Supporting Information for: Resin-Immobilized Pyrrolidine-Based Chiral Organocatalysts for Asymmetric Michael Additions of Ketones and Aldehydes to Nitroolefins

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General Methods: ^{1}H and ^{13}C NMR were recorded on Varian-500 or Avance III 600 instruments.Chemical shifts were reported in ppm down field from internal Me4Si. Mass spectra were recorded using electrospray ionization (ESI) on LCQ Advanted MAX Mass instruments. HPLC analysis was measured using ChiralPak AS-H column.

Materials: Commercial reagents were used without purification except for otherwise explanation. Analytical thin layer chromatography was performed on 0.20 mm silica gel plates and silica gel (200-300 mesh) was used for flash chromatography both purchased from Qingdao Haiyang Chem. Company, Ltd..

Preparation of catalysts:

1. **Preparation of catalyst 1:**

To a stirred solution of L-proline (10 g, 0.1 mol) in dioxane (200 ml) were added K_2CO_3 (16.4 g, 0.12 mol) and benzyl chloride (15 g, 0.12 mol). The mixture was refluxed for 3 hours, then concentrated in vacuo. The residure was dissolved in 200 ml 2 M sodium hydroxide aqueous solution. Then it was extracted by CH_2Cl_2 (200 ml*2). The organic phase was dried by $MgSO_4$ then purified by column chromatography (CH_3OH:EA=1:10) to afford product **4** (18.1 g, 97.3%), ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.67-1.72 (2H, m), 1.80-1.86 (1H, m), 1.90-1.95 (1H, m), 2.27-2.31 (1H, m), 2.71-2.75 (1H, m), 2.96-2.99 (1H, m), 3.35 (1H, d, *J*=12.6 Hz), 3.41-3.44 (1H, m), 3.64-3.67 (1H, m), 3.87 (1H, d, *J*=13.2 Hz), 7.24-7.33 (5H, m).

To a stirred solution of **4** (11.64 g, 0.06 mol) in CH_2Cl_2 (150 ml) was added triethylamine (8.62 g, 0.085 mol), then the methylsufonyl chloride (9.73 g, 0.085 mol) was added dropwise under ice-bath cooling. The reaction mixture was stirred at room temperature for 2 hours and washed by 100 ml 2 M sodium hydroxide aqueous solution. The organic phase was dried by $MgSO_4$, filtered, and evaporated to dryness to afford product **5** (16.2 g, 98.8%).

To a stirred solution of **5** (7.0 g, 0.026 mol) in CH_3OH (100 ml) was added piperidine (11.0 g, 0.13 mol). The reaction mixture was refluxed for 12 hours, then concentrated in vacuo to remove CH_3OH and remainder piperidine. The residue was dissolved in 200 ml 2 M sodium hydroxide aqueous solution. Then it was extracted by CH_2Cl_2 (200 ml). The organic phase was dried by $MgSO_4$ then purified by column chromatography (CH_3OH:EA=1:10) to afford product **6** (4.73 g, 70.6%). ^1H NMR (600 MHz, $CDCl_3$) δ: 1.22-1.26 (2H, m), 1.41 (2H, m), 1.51-1.74 (8H, m), 1.94-2.00 (1H, m), 2.11-2.15 (1H, m), 2.27-2.31 (1H, m), 2.52-2.55 (1H, m), 2.60-2.65 (1H, m), 2.88-2.92 (1H, m), 3.24 (1H, d, *J*=12.6 Hz), 3.69-3.73 (1H, q, *J*=7.2 Hz), 4.22 (1H, d, *J*=12.6 Hz), 7.21-7.23 (1H, m), 7.28-7.33 (4H, m).

To a solution of **6** (4.73 g, 0.018 mol) in CH_3OH (50 ml) was added Pd/C (10%, 2.5 g). The reaction mixture was stirred at 80 ℃, 1.0 MPa H_2 atmosphere for 10 hours. Then the mixture was filtered to remove Pd/C, and purified by column chromatography (ammonia water: CH_3OH=1:30) to afford product **7** (2.26 g, 73.4%). ^1H NMR (600 MHz, $CDCl_3$) δ: 1.32-1.42 (3H, m), 1.50-1.64 (4H, m), 1.73-1.77 (2H, m), 1.87-1.90 (1H, m), 2.27-2.33 (4H, m), 2.42-2.58 (2H, m), 2.87-3.02 (2H, m), 3.31-3.33 (1H, m).

To a solution of **7** (1.0 g, 5.95 mmol) in CH_2Cl_2 (20 ml) was added activated resin (2.58 g, contain sulfonic acid group 4.96 mmol). The reaction mixture was stirred for 24 hours at room temperature and then filtered. The insoluble substance was washed by CH_2Cl_2 (10 ml*2) and dried at 40 ℃ for 2 hours to afford catalyst **1**. Elemental analysis: C: 53.92%, H: 6.93%, N: 5.21%, S: 9.71%, organic catalyst loading: 1.861 mmol/g.

2. Preparation of catalyst 2:

The product **8** was synthesized from **5** utilizing the similar procedure of synthesizing **6**. The product **8** ^1H NMR (600 MHz, $CDCl_3$) δ: 1.51-1.73 (2H, m), 1.82-1.99 (2H, m), 2.27 (3H, s), 2.32-2.66 (11H, m), 2.78-2.79 (0.5H, m), 2.89-2.93 (0.5H, m), 3.03-3.05 (0.5H, m), 3.26 (0.5H, d, *J*=13.2 Hz), 3.48-3.54 (1H, m), 3.67-3.71 (1H, m), 7.21-7.33 (5H, m).

The product **9** was synthesized from **8** utilizing the similar procedure of synthesizing **7**. The product **9** ^1H NMR (600 MHz, $CDCl_3$) δ: 1.29-1.46 (2H,m), 1.69-1.76 (2H, m), 2.26 (3H, s), 2.29-2.60 (10H, m), 2.81-2.86 (1H, m), 2.93-3.00 (1H, m), 3.19-3.27 (1H, m).

To a solution of **9** (1.0 g, 5.46 mmol) in CH_2Cl_2 (20 ml) was added activated resin (4.74 g, contain sulfonic acid group 9.11 mmol). The reaction mixture was stirred for 24 hours at room temperature and then filtered. The insoluble substance was washed by CH_2Cl_2 (10 ml*2) and dried at 40 ℃ for 2 hours to afford catalyst **2**. Elemental analysis: C: 52.81%, H: 7.22%, N: 4.74%, S: 10.61%, organic catalyst loading: 1.129 mmol/g.

3. Preparation of catalyst 3:

The product **10** was synthesized from **5** utilizing the similar procedure of synthesizing **6**. The product **10** ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.56-1.71 (3H, m), 1.85-1.98 (2H, m), 2.12-2.19 (1H, m), 2.31-2.36 (1H, m), 2.51-2.65 (12H, m), 2.89-2.93 (1H, m), 3.25-3.28 (1H, m), 3.59-3.61 (2H, m), 7.23-7.33 (5H, m).

The product **11** was synthesized from **10** utilizing the similar procedure of synthesizing **5**.

The product **12** was synthesized from **11** utilizing the similar procedure of synthesizing **6**. The product **12** ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.29 (6H, t, J=10.8 Hz), 1.73-2.07 (4H, m), 2.41-2.46 (2H, m), 2.49-2.68 (8H, m), 2.78-2.91 (2H, m), 2.93-3.14 (8H, m), 3.47-3.69 (1H, m), 4.26-4.43 (2H, m), 7.27-7.43 (5H, m).

The product **13** was synthesized from **12** utilizing the similar procedure of synthesizing **7**. The product **13** ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.76 (6H, t, J=10.8 Hz), 1.06-1.21 (2H, m), 1.47-1.73 (2H, m), 2.02-2.11 (2H, m), 2.21-2.33 (16H, m), 2.56-2.74 (2H, m), 2.93-3.01 (1H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 11.59, 24.75, 29.72, 45.79, 47.24, 49.12, 50.09, 53.54, 55.11, 56.59, 63.76.

To a solution of **13** (1.0 g, 3.73 mmol) in CH_2Cl_2 (20 ml) was added activated resin (4.86 g, contain sulfonic acid group 9.33 mmol). The reaction mixture was stirred for 24 hours at room temperature and then filtered. The insoluble substance was washed by CH_2Cl_2 (10 ml*2) and dried at 40 ℃ for 2 hours to afford catalyst **3**. Elemental analysis: C: 52.27%, H: 6.95%, N: 4.95%, S: 12.08%, organic catalyst loading: 0.084 mmol/g.

General experimental procedure for the Michael addition of cyclohexanone to nitroalkene by catalyst 1, 2 and 3.

To a solution of cyclohexanone (10 mmol) and nitroalkene (1 mmol) was added resin-immobilized catalyst (contain 0.1 mmol organic catalyst). The mixture was stirred at room temperature for 48 hours. Then the mixture was filtered and washed by CH_2Cl_2 (10 ml*2), and the product was purified by flash chromatography on silica gel.

Other asymmetric Michael additions of ketones and aldehydes to nitroolefins utilized the similar procedure.

NMR data and HPLC data for Michael addition products of Table 4.

The product of entry 1:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.10-1.22 (1H, m), 1.43-1.74 (4H, m), 1.96-2.04 (1H, m), 2.27-2.45 (2H, m), 2.57-2.66 (1H, m), 3.67-3.74 (1H, m), 4.58 (1H, dd, *J*=12.5 Hz, 10.0 Hz), 4.89 (1H, dd, *J*=12.5Hz, 4.5 Hz), 7.10-7.28 (5H, m);

^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.2, 28.6, 33.3, 42.7, 44.2, 52.4, 79.0, 127.8, 128.3, 129.0, 137.7, 211.1

MS (ESI, m/z): 248.1 (M+H$^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=15.4 min (minor), 23.8 min (major).

The product of entry 2:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.21-1.29 (1H, m), 1.58-1.83 (4H, m), 2.04-2.11 (1H, m), 2.33 (3H, s), 2.36-2.43 (1H, m), 2.47-2.50 (1H, m), 2.66-2.70 (1H, m), 3.70-3.75 (1H, m), 4.60-4.63 (1H, m), 4.91-4.94 (1H, m), 7.05 (2H, d, *J*=8.0 Hz) , 7.13 (2H, d, *J*=8.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.0, 24.8, 28.5, 33.2, 42.6, 43.5, 52.5, 79.1, 127.9, 129.5, 134.5, 137.3, 211.8

MS (ESI, m/z): 266.3 (M+H$^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=10.8 min (minor), 19.8 min (major).

The product of entry 3:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.18-1.28 (1H, m), 1.56-1.82 (4H, m), 2.05-2.12 (1H, m), 2.34-2.42 (1H, m), 2.46-2.51 (1H, m), 2.61-2.68 (1H, m), 3.68-3.74 (1H, m), 3.79 (3H, s), 4.58-4.61 (1H, m), 4.90-4.93 (1H, m) , 6.85 (2H, d, J=8.5 Hz) , 7.05 (2H, d, *J*=8.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.8, 28.5, 33.1, 42.5, 43.1, 52.4, 55.1, 78.9, 114.1, 129.1, 129.6, 158.8, 211.8.

MS (ESI, m/z): 278.1 (M+H$^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=33.0 min (minor), 47.8

min (major).

The product of entry 4:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.19-1.28 (1H, m), 1.56-1.83 (4H, m), 2.06-2.13 (1H, m), 2.34-2.42 (1H, m), 2.46-2.52 (1H, m), 2.63-2.67 (1H, m), 3.74-3.78 (1H, m), 4.59-4.63 (1H, m), 4.92-4.96 (1H, m) , 7.12-7.14 (2H, m) , 7.29-7.33 (2H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.1, 28.4, 33.3, 42.6, 43.5, 52.3, 78.4, 129.1, 129.5, 133.5, 136.2, 211.7.

MS (ESI, m/z): 282.0 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=16.3 min (minor), 29.0 min (major).

The product of entry 5:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.24-1.33 (1H, m), 1.57-1.84 (4H, m), 2.07-2.14 (1H, m), 2.35-2.44 (1H, m), 2.46-2.51 (1H, m), 2.77-2.82 (1H, m), 3.89-3.93 (1H, m), 4.85-4.96 (2H, m) , 7.15-7.37 (4H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.1, 28.5, 33.2, 41.8, 43.3, 51.8, 77.9, 129.0, 129.8, 134.1, 136.1, 211.7.

MS (ESI, m/z): 282.0 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=16.3 min (minor), 31.0 min (major).

The product of entry 6:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.31-1.38 (1H, m), 1.59-1.83 (4H, m), 2.09-2.15 (1H, m), 2.37-2.45 (1H, m), 2.47-2.51 (1H, m), 2.90-2.96 (1H, m), 4.27-4.33 (1H, m), 4.87-4.94 (2H, m), 7.20-7.25 (3H, m) , 7.36-7.39 (1H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.2, 28.5, 33.1, 41.1, 42.8, 51.5, 77.3, 128.8, 130.4,134.7, 135.5, 211.8,

MS (ESI, m/z): 282.1 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=14.0 min (minor), 20.9 min (major).

The product of entry 7:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.31-1.38 (1H, m), 1.60-1.85 (4H, m), 2.11-2.15 (1H, m), 2.35-2.42 (1H, m), 2.46-2.52 (1H, m), 2.84-2.94 (1H, m), 4.11-4.24 (1H, m), 4.86-4.92 (2H, m) , 7.16 (1H, d, J=8.5 Hz) , 7.24 (1H, dd, J_1=8.5 Hz, J_2=2.0 Hz), 7.43 (1H, d, J=2.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.1, 27.0, 28.3, 32.9, 40.4, 42.7, 51.5, 77.4, 127.8, 130.0, 133.9, 134.4, 135.2, 211.5.

MS (ESI, m/z): 316.2 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=11.1 min (minor), 20.1 min (major).

The product of entry 8:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.23-1.31 (1H, m), 1.55-1.84 (4H, m), 2.07-2.14 (1H, m), 2.35-2.44 (1H, m), 2.48-2.54 (1H, m), 2.65-2.69 (1H, m), 3.75-3.81 (1H, m), 4.59-4.63 (1H, m), 4.93-4.96 (1H, m) , 7.16-7.21 (2H, m) , 7.32-7.38 (2H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.0, 28.3, 33.4, 42.5, 43.6, 52.2, 78.5, 129.2, 129.6, 133.4, 140.2, 211.7.

MS (ESI, m/z): 326.0 ($M+H^+$), 328.0 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=16.9 min (minor), 30.3 min (major).

The product of entry 9:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.22-1.32 (1H, m), 1.56-1.77 (3H, m), 1.78-1.85 (1H, m), 2.08-2.16 (1H, m), 2.44-2.35 (1H, m), 2.52-2.45 (1H, m), 2.78-2.69 (1H, m), 3.91-4.01 (1H, m), 4.66-4.73 (1H, m), 4.97-5.05 (1H, m), 7.41 (2H, d, J=8.5 Hz), 8.15 (2H, d, J=8.5 Hz).

^{13}C NMR (125MHz, $CDCl_3$) δ: 24.9, 28.2, 33.0, 42.4, 43.6, 52.1, 77.9, 123.8, 129.2, 145.5, 147.3, 210.9.

MS (ESI, m/z): 315.1 ($M+Na^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=7:3), 1.0 ml/min; t_r=30.0 min (major).

The product of entry 10:

^{1}H NMR (500 MHz, $CDCl_3$) δ : 1.19-1.29 (1H, m), 1.57-1.83 (4H, m), 2.05-2.11 (1H, m), 2.36-2.44 (1H, m), 2.46-2.51 (1H, m), 2.62-2.68 (1H, m), 3.69-3.75 (1H, m), 3.79 (3H, s), 4.57-4.61 (1H, m), 4.90-4.94 (1H, m) , 6.85 (2H, d, J=8.5 Hz) , 7.08 (2H, d, J=8.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.1, 28.1, 33.0, 41.9, 42.7, 52.1, 77.5, 124.7, 128.4, 129.0, 132.8, 133.0, 150.7, 211.1.

MS (ESI, m/z): 293.2 (M+H$^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=7:3), 1.0 ml/min; t_r=14.1 min (minor), 18.4 min (major).

The product of entry 11:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.52-2.57 (1H, m), 2.60-2.68 (1H, m), 2.85-2.90 (1H, m), 3.26 (1H, dd, J_1=20.0 Hz, J_2=8.5 Hz), 3.64-3.86 (3H, m), 4.11-4.18 (1H, m), 4.62-4.68 (1H, m), 4.94 (1H, dd, J_1=12.5 Hz, J_2=4.5 Hz), 7.18-7.35 (5H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 41.3, 42.8, 53.4, 68.8, 71.5, 78.5, 127.7, 128.3, 129.1, 136.3, 208.3.

MS (ESI, m/z): 250.1(M+H$^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=28.9 min (minor), 38.8 min (major).

The product of entry 12:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.14 (3H, s)，2.93 (2H, d, J=5.0 Hz)，3.99-4.04 (1H, m), 4.58-4.63 (1H, m), 4.68-4.73 (1H, m), 7.21-7.55 (5H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 30.3, 39.0, 46.1, 55.4, 79.4, 127.2, 127.9, 129.1, 138.8, 205.6.

MS (ESI, m/z): 208.0 (M+H$^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=30.2 min (minor), 37.1 min (major).

The product of entry 13:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.98 (3H, d, J=7.5 Hz,), 1.08 (3H, t, J=7.5 Hz), 2.34−2.44 (1H, m), 2.55–2.65 (1H, m), 2.93−3.02 (1H, m), 3.67−3.72 (1H, m), 4.58 (1H, dd, J_1=12.5 Hz, J_2=4.5 Hz), 4.65 (1H, dd, J_1=12.5 Hz, J_2=9.0 Hz), 7.14−7.16 (2H, m), 7.24−7.32 (3H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 7.1, 14.4, 35.5, 45.9, 49.0, 77.8, 128.8, 138.5, 212.7.

MS (ESI, m/z): 236.2(M+H$^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-

H column at 254 nm (hexane:2-propanol=95:5), 1.0 ml/min; t_r=11.8 min (minor), 16.7 min (major).

The product of entry 14:

^{1}H NMR (500MHz, $CDCl_3$) δ: 1.56-1.78 (2H, m), 1.78-1.97 (2H, m), 2.04-2.54 (3H, m), 3.66–3.73 (1H, m), 5.02 (1H, d, *J*=8.5 Hz), 7.15-7.35 (5H, m).

^{13}C NMR (125 MHz, $CDCl_3$): 20.1, 28.1, 38.5, 44.0, 50.3, 78.1, 127.7, 127.9, 128.3, 137.3, 218.4.

MS (ESI, m/z): 266.1 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=16.5 min (minor), 28.7 min (major).

The product of entry 15:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.21-1.31 (1H, m), 1.42-1.83 (6H, m), 1.99-2.07 (1H, m), 2.28-2.47 (2H, m), 2.58-2.69 (1H, m), 3.70-3.77 (1H, m), 4.61-4.64 (1H, m), 4.89-4.93 (1H, m), 7.11-7.29 (5H, m).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.9, 26.3, 28.5, 33.5, 43.1, 44.5, 52.7, 79.7, 127.8, 128.5, 129.0, 138.5, 211.5

MS (ESI, m/z): 262.1 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=95:5), 1.0 ml/min; t_r=15.6 min (minor), 26.0 min (major).

The product of entry 16:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.99 (3H, d, *J*=9.0 Hz), 2.71-2.83 (1H, m), 3.75-3.80 (1H, m), 4.61-4.69 (1H, m), 4.72-4.78 (1H, m), 7.16-7.35 (5H, m), 9.72 (1H, d, *J*=2.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 12.2, 44.0, 48.5, 78.1, 128.0, 128.1, 129.1, 136.6, 202.1.

MS (ESI, m/z): 208.2 ($M+H^+$)

The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=8:2), 1.0 ml/min; t_r=22.6 min (major), 32.1 min (minor).

The product of entry 17:

^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.81-0.92 (3H, m), 1.48-1.56 (2H, m), 2.66-2.72 (1H, m), 3.77-3.83 (1H, m), 4.61-4.75 (2H, m), 7.18-7.21 (2H, m), 7.29-7.38 (2H, m), 9.72 (1H, d, *J*=2.5 Hz).

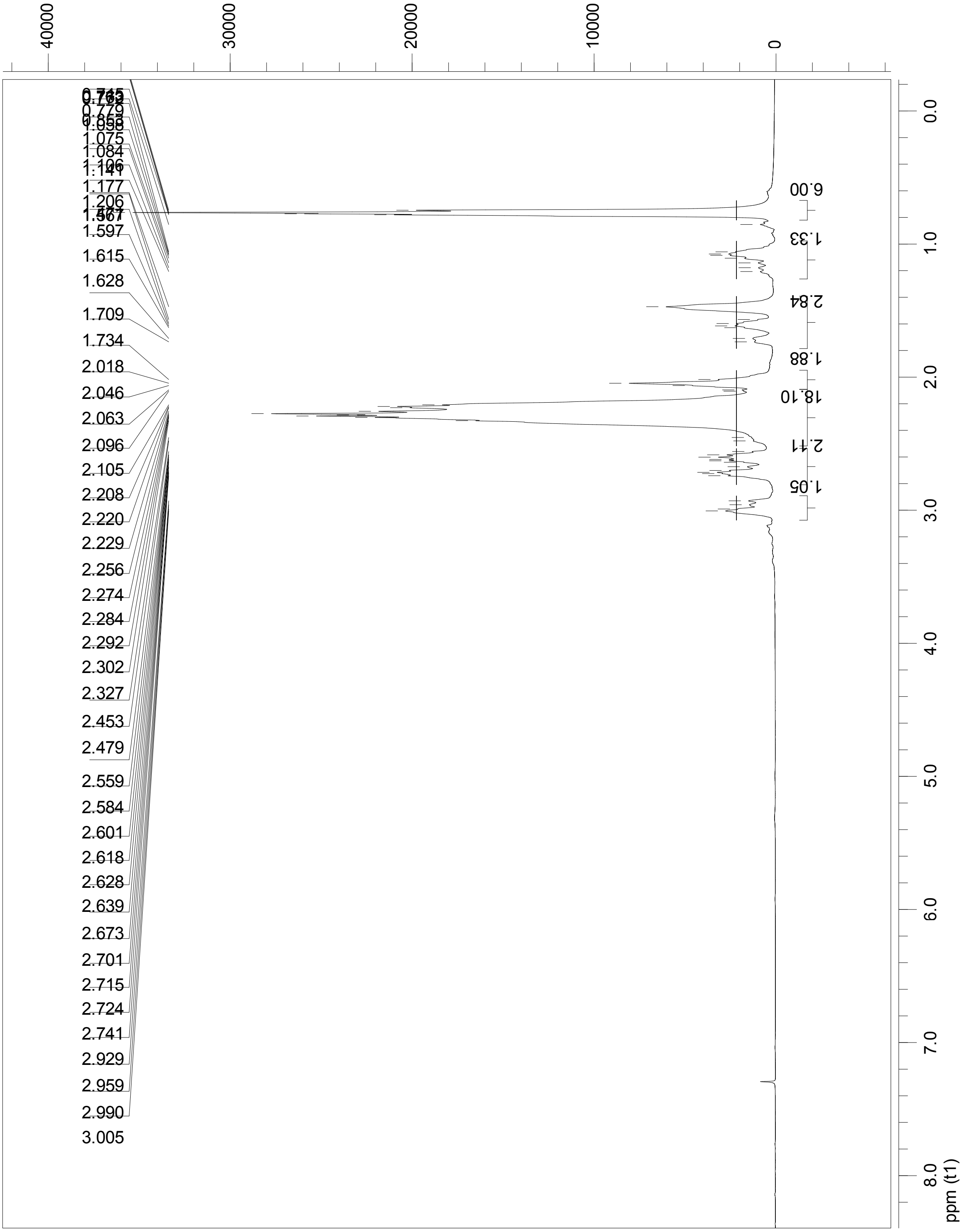
^{13}C NMR (125 MHz, $CDCl_3$) δ: 10.8. 20.5, 42.7, 55.0, 78.4, 128.0, 128.1, 129.1, 136.7, 203.1.

MS (ESI, m/z): 222.3 ($M+H^+$)

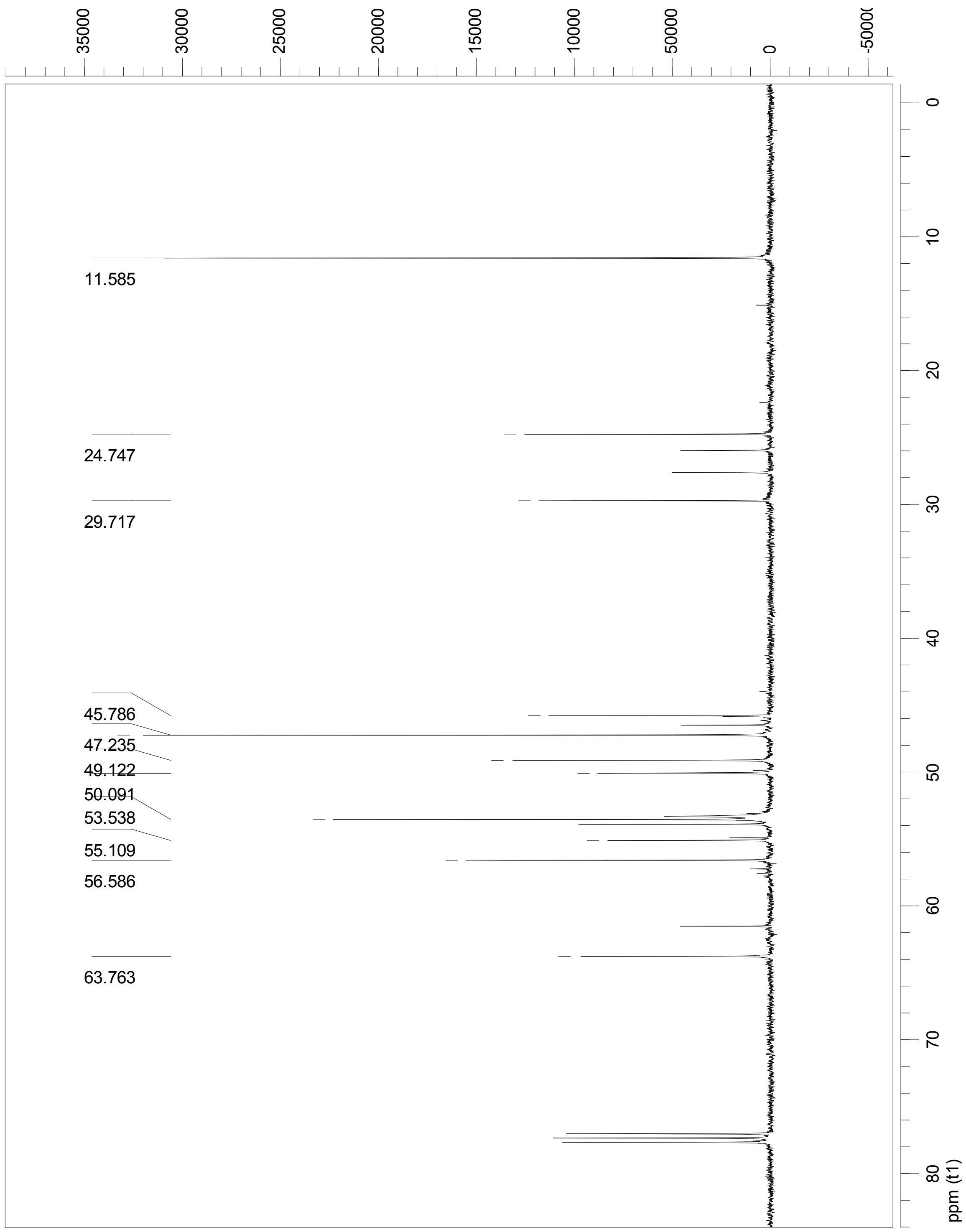
The enantiomeric excess was determined by chiral HPLC with a Chiralpack AS-H column at 254 nm (hexane:2-propanol=9:1), 1.0 ml/min; t_r=12.7 min (major), 26.1 min (minor).

NMR of compound **13**:

^{1}H NMR

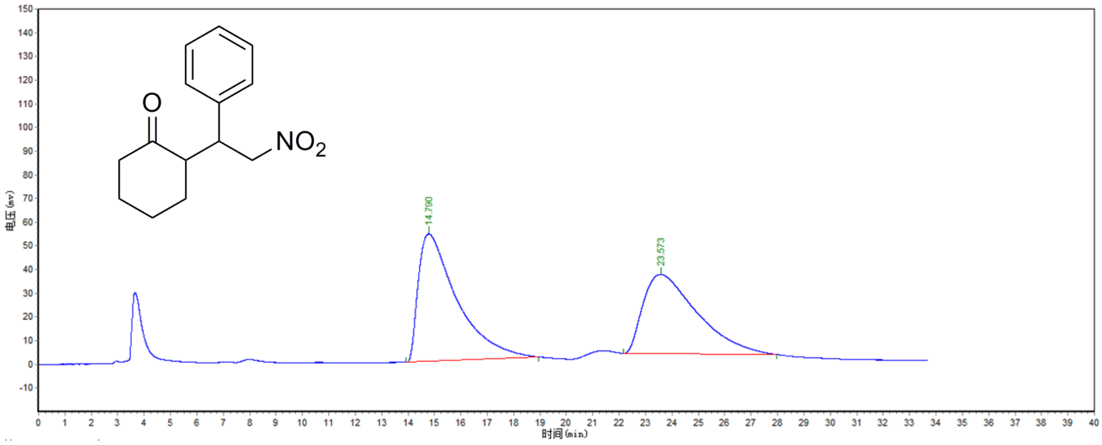


^{13}C NMR



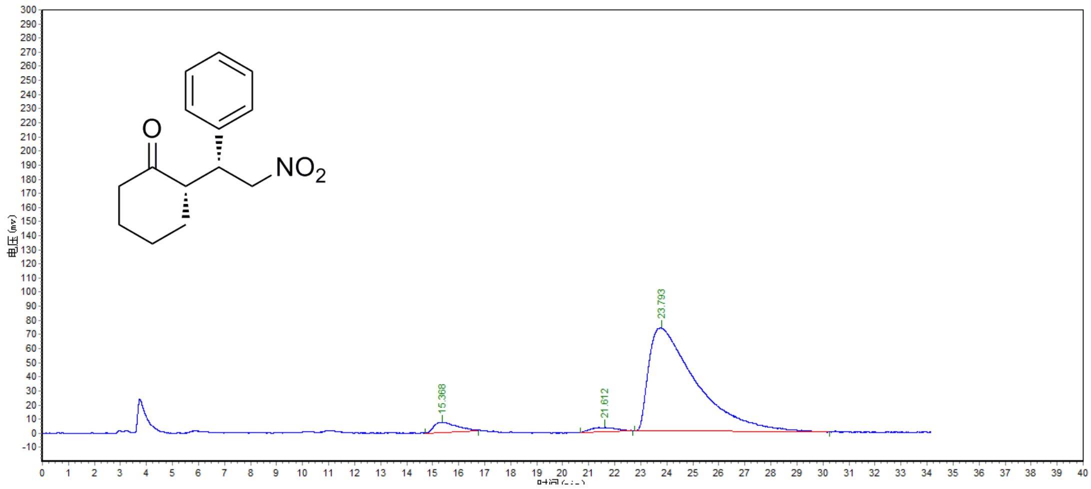
HPLC analysis results:

Table 4 Entry 1



Analysis Result

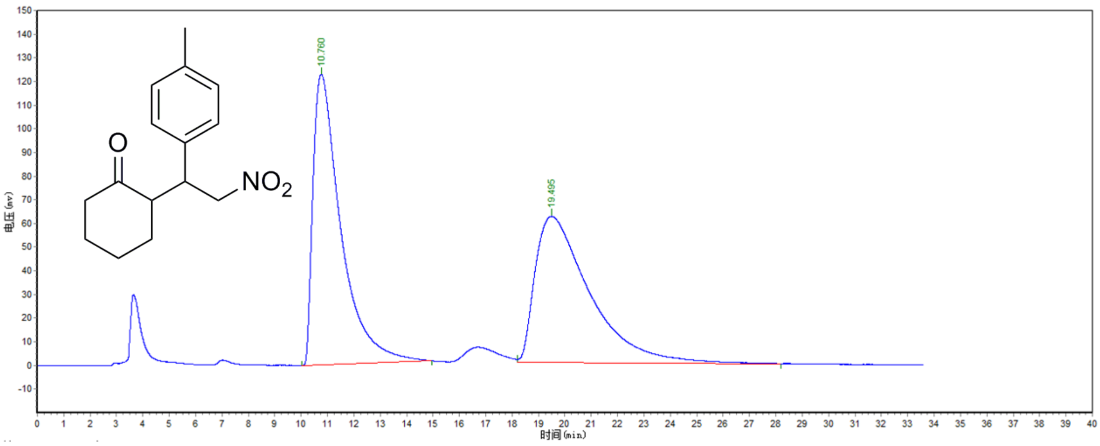
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	14.790	53826.652	5476112.000	53.3610
2	23.573	33581.625	4786269.500	46.6390
Total		87408.277	10262381.500	100.0000



Analysis Result

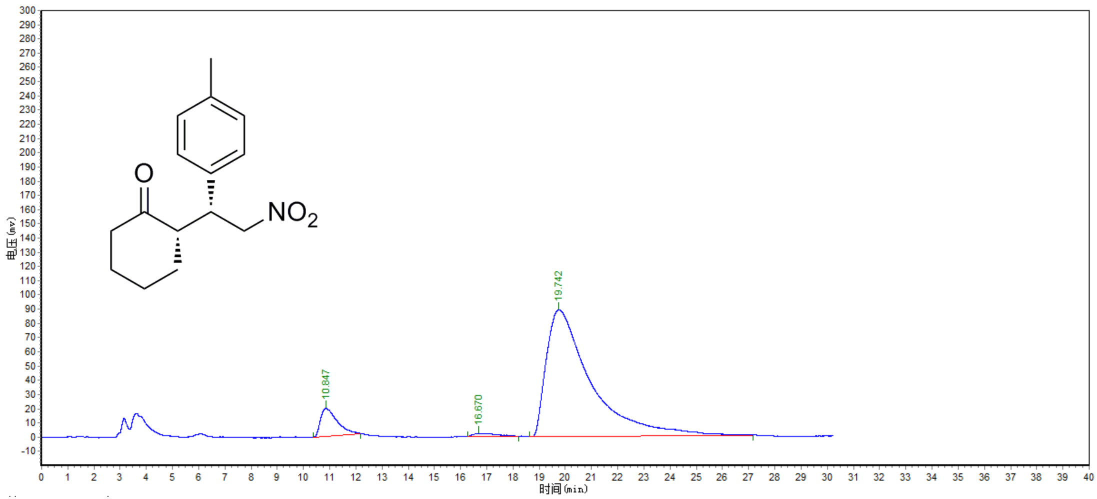
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	15.368	7077.769	417198.844	4.1927
2	21.612	3024.380	209476.609	2.1052
3	23.793	73270.852	9323860.000	93.7021
Total		83373.000	9950535.453	100.0000

Table 4 Entry 2



Analysis Result

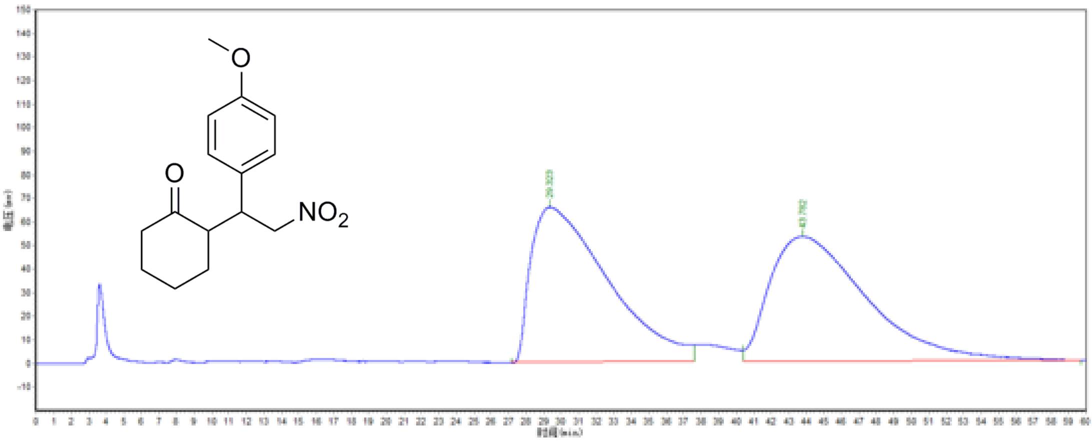
Peak#	RT (min)	Height (µV)	Area (µV*Sec)	Area%
1	10.760	122714.406	9017093.000	50.3714
2	19.495	61737.625	8884140.000	49.6286
Total		184452.031	17901233.000	100.0000



Analysis Result

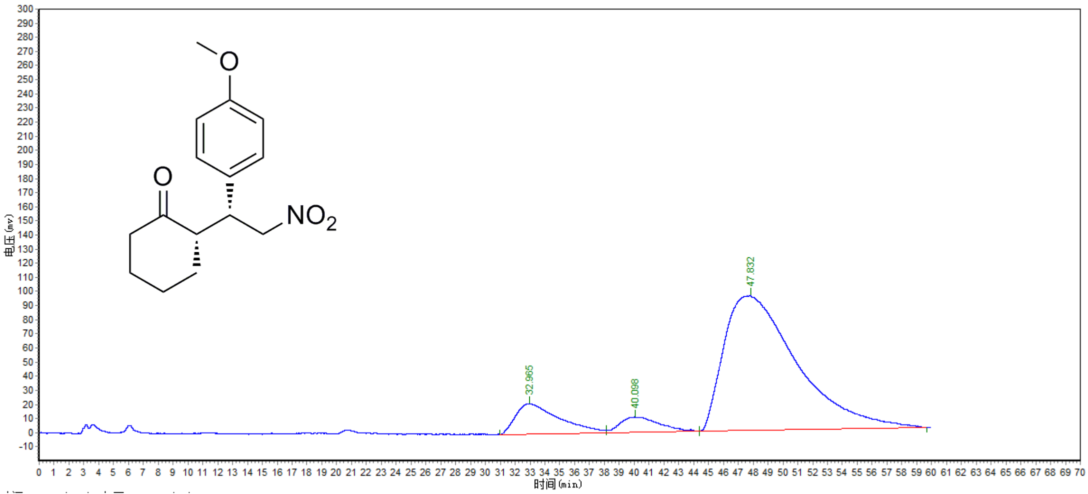
Peak#	RT (min)	Height (µV)	Area (µV*Sec)	Area%
1	10.847	19730.707	863682.000	7.5368
2	16.670	1971.928	123015.492	1.0735
3	19.742	89059.398	10472875.000	91.3898
Total		110762.034	11459572.492	100.0000

Table 4 Entry 3



Analysis Result

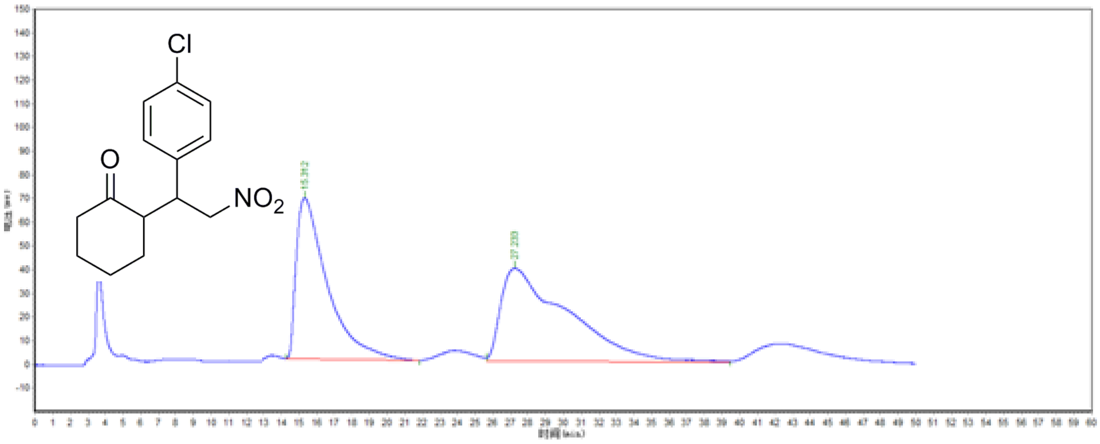
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	29.323	65586.398	20023696.000	49.7180
2	43.782	52790.691	20250874.000	50.2820
Total		118377.090	40274570.000	100.0000



Analysis Result

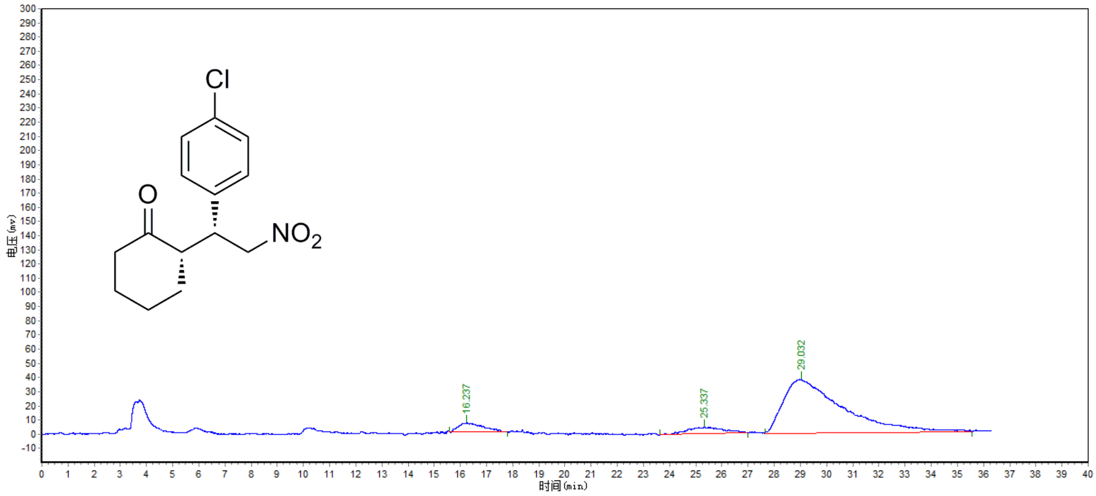
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	32.965	21500.307	4407238.500	11.3307
2	40.098	10788.599	1996650.750	5.1333
3	47.832	95503.383	32492468.000	83.5360
Total		127792.288	38896357.250	100.0000

Table 4 Entry 4



Analysis Result

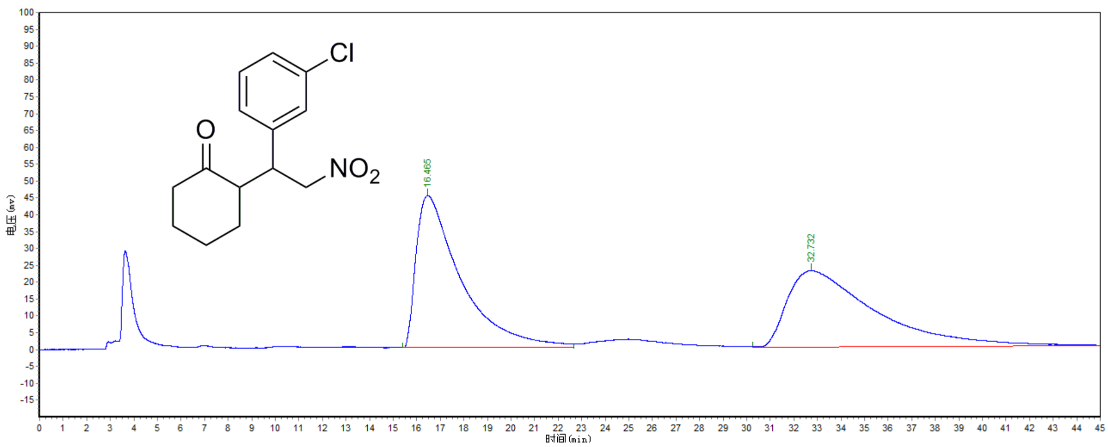
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	15.312	67863.359	8339949.500	44.7806
2	27.233	39212.293	10284056.000	55.2194
Total		107075.652	18624005.500	100.0000



Analysis Result

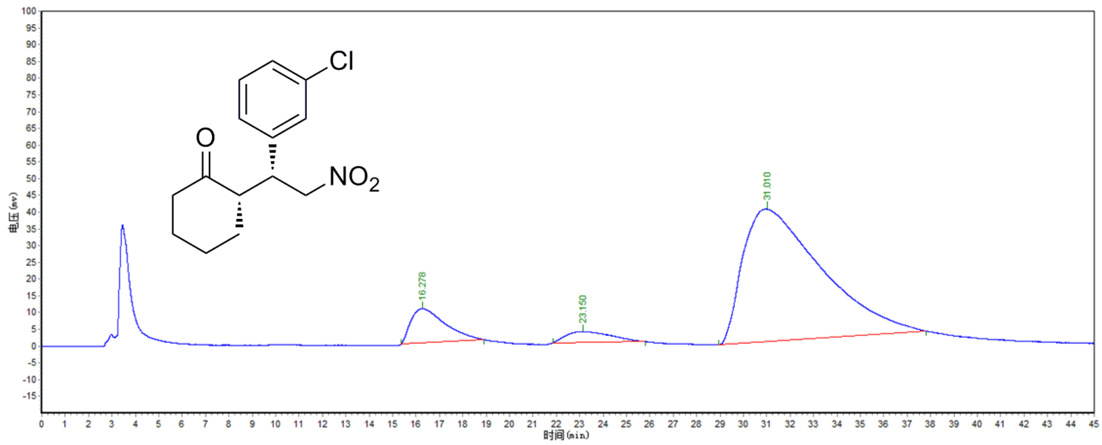
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	16.237	5890.376	367247.406	5.4995
2	25.337	4461.787	441692.156	6.6143
3	29.032	37642.684	5868873.000	87.8862
Total		47994.847	6677812.563	100.0000

Table 4 Entry 5



Analysis Result

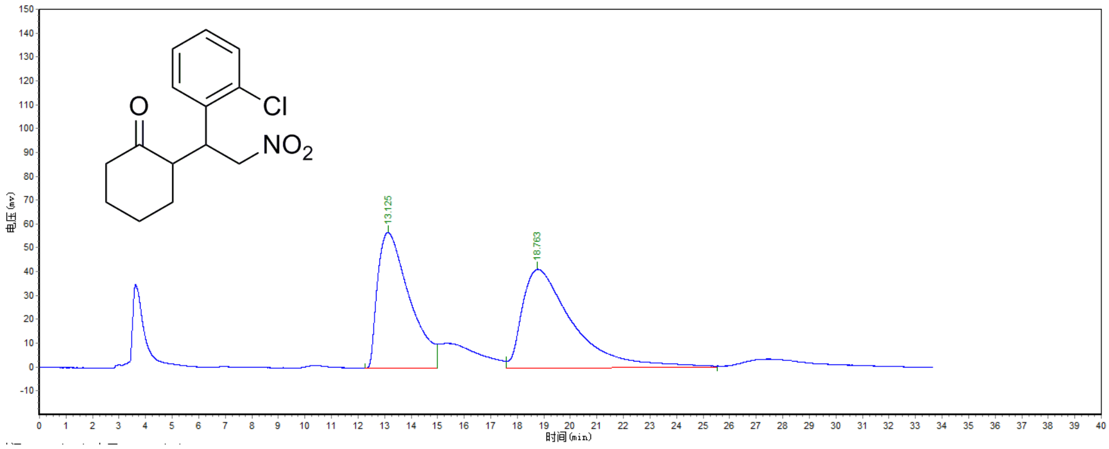
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	16.465	45082.438	5922708.000	50.5291
2	32.732	22478.158	5798669.500	49.4709
Total		67560.596	11721377.500	100.0000



Analysis Result

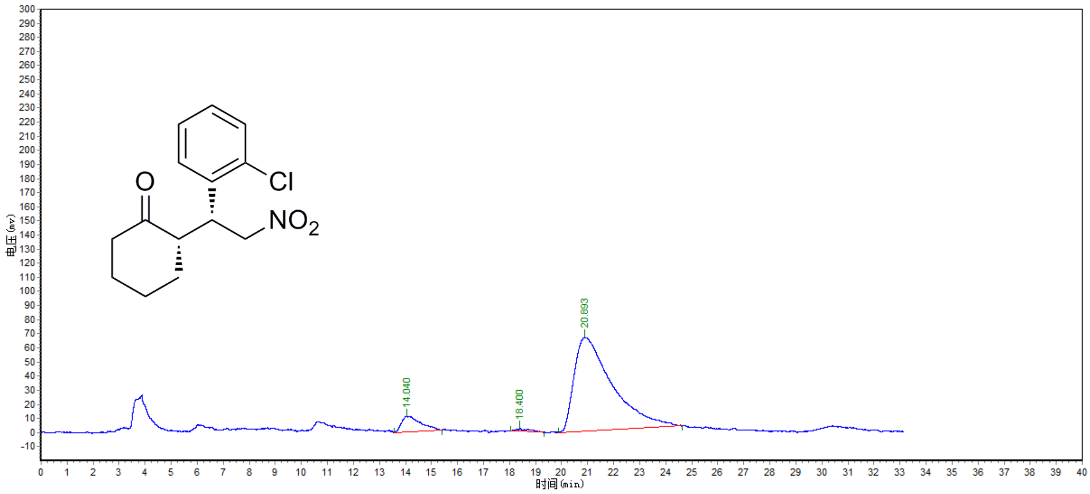
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	16.278	10285.205	1043212.188	9.7476
2	23.150	3238.591	422838.594	3.9509
3	31.010	39538.008	9236197.000	86.3015
Total		53061.804	10702247.781	100.0000

Table 4 Entry 6



Analysis Result

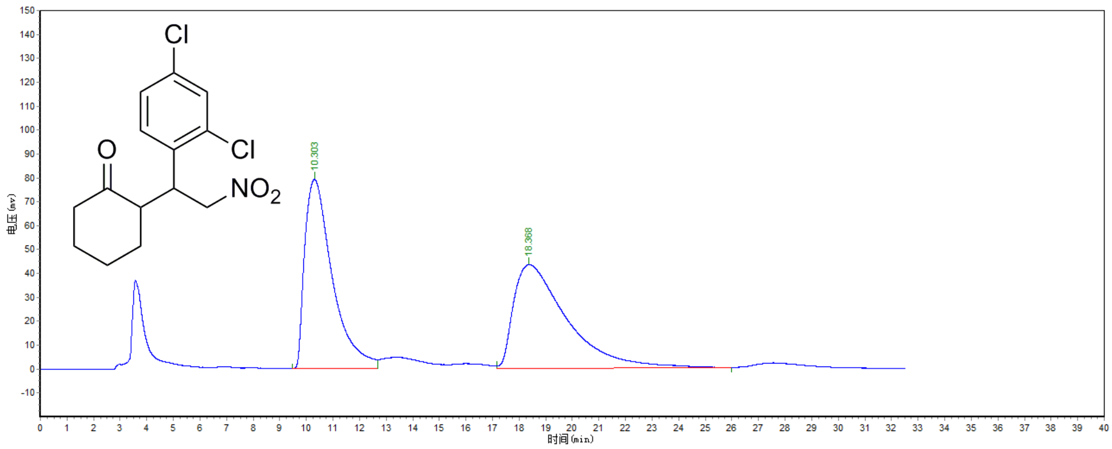
Peak#	RT (min)	Height (μV)	Area (μV*Sec)	Area%
1	13.125	56786.285	4738040.000	46.2078
2	18.763	41309.098	5515724.000	53.7922
Total		98095.383	10253764.000	100.0000



Analysis Result

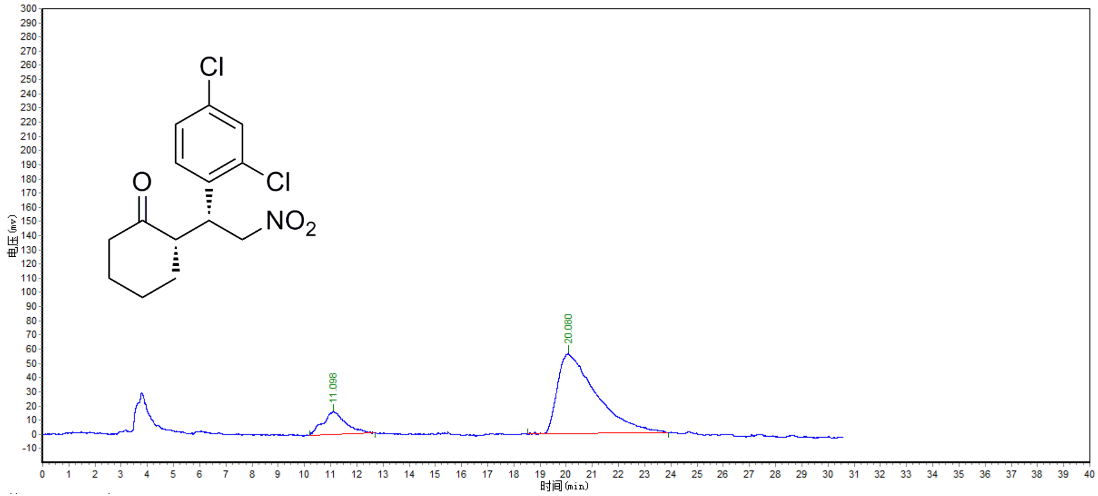
Peak#	RT (min)	Height (μV)	Area (μV*Sec)	Area%
1	14.040	11324.587	574376.563	7.7897
2	18.400	2097.152	65977.453	0.8948
3	20.893	66391.016	6733215.500	91.3156
Total		79812.754	7373569.516	100.0000

Table 4 Entry 7



Analysis Result

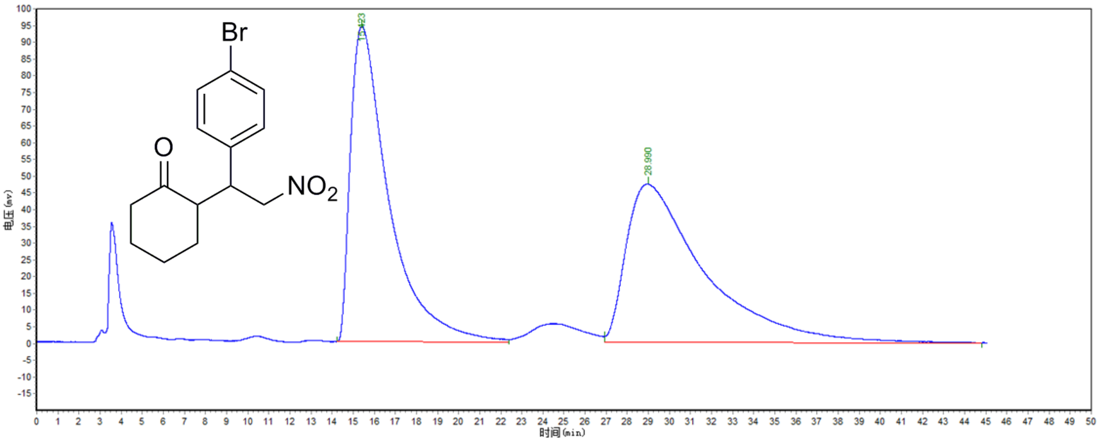
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	10.303	79064.203	5703810.000	48.6955
2	18.368	43301.738	6009399.000	51.3045
Total		122365.941	11713209.000	100.0000



Analysis Result

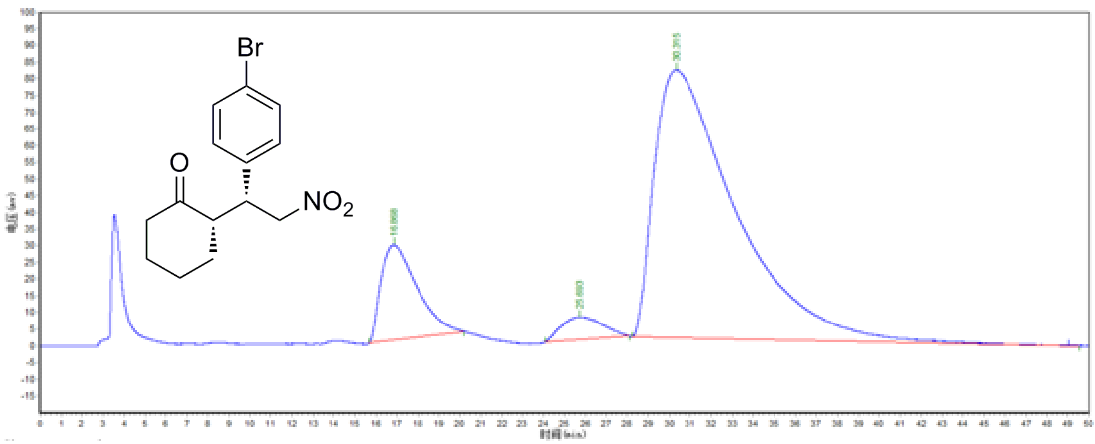
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	11.098	15992.151	942723.563	14.0263
2	20.080	56700.484	5778410.000	85.9737
Total		72692.636	6721133.563	100.0000

Table 4 Entry 8



Analysis Result

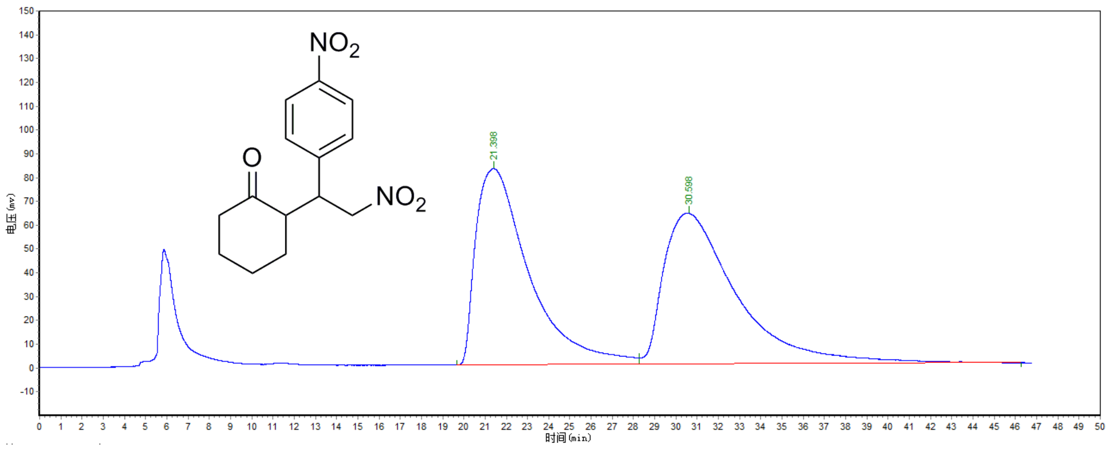
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	15.423	94377.977	11961047.000	49.4972
2	28.990	47337.816	12204049.000	50.5028
Total		141715.793	24165096.000	100.0000



Analysis Result

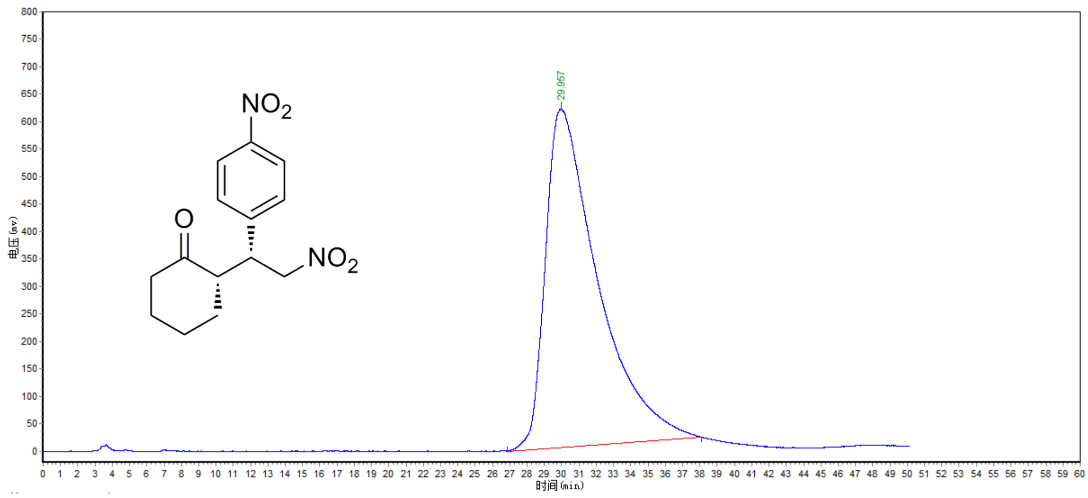
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	16.868	28380.660	3373223.000	13.0806
2	25.693	6694.212	920293.563	3.5687
3	30.315	80084.531	21494562.000	83.3508
Total		115159.403	25788078.563	100.0000

Table 4 Entry 9



Analysis Result

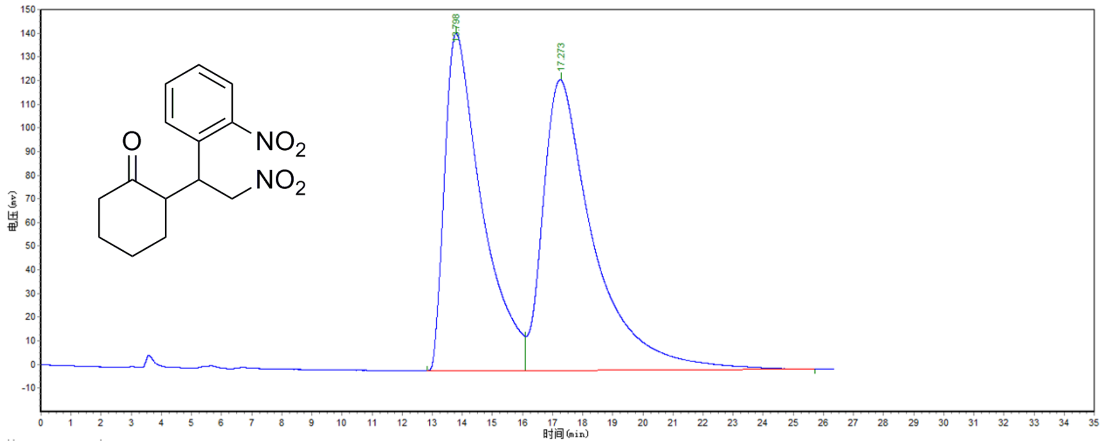
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	21.398	82421.938	14435415.000	48.6479
2	30.598	63457.465	15237813.000	51.3521
Total		145879.402	29673228.000	100.0000



Analysis Result

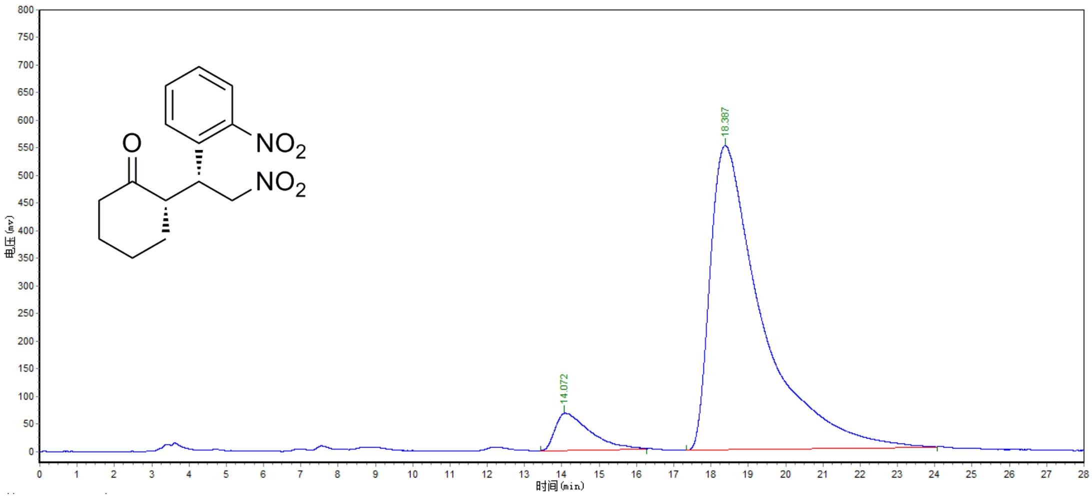
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	29.957	615853.938	129882296.000	100.0000
Total		615853.938	129882296.000	100.0000

Table 4 Entry 10



Analysis Result

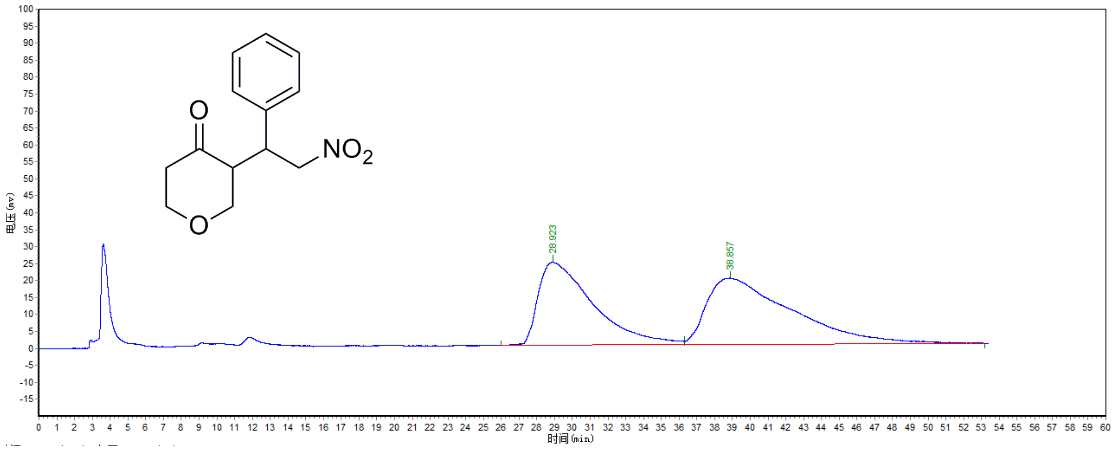
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	13.798	142498.188	12231177.000	45.9604
2	17.273	122675.844	14381274.000	54.0396
Total		265174.031	26612451.000	100.0000



Analysis Result

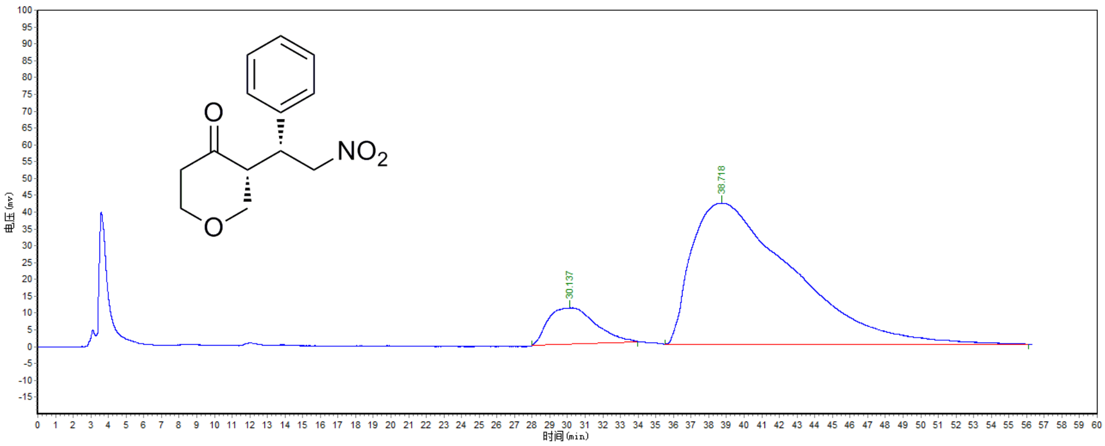
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	14.072	67007.227	4308485.500	7.4579
2	18.387	551076.938	53462024.000	92.5421
Total		618084.164	57770509.500	100.0000

Table 4 Entry 11



Analysis Result

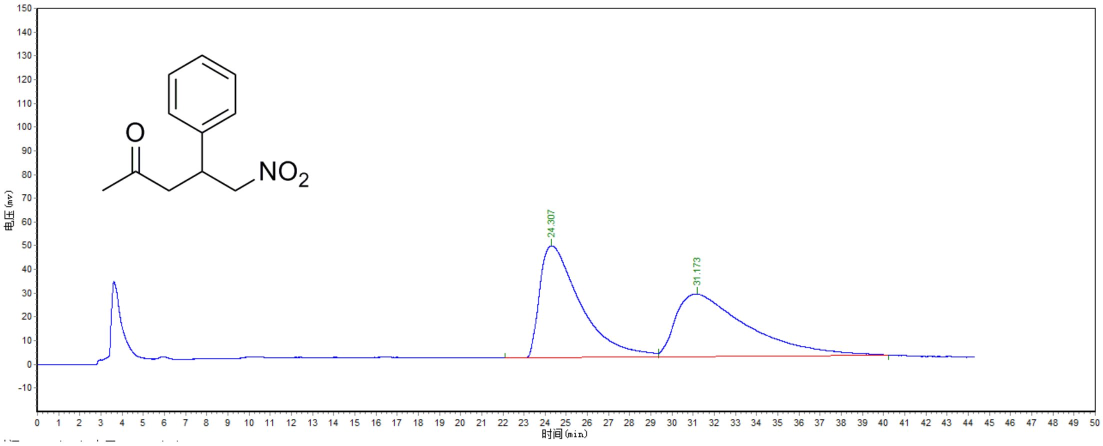
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	28.923	24530.600	5304054.000	44.7906
2	38.857	19564.703	6537829.000	55.2094
Total		44095.303	11841883.000	100.0000



Analysis Result

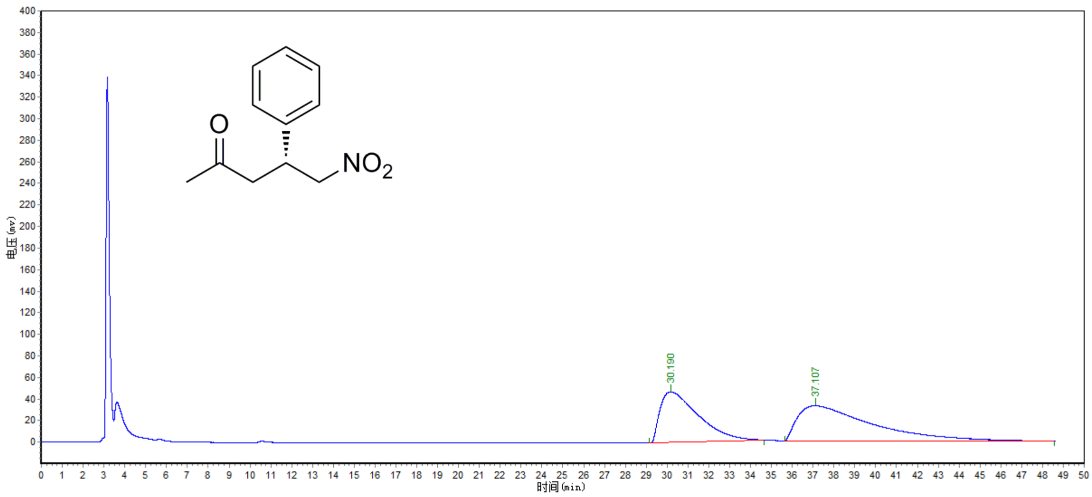
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	30.137	10763.868	1999865.000	10.6702
2	38.718	41913.688	16742610.000	89.3298
Total		52677.556	18742475.000	100.0000

Table 4 Entry 12



Analysis Result

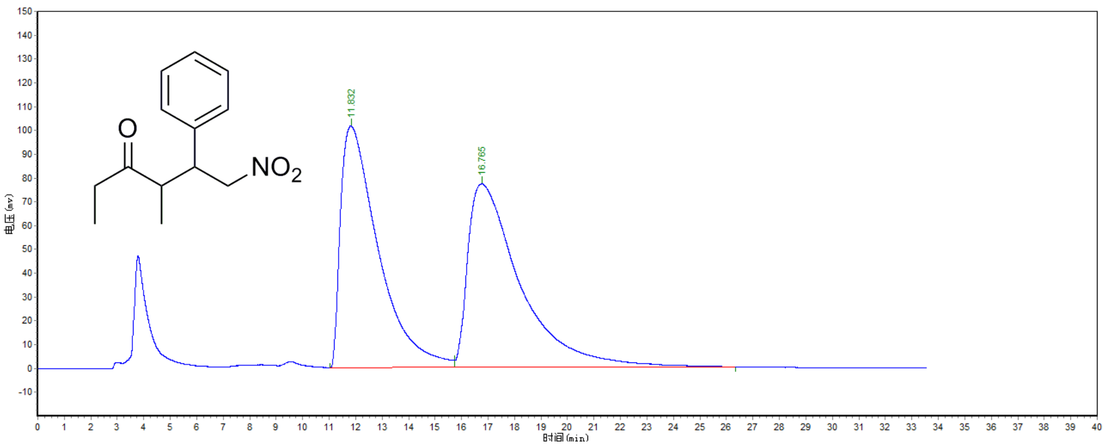
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	24.307	47030.793	6302139.000	50.4938
2	31.173	26371.750	6178874.000	49.5062
Total		73402.543	12481013.000	100.0000



Analysis Result

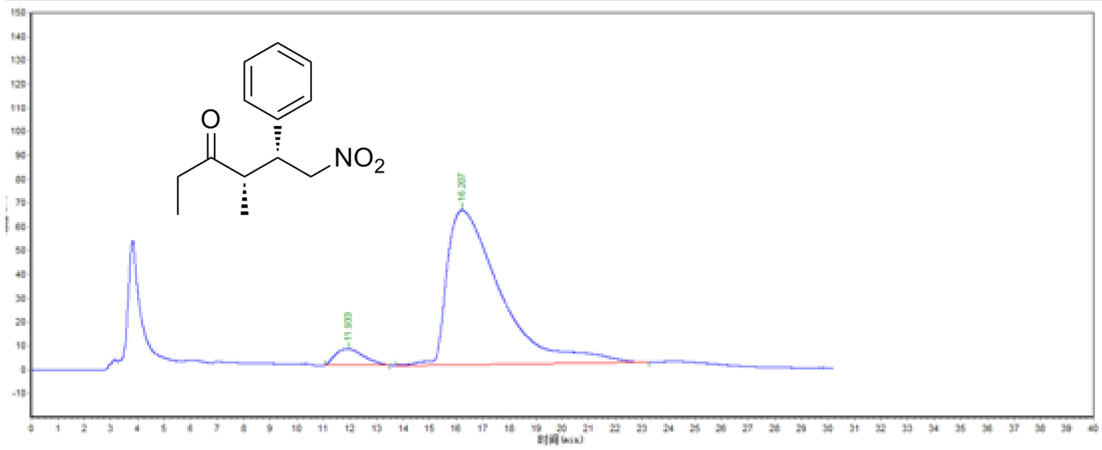
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	30.190	46975.465	5997621.500	42.5935
2	37.107	32434.793	8083439.000	57.4065
Total		79410.258	14081060.500	100.0000

Table 4 Entry 13



Analysis Result

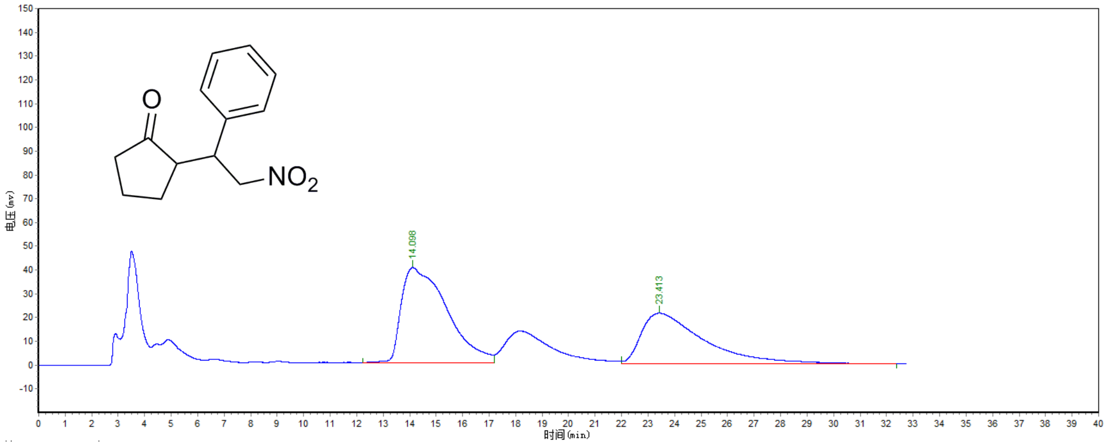
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	11.832	101463.625	10048938.000	48.6692
2	16.765	77076.828	10598503.000	51.3308
Total		178540.453	20647441.000	100.0000



Analysis Result

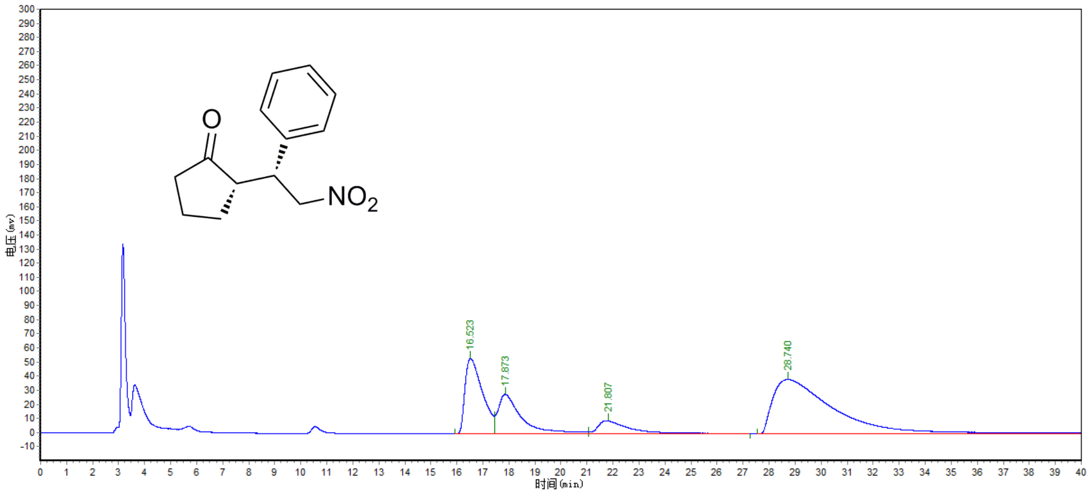
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	11.933	6792.436	497742.656	5.2073
2	16.207	64870.738	9060862.000	94.7927
Total		71663.174	9558604.656	100.0000

Table 4 Entry 14



Analysis Result

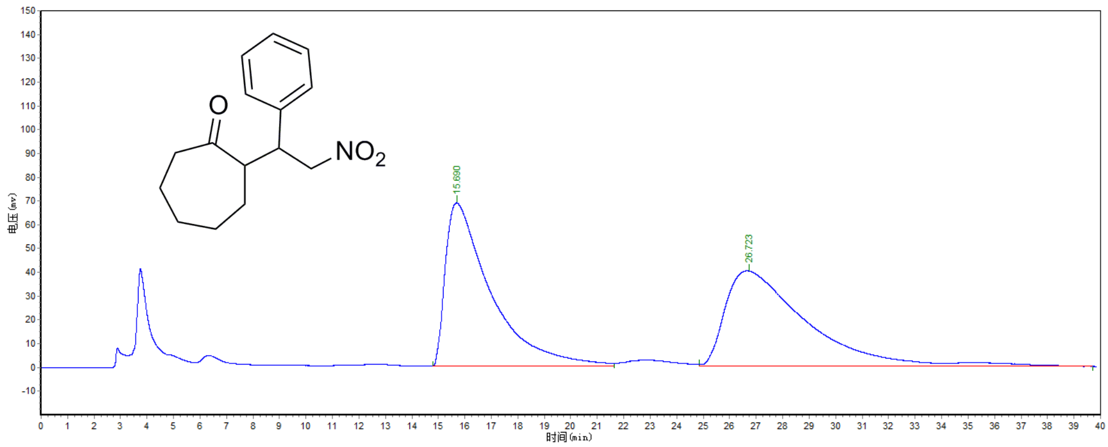
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	14.098	40058.582	4808921.500	58.0789
2	23.413	21163.809	3471055.750	41.9211
Total		61222.391	8279977.250	100.0000



Analysis Result

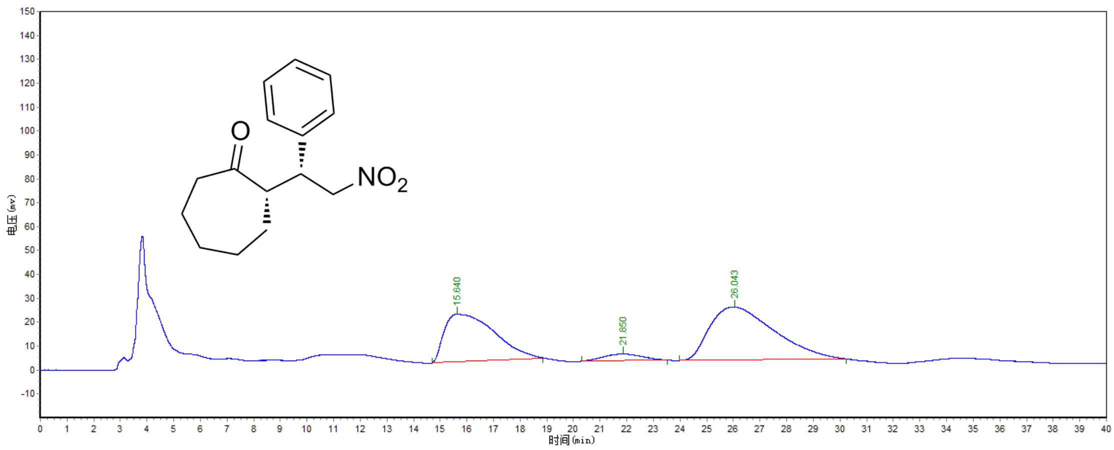
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	16.523	53265.926	2502649.500	20.9178
2	17.873	27991.076	1764279.625	14.7463
3	21.807	9135.583	788902.250	6.5939
4	28.740	38378.391	6908371.000	57.7420
Total		128770.976	11964202.375	100.0000

Table 4 Entry 15



Analysis Result

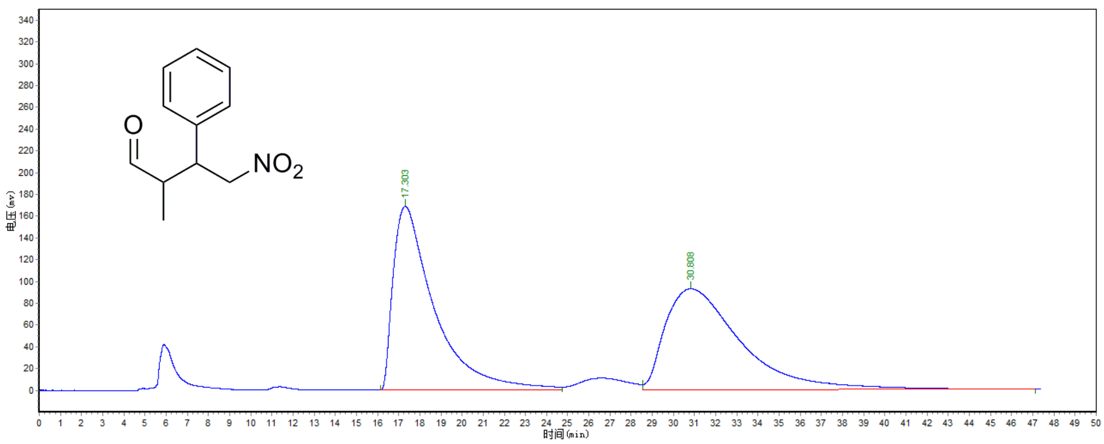
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	15.690	68585.500	8193990.000	48.9498
2	26.723	40098.426	8545589.000	51.0502
Total		108683.926	16739579.000	100.0000



Analysis Result

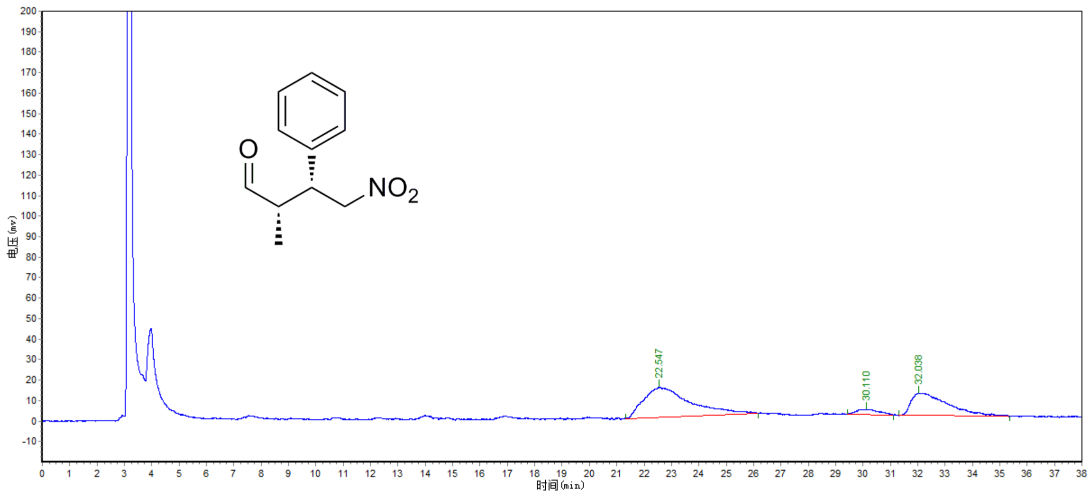
Peak#	RT(min)	Height(µV)	Area(µV*Sec)	Area%
1	15.640	19913.268	2582301.750	39.2885
2	21.850	2780.016	277117.844	4.2162
3	26.043	22149.949	3713245.000	56.4953
Total		44843.233	6572664.594	100.0000

Table 4 Entry 16



Analysis Result

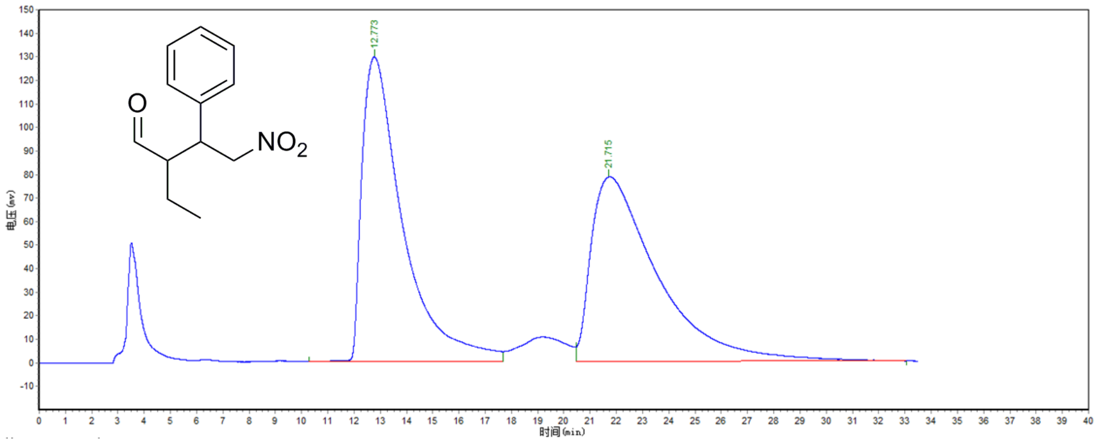
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	17.303	168673.984	22888412.000	49.6842
2	30.808	92737.172	23179366.000	50.3158
Total		261411.156	46067778.000	100.0000



Analysis Result

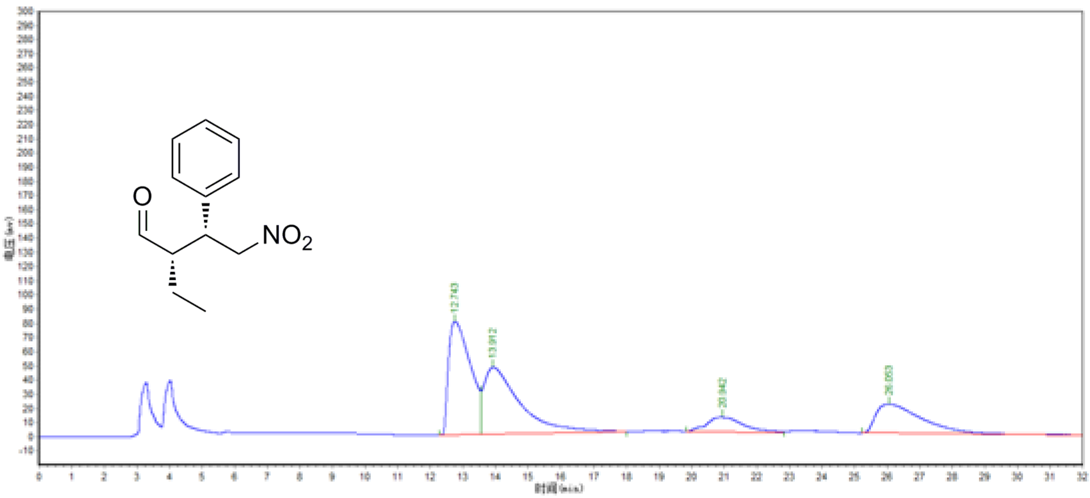
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	22.547	14475.535	1706031.375	59.5330
2	30.110	2395.877	140047.266	4.8870
3	32.038	10872.851	1019613.938	35.5800
Total		27744.262	2865692.578	100.0000

Table 4 Entry 17



Analysis Result

Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	12.773	129417.828	13990152.000	50.3537
2	21.715	78343.961	13793603.000	49.6463
Total		207761.789	27783755.000	100.0000



Analysis Result

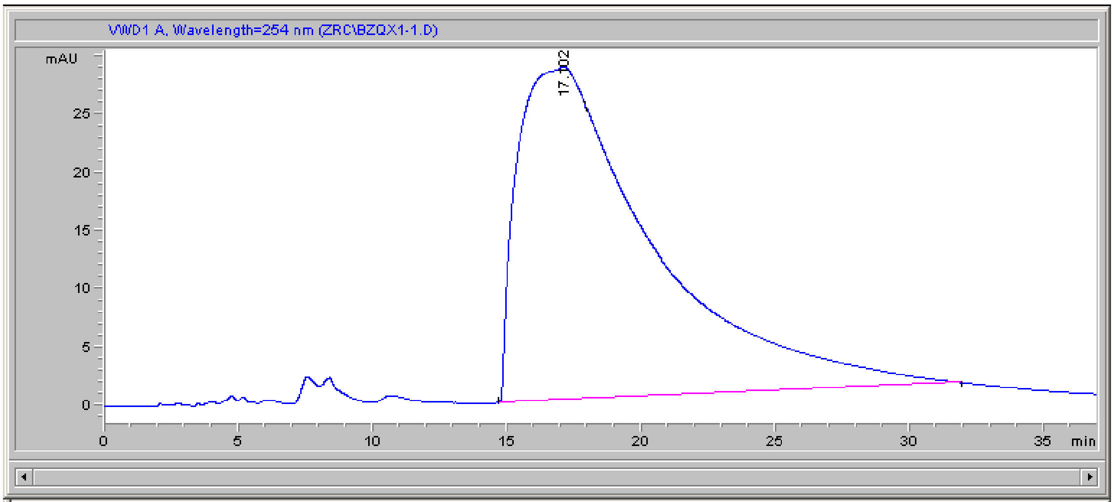
Peak#	RT(min)	Height(μV)	Area(μV*Sec)	Area%
1	12.743	79898.023	3736924.000	37.0849
2	13.912	47119.488	3646401.500	36.1865
3	20.942	10112.525	788804.625	7.8280
4	26.053	20122.066	1904552.625	18.9006
Total		157252.104	10076682.750	100.0000

HPLC analysis results of Fig. 3:

Column model: Agilent Prep-C18 Scalar PN440910-902;

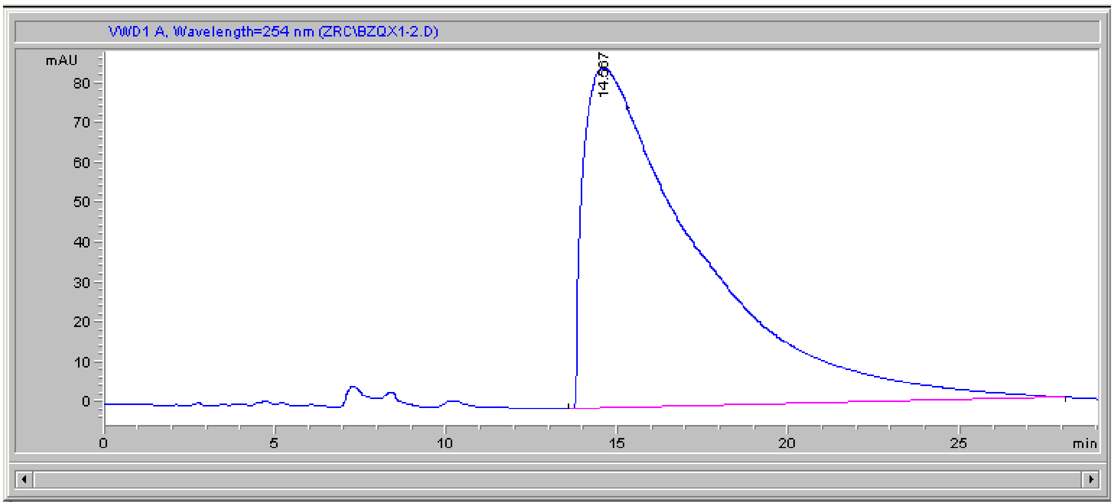
Mobile phase: CH_3OH:H_2O=3:2; Flow rate: 0.7 mL/min; Injected volume: 10μL

Concentration: 0.1 mol/L



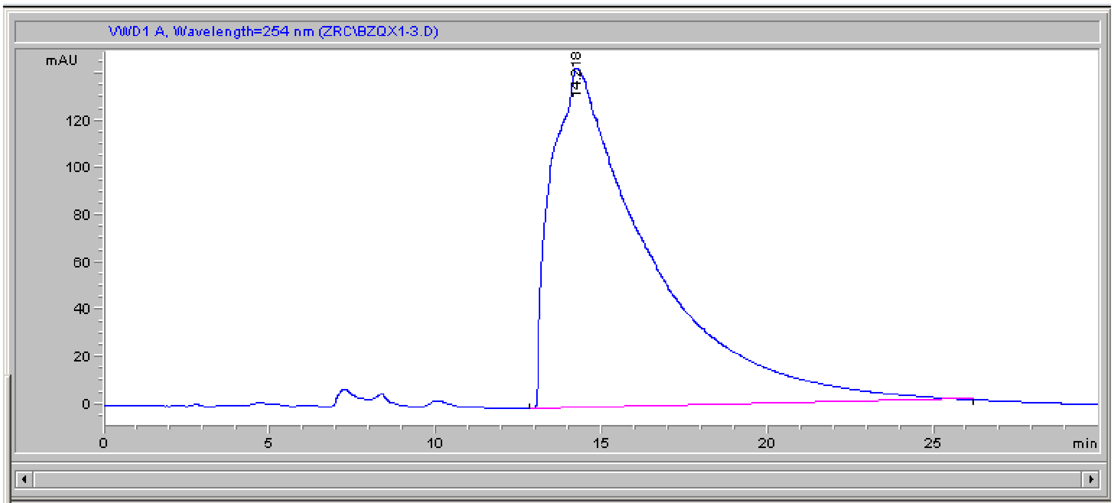
#	Time	Area	Height	Width	Symmetry
1	17.102	10061.3	28.6	5.8557	0.477

Concentration: 0.2 mol/L



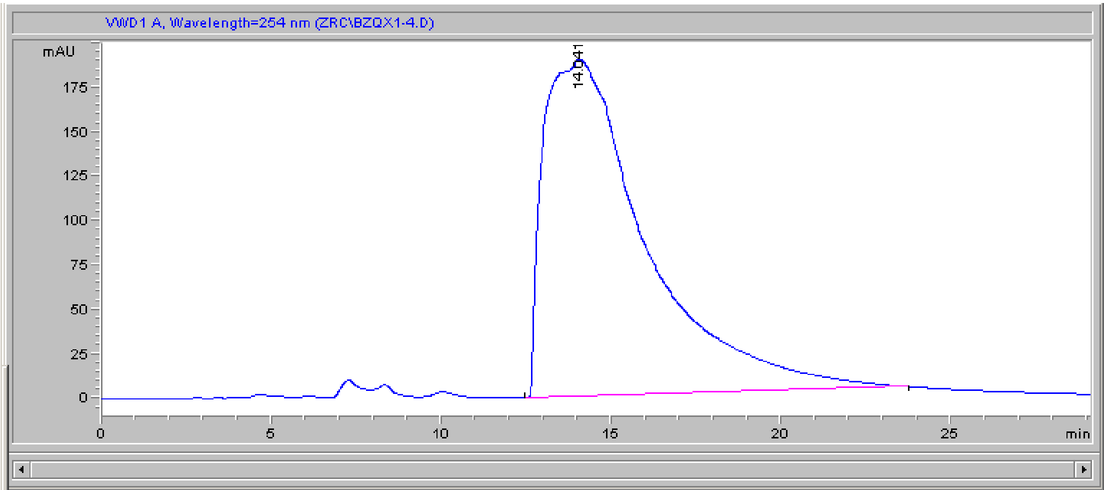
#	Time	Area	Height	Width	Symmetry
1	14.567	19971.5	85.1	3.9094	0.197

Concentration: 0.3 mol/L



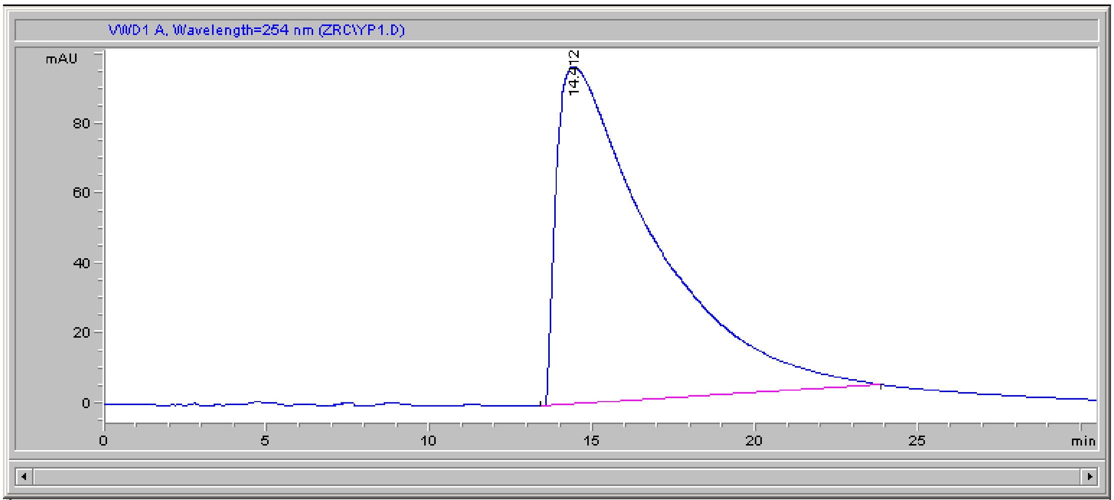
#	Time	Area	Height	Width	Symmetry
1	14.218	29948.5	143.8	3.4705	0.329

Concentration: 0.4 mol/L



#	Time	Area	Height	Width	Symmetry
1	14.041	39992.7	189.5	2.5591	0.488

Sample:



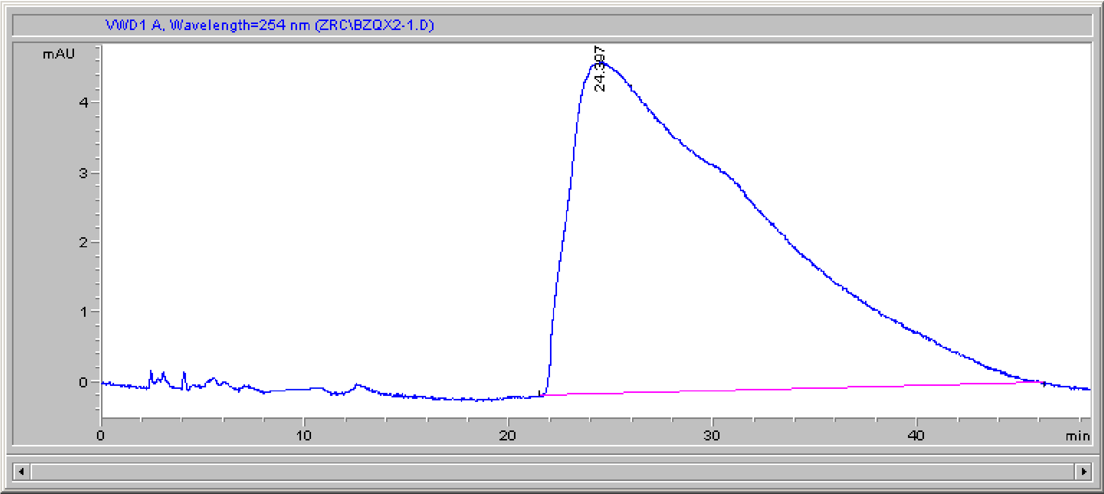
#	Time	Area	Height	Width	Symmetry
1	14.412	20293.6	96.6	2.7051	0.206

HPLC analysis results of Fig. 4:

Column model: Agilent Prep-C18 Scalar PN440910-902;

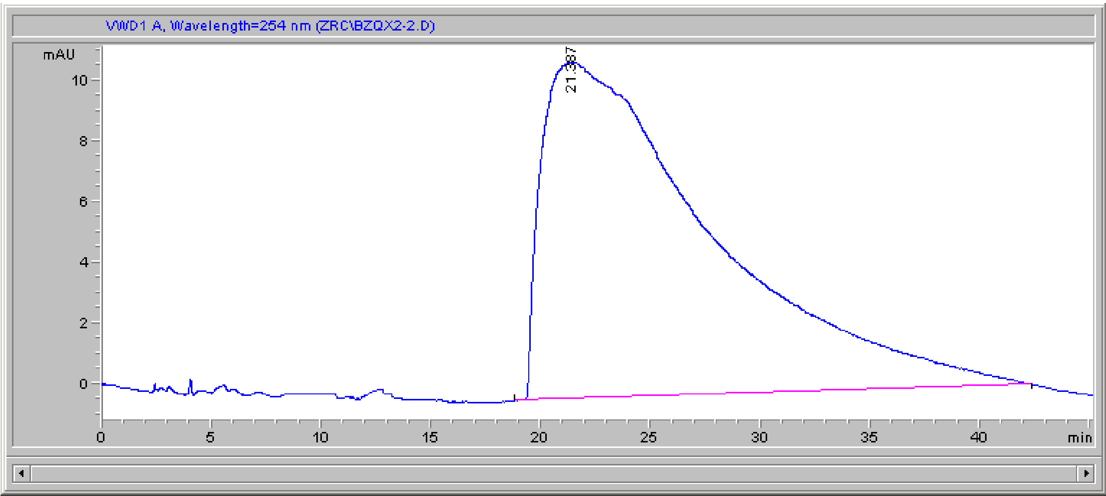
Mobile phase: CH_3OH:H_2O=3:2; Flow rate: 0.7 mL/min; Injected volume: 10μL

Concentration: 0.025 mol/L



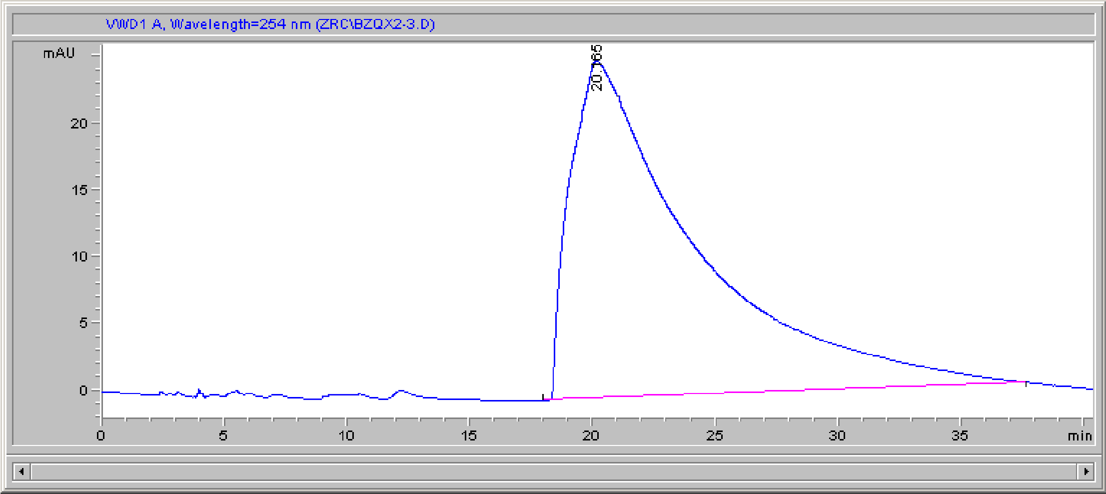
#	Time	Area	Height	Width	Symmetry
1	24.397	3057.7	4.8	10.6757	0.191

Concentration: 0.05 mol/L



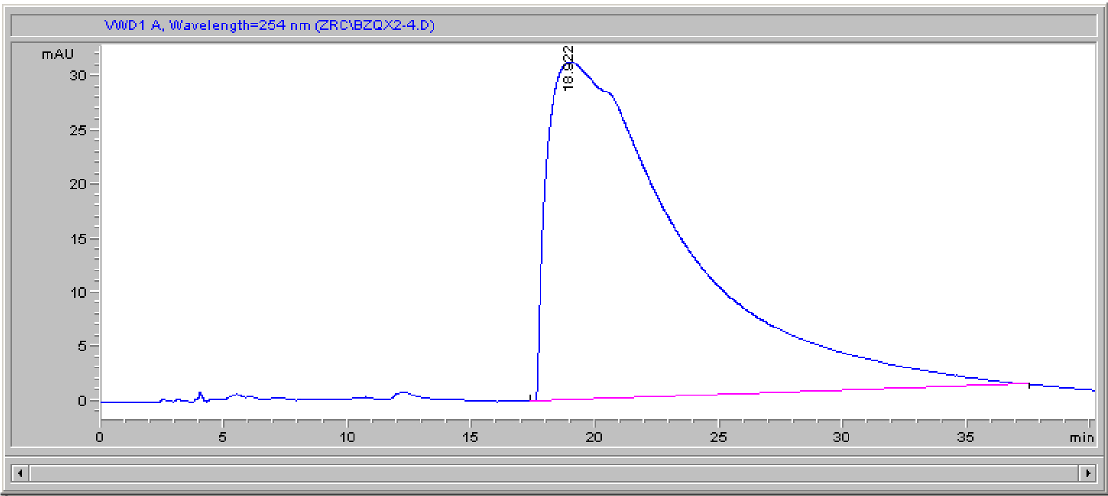
#	Time	Area	Height	Width	Symmetry
1	21.387	5978.8	11.1	8.9947	0.211

Concentration: 0.075 mol/L



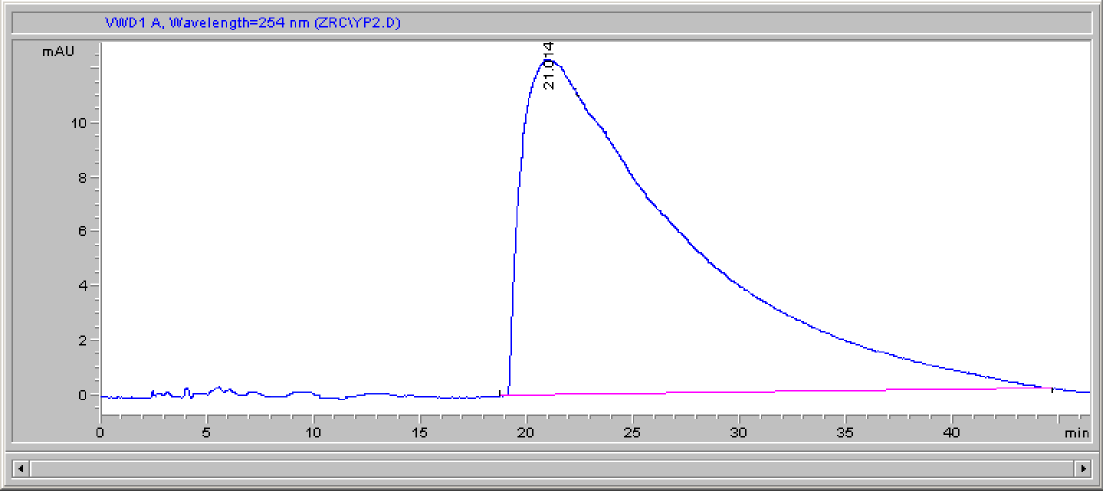
#	Time	Area	Height	Width	Symmetry
1	20.165	8983.9	25.2	5.9316	0.271

Concentration: 0.10 mol/L



#	Time	Area	Height	Width	Symmetry
1	18.922	12043.3	31.2	6.434	0.185

Sample:



#	Time	Area	Height	Width	Symmetry
1	21.014	6524.1	12.3	8.8058	0.195