Application of chiral *N-tert*-butylsulfinyl vinyl aziridines in Rh(I) catalyzed 1,4-addition of aryl boronic acids with cyclic enones

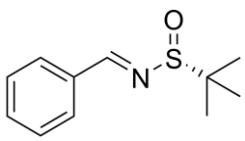
Qian Chen,* Chao Chen, Fang Guo, and Wujiong Xia*

State Key Lab of Urban Water Resource and Environment (SKLUWRE) & Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin, Heilongjiang, 150080, P. R. China.. E-mail: chenqian@hit.edu.cn xiawj@hit.edu.cn

Melting points were determined on a FishereJohns apparatus and not corrected. HRMS were obtained from Agilent 6520 Q-TOF LC/MS. ^{1}H and ^{13}C NMR data was acquired on a Bruker AV-400 MHz spectrometer. Commercial reagents were purchased and used without further purification. THF was distilled over benzophenone ketyl under nitrogen. CH_2Cl_2 was distilled over CaH_2 under nitrogen. Dioxane was distilled over $LiAlH_4$ under nitrogen.

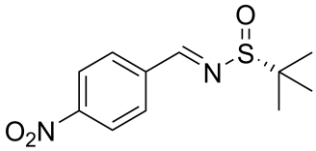
General Procedure for the Synthesis of tert-Butanesulfinyl Aldimines from $CuSO_4$[1]:

To a 0.5 M solution of *(R)*- *tert*-butanesulfinamide (1 equiv, 5mmol) in CH_2Cl_2 was added anhydrous $CuSO_4$ (2.2equiv, 11mmol) followed by the aldehyde (1.1 equiv, 5.5mmol). The mixture was stirred at room temperature for 12-24 h. The reaction mixture was filtered through a pad of Celite, and the filter cake was washed well with CH_2Cl_2. The residue obtained after filtration was purified by chromatography.

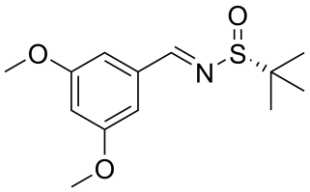


a pale oil, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.89 – 7.84 (m, 2H), 7.55 – 7.45 (m, 3H),

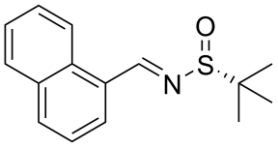
1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 134.1, 132.4, 129.4, 129.0, 57.8, 22.6. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{11}H_{16}NOS$: 210.0947, found 210.0955.



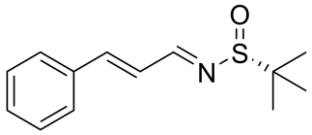
a yellow solid of mp140-141 °C, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.34 (d, *J* = 8.7 Hz, 2H), 8.03 (d, *J* = 8.7 Hz, 2H), 1.30 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 149.9, 138.9, 130.1, 124.2, 58.5, 22.7. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{11}H_{15}N_2O_3S$ 255.0798, found 255.0800.



a colourless oil, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 7.00 (d, *J* = 2.2Hz, 2H), 6.62 (t, *J* = 2.1Hz, 1H), 3.84 (s, 6H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 161.1, 135.93, 107.0, 104.9, 57.9, 55.6, 22.6. HRMS-ESI(*m/z*):$[M+H]^+$ calcd for $C_{13}H_{20}NO_3S$ 270.1158, found 270.1174.



a pale oil, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (s, 1H), 9.04 (d, *J* = 8.5Hz, 1H), 8.03 (dd, *J* = 12.2Hz, 7.7Hz, 2H), 7.92 (d, *J* = 8.1Hz, 1H), 7.65 (t, *J* =7.6Hz, 1H), 7.57 (t, *J* = 7.6Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 133.9, 133.3, 132.0, 131.3, 129.4, 128.9, 128.1, 126.5, 125.3, 124.4, 57.7, 22.7. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{15}H_{18}NOS$ 260.1104, found 260.1105.

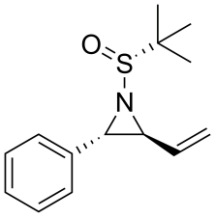


a yellow solid of mp 60-61°C, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 9.2 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.40 (d, *J* = 6.2 Hz, 3H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.09 (dd, *J* = 15.9, 9.2 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 146.4, 135.0, 130.3, 129.0, 127.9, 125.6, 57.6 22.5. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{13}H_{18}NOS$ 236.1104, found 236.1110.

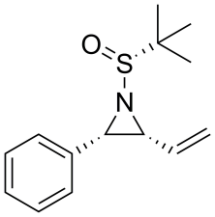
General procedure for the preparation of tert-butylsulfinyl vinyl aziridines[2]:

A solution of the tetrahydrothiophene allyl sulfur salt (1.5mmol, 1.5eq) in anhydrous tetrahydrofuran was stirred at room temperature under an atmosphere of nitrogen. After 10 minutes, a solution of the *tert*-butylsulfinylimine (1 mmol) in anhydrous tetrahydrofuran (5 ml), was added to the reaction mixture. The cloudy dispersion was then stirred for a further 20 minutes. At this stage the cesium carbonate (1.5 mmol, 1.5 eq) was added portion-wise to the reaction mixture. Once the reaction was complete by TLC, ice-cold brine (15 ml) was added, and the biphasic reaction was stirred rapidly for 10 minutes. The resulting cloudy mixture was then filtered through a pad of celite, the product extracted into diethyl ether, washed with brine and dried over sodium sulfate. The organic fraction was concentrated in vacuo to yield a crude mixture containing the azirdine. The desired products were isolated by column

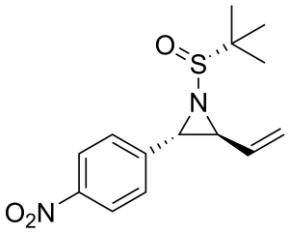
chromatography.



a pale oil, total 65% yield, *trans*:*cis* =2.5:1, $[\alpha]_D^{20}$ -88(c 0.072, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.25 (m, 5H), 6.27 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.46 (d, *J* = 17.0 Hz, 1H), 5.35 (d, *J* = 10.2 Hz, 1H), 3.54 (d, *J* = 3.5 Hz, 1H), 3.16 (dd, *J* = 9.4, 3.5 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 133.3, 128.6, 128.0, 126.3, 120.8, 57.4, 54.1, 44.5, 23.0. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}NOS$, 250.1260, found 250.1244.

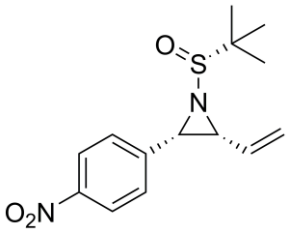


a pale oil, $[\alpha]_D^{20}$ -74(c 0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.25 (m, 5H), 5.98 (dt, *J* = 17.2, 9.9 Hz, 1H), 5.52 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.40 (d, *J* = 10.3 Hz, 1H), 3.71 (d, *J* = 3.6 Hz, 1H), 3.07 (d, *J* = 6.6 Hz, 1H), 1.17 (s, 9H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 132.6, 128.6, 127.8, 126.7, 121.9, 57.2, 50.9, 38.2, 22.8. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}NOS$ 250.1260, found 250.1100.

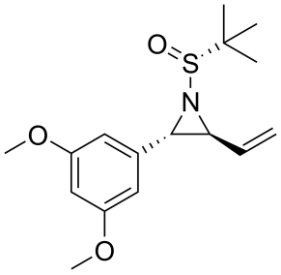


a pale yellow oil, total 55% yield, *trans*:*cis* =2:1, $[\alpha]_D^{20}$ -69 (c 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.7Hz, 2H), 7.46 (d, *J* = 8.7Hz, 2H), 6.32 (ddd, *J* = 17.0Hz, 9.9 Hz, 9.8Hz 1H), 5.49 (d, *J* = 17.0Hz, 1H), 5.39 (d, *J* = 10.3Hz, 1H), 3.67 (d, *J* = 3.3Hz, 1H), 3.18 (dd, *J* = 3.4Hz, 9.5Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

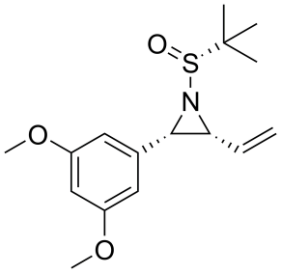
147.6, 144.4, 132.8, 127.1, 123.9, 121.5, 57.8, 55.2, 43.1, 23.1. HRMS-ESI(m/z): $[M+H]^+$ calcd for $C_{14}H_{19}N_2O_3S$ 295.1111, found 295.1138.



a pale oil, $[\alpha]_D^{20}$ -59 (c 0.092, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.7Hz, 2H), 7.46 (d, *J* = 8.6Hz, 2H), 5.97 (ddd, *J* = 16.9Hz, 9.9 Hz, 9.6 Hz 1H), 5.57 (d, *J* = 17.0Hz, 1H), 5.46 (d, *J* = 10.4Hz, 1H), 3.79 (d, *J* = 3.4Hz, 1H), 3.11 (d, *J* = 6.9Hz, 1H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 144.7, 131.7, 127.5, 123.9, 122.9, 57.4, 29.7, 28.3, 22.9. HRMS-ESI(m/z): $[M+H]^+$ calcd for $C_{14}H_{19}N_2O_3S$ 295.1111, found 295.1131.

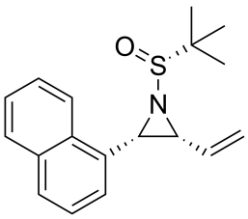


a pale oil, total 90% yield, *trans*:*cis* =6:1, $[\alpha]_D^{20}$-60(c0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 6.45 (d, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 1H), 6.23 (dt, *J* = 17.0, 9.9 Hz, 1H), 5.47 (d, *J* = 16.9 Hz, 1H), 5.36 (d, *J* = 10.2 Hz, 1H), 3.78 (s, 6H), 3.47 (d, *J* = 3.5 Hz, 1H), 3.14 (dd, *J* = 9.4, 3.5 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 139.1, 133.0, 121.0, 104.2, 99.9, 57.4, 55.4, 53.8, 44.8, 22.9. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{16}H_{24}NO_3S$ 310.1471, found 310.1470.

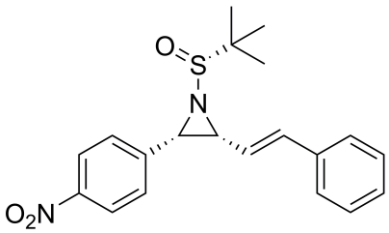


a pale oil, $[\alpha]_D^{20}$ -53 (c 0.132, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 6.47 (d, *J* = 2.19Hz, 2H), 6.40 (t, *J*

= 4.3Hz, 1H), 6.25 (ddd, *J* = 17.0Hz, 9.9 Hz, 9.8Hz 1H), 5.49 (d, *J* = 17.0Hz, 1H), 5.38 (d, *J* = 10.3Hz, 1H), 3.80 (s, 6H), 3.49 (d, *J* = 3.5Hz, 1H), 3.15 (d, *J* = 9.4Hz, 3.5Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 138.4, 131.4, 120.9, 103.5, 98.8, 56.3, 54.3, 49.7, 37.3, 21.8. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{16}H_{24}NO_3S$ 310.1471, found 310.1477.

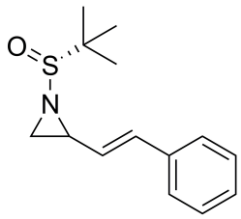


a yellow solid of mp 112-124°C, 16% yield, $[\alpha]_D^{20}$ -30 (c 0.08, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.59 – 7.49 (m, 2H), 7.46 (d, *J* = 5.1 Hz, 2H), 6.18 (s, 1H), 5.54 (d, *J* = 17.0 Hz, 1H), 5.45 (d, *J* = 10.3 Hz, 1H), 4.44 (s, 1H), 3.06 (s, 1H), 1.25 (s, 9H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 133.5, 132.7, 128.8, 128.1, 126.5, 126.0, 125.5, 123.1, 57.3, 51.4, 35.8, 22.8. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{18}H_{22}NOS$ 300.1417, found 300.1422.



a pale oil, 35% yield. $[\alpha]_D^{20}$ -88 (c 0.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.24 (m, 3H), 6.84 (d, *J* = 15.8 Hz, 1H), 6.34 (dd, *J* = 15.8, 9.4 Hz, 1H), 3.91 (d, *J* = 3.4 Hz, 1H), 3.27 (d, *J* = 7.2 Hz, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 137.6, 135.8, 130.2, 128.7, 128.4, 127.5, 126.6, 124.1 122.9, 57.5, 51.5, 38.0,

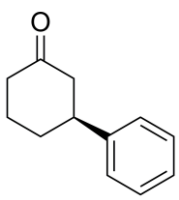
22.7. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{20}H_{23}N_2O_3S$ 371.1424, found 371.1447.



a pale oil, 15% yield, $[\alpha]_D^{20}$ -65 (c 0.02, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 6.72 (dd, *J* = 15.5, 8.6 Hz, 1H), 5.97 – 5.91 (m, 1H), 3.34 – 3.24 (m, 1H), 2.34 (d, *J* = 6.8 Hz, 1H), 2.16 (d, *J* = 9.6 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 133.4, 128.7, 128.0, 127.0, 126.4, 57.0, 34.8, 26.8, 22.9. HRMS-ESI(*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}NOS$ 250.1260, found 250.1260.

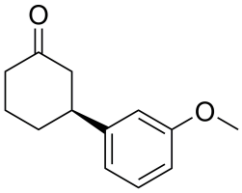
General procedure for Rhodium(I)-catalyzed asymmetric 1,4-addition of phenylboronic Acid to cycloalkenones:

Under N_2 atmosphere, a reaction flask was charged with $RhCl(C_2H_4)_2$ (0.015eq, 0.0075 mmol) and $PhB(OH)_2$ (5eq, 2.5 mmol). To the flask were added successively 1,4-dioxane (2.50 mL), ligand (0.036eq, 0.018 mmol), cyclohexenone (1eq, 1.0 mmol), and 4M aq potassium hydroxide (1eq, 1.0 mmol). The mixture was stirred at 70°C. After dilution with AcOEt, the mixture was washed with 10% aq NaOH and brine, and then dried over Na_2SO_4. Concentration and purification by silica gel column chromatography.

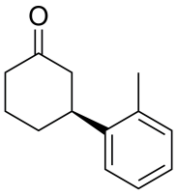


99% yield, $[\alpha]_D^{20}$ -22 (c 0.1, $CHCl_3$), 99% ee (AD, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 15.7 and 18.9 min for major and minor). ^1H NMR (400 MHz, $CDCl_3$):

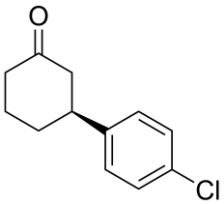
δ 7.36 – 7.29 (m, 2H), 7.27 – 7.20 (m, 3H), 3.01 (tt, *J* = 11.7, 4.0 Hz, 1H), 2.65 – 2.33 (m, 4H), 2.20 – 2.04 (m, 2H), 1.91 – 1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1, 144.4, 128.7, 126.7, 48.9, 44.8, 41.2, 32.8, 25.6.



99% yield, $[\alpha]_D^{20}$ -15 (c 0.08, $CHCl_3$), 96% ee (OD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 42.8 and 46.8 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (td, *J* = 7.7, 1.3 Hz, 1H), 6.84 – 6.75 (m, 3H), 3.80 (s, 3H), 2.98 (tt, *J* = 11.8, 3.9 Hz, 1H), 2.62 – 2.32 (m, 4H), 2.18 – 2.04 (m, 2H), 1.91 – 1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.0, 159.8, 146.1, 129.7, 118.9, 112.7, 111.7, 55.2, 48.9, 44.8, 41.2, 32.7, 25.5.

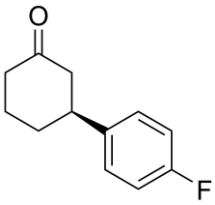


95% yield, $[\alpha]_D^{20}$ -70 (c 0.06, $CHCl_3$), 87% ee (AD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 13.9 and 16.8 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.11 (m, 4H), 3.27 – 3.14 (m, 1H), 2.56 – 2.35 (m, 4H), 2.32 (s, 3H), 2.17 (ddd, *J* = 12.5, 6.3, 3.4 Hz, 1H), 2.00 (d, *J* = 10.2 Hz, 1H), 1.90 – 1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.3, 142.3, 135.1, 130.7, 126.5, 126.4, 125.1, 48.4, 41.3, 40.3, 32.0, 25.8, 19.3.

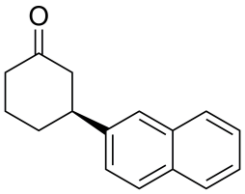


77% yield, $[\alpha]_D^{20}$ -12 (c 0.132, $CHCl_3$), 98% ee (AD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 18.6 and 20.9 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.99 (tt, *J* =

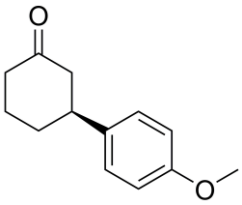
11.8, 3.9 Hz, 1H), 2.60 – 2.33 (m, 4H), 2.19 – 2.03 (m, 2H), 1.88 – 1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 142.8, 132.4, 128.8, 128.0, 48.8, 44.1, 41.1, 32.7, 25.4.



70% yield, $[\alpha]_D^{20}$ -20 (c 0.04, $CHCl_3$) 98% ee (AD, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm, 24.6 and 34.4 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.14 (m, 2H), 7.05 – 6.97 (m, 2H), 3.00 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.62 – 2.32 (m, 4H), 2.19 – 2.00 (m, 2H), 1.88 – 1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 161.6 (d, *J* = 244.8 Hz) 140.1 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 7.8 Hz),115.5 (d, *J* = 21.2 Hz) , 49.1, 44.0, 41.1, 32.9, 25.4.

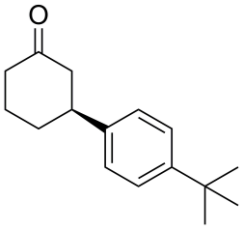


99% yield, $[\alpha]_D^{20}$ -8,7 (c 0.072, $CHCl_3$), 96% ee (AD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 21.6 and 24.0 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 8.7, 4.2 Hz, 3H), 7.63 (s, 1H), 7.50 – 7.41 (m, 2H), 7.35 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.22 – 3.10 (m, 1H), 2.72 – 2.57 (m, 2H), 2.45 (dddd, *J* = 26.8, 19.6, 8.5, 3.8 Hz, 2H), 2.17 (tdd, *J* = 9.8, 6.9, 3.3 Hz, 2H), 2.01 – 1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.0, 141.8, 133.6, 132.4, 128.4, 127.7, 126.2, 125.7, 125.4, 124.8, 48.9, 44.8, 41.3, 32.7, 25.6.

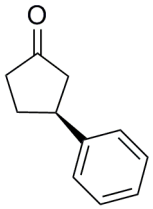


85%yield, $[\alpha]_D^{20}$ -17.8 (c 0.047, $CHCl_3$), 85% ee (OJ-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 39.1

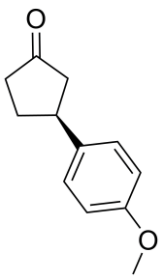
and 43.5 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 2.97 (tt, *J* = 11.7, 3.9 Hz, 1H), 2.60 – 2.34 (m, 4H), 2.18 – 2.02 (m, 2H), 1.85 – 1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 158.5, 136.6, 127.5, 114.0, 55.3, 49.3, 44.0, 41.2, 33.0, 25.



99% yield, $[\alpha]_D^{20}$ -17.9 (c 0.29, $CHCl_3$), 93% ee (OJ-H, hexane/2-propanol = 99/1, 0.3 mL/min, 254 nm, 21.2 and 30.0 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 3.03 (tt, *J* = 11.7, 3.9 Hz, 1H), 2.66 – 2.39 (m, 4H), 2.22 – 2.08 (m, 2H), 1.92 – 1.75 (m, 2H), 1.35 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 149.5, 141.3, 126.2, 125.6, 49.0, 44.3, 41.3, 34.4, 32.8, 31.4, 25.6.

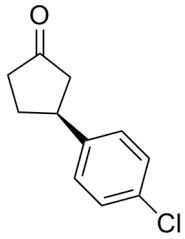


85% yield, $[\alpha]_D^{20}$ -78 (*c* 0.012 $CHCl_3$), 51% ee (AS-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 41.5 and 45.5 min for minor and major).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 9.8, 5.3 Hz, 2H), 7.34 – 7.23 (m, 3H), 3.45 (tt, *J* = 11.1, 7.0 Hz, 1H), 2.70 (dd, *J* = 18.2, 7.6 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.43 – 2.26 (m, 2H), 2.11 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.4, 143.1, 128.7, 126.8, 45.8, 42.2, 38.9, 31.2.

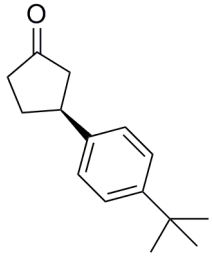


55% yield, $[\alpha]_D^{20}$ -86 (c 0.036, $CHCl_3$), 85% ee (OD-H, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm, 33.8 and 35.4 min for minor and major). ^{1}H NMR (400 MHz, $CDCl_3$):

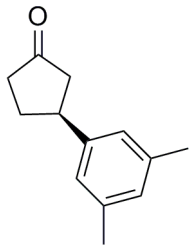
δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.43 – 3.31 (m, 1H), 2.65 (dd, *J* = 18.1, 7.5 Hz, 1H), 2.42 (dddd, *J* = 10.0, 8.0, 6.0, 5.0 Hz, 2H), 2.35 – 2.23 (m, 2H), 2.01 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.7, 158.4, 135.1, 127.7, 114.1, 55.3, 46.1, 41.5, 38.9, 31.4.



88% yield, $[\alpha]_D^{20}$ -53 (*c* 0.02 $CHCl_3$), 30% ee (AS-H, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm, 60.6 and 67.5 min for minor and major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.40 (ddd, *J* = 18.0, 11.1, 6.9 Hz, 1H), 2.66 (dd, *J* = 18.1, 7.6 Hz, 1H), 2.53 – 2.39 (m, 2H), 2.38 – 2.20 (m, 2H), 2.02 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.8, 141.5, 132.4, 128.8, 128.1, 45.7, 41.6, 38.8, 31.1.

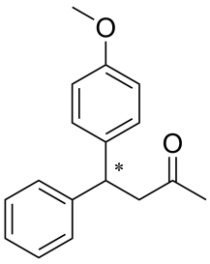


99% yield, $[\alpha]_D^{20}$ -65 (*c* 0.11 $CHCl_3$), 64% ee (AD, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 15.6 and 18.3 min for major and minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.43 (ddd, *J* = 13.4, 11.1, 6.9 Hz, 1H), 2.69 (dd, *J* = 18.2, 7.5 Hz, 1H), 2.54 – 2.28 (m, 4H), 2.08 – 1.95 (m, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.6, 149.7, 140.0, 126.4, 125.6, 45.9, 41.8, 38.9, 34.5, 31.3.



99% yield, $[\alpha]_D^{20}$ -49 (*c* 0.2 $CHCl_3$), 41% ee (AS-H, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm, 29.5 and

33.3 min for minor and major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.87 (s, 2H), 3.43 – 3.22 (m, 1H), 2.64 (dd, *J* = 18.3, 7.3 Hz, 2H), 2.43 (ddd, *J* = 12.3, 8.2, 5.3 Hz,2H), 2.31 (s, 6H), 2.30 – 2.10 (m, 2H), 2.06 – 1.88 (m, 1H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 219.0, 143.1, 138.2, 128.4, 124.6, 113.1, 45.9, 42.2, 38.9, 31.4， 31.3, 21.4.

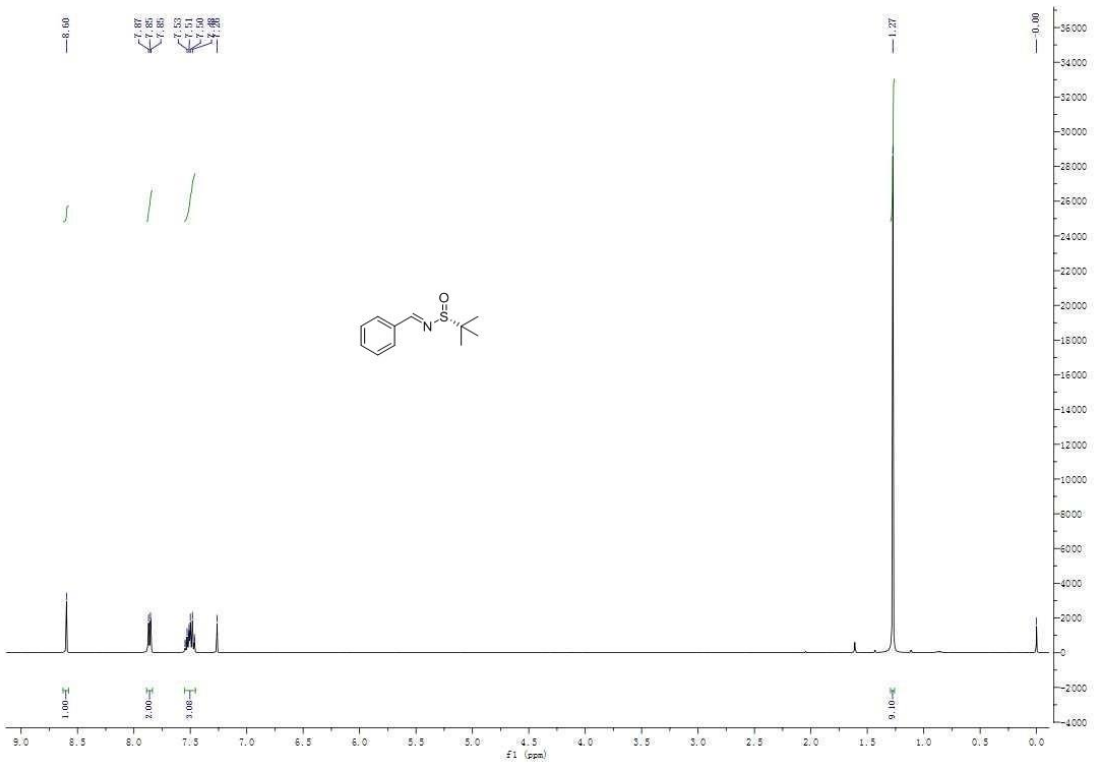


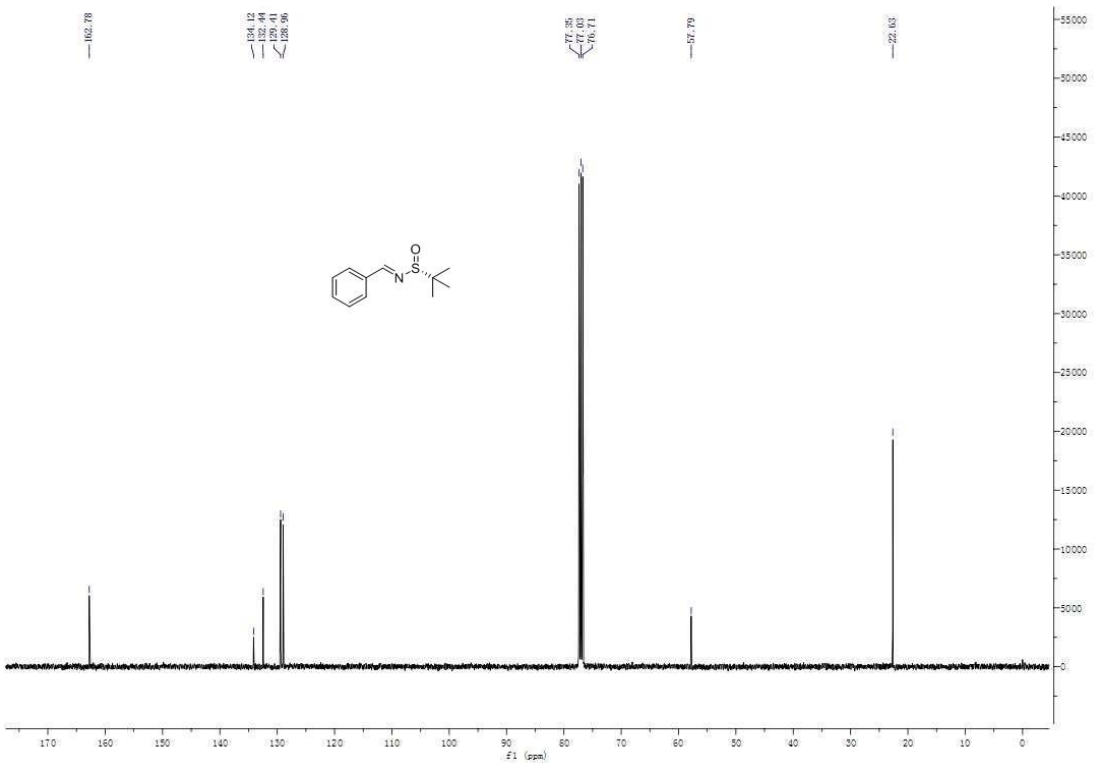
30% yield, $[\alpha]_D^{20}$ -8 (*c* 0.088 $CHCl_3$), 67% ee (OD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm, 21.9 and 23.4 min for minor and major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 7H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.53 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.14 (d, *J* = 7.6 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) :δ 207.1, 158.1, 144.25, 135.9, 128.6, 127.6, 126.4, 113.9, 55.2, 49.9, 45.3, 30.7.

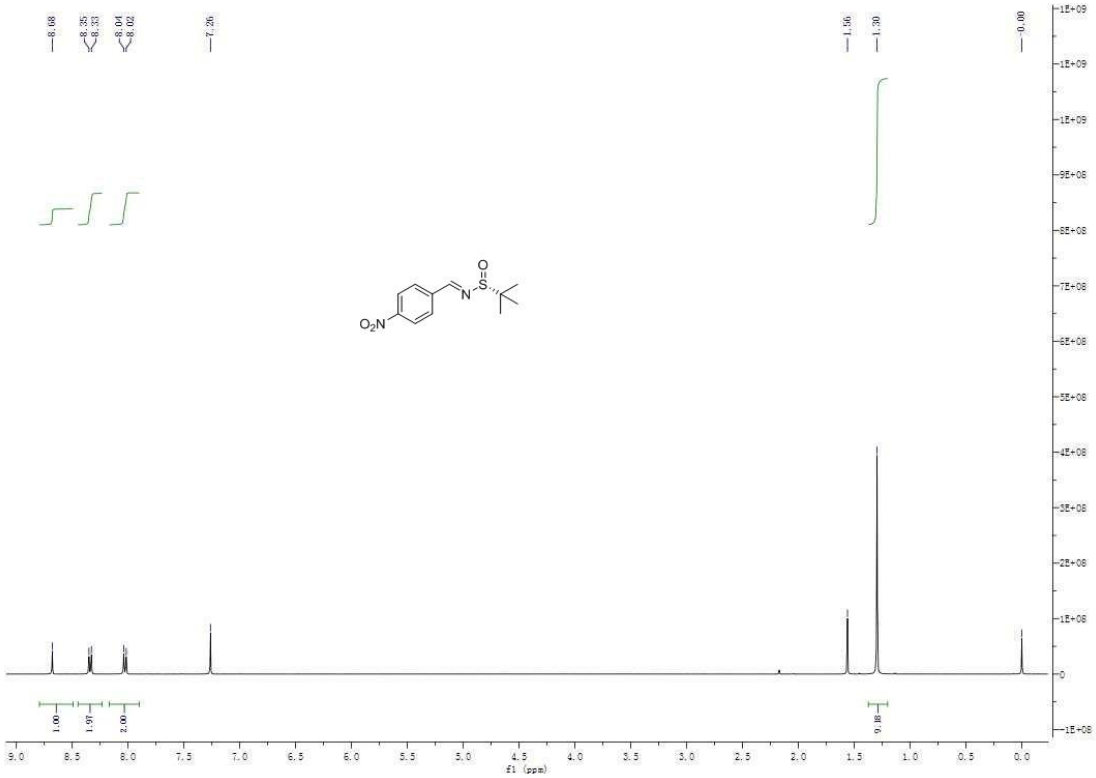
References

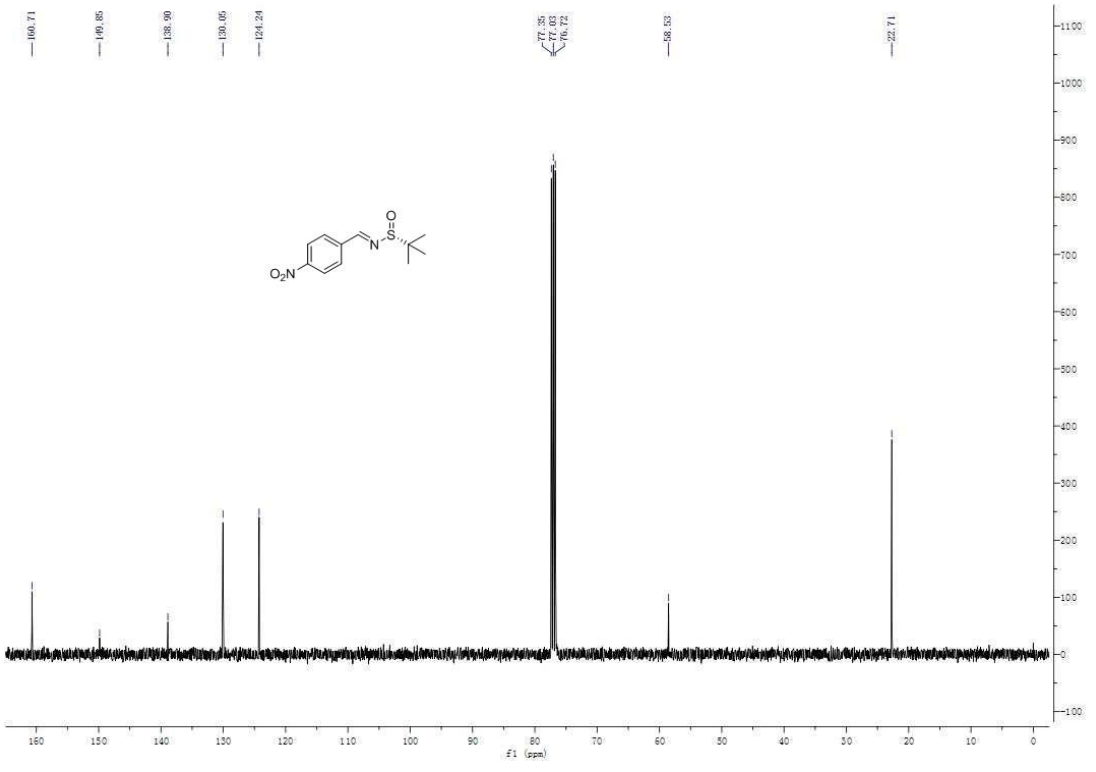
(1) Guang, C.; Derek, C.; Timothy, O.; Tony, T.; Jonathan, E. *J. Org. Chem.* **1999**, *64*, 1278-1284.

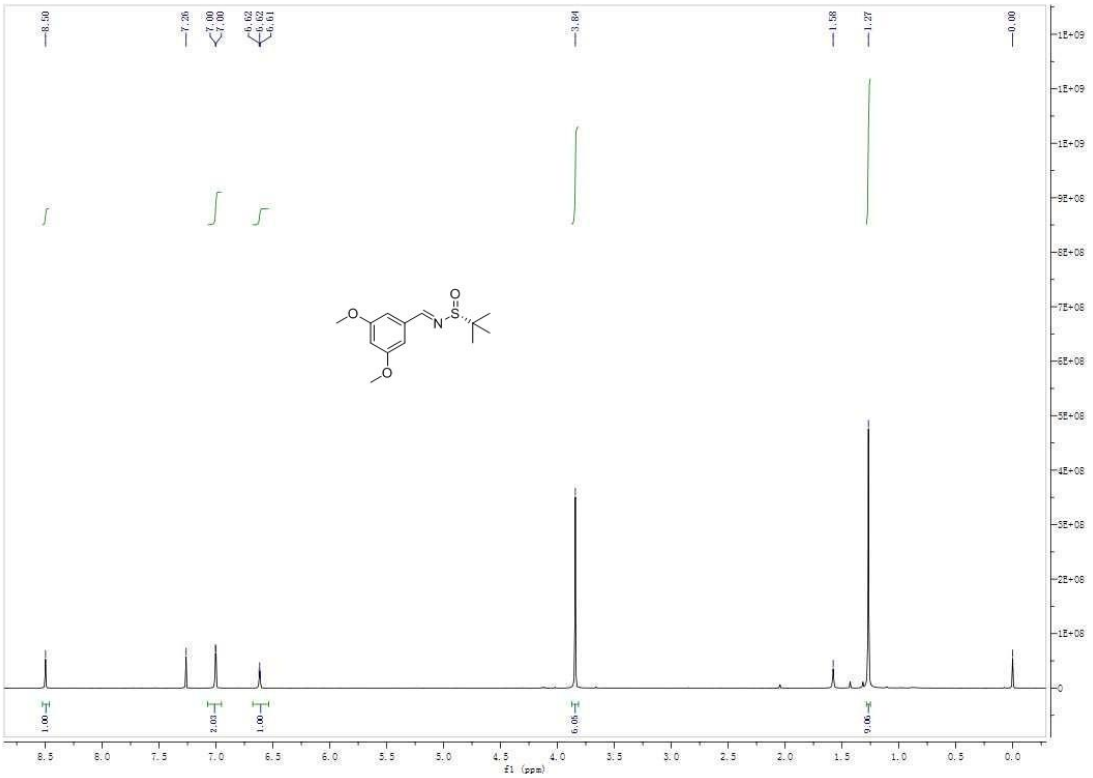
(2) Daniel, M.; David, P.; Robert, F.; Robert, S. *Org. Lett*. **2004**, *6*, 2377-2380.

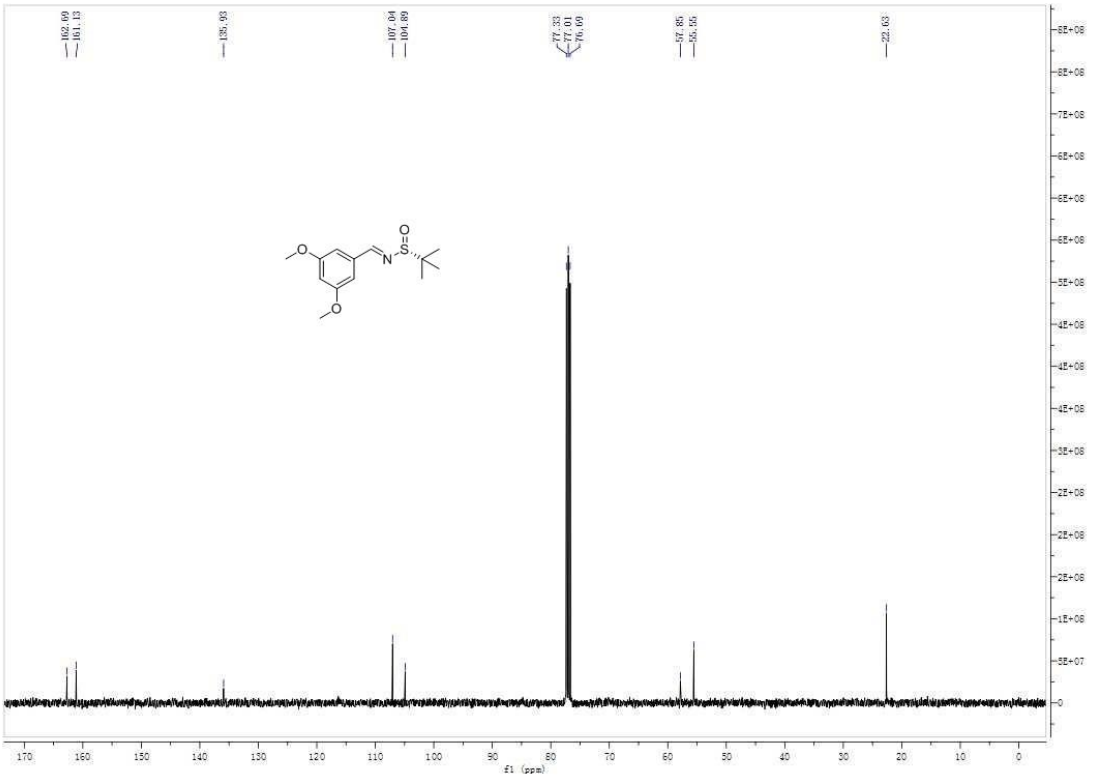


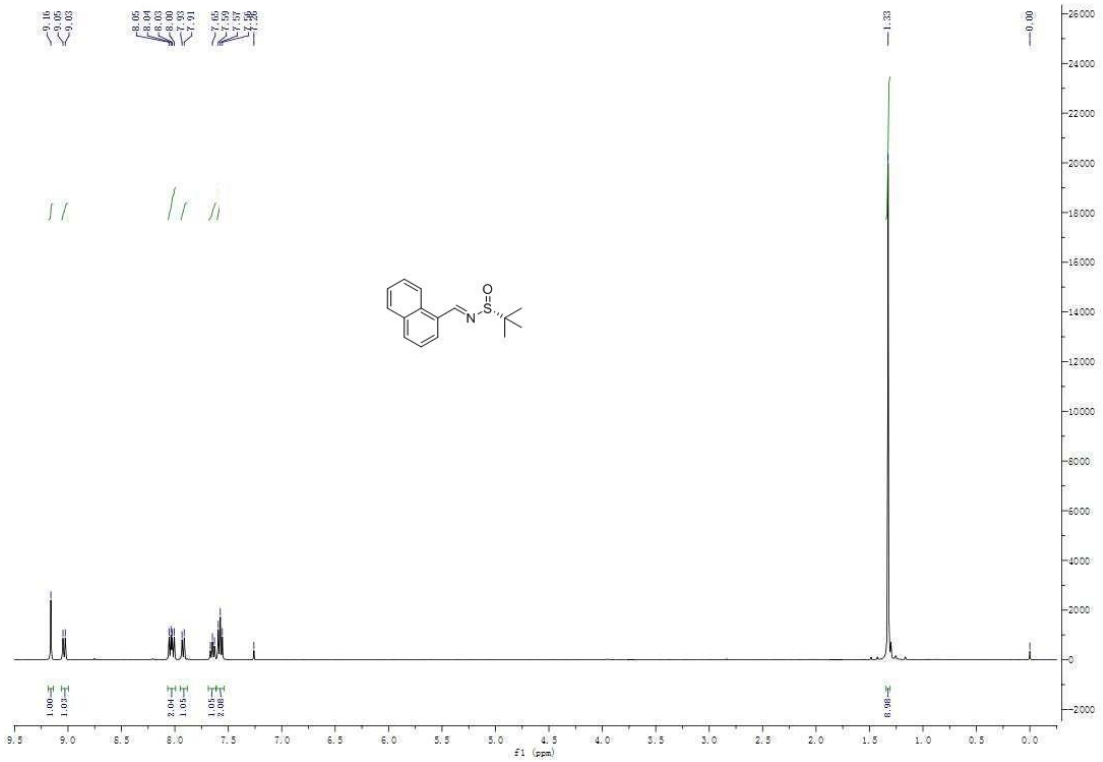


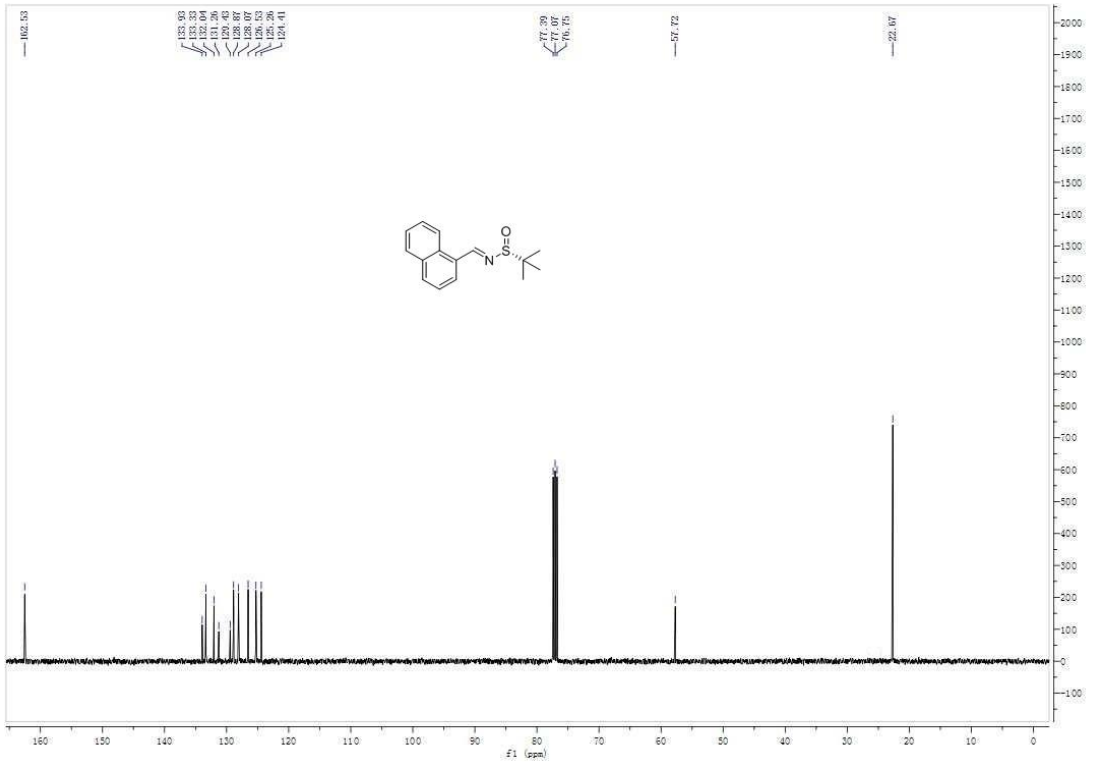


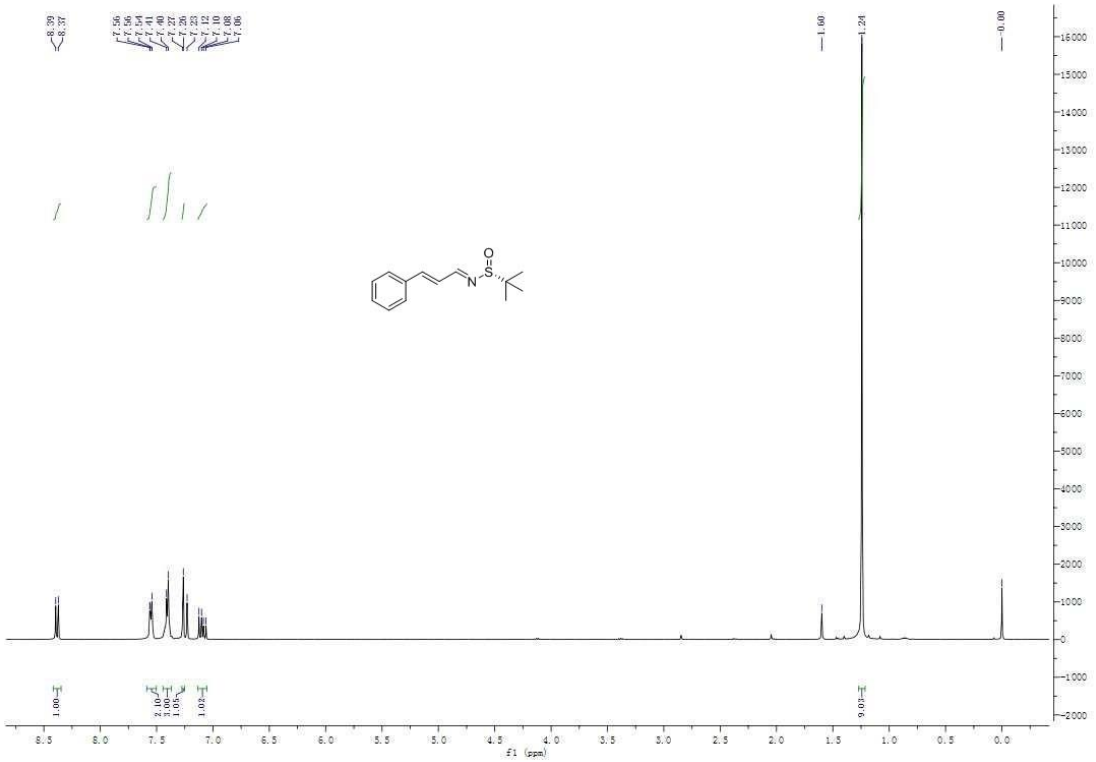


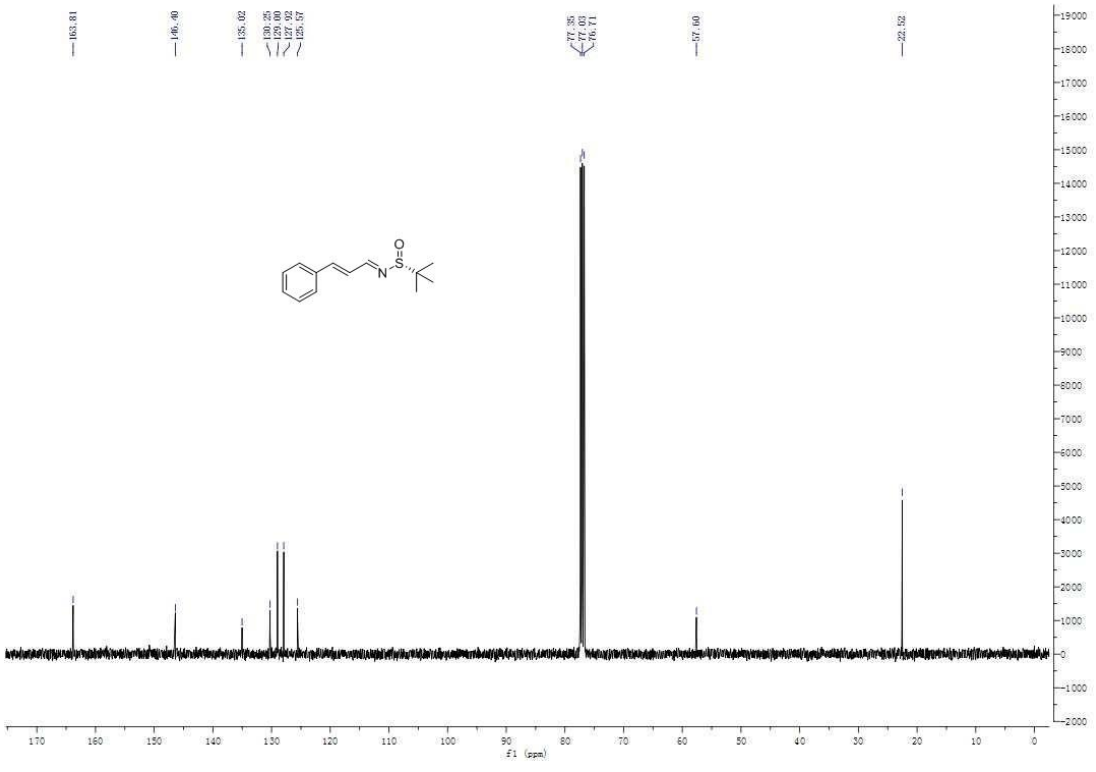


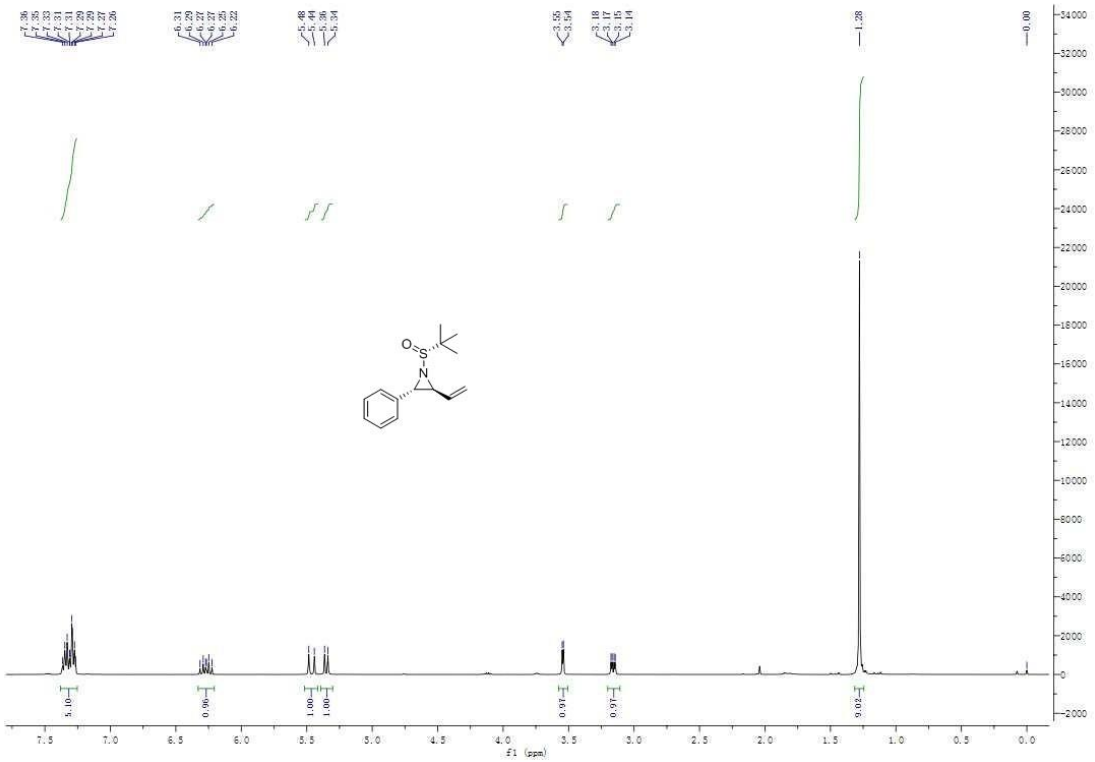


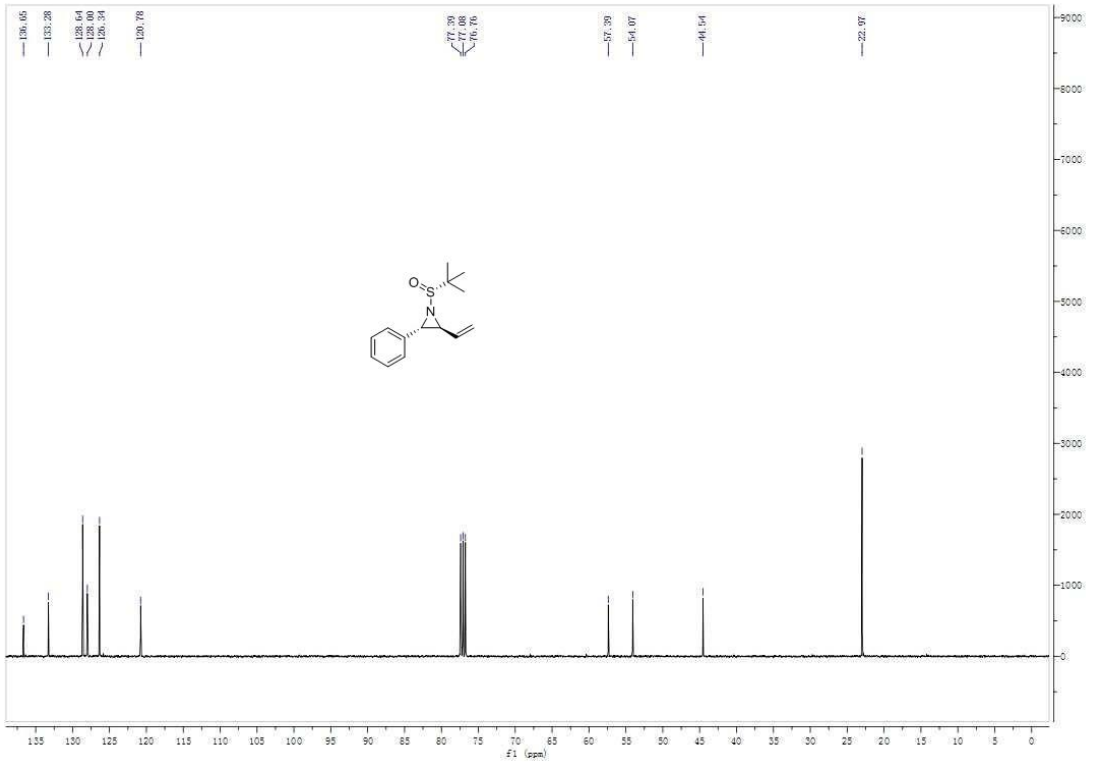


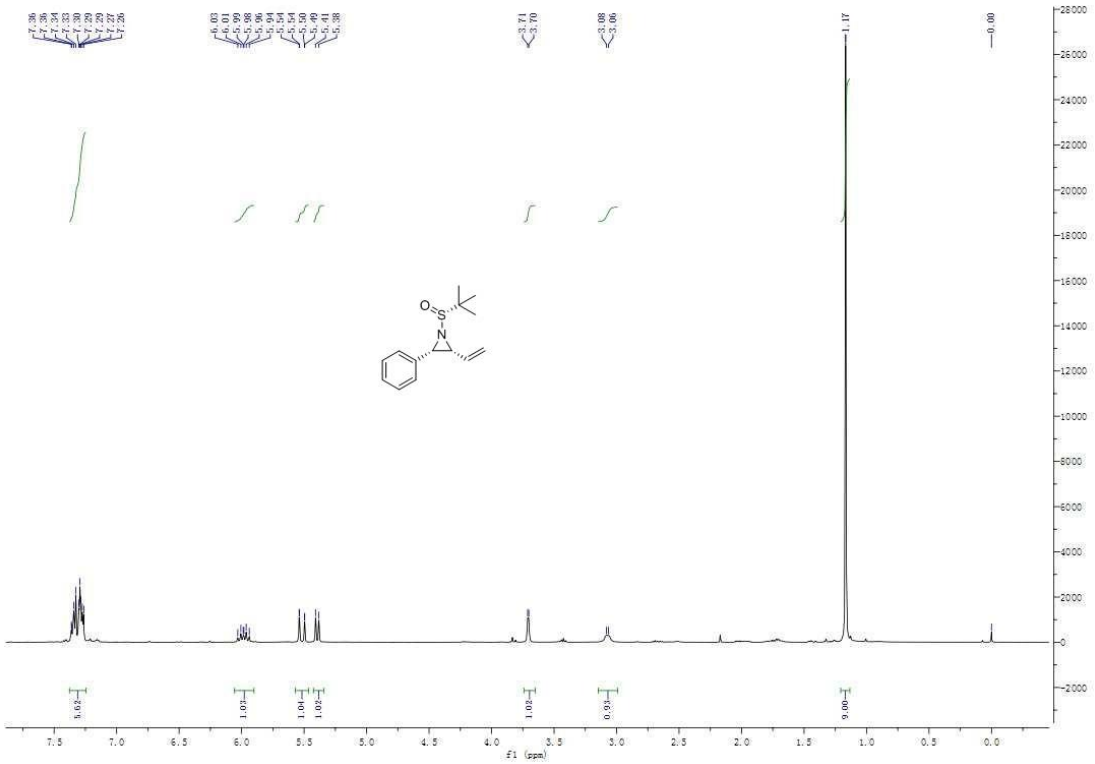


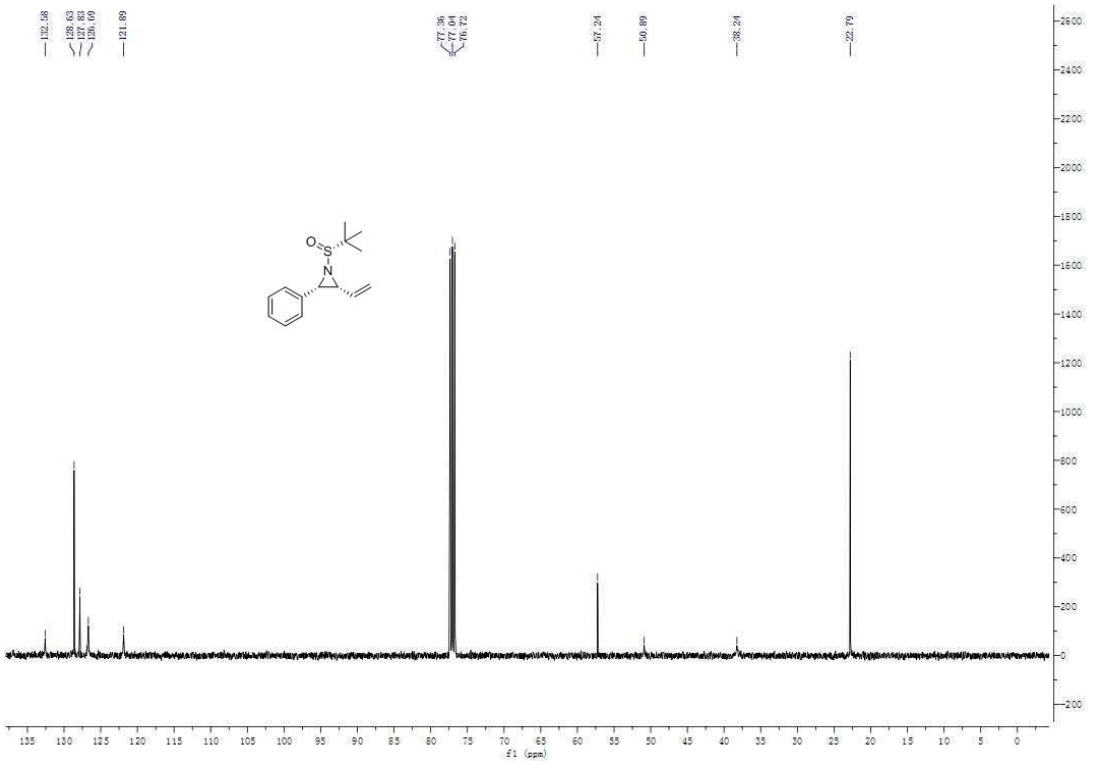


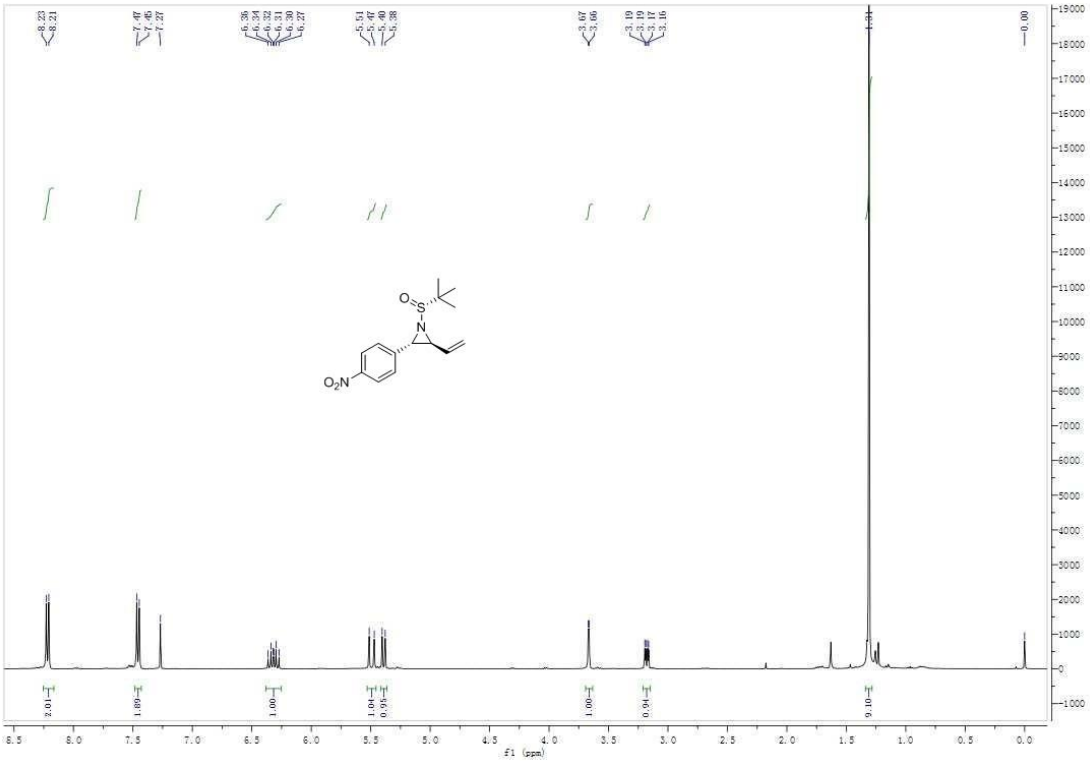


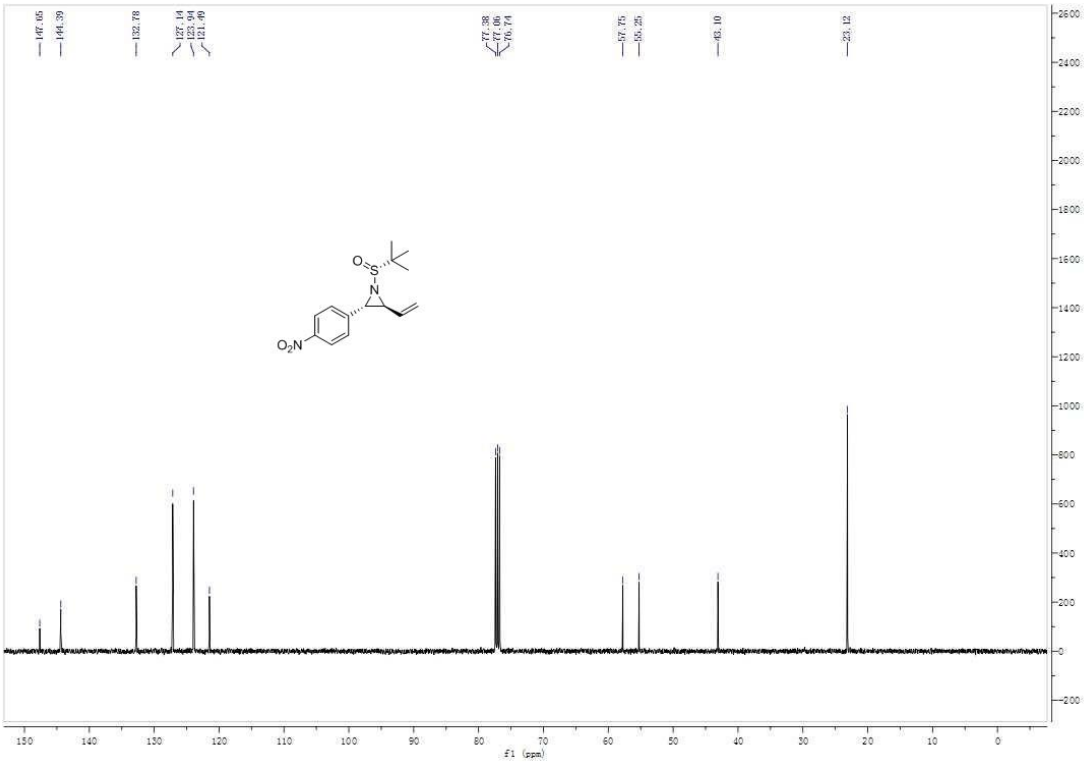


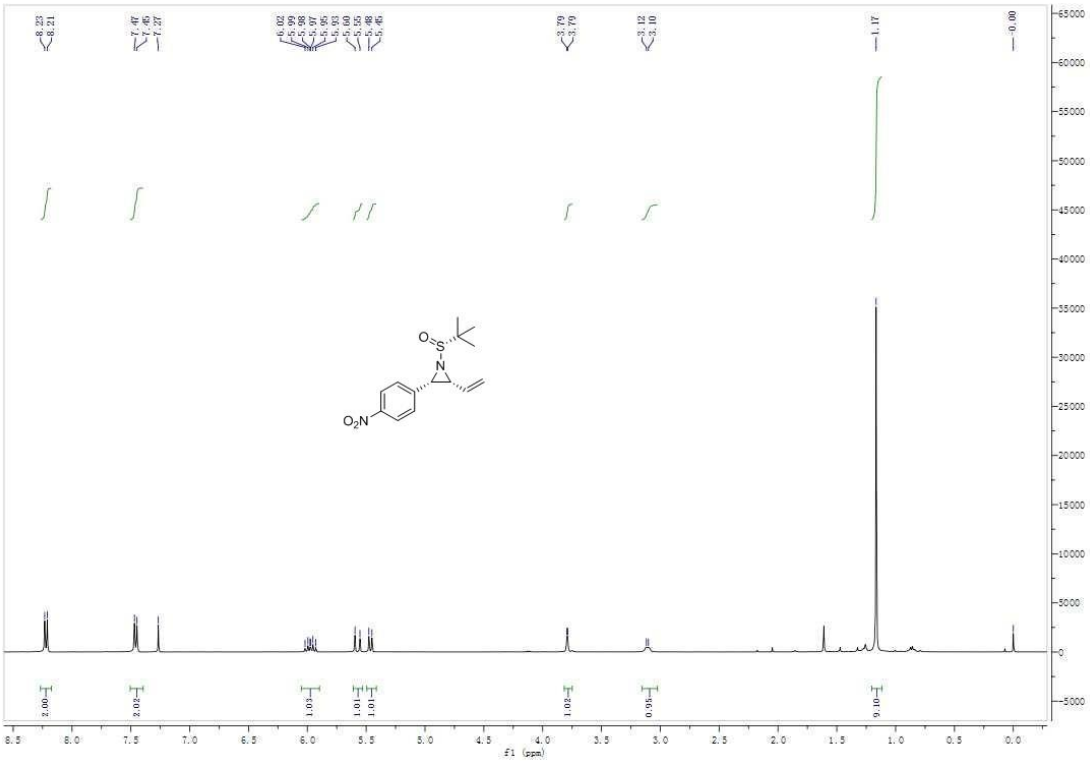


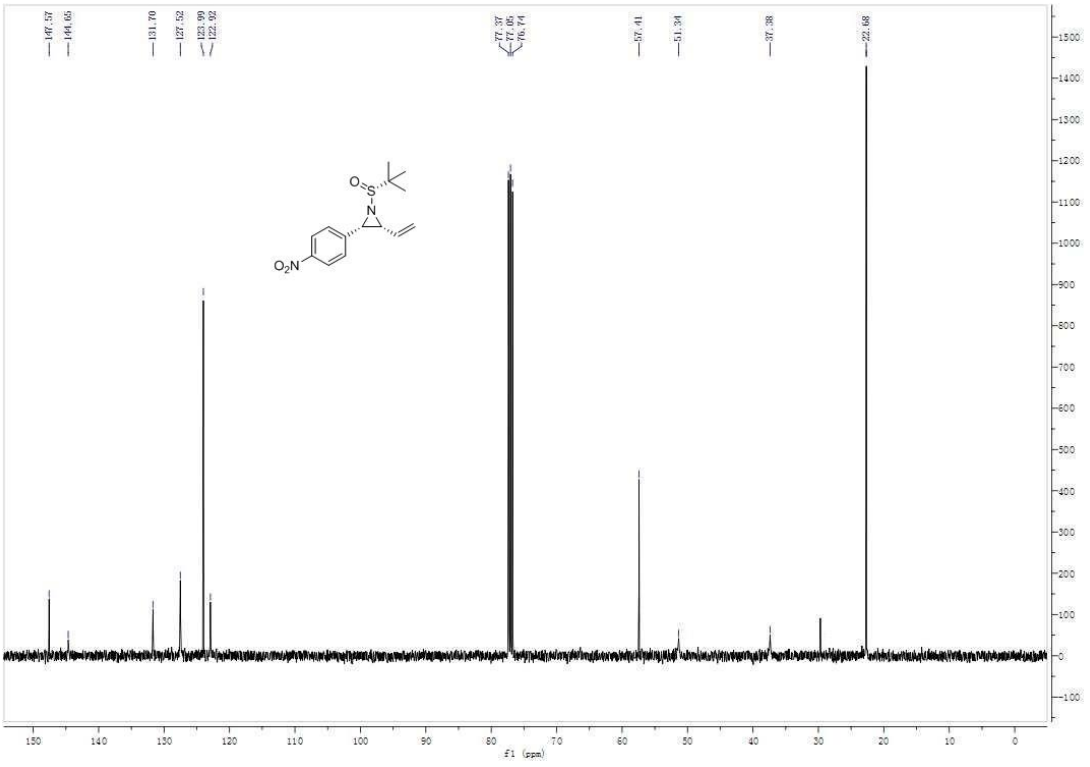


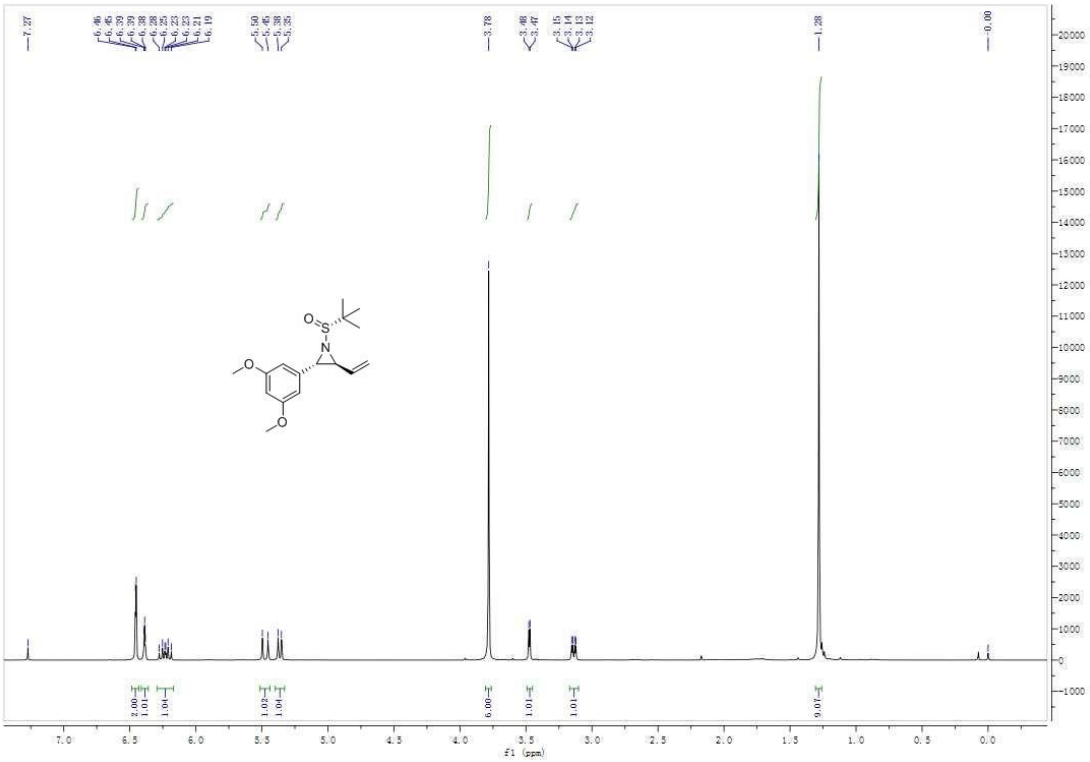


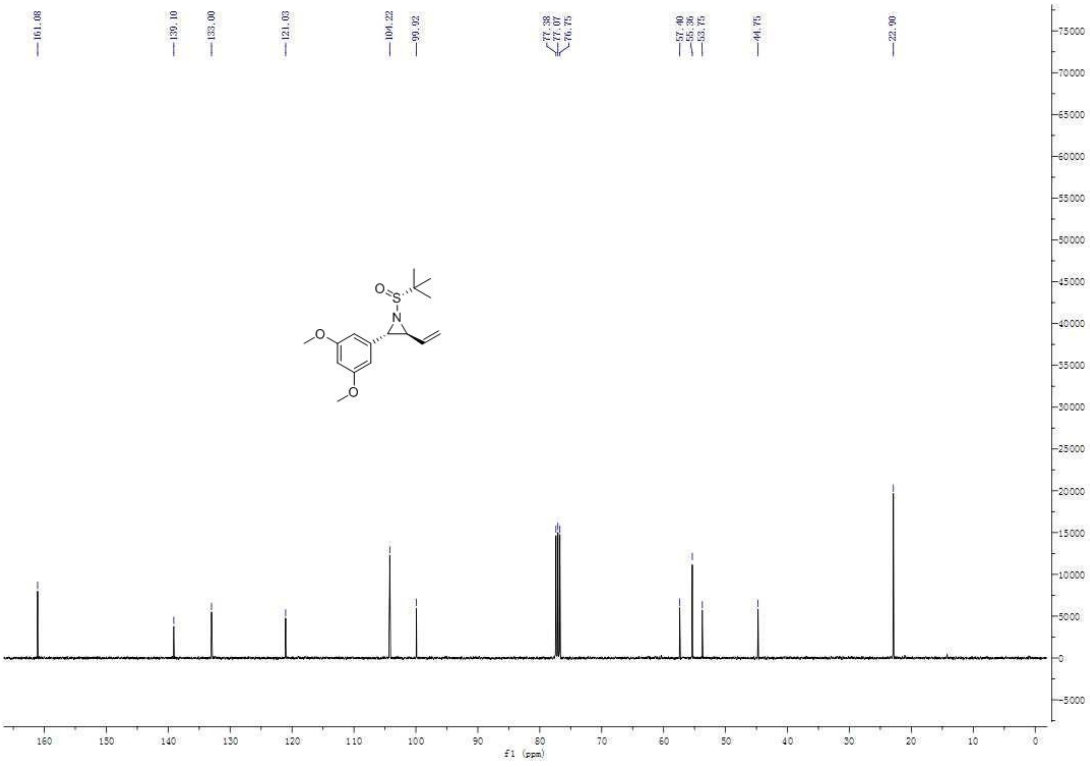


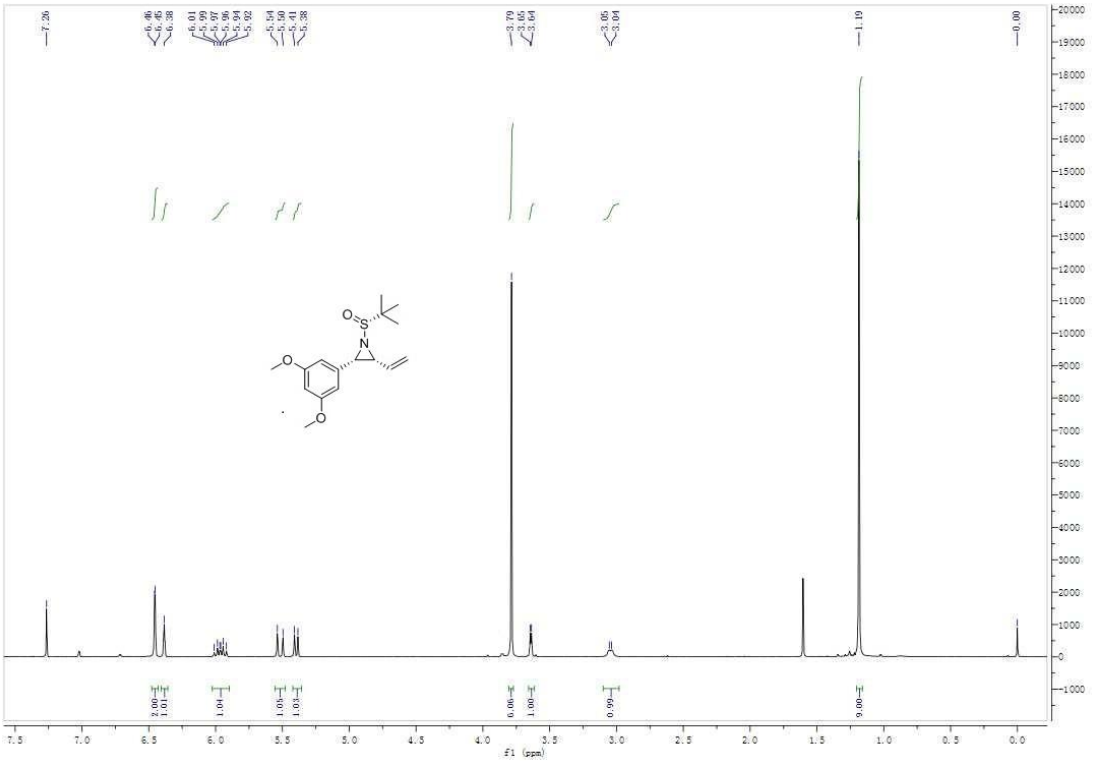


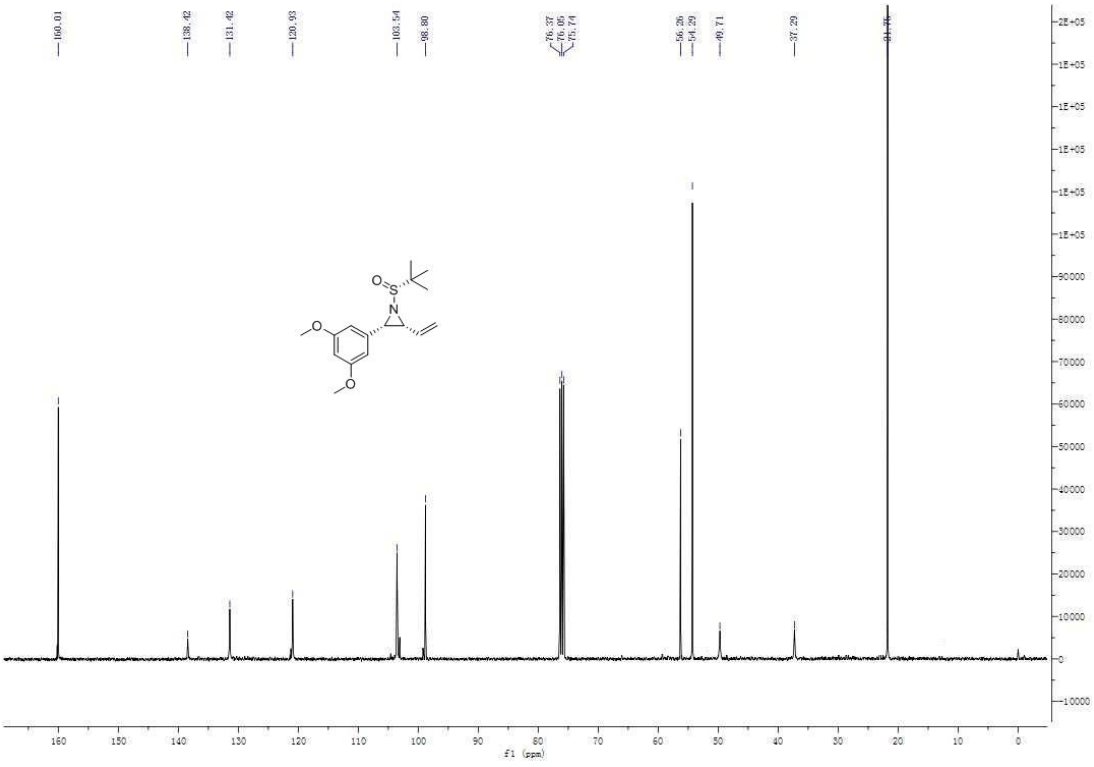


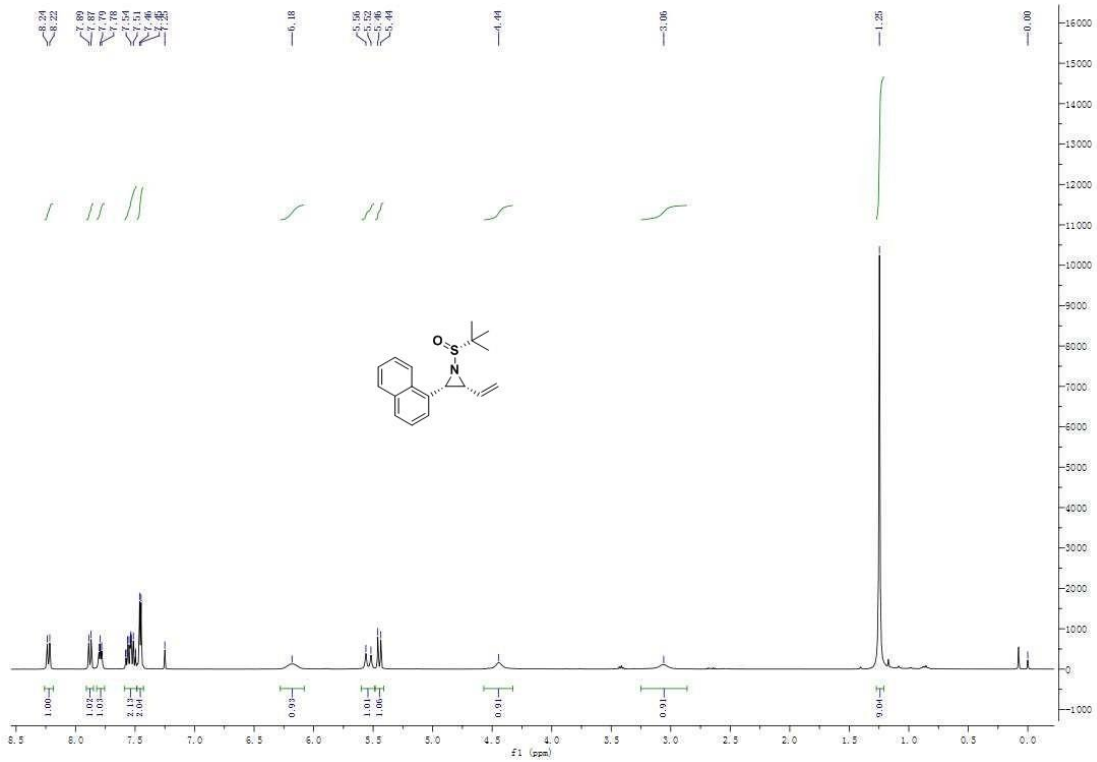


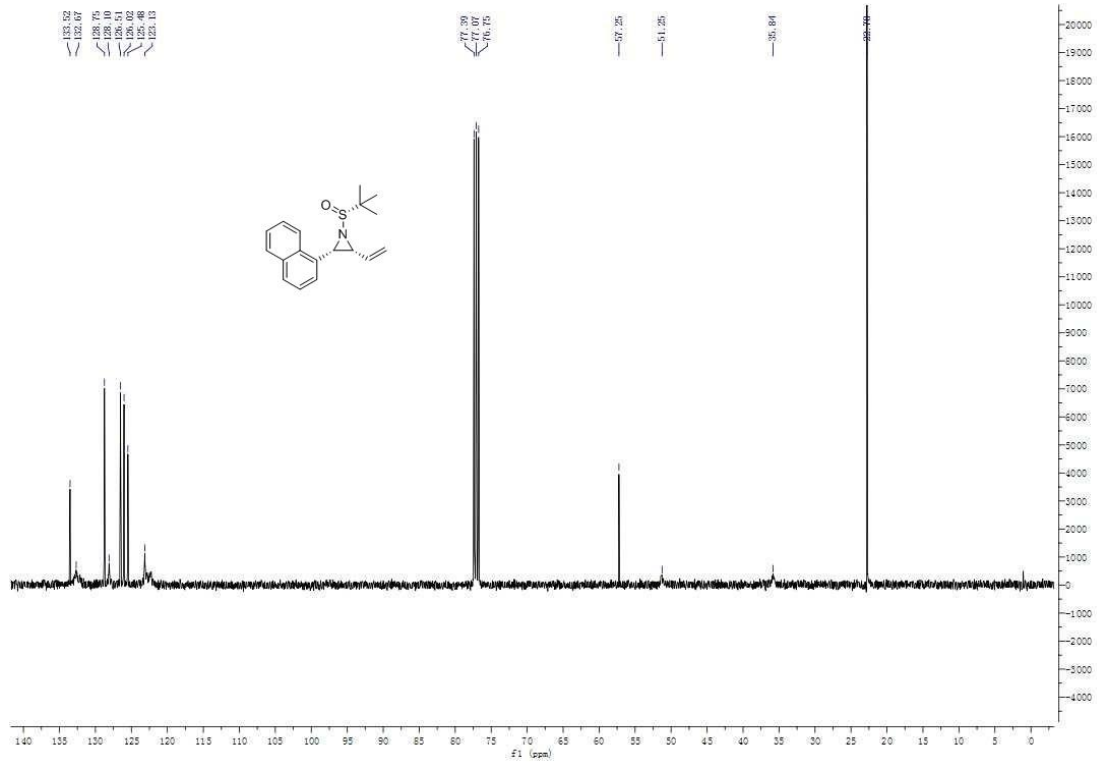


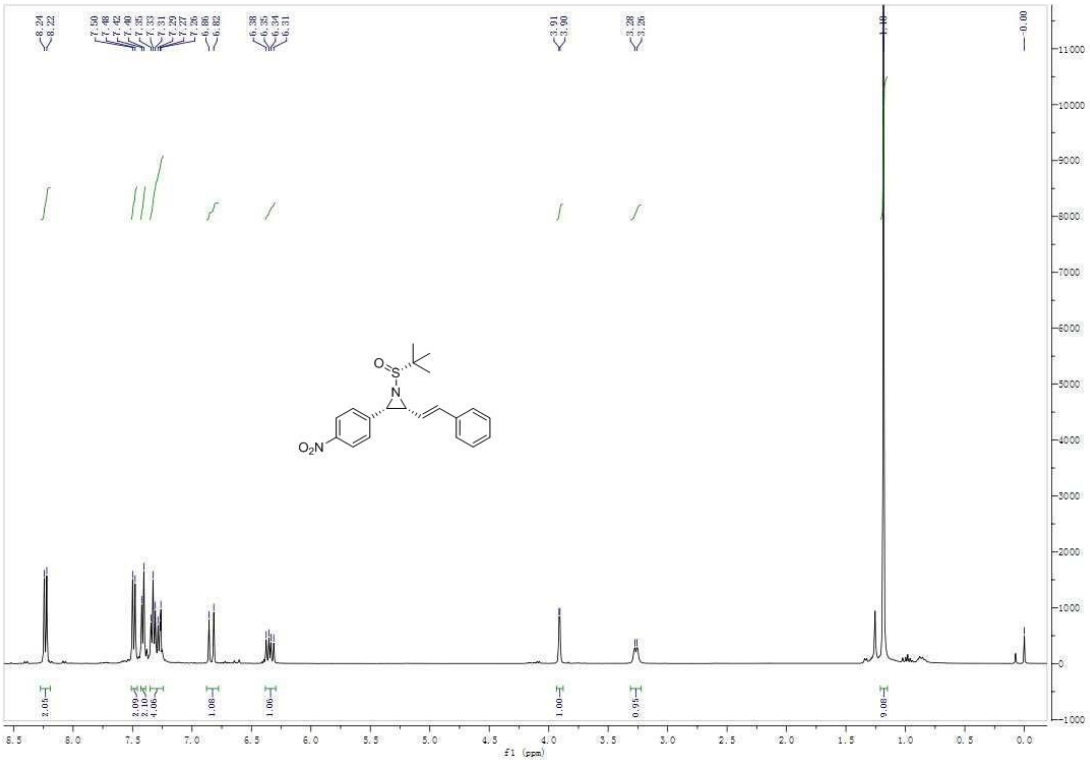


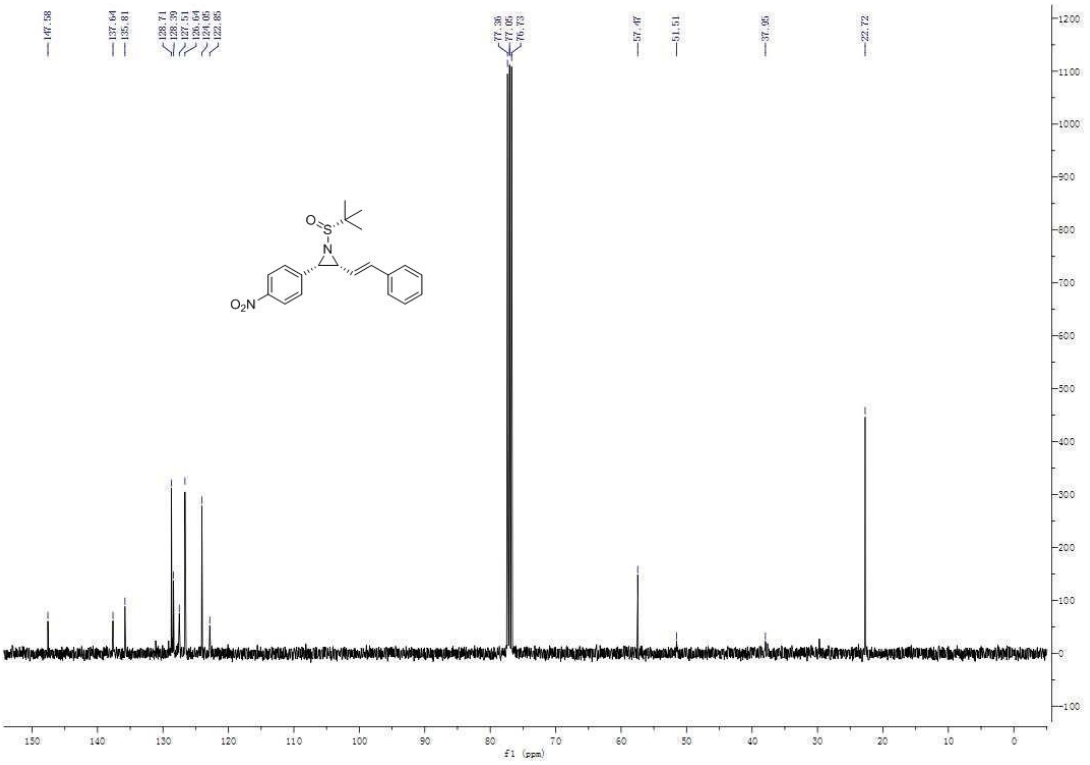


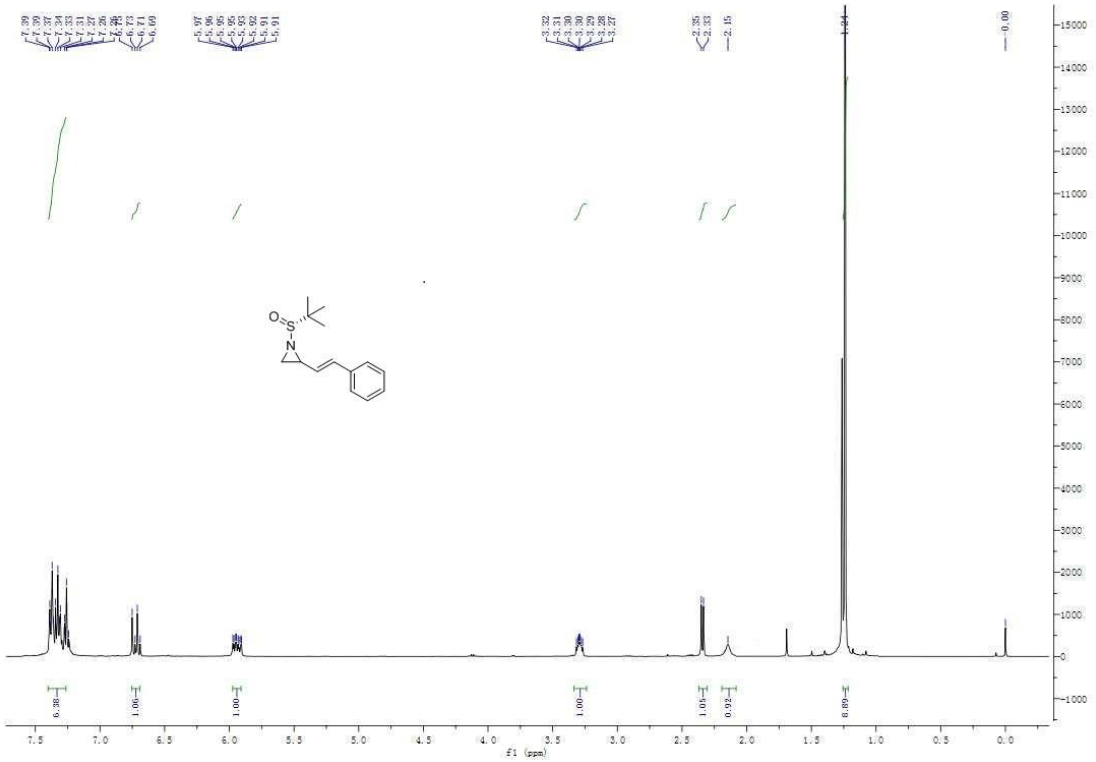


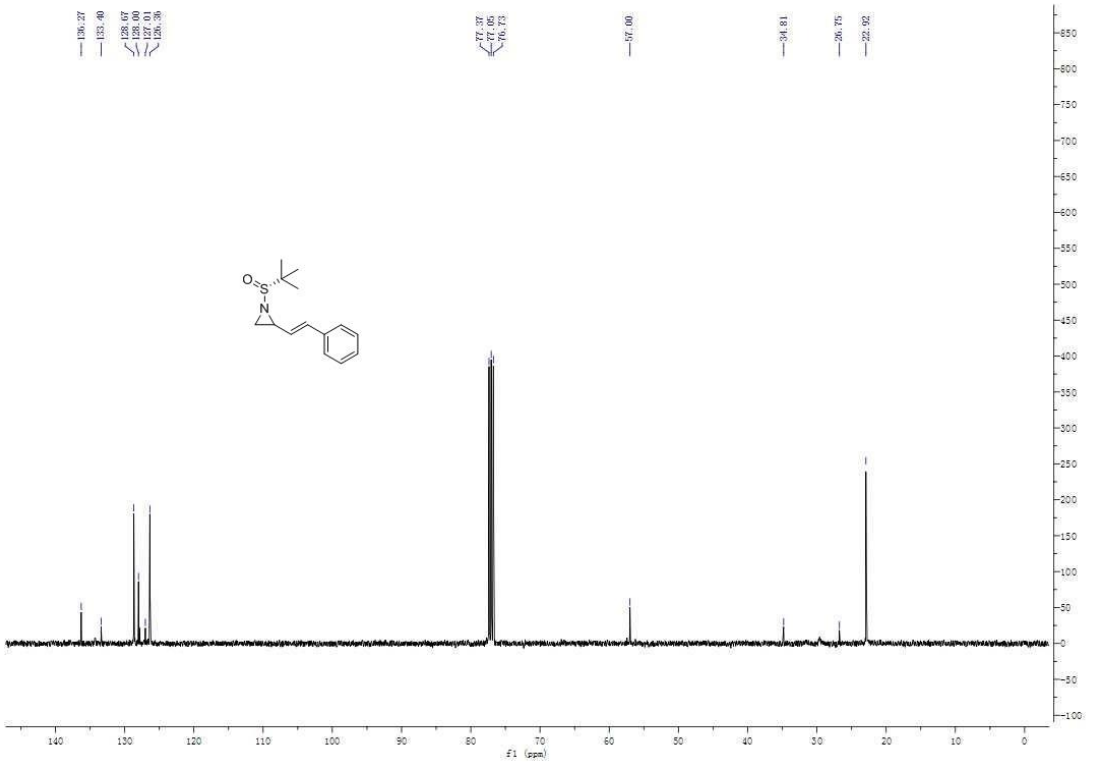


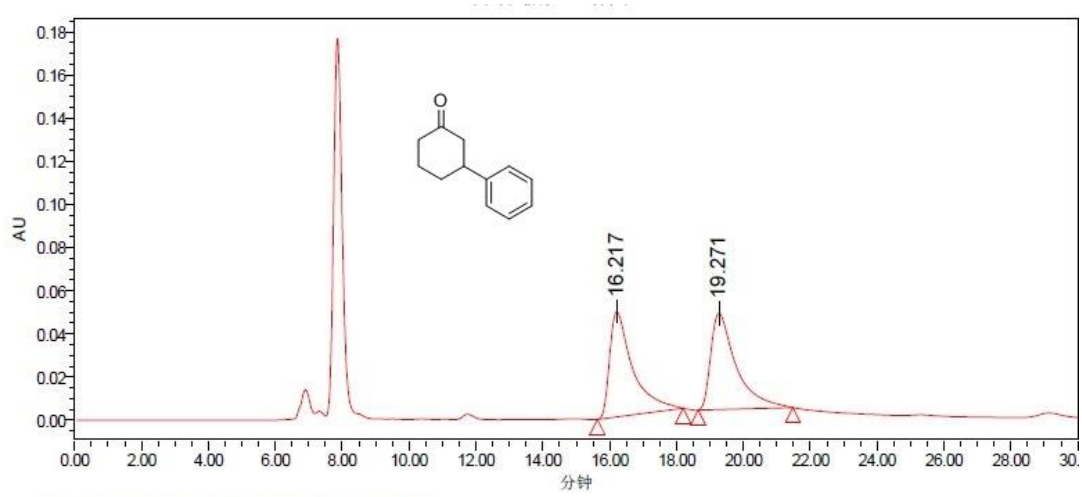






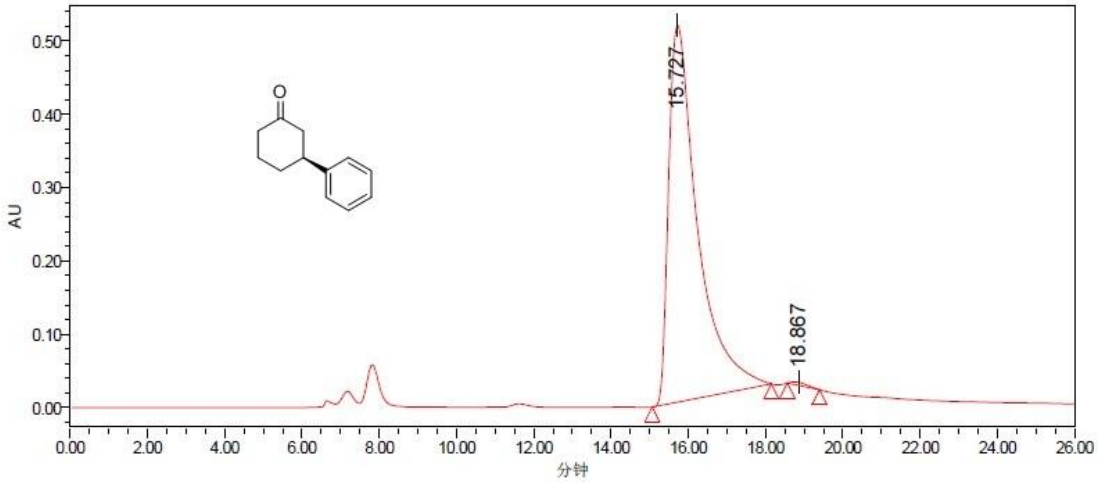






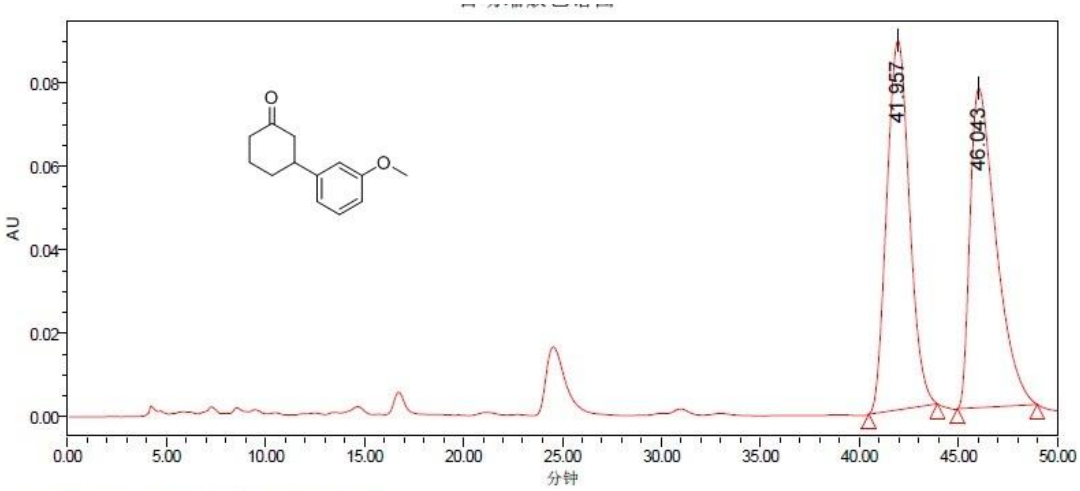
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	16.217	2343250	49.93	48706
2	W2489 ChA 254nm	19.271	2349419	50.07	44601



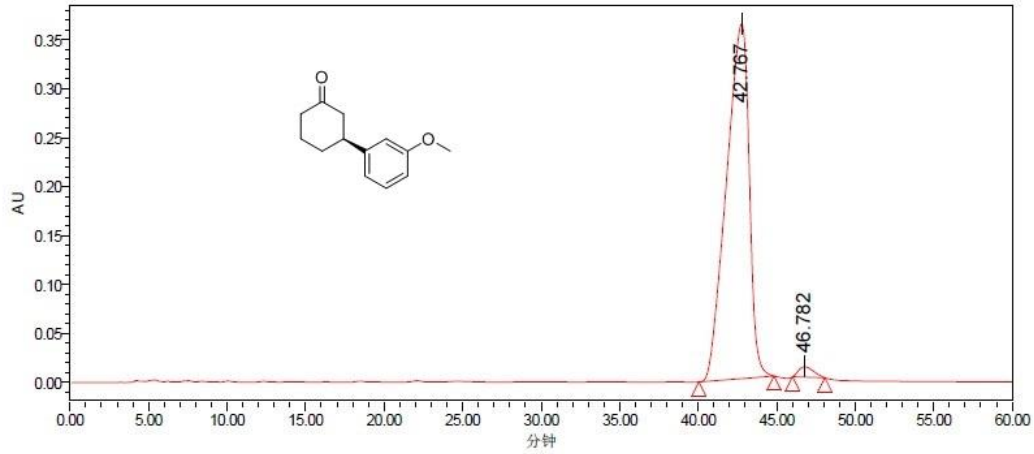
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	15.727	26814808	99.55	514178
2	W2489 ChA 254nm	18.867	121202	0.45	4199



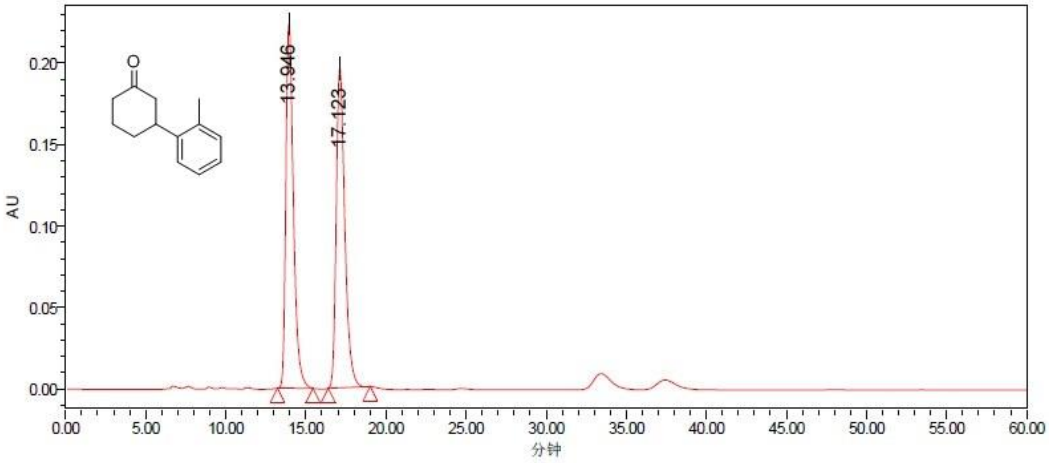
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	41.957	7049581	50.15	88438
2	W2489 ChA 254nm	46.043	7007276	49.85	76473



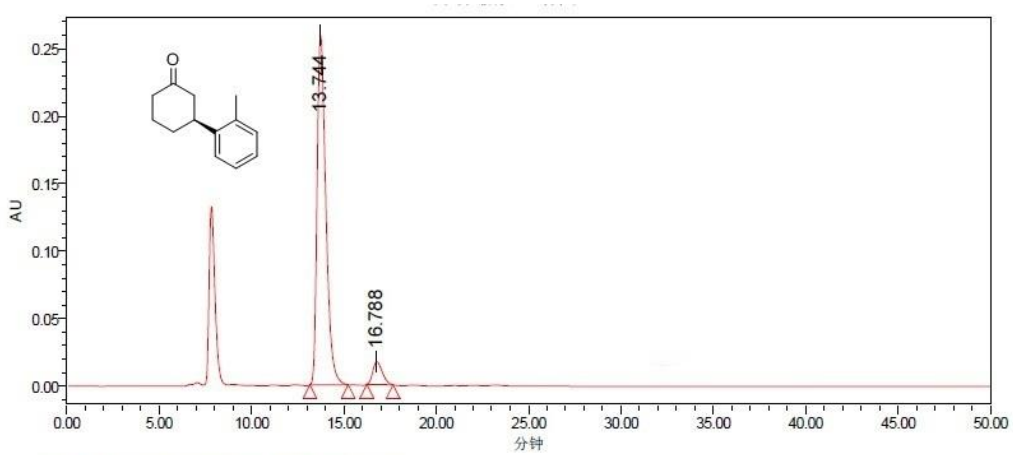
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	42.767	36569979	98.10	362212
2	W2489 ChA 254nm	46.782	709499	1.90	10685



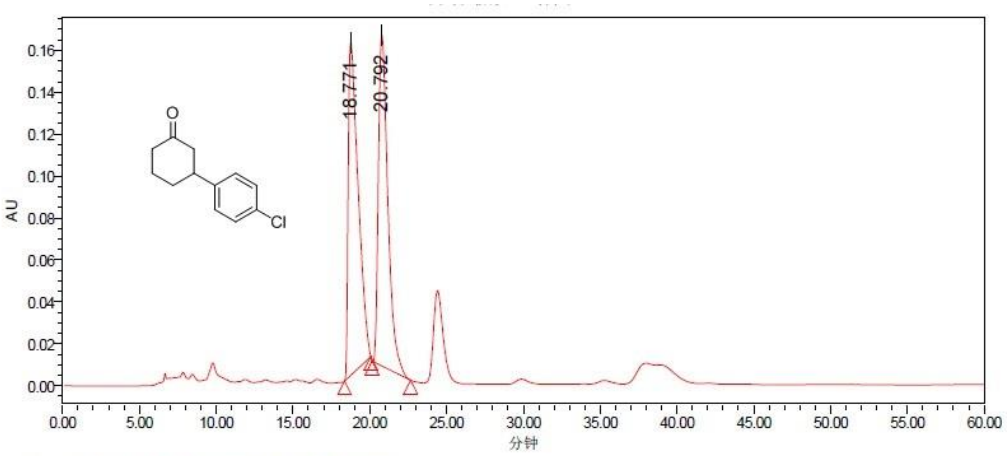
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	13.946	7333718	50.18	223393
2	W2489 ChA 254nm	17.123	7281148	49.82	196069



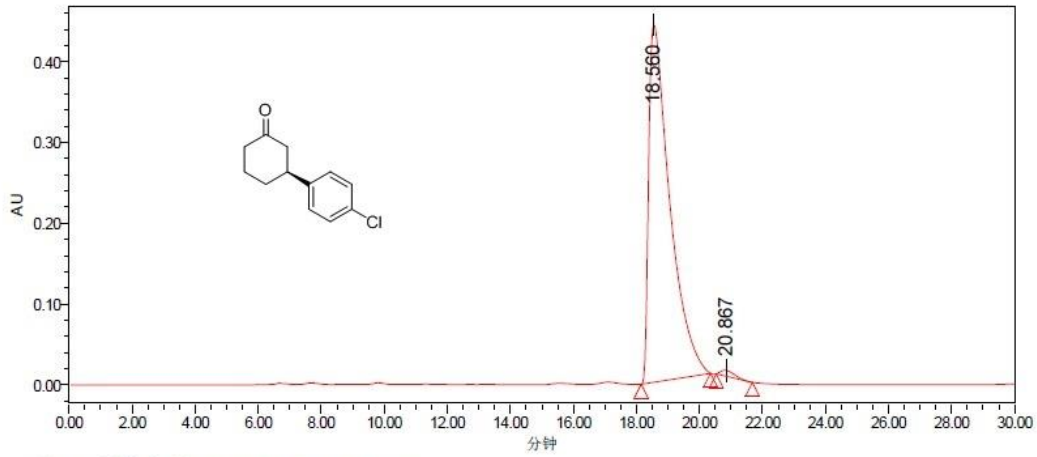
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	13.744	8544683	93.40	258984
2	W2489 ChA 254nm	16.788	603859	6.60	16861



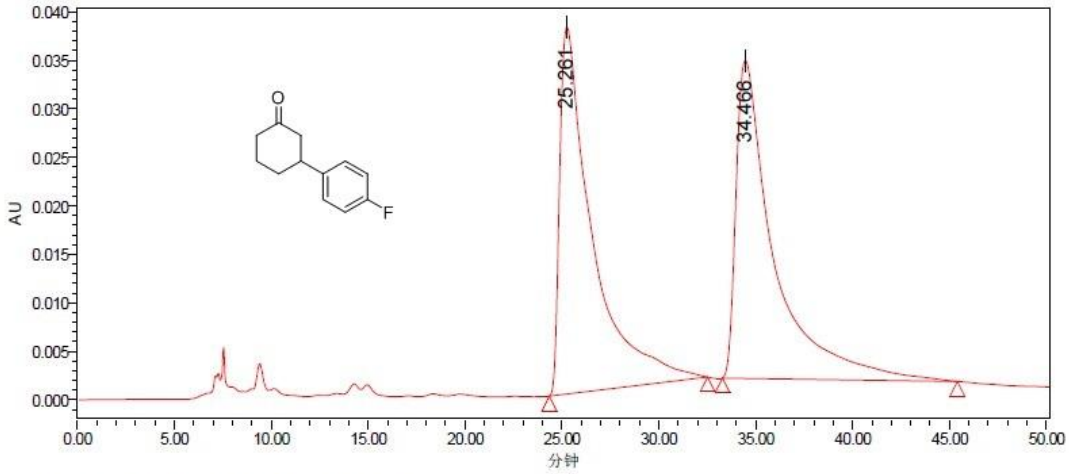
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	18.771	7109362	51.12	158953
2	W2489 ChA 254nm	20.792	6797895	48.88	157808



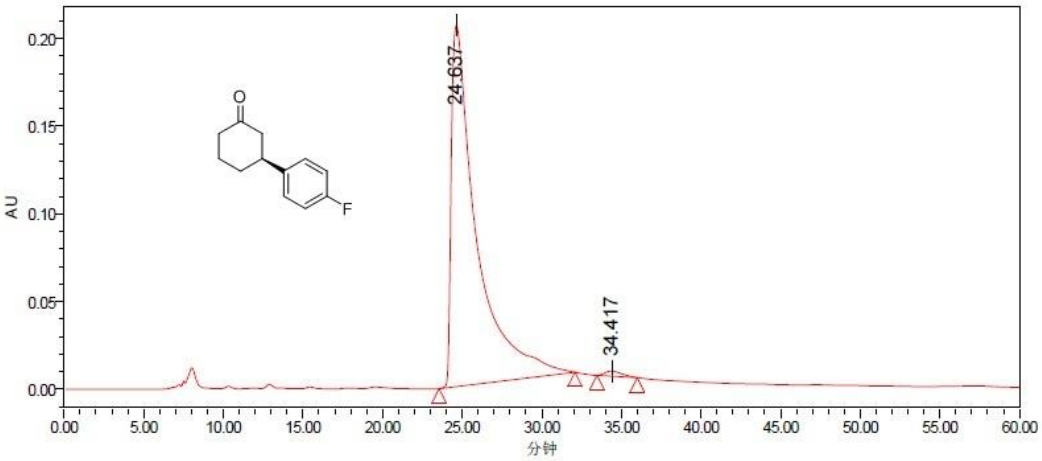
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	18.560	20593583	98.94	442450
2	W2489 ChA 254nm	20.867	221658	1.06	7225



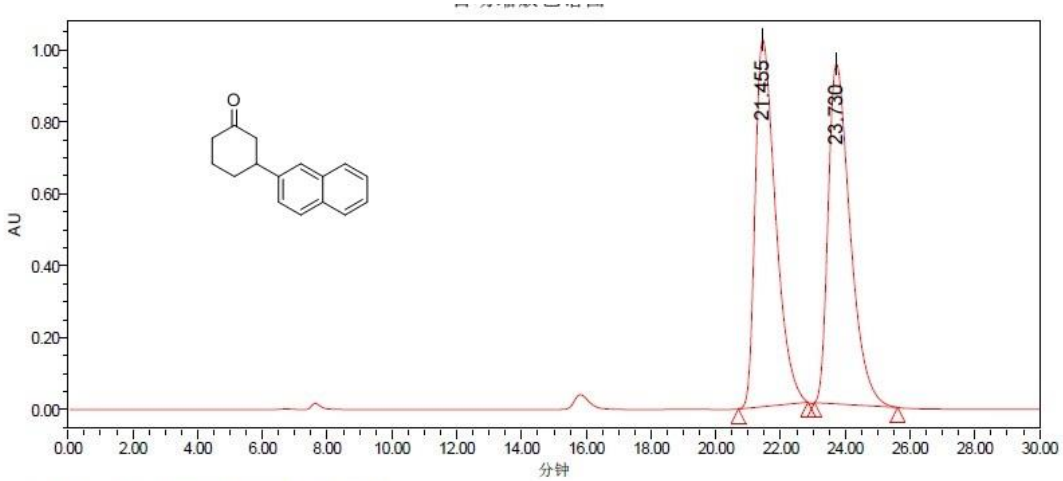
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	25.261	4423547	49.87	37802
2	W2489 ChA 254nm	34.466	4446520	50.13	32774



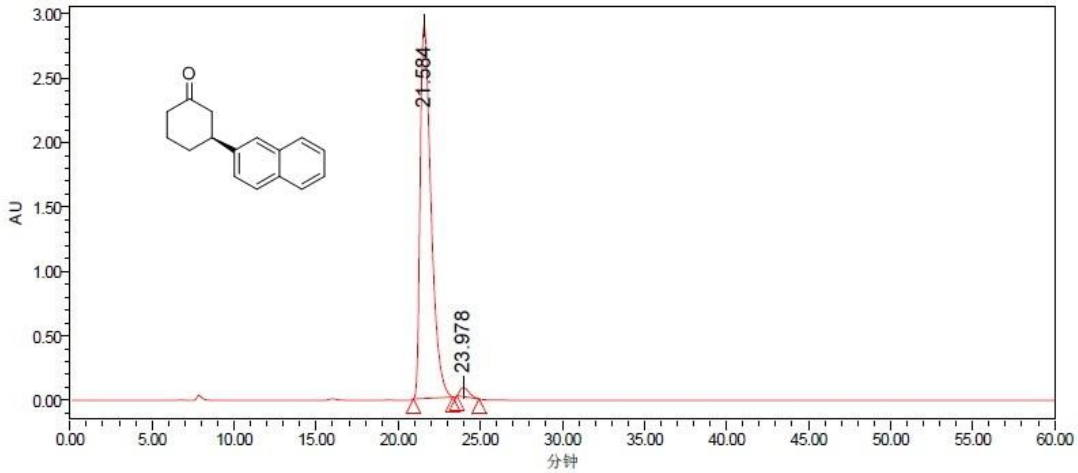
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	24.637	22746627	99.06	206052
2	W2489 ChA 254nm	34.417	215109	0.94	2884



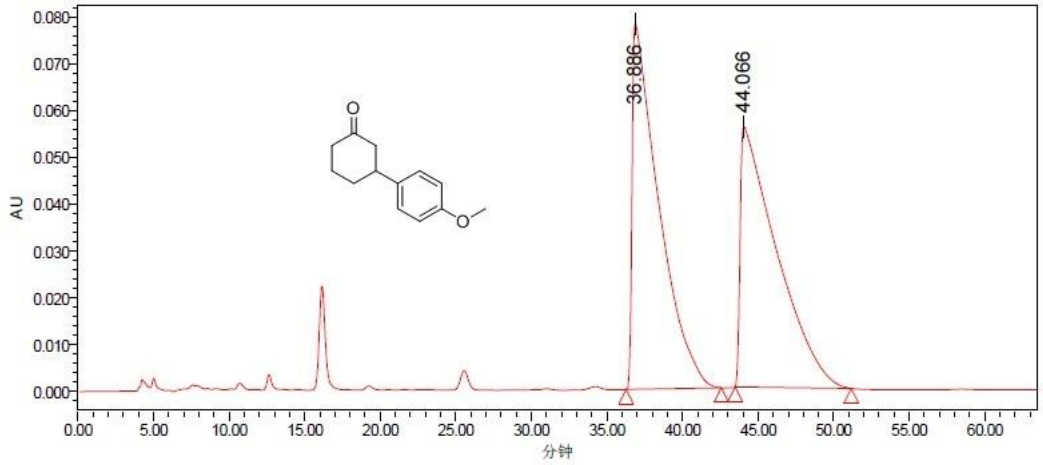
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	21.455	44774471	50.02	1020510
2	W2489 ChA 254nm	23.730	44741640	49.98	945238



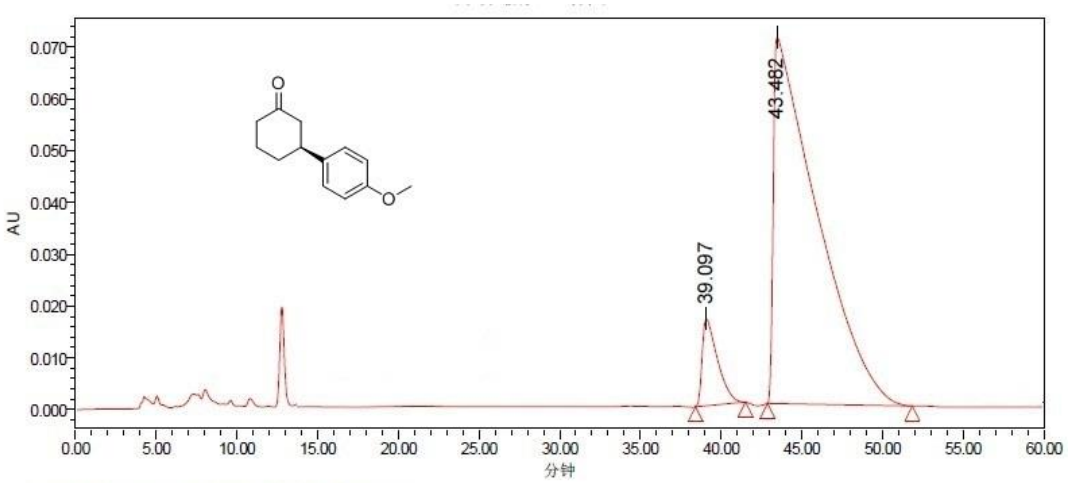
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	21.584	134088544	98.05	2893318
2	W2489 ChA 254nm	23.978	2670028	1.95	69895



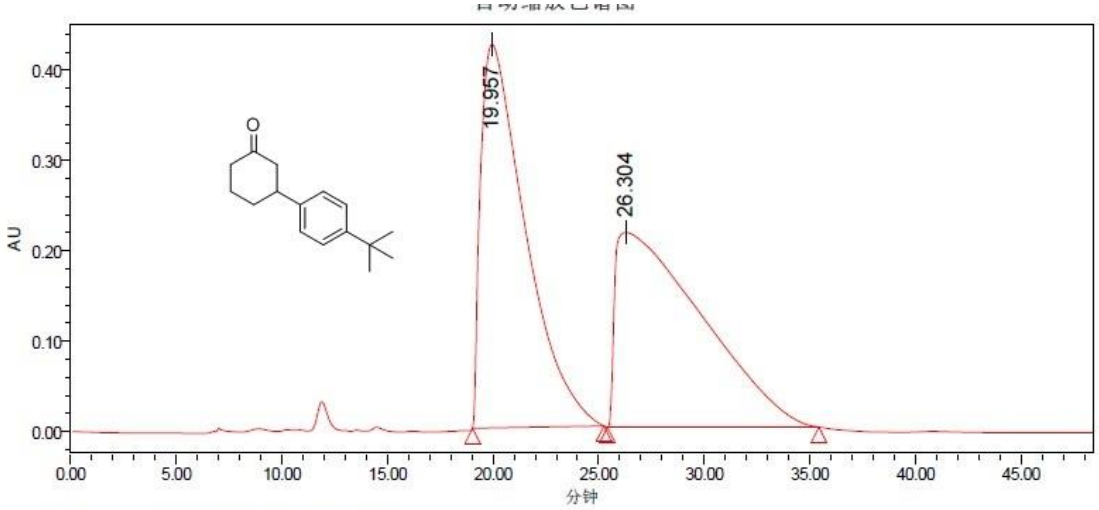
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	36.886	9517607	50.49	77935
2	W2489 ChA 254nm	44.066	9333339	49.51	55563



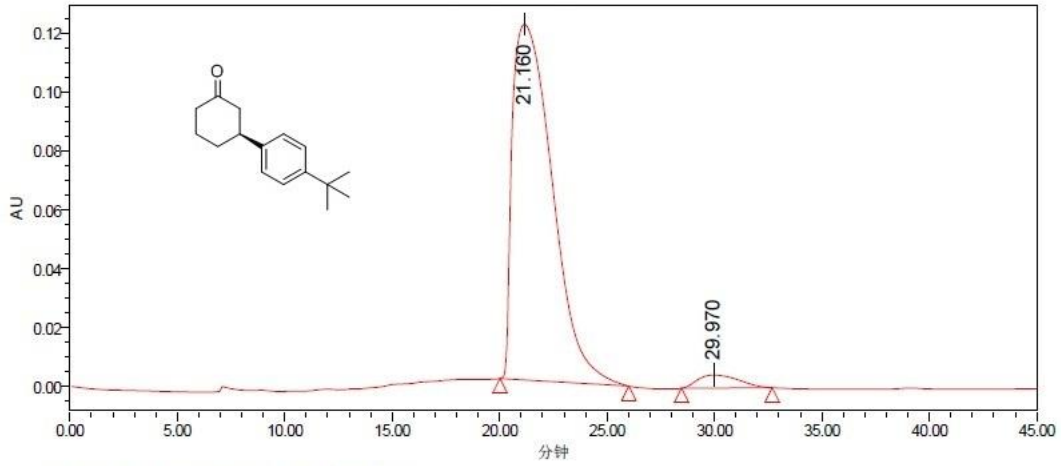
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	39.097	1107475	7.68	16800
2	W2489 ChA 254nm	43.482	13321928	92.32	70714



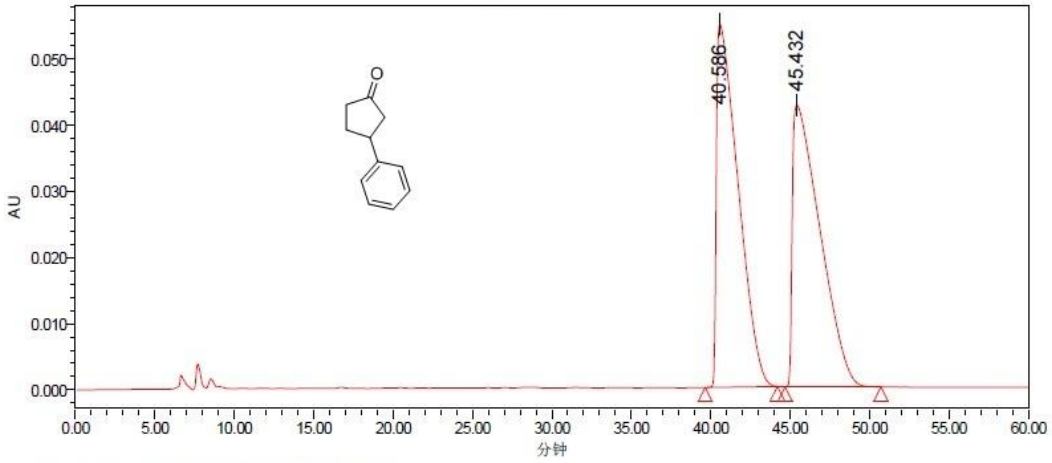
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	19.957	62492613	50.38	424369
2	W2489 ChA 254nm	26.304	61537875	49.62	215497



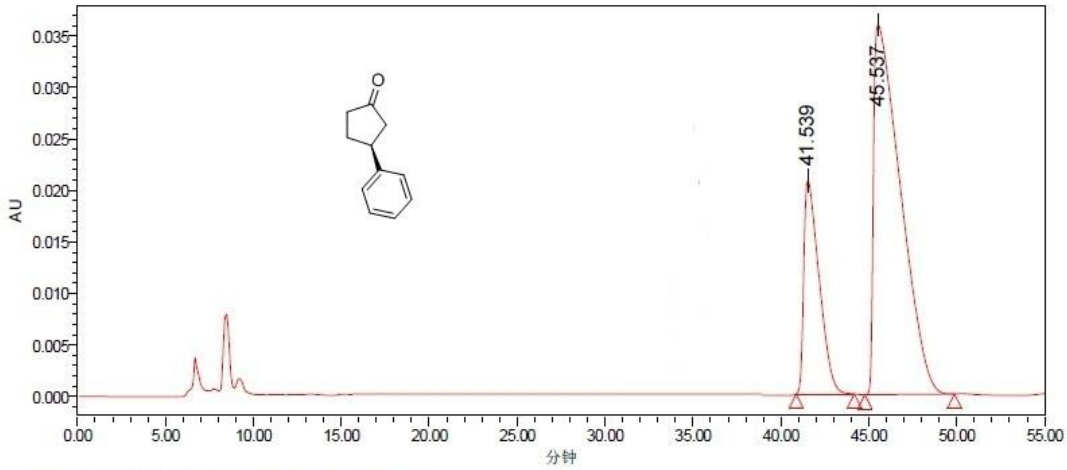
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	21.160	15642066	96.36	120855
2	W2489 ChA 254nm	29.970	591245	3.64	4454



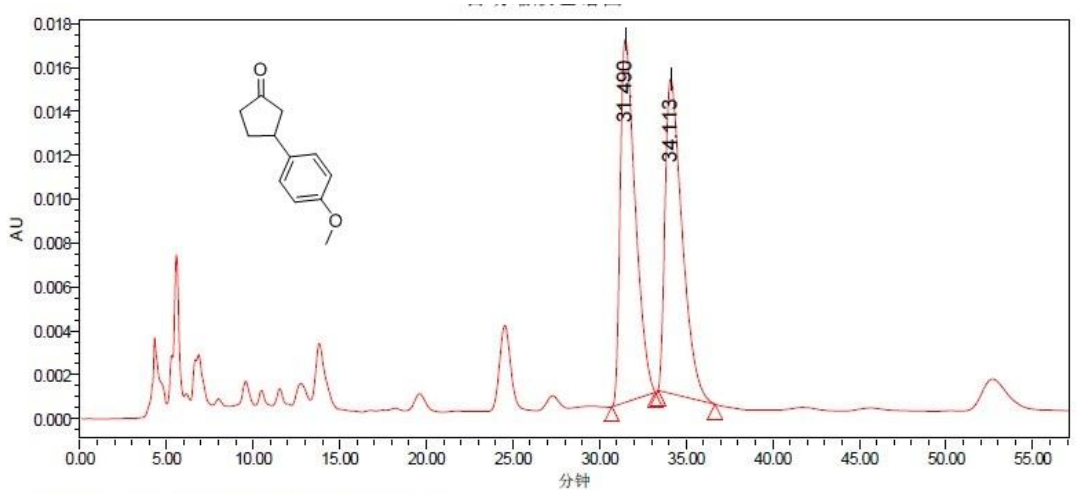
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	40.586	5203829	50.26	54895
2	W2489 ChA 254nm	45.432	5149785	49.74	42624



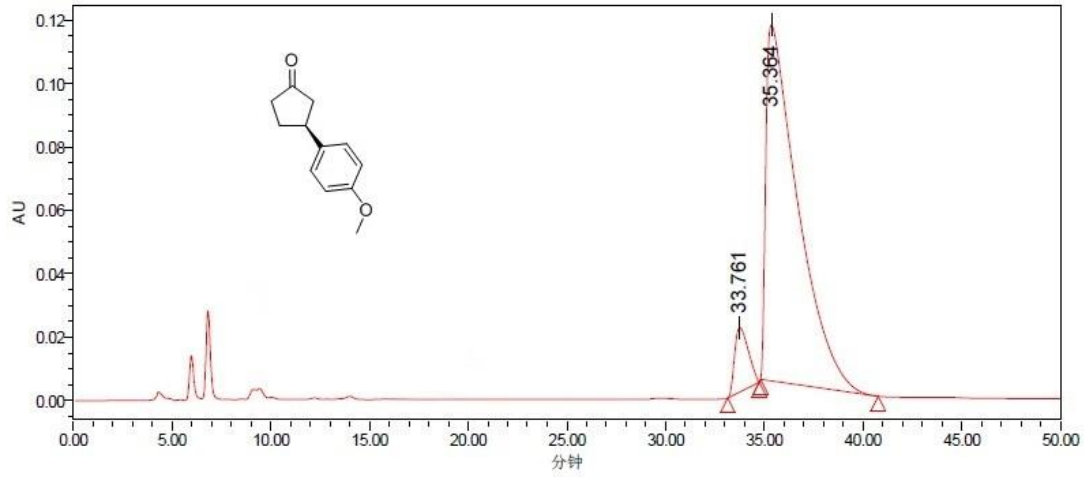
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	41.539	1258422	24.80	20731
2	W2489 ChA 254nm	45.537	3814995	75.20	35897



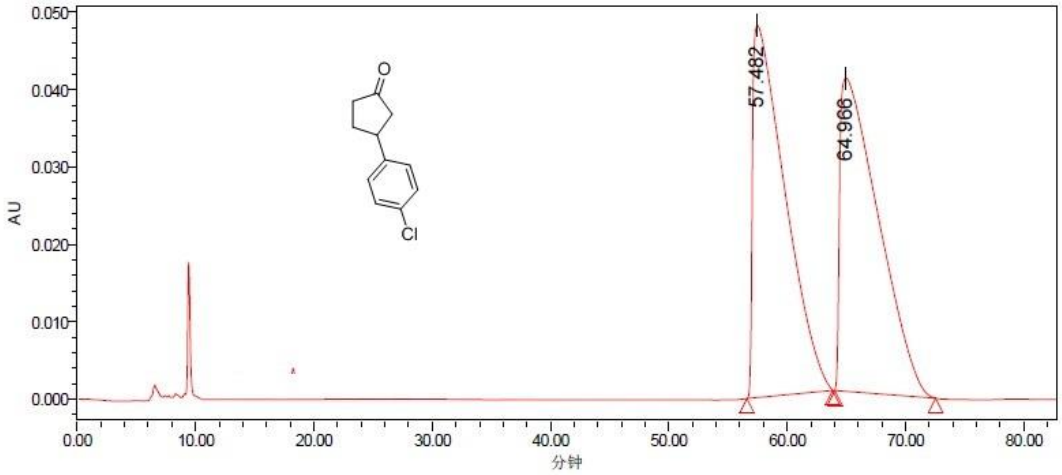
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	31.490	994322	50.35	16543
2	W2489 ChA 254nm	34.113	980623	49.65	14344



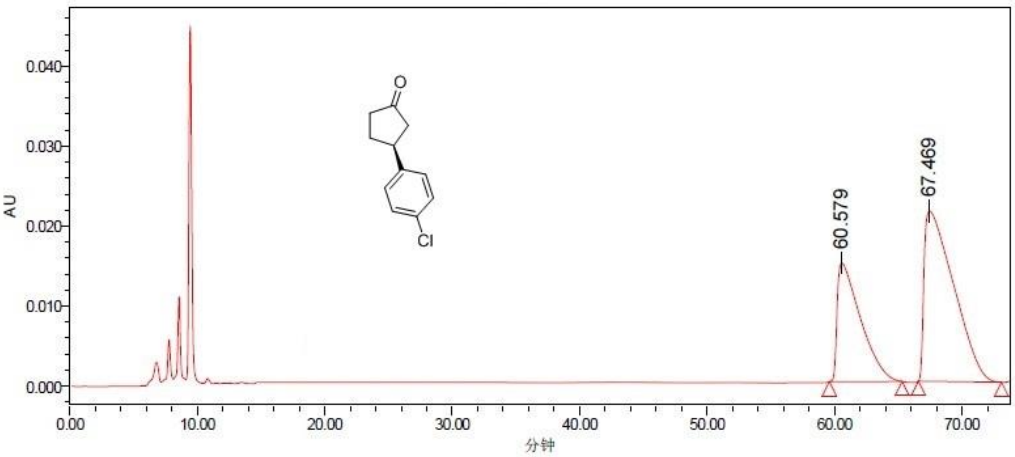
处理通道说明: W2489 ChA 254nm

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	33.761	978513	7.21	20363
2	W2489 ChA 254nm	35.364	12597150	92.79	112231



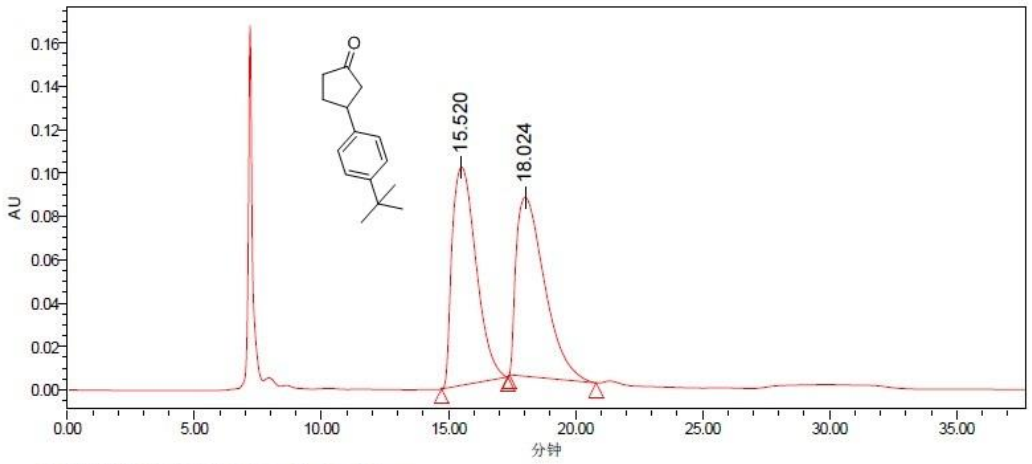
处理通道说明:**W2489 ChA 254nm**

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	57.482	9131537	49.89	48087
2	W2489 ChA 254nm	64.966	9171103	50.11	40488



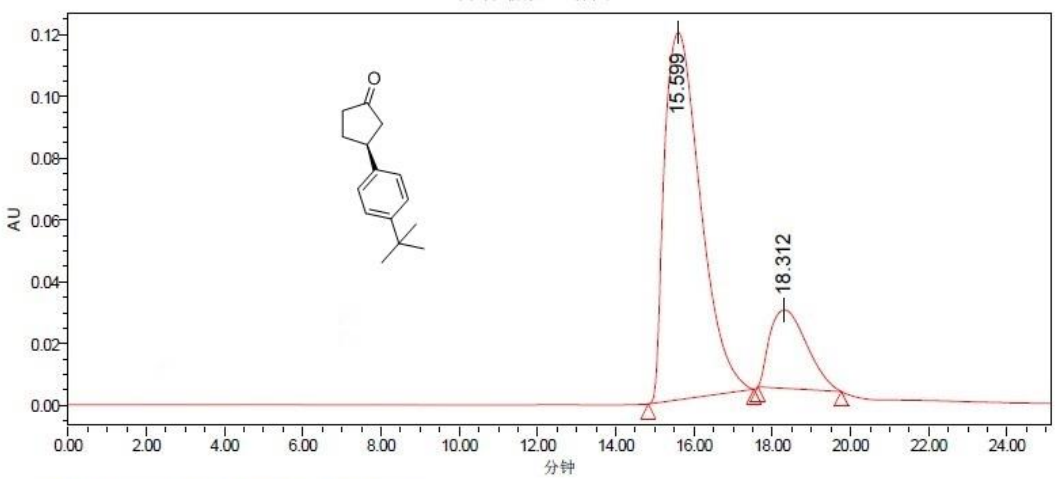
处理通道说明:**W2489 ChA 254nm**

	处理通道说明	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	W2489 ChA 254nm	60.579	1889922	35.53	14841
2	W2489 ChA 254nm	67.469	3429792	64.47	21286



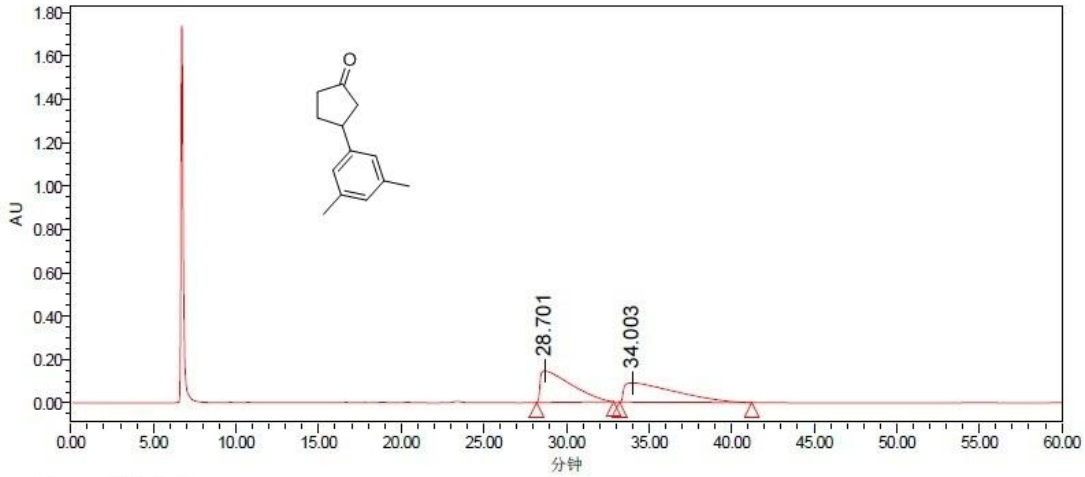
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	15.520	6608696	50.71	100685
2	W2489 ChA 254nm	18.024	6422565	49.29	82539



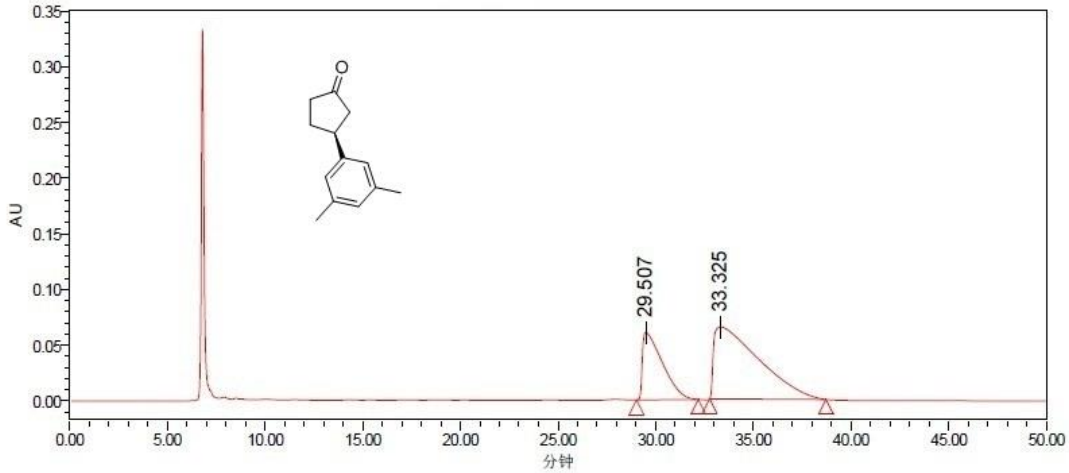
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	15.599	7619212	82.00	118927
2	W2489 ChA 254nm	18.312	1672905	18.00	25396



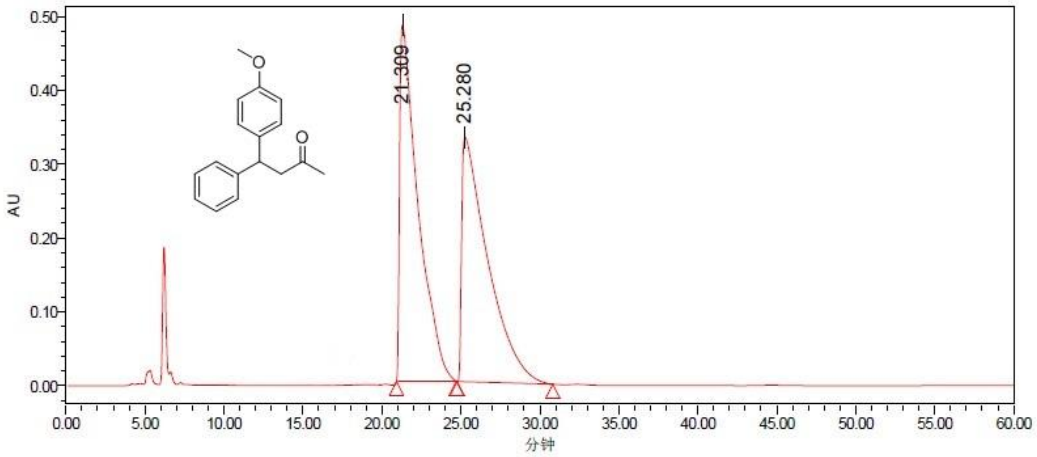
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	28.701	19033442	49.99	145148
2	W2489 ChA 254nm	34.003	19042490	50.01	88410



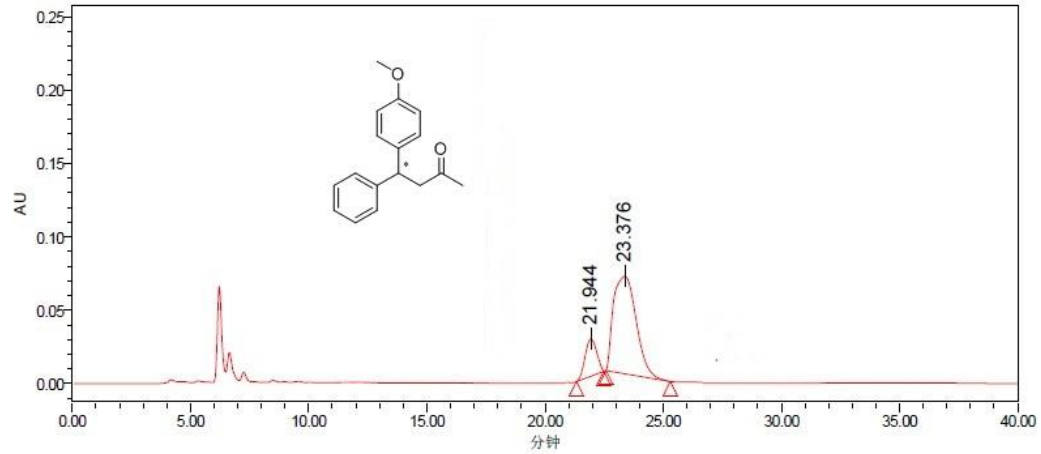
处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	29.507	4319950	29.33	60592
2	W2489 ChA 254nm	33.325	10407485	70.67	64598



处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	21.309	39040087	50.73	482751
2	W2489 ChA 254nm	25.280	37922434	49.27	330750



处理通道说明:W2489 ChA 254nm

	处理通道说明	保留时间(分钟)	面积(微伏*秒)	% 面积	高度(微伏)
1	W2489 ChA 254nm	21.944	861287	16.28	25393
2	W2489 ChA 254nm	23.376	4429311	83.72	66451