

Supporting Information

Asymmetric Counter-Anion-Directed Aminomethylation: Synthesis of Chiral β -Amino Acids via Trapping of an Enol Intermediate

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1. General information & materials

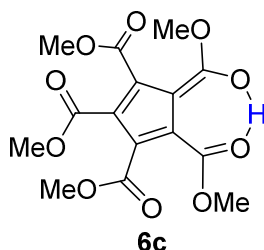
General: All ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Bruker spectrometers in CDCl_3 . ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 on a 400 MHz spectrometer; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (J) were given in Hertz. The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectrometry (HRMS) were recorded on a commercial apparatus (ESI or CI Source). Enantioselectivities were determined with HPLC using Chiralpak IA, IC, ID and AD-H columns. The racemic standards used in HPLC studies were prepared according to the general procedure using racemic BINOL-derived phosphoric acid catalyst *rac*-PPA.

Materials: Solvent CHCl_3 was distilled over calcium hydride. α -aminomethyl ether **3** were prepared according to the literature method.¹ Chiral BINOL-derived phosphoric acids (**5a-5f**) were prepared according to the literature procedures.² 4 Å molecular sieve was dried in a Muffle furnace at 250 °C over 5 h. All reactions were carried out under nitrogen atmosphere in a well-dried glassware.

2. Experimental procedures

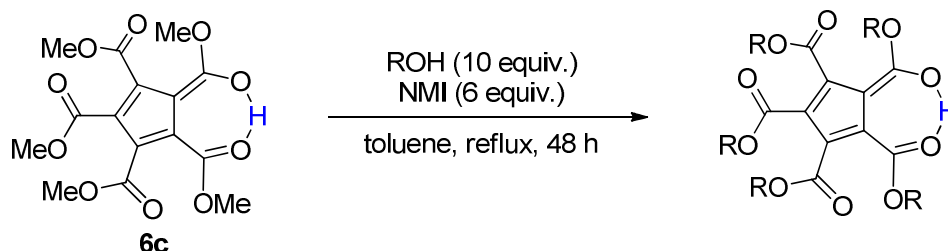
2.1 Synthesis of organocatalysts 6

Pentakis(methoxycarbonyl)cyclopentadiene (6c):



Cyclopentadiene acid **6c** was prepared according to the reported procedure to produce.³

General procedure for the Synthesis of chiral PCCPs (6a, 6b, 6d, and 6e):⁴



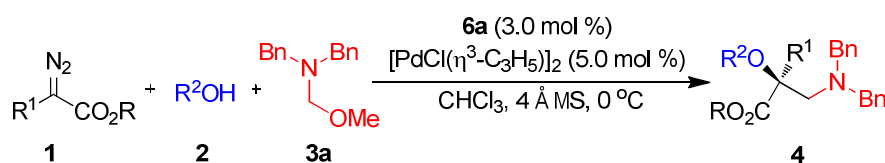
According to the reported method by Lambert, cyclopentadiene **6c** (1.0 equiv), chiral alcohol (10 equiv), and 1-methylimidazole (6.0 equiv) were dissolved in toluene. The reaction solution was refluxing for 48 h at 125 °C, then cooled to room temperature, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (MeOH/DCM=1/50-1/20). The purified product was subsequently washed with 6 M HCl (3 x), dried with anhydrous sodium sulfate, and concentrated *in vacuo* after filtration to yield a brown solid product **6**. The characterization data of these catalysts are identical to those earlier reported.⁴

2.2 General procedure for optimization of conditions of three-component reaction

To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added metal catalyst (5 mol %), chiral Brønsted acid, and 4 Å molecular sieve (100 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Then, benzyl alcohol **2a** (32.4 mg, 0.3 mmol, 1.5 eq) and α -aminomethyl ether **3a** (48.2 mg, 0.2 mmol, 1.0 eq) in corresponding solvent (1.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1a** (52.8 mg, 0.3 mmol, 1.5 eq) in 1.5 mL of same solvent was added to the

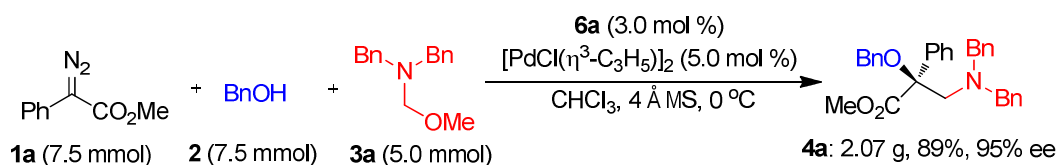
above reaction mixture for 2 h *via* a syringe pump at indicate temperature. After completion of the addition, stirring was continued at indicate temperature until the diazo compound was consumed completely. The solvent was evaporated under vacuum after filtering through Celite. The residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/100~1/10) to give the product **4a**.

2.3 General procedure for the enantioselective three-component reaction



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (3.7 mg, 5.0 mol %), chiral PCCP **6a** (5.9 mg, 3.0 mol %), and 4 Å molecular sieve (100 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Then, benzyl alcohol **2** (0.3 mmol, 1.5 eq) and α -aminomethyl ether **3a** (48.2 mg, 0.2 mmol, 1.0 eq) in CHCl_3 (1.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1** (0.3 mmol, 1.5 eq) in 1.5 mL of CHCl_3 was added to the above reaction mixture for 2 h *via* a syringe pump at 0 °C. After completion of the addition, stirring was continued at 0 °C until the diazo compound was consumed completely. The solvent was evaporated under vacuum after filtering through Celite. The residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/100~1/10) to give the products **4** in high yields.

2.4 Procedure for the gram scale three-component reaction

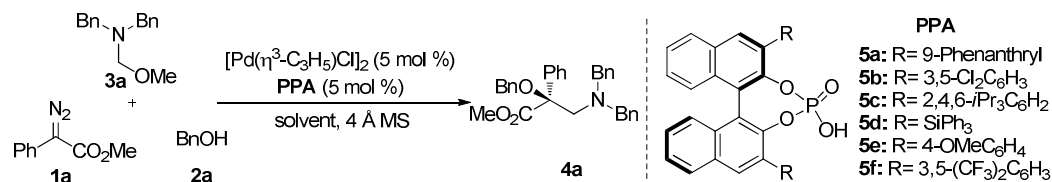


To a 25 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (90 mg, 5.0 mol %), chiral PCCP **6a** (146 mg, 3.0 mol %), and 4 Å molecular sieve (300 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen

(3 cycles). Then, benzyl alcohol **2a** (810 mg, 7.5 mmol, 1.5 eq) and α -aminomethyl ether **3a** (1.22 g, 5.0 mmol, 1.0 eq) in CHCl_3 (10 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1a** (1.32 g, 7.5 mmol, 1.5 eq) in 5 mL of CHCl_3 was added to the above reaction mixture for 2 h via a syringe pump at 0 °C. After completion of the addition, stirring was continued at 0 °C for 10 h. Upon completion (monitored by TLC), the solvent was evaporated under vacuum after filtering through Celite. The residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/100~1/10) to give 2.07 g pure product **4a** (89% yield, 95% ee).

3. Complete data for optimization of the reaction conditions

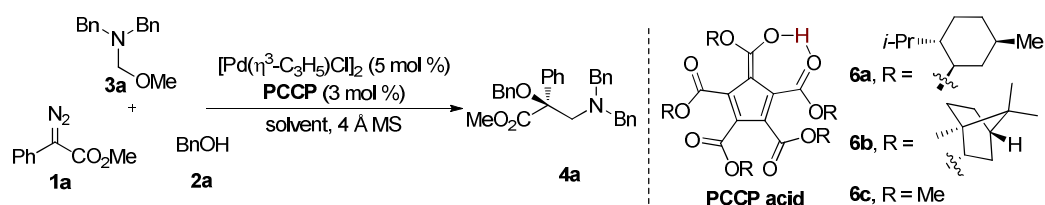
Table S1. Preliminary Optimization of Three-component Reaction with PPA^a



entry	solvent	T/°C	PPA	yield ^b (%)	ee ^c (%)
1	DCM	25	5a	90	0
2	DCM	25	5b	87	5
3	DCM	25	5c	92	37
4	DCM	25	5d	90	31
5	DCM	25	5e	93	0
6	DCM	25	5f	87	12
7	DCM	0	5a	93	0
8	DCM	0	5b	89	5
9	DCM	0	5c	95	51
10	DCM	0	5d	92	27
11	DCM	0	5e	90	0
12	DCM	0	5f	89	15
13	DCM	-20	5c	87	48
14	DCM	-20	5d	89	27
15 ^d	DCM	0	5c	88	51
16 ^e	DCM	0	5c	68	53
17	THF	0	5c	< 20	-
18	toluene	0	5c	72	47
19	EA	0	5c	50	60
20	CHCl ₃	0	5c	89	53

^aUnless otherwise indicated, all reactions were conducted on a 0.2 mmol scale for **3**, **1:2:3** = 1.5:1.5:1 ^bIsolated yields. ^cDetermined by HPLC analysis of the major product using a chiral stationary phase. ^d10 mol % **5c** was used. ^e20 mol % **5a** was used.

Table S2. Optimization of Three-component Reaction with PCCP^a

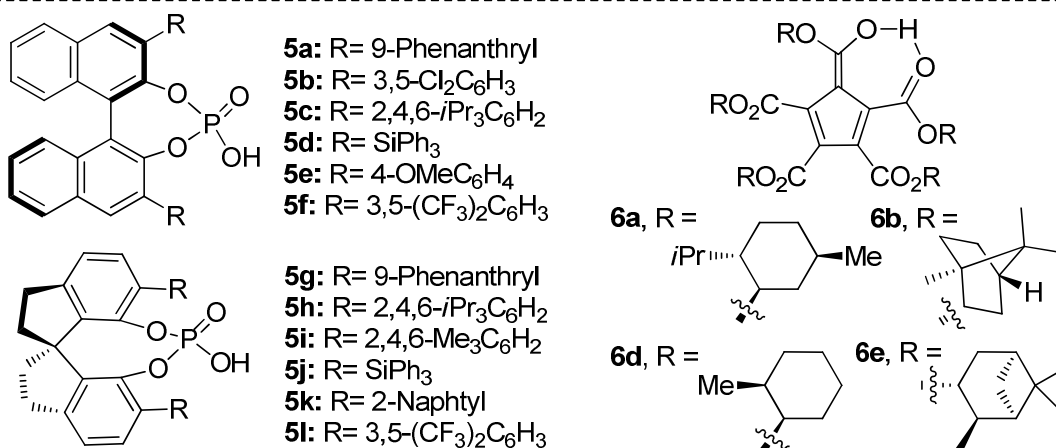
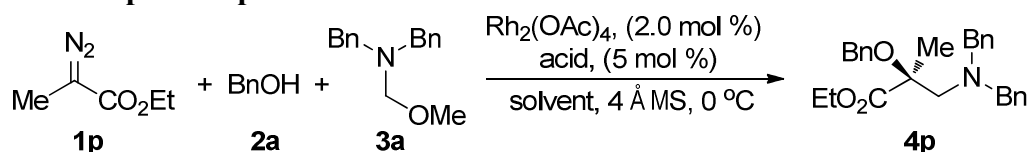


entry	solvent	T/°C	PCCP	yield ^b (%)	ee ^c (%)
1	DCM	25	6c	92	-
2	DCM	25	6a	90	85
3	DCM	25	6b	89	80
4	DCM	0	6a	90	88
5	DCM	0	6b	88	84
6	DCM	-20	6a	75	90
7	DCM	-20	6b	75	86
8	CHCl ₃	0	6a	92	96
9	toluene	0	6a	78	88
10	EA	0	6a	50	80
11	DCE	0	6a	90	93
12	THF	0	6a	< 20	-
13 ^d	CHCl ₃	0	6a	91	94
14 ^e	CHCl ₃	0	6a	75	93
15 ^f	CHCl ₃	0	6a	40	93
16 ^g	CHCl ₃	0	6a	90	96

^aUnless otherwise indicated, all reactions were conducted on a 0.2 mmol scale for **3**, **1**:**2**:**3** = 1.5:1.5:1. ^bIsolated yield. ^cDetermined by HPLC analysis of the major product using a chiral stationary phase. ^d5.0 mol % **6a** was used. ^e1.0 mol % **6a** was used. ^f0.5 mol % **6a** was used.

^gThe reaction was catalyzed by Rh₂(OAc)₄ instead of the Pd-catalyst.

Table S3. Condition Optimization of Three-Component Reaction with Alkyl Diazo Compound 1p^a



entry	solvent	acid	yield (%) ^b	ee (%) ^c
1	CHCl ₃	5a	86	0
2	CHCl ₃	5b	79	0
3	CHCl ₃	5c	82	16
4	CHCl ₃	5d	80	10
5	CHCl ₃	5e	74	0
6	CHCl ₃	5f	83	5
7	CHCl ₃	5g	76	64
8	CHCl ₃	5h	81	60
9	CHCl ₃	5i	85	43
10	CHCl ₃	5j	92	29
11	CHCl ₃	5k	80	51
12	CHCl ₃	5l	89	43
13	CHCl ₃	6a	85	80
14 ^d	CHCl ₃	6a	23	81
15	CHCl ₃	6b	81	76
16	CHCl ₃	<i>ent</i> - 6a	82	-80
17	CHCl ₃	6d	78	64

18	CHCl ₃	6e	70	52
19	DCM	6a	88	63
20	THF	6a	< 10	-
21	toluene	6a	42	47
22	EA	6a	27	57

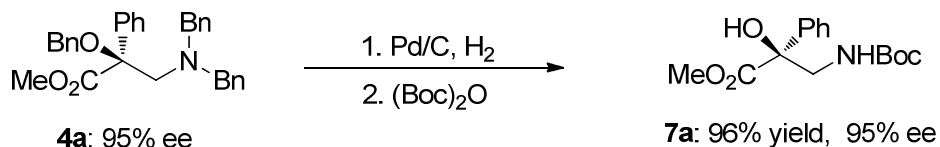
^aUnless otherwise indicated, all reactions were conducted in 0.2 mmol scale for **3a**, **1n:2a:3a** = 1.5:1.5:1. ^bIsolated yields. ^cDetermined by HPLC analysis using a chiral stationary phase. ^dThe reaction was catalyzed by [PdCl(η³-C₃H₅)]₂ instead of Rh₂(OAc)₄.

Table S4. Investigation the Reaction of Alkyl Diazo Compound 1p with a Variety of Alcohols 2.^a

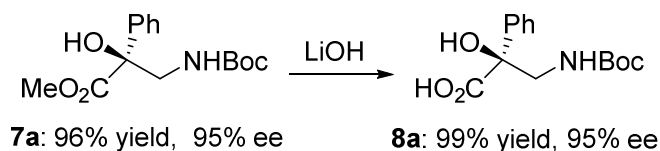
entry	ROH	yield (%) ^b	ee (%) ^c
1	EtOH	83	40
2		76	52
3		87	75
4		85	67
5		89	85
6		90	90

^aUnless otherwise indicated, all reactions were conducted in 0.2 mmol scale for **3a**, **1n:2a:3a** = 1.5:1.5:1. ^bIsolated yields. ^cDetermined by HPLC analysis using a chiral stationary phase.

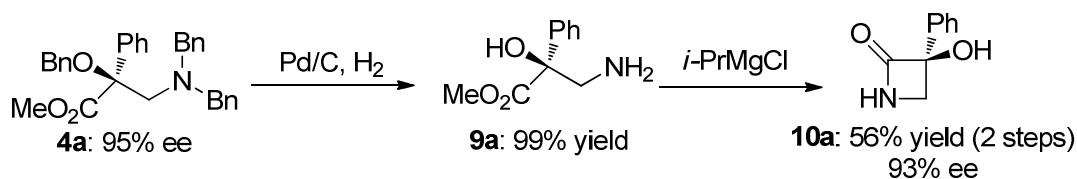
4. Product derivatizations



Synthesis of 7a: To a 50-mL hydrogenation reactor containing a magnetic stirring bar, **4a** (930 mg, 2.0 mmol) in 25 mL of MeOH, was added wet 10% Pd/C (200 mg, 20 %). The heterogeneous mixture was placed under 40-60 psi H₂ atmosphere and stirred overnight at room temperature. After the hydrogenolysis was complete, as indicated by LC-MS analysis, the reaction mixture was diluted with 25 mL of DCM. DIPEA (387 mg, 3 mmol, 1.5 eq) and Boc₂O (654 mg, 2.4 mmol, 1.2 eq) were added in sequence at room temperature. The mixture was stirred at room temperature overnight and then filtered through a pad of Celite to remove Pd/C, and the solid was washed with MeOH. The combined filtrate was concentrated under vacuum, and the residue was purified by silica chromatography column (eluent: EtOAc/light petroleum ether = 1/10~1/5) to give 566 mg **7a** (96% yield and 95% ee).

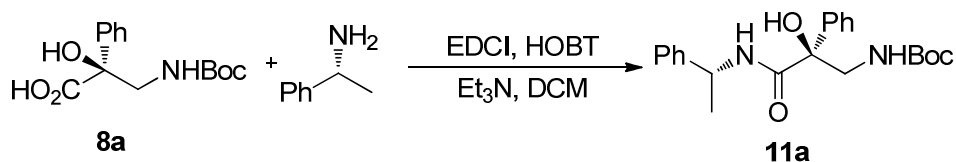


Synthesis of 8a: To a 50-mL oven-dried flask containing a magnetic stirring bar, *N*-Boc- α -hydroxyl- β -amino acid ester **7a** (590 mg, 2.0 mmol), THF (20 mL), H₂O (10 mL), and LiOH (3.0 mmol, 1.5 eq) were added in sequence at room temperature. The reaction mixture was then stirred at room temperature for 24 hours. After completion of the reaction, as indicated by LC-MS analysis, the reaction mixture was acidified to pH = 3 with 1N HCl aqueous solution and extracted with CH₂Cl₂ (3 $\times$ 100 mL). The combined CH₂Cl₂ layers was washed with brine and dried over anhydrous Na₂SO₄. The solvent was evaporated under vacuum after filtration to afford 560 mg pure *N*-Boc- α -hydroxyl- β -amino acid **8a** (99% yield and 95% ee).



Synthesis of 9a: To a 50-mL hydrogenation reactor containing a magnetic stirring bar, **4a** (465 mg, 1.0 mmol) in 15 mL of MeOH, was added wet 10% Pd/C (100 mg, 20 %). The heterogeneous mixture was placed under 40-60 psi H₂ atmosphere and stirred overnight at room temperature. After the hydrogenolysis was complete, as indicated by LC-MS analysis. The mixture was filtered through a pad of Celite to remove Pd/C, and the solid was washed with MeOH. The combined filtrate was concentrated under vacuum to give crude product α -hydroxyl- β -amino acid ester **9a**.

Synthesis of 10a: To a 50-mL oven-dried flask containing a magnetic stirring bar, the above obtained **9a** (195 mg, 1.0 mmol) in anhydrous THF (5.0 mL), was added *i*PrMgCl (2.5 mL, 2.0 M in THF, 5.0 mmol) drop wisely *via* a syringe at 0 °C. The resulting reaction mixture was stirred at room temperature overnight. Upon completion (monitored by LC-MS), the reaction was quenched with NH₄Cl aq. (20 mL) and extracted with ethyl acetate (50 mL). The organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo after filtration and the residue was purified by flash chromatography (eluent: EtOAc/light petroleum ether = 1/10~1/2) to give 91 mg **10a** as a white powder (56% yield over 2 steps from **4a**, 93% ee).

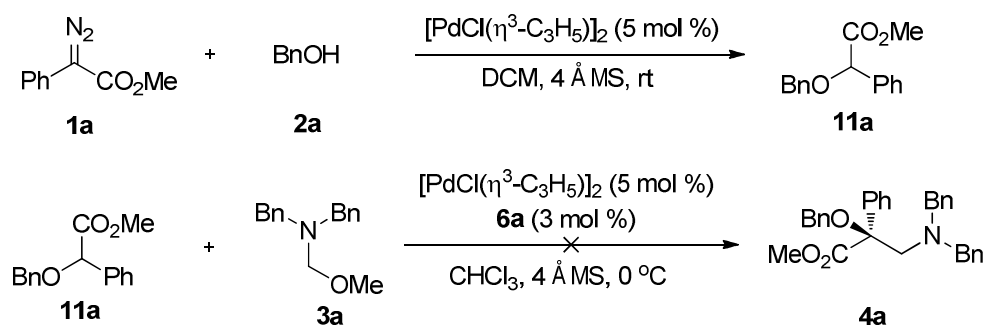


Synthesis of 11a: To a 50-mL oven-dried flask containing a magnetic stirring bar, *N*-Boc- α -hydroxyl- β -amino acid **8a** (281 mg, 1.0 mmol) in DCM (15 mL), was added HOBT (200 mg, 1.5 mmol) and EDCI (290 mg, 1.5 mmol) in sequence under a nitrogen atmosphere at room temperature. The mixture was stirred for 10 minutes at room temperature and cooled down to 0 °C. (*R*)-1-phenylethylamine (0.15 mL, 1.2 mmol) and Et₃N (0.6 mL) were added to the above reaction mixture in sequence. The mixture was stirred for 24 h at room temperature. After completion of the reaction, as indicated by LC-MS analysis, diluted with DCM (25 mL), washed with 1N HCl aqueous solution (4 × 20 mL) and NaHCO₃ saturated solution in sequence. The organic phase was

dried over anhydrous Na_2SO_4 , the solvent was evaporated under vacuum after filtration to give crude product **11a** as a white solid (256 mg, 67% yield) with dr >19:1, which indicates that no racemization was occurred during the hydrolysis of **7a** to produce **8a** under the reaction conditions.

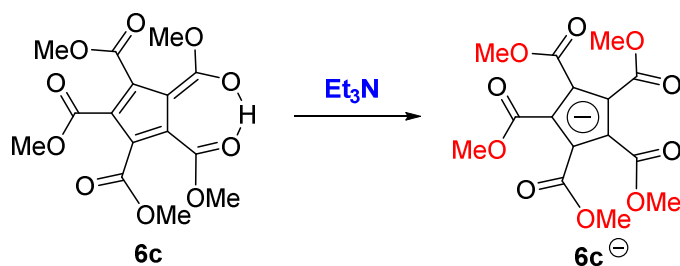
5. Control experiments

Control reaction with insertion product **11a**



Control experiment with the O-H insertion product **11a** and **3a** was conducted under the standard condition, in which no three-component product was observed. These results exclude the possibility that the product is generated from the O-H insertion product **11a**.

Proton NMR observation of the formation of V-6c⁻



To a NMR tube, **6c** (15 mg) in CDCl_3 (0.5 ml) was added, and the sample was subjected to ^1H NMR analysis. Et_3N (10 mg) was then added to the above NMR tube, mixed uniformly, and followed by ^1H NMR analysis. After the addition of Et_3N into **6c**, three singlet peaks were observed around 3.64 ppm, and the acidic H signal at 20.08 ppm was disappear (see Figure S1).

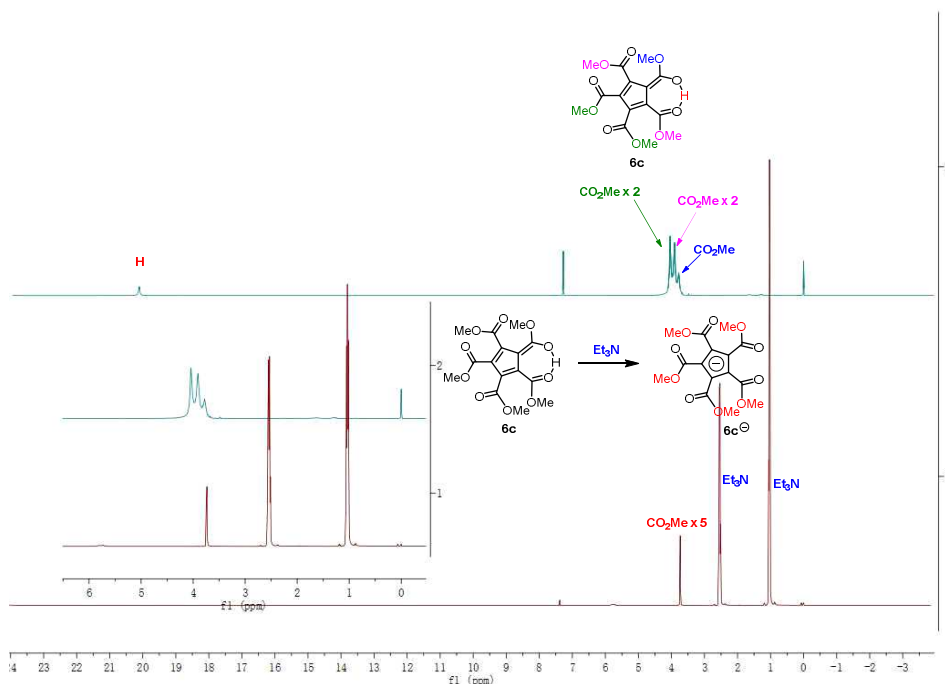
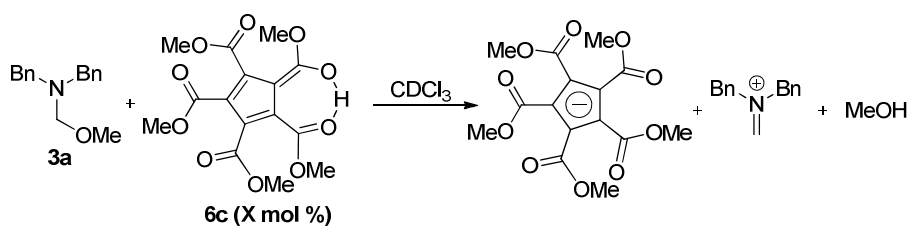


Figure S1. ^1H NMR comparison of **6c** and its conjugate base.

Proton NMR observation of the formation of methylene iminium ion intermediate



To six NMR tubes, each was added **3a** (24 mg), and followed by adding variety amount of **6c**: (1.8 mg, 5 mol %), (7.5 mg, 20 mol %), (17.5 mg, 50 mol %), (28.5 mg, 80 mol %), (35.6 mg, 100 mol %), and (42.7 mg, 120 mol %) in CDCl_3 (0.5 ml) respectively. The above mixtures were shaking for 5 min followed by subjected to ^1H NMR analysis.

With the addition of **6c** into **3a**, **6c** was convert into its conjugate base and MeOH was formed at same time, which indicates that the ion pair was generated from **3a** *via* desorption of MeOH (see Figure S2 for details). Furthermore, the methylene iminium ion intermediate was also detected by HR-MS of the mixture of **3a** and **6c** (see Figure S3).

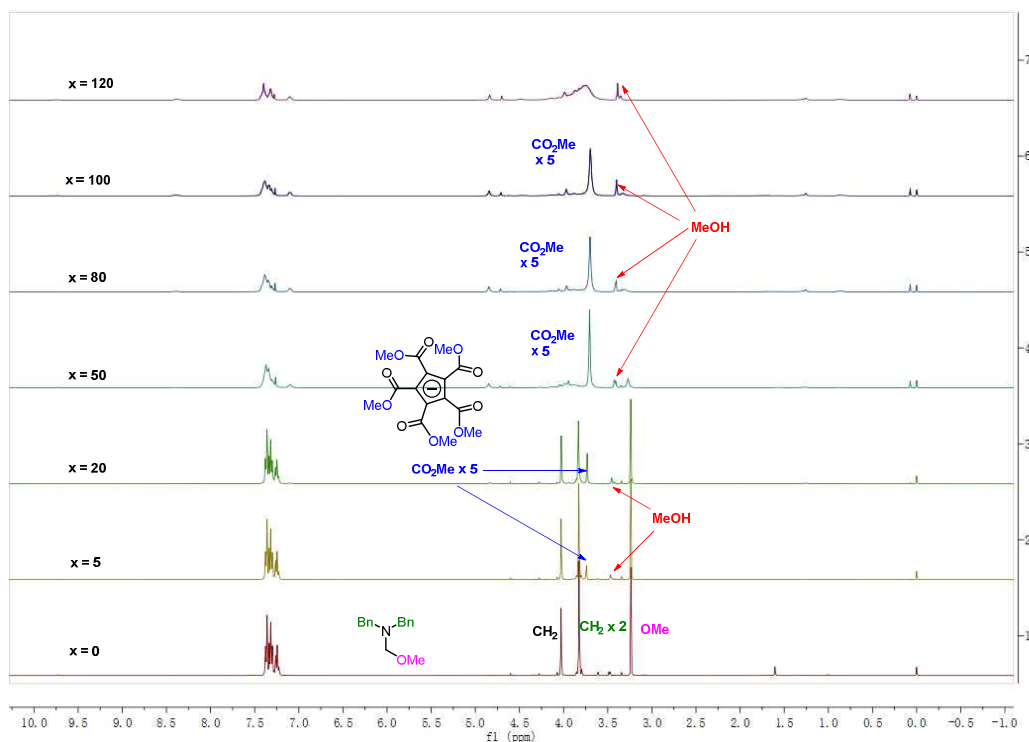


Figure S2. ^1H NMR monitoring of the reaction mixture of **3a** with different amount of **6c**.

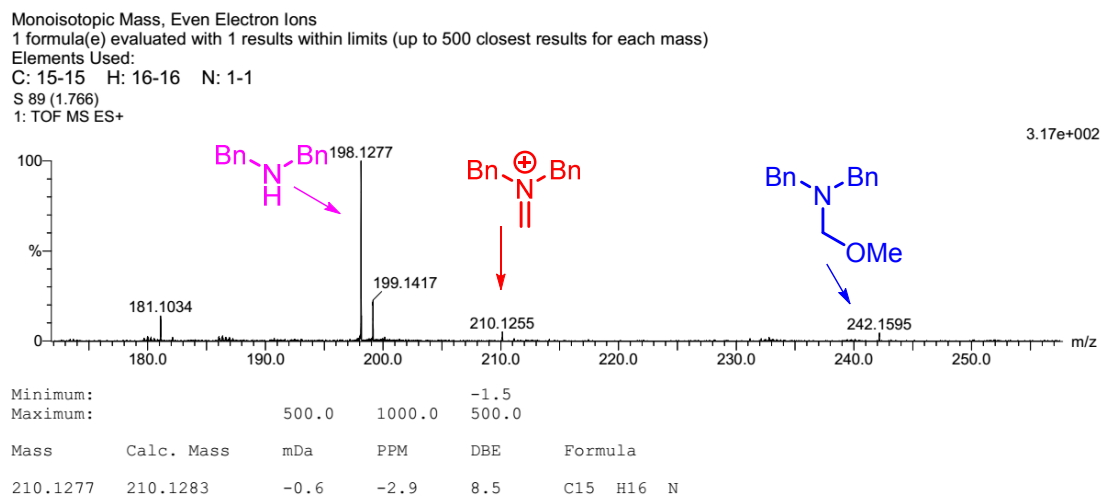
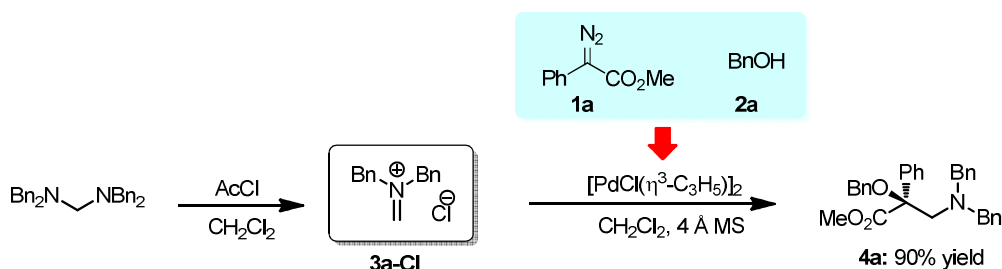


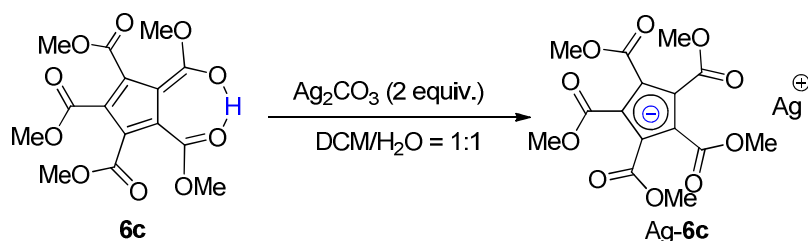
Figure S3. HR-MS spectrum for the reaction mixture of **3a** with **6c**.

Control reaction with iminium ion intermediate **3a-Cl**



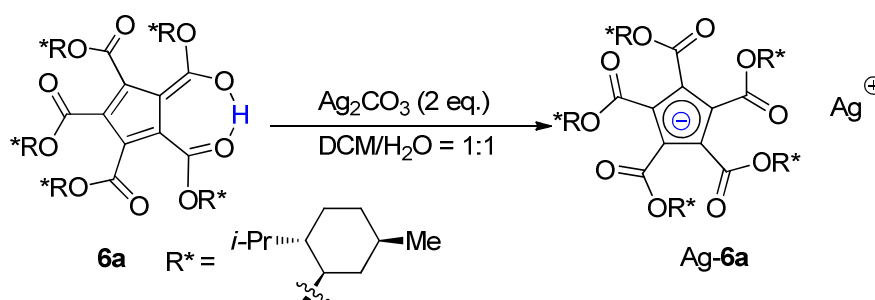
To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, *N, N, N', N'*-tetrabenzylmethanediamine (81 mg, 0.2 mmol), 4 Å molecular sieve (100 mg) in CH_2Cl_2 (2.0 mL), was added acetyl chloride (16 mg, 0.2 mmol) slowly at 0 °C. After stirring at room temperature for 1 h, $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (3.7 mg, 5.0 mol %) in CH_2Cl_2 (0.5 mL) was added to the above reaction tube *via* syringe. Then, the solution of the diazo compound **1a** (53 mg, 0.3 mmol, 1.5 eq) and benzyl alcohol **2a** (32 mg, 0.3 mmol, 1.5 eq) in CH_2Cl_2 (1.0 mL) was added to the reaction mixture for 1 h *via* a syringe pump at room temperature. After completion of the addition, stirring was continued at room temperature until the diazo compound decomposed completely. The solvent was evaporated under vacuum after filtering through Celite. The residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/100~1/10) to give 83 mg products **4a** (90% yield).

Chiral anion metathesis reaction



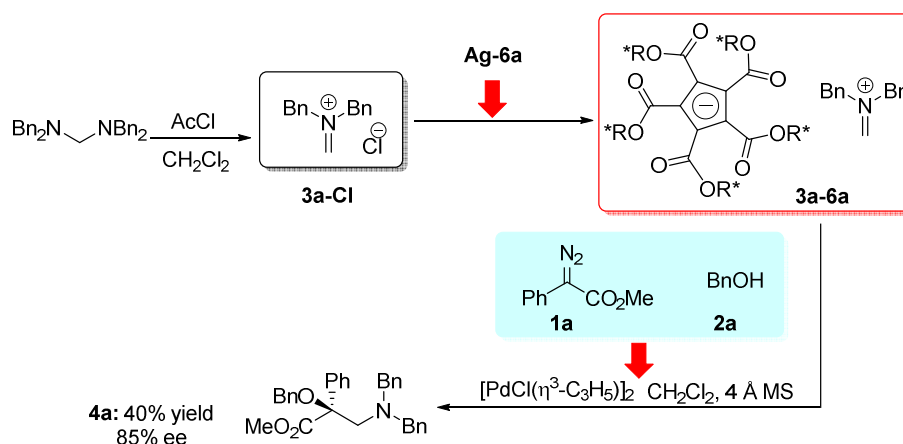
Synthesis of Ag-6c: To a 25 mL oven-dried flask containing a magnetic stirring bar, PCCP (**6c**) (178 mg, 0.5 mmol, 1.0 eq.) in 20 mL mixed solvent ($\text{CH}_2\text{Cl}_2/\text{H}_2\text{O} = 1:1$) in dark, was added Ag_2CO_3 (276 mg, 2.0 eq.) in one portion under vigorous stirring at room temperature, and the reaction mixture was stirred overnight under these conditions. The reaction mixture was filtered and the filtrate was diluted with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (20 mL). The aqueous layer was separated, and

washed with CH₂Cl₂. The aqueous layer concentrated under reduced pressure to give 180 mg desired silver salt Ag-**6c** as a gray solid. ¹H NMR (400 MHz, CD₃OD) 3.75 (s, 15H). ¹³C NMR (100 MHz, CD₃OD) δ 169.7, 118.2, 52.1. Single crystal X-ray diffraction data for Ag-**6c** was attached below.



Synthesis of Ag-6a: To a 25 mL oven-dried flask containing a magnetic stirring bar, PCCP (**6a**) (200 mg, 0.2 mmol, 1.0 eq.) in 20 mL solution (CH₂Cl₂/H₂O = 1:1) in dark, was added Ag₂CO₃ (113 mg, 2.0 eq.) in one portion under vigorous stirring at room temperature, and the reaction mixture was stirred overnight under these conditions. The reaction mixture was filtered and the filtrate was diluted with CH₂Cl₂/H₂O (20 mL). The organic layer was separated, and washed with H₂O. The aqueous layer concentrated under reduced pressure to give 156 mg desired silver salt Ag-**6a** as a black solid. ¹H NMR (400 MHz, CDCl₃) δ 4.89 – 4.62 (m, 5H), 2.14 – 0.71 (m, 90H). ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 116.8, 74.7, 46.7, 40.0, 34.3, 31.6, 25.2, 23.1, 22.2, 21.2, 16.5.

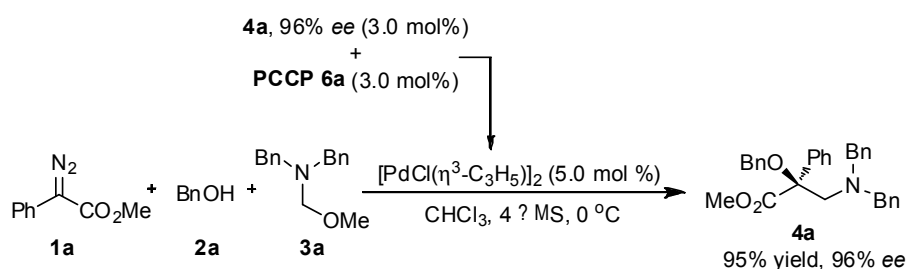
Control reaction with iminium ion intermediate 3a-6a



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, *N, N, N', N'*-tetrabenzylmethanediamine (81 mg, 0.2 mmol), 4 Å molecular sieve (100 mg) in CH₂Cl₂ (2.0

mL), was added acetyl chloride (16 mg, 0.2 mmol) slowly at 0 °C. After stirring at room temperature for 1 h, the solution of Ag-**6a** (264 mg, 0.24 mmol, 1.2 eq) in CH₂Cl₂ (0.5 mL) was added to the reaction mixture and stirred for 4 h at room temperature in dark. Then [PdCl(η³-C₃H₅)]₂ (3.7 mg, 5.0 mol %) in CH₂Cl₂ (0.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1a** (53 mg, 0.3 mmol, 1.5 eq) and benzyl alcohol **2a** (32 mg, 0.3 mmol, 1.5 eq) in CH₂Cl₂ (1.0 mL) was added to the reaction mixture for 1 h *via* a syringe pump at room temperature. After completion of the addition, stirring was continued at room temperature until the diazo compound decomposed completely. The solvent was evaporated under vacuum after filtering through Celite. The residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/100~1/10) to give 37 mg products **4a** in 40% yield with 85% *ee*.

Control reaction with a combination of **4a** (96% *ee*) and PCCP **6a** as co-catalyst



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added [PdCl(η³-C₃H₅)]₂ (3.7 mg, 5.0 mol %) and 4 Å molecular sieve (100 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). The premixed complex (see Figure S4): **4a** (2.8 mg, 3.0 mol %, 96% *ee*) and chiral PCCP **6a** (5.9 mg, 3.0 mol %) in CHCl₃ (1.0 mL) was added and the mixture was stirred for 10 min. Then, benzyl alcohol **2a** (32 mg, 0.3 mmol) and α-aminomethyl ether **3a** (48.8 mg, 0.2 mmol) in CHCl₃ (1.0 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1a** (52.5 mg, 0.3 mmol) in 1.5 mL of CHCl₃ was added to the suspension for 2 h *via* a syringe pump at 0 °C. After completion of the addition, stirring was continued at 0 °C until the diazo compound decomposed completely. The solvent was evaporated under vacuum after filtering through Celite. The residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/100~1/10) to give 88 mg pure product **4a** in 95% yield with 96% *ee*.

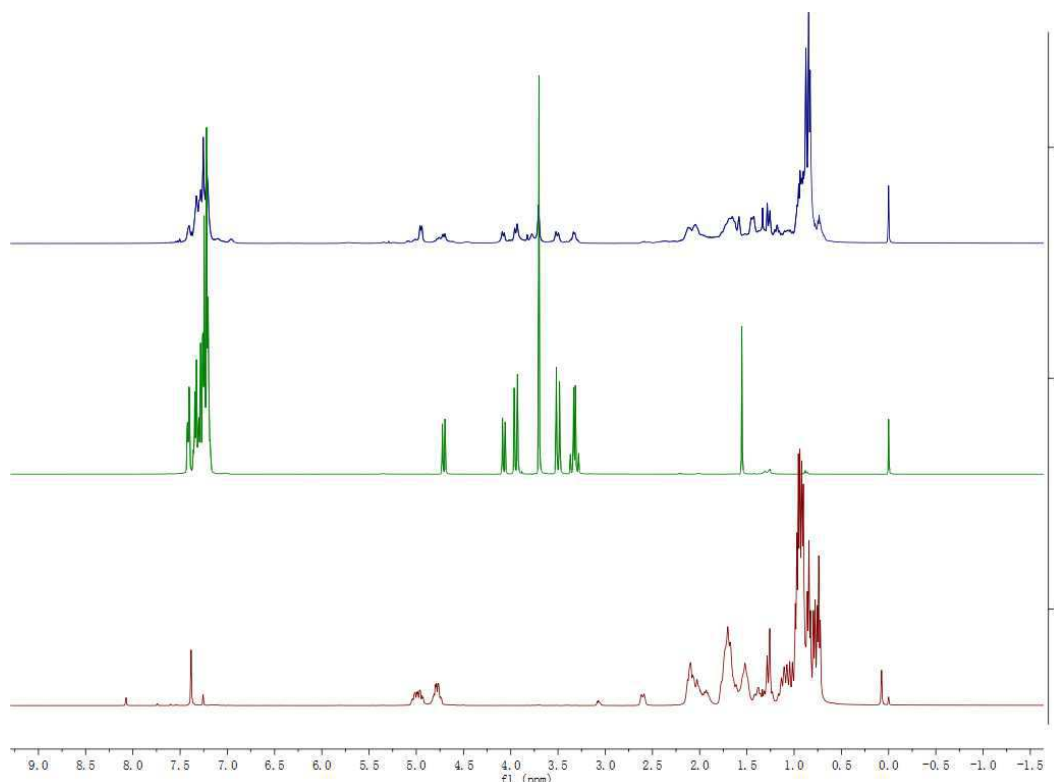
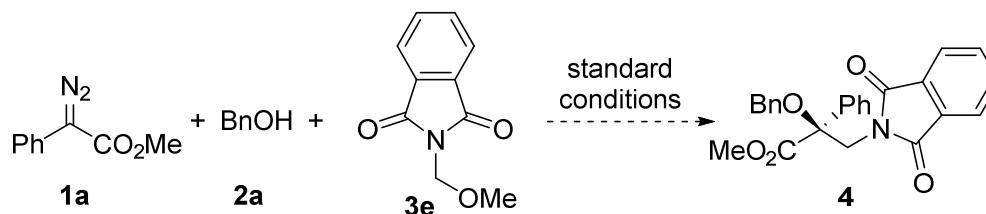


Figure S4. Proton NMR of a combination of chiral **4a** (96% *ee*) with PCCP **6a**.

Reaction with phthalimide substituted methyl amino **3e**



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (3.7 mg, 5.0 mol %), chiral PCCP **6a** (5.9 mg, 3.0 mol %), and 4 Å molecular sieve (100 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Then, benzyl alcohol **2a** (32.4 mg, 0.3 mmol) and α -aminomethyl ether **3e** (38.2 mg, 0.2 mmol) in CHCl_3 (1.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1a** (52.8 mg, 0.3 mmol) in 1.5 mL of CHCl_3 was added to the suspension for 2 h *via* a syringe pump at 0 °C. After completion of the addition, stirring was continued at 0 °C until the diazo compound decomposed completely. The solvent was evaporated under vacuum after filtering through Celite and the residue was recorded with ^1H NMR spectra in CDCl_3 (see

Figure S5). Most of the material **3e** remained intact according to these spectra.

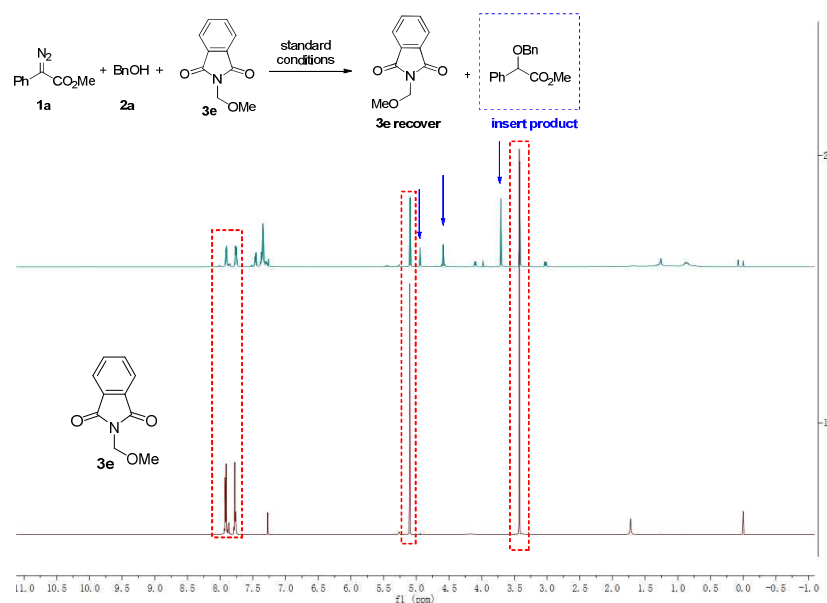
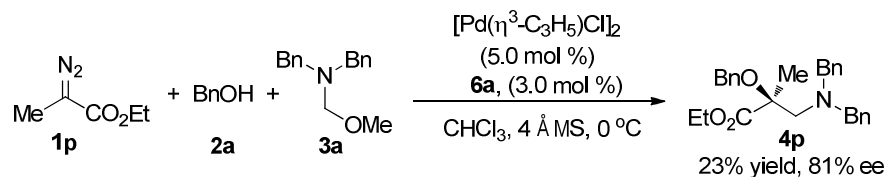


Figure S5. Proton NMR of crude reaction mixture of **1a**, **2a**, and **3e** under the standard conditions.

Pd-Catalyzed reaction of α -alkyl diazoacetate **1p**



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}_2]$, chiral PCCP **6a** (5.9 mg, 3.0 mol %), and 4 Å molecular sieve (100 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Then, benzyl alcohol **2a** (32.4 mg, 0.3 mmol) and α -aminomethyl ether **3a** (48.8 mg, 0.2 mmol) in CHCl_3 (1.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1p** (38.4 mg, 0.3 mmol) in 1.5 mL of CHCl_3 was added to the suspension for 2 h *via* a syringe pump at 0 °C. After completion of the addition, stirring was continued at 0 °C until the diazo compound decomposed completely. The solvent was evaporated under vacuum after filtering through Celite. The residue was recorded with ^1H NMR spectra in CDCl_3 (see Figure S6) and purified by column chromatography on silica gel (eluent: EtOAc /light petroleum ether = 1/100~1/10) to give **4p** in 23% yield with 81% ee (combined with oxidation product and β -H shift product).

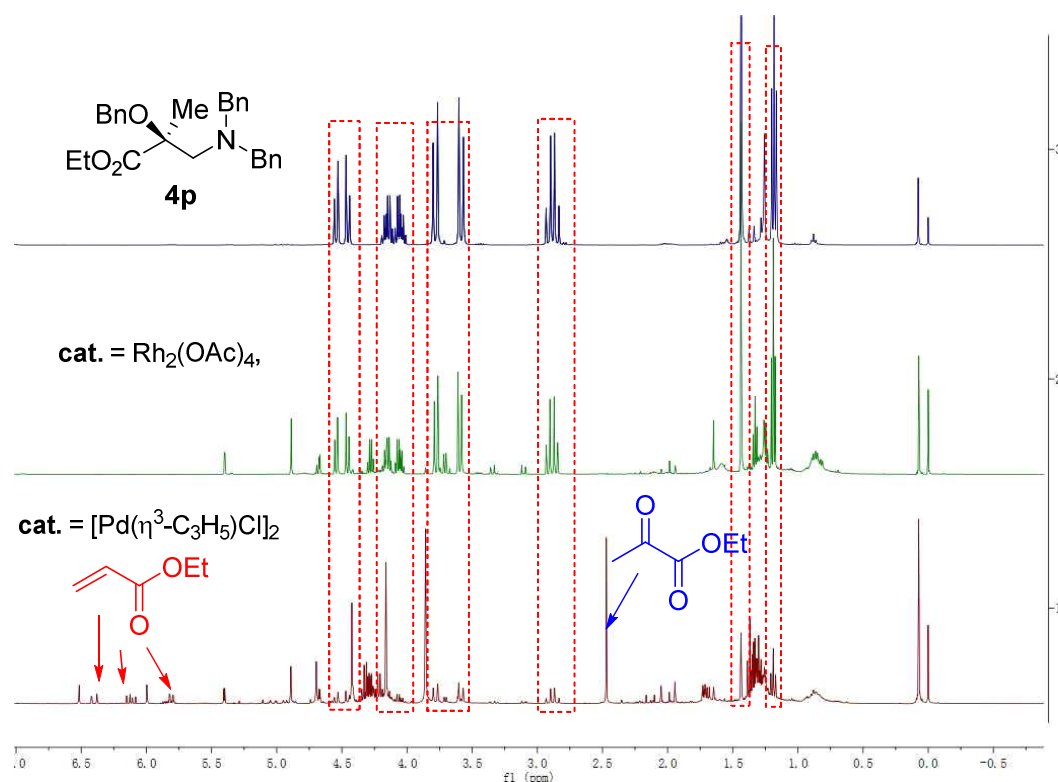
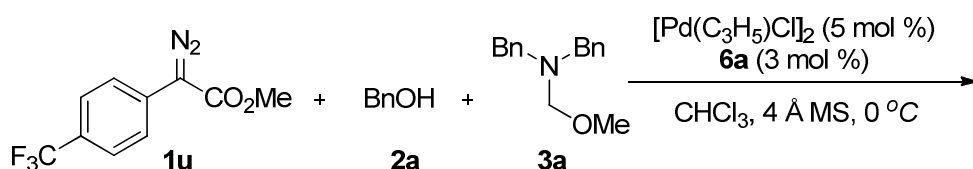


Figure S6. Proton NMR of the crude reaction mixture of **1p** with **2a** and **3a** in the presence of Pd-catalyst.

Catalytic reaction of α -aryl diazoacetate **1u**



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (3.7 mg, 5.0 mol %), chiral PCCP **6a** (5.9 mg, 3.0 mol %), and 4 Å molecular sieve (100 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Then, benzyl alcohol **2a** (32.4 mg, 0.3 mmol) and α -aminomethyl ether **3a** (48.8 mg, 0.2 mmol) in CHCl_3 (1.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1u** (0.3 mmol, 73.2 mg) in 1.5 mL of CHCl_3 was added to the suspension for 2 h *via* a syringe pump at 0 °C. After completion of the addition, stirring was continued at 0 °C until the diazo compound decomposed completely. The solvent was evaporated under vacuum

after filtering through Celite and the residue was recorded with ^1H NMR spectra in CDCl_3 . (see Figure S7). Only O-H insertion product of **1u** with **2a** was observed according to these spectra.

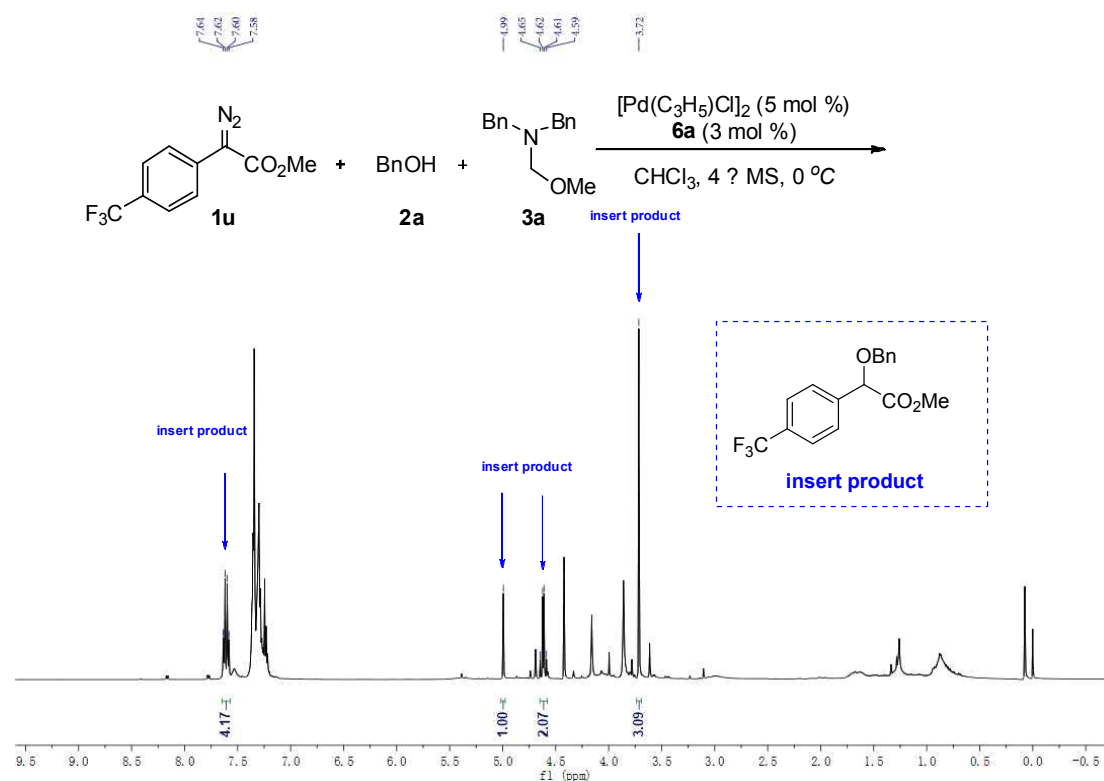
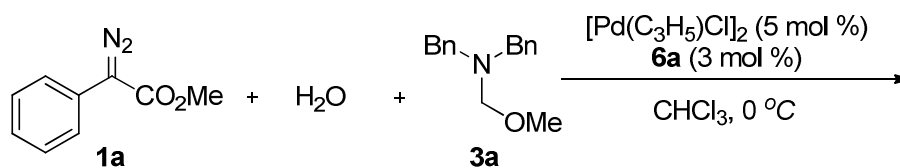


Figure S7. Proton NMR of crude reaction mixture of **1u**, **2a**, and **3a** under the standard conditions.

Control experiment of model reaction with water instead of alcohol



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (3.7 mg, 5.0 mol %) and chiral PCCP **6a** (5.9 mg, 3.0 mol %). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Then, H_2O (5.4 mg, 0.3 mmol) and α -aminomethyl ether **3a** (48.8 mg, 0.2 mmol) in CHCl_3 (1.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1a** (52.8 mg, 0.3 mmol) in 1.5 mL of CHCl_3 was added to the suspension for 2 h *via* a syringe pump at 0°C . After completion of the addition, stirring was continued at 0°C until the diazo compound decomposed completely.

The solvent was evaporated under vacuum after filtering through Celite and the residue was recorded with ^1H NMR spectra in CDCl_3 (see Figure S8). And only oxidation product and O-H insertion product were observed according to these spectra.

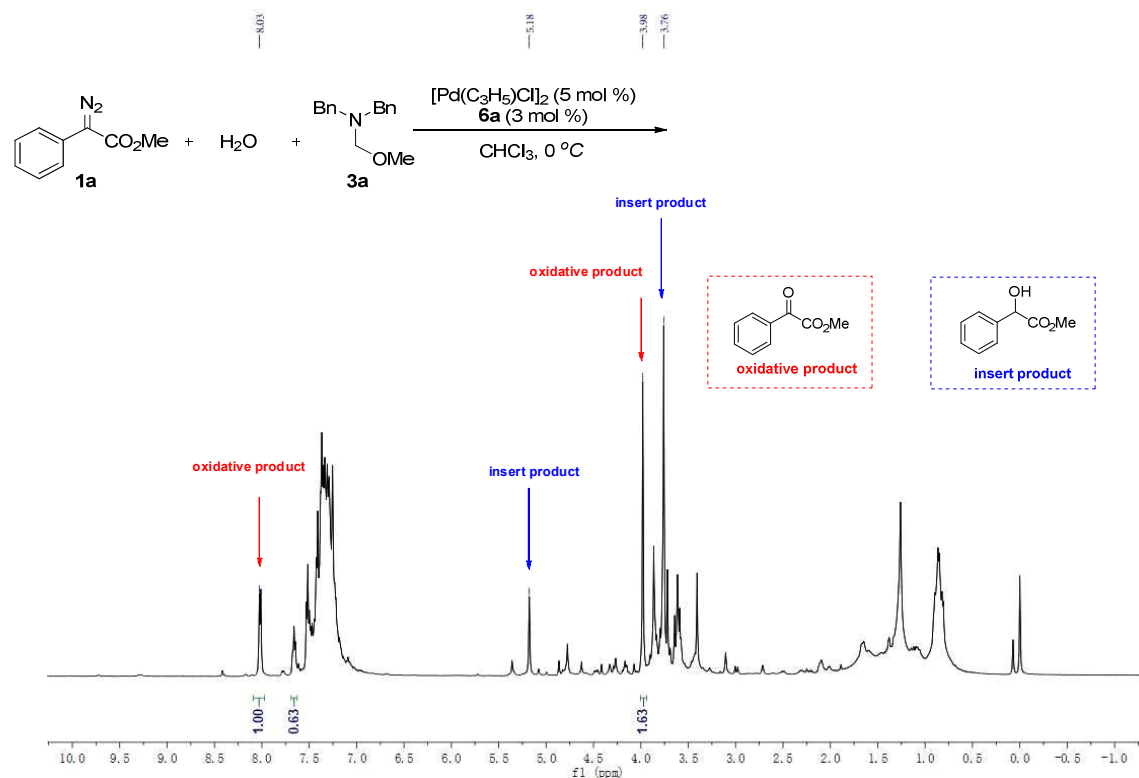
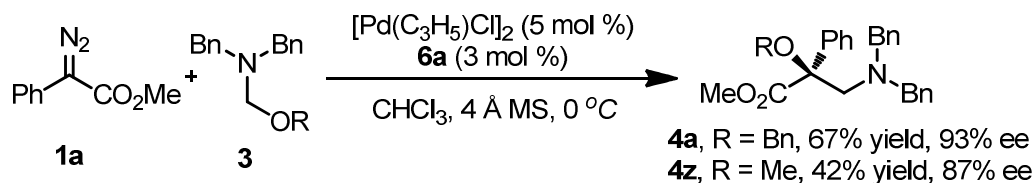


Figure S8. Proton NMR of crude reaction mixture of **1a**, H_2O , and **3a** under the standard conditions.

Control experiment in the absence of alcohol under standard conditions



To a 10 mL oven-dried Schlenk reaction tube equipped with a magnetic stir bar, was added $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (3.7 mg, 5.0 mol %), chiral PCCP **6a** (5.9 mg, 3.0 mol %), and 4 Å molecular sieve (100 mg). The Schlenk tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Then, α -aminomethyl ether **3** (0.2 mmol, 1.0 eq) in CHCl_3 (1.5 mL) was added to the above reaction tube *via* syringe. The solution of the diazo compound **1a** (52.8 mg, 0.3 mmol) in

1.5 mL of CHCl_3 was added to the suspension for 2 h *via* a syringe pump at 0 °C. After completion of the addition, stirring was continued at 0 °C until the diazo compound decomposed completely. The solvent was evaporated under vacuum after filtering through Celite. The residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/100~1/10) to give the corresponding products **4a** or **4z** in moderate to high yields with high enantioselectivity. For the proton NMR of crude reaction mixture of **1a** and **3a** in the absence of alcohol **2a** under the standard conditions, see Figure S9.

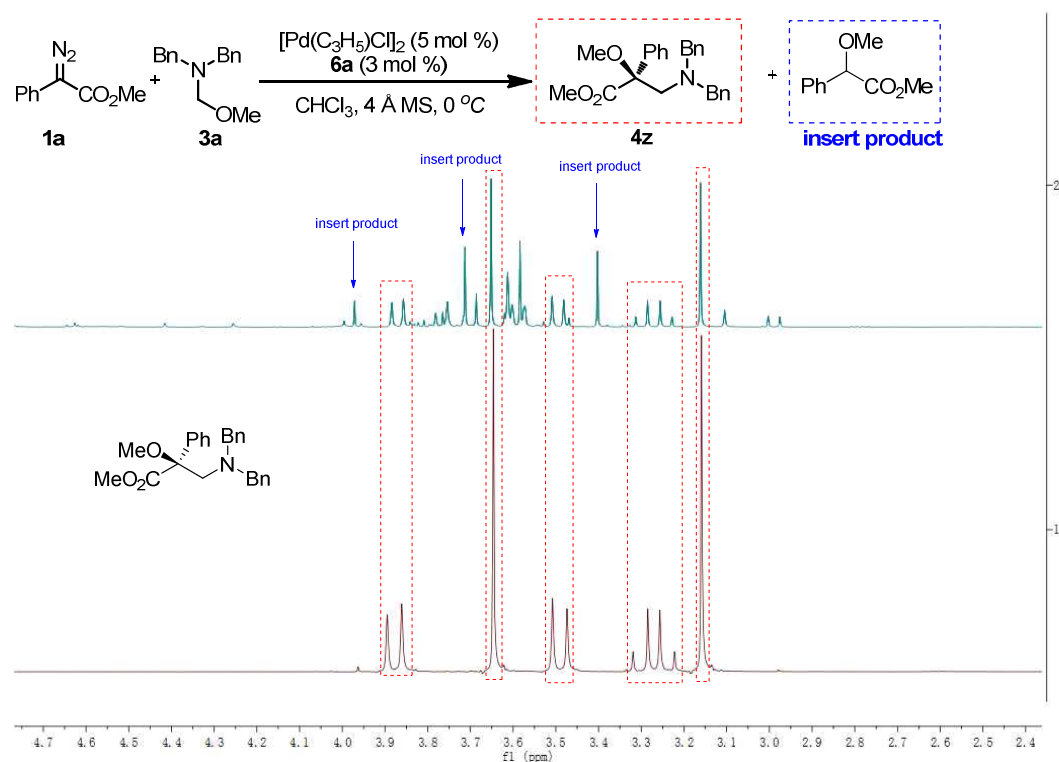


Figure S9. Proton NMR of crude reaction mixture of model reaction in the absence of alcohol under the standard conditions.

6. Computational details

All calculations were carried out using the Gaussian 09 program.⁵ The hybrid density functional M06-2X⁶ was used in combination with the standard 6-31G(d) basis set for C, H, N, O and Cl, and the Lanl (Los Alamos National Laboratory) basis sets,⁷ also known as LanL2DZ (Lanl-2-double zeta)⁸ for Pd. All structures were fully optimized in chloroform solvent ($\epsilon = 4.7113$) using the SMD method of Truhlar and Cramer.⁹ Vibrational analyses at the same level of theory were performed to confirm each stationary point to be either a local minimum or a transition state (TS), and to obtain thermal correction.¹⁰ The connection of each TS to its corresponding reactant and product was confirmed by IRC (intrinsic reaction coordinate) calculations.¹¹ To consider solvent effect, single-point energy calculations for key transition states were performed in dichloromethane ($\epsilon = 8.93$). All discussed energies are relative Gibbs free energies in solvent (ΔG) at 273 K unless specified.

Free energy profiles for the formation of enolate **III** and enol **IV** from ylide **II**. To form enolate **III**, **II** has to overcome a free energy barrier of 14.6 kcal/mol through **TS1** and is endothermic with 5.4 kcal/mol; while to form enol **IV**, **II** only need to overcome a free energy barrier of 9.3 kcal/mol through **TS2** and is exothermic with 8.4 kcal/mol. Thus, enol **IV** is more likely to be the reactive intermediate participating in the next step (Figure S10).

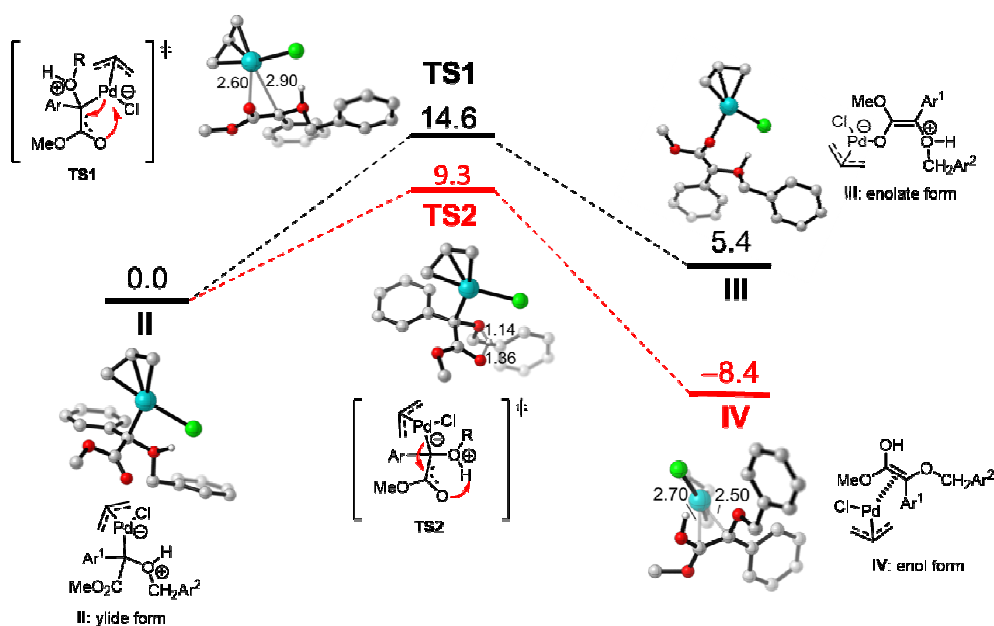


Figure S10 Free energy profiles for the formation of intermediates **III** and **IV** from intermediate **II**.

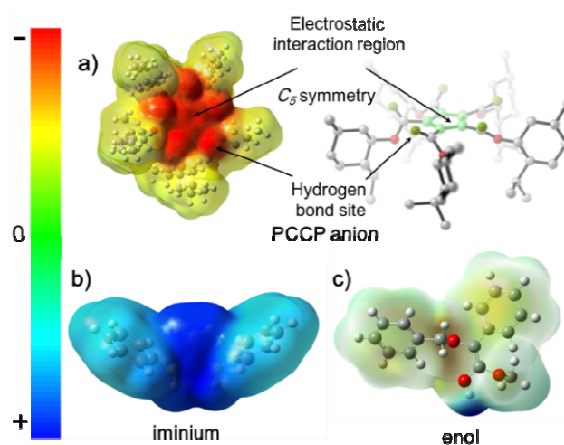
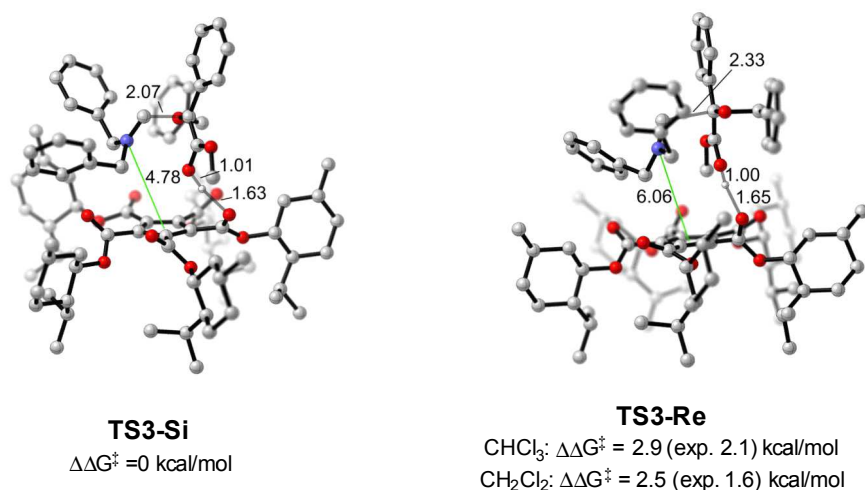


Figure S11. DFT-calculated electrostatic potential map. (a) DFT-calculated electrostatic potential map and three-dimensional structure, with C_5 symmetry of the PCCP anion, the negative charges are mainly located at the center 5-membered ring and the carbonyl groups, thus this region may electrostatically interact with the positive iminium and the carbonyl groups may form hydrogen bond with the enol. (b) DFT-calculated electrostatic potential map of the iminium, the positive charges are mainly around the N-atom, which may interact with the electrostatic region of the PCCP anion. (c) DFT-calculated electrostatic potential map of the enol, the electrostatic potential near the hydroxyl hydrogen is positive, in favor of the formation of hydrogen bond with one of the carbonyl groups in the PCCP anion.

Molecular Geometries and Energies

M06-2X (SMD, CHCl_3) Cartesian coordinates and energies in Hartree

II

Number of imaginary frequencies: 0

C	-0.570488000	2.010523000	-1.044904000
C	0.343603000	1.733474000	-0.011707000
C	1.188786000	2.773529000	0.408127000
C	1.118391000	4.032041000	-0.185366000

C	0.204645000	4.295268000	-1.201868000
C	-0.640440000	3.272197000	-1.626350000
H	-1.230697000	1.225080000	-1.400026000
H	1.908860000	2.600547000	1.197466000
H	1.785386000	4.815990000	0.162223000
H	0.153199000	5.279168000	-1.657524000
H	-1.359300000	3.450439000	-2.421138000
C	0.387726000	0.350197000	0.554304000
O	-0.953243000	-0.231405000	0.430943000
C	-2.045970000	0.128831000	1.360141000
H	-1.915104000	-0.476793000	2.255355000
H	-1.877879000	1.183926000	1.582909000
C	-3.346064000	-0.113003000	0.659747000
C	-3.976421000	0.920960000	-0.037083000
C	-3.919775000	-1.386600000	0.676639000
C	-5.172240000	0.684036000	-0.708185000
H	-3.526736000	1.911047000	-0.048189000
C	-5.111971000	-1.625511000	-0.001560000
H	-3.429588000	-2.189521000	1.222273000
C	-5.739016000	-0.589797000	-0.691680000
H	-5.662665000	1.491775000	-1.242608000
H	-5.553103000	-2.617227000	0.012949000
H	-6.671556000	-0.774678000	-1.216419000
C	0.896584000	0.040673000	1.910029000
O	0.378398000	-0.755494000	2.671597000
H	-0.881368000	-1.238280000	0.203107000
O	2.059119000	0.655673000	2.193688000
C	2.667940000	0.269071000	3.428202000
H	3.579067000	0.861649000	3.503314000
H	2.005644000	0.481604000	4.270003000
H	2.909144000	-0.796678000	3.416758000
Pd	1.635797000	-1.005376000	-0.665112000
Cl	-0.174389000	-2.784945000	-0.534566000
C	3.384582000	0.161835000	-0.759828000
H	3.899342000	-0.151545000	0.148144000
H	3.259697000	1.234116000	-0.884289000
C	3.414943000	-0.672191000	-1.910062000
H	3.196392000	-0.242175000	-2.885170000
C	3.319946000	-2.049566000	-1.733112000
H	3.102137000	-2.696296000	-2.577015000
H	3.724320000	-2.526778000	-0.842087000

Total Energy (CHCl₃): -1548.737496

Thermal correction to Gibbs Free Energy (273 K): 0.311316

III

Number of imaginary frequencies: 0

C	0.303514000	2.301710000	-1.074994000
C	0.734137000	1.849939000	0.183002000
C	1.692681000	2.604610000	0.875455000
C	2.223700000	3.759069000	0.305349000
C	1.804409000	4.190617000	-0.951319000
C	0.834813000	3.458377000	-1.635046000
H	-0.451059000	1.730981000	-1.608899000
H	2.022435000	2.293128000	1.858833000
H	2.965632000	4.329888000	0.856441000
H	2.221296000	5.092523000	-1.388894000
H	0.489566000	3.787922000	-2.610689000
C	0.134230000	0.598095000	0.701934000
O	-1.114522000	0.258274000	0.201449000
C	-2.177457000	1.003050000	0.796761000
H	-2.143066000	0.864324000	1.887378000
H	-2.045099000	2.073457000	0.590299000
C	-3.489500000	0.513729000	0.240203000
C	-3.600011000	-0.751333000	-0.339298000
C	-4.620268000	1.328915000	0.331029000
C	-4.832238000	-1.192843000	-0.819554000
H	-2.718767000	-1.382110000	-0.420555000
C	-5.850874000	0.883049000	-0.142219000
H	-4.534685000	2.318824000	0.773830000
C	-5.959254000	-0.380546000	-0.721643000
H	-4.908043000	-2.176730000	-1.273343000
H	-6.723521000	1.525152000	-0.066648000
H	-6.917327000	-0.727755000	-1.096960000
C	0.527410000	-0.133590000	1.800159000
O	-0.190741000	-1.149145000	2.280462000
H	-0.677025000	-1.576938000	1.535389000
O	1.618222000	0.167510000	2.503262000
C	2.296926000	-0.937664000	3.119349000
H	3.245067000	-0.533538000	3.472147000
H	1.718853000	-1.330636000	3.956618000
H	2.473533000	-1.730182000	2.384015000
Pd	1.456828000	-1.116223000	-0.542263000
Cl	-0.260001000	-2.882181000	-0.269995000
C	3.314911000	-0.032154000	-0.827926000
H	3.880262000	-0.467186000	-0.004128000
H	3.265913000	1.052465000	-0.863086000
C	3.056541000	-0.781148000	-1.984820000
H	2.732026000	-0.279583000	-2.893437000

C	2.816775000	-2.160548000	-1.814667000
H	2.373389000	-2.736739000	-2.620735000
H	3.370168000	-2.725061000	-1.065499000

Total Energy (CHCl₃): -1548.750782

Thermal correction to Gibbs Free Energy (273 K) : 0.311197

IV

Number of imaginary frequencies: 0

C	-3.451634000	-1.198072000	0.744980000
C	-2.379545000	-1.868909000	0.120542000
C	-2.532960000	-3.249405000	-0.125814000
C	-3.697649000	-3.912967000	0.240790000
C	-4.750447000	-3.237021000	0.855551000
C	-4.613422000	-1.873317000	1.102164000
H	-3.364960000	-0.139089000	0.965205000
H	-1.735662000	-3.798740000	-0.609136000
H	-3.781688000	-4.977044000	0.036701000
H	-5.657452000	-3.762906000	1.136781000
H	-5.416840000	-1.323389000	1.584730000
C	-1.185997000	-1.133494000	-0.254274000
O	-1.297549000	0.285929000	-0.065024000
C	-1.532321000	1.091870000	-1.284491000
H	-0.671451000	0.930326000	-1.934204000
H	-2.433321000	0.652616000	-1.714851000
C	-1.713056000	2.521148000	-0.883771000
C	-2.957684000	2.971308000	-0.435610000
C	-0.630455000	3.402081000	-0.921474000
C	-3.118806000	4.292579000	-0.031135000
H	-3.798985000	2.282681000	-0.411680000
C	-0.791366000	4.724849000	-0.517762000
H	0.337737000	3.046163000	-1.265732000
C	-2.034857000	5.169034000	-0.072696000
H	-4.087869000	4.639976000	0.313325000
H	0.051921000	5.407606000	-0.549659000
H	-2.160508000	6.201027000	0.240876000
C	0.027717000	-1.498082000	-0.805577000
O	0.927141000	-0.666916000	-1.157144000
H	-0.512486000	0.649235000	0.516582000
O	0.228029000	-2.826231000	-0.984971000
C	1.532053000	-3.211190000	-1.403244000
H	1.482800000	-4.288582000	-1.563849000
H	1.817011000	-2.707068000	-2.329464000
H	2.267947000	-2.989134000	-0.622829000
Pd	2.525524000	-0.087466000	0.228652000

Cl	0.845284000	1.077951000	1.684552000
C	4.288255000	-0.706326000	-0.843848000
H	4.438457000	0.186073000	-1.449705000
H	4.256919000	-1.650446000	-1.379124000
C	4.584055000	-0.687501000	0.529193000
H	4.701212000	-1.620264000	1.075707000
C	4.307092000	0.509195000	1.221748000
H	4.286415000	0.510604000	2.307409000
H	4.482061000	1.471685000	0.743050000

Total Energy (CHCl₃): -1548.728098

Thermal correction to Gibbs Free Energy (273 K) : 0.310532

TS1

Number of imaginary frequencies: 1

C	0.645241000	2.057619000	-1.439726000
C	0.755109000	1.776969000	-0.067550000
C	1.322167000	2.742395000	0.771951000
C	1.786677000	3.947742000	0.246858000
C	1.666494000	4.221300000	-1.112201000
C	1.083779000	3.271720000	-1.953173000
H	0.220555000	1.305327000	-2.101505000
H	1.412412000	2.550443000	1.835694000
H	2.233253000	4.680667000	0.912356000
H	2.023116000	5.164052000	-1.515214000
H	0.984230000	3.472202000	-3.015808000
C	0.303798000	0.454400000	0.426983000
O	-1.064893000	0.079214000	0.004216000
C	-2.085079000	1.118136000	0.082434000
H	-2.018803000	1.605216000	1.062085000
H	-1.846704000	1.849347000	-0.691986000
C	-3.430973000	0.482505000	-0.143550000
C	-4.574108000	1.188727000	0.239505000
C	-3.560354000	-0.765931000	-0.754489000
C	-5.837439000	0.655926000	0.006406000
H	-4.472582000	2.157619000	0.722595000
C	-4.829203000	-1.300376000	-0.975900000
H	-2.675670000	-1.326758000	-1.043996000
C	-5.967528000	-0.592038000	-0.602329000
H	-6.720688000	1.211581000	0.306573000
H	-4.922468000	-2.275422000	-1.444273000
H	-6.953395000	-1.011532000	-0.778446000
C	0.282866000	0.032137000	1.816686000
O	-0.695358000	-0.670980000	2.171287000

H	-1.224683000	-0.581931000	0.923993000
O	1.291628000	0.310610000	2.612758000
C	1.268488000	-0.327480000	3.903389000
H	2.168833000	0.016340000	4.408703000
H	0.377599000	-0.025990000	4.456331000
H	1.285068000	-1.411966000	3.780539000
Pd	1.616800000	-1.153719000	-0.416929000
Cl	-0.145779000	-2.889225000	-0.339303000
C	3.464661000	-0.076134000	-0.456871000
H	3.864776000	-0.330478000	0.524291000
H	3.433083000	0.983047000	-0.697457000
C	3.512339000	-1.024469000	-1.503965000
H	3.401513000	-0.688466000	-2.532939000
C	3.290346000	-2.370027000	-1.192853000
H	3.085830000	-3.085787000	-1.982410000
H	3.615456000	-2.779098000	-0.237944000

Total Energy (CHCl₃): -1548.719084

Thermal correction to Gibbs Free Energy (273 K) : 0.307637

TS2

Number of imaginary frequencies: 1

C	-0.737838000	2.761788000	-0.915709000
C	0.297929000	2.271853000	-0.090969000
C	1.409127000	3.117994000	0.118735000
C	1.464012000	4.380986000	-0.458397000
C	0.428865000	4.854392000	-1.263366000
C	-0.669541000	4.028106000	-1.486278000
H	-1.599501000	2.135326000	-1.121833000
H	2.229165000	2.781994000	0.739806000
H	2.334752000	5.004269000	-0.272094000
H	0.479917000	5.842533000	-1.709496000
H	-1.487958000	4.367616000	-2.115484000
C	0.200197000	0.941592000	0.483552000
O	-1.058136000	0.298741000	0.205318000
C	-2.071482000	0.322572000	1.286768000
H	-1.680886000	-0.301745000	2.091484000
H	-2.104817000	1.370664000	1.586571000
C	-3.370479000	-0.166929000	0.730924000
C	-4.236267000	0.721903000	0.087708000
C	-3.709402000	-1.518779000	0.823127000
C	-5.431072000	0.262923000	-0.457591000
H	-3.973104000	1.775215000	0.024269000
C	-4.904397000	-1.978378000	0.276104000

H	-3.032634000	-2.208261000	1.321324000
C	-5.764224000	-1.087888000	-0.363778000
H	-6.103346000	0.957134000	-0.952219000
H	-5.163765000	-3.029870000	0.349477000
H	-6.697258000	-1.446266000	-0.788280000
C	0.921340000	0.287226000	1.503547000
O	0.660070000	-0.865723000	1.918951000
H	-0.961696000	-0.648605000	-0.209659000
O	1.972779000	0.983275000	2.008358000
C	2.732774000	0.301782000	3.002620000
H	3.571828000	0.959745000	3.231237000
H	2.134781000	0.132923000	3.901425000
H	3.097790000	-0.660696000	2.634764000
Pd	1.689307000	-1.379582000	-0.409232000
Cl	-0.567604000	-2.254602000	-1.031114000
C	3.760071000	-0.895652000	-0.120754000
H	4.038555000	-1.672890000	0.589289000
H	3.974361000	0.130883000	0.165233000
C	3.556005000	-1.221057000	-1.471790000
H	3.557099000	-0.450351000	-2.237943000
C	2.955933000	-2.476474000	-1.711358000
H	2.533362000	-2.696624000	-2.687116000
H	3.207491000	-3.332113000	-1.086749000

Total Energy (CHCl₃): -1548.714344

Thermal correction to Gibbs Free Energy (273 K): 0.311461

TS3-Si

Number of imaginary frequencies: 1

O	-2.976291000	-2.093238000	-0.189983000
O	-2.436899000	1.262976000	1.921545000
O	0.836382000	3.008800000	1.015398000
O	2.866745000	0.643062000	-1.201182000
O	0.072124000	-2.652237000	-2.320827000
O	-2.716988000	-1.825402000	-2.413427000
O	-3.904652000	0.675859000	0.323417000
O	-1.268241000	3.516275000	0.387903000
O	1.829870000	2.566604000	-1.744475000
O	1.550132000	-1.101719000	-3.019755000
C	-1.431136000	-0.475071000	-1.002582000
C	-1.614417000	0.659771000	-0.200344000
C	-0.433359000	1.435362000	-0.253899000
C	0.478939000	0.778306000	-1.088250000
C	-0.134210000	-0.416570000	-1.550736000

C	-2.434452000	-1.554507000	-1.135554000
C	-3.653272000	-2.888252000	-2.668456000
H	-4.382300000	-2.901629000	-1.851042000
C	-2.920517000	-4.221333000	-2.704614000
H	-2.138771000	-4.174232000	-3.475844000
H	-2.419160000	-4.382558000	-1.743052000
C	-3.890557000	-5.366899000	-3.008962000
H	-4.621236000	-5.417884000	-2.187217000
C	-4.657424000	-5.069084000	-4.301591000
H	-3.946773000	-5.085077000	-5.141338000
H	-5.389873000	-5.863115000	-4.492539000
C	-5.357012000	-3.705834000	-4.265877000
H	-6.137012000	-3.715947000	-3.490866000
H	-5.861907000	-3.529906000	-5.221353000
C	-4.362631000	-2.569958000	-3.981839000
H	-3.602256000	-2.591220000	-4.778818000
C	-4.976730000	-1.151701000	-3.981159000
H	-4.130684000	-0.454045000	-3.981435000
C	-5.794930000	-0.888536000	-5.246211000
H	-6.041447000	0.175377000	-5.328128000
H	-6.739347000	-1.444819000	-5.237862000
H	-5.242449000	-1.175175000	-6.148848000
C	-3.154584000	-6.701187000	-3.083658000
H	-3.846117000	-7.527969000	-3.280462000
H	-2.627896000	-6.914636000	-2.147027000
H	-2.410840000	-6.685892000	-3.889765000
C	-5.806226000	-0.846799000	-2.730283000
H	-5.185685000	-0.827045000	-1.827001000
H	-6.606896000	-1.582253000	-2.581103000
H	-6.278246000	0.138480000	-2.824154000
C	-2.679281000	0.892894000	0.764179000
C	-4.994119000	0.793185000	1.268914000
H	-4.765733000	1.633059000	1.934150000
C	-5.117275000	-0.484837000	2.086301000
H	-4.175837000	-0.677211000	2.614220000
H	-5.288429000	-1.326873000	1.402021000
C	-6.277832000	-0.368963000	3.081086000
H	-6.046125000	0.455535000	3.772806000
C	-7.567547000	-0.007577000	2.337054000
H	-8.385561000	0.126579000	3.055049000
H	-7.846973000	-0.853167000	1.691286000
C	-7.412702000	1.249138000	1.473887000
H	-7.231193000	2.118955000	2.121320000
H	-8.347812000	1.440899000	0.938242000

C	-6.258687000	1.098161000	0.471419000
H	-6.479614000	0.213117000	-0.145870000
C	-6.070219000	2.285160000	-0.497908000
H	-5.358170000	1.943685000	-1.259862000
C	-5.461589000	3.525552000	0.162057000
H	-4.438125000	3.340431000	0.507609000
H	-6.057950000	3.867598000	1.016975000
H	-5.416955000	4.349052000	-0.559684000
C	-7.376176000	2.639727000	-1.210883000
H	-7.182648000	3.311614000	-2.053691000
H	-8.076766000	3.148502000	-0.538700000
H	-7.876738000	1.745649000	-1.601629000
C	-6.436614000	-1.651915000	3.891118000
H	-7.249619000	-1.563208000	4.619988000
H	-5.518229000	-1.894257000	4.436671000
H	-6.666665000	-2.497283000	3.231655000
C	-0.199605000	2.705465000	0.450933000
C	-1.125029000	4.844160000	0.925228000
H	-0.085622000	5.156307000	0.771595000
C	-1.427965000	4.859314000	2.416673000
H	-0.726569000	4.193305000	2.932244000
H	-2.443632000	4.470487000	2.580122000
C	-1.312304000	6.278679000	2.983251000
H	-0.267629000	6.602266000	2.860020000
C	-2.197180000	7.237419000	2.181171000
H	-3.250478000	6.967424000	2.349844000
H	-2.069410000	8.260475000	2.555066000
C	-1.902468000	7.183444000	0.678700000
H	-0.881650000	7.546091000	0.491117000
H	-2.581585000	7.860219000	0.150588000
C	-2.056361000	5.757281000	0.130439000
H	-3.089238000	5.438511000	0.343114000
C	-1.844416000	5.616601000	-1.393942000
H	-2.206846000	4.616438000	-1.661095000
C	-2.675300000	6.635305000	-2.175680000
H	-2.684830000	6.383336000	-3.241258000
H	-2.265416000	7.647508000	-2.081264000
H	-3.715045000	6.659763000	-1.827835000
C	-0.372209000	5.686584000	-1.812092000
H	-0.291805000	5.685653000	-2.905198000
H	0.196271000	4.824015000	-1.445197000
H	0.112747000	6.600875000	-1.446861000
C	-1.655642000	6.304950000	4.469486000
H	-1.005649000	5.632429000	5.040751000

H	-2.692647000	5.986997000	4.631706000
H	-1.545194000	7.312156000	4.885449000
C	1.842728000	1.282443000	-1.350842000
C	3.107577000	3.227451000	-1.836258000
H	3.851371000	2.477299000	-2.125558000
C	3.484143000	3.811296000	-0.483172000
H	3.448673000	3.029016000	0.282010000
H	2.738208000	4.567168000	-0.199075000
C	4.875257000	4.443462000	-0.552889000
H	5.589128000	3.648799000	-0.822092000
C	4.898838000	5.500290000	-1.663300000
H	4.238810000	6.329005000	-1.366056000
H	5.907679000	5.919663000	-1.761977000
C	4.426619000	4.947679000	-3.014347000
H	5.149785000	4.202730000	-3.375562000
H	4.410930000	5.757106000	-3.751738000
C	3.033013000	4.304567000	-2.914756000
H	2.339213000	5.083194000	-2.559727000
C	2.466118000	3.768732000	-4.245907000
H	1.418018000	3.511956000	-4.046697000
C	3.155854000	2.492673000	-4.737021000
H	2.998415000	1.652763000	-4.050184000
H	4.236320000	2.636059000	-4.863620000
H	2.747103000	2.200993000	-5.710991000
C	5.287390000	5.020334000	0.797545000
H	6.303497000	5.429174000	0.763488000
H	5.256473000	4.251845000	1.578971000
H	4.608728000	5.829593000	1.094446000
C	2.482868000	4.840068000	-5.337467000
H	2.068897000	5.789345000	-4.976778000
H	1.886612000	4.519933000	-6.198409000
H	3.500516000	5.031944000	-5.696437000
C	0.474056000	-1.501426000	-2.322237000
C	2.448538000	-2.131506000	-3.471398000
H	1.853154000	-2.982130000	-3.820173000
C	3.327495000	-2.573694000	-2.305451000
H	2.692754000	-2.969976000	-1.500934000
H	3.847100000	-1.690279000	-1.908715000
C	4.348210000	-3.625710000	-2.746958000
H	3.793525000	-4.511404000	-3.093310000
C	5.162053000	-3.087887000	-3.927456000
H	5.862687000	-3.855508000	-4.278923000
H	5.769300000	-2.240360000	-3.575682000
C	4.271010000	-2.622081000	-5.082930000

H	3.735652000	-3.487992000	-5.497605000
H	4.895639000	-2.220773000	-5.887914000
C	3.259364000	-1.558583000	-4.629431000
H	3.833102000	-0.705794000	-4.230302000
C	2.358753000	-1.007975000	-5.756663000
H	1.814998000	-0.159296000	-5.323630000
C	3.189718000	-0.480311000	-6.927937000
H	2.567649000	0.113666000	-7.606385000
H	3.621502000	-1.299765000	-7.514355000
H	4.014055000	0.155791000	-6.583360000
C	5.244642000	-4.038198000	-1.583424000
H	5.964552000	-4.806409000	-1.888429000
H	4.654526000	-4.435433000	-0.749998000
H	5.810766000	-3.175537000	-1.211210000
C	1.312949000	-2.010647000	-6.252047000
H	0.591384000	-2.270091000	-5.470034000
H	1.776907000	-2.937469000	-6.610436000
H	0.748734000	-1.582754000	-7.088107000
C	0.861792000	-3.595967000	5.482862000
C	0.479022000	-2.246119000	5.399541000
C	0.249804000	-1.545961000	6.595179000
C	0.383726000	-2.187544000	7.823674000
C	0.751915000	-3.528785000	7.893900000
C	0.992431000	-4.228799000	6.714464000
H	1.056477000	-4.145441000	4.566656000
H	-0.044300000	-0.505217000	6.576798000
H	0.193606000	-1.627956000	8.734949000
H	0.851793000	-4.021594000	8.856079000
H	1.285010000	-5.274115000	6.748995000
C	0.413519000	-1.657126000	4.037489000
O	0.393864000	-2.568173000	2.993342000
C	-0.899235000	-3.112473000	2.673034000
H	-1.493697000	-2.350139000	2.154399000
H	-1.409861000	-3.410114000	3.597381000
C	-0.641834000	-4.294336000	1.782595000
C	-0.507362000	-5.575966000	2.320318000
C	-0.400467000	-4.091987000	0.421951000
C	-0.135296000	-6.645252000	1.507265000
H	-0.692204000	-5.734272000	3.380763000
C	-0.021627000	-5.157332000	-0.392488000
H	-0.495582000	-3.096378000	-0.003638000
C	0.112737000	-6.435145000	0.151030000
H	-0.036607000	-7.640020000	1.931970000
H	0.169812000	-4.975048000	-1.445791000

H	0.408533000	-7.267130000	-0.481665000
C	-0.111827000	-0.395117000	3.716646000
O	-0.279885000	-0.105911000	2.457558000
H	-0.988059000	0.595395000	2.279403000
O	-0.275051000	0.521500000	4.648740000
C	-0.512917000	1.888997000	4.256215000
H	-1.567167000	2.020295000	4.008674000
H	0.121127000	2.159670000	3.406818000
H	-0.251804000	2.486382000	5.128631000
C	6.214964000	1.823433000	3.595112000
C	4.858289000	1.515080000	3.527764000
C	4.264258000	1.171499000	2.310074000
C	5.052458000	1.146191000	1.153914000
C	6.411909000	1.450556000	1.221333000
C	6.995900000	1.787811000	2.440908000
H	6.661505000	2.093941000	4.547345000
H	4.251335000	1.549427000	4.430103000
H	4.593409000	0.902521000	0.198251000
H	7.012993000	1.428459000	0.316800000
H	8.053409000	2.029372000	2.491337000
C	2.801559000	0.777371000	2.267642000
H	2.336819000	1.032190000	1.312608000
H	2.247518000	1.299683000	3.052877000
N	2.648800000	-0.669442000	2.493881000
C	2.749576000	-1.562672000	1.320918000
H	1.740240000	-1.859670000	1.019663000
H	3.173028000	-0.964551000	0.509680000
C	3.611683000	-2.772171000	1.596871000
C	4.987339000	-2.616987000	1.800141000
C	3.053050000	-4.049788000	1.663266000
C	5.791157000	-3.723404000	2.056170000
H	5.425979000	-1.621783000	1.752377000
C	3.858400000	-5.160169000	1.921235000
H	1.984027000	-4.172232000	1.513900000
C	5.227392000	-4.999070000	2.116534000
H	6.859048000	-3.592927000	2.205149000
H	3.409842000	-6.148364000	1.966512000
H	5.855569000	-5.862341000	2.315856000
C	2.388348000	-1.137381000	3.703323000
H	2.613156000	-2.187440000	3.880271000
H	2.521569000	-0.453895000	4.540055000

Total Energy (CHCl₃): -4575.098028

Total Energy (DCM): -4575.102125

Thermal correction to Gibbs Free Energy (273 K) : 1.933803

TS3-Re

Number of imaginary frequencies: 1

symmetry c1

O	3.700868000	0.088573000	-2.623240000
O	1.464575000	3.267133000	-1.228810000
O	-1.245576000	2.024921000	0.601720000
O	-0.608779000	-2.144617000	1.679264000
O	2.435146000	-3.143273000	-0.800815000
O	4.589874000	-1.193080000	-0.993562000
O	3.618846000	2.604301000	-1.097752000
O	0.485479000	3.027282000	1.600670000
O	-0.681449000	-0.100155000	2.644168000
O	2.094585000	-3.057683000	1.425146000
C	2.556248000	-0.123776000	-0.549186000
C	1.967663000	1.139929000	-0.322692000
C	0.902468000	0.969042000	0.574152000
C	0.823949000	-0.396723000	0.911577000
C	1.856172000	-1.071316000	0.210815000
C	3.649156000	-0.384311000	-1.506017000
C	5.665670000	-1.574622000	-1.867868000
H	5.876218000	-0.729198000	-2.532630000
C	5.256486000	-2.778060000	-2.706719000
H	4.994012000	-3.605839000	-2.033388000
H	4.358353000	-2.529835000	-3.284280000
C	6.398425000	-3.199107000	-3.637344000
H	6.594779000	-2.363322000	-4.326178000
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H	7.510222000	-4.323965000	-2.179860000
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C	8.044619000	-2.247367000	-1.940874000
H	8.305192000	-1.391065000	-2.579528000
H	8.937391000	-2.490049000	-1.355310000
C	6.891030000	-1.860382000	-1.003082000
H	6.661080000	-2.744753000	-0.387251000
C	7.202639000	-0.702819000	-0.029091000
H	6.378366000	-0.684565000	0.694428000
C	8.497025000	-0.952170000	0.746911000
H	8.589639000	-0.243772000	1.576873000
H	9.379197000	-0.826439000	0.108598000
H	8.527266000	-1.965400000	1.165185000
C	6.016300000	-4.425977000	-4.460044000
H	6.821952000	-4.711989000	-5.145324000

H	5.115394000	-4.240936000	-5.054879000
H	5.814644000	-5.281035000	-3.803385000
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H	7.539083000	1.436642000	0.017501000
C	2.301047000	2.429099000	-0.935503000
C	4.053897000	3.823835000	-1.726879000
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C	4.222901000	3.592213000	-3.221969000
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H	4.949523000	2.782189000	-3.376931000
C	4.705074000	4.870393000	-3.916233000
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H	1.360830000	5.051326000	2.850386000
C	0.284214000	3.944498000	4.351222000
H	0.518468000	2.930001000	4.001468000
C	1.369744000	4.348953000	5.349882000
H	1.374168000	3.677022000	6.215301000
H	1.208923000	5.367087000	5.724330000
H	2.363552000	4.310545000	4.891019000
C	-1.080434000	3.902277000	5.045582000
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H	-1.895167000	3.667642000	4.349798000
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C	-0.887469000	7.341110000	-0.337646000
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H	0.155567000	7.540239000	-0.611867000
H	-1.379755000	8.304657000	-0.166217000
C	-0.203725000	-0.998930000	1.757748000
C	-1.804791000	-0.467466000	3.458130000
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H	-2.871685000	1.311110000	2.904141000
C	-4.274837000	-0.094066000	3.771625000
H	-4.446860000	-1.181288000	3.728743000
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H	-4.848828000	0.011187000	5.856867000
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C	-0.161078000	-0.642550000	5.402198000
H	0.619920000	-0.213166000	4.762131000
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H	-0.115399000	-2.491824000	4.228172000
H	-0.871038000	-2.668057000	5.826853000
H	0.883862000	-2.518101000	5.684365000

C	-5.519661000	0.616683000	3.249207000
H	-6.395426000	0.391235000	3.868008000
H	-5.753479000	0.321320000	2.219913000
H	-5.369563000	1.703888000	3.261321000
C	0.132251000	-0.209122000	6.839389000
H	0.000116000	0.872042000	6.968687000
H	1.164822000	-0.453678000	7.109980000
H	-0.523415000	-0.716559000	7.556254000
C	2.150312000	-2.515982000	0.201478000
C	2.266169000	-4.482344000	1.513225000
H	2.984785000	-4.786236000	0.744187000
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H	0.204688000	-4.834604000	1.995299000
C	1.107259000	-6.703058000	1.360137000
H	1.814407000	-7.017518000	0.577252000
C	1.717134000	-7.066124000	2.717934000
H	1.884468000	-8.148777000	2.775217000
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H	-0.098534000	-8.506787000	1.163565000
H	-0.643661000	-7.154630000	0.152711000
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C	-3.318118000	0.125737000	-5.341684000
C	-3.635367000	-0.106647000	-6.676387000
C	-4.961486000	-0.204964000	-7.092496000
C	-5.978008000	-0.071294000	-6.150303000

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H	-2.278458000	0.201609000	-5.052491000
H	-2.831005000	-0.209890000	-7.398986000
H	-5.198374000	-0.385268000	-8.136487000
H	-7.018140000	-0.149559000	-6.453472000
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C	-5.541969000	2.174862000	-2.130664000
H	-4.676705000	2.716642000	-1.730702000
H	-5.751385000	2.538718000	-3.144255000
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C	-8.029225000	2.302277000	-1.762012000
C	-6.563986000	2.353464000	0.152398000
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H	-5.555376000	2.360118000	0.562533000
C	-8.956950000	2.339971000	0.465877000
H	-10.138794000	2.299581000	-1.334734000
H	-7.527129000	2.389253000	2.076857000
H	-9.818829000	2.346097000	1.126311000
C	-2.906620000	0.641148000	-2.282710000
O	-2.943497000	0.878502000	-0.985168000
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O	-1.761370000	0.463000000	-2.923889000
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H	-0.477799000	-0.012549000	-1.343083000
H	0.256734000	0.351445000	-2.927902000
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C	0.005339000	-4.068476000	-2.495001000
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C	-1.987949000	-5.428379000	-2.496705000
C	-0.662601000	-5.224233000	-2.886890000
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H	-2.512168000	-6.330882000	-2.796645000
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C	-2.661283000	-2.296622000	-0.445561000
H	-2.821031000	-2.707039000	0.554616000
H	-2.041079000	-1.403598000	-0.324660000
N	-3.992124000	-1.887869000	-0.949115000

C	-5.008996000	-1.465037000	0.047623000
H	-5.051589000	-0.372660000	0.038367000
H	-4.638071000	-1.791972000	1.022693000
C	-6.364733000	-2.064556000	-0.234028000
C	-6.551813000	-3.446803000	-0.126719000
C	-7.437291000	-1.252084000	-0.601032000
C	-7.796922000	-4.008489000	-0.386079000
H	-5.718272000	-4.080571000	0.169827000
C	-8.687953000	-1.815357000	-0.855851000
H	-7.290051000	-0.178961000	-0.688851000
C	-8.868268000	-3.191357000	-0.751354000
H	-7.936187000	-5.081672000	-0.298052000
H	-9.517664000	-1.173891000	-1.137904000
H	-9.841021000	-3.630583000	-0.951089000
C	-4.224610000	-1.732770000	-2.219593000
H	-5.249193000	-1.554527000	-2.532780000
H	-3.493280000	-2.093379000	-2.936875000

Total Energy (CHCl₃): -4575.089533

Total Energy (DCM): -4575.094281

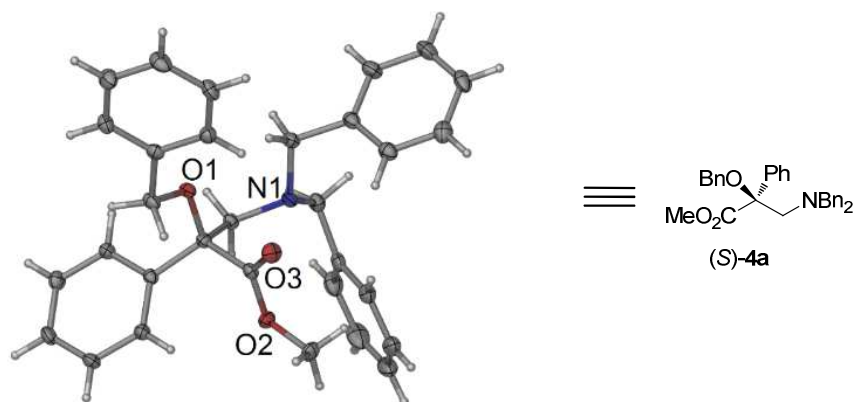
Thermal correction to Gibbs Free Energy (273 K) : 1.929899

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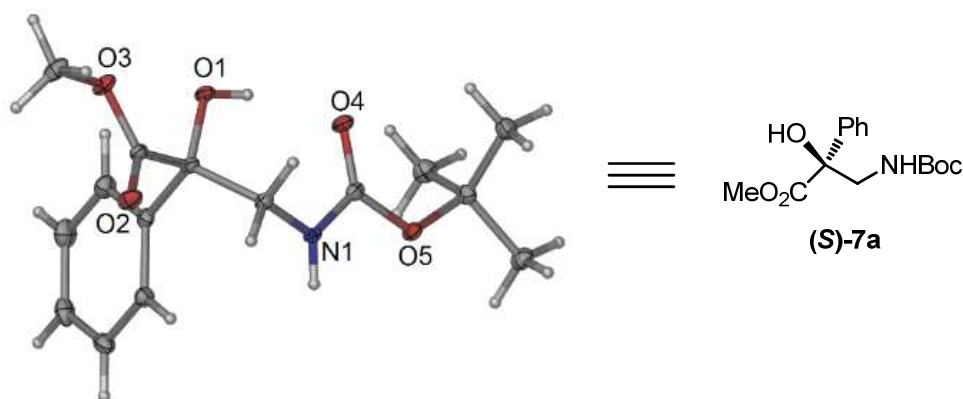
8. Single crystal X-ray diffraction data

Single crystal X-ray diffraction data of (S)-4a (CDCC NO.: 1849954)



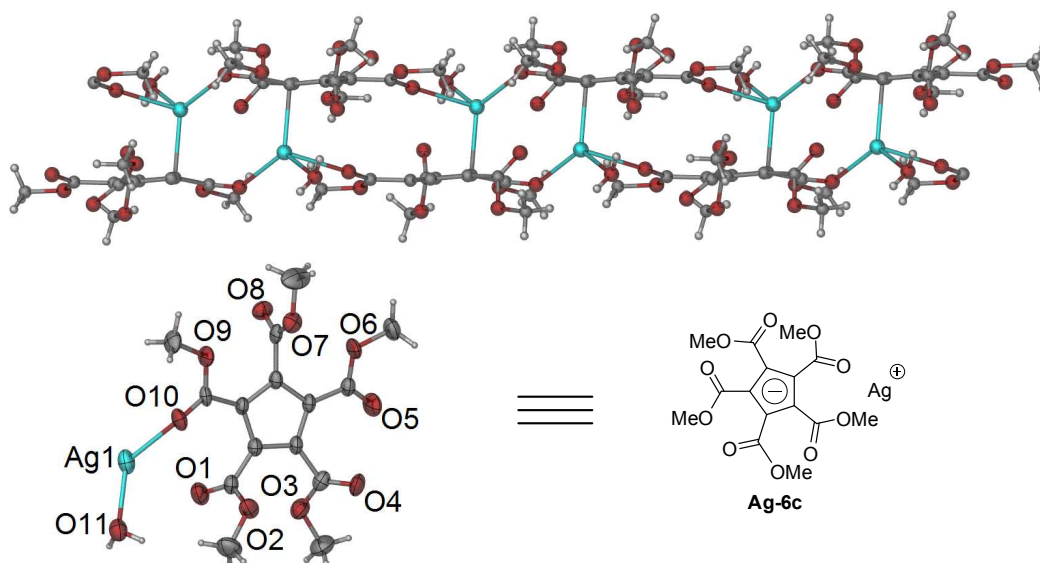
Bond precision:	C-C = 0.0019 Å	Wavelength=1.54184
Cell:	a=9.6616(1) b=11.6145(1) c=11.4666(1)	
	alpha=90 beta=96.814(1) gamma=90	
Temperature:	293 K	
	Calculated	Reported
Volume	1277.63(2)	1277.63(2)
Space group	P 21	P2(1)
Hall group	P 2yb	?
Moiety formula	C31 H31 N O3	?
Sum formula	C31 H31 N O3	C31 H31 N O3
Mr	465.57	465.57
Dx, g cm ⁻³	1.210	1.210
Z	2	2
Mu (mm ⁻¹)	0.609	0.609
F000	496.0	496.0
F000'	497.41	
h,k,lmax	11,14,13	11,14,13
Nref	4846[2550]	4833
Tmin,Tmax	0.823,0.875	0.829,0.878
Tmin'	0.823	
Correction method=	# Reported T Limits: Tmin=0.829 Tmax=0.878	
AbsCorr =	MULTI-SCAN	
Data completeness=	1.90/1.00	Theta(max)= 69.990
R(reflections)=	0.0273(4811)	wR2(reflections)= 0.0714(4833)
S =	1.033	Npar= 317

Single crystal X-ray diffraction data of (S)-7a (CDCC NO.: 1849960)



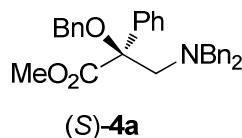
Bond precision:	C-C = 0.0019 Å	Wavelength=1.54184
Cell:	a=5.9401 (1) b=10.6560 (1)	c=23.6934 (2)
	alpha=90 beta=90	gamma=90
Temperature:	100 K	
	Calculated	Reported
Volume	1499.74 (3)	1499.74 (3)
Space group	P 21 21 21	P2 (1) 2 (1) 2 (
Hall group	P 2ac 2ab	?
Moiety formula	C15 H21 N O5	?
Sum formula	C15 H21 N O5	C15 H21 N O5
Mr	295.33	295.33
Dx, g cm ⁻³	1.308	1.308
Z	4	4
Mu (mm ⁻¹)	0.815	0.815
F000	632.0	632.0
F000'	634.11	
h, k, lmax	7, 13, 29	7, 13, 29
Nref	3081 [1808]	3062
Tmin, Tmax	0.710, 0.809	0.696, 0.816
Tmin'	0.644	
Correction method=	# Reported T Limits: Tmin=0.696 Tmax=0.816	
AbsCorr =	MULTI-SCAN	
Data completeness=	1.69/0.99	Theta(max)= 74.720
R(reflections)=	0.0318 (3039)	wR2(reflections)= 0.0860 (3062)
S =	1.089	Npar= 190

Single crystal X-ray diffraction data of Ag-6c (CDCC NO.: 1849959)



Bond precision:	C-C = 0.0075 Å	Wavelength=1.54184
Cell:	a=8.8042(3) b=10.5315(4) c=10.8818(4)	
	alpha=107.990(4) beta=100.432(3) gamma=104.927(4)	
Temperature: 293 K		
	Calculated	Reported
Volume	889.20(7)	889.19(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H17 Ag O11	C15 H17 Ag O11
Sum formula	C15 H17 Ag O11	C15 H17 Ag O11
Mr	481.16	481.15
Dx, g cm ⁻³	1.797	1.797
Z	2	2
Mu (mm ⁻¹)	9.650	9.650
F000	484.0	484.0
F000'	485.94	
h, k, lmax	10, 12, 12	10, 12, 12
Nref	3177	3144
Tmin, Tmax	0.061, 0.176	0.234, 1.000
Tmin'	0.006	
Correction method= # Reported T Limits: Tmin=0.234 Tmax=1.000 AbsCorr = MULTI-SCAN		
Data completeness= 0.990	Theta(max)= 67.079	
R(reflections)= 0.0691(2822)	wR2(reflections)= 0.1836(3144)	
S = 1.015	Npar= 251	

9. Analytical data of products



(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-phenylpropanoate

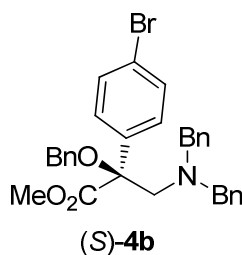
(S)-4a: 92% yield, 96% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.16 (m, 20H), 4.71 (d, *J* = 11.2 Hz, 1H), 4.07 (d, *J* = 11.2 Hz, 1H), 3.95 (d, *J* = 13.7 Hz, 2H), 3.70 (s, 3H), 3.50 (d, *J* = 13.7 Hz, 2H), 3.35 (d, *J* = 13.8 Hz, 1H), 3.30 (d, *J* = 13.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.4, 139.3, 138.7, 138.5, 129.4, 128.3, 128.2, 128.2, 128.0, 127.5, 127.2, 127.1, 126.7, 87.8, 67.6, 61.0, 58.7, 51.9.

HRMS-ESI: calcd. for C₃₁H₃₂NO₃ [M + H]⁺: 466.2382 found: 466.2385

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 10.16 min, t_{minor} = 11.00 min.



(S)-Methyl 2-(benzyloxy)-2-(4-bromophenyl)-3-(dibenzylamino)propanoate

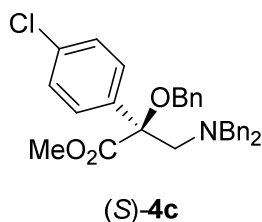
(S)-4b: 89% yield, 92% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.41 (m, 2H), 7.32 – 7.15 (m, 17H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.11 (d, *J* = 11.1 Hz, 1H), 3.84 (d, *J* = 13.7 Hz, 2H), 3.68 (s, 3H), 3.53 (d, *J* = 13.7 Hz, 2H), 3.33 – 3.21 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 171.9, 139.1, 138.4, 137.7, 131.4, 129.3, 128.9, 128.3, 128.1, 127.5, 127.4, 126.7, 122.2, 87.3, 67.7, 60.6, 58.8, 52.1.

HRMS-ESI: calcd. for C₃₁H₃₁BrNO₃ [M + H]⁺: 544.1487 found: 544.1492

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 12.88 min, t_{minor} = 15.20 min.



(S)-Methyl 2-(benzyloxy)-2-(4-chlorophenyl)-3-(dibenzylamino)propanoate

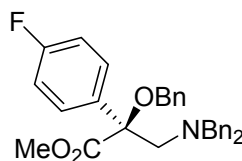
(S)-4c: 91% yield, 94% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.12 (m, 17H), 4.69 (d, J = 11.1 Hz, 1H), 4.12 (d, J = 11.1 Hz, 1H), 3.86 (d, J = 13.7 Hz, 2H), 3.69 (s, 3H), 3.54 (d, J = 13.6 Hz, 2H), 3.33 – 3.22 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 139.1, 138.4, 137.1, 134.0, 129.3, 128.6, 128.4, 128.3, 128.1, 127.4, 127.4, 126.8, 87.2, 67.7, 60.6, 58.8, 52.1.

HRMS-ESI: calcd. for $\text{C}_{31}\text{H}_{31}\text{ClNO}_3$ $[\text{M} + \text{H}]^+$: 500.1992 found: 500.2004

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 12.18 min, t_{minor} = 13.89 min.



(S)-4d

(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-(4-fluorophenyl) propanoate

(S)-4d: 78% yield, 90% ee.

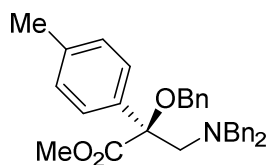
^1H NMR (400 MHz, CDCl_3) δ 7.39 (M, 2H), 7.33 – 7.11 (m, 15H), 7.06 – 6.95 (m, 2H), 4.69 (d, J = 11.2 Hz, 1H), 4.09 (d, J = 11.2 Hz, 1H), 3.87 (d, J = 13.7 Hz, 2H), 3.69 (s, 3H), 3.53 (d, J = 13.7 Hz, 2H), 3.28 (M, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.2, 162.4 (d, J = 247.2 Hz), 139.2, 138.5, 134.4 (d, J = 3.0 Hz), 129.3, 128.9 (d, J = 8.1 Hz), 128.2, 128.1, 127.4, 127.4, 126.8, 115.2 (d, J = 21.3 Hz), 87.2, 67.6, 60.8, 58.8, 52.0.

^{19}F NMR (376 MHz, CDCl_3) δ -113.96.

HRMS-ESI: calcd. for $\text{C}_{31}\text{H}_{31}\text{FNO}_3$ $[\text{M} + \text{H}]^+$: 484.2288 found: 484.2296

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 12.13 min, t_{minor} = 13.79 min.



(S)-4e

(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-(p-tolyl) propanoate

(S)-4e: 96% yield, 93% ee.

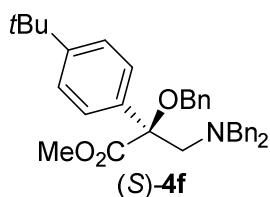
^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.16 (m, 17H), 7.14 (d, J = 8.1 Hz, 2H), 4.69 (d, J = 11.2 Hz, 1H), 4.06 (d, J = 11.2 Hz, 1H), 3.99 (d, J = 13.7 Hz, 2H), 3.68 (s, 3H), 3.47 (d, J = 13.7 Hz, 2H), 3.36 – 3.25 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 139.4, 138.9, 138.0, 135.5, 129.4, 129.0, 128.1, 128.0, 127.5, 127.1, 126.7, 87.7, 67.5, 61.3, 58.8, 51.8, 21.1.

HRMS-ESI: calcd. for $\text{C}_{32}\text{H}_{34}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 480.2539 found: 480.2528

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 6.20 min,

$t_{\text{minor}} = 5.33$ min.



(S)-Methyl 2-(benzyloxy)-2-(4-(*tert*-butyl)phenyl)-3-(dibenzylamino) propanoate

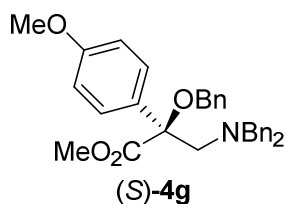
(S)-4f: 96% yield, 94% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.15 (m, 19H), 4.71 (d, $J = 11.3$ Hz, 1H), 4.08 (d, $J = 11.3$ Hz, 1H), 3.99 (d, $J = 13.8$ Hz, 2H), 3.69 (s, 3H), 3.50 (d, $J = 13.8$ Hz, 2H), 3.35 (d, $J = 13.8$ Hz, 1H), 3.29 (d, $J = 13.8$ Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 151.1, 139.4, 139.0, 135.4, 129.4, 128.1, 128.0, 127.5, 127.1, 126.9, 126.7, 125.2, 87.8, 67.6, 61.3, 58.7, 51.8, 34.6, 31.4.

HRMS-ESI: calcd. for $\text{C}_{35}\text{H}_{40}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 522.3008 found: 522.3016

HPLC: (Chiral IC, $\lambda = 254$ nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 5.67$ min, $t_{\text{minor}} = 4.76$ min.



(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-(4-methoxyphenyl) propanoate

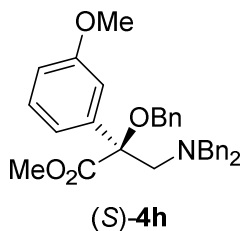
(S)-4g: 95% yield, 95% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.30 (m, 2H), 7.30 – 7.11 (m, 15H), 6.86 (d, $J = 8.9$ Hz, 1H), 4.69 (d, $J = 11.2$ Hz, 1H), 4.06 (d, $J = 11.2$ Hz, 1H), 3.98 (d, $J = 13.7$ Hz, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 3.48 (d, $J = 13.8$ Hz, 2H), 3.37 – 3.23 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 159.3, 139.3, 138.9, 130.6, 129.4, 128.5, 128.1, 128.0, 127.5, 127.1, 126.7, 113.6, 87.5, 67.5, 61.3, 58.7, 55.3, 51.8.

HRMS-ESI: calcd. for $\text{C}_{32}\text{H}_{34}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 496.2488 found: 496.2502

HPLC: (Chiral OD-H, $\lambda = 254$ nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 9.14$ min, $t_{\text{minor}} = 10.10$ min.



(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-(3-methoxyphenyl)propanoate

(S)-4h: 95% yield, 90% ee.

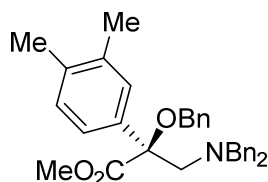
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.14 (m, 16H), 7.06 – 6.94 (m, 2H), 6.85 (M, 1H), 4.72 (d, $J =$

11.3 Hz, 1H), 4.11 (d, J = 11.3 Hz, 1H), 3.95 (d, J = 13.8 Hz, 2H), 3.74 (s, 3H), 3.70 (s, 3H), 3.50 (d, J = 13.8 Hz, 2H), 3.31 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 159.5, 140.0, 139.3, 138.8, 129.3, 129.3, 128.4, 128.0, 127.4, 127.2, 126.7, 119.5, 113.4, 113.2, 87.8, 67.6, 61.1, 58.7, 55.2, 51.9.

HRMS-ESI: calcd. for $\text{C}_{32}\text{H}_{34}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 496.2488 found: 496.2465

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 14.53 min, t_{minor} = 11.21 min.



(S)-4i

(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-(3,4-dimethylphenyl) propanoate

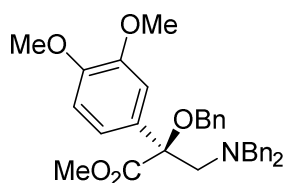
(S)-4i: 95% yield, 95% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.03 (m, 18H), 4.69 (d, J = 11.2 Hz, 1H), 4.06 (d, J = 11.2 Hz, 1H), 4.00 (d, J = 13.7 Hz, 2H), 3.69 (s, 3H), 3.47 (d, J = 13.7 Hz, 2H), 3.32 (t, J = 8.3 Hz, 2H), 2.25 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 139.4, 139.0, 136.7, 136.5, 135.8, 129.5, 129.4, 128.4, 128.1, 128.0, 127.5, 127.1, 126.7, 124.1, 87.8, 67.5, 61.3, 58.8, 51.7, 20.0, 19.5.

HRMS-ESI: calcd. for $\text{C}_{33}\text{H}_{36}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 494.2695 found: 494.2671

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 6.55 min, t_{minor} = 5.46 min.



(S)-4j

(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-(3,4-dimethoxyphenyl)propanoate

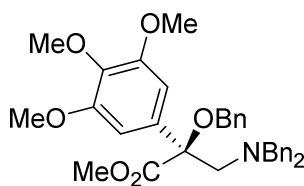
(S)-4j: 95% yield, 90% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.17 (m, 15H), 7.01 – 6.87 (m, 2H), 6.80 (d, J = 8.4 Hz, 1H), 4.72 (d, J = 11.4 Hz, 1H), 4.11 (d, J = 11.4 Hz, 1H), 3.96 (d, J = 13.7 Hz, 2H), 3.88 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.50 (d, J = 13.7 Hz, 2H), 3.34 – 3.22 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 148.8, 148.7, 139.3, 138.9, 131.0, 129.3, 128.2, 128.0, 127.4, 127.2, 126.7, 119.6, 110.5, 110.3, 87.7, 67.6, 61.4, 58.8, 55.9, 55.8, 51.9.

HRMS-ESI: calcd. for $\text{C}_{33}\text{H}_{36}\text{NO}_5$ $[\text{M} + \text{H}]^+$: 526.2593 found: 526.2605

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 10/1, Flow rate = 1.0 mL/min), t_{major} = 9.13 min, t_{minor} = 8.57 min.



(S)-4k

(S)-Methyl 2-(benzyloxy)-3-(dibenzylamino)-2-(3,4,5-trimethoxyphenyl) propanoate

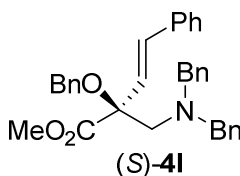
(S)-4k: 90% yield, 90% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.14 (m, 15H), 6.64 (s, 2H), 4.75 (d, *J* = 11.5 Hz, 1H), 4.20 (d, *J* = 11.5 Hz, 1H), 3.93 – 3.80 (m, 5H), 3.72 (s, 9H), 3.57 (d, *J* = 13.7 Hz, 2H), 3.35 – 3.19 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 152.9, 139.3, 138.8, 137.7, 134.0, 129.2, 128.2, 128.0, 127.3, 126.8, 104.3, 87.9, 67.7, 61.2, 60.9, 58.8, 56.0, 51.9.

HRMS-ESI: calcd. for C₃₄H₃₈NO₆ [M + H]⁺: 556.2699 found: 556.2662

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 95/5, Flow rate = 1.0 mL/min), *t*_{major} = 19.11 min, *t*_{minor} = 13.30 min.



(S)-4l

(S, E)-Methyl 2-(benzyloxy)-2-((dibenzylamino)methyl)-4-phenylbut-3-enoate

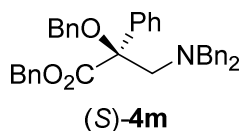
(S, E)-4l: 88% yield, 72% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.23 (m, 20H), 6.72 (d, *J* = 16.5 Hz, 1H), 6.52 (d, *J* = 16.5 Hz, 1H), 4.77 (d, *J* = 11.3 Hz, 1H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.02 (d, *J* = 13.7 Hz, 2H), 3.74 (s, 3H), 3.55 (d, *J* = 13.7 Hz, 2H), 3.15 (d, *J* = 13.7 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.1, 139.5, 138.9, 136.3, 132.3, 129.3, 128.6, 128.3, 128.1, 128.0, 127.6, 127.3, 126.9, 126.8, 126.7, 86.5, 67.8, 62.8, 59.1, 52.1.

HRMS-ESI: calcd. for C₃₃H₃₄NO₃ [M + H]⁺: 492.2533 found: 492.2534

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), *t*_{major} = 6.84 min, *t*_{minor} = 8.28 min.



(S)-4m

(S)-Benzyl 2-(benzyloxy)-3-(dibenzylamino)-2-phenylpropanoate

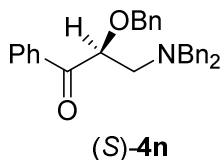
(S)-4m: 78% yield, 94% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.37 (m, 2H), 7.36 – 7.10 (m, 24H), 5.34 (d, *J* = 12.2 Hz, 1H), 5.08 (d, *J* = 12.3 Hz, 1H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.08 (d, *J* = 11.1 Hz, 1H), 3.85 (d, *J* = 13.8 Hz, 2H), 3.54 (d, *J* = 13.8 Hz, 2H), 3.43 – 3.31 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 171.8, 139.1, 138.7, 138.4, 135.5, 129.3, 128.5, 128.5, 128.3, 128.1, 128.1, 128.0, 127.4, 127.2, 126.7, 87.7, 67.6, 66.9, 61.0, 58.3.

HRMS-ESI: calcd. for $C_{37}H_{36}NO_3$ $[M + H]^+$: 542.2695 found: 542.2700

HPLC: (Chiral OD-H, $\lambda = 254$ nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 29.66$ min, $t_{\text{minor}} = 25.47$ min.



(S)-2-(Benzyloxy)-3-(dibenzylamino)-1-phenylpropan-1-one

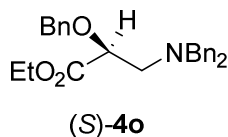
(S)-4n: 90% yield, 87% ee.

1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, $J = 7.5$ Hz, 2H), 7.52 – 7.44 (m, 1H), 7.35 – 7.24 (m, 7H), 7.25 – 7.14 (m, 10H), 4.88 (dd, $J = 6.9, 4.7$ Hz, 1H), 4.65 (d, $J = 11.6$ Hz, 1H), 4.38 (d, $J = 11.6$ Hz, 1H), 3.70 (d, $J = 13.6$ Hz, 2H), 3.60 (d, $J = 13.6$ Hz, 2H), 3.05 – 2.90 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 139.4, 137.6, 135.3, 133.2, 129.0, 128.6, 128.5, 128.5, 128.3, 128.2, 127.9, 126.9, 82.0, 72.2, 59.0, 55.8.

HRMS-ESI: calcd. for $C_{30}H_{30}NO_2$ $[M + H]^+$: 436.2277 found: 436.2271

HPLC: (Chiral OD-H, $\lambda = 254$ nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 5.70$ min, $t_{\text{minor}} = 5.25$ min.



(S)-Ethyl 2-(benzyloxy)-3-(dibenzylamino) propanoate

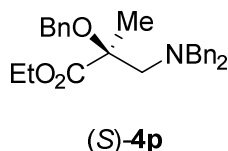
(S)-4o: 78% yield, 59% ee.

1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.12 (m, 15H), 4.66 (d, $J = 11.6$ Hz, 1H), 4.39 (d, $J = 11.6$ Hz, 1H), 4.20 – 4.04 (m, 3H), 3.69 (d, $J = 13.7$ Hz, 2H), 3.58 (d, $J = 13.7$ Hz, 2H), 2.90 (d, $J = 5.6$ Hz, 2H), 1.19 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 139.3, 137.5, 129.0, 128.4, 128.2, 128.1, 127.9, 127.0, 78.1, 72.5, 60.8, 58.8, 55.6, 14.2.

HRMS-ESI: calcd. for $C_{26}H_{30}NO_3$ $[M + H]^+$: 404.2226 found: 404.2252

HPLC: (Chiral OD-H, $\lambda = 254$ nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 22.07$ min, $t_{\text{minor}} = 33.06$ min.



(S)-Ethyl 2-(benzyloxy)-3-(dibenzylamino)-2-methylpropanoate

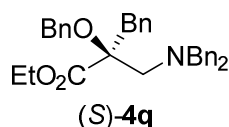
(S)-4p: 85% yield, 80% ee.

1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.02 (m, 15H), 4.47 (d, $J = 11.0$ Hz, 1H), 4.38 (d, $J = 11.0$ Hz, 1H), 4.15 – 3.90 (m, 2H), 3.71 (d, $J = 13.7$ Hz, 2H), 3.51 (d, $J = 13.7$ Hz, 2H), 2.84 (d, $J = 13.7$ Hz, 1H), 2.77 (d, $J = 13.7$ Hz, 1H), 1.36 (s, 3H), 1.11 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.5, 139.6, 138.8, 129.2, 128.2, 128.1, 127.6, 127.4, 126.8, 82.8, 67.1, 61.3, 60.9, 59.4, 19.9, 14.2.

HRMS-ESI: calcd. for C₂₇H₃₂NO₃ [M + H]⁺: 418.2382 found: 418.2336

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 5.80 min, t_{minor} = 5.12 min.



(S)-Ethyl 2-benzyl-2-(benzyloxy)-3-(dibenzylamino) propanoate

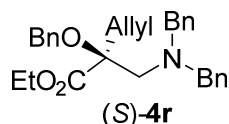
(S)-4q: 90% yield, 55% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.18 (m, 20H), 4.77 (d, *J* = 10.9 Hz, 1H), 4.63 (d, *J* = 11.0 Hz, 1H), 4.18 – 3.94 (m, 2H), 3.75 (d, *J* = 13.6 Hz, 2H), 3.56 (d, *J* = 13.7 Hz, 2H), 3.37 – 3.19 (m, 2H), 3.00 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.1 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 172.6, 139.3, 138.5, 136.4, 130.4, 129.3, 128.2, 128.2, 128.1, 127.6, 127.4, 126.9, 126.6, 85.7, 66.9, 61.0, 58.7, 57.6, 39.5, 14.1.

HRMS-ESI: calcd. for C₃₃H₃₆NO₃ [M + H]⁺: 494.2695 found: 494.2671

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 5.38 min, t_{minor} = 4.99 min.



(S)-Ethyl 2-(benzyloxy)-2-((dibenzylamino)methyl)pent-4-enoate

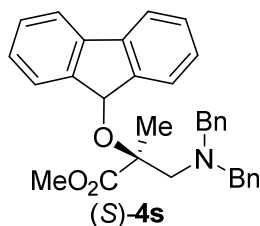
(S)-4r: 76% yield, 72% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.34 (m, 2H), 7.31 – 7.25 (m, 9H), 7.26 – 7.18 (m, 4H), 5.77 – 5.63 (m, 1H), 5.16 – 5.00 (m, 2H), 4.62 (d, *J* = 10.6 Hz, 1H), 4.50 (d, *J* = 10.6 Hz, 1H), 4.25 – 4.12 (m, 1H), 4.11 – 3.99 (m, 1H), 3.84 (d, *J* = 13.8 Hz, 2H), 3.48 (d, *J* = 13.8 Hz, 2H), 2.98 (d, *J* = 14.0 Hz, 1H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.82 (dd, *J* = 15.2, 6.4 Hz, 1H), 2.68 (dd, *J* = 15.2, 7.7 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 172.6, 139.4, 138.4, 132.6, 129.2, 128.2, 128.1, 127.7, 127.4, 126.8, 118.4, 84.2, 66.6, 60.9, 58.9, 58.4, 37.5, 14.2.

HRMS-ESI: calcd. for C₂₉H₃₄NO₃ [M + H]⁺: 444.2533 found: 444.2535

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 6.02 min, t_{minor} = 5.54 min.



(S)-Methyl 2-((9H-fluoren-9-yl)oxy)-3-(dibenzylamino)-2-methylpropanoate

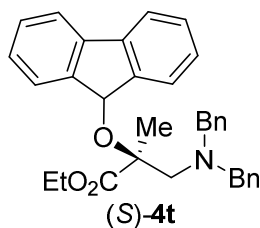
(S)-4s: 89% yield, 90% ee.

¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.45 (m, 3H), 7.30 (dd, *J* = 15.9, 6.0 Hz, 10H), 7.23 – 7.11 (m, 4H), 5.63 (s, 1H), 3.83 (d, *J* = 13.7 Hz, 2H), 3.65 (s, 3H), 3.44 (d, *J* = 13.7 Hz, 2H), 2.99 (d, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 1.74 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 174.1, 144.9, 144.5, 140.9, 139.8, 139.6, 129.2, 128.7, 128.7, 128.1, 127.7, 127.3, 126.9, 126.8, 125.7, 119.9, 119.4, 83.6, 78.5, 62.0, 59.5, 52.0, 23.2.

HRMS-ESI: calcd. for C₃₂H₃₂NO₃ [M + H]⁺: 477.2377 found: 477.2386

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 8.10 min, t_{minor} = 7.31 min.



(S)-Ethyl 2-((9H-fluoren-9-yl)oxy)-3-(dibenzylamino)-2-methylpropanoate

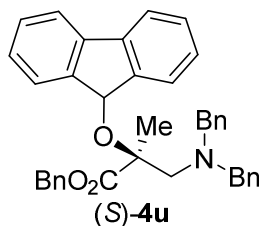
(S)-4t: 90% yield, 90% ee.

¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.68 – 7.53 (m, 3H), 7.39 – 7.30 (m, 10H), 7.28 – 7.22 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 5.69 (s, 1H), 4.35 – 4.26 (m, 1H), 4.17 – 4.01 (m, 1H), 3.86 (d, *J* = 13.8 Hz, 2H), 3.53 (d, *J* = 13.8 Hz, 2H), 3.04 (d, *J* = 13.7 Hz, 1H), 2.94 (d, *J* = 13.6 Hz, 1H), 1.81 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.7, 144.9, 144.6, 140.8, 139.8, 139.5, 129.2, 128.7, 128.6, 128.1, 127.6, 127.3, 126.9, 126.8, 125.7, 119.8, 119.3, 83.5, 78.4, 62.0, 61.2, 59.3, 23.2, 14.1.

HRMS-ESI: calcd. for C₃₃H₃₄NO₃ [M + H]⁺: 492.2533 found: 492.2531

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 7.54 min, t_{minor} = 6.60 min.



(S)-Benzyl 2-((9H-fluoren-9-yl)oxy)-3-(dibenzylamino)-2-methylpropanoate

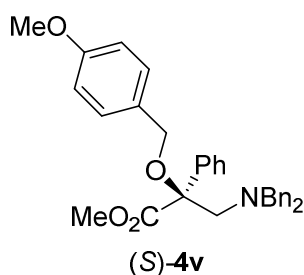
(S)-4u: 83% yield, 92% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.44 (m, 3H), 7.32 – 7.21 (m, 15H), 7.20 – 7.14 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.63 (s, 1H), 5.28 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 3.77 (d, *J* = 13.8 Hz, 2H), 3.48 (d, *J* = 13.8 Hz, 2H), 3.01 (d, *J* = 13.7 Hz, 1H), 2.92 (d, *J* = 13.7 Hz, 1H), 1.77 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 173.6, 144.9, 144.6, 140.9, 139.8, 139.5, 135.7, 129.3, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 127.7, 127.4, 127.0, 126.9, 125.7, 119.9, 119.4, 83.7, 78.6, 66.9, 62.1, 59.3, 23.2.

HRMS-ESI: calcd. for C₃₈H₃₆NO₃ [M + H]⁺: 554.2690 found: 554.2698

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 9.45 min, t_{minor} = 8.53 min.



(S)-Methyl 3-(dibenzylamino)-2-((4-methoxybenzyl)oxy)-2-phenylpropanoate

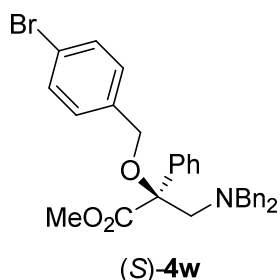
(S)-4v: 89% yield, 94% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 7.27 – 7.14 (m, 13H), 6.80 – 6.73 (m, 2H), 4.63 (d, *J* = 10.6 Hz, 1H), 3.99 (d, *J* = 10.6 Hz, 1H), 3.93 (d, *J* = 13.7 Hz, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 3.49 (d, *J* = 13.7 Hz, 2H), 3.33 (d, *J* = 13.8 Hz, 1H), 3.28 (d, *J* = 13.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.4, 158.9, 139.3, 138.6, 131.0, 129.4, 129.1, 128.3, 128.2, 128.1, 127.2, 126.8, 113.6, 87.7, 67.3, 61.0, 58.8, 55.3, 51.9.

HRMS-ESI: calcd. for C₃₂H₃₄NO₄ [M + H]⁺: 496.2488 found: 496.2509

HPLC: (Chiral ID, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 20.57 min, t_{minor} = 18.01 min.



(S)-Methyl 2-((4-bromobenzyl)oxy)-3-(dibenzylamino)-2-phenylpropanoate

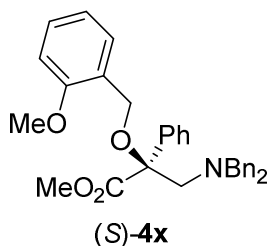
(S)-4w: 78% yield, 93% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 7H), 7.30 – 7.18 (m, 10H), 7.18 – 7.07 (m, 2H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.05 – 3.88 (m, 3H), 3.69 (s, 3H), 3.48 (d, *J* = 13.8 Hz, 2H), 3.36 – 3.27 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 139.2, 138.2, 137.8, 131.2, 129.3, 129.2, 128.4, 128.3, 128.1, 127.1, 126.8, 121.0, 88.0, 67.0, 61.3, 58.8, 51.9.

HRMS-ESI: calcd. for C₃₁H₃₁BrNO₃ [M + H]⁺: 544.1487 found: 544.1473

HPLC: (Chiral ID, $\lambda = 254$ nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 17.62$ min, $t_{\text{minor}} = 15.86$ min.



(S)-Methyl 3-(dibenzylamino)-2-((2-methoxybenzyl)oxy)-2-phenylpropanoate

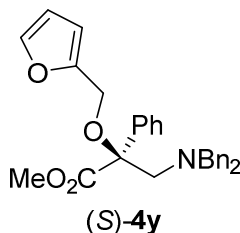
(S)-4x: 91% yield, 93% ee.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 – 7.48 (m, 1H), 7.48 – 7.38 (m, 2H), 7.35 – 7.13 (m, 14H), 6.88 (d, $J = 7.3$ Hz, 1H), 6.75 (d, $J = 8.1$ Hz, 1H), 4.72 (d, $J = 12.3$ Hz, 1H), 4.25 (d, $J = 12.3$ Hz, 1H), 3.89 (d, $J = 13.7$ Hz, 2H), 3.67 (s, 1H), 3.66 (s, 1H), 3.56 (d, $J = 13.8$ Hz, 2H), 3.44 – 3.26 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.4, 156.5, 139.4, 138.7, 129.3, 128.3, 128.2, 128.0, 128.0, 127.3, 127.1, 126.7, 120.4, 109.8, 87.5, 62.3, 60.2, 58.7, 55.1, 51.9.

HRMS-ESI: calcd. for $\text{C}_{32}\text{H}_{34}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 496.2488 found: 496.2521

HPLC: (Chiral ID, $\lambda = 254$ nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 19.28$ min, $t_{\text{minor}} = 17.74$ min.



(S)-Methyl 3-(dibenzylamino)-2-(furan-2-ylmethoxy)-2-phenylpropanoate

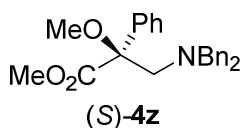
(S)-4y: 90% yield, 87% ee.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 – 7.39 (m, 2H), 7.33 (dd, $J = 8.4, 4.6$ Hz, 4H), 7.30 – 7.10 (m, 10H), 6.21 (d, $J = 33.8$ Hz, 2H), 4.66 (d, $J = 11.9$ Hz, 1H), 4.09 (d, $J = 11.9$ Hz, 1H), 3.91 (d, $J = 13.5$ Hz, 2H), 3.70 (s, 3H), 3.50 (d, $J = 13.6$ Hz, 2H), 3.28 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.2, 152.2, 142.3, 139.3, 138.1, 129.4, 128.4, 128.3, 128.1, 127.3, 126.8, 110.2, 108.4, 87.8, 61.1, 60.2, 58.7, 51.9.

HRMS-ESI: calcd. for $\text{C}_{29}\text{H}_{29}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 456.2175 found: 456.2172

HPLC: (Chiral ID, $\lambda = 254$ nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 7.45$ min, $t_{\text{minor}} = 6.51$ min.



(S)-Methyl 3-(dibenzylamino)-2-methoxy-2-phenylpropanoate

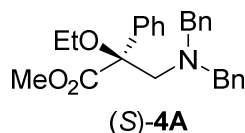
(S)-4z: 92% yield, 87% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 6.97 (m, 15H), 3.80 (d, *J* = 13.6 Hz, 2H), 3.57 (s, 3H), 3.41 (d, *J* = 13.7 Hz, 2H), 3.22 (d, *J* = 13.8 Hz, 1H), 3.16 (d, *J* = 13.8 Hz, 1H), 3.08 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 139.3, 138.4, 129.3, 128.3, 128.1, 128.1, 127.0, 126.8, 87.2, 58.8, 58.5, 52.7, 52.0.

HRMS-ESI: calcd. for C₂₅H₂₈NO₃ [M + H]⁺: 390.2070 found: 390.2085

HPLC: (Chiral ID, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 16.42 min, t_{minor} = 13.57 min.



(S)-Methyl 3-(dibenzylamino)-2-ethoxy-2-phenylpropanoate

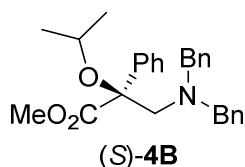
(S)-4A: 90% yield, 96% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.16 (m, 15H), 3.86 (d, *J* = 13.7 Hz, 2H), 3.65 (s, 3H), 3.60 – 3.46 (m, 3H), 3.26 (d, *J* = 13.8 Hz, 1H), 3.21 (d, *J* = 13.8 Hz, 1H), 3.17 – 3.06 (m, 1H), 1.15 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.5, 138.3, 137.9, 128.3, 127.1, 127.0, 126.8, 125.8, 125.7, 86.1, 76.3, 76.0, 75.7, 59.7, 58.7, 57.7, 50.8, 14.5.

HRMS-ESI: calcd. for C₂₆H₃₀NO₃ [M + H]⁺: 404.2220 found: 404.2226

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 11.86 min, t_{minor} = 9.48 min.



(S)-Methyl 3-(dibenzylamino)-2-isopropoxy-2-phenylpropanoate

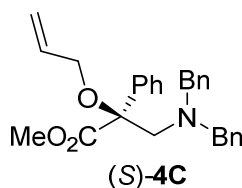
(S)-4B: 88% yield, 90% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.10 (m, 15H), 3.94 (d, *J* = 13.6 Hz, 2H), 3.77 – 3.69 (m, 1H), 3.55 (d, *J* = 1.0 Hz, 3H), 3.35 (d, *J* = 13.6 Hz, 2H), 3.30 (d, *J* = 13.4 Hz, 1H), 3.13 (d, *J* = 13.3 Hz, 1H), 1.18 (d, *J* = 5.9 Hz, 3H), 0.50 (d, *J* = 5.8 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 173.2, 139.7, 139.4, 129.5, 128.1, 128.0, 128.0, 127.7, 126.7, 87.6, 68.8, 61.0, 58.8, 51.5, 24.3, 23.5.

HRMS-ESI: calcd. for C₂₇H₃₂NO₃ [M + H]⁺: 418.2377 found: 418.2371

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 8.91 min, t_{minor} = 6.77 min.



(S)-Methyl 2-(allyloxy)-3-(dibenzylamino)-2-phenylpropanoate

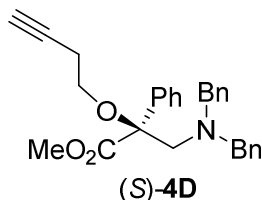
(S)-4C: 85% yield, 89% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.21 (m, 15H), 6.00 – 5.85 (m, 1H), 5.26 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.10 (dd, *J* = 10.5, 1.6 Hz, 1H), 4.21 – 4.10 (m, 1H), 3.97 (d, *J* = 13.7 Hz, 2H), 3.73 (s, 3H), 3.69 – 3.61 (m, 1H), 3.56 (d, *J* = 13.7 Hz, 2H), 3.34 (d, *J* = 13.8 Hz, 1H), 3.30 (d, *J* = 13.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 139.3, 138.5, 135.1, 129.4, 128.3, 128.1, 128.1, 127.0, 126.8, 115.8, 87.6, 66.7, 60.6, 58.7, 51.9.

HRMS-ESI: calcd. for C₂₇H₃₀NO₃ [M + H]⁺: 416.2220 found: 416.2217

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 5.88 min, t_{minor} = 4.87 min.



(S)-Methyl 2-(but-3-yn-1-yloxy)-3-(dibenzylamino)-2-phenylpropanoate

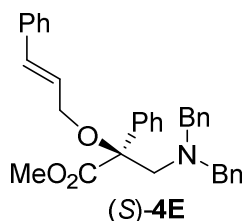
(S)-4D: 82% yield, 83% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.26 (m, 15H), 4.01 (d, *J* = 13.7 Hz, 2H), 3.80 – 3.68 (m, 4H), 3.58 (d, *J* = 13.7 Hz, 2H), 3.34 (d, *J* = 13.8 Hz, 1H), 3.30 – 3.19 (m, 2H), 2.58 – 2.40 (m, 2H), 1.90 (t, *J* = 2.5 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.2, 139.3, 138.2, 129.4, 128.3, 128.2, 128.1, 127.1, 126.8, 87.9, 81.4, 69.2, 63.7, 60.9, 58.8, 51.8, 20.2.

HRMS-ESI: calcd. for C₂₈H₃₀NO₃ [M + H]⁺: 428.2220 found: 428.2217

HPLC: (Chiral OD-H, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 6.19 min, t_{minor} = 6.89 min.



(S)-Methyl 2-(cinnamyloxy)-3-(dibenzylamino)-2-phenylpropanoate

(S)-4E: 90% yield, 87% ee.

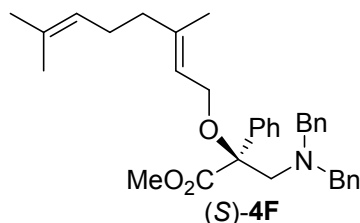
¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.30 (m, 3H), 7.30 – 7.16 (m, 15H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.28 – 4.19 (m, 1H), 3.95 (d, *J* = 13.7 Hz, 2H), 3.81 – 3.73 (m, 1H), 3.70 (s, 3H), 3.52 (d, *J* = 13.7 Hz, 2H), 3.32 (d, *J* = 14.0 Hz, 1H), 3.28 (d, *J* = 13.9 Hz,

1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 139.3, 138.5, 137.0, 131.2, 129.3, 128.4, 128.3, 128.1, 127.4, 127.1, 126.7, 126.5, 126.4, 87.6, 66.4, 60.8, 58.8, 51.9.

HRMS-ESI: calcd. for C₃₃H₃₄NO₃ [M + H]⁺: 492.2533 found: 492.2535

HPLC: (Chiral IE, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 8.48 min, t_{minor} = 9.70 min.



(S, E)-Methyl 3-(dibenzylamino)-2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-phenylpropanoate

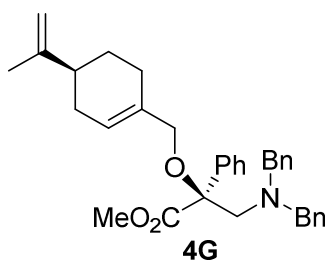
(S, E)-**4F**: 90% yield, 90% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.26 (m, 13H), 5.44 (t, *J* = 6.4 Hz, 1H), 5.15 (t, *J* = 6.6 Hz, 1H), 4.21 (dd, *J* = 11.0, 6.4 Hz, 1H), 3.97 (d, *J* = 13.7 Hz, 2H), 3.76 (s, 3H), 3.72 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.62 (d, *J* = 13.7 Hz, 2H), 3.38 (d, *J* = 13.8 Hz, 1H), 3.33 (d, *J* = 13.8 Hz, 1H), 2.18 – 2.08 (m, 2H), 2.09 – 2.00 (m, 2H), 1.73 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 172.5, 139.4, 139.0, 138.9, 131.5, 129.4, 128.2, 128.1, 127.9, 127.1, 126.7, 124.1, 121.3, 87.2, 62.4, 60.3, 58.8, 51.8, 39.6, 26.5, 25.7, 17.7, 16.5.

HRMS-ESI: calcd. for C₃₄H₄₂NO₃ [M + H]⁺: 512.3159 found: 512.3150

HPLC: (Chiral IC, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 6.20 min, t_{minor} = 5.38 min.



(S)-Methyl

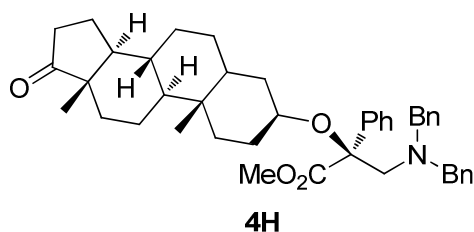
3-(dibenzylamino)-2-phenyl-2-(((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methoxy)propanoate

(S, S)-**4G**: 90% yield, *dr* > 95:5

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.26 (m, 2H), 7.25 – 7.20 (m, 3H), 7.20 – 7.16 (m, 4H), 7.14 – 7.10 (m, 6H), 5.54 (s, 1H), 4.58 (d, *J* = 7.9 Hz, 2H), 3.91 (d, *J* = 10.7 Hz, 1H), 3.80 (d, *J* = 13.7 Hz, 2H), 3.58 (s, 3H), 3.44 (d, *J* = 13.7 Hz, 2H), 3.35 (d, *J* = 10.8 Hz, 1H), 3.23 (d, *J* = 13.8 Hz, 1H), 3.16 (d, *J* = 13.8 Hz, 1H), 2.07 – 1.89 (m, 4H), 1.80 (t, *J* = 13.8 Hz, 1H), 1.70 – 1.63 (m, 1H), 1.61 (s, 3H), 1.38 – 1.26 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 171.3, 149.0, 138.3, 137.6, 133.7, 128.3, 127.1, 127.0, 126.9, 126.0, 125.7, 122.0, 107.4, 86.1, 68.6, 59.3, 57.6, 50.7, 40.0, 29.4, 26.4, 25.6, 19.7.

HRMS-ESI: calcd. for $C_{34}H_{40}NO_3$ $[M + H]^+$: 510.3003 found: 510.3001



(S)-Methyl

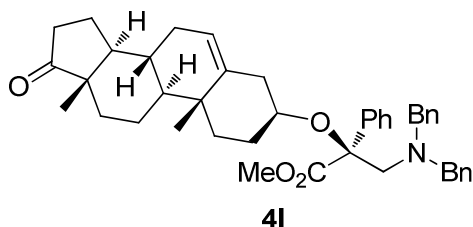
3-(dibenzylamino)-2-(((3S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-2-phenylpropanoate

4H: 95% yield, *dr* > 95:5

1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 8H), 7.26 – 7.17 (m, 8H), 3.99 (d, J = 13.6 Hz, 2H), 3.61 (s, 3H), 3.49 – 3.33 (m, 4H), 3.20 (d, J = 13.4 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.18 – 2.07 (m, 1H), 2.07 – 1.96 (m, 1H), 1.90 – 1.81 (m, 1H), 1.77 – 1.71 (m, 1H), 1.62 – 1.54 (m, 2H), 1.49 – 1.39 (m, 3H), 1.20 – 1.12 (m, 2H), 1.10 – 0.99 (m, 2H), 0.94 – 0.77 (m, 7H), 0.76 – 0.67 (m, 4H), 0.58 – 0.48 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.5, 173.1, 140.0, 139.4, 129.5, 128.1, 128.0, 127.5, 126.7, 87.1, 75.3, 60.8, 58.9, 54.5, 51.6, 51.4, 47.8, 44.9, 37.3, 36.3, 35.9, 35.5, 35.0, 31.6, 30.8, 29.7, 28.5, 21.8, 20.4, 13.8, 12.2.

HRMS-ESI: calcd. for $C_{43}H_{54}NO_4$ $[M + H]^+$: 648.4047 found: 648.4045



(S)-Methyl

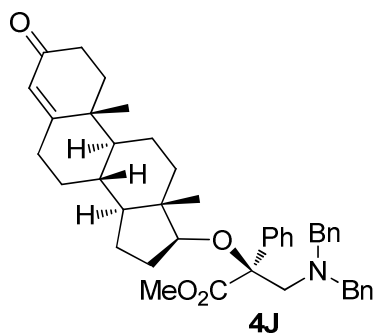
3-(dibenzylamino)-2-(((3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-2-phenylpropanoate

4I: 93% yield, *dr* > 95:5

1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 6H), 7.28 – 7.26 (m, 2H), 7.26 – 7.17 (m, 7H), 4.80 – 4.68 (m, 1H), 4.07 (d, J = 13.6 Hz, 2H), 3.62 (s, 3H), 3.44 – 3.33 (m, 4H), 3.23 (d, J = 13.3 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.25 – 2.15 (m, 1H), 2.11 – 2.00 (m, 1H), 1.96 – 1.72 (m, 5H), 1.55 – 1.38 (m, 5H), 1.24 – 1.15 (m, 2H), 1.13 – 1.05 (m, 1H), 1.04 – 0.96 (m, 1H), 0.92 – 0.79 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.3, 173.0, 141.7, 139.9, 139.4, 129.5, 128.2, 128.1, 128.0, 127.6, 126.7, 120.1, 87.6, 75.9, 60.8, 58.9, 51.8, 51.6, 50.3, 47.6, 40.6, 37.6, 36.6, 35.9, 31.5, 31.4, 30.8, 30.0, 21.9, 20.3, 19.3, 13.5.

HRMS-ESI: calcd. for $C_{43}H_{52}NO_4$ $[M + H]^+$: 646.3891 found: 646.3888



(S)-Methyl

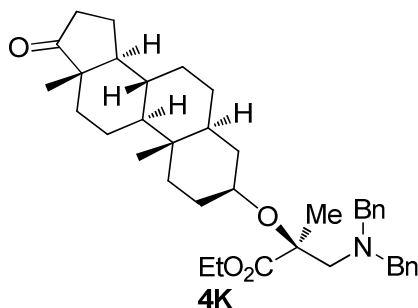
3-(dibenzylamino)-2-(((8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)oxy)-2-phenylpropanoate

4J: 92% yield, *dr* > 95:5

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.29 (m, 3H), 7.30 – 7.24 (m, 7H), 7.21 – 7.16 (m, 5H), 5.68 (s, 1H), 3.92 (d, *J* = 13.7 Hz, 2H), 3.60 (s, 3H), 3.48 (s, 1H), 3.46 – 3.36 (m, 3H), 3.19 (d, *J* = 13.4 Hz, 1H), 2.42 – 2.25 (m, 3H), 2.24 – 2.13 (m, 2H), 1.96 – 1.88 (m, 1H), 1.86 – 1.71 (m, 2H), 1.62 – 1.41 (m, 4H), 1.25 – 1.15 (m, 2H), 1.13 – 1.05 (m, 4H), 0.94 – 0.81 (m, 2H), 0.77 – 0.64 (m, 5H), 0.29 – 0.17 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 199.6, 173.1, 171.5, 139.9, 139.3, 129.4, 128.2, 128.0, 127.8, 126.7, 123.7, 87.7, 84.7, 61.1, 58.7, 53.7, 51.6, 50.0, 42.8, 38.6, 35.7, 35.6, 35.5, 34.0, 32.8, 31.5, 30.0, 23.6, 20.6, 17.4, 12.1.

HRMS-ESI: calcd. for C₄₃H₅₂NO₄ [M + H]⁺: 646.3891 found: 646.3876



(S)-Ethyl

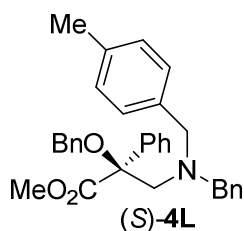
3-(dibenzylamino)-2-(((3S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-2-methylpropanoate

4K: 96% yield, *dr* > 95:5

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.26 (m, 8H), 7.25 – 7.18 (m, 2H), 4.14 – 3.98 (m, 2H), 3.75 (d, *J* = 13.7 Hz, 2H), 3.56 (d, *J* = 13.7 Hz, 2H), 3.39 – 3.26 (m, 1H), 2.78 (d, *J* = 13.5 Hz, 1H), 2.72 (d, *J* = 13.5 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.10 – 1.85 (m, 3H), 1.81 – 1.73 (m, 2H), 1.71 – 1.57 (m, 3H), 1.51 – 1.42 (m, 3H), 1.38 – 1.32 (m, 4H), 1.27 – 1.22 (m, 4H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.10 – 1.01 (m, 1H), 0.97 – 0.87 (m, 2H), 0.83 (s, 3H), 0.78 (s, 3H), 0.63 (t, *J* = 10.9 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 221.5, 174.2, 139.7, 129.2, 128.1, 126.8, 82.5, 74.9, 62.0, 60.7, 59.3, 54.6, 51.4, 47.8, 45.2, 37.8, 37.4, 35.9, 35.6, 35.0, 31.6, 31.0, 29.5, 28.6, 21.8, 21.0, 20.4, 14.1, 13.8, 12.3.

HRMS-ESI: calcd. for C₃₉H₅₄NO₄ [M + H]⁺: 600.4047 found: 600.4041



(S)-Methyl 3-(benzyl(4-methylbenzyl)amino)-2-(benzyloxy)-2-phenylpropanoate

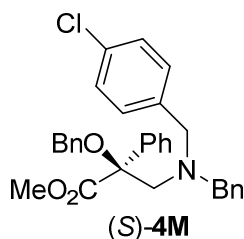
(S)-4L: 95% yield, 90% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.36 – 7.27 (m, 5H), 7.26 – 7.16 (m, 8H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 4.71 (d, *J* = 11.2 Hz, 1H), 4.07 (d, *J* = 11.2 Hz, 1H), 3.93 (d, *J* = 13.7 Hz, 1H), 3.88 (d, *J* = 13.7 Hz, 1H), 3.70 (s, 3H), 3.50 (d, *J* = 5.5 Hz, 1H), 3.47 (d, *J* = 5.4 Hz, 1H), 3.34 (d, *J* = 13.9 Hz, 1H), 3.29 (d, *J* = 13.8 Hz, 1H), 2.30 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 172.4, 139.4, 138.8, 138.6, 136.2, 136.1, 129.4, 128.8, 128.3, 128.2, 128.1, 127.5, 127.2, 127.2, 126.7, 87.8, 67.6, 60.9, 58.6, 58.3, 51.9, 21.2.

HRMS-ESI: calcd. for C₃₂H₃₄NO₃ [M + H]⁺: 480.2533 found: 480.2532

HPLC: (Chiral IA, λ = 254 nm, hexane/2-propanol = 300/1, Flow rate = 1.0 mL/min), t_{major} = 6.76 min, t_{minor} = 5.36 min.



(S)-Methyl 3-(benzyl(4-chlorobenzyl)amino)-2-(benzyloxy)-2-phenylpropanoate

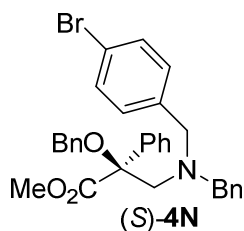
(S)-4M: 92% yield, 94% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.19 (m, 10H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.07 (d, *J* = 11.1 Hz, 1H), 3.93 (d, *J* = 13.8 Hz, 1H), 3.88 (d, *J* = 13.7 Hz, 1H), 3.70 (s, 3H), 3.49 (d, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 7.7 Hz, 1H), 3.33 (d, *J* = 13.9 Hz, 1H), 3.28 (d, *J* = 13.8 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 172.3, 138.9, 138.7, 138.3, 137.9, 132.4, 130.6, 129.3, 128.4, 128.3, 128.2, 128.2, 128.1, 127.5, 127.3, 127.1, 126.9, 87.8, 67.7, 61.0, 58.8, 58.1, 52.6, 51.9.

HRMS-ESI: calcd. for C₃₁H₃₁ClNO₃ [M + H]⁺: 500.1987 found: 500.1983

HPLC: (Chiral IA, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 9.74 min, t_{minor} = 8.73 min.



(S)-Methyl 3-(benzyl(4-bromobenzyl)amino)-2-(benzyloxy)-2-phenylpropanoate

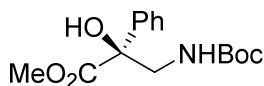
(S)-4N: 92% yield, 92% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.30 (m, 7H), 7.29 – 7.15 (m, 10H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.07 (d, *J* = 11.1 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 3.88 (d, *J* = 13.9 Hz, 1H), 3.70 (s, 3H), 3.49 (d, *J* = 10.5 Hz, 1H), 3.45 (d, *J* = 10.6 Hz, 1H), 3.33 (d, *J* = 13.8 Hz, 1H), 3.28 (d, *J* = 13.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 138.9, 138.7, 138.5, 138.3, 131.1, 131.0, 129.3, 128.4, 128.3, 128.2, 128.1, 127.5, 127.3, 127.1, 126.9, 120.5, 87.8, 67.7, 61.0, 58.9, 58.1, 51.9.

HRMS-ESI: calcd. for C₃₁H₃₁BrNO₃ [M + H]⁺: 544.1482 found: 544.1479

HPLC: (Chiral IA, λ = 254 nm, hexane/2-propanol = 100/1, Flow rate = 1.0 mL/min), t_{major} = 15.39 min, t_{minor} = 14.24 min.



(*S*)-**7a**

(*S*)-Methyl 3-((*tert*-butoxycarbonyl)amino)-2-hydroxy-2-phenylpropanoate

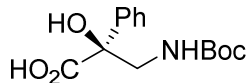
(*S*)-**7a**: 96% yield, 95% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.52 (m, 2H), 7.47 – 7.29 (m, 3H), 5.03 (s, 1H), 4.32 (s, 1H), 4.12 (d, *J* = 13.7 Hz, 1H), 3.79 (s, 3H), 3.46 (d, *J* = 13.9 Hz, 1H), 1.42 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 174.2, 156.3, 139.0, 128.4, 128.3, 125.6, 79.9, 78.9, 53.4, 48.6, 28.3.

HRMS-ESI: calcd. for C₁₅H₂₁NO₅Na [M + Na]⁺: 318.1317 found: 318.1317

HPLC: (Chiral OD-H, λ = 210 nm, hexane/2-propanol = 50/1, Flow rate = 1.0 mL/min), t_{major} = 20.03 min, t_{minor} = 22.11 min.



(*S*)-**8a**

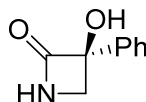
(*S*)-3-((*tert*-butoxycarbonyl) amino)-2-hydroxy-2-phenylpropanoic acid

(*S*)-**8a**: 99% yield, 95% ee

¹H NMR (400 MHz, CDCl₃) δ 7.68 (M, 2H), 7.35 (M, 3H), 5.26 (s, 1H), 4.06 – 3.76 (m, 1H), 3.73 – 3.34 (m, 1H), 1.43 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 174.3, 159.1, 138.0, 128.5, 125.5, 81.6, 80.8, 49.8, 28.2.

HRMS-ESI: calcd. for C₁₄H₁₉NO₅Na [M + Na]⁺: 304.1161 found: 304.1146.



(*S*)-**10a**

(*S*)-3-hydroxy-3-phenylazetidin-2-one

(*S*)-**10a**: 56% yield, 93% ee.

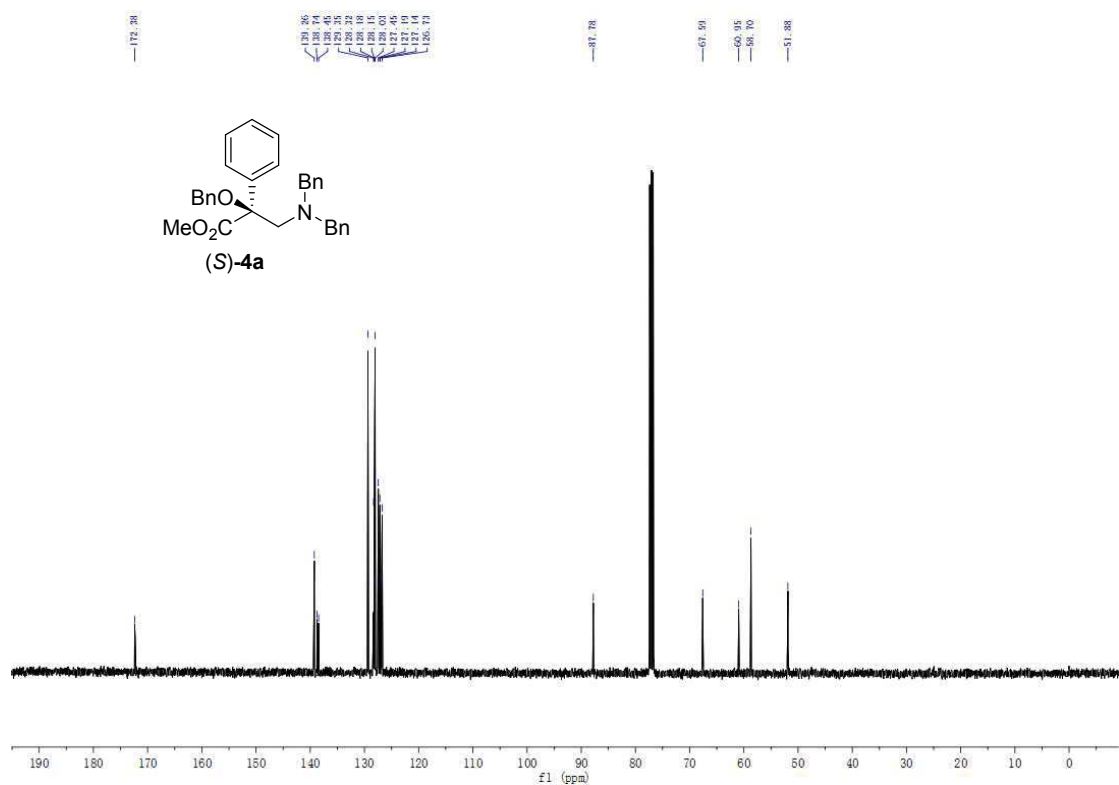
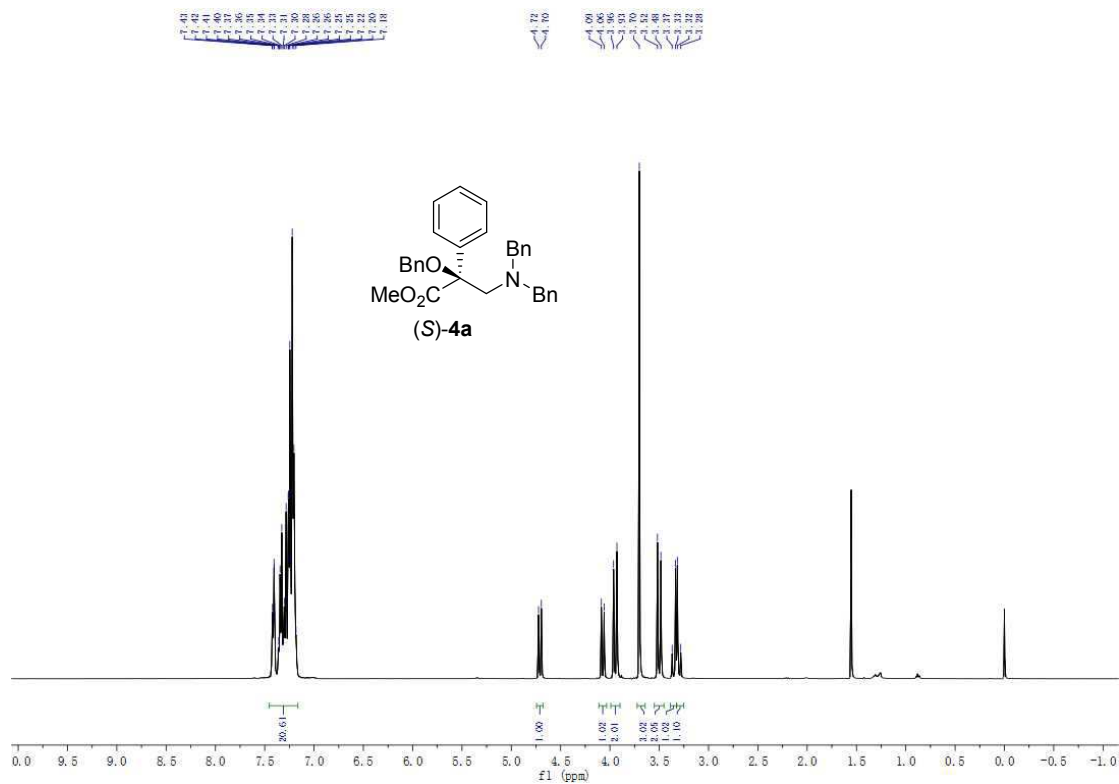
¹H NMR (400 MHz, Acetone) δ 7.47 – 7.41 (m, 2H), 7.29 – 7.14 (m, 4H), 5.55 (s, 1H), 3.43 (s, 2H).

¹³C NMR (100 MHz, Acetone) δ 170.9, 140.9, 129.1, 128.6, 126.3, 88.5, 54.4.

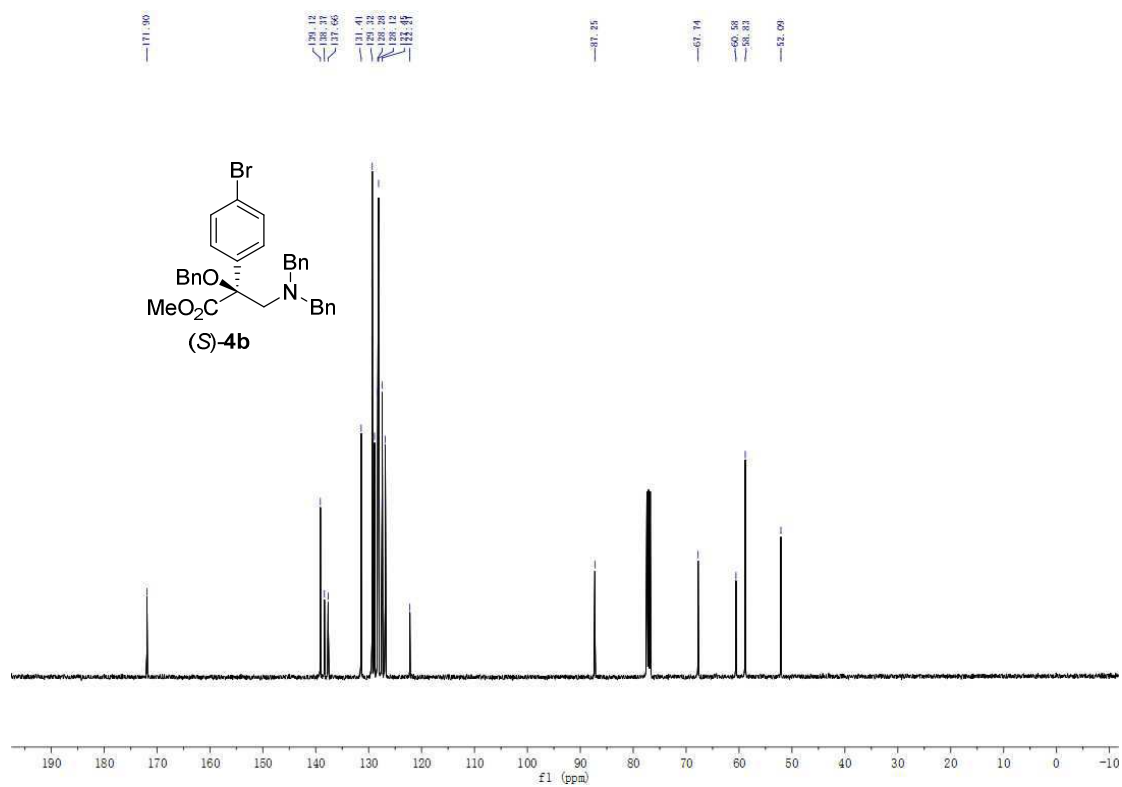
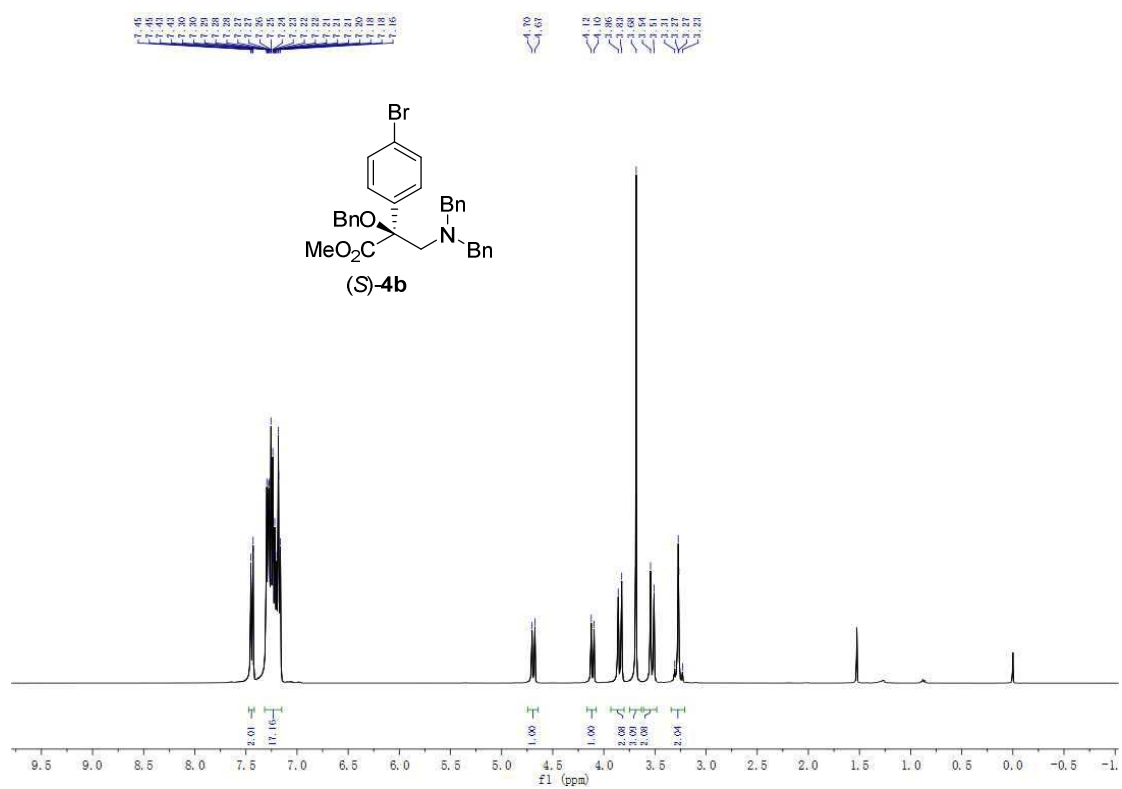
HPLC: (Chiral OD-H, λ = 210 nm, hexane/2-propanol = 10/1, Flow rate = 1.0 mL/min), t_{major} = 14.50 min, t_{minor} = 13.06 min.

10. NMR spectra of products

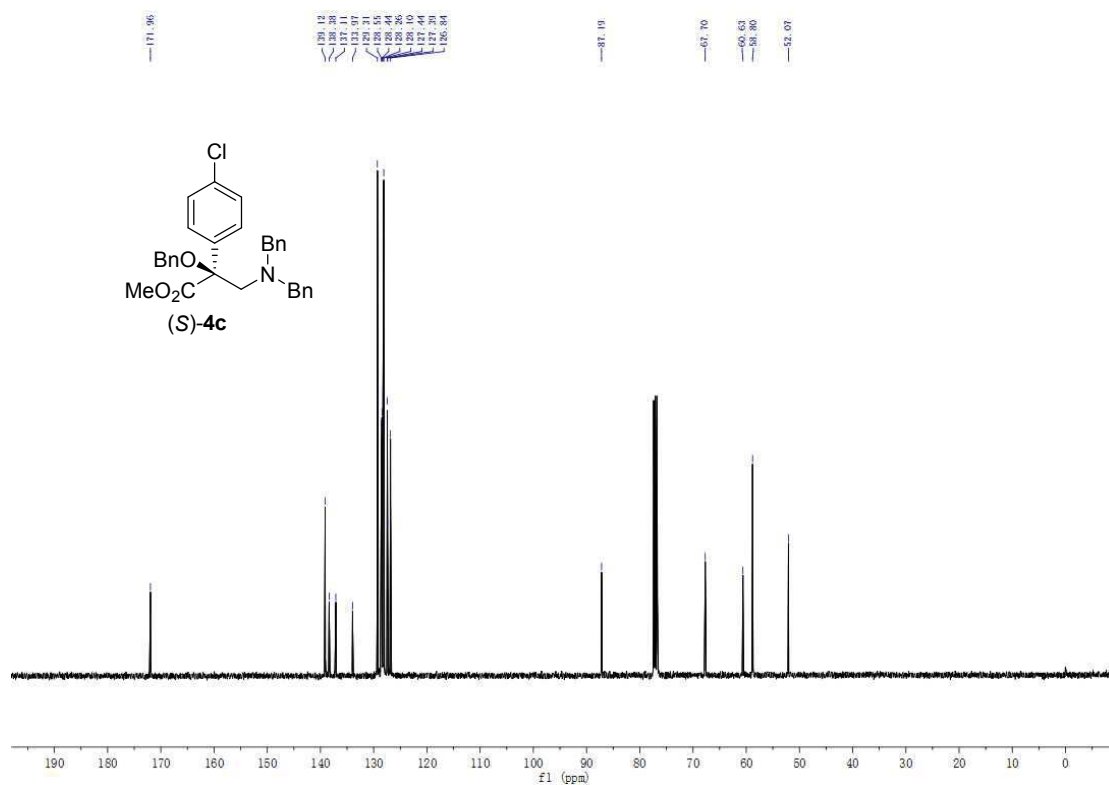
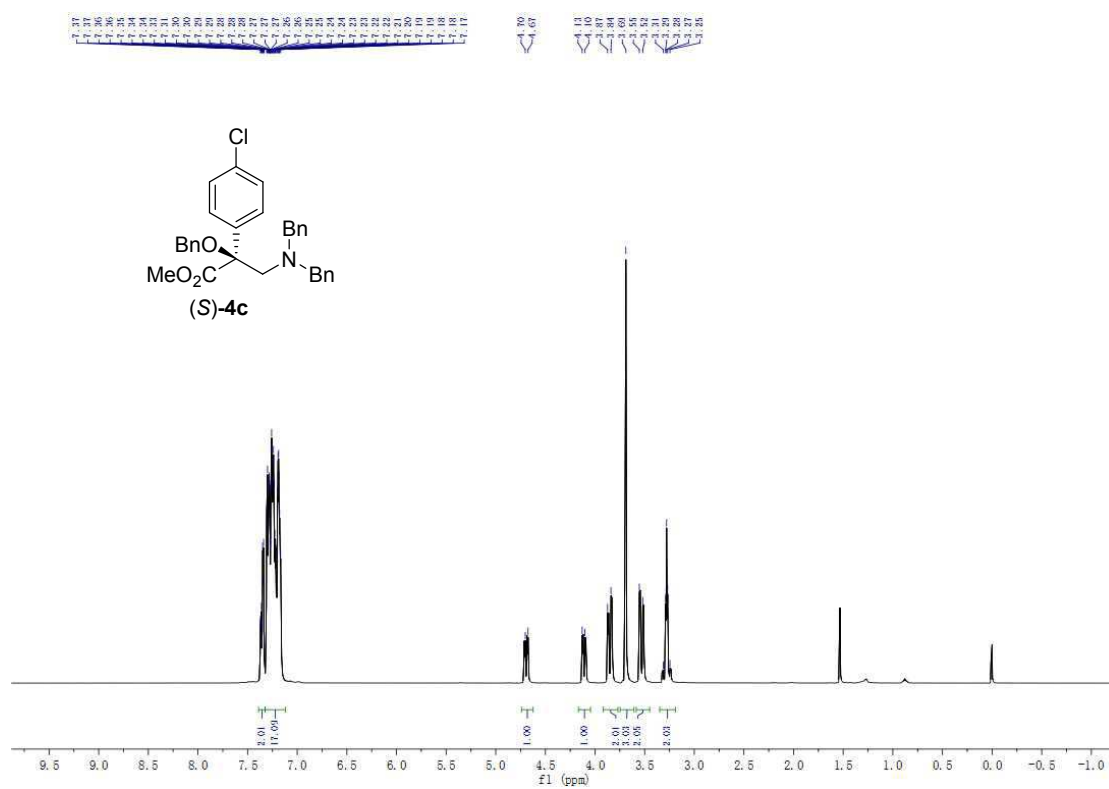
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4a



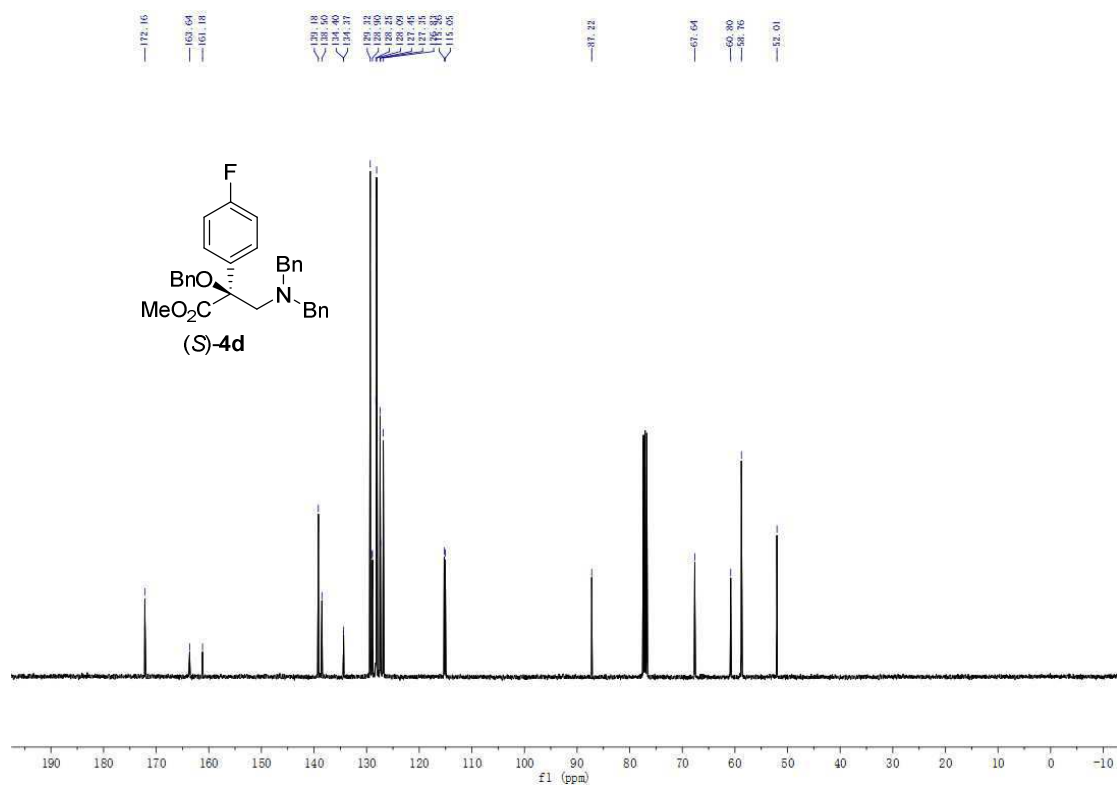
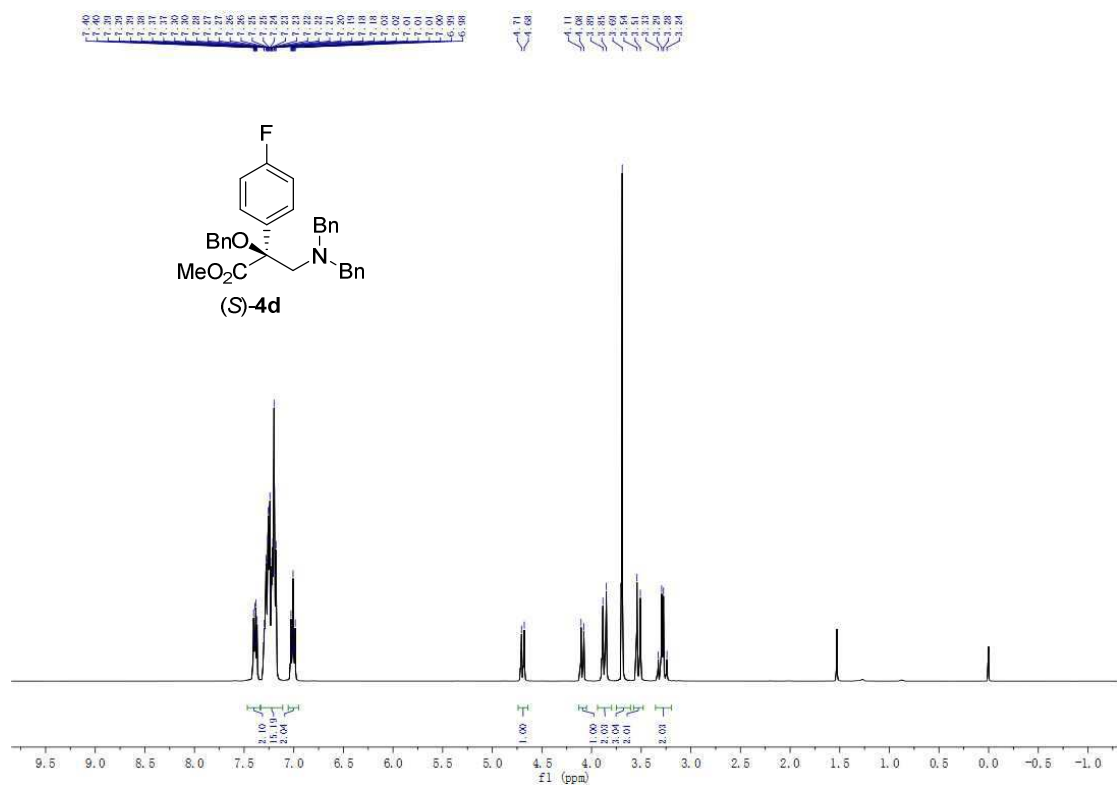
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (*S*)-**4b**



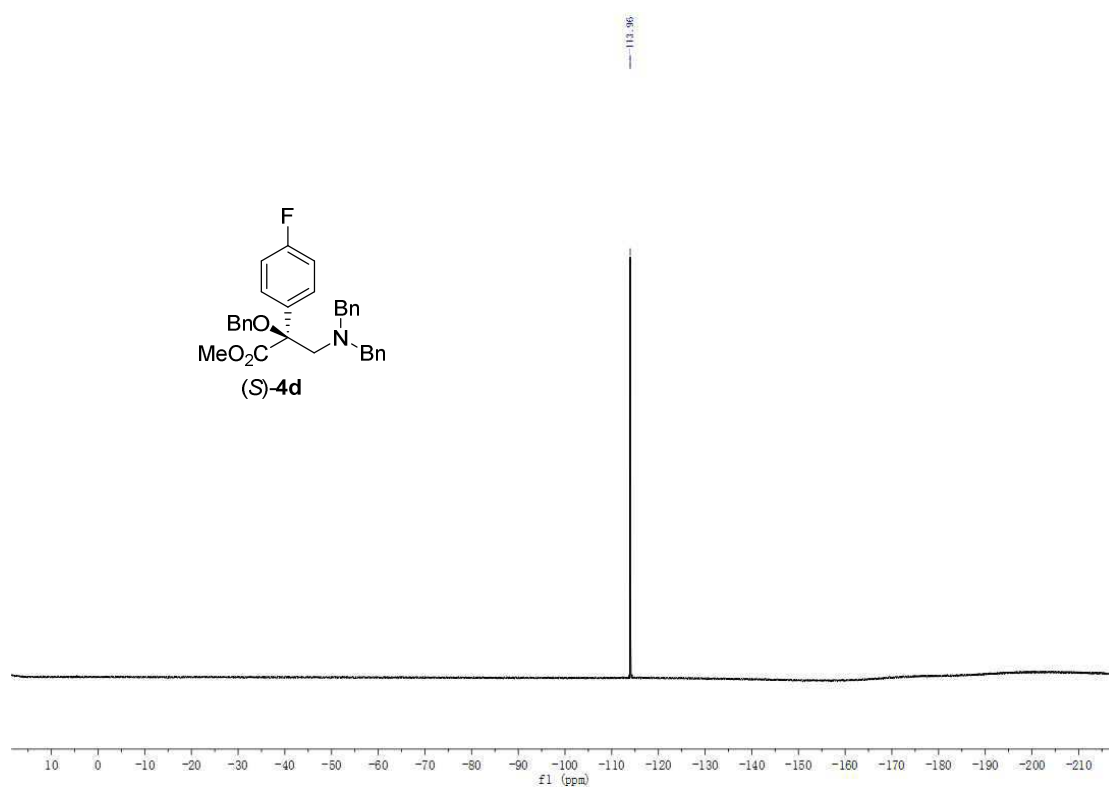
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4c



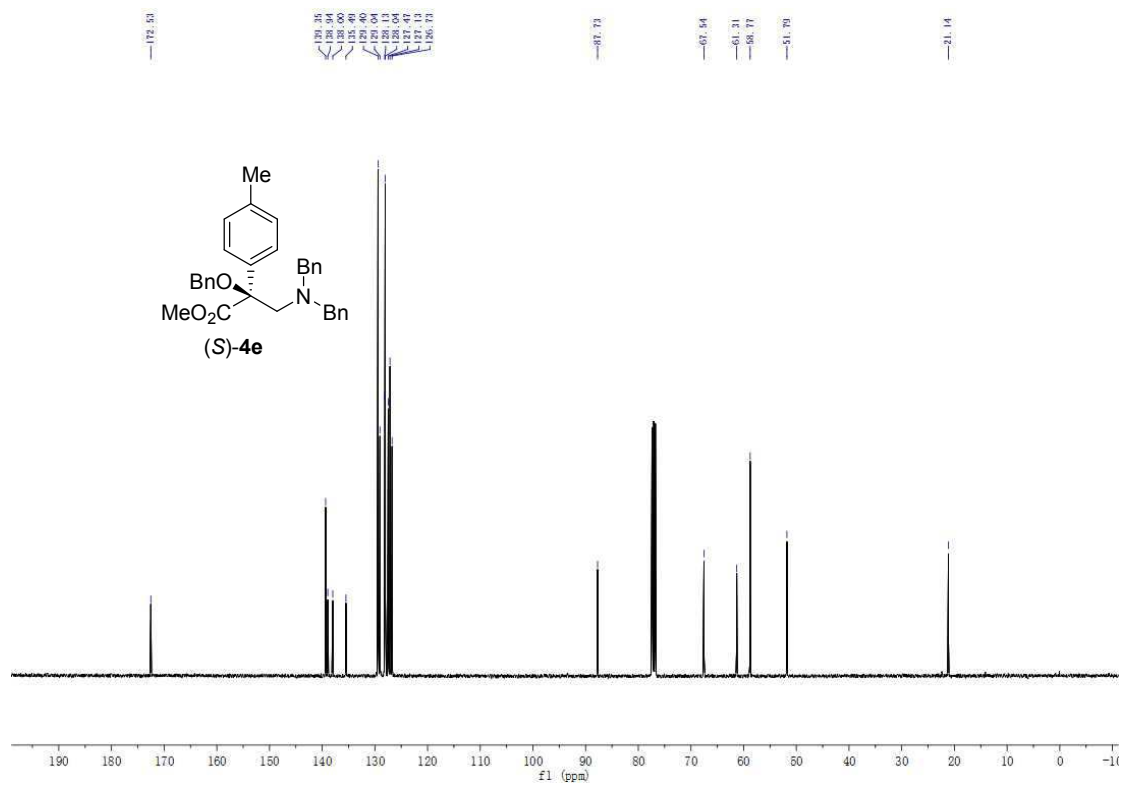
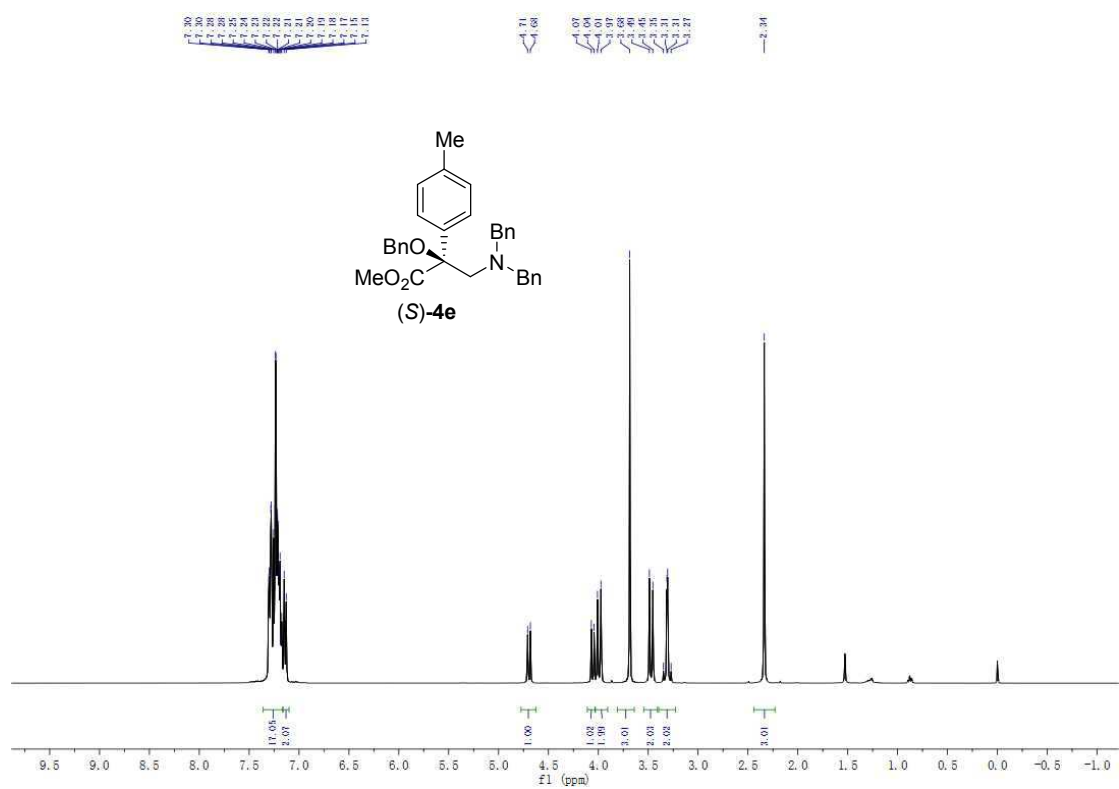
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (*S*)-4d



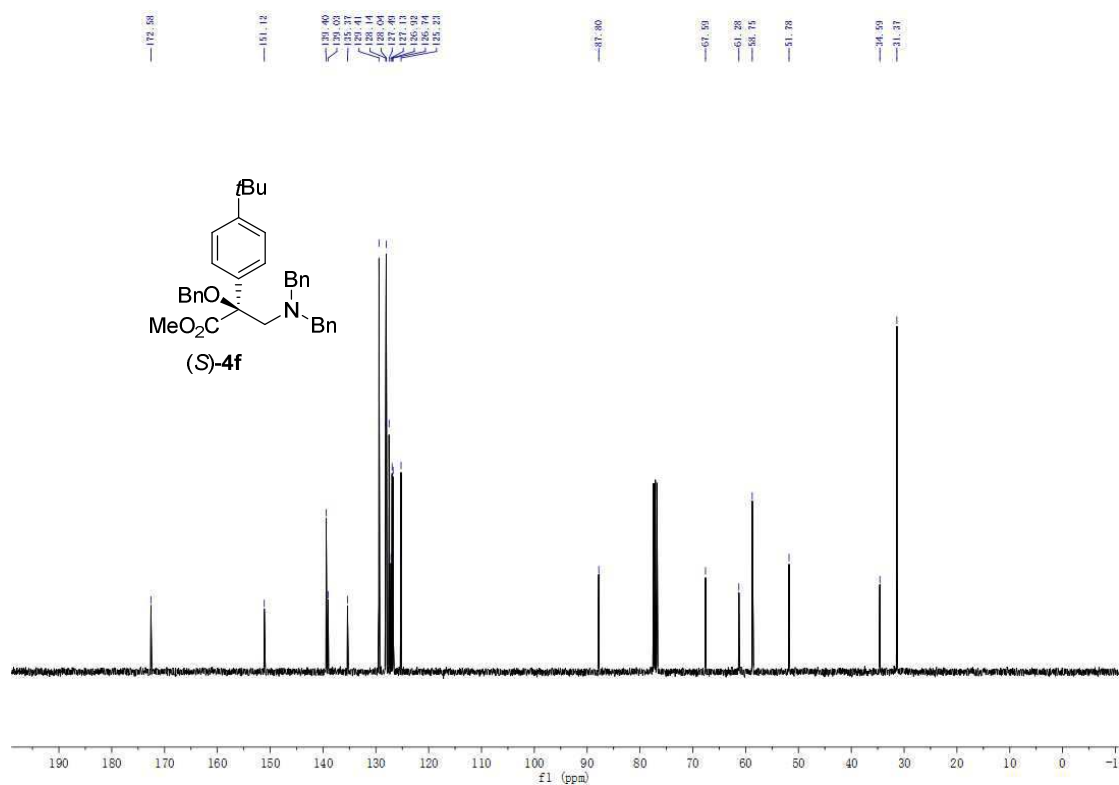
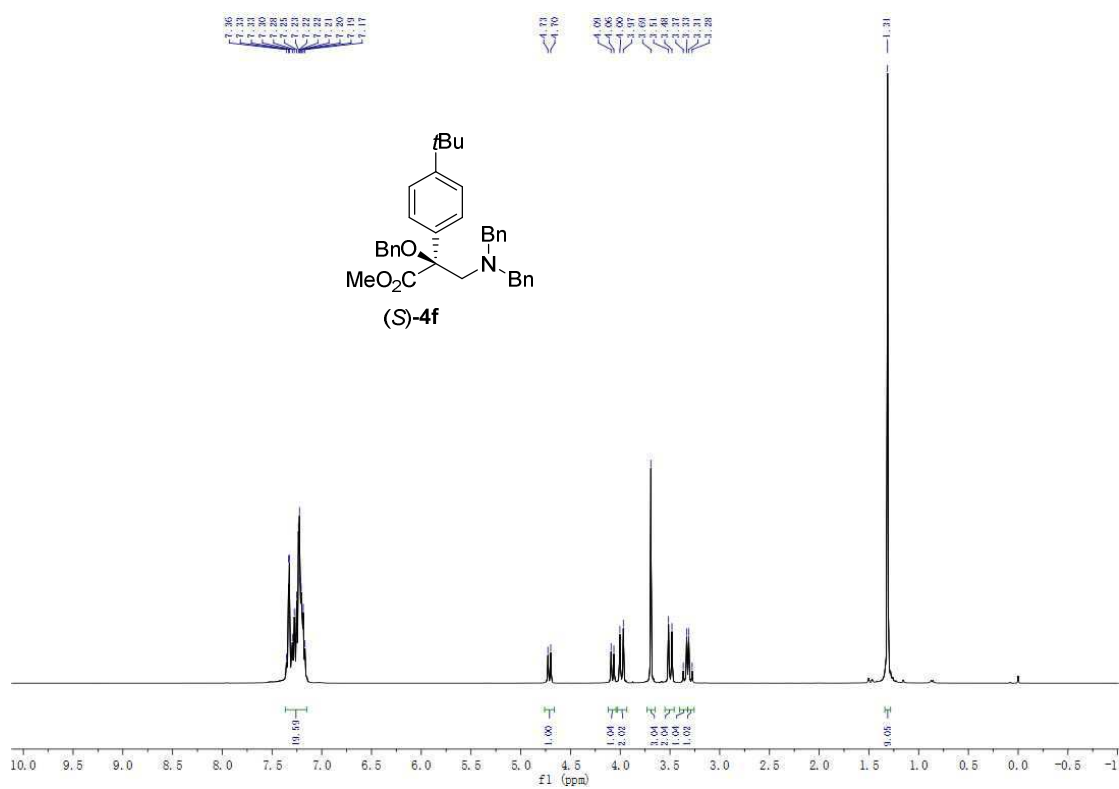
^{19}F NMR (376 MHz, CDCl_3) spectra for (S)-4d



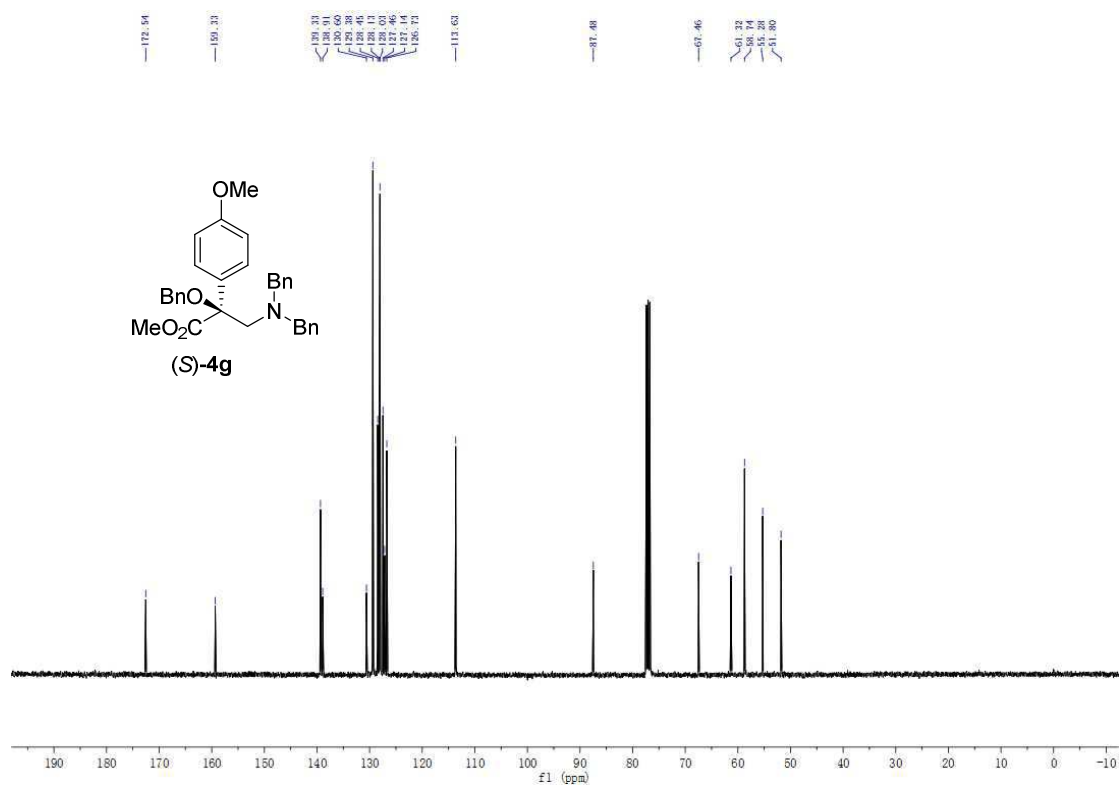
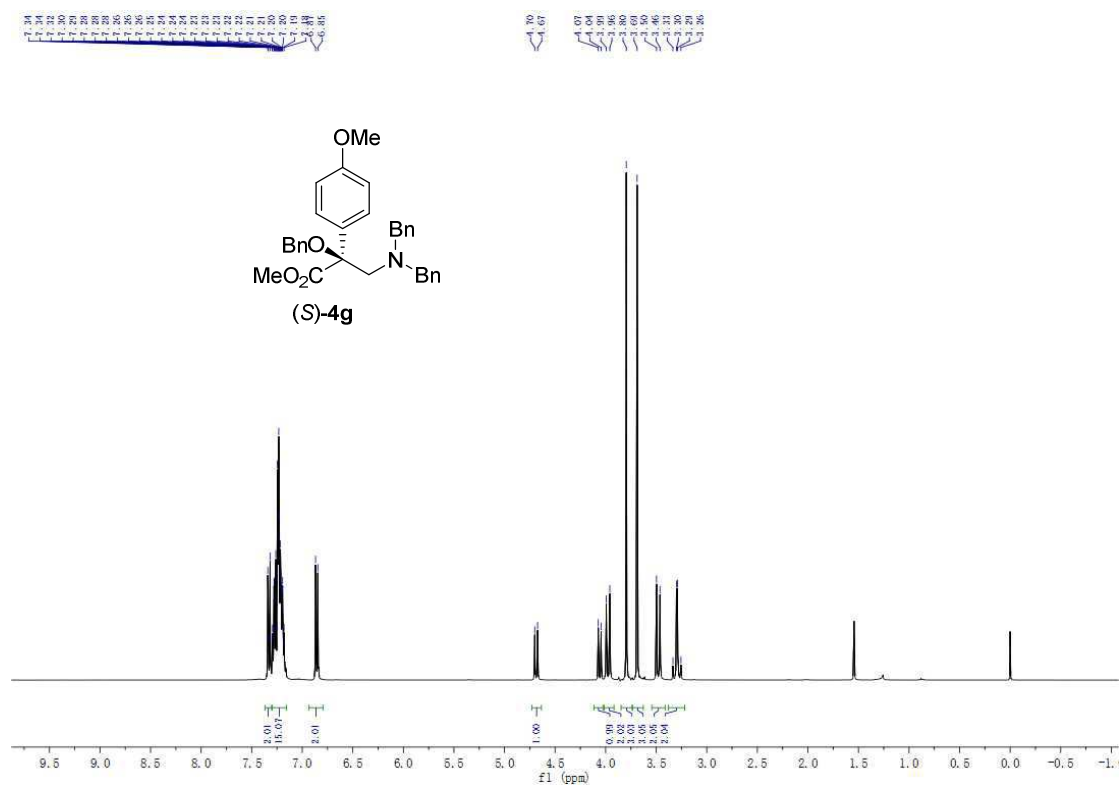
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4e



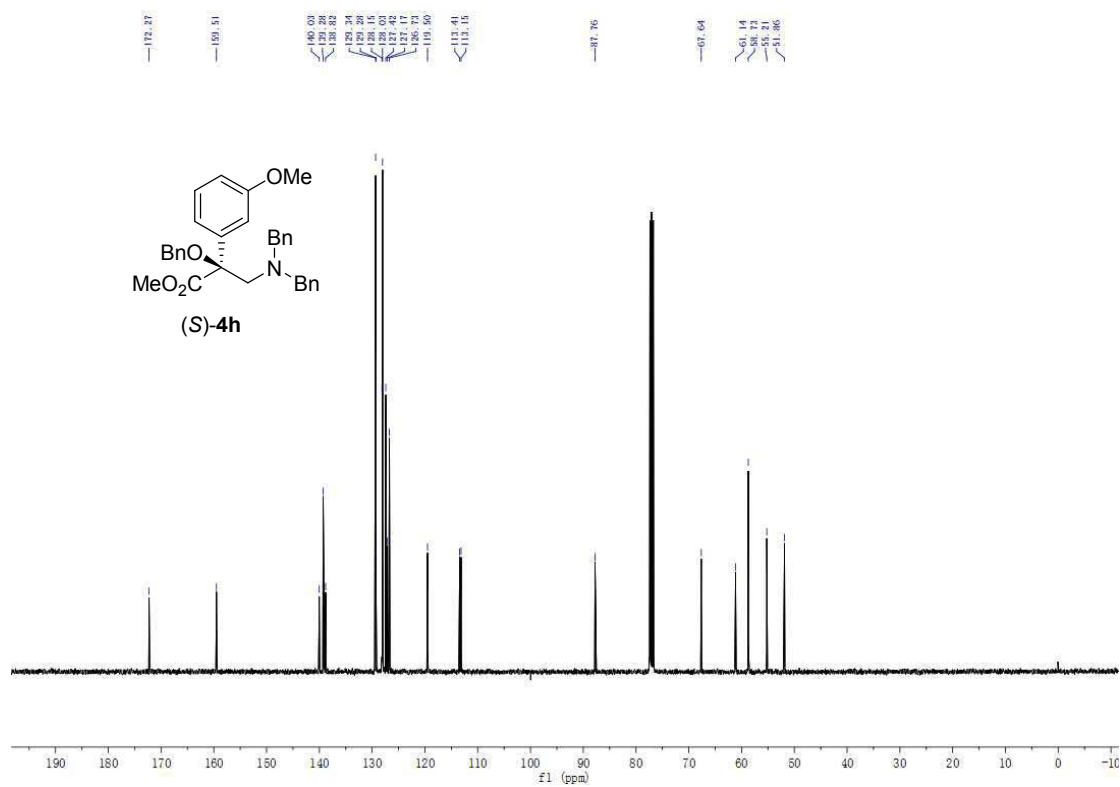
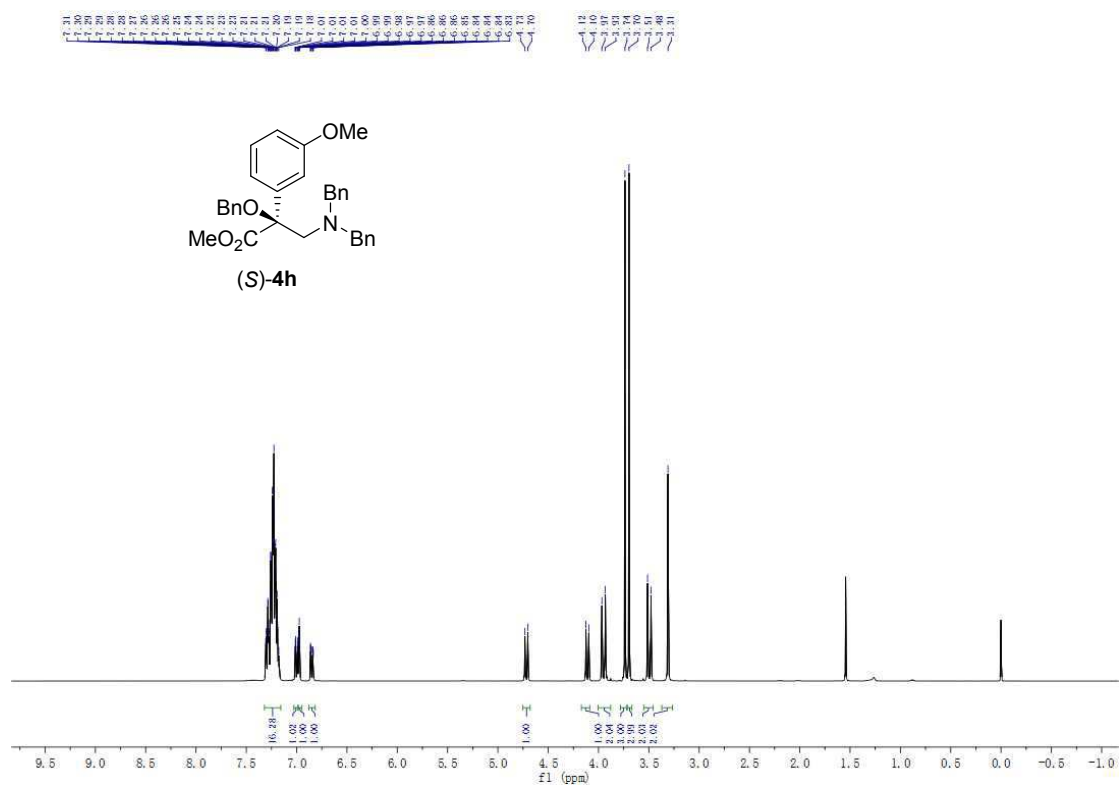
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4f



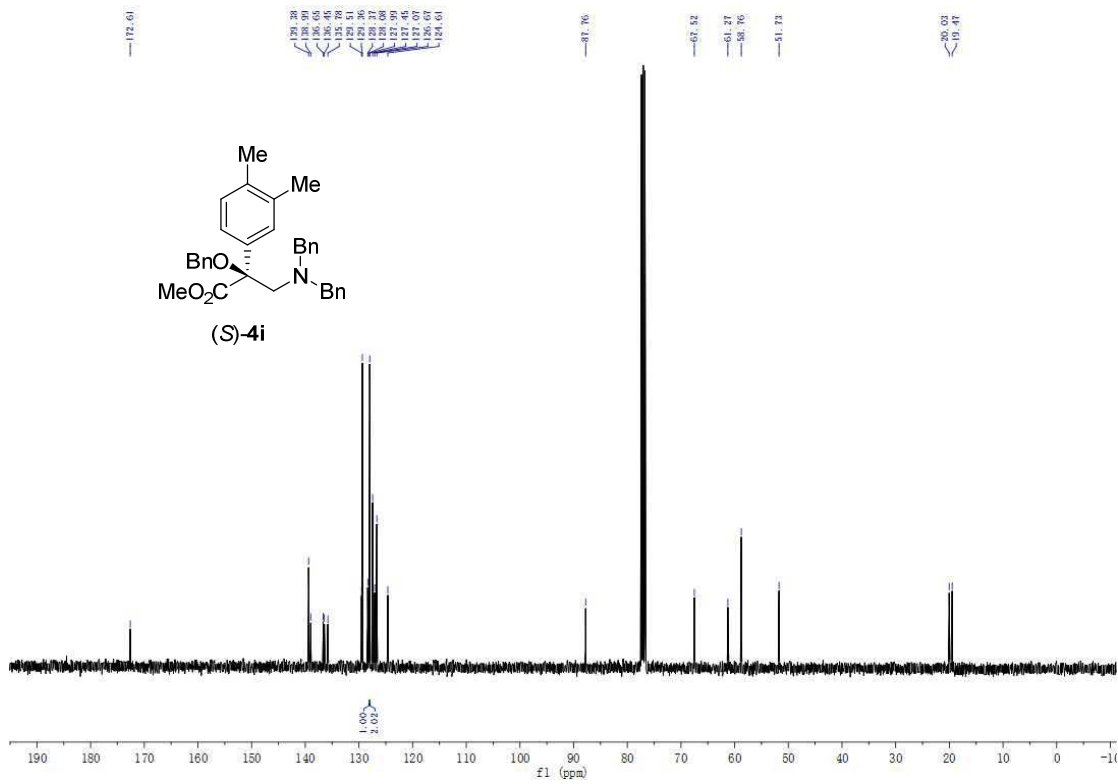
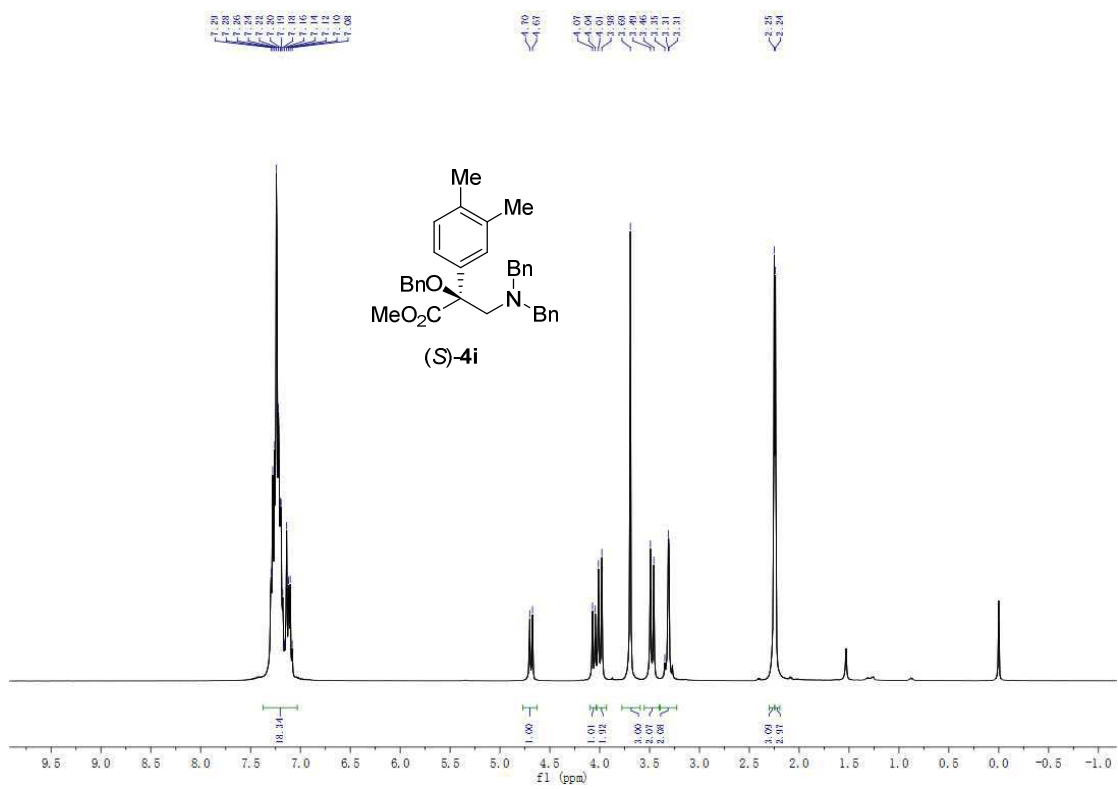
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4g



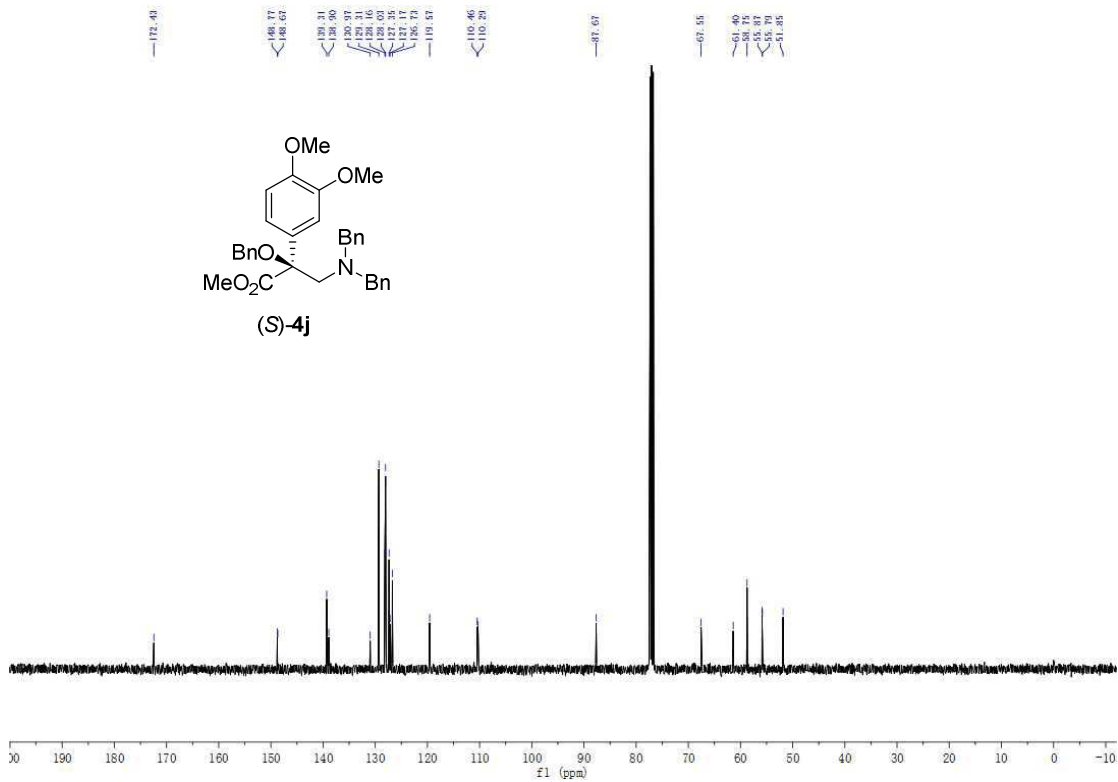
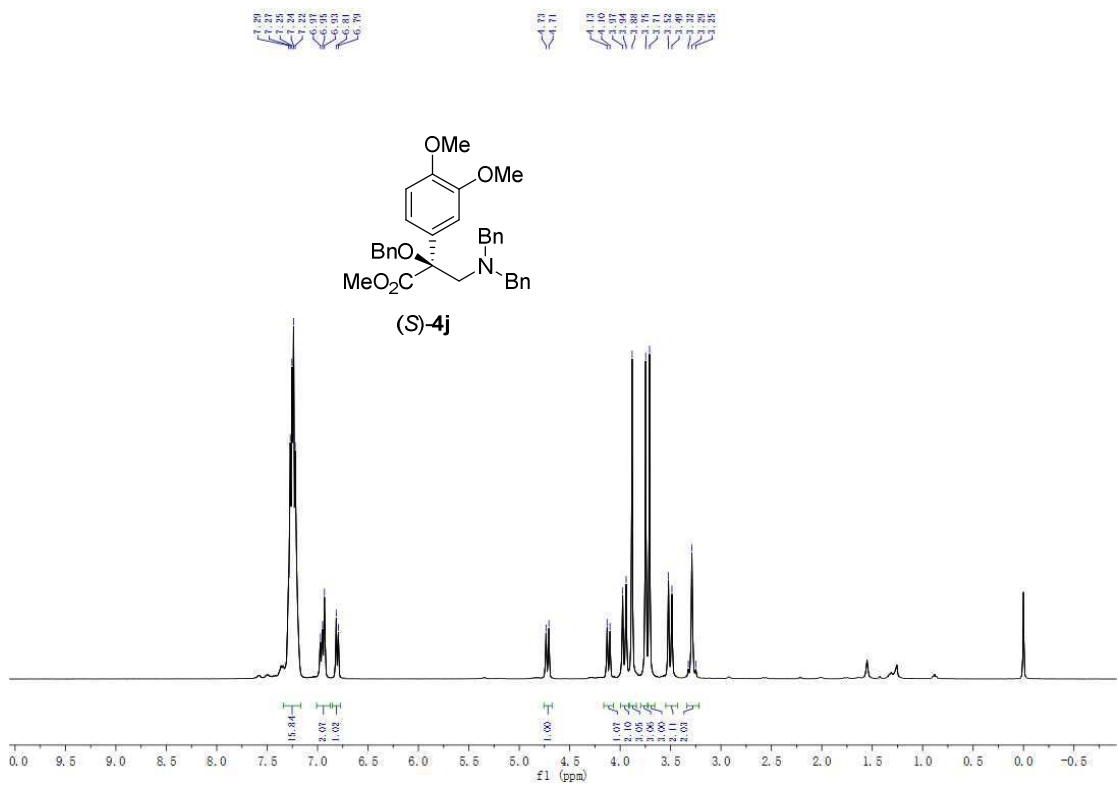
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4h



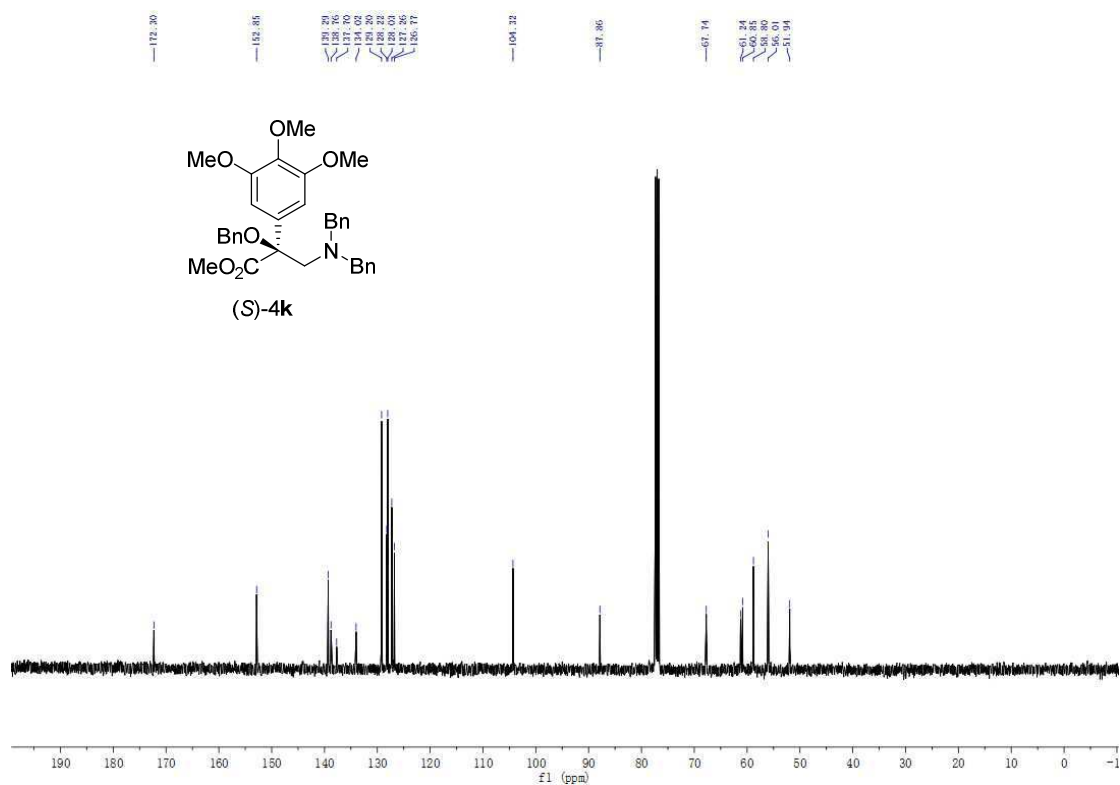
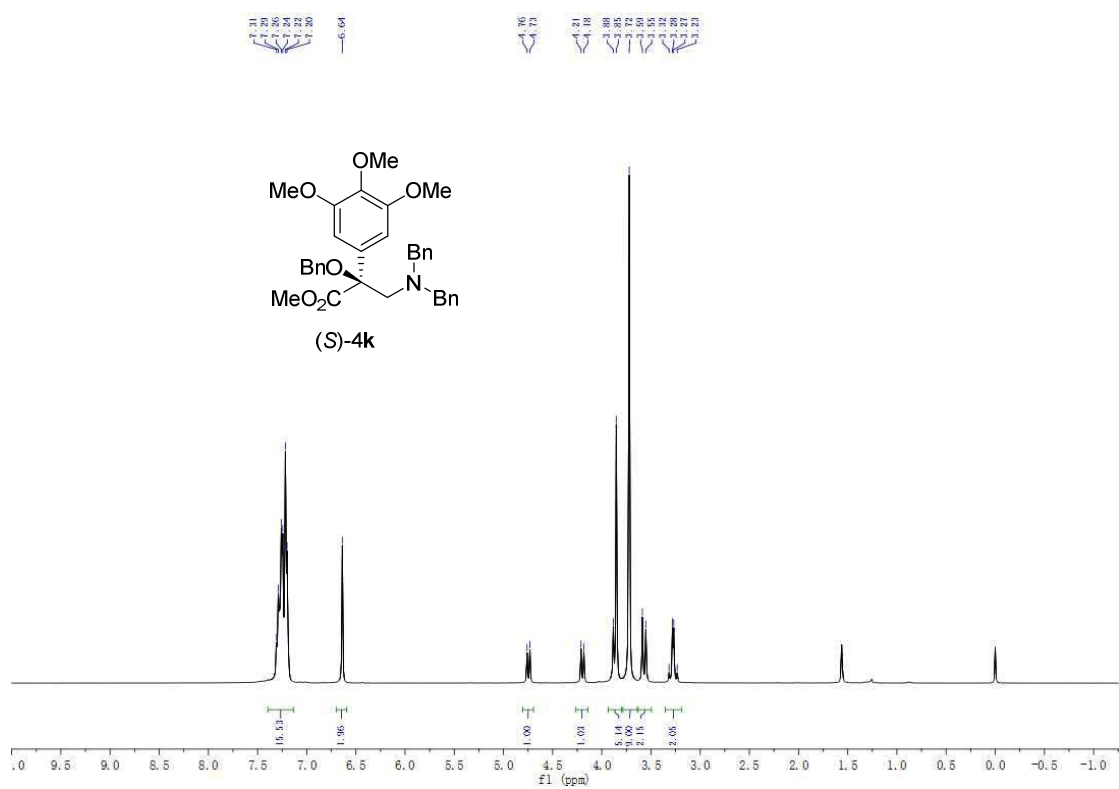
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4i



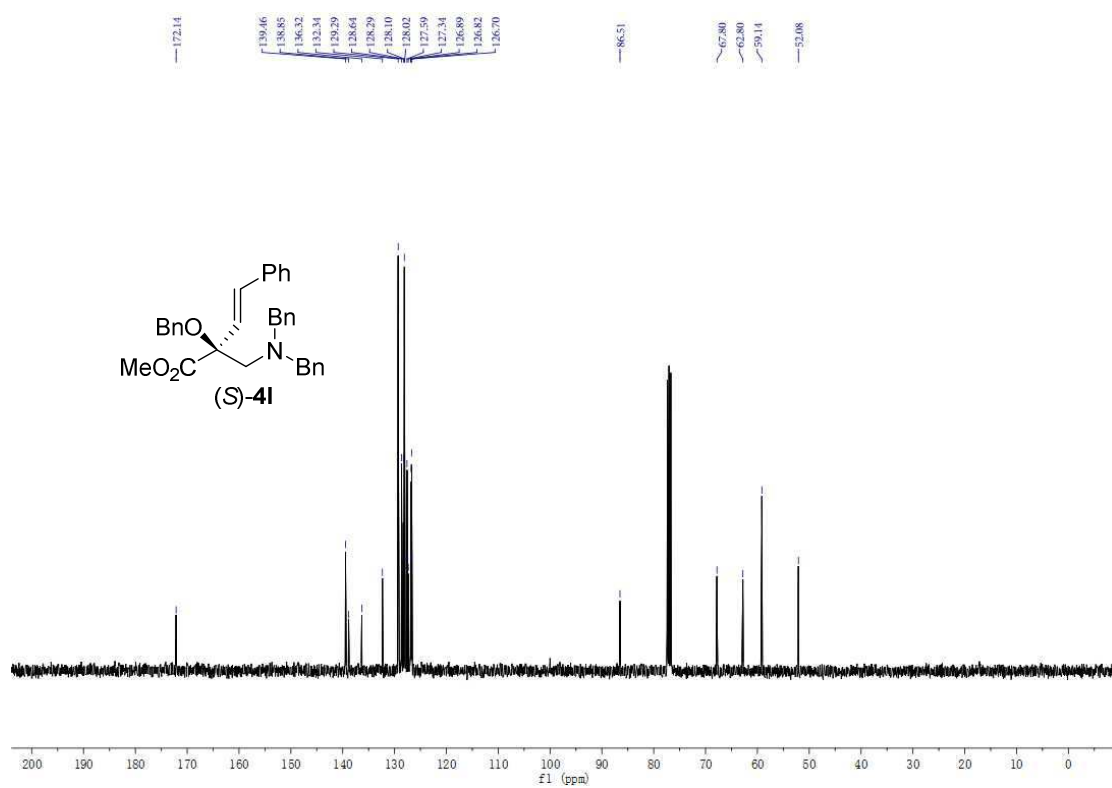
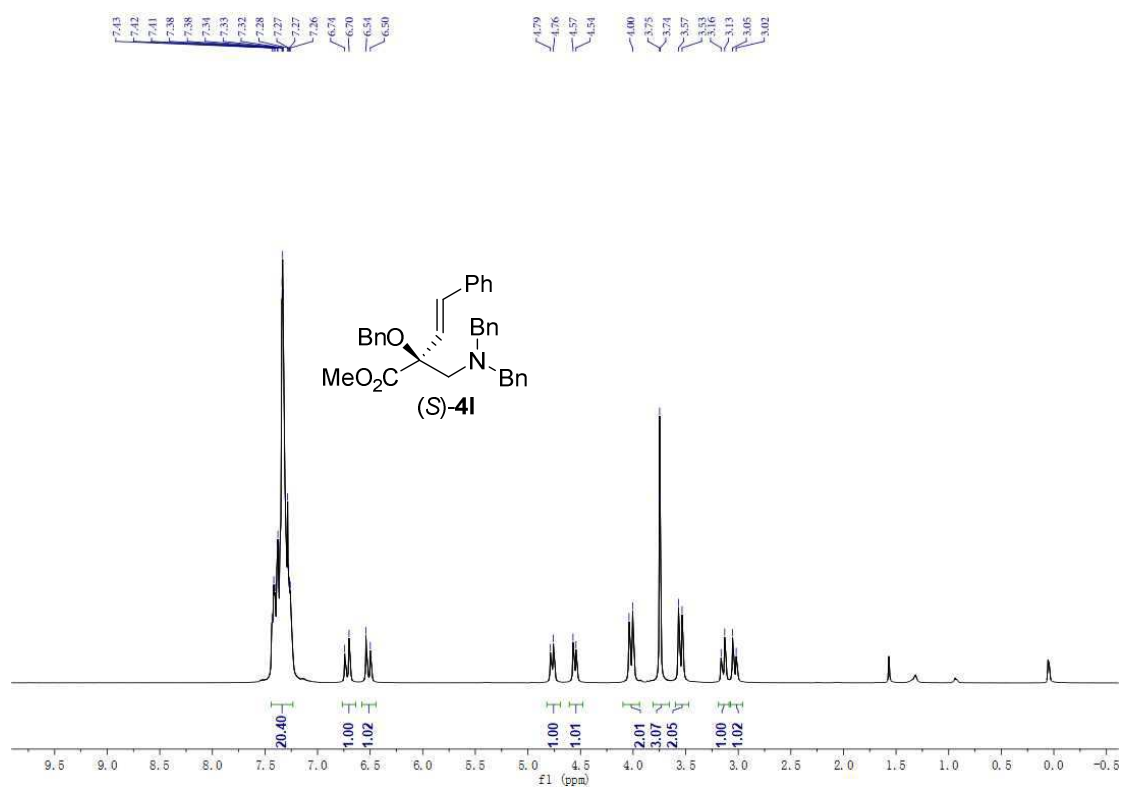
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4j



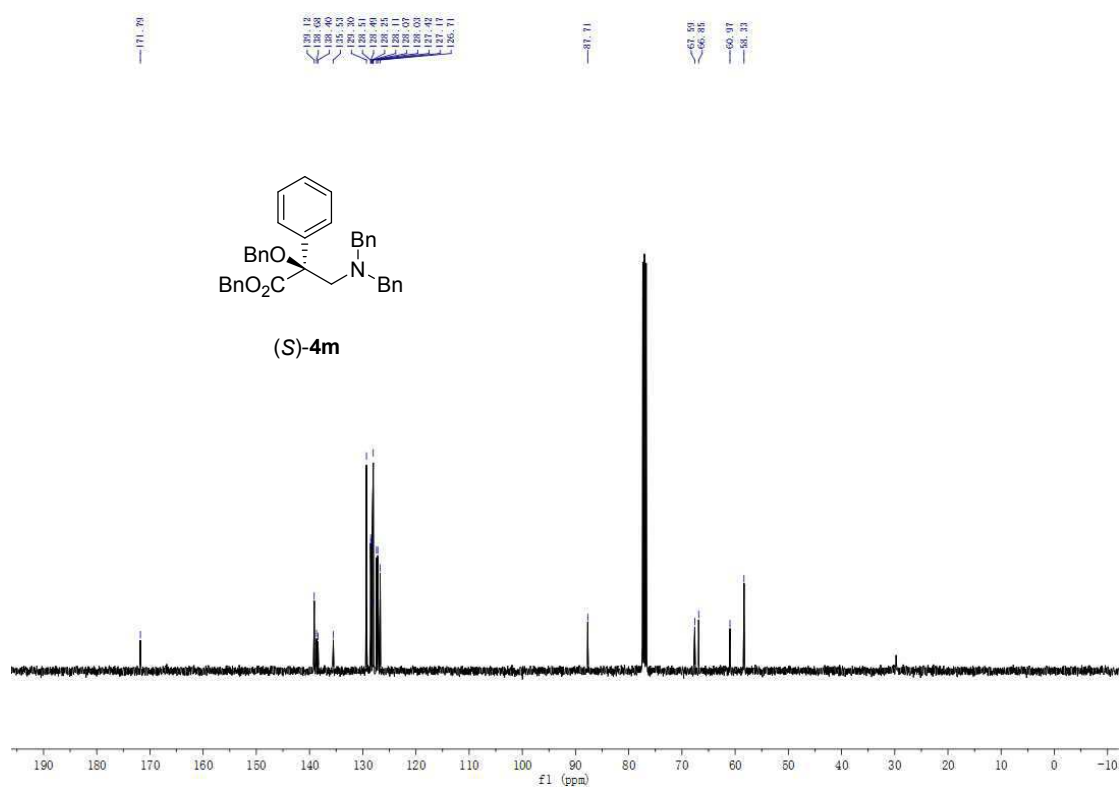
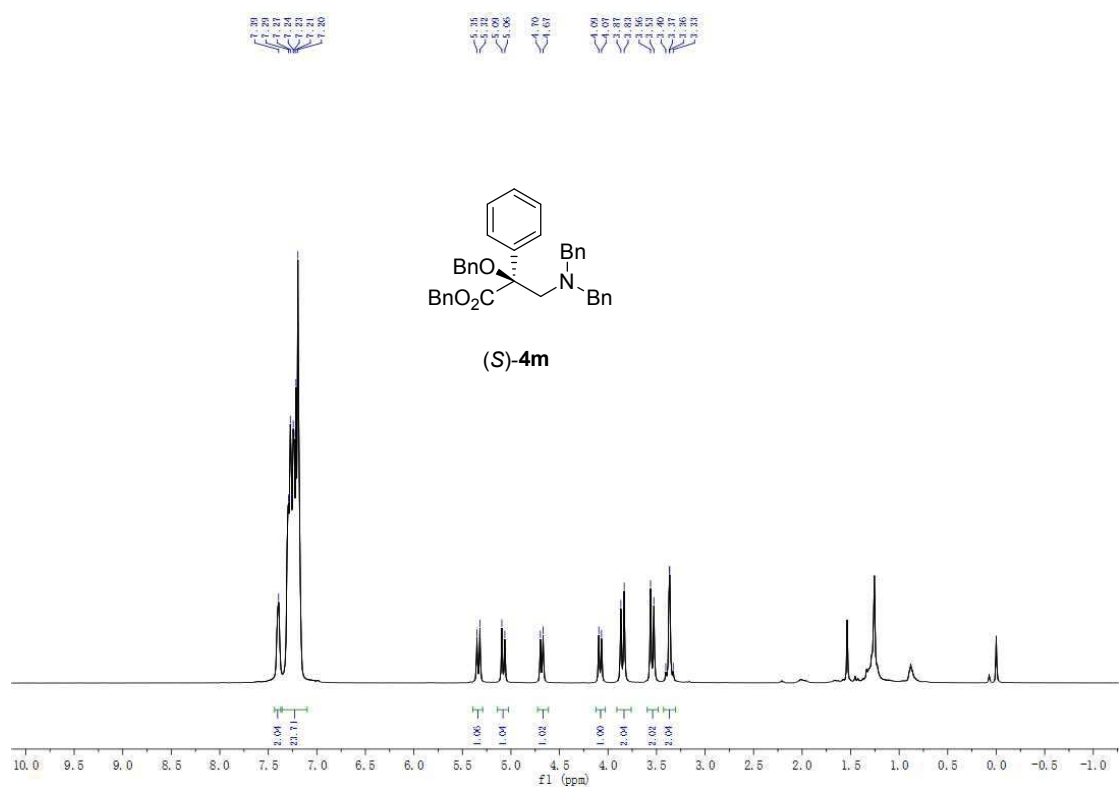
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4k



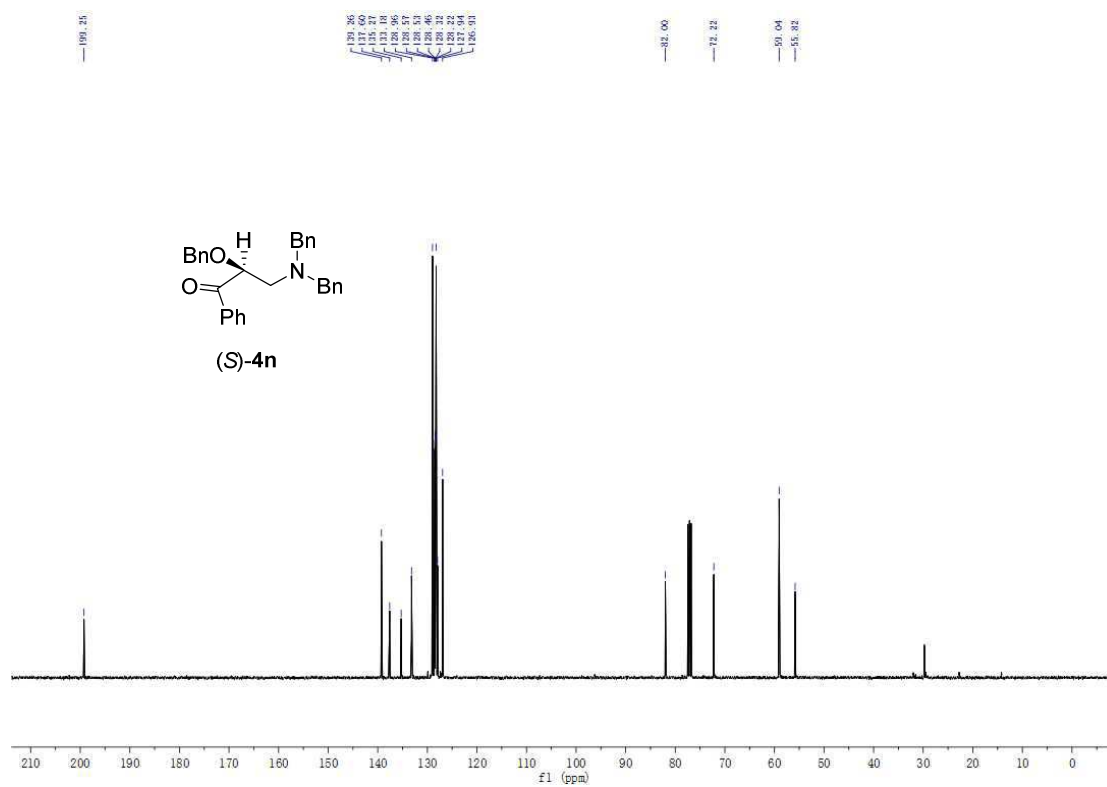
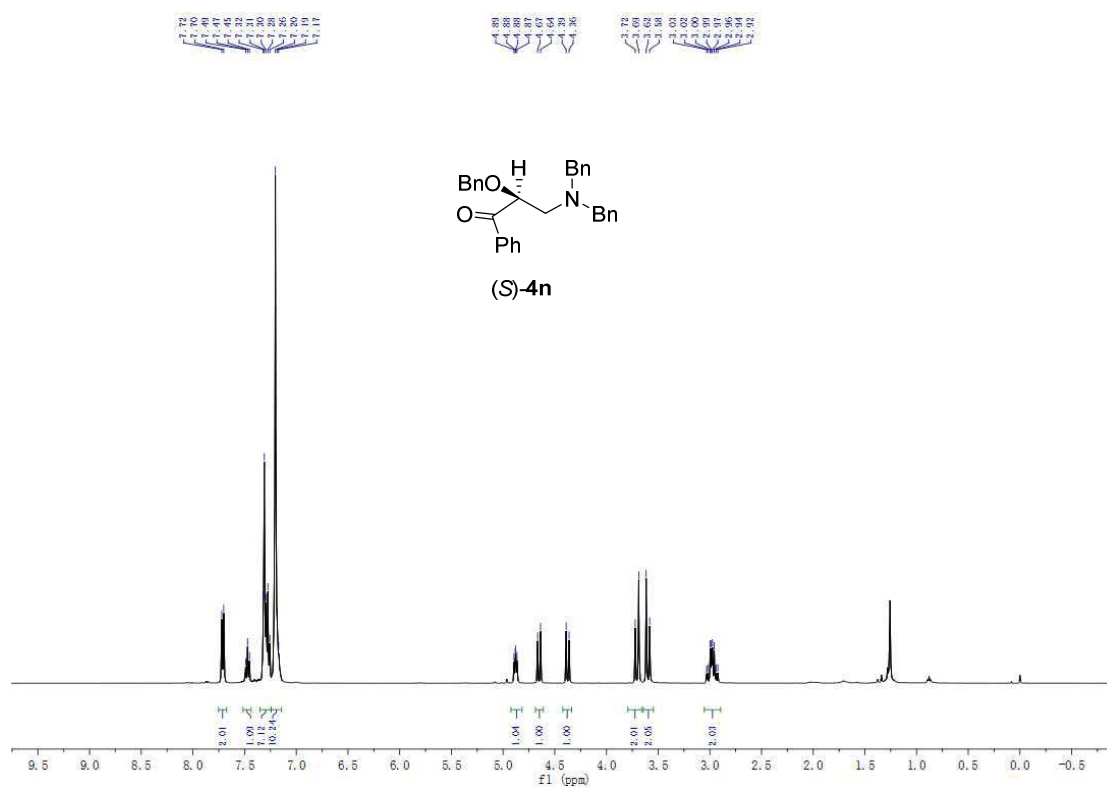
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4I



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4m



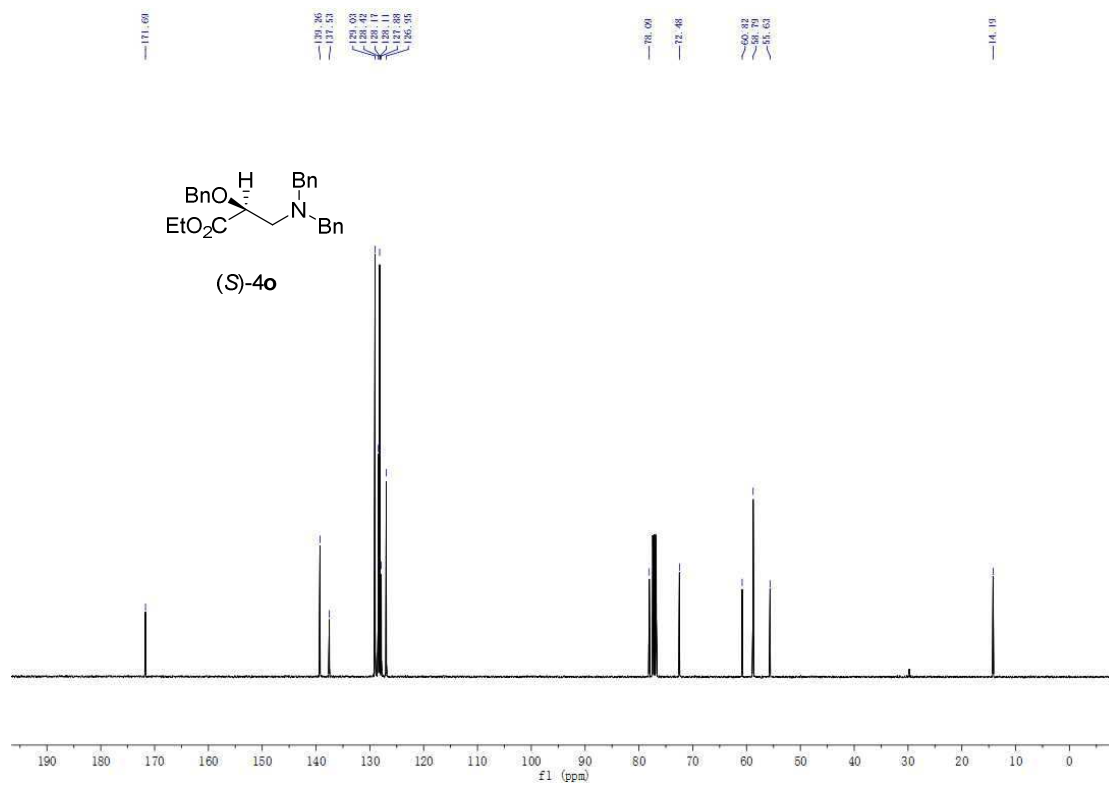
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4n



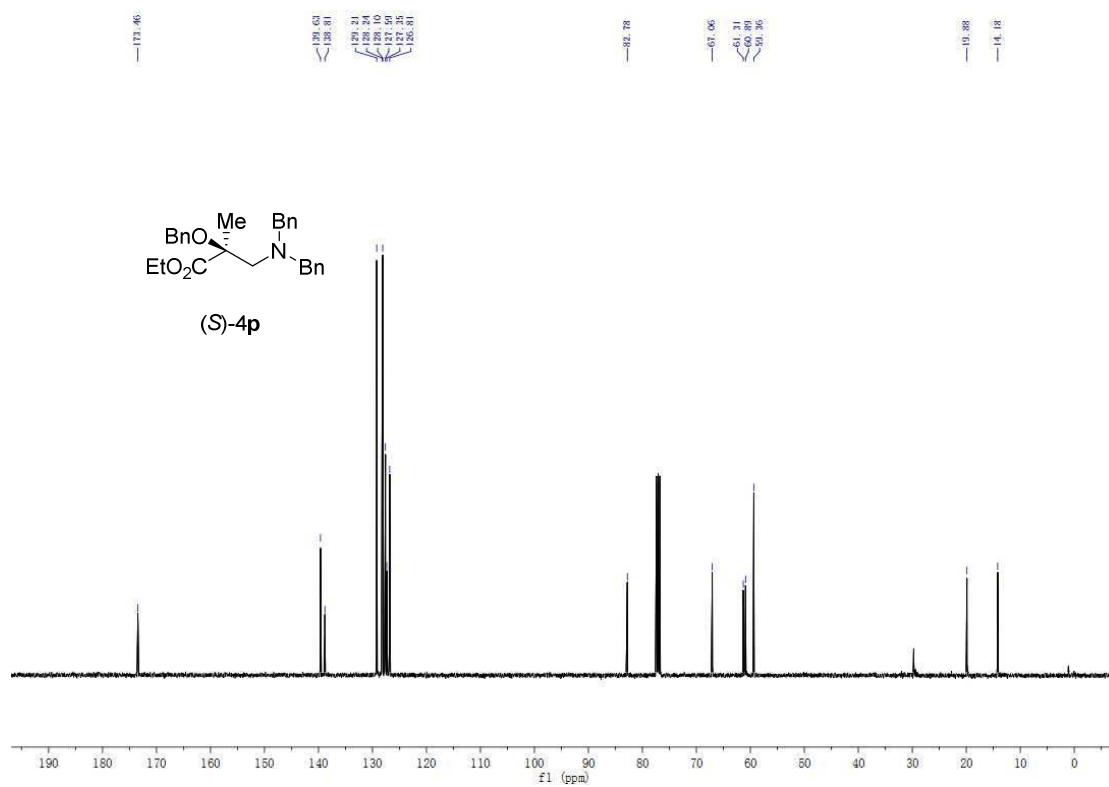
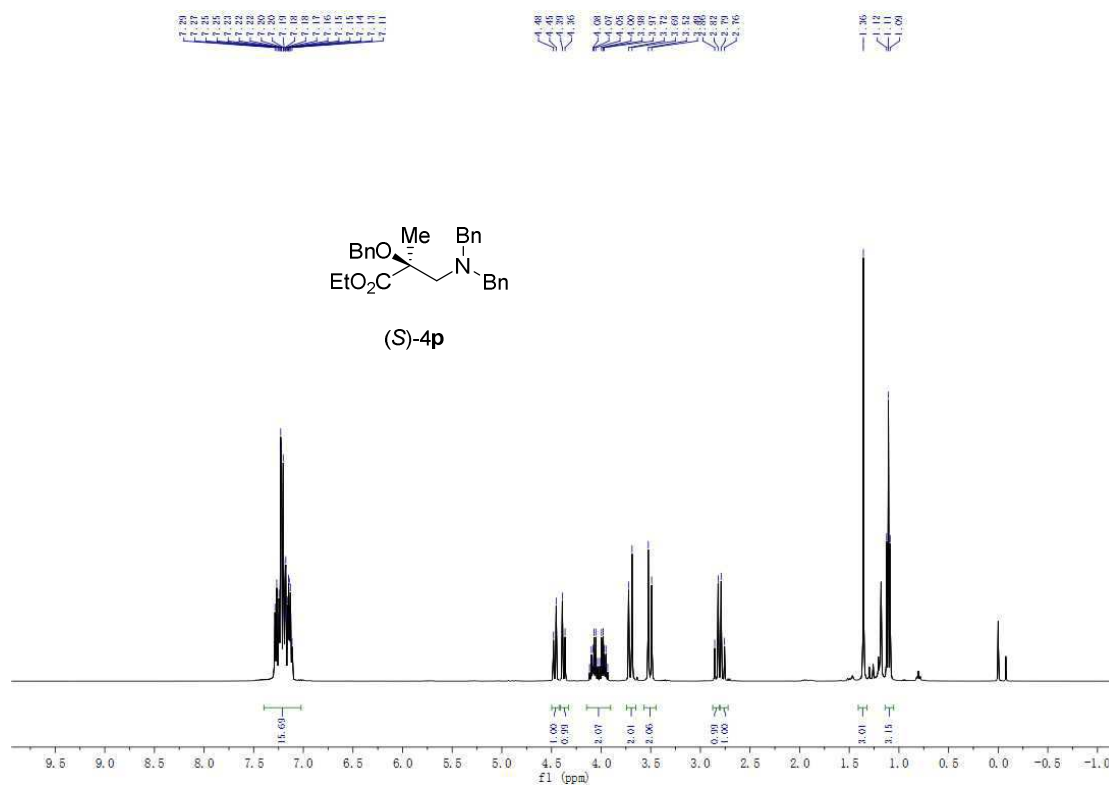
(S)-4o

¹H NMR spectrum (CDCl₃) of (S)-4o. The spectrum shows peaks corresponding to the structure, with integration values indicated below the peaks.

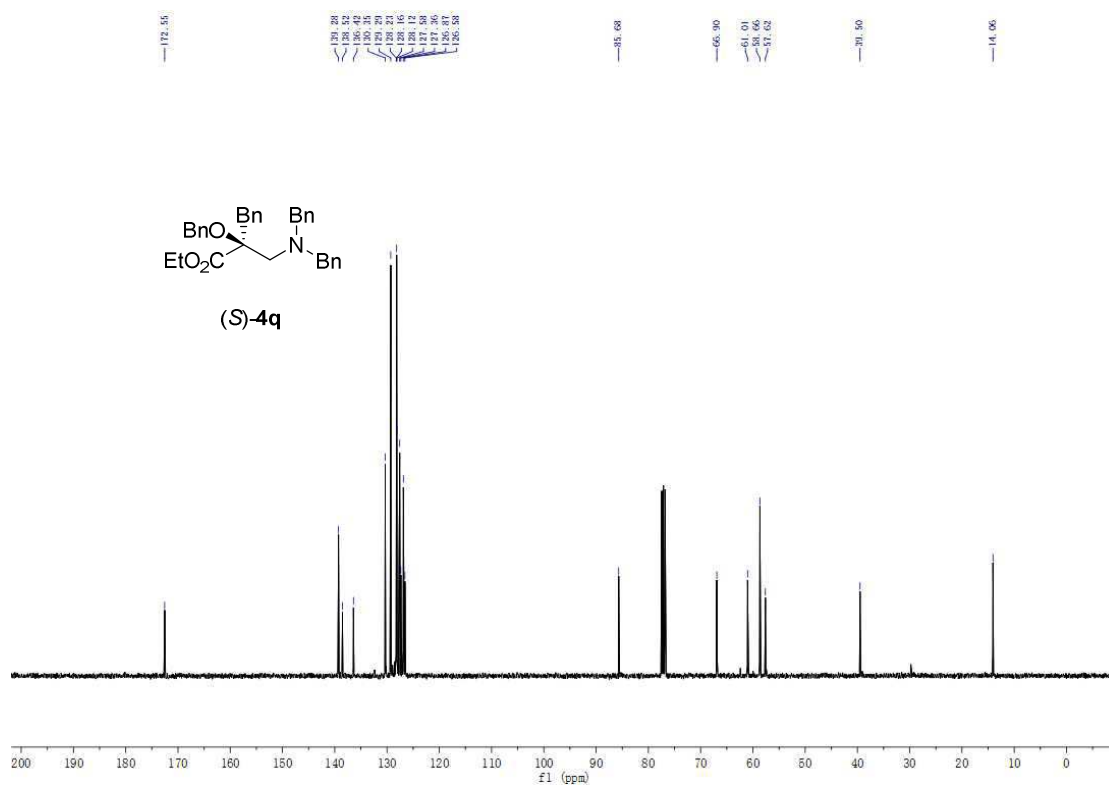
Chemical Shift (ppm)	Integration
7.1 - 7.5	15.21
4.4 - 4.5	1.00
4.2 - 4.3	0.98
4.0 - 4.1	2.99
3.6 - 3.7	3.05
3.4 - 3.5	2.01
3.1	1.00
3.7	3.02
1.3	2.00
1.1	3.02



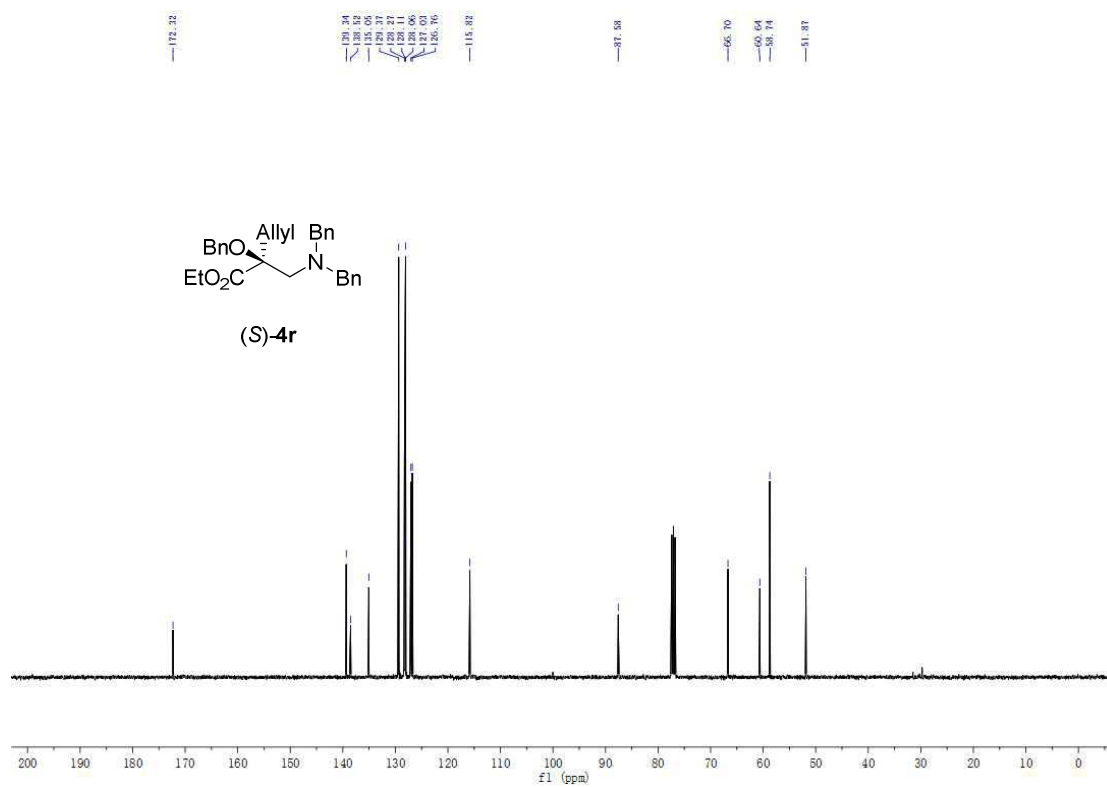
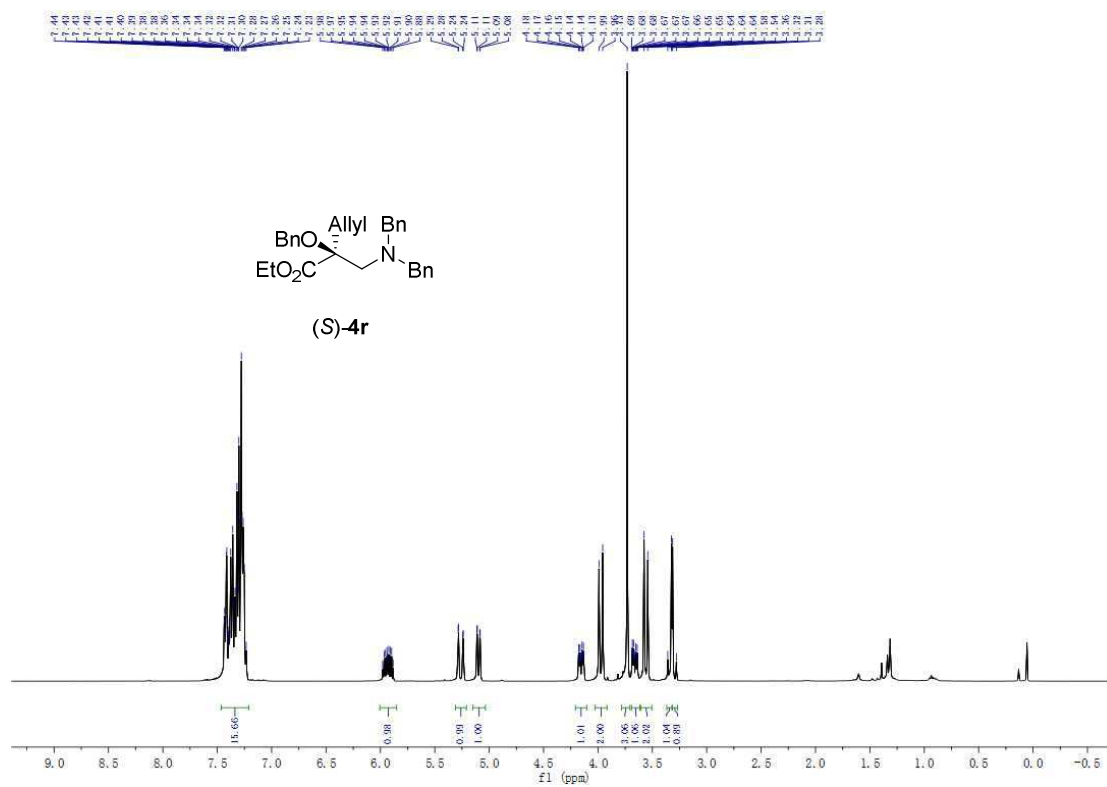
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4p



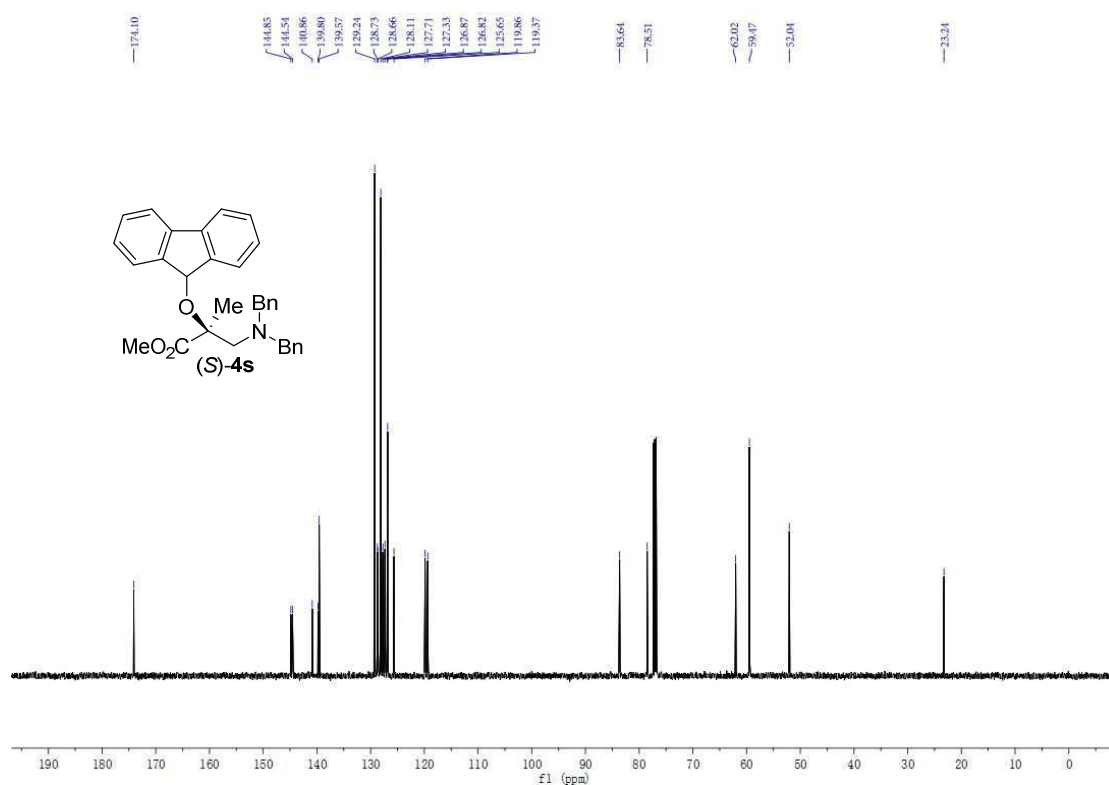
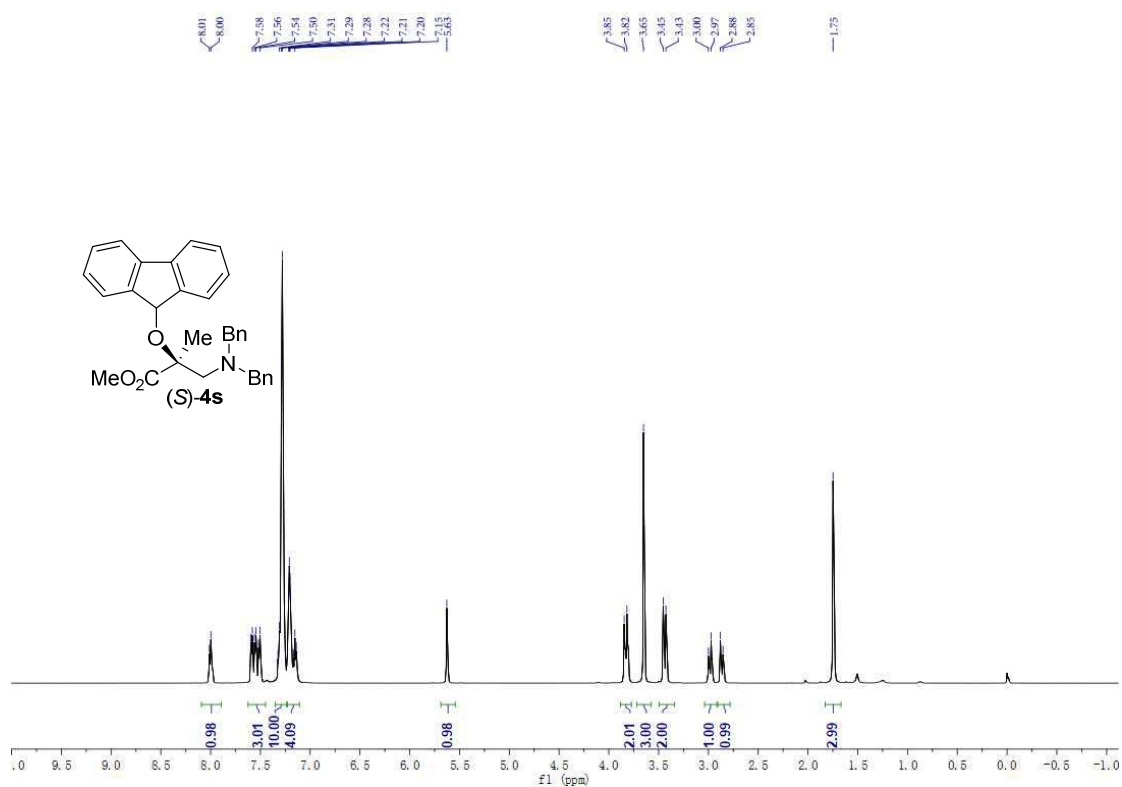
(S)-4q



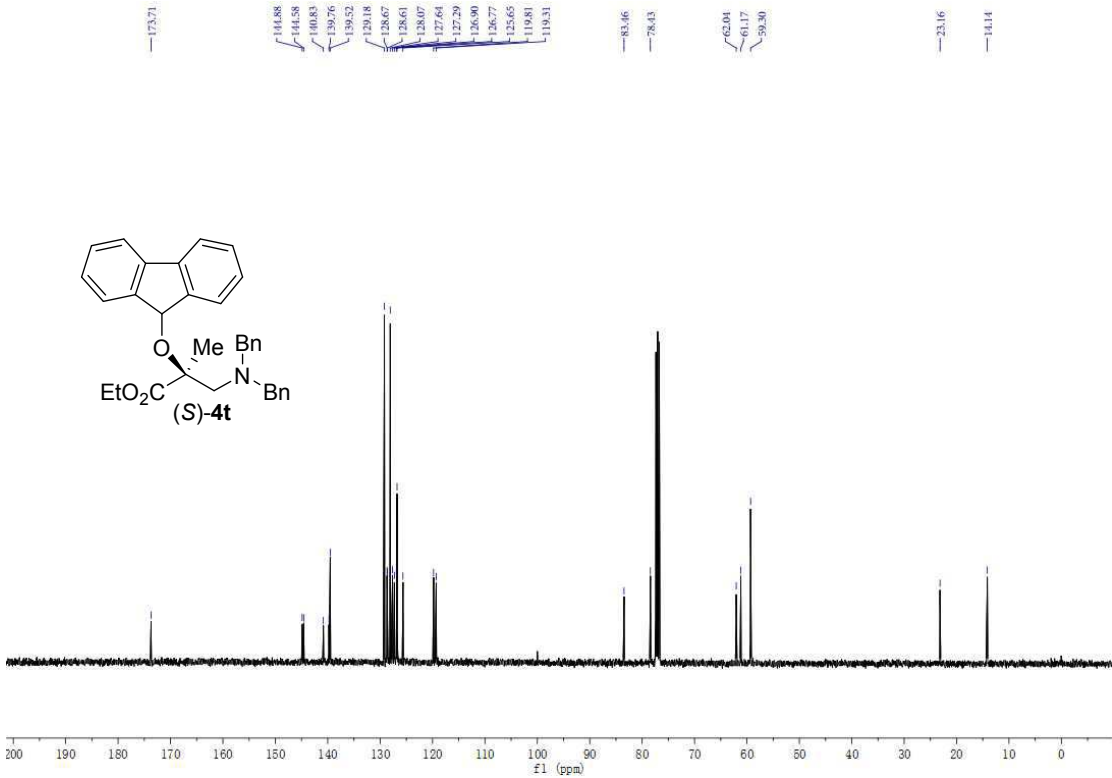
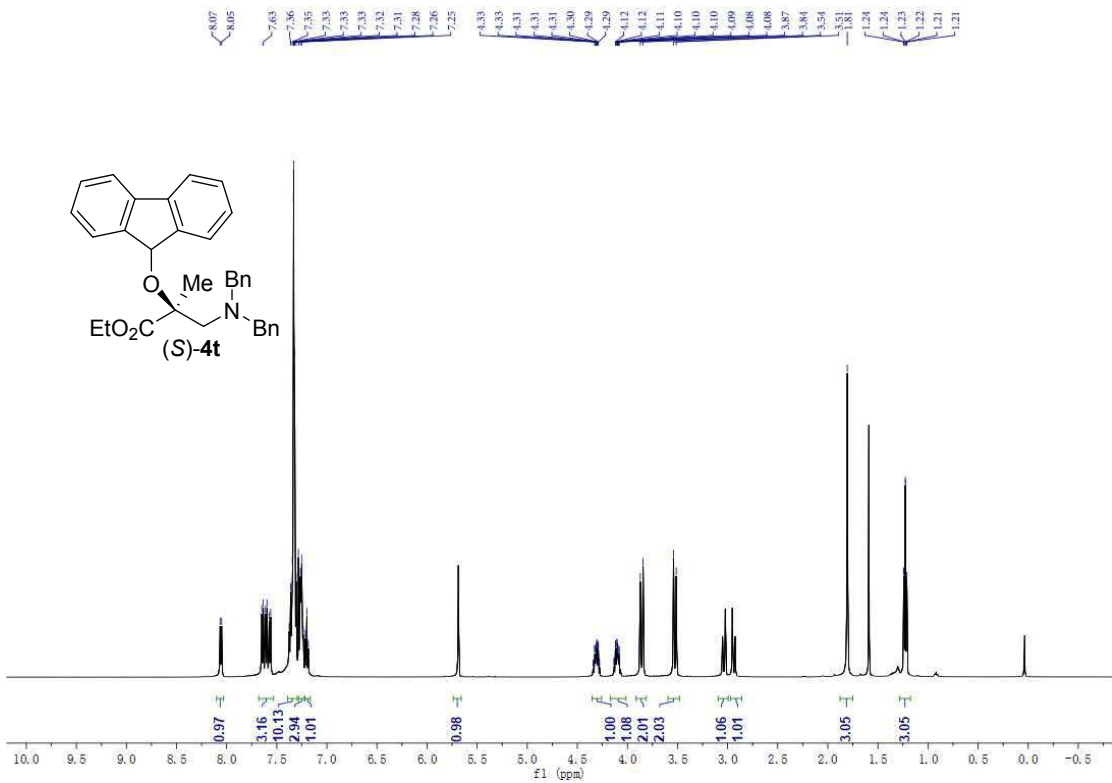
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4r



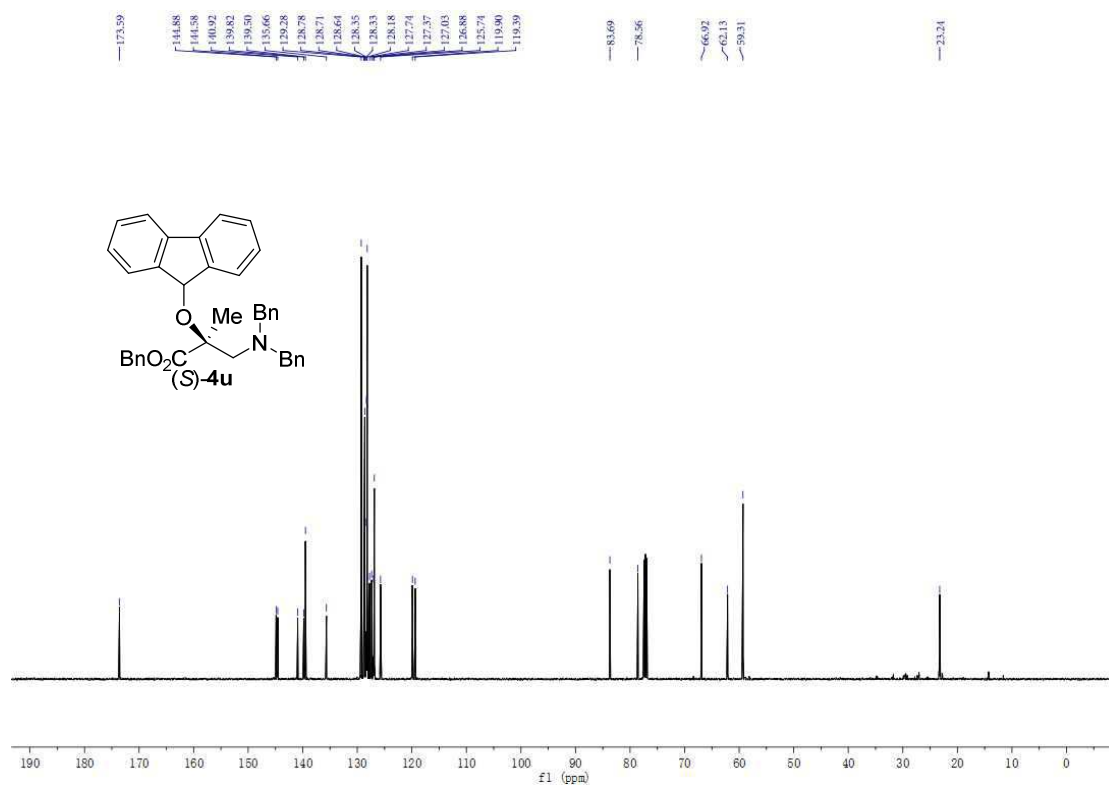
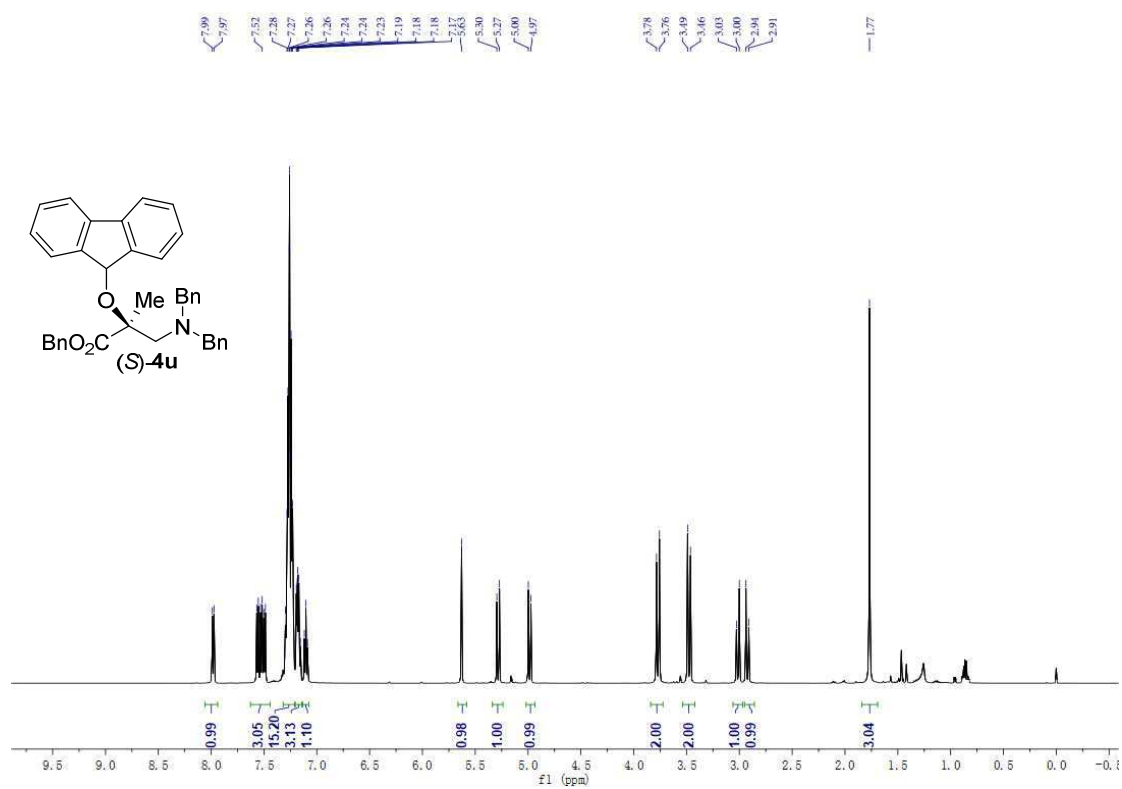
¹H NMR (500 MHz, CDCl₃) and ¹³C NMR (500 MHz, CDCl₃) spectra for (S)-4s



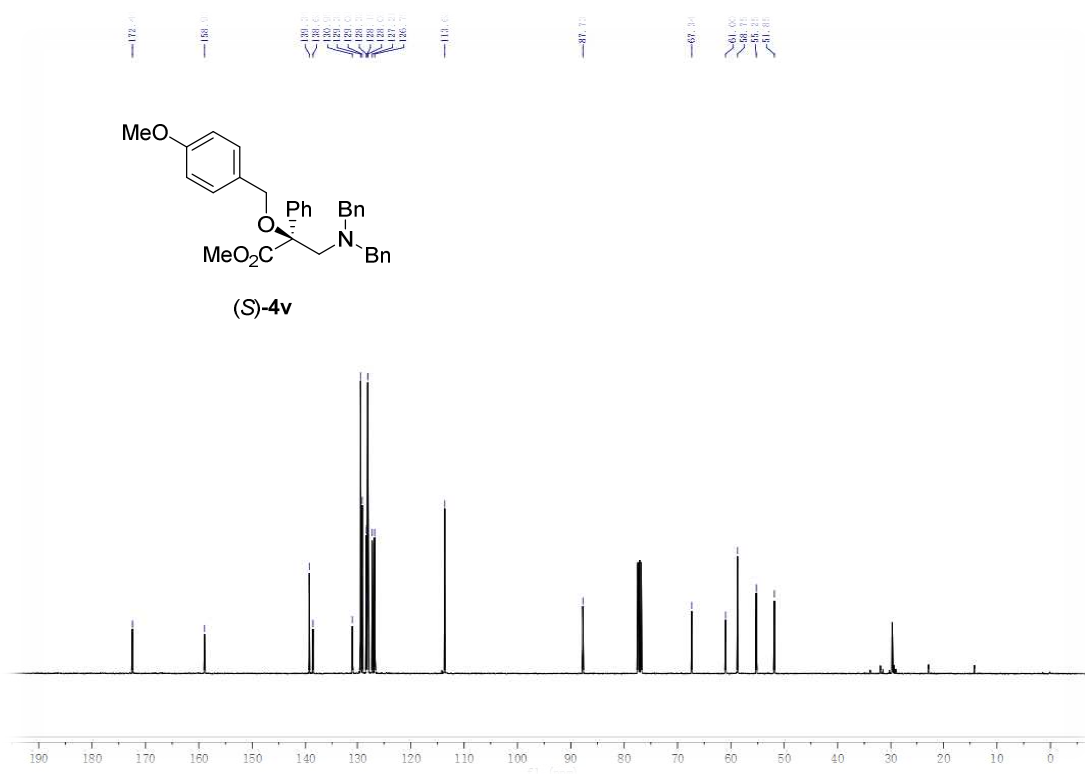
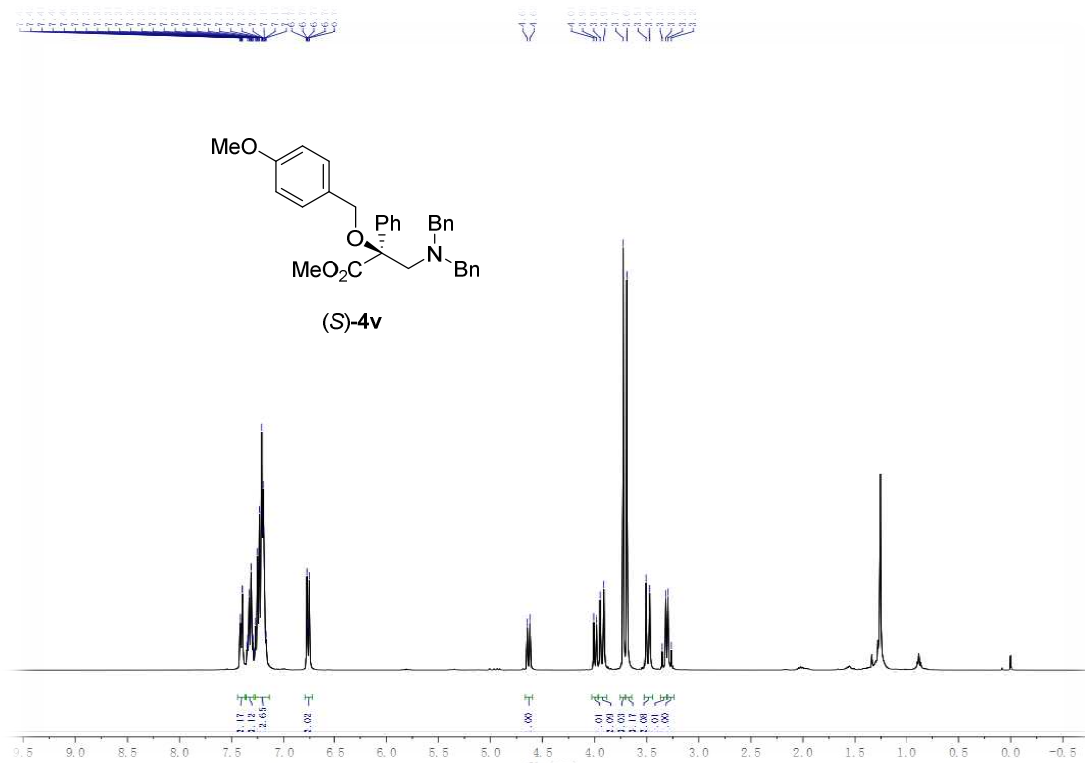
¹H NMR (500 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4t



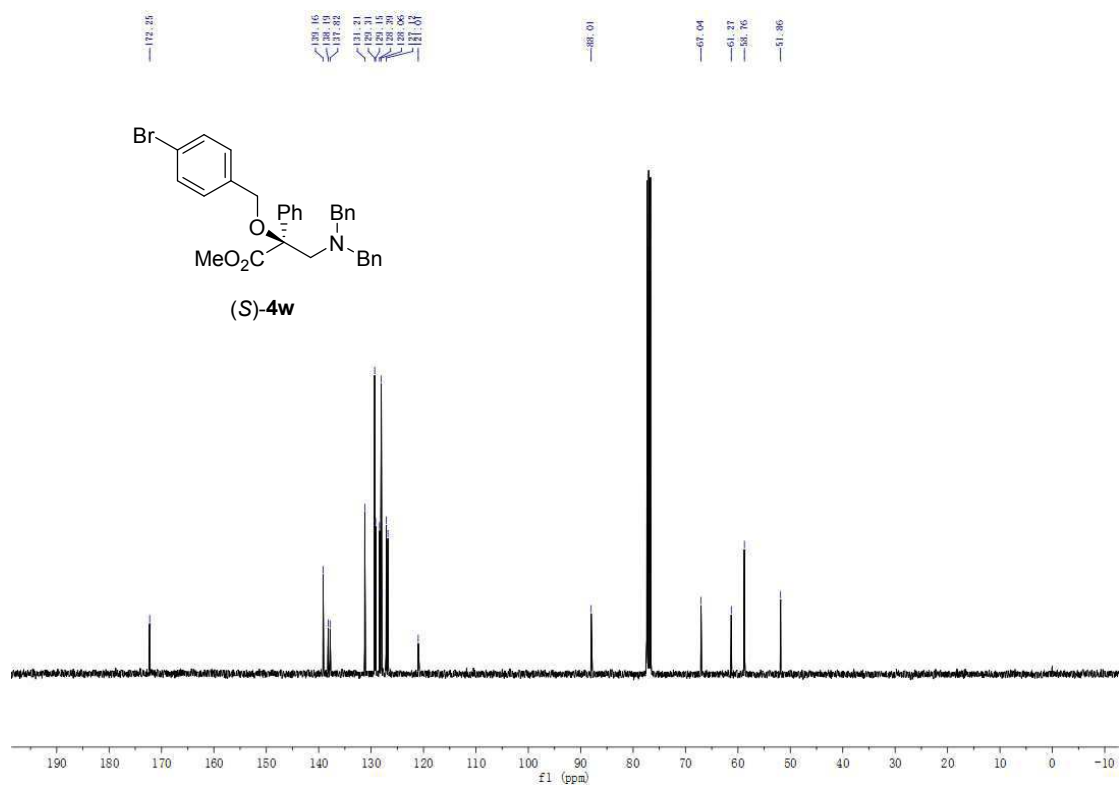
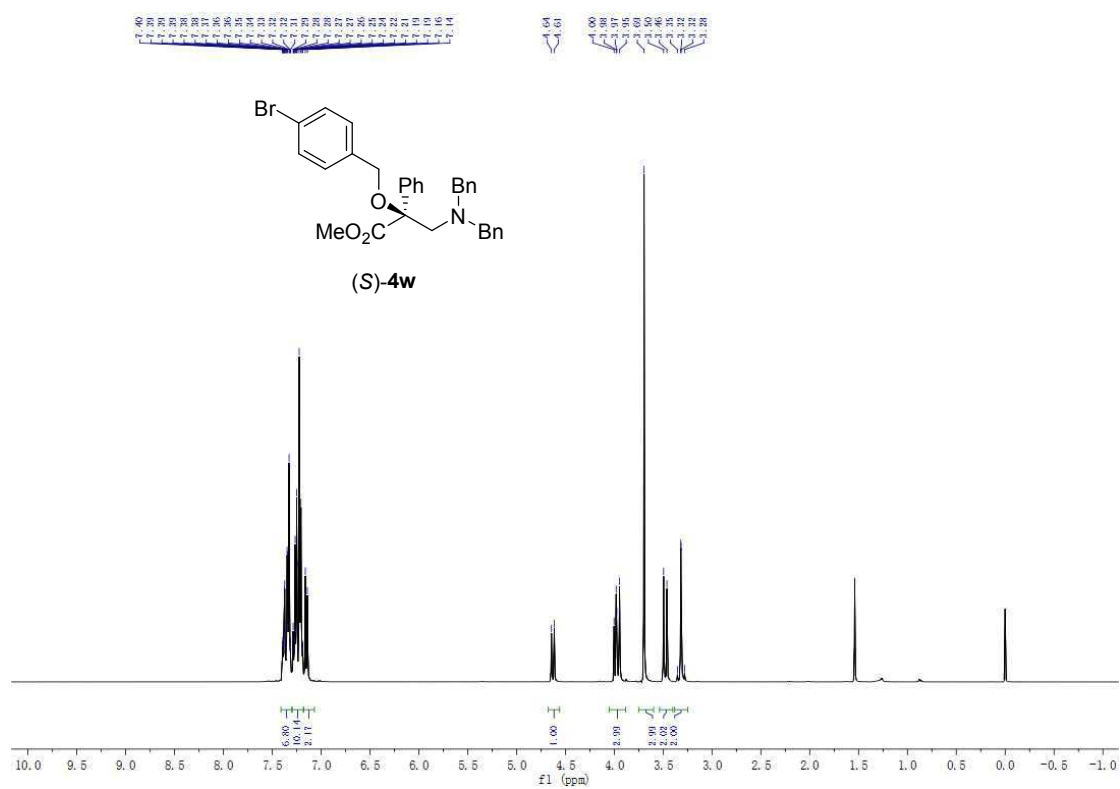
¹H NMR (500 MHz, CDCl₃) and ¹³C NMR (500 MHz, CDCl₃) spectra for (*S*)-4u



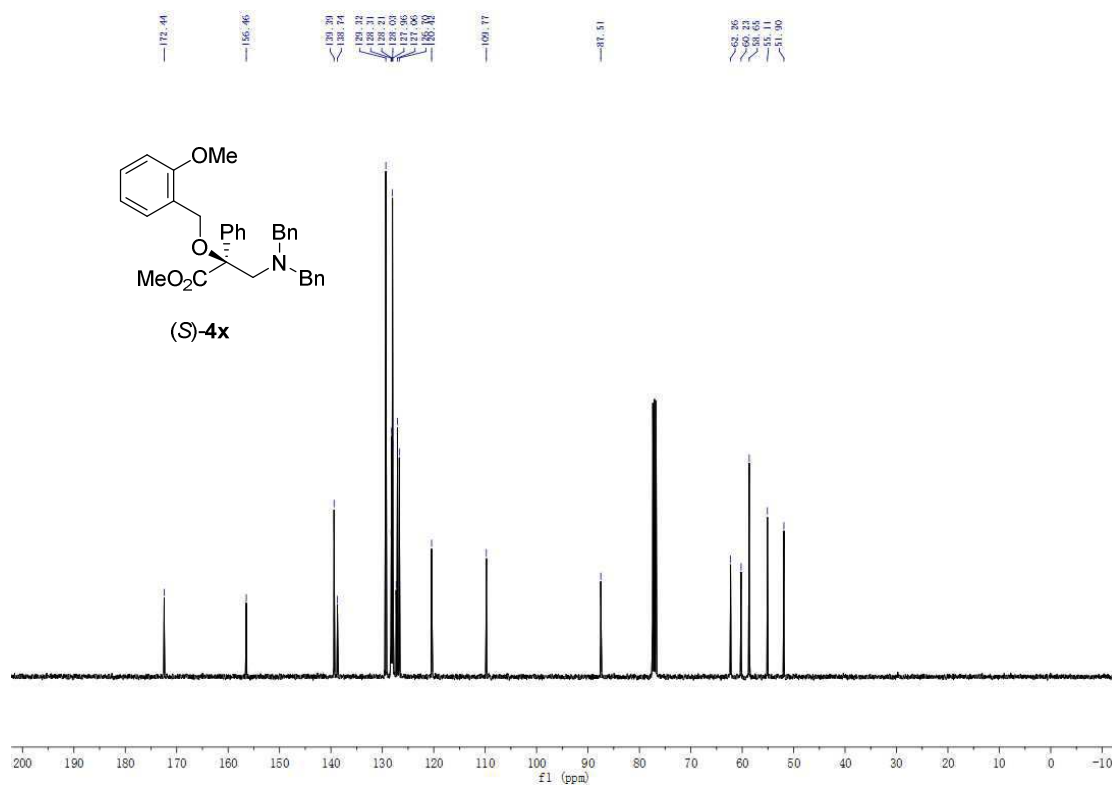
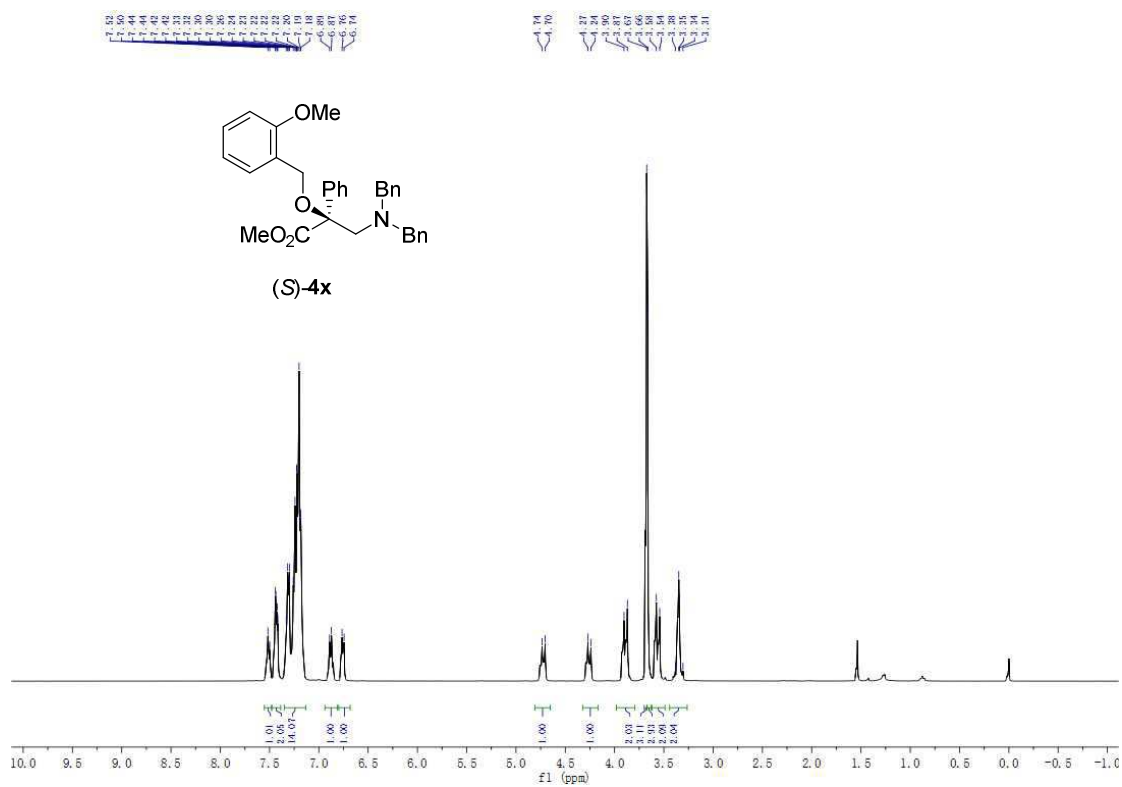
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4v



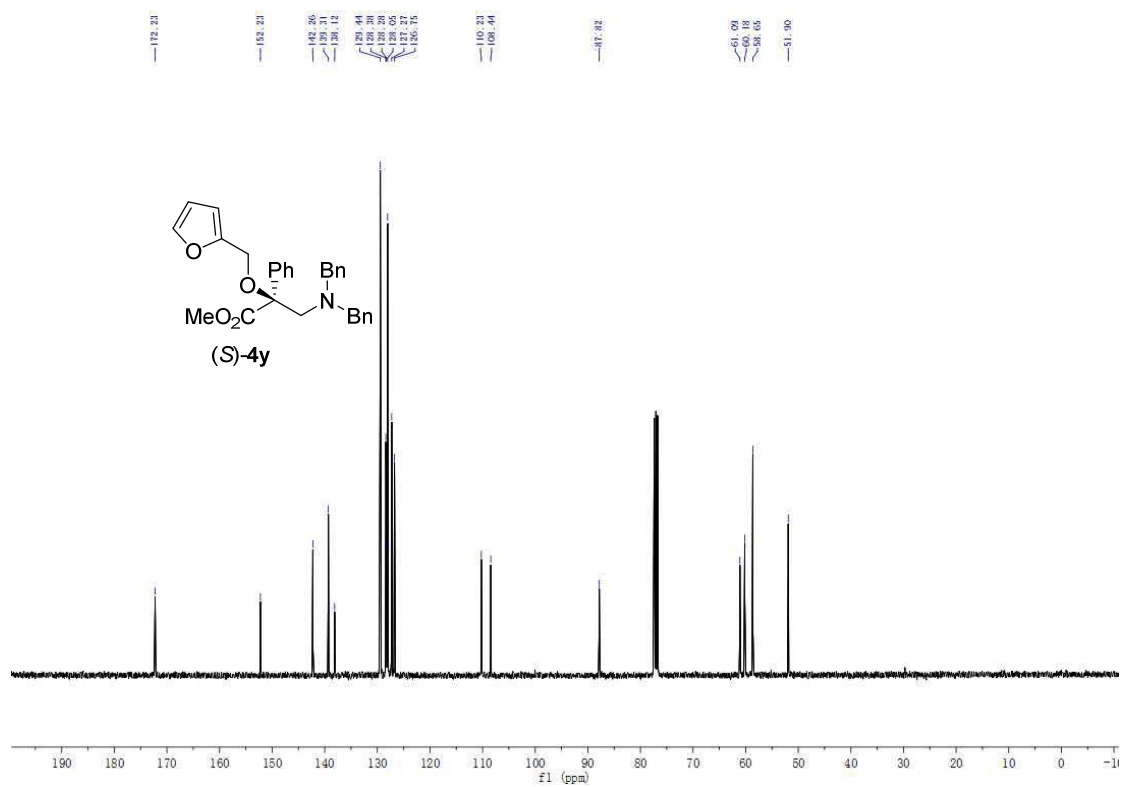
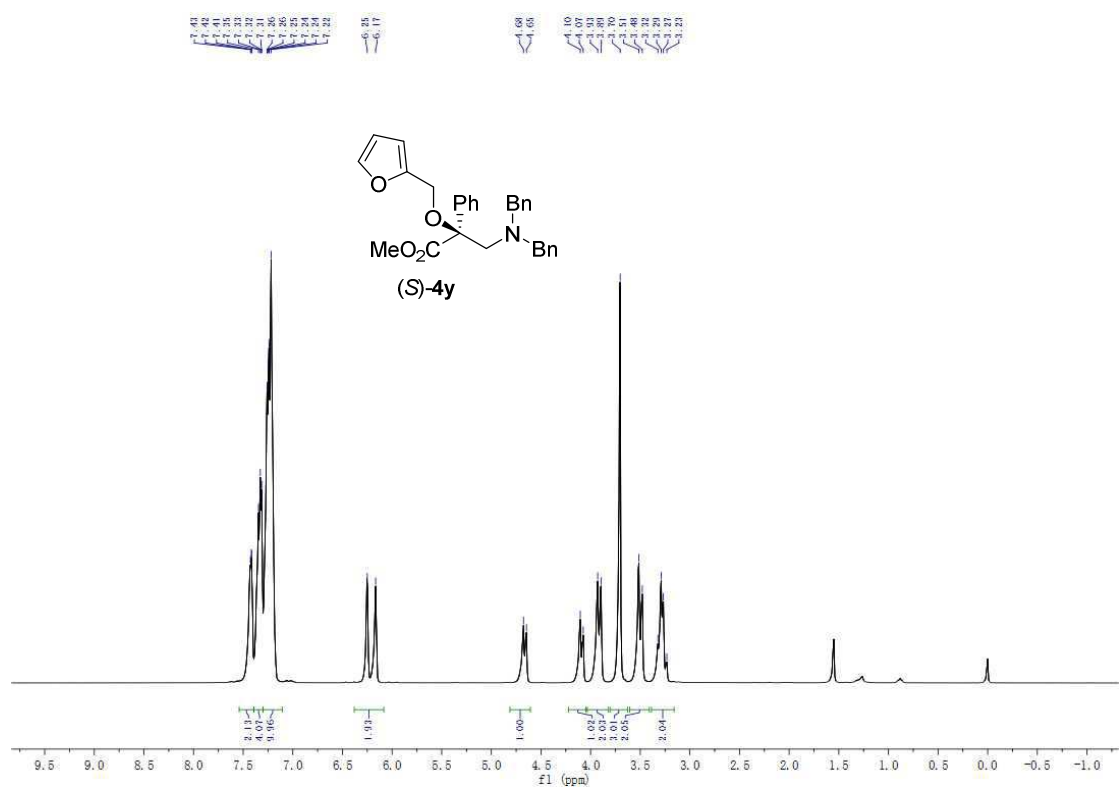
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4w



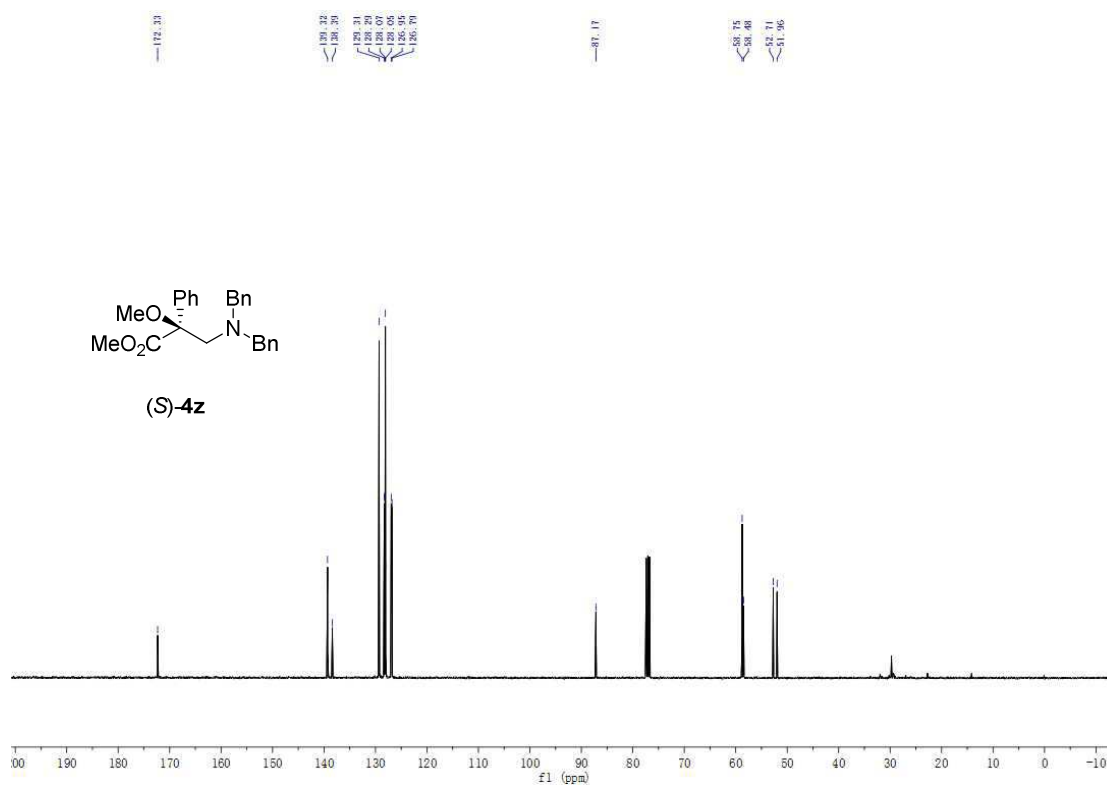
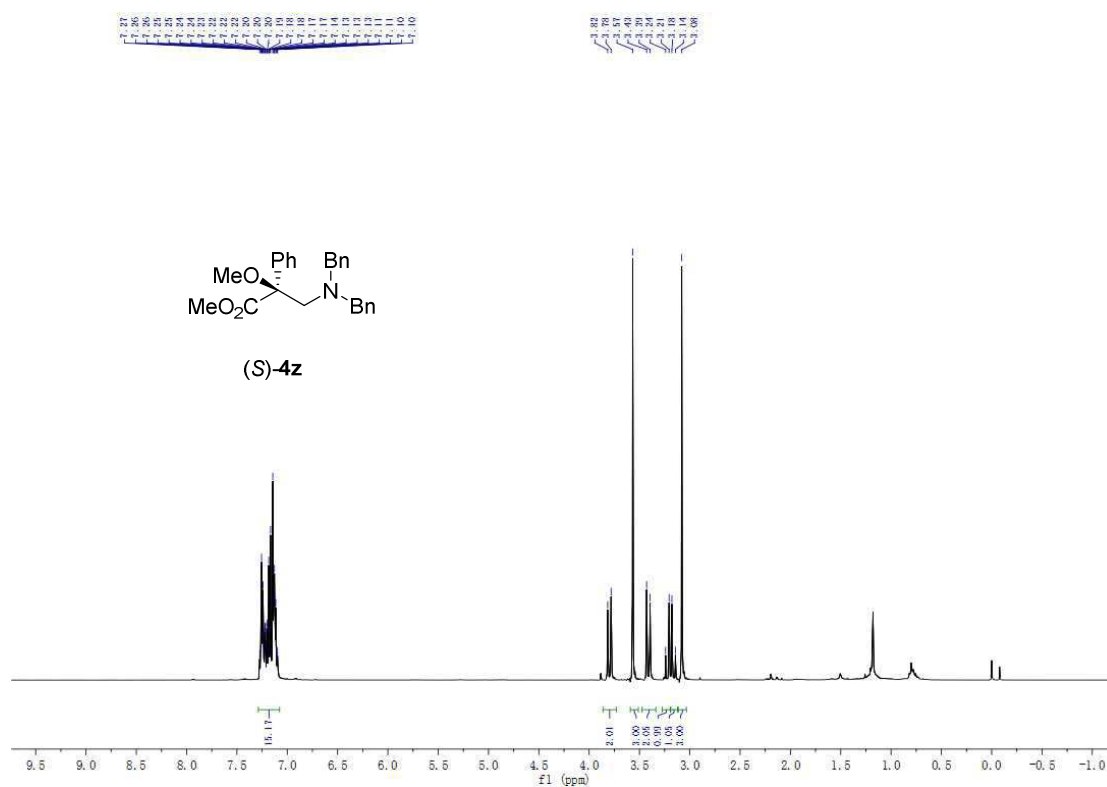
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4x



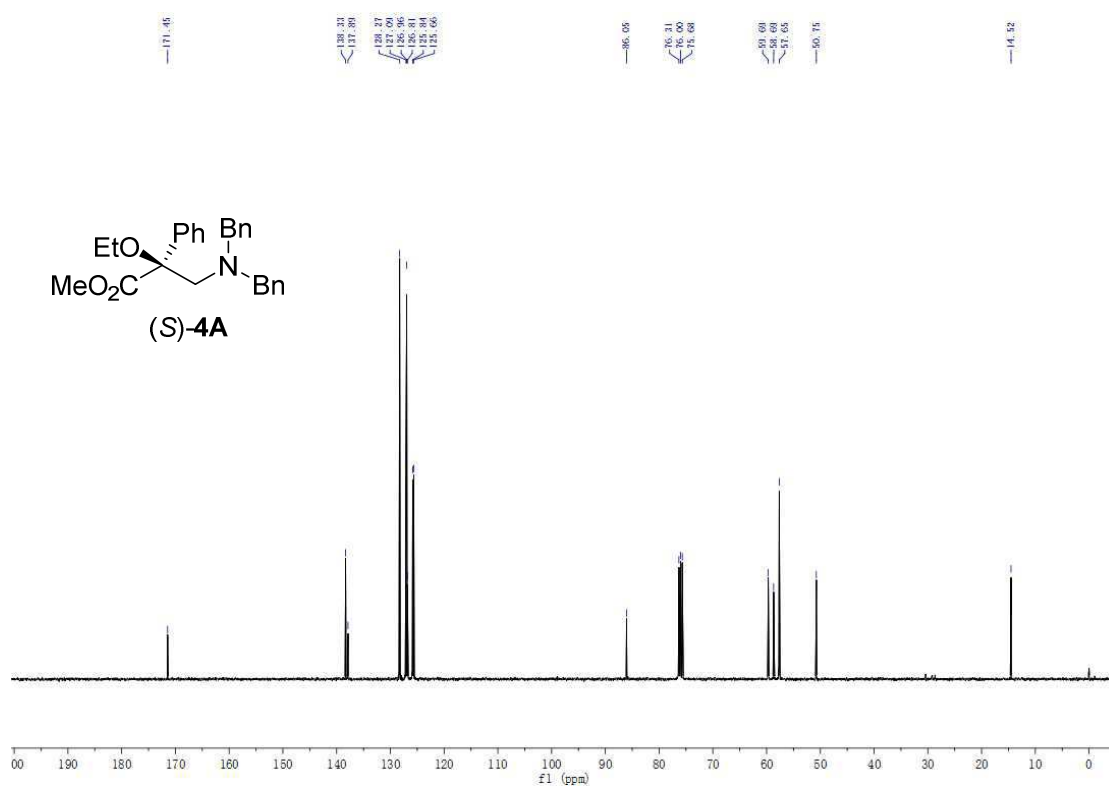
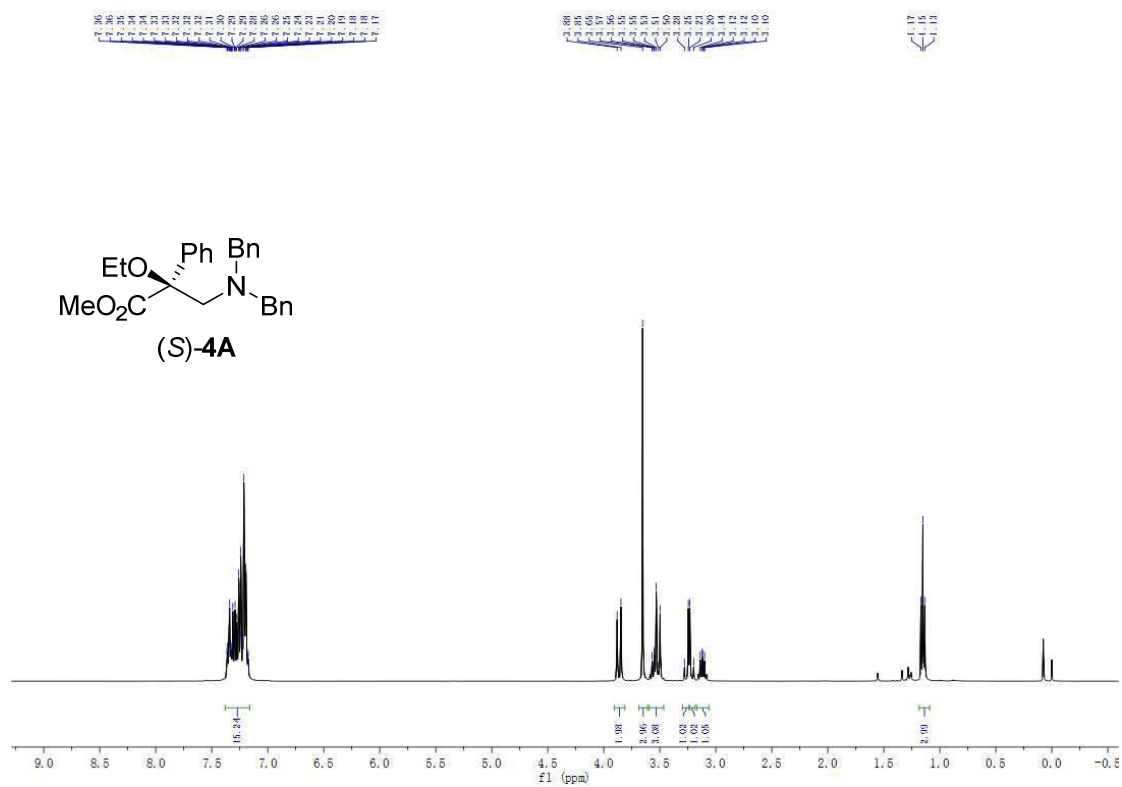
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4y



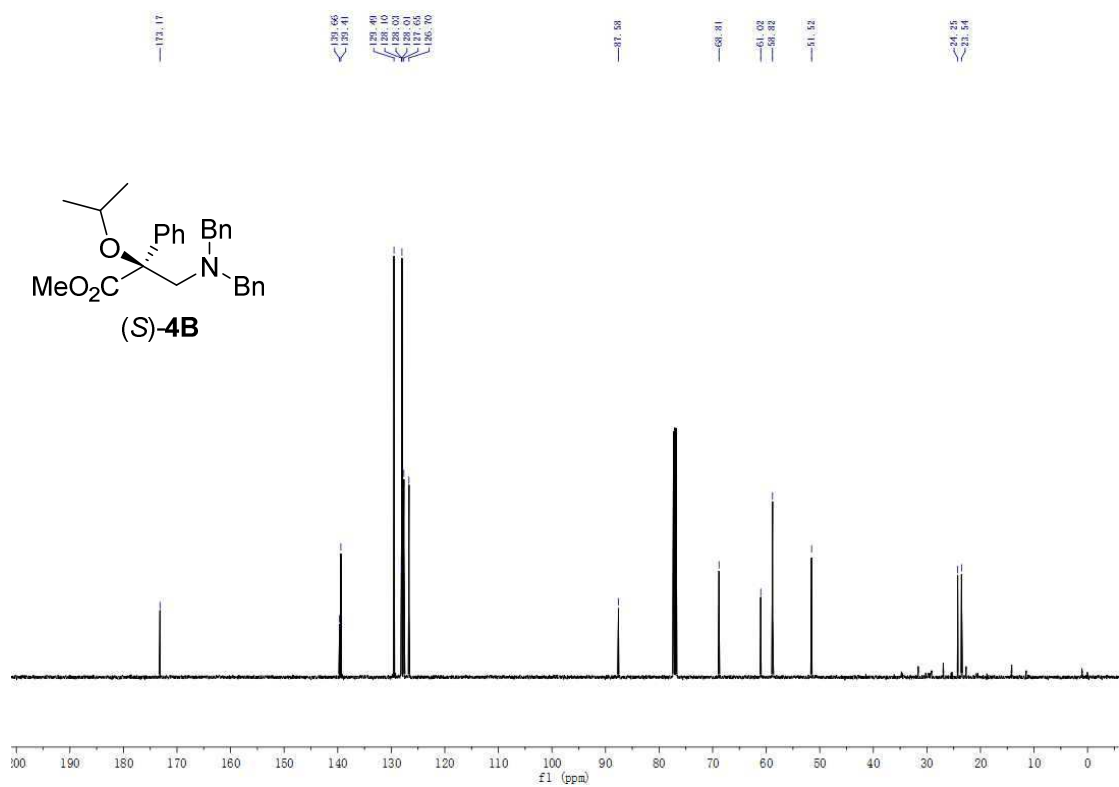
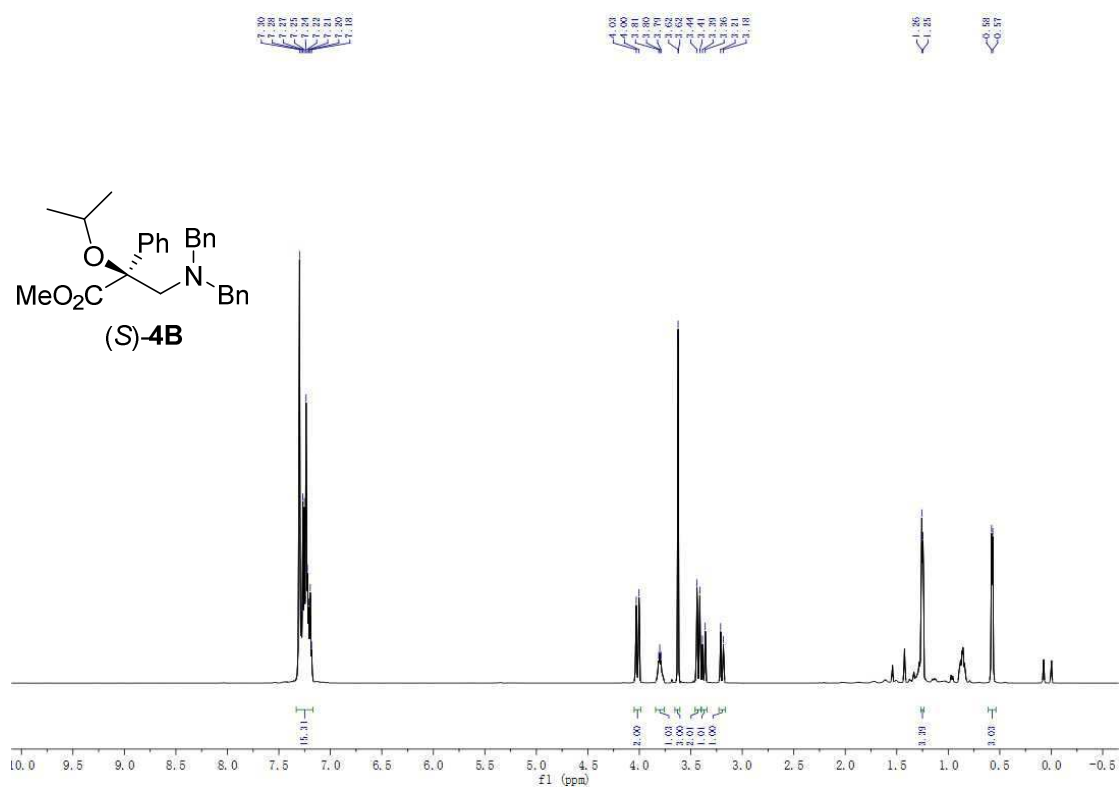
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4z



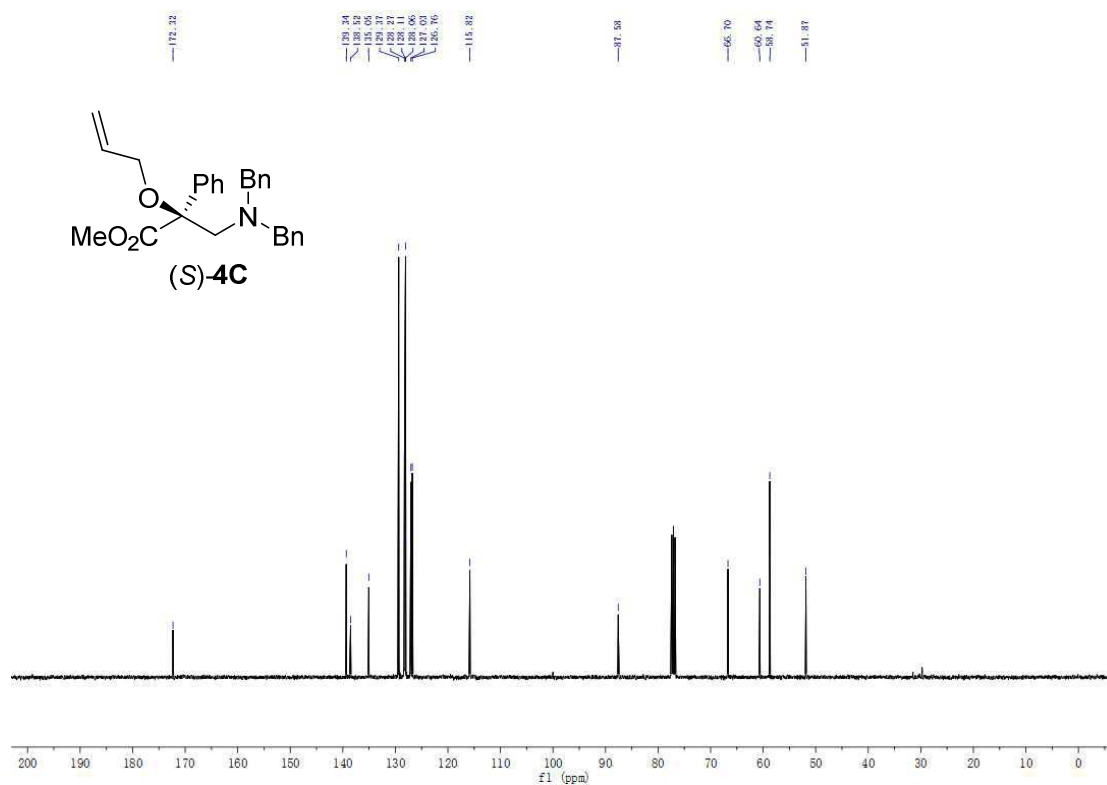
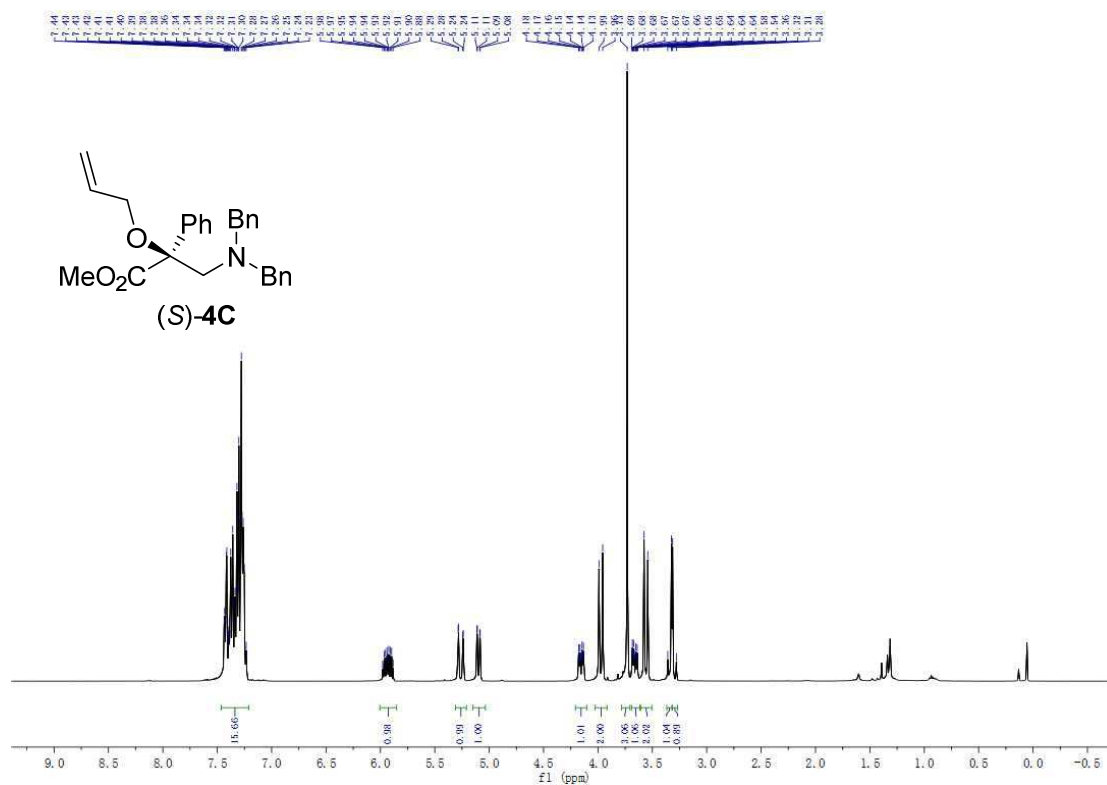
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4A



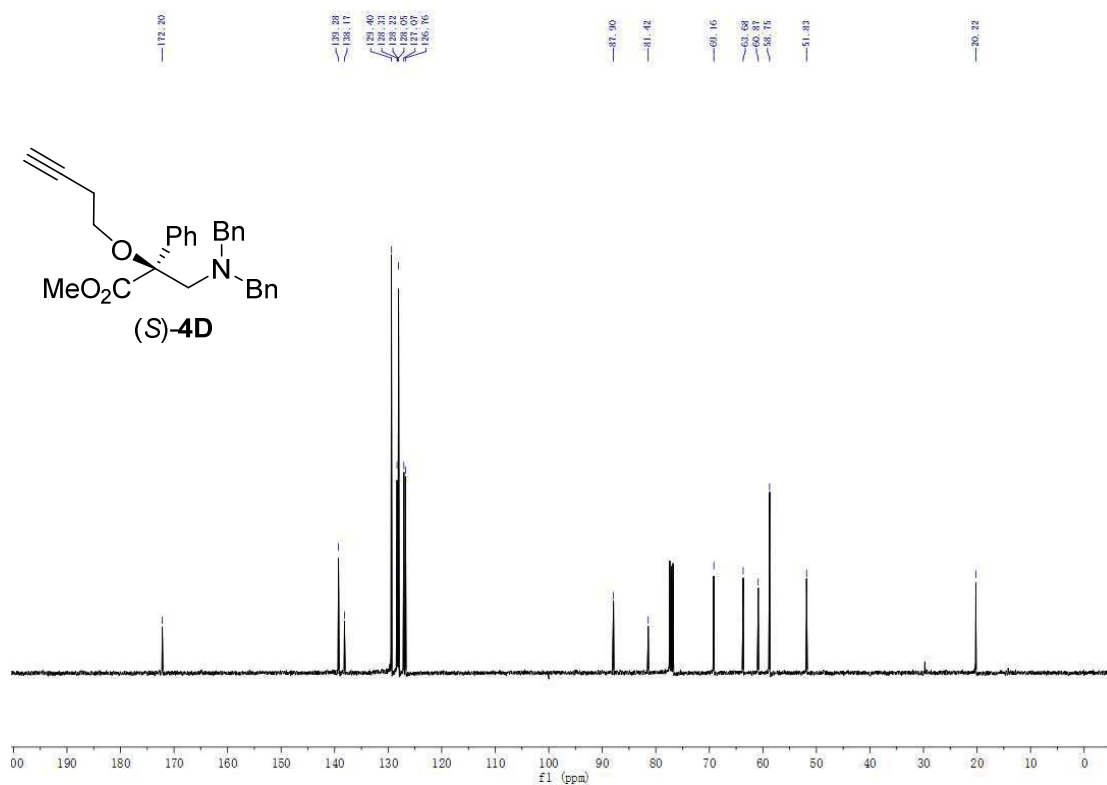
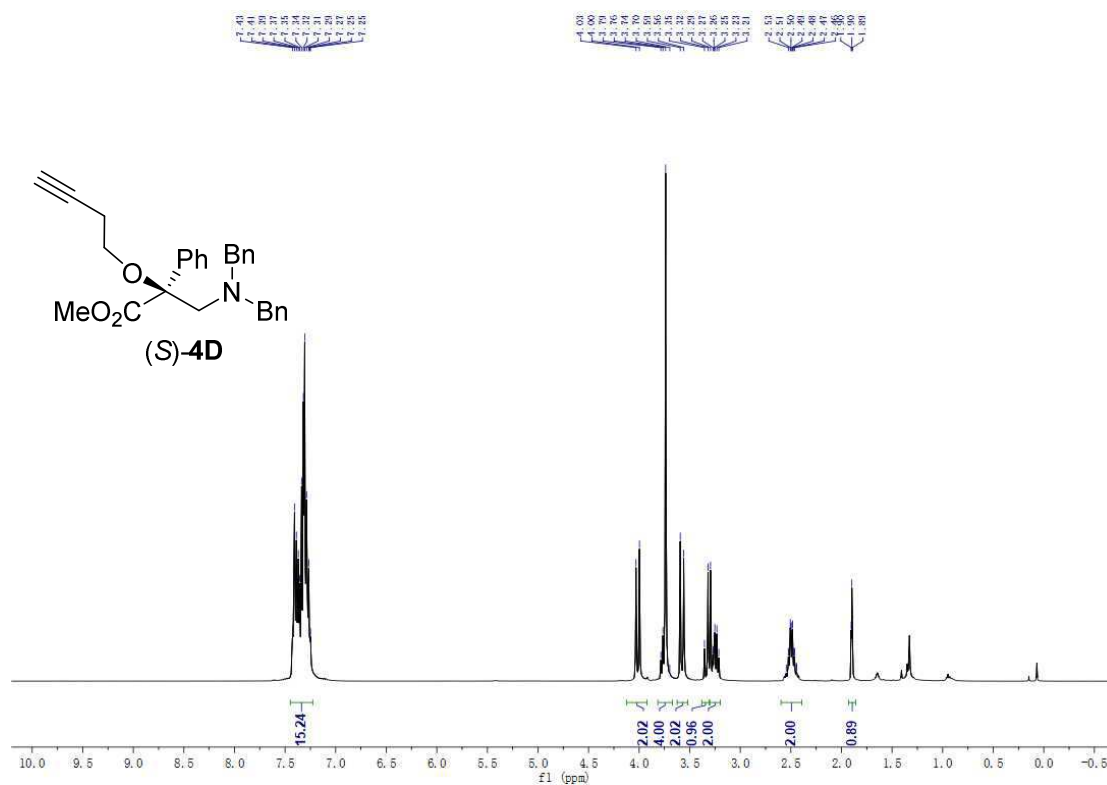
¹H NMR (500 MHz, CDCl₃) and ¹³C NMR (500 MHz, CDCl₃) spectra for (S)-4B



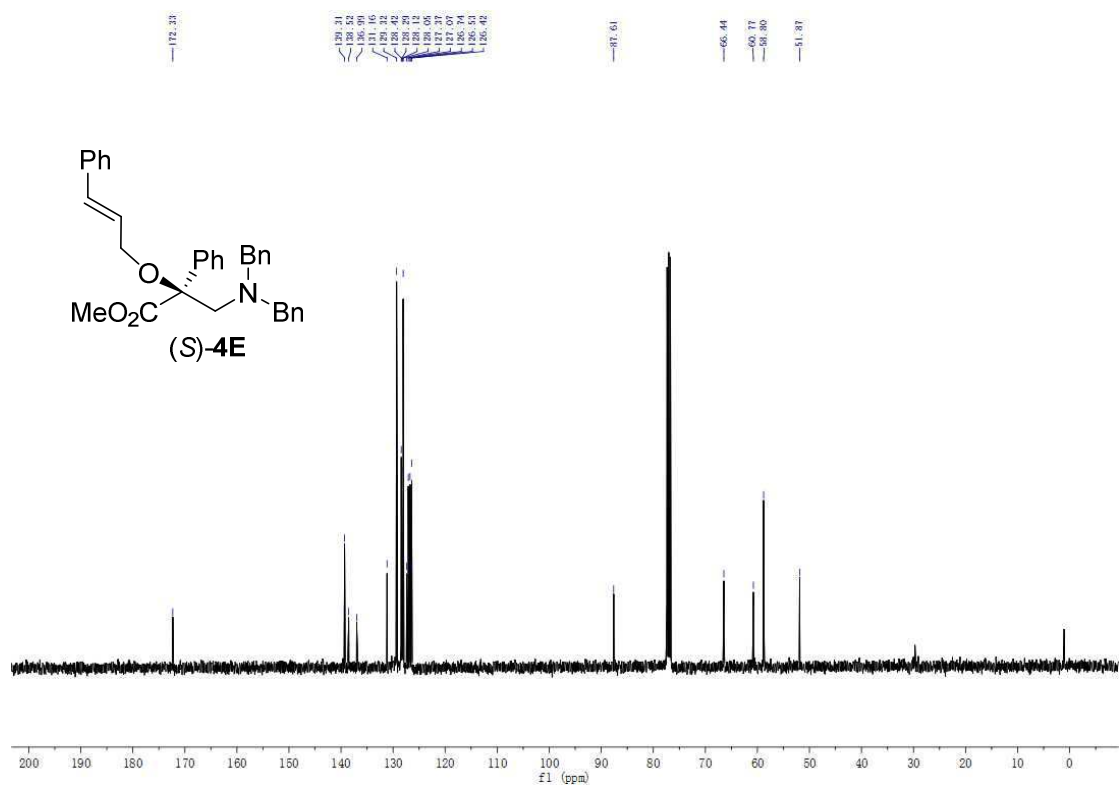
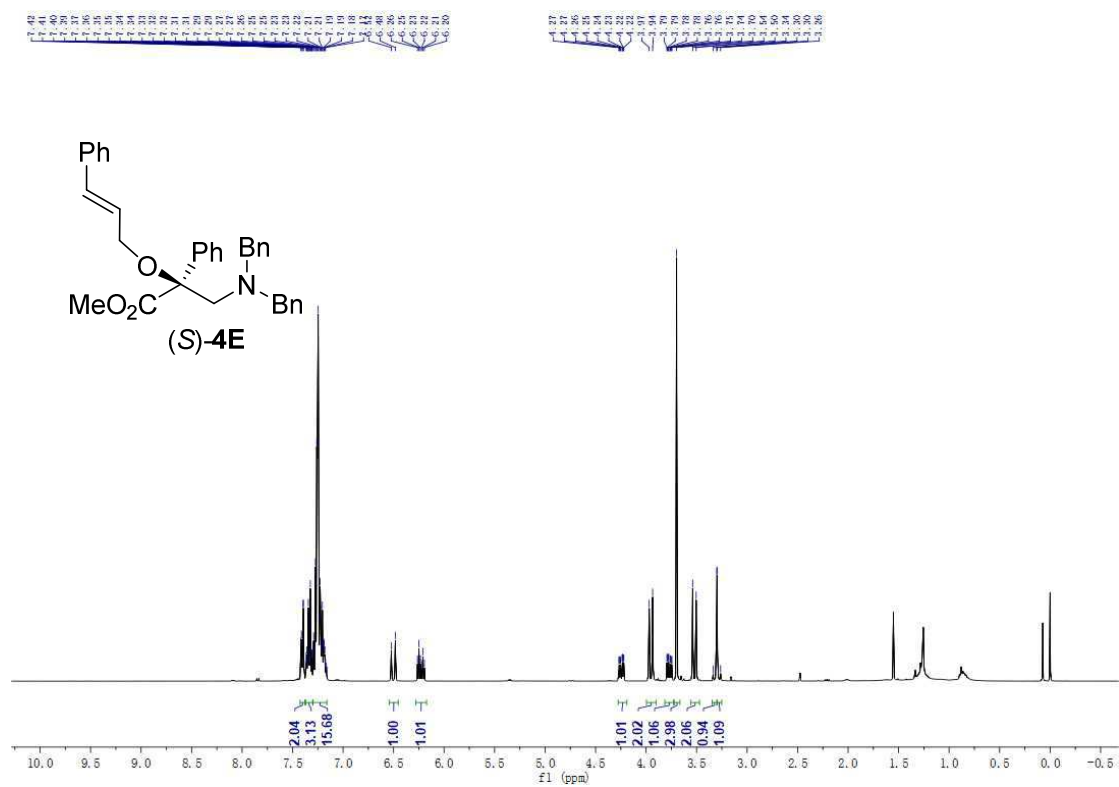
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4C



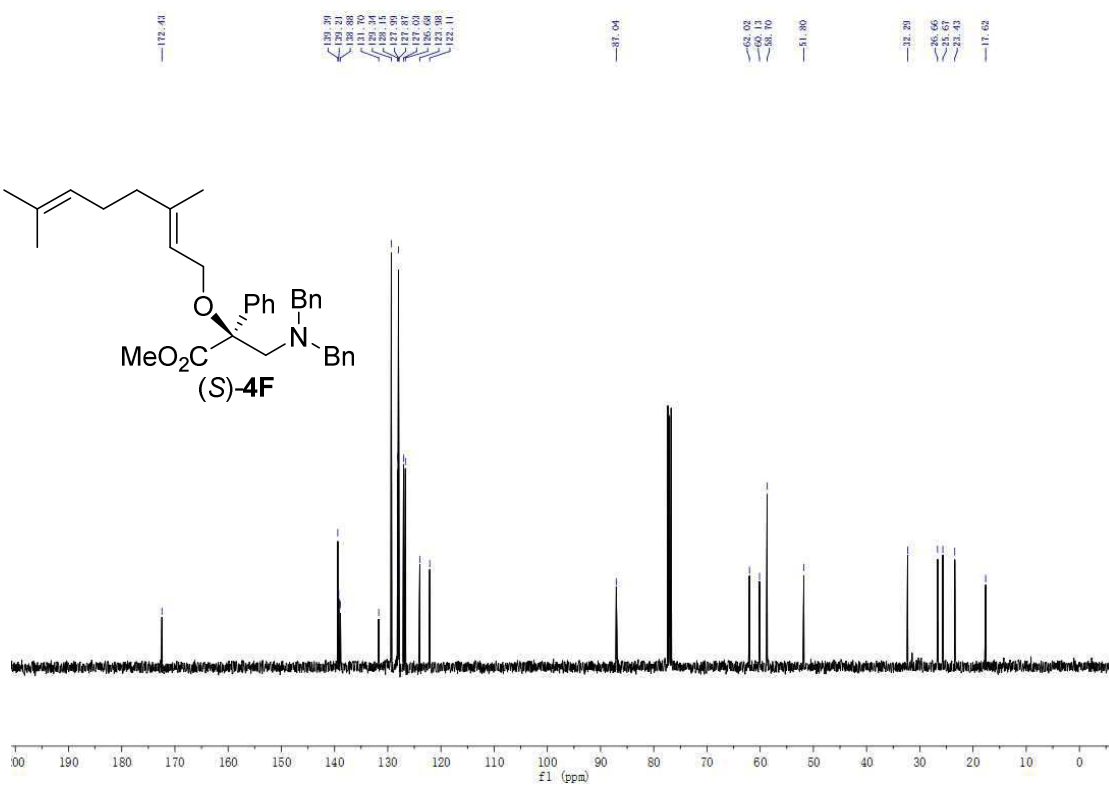
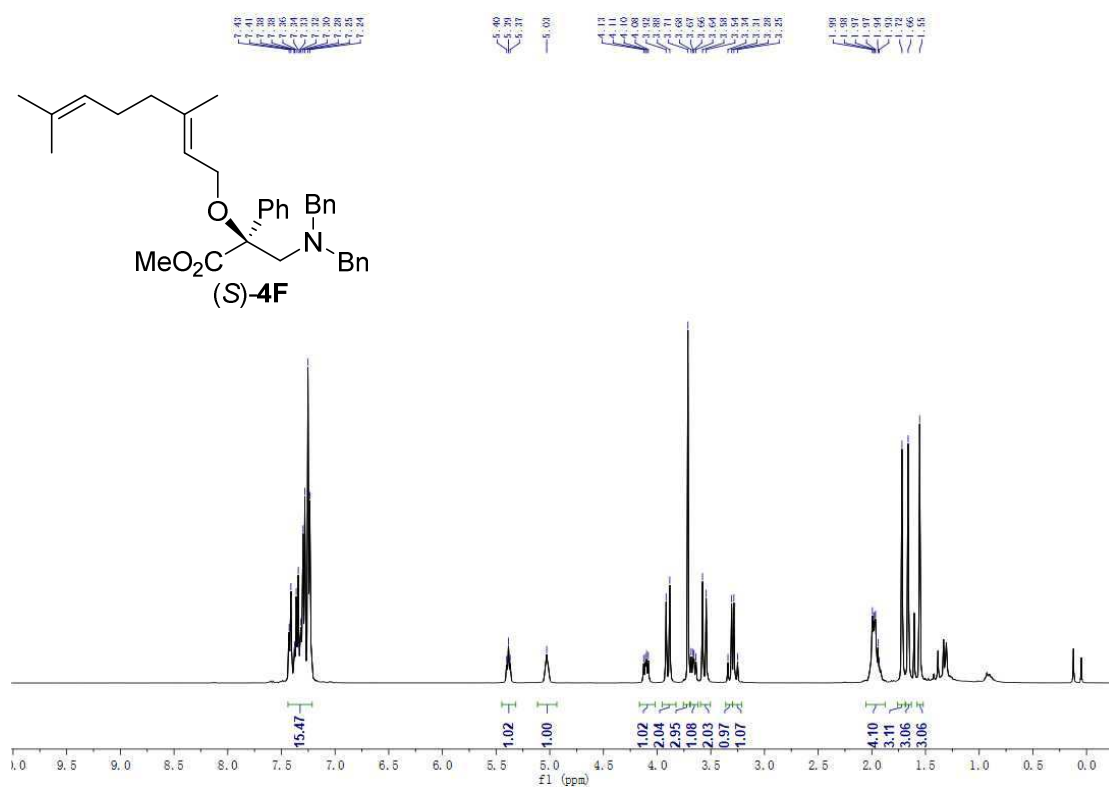
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (*S*)-4D



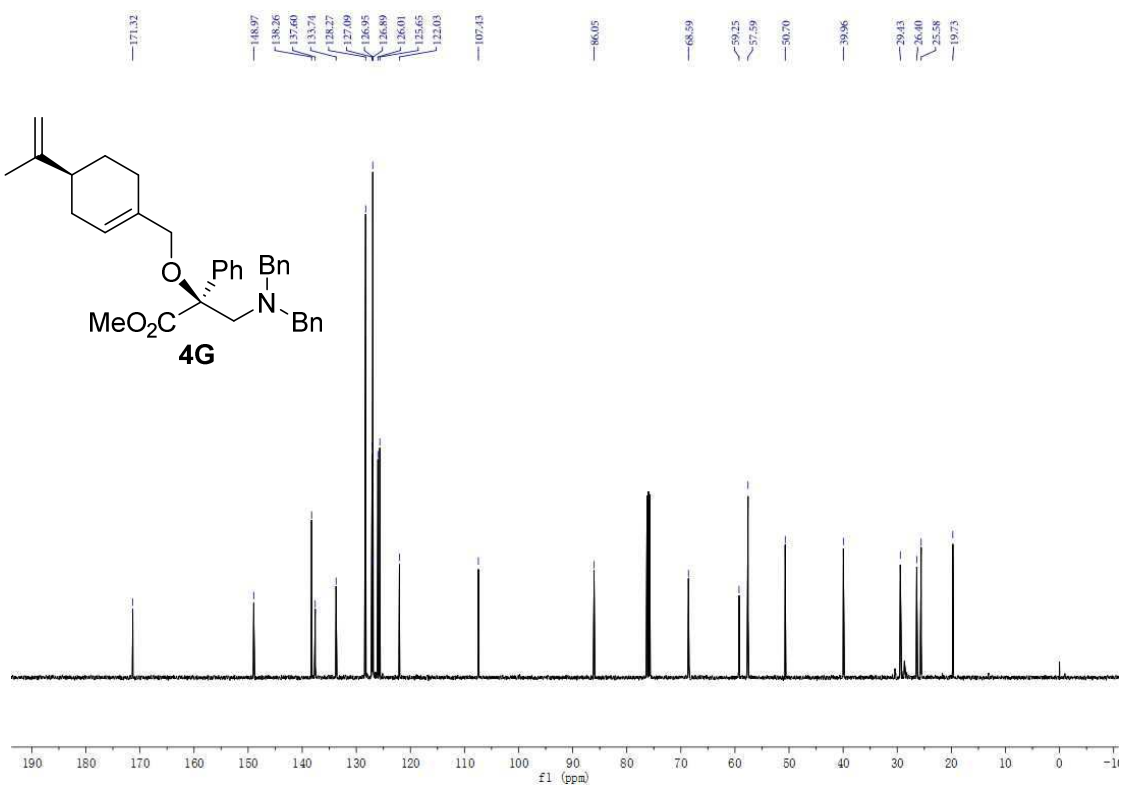
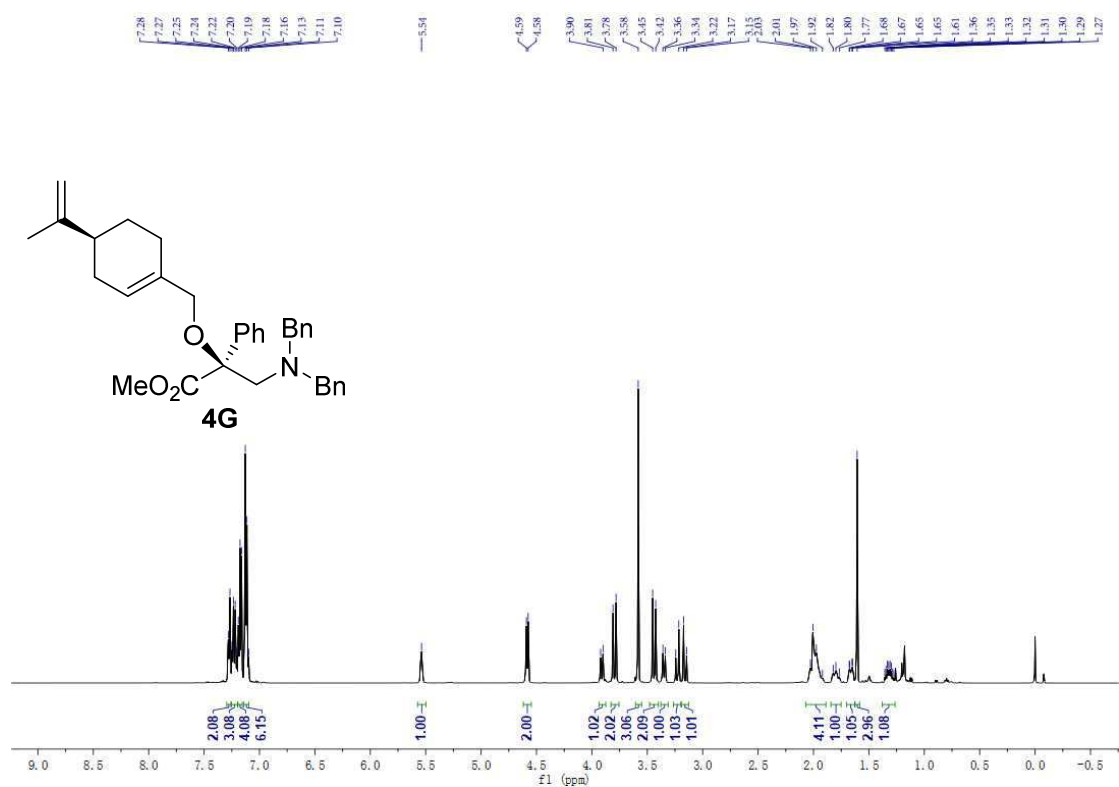
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (*S*)-4E



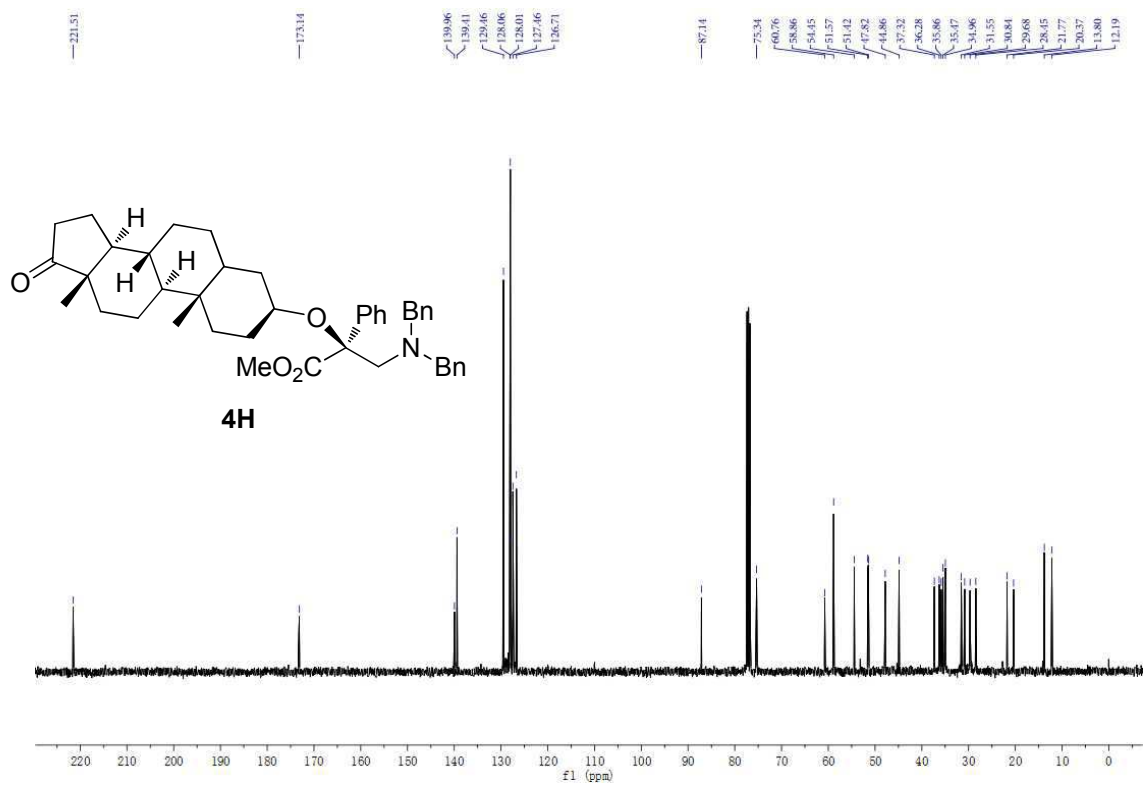
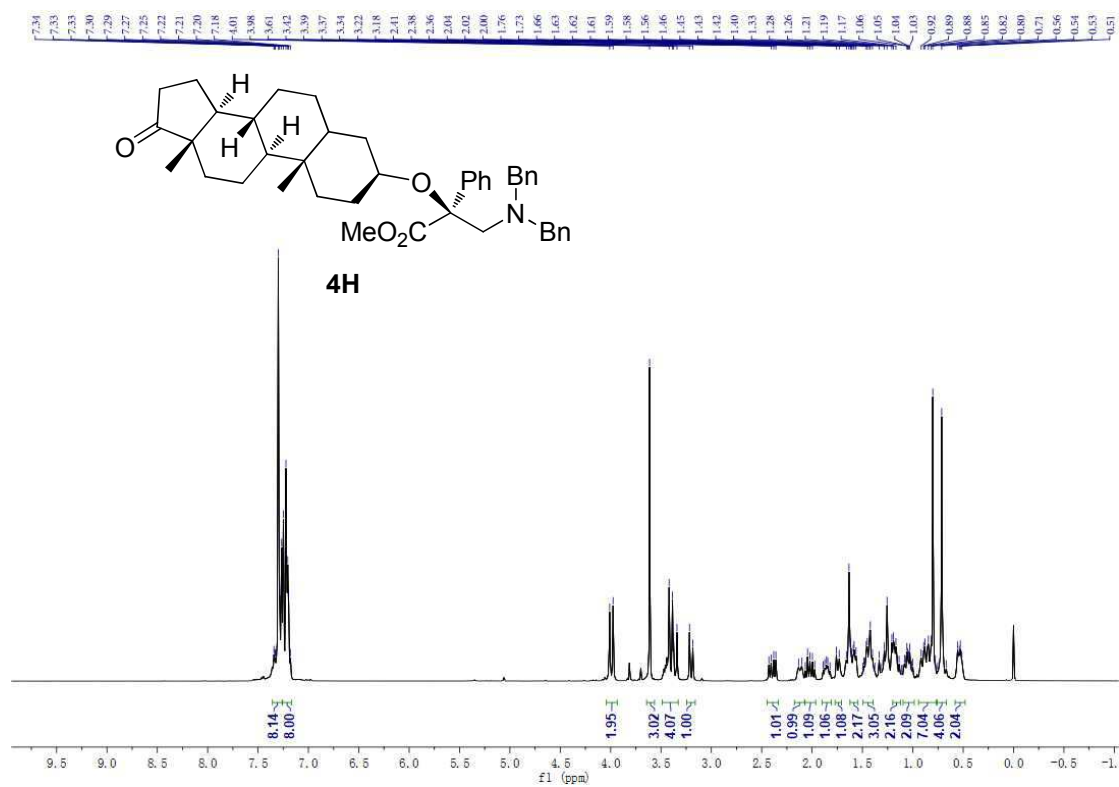
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-4F



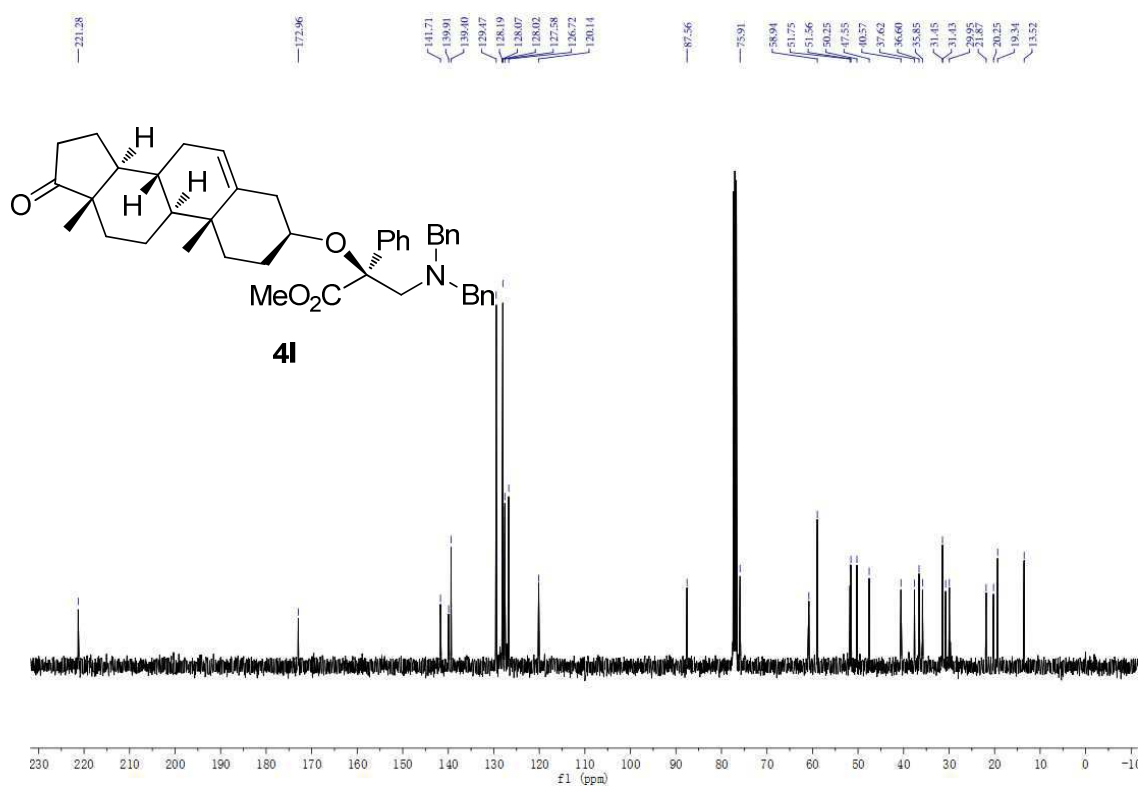
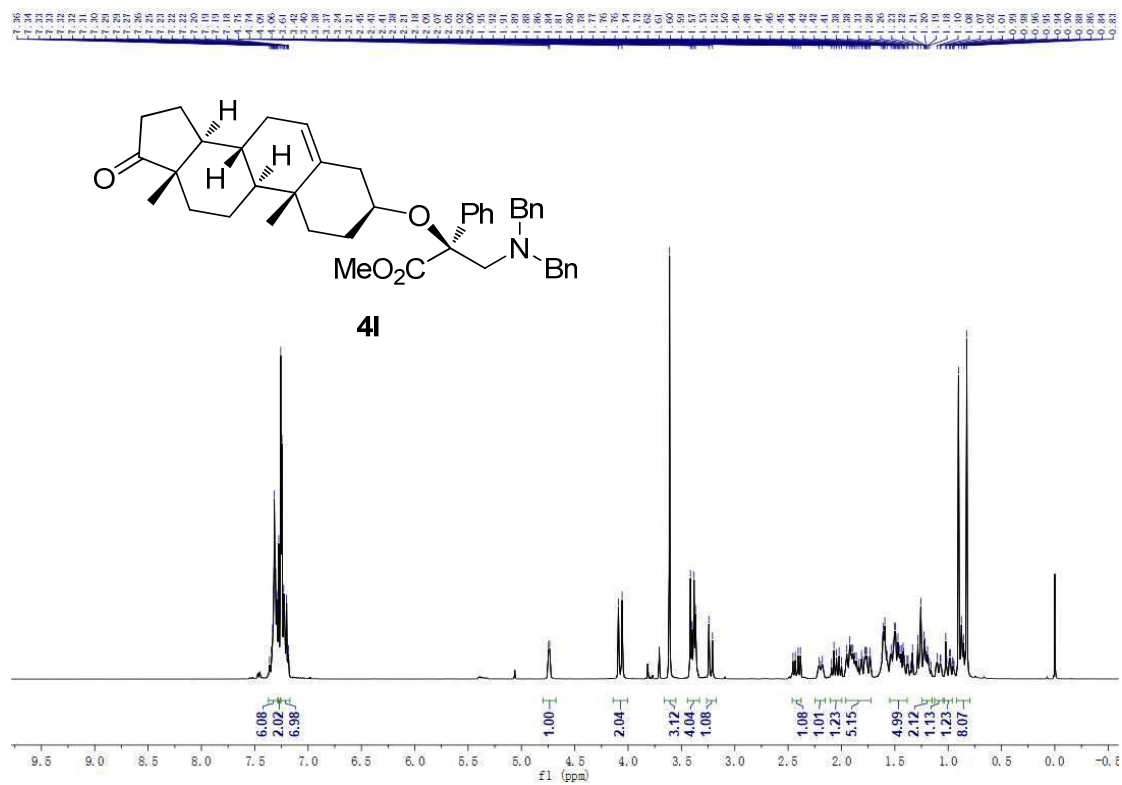
¹H NMR (500 MHz, CDCl₃) and ¹³C NMR (500 MHz, CDCl₃) spectra for 4G



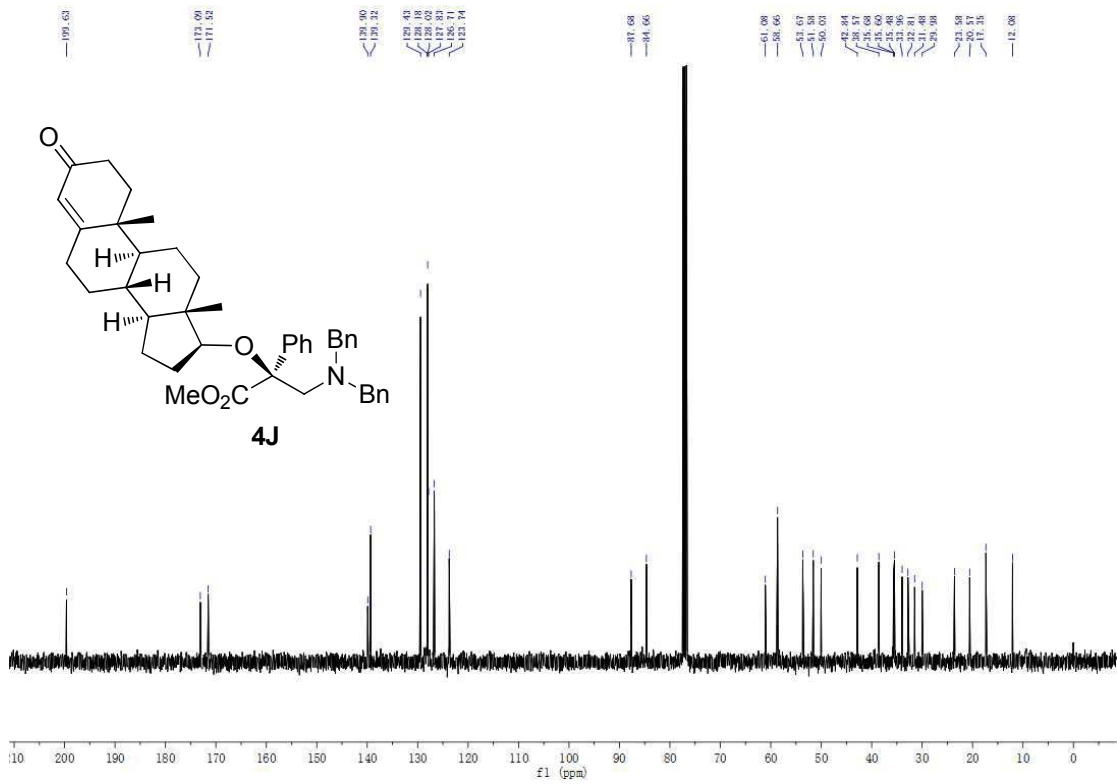
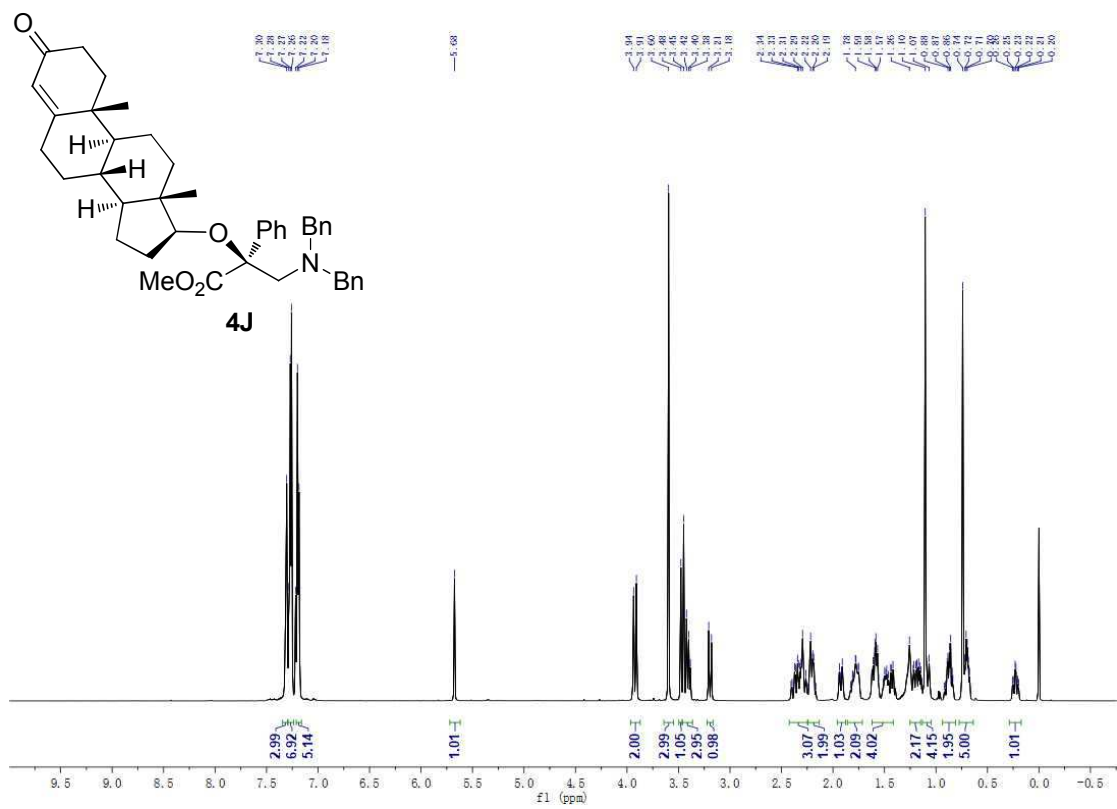
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for 4H



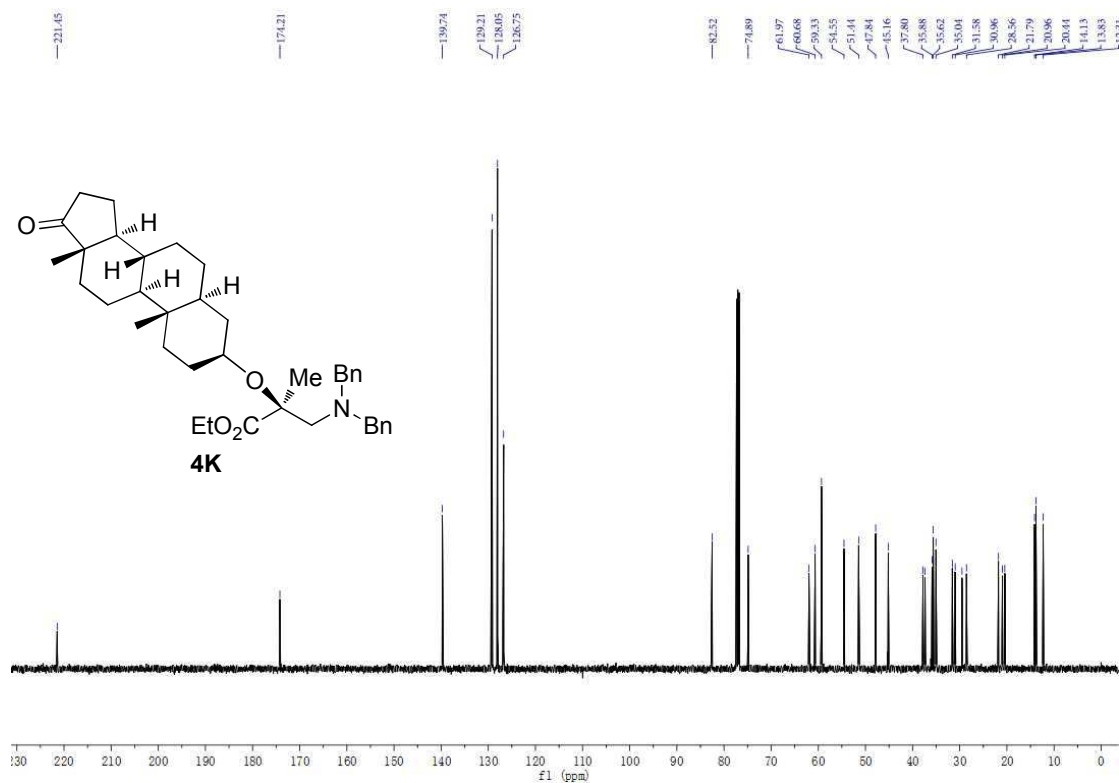
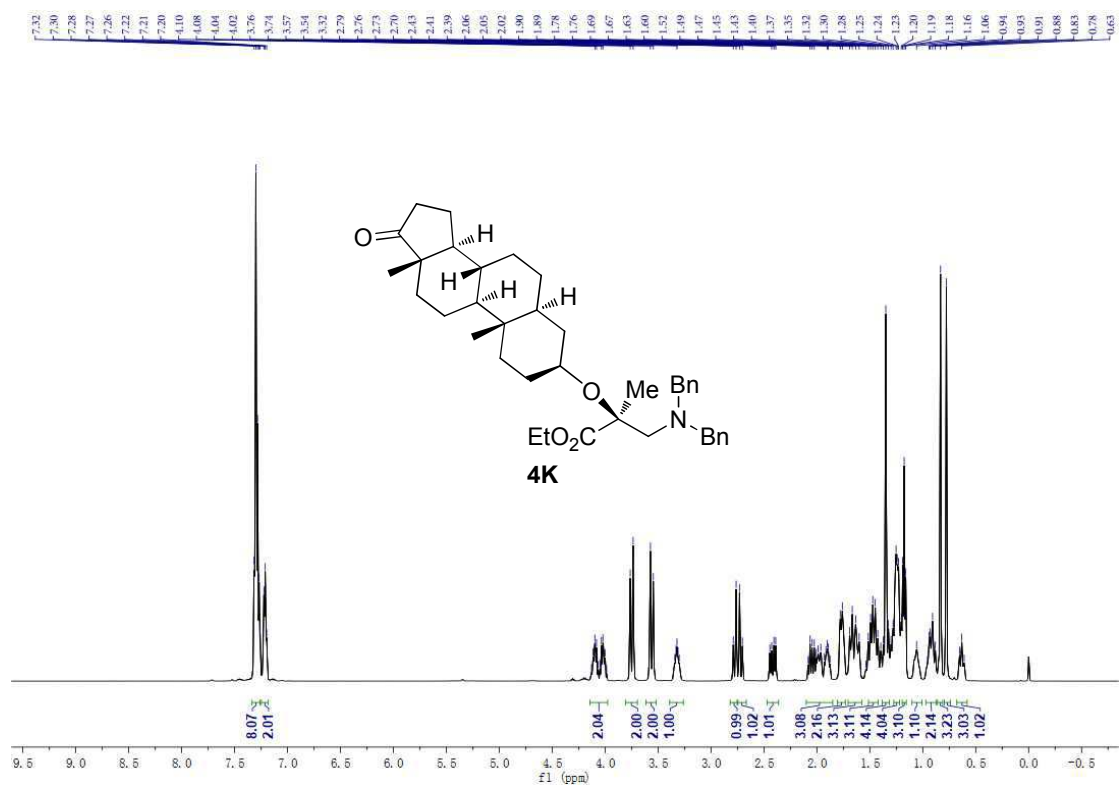
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for 4I



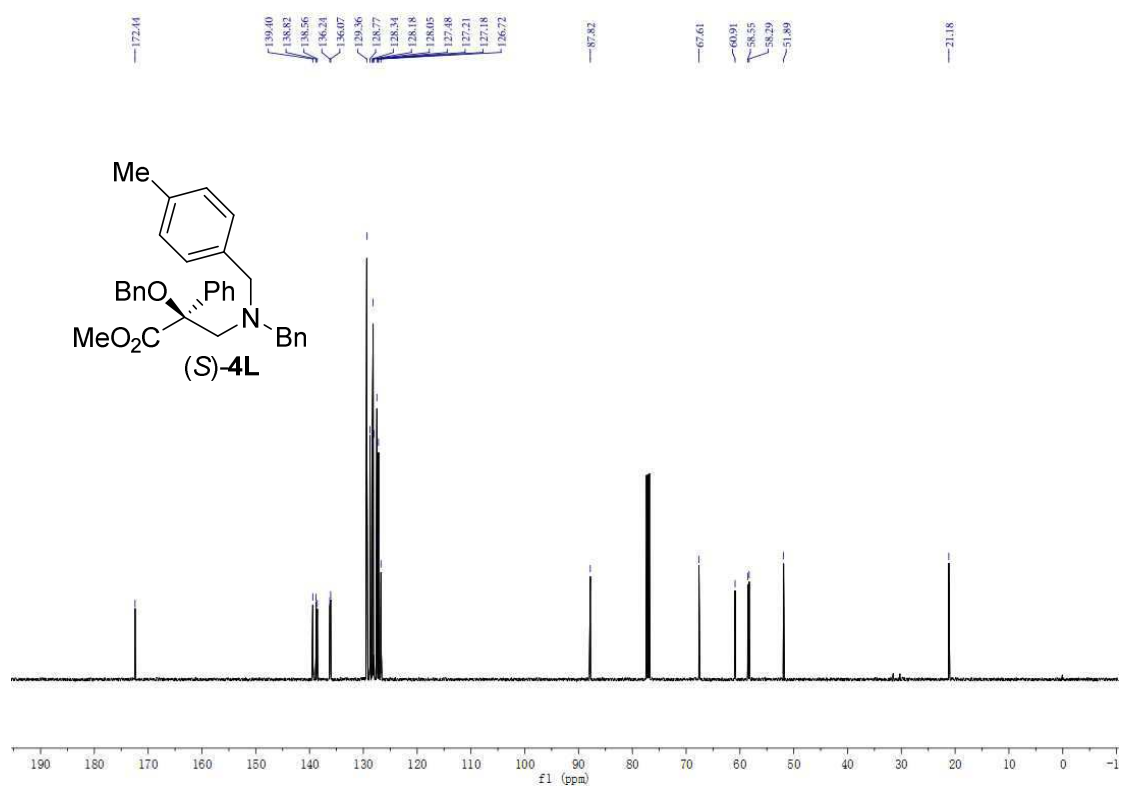
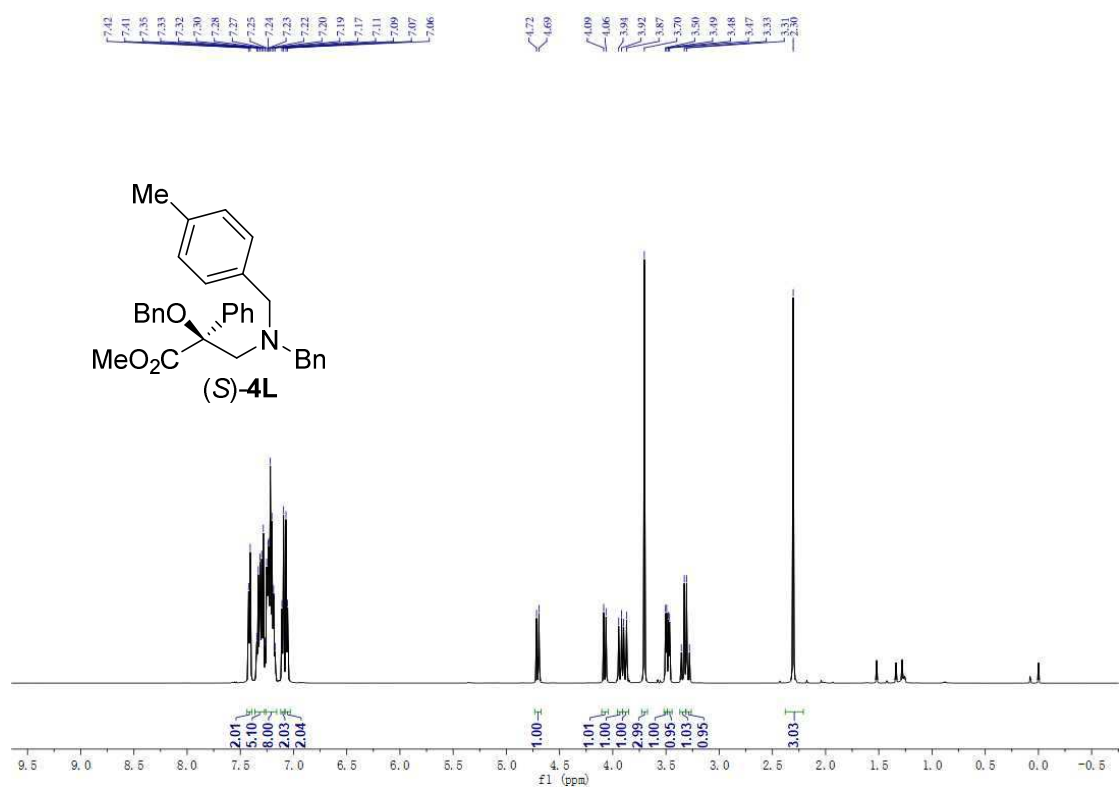
¹H NMR (500 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for 4J



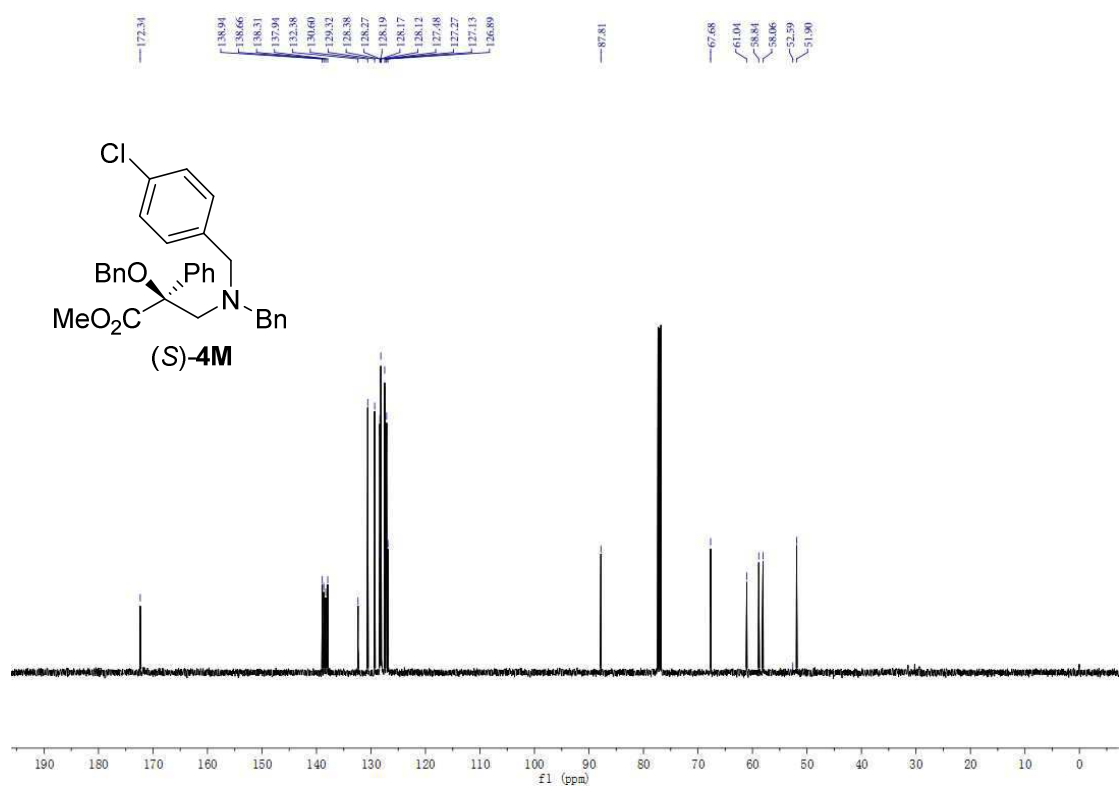
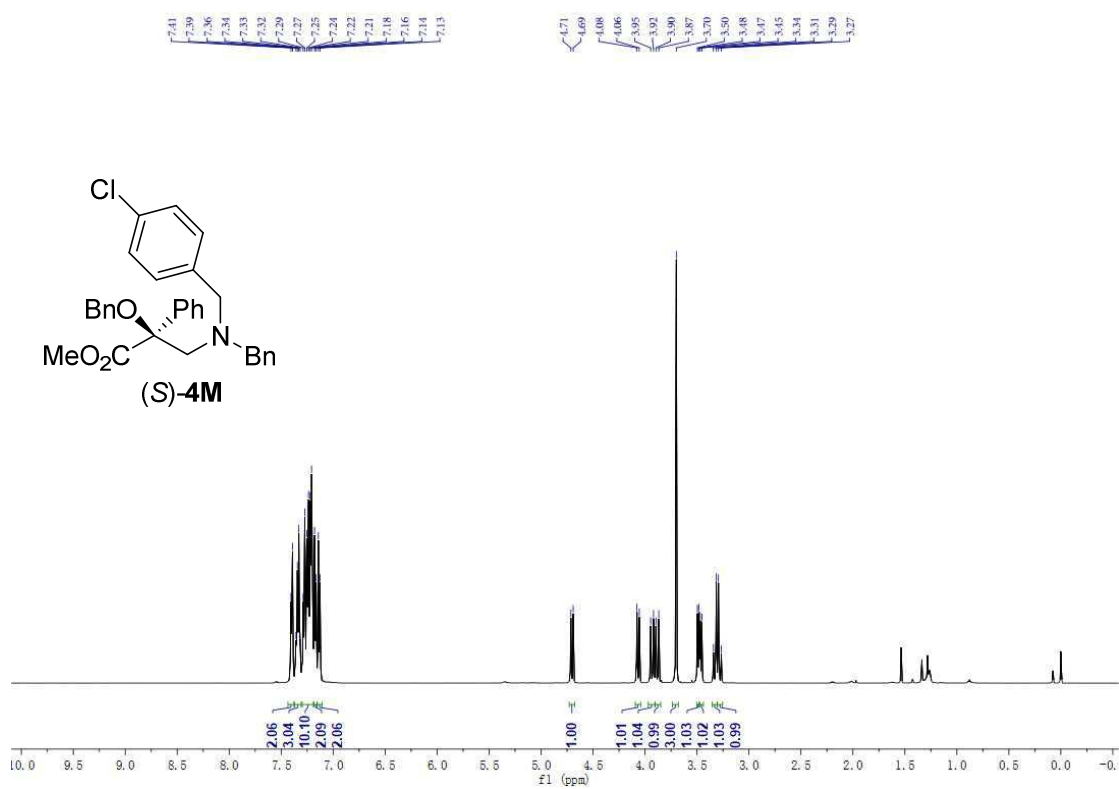
^1H NMR (500 MHz, CDCl_3) and ^{13}C NMR (500 MHz, CDCl_3) spectra for 4K



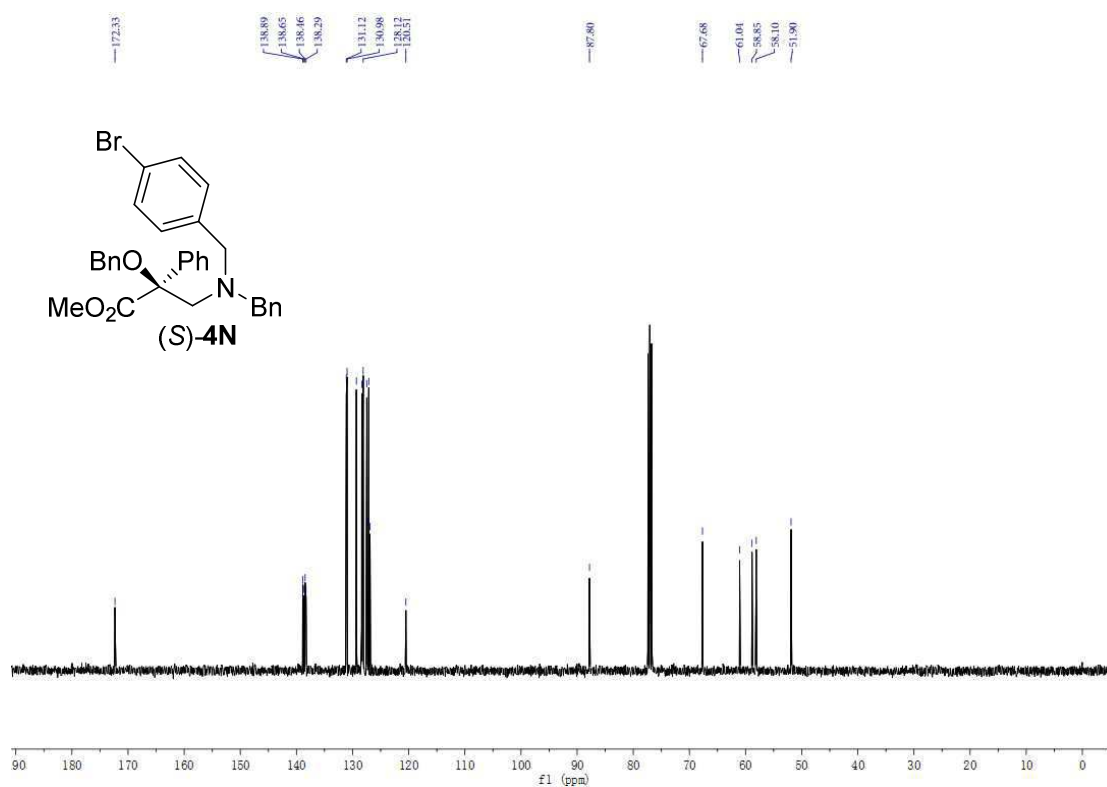
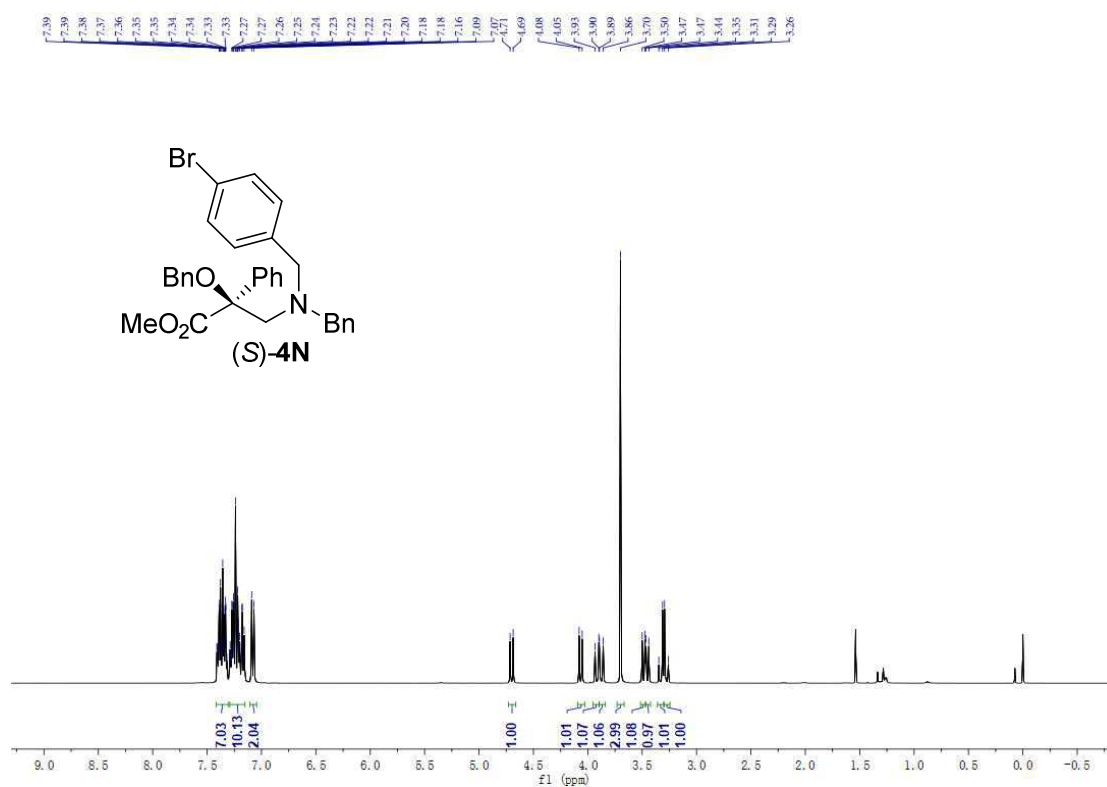
^1H NMR (500 MHz, CDCl_3) and ^{13}C NMR (500 MHz, CDCl_3) spectra for (*S*)-4L



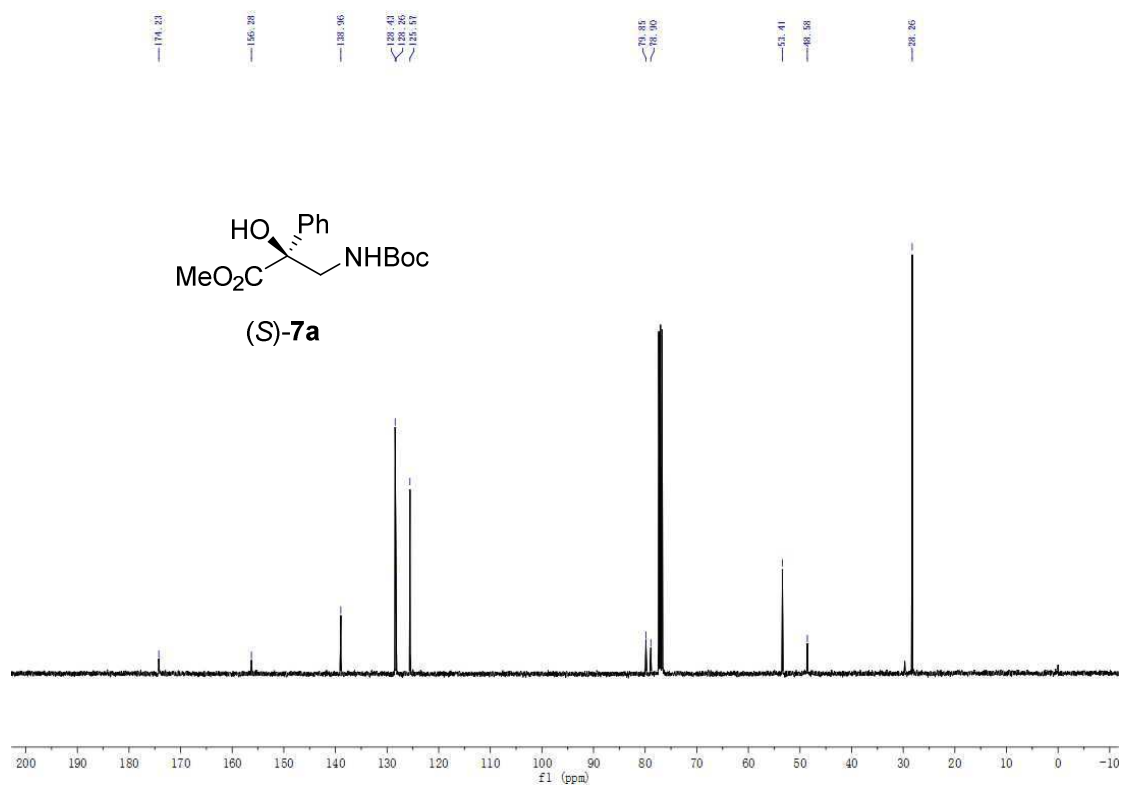
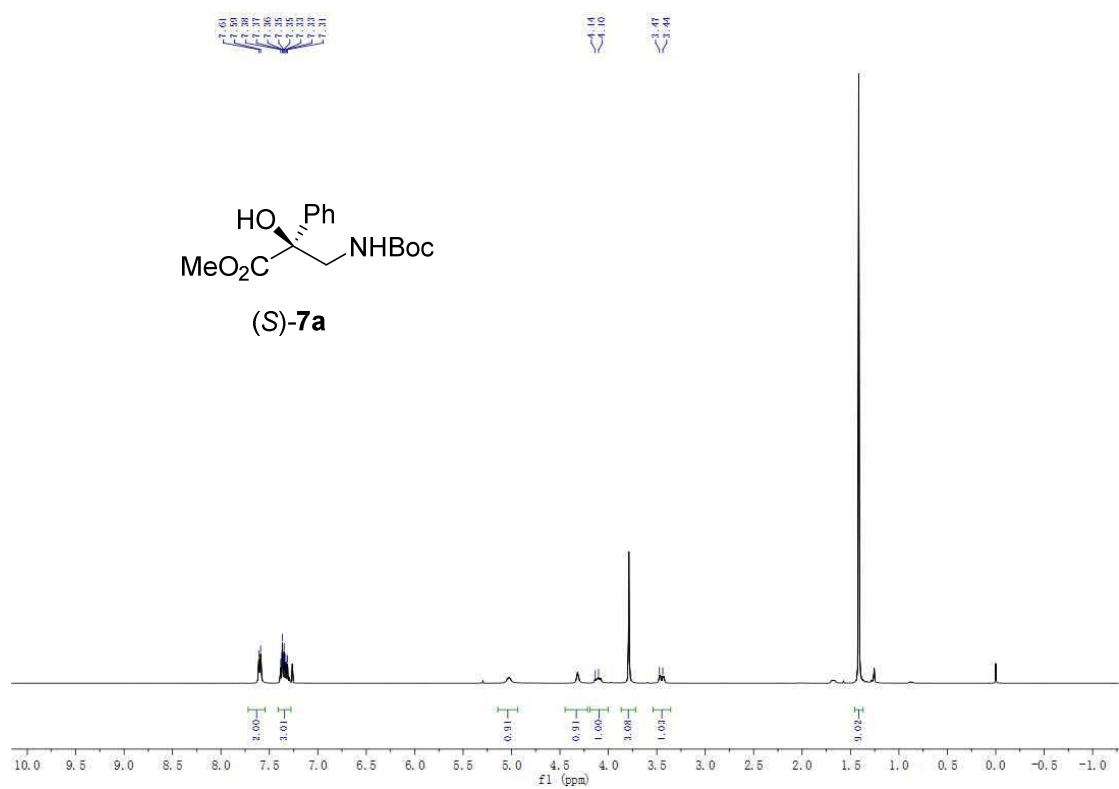
^1H NMR (500 MHz, CDCl_3) and ^{13}C NMR (500 MHz, CDCl_3) spectra for (S)-4M



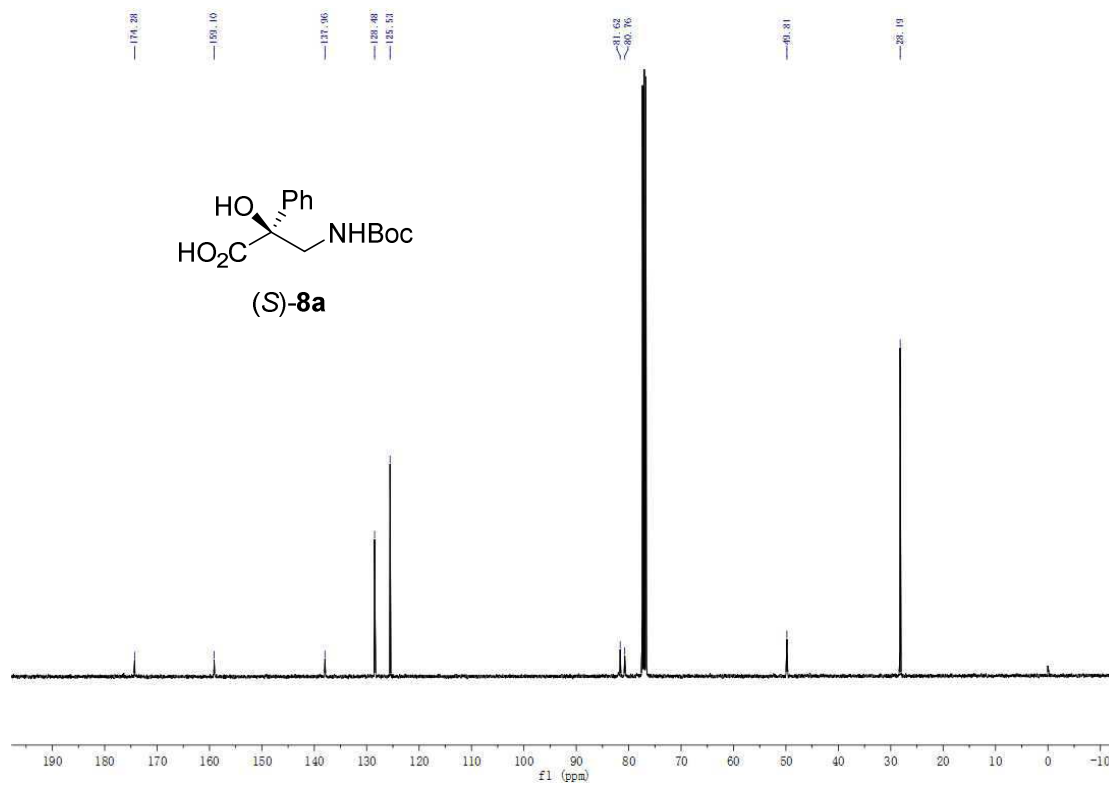
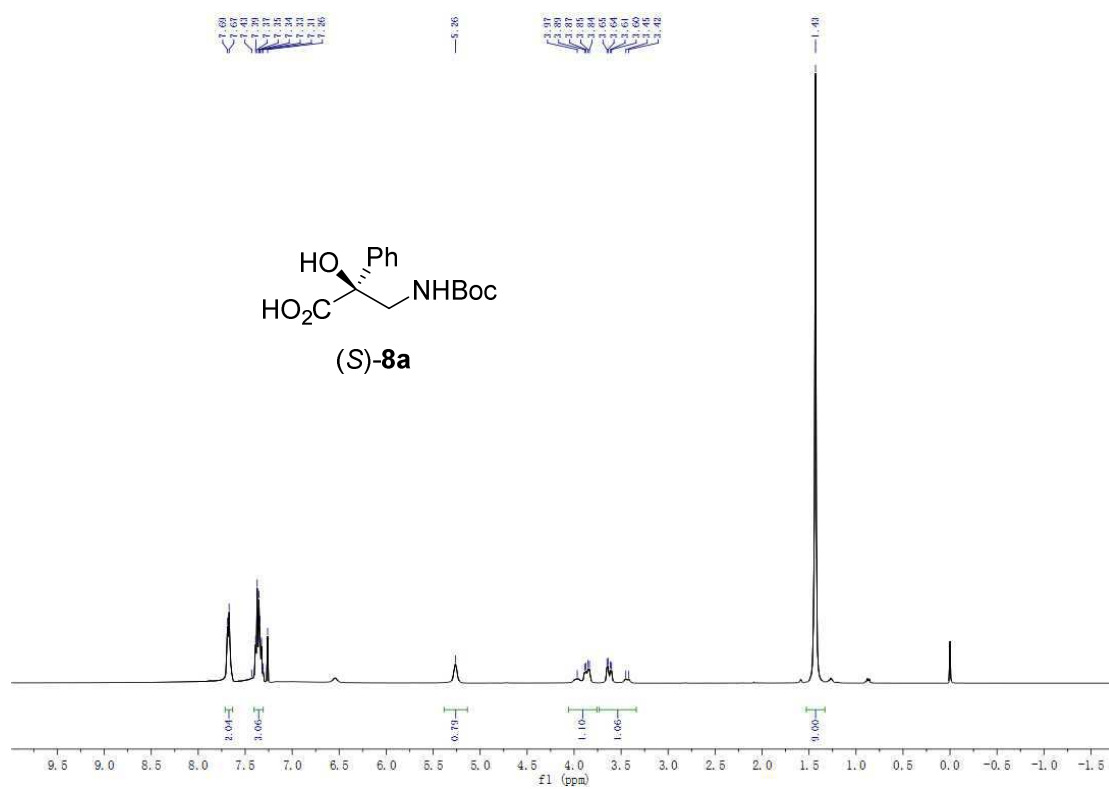
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-4N



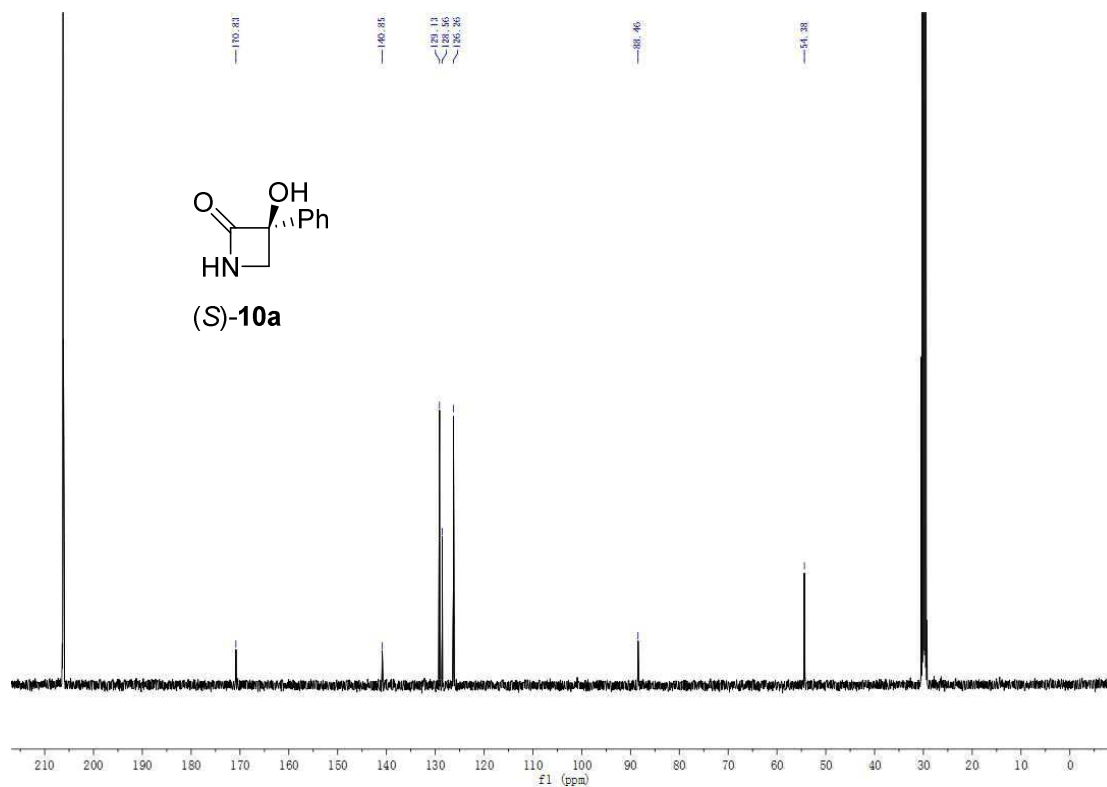
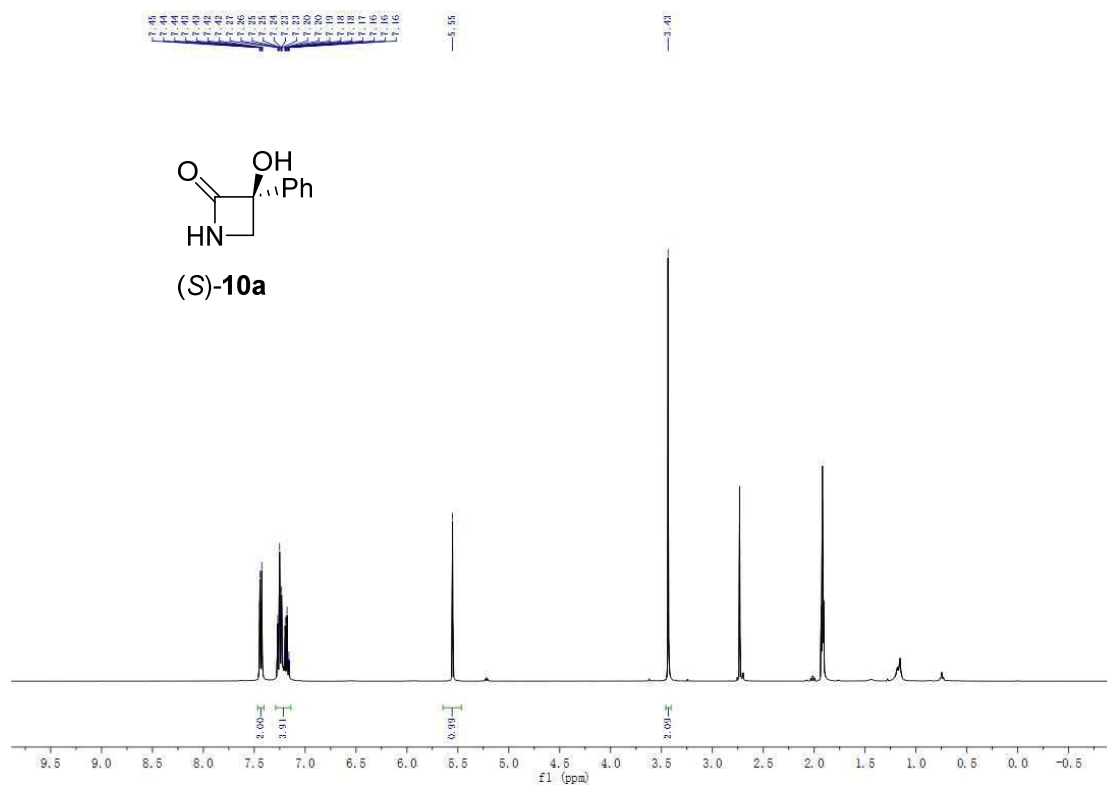
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra for (S)-7a



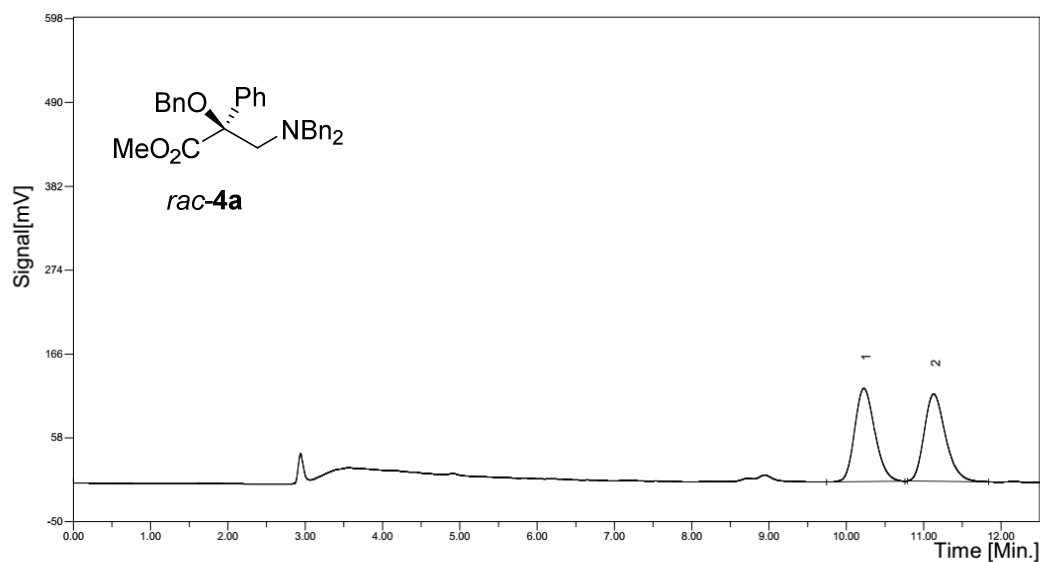
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra for (S)-8a



¹H NMR (400 MHz, Acetone) and ¹³C NMR (100 MHz, Acetone) spectra for (S)-10a

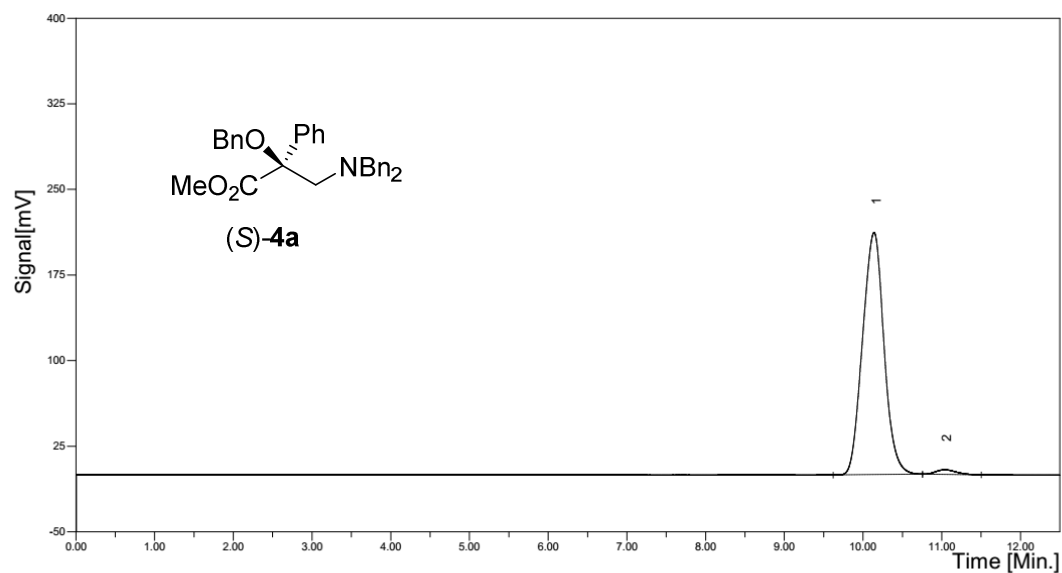


11. HPLC chromatograms of all products



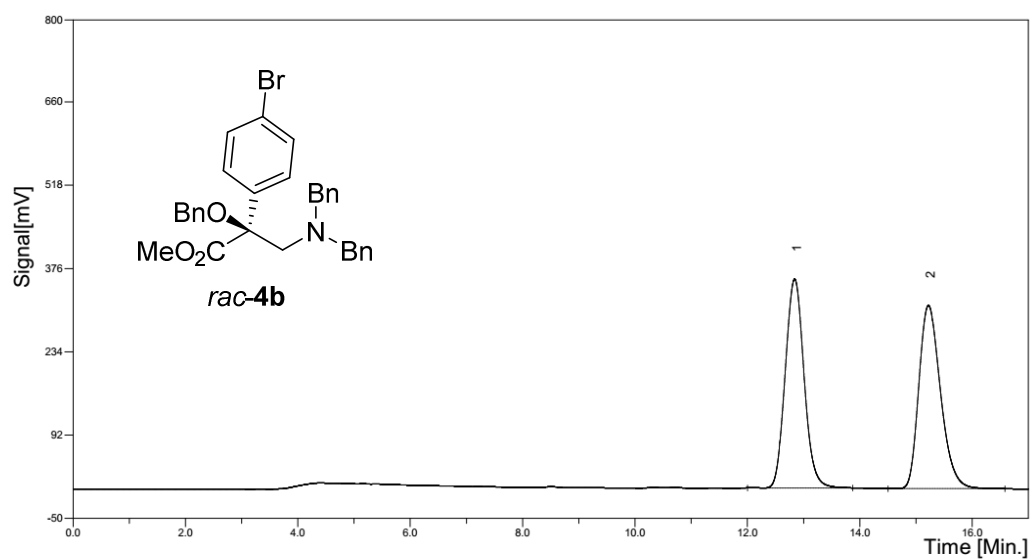
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	10.22667	119.97	2172.36	50.2096	0.0000	100.0000
2	Unknown	11.12917	112.32	2154.23	49.7904	0.0000	100.0000
合计			232.29	4326.59	100		



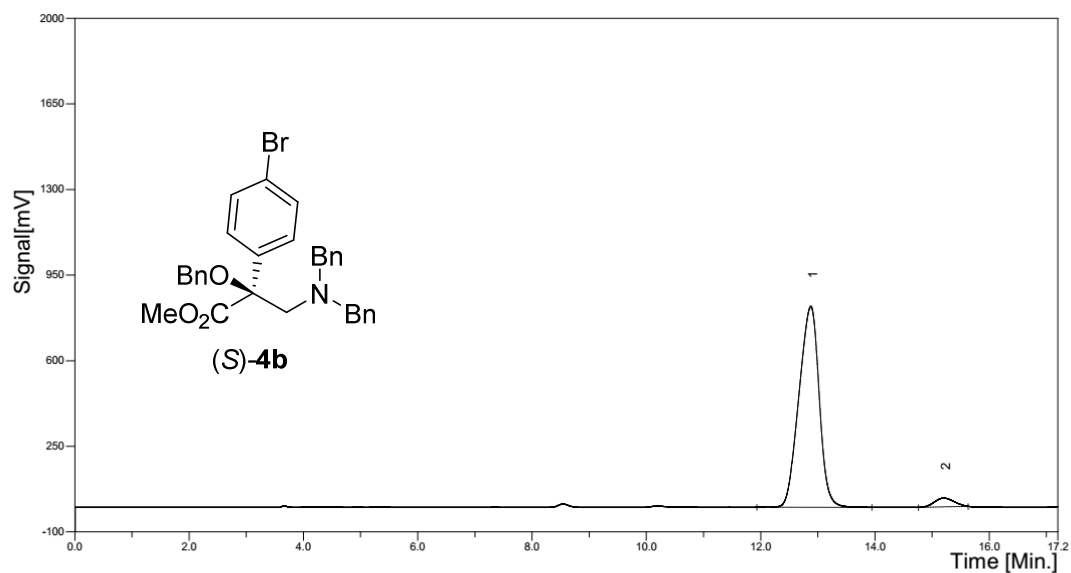
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	10.14000	212.03	4006.15	98.1924	0.0000	0.0000
2	Unknown	11.03667	4.09	73.75	1.8076	0.0000	100.0000
合计			216.12	4079.90	100		



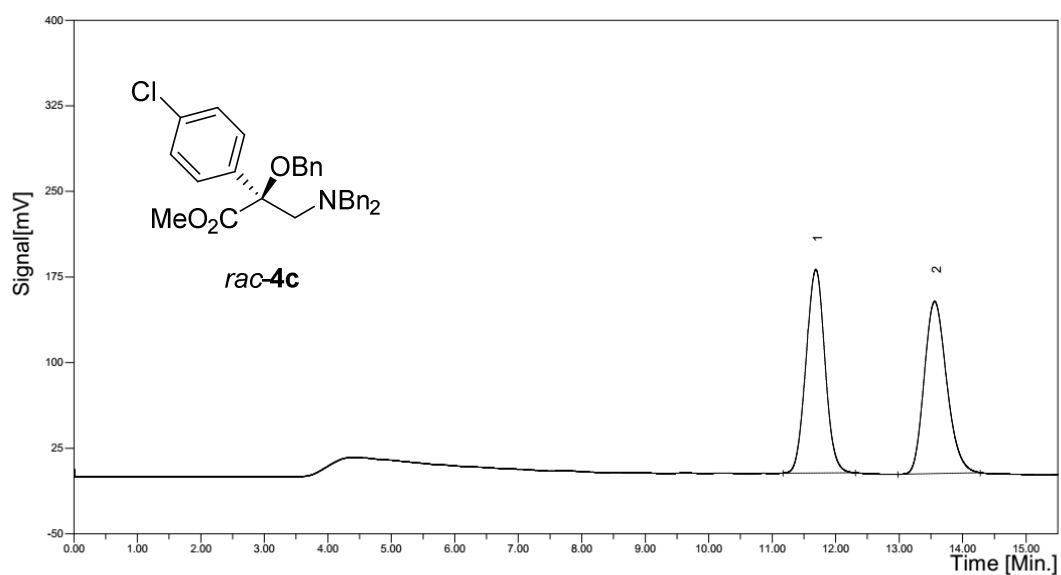
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	12.84083	356.12	8282.41	49.7692	0.0000	100.0000
2	Unknown	15.22167	312.30	8359.23	50.2308	0.0000	100.0000
合计			668.42	16641.63	100		



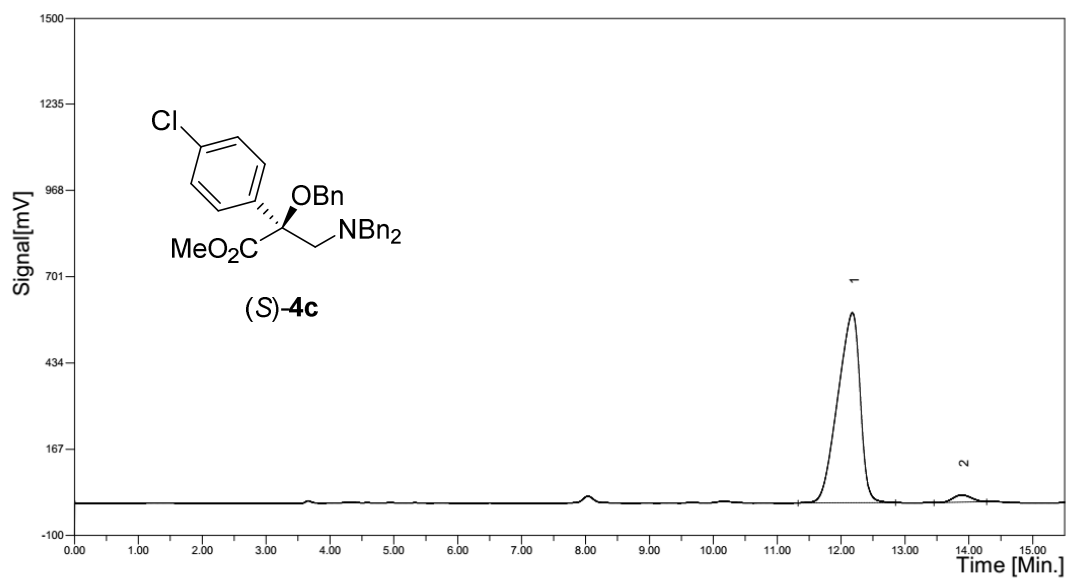
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	12.87667	821.01	20210.69	95.9467	0.0000	0.0000
2	Unknown	15.20333	35.84	853.80	4.0533	0.0000	100.0000
合计			856.85	21064.49	100		



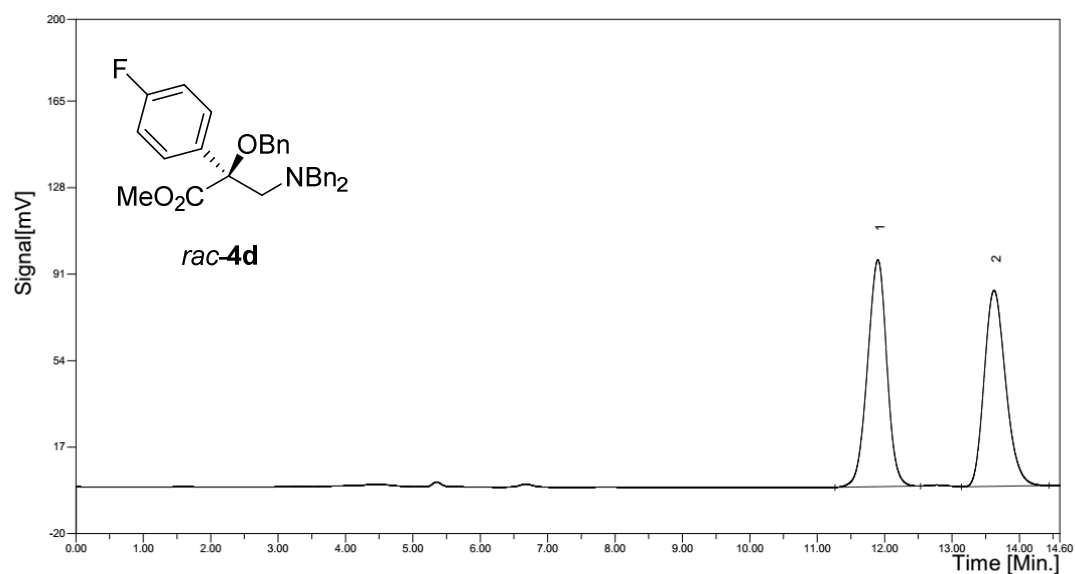
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	11.68667	178.26	3707.76	49.9500	0.0000	100.0000
2	Unknown	13.55833	150.84	3715.18	50.0500	0.0000	100.0000
合计			329.10	7422.95	100		



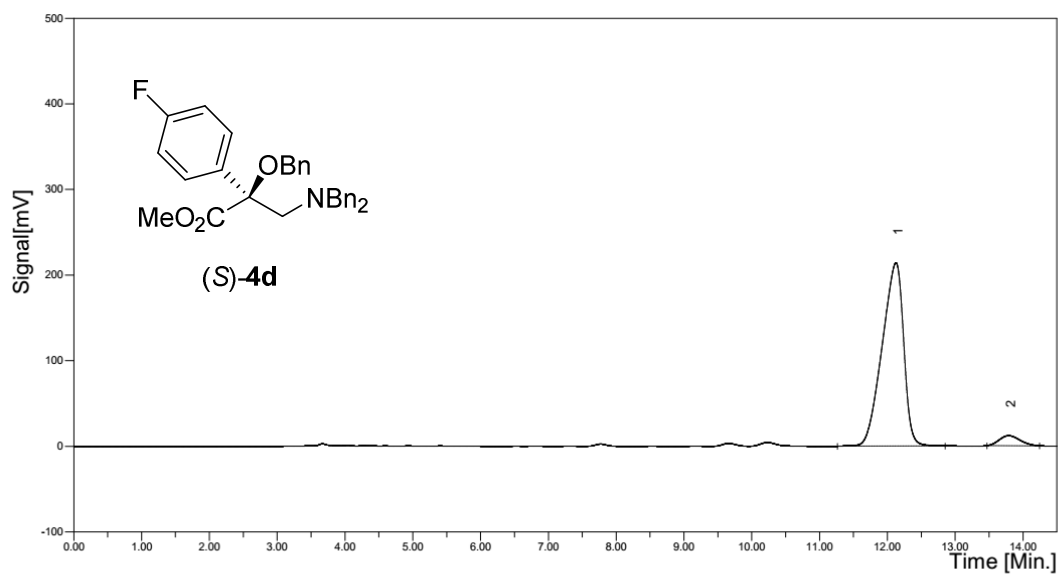
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	12.17583	587.58	14298.88	97.0413	0.0000	100.0000
2	Unknown	13.88833	22.09	435.96	2.9587	0.0000	100.0000
合计			609.67	14734.84	100		



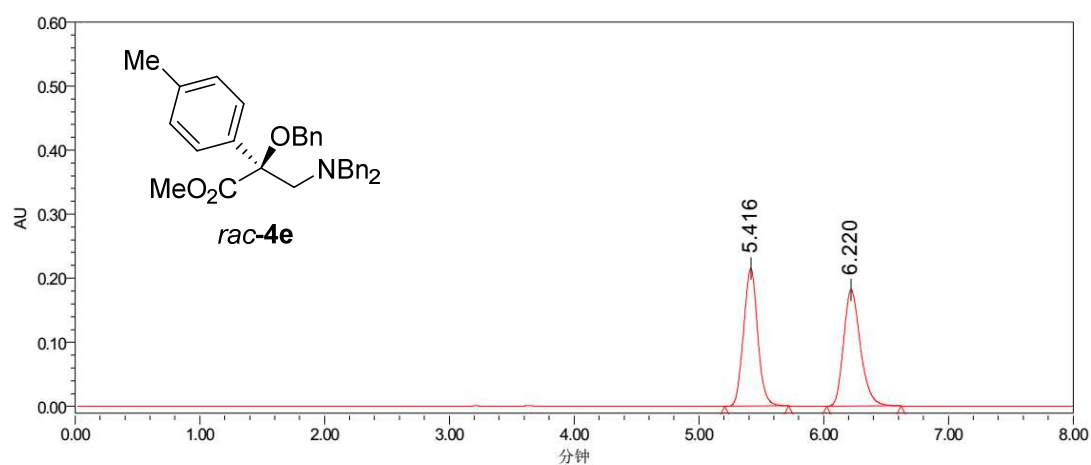
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	11.90083	97.03	1931.92	51.0697	0.0000	100.0000
2	Unknown	13.62417	83.80	1850.98	48.9303	0.0000	100.0000
合计			180.83	3782.90	100		



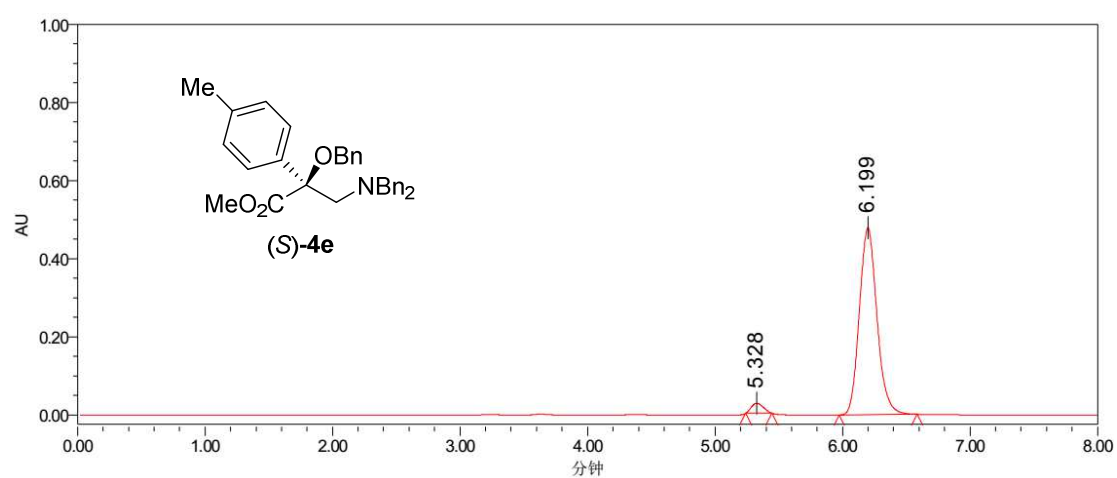
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	12.12583	214.15	4722.66	95.0297	0.0000	0.0000
2	Unknown	13.78750	11.68	247.01	4.9703	0.0000	100.0000
合计			225.83	4969.67	100		



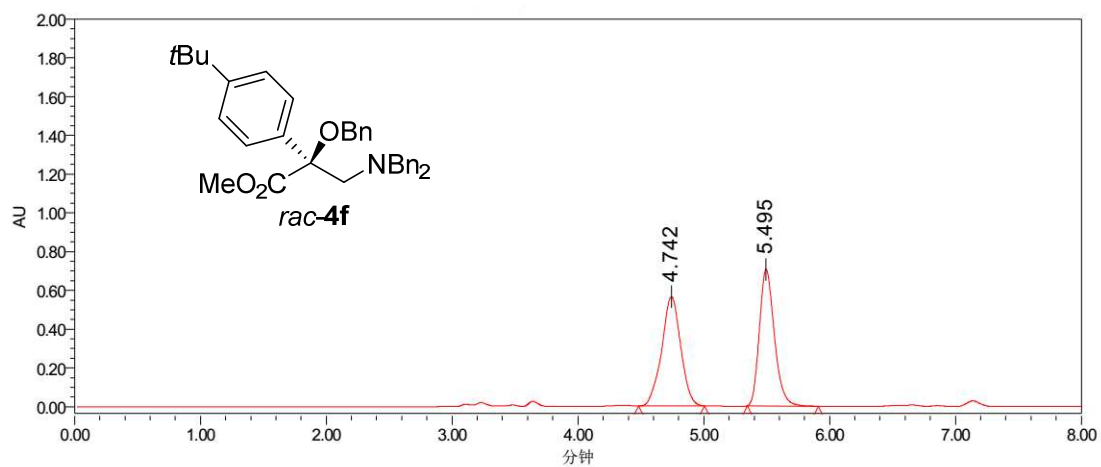
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.416	1688030	215164	49.86
2	6.220	1697281	181639	50.14



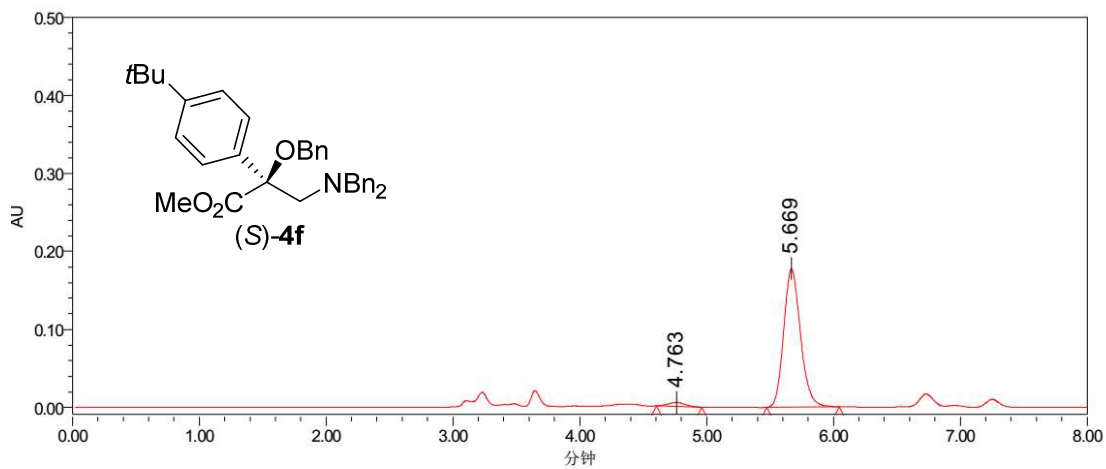
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.328	165007	25676	3.48
2	6.199	4577282	478566	96.52



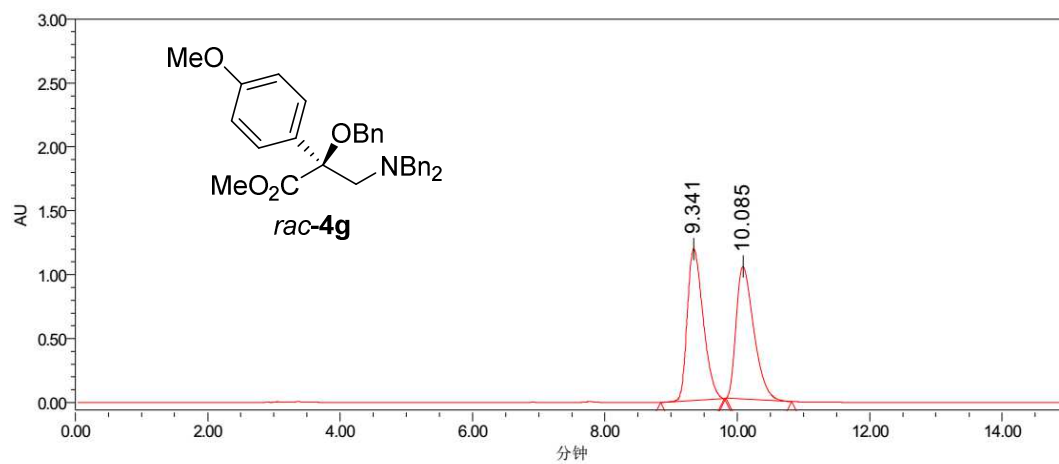
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	4.742	5924872	563820	50.28
2	5.495	5859394	703783	49.72



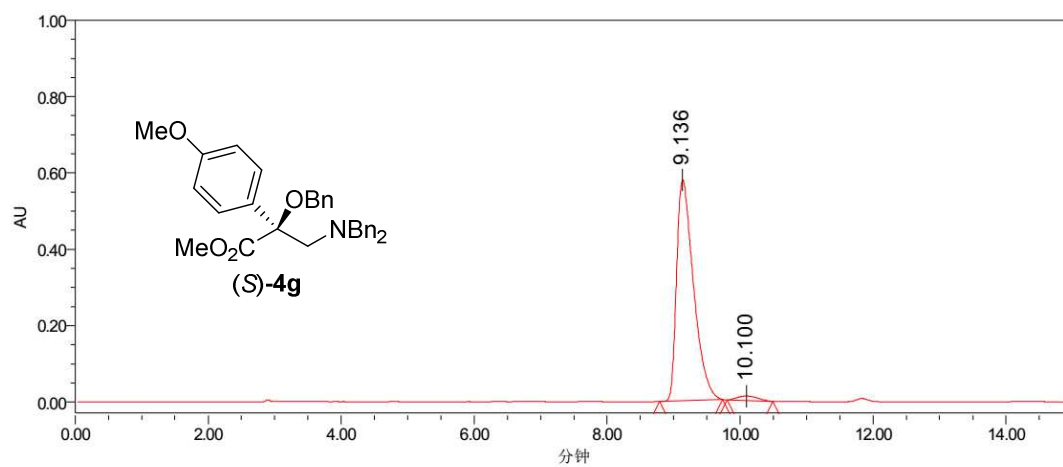
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	4.763	47260	5132	2.81
2	5.669	1634568	177347	97.19



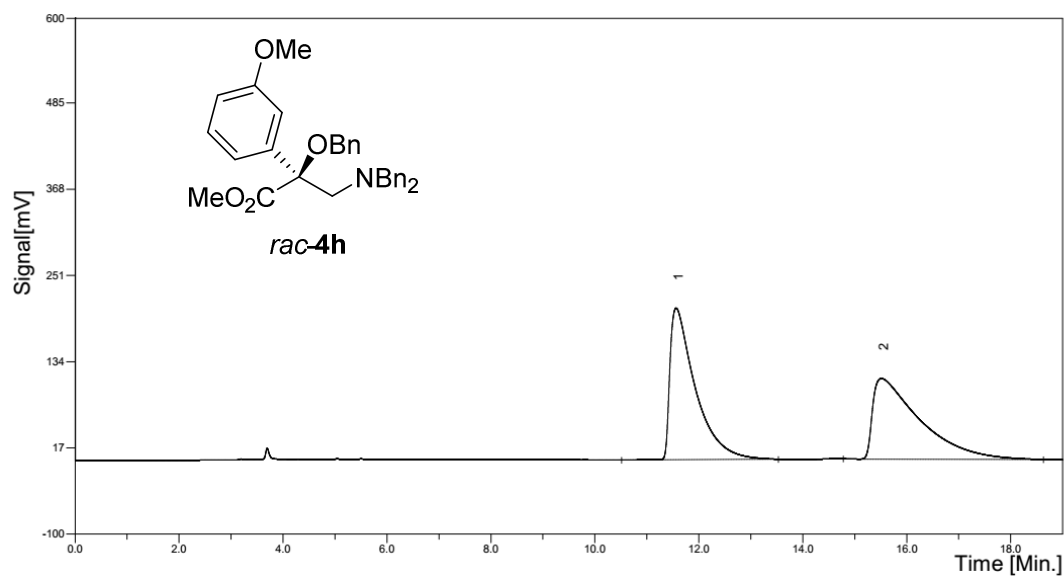
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		9.341	19631589	1186152	50.37
2		10.085	19343266	1036473	49.63



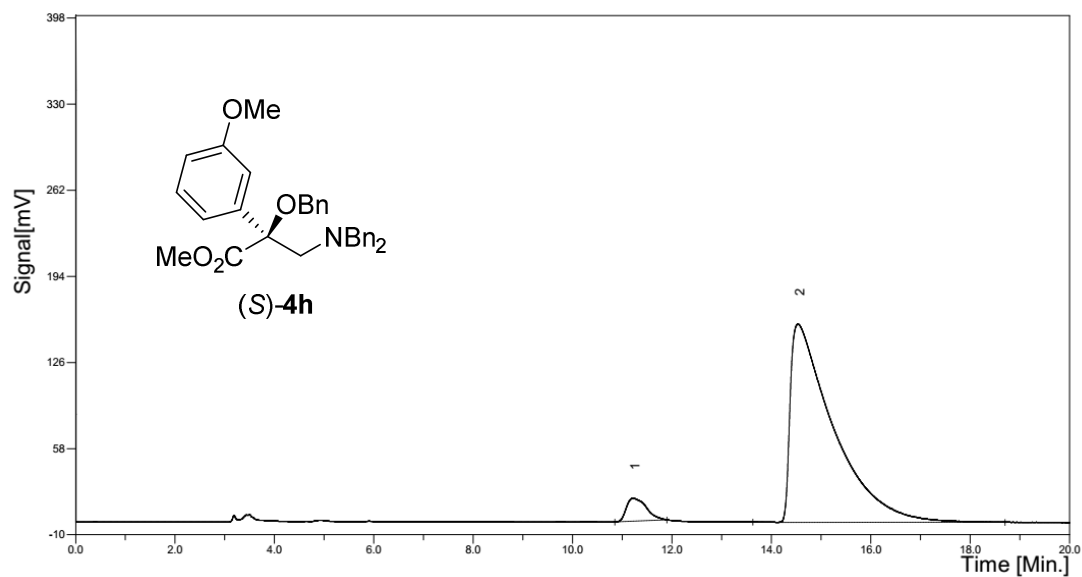
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		9.136	10149347	578997	97.61
2		10.100	248743	11761	2.39



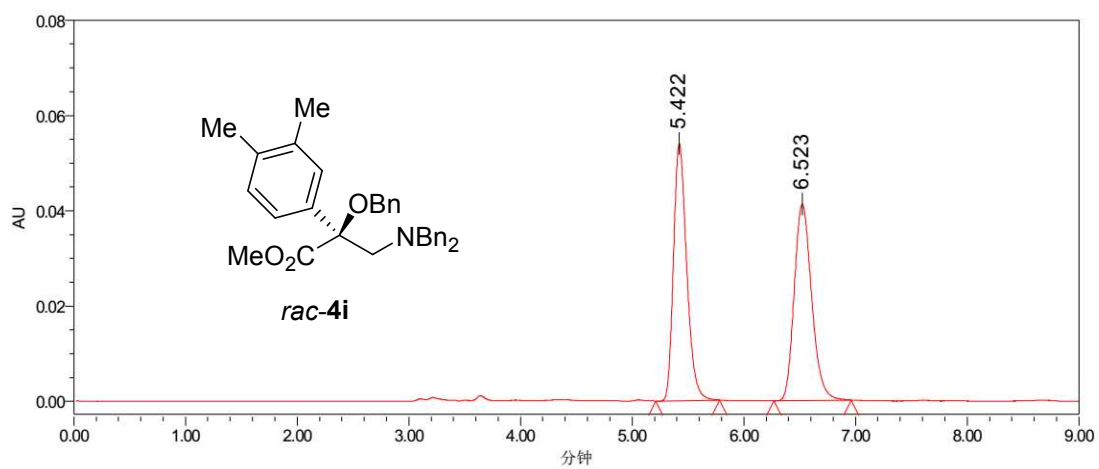
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	11.56333	205.73	6949.28	50.4434	0.0000	0.0000
2	Unknown	15.51417	109.15	6827.12	49.5566	0.0000	0.0000
合计			314.88	13776.41	100		



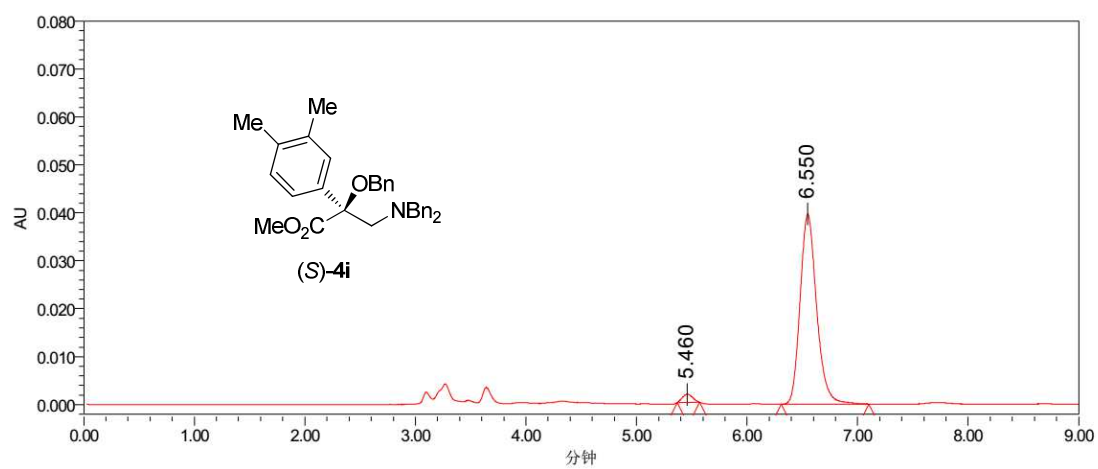
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	11.21333	18.17	502.19	5.1015	0.0000	100.0000
2	Unknown	14.53167	156.25	9341.70	94.8985	0.0000	0.0000
合计			174.42	9843.89	100		



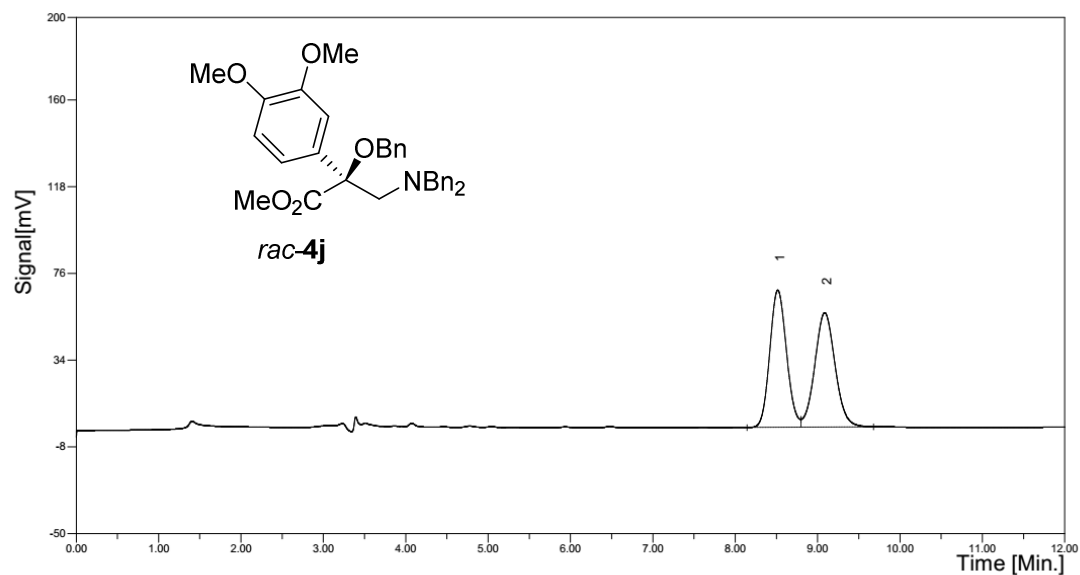
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.422	440391	53946	49.67
2	6.523	446250	41229	50.33



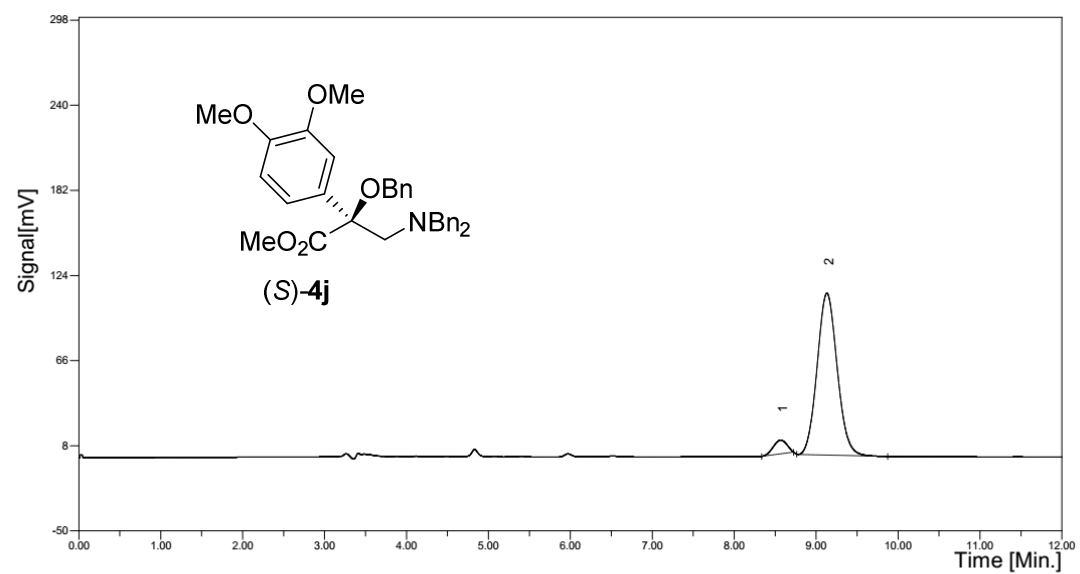
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.460	11353	1725	2.68
2	6.550	411553	39699	97.32



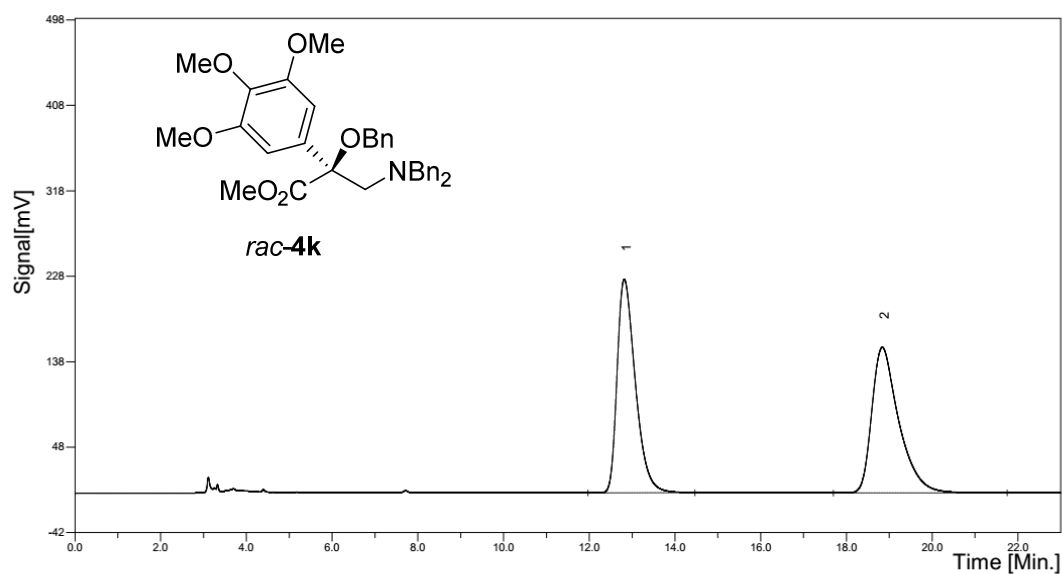
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	浓 度	样品含量(%)
1	Unknown	8.51667	66.40	939.53	0.0000	0.0000
2	Unknown	9.08667	55.38	949.10	0.0000	0.0000
合计			121.78	1888.63		



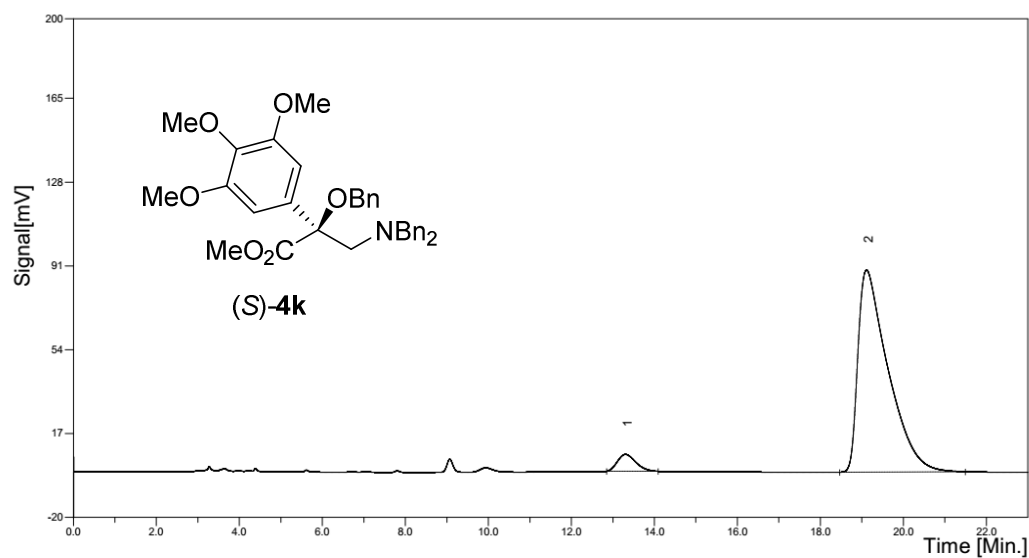
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	8.56667	9.39	108.32	5.4822	0.0000	100.0000
2	Unknown	9.13167	110.13	1867.51	94.5178	0.0000	100.0000
合计			119.51	1975.83	100		



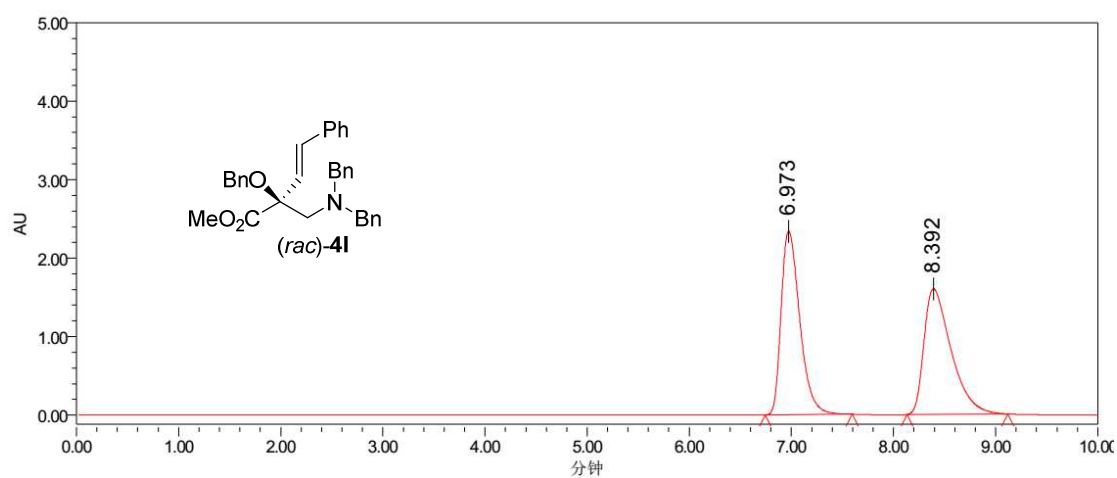
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	12.81667	224.72	6619.78	49.7033	0.0000	100.0000
2	Unknown	18.83667	153.29	6698.80	50.2967	0.0000	100.0000
合计			378.00	13318.58	100		



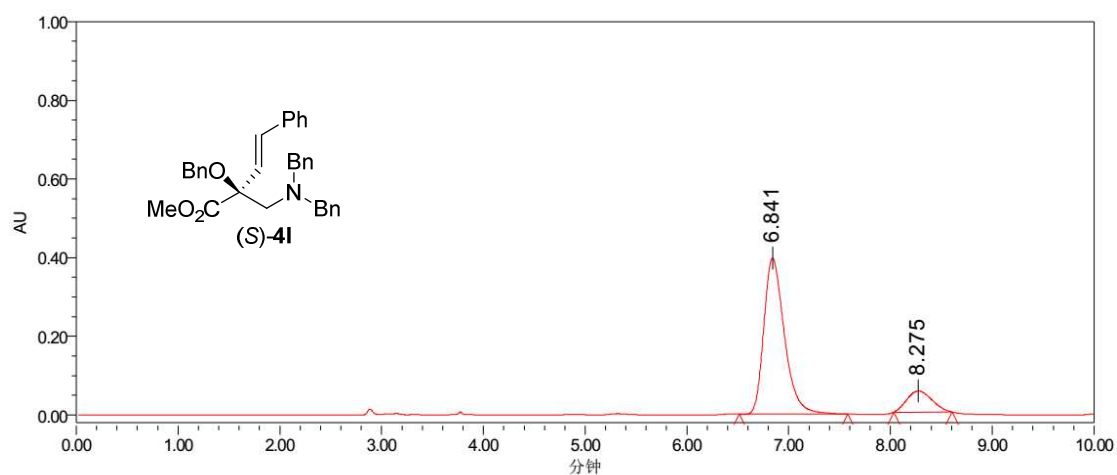
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	13.30250	7.48	229.76	4.8713	0.0000	0.0000
2	Unknown	19.11083	89.25	4486.81	95.1287	0.0000	0.0000
合计			96.73	4716.57	100		



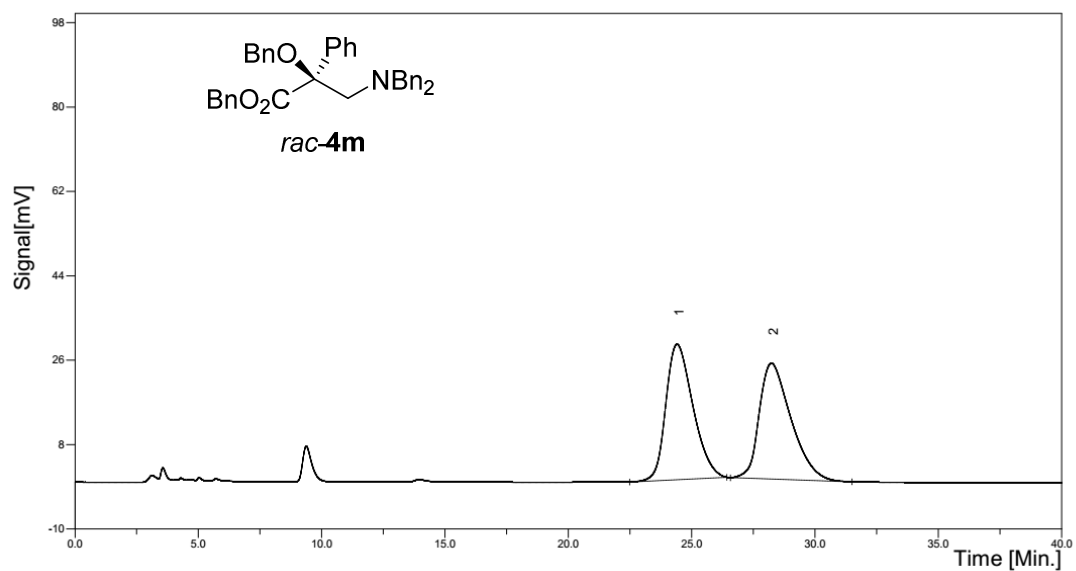
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.973	29661647	2338941	50.08
2		8.392	29571682	1599249	49.92



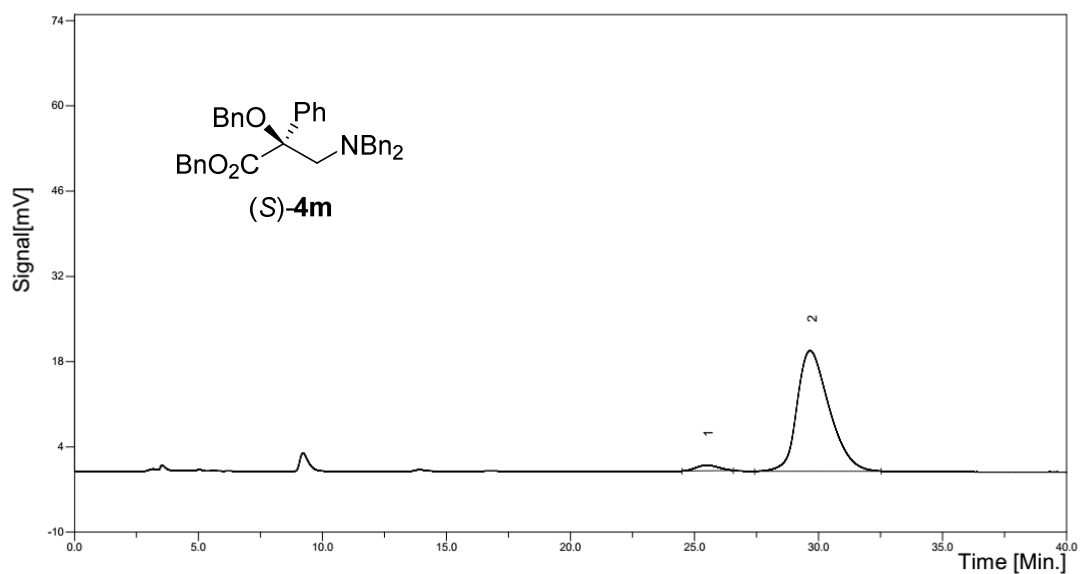
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.841	5572420	396472	85.82
2		8.275	920872	53681	14.18



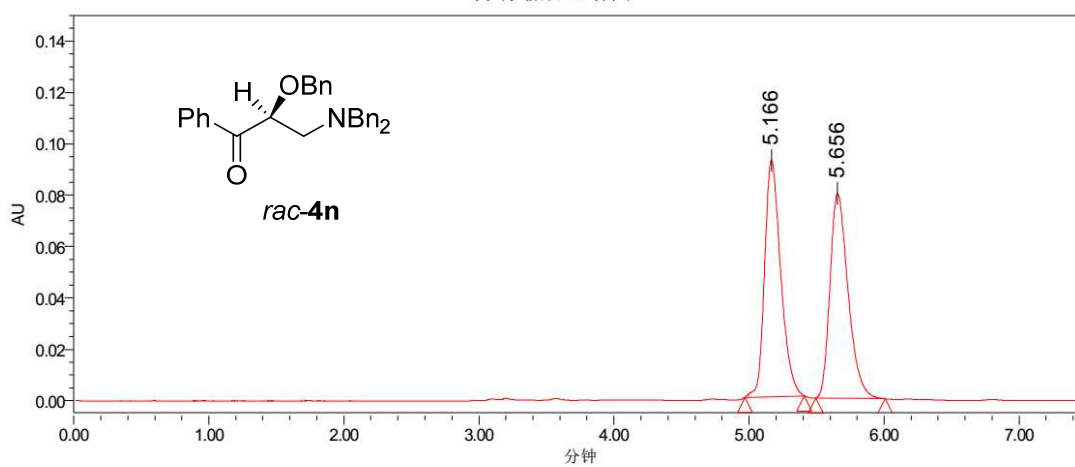
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	24.40000	28.89	2203.48	50.0298	0.0000	100.0000
2	Unknown	28.23000	24.70	2200.86	49.9702	0.0000	0.0000
合计			53.59	4404.34	100		



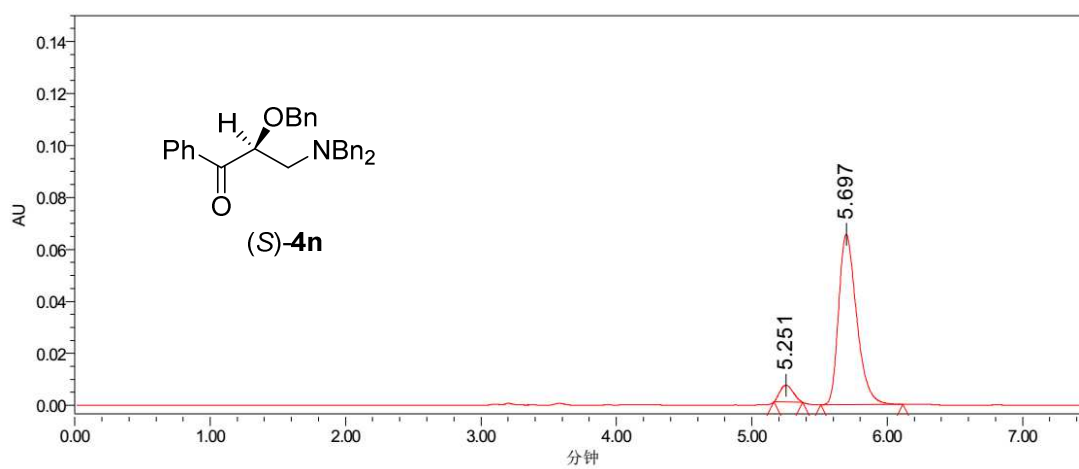
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	25.46750	0.91	57.19	3.1198	0.0000	100.0000
2	Unknown	29.65667	19.81	1775.92	96.8802	0.0000	0.0000
合计			20.72	1833.11	100		



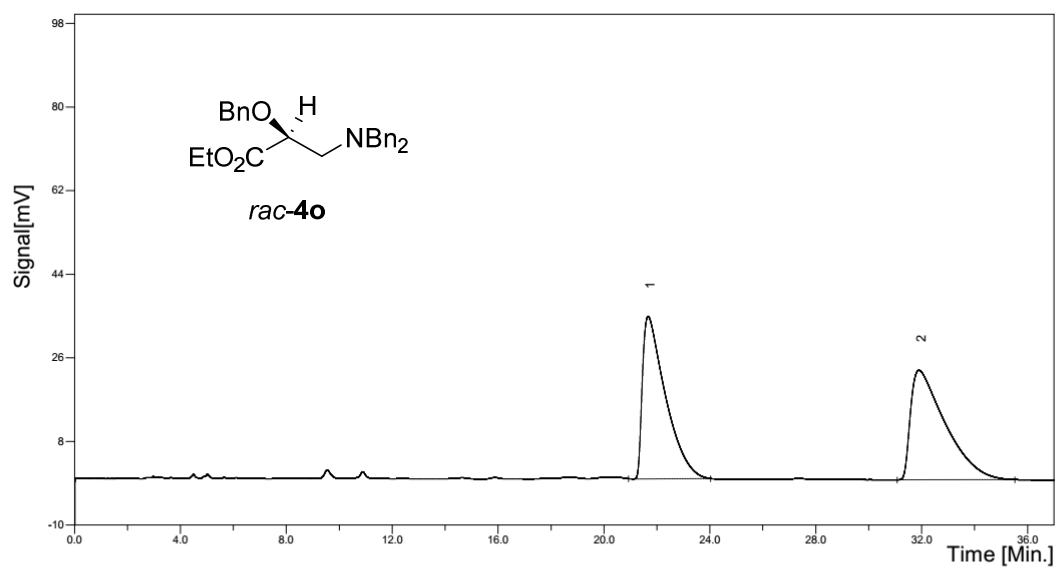
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.166	763976	92068	50.67
2	5.656	743678	79702	49.33



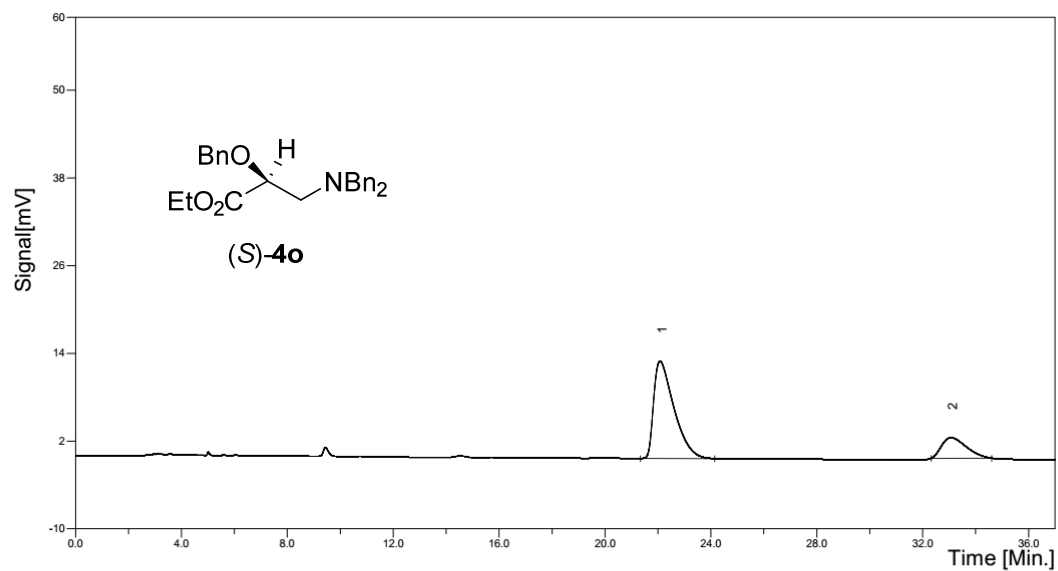
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.251	43918	6488	6.77
2	5.697	604487	65535	93.23



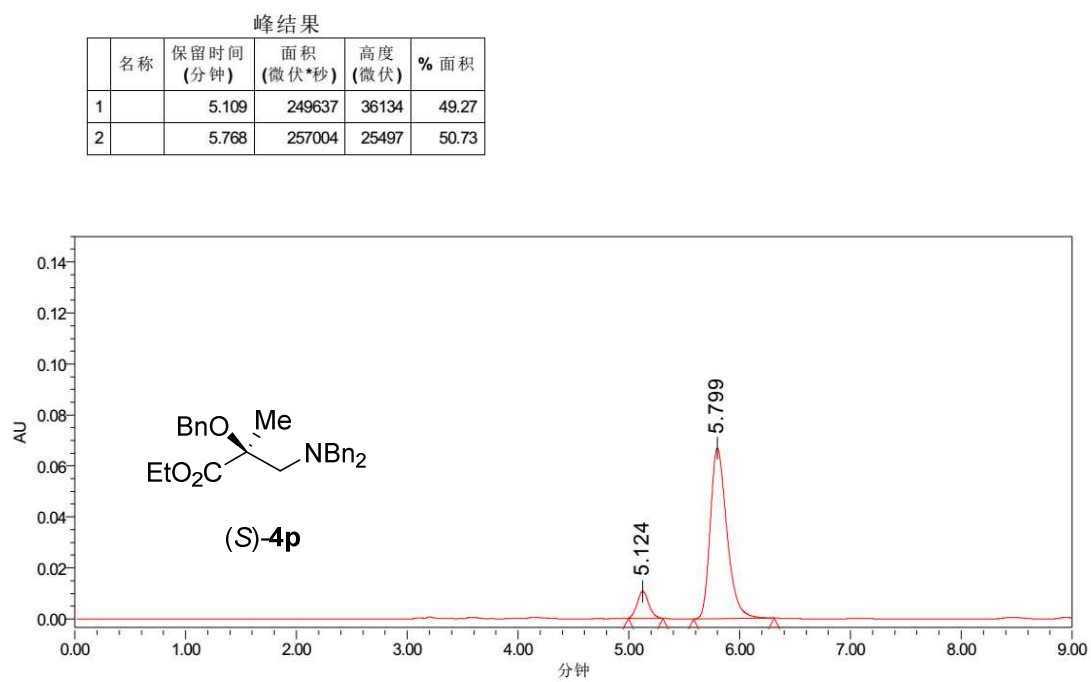
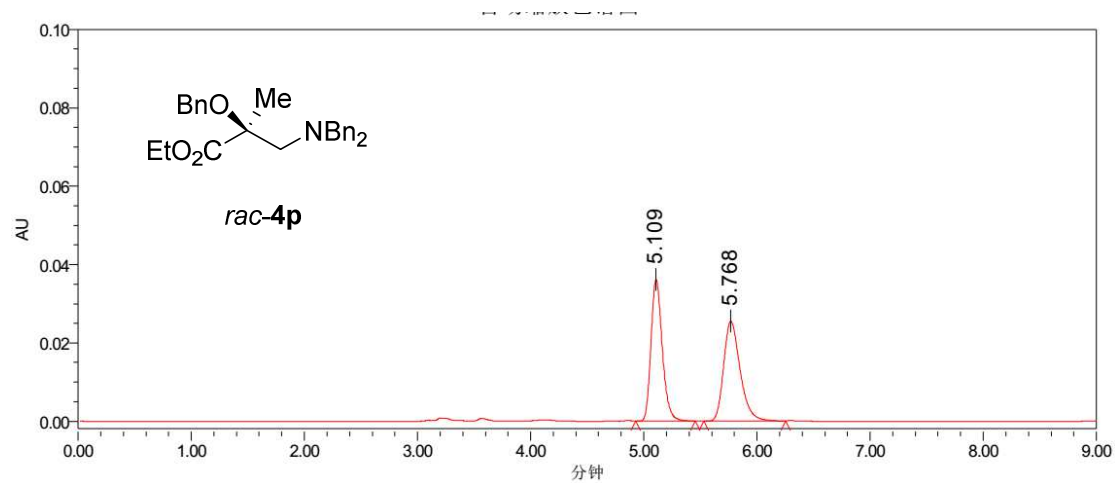
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	21.66500	34.94	2103.27	49.6371	0.0000	100.0000
2	Unknown	31.90000	23.57	2134.03	50.3629	0.0000	0.0000
合计			58.51	4237.31	100		



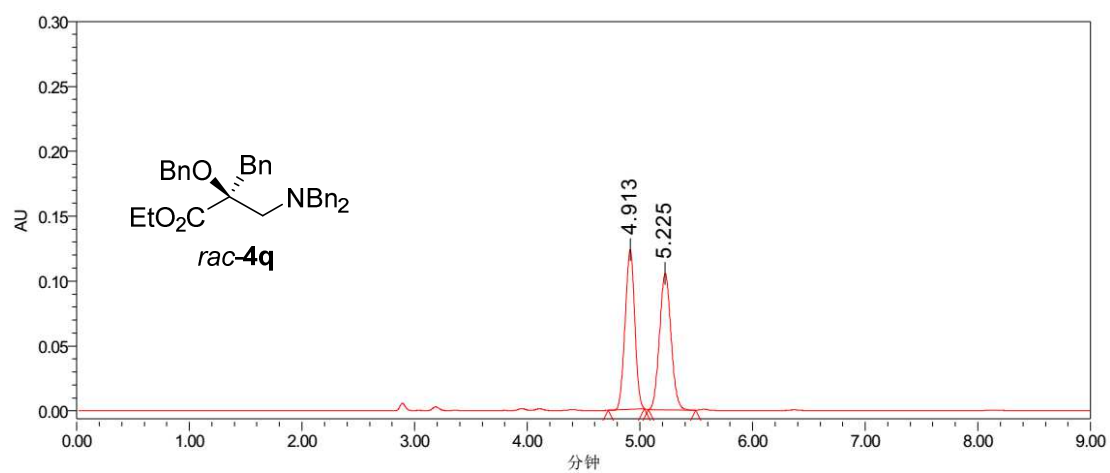
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	22.07333	13.33	707.63	79.4818	0.0000	100.0000
2	Unknown	33.06417	2.82	182.68	20.5182	0.0000	0.0000
合计			16.15	890.31	100		



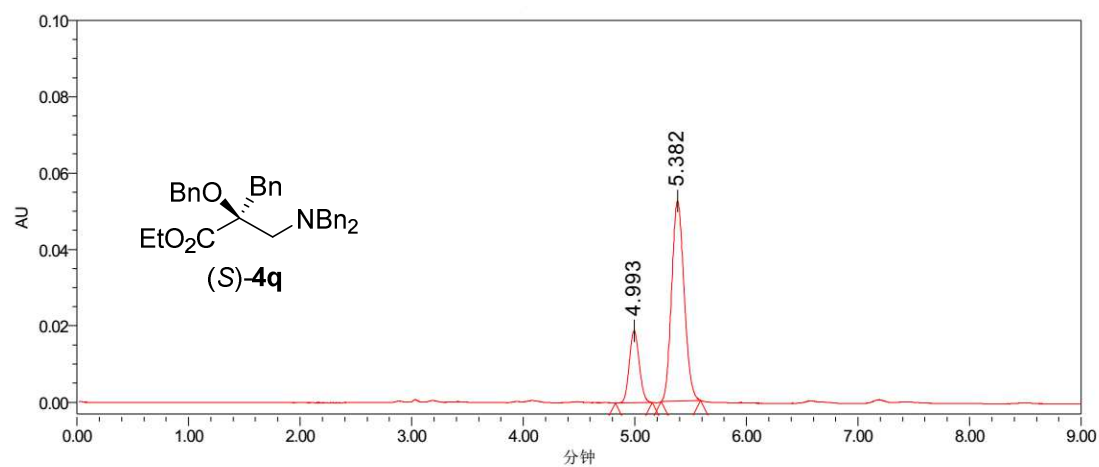
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.124	76880	10648	9.97
2	5.799	694394	66863	90.03



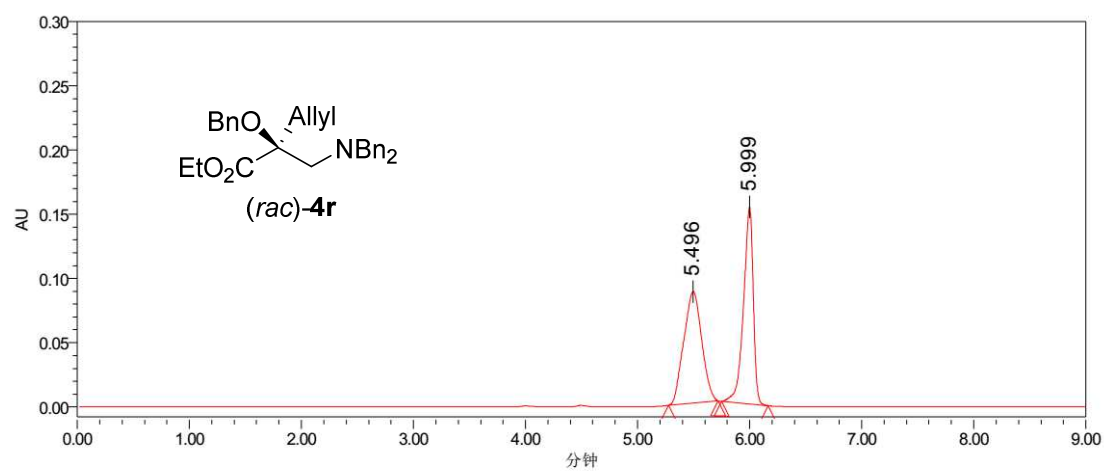
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	4.913	731623	122875	49.51
2	5.225	746214	104925	50.49



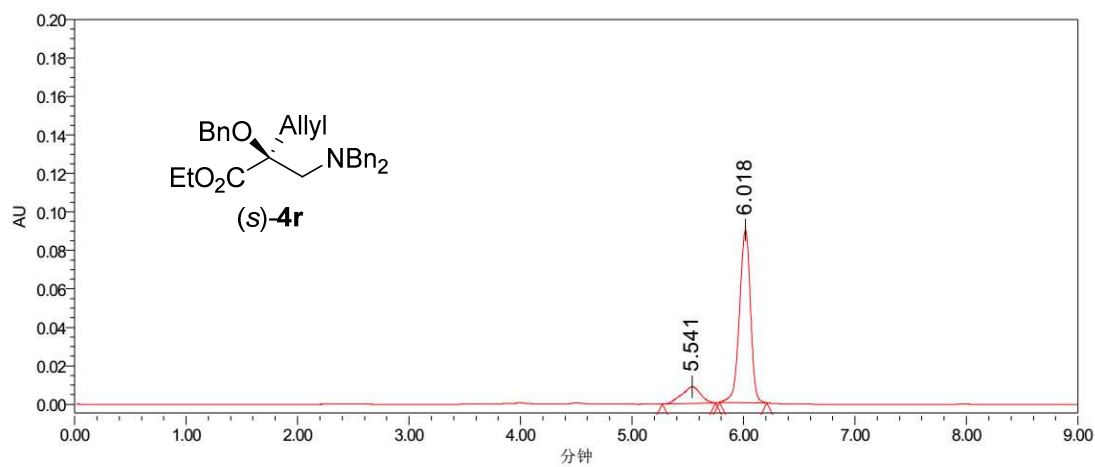
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	4.993	116861	18845	22.28
2	5.382	407532	52356	77.72



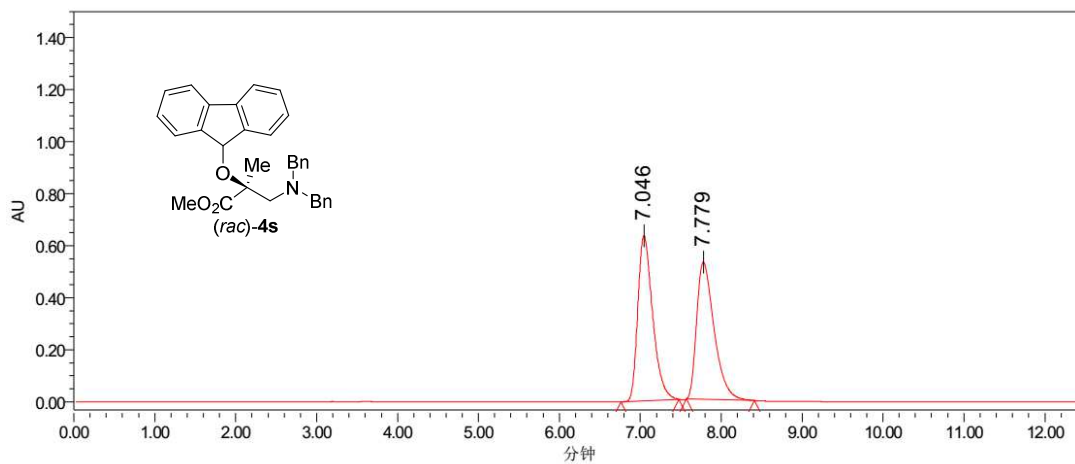
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		5.496	970733	86801	50.88
2		5.999	937154	153470	49.12



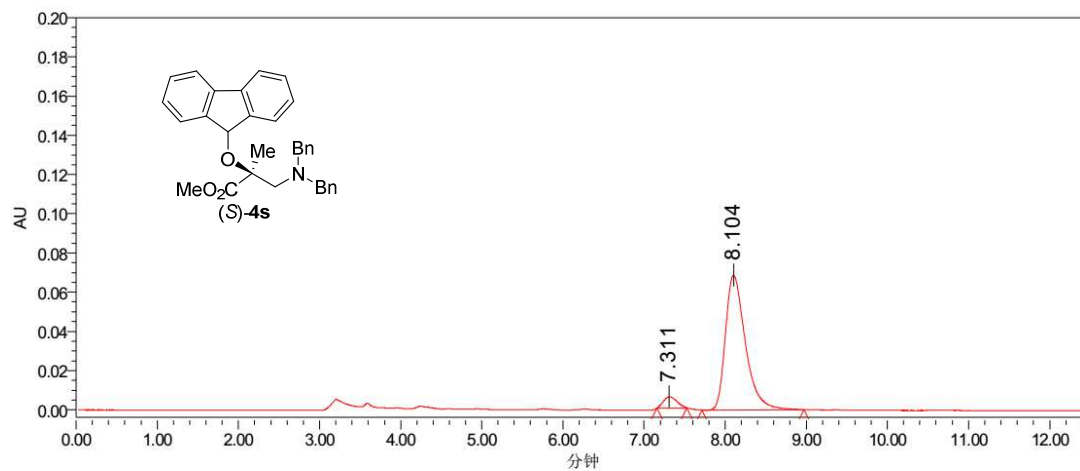
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		5.541	99282	8565	13.88
2		6.018	616215	89690	86.12



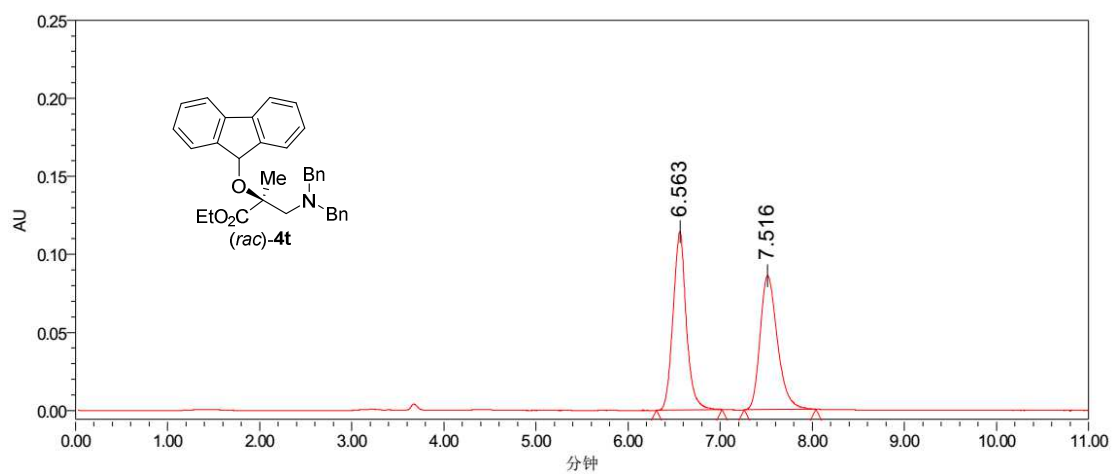
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	7.046	8039425	633970	50.21
2	7.779	7971819	528079	49.79



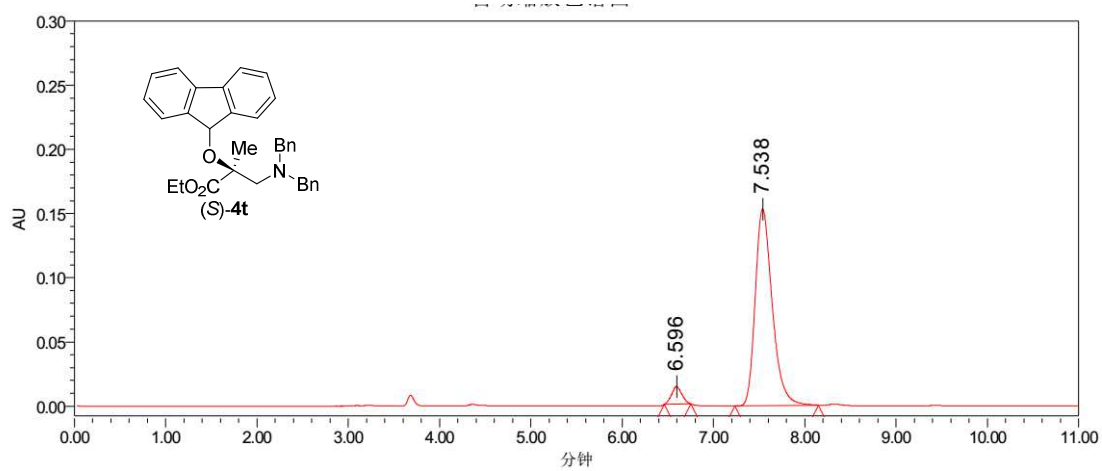
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	7.311	66116	5709	5.35
2	8.104	1169262	68672	94.65



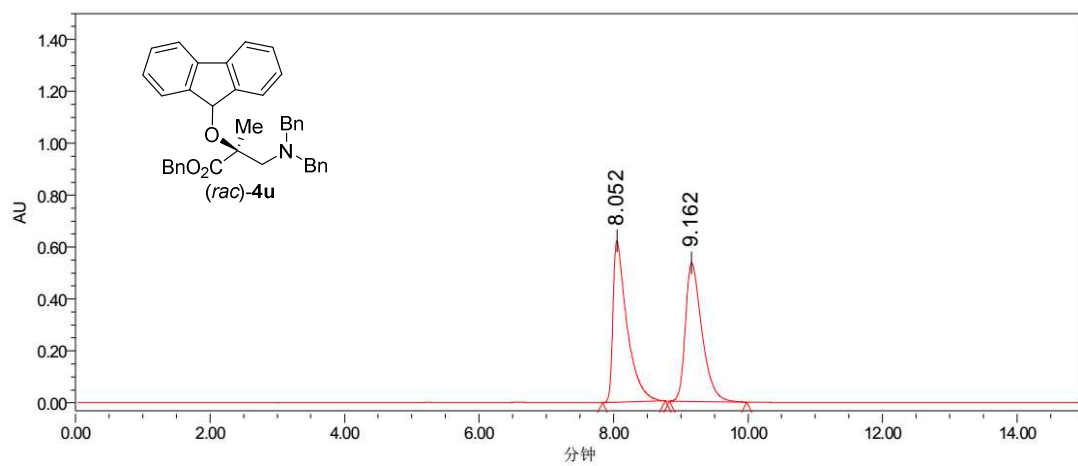
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.563	1139353	114262	50.28
2		7.516	1126838	85876	49.72



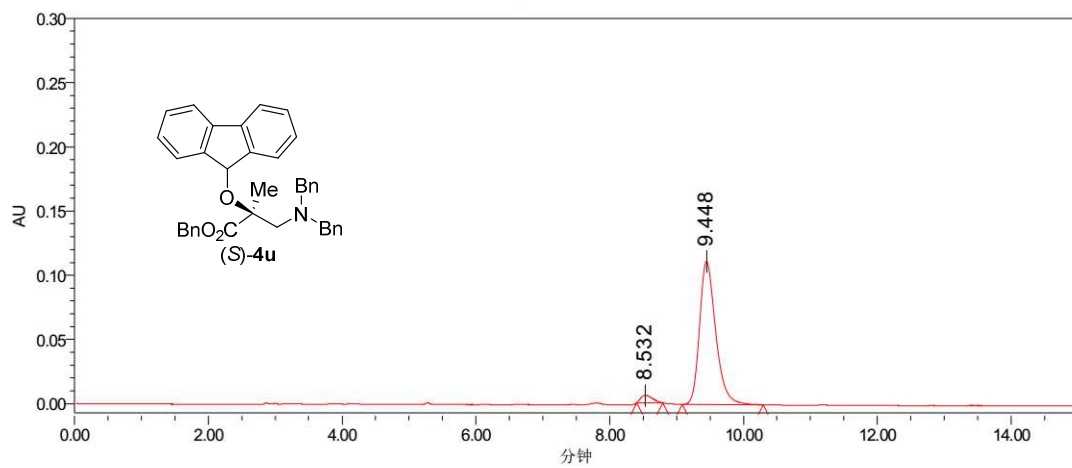
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.596	107159	13716	5.10
2		7.538	1995297	153271	94.90



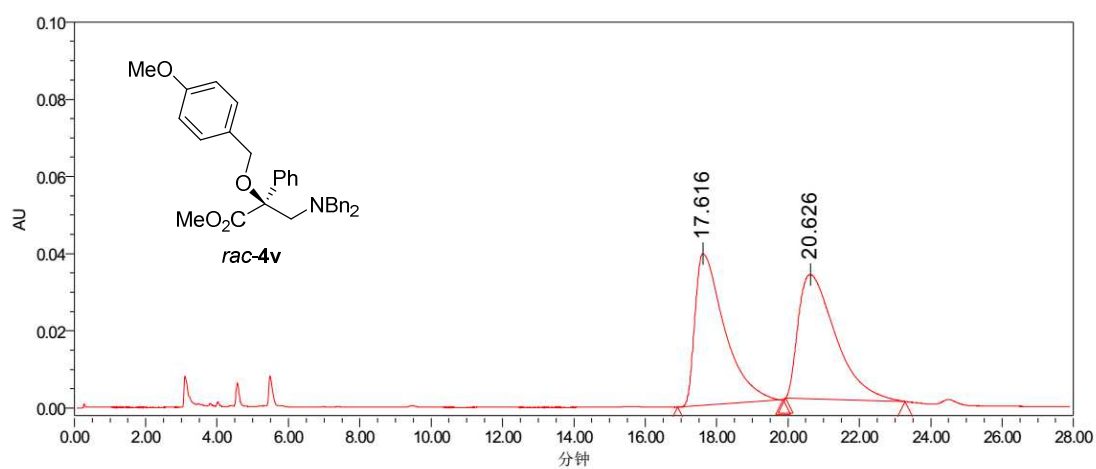
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		8.052	9024694	622113	49.66
2		9.162	9150063	533984	50.34



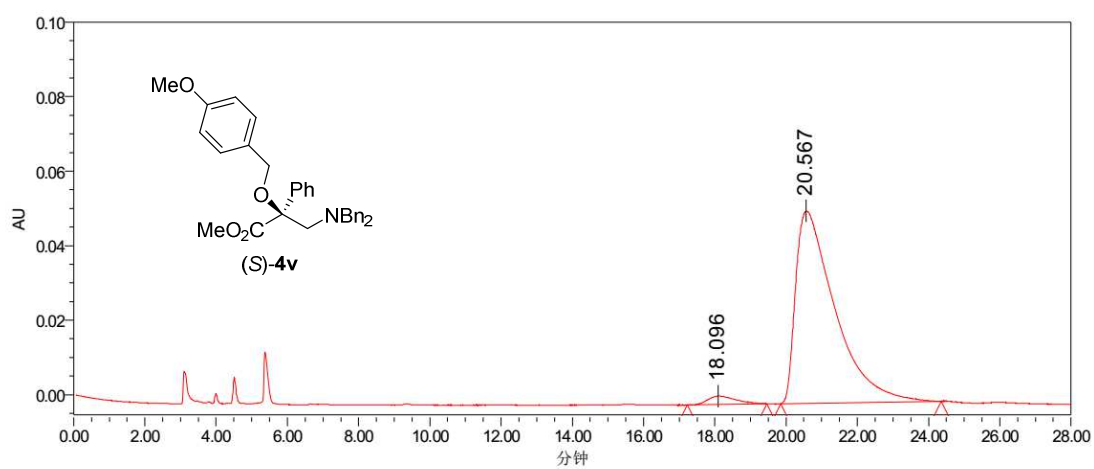
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		8.532	72398	5938	3.70
2		9.448	1882951	111558	96.30



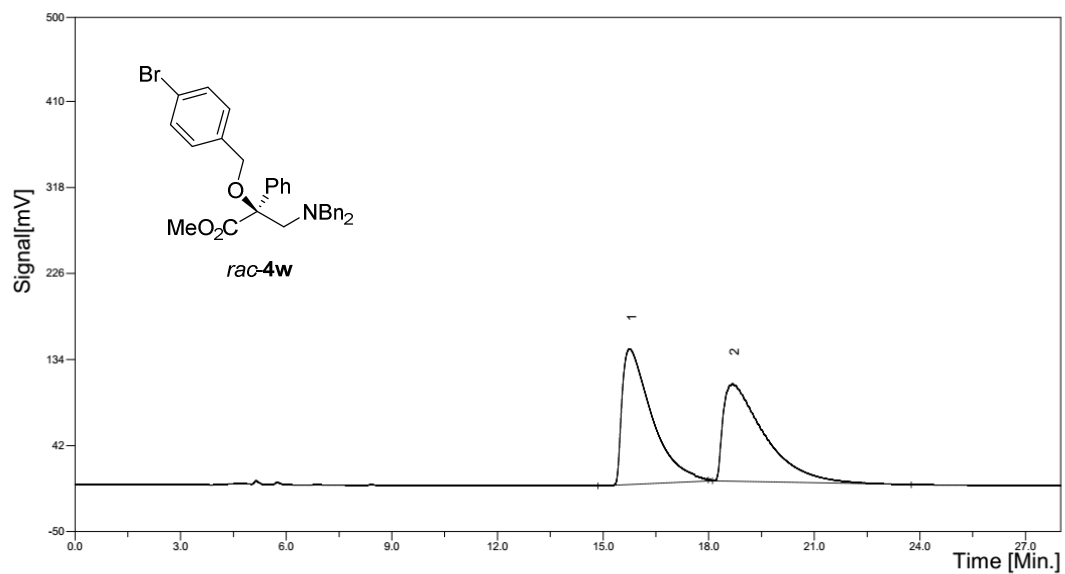
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		17.616	2272440	39329	49.30
2		20.626	2337008	32174	50.70



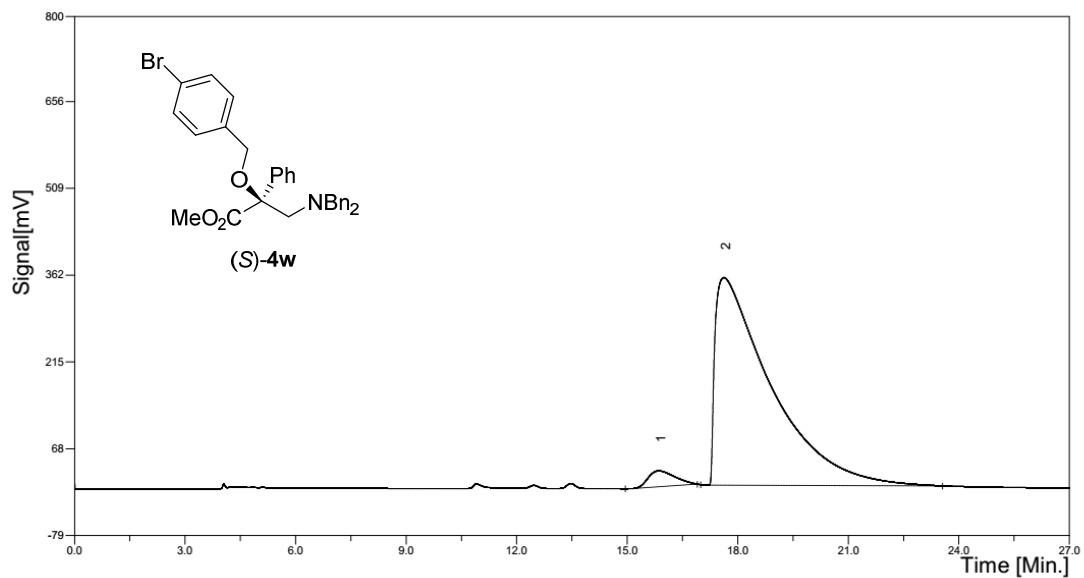
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		18.096	125604	2276	3.09
2		20.567	3933964	51597	96.91



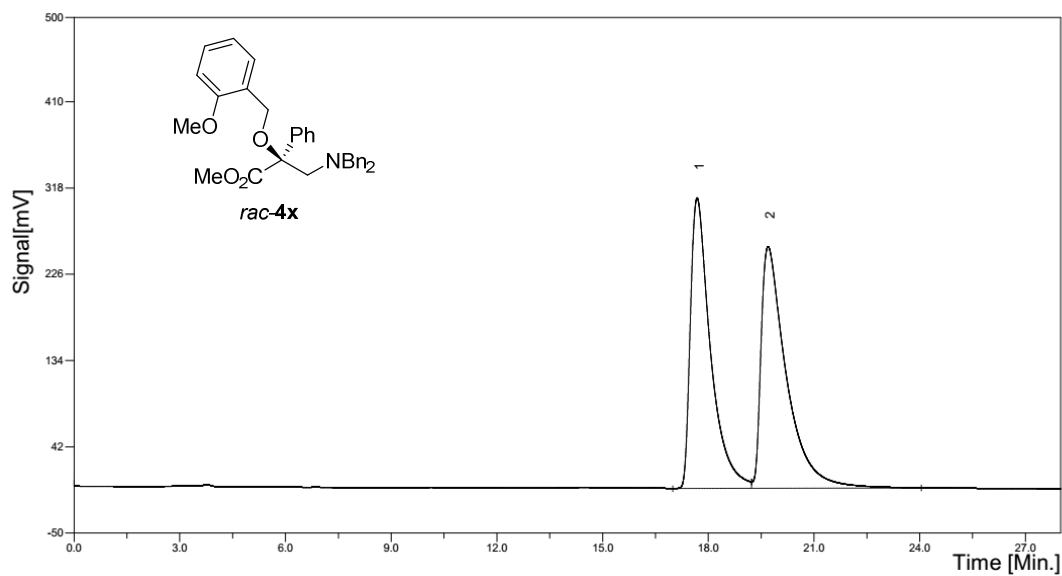
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	15.75167	144.63	8513.24	50.6523	0.0000	0.0000
2	Unknown	18.67167	103.32	8293.98	49.3477	0.0000	100.0000
合计			247.95	16807.22	100		



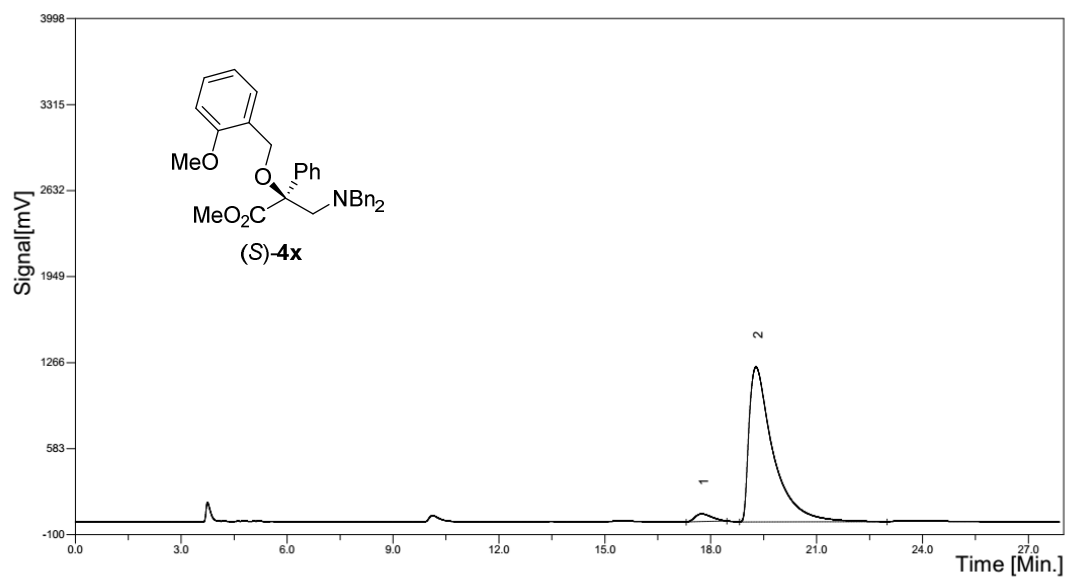
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	15.85500	26.62	1312.98	3.4402	0.0000	0.0000
2	Unknown	17.62167	350.81	36853.01	96.5598	0.0000	100.0000
合计			377.43	38165.99	100		



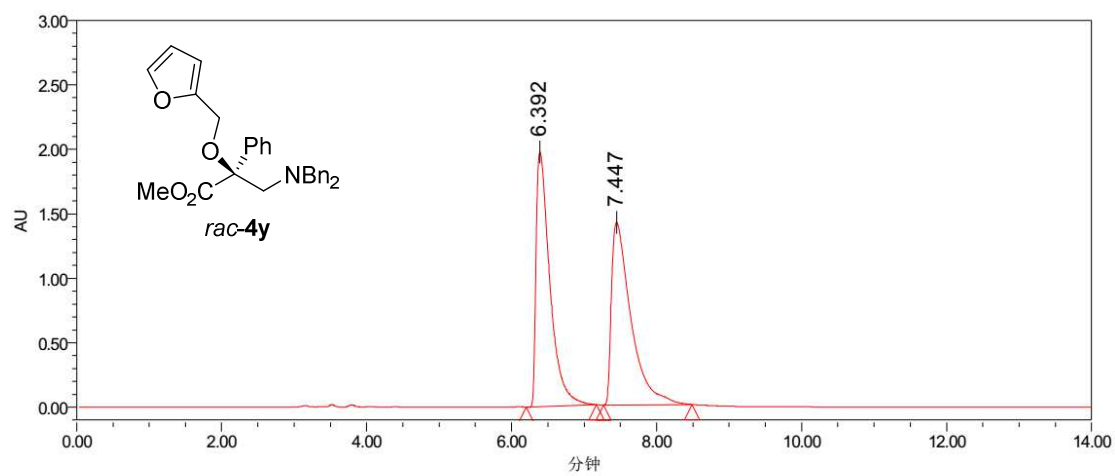
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	17.68083	309.85	12277.99	48.8586	0.0000	0.0000
2	Unknown	19.69583	257.77	12851.65	51.1414	0.0000	0.0000
合计			567.62	25129.65	100		



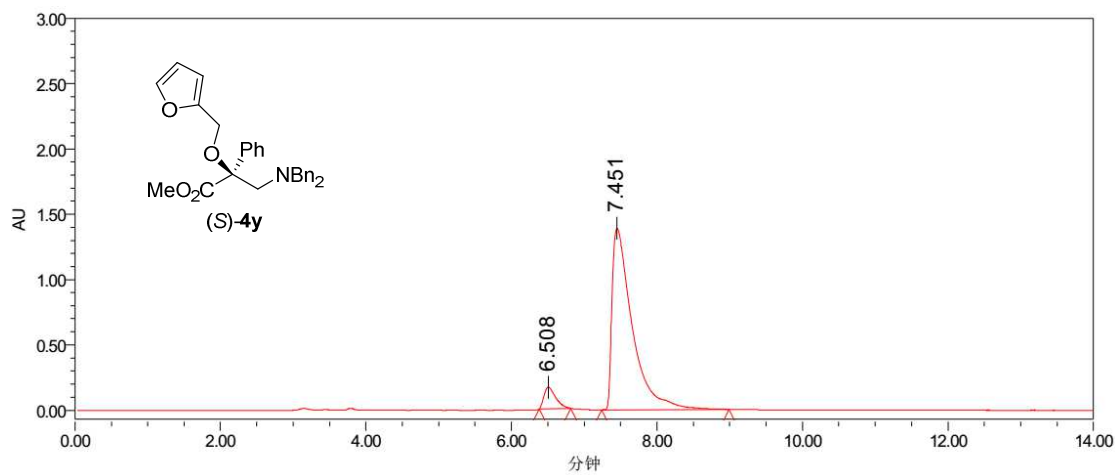
组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	17.74333	61.17	2014.37	3.3531	0.0000	100.0000
2	Unknown	19.28167	1229.60	58060.26	96.6469	0.0000	0.0000
合计			1290.77	60074.62	100		



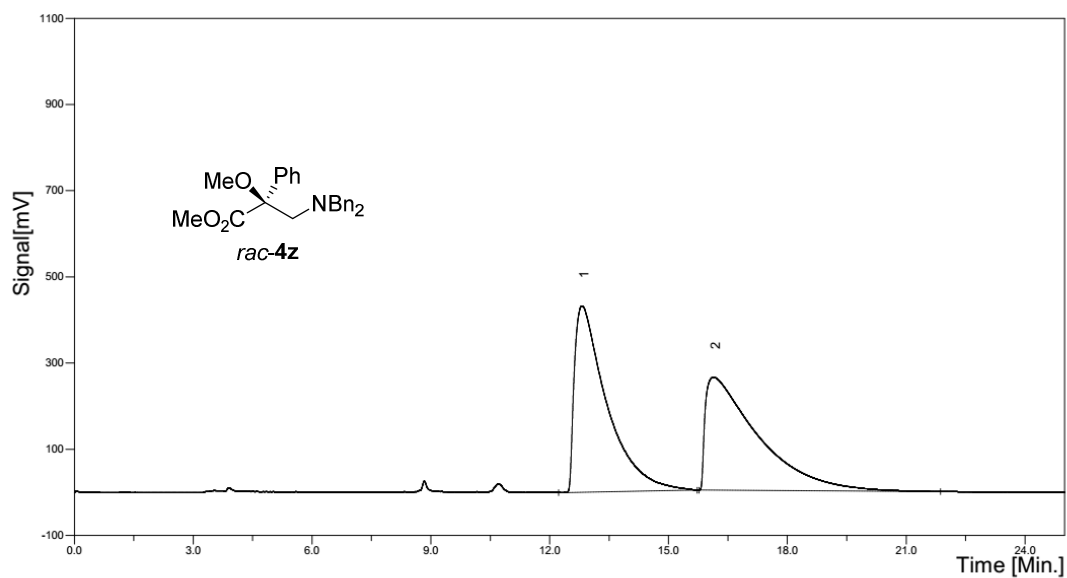
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.392	26239301	1974406	49.77
2		7.447	26483219	1415552	50.23



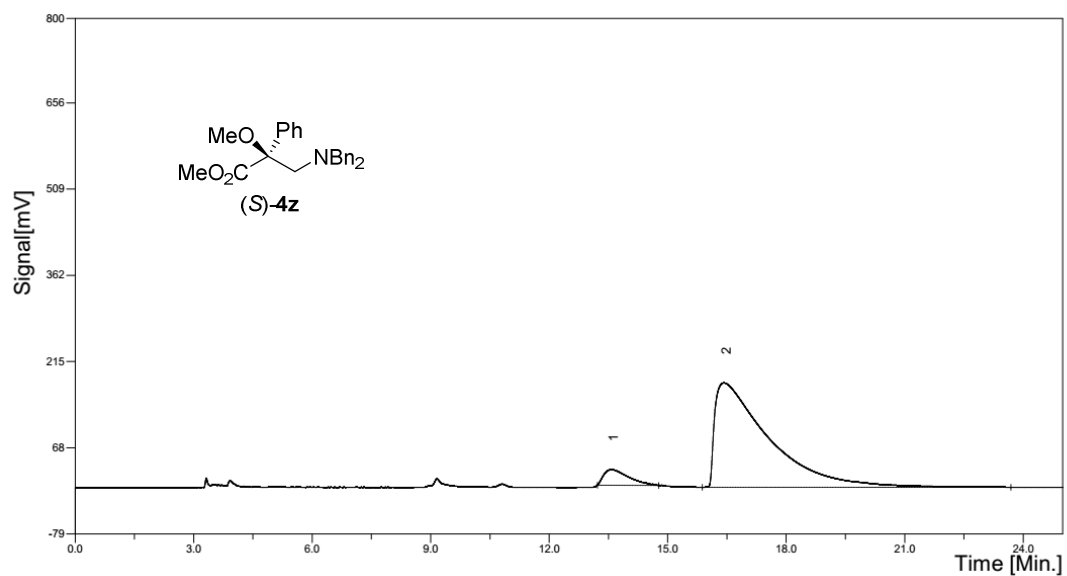
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.508	1821869	164656	6.35
2		7.451	26848721	1390495	93.65



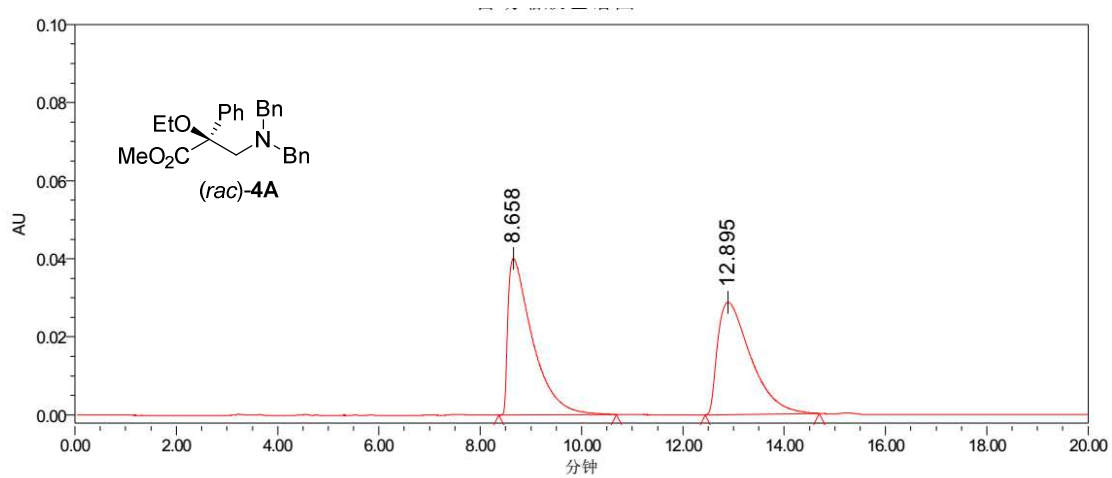
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	12. 81583	431. 46	24486. 35	50. 2916	0. 0000	100. 0000
2	Unknown	16. 13250	262. 09	24202. 37	49. 7084	0. 0000	0. 0000
合计			693. 55	48688. 72	100		



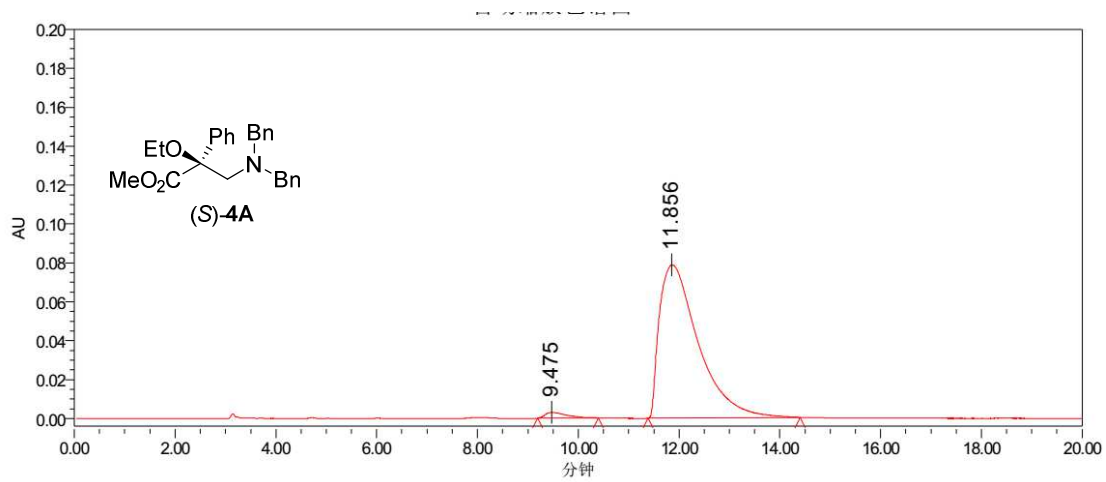
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	13. 57250	26. 40	1145. 94	6. 3414	0. 0000	100. 0000
2	Unknown	16. 42333	177. 90	16924. 86	93. 6586	0. 0000	0. 0000
合计			204. 30	18070. 80	100		



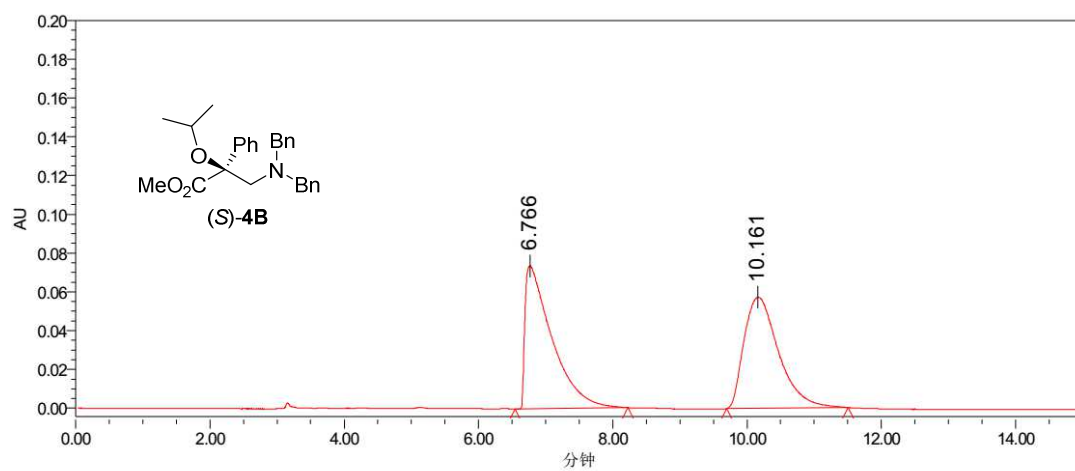
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		8.658	1341762	40044	50.66
2		12.895	1306756	28754	49.34



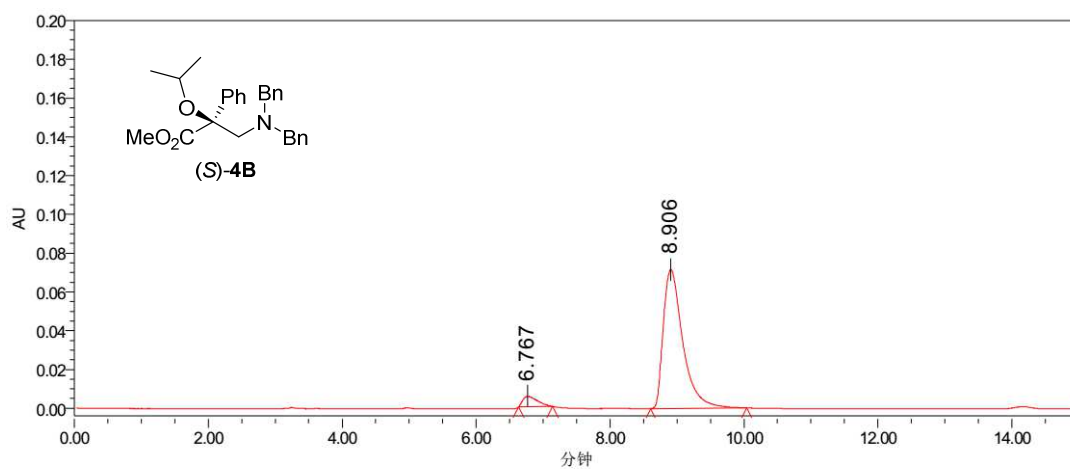
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		9.475	87246	2955	2.02
2		11.856	4227744	78712	97.98



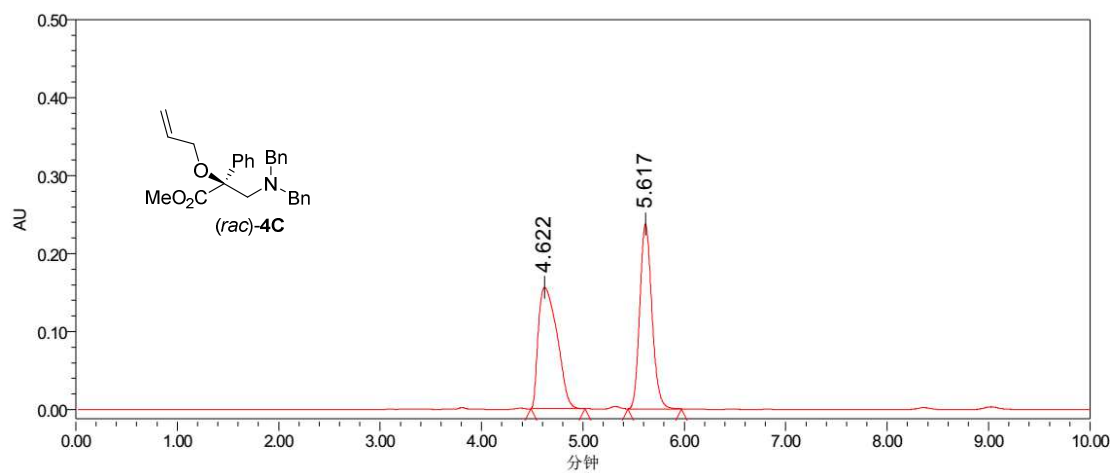
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.766	2045413	73676	50.01
2		10.161	2044518	57341	49.99



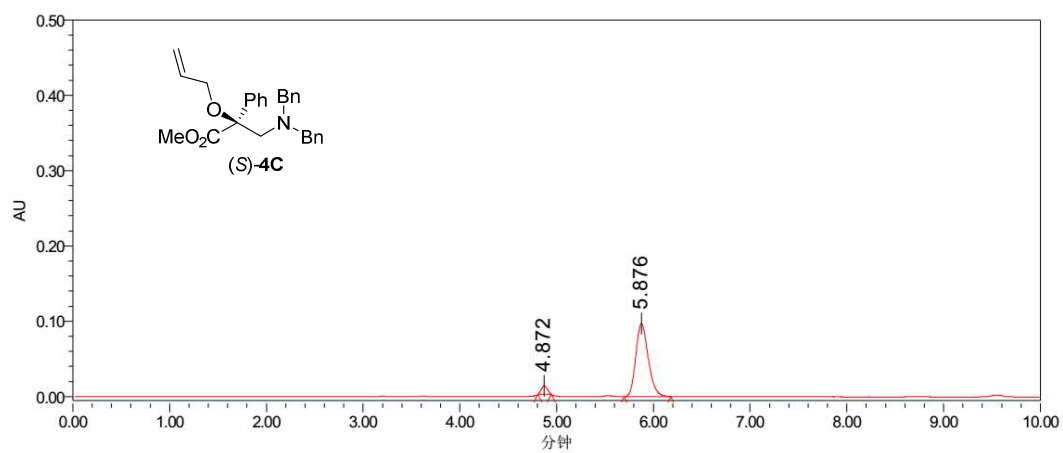
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		6.767	82747	5417	5.38
2		8.906	1455310	71613	94.62



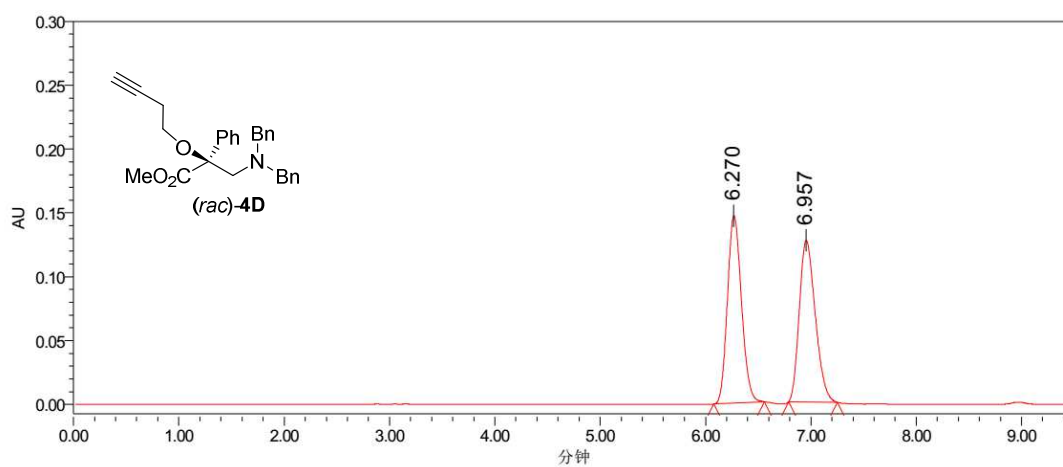
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		4.622	1989844	155313	50.34
2		5.617	1963203	237146	49.66



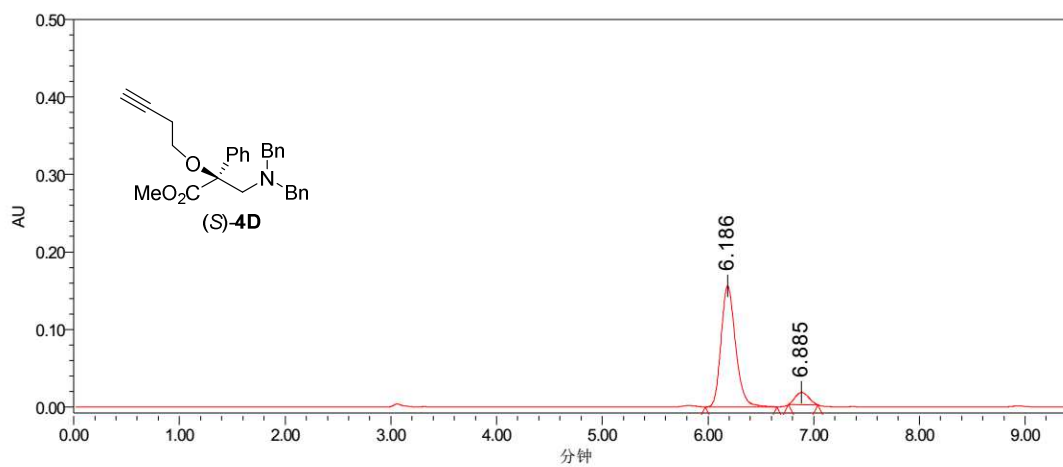
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		4.872	48270	10949	5.30
2		5.876	862605	96656	94.70



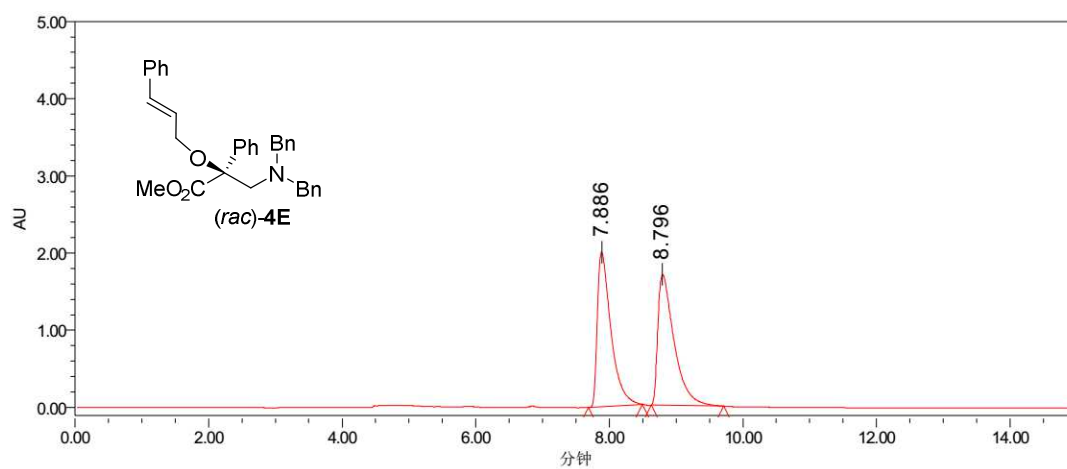
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	6.270	1356964	146851	50.34
2	6.957	1338670	126470	49.66



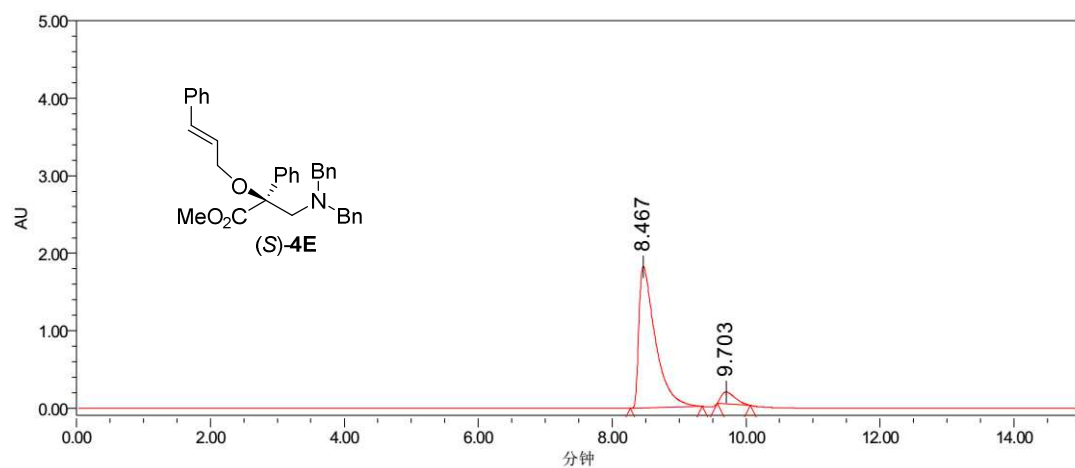
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	6.186	1479109	155766	91.32
2	6.885	140612	15749	8.68



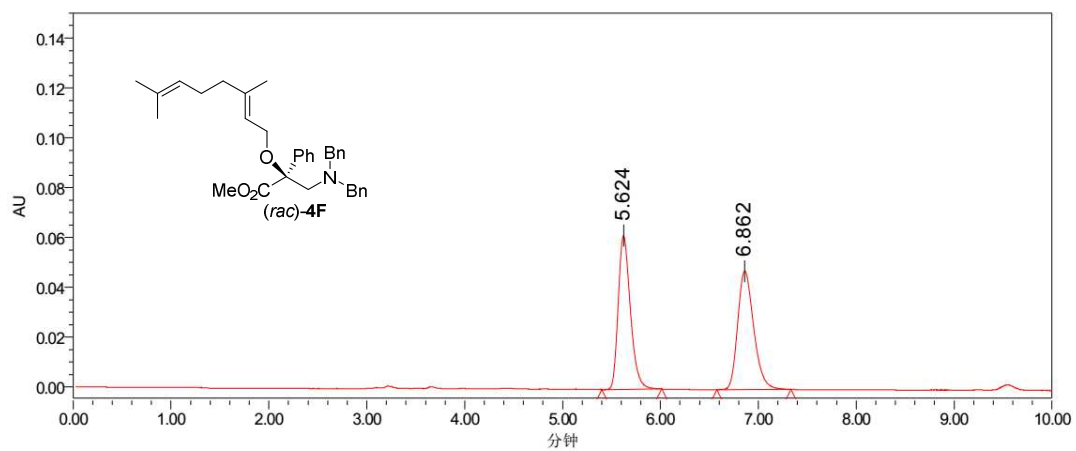
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		7.886	28359715	2000516	49.71
2		8.796	28688847	1694636	50.29



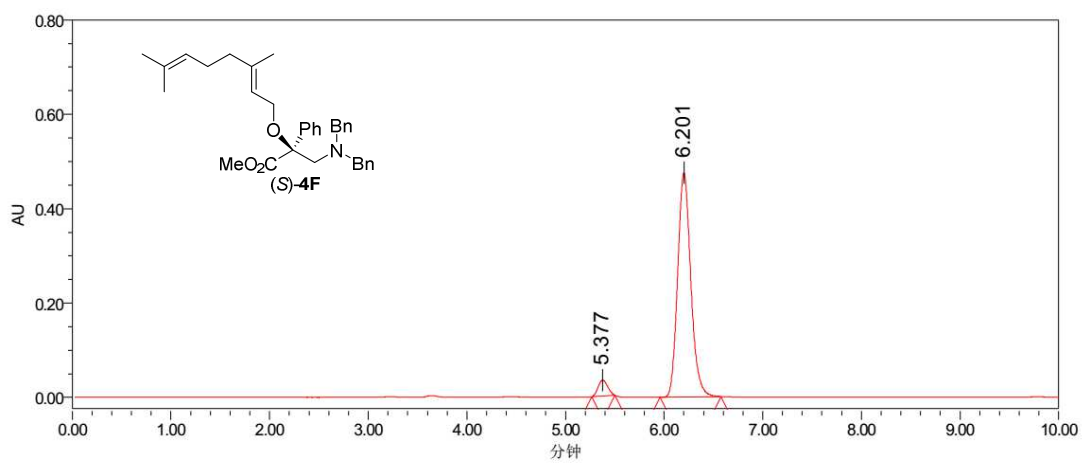
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		8.467	31043266	1822551	93.35
2		9.703	2212610	153282	6.65



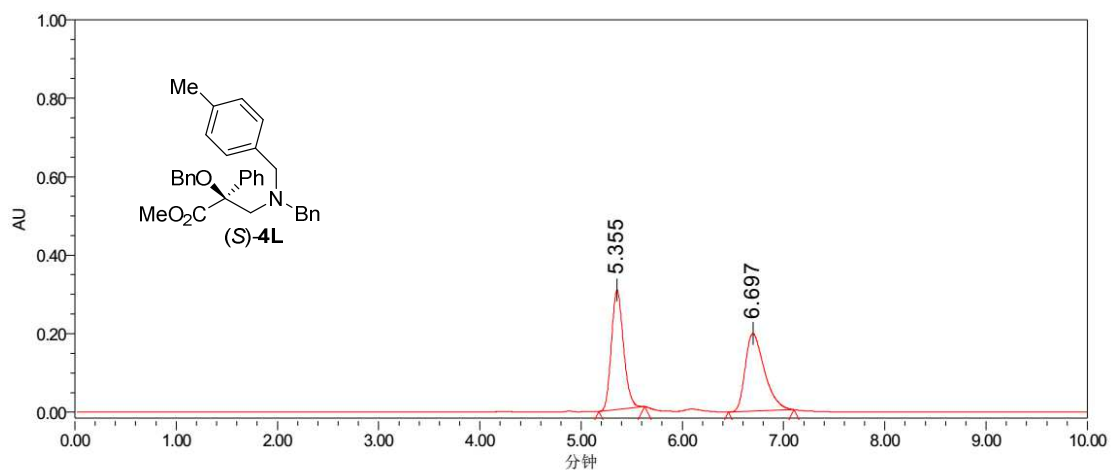
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		5.624	533772	61653	49.62
2		6.862	541942	47517	50.38



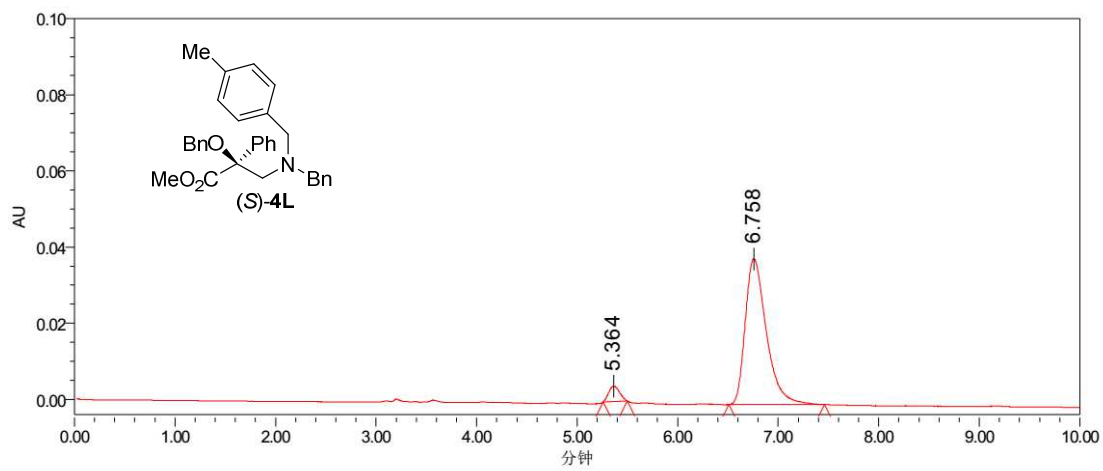
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		5.377	229125	33811	4.97
2		6.201	4383111	475479	95.03



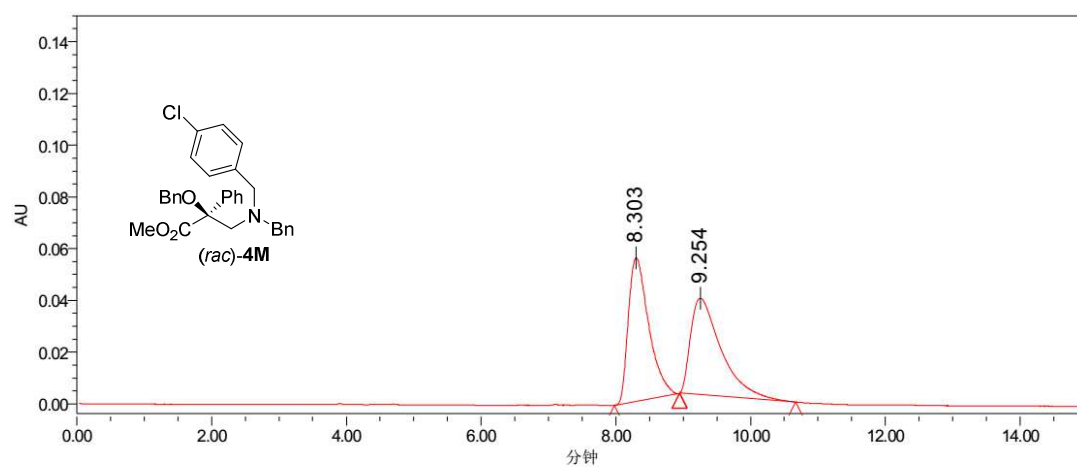
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.355	2535320	304883	49.35
2	6.697	2602281	197658	50.65



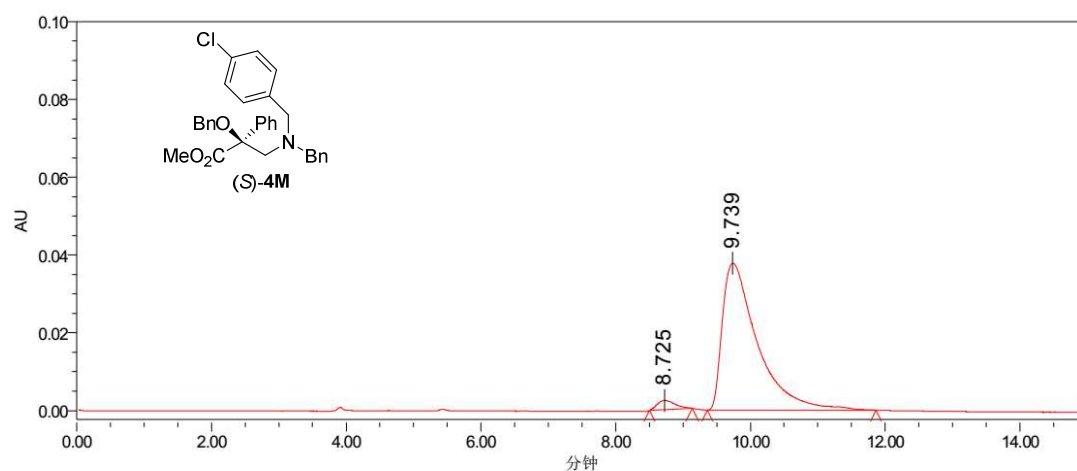
峰结果

名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1	5.364	29798	4010	5.06
2	6.758	558705	38278	94.94



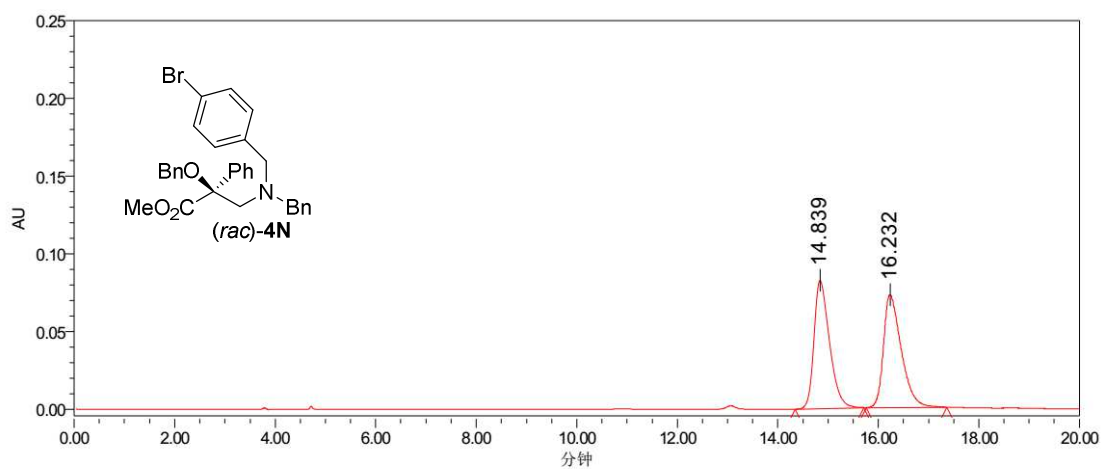
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		8.303	1164286	55477	49.73
2		9.254	1177075	37231	50.27



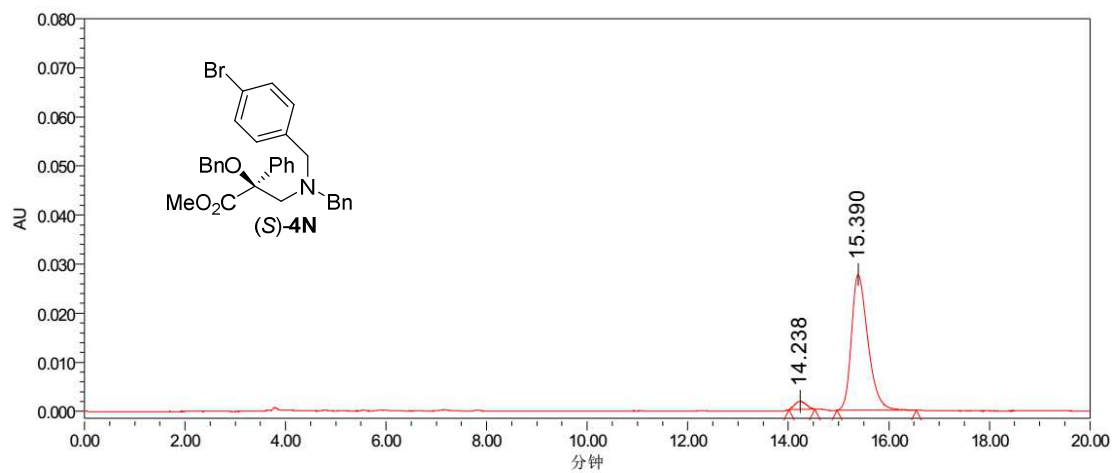
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		8.725	43725	2371	3.10
2		9.739	1367537	37734	96.90



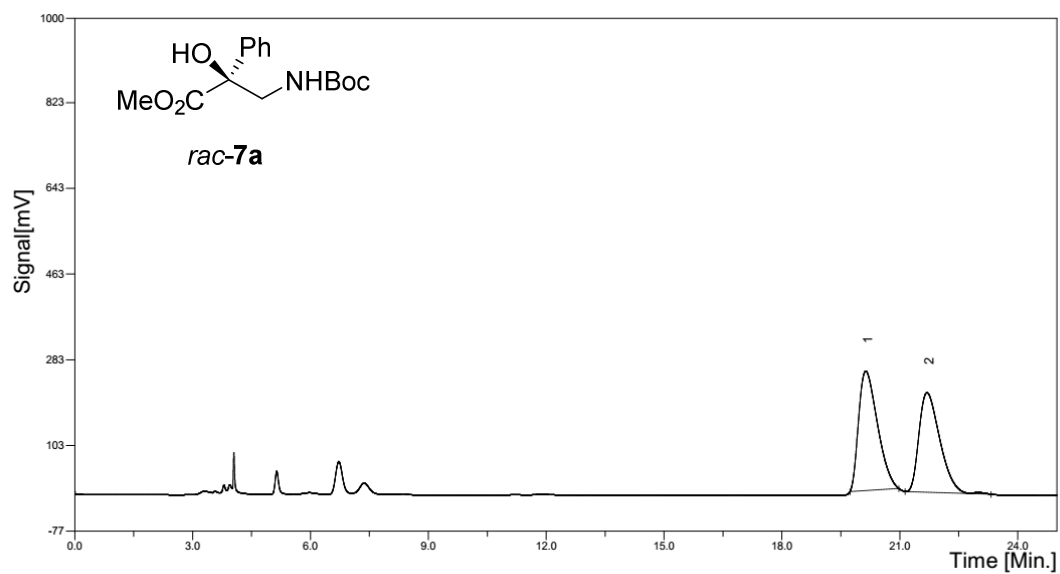
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		14.839	1769631	82452	49.91
2		16.232	1776241	72513	50.09



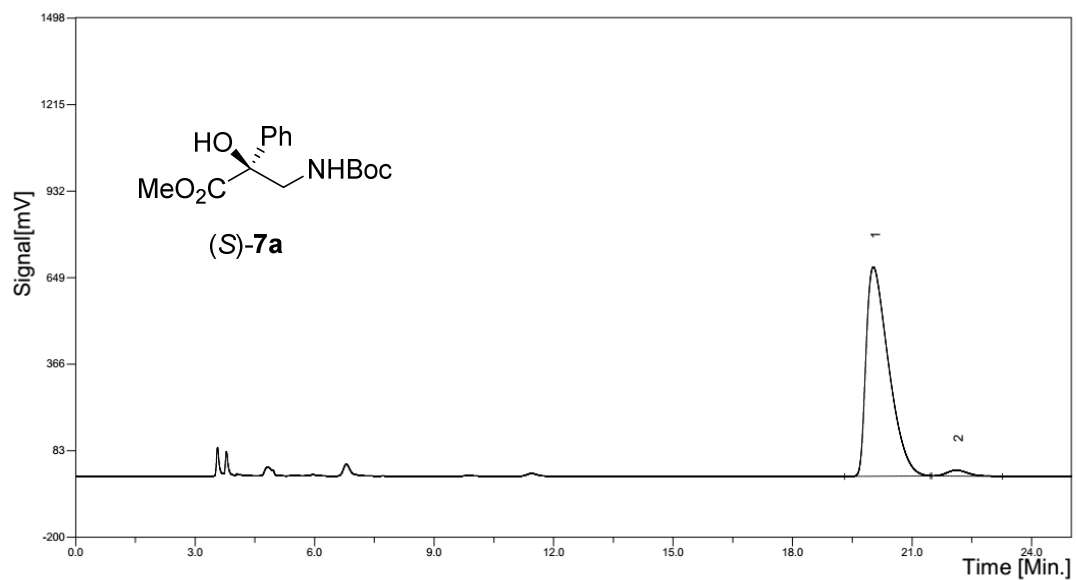
峰结果

	名称	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		14.238	25266	1627	3.88
2		15.390	625431	27622	96.12



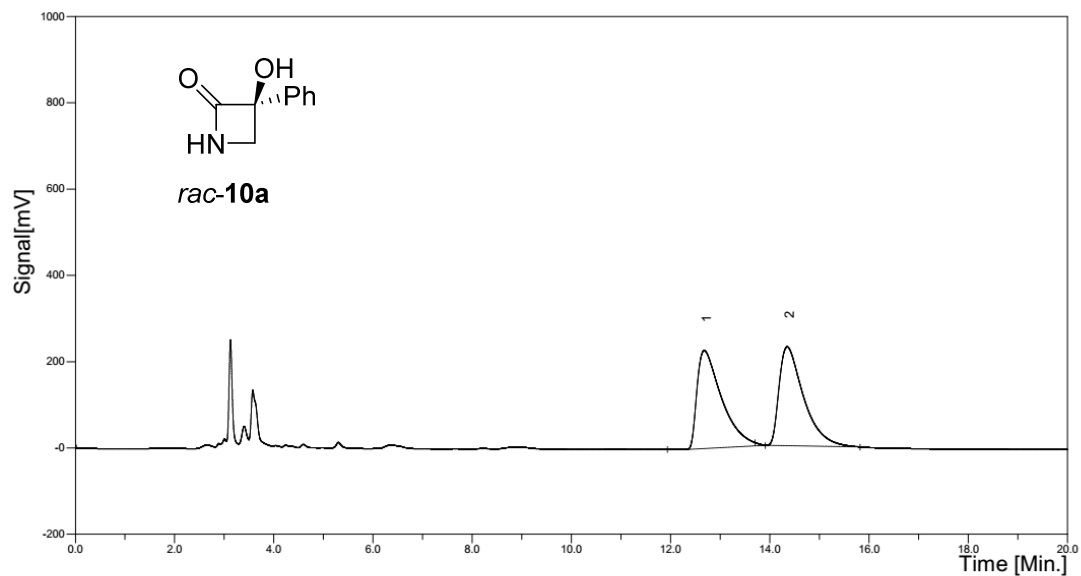
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	20.13250	251.05	8392.28	52.0810	0.0000	100.0000
2	Unknown	21.69250	209.11	7721.63	47.9190	0.0000	0.0000
合计			460.16	16113.91	100		



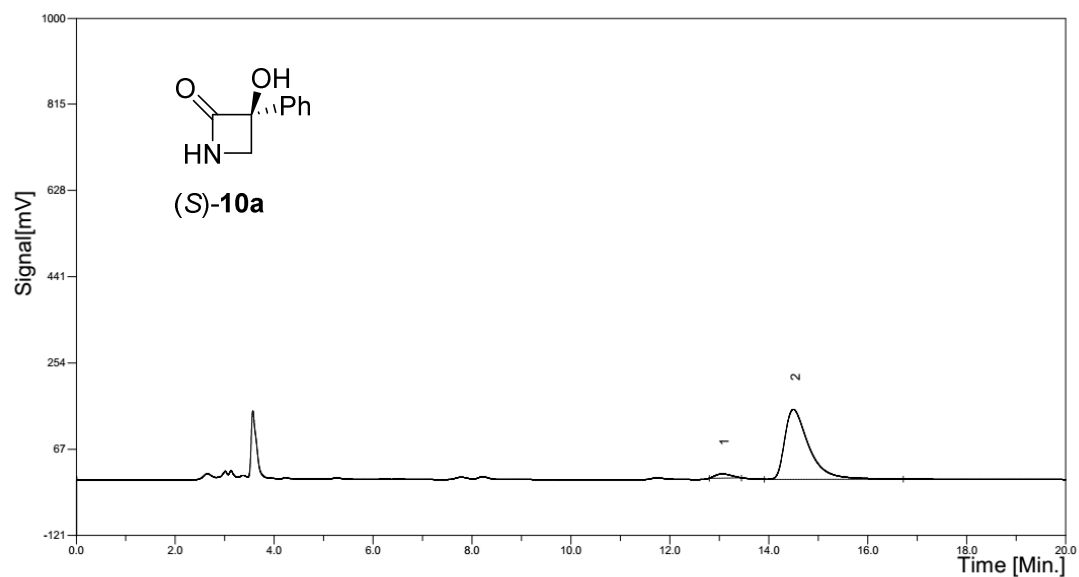
组分表

#	组分名	保留时间 (min)	峰高 (mV)	峰面积 (mV. sec)	面积百分比 (%)	浓 度	样品含量 (%)
1	Unknown	20.02917	684.48	26799.18	97.5285	0.0000	100.0000
2	Unknown	22.10917	18.99	679.14	2.4715	0.0000	100.0000
合计			703.47	27478.31	100		



组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	12. 67750	225. 64	7715. 61	50. 6635	0. 0000	100. 0000
2	Unknown	14. 34750	225. 09	7513. 51	49. 3365	0. 0000	100. 0000
合计			450. 72	15229. 12	100		



组分表

#	组分名	保留时间(min)	峰高(mV)	峰面积(mV. sec)	面积百分比(%)	浓 度	样品含量(%)
1	Unknown	13. 05750	9. 01	198. 06	3. 7507	0. 0000	100. 0000
2	Unknown	14. 49500	151. 42	5082. 46	96. 2493	0. 0000	0. 0000
合计			160. 42	5280. 51	100		