

## Supporting Information

### Palladium-Catalyzed Asymmetric [3+2] Cycloaddition of Vinyl Aziridines and $\alpha$ , $\beta$ -Unsaturated Imines Generated *in situ* from Aryl Sulfonyl Indoles

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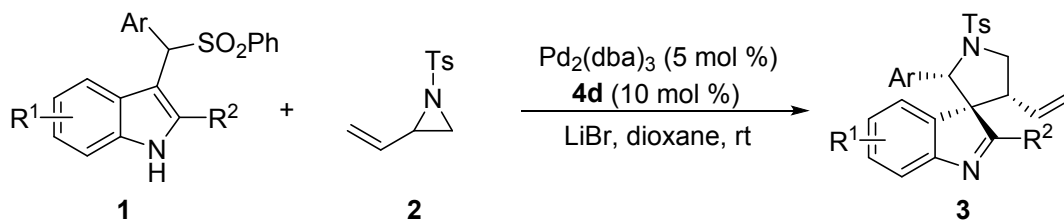
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## 1. General information

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents used in the reactions were distilled from appropriate drying agents prior to use. The sulfonyl indoles **1a-1x**<sup>1</sup>, **1y**<sup>2</sup>, **1z**<sup>1</sup> and vinyl aziridine **2**<sup>3</sup> were prepared according to the literature procedures. If not noted, catalysts **4a-f** and other chemicals were commercially available and used without further purification.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded respectively at 400 MHz and 100 MHz. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Optical rotations were measured in the indicated solvents on Perkin Elmer polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Flash column chromatography was performed using 200-300 mesh silica gel. Enantiomeric excess (*ee*) were determined by HPLC analysis on a Shimadzu LC-20A, using Daicel Chiracel IC columns. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruker P-SIMS-Gly FT-ICR mass spectrometer. The relative and absolute configuration of **3b** were assigned by the X-ray analysis and the configurations of other cycloaddition products were assigned by analogy.

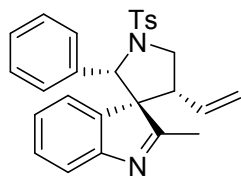
## 2. Asymmetric formal [3+2] cycloadditions



To a dried tube filled with sulfonyl indole **1** (0.1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5 mol %), LiBr (0.3 mmol) and (S)-(-)-XylBINAP (10 mol %) was added a solution of vinyl aziridine **2** (0.3 mmol) in 1,4-dioxane (2 mL). The reaction mixture was stirred under an atmosphere of argon at 25 °C. Upon completion of the reaction, distilled water was added dropwise to quench the reaction. The resulting solution was extracted with ethyl acetate (3 × 3 mL). The combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether and ethyl acetate (petroleum ether/ethyl acetate = 2:1) to give the corresponding product **3**.

### 3.1. Products 3a - 3z in Scheme 2.

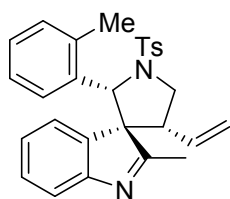
#### (2'S,3S,4'R)-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3a)



White solid, yield 72%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 7:1, mp = 182.0 -183.4 °C, [α]<sub>D</sub><sup>20</sup> = +19.8 (c = 0.1, THF), 97% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 25.1 min, t (major) = 28.3 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.81 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.27-7.22 (m, 2H), 7.10 (t, J = 7.3 Hz, 1H), 7.02 -6.88 (m, 6H), 5.11 (s, 1H), 4.89-4.68 (m, 3H), 4.18 (dd, J = 12.1, 7.9 Hz, 1H), 3.97 (t, J = 11.9 Hz, 1H), 2.85-2.67 (m, 1H), 2.48 (s, 3H), 2.25 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.4, 154.6, 144.4, 136.2, 135.4, 133.9, 130.8, 129.9, 128.4, 128.1, 127.5, 127.4, 126.0, 125.0, 124.7, 120.0, 119.0, 73.3, 67.9, 53.1, 49.1, 21.7, 15.8. HRMS (ESI): calcd for C<sub>27</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 443.1788, found 443.1791.

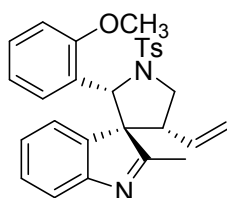
**(2'S,3S,4'R)-2-methyl-2'-(*o*-tolyl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine]**

**(3b)**



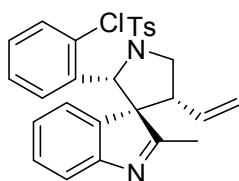
White solid, yield 73%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 6:1, mp = 173.6-175.5 °C.  $[\alpha]_D^{20} = -28.2$  (c = 0.1, THF), 96% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 20.6 min, t (major) = 24.6 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.78 (d,  $J = 8.2$  Hz, 2H), 7.46 (d,  $J = 7.4$  Hz, 2H), 7.40 - 7.29 (m, 3H), 7.11 (t,  $J = 7.3$  Hz, 1H), 7.04-6.84 (m, 4H), 6.77 (m, 1H), 5.55 (s, 1H), 4.88 - 4.75 (m, 1H), 4.34 (dd,  $J = 12.0$ , 7.4 Hz, 1H), 3.95 (t,  $J = 11.6$  Hz, 1H), 2.98- 2.93 (m, 3H), 2.48 (s, 2H), 2.26 (s, 3H), 1.92 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 1180.7, 154.7, 144.1, 136.0, 135.5, 134.2, 131.2, 130.1, 129.8, 128.2, 128.0, 127.7, 127.1, 125.7, 124.9, 124.3, 120.0, 118.7, 72.3, 63.9, 53.0, 50.6, 21.6, 19.2, 16.0. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 457.1944, found 457.1949.

**(2'R,3S,4'R)-2'-(2-methoxyphenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3c)**



White solid, yield 80%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 8:1, mp = 171.5-173.2 °C.  $[\alpha]_D^{20} = +21.15$  (c = 0.1, THF), 94% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 23.1 min, t (major) = 25.1 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.89 (d,  $J = 7.2$  Hz, 2H), 7.65 (d,  $J = 6.9$  Hz, 1H), 7.44-7.42 (m, 1H), 7.27 - 6.73 (m, 3H), 6.42 - 6.40 (m, 1H), 5.54 (s, 1H), 4.88 - 4.54 (m, 3H), 4.31 - 4.08 (m, 1H), 3.90 (t,  $J = 12.0$  Hz, 1H), 3.42 (s, 3H), 2.69 - 2.54 (m, 1H), 2.50 (s, 3H), 2.10 (s, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 181.0, 155.7, 154.8, 144.3, 135.9, 134.5, 130.5, 130.0, 128.1, 128.0, 127.9, 126.5, 124.7, 124.1, 119.7, 119.5, 118.6, 109.2, 72.0, 62.9, 54.3, 52.9, 50.1, 21.7, 15.4. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 473.1893, found 473.1893.

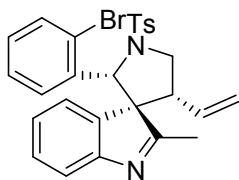
**(2'R,3S,4'R)-2'-(2-chlorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3d)**



White solid, yield 65%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 6:1, mp = 181.5-184.9°C.  $[\alpha]_D^{20} = -63.8$  (c = 0.1, THF) 86% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm).

Retention time: t (minor) = 20.3 min, t (major) = 22.3 min.  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.86 (d,  $J = 8.1$  Hz, 2H), 7.66 (d,  $J = 7.7$  Hz, 1H), 7.44-7.42 (m, 2H), 7.29-7.25 (m, 1H), 7.17-7.10 (m, 2H), 7.05-6.92 (m, 4H), 5.58 (s, 1H), 4.89- 4.70 (m, 3H), 4.23 (dd,  $J = 12.3, 7.6$  Hz, 1H), 4.00 (t,  $J = 12.0$  Hz, 1H), 2.77-2.70 (m, 1H), 2.50 (s, 3H), 2.17 (s, 3H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  180.0, 155.0, 144.5, 135.1, 134.8, 134.0, 131.6, 130.5, 130.3, 130.1, 129.0, 128.6, 128.4, 128.1, 125.7, 125.2, 124.3, 120.2, 119.1, 72.2, 64.4, 53.1, 49.9, 21.7, 16.3. **HRMS (ESI)**: calcd for  $\text{C}_{27}\text{H}_{25}\text{ClN}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  477.1398, found 477.1400.

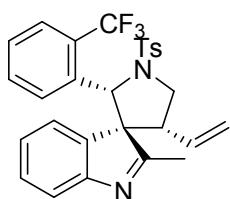
**(2'R,3S,4'R)-2'-(2-bromophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3e)**



White solid, yield 64%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 5:1, mp = 162.8-164.6 °C.  $[\alpha]_D^{20} = +36.2$  (c = 0.1, THF), 90% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time:

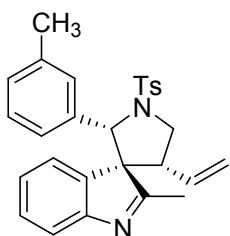
t (minor) = 24.3 min, t (major) = 28.1 min.  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.89 (d,  $J = 7.5$  Hz, 2H), 7.65 (d,  $J = 7.5$  Hz, 1H), 7.45-7.43 (m, 2H), 7.34-7.25 (m, 1H), 7.23-7.04 (m, 4H), 6.99-6.83 (m, 2H), 5.56 (s, 1H), 4.88 -4.71 (m, 3H), 4.27 (dd,  $J = 11.7, 7.7$  Hz, 1H), 4.02 (t,  $J = 11.8$  Hz, 1H), 2.83-2.73 (m, 1H), 2.51 (s, 3H), 2.21 (s, 3H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  180.3, 155.1, 144.5, 136.9, 134.8, 134.1, 132.3, 130.73, 130.66, 130.1, 129.0, 128.4, 128.1, 126.3, 125.4, 124.2, 121.7, 120.1, 119.0, 72.1, 66.3, 53.2, 49.9, 21.7, 16.9. **HRMS (ESI)**: calcd for  $\text{C}_{27}\text{H}_{25}\text{BrN}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  521.0893, found 521.0892.

**(2'S,3S,4'R)-2-methyl-1'-tosyl-2'-(2-(trifluoromethyl)phenyl)-4'-vinylspiro[indole-3,3'-pyrrolidine] (3f)**



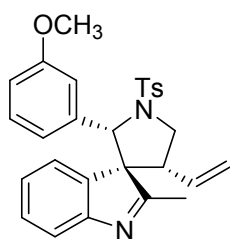
White solid, yield 65%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 8:1, mp = 119.5-120.4°C.  $[\alpha]_D^{20} = +14.7$  (c = 0.1, THF), 84% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 15.7 min, t (major) = 19.7 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.99 (d,  $J = 6.8$  Hz, 1H), 7.85 (d,  $J = 6.4$  Hz, 2H), 7.51-7.29 (m, 5H), 7.20-7.06 (m, 1H), 6.95-6.85 (m, 1H), 5.65 (s, 1H), 4.85-4.72 (m, 3H), 4.35-4.25 (m, 1H), 4.06 (t,  $J = 11.2$  Hz, 1H), 2.80-2.69 (m, 1H), 2.50 (s, 3H), 2.01 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.0, 155.0, 144.5, 136.8, 134.6, 134.5, 131.0, 130.9, 130.8, 130.1, 128.4, 127.8, 127.7, 126.6 (q,  $J = 30.2$  Hz), 125.9 (q,  $J = 6$  Hz), 125.8, 124.0 (q,  $J = 272.0$  Hz), 120.1, 119.0, 72.6, 62.7, 53.2, 50.3, 21.6, 15.7. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 511.1662, found 511.1663.

**(2'S,3S,4'R)-2-methyl-2'-(m-tolyl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3g)**



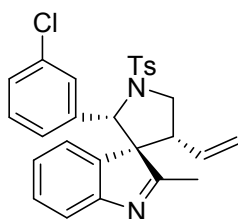
White solid, yield 78%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 9:1, mp = 168.8-170.0°C.  $[\alpha]_D^{20} = +21.4$  (c = 0.1, THF), 92% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 22.2 min, t (major) = 24.2 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.81 (d,  $J = 8.1$  Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.27-7.25 (m, 2H), 7.12 (t,  $J = 7.4$  Hz, 1H), 7.03-6.99 (m, 1H), 6.91-6.67 (m, 4H), 5.12 (s, 1H), 4.89 - 4.72 (m, 3H), 4.22 (dd,  $J = 12.1, 7.9$  Hz, 1H), 3.98 (t,  $J = 11.8$  Hz, 1H), 2.83-2.77 (m, 1H), 2.49 (s, 3H), 2.28 (s, 3H), 2.09 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.5, 154.6, 144.3, 136.8, 135.9, 135.5, 134.2, 130.9, 129.8, 128.3, 128.2, 128.0, 127.3, 126.8, 125.0, 124.5, 123.2, 120.0, 118.9, 73.3, 67.9, 53.0, 49.1, 21.6, 21.3, 15.8. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 457.1944, found 457.1942.

**(2'S,3S,4'R)-2'-(3-methoxyphenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3h)**



White solid, yield 78%.  $R_f$  = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 7:1, mp = 161.4-162.8°C.  $[\alpha]_D^{20}$  = -23.6 (c = 0.1, THF), 91% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 28.9 min, t (major) = 34.8 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.31 (s, 1H), 7.27 (s, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.64 - 6.45 (m, 3H), 5.11 (s, 1H), 4.91 - 4.68 (m, 3H), 4.22 (dd, *J* = 12.1, 7.9 Hz, 1H), 3.98 (t, *J* = 11.8 Hz, 1H), 3.58 (s, 3H), 2.87 - 2.74 (m, 1H), 2.50 (s, 3H), 2.27 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.5, 158.7, 154.6, 144.4, 137.6, 135.5, 134.1, 130.8, 129.9, 128.5, 128.0, 124.9, 124.7, 120.1, 119.0, 118.5, 113.3, 111.9, 73.2, 67.8, 55.0, 53.0, 49.0, 21.7, 15.8. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 473.1893, found 473.1893.

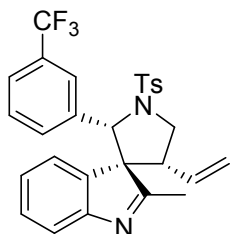
**(2'S,3S,4'R)-2'-(3-chlorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3i)**



White solid, yield 76%.  $R_f$  = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 6:1, mp = 132.4-135.9°C.  $[\alpha]_D^{20}$  = -31.8 (c = 0.1, THF), 84% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 17.8 min, t (major) = 20.4 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.32-7.20 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.05-7.01 (m, 1H), 6.96 (s, 1H), 6.92-6.80 (m, 3H), 5.10 (s, 1H), 4.91-4.67 (m, 3H), 4.21 (dd, *J* = 12.0, 7.9 Hz, 1H), 3.95 (t, *J* = 11.8 Hz, 1H), 2.89-2.75 (m, 1H), 2.48 (s, 3H), 2.26 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.1, 154.6, 144.6, 138.3, 135.0, 133.0, 133.5, 130.6, 130.0, 128.8, 128.6, 128.0, 127.6, 126.4, 124.9, 124.8, 124.1, 120.3, 119.1, 73.2, 67.2, 53.0, 49.1, 21.6, 15.7. **HRMS (ESI)**: calcd for C<sub>27</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 477.1398, found

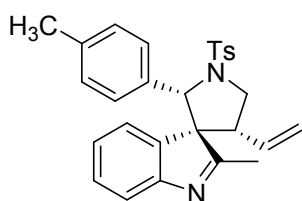
477.1399.

**(2'S,3S,4'R)-2-methyl-1'-tosyl-2'-(3-(trifluoromethyl)phenyl)-4'-vinylspiro[indole-3,3'-pyrrolidine] (3j)**



White solid, yield 75%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 8:1, mp = 130.1-132.7°C.  $[\alpha]_D^{20} = +12.7$  (c = 0.1, THF), 86% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 10.5 min, t (major) = 11.3 min.  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.78 (d,  $J = 8.2$  Hz, 2H), 7.39 (d,  $J = 8.1$  Hz, 2H), 7.25-7.20 (m, 4H), 7.16 - 6.98 (m, 4H), 5.21 (s, 1H), 4.94 - 4.76 (m, 3H), 4.28 (dd,  $J = 12.0, 8.0$  Hz, 1H), 3.98 (t,  $J = 11.8$  Hz, 1H), 2.93 (m, 1H), 2.49 (s, 3H), 2.32 (s, 3H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  177.9, 154.5, 144.7, 137.3, 134.9, 134.1, 130.6, 130.0, 129.7 (q,  $J = 32.0$  Hz), 129.1, 128.7, 128.0, 124.9, 124.7, 124.2 (q,  $J = 3.0$  Hz), 123.8 (q,  $J = 271.0$  Hz), 123.2, 120.3, 119.2, 73.2, 67.4, 53.0, 49.1, 21.6, 15.8. **HRMS (ESI)**: calcd for  $\text{C}_{28}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  511.1662, found 511.1663.

**(2'S,3S,4'R)-2-methyl-2'-(p-tolyl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3k)**

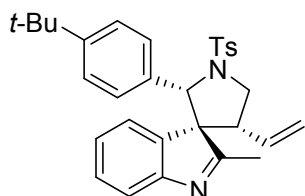


White solid, yield 77%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 7:1, mp = 159.0-161.5°C.  $[\alpha]_D^{20} = +28.7$  (c = 0.1, THF), 92% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 21.5 min, t (major) = 30.1 min.  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.81 (d,  $J = 8.1$  Hz, 2H), 7.42 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 7.4$  Hz, 2H), 7.26 (s, 1H), 7.17-7.03 (m, 2H), 6.90-6.78 (m, 4H), 5.07 (s, 1H), 4.93-4.71 (m, 2H), 4.18 (dd,  $J = 12.1, 8.0$  Hz, 1H), 3.99 (t,  $J = 11.8$  Hz, 1H), 2.83 - 2.72 (m, 1H), 2.51 (s, 3H), 2.26 (s, 3H), 2.12 (s, 3H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  178.4, 154.6, 144.3, 137.0, 135.5, 133.9, 132.9, 130.9, 129.9, 128.3, 128.2, 128.1,



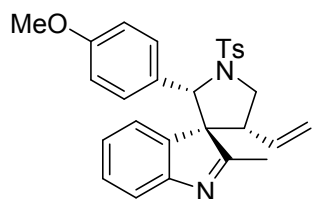
126.0, 125.0, 124.7, 120.0, 118.9, 73.3, 67.9, 53.0, 48.9, 21.7, 21.0, 15.8. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 457.1944, found 457.1945.

**(2'S,3S,4'R)-2'-(4-(tert-butyl)phenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3l)**



White solid, yield 71%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 9:1, mp = 131.1-134.7°C.  $[\alpha]_D^{20} = +24.5$  (c = 0.1, THF), 94% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 18.5 min, t (major) = 32.3 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.14-7.00 (m, 2H), 6.94-6.84 (m, 4H), 5.10 (s, 1H), 4.92 - 4.71 (m, 3H), 4.23 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.98 (t, *J* = 11.8 Hz, 1H), 2.87-2.80 (m, 1H), 2.49 (s, 3H), 2.27 (s, 3H), 1.12 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.5, 154.6, 150.1, 144.1, 135.5, 134.3, 132.5, 131.0, 129.8, 128.2, 128.1, 125.8, 125.0, 124.6, 124.2, 112.0, 118.8, 73.4, 67.9, 52.9, 48.9, 34.2, 31.1, 21.6, 15.9. **HRMS (ESI)**: calcd for C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 499.2414, found 499.2412.

**(2'S,3S,4'R)-2'-(4-methoxyphenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3m)**

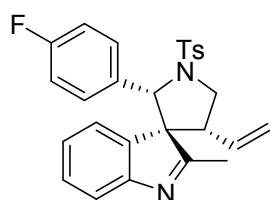


White solid, yield 83%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 5:1, mp = 106.8-107.2°C.  $[\alpha]_D^{20} = +27.0$  (c = 0.1, THF), 92% *ee*, determined by HPLC analysis (chiral IC column, 25% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 23.6 min, t (major) = 32.7 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.25 - 7.02 (m, 3H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 5.01 (s, 1H), 4.89 - 4.65 (m, 3H), 4.17 (dd, *J* = 12.1, 8.1 Hz, 1H), 3.97 (t, *J* = 11.8 Hz, 1H), 3.60 (s, 3H), 2.83 - 2.70 (m, 1H), 2.48 (s, 3H), 2.23 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.4, 158.7, 154.6, 144.3, 135.5, 133.8, 130.9, 129.9, 128.4, 128.0,

127.9, 127.4, 125.0, 124.8, 120.1, 118.9, 112.8, 73.3, 67.8, 55.0, 53.0, 48.7, 21.7, 15.9.

**HRMS (ESI):** calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 473.1893, found 473.1891.

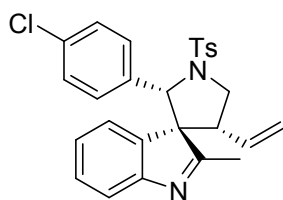
**(2'S,3S,4'R)-2'-(4-fluorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3n)**



White solid, yield 71%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 7:1, mp = 149.2-150.6°C. [α]<sub>D</sub><sup>20</sup> = +29.7 (c = 0.1, THF), 90% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm).

Retention time: t (minor) = 16.0 min, t (major) = 19.8 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.27-7.25 (m, 1H), 7.20 - 6.90 (m, 4H), 6.65 (t, *J* = 8.8 Hz, 2H), 5.06 (s, 1H), 4.89 - 4.71 (m, 3H), 4.18 (dd, *J* = 12.2, 8.0 Hz, 1H), 3.97 (t, *J* = 11.9 Hz, 1H), 2.79-2.73 (m, 1H), 2.50 (s, 3H), 2.24 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.2, 160.84 (d, *J* = 246.0 Hz), 154.6, 144.6, 135.3, 133.8, 131.92 (d, *J* = 3.1 Hz), 130.7, 130.0, 128.6, 128.1, 127.70 (d, *J* = 8.2 Hz), 124.9 (d, *J* = 4.4 Hz), 120.3, 120.0, 114.6, 114.3, 73.3, 67.4, 53.1, 48.9, 21.7, 15.8. **HRMS (ESI):** calcd for C<sub>27</sub>H<sub>25</sub>FN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 461.1694, found 461.1694.

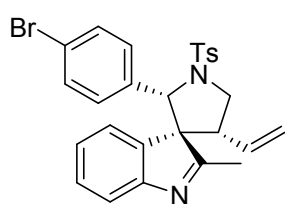
**(2'S,3S,4'R)-2'-(4-chlorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3o)**



White solid, yield 60%. R<sub>f</sub> = 0.3 (petroleum ether/ethylacetate = 2:1), dr = 6:1, mp = 173.8-176.3°C. [α]<sub>D</sub><sup>20</sup> = +48.4 (c = 0.1, THF), 90% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 16.7 min, t (major) = 24.2 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 - 7.02 (m, 4H), 7.01 - 6.87 (m, 4H), 5.06 (s, 1H), 4.86 - 4.73 (m, 3H), 4.18 (dd, *J* = 12.1, 8.0 Hz, 1H), 3.98 (t, *J* = 11.9 Hz, 1H), 2.85 - 2.68 (m, 1H), 2.50 (s, 3H), 2.25 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.1, 154.5, 144.6, 135.1, 134.8, 133.6,

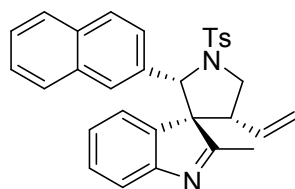
133.1, 130.6, 130.0, 128.6, 128.0, 127.7, 127.4, 124.9, 124.8, 120.3, 119.1, 73.1, 67.3, 53.1, 48.9, 21.7, 15.8. **HRMS (ESI)**: calcd for C<sub>27</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 477.1398, found 477.1397.

**(2'S,3S,4'R)-2'-(4-bromophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3p)**



White solid, yield 72%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 10:1, mp = 167.5-171.2 °C. [α]<sub>D</sub><sup>20</sup> = +62.6 (c = 0.1, THF), 90% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 17.4 min, t (major) = 26.1 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.25-7.24 (m, 2H), 7.19-6.99 (m, 4H), 6.87-7.65 (m, 2H), 5.03 (s, 1H), 4.79 (m, 3H), 4.16 (dd, *J* = 11.9, 8.1 Hz, 1H), 3.96 (t, *J* = 11.8 Hz, 1H), 2.86-2.69 (m, 1H), 2.49 (s, 3H), 2.24 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.0, 154.5, 144.6, 135.3, 135.1, 133.6, 130.60, 130.55, 130.0, 128.7, 128.0, 127.8, 125.0, 124.8, 121.3, 120.3, 119.1, 73.0, 67.4, 53.0, 49.0, 21.7, 15.8. **HRMS (ESI)**: calcd for C<sub>27</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 521.0893, found 521.0896.

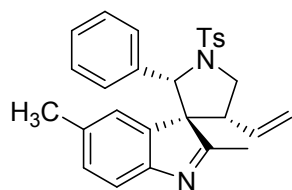
**(2'S,3S,4'R)-2-methyl-2'-(naphthalen-2-yl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3q)**



White solid, yield 73%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 10:1, mp = 157.2-158.6 °C. [α]<sub>D</sub><sup>20</sup> = -76.9 (c = 0.1, THF), 94% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 25.0 min, t (major) = 29.3 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.1 Hz, 1H), 7.62 - 7.51 (m, 2H), 7.42 - 7.32 (m, 5H), 7.13 - 6.64 (m, 5H), 6.09 (s, 1H), 4.93 - 4.71 (m, 3H), 4.41 (dd, *J* = 11.9, 7.3 Hz, 1H), 4.02 (t, *J* = 11.7 Hz, 1H), 3.10-2.90 (m, 1H), 2.49 (s, 3H), 2.39 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 180.0, 154.5,

144.3, 135.3, 133.5, 133.2, 131.1, 130.3, 129.9, 128.6, 128.0, 127.9, 127.8, 125.6, 125.4, 125.3, 125.25, 125.22, 124.4, 124.1, 121.6, 119.8, 118.8, 72.5, 63.5, 53.1, 50.7, 21.6, 16.1. **HRMS (ESI)**: calcd for C<sub>31</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 493.1944, found 493.1951.

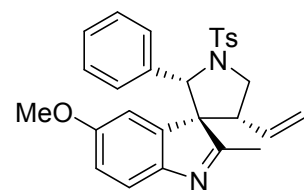
**(2'S,3S,4'R)-2,5-dimethyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine (3r)**



White solid, yield 72%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 9:1, mp =181.6-188.5°C. [α]<sub>D</sub><sup>20</sup> = +44.0 (c = 0.1, THF), 92% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210nm).

Retention time: t (minor) = 23.9 min, t (major) = 30.1 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.15 - 6.88 (m, 8H), 5.09 (s, 1H), 4.88 - 4.73 (m, 3H), 4.20 - 4.13 (m, 1H), 4.00 (t, *J* = 11.8 Hz, 1H), 2.77-2.67 (m, 1H), 2.52 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 177.2, 152.4, 144.4, 136.2, 135.5, 134.4, 133.7, 130.9, 129.9, 128.8, 128.1, 127.4, 126.0, 125.8, 119.5, 118.9, 73.1, 67.9, 53.2, 49.0, 21.7, 21.4, 15.7. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 457.1944, found 457.1939.

**(2'S,3S,4'R)-5-methoxy-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3s)**

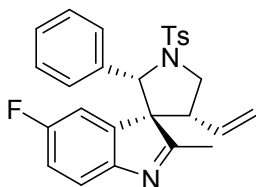


White solid, yield 65%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 13:1, mp =154.6-155.6°C. [α]<sub>D</sub><sup>20</sup> = +89.3 (c = 0.1, THF), 96% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min,

210 nm). Retention time: t (minor) = 29.9 min, t (major) = 33.6 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.17-7.01 (m, 6H), 6.84 - 6.59 (m, 2H), 5.14 (s, 1H), 4.84 - 4.78 (m, 3H), 4.18 (dd, *J* = 12.2, 7.9 Hz, 1H), 3.96 (t, *J* = 11.9 Hz, 1H), 3.74 (s, 3H), 2.81 - 2.69 (m, 1H), 2.52 (s, 3H), 2.23 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 176.2, 157.3, 148.5, 144.4, 137.0, 136.3, 133.9, 130.8, 129.9, 128.1, 127.5, 127.4, 125.9, 120.1, 119.0, 112.7, 112.2, 73.4, 67.7,

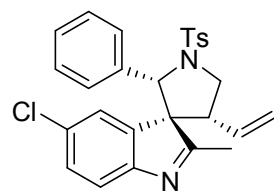
55.8, 52.9, 49.1, 21.7, 15.6. **HRMS (ESI)**: calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 473.1893, found 473.1900.

**(2'S,3S,4'R)-5-fluoro-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3t)**



White solid, yield 78%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 13:1, mp = 198.5-199.9 °C. [α]<sub>D</sub><sup>20</sup> = +33.6 (c = 0.1, THF), 90% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 17.9 min, t (major) = 21.5 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.20 - 7.17 (m, 1H), 7.01 - 6.96 (m, 6H), 6.85 - 6.80 (m, 1H), 5.16 (s, 1H), 4.95 - 4.75 (m, 1H), 4.22 (dd, *J* = 12.2, 7.9 Hz, 1H), 3.91 (t, *J* = 11.9 Hz, 1H), 2.88 - 2.78 (m, 1H), 2.51 (s, 3H), 2.27 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.4, 160.4 (d, *J* = 244.2 Hz), 144.5, 137.40 (d, *J* = 8.9 Hz), 135.9, 134.0, 130.4, 130.0, 128.0, 127.6, 125.9, 120.6 (d, *J* = 9.0 Hz), 119.3, 115.0, 114.9, 112.7 (d, *J* = 25.4 Hz), 73.8, 67.7, 52.9, 48.9, 29.7, 21.7, 15.8. **HRMS (ESI)**: calcd for C<sub>27</sub>H<sub>25</sub>FN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 461.1694, found 461.1700.

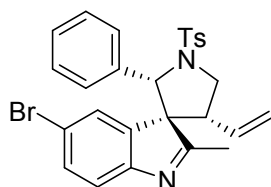
**(2'S,3S,4'R)-5-chloro-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3u)**



White solid, yield 73%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 10:1, mp = 158.3-166.1 °C. [α]<sub>D</sub><sup>20</sup> = -86.9 (c = 0.1, THF), 93% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 18.5 min, t (major) = 21.6 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.27 - 7.05 (m, 3H), 7.04 - 6.90 (d, *J* = 5.1 Hz, 5H), 5.12 (s, 1H), 4.90 - 4.75 (m, 3H), 4.19 (dd, *J* = 12.2, 7.9 Hz, 1H), 3.91 (t, *J* = 11.9 Hz, 1H), 2.85 - 2.73 (m, 1H), 2.49 (s, 3H), 2.26 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 179.1, 153.1, 144.5, 135.8, 133.9, 130.6, 130.4,

130.0, 128.5, 128.1, 127.6, 125.9, 125.3, 120.8, 119.4, 73.7, 67.8, 53.0, 49.0, 21.7, 15.8. **HRMS (ESI)**: calcd for C<sub>27</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 477.1398, found 477.1396.

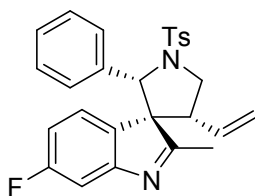
**(2'S,3S,4'R)-5-bromo-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3v)**



White solid, yield 70%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 11:1, mp = 154.7-155.6 °C. [α]<sub>D</sub><sup>20</sup> = -28.1 (c = 0.1, THF), 96% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm).

Retention time: t (minor) = 19.7 min, t (major) = 22.4 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.41 (m, 3H), 7.27 - 7.08 (m, 1H), 7.05 - 6.95 (m, 5H), 5.14 (s, 1H), 4.95 - 4.75 (m, 3H), 4.21 (dd, *J* = 12.2, 7.9 Hz, 1H), 3.93 (t, *J* = 11.9 Hz, 1H), 2.85-2.79 (m, 1H), 2.52 (s, 3H), 2.28 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 179.1, 153.6, 144.5, 137.7, 135.8, 133.9, 131.4, 130.4, 130.0, 128.1, 128.1, 127.7, 127.6, 125.8, 121.3, 119.4, 118.5, 73.8, 67.8, 53.1, 49.0, 21.7, 15.8. **HRMS (ESI)**: calcd for C<sub>27</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 521.0892, found 521.0896.

**(2'S,3S,4'R)-6-fluoro-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3w)**

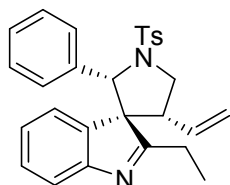


White solid, yield 78%. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 2:1), dr = 12:1, mp = 128.9-133.0 °C. [α]<sub>D</sub><sup>20</sup> = +30.5 (c = 0.1, THF), 92% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm).

Retention time: t (minor) = 17.9 min, t (major) = 21.5 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.21-7.18 (m, 1H), 7.07 - 6.65 (m, 7H), 5.12 (s, 1H), 4.91 - 4.68 (m, 2H), 4.20 (dd, *J* = 12.1, 7.9 Hz, 1H), 3.94 (t, *J* = 11.9 Hz, 1H), 2.81- 2.74 (m, 1H), 2.51 (s, 3H), 2.28 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 180.9, 162.90 (d, *J* = 245.3 Hz), 156.1 (d, *J* = 11.0 Hz), 144.5, 136.0, 133.9, 131.1 (d, *J* = 3.0 Hz), 130.5, 130.0, 128.0, 127.6, 125.9, 125.4 (d,

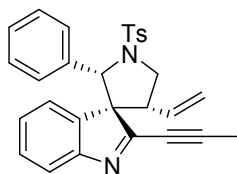
$J = 9.6$  Hz), 119.1, 111.5, 115.3, 107.88 (d,  $J = 23.9$  Hz), 73.0, 67.8, 53.0, 49.0, 21.7, 15.9. **HRMS (ESI)**: calcd for  $C_{27}H_{25}FN_2O_2S$   $[M+H]^+$  461.1693, found 461.1697.

**(2'S,3S,4'R)-2-ethyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3x)**



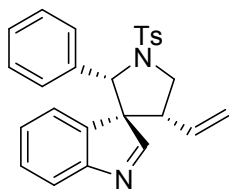
White solid, yield 76%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 6:1, mp = 111.4-118.1°C.  $[\alpha]_D^{20} = +26.7$  (c = 0.1, THF), 94% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 20.2 min, t (major) = 23.8 min.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ , ppm)  $\delta$  7.82 (d,  $J = 7.5$  Hz, 2H), 7.42 (d,  $J = 7.4$  Hz, 2H), 7.32 - 7.30 (m, 1H), 7.25 - 7.11 (m, 2H), 7.08 - 6.89 (m, 6H), 5.14 (s, 1H), 4.81 - 4.76 (m, 1H), 4.29 - 4.09 (m, 1H), 3.97 (t,  $J = 11.7$  Hz, 1H), 2.82 (s, 1H), 2.69 - 2.56 (m, 1H), 2.52 (s, 3H), 2.36 (dd,  $J = 16.6, 7.6$  Hz, 1H), 1.41 (t,  $J = 6.9$  Hz, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ , ppm)  $\delta$  144.4, 136.1, 135.4, 134.0, 130.9, 129.9, 128.8, 128.6, 128.4, 128.1, 127.5, 125.9, 125.0, 120.1, 119.0, 73.4, 67.9, 53.1, 49.0, 22.2, 21.7, 10.8. **HRMS (ESI)**: calcd for  $C_{28}H_{28}N_2O_2S$   $[M+H]^+$  457.1943, found 457.1949.

**(2'S,3S,4'R)-2'-phenyl-2-(prop-1-yn-1-yl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3y)**



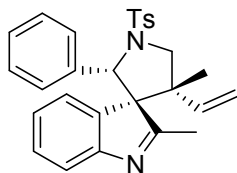
White solid, yield 70%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 11:1, mp = 113.4-115.8°C.  $[\alpha]_D^{20} = +46.4$  (c = 0.1, THF), 92% *ee*, determined by HPLC analysis (chiral IC column, 25% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 24.9 min, t (major) = 26.4 min.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ , ppm)  $\delta$  7.84 (d,  $J = 6.7$  Hz, 2H), 7.41 (d,  $J = 6.8$  Hz, 2H), 7.36 - 7.29 (m, 2H), 7.14 - 7.08 (m, 4H), 6.98 - 6.96 (m, 1H), 5.30 (s, 1H), 4.96 - 4.63 (m, 1H), 4.19 - 4.15 (m, 1H), 4.02 (t,  $J = 11.7$  Hz, 1H), 3.05 - 2.91 (s, 1H), 2.46 (s, 3H), 2.10 (s, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ , ppm)  $\delta$  163.5, 154.9, 144.1, 136.1, 134.5, 133.6, 130.4, 129.9, 128.6, 128.3, 127.4, 126.1, 125.9, 124.9, 121.3, 119.1, 98.4, 74.3, 73.7, 68.3, 53.2, 48.7, 21.7, 4.9. **HRMS (ESI)**: calcd for  $C_{29}H_{26}N_2O_2S$   $[M+H]^+$  467.1788, found 467.1785.

**(2'S,3S,4'R)-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3z)**



White solid, yield 54%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 2:1, mp = 116.5-117.8°C.  $[\alpha]_D^{20} = +16.5$  (c = 0.1, THF), 94% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 29.1 min, t (major) = 37.2 min.  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.92 (s, 1H), 7.81 (d,  $J = 7.6$  Hz, 2H), 7.56 - 7.29 (m, 5H), 7.19 - 7.02 (m, 4H), 6.93 (s, 2H), 5.24 - 5.14 (m, 1H), 5.11 (s, 1H), 4.77 (dd,  $J = 32.0, 13.7$  Hz, 2H), 4.33 (dd,  $J = 11.6, 7.6$  Hz, 1H), 3.94 (t,  $J = 11.8$  Hz, 1H), 2.85 - 2.75 (m, 1H), 2.52 (s, 3H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  171.2, 155.8, 144.3, 136.5, 136.2, 134.5, 129.99, 129.93, 129.1, 128.1, 128.0, 127.9, 126.8, 125.3, 121.5, 121.3, 118.9, 71.5, 70.2, 53.9, 50.1, 21.7. **HRMS (ESI)**: calcd for  $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  429.1631, found 429.1635.

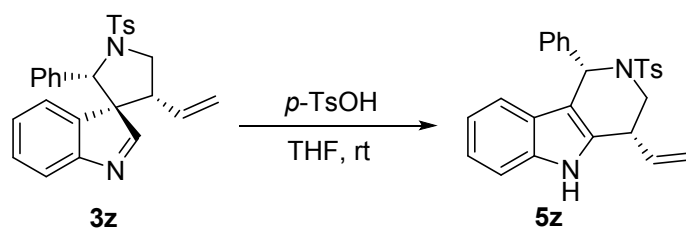
**(2'S,3S,4'R)-2,4'-dimethyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (6a)**



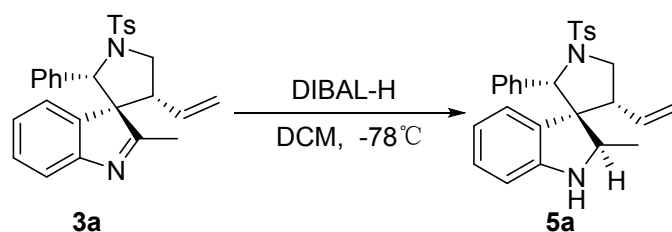
White solid, yield 51%.  $R_f = 0.3$  (petroleum ether/ethyl acetate = 2:1), dr = 5:1, mp = 158.2-163.7°C.  $[\alpha]_D^{20} = -30.4$  (c = 0.1, THF), 17% ee, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) = 30.6 min, t (major) = 35.9 min.  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.71 (d,  $J = 8.1$  Hz, 2H), 7.39 - 7.28 (m, 3H), 7.16 (t,  $J = 7.6$  Hz, 1H), 7.08 - 7.00 (m, 3H), 6.91 - 6.84 (m, 3H), 6.53 (d,  $J = 7.6$  Hz, 1H), 5.40 - 5.28 (m, 1H), 5.07 (s, 1H), 4.95 - 4.89 (m, 2H), 3.97 (dd,  $J = 10.92, 10.14$  Hz, 2H), 2.47 (s, 3H), 2.02 (s, 3H), 1.09 (s, 3H).  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  180.8, 154.7, 144.2, 140.0, 137.6, 135.7, 134.3, 129.8, 128.4, 128.0, 127.5, 127.5, 127.2, 127.1, 124.2, 119.8, 113.8, 75.2, 66.2, 58.7, 48.4, 23.5, 21.6, 19.8. **HRMS (ESI)**: calcd for  $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  456.1871, found 456.1874.



### 3.2 The Compound 4 and 5 in Scheme 3



To a solution of **3z** (46.5 mg 0.11 mmol) in THF (2 mL) was added *p*-TsOH (6.3 mg 0.033 mmol) and then stirred at room temperature under argon atmosphere for 20 h. Upon completion of the reaction, the solvent was removed under reduced pressure, added saturated NaHCO<sub>3</sub> (2 mL), and the aqueous phase was extracted with ethyl acetate (3×3 mL). The organic phases was washed by water (5 mL) and saturated brine (5 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the residue was purified by column chromatography on silica gel to give compound **5z** (39 mg, 91% yield, 94% *ee*) as a white solid. Dr =12:1. R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 4:1), mp = 112-114 °C, [α]<sub>D</sub><sup>20</sup> = +54.9 (c = 0.1, THF), 94% *ee*, determined by HPLC analysis (chiral IC column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: t (minor) =6.0 min, t (major) = 7.2 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.77 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.22 (s, 4H), 7.19 - 7.17 (m, 1H), 7.09-7.05 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.22 (s, 1H), 5.71 -5.62 (m, 1H), 5.31 - 5.14 (m, 2H), 3.77 (dd, *J* = 14.5, 5.9 Hz, 1H), 3.44 -3.37 (m, 1H), 2.90 (dd, *J* = 14.5, 10.9 Hz, 1H), 2.18 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 143.3, 138.9, 138.1, 137.5, 136.2, 130.5, 129.4, 128.7, 128.6, 126.9, 126.5, 122.2, 120.0, 119.5, 117.9, 111.0, 55.7, 46.2, 44.8, 37.5, 21.4, 11.4. **HRMS (ESI)**: calcd for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 429.1631, found 429.1631.



To a solution of **3a** (44.3 mg 0.1 mmol) in DCM (2 mL) was added DIBAL-H (0.2 mmol), and then stirred at -78 °C under argon atmosphere for 4 h. Upon completion of

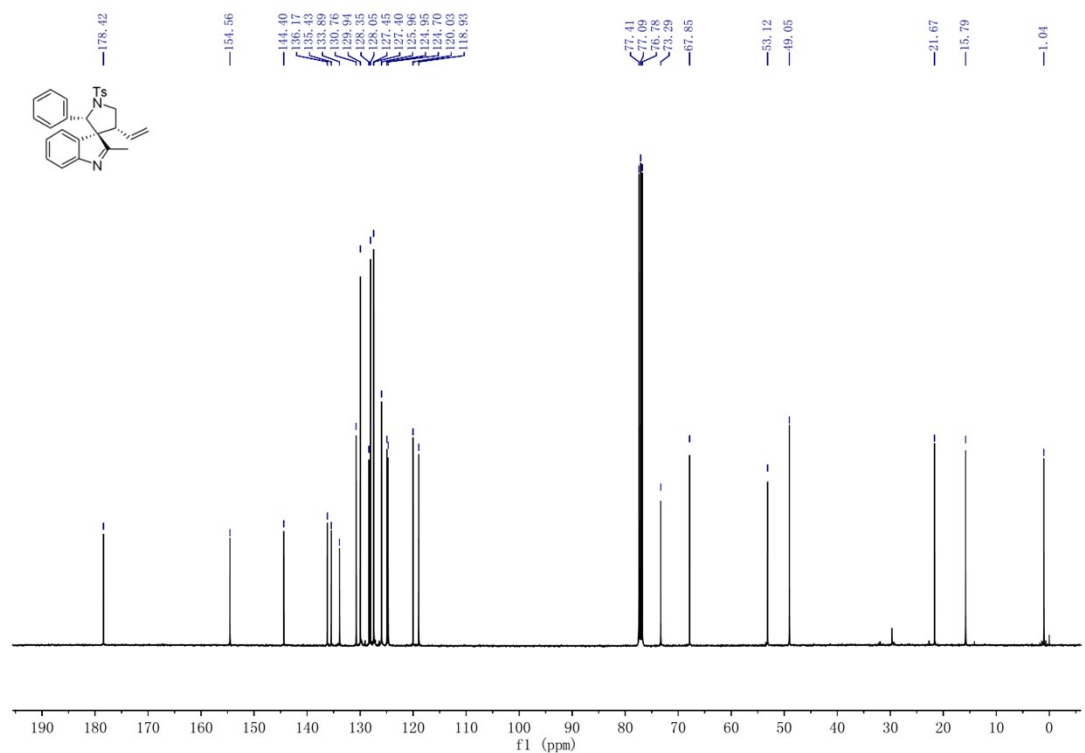
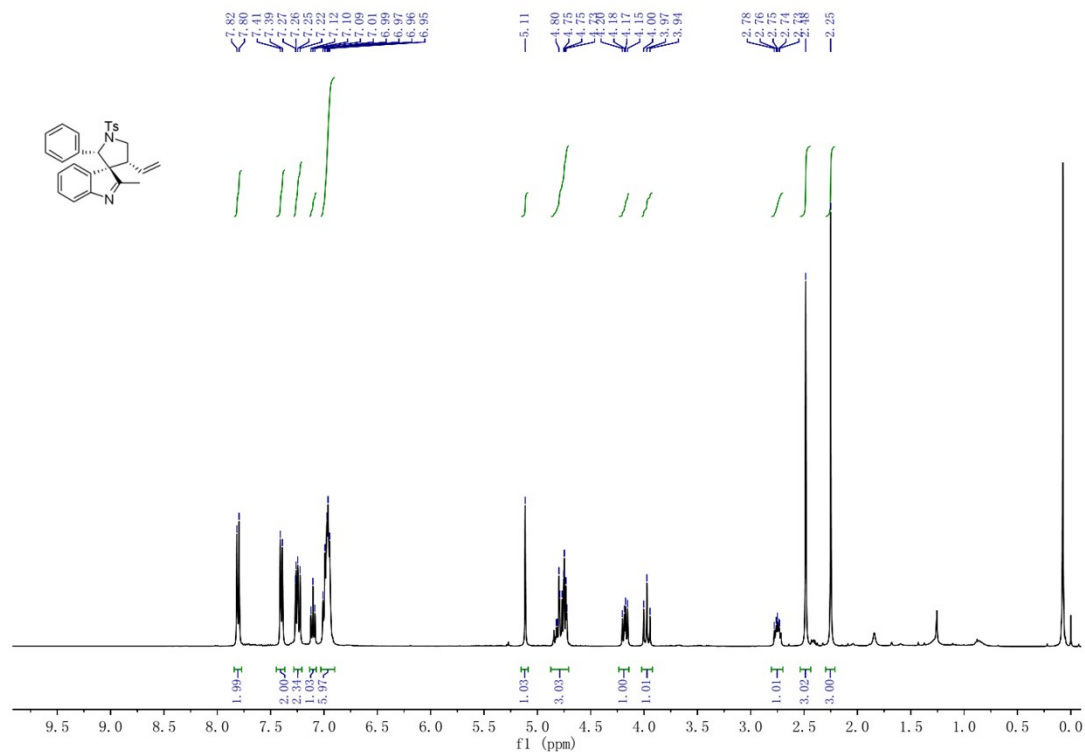
the reaction, the reaction was quenched with water (5 mL). The mixture was extracted with Dichloromethane (3 × 5 mL), the combined organic layer was dried MgSO<sub>4</sub>. After removal of the solvents under reduced pressure, the residual was purified by column chromatography, affording the title compound **5a** (38.7 mg, 87% yield, 96% *ee*) as a white solid. *dr*=7:1. *R<sub>f</sub>* = 0.3 (petroleum ether/ethyl acetate = 5:1), *mp* = 98-100 °C,  $[\alpha]_{\text{D}}^{20} = -52.13$  (*c* = 0.1, THF), 96% *ee*, determined by HPLC analysis (chiral IE column, 20% IPA in hexane, rate: 1.0 mL/min, 210 nm). Retention time: *t* (minor) = 22.7 min, *t* (major) = 24.8 min. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.43 - 7.22 (m, 2H), 7.03 - 6.85 (m, 7H), 6.60 (t, *J* = 7.4 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 5.82 - 5.60 (m, 1H), 5.09 - 5.1 (m, 2H), 4.91 (s, 1H), 4.11 (dd, *J* = 11.6, 9.0 Hz, 1H), 3.90 (t, *J* = 11.5 Hz, 1H), 3.74 - 3.70 (m, 1H), 2.46 (s, 1H), 2.41 (dd, *J* = 19.5, 9.2 Hz, 1H), 1.31 (d, *J* = 6.6 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, ppm) δ 150.7, 143.5, 138.1, 135.2, 134.9, 129.6, 128.2, 128.11, 128.06, 127.8, 127.0, 126.8, 126.7, 119.4, 118.3, 110.0, 67.5, 62.9, 60.0, 52.8, 50.0, 21.6, 15.0. **HRMS (ESI)**: calcd for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> 445.1944, found 445.1948.

#### 4. References

- [1] (a) Z. S. Liu, W. K. Li, T. R. Kang, L. He and Q. Z. Liu, Palladium-Catalyzed Asymmetric Cycloadditions of Vinylcyclopropanes and in Situ Formed Unsaturated Imines: Construction of Structurally and Optically Enriched Spiroindolenines, *Org. Lett.*, 2015, **17**, 150. (b) Y. Chen, X. Q. Guo, C. Zhou, L. M. Chen and T. R. Kang, Direct N-sec-Alkylation of Amides by Reaction of Halohydroxamates and Sulfonylindoles: An Approach to 3-Indolyl Methanamines, *Synlett*, 2019, **30**, 851.
- [2] E. Rossi, G. Abbiati, V. Canevari, G. Celentano, E. Magri, 2-Trifluoromethanesulfonyloxyindole-1-carboxylic Acid Ethyl Ester: A Practical Intermediate for the Synthesis of 2-Carbo-substituted Indoles, *Synthesis*, 2006, **2**, 299.
- [3] S. I. Ali, M. D. Nikalje and A. Sudalai, Pyridinium Hydrobromide Perbromide: A Versatile Catalyst for Aziridination of Olefins Using Chloramine-T, *Org. Lett.*, 1999, **1**, 705.

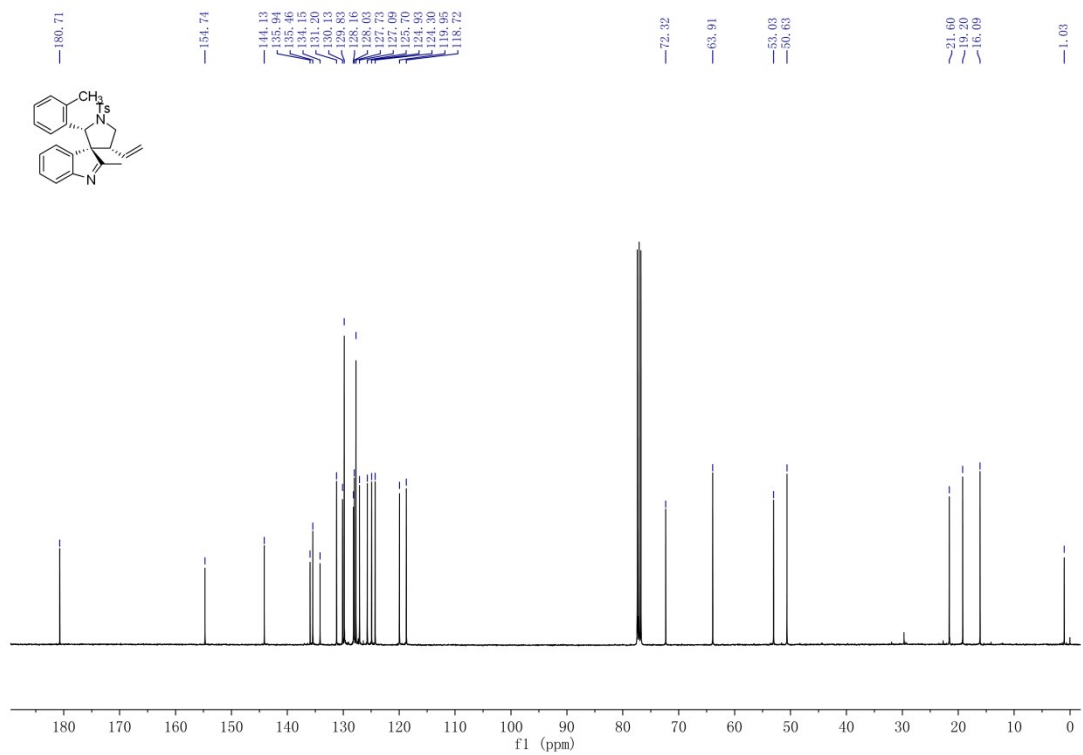
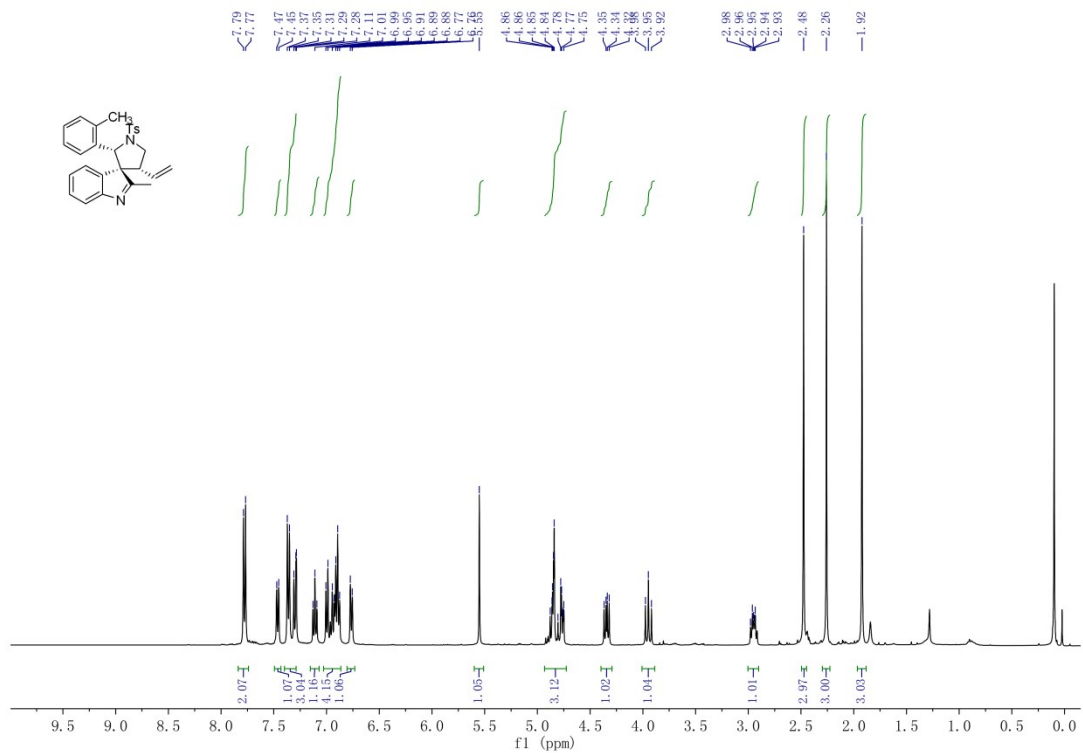
## 5. NMR spectra of the products

### (2'S,3S,4'R)-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3a)

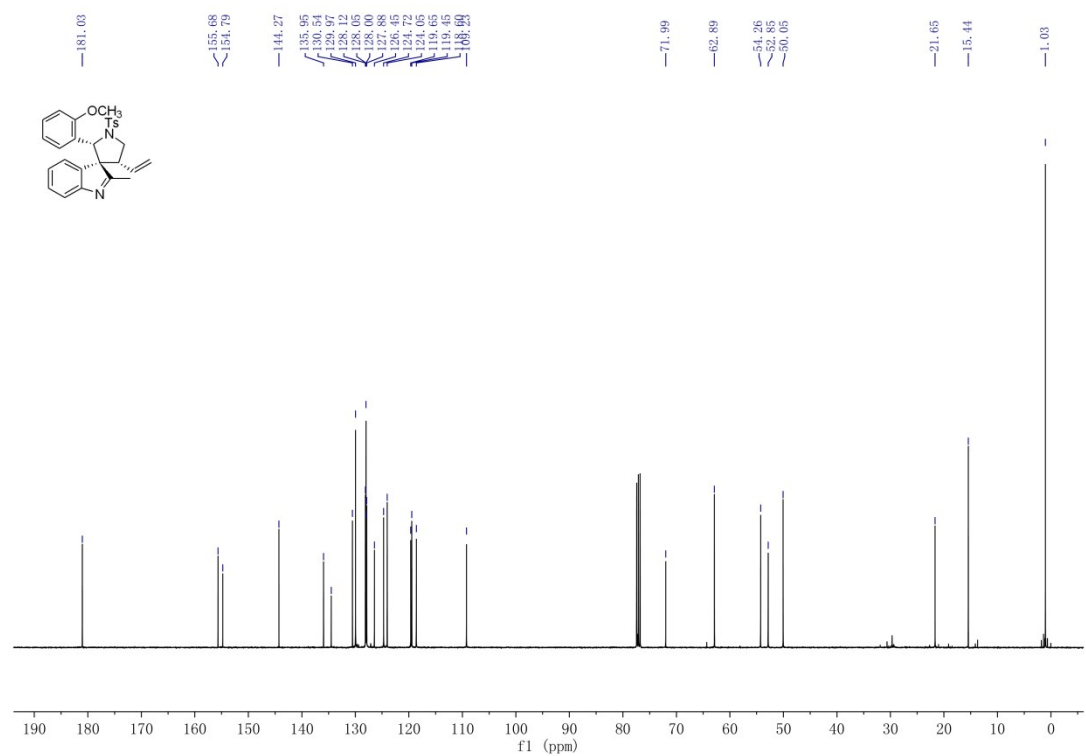
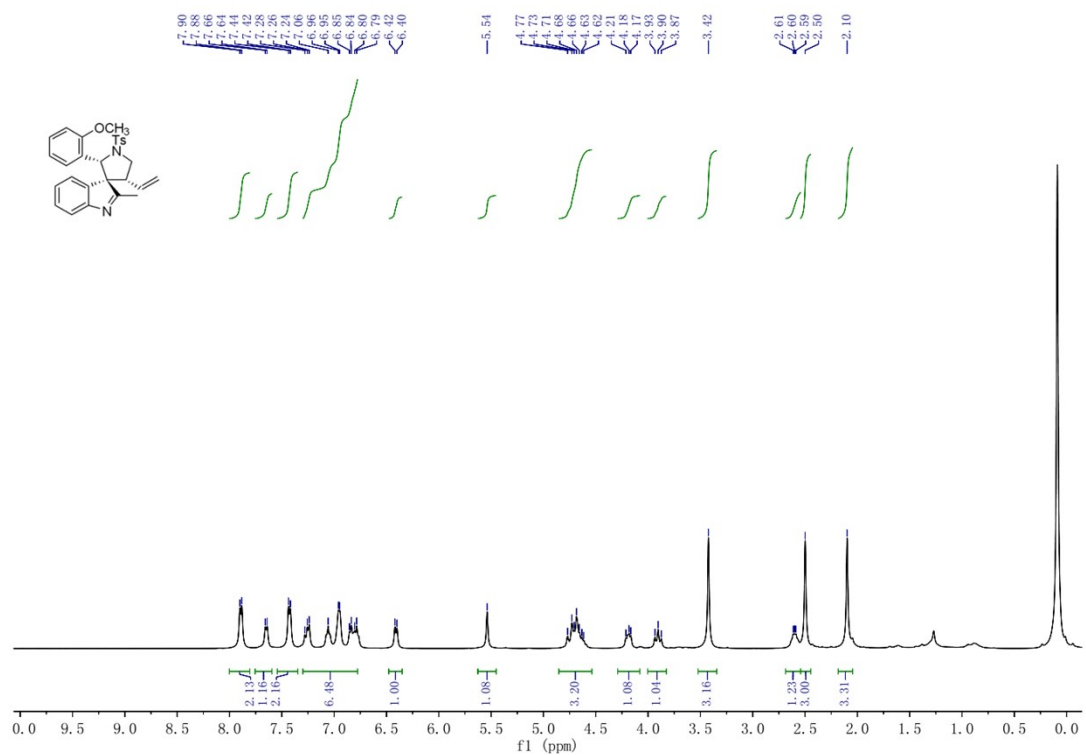


### (2'S,3S,4'R)-2-methyl-2'-(o-tolyl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine]

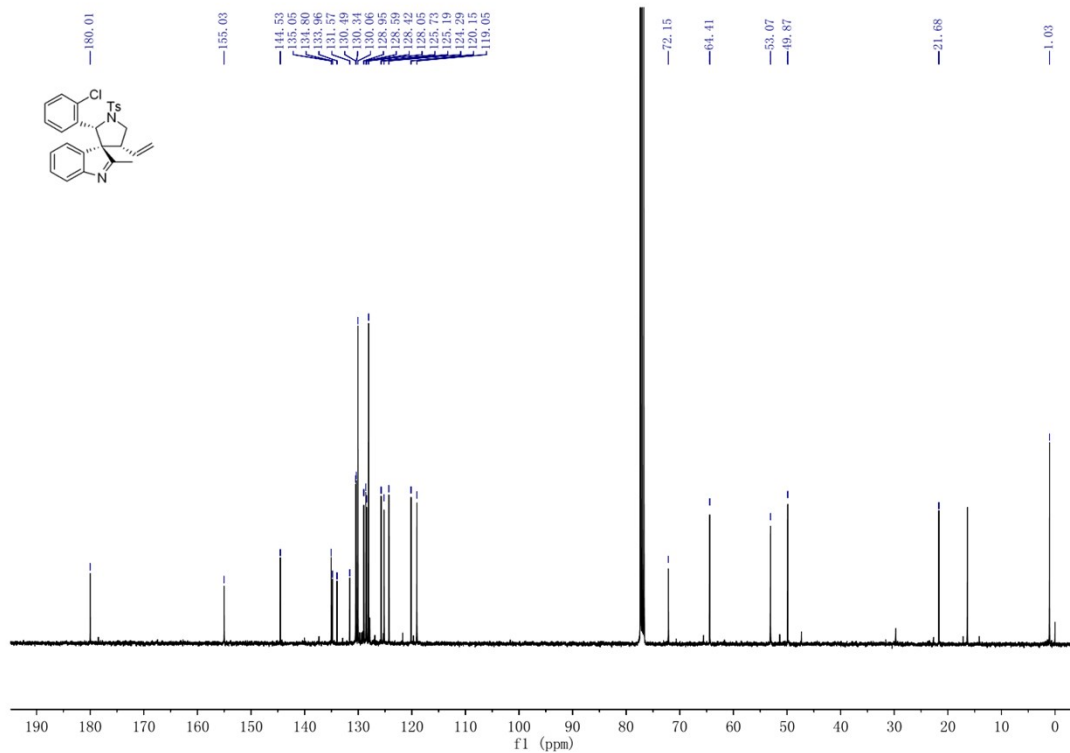
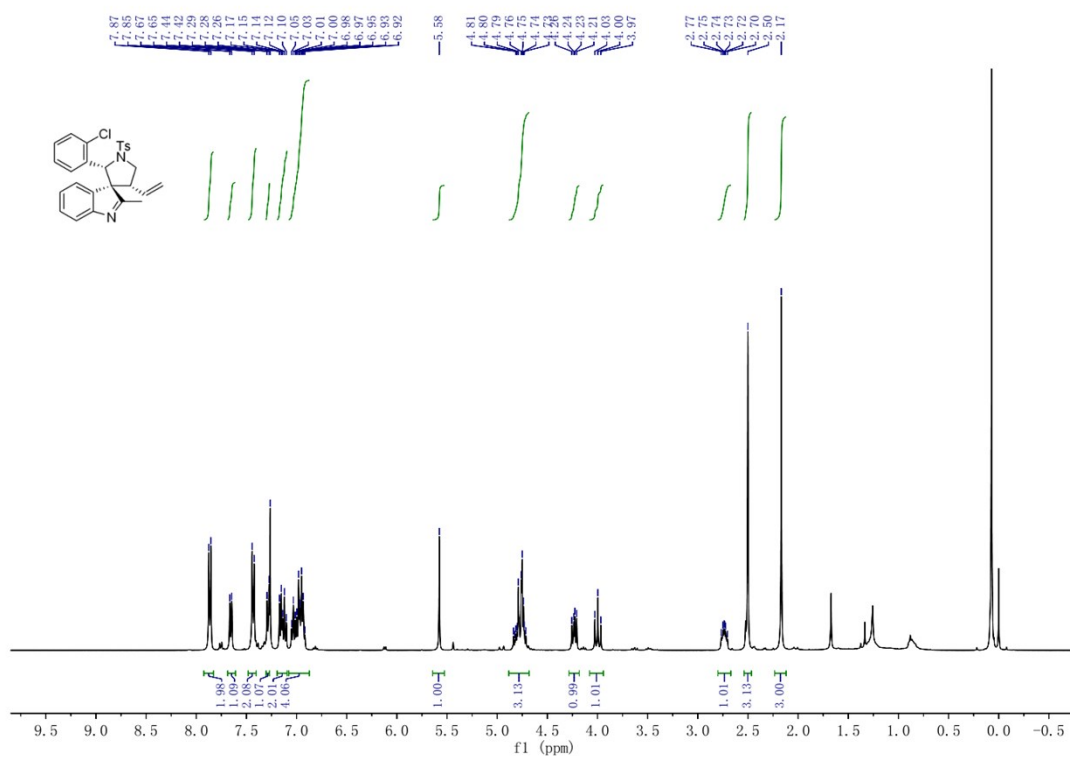
(3b)



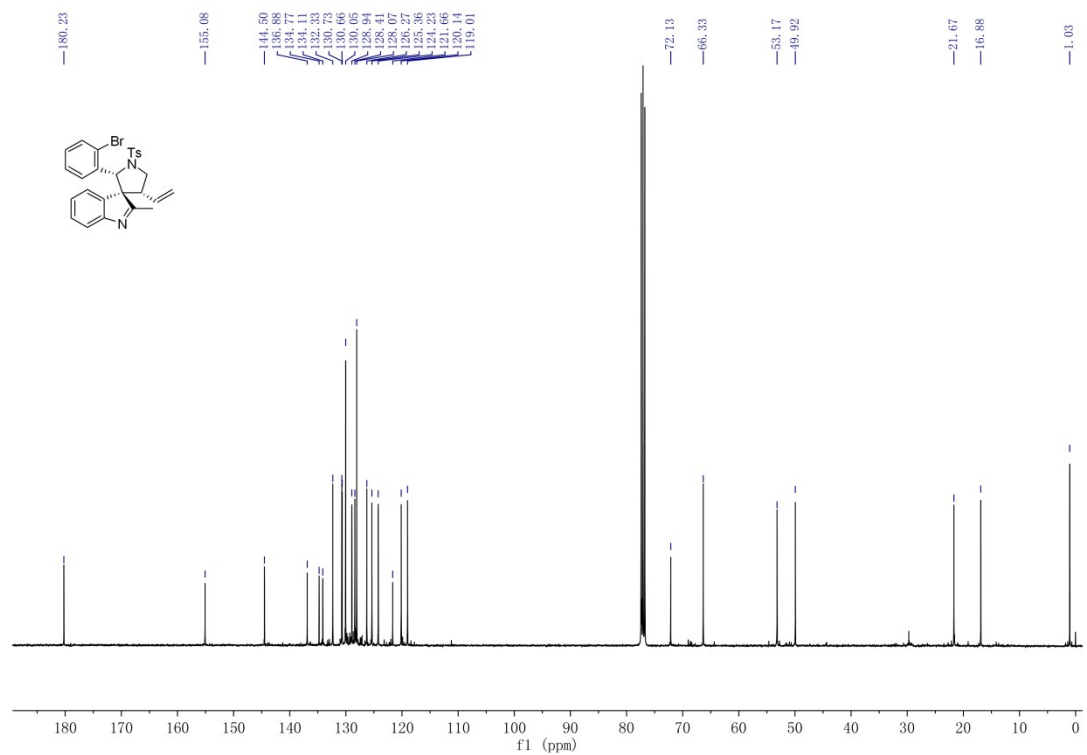
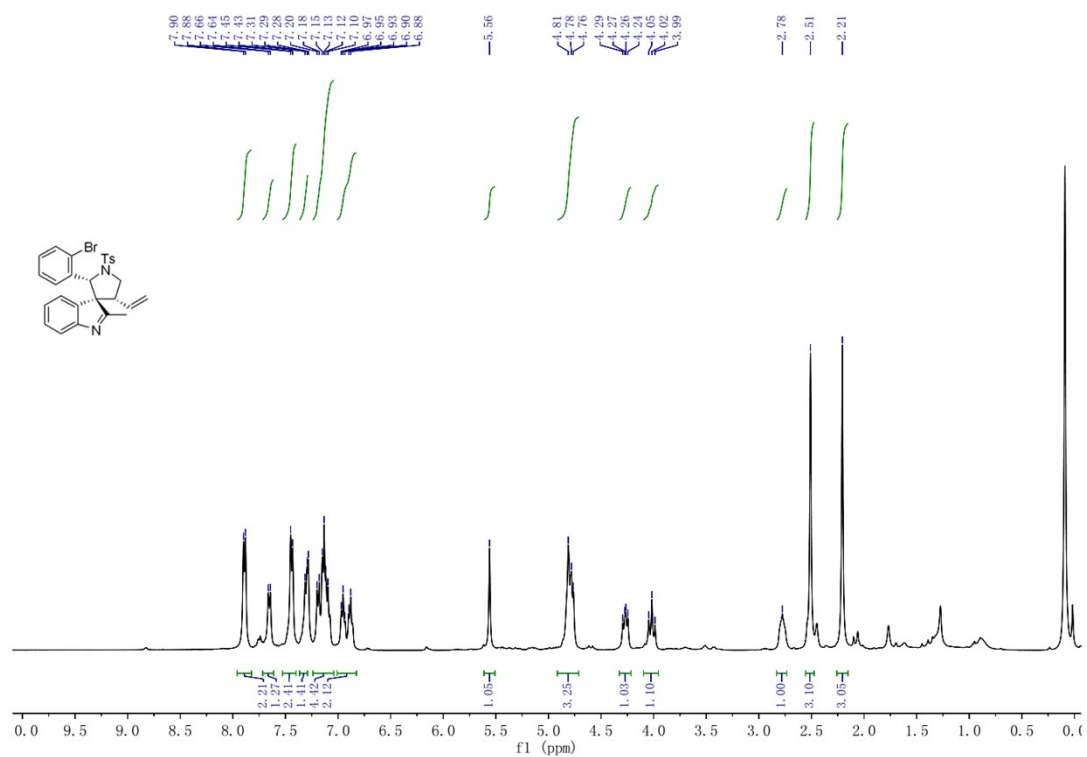
**(2'R,3S,4'R)-2'-(2-methoxyphenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3c)**



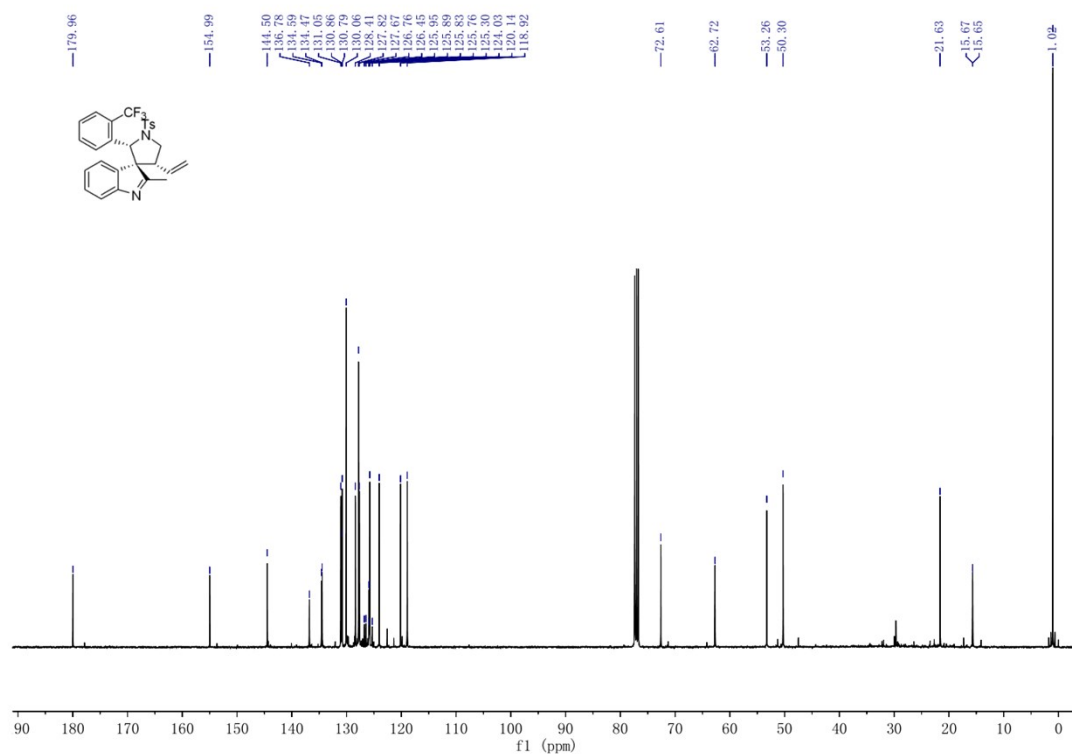
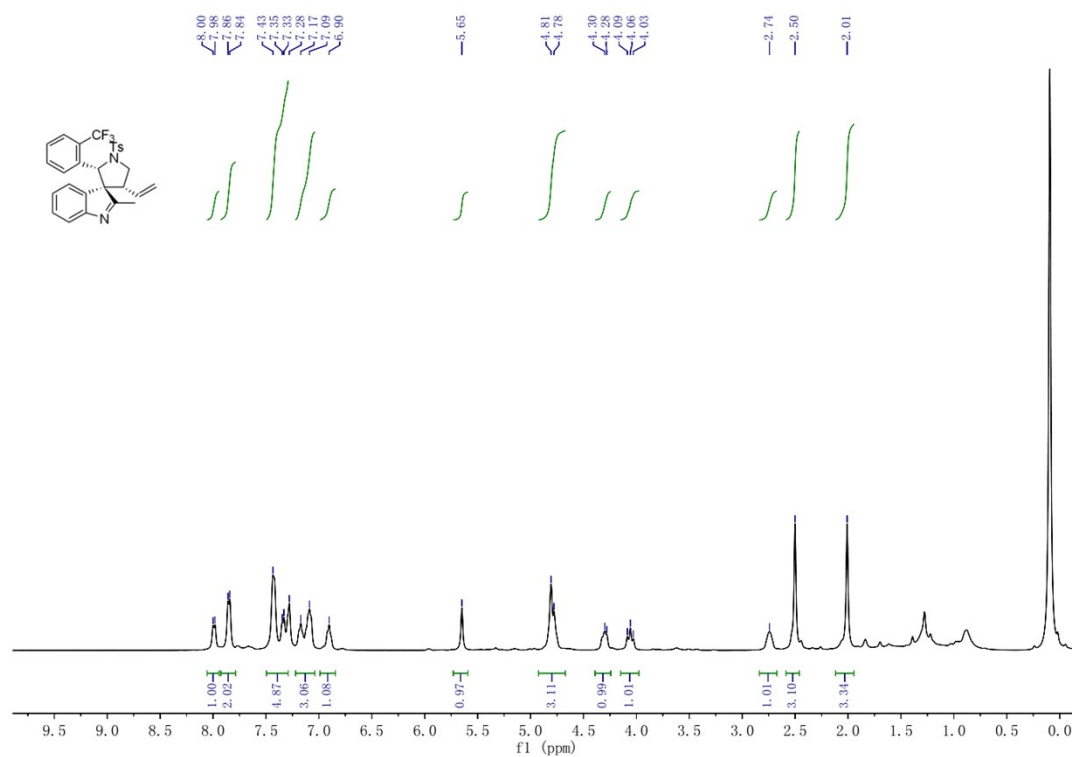
**(2'R,3S,4'R)-2'-(2-chlorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3d)**



**(2'R,3S,4'R)-2'-(2-bromophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3e)**

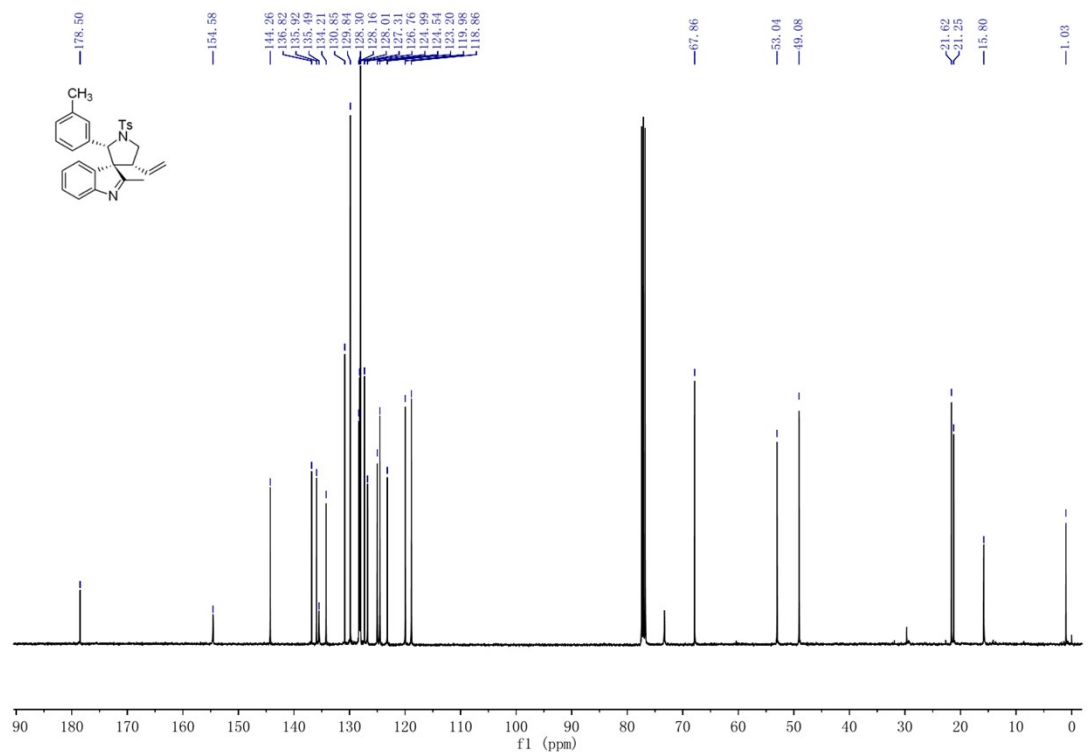
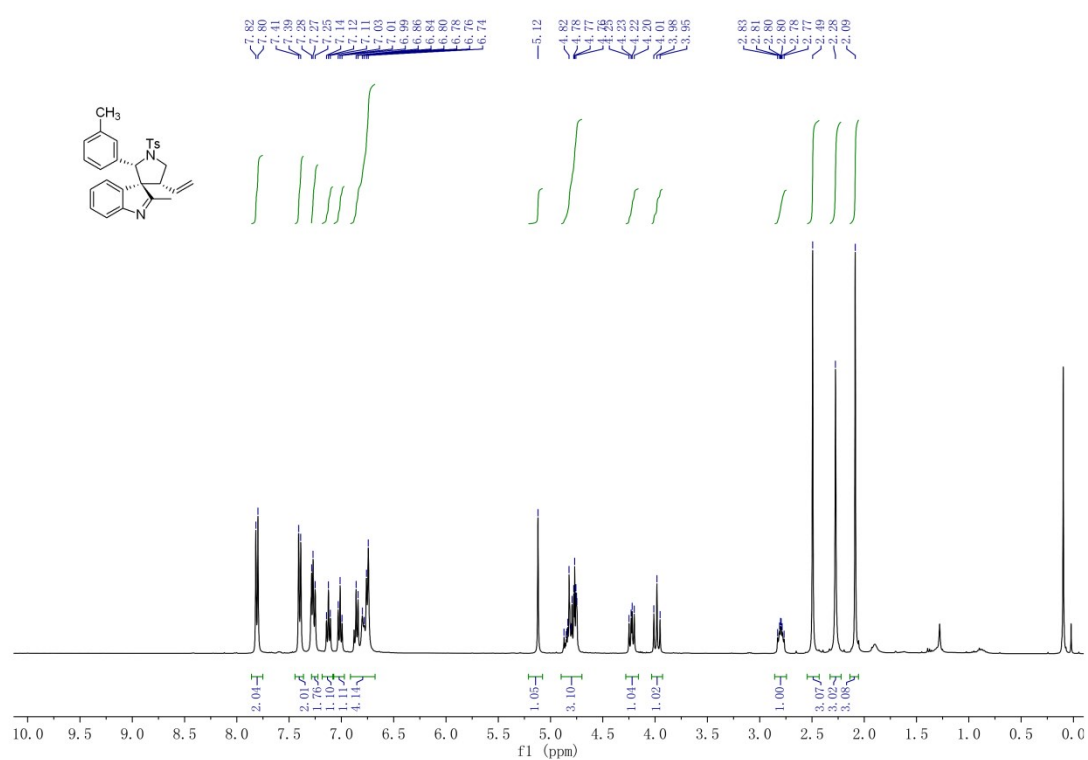


**(2'S,3S,4'R)-2-methyl-1'-tosyl-2'-(2-(trifluoromethyl)phenyl)-4'-vinylspiro[indole-3,3'-pyrrolidine] (3f)**

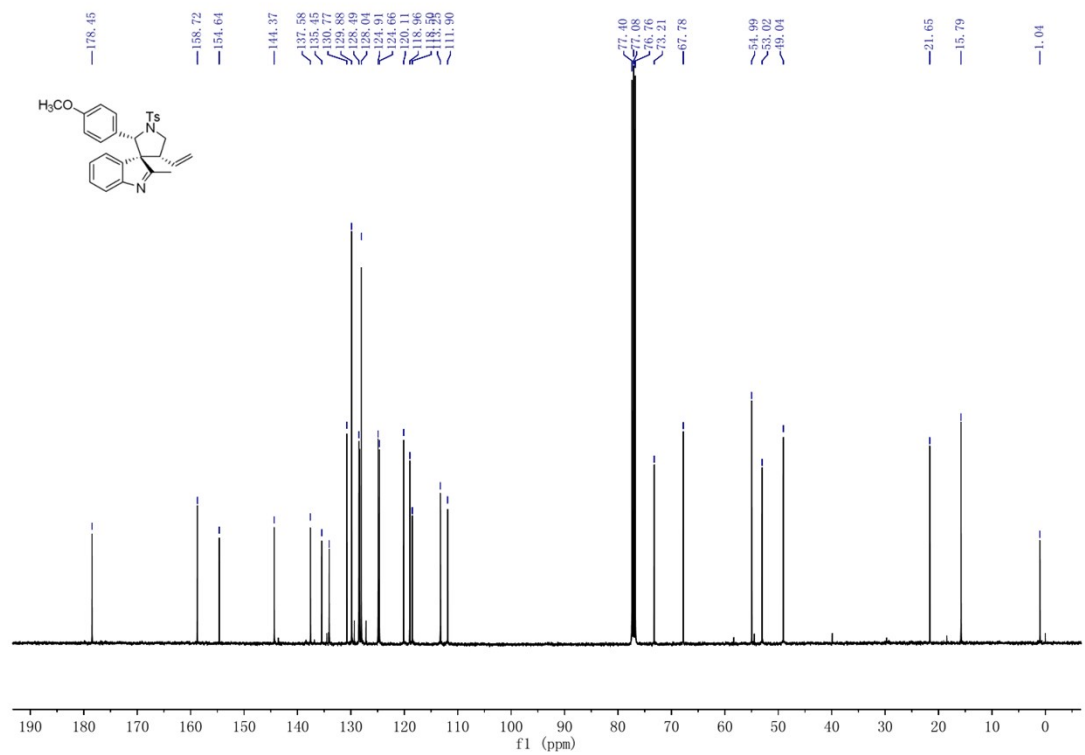
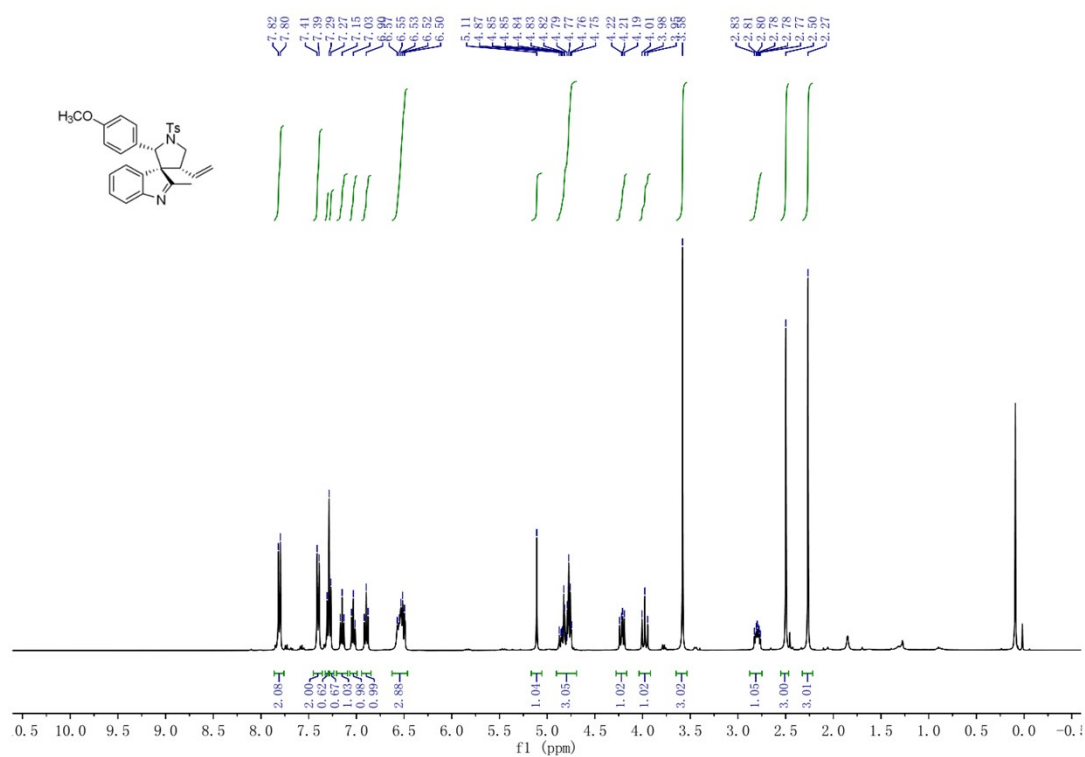




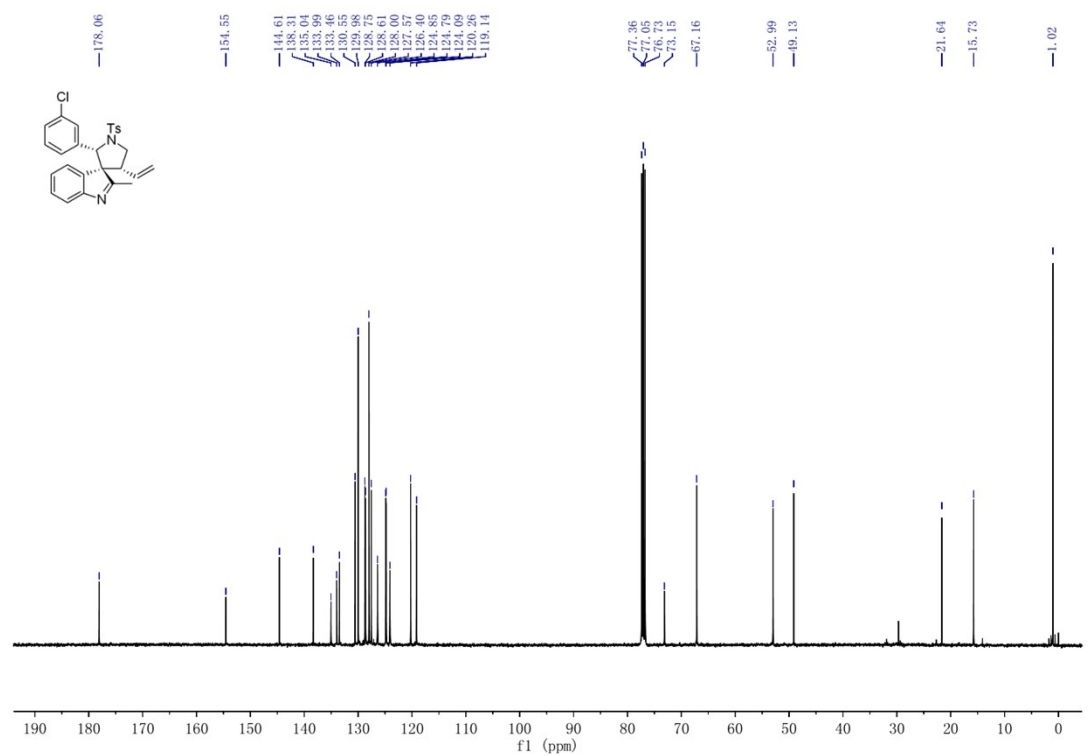
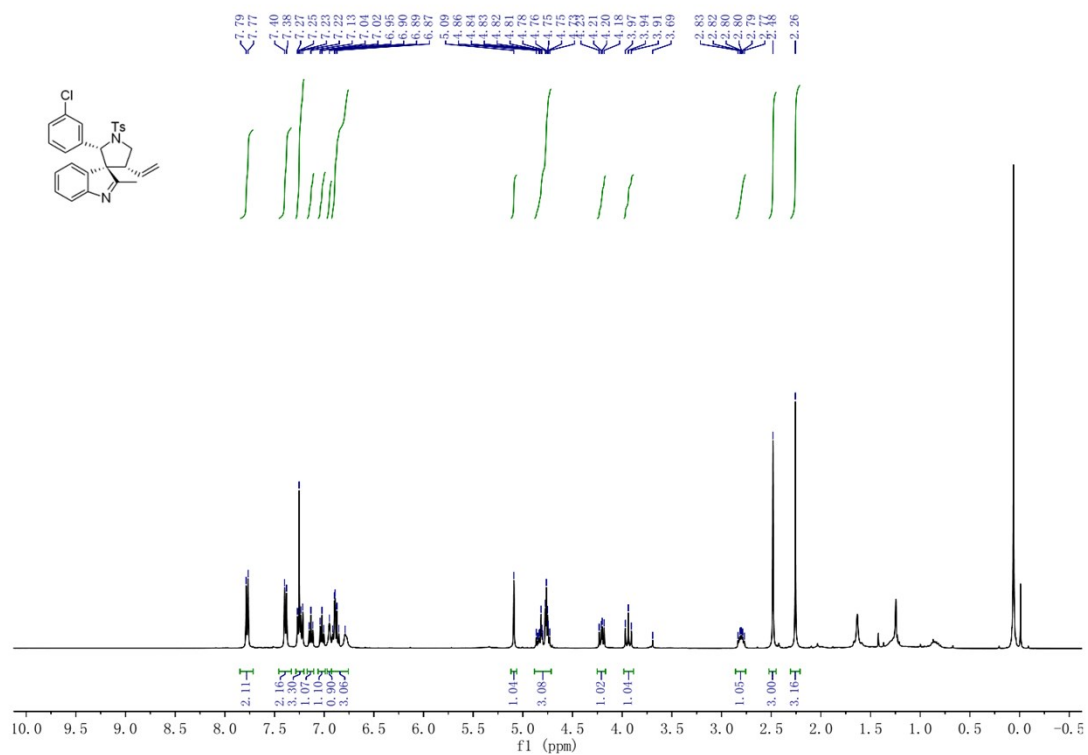
**(2'S,3S,4'R)-2-methyl-2'-(m-tolyl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine]**  
**(3g)**



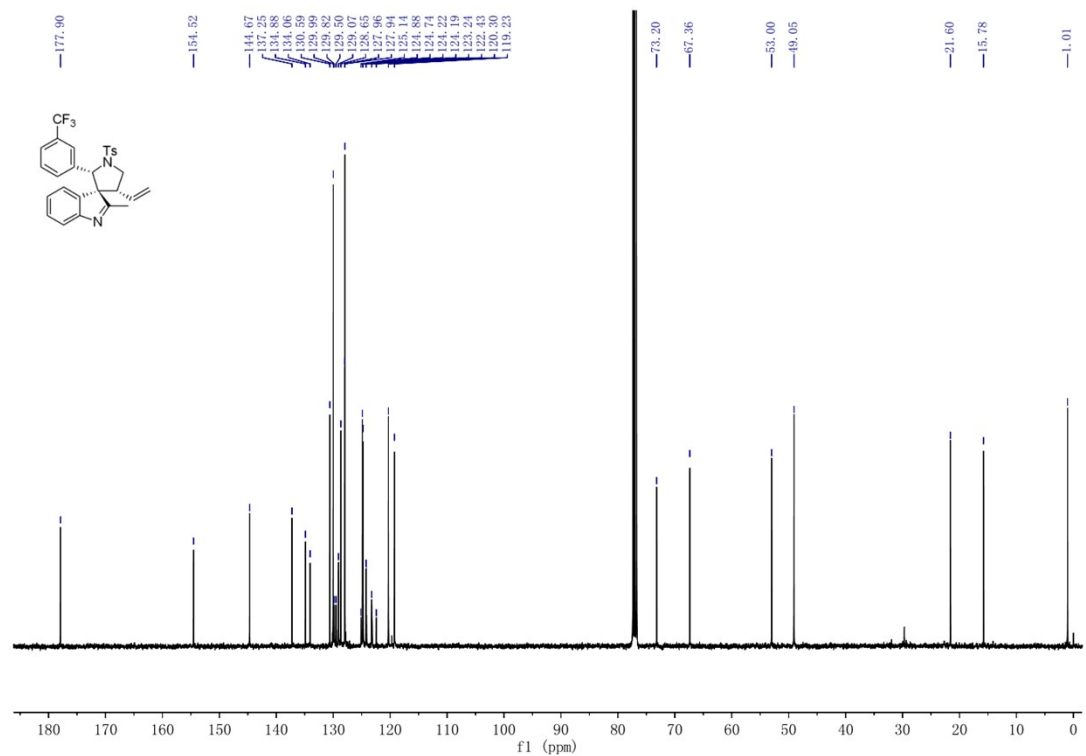
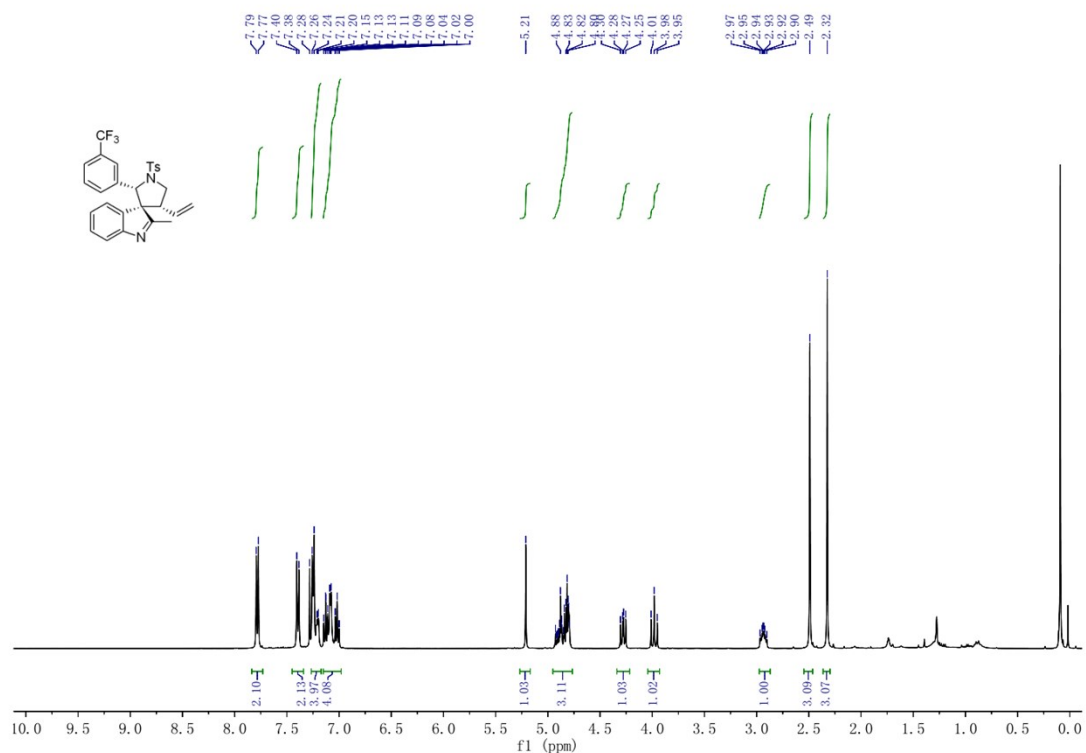
**(2'S,3S,4'R)-2'-(3-methoxyphenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3h)**



**(2'S,3S,4'R)-2'-(3-chlorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3i)**

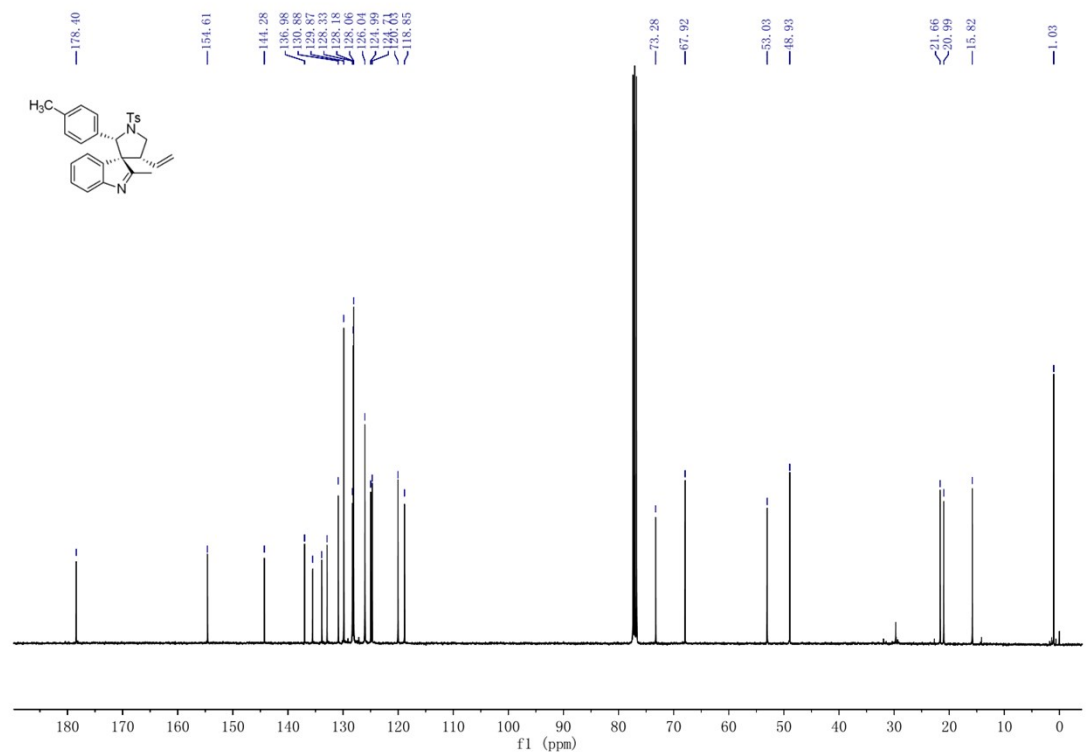
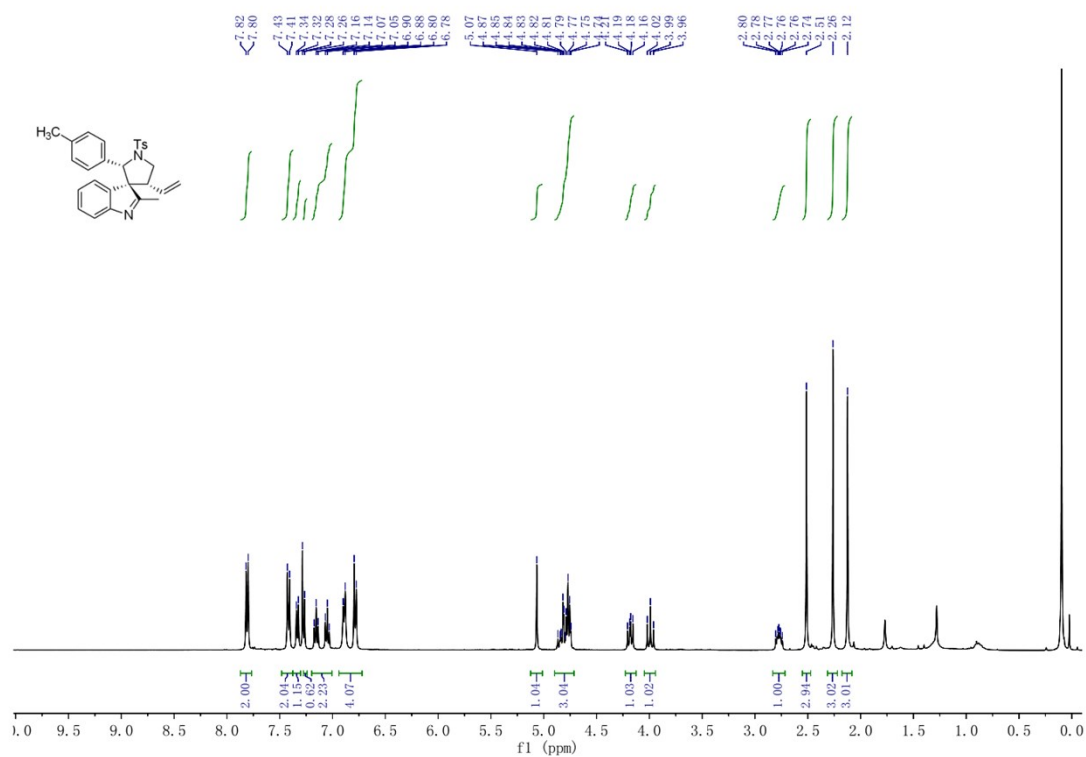


**(2'S,3S,4'R)-2-methyl-1'-tosyl-2'-(3-(trifluoromethyl)phenyl)-4'-vinylspiro[indole-3,3'-pyrrolidine] (3j)**

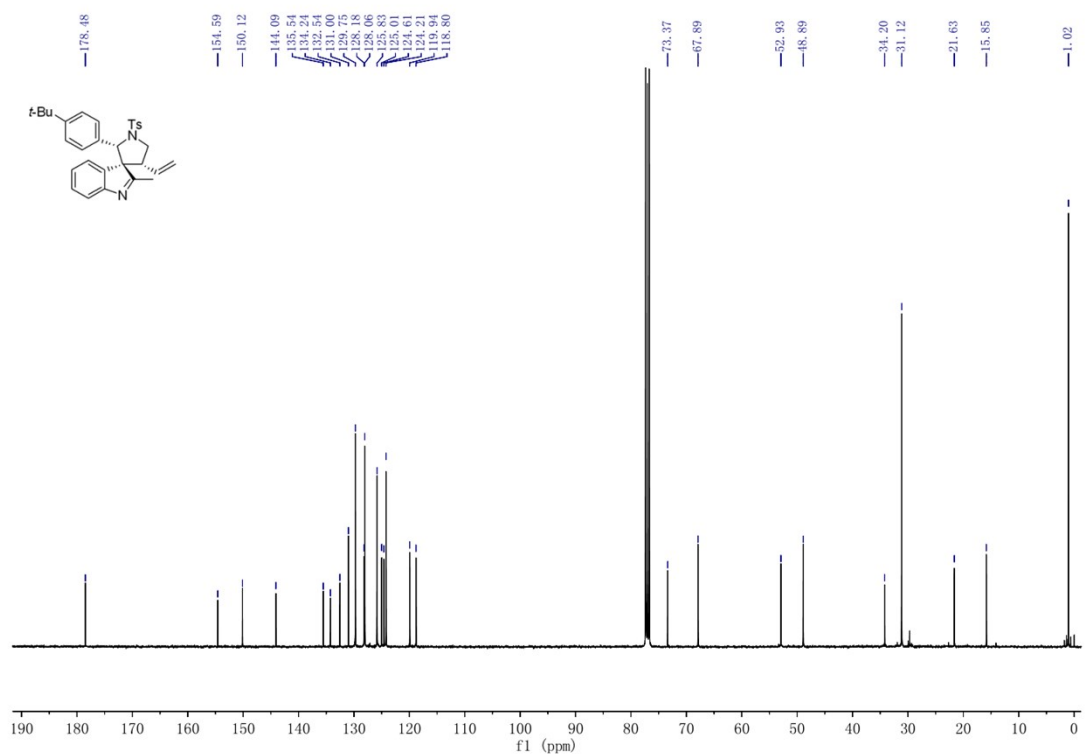
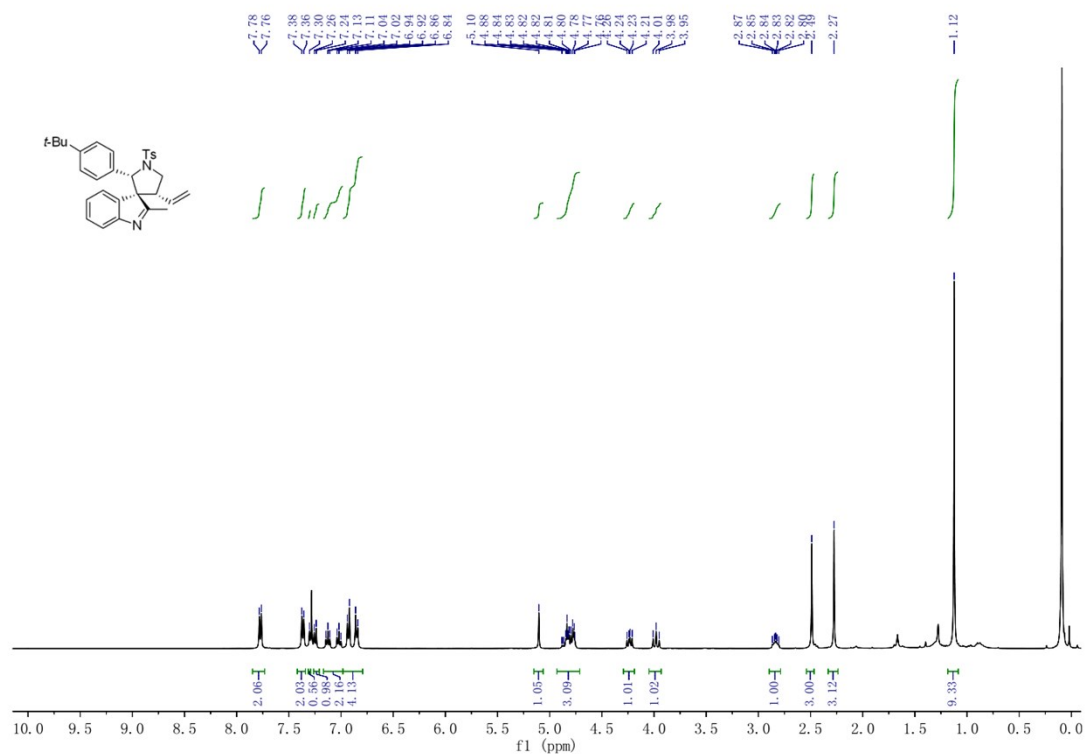


**(2'S,3S,4'R)-2-methyl-2'-(p-tolyl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine]**

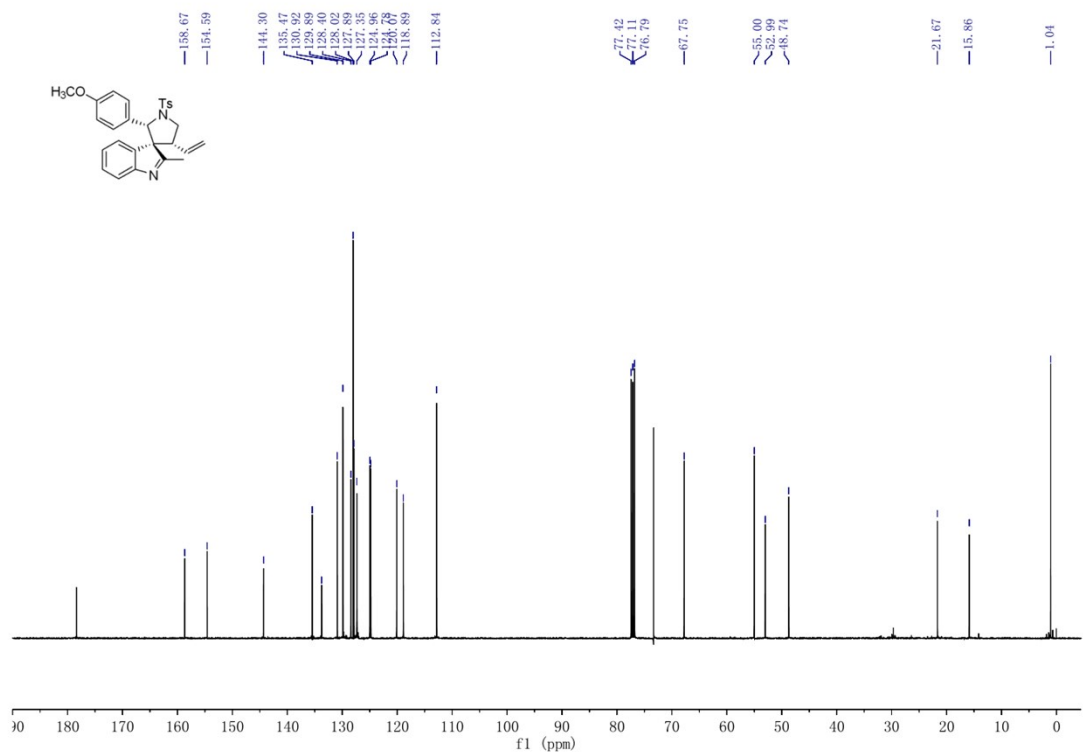
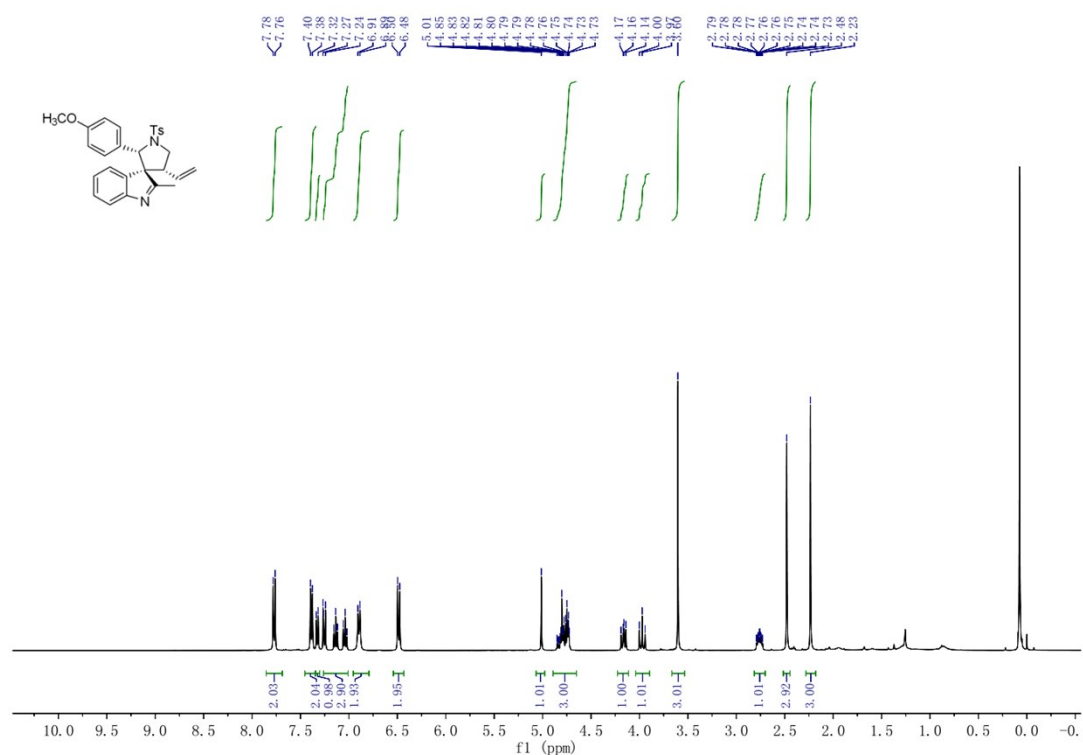
**(3k)**



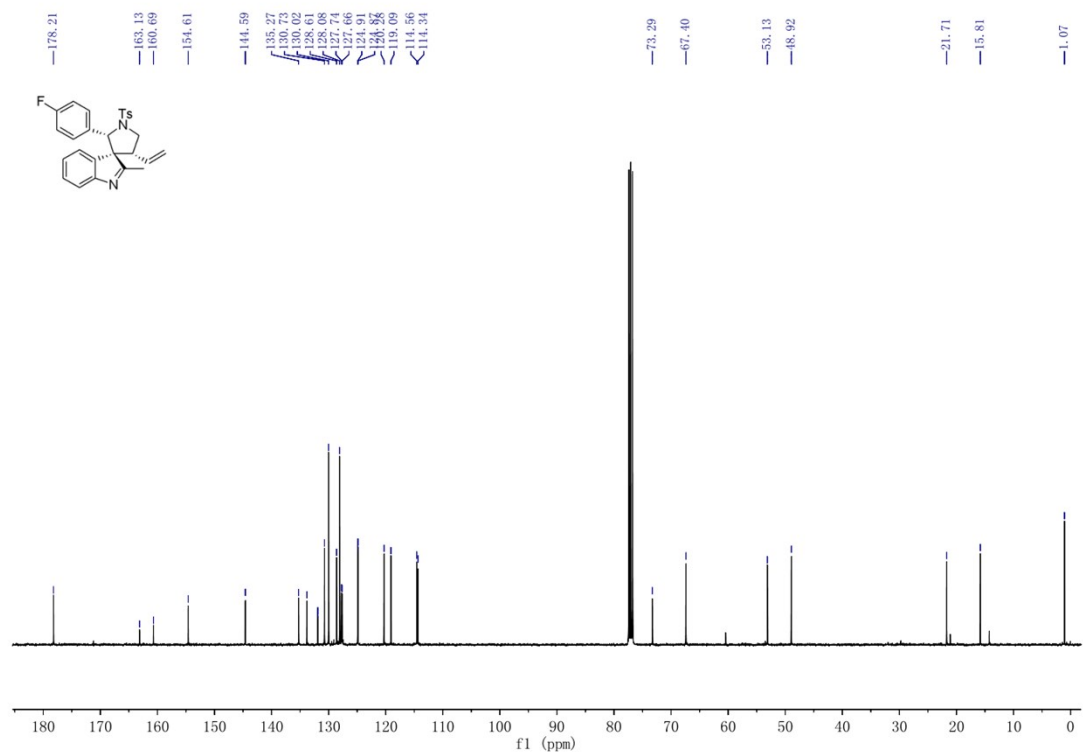
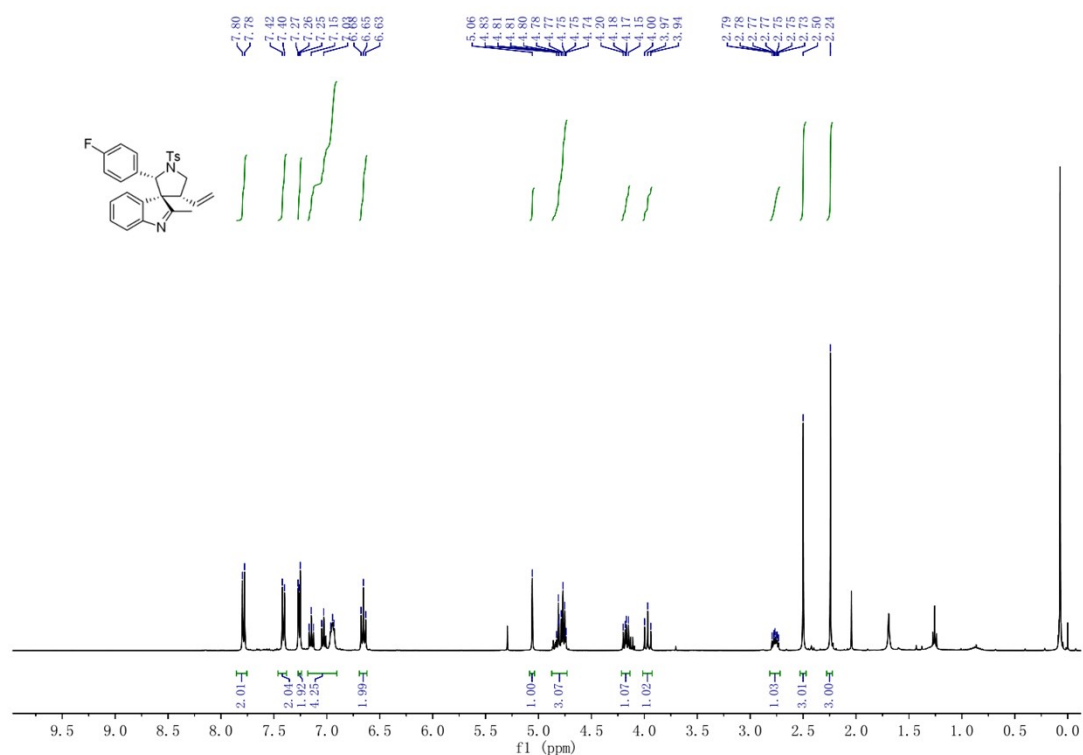
**(2'S,3S,4'R)-2'-(4-(tert-butyl)phenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3l)**



**(2'S,3S,4'R)-2'-(4-methoxyphenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3m)**

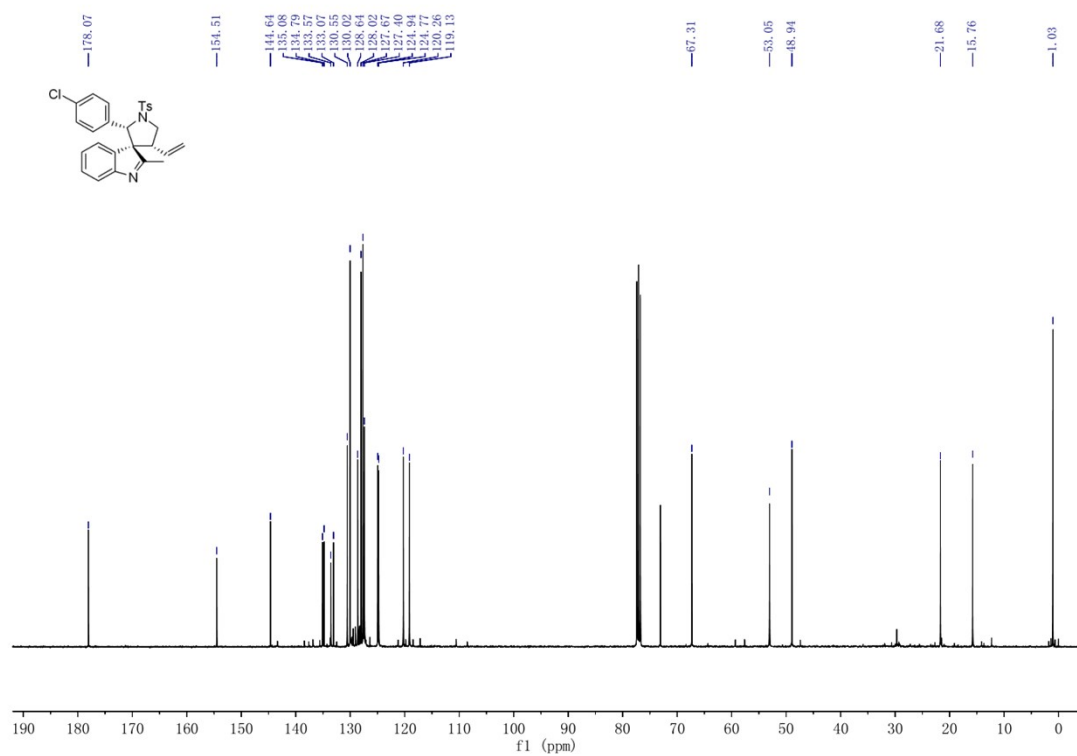
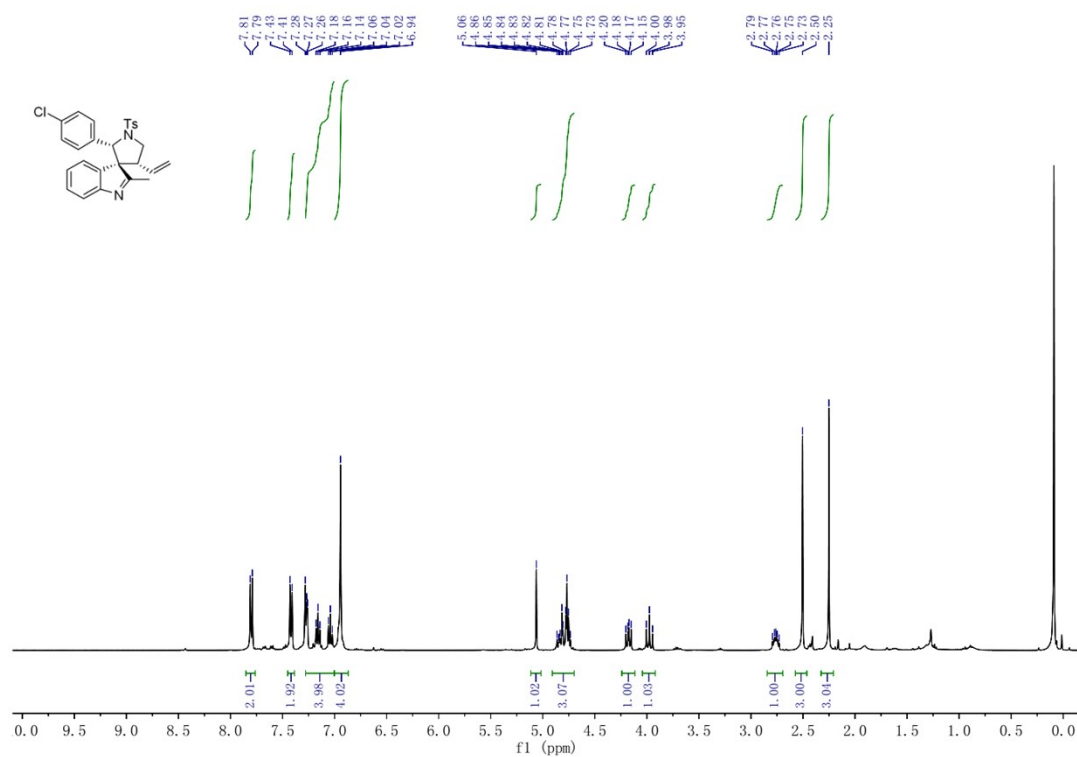


**(2'S,3S,4'R)-2'-(4-fluorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3n)**

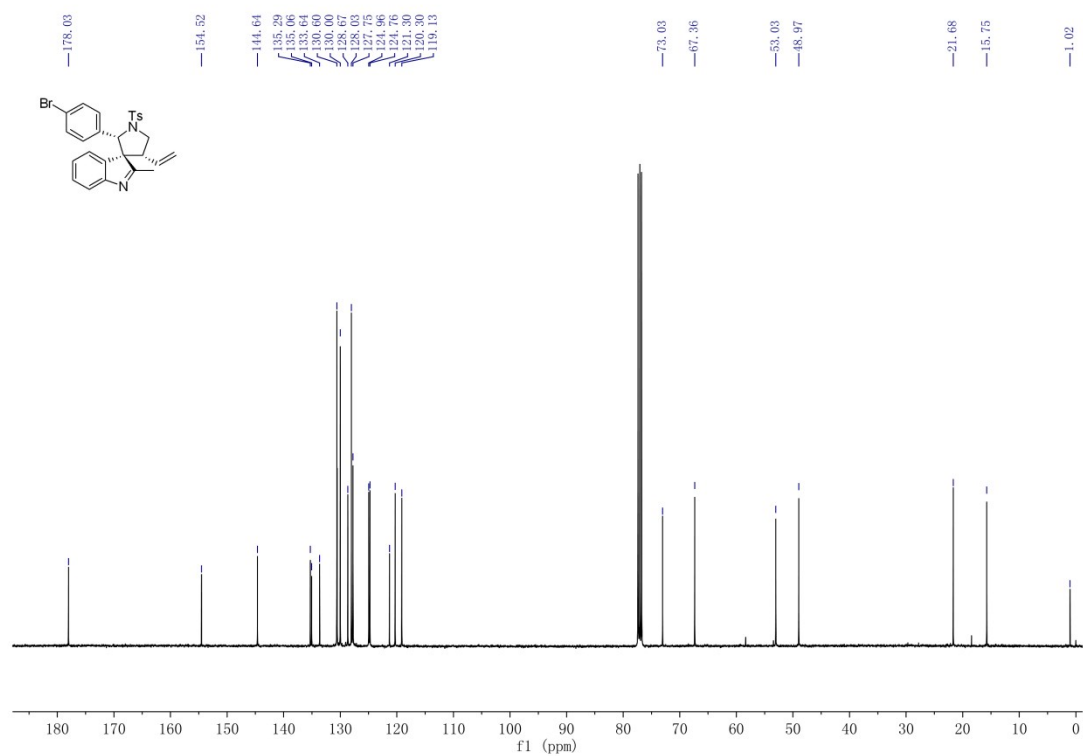
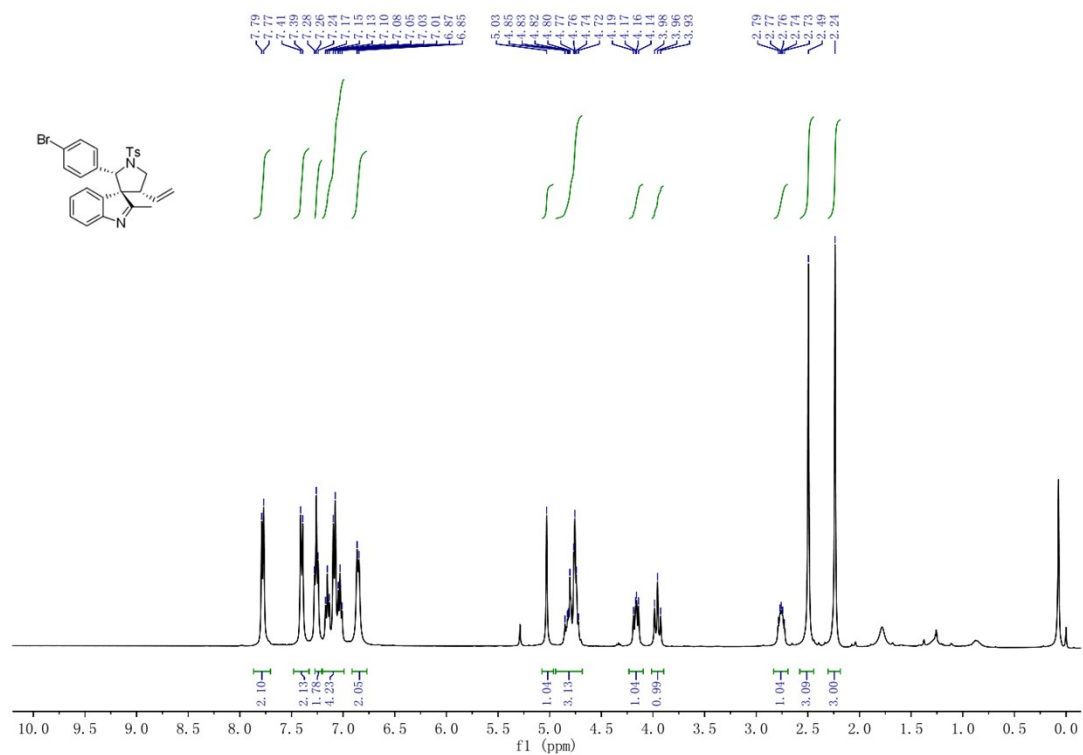




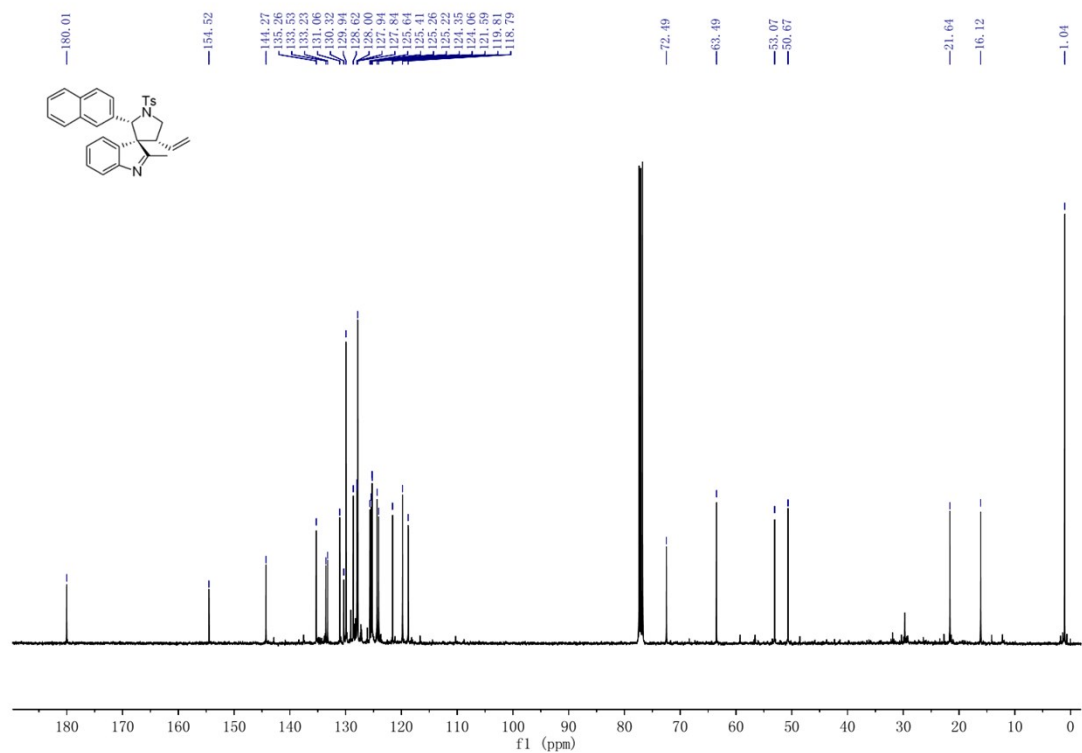
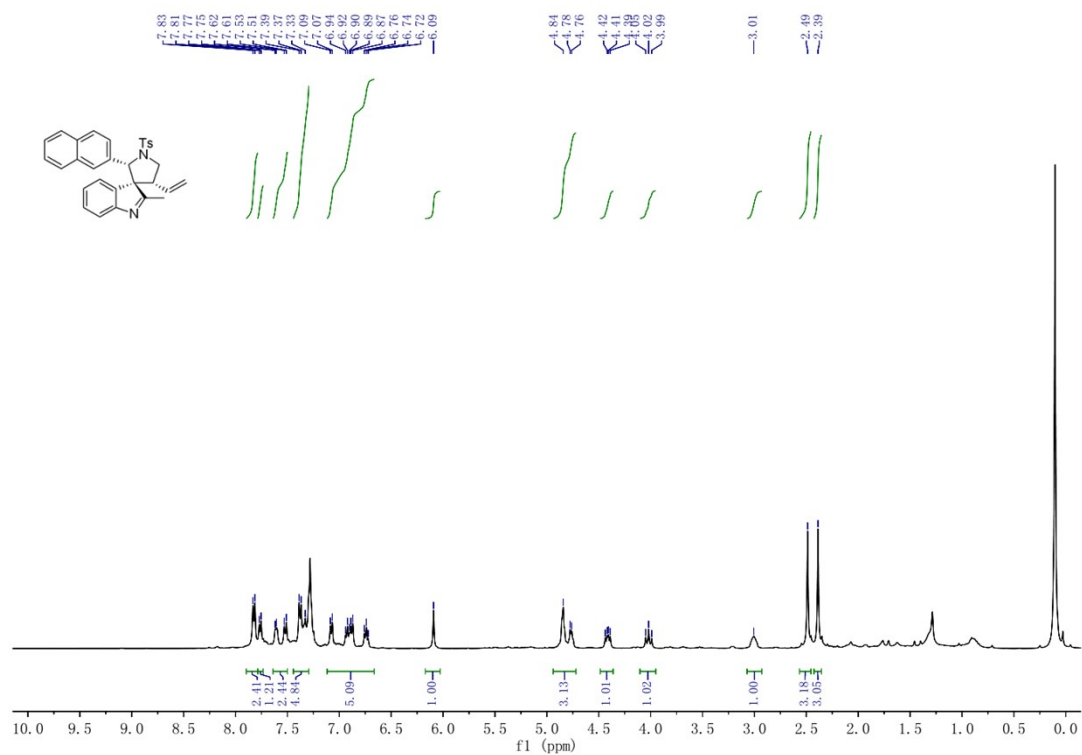
**(2'S,3S,4'R)-2'-(4-chlorophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3o)**



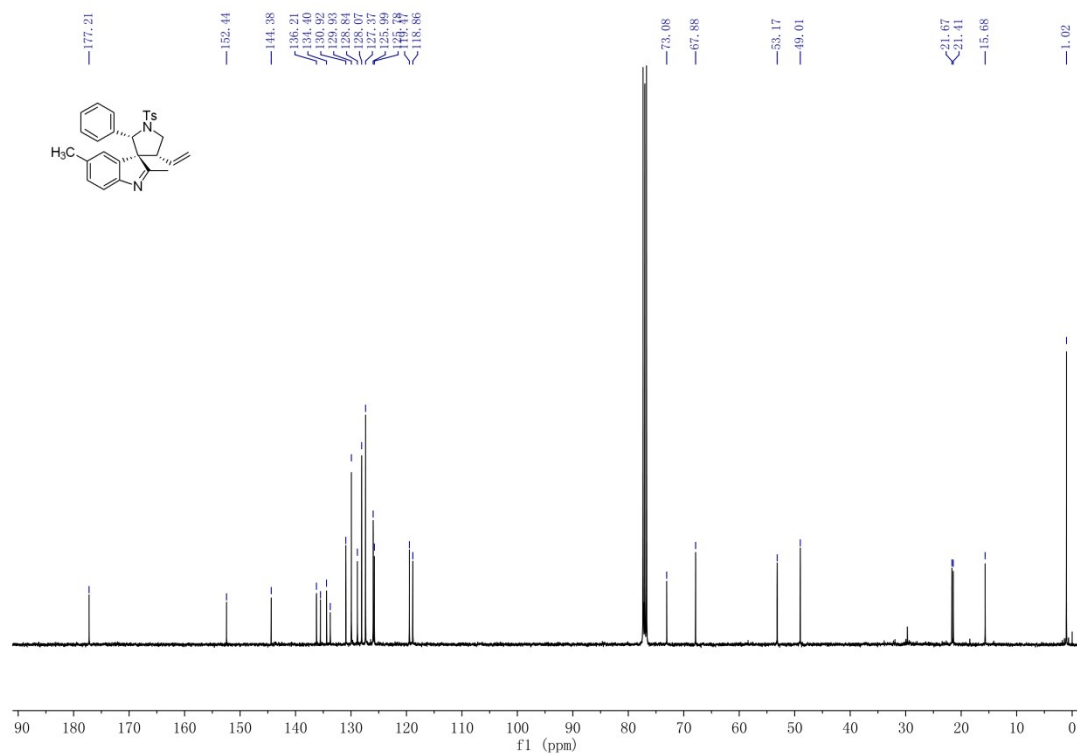
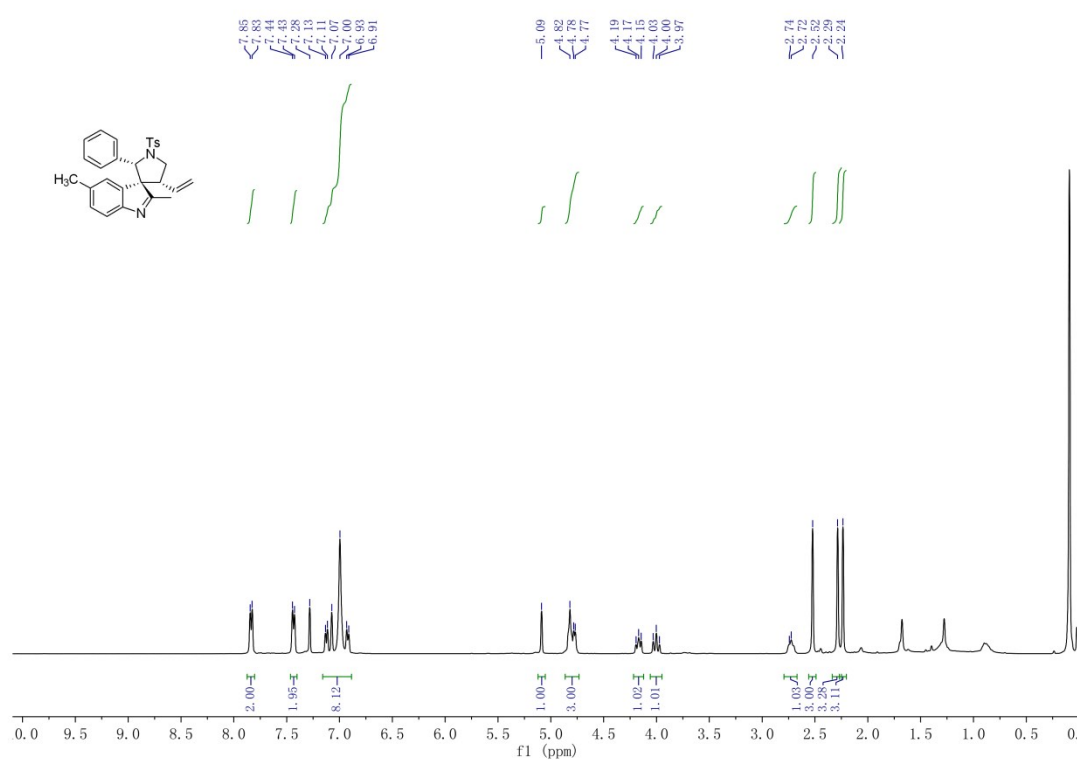
**(2'S,3S,4'R)-2'-(4-bromophenyl)-2-methyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3p)**



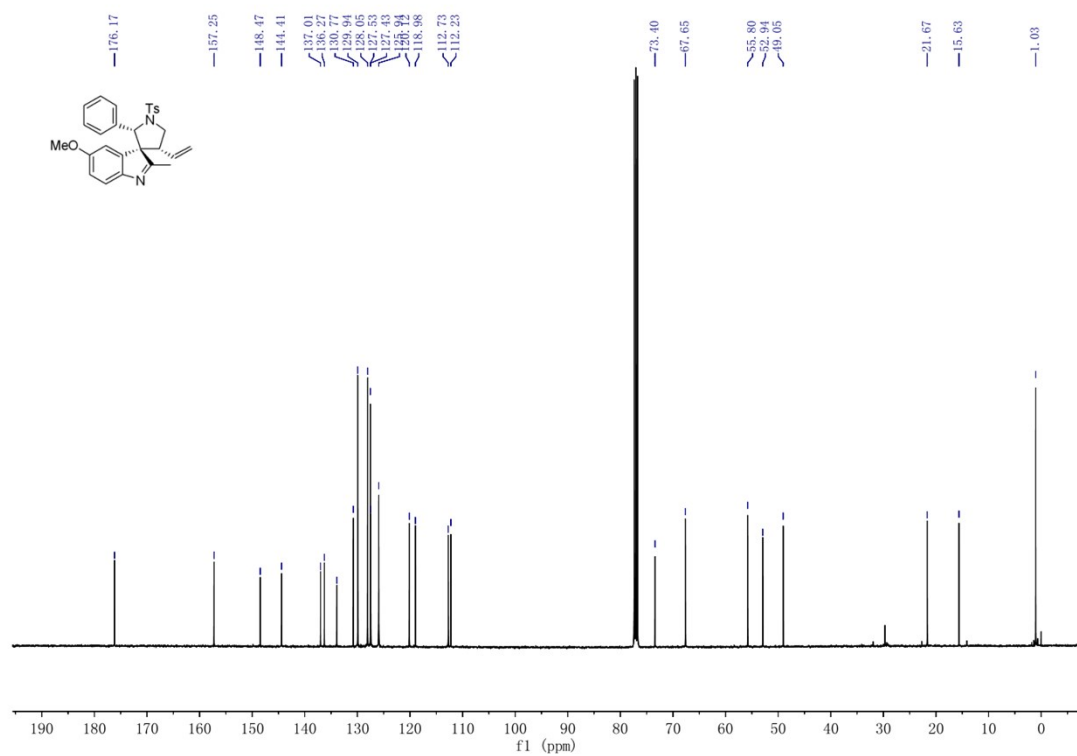
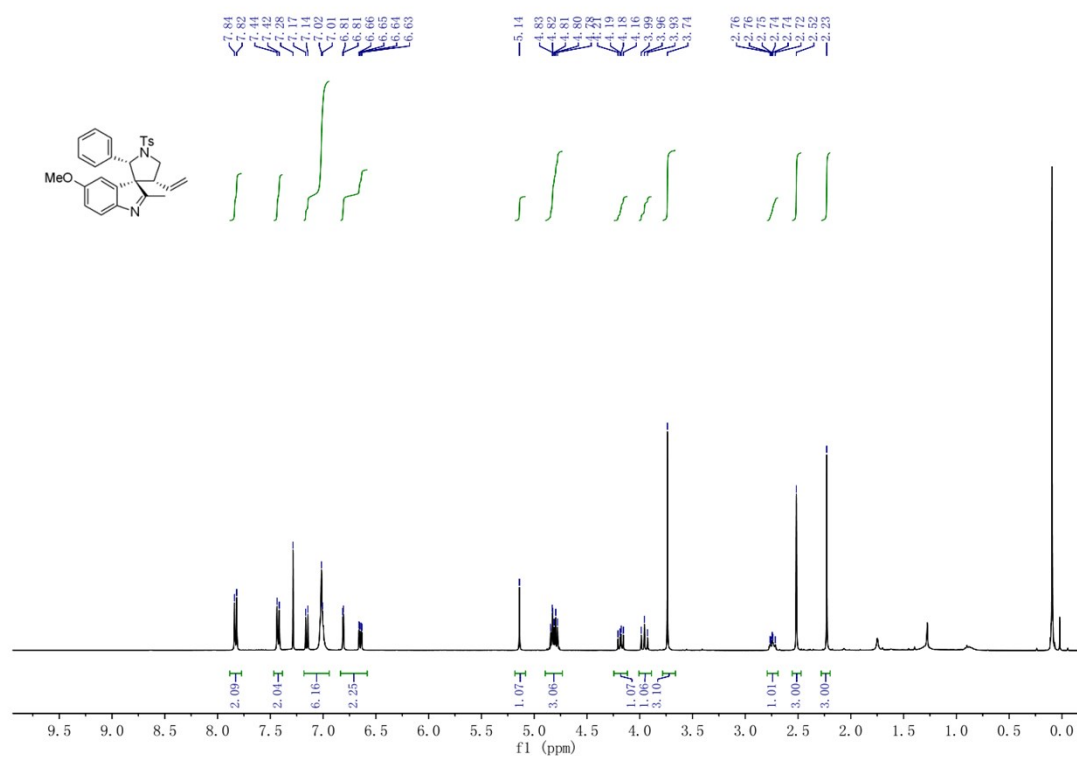
**(2'S,3S,4'R)-2-methyl-2'-(naphthalen-2-yl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3q)**



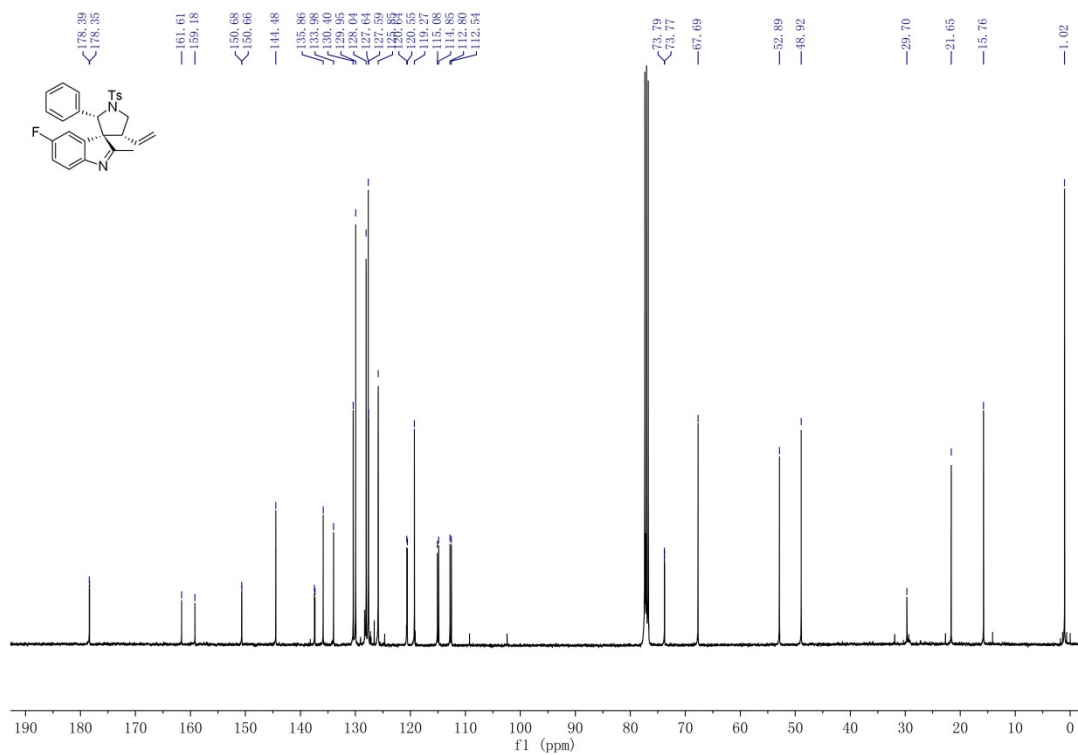
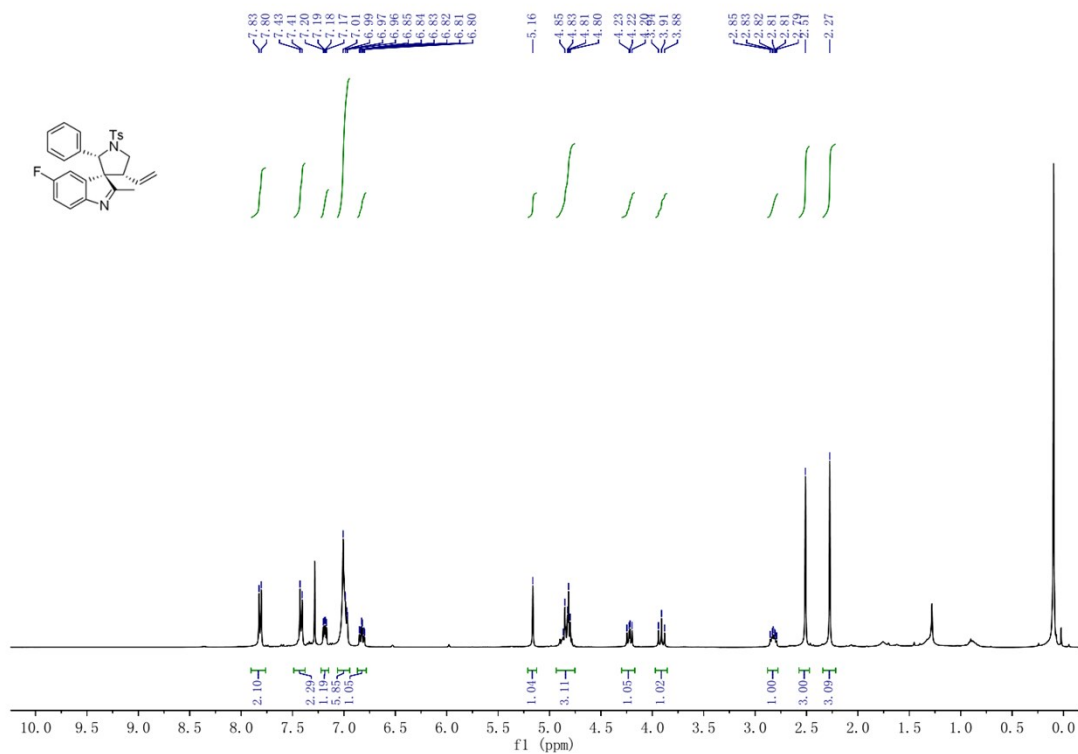
**(2'S,3S,4'R)-2,5-dimethyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine]**  
**(3r)**



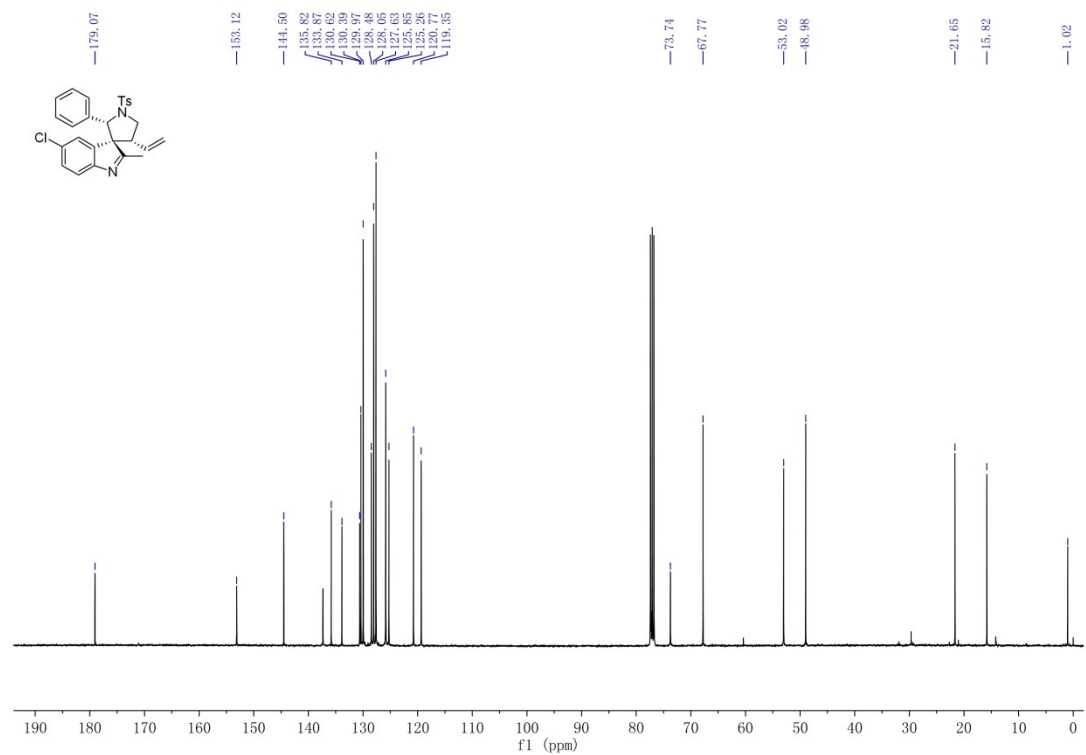
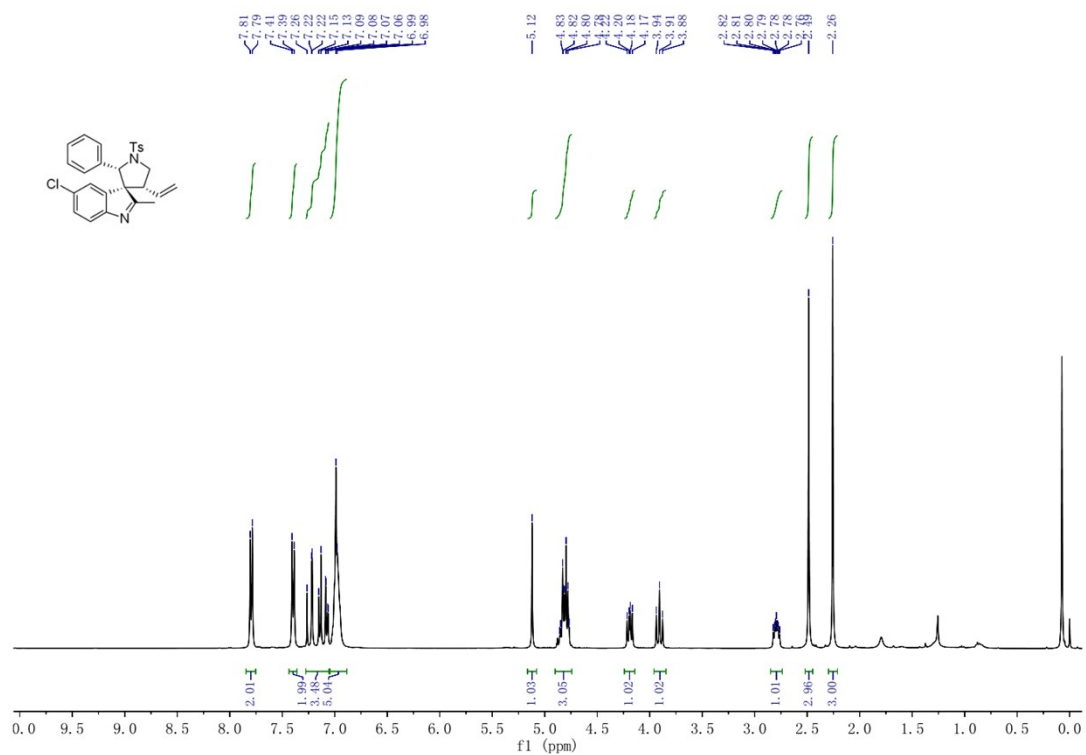
**(2'S,3S,4'R)-5-methoxy-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3s)**



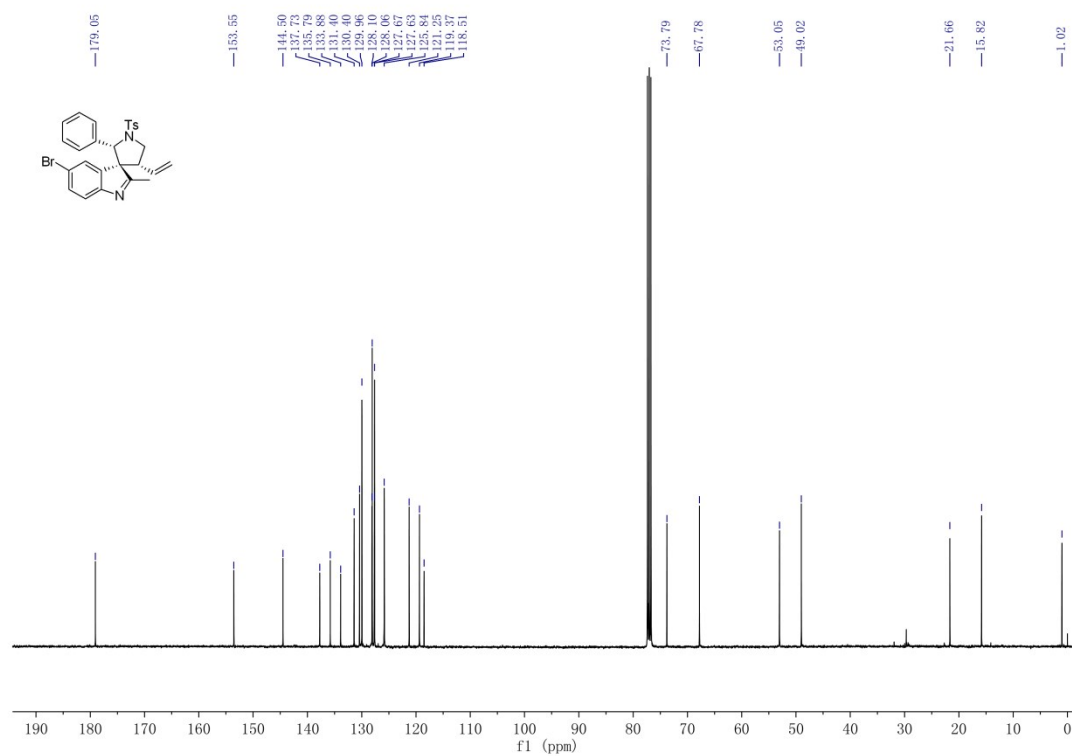
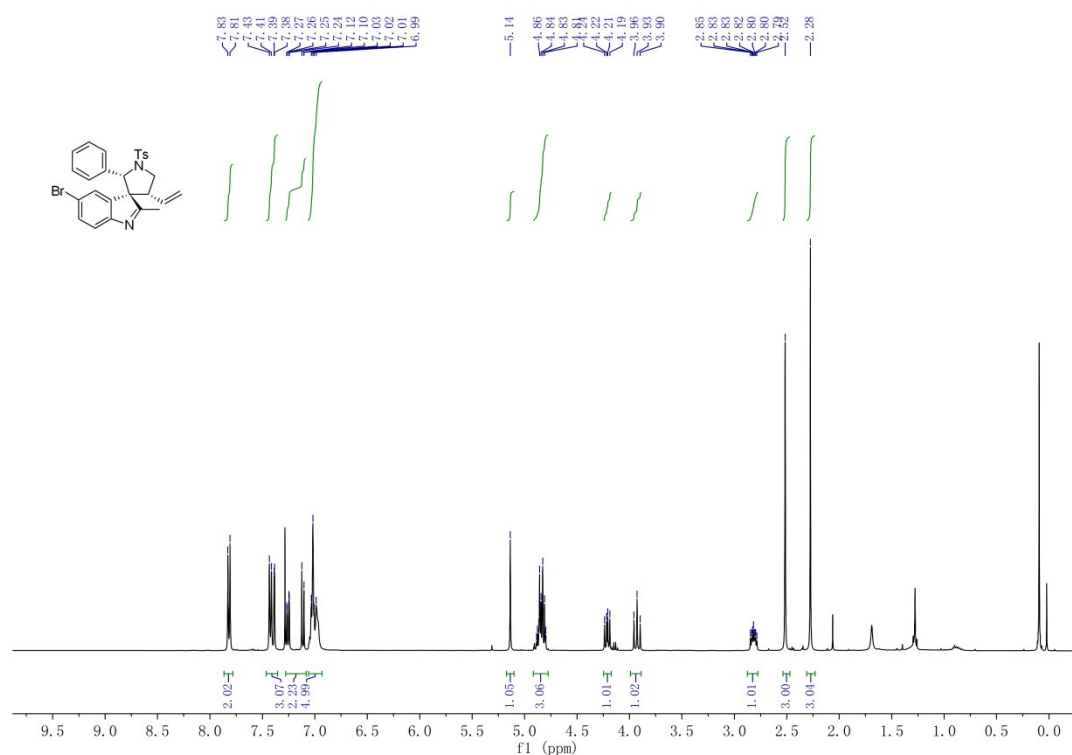
**(2'S,3S,4'R)-5-fluoro-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3t)**



**(2'S,3S,4'R)-5-chloro-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3u)**

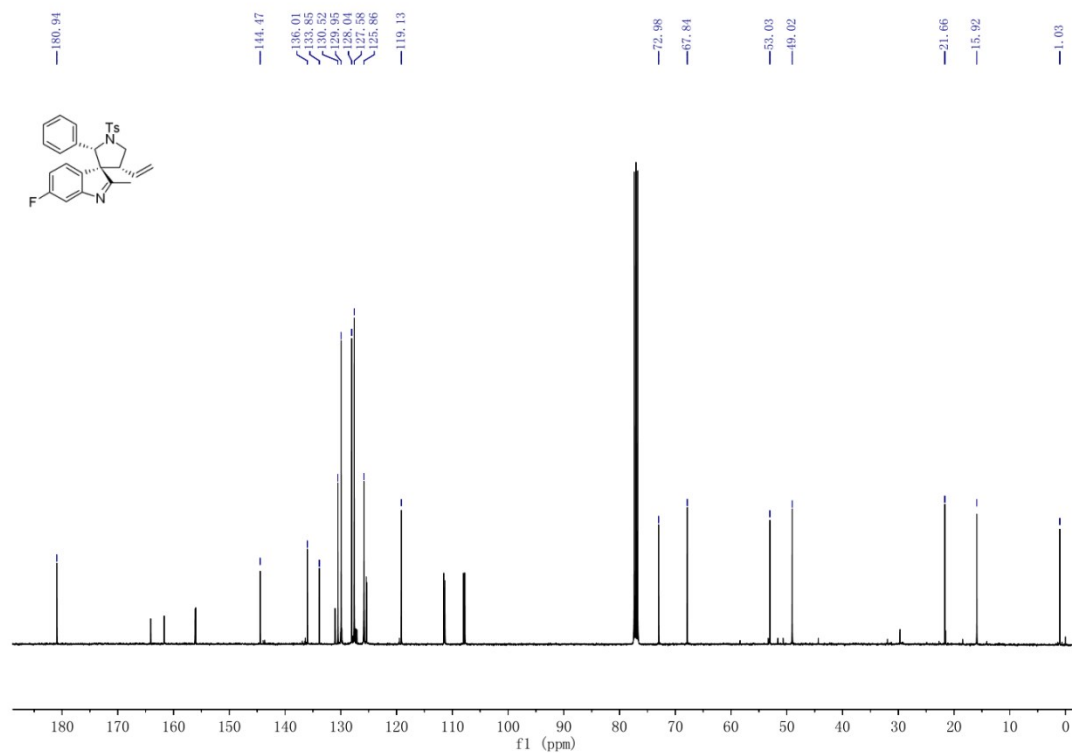
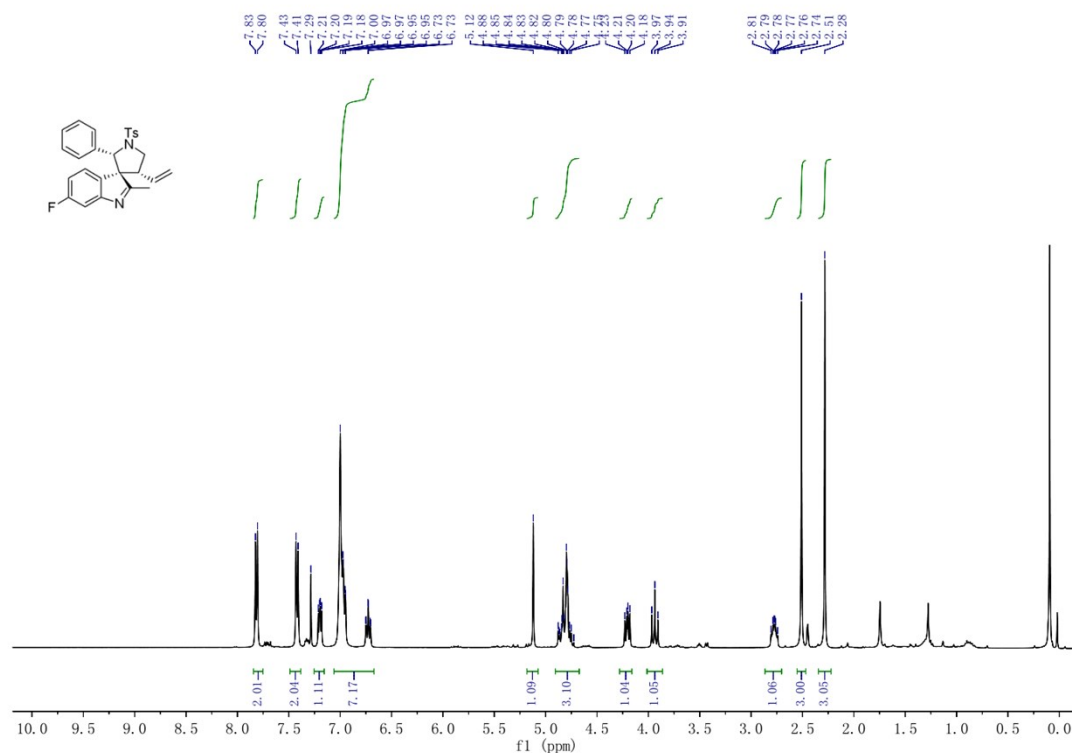


**(2'S,3S,4'R)-5-bromo-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3v)**

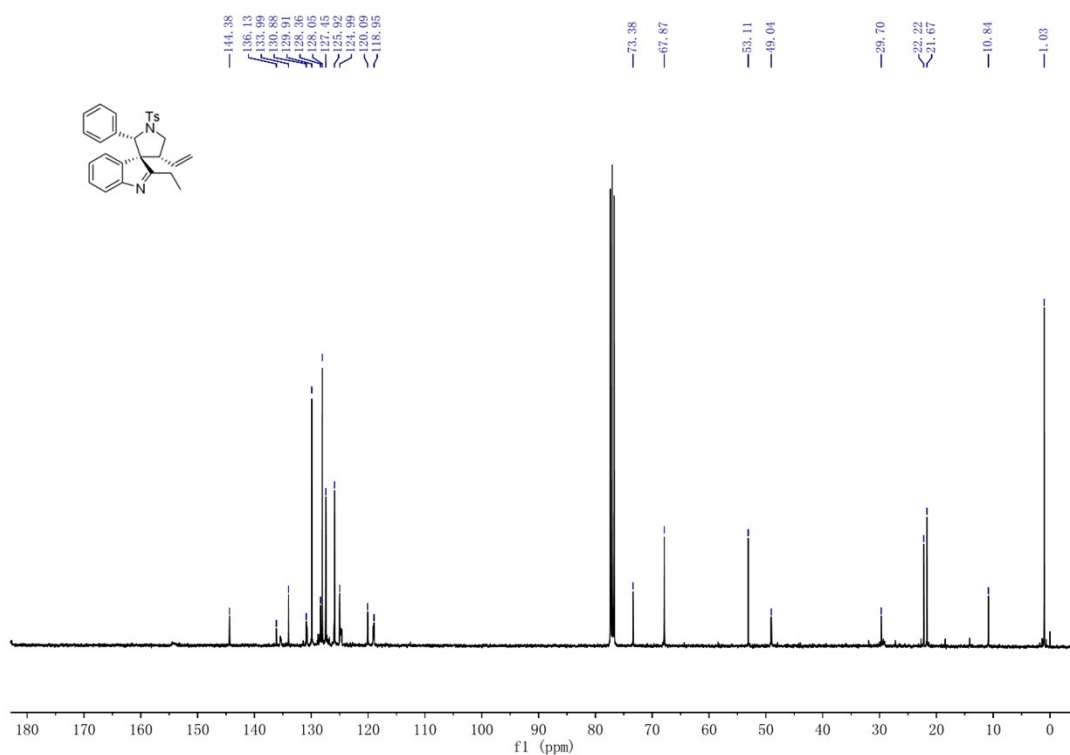
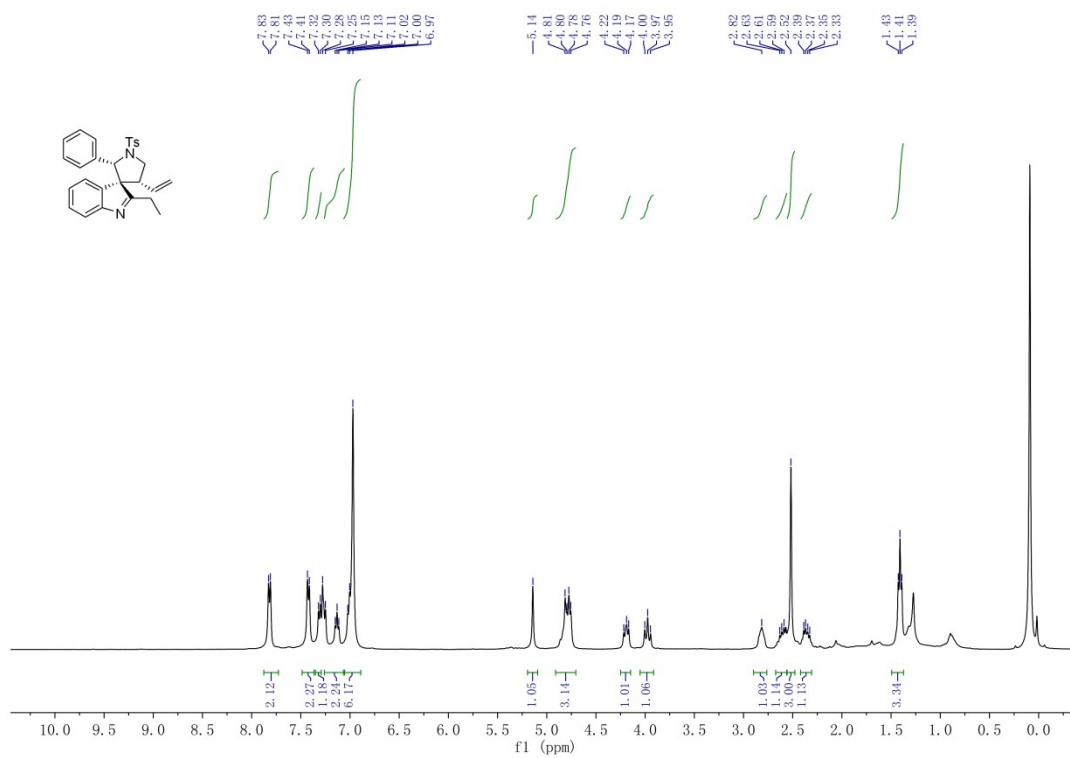




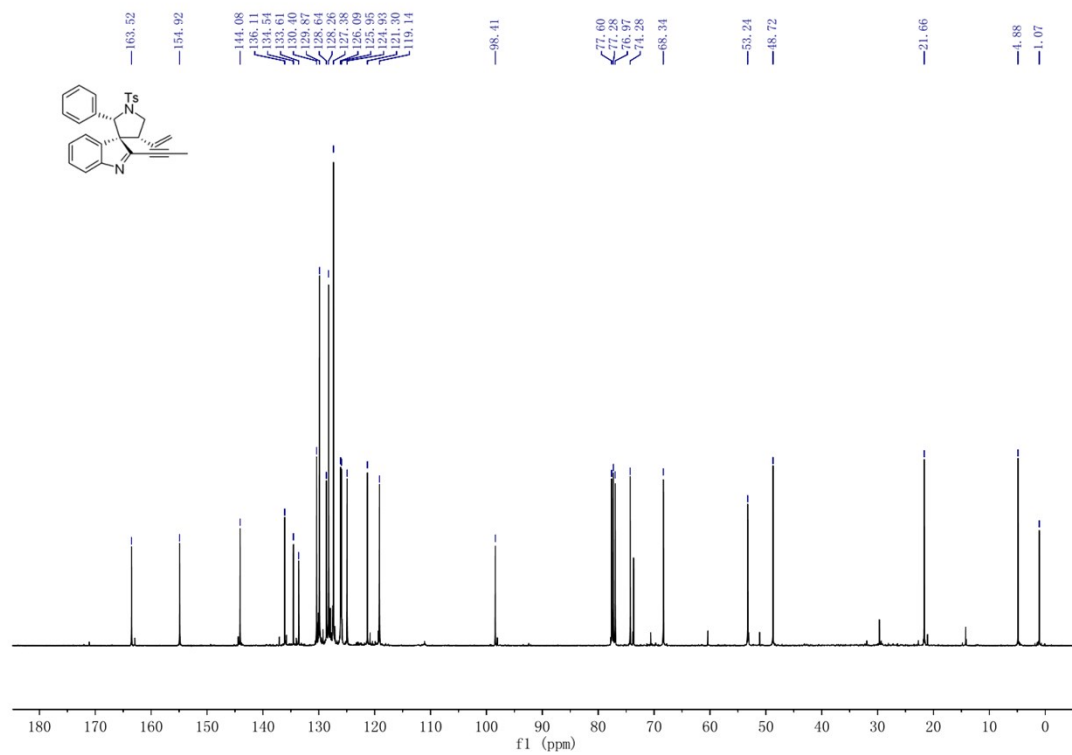
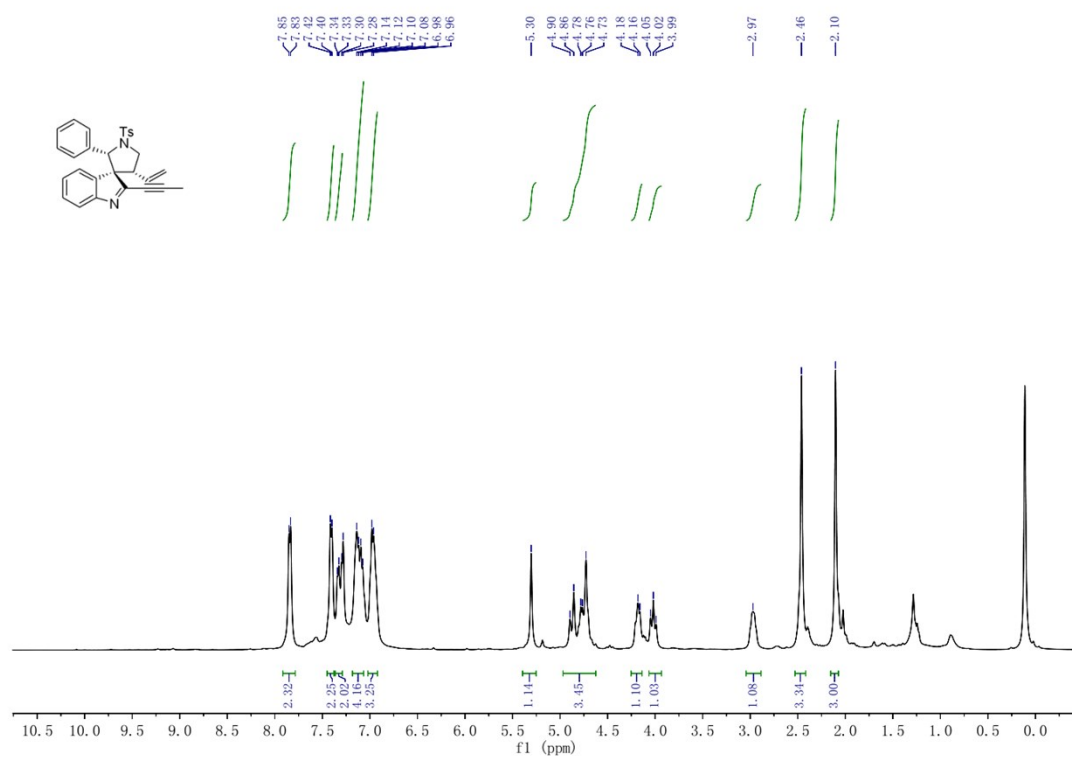
**(2'S,3S,4'R)-6-fluoro-2-methyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3w)**



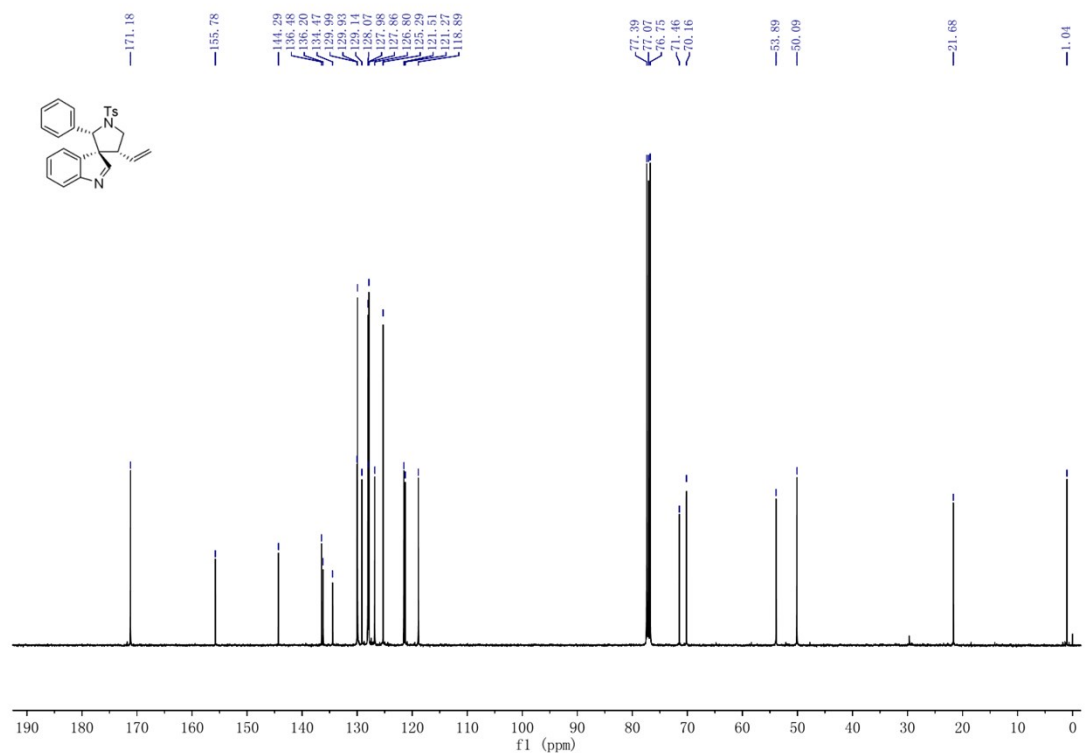
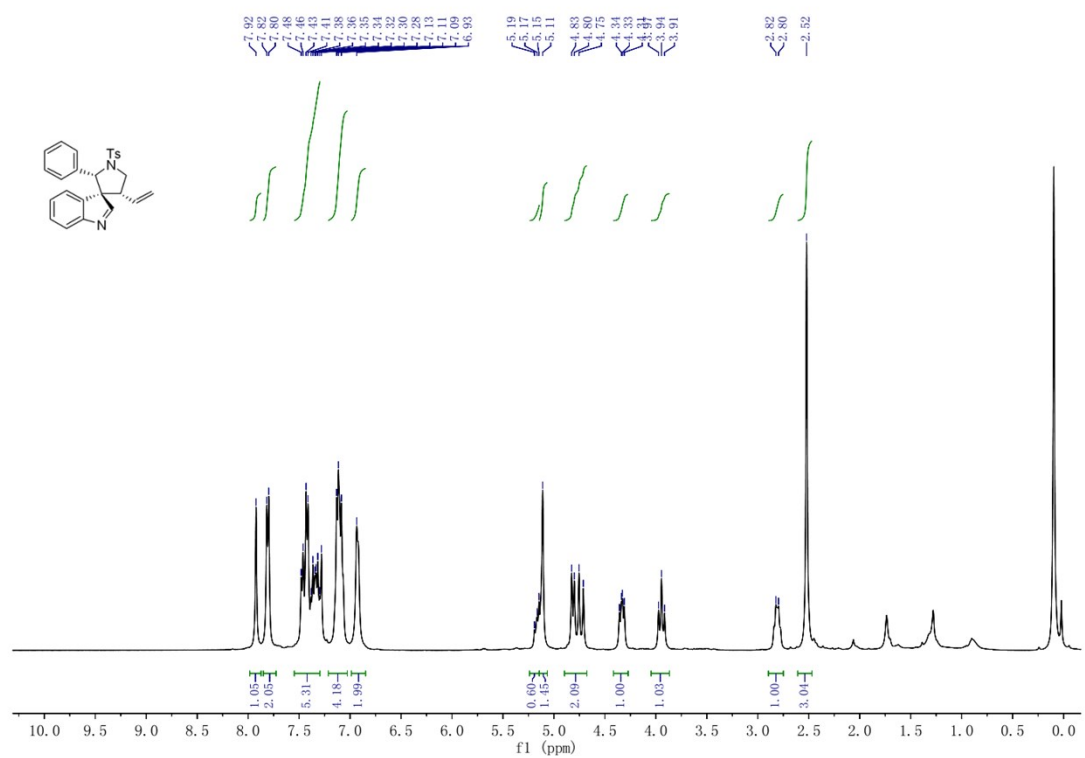
**(2'S,3S,4'R)-2-ethyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3x)**



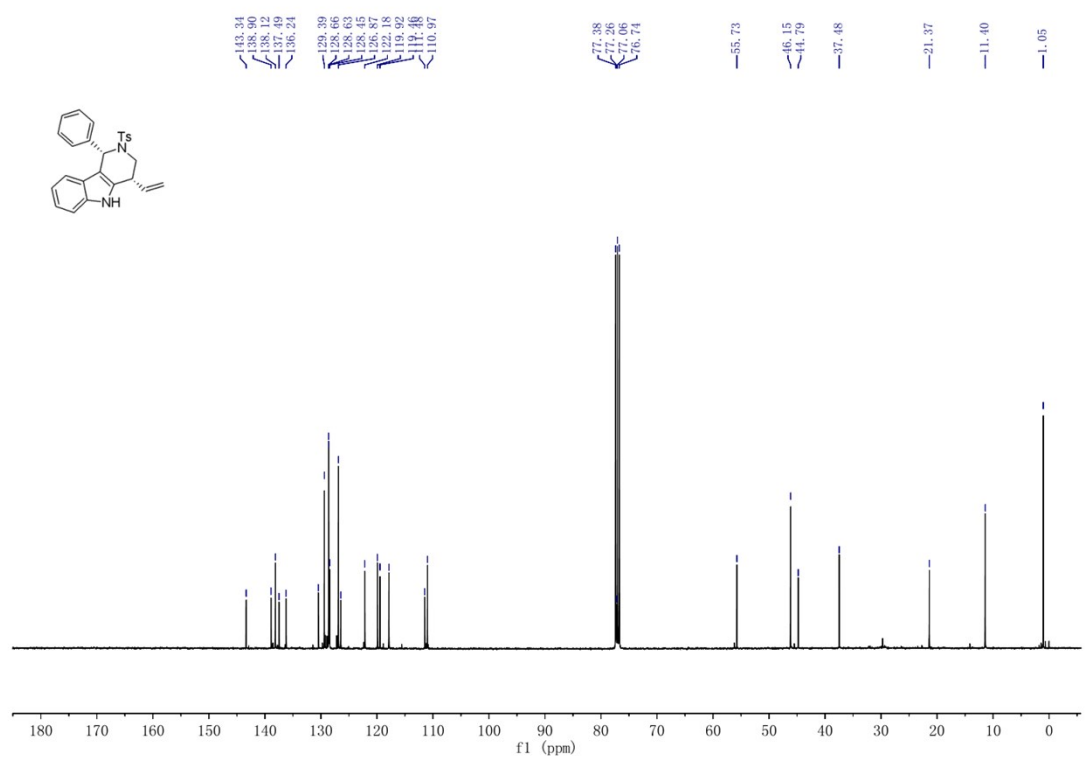
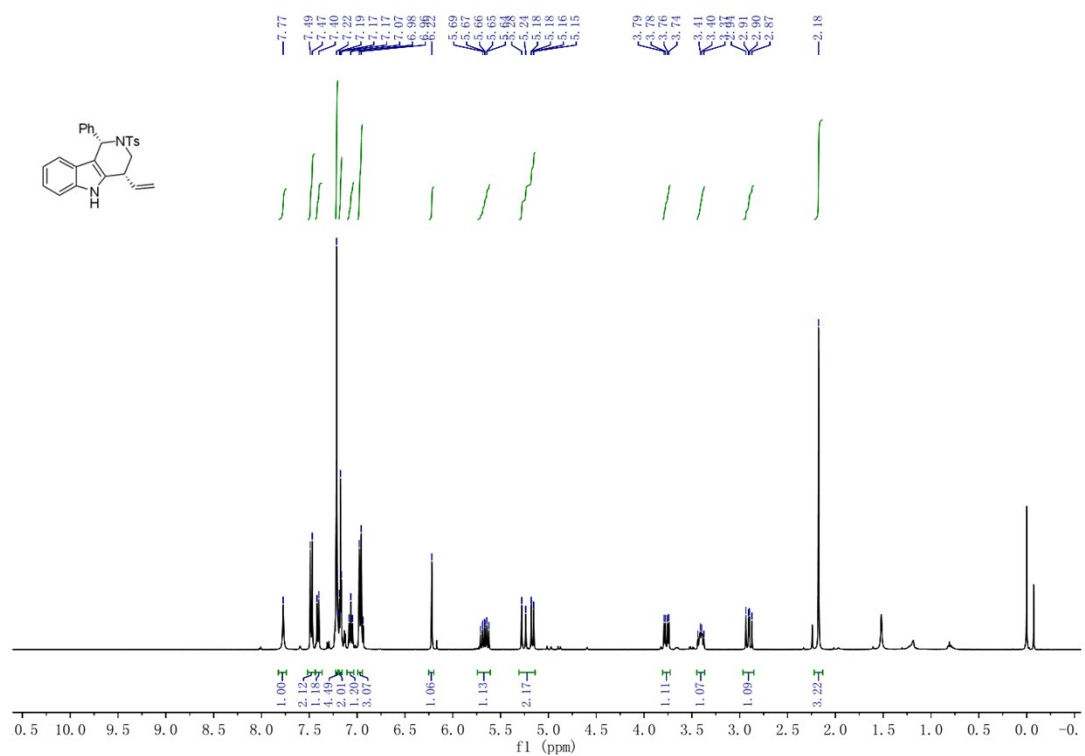
**(2'S,3S,4'R)-2'-phenyl-2-(prop-1-yn-1-yl)-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3y)**



**(2'S,3S,4'R)-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine] (3z)**

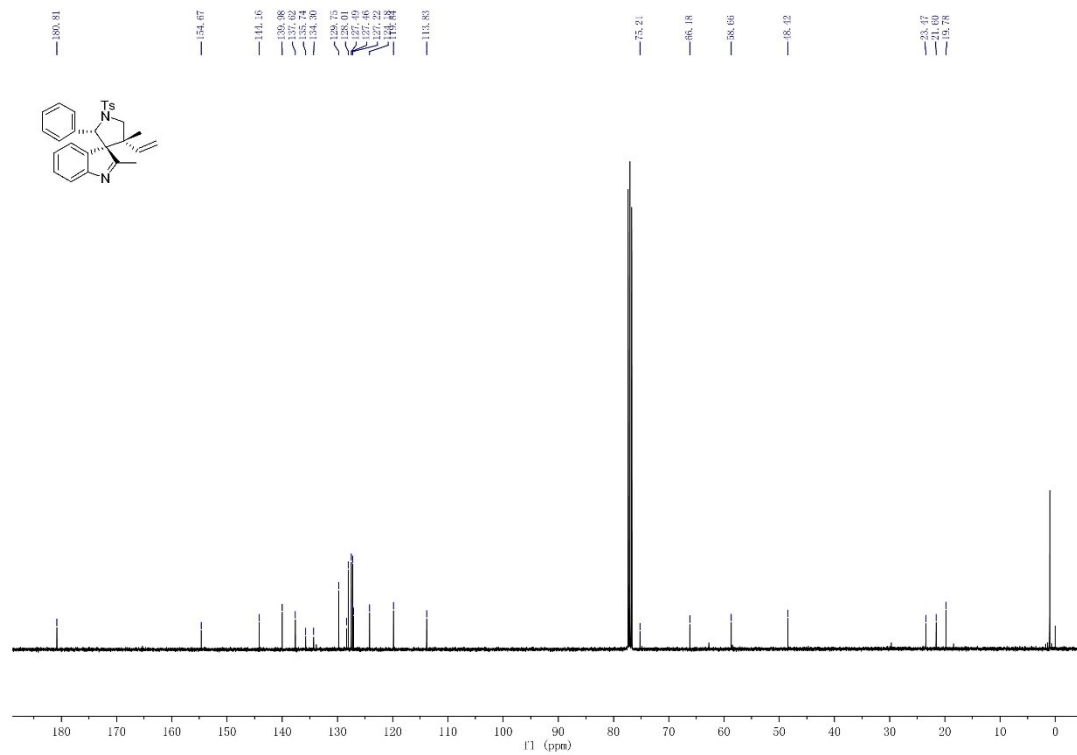
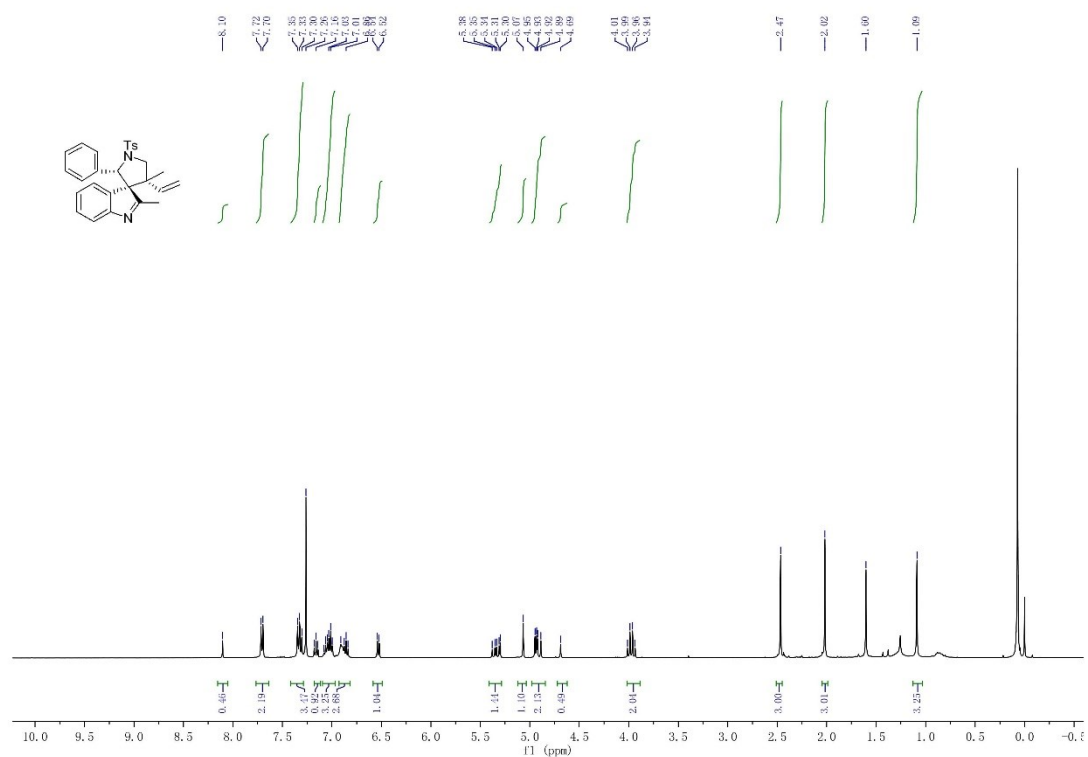


**(1S,4S)-1-phenyl-2-tosyl-4-vinyl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (5z)**





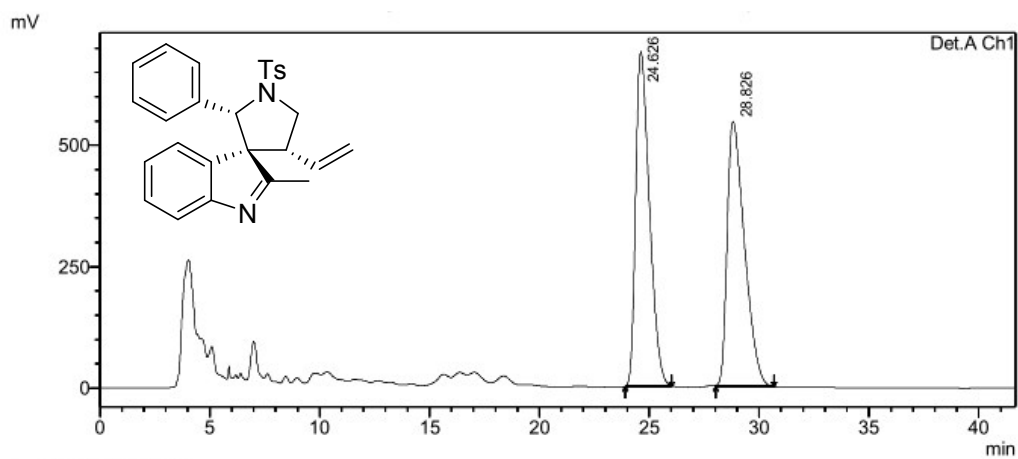
**(2'S,3S,4'R)-2,4'-dimethyl-2'-phenyl-1'-tosyl-4'-vinylspiro[indole-3,3'-pyrrolidine]**  
**(6a)**



## 6.HPLC spectra of the products

### HPLC of 3a

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 254$  nm

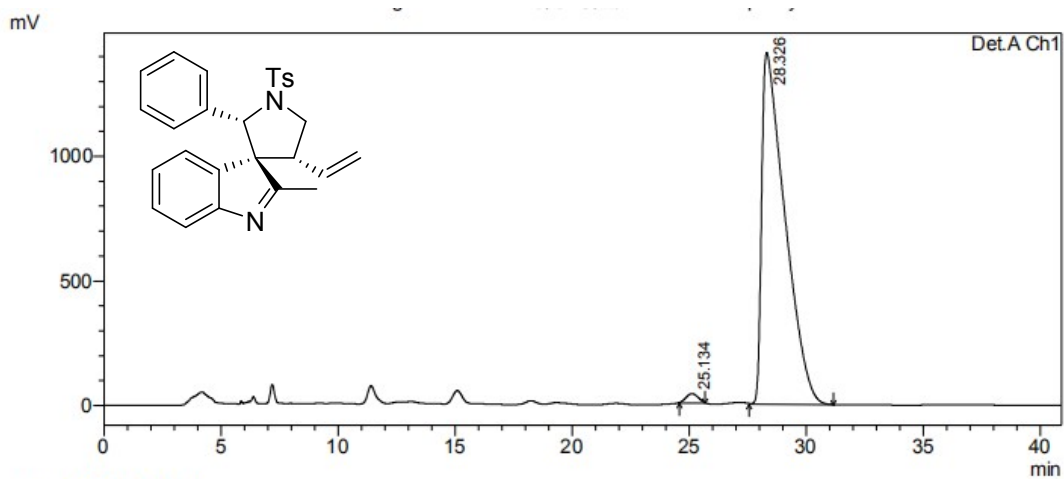


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.626	30114362	690088	50.206
2	28.826	29866777	546317	49.794
Total		59981139	1236405	100.000



1 Det.A Ch1/254nm

PeakTable

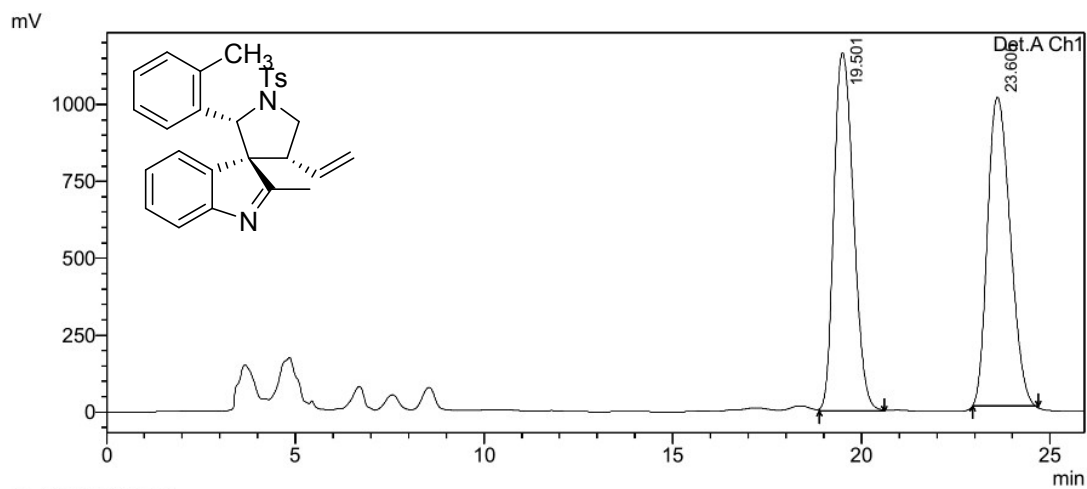
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.134	1421449	38584	1.437
2	28.326	97477769	1411768	98.563
Total		98899218	1450352	100.000



## HPLC of 3b

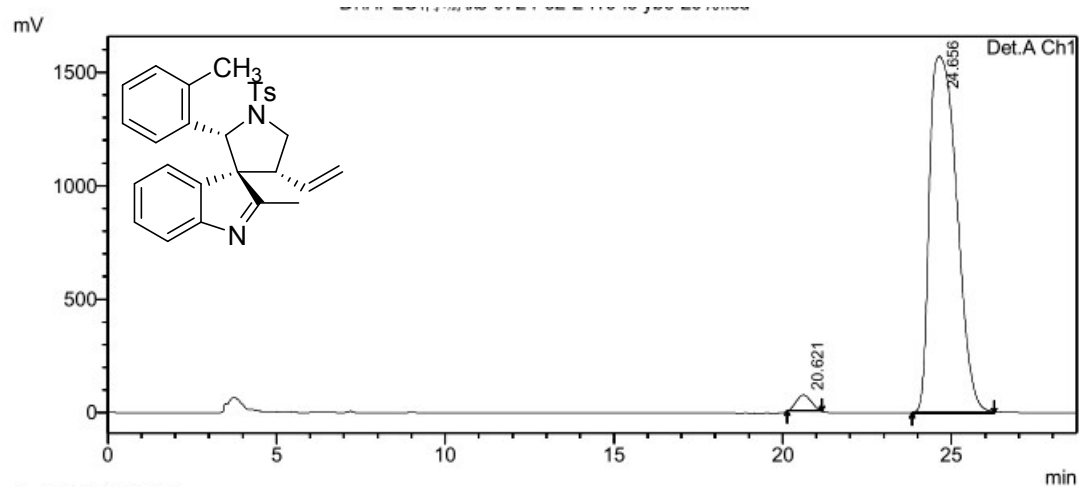
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v= 1.0$  mL/min,  $\lambda=210$  nm



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	19.501	42109086	1164491	50.005
2	23.605	42099972	1004570	49.995
Total		84209057	2169062	100.000



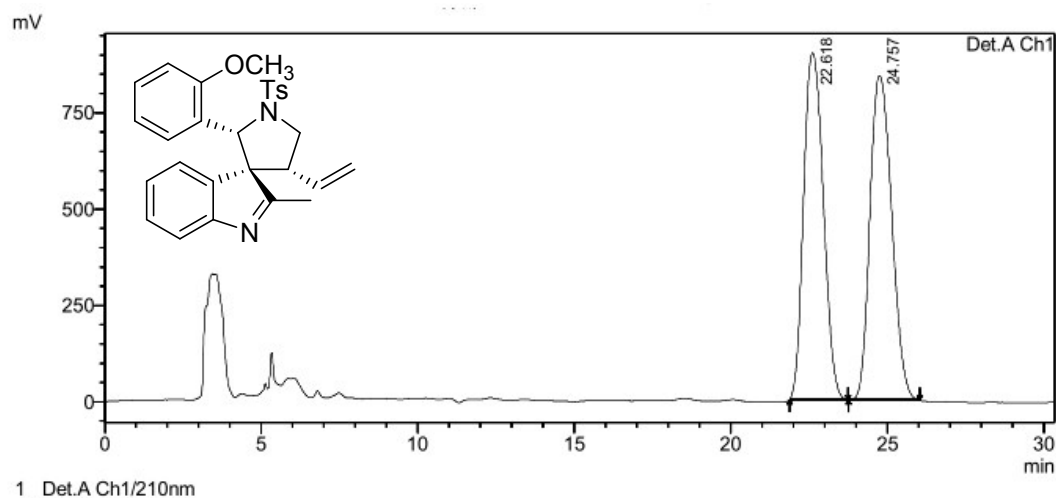
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	20.621	2101997	69713	2.319
2	24.656	88521663	1569456	97.681
Total		90623659	1639169	100.000

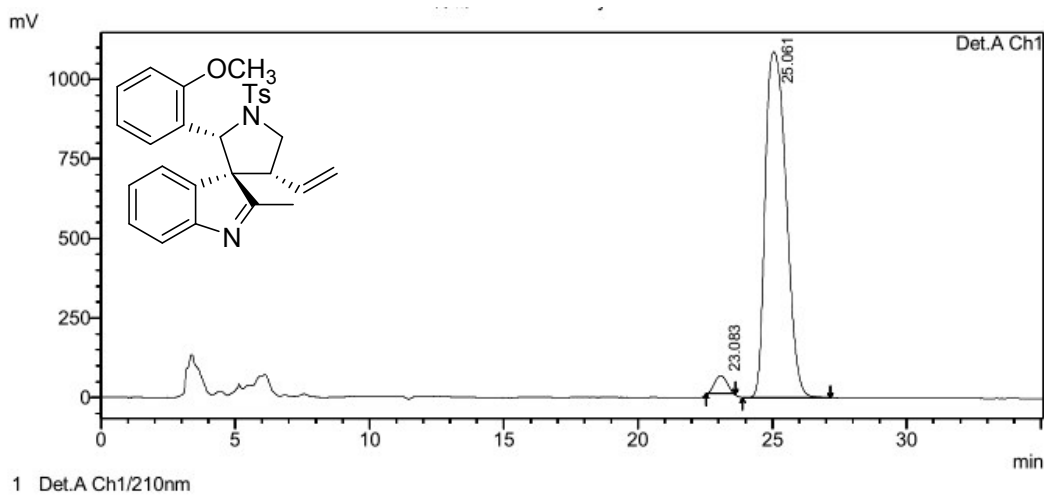
### HPLC of 3c

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	22.618	39503821	899816	49.340
2	24.757	40560179	841008	50.660
Total		80064000	1740825	100.000

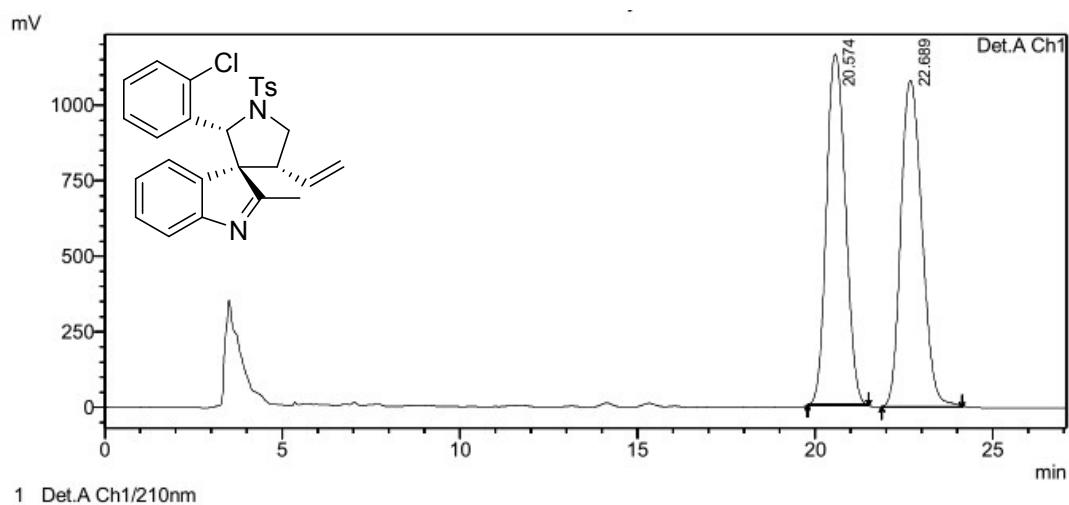


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	23.083	1767715	56492	2.916
2	25.061	58851743	1087002	97.084
Total		60619457	1143493	100.000

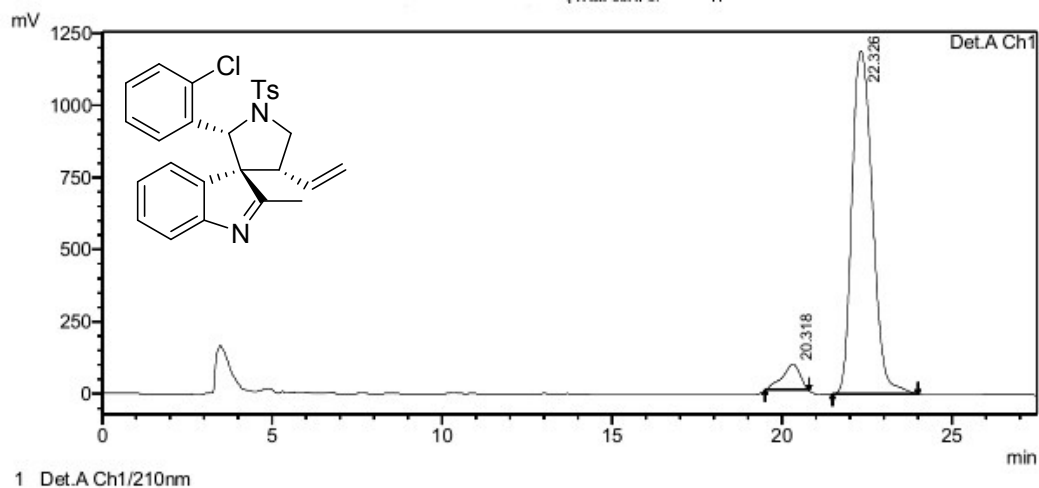
## HPLC of 3d

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



PeakTable

Detector A Ch1 210nm				
Peak#	Ret. Time	Area	Height	Area %
1	20.574	43329262	1159719	49.168
2	22.689	44796390	1080972	50.832
Total		88125651	2240691	100.000

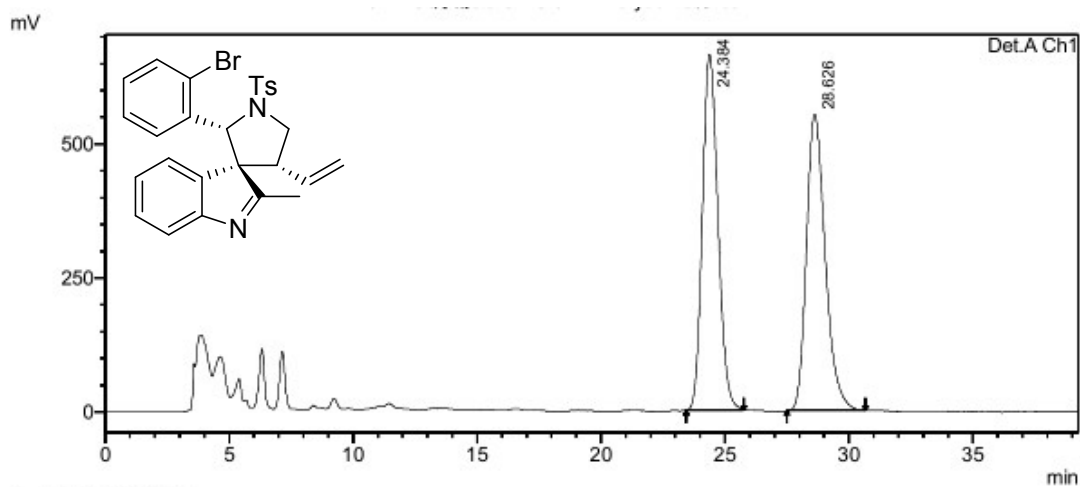


PeakTable

Detector A Ch1 210nm				
Peak#	Ret. Time	Area	Height	Area %
1	20.318	3221992	88366	6.065
2	22.326	49898614	1189319	93.935
Total		53120606	1277685	100.000

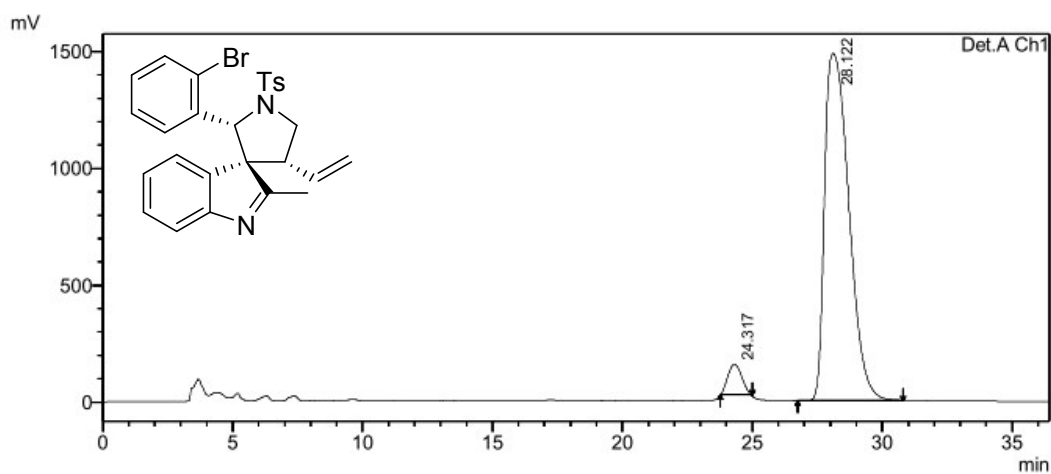
## HPLC of 3e

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	24.384	29051191	663839	49.923
2	28.626	29140902	552519	50.077
Total		58192093	1216358	100.000

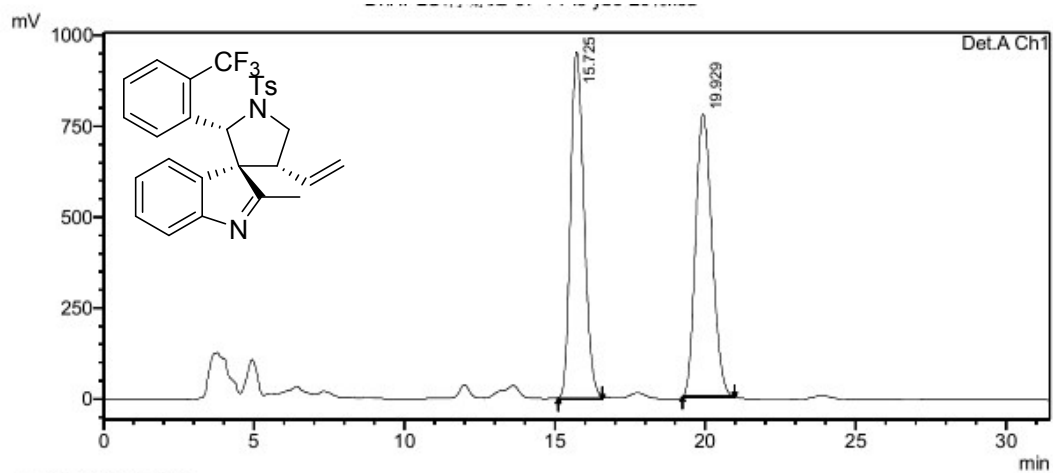


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	24.317	4688227	128789	4.624
2	28.122	96693321	1486342	95.376
Total		101381548	1615131	100.000

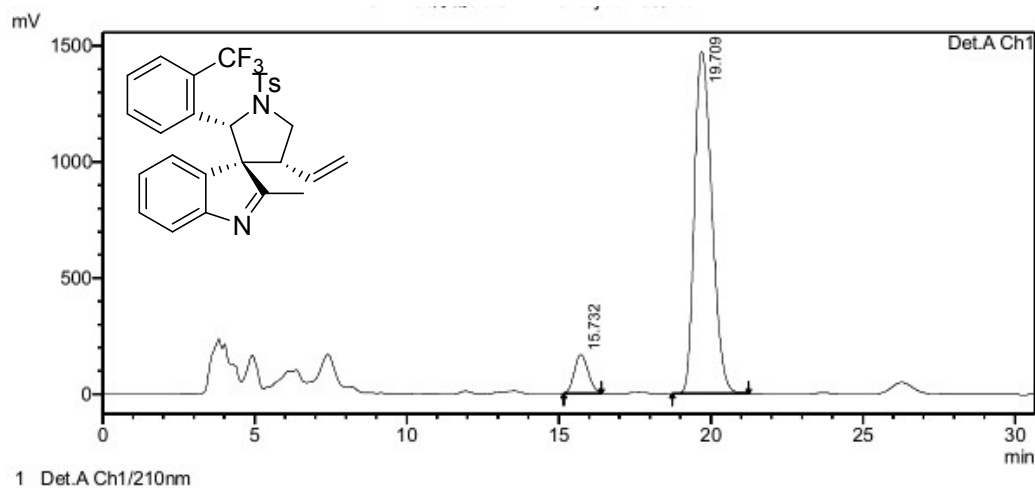
## HPLC of 3f

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	15.725	29866506	954027	50.203
2	19.929	29624998	777828	49.797
Total		59491504	1731856	100.000

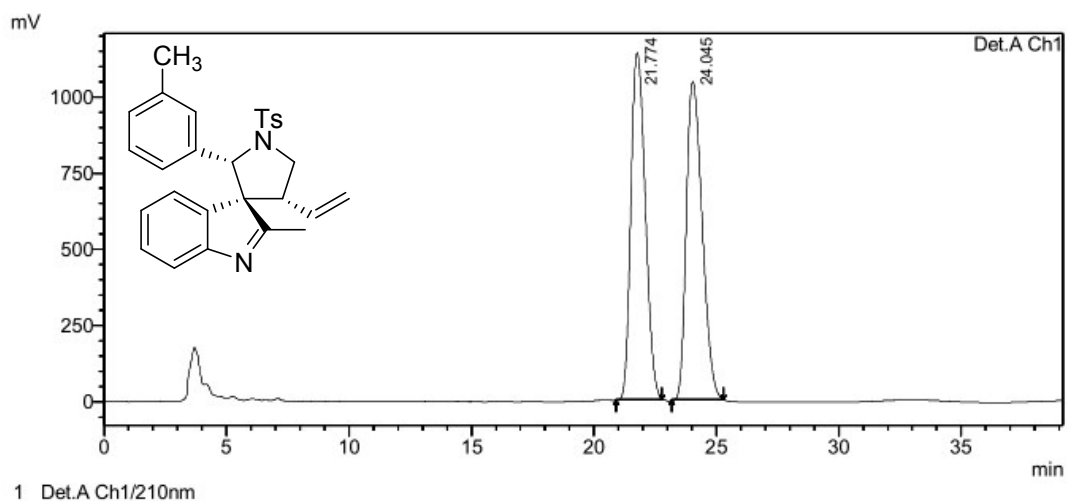


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	15.732	5341977	167249	8.334
2	19.709	58753623	1472433	91.666
Total		64095600	1639682	100.000

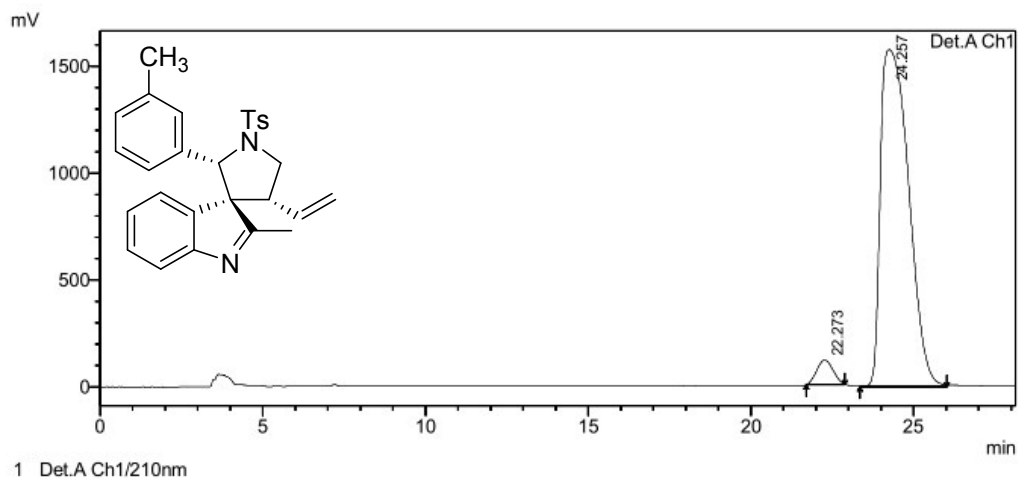
## HPLC of 3g

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	21.774	46279659	1136345	49.562
2	24.045	47098272	1042700	50.438
Total		93377931	2179045	100.000

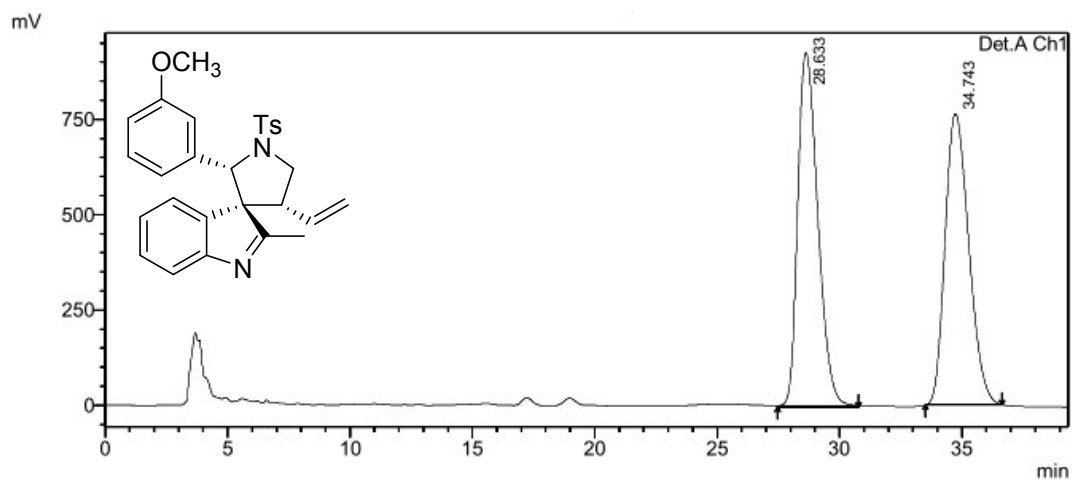


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	22.273	4052899	115333	4.096
2	24.257	94899013	1575689	95.904
Total		98951912	1691022	100.000

## HPLC of 3h

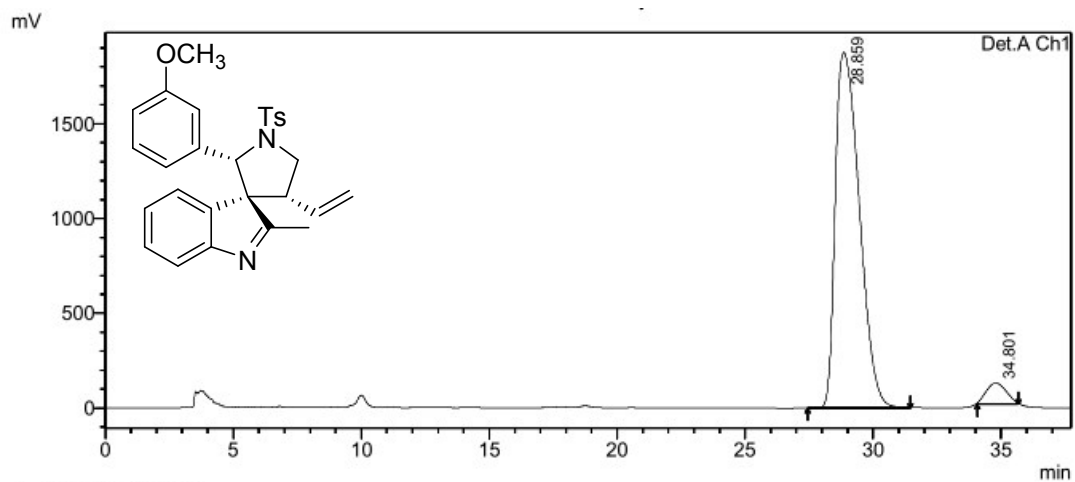
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	28.633	52943986	928305	50.710
2	34.743	51461503	763822	49.290
Total		104405489	1692127	100.000



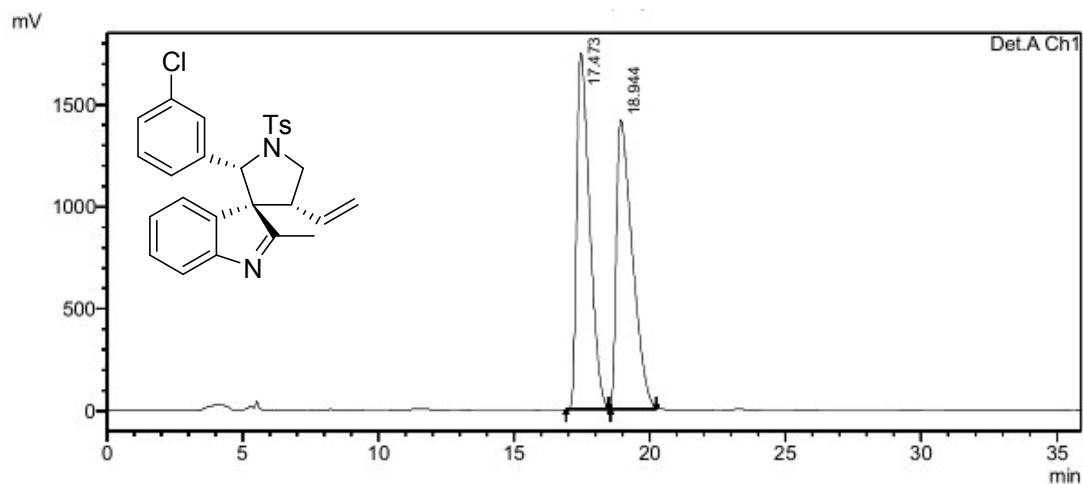
Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	28.859	122436390	1874729	95.270
2	34.801	6078593	110584	4.730
Total		128514983	1985312	100.000

## HPLC of 3i

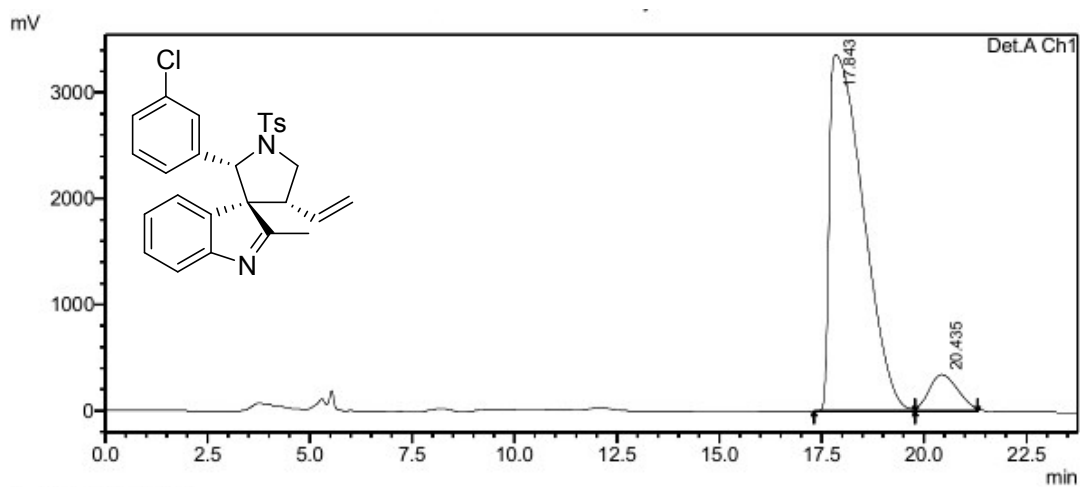
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	17.473	57894113	1745569	49.864
2	18.944	58210135	1417944	50.136
Total		116104248	3163514	100.000



1 Det.A Ch1/254nm

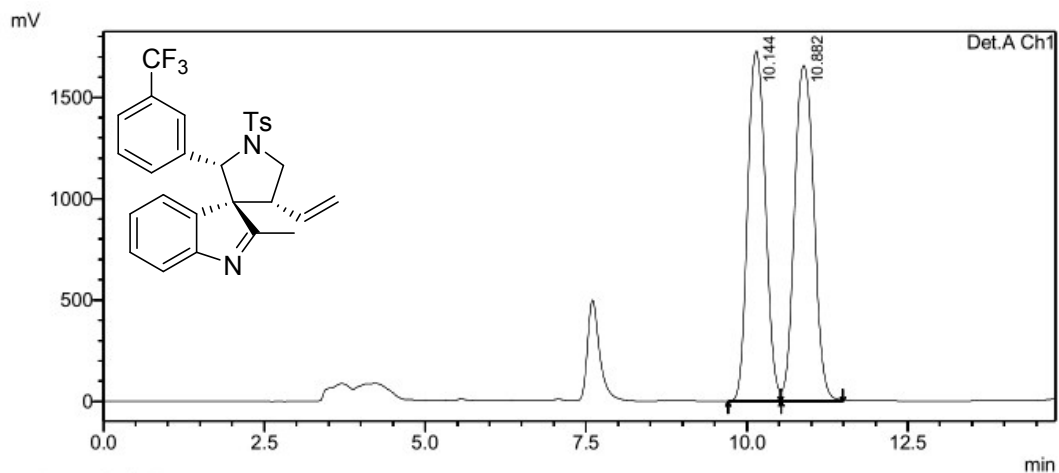
PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	17.843	193159229	3363115	91.911
2	20.435	16999578	343964	8.089
Total		210158808	3707079	100.000



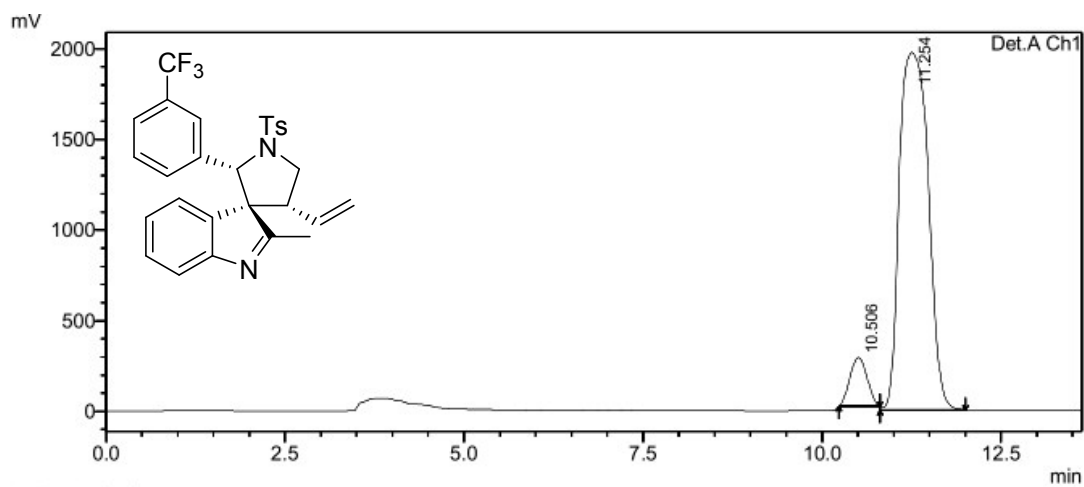
## HPLC of 3j

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



PeakTable

Detector A Ch1 210nm				
Peak#	Ret. Time	Area	Height	Area %
1	10.144	33701022	1726893	49.181
2	10.882	34822908	1656056	50.819
Total		68523930	3382949	100.000

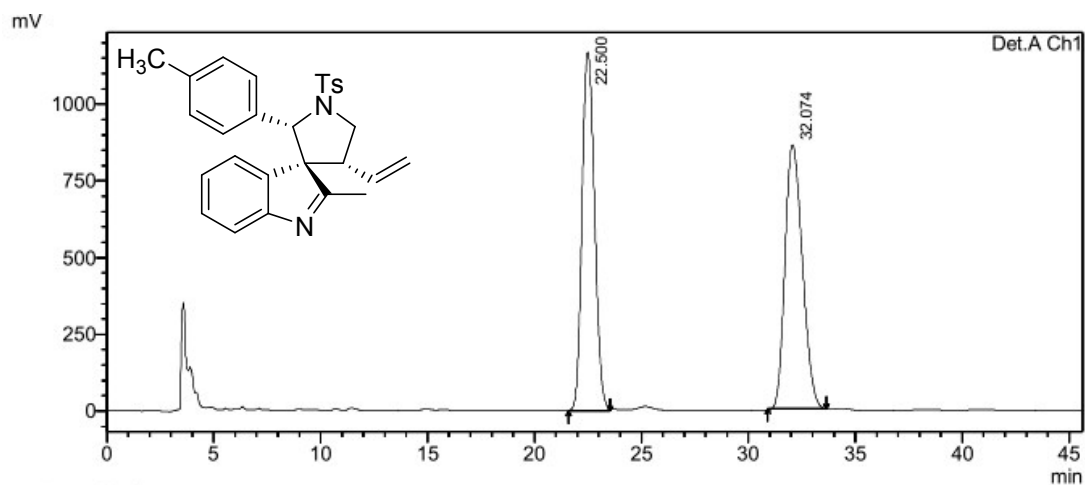


PeakTable

Detector A Ch1 210nm				
Peak#	Ret. Time	Area	Height	Area %
1	10.506	4474785	268360	7.465
2	11.254	55464987	1973795	92.535
Total		59939772	2242155	100.000

## HPLC of **3k**

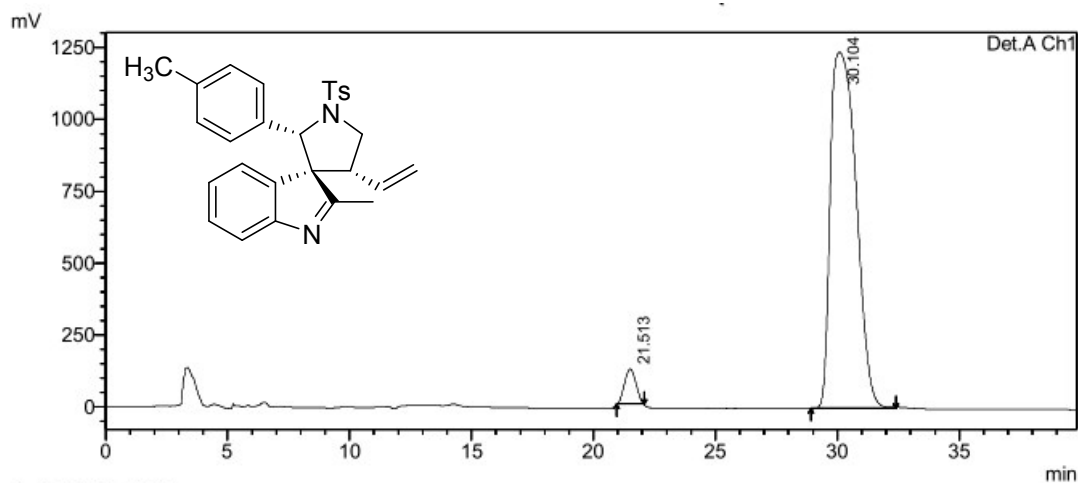
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	22.500	47660930	1167703	49.446
2	32.074	48728182	860740	50.554
Total		96389112	2028443	100.000



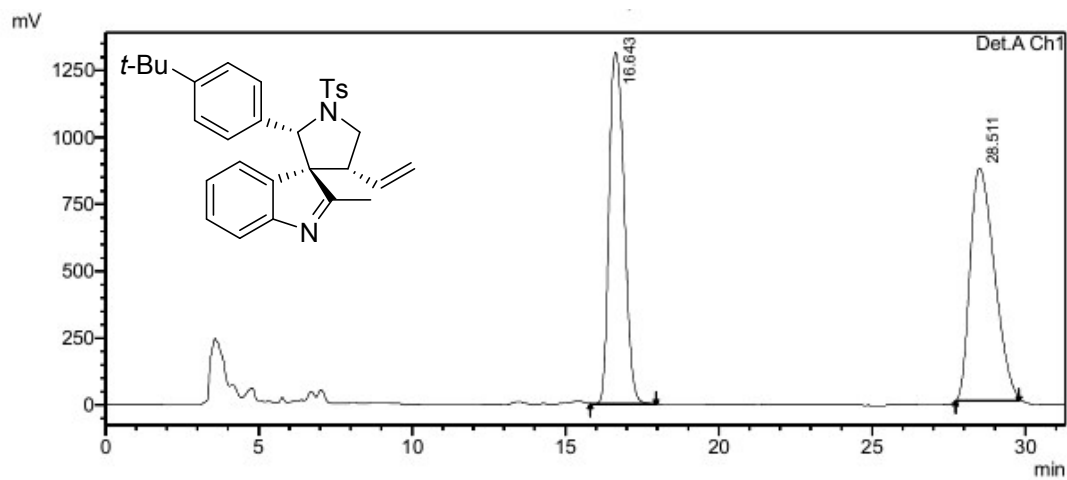
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	21.513	3932058	121540	4.142
2	30.104	90991659	1237564	95.858
Total		94923717	1359104	100.000

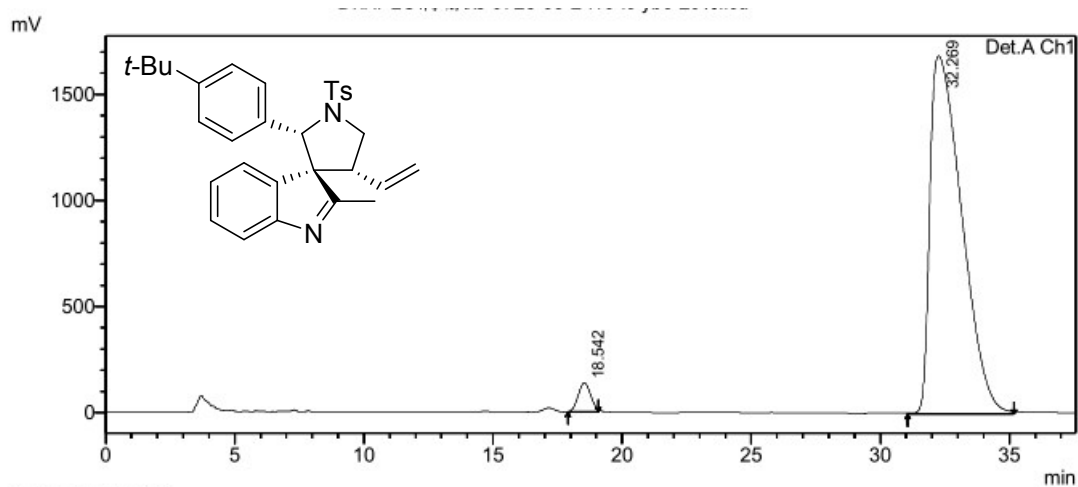
## HPLC of 31

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	16.643	44874381	1313744	48.226
2	28.511	48175728	869743	51.774
Total		93050109	2183488	100.000

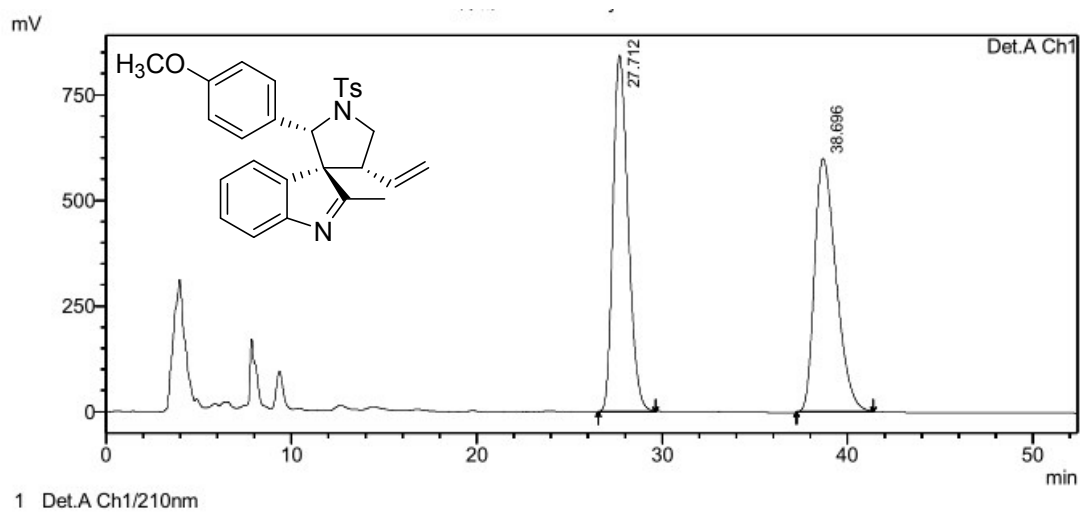


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	18.542	4626809	136714	3.100
2	32.269	144604180	1687510	96.900
Total		149230989	1824223	100.000

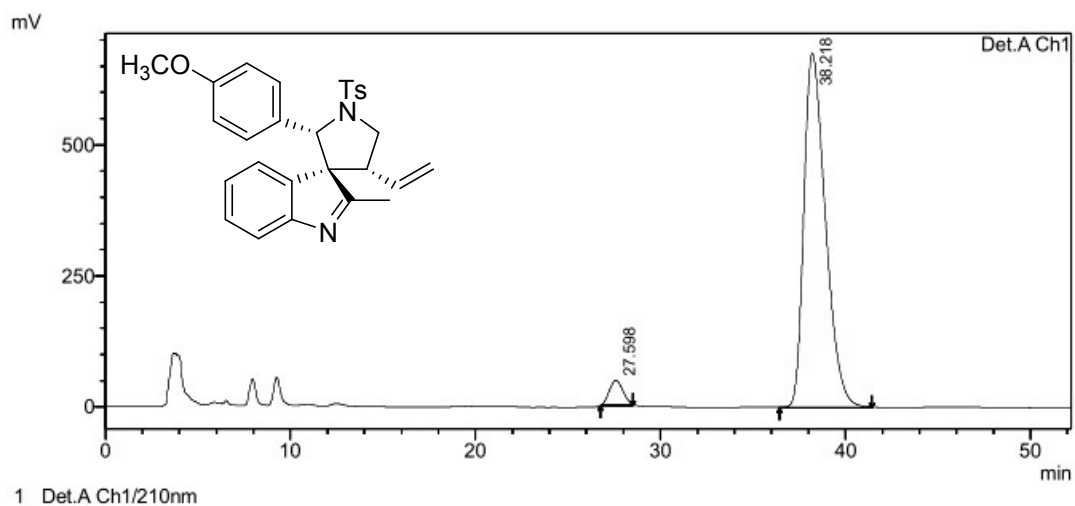
### HPLC of 3m

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



PeakTable

Detector A Ch1 210nm				
Peak#	Ret. Time	Area	Height	Area %
1	27.712	47925058	843967	49.735
2	38.696	48436010	599801	50.265
Total		96361068	1443768	100.000

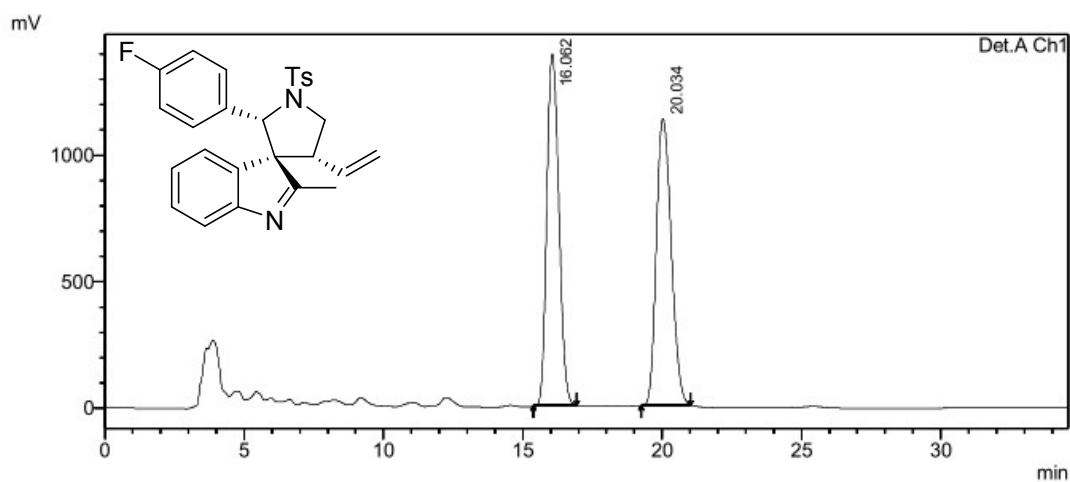


PeakTable

Detector A Ch1 210nm				
Peak#	Ret. Time	Area	Height	Area %
1	27.598	2515143	48042	4.383
2	38.218	54875351	676008	95.617
Total		57390494	724050	100.000

## HPLC of 3n

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm

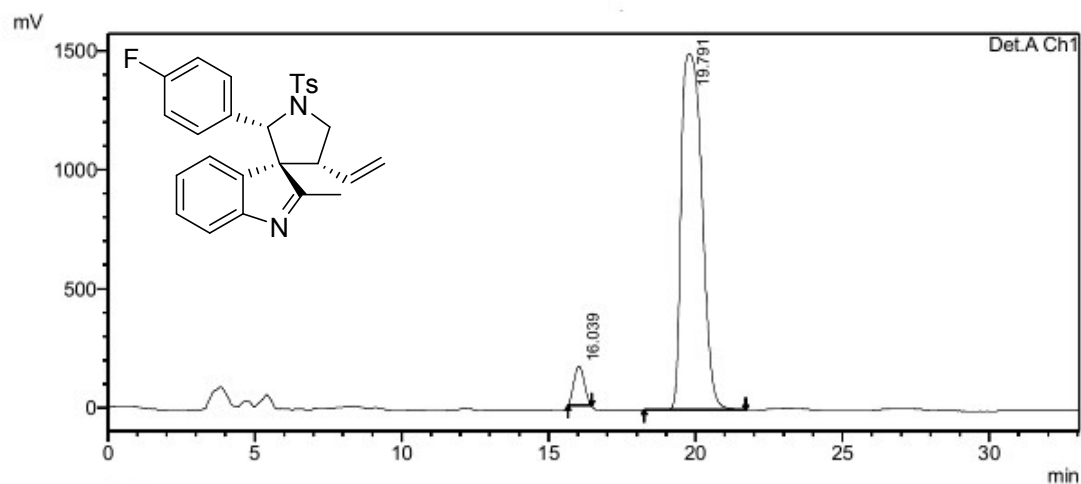


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	16.062	41871064	1388181	49.764
2	20.034	42267688	1133925	50.236
Total		84138753	2522106	100.000



1 Det.A Ch1/210nm

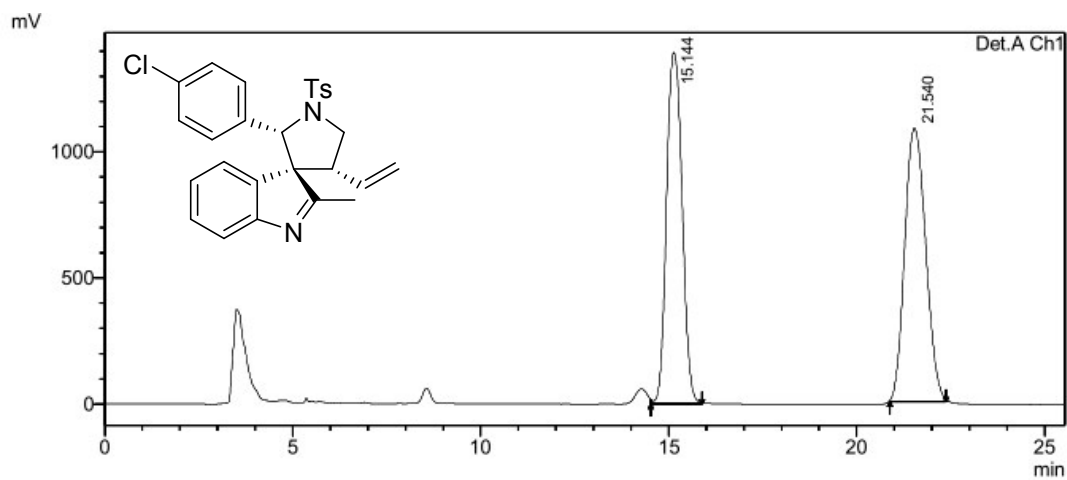
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	16.039	4059218	164953	5.285
2	19.791	72746743	1495632	94.715
Total		76805960	1660584	100.000

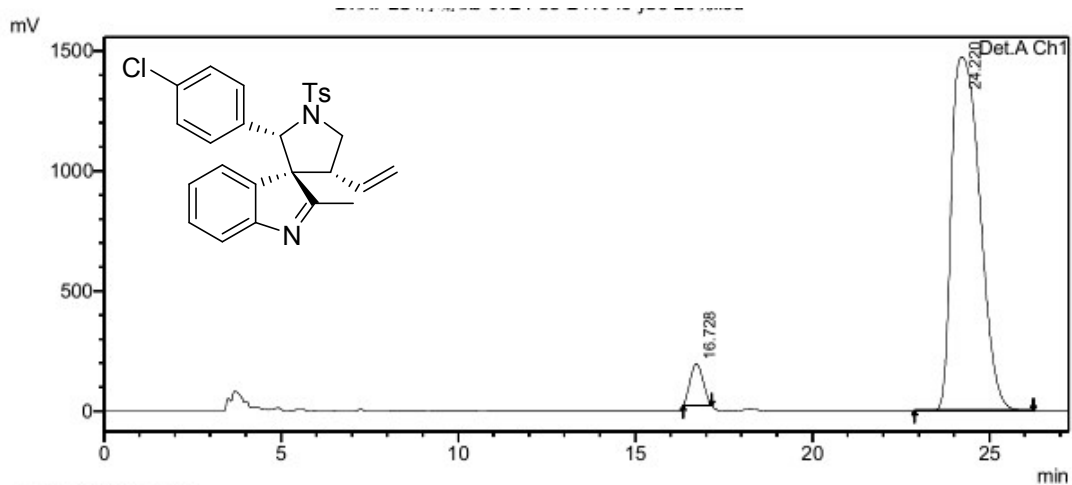
### HPLC of 3o

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	15.144	40182968	1393065	48.850
2	21.540	42074441	1084914	51.150
Total		82257409	2477979	100.000

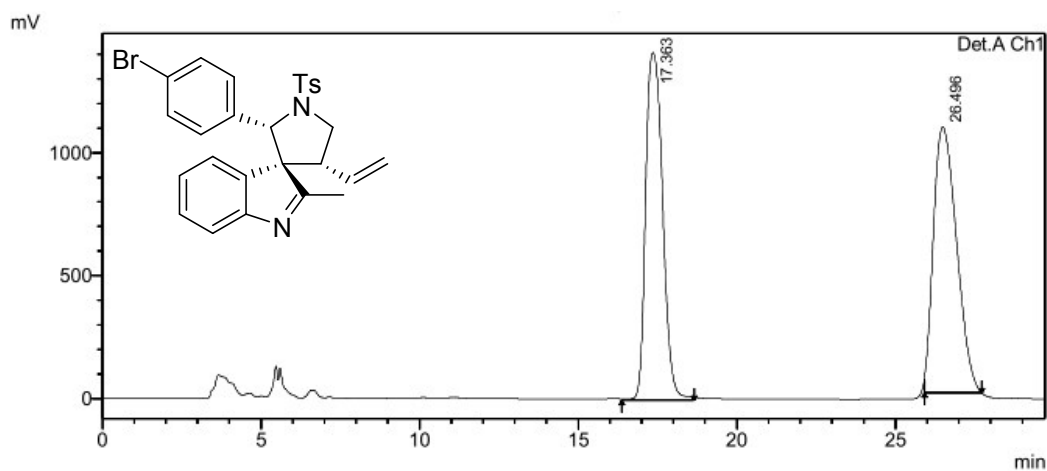


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	16.728	4358554	172753	5.053
2	24.220	81891385	1472099	94.947
Total		86249939	1644852	100.000

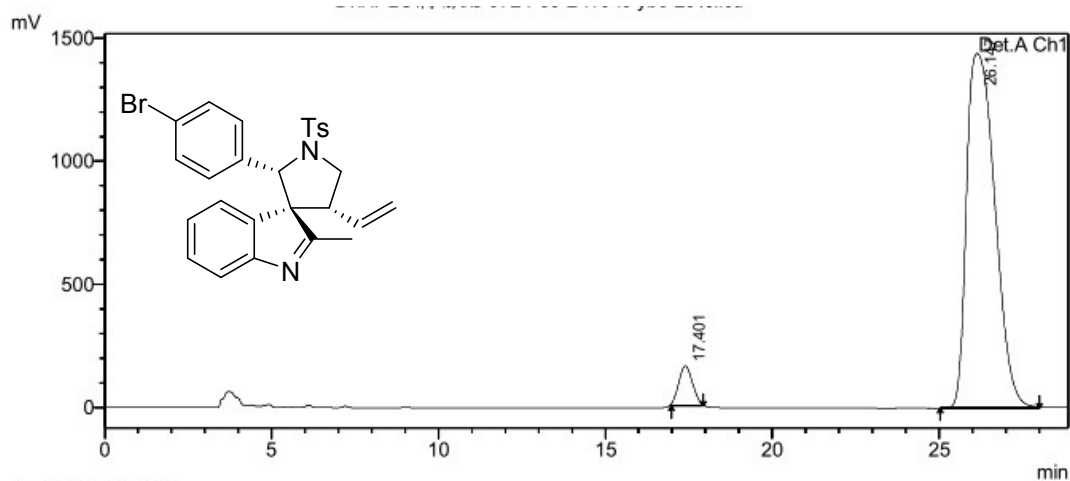
## HPLC of 3p

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	17.363	52582396	1411394	48.926
2	26.496	54890945	1079982	51.074
Total		107473342	2491376	100.000

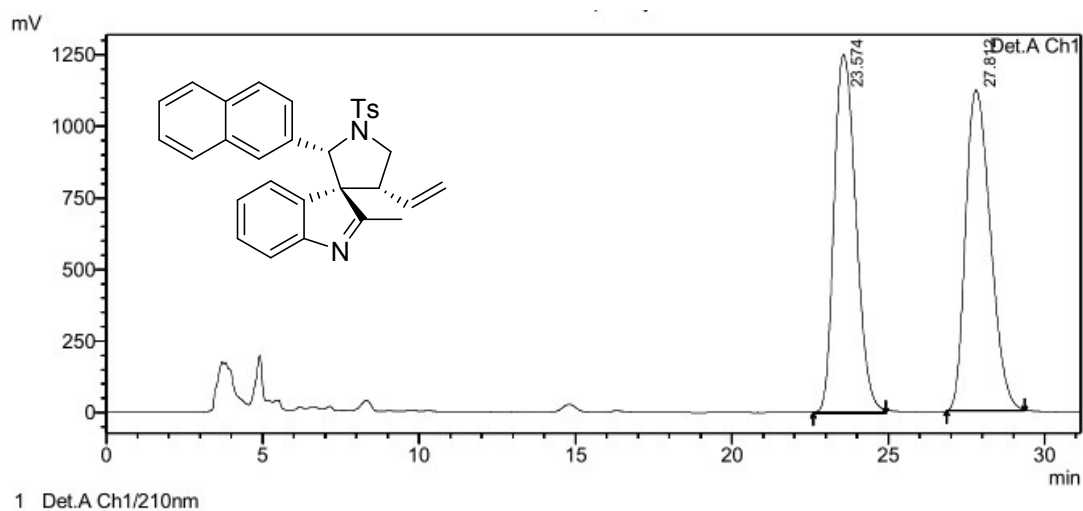


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	17.401	4685534	161695	5.235
2	26.147	84812495	1438174	94.765
Total		89498029	1599868	100.000

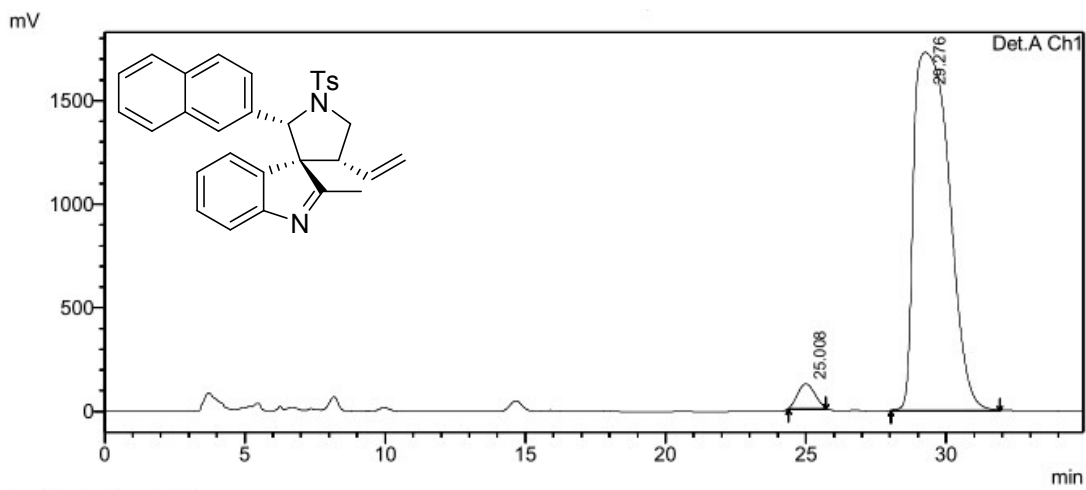
## HPLC of 3q

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	23.574	60955246	1250453	49.569
2	27.812	62014536	1120293	50.431
Total		122969781	2370746	100.000



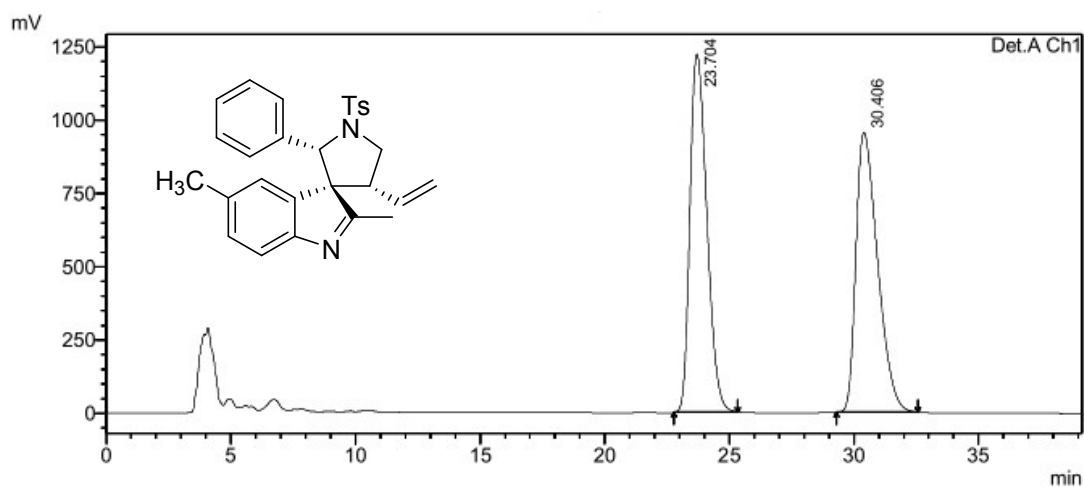
PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	25.008	5212845	120724	3.300
2	29.276	152740582	1730435	96.700
Total		157953427	1851159	100.000



## HPLC of 3r

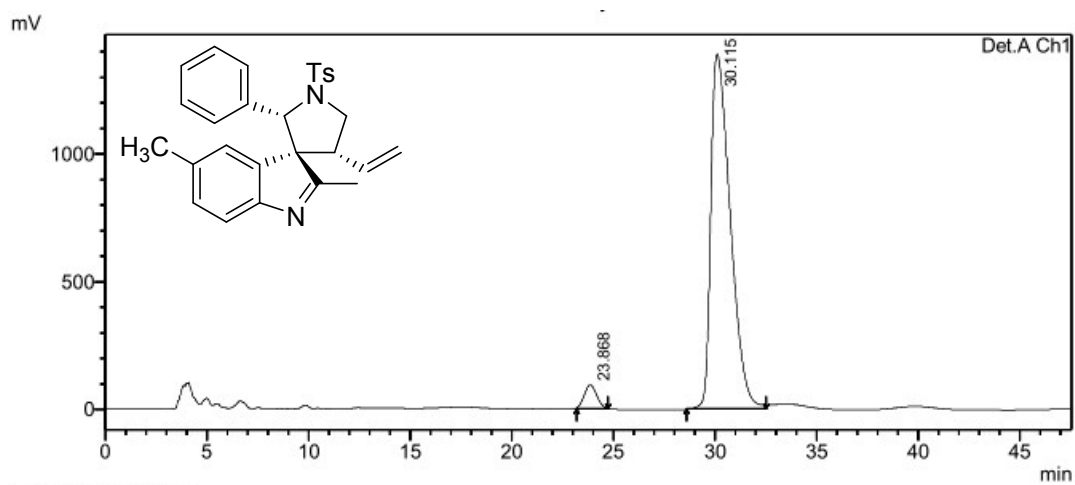
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	23.704	57563105	1220713	49.913
2	30.406	57764171	953895	50.087
Total		115327276	2174608	100.000



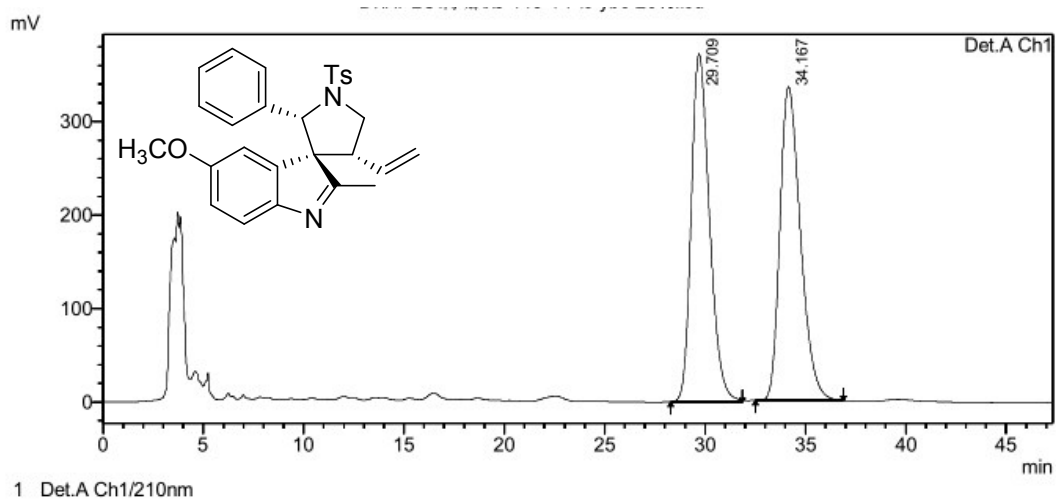
Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	23.868	3988395	92997	4.150
2	30.115	92110069	1386031	95.850
Total		96098464	1479028	100.000

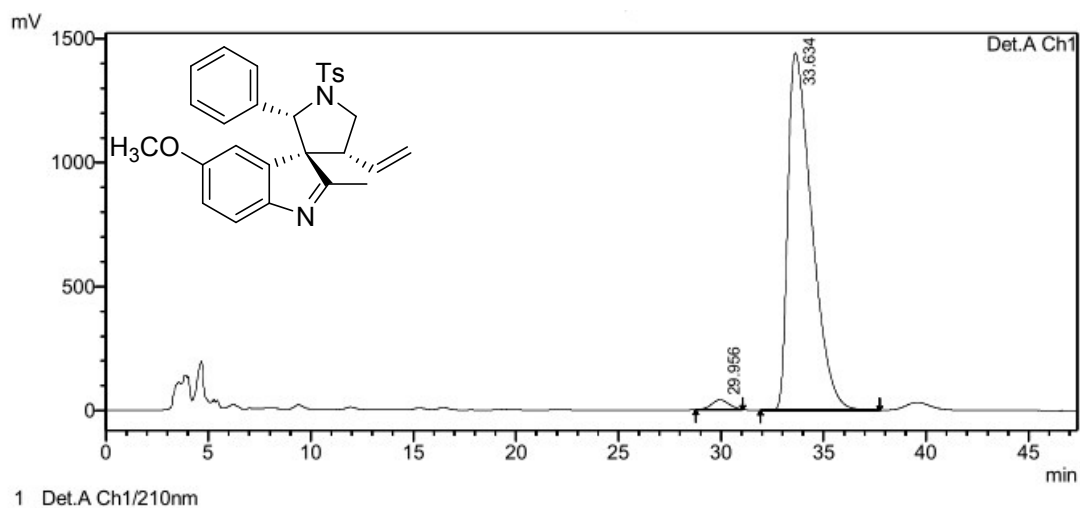
## HPLC of 3s

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0 \text{ mL/min}$ ,  $\lambda = 210 \text{ nm}$



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	29.709	23538985	372274	49.582
2	34.167	23935892	335613	50.418
Total		47474877	707887	100.000

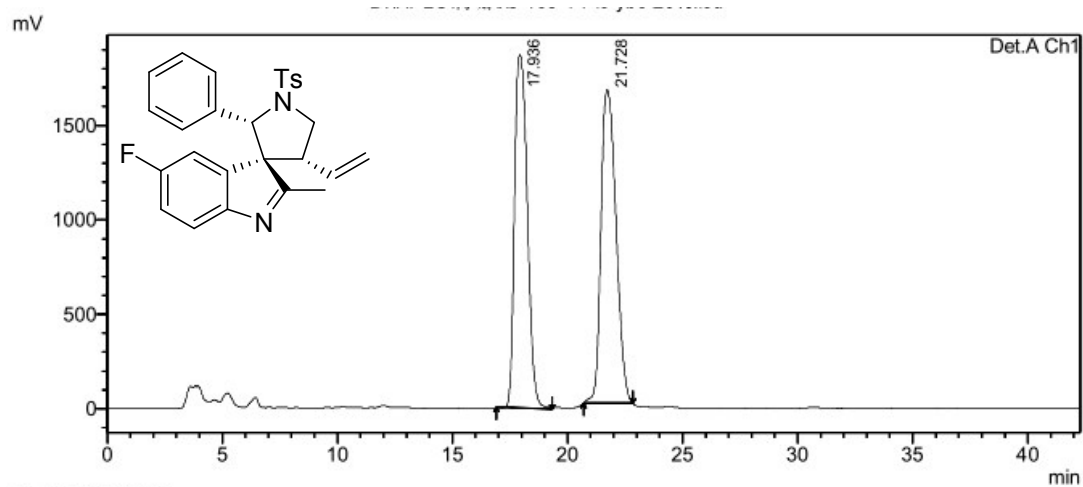


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	29.956	2446035	40077	2.047
2	33.634	117042530	1440869	97.953
Total		119488566	1480946	100.000

HPLC of **3t**

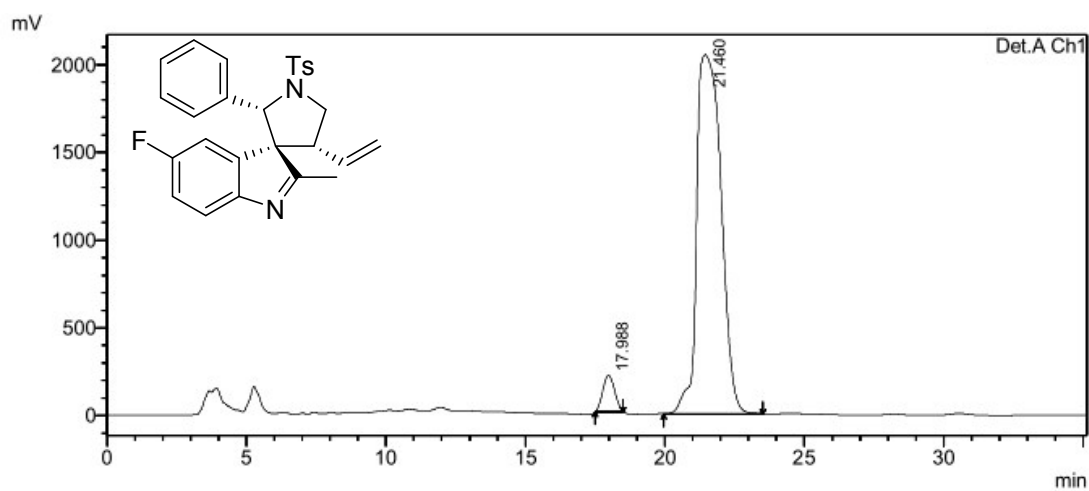
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v= 1.0$  mL/min,  $\lambda=210$  nm



1 Det.A Ch1/210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	17.936	72118157	1869560	48.941
2	21.728	75238195	1657959	51.059
Total		147356352	3527518	100.000



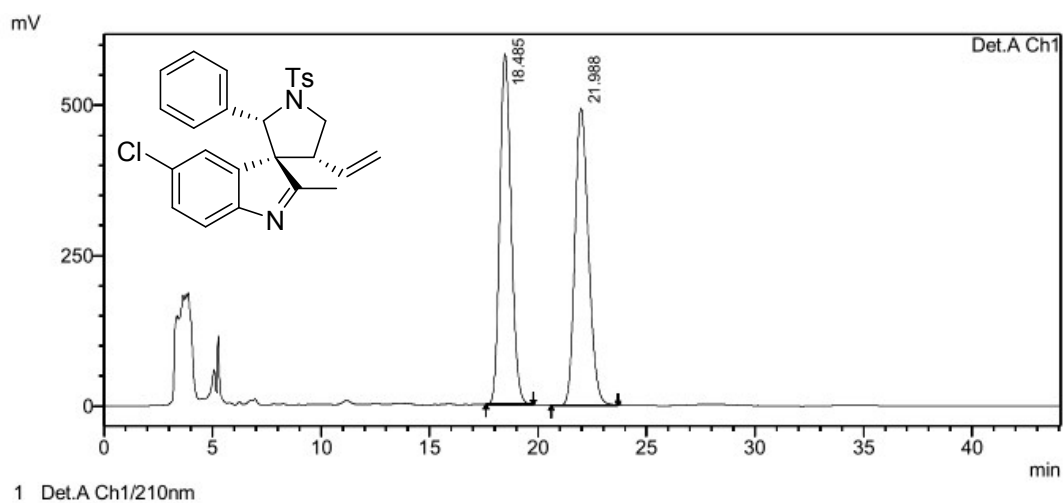
1 Det.A Ch1/210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	17.988	6172675	208377	4.697
2	21.460	125234591	2048611	95.303
Total		131407265	2256988	100.000

HPLC of **3u**

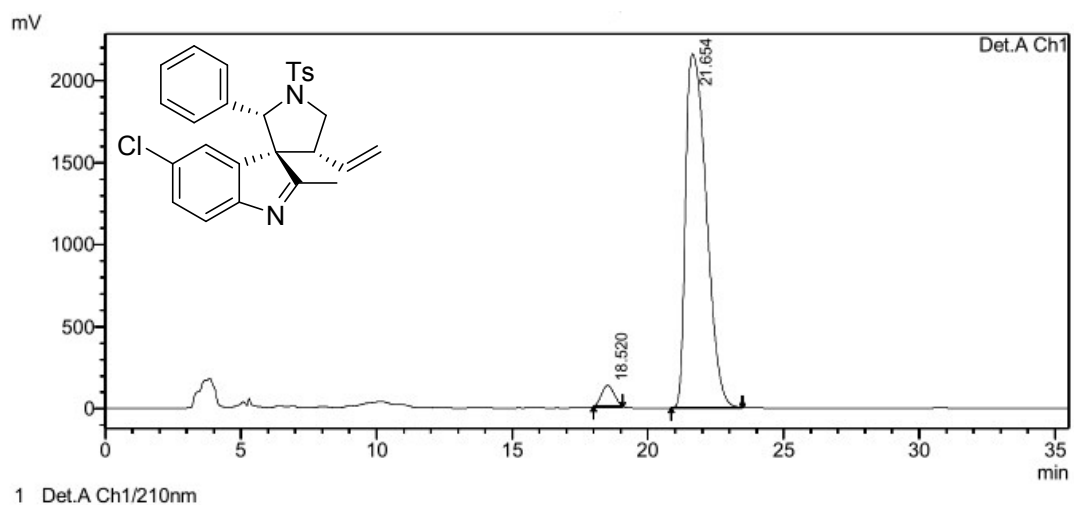
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v= 1.0 \text{ mL/min}$ ,  $\lambda=210 \text{ nm}$



Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	18.485	21124711	582665	49.592
2	21.988	21472459	494431	50.408
Total		42597170	1077096	100.000



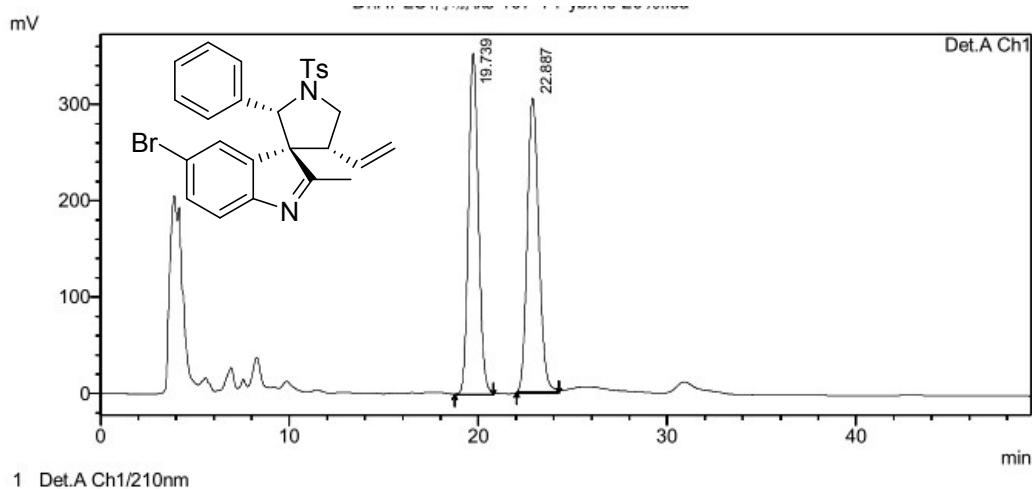
Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	18.520	4187290	128955	3.520
2	21.654	114768294	2159503	96.480
Total		118955584	2288458	100.000

HPLC of **3v**

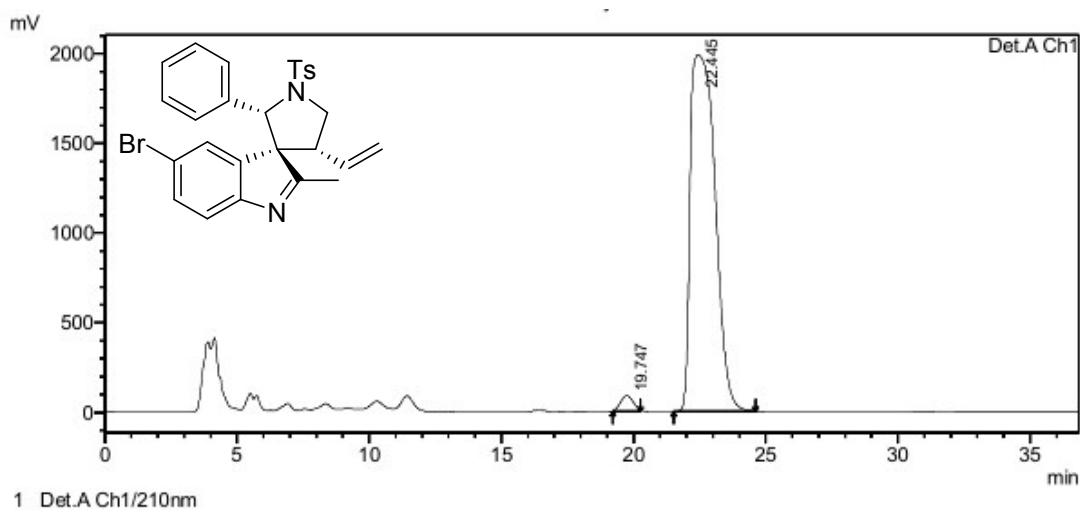
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v= 1.0 \text{ mL/min}$ ,  $\lambda=210 \text{ nm}$



Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	19.739	12945606	353999	49.956
2	22.887	12968297	305712	50.044
Total		25913903	659711	100.000



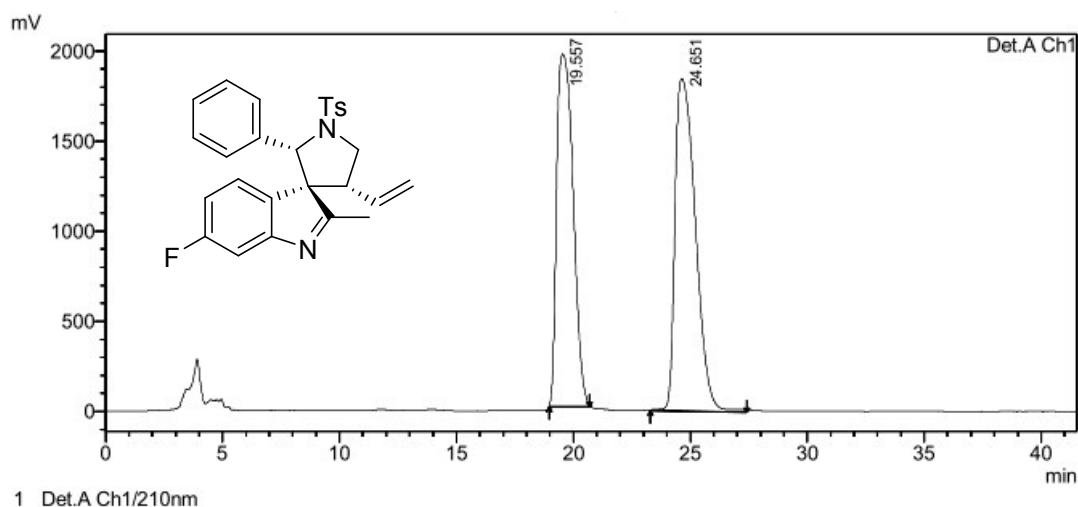
Detector A Ch1 210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	19.747	2989276	88207	2.248
2	22.445	130003470	1989406	97.752
Total		132992747	2077613	100.000

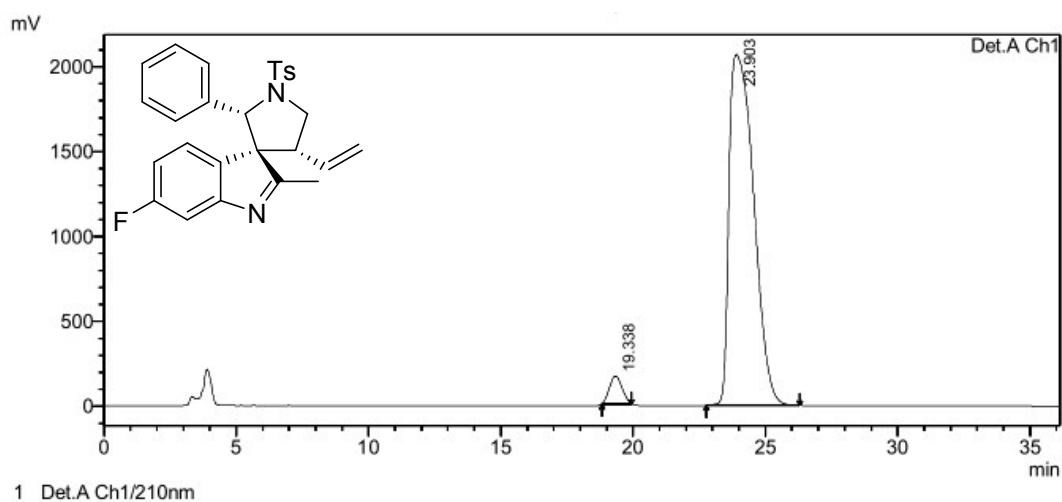
HPLC of **3w**

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v= 1.0 \text{ mL/min}$ ,  $\lambda=210 \text{ nm}$



PeakTable

Peak#	Ret. Time	Area	Height	Height %
1	19.557	96141717	1957316	51.458
2	24.651	112149712	1846431	48.542
Total		208291430	3803747	100.000

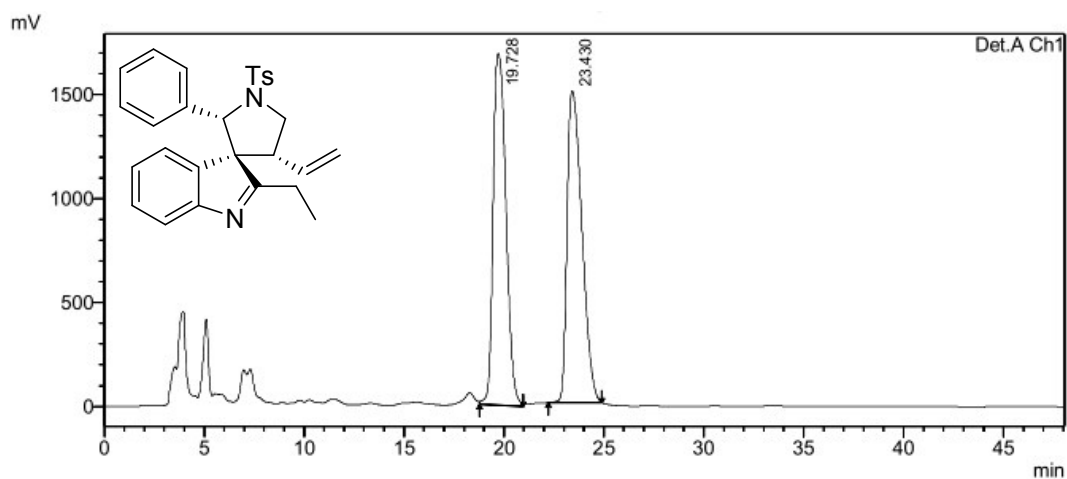


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	19.338	5536302	164575	3.981
2	23.903	133523761	2067630	96.019
Total		139060063	2232205	100.000

### HPLC of 3x

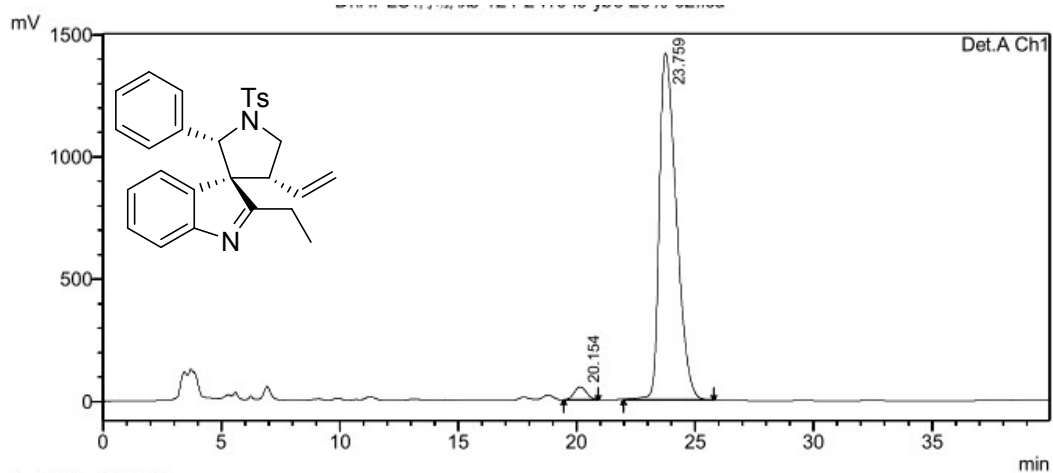
Conditions: Chiralpak IC column, 20% IPA in hexane,  $v= 1.0 \text{ mL/min}$ ,  $\lambda=210 \text{ nm}$



1 Det.A Ch1/210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	19.728	75755803	1691812	49.411
2	23.430	77562564	1500289	50.589
Total		153318366	3192101	100.000



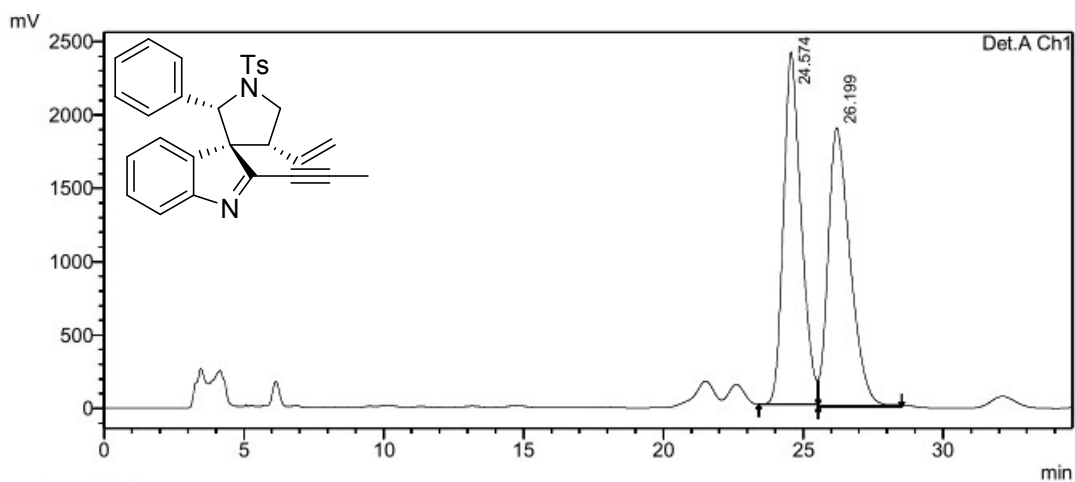
1 Det.A Ch1/210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	20.154	1918130	52921	2.639
2	23.759	70770872	1417686	97.361
Total		72689001	1470607	100.000

### HPLC of **3y**

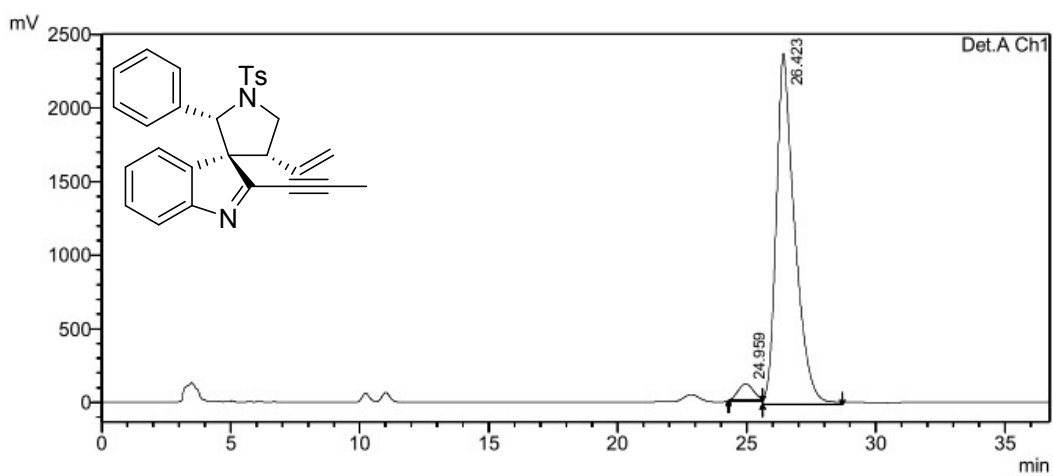
Conditions: Chiralpak IC column, 25% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



1 Det.A Ch1/210nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	24.574	105217277	2401098	50.250
2	26.199	104171234	1898076	49.750
Total		209388512	4299175	100.000



1 Det.A Ch1/210nm

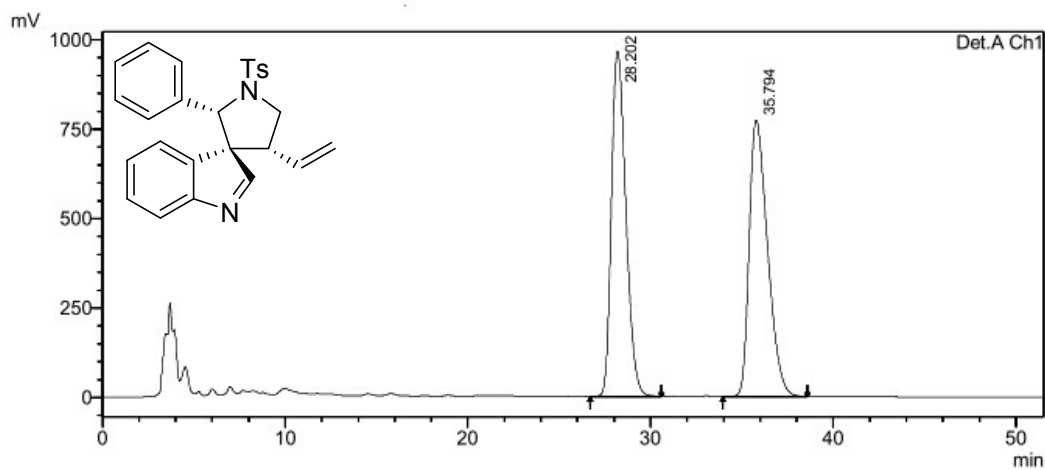
PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	24.959	4681095	111955	3.799
2	26.423	118531570	2384162	96.201
Total		123212665	2496117	100.000

### HPLC of **3z**

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



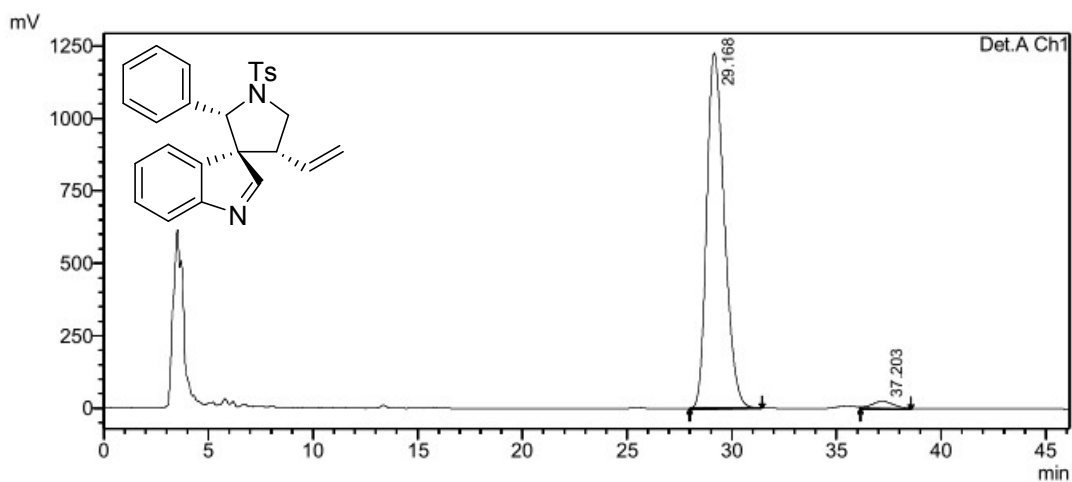


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	28.202	53281650	966578	49.501
2	35.794	54355219	773589	50.499
Total		107636869	1740167	100.000



1 Det.A Ch1/210nm

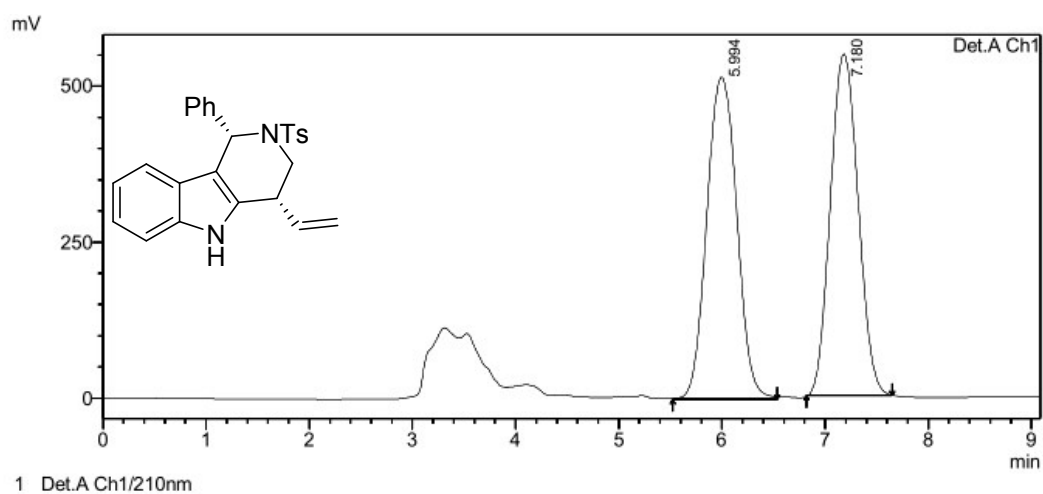
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	29.168	71630491	1225865	97.309
2	37.203	1980982	25592	2.691
Total		73611473	1251457	100.000

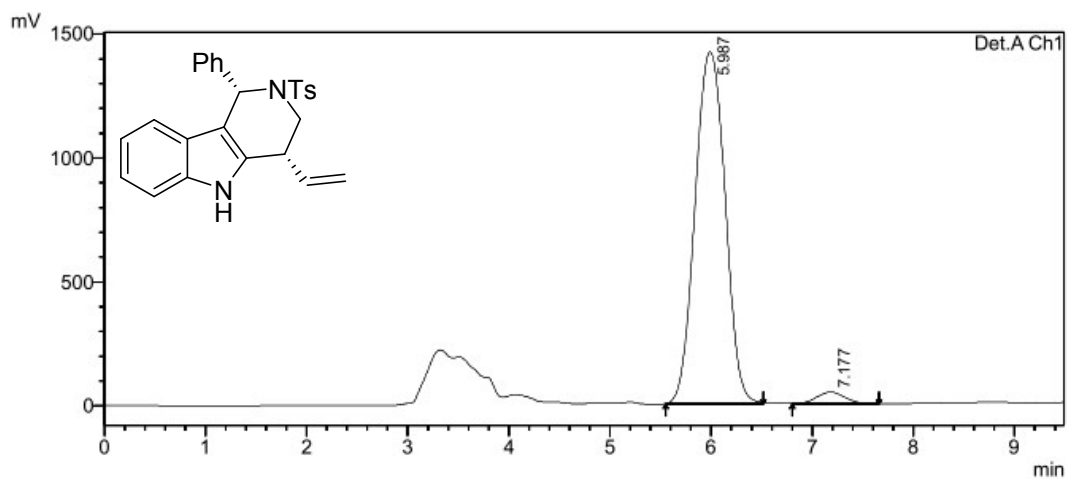
## HPLC of 5z

Conditions: Chiralpak IC column, 20% IPA in hexane,  $v = 1.0$  mL/min,  $\lambda = 210$  nm



PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	5.994	10473004	516454	50.517
2	7.180	10258745	547202	49.483
Total		20731749	1063656	100.000

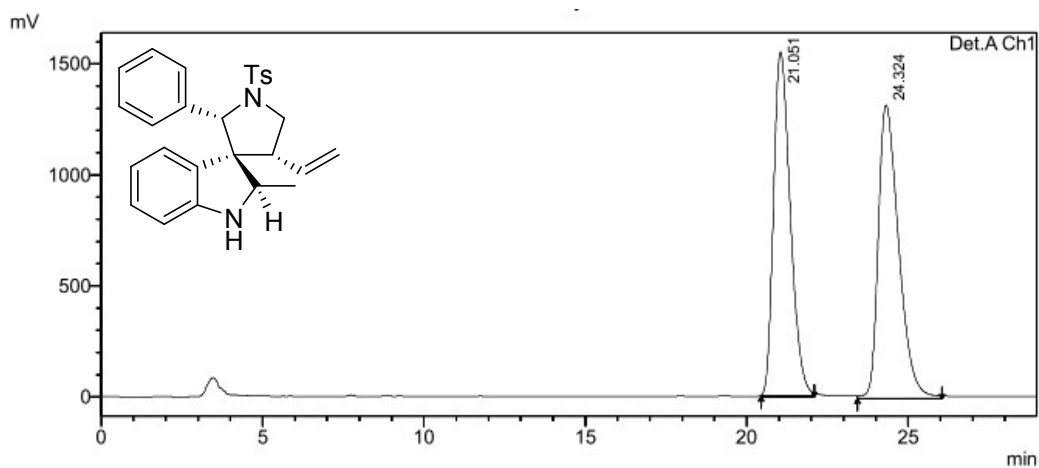


PeakTable

Peak#	Ret. Time	Area	Height	Area %
1	5.987	29398217	1418648	97.020
2	7.177	902986	46758	2.980
Total		30301204	1465406	100.000

## HPLC of 5a

Conditions: Chiralpak IE column, 20% IPA in hexane,  $v= 1.0 \text{ mL/min}$ ,  $\lambda=210 \text{ nm}$

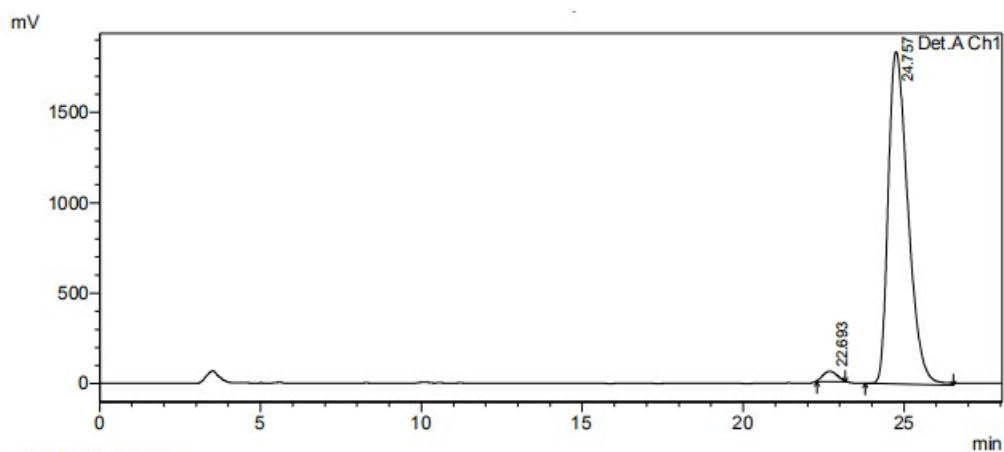


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	21.051	56361001	1552115	49.161
2	24.324	58285781	1322350	50.839
Total		114646782	2874465	100.000



1 Det.A Ch1/210nm

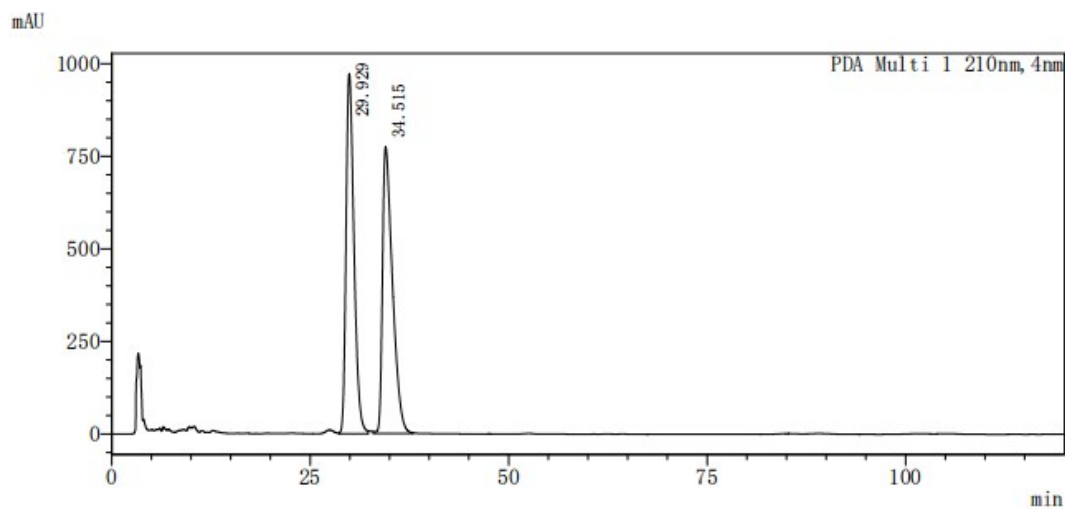
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	22.693	1724885	56395	2.150
2	24.757	78507541	1838375	97.850
Total		80232426	1894770	100.000

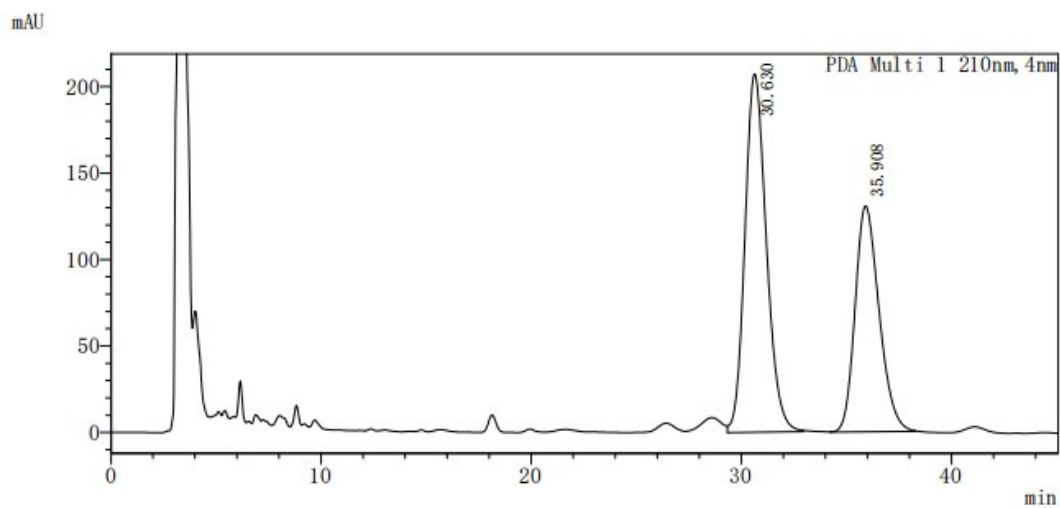
## HPLC of 6a

Conditions: Chiralpak IE column, 20% IPA in hexane,  $v=1.0$  mL/min,  $\lambda=210$  nm



<峰表>

峰号	保留时间	面积	高度	标记	化合物名	面积%
1	29.929	67546674	973056	M		49.971
2	34.515	67625261	774144	M		50.029
总计		135171936	1747200			100.000

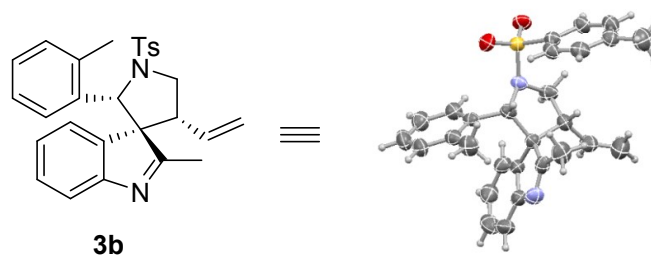


<峰表>

峰号	保留时间	面积	高度	标记	化合物名	面积%
1	30.630	14688312	207224	M		58.616
2	35.908	10370125	130649	M		41.384
总计		25058437	337873			100.000

## 7.X-ray crystallographic data of **3b** and **5a**

CCDC 2027183 (**3b**) and CCDC 2069356 (**5a**) contain the structure and supplementary crystallographic data. These data can be obtained free of charge on application to the Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336033; or e-mail [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)) or via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Table S1** Crystal data and structure refinement for Compounds **3b**.

Identification code	<b>3b</b>	<b>5a</b>
CCDC Deposit number	2027183	2069356
Empirical formula	C <sub>28</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> S	C <sub>27</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> S
Formula weight	472.60	444.57
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
space group	P 21 21 21	P 1 21 1
Unit cell dimensions	a=10.783(4)	a=8.546(6)
Å	b=11.947(7)	b=14.915(10)
	c=18.807(8)	c=10.120(7)
(°)	α = 90	α = 90
	β = 90	β = 11.501(17)
	γ = 90	γ = 90

Volume	2423(2)Å <sup>3</sup>	1192(14)
Z	4	2
Calcd. density (Mg/m <sup>3</sup> )	1.257	1.236
F(000)	968.0	472.0
Limiting indices	-10 ≤ h ≤ 12	-10 ≤ h ≤ 10
	-13 ≤ k ≤ 13	-18 ≤ k ≤ 18
	-22 ≤ l ≤ 21	-12 ≤ l ≤ 12
GOOF	0.941	1.061
R(int)	4.97%	4.86%
R <sub>1</sub>	3.92%	4.00%
wR <sub>2</sub>	9.12%	9.00%