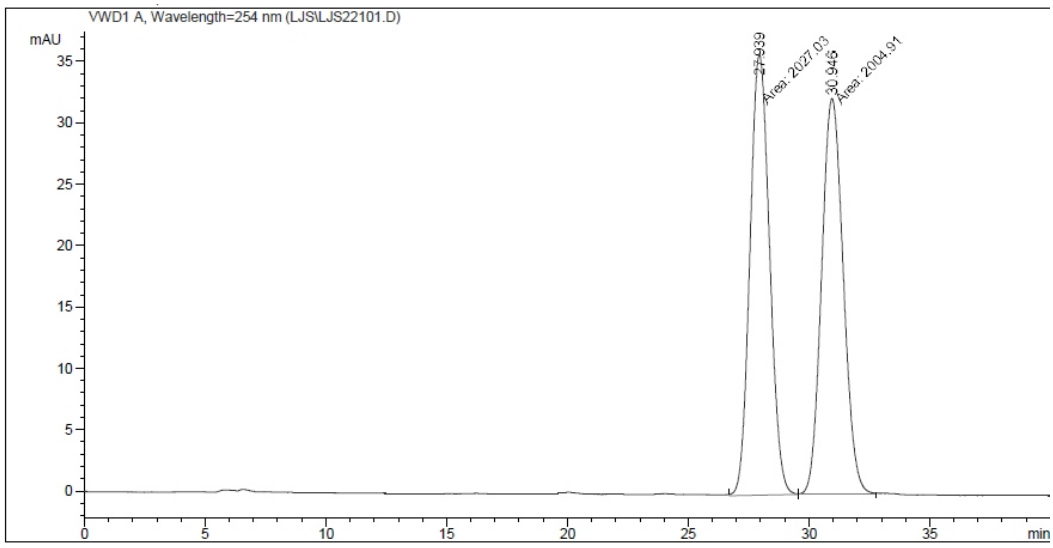
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  24.315 MM    0.9897   85.65887   1.44257   3.2626
   2  45.473 MM    1.3903 2539.79834  30.44698  96.7374
```

HPLC analysis

racemic



***cis*-2l**

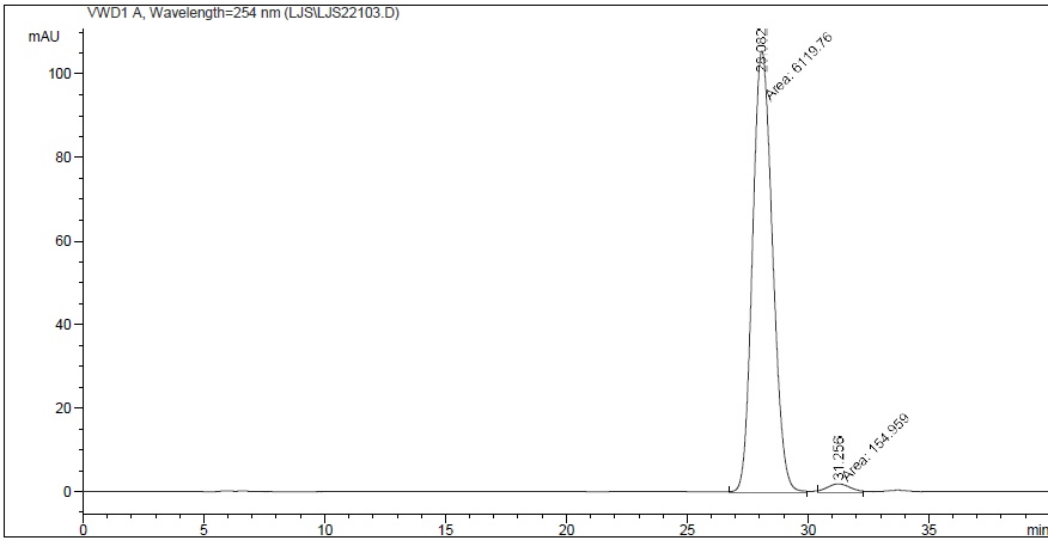



```
================================================================
                    Area Percent Report
================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  27.939 MM    0.9402 2027.03088   35.93351  50.2743
   2  30.946 MM    1.0373 2004.90955   32.21498  49.7257
```

chiral



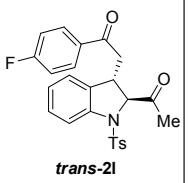

```
================================================================
                    Area Percent Report
================================================================

Signal 1: VWD1 A, Wavelength=254 nm

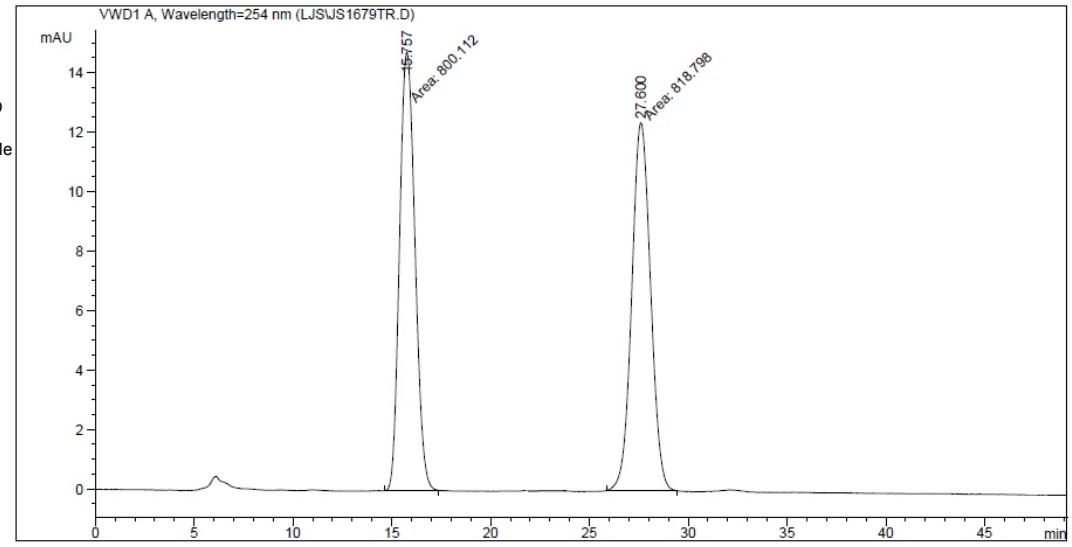
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  28.082 MM    0.9635 6119.76025  105.86341  97.5304
   2  31.256 MM    1.1634  154.95877    2.22000   2.4696
```

HPLC analysis

racemic



***trans*-2l**

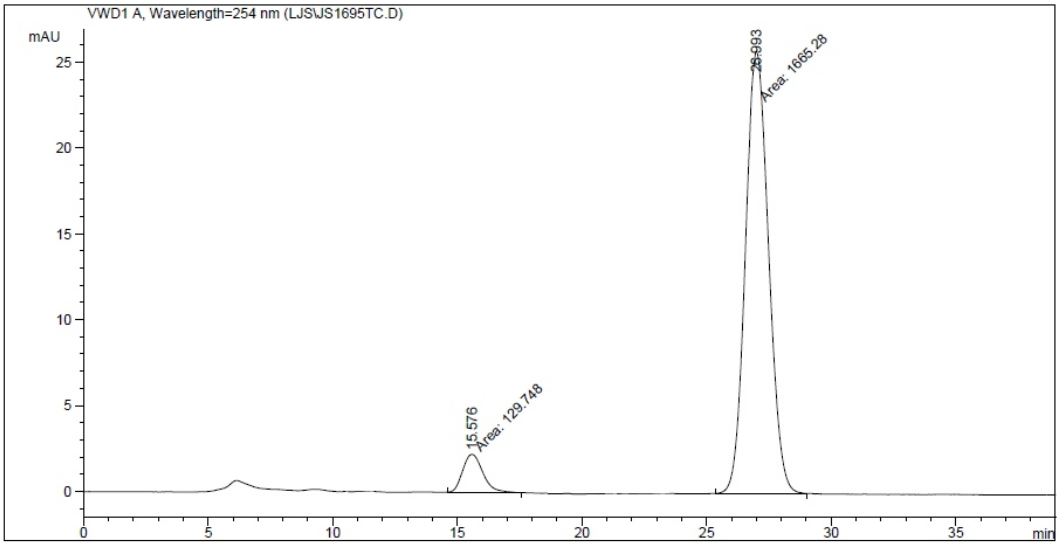



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.757 MM    0.9049  800.11237   14.73636  49.4229
   2  27.600 MM    1.1033  818.79816   12.36874  50.5771
```

chiral



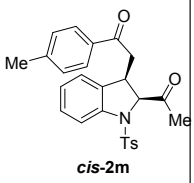

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

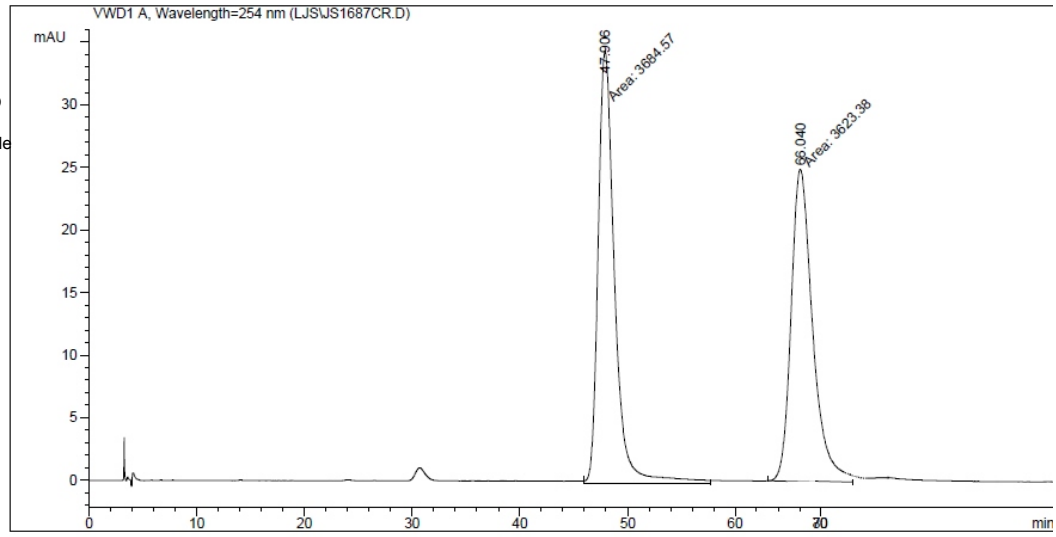
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.576 MM    0.9588  129.74789    2.25547   7.2282
   2  26.993 MM    1.0764 1665.27661   25.78492  92.7718
```

HPLC analysis

racemic



***cis*-2m**

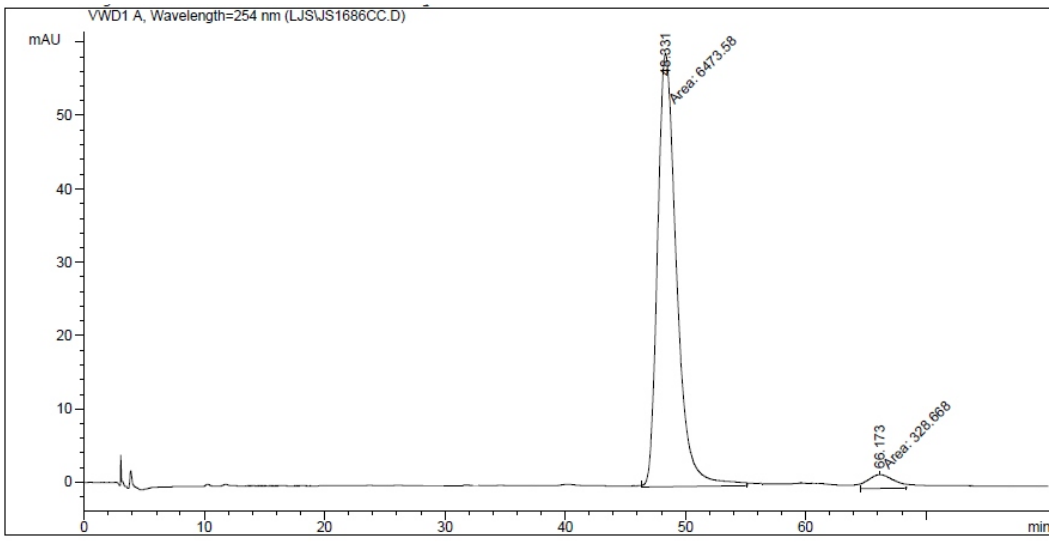



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  47.906 MM    1.7787 3684.56689   34.52538  50.4186
   2  66.040 MM    2.4262 3623.38330   24.89041  49.5814
```

chiral



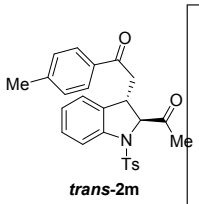

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

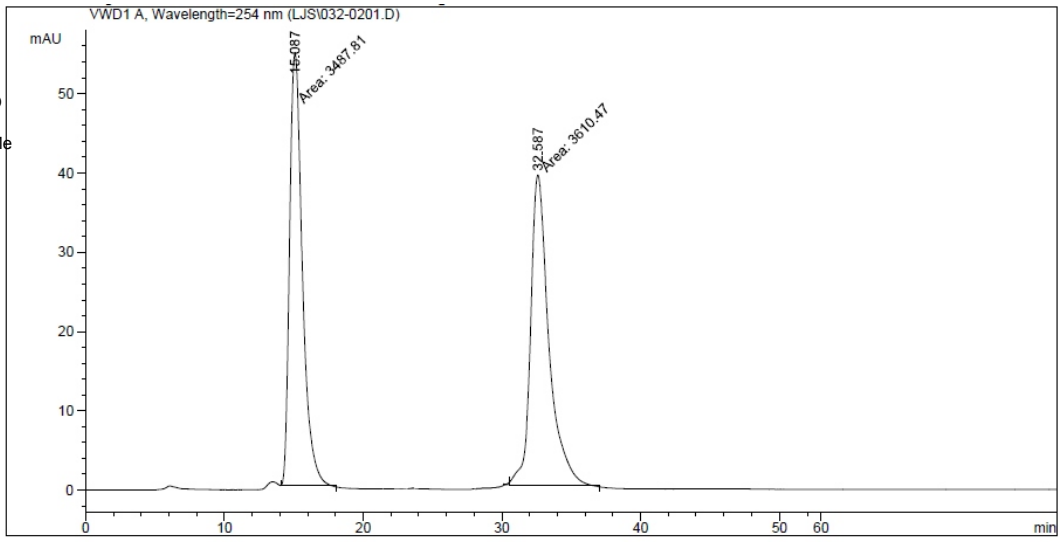
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  48.331 MM    1.8282 6473.57568   59.01686  95.1682
   2  66.173 MM    2.9653  328.66769    1.84728   4.8318
```

HPLC analysis

racemic



***trans*-2m**

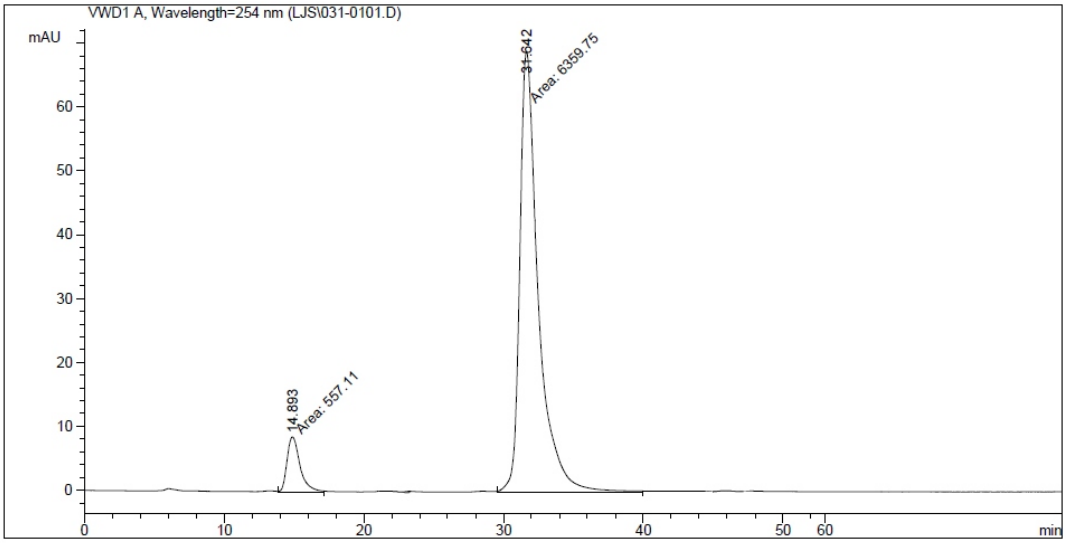



```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  15.087 MM    1.0630 3487.80957   54.68661  49.1360
   2  32.587 MM    1.5334 3610.46582   39.24264  50.8640
```

chiral



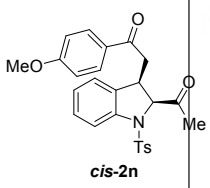

```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

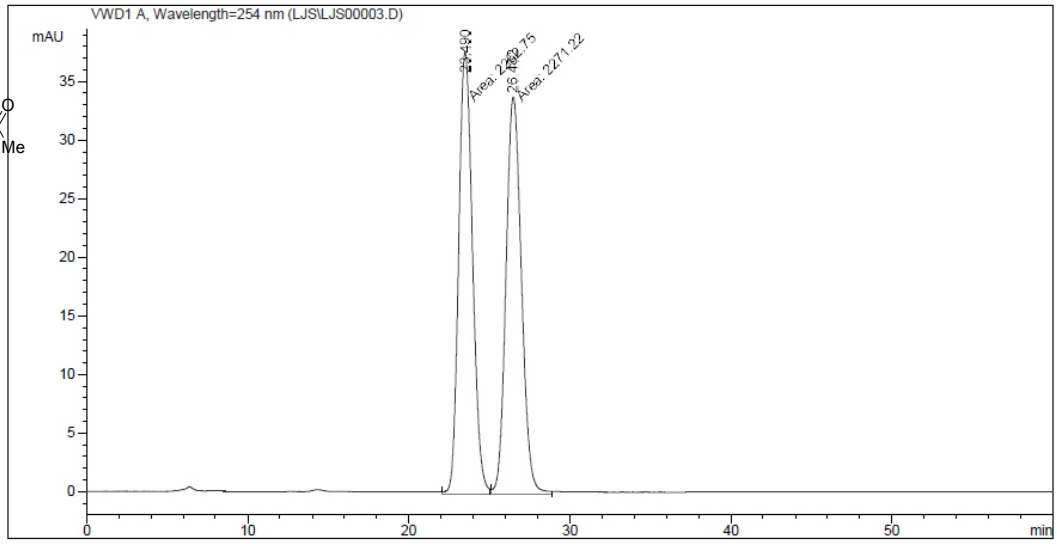
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  14.893 MM    1.0796  557.11041    8.60077   8.0544
   2  31.642 MM    1.5365 6359.74609   68.98383  91.9456
```

HPLC analysis

racemic



***cis*-2n**

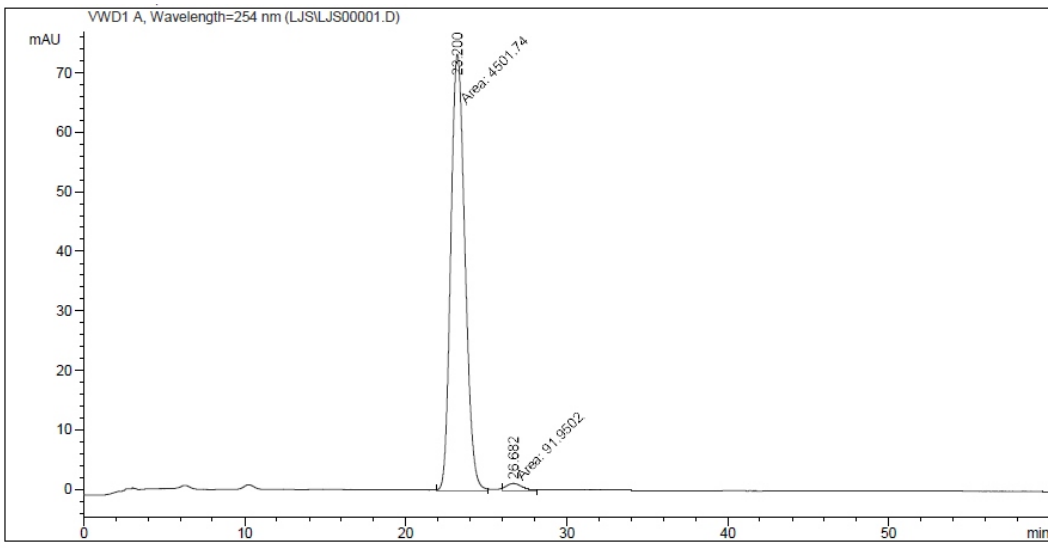



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  23.490 MM    0.9972 2262.75269   37.81823  49.9066
   2  26.482 MM    1.1157 2271.21924   33.92888  50.0934
```

chiral



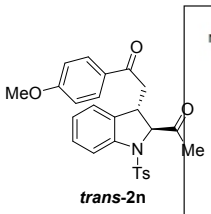

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

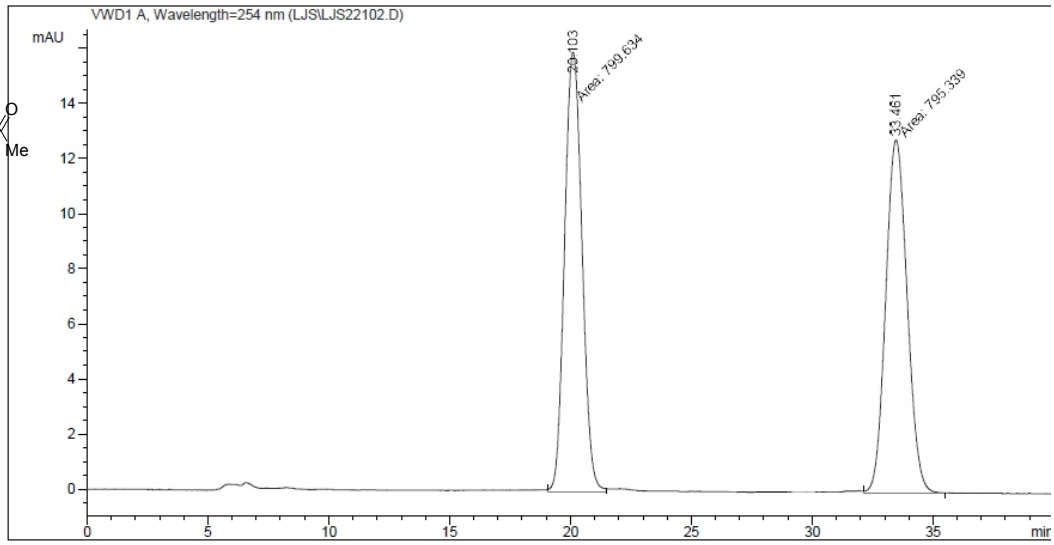
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  23.200 MM    1.0223 4501.73584   73.39381  97.9983
   2  26.682 MM    1.1954   91.95019    1.28202   2.0017
```

HPLC analysis

racemic



***trans*-2n**

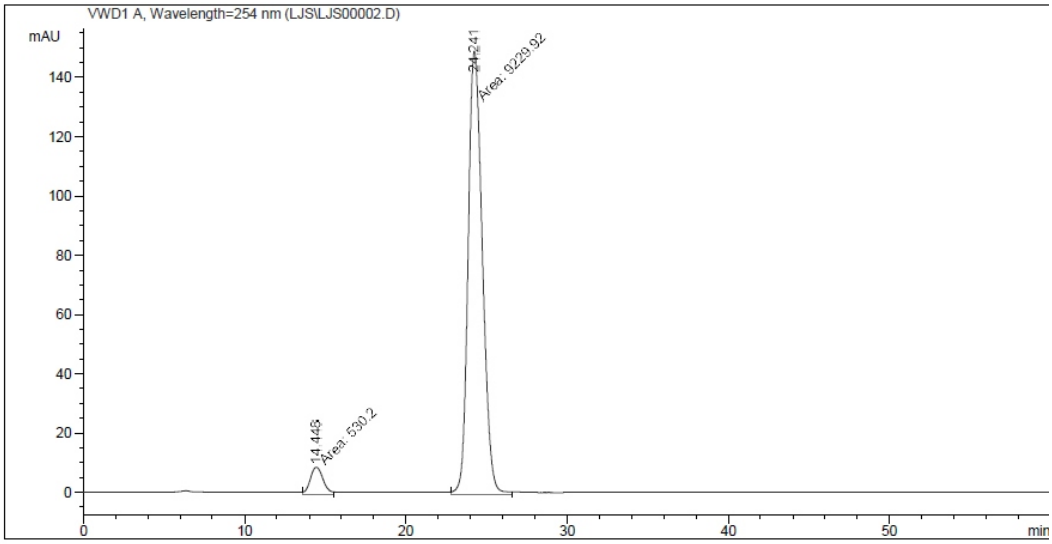



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  20.103 MM    0.8357  799.63440   15.94744  50.1347
   2  33.461 MM    1.0325  795.33850   12.83814  49.8653
```

chiral



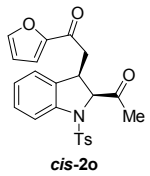

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

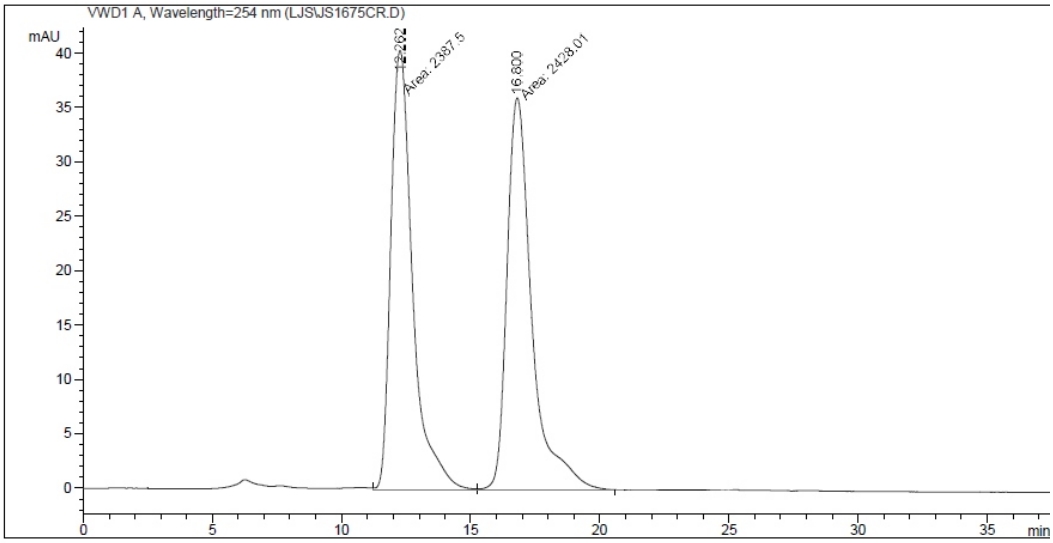
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.448 MM    0.9518  530.20038    9.28434   5.4323
   2  24.241 MM    1.0274 9229.92285  149.72507  94.5677
```

HPLC analysis

racemic



***cis*-2o**

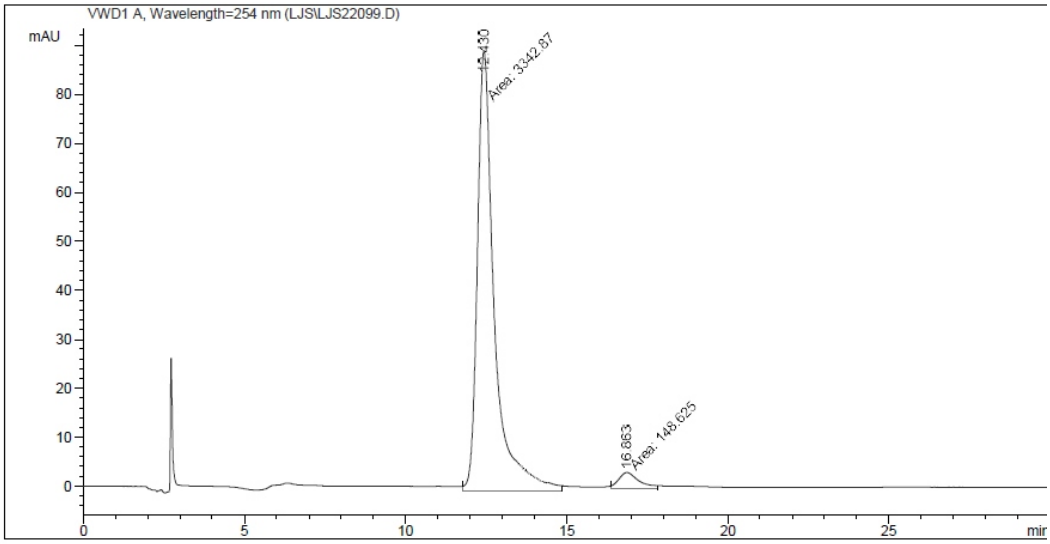



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.262 MM    0.9843 2387.50000   40.42767  49.5794
   2  16.800 MM    1.1219 2428.00879   36.07024  50.4206
```

chiral



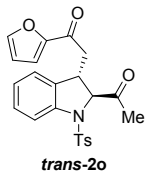

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

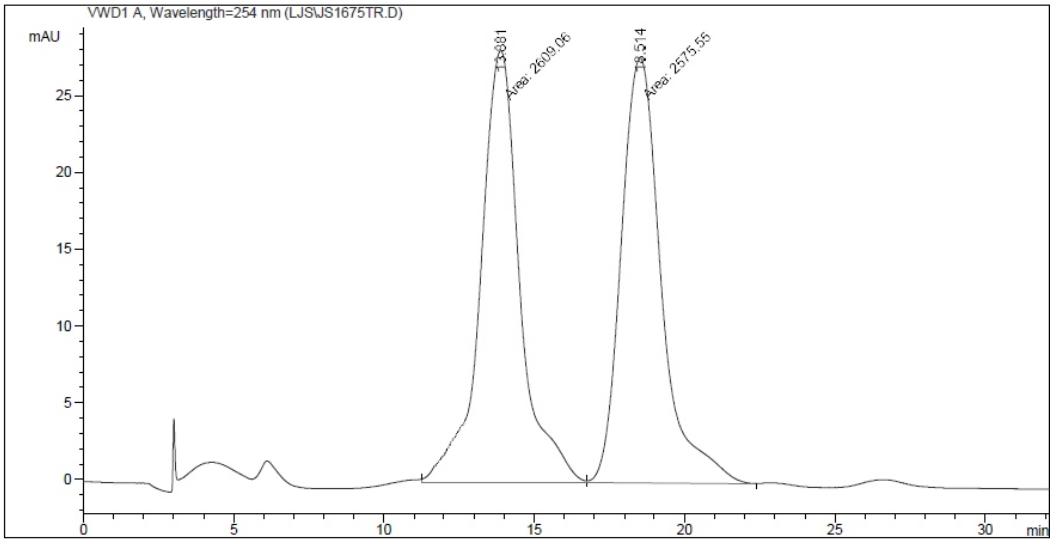
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.430 MM    0.6210 3342.87329   89.72073  95.7432
   2  16.863 MM    0.7504  148.62537    3.30113   4.2568
```

HPLC analysis

racemic



***trans*-2o**

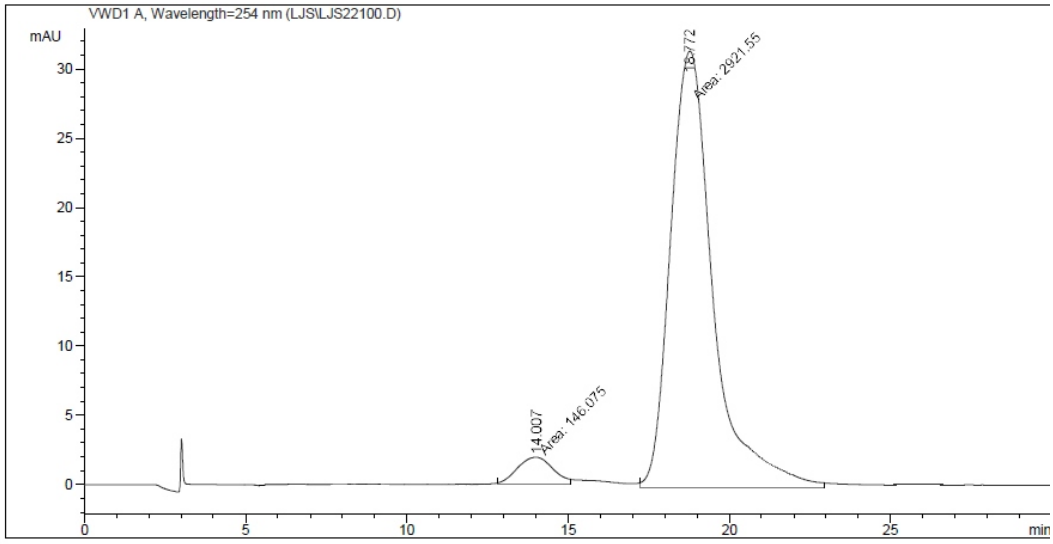



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.881 MM    1.5451 2609.05713   28.14383  50.3231
   2  18.514 MM    1.5498 2575.55176   27.69692  49.6769
```

chiral



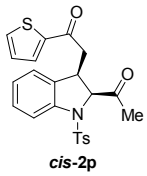

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

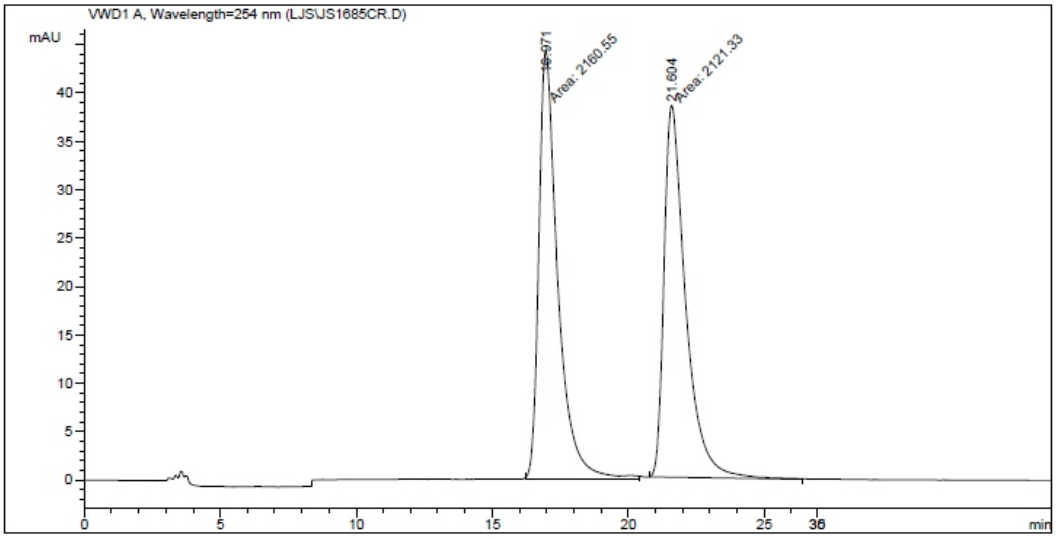
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.007 MM    1.2646  146.07489    1.92514   4.7618
   2  18.772 MM    1.5450 2921.54785   31.51534  95.2382
```

HPLC analysis

racemic



***cis*-2p**

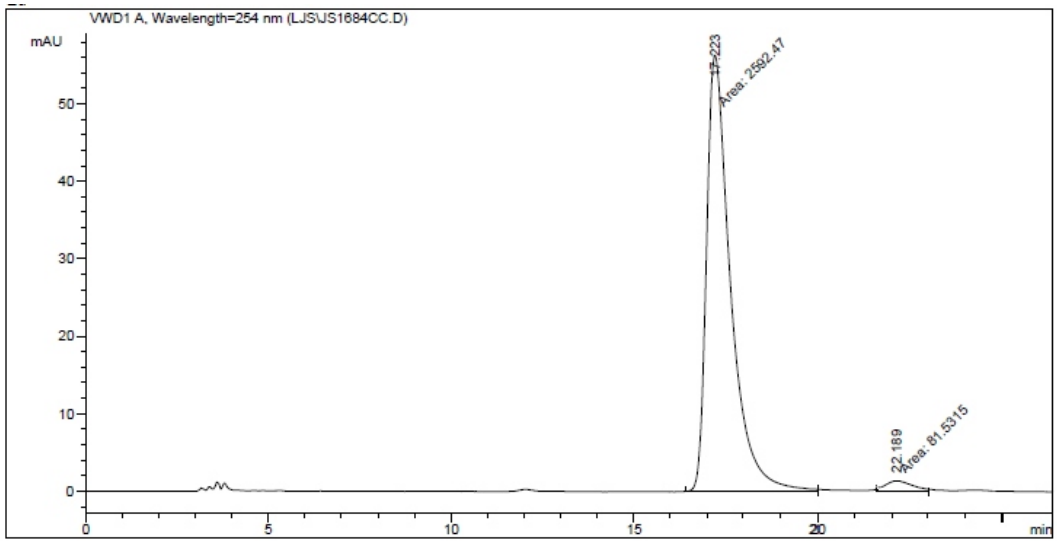



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.971 MM    0.8136 2160.55322   44.26115  50.4580
   2  21.604 MM    0.9199 2121.32886   38.43588  49.5420
```

chiral



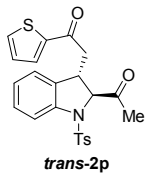

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

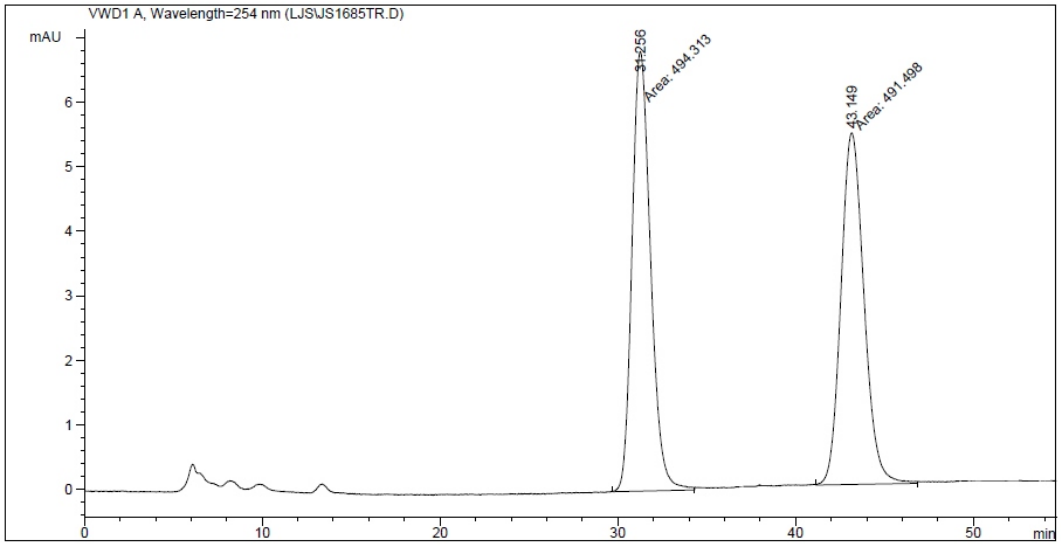
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  17.223 MM    0.7670 2592.46606   56.33123  96.9510
   2  22.189 MM    0.9959   81.53149    1.36441   3.0490
```

HPLC analysis

racemic



***trans*-2p**

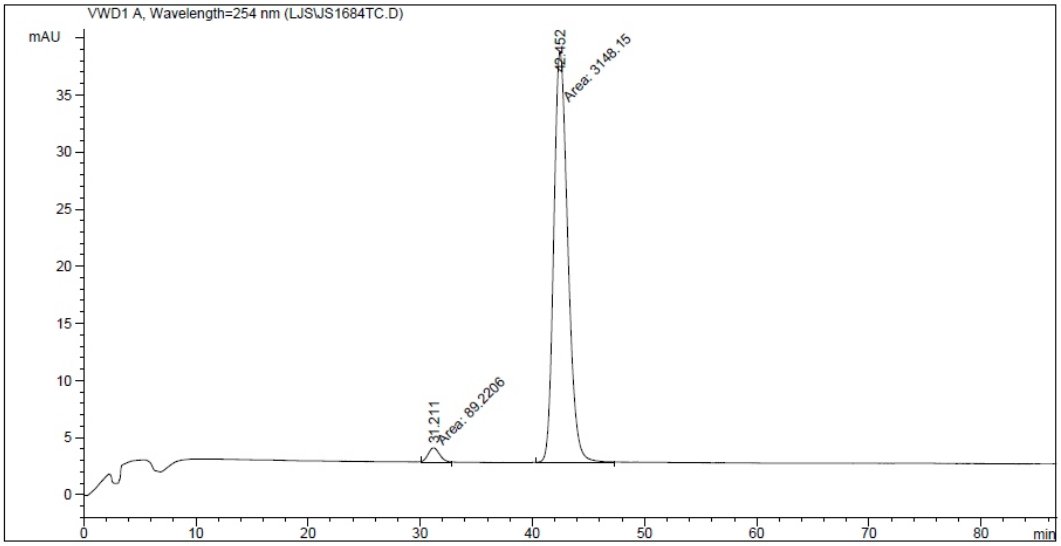



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  31.256 MM    1.2091  494.31296    6.81369  50.1428
   2  43.149 MM    1.5031  491.49774    5.44989  49.8572
```

chiral



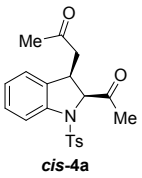

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

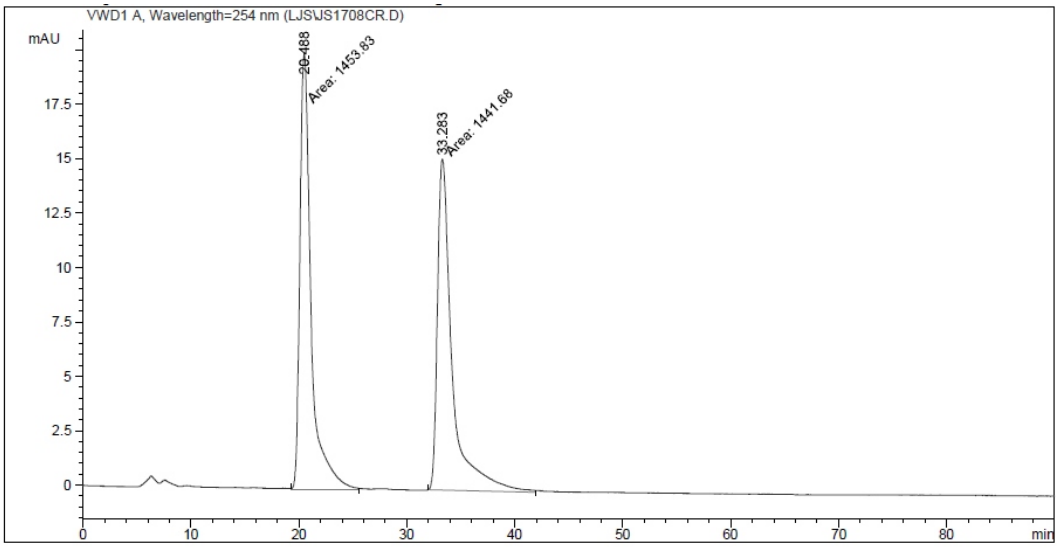
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  31.211 MM    1.1823   89.22057    1.25777   2.7560
   2  42.452 MM    1.4569 3148.15479   36.01451  97.2440
```

HPLC analysis

racemic



***cis*-4a**

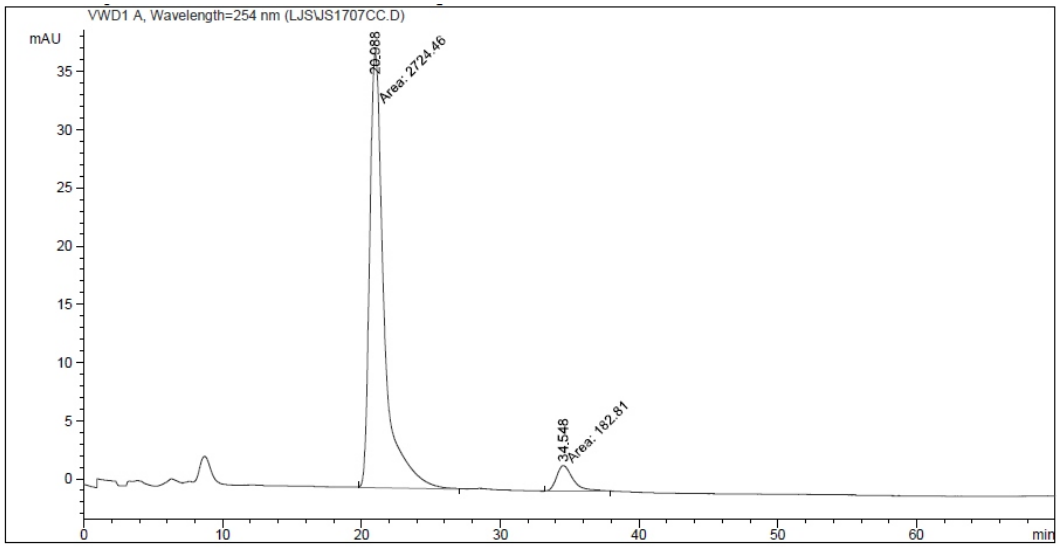



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  20.488 MM    1.2075 1453.83105   20.06620  50.2097
   2  33.283 MM    1.5797 1441.68457   15.21083  49.7903
```

chiral



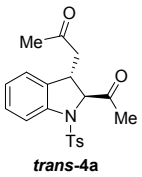

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

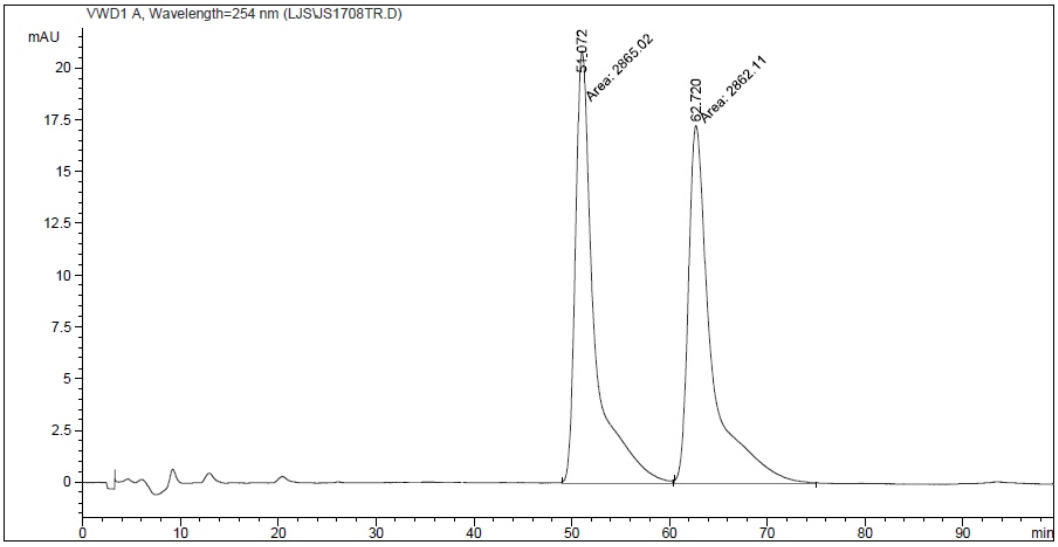
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  20.988 MM    1.2164 2724.46045   37.33106  93.7120
   2  34.548 MM    1.3867  182.81038    2.19726   6.2880
```

HPLC analysis

racemic



***trans*-4a**

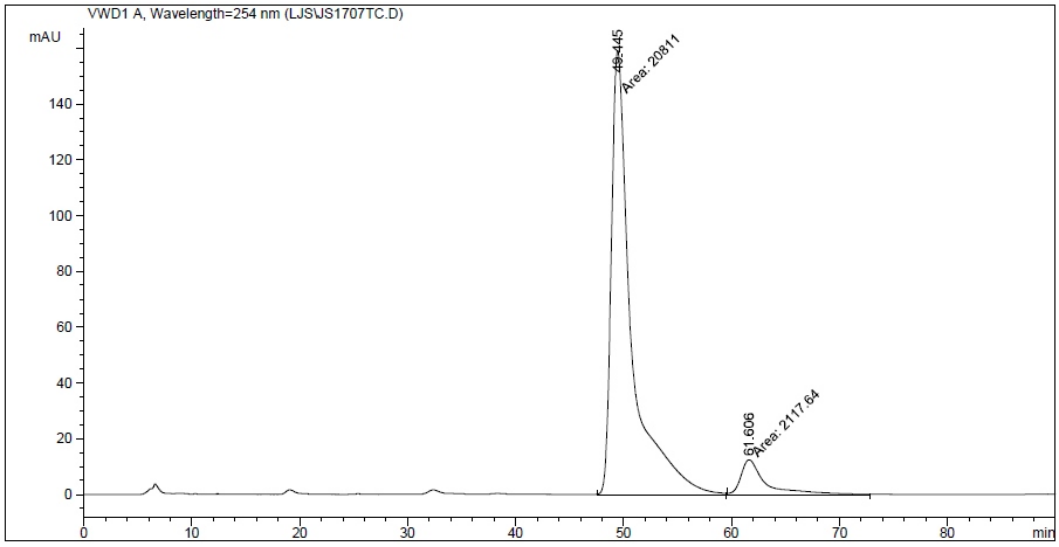



```
================================================================================
                          Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  51.072 MM    2.2874 2865.02075   20.87576  50.0254
   2  62.720 MM    2.7596 2862.11108   17.28574  49.9746
```

chiral



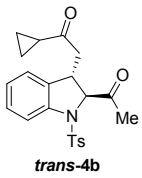

```
================================================================================
                          Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

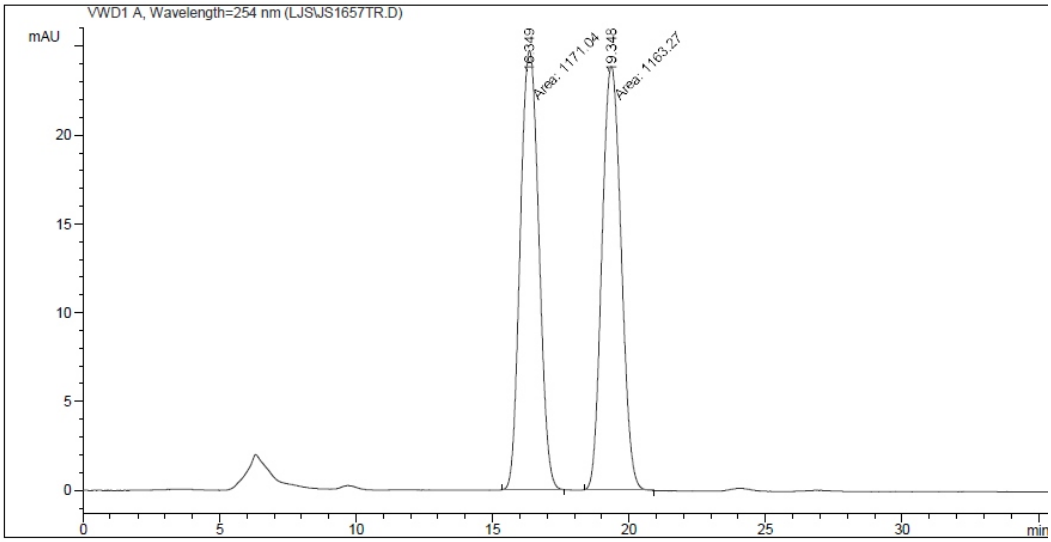
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  49.445 MM    2.1802 2.08110e4   159.08881  90.7642
   2  61.606 MM    2.7936 2117.64185   12.63395   9.2358
```

HPLC analysis

racemic



***trans*-4b**

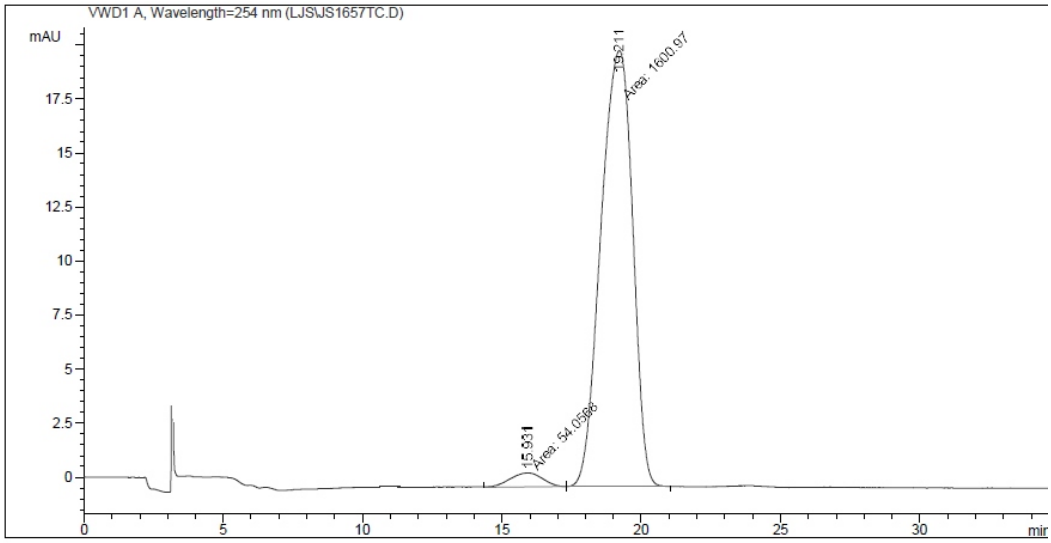



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.349 MM    0.7896 1171.04382   24.71677  50.1665
   2  19.348 MM    0.8133 1163.27063   23.83787  49.8335
```

chiral



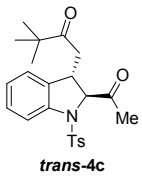

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

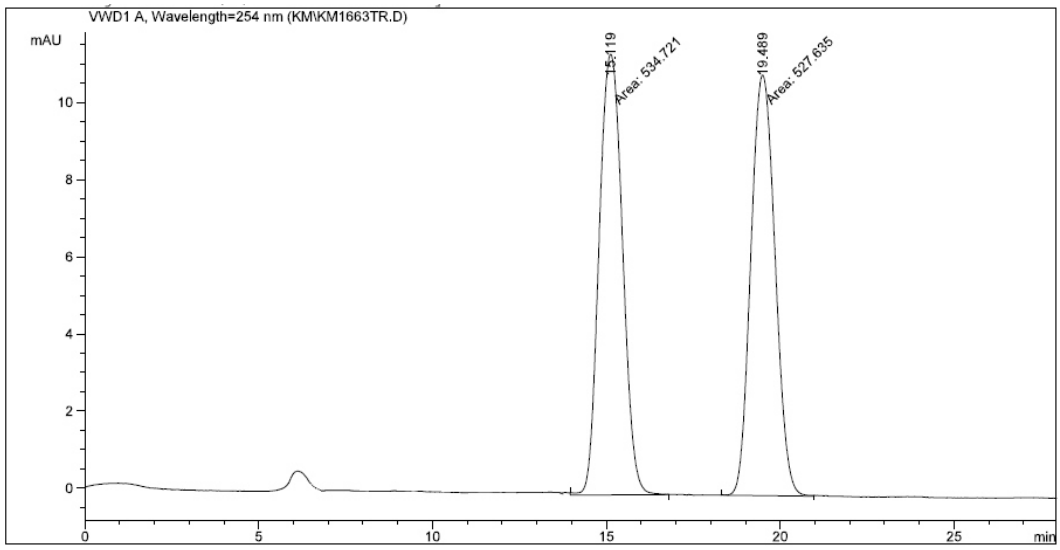
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.931 MM    1.3686   54.05675 6.58302e-1   3.2662
   2  19.211 MM    1.3219 1600.96790   20.18509  96.7338
```

HPLC analysis

racemic



***trans*-4c**

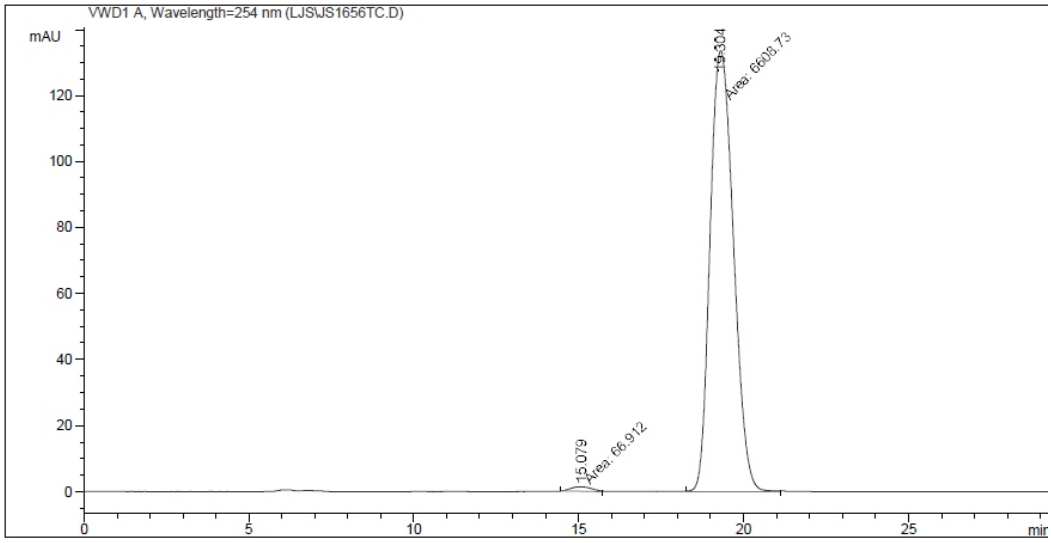



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.119 MM    0.7803  534.72113   11.42099  50.3335
   2  19.489 MM    0.8064  527.63477   10.90473  49.6665
```

chiral



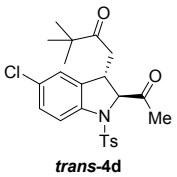

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

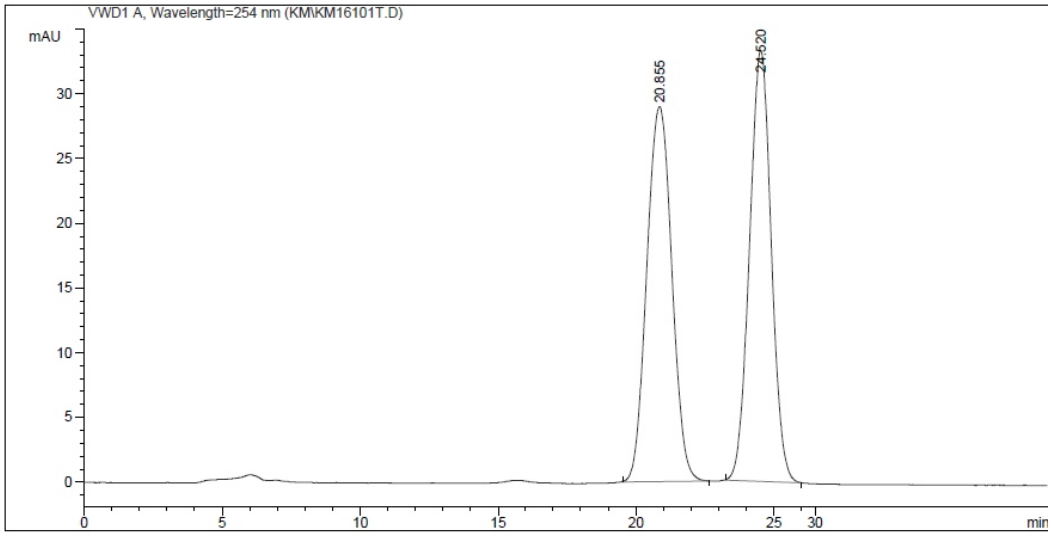
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.079 MM    0.7751   66.91203    1.43879   1.0023
   2  19.304 MM    0.8234 6608.73047  133.76910  98.9977
```

HPLC analysis

racemic



***trans*-4d**

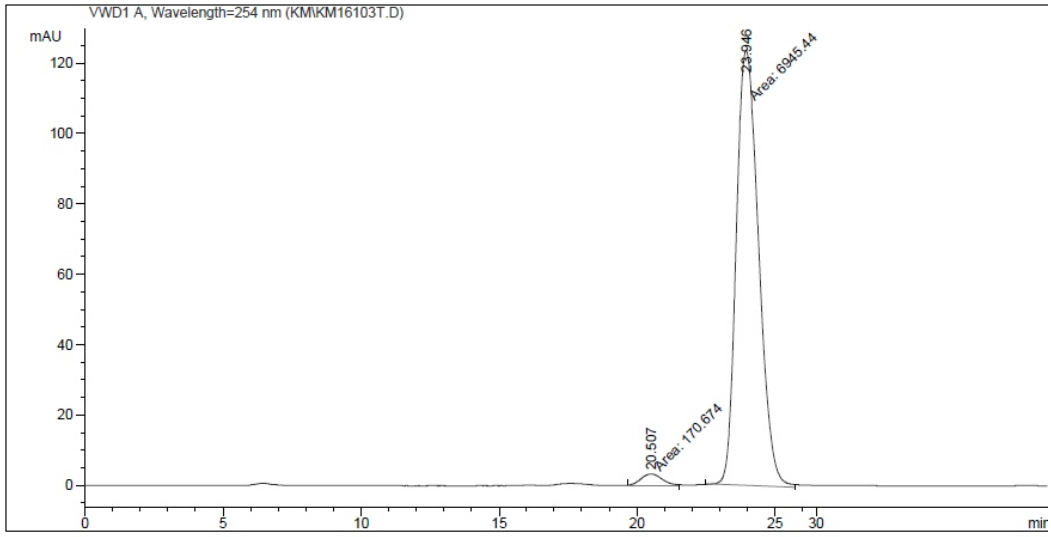



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  20.855 BB    1.0054 1831.12183   28.96747  50.0093
   2  24.520 BB    0.8523 1830.43787   33.30648  49.9907
```

chiral



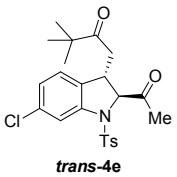

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

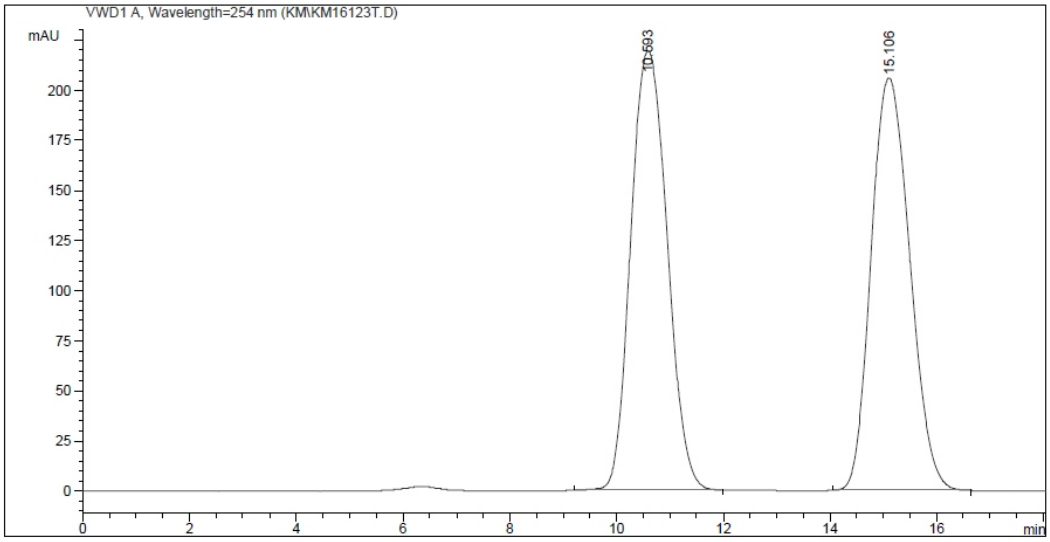
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  20.507 MM    0.8840  170.67426    3.21779   2.3984
   2  23.946 MM    0.9369 6945.43994  123.55561  97.6016
```

HPLC analysis

racemic



***trans*-4e**

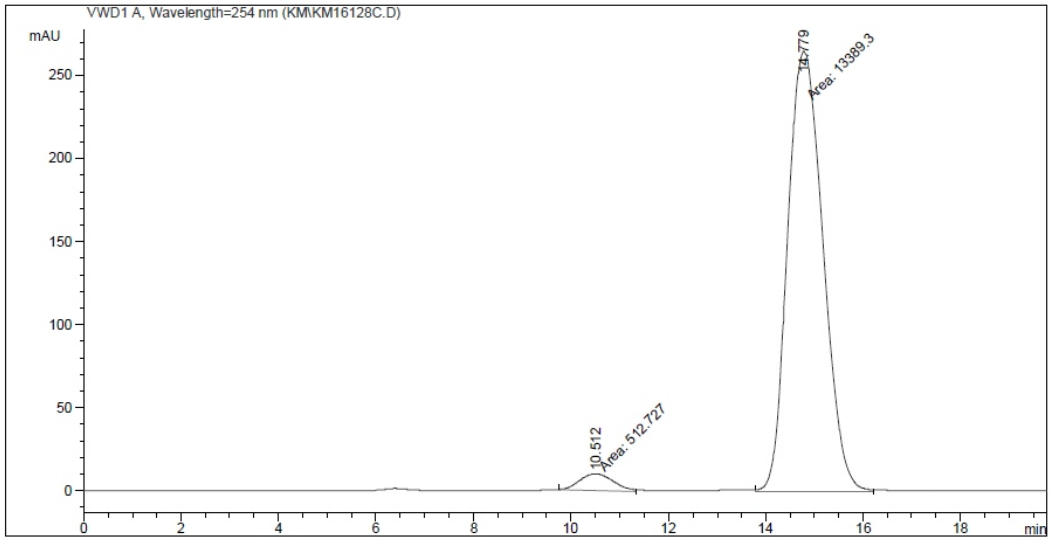



```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.593 BB    0.7617 1.04045e4   219.32442  50.0353
   2  15.106 BB    0.8038 1.03898e4   206.04263  49.9647
```

chiral



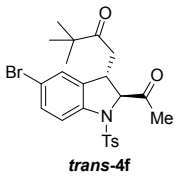

```
================================================================================
                            Area Percent Report
================================================================================

Signal 1: VWD1 A, Wavelength=254 nm

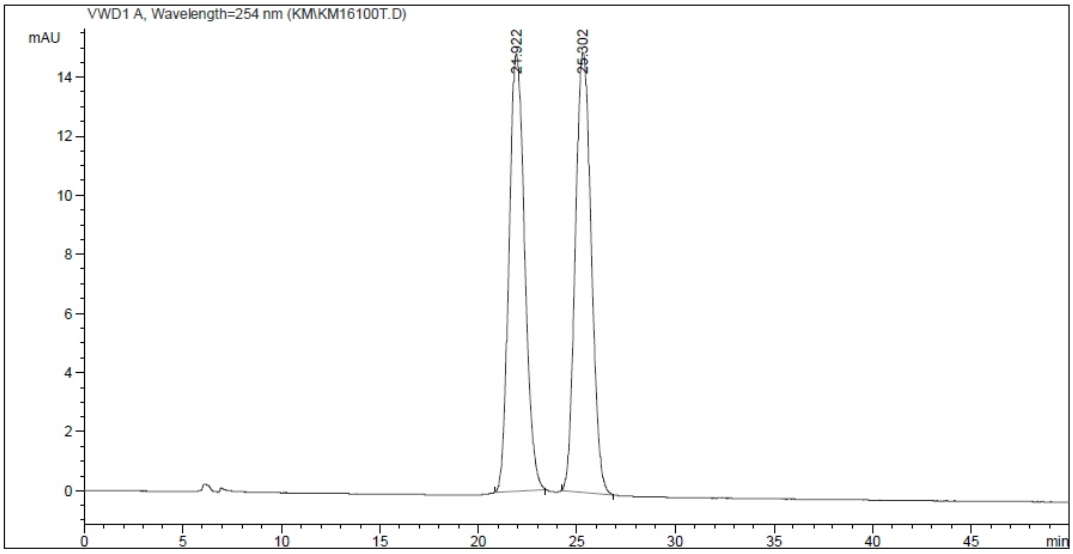
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.512 MM    0.8367  512.72705   10.21337   3.6881
   2  14.779 MM    0.8414 1.33893e4   265.22925  96.3119
```

HPLC analysis

racemic



***trans*-4f**

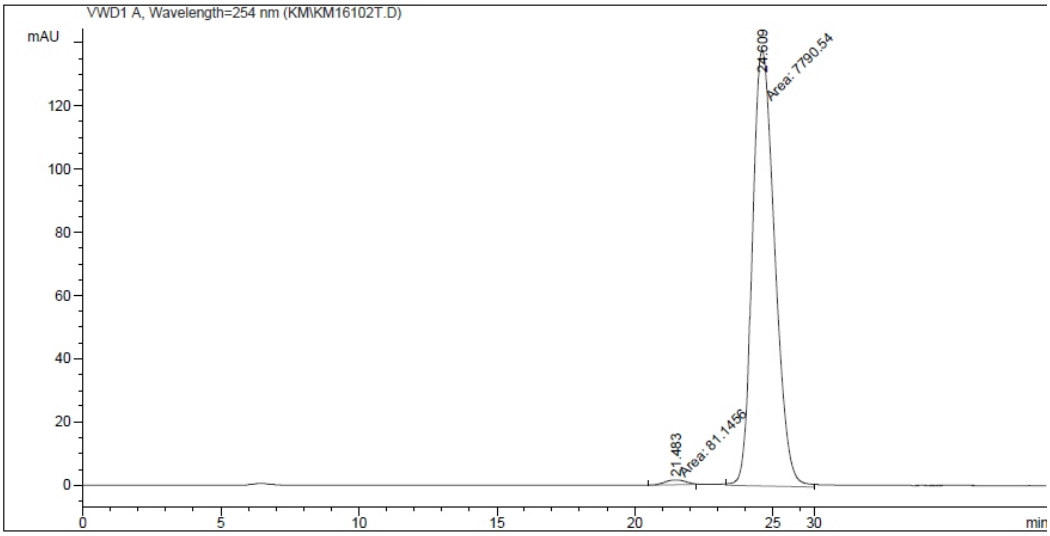



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  21.922 BB    0.8722  827.82513   14.80578  49.6808
   2  25.302 BB    0.8915  838.46198   14.91930  50.3192
```

chiral



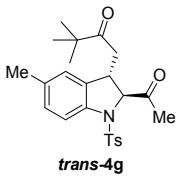

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

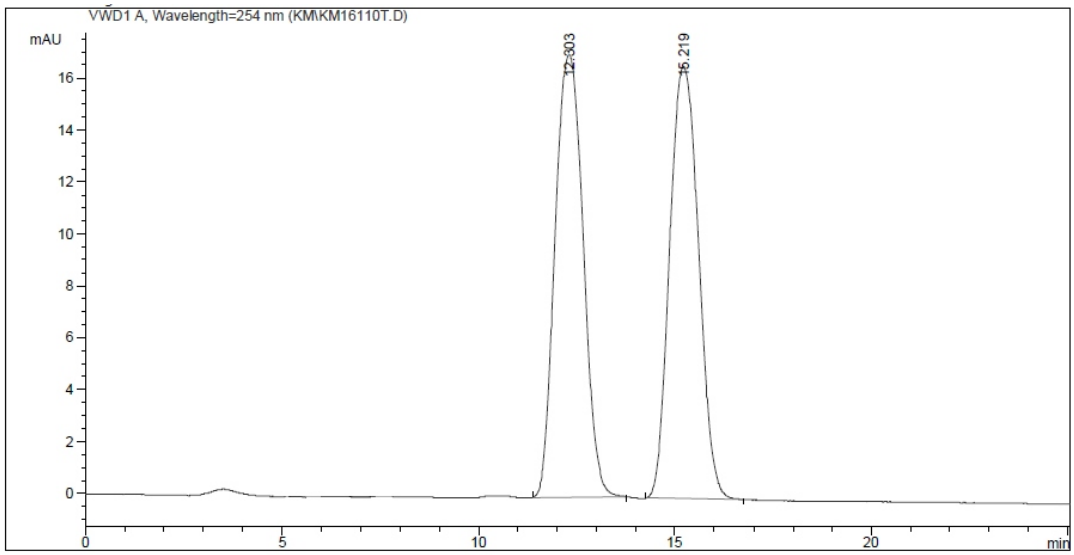
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  21.483 MM    0.6322   81.14555    1.54865   1.0309
   2  24.609 MM    0.9422 7790.54102  137.81384  98.9691
```

HPLC analysis

racemic



***trans*-4g**

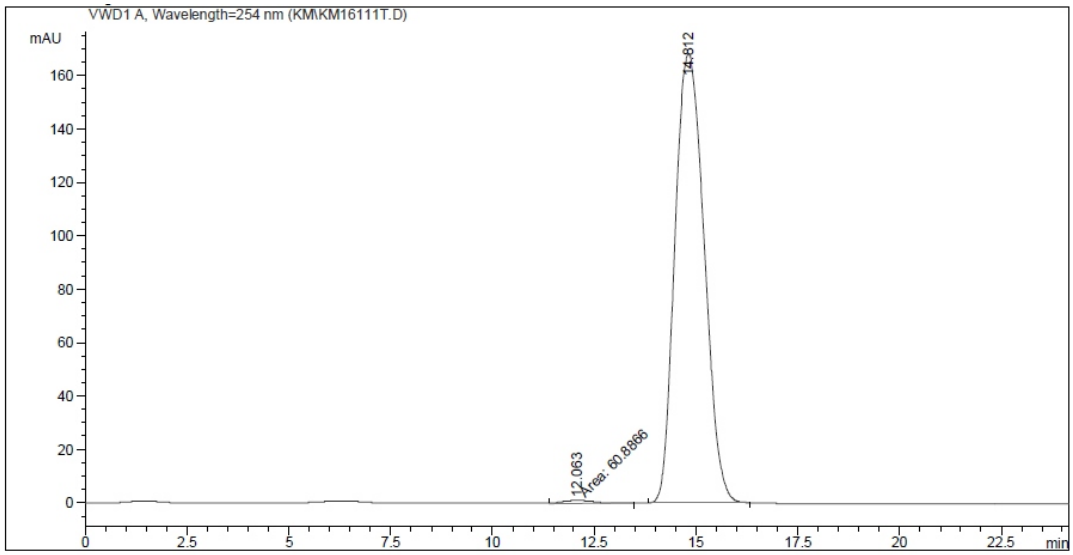



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.303 BB    0.7970  846.95081   17.03452  49.9874
   2  15.219 BB    0.8234  847.37939   16.66278  50.0126
```

chiral



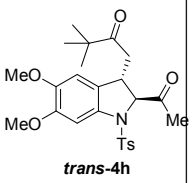

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

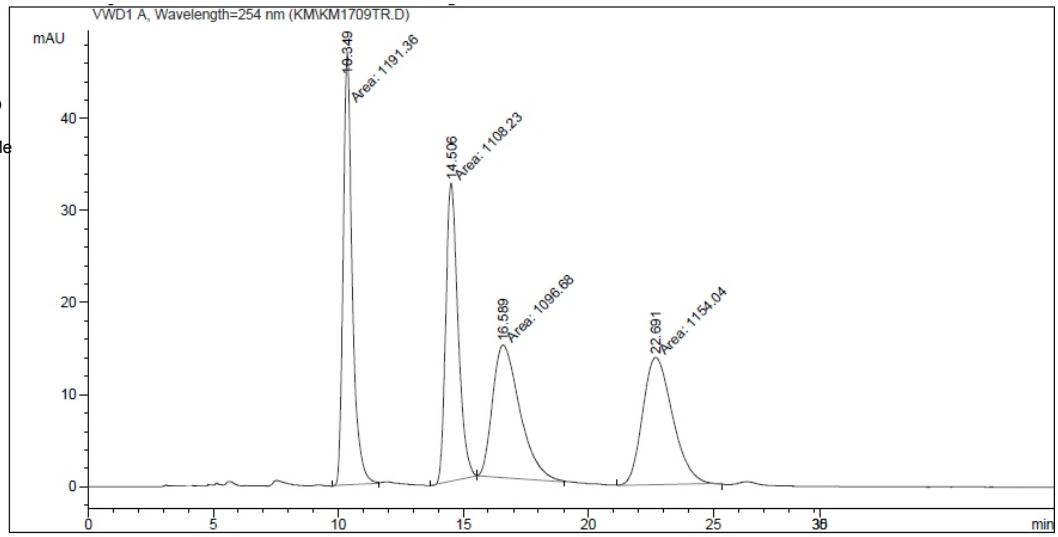
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.063 MM    0.8480   60.88659    1.19669   0.7150
   2  14.812 BB    0.8120 8454.27246  168.20999  99.2850
```

HPLC analysis

racemic (*cis* + *trans*)



***trans*-4h**

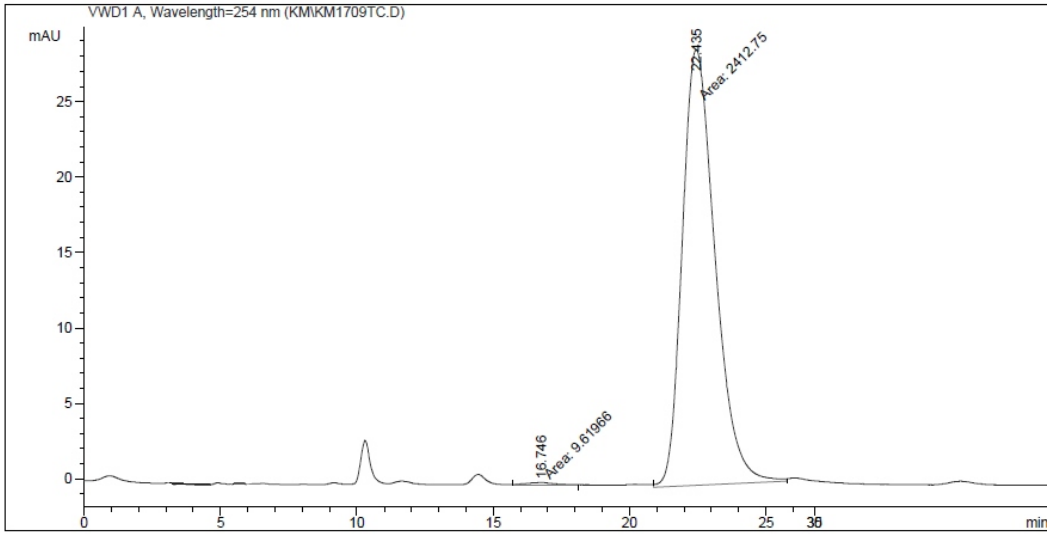



```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.349 MM    0.4224 1191.36401   47.00374  26.1820
   2  14.506 MM    0.5702 1108.23083   32.39037  24.3550
   3  16.589 MM    1.2673 1096.68298   14.42241  24.1012
   4  22.691 MM    1.3912 1154.03809   13.82582  25.3617
```

chiral



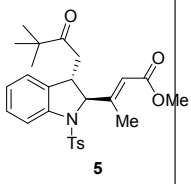

```
=====================================================================
                      Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

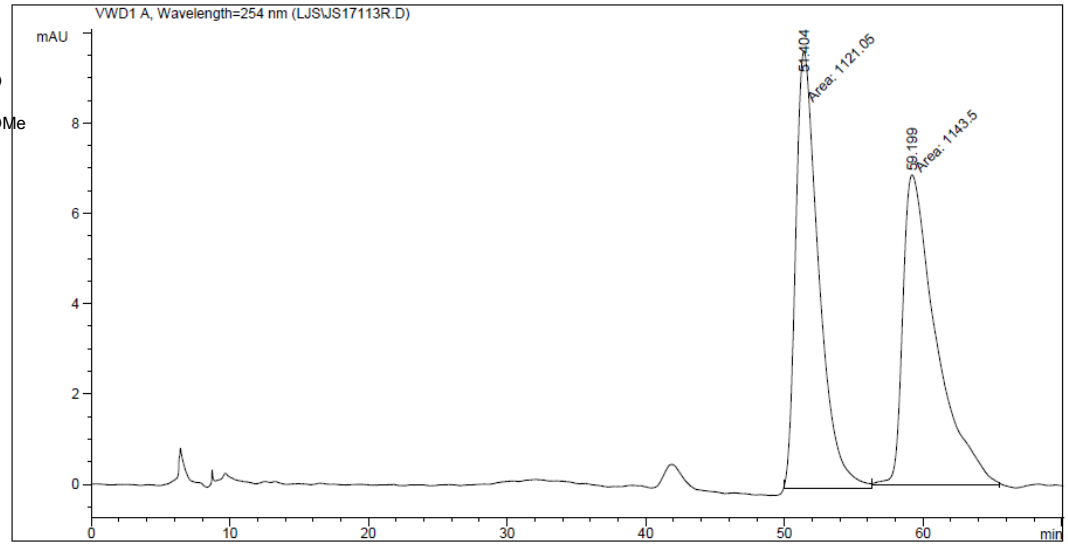
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.746 MM    1.0399    9.61966 1.54170e-1   0.3971
   2  22.435 MM    1.3927 2412.74707   28.87442  99.6029
```

HPLC analysis

racemic



5

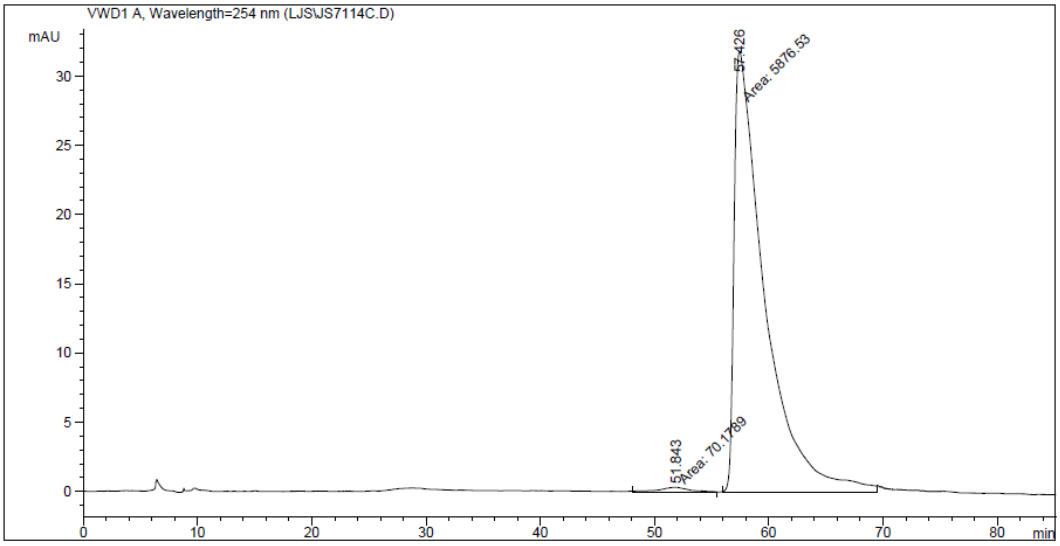



```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  51.404 MM    1.9304 1121.04614    9.67889  49.5042
   2  59.199 MM    2.7793 1143.50171    6.85725  50.4958
```

chiral




```
=====================================================================
                        Area Percent Report
=====================================================================

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  51.843 MM    3.2659   70.17892 3.58139e-1   1.1801
   2  57.426 MM    3.0783 5876.52783   31.81671  98.8199
```