Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Solvent Directed Chemical Divergent Synthesis of β-Lactams and α-Amino Acid Derivatives with Chiral Isothiourea

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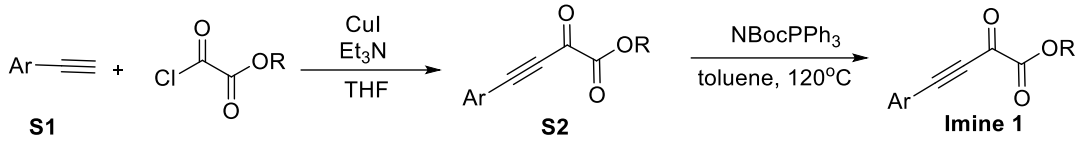
Contents

1. General information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silicycle silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AM-400 or 600 spectrometer (400 or 600 MHz ^{1}H, 100 or 151 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as the solvent at room temperature, ^{1}H and ^{13}CNMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.0 ppm) or TMS (^{1}H) (δ = 0.00 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on Bruker Apex II mass instrument (ESI). Enantiomeric excess values were determined by HPLC with a Daicel Chirapak IA and IF-3 column on Agilent 1260/1100 series with *i*-PrOH and *n*-hexane. Optical rotation was measured on the Perkin Elmer 341 polarimeter with $[\alpha]_D$ values reported in degrees. Concentration (c) is in g/100 mL. Substrate imine[1] and phenyl acetate[2] were prepared according to the procedures in the literature reports, all the isothiourea catalysts[3] were synthesized according to the procedures in the literature reports in laboratory.

2 Substrates synthesis

2.1 The general procedures for synthesis Imine 1



Imine 1 was prepared based on the reported procedures[1]

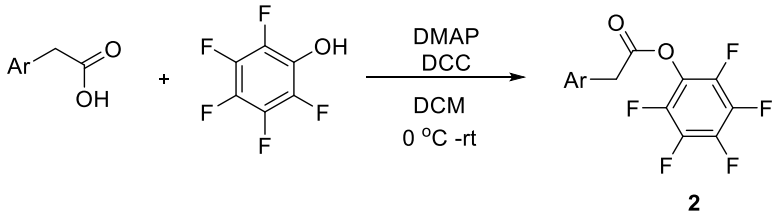
Step 1

A two necked round bottomed flask was charged with CuI (10 mol%) and THF (0.4 M), trimethylamine (2.0 equiv), S1 alkyne(1.0 equiv) and ethyl 2 –chloro-2-oxoacetate (1.5 equiv) were added sequentially and the resulting mixture was stirred at room temperature for 24 hours. The reaction was quenched by saturated $NaHCO_3$ aqueous solution and the aqueous phase was extracted with ethyl acetate. The organic phases were combined, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel chromatography (PE/ ethyl acetate 95:5) to give the S2.

Step 2

An oven-dried round bottom two necks flask was added ketoesters S2 (1.0 equiv), N-Boc-triphenyliminophosphorane and toluene. The mixture was heated to 120 ℃ and stirred for 24h - 72h. After cooling to room temperature, the mixture was concentrated under vacuum. The residue was purified by silica gel chromatography (PE/ ethyl acetate 10:1 - 6:1) to give the Imine **1c**-**1m**.

2.2 The general procedures for synthesis phenylacetic acid ester 2

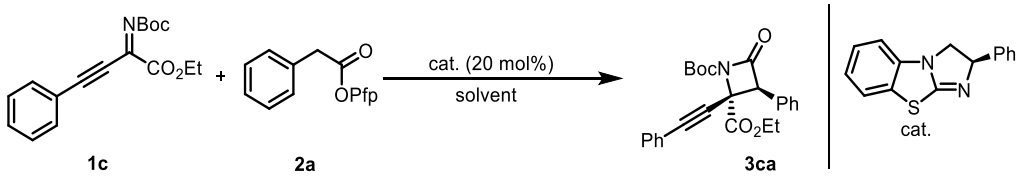


Phenylacetic acid ester 2 was prepared based on the reported procedures[2].

The specified phenylacetic acid (5 mmol, 1.0 equiv.), the specified phenol (0.75 g, 5.5 mmol, 1.1 equiv.) and dry CH_2Cl_2 (60mL) were added sequentially to a dry round-bottom flask at room temperature under an atmosphere of nitrogen. The reaction was cooled to 0 ℃ using an ice bath and DCC (1.11 g, 5.5 mmol, 1.1 equiv.) and DMAP (60 mg, 0.5 mmol, 0.1 equiv.) added sequentially. The reaction was allowed to slowly warm to room temperature and further stirred for 12 hours. Thereafter, aq. HCl (3N, 6 mL) was added and the reaction placed in a freezer (–20 ℃) for a minimum of 6 h The resulting suspension was filtered over celite and the residue washed with ice-cold CH_2Cl_2. The combined filtrates were successively washed with sat. aq. $NaHCO_3$ and water before being dried (MgSO4) and concentrated under reduced pressure. The residue was purified by column chromatography (PE/ ethyl acetate 20:1) to give the phenylacetic acid ester **2**.

3 Condition optimization

3.1 The attempt of Lewis acid and Lewis base cooperative catalysis

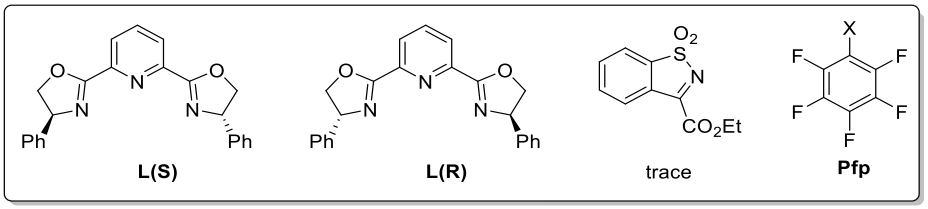


1c 2a 3ca

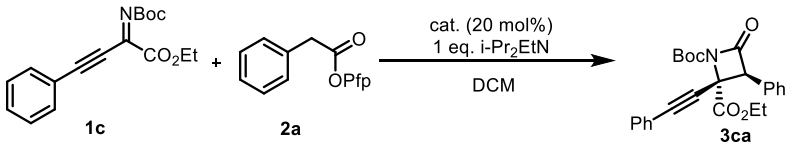
Table S1. The initial experiments

Entry[a]	Loading of Cat.	solvent	[Cu][b]	L	Yield[c]	dr	Ee[d]
1	20%	DCM	-	-	53	-	90
2	20%	DCM	10%	11%(S)	25	-	90
3	-	DCM	10%	11%	/	/	/
4	20%	DCM	10%	11%(R)	25-27	-	90

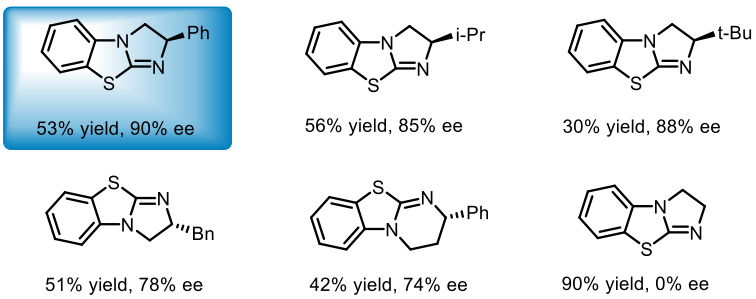
Conditions: [a] Reactions performed with 0.1 mmol **1c**, 0.1 mmol **2a**, catalyst (20 mol%) in DCM(1 mL) at 15°C for 24h. [b] [Cu]: $Cu(CH_3CN)_4PF_6$ [c] Isolated yield. [d] Determined by chiral-phase HPLC analysis



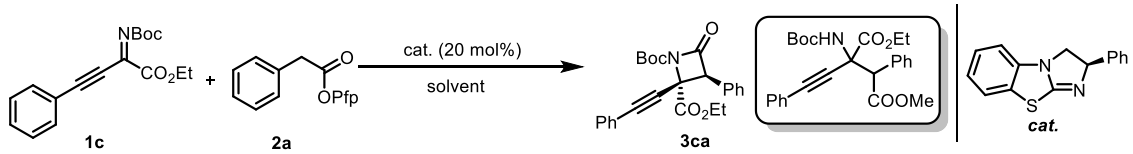
3.2 The optimization of catalyst (Table S2)



1c 2a 3ca



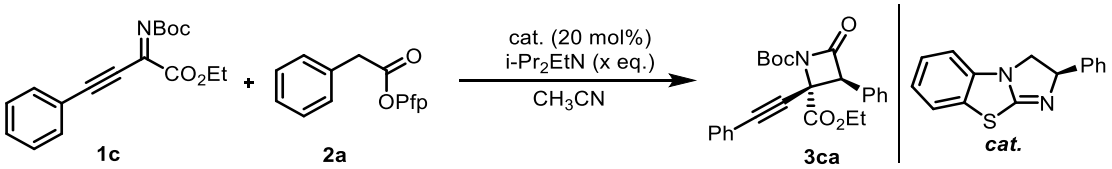
3.3 The detailed optimization of solvents (Table S3)



entry	solvent	dr[d]	yield[c]	ee[e]
1[a]	DCM	10:1	49%	90
2[a,b]	DCM	3:1	53%	90
3[a,b]	$CHCl_3$	3:1	56%	88
4[a,b]	Acetone	3:1	72%	85
5[a,b]	Et_2O or toluene	-	trace	-
6[a,b]	CH_3CN	3:1	70%	90
7[a,b]	MeOH	4:1	75%	0
8[a,b]	EtOH	5:1	72%	92

Conditions: [a]Reactions performed with 0.1 mmol **1c**, 0.1 mmol **2a**, catalyst (20% mol) in solvent(1 mL) at 15°C for 24h. [b]1 equiv i-Pr_2EtN was added. [c]Isolated yield. [d]Determined by ^{1}H NMR analysis of the crude products. [e]Determined by chiral-phase HPLC analysis of major isomer.

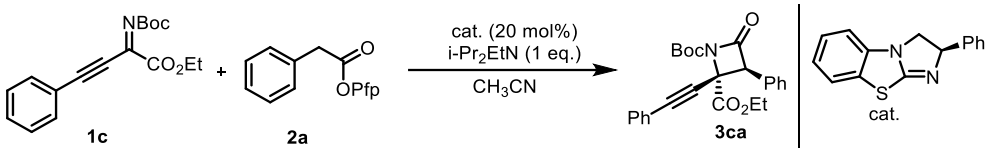
3.4 Optimization of the loading of base(Table S4)



Entry[a]	base(x eq.)	dr[c]	ee/%[d]	yield[b]
1	0.5	2:1	89	67%
2	1	3:1	90	70%
3	1.25	3:1	89	71%
4	1.5	3:1	89	66%

Conditions: [a]Reactions performed with 0.1 mmol **1c**, 0.1 mmol **2a**, catalyst(20% mol) and x equiv base in CH_3CN(1 mL) at 15-20°C for 24h. [b]Isolated yield. [c]Determined by ^{1}H NMR analysis of the crude products. [d]Determined by chiral-phase HPLC analysis of major isomer.

3.5 Further optimization of stereoselectivity(Table S5)

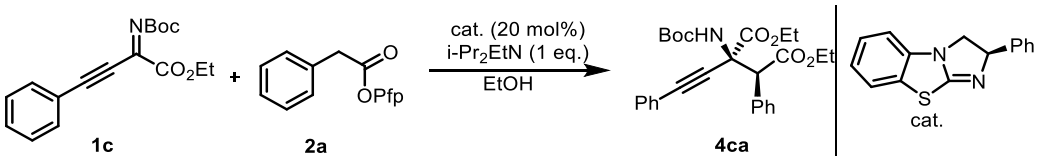


1c 2a 3ca

Entry[a]	t/ °C	dr[c]	ee/%[d]	yield[b]
1	15-20 °C	3:1	90	85%
2	0	3:1	90	85%
3	-10	3:1	91	85%
4	-20	3:1	90	85%
5	-30	-	93	85%
6	-40	6:1	99	84%
9[e]	-50	8:1	99	85%

Conditions: [a]Reactions performed with 0.1 mmol **1c**, 0.1 mmol **2a**, catalyst(20% mol) and 1 equiv base in CH_3CN(1 mL) at t °C for 24h. [b]Isolated yield. [c]Determined by ^1H NMR analysis of the crude products. [d]Determined by chiral-phase HPLC analysis of major isomer. [e]CH_3CN/DCM=3:1, 0.12 mmol **2a.**

3.6 Optimization of the conditions of synthesis α-amino acid derivatives(Table S6)



1c 2a 4ca

Entry[a]	dr[b]	Ee/%[c]	Yield/%[d]
1	5:1	91	72
2[e]	20:1	99	75
3[f,e]	20:1	99	79
4[g,e]	20:1	99	81

Conditions: [a]Reactions performed with 0.1 mmol **1c**, 0.1 mmol **2a**, 1 equiv i-Pr_2EtN, catalyst (20 mol%) in EtOH(1 mL) at 15-30°C for 24h. [b]Determined by ^1H NMR analysis of the crude products. [c]Determined by chiral-phase HPLC analysis. [d]Isolated yield. [e]at 0°C. [f]0.12eq. **1c** was used. [g]0.12eq. **2a** was used.

3.7 The testing to the others nucleophile

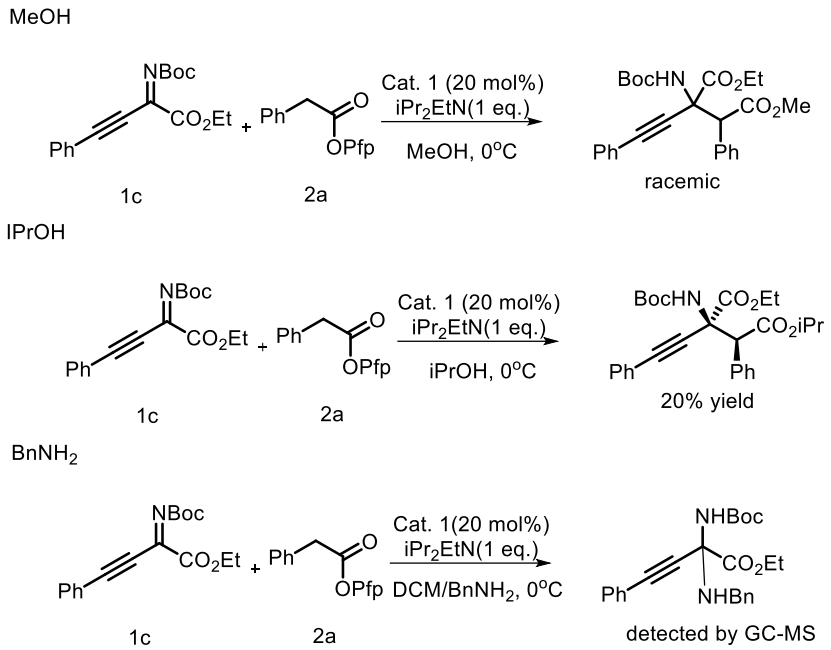


Figure 2

4 General procedures

4.1 General procedures for the synthesis *β*-lactam derivatives

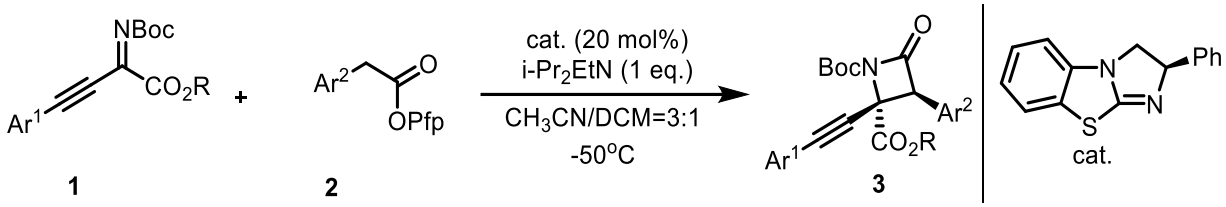


Figure 4.1

In a 10 ml tube with a stirring imine **1** (0.1 mmol), phenyl ester **2**(0.12 mmol), **Cat.** (0.02 mmol) and 18μL **i-Pr$_2$EtN** were successively added, then 1 mL solvent (CH_3CN/DCM_{volume} =3:1) that precooled at -50^{o}C was added by syringe, after that the device was put into low-temperature reactor which controled the temperature at -50^{o}C(**Figure 4.1**). When TLC analysis showed imine **1** was mainly consumed, 1 mL 10% HCl was added to quench the reaction, then the mixture will be extracted three times by DCM(1mL*3), the combined organic phases were washed by NaCl(aq), dried over Na_2SO_4, filtered, and concentrated under reduced pressure, then this mixture was used to test d.r. value and purify. The product **3** was purified by flash column chromatography(PE/EA=20:1 to 10:1).

4.2 General procedures for the synthesis *α*-amino acids derivatives

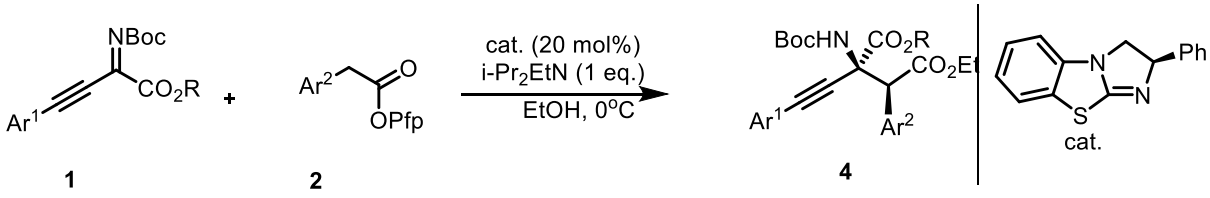


Figure 4.2

In a 10 ml tube with a stirring imine **1** (0.1 mmol), phenyl ester **2**(0.12 mmol), **Cat.** (0.02 mmol) and 18μL **i-Pr$_2$EtN** were successively added, then 1 mL EtOH (HPLC) that precooled at -0^{o}C was added by syringe, after that the device was put into low-temperature reactor which controled the temperature at -0^{o}C(**Figure 4.2**). When TLC analysis showed imine **1** was mainly consumed, the reaction was concentrated under reduced pressure with silica gel and have a mixture, then this mixture was loaded on column chromatography to access the product **4** (PE/EA=20:1).

4.3 The synthesis of racemic product

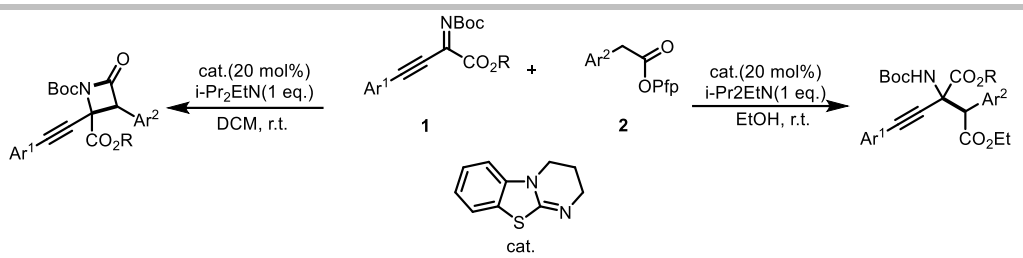


Figure 4.3

In a 10 mL tube with stir bar imine **1** (0.1 mmol), phenyl ester **2**(0.12 mmol), **Cat.** (0.02 mmol) and 18μL **i-Pr$_2$EtN** were successively added, then the 1mL corresponding solvent (DCM or EtOH) was added by syringe. The reaction mixture was stirred 24 hours at room temperature, then the reaction was concentrated under reduced pressure with silica gel and have a mixture, this mixture was loaded on column chromatography, after a flash column chromatography by solvent (PE/EA=20:1), the racemic product would be accessed (**Figure 4.3**).

5 The Mechanism exploration

5.1 Isotope labeling experiments

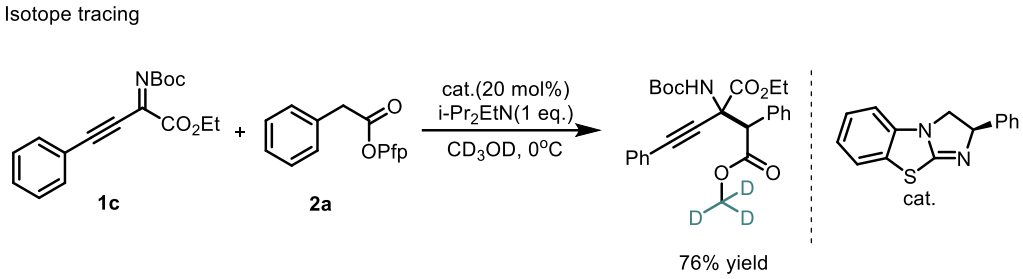


Figure 5.1

In a 10 ml tube with a stirring imine **1c** (0.1 mmol), phenyl ester **2a**(0.12 mmol), **Cat.** (0.02 mmol) and 18μL **i-Pr$_2$EtN** were successively added, then 1 mL CD_3OD that precooled at -0°C was added by syringe, after that the device was putinto low-temperature reactor which controled the temperature at -0°C(**Figure 5.1**). When TLC analysis showed imine **1** was mainly consumed, the reaction was concentrated under reduced pressure with silica gel and have a mixture, then this mixture was loaded on column chromatography to access the product.

5.2 The identification of divergent synthesis

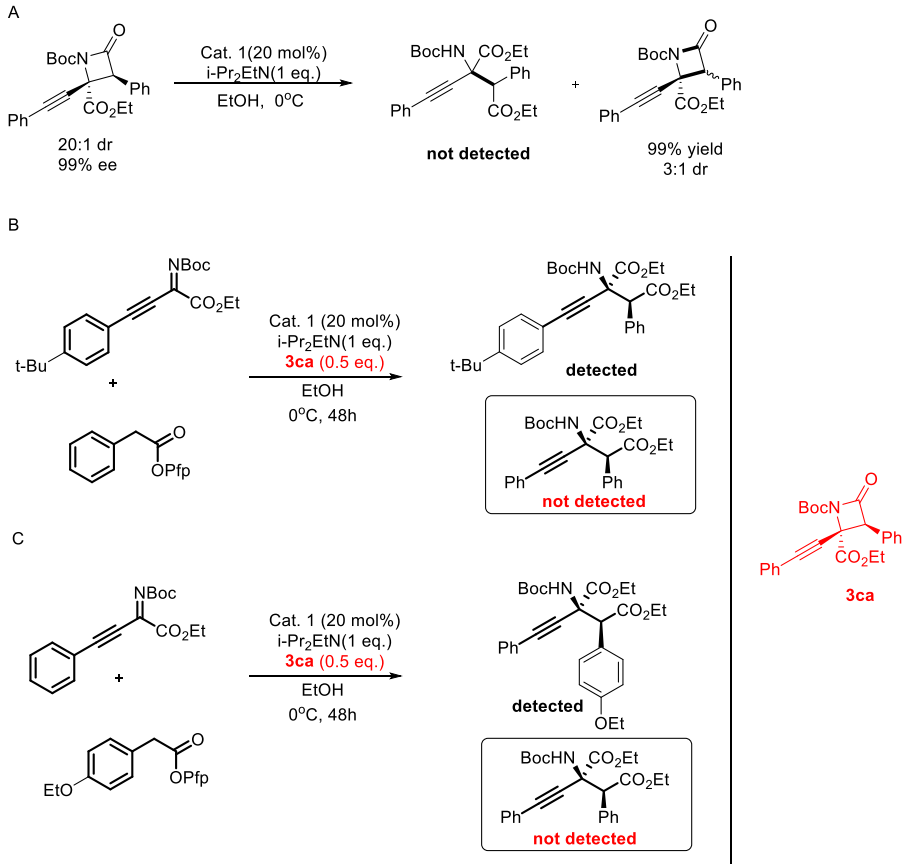


Figure 5.2

So in order to exclude the machanism which α-amino acid derivatives **4** would come from the ring opening of β-lactam **3** at the conditions of model reaction, the enantiomerically pure **3ca** was used as ***starting material*** or

additive in another reaction of another substrate at the optimal reaction conditions for accessing amino acid derivatives. But only the diastereoisomer of **3ca** was observed(**Figure 5.2**).

5.3 The mixed solvent experiment

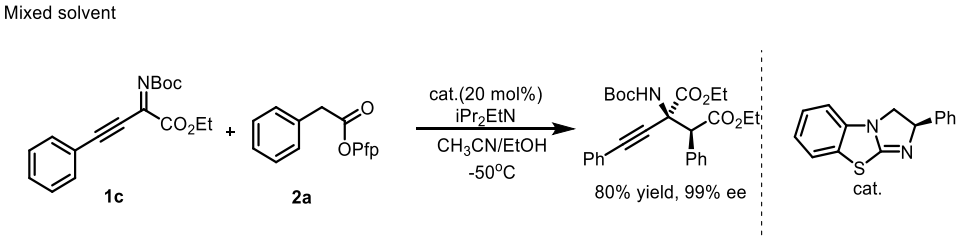


Figure 5.3

In a 10 ml tube with a stirring imine **1c** (0.1 mmol, 30.1mg), phenyl ester **2a**(0.12 mmol, 36mg), **Cat.** (0.02 mmol, 5mg) and 18μL **i-Pr$_2$EtN** were successively added, then 1 mL solvent ($CH_3CN/EtOH$ $_{volume}$ =1:1) that precooled at -50°C was added by syringe, after that the device was putinto low-temperature reactor which controled the temperature at -50°C. (**Figure 5.3**) When TLC analysis showed imine **1** was mainly consumed, 1 mL 10% HCl was added to quench the reaction, then the mixture will be extracted three times by DCM(1mL*3), the combined organic phases were washed by NaCl(aq), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product **4ca** was purified by flash column chromatography.

5.4 Ths studies to the others species that might influenced the epimerization of product 3.

In the conditions of optimal conditions for synthesis lactam, we studied the role of the iPr_2EtN(**Equation A**), isothiouera(**Equation B**), pentafluorophenol(**Equation C**) and the corresponding pentafluorophenolate (**Equation D**) in the epimerisation process(**Figure 5.4**). At -50°C, the obvious epimerization only in the presence of iPr_2EtN was observed.

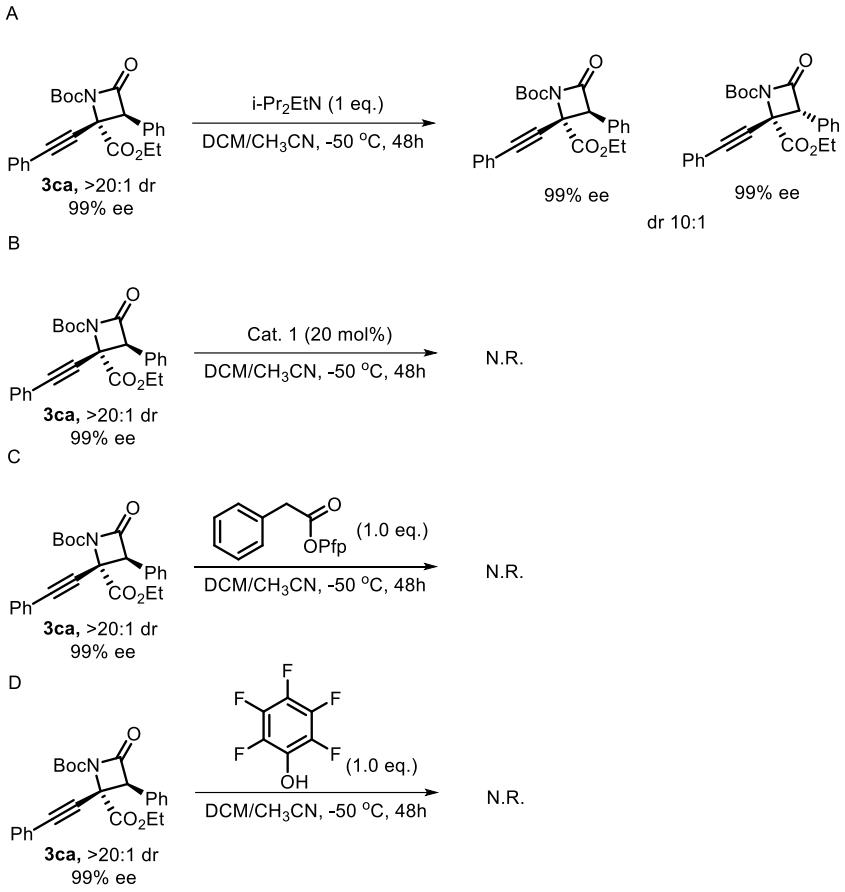


Figure 5.4

5.5 Non-linear effects experiments

In order to have a deeper interpretation to mechanism of this protocol, a non-liner effects experiment was conducted (Figure 5.5). At –50°C, to a 10-mL tube charged with a solution of the catalyst (R)-BTM(5.0 mg, 20mol%) with different enantiopurity(1st run: 0% ee, 2nd run: 20% ee; 3rd run: 40% ee; 4th run: 60% ee; 5th run: 80% ee; 6th run: 100% ee)in DCM (0.25 mL) was added a solution of **1c** (30.2 mg, 0.1mmol) and **2a**(36 mg, 0.12 mmol) in CH_3CN(0.75mL). The reaction mixture was stirred at –50°C for 48h. After that, the reaction was quenched by HCl and extracted with DCM, the combined organic phases were washed by NaCl(aq), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product **3ca** was purified by flash column chromatography. The ee values of the product **3ca** were determined by HPLC.

entry	ee of cat	ee of 3ca
1	0	0
2	17	15
3	38	38
4	59	58
5	80	79

6	99	99

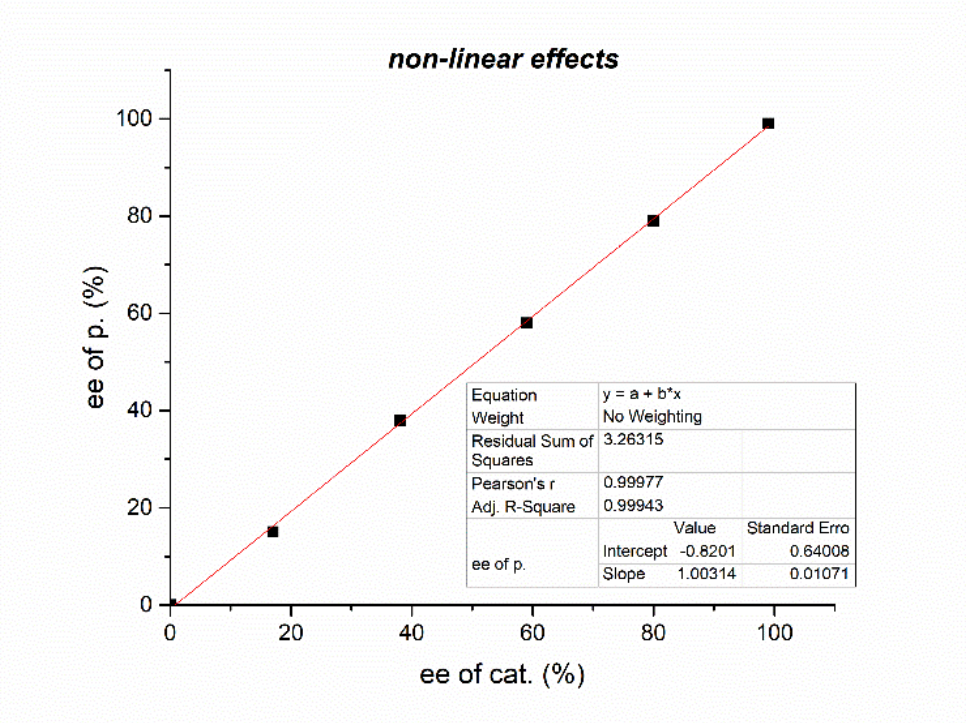


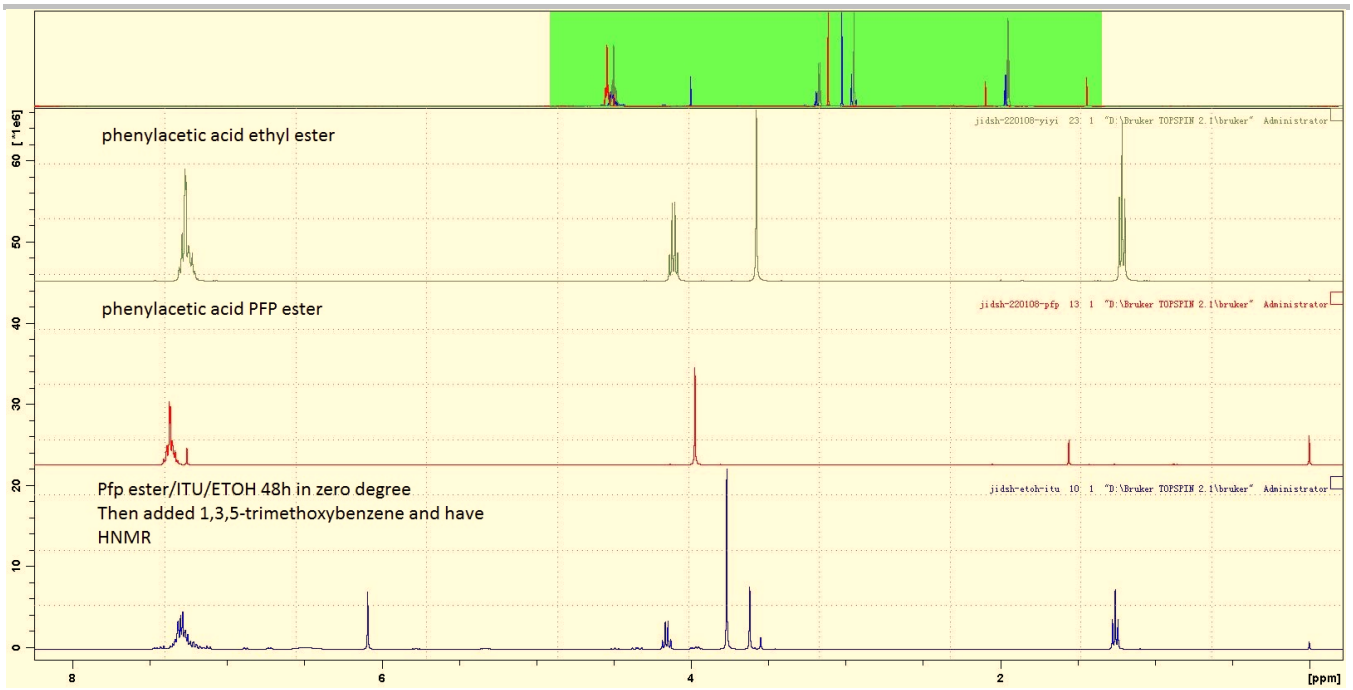
Figure 5.5

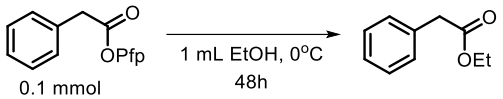
This results showed there is one catalyst was involved in a catalytic cycle.

5.6 The exploration competitive process of acyl ammonium ion pair

The phenylacetic acid ethylester was detected by HRMS in reaction mixture of the synthesis 4ca but never observed in TLC analysis or separated on column chromatography.

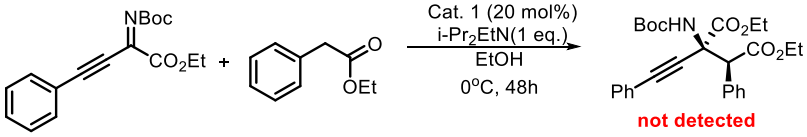
Some control experiments were conducted to explore the process of the Pfp ester transesterified in the presence of EtOH, the results showed base and catalyst all could contribute to this process, so we can't exclude the competitive process between deprotonation and acylated by EtOH when acyl ammonium ion pair is formed. In the control experiments, at the conditions of no ITU catalyst, the phenylacetic acid ethyl ester only can be detected by GC-MS as a weak peak, it cannot be observed by HNMR or separated, so the conversion cannot be quantified. In the presence of ITU catalyst, we analyzed the reaction mixture by HNMR and observed the signal of phenylacetic acid ethyl ester, the conversion of the starting material is 100% and the isolated yield of phenylacetic acid ethyl ester is 88%.





i-Pr_2EtN	Cat.1	phenylacetic acid ethylester	Observed by HNMR?
-	-	Detected by GC-MS	No
	√	detected by GC-MS	Yes
√		detected by GC-MS	No

Additional, we found when phenylacetic acid ethylester was used as starting material there any desirable product was detected.



6. The model of stereochemistry of reaction

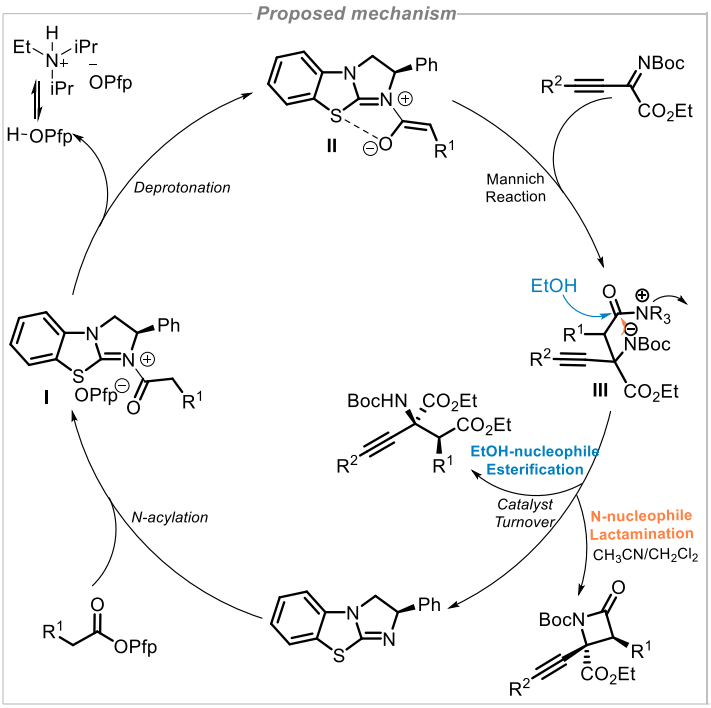


Figure 6.1

The stereochemical outcome of the reaction is determined in the step of the Mannich reaction, where ammonium enolate II adopts a Z-conformation aided by the 1,5-O S interaction (chalcogen-bonding catalysis) between the enolate oxygen anion and the S atom of the catalyst, which forms a conformational lock. The phenyl group shields the Si face of ammonium enolate, and the Re face is open for the imine approaching from the least hindered Re face. There are two orientations when imine approaches the enolate which affords two diastereomers, at the favored transition state, 1,5-O S interaction and π-π stacking interaction all contribute to induce the formation of the favored transition state; at the unfavored transition state, there is no π-π stacking interaction. Whatever orientation it takes when imine approaches the Re face of enolate, the configuration of the products at C3 is definite. When imine approaches the Re

face of enolate from different orientations, it will affect the configuration of the products at C2 as shown below. This rational is consistent with single X-ray crystal structure of 3ca and 4cm. (**Figure 6.2**)

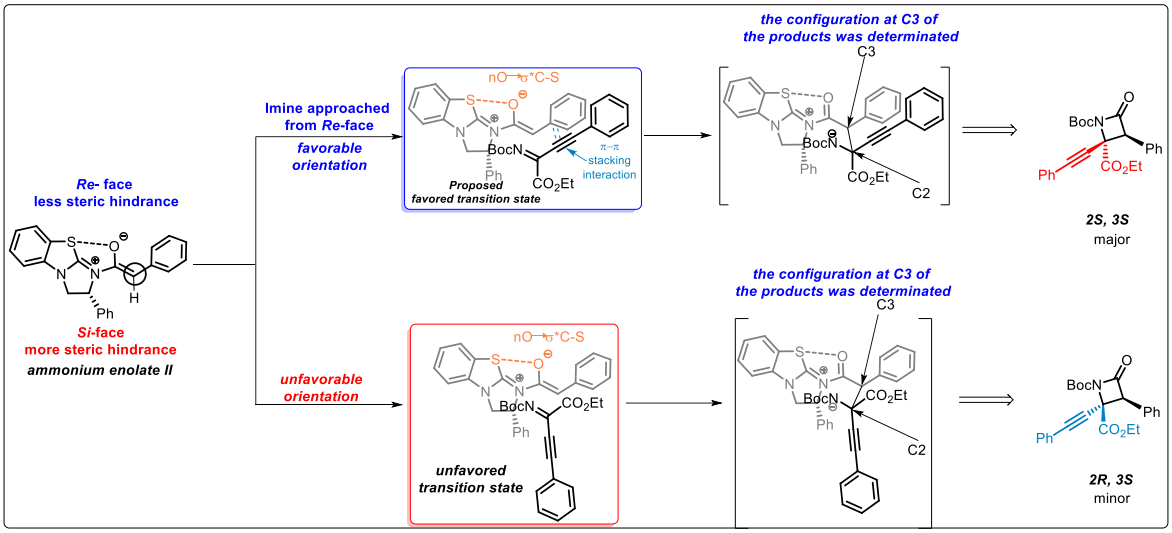


Figure 6.2

. In the reaction, the absolute configuration of the isothiourea catalyst is R configuration, therefore, according to our rational, the absolute configuration of the major product is (2S, 3S), and the minor is (2R, 3S), the relationship between them is diastereoisomer. At the same time, in the reaction, once β-lactam products were formed there would be the epimerization of carbonyl α-site, which afforded (2S, 3R) lactam as another diastereoisomer of (2S, 3S), it is the enantiomer of compound (2R, 3S) (**Figure 6.3**). **Therefore the ee value of the minor product is lower. In another word, the minor diastereoisomers in one pot reaction with our protocol were derived from two pathways.**

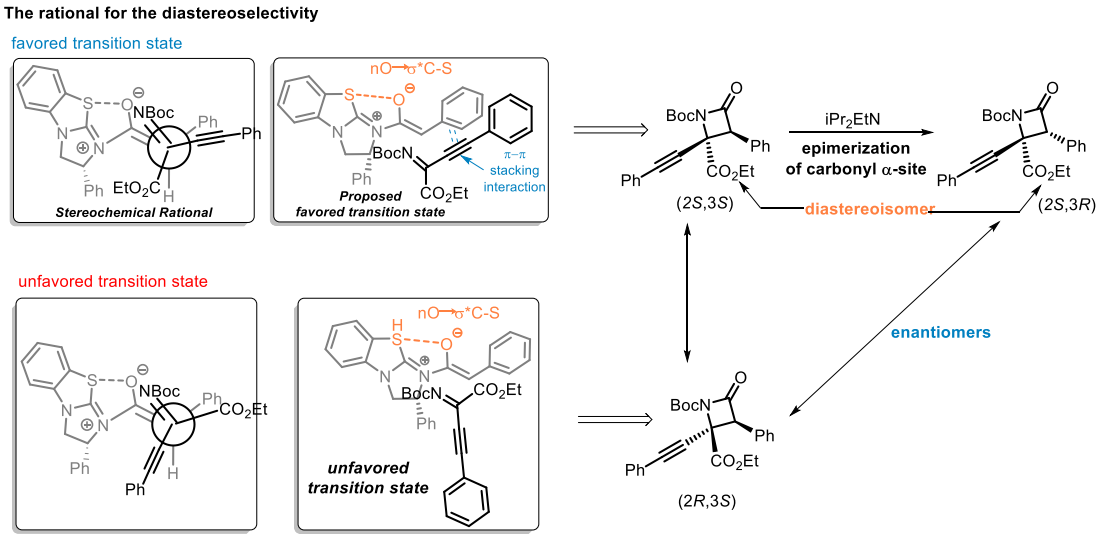


Figure 6.3 The rational for the stereochemistry and diastereoselectivity

This assumption was proved by experiments(**Figure 6.4**):

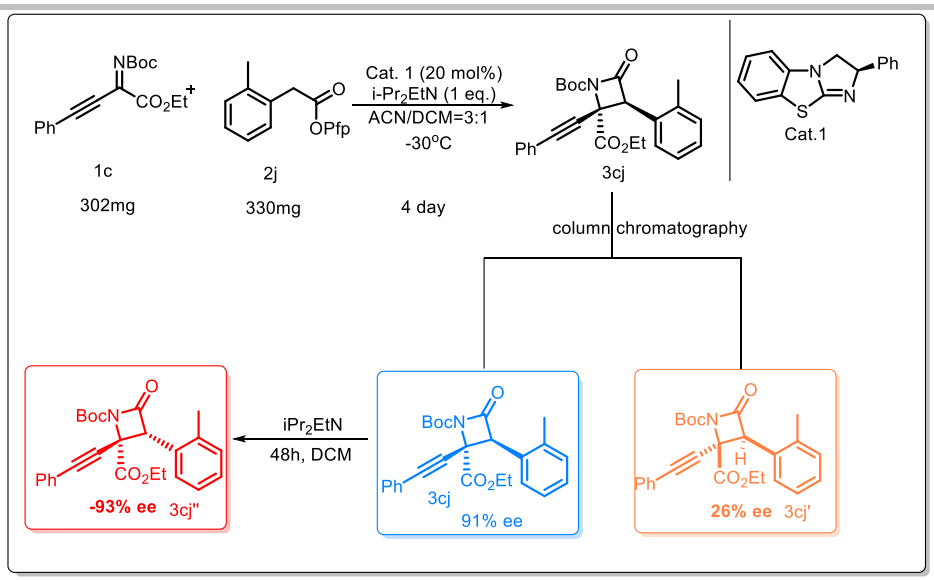
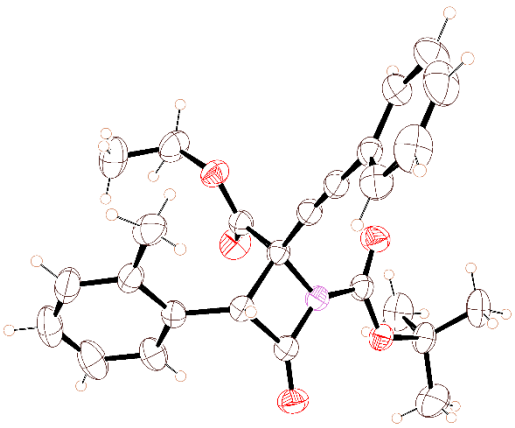


Figure 6.4

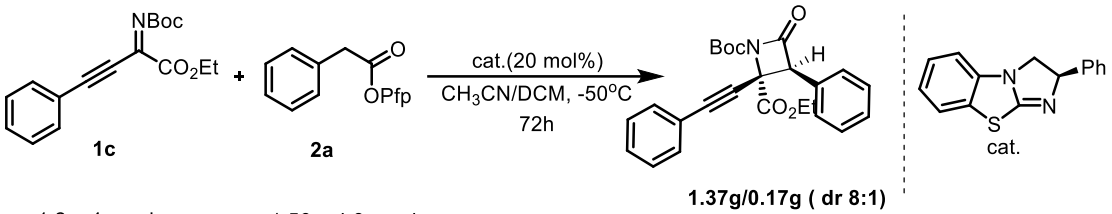
In order to as much as possible obtained the amount of **3cj'** obtained the single crystal we performed the reaction at -30°C (**Figure 6.4**). After stiring 4 days at the above conditions, we obtained two diastereoisomers by column chromatography, the ee value of **major product** (blue) is **91%**, the ee value of **minor product**(orange) is **26%**, then the **pure major product** was dissolved in DCM(1M) and stirred at 20°C in the presence of. iPr_2EtN(1 eq.), after 48h, we separated the **product 3cj''** that derived from epimerization by column chromatography, the ee value of **this product**(red) is -93%(compared with **3cj'**). But because the lower ee value **3cj'** afforded the racemic single crystal. This results indicated the minor diastereoisomers in one pot reaction with our protocol were derived from two pathways.



3cj' racemic CCDC 2118205

7 The gram scale synthesis and further transformation of product

7.1 The gram scale synthesis

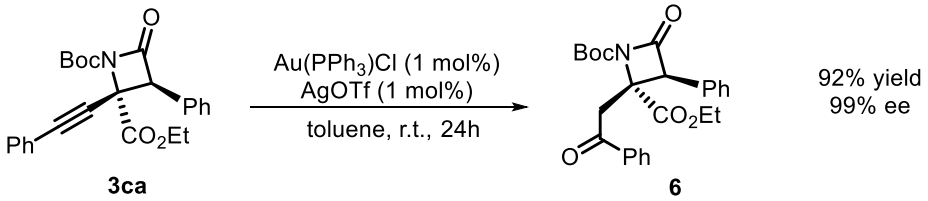


To a 100 mL round-bottom flask equipped with a magnetic stir bar was successively added **1c** (1.2g, 4mmol), **2a**(1.56g, 4.8mmol), cat(0.2g, 0.8mmol) and 0.32 mL i-Pr_2EtN, 40 mL precooled solvent(V_{CH3CN}/V_{DCM}=3/1), immediately the flask was put on low-temperature reactor. When TLC analysis showed the imine has been compeletly consumed, 40 mL 10% HCl was added to quench the reaction, then the mixture will be extracted three times by DCM (20mL*3), the combined organic phases were washed by NaCl(aq), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product **3ca** was purified by flash column chromatography. **4ca** was obtained by the similar procedurde.

7.2 The synthesis of 5

AgOTf(0.25mg, 0.01 mmol) and $AgClPPh_3$(0.49mg, 0.01mmol) was added in a 10 ml reaction tube equipped with a magnetic stir bar, 0.5 mL toluene was added and the mixture was stirred 10 minutes at room temperature. Later, **4ca** (47mg, 0.1 mmol) was added into reaction tube as well as another 0.5 mL. This mixture was stirred 24 hours at room temperature, after that this mixture was directly subjected to column chromatography on silica gel (9:1~3:1, PE/ EA) to afford the desired product **5**.

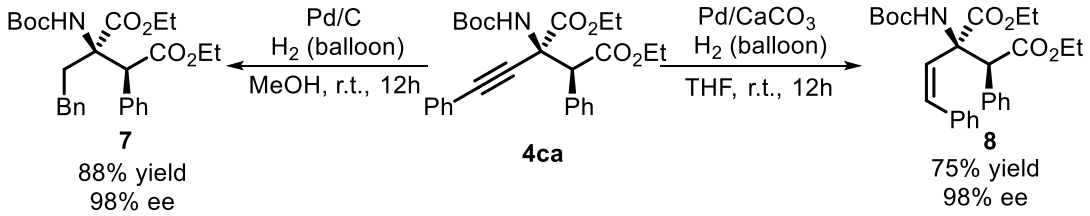
7.3 The synthesis of 6



AgOTf(0.25mg, 0.01 mmol) and $AgClPPh_3$(0.49mg, 0.01mmol) was added in a 10 ml reaction tube equipped with a magnetic stir bar, 0.5 mL toluene was added and the mixture was stirred 10 minutes at

room temperature. Later, **3ca** (42mg, 0.1 mmol) was added into reaction tube as well as another 0.5 mL. This mixture was stirred 24 hours at room temperature, after that this mixture was directly subjected to column chromatography on silica gel (9:1 PE/ EA) to afford the desired product **6**.

7.4 The synthesis of 7 and 8

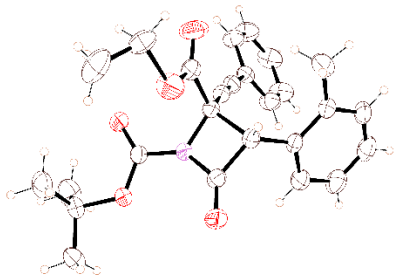


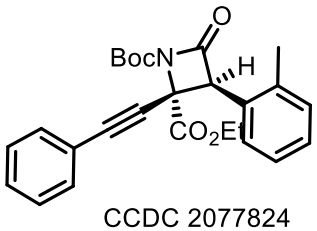
To a 10 mL reaction tube equipped with a magnetic stir bar was successively added $Pd/CaCO_3$(20mg, 50%wt), **4ca**(42mg, 0.1mmol) and 1mL THF, a hydrogen balloon was linked to the tube, then repeat the procudure evacuation and inflation three times, then stired overnight, after this, the reaction mixture was added silica gel and concentrated under reduced pressure, this mixture subjected to column chromatography on silica gel (10:1, PE/ EA) to afford the desired product **7**.

To a 10 mL reaction tube equipped with a magnetic stir bar was successively added $Pd/CaCO_3$ (6mg,), **4ca**(42mg, 0.1mmol) and 1mL THF, a hydrogen balloon was linked to the tube, then repeat the procudure evacuation and inflation three times, then stired overnight, after this, the reaction mixture was added silica gel and concentrated under reduced pressure, this mixture subjected to column chromatography on silica gel (10:1, PE/ EA) to afford the desired product **8**.

8 Crystal information

X-ray Crystallographic Data of Compound 3cj





CCDC 2077824

Bond precision:	C-C = 0.0047 A	Wavelength=1.54184	
Cell:	a = 8.3138(4)	b = 11.6732(4)	c = 25.1129(10)
	Alpha = 90	Beta = 90	Gamma = 90
Temperature:	292 K		
	Calculated	Reported	
Volume	2437.94(17)	2437.94(18)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	$C_{26}H_{27}NO_5$	$C_{26}H_{27}NO_5$	
Sum formula	$C_{26}H_{27}NO_5$	$C_{26}H_{27}NO_5$	
Mr	433.49	433.48	
Dx,g cm^{-3}	1.181	1.181	
Z	4	4	
Mu (mm^{-1})	0.664	0.664	
F000	920.0	920.0	
F000’	922.87		
h, k, lmax	10, 14, 30	9, 13, 30	
Nref	4608[2640]	3876	
Tmin,Tmax	0.911, 0.936	0.827, 1.000	
Tmin’	0.911		

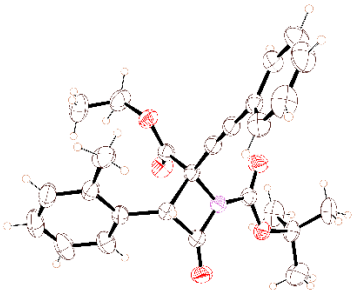
Correction method = # Reported T Limits: Tmin = 0.827 Tmax = 1.000
AbsCorr = MULTI-SCAN

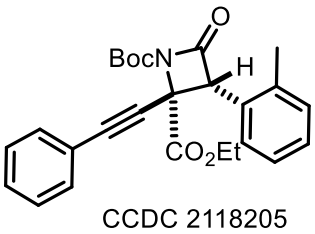
Data completeness = 1.47/0.84	Theta(max) = 69.736
R(reflections) = 0.0457(3241)	wR2(reflections) = 0.1204(3876)
S = 1.059	Npar= 313

Displacement ellipsoids are drawn at 50% probability level

Attention: The pure compouds (30 mg) of 3cj was dissolved in $CDCl_3$ and was removed in NMR tube. After the NMR experiments were finished, the tube was placed in the lab for about 20 days, during which the crystal was formed. The X-ray was detected after the crystal was formed.

X-ray Crystallographic Data of Compound 3cj‘





CCDC 2118205

No syntax errors found. CIF dictionary Interpreting this report

Datablock: jidongsheng_1014_auto

Bond precision: C-C = 0.0027 A Wavelength=1.54184

Cell: a=8.76363(11) b=11.32074(14) c=13.30299(13)
alpha=97.5000(9) beta=93.5092(9) gamma=110.6596(12)
Temperature: 293 K

	Calculated	Reported
Volume	1216.15(3)	1216.15(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C26 H27 N O5	C26 H27 N O5
Sum formula	C26 H27 N O5	C26 H27 N O5
Mr	433.49	433.48
Dx,g cm-3	1.184	1.184
Z	2	2
Mu (mm-1)	0.666	0.666
F000	460.0	460.0
F000’	461.44	
h,k,lmax	11,14,16	10,14,16
Nref	5107	4883
Tmin,Tmax	0.916,0.948	0.549,1.000
Tmin’	0.905	

Correction method= # Reported T Limits: Tmin=0.549 Tmax=1.000
AbsCorr = MULTI-SCAN

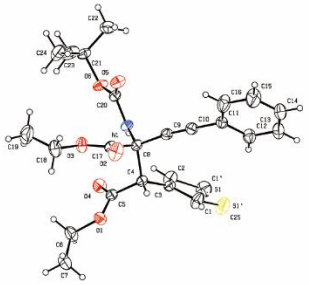
Data completeness= 0.956 Theta(max)= 76.385

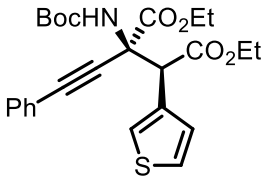
R(reflections)= 0.0467(4026) wR2(reflections)= 0.1406(4883)

S = 1.092 Npar= 304

Attention: The pure compouds (20 mg) of 3cj‘ was dissolved in EA as a saturated solution, then 0.1-0.2 mL hexane was added, then this solution was placed at the refrigerator(-5 ^{o}C) after volatilize of solvents in 3 days the crystal was formed. The X-ray was detected after the crystal was formed.

X-ray Crystallographic Data of Compound 4cm





CCDC 2111690

No syntax errors found. CIF dictionary Interpreting this report

Datablock: jidongs-0923-1_auto

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Cell:           a=10.34486(14)   b=10.19459(12)       c=12.07537(18)
                alpha=90         beta=105.0474(15)    gamma=90
Temperature:    303 K

                 Calculated                Reported
Volume           1229.82(3)                1229.82(3)
Space group      P 21                      P 1 21 1
Hall group       P 2yb                     P 2yb
Moiety formula   C25 H28 N O6 S            C25 H28 N O6 S
Sum formula      C25 H28 N O6 S            C25 H28 N O6 S
Mr               470.54                    470.54
Dx,g cm-3        1.271                     1.271
Z                2                         2
Mu (mm-1)        1.501                     1.501
F000             498.0                     498.0
F000'            500.17
h,k,lmax         13,12,15                  13,12,15
Nref             5139[ 2721]               4877
Tmin,Tmax        0.820,0.900               0.796,1.000
Tmin'            0.810

Correction method= # Reported T Limits: Tmin=0.796 Tmax=1.000
AbsCorr = MULTI-SCAN

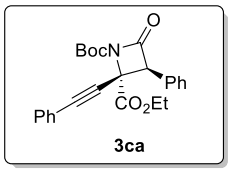
Data completeness= 1.79/0.95        Theta(max)= 76.245

R(reflections)= 0.0357( 4501)                    wR2(reflections)=
                                                 0.1001( 4877)
S = 1.065                  Npar= 304
```

Attention: The pure compouds (150 mg) of 4cm was dissolved in EA as a saturated solution, then 0.1mL hexane was added, then this solution was placed refrigerator (temperature approximately -5^{o}C) after 7 days the crystal was formed. The X-ray was detected after the crystal was formed.

9 The characterization data of product

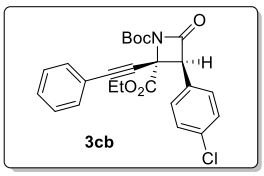
1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-3-phenyl-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3ca)



Chemical Formula: $C_{25}H_{25}NO_5$

An coloress liquid, 85% yield (36 mg). $[\alpha]_D^{23}$ = -19 (*c* 1.0, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.33(m, 5H), 7.24-7.29(m, 1H), 7.22-7.17(m, 2H), 7.04-6.99(m, 2H), 4.75(s, 1H), 4.47-4.33(m, 2H), 1.56(m, 9H), 1.38(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.6, 146.2, 131.7, 130.6, 129.2, 128.9, 128.7, 128.5, 128.0, 121.3, 89.9, 84.3, 80.7, 66.0, 63.1, 61.1, 27.9, 14.1. HPLC : Chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 13.98 min, minor enantiomer t_R = 17.34 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{25}NO_5Na]$:442.1625, found:442.1626.

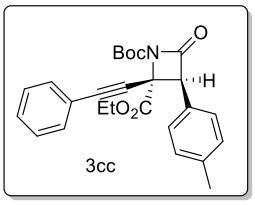
1-(tert-butyl) 2-ethyl (2S,3S)-3-(4-chlorophenyl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3cb)



An coloress liquid, 80% yield (36 mg). $[\alpha]_D^{23}$ = 16 (*c* 1.0, CH_2Cl_2, 98% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.36(m, 2H), 7.33-7.28(m, 3H), 7.27-7.22(m, 2H), 7.08-7.03(m, 2H), 7.72(s, 1H), 4.47-4.43(m, 2H), 1.56(s, 9H), 1.39(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.4, 163.0, 146.1, 134.8, 131.8, 130.6, 129.2, 129.1, 128.7, 128.2, 121.1, 90.3, 84.5, 80.5, 65.1, 63.3, 60.9, 27.9, 14.1. HPLC : chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 12.90 min, minor enantiomer t_R = 14.87 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{24}ClNO_5Na]$:476.1235, found:476.1229.

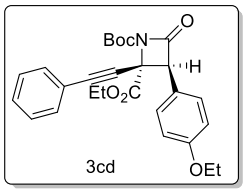
1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-2-(phenylethynyl)-3-(p-tolyl)azetidine-1,2-dicarboxylate (3cc)

An coloress liquid, 80% yield (35 mg). $[\alpha]_D^{23}$ = 17 (*c* 1.0, CH_2Cl_2, >99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 1H), 7.25 – 7.19 (m, 6H), 7.05 – 7.02 (m, 2H), 4.71 (s, 1H), 4.47 – 4.31 (m, 2H), 2.37 (s, 3H), 1.55 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, cdcl$_3$) δ 167.6, 163.6, 146.3, 138.6, 131.8, 129.2, 129.1, 128.8, 128.1, 127.7, 121.6, 89.9, 84.2, 81.2, 66.1, 63.0, 61.3, 28.0, 21.2, 14.1. HPLC : chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 14.14 min, minor enantiomer t_R = 16.30 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{27}NO_5Na]$:456.1781, found:456.1775.

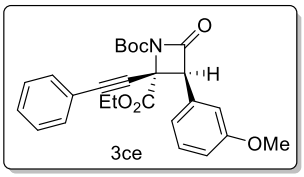


1-(tert-butyl) 2-ethyl (2S,3S)-3-(4-ethoxyphenyl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3cd)

An coloress liquid, 78% yield (36 mg). $[\alpha]_D^{23}$ = 6 (*c* 1.0, CH_2Cl_2, >99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (m, 3H), 7.21 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 1H), 4.45 – 4.34 (m, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 1.55 (s, 9H), 1.40 (m, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.7, 163.9, 159.3, 146.3, 131.8, 130.6 , 128.9 , 128.0 , 122.5 , 114.6 , 89.9, 84.3, 81.1, 65.9 , 63.6 , 63.0 , 61.5 , 28.0 , 14.7 , 14.1. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 12.25 min, minor enantiomer t_R = 20.78 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{27}H_{29}NO_6Na]$:486.1887, found:486.1882.



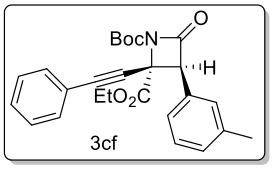
1-(tert-butyl) 2-ethyl (2S,3S)-3-(3-methoxyphenyl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3ce)



Chemical Formula: $C_{26}H_{27}NO_6$

An coloress liquid, 81% yield (37 mg). $[\alpha]_D^{23}$ = 11 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H NMR (100 MHz, Chloroform-*d*) δ 7.34-7.26(m, 2H), 9.25-9.19(m, 2H), 7.09-7.01(m, 2H), 6.95 (m, 1H), 6.92(m, 1H), 6.89(m, 1H), 4.73(s ,1H), 4.47-4.33(m, 2H), 3.78(s, 3H), 1.56(s, 9H), 1.39(t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ167.6, 163.3, 159.6, 146.2, 131.8, 131.8, 129.5, 128.9, 128.1, 121.7, 121.4, 114.6, 114.5, 89.9, 84.4, 80.7, 66.0, 63.2, 61.0, 55.3, 28.0, 14.1. HPLC : chiral IF column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; major enantiomer t_R = 17.56 min, minor enantiomer t_R = 22.67 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{27}NO_6Na]$:472.1731, found:472.1726.

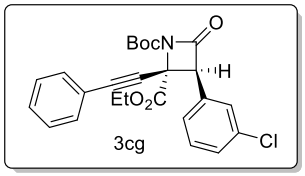
1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-2-(phenylethynyl)-3-(m-tolyl)azetidine-1,2-dicarboxylate (3cf)



Chemical Formula: $C_{26}H_{27}NO_5$

An coloress liquid, 73% yield (32 mg). $[\alpha]_D^{20}$ = 22 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (m, 1H), 7.27 (m, 1H), 7.21 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.93 (m, 2H), 6.89 (s, 1H), 4.72 (s, 1H), 4.46 – 4.34 (m, 2H), 3.78 (s, 3H), 1.56 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.6, 163.2, 159.7, 146.2, 132.0, 131.8, 129.5, 128.9, 128.1, 121.7, 121.6, 114.6, 90.0, 84.3, 81.0, 66.1, 63.1, 61.1, 55.3, 28.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 13.33 min, minor enantiomer t_R = 16.88 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{27}NO_5Na]$: 456.1781, found: 456.1774.

1-(tert-butyl) 2-ethyl (2S,3S)-3-(3-chlorophenyl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate(3cg)

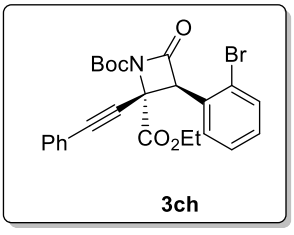


Chemical Formula: $C_{25}H_{24}ClNO_5$

An coloress liquid, 65% yield (31 mg). $[\alpha]_D^{24}$ = 6 (*c* 1.0, CH_2Cl_2, 95% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.38(m, 1H), 7.38-7.34(m, 1H), 7.34-7.31(m, 1H), 7.30-7.27(m, 1H), 7.27-7.20(m, 3H), 7.14-7.08(m, 2H), 4.71(s, 1H), 4.47-4.34(m, 2H), 1.56(s, 9H), 1.39(t, *J* = 7.2Hz, 3H); ^{13}C NMR (100MHz, Chloroform-*d*) δ167.3, 162.7, 146.0, 134.4, 132.5, 131.8, 129.8, 129.4, 129.1, 129.0, 128.2, 127.5, 121.1, 90.5, 84.6, 80.4, 65.1, 63.3, 60.8, 27.9, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 11.67 min, minor enantiomer t_R = 14.1 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{24}ClNO_5Na]$:476.1235, found:476.1231.

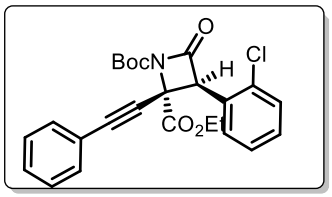
1-(tert-butyl) 2-ethyl (2S,3S)-3-(2-bromophenyl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3ch major enantiomer seprated by preparative liquid chromatography**)**

An coloress liquid, 78% yield (39 mg). $[\alpha]_D^{27.2}$ = 62 (*c* 0.5, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63(d, *J* = 8 Hz, 1H), 7.55-7.52(m, 1H), 7.39-7.35(m, 1H), 7.28-7.24(m, 2H), 7.21-7.17(m, 2H), 6.98(d, *J* = 7.2 Hz, 2H), 5.22(s, 1H), 4.48-4.38(m, 2H), 1.55(s, 9H), 1.39(t, *J* = 7.2 Hz,3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.4, 163.1, 146.1, 132.7, 131.8, 131.5, 130.4, 130.2, 128.8, 128.0, 127.5, 125.5, 121.5, 89.5, 84.6, 80.5, 66.1, 63.1, 61.0, 28.0, 14.2. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 11.38 min, minor enantiomer t_R = 12.96 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{25}BrNO_5Na]$: 520.0730, 522.0710, found: 520.0725, 522.0704.



1-(tert-butyl) 2-ethyl (2S,3S)-3-(2-chlorophenyl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate(3ci major enantiomer major enantiomer seprated by preparative liquid chromatography**)**

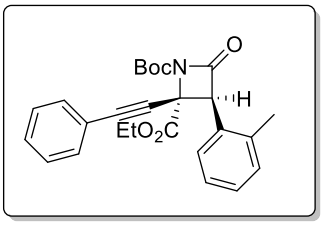
An coloress liquid, 80% yield (35 mg). $[\alpha]_D^{27.2}$ = 35 (*c* 0.5, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 6.6 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.33 (m, 2H), 7.25 (m, 1H), 7.18 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 5.20 (s, 1H), 4.49 – 4.35 (m, 2H), 1.55 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 167.4, 163.0, 146.1, 134.9, 131.8, 130.2, 130.0, 129.6, 129.4, 128.9, 128.0, 126.9, 121.4, 89.3, 84.5, 80.4, 63.9, 63.1, 60.9, 28.0, 14.1HPLC: chiral If column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 8.857 min, minor enantiomer t_R =9.976 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{24}ClNO_5Na]$: 476.1235, found:476.1233.



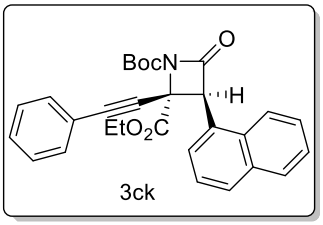
Chemical Formula: $C_{25}H_{24}ClNO_5$

(2S,3S)-4-oxo-2-(phenylethynyl)-3-(o-tolyl)azetidine-1,2-dicarboxylate (3cj)

An coloress liquid, 80% yield (35 mg). $[\alpha]_D^{27.2}$ = 56 (*c* 0.5, CH_2Cl_2, 90% ee); ^{1} H NMR (600 MHz, Chloroform-d) δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.30 (m, 1H), 7.27 – 7.22 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 7.2Hz, 2H), 4.92 (s, 1H), 4.49 – 4.34 (m, 2H), 2.24 (s, 3H), 1.55(s, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 167.9, 163.9, 146.2, 137.4, 131.9, 130.3, 129.8, 128.8, 128.7, 128.0, 126.1, 121.5, 89.3, 84.4, 80.4, 64.3, 63.1, 61.1, 28.0, 19.6, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; major enantiomer t_R = 23.86 min, minor enantiomer t_R = 26.12 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{27}NO_5Na]$: 456.1775, found: 456.1781.

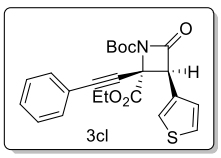


1-(tert-butyl) 2-ethyl (2S,3S)-3-(naphthalen-1-yl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3ck)



An coloress liquid, 85% yield (41 mg). $[\alpha]_D^{27.1}$ = 384 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (m, 2H), 7.69 (m, 2H), 7.54 – 7.48 (m, 3H), 7.14 (m, 1H), 7.04 (m, 2H), 6.58 (d, *J* = 7.8 Hz, 2H), 5.47 (s, 1H), 4.57 (m, 1H), 4.44 (m, 1H), 1.57 (s, 9H), 1.45 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, cdcl$_3$) δ 168.0, 163.8, 146.3, 133.8, 131.9, 131.6, 129.4, 128.9, 128.6, 127.8, 127.4, 127.0, 126.6, 126.0, 125.3, 123.0, 121.3, 89.3, 84.4, 80.7, 63.7, 63.2, 61.5, 28.0, 14.2. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; minor enantiomer t_R = 32.54 min, major enantiomer t_R = 42.9 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{29}H_{27}NO_5Na]$: 492.1781, found: 492.1773.

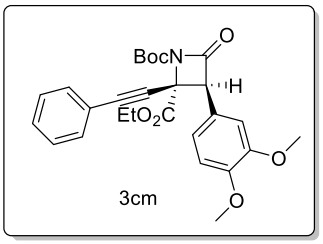
1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-2-(phenylethynyl)-3-(thiophen-2-yl)azetidine-1,2-dicarboxylate (3cl)



An coloress liquid, 69% yield (30 mg). $[\alpha]_D^{20}$ = 4 (*c* 0.5, CH_2Cl_2, >99% ee); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (s, 1H), 7.37 (m, 1H), 7.30 (m, 1H), 7.26 (d, *J* = 3.0 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 4.8 Hz, 1H), 4.78 (s, 1H), 4.45 – 4.34 (m, 2H), 1.55 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.5, 163.3, 146.3, 131.9, 130.5, 129.0, 128.2, 127.8, 125.9, 125.4, 121.6, 89.7, 84.4, 80.8, 63.1, 61.6, 61.0, 28.0, 14.2. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 15.27 min, minor enantiomer t_R = 19.86 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{23}H_{23}NO_5SNa]$: 448.1189, found: 448.1184.

1-(tert-butyl) 2-ethyl (2S,3S)-3-(3,4-dimethoxyphenyl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3cm)

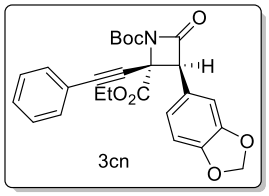
An coloress liquid,79% yield (38 mg). $[\alpha]_D^{27.2}$ = -12 (*c* 1.0, CH_2Cl_2, >99% ee); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 1H), 7.23 (m, 2H), 7.09 (m, 2H), 6.92 – 6.85 (m, 3H), 4.71 (s, 1H), 4.46 – 4.34 (m, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 1.56 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.6, 163.7, 149.6, 149.0, 146.2, 131.7, 128.9, 128.1, 123.0, 122.2, 121.5, 112.4, 111.3, 89.9, 84.2, 81.1, 66.1, 63.0, 61.4, 56.07, 56.02, 28.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 39.81min, minor enantiomer t_R = 36.72 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{27}H_{29}NO_7Na]$:502.1836, found:502.1829.



Chemical Formula: $C_{27}H_{29}NO_7$

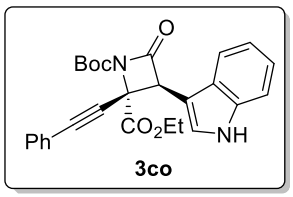
1-(tert-butyl) 2-ethyl (2S,3S)-3-(benzo[d][1,3]dioxol-5-yl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3cn)

An coloress liquid, 82% yield (38 mg). $[\alpha]_D^{23.8}$ = 14 (*c* 1.0, CH_2Cl_2, 99% ee); ^{1}H NMR (600 MHz, Chloroform-d) δ 7.30 (m, 1H), 7.24 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.83 (s, 3H), 5.95 (s, 2H), 4.66 (s, 1H), 4.44 – 4.34 (m, 2H), 1.55 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 167.5, 163.4, 148.1, 147.8, 146.2, 131.8, 129.0, 128.2, 124.1, 123.2, 121.6, 109.7, 108.3, 101.3, 90.0, 84.3, 81.0, 66.1, 63.1, 61.4, 28.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 22.04 min, minor major enantiomer t_R = 27.11 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{25}NO_7Na]$: 486.1817, found: 486.1523.

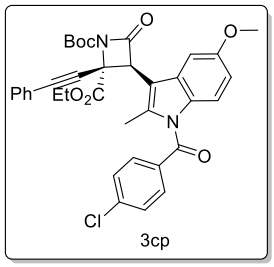


1-(tert-butyl) 2-ethyl (2S,3S)-3-(1H-indol-3-yl)-4-oxo-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3co)

An coloress liquid, 82% yield (37 mg). $[\alpha]_D^{23.4}$ = -4 (*c* 0.5, CH_2Cl_2, >99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54(br, 1H), 7.60(d, *J* = 8 Hz, 1H), 7.40(d, *J* = 8.4 Hz, 1H),7.23-7.21(m, 1H), 7.21-7.09(m, 3H), 7.08-7.02(m, 2H), 6.64(d, *J* = 7.2 Hz, 2H), 4.98(s, 1H), 4.51-4.35(m, 2H), 1.57(s, 9H), 1.40(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ167.9, 164.6 ,146.5 ,136.2 ,128.6 ,127.9 ,126.8 , 124.8, 122.4, 121.4 , 120.1, 119.3, 111.4, 105.2, 89.1, 84.3, 81.1, 63.1, 61.5, 59.8, 28.0, 14.2. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 21.25 min, minor enantiomer t_R = 19.80 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{27}H_{26}N_2O_5Na]$: 481.1734, found: 481.1739



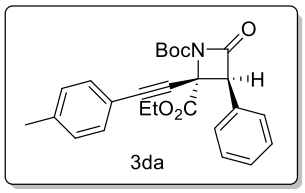
tert-butyl-(2S,3S)-3-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-4-oxo-2-(phenylethynyl)-2-(propionyloxy)azetidine-1-carboxylate (3cp)



An coloress liquid, 66% yield (43 mg). $[\alpha]_D^{23.4}$ = -16 (*c* 1.0, CH_2Cl_2, 85% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53(d, *J* = 8 Hz, 2H), 7.34(d, *J* = 8 Hz, 2H), 7.29-7.24(m, 1H), 7.20-7.11(m, 2H), 6.98(s, 1H), 6.86-6.80(m, 2H), 6.72-3.67(m, 1H), 4.93(s, 1H), 4.49-4.36(m, 2H), 3.77(s, 3H), 2.39(m, 3H), 1.58(s, 9H), 1.40(t, *J* = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) 168.2, 167.6, 163.5, 156.0, 146.2, 139.7, 138.7, 133.2, 131.7, 131.3, 130.8, 129.1, 129.0, 128.1, 121.3, 114.7, 111.8, 108.6, 89.5, 84.5, 80.8, 63.2, 60.8, 58.9, 55.6, 28.0, 14.2. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 0.8 mL/min; major enantiomer t_R = 57.60 min, minor enantiomer t_R = 74.16 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{36}H_{33}N_2O_7ClNa]$: 663.1869, found: 663.1871.

1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-3-phenyl-2-(p-tolylethynyl)azetidine-1,2-dicarboxylate (3da)

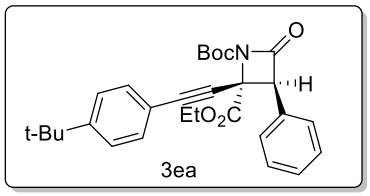
An coloress liquid, 80% yield (35 mg). $[\alpha]_D^{23.4}$ = 35 (*c* 1.0, CH_2Cl_2, >99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 3H), 7.35-7.33(m, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 4.74 (s, 1H), 4.49 – 4.31 (m, 3H), 2.29 (s, 3H), 1.55 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, cdcl$_3$) δ 167.7, 163.5, 146.3, 139.2, 131.7, 130.8, 129.3, 128.8, 128.7, 128.5, 118.4, 97.0, 90.3, 84.3, 80.2, 66.1, 63.1, 61.3, 28.0, 21.4, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 14.61 min, minor enantiomer t_R = 18.10 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{27}NO_5Na]$: 456.1775, found: 456.1781.



Chemical Formula: $C_{26}H_{27}NO_5$

1-(tert-butyl) 2-ethyl (2S,3S)-2-((4-(tert-butyl)phenyl)ethynyl)-4-oxo-3-phenylazetidine-1,2-dicarboxylate (3ea)

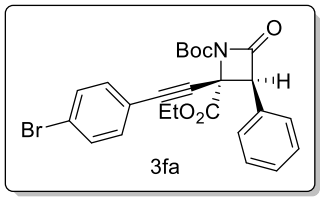
An coloress liquid, 80% yield (38 mg). $[\alpha]_D^{24}$ = 31 (*c* 1.0, CH_2Cl_2, 98% ee); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 (m, , 3H), 7.34 (m, , 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.74 (s, 1H), 4.40 (m, 2H), 1.56 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 9H).^{13}C NMR (151 MHz, Chloroform-d) δ 167.7, 163.5, 152.4, 146.3, 131.6, 130.8, 129.3, 128.7, 128.5, 125.1, 118.4, 90.2, 84.4, 80.1, 66.1, 63.1, 61.3, 34.8, 31.0, 28.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 13.13 min, minor enantiomer t_R = 16.12 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{29}H_{33}NO_5Na]$:498.2251, found:498.2256.



Chemical Formula: $C_{29}H_{33}NO_5$

1-(tert-butyl) 2-ethyl (2S,3S)-2-((4-bromophenyl)ethynyl)-4-oxo-3-phenylazetidine-1,2-dicarboxylate (3fa)

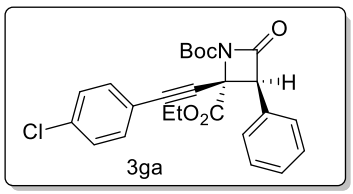
An coloress liquid, 82% yield (47 mg). $[\alpha]_D^{23.3}$ = 58 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 (m, 3H), 7.36 – 7.32 (m, 4H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.75 (s, 1H), 4.47 – 4.34 (m, 2H), 1.56 (s, 9H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, cdcl$_3$) δ 167.4, 163.1, 146.3, 133.2, 131.5, 130.8, 129.3, 128.8, 128.6, 123.4, 120.4, 88.9, 84.5, 82.2, 66.1, 63.2, 61.1, 28.0, 14.2. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 20.11 min, major enantiomer t_R = 15.96 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{24}BrNO_5Na]$:522.0710, 520.0730, found:522.0714, 520.0725.



Chemical Formula: $C_{25}H_{24}BrNO_5$

1-(tert-butyl) 2-ethyl (2S,3S)-2-((4-chlorophenyl)ethynyl)-4-oxo-3-phenylazetidine-1,2-dicarboxylate (3ga)

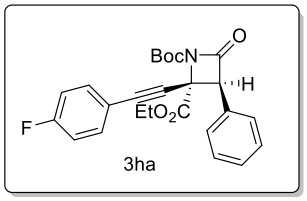
An coloress liquid, 69% yield (39 mg). $[\alpha]_D^{22.6}$ = 41 (*c* 1.0, CH_2Cl_2, 96% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42-7.37 (m, 3H), 7.36 – 7.31 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 4.75 (s, 1H), 4.47 – 4.34 (m, 2H), 1.56 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.5, 163.1, 146.3, 135.1, 133.0, 130.8, 129.3, 128.8, 128.6, 128.5, 120.0, 88.9, 84.4, 82.1, 66.2, 63.2, 61.0, 28.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 12.4 min, minor enantiomer t_R = 14.19 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{24}ClNO_5Na]$:476.1235, found:476.1231.



Chemical Formula: $C_{25}H_{24}ClNO_5$

1-(tert-butyl) 2-ethyl (2S,3S)-2-((4-fluorophenyl)ethynyl)-4-oxo-3-phenylazetidine-1,2-dicarboxylate (3ha)

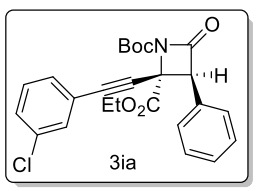
An coloress liquid, 91% yield (39 mg). $[\alpha]_D^{23}$ = 27 (*c* 1.0, CH_2Cl_2, 98% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (m, 3H), 7.34 (m, 2H), 6.98 (m, 2H), 6.89 (t, *J* = 8.6 Hz, 2H), 4.75 (s, 1H), 4.49 – 4.33 (m, 2H), 1.56 (s, 9H), 1.39 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.5, 163.2, 163.0(d, J_{C-F} = 250.6 Hz), 162.0, 146.2, 133.8(d, J_{C-F} = 9.1 Hz), 130.7, 129.2, 128.7, 128.5, 117.5 (d, J_{C-F} = 3.0 Hz), 115.5(d, J_{C-F} = 22.6 Hz), 89.0, 84.4, 80.7, 66.1, 63.1, 61.1, 28.0, 14.1.HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 12.3 min, minor enantiomer t_R = 15.4 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{24}FNO_5Na]$:460.1531, found:460.1526.



Chemical Formula: $C_{25}H_{24}FNO_5$

1-(tert-butyl) 2-ethyl (2S,3S)-2-((3-chlorophenyl)ethynyl)-4-oxo-3-phenylazetidine-1,2-dicarboxylate (3ia)

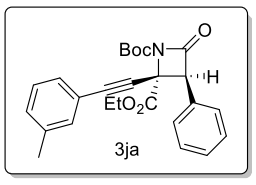
An coloress liquid, 65% yield (29 mg). $[\alpha]_D^{24}$ = 29 (*c* 1.0, CH_2Cl_2, 98% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (s, 3H), 7.36 – 7.32 (m, 2H), 7.28 – 7.23 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.95 (s, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.76 (s, 1H), 4.46 – 4.36 (m, 2H), 1.56 (s, 9H), 1.39 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.4, 163.0, 146.2, 134.0, 131.8, 130.7, 129.8, 129.4, 129.2, 128.9, 128.6, 123.2, 88.5, 84.5, 82.3, 66.2, 63.2, 61.0, 28.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 21.21 min, minor enantiomer t_R = 13.15 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{25}H_{24}ClNO_5Na]$:476.1235, found:476.1229.



Chemical Formula: $C_{25}H_{24}ClNO_5$

1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-3-phenyl-2-(m-tolylethynyl)azetidine-1,2-dicarboxylate (3ja)

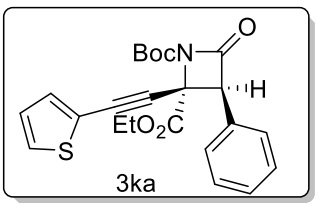
An coloress liquid, 77% yield (33 mg). $[\alpha]_D^{24}$ = 34 (*c* 1.0, CH_2Cl_2, 98% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43-7.38 (m, 3H), 7.37-7.33 (m, 2H), 7.11-7.06 (m, 2H), 6.82 (s, 2H), 4.75 (s, 1H), 4.47 – 4.34 (m, 2H), 2.24 (s, 3H), 1.56 (s, 9H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, cdcl$_3$) δ 167.7, 163.4, 146.3, 137.8, 132.4, 130.8, 129.8, 129.3, 128.8, 128.7, 128.5, 128.0, 121.3, 90.2, 84.3, 80.6, 66.2, 63.1, 61.2, 28.0, 21.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 13.76 min, major enantiomer t_R = 11.41 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{26}H_{27}NO_5Na]$:456.1181, found:456.1176.



Chemical Formula: $C_{26}H_{27}NO_5$

1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-3-phenyl-2-(thiophen-2-ylethynyl)azetidine-1,2-dicarboxylate (3ka)

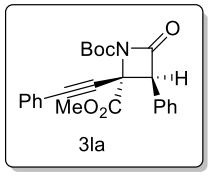
An coloress liquid, 69% yield (29 mg). $[\alpha]_D^{24}$ = 25 (*c* 1.0, CH_2Cl_2, 98% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43-7.37(m, 3H), 7.36 – 7.31 (m, 2H), 7.22 – 7.18 (m, 1H), 6.90 – 6.85 (m, 2H), 4.75 (s, 1H), 4.46 – 4.34 (m, 2H), 1.55 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.4, 163.2, 146.2, 133.1, 130.5, 129.2, 128.8, 128.6, 128.1, 126.8, 121.3, 84.9, 84.5, 83.5, 66.3, 63.2, 61.4, 28.0, 14.1. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 10.59 min, major enantiomer t_R = 13.18 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{23}H_{23}NO_5SNa]$:448.1189, found:448.1183.



Chemical Formula: $C_{23}H_{23}NO_5S$

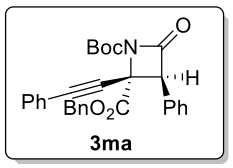
1-(tert-butyl) 2-methyl (2S,3S)-4-oxo-3-phenyl-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3la)

An coloress liquid, 82% yield (33 mg). $[\alpha]_D^{23}$ = 16 (*c* 1.0, CH_2Cl_2, 95% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.39(m, 3H), 7.37-7.33(m, 2H), 7.29-7.24(m, 1H), 7.23-7.17(m, 2H), 7.04-6.99(m, 2H), 4.77(s, 1H), 3.95(s, 3H), 1.56(s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 163.3, 146.2, 131.8, 130.6, 129.3, 129.0, 128.8, 128.5, 128.1, 121.2, 90.0, 84.5, 80.6, 66.1, 60.9, 53.9, 28.0. HPLC : chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 13.2 min, minor enantiomer t_R = 19.6 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{24}H_{23}NO_5Na]$:428.1468, found:428.1472.



Chemical Formula: $C_{24}H_{23}NO_5$

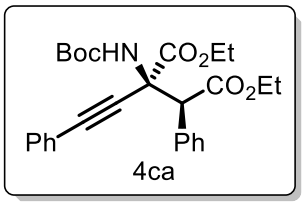
1-(tert-butyl) 2-ethyl (2S,3S)-4-oxo-3-phenyl-2-(phenylethynyl)azetidine-1,2-dicarboxylate (3ma)



Chemical Formula: $C_{30}H_{27}NO_5$

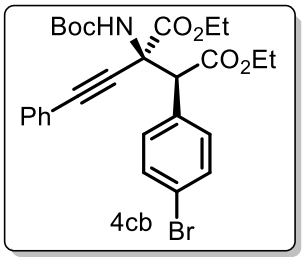
An coloress liquid, 87% yield (42 mg). $[\alpha]_D^{24}$ = 20 (*c* 1.0, CH_2Cl_2, 95% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45-7.40(m, 2H), 7.41-7.34(m, 6H), 7.33-7.28(m, 2H), 7.28-7.24(m, 1H), 7.23-7.17(m, 2H), 7.03-6.98(m, 2H), 5.42(d, *J* = 12Hz, 1H), 5.32(d, *J* = 12Hz 1H), 4.70(s, 1H), 1.47(s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.4, 163.3, 146.1, 134.8, 131.8, 130.5, 129.3, 129.0, 128.8, 128.7, 128.5, 128.3, 128.1, 121.3, 90.0, 84.4, 80.6, 68.4, 66.1, 61.1, 27.8. HPLC : chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 20.12 min, minor enantiomer t_R = 25.88 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{30}H_{27}NO_5Na]$:504.1781, found:504.1786.

diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-phenyl-2-(phenylethynyl)succinate (4ca)



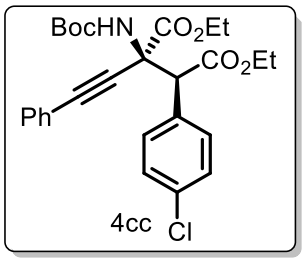
An coloress liquid, 81% yield (41 mg). $[\alpha]_D^{20}$ = -17 (*c* 1.0, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.43 – 7.37 (m, 2H), 7.35 – 7.27 (m, 6H), 6.32 (s, 1H), 4.37 (s, 1H), 4.28 – 4.14 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.44 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 168.29, 154.2, 132.7, 131.7, 130.5, 128.4, 128.3, 128.1, 127.9 , 80.5, 62.4 , 61.6 , 60.8, 57.3, 28.20, 14.0, 13.7. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; minor enantiomer t_R = 29.83 min, major enantiomer t_R = 31.98 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{31}NO_6Na]$:488.2044 found:488.2048.

diethyl (2S,3S)-3-(4-bromophenyl)-2-((tert-butoxycarbonyl)amino)-2-(phenylethynyl)succinate (4cb)



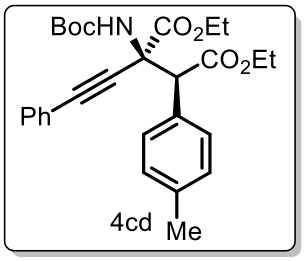
An coloress liquid, 75% yield (41 mg). $[\alpha]_D^{20}$ = -2 (*c* 1.0, CH_2Cl_2, 98% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48-7.44(m, 4H), 7.42-7.39(m, 2H), 7.35-7.29(m, 3H), 6.19(br, 1H), 4.40(s, 1H), 4.19-4.16(m, 2H), 4.12(q, 2H), 1.44(s, 9H), 1.24(t, *J* = 7.2 Hz, 3H), 1.16(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.2, 168.1, 154.1, 132.3, 132.0, 131.7, 131.1, 128.7, 128.2, 122.7, 122.2, 87.2, 84.5, 80.7, 62.6, 61.8, 60.5, 56.6, 28.2, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; minor enantiomer t_R = 9.83 min, major enantiomer t_R = 10.99 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{30}BrNO_6Na]$:566.1149, 568.1128 found:566.1149, 568.1126.

diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-(4-chlorophenyl)-2-(phenylethynyl)succinate (4cc)



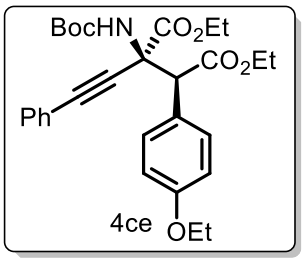
An coloress liquid, 73% yield (37 mg). $[\alpha]_D^{20}$ = 22 (*c* 1.0, CH_2Cl_2, >99% ee); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 2H), 7.35 – 7.30 (m, 5H), 7.28 – 7.25 (m, 2H), 6.33 (s, 1H), 4.34 (s, 1H), 4.20 (m, 2H), 4.11 (m, 2H), 1.43 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-d)170.3, 168.0, 154.1, 134.4, 131.9, 131.7, 131.4, 28.7, 128.2, 128.1, 122.2, 87.1, 84.5, 80.7, 62.6, 61.8, 60.6, 56.5, 28.2, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 15.25 min, major enantiomer t_R = 16.87 min,. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{30}ClNO_6Na]$:474.1887 found:474.1884.

diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-2-(phenylethynyl)-3-(p-tolyl)succinate (4cd)



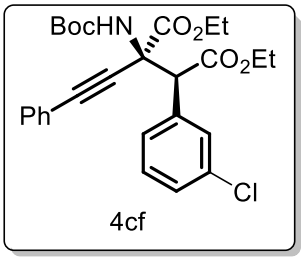
An coloress liquid, 79% yield (38 mg). $[\alpha]_D^{20}$ = -11 (*c* 1.0, CH_2Cl_2, 90% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44(d, *J* = 7.8 Hz, 2H), 7.42-7.39(m, 2H), 7.31-7.27(m, 3H), 7.13(m, 2H), 6.28(br, 1H), 4.34(s, 3H), 4.24-4.15(m, 2H), 4.14-4.07(m, 2H), 2.33(s, 3H), 1.43(s, 9H), 1.23(t, *J* = 7.2 Hz, 3H), 1.14(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 168.3, 154.3, 138.1, 131.8, 130.4, 129.7, 128.7, 128.4, 128.1, 122.6, 86.6, 85.1, 80.4, 62.4, 61.6, 60.9, 57.0, 28.2, 21.1, 14.1, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 24.16 min, major enantiomer t_R = 16.39 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{28}H_{33}NO_6Na]$:502.2200, found:502.2195.

diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-(4-ethoxyphenyl)-2-(phenylethynyl)succinate (4ce)

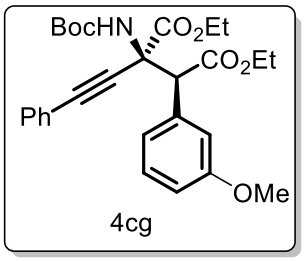


An coloress liquid, 80% yield (41 mg). $[\alpha]_D^{20}$ = -11 (*c* 1.0, CH_2Cl_2, 98% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 3H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.28 (s, 1H), 4.31 (s, 1H), 4.24 – 4.16 (m, 2H), 4.10 (q, *J* = 6.6 Hz, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 1.44 (s, 9H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 168.4, 159.1, 154.3, 131.8, 131.7, 128.4, 128.1, 124.7, 114.0, 86.7, 85.2, 80.5, 63.4, 62.4, 61.6, 61.0, 56.7, 28.3, 14.8, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 15.03 min, major enantiomer t_R = 16.67 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{29}H_{35}NO_7Na]$:532.2306, found:532.2303.

diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-(3-chlorophenyl)-2-(phenylethynyl)succinate (4cf)

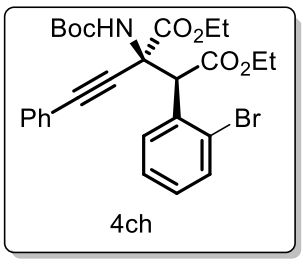


An coloress liquid, 71% yield (35 mg). $[\alpha]_D^{20}$ = -6 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.45 (m, 3H), 7.37 – 7.21 (m, 5H), 6.19 (s, 1H), 4.43 (s, 1H), 4.27 – 4.10 (m, 4H), 1.44 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 168.0, 154.1, 134.8, 133.6, 131.8, 130.8, 129.1, 128.9, 128.7, 128.5, 128.2, 122.2, 87.3, 84.3, 80.7, 62.6, 61.8, 60.5, 56.6, 28.2, 14.0,13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 9.61 min, major enantiomer t_R = 11.08 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{30}ClNO_6Na]$:522.1654 found:522.1656.



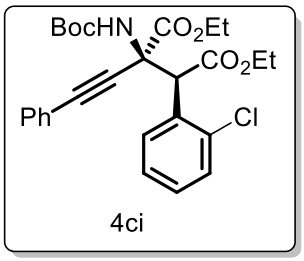
diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-(3-methoxyphenyl)-2-(phenylethynyl)succinate (4cg)

An coloress liquid, 80% yield (39 mg). $[\alpha]_D^{20}$ = -10 (*c* 1.0, CH_2Cl_2, 98% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 6.6 Hz, 2H), 7.29 (d, *J* = 6.6 Hz, 3H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.18 (s, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 4.35 (s, 1H), 4.21 (m 2H), 4.15 – 4.08 (m, 2H), 3.74 (s, 3H), 1.44 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 168.2, 159.0, 154.2, 134.0, 131.7, 128.8, 128.5, 122.9, 122.5, 116.1, 114.1, 86.7, 85.0, 80.5, 62.5, 61.7, 60.7, 57.2, 55.1, 28.2, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 13.96 min, major enantiomer t_R = 17.86 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{28}H_{33}NO_7Na]$:518.2149 found:518.2147.



diethyl (2S,3S)-3-(2-bromophenyl)-2-((tert-butoxycarbonyl)amino)-2-(phenylethynyl)succinate (4ch)

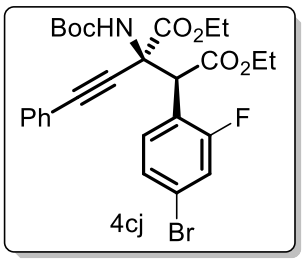
An coloress liquid, 68% yield (37 mg). $[\alpha]_D^{20}$ = -49 (*c* 1.0, CH_2Cl_2, 99% ee); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 6.6 Hz, 2H), 7.31 (m, 4H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.45 (s, 1H), 5.11 (s, 1H), 4.27 – 4.17 (m, 2H), 4.17 – 4.11 (m, 1H), 4.11 – 4.04 (m, 1H), 1.44 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.0 , 167.6 , 154.1, 132.9, 132.7, 131.8, 131.3, 129.6, 128.5, 128.1, 127.1, 126.5, 122.4, 86.7, 84.9, 80.6, 62.5, 62.0, 60.4 , 55.1, 28.2, 14.0, 13.7 . HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 13.93 min, minor enantiomer t_R = 16.51 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{30}BrNO_6Na]$:566.1149, 568.1128 found:566.1149, 568.1125.



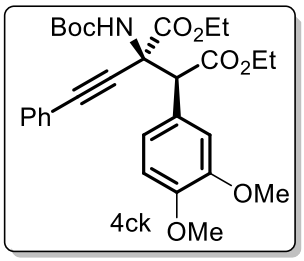
diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-(2-chlorophenyl)-2-(phenylethynyl)succinate (4ci)

An coloress liquid, 75% yield (37 mg). $[\alpha]_D^{20}$ = 48 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03-7.99(m, 1H), 7.43-7.37(m, 3H), 7.33-7.27(m, 3H), 7.25-7.22(m, 2H), 6.40(br, 1H), 5.12(s, 1H), 4.26-4.05(m, 2H), 1.44(s, 9H), 1.23(t, *J* = 7.2 Hz, 3H), 1.14(t, *J* = 7.2 Hz 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 167.7, 154.1, 135.3, 131.8, 131.3, 131.1, 129.3, 128.5, 128.1, 126.5, 122.4, 86.6, 84.8, 80.6, 62.5, 62.0, 60.4, 52.4, 28.2, 14.0, 13.7. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 13.47 min, minor enantiomer t_R = 14.93 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{30}ClNO_6Na]$:522.1654 found:522.1650.

diethyl (2S,3S)-3-(4-bromo-2-fluorophenyl)-2-((tert-butoxycarbonyl)amino)-2-(phenylethynyl)succinate (4cj)

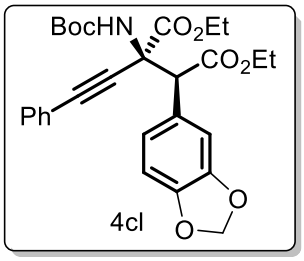


An coloress liquid, 64% yield (36 mg). $[\alpha]_D^{20}$ = -10 (*c* 1.0, CH_2Cl_2, 96% ee); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.24 (m, 5H), 6.15 (s, 1H), 4.84 (s, 1H), 4.25 – 4.13 (m, 4H), 1.43 (s, 9H), 1.22 (dt, *J* = 13.2, 7.2Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.7, 167.8, 166.1, 161.7, 154.0, 132.7, 131.7, 128.7, 128.2, 127.1, 122.2, 120.3, 118.9, 118.7, 87.0, 84.3, 80.7, 62.7, 61.9, 60.2, 49.1, 28.2, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 10.42 min, major enantiomer t_R = 11.49 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{27}H_{29}BrFNO_6Na]$:584.1054 586.1034 , found:584.1058, 586.1035.



diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-(3,4-dimethoxyphenyl)-2-(phenylethynyl)succinate (4ck)

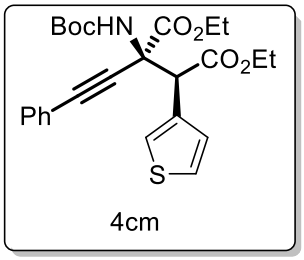
An coloress liquid, 70% yield (37 mg). $[\alpha]_D^{20}$ = 7 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.30 (m, 3H), 7.21 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.25 (s, 1H), 4.31 (s, 1H), 4.26 – 4.18 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H), 1.44 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 168.3, 154.2, 149.3, 148.4, 131.7, 128.5, 128.2, 125.1, 122.6, 123.1, 114.0, 110.6, 97.0, 86.8, 85.3, 80.6, 62.4 , 61.6, 60.9, 56.9, 55.8, 28.2, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 22.05 min, major enantiomer t_R = 31.15 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{29}H_{35}NO_8Na]$:548.2255, found:548.2254.



diethyl (2S,3S)-3-(benzo[d][1,3]dioxol-5-yl)-2-((tert-butoxycarbonyl)amino)-2-(phenylethynyl)succinate (4cl)

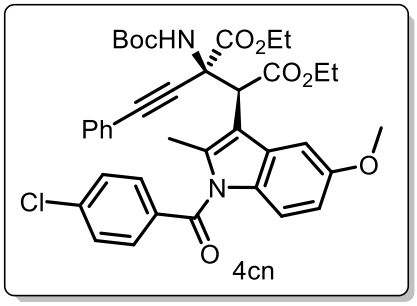
An coloress liquid, 74% yield (38 mg). $[\alpha]_D^{20}$ = -20 (*c* 1.0, CH_2Cl_2, 99% ee)^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.30 (m, 3H), 7.18 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.25 (s, 1H), 5.96 – 5.94 (m, 2H), 4.30 (s, 1H), 4.26 – 4.11 (m, 4H), 1.44 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 168.3, 154.2, 147.8, 147.3, 131.8, 128.5, 128.2, 126.4, 124.5, 122.6, 110.7, 107.6, 101.1, 86.9,85.0, 80.5, 62.5,

61.7, 60.9, 57.0, 28.3, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 15.01 min, major enantiomer t_R = 18.81 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{28}H_{31}NO_8Na]$:532.1942, found:532.1939.



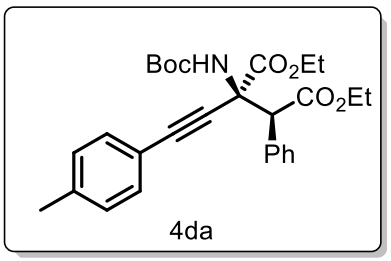
diethyl (2S,3R)-2-((tert-butoxycarbonyl)amino)-2-(phenylethynyl)-3-(thiophen-2-yl)succinate (4cm)

An coloress liquid, 70% yield (33 mg). $[\alpha]_D^{20}$ = 4 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44(d, *J* = 7.6 Hz, 1H), 7.43-7.40(m, 2H), 7.34-7.32(m, 1H), 7.32-7.28(m, 3H), 7.27-7.24(m, 1H), 6.25(br, 1H), 4.54(s, 1H), 4.26-4.18(m, 2H), 4.12(q, *J* = 7.2 Hz, 2H), 1.45(s, 9H), 1.26(t, *J* = 7.2 Hz ,3H), 1.17(t, *J* = 7.2 Hz 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 168.2, 154.2, 132.6, 132.0, 131.8, 129.3, 128.5, 128.3, 125.8, 124.5, 122.4, 86.4, 85.0, 80.6, 62.5, 61.8, 52.9, 28.2, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 8.63 min, minor enantiomer t_R = 7.55 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{25}H_{29}NO_6SNa]$:494.1608 found:494.1606.



(2S,3S) ethyl 3-((tert-butoxycarbonyl)amino)-2-(1-(4-chlorobenzoyl)-1H-indol-3-yl)-5-phenyl-3-(propionyloxy)pent-4-ynoate (4cn)

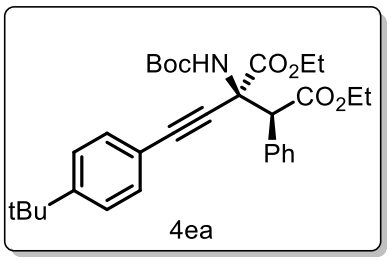
An coloress liquid, 62% yield (39 mg). $[\alpha]_D^{20}$ = 21 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65(s, 2H), 7.40-7.22(m, 7H), 7.15-7.05(m, 2H), 6.68-6.65(m, 1H), 6.23(s, 1H), 4.76(s, 1H), 4.33-4.12(m, 4H), 3.70(s, 3H), 2.39(s, 3H), 1.22(s, 9H), 1.17(t, J = 7.2Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ168.8, 168.6, 155.7,139.3, 137.3, 133.7, 131.7, 131.4, 129.0, 128.6, 128.2, 122.4, 114.3, 112.1, 102.4, 86.2, 85.2, 62., 61.9, 60.4, 55.4, 28.0, 14.1, 13.8 HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 10.39 min, major enantiomer t_R = 16.46 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{38}H_{39}ClN_2O_8Na]$:709.2287 found:709.2271.



Diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-phenyl-2-(p-tolylethynyl)succinate (4da)

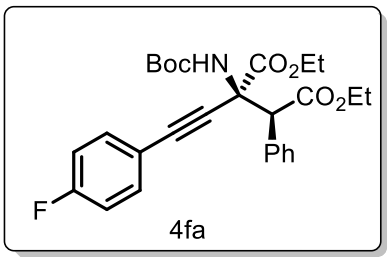
An coloress liquid, 79% yield (38 mg). $[\alpha]_D^{20}$ = -14 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (s, 2H), 7.38 – 7.26 (m, 5H), 7.10 (d, *J* = 7.2Hz, 2H), 6.31 (s, 1H), 4.37 (s, 1H), 4.20 (m, 2H), 4.09 (d, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 1.43 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.3 , 154.2 , 138.54 , 132.87 , 131.60 , 130.58 , 128.85 , 128.24 , 127.85 , 119.5 , 80.4 , 62.4 , 60.8 , 57.4 , 28.2 , 21.4 , 14.0 , 13.7 . HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; minor enantiomer t_R = 28.25 min, major enantiomer t_R = 31.06 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{28}H_{33}NO_6Na]$:502.2200, found:502.2196.

diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-2-((4-(tert-butyl)phenyl)ethynyl)-3-phenylsuccinate (4ea)



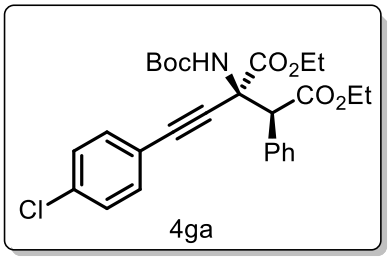
An coloress liquid, 71% yield (37 mg). $[\alpha]_D^{20}$ = -14 (*c* 1.0, CH_2Cl_2, 91% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.56 (m, 2H), 7.33 (q, *J* = 8.4 Hz, 7H), 6.30 (br, 1H), 4.36 (s, 1H), 4.26 – 4.14 (m, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.43 (s, 9H), 1.30 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 168.4, 154.2, 151.8, 133.0, 131.5, 130.6, 128.3, 127.9, 125.1, 119.6, 97.0, 86.9, 84.4, 80.5, 62.4, 61.6, 60.9, 57.5, 34.8, 31.1, 28.3, 14.0, 13.7. HPLC: chiral IF

column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 10.31 min, minor enantiomer t_R = 11.18 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{31}H_{39}NO_6Na]$:544.2670, found:544.2667.



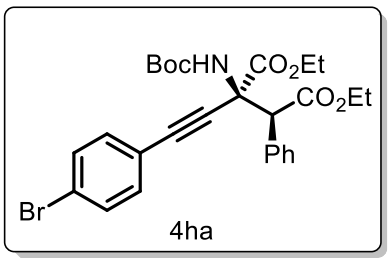
diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-2-((4-fluorophenyl)ethynyl)-3-phenylsuccinate (4fa)

An coloress liquid, 54% yield (26 mg). $[\alpha]_D^{20}$ = 25.5 (*c* 1.0, CH_2Cl_2, 99% ee);v^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 2H), 7.39 – 7.35 (m, 2H), 7.33 (d, *J* = 4.8 Hz, 3H), 6.98 (t, *J* = 8.4 Hz, 2H), 6.31 (s, 1H), 4.35 (s, 1H), 4.25 – 4.16 (m, 2H), 4.14 – 4.08 (m, 2H), 1.44 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 168.2, 162.7(d, J_{C-F} = 250.2 Hz), 154.2, 133.7(d, J_{C-F} =8.4 Hz), 132.9, 130.5, 128.4, 128.0, 118.6, 115.4(d, J_{C-F} = 22.0 Hz), 90.7, 85.8, 84.8, 80.5, 62.5, 61.7, 60.9, 57.4, 28.3, 14.0, 13.8. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; minor enantiomer t_R = 23.63 min, major enantiomer t_R = 25.76 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{27}H_{30}FNO_6Na]$:506.1949, found:506.1948.



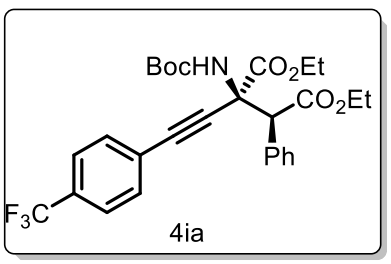
diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-2-((4-chlorophenyl)ethynyl)-3-phenylsuccinate (4ga)

An coloress liquid, 69% yield (34 mg). $[\alpha]_D^{20}$ = -8 (*c* 1.0, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57-7.49(m, 2H), 7.35-7.29(m, 5H), 7.28-7.24(m, 2H), 6.31(br, 1H), 4.34(s, 1H), 4.25-4.16(m, 2H), 4.11(q, *J* = 7.2 Hz, 2H), 1.43(s, 9H), 1.23(t, *J* = 7.2 Hz ,3H), 1.13(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 168.2, 154.3, 134.5, 132.9, 132.7, 130.4, 128.5, 128.4, 128.0, 121.0, 86.0, 85.6, 80.6, 62.5, 61.7, 60.8, 57.2, 28.2, 14.0, 13.7. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 11.31 min, major enantiomer t_R = 12.25 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{27}H_{30}ClNO_6Na]$:522.1654, found:522.1653.



diethyl (2S,3S)-2-((4-bromophenyl)ethynyl)-2-((tert-butoxycarbonyl)amino)-3-phenylsuccinate (4ha)

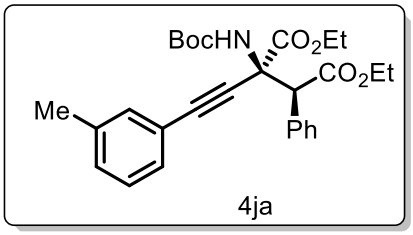
An coloress liquid, 73% yield (39 mg). $[\alpha]_D^{20}$ = -7 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 4.34 (s, 1H), 4.26 – 4.14 (m, 2H), 4.10 (m 2H), 1.43 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 168.2, 154.3, 133.2, 132.8, 131.4, 130.5, 128.4, 128.0, 122.8, 121.6, 86.3, 85.7, 80.6, 62.5, 61.7, 60.9, 57.3, 28.2, 14.0, 13.7. HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 11.67min, major enantiomer t_R = 12.63 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{27}H_{30}BrNO_6Na]$:566.1149,568.1128, found:566.1129, 568.1127.



diethyl (2S,3S)-3-((tert-butoxycarbonyl)amino)-2-phenyl-3-(propionyloxy)-5-(4-(trifluoromethyl)phenyl)pent-4-ynoate (4ia）

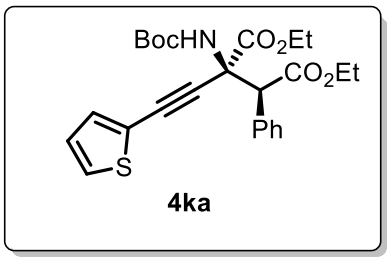
An coloress liquid, 55% yield (29 mg). $[\alpha]_D^{20}$ = -10 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ7.57-5.51(m, 4H), 7.48(d, J = 7.8 Hz, 2H), 7.31-7.37(m, 3H), 6.34(s, 1H), 4.34(s, 1H), 4.26-4.17(m, 2H), 4.15-4.09(m, 2H), 1.44(s, 9H), 1.24(t, J = 7.2Hz, 3H), 1.14(t, J = 7.2Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ170.5,

168.1, 154.3, 132.6, 132.0, 130.5, 130.4, 130.1, 129.9, 128.5, 128.1, 126.3(d, J_{C-F} =1.68 Hz), 125.1(q, J_{C-F} =3.7 Hz), 123.9(q, J_{C-F} = 272.7 Hz) 123.9, 87.6, 85.3, 80.7, 62.6, 61.8, 60.9, 57.2, 28.2, 14.0, 13.8 HPLC: chiral IF column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; minor enantiomer t_R = 19.99 min, major enantiomer t_R = 21.57 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{28}H_{30}F_3NO_6Na]$:556.1917, found:556.1913.



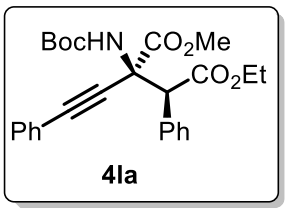
diethyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-phenyl-2-(m-tolylethynyl)succinate （4ja）

An coloress liquid, 80% yield (38 mg). $[\alpha]_D^{20}$ = -9 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (m, 2H), 7.34 – 7.31 (m, 3H), 7.24 – 7.16 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.29 (s, 1H), 4.37 (s, 1H), 4.20 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.44 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 168.3, 154.2, 137.8, 132.8, 132.3, 130.6, 129.3, 128.8, 128.3, 128.0, 127.9, 122.3, 86.9, 84.5, 80.4, 62.4, 61.7, 60.8, 57.3, 28.2, 21.1, 14.0, 13.7. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 98:2), 1 mL/min; major enantiomer t_R = 26.21 min, minor enantiomer t_R = 33.3 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{28}H_{33}NO_6Na]$:502.2200, found:502.2196



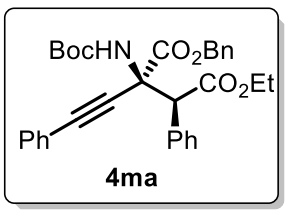
4-ethyl 1-methyl (2S,3S)-2-((tert-butoxycarbonyl)amino)-3-phenyl-2-(thiophen-2-ylethynyl)succinate (4ka)

An coloress liquid, 71% yield (32.4 mg). $[\alpha]_D^{20}$ =14 (*c* 1.0, CH_2Cl_2, 87% ee); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57-7.51(m, 2H), 7.36-7.30(m, 3H), 7.26-7.23(m, 1H), 7.18(d, *J* = 2.4 Hz, 1H), 6.99-6.90(m, 1H), 6.30(br, 1H), 4.35(s, 1H), 4.26-4.15(m, 2H), 4.10(q, *J* = 7.2 Hz ,2H), 1.43(s, 9H), 1.24(t, *J* = 7.2 Hz, 3H), 1.13(t, *J* = 7.2 Hz, 3H); 13C NMR (151 MHz, Chloroform-d) δ 168.1, 154.3, 130.5, 128.4, 128.0, 127.3, 126.8, 122.4, 88.8, 80.6, 80.2, 62.6, 61.8, 61.0, 57.3, 28.2, 14.0, 13.7. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 95:5), 0.7 mL/min; minor enantiomer t_R = 38.01 min, major enantiomer t_R = 34.56 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{24}H_{27}NO_6SNa]$:480.1451 found:480.1452.



4-ethyl 1-methyl (2S,3R)-2-((tert-butoxycarbonyl)amino)-3-phenyl-2-(phenylethynyl)succinate (4la)

An coloress liquid, 77% yield (35 mg). $[\alpha]_D^{20}$ = 10 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58-7.51(m, 2H), 7.42-7.38(m, 2H), 7.35-7.32(m, 3H), 7.31-7.28(m, 2H), 6.31(br, 1H), 4.36(s, 1H), 4.27-4.16(m, 2H), 3.62(s, 3H), 1.44(s, 9H), 1.24(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 168.9, 154.3, 132.7, 131.8, 130.5, 128.5, 128.4, 128.1, 128.0, 122.4, 86.8, 84.7, 80.7, 61.7, 60.9, 57.4, 53.2, 28.2, 14.0. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 13.20 min, minor enantiomer t_R = 15.16 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{26}H_{29}NO_6Na]$:474.1887 found:474.1887.

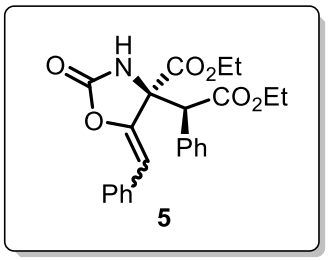


1-benzyl 4-ethyl (2S,3R)-2-((tert-butoxycarbonyl)amino)-3-phenyl-2-(phenylethynyl)succinate (4ma)

An coloress liquid, 86% yield (45 mg). $[\alpha]_D^{20}$ = -20 (*c* 1.0, CH_2Cl_2, 99% ee);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55-7.49(m, 2H), 7.36(d, 2H), 7.33-7.23(m, 11H), 6.30(br, 1H), 5.11(d, *J* = 12 Hz, 1H), 5.05(d, *J* = 12 Hz, 1H), 4.39(s, 1H), 4.14, (q, *J* = 7.2 Hz, 2H), 1.40(s, 9H), 1.19(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 168.1, 154.2, 135.1, 132.7, 131.8, 130.5, 128.5, 128.4, 128.3,

128.2, 128.1, 128.1, 128.0, 122.4, 87.0, 84.8, 80.6, 68.0, 61.7, 61.0, 57.3, 28.2, 14.0. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; major enantiomer t_R = 17.57 min, minor enantiomer t_R = 15.6 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{32}H_{33}NO_6Na]$:550.2200 found:550.2205.

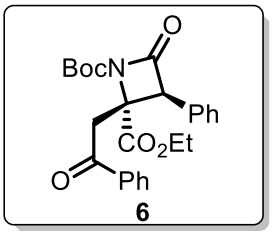
ethyl (4S)-5-benzylidene-4-(2-ethoxy-2-oxo-1-phenylethyl)-2-oxooxazolidine-4-carboxylate (5)



5

An coloress liquid, 71% yield (31 mg). $[\alpha]_D^{20}$ = -477(*c* 1.0, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (m, 2H), 7.36 – 7.26 (m, 6H), 7.20 (m, 2H), 6.68 (s, 1H), 5.39 (d, *J* = 2 Hz, 1H), 4.43 (s, 1H), 4.31 (m, 2H), 4.18 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2 , 170.9 , 150.6, 148.8 , 130.7 , 129.9 , 129.5 , 128.5 , 128.4 , 128.4 , 124.8 , 95.0 , 65.0 , 62.9 , 61.8 , 57.96, 14.0 , 13.9 . HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 12.03 min, major enantiomer t_R = 18.20 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{23}H_{23}NO_6Na]$:432.1418 found:432.1418.

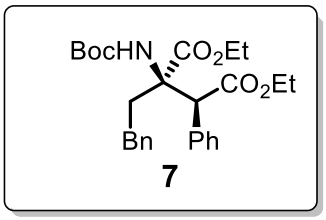
1-(tert-butyl) 2-ethyl (2R,3S)-4-oxo-2-(2-oxo-2-phenylethyl)-3-phenylazetidine-1,2-dicarboxylate (6)



6

Chemical Formula: $C_{25}H_{27}NO_6$

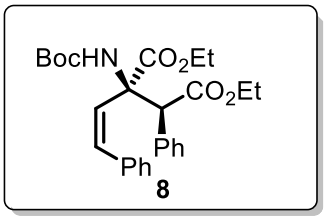
An coloress liquid, 91% yield (41 mg). $[\alpha]_D^{20}$ = 52 (*c* 1.0, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.32 (m, 2H), 7.26 – 7.21 (m, 2H), 7.21 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 5.10 (s, 1H), 4.35 (m, 2H), 4.05 (d, *J* = 17.6 Hz, 1H), 3.24 (d, *J* = 17.6Hz, 1H), 1.52 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.0 , 165.3 , 136.2 , 133.0 , 130.7 , 130.2 , 128.3 , 127.4 , 84.3 , 64.8 , 62.9 , 62.3 , 38.1 , 27.9 , 14.0 . HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 18.41 min, major enantiomer t_R = 22.9 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{25}H_{27}NO_6Na]$:460.1731 found: 460.1736.



7

ethyl (3S)-3-((tert-butoxycarbonyl)amino)-2,5-diphenyl-3-(propionyloxy)pentanoate (7)

An coloress liquid, 88% yield (42 mg). $[\alpha]_D^{20}$ = 56 (*c* 1.0, CH_2Cl_2, 98% ee); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30-7.26(m, 5H), 7.25-7.22(m, 2H), 7.17-7.14(m, 1H), 7.12(d, J = 7.2Hz, 2H), 5.74(s, 1H), 4.39(s, 1H), 4.29-4.22(m, 2H), 4.17-4.05(m, 2H), 3.05(t, J = 12Hz, 1H), 2.63-2.51(m, 1H), 2.34-2.24(m, 1H), 2.23-2.15(m, 1H), 1.37(s, 9H), 1.33(t, J = 7.2Hz, 3H), 1.18(t, J = 7.2Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4,171.7, 153.5, 141.5, 134.0, 129.9, 128.5, 128.3, 128.2, 127.9, 125.8, 78.9, 65.4, 62.1, 61.0, 57.8, 35.9, 30.9, 28.3, 14.1,14.0. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 13.74 min, major enantiomer t_R = 21.86 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{35}NO_6Na]$:492.2357 found:492.2359.



8

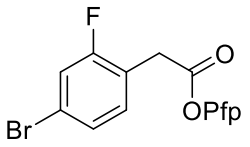
diethyl (2R,3S)-2-((tert-butoxycarbonyl)amino)-3-phenyl-2-((Z)-styryl)succinatee (8)

An coloress liquid, 75% yield (35 mg). $[\alpha]_D^{20}$ = 45 (*c* 1.0, CH_2Cl_2, 98% ee); ^{1}H NMR (400 MHz, Chloroform-*d*) δ7.42 – 7.26 (m, 2H), 7.32-7.26(m, 2H), 7.22-7.12(m, 3H), 7.00(d, J = 6.8Hz, 2H), 6.66(d, J = 12.8Hz, 1H), 6.28(d, J = 12Hz, 1H), 5.73(s, 1H), 4.65(s, 1H), 4.23-4.03(m, 2H), 3.89-3.63(m, 2H), 1.29(s, 9H), 1.26(t, J = 7.2Hz, 3H), 1.08(t, J = 7.2Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ172.3, 171.7, 153.6 , 141.5, 134.13, 4, 130.0 , 128.5, 128.3, 128.0, 127.9, 125.8, 79.0,

65.45, 62.1, 61.0, 57.9, 35..9, 30.9. 28.3, 14.1, 14.0. HPLC: chiral IA column. (*n*-hexane:*i*-PrOH = 90:10), 1 mL/min; minor enantiomer t_R = 13.15 min, major enantiomer t_R = 22.21 min. HRMS (ESI): $[M+Na]^+$ calcd $[C_{27}H_{.33}NO_6Na]$:490.2200, found:490.2206.

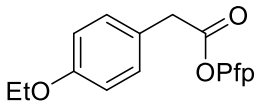
Novel substrates

perfluorophenyl 2-(4-bromo-2-fluorophenyl)acetate (2j)



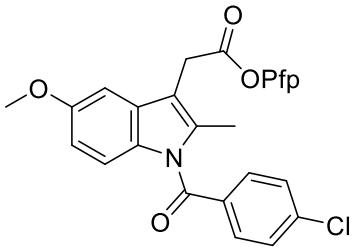
Following the general procedure 2.2, 2j was obtained as a white solid, mp 58.0–59.5 °C, in a 5 mmol scale with 75% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ7.31 – 7.26 (m, 2H), 7.23-7.19(m, 1H), 3.97(s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ166.1, 161.6, 159.9, 142.0-141.7(m, ArCF), 140.6-140.0(m, ArCF), 138.9-138.5(m, ArCF), 137.2-136.8(m, ArCF), 132.3, 132.2, 127.8, 127.7, 125.1-124.7(m, ArCF) 122.3, 122.2, 119.4, 119.2, 118.8, 118.7, 33.0, 32.9. ^{19}F NMR (376 MHz, $CDCl_3$): -113.8, -152.6- -153.0(m), -157.7 - -157.9(m), -162.3- -162.5(m) HRMS (ESI): $[M+H]^+$ calcd $[C_{14}H_5BrF_6O_2]$:399.9483, 400.9429, found:399.9477, 400.9435.

perfluorophenyl 2-(4-ethoxyphenyl)acetate (2e)



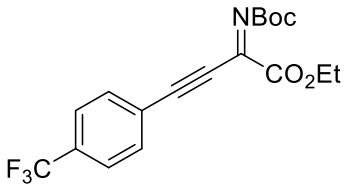
Following the general procedure 2.2, 2e was obtained as a white solid, mp56.5–57.5 °C, in a 5 mmol scale with 80% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.22(d, *J* = 8.4 Hz, 2H), 6.89-6.84(m, 2H), 3.99(q, *J* = 6.96 Hz, 2H), 3.85(s, 2H), 1.38(m, *J* = 6.96 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.7, 158.6, 142.0-141.8(m, ArCF), 140.0-140.3(m, ArCF), 138.8-138.5(m, ArCF), 137.1-136.8(m, ArCF), 130.2, 125.2-125.0(m, ArCF), 123.8, 114.6, 63.3, 39.1, 14.6. ^{19}F NMR (376 MHz, $CDCl_3$):-152.82- -152.89(m), -158.30(t, J = 22.10 Hz), -162.60- -162.78(m). HRMS (ESI): $[M+H]^+$ calcd $[C_{16}H_{11}F_5O_3]$:347.0701, found:347.0710.

perfluorophenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (2n)



Following the general procedure 2.2, 2n was obtained as a white solid, mp 128.0–129.5 °C, in a 5 mmol scale with 55% yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.69-7.63(m, 2H), 7.49-7.45(m, 2H), 6.98-6.95(m, 1H), 6.90-6.87(m, 1H), 6.72-6.68(m, 1H), 4.01(s, 2H), 3.84(s, 3H), 2.43(s, 3H); ^{13}C NMR (151 MHz, Chloroform-d) δ 168.2, 166.8, 156.2, 141.9-141.7(m, ArCF), 140.5-140.0(m, ArCF), 139.5, 138.8-138.4(m, ArCF), 137.1-136.8(m, ArCF), 136.5, 133.6, 131.2, 130.8, 130.0, 129.2 , 125.2-124.8(m, ArCF), 115.0, 112.1, 110.6, 100.7, 55.6, 29.3, 13.2. ^{19}F NMR (376 MHz, CDCl3):-152.5- -152.7 (m), -157.52(t, J = 21.72 Hz), -161.90- -162.01(m). HRMS (ESI): $[M+H]^+$ calcd $[C_{25}H_{15}ClF_5NO_4]$:524.0683, found:524.0685.

ethyl (Z)-2-((tert-butoxycarbonyl)imino)-4-(4-(trifluoromethyl)phenyl)but-3-ynoate (1i)



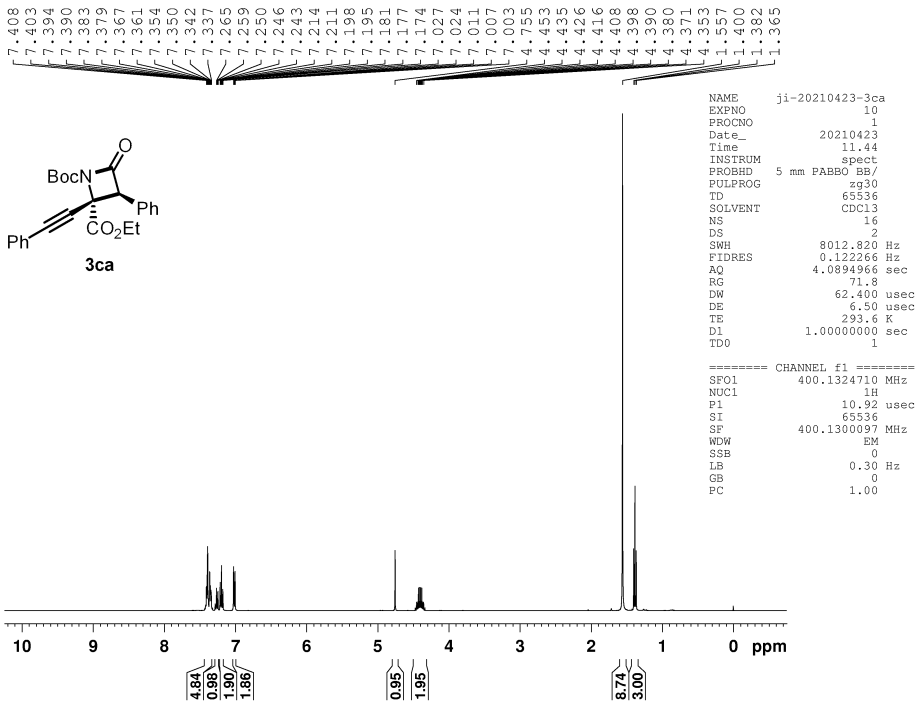
Following the general procedure 2.1, 1i was obtained as yellow oil, 40% yield in two steps with 10 mmol scale. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75-7.63(m, 4H), 4.44(q, 2H, *J* = 7.2Hz), 1.60(s, 9H), 1.43(t, 3H, *J* = 7.2Hz); ^{13}C NMR (100 MHz, Chloroform-d) δ 160.6, 159.4, 144.1, 133.5, 132.0(q, $J_{c\text{-}f}$ = 32.8Hz), 132.7, 127.8, 125.4(q, $J_{c\text{-}f}$ = 3.7Hz) , 123.4, 121.2(q, $J_{c\text{-}f}$ = 272.2Hz), 98.2, 84.1, 81.9, 63.1, 27.7, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$):-63.3. HRMS (ESI): $[M+H]^+$ calcd $[C_{18}H_{18}F_3NO_4]$:370.1261, found:370.1266.

REFERENCES

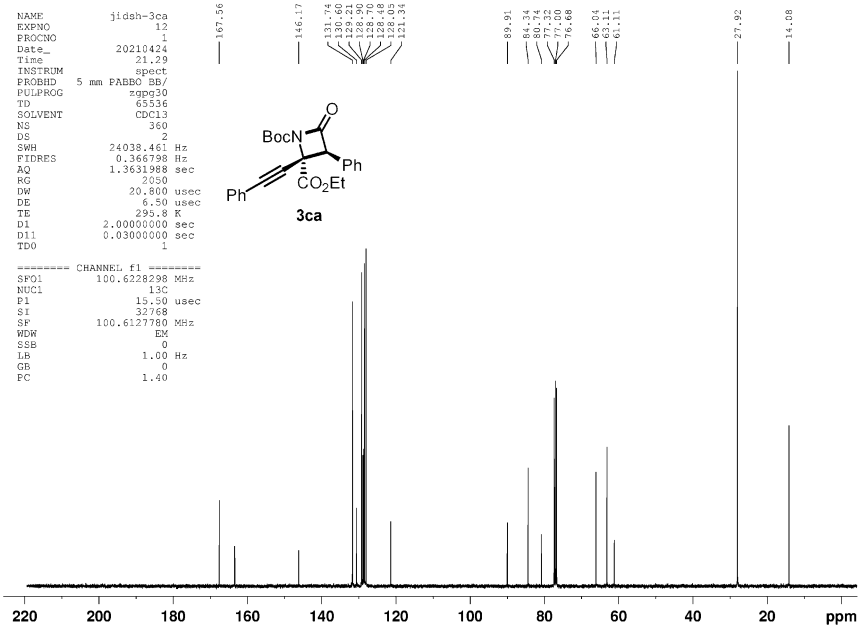
1. *Angew Chem. Int. Ed.* **2020**, *59*, 642-647.
2. *J. Am. Chem. Soc.* **2016**, *138*, 5214-5217.
3. *J. Am. Chem. Soc.* **2010**, *132*, 11629-11641.

10 The copy of NMR and HPLC

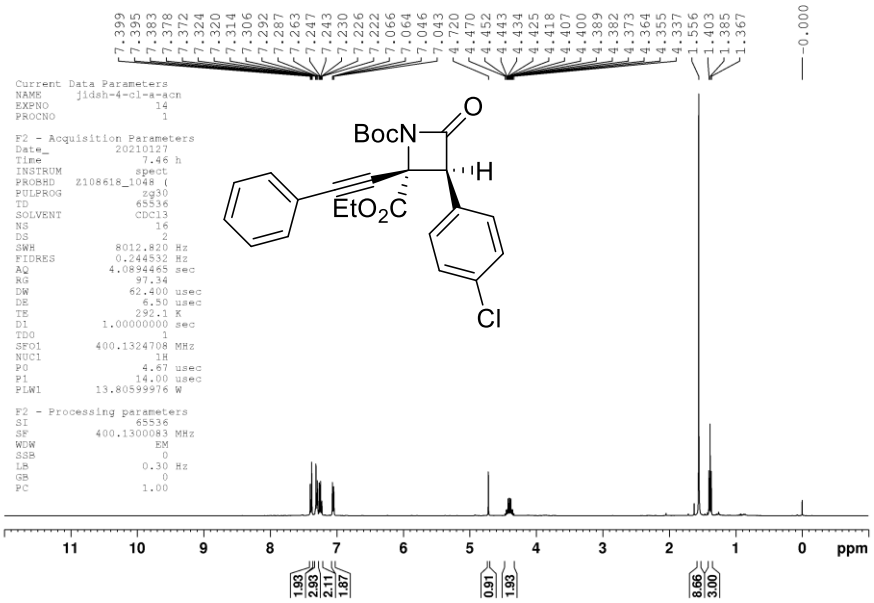
3ca-^{1}HNMR (400M, $CDCl_3$)



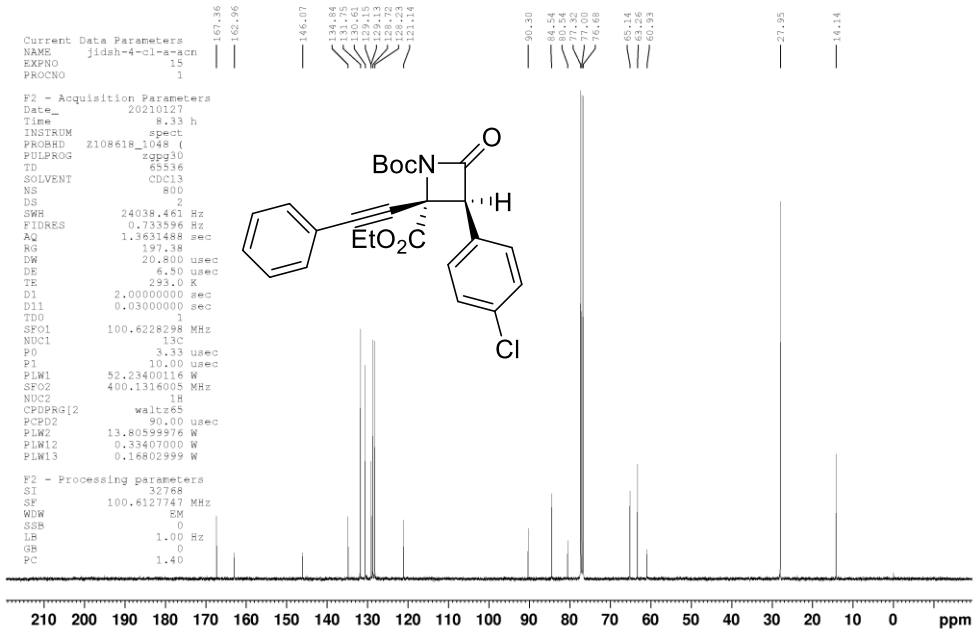
3ca-^{13}CNMR (100M, $CDCl_3$)



3cb-^{1}HNMR (400M, $CDCl_3$)

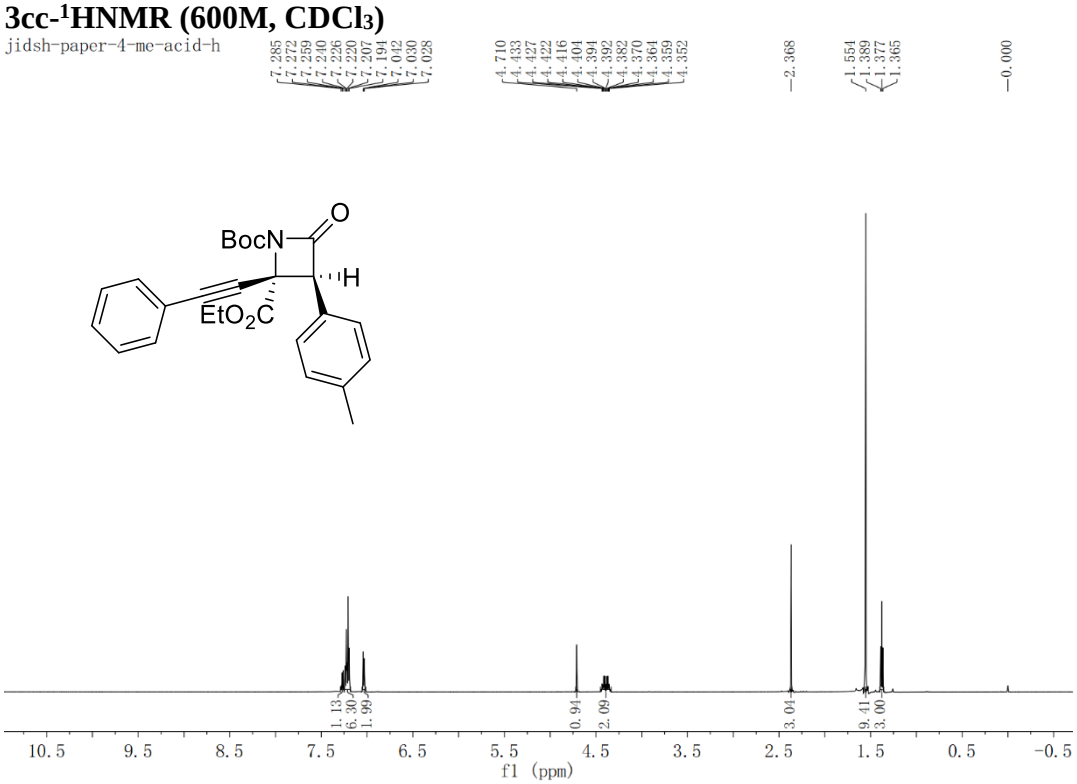


3cb-^{13}CNMR (100M, $CDCl_3$)



3cc-^{1}HNMR (600M, $CDCl_3$)

jidsh-paper-4-me-acid-h



3cc-^{13}CNMR (151M, $CDCl_3$)

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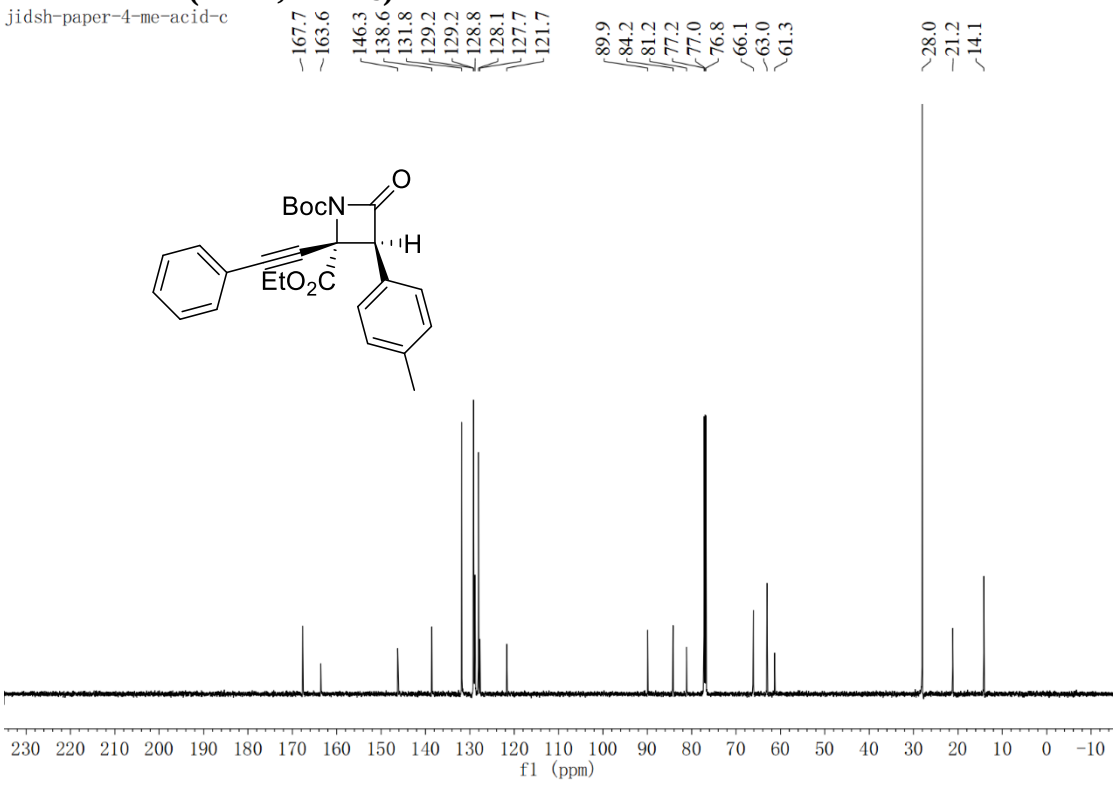

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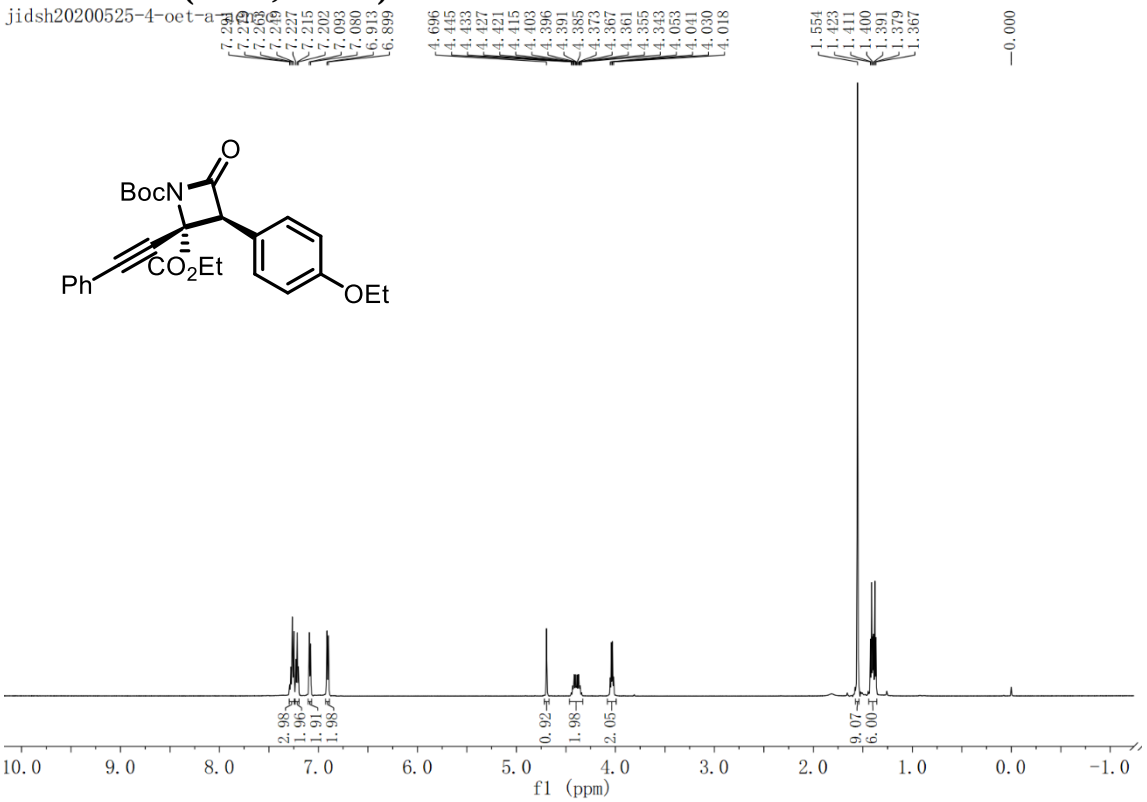
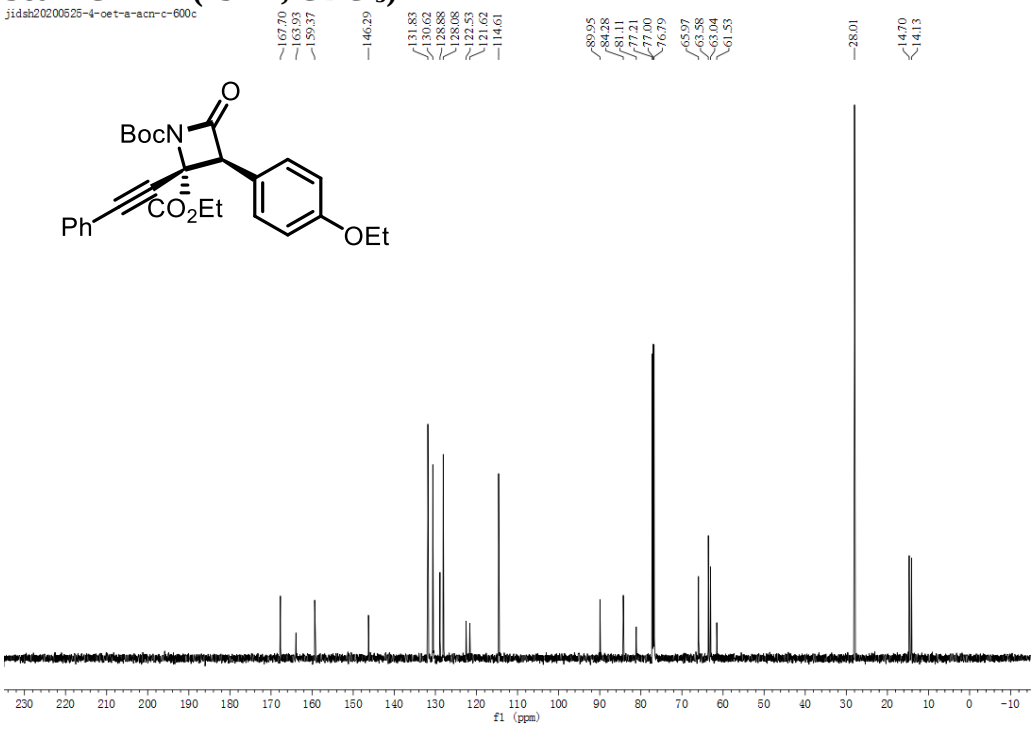
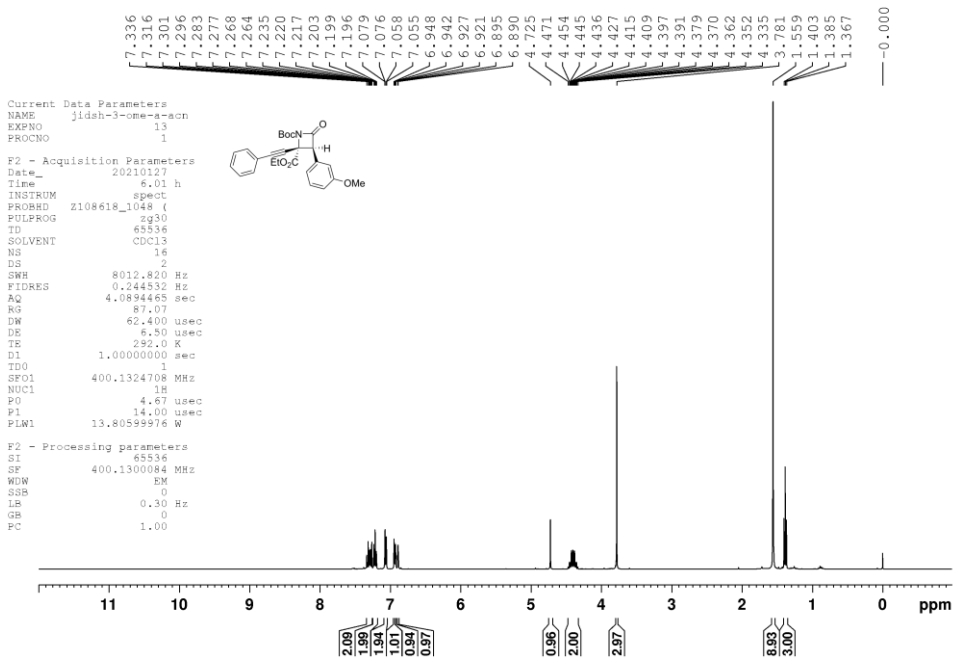


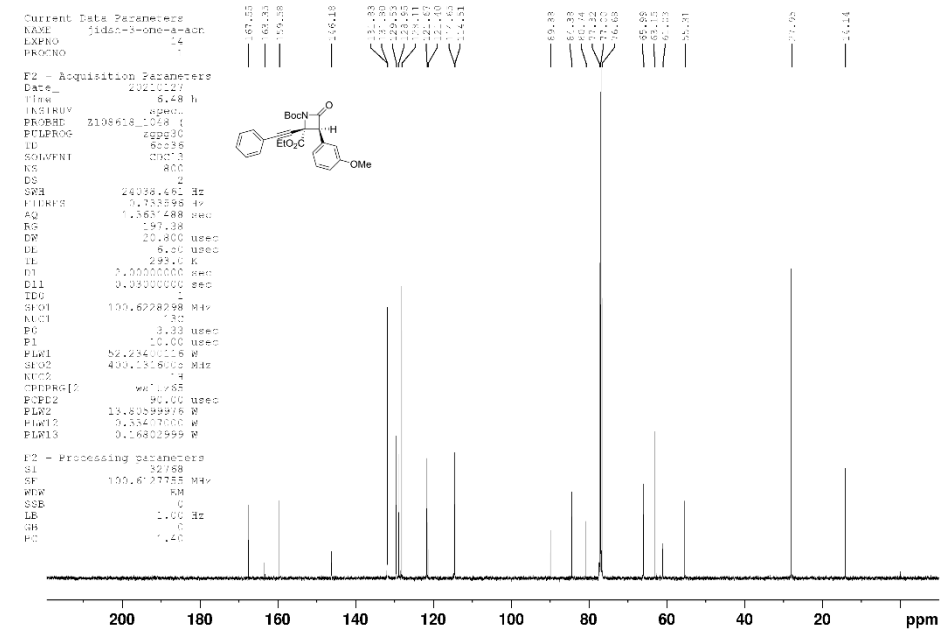
3cd-^{13}CNMR (151M, $CDCl_3$)



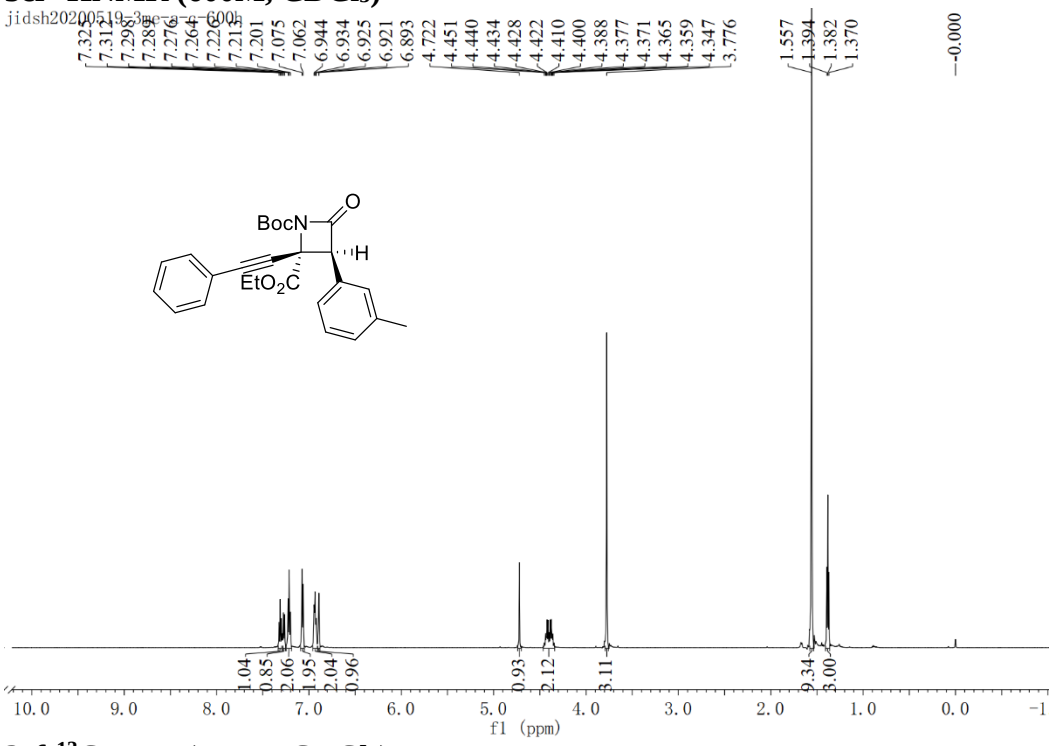
3ce-^{1}HNMR (400M, $CDCl_3$)



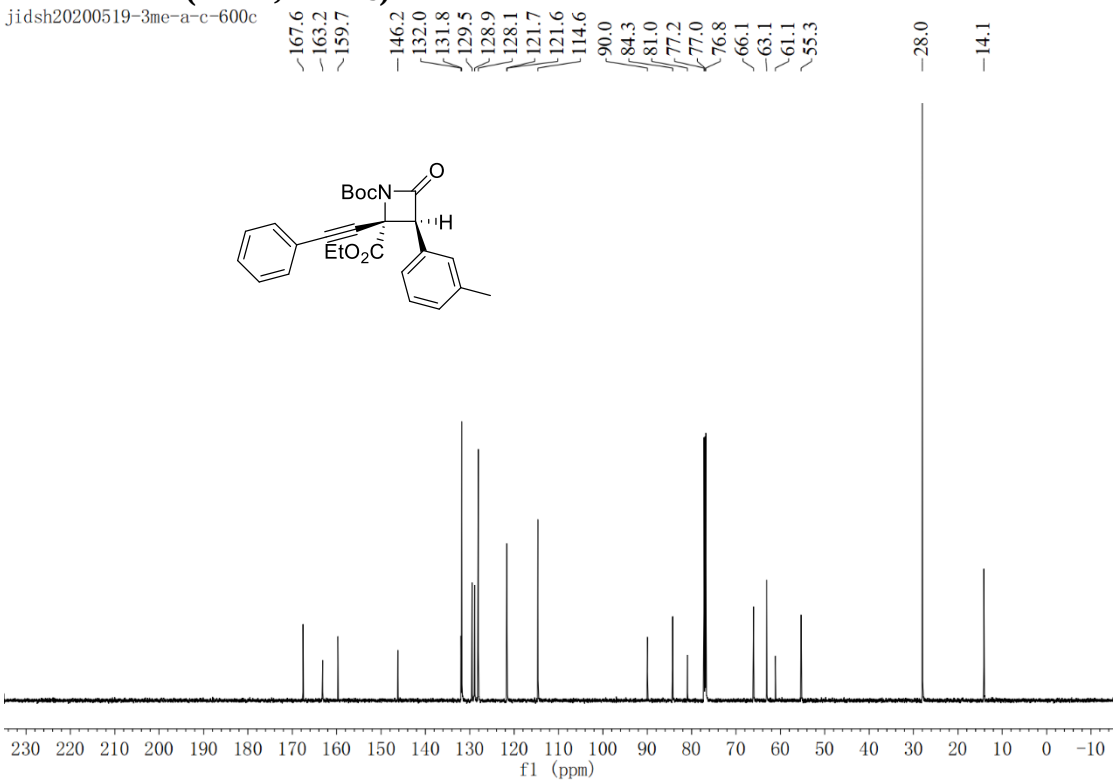
3ce-^{13}CNMR (100M, $CDCl_3$)



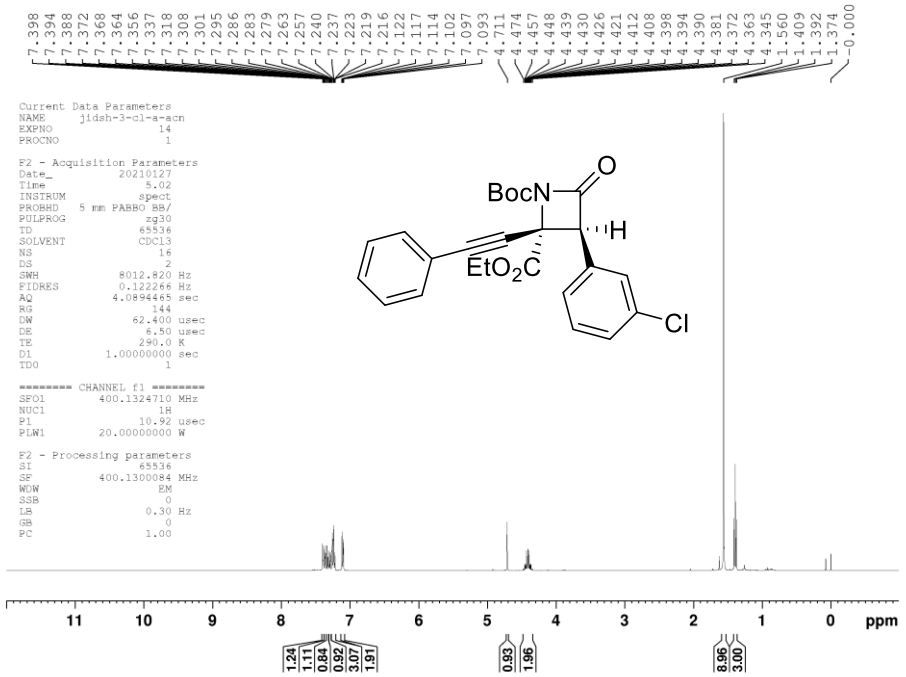
3cf-^{1}HNMR (600M, $CDCl_3$)



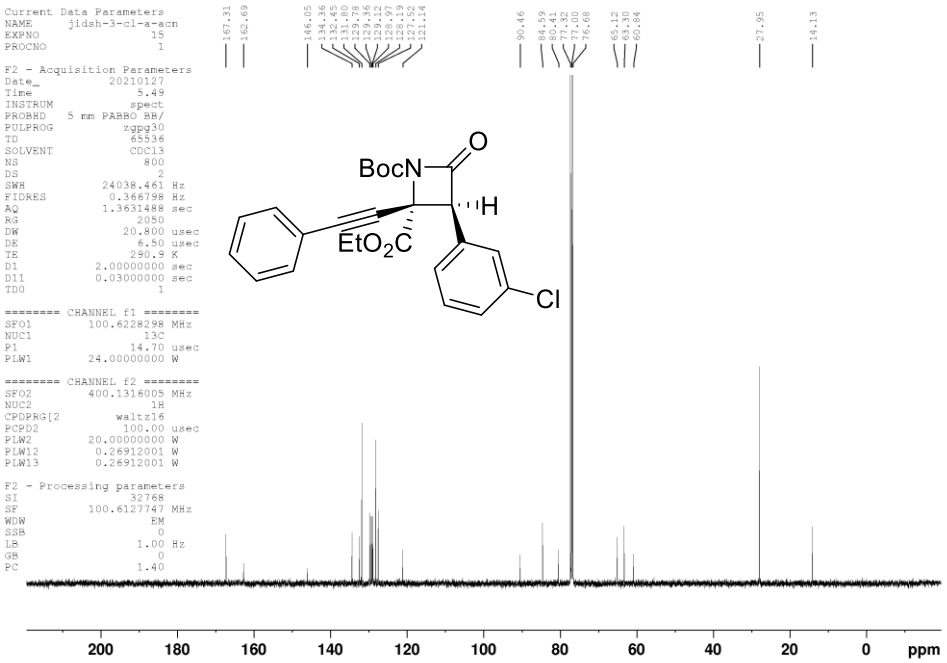
3cf-^{13}CNMR (151M, $CDCl_3$)



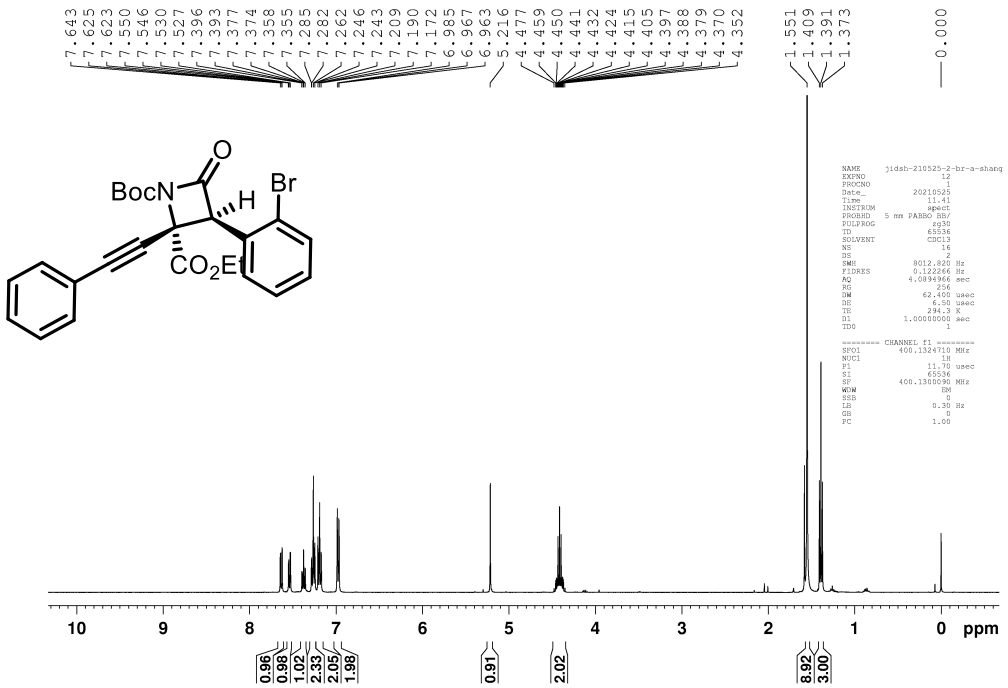
3cg-**^{1}HNMR** (400M, $CDCl_3$)



3cg-^{13}CNMR (100M, $CDCl_3$)



3ch-^{1}HNMR (400M, $CDCl_3$)



3ch-^{13}CNMR (151M, $CDCl_3$)

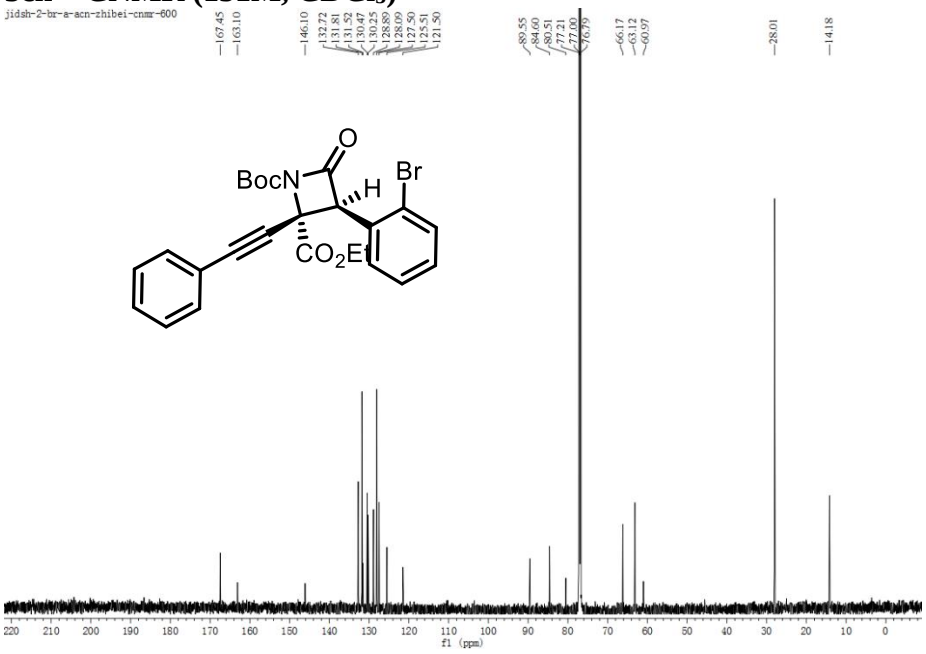
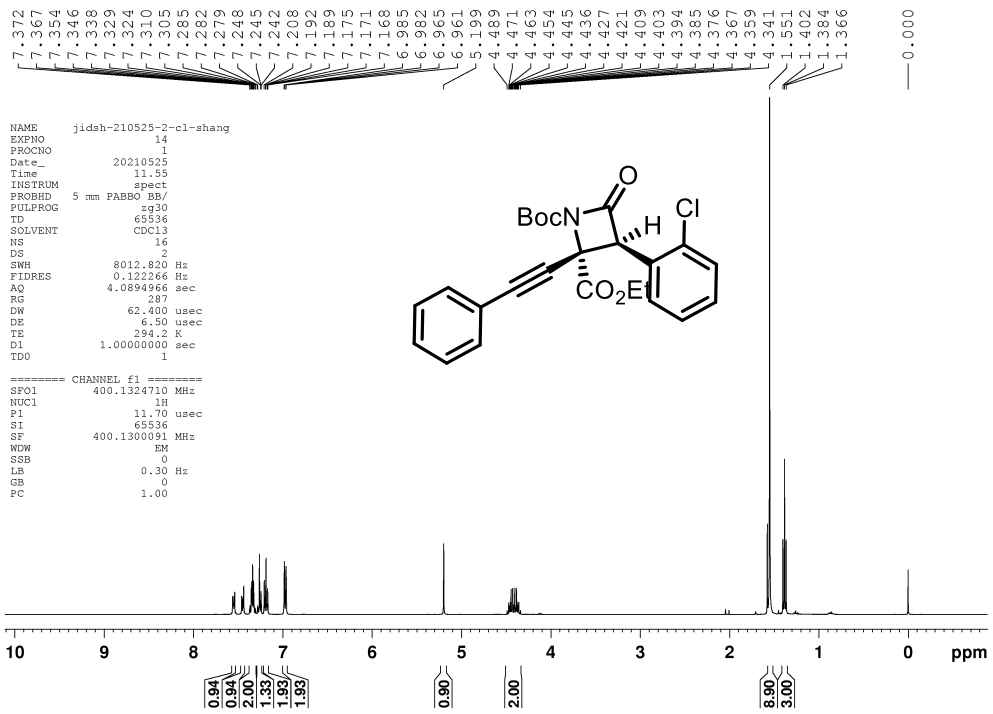
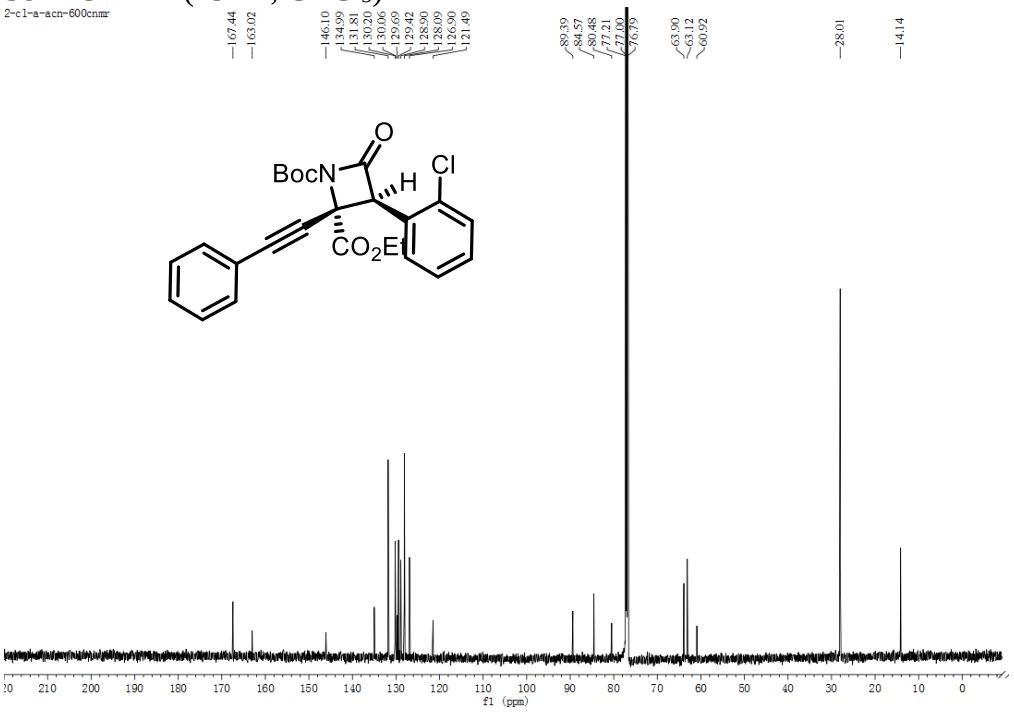


图 1

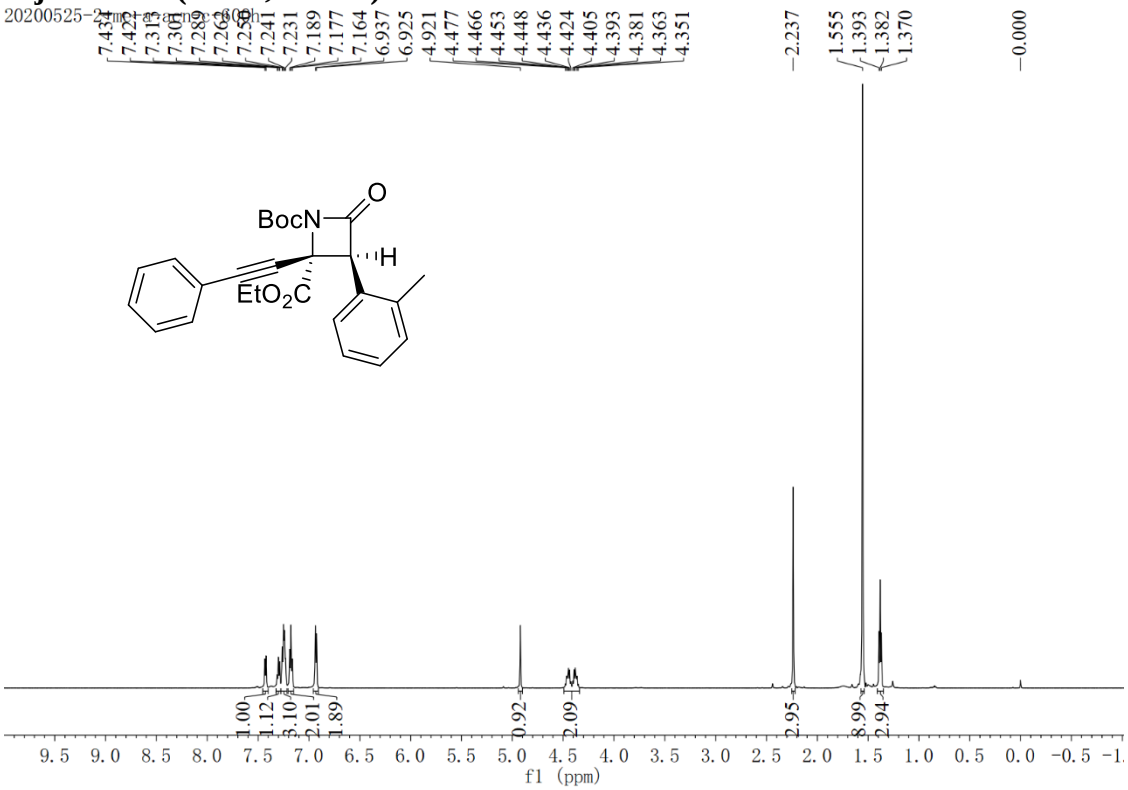
3ci-**^{1}HNMR** (400M, $CDCl_3$)



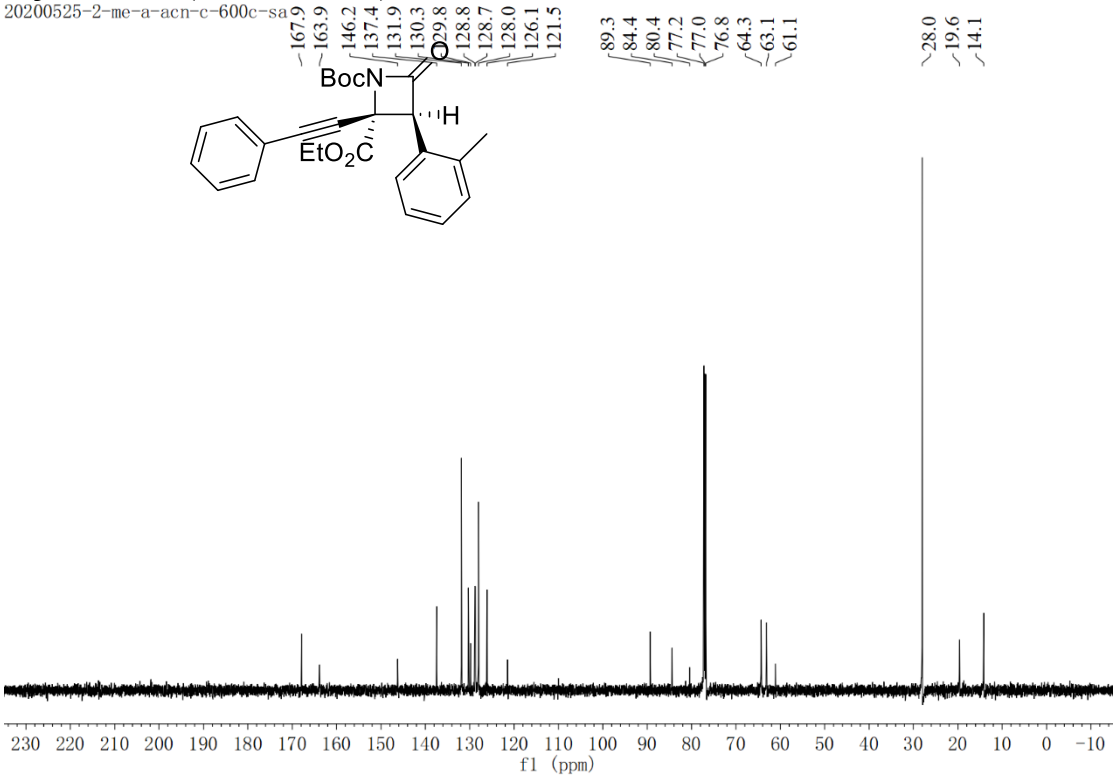
3ci-**^{13}CNMR** (151M, $CDCl_3$)



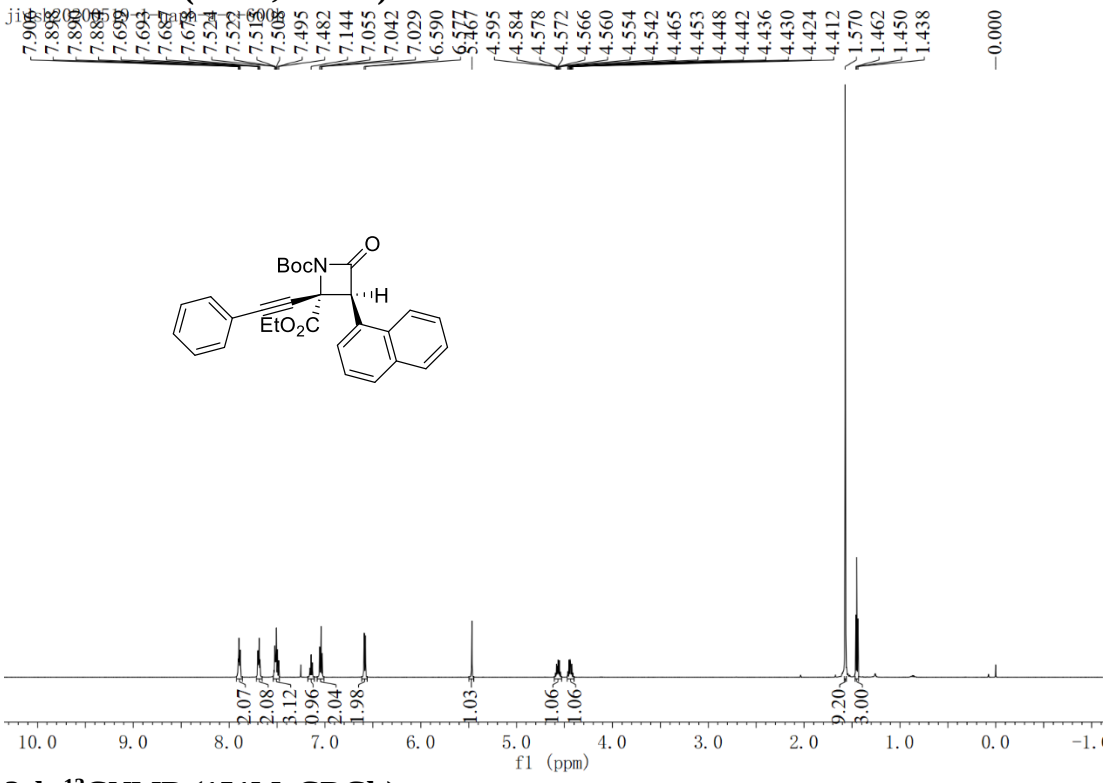
3cj-^{1}HNMR (600M, CDCl$_3$)



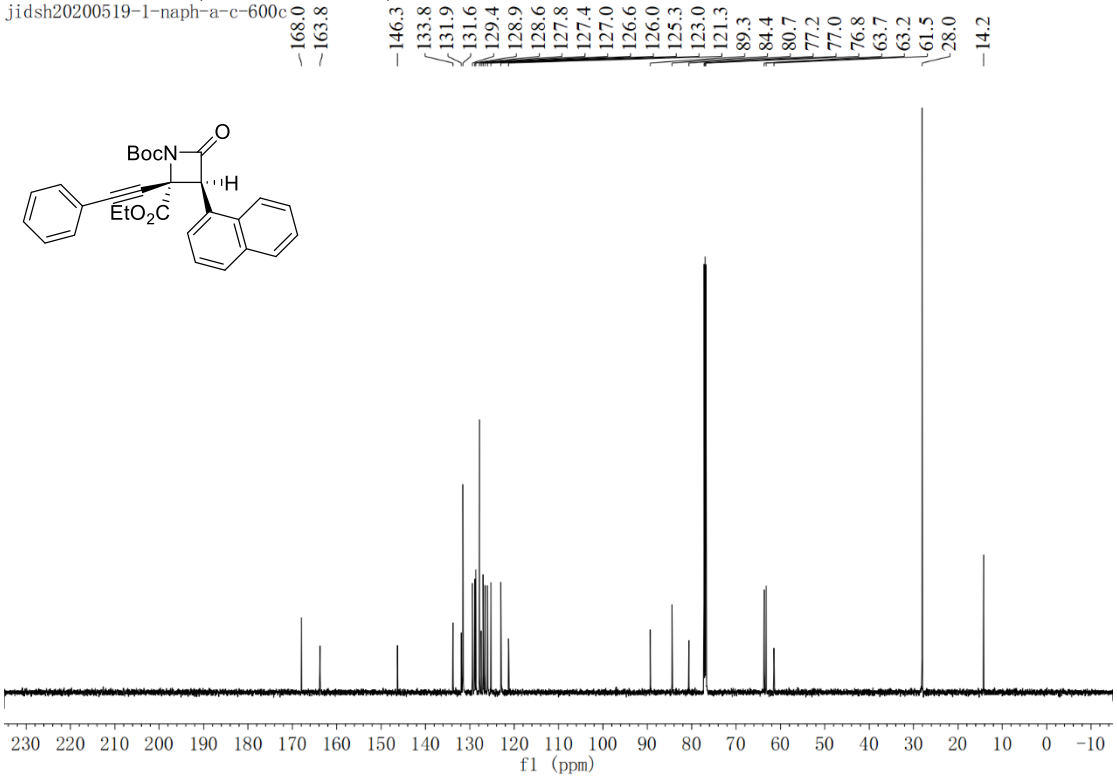
3cj-^{13}CNMR (151M, CDCl$_3$)



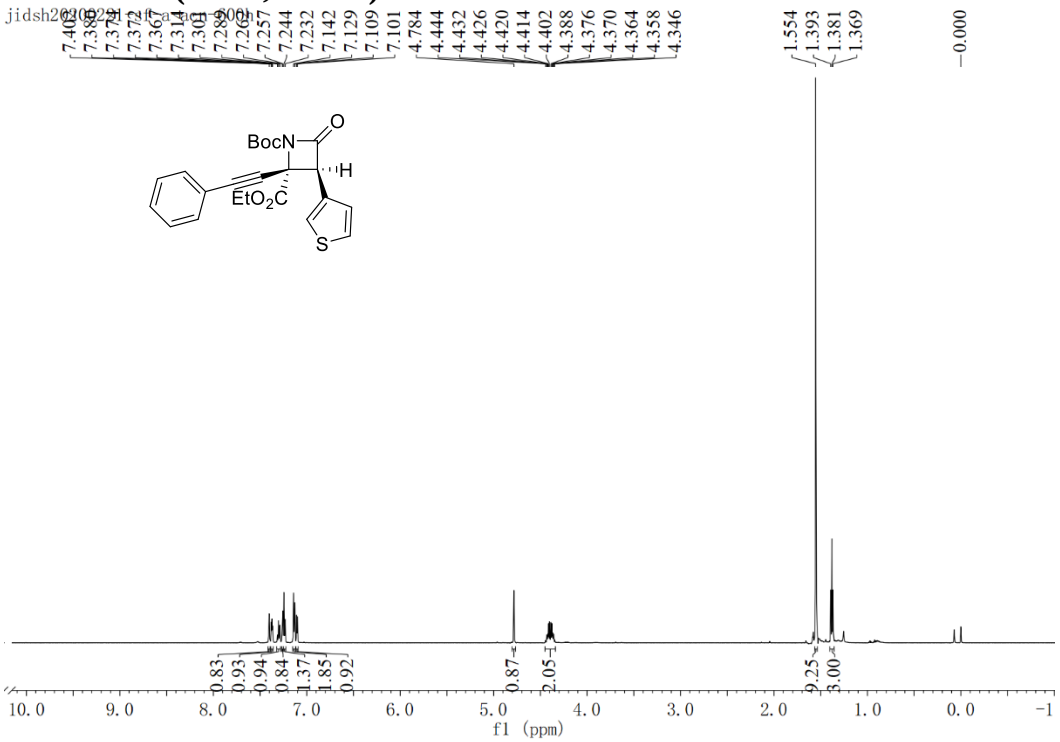
3ck-^{1}HNMR (600M, $CDCl_3$)



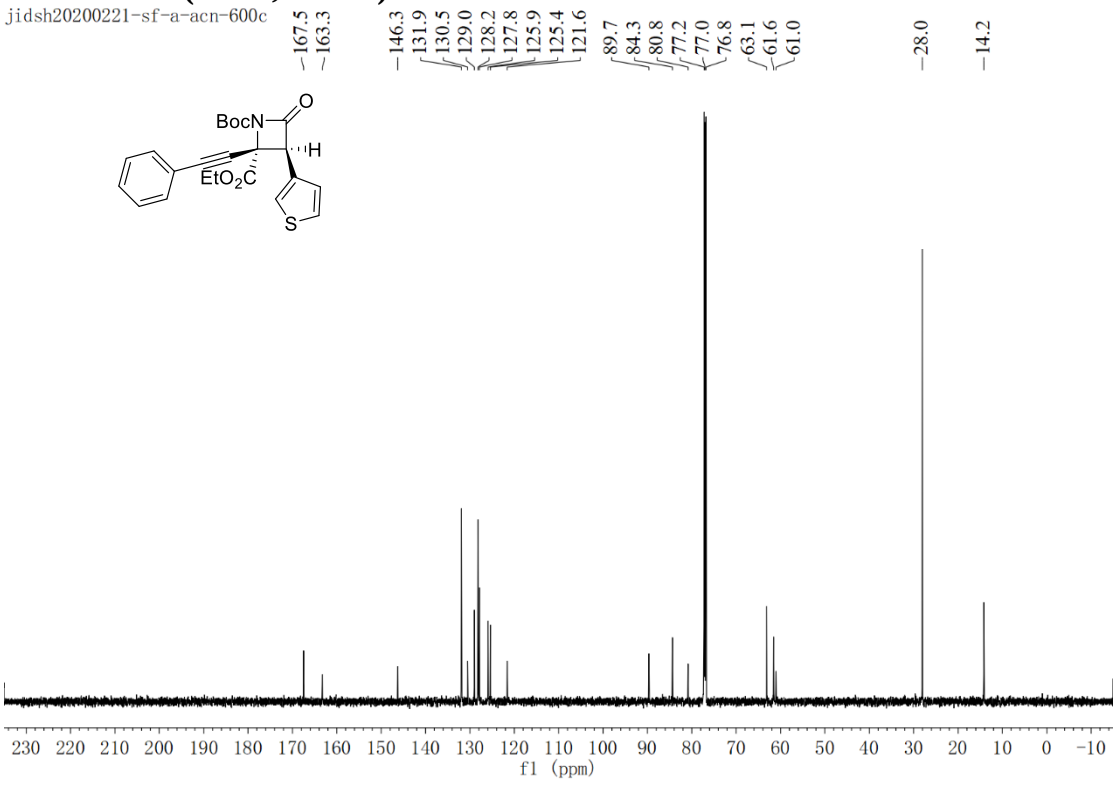
3ck-^{13}CNMR (151M, $CDCl_3$)



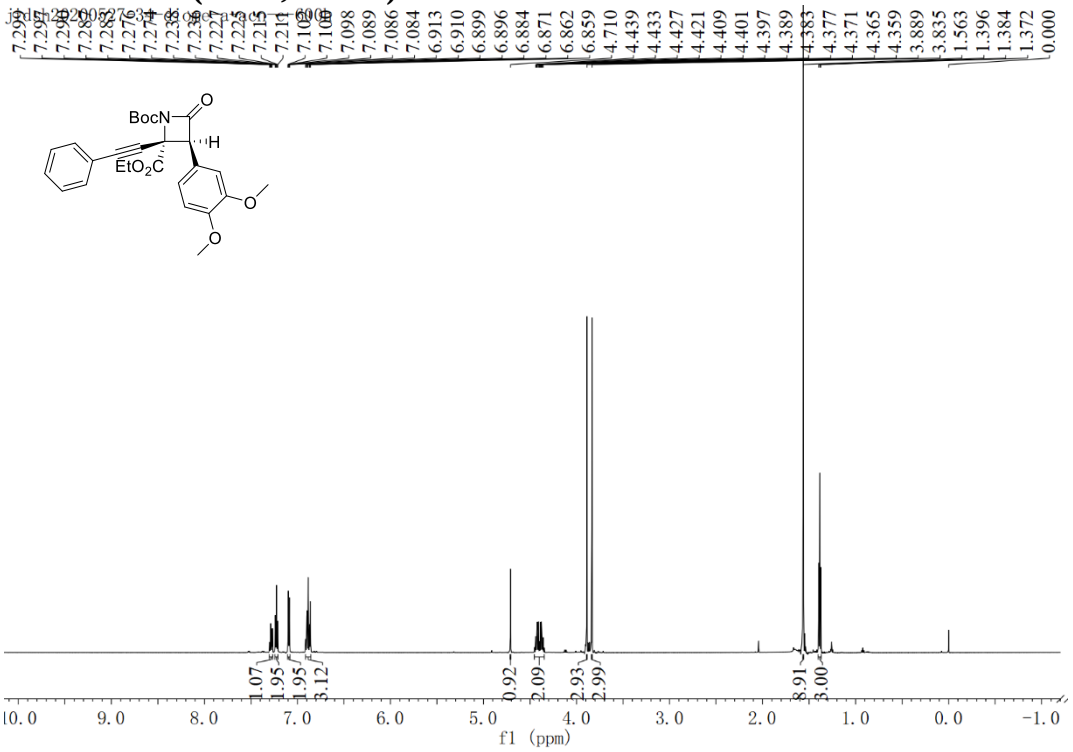
3cl-^{1}HNMR (600M, $CDCl_3$)



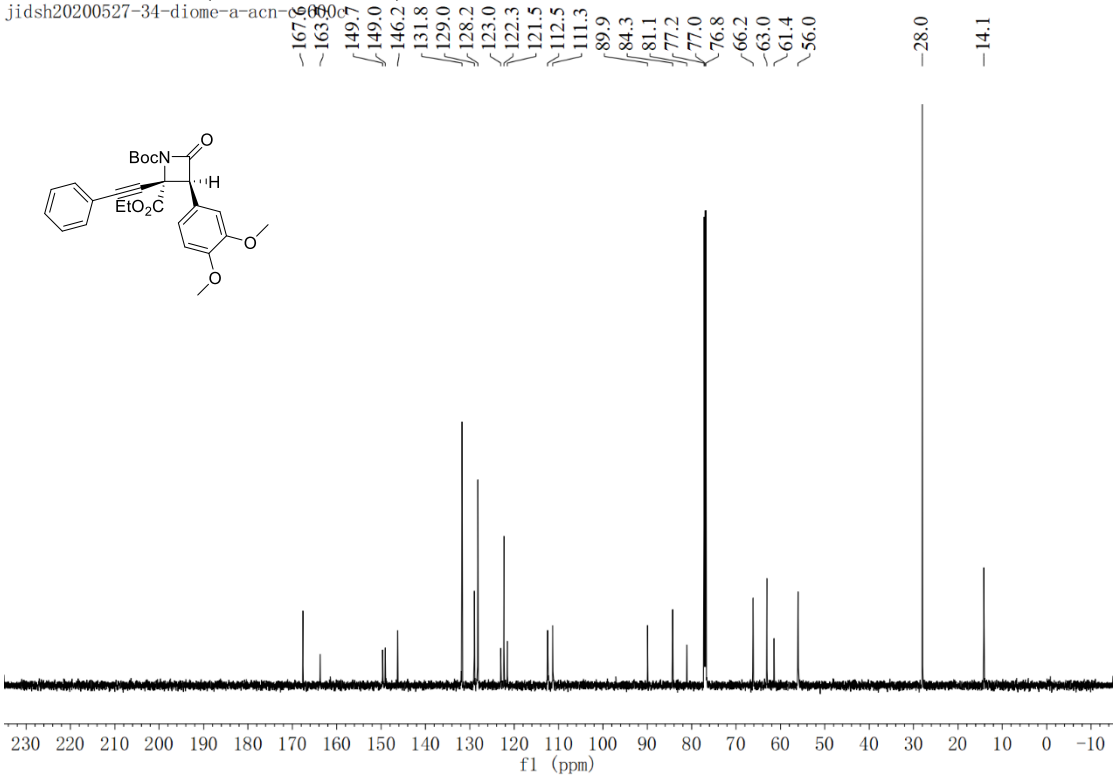
3cl-^{13}CNMR (151M, $CDCl_3$)



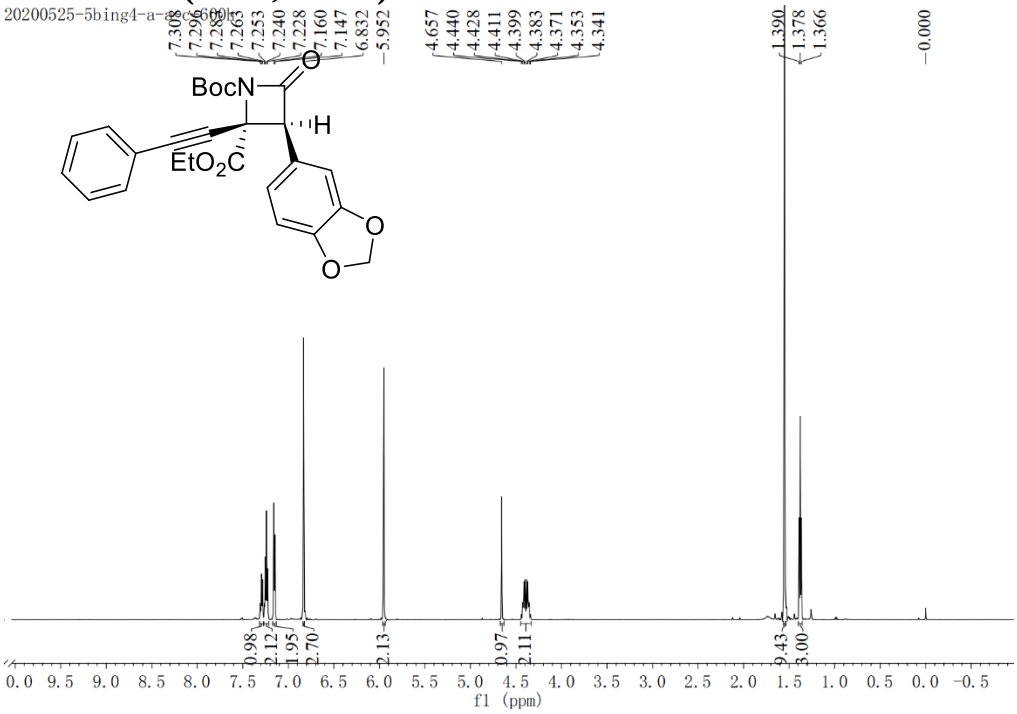
3cm-^{1}HNMR (600M, $CDCl_3$)



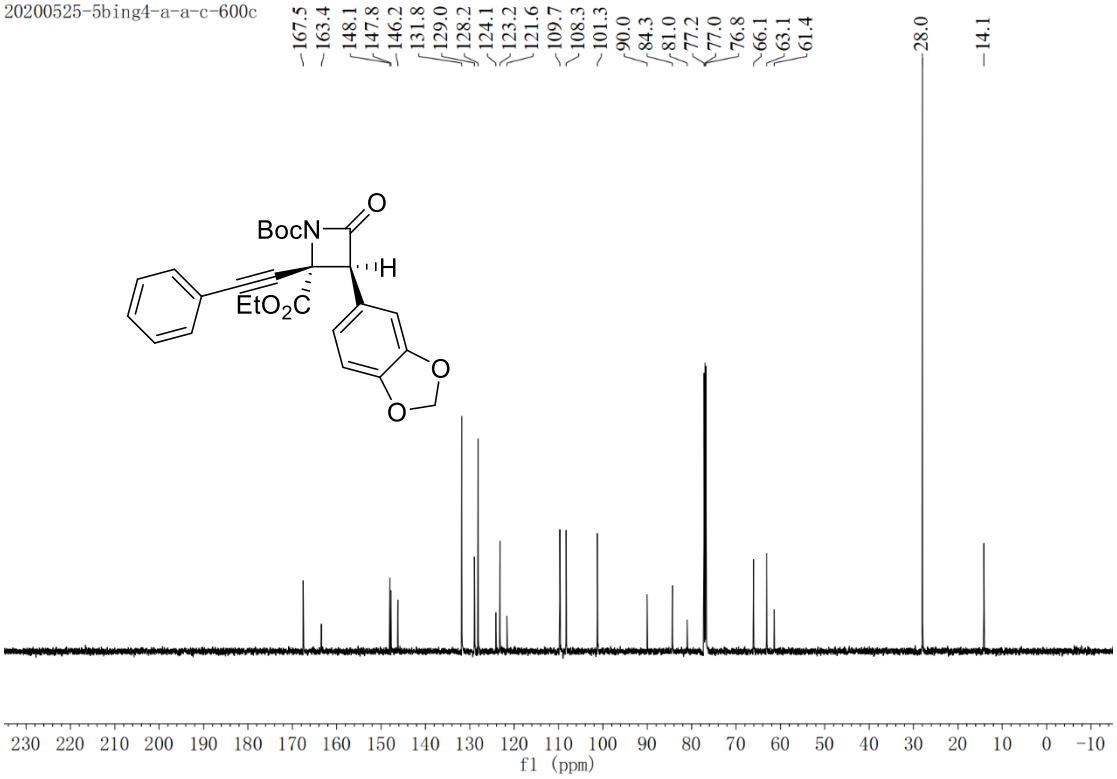
3cm-^{13}CNMR (151M, $CDCl_3$)



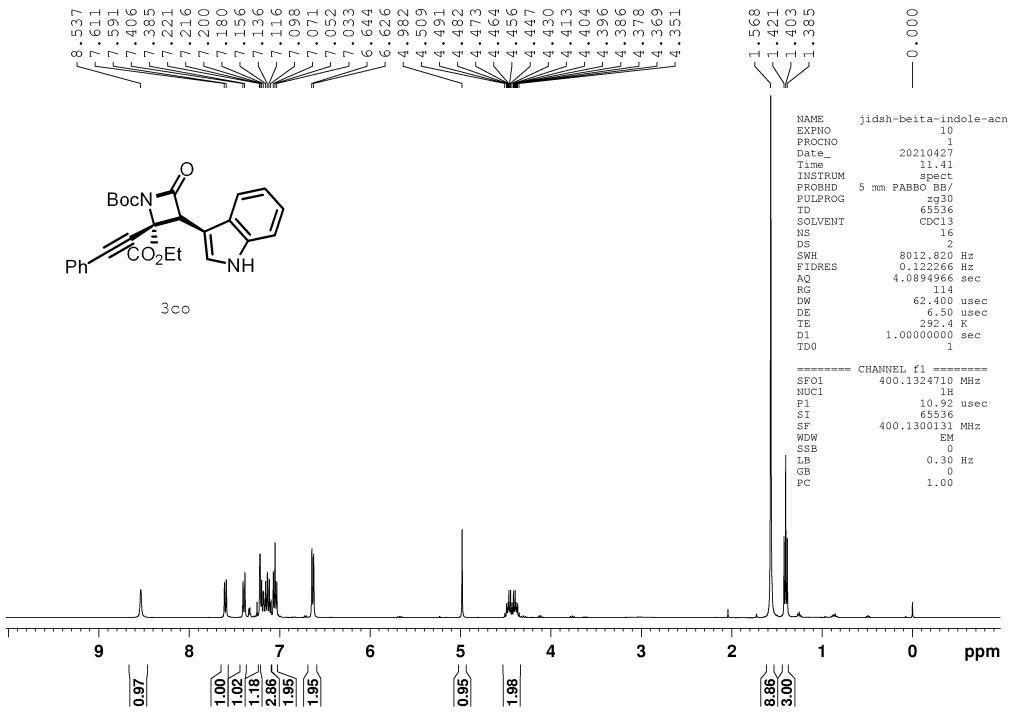
3cn-^{1}HNMR (600M, $CDCl_3$)



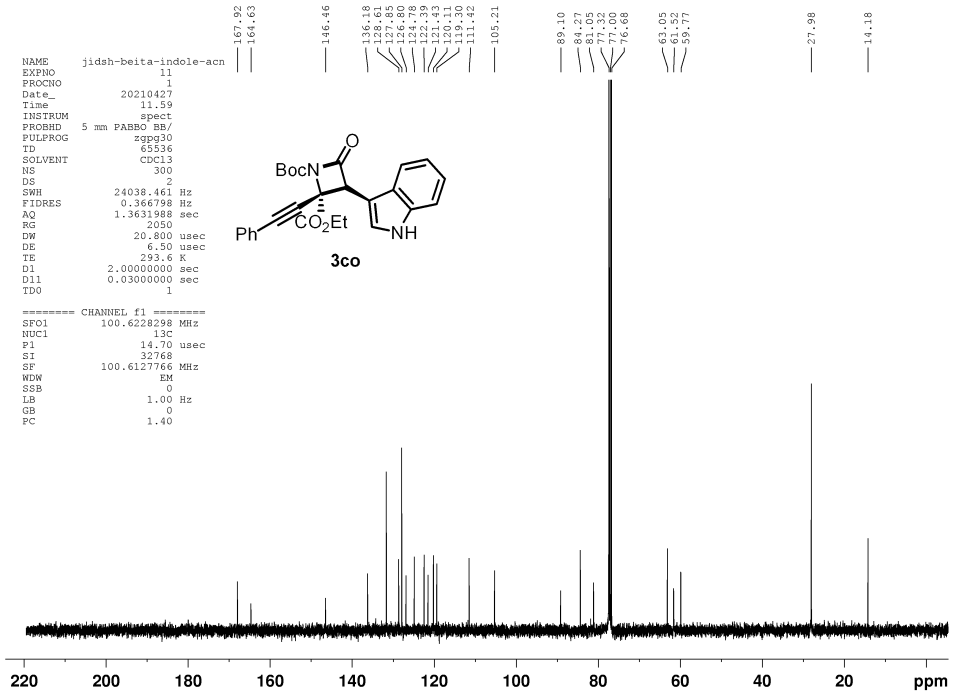
3cn-^{13}CNMR (151M, $CDCl_3$)



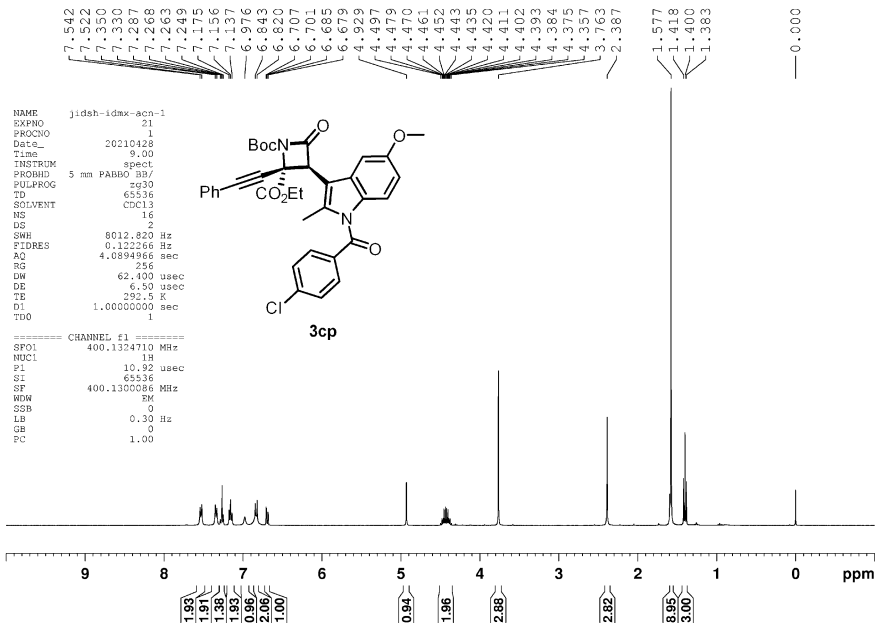
3co-^{1}HNMR (400M, $CDCl_3$)



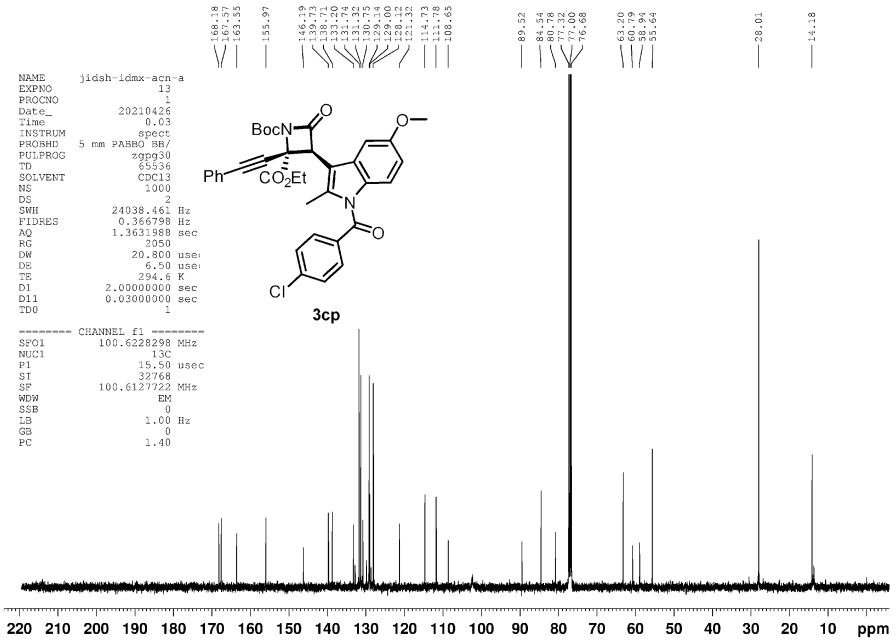
3co-^{13}CNMR (100M, $CDCl_3$)



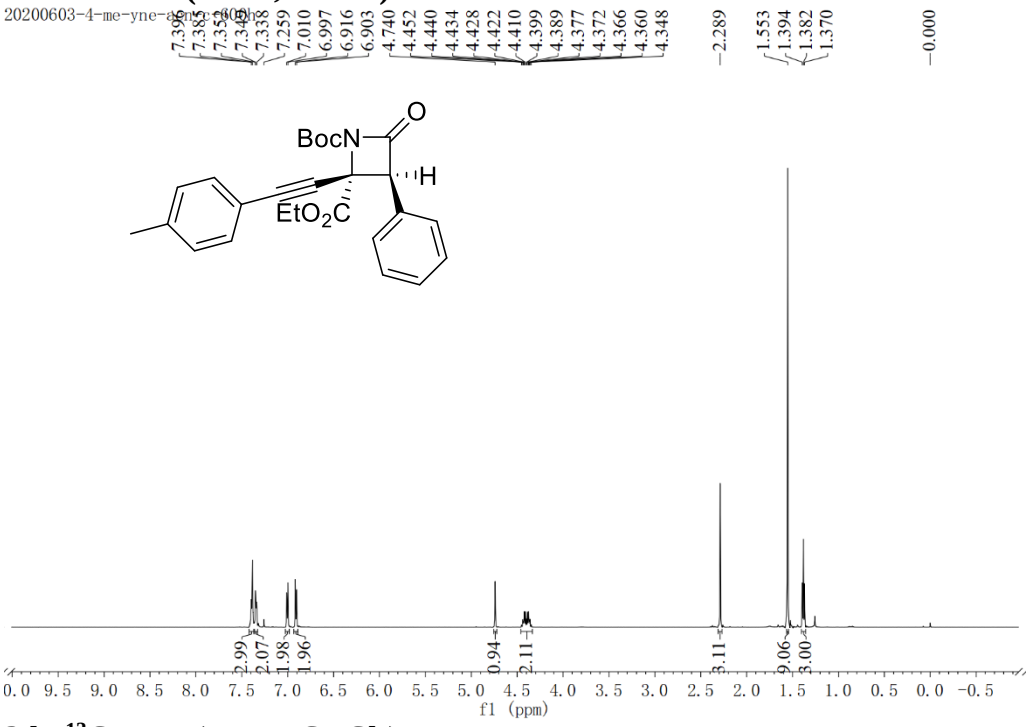
3cp-^{1}HNMR (400M, $CDCl_3$)



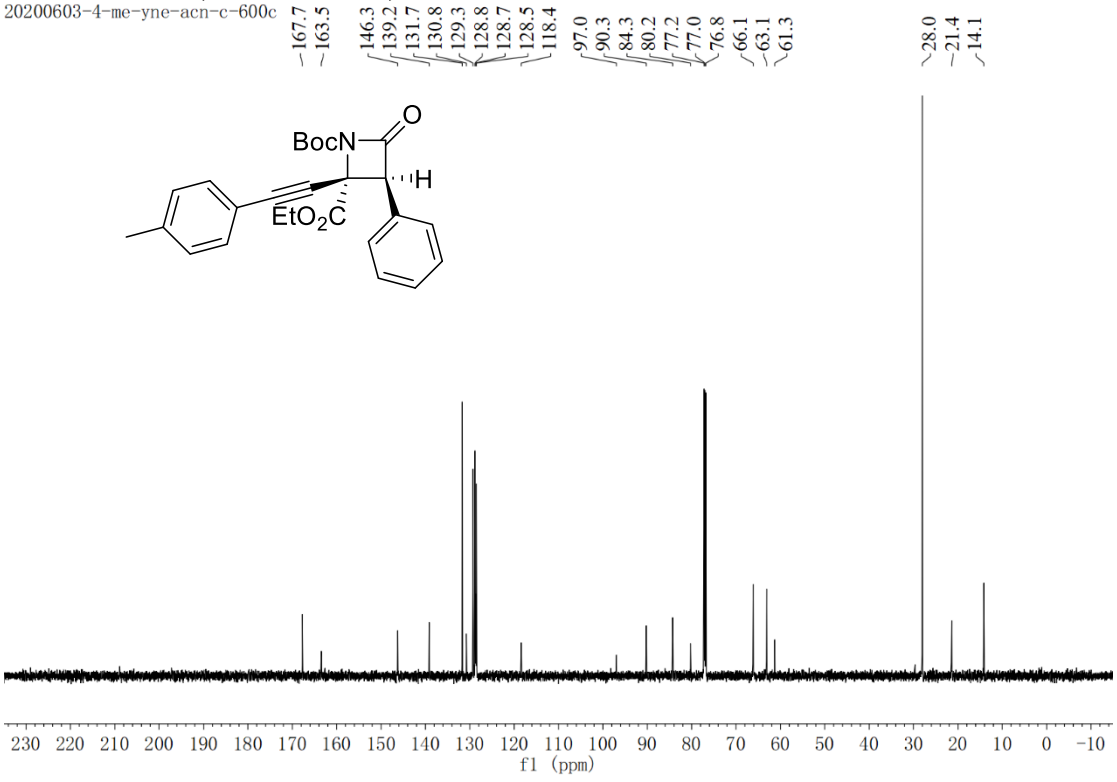
3cp-^{13}CNMR (100M, $CDCl_3$)



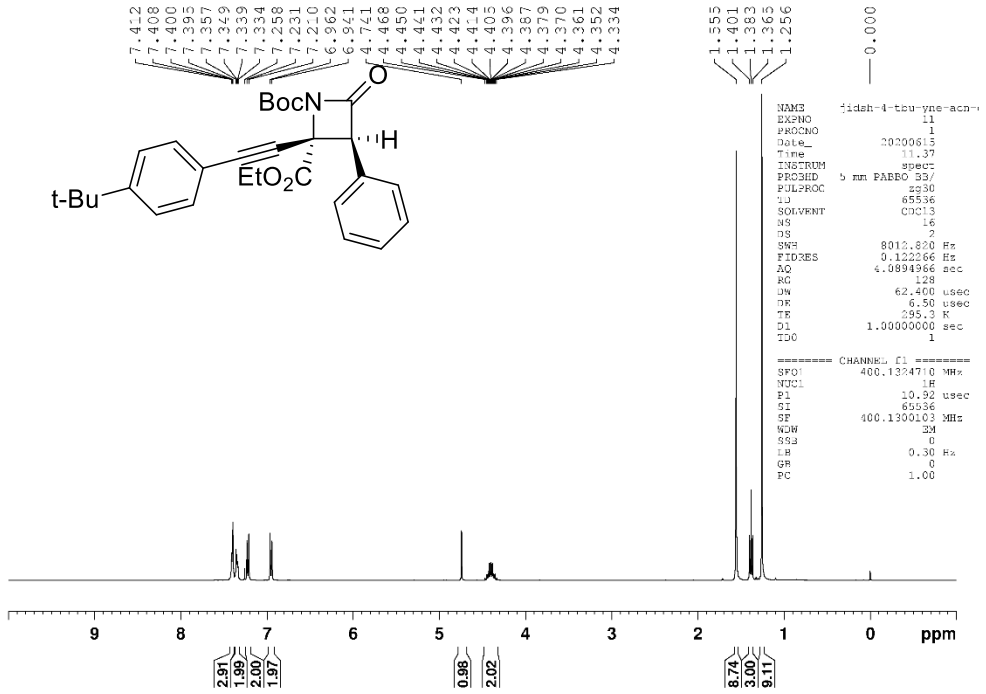
3da-^{1}HNMR (600M, $CDCl_3$)



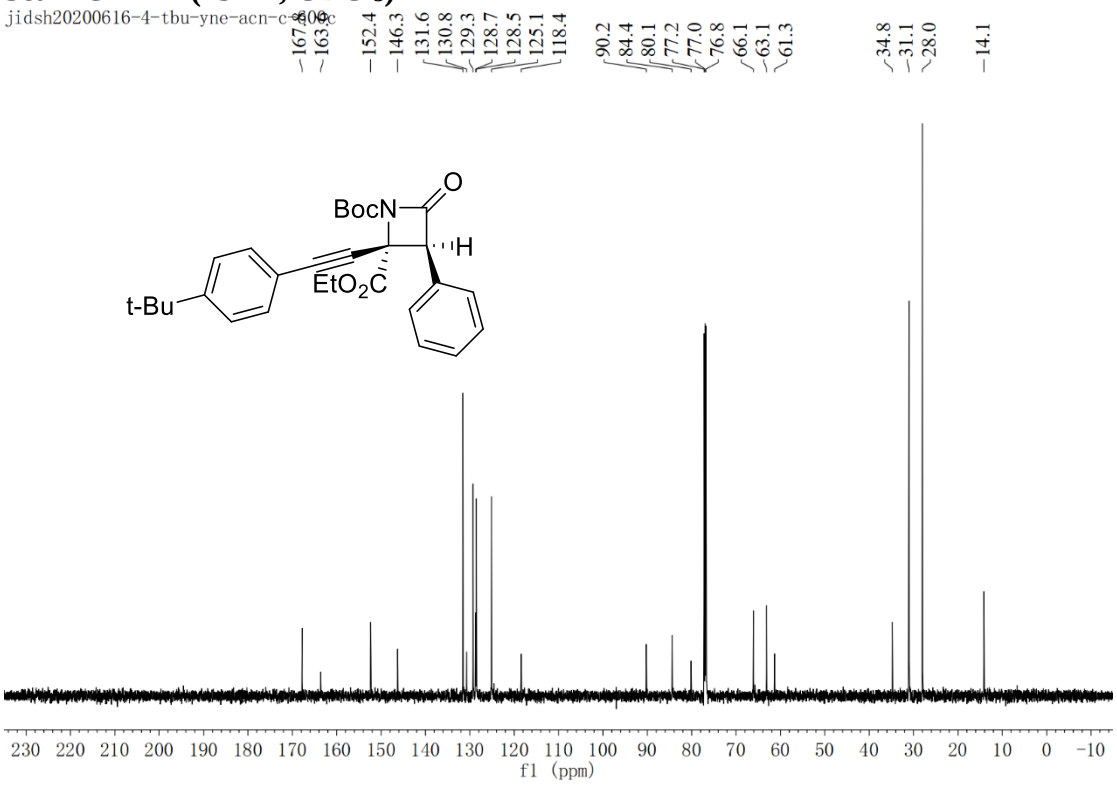
3da-^{13}CNMR (151M, $CDCl_3$)



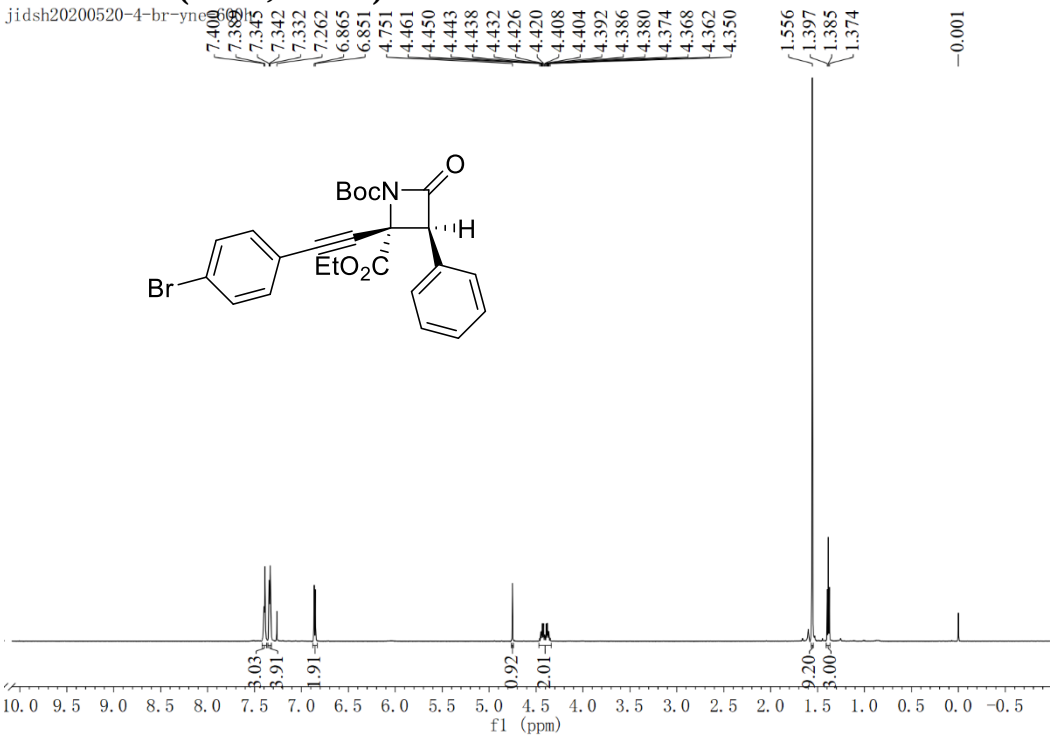
3ea-^{1}HNMR (400M, $CDCl_3$)



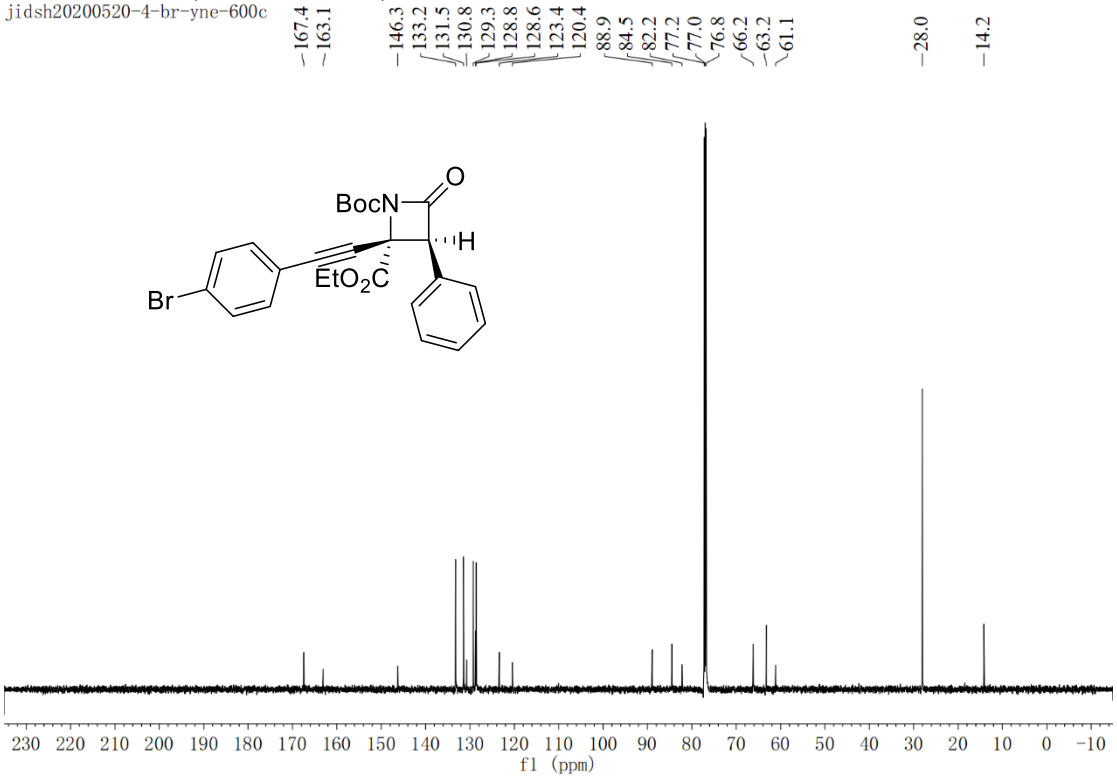
3ea-^{13}CNMR (151M, $CDCl_3$)



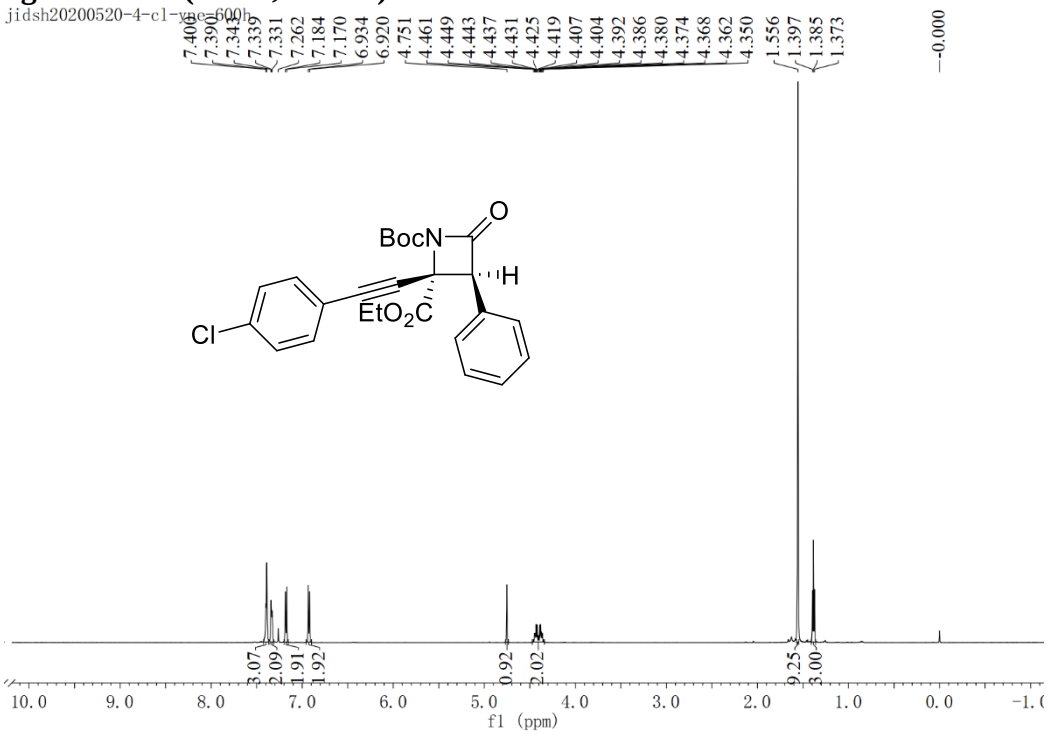
3fa-^{1}HNMR (600M, $CDCl_3$)



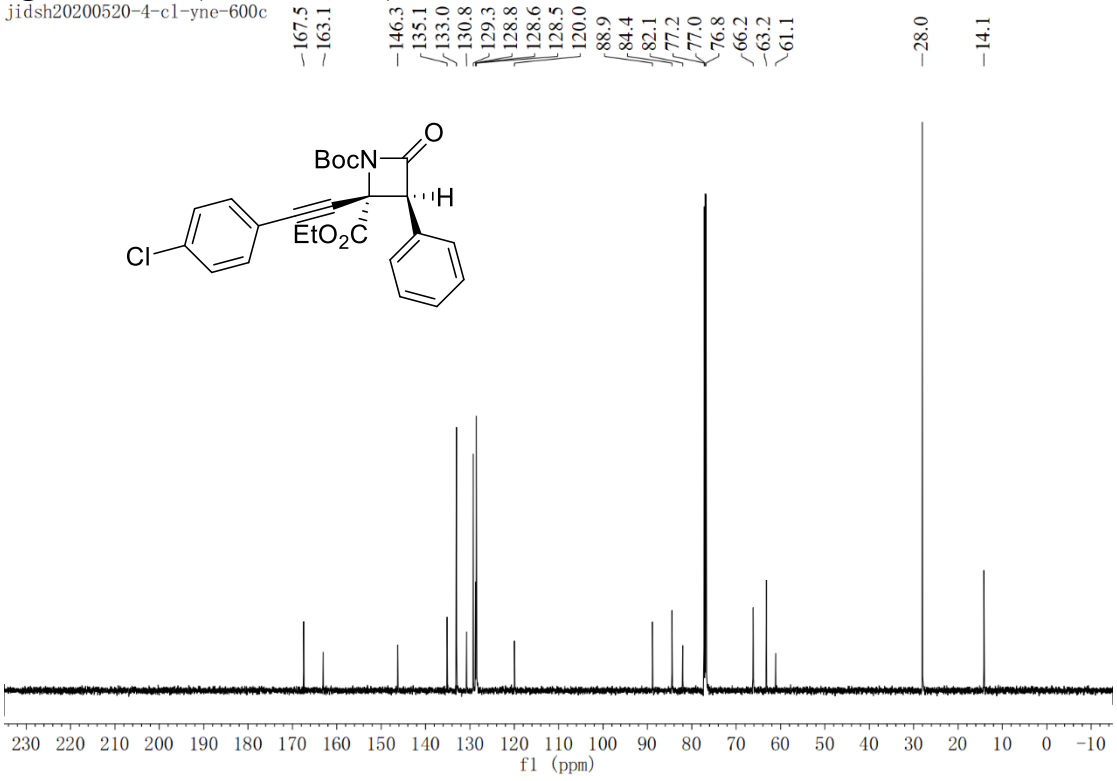
3fa-^{13}CNMR (151M, $CDCl_3$)



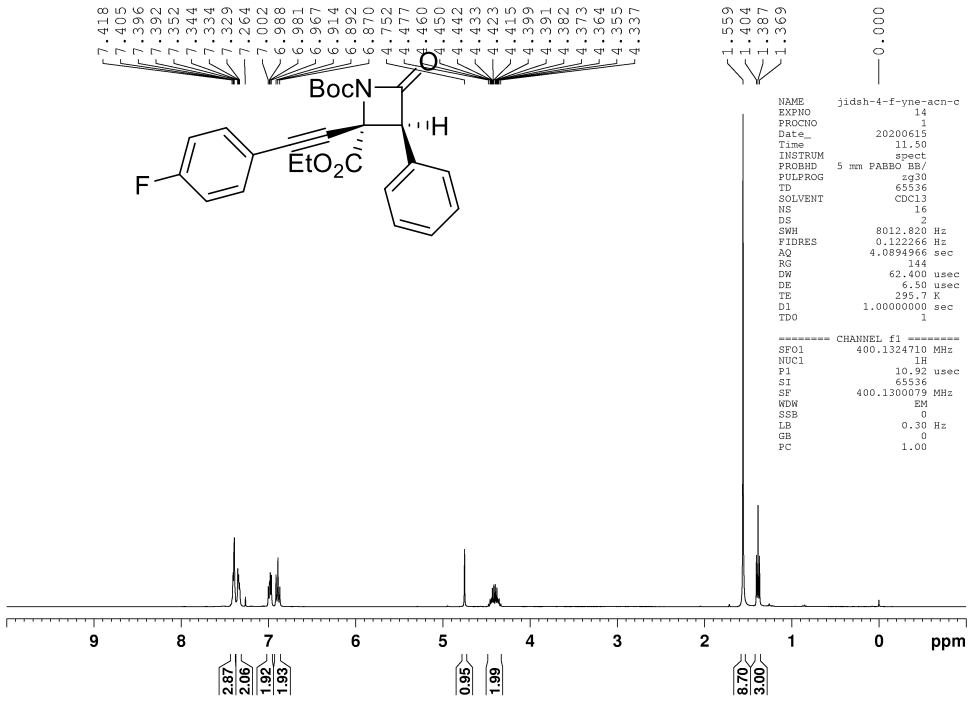
3ga-^{1}HNMR (600M, $CDCl_3$)



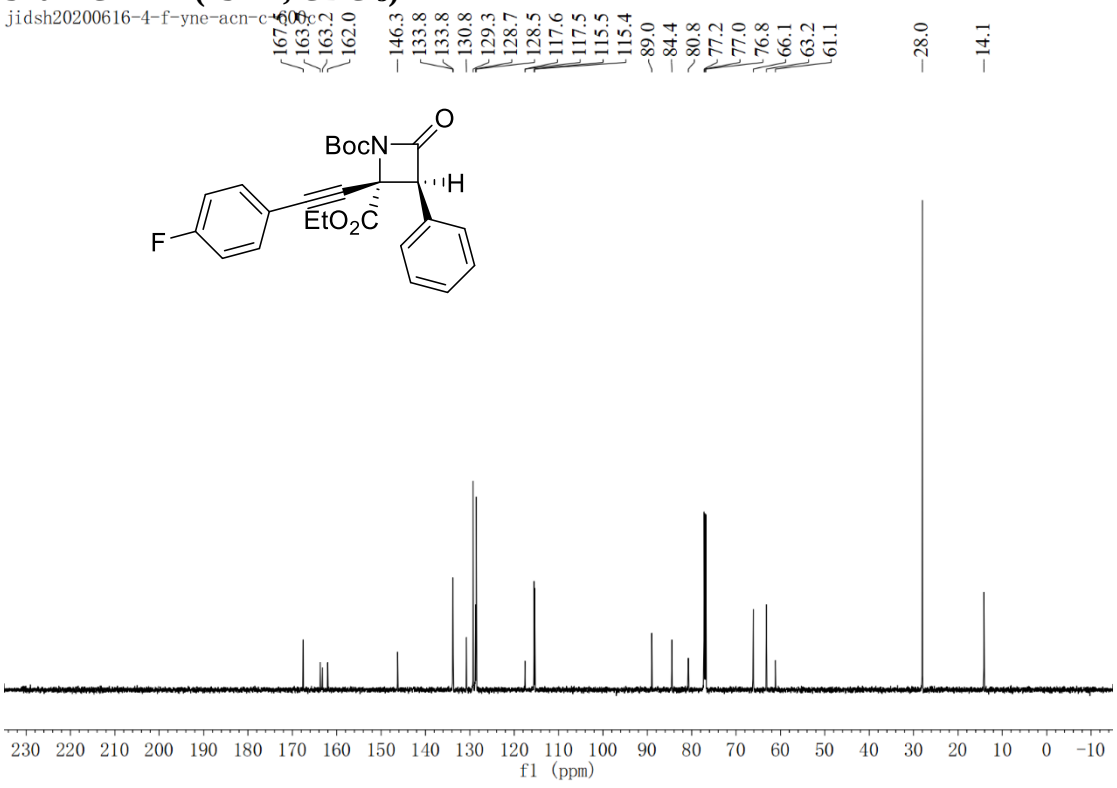
3ga-^{13}CNMR (151M, $CDCl_3$)



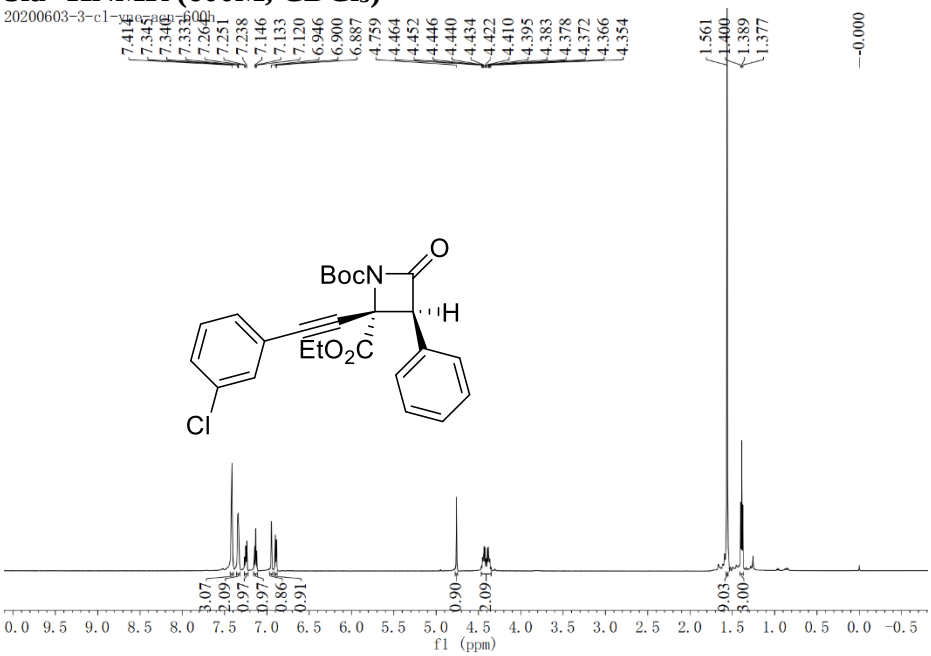
3ha-^{1}HNMR (400M, $CDCl_3$)



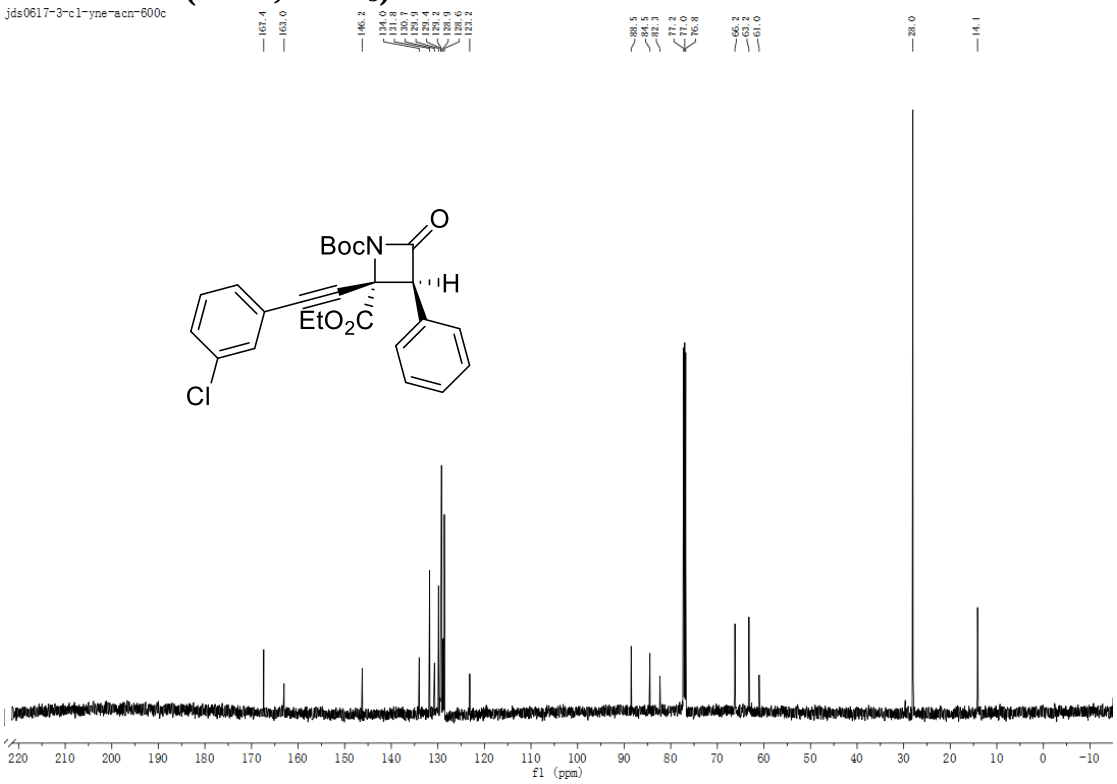
3ha-^{13}CNMR (151M, $CDCl_3$)



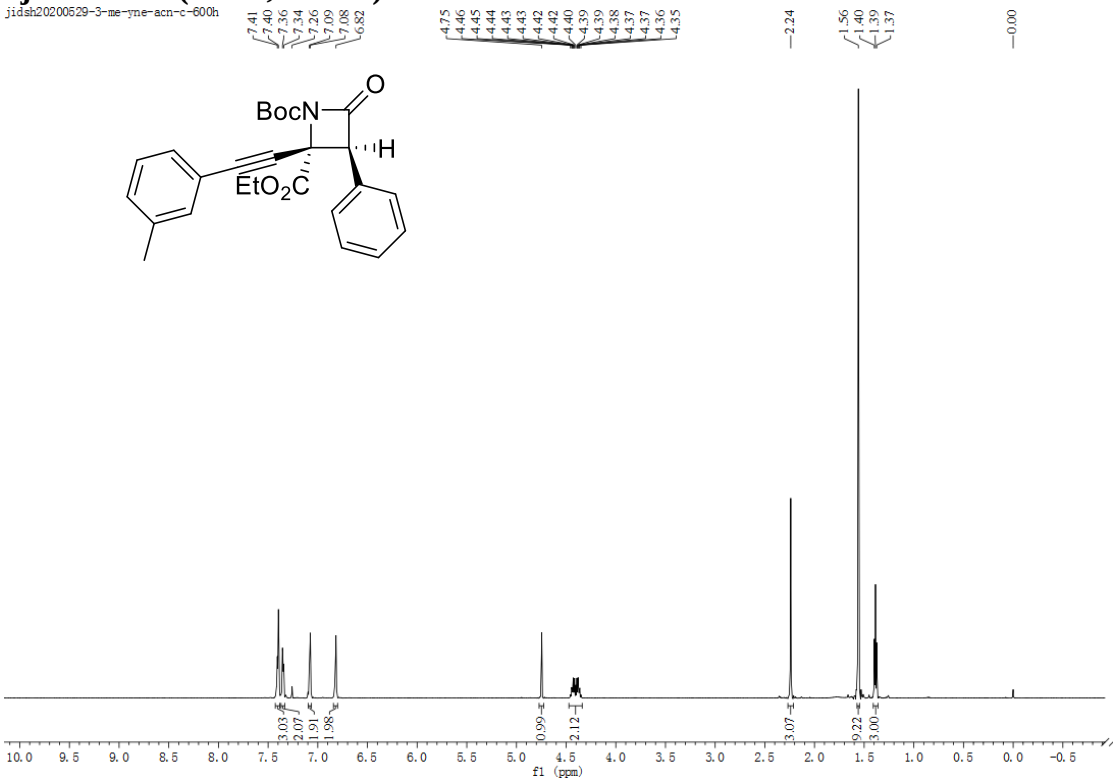
3ia-^{1}HNMR (600M, $CDCl_3$)



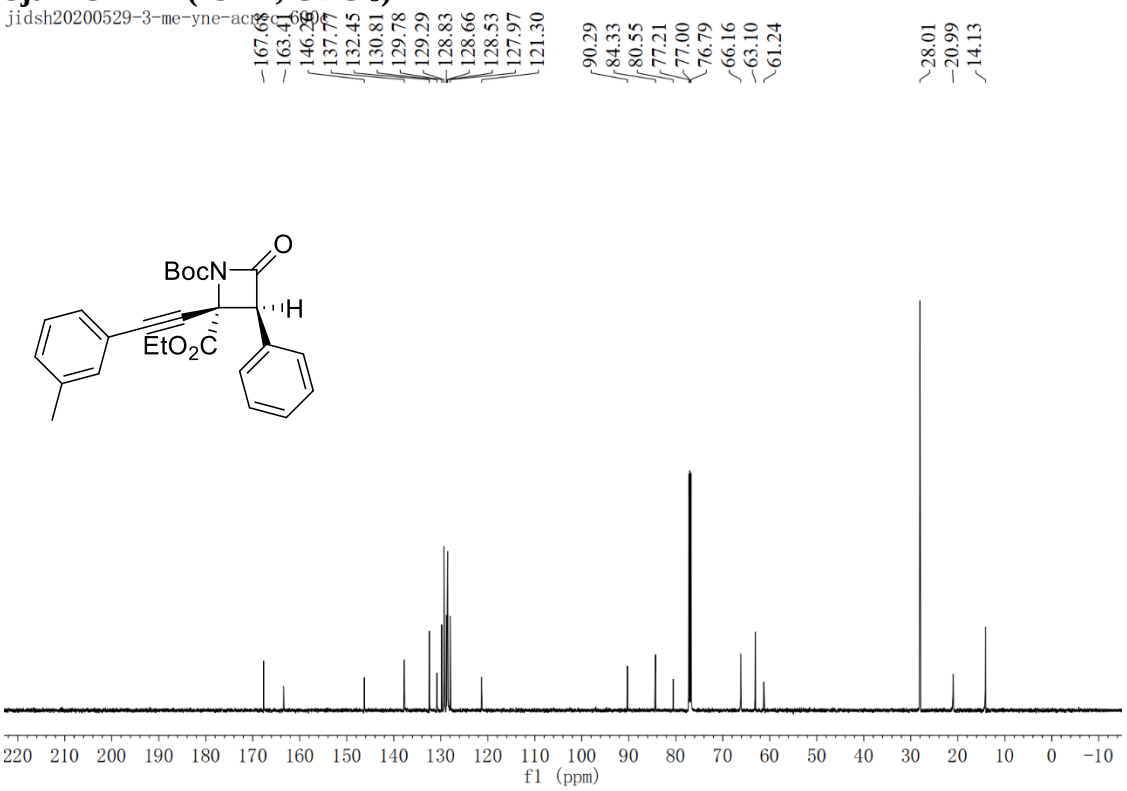
3ia-^{13}CNMR (151M, $CDCl_3$)



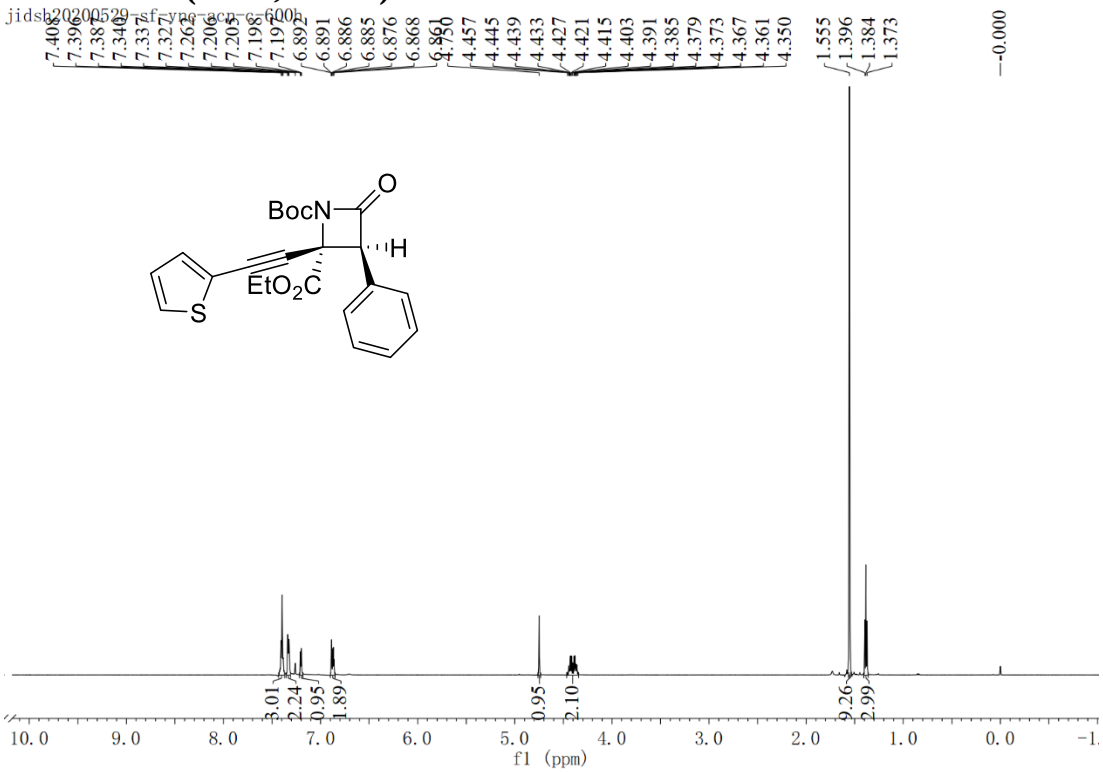
3ja-^{1}HNMR (600M, $CDCl_3$)



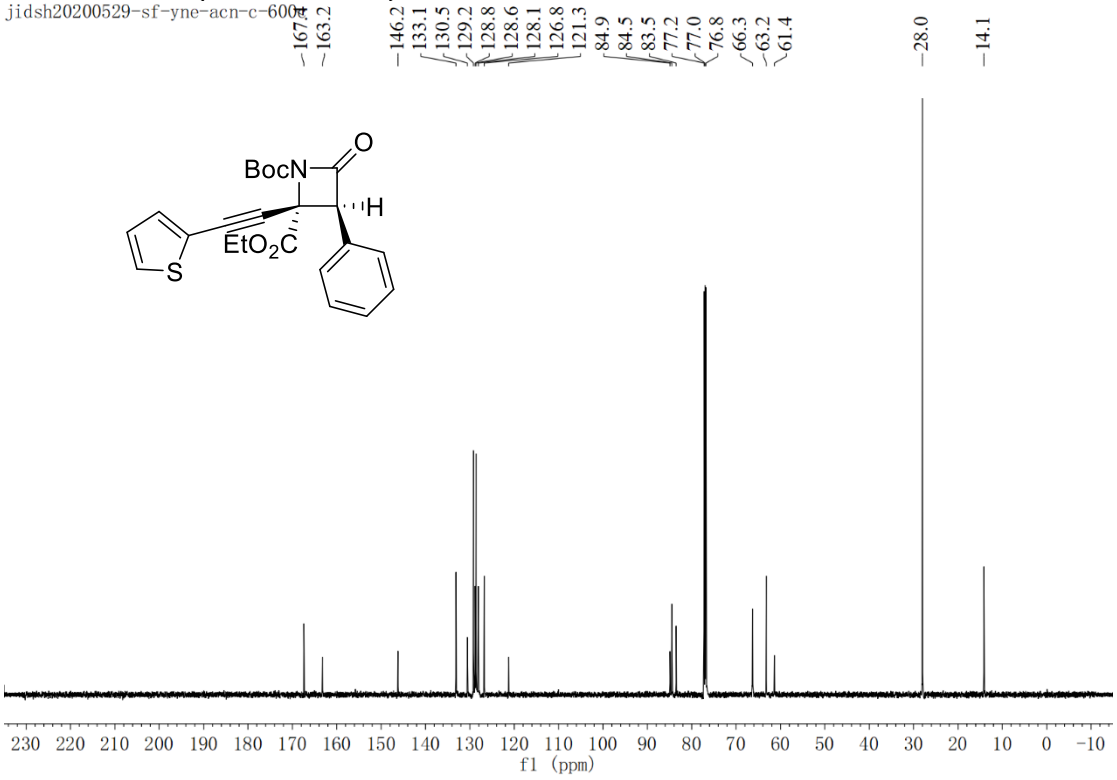
3ja-^{13}CNMR (151M, $CDCl_3$)



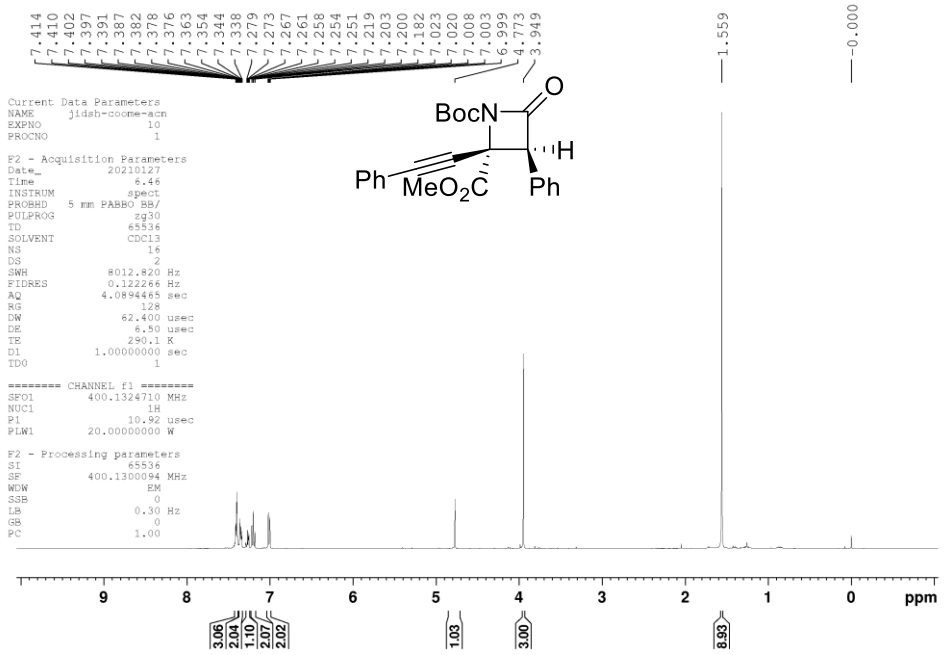
3ka-^{1}HNMR (600M, $CDCl_3$)



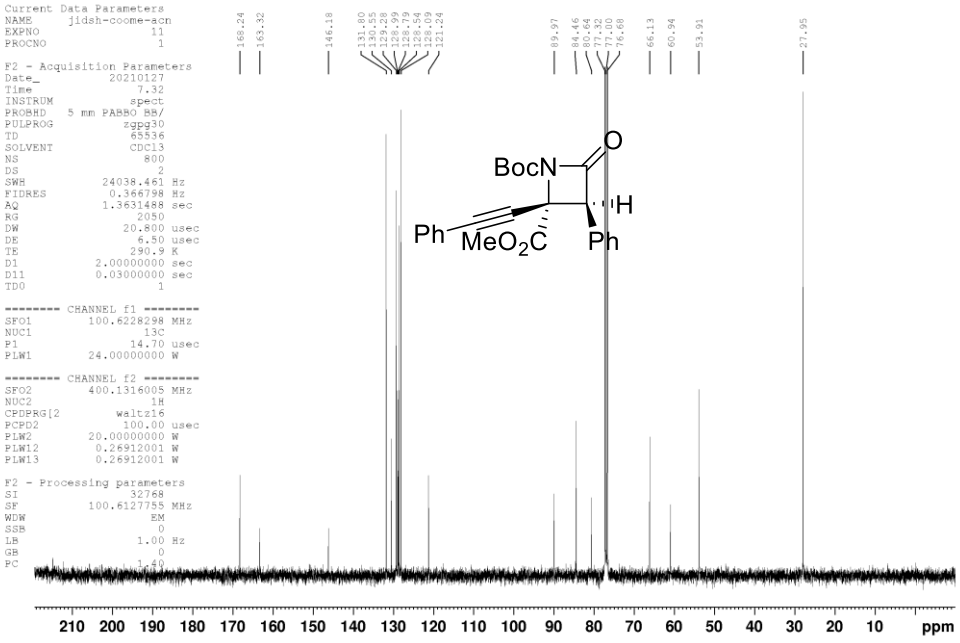
3ka-^{13}CNMR (151M, $CDCl_3$)



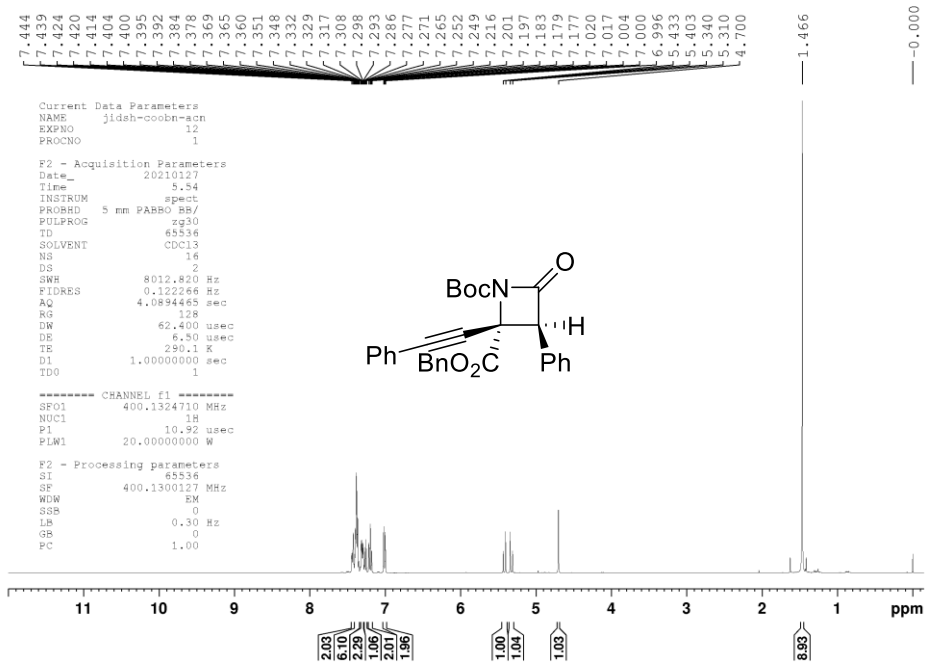
3la-^{1}HNMR (400M, $CDCl_3$)



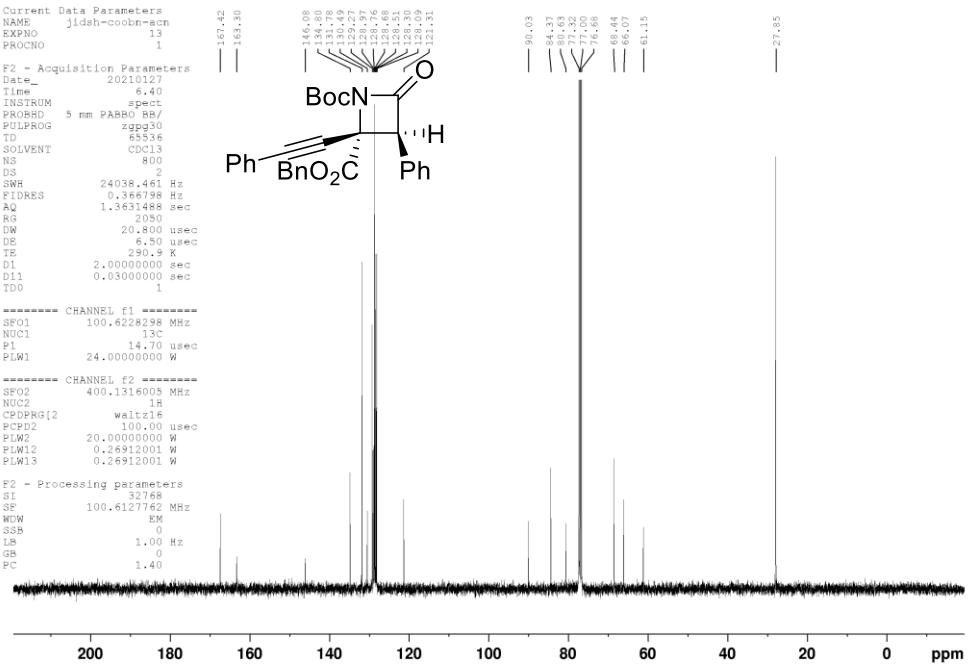
3la-^{13}CNMR (100M, $CDCl_3$)



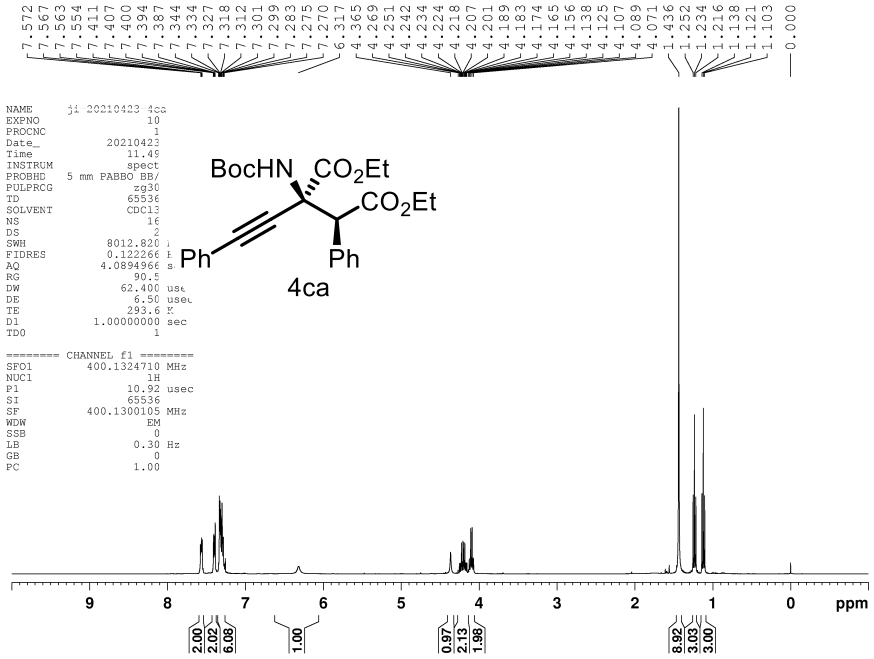
3ma-^{1}HNMR (400M, $CDCl_3$)



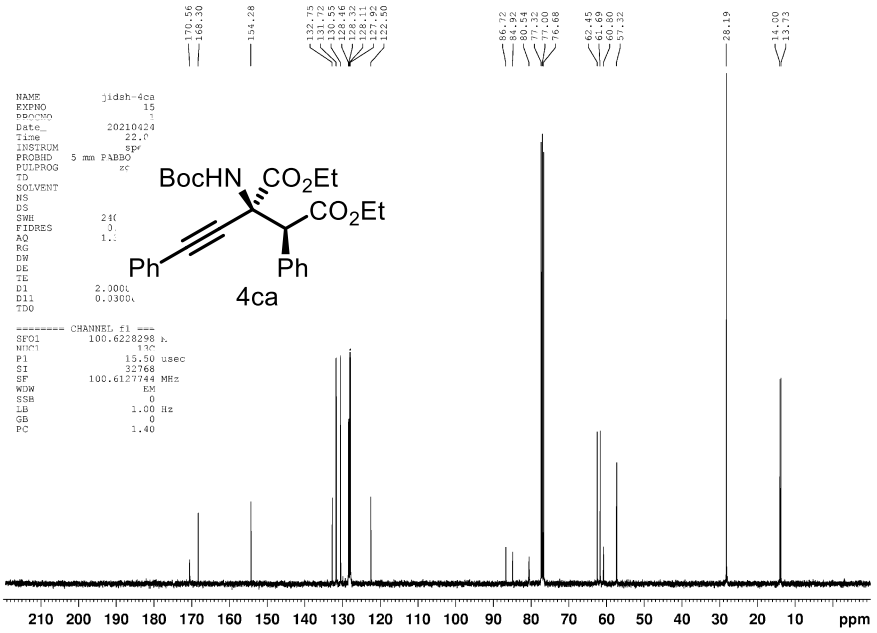
3ma-^{13}CNMR (100M, $CDCl_3$)



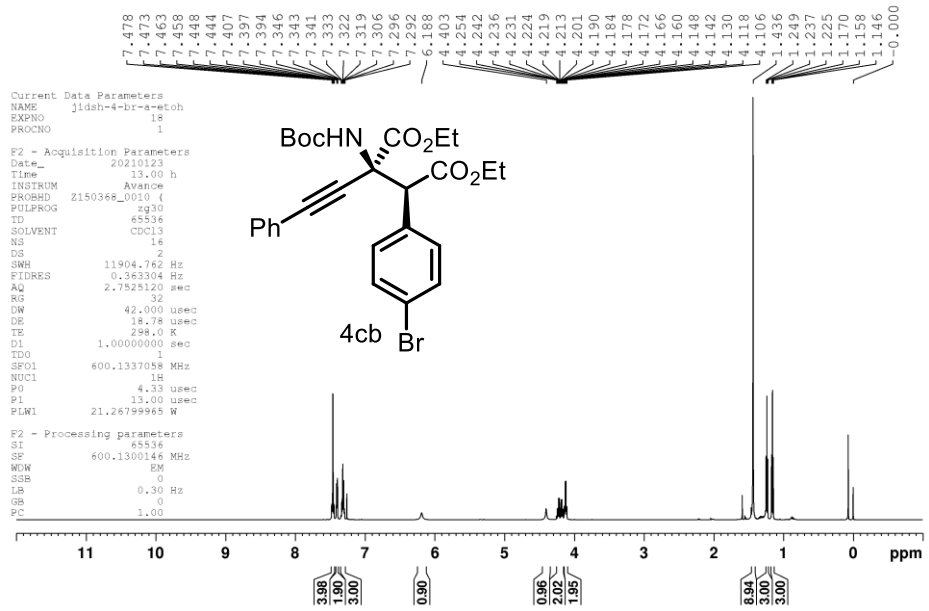
4ca-^{1}HNMR (400M, $CDCl_3$)



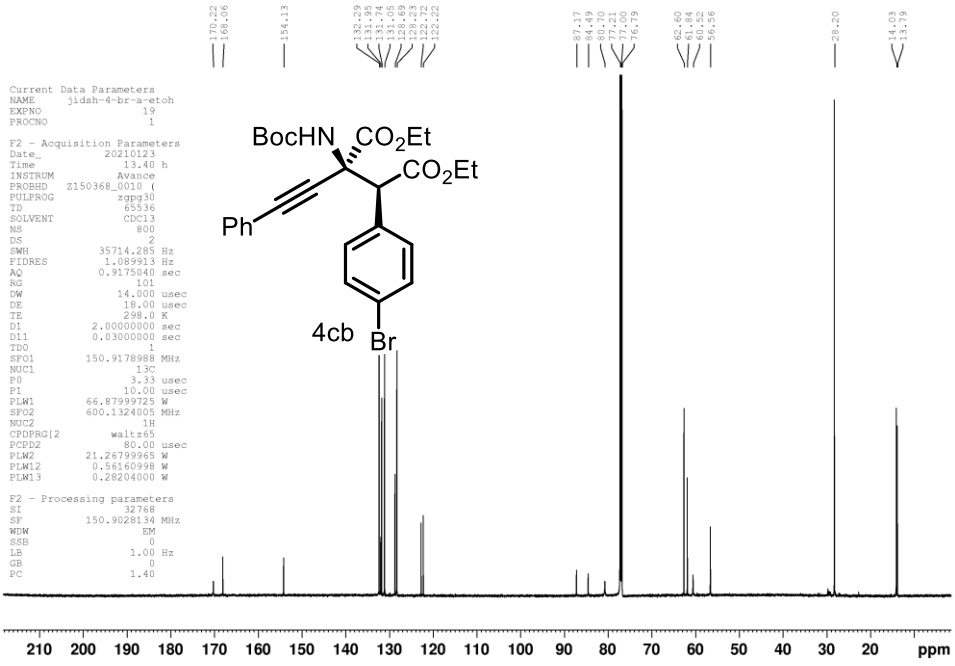
4ca-^{13}CNMR (100M, $CDCl_3$)



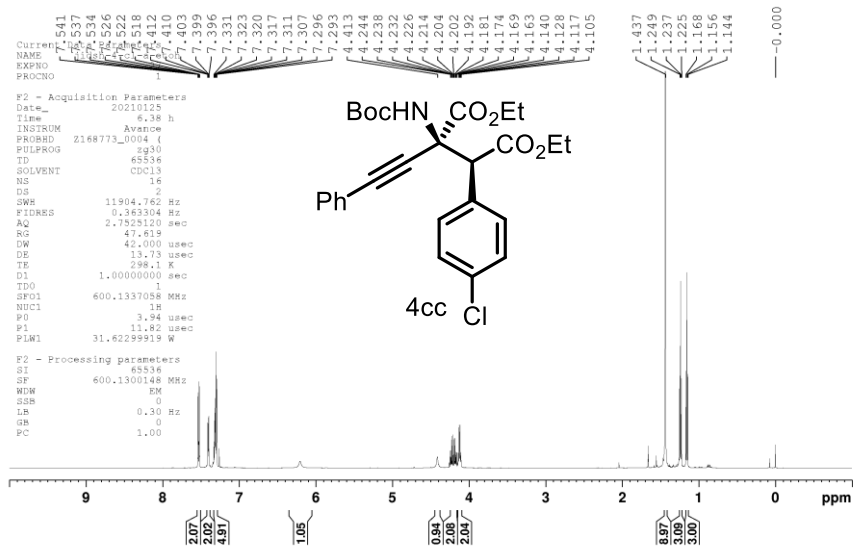
4cb-^{1}HNMR (600M, $CDCl_3$)



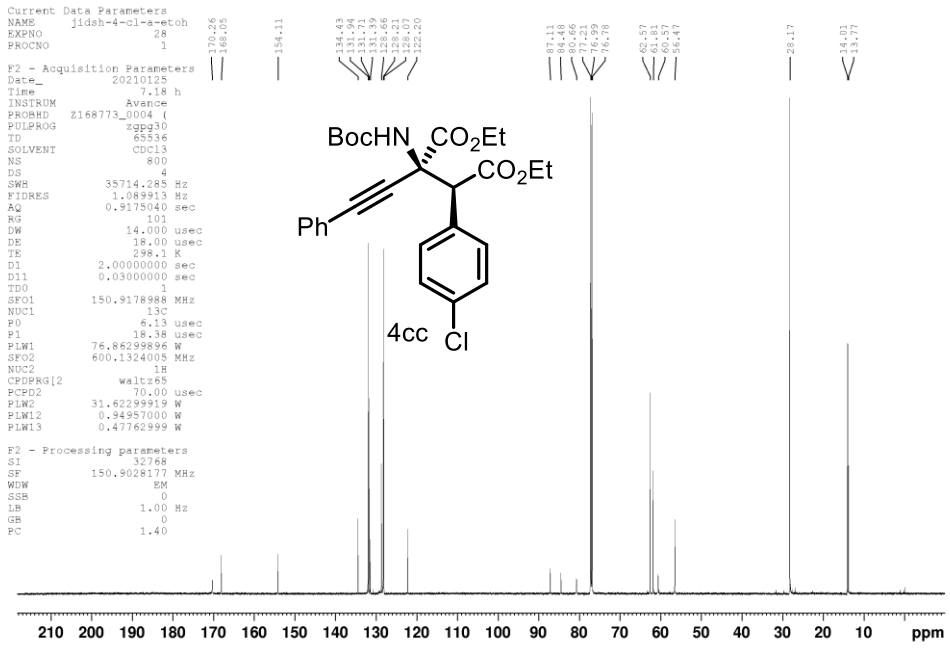
4cb-^{13}CNMR (151M, $CDCl_3$)



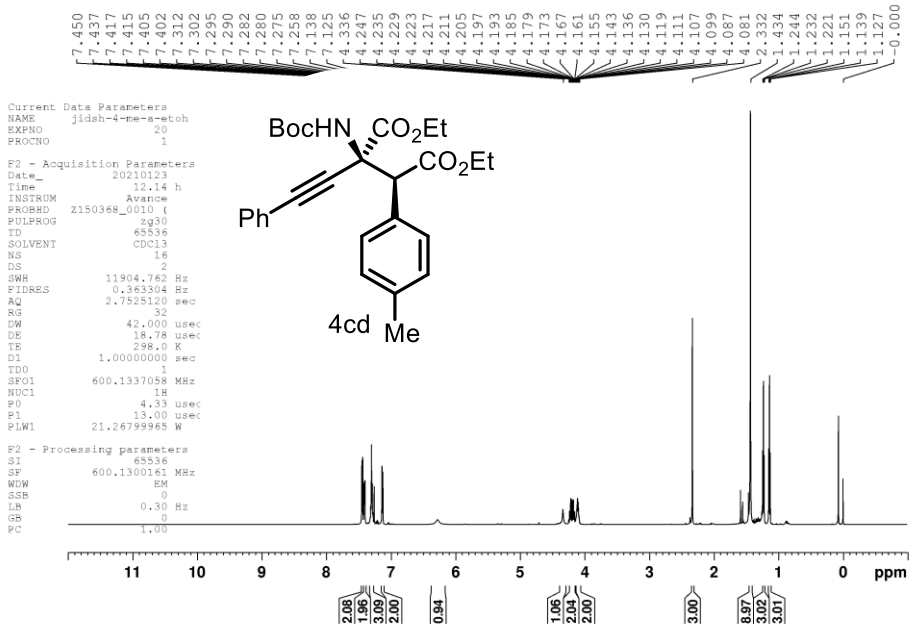
4cc-^{1}HNMR (600M, $CDCl_3$)



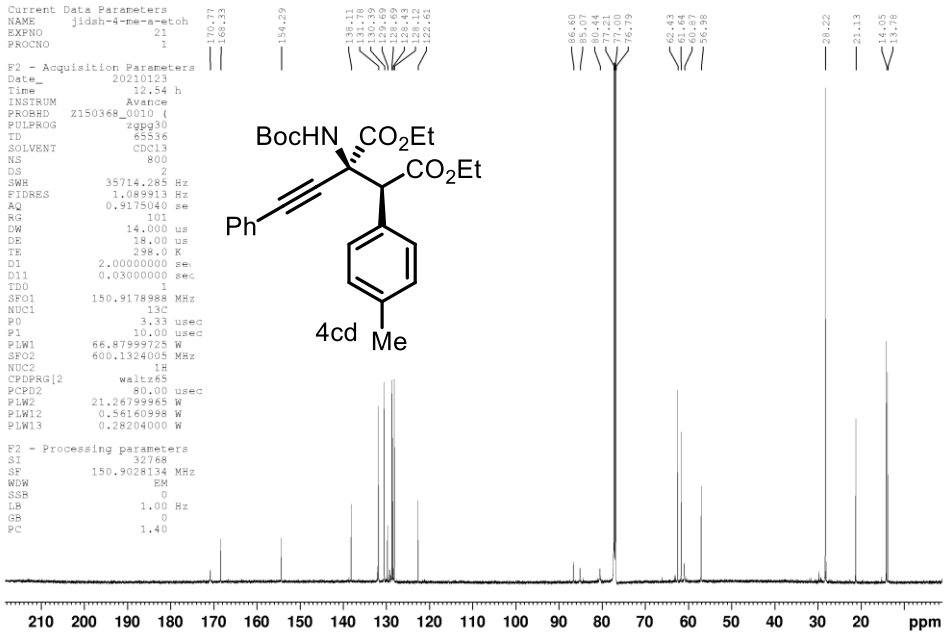
4cc-^{13}CNMR (151M, $CDCl_3$)



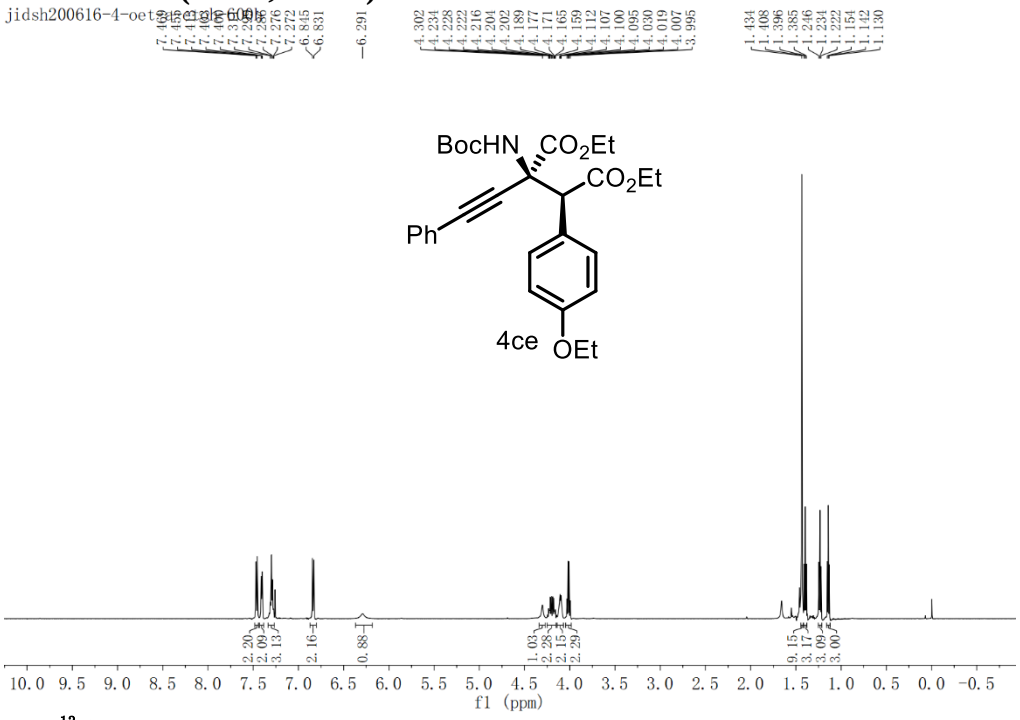
4cd-^{1}HNMR (600M, $CDCl_3$)



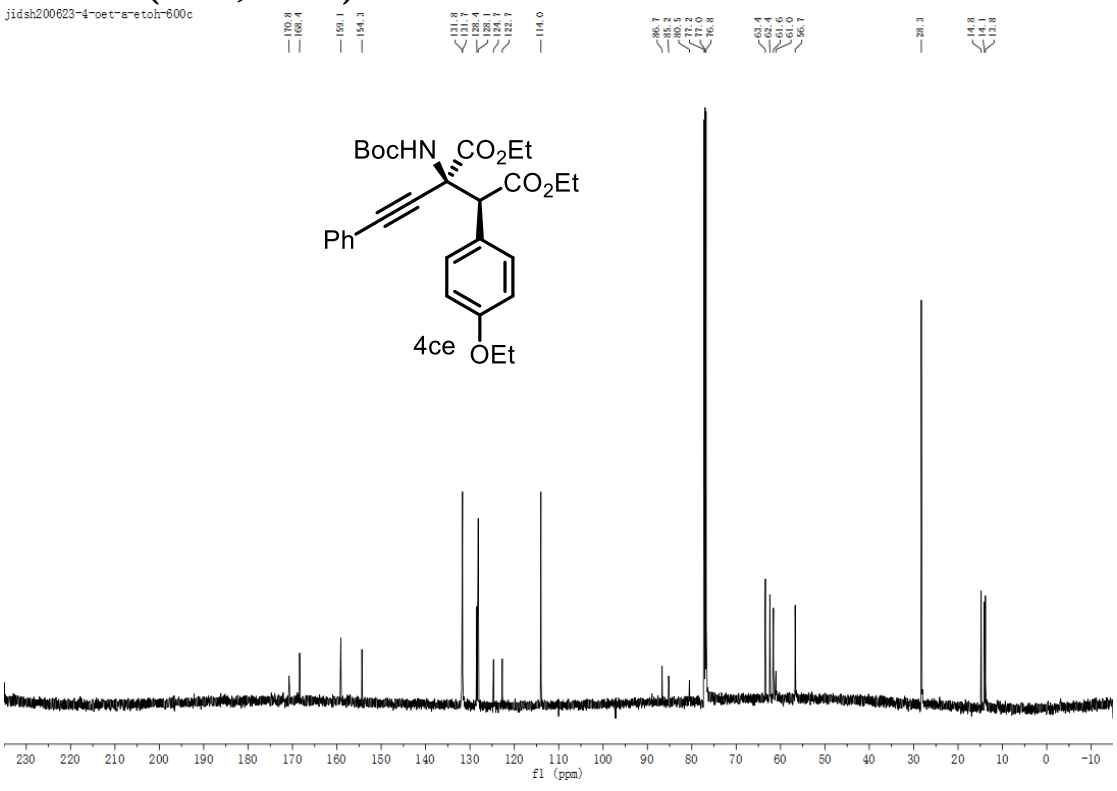
4cd-^{13}CNMR (151M, $CDCl_3$)



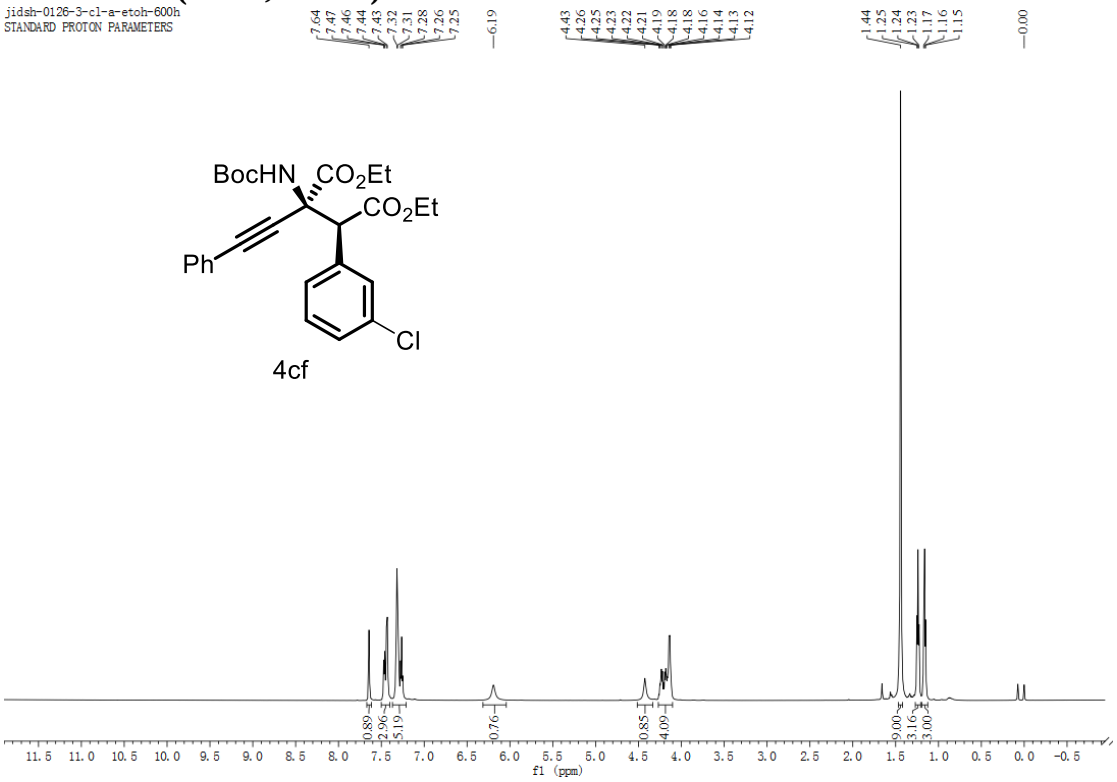
4ce-^{1}HNMR (600M,CDCl$_3$)



4ce-^{13}CNMR (151M, CDCl$_3$)



4cf-^{1}HNMR (600M, $CDCl_3$)



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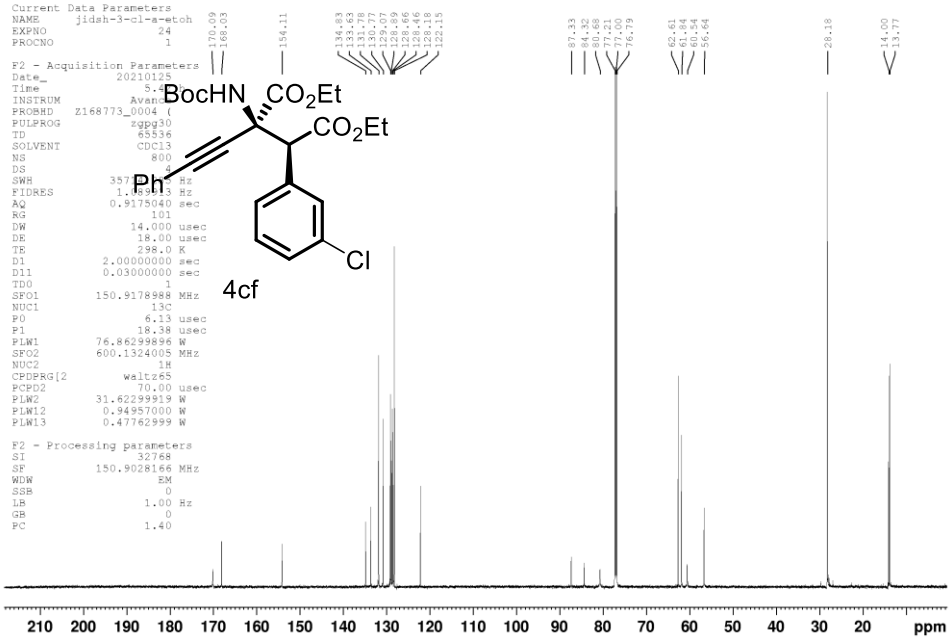

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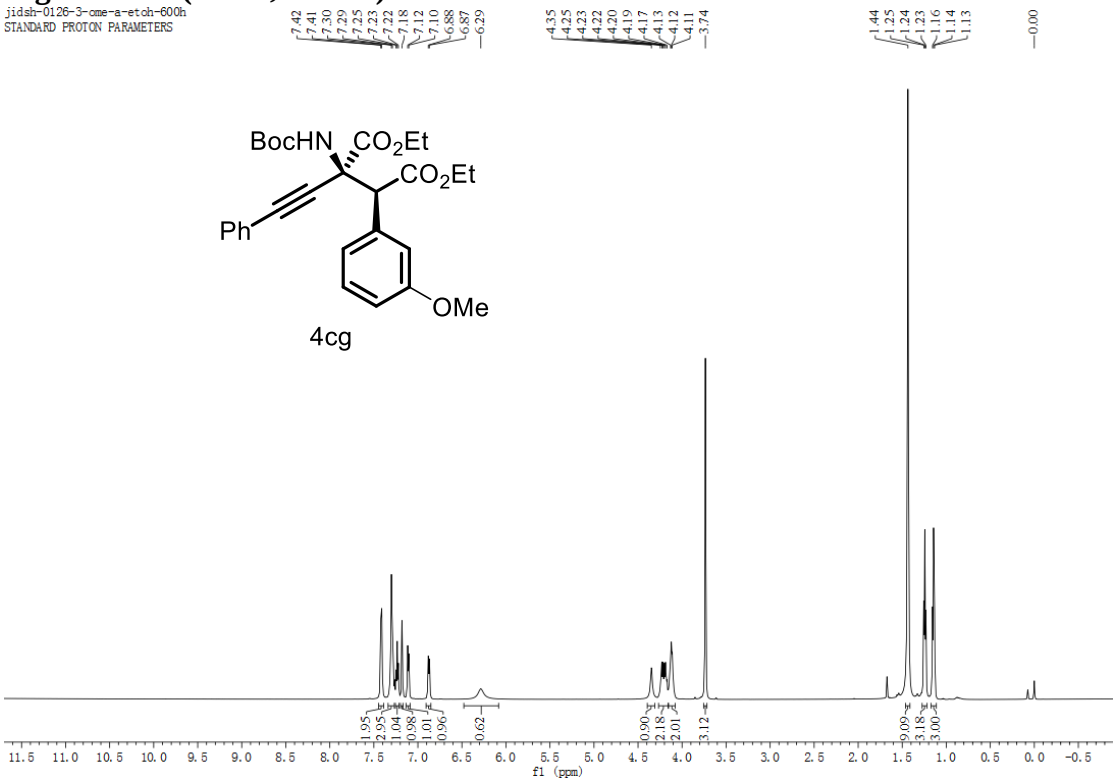

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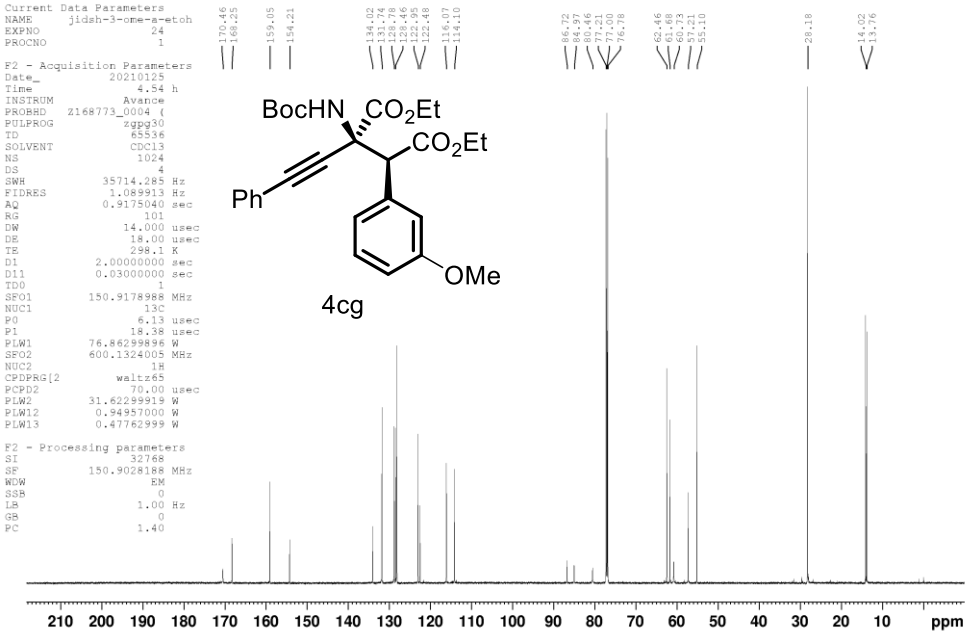
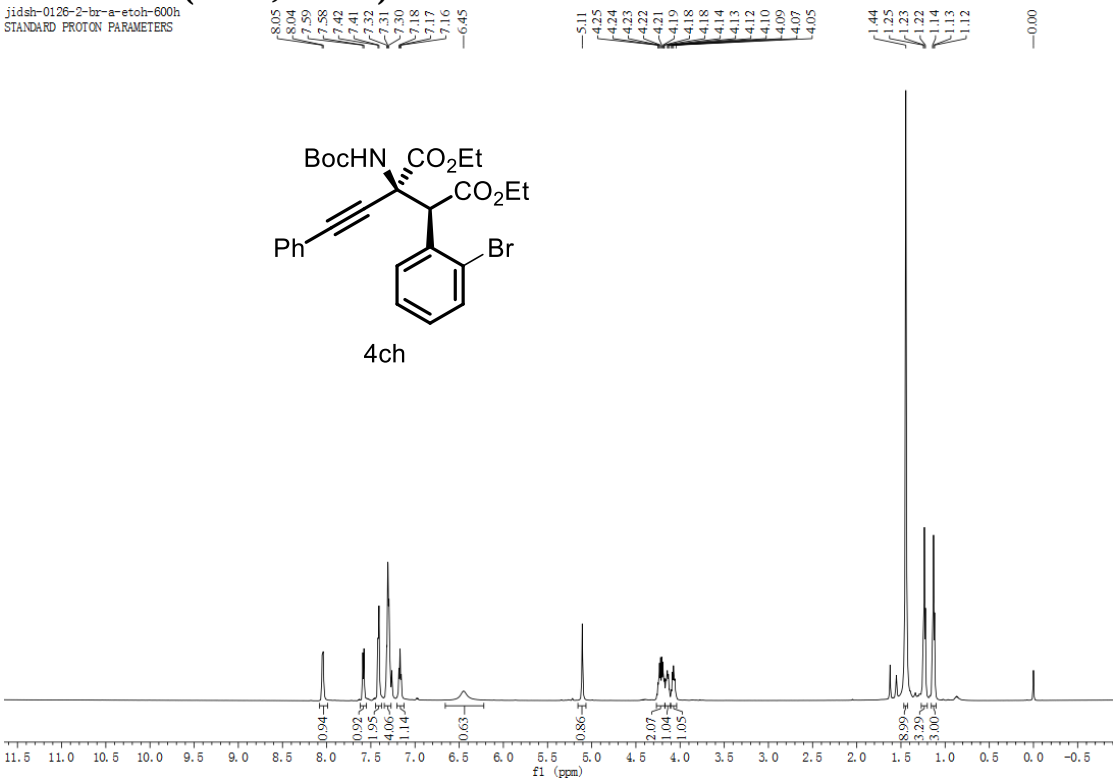


4ch-^{1}HNMR (600M, $CDCl_3$)



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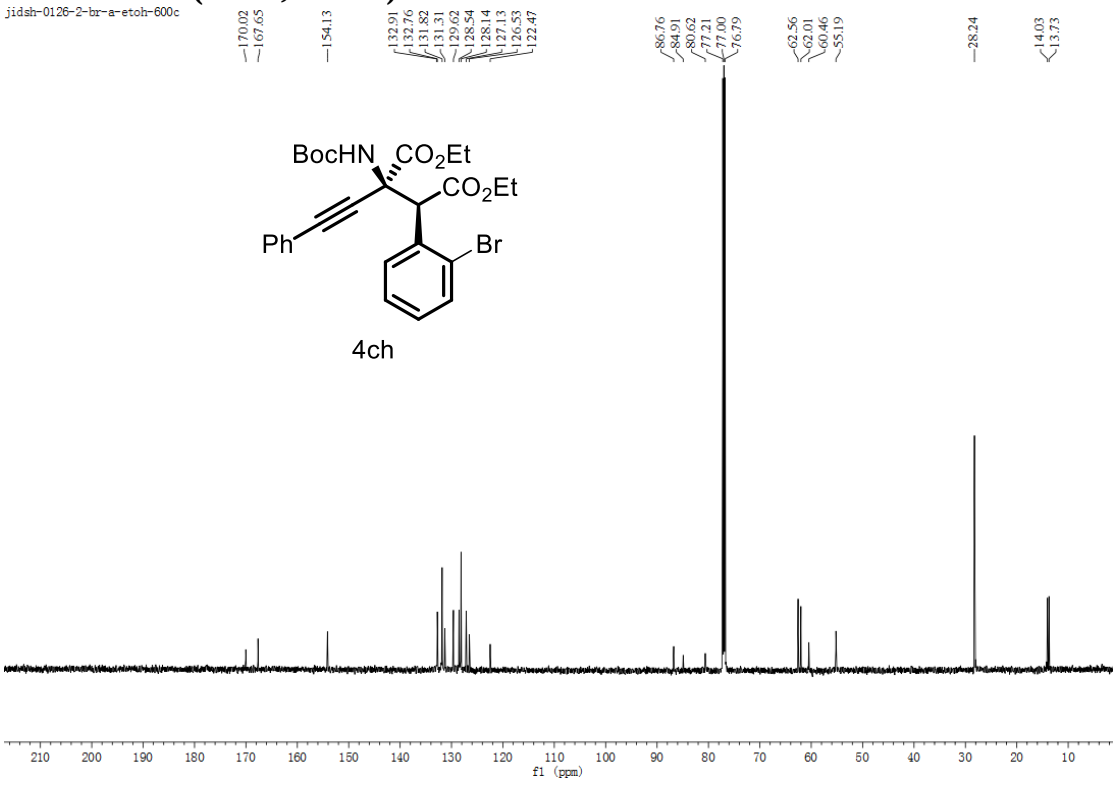
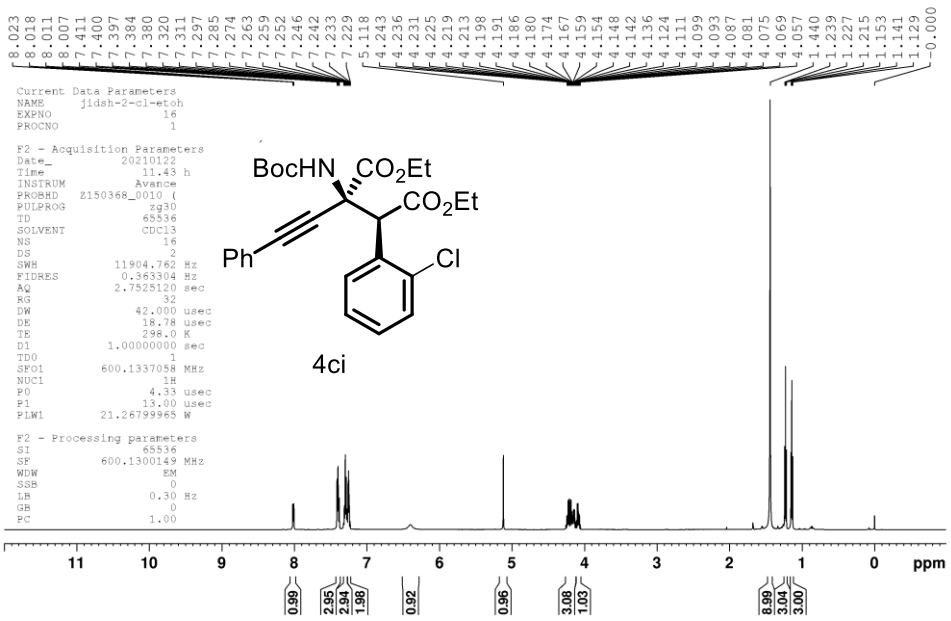


4ci-^{1}HNMR (600M, $CDCl_3$)



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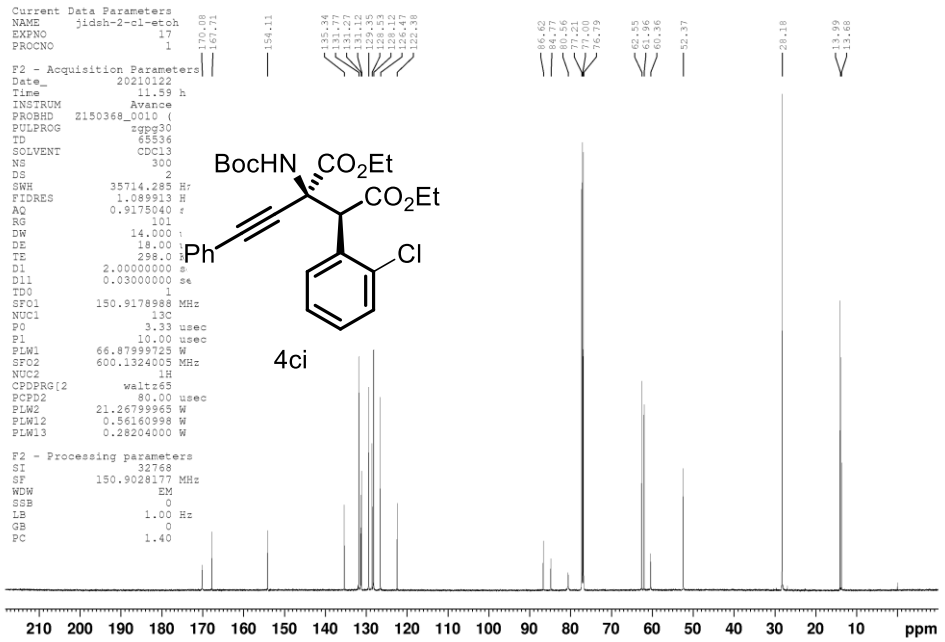

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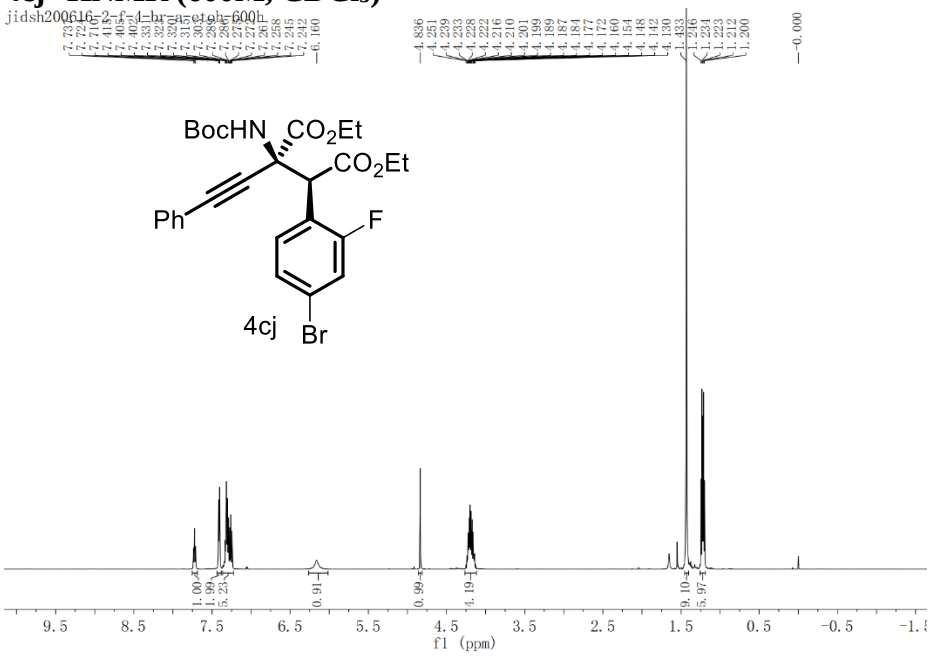
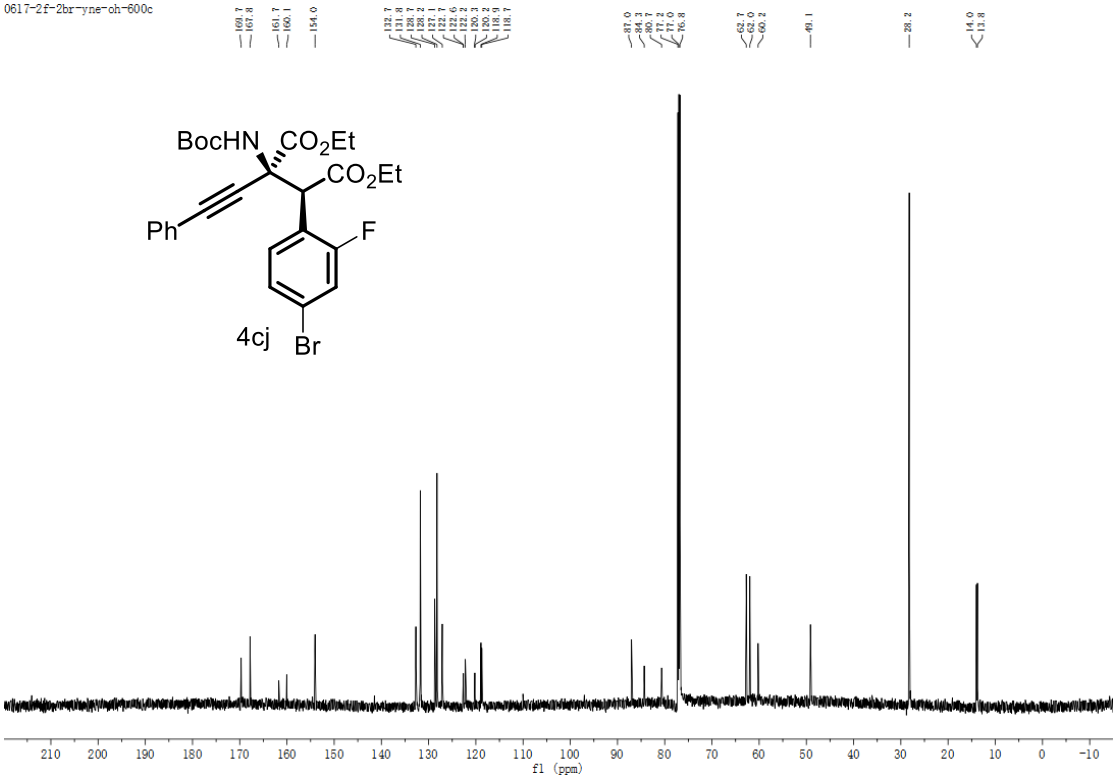


4cj-^{13}CNMR (151M, $CDCl_3$)



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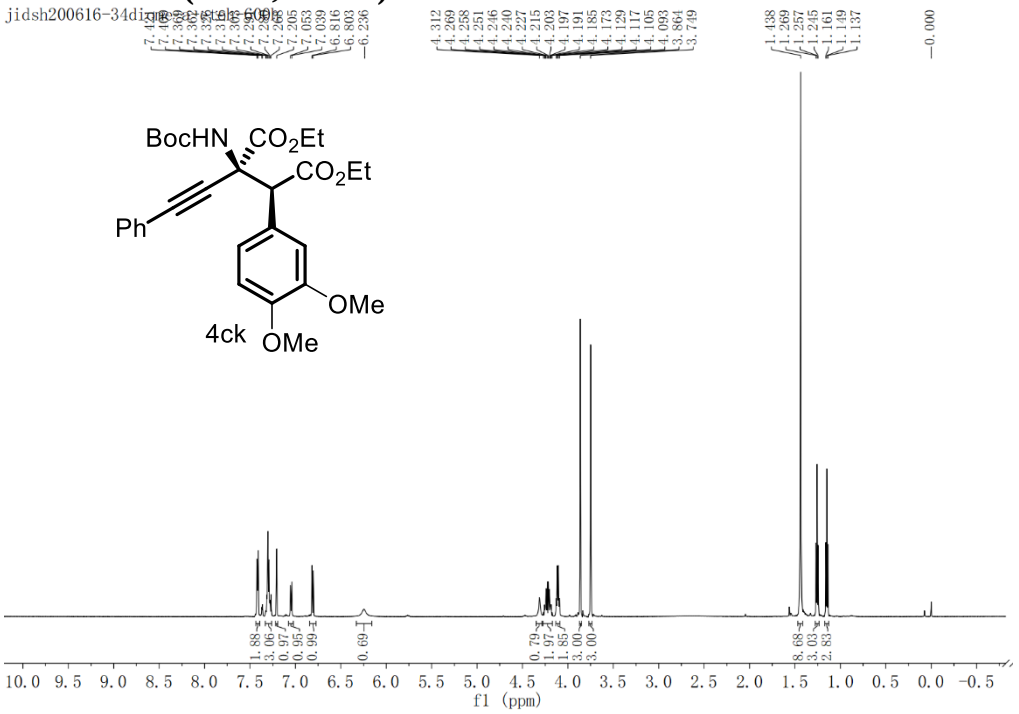

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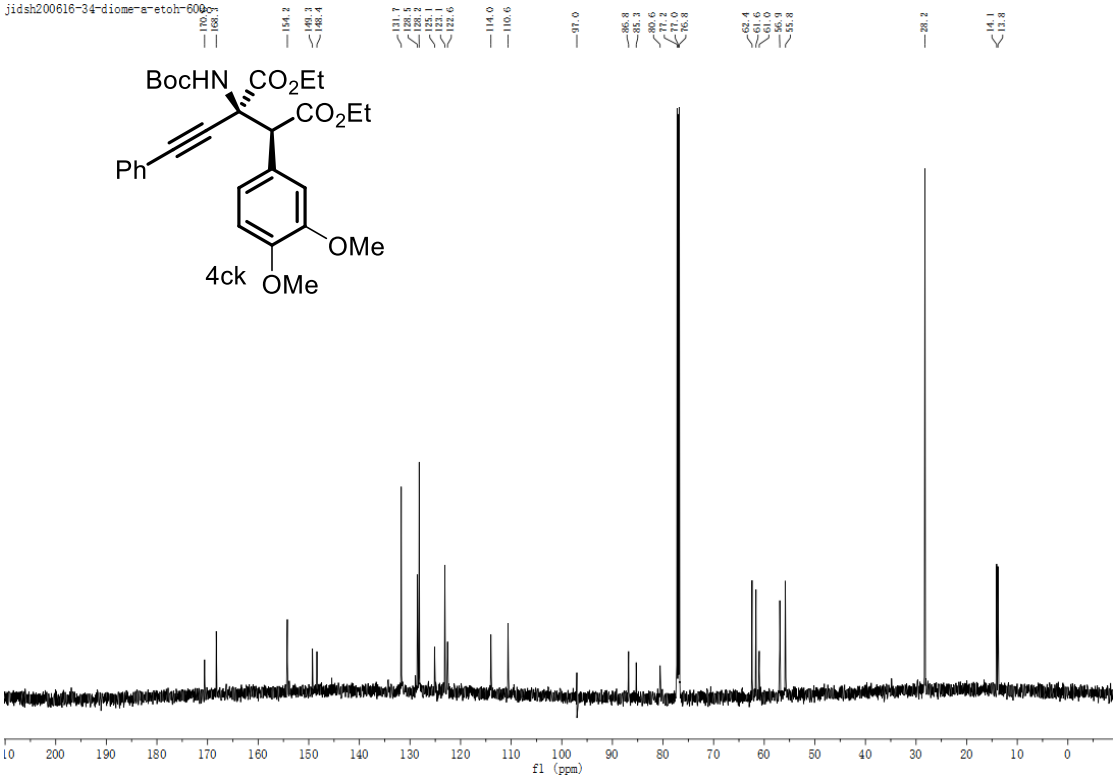

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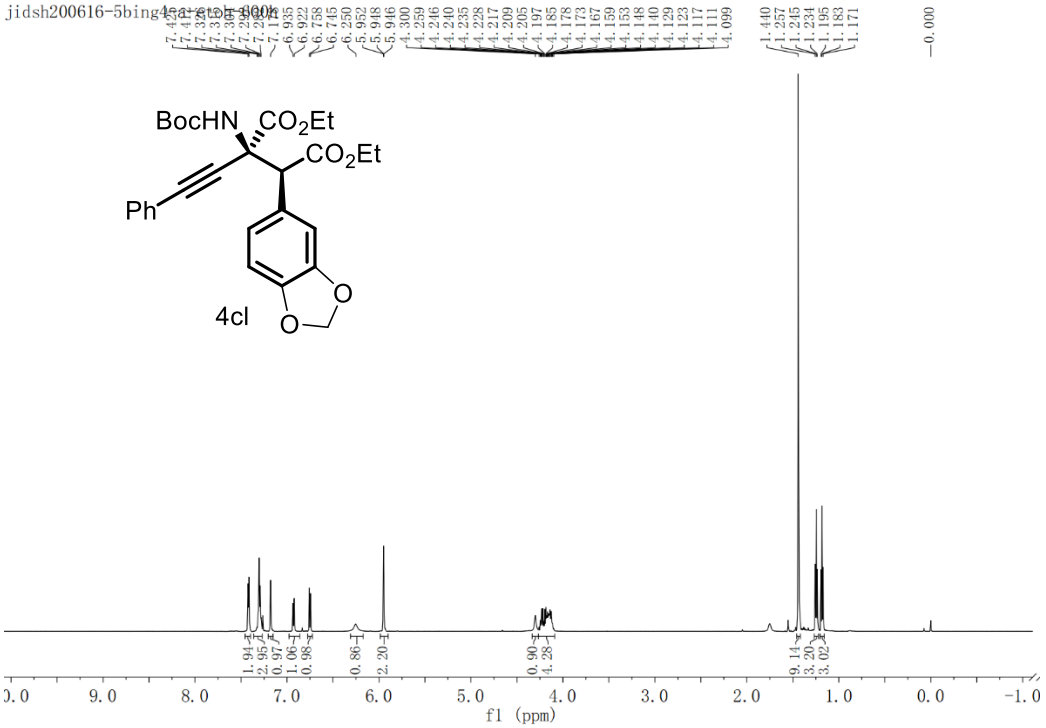

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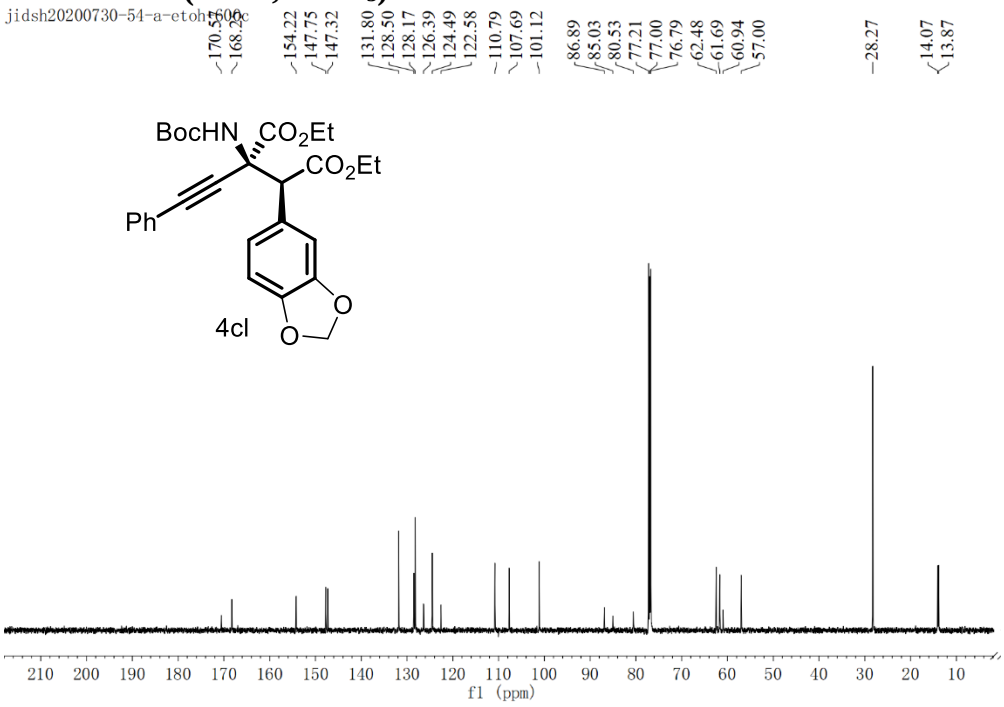
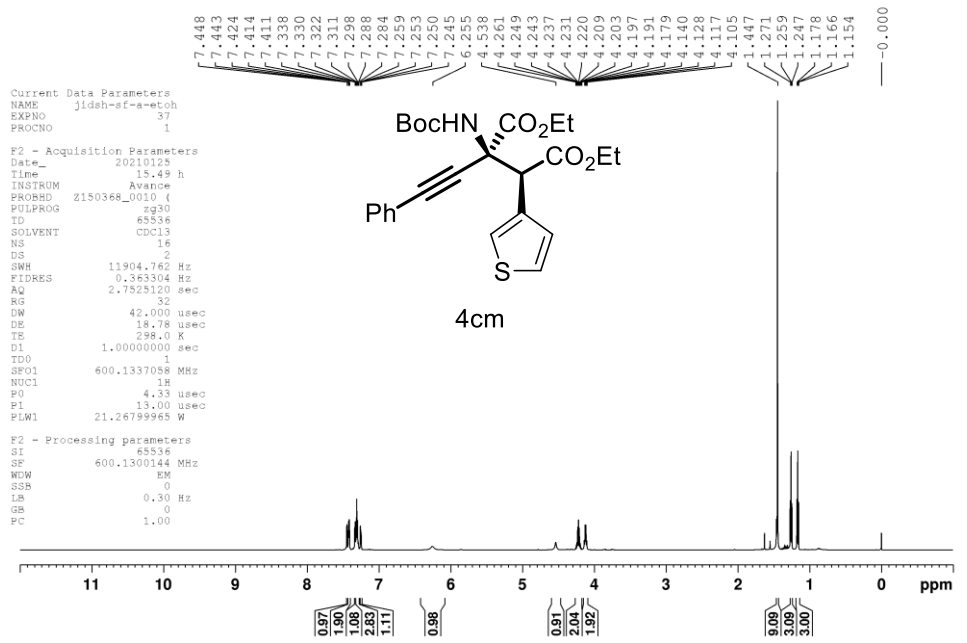
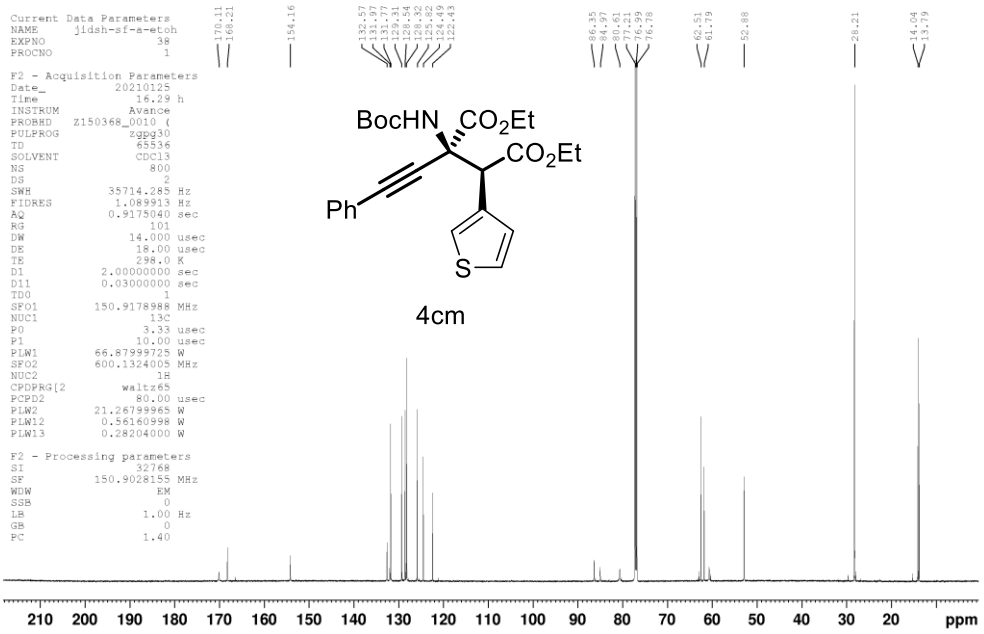


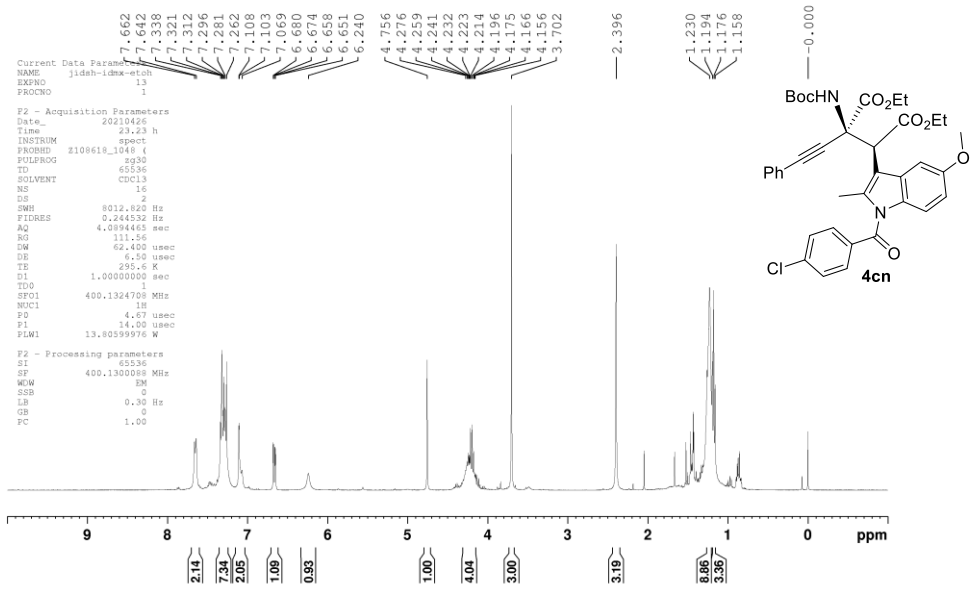
4cm-^{1}HNMR (600M, $CDCl_3$)



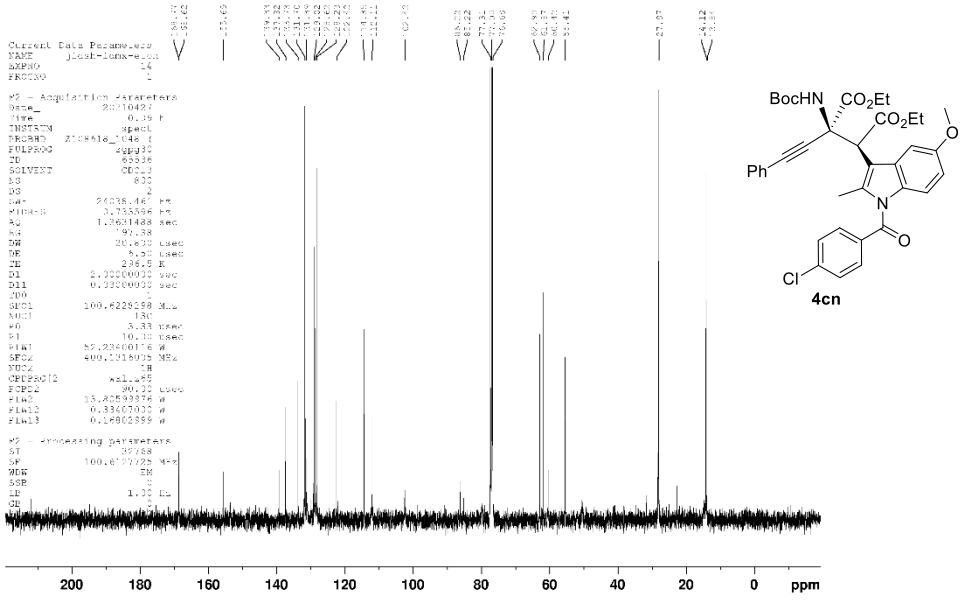
4cm-^{13}CNMR (150M, $CDCl_3$)



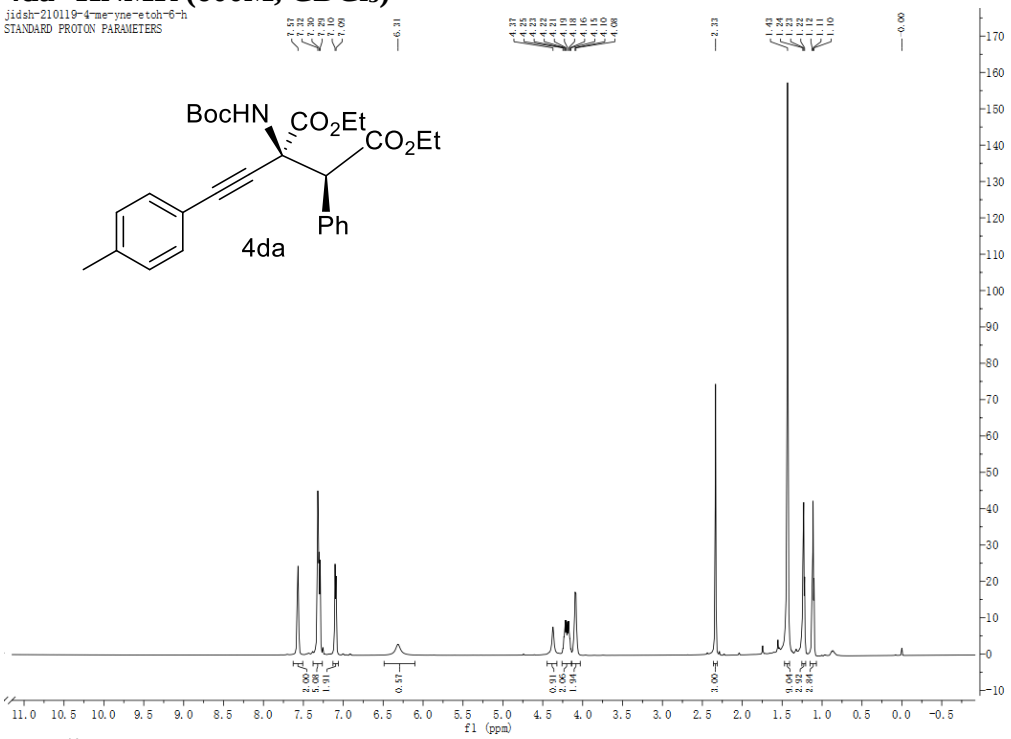
4cn-^{1}HNMR (600M, $CDCl_3$)



4cn-^{13}CNMR (150M, $CDCl_3$)



4da-^{1}HNMR (600M, $CDCl_3$)



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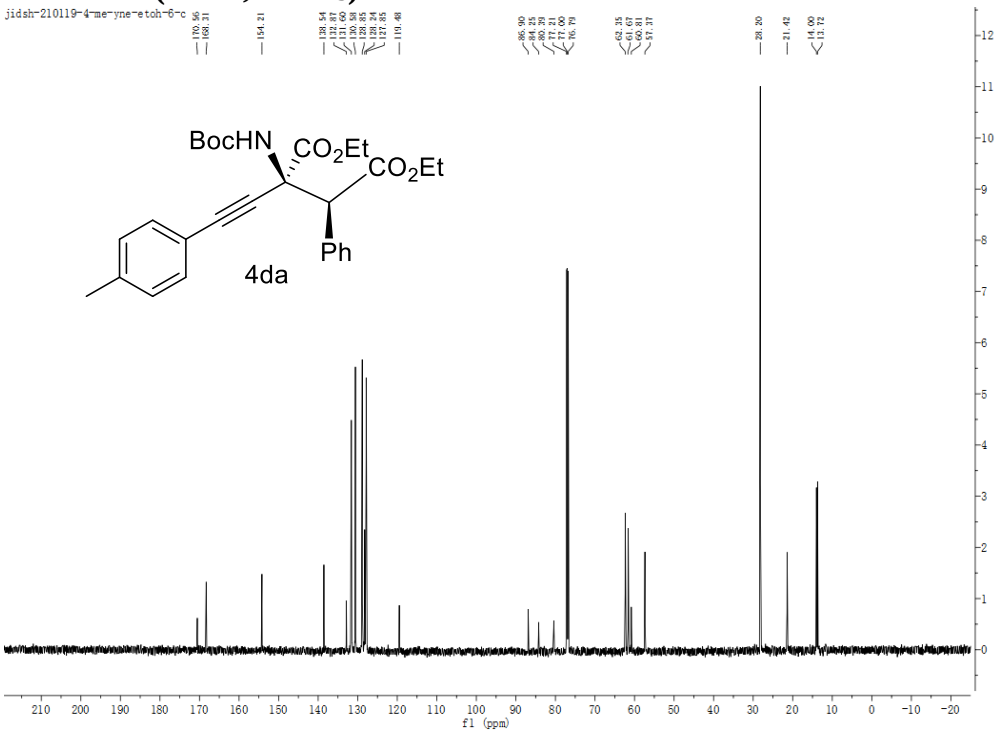

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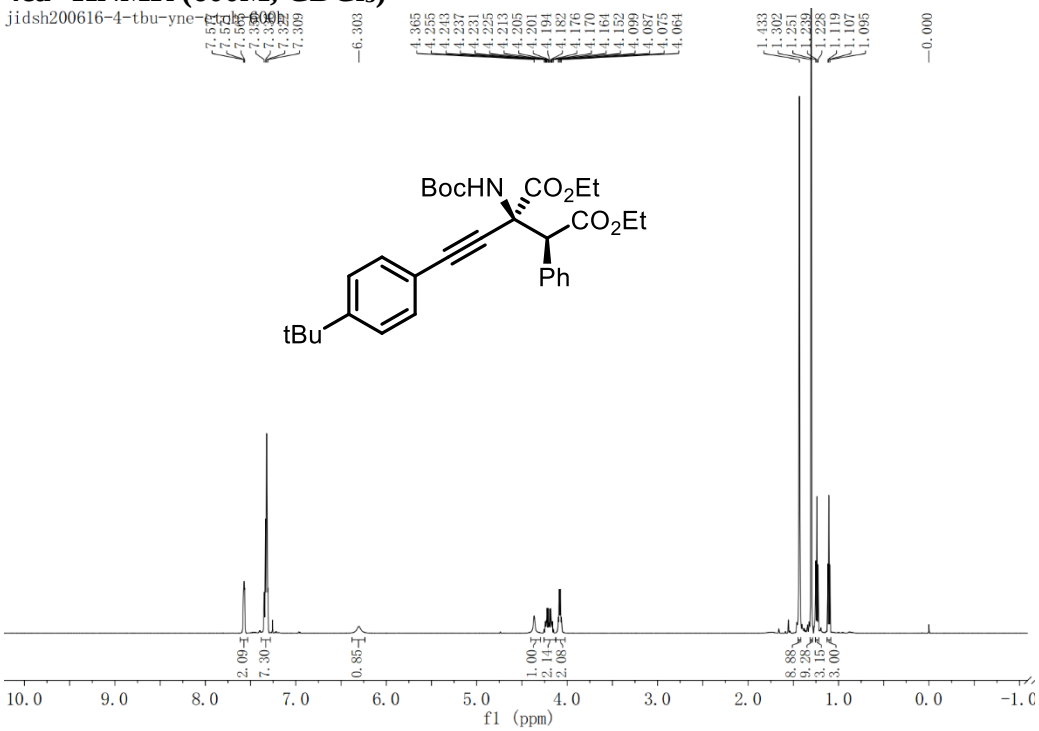
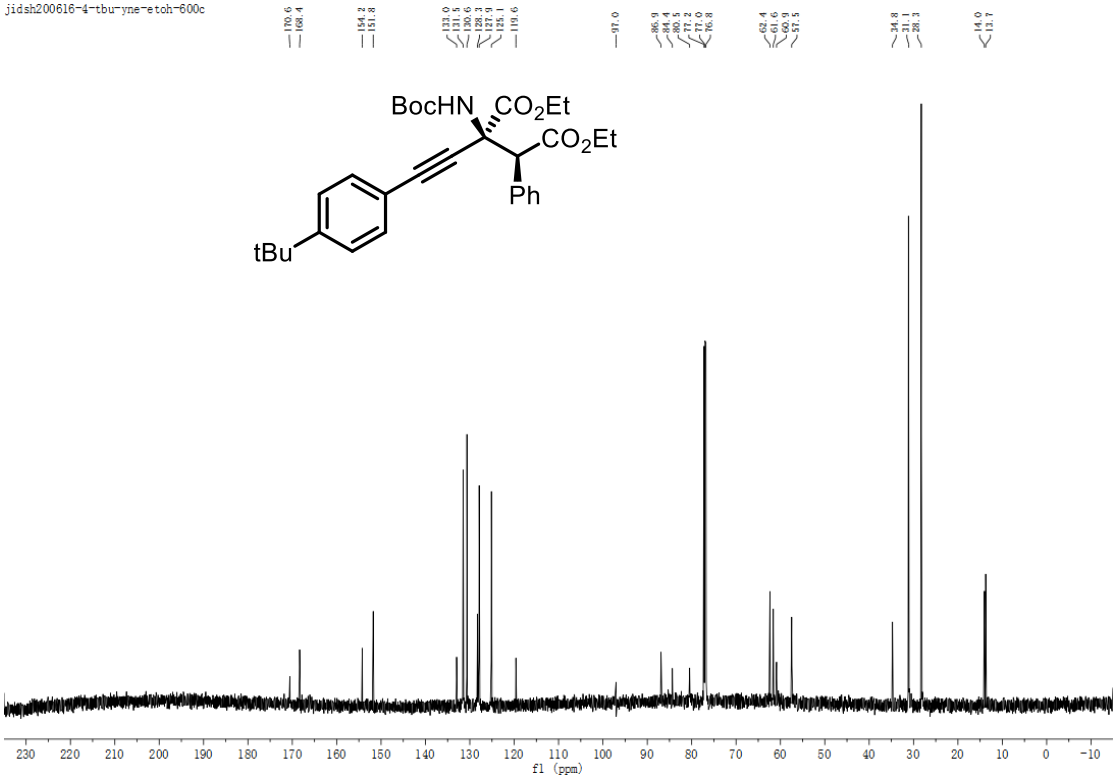


4ea-^{13}CNMR (151M, $CDCl_3$)



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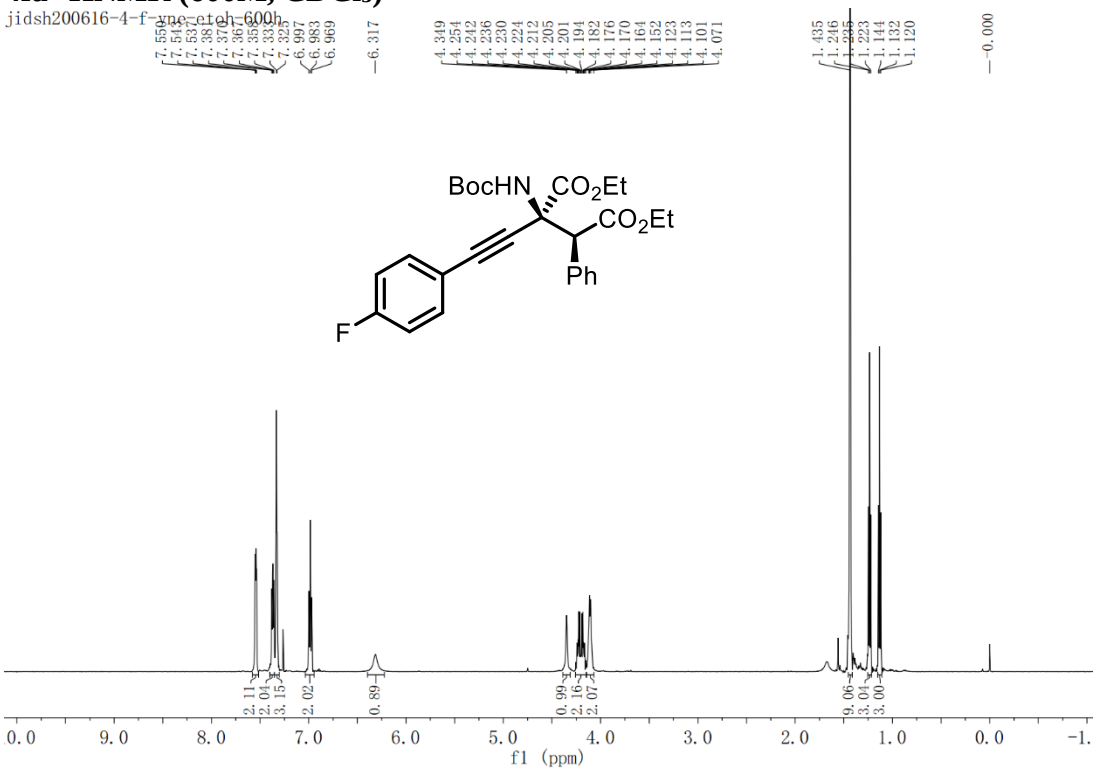

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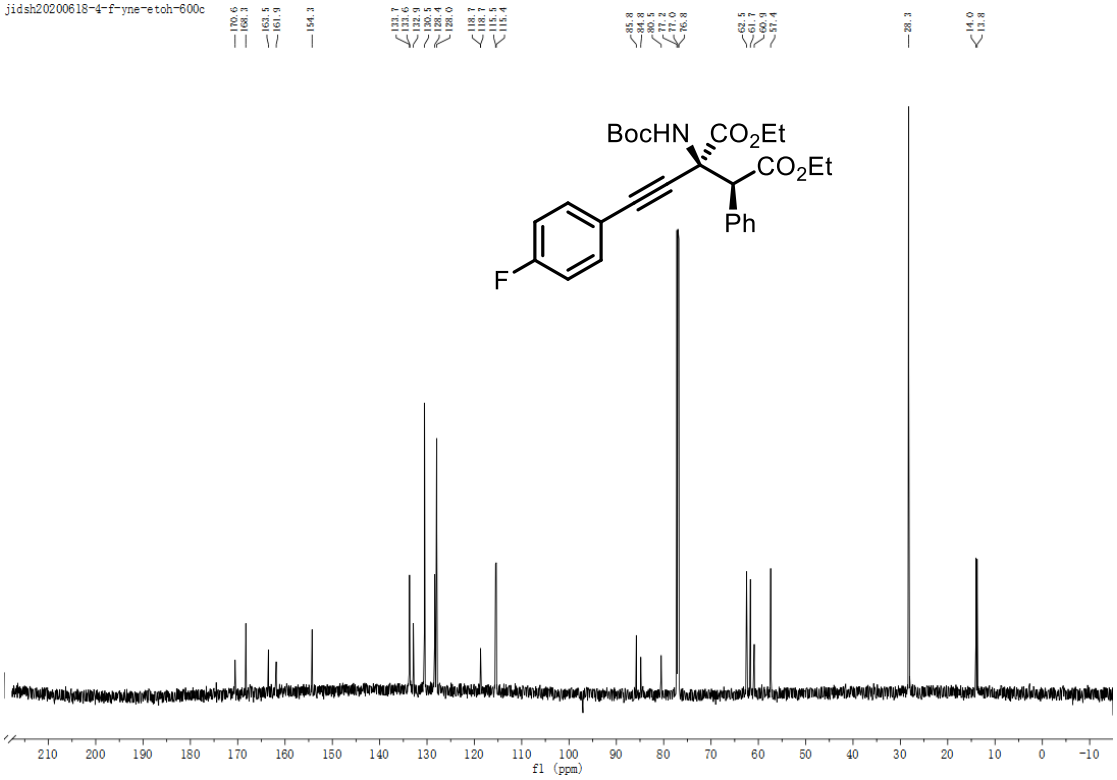
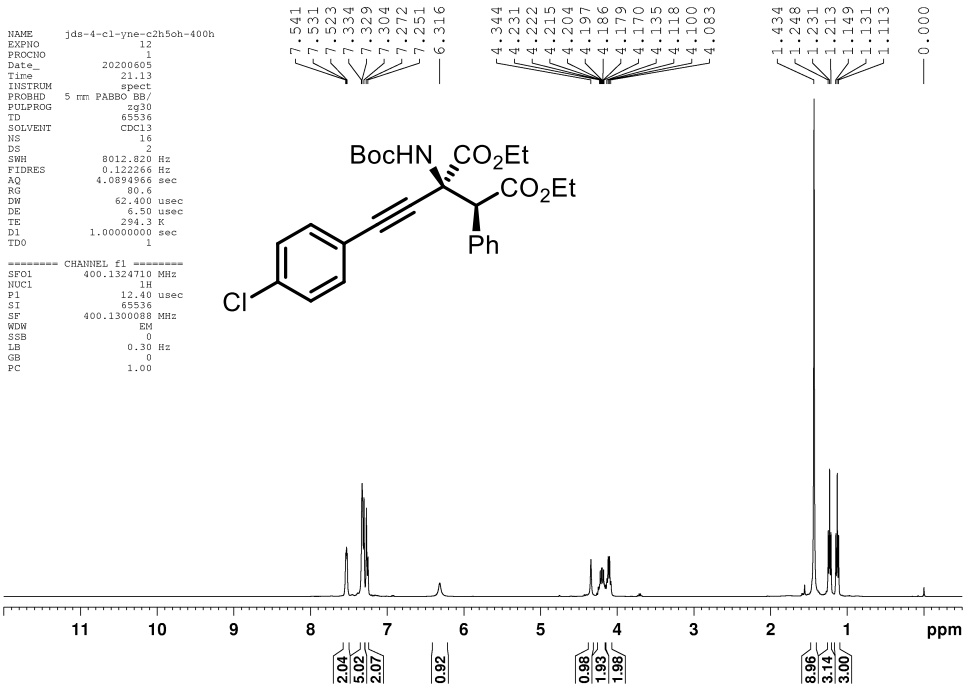
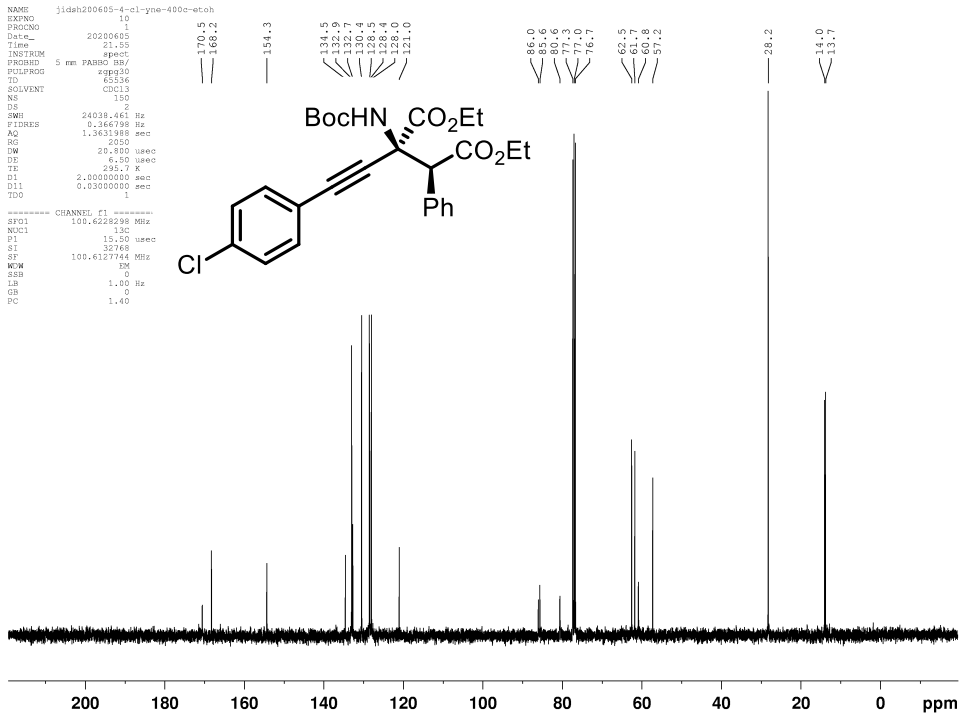


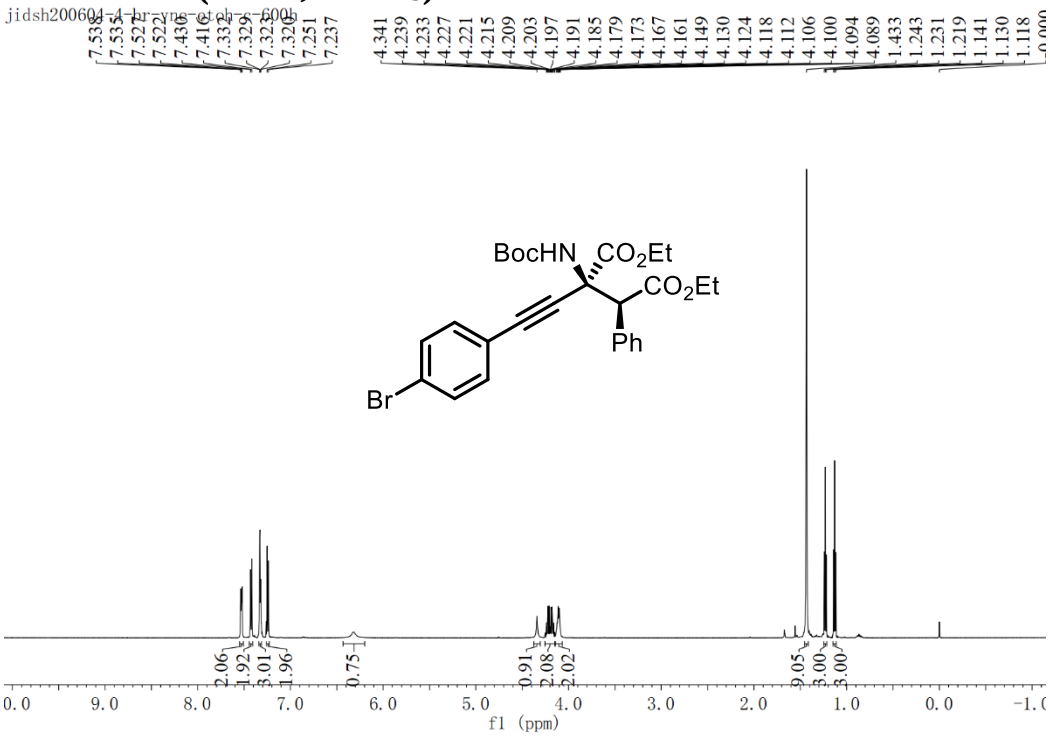
4ga-^{1}HNMR (400M, $CDCl_3$)



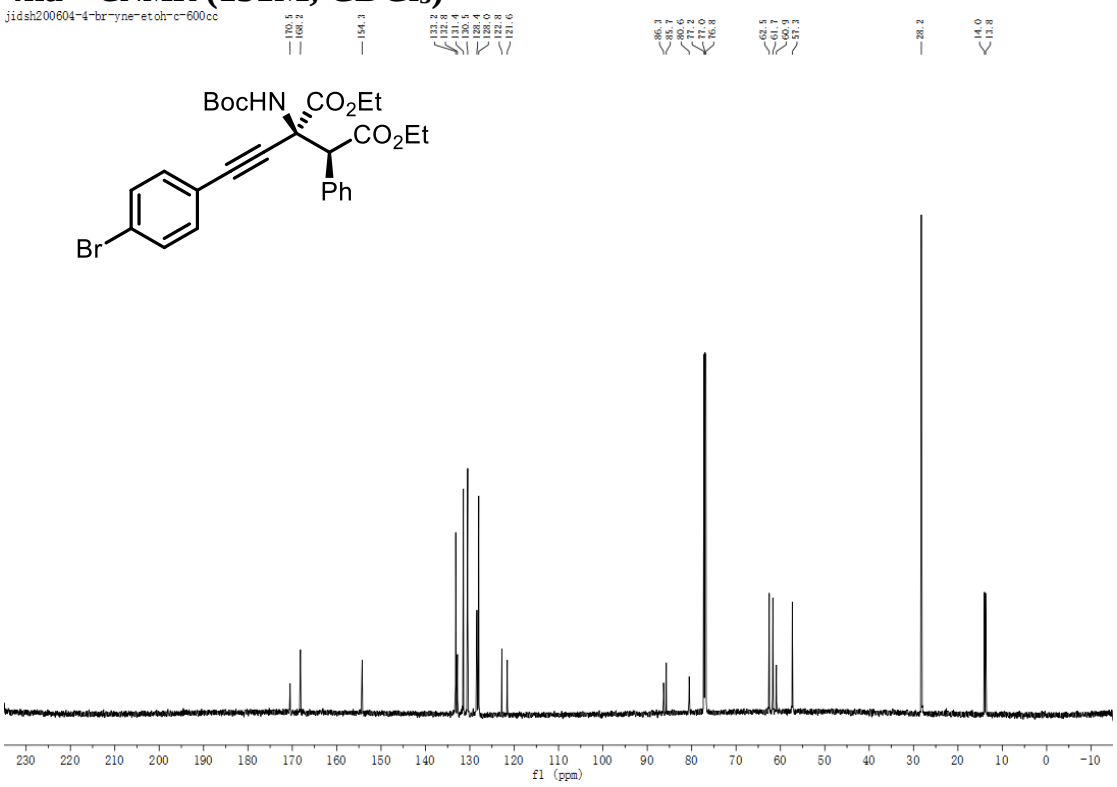
4ga-^{13}CNMR (100M, $CDCl_3$)



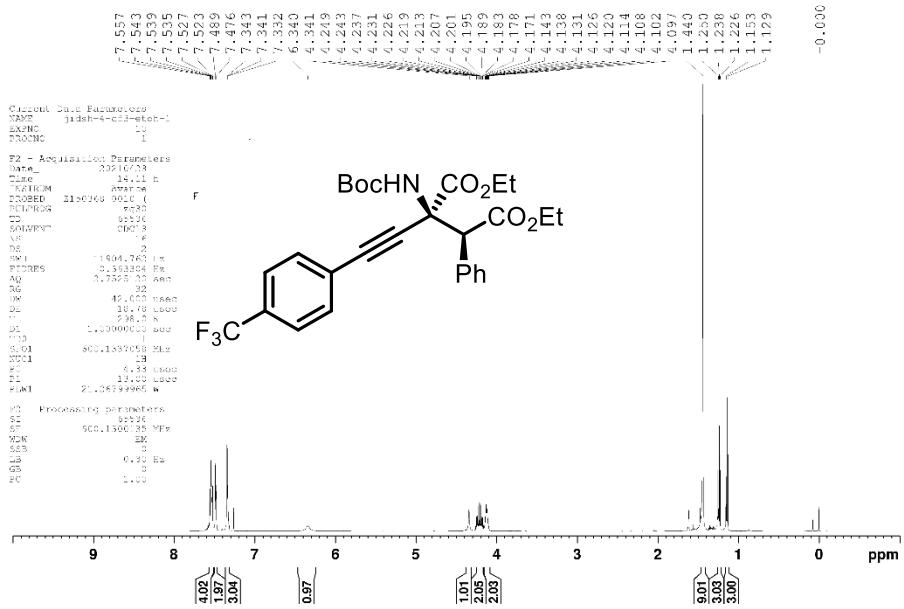
4ha-^{1}HNMR (600M, $CDCl_3$)



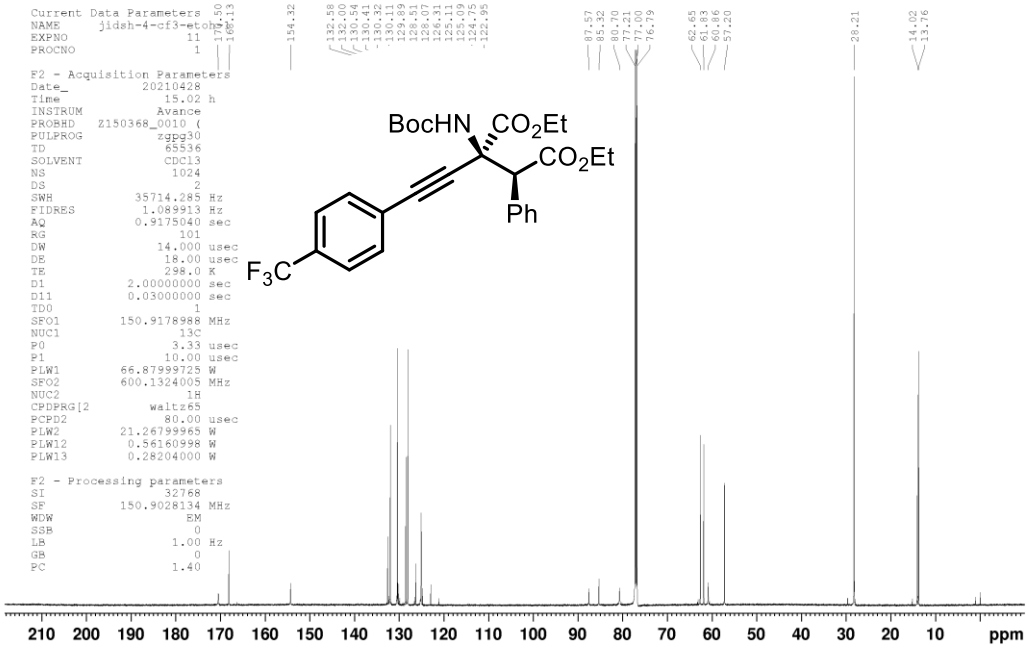
4ha-^{13}CNMR (151M, $CDCl_3$)



4ia—^{1}HNMR (600M, $CDCl_3$)



4ia—^{13}CNMR (151M, $CDCl_3$)



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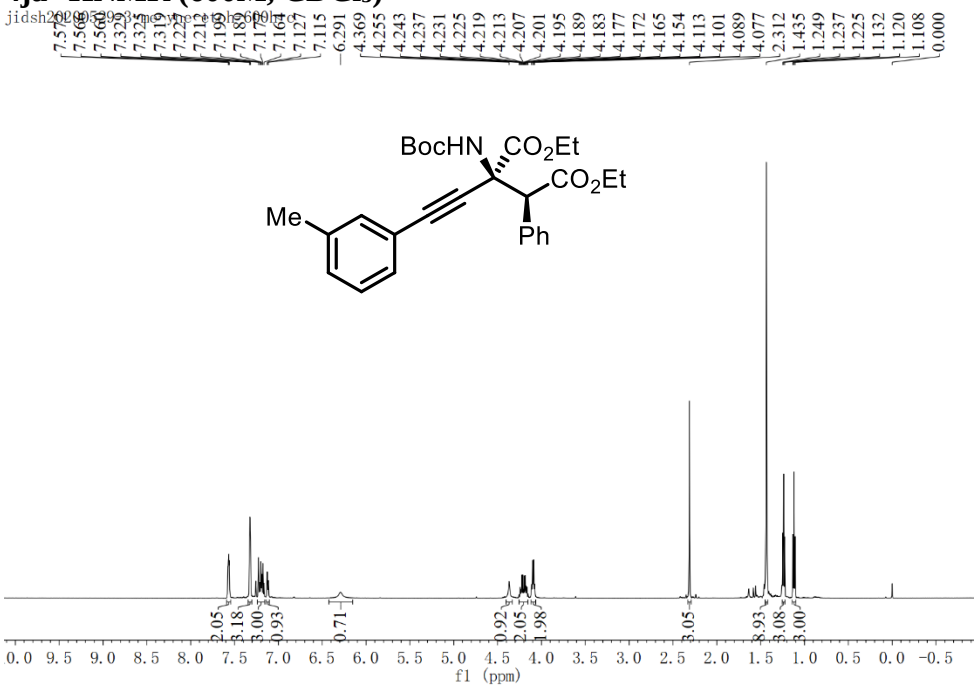

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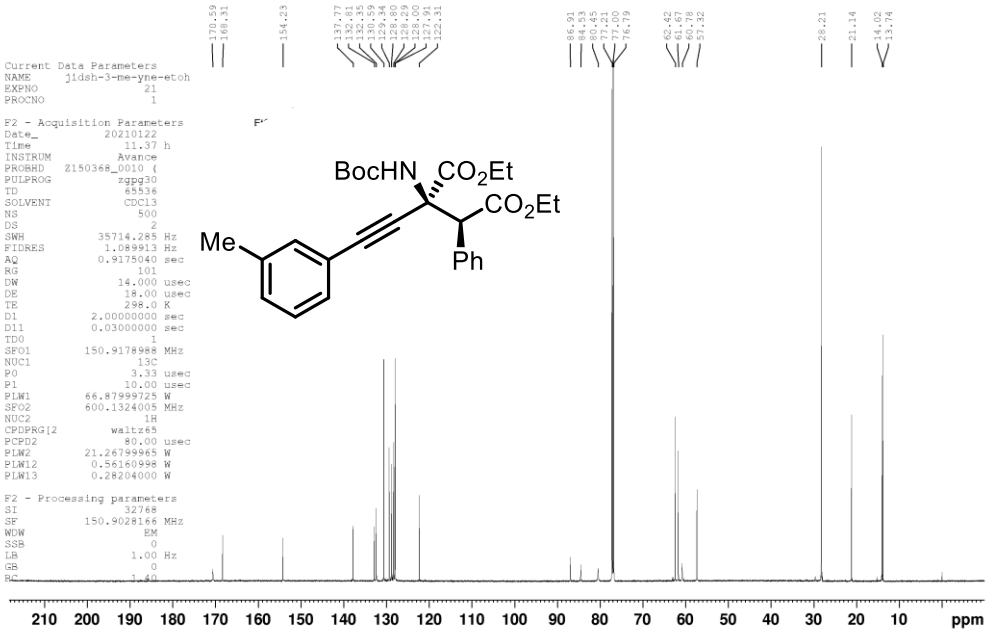

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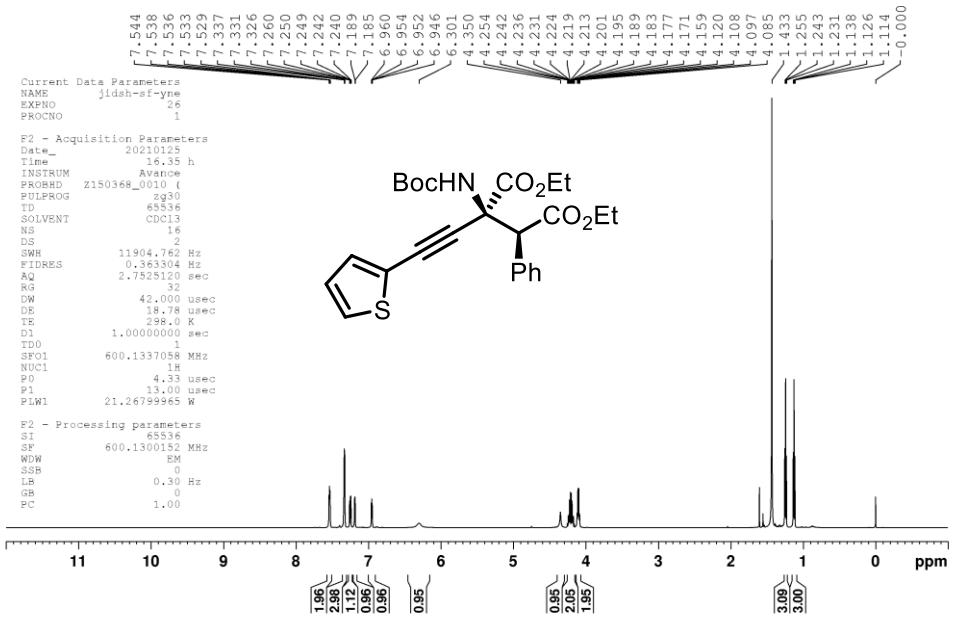
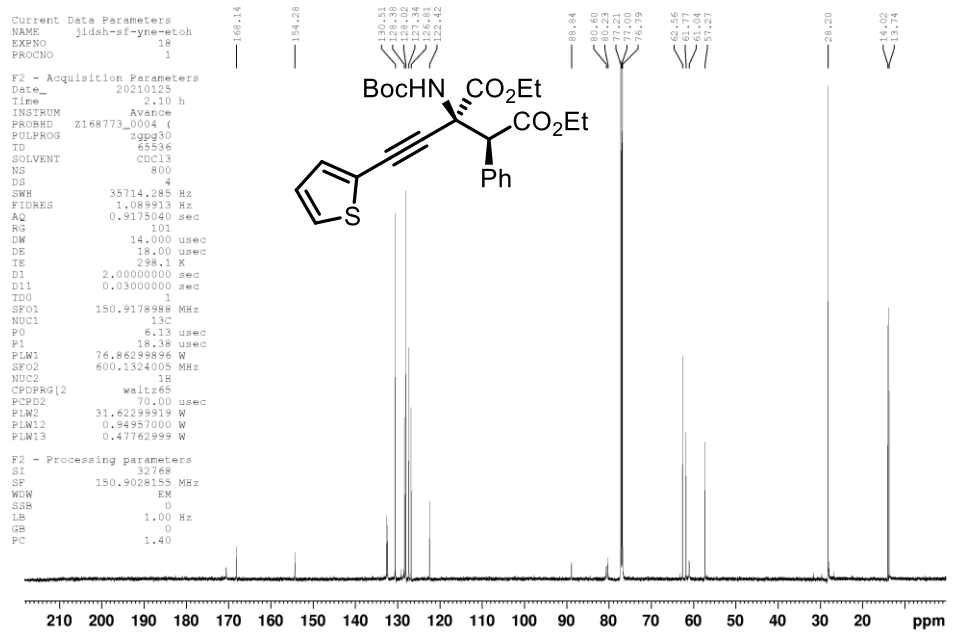
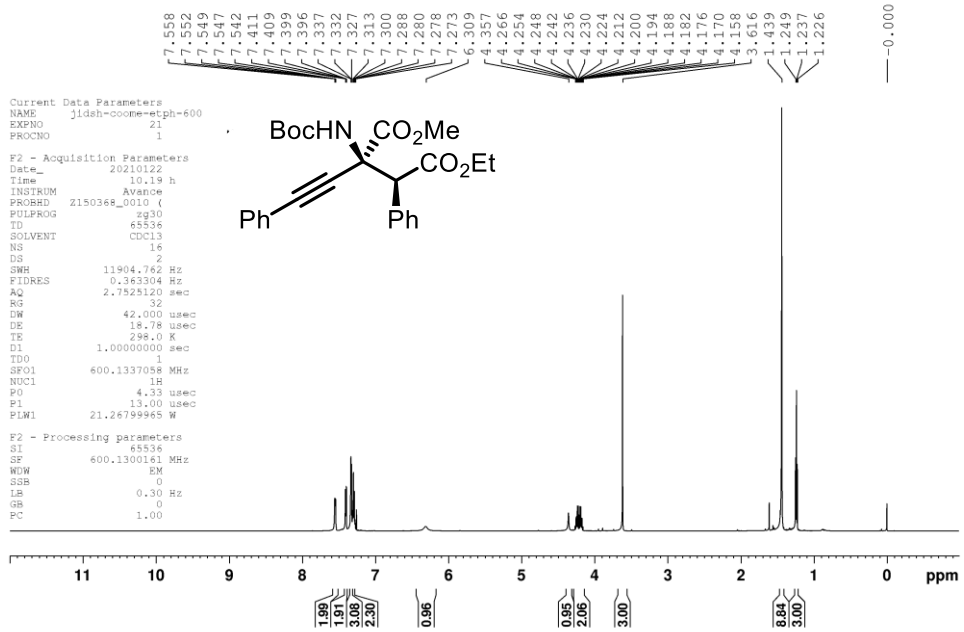


4ka-^{13}CNMR (151M, $CDCl_3$)



4la-^{1}HNMR(600M, $CDCl_3$)



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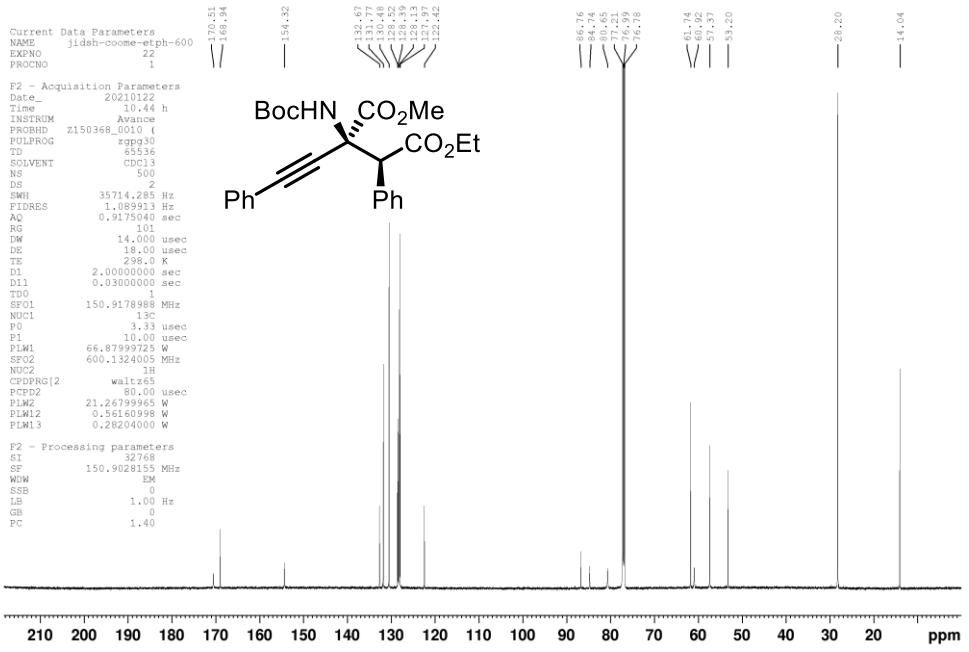

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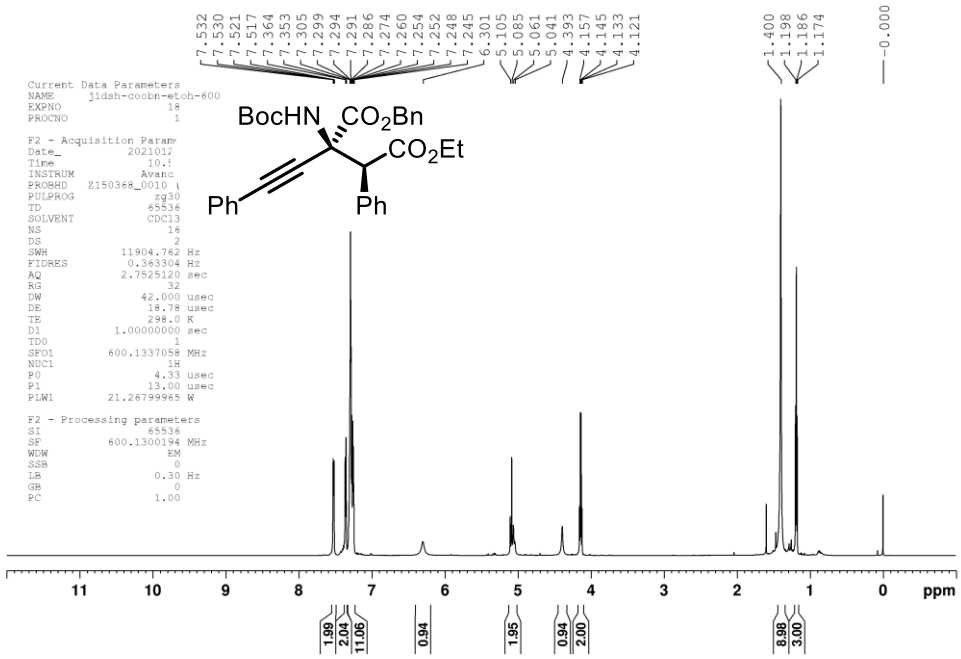
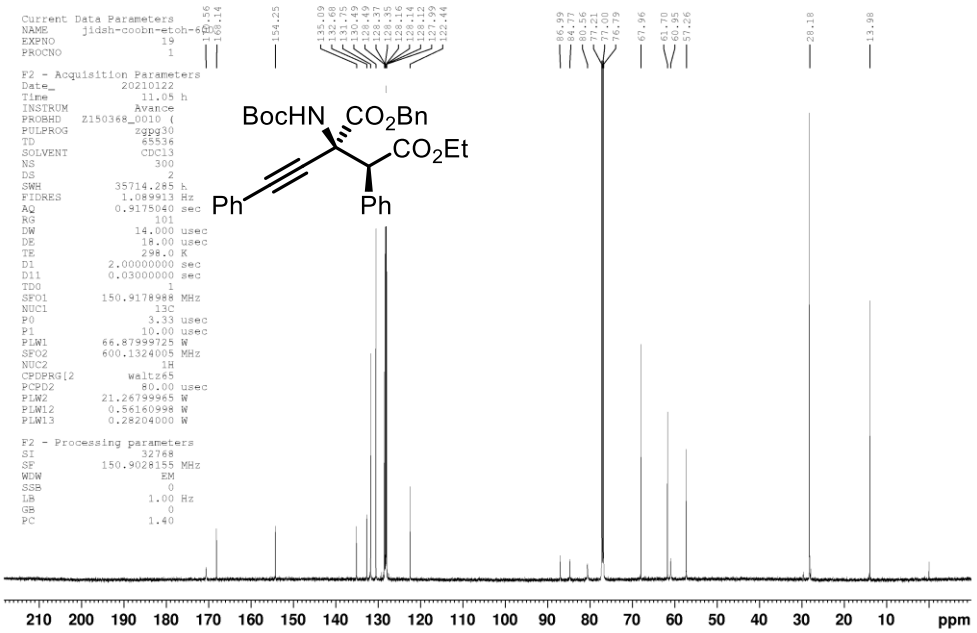
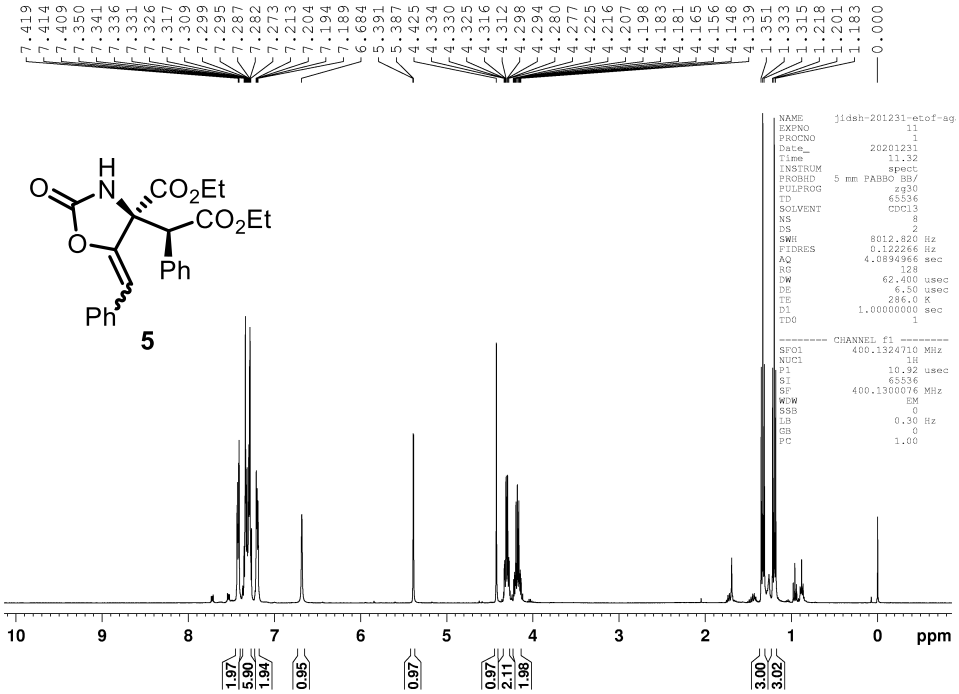


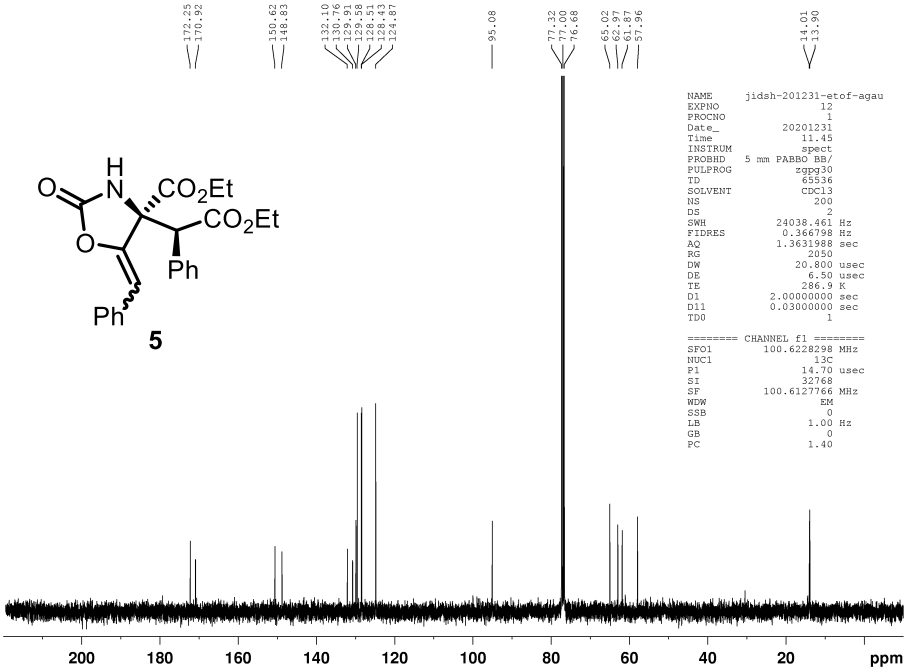
4ma-^{13}CNMR (151M, $CDCl_3$)



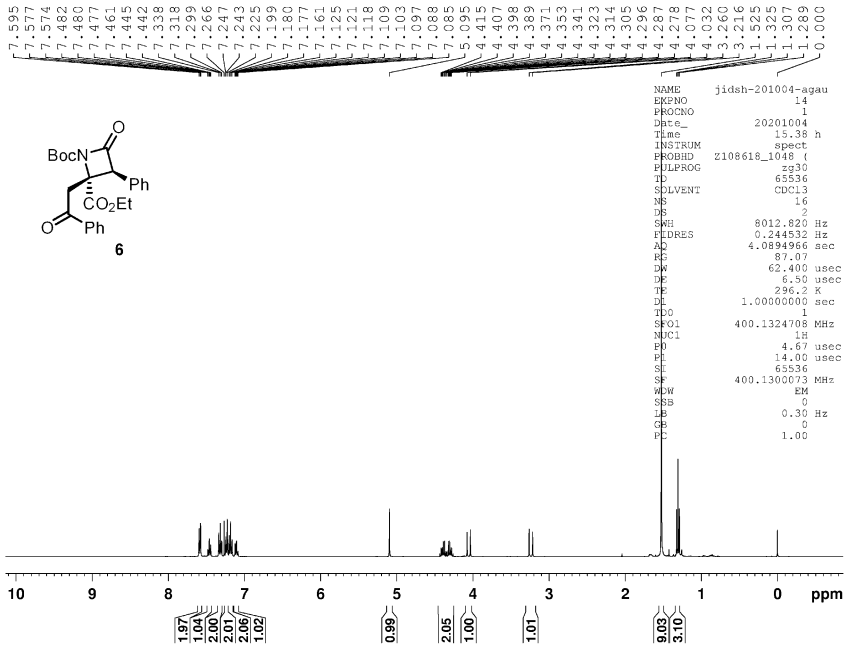
5-^{1}HNMR (400M, $CDCl_3$)



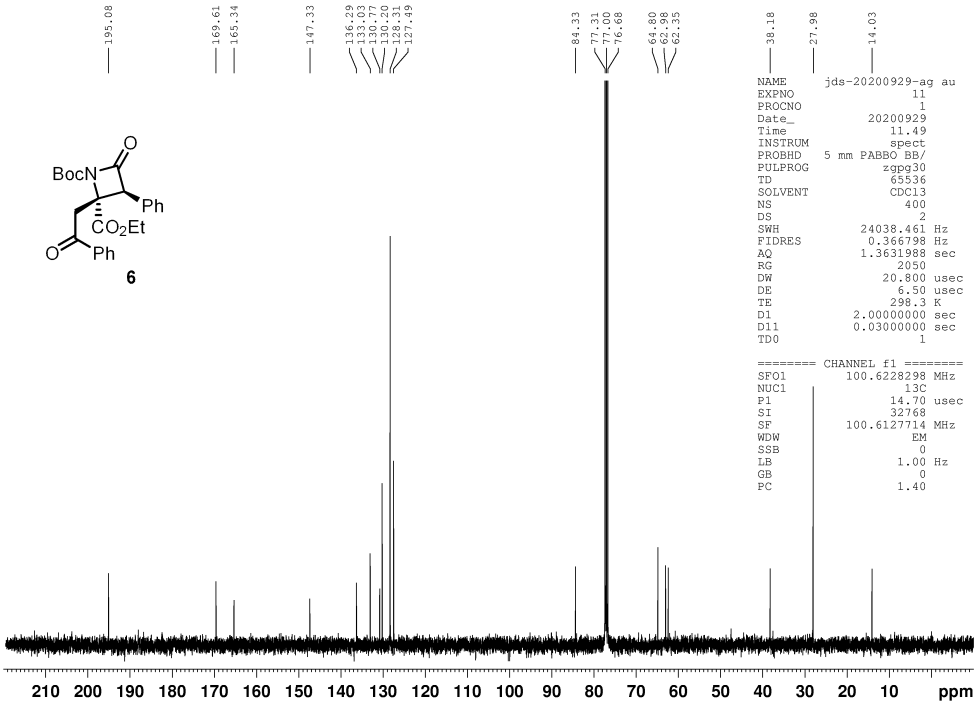
5-^{13}CNMR (100M, $CDCl_3$)



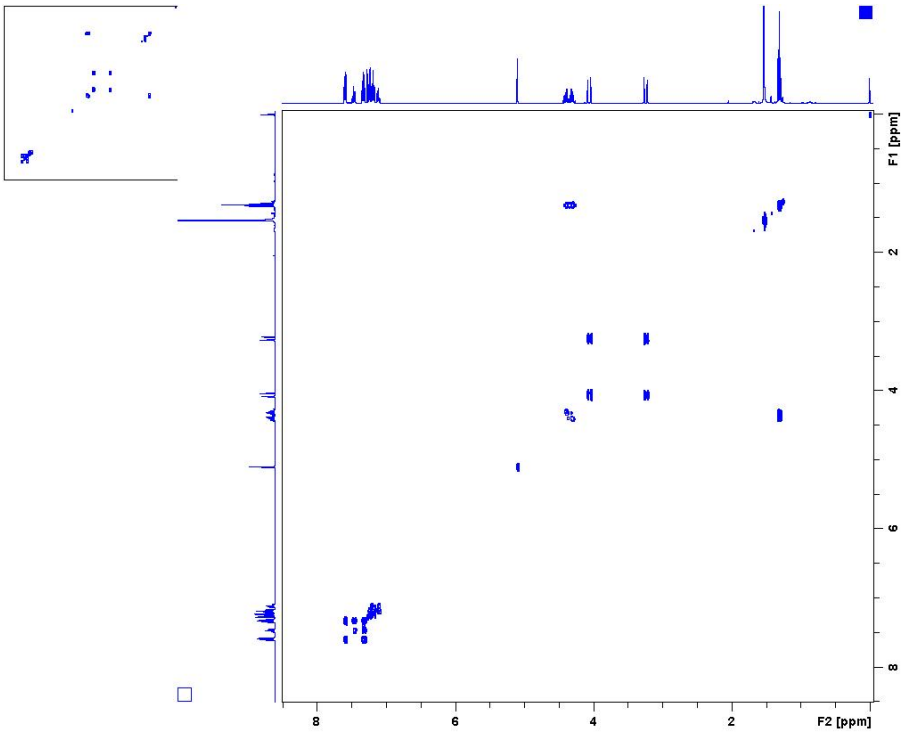
6-^{1}HNMR (400M, $CDCl_3$)



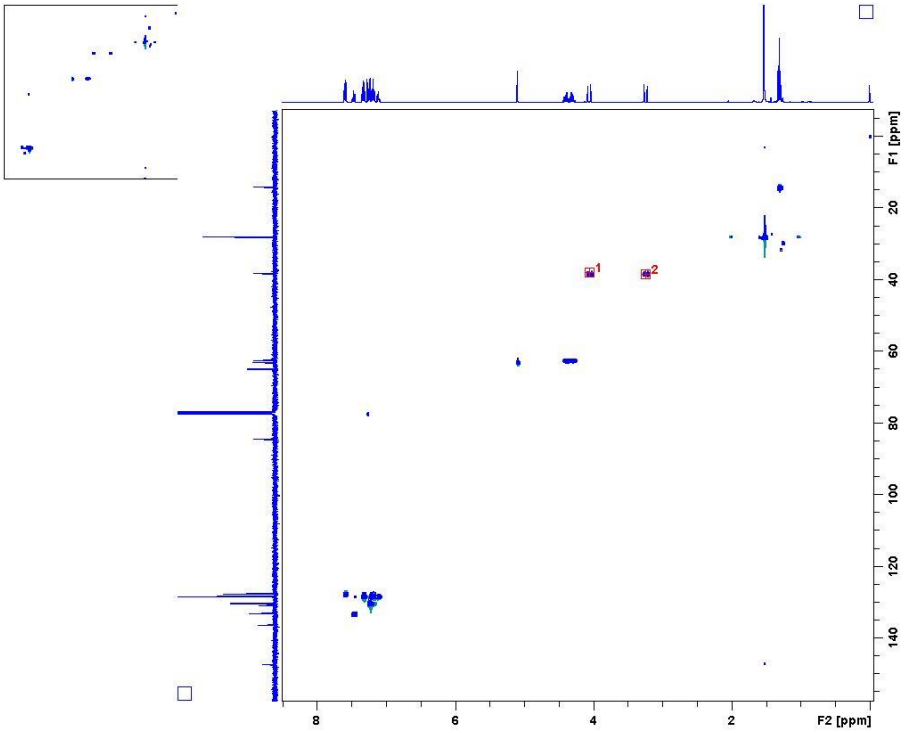
6-^{13}CNMR (100M, $CDCl_3$)



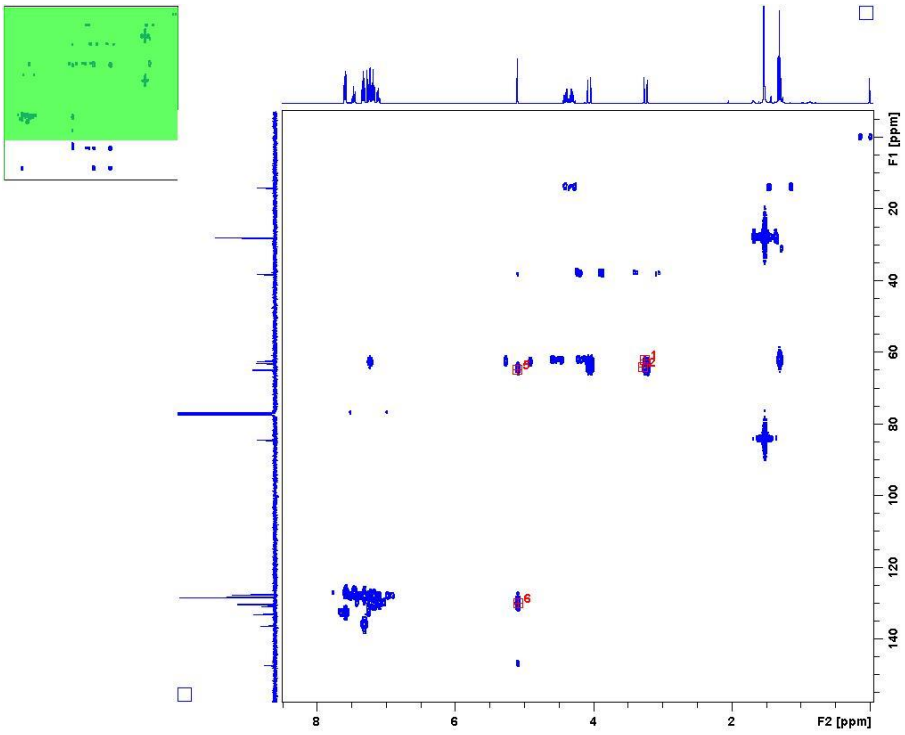
H-H COSY OF 6



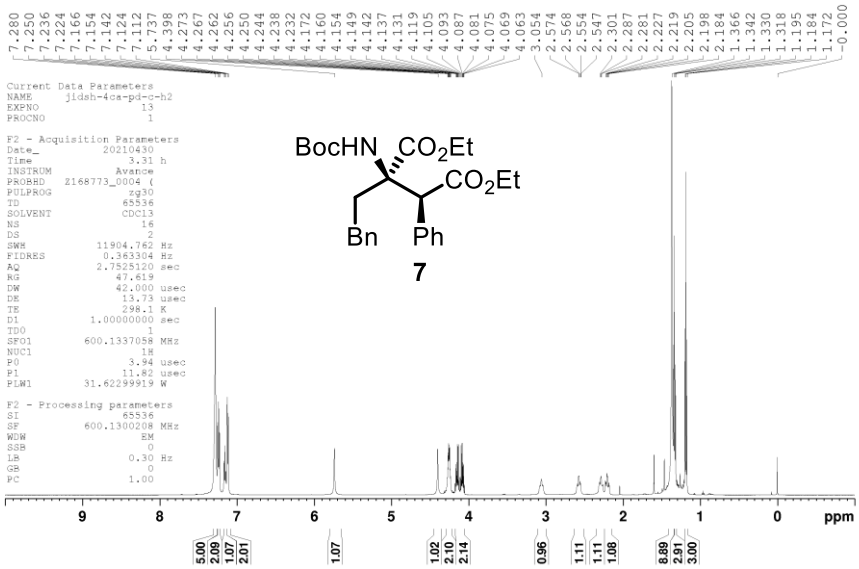
C-H COSY OF 6



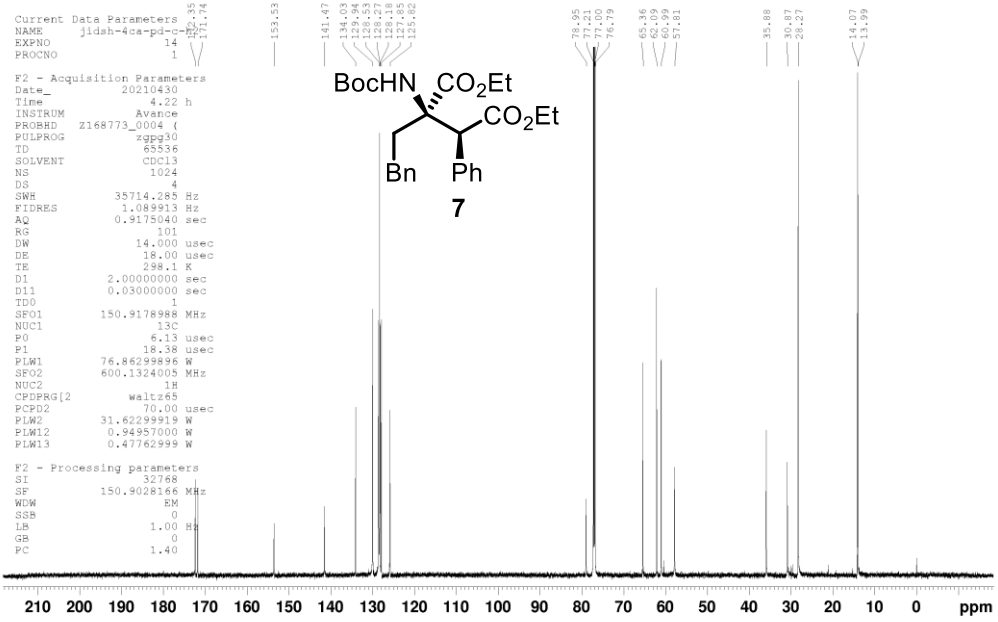
HMBC of 6



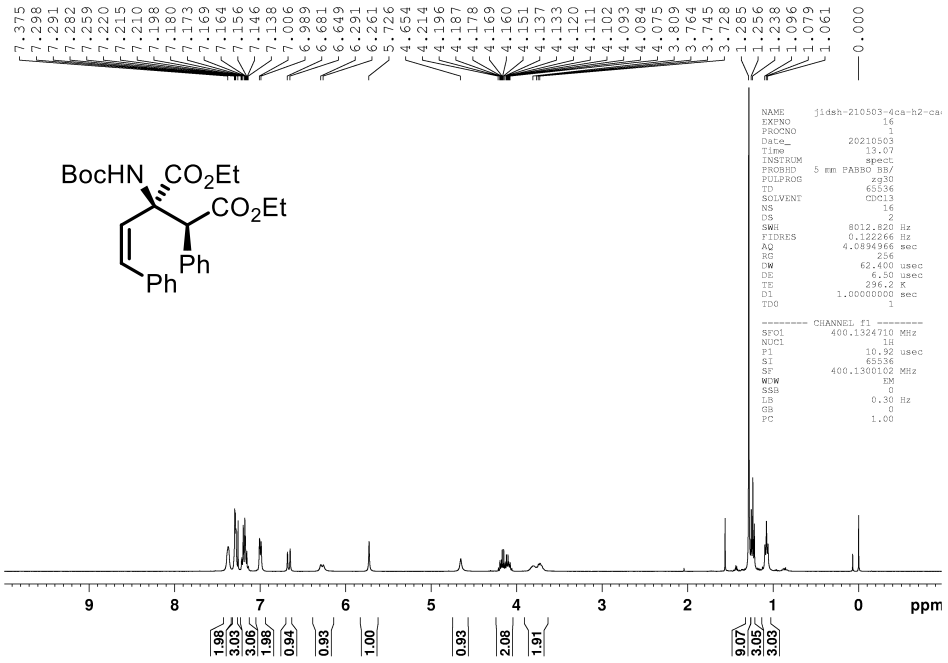
7-^{1}HNMR (600M, $CDCl_3$)



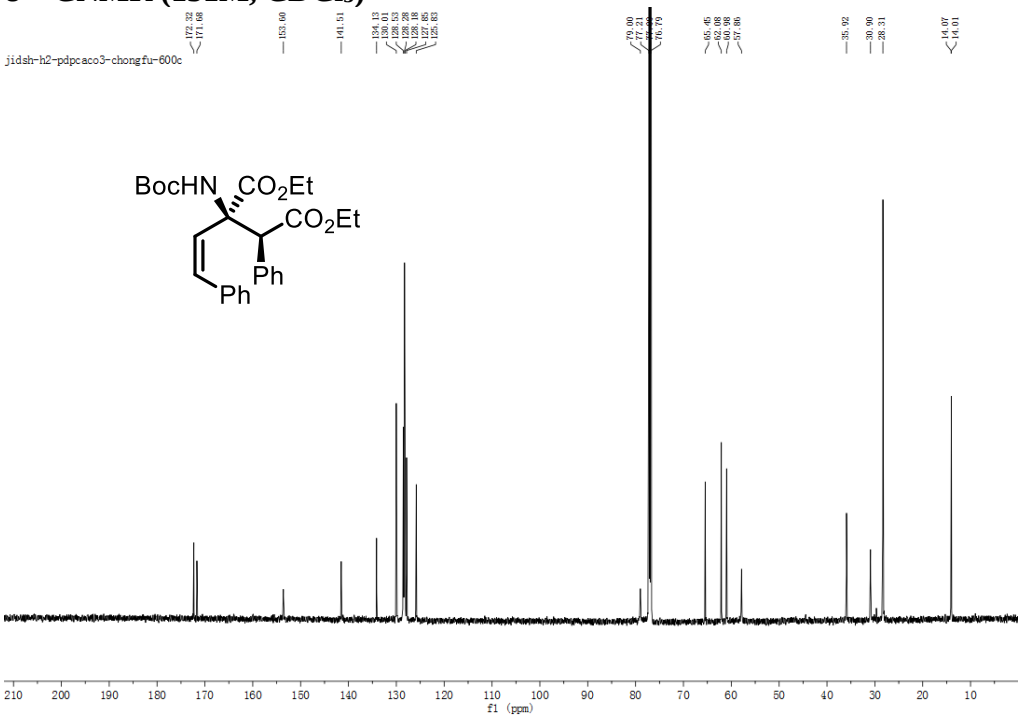
7-^{13}CNMR (151M, $CDCl_3$)

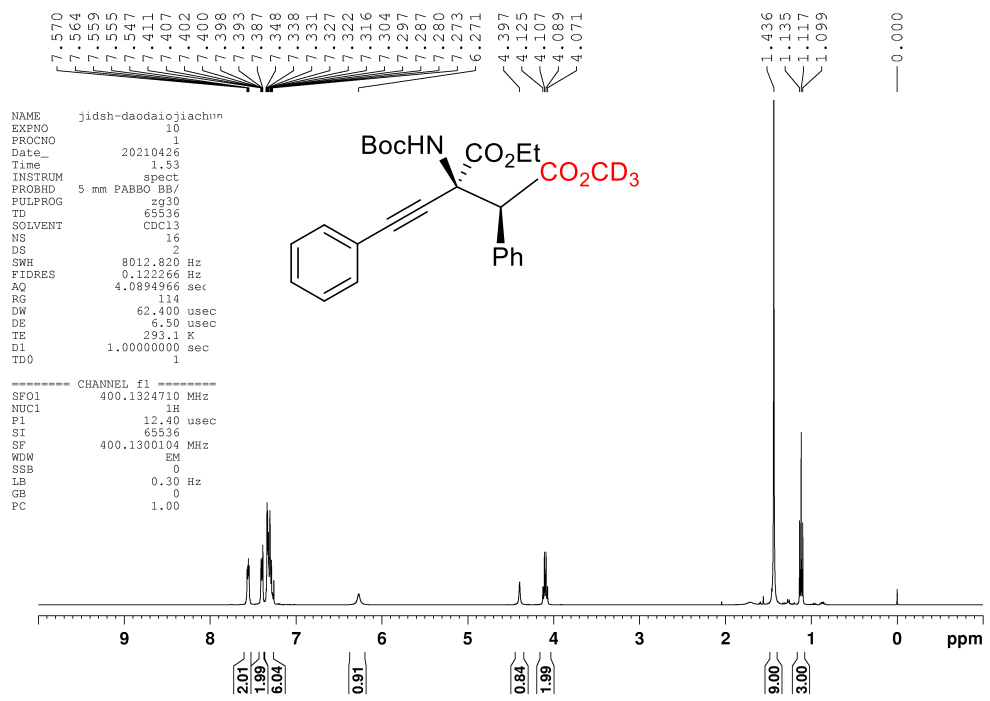


8-^{1}HNMR (400M, $CDCl_3$)



8-^{13}CNMR (151M, $CDCl_3$)

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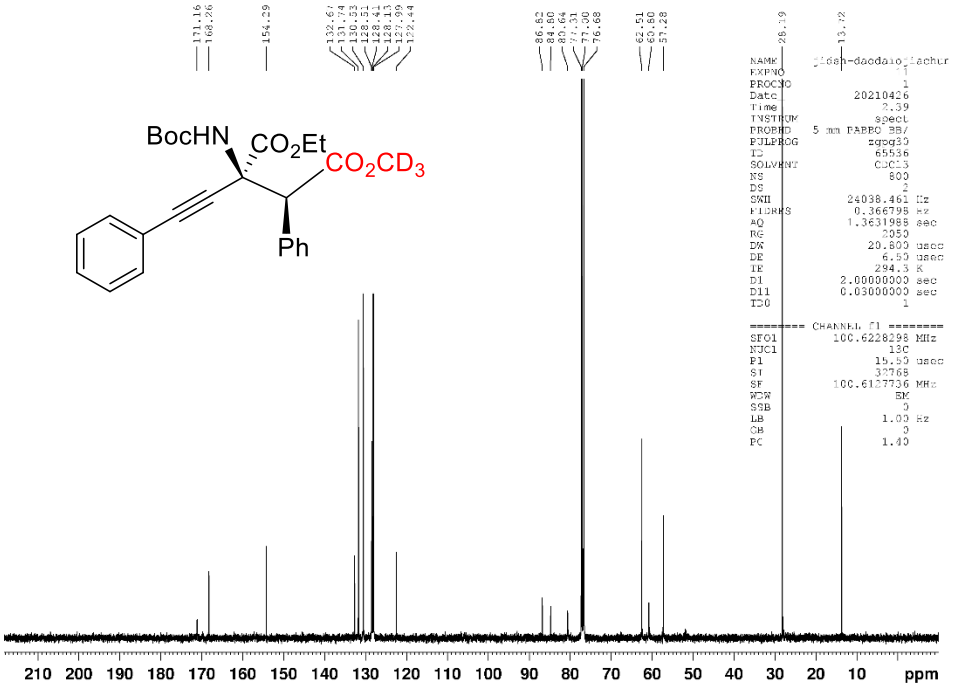
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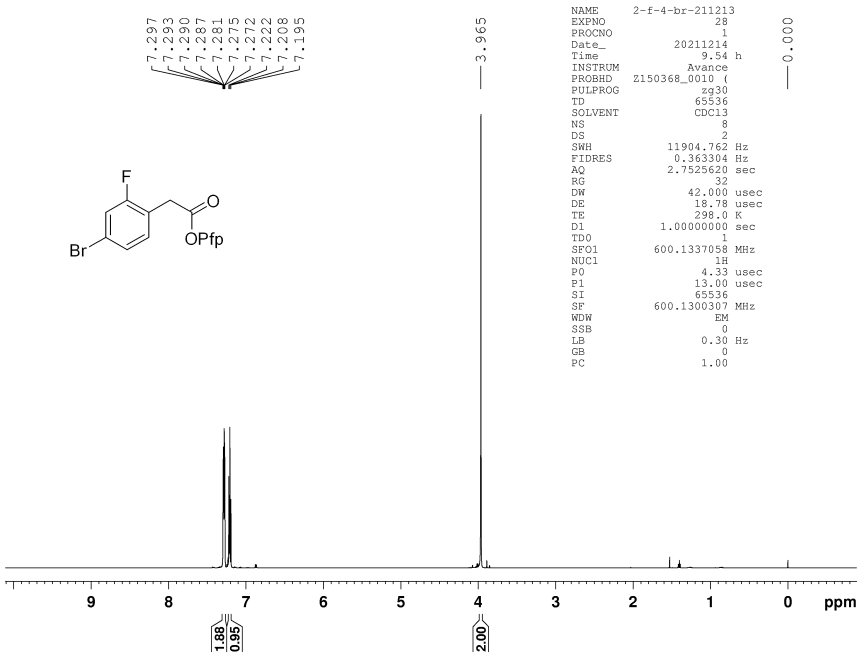
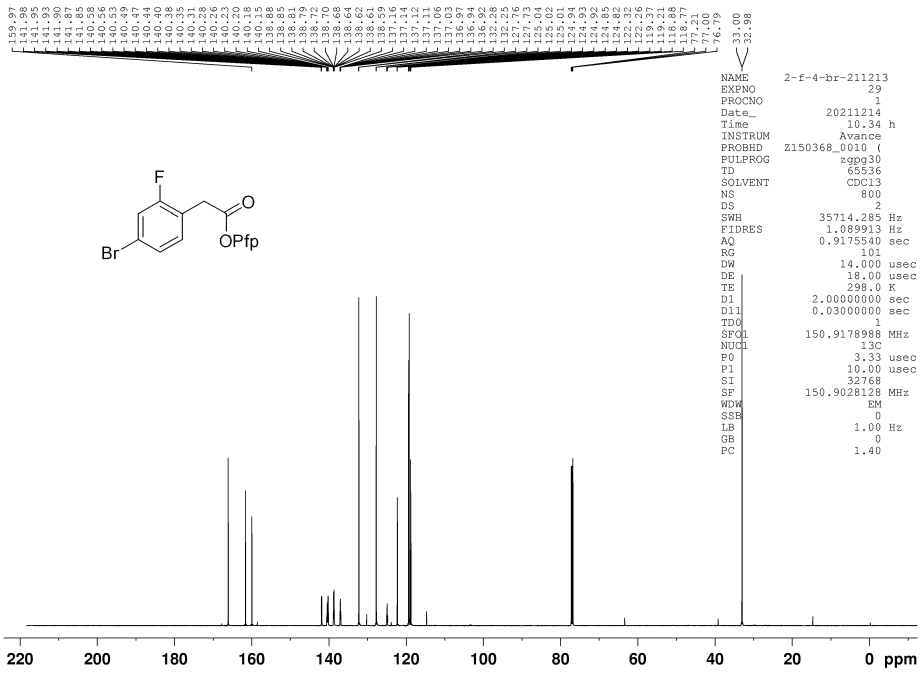
132.67
131.74
130.53
128.21
128.44
128.13
127.99
122.44
86.62
84.80
80.64
77.31
77.00
76.68
62.51
60.60
57.28
28.19
13.72
BocHN
CO2Et
CO2CD3
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

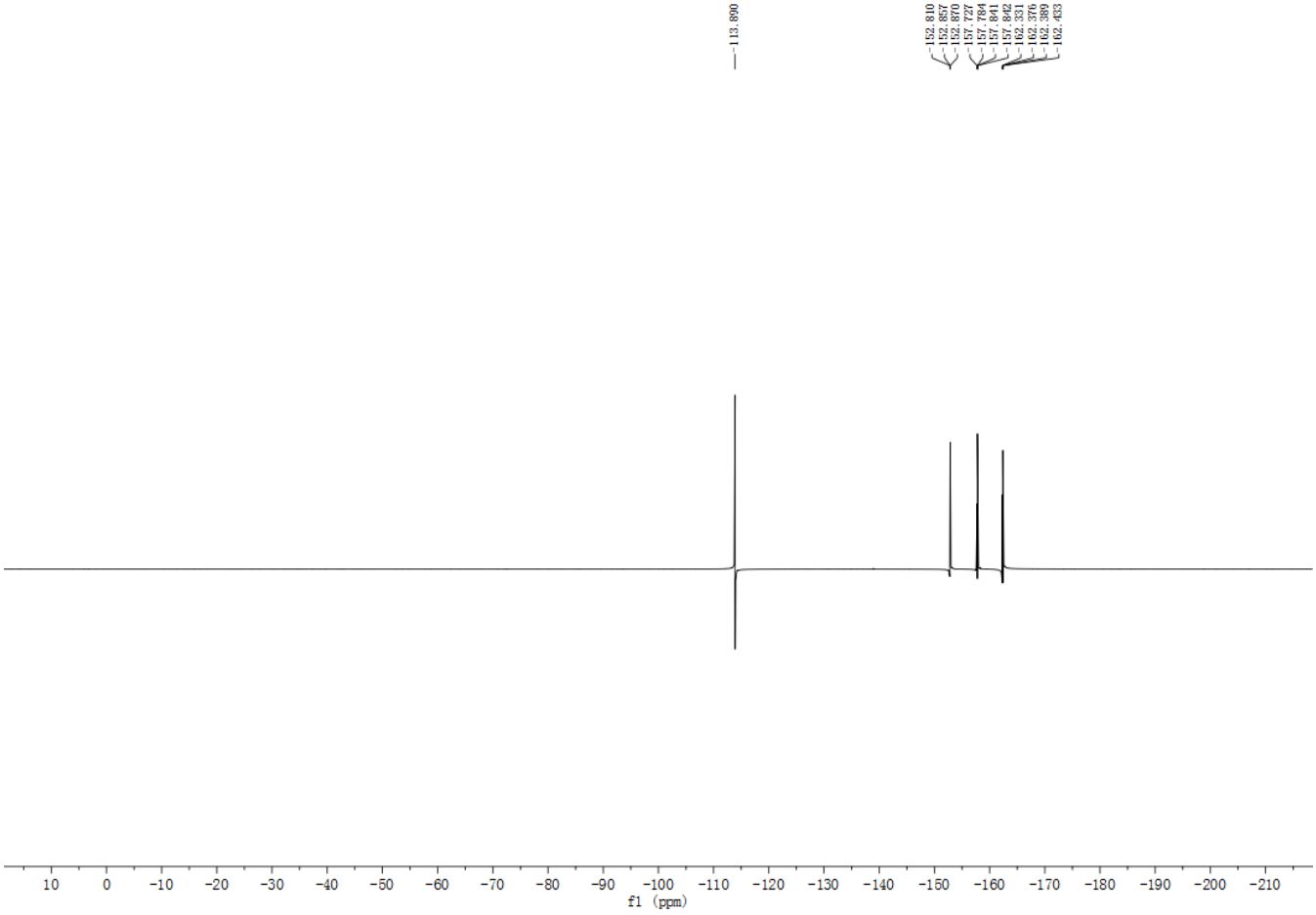
2j ^{1}HNMR($CDCl_3$, 600M)



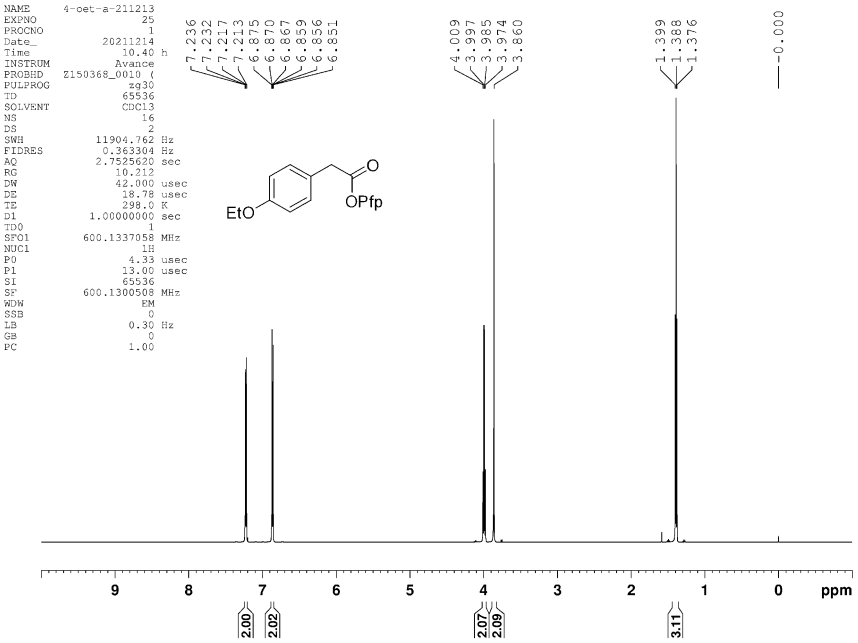
2j-^{13}CNMR($CDCl_3$, 151M)



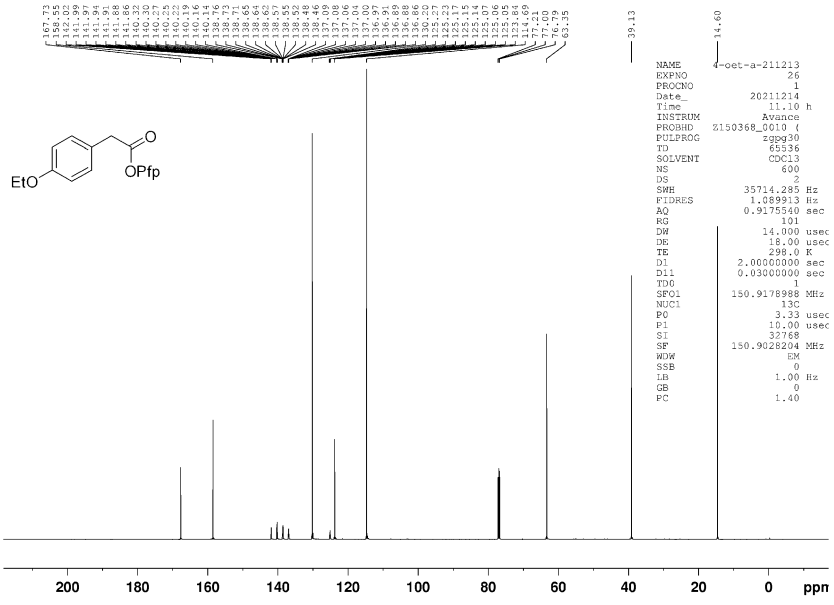
2j-^{19}FNMR($CDCl_3$, 376M)



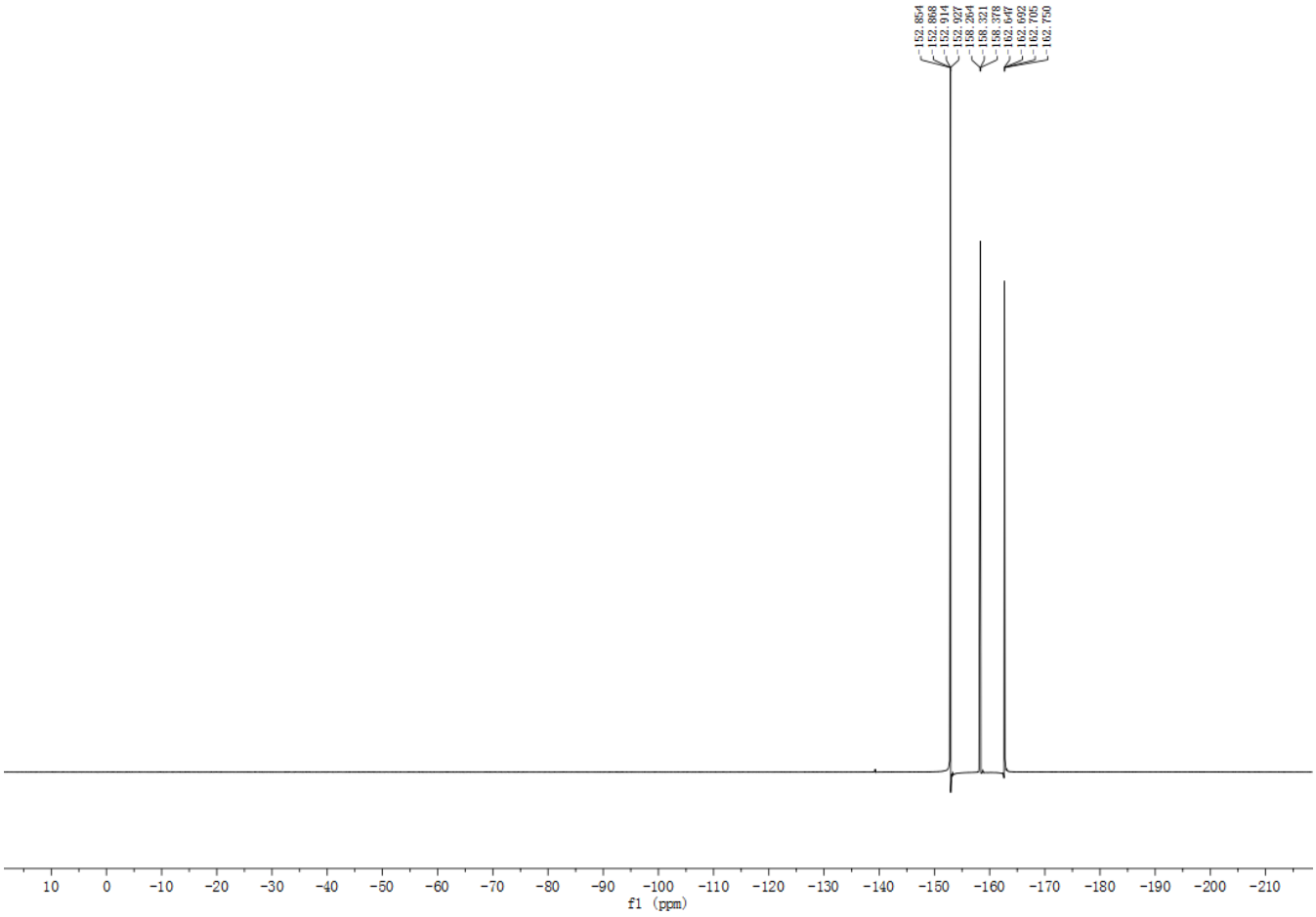
2e-^{1}HNMR($CDCl_3$, 600M)



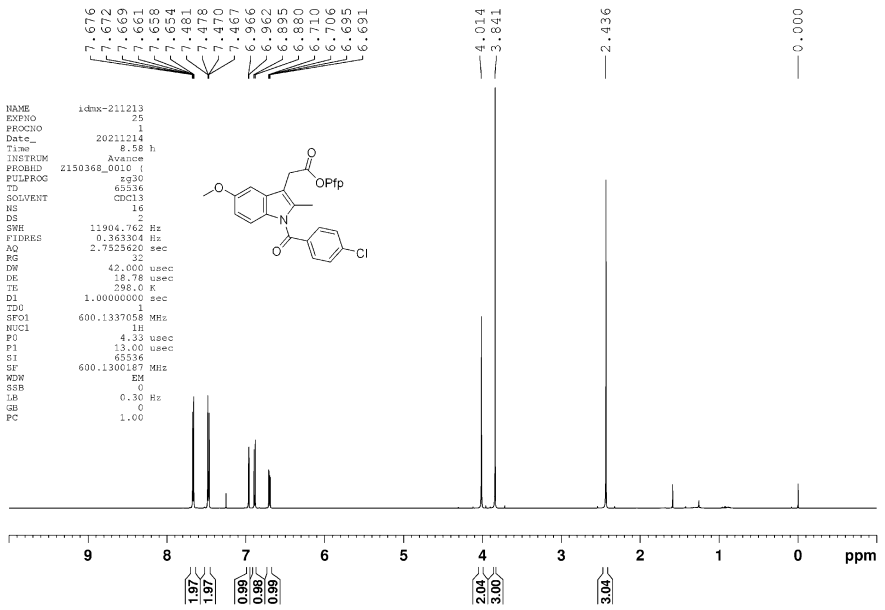
2e-^{13}CNMR($CDCl_3$, 151M)



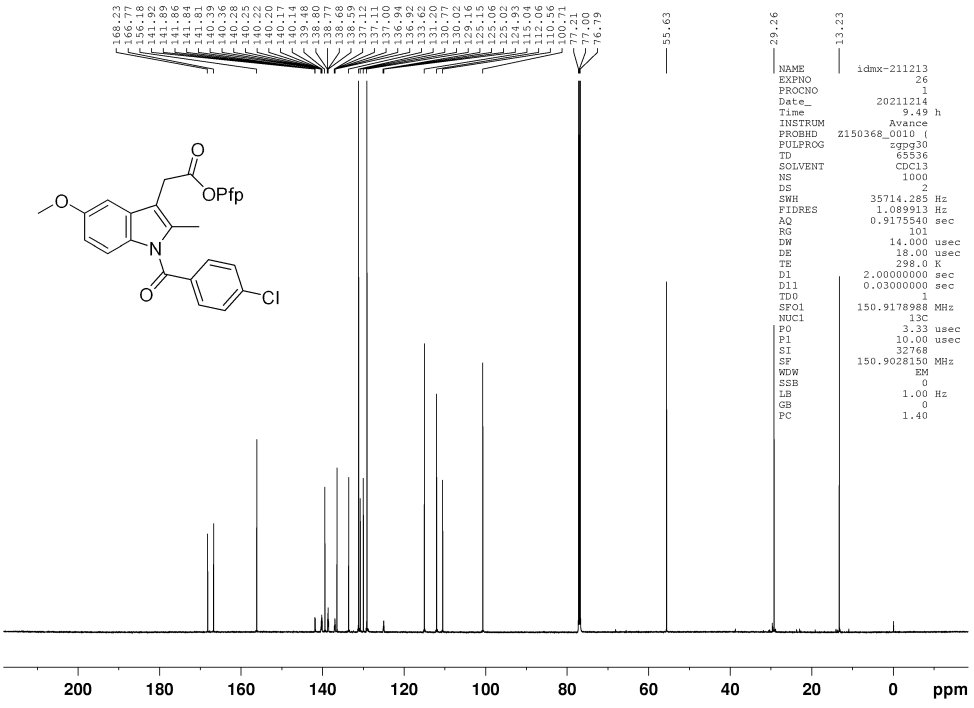
2e-^{19}FNMR($CDCl_3$, 376M)



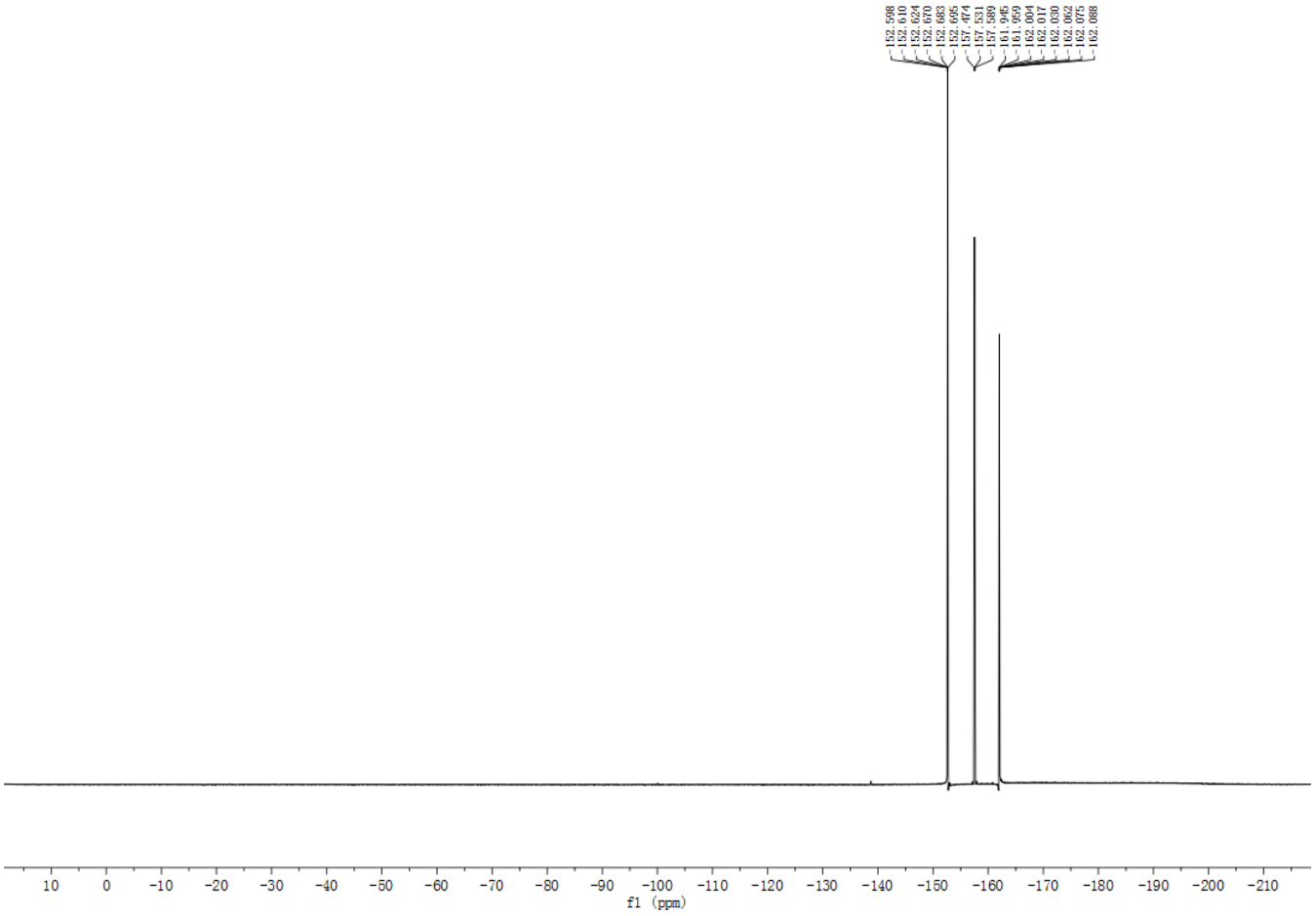
2n-^{1}HNMR($CDCl_3$, 600M)



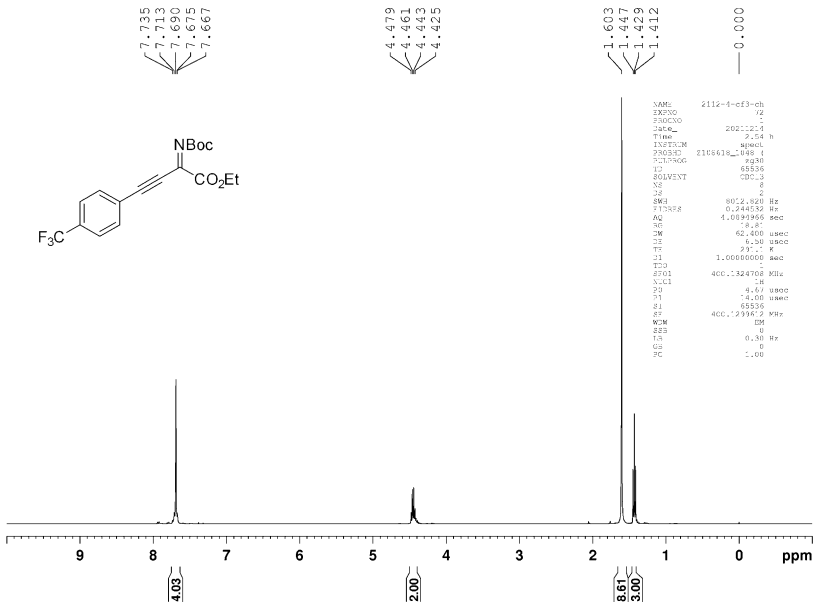
2n-^{13}CNMR($CDCl_3$, 151M)



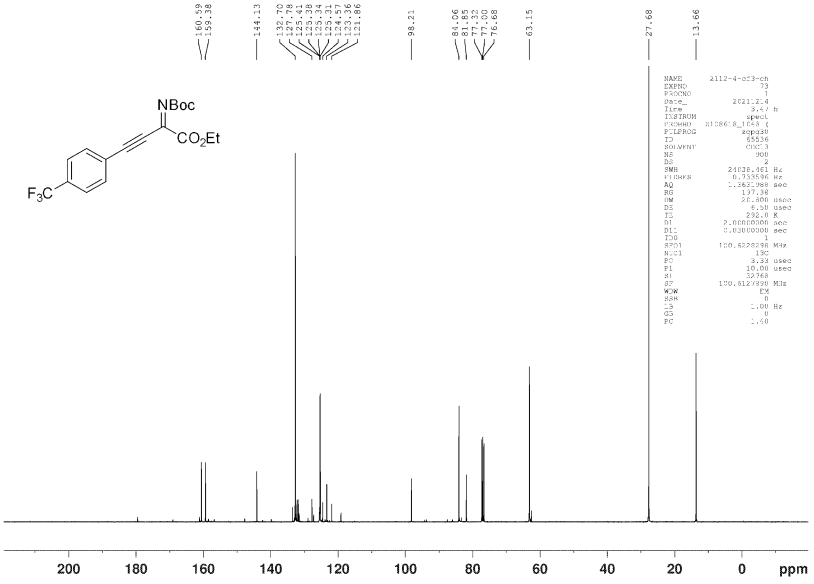
2n-^{19}FNMR($CDCl_3$, 376M)



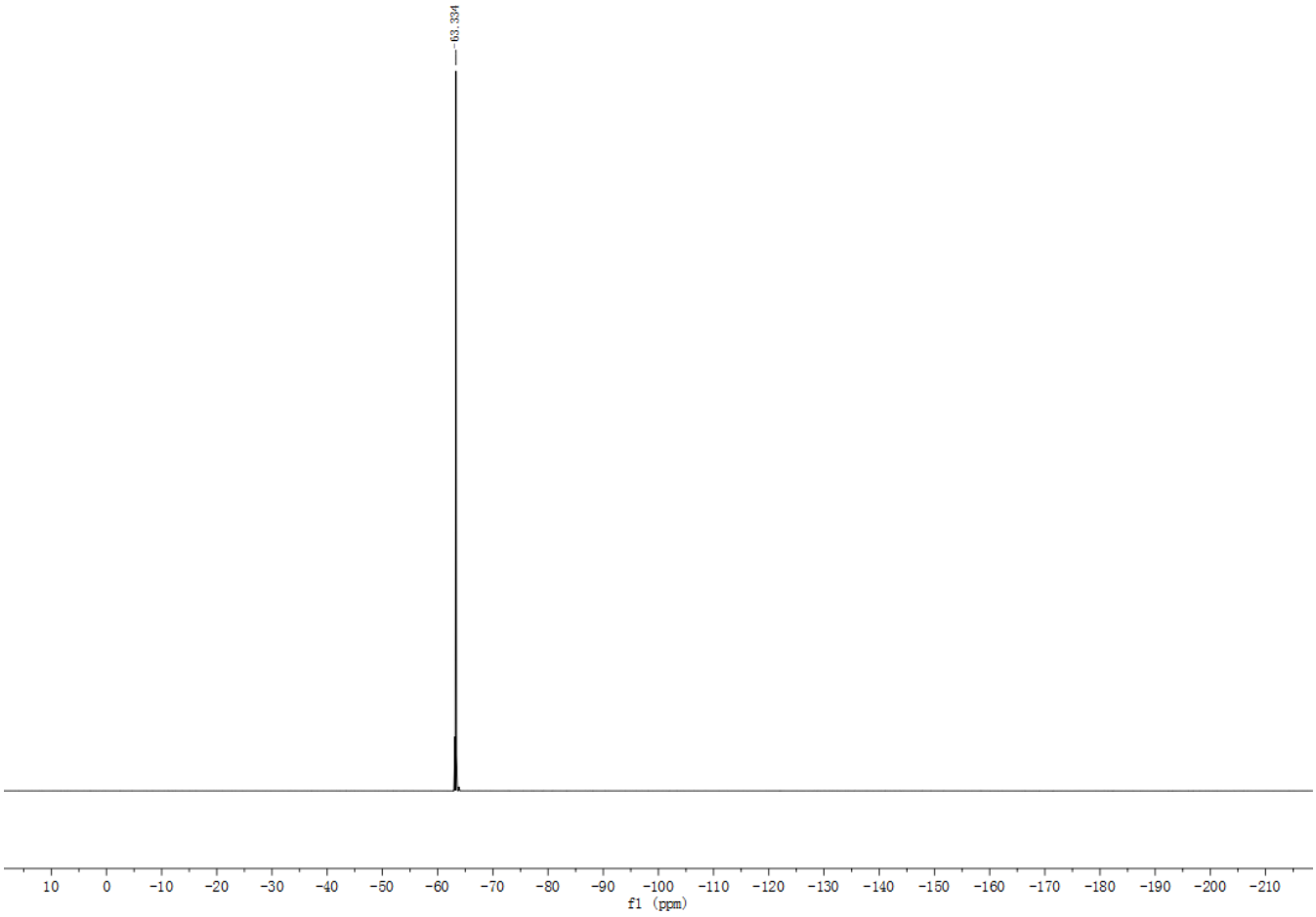
1i-^{1}HNMR(CDCl$_3$, 400M)



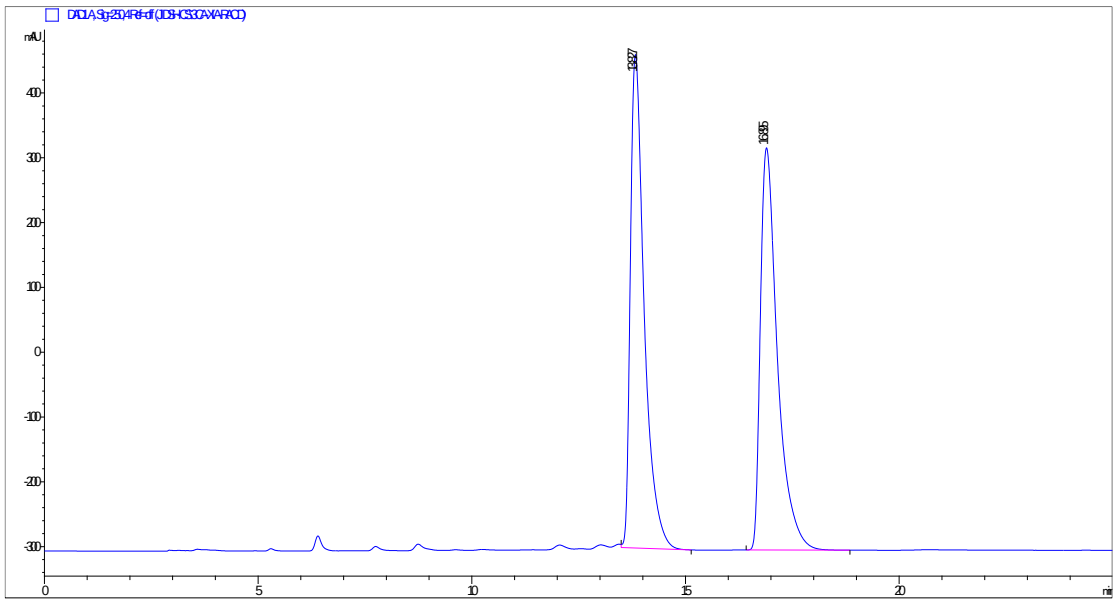
1i-^{13}CNMR(CDCl$_3$, 100M)



1i-^{19}FNMR($CDCl_3$, 376M)

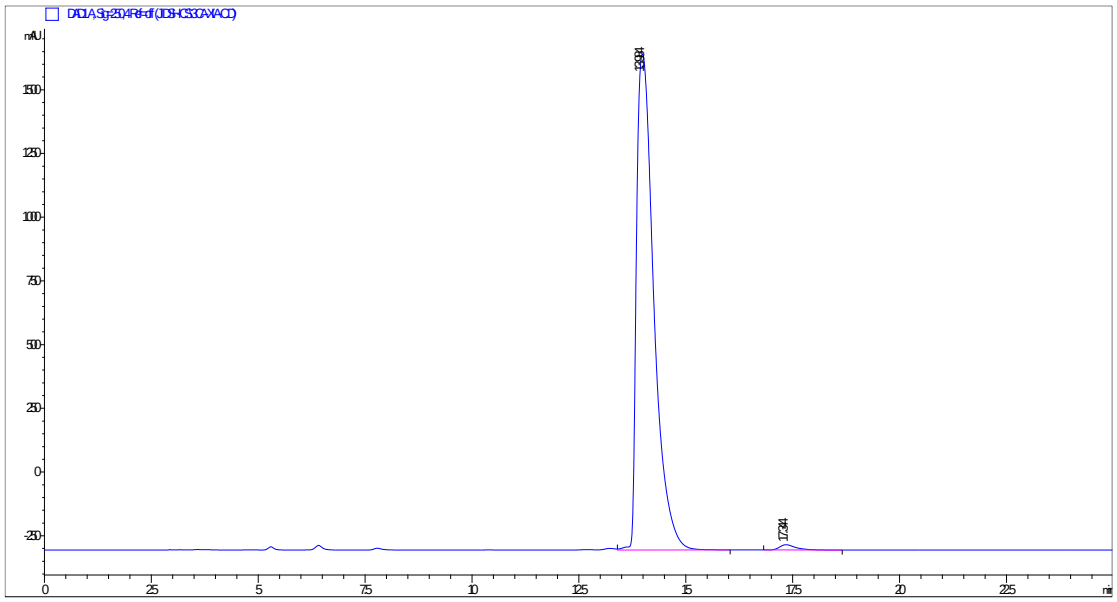


Racemic-3ca



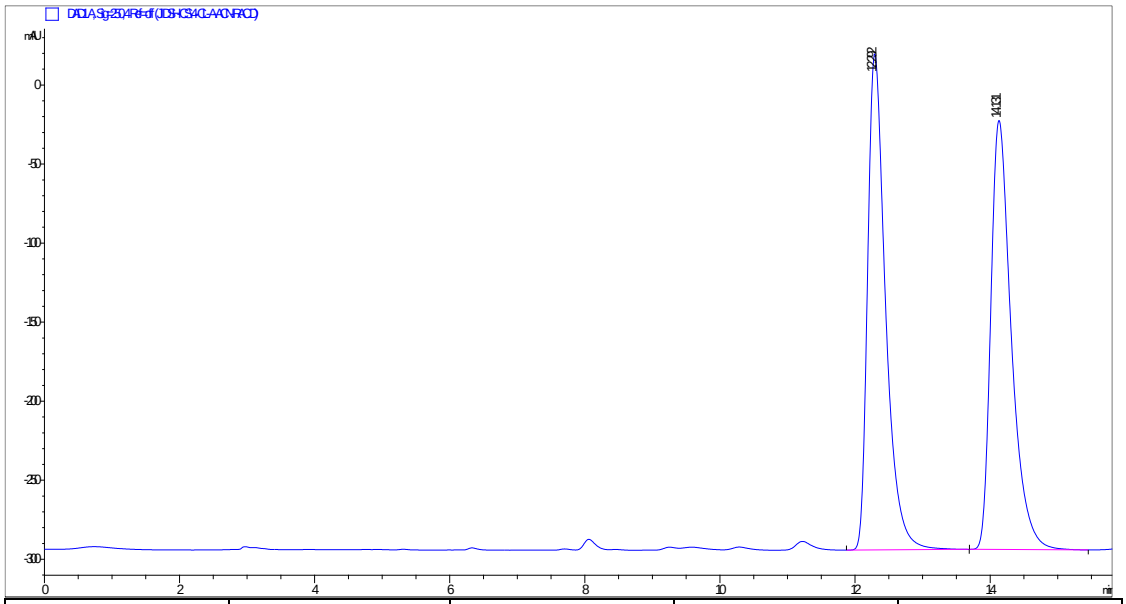
t_R	Channel	Area	Height	Area%
13.827	254nm	17160.7	761.3	49.89
16.895	254nm	17232.6	620.7	50.11

Enantioenriched-3ca



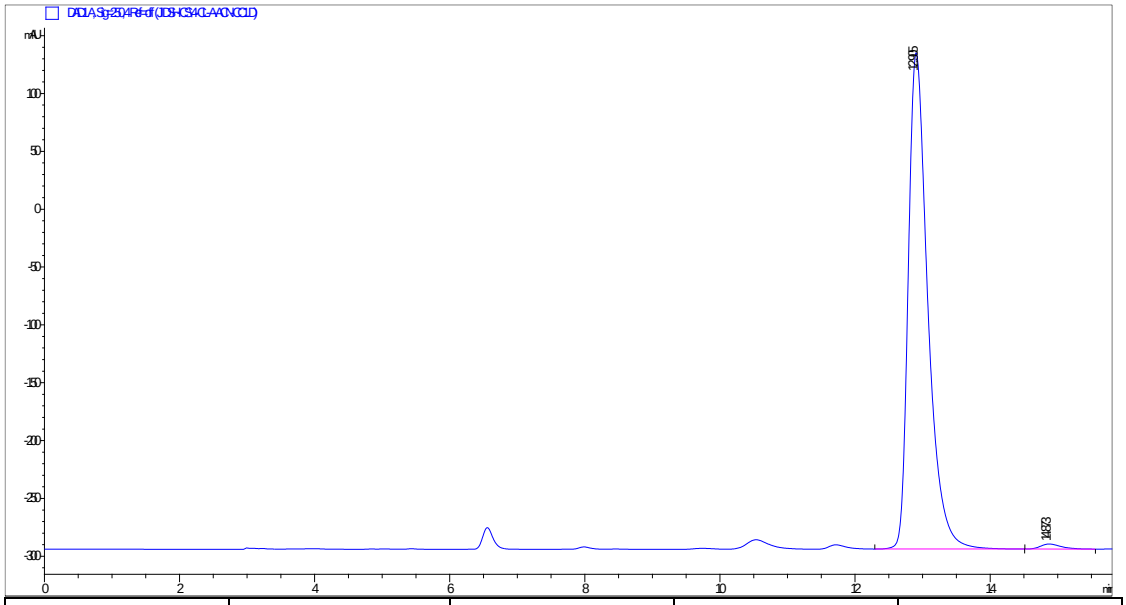
t_R	Channel	Area	Height	Area%
13.984	254nm	54782.8	1946.8	99.541
17.344	254nm	545.2	20.7	0.459

Racemic-3cb



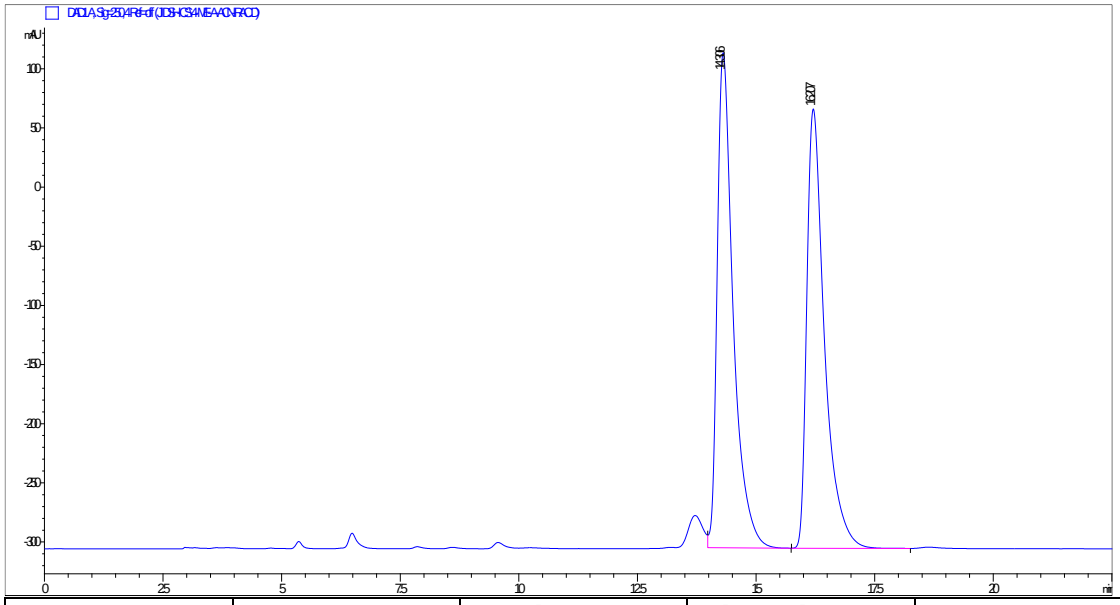
t_R	Channel	Area	Height	Area%
12.292	254nm	5790.4	313.8	50.273
14.131	254nm	5727.5	271.5	49.727

Enantioenriched-3cb



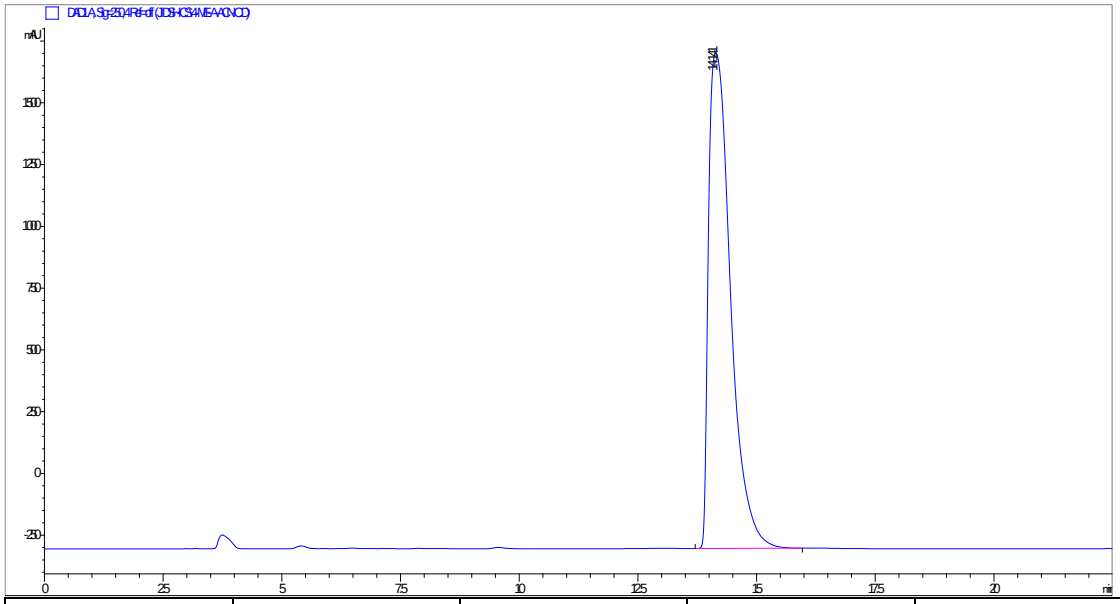
t_R	Channel	Area	Height	Area%
12.905	254nm	8599.2	428.9	98.958
14.873	254nm	90.6	4.3	1.042

Racemic- 3cc



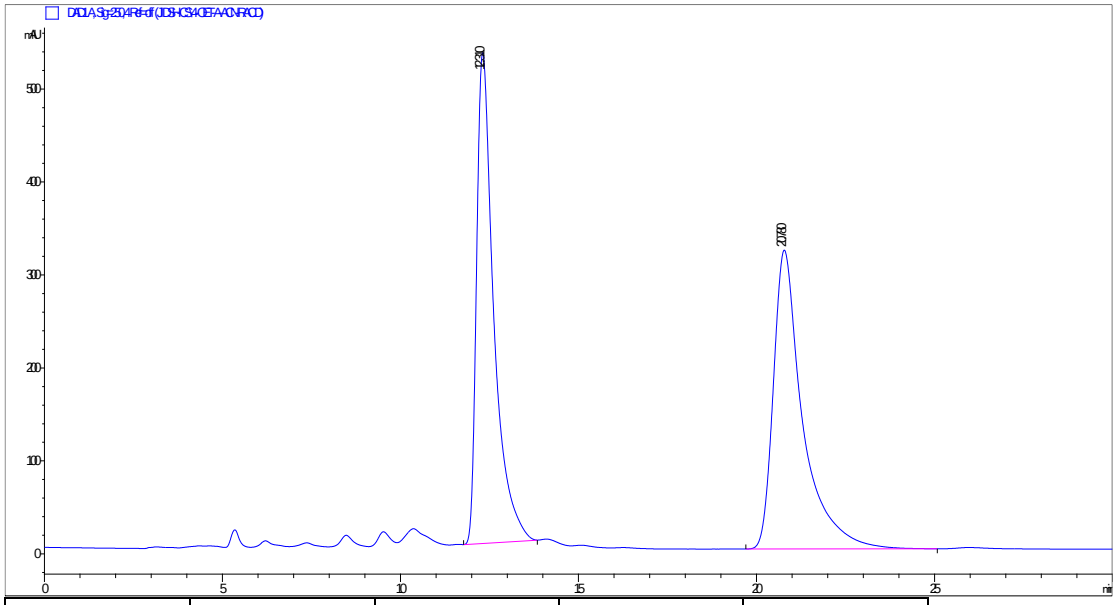
t_R	Area	Height	Channel	Area%
14.306	9789.4	418.6	254nm	50.48
16.207	9603.1	371.3	254nm	49.52

Enantioenriched-3cc



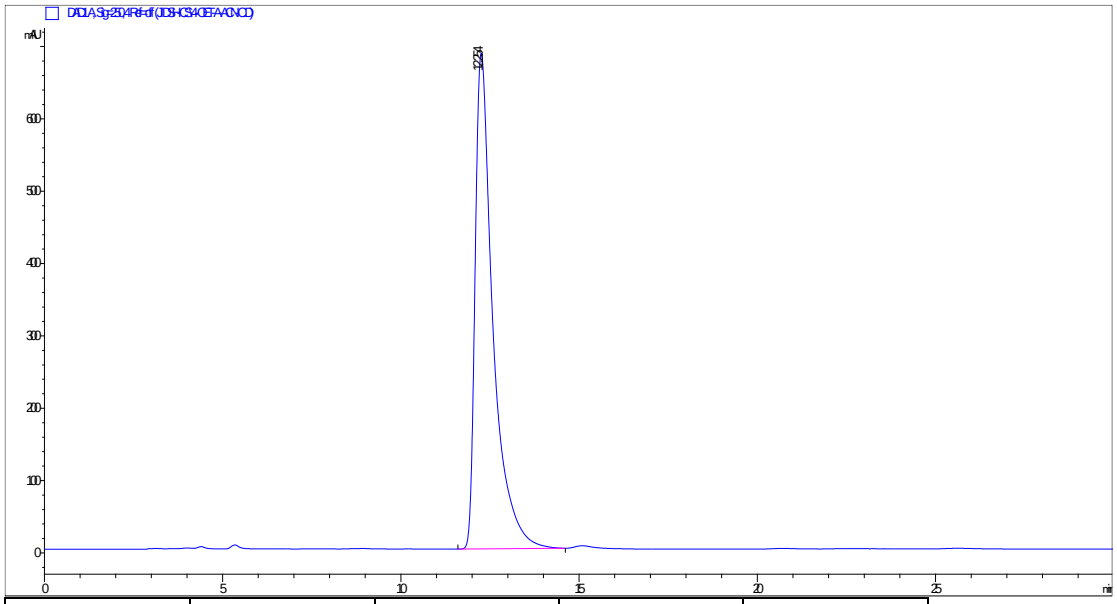
t_R	Area	Height	Channel	Area%
14.141	64697.3	2006.7	254nm	100
-	-	-	254nm	-

Racemic-3cd



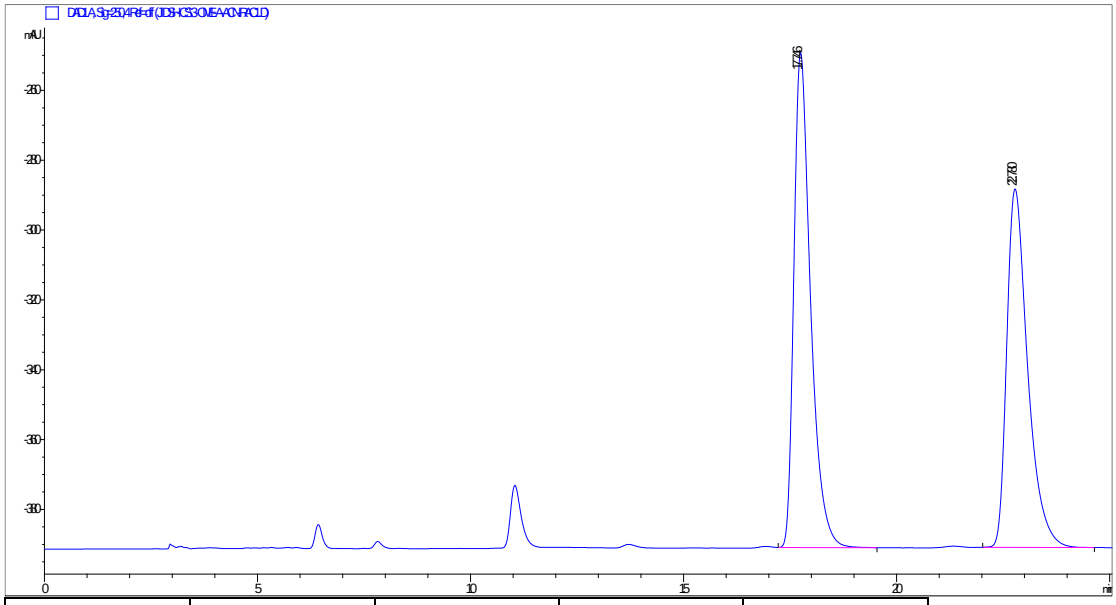
t_R	Channel	Area	Height	Area%
12.31	254nm	17701.5	527.9	49.3
20.78	254nm	18350.2	321.4	50.7

Enantioenriched-3cd



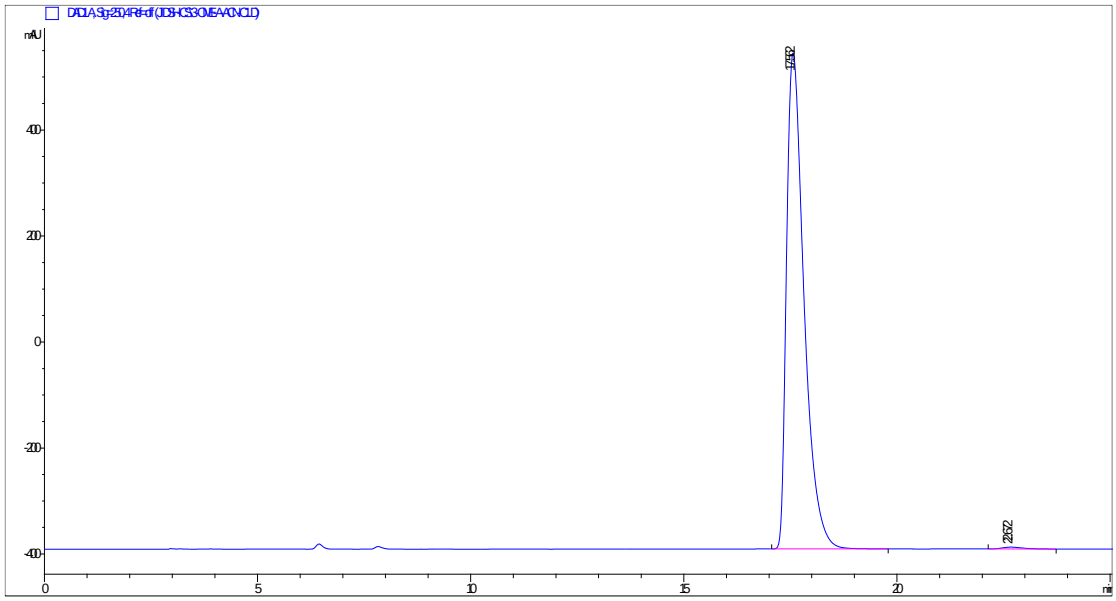
t_R	Channel	Area	Height	Area%
12.254	254nm	23819.8	685.6	100
-	254nm	-	-	-

Racemic- 3ce



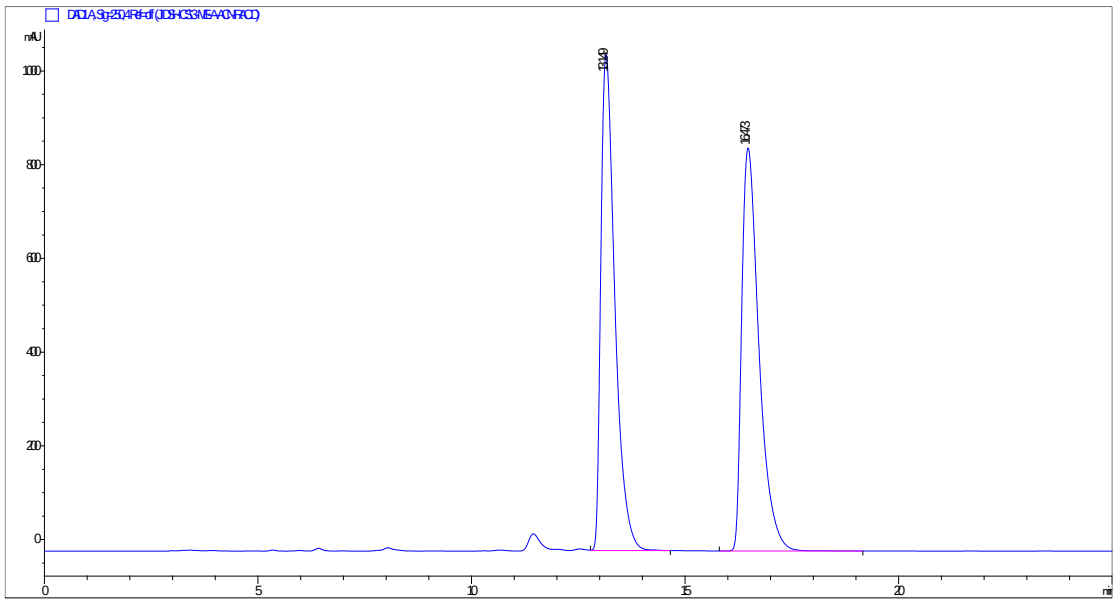
t_R	Channel	Area	Height	Area%
17.746	254nm	3857.9	141.7	50.413
22.78	254nm	3502.6	102.6	49.587

Enantioenriched-3ce



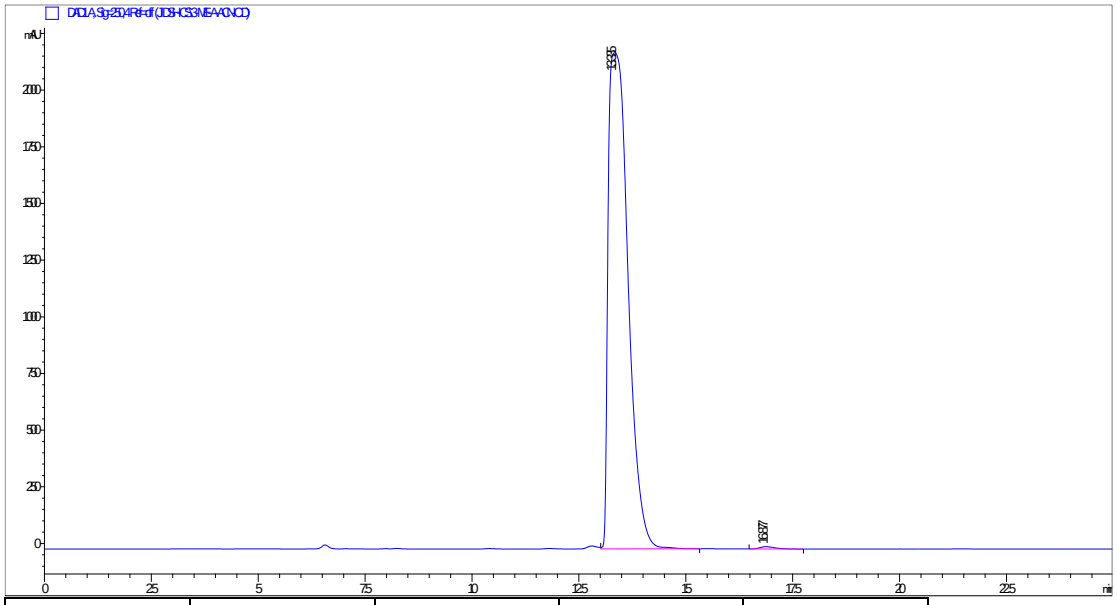
t_R	Channel	Area	Height	Area%
17.562	254nm	26630.7	935.7	99.604
22.672	254nm	105.8	3.3	0.396

Racemic-3cf



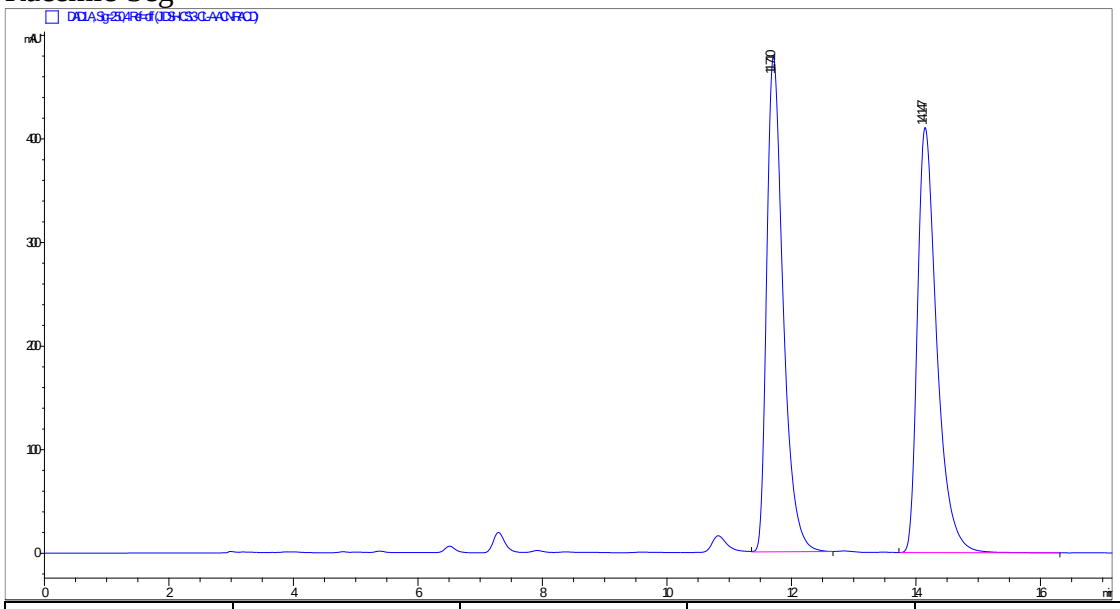
t_R	Channel	Area	Height	Area%
13.149	254nm	24171.2	1058.2	49.98
16.473	254nm	24192.6	860.2	50.02

Enantioenriched-3cf



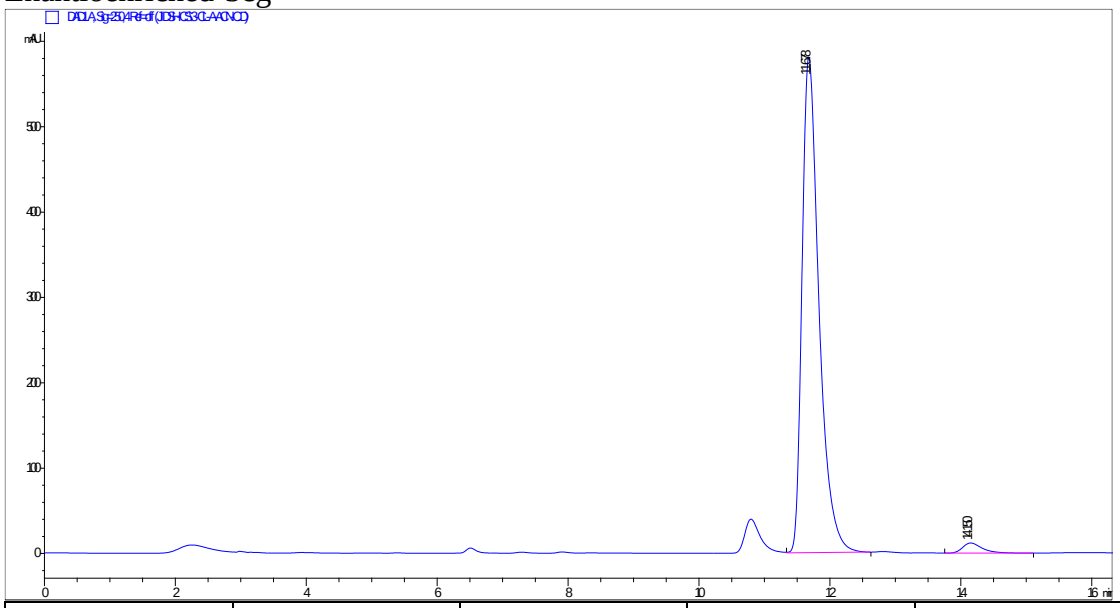
t_R	Channel	Area	Height	Area%
13.335	254nm	70486.8	2188.6	99.642
16.877	254nm	253.3	10.3	0.358

Racemic-3cg



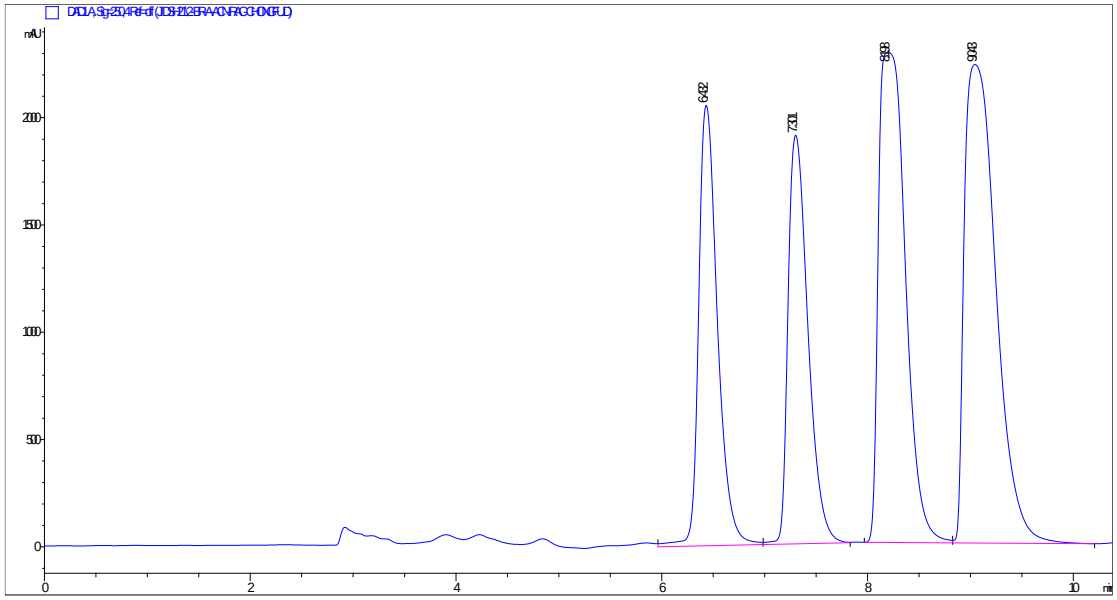
t_R	Channel	Area	Height	Area%
11.71	254nm	8793.8	478.3	49.786
13.721	254nm	8869.4	410.4	50.214

Enantioenriched-3cg



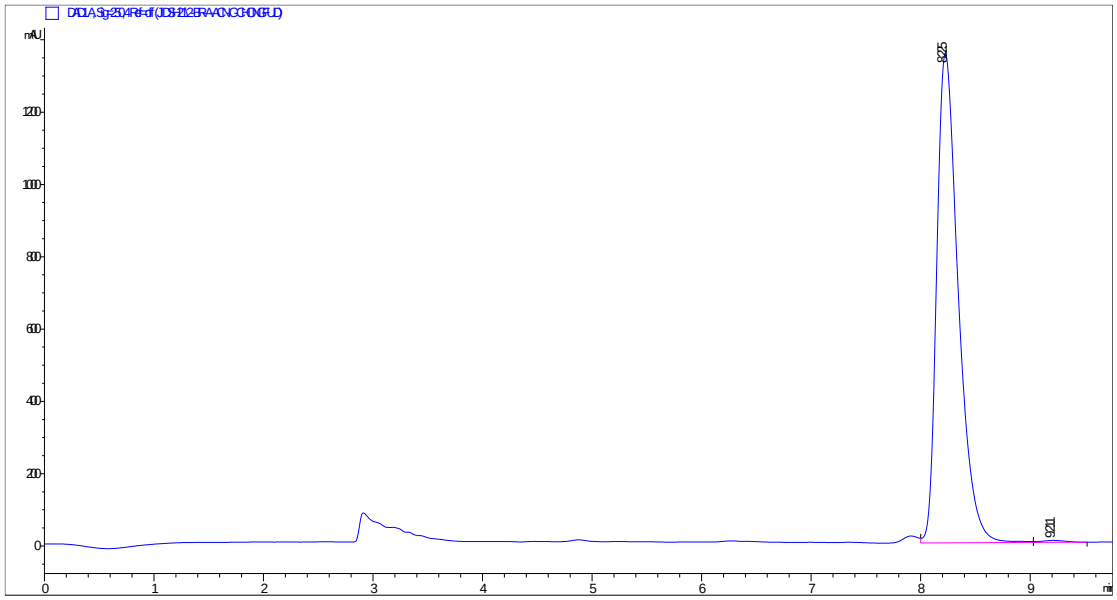
t_R	Channel	Area	Height	Area%
11.678	254nm	10438.8	580.6	97.727
14.15	254nm	242.7	11.8	2.273

Racemic-3ch (the racemic product was obtained as an inseparable mixture of diastereoisomers)



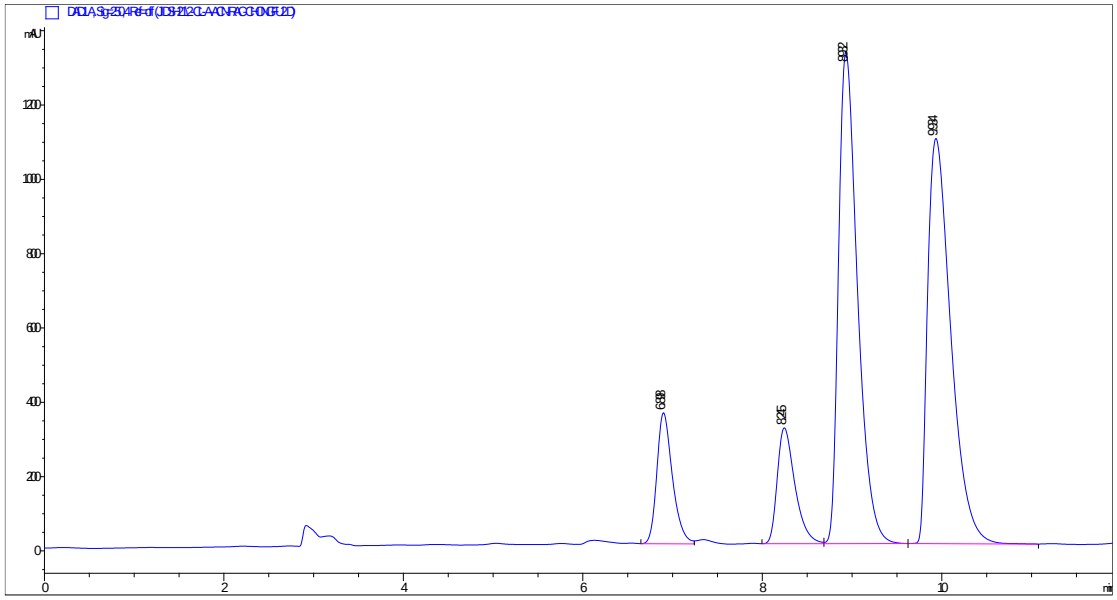
t_R	Channel	Area	height	Area/%
8.198	254nm	41451.6	2284.8	29.460
9.043	254nm	47585.6	2230.4	33.819

Enantioenriched-3ch



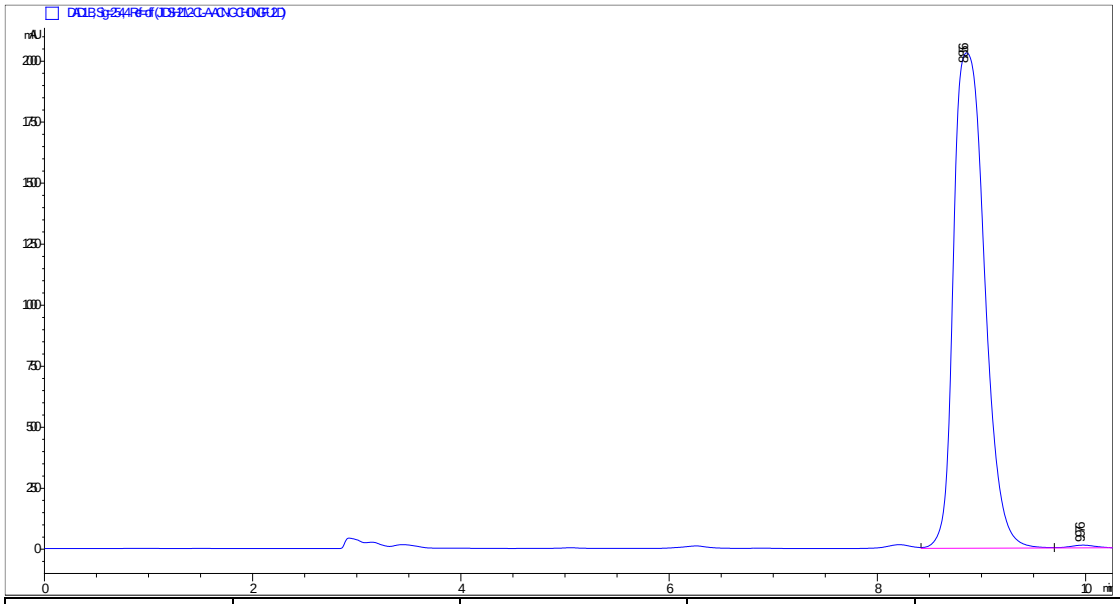
t_R	Channel	Area	height	Area/%
8.225	254nm	18519.9	1355.6	99.547
9.211	254nm	84.2	5.5	0.453

Racemic-3ci (the racemic product was obtained as an inseparable mixture of diastereoisomers)



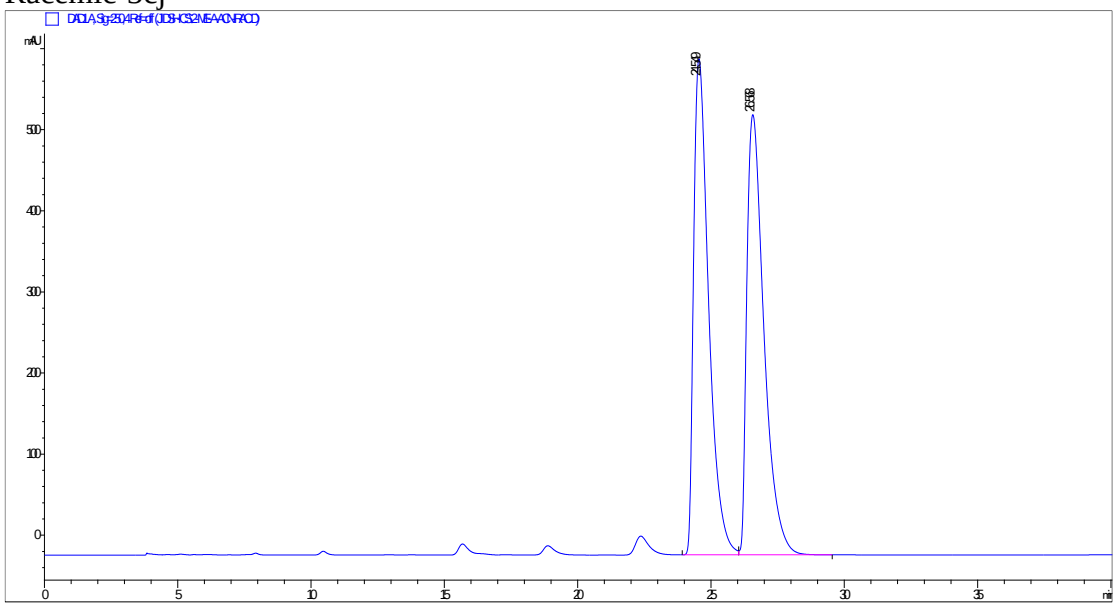
t_R	Channel	Area	height	Area/%
8.932	254nm	19436.9	1322.4	49.718
9.934	254nm	19657.6	1090.5	50.282

Enantioenriched-3ci



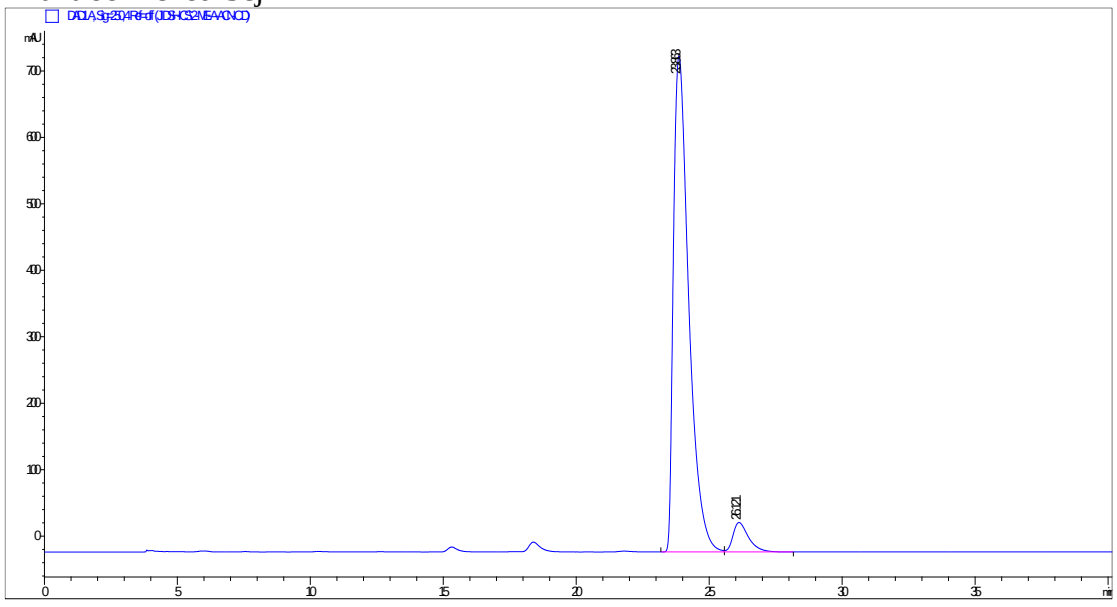
t_R	Channel	Area	height	Area/%
8.857	254nm	42047.5	2029.9	99.567
9.976	254nm	182.8	11	0.433

Racemic-3cj



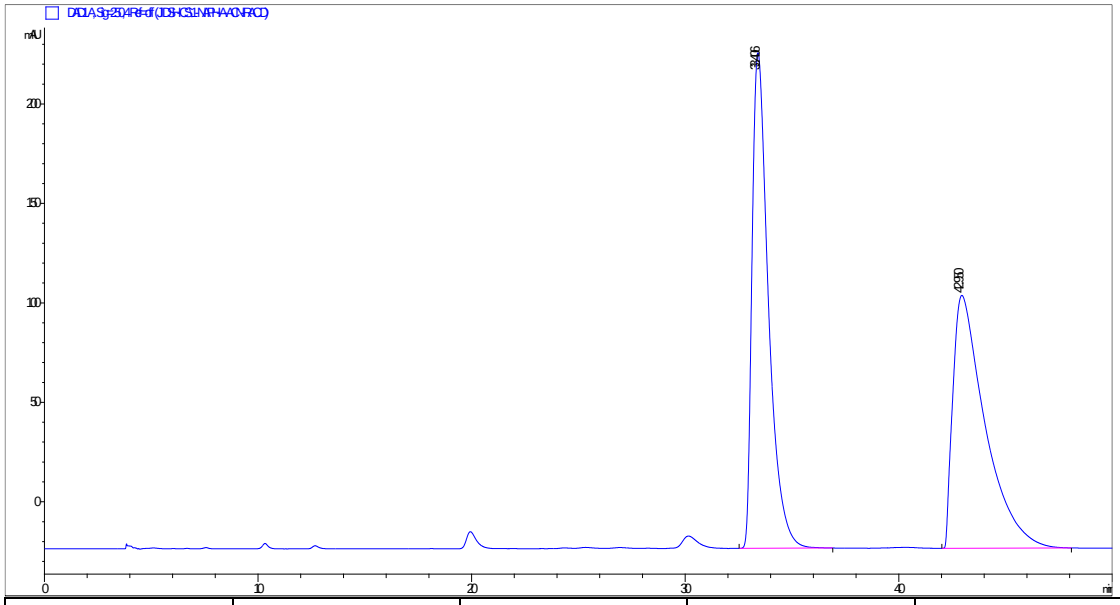
t_R	Channel	Area	Height	Area%
24.549	254nm	23973.8	611.8	49.65
26.568	254nm	24310.8	542.8	50.34

Enantioenriched-3cj



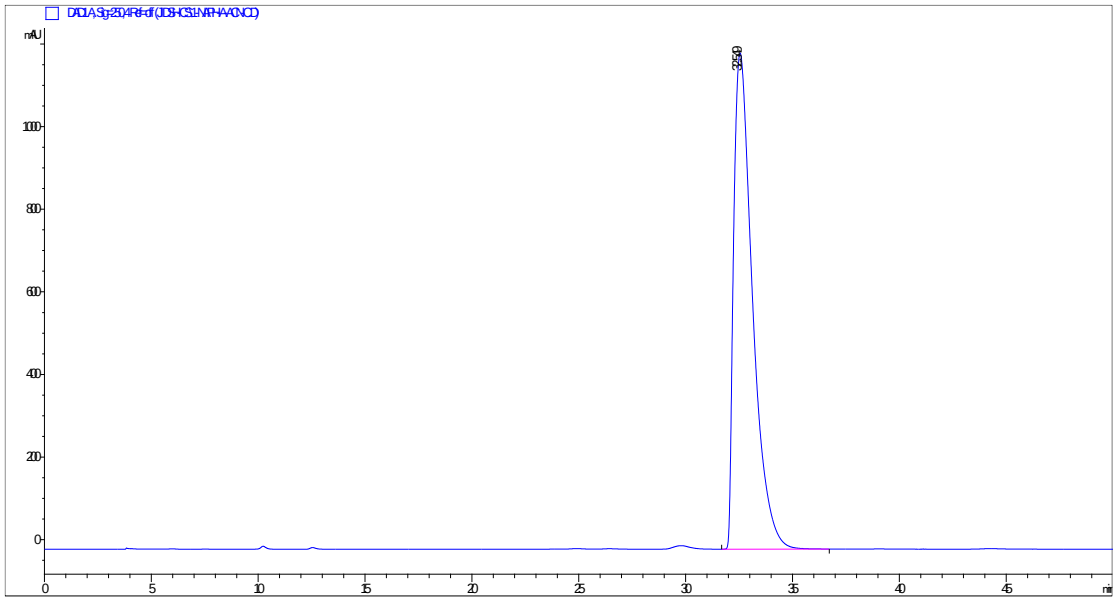
t_R	Channel	Area	Height	Area%
23.863	254nm	29918.1	746.5	95.001
26.121	254nm	1800.6	44.3	4.999

Racemic-3ck



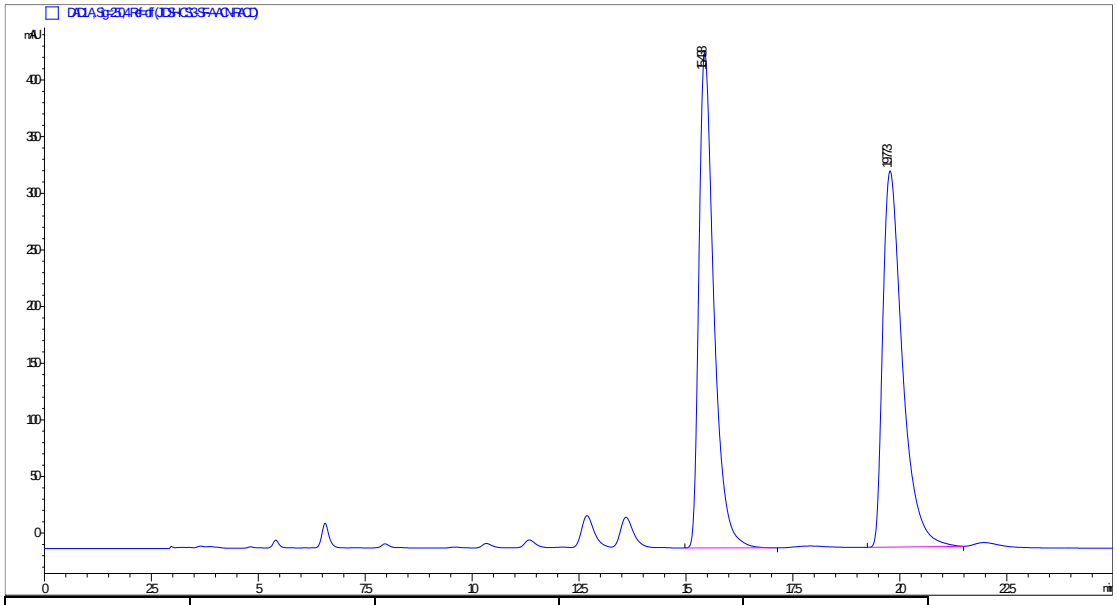
t_R	Channel	Area	Height	Area%
33.406	254nm	13296.6	249.2	49.991
42.95	254nm	13301.6	127.1	50.009

Enantioenriched-3ck



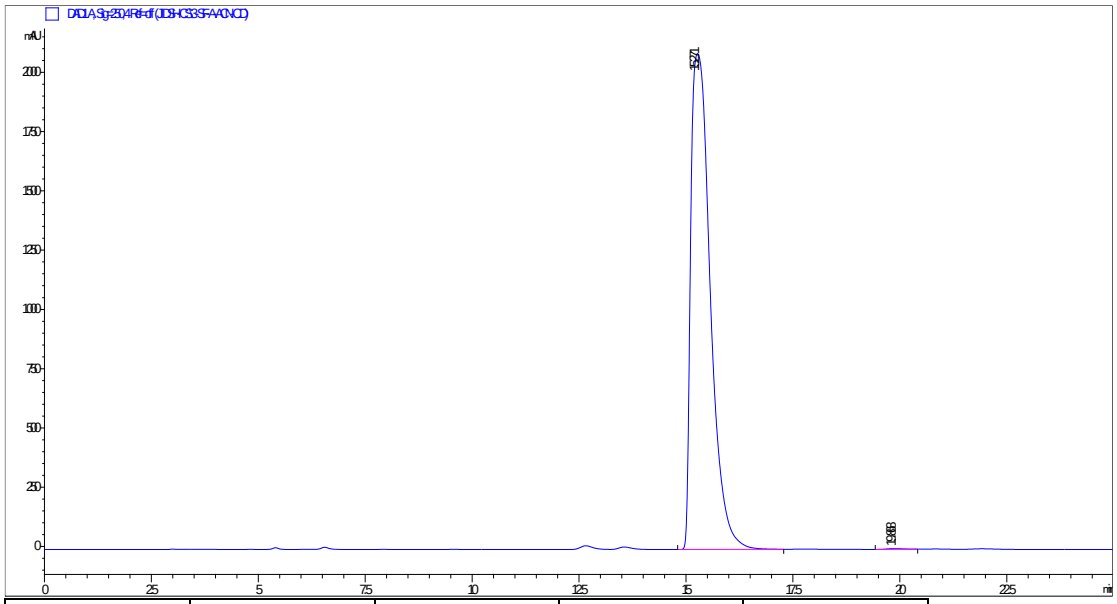
t_R	Channel	Area	Height	Area%
32.549	254nm	73586.7	1201.2	100
-	254nm	-	-	-

Racemic-3cl



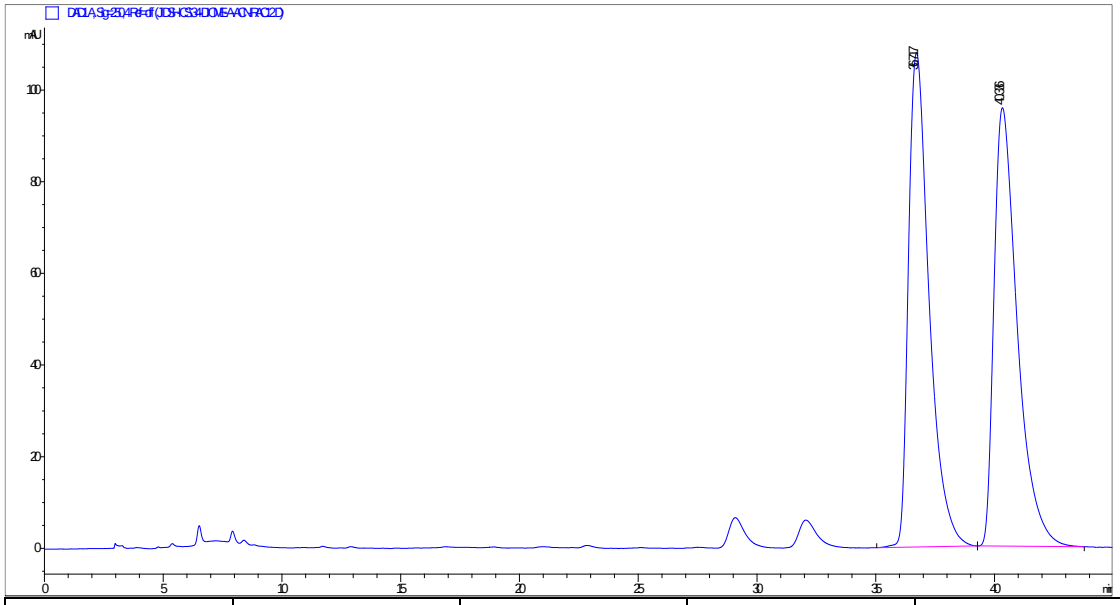
t_R	Channel	Area	Height	Area%
15.438	254nm	10670.4	511.4	50.041
19.773	254nm	10653.1	457.4	49.959

Enantioenriched-3cl



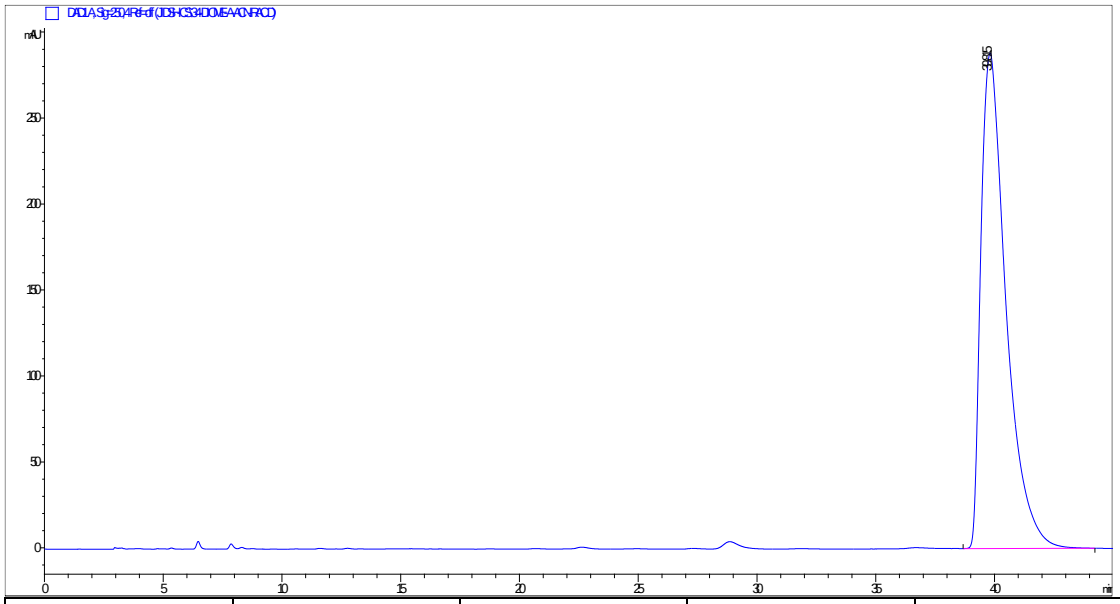
t_R	Channel	Area	Height	Area%
15.271	254nm	66352.5	2092.5	99.881
19.868	254nm	78.8	3	0.119

Racemic-3cm



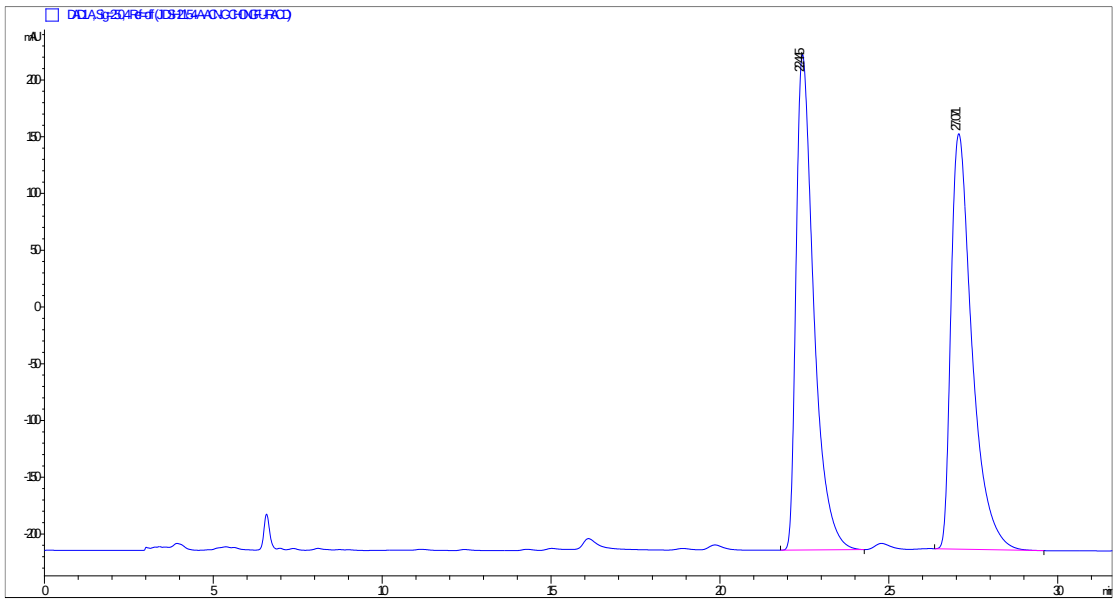
t_R	Channel	Area	height	Area/%
36.717	254nm	6525.5	107.9	49.995
40.336	254nm	6526.8	95.7	50.005

Enantioenriched-3cm



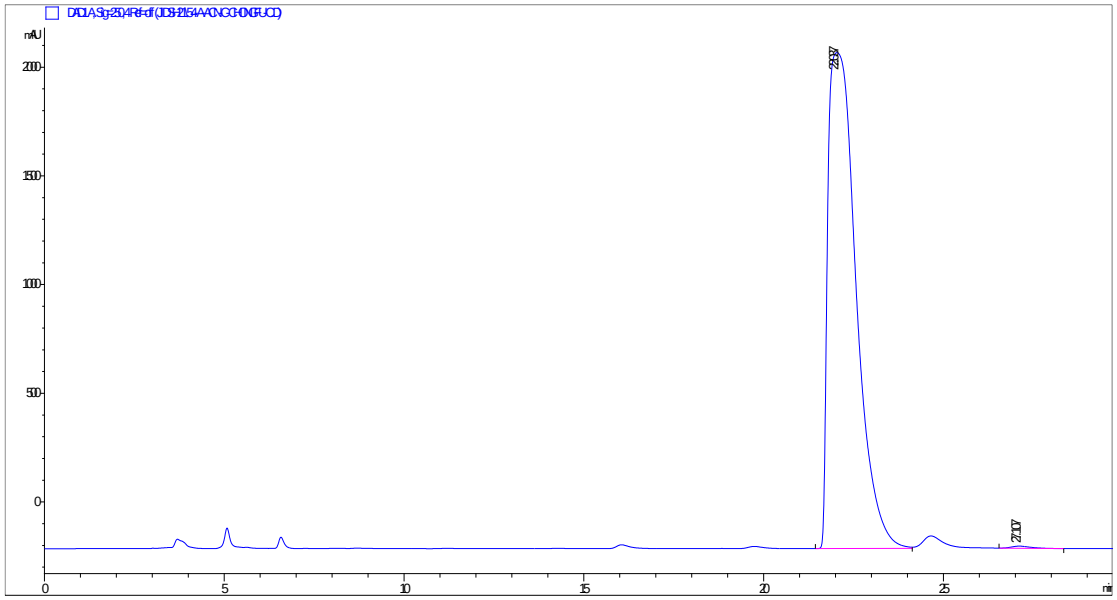
t_R	Channel	Area	height	Area/%
36.717	254nm	-	-	-
39.815	254nm	21212.5	288.2	100

Racemic-3cn



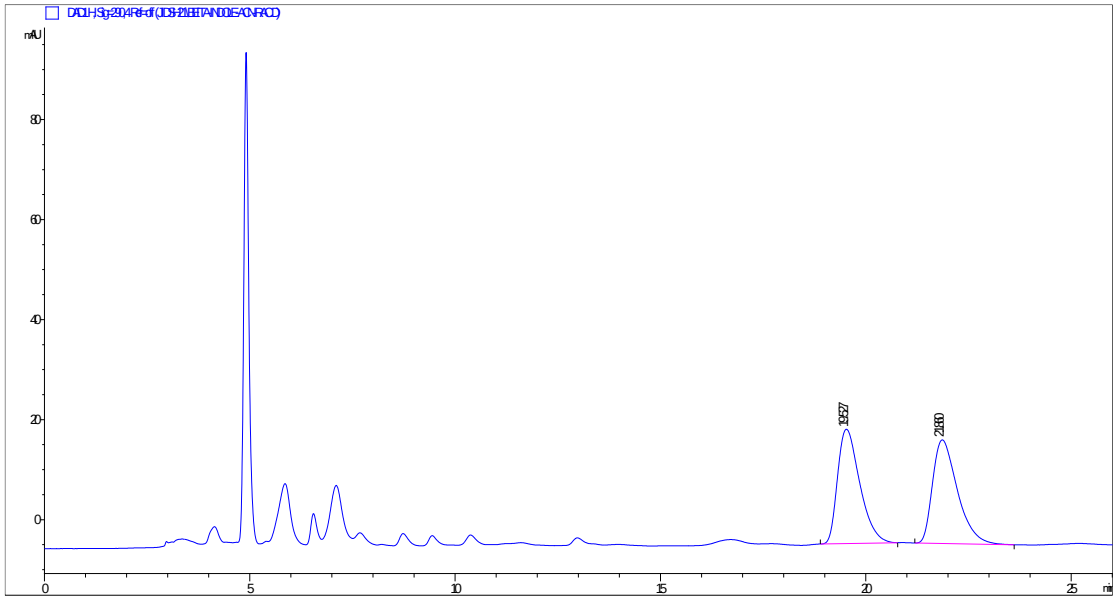
t_R	Channel	Area	height	Area/%
22.445	254nm	15893.7	436.5	50.062
27.071	254nm	15854.1	365.9	49.938

Enantioenriched-3cn



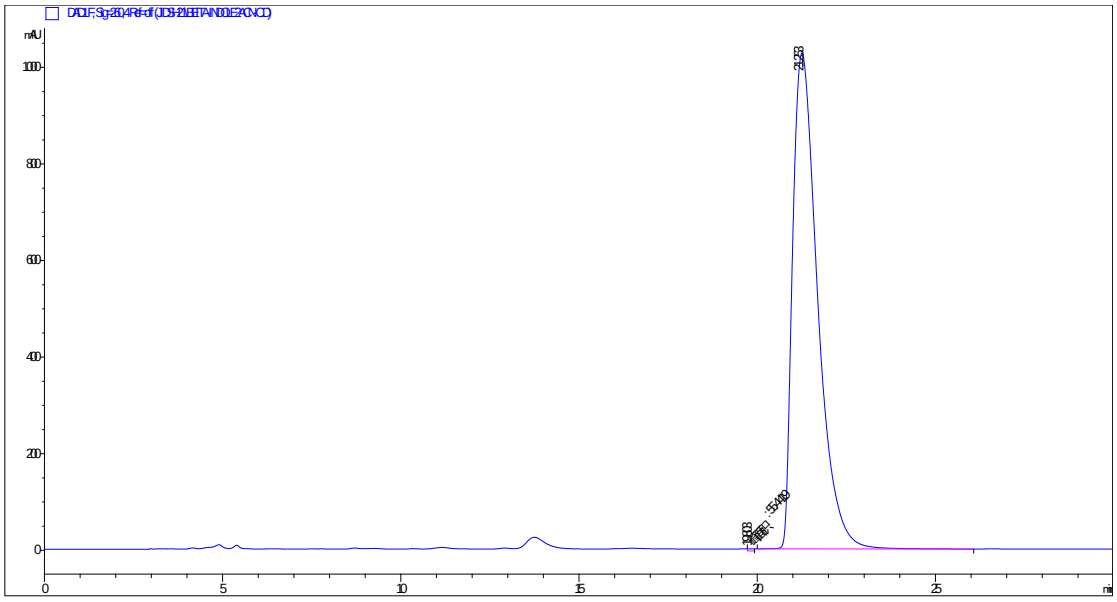
t_R	Channel	Area	height	Area/%
22.037	254nm	97068.7	2205.1	99.71
27.107	254nm	247.2	8.5	0.29

Racemic-3co



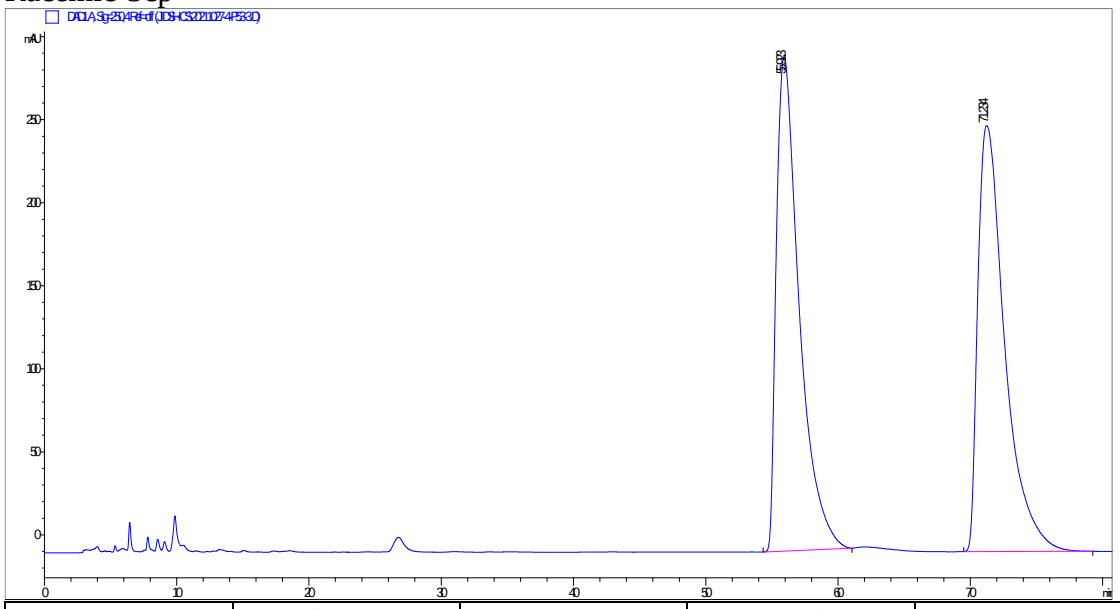
t_R	Channel	Area	height	Area/%
19.527	254nm	861.2	22.9	49.7
21.86	254nm	871.4	20.7	50.3

Enantioenriched-3co



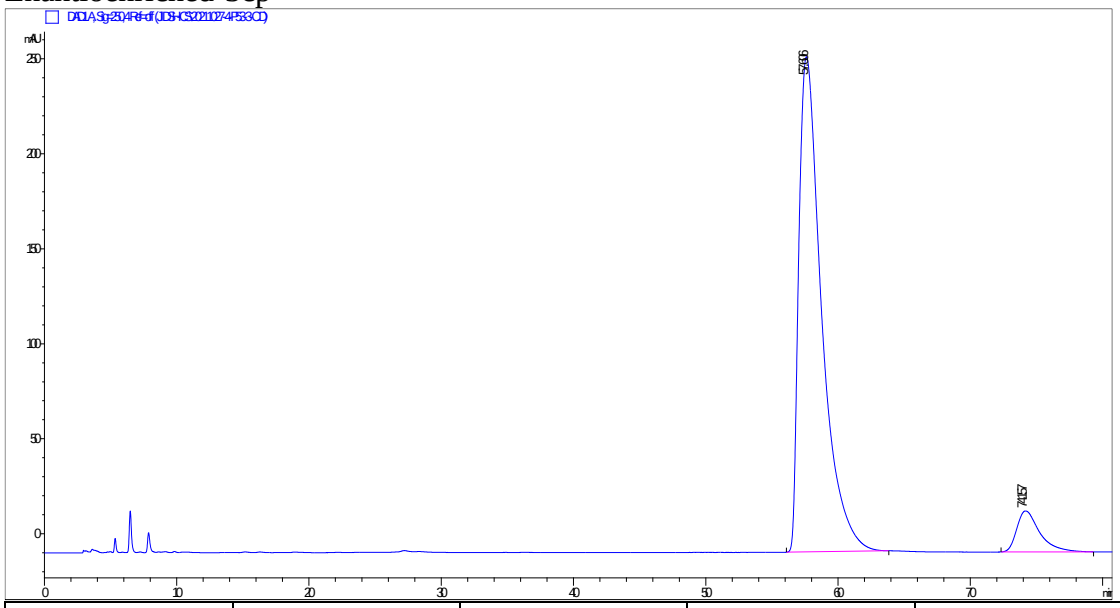
t_R	Channel	Area	height	Area/%
19.803	254nm	55.4	4.5	0.11
21.253	254nm	50007.3	1026.5	99.89

Racemic-3cp



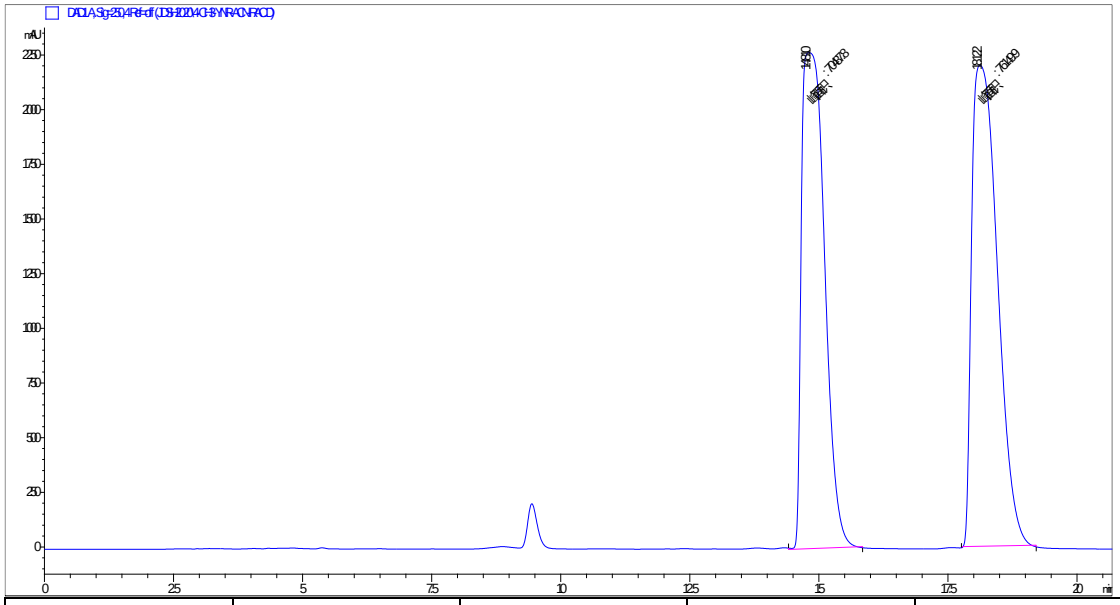
t_R	Channel	Area	height	Area/%
55.923	254nm	35861.2	297.7	49.689
71.235	254nm	36310.5	256.5	50.311

Enantioenriched-3cp



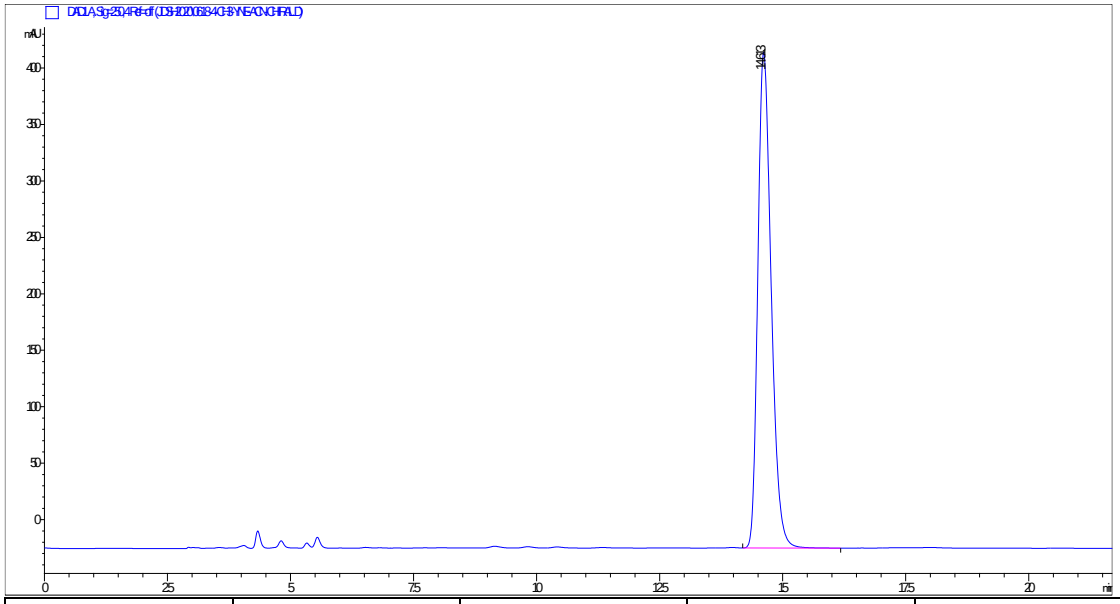
t_R	Channel	Area	height	Area/%
57.606	254nm	31158.8	260.2	92.298
74.157	254nm	2600	21.6	7.702

Racemic-3da



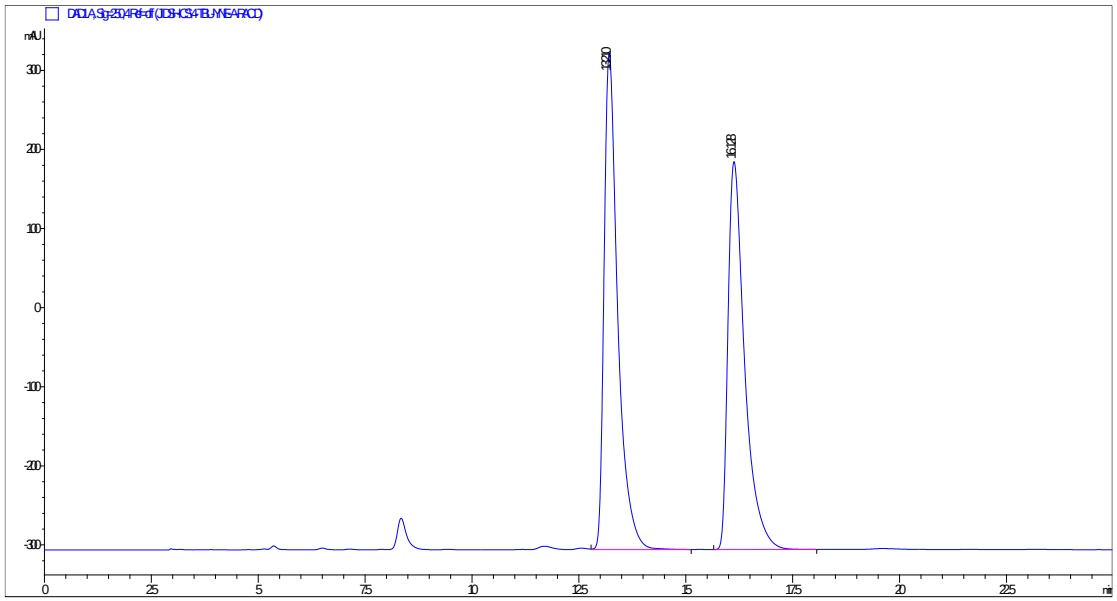
t_R	Channel	Area	Height	Area%
14.81	254nm	76487.8	2268.9	51.0
18.122	254nm	76149.9	2199.8	49.0

Enantioenriched -3da



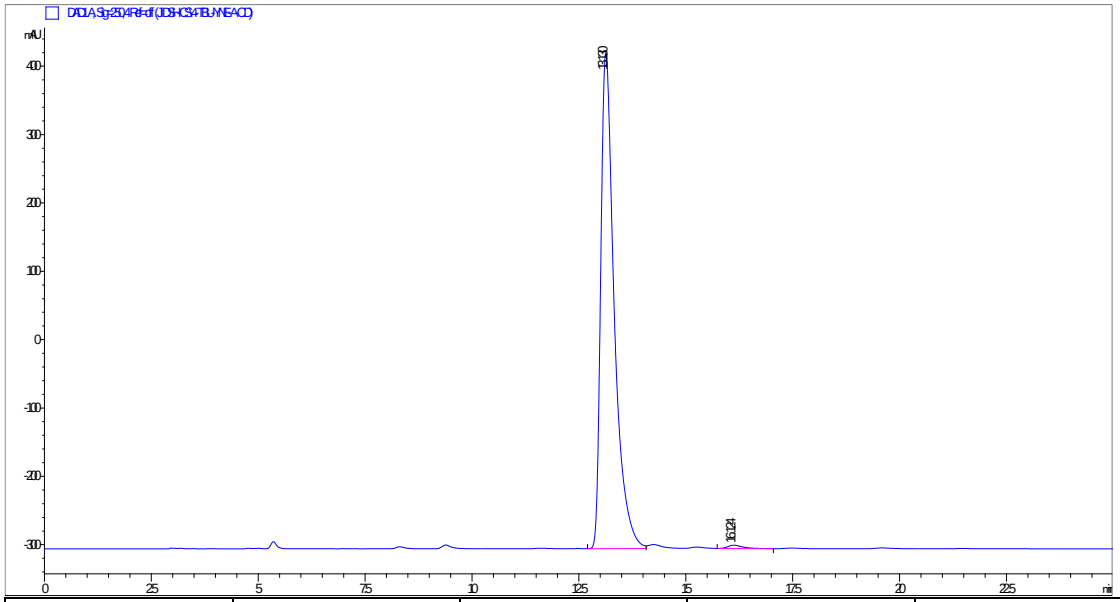
t_R	Channel	Area	Height	Area%
14.61	254nm	76487.8	8272.1	100
-	254nm	-	-	-

Racemic-3ea



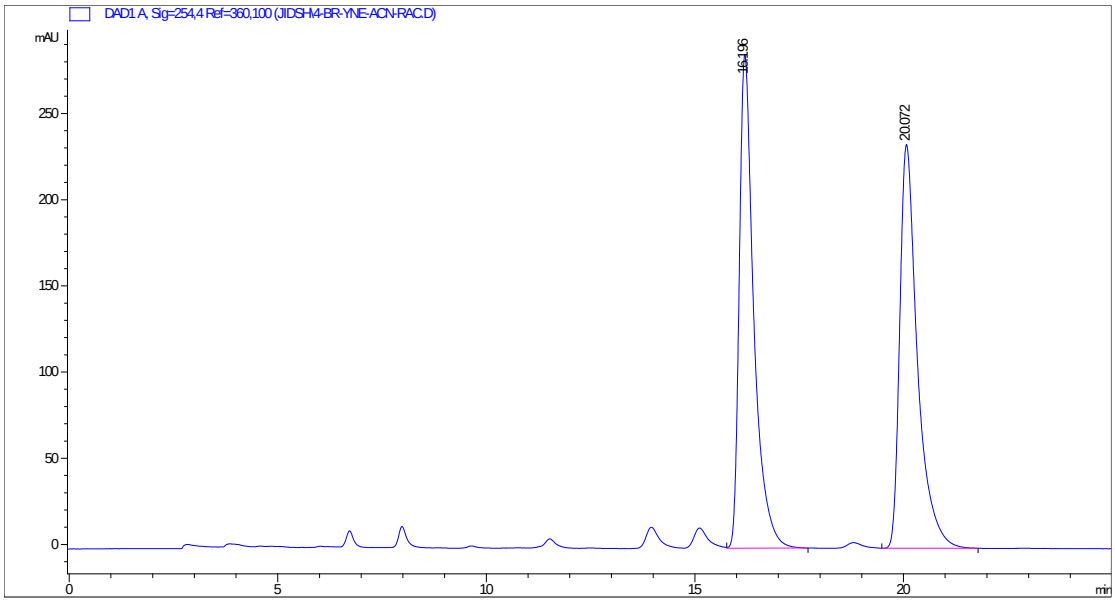
t_R	Channel	Area	Height	Area%
13.21	254nm	13969	627.4	50.091
16.128	254nm	13815.9	480.6	49.909

Enantioenriched-3ea



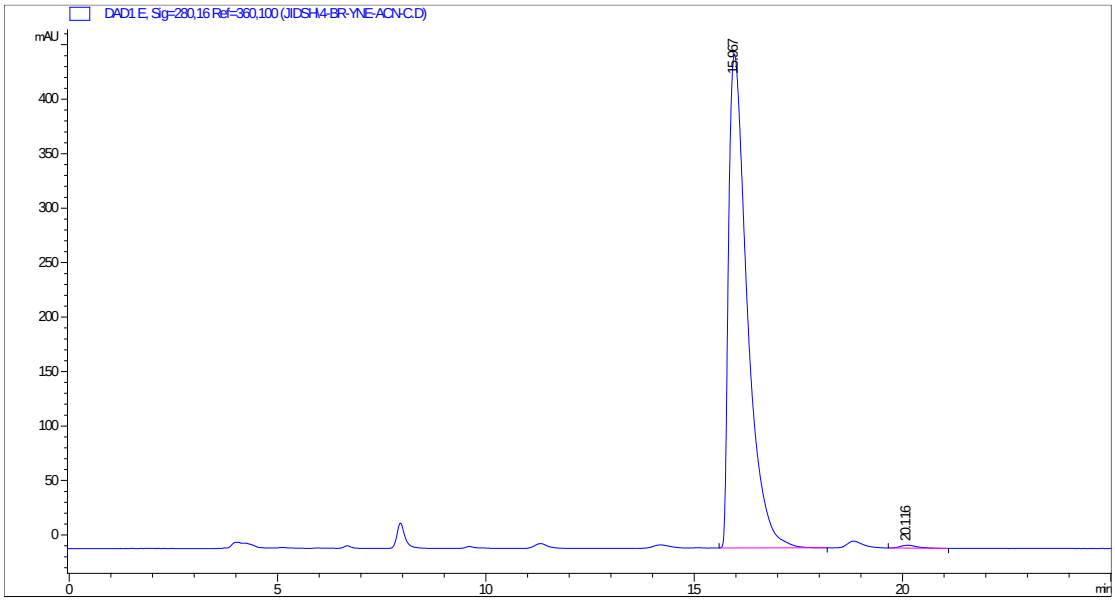
t_R	Channel	Area	Height	Area%
13.13	254nm	15943	725.7	99.277
16.124	254nm	116.1	4.8	0.723

Racemic-3fa



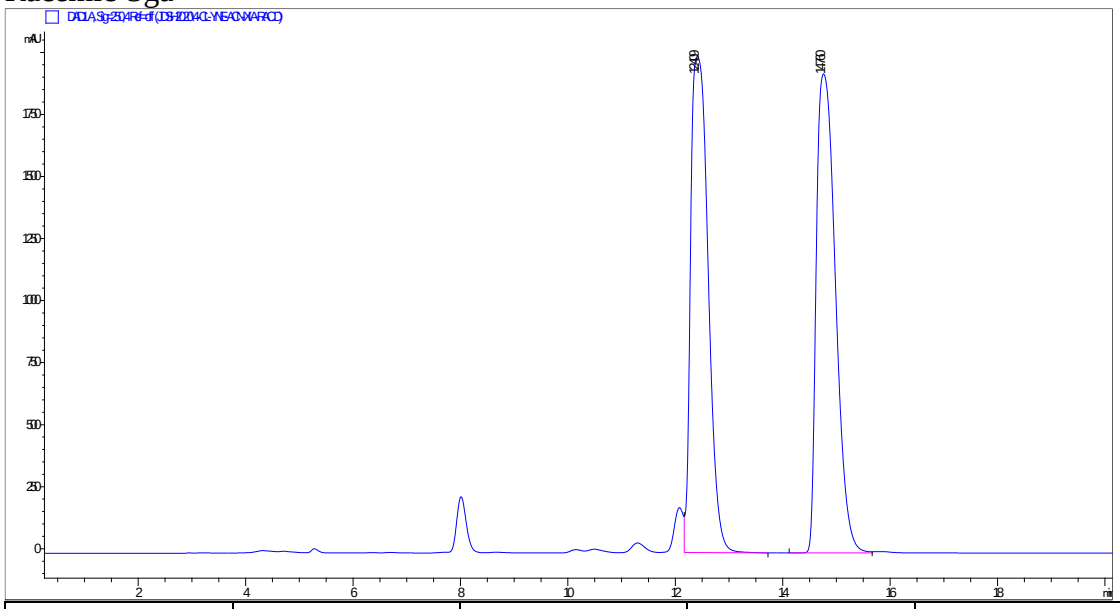
t_R	Channel	Area	Height	Area%
16.196	254nm	6939	286.2	50.172
20.072	254nm	6891.4	234.3	49.828

Enantioenriched-3fa



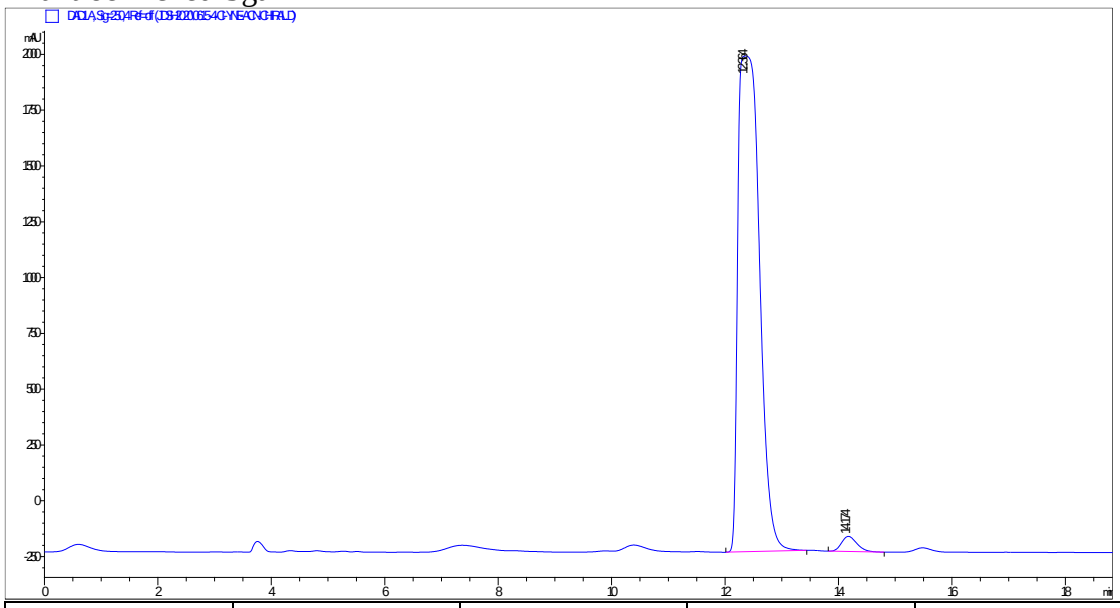
t_R	Channel	Area	Height	Area%
15.967	254nm	14107.2	453.2	99.474
20.116	254nm	74.5	2.6	0.526

Racemic-3ga



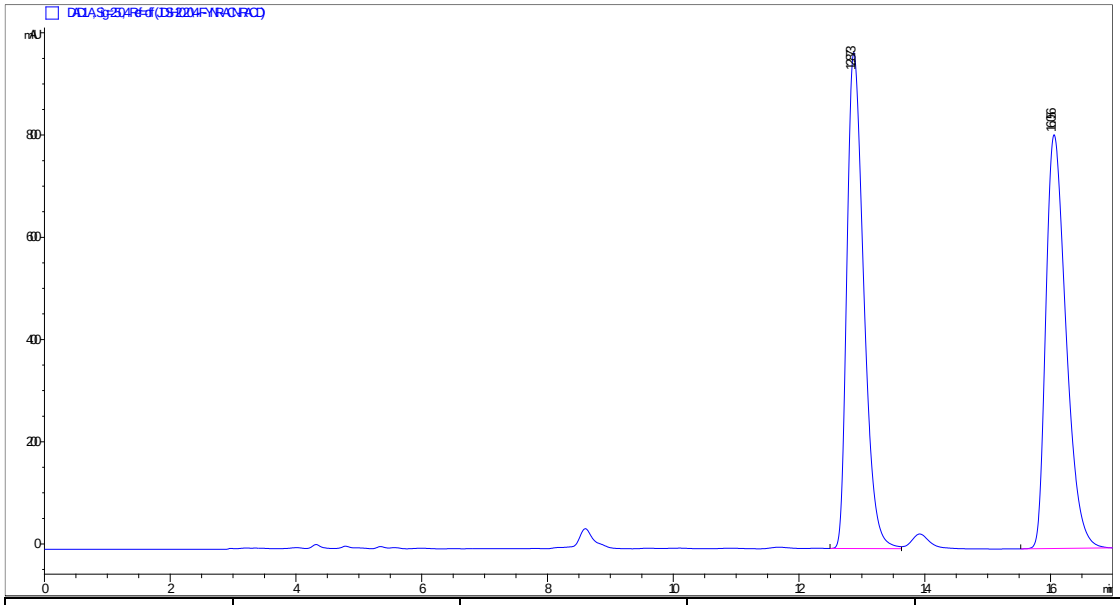
t_R	Channel	Area	Height	Area%
12.4	254nm	45449	1998.5	48.8
14.7	254nm	47714	1929.7	51.2

Enantioenriched-3ga



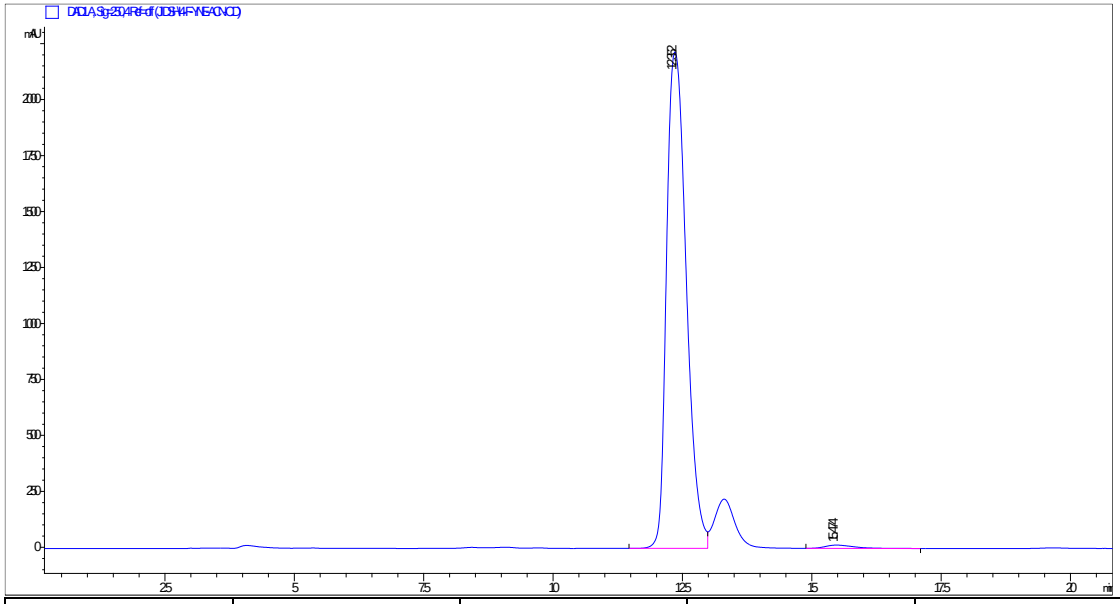
t_R	Channel	Area	Height	Area%
12.4	254nm	58440	2221.7	98.0
14.2	254nm	1281	67.8	2.0

Racemic-3ha



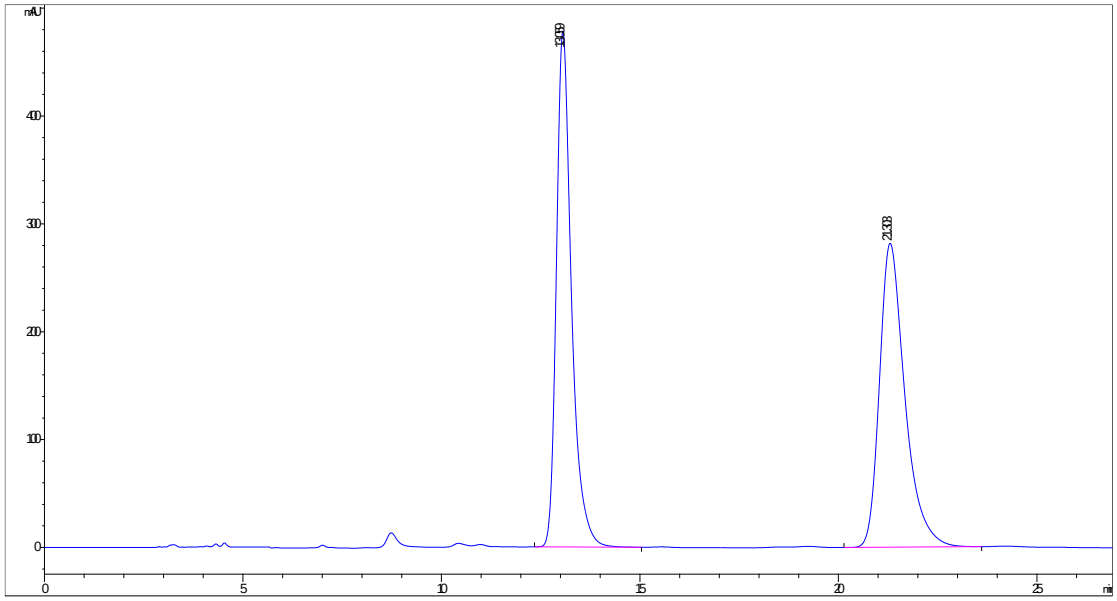
t_R	Channel	Area	Height	Area%
12.8	254nm	18046	970.3	50
16.0	254nm	18050	809.6	50

Enantioenriched-3ha



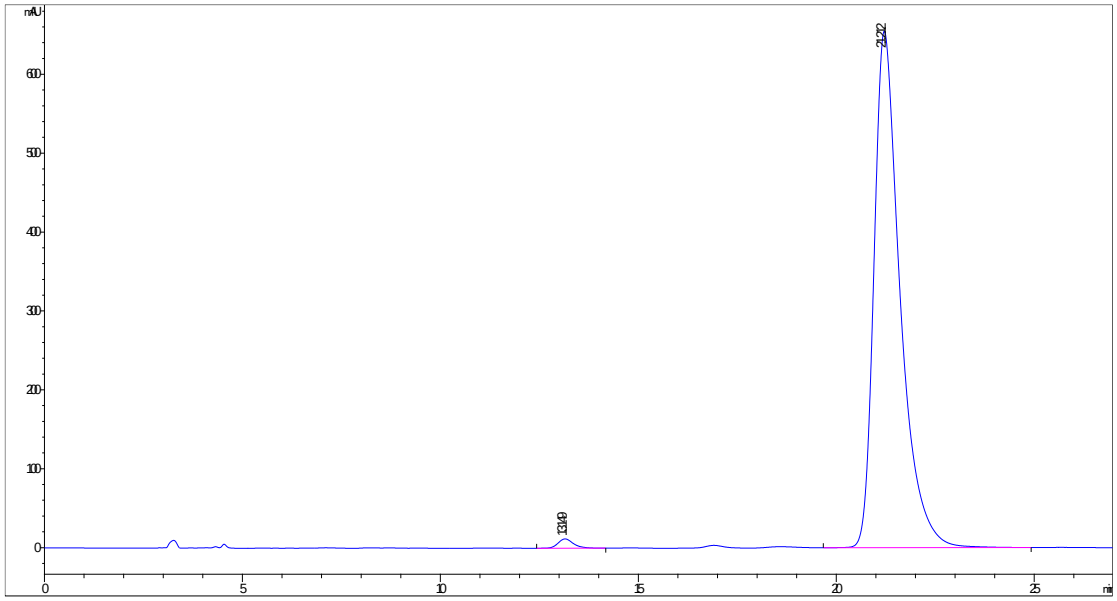
t_R	Channel	Area	Height	Area%
12.3	254nm	58595.4	2217.4	99.1
15.4	254nm	530.1	14.6	0.9

Racemic-3ia



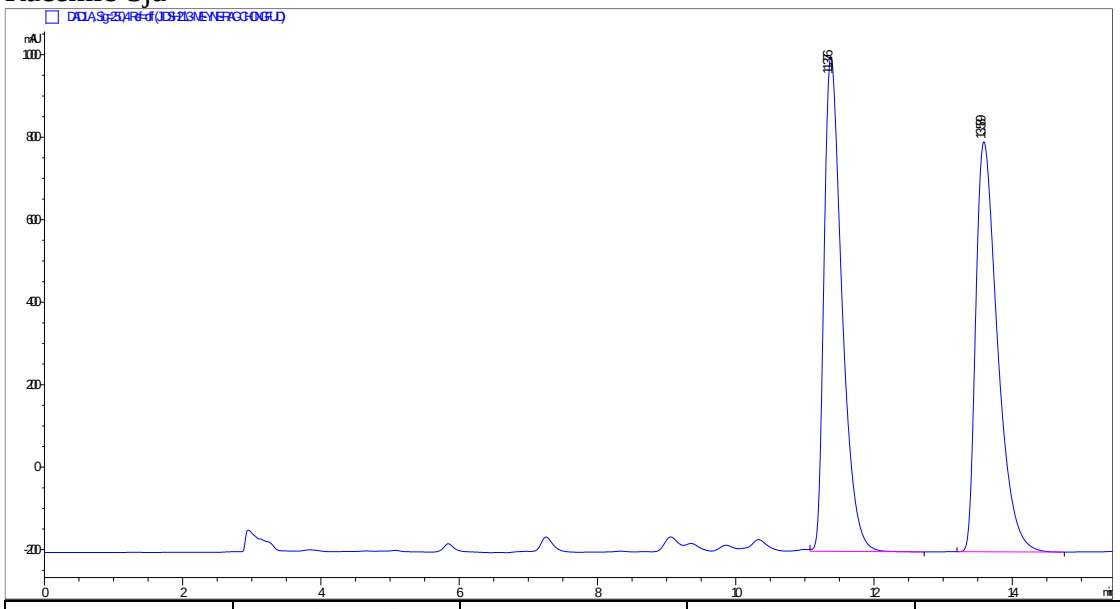
t_R	Channel	Area	Height	Area%
13.059	254nm	12638.6	478.3	50.21
21.303	254nm	12522.9	281.7	49.79

Enantioenriched-3ia



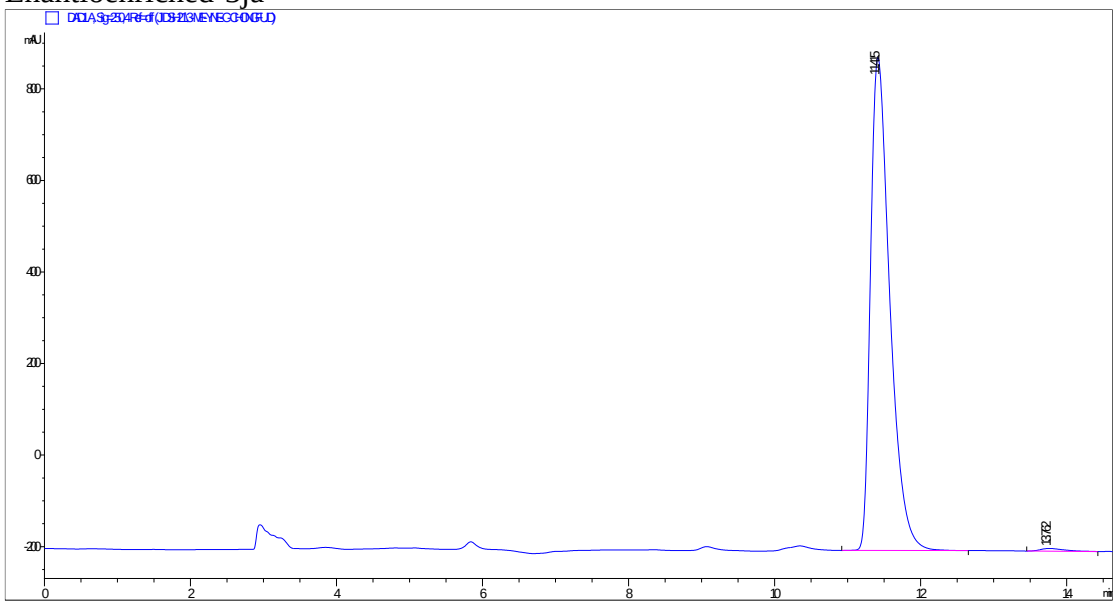
t_R	Channel	Area	Height	Area%
13.149	254nm	318.6	11.8	1.05
21.212	254nm	29985	654.8	98.95

Racemic-3ja



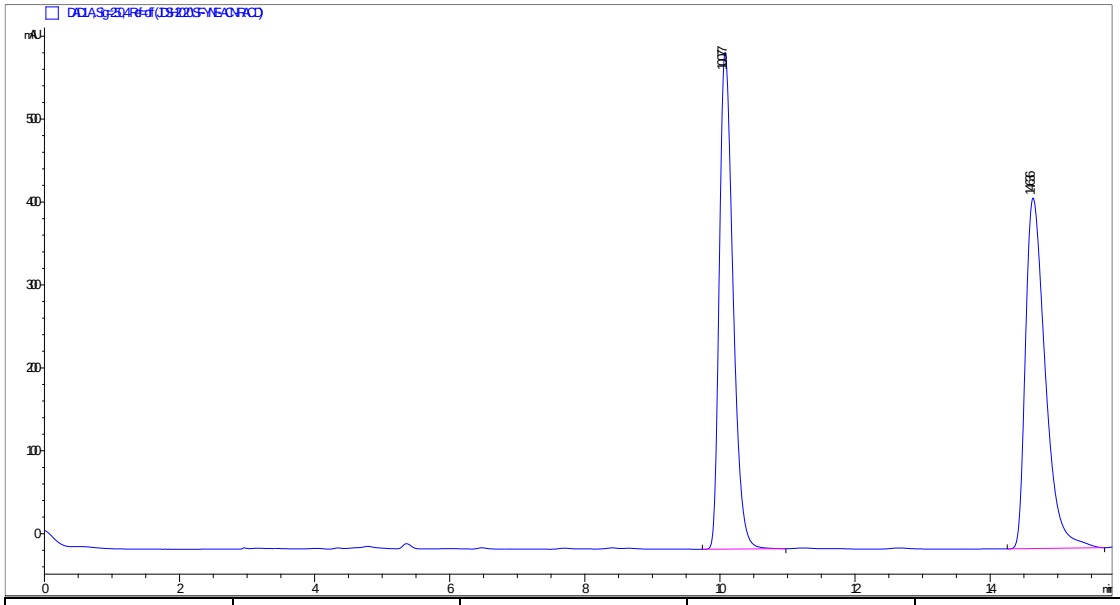
t_R	Channel	Area	height	Area/%
11.376	254nm	16111.8	1386.6	50.7
13.589	254nm	15617.2	15617.2	49.3

Enantioenriched-3ja



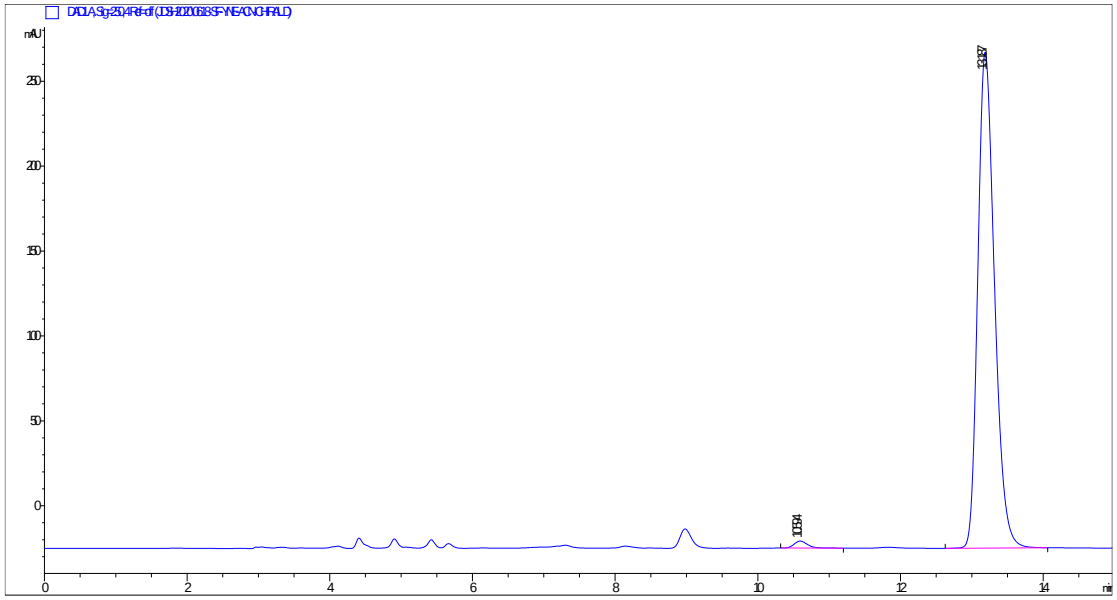
t_R	Channel	Area	height	Area/%
11.415	254nm	19792.9	1077.1	99.322
13.762	254nm	135.1	6.1	0.678

Racemic-3ka



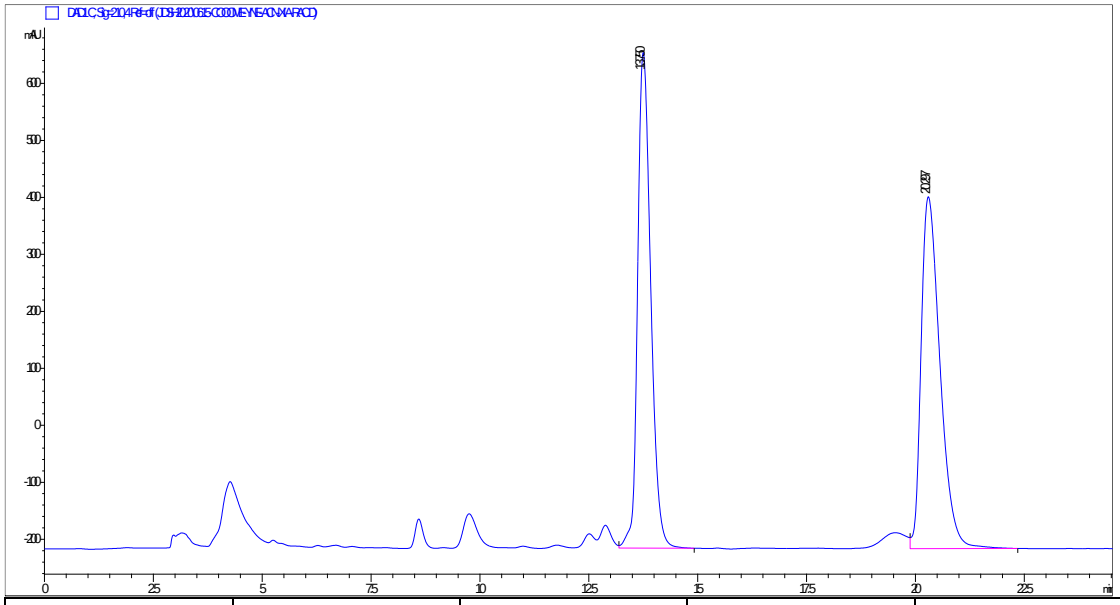
t_R	Channel	Area	Height	Area%
10.07	254nm	8429.1	599	49.4
14.64	254nm	8617.1	422.9	50.5

Enantioenriched-3ka



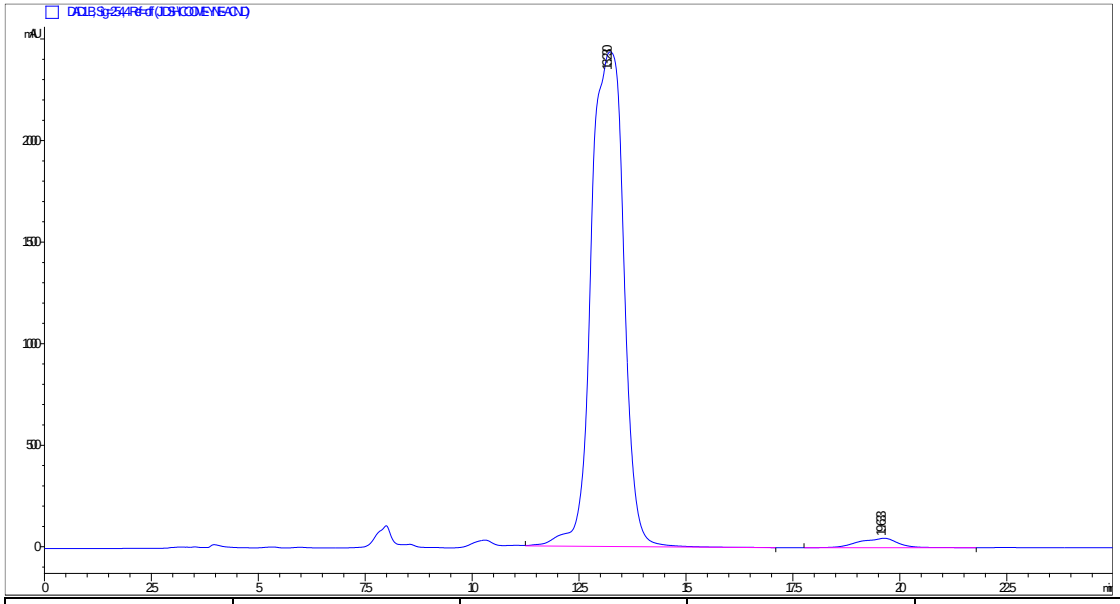
t_R	Channel	Area	Height	Area%
10.59	254nm	54.5	4.1	1.1
13.18	254nm	4742	292.1	98.9

Racemic-3la



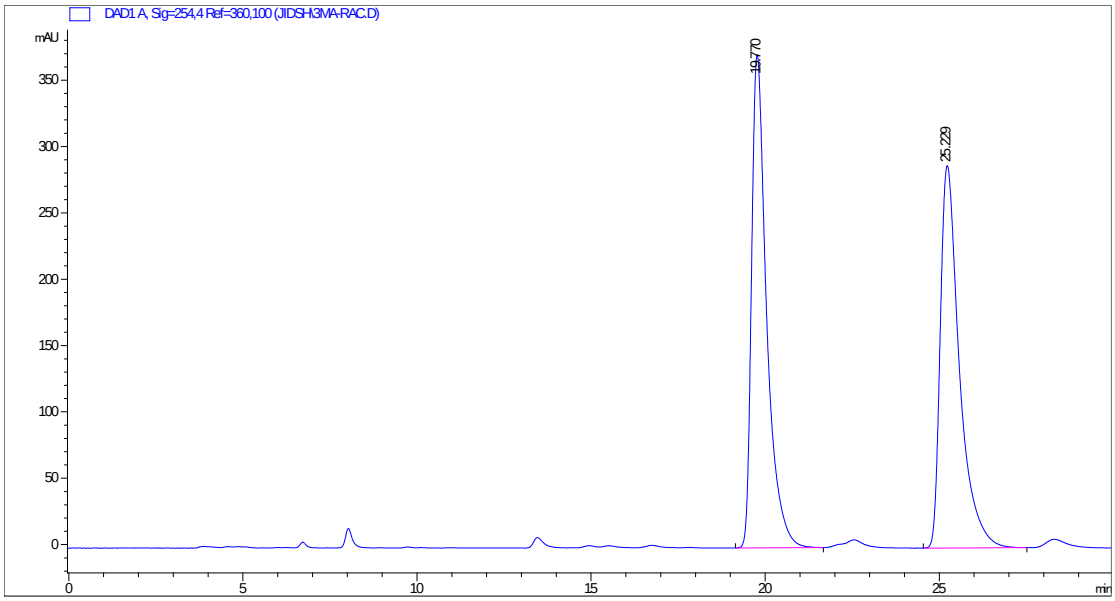
t_R	Channel	Area	Height	Area%
13.7	254nm	18186.7	869.7	49
20.3	254nm	18652	617.4	51

Enantioenriched-3la



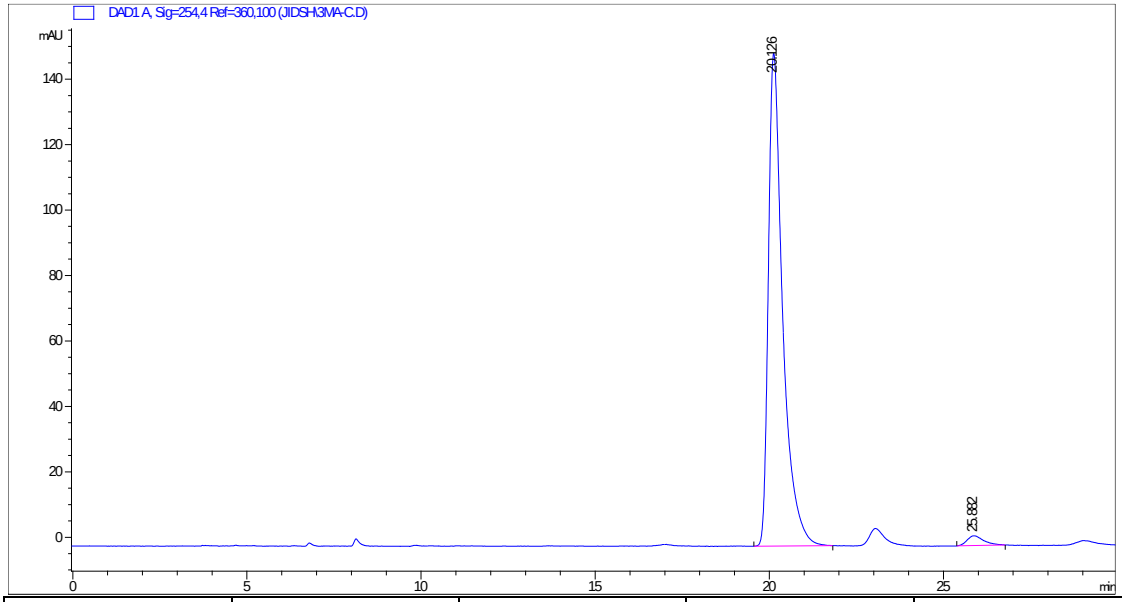
t_R	Channel	Area	Height	Area%
13.2	254nm	128518	2435	97.7
19.6	254nm	2984.7	46.8	2.3

Racemic-3ma



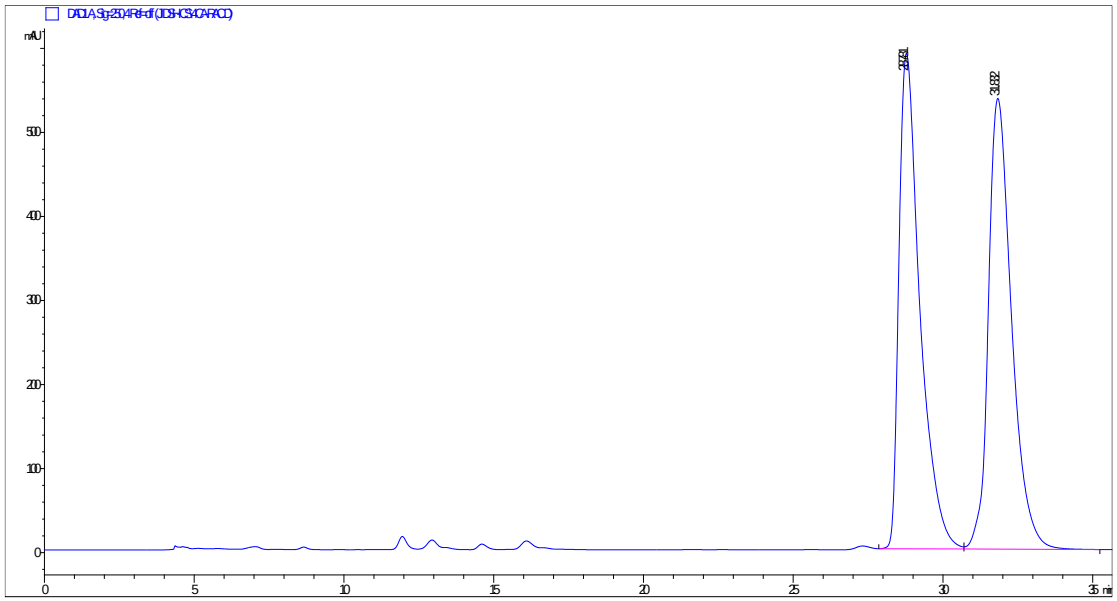
t_R	Channel	Area	height	Area/%
19.77	254nm	11185.8	371.7	50.469
25.229	254nm	10977.8	288.2	49.531

Enantioenriched-3ma



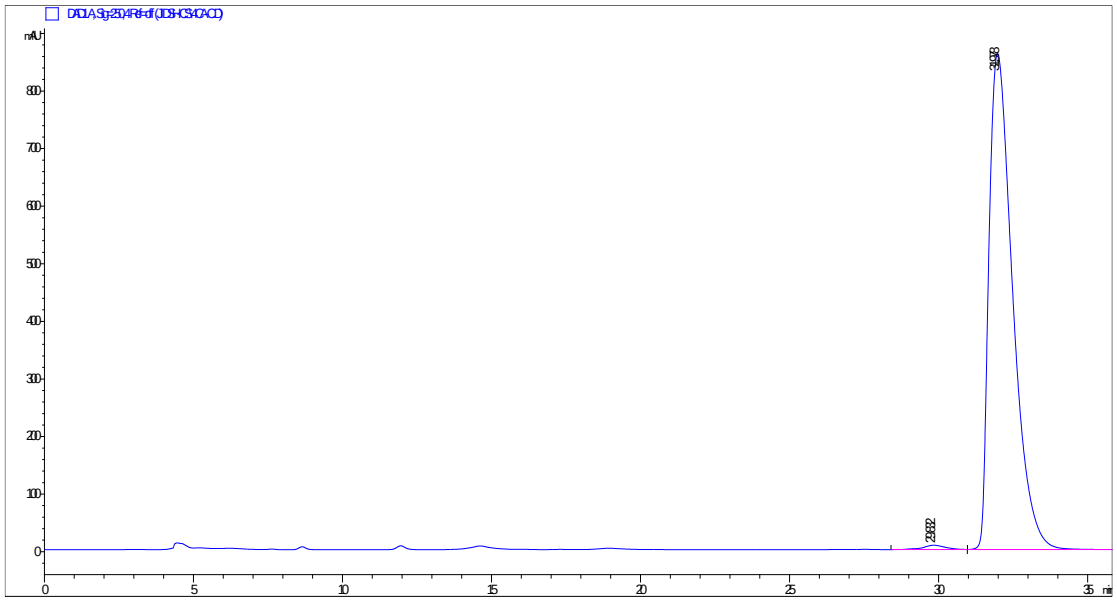
t_R	Channel	Area	height	Area/%
20.126	254nm	4306.7	150.6	97.737
25.882	254nm	99.7	3	2.263

Racemic-4ca



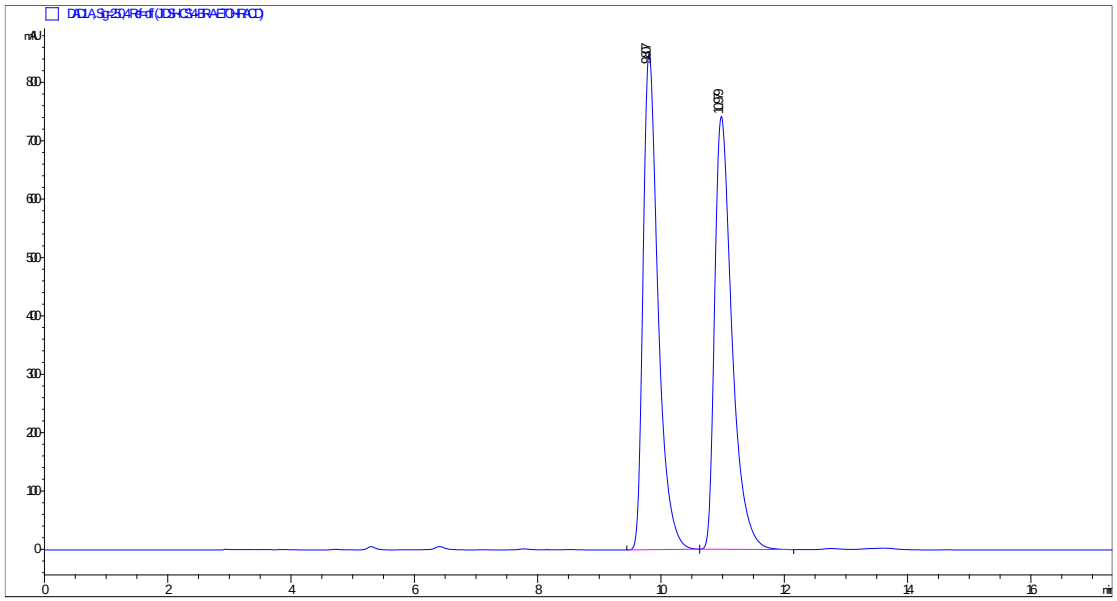
t_R	Channel	Area	Height	Area%
28.781	254nm	28653.2	589.5	49.81
31.832	254nm	28868	536.3	50.19

Enantioenriched-4ca



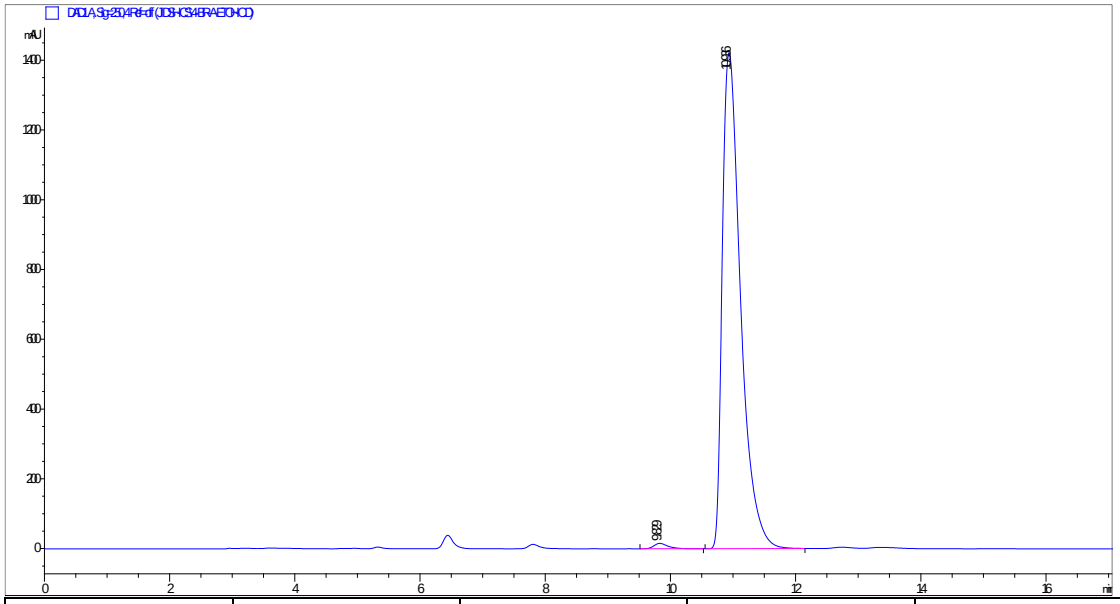
t_R	Channel	Area	Height	Area%
29.832	254nm	332.1	7.5	0.498
31.987	254nm	47725.8	861.3	99.502

Racemic-4cb



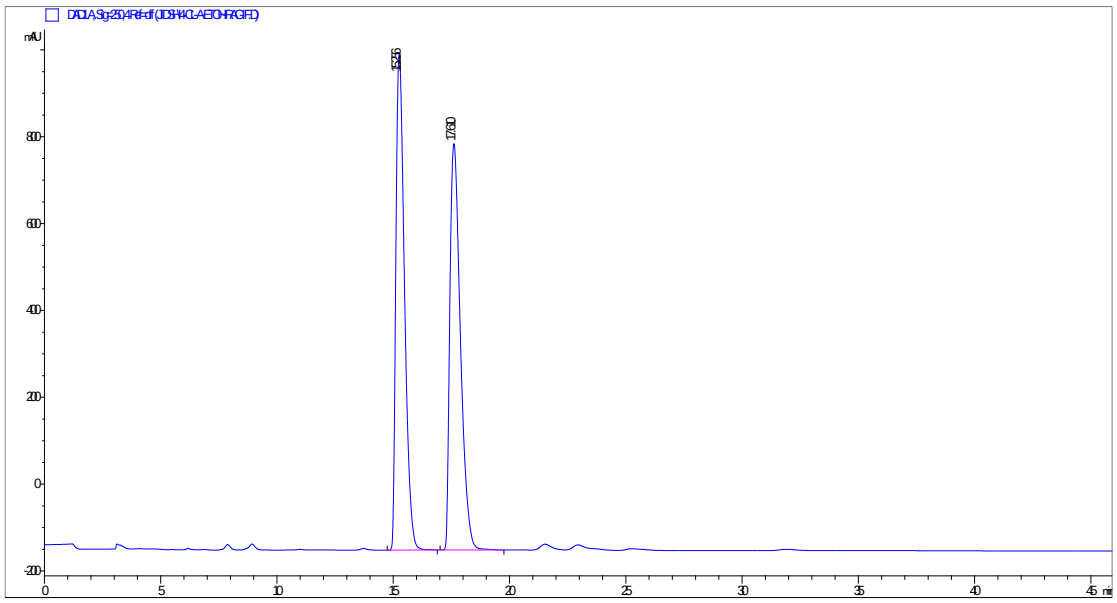
t_R	Channel	Area	Height	Area%
9.807	254nm	14413	850.1	49.875
10.979	254nm	14485.6	741.6	50.125

Enantioenriched-4cb



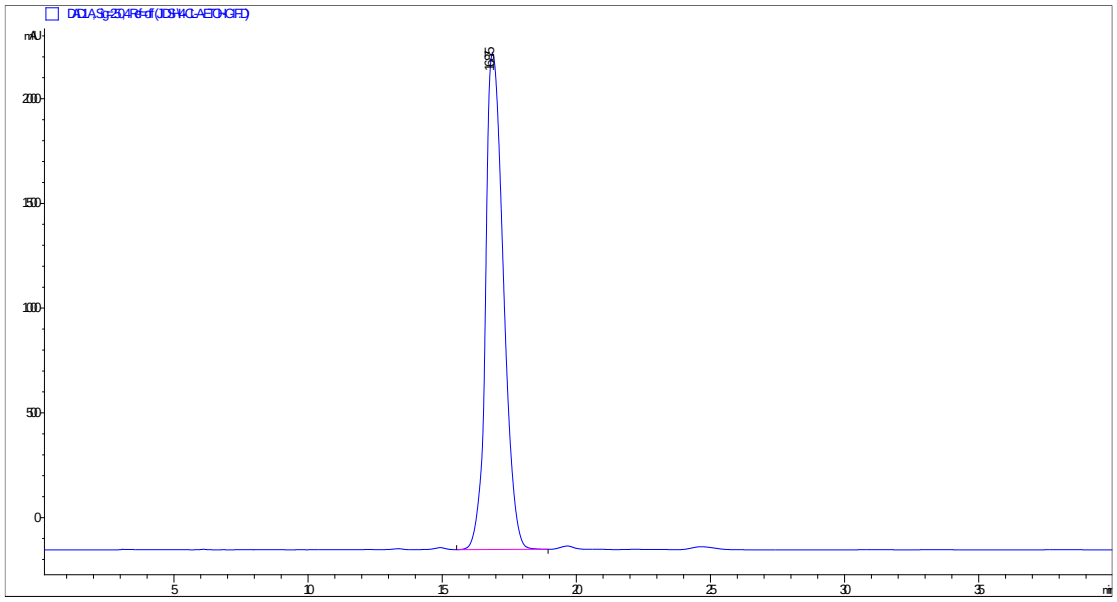
t_R	Channel	Area	Height	Area%
9.829	254nm	244.1	15.4	0.839
10.939	254nm	28855.4	1422.4	99.161

Racemic-4cc



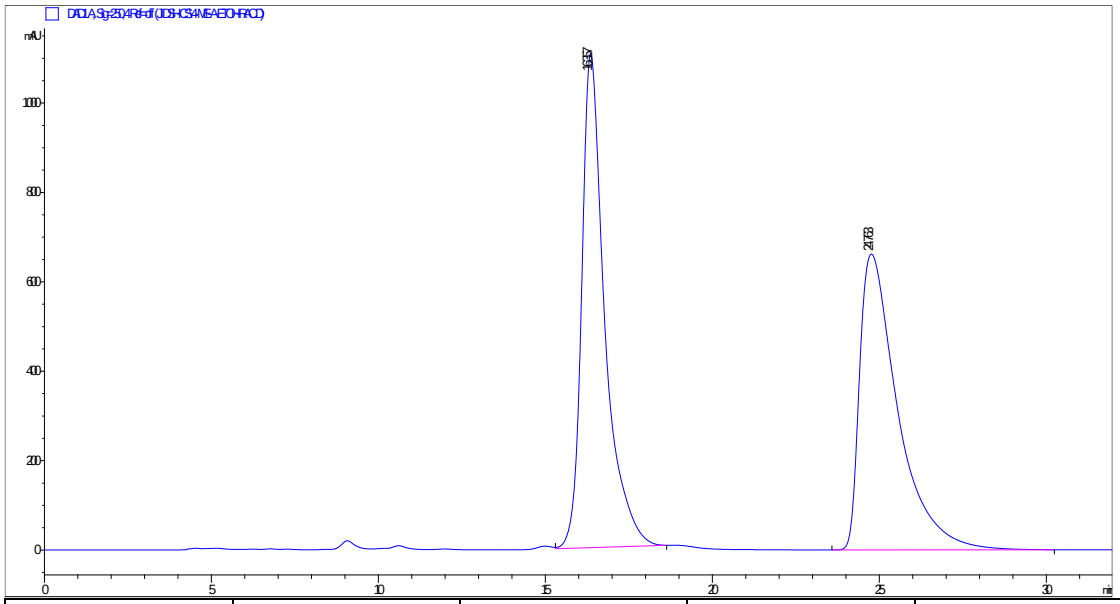
t_R	Channel	Area	Height	Area%
15.256	254nm	29478.7	1141.3	50
17.61	254nm	29469.8	935.7	50

Enantioenriched-4cc



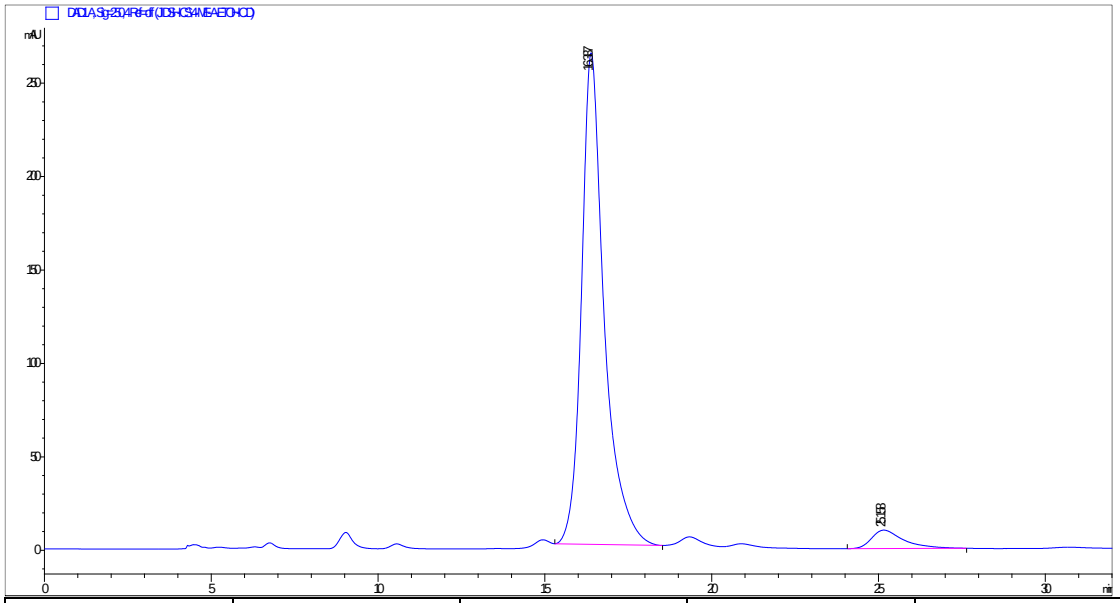
t_R	Channel	Area	Height	Area%
-	254nm	-	-	-
16.875	254nm	109713.1	2368.4	100

Racemic-4cd



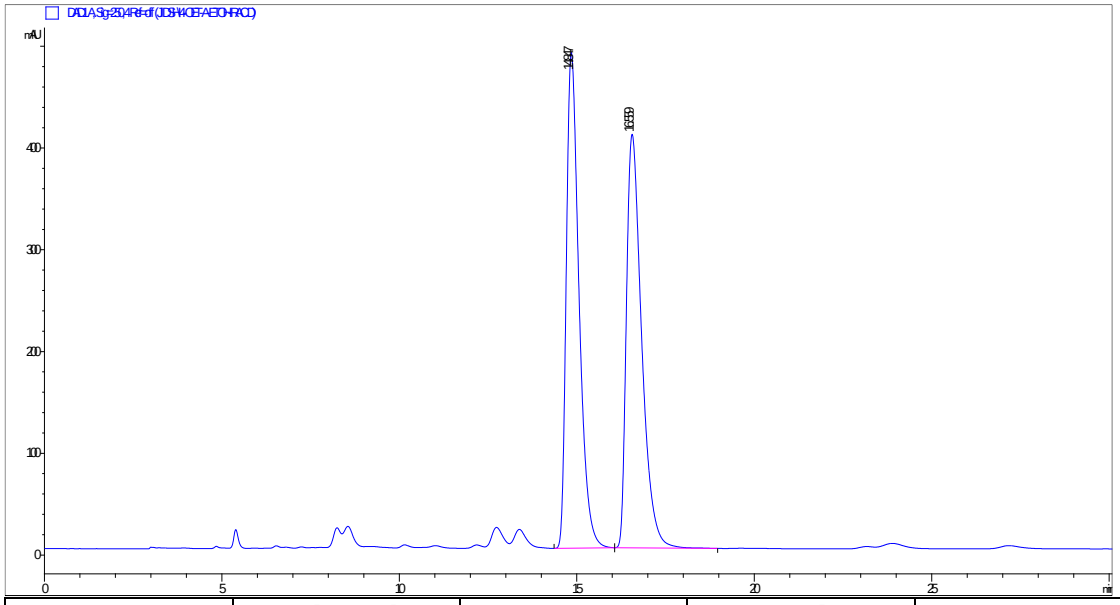
t_R	Channel	Area	Height	Area%
16.357	254nm	52969.2	1105.3	50.271
24.763	254nm	52397.9	661.6	49.729

Enantioenriched-4cd



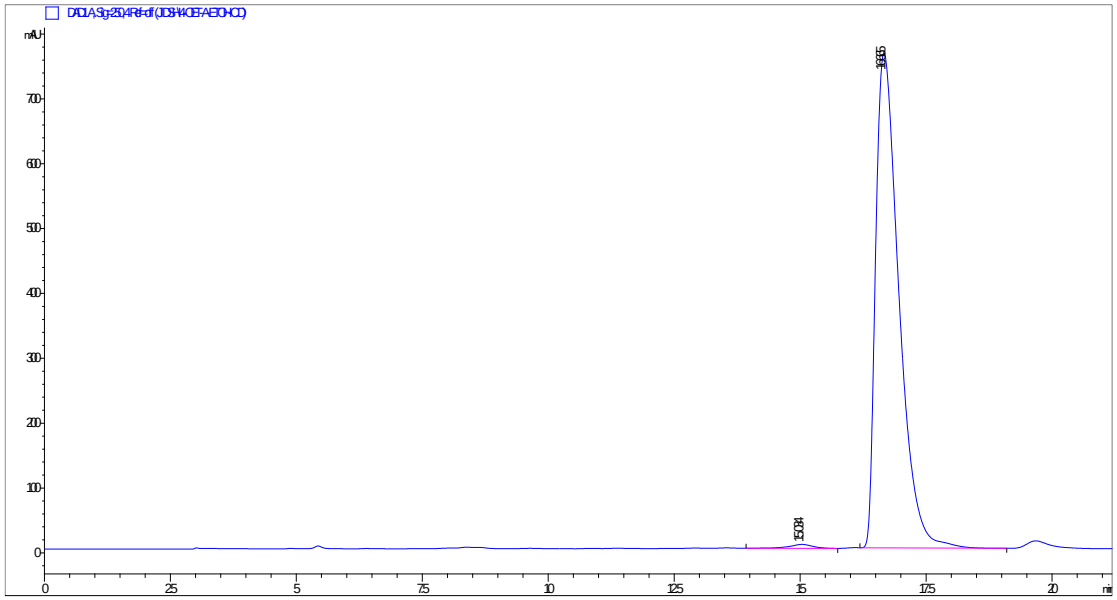
t_R	Channel	Area	Height	Area%
16.387	254nm	12422.5	263.1	94.975
24.158	254nm	658.3	9.9	5.025

Racemic-4ce



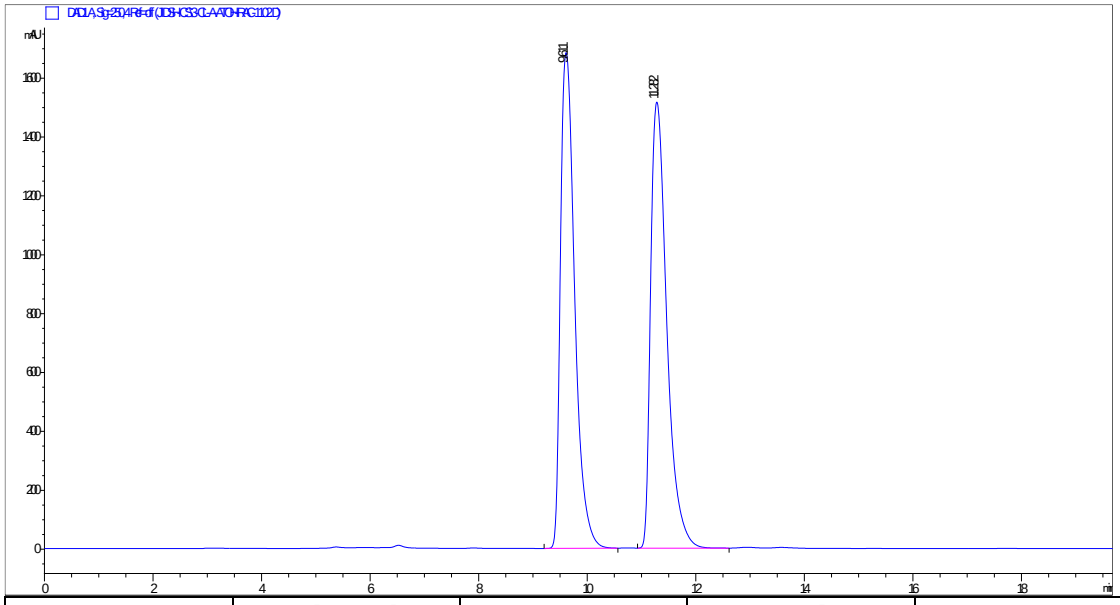
t_R	Channel	Area	Height	Area%
14.847	254nm	12127.4	487.1	50
16.559	254nm	12090.8	406.5	50

Enantioenriched-4ce



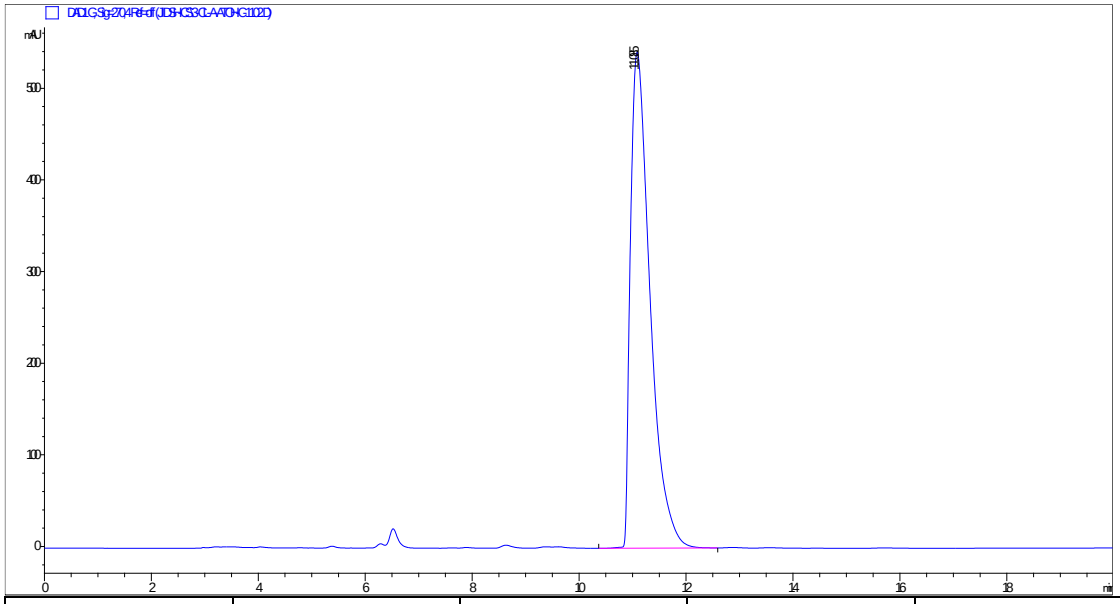
t_R	Channel	Area	Height	Area%
15.034	254nm	198.7	6	0.8
16.665	254nm	24457.1	763.8	99.2

Racemic-4cf



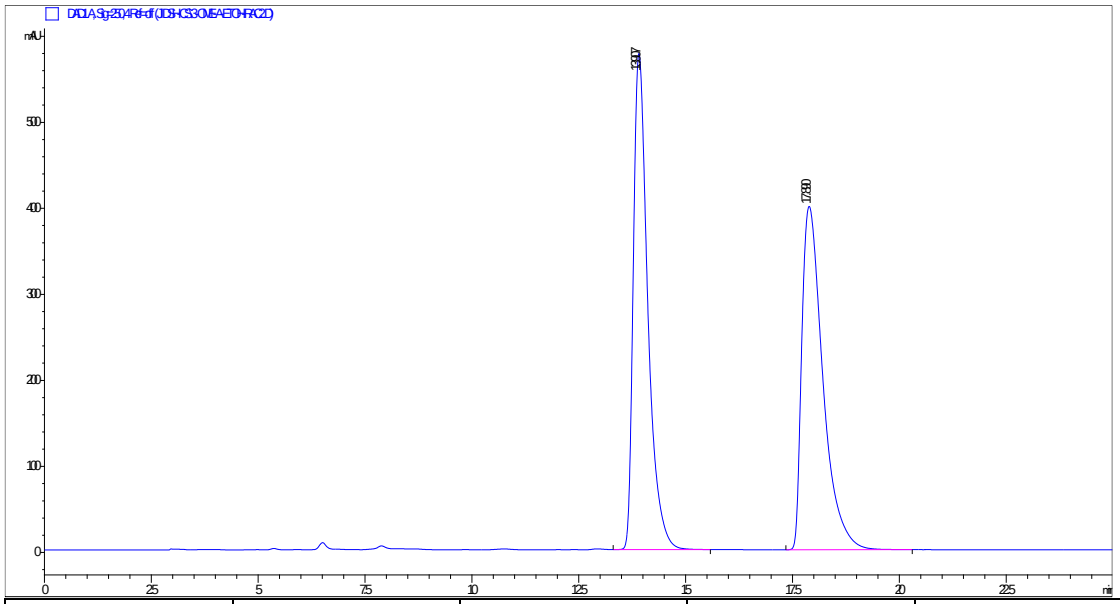
t_R	Channel	Area	Height	Area%
9.611	254nm	30768.9	1684.2	49.565
11.282	254nm	31309.2	1515.4	50.435

Enantioenriched-4cf



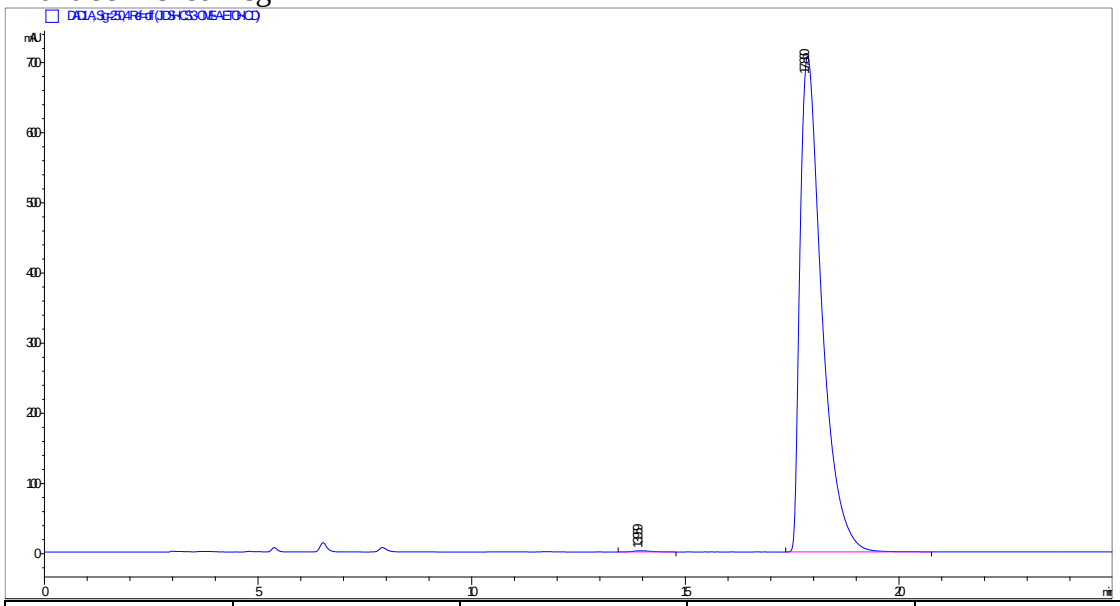
t_R	Channel	Area	Height	Area%
9.611	254nm	-	-	-
11.085	254nm	13789.9	541	100

Racemic-4cg



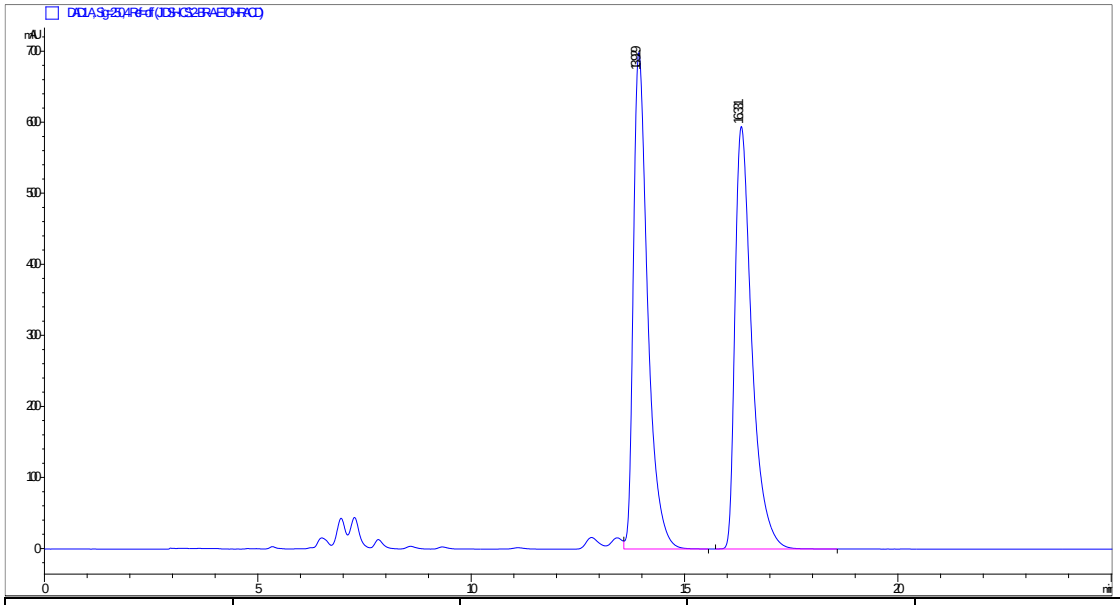
t_R	Channel	Area	Height	Area%
13.907	254nm	13598.3	576.7	49.878
17.89	254nm	13665	399.2	50.122

Enantioenriched-4cg



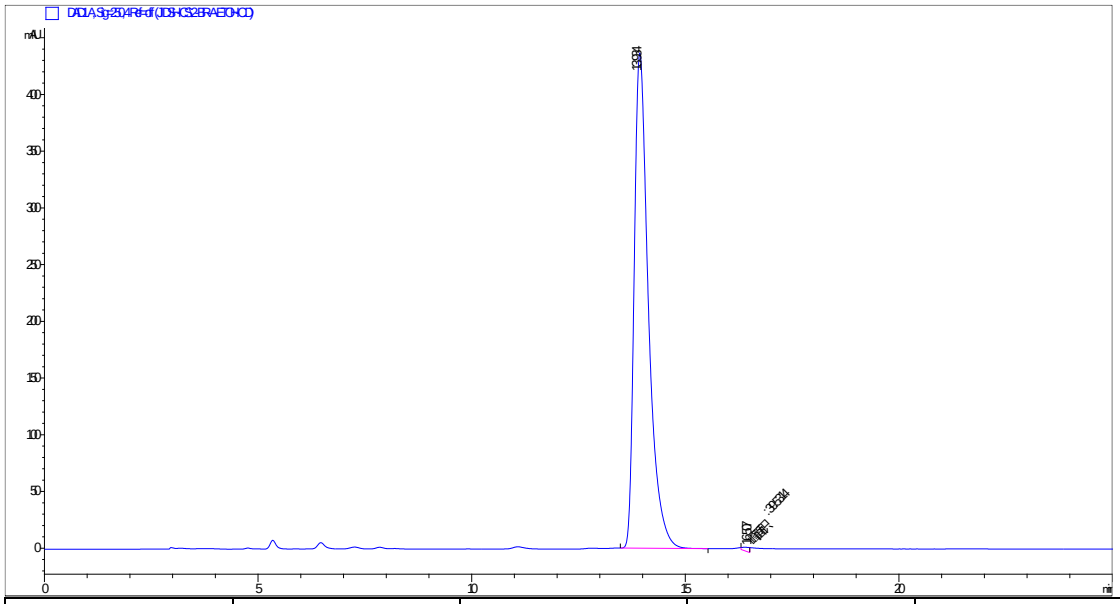
t_R	Channel	Area	Height	Area%
13.959	254nm	50	1.7	0.199
17.86	254nm	25078.7	706.9	99.801

Racemic-4ch



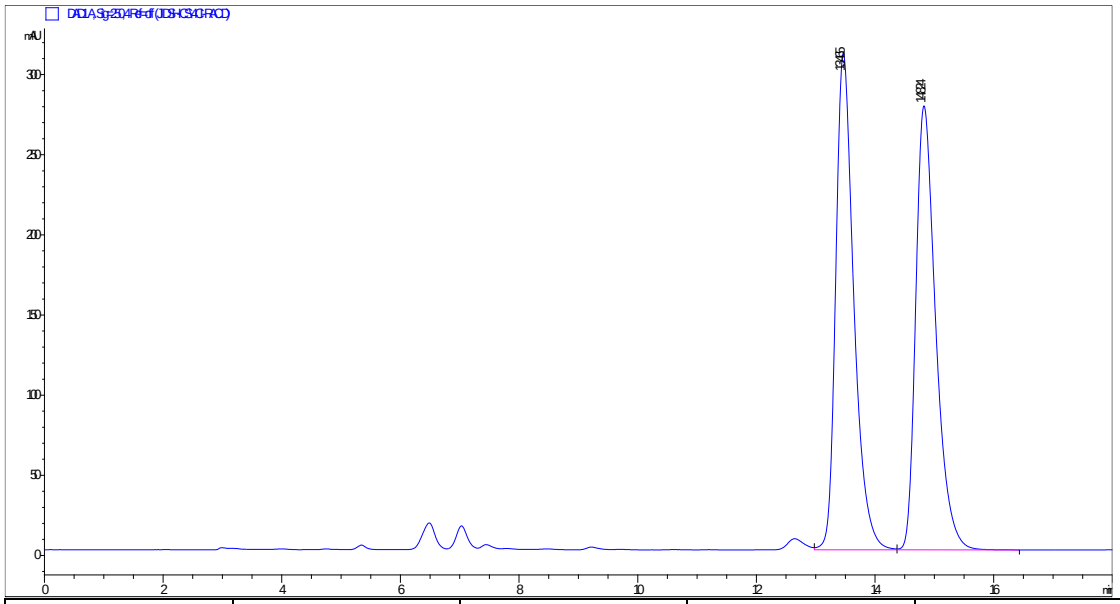
t_R	Channel	Area	Height	Area%
13.929	254nm	16383	698.7	50.106
16.331	254nm	16316.5	594.6	49.894

Enantioenriched-4ch



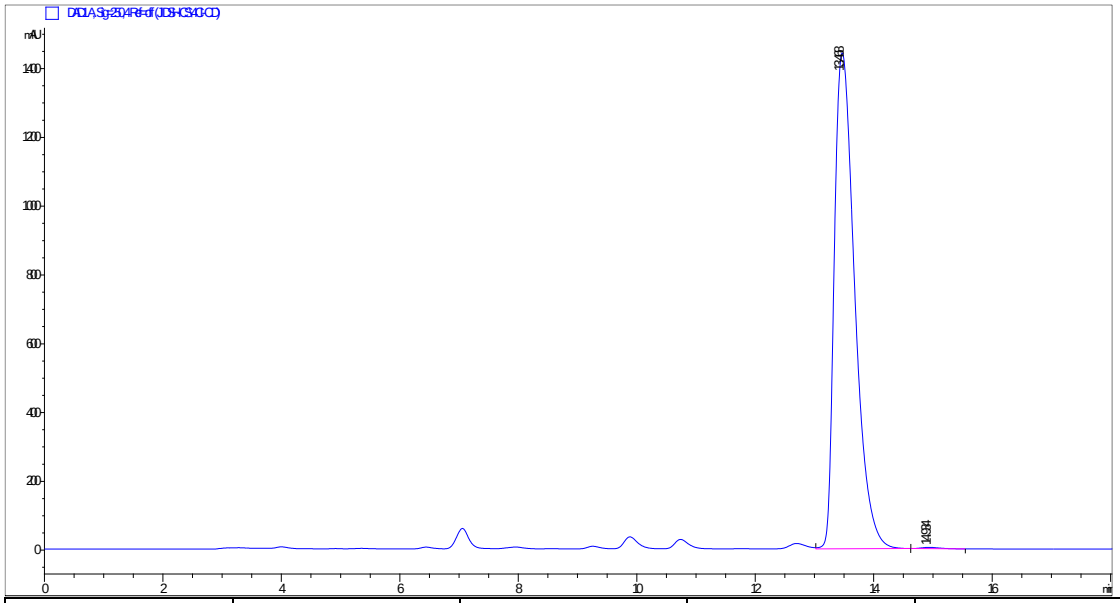
t_R	Channel	Area	Height	Area%
13.934	254nm	10087.3	436.5	99.610
16.507	254nm	39.5	4.3	0.390

Racemic-4ci



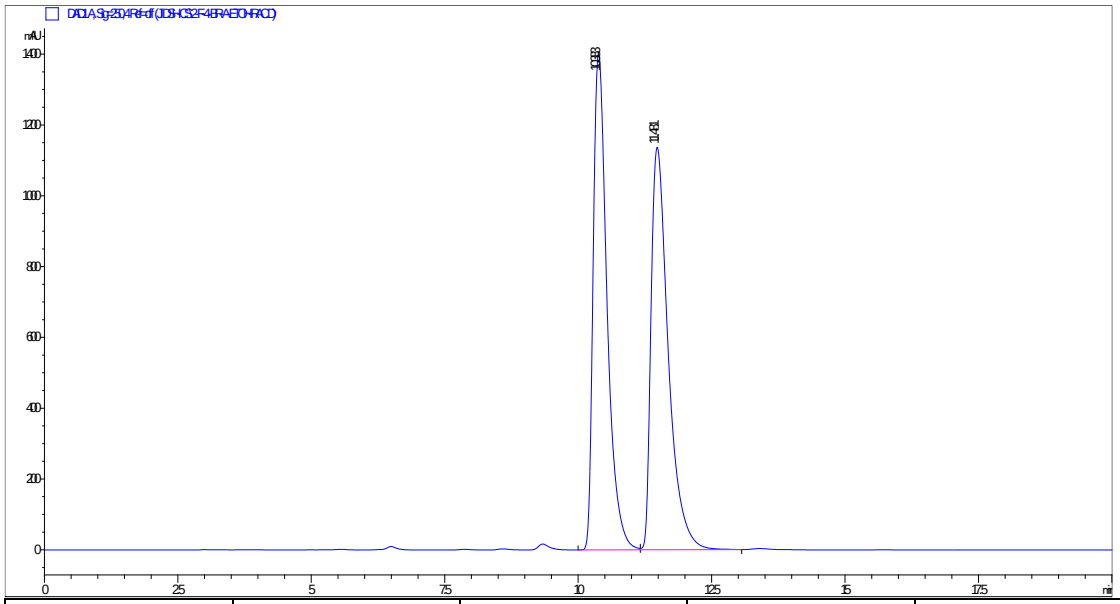
t_R	Channel	Area	Height	Area%
13.465	254nm	6569.5	309.7	50.431
14.824	254nm	6457.2	277.1	49.569

Enantioenriched-4ci



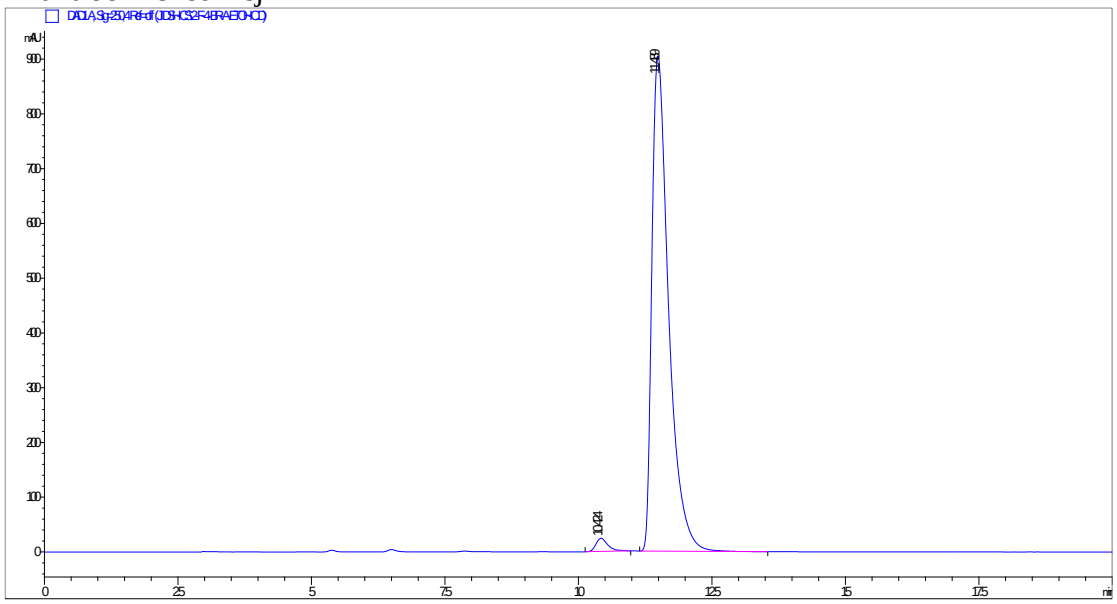
t_R	Channel	Area	Height	Area%
13.468	254nm	34494.6	1441.8	99.782
14.934	254nm	75.5	3.6	0.218

Racemic-4cj



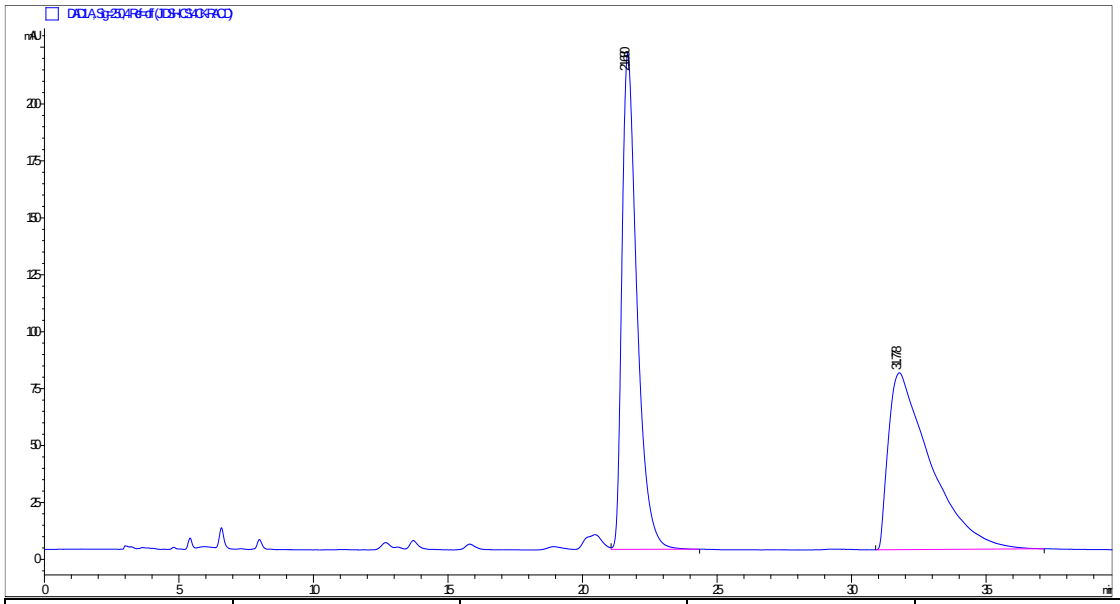
t_R	Channel	Area	Height	Area%
10.383	254nm	25374	1402.6	49.895
11.481	254nm	25491.2	1137	50.115

Enantioenriched-4cj



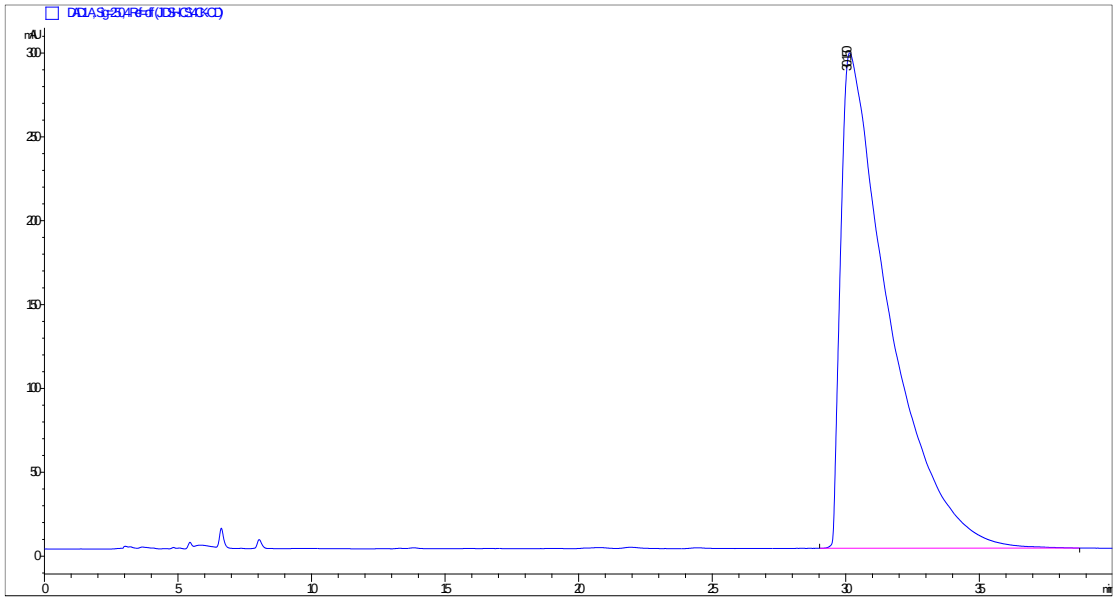
t_R	Channel	Area	Height	Area%
10.424	254nm	373.5	24.1	1.860
11.489	254nm	19713.2	904.7	98.140

Racemic-4ck



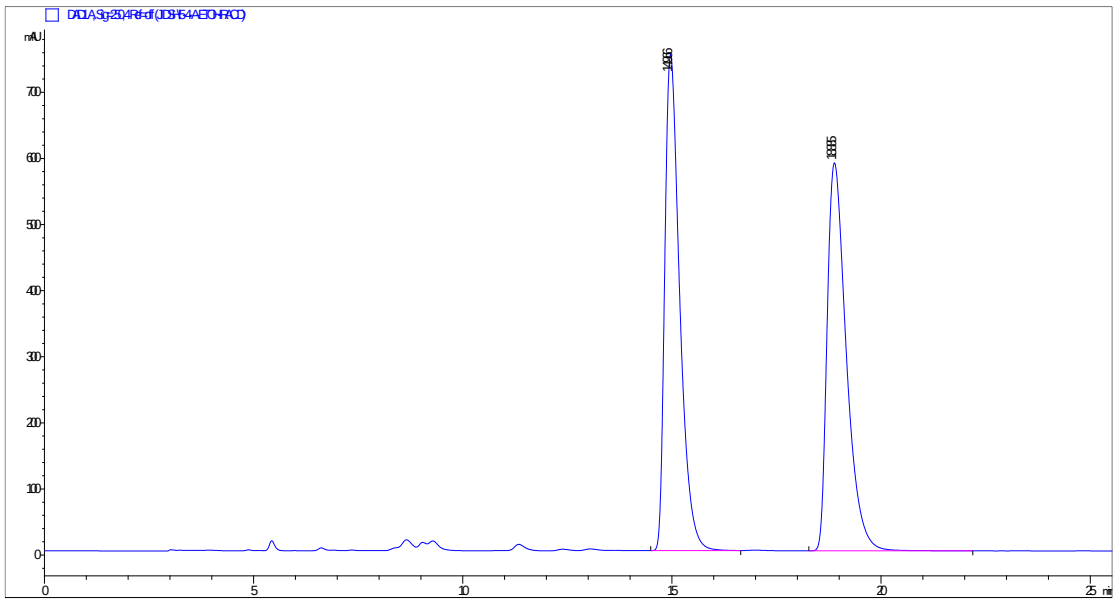
t_R	Channel	Area	Height	Area%
21.68	254nm	8507.4	217.8	50.103
31.778	254nm	8472.4	77.7	49.897

Enantioenriched-4ck



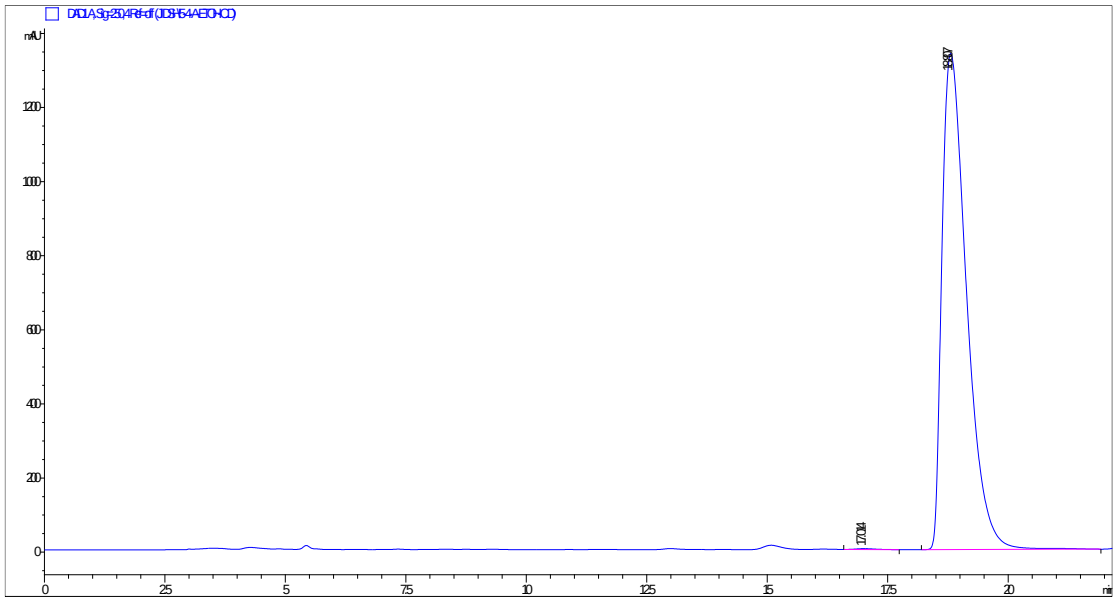
t_R	Channel	Area	Height	Area%
21.68	254nm	-	-	-
31.15	254nm	37151.1	295.4	100

Racemic-4cl



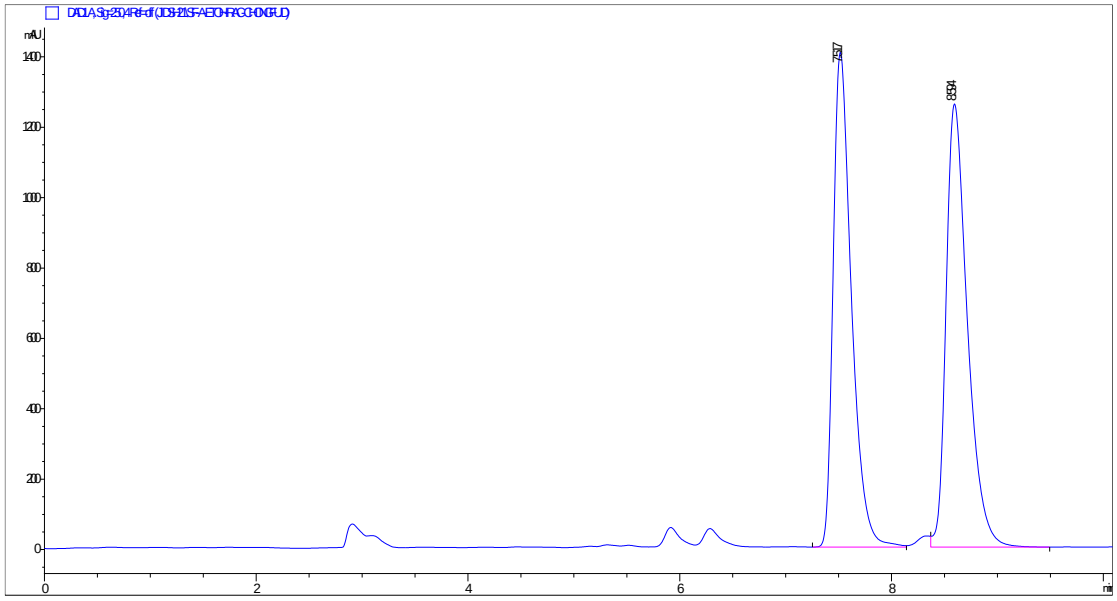
t_R	Channel	Area	Height	Area%
14.966	254nm	18634.3	750.3	50
18.885	254nm	18662.4	587	50

Enantioenriched-4cl



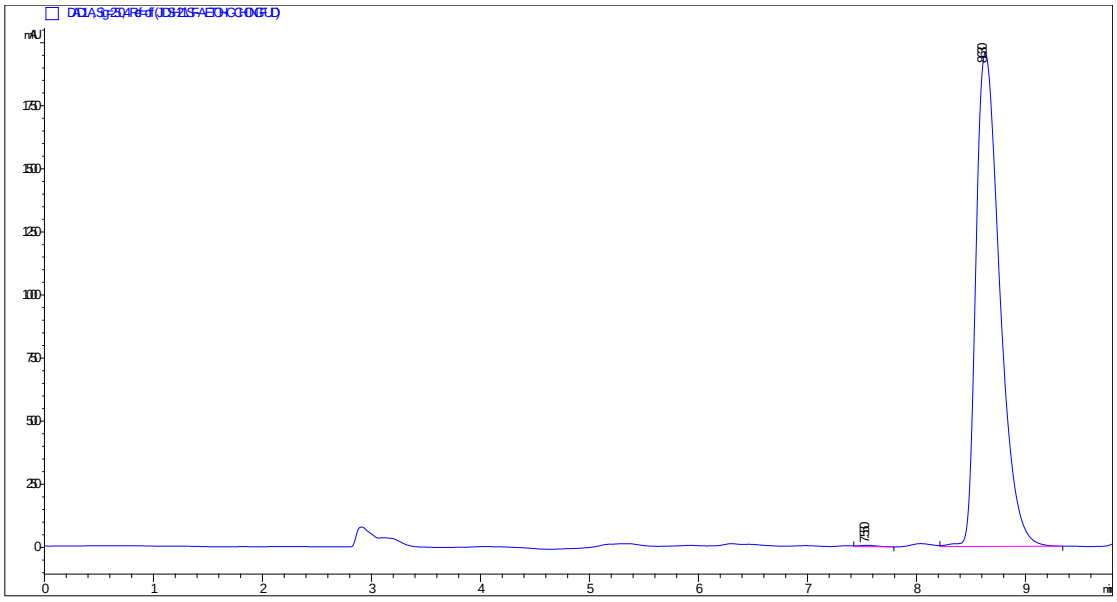
t_R	Channel	Area	Height	Area%
15.014	254nm	63.3	2.3	0.14
18.807	254nm	47465.6	1339.1	99.86

Racemic-4cm



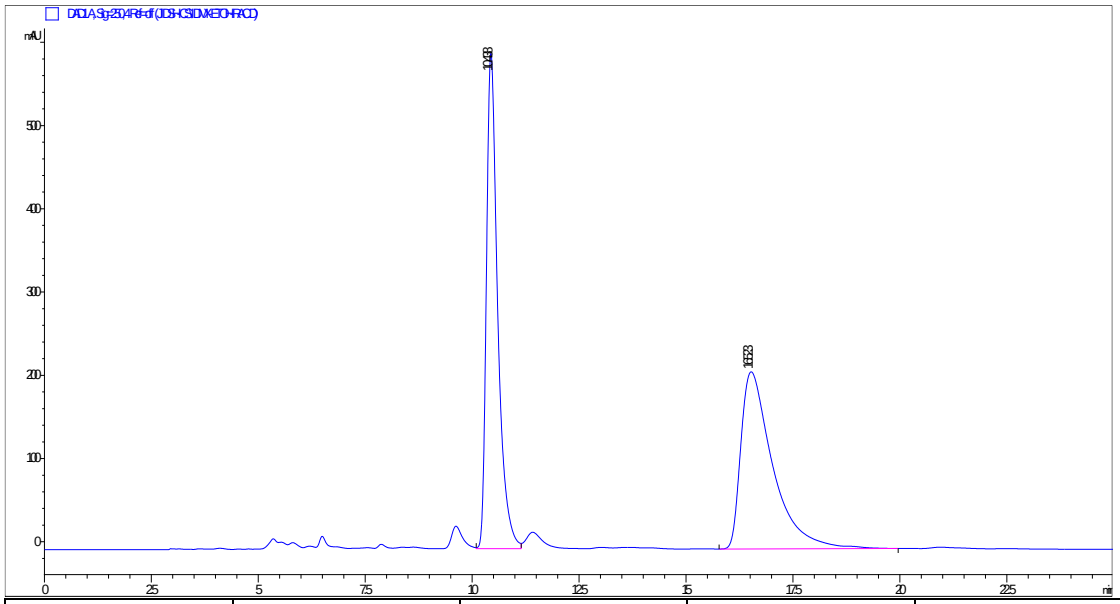
t_R	Channel	Area	height	Area/%
7.517	254nm	16864.5	1406.3	48.866
8.594	254nm	17647	1259.6	53.137

Enantioenriched-4cm



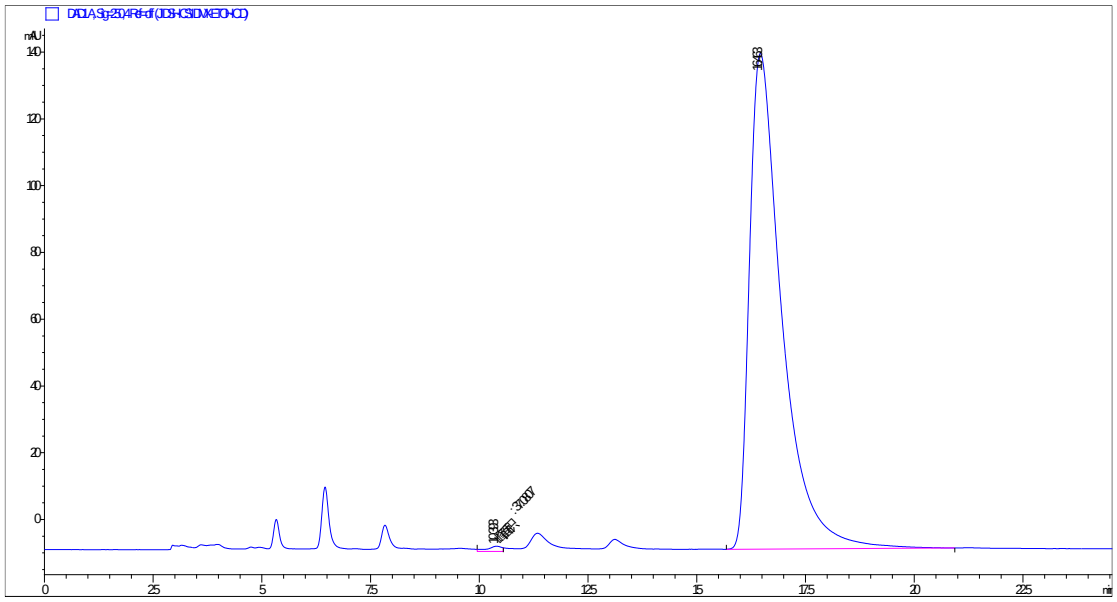
t_R	Channel	Area	height	Area/%
7.55	254nm	67.3	5.6	0.226
8.63	254nm	29744.9	1955.7	99.774

Racemic-4cn



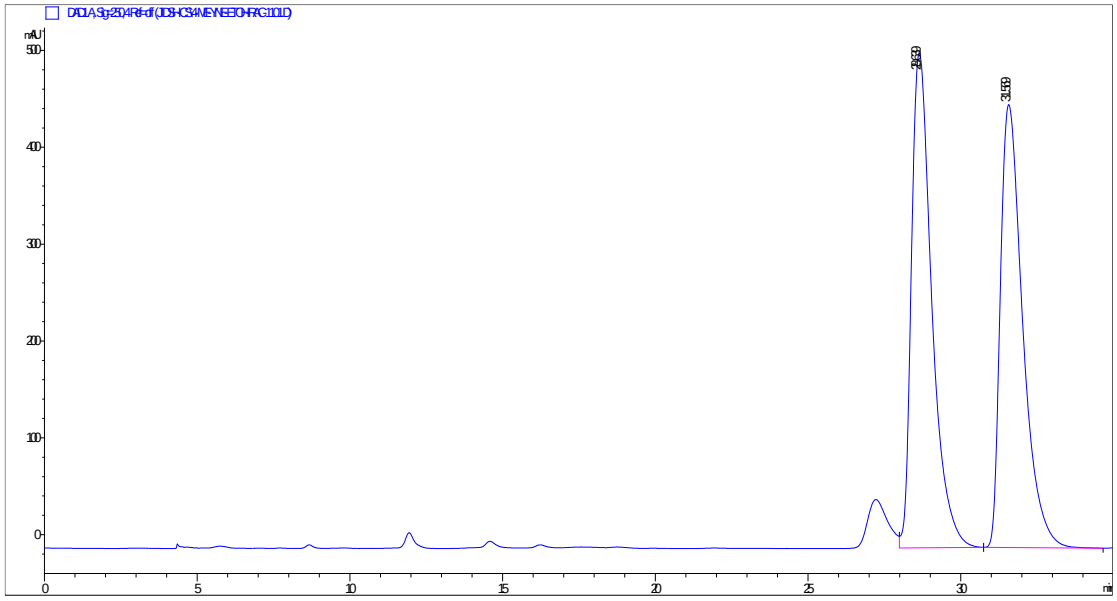
t_R	Channel	Area	height	Area/%
10.438	254nm	10901.9	594.9	49.659
16.523	254nm	11051.6	212.7	50.341

Enantioenriched-4cn



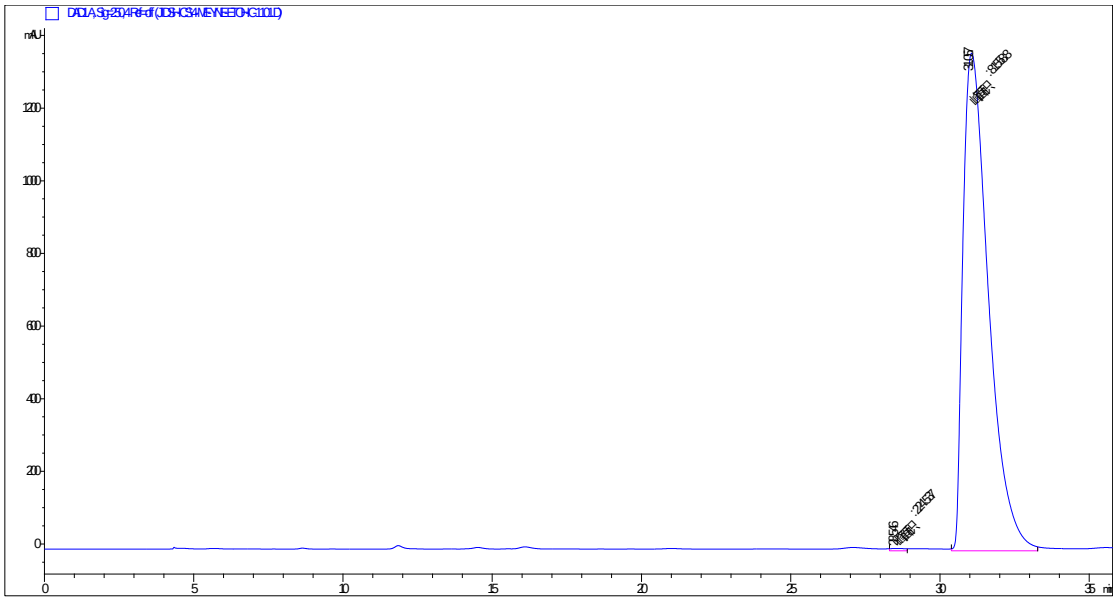
t_R	Channel	Area	height	Area/%
10.393	254nm	37.1	1.6	0.478
16.463	254nm	7720.6	148.4	99.522

Racemic- 4da



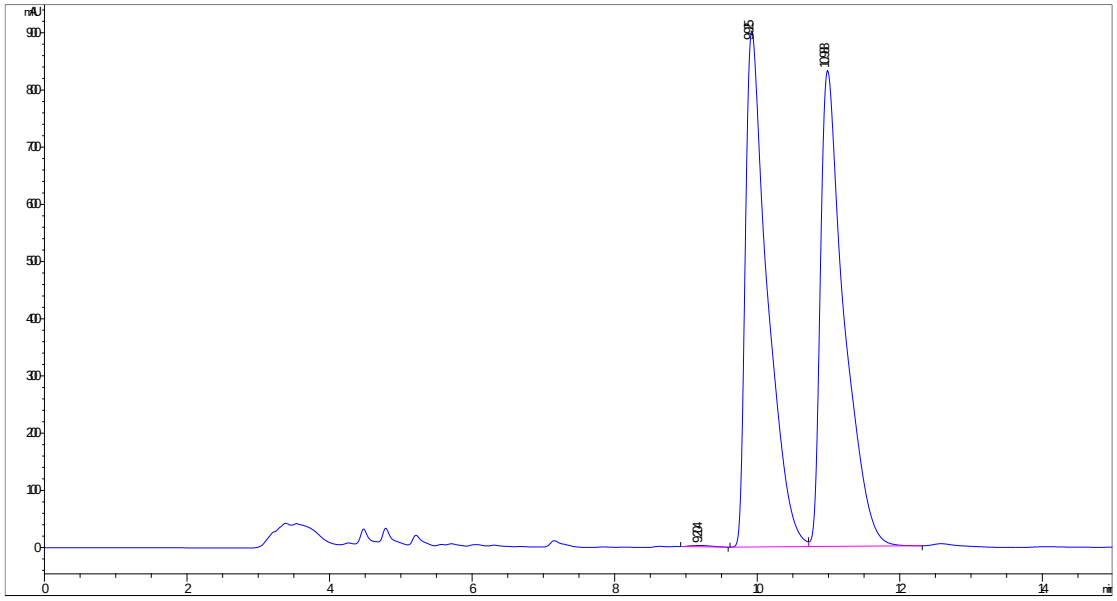
t_R	Channel	Area	Height	Area%
28.639	254nm	23681	511.4	50.466
31.569	254nm	23243.4	457.4	49.534

Enantioenriched-4da



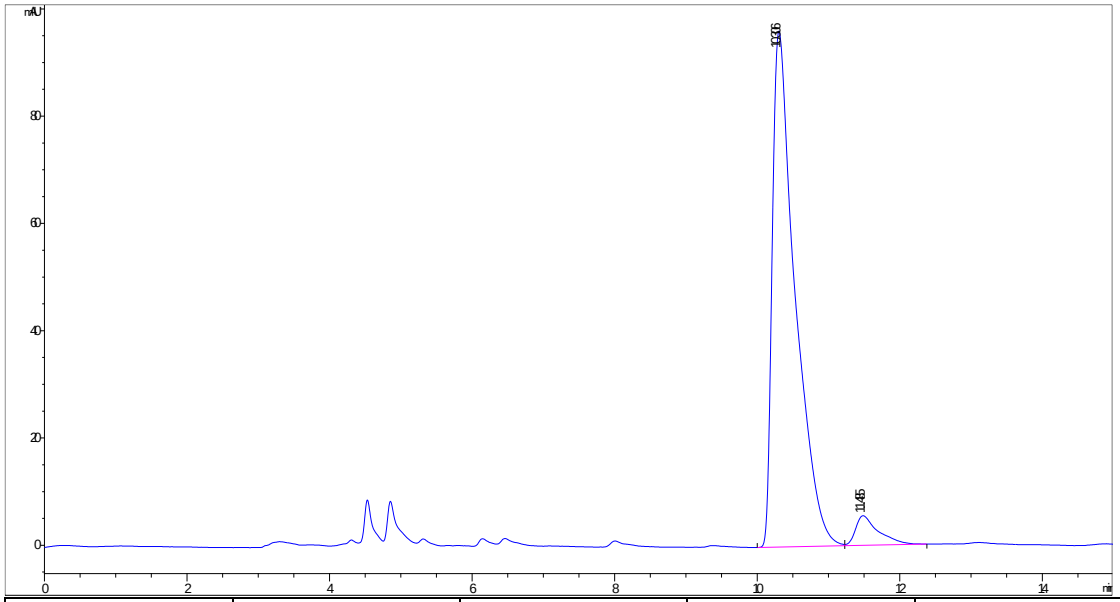
t_R	Channel	Area	Height	Area%
28.546	254nm	224.5	6.6	0.275
31.057	254nm	81558.8	1370.2	99.725

Racemic-4ea



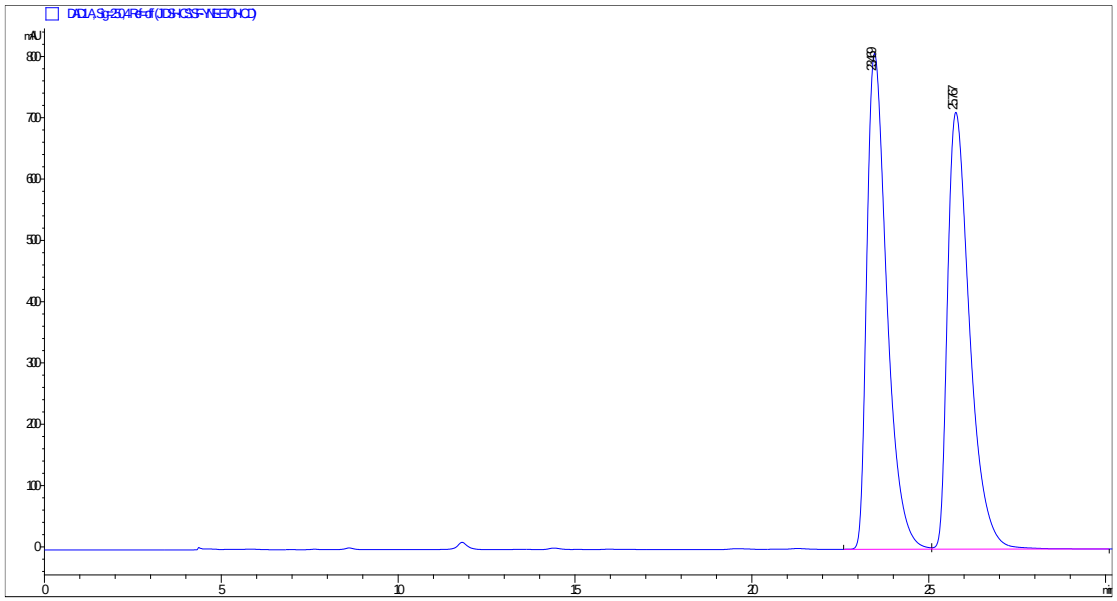
t_R	Channel	Area	Height	Area%
9.925	254nm	19387.9	902.3	50.266
10.988	254nm	19182.8	832	49.734

Enantioenriched-4ea



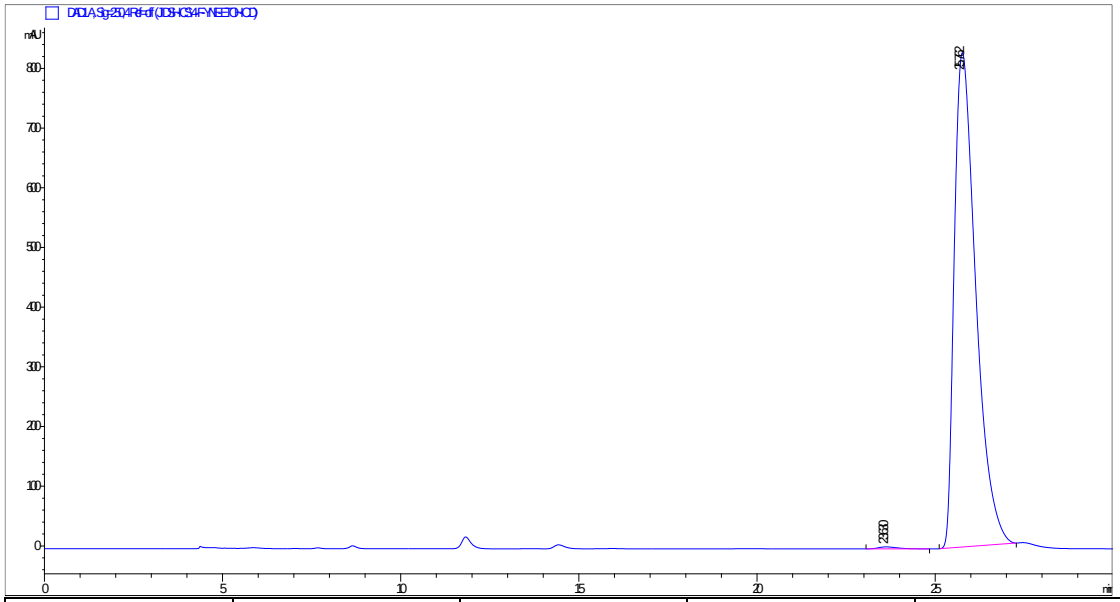
t_R	Channel	Area	Height	Area%
10.306	254nm	2138	96.2	95.56
11.185	254nm	123.2	5.5	4.46

Racemic-4fa



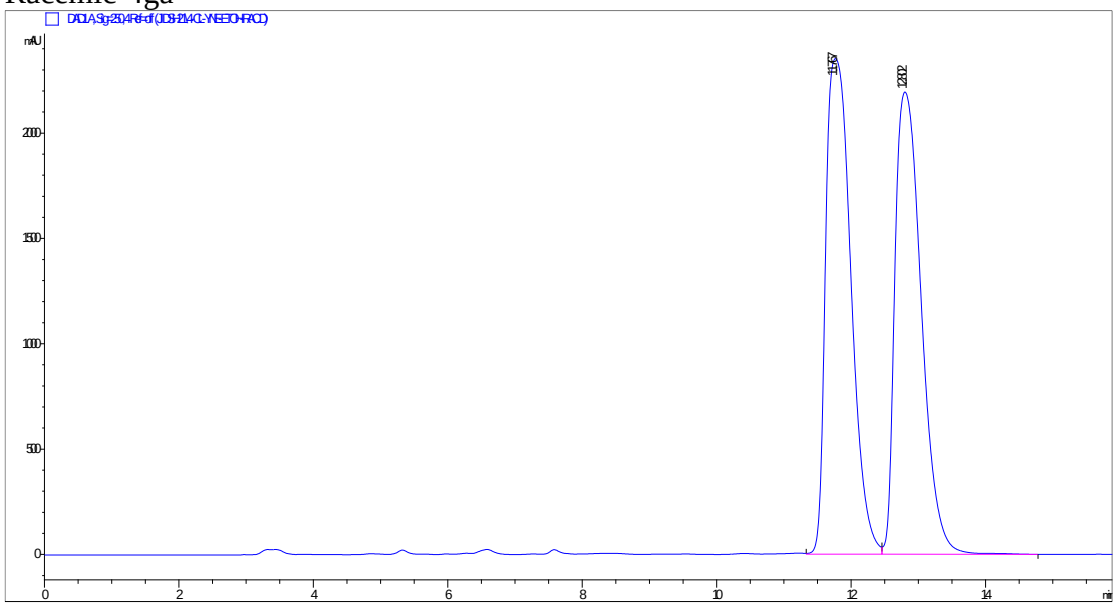
t_R	Channel	Area	Height	Area%
23.469	254nm	31813	808.8	50.666
25.767	254nm	30976.5	712.7	49.334

Enantioenriched-4fa



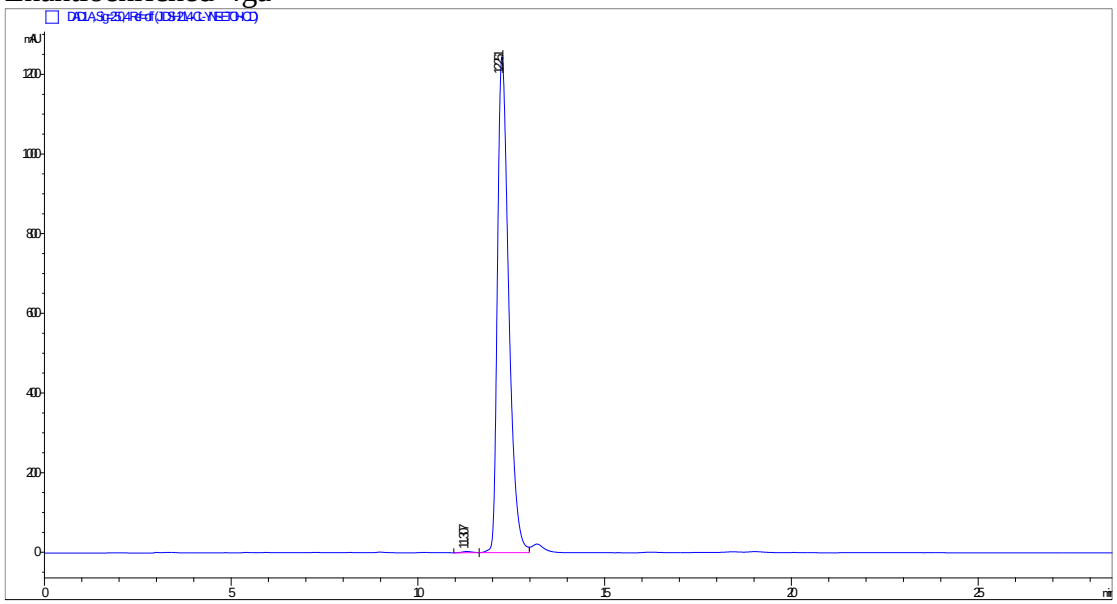
t_R	Channel	Area	Height	Area%
23.63	254nm	124.2	3.3	0.356
25.762	254nm	34761.8	828.2	99.644

Racemic-4ga



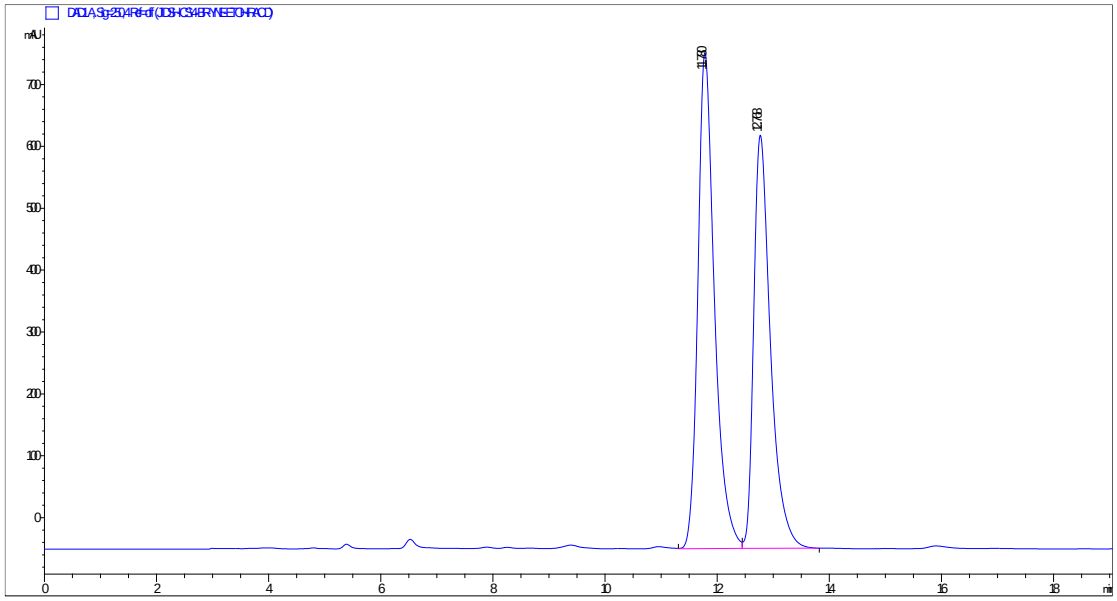
t_R	Channel	Area	Height	Area%
11.767	254nm	61509.3	23524	50.788
12.802	254nm	59601.5	2194.5	49.212

Enantioenriched-4ga



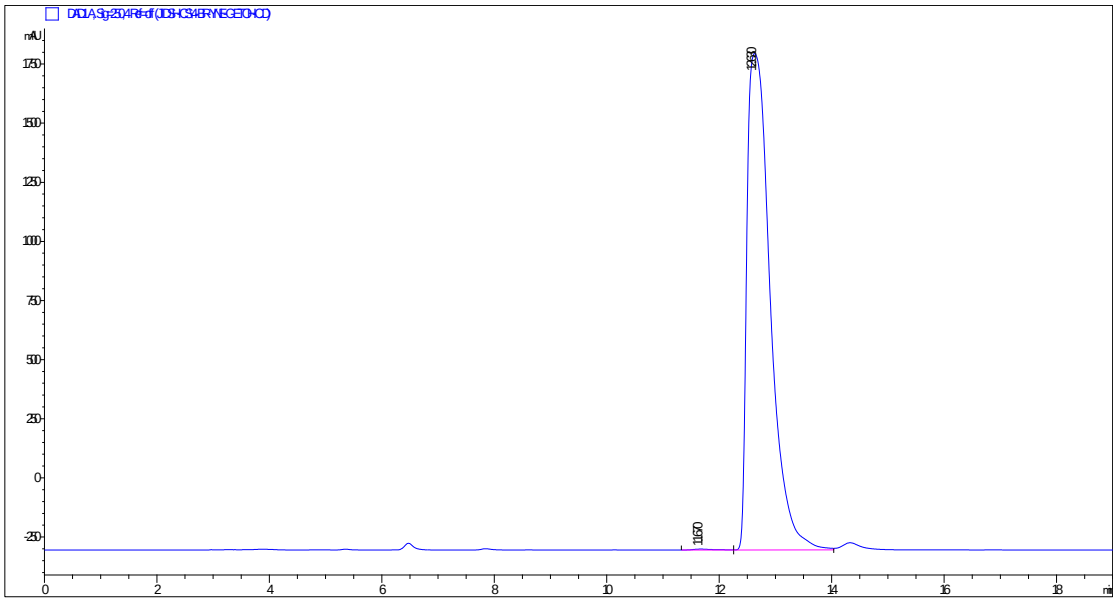
t_R	Channel	Area	Height	Area%
11.307	254nm	58.1	3.2	0.221
12.251	254nm	26187.9	1245.5	99.779

Racemic-4ha



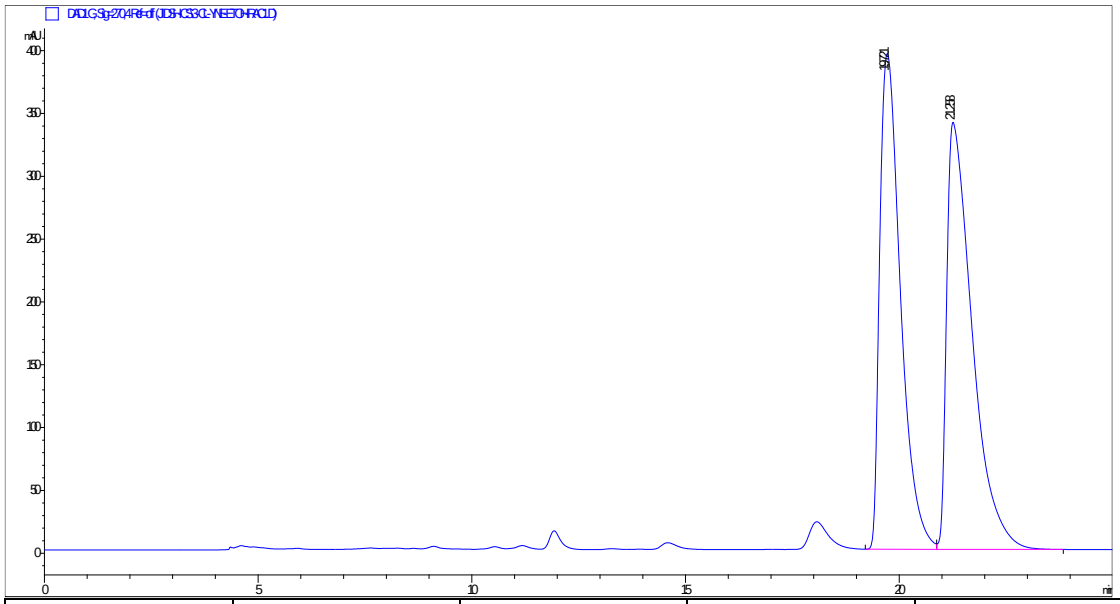
t_R	Channel	Area	Height	Area%
11.78	254nm	16557.8	801.3	50.365
12.768	254nm	14898.9	667.8	49.635

Enantioenriched-4ha



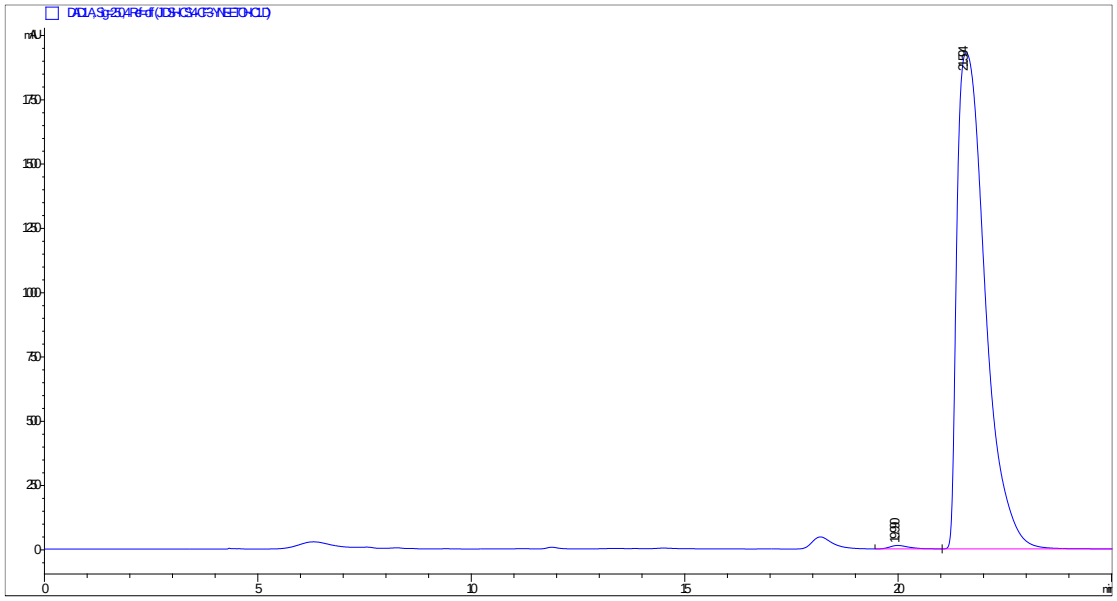
t_R	Channel	Area	Height	Area%
11.67	254nm	97.8	3.8	0.162
12.63	254nm	60316.5	2099.5	99.838

Racemic-4ia



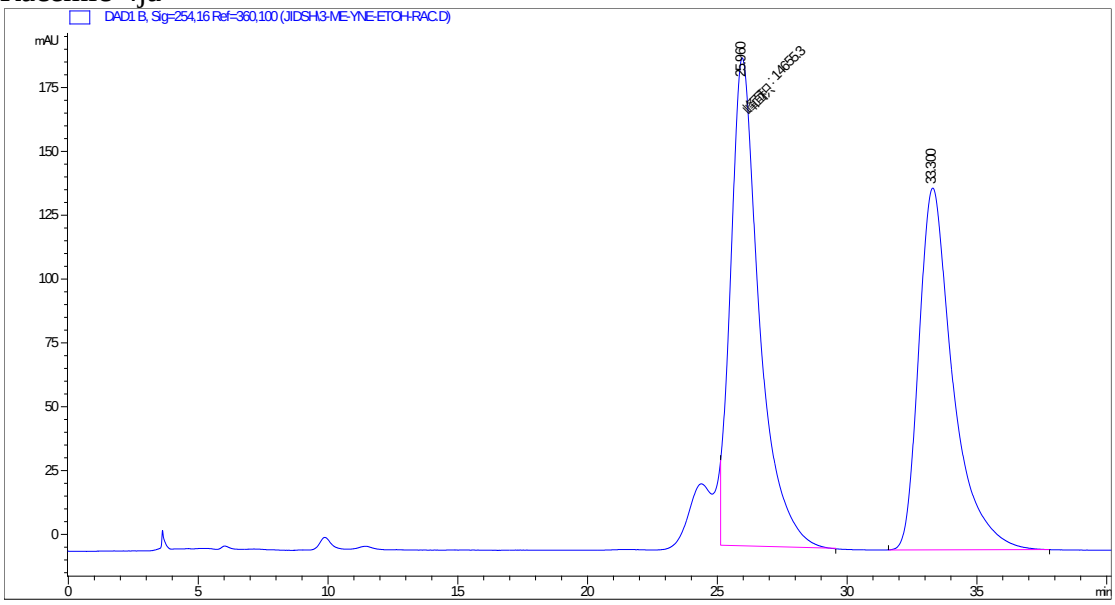
t_R	Channel	Area	Height	Area%
19.721	254nm	13352.9	394.6	49.68
21.258	254nm	14075.9	339.9	50.32

Enantioenriched-4ia



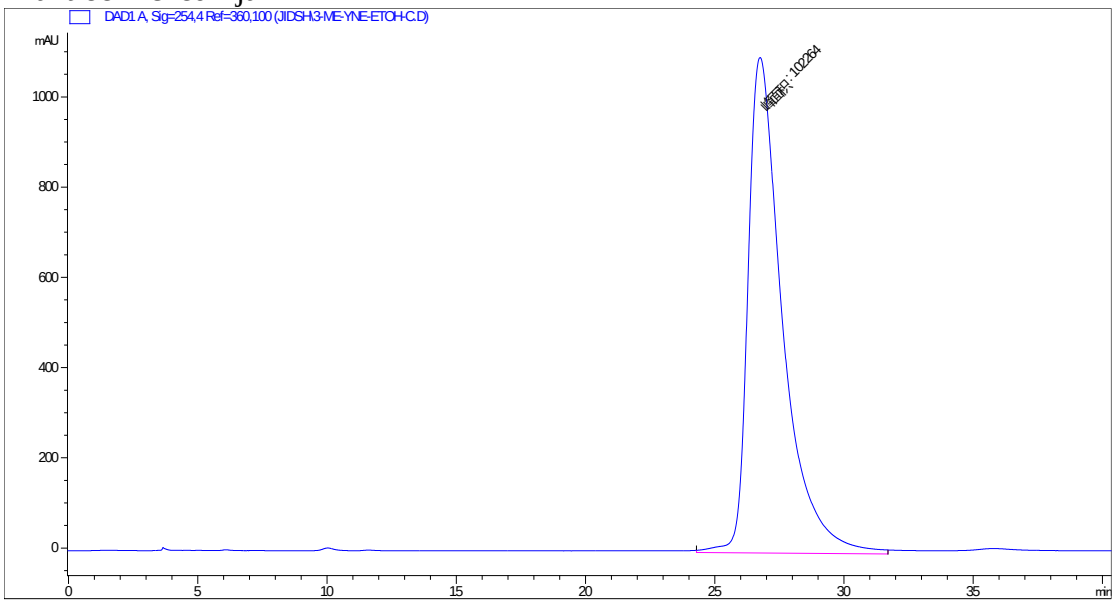
t_R	Channel	Area	Height	Area%
19.99	254nm	420.4	13.3	0.474
21.594	254nm	88205.2	1928.6	99.526

Racemic-4ja



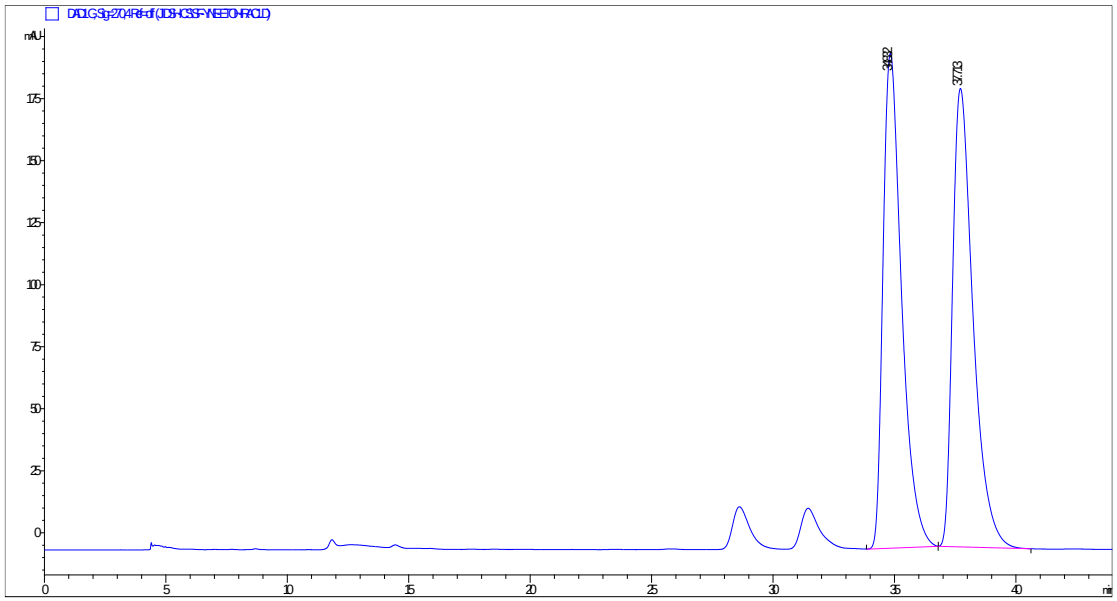
t_R	Channel	Area	Height	Area%
25.96	254nm	14255.4	1418.6	50.821
33.3	254nm	13766.3	1332.6	49.179

Enantioenriched-4ja



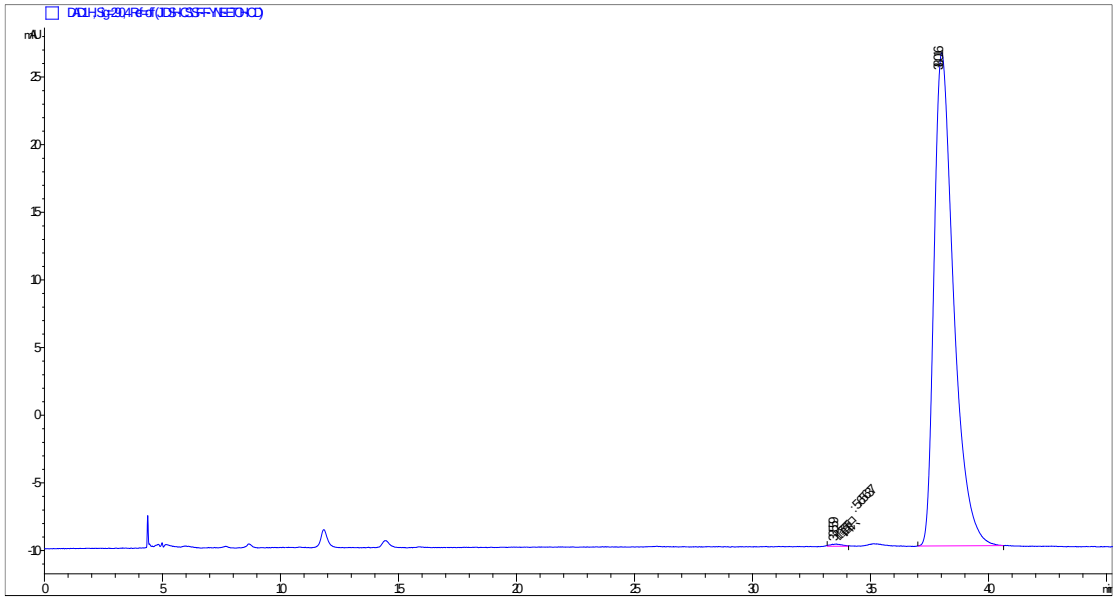
t_R	Channel	Area	Height	Area%
26.21	254nm	1022643	1233	100
-	254nm	-	-	-

Racemic-4ka



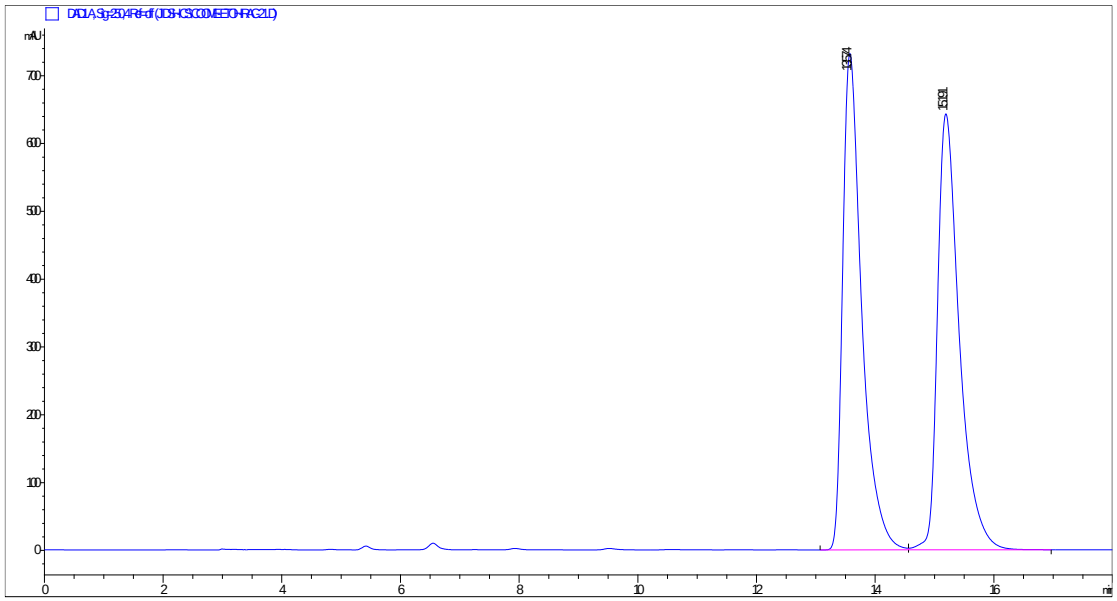
t_R	Channel	Area	Height	Area%
34.832	254nm	10623.4	199.4	49.53
37.713	254nm	10824.6	184.8	50.47

Enantioenriched-4ka



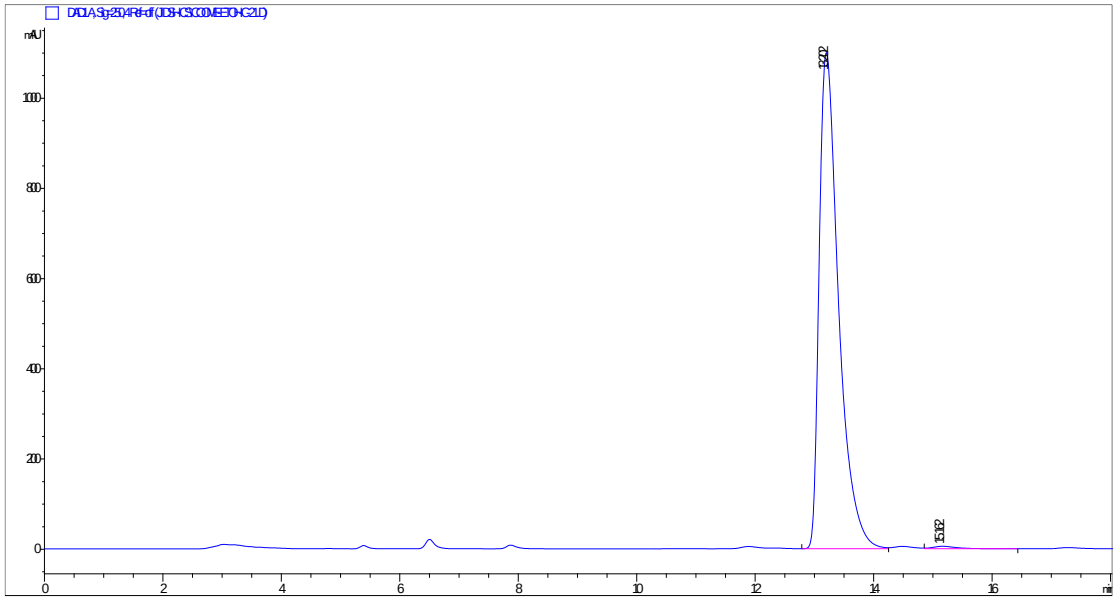
t_R	Channel	Area	Height	Area%
34.559	254nm	5.7	0.017	0.268
38.016	254nm	2108.2	36.5	99.832

Racemic-4la



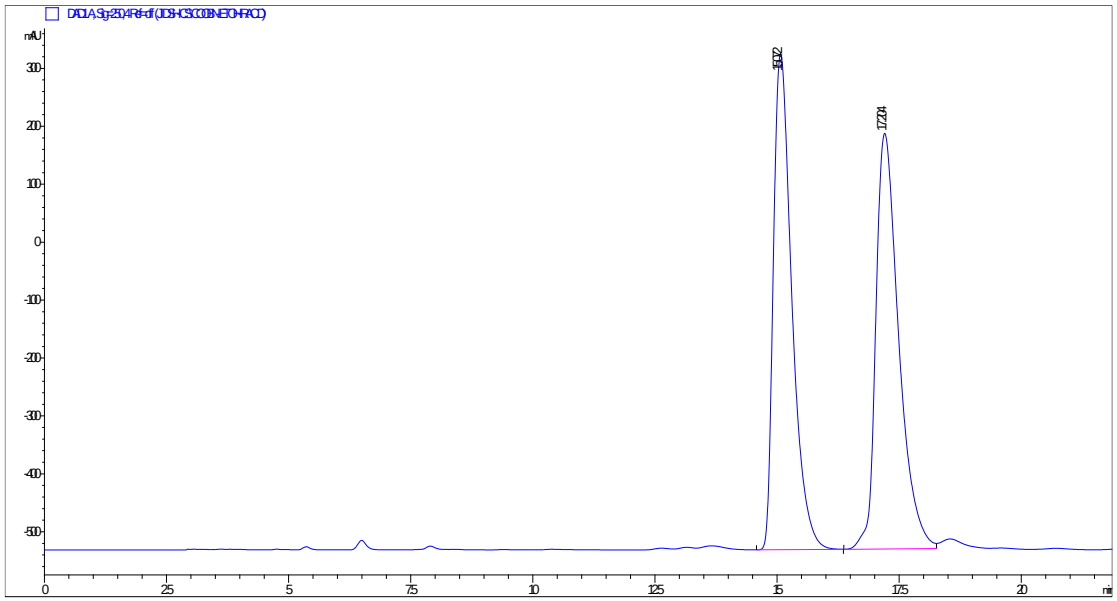
t	Channel	Area	height	Area/%
13.574	254nm	16388	732.1	49.908
15.191	254nm	16448.8	643	50.092

Enantioenriched-4la



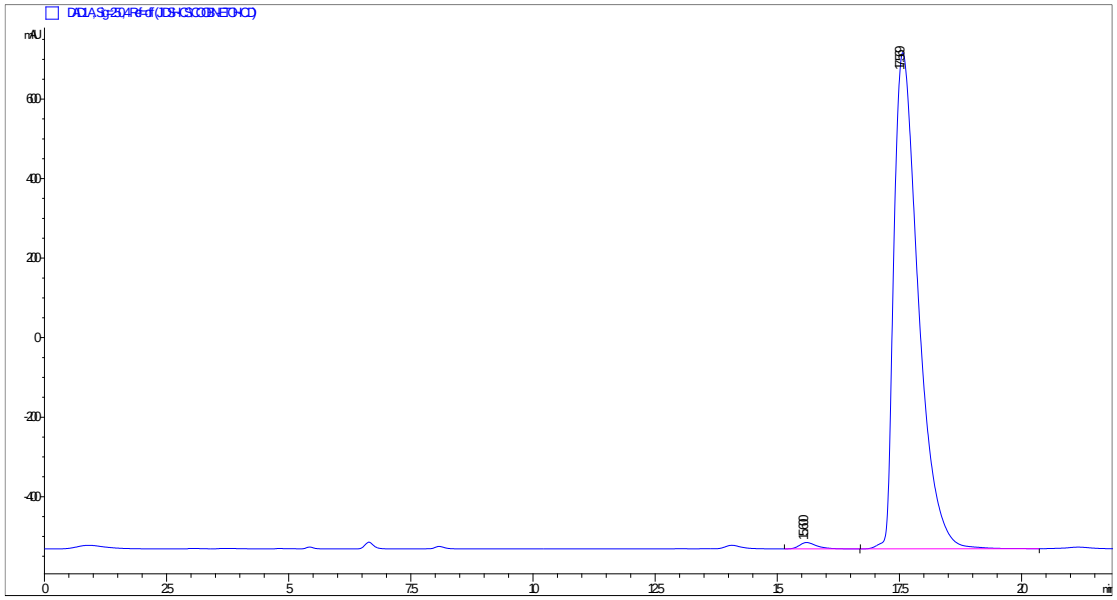
t	Channel	Area	height	Area/%
13.202	254nm	25024.1	1099.7	99.407
15.162	254nm	149.2	5.4	0.593

Racemic-4ma



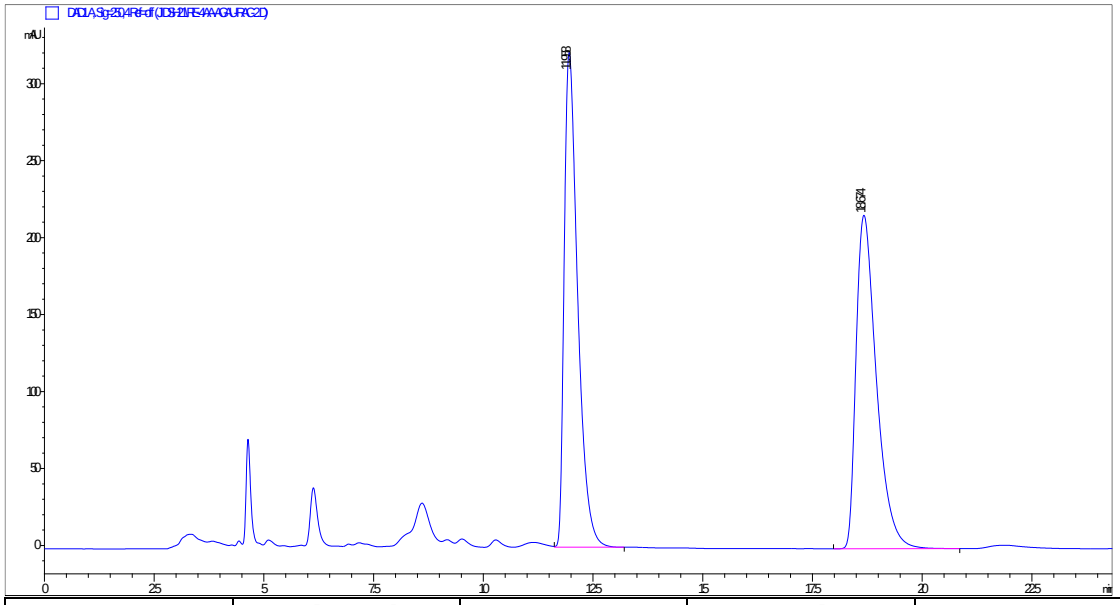
t	Channel	Area	height	Area/%
15.072	254nm	22909.7	856.6	49.568
17.204	254nm	23365.2	717.7	50.432

Enantioenriched-4ma



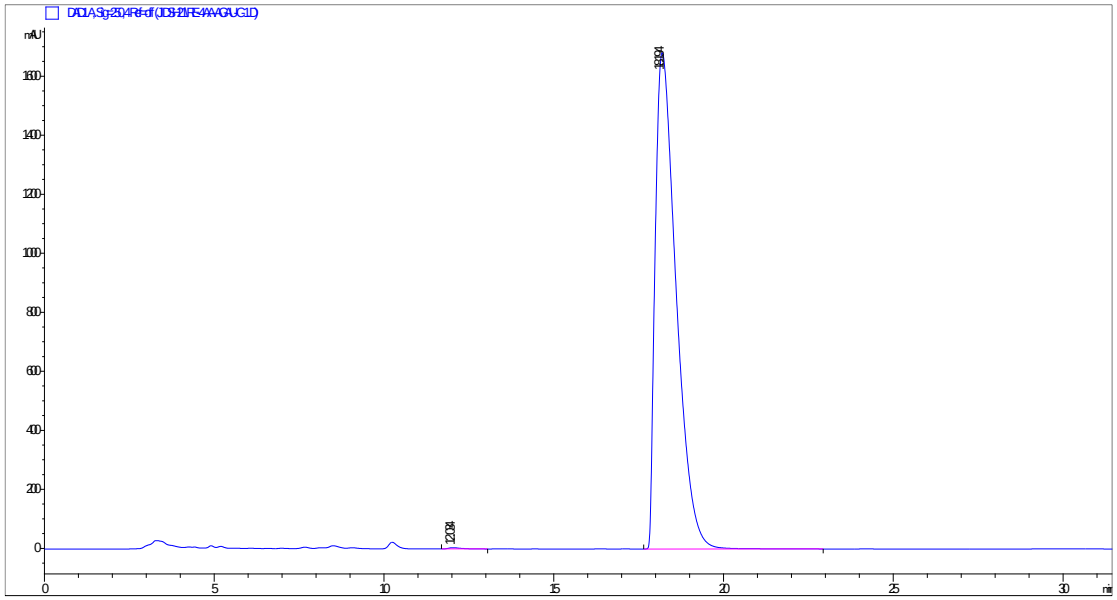
t	Channel	Area	height	Area/%
15.6	254nm	386.7	15.9	0.886
17.569	254nm	43255.2	1247.9	99.114

Racemic-5



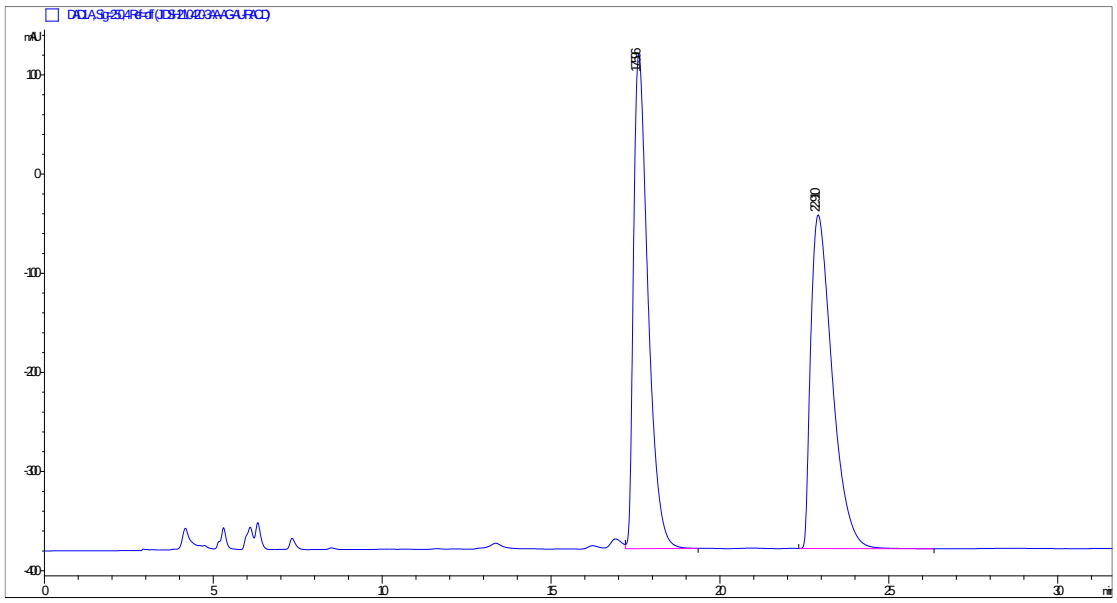
t_R	Channel	Area	Height	Area%
11.958	254nm	6366.2	699.3	49.95
18.611	254nm	6238.6	681.7	50.05

Enantioenriched-5



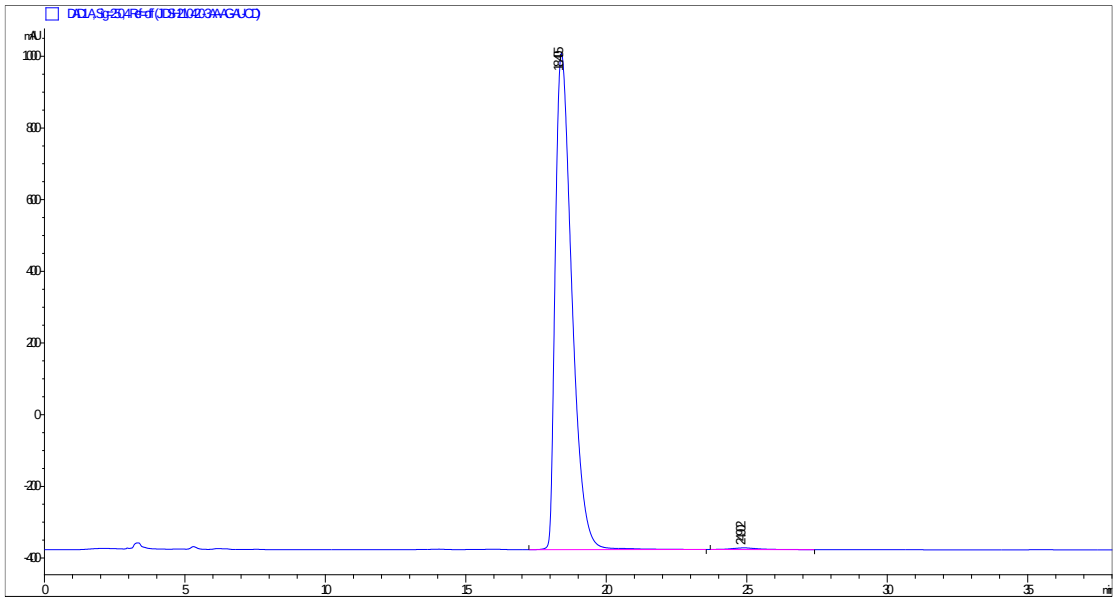
t_R	Channel	Area	Height	Area%
12.034	254nm	103.6	4	0.144
18.194	254nm	71750.1	1681.7	99.985

Racemic-6



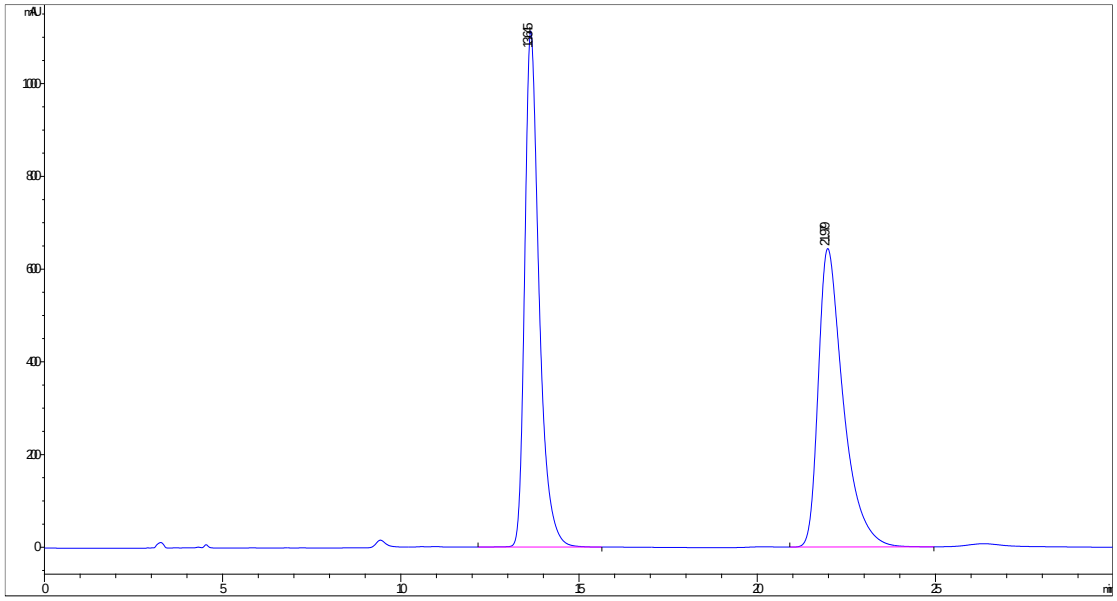
t_R	Channel	Area	Height	Area%
17.596	254nm	14941.2	498.4	50.155
22.91	254nm	14848.9	336.5	49.845

Enantioenriched-6



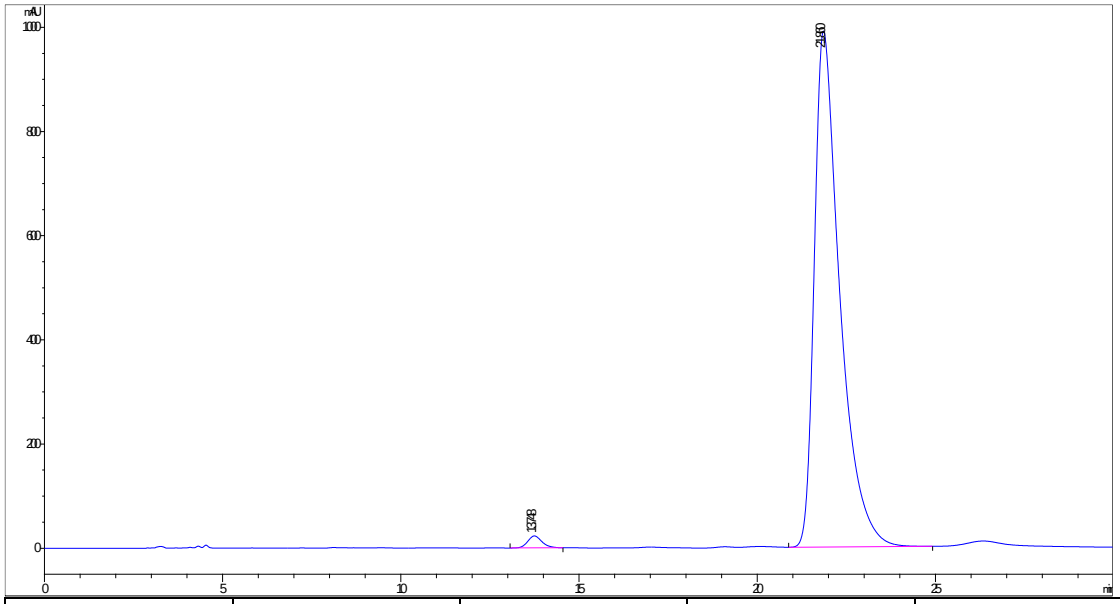
t_R	Channel	Area	Height	Area%
18.405	254nm	56824.4	1384.2	99.498
24.902	254nm	286.7	4.5	0.502

Racemic-7



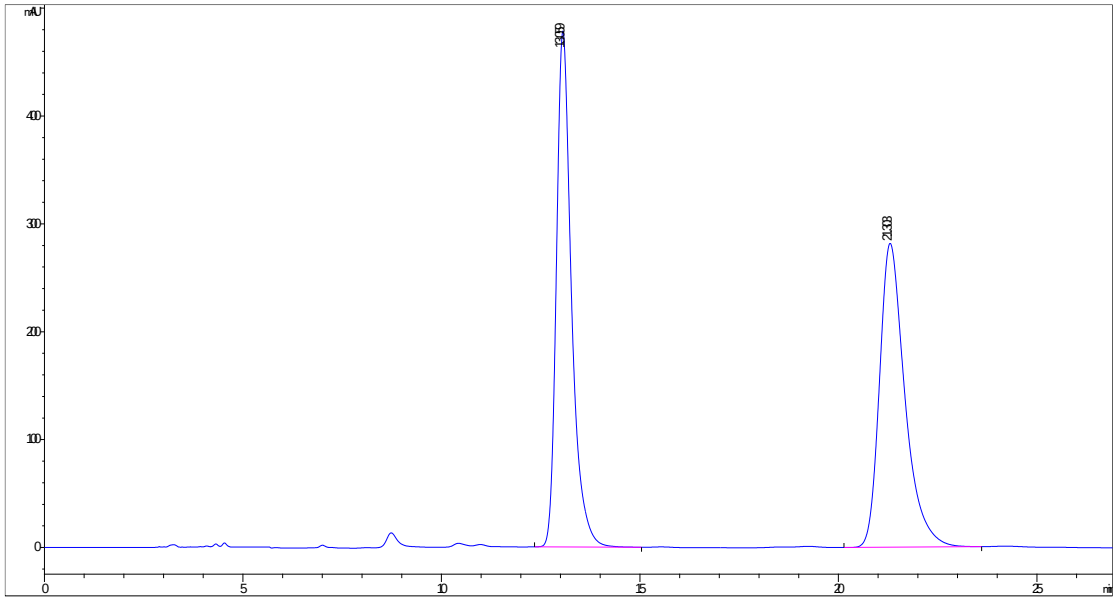
t_R	Channel	Area	Height	Area%
13.645	254nm	31254.3	1113.1	49.93
21.979	254nm	31350.5	643.8	50.07

Enantioenriched-7



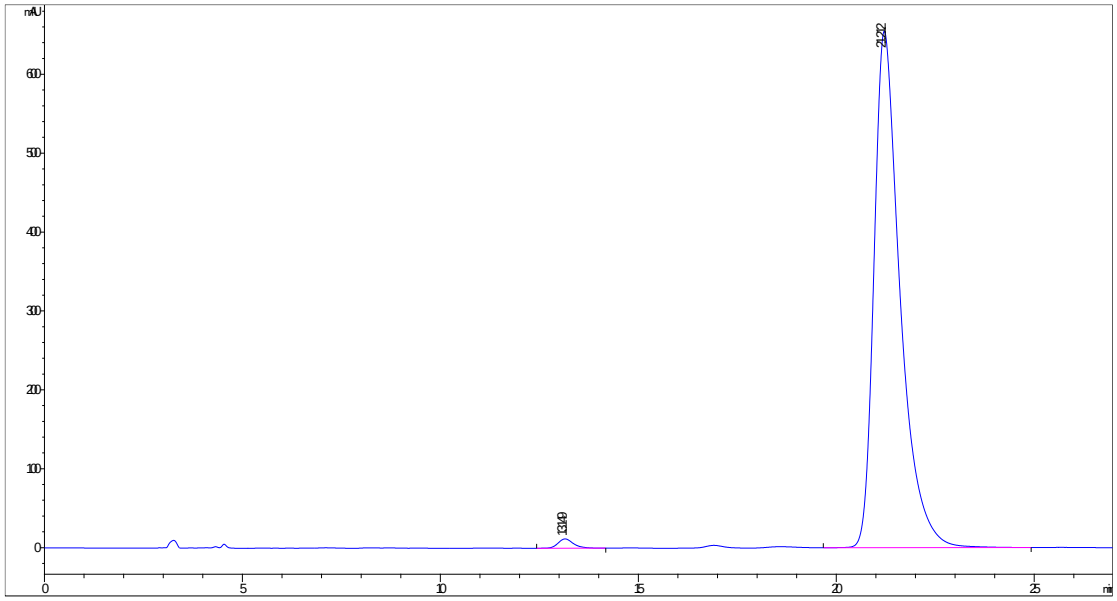
t_R	Channel	Area	Height	Area%
13.74	254nm	631.7	22.9	1
21.86	254nm	31350.5	990.5	99

Racemic-8



t_R	Channel	Area	Height	Area%
13.059	254nm	12628.6	478.3	50.2
21.303	254nm	12522,9	281.7	49.8

Enantioenriched-8



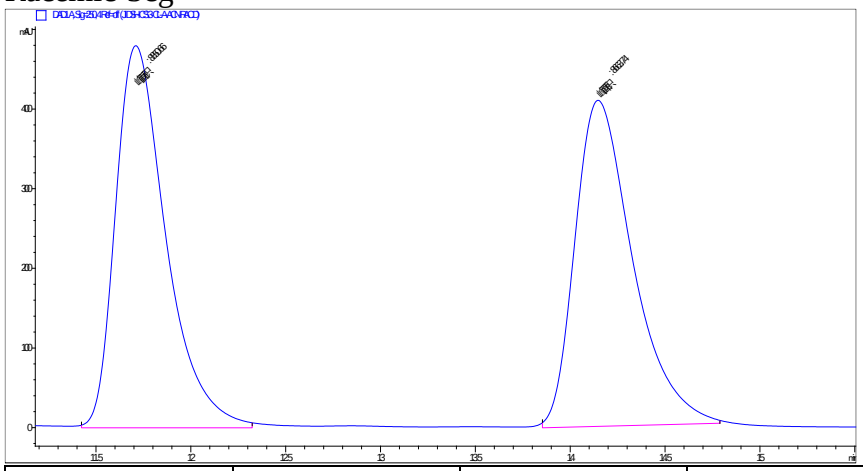
t_R	Channel	Area	Height	Area%
13.149	254nm	318.6	11.8	0.95
21.212	254nm	29985	654.8	99.05

Some example with 10 mol% catalyst loading results:

	t/h	dr	ee/%	Yield/%
3cg	78h	4:1	93	57
3cb	56h	7:1	93	77
3cl	56h	9:1	94	62
4ce	72h	20:1	93	68
4cg	72h	20:1	98	70
4ci	72h	20:1	99	52
4ch	72h	20:1	98	48

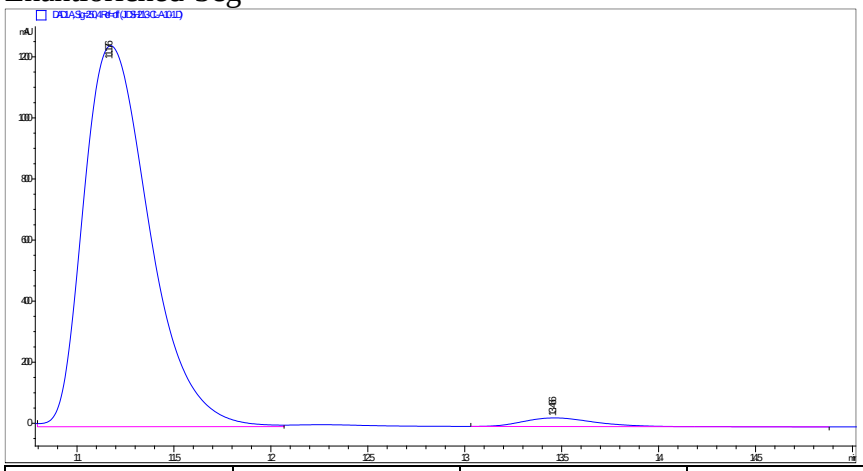
HPLC

Racemic-3cg



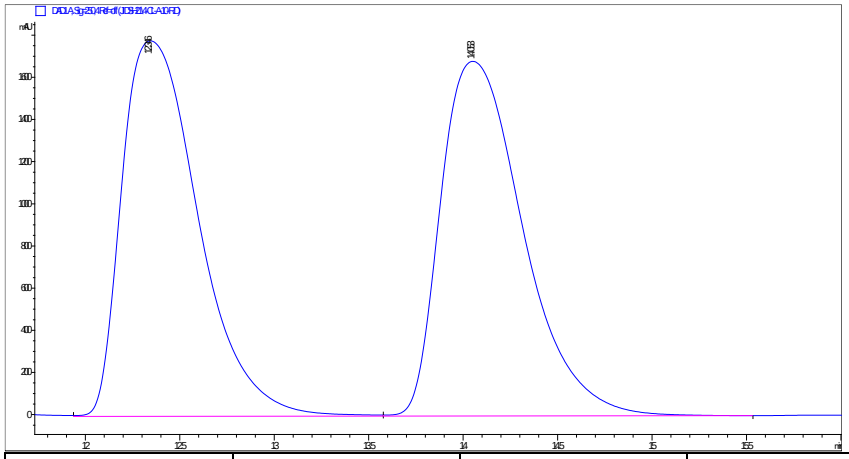
t_R	Channel	Area	Height	Area%
11.71	254nm	8850.7	479.9	50.534
14.14	254nm	8663.7	409.7	49.466

Enantioriched-3cg



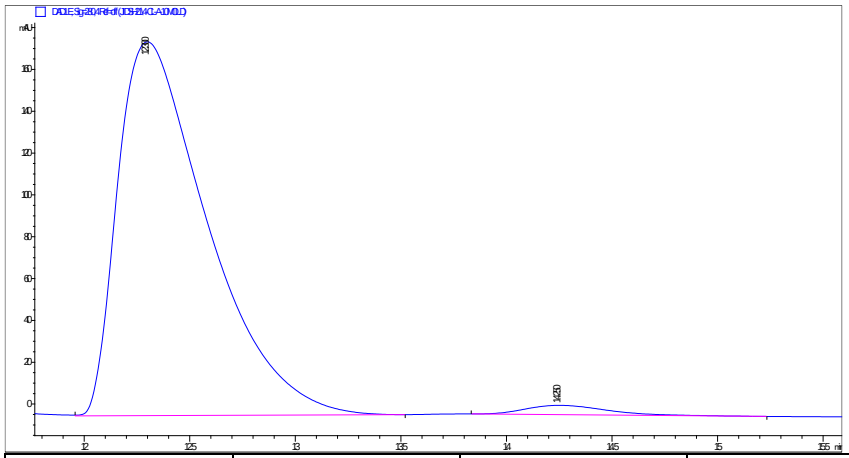
t_R	Channel	Area	Height	Area%
11.176	254nm	29452.2	1247.8	97.607
13.466	254nm	721.9	28.1	2.393

Racemic-3cb



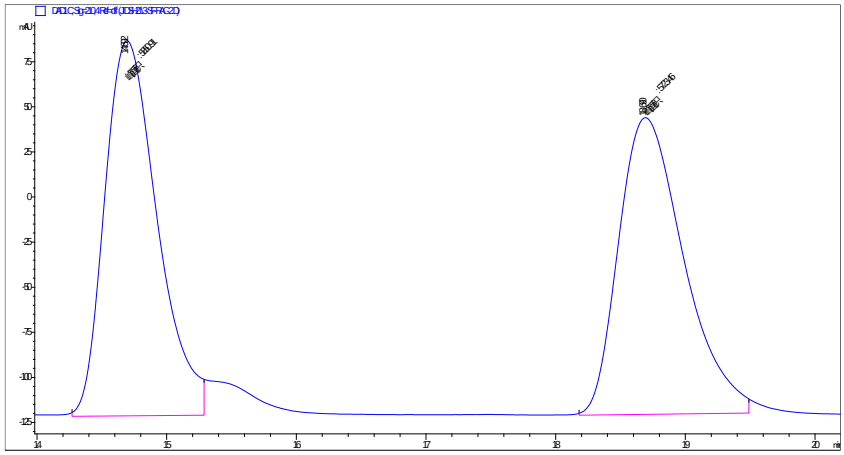
t_R	Channel	Area	Height	Area%
12.346	254nm	50521.0	1780.9	49.628
14.053	254nm	50962.1	1682.2	50.372

Enantioriched-3cb



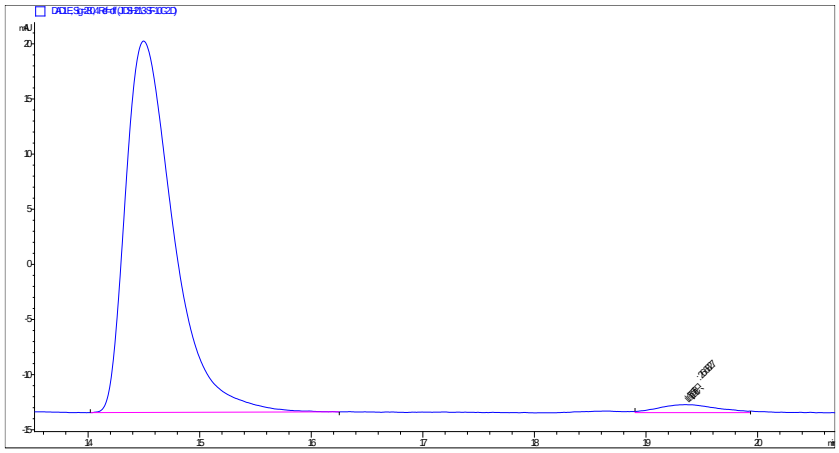
t_R	Channel	Area	Height	Area%
12.3	254nm	5272.7	178.8	96.3
14.25	254nm	129.3	4.5	3.7

Racemic-3cl



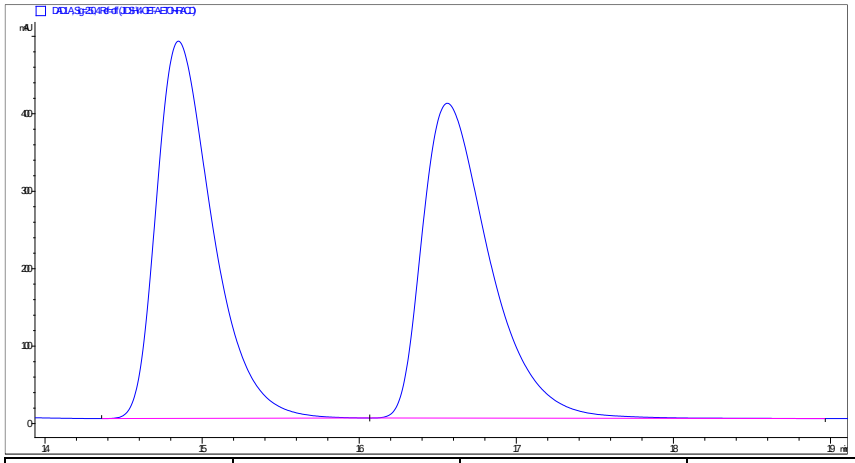
t_R	Channel	Area	Height	Area%
14.692	254nm	5850.9	207.9	50.551
18.69	254nm	5723.5	164.5	49.449

Enantioriched-3cl



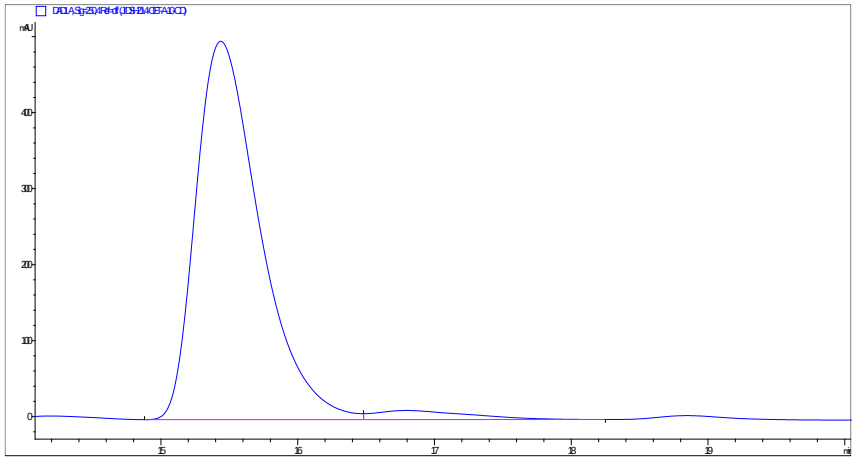
t_R	Channel	Area	Height	Area%
14.497	254nm	1004.9	33.7	97.007
19.359	254nm	26.9	0.0072	2.9929

Racemic-4ce



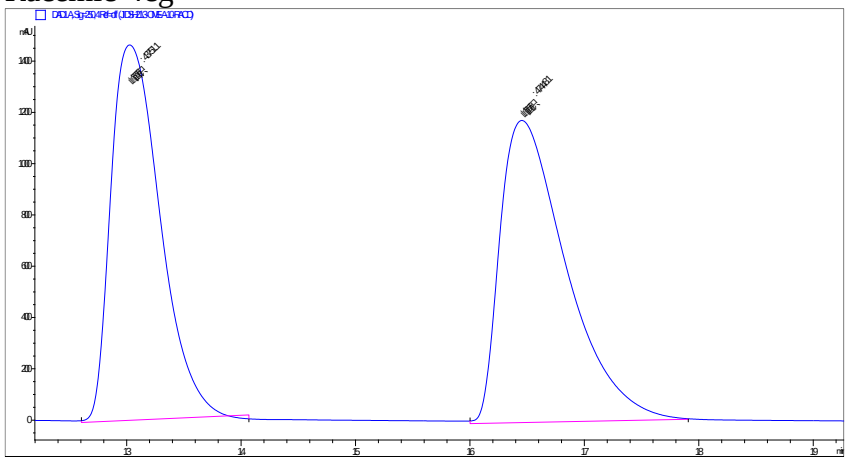
t_R	Channel	Area	Height	Area%
14.997	254nm	12127.4	487.1	50.075
16.559	254nm	12090.8	406.5	49.925

Enantioriched-4ce



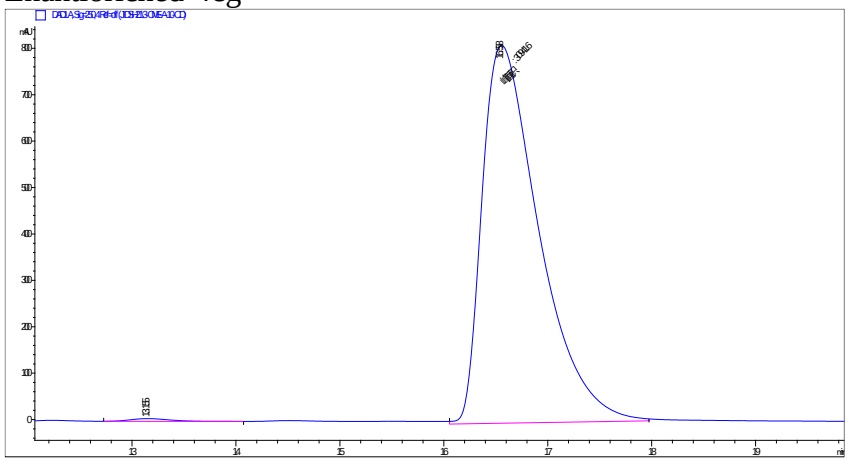
t_R	Channel	Area	Height	Area%
15.438	254nm	16157.2	497.9	96.61
16.795	254nm	566.5	12	3.39

Racemic-4cg



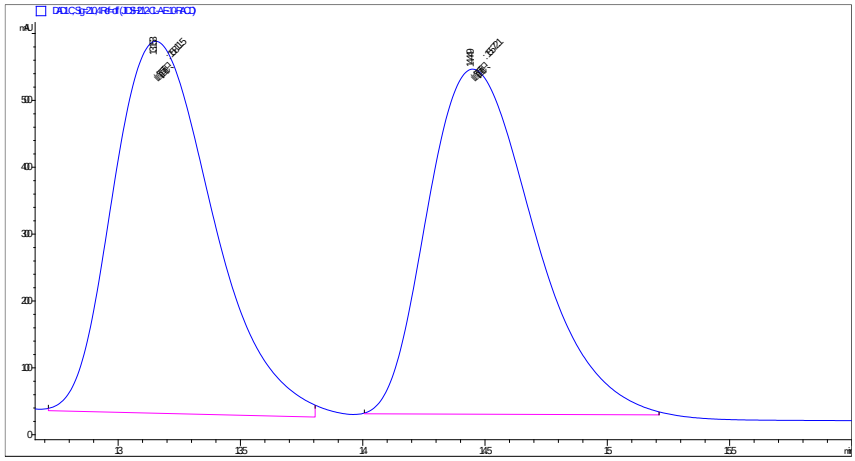
t_R	Channel	Area	Height	Area%
13.029	254nm	43751.1	1463.5	49.71
16.456	254nm	47449.1	1178	50.39

Enantioriched-4cg



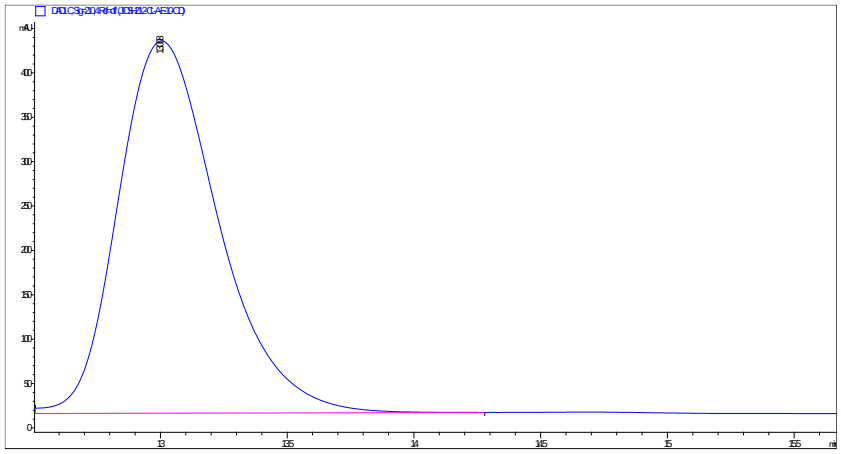
t_R	Channel	Area	Height	Area%
13.155	254nm	148.7	5.8	0.988
16.558	254nm	30941.6	814.4	90.012

Racemic-4ci



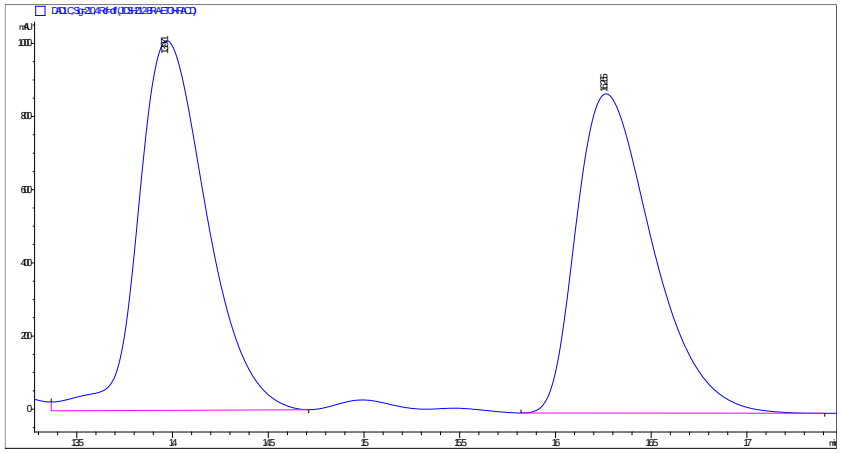
t_R	Channel	Area	Height	Area%
13.153	254nm	15811.5	556.1	50.381
14.449	254nm	15572.1	516	49.619

Enantioriched-4ci



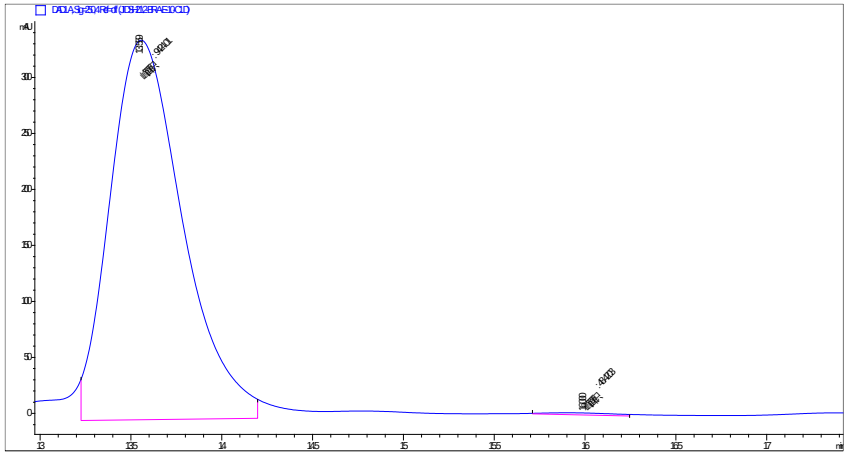
t_R	Channel	Area	Height	Area%
13.005	254nm	9579.8	353.5	100
14.449	254nm	-	-	-

Racemic-4ch



t_R	Channel	Area	Height	Area%
13.971	254nm	25142.7	1010.4	50.956
16.265	254nm	24199.4	872.5	49.044

Enantioriched-4ch



t_R	Channel	Area	Height	Area%
13.559	254nm	9424	338.9	99.489
14.449	254nm	48.9	1.9	0.511