Supporting Information for

Catalytic Asymmetric Construction of Tetrahydroquinoline-Based Spirooxindole Framework via a Diastereo- and Enantioselective Decarboxylative [4 + 2] Cycloaddition

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1. General method

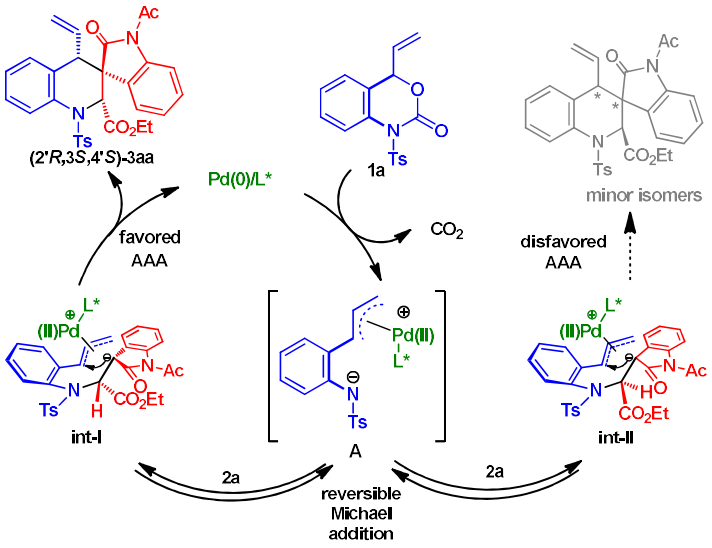
^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$, usingtetramethylsilane as the internal reference. HRMS (ESI) was determined by amicrOTOF-Q Ⅱ HRMS/MS instrument (Bruker). Enantiomeric ratios (er) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiralpak IC, IB, AD-H and IA columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at thetemperatures indicated. The X-ray source used for the single crystal X-ray diffraction analysis of compound **3aa** was CuKα (λ = 1.54178), and the thermal ellipsoid was drawn at the 30% probability level. Analytical grade solvents for the column chromatography were distilled before use. All starting materials commercially available were used directly. Substrates **1** were synthesized according to the literature methods.[1]

2. Proposed reaction pathway

Based on the experimental results, we suggested a possible reaction pathway to explain the chemistry and stereochemistry of this decarboxylative [4+2] cycloaddition. As show in Scheme S1, the reaction was initialized by Pd(0)/L* catalyzed decarboxylation of **1a**, affording palladium-stabilized zwitterionic intermediate **A**. Two new zwitterionic intermediates **int-I** and **int-II** could be generated from the reversible Michael addition between the intermediate **A** and methyleneindolinone **2a**. Finally, an intramolecular asymmetric allylic alkylation (AAA) reaction occurred to accomplish the [4+2] cyclization. There might exist a kinetic resolution process during the formation of intermediates **int-I** and **int-II**. Namely, the favorable **int-I** could rapidly undergo the intramolecular AAA reaction to generate product **3aa** with

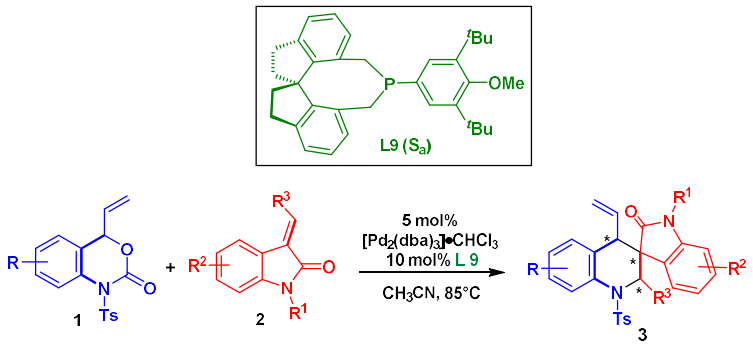
[1](a) Jia, M.-Q.; You, S.-L. *ACS Catal.* **2013**, *3*, 622. (b) Chong, P. Y.; Janicki, S. Z.; Petillo, P. A. *J. Org. Chem.* **1998**, *63*, 8515. (c) Rauno, G.; Luis, J.; Concepcion, P.; Jesus H. R. *Tetrahedron*, **1989**, *45*, 203. (d) Guo, C.; Fleige, M.; Janssen-Müller, D.; Daniliuc, C. G.; Glorius, F. *J. Am. Chem. Soc.* **2016**, *138*, 7840. (e) Wei, Y.; Lu, L.; Li, T.; Feng, B.; Wang, Q.; Xiao, W.-J.; Alper, H. *Angew. Chem. Int. Ed.* **2016**, *55*, 2200. (f) Mei, G.-J.; Bian, C.-Y.; Li, G.-H.; Xu, S.-L.; Zheng, W.-Q.; Shi, F. *Org. Lett*. **2017**, *19*, 3219.

the observed configuration, while the unfavourable **int-II** would transform into the favourable **int-I** via reversible Michael addition and the induction of chiral ligand. As far as the stereochemistry is concerned, in the first step of Michael addition, the chiral ligand might have some interactions with the moiety of methyleneindolinone **2a** and the nucleophilic amide group, thus controlling the enantioselectivity of the first step, which resulted in the excellent diastereoselectivity of the final product. In the second step of intramolecular AAA reaction, the induction effect of the first chiral center to the newly formed chiral centers, along with the interaction between the chiral ligand and the substrate, led to the high enantioselectivity of the final product **3aa** with (2'*R*,3*S*,4'*S*)-configuration.



Scheme S1. Proposed reaction pathway.

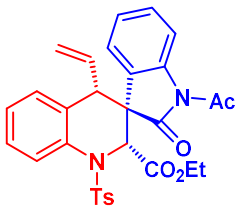
3. General procedure for the synthesis of products 3



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (0.005 mmol), **ligand L9**

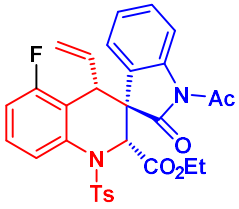
(0.01 mmol), vinyl benzoxazinanones **1** (0.1 mmol) and methyleneindolinones **2** (0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel to get chiral 3,3'-spirooxindole tetrahydroquinoline products **3**.

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indolie-3,3'-quinoline]-2'-carboxylate (3aa):



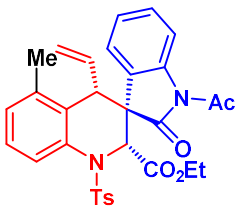
In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3aa** (52 mg) was obtained in 96% yield as a yellowish solid. m.p. 155–156°C; $[\alpha]_D^{20}$ =+34 (c = 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.45 (m, 1H), 7.30 (d, *J* = 9.4, 2H), 7.27 – 7.19 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.74 (td, *J* = 7.7, 1.0 Hz, 1H), 5.54 (s, 1H), 5.48 (dd, *J* = 7.7, 0.9 Hz, 1H), 5.11 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.88 (dd, *J* = 18.1, 8.5 Hz, 1H), 4.77 (dd, *J* = 16.9, 2.0 Hz, 1H), 3.75 – 3.57 (m, 2H), 2.68 (s, 3H), 2.50 – 2.38 (m, 4H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 170.6, 167.6, 144.2, 140.5, 135.7, 135.2, 133.3, 130.4, 129.6, 129.4, 128.7, 128.3, 127.3, 127.1, 126.7, 124.8, 124.7, 123.9, 122.4, 115.9, 64.9, 61.5, 60.3, 48.9, 26.6, 21.5, 13.2; IR (KBr): 2980, 1685, 1508, 1246, 800 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{28}N_2O_6S+Na)^+$ requires m/z 567.1560, found m/z 567.1562. Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 17.487 min (minor), t_R= 30.970 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-5'-fluoro-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ba):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1b** (19.3 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ba** (50 mg) was obtained in 89% yield as a yellowish solid. m.p. 158–159°C; $[\alpha]_D^{20}$ =+22 (c = 0.27, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.47 (td, *J* = 8.1, 5.7 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.22 (m, 1H), 6.97 (dd, *J* = 9.9, 8.7 Hz, 1H), 6.82 (td, *J* = 7.7, 0.8 Hz, 1H), 5.62 (d, *J* = 7.0 Hz, 1H), 5.58 (s, 1H), 5.28 – 5.16 (m, 1H), 4.93 (d, *J* = 9.9 Hz, 1H), 4.71 – 4.61 (m, 1H), 3.77 – 3.54 (m, 2H), 2.67 (s, 3H), 2.51 (d, *J* = 10.3 Hz, 1H), 2.46 (s, 3H), 0.66 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 170.5, 167.4, 160.8 (*J* = 249 Hz), 144.5, 140.6, 137.6, 137.5, 135.3, 131.4, 131.3, 129.8, 129.6, 129.4, 129.3, 127.3, 125.0, 124.8, 124.7, 124.6, 123.4, 120.3 (*J* = 12 Hz), 119.3, 116.1, 115.4 (*J* = 22 Hz), 64.9, 61.6, 61.0, 48.4, 26.6, 21.6, 13.2; IR (KBr): 2985, 1647, 1396, 1155, 800 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}FN_2O_6S+Na)^+$ requires m/z 585.1466, found m/z 585.1465. Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 12.137 min (minor), t_R= 21.547 min(major).

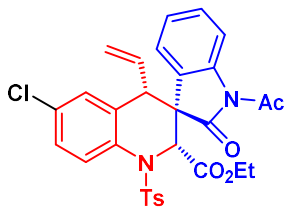
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-5'-methyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ca):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1c** (17.6 mg, 0.1 mmol) and

methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ca** (51 mg) was obtained in 92% yield as a yellowish solid. m.p. 160–161°C; $[\alpha]_D^{20}$=+20 (c = 0.24, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.31 (m, 3H), 7.25 – 7.20 (m, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.78 (td, *J* = 7.7, 0.8 Hz, 1H), 5.63 (s, 1H), 5.49 (dd, *J* = 7.8, 0.8 Hz, 1H), 5.27 – 5.17 (m, 1H), 4.95 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.60 (dd, *J* = 16.8, 1.5 Hz, 1H), 3.70 – 3.56 (m, 2H), 2.66 (s, 3H), 2.51 – 2.32 (m, 4H), 1.99 (s, 3H), 0.64 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 170.6, 167.7, 144.0, 140.6, 137.4, 136.4, 135.8, 133.4, 131.5, 131.3, 129.8, 129.6, 129.3, 128.8, 128.0, 127.5, 127.4, 125.3, 124.9, 123.7, 119.8, 115.9, 65.0, 61.9, 61.4, 51.5, 26.6, 22.6, 21.5, 13.2; IR (KBr): 2950, 1645, 1507, 1396, 1090 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{30}N_2O_6S+Na)^+$ requires m/z 581.1717, found m/z 581.1720. Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 17.630 min (minor), t_R= 44.980 min(major).

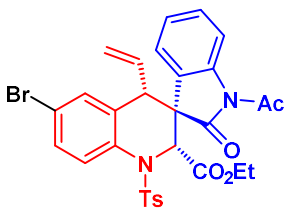
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-6'-chloro-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3da):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1d** (21 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3da** (44 mg) was obtained in 76% yield as a yellowish oil; $[\alpha]_D^{20}$=+24 (c = 0.87, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.49 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.25 (td, *J* =

8.2, 1.3 Hz, 1H), 6.87 – 6.77 (m, 2H), 5.61 (dd, *J* = 7.7, 0.8 Hz, 1H), 5.51 (s, 1H), 5.14 (dd, *J* = 9.3, 2.4 Hz, 1H), 4.91 – 4.74 (m, 2H), 3.75 – 3.57 (m, 2H), 2.68 (s, 3H), 2.50 – 2.40 (m, 4H), 0.68 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 170.5, 167.3, 144.5, 140.6, 135.1, 134.9, 134.4, 132.9, 129.8, 129.6, 129.4, 128.8, 127.3, 126.9, 124.9, 124.4, 123.7, 123.2, 116.1, 64.9, 61.7, 60.0, 48.8, 26.6, 21.6, 13.2; IR (KBr): 2980, 1760, 1369, 1170, 800 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}ClN_2O_6S+Na)^+$ requires m/z 601.1171, found m/z 601.1170. Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.570 min (minor), t_R= 7.233 min(major).

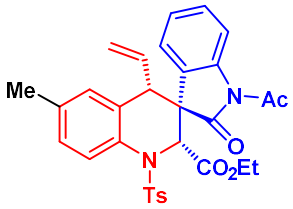
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-6'-bromo-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ea):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1e** (25.2 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ea** (50 mg) was obtained in 81% yield as a yellowish oil; $[\alpha]_D^{20}$ =+7 (c = 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.67 – 7.54 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.25 (td, *J* = 8.2, 1.2 Hz, 1H), 6.96 – 6.91 (m, 1H), 6.83 (td, *J* = 7.7, 0.9 Hz, 1H), 5.61 (dd, *J* = 7.7, 0.8 Hz, 1H), 5.50 (s, 1H), 5.14 (dd, *J* = 9.3, 2.5 Hz, 1H), 4.92 – 4.73 (m, 2H), 3.73 – 3.59 (m, 2H), 2.67 (s, 3H), 2.50 – 2.40 (m, 4H), 0.68 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 170.5, 167.3, 144.5, 140.6, 135.4, 134.9, 134.9, 131.8, 129.8, 129.8, 129.6, 129.6, 127.3, 124.9, 124.4, 123.7, 123.2, 120.8, 116.1, 64.9, 61.7, 60.0, 48.7, 26.6, 21.6, 13.2; IR (KBr): 2965, 1653, 1507, 1395, 1261 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}BrN_2O_6S+Na)^+$ requires m/z 645.0665, found m/z 645.0660. Enantiomeric

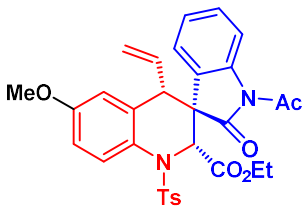
excess: 98%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70310, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.653 min (minor), t_R= 7.507 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-6'-methyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3fa):



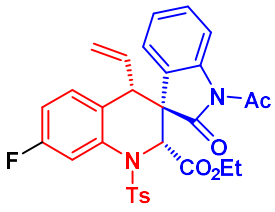
In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1f** (17.6 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3fa** (45 mg) was obtained in 80% yield as a yellowish oil; $[\alpha]_D^{20}$ =+27 (c = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.21 (td, *J* = 8.2, 1.3 Hz, 1H), 6.76 (td, *J* = 7.7, 1.0 Hz, 1H), 6.59 (s, 1H), 5.57 – 5.48 (m, 2H), 5.10 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.88 (dt, *J* = 16.9, 9.7 Hz, 1H), 4.75 (dd, *J* = 16.9, 2.0 Hz, 1H), 3.74 – 3.57 (m, 2H), 2.67 (s, 3H), 2.47 – 2.39 (m, 4H), 2.33 (s, 3H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 170.6, 167.6, 144.1, 140.6, 137.0, 135.2, 133.0, 133.0, 130.6, 129.6, 129.3, 129.3, 128.1, 127.4, 127.3, 124.9, 124.7, 124.0, 122.2, 115.8, 65.0, 61.5, 60.3, 49.0, 26.6, 21.5, 21.3, 13.2; IR (KBr): 2955, 1716, 1507, 1395, 799 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{30}N_2O_6S+Na)^+$ requires m/z 581.1717, found m/z 581.1719. Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.853 min (minor), t_R= 6.373 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-6'-methoxy-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ga):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1g** (20.5 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ga** (45 mg) was obtained in 78% yield as a yellowish oil; $[\alpha]_D^{20}$ =+43 (c = 0.92, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.01 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.33 (d, *J* = 2.7 Hz, 1H), 5.57 (d, *J* = 7.7 Hz, 1H), 5.50 (s, 1H), 5.09 (dd, *J* = 9.9, 1.4 Hz, 1H), 4.84 (dt, *J* = 19.2, 9.6 Hz, 1H), 4.76 – 4.64 (m, 1H), 3.80 (s, 3H), 3.72 – 3.57 (m, 2H), 2.67 (s, 3H), 2.45 (s, 3H), 2.34 (d, *J* = 9.4 Hz, 1H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 170.6, 167.6, 158.5, 144.1, 140.5, 135.0, 135.0, 130.3, 129.7, 129.6, 129.4, 128.3, 127.4, 124.9, 124.8, 124.0, 122.5, 115.9, 113.2, 112.8, 65.0, 61.5, 60.1, 55.5, 49.0, 26.6, 21.5, 13.2; IR (KBr): 2950, 1521, 1395, 1156, 953 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{30}N_2O_7S+Na)^+$ requires m/z 597.1666, found m/z 597.1669. Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 6.407 min (minor), t_R= 6.993 min(major).

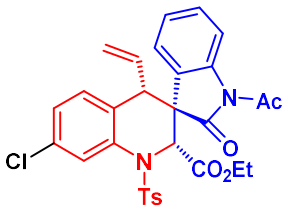
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-7'-fluoro-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ha):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1h** (17.5 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude

products were purified by column chromatography on silica gel (PE:EA=5:1), **3ha** (53 mg) was obtained in 95% yield as a yellowish oil; $[\alpha]_D^{20}$ =+25 (c = 0.32, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 (td, *J* = 8.2, 1.3 Hz, 1H), 6.96 (td, *J* = 8.3, 2.6 Hz, 1H), 6.85 – 6.72 (m, 2H), 5.59 (dd, *J* = 7.7, 0.9 Hz, 1H), 5.53 (s, 1H), 5.13 (dd, *J* = 9.2, 2.6 Hz, 1H), 4.94 – 4.77 (m, 2H), 3.76 – 3.60 (m, 2H), 2.68 (s, 3H), 2.55 – 2.39 (m, 4H), 0.69 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 170.5, 167.4, 162.4 (*J* = 246 Hz), 144.5, 140.6, 137.0 (*J* = 8 Hz), 135.0, 130.1, 129.6 (*J* = 18 Hz), 128.8, 127.8, 127.7, 127.3, 124.6 (*J* = 25 Hz), 123.8, 122.7, 116.0, 115.7, 115.5, 114.0, 113.7, 65.0, 61.7, 60.1, 48.6, 26.6, 21.6, 13.2; IR (KBr): 2950, 1636, 1507, 1398, 1261 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}FN_2O_6S+Na)^+$ requires m/z 585.1466, found m/z 585.1465. Enantiomeric excess: 96%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 7.803 min (minor), t_R= 5.457 min(major).

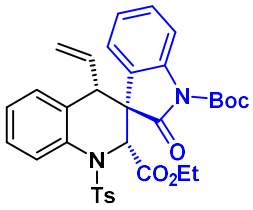
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-7'-chloro-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ia):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1i** (21 mg, 0.1 mmol) and methyleneindolinones **2a** (31 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ia** (49 mg) was obtained in 85% yield as a yellowish solid. m.p. 91–92°C; $[\alpha]_D^{20}$ =+12 (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.81 (t, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.60 (d, *J* = 7.6 Hz, 1H), 5.51 (s, 1H), 5.12 (dd, *J* = 9.3, 2.3 Hz, 1H), 4.91 – 4.76 (m, 2H), 3.74 – 3.60 (m, 2H), 2.67 (s, 3H), 2.45 – 2.43 (m, 4H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4,

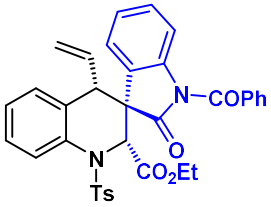
170.5, 167.3, 144.5, 140.5, 136.8, 135.0, 134.3, 131.7, 129.9, 129.8, 129.6, 128.1, 127.6, 127.3, 127.1, 124.9, 124.5, 123.8, 122.9, 116.0, 64.9, 61.7, 60.1, 48.6, 26.6, 21.6, 13.2; IR (KBr): 2960, 1792, 1540, 1507, 1418 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}ClN_2O_6S+Na)^+$ requires m/z 601.1171, found m/z 601.1170. Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 7.143 min (minor), t_R= 4.973 min(major).

(2'*R*,3*S*,4'*S*)-1-(tert-butyl)-2'-ethyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro [indoline-3,3'-quinoline]-1,2'-dicarboxylate (3ab):



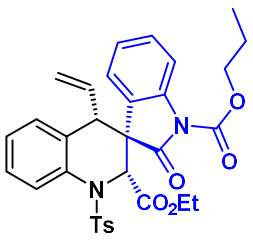
In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2b** (36 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ab** (52 mg) was obtained in 86% yield as a yellowish oil; $[\alpha]_D^{20}$ =+53 (c = 0.36, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.14 (m, 3H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.69 (dd, *J* = 11.2, 4.1 Hz, 1H), 5.56 (s, 1H), 5.46 (d, *J* = 7.7 Hz, 1H), 5.09 (dd, *J* = 9.7, 2.1 Hz, 1H), 4.94 – 4.69 (m, 2H), 3.72 – 3.55 (m, 2H), 2.44 – 2.41 (m, 4H), 1.65 (s, 9H), 0.70 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 167.7, 148.6, 144.1, 140.2, 135.7, 135.1, 133.6, 130.0, 129.6, 129.2, 128.5, 128.4, 127.3, 127.0, 126.7, 124.7, 124.1, 124.0, 122.6, 114.4, 84.8, 64.9, 61.3, 60.2, 48.7, 28.1, 21.5, 13.2; IR (KBr): 2980, 1635, 1400, 1260, 801 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{34}N_2O_7S+Na)^+$ requires m/z 625.1979, found m/z 625.1981. Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IB, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 30.773 min (minor), t_R= 43.147 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-benzoyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ac):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2c** (39 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ac** (47 mg) was obtained in 86% yield as a yellowish solid. m.p. 157–158°C; $[\alpha]_D^{20}$ =+45 (c = 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.67 (dd, *J* = 14.8, 7.5 Hz, 2H), 7.58 – 7.48 (m, 5H), 7.27 – 7.23 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.76 (td, *J* = 7.7, 0.9 Hz, 1H), 5.54 (s, 1H), 5.50 (dd, *J* = 7.7, 0.7 Hz, 1H), 5.24 (dd, *J* = 10.0, 1.9 Hz, 1H), 5.03 (dt, *J* = 17.0, 9.8 Hz, 1H), 4.82 (dd, *J* = 16.9, 1.8 Hz, 1H), 3.86 – 3.70 (m, 2H), 2.53 (d, *J* = 9.6 Hz, 1H), 2.38 (s, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 168.9, 167.8, 144.01, 140.8, 135.6, 135.1, 133.5, 133.5, 130.6, 129.9, 129.6, 129.4, 128.7, 128.3, 128.2, 127.2, 127.1, 126.8, 125.2, 124.4, 124.3, 122.8, 114.2, 65.4, 61.8, 60.4, 48.7, 21.5, 13.5; IR (KBr): 2980, 1750, 1510, 1260, 750 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{30}N_2O_6S+Na)^+$ requires m/z 629.1717, found m/z 629.1715. Enantiomeric excess: 86%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 11.893 min (minor), t_R= 8.057 min(major).

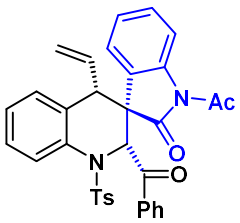
(2'*R*,3*S*,4'*S*)-2'-ethyl1-propyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-1,2'-dicarboxylate (3ad):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl

benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2d** (36 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ad** (56 mg) was obtained in 95% yield as a yellowish solid. m.p. 147–148°C; $[\alpha]_D^{20}$ =+31 (c = 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.16 (m, 4H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 5.55 (s, 1H), 5.46 (d, *J* = 7.2 Hz, 1H), 5.09 (dd, *J* = 9.7, 2.0 Hz, 1H), 4.81 (ddd, *J* = 18.9, 16.9, 4.7 Hz, 2H), 4.41 (t, *J* = 6.7 Hz, 2H), 3.75 – 3.55 (m, 2H), 2.44 – 2.41 (m, 4H), 1.86 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 167.6, 150.5, 144.1, 134.0, 135.7, 135.1, 133.5, 129.9, 129.6, 129.3, 128.6, 128.4, 127.3, 127.0, 126.7, 124.7, 124.3, 124.1, 122.7, 114.5, 69.1, 65.0, 61.4, 60.3, 48.8, 22.0, 21.5, 13.2, 10.2; IR (KBr): 2985, 1733, 1716, 1540, 800 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{32}N_2O_7S+Na)^+$ requires m/z 611.1822, found m/z 611.1830. Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.667 min (minor), t_R= 7.047 min(major).

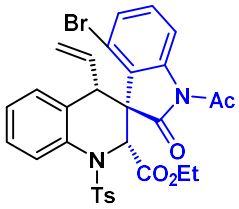
(2'*R*,3*S*,4'*S*)-1-acetyl-2'-benzoyl-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinolin]-2-one (3ae):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2e** (35 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ae** (51 mg) was obtained in 88% yield as a yellowish solid. m.p. 136–137°C; $[\alpha]_D^{20}$ =+30 (c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.70 (dd, *J* =

8.2, 3.9 Hz, 3H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26 (td, *J* = 7.7, 1.1 Hz, 1H), 7.22 – 7.12 (m, 4H), 7.11 – 7.05 (m, 1H), 6.81 – 6.73 (m, 2H), 6.47 (s, 1H), 5.44 (dd, *J* = 7.7, 0.9 Hz, 1H), 5.05 (dd, *J* = 9.5, 2.4 Hz, 1H), 4.84 – 4.71 (m, 2H), 2.66 (d, *J* = 9.0 Hz, 1H), 2.47 – 2.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 177.1, 169.8, 144.1, 139.9, 136.3, 136.1, 135.8, 133.5, 132.9, 130.2, 129.6, 129.2, 128.7, 128.7, 128.1, 127.7, 127.4, 127.0, 126.6, 125.1, 124.8, 124.1, 122.4, 115.5, 68.3, 60.6, 49.4, 26.5, 21.6; IR (KBr): 2945, 1716, 1558, 1540, 960 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{28}N_2O_5S+Na)^+$ requires m/z 599.1611, found m/z 599.1610. Enantiomeric excess: 82%, determined by HPLC (Daicel Chiralpak IA, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 15.950 min (minor), t_R= 17.880 min(major).

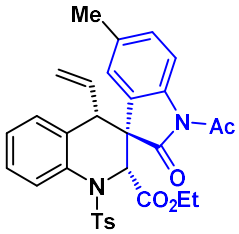
(2'*R*,3*S*,4'*S*)-1-acetyl-2'-benzoyl-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinolin]-2-one (3af):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2f** (41 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3af** (59 mg) was obtained in 95% yield as a yellowish solid. m.p. 122–123°C; $[\alpha]_D^{20}$ =+33 (c = 0.57, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.26 (s, 1H), 5.42 (dt, *J* = 16.3, 10.3 Hz, 1H), 5.10 – 5.06 (m, 2H), 4.39 (d, *J* = 10.2 Hz, 1H), 4.20 – 3.92 (m, 2H), 2.44 – 2.43 (m, 6H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 170.3, 169.4, 144.1, 142.0, 137.2, 135.6, 132.7, 130.5, 129.9, 129.7, 129.3, 128.0, 127.2, 126.6, 126.5, 125.1, 122.9, 118.1, 115.3, 62.3, 61.7, 61.3, 46.1, 26.9, 21.6, 13.7; IR (KBr): 2935, 1716, 1653, 1540, 799 cm^{-1}; ESI FTMS exact mass calcd for

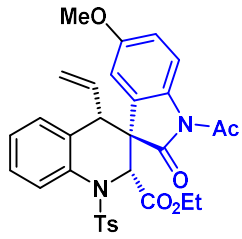
$(C_{30}H_{27}BrN_2O_6S+Na)^+$ requires m/z 645.0665, found m/z 645.0660. Enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 19.470 min (minor), t_R= 10.207 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-5-methyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ag):



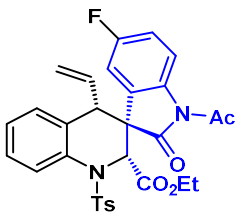
In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2g** (33 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ag** (51 mg) was obtained in 92% yield as a yellowish oil; $[\alpha]_D^{20}$=+24 (c = 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.24 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.52 (s, 1H), 5.20 (d, *J* = 1.1 Hz, 1H), 5.09 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.87 (dd, *J* = 18.1, 8.5 Hz, 1H), 4.75 (dd, *J* = 16.9, 2.0 Hz, 1H), 3.74 – 3.61 (m, 2H), 2.66 (s, 3H), 2.45 – 2.43 (m, 4H), 1.95 (s, 3H), 0.67 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 170.5, 167.6, 144.2, 138.2, 135.7, 135.1, 134.3, 133.5, 130.5, 129.7, 129.6, 128.6, 128.4, 127.3, 126.9, 126.8, 124.7, 124.5, 122.3, 115.6, 26.6, 21.5, 21.0, 13.2; IR (KBr): 2985, 1745, 1636, 1540, 1089, 799 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{30}N_2O_6S+Na)^+$ requires m/z 581.1717, found m/z 581.1718. Enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.120 min (minor), t_R= 5.923 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-5-methoxy-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ah):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2h** (35 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ah** (51 mg) was obtained in 89% yield as a yellowish solid. m.p. 148–149 °C; $[\alpha]_D^{20}$ =+27 (c = 0.52, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.25 (m, 3H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.7 Hz, 1H), 5.52 (s, 1H), 5.11 (dd, *J* = 9.9, 1.9 Hz, 1H), 4.99 (d, *J* = 2.7 Hz, 1H), 4.90 (dt, *J* = 19.3, 9.7 Hz, 1H), 4.77 (dd, *J* = 16.9, 1.9 Hz, 1H), 3.84 – 3.65 (m, 2H), 3.34 (s, 3H), 2.65 (s, 3H), 2.50 – 2.41 (m, 4H), 0.71 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 170.3, 167.5, 156.3, 144.2, 135.8, 135.1, 133.9, 133.5, 130.3, 129.6, 128.6, 128.4, 127.3, 127.1, 127.0, 125.8, 122.5, 116.9, 115.1, 109.0, 65.0, 61.6, 60.5, 55.0, 48.9, 26.4, 21.6, 13.3; IR (KBr): 2980, 1684, 1558, 1246, 952, 688 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{30}N_2O_7S+Na)^+$ requires m/z 597.1666, found m/z 597.1669. Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 14.963 min (minor), t_R= 13.073 min(major).

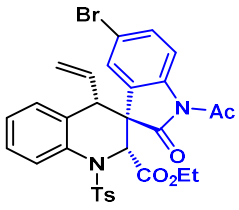
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-5-fluoro-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ai):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2i** (33 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products

were purified by column chromatography on silica gel (PE:EA=5:1), **3ai** (53 mg) was obtained in 95% yield as a yellowish solid. m.p. 148–149 °C; $[\alpha]_D^{20}$ =+29 (c = 0.45, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 9.0, 4.8 Hz, 1H), 8.08 – 7.98 (m, 1H), 7.54 (dd, *J* = 14.5, 8.0 Hz, 3H), 7.35 – 7.25 (m, 3H), 6.91 (td, *J* = 8.9, 2.7 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.53 (s, 1H), 5.20 – 5.08 (m, 2H), 4.95 – 4.72 (m, 2H), 3.79 – 3.68 (m, 2H), 2.66 (s, 3H), 2.50 – 2.36 (m, 4H), 0.74 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 170.4, 167.4, 159.2 (*J* = 244 Hz), 144.3, 136.6, 136.6, 135.5, 135.0, 132.9, 123.0, 129.7, 129.0, 128.4, 127.3, 126.8, 126.7, 122.8, 117.3 (*J* = 8.0 Hz), 115.9 (*J* = 22.0 Hz), 111.6 (*J* = 26.0 Hz), 64.9, 61.7, 60.5, 60.5, 48.9, 26.5, 21.6, 13.3; IR (KBr): 2983, 1716, 1540, 1246, 800, 688 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}FN_2O_6S+Na)^+$ requires m/z 585.1466, found m/z 5585.1465. Enantiomeric excess: 96%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.837 min (minor), t_R= 5.123 min(major).

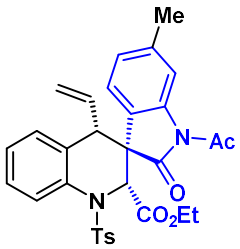
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-5-bromo-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3aj):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2j** (40 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3aj** (58 mg) was obtained in 93% yield as a yellowish oil; $[\alpha]_D^{20}$ =+34 (c = 0.64, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.64 – 7.51 (m, 3H), 7.37 – 7.26 (m, 4H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.52 (s, 1H), 5.47 (d, *J* = 2.1 Hz, 1H), 5.13 (dd, *J* = 9.8, 2.0 Hz, 1H), 4.95 – 4.69 (m, 2H), 3.85 – 3.67 (m, 2H), 2.66 (s, 3H), 2.53 – 2.35 (m, 4H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 170.4, 167.4, 144.3, 139.5, 135.5, 135.0, 132.9, 132.3, 129.9, 129.7, 129.0, 128.5, 127.3, 127.3, 127.0,

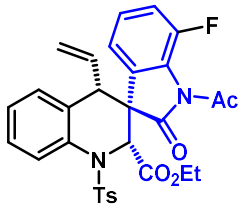
126.9, 126.8, 122.8, 117.7, 117.4, 64.9, 61.8, 60.4, 48.9, 26.6, 21.6, 13.4; IR (KBr): 2980, 1771, 1636, 1473, 799 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}BrN_2O_6S+Na)^+$ requires m/z 645.0665, found m/z 645.0660. Enantiomeric excess: 96%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 9.773 min (minor), t_R= 11.407 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-6-methyl-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3ak):



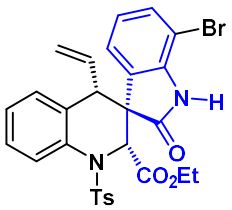
In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2k** (35 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3ak** (48 mg) was obtained in 86% yield as a yellowish oil; $[\alpha]_D^{20}$=+49 (c = 0.66, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.97 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.20 (m, 3H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.51 (s, 1H), 5.34 (d, *J* = 7.8 Hz, 1H), 5.09 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.90 (dt, *J* = 17.0, 9.7 Hz, 1H), 4.75 (dd, *J* = 16.9, 1.9 Hz, 1H), 3.75 – 3.58 (m, 2H), 2.66 (s, 3H), 2.43 – 2.41 (m, 4H), 2.25 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 170.7, 167.6, 144.2, 140.6, 139.7, 135.70, 135.1, 133.4, 130.5, 129.6, 128.6, 128.3, 127.3, 127.0, 126.7, 125.3, 123.6, 122.2, 121.6, 116.5, 65.0, 61.5, 60.1, 48.9, 26.7, 21.8, 21.6, 13.3; IR (KBr): 2960, 1733, 1646, 1540, 1010, 799 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{30}N_2O_6S+Na)^+$ requires m/z 581.1717, found m/z 581.1720. Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.367 min (minor), t_R= 7.420 min(major).

(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-7-fluoro-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3al):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2l** (33 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3al** (48 mg) was obtained in 85% yield as a yellowish solid. m.p. 129–130°C; $[\alpha]_D^{20}$ =+33 (c = 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 1H), 7.59 – 7.48 (m, 3H), 7.30 – 7.25 (m, 3H), 6.99 (ddd, *J* = 10.8, 8.5, 0.8 Hz, 1H), 6.83 – 6.70 (m, 2H), 5.54 (s, 1H), 5.30 (dd, *J* = 7.6, 0.9 Hz, 1H), 5.13 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.94 (dt, *J* = 16.9, 9.8 Hz, 1H), 4.76 (dd, *J* = 16.9, 1.8 Hz, 1H), 3.77 – 3.65 (m, 2H), 2.67 (s, 3H), 2.43 – 2.41 (m, 4H), 0.73 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 167.9, 167.4, 149.5 (*J* = 253 Hz), 144.3, 135.6, 135.0, 133.0, 130.0, 129.6, 128.8, 128.4, 128.4, 128.3, 127.3, 127.2, 126.8, 126.7, 126.1 (*J* = 7 Hz), 122.7, 119.7, 119.6, 117.9 (*J* = 20 Hz), 64.5, 61.8, 61.7, 49.1, 25.9, 21.6, 13.3; IR (KBr): 2950, 1653, 1558, 1473, 1264, 799 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{27}FN_2O_6S+Na)^+$ requires m/z 585.1466, found m/z 585.1465. Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 17.277 min (minor), t_R= 32.587 min(major).

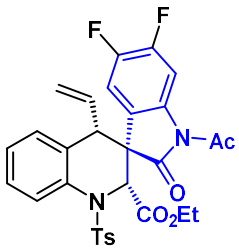
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-7-bromo-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3am):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and

methyleneindolinones **2m** (40 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=2:1), **3am** (52 mg) was obtained in 90% yield as a yellowish oil; $[\alpha]_D^{20}$ =+24 (c = 0.41, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 6.0, 1.8 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 4H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.50 (t, *J* = 7.9 Hz, 1H), 5.48 (s, 1H), 5.34 (d, *J* = 7.5 Hz, 1H), 5.12 (dd, *J* = 9.8, 1.9 Hz, 1H), 4.91 (dt, *J* = 16.9, 9.6 Hz, 1H), 4.78 (dd, *J* = 16.9, 1.9 Hz, 1H), 3.78 – 3.71 (m, 2H), 2.43 – 2.41 (m, 4H), 0.72 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 167.7, 144.1, 140.8, 135.6, 135.2, 133.8, 131.7, 130.0, 129.6, 128.6, 128.5, 127.6, 127.3, 127.0, 126.5, 123.7, 123.4, 122.6, 102.4, 64.4, 61.7, 61.5, 47.9, 21.6, 13.3; IR (KBr): 2950, 1646, 1473, 1152, 800, 688 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{25}BrN_2O_5S+Na)^+$ requires m/z 603.0560, found m/z 603.0561. Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 5.457 min (minor), t_R= 4.513 min(major).

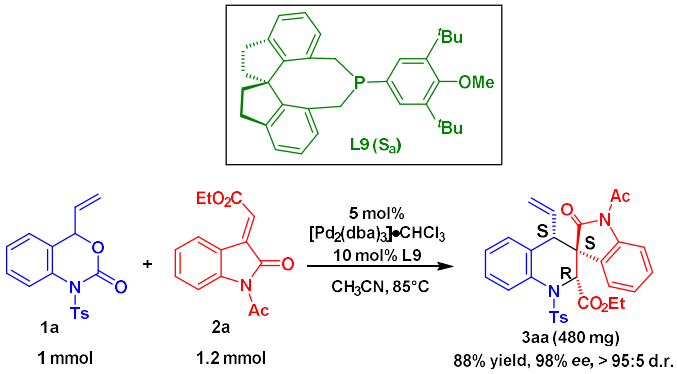
(2'*R*,3*S*,4'*S*)-ethyl-1-acetyl-5,6-difluoro-2-oxo-1'-tosyl-4'-vinyl-1',4'-dihydro-2'*H*-spiro[indoline-3,3'-quinoline]-2'-carboxylate (3an):



In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (5.2 mg, 0.005 mmol), **ligand L9** (5.0 mg, 0.01 mmol), vinyl benzoxazinanones **1a** (17.5 mg, 0.1 mmol) and methyleneindolinones **2n** (35 mg, 0.12 mmol) were mixed in dry CH_3CN (1 mL) at room temperature. Then the resulting solution was stirred at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3an** (47 mg) was obtained in 82% yield as a yellowish solid. m.p. 125–126°C; $[\alpha]_D^{20}$ =+38 (c = 0.45, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 11.5, 7.2 Hz, 1H), 8.02 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 3H), 7.34 – 7.24 (m, 3H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.50 (s, 1H), 5.24 (dd, *J* = 9.8, 7.9 Hz, 1H),

5.14 (dd, J = 9.6, 2.1 Hz, 1H), 4.90 – 4.76 (m, 2H), 3.86 – 3.69 (m, 2H), 2.66 (s, 3H), 2.51 – 2.40 (m, 4H), 0.80 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 170.2, 167.4, 150.2 (dd, J = 248, 13 Hz), 147.0 (dd, J = 247, 13 Hz), 144.4, 136.6 (J = 10 Hz), 135.5, 134.9, 132.7, 129.7, 129.2, 128.5, 127.4, 127.3, 126.8, 123.1, 120.7 (J = 7 Hz), 113.2 (J = 21 Hz), 106.6 (J = 25 Hz), 64.9, 61.8, 60.2, 48.8, 26.4, 21.6, 13.4; IR (KBr): 2945, 1636, 1397, 1260, 799 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{26}F_2N_2O_6S+Na)^+$ requires m/z 603.1372, found m/z 603.1374. Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 4.967 min (minor), t_R= 4.597 min(major).

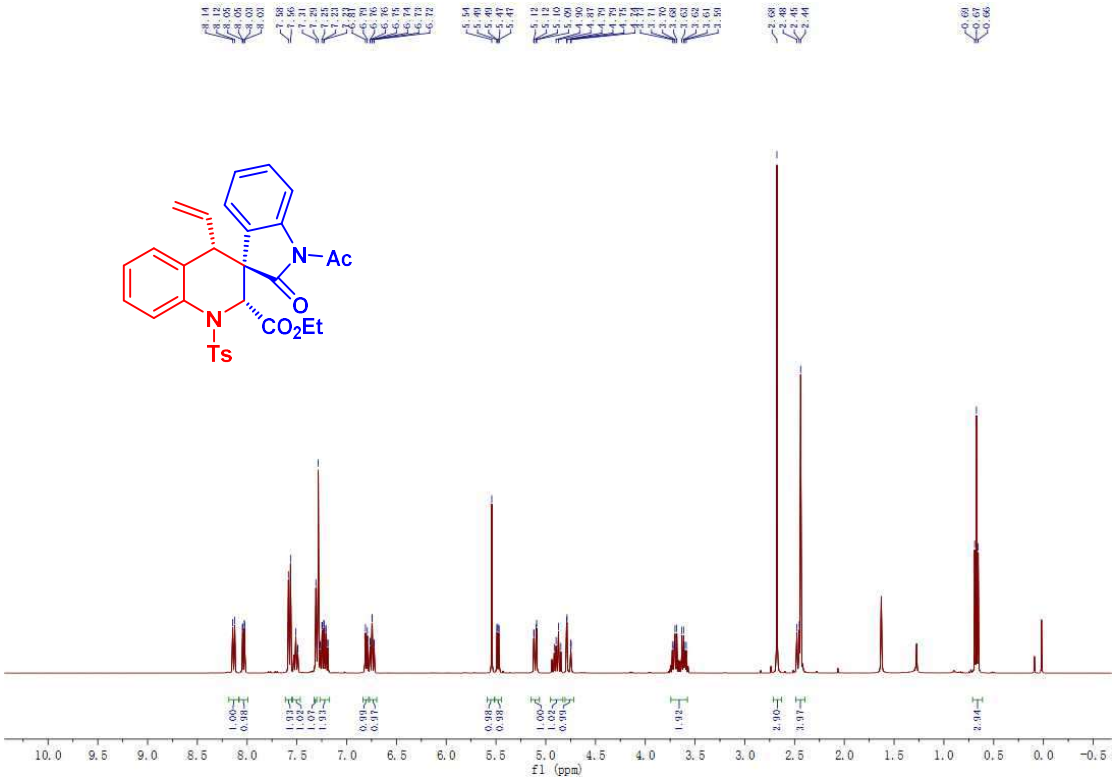
4. Procedure for the preparative scale synthesis of product 3aa



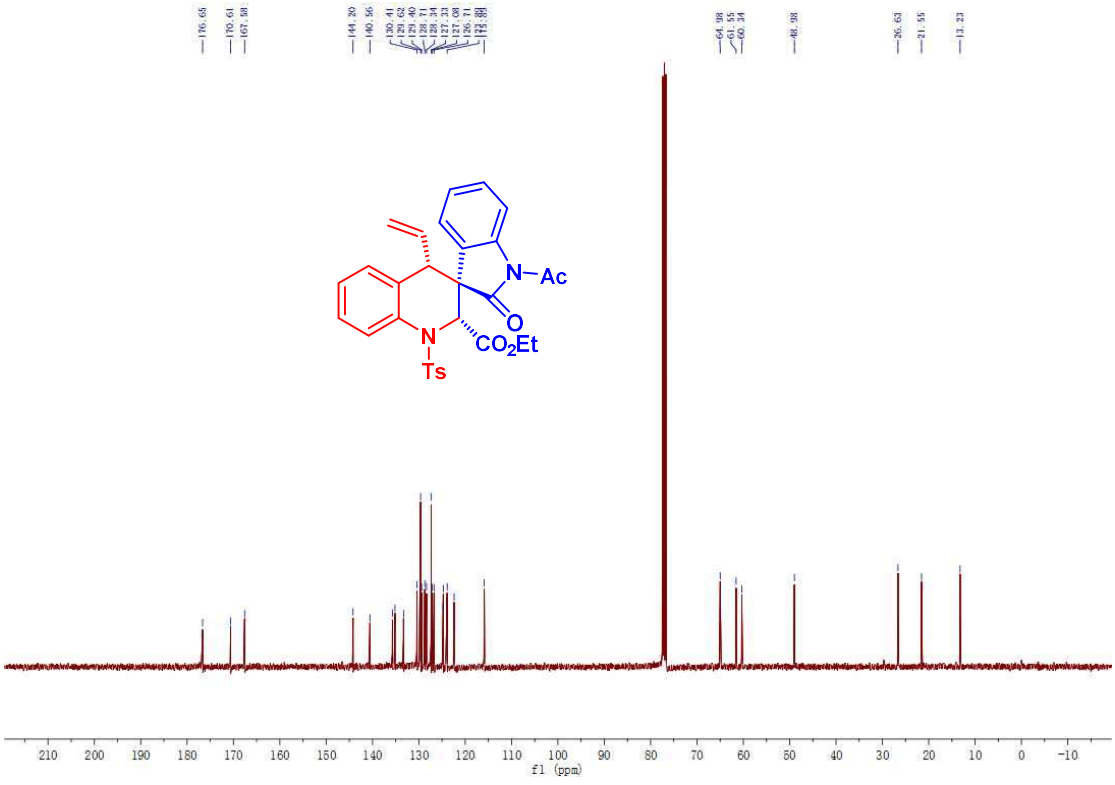
In a flame dried Schlenk tube under N_2, $Pd_2(dba)_3$•$CHCl_3$ (52 mg, 0.05 mmol), **ligand L9** (50 mg, 0.1 mmol), vinyl benzoxazinanones **1a** (175 mg, 1.0 mmol) and methyleneindolinones **2a** (310 mg, 1.2 mmol) were mixed in dry CH_3CN (20 mL) at room temperature. Then the resulting solution was refluxed at 85 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude products were purified by column chromatography on silica gel (PE:EA=5:1), **3aa** (480 mg) was obtained as a yellow solid in 88% yield, Enantiomeric excess: 98%.

5. Copies of NMR spectra

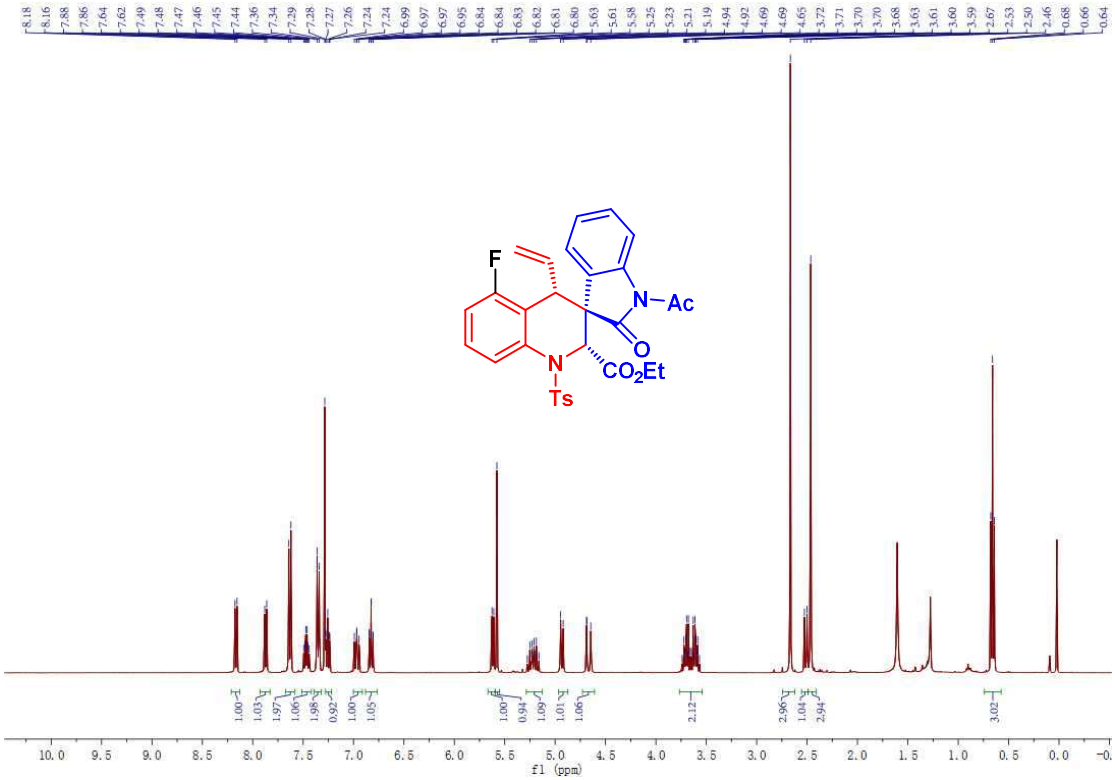
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**



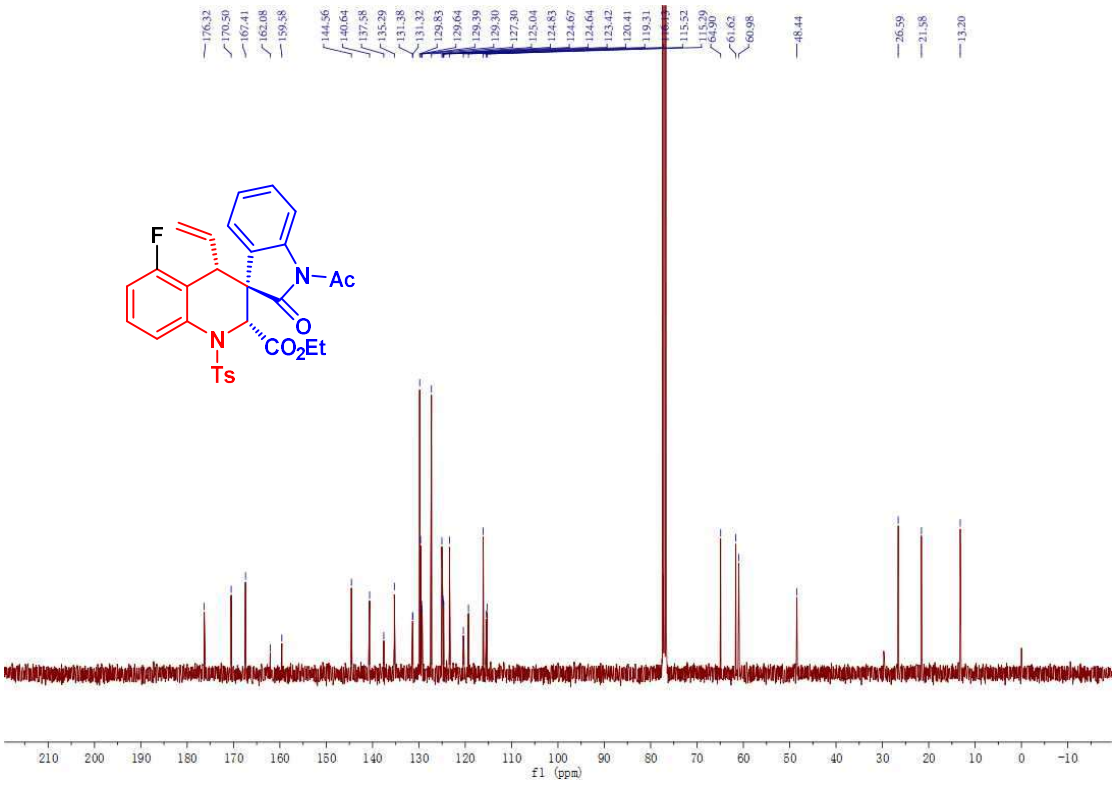
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aa**



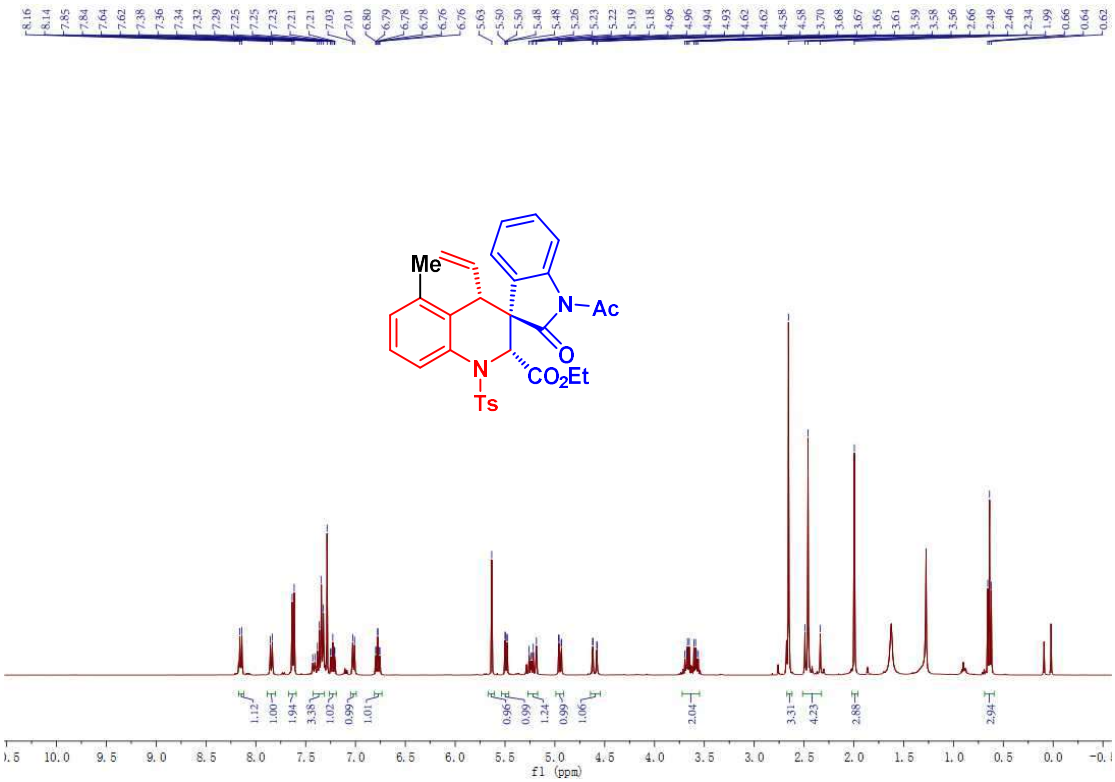
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ba**



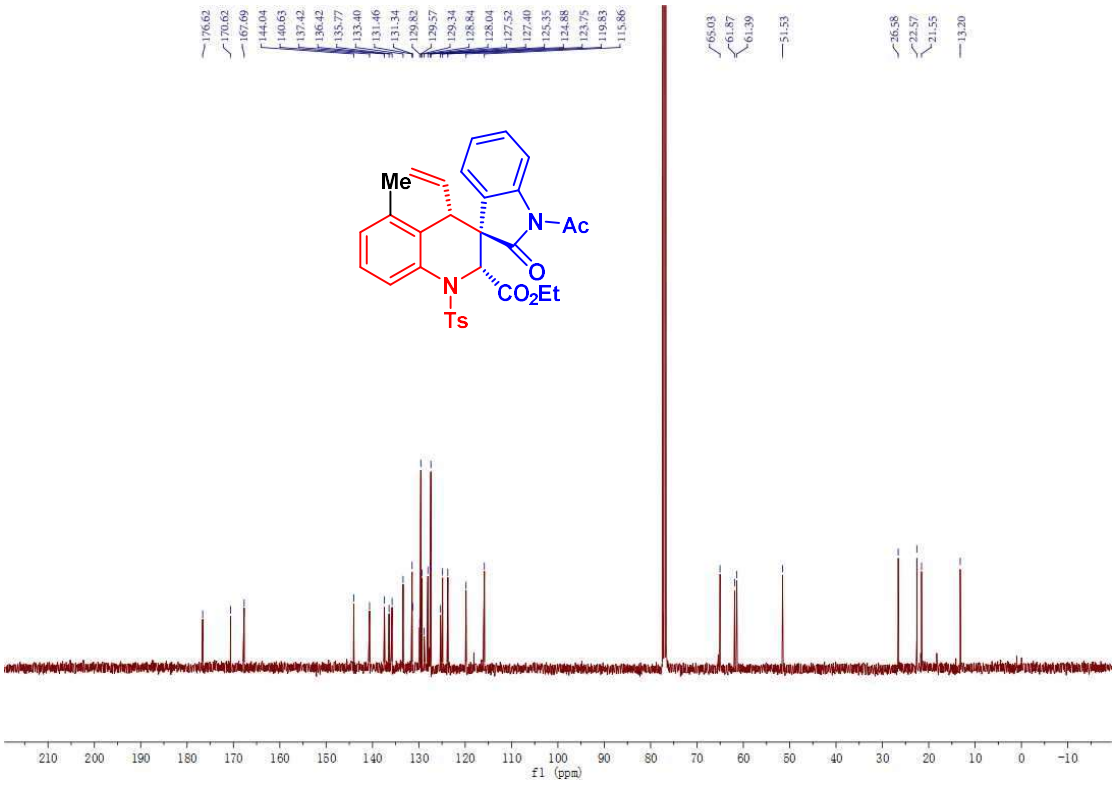
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ba**



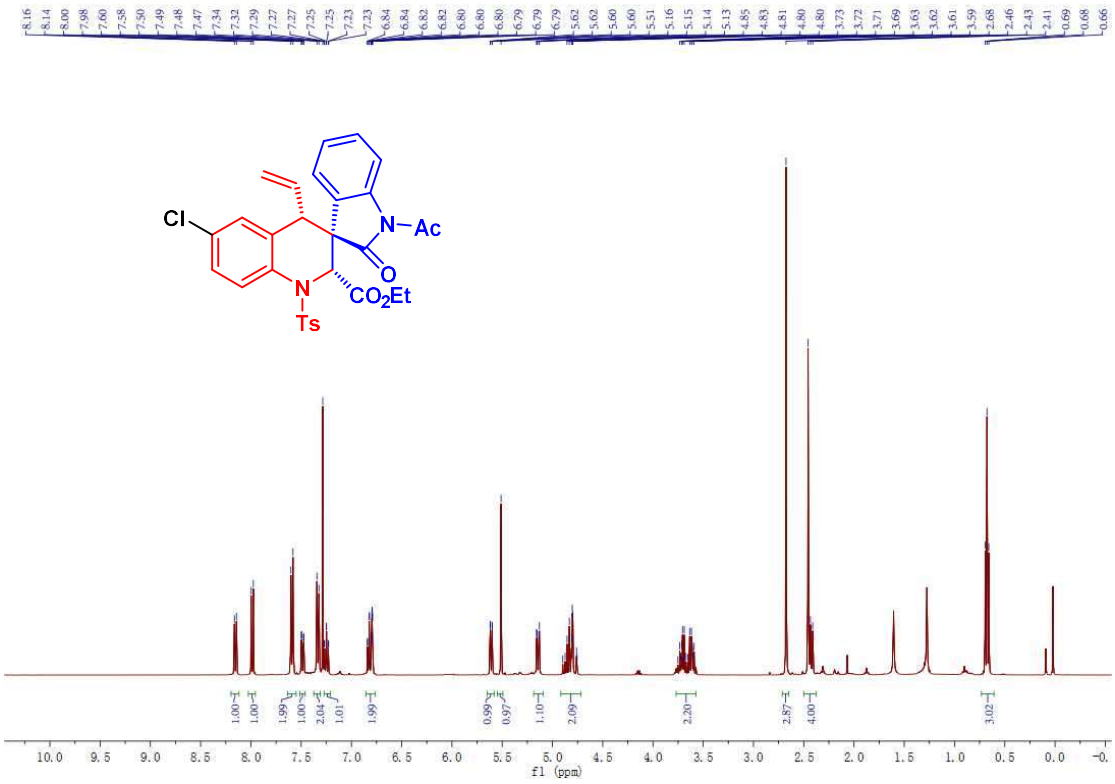
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ca**



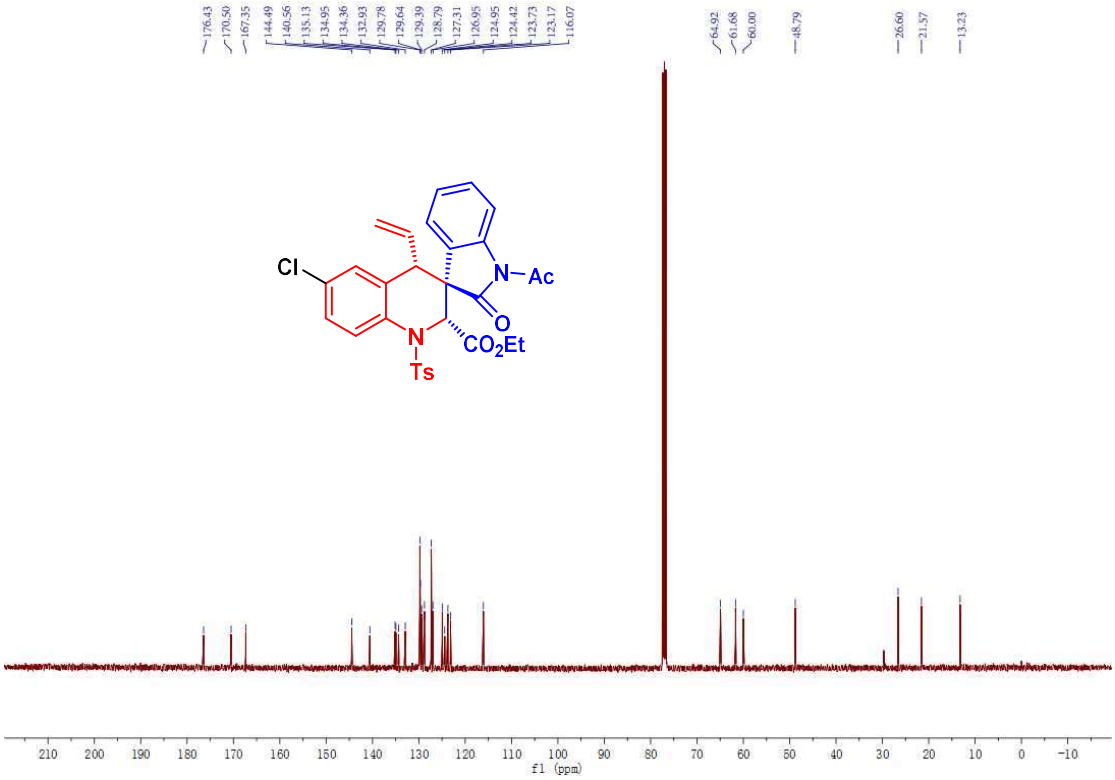
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ca**



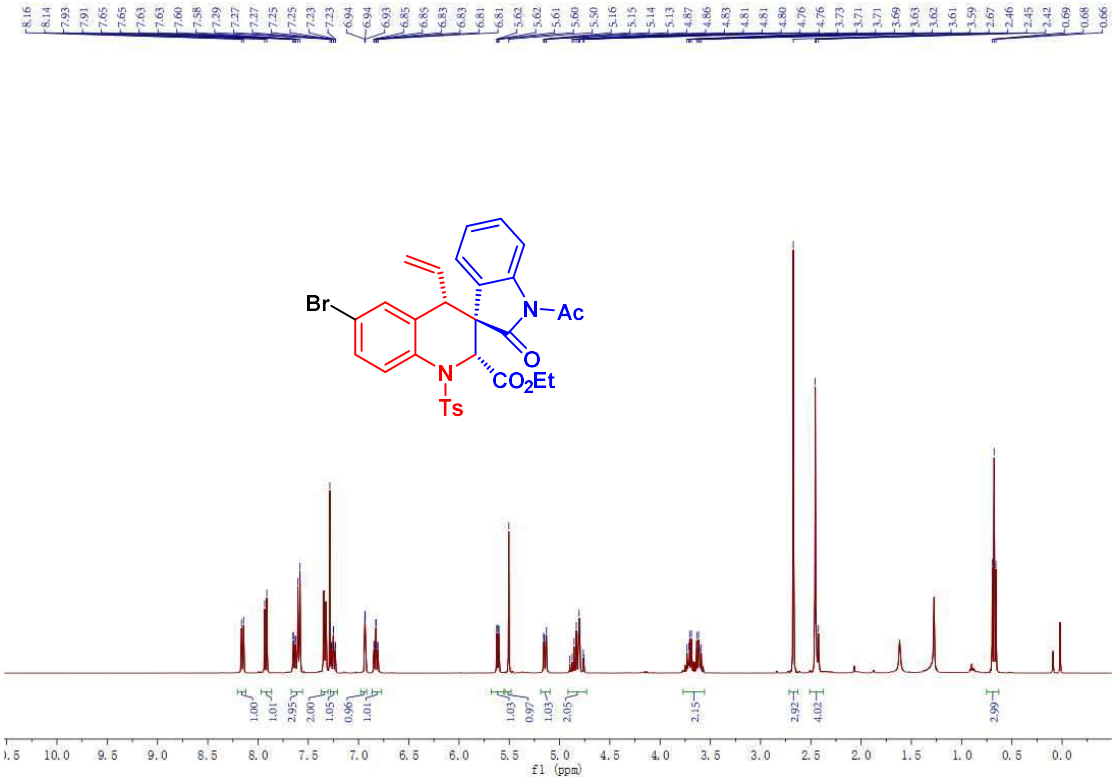
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3da**



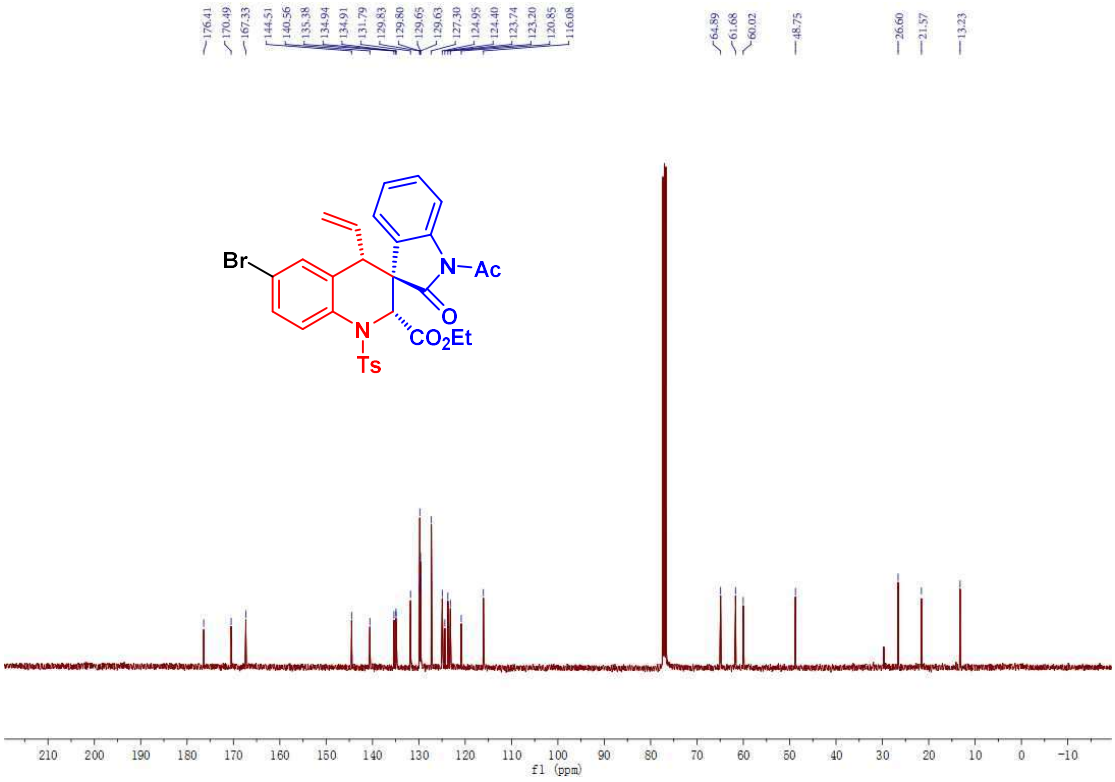
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3da**



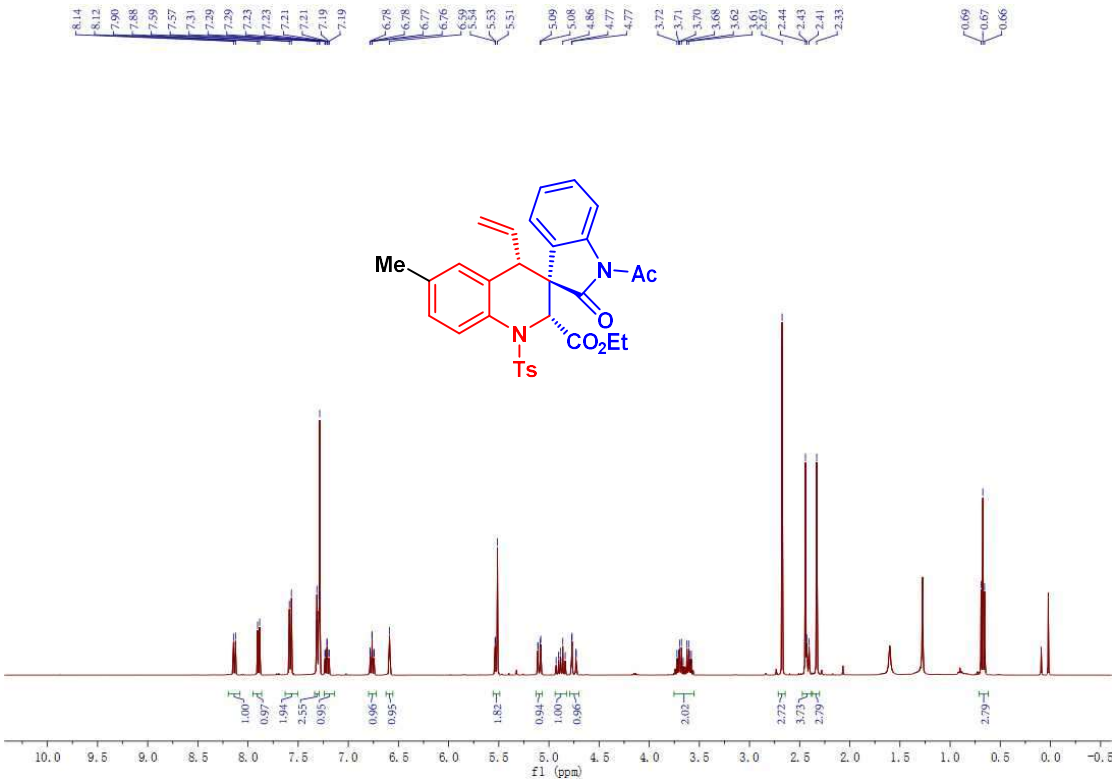
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ea**



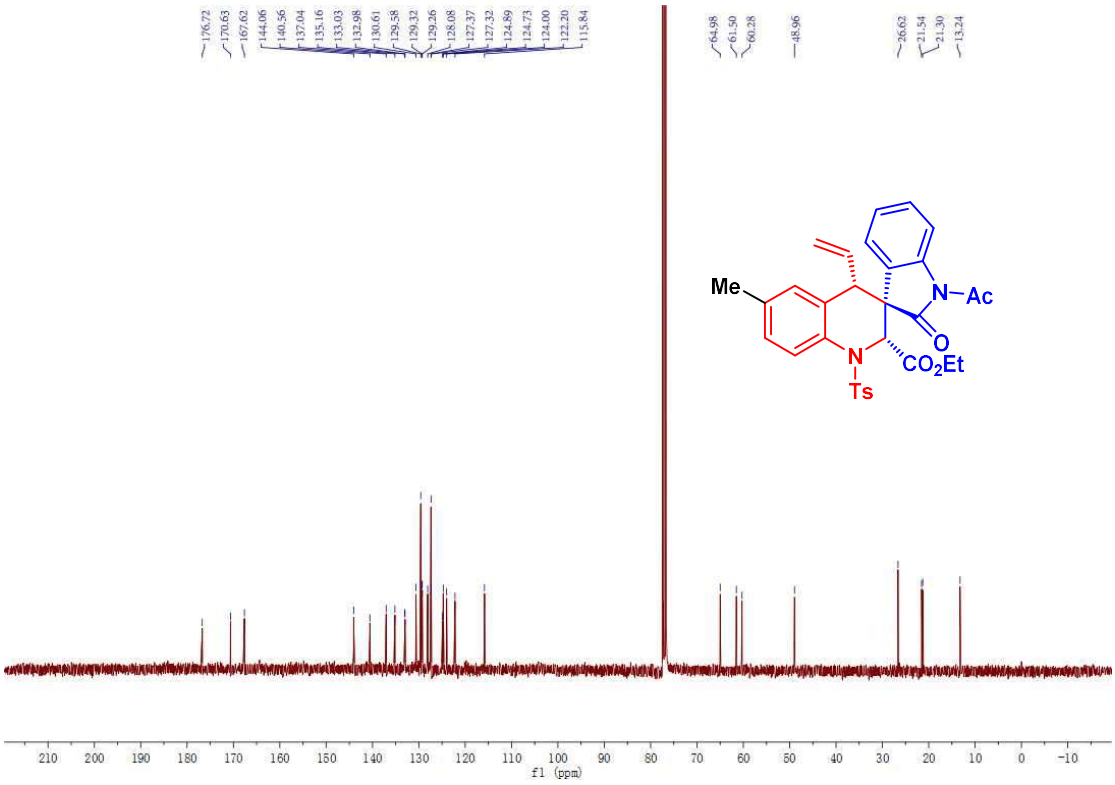
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ea**



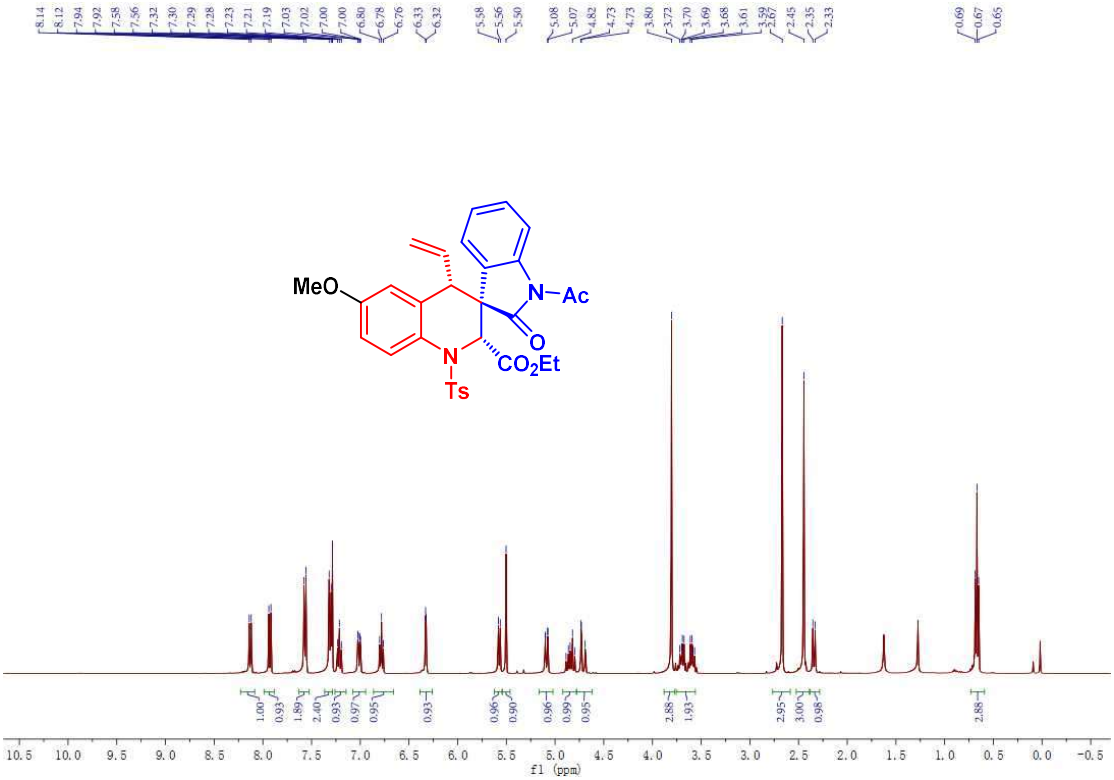
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3fa**



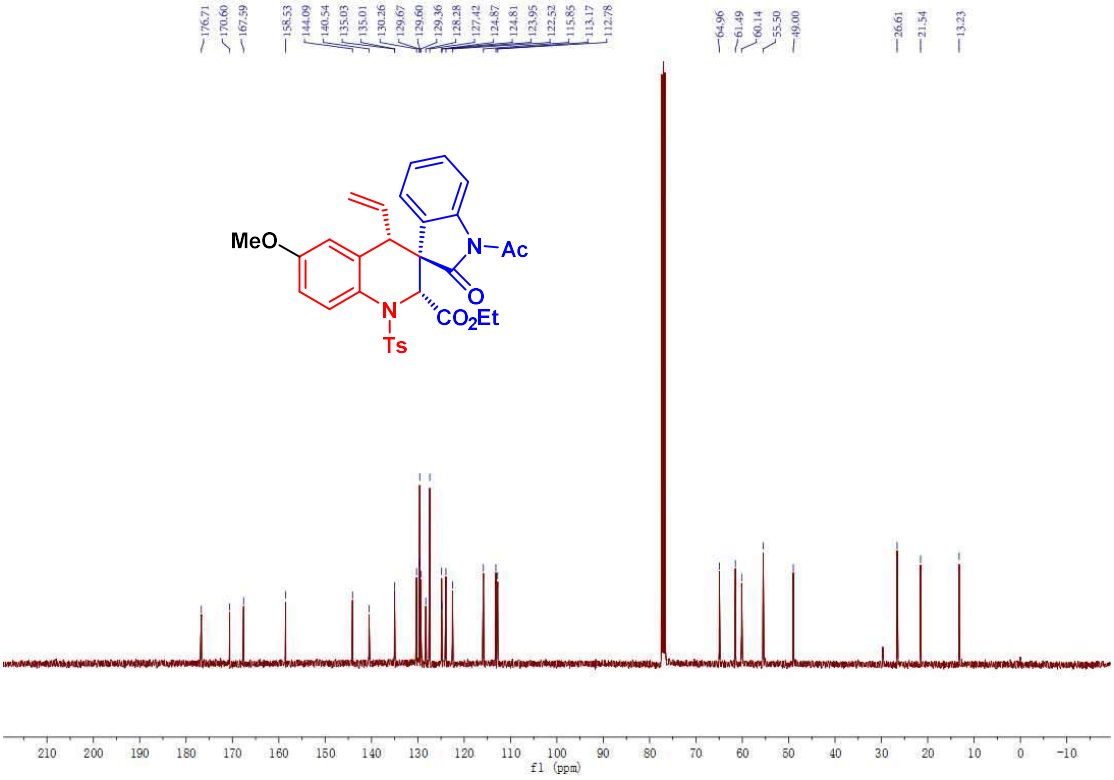
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3fa**



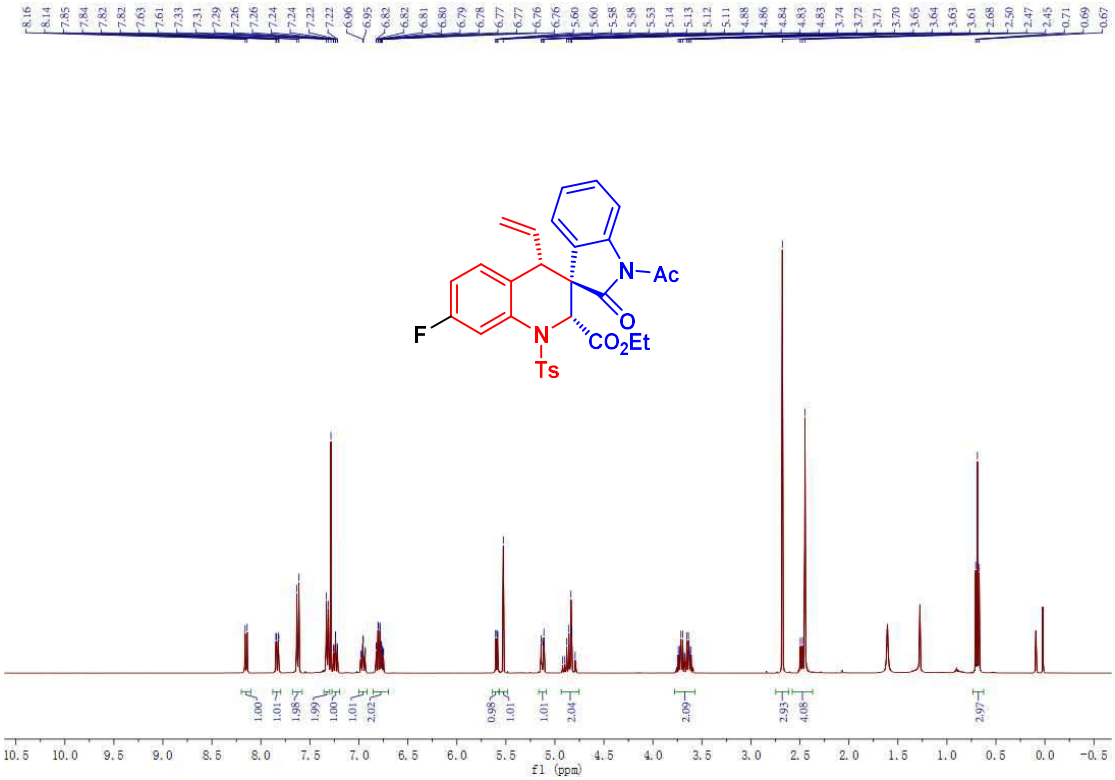
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ga**



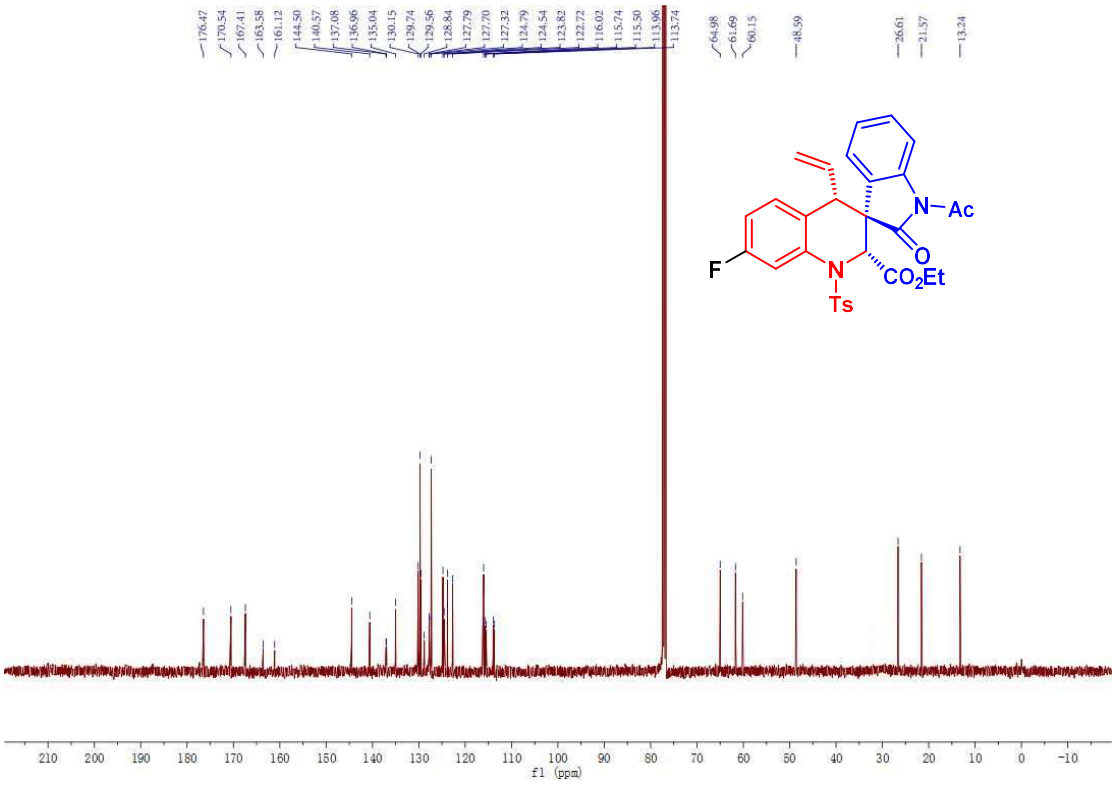
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ga**



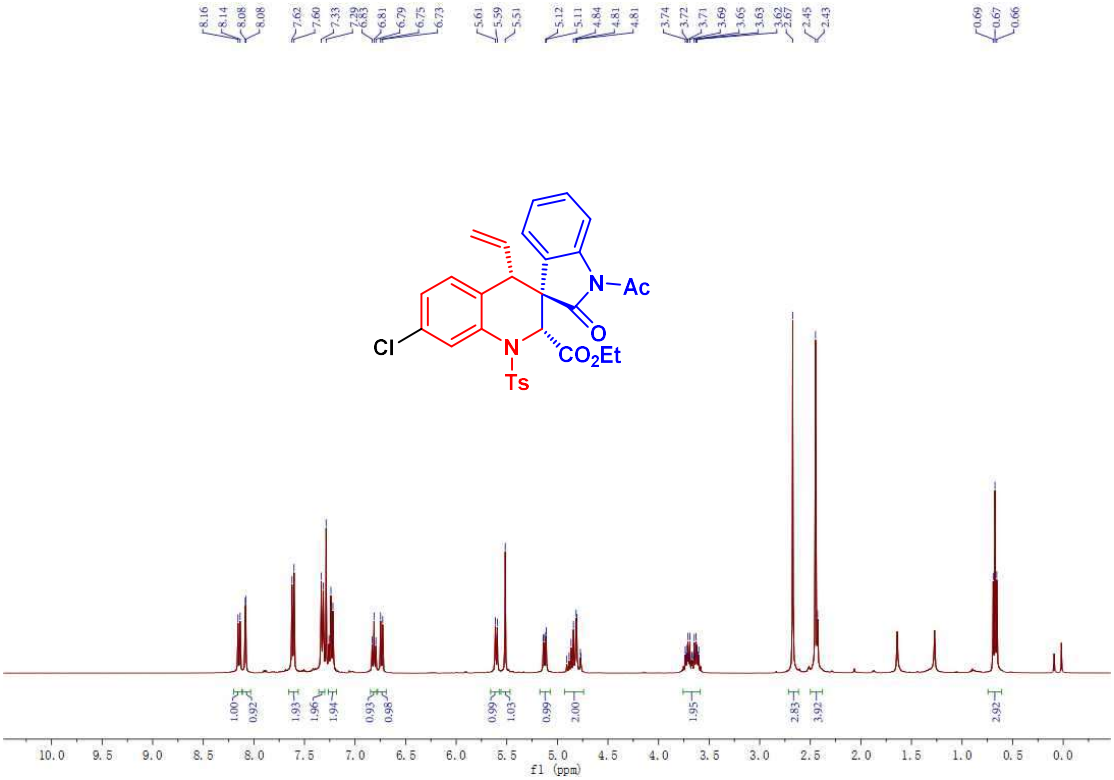
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ha**



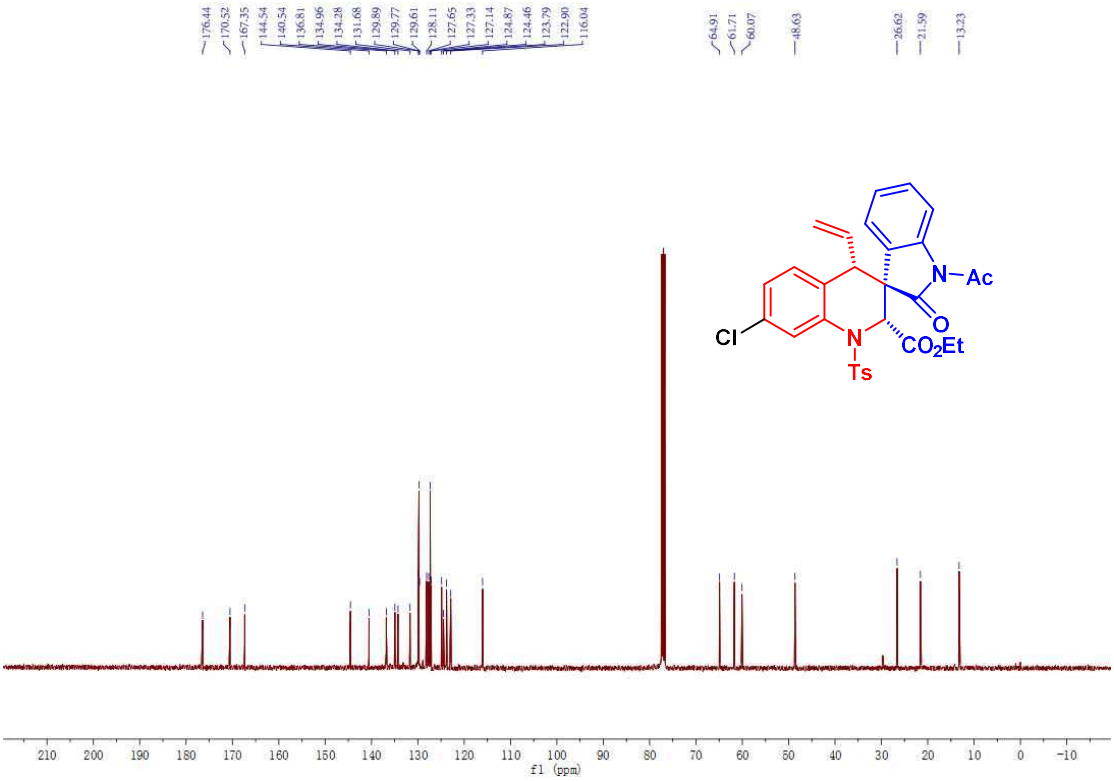
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ha**



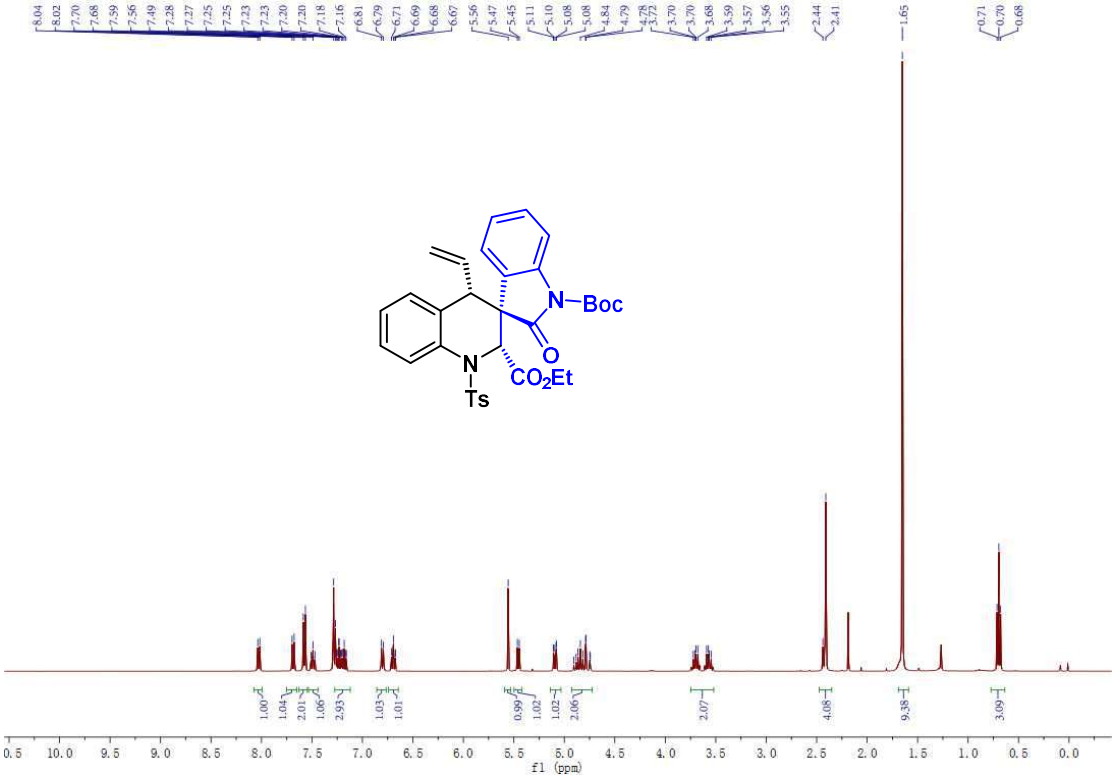
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ia**



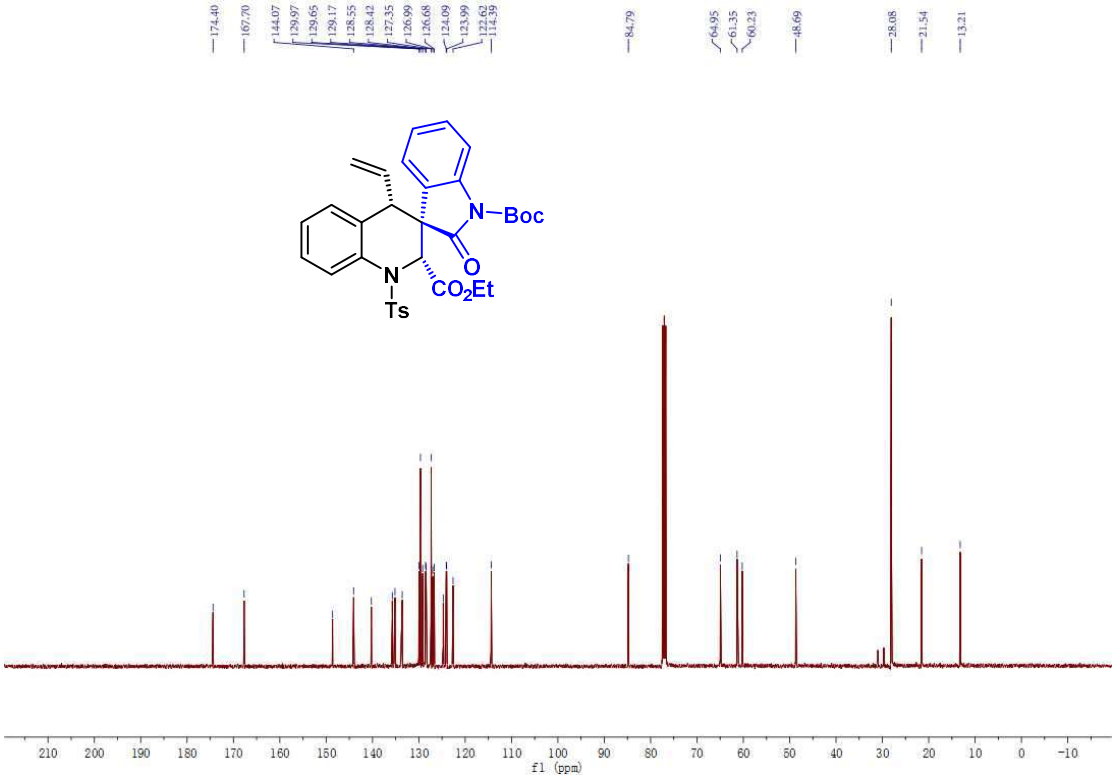
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ia**



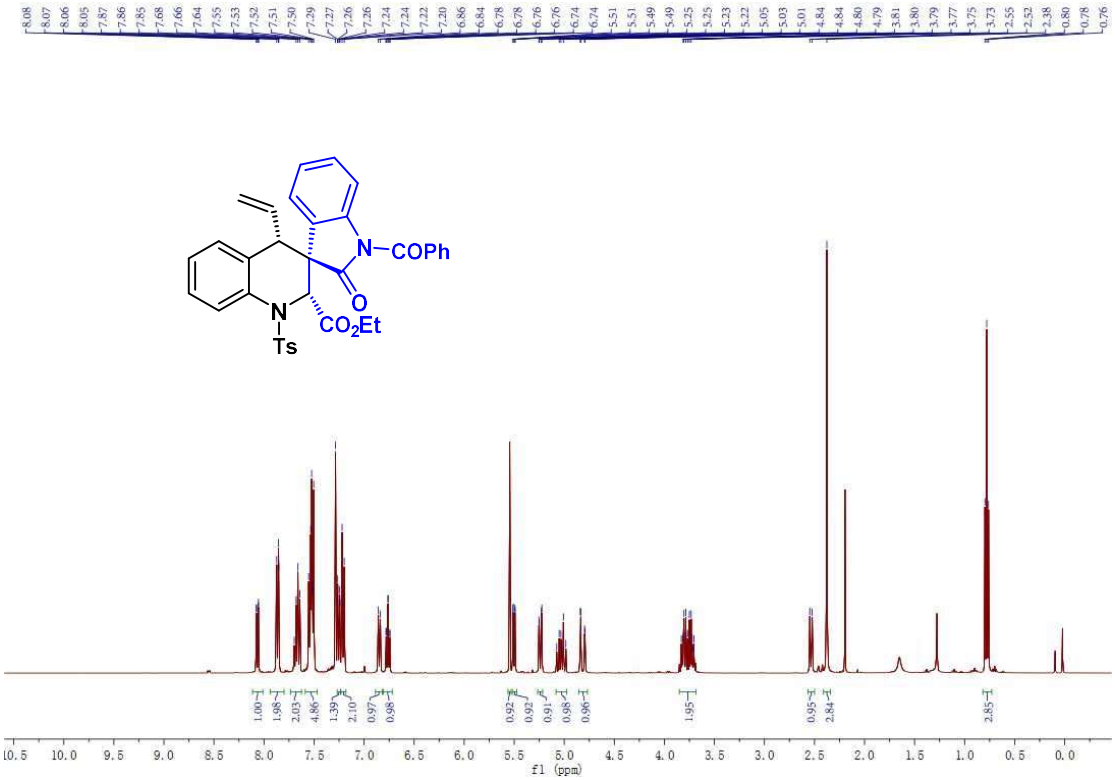
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ab**



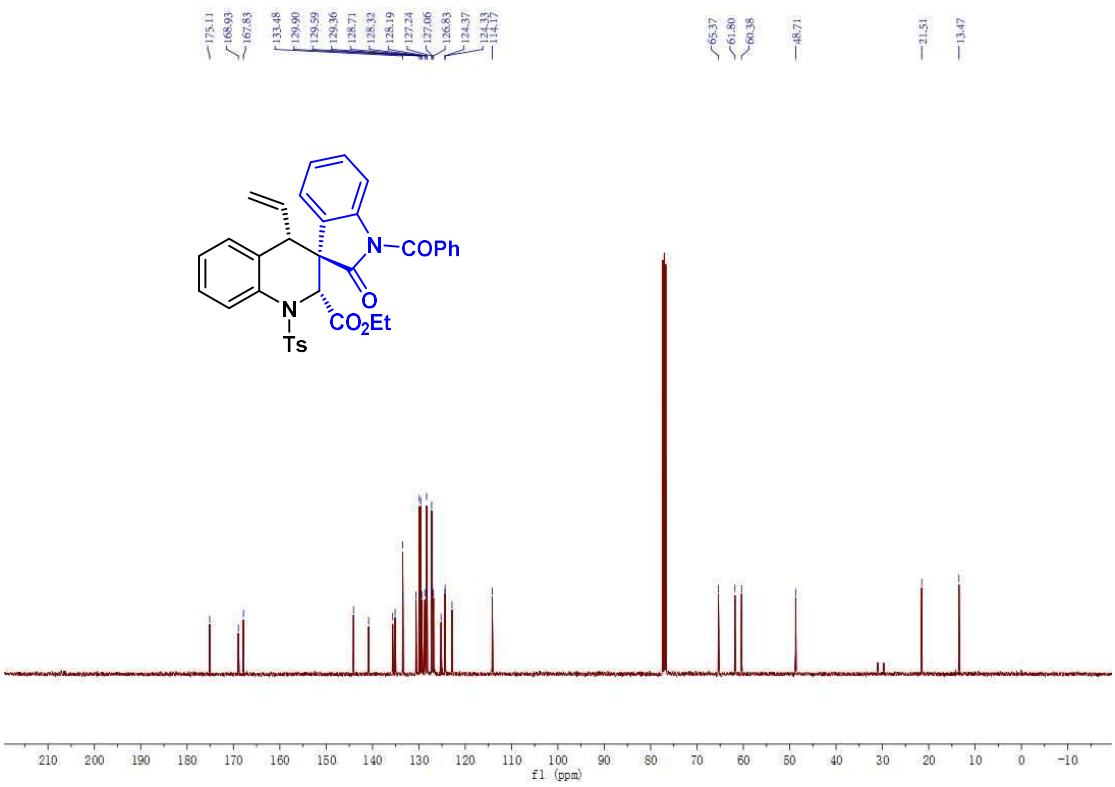
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ab**



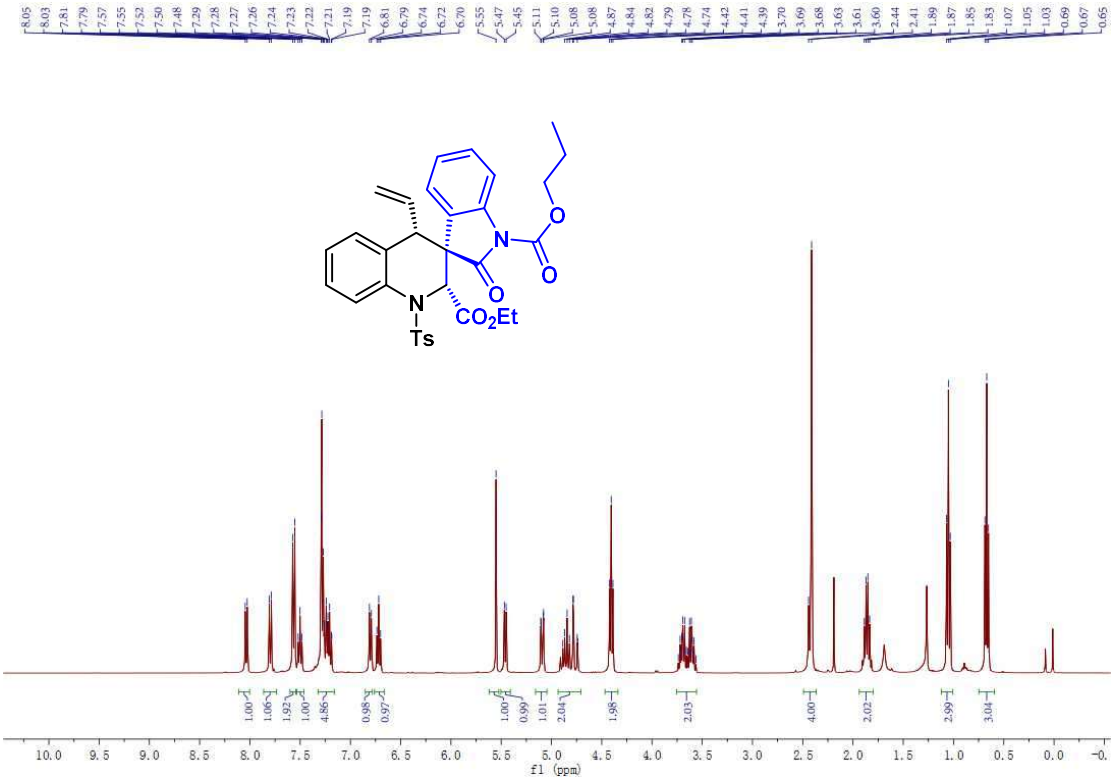
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ac**



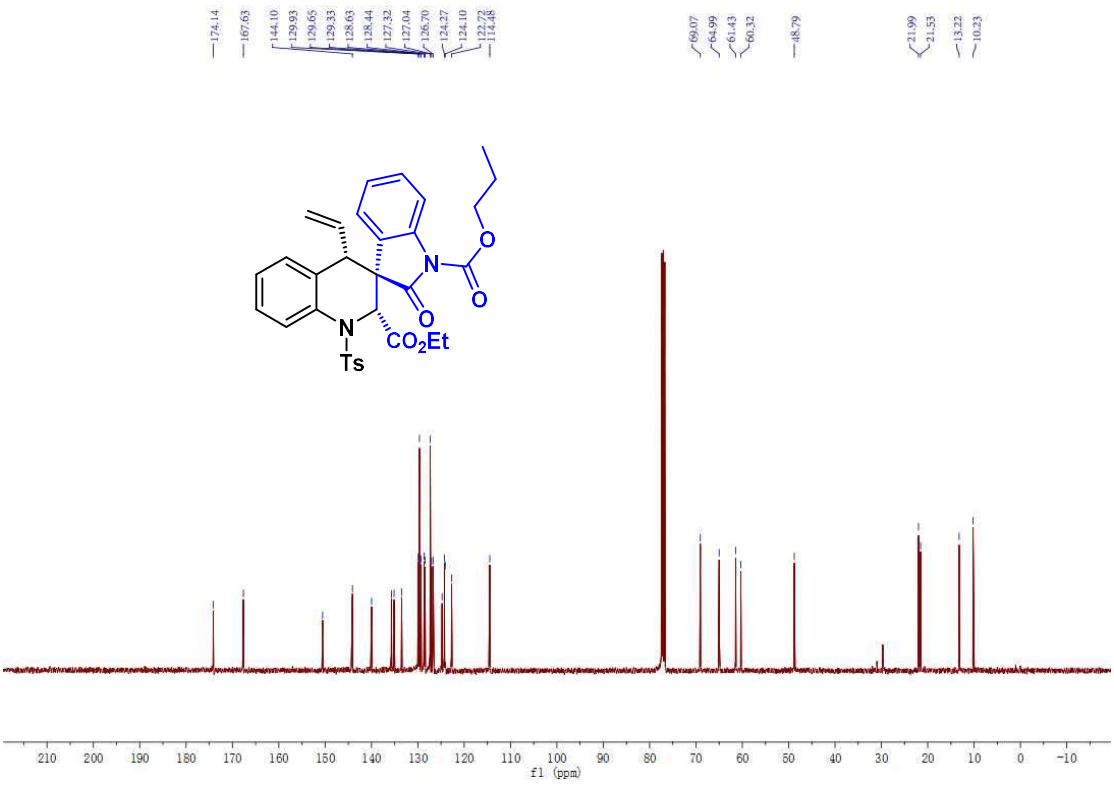
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ac**



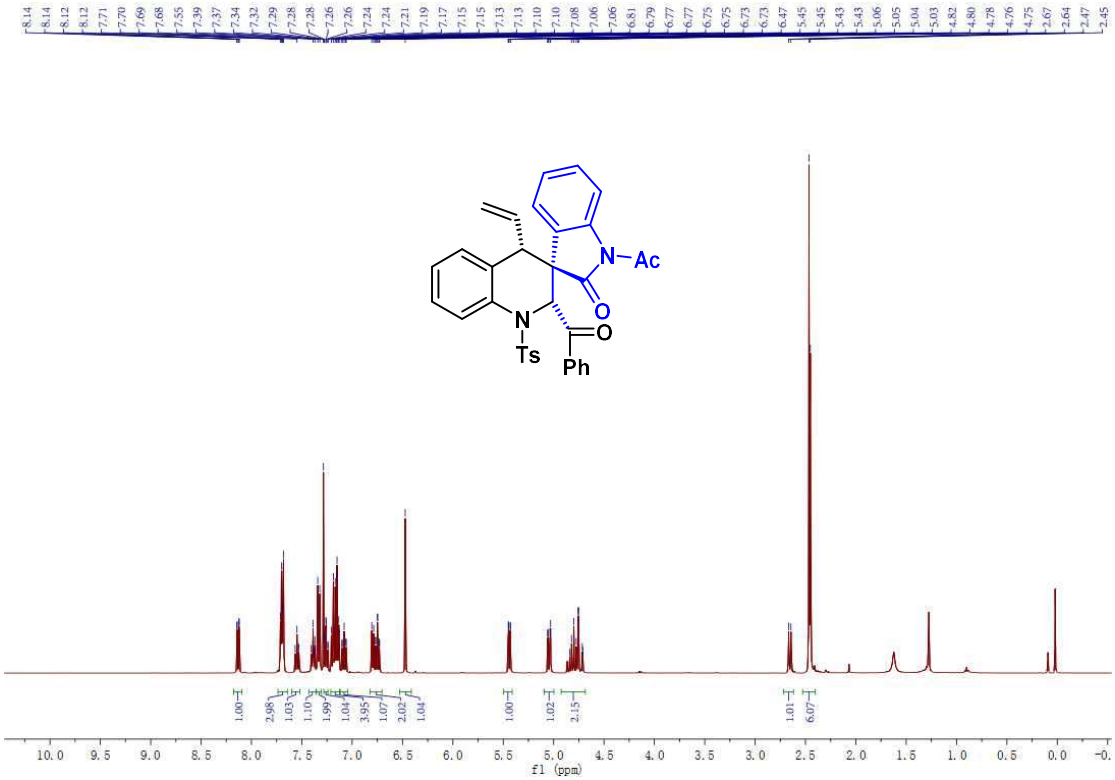
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ad**



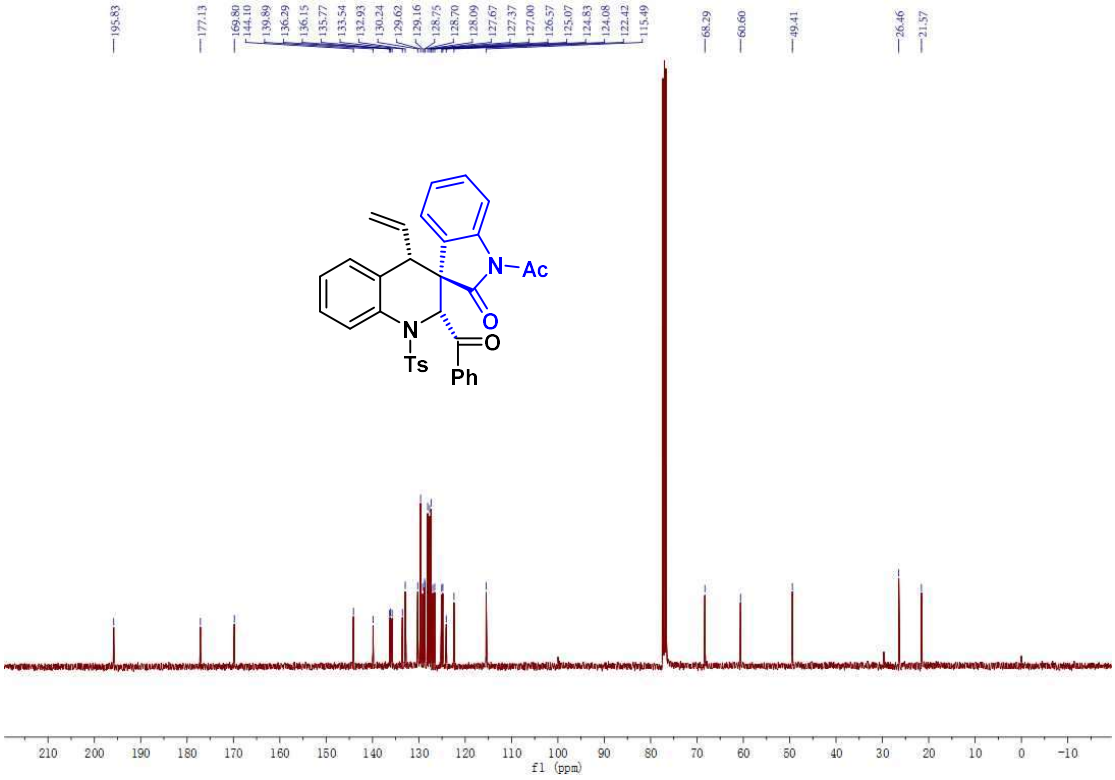
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ad**



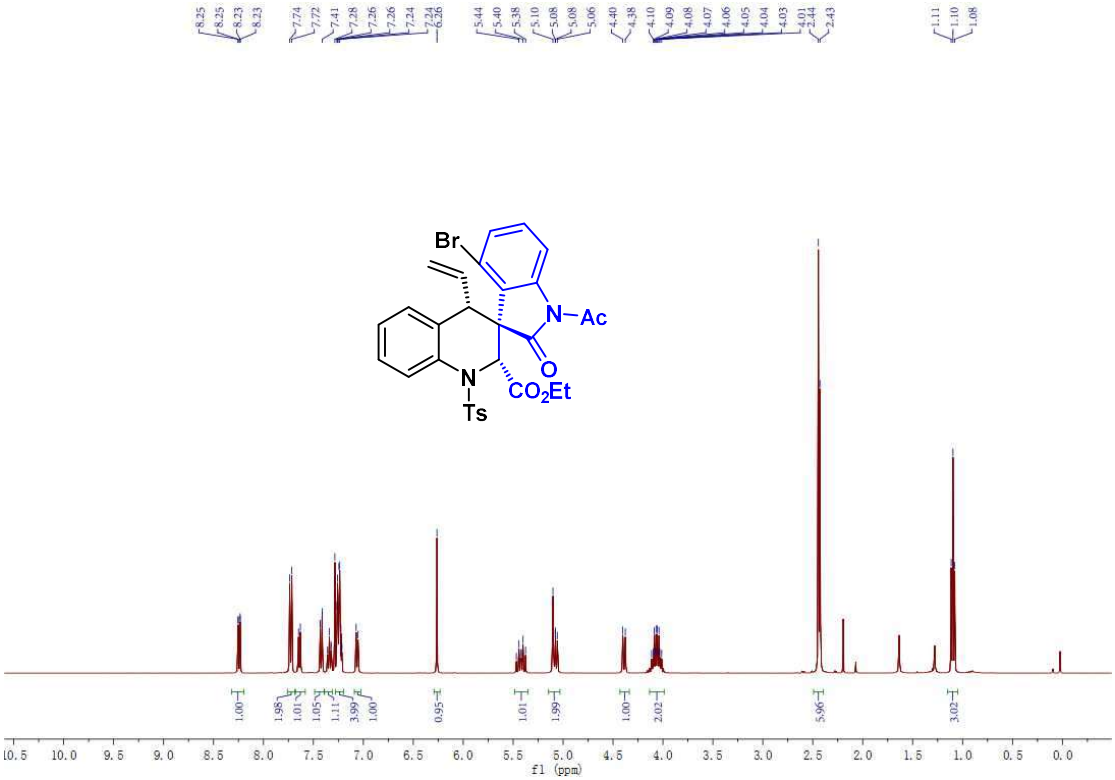
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ae**



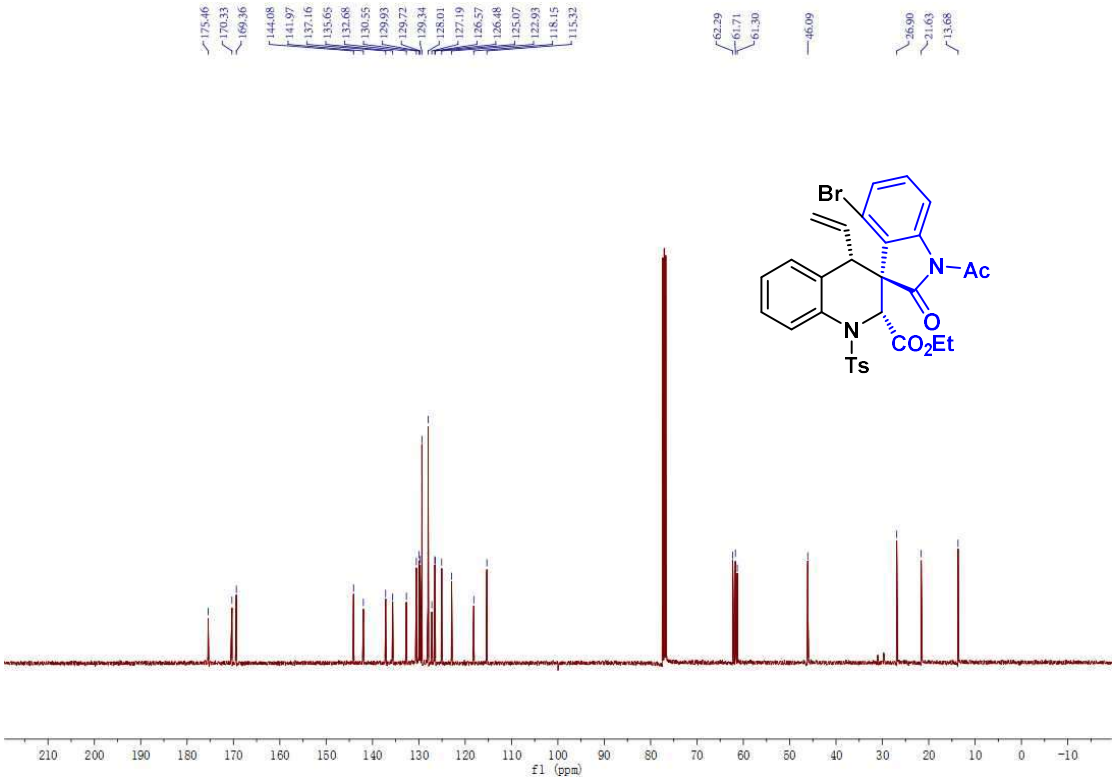
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ae**



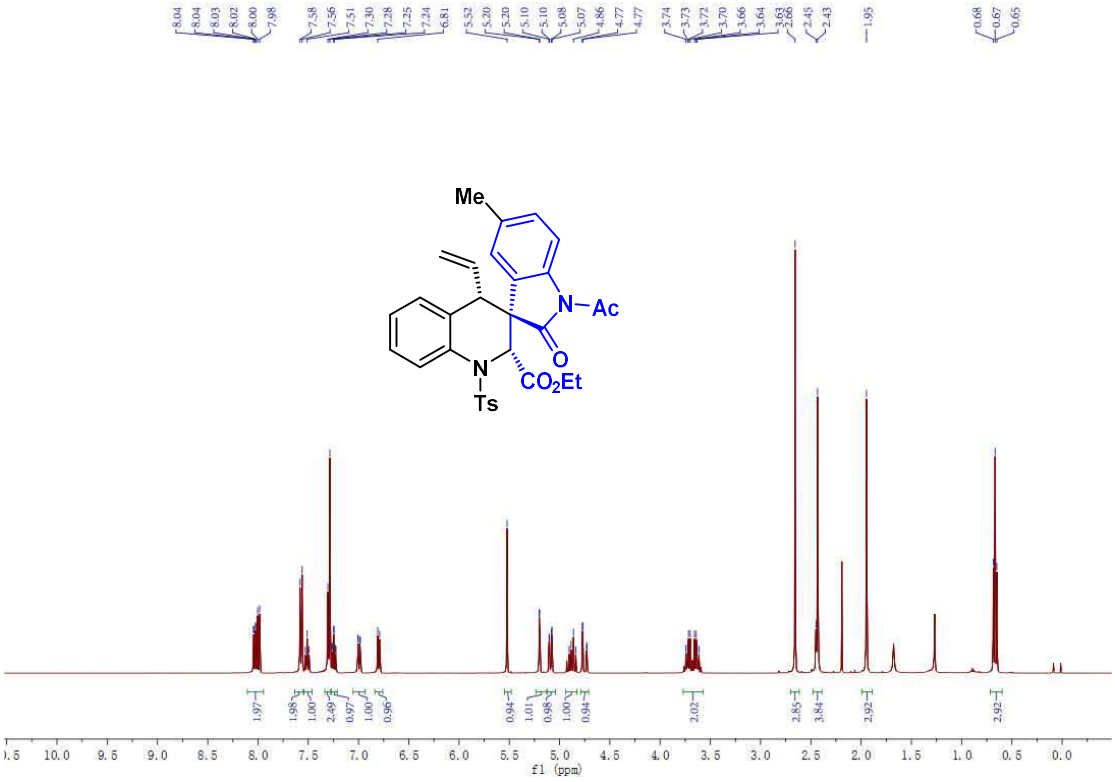
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3af**



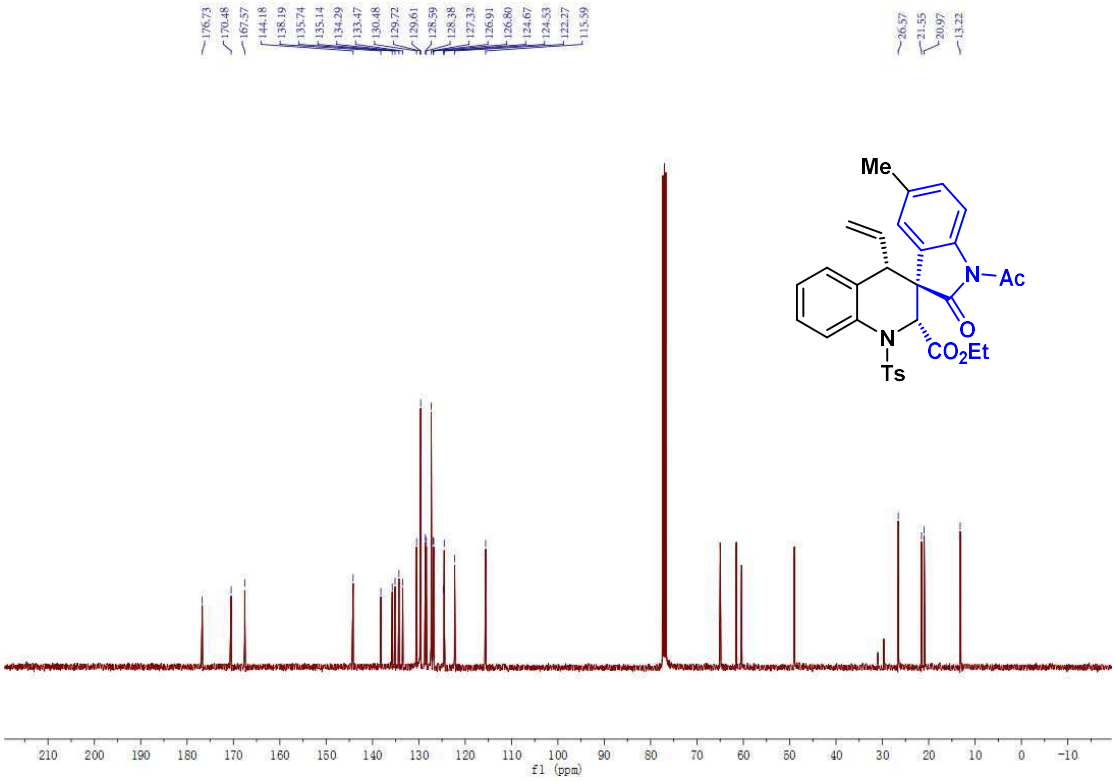
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3af**



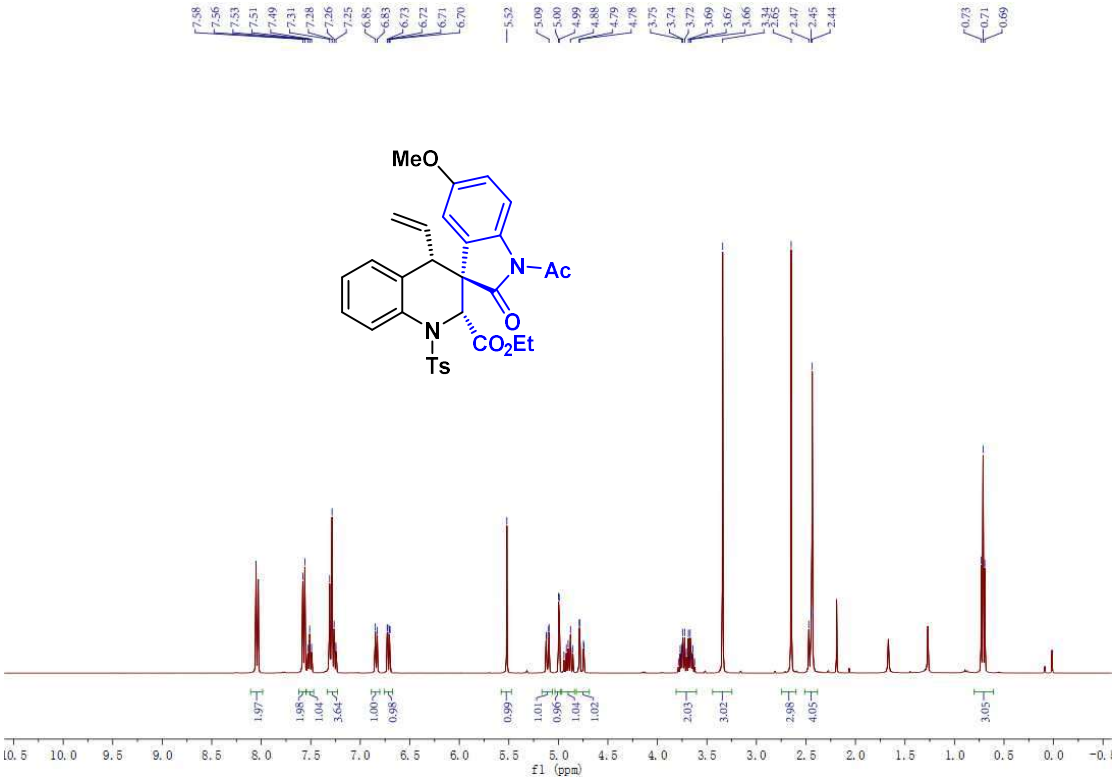
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ag**



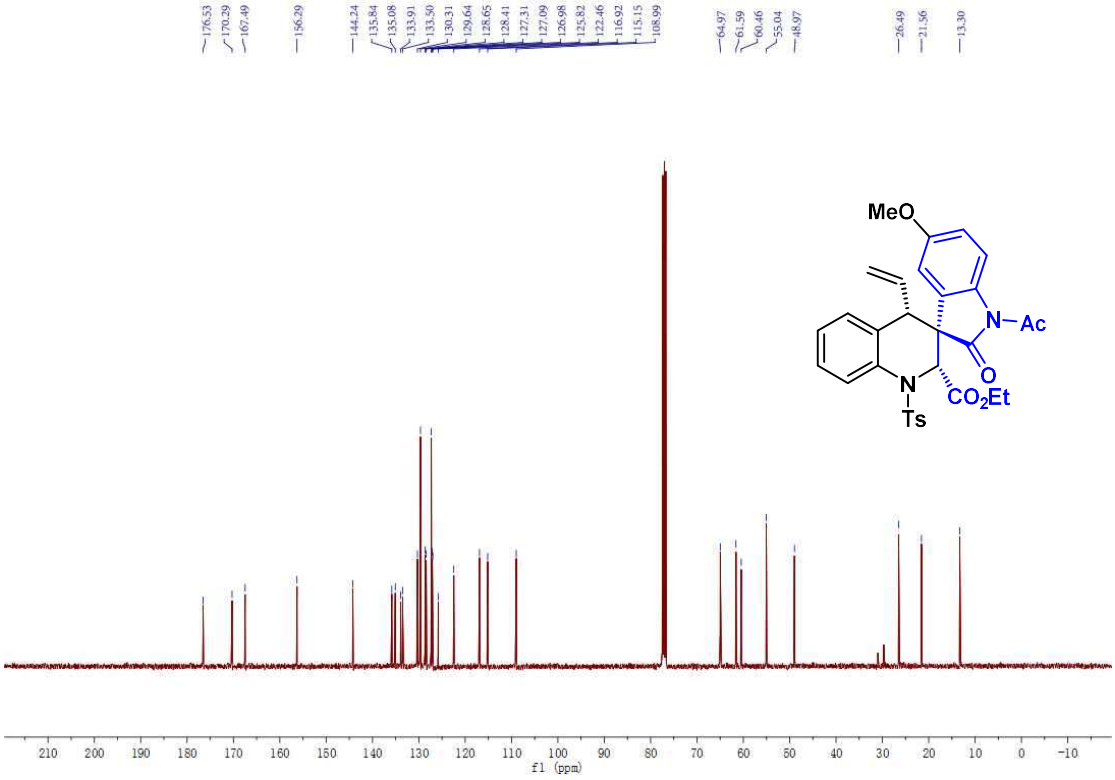
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ag**



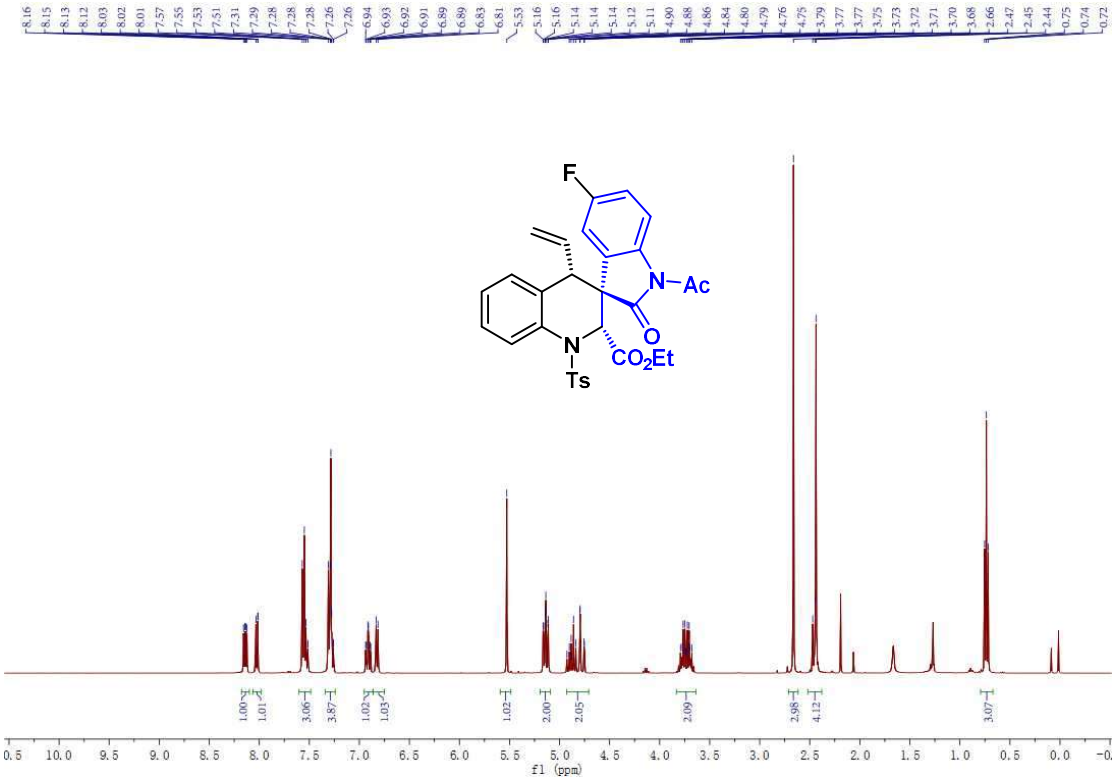
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ah**



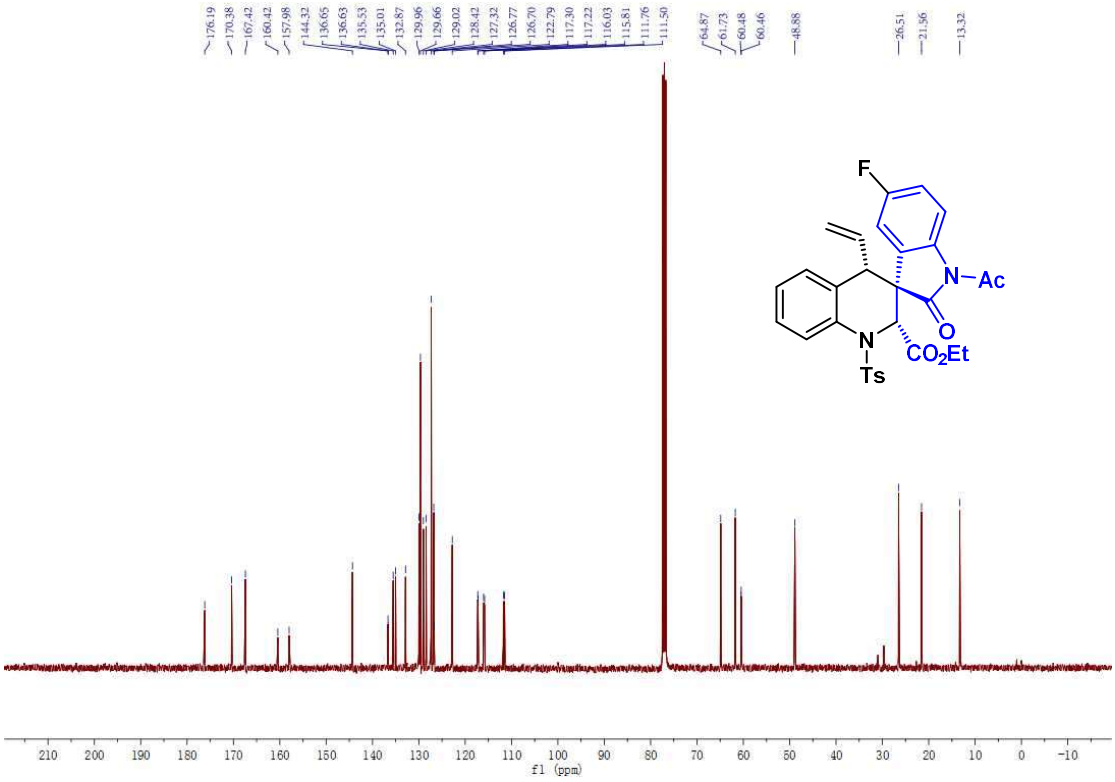
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ah**



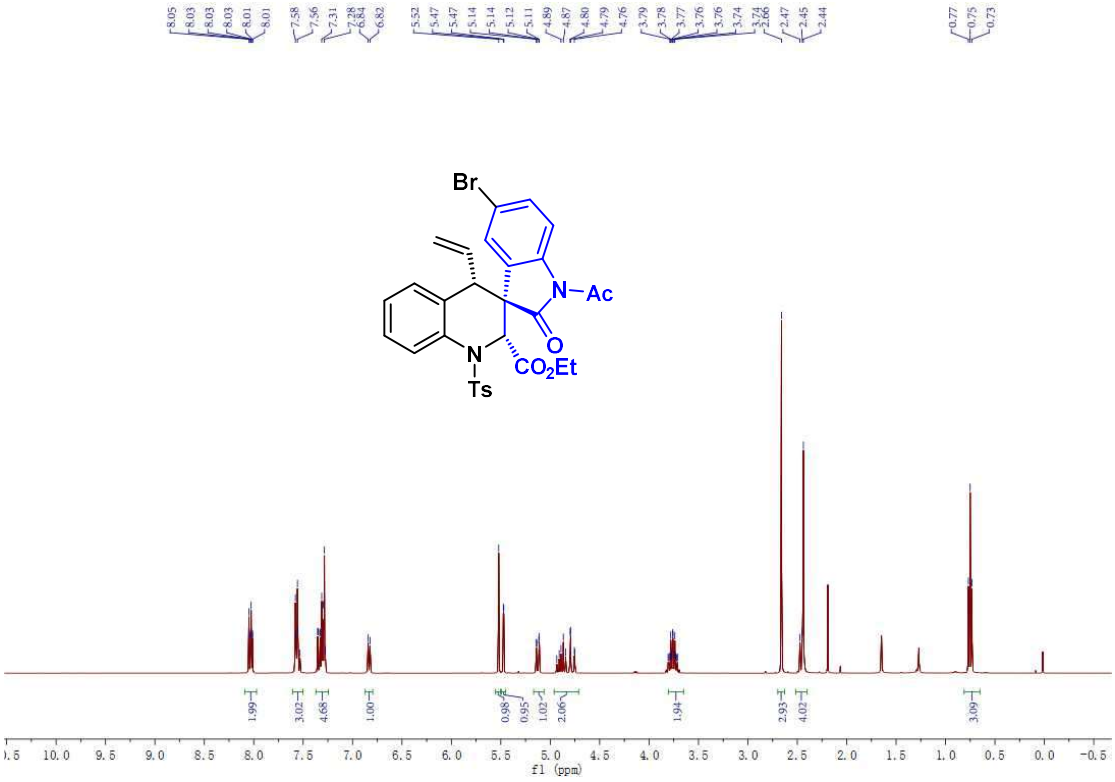
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ai**



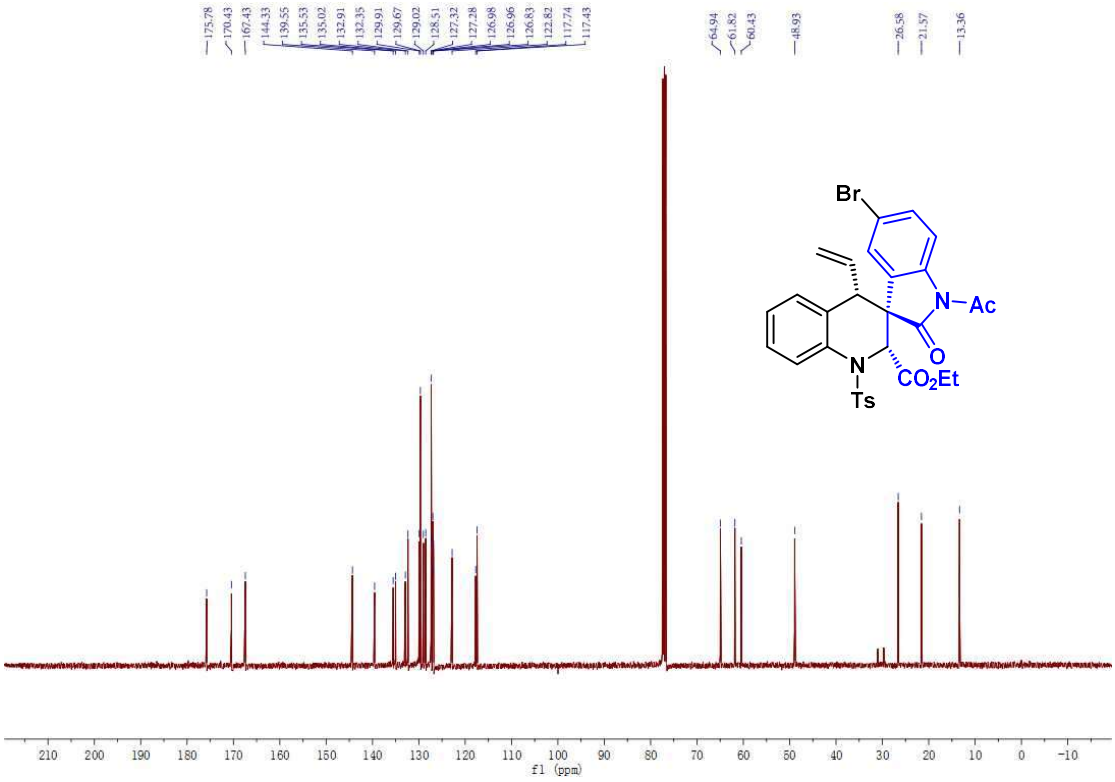
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ai**



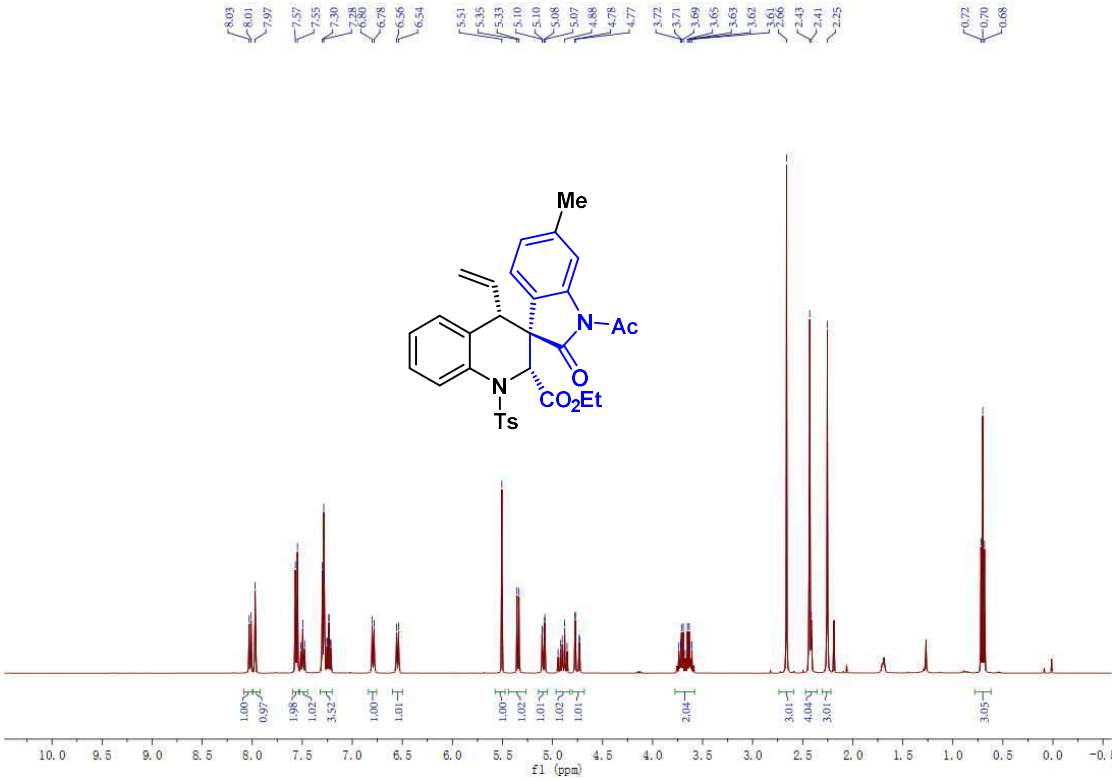
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aj**



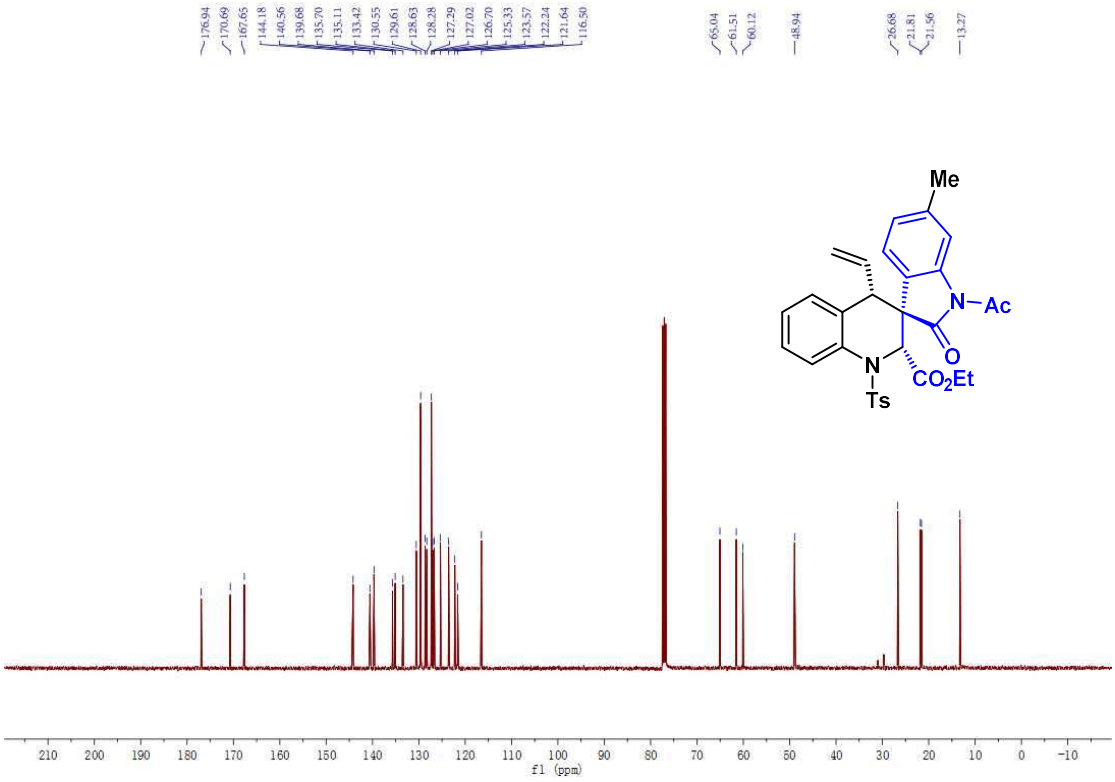
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aj**



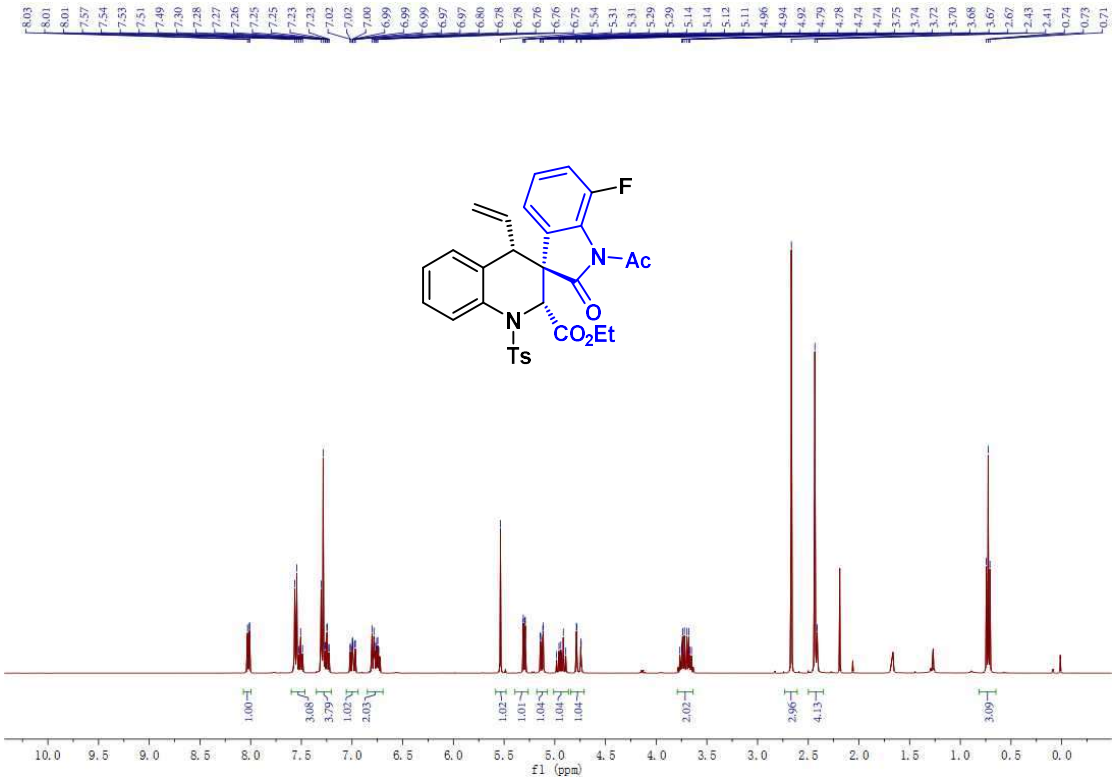
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ak**



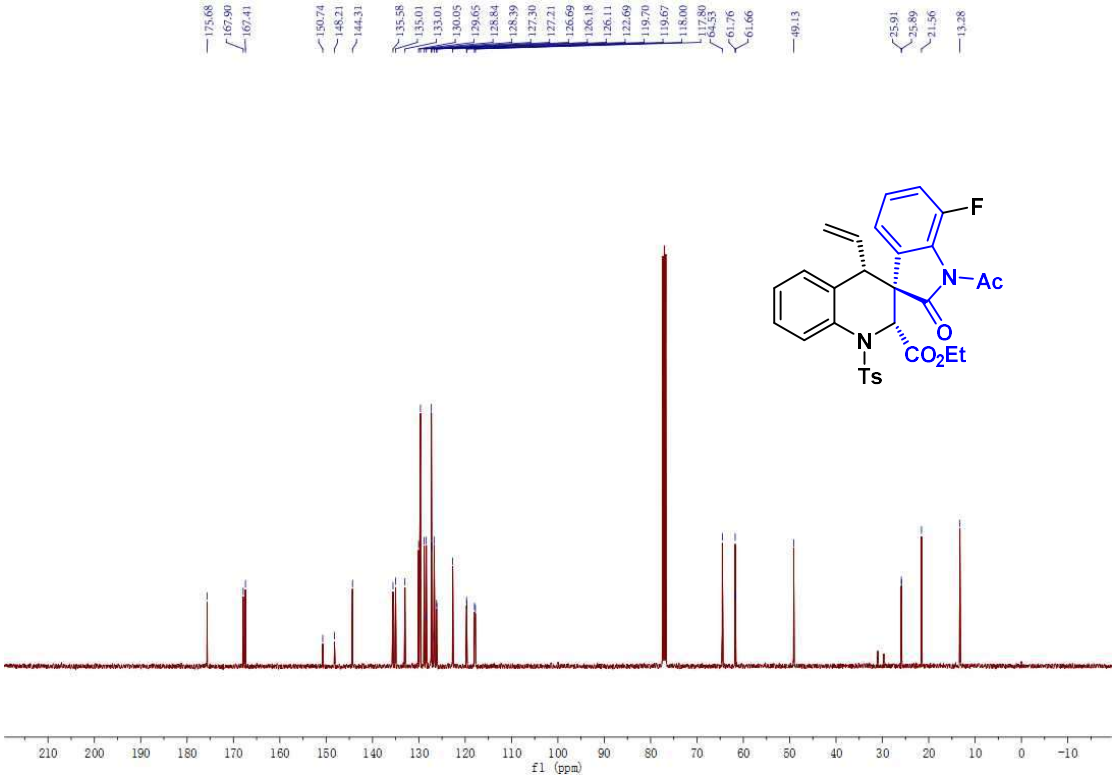
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ak**



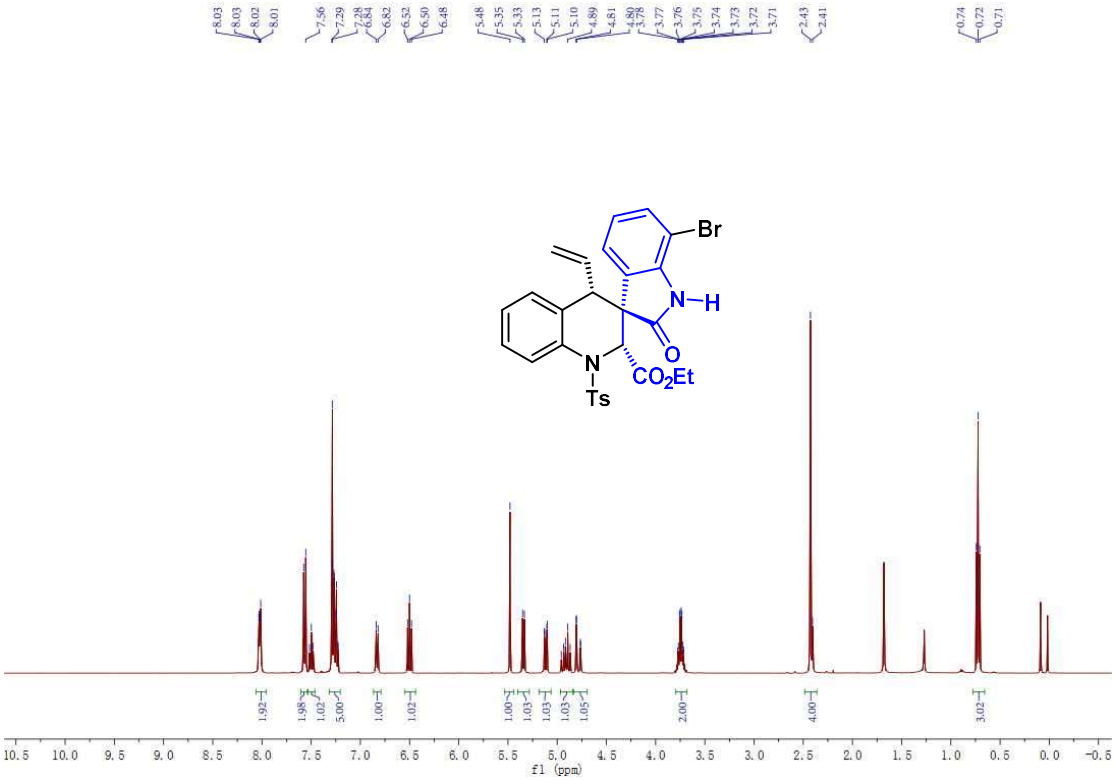
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3al**



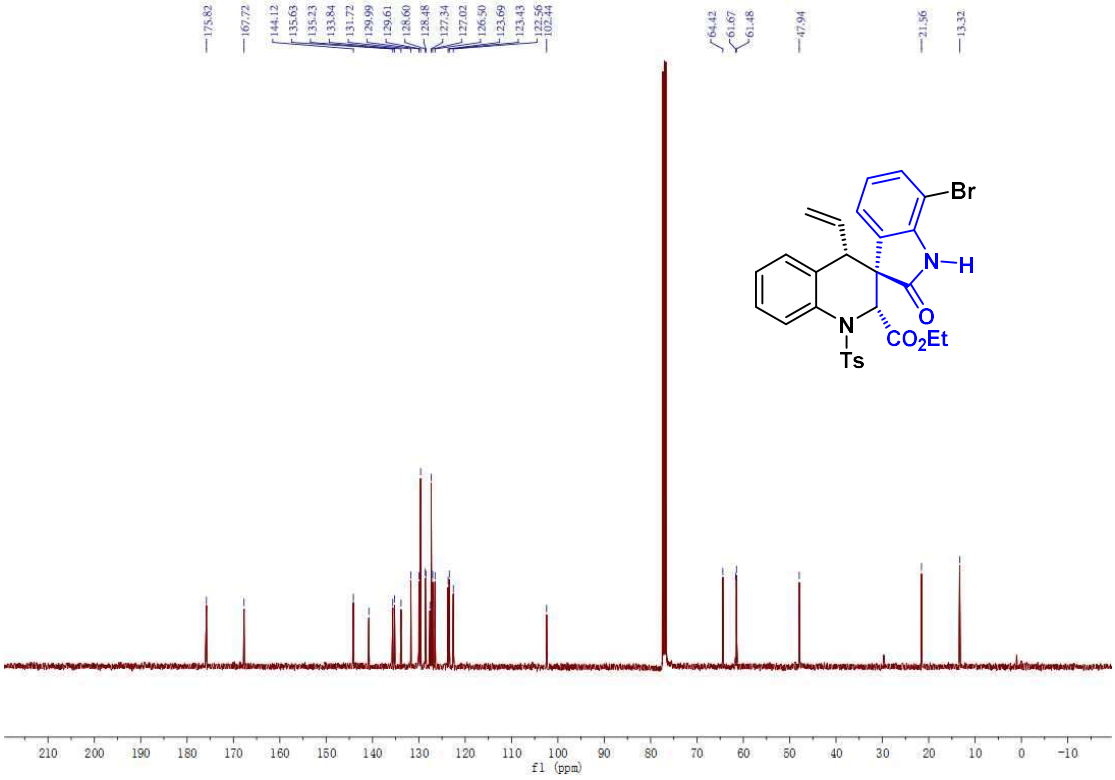
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3al**



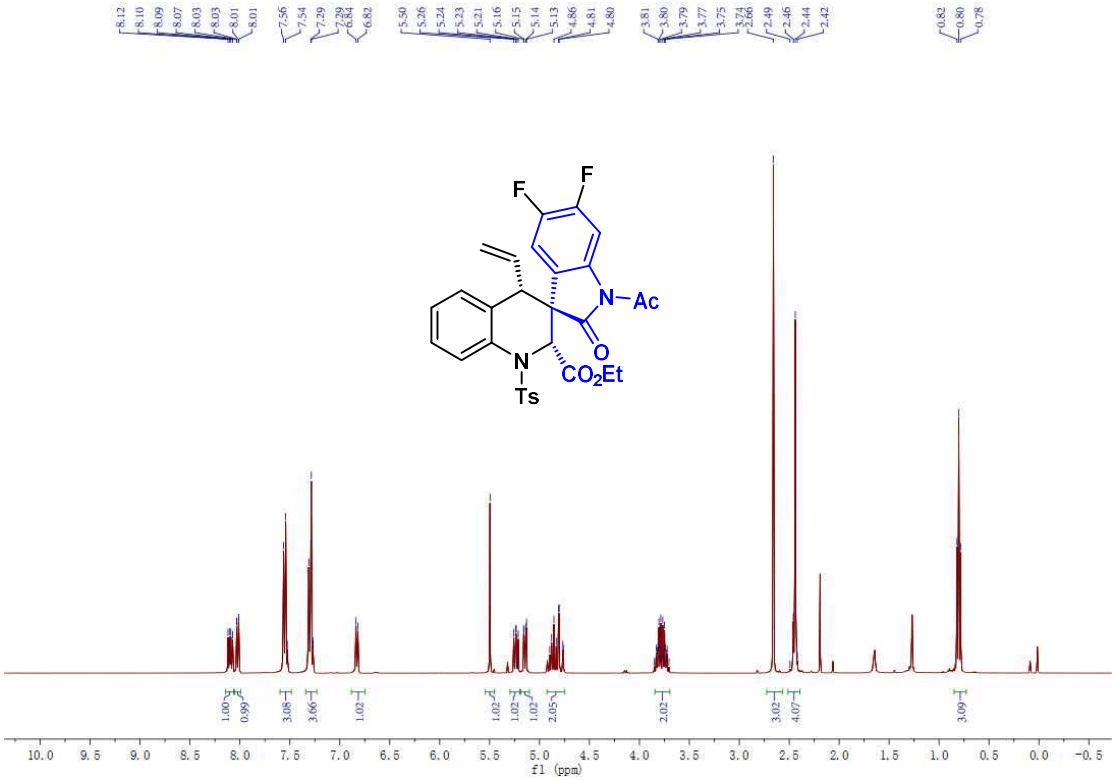
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3am**



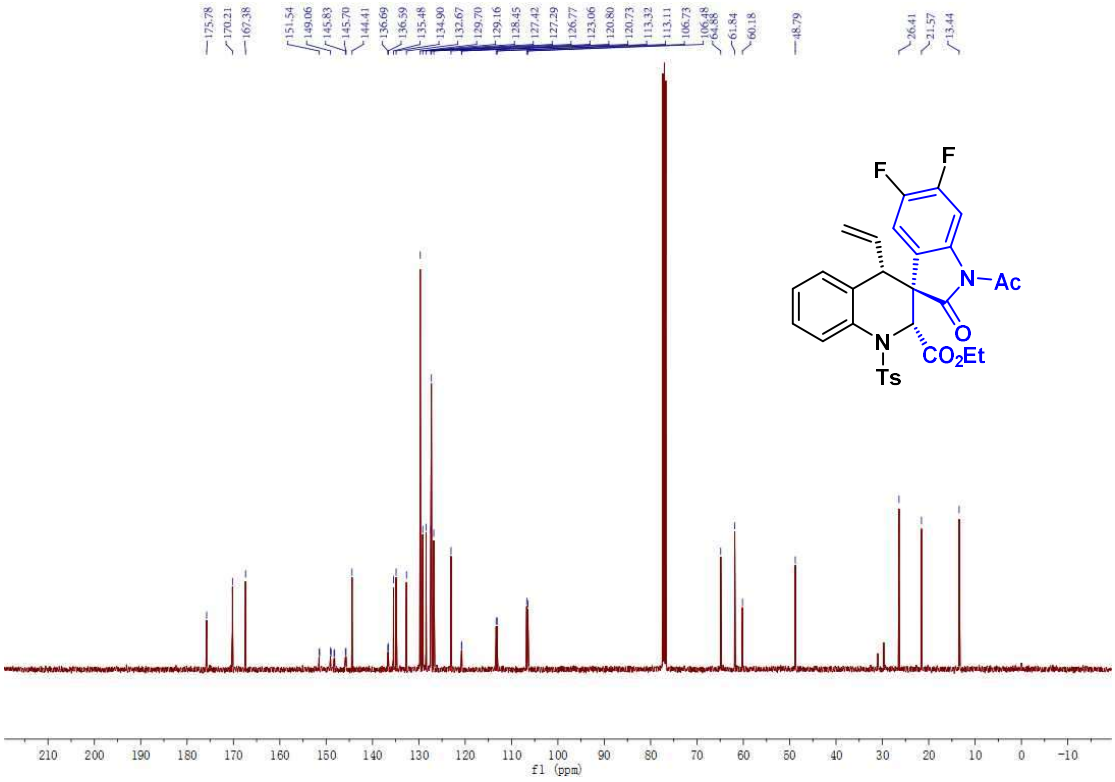
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3am**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3an**



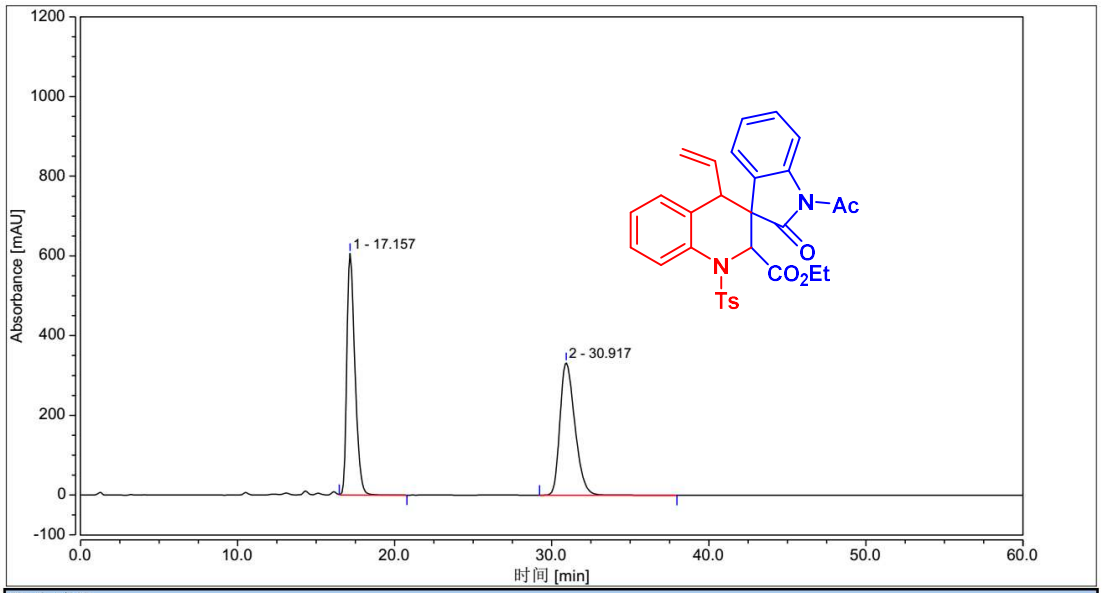
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3an**



6. Chiral HPLC analyses of products 3

3aa

racemic:

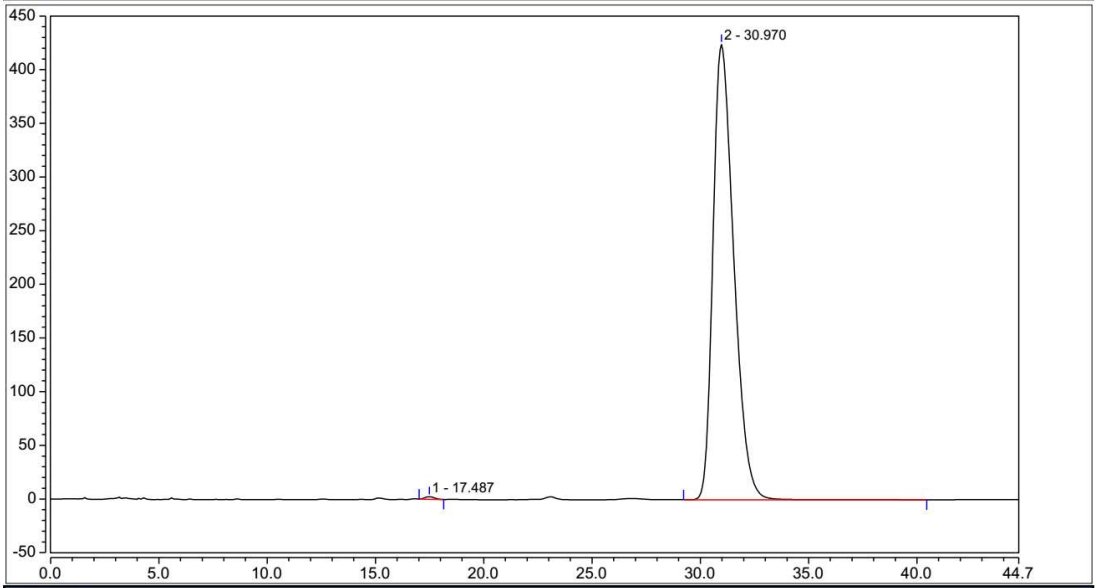


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		17.157	362.976	605.978	49.84	64.59	n.a.
2		30.917	365.377	332.245	50.16	35.41	n.a.
总和:			**728.353**	**938.223**	**100.00**	**100.00**	

enantioselective:

色谱图



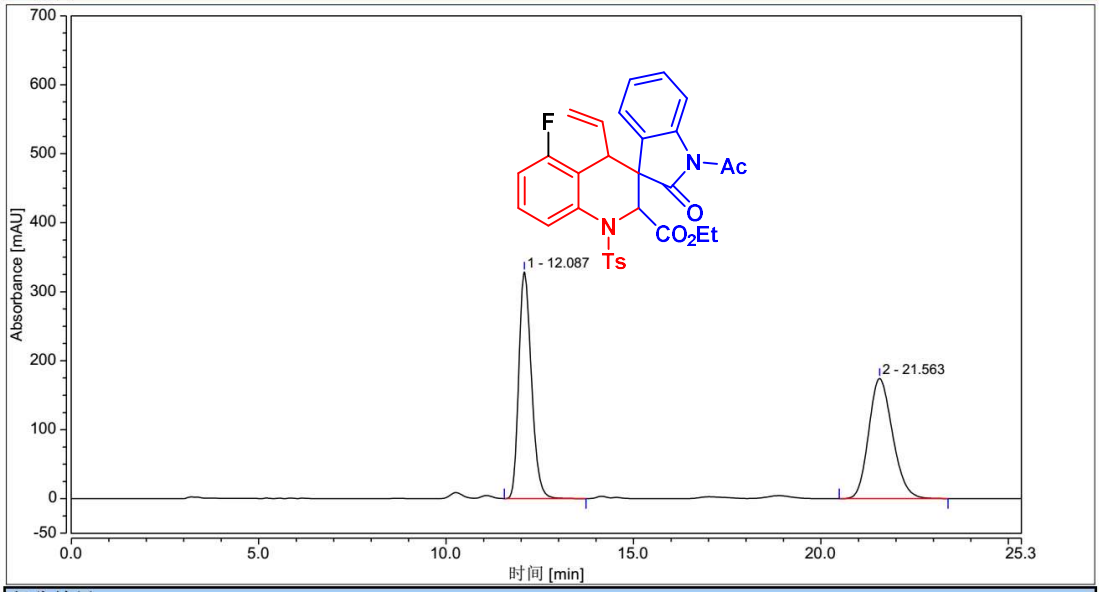
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		17.487	1.168	2.309	0.25	0.54	n.a.
2		30.970	471.775	424.262	99.75	99.46	n.a.
总和:			**472.943**	**426.571**	**100.00**	**100.00**	

3ba

racemic:

色谱图

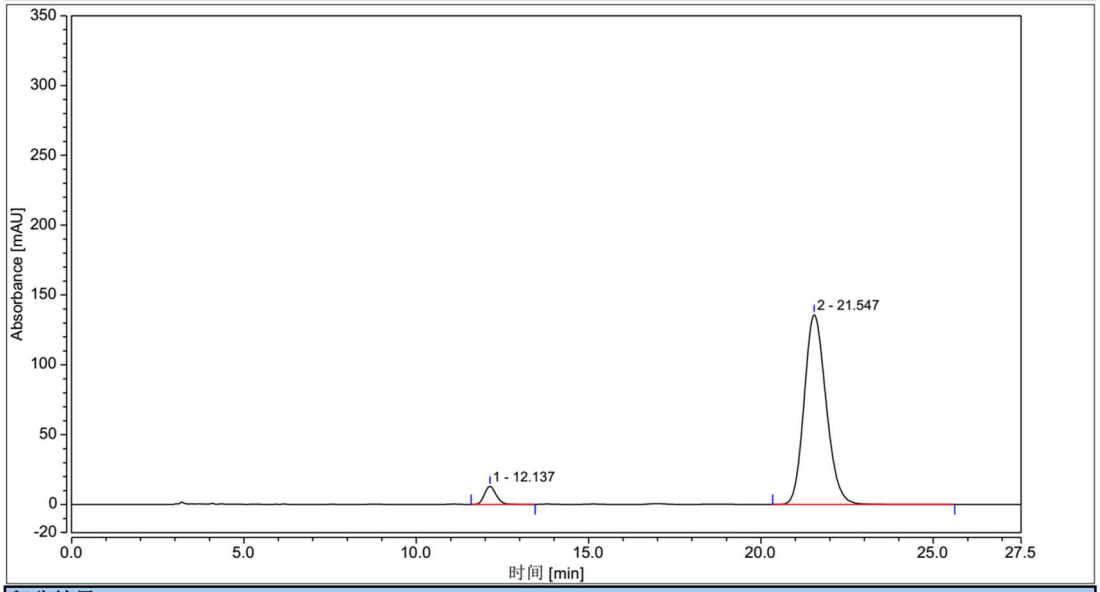


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.087	128.626	328.425	50.01	65.33	n.a.
2		21.563	128.580	174.307	49.99	34.67	n.a.
总和:			**257.206**	**502.732**	**100.00**	**100.00**	

enantioselective:

色谱图



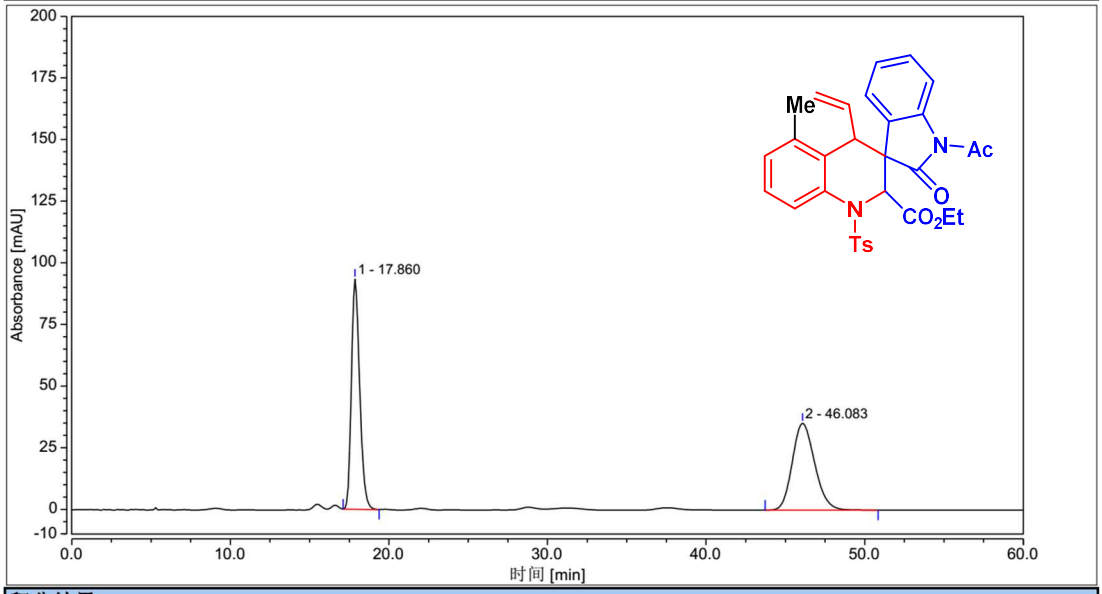
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.137	5.138	13.005	4.88	8.73	n.a.
2		21.547	100.255	135.918	95.12	91.27	n.a.
总和:			**105.394**	**148.923**	**100.00**	**100.00**	

3ca

racemic:

色谱图

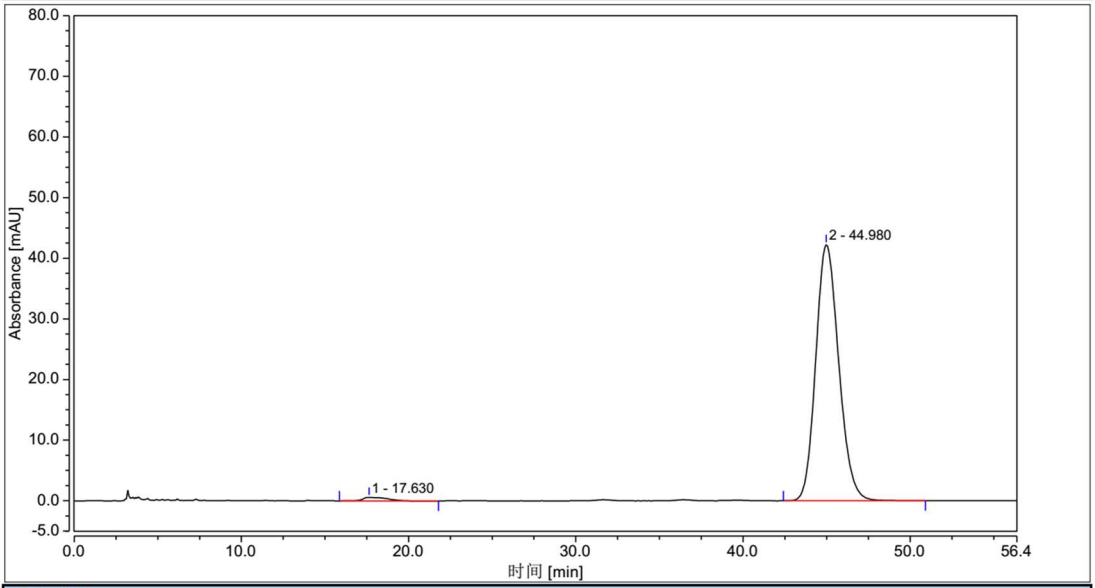


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		17.860	57.146	93.446	49.78	72.63	n.a.
2		46.083	57.652	35.216	50.22	27.37	n.a.
总和:			**114.798**	**128.661**	**100.00**	**100.00**	

enantioselective:

色谱图



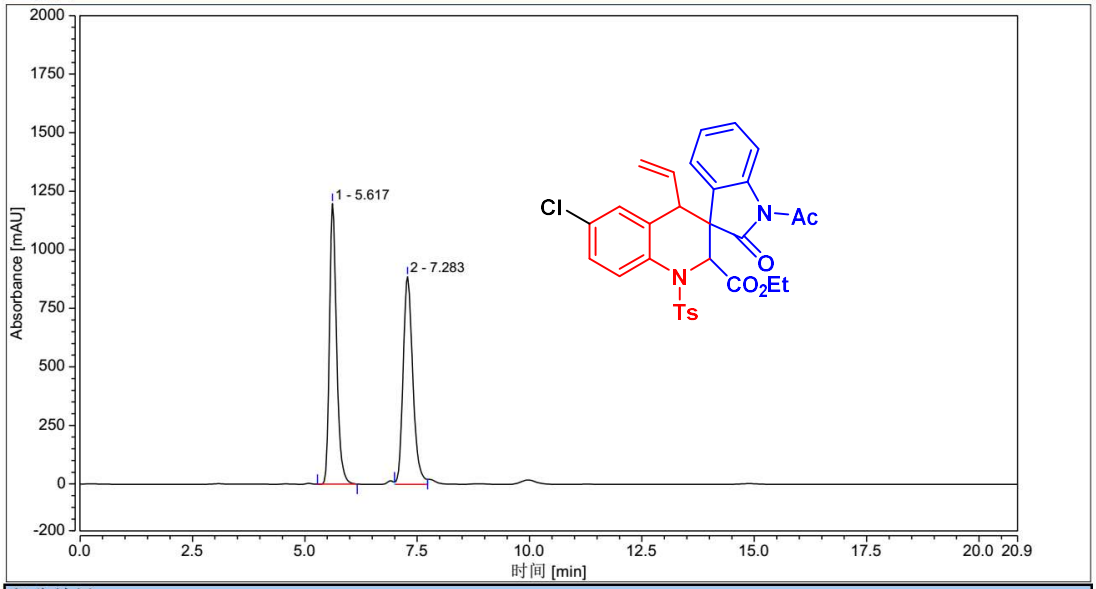
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		17.630	0.945	0.576	1.39	1.35	n.a.
2		44.980	67.231	42.214	98.61	98.65	n.a.
总和:			**68.176**	**42.790**	**100.00**	**100.00**	

3da

racemic:

色谱图

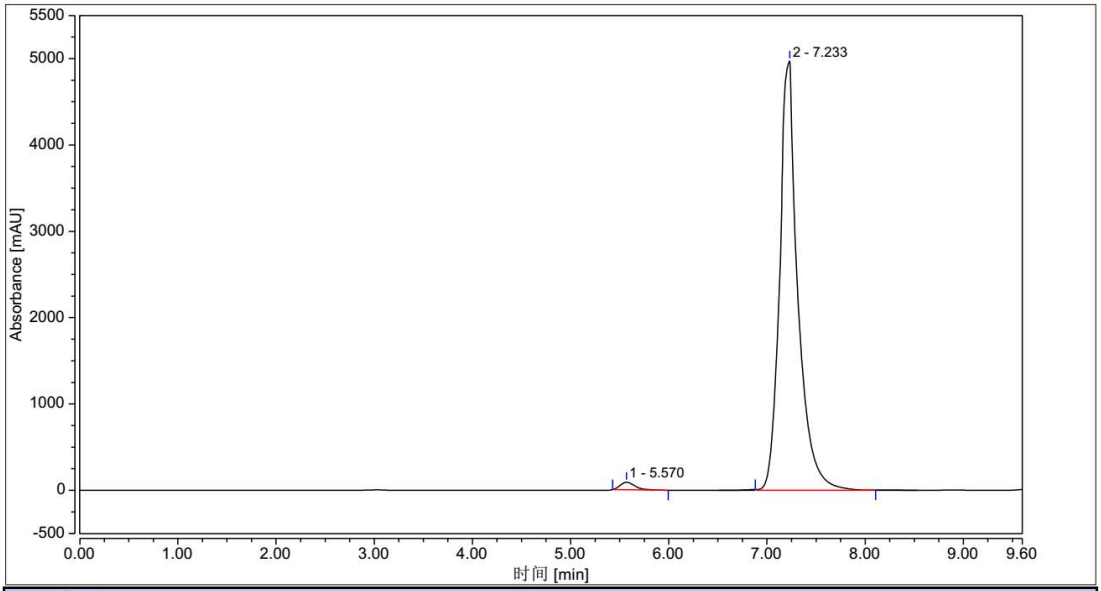


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.617	221.049	1197.752	49.93	57.48	n.a.
2		7.283	221.626	885.928	50.07	42.52	n.a.
总和:			**442.676**	**2083.680**	**100.00**	**100.00**	

enantioselective:

色谱图



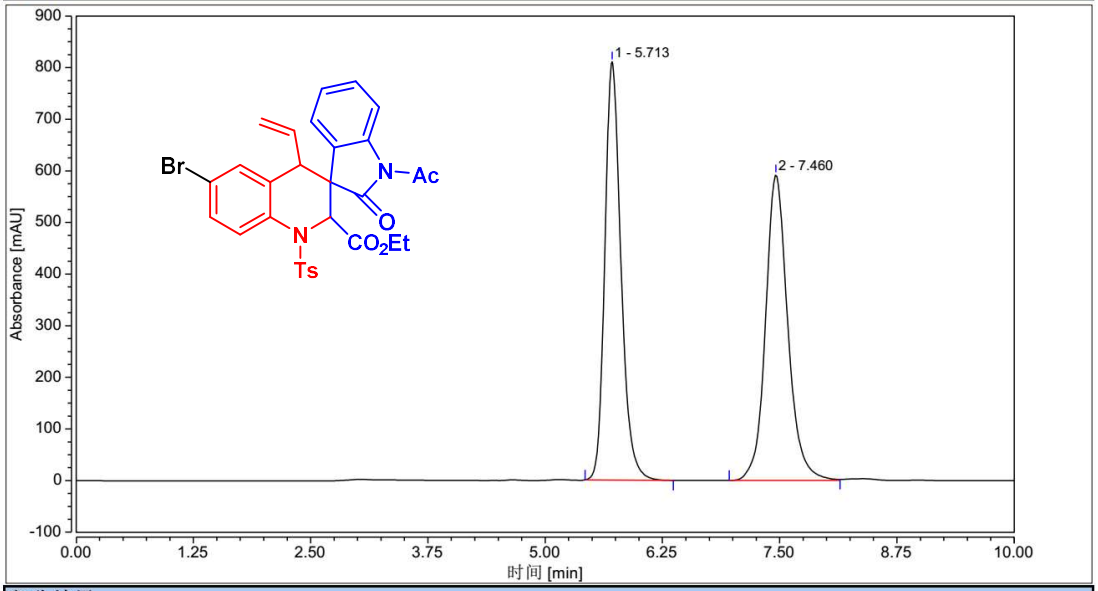
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.570	15.399	87.774	1.42	1.73	n.a.
2		7.233	1070.069	4972.960	98.58	98.27	n.a.
总和:			**1085.467**	**5060.734**	**100.00**	**100.00**	

3ea

racemic:

色谱图

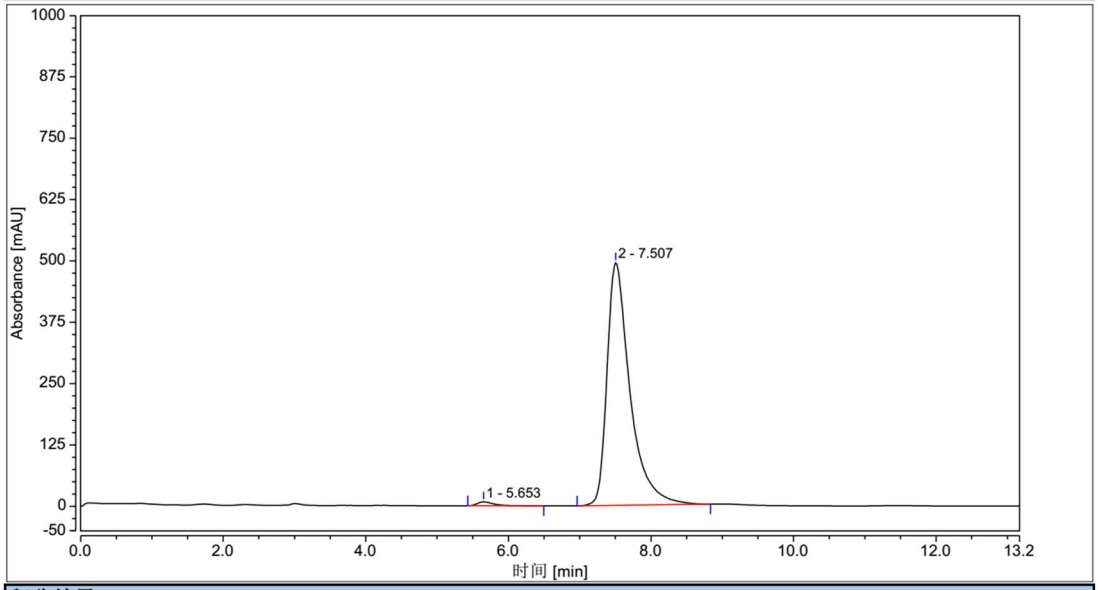


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.713	161.519	810.273	49.72	57.77	n.a.
2		7.460	163.340	592.384	50.28	42.23	n.a.
总和:			**324.859**	**1402.657**	**100.00**	**100.00**	

enantioselective:

色谱图



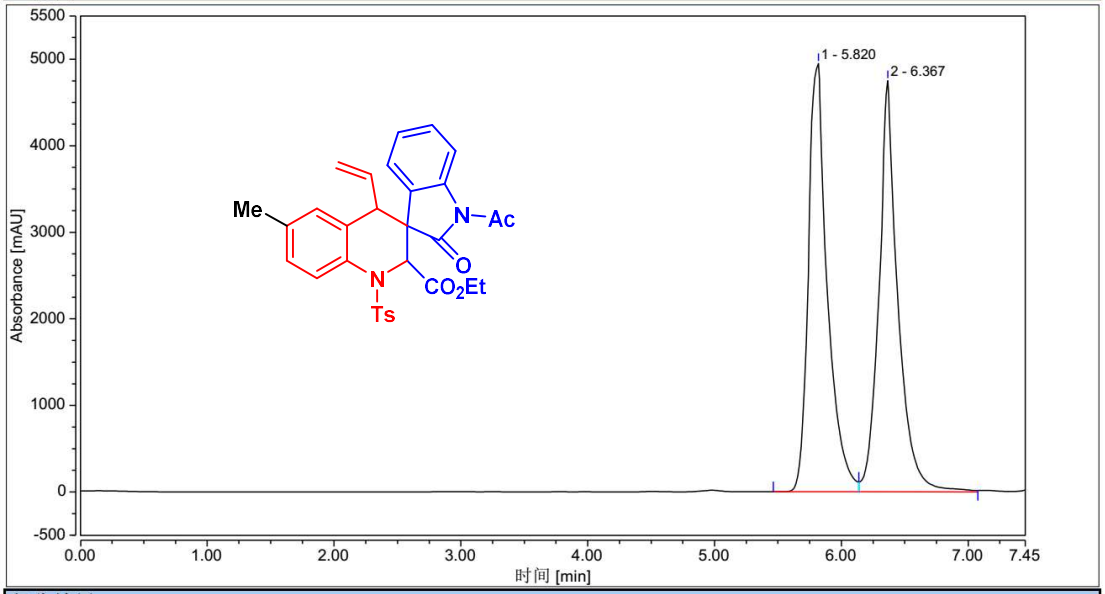
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.653	2.129	7.914	1.14	1.57	n.a.
2		7.507	184.991	494.677	98.86	98.43	n.a.
总和:			**187.121**	**502.590**	**100.00**	**100.00**	

3fa

racemic:

色谱图

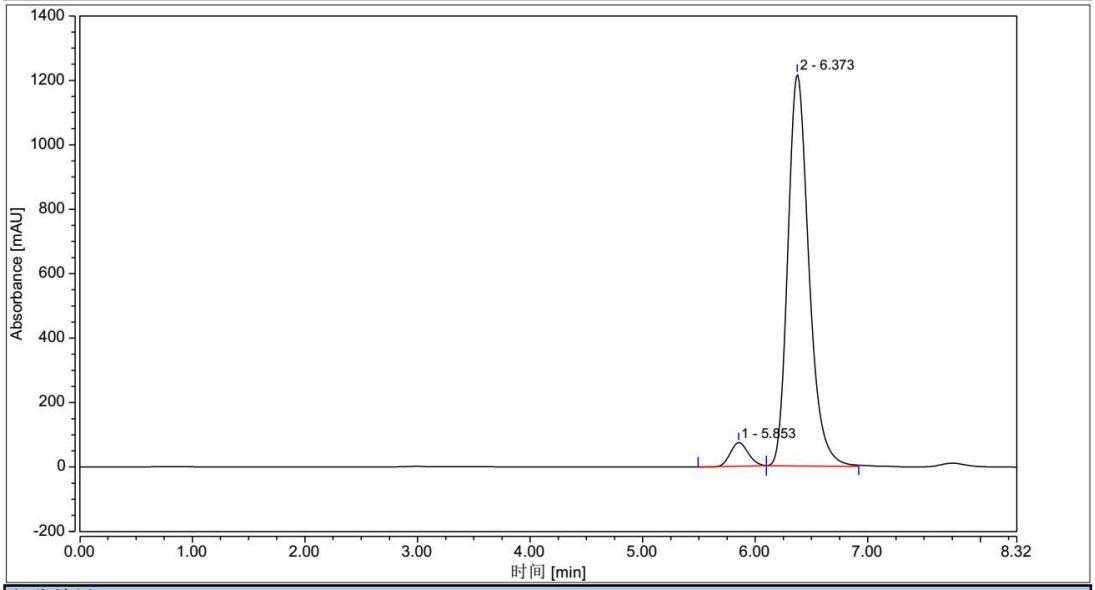


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.820	857.292	4947.913	51.01	51.02	n.a.
2		6.367	823.483	4749.820	48.99	48.98	n.a.
总和:			**1680.775**	**9697.733**	**100.00**	**100.00**	

enantioselective:

色谱图



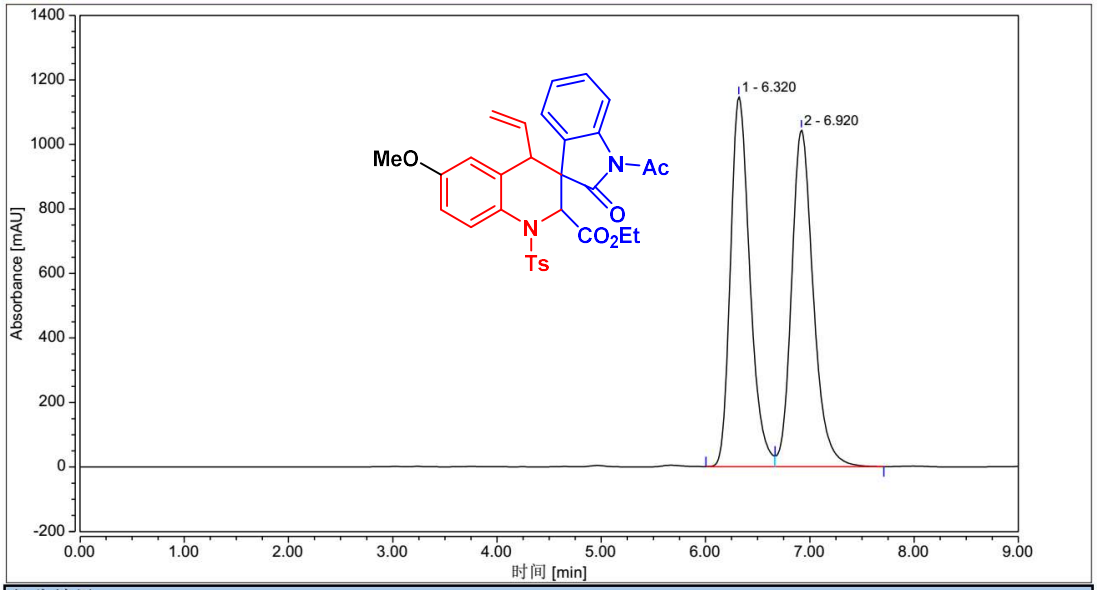
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.853	13.375	73.087	4.84	5.67	n.a.
2		6.373	263.211	1215.220	95.16	94.33	n.a.
总和:			**276.586**	**1288.308**	**100.00**	**100.00**	

3ga

racemic:

色谱图

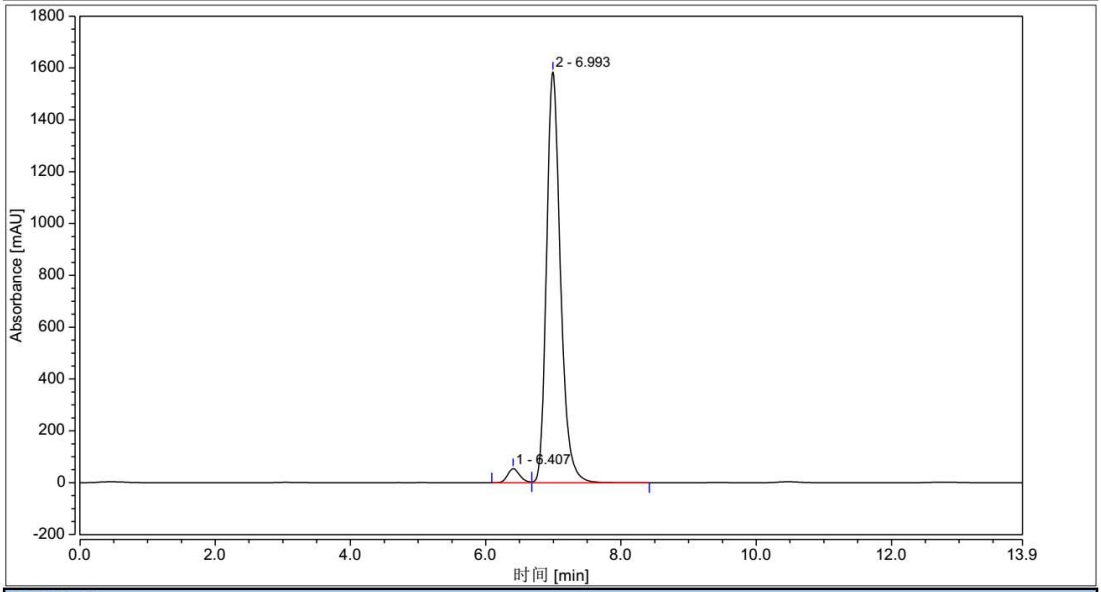


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		6.320	247.172	1146.383	49.48	52.35	n.a.
2		6.920	252.397	1043.289	50.52	47.65	n.a.
总和:			**499.569**	**2189.672**	**100.00**	**100.00**	

enantioselective:

色谱图

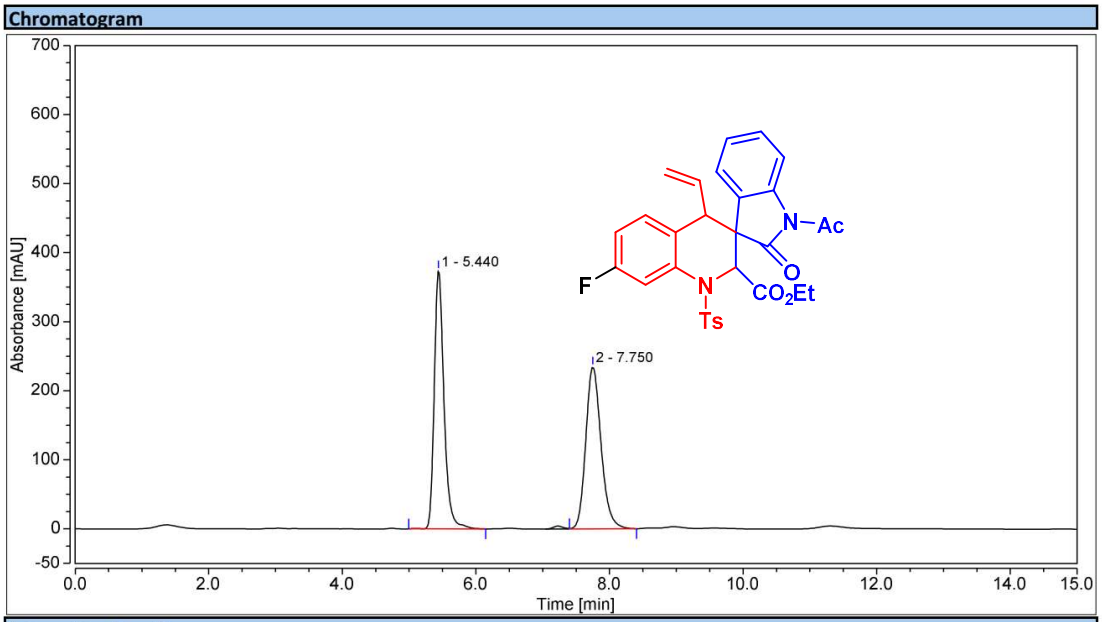


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		6.407	11.309	54.028	2.90	3.30	n.a.
2		6.993	378.867	1584.899	97.10	96.70	n.a.
总和:			**390.176**	**1638.927**	**100.00**	**100.00**	

3ha

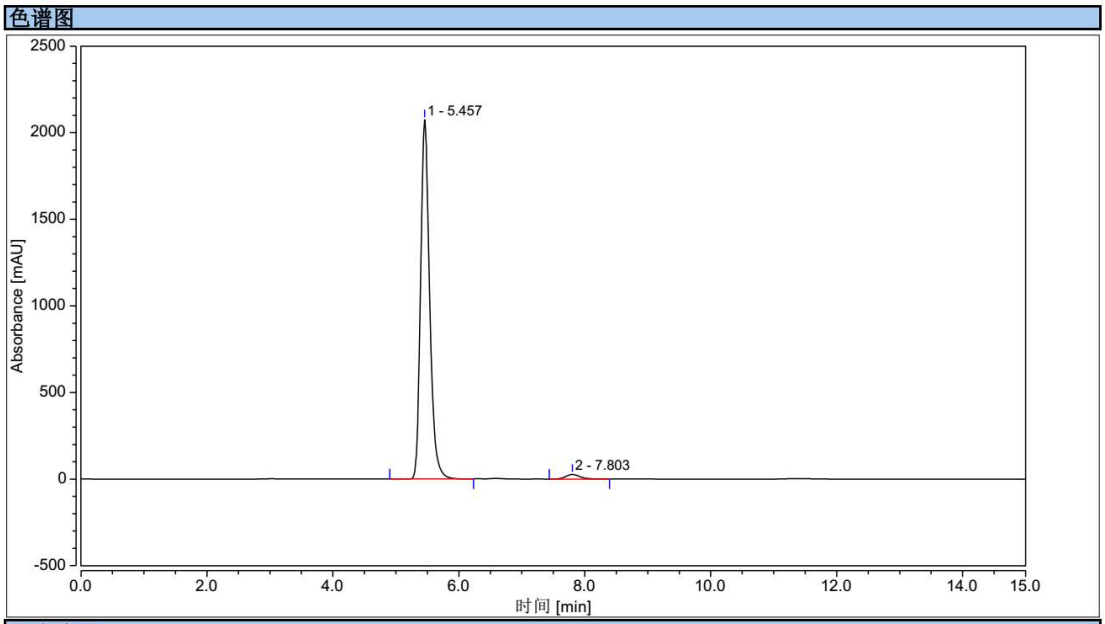
racemic:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.440	63.138	373.776	50.31	61.43	n.a.
2		7.750	62.372	234.641	49.69	38.57	n.a.
Total:			**125.510**	**608.417**	**100.00**	**100.00**	

enantioselective:



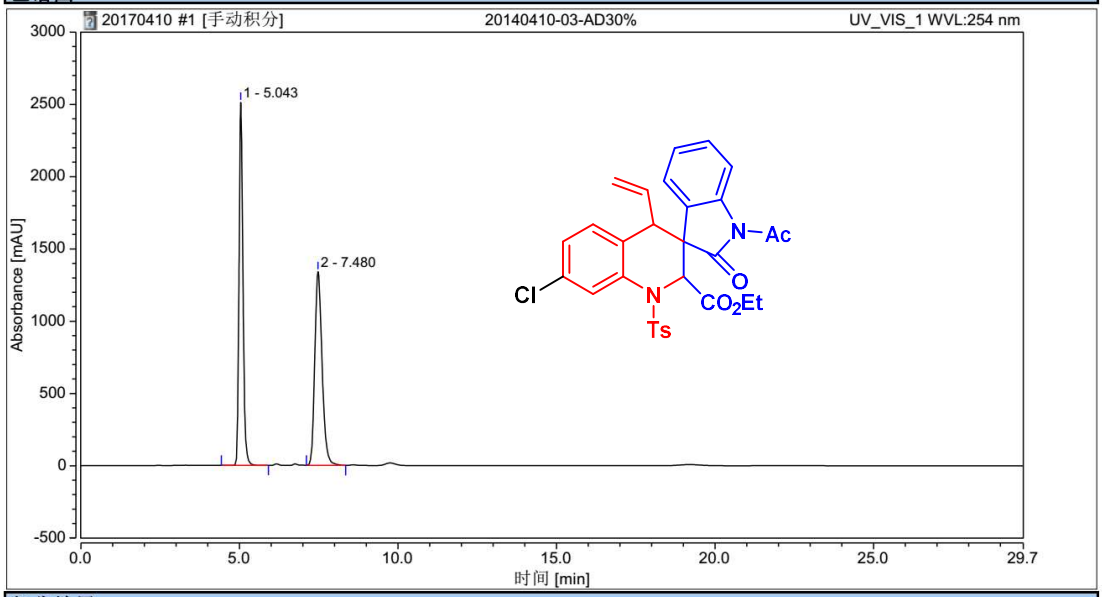
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.457	344.870	2073.869	97.98	98.73	n.a.
2		7.803	7.109	26.608	2.02	1.27	n.a.
总和:			**351.979**	**2100.477**	**100.00**	**100.00**	

3ia

racemic:

色谱图

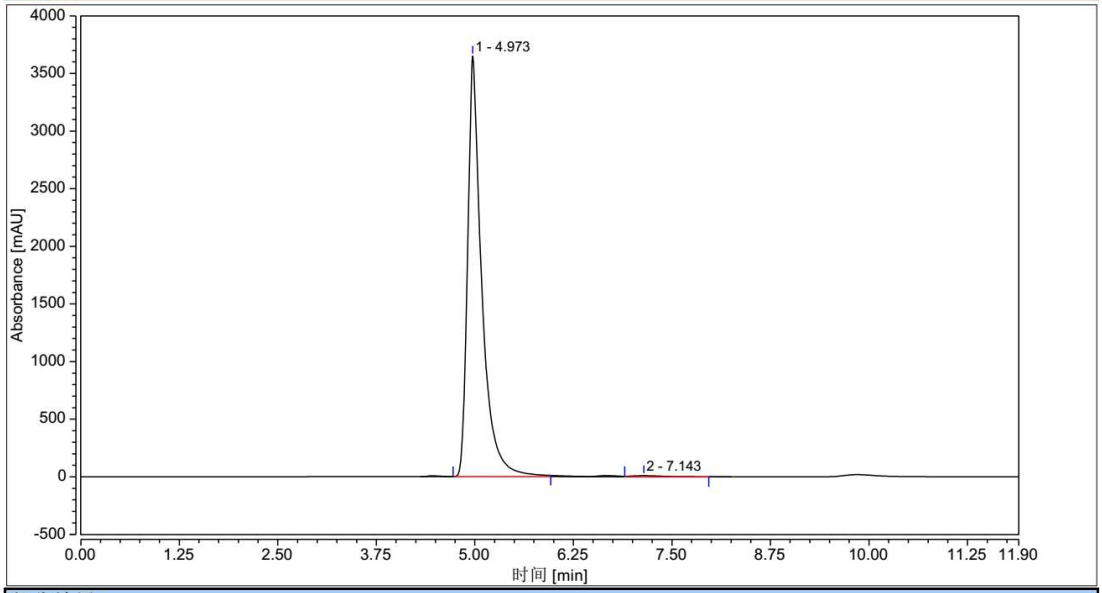


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.043	356.076	2511.100	49.93	65.21	n.a.
2		7.480	357.139	1339.975	50.07	34.79	n.a.
总和:			**713.216**	**3851.075**	**100.00**	**100.00**	

enantioselective:

色谱图



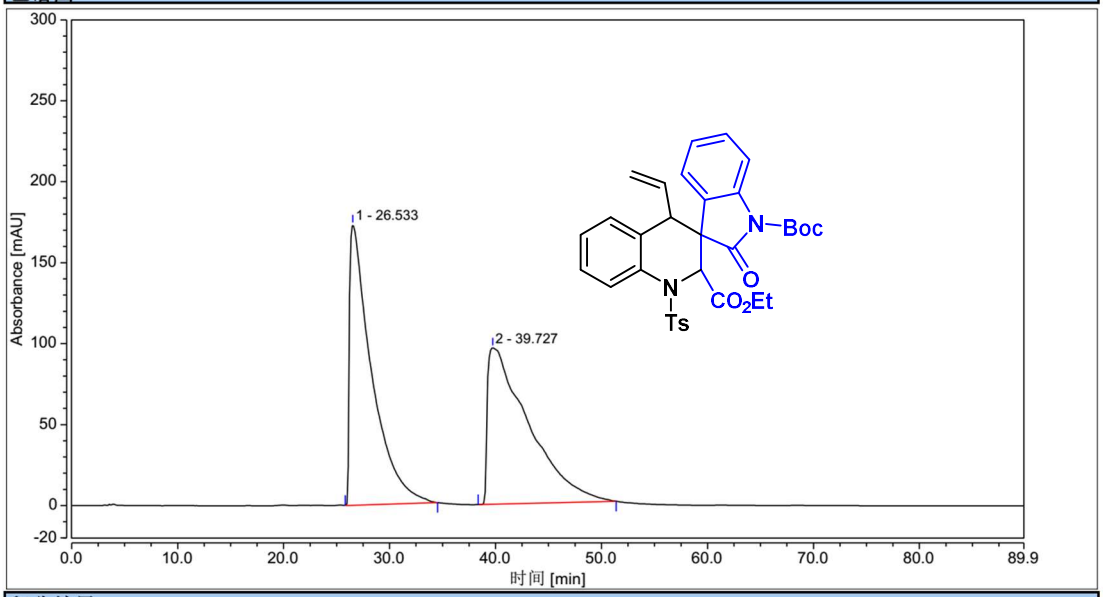
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.973	756.575	3650.528	99.45	99.74	n.a.
2		7.143	4.172	9.361	0.55	0.26	n.a.
总和:			**760.747**	**3659.889**	**100.00**	**100.00**	

3ab

racemic:

色谱图

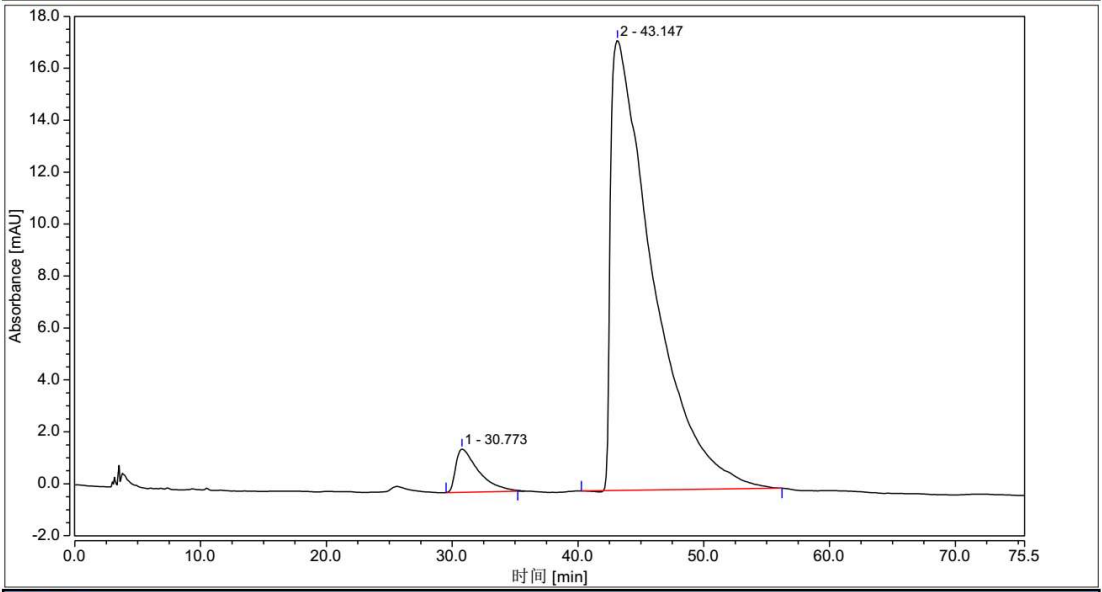


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		26.533	417.153	173.198	49.12	64.19	n.a.
2		39.727	432.068	96.609	50.88	35.81	n.a.
总和:			**849.221**	**269.807**	**100.00**	**100.00**	

enantioselective:

色谱图



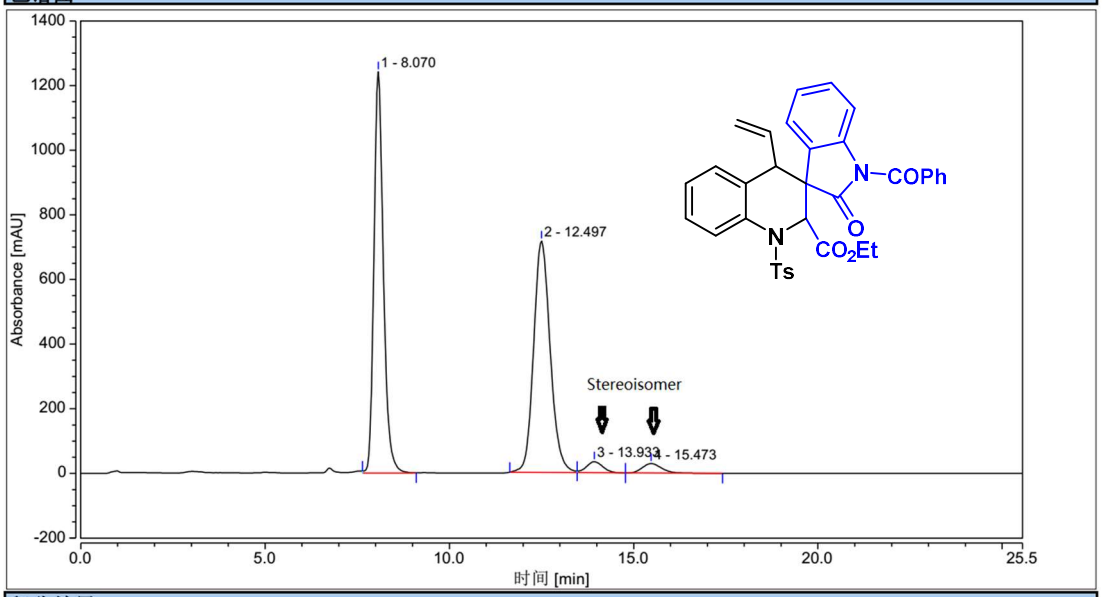
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		30.773	3.508	1.665	4.97	8.77	n.a.
2		43.147	67.082	17.326	95.03	91.23	n.a.
总和:			**70.589**	**18.990**	**100.00**	**100.00**	

3ac

racemic:

色谱图

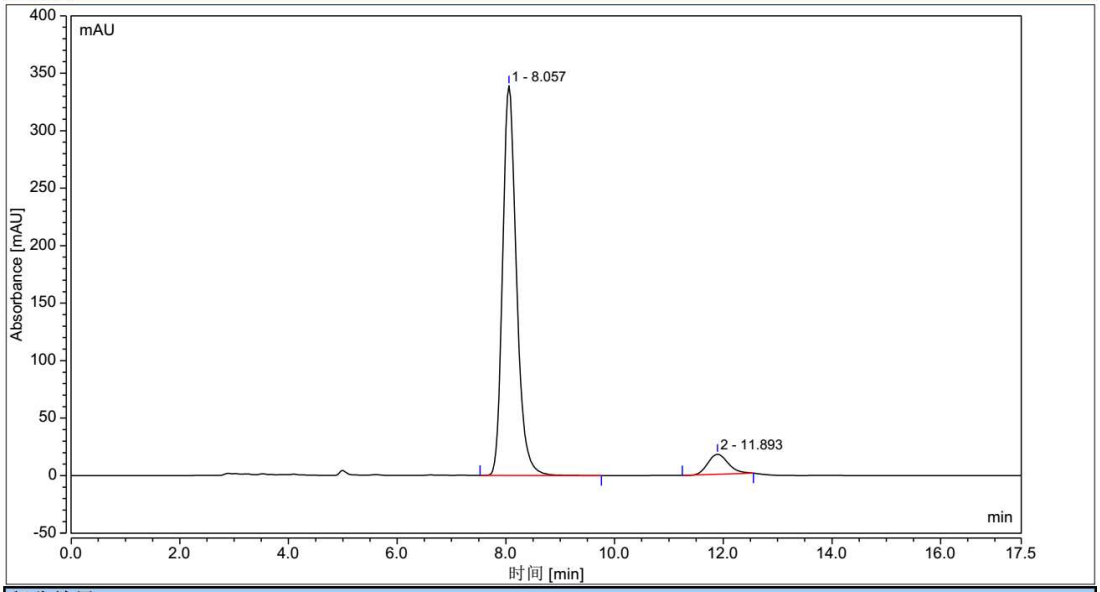


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.070	370.058	1241.595	47.59	61.44	n.a.
2		12.497	373.439	716.261	48.02	35.44	n.a.
3		13.933	17.226	33.977	2.22	1.68	n.a.
4		15.473	16.878	28.999	2.17	1.43	n.a.
总和:			**777.601**	**2020.833**	**100.00**	**100.00**	

enantioselective:

色谱图



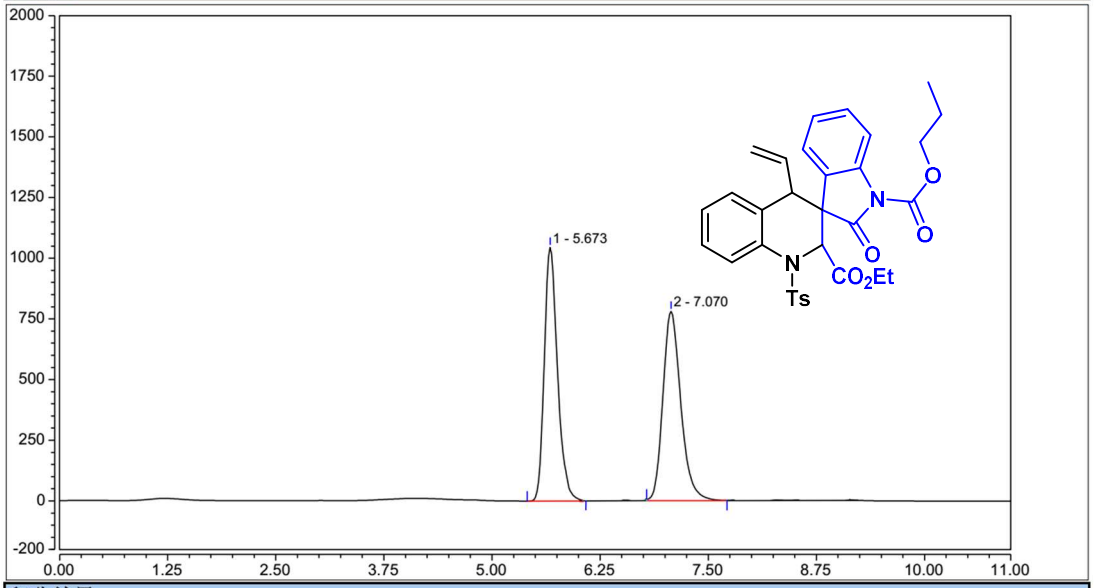
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		8.057	100.318	339.010	92.93	95.11	n.a.
2		11.893	7.630	17.445	7.07	4.89	n.a.
总和:			**107.948**	**356.455**	**100.00**	**100.00**	

3ad

racemic:

色谱图

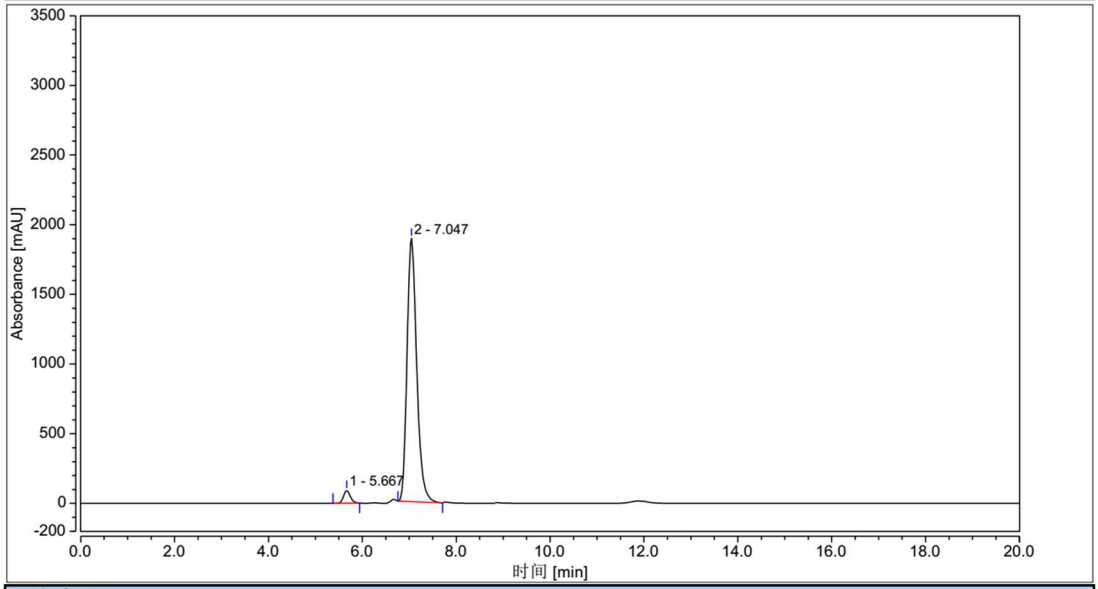


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.673	189.108	1045.203	50.24	57.26	n.a.
2		7.070	187.271	780.209	49.76	42.74	n.a.
总和:			**376.379**	**1825.412**	**100.00**	**100.00**	

enantioselective:

色谱图



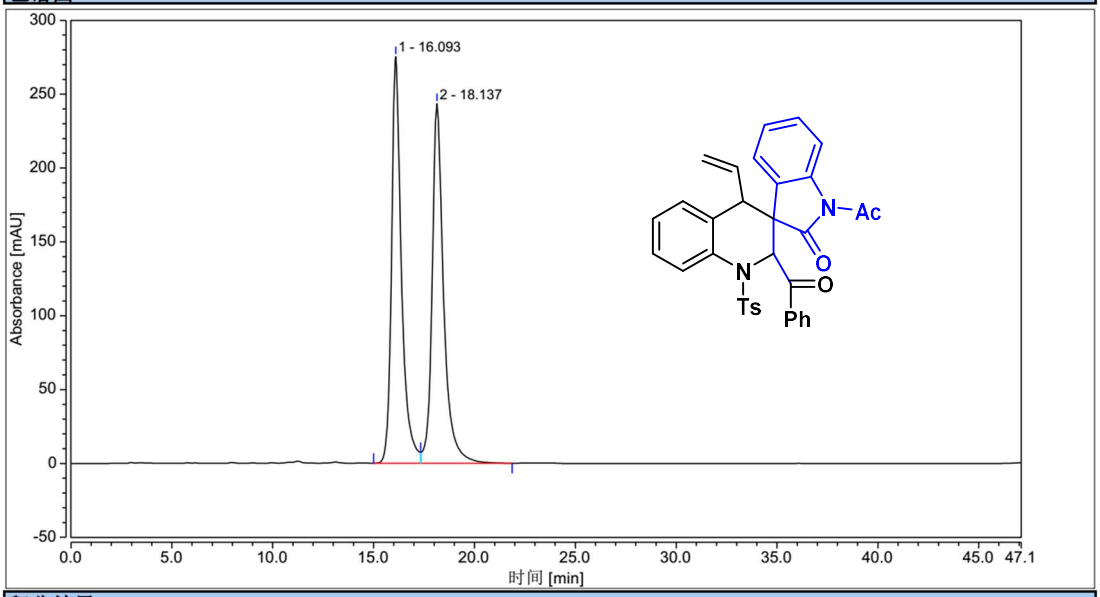
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.667	15.402	91.084	3.31	4.60	n.a.
2		7.047	449.866	1888.628	96.69	95.40	n.a.
总和:			**465.268**	**1979.712**	**100.00**	**100.00**	

3ae

racemic:

色谱图

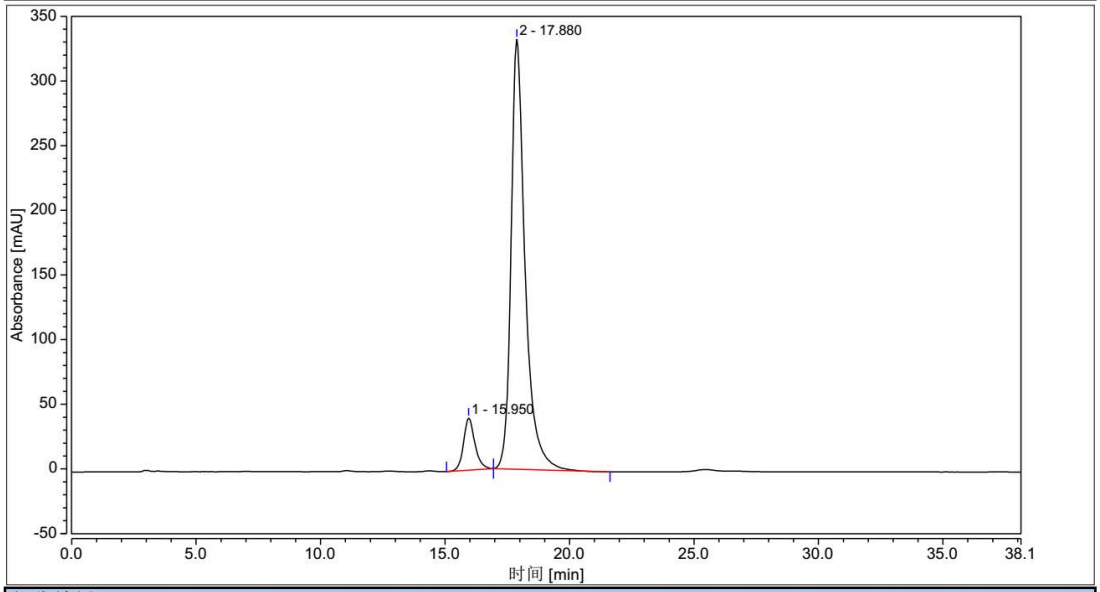


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		16.093	157.187	275.266	49.27	53.06	n.a.
2		18.137	161.835	243.491	50.73	46.94	n.a.
总和:			**319.022**	**518.757**	**100.00**	**100.00**	

enantioselective:

色谱图



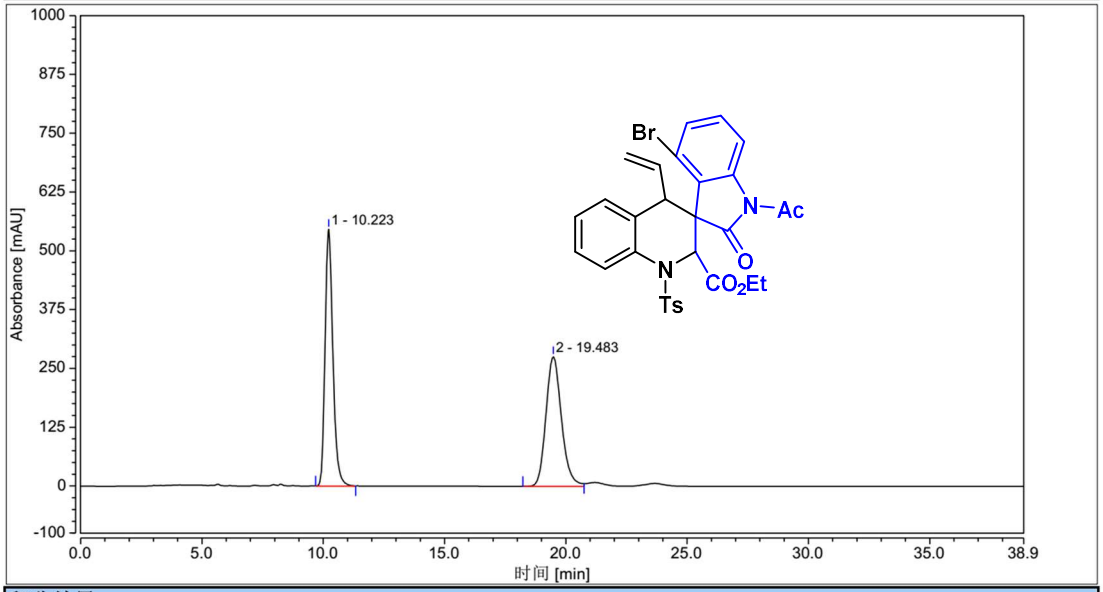
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		15.950	21.336	40.245	8.96	10.80	n.a.
2		17.880	216.902	332.487	91.04	89.20	n.a.
总和:			**238.238**	**372.732**	**100.00**	**100.00**	

3af

racemic:

色谱图

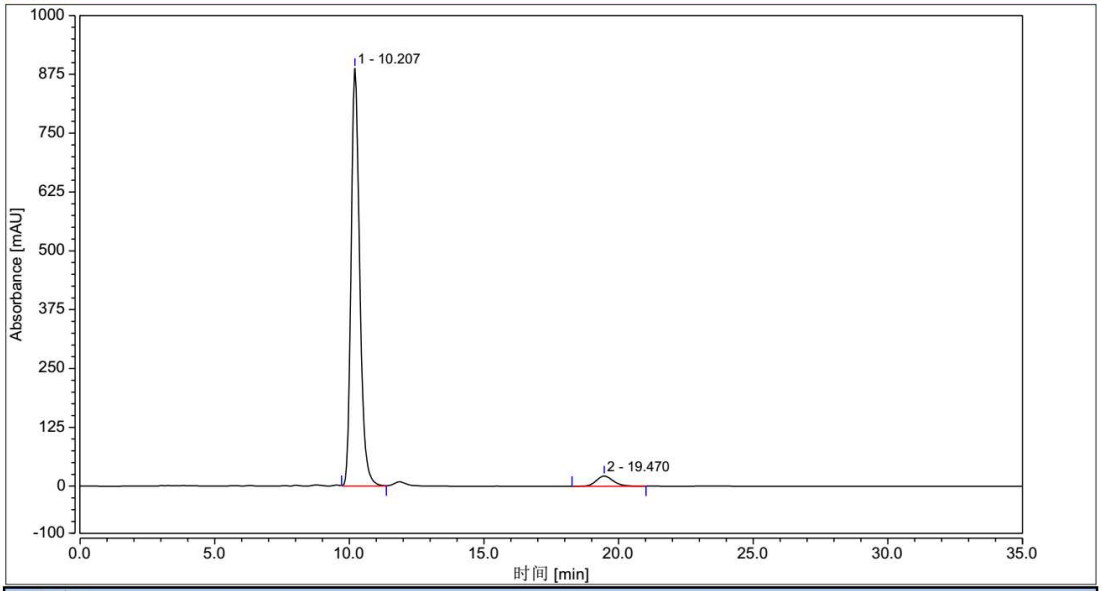


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		10.223	203.112	545.774	49.82	66.44	n.a.
2		19.483	204.559	275.698	50.18	33.56	n.a.
总和:			**407.671**	**821.472**	**100.00**	**100.00**	

enantioselective:

色谱图



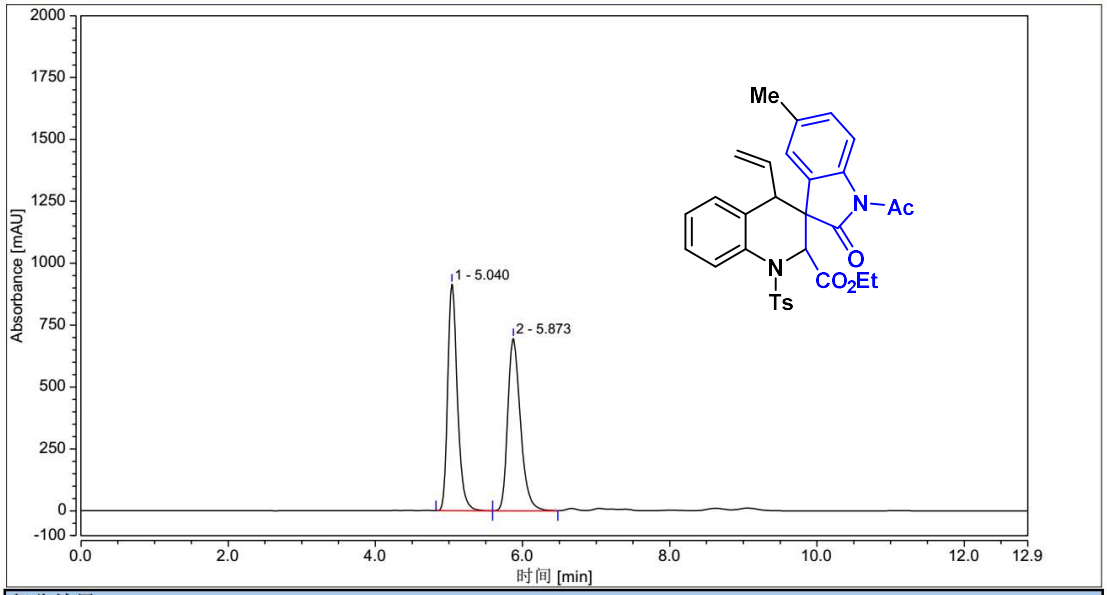
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		10.207	330.863	887.438	95.43	97.62	n.a.
2		19.470	15.851	21.602	4.57	2.38	n.a.
总和:			**346.714**	**909.041**	**100.00**	**100.00**	

3ag

racemic:

色谱图

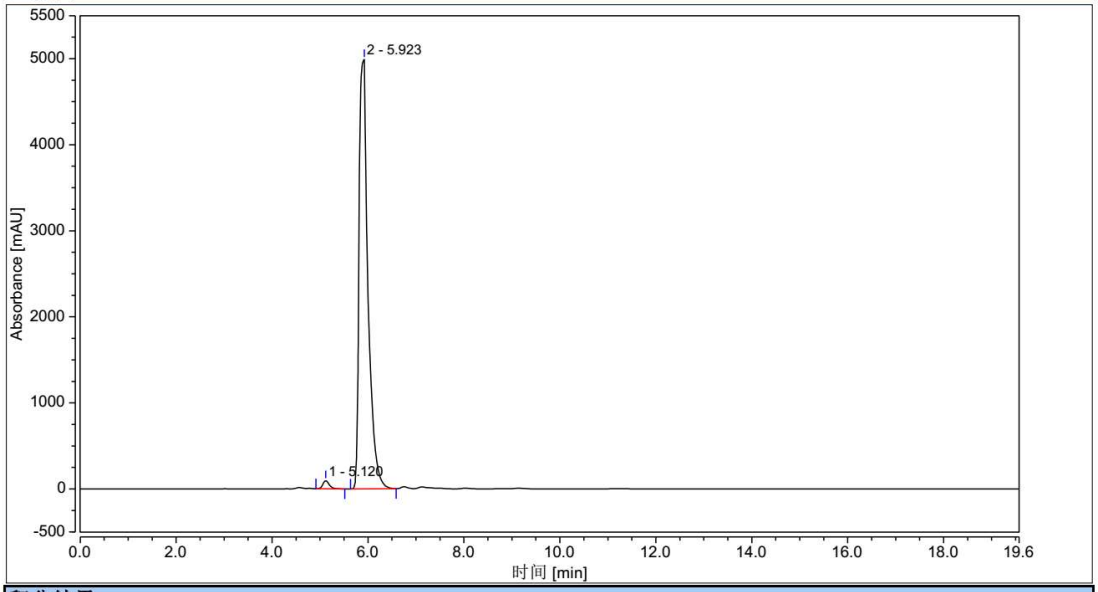


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.040	139.255	915.513	49.89	56.80	n.a.
2		5.873	139.896	696.164	50.11	43.20	n.a.
总和:			**279.151**	**1611.677**	**100.00**	**100.00**	

enantioselective:

色谱图



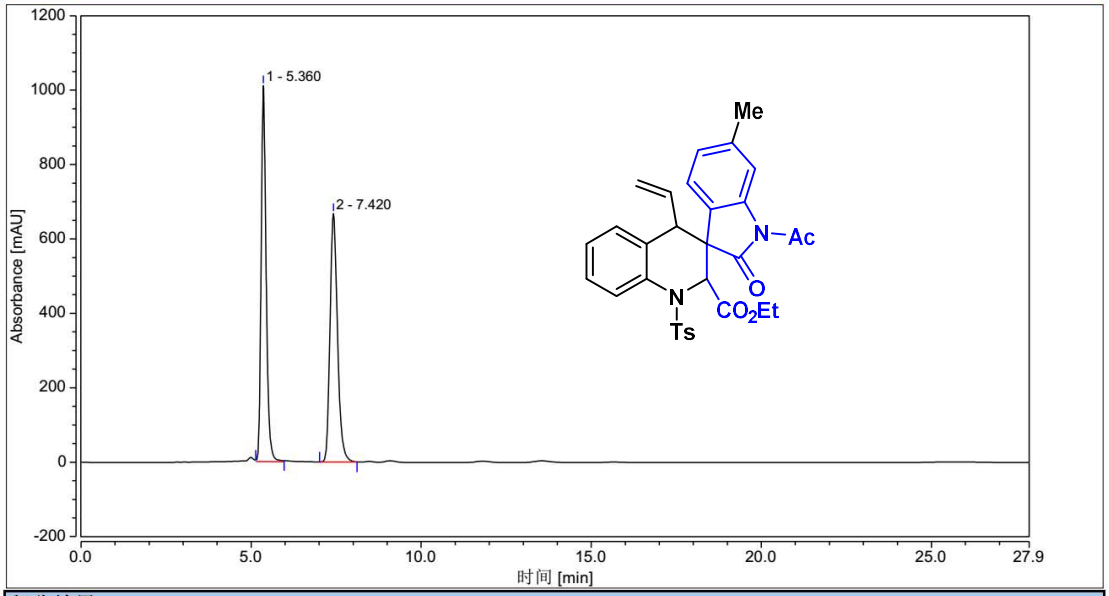
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.120	14.454	95.334	1.33	1.87	n.a.
2		5.923	1068.816	4990.846	98.67	98.13	n.a.
总和:			**1083.269**	**5086.180**	**100.00**	**100.00**	

3ak

racemic:

色谱图

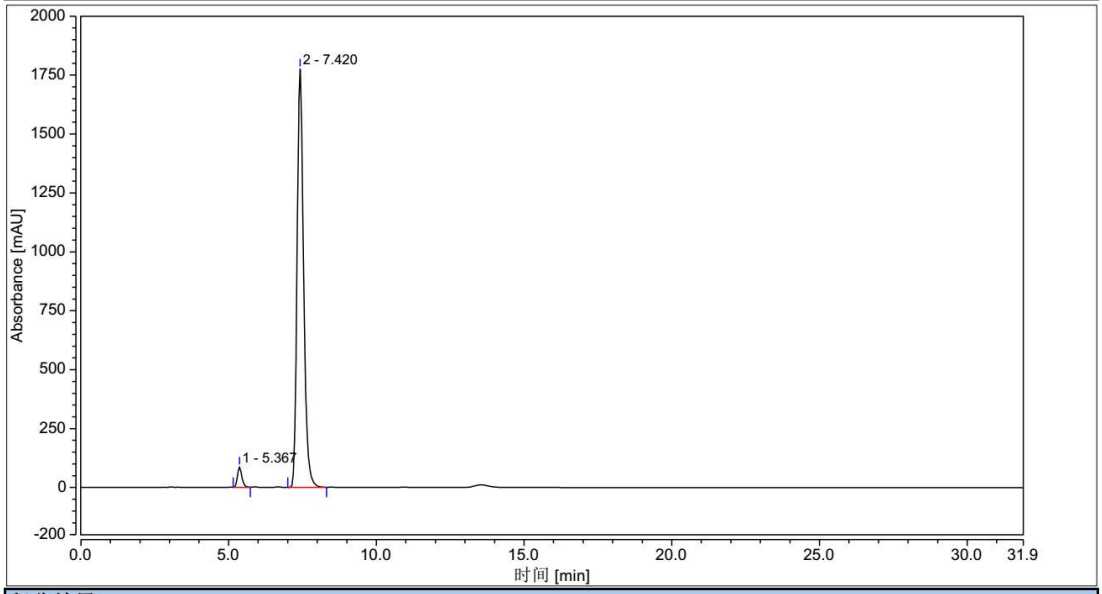


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.360	172.583	1010.068	50.39	60.20	n.a.
2		7.420	169.899	667.790	49.61	39.80	n.a.
总和:			**342.482**	**1677.858**	**100.00**	**100.00**	

enantioselective:

色谱图



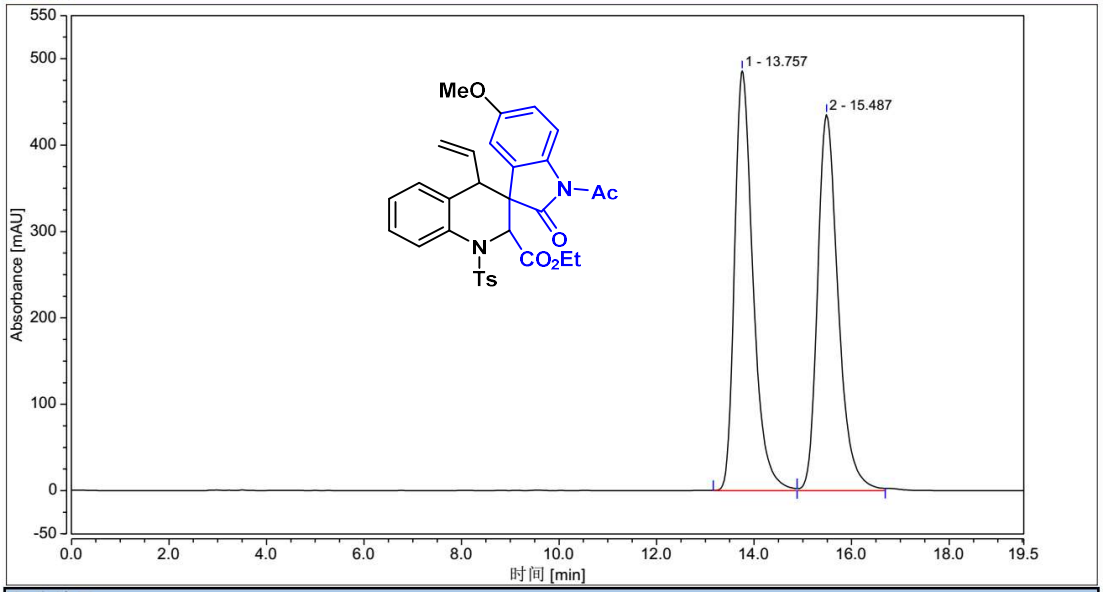
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.367	15.373	87.099	3.27	4.68	n.a.
2		7.420	455.070	1775.777	96.73	95.32	n.a.
总和:			**470.443**	**1862.876**	**100.00**	**100.00**	

3ah

racemic:

色谱图

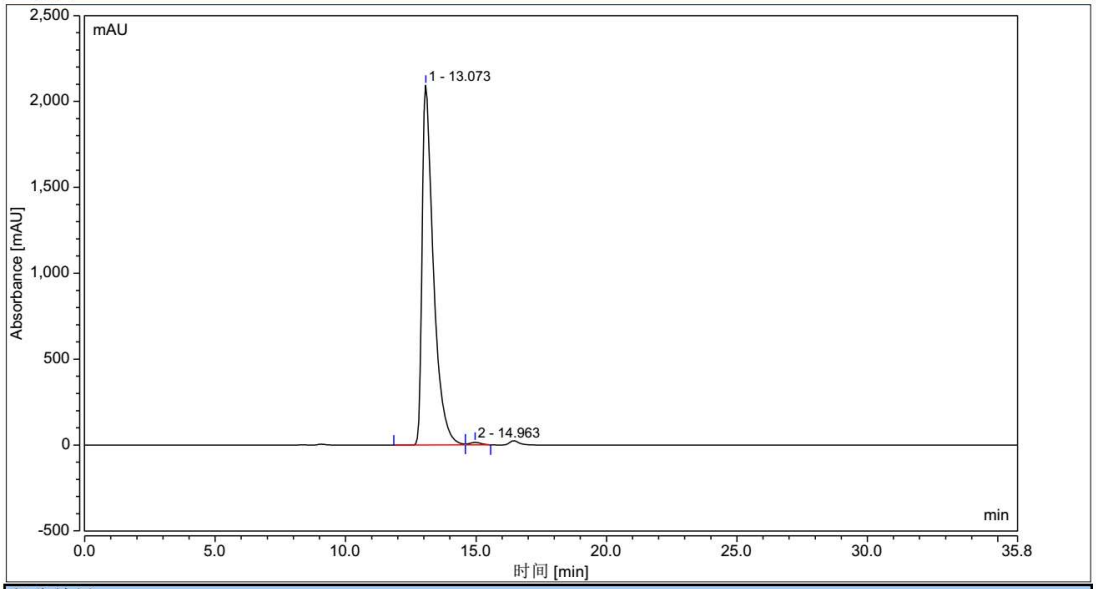


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.757	213.262	485.893	49.92	52.75	n.a.
2		15.487	213.905	435.304	50.08	47.25	n.a.
总和:			**427.167**	**921.197**	**100.00**	**100.00**	

enantioselective:

色谱图



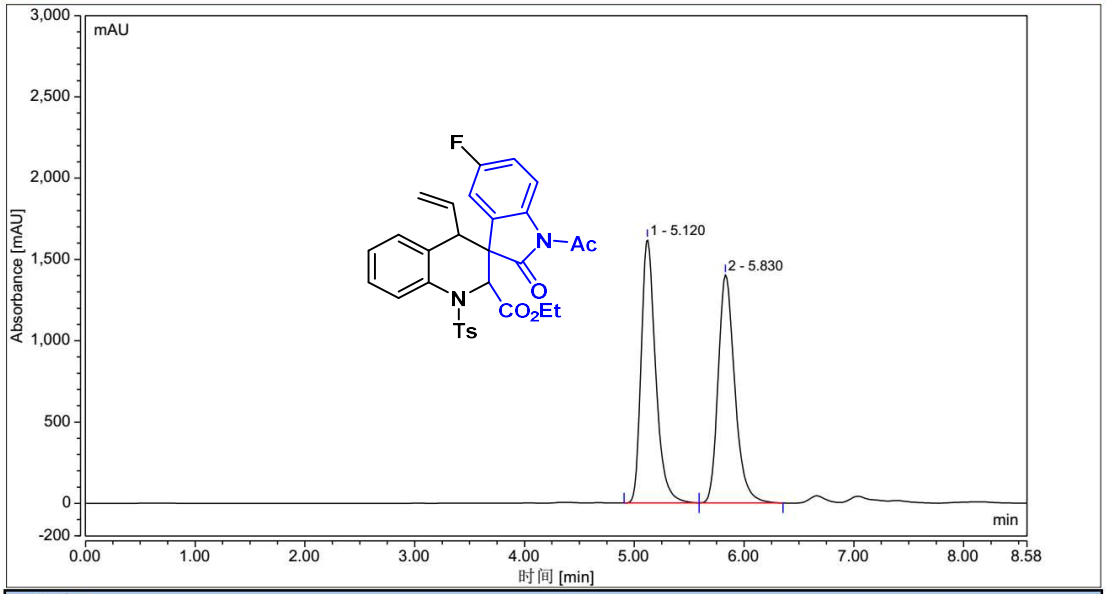
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.073	1052.455	2093.650	99.29	99.28	n.a.
2		14.963	7.525	15.111	0.71	0.72	n.a.
总和:			**1059.980**	**2108.760**	**100.00**	**100.00**	

3ai

racemic:

色谱图

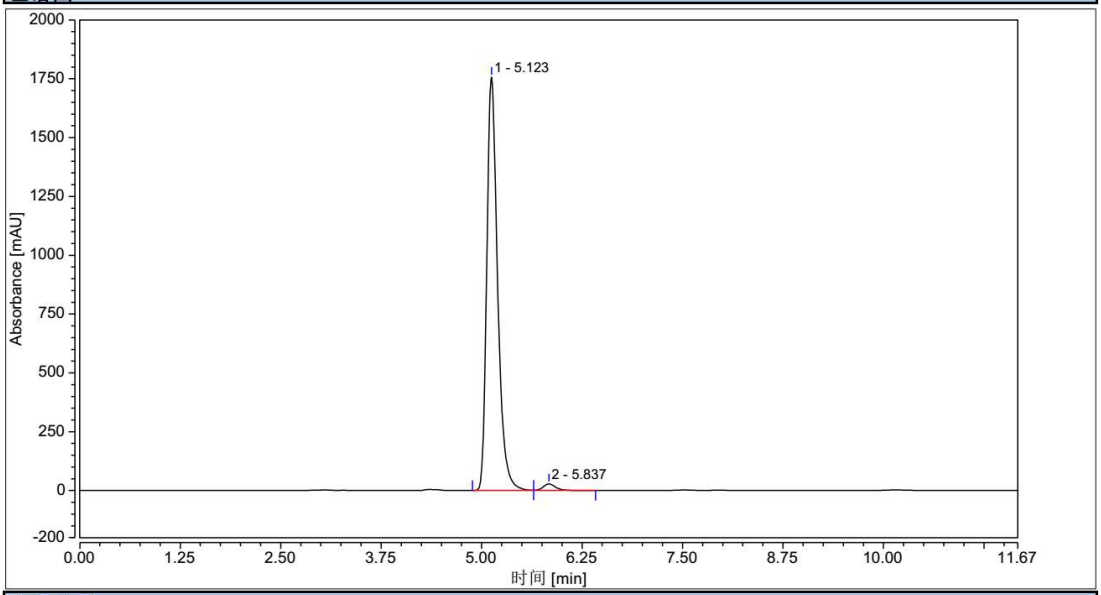


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.120	247.797	1620.748	50.02	53.60	n.a.
2		5.830	247.568	1403.258	49.98	46.40	n.a.
总和:			**495.365**	**3024.006**	**100.00**	**100.00**	

enantioselective:

色谱图



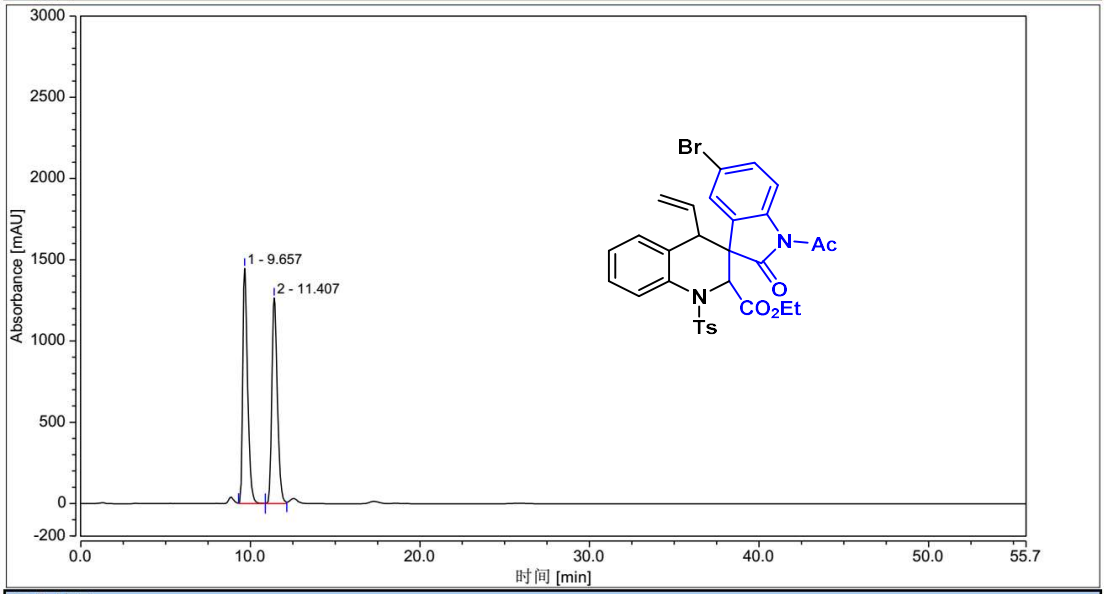
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		5.123	273.038	1756.604	98.17	98.43	n.a.
2		5.837	5.083	28.054	1.83	1.57	n.a.
总和:			**278.121**	**1784.659**	**100.00**	**100.00**	

3aj

racemic:

色谱图

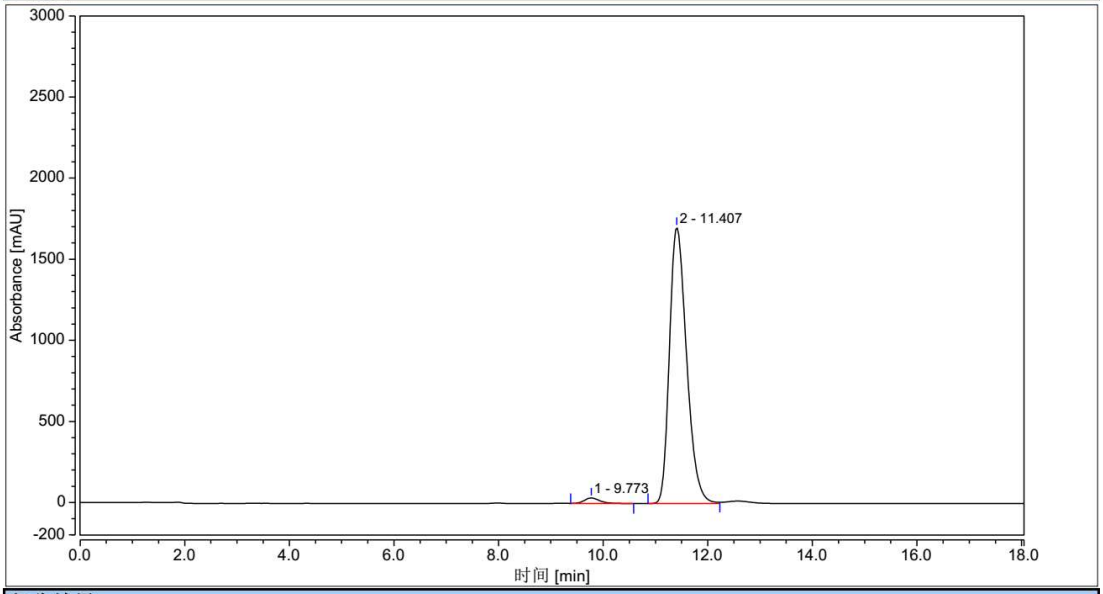


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.657	486.958	1447.317	50.35	53.35	n.a.
2		11.407	480.169	1265.444	49.65	46.65	n.a.
总和:			**967.127**	**2712.761**	**100.00**	**100.00**	

enantioselective:

色谱图



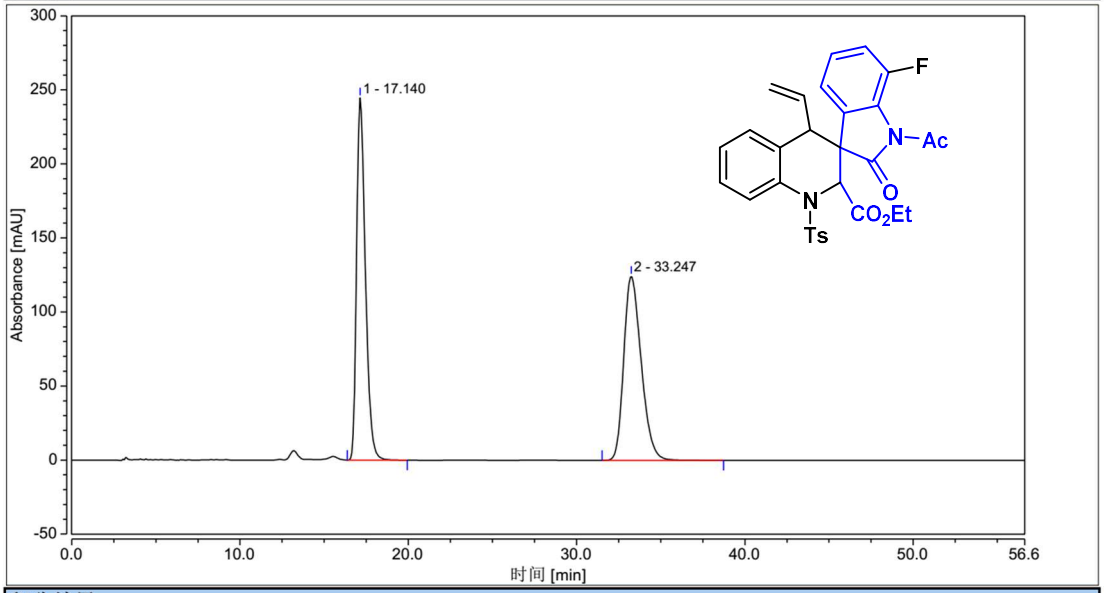
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.773	12.252	34.860	1.86	2.01	n.a.
2		11.407	645.744	1702.430	98.14	97.99	n.a.
总和:			**657.997**	**1737.290**	**100.00**	**100.00**	

3al

racemic:

色谱图

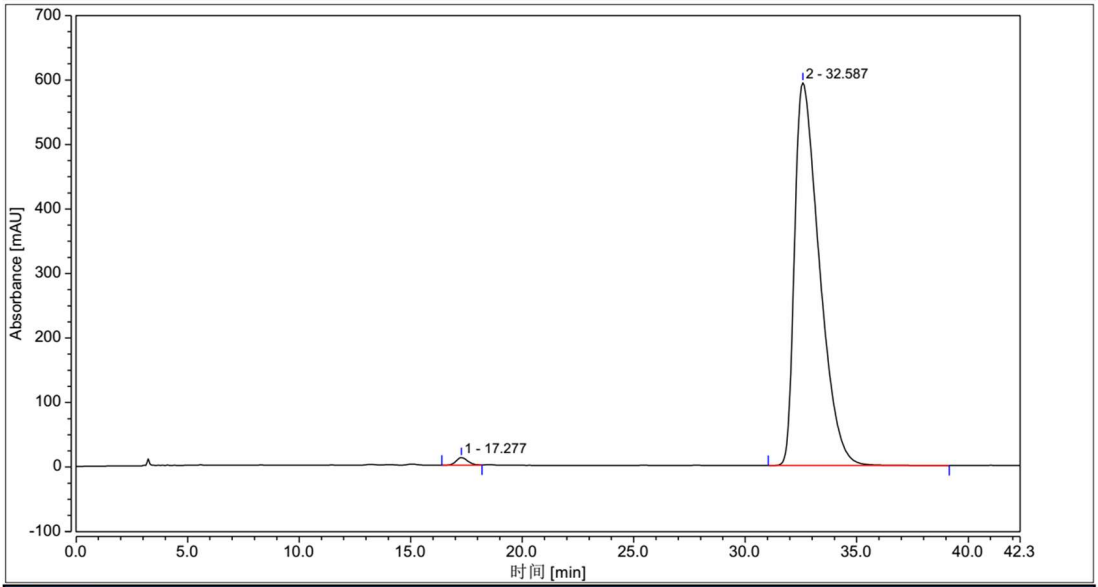


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		17.140	148.639	244.645	49.91	66.29	n.a.
2		33.247	149.148	124.390	50.09	33.71	n.a.
总和:			**297.787**	**369.036**	**100.00**	**100.00**	

enantioselective:

色谱图



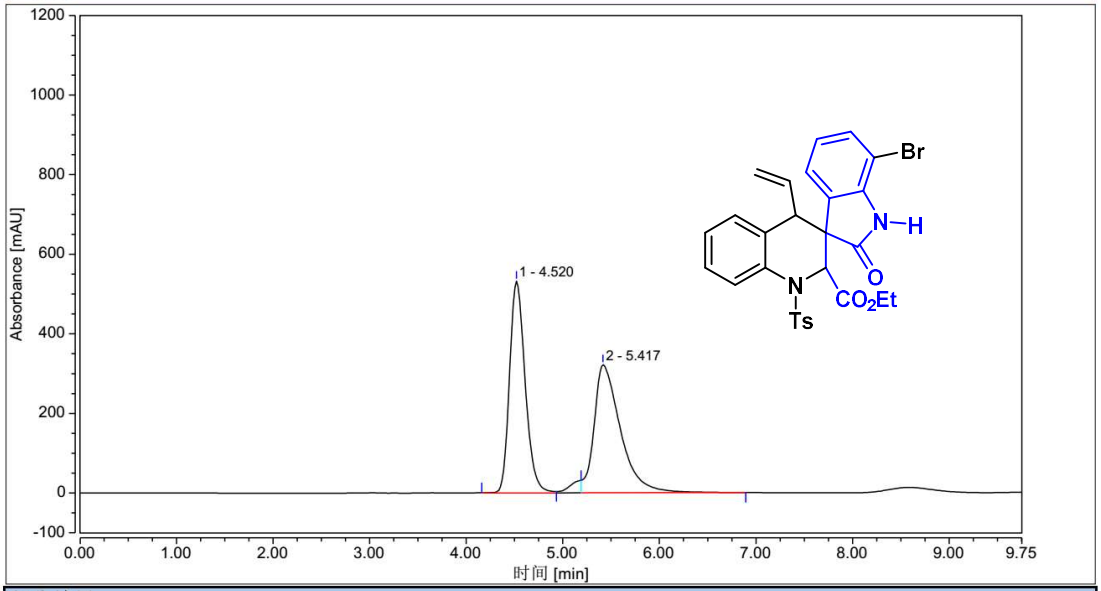
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		17.277	7.432	11.953	0.97	1.98	n.a.
2		32.587	760.364	593.235	99.03	98.02	n.a.
总和:			**767.796**	**605.188**	**100.00**	**100.00**	

3am

racemic:

色谱图

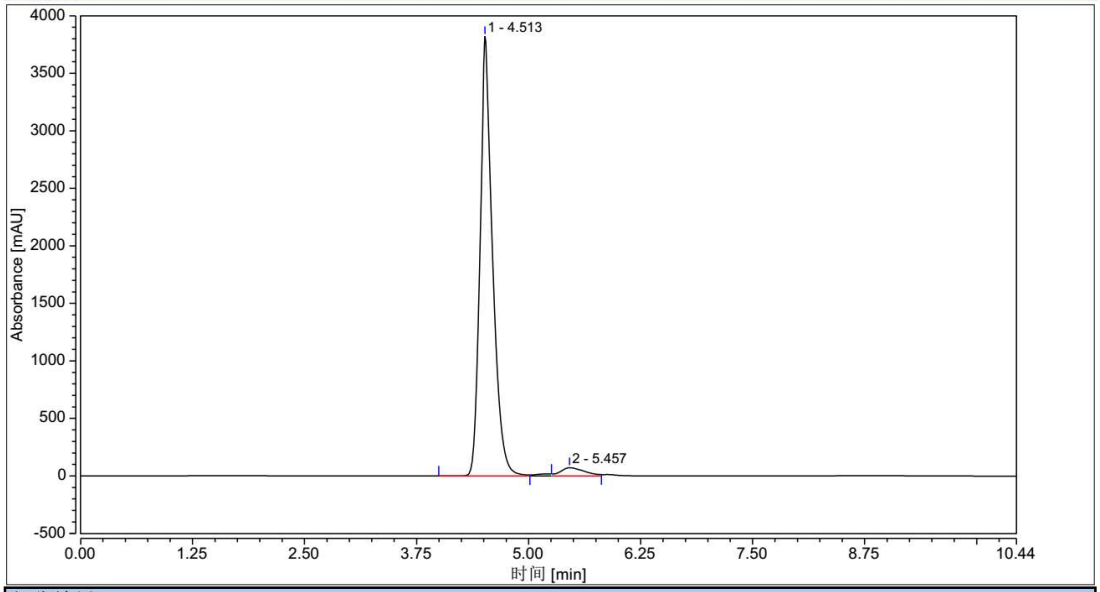


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.520	99.943	531.845	49.51	62.28	n.a.
2		5.417	101.941	322.058	50.49	37.72	n.a.
总和:			**201.884**	**853.903**	**100.00**	**100.00**	

enantioselective:

色谱图



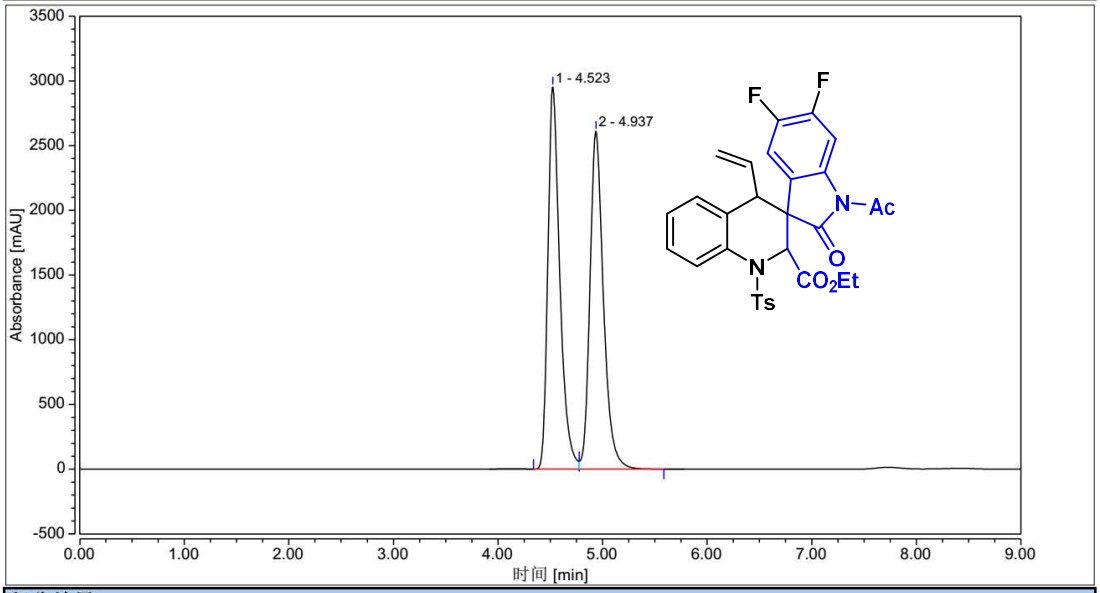
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.513	619.091	3820.548	96.48	98.15	n.a.
2		5.457	22.572	71.897	3.52	1.85	n.a.
总和:			**641.664**	**3892.445**	**100.00**	**100.00**	

4an

racemic:

色谱图

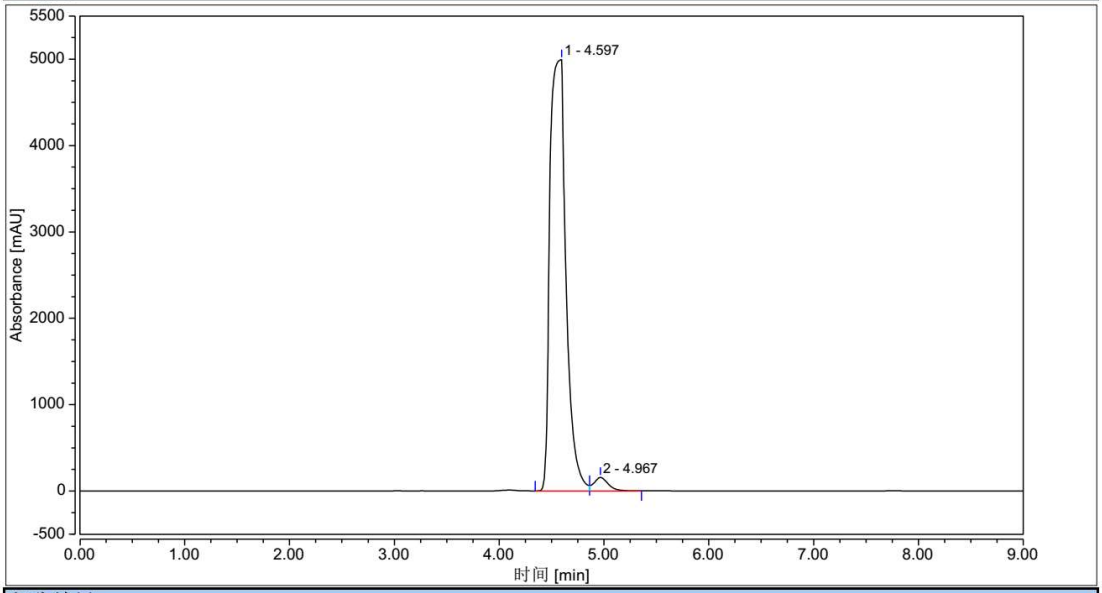


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.523	390.390	2953.024	49.99	53.09	n.a.
2		4.937	390.489	2609.679	50.01	46.91	n.a.
总和:			**780.879**	**5562.703**	**100.00**	**100.00**	

enantioselective:

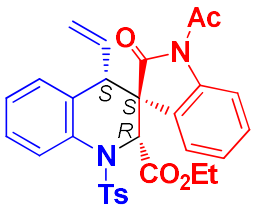
色谱图



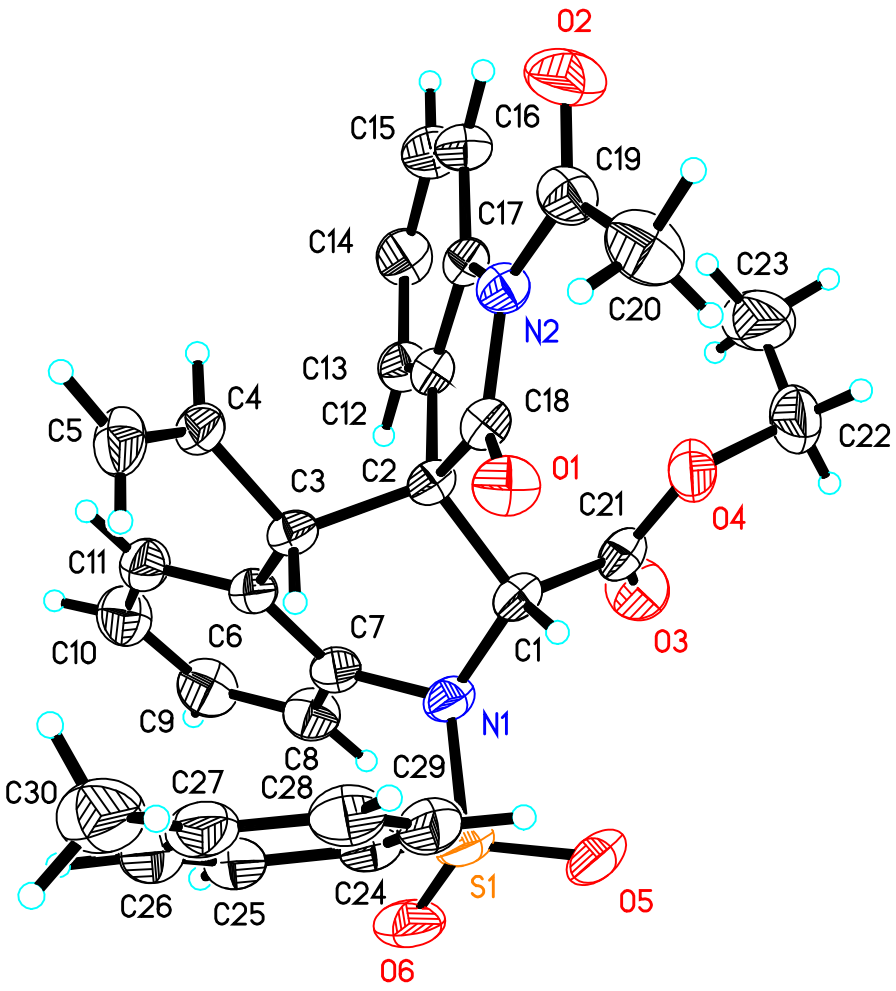
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.597	886.465	4993.829	97.24	96.96	n.a.
2		4.967	25.121	156.592	2.76	3.04	n.a.
总和:			**911.586**	**5150.421**	**100.00**	**100.00**	

7. X-ray single crystal data for product 3aa



(2'*R*,3*S*,4'*S*)-3aa



The thermal ellipsoid was drawn at the 30% probability level.

Identification code	cu_dm17218_0m	
Empirical formula	C30 H28 N2 O6 S	
Formula weight	544.60	
Temperature	296.15 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.0717(2) Å	α= 90°.

	b = 12.8155(2) Å	β= 90°.
	c = 23.4747(5) Å	γ = 90°.
Volume	2729.13(9) Å^3	
Z	4	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	1.444 mm^{-1}	
F(000)	1144	
Crystal size	0.22 x 0.2 x 0.15 mm^3	
Theta range for data collection	3.766 to 69.678°.	
Index ranges	-10<=h<=8, -12<=k<=15, -27<=l<=28	
Reflections collected	14759	
Independent reflections	4909 [R(int) = 0.0590]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.3889	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4909 / 0 / 355	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1098	
R indices (all data)	R1 = 0.0443, wR2 = 0.1127	
Absolute structure parameter	0.058(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.210 and -0.237 e.Å^{-3}	