Supporting Information

Pd/Cu Dual Catalysis: Highly Enantioselective Access to α-Substituted α-Amino Acids and α-Amino Amides

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CONTENTS

1. General Experimental Details

All reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen, and the workup was carried out in air, unless otherwise noted. Toluene, dichloromethane (CH_2Cl_2), triethylamine (Et_3N) and N,N-dimethylformamide (DMF) were dried and distilled from calcium hydride. Ether (Et_2O), tetrahydrofuran (THF) and 1.4-dioxane were dried and distilled from metal sodium and benzophenone. Acetone was dried and distilled from potassium carbonate. Column chromatographic purification of products was carried out using basic silica gel or neutral Al_2O_3 (100~200 mesh). Commercially available reagents were used without further purification. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^1H; 100 MHz, ^{13}C) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane. The ee values were determined by HPLC using a Daicel chiral column. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50-mm path-length cell at 589 nm. IR was measured on a PerkinElmer Spectrum 100 FT-IR Spectrometer. The racemic samples were prepared by running reactions with a racemic catalyst. The absolute configuration of products was assigned by comparison with the literature's results.

2. Preparation of Starting Materials

Reagents were purchased from Sigma-Aldrich, TCI, or Alfa Aesar and used as received unless otherwise stated. Diphenylimino glycinate **1** was purchased from Energy Chemical. [(S,S_p)−(**L1**−**L8**)],[1] allylic acetates,[2] and glycine amide derivatives (**5a** and **5b**)[3] were prepared according to literature procedures. The racemic samples were prepared by running reactions with a racemic catalyst.

3. Pd/Cu Dual Catalysis for the Asymmetric Alkylation of Glycine Derivatives

3.1 General Procedure

The preparation of Pd catalyst: [Pd(η^3-allyl)Cl]$_2$ (2.5 mol%, 2.25 mg), **L** (5.0 mol%) were stirred in THF (1 mL) in a Schlenk flask under a nitrogen atmosphere at room temperature for 40 min.

The preparation of Cu catalyst: $Cu(OTf)_2$ (5.0 mol%, 4.5 mg), **L** (5.0 mol%) were stirred in THF (1 mL) in a Schlenk flask under nitrogen atmosphere at room temperature for 40 min.

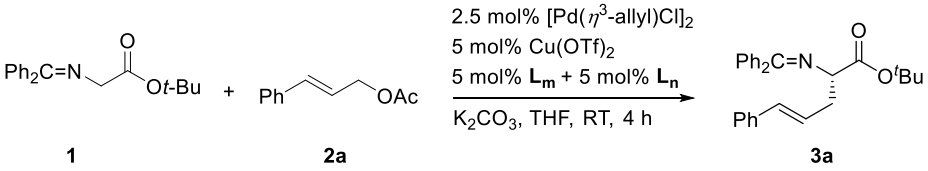
To a Schlenk flask was added glycine derivatives **1** (0.25 mmol, 73.8 mg) and Cs_2CO_3 (81.5 mg, 0.25 mmol), and the flask was degassed via an alternating vacuum/evacuation N_2 backfill. Cu catalyst (1 mL) and Pd catalyst (1 mL) was then added, and the mixture was cooled to -10 ºC. Cinnamyl acetate **2a** (0.30 mmol, 52.8 mg) was then injected in one portion. After completion, the reaction mixture was filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography with basic silica gel or neutral Al_2O_3 (100~200 mesh) afforded the desired product. The ee was determined by chiral HPLC.

3.2 The Details for Optimizing the Reaction Conditions

3.2.1 Creation of the Chiral Catalyst Library and High Throughput Evaluation of the Library

Various chiral metal complexes (Pd/**L*** and Cu/**L***) were first prepared by the combination of chiral P,N-ligands (**L1**-**L8**) and metal precursors (Pd and Cu). A larger structurally diverse and efficient dual-catalyst system library involving two chiral metal catalysts was then set up by the random combination of any two of the in situ-prepared chiral metal complexes. These chiral metal complexes simultaneously activate cinnamyl acetate and diphenylimino glycinate. After completion, the reaction mixture was filtered and concentrated under reduced pressure. The crude products were submitted for NMR and HPLC analysis for the determination of yields and enantiomeric excesses (ee). The enantiomeric excesses were determined by using the same HPLC analytical system on Chiralcel OD-H column: eluent hexane/2-propanol (95:5); flow rate 1.0 mL/min; UV detection at λ = 254 nm; retention time = 4.3 min (*S* enantiomer), 4.8 min (*R* enantiomer). The results of the primary screening of the dual-catalyst system library are summarized in *Table S1* and *Figure S1*.

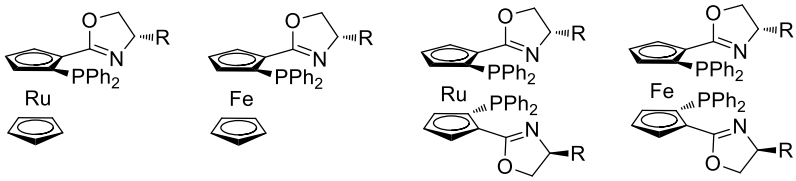
Table S1 Optimization of the reaction conditions through the screening of a chiral metal complex library (the ee of products)[a]



1 **2a** **3a**

PdL / CuL	PPh_3	L1	L2	L3	L4	L5	L6	L7	L8
PPh_3	0	60	81	59	88	55	64	80	70
L1	74	76	84	84	86	83	83	86	90
L2	88	65	**94**	92[b]	91	91	91	92	92
L3	73	85	70	88	92	86	90	89	90
L4	89	90	92	91	**94**	88	91	91	91
L5	52	75	88	82	75	75	86	80	86
L6	51	86	89	89	92	89	92	88	90
L7	63	86	89	85	92	82	90	80	86
L8	46	87	88	86	89	88	90	85	84

[a] Conditions: **1** (0.25 M), **2a** (1.2 equiv), CuL* (5 mol%), PdL* (5 mol%), K_2CO_3 (1.0 equiv), THF (2 mL); [b] All the reaction gave the desired product in >95% yields, except the reaction using (Cu/L2+Pd/L3); [c] The ee values were determined by HPLC using chiral columns.

Metal	Chiral metallocene-based P,N ligands
Cu / **Pd**	

L1: *i*-Pr; **L2**: *t*-Bu **L3**: *i*-Pr; **L4**: *t*-Bu **L5**: *i*-Pr; **L6**: *t*-Bu **L7**: *i*-Pr; **L8**: *t*-Bu

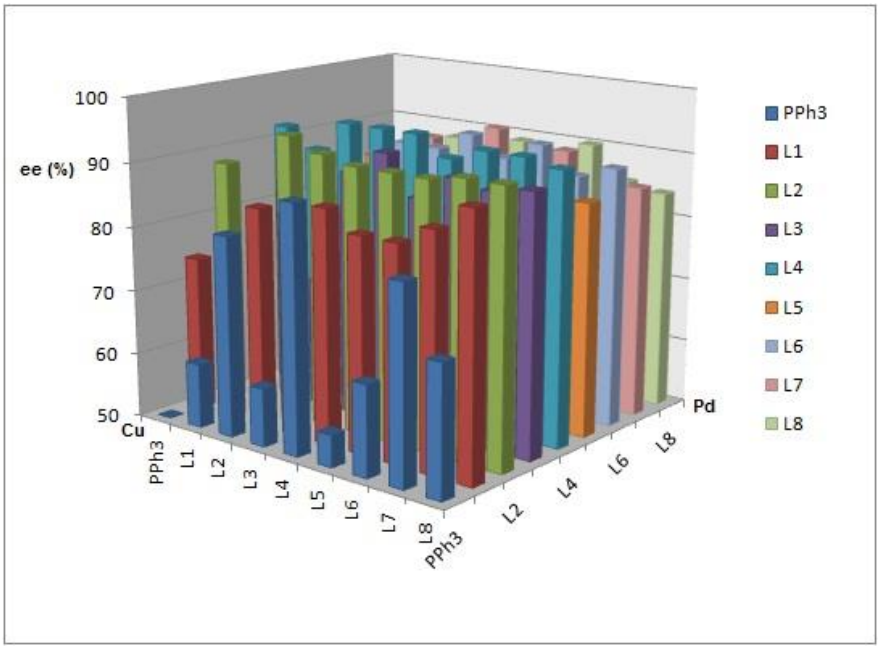
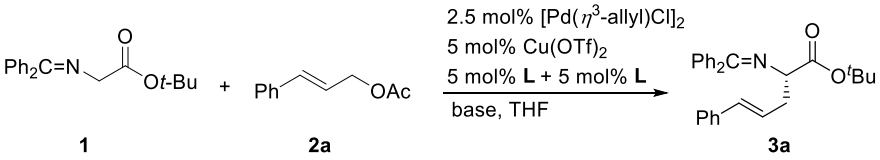


Figure S1. High throughput screening of chiral dual-catalyst system library (*ee* of the products)

3.2.2 Further Optimizing the Reaction Conditions

Table S2 Further optimization of the reaction conditions[a]

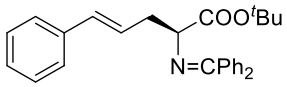


Entry	Pd/L*	Cu/L*	Base	Temp (°C)	t (h)	Yield (%)[b]	Ee (%)[c]
1	L2	L2	K_2CO_3	20	4	93	94 (*S*)
2	L4	L4	K_2CO_3	20	4	93	94 (*S*)
3	L2	L2	K_2CO_3	-10	12	NR	ND
4	L4	L4	K_2CO_3	-10	12	NR	ND
5	L2	L2	Cs_2CO_3	-10	12	96	97 (*S*)
6	L4	L4	Cs_2CO_3	-10	12	25	ND
7	no Pd	L2	Cs_2CO_3	-10	12	NR	NR
8	L2	no Cu	Cs_2CO_3	-10	12	18	ND
9	L2	ent-L2	Cs_2CO_3	-10	12	86	5 (*R*)
10	ent-L2	L2	Cs_2CO_3	-10	12	88	4 (*S*)

[a] Condition: **1** (0.25 M), **2a** (1.2 equiv), CuL* (5 mol%), PdL* (5 mol%), base (1.0 equiv), THF (2 mL); [b] The yields were calculated from ^{1}H NMR spectra; [c] The ee values were determined by HPLC using chiral columns. NR = not reaction, ND = not determined.

3.3 The Data of Characterization

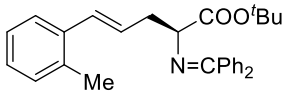
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-phenylpent-4-enoate (3a)[4]



(*S*)-3a

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 6.8 Hz, 2H), 7.52 – 7.17 (m, 13H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.16 (dt, *J* = 15.2, 7.2 Hz, 1H), 4.17 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.99 – 2.76 (m, 2H), 1.51 (s, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 170.5, 139.9, 137.8, 136.9, 132.7, 130.4, 129.0, 128.7, 128.7, 128.6, 128.2, 128.2, 127.2, 126.8, 126.3, 81.3, 66.5, 37.5, 28.3; IR (v/cm^{-1}) 3445, 2922, 1732, 1622, 1446, 1367, 1148, 966, 744, 694 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 4.7 min (minor), t_{R2} = 5.2 min (major)]; ee = 97%, $[\alpha]_D^{20}$ = –38.2 (*c* 1.0, $CHCl_3$).

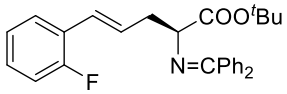
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(*o*-tolyl)pent-4-enoate (3b)



(*S*)-3b

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 6.8 Hz, 2H), 7.53 – 7.29 (m, 8H), 7.20 – 7.05 (m, 4H), 6.65 (d, *J* = 14.4 Hz, 1H), 6.07 – 5.92 (m, 1H), 4.17 – 4.09 (m, 1H), 2.94 – 2.74 (m, 2H), 2.28 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.5, 153.2, 141.7, 139.9, 136.9, 130.4, 129.0, 128.7, 128.6, 128.5, 128.2, 128.1, 125.7, 121.2, 117.2, 111.3, 106.7, 81.3, 66.4, 37.3, 28.3, 19.6; IR (v/cm^{-1}) 2977, 1732, 1622, 1367, 1279, 1150, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 4.1 min (major), t_{R2} = 4.4 min (minor)]; ee = 99.1%, $[\alpha]_D^{20}$ = –42.6 (*c* 1.0, $CHCl_3$).

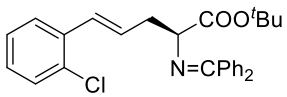
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(2-fluoro phenyl)pent-4-enoate (3c)



(*S*)-3c

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 – 7.63 (m, 2H), 7.46 – 7.27 (m, 7H), 7.19 – 7.10 (m, 3H), 7.08 – 6.94 (m, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.25 – 6.12 (m, 1H), 4.15 – 4.10 (m, 1H), 2.94 – 2.74 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.6, 160.2 (*J* = 247.1 Hz), 139.9, 132.6, 130.5, 130.3, 129.6 (*J* = 4.0 Hz), 129.1, 128.8, 128.7, 128.5 (*J* = 7.8 Hz), 128.2, 128.1, 127.4 (*J* = 3.0 Hz), 125.1 (*J* = 2.4 Hz), 124.2 (*J* = 2.0 Hz), 115.8 (*J* = 22.0 Hz), 81.4, 66.3, 38.0, 28.3; IR (v/cm^{-1}) 2977, 1732, 1487, 1150, 968, 754, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 98/2, 254 nm, 1.0 mL/min; t_{R1} = 4.1 min (minor), t_{R2} = 4.8 min (major)]; ee = 99.3%, $[\alpha]_D^{25}$ = –40.8 (*c* 1.0, $CHCl_3$).

(*E*)-*Tert*-butyl 5-(2-chlorophenyl)-2-((diphenylmethylene) amino)pent-4-enoate (3d)

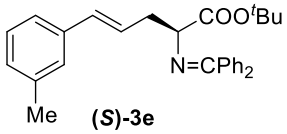


(*S*)-3d

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.80 (m, 1H), 7.73 – 7.66 (m, 2H), 7.53 –

7.28 (m, 8H), 7.22 – 7.08 (m, 3H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.22 – 6.09 (m, 1H), 4.22 – 4.05 (m, 1H), 2.94 – 2.74 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.7, 139.9, 136.9, 135.8, 132.9, 130.5, 130.3, 129.8, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 127.0, 81.5, 66.2, 37.7, 28.3; IR (v/cm^{-1}) 2977, 1470, 1623, 1445, 1096, 966, 751, 699 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min; t_{R1} = 4.7 min (major), t_{R2} = 5.4 min (minor)]; ee = 99%, $[\alpha]_D^{20}$ = –35.1 (*c* 1.0, $CHCl_3$).

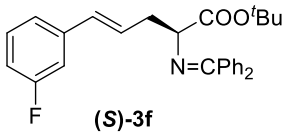
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(*m*-tolyl) pent-4-enoate (3e)



(*S*)-3e

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 – 7.94 (m, 2H), 7.88 – 7.61 (m, 6H), 7.60 – 7.28 (m, 6H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.48 – 6.36 (m, 1H), 4.50 – 4.42 (m, 1H), 3.23 – 3.05 (m, 2H), 2.66 (s, 3H), 1.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 170.5, 139.9, 138.2, 137.7, 136.9, 132.7, 130.4, 129.1, 128.8, 128.6, 128.2, 128.1, 127.1, 126.5, 123.4, 81.3, 66.5, 37.6, 28.4, 21.7; IR (v/cm^{-1}) 2976, 1732, 1622, 1367, 1149, 965, 776, 695 cm^{-1}; HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 4.0 min (minor), t_{R2} = 4.6 min (major)]; ee = 97%, $[\alpha]_D^{20}$ = –31.5 (*c* 1.0, $CHCl_3$).

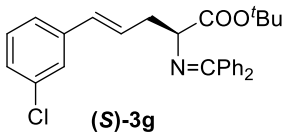
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(3-fluoro phenyl)pent-4-enoate (3f)



(*S*)-3f

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.67 (m, 2H), 7.54 – 7.15 (m, 9H), 7.12 – 6.97 (m, 2H), 6.92-6.86 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.24 – 6.09 (m, 1H), 4.17 – 4.12 (m, 1H), 2.93 – 2.71 (m, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.5, 163.3 (*J* = 243.4 Hz), 140.2 (*J* = 8.0 Hz), 139.9, 136.9, 131.7, 130.5, 130.2 (*J* = 7.3 Hz), 129.1, 128.8, 128.7, 128.4, 128.3, 128.1, 122.2, 114.1 (*J* = 20.2 Hz), 112.7 (*J* = 22.5 Hz), 81.4, 66.3, 37.5, 28.4; IR (v/cm^{-1}) 3027, 1732, 1582, 1276, 1149, 969, 779, 702 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_{R1} = 4.2 min (major), t_{R2} = 4.9 min (minor)]; ee = 96%, $[\alpha]_D^{20}$ = –30.2 (*c* 1.0, $CHCl_3$).

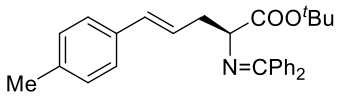
(*E*)-*Tert*-butyl 5-(3-chlorophenyl)-2-((diphenylmethylene) amino)pent-4-enoate (3g)



(*S*)-3g

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.67 (m, 2H), 7.50 – 7.30 (m, 8H), 7.25 – 7.16 (m, 4H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.24 – 6.08 (m, 1H), 4.19-4.13 (m, 1H), 2.94 – 2.76 (m, 2H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.6, 139.9, 139.6, 136.9, 134.7, 131.4, 130.6, 130.0, 129.1, 128.9, 128.7, 128.5, 128.3, 128.2, 127.3, 126.2, 124.5, 81.5, 66.3, 37.5, 28.4; IR (v/cm^{-1}) 2977, 1732, 1621, 1367, 1149, 964, 777, 695 cm^{-1}; HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 4.7 min (minor), t_{R2} = 5.2 min (major)]; ee = 97%, $[\alpha]_D^{20}$ = –35.8 (*c* 1.0, $CHCl_3$).

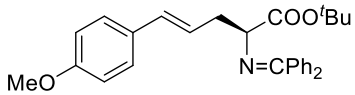
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(*p*-tolyl) pent-4-enoate (3h)[5]



(*S*)-3h

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 – 7.69 (m, 2H), 7.56 – 7.33 (m, 6H), 7.37 – 7.11 (m, 6H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.19 – 6.02 (m, 1H), 4.20 – 4.15 (m, 1H), 2.96 – 2.78 (m, 2H), 2.38 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 170.5, 140.0, 137.0, 135.0, 132.6, 130.5, 129.5, 129.4, 129.1, 128.8, 128.7, 128.3, 128.2, 126.2, 125.7, 81.3, 66.6, 37.6, 28.4, 21.5; IR (v/cm^{-1}) 2976, 1724, 1623, 1446, 968, 702, 638 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min. t_{R1} = 4.6 min (major), t_{R2} = 5.2 min (minor)]; ee = 94%, $[\alpha]_D^{20}$ = –32.6 (*c* 1.0, $CHCl_3$).

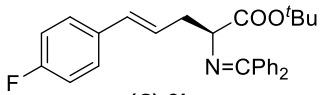
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(4-methoxyphenyl)pent-4-enoate (3i)[5]



(*S*)-3i

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.60 (m, 2H), 7.45 – 7.35 (m, 4H), 7.34 – 7.28 (m, 2H), 7.23 – 7.18 (m, 2H), 7.15 – 7.10 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.42 – 6.28 (m, 1H), 5.98 – 5.84 (m, 1H), 4.15 – 4.02 (m, 1H), 3.79 (s, 3H), 2.90 – 2.65 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 170.5, 156.6, 140.0, 136.9, 130.4, 129.1, 128.7, 128.6, 128.2, 127.5, 127.4, 126.9, 126.8, 120.8, 111.0, 81.3, 66.5, 55.6, 38.0, 28.3; IR (v/cm^{-1}) 2977, 1733, 1510, 1248, 1149, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min, t_{R1} = 5.1 min (major), t_{R2} = 5.9 min (minor)]; ee = 98%, $[\alpha]_D^{20}$ = –38.7 (*c* 1.0, $CHCl_3$).

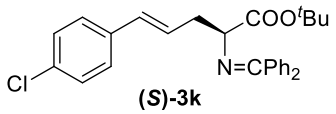
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(4-fluoro phenyl)pent-4-enoate (3j)[5]



(*S*)-3j

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67-7.61 (m, 2H), 7.45 – 7.36 (m, 4H), 7.34 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.15 – 7.09 (m, 2H), 6.99 – 6.92 (m, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.06 – 5.95 (m, 1H), 4.12-4.04 (m, 1H), 2.87 – 2.69 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.5, 162.2 (*J* = 244.4 Hz), 133.9, 132.6, 131.5, 130.4 (*J* = 23.4 Hz), 129.1, 128.8, 128.6, 128.5, 128.2, 128.1, 127.7 (*J* = 8.0 Hz), 126.5, 115.6 (*J* = 11.4 Hz), 81.4, 66.3, 37.4, 28.3; IR (v/cm^{-1}) 2978, 1732, 1554, 1227, 1123, 967, 845, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_{R1} = 4.3 min (major), t_{R2} = 5.0 min (minor)]; ee = 97%, $[\alpha]_D^{20}$ = –42.8 (*c* 1.0, $CHCl_3$).

(*E*)-*Tert*-butyl 5-(4-chlorophenyl)-2-((diphenylmethylene) amino)pent-4-enoate (3k)[5]

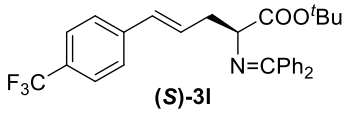


(*S*)-3k

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 – 7.64 (m, 2H), 7.45 – 7.30 (m, 6H), 7.27 – 7.20 (m, 4H), 7.18 – 7.12 (m, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.17 – 6.03 (m, 1H), 4.11 (dd, *J* =

7.2, 5.2 Hz, 1H), 2.88 – 2.73 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.5, 139.9, 136.9, 136.2, 132.9, 131.5, 130.5, 129.1, 128.9, 128.7, 128.5, 128.3, 128.1, 127.6, 127.5, 81.4, 66.3, 37.5, 28.3; IR (v/cm^{-1}) 2976, 1736, 1623, 1150, 749, 699 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_{R1} = 4.2 min (major), t_{R2} = 4.9 min (minor)]; ee = 98%, $[\alpha]_D^{20}$ = –27.9 (*c* 1.0, $CHCl_3$).

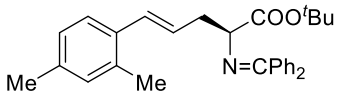
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (3l)



(*S*)-3l

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.46 – 7.29 (m, 8H), 7.16 – 7.10 (m, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.29 – 6.15 (m, 1H), 4.15 – 4.08 (m, 1H), 2.93 – 2.74 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 170.5, 140.9, 139.6, 136.5, 132.4, 131.2, 130.2 (*J* = 27 Hz), 129.5, 128.8, 128.6, 128.5, 128.1, 127.9, 126.9 (*J* = 281 Hz), 126.2, 81.3, 65.9, 37.3, 28.1; IR (v/cm^{-1}) 2975, 1732, 1134, 967, 845, 698 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_{R1} = 4.0 min (major), t_{R2} = 5.0 min (minor)]; ee = 97%, $[\alpha]_D^{20}$ = –23.7 (*c* 1.0, $CHCl_3$).

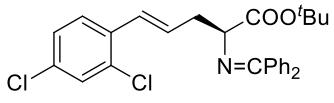
(*E*)-*Tert*-butyl 5-(2,4-dimethylphenyl)-2-((diphenylmethylene)amino)pent-4-enoate (3m)



(*S*)-3m

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.80 (m, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.30 (m, 6H), 7.19 – 7.12 (m, 2H), 7.10 – 7.00 (m, 2H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.09 – 5.97 (m, 1H), 4.11 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.92 – 2.66 (m, 2H), 2.25 (s, 6H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 170.4, 136.7, 135.7, 135.4, 132.6, 130.4, 130.3, 129.9, 129.1, 128.6, 128.5, 128.2, 127.6, 125.4, 123.7, 81.3, 66.5, 37.5, 28.3, 20.0, 19.7; IR (v/cm^{-1}) 2976, 1733, 1446, 1277, 1150, 967, 701 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min. t_{R1} = 4.5 min (major), t_{R2} = 5.1 min (minor)]; ee = 96%, $[\alpha]_D^{25}$ = –41.0 (*c* 1.0, $CHCl_3$); HRMS (Q–TOF Premier) calcd for $C_{30}H_{34}NO_2$ $(M+2H)^{2+}$: 440.2578; found: 440.2590.

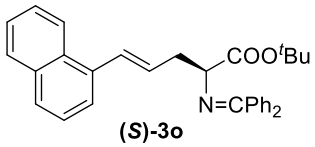
(*E*)-*Tert*-butyl 5-(2,4-dichlorophenyl)-2-((diphenylmethylene)amino)pent-4-enoate (3n)



(*S*)-3n

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.50 – 7.28 (m, 8H), 7.17 – 7.09 (m, 2H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.21 – 6.05 (m, 1H), 4.10 (t, *J* = 6.4 Hz, 1H), 2.82 (t, *J* = 6.4 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 170.5, 139.6, 136.6, 134.1, 133.1, 132.4, 130.6, 130.1, 128.9, 128.5, 128.0, 127.8, 127.7, 127.4, 127.1, 81.3, 65.8, 37.5, 28.1; IR (v/cm^{-1}) 2977, 1732, 1623, 1470, 1155, 967, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min; t_{R1} = 4.3 min (minor), t_{R2} = 5.5 min (major)]; ee = 99%, $[\alpha]_D^{25}$ = –32.3 (*c* 1.0, $CHCl_3$); HRMS (Q–TOF Premier) calcd for $C_{28}H_{28}NO_2Cl_2$ $(M+2H)^{2+}$: 480.1498; found: 480.1497.

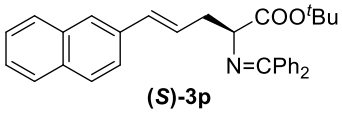
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(naphthalen-1-yl)pent-4-enoate (3o)



(*S*)-3o

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.56 (m, 3H), 7.52 – 7.27 (m, 8H), 7.21 – 7.04 (m, 6H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.18 – 6.08 (m, 1H), 4.11 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.86 – 2.70 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 170.7, 140.7, 139.7, 136.8, 135.2, 132.6, 130.6, 130.3, 130.3, 129.0, 128.9, 128.7, 128.5, 128.3, 128.1, 127.1, 124.6, 81.5, 66.0, 37.4, 28.3; IR (v/cm^{-1}) 2977, 1732, 1622, 1367, 1277, 1150, 967, 777, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min, t_{R1} = 5.1 min (minor), t_{R2} = 6.0 min (major)]; ee = 94%, $[\alpha]_D^{20}$ = –41.4 (*c* 1.0, $CHCl_3$); HRMS (Q–TOF Premier) calcd for $C_{32}H_{32}NO_2$ $(M+2H)^{2+}$: 462.2431; found: 462.2433.

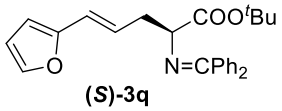
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(naphthalen-2-yl) pent-4-enoate (3p)



(*S*)-3p

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 – 8.00 (m, 1H), 7.86 – 7.78 (m, 2H), 7.76 – 7.67 (m, 2H), 7.53 – 7.45 (m, 3H), 7.43 – 7.30 (m, 6H), 7.21 – 7.18 (m, 1H), 7.14 (m, 2H), 6.18 – 6.10 (m, 1H), 4.18 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.98 – 2.88 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6, 170.5, 140.5, 139.5, 136.5, 135.0, 132.4, 130.4, 130.1, 130.0, 129.9, 128.8, 128.7, 128.5, 128.3, 128.1, 127.9, 126.8, 124.4, 81.3, 65.8, 37.2, 28.1; IR (v/cm^{-1}) 2977, 1732, 1366, 1150, 967, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min; t_{R1} = 4.3 min (major), t_{R2} = 7.2 min (minor)]; ee = 98%, $[\alpha]_D^{25}$ = –32.4 (*c* 1.0, $CHCl_3$); HRMS (Q–TOF Premier) calcd for $C_{32}H_{32}NO_2$ $(M+2H)^{2+}$: 462.2431; found: 462.2433.

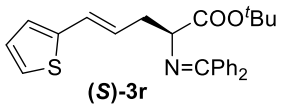
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(furan-2-yl) pent-4-enoate (3q)



(*S*)-3q

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 – 7.59 (m, 2H), 7.48 – 7.27 (m, 7H), 7.21 – 7.08 (m, 2H), 6.34 – 6.30 (m, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 6.07 – 5.94 (m, 1H), 4.06 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.85 – 2.64 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.5, 153.2, 141.7, 139.9, 136.9, 130.4, 129.0, 128.7, 128.6, 128.2, 128.1, 125.7, 121.2, 111.2, 106.7, 81.3, 66.4, 37.3, 28.3; IR (v/cm^{-1}) 2977, 2921, 1732, 1660, 1367, 1277, 1150, 962, 701 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min; t_{R1} = 4.6 min (major), t_{R2} = 5.1 min (minor)]; ee = 95%, $[\alpha]_D^{20}$ = –33.9 (*c* 1.0, $CHCl_3$); HRMS (Q–TOF Premier) calcd for $C_{26}H_{28}NO_3$ $(M+2H)^{2+}$: 402.2069; found: 402.2065.

(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-5-(thiophen-2-yl)pent-4-enoate (3r)

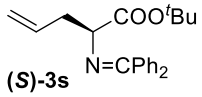


(*S*)-3r

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 – 7.60 (m, 2H), 7.47 – 7.34 (m, 6H), 7.22 – 7.12 (m, 2H), 7.10 – 7.06 (m, 1H), 6.93 – 6.88 (m, 1H), 6.85 – 6.80 (m, 1H), 6.53 (d, *J* = 15.6 Hz,

1H), 5.97 – 5.80 (m, 1H), 4.06 (dd, *J* = 8.2, 5.2 Hz, 1H), 2.83 – 2.66 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 170.6, 142.9, 139.9, 136.9, 130.4, 129.0, 128.7, 128.6, 128.2, 128.1, 127.4, 126.7, 125.8, 124.8, 123.6, 81.3, 66.3, 37.3, 28.3; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 97/3, 254 nm, 1.0 mL/min. t_{R1} = 5.1 min (major), t_{R2} = 5.8 min (minor)]; ee = 97%, $[\alpha]_D^{20}$ = –32.1 (*c* 1.0, $CHCl_3$); HRMS (Q–TOF Premier) calcd for $C_{26}H_{28}NO_2S$ $(M+2H)^{2+}$: 418.1841; found: 418.1848.

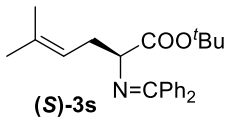
***Tert*-butyl 2-((diphenylmethylene)amino)pent-4-enoate (3s)**



(*S*)-3s

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 – 7.62 (m, 2H), 7.47 – 7.42 (m, 3H), 7.42 – 7.28 (m, 3H), 7.22 – 7.16 (m, 2H), 5.80 – 5.68 (m, 1H), 5.08 (dd, *J* = 0.4, 20.0 Hz, 1H), 5.03 (dd, *J* = 0.5, 8.0 Hz, 1H), 4.03 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.72 – 2.58 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 170.3, 139.9, 136.9, 134.9, 130.4, 130.3, 129.0, 128.7, 128.6, 128.2, 117.5, 81.2, 66.1, 38.4, 28.3; IR (v/cm^{-1}) 2977, 1732, 1624, 1367, 1152, 780, 696 cm^{-1}; HPLC [DAICEL CHIRALPAK OD-H, hexane/*i*-PrOH = 99/1, 254 nm, 1.0 mL/min. t_{R1} = 5.2 min (major), t_{R2} = 5.7 min (minor)]; ee = 98%, $[\alpha]_D^{20}$ = –1.0 (*c* 1.0, $CHCl_3$).

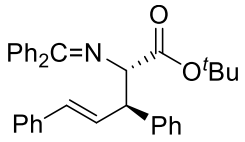
***Tert*-butyl (*S*)-2-((diphenylmethylene)amino)-5-methylhex-4-enoate (3t)**[6]



(*S*)-3s

Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.78 (m, 1H), 7.61 (dd, *J* = 21.6, 7.5 Hz, 2H), 7.52 – 7.28 (m, 5H), 7.19 – 7.12 (m, 2H), 5.02 (t, *J* = 7.7 Hz, 1H), 3.95 (dd, *J* = 7.7, 5.4 Hz, 1H), 2.55 (hept, *J* = 8.0 Hz, 2H), 1.65 (s, 3H), 1.56 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 169.8, 140.0, 136.9, 134.1, 132.7, 130.3, 129.0, 128.6, 128.5, 128.2, 120.4, 81.0, 66.6, 32.6, 28.3, 26.0, 18.2. HPLC [DAICEL CHIRALPAK IC-3, hexane/*i*-PrOH = 95/5, 254 nm, 0.5 mL/min. t_{R1} = 7.4 min (major), t_{R2} = 7.9 min (minor)]; ee = 90%, $[\alpha]_D^{20}$ = –2.9 (*c* 1.0, $CHCl_3$).

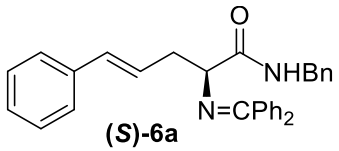
(*E*)-*Tert*-butyl 2-((diphenylmethylene)amino)-3,5-diphenylpent-4 -enoate (4)



(*R*,*S*)-4

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 – 7.80 (m, 1H), 7.74 – 7.65 (m, 2H), 7.55 – 7.14 (m, 15H), 6.94 – 6.85 (m, 2H), 6.70 – 6.53 (m, 2H), 4.45 – 4.36 (m, 1H), 4.36 – 4.27 (m, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 170.2, 141.7, 139.9, 137.8, 136.9, 132.7, 132.5, 130.5, 130.3, 129.9, 129.2, 128.9, 128.7, 128.5, 128.2, 128.1, 127.4, 126.8, 126.6, 81.4, 71.5, 53.3, 28.2; HPLC [DAICEL CHIRAL PAK IE, hexane/*i*-PrOH = 99/1, 254 nm, 1.0 mL/min. t_{R1} = 7.3 min (minor), t_{R2} = 8.3 min (major)]; ee = 98%.

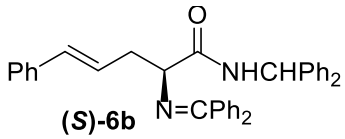
(*S*,*E*)-N-Benzyl-2-((diphenylmethylene)amino)-5-phenylpent-4-enamide [**6a**]



(*S*)-6a

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). 93% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min; t_{R1} = 19.4 min (major), t_{R2} = 28.5 min (minor)]; $[\alpha]_D^{20}$ = –7.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 – 7.63 (m, 2H), 7.49 – 7.42 (m, 4H), 7.41 – 7.35 (m, 2H), 7.34 – 7.30 (m, 6H), 7.30 – 7.25 (m, 4H), 7.13 – 7.07 (m, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.23 – 6.02 (m, 1H), 4.78 (dd, *J* = 15.1, 7.1 Hz, 1H), 4.40 (dd, *J* = 15.1, 5.2 Hz, 1H), 4.31 (dd, *J* = 6.6, 4.6 Hz, 1H), 2.91 – 2.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.8, 170.0, 139.2, 138.5, 137.4, 135.8, 132.9, 130.7, 128.9, 128.7, 128.7, 128.5, 128.2, 127.8, 127.5, 127.3, 127.2, 126.2, 125.8, 66.0, 42.9, 39.2. IR (v/cm^{-1}) 3056, 3025, 2927, 1733, 1484, 1437, 1374, 1259, 1181, 1119, 747, 721, 695, 541 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{31}H_{29}N_2O$ $(M+H)^+$: 445.2280; found: 445.2285.

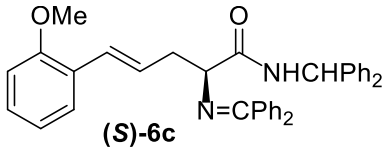
(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-phenylpent-4-enamide [**6b**]



(*S*)-6b

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (124.8 mg, 96% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 35.6 min (minor), t_{R2} = 40.5 min (major)]; $[\alpha]_D^{20}$ = 0.38 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.80 (m, 1H), 7.68 – 7.62 (m, 2H), 7.49 – 7.41 (m, 4H), 7.40 – 7.22 (m, 16H), 7.11 – 7.05 (m, 2H), 6.47 – 6.35 (m, 2H), 6.15 (ddd, *J* = 15.4, 8.4, 6.5 Hz, 1H), 4.29 (dd, *J* = 6.6, 4.4 Hz, 1H), 2.81 (dt, *J* = 14.7, 7.8 Hz, 1H), 2.76 – 2.68 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 170.0, 141.8, 141.7, 139.2, 137.3, 135.8, 133.0, 132.4, 130.7, 130.1, 128.9, 128.7, 128.7, 128.6, 128.6, 128.5, 128.3, 128.3, 127.7, 127.4, 127.3, 127.3, 127.2, 126.2, 125.6, 65.9, 56.3, 39.1. IR (v/cm^{-1}) 3311, 3059, 3027, 1651, 1505, 1447, 1317, 1278, 967, 919, 742, 695, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{31}H_{29}N_2O$ $(M+H)^+$: 445.2280; found: 445.2285.

(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(2-methoxyphenyl)pent-4-enamide [**6c**]

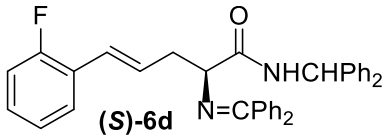


(*S*)-6c

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). 99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 43.9 min (minor), t_{R2} = 45.6 min (major)]; $[\alpha]_D^{20}$ = –0.35 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.48 – 7.41 (m, 4H), 7.40 – 7.37 (m, 2H), 7.37 – 7.23 (m, 11H), 7.09 (dt, *J* = 7.7, 2.7 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 15.9 Hz, 1H), 6.38 (d, *J* = 8.6 Hz, 1H), 6.12 (ddd, *J* =

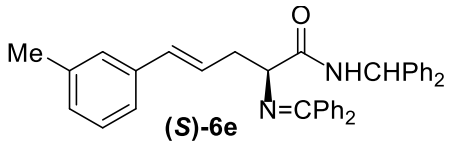
15.4, 8.2, 6.5 Hz, 1H), 4.28 (dd, *J* = 6.8, 4.3 Hz, 1H), 3.77 (s, 3H), 2.92 – 2.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 169.9, 156.5, 141.8, 141.8, 139.3, 135.9, 130.6, 128.8, 128.7, 128.7, 128.6, 128.6, 128.2, 128.1, 127.8, 127.7, 127.4, 127.4, 127.3, 127.3, 126.6, 126.5, 126.2, 120.6, 110.8, 66.0, 56.3, 55.3, 39.5. IR (v/cm^{-1}) 3308, 3060, 3028, 2917, 1659, 1598, 1494, 1447, 1317, 1278, 1244, 1028, 754, 699, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{38}H_{35}N_2O_2$ $(M+H)^+$: 551.2693; found: 551.2701.

(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(2-fluorophenyl)pent-4-enamide [**6d**]



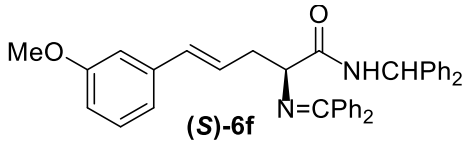
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 38.5 min (minor), t_{R2} = 43.0 min (major)]; $[\alpha]_D^{20}$ = 0.50 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 12.3, 7.8 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.49 – 7.42 (m, 4H), 7.41 – 7.37 (m, 2H), 7.37 – 7.23 (m, 11H), 7.14 – 7.01 (m, 4H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.37 (d, *J* = 8.6 Hz, 1H), 6.23 (ddd, *J* = 15.6, 8.2, 6.6 Hz, 1H), 4.29 (dd, *J* = 6.6, 4.5 Hz, 1H), 2.87 – 7.78 (m, 1H), 2.77 – 7.68 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 170.1, 160.0 (*J* = 247.5 Hz), 141.7 (*J* = 2.5 Hz), 139.2, 135.8, 130.7, 130.1, 128.9, 128.7, 128.7, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 127.7, 127.4, 127.3, 127.3, 125.3 (*J* = 3.5 Hz), 125.0 (*J* = 12.2 Hz), 124.0 (*J* = 3.6 Hz), 115.7 (*J* = 22.0 Hz), 65.8, 56.3, 39.5. IR (v/cm^{-1}) cm^{-1}. 3304, 3061, 2926, 1659, 1598, 1494, 1447, 1318, 1278, 941, 762, 701, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{37}H_{32}FN_2O$ $(M+H)^+$: 539.2493; found: 539.2501.

(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(*m*-tolyl)pent-4-enamide [**6e**]



Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} = 20.3 min (minor), t_{R2} = 24.1 min (major)]; $[\alpha]_D^{20}$ = 0.31 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.80 (m, 1H), 7.66 – 7.61 (m, 2H), 7.48 – 7.42 (m, 4H), 7.40 – 7.31 (m, 4H), 7.30 – 7.22 (m, 8H), 7.13 – 7.05 (m, 5H), 6.43 – 6.33 (m, 2H), 6.11 (ddd, *J* = 15.5, 8.4, 6.5 Hz, 1H), 4.27 (dd, *J* = 6.7, 4.4 Hz, 1H), 2.84 – 2.66 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 170.0, 141.8, 141.7, 139.2, 137.9, 137.3, 135.8, 133.0, 130.7, 130.1, 128.9, 128.7, 128.6, 128.6, 128.4, 128.3, 128.3, 127.9, 127.7, 127.4, 127.3, 127.3, 127.0, 125.3, 123.3, 65.9, 56.3, 39.2, 21.5. IR (v/cm^{-1}) 3307, 3060, 3028, 2921, 1651, 1505, 1446, 1317, 941, 919, 762, 703, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{38}H_{35}N_2O$ $(M+H)^+$: 535.2744; found: 535.2746.

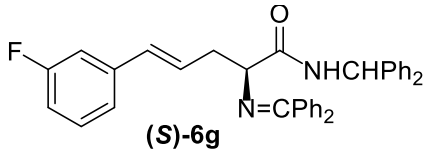
(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(3-methoxyphenyl)pent-4-enamide [**6f**]



(*S*)-6f

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} = 26.0 min (minor), t_{R2} = 30.5 min (major)]; $[\alpha]_D^{20}$ = 0.39 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.48 – 7.41 (m, 4H), 7.40 – 7.31 (m, 4H), 7.30 – 7.23 (m, 8H), 7.11 – 7.04 (m, 2H), 6.91 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.46 – 6.29 (m, 2H), 6.13 (ddd, *J* = 15.5, 8.4, 6.4 Hz, 1H), 4.27 (dd, *J* = 6.7, 4.4 Hz, 1H), 3.82 (s, 3H), 2.86 – 2.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 170.1, 159.8, 141.8, 141.7, 139.2, 138.8, 135.8, 132.9, 130.7, 129.5, 128.9, 128.7, 128.7, 128.6, 128.6, 128.3, 128.3, 127.7, 127.4, 127.3, 127.3, 125.9, 118.8, 112.7, 119.7, 65.9, 56.4, 55.2, 39.1. IR (v/cm^{-1}) 3307, 3060, 3028, 2931, 1651, 1505, 1447, 1317, 1277, 1155, 763, 702, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{38}H_{35}N_2O_2$ $(M+H)^+$: 551.2693; found: 551.2704.

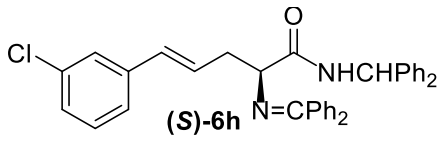
(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(3-fluorophenyl)pent-4-enamide [**6g**]



(*S*)-6g

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). 99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} = 30.4 min (major), t_{R2} = 33.1 min (minor)]; $[\alpha]_D^{20}$ = 0.62 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.81 (m, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.46 (dt, *J* = 5.4, 2.5 Hz, 4H), 7.43 – 7.32 (m, 4H), 7.32 – 7.24 (m, 8H), 7.12 – 6.91 (m, 5H), 6.39 (dd, *J* = 12.5, 3.6 Hz, 2H), 6.16 (ddd, *J* = 15.4, 8.3, 6.5 Hz, 1H), 4.30 (dd, *J* = 6.4, 4.4 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.76 – 2.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 170.2, 163.1 (*J* = 243.3 Hz), 141.7 (*J* = 3.1 Hz), 139.7 (*J* = 7.6 Hz), 139.1, 135.8, 131.9 (*J* = 2.5 Hz), 130.8, 130.1, 129.9, 129.9, 128.9, 128.8, 128.7, 128.7, 128.6, 128.3, 127.7, 127.4, 127.4, 127.3, 127.1, 122.2 (*J* = 2.6 Hz), 114.0 (*J* = 21.2 Hz), 112.5 (*J* = 21.5 Hz), 65.7, 56.3, 39.0. IR (v/cm^{-1}) 3372, 3061, 3028, 2924, 1682, 1505, 1447, 1278, 1227, 1157, 696, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{37}H_{31}FN_2O$ $(M+H)^+$: 539.2493; found: 539.2496.

(*S*,*E*)-N-Benzhydryl-5-(3-chlorophenyl)-2-((diphenylmethylene)amino)pent-4-enamide [**6h**]

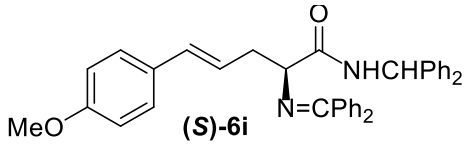


(*S*)-6h

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} = 32.3 min (major), t_{R2} = 34.1 min (minor)]; $[\alpha]_D^{20}$ = 0.38 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.79 (m, 1H), 7.66 – 7.60 (m, 2H), 7.48 – 7.42 (m, 4H), 7.40 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.23 (m, 9H), 7.21 – 7.17 (m, 2H), 7.08 – 7.03

(m, 2H), 6.40 – 6.30 (m, 2H), 6.09 (ddd, *J* = 15.5, 8.4, 6.5 Hz, 1H), 4.26 (dd, *J* = 6.5, 4.5 Hz, 1H), 2.82 – 2.73 (m, 1H), 2.72 – 2.62 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 170.1, 141.7, 141.7, 139.1, 135.8, 135.7, 132.7, 131.7, 130.7, 130.0, 128.9, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.2, 127.6, 127.4, 127.3, 127.3, 127.3, 127.2, 126.3, 65.7, 56.3, 39.0. IR (v/cm^{-1}) 3307, 3061, 2923, 1651, 1505, 1317, 1177, 919, 763, 702, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{37}H_{32}ClN_2O$ $(M+H)^+$: 555.2198; found: 555.2208.

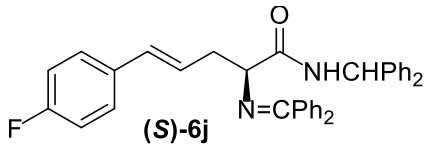
(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(4-methoxyphenyl)pent-4-enamide [**6i**]



(*S*)-6i

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 48.9 min (minor), t_{R2} = 54.7 min (major)]; $[\alpha]_D^{20}$ = 0.56 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.48 – 7.41 (m, 4H), 7.40 – 7.31 (m, 4H), 7.31 – 7.21 (m, 10H), 7.10 – 7.04 (m, 2H), 6.96 – 6.83 (m, 2H), 6.43 – 6.30 (m, 2H), 5.98 (ddd, *J* = 15.5, 8.4, 6.6 Hz, 1H), 4.26 (dd, *J* = 6.7, 4.4 Hz, 1H), 3.85 (s, 3H), 2.86 – 2.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 169.9, 158.9, 141.8, 139.2, 135.8, 132.3, 130.6, 130.2, 128.8, 128.7, 128.6, 128.6, 128.2, 127.7, 127.4, 127.3, 127.3, 123.3, 113.9, 66.0, 56.3, 55.3, 39.2. IR (v/cm^{-1}) 3308, 3060, 3029, 2931, 1651, 1599, 1506, 1447, 1317, 1249, 1177, 1030, 941, 763, 702, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{38}H_{35}N_2O_2$ $(M+H)^+$: 551.2693; found: 551.2699.

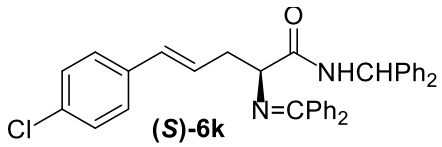
(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(4-fluorophenyl)pent-4-enamide [**6j**]



(*S*)-6j

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 51.3 min (major), t_{R2} = 55.2 min (minor)]; $[\alpha]_D^{20}$ = 0.44 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.49 – 7.42 (m, 4H), 7.41 – 7.38 (m, 1H), 7.37 – 7.31 (m, 3H), 7.27 (tdd, *J* = 8.6, 5.3, 2.8 Hz, 9H), 7.11 – 7.06 (m, 2H), 7.04 – 6.98 (m, 2H), 6.37 (dd, *J* = 12.3, 3.6 Hz, 2H), 6.05 (ddd, *J* = 15.5, 8.4, 6.5 Hz, 1H), 4.27 (dd, *J* = 6.5, 4.4 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.72 – 2.64 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 170.1, 162.1 (*J* = 244.6 Hz), 141.7 (*J* = 4.7 Hz), 139.1, 135.8, 133.5 (*J* = 3.3 Hz), 131.7, 130.7, 128.9, 128.7, 128.7, 128.6, 128.6, 128.3, 127.7, 127.7, 127.6, 127.4, 127.3, 127.3, 125.3 (*J* = 2.2 Hz), 115.4 (*J* = 21.3 Hz), 65.8, 56.3, 39.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.1. IR (v/cm^{-1}) 3372, 3061, 3028, 2924, 1683, 1506, 1447, 1227, 1157, 967, 760, 696, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{37}H_{31}FN_2O$ $(M+H)^+$: 539.2493; found: 539.2505.

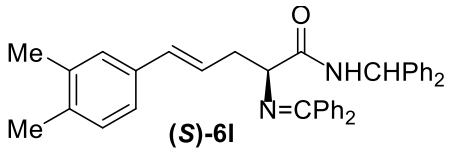
(*S*,*E*)-N-Benzhydryl-5-(4-chlorophenyl)-2-((diphenylmethylene)amino)pent-4-enamide [**6k**]



(*S*)-6k

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). 99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} = 33.1 min (major), t_{R2} = 42.2 min (minor)]; $[\alpha]_D^{20}$ = 0.43 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.46 (dt, *J* = 5.3, 2.6 Hz, 4H), 7.41 – 7.22 (m, 16H), 7.13 (dt, *J* = 6.8, 2.0 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.45 – 6.28 (m, 2H), 6.14 (ddd, *J* = 15.5, 8.4, 6.4 Hz, 1H), 4.29 (dd, *J* = 6.5, 4.4 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.74 – 2.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 170.2, 141.7, 141.7, 139.2, 139.1, 135.7, 134.4, 131.6, 130.8, 129.7, 128.9, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 128.3, 128.2, 127.7, 127.4, 127.4, 127.3, 127.3, 127.1, 126.0, 124.5, 65.7, 56.3, 39.0. IR (v/cm^{-1}) 3307, 3060, 2920, 1651, 1505, 1455, 1317, 1177, 1076, 1029, 941, 919, 763, 702, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{37}H_{32}ClN_2O$ $(M+H)^+$:555.2198; found: 555.2205.

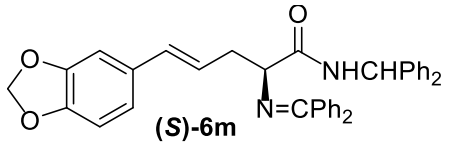
(*S*,*E*)-N-Benzhydryl-5-(3,4-dimethylphenyl)-2-((diphenylmethylene)amino)pent-4-enamide [**6l**]



(*S*)-6l

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 26.0 min (minor), t_{R2} = 36.9 min (major)]; $[\alpha]_D^{20}$ = 0.36 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 10.1, 8.0 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.42 (m, 4H), 7.41 – 7.24 (m, 11H), 7.15 – 7.03 (m, 5H), 6.44 – 6.30 (m, 2H), 6.05 (ddd, *J* = 15.3, 8.2, 6.5 Hz, 1H), 4.28 (dd, *J* = 6.6, 4.5 Hz, 1H), 2.77 (tq, *J* = 15.0, 8.2, 7.4 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 169.9, 141.8, 141.8, 139.2, 136.5, 135.9, 135.6, 135.0, 132.9, 130.6, 129.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 128.3, 128.3, 127.8, 127.6, 127.4, 127.4, 127.3, 127.3, 124.4, 123.7, 66.0, 56.4, 39.2, 19.9, 19.5. IR (v/cm^{-1}) 3307, 3060, 3027, 2919, 1660, 1576, 1495, 1277, 698, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{39}H_{37}N_2O$ $(M+H)^+$: 549.2901; found: 549.2906.

(*S*,*E*)-N-Benzhydryl-5-(benzo[d][1,3]dioxol-5-yl)-2-((diphenylmethylene)amino)pent-4-enamide [**6m**]

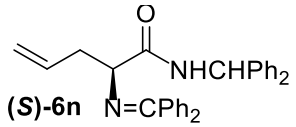


(*S*)-6m

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). >99% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} = 34.7 min (minor), t_{R2} = 47.9 min (major)]; $[\alpha]_D^{20}$ = 0.50 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.79 (m, 1H), 7.66 – 7.59 (m, 2H), 7.45 (dt, *J* = 4.9, 2.3 Hz, 4H), 7.40 – 7.37 (m, 2H), 7.36 – 7.24 (m, 11H), 7.13 – 7.04 (m, 2H), 6.84 (d, *J* = 1.6 Hz,

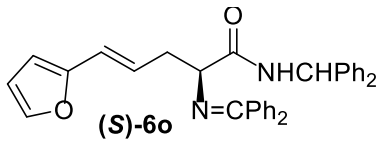
1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.40 – 6.28 (m, 2H), 6.03 – 5.89 (m, 3H), 4.26 (dd, *J* = 6.6, 4.4 Hz, 1H), 2.81 – 2.71 (m, 1H), 2.71 – 2.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 169.9, 147.9, 146.9, 141.8, 141.8, 139.2, 135.8, 132.5, 131.9, 130.7, 130.1, 128.9, 128.7, 128.7, 128.7, 128.6, 128.3, 127.7, 127.4, 127.3, 127.3, 123.7, 120.8, 108.2, 105.5, 101.0, 65.9, 56.3, 39.0. IR (v/cm^{-1}) 3307, 3060, 3028, 2898, 1651, 1599, 1505, 1446, 1317, 1250, 1038, 921, 762, 698, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{38}H_{33}N_2O_3$ $(M+H)^+$: 565.2486; found: 565.2491.

(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)pent-4-enamide [6n]



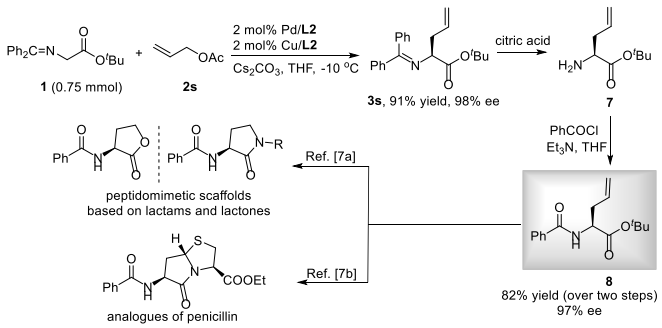
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). 98% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 27.6 min (major), t_{R2} = 47.5 min (minor)]; $[\alpha]_D^{20}$ = 0.094 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.49 – 7.43 (m, 4H), 7.40 – 7.36 (d, *J* = 7.6 Hz, 3H), 7.36 – 7.30 (m, 5H), 7.27 (m, 3H), 7.16 – 7.05 (m, 2H), 6.35 (d, *J* = 8.6 Hz, 1H), 5.79 – 5.66 (m, 1H), 5.13 – 4.96 (m, 2H), 4.17 (dd, *J* = 6.8, 4.9 Hz, 1H), 2.70 – 2.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 169.9, 141.8, 141.8, 139.2, 135.7, 133.9, 130.6, 130.1, 128.9, 128.7, 128.7, 128.6, 128.6, 128.2, 127.8, 127.4, 127.4, 127.3, 117.9, 65.8, 56.3, 39.9. IR (v/cm^{-1}) 3316, 3061, 3028, 2922, 1659, 1598, 1495, 1447, 1317, 1277, 941, 919, 762, 699, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{31}H_{29}N_2O$ $(M+H)^+$: 445.2275; found: 445.2281.

(*S*,*E*)-N-Benzhydryl-2-((diphenylmethylene)amino)-5-(furan-2-yl)pent-4-enamide [6o]



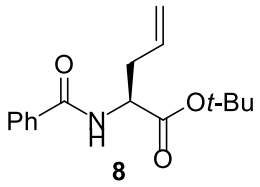
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (57.4 mg, 88% yield). 98% ee, HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 53.1 min (major), t_{R2} = 58.4 min (minor)]; $[\alpha]_D^{20}$ = 0.32 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.45 (q, *J* = 5.9, 5.1 Hz, 4H), 7.41 – 7.35 (m, 4H), 7.34 – 7.24 (m, 10H), 7.13 – 7.06 (m, 2H), 6.43 – 6.31 (m, 2H), 6.24 (d, *J* = 15.8 Hz, 1H), 6.17 – 6.06 (m, 2H), 4.24 (dd, *J* = 6.5, 4.5 Hz, 1H), 2.71 (dtt, *J* = 18.6, 13.5, 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 170.2, 152.9, 141.8, 141.7, 141.6, 139.1, 135.7, 130.7, 128.9, 128.7, 128.6, 128.6, 128.6, 128.3, 127.7, 127.4, 127.4, 127.3, 127.3, 124.5, 121.5, 111.2, 106.9, 65.9, 56.4, 38.9. IR (v/cm^{-1}) 3306, 3060, 3029, 2925, 1651, 1505, 1447, 1318, 1278, 742, 702, 638 cm^{-1}. HRMS (Q–TOF Premier) calcd for $C_{35}H_{31}N_2O_2$ $(M+H)^+$: 511.2380; found: 511.2386.

4. Synthetic Transformation



To a solution of **3s** (226 mg, 0.675 mmol) in THF (10 mL) was added a 15% citric acid solution (5 mL) at room temperature and the mixture was stirred for 12 h. After being washed with ether, the mixture was neutralized with solid K_2CO_3 and extracted with EtOAc. The combined extracts were dried over Na_2SO_4 and concentrated in vacuo. To a solution of the residue in THF (9 mL) were added Et_3N (102 mg, 1.05 mmol) and benzoyl chloride (105 mg, 0.75 mmol) at 0 °C. After being stirred for 5 h, the mixture was quenched with a saturated NH_4Cl solution and extracted with EtOAc. The combined extracts were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and then concentrated in vacuo. The residue was purified by preparative TLC on silica gel.

(*S*)-*Tert*-butyl 2-benzamidopent-4-enoate (5)[8]



8

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 7.2, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 6.75 (d, *J* = 6.8 Hz, 1H), 5.85 – 5.66 (m, 1H), 5.17 – 5.13 (m, 1H), 5.12 (s, 1H), 4.80 – 4.72 (m, 1H), 2.77 – 2.66 (m, 1H), 2.66 – 2.55 (m, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 167.0, 134.4, 132.5, 131.8, 128.8, 127.2, 119.3, 82.7, 52.6, 37.0, 28.3; HPLC [DAICEL CHIRAL PAK OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 5.3 min (major), t_{R2} = 11.6 min (minor)]; ee = 97%.

5. **References**

(1) (a) Liu, D.; Xie, F.; Zhang, W. *Tetrahedron Lett.* **2007**, *48*, 585. (b) Schaarschmidt, D.; Lang, H. *Organometallics*, **2013**, *32*, 5668.

(2) (a) Watson, I. D. G.; Styler, S. A.; Yudin, A. K. *J. Am. Chem. Soc.*, **2004**, *126*, 5086. (b) Chu, J. C. K.; Dalton, D. M.; Rovis, T. *J. Am. Chem. Soc.*, **2015**, *137*, 4445. (c) Jautze, S.; Peters, R. *Angew. Chem. Int. Ed.* **2008**, *47*, 9284. (d) Liu, X.; Xu, X.; Pan, L.; Zhang, Q.; Liu, Q. *Org. Biomol. Chem.*, **2013**, *11*, 6703.

(3) Huo, X.; He, R.; Fu, J.; Zhang, J.; Yang, G.; Zhang, W. *J. Am. Chem. Soc.* **2017**, *139*, 9819.

(4) Jew, S.-S.; Jeong, B.-S.; Yoo, M.-S.; Huh, H.; Park, H.-G. *Chem. Commun.* **2001**, 1244.

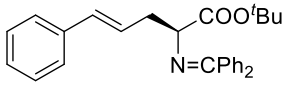
(5) Nakoji, M.; Kanayama, T.; Okino, T.; Takemoto, Y. *Org. Lett.* **2001**, *3*, 3329.

(6) Siebum, A. H. G.; Woo, W. S.; Raap, J.; Lugtenburg, J. *Eur. J. Org. Chem.* **2004**, 2905.

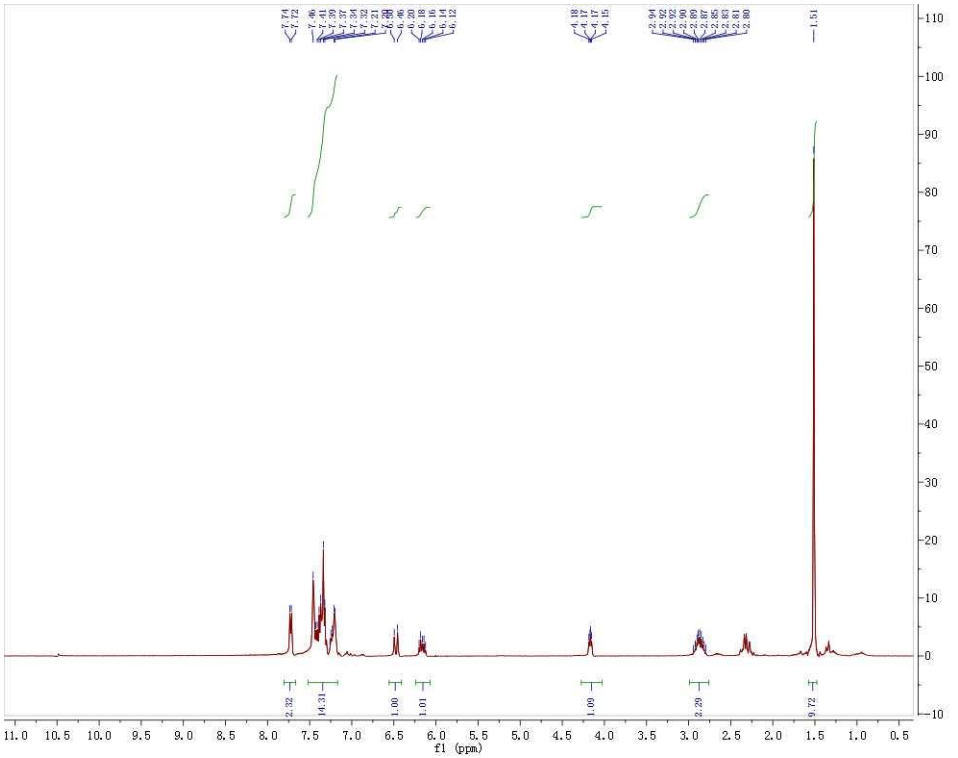
(7) (a) Matagne, A.; Dubus, A.; Galleni, M.; Frère, J.-M. *Nat. Prod. Rep.* **1999**, *16*, 1; (b) J. Marchand-Brynaert, L. Ghosez, *Non β-lactam analogues of penicillins and cephalosporins*, Lukacs, G.; Ohno, M., Eds.; Springer-Verlag: Berlin, **1990**, 727-794.

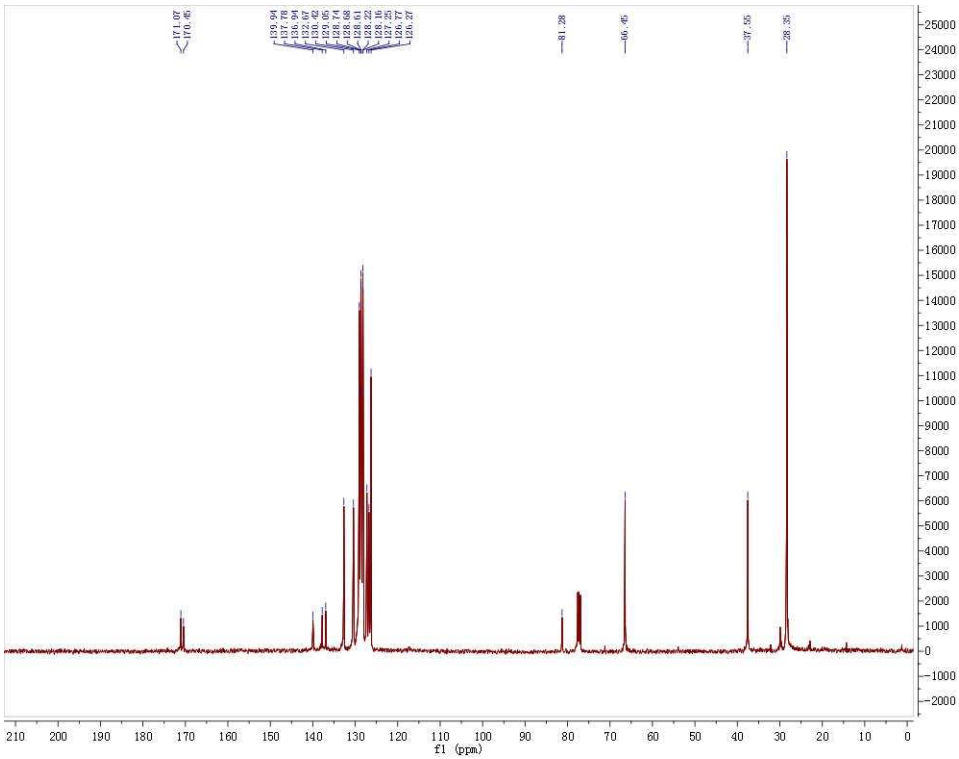
(8) H.-g. Park, M.-J. Kim, M.-K. Park, H.-J. Jung, J. Lee, S.-h. Choi, Y.-J. Lee, B.-S. Jeong, J.-H. Lee, M.-S. Yoo, J.-M. Ku, S.-s. Jew *J. Org. Chem.* **2005**, *70*, 1904.

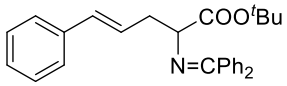
6. NMR and HPLC spectra



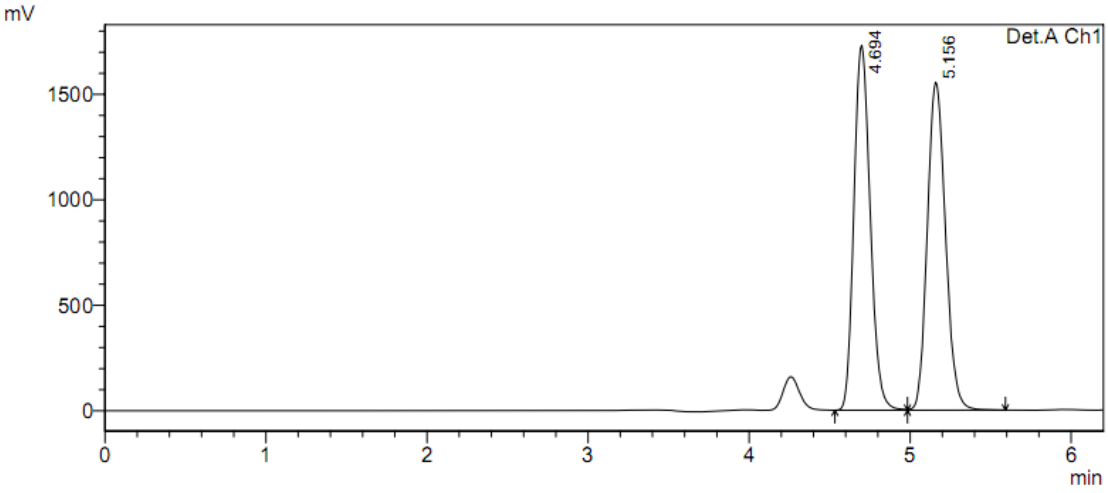
(*S*)-3a







***(rac)*-3a**

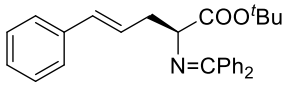


1 Det.A Ch1/254nm

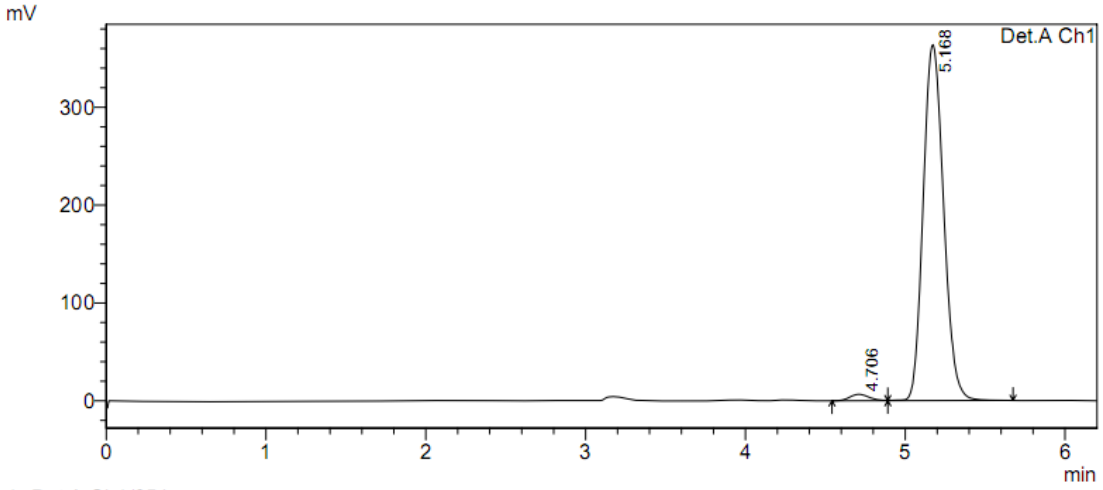
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.694	12164256	1730704	49.966	52.683
2	5.156	12180715	1554441	50.034	47.317
Total		24344970	3285145	100.000	100.000



***(S)*-3a**

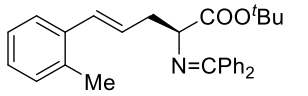


1 Det.A Ch1/254nm

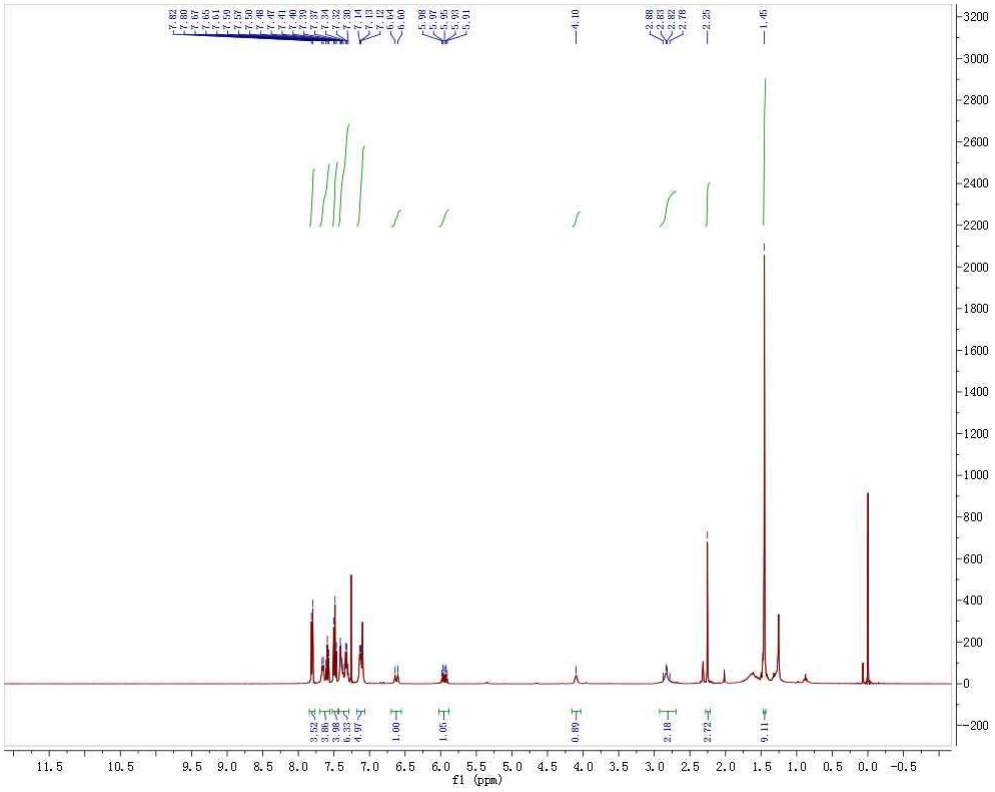
PeakTable

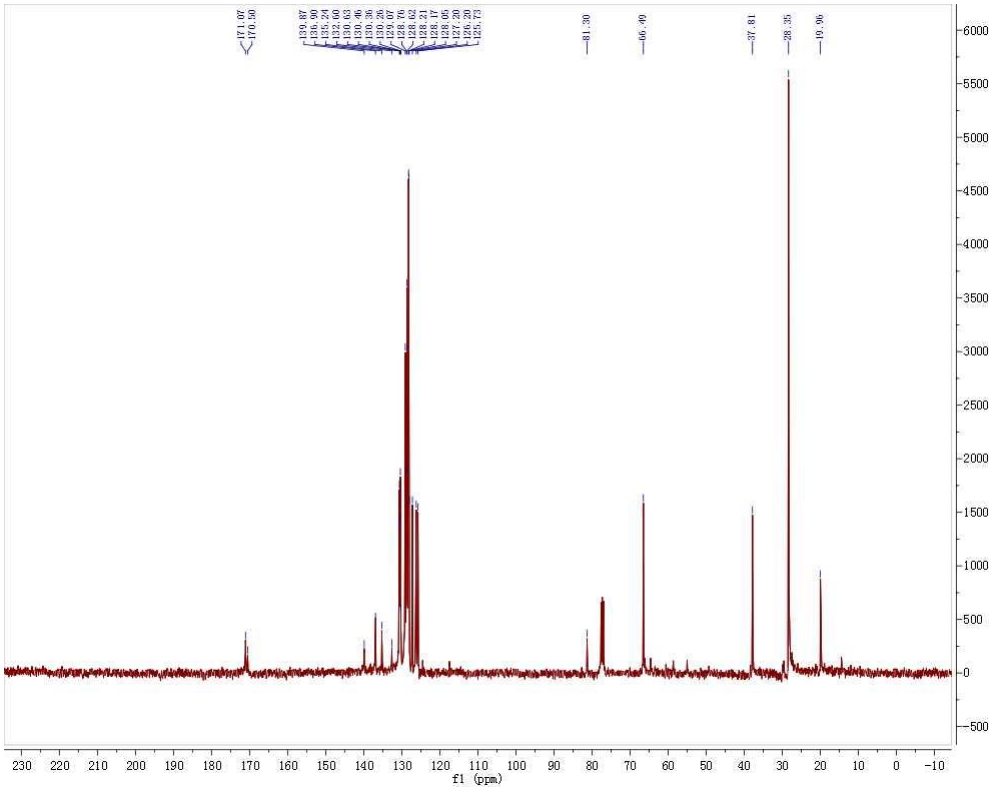
Detector A Ch1 254nm

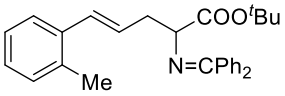
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.706	54430	6493	1.659	1.753
2	5.168	3227233	363788	98.341	98.247
Total		3281663	370280	100.000	100.000



(*S*)-3b







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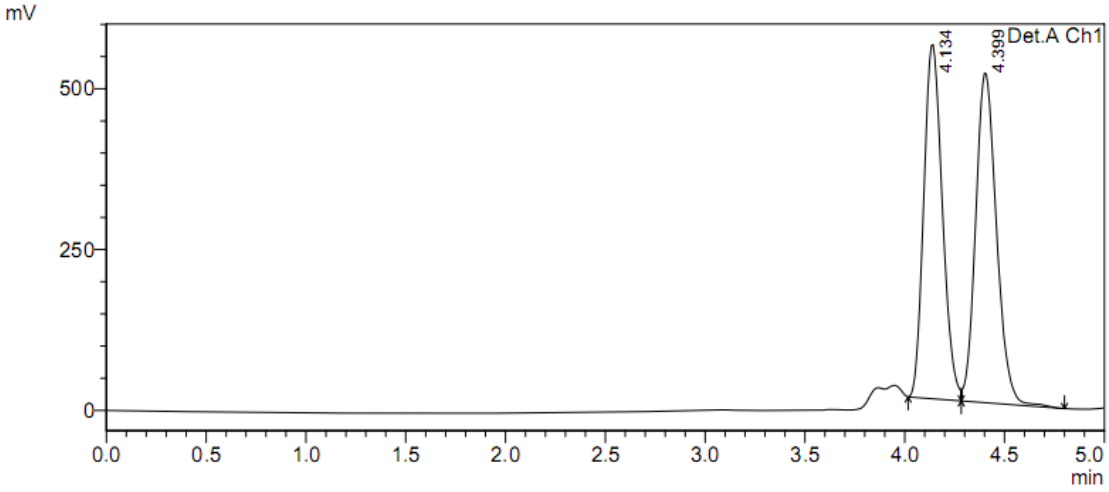

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

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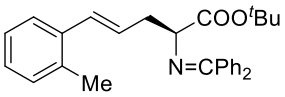
Total		7283092	1063151	100.000	100.000



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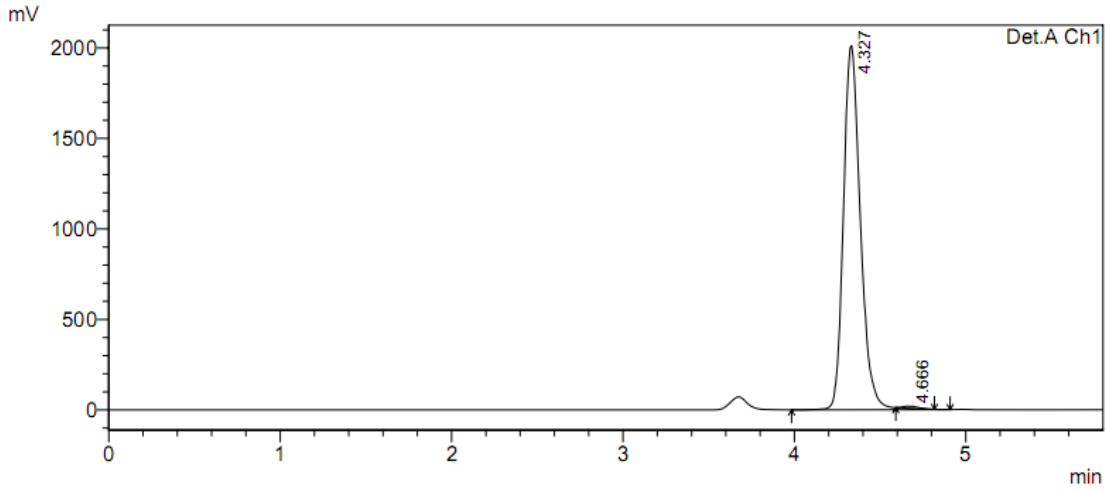

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

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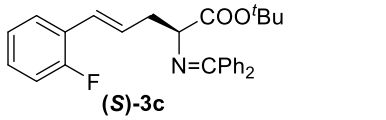
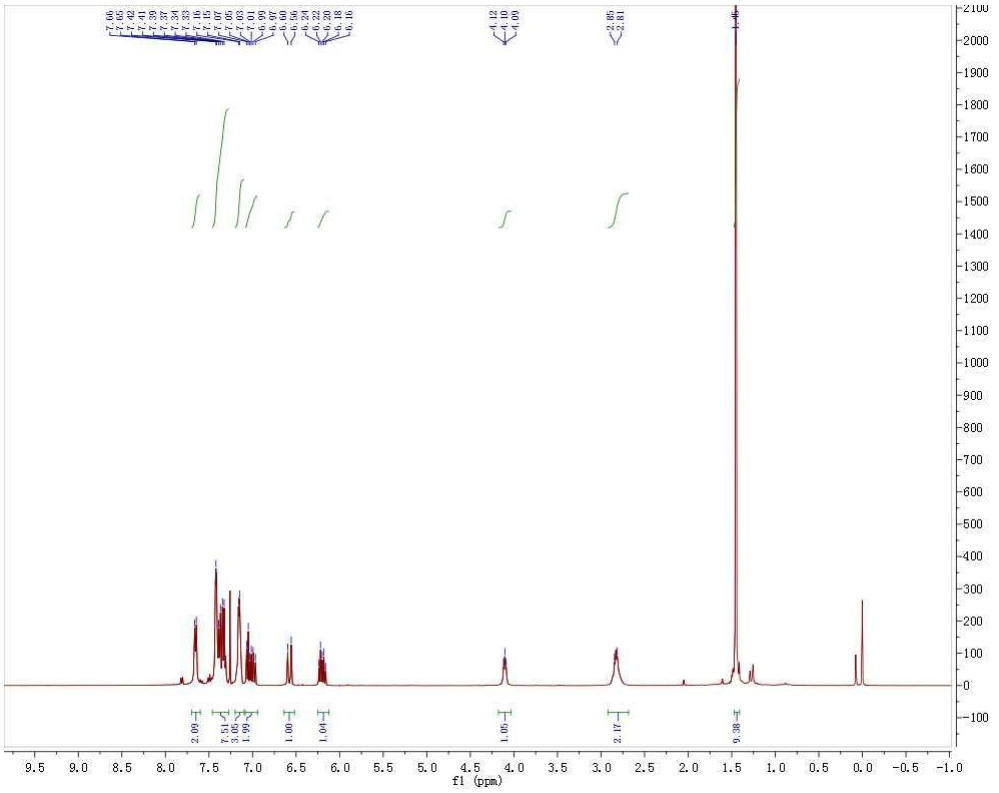
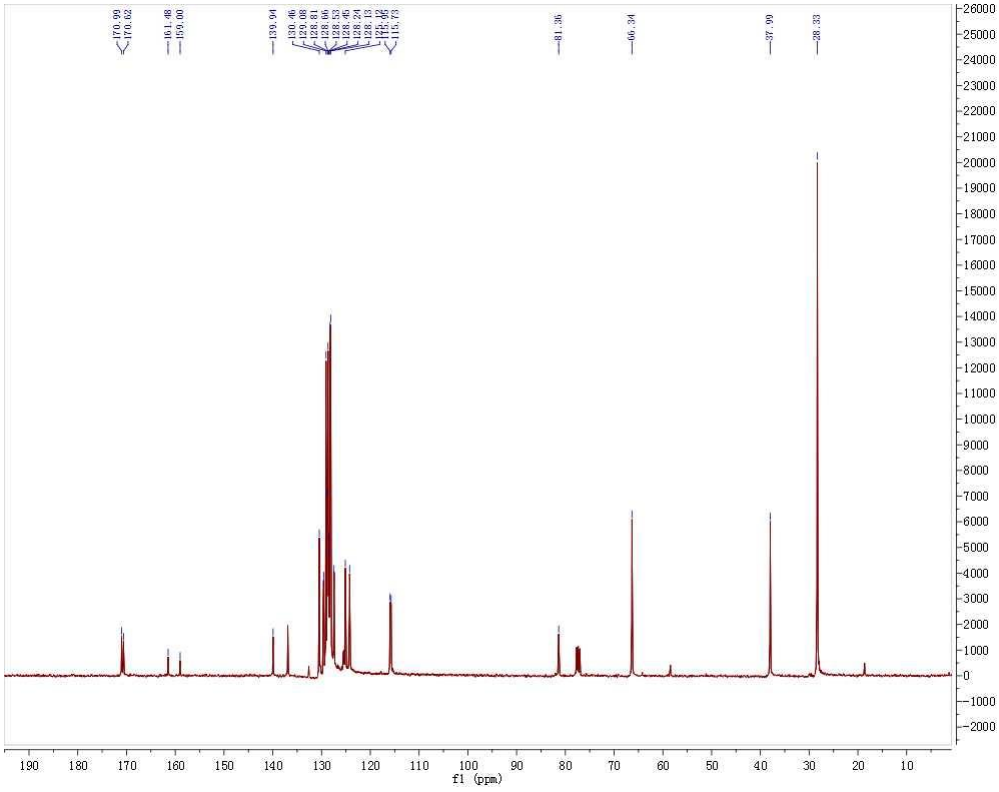
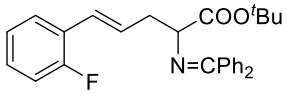


(*S*)-3c







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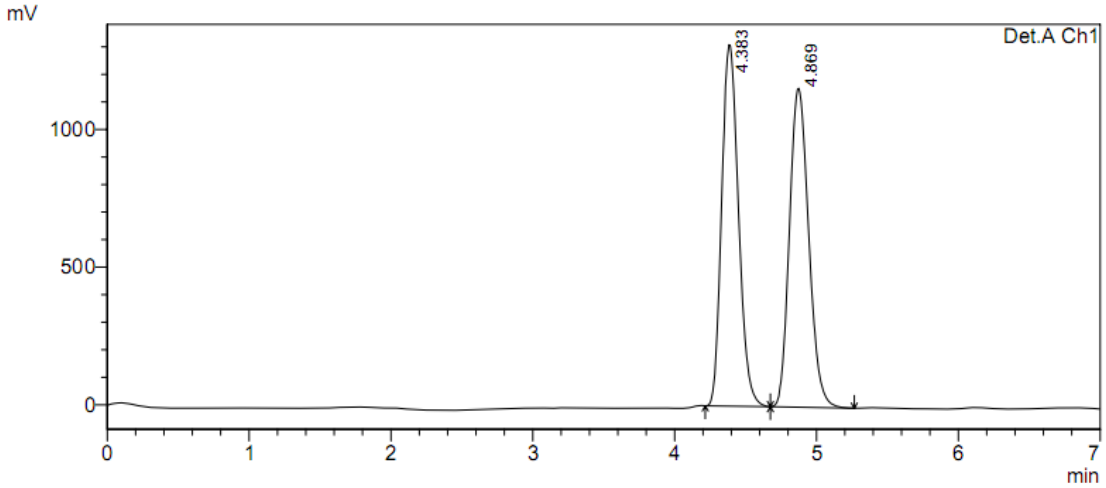

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

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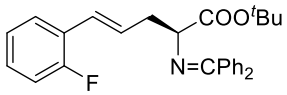

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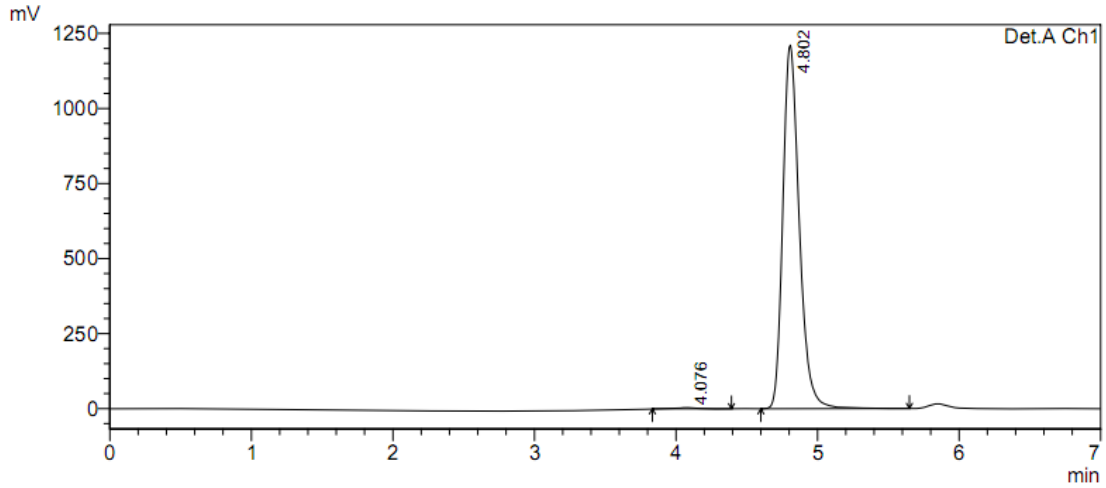

1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

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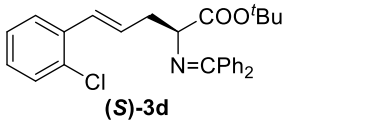

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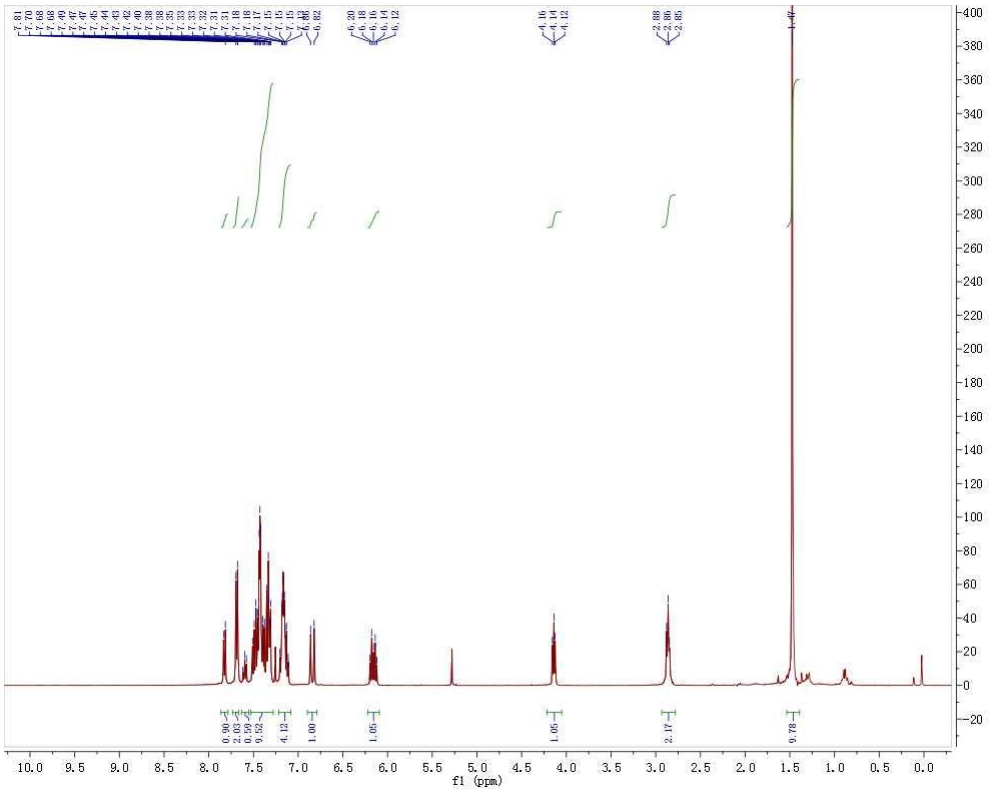
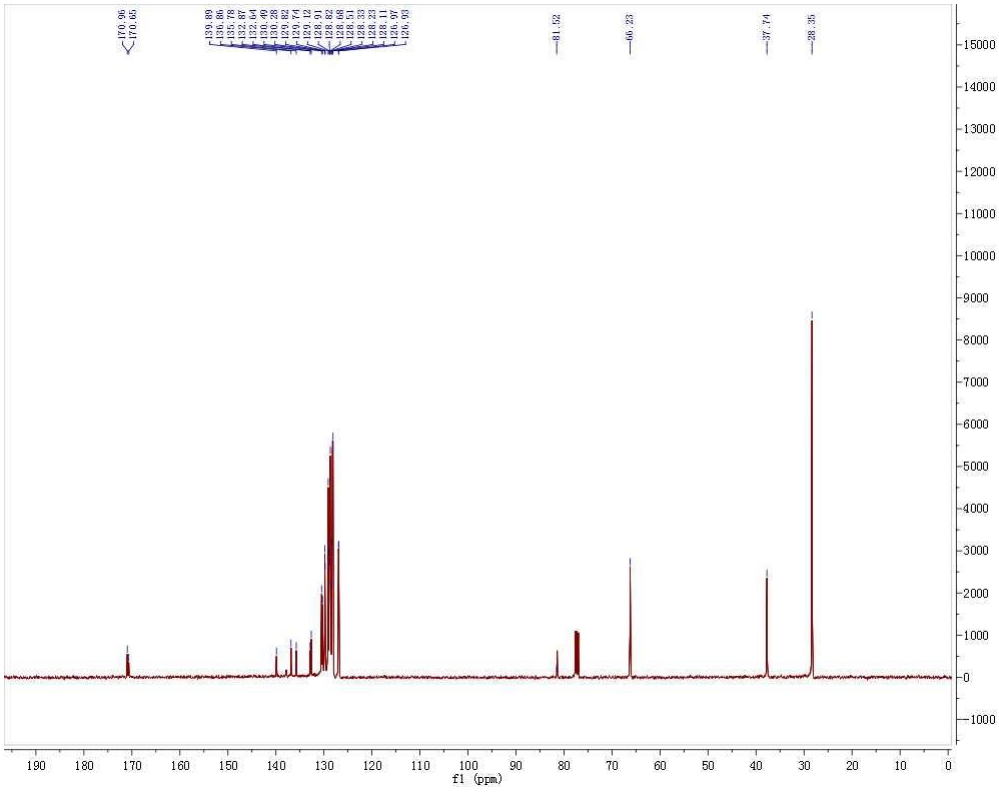
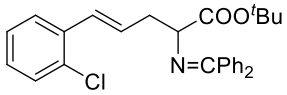
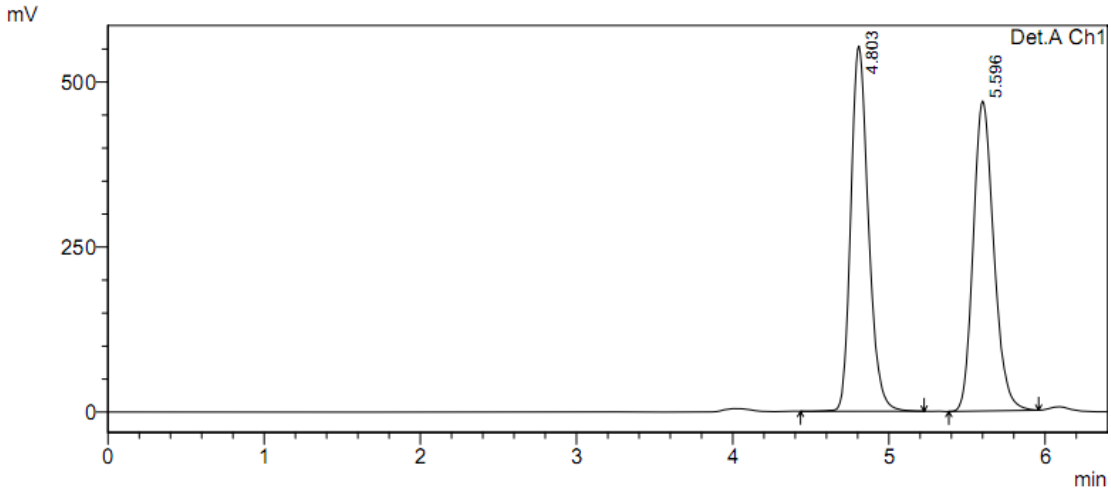






(*rac*)-3d

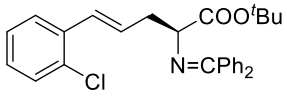


1 Det.A Ch1/254nm

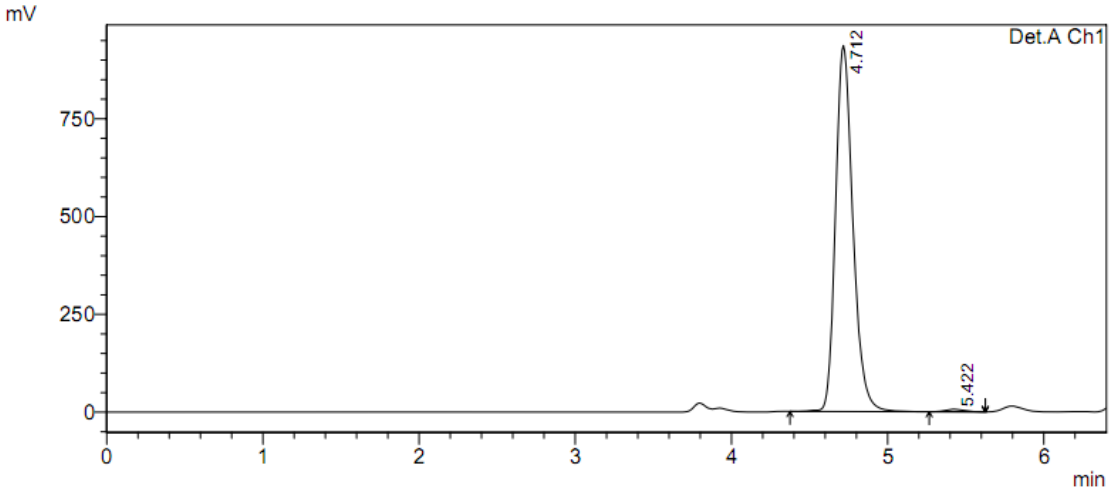
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.803	4324860	553546	50.204	54.095
2	5.596	4289673	469735	49.796	45.905
Total		8614532	1023281	100.000	100.000



(*S*)-3d

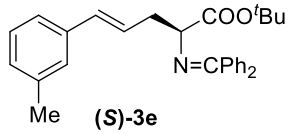


1 Det.A Ch1/254nm

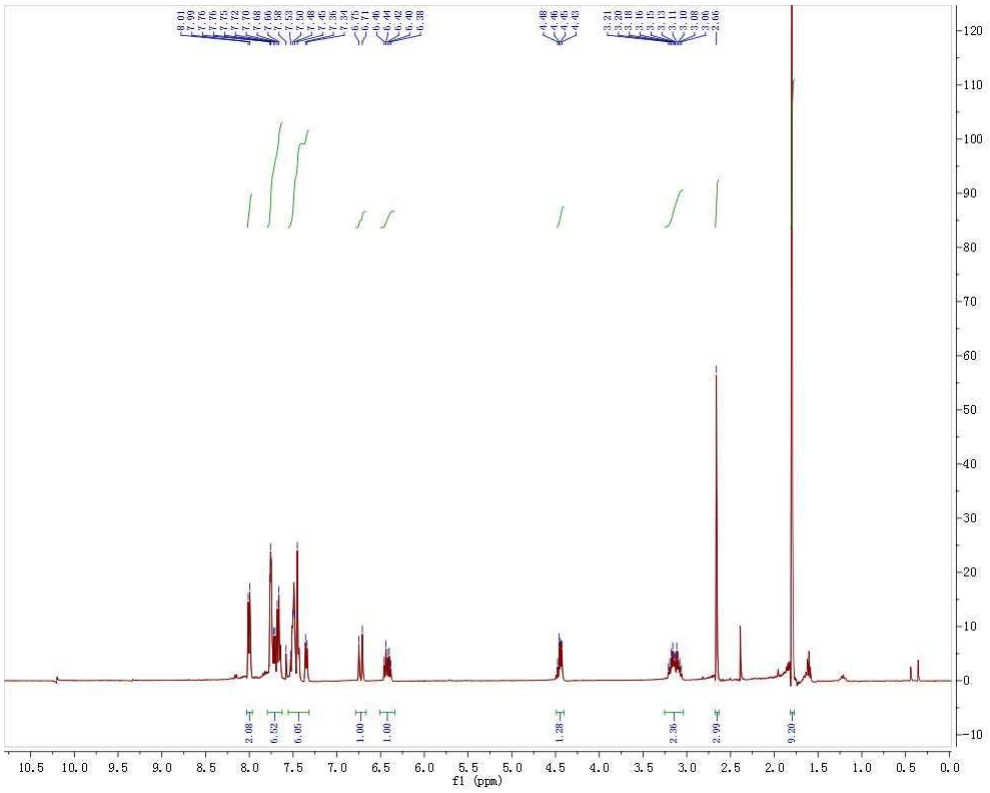
PeakTable

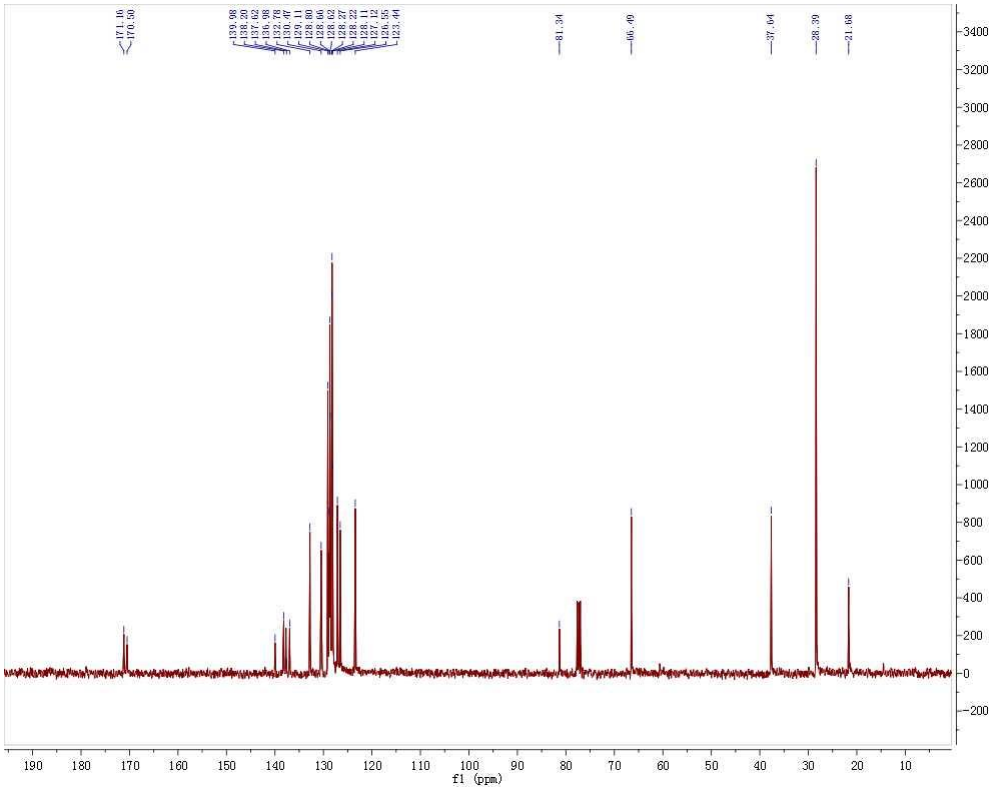
Detector A Ch1 254nm

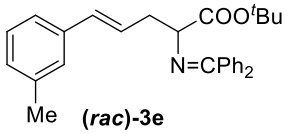
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.712	7240467	936042	99.274	99.323
2	5.422	52953	6381	0.726	0.677
Total		7293420	942423	100.000	100.000



(*S*)-3e







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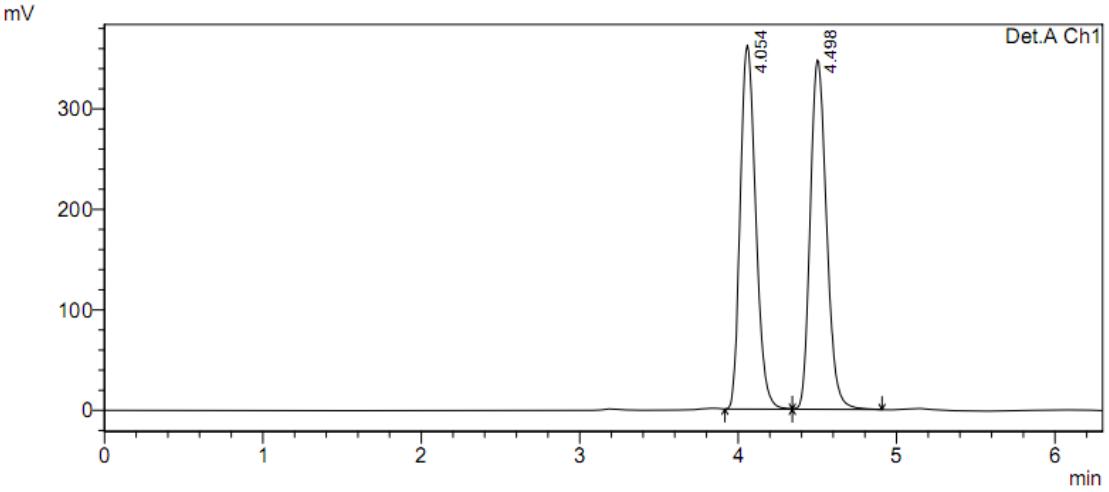
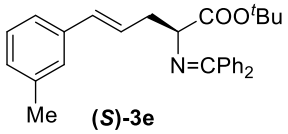


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.054	2467022	362354	49.748	51.034
2	4.498	2491997	347669	50.252	48.966
Total		4959019	710023	100.000	100.000



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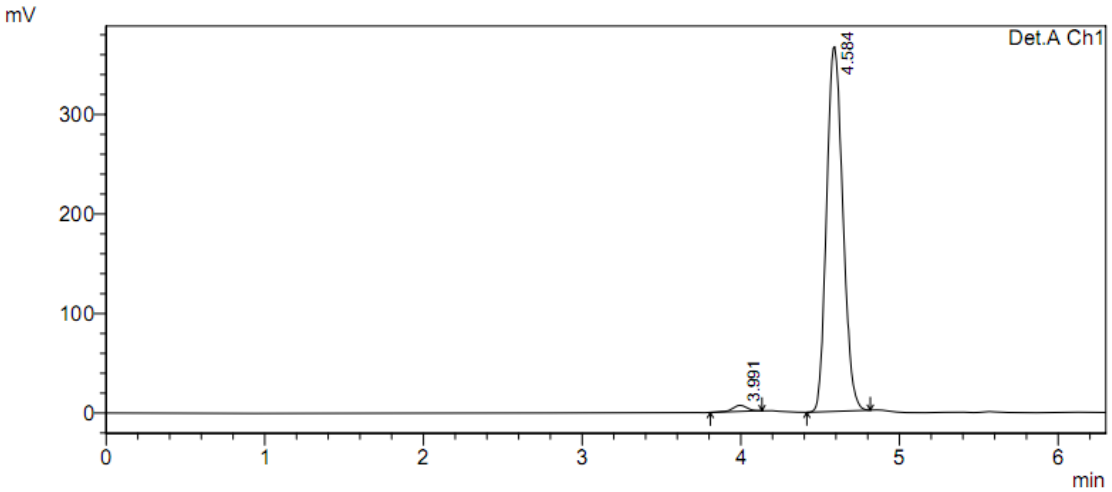
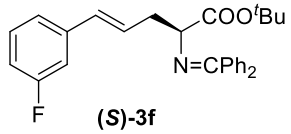


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.991	39633	6163	1.497	1.653
2	4.584	2607195	366552	98.503	98.347
Total		2646828	372715	100.000	100.000



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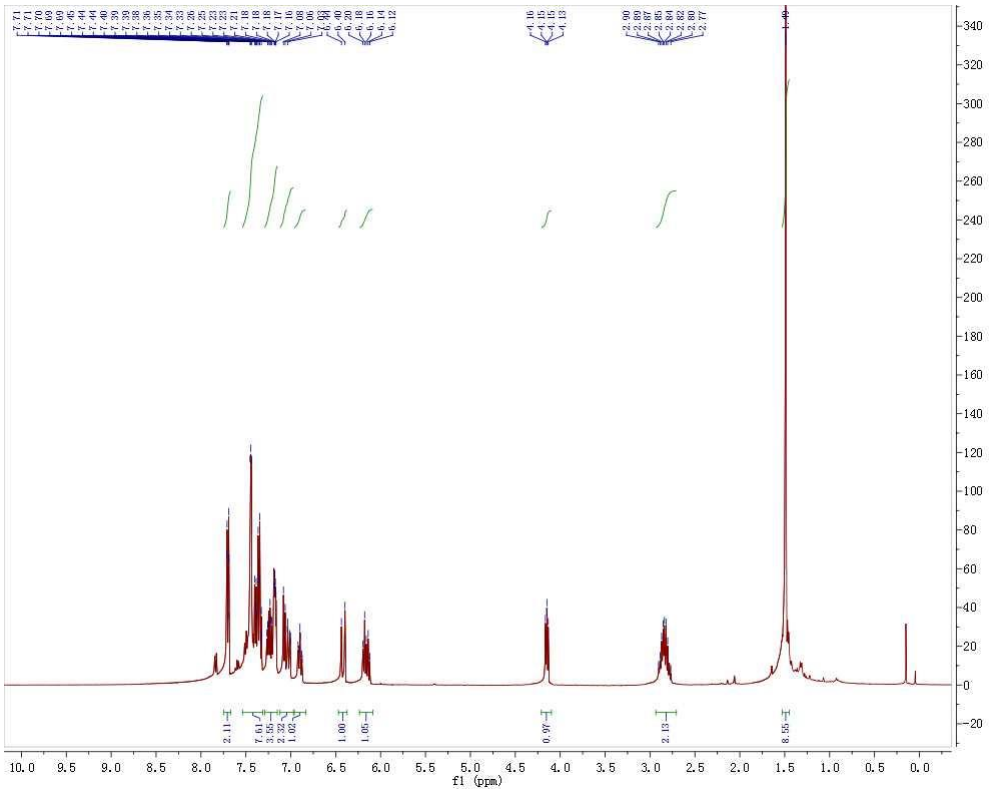
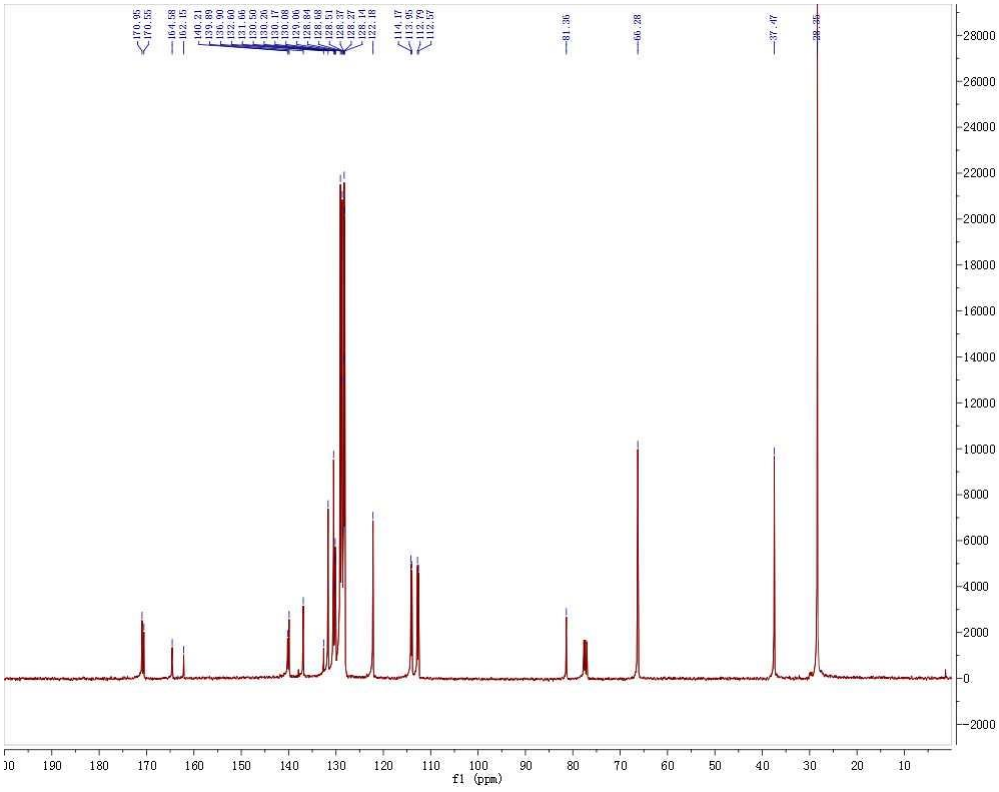
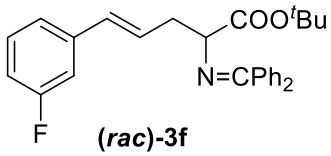
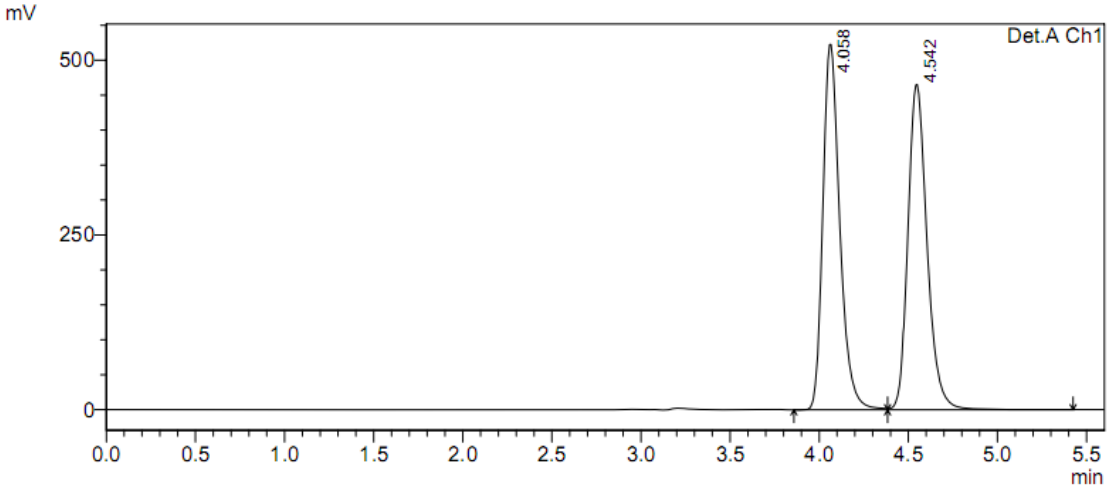






(*rac*)-3f

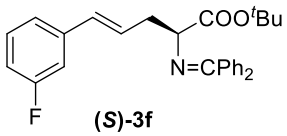


1 Det.A Ch1/254nm

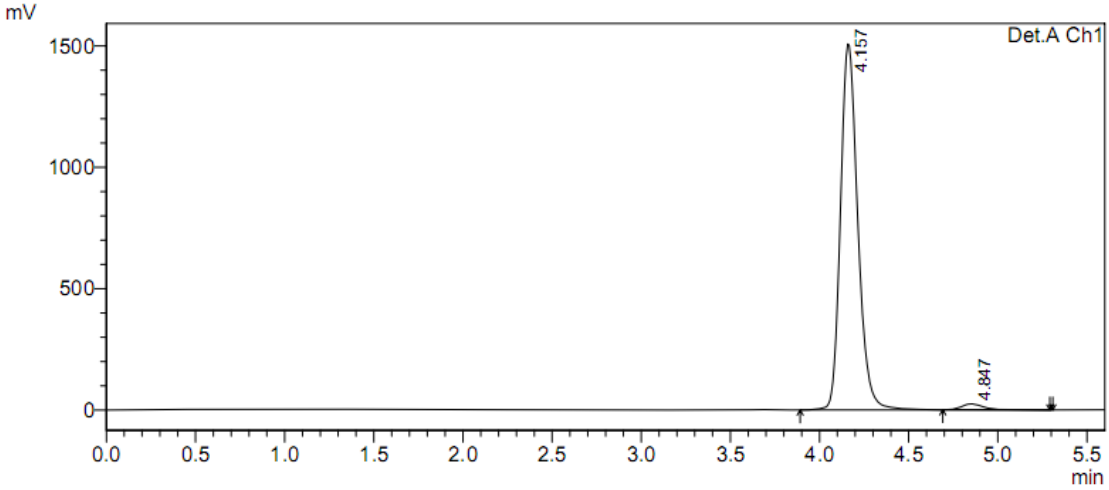
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.058	3458047	522865	49.836	52.897
2	4.542	3480754	465594	50.164	47.103
Total		6938801	988459	100.000	100.000



(*S*)-3f

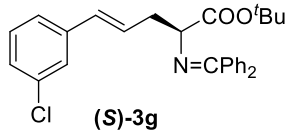


1 Det.A Ch1/254nm

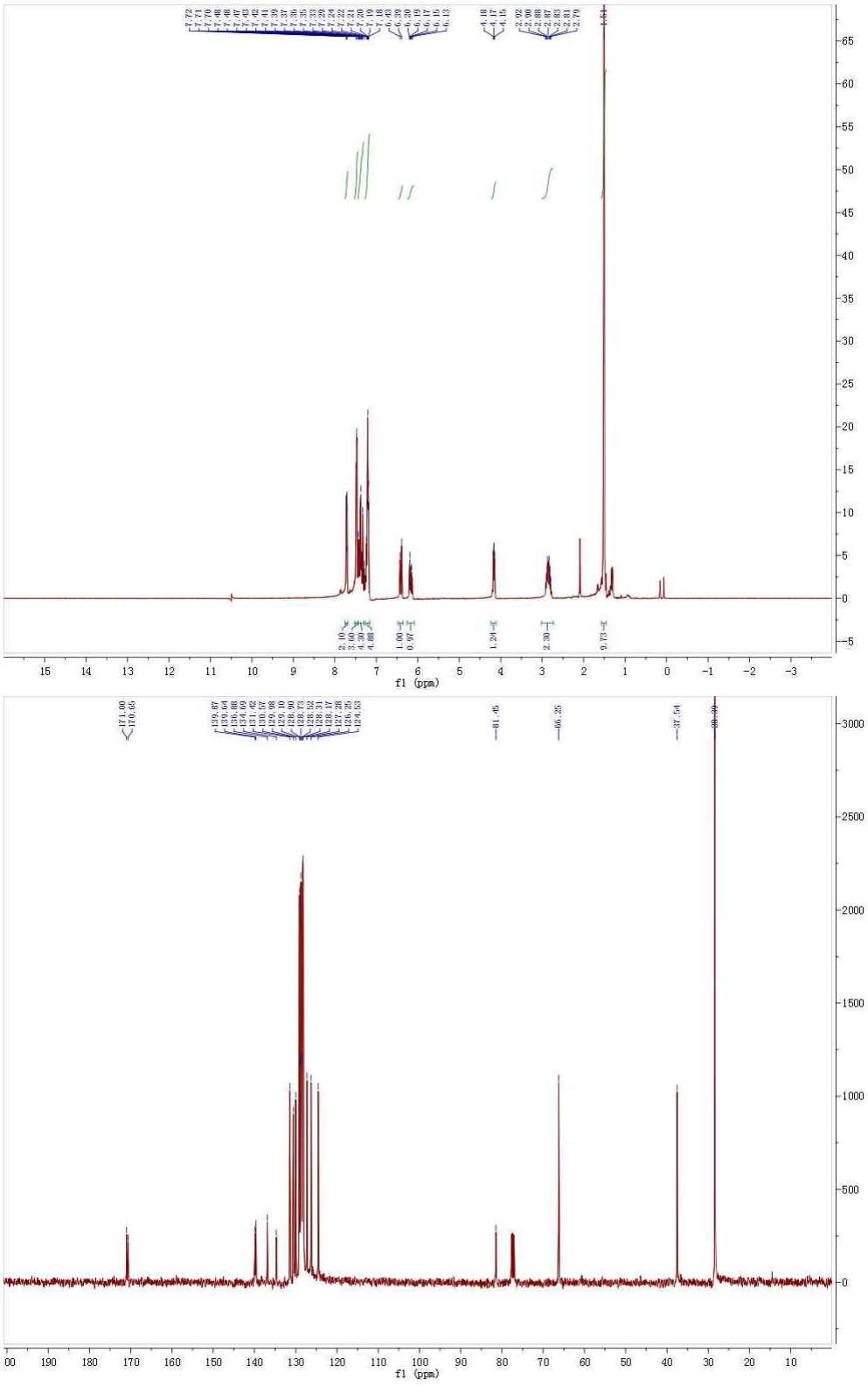
PeakTable

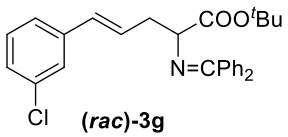
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.157	10211670	1507705	98.031	98.419
2	4.847	205088	24225	1.969	1.581
Total		10416759	1531929	100.000	100.000



(*S*)-3g





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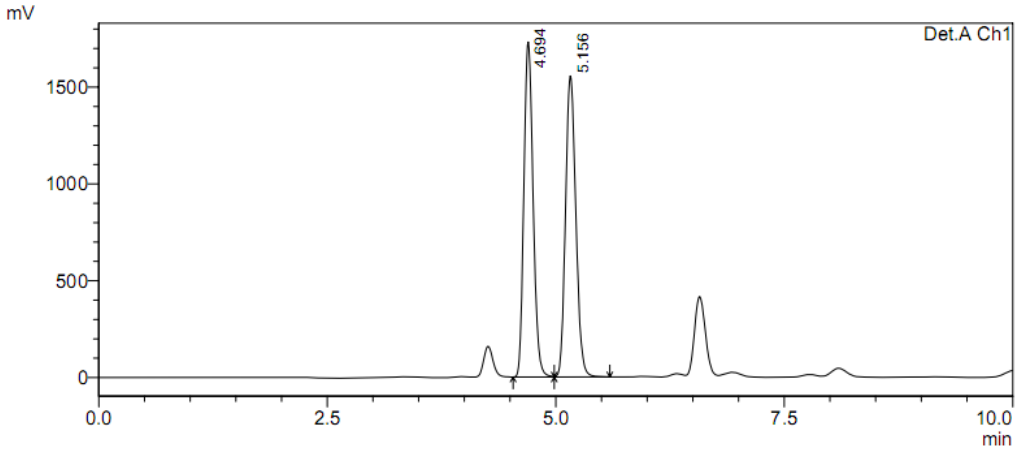
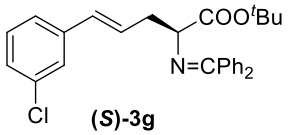


1 Det.A Ch1/254nm

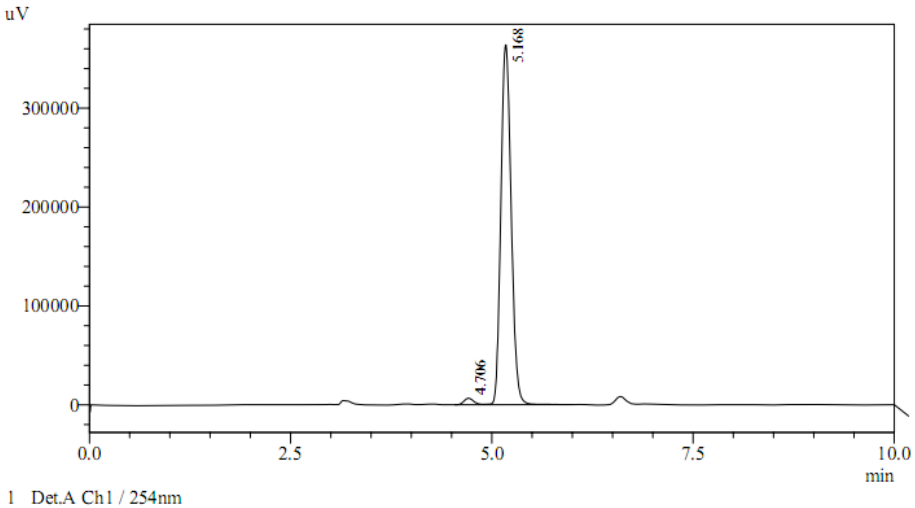
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.694	12164256	1730704	49.966	52.683
2	5.156	12180715	1554441	50.034	47.317
Total		24344970	3285145	100.000	100.000



(*S*)-3g

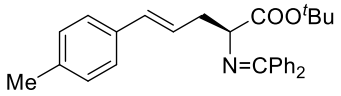


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.706	55391	6536	1.681	1.764
2	5.168	3238855	363952	98.319	98.236
Total		3294246	370487	100.000	100.000



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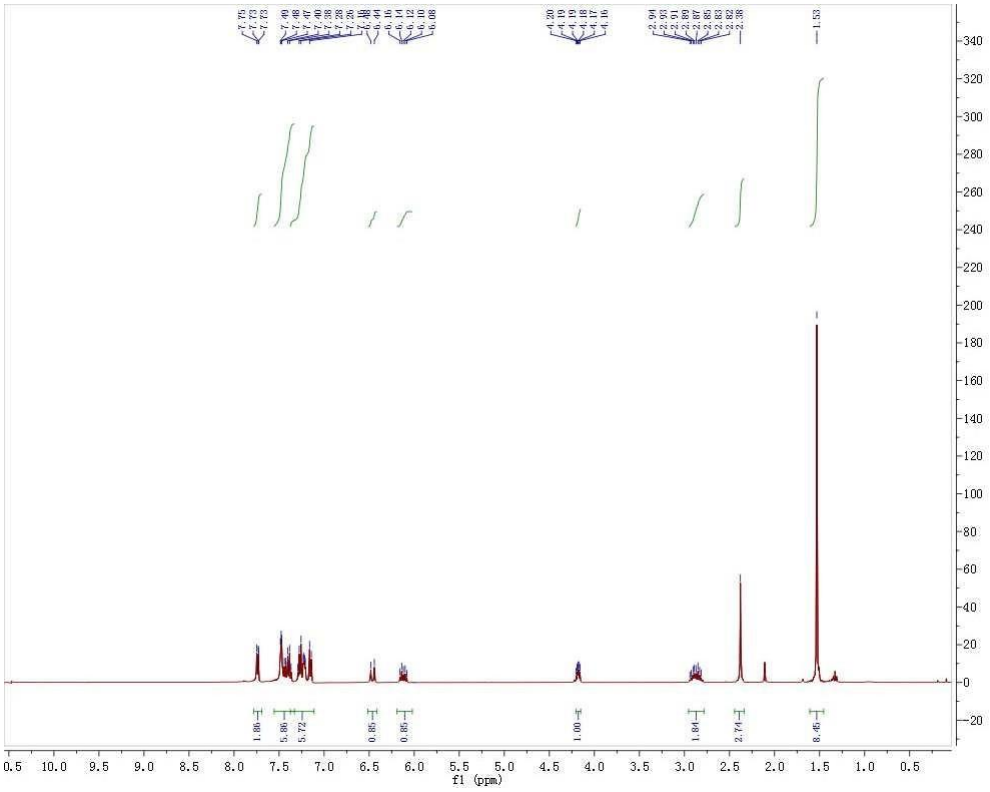

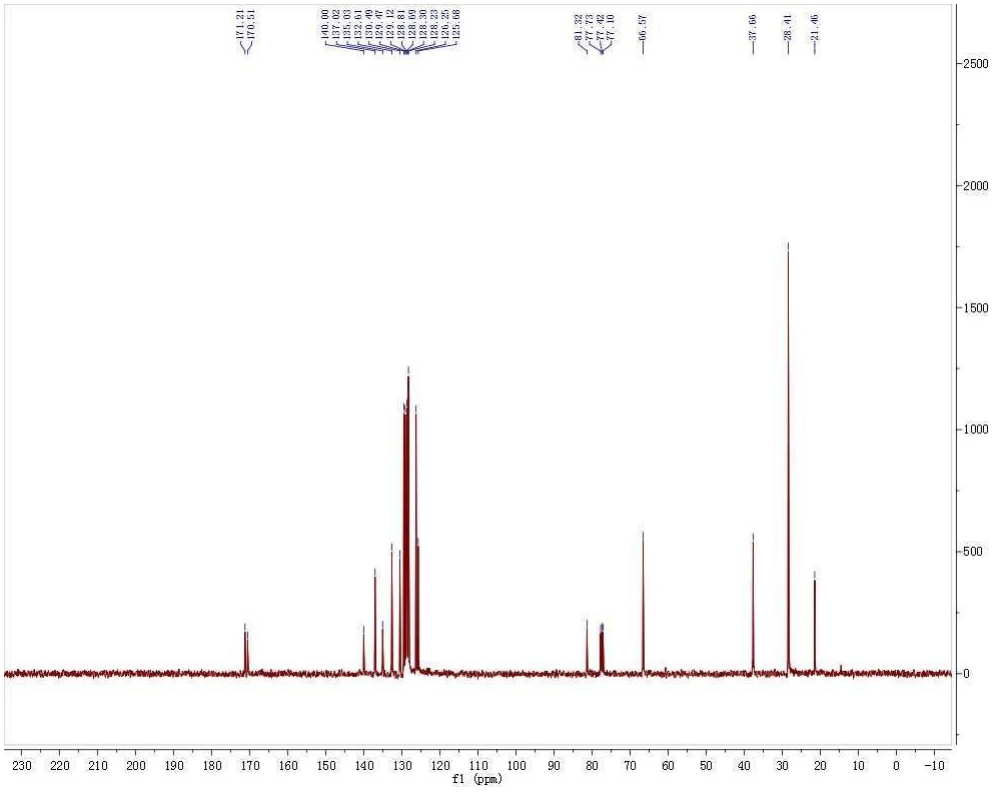

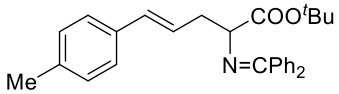

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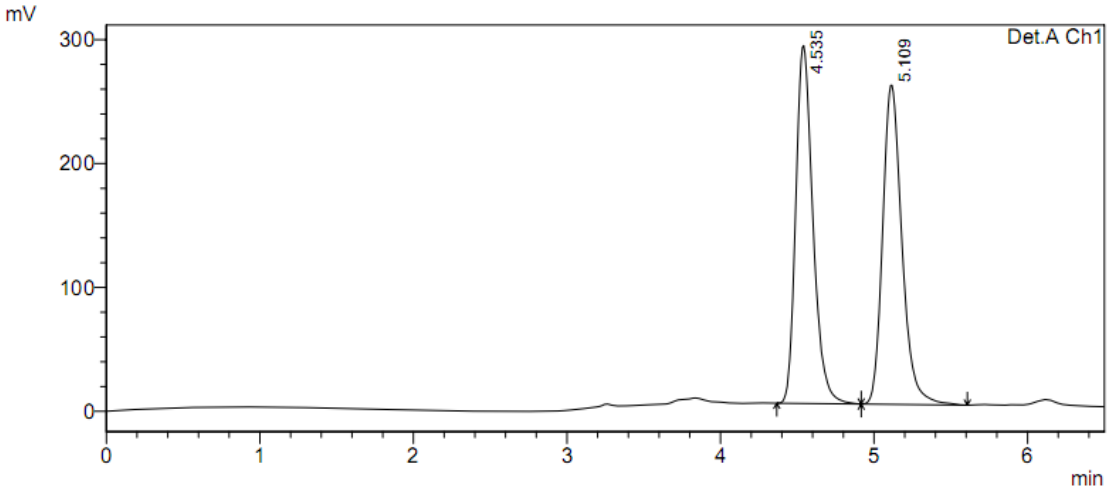
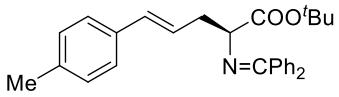


1 Det.A Ch1/254nm

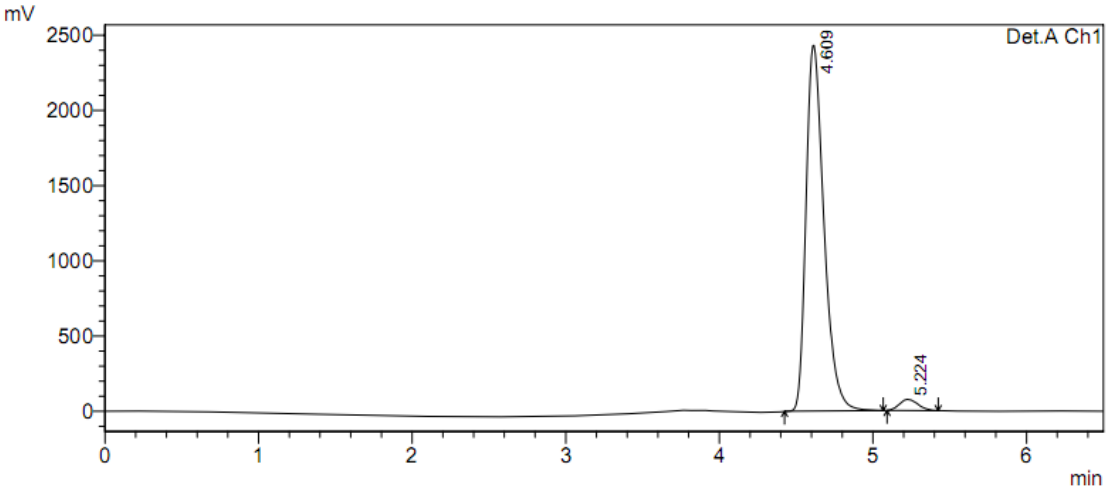
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.535	2247561	288924	49.923	52.880
2	5.109	2254530	257453	50.077	47.120
Total		4502091	546377	100.000	100.000



(*S*)-3h

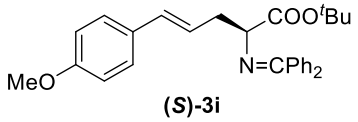


1 Det.A Ch1/254nm

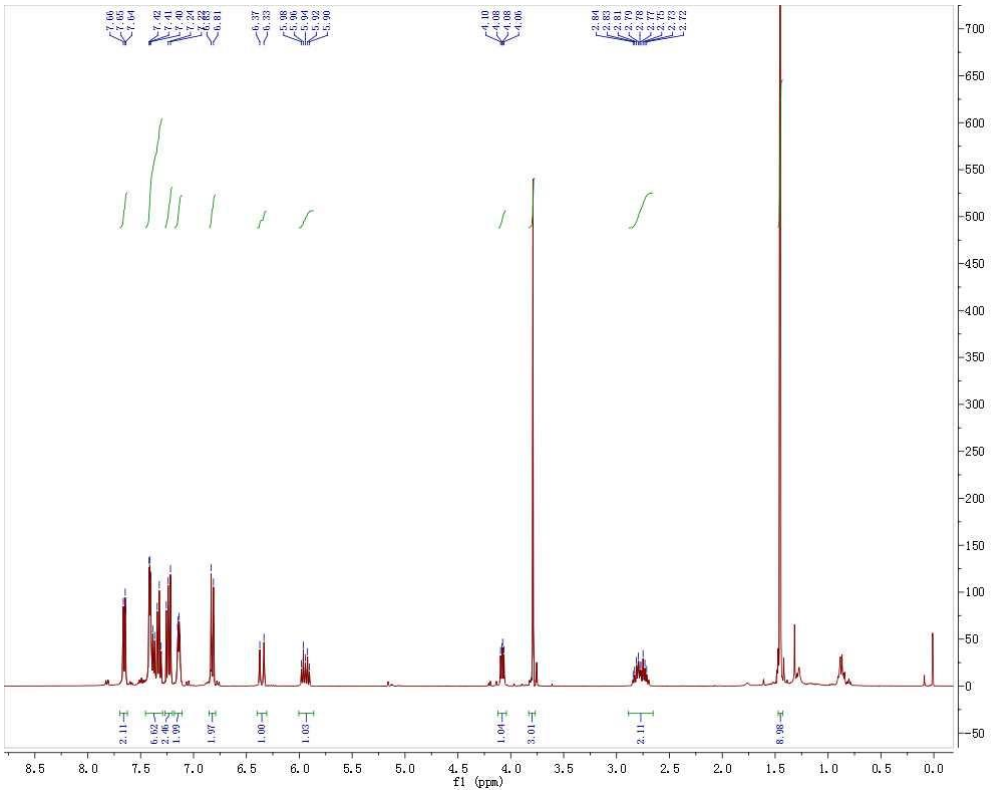
PeakTable

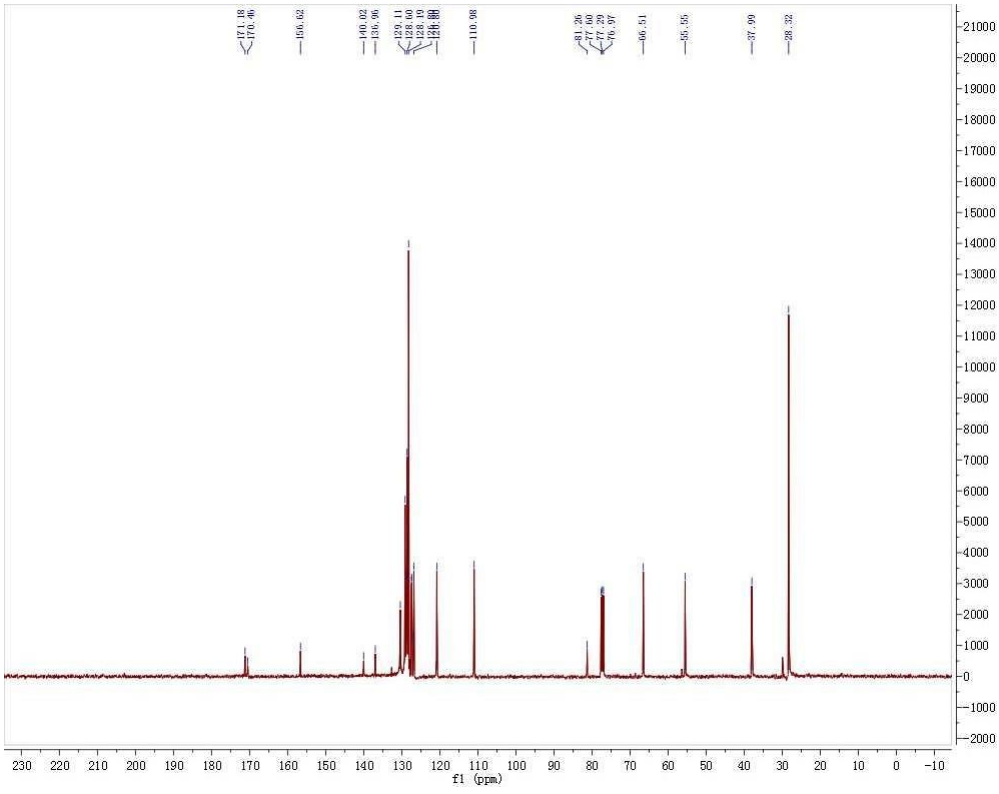
Detector A Ch1 254nm

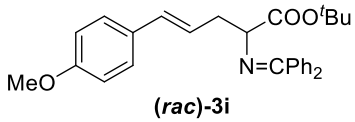
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.609	19775702	2431478	96.944	97.017
2	5.224	623443	74771	3.056	2.983
Total		20399145	2506248	100.000	100.000



(*S*)-3i







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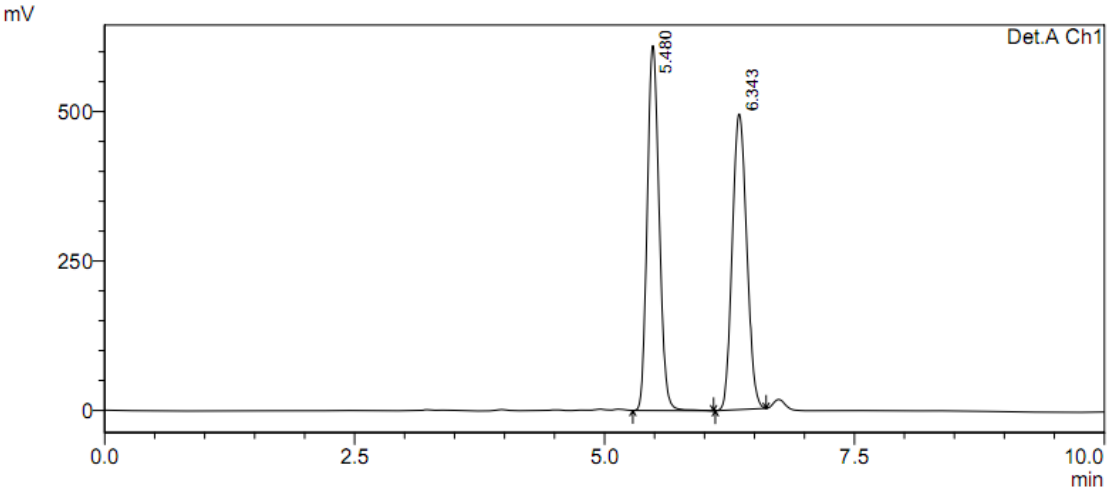
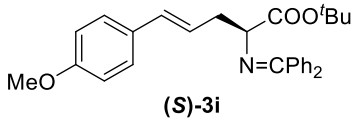


1 Det.A Ch1/254nm

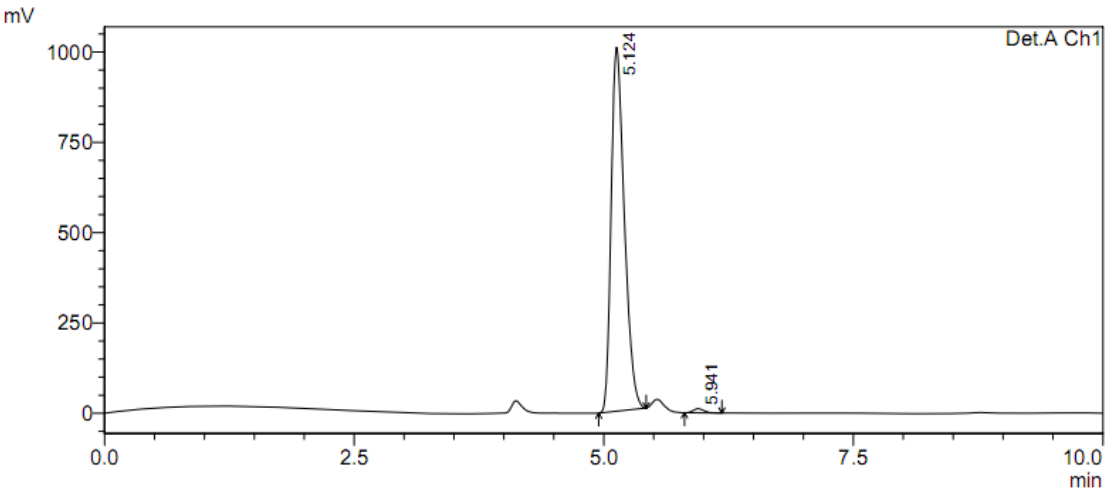
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.480	5061359	610746	50.398	55.244
2	6.343	4981400	494804	49.602	44.756
Total		10042759	1105551	100.000	100.000



(*S*)-3i

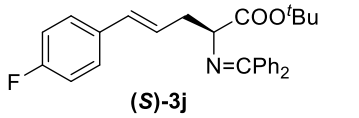


1 Det.A Ch1/254nm

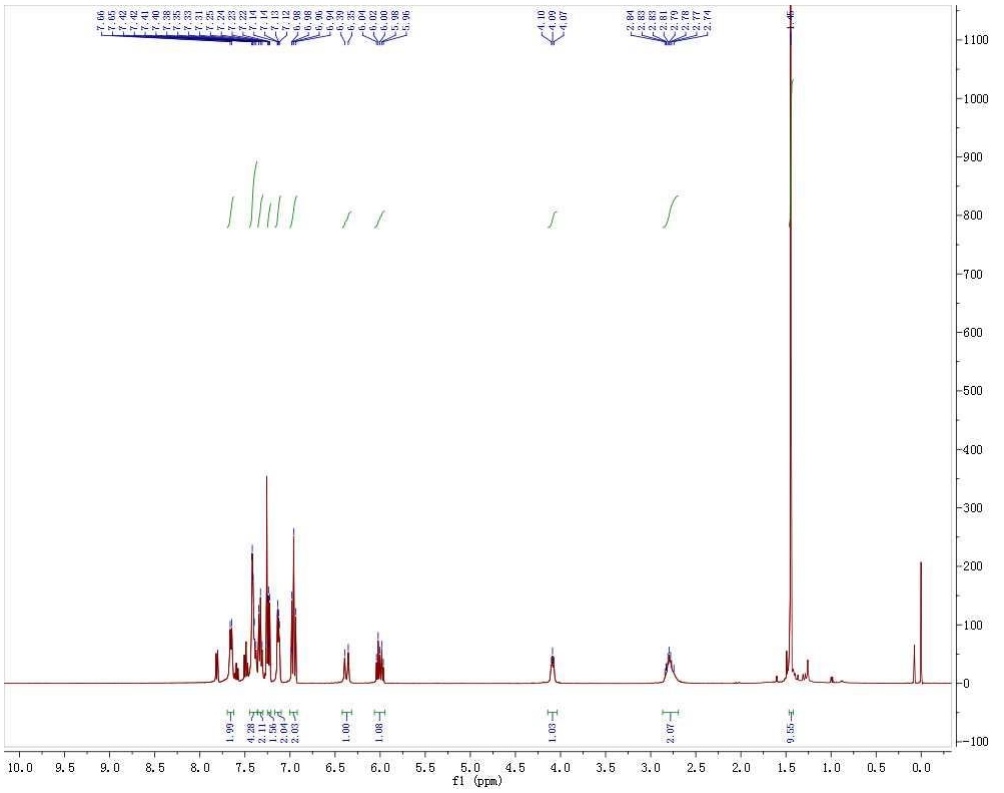
PeakTable

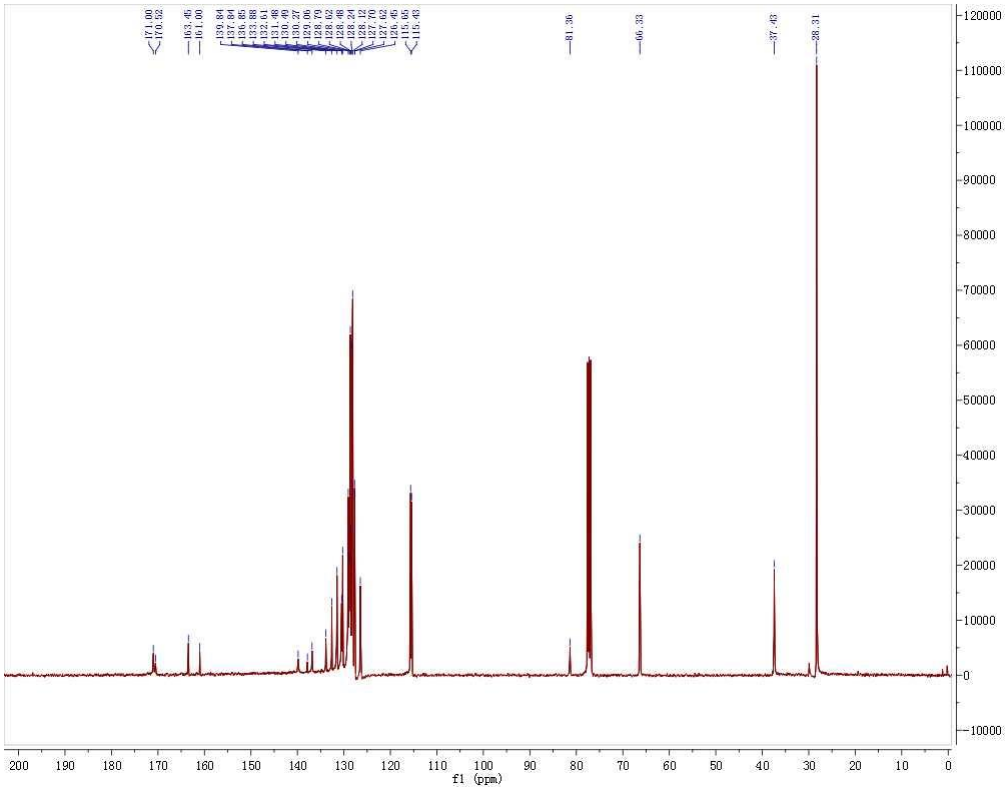
Detector A Ch1 254nm

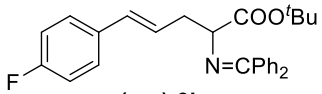
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.124	9258633	1007433	99.071	98.855
2	5.941	86814	11670	0.929	1.145
Total		9345447	1019103	100.000	100.000



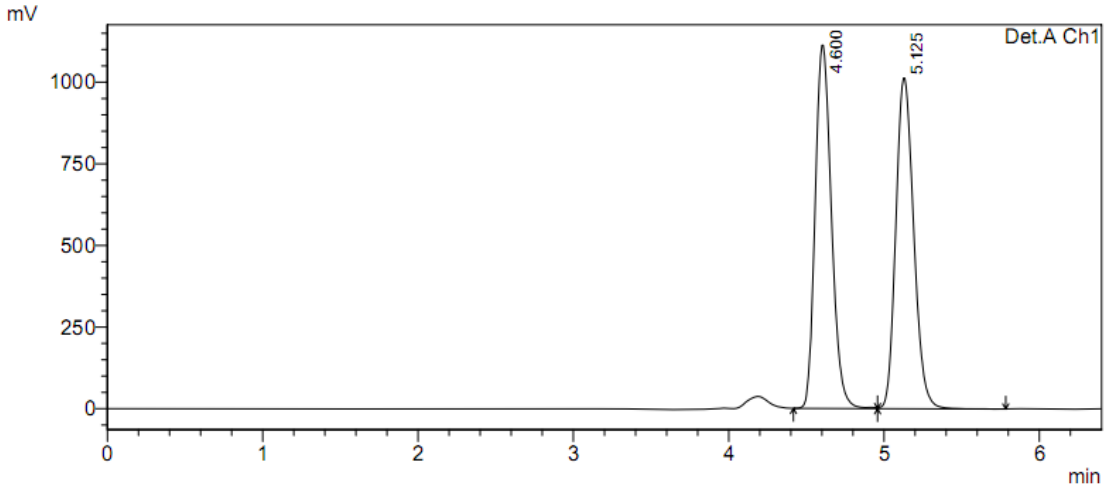
(*S*)-3j







(*rac*)-3j

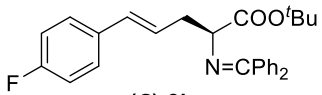


1 Det.A Ch1/254nm

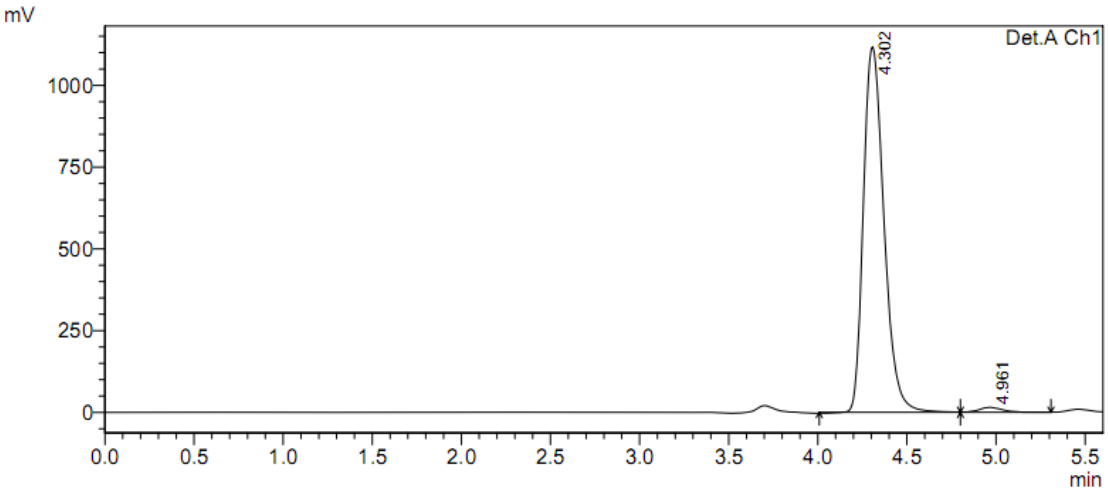
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.600	8104663	1112221	50.005	52.346
2	5.125	8102900	1012548	49.995	47.654
Total		16207563	2124769	100.000	100.000



(*S*)-3j

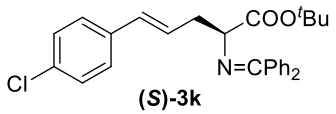


1 Det.A Ch1/254nm

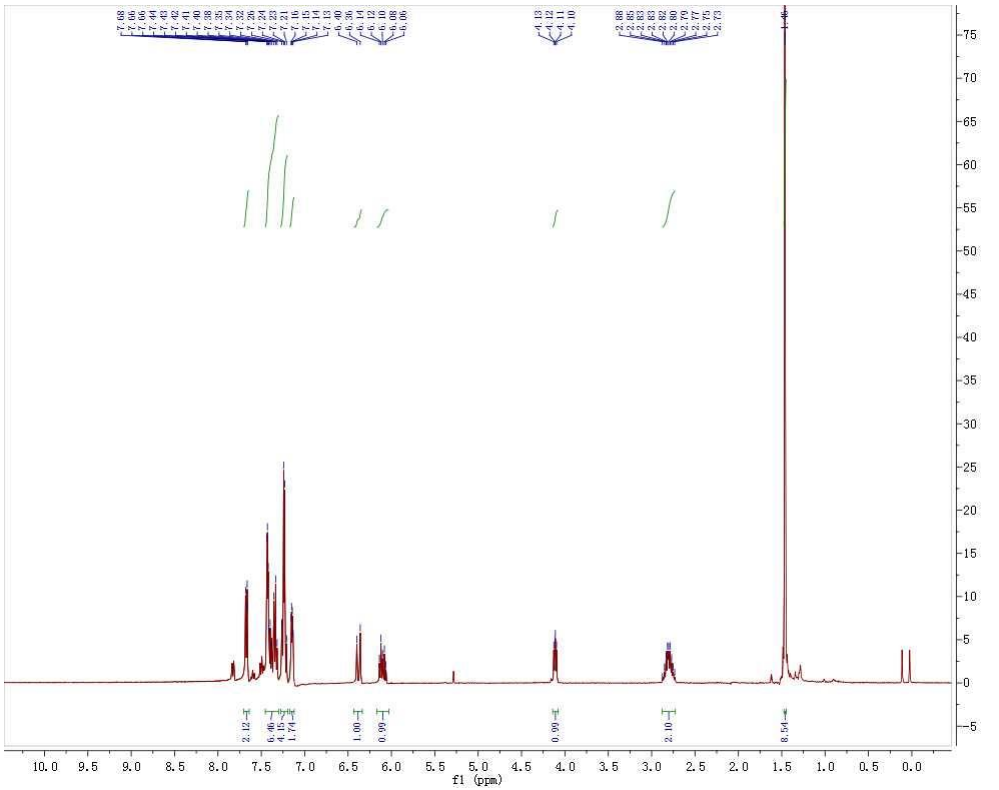
PeakTable

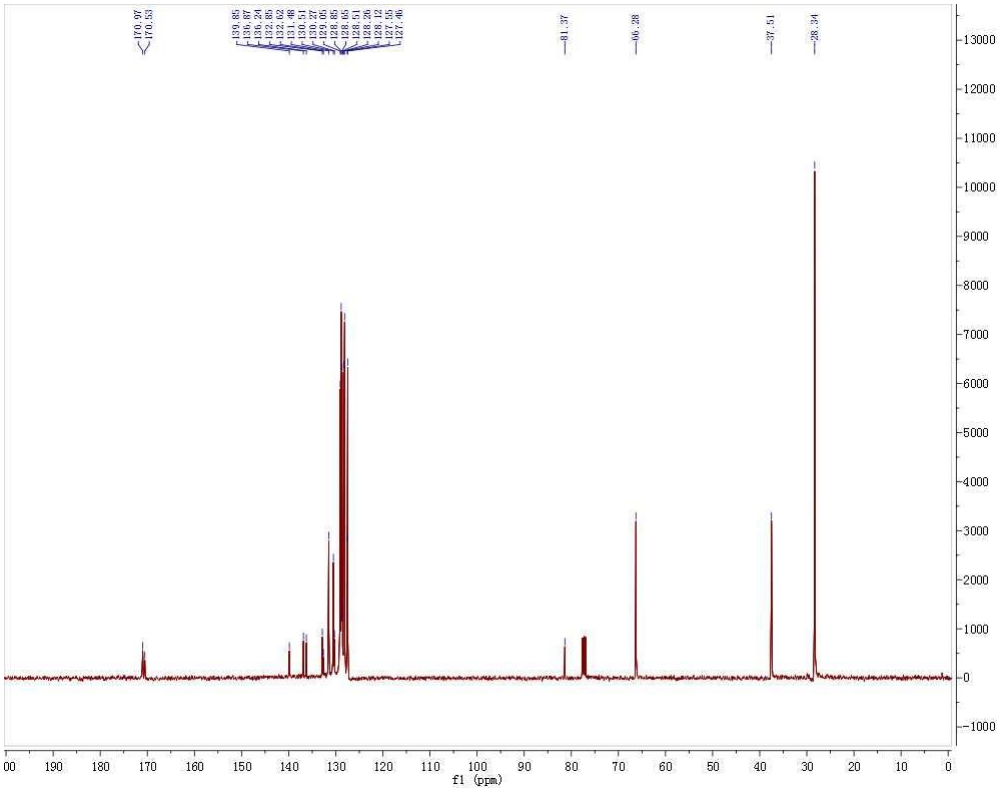
Detector A Ch1 254nm

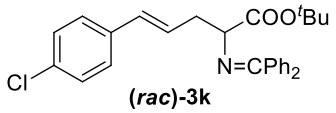
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.302	8963748	1118776	98.498	98.668
2	4.961	136731	15100	1.502	1.332
Total		9100479	1133876	100.000	100.000



(*S*)-3k







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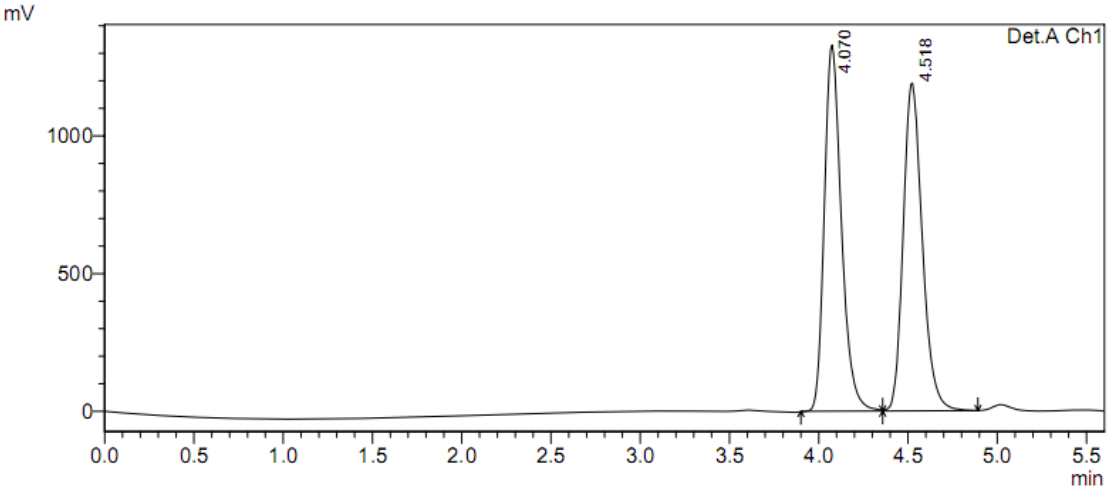
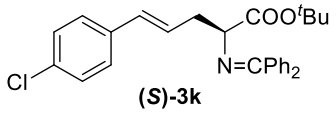


1 Det.A Ch1/254nr

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.070	8851397	1329798	50.006	52.775
2	4.518	8849422	1189939	49.994	47.225
Total		17700819	2519737	100.000	100.000



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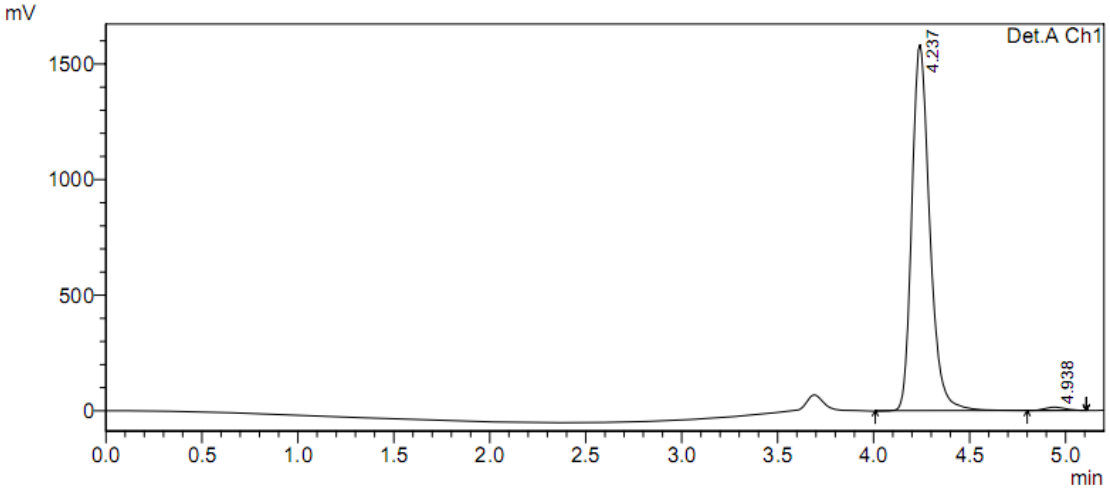
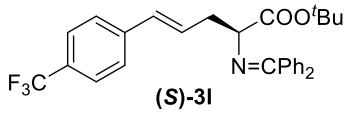


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.237	10270085	1583455	99.002	99.096
2	4.938	103521	14442	0.998	0.904
Total		10373605	1597896	100.000	100.000



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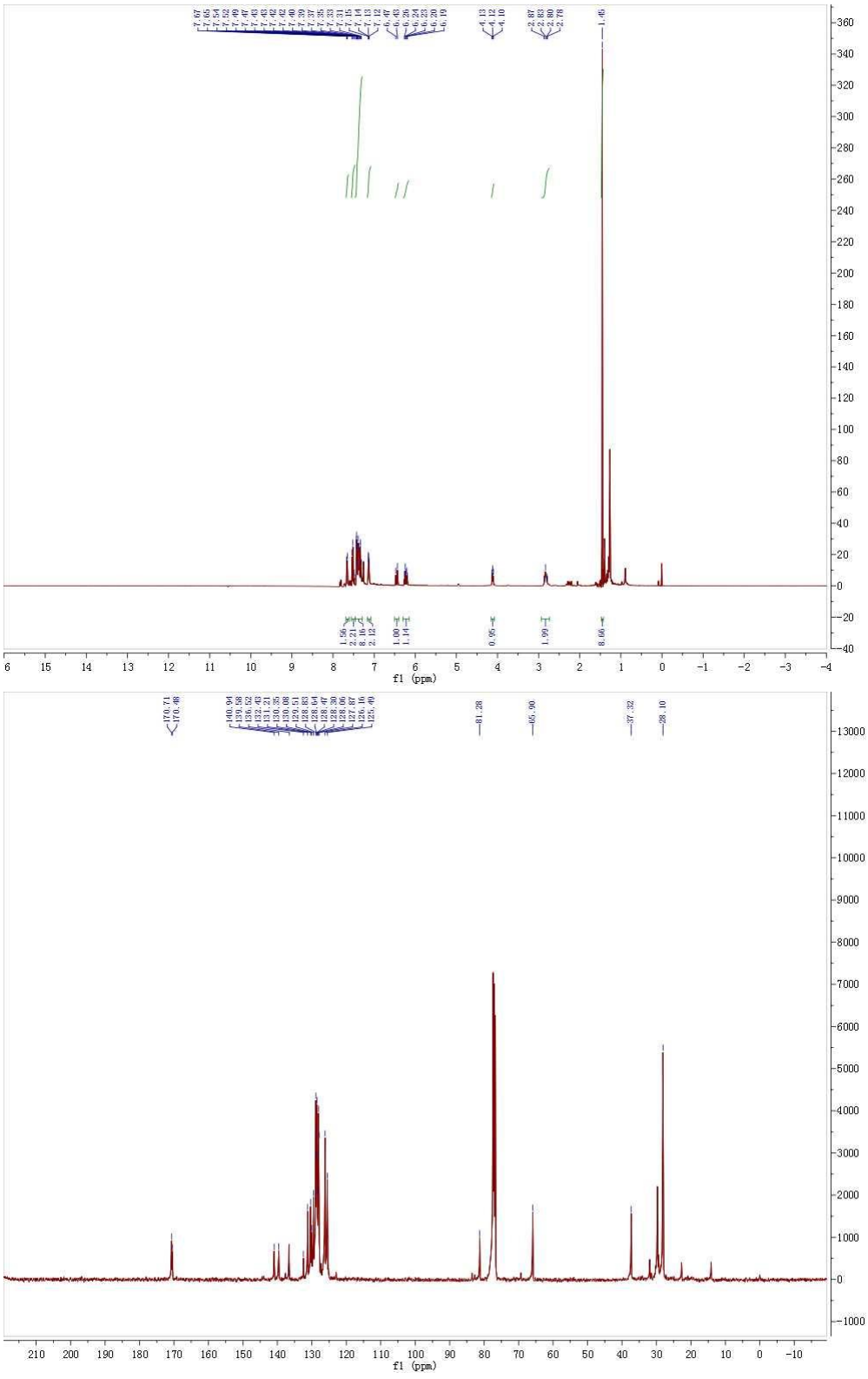

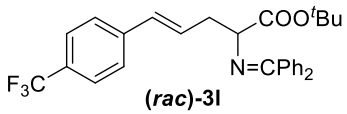

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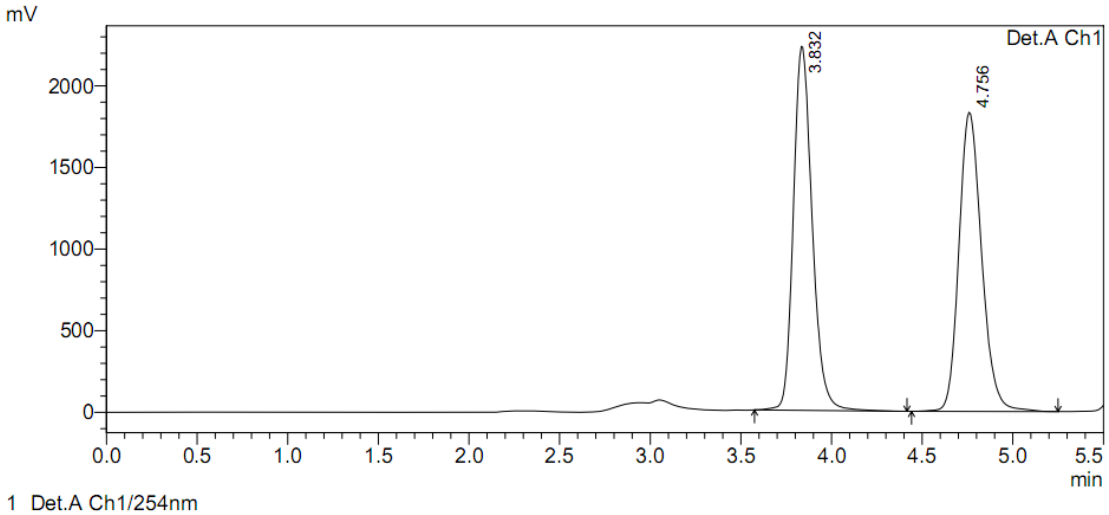
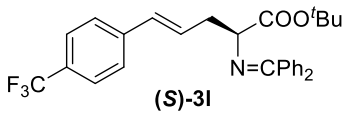


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.832	16109585	2230940	50.228	54.903
2	4.756	15963067	1832478	49.772	45.097
Total		32072652	4063418	100.000	100.000



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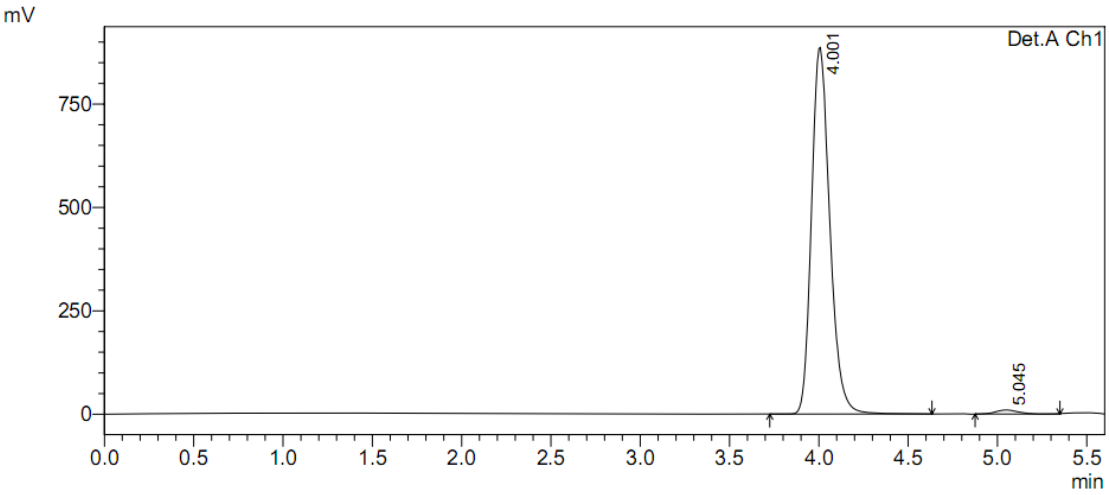
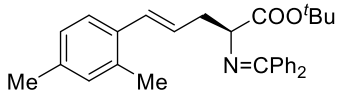


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.001	6343468	887224	98.688	98.921
2	5.045	84327	9673	1.312	1.079
Total		6427795	896898	100.000	100.000



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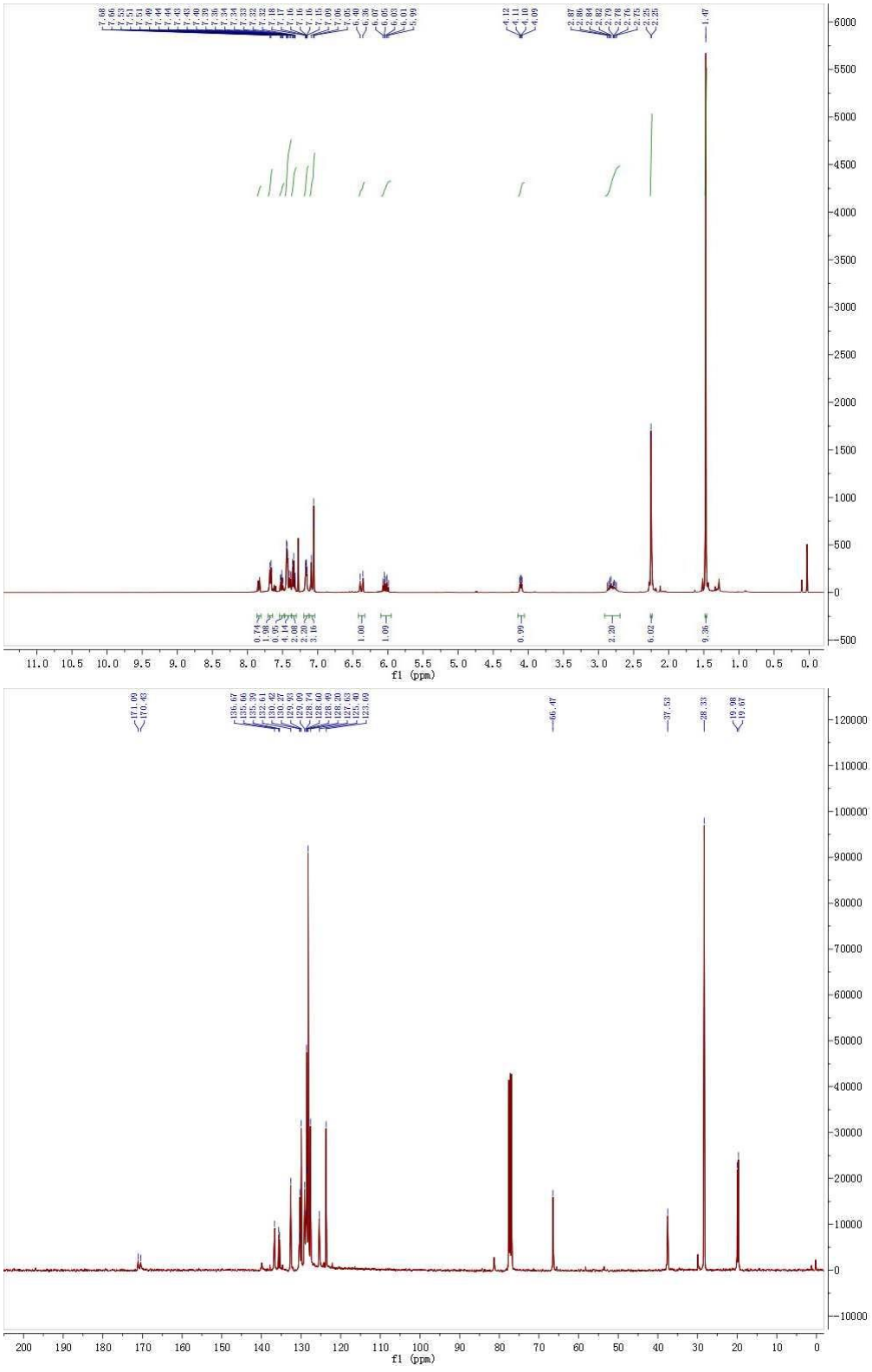

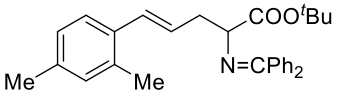

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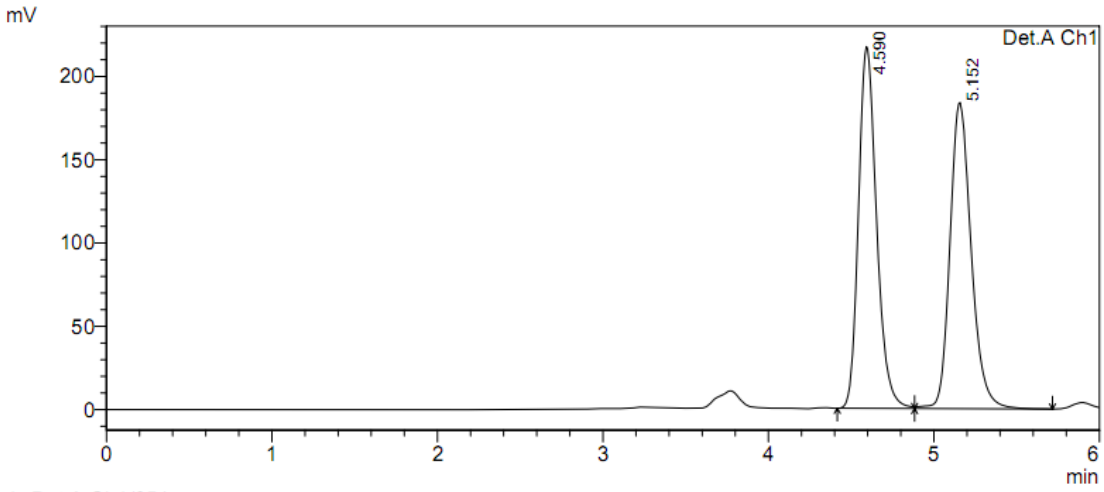
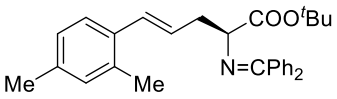


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.590	1648790	217241	50.079	54.170
2	5.152	1643563	183792	49.921	45.830
Total		3292353	401033	100.000	100.000



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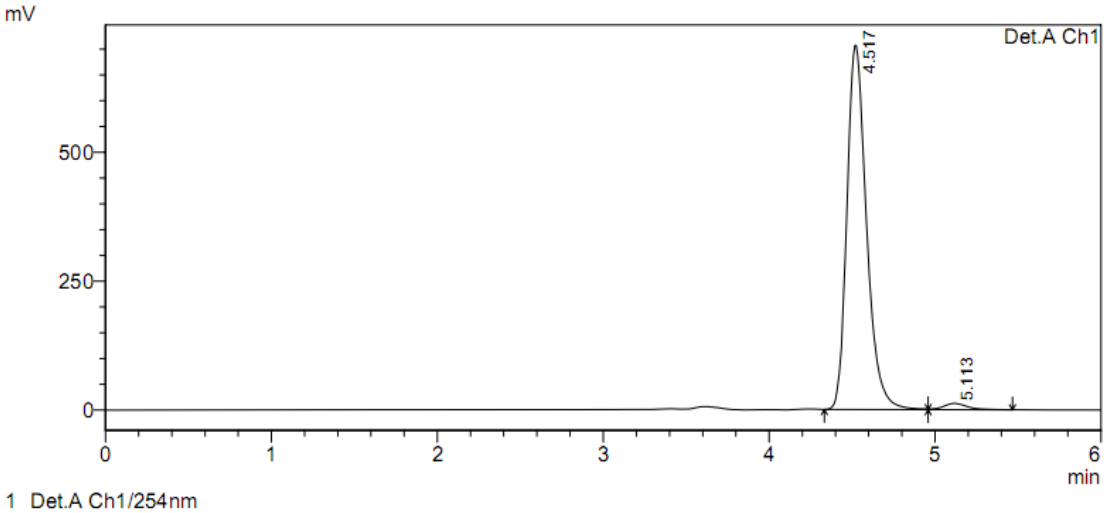
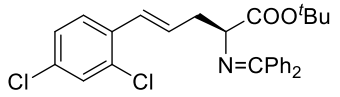


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.517	5811556	706309	97.909	98.292
2	5.113	124142	12277	2.091	1.708
Total		5935698	718586	100.000	100.000



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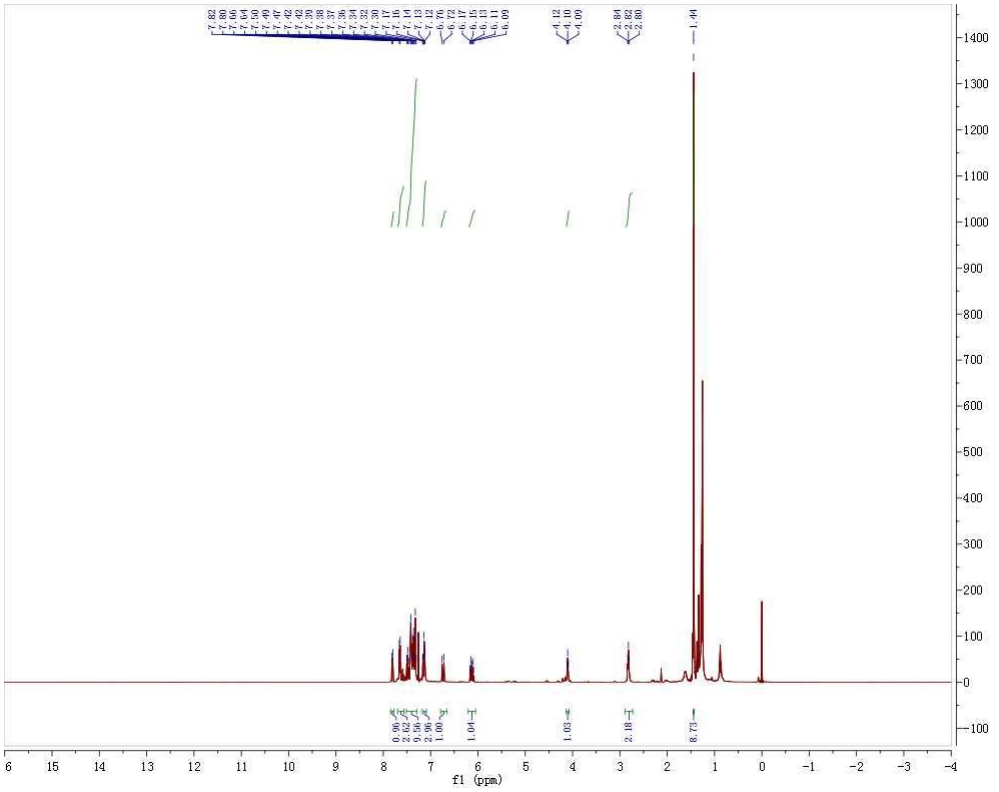

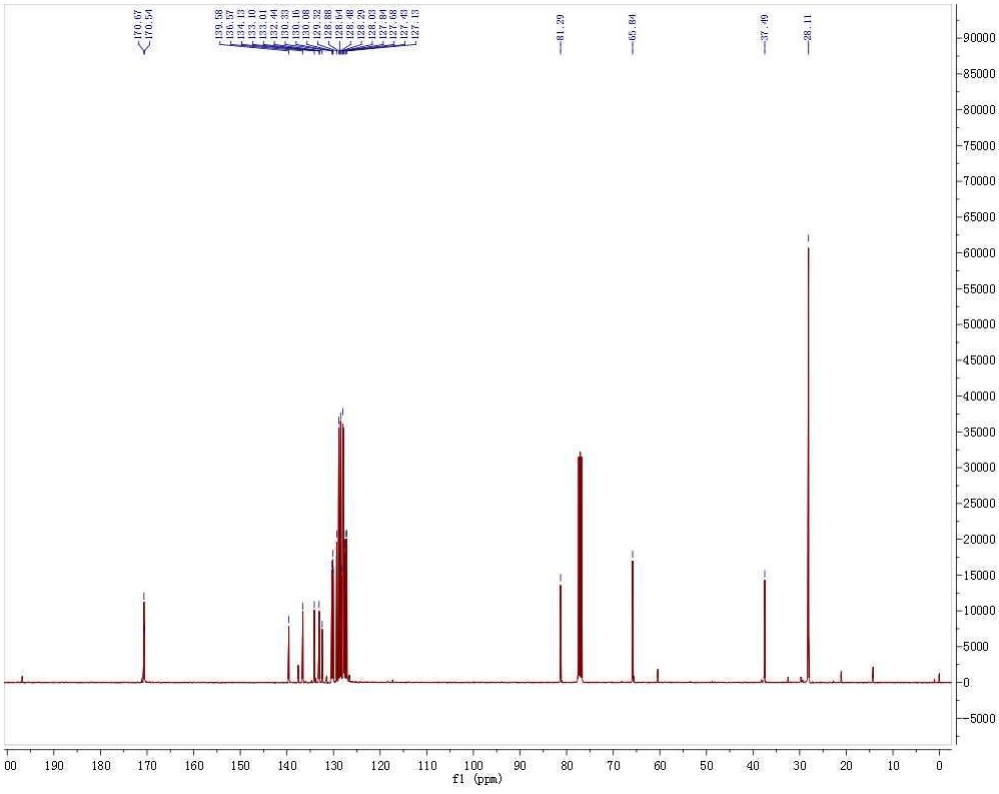

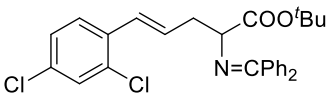

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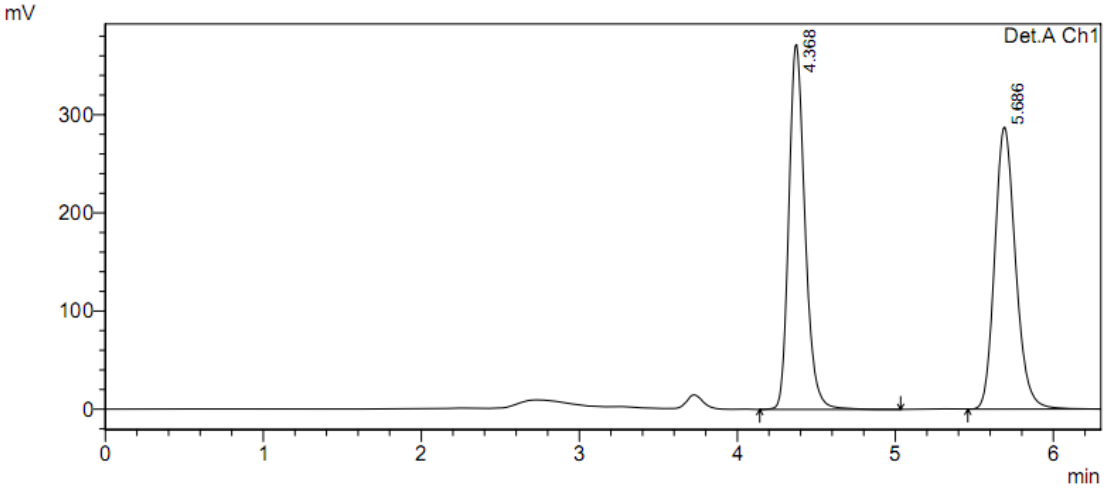
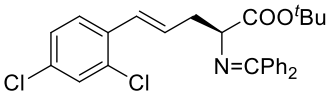


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.368	2649668	371971	50.105	56.412
2	5.686	2638584	287412	49.895	43.588
Total		5288252	659383	100.000	100.000



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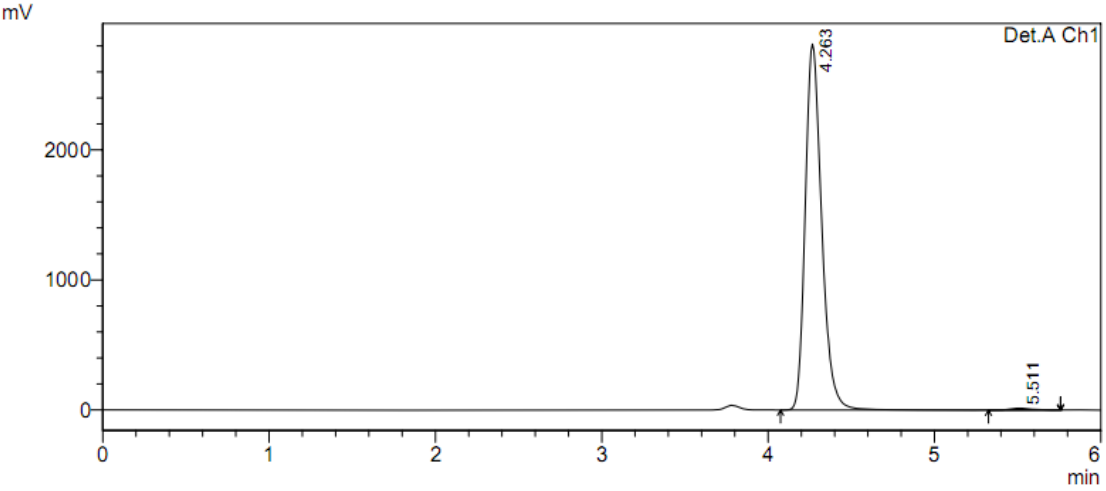
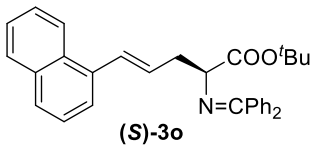


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.263	19323773	2816342	99.338	99.477
2	5.511	128782	14815	0.662	0.523
Total		19452555	2831157	100.000	100.000



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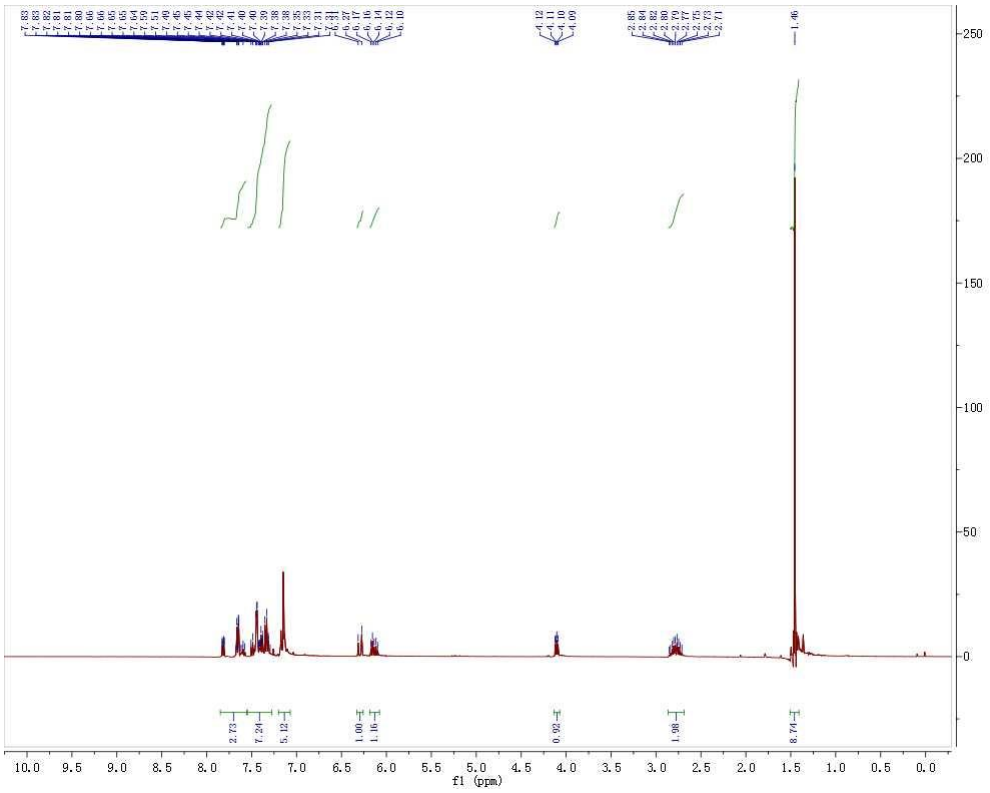

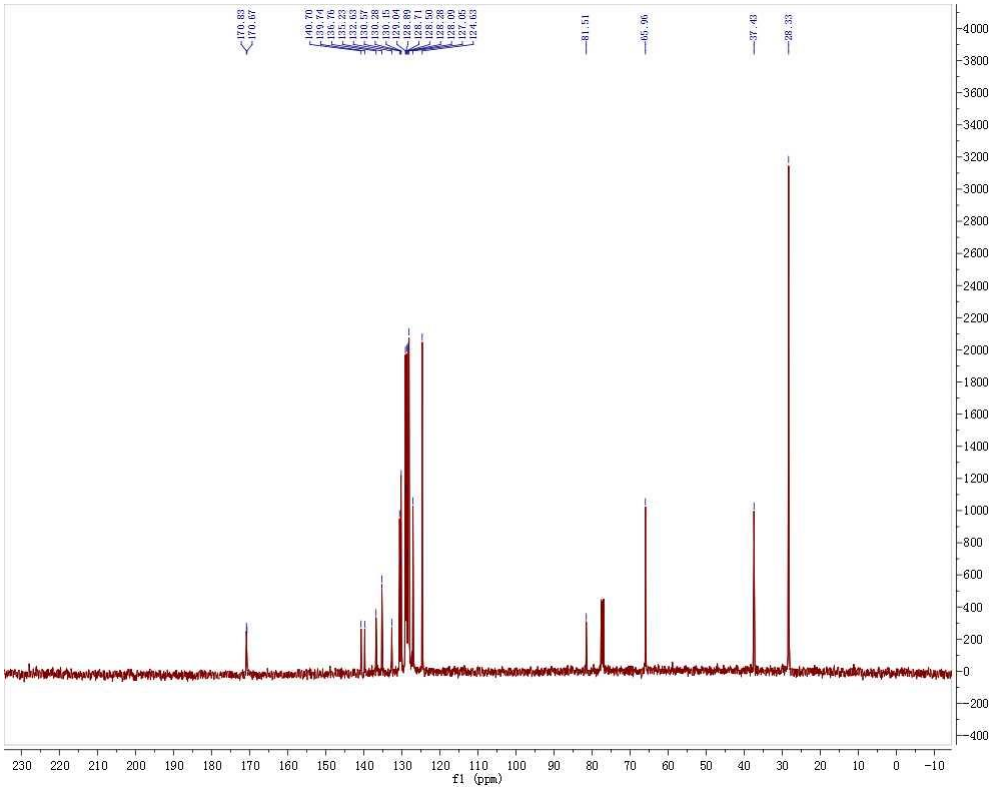

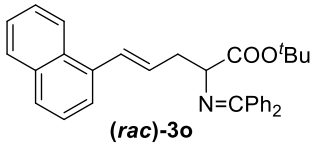

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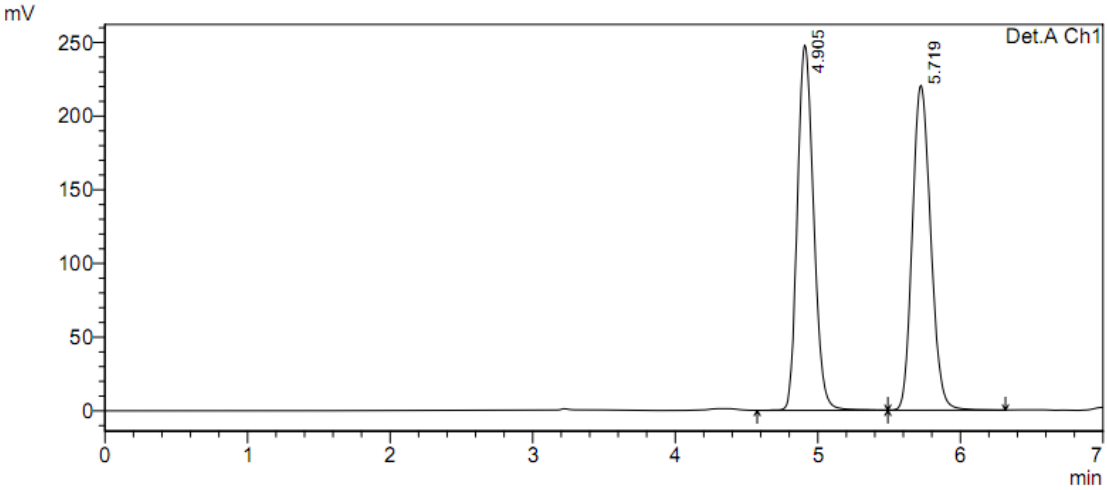
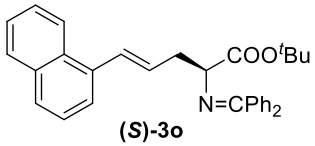


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.905	1966101	247974	49.920	52.938
2	5.719	1972372	220448	50.080	47.062
Total		3938473	468423	100.000	100.000



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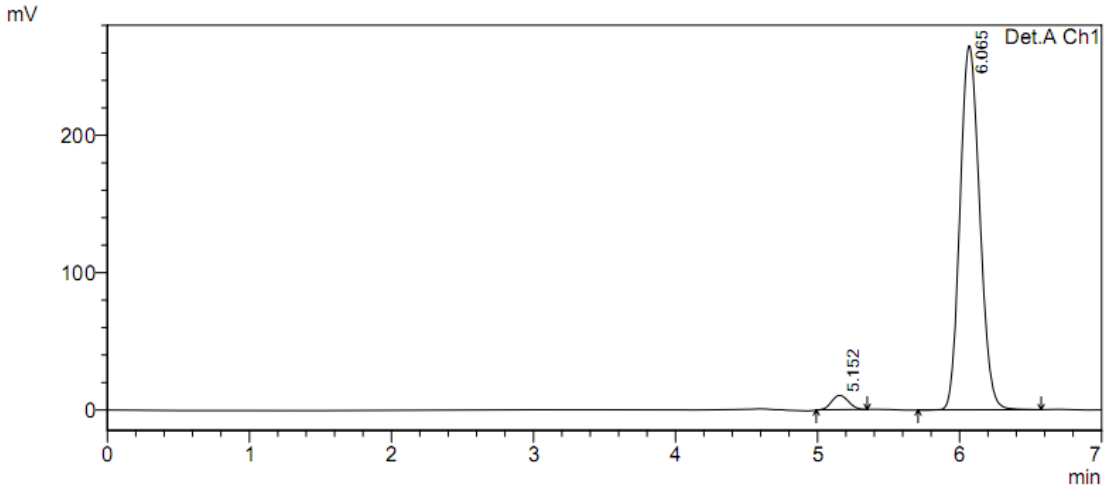
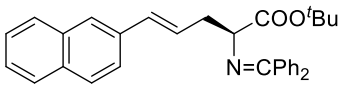


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.152	85893	10423	3.258	3.781
2	6.065	2550121	265222	96.742	96.219
Total		2636015	275645	100.000	100.000



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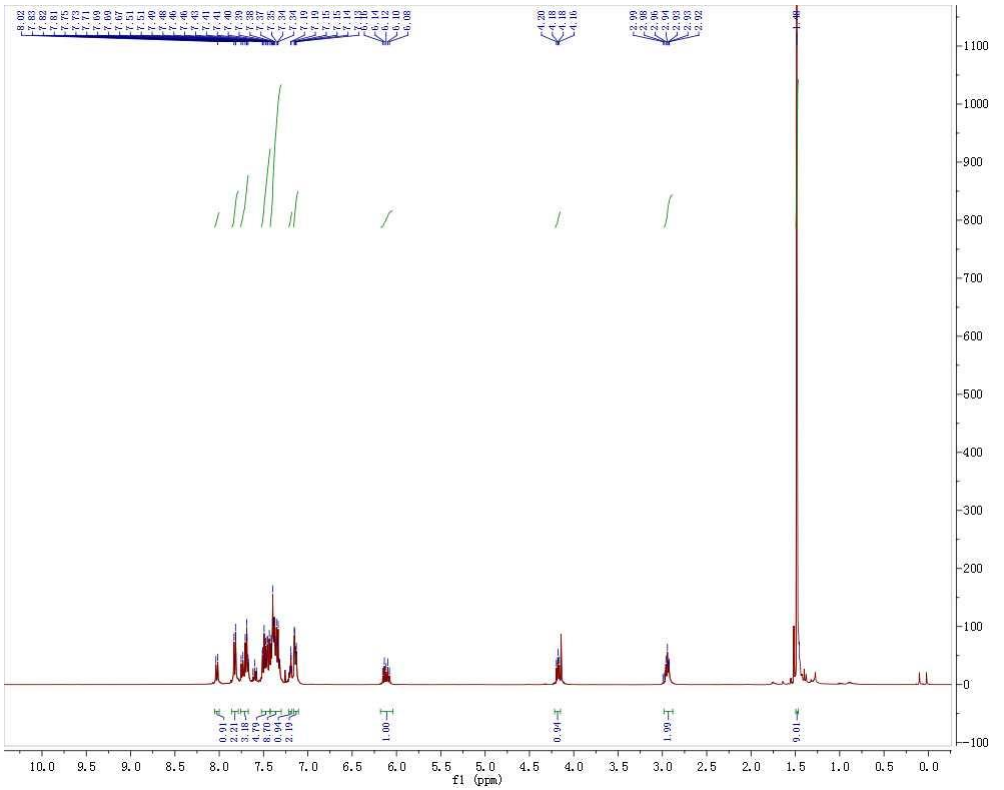

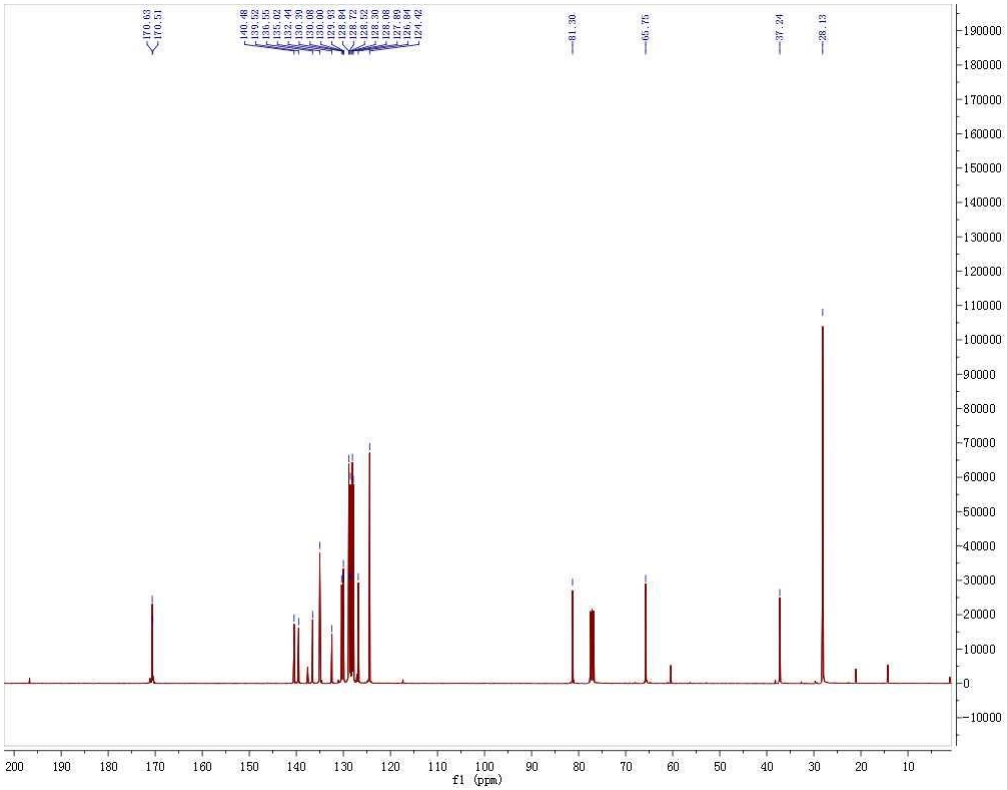

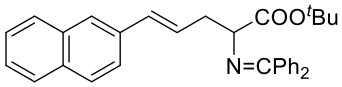

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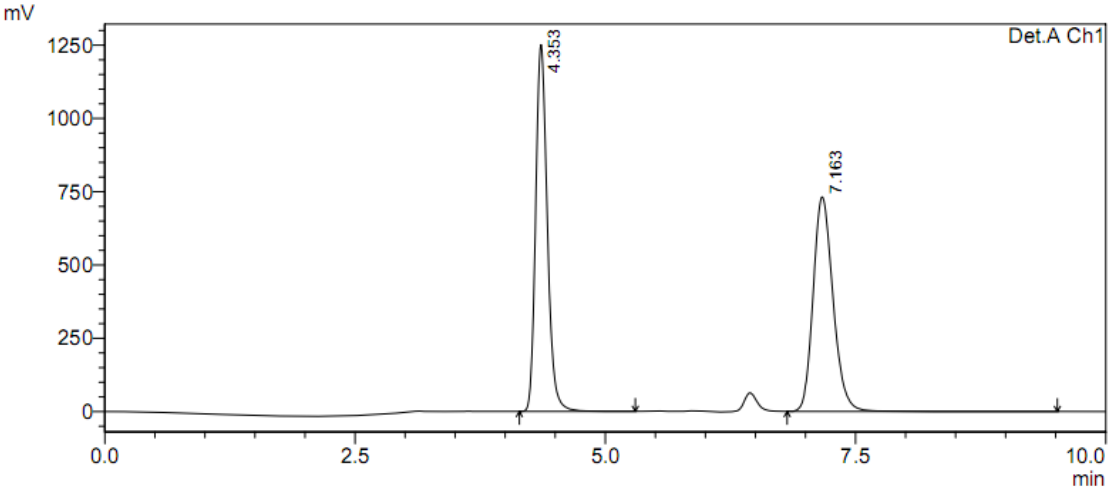
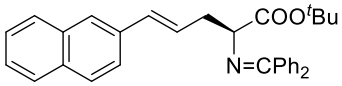


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.353	10116010	1251684	50.002	63.096
2	7.163	10115080	732101	49.998	36.904
Total		20231090	1983785	100.000	100.000



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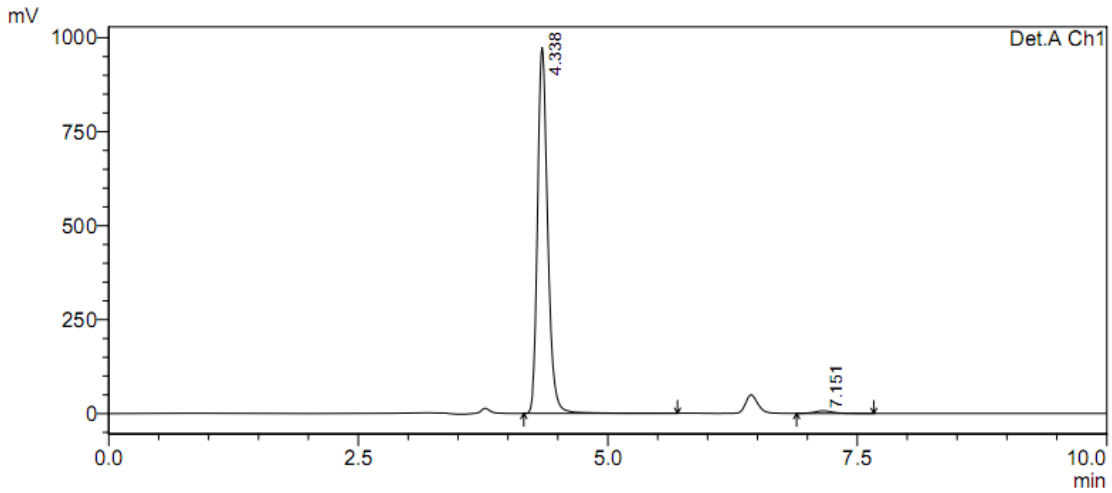
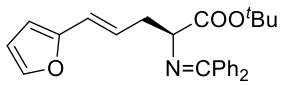


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.338	6904900	973865	98.781	99.306
2	7.151	85235	6803	1.219	0.694
Total		6990135	980668	100.000	100.000



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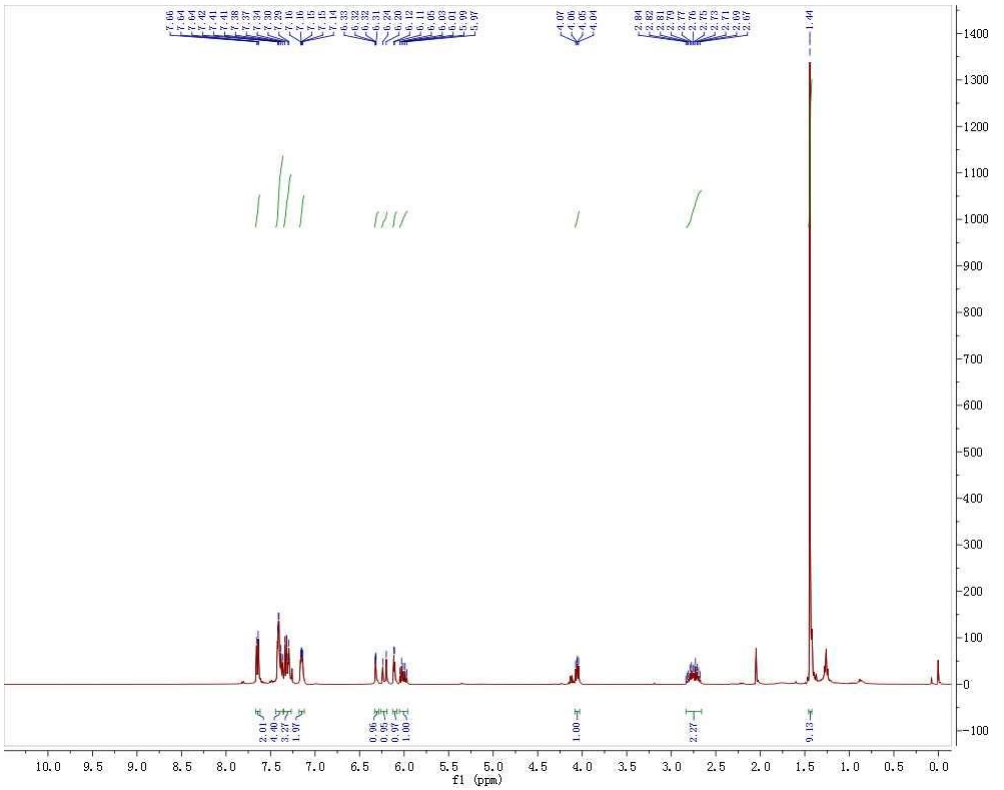

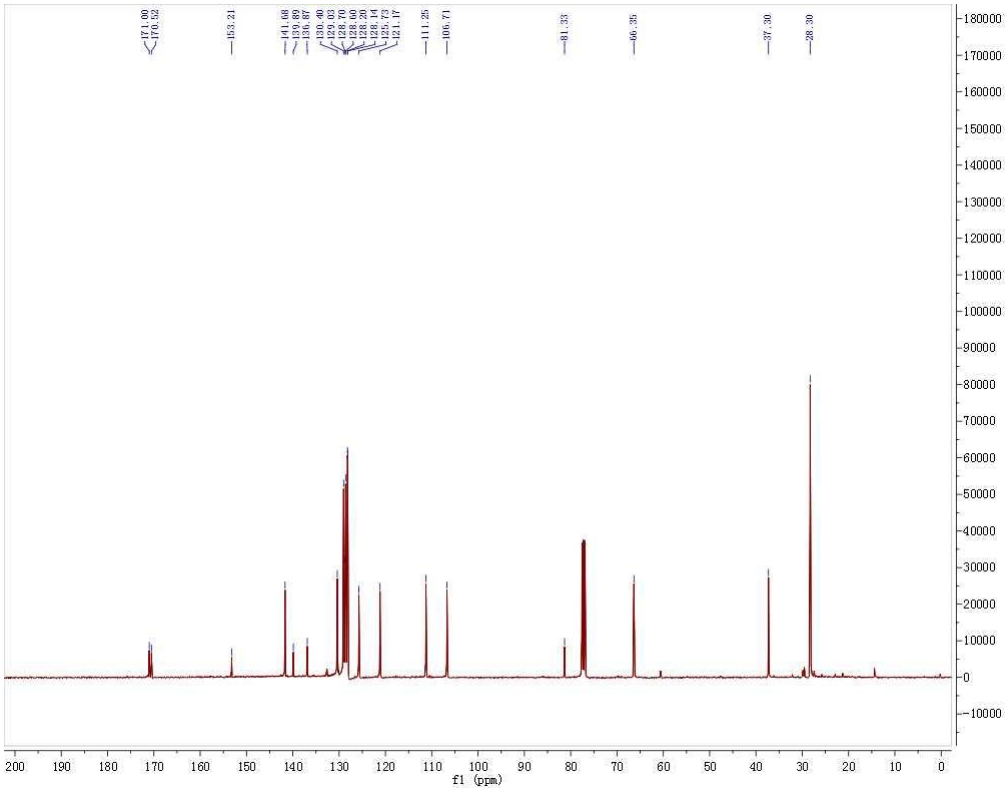

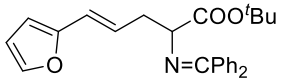

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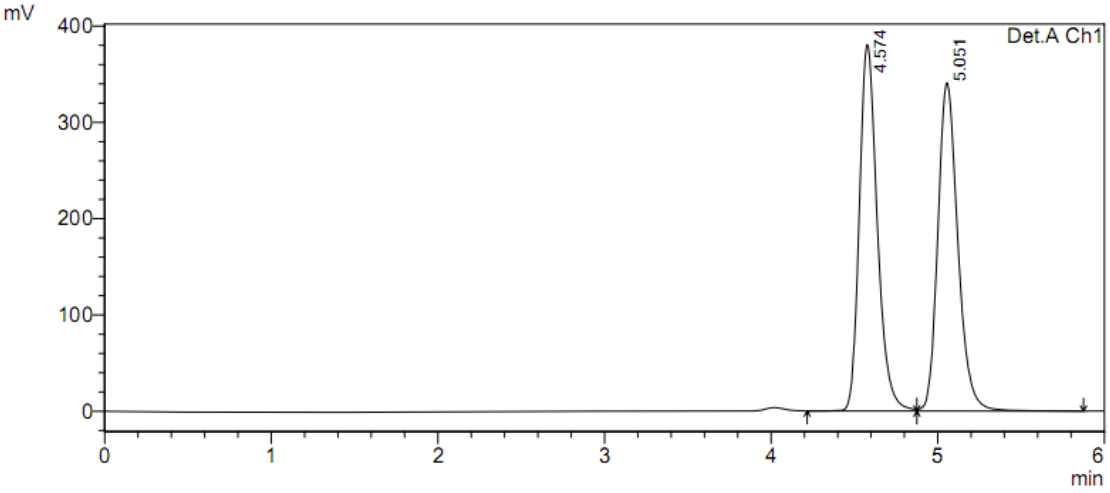
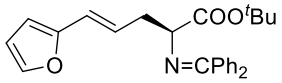


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.574	2847167	380568	50.015	52.746
2	5.051	2845463	340944	49.985	47.254
Total		5692630	721513	100.000	100.000



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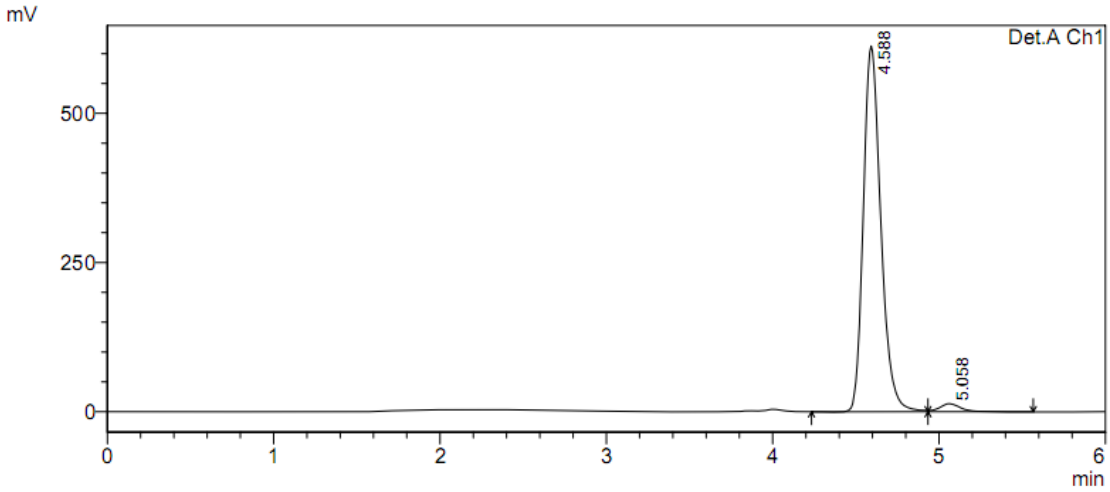
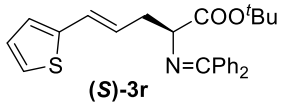


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.588	4484162	613077	97.471	97.855
2	5.058	116349	13438	2.529	2.145
Total		4600512	626515	100.000	100.000



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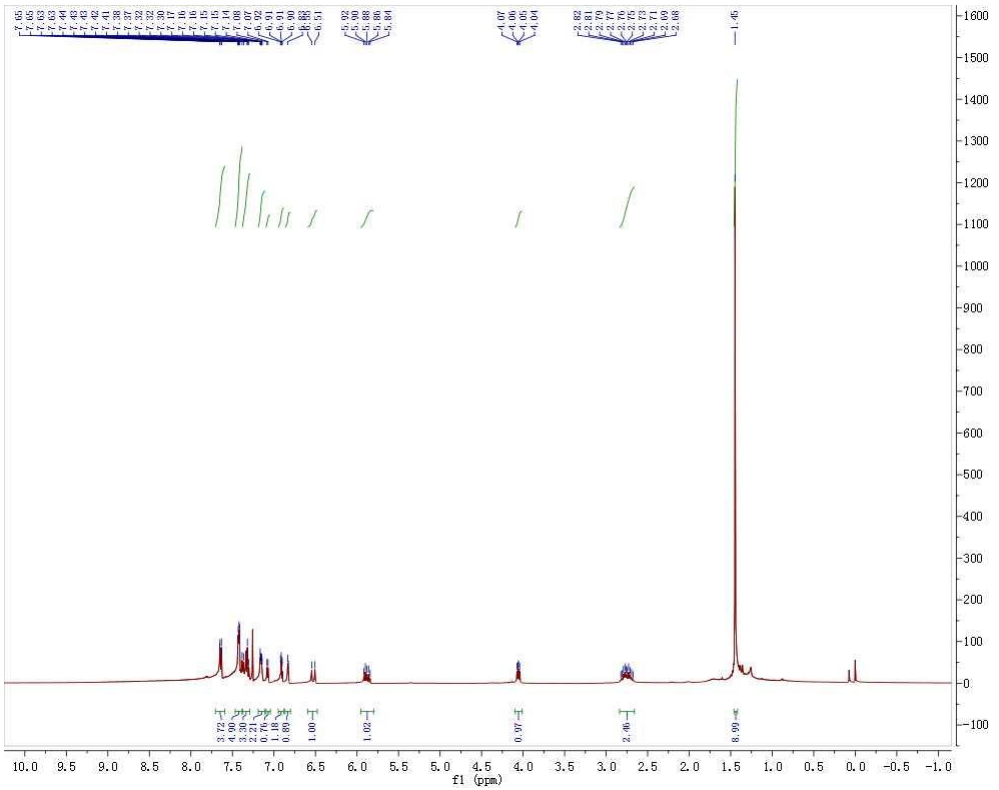

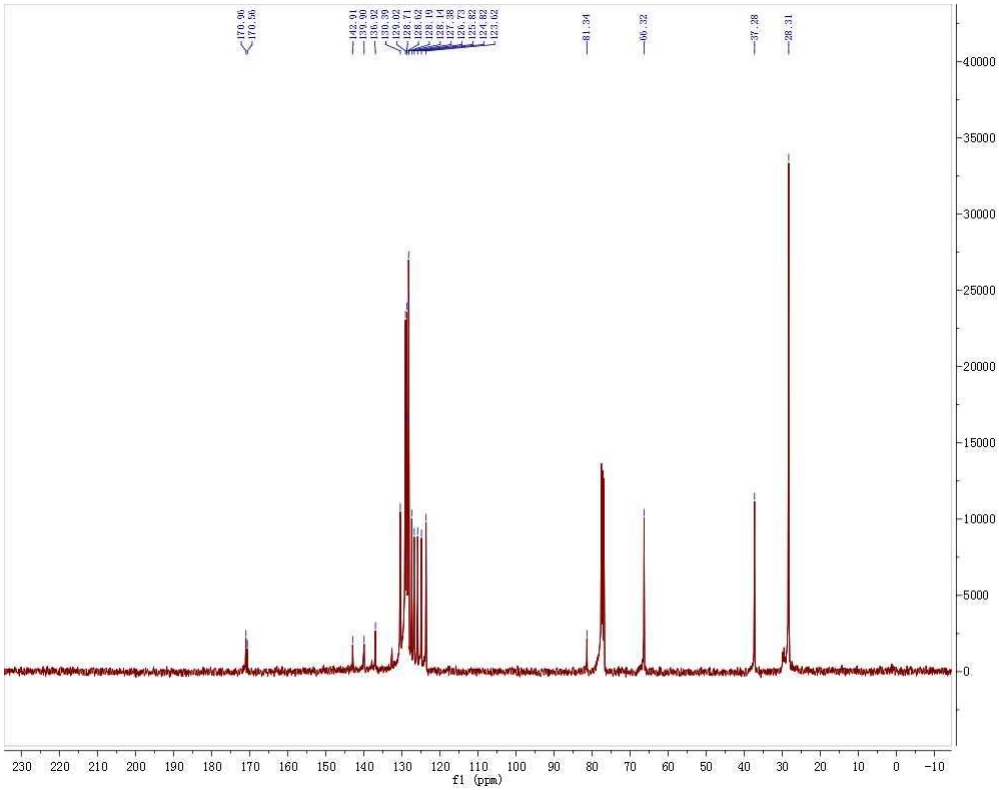

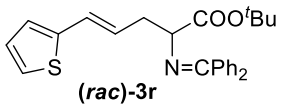

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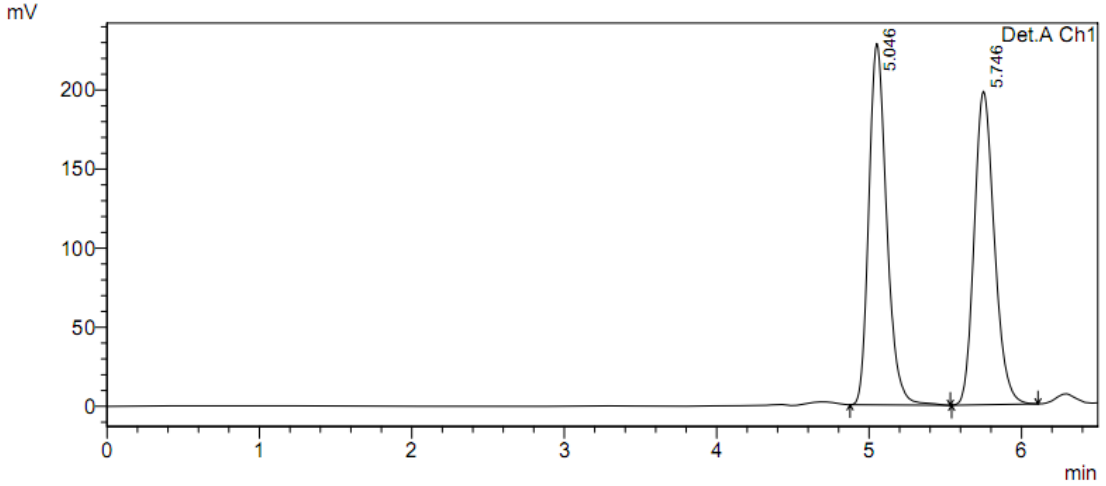
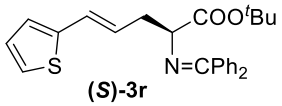


1 Det.A Ch1/254nm

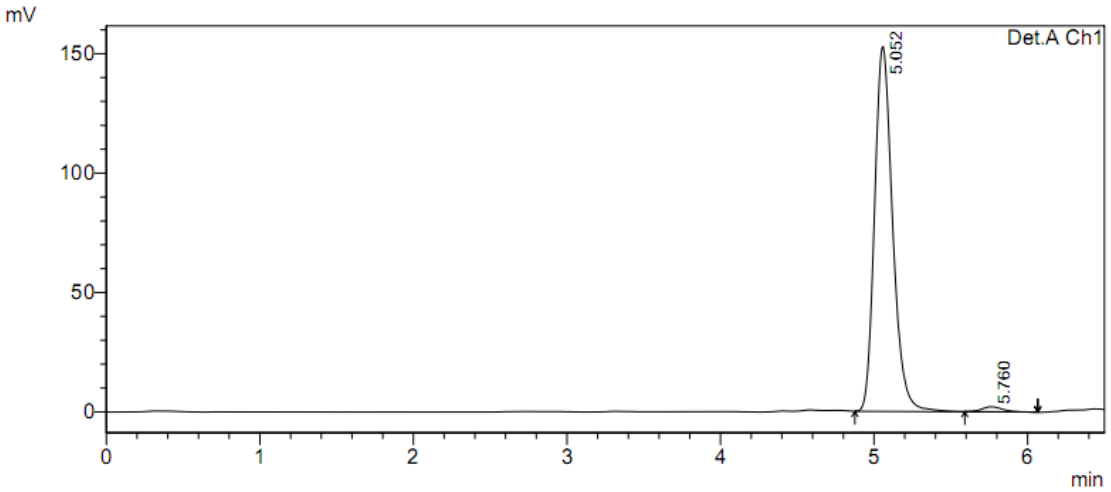
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.046	1854177	228592	50.434	53.549
2	5.746	1822269	198289	49.566	46.451
Total		3676445	426881	100.000	100.000



(*S*)-3r

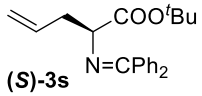


1 Det.A Ch1/254nm

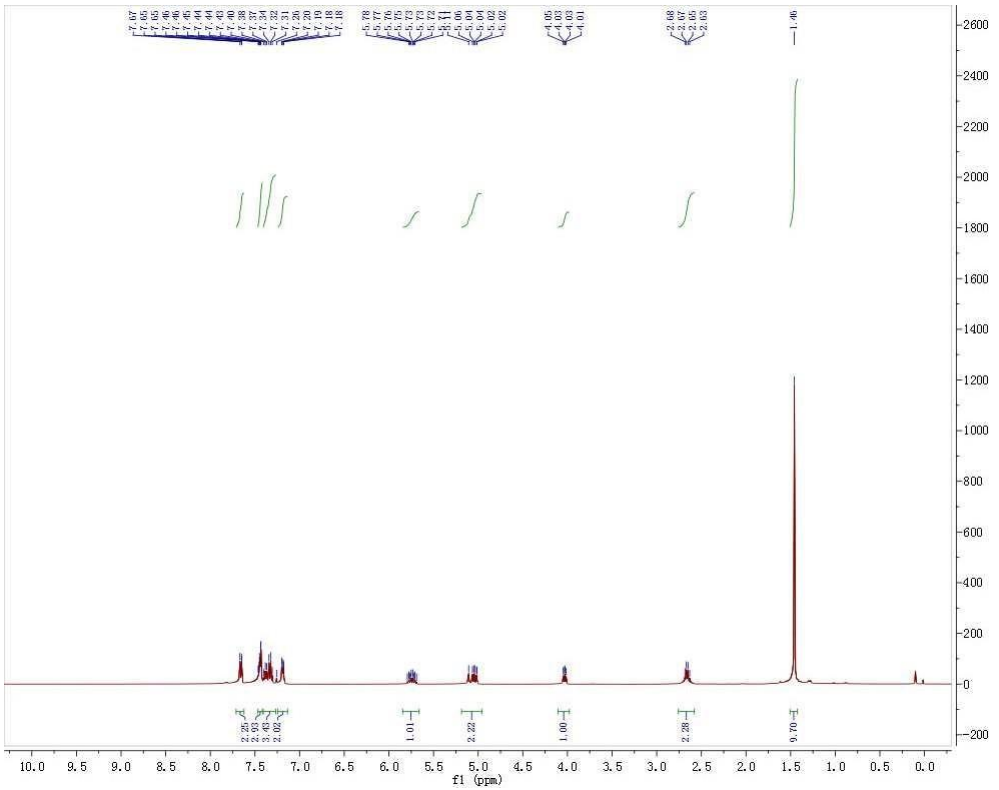
PeakTable

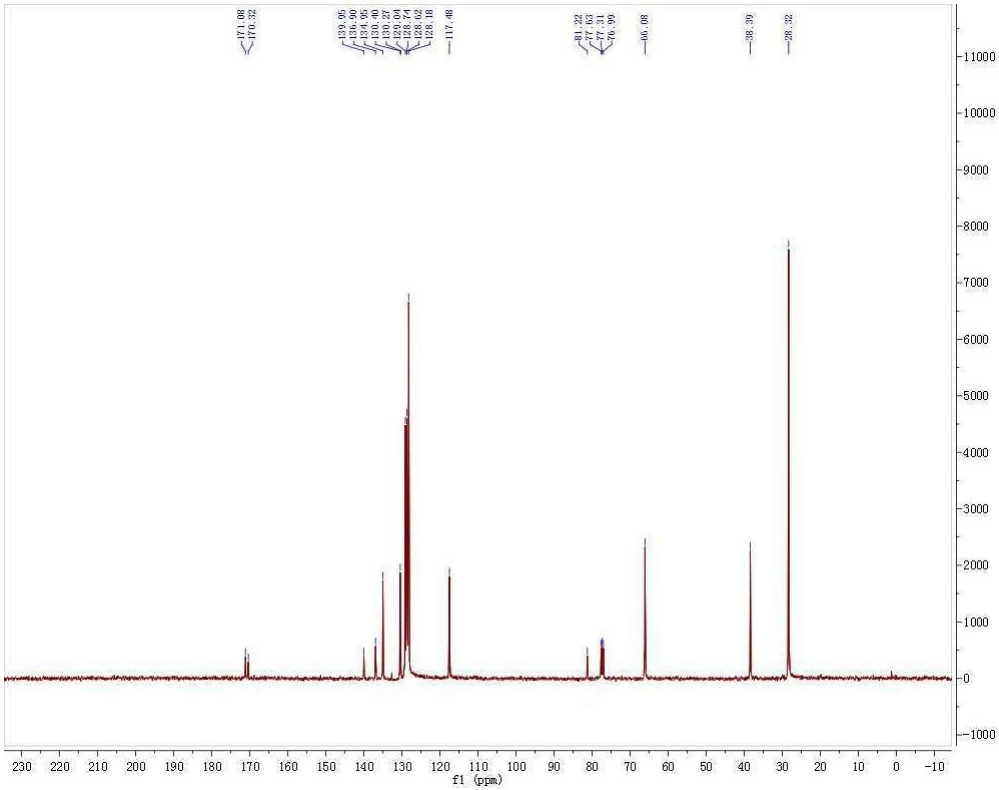
Detector A Ch1 254nm

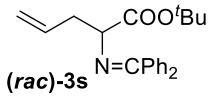
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.052	1247755	152874	98.502	98.661
2	5.760	18980	2075	1.498	1.339
Total		1266734	154949	100.000	100.000



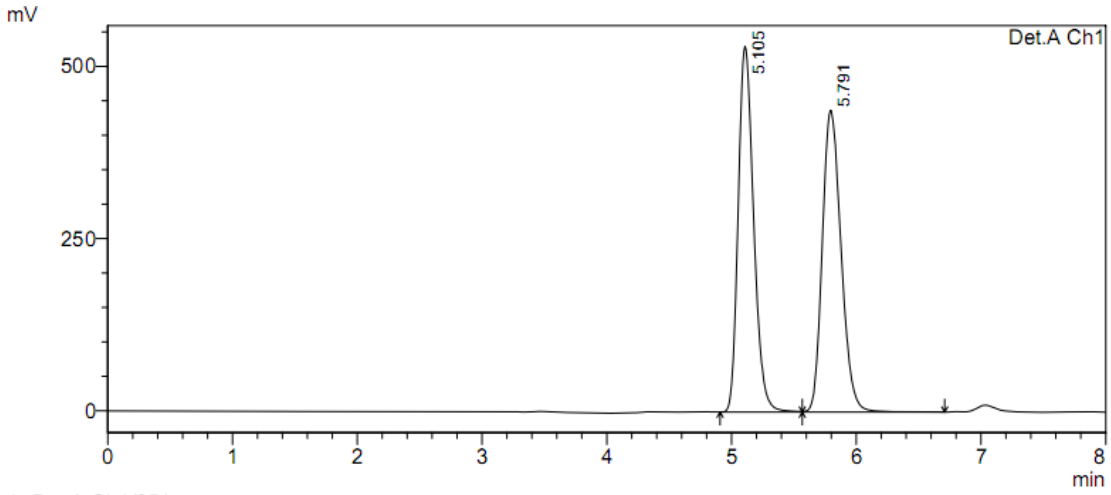
(*S*)-3s







(*rac*)-3s

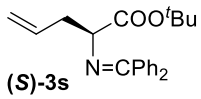


1 Det.A Ch1/254nm

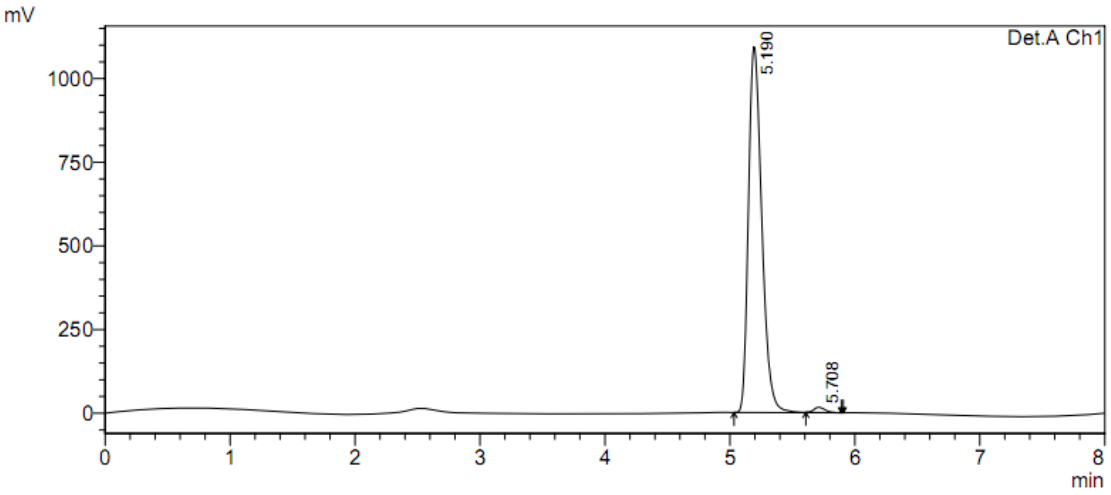
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.105	4568106	531311	49.912	54.824
2	5.791	4584173	437811	50.088	45.176
Total		9152279	969122	100.000	100.000



(*S*)-3s

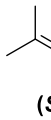


1 Det.A Ch1/254nm

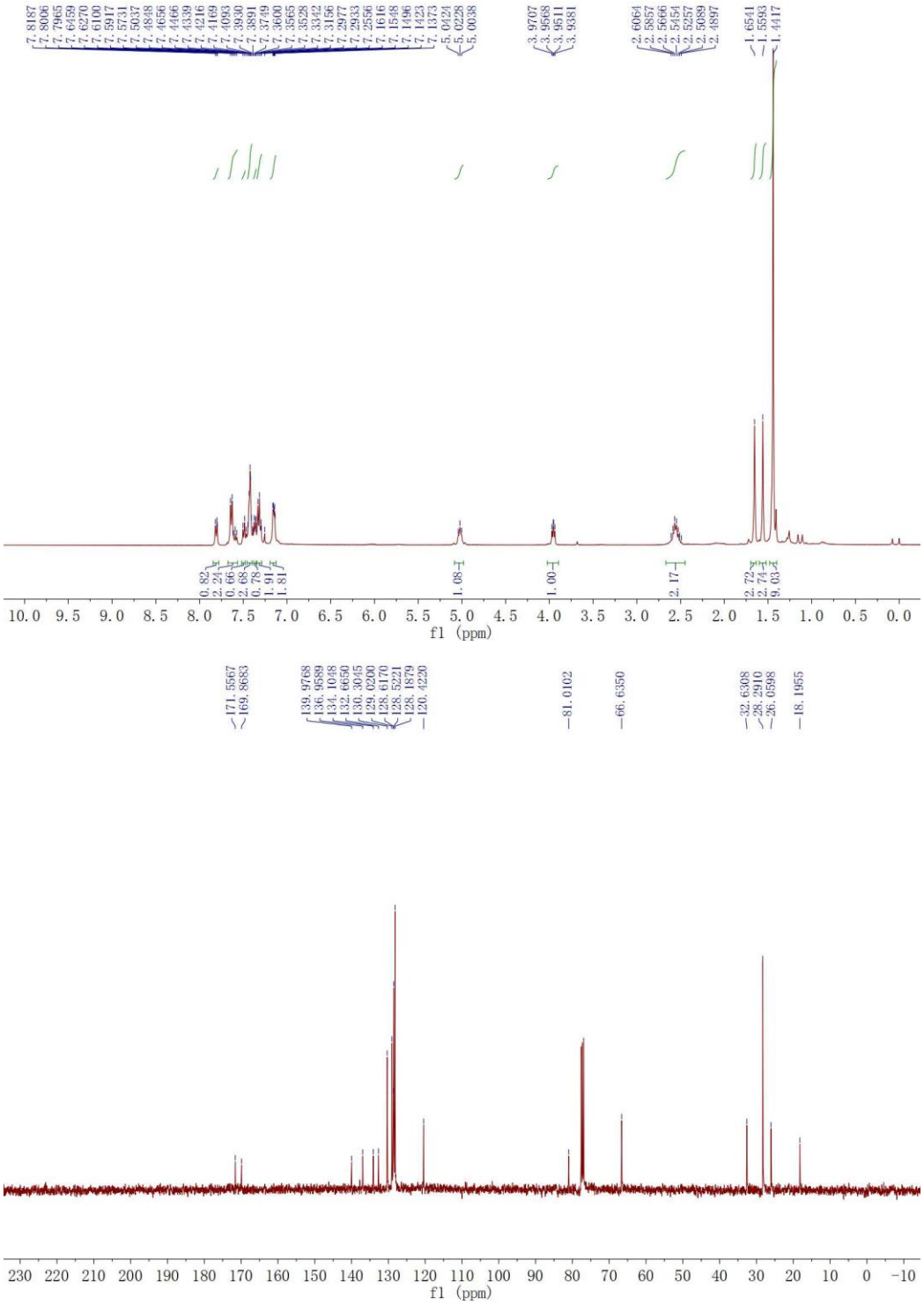
PeakTable

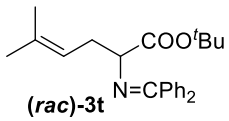
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.190	8110612	1093764	98.830	98.574
2	5.708	96025	15821	1.170	1.426
Total		8206637	1109585	100.000	100.000

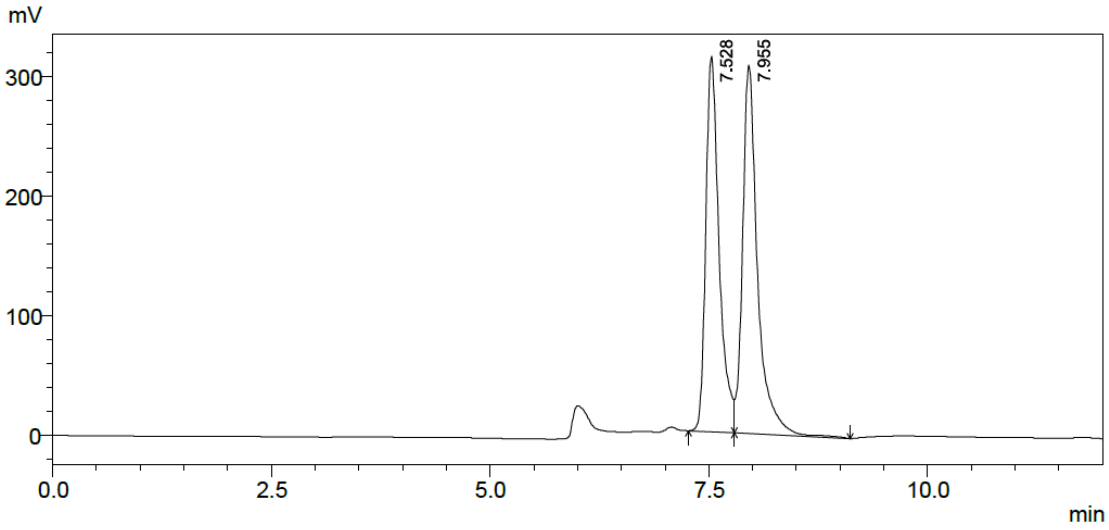


(*S*)-3t



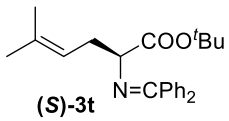


(*rac*)-3t

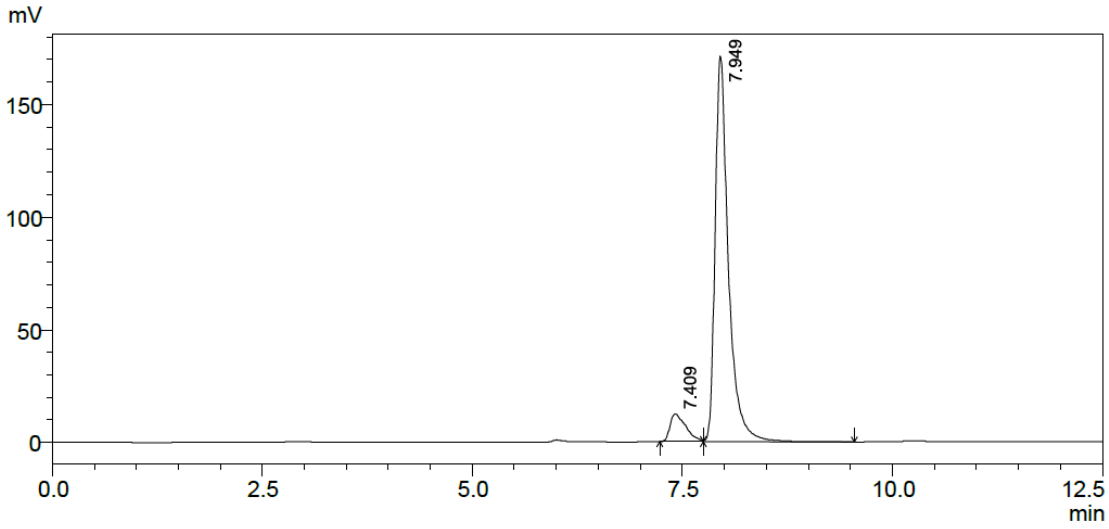


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.528	3331906	314128	47.570	50.483
2	7.955	3672275	308116	52.430	49.517
total		7004181	622244	100.000	100.000

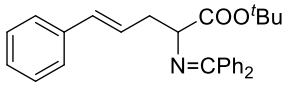


(*S*)-3t

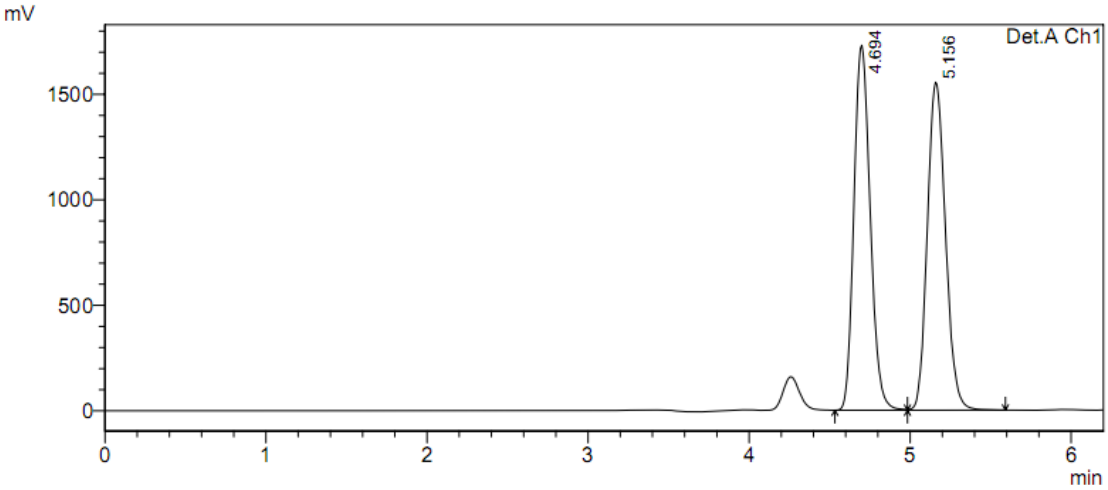


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.409	160002	12311	7.838	6.702
2	7.949	1881339	171384	92.162	93.298
total		2041341	183695	100.000	100.000



***(rac)*-3u**

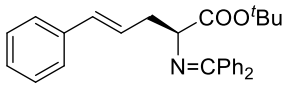


1 Det.A Ch1/254nm

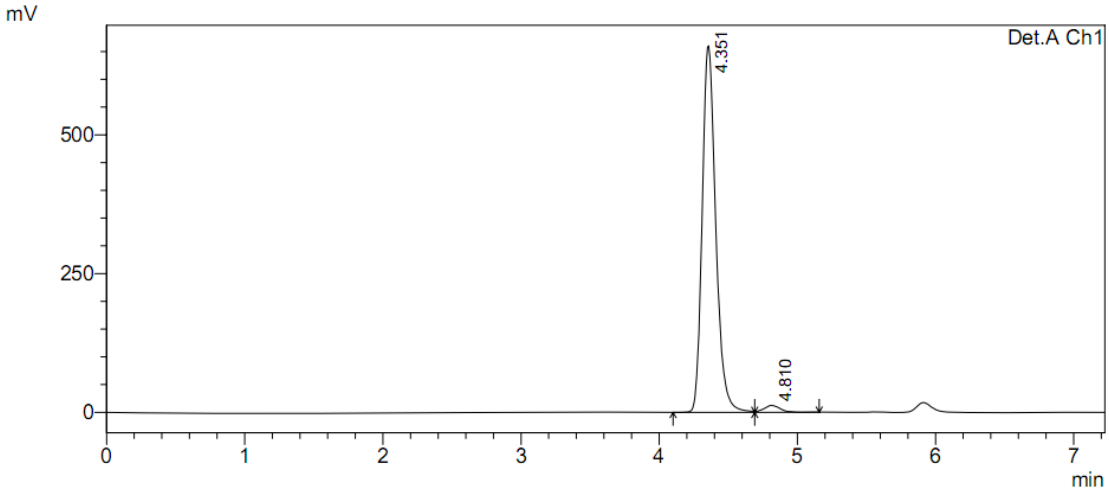
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.694	12164256	1730704	49.966	52.683
2	5.156	12180715	1554441	50.034	47.317
Total		24344970	3285145	100.000	100.000



***(S)*-3u**

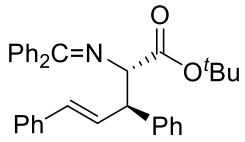


1 Det.A Ch1/254nm

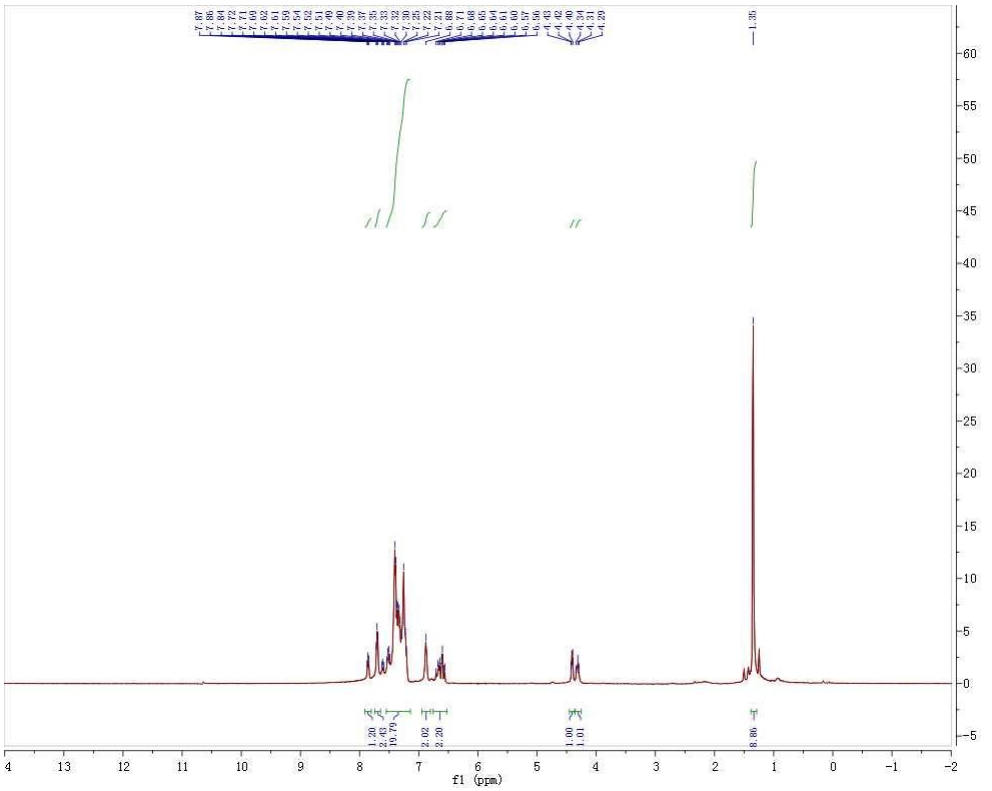
PeakTable

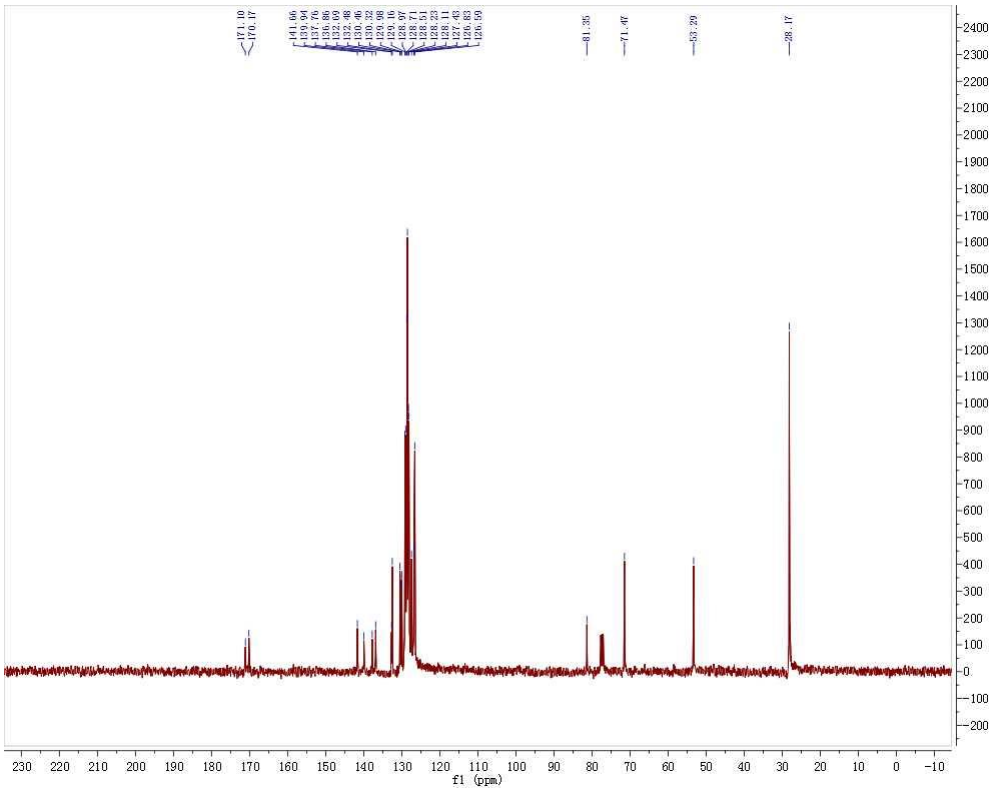
Detector A Ch1 254nm

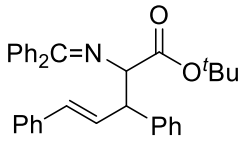
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.351	4503158	660624	97.787	98.124
2	4.810	101912	12633	2.213	1.876
Total		4605069	673256	100.000	100.000



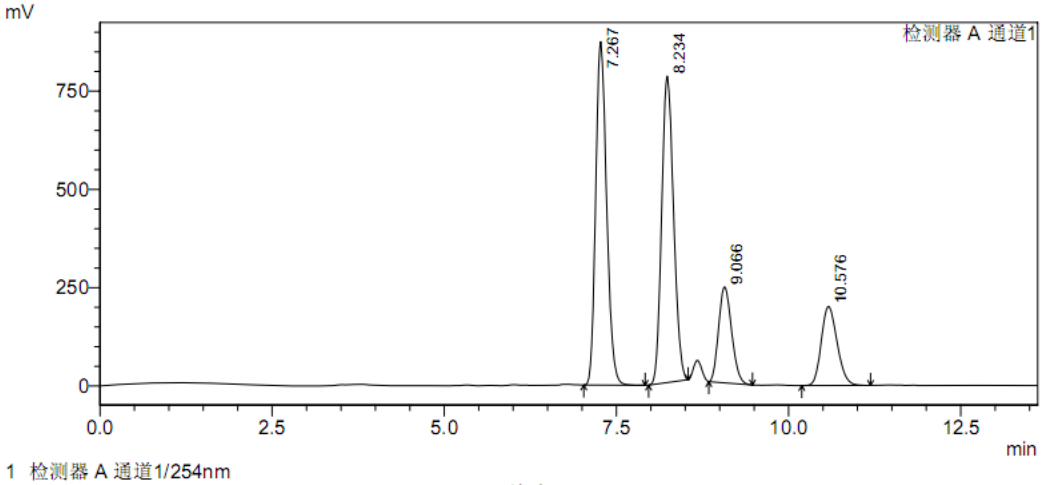
(*R*,*S*)-4







(*rac*)-4

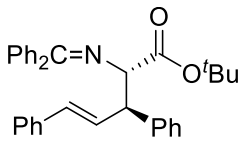


1 检测器 A 通道1/254nm

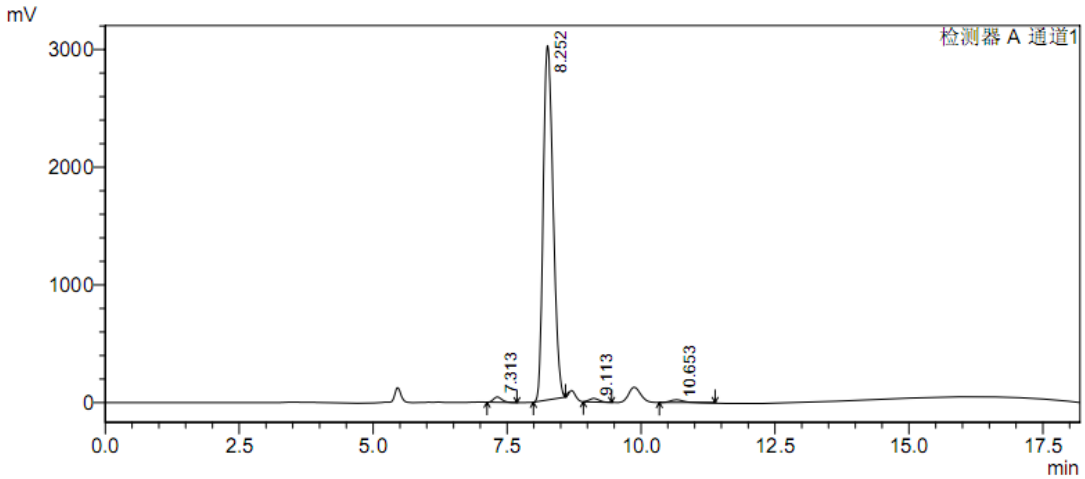
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	7.267	9628283	873252	37.858	41.635
2	8.234	9393042	779418	36.933	37.161
3	9.066	3202755	243791	12.593	11.624
4	10.576	3208624	200926	12.616	9.580
总计		25432703	2097387	100.000	100.000



(*R*,*S*)-4

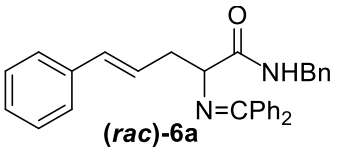


1 检测器 A 通道1/254nm

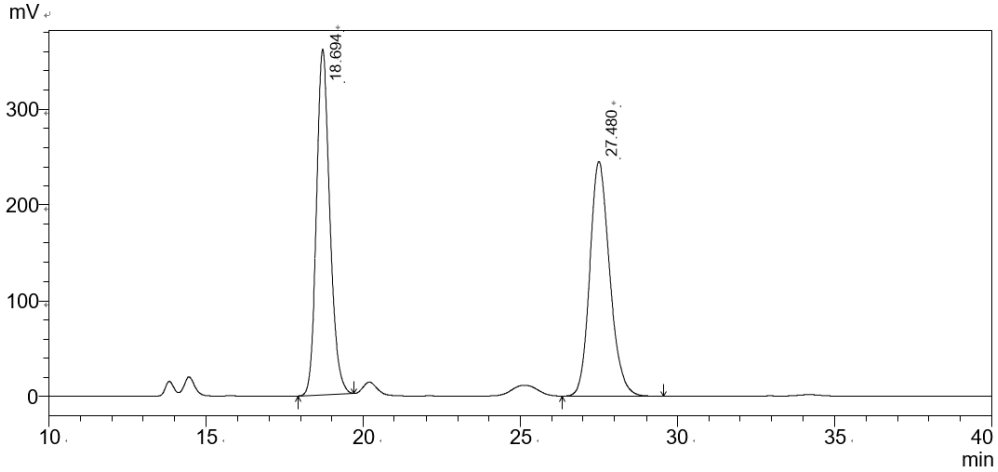
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	7.313	498942	45643	1.252	1.467
2	8.252	38596524	3012335	96.836	96.812
3	9.113	382479	30397	0.960	0.977
4	10.653	379783	23168	0.953	0.745
总计		39857728	3111543	100.000	100.000

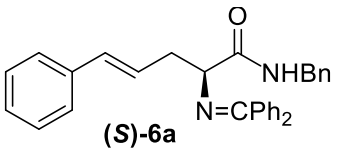


(*rac*)-6a

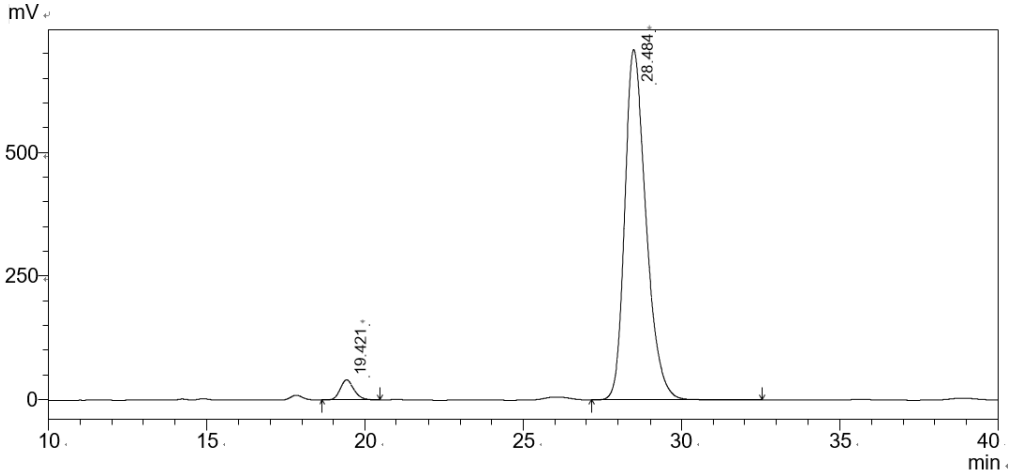


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.694	10688348	360864	49.680	59.512
2	27.480	10825830	245507	50.320	40.488
Total		21514178	606371	100.000	100.000

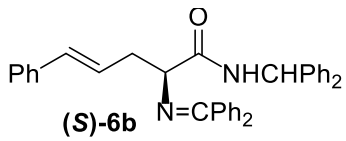


(*S*)-6a

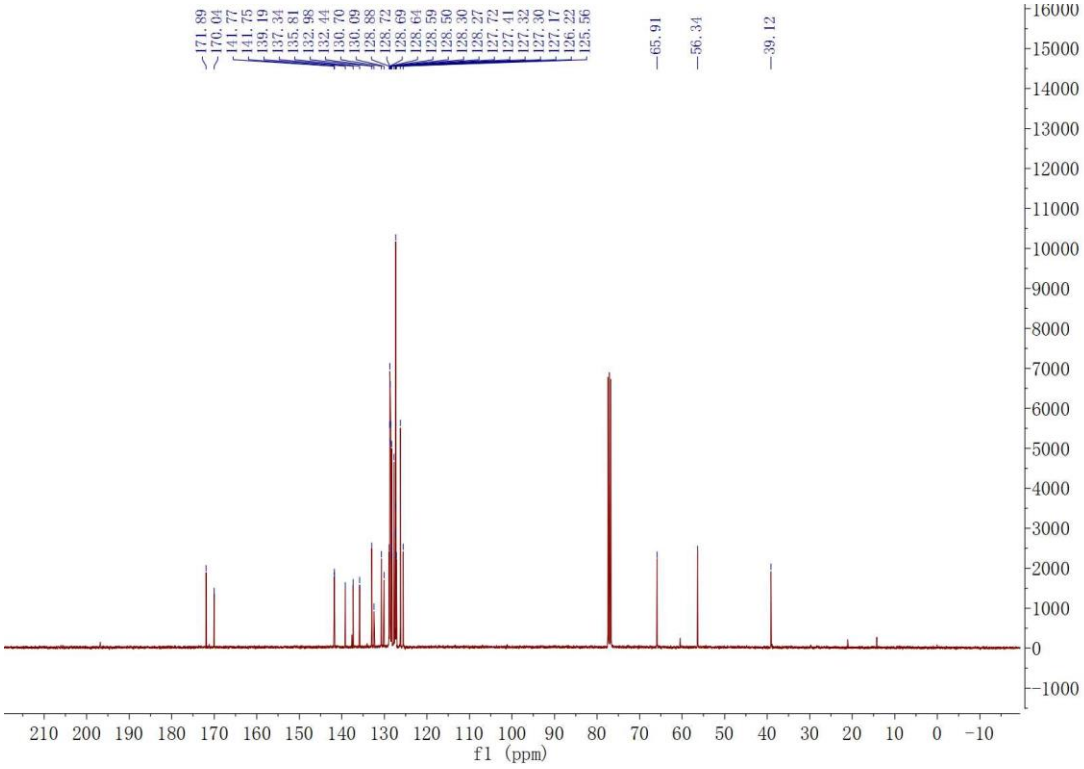


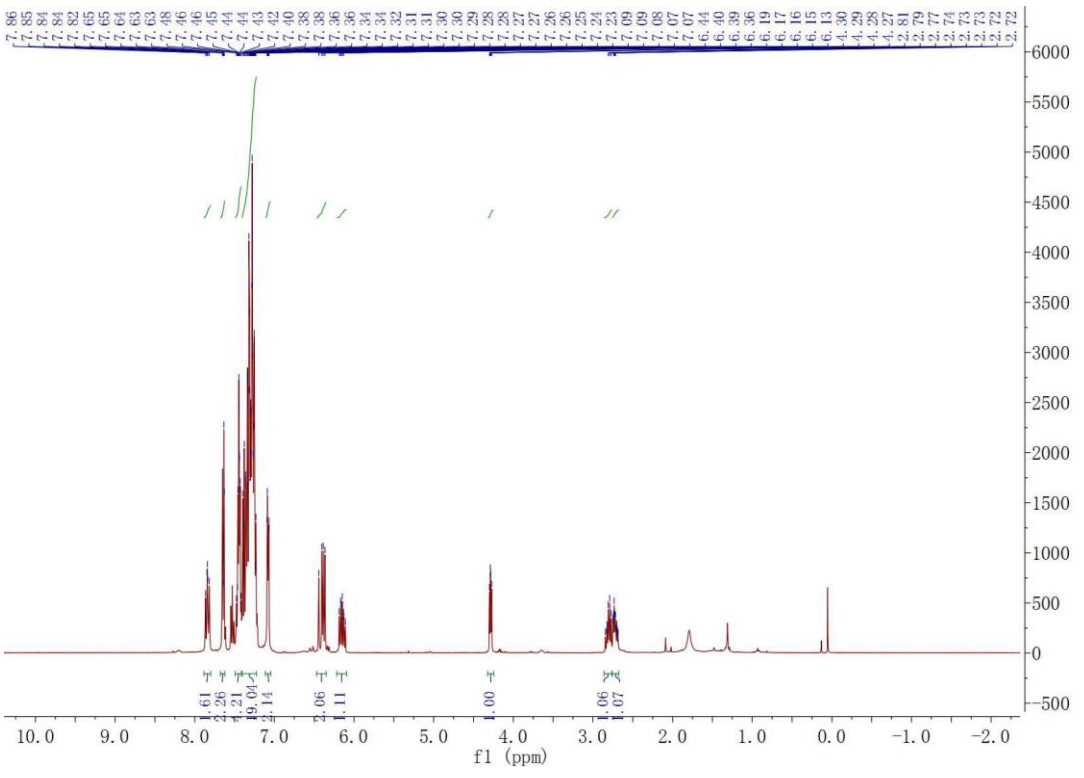
PeakTable

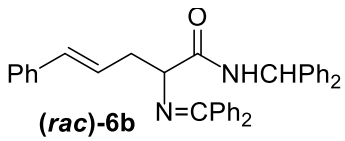
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.421	1220595	39589	3.511	5.293
2	28.484	33549175	708357	96.489	94.707
total		34769770	747945	100.000	100.000


O
Ph
NHCHPh2
N=CPh2

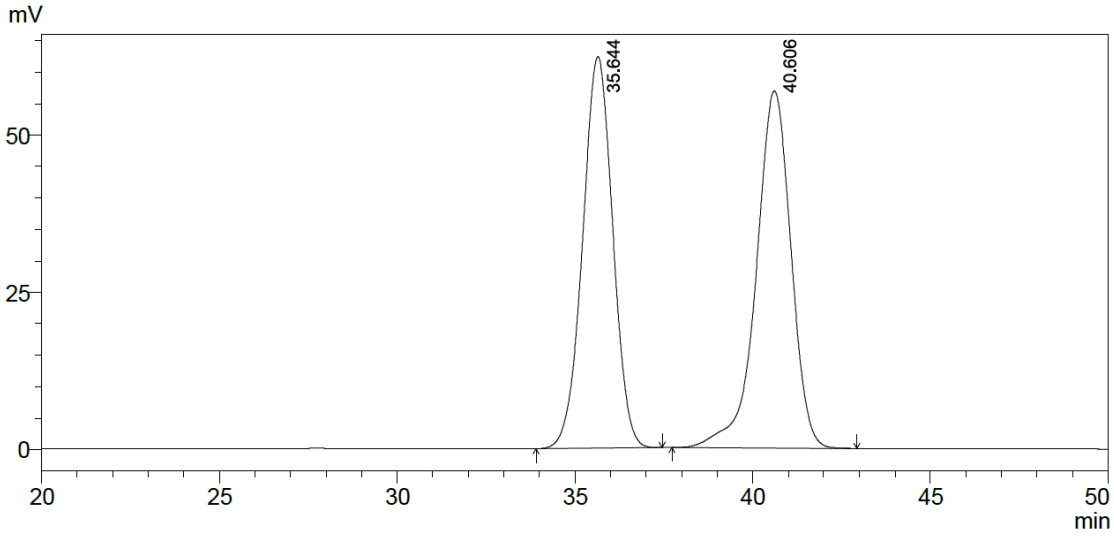
(*S*)-6b


171.89
170.04
141.77
141.75
139.19
137.34
135.81
132.98
132.44
130.70
130.09
128.88
128.72
128.69
128.64
128.59
128.50
128.30
128.27
127.72
127.41
127.32
127.30
127.17
126.22
125.56
65.91
56.34
39.12
f1 (ppm)


7.86
7.85
7.84
7.84
7.82
7.65
7.64
7.63
7.48
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.40
7.38
7.38
7.36
7.36
7.34
7.34
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.23
7.09
7.08
7.07
7.07
6.44
6.40
6.39
6.36
6.19
6.17
6.16
6.15
6.13
4.30
4.29
4.28
4.27
2.81
2.79
2.77
2.74
2.73
2.73
2.72
2.72
1.61
2.26
4.21
19.04
2.14
2.06
1.11
1.00
1.06
1.07
f1 (ppm)

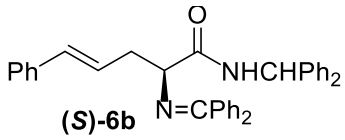


(*rac*)-6b

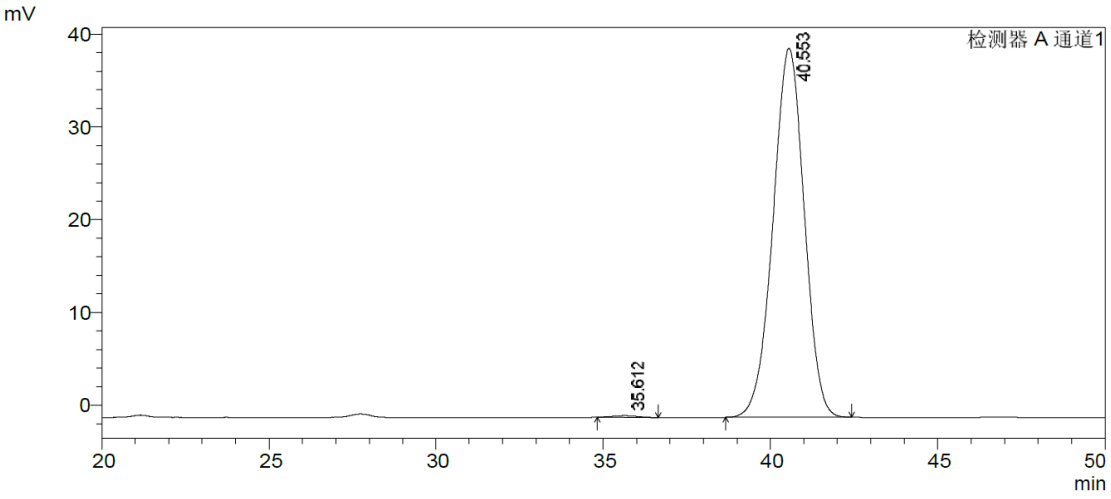


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.644	3672499	62269	48.646	52.299
2	40.606	3876893	56794	51.354	47.701
Total		7549392	119063	100.000	100.000

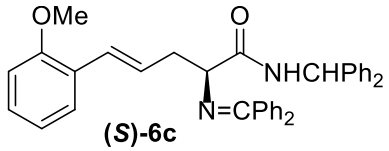


(*S*)-6b

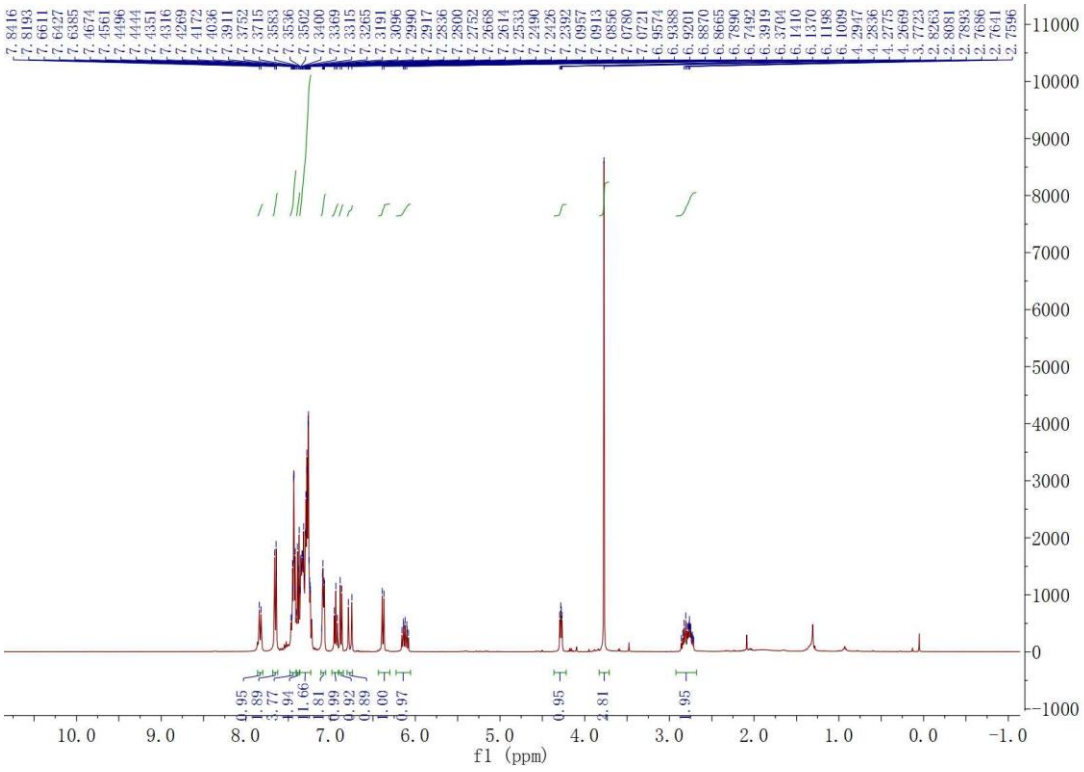


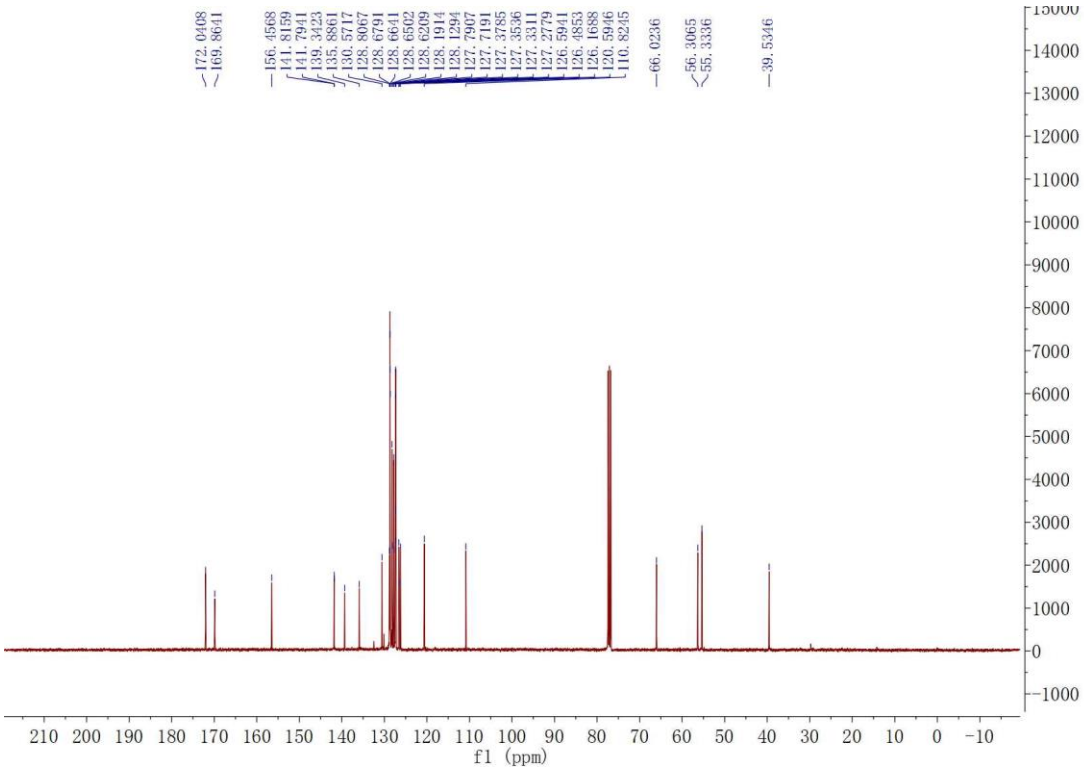
PeakTable

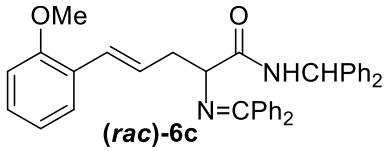
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.612	10227	190	0.394	0.476
2	40.553	2584341	39772	99.606	99.524
Total		2594568	39963	100.000	100.000



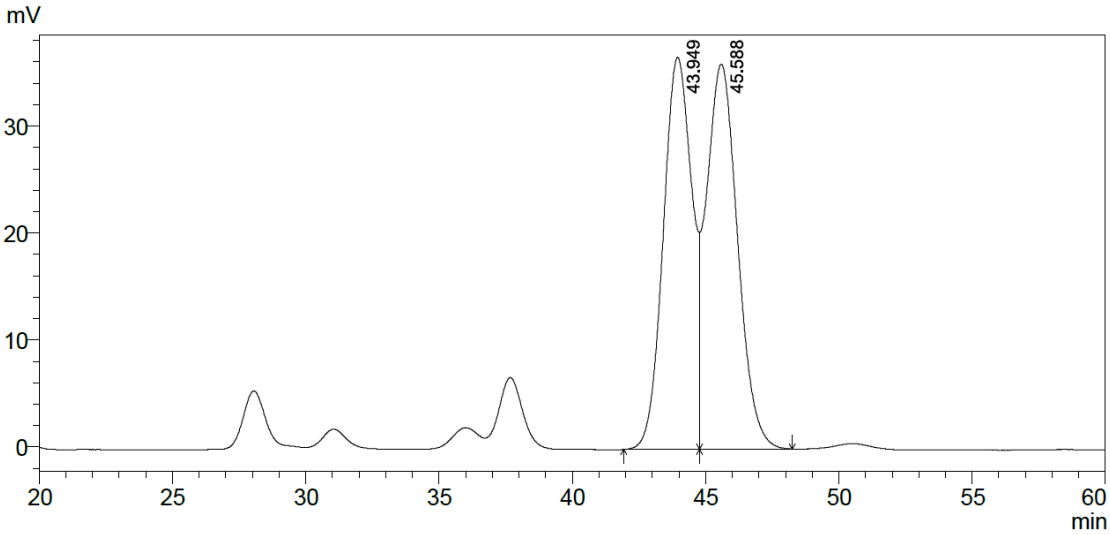
(*S*)-6c





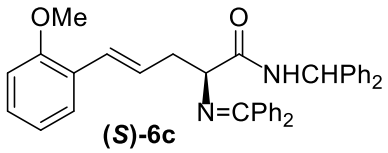


(*rac*)-6c

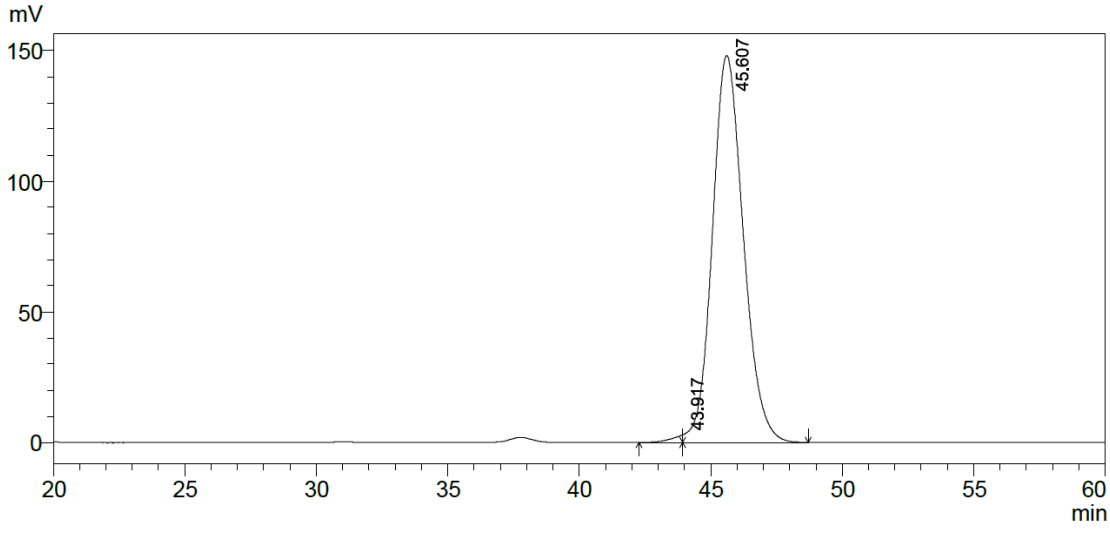


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.949	2757555	36656	48.381	50.441
2	45.588	2942124	36015	51.619	49.559
Total		5699678	72671	100.000	100.000

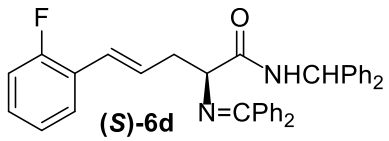


(*S*)-6c



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.917	86024	2858	0.703	1.894
2	45.607	12156986	148041	99.297	98.106
Total		12243010	150899	100.000	100.000



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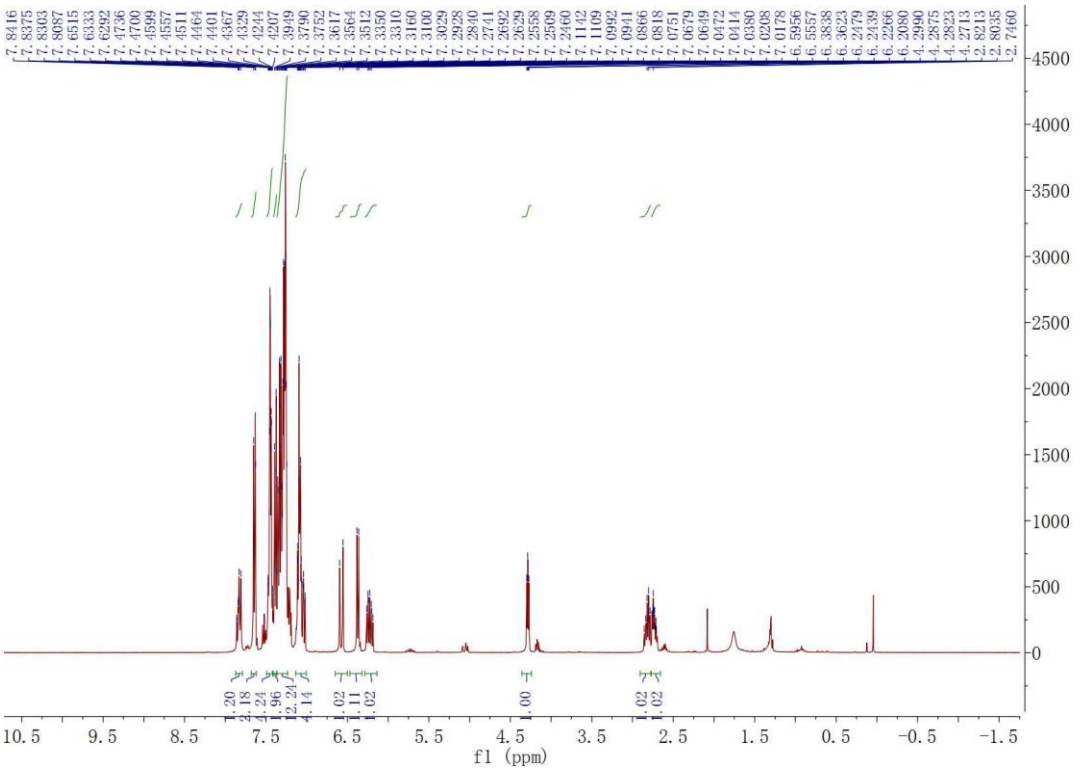

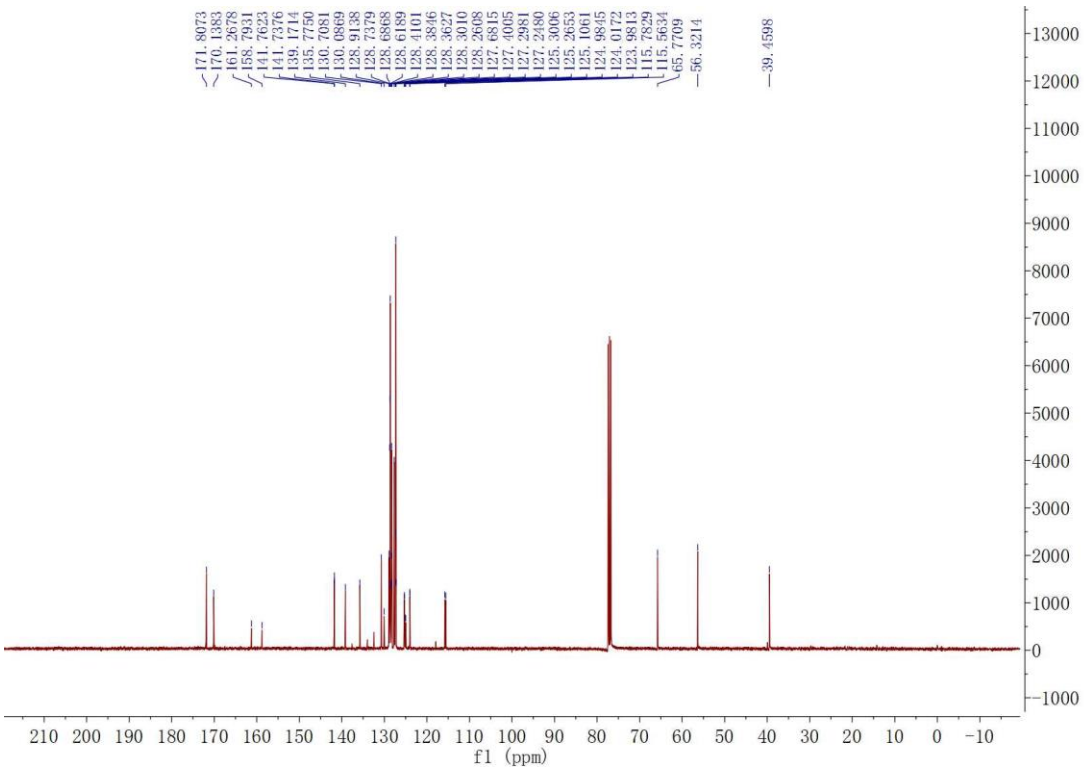

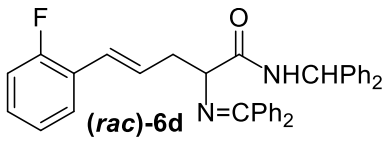

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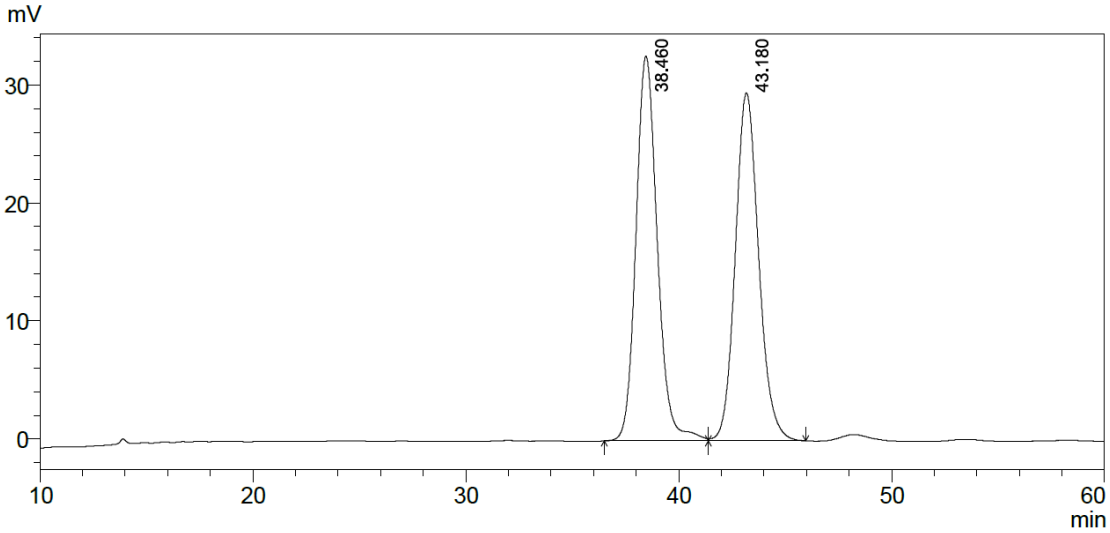
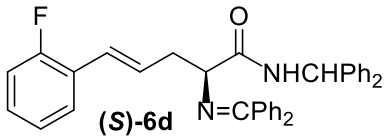


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.460	2275765	32629	50.212	52.504
2	43.180	2256525	29517	49.788	47.496
Total		4532289	62146	100.000	100.000



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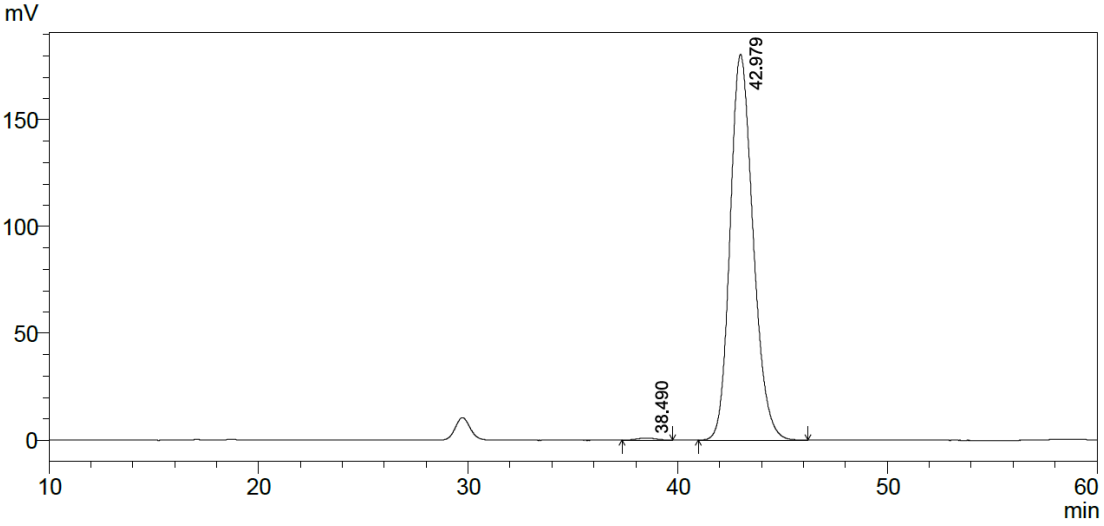
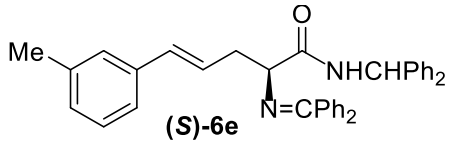


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.490	62774	989	0.453	0.545
2	42.979	13782758	180622	99.547	99.455
Total		13845532	181612	100.000	100.000



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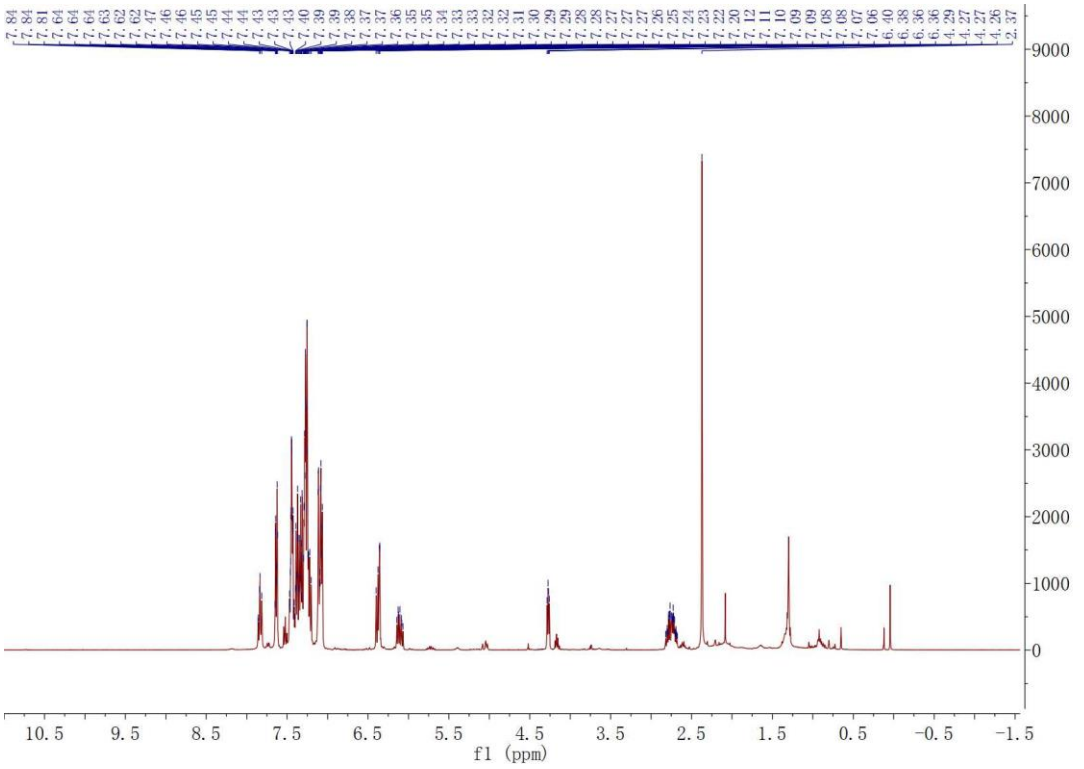

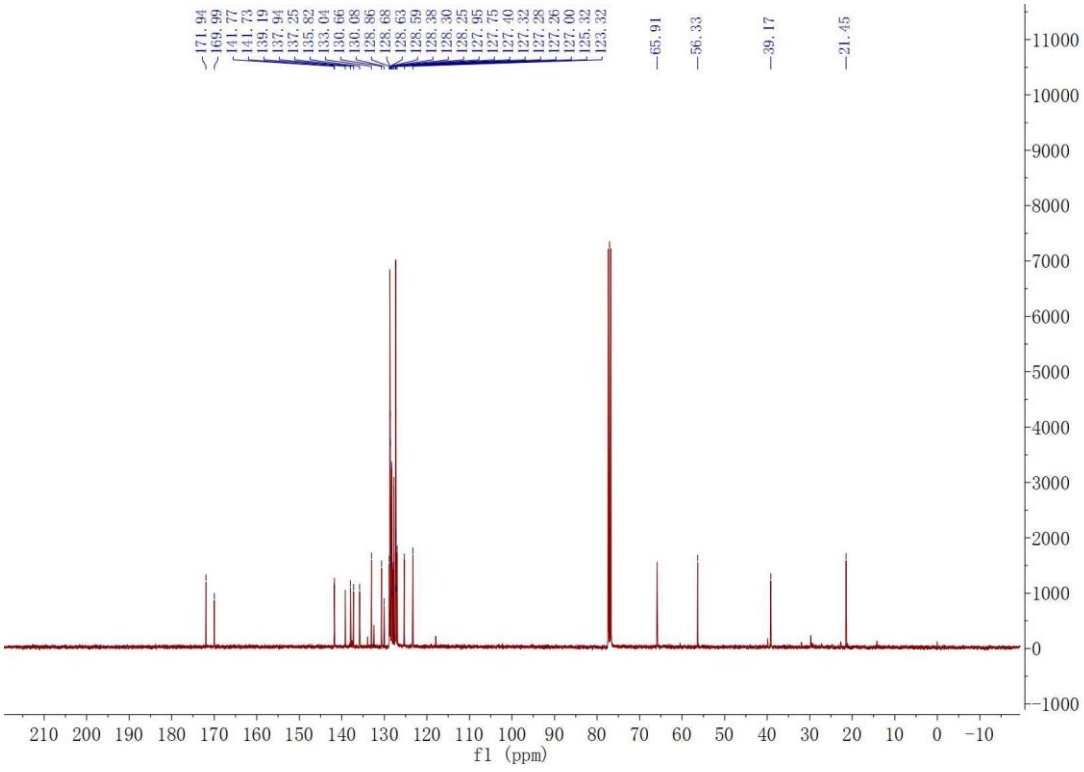

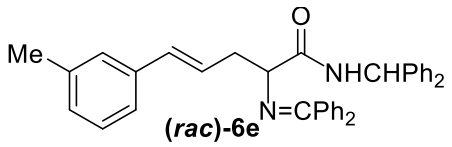

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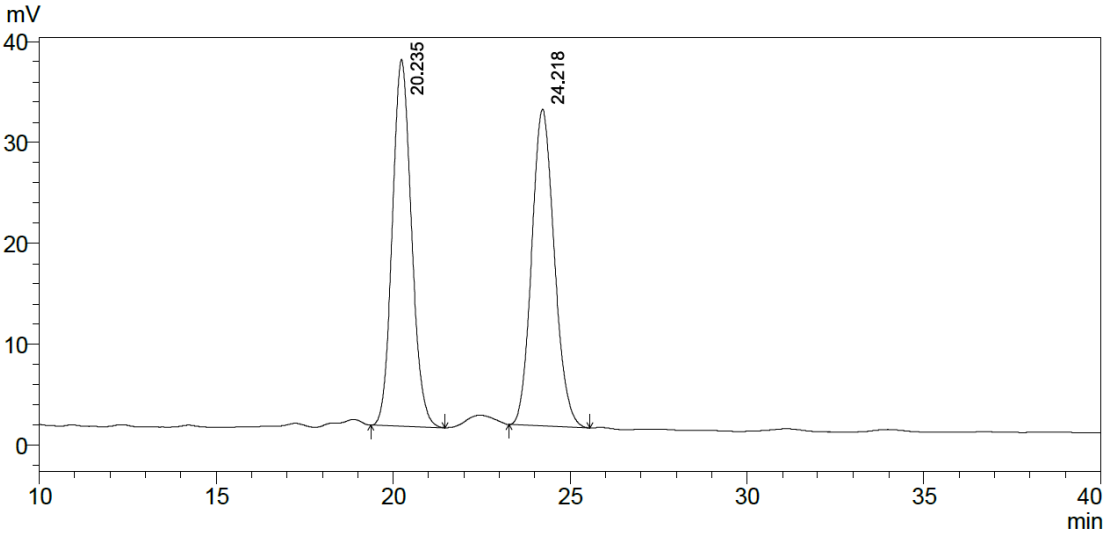
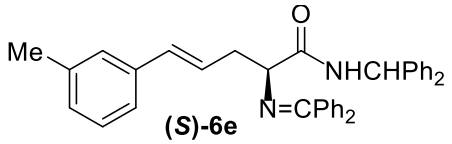


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.235	1367663	36346	49.529	53.673
2	24.218	1393693	31372	50.471	46.327
Total		2761357	67717	100.000	100.000



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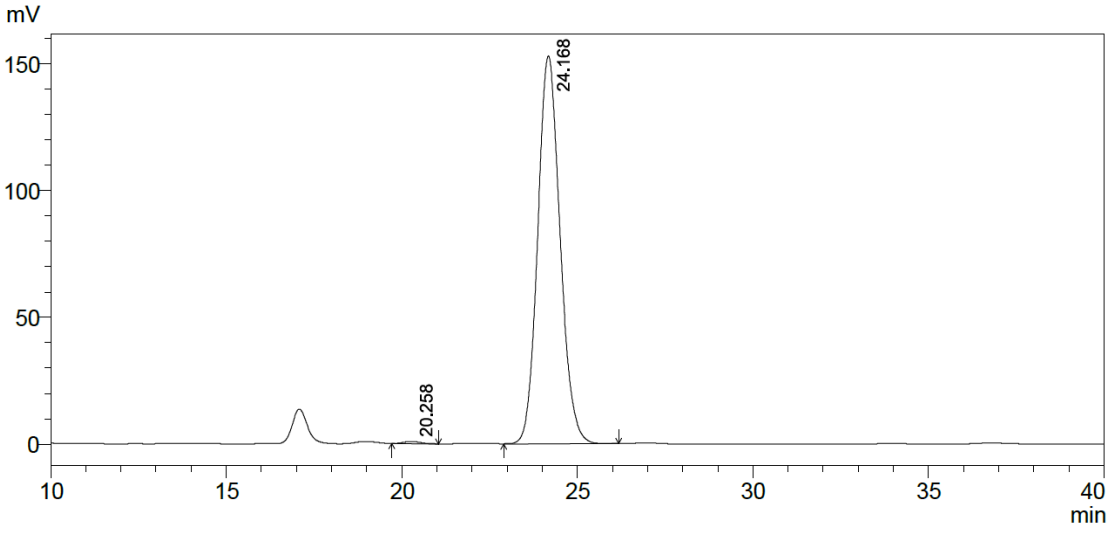
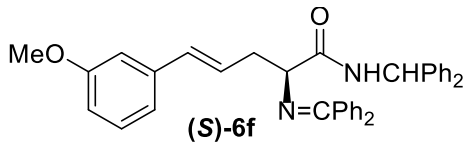


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.258	29320	874	0.431	0.569
2	24.168	6772322	152790	99.569	99.431
Total		6801642	153664	100.000	100.000



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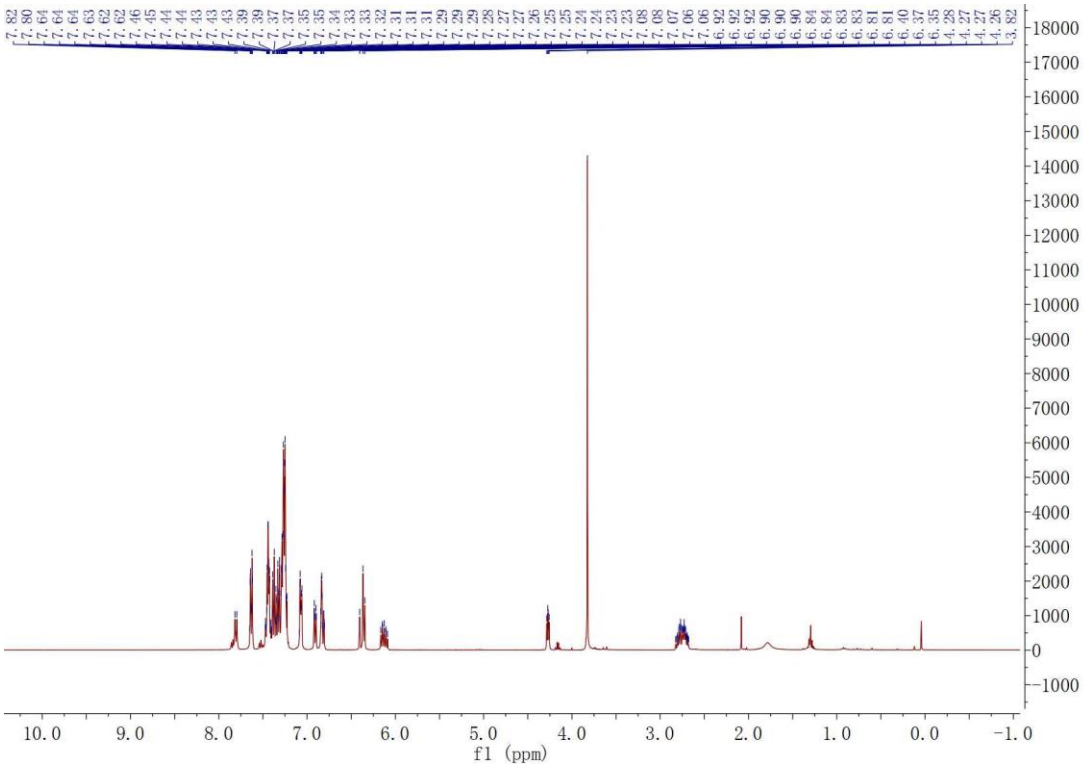

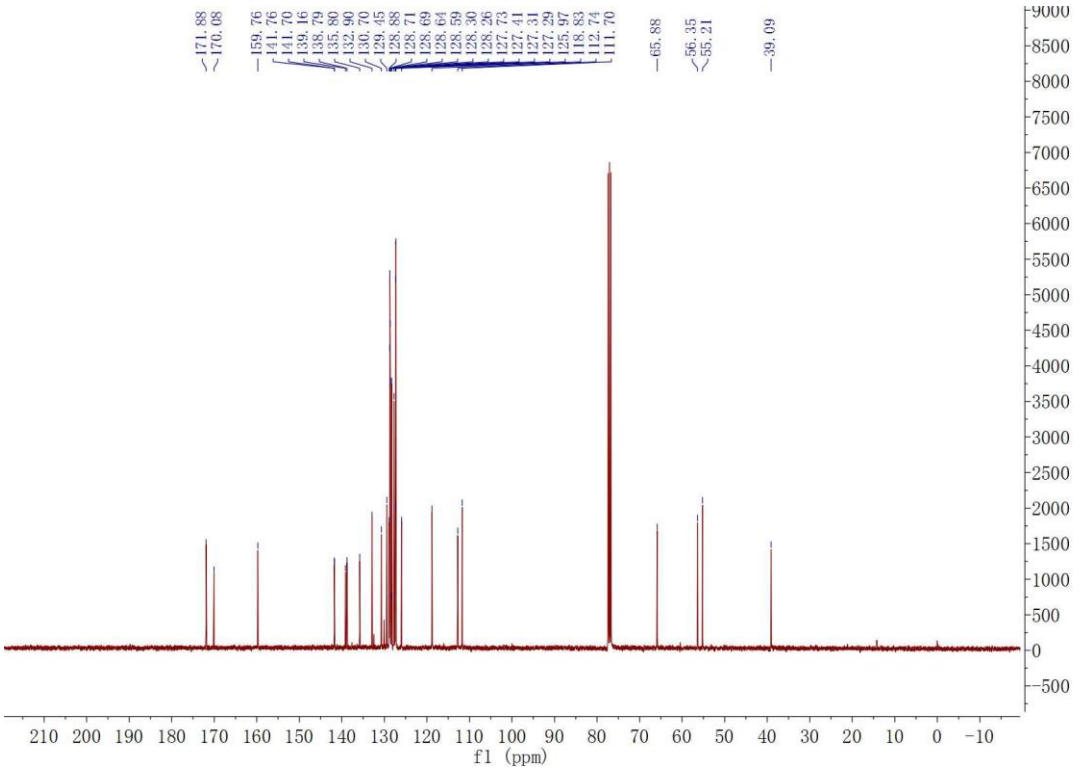

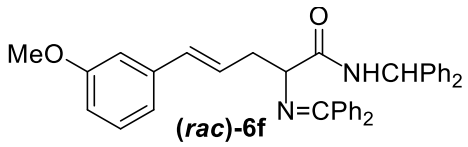

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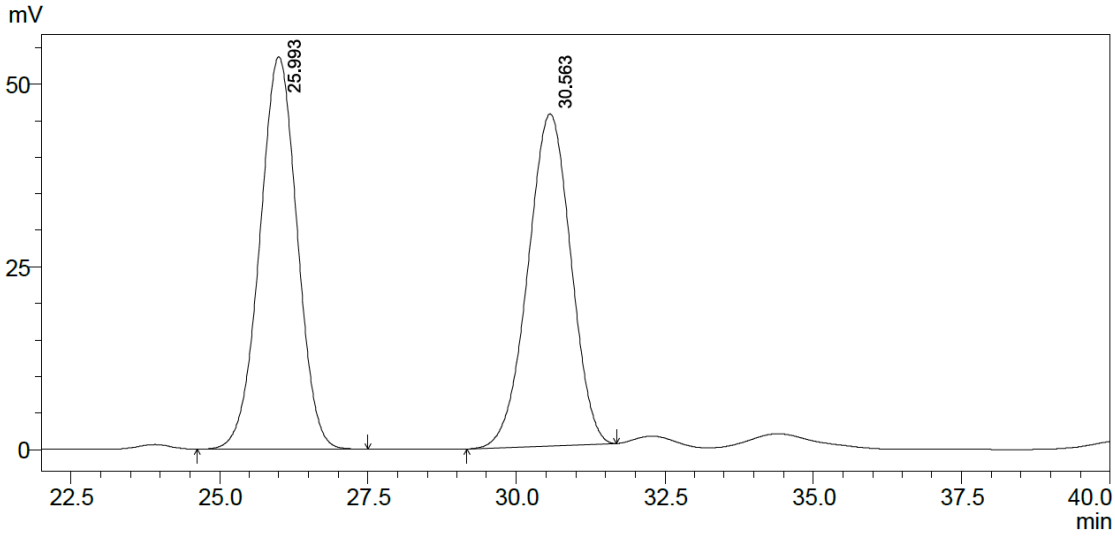
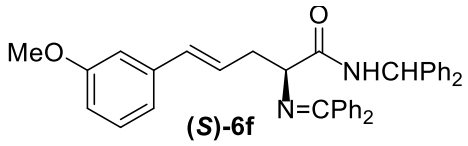


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.993	2350440	53670	50.730	54.161
2	30.563	2282834	45424	49.270	45.839
Total		4633274	99095	100.000	100.000



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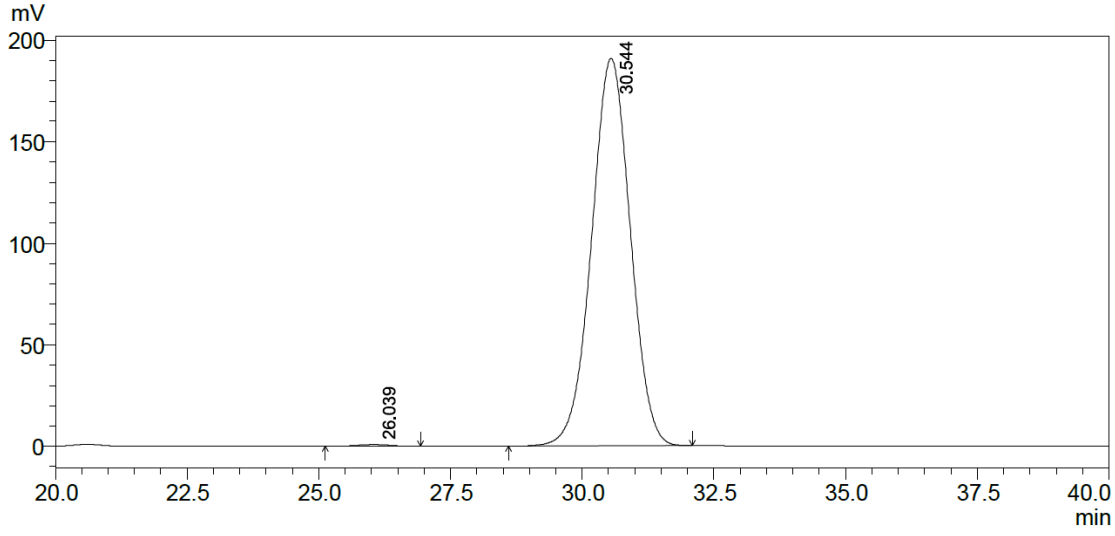
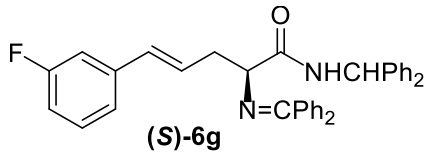


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.039	38456	889	0.392	0.464
2	30.544	9776934	190746	99.608	99.536
Total		9815390	191635	100.000	100.000



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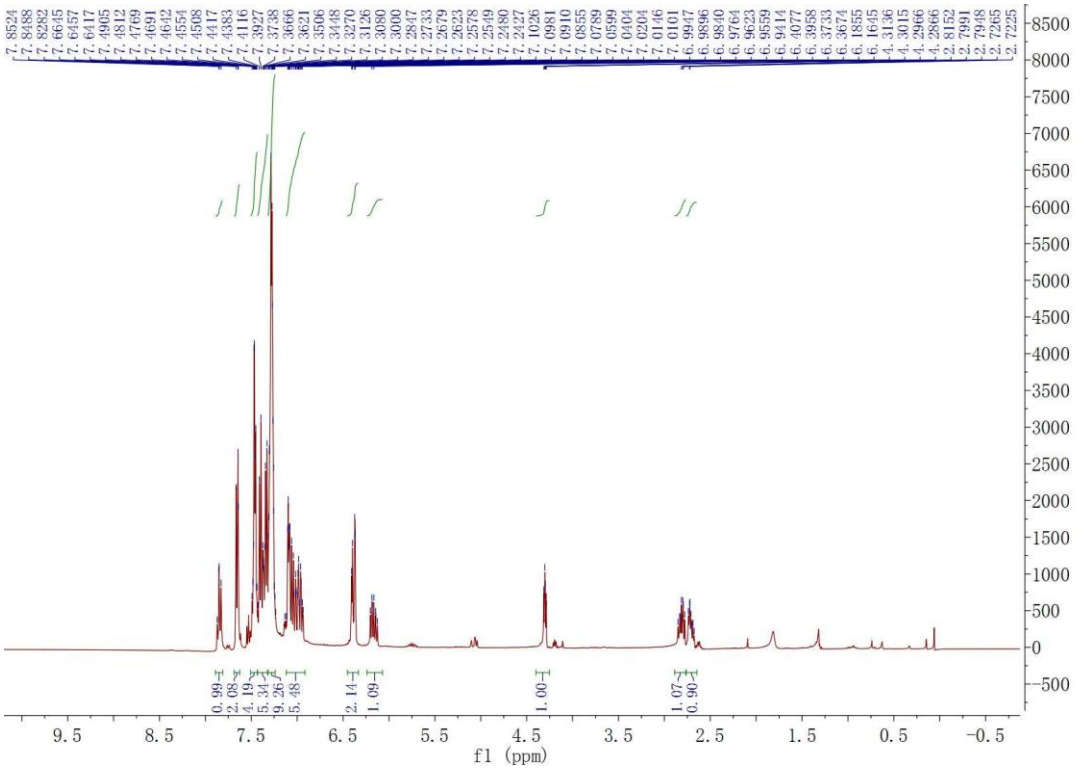

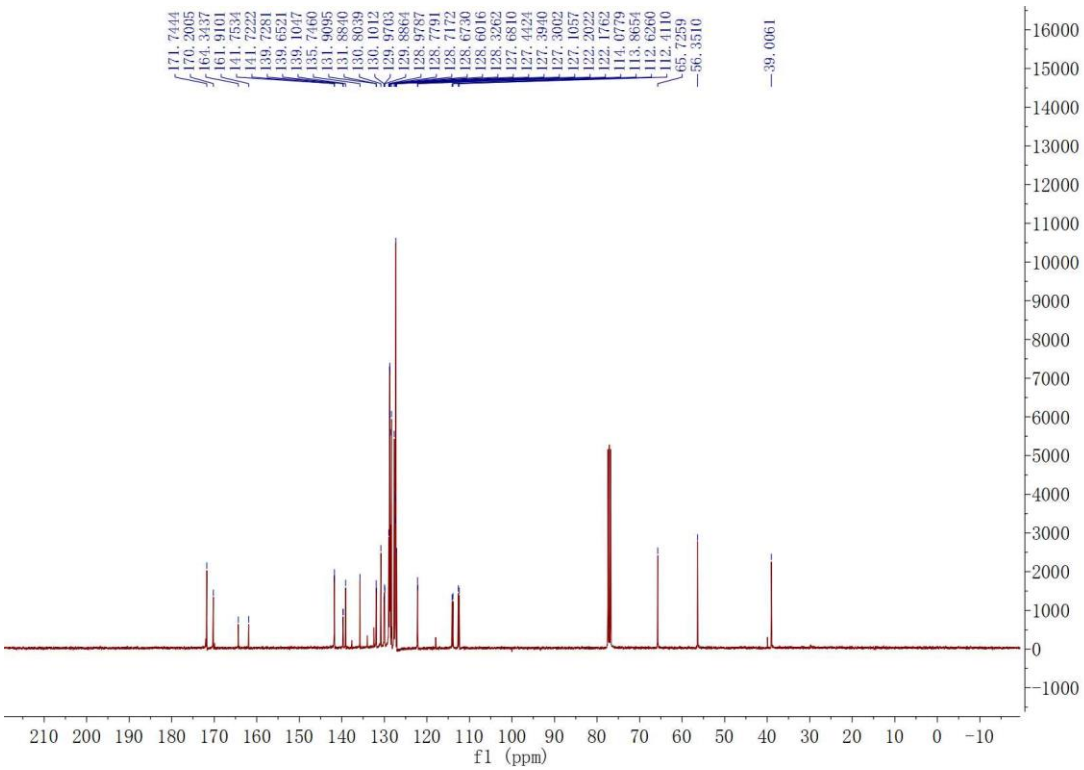

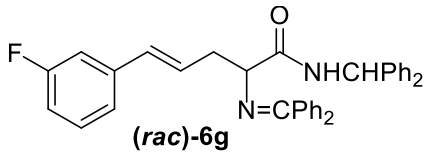

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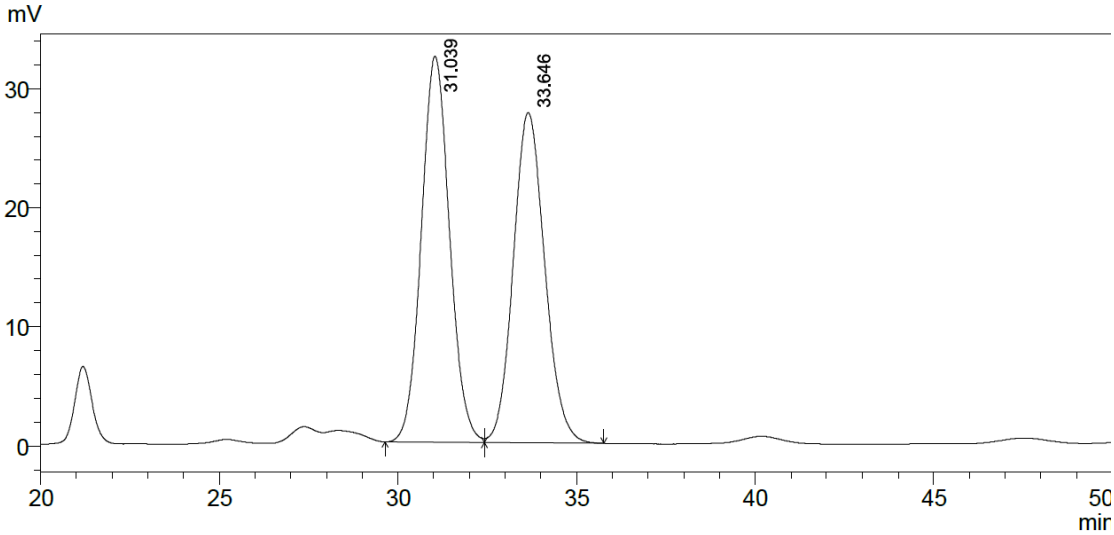
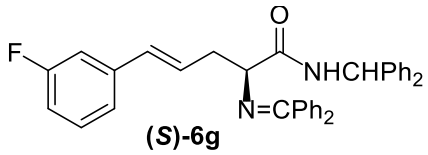


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.039	1784936	32433	51.188	53.884
2	33.646	1702077	27757	48.812	46.116
Total		3487012	60189	100.000	100.000



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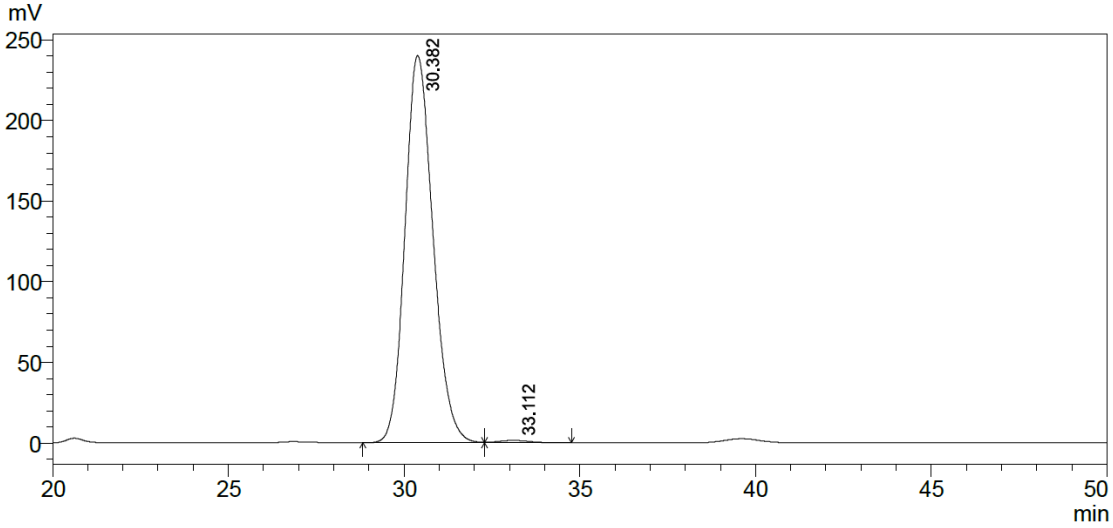
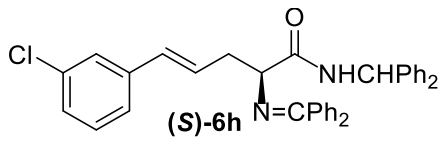


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.382	13350991	240090	99.275	99.359
2	33.112	97544	1549	0.725	0.641
Total		13448536	241639	100.000	100.000



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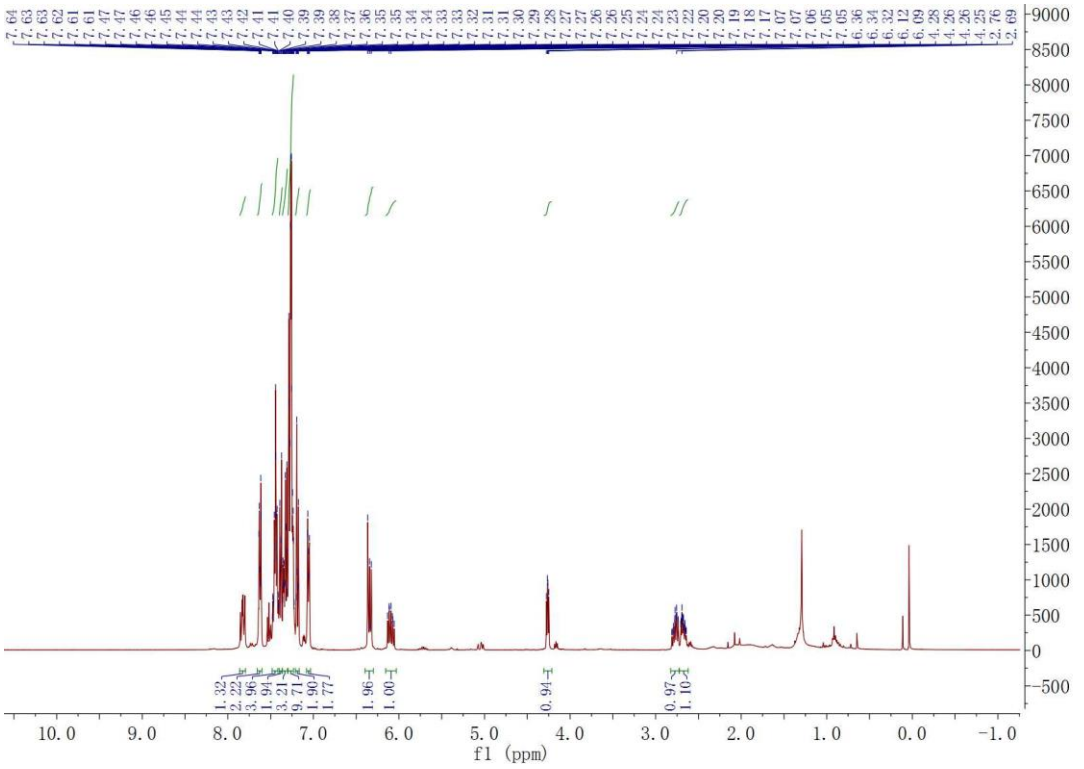

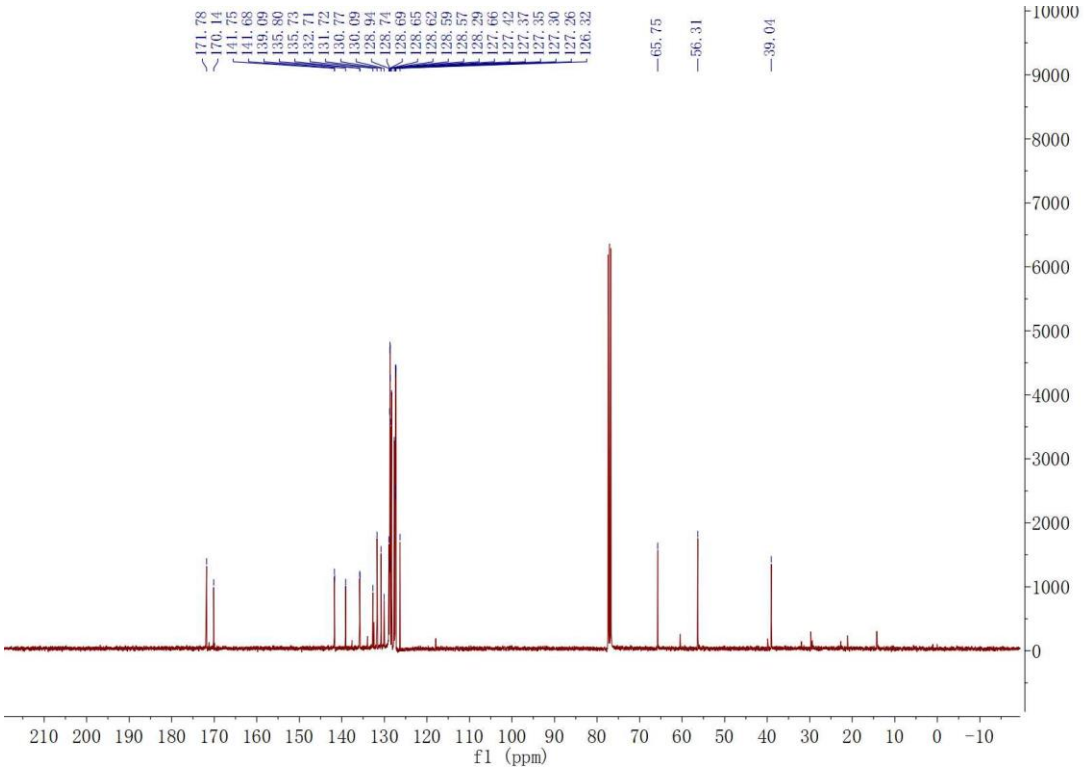

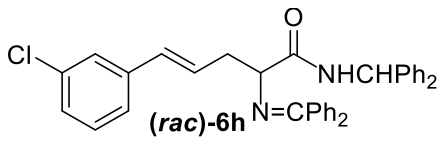

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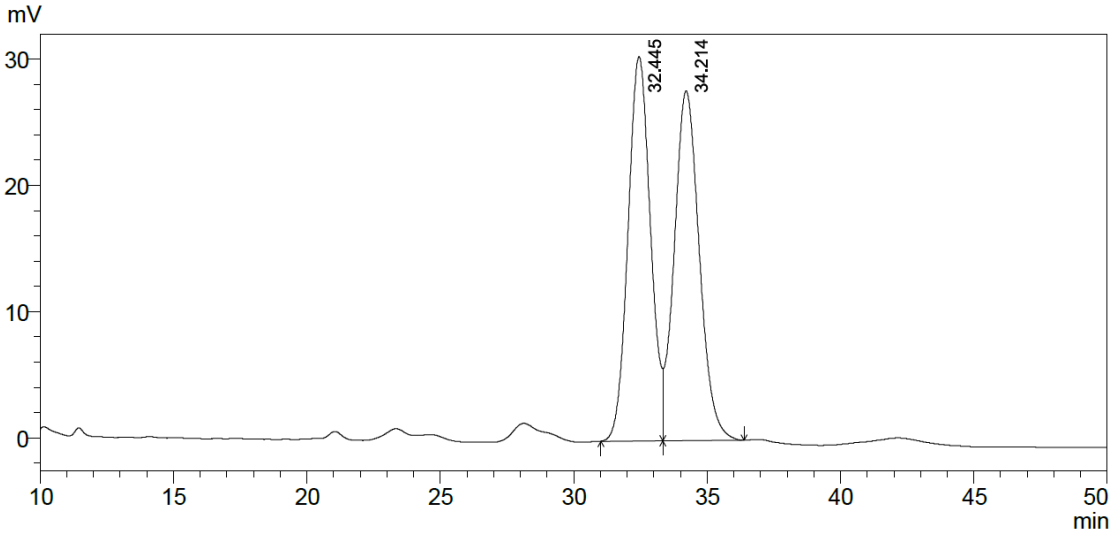
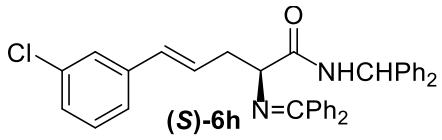


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.445	1782038	30457	49.536	52.352
2	34.214	1815454	27720	50.464	47.648
Total		3597493	58178	100.000	100.000



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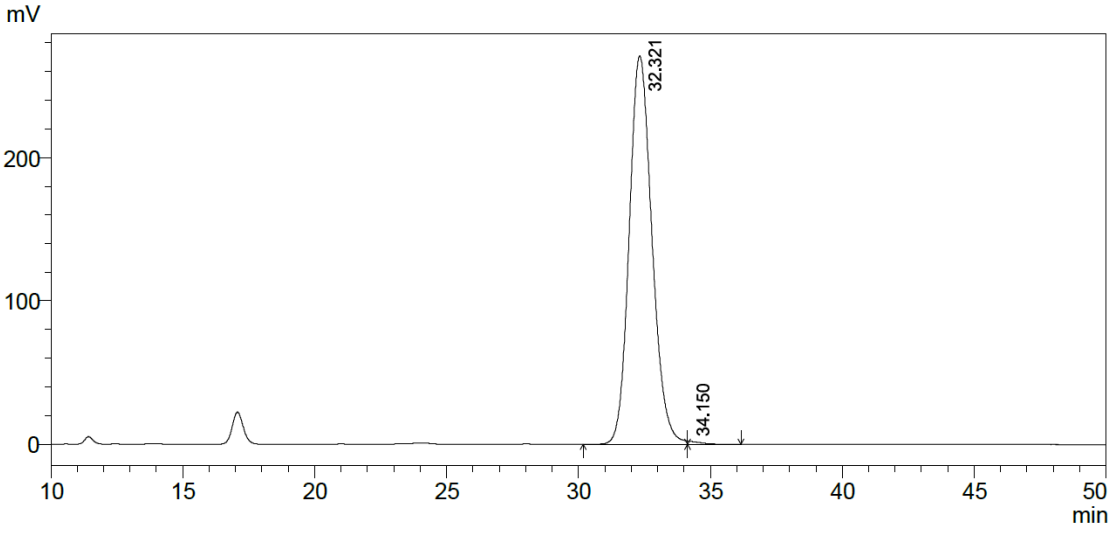
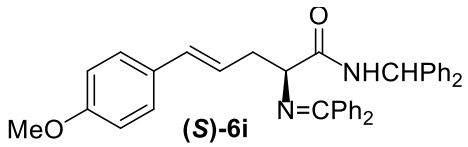


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.321	16266170	271036	99.562	99.163
2	34.150	71485	2288	0.438	0.837
Total		16337656	273324	100.000	100.000



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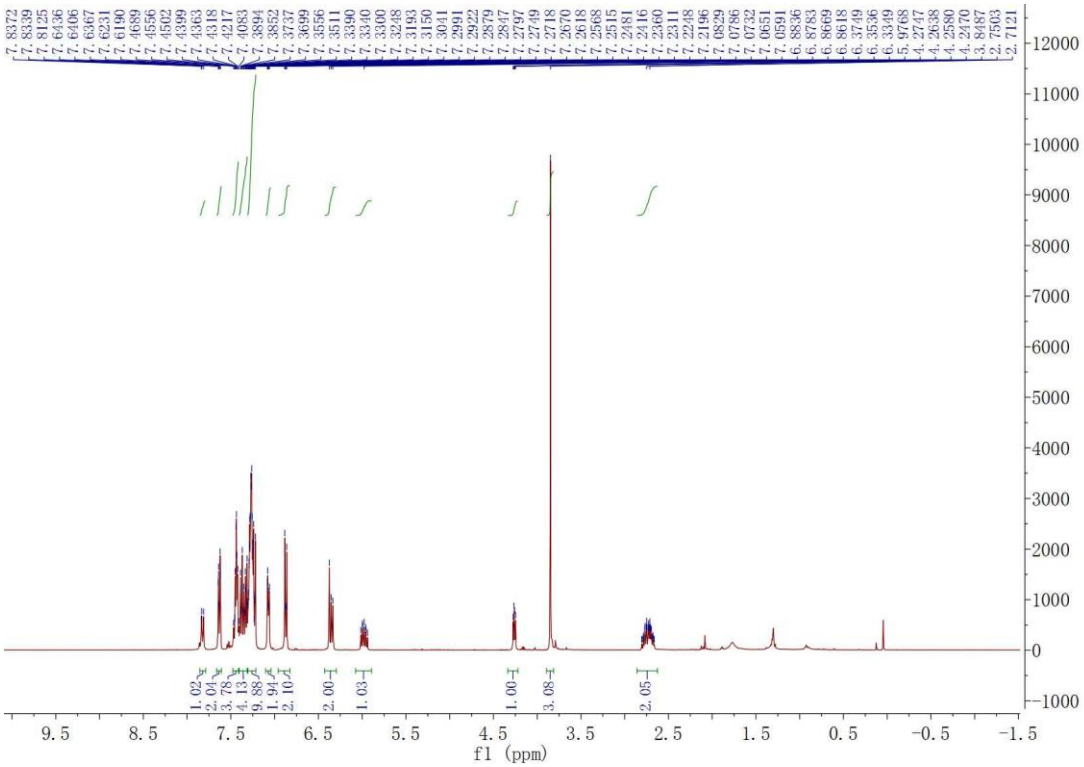

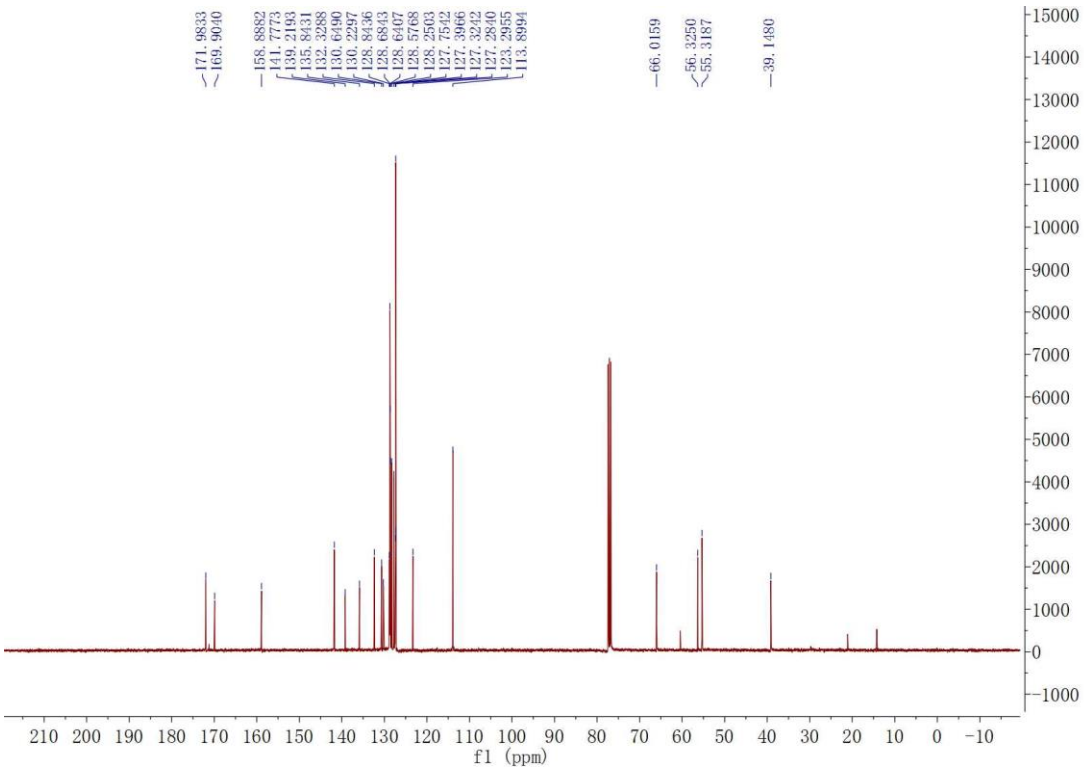

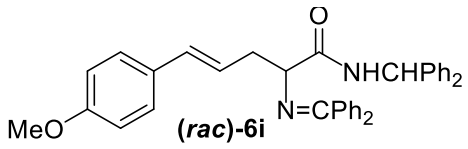

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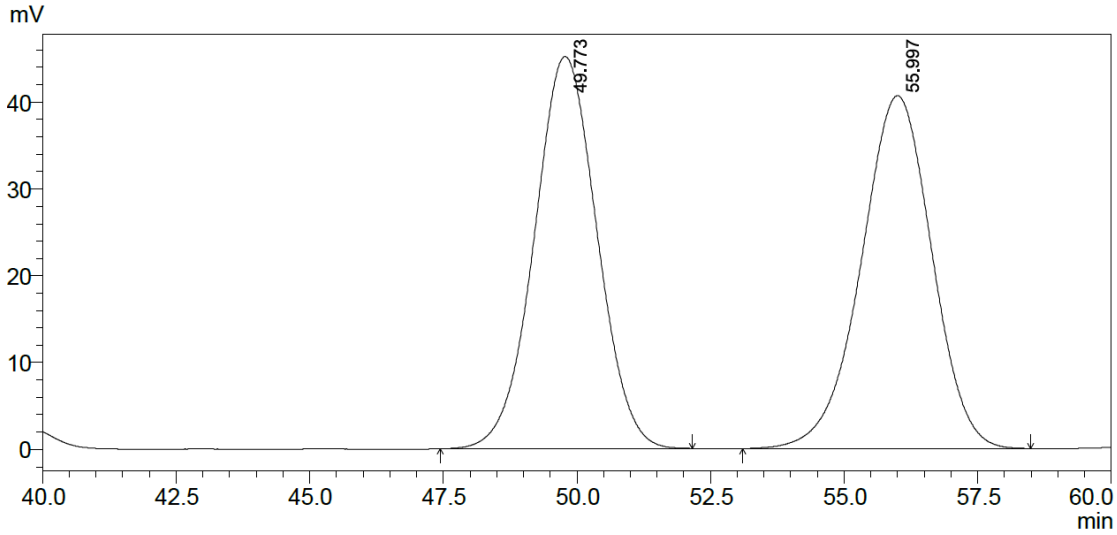
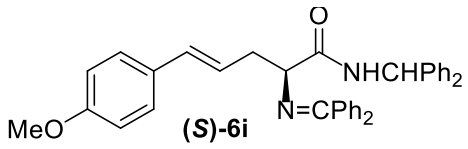


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.773	3698676	45146	49.727	52.636
2	55.997	3739332	40625	50.273	47.364
Total		7438008	85771	100.000	100.000



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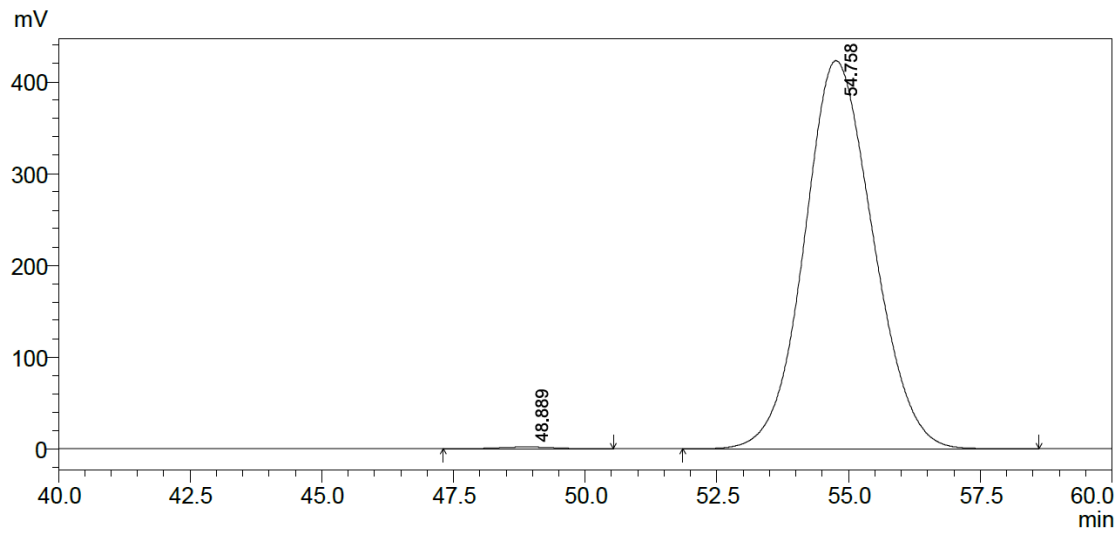
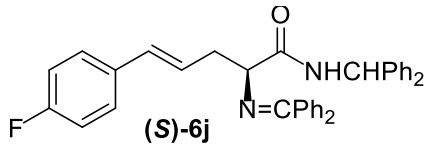


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.889	162558	2115	0.421	0.498
2	54.758	38492222	422893	99.579	99.502
Total		38654780	425008	100.000	100.000



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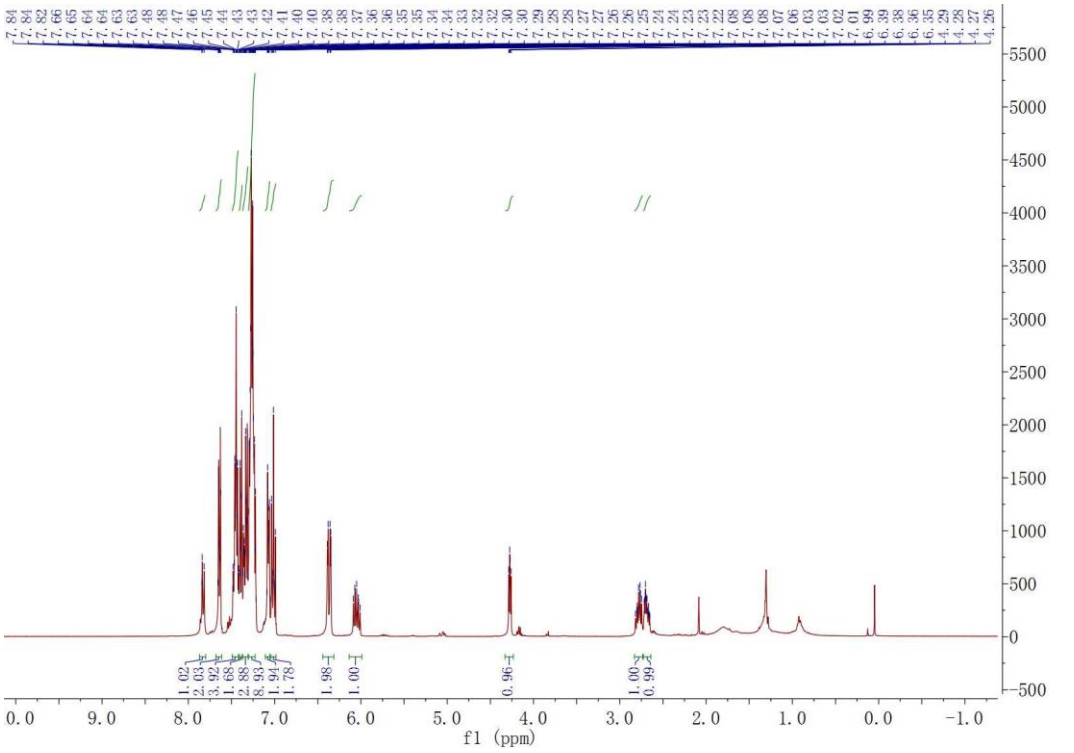
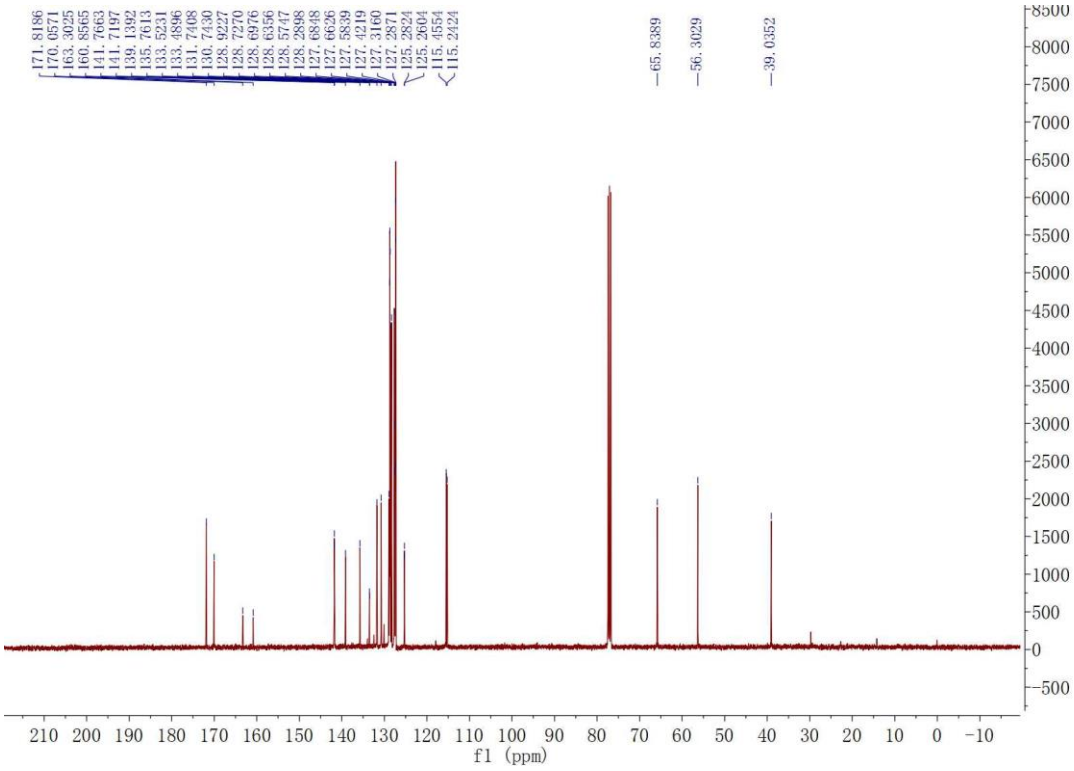
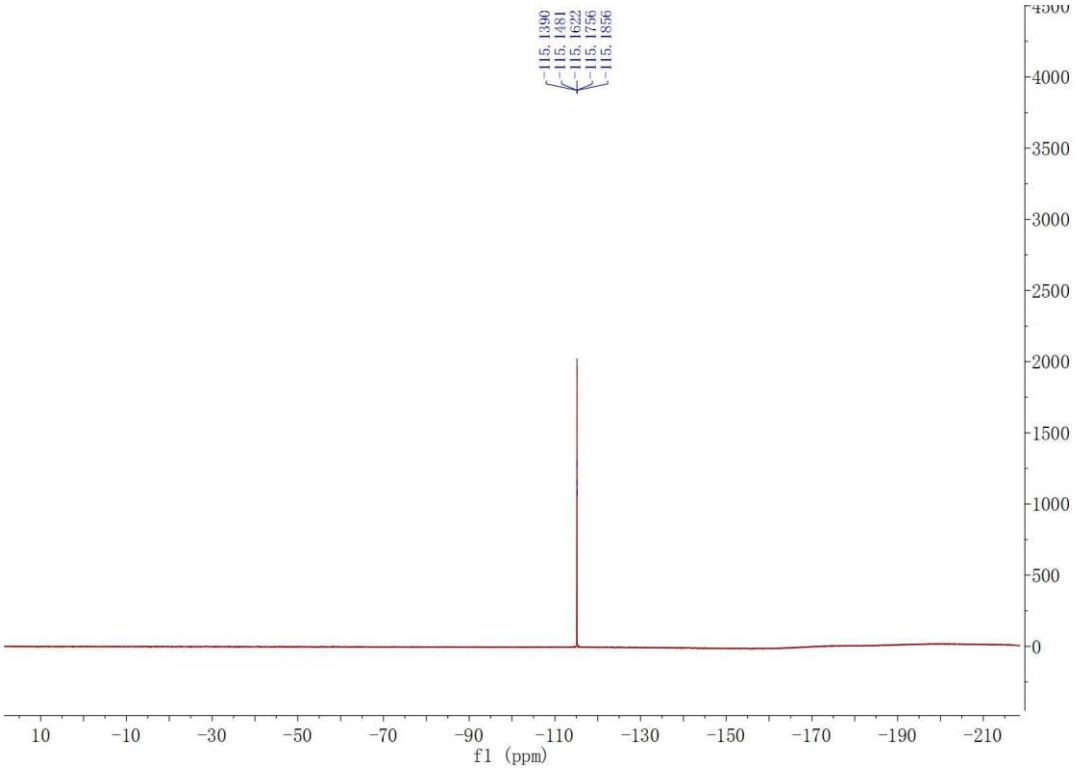
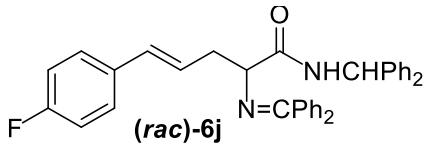





-115.1390
-115.1481
-115.1622
-115.1756
-115.1856
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)



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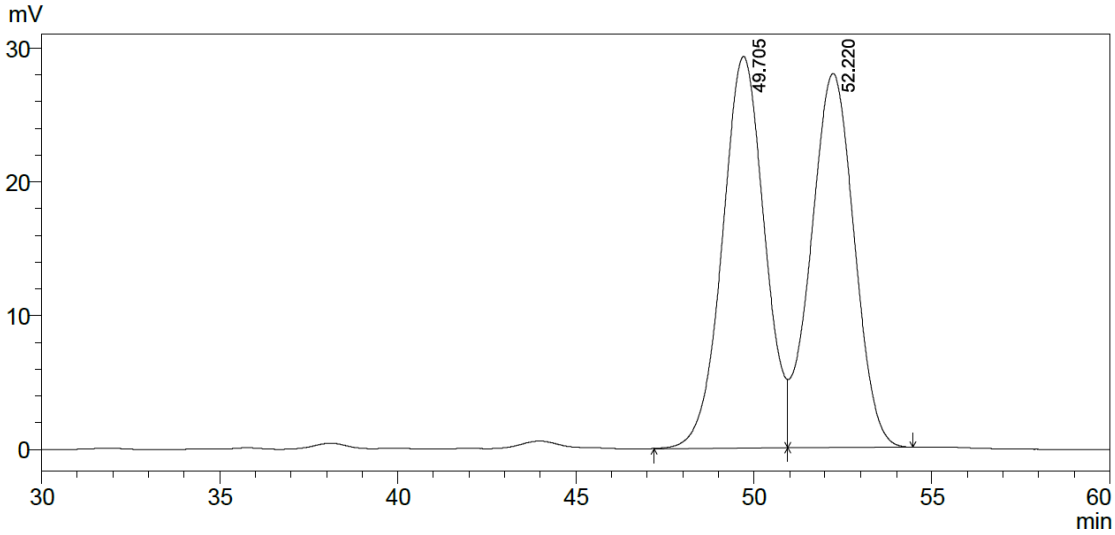
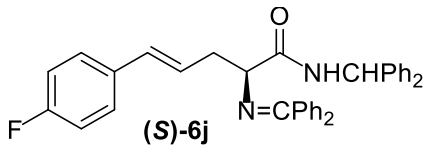


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.705	2418164	29271	50.547	51.158
2	52.220	2365803	27945	49.453	48.842
Total		4783967	57216	100.000	100.000



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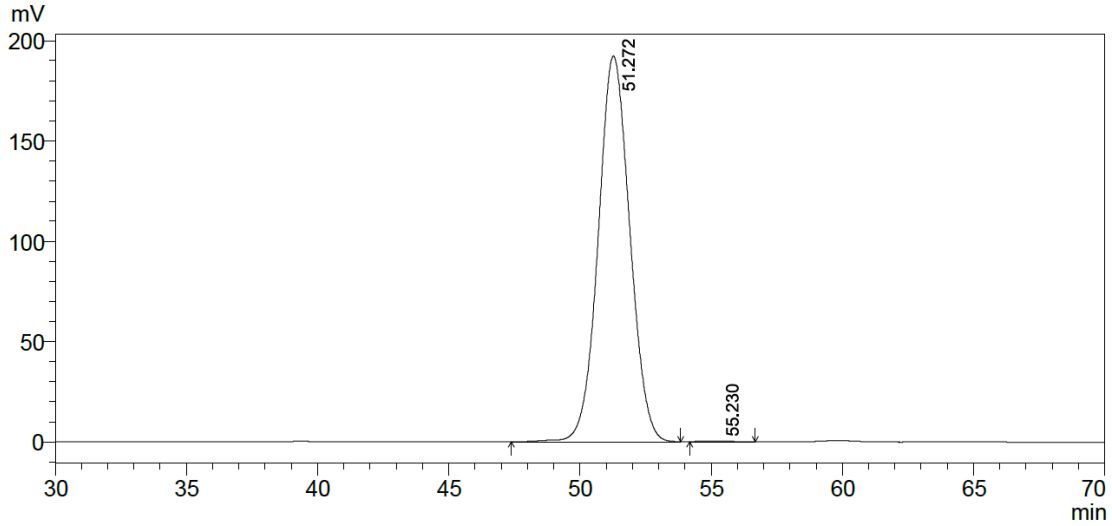
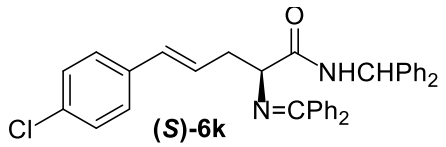
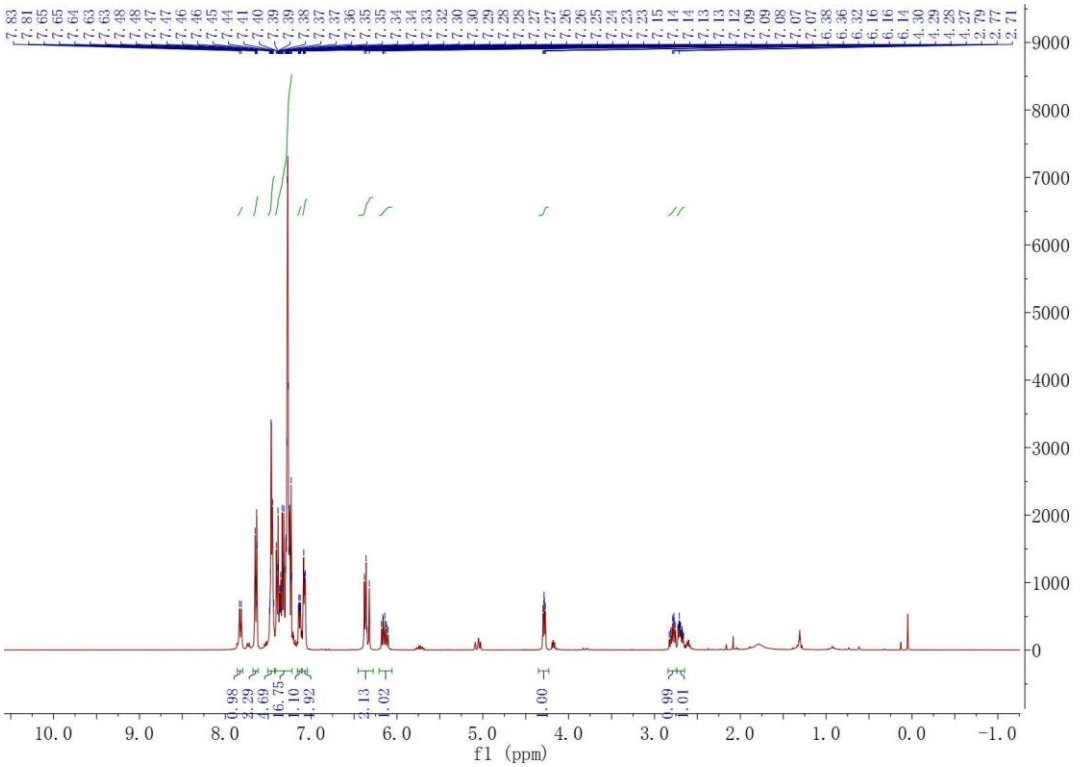
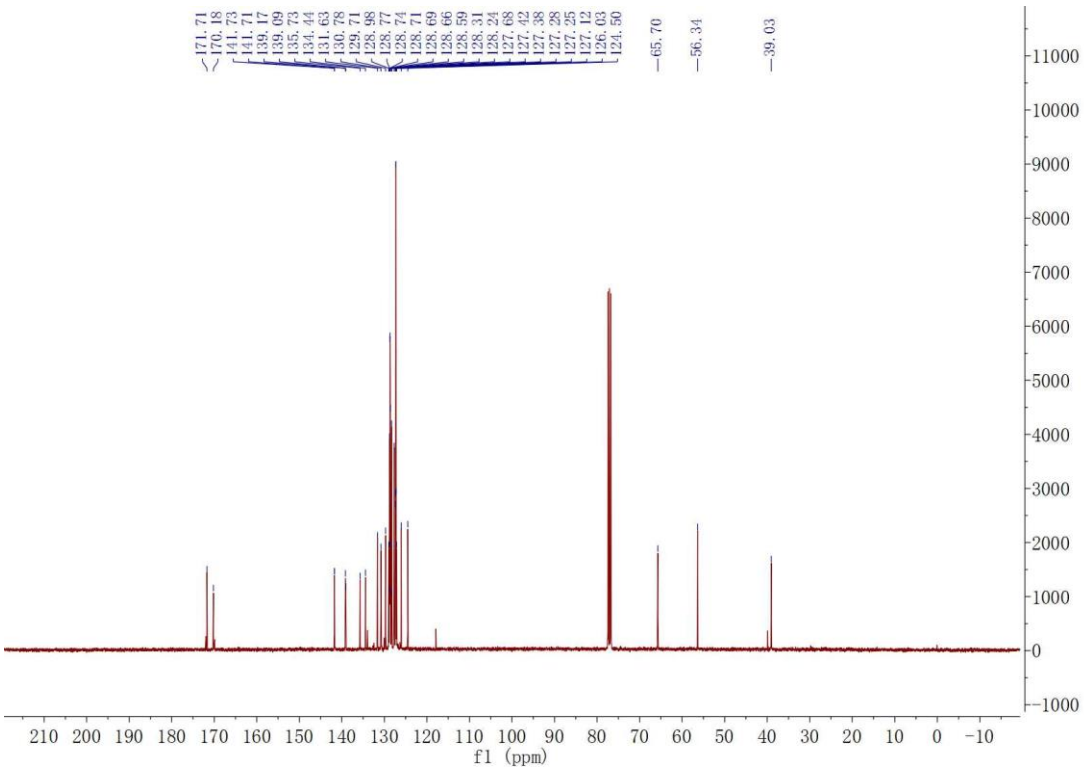


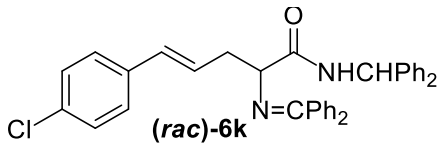
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	51.272	16086223	192215	99.842	99.827
2	55.230	25396	334	0.158	0.173
Total		16111619	192548	100.000	100.000

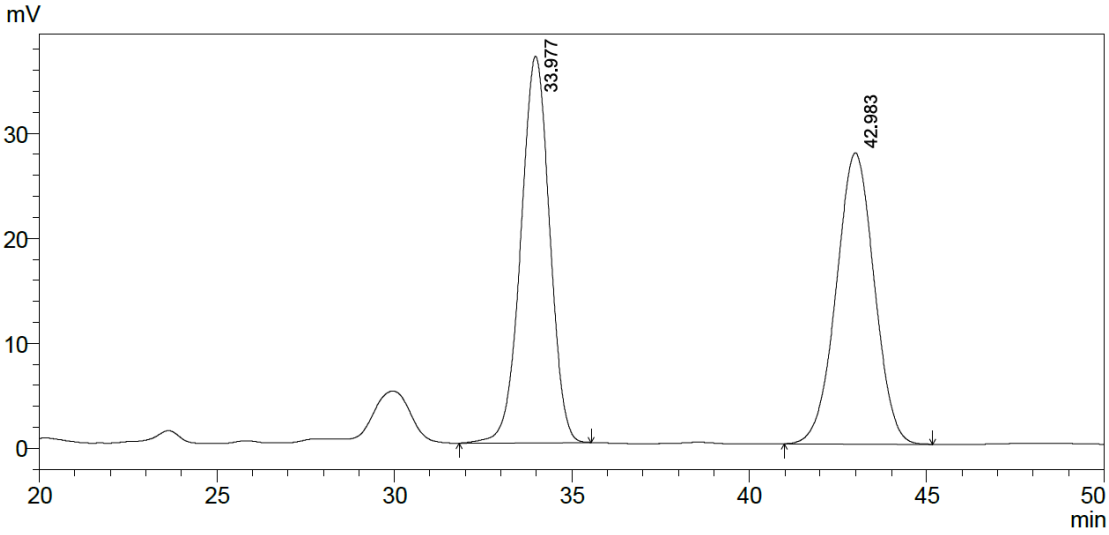

O
NHCHPh2
N=CPh2
Cl
(S)-6k


f1 (ppm)


f1 (ppm)

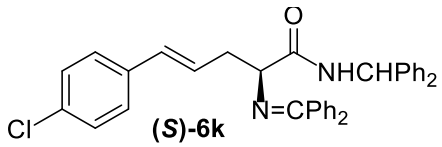


(*rac*)-6k

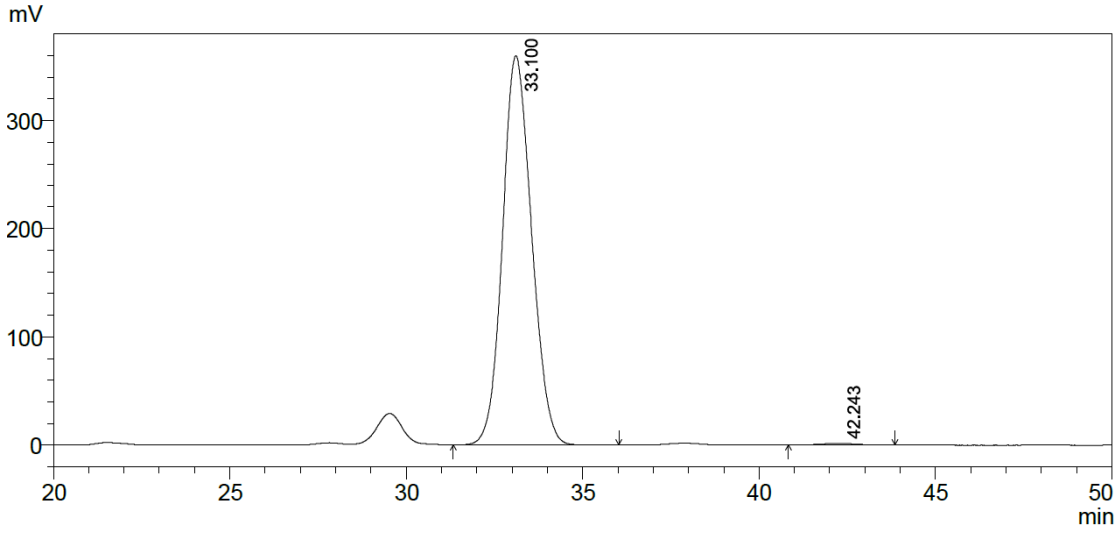


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.977	2077725	36813	50.126	57.031
2	42.983	2067271	27736	49.874	42.969
Total		4144996	64549	100.000	100.000

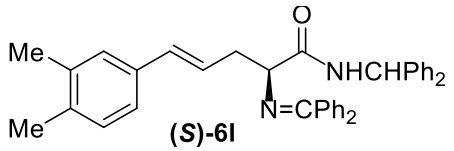


(*S*)-6k

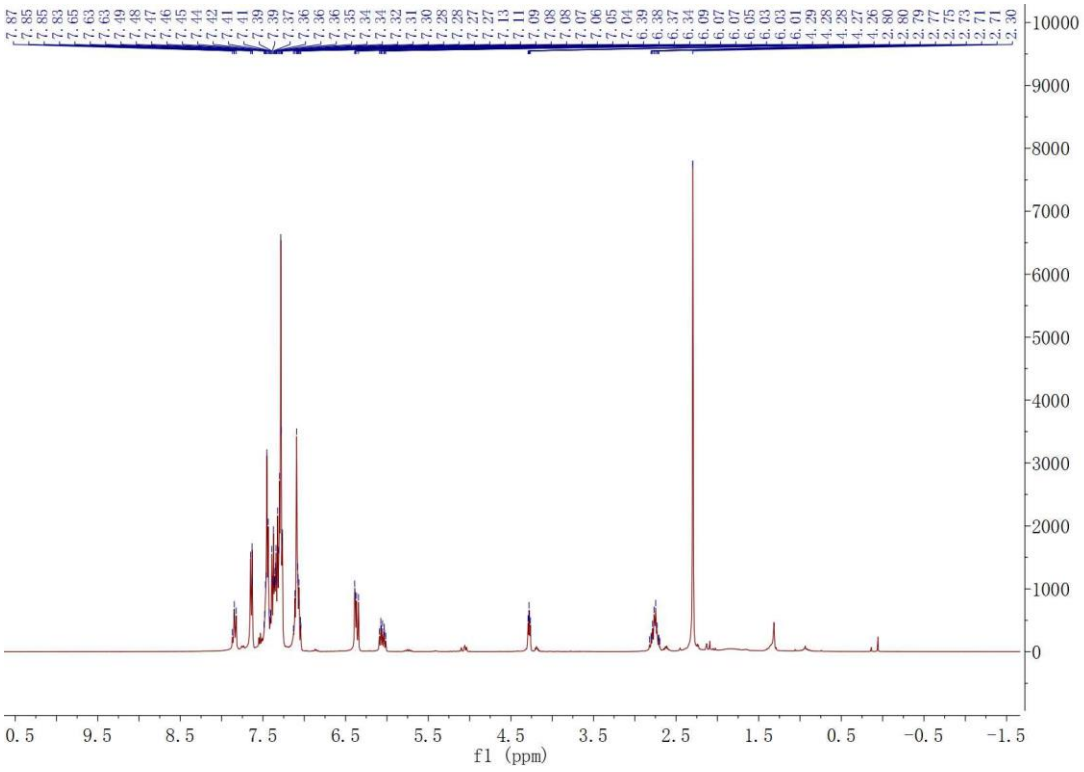


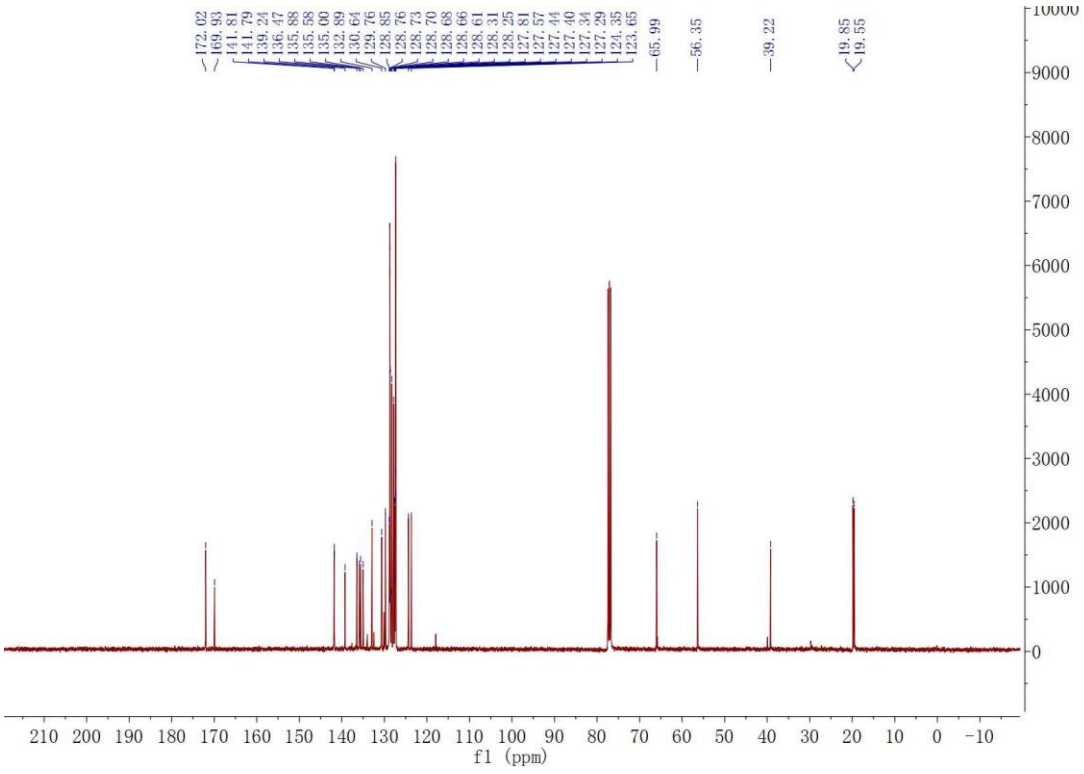
PeakTable

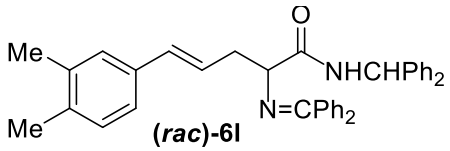
Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.100	20633488	359707	99.492	99.598
2	42.243	105342	1453	0.508	0.402
Total		20738830	361160	100.000	100.000



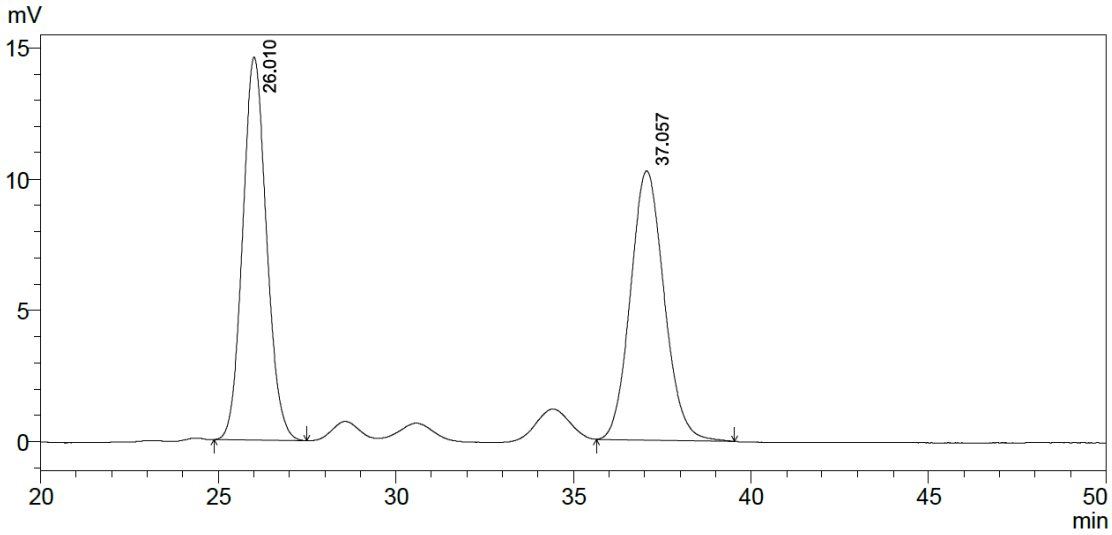
(*S*)-6l





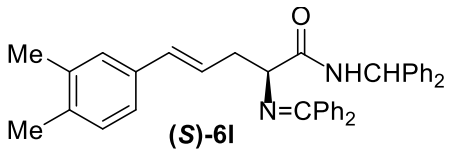


(*rac*)-6l

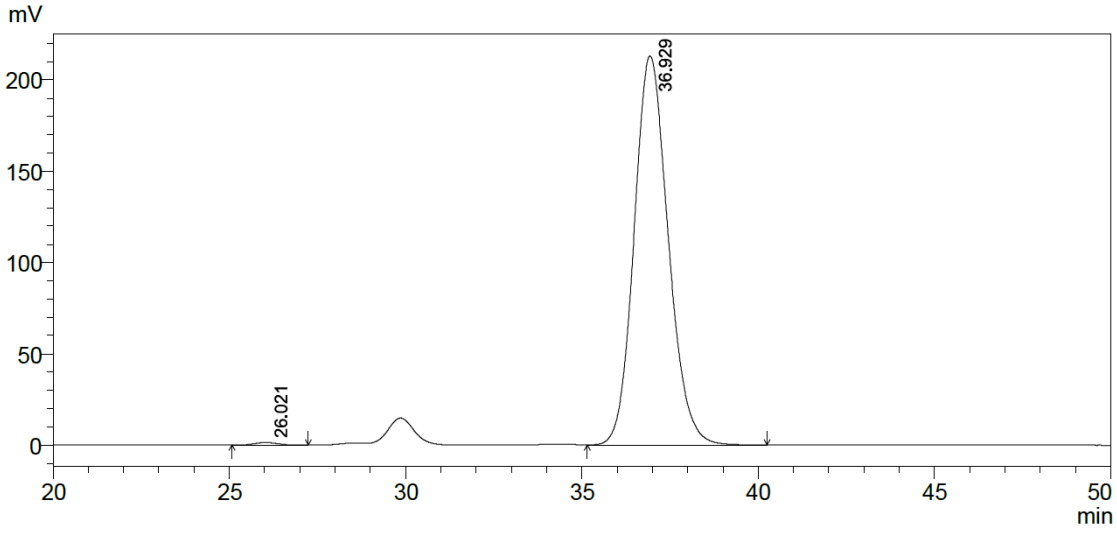


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.010	680997	14586	50.177	58.742
2	37.057	676188	10245	49.823	41.258
Total		1357185	24831	100.000	100.000

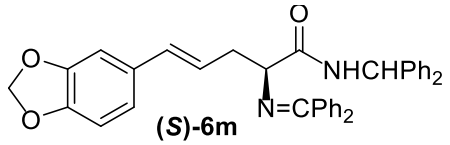


(*S*)-6l

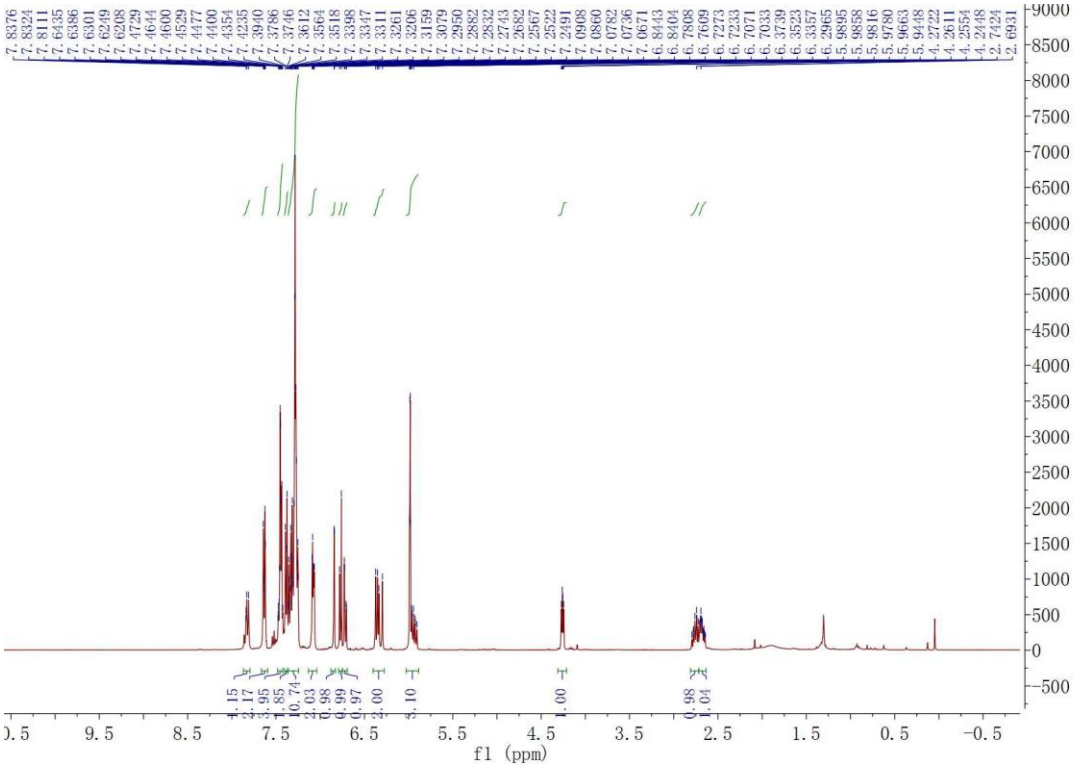


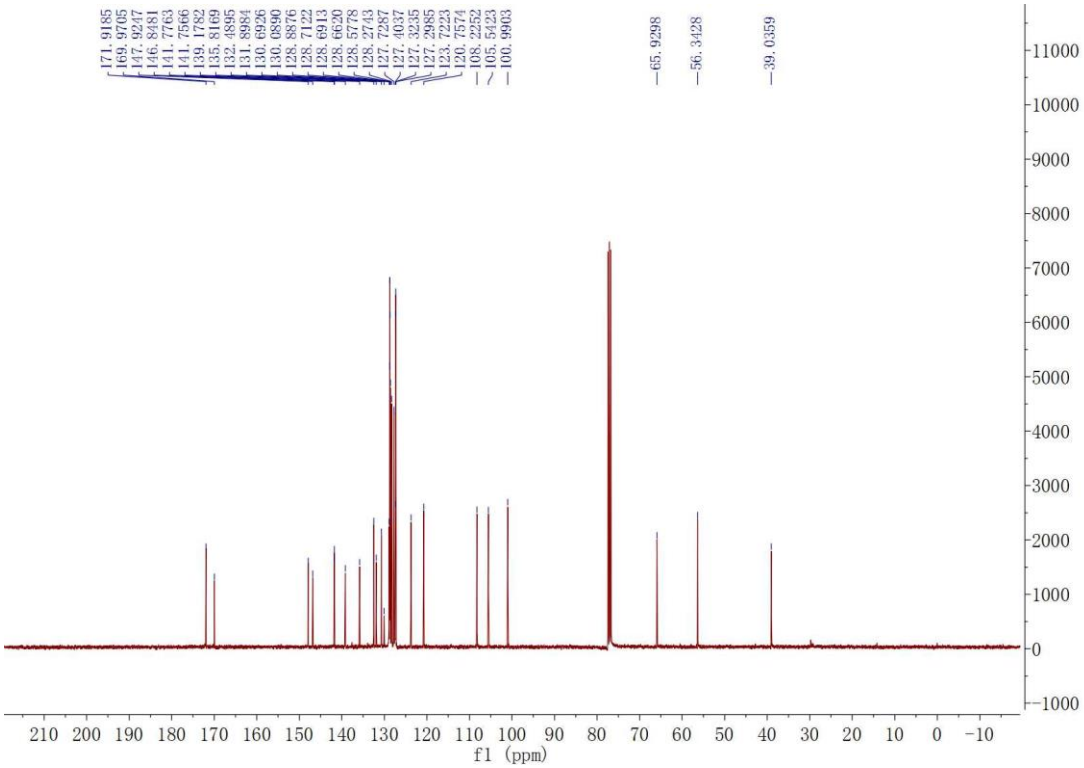
PeakTable

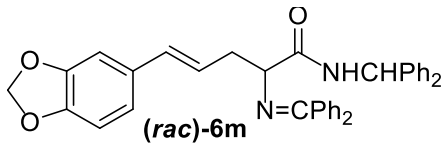
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.021	67504	1432	0.469	0.668
2	36.929	14322389	213015	99.531	99.332
Total		14389893	214446	100.000	100.000



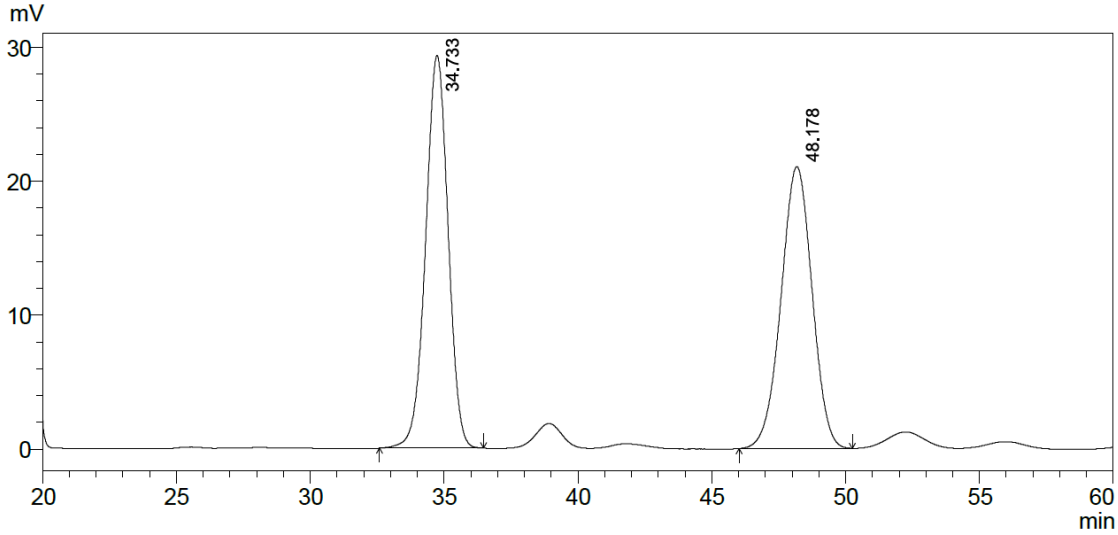
(*S*)-6m





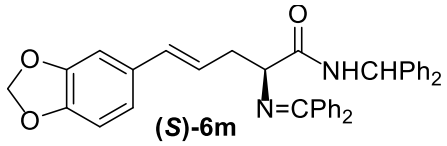


(*rac*)-6m

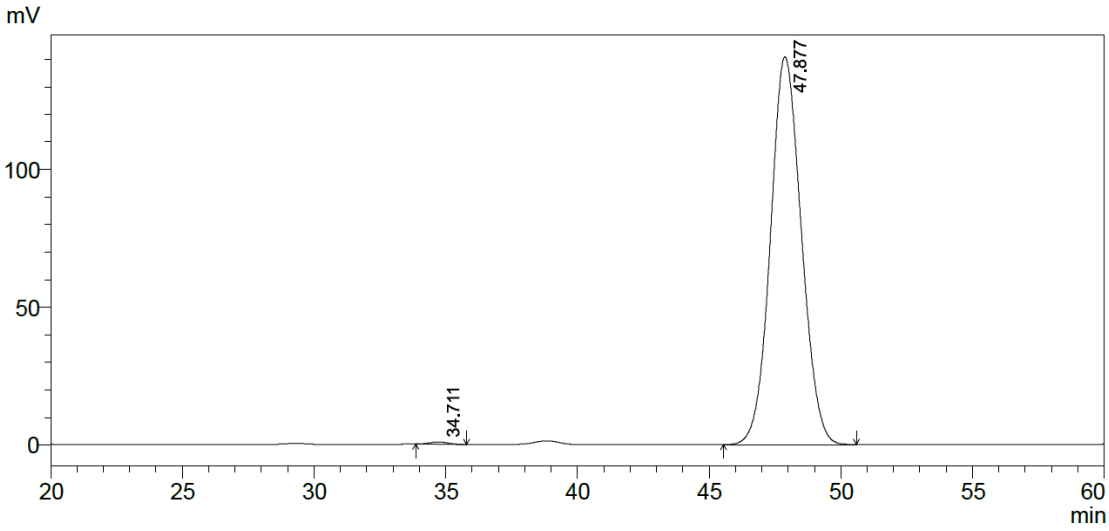


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.733	1716657	29311	50.281	58.214
2	48.178	1697458	21040	49.719	41.786
Total		3414115	50351	100.000	100.000

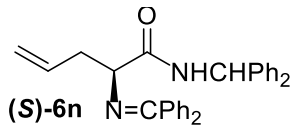


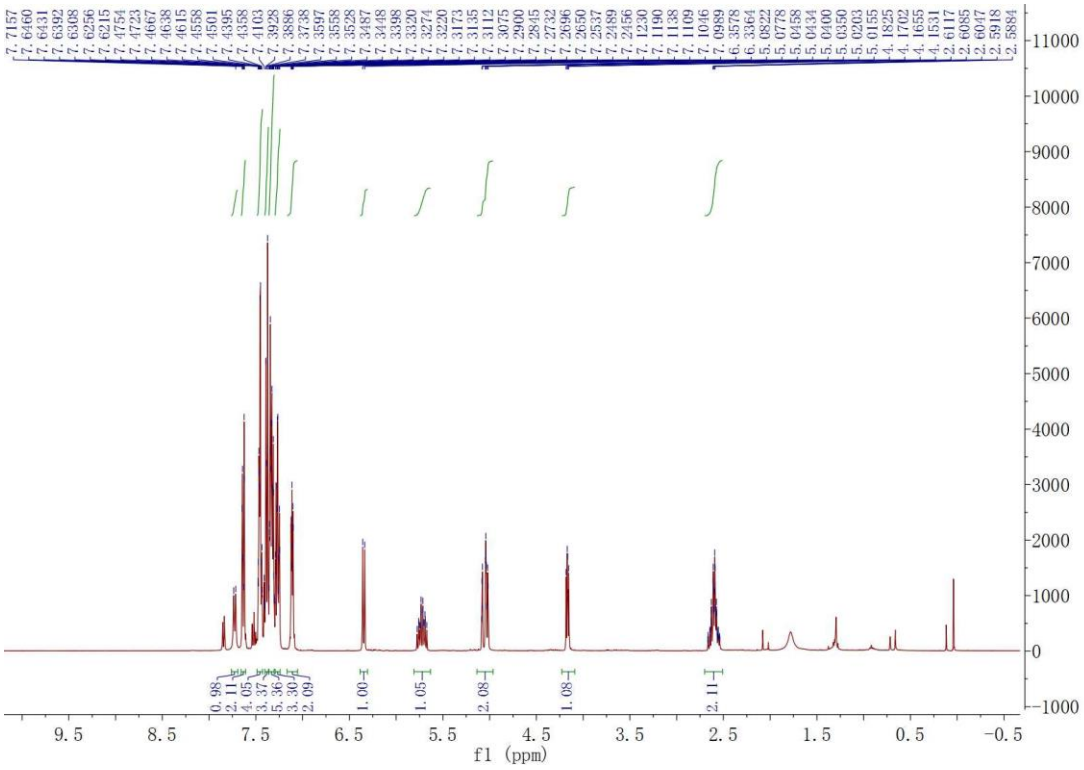
(*S*)-6m

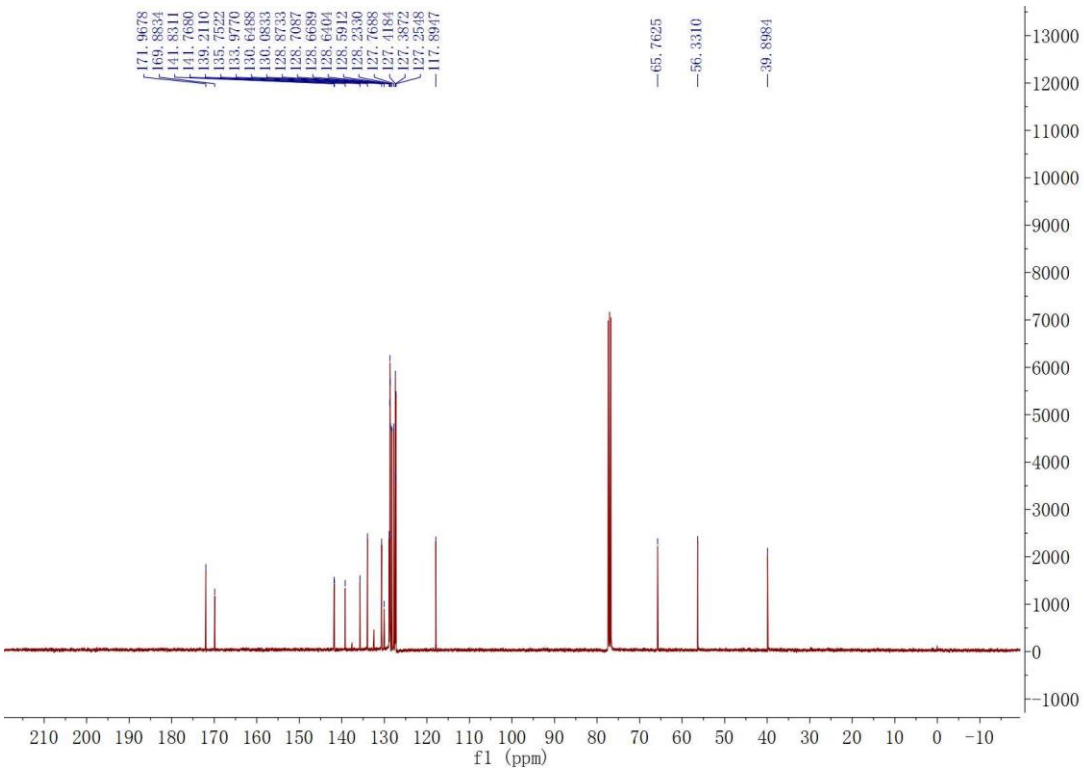


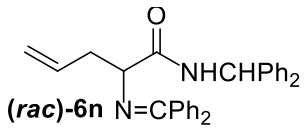
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.711	43991	854	0.381	0.603
2	47.877	11496044	140826	99.619	99.397
Total		11540035	141680	100.000	100.000

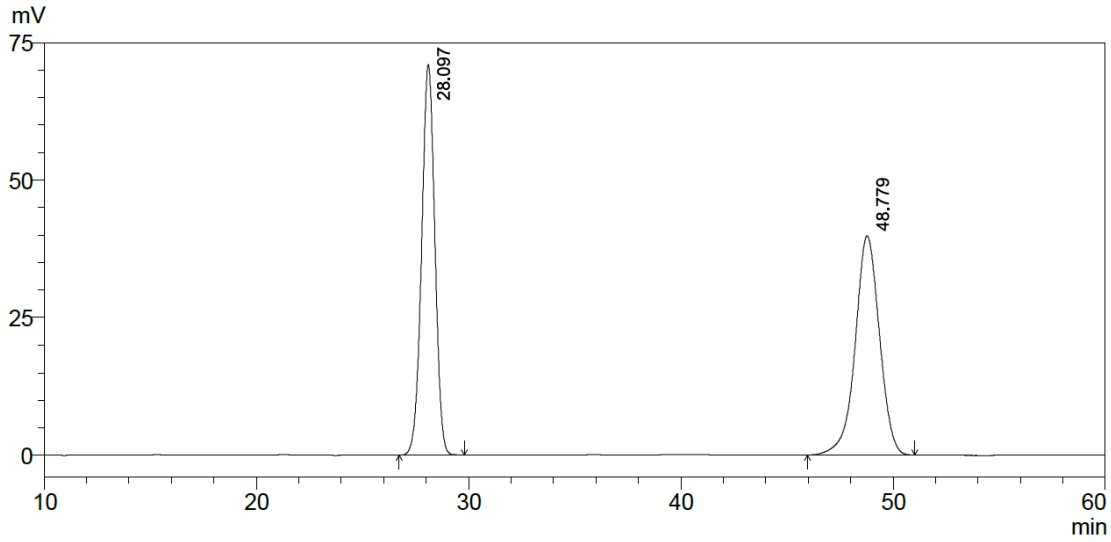

O
NHCHPh2
(S)-6n
N=CPh2


f1 (ppm)


f1 (ppm)

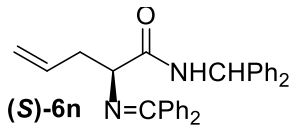


(*rac*)-6n

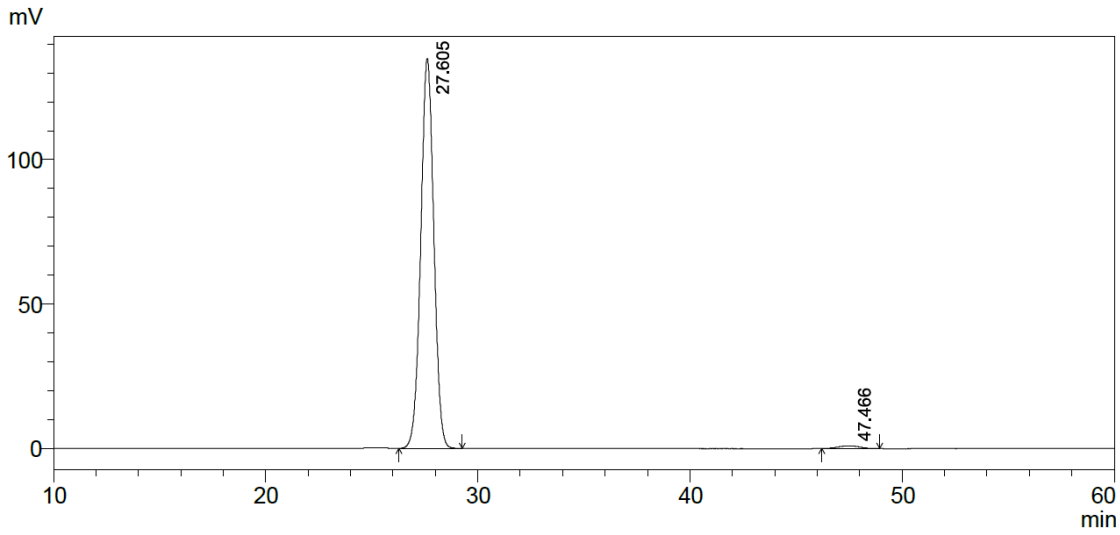


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.097	3079151	70912	49.283	64.046
2	48.779	3168806	39808	50.717	35.954
Total		6247958	110720	100.000	100.000

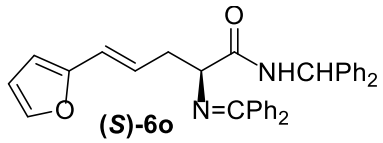


(*S*)-6n

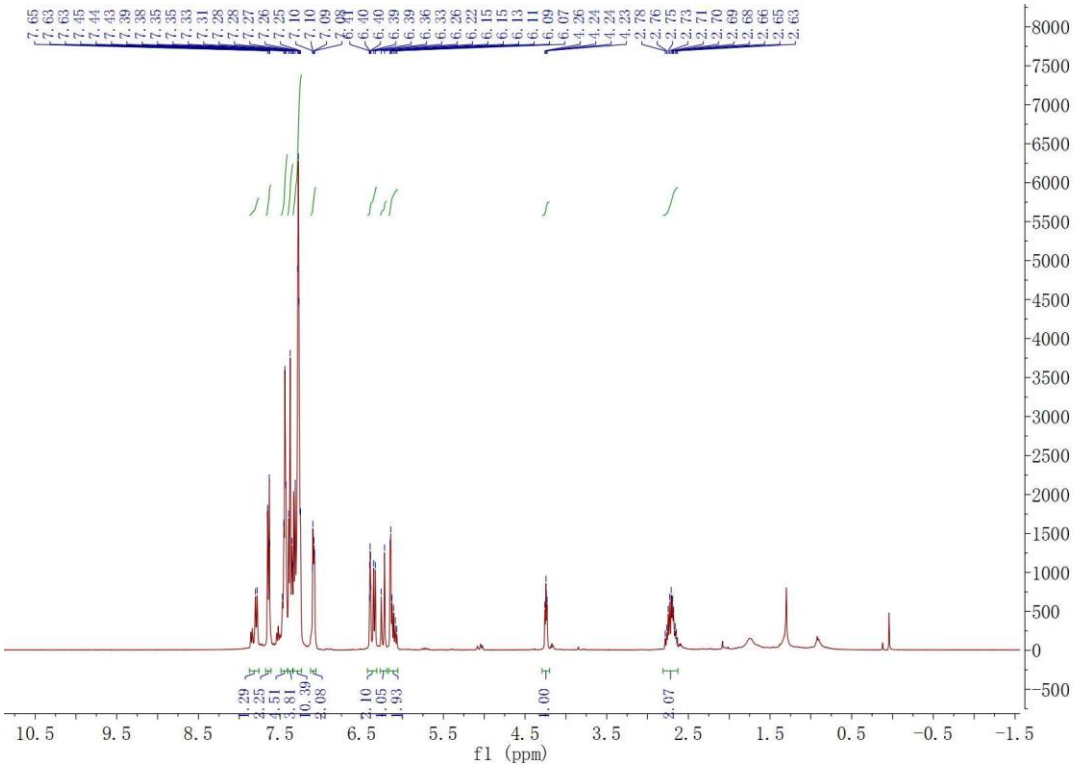


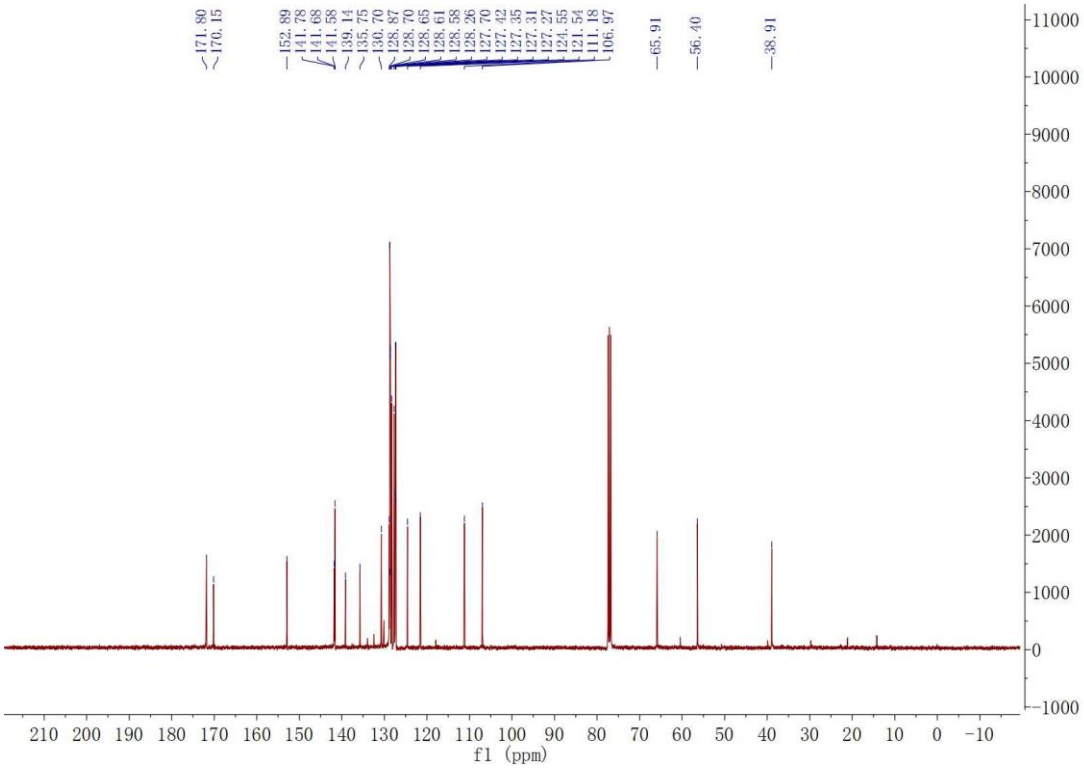
PeakTable

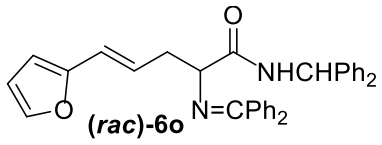
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.605	5784462	134985	98.846	99.297
2	47.466	67506	956	1.154	0.703
Total		5851968	135941	100.000	100.000



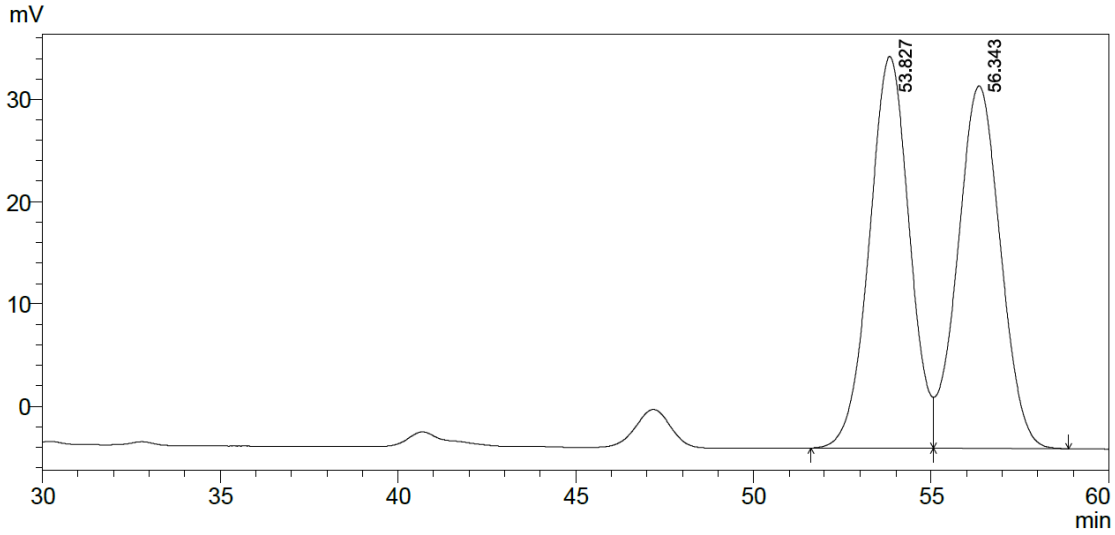
(*S*)-6o





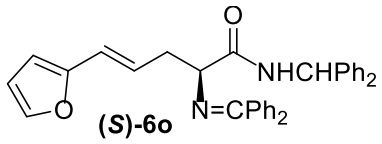


(*rac*)-6o

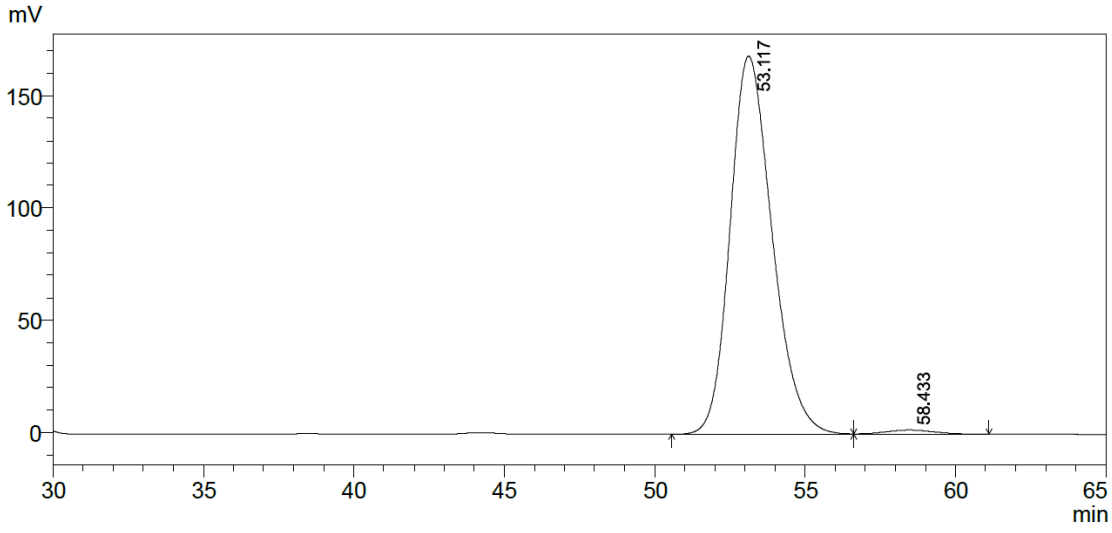


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.827	3000879	38294	50.292	51.928
2	56.343	2965997	35450	49.708	48.072
Total		5966876	73744	100.000	100.000

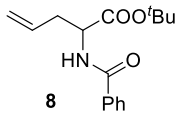


(*S*)-6o



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.117	16367710	168524	98.708	98.916
2	58.433	214296	1846	1.292	1.084
Total		16582006	170370	100.000	100.000



8