Supporting information

Asymmetric [3+2] Annulation of Allenes with Maleimides Catalyzed by Dipeptide-Derived Phosphines: Facile Creation of Functionalized Bicyclic Cyclopentenes Containing two Tertiary Stereogenic Centers

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Contents:

1. General Methods: ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz or 300 and 75 MHz, respectively. Low- and high-resolution mass spectra were recorded by EI or ESI method. The used organic solvents were dried by standard methods if it was necessary. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, OD-H and IC-H columns 4.6 x 250 mm, (Daicel Chemical Ind., Ltd.)). Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica-gel-coated plates. Flash column chromatography was carried out by using silica gel at increased pressure.

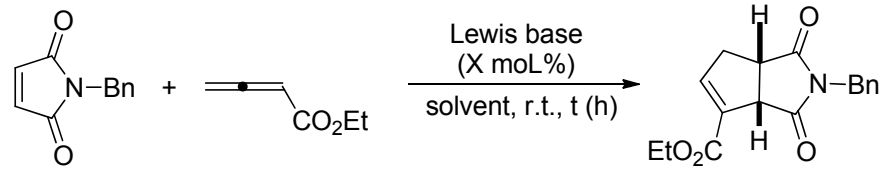
Allenoates **2b**-**2d**[1] and allenic ketone **2e**[2] were prepared according to the previously reported procedures.

Cat. 1-**Cat. 5** were purchased from J&K Chemical Ltd. and used directly without further purification. **Cat. 6**,[3] **Cat. 7**,[4] **Cat. 8**,[5] **Cat. 9**,[6] **Cat. 10**,[7] and **Cat. 11**,[8] were prepared according to the previously reported procedures.

2. General procedure for the PPh_3- or Cat. 11-catalyzed [3+2] annulation of maleimide 1 with electron-deficient allene 2: maleimide **1** (0.15 mmol), allene **2** (0.30 mmol), PPh_3 (0.0075 mmol) or **Cat. 11** (0.015 mmol), and toluene or toluene/$CHCl_3$ = 1:1 (v/v) (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for the time indicated in the Table. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/EA = 4/1~2/1).

Several phosphine-containing achiral Lewis bases were tested in the reaction of maleimide **1a** with ethyl allenoate **2a** in toluene at room temperature for 3 h. Triphenylphosphine (PPh_3) was the most effective catalyst, giving the corresponding racemic annulation product **3a** in 99% yield (Table S1, entry 1). Another phosphine-containing Lewis base methyldiphenylphosphine (PPh_2Me) did not catalyze this reaction under the standard conditions, while dimethyl(phenyl)phosphine ($PPhMe_2$) gave the complex product mixture (Table S1, entries 3 and 4). Tributylphosphine (PBu_3), tris(4-methoxyphenyl)phosphine ($P(p\text{-}MeOC_6H_4)_3$), tri-*p*-tolylphosphine ($P(p\text{-}MeC_6H_4)_3$) and tris(4-fluorophenyl)phosphine ($P(p\text{-}FC_6H_4)_3$) could also promote the reaction smoothly to give the desired product in 10%-97% yields (Table S1, entries 2 and 5-7). Solvent effects were subsequently examined with the use of 20 mol% of PPh_3 as the catalyst. Tetrahydrofuran (THF), dichloromethane, acetonitrile and 1,4-dioxane were then tested and the desired product was obtained in a range of 15-97% yields (Table S1, entries 8-11). Decreasing the employed amount of PPh_3 from 20 mol% to 10 mol% and 5 mol% led to the formation of **3a** in the same yield (99%) in toluene by extending the reaction time to 4 h and 9 h, respectively (Table S1, entries 12 and 13). Therefore, the best reaction conditions have been identified as that using 5 mol% of PPh_3 as the catalyst and carrying out the reaction in toluene at room temperature for 9 h.

Table S1. Optimization of the Reaction Conditions for the Phosphine-Catalyzed Reactions of Ethyl Allenoate **2a** with Maleimide **1a**[a]



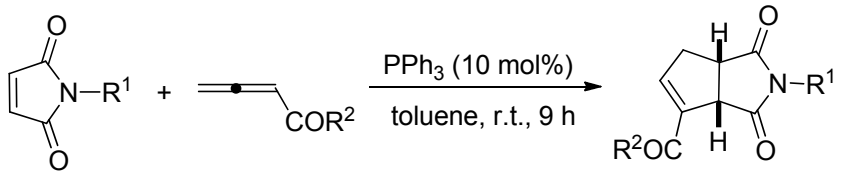
1a **2a** **3a**

entry	Lewis base	X	solvent	time (h)	yield (%)[b]
1	PPh_3	20	toluene	3	99
2	PBu_3	20	toluene	3	10
3	PPh_2Me	20	toluene	3	NR[c]
4	$PPhMe_2$	20	toluene	3	complex
5	P(*p*-$MeOC_6H_4)_3$	20	toluene	3	25
6	P(*p*-$MeC_6H_4)_3$	20	toluene	3	97
7	P(*p*-$FC_6H_4)_3$	20	toluene	3	75
8	PPh_3	20	THF	3	85
9	PPh_3	20	CH_2Cl_2	3	97
10	PPh_3	20	CH_3CN	3	15
11	PPh_3	20	dioxane	3	96
12	PPh_3	10	toluene	4	99
13	PPh_3	5	toluene	9	99

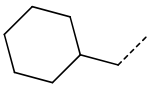
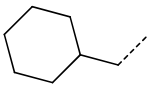
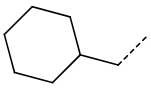
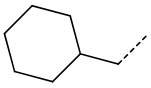
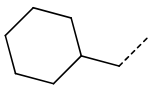
[a] The reaction was carried out on a 0.15 mmol scale with X mol% catalyst under Ar in solvent (1.0 mL) at rt, and the ratio of **1a/2a** was 1.0/2.0. [b] Isolated yield. [c] NR = No reaction.

Having identified the optimal reaction conditions, we next set out to examine the scope and limitations of this reaction by using various maleimides **1** and allenes **2a-2e**, and the results are summarized in Table S2. It was found that all of these *N*-alkyl, *N*-aryl, and *N*-benzyl substituted maleimides **1** could react with **2a-2e** smoothly to give the corresponding [3+2] cycloaddition products **3** in excellent yields (90-99%) under the standard conditions (Table S2, entries 1-19).

Table S2. Substrate Scope of the Reactions of Maleimide **1** with Electron Deficient Allenes **2** Catalyzed by PPh_3[a]



1 **2** **3**

entry	R^1	R^2	yield (%)[b]
1	**1a**, Bn	**2a**, OEt	**3a**, 98
2	**1b**, 1-naphthalenemethyl	**2a**, OEt	**3b**, 99
3	**1c**, 4-$MeOC_6H_4CH_2$	**2a**, OEt	**3c**, 99
4	**1d**, 3-$MeOC_6H_4CH_2$	**2a**, OEt	**3d**, 99
5	**1e**, 3,4-$(MeO)_2C_6H_3CH_2$	**2a**, OEt	**3e**, 99
6	**1f**, 4-$BrC_6H_4CH_2$	**2a**, OEt	**3f**, 98
7	**1g**, 4-$FC_6H_4CH_2$	**2a**, OEt	**3g**, 99
8	**1h**, 2-thienylmethyl	**2a**, OEt	**3h**, 97
9	**1i**, 	**2a**, OEt	**3i**, 99
10	**1i**, 	**2b**, O^iPr	**3j**, 99
11	**1i**, 	**2c**, O^tBu	**3k**, 99
12	**1i**, 	**2d**, OBn	**3l**, 98
13	**1i**, 	**2e**, Me	**3m**, 99
14	**1j**, Me	**2a**, OEt	**3n**, 99
15	**1k**, H	**2a**, OEt	**3o**, 96[d]
16	**1l**, Ph	**2a**, OEt	**3p**, 96
17	**1m**, 4-$MeOC_6H_4$	**2a**, OEt	**3q**, 99
18	**1n**, 3,5-$(MeO)_2C_6H_3$	**2a**, OEt	**3r**, 99
19	**1o**, 2,4,6-$Br_3C_6H_2$	**2a**, OEt	**3s**, 95
20	**1p**, 2-$NO_2C_6H_4$	**2a**, OEt	**3t**, 90[e]

[a] The reaction was carried out on a 0.15 mmol scale with 5 mol% catalyst under Ar in toluene (1.0 mL) at rt for 9 h, and the ratio of **1/2** was 1.0/2.0. [b] Isolated yield. [d] The ratio of **1/2** was 1.0/3.0, and R^1 = (*E*)-$CH_2CH{=}CHCO_2Et$ in the annulation product **3o**, *E*/*Z* > 20/1. [e] dr = 3:2. An axial chirality caused by the nitro substituent at the *ortho* position of the phenyl ring was discovered and confirmed by X-ray structure (see Figure SI-3)

The reactions were initially carried out on a 0.15 mmol scale with 10 mol% chiral phosphine catalysts under Ar in toluene (1.0 mL) at room temperature for 24 h and the ratio of **1a**/**2a** was 1.0/2.0 (Figure S1). First, chiral bidentate phosphine catalysts **Cat. 1**-**Cat. 4** were tested in this asymmetric [3+2] cycloaddition of **1a** with **2a**. We found that **Cat. 1**, **Cat. 2** and **Cat. 3** led to the formation of the desired products **3aa** in high yields along with 5%-50% ee values and **Cat. 4** almost had no catalytic activity in this reaction. Using monodentate chiral phosphine such as the eight-membered spirocyclic phosphine **Cat. 5** as the catalyst, the reaction nearly could not proceed. We then turned to test some bifunctional phosphine catalysts involving some substitutes, such as OH group, NH group, which could provide good opportunity to form a hydrogen bond. Catalyst 1,1'-bi-2-naphthol-derived chiral phosphine **Cat. 6** bearing a phenolic hydroxy group developed by our group[9] led to the formation of **3aa** in high yield (95%) with 15% ee. Chiral binaphthyl-derived bifunctional thiourea-phosphine catalysts **Cat. 7**-**Cat. 9** did not improve the ee value of **3aa** either, affording the product **3aa** in 60-98% yields with 13-23% ee values. L-valine-derived bifunctional thiourea-phosphine **Cat. 10** was also examined but gave a racemic product. Gratifyingly, it was found that D-threonine-L-tert-leucine-derived bifunctional phosphine **Cat. 11** developed by Lu's group[10] was the most effective catalyst in this reaction, giving **3aa** in 97% yield and 86% ee within 24 h.

Using **Cat. 11** (10 mol%) as the catalyst, we next examined the solvent effects and reaction temperature on the reaction outcome to further optimize the reaction conditions and the results are summarized in Table S3. In solvents such as CH_2Cl_2, THF, CH_3CN, $CHCl_3$ and Et_2O, the desired product **3aa** was obtained in moderate to good yields (from 61% to 88%) but with lower ee values (from 18% to 86%) (Table S3, entries 2-7). Protic solvent such as methanol was not suitable media for this reaction, affording no product (Table S3, entry 8). Decreasing the reaction temperature from 25 ^oC to 0 ^oC, we found that **3aa** could be obtained in 97% yield with 88% ee in toluene (Table S3, entry 9). Further decreasing the reaction temperature from 0 ^oC to -20 ^oC or -40 ^oC did not improve the enantioselectivity (Table S3, entries 10 and 11). Fortunately, in the mixed solvent of toluene/$CHCl_3$ = 1:1 (v/v), **3aa** was given in 92% yield with 92% ee at 0 ^oC after 72 h (Table S3, entry 12). Changing the mixed solvent to fluorobenzene/$CHCl_3$ = 1:1 (v/v) and chlorobenzene/$CHCl_3$ = 1:1 (v/v), lower yields (87-89%) and enantiomeric excesses (89-90%) were observed in the reaction system (Table S3, entries 13

and 14). Reducing the catalyst loading from 10 mol% to 5 mol% resulted in the longer reaction time and lower yield (Table S3, entry 15). Therefore, the optimal reaction conditions have been identified as that using 10 mol% of **Cat. 11** as the catalyst and carrying out the reaction in toluene/$CHCl_3$ = 1:1 (v/v) at 0 ^oC for 72 h.

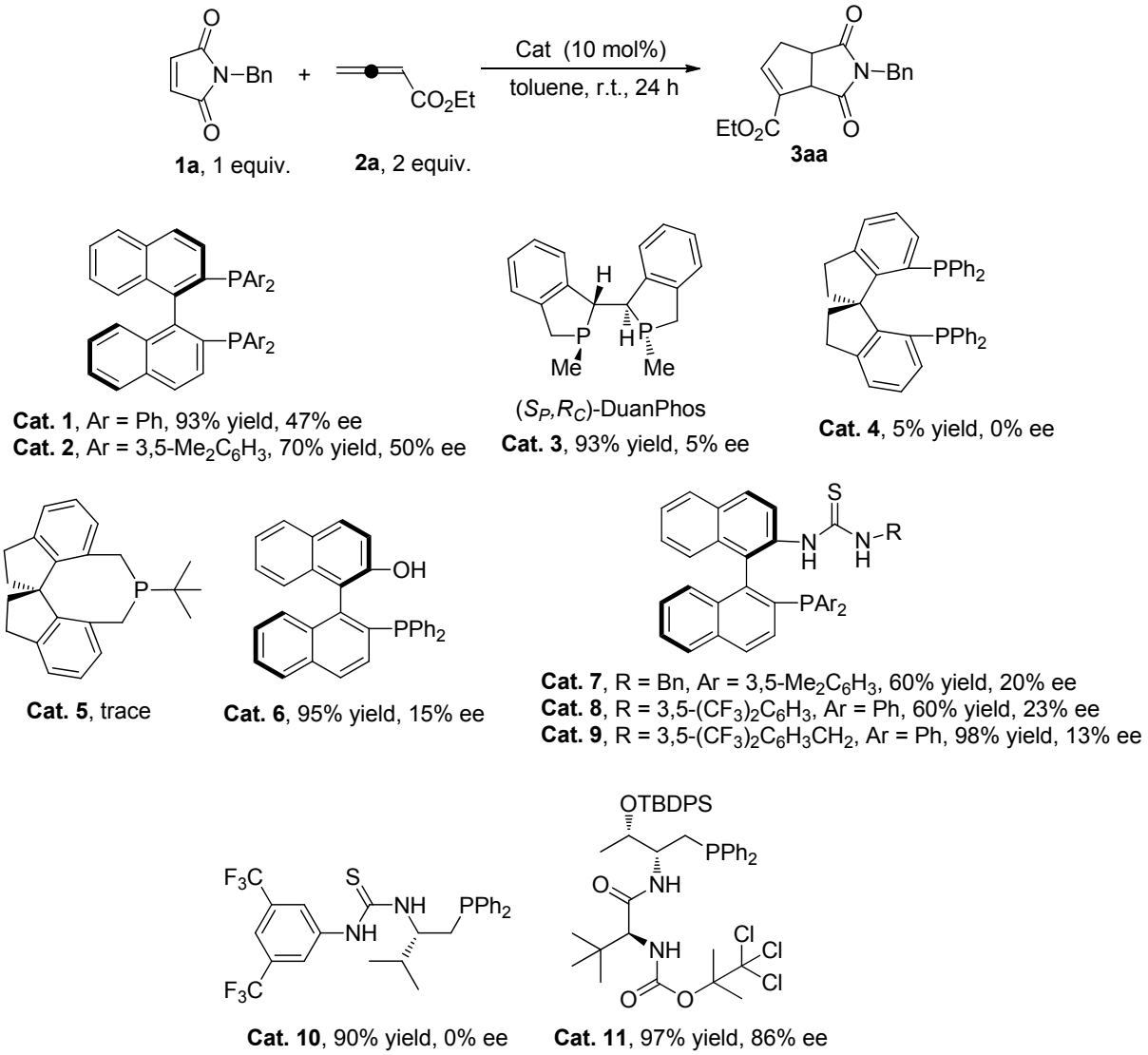
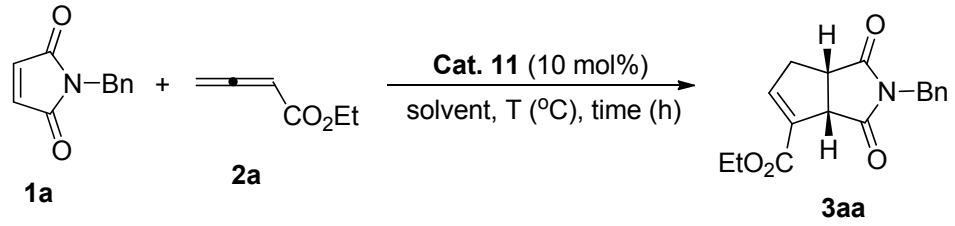


Figure S1. Chiral Phosphine Catalysts Screening for the Asymmetric [3+2] Cycloaddition.

Table S3. Optimization of the Reaction Conditions in the Asymmetric [3+2] Cycloaddition of **1a** with **2a** Catalyzed by **Cat. 11**[a]



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

entry	solvent	T (°C)	time (h)	yield (%)[b] **3a**	ee (%)[c] **3a**
1	toluene	25	24	97	86
2	CH_2Cl_2	25	24	64	80
3	THF	25	24	88	54
4	CH_3CN	25	24	68	18
5	Et_2O	25	24	80	47
6	$CHCl_3$	25	24	61	86
7	chlorobenzene	25	24	85	85
8	MeOH	25	24	trace	-
9	toluene	0	24	97	88
10	toluene	-20	24	93	85
11	toluene	-40	48	98	80
12	toluene/$CHCl_3$ = 1:1 (v/v)	0	72	92	92
13	fluorobenzene/$CHCl_3$ = 1:1 (v/v)	0	72	87	89
14	chlorobenzene/$CHCl_3$ = 1:1 (v/v)	0	72	89	90
15[e]	toluene/$CHCl_3$ = 1:1 (v/v)	0	96	79	90

[a] Unless otherwise specified, reactions were performed with **1a** (0.15 mmol), **2a** (0.30 mmol), and **Cat. 11** (10 mol %). [b] Isolated yields. [c] Determined by chiral HPLC. [d] The catalyst loading was 5 mol %.

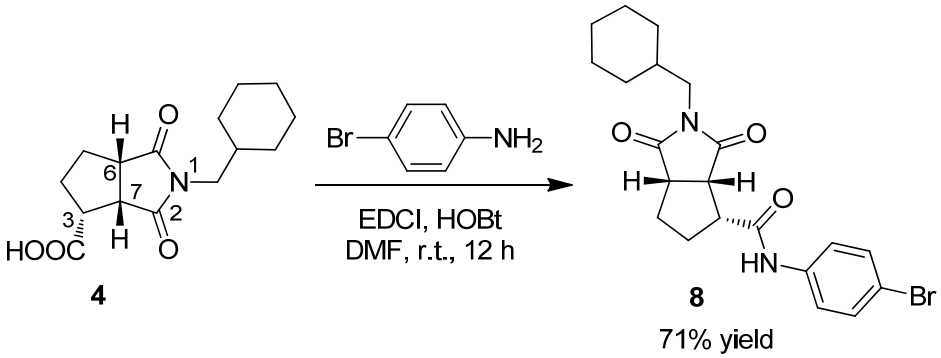
3. General procedure for the synthesis of 4

Compound **3id** (28 mg, 0.10 mmol) was stirred in anhydrous tetrahydrofuran (5.0 mL) in the presence of 10% palladium on carbon (11.0 mg) under an atmosphere of hydrogen for 7 h. After removal of the catalyst through Celite and concentration of the filtrate, the product **4** was obtained in over 99% yield.

4. General procedure for the synthesis of 5

Compound **4** (28 mg, 0.10 mmol) was added to a solution of *m*-bromoaniline (34 mg, 0.20 mmol), N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (58 mg, 0.30 mmol) and 1-hydroxy benzotriazole (HOBt) (54 mg, 0.40 mmol) in N,N-dimethylformamide (DMF) (5.0 mL). The resulted mixture was stirred for 12 h at room temperature (22 ^{o}C). Then, the solvent was removed from the flask under reduced pressure. The resulting residue was diluted with EtOAc, washed with saturated NaCl solution twice, and extracted by EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (elution with petroleum ether/EtOAc = 2:1) to give compound **5**.

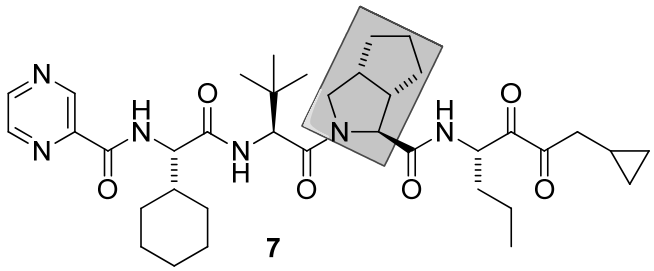
Compound **8** was also obtained according to the same procedure for the synthesis of **5** above (Scheme S1).



Scheme S1. Transformation of **4** to **8**

5. General procedure for the synthesis of 6

Compound **4** (28 mg, 0.1 mmol) was dissolved in dry THF (10mL) and cooled to 0 ^{o}C. $LiAlH_4$ (38 mg, 1.0 mmol) was added in one portion. The reaction mixture was refluxed for 18 h, then cooled to 0 ^{o}C, and the excess lithium aluminum hydride was quenched by cautious addition of water. Filtration through a pad of celite and evaporation of the filtrate under reduced pressure gave the pure product **6**.



7

Figure S2. hepatitis C virus protease inhibitors telaprevir **7**

6. Determination of absolute configuration and the X-ray structure of 3fa

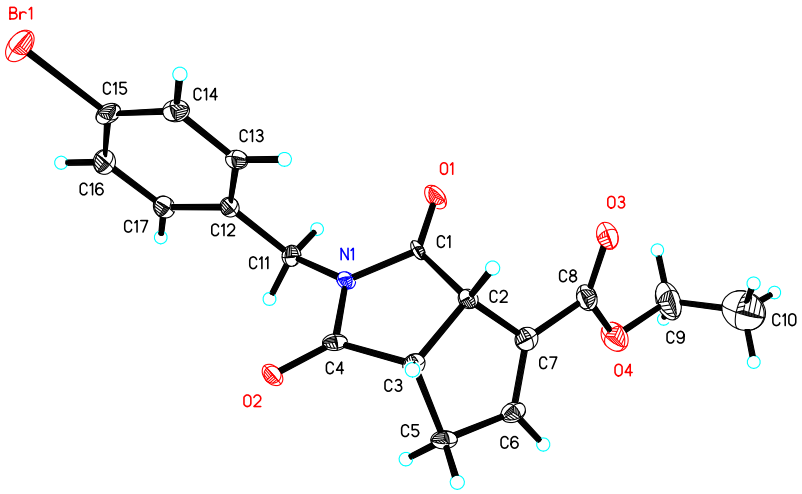


Figure S3. ORTEP Drawing of **3fa**.

Single crystal of $C_{17}H_{16}BrNO_4$ **3fa** was recrystallized from mixed solvents of dichloromethane and petroleum ether. Its absolute configuration has been identified as (*S*,*S*)-configuration.

The crystal data of **3fa** have been deposited in CCDC with number 783732. Empirical Formula: $C_{20}H_{18}BrF_2NO_2$; Formula Weight: 422.26; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.485 x 0.451 x 0.397 mm; Crystal System: Monoclinic; Lattice Parameters: a = 9.2224(14)Å, b = 10.4748(16)Å, c = 10.2384(16)Å, $\alpha = 90^o$, $\beta = 104.482(3)^o$, $\gamma = 90^o$, V = 957.6(3)Å^3; Space group: P2(1); Z = 2; D_{calc}= 1.464 g/cm^3; F_{000} = 957.6(3); Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0402, 0.0880.

7. Determination of relative configuration and the X-ray structure of *rac*-5

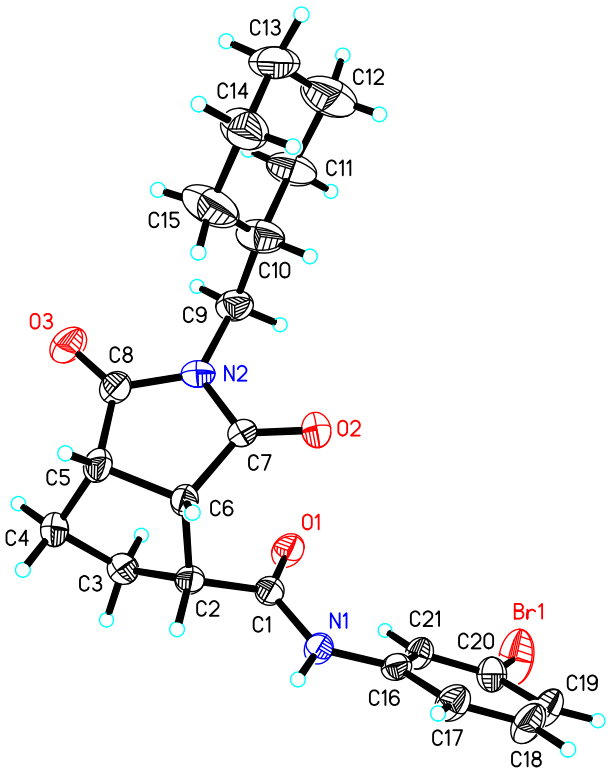


Figure S4. ORTEP Drawing of *rac*-**5**.

Single crystal of $C_{21}H_{25}BrN_2O_3$ *rac*-**5** was recrystallized from chloroform-d.

The crystal data of *rac*-**5** have been deposited in CCDC with number 844461. Empirical Formula: $C_{21}H_{25}BrN_2O_3$; Formula Weight: 433.34; Crystal Color, Habit: colorless, Crystal Dimensions: 0.265 x 0.071 x 0.063 mm; Crystal System: Monoclinic; Lattice Parameters: a = 8.960(7)Å, b = 21.905(17)Å, c = 20.488(16)Å, α = 90°, β = 98.968(17)°, γ = 90°, V = 3972(5)Å^3; Space group: P2(1)/c; Z = 8; D_{calc}= 1.449 g/cm^3; F_{000} = 1792; Final R indices [I>2sigma(I)] R1 = 0.0646, wR2 = 0.1571.

8. Determination of relative configuration and the X-ray structure of 3t

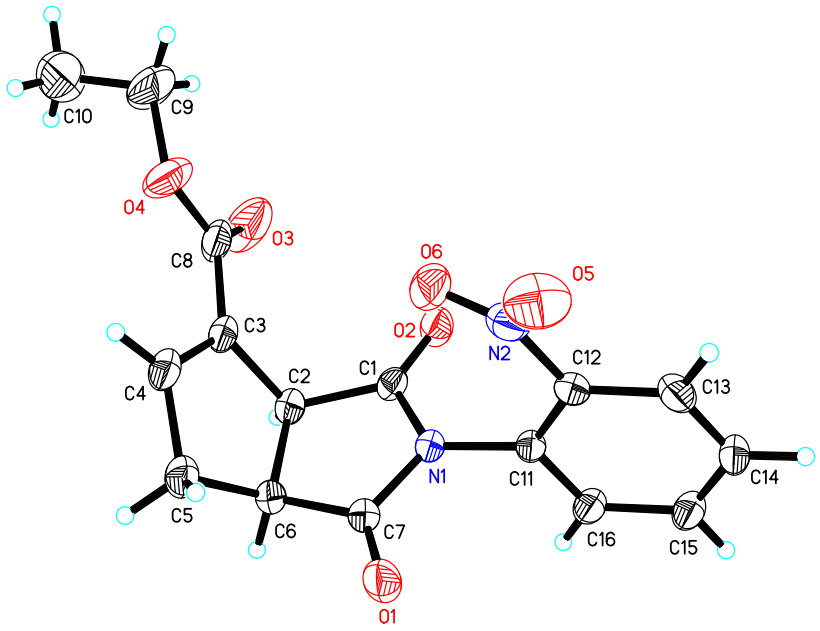


Figure S5. ORTEP Drawing of **3t**.

Single crystal of $C_{17}H_{16}BrNO_4$ **3t** was recrystallized from mixed solvents of dichloromethane and petroleum ether.

The crystal data of **3t** have been deposited in CCDC with number 805801. Empirical Formula: $C_{16}H_{14}N_2O_6$; Formula Weight: 330.29; Crystal Color, Habit: colorless, Crystal Dimensions: 0.30 x 0.28 x 0.25 mm; Crystal System: Monoclinic; Lattice Parameters: a = 14.2927(11)Å, b = 6.5471(5)Å, c = 16.4441(14)Å, $\alpha = 90^o$, $\beta = 93.366(2)^o$, $\gamma = 90^o$, V = 1536.1(2)Å^3; Space group: P2(1)/n; Z = 4; D_{calc}= 1.428 g/cm^3; F_{000} = 688; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0547, 0.1648.

9. References

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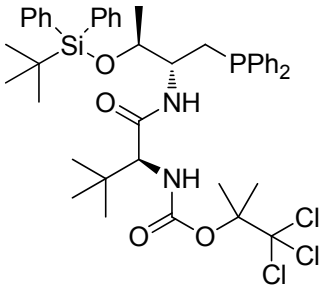
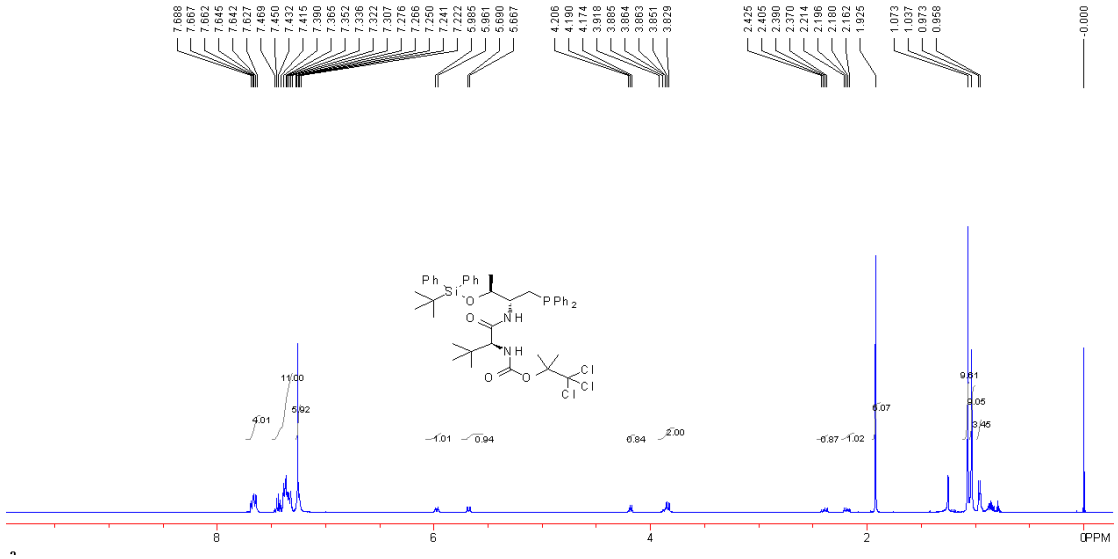
9. (a) M. Shi, L.-H. Chen, *Chem. Commun.* **2003**, 1310; (b) M. Shi, L.-H. Chen, C.-Q. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3790.

10. X. Han, Y. Wang, F. Zhong, Y. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 1726.

10. Characterization and spectra charts containing HPLC for products



Compound Cat. 11. This is a known compound.[6] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.97 (3H, d, J = 6.0 Hz), 1.04 (9H, s), 1.07 (9H, s), 1.93 (6H, s), 2.19 (1H, dd, J = 7.2, 13.6 Hz), 2.40 (1H, dd, J = 8.0, 13.6 Hz), 3.83-3.92 (2H, m), 4.19 (1H, t, J = 6.4 Hz), 5.68 (1H, d, J = 9.2 Hz), 5.98 (1H, d, J = 9.6 Hz), 7.22-7.28 (5H, m), 7.31-7.47 (11H, m), 7.63-7.69 (4H, m); ^{31}P NMR (161 MHz, $CDCl_3$, 85% H_3PO_4): δ 23.8.


7.688
7.667
7.662
7.645
7.642
7.627
7.469
7.450
7.432
7.415
7.390
7.365
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7.336
7.322
7.307
7.276
7.266
7.250
7.241
7.222
5.985
5.961
5.690
5.667
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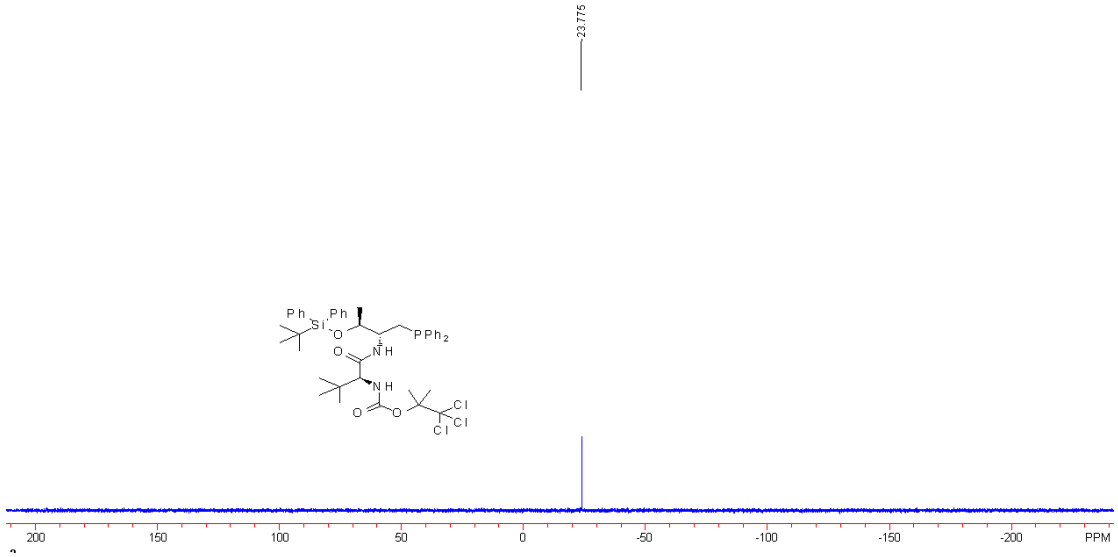
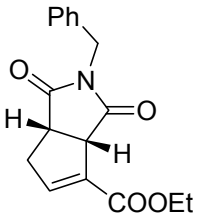
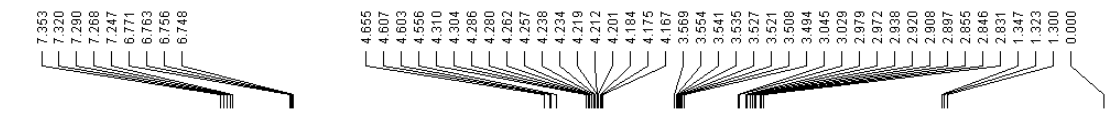
4.190
4.174
3.918
3.885
3.864
3.863
3.851
3.829
2.425
2.405
2.390
2.370
2.214
2.196
2.180
2.162
1.925
1.073
1.037
0.973
0.956
0.000
Ph
Si
Ph
O
PPh2
O
NH
NH
O
O
Cl
Cl
Cl
11.00
5.92
4.01
1.01
0.94
0.84
2.00
0.87
1.02
6.07
9.81
3.05
3.45
8
6
4
2
0
PPM


23.775
Ph
Si
Ph
O
PPh2
O
NH
NH
O
O
Cl
Cl
Cl
200
150
100
50
0
-50
-100
-150
-200
PPM



Compound 3aa. 41 mg, Yield: 92%, colorless oil; IR (neat): ν 2979, 2925, 2854, 1780, 1708, 1631, 1491, 1440, 1372, 1272, 1183, 1092, 1039, 921, 829, 758, 735, 691, 625 □cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.32 (3H, t, *J* = 7.2 Hz)□, 2.83-3.05 (2H, m), 3.53 (1H, ddd, *J* = 4.5, 8.4, 12.6 Hz), 4.17-4.22 (1H, m), 4.27 (1H, qd, *J* = 1.8, 7.2 Hz), 4.61 (2H, dd, *J* = 14.4, 15.6 Hz), 6.76 (1H, dd, *J* = 2.4, 4.5 Hz), 7.25-7.35 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.5, 42.4, 43.1, 51.6, 60.9, 127.9, 128.5, 128.6, 133.1, 135.5, 143.8, 163.1, 175.1, 178.5; MS (EI) *m/z* (%): 299 [M^+] (100.0), 253 (19.6), 225 (81.1), 197 (10.1), 132 (15.9), 110 (13.8), 91 (67.2), 79 (27.6), 65 (68.8), 41 (6.4); HRMS (EI) Calcd. for $C_{17}H_{17}NO_4$ requires (M^+) 299.1158, Found: 299.1162; $[\alpha]^{20}_D$ = +29.0 (c 0.5, CH_2Cl_2, 92% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 70/30, 0.6 mL/min, 214 nm, t_{minor} = 18.57 min, t_{major} = 16.58 min).

Compound 3a (the racemate of **3aa**). 44 mg, Yield: 98%, colorless oil.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6.756
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4.603
4.556
4.310
4.304
4.286
4.280
4.262
4.257
4.238
4.234
4.219
4.212
4.201
4.184
4.175
4.167
3.569
3.554
3.541
3.535
3.527
3.521
3.508
3.494
3.045
3.029
2.979
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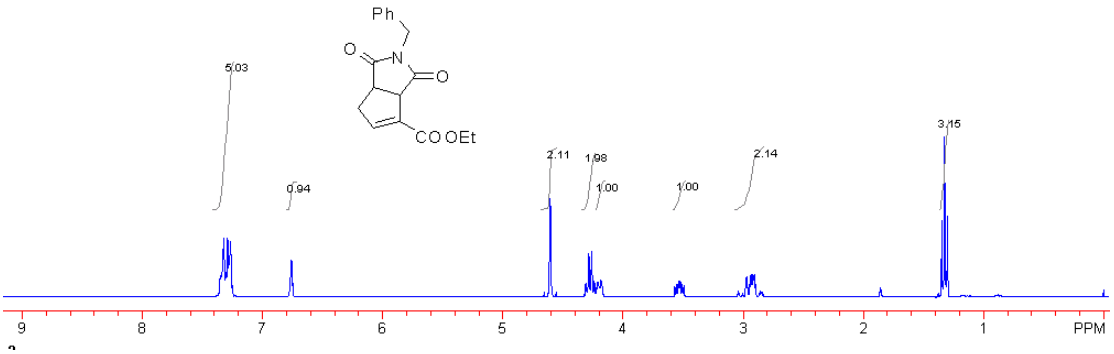
2.831
1.347
1.323
1.300
0.000


Ph
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N
O
COOEt
5.03
0.94
2.11
1.98
1.00
1.00
2.14
3.15
9
8
7
6
5
4
3
2
1
PPM


178.466
175.074
163.058
143.756
135.528
133.067
128.642
128.568
127.861
77.312
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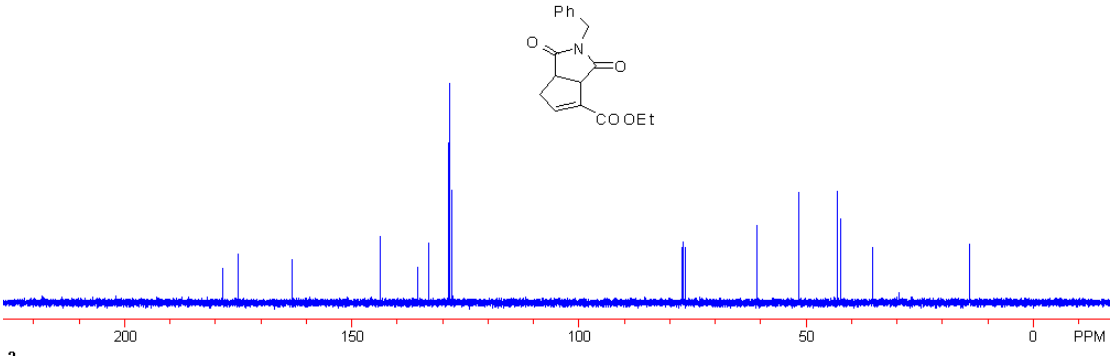
60.903
51.565
43.109
42.402
35.451
14.125


Ph
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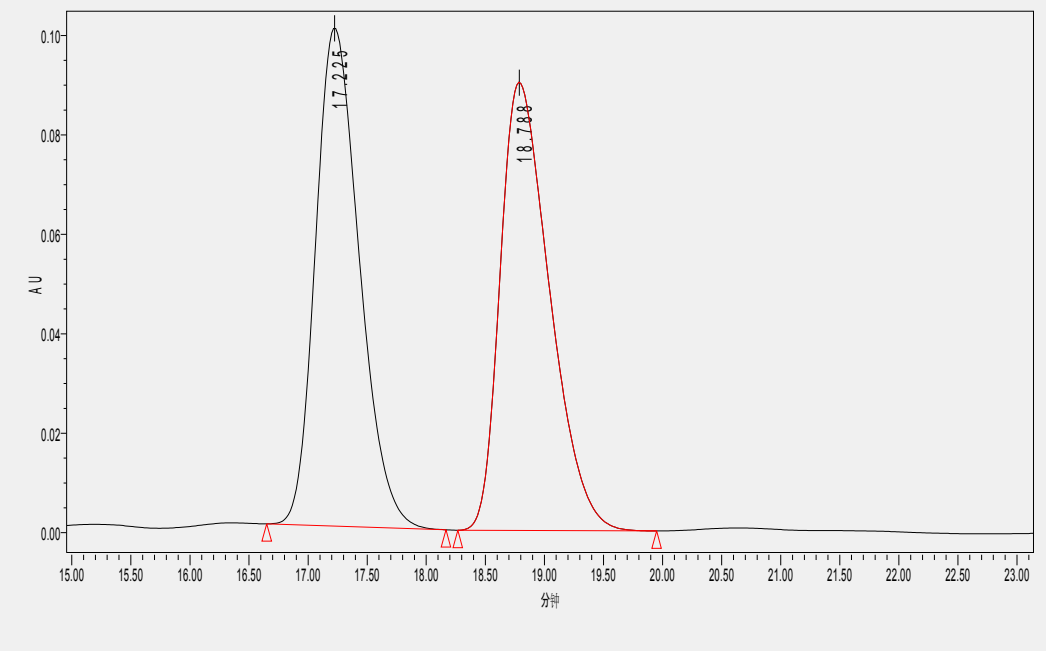
N
O
COOEt
200
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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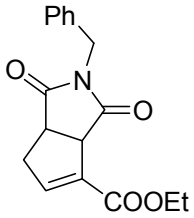
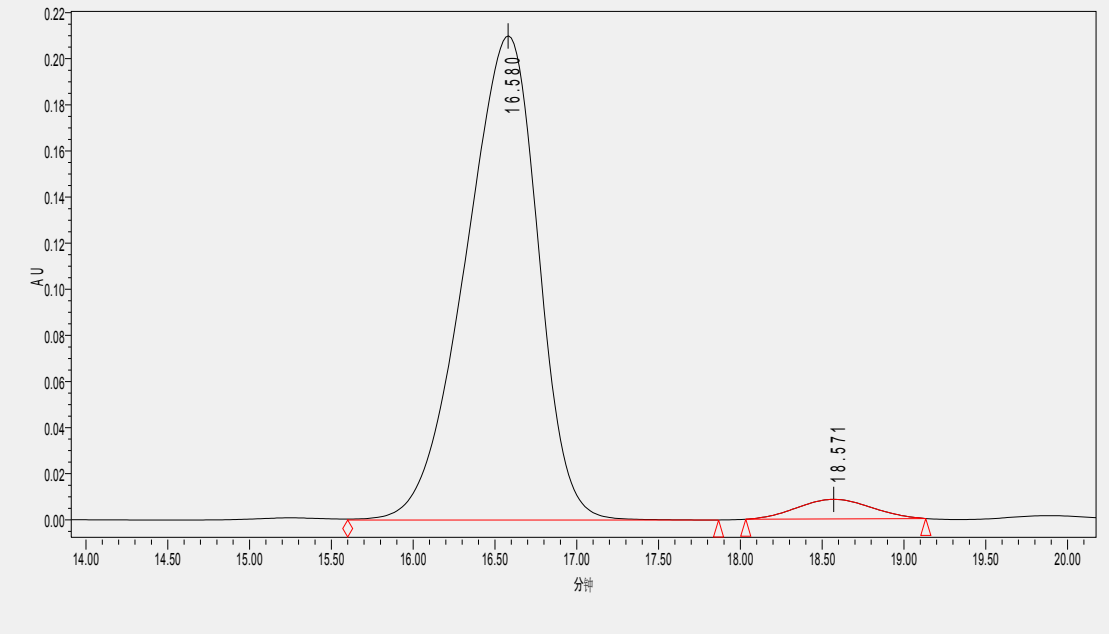
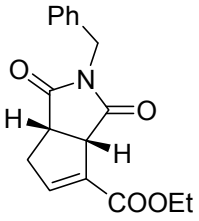
2	2	18.788	2620838	50.31	90134



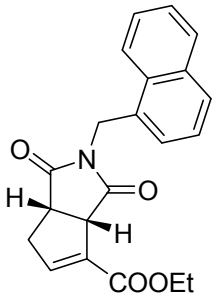
AD-H, *n*-hexane/*i*-PrOH = 70/30, 0.6 mL/min, 214 nm.



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	16.580	6481333	96.05	210065
2	2	18.571	266602	3.95	8446

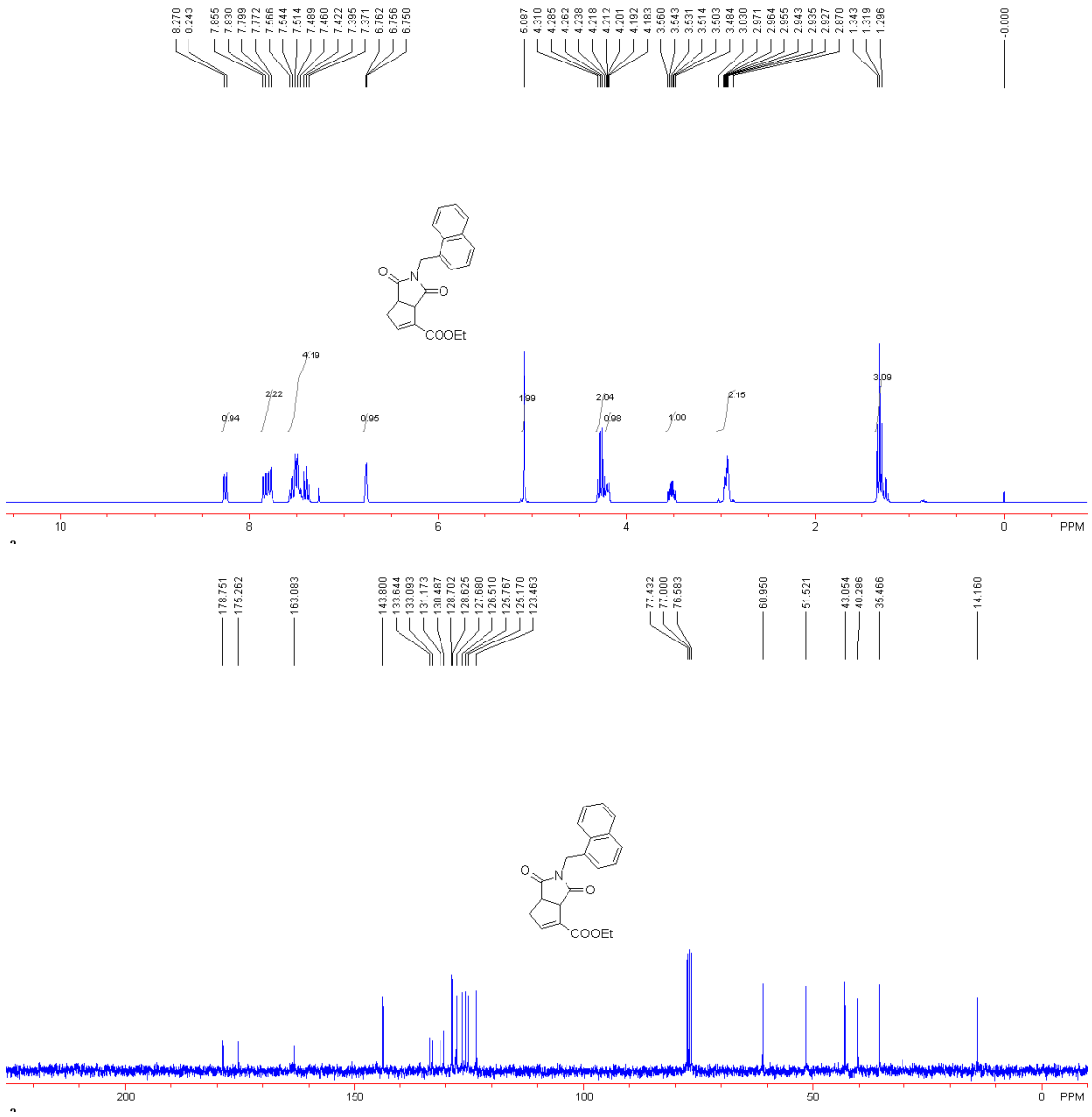


AD-H, *n*-hexane/*i*-PrOH = 70/30, 0.6 mL/min, 214 nm.



Compound 3ba. 44 mg, Yield: 84%, white solid, m.p. 140-141 °C; IR (neat): ν 3048, 2987, 1776, 1698, 1437, 1347, 1292, 1276, 1274, 1113, 854, 773, 724, 682 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.32 (3H, t, *J* = 7.2 Hz), 2.87-3.03 (2H, m), 3.52 (1H, td, *J* = 5.1, 8.7 Hz), 4.18-4.22 (1H, m), 4.28 (2H, q, *J* = 7.2 Hz), 5.09 (2H, s), 6.76 (1H, dd, *J* = 1.8, 3.6 Hz), 7.37-7.57 (4H, m), 7.82 (2H, dd, *J* = 7.8, 17.4 Hz), 8.26 (1H, d, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2, 35.5, 40.3, 43.1, 51.5, 61.0, 123.5, 125.2, 125.8, 126.5, 127.7, 128.6, 128.7, 130.5, 131.2, 133.1, 133.6, 143.8, 163.1, 175.3, 178.8; MS (EI) *m/z* (%): 349 [M^+] (100.0), 275 (25.9), 259 (13.2), 182 (20.7), 131 (51.8), 115 (14.8), 57 (17.8), 43 (12.1); HRMS (EI) Calcd. for $C_{21}H_{19}NO_4$ requires (M^+) 349.1314, Found: 349.1312; $[\alpha]^{20}_D$ = -5.7 (c 0.1, CH_2Cl_2, 85% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm, t_{minor} = 19.27 min, t_{major} = 12.62 min).

Compound 3b (the racemate of **3ba**). 52 mg, Yield: 99%, white solid, m.p. 131-132 °C.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4.310
4.285
4.262
4.238
4.218
4.212
4.201
4.192
4.183
3.560
3.543
3.531
3.514
3.503
3.484
3.030
2.971
2.964
2.955
2.943
2.935
2.927
2.870
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1.319
1.296
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COOEt
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2.22
4.19
0.95
1.99
2.04
0.98
1.00
2.15
3.09
10
8
6
4
2
0
PPM

178.751
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163.083
143.800
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133.093
131.173
130.487
128.702
128.625
127.660
126.510
125.767
125.170
123.463
77.432
77.000
76.583
60.950
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COOEt
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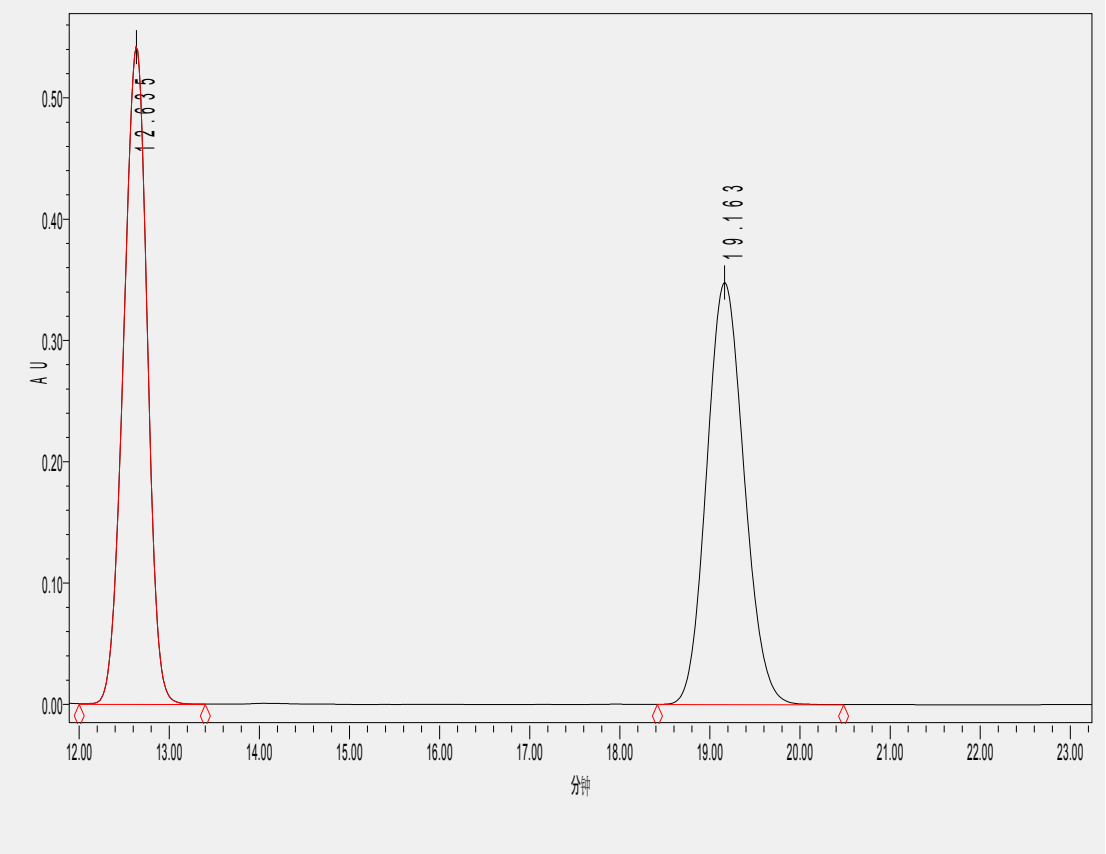
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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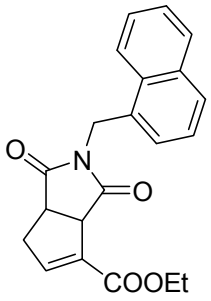
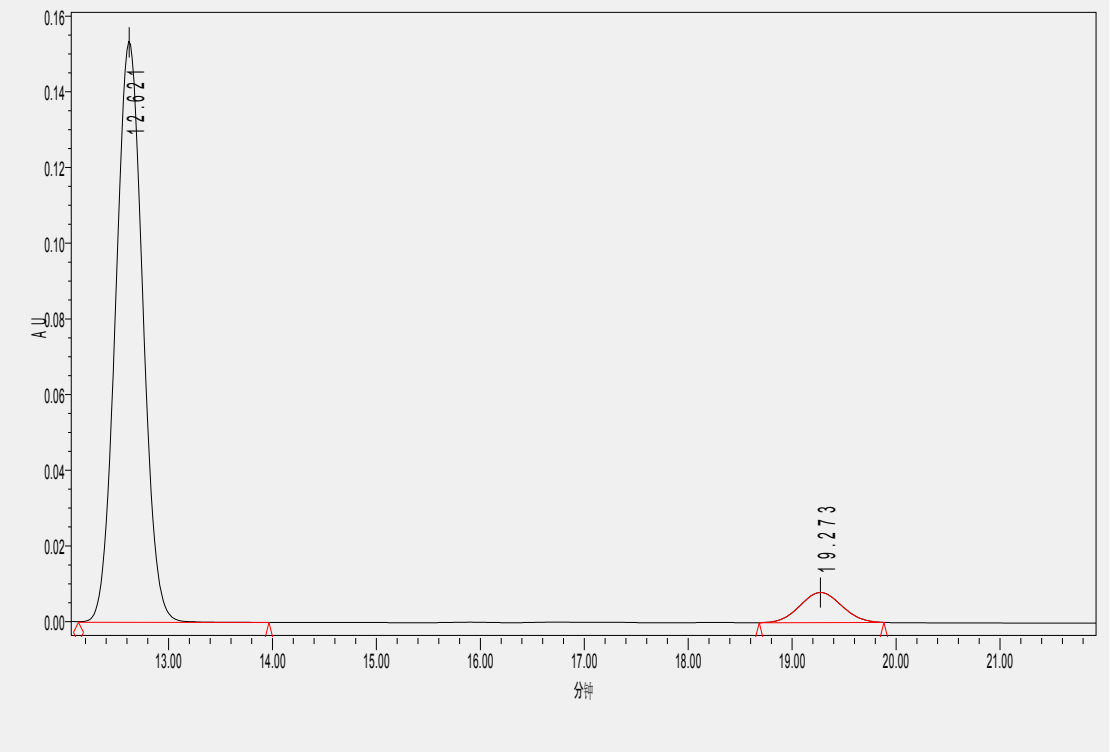
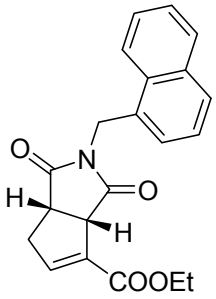


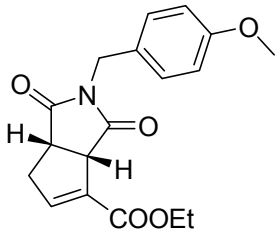
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm.



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	12.621	2784964	92.61	153560
2	2	19.273	222247	7.39	7946

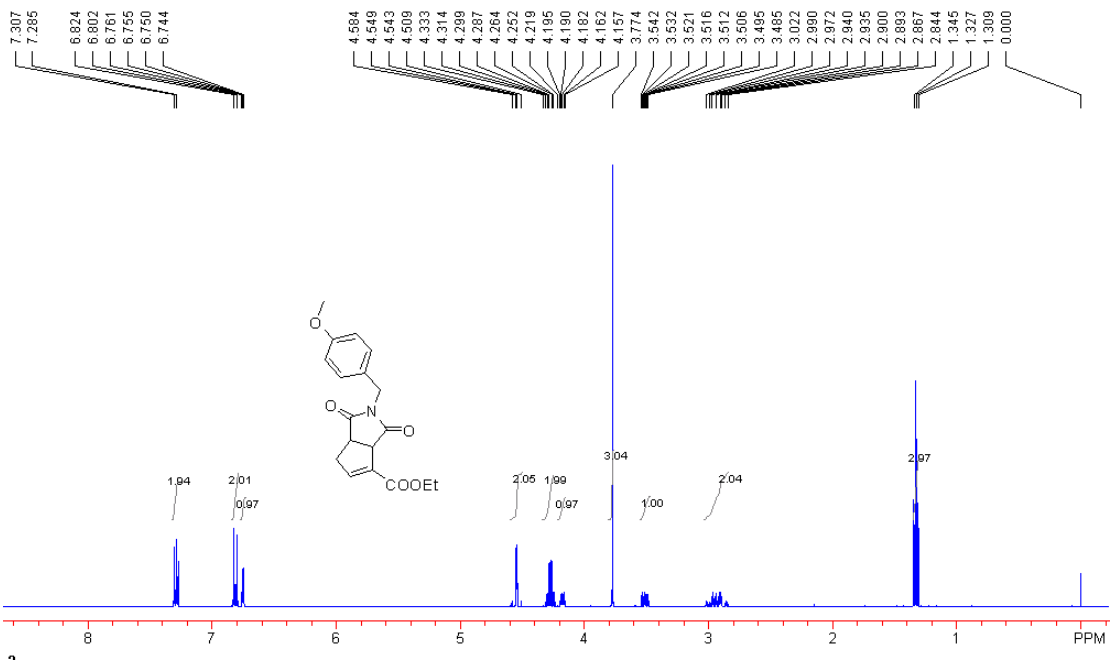


AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm.



Compound 3ca. 39 mg, Yield: 80%, white solid, m.p. 52-53 ^{o}C; IR (neat): ν 3053, 2962, 2861, 1724, 1615, 1556, 1453, 1362, 1298, 1173, 1122, 1038, 873, 806, 673, 629 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 7.2 Hz)□, 2.84-3.02 (2H, m), 3.52 (1H, ddd, *J* = 4.0, 8.4, 10.4 Hz), 3.77 (3H, s), 4.16-4.20 (1H, m), 4.22-4.33 (2H, m), 4.55 (2H, dd, *J* = 13.6, 16.0 Hz), 6.75 (1H, dd, *J* = 2.4, 4.4 Hz), 6.81 (2H, d, *J* = 8.8 Hz), 7.30 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.2, 35.5, 41.9, 43.1, 51.6, 55.2, 60.9, 113.9, 127.9, 130.2, 133.1, 143.8, 159.2, 163.1, 175.1, 178.5; MS (EI) *m/z* (%): 329 [M^+] (100.0), 255 (72.3), 227 (13.6), 162 (16.2), 121 (70.1), 93 (10.8), 65 (13.2), 43 (6.0); HRMS (EI) Calcd. for $C_{18}H_{19}NO_5$ requires (M^+) 329.1263, Found: 329.1260; $[\alpha]^{20}_D$ = +21.0 (c 0.1, CH_2Cl_2, 91% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm, t_{minor} = 9.14 min, t_{major} = 7.55 min).

Compound 3c (the racemate of **3ca**). 49 mg, Yield: 99%, colorless oil.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6.761
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6.750
6.744
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4.543
4.509
4.333
4.314
4.299
4.287
4.264
4.252
4.219
4.195
4.190
4.182
4.162
4.157
3.774
3.542
3.532
3.521
3.516
3.512
3.506
3.495
3.485
3.022
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2.940
2.935
2.900
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1.309
0.000
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O
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O
COOEt
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0.97
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3.04
1.00
2.04
2.97
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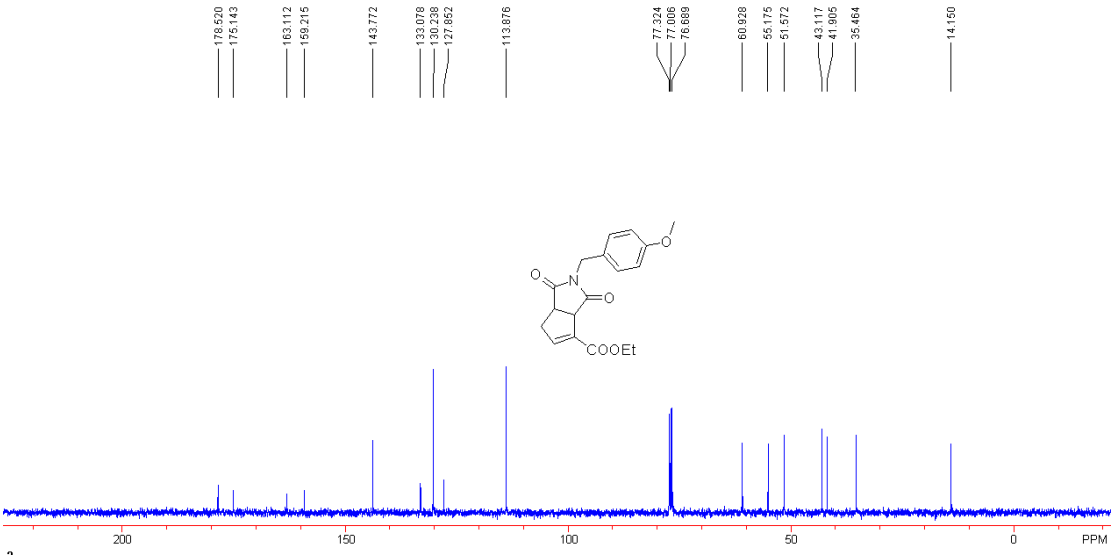
7
6
5
4
3
2
1
PPM


178.520
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133.078
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77.006
76.689
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55.175
51.572
43.117
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35.464
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COOEt
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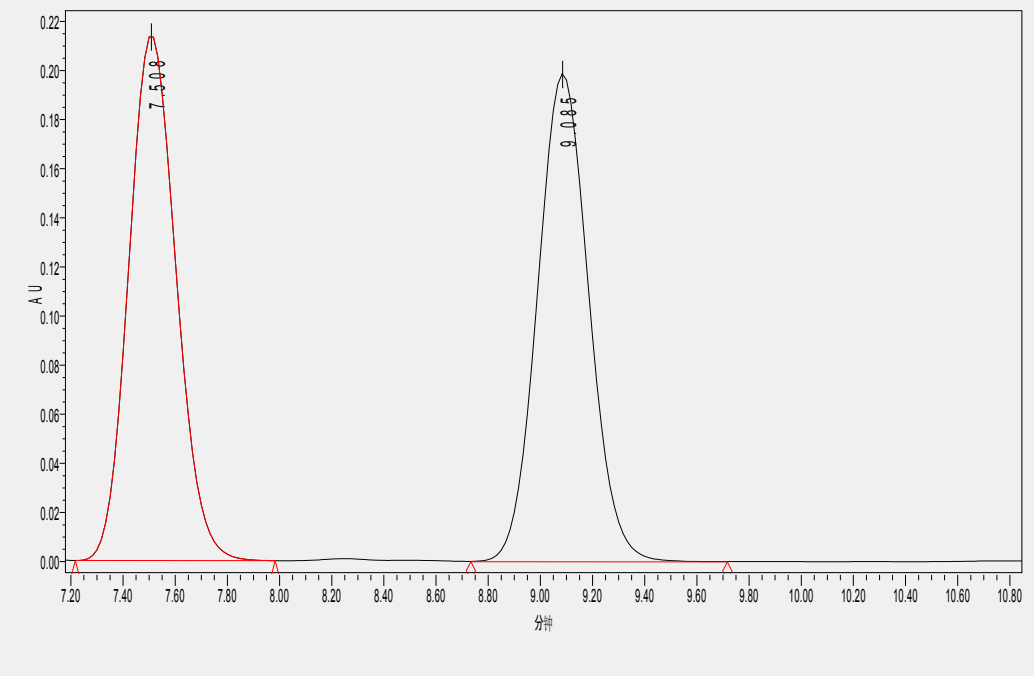
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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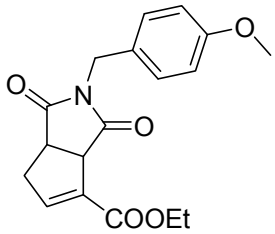
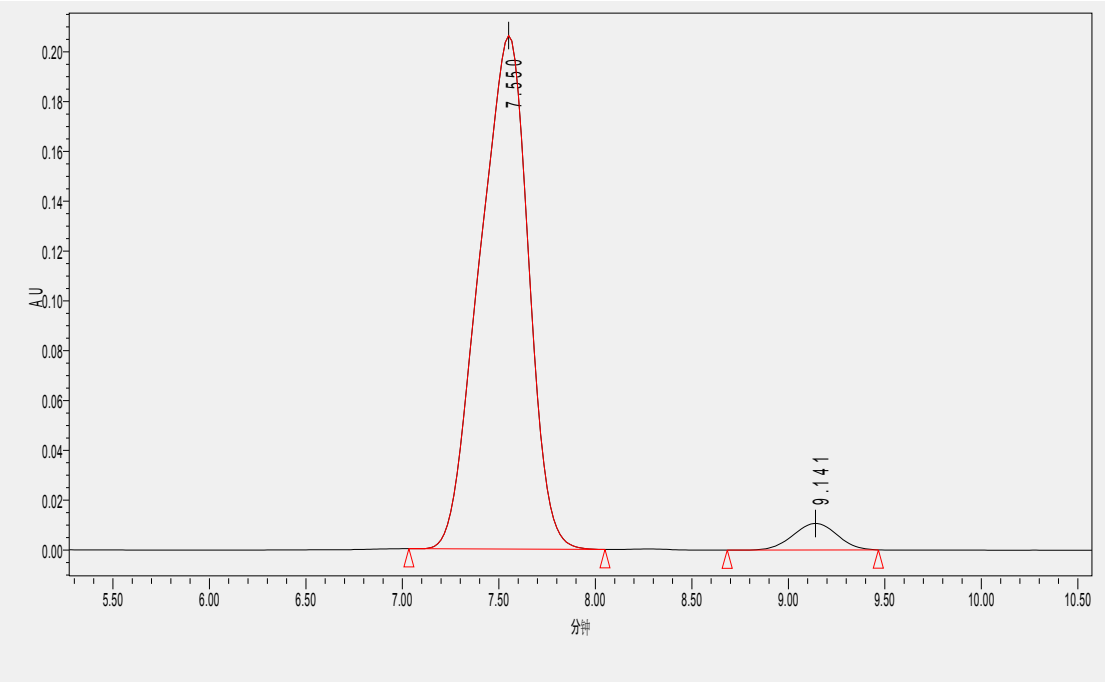
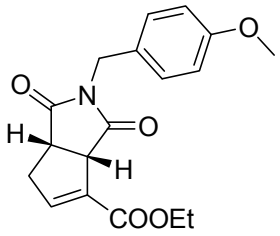


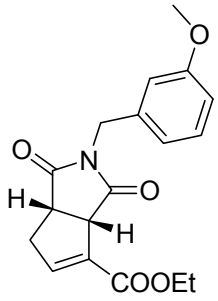
AD-H, *n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	7.550	3614318	95.55	206154
2	2	9.141	168402	4.45	10640

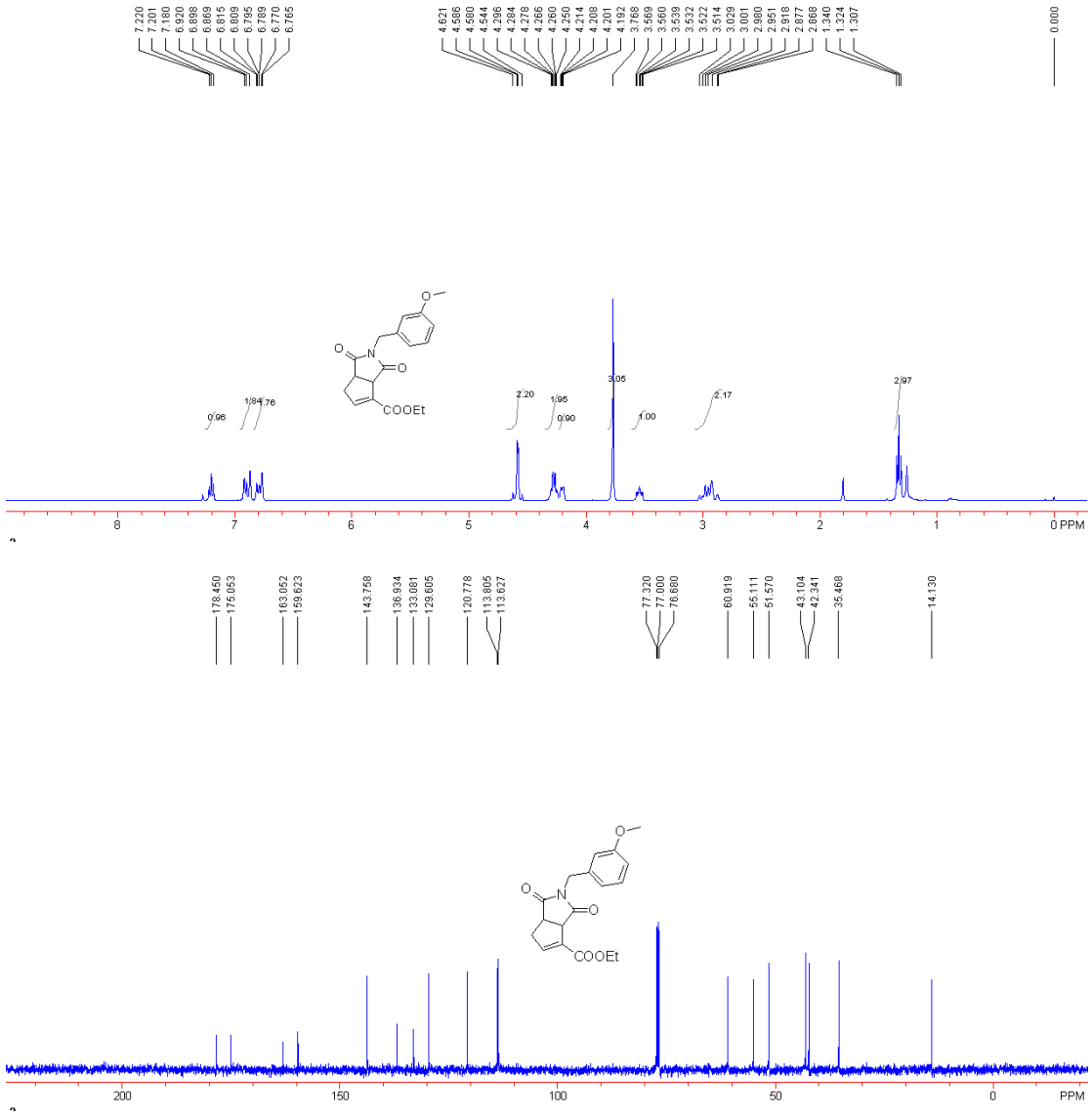


AD-H, *n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm



Compound 3da. 39 mg, Yield: 79%, white solid, m.p. 61-62 ^{o}C; IR (neat): ν 3044, 2984, 2839, 1704, 1610, 1495, 1391, 1349, 1252, 1161, 1093, 1031, 869, 769, 730, 678 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.32 (3H, t, *J* = 6.8 Hz)□, 2.87-3.03 (2H, m), 3.51-3.57 (1H, m), 3.77 (3H, s), 4.19-4.21 (1H, m), 4.25-4.30 (2H, m), 4.58 (2H, dd, *J* = 14.4, 16.8 Hz), 6.77-6.82 (2H, m), 6.87-6.92 (2H, m), 7.20 (1H, t, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.5, 42.3, 43.1, 51.6, 55.1, 60.9, 113.6, 113.8, 120.8, 129.6, 133.1, 136.9, 143.8, 159.6, 163.1, 175.1, 178.5; MS (EI) *m/z* (%): 329 [M^+] (100.0), 283 (23.8), 255 (83.6), 227 (8.2), 163 (18.7), 121 (30.1), 93 (22.3), 65 (24.2), 49 (14.7); HRMS (EI) Calcd. for $C_{18}H_{19}NO_5$ requires (M^+) 329.1263, Found: 329.1259; $[\alpha]^{20}_{D}$ = +32.0 (c 0.1, CH_2Cl_2, 92% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm, t_{minor} = 17.97 min, t_{major} = 14.36 min).

Compound 3d (the racemate of **3da**). 49 mg, Yield: 99%, white solid, m.p. 80-81 ^{o}C.


7.220
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6.809
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4.278
4.266
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4.214
4.208
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4.192
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3.539
3.532
3.522
3.514
3.029
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2.951
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2.877
2.868
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1.324
1.307
0.000
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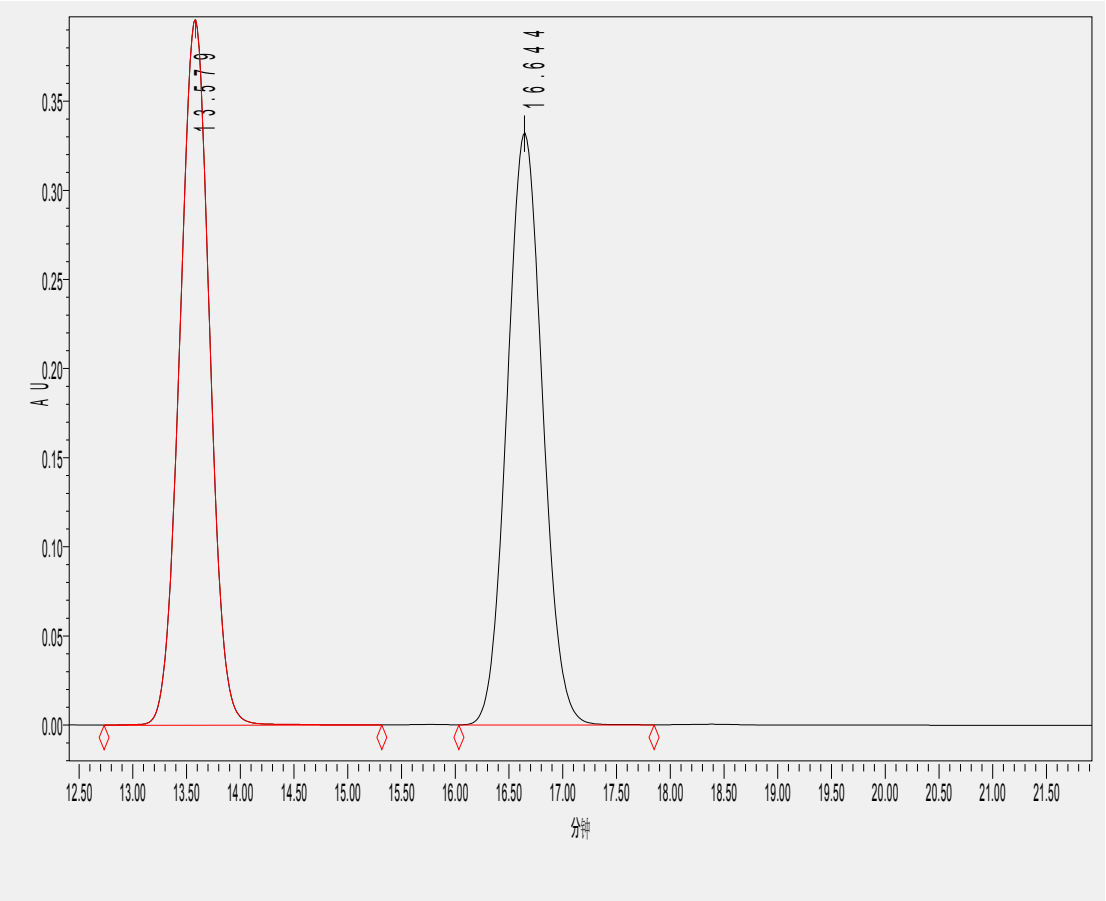
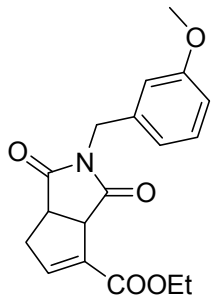
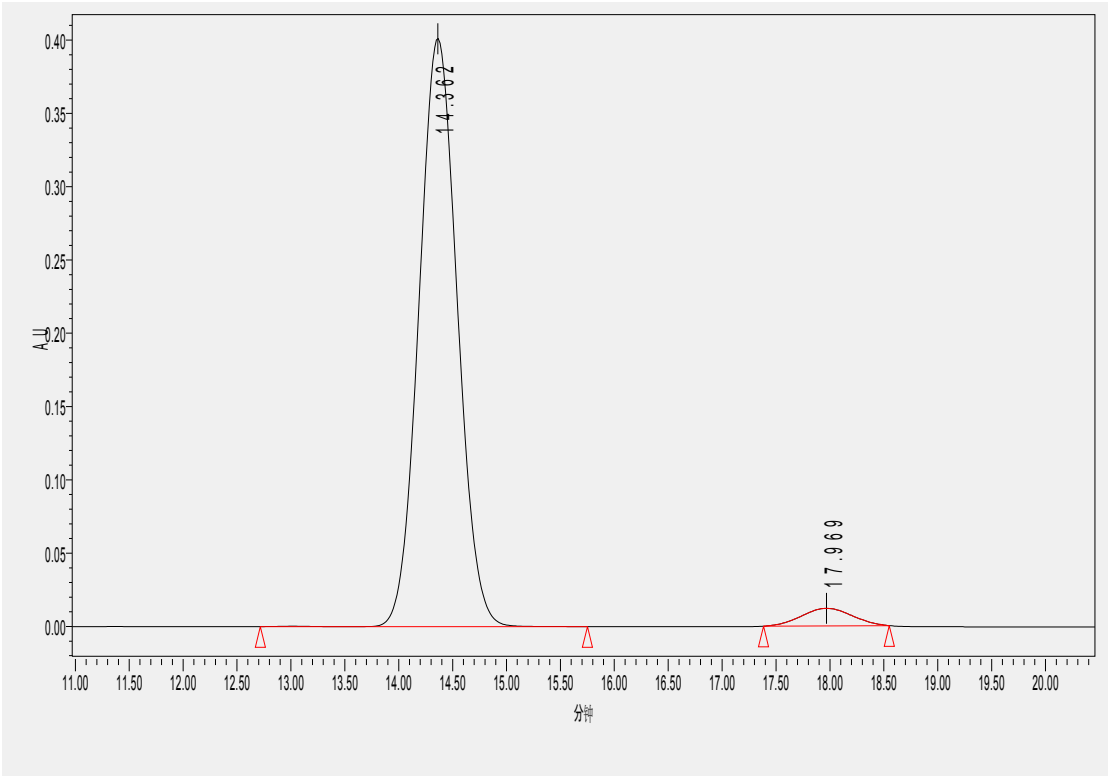
N
O
O
COOEt
0.96
1.84
1.76
2.20
1.95
0.90
3.05
1.00
2.17
2.97
8
7
6
5
4
3
2
1
0 PPM
178.450
175.053
163.052
159.623
143.758
136.934
133.081
129.605
120.778
113.805
113.627
77.320
77.000
76.680
60.919
55.111
51.570
43.104
42.341
35.468
14.130
200
150
100
50
0
PPM



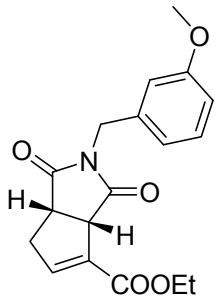
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	13.579	7699647	50.14	396313
2	2	16.644	7655984	49.86	332345



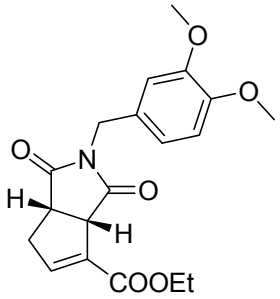
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	14.362	9895186	96.19	401504
2	2	17.969	391488	3.81	12021

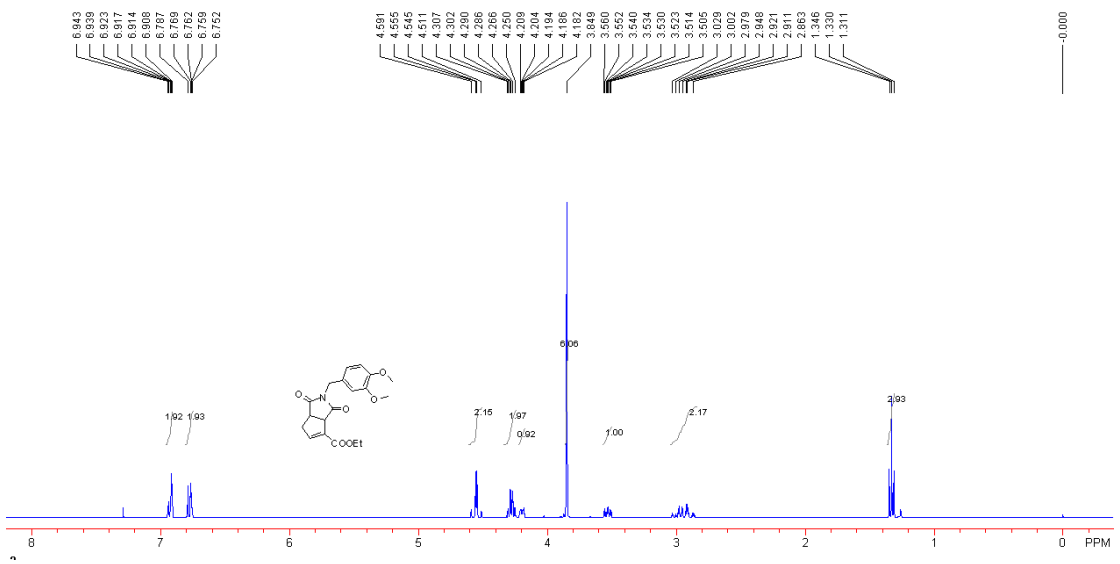


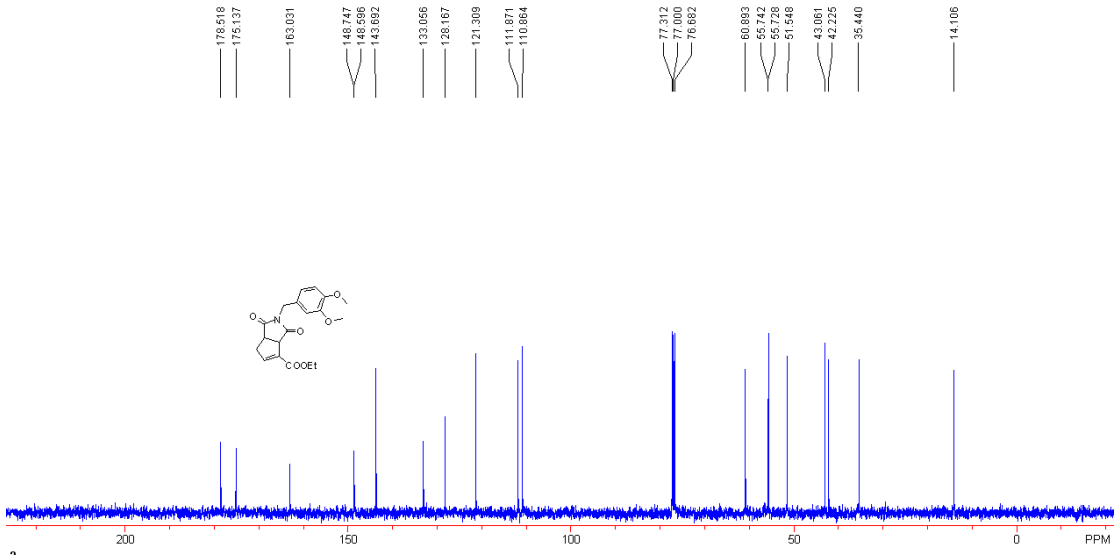
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm



Compound 3ea. 42 mg, Yield: 78%, white solid, m.p. 128-129 ^{o}C; IR (neat): ν 3052, 2995, 2846, 1775, 1700, 1697, 1512, 1386, 1334, 1251, 1161, 1143, 1035, 866, 744, 667 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 6.8 Hz)□, 2.86-3.03 (2H, m), 3.53 (1H, ddd, *J* = 3.2, 8.8, 10.4 Hz), 3.85 (6H, s), 4.18-4.21 (1H, m), 4.25-4.31 (2H, m), 4.55 (2H, dd, *J* = 13.6, 17.6 Hz), 6.75-6.79 (2H, m), 6.91-6.94 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.4, 42.2, 43.1, 51.5, 55.7, 55.8, 60.9, 110.9, 111.9, 121.3, 128.2, 133.1, 143.7, 148.6, 148.7, 163.0, 175.1, 178.5; MS (EI) *m/z* (%): 359 [M^+] (100.0), 285 (21.4), 257 (5.1), 192 (5.5), 151 (22.3), 107 (6.0), 93 (6.8), 65 (8.8); HRMS (EI) Calcd. for $C_{19}H_{21}NO_6$ requires (M^+) 359.1369, Found: 359.1366; $[\alpha]^{20}_{D}$ = +7.0 (c 0.1, CH_2Cl_2, 92% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm, t_{minor} = 19.50 min, t_{major} = 23.79 min).

Compound 3e (the racemate of **3ea**). 53 mg, Yield: 99%, white solid, m.p. 108-109 ^{o}C.


6.943
6.939
6.923
6.917
6.914
6.908
6.787
6.769
6.762
6.759
6.752
4.591
4.555
4.545
4.511
4.307
4.302
4.290
4.286
4.266
4.250
4.209
4.204
4.194
4.186
4.182
3.849
3.560
3.552
3.540
3.534
3.530
3.523
3.514
3.505
3.029
3.002
2.979
2.948
2.921
2.911
2.863
1.346
1.330
1.311
0.000
1.92
1.93
2.15
1.97
0.92
6.06
1.00
2.17
2.93
COOEt
8
7
6
5
4
3
2
1
0
PPM


178.618
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163.031
148.747
148.596
143.692
133.056
128.167
121.309
111.871
110.864
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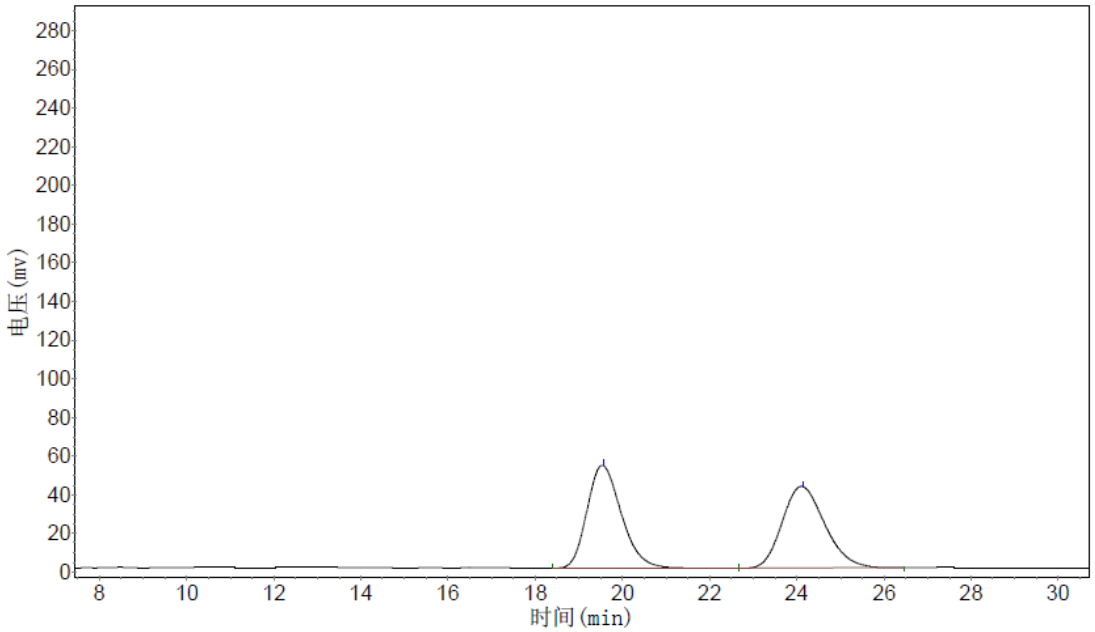
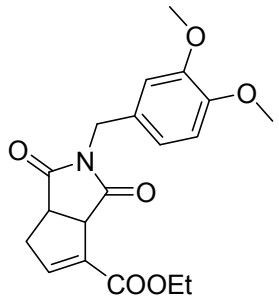
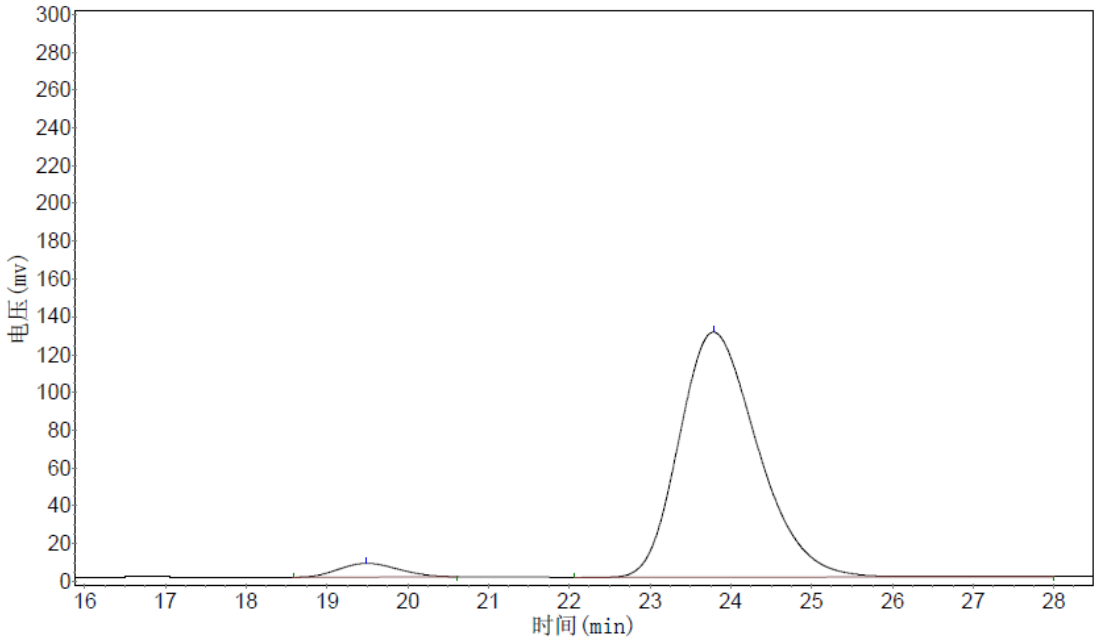
77.000
76.682
60.893
55.742
55.728
51.548
43.061
42.225
35.440
14.106
COOEt
200
150
100
50
0
PPM



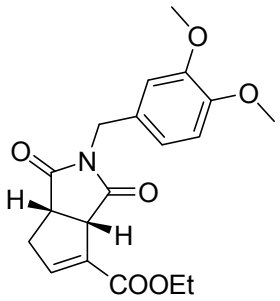
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	19.559	2907821	50.05	53129
2	2	24.135	2903374	49.95	42370



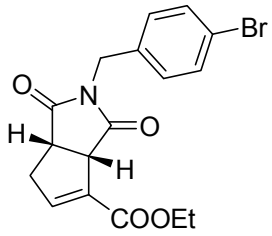
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	19.502	372498	4.03	7277
2	2	23.791	8853328	95.92	129622

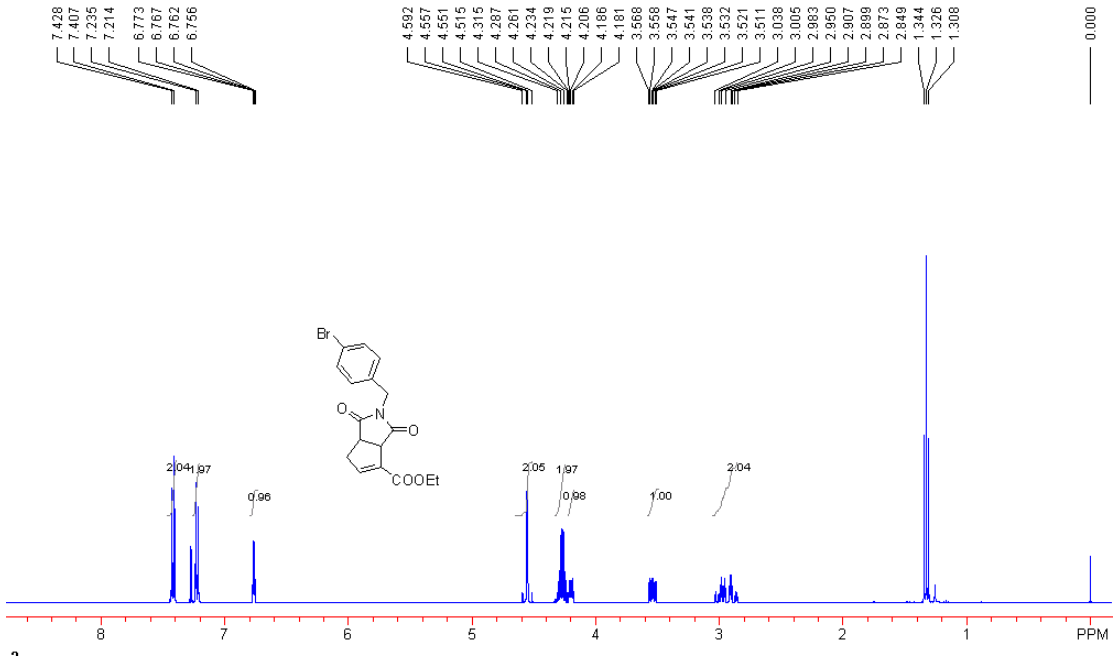


AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 214 nm



Compound 3fa. 46 mg, Yield: 81%, white solid, m.p. 47-48 ^{o}C; IR (neat): ν 3035, 2984, 2853, 1767, 1701, 1604, 1498, 1350, 1253, 1161, 1072, 1022, 821, 725, 669 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 7.2 Hz)□, 2.85-3.04 (2H, m), 3.54 (1H, ddd, *J* = 4.0, 8.4, 10.8 Hz), 4.18-4.22 (1H, m), 4.23-4.32 (2H, m), 4.55 (2H, dd, *J* = 14.0, 16.4 Hz), 6.76 (1H, dd, *J* = 2.4, 4.4 Hz), 7.22 (2H, d, *J* = 8.4 Hz), 7.42 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.4, 41.8, 43.1, 51.6, 60.9, 122.0, 130.5, 131.7, 132.9, 134.5, 143.8, 163.0, 175.0, 178.4; MS (EI) *m/z* (%): 379 [M^{+2}] (100.0), 378 [M^{+1}] (32.1), 378 [M^{+}] (99.5), 333 (27.8), 305 (95.1), 169 (25.2), 110 (23.9), 93 (55.0), 79 (26.0), 65 (53.8), 43 (18.7); HRMS (EI) Calcd. for $C_{17}H_{16}NO_4Br$ requires (M^{+}) 377.0263, Found: 377.0261; $[\alpha]^{20}_{D}$ = +10.0 (c 0.2, CH_2Cl_2, 91% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 80/20, 0.6 mL/min, 230 nm, t_{minor} = 28.36 min, t_{major} = 20.70 min).

Compound 3f (the racemate of **3fa**). 55 mg, Yield: 98%, white solid, m.p. 57-58 ^{o}C.


7.428
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6.762
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4.551
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4.287
4.261
4.234
4.219
4.215
4.206
4.186
4.181
3.568
3.558
3.547
3.541
3.538
3.532
3.521
3.511
3.038
3.005
2.983
2.950
2.907
2.899
2.873
2.849
1.344
1.326
1.308
0.000
Br
O
N
O
COOEt
2.04
1.97
0.96
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1.97
0.98
1.00
2.04
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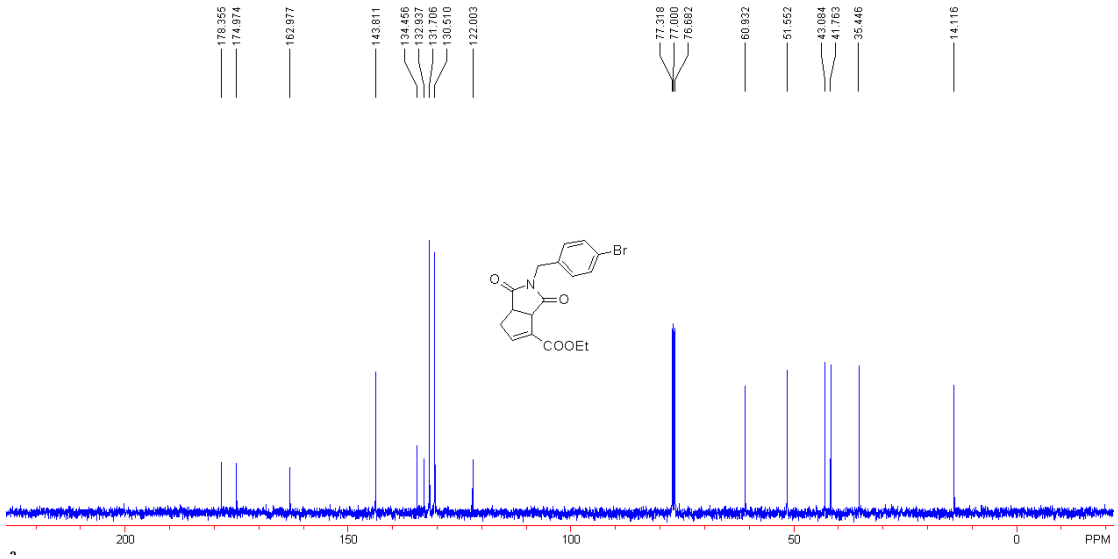
7
6
5
4
3
2
1
PPM


178.355
174.974
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134.456
132.937
131.706
130.510
122.003
77.318
77.000
76.682
60.932
51.552
43.084
41.763
35.446
14.116
Br
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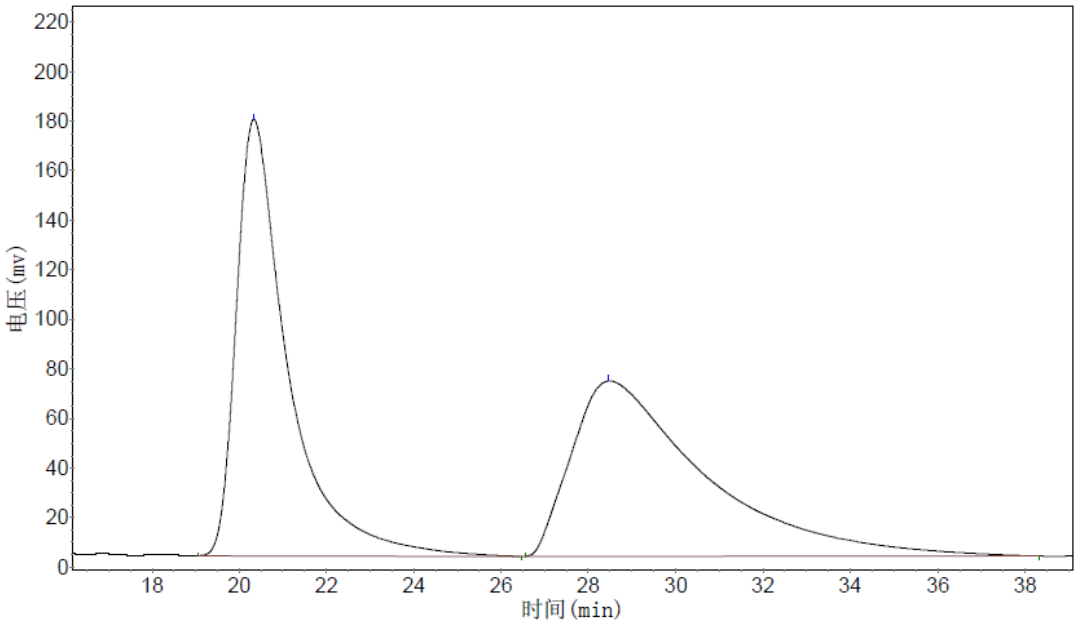
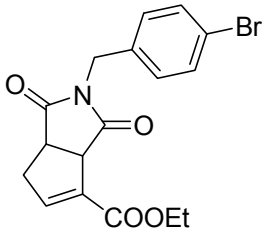
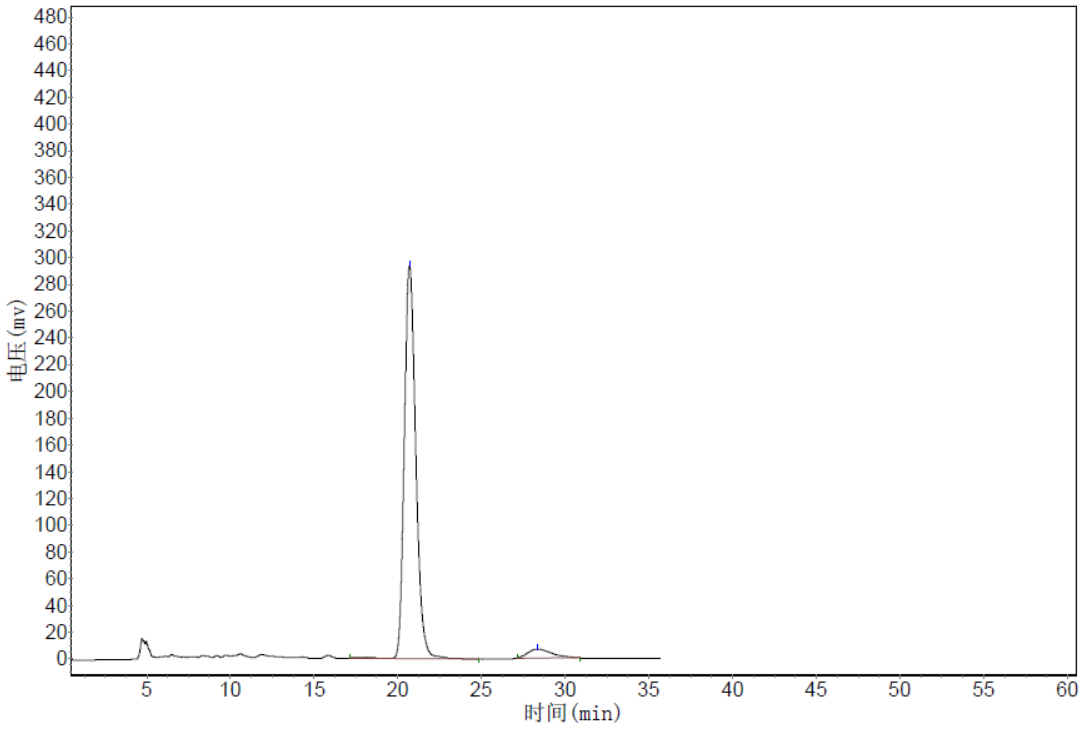
N
O
COOEt
200
150
100
50
0
PPM



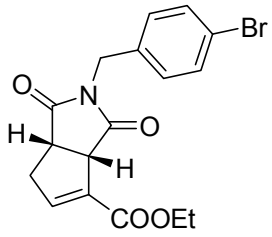
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	20.342	14560643	49.40	176198
2	2	28.462	14975217	50.71	70817



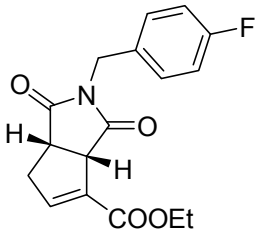
AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.6 mL/min, 230 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	20.699	13916711	95.43	293406
2	2	28.361	667421	4.48	6605

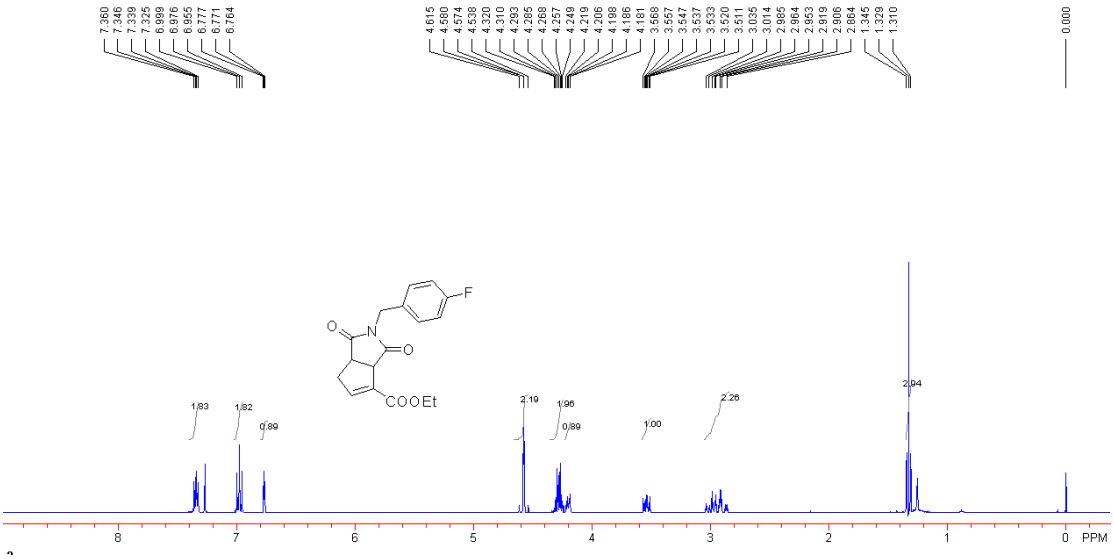


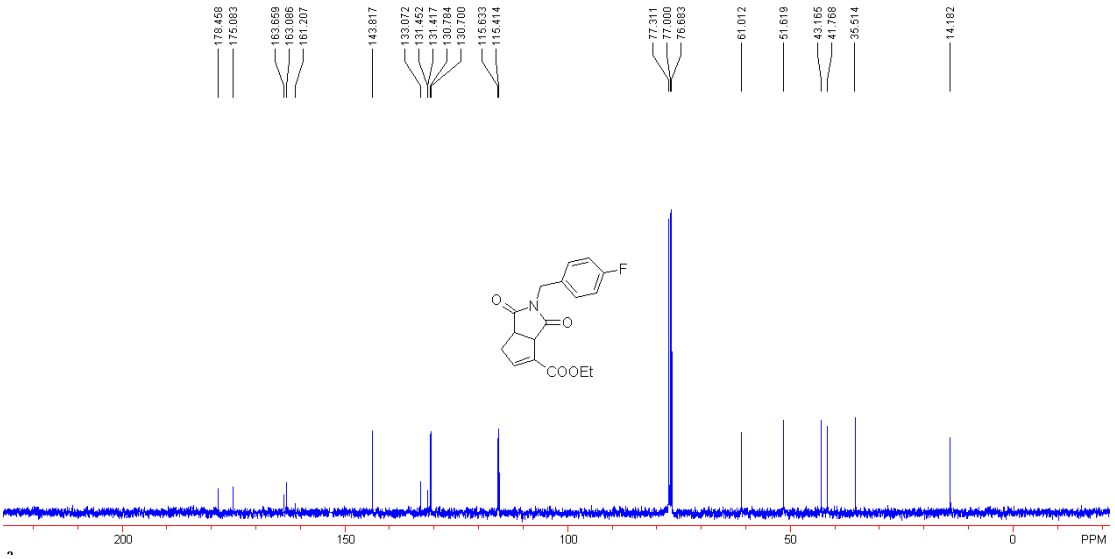
AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.6 mL/min, 230 nm



Compound 3ga. 41 mg, Yield: 86%, colorless oil; IR (neat): ν 3066, 2982, 2883, 1768, 1689, 1501, 1393, 1352, 1293, 1226, 1151, 1031, 906, 853, 735, 681, 625 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 7.2 Hz)□, 2.86-3.04 (2H, m), 3.51-3.57 (1H, m), 4.19-4.22 (1H, m), 4.25-4.32 (2H, m), 4.58 (2H, dd, *J* = 14.0, 16.4 Hz), 6.77 (1H, dd, *J* = 2.4, 5.2 Hz), 6.96-7.00 (2H, m), 7.34 (2H, dd, *J* = 5.6, 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.2, 35.5, 41.8, 43.2, 51.6, 61.0, 115.5 (d, *J* = 21.9 Hz), 130.7 (d, *J* = 8.4 Hz), 131.4 (d, *J* = 3.5 Hz), 133.1, 143.8, 162.4 (d, *J* = 245.2 Hz), 163.1, 175.1, 178.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -114.0- -114.1 (1F, m); MS (EI) *m/z* (%): 317 [M^+] (100.0), 271 (18.1), 243 (94.2), 109 (69.7), 93 (26.9), 79 (16.1), 65 (30.0), 49 (7.0); HRMS (EI) Calcd. for $C_{17}H_{16}NO_4F$ requires (M^+) 317.1063, Found: 317.1062; $[\alpha]^{20}_D$ = +21.0 (c 0.1, CH_2Cl_2, 90% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 80/20, 0.6 mL/min, 214 nm, t_{minor} = 25.66 min, t_{major} = 18.80 min).

Compound 3g (the racemate of **3ga**). 47 mg, Yield: 99%, colorless oil.

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77.311
77.000
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61.012
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COOEt
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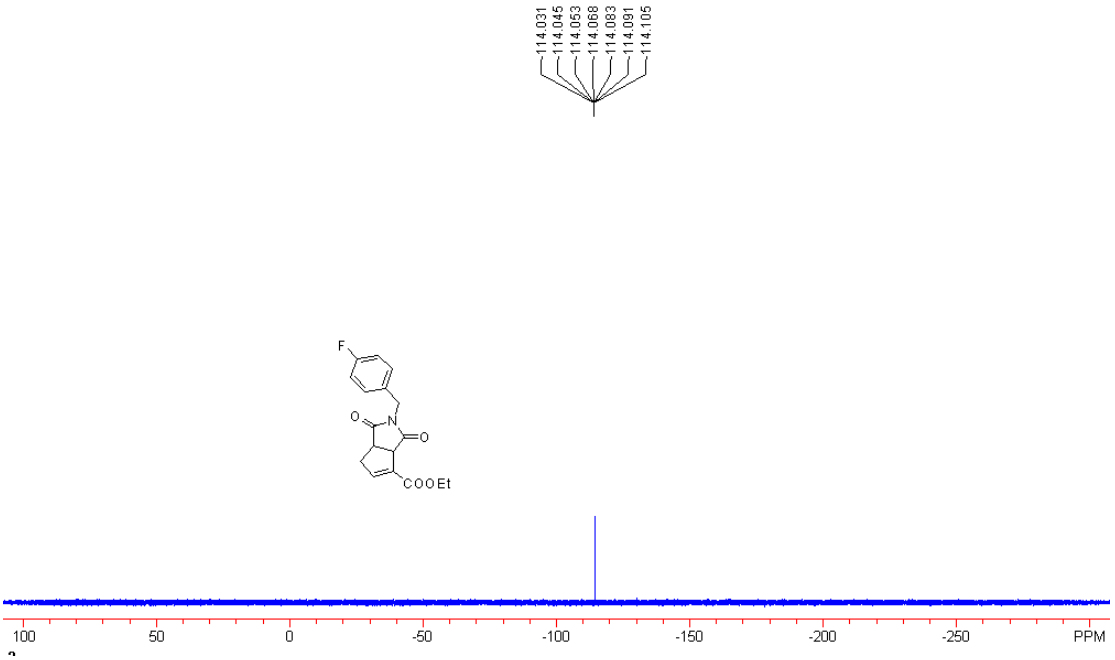
PPM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COOEt
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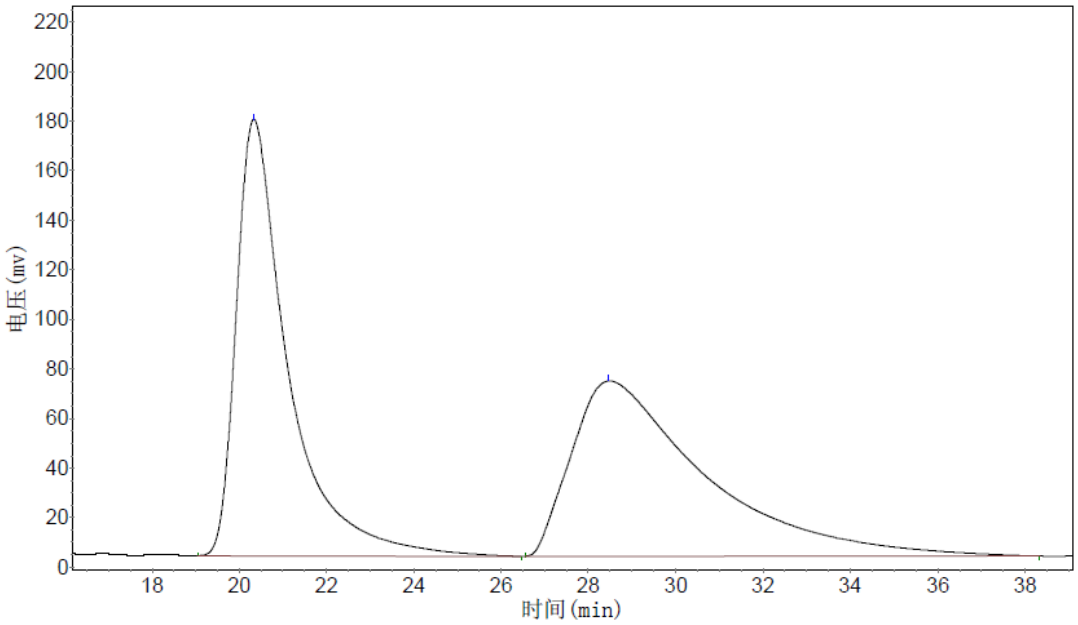
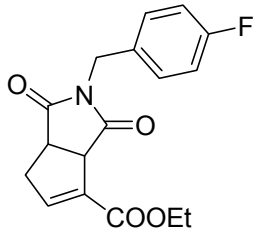
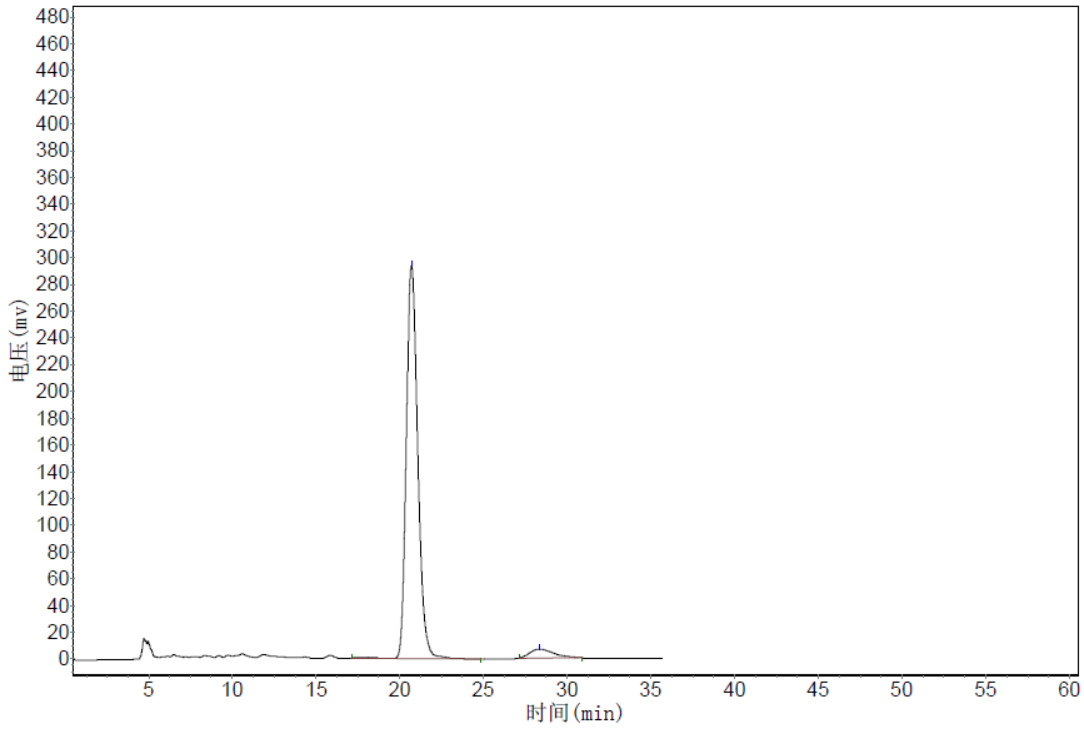
-50
-100
-150
-200
-250
PPM



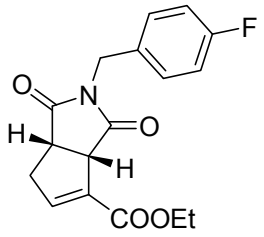
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	20.342	14560643	49.40	176198
2	2	28.462	14975217	50.71	70817



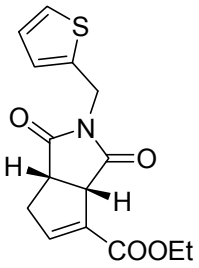
AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	20.699	13916711	95.43	293406
2	2	28.361	667421	4.48	6605

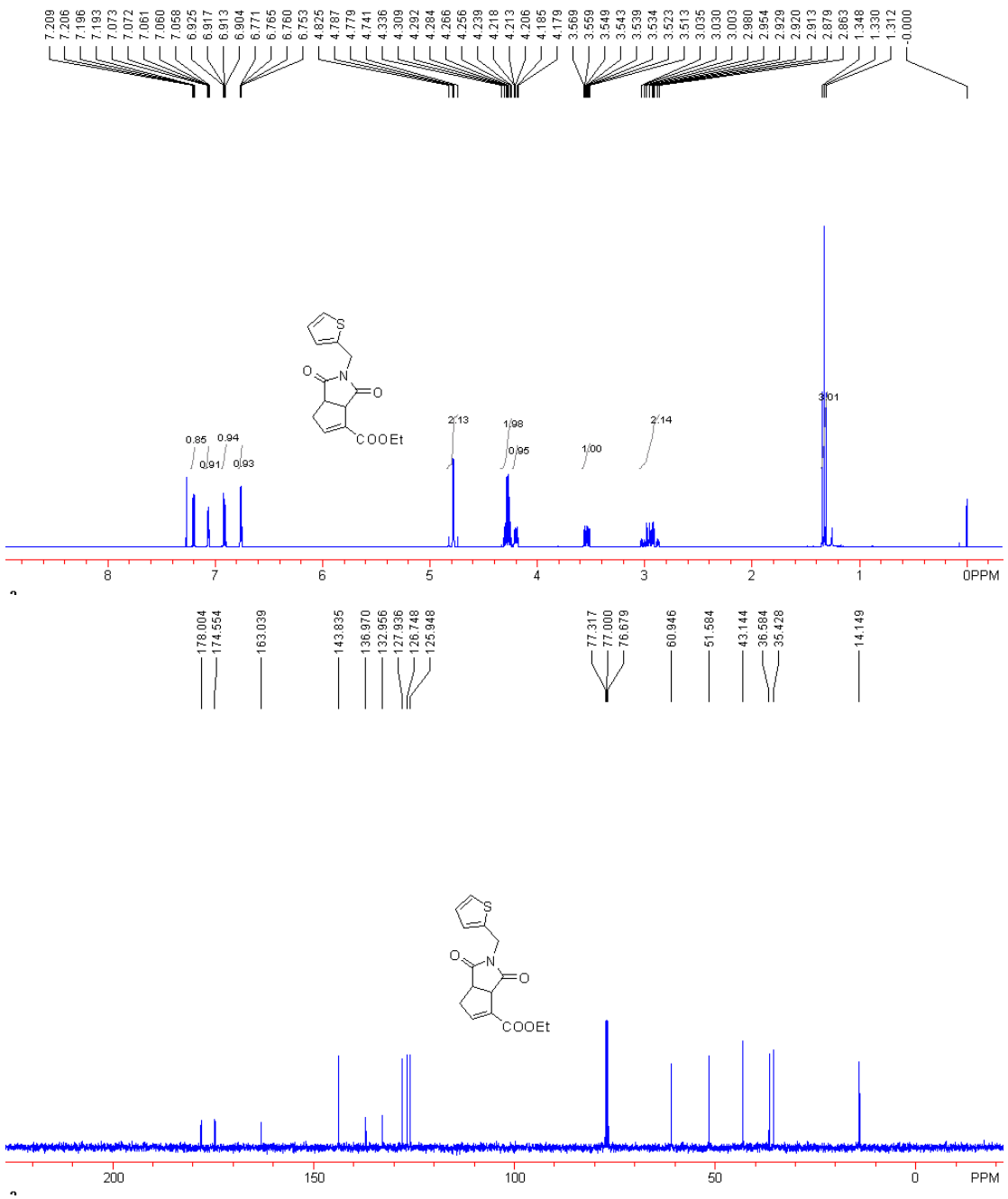


AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.6 mL/min, 214 nm



Compound 3ha. 38 mg, Yield: 82%, colorless oil; IR (neat): ν 3051, 2995, 2882, 1775, 1701, 1635, 1393, 1342, 1255, 1182, 1153, 1139, 1026, 885, 857, 733, 630 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, J = 7.2 Hz)□, 2.86-3.04 (2H, m), 3.54 (1H, ddd, J = 4.0, 8.0, 10.4 Hz), 4.18-4.22 (1H, m), 4.24-4.34 (2H, m), 4.78 (2H, dd, J = 15.2, 18.4 Hz), 6.76 (1H, dd, J = 2.4, 4.4 Hz), 6.92 (1H, dd, J = 3.2, 5.2 Hz), 7.06-7.07 (1H, m), 7.20 (1H, dd, J = 1.4, 5.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.4, 36.6, 43.1, 51.6, 60.9, 125.9, 126.7, 127.9, 133.0, 137.0, 143.8, 163.0, 174.6, 178.0; MS (EI) *m/z* (%): 305 [M^+] (79.1), 259 (20.7), 231 (100.0), 203 (13.6), 138 (10.8), 97 (61.1), 65 (15.4); HRMS (EI) Calcd. for $C_{15}H_{15}NO_4S$ requires (M^+) 305.0722, Found: 305.0726; $[\alpha]^{20}_D$ = +28.1 (c 0.1, CH_2Cl_2, 90% ee). Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm, t_{minor} = 26.45 min, t_{major} = 32.74 min).

Compound 3h (the racemate of **3ha**). 44 mg, Yield: 97%, colorless oil.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7.072
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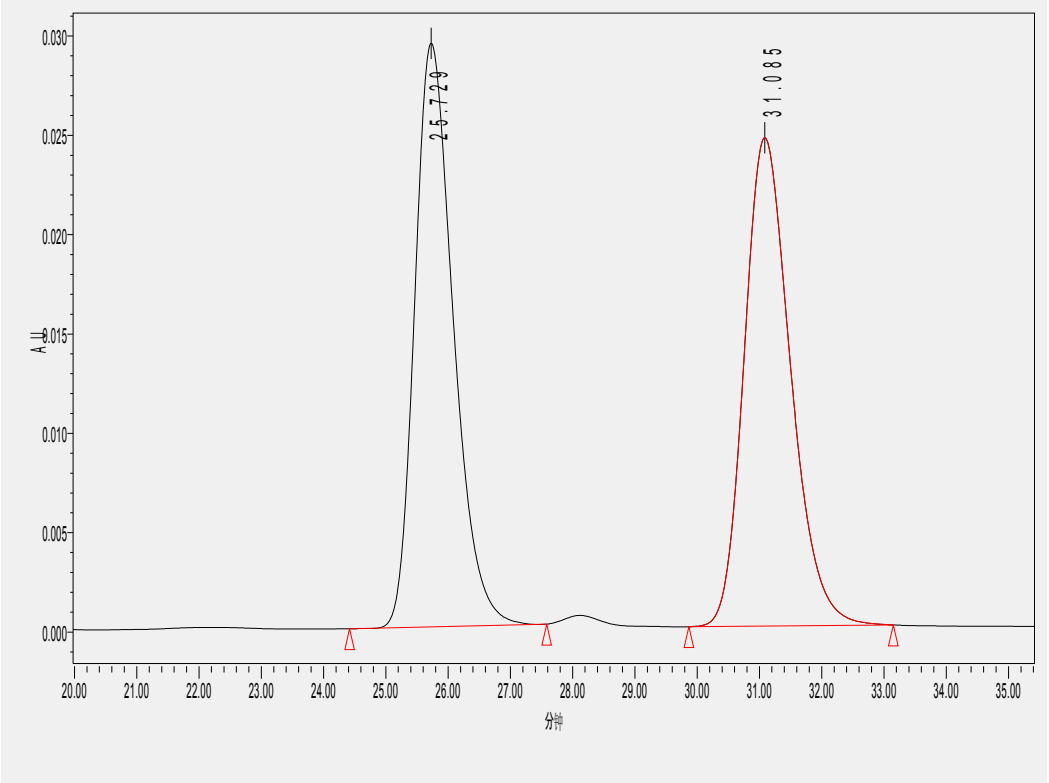
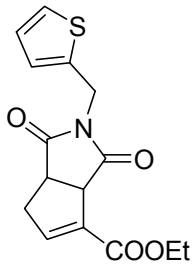
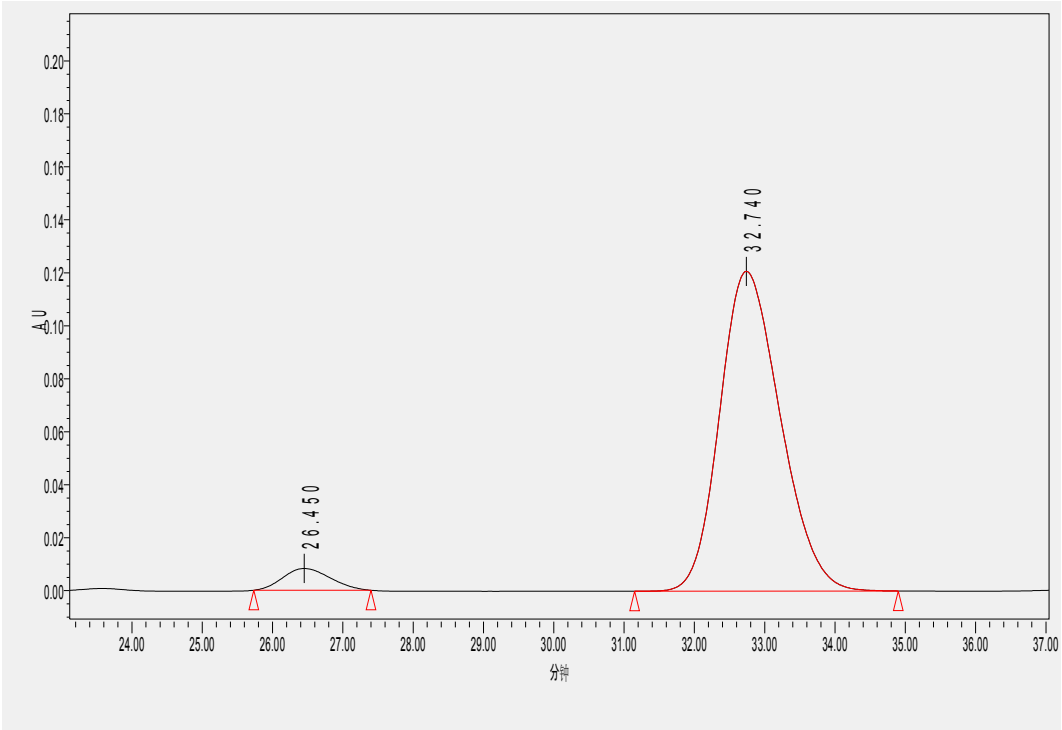
6.771
6.765
6.760
6.753
4.825
4.787
4.779
4.741
4.336
4.309
4.292
4.284
4.266
4.256
4.239
4.218
4.213
4.206
4.185
4.179
3.569
3.559
3.549
3.543
3.539
3.534
3.523
3.513
3.035
3.030
3.003
2.980
2.954
2.929
2.920
2.913
2.879
2.863
1.348
1.330
1.312
-0.000
S
O
N
O
COOEt
0.85
0.91
0.94
0.93
2.13
1.98
0.95
1.00
2.14
3.01
8
7
6
5
4
3
2
1
0PPM
178.004
174.554
163.039
143.835
136.970
132.956
127.936
126.748
125.948
77.317
77.000
76.679
60.946
51.584
43.144
36.584
35.428
14.149
S
O
N
O
COOEt
200
150
100
50
0
PPM



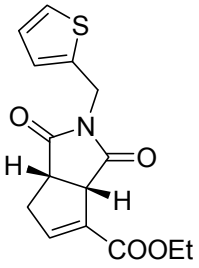
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	25.729	1265319	49.86	29381
2	2	31.085	1272658	50.14	24585



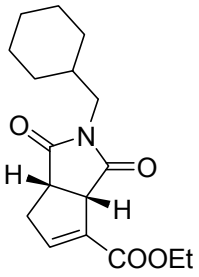
IC-H, *n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	26.450	384293	5.04	8224
2	2	32.740	7237552	94.96	120715

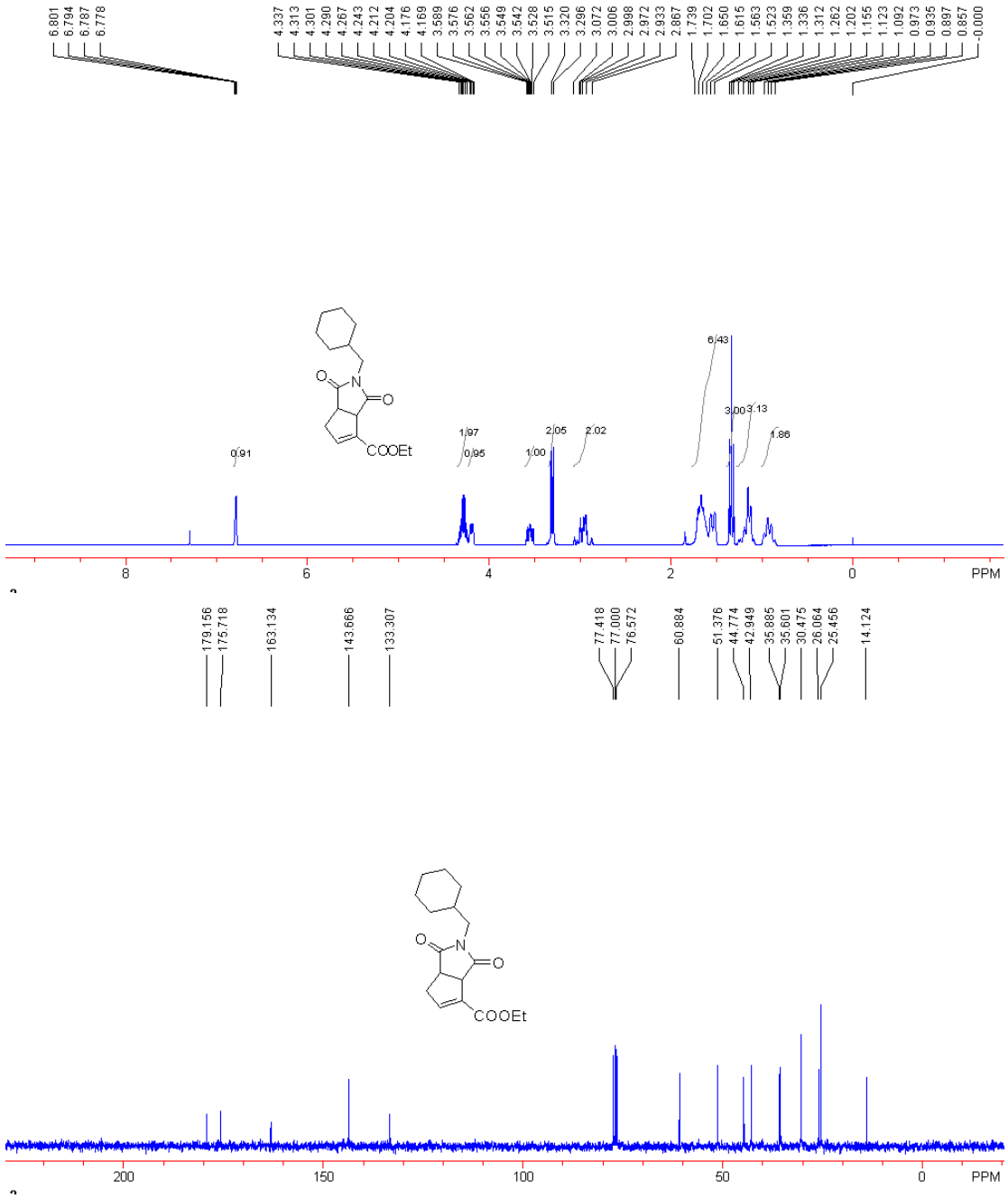


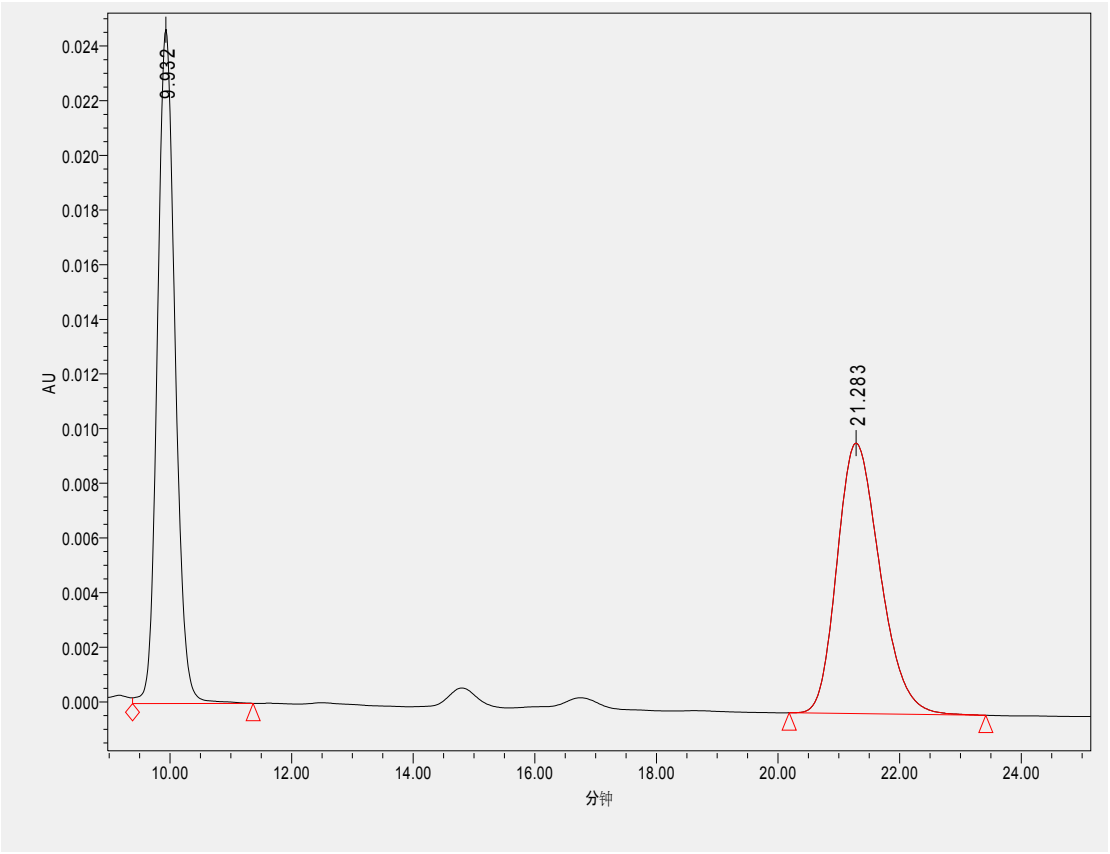
IC-H, *n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm



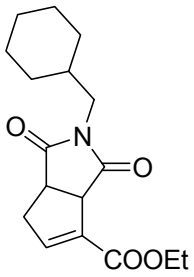
Compound 3ia. 41 mg, Yield: 89%, white solid, m.p. 78-79 ^{o}C; IR (neat): ν 2964, 2918, 2851, 1703, 1555, 1363, 1263, 1176, 1108, 863, 803, 680 □cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.86-0.97 (2H, m), 1.09-1.26 (3H, m), 1.34 (3H, t, *J* = 7.2 Hz)□, 1.52-1.74 (6H, m), 2.87-3.07 (2H, m), 3.31 (2H, d, *J* = 7.2 Hz), 3.55 (1H, ddd, *J* = 3.9, 8.1, 9.9 Hz), 4.17-4.21 (1H, m), 4.24-4.34 (2H, m), 6.79 (1H, dd, *J* = 2.1, 4.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □14.1, 25.5, 26.1, 30.5, 35.6, 35.9, 42.9, 44.8, 51.4, 60.9, 133.3, 143.7, 163.1, 175.7, 179.2; MS (EI) *m/z* (%): 305 [M^+] (12.1), 260 (10.2), 223 (49.6), 210 (100.0), 177 (25.5), 164 (55.0), 93 (20.1), 65 (17.9), 55 (17.2); HRMS (EI) Calcd. for $C_{17}H_{23}NO_4$ requires (M^+) 305.1627, Found: 305.1630; $[\alpha]^{20}_{D}$ = +20.3 (c 0.2, CH_2Cl_2, 95% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm, t_{minor} = 23.28 min, t_{major} = 10.35 min).

Compound 3i (the racemate of **3ia**). 45 mg, Yield: 99%, white solid, m.p. 99-100 ^{o}C.

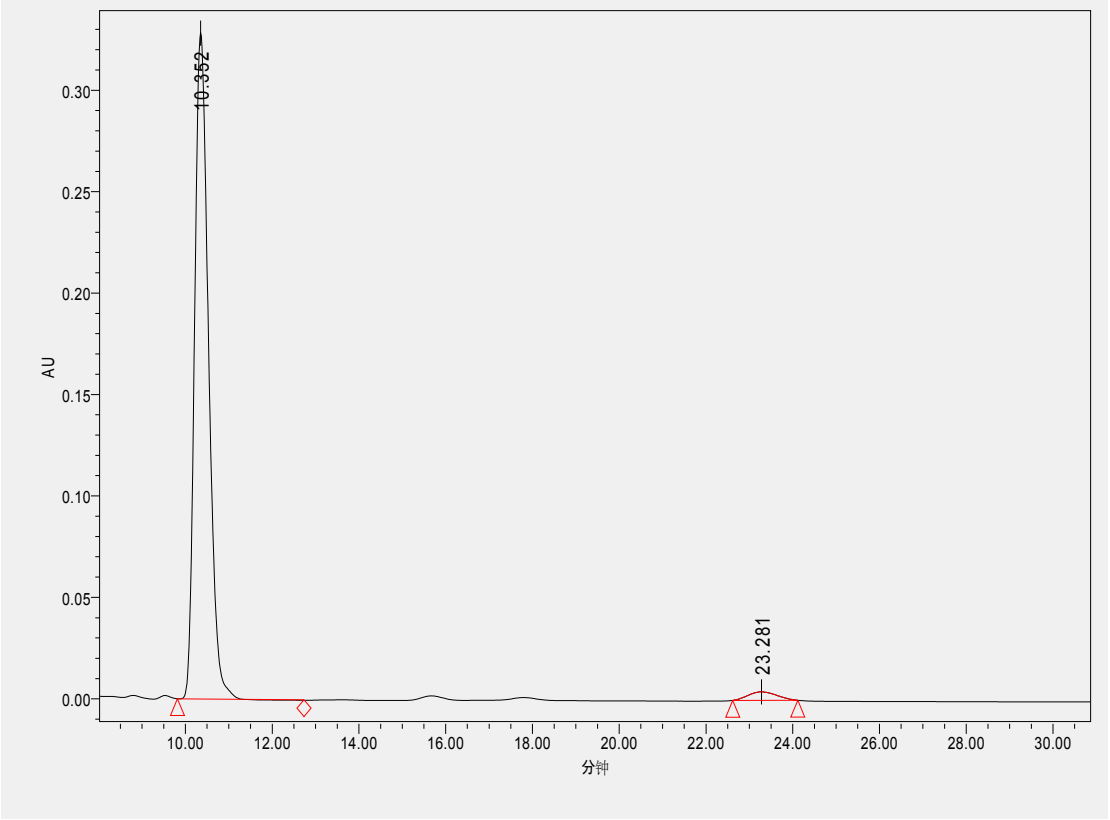

6.801
6.794
6.787
6.778
4.337
4.313
4.301
4.290
4.267
4.243
4.212
4.204
4.176
4.169
3.589
3.576
3.562
3.556
3.549
3.542
3.528
3.515
3.320
3.296
3.072
3.006
2.998
2.972
2.933
2.867
1.739
1.702
1.650
1.615
1.563
1.523
1.359
1.336
1.312
1.262
1.202
1.155
1.123
1.092
0.973
0.935
0.897
0.857
-0.000
COOEt
0.91
1.97
0.95
1.00
2.05
2.02
6.43
3.00
3.13
1.86
8
6
4
2
0
PPM
179.156
175.718
163.134
143.666
133.307
77.418
77.000
76.572
60.884
51.376
44.774
42.949
35.885
35.601
30.475
26.064
25.456
14.124
COOEt
200
150
100
50
0
PPM



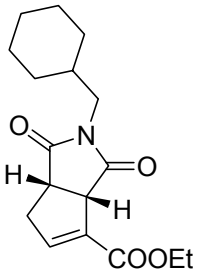
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	9.932	501529	50.81	24664
2	2	21.283	485562	49.19	9899



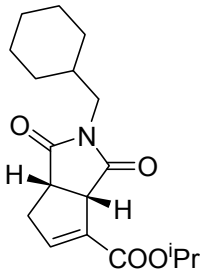
OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	10.352	7334562	97.45	328457
2	2	23.281	192055	2.55	4188

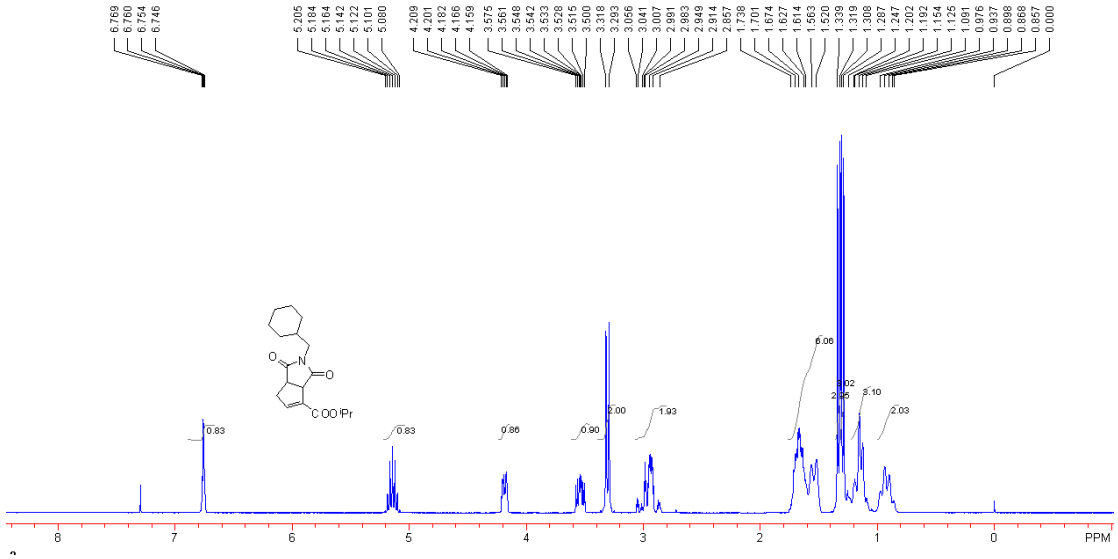


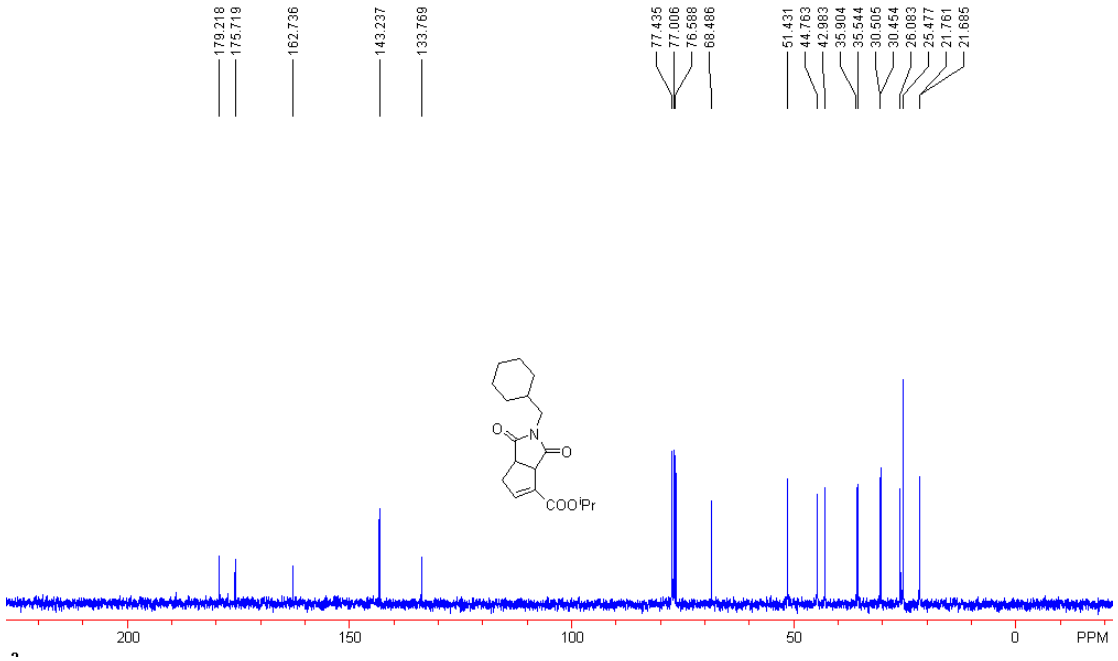
OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm

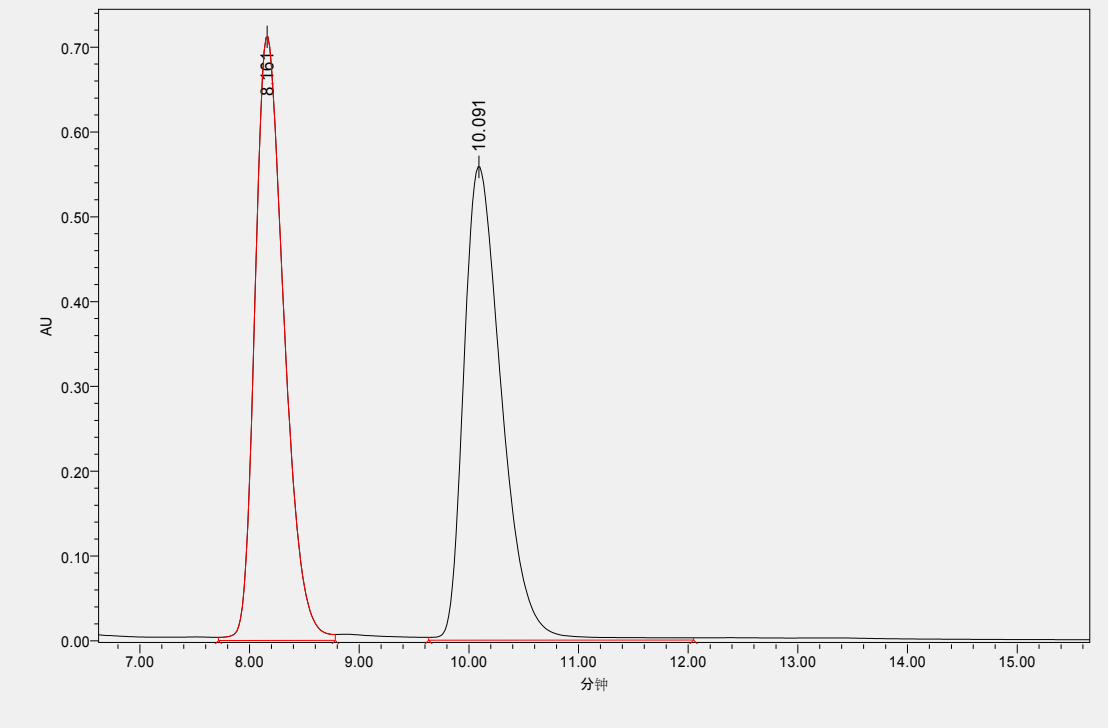


Compound 3ib. 38 mg, Yield: 80%, white solid, m.p. 131-132 ^{o}C; IR (neat): ν 2955, 2913, 2847, 1714, 1557, 1364, 1264, 1176, 1109, 862, 804, 688 □cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.86-0.98 (2H, m), 1.09-1.25 (3H, m), 1.30 (3H, d, *J* = 6.6 Hz)□, 1.33 (3H, d, *J* = 6.6 Hz)□, 1.52-1.74 (6H, m), 2.86-3.06 (2H, m), 3.31 (2H, d, *J* = 7.5 Hz), 3.54 (1H, ddd, *J* = 4.2, 8.1, 9.9 Hz), 4.16-4.21 (1H, m), 5.14 (1H, sept, *J* = 6.0 Hz), 6.76 (1H, dd, *J* = 2.4, 4.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □21.7, 21.8, 25.5, 26.1, 30.4, 30.5, 35.6, 35.9, 43.0, 44.8, 51.4, 68.5, 133.8, 143.2, 162.7, 175.7, 179.2; MS (EI) *m/z* (%): 319 [M^{+}] (13.1), 260 (30.2), 224 (73.1), 218 (100.0), 164 (55.6), 93 (31.2), 65 (29.6), 43 (44.9); HRMS (EI) Calcd. for $C_{18}H_{25}NO_4$ requires (M^{+}) 319.1784, Found: 319.1786; $[\alpha]^{20}_{D}$ = +59.5 (c 0.1, CH_2Cl_2, 91% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm, t_{minor} = 10.84 min, t_{major} = 8.60 min).

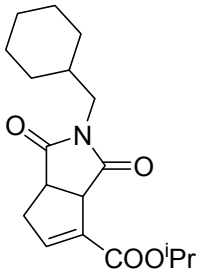
Compound 3j (the racemate of **3ib**). 47 mg, Yield: 99%, white solid, m.p. 112-113 ^{o}C.


6.769
6.760
6.754
6.746
5.205
5.184
5.164
5.142
5.122
5.101
5.080
4.209
4.201
4.182
4.166
4.159
3.575
3.561
3.548
3.542
3.533
3.528
3.515
3.500
3.318
3.293
3.066
3.041
3.007
2.991
2.983
2.949
2.914
2.857
1.738
1.701
1.674
1.627
1.614
1.563
1.520
1.339
1.319
1.308
1.287
1.247
1.202
1.192
1.154
1.125
1.091
0.976
0.937
0.898
0.868
0.857
0.000
COO'Pr
0.83
0.83
0.86
0.90
2.00
1.93
6.06
2.02
2.05
3.10
2.03
8
7
6
5
4
3
2
1
0
PPM

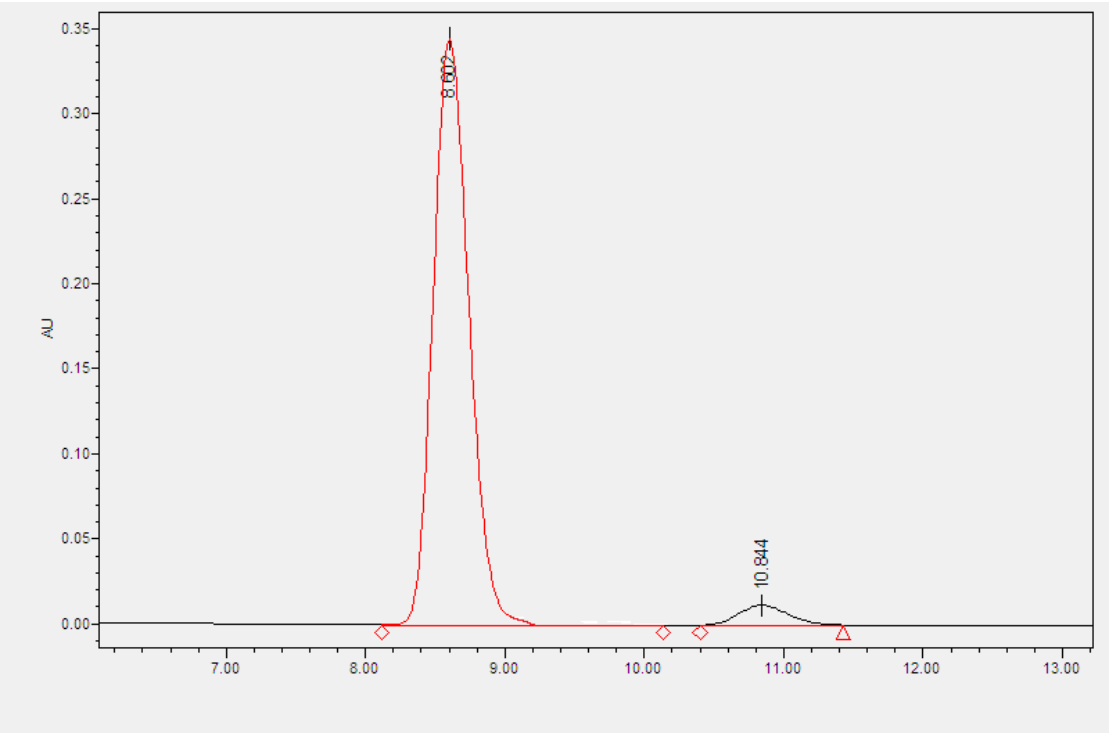

179.218
175.719
162.736
143.237
133.769
77.435
77.006
76.588
68.486
51.431
44.763
42.983
35.904
35.544
30.505
30.454
26.083
25.477
21.761
21.685
COO'Pr
200
150
100
50
0
PPM



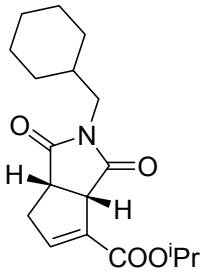
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	8.161	13208915	49.49	712842
2	2	10.091	13479604	50.51	559179



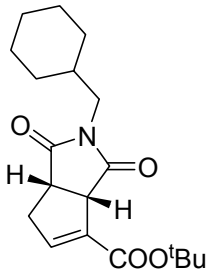
OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	8.602	6136001	95.63	344722
2	2	10.844	280729	4.37	11640

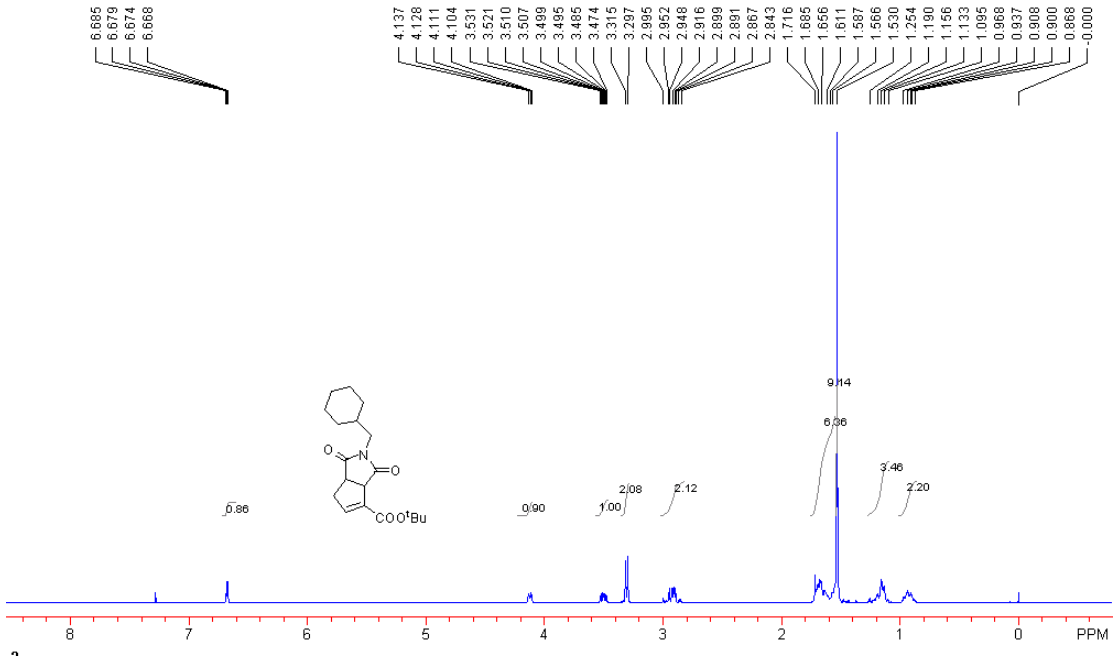


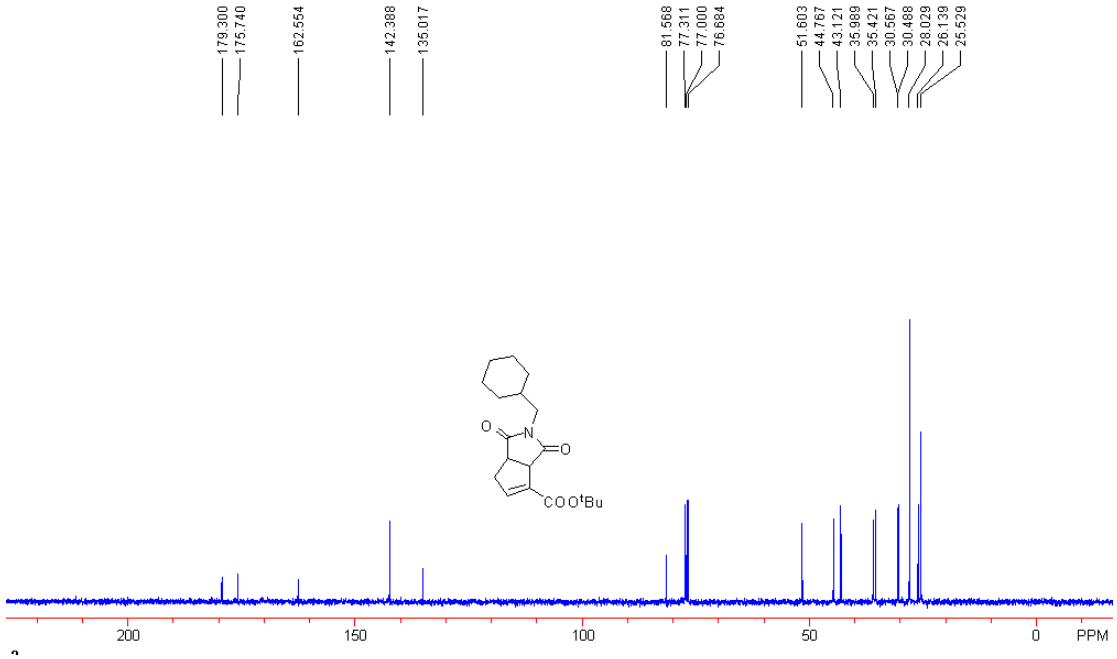
OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm

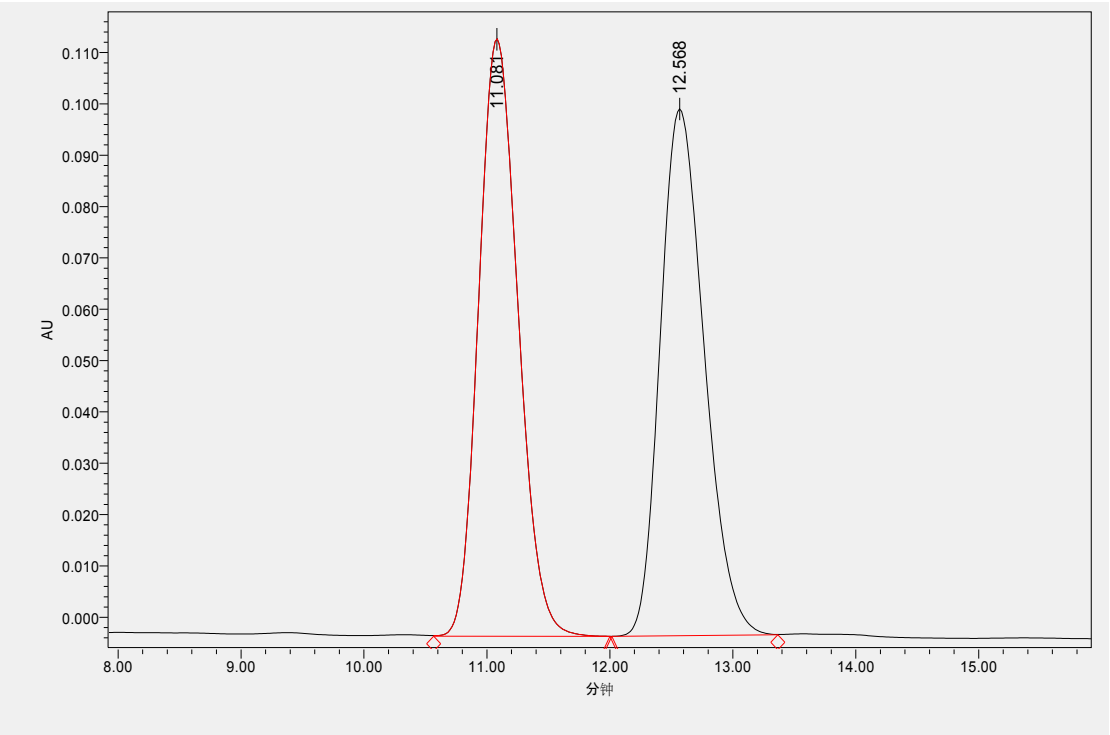


Compound 3ic. 41 mg, Yield: 82%, white solid, m.p. 76-77 ^{o}C; IR (neat): ν 3051, 2923, 2857, 1709, 1698, 1410, 1356, 1304, 1263, 1128, 847, 803, 673 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87-0.97 (2H, m), 1.10-1.25 (3H, m), 1.53 (9H, s)□, 1.57-1.72 (6H, m), 2.84-3.00 (2H, m), 3.31 (2H, d, J = 7.2 Hz), 3.50 (1H, ddd, J = 4.0, 8.4, 9.6 Hz), 4.10-4.14 (1H, m), 6.68 (1H, dd, J = 2.4, 4.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □25.5, 26.1, 28.0, 30.5, 30.6, 35.4, 36.0, 43.1, 44.8, 51.6, 81.6, 135.0, 142.4, 162.6, 175.7, 179.3; MS (EI) *m/z* (%): 333 [M^+] (5.1), 277 (35.1), 260 (35.5), 195 (38.3), 182 (100.0), 164 (49.1), 93 (16.9), 57 (36.8), 55 (18.9), 41 (17.1); HRMS (EI) Calcd. for $C_{19}H_{27}NO_4$ requires (M^+) 333.1940, Found: 333.1938; $[\alpha]^{20}_{D}$ = +7.7 (c 0.1, CH_2Cl_2, 77% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 214 nm, t_{minor} = 12.61 min, t_{major} = 11.34 min).

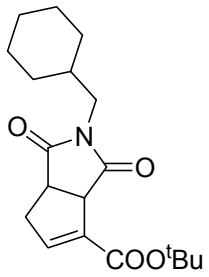
Compound 3k (the racemate of **3ic**). 49 mg, Yield: 99%, white solid, m.p. 109-110 ^{o}C.


6.685
6.679
6.674
6.668
4.137
4.128
4.111
4.104
3.531
3.521
3.510
3.507
3.499
3.495
3.485
3.474
3.315
3.297
2.995
2.952
2.948
2.916
2.899
2.891
2.867
2.843
1.716
1.685
1.656
1.611
1.587
1.566
1.530
1.254
1.190
1.156
1.133
1.095
0.968
0.937
0.908
0.900
0.868
-0.000
9.14
6.06
3.46
2.20
2.12
2.08
1.00
0.90
0.86
COO^{t}Bu
PPM

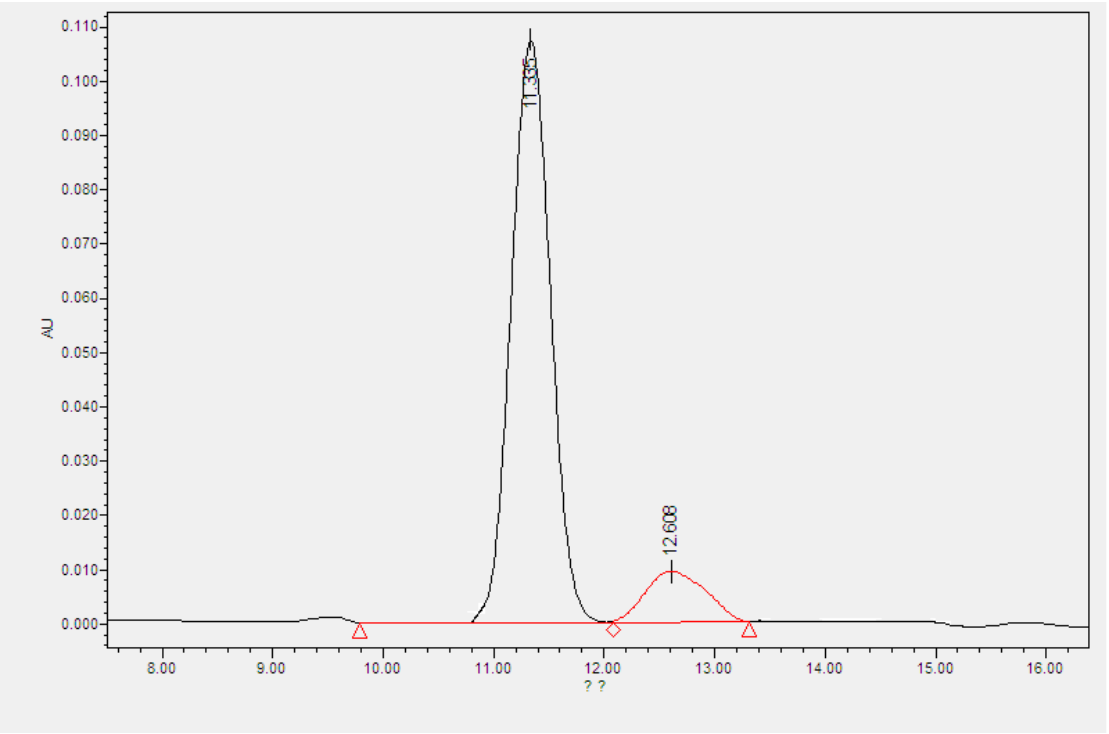

179.300
175.740
162.554
142.388
135.017
81.568
77.311
77.000
76.684
51.603
44.767
43.121
35.989
35.421
30.567
30.488
28.029
26.139
25.529
COO^{t}Bu
PPM



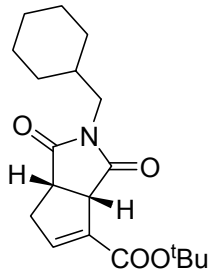
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	11.081	2592995	50.42	116353
2	2	12.568	2549697	49.58	102603



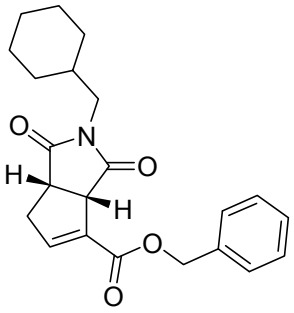
OD-H, *n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	11.335	2823024	88.80	107283
2	2	12.608	356089	11.20	9416

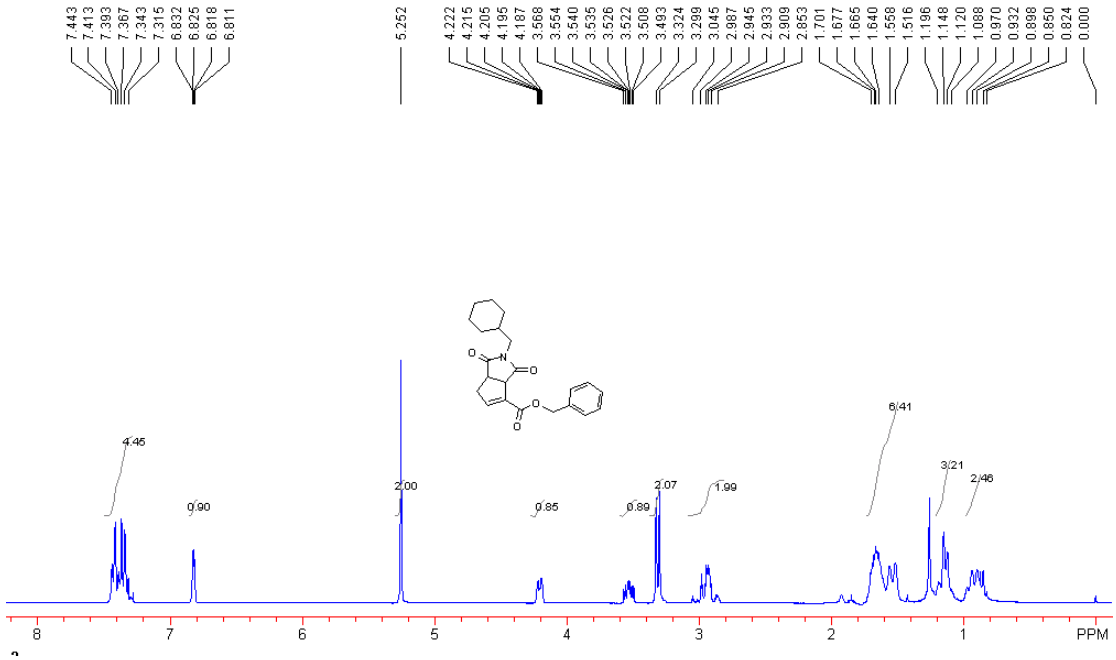


OD-H, *n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 214 nm



Compound 3id. 54 mg, Yield: 98%, colorless oil; IR (neat): ν 3013, 2985, 2858, 1769, 1746, 1699, 1450, 1362, 1375, 1277, 1242, 1158, 866, 801, 638 □cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.82-0.97 (2H, m), 1.09-1.20 (3H, m), 1.52-1.70 (6H, m), 2.85-3.05 (2H, m), 3.31 (2H, d, *J* = 7.5 Hz), 3.53 (1H, ddd, *J* = 4.2, 8.4, 9.9 Hz), 4.19-4.22 (1H, m), 5.25 (2H, s), 6.82 (1H, dd, *J* = 2.1, 4.2 Hz), 7.32-7.44 (5H, m); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □25.4, 26.0, 30.4, 35.6, 35.9, 42.9, 44.7, 51.3, 66.6, 128.1, 128.4, 132.9, 135.6, 144.4, 162.9, 175.6, 179.1; MS (EI) *m/z* (%): 367 [M^+] (5.9), 261 (25.8), 233 (16.0), 166 (8.8), 138 (12.9), 91 (100.0), 65 (30.8), 55 (38.7), 41 (35.1); HRMS (EI) Calcd. for $C_{22}H_{25}NO_4$ requires (M^+) 367.1784, Found: 367.1788; $[\alpha]^{20}_D$ = +20.7 (c 0.5, CH_2Cl_2, 87% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm, t_{minor} = 25.61 min, t_{major} = 13.00 min).

Compound 3l (the racemate of **3id**). 54 mg, Yield: 98%, colorless oil.


7.443
7.413
7.393
7.367
7.343
7.315
6.832
6.825
6.818
6.811
5.252
4.222
4.215
4.205
4.195
4.187
3.568
3.554
3.540
3.535
3.526
3.522
3.508
3.493
3.324
3.299
3.045
2.987
2.945
2.933
2.909
2.853
1.701
1.677
1.665
1.640
1.558
1.516
1.196
1.148
1.120
1.088
0.970
0.932
0.898
0.850
0.824
0.000
4.45
0.90
2.00
0.85
0.89
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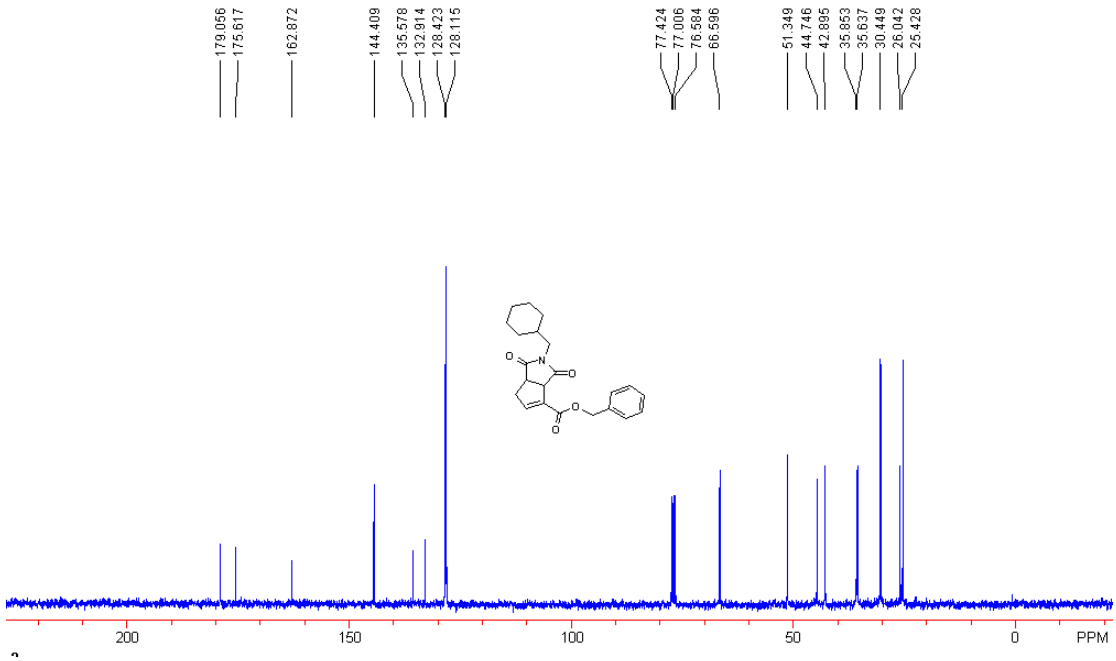
1.99
6.41
3.21
2.46
8
7
6
5
4
3
2
1
PPM


179.056
175.617
162.872
144.409
135.578
132.914
128.423
128.115
77.424
77.006
76.584
66.596
51.349
44.746
42.895
35.853
35.637
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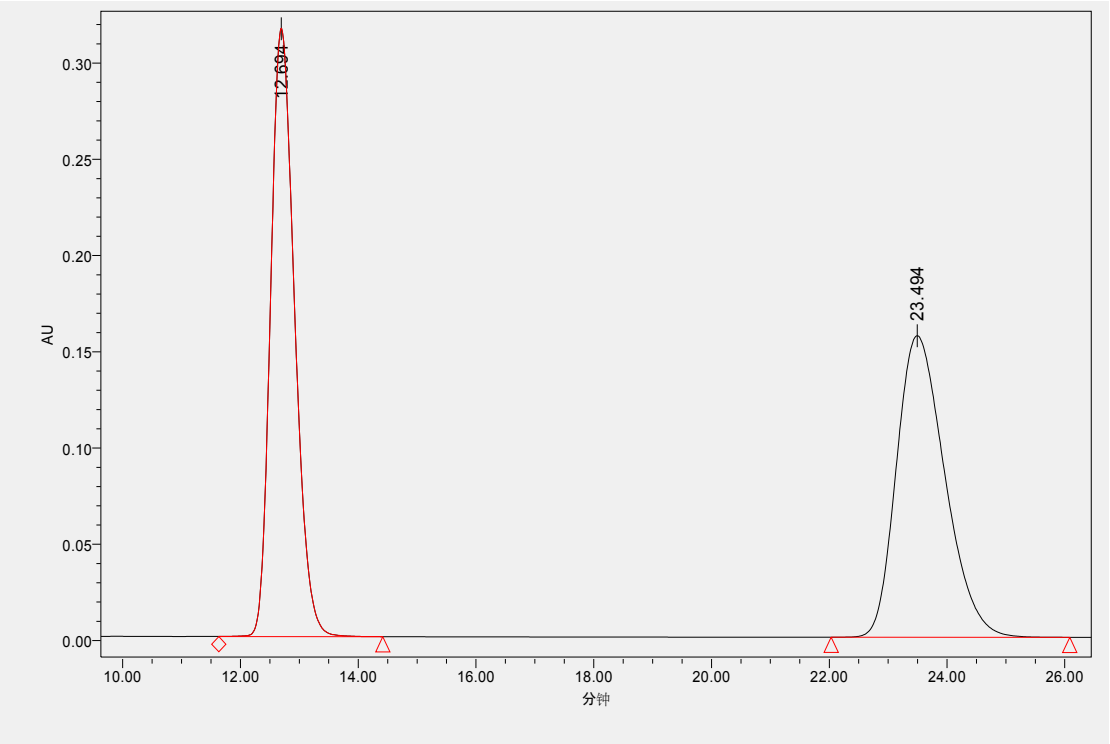
26.042
25.428
200
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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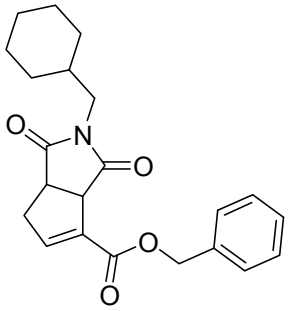
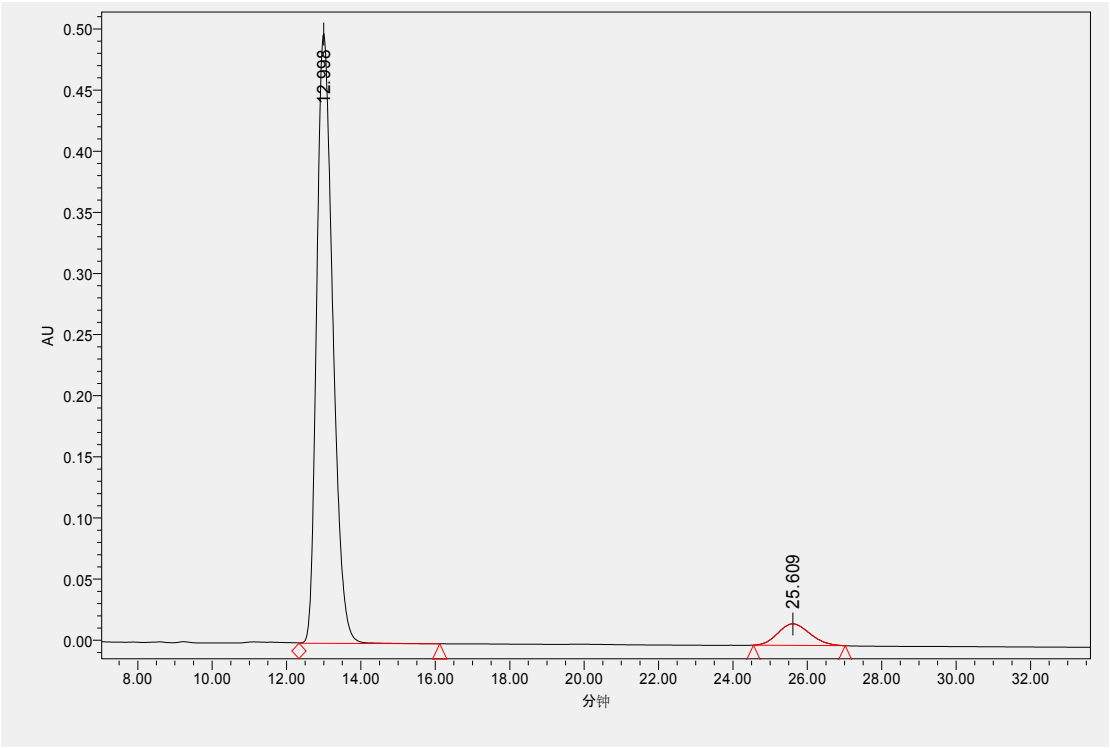


OD-H, *n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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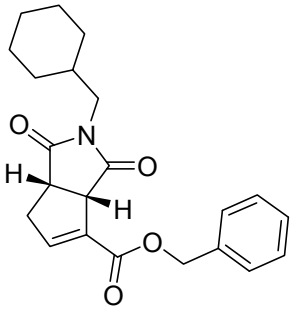
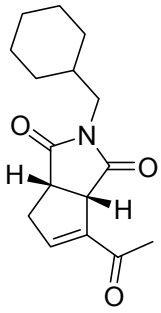
2	2	25.609	1051734	6.54	17582

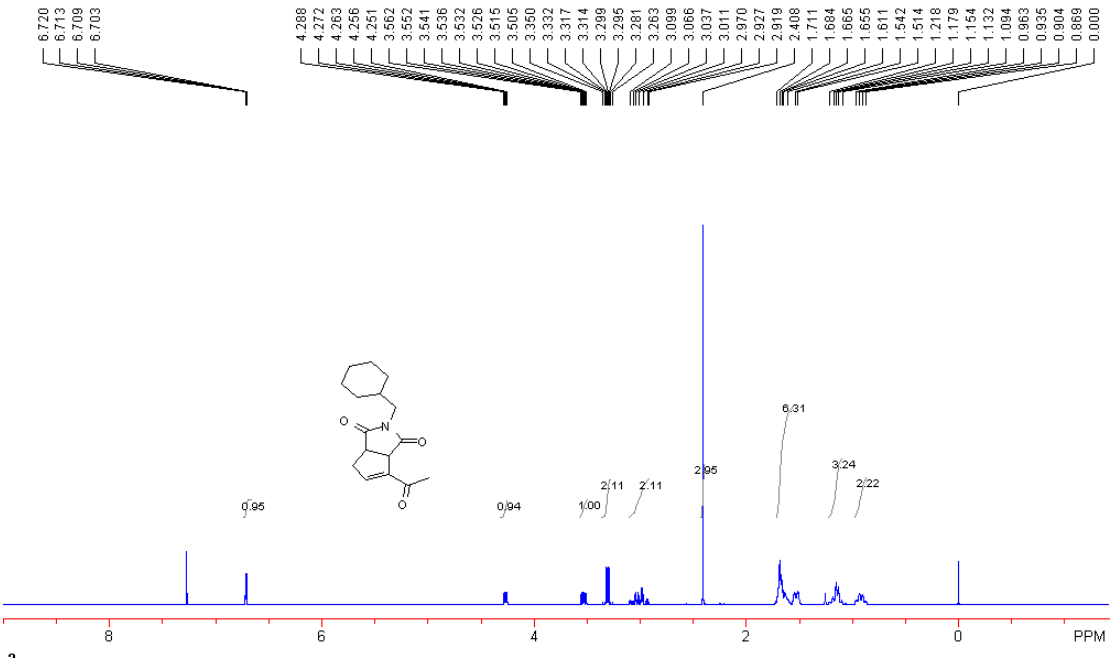


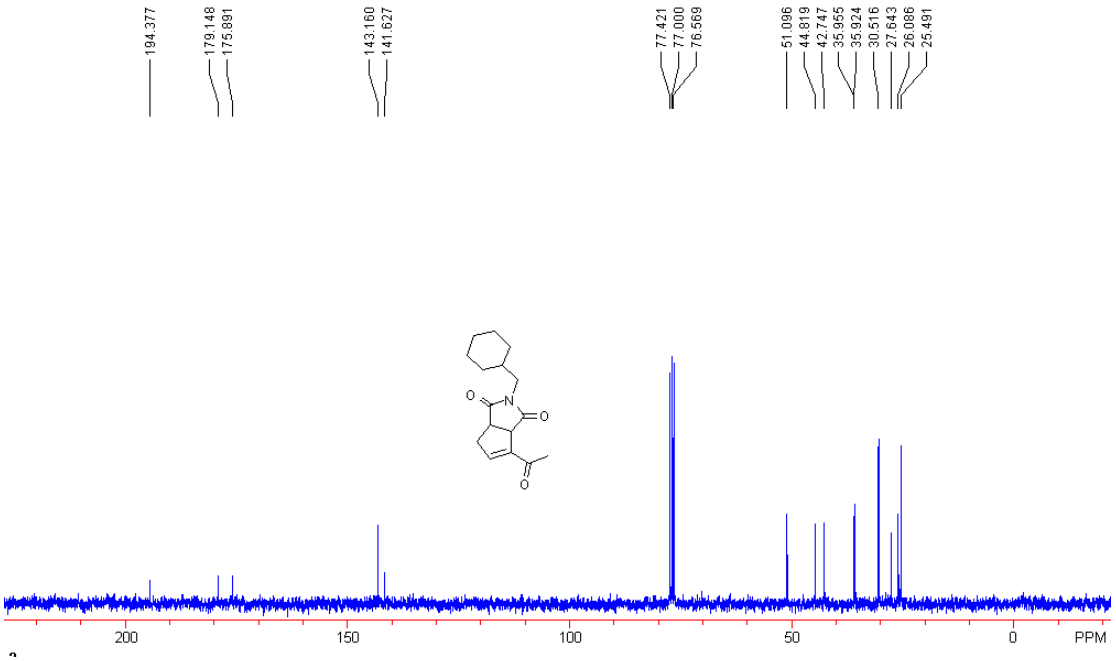
OD-H, *n*-hexane/*i*-PrOH = 50/50, 0.6 mL/min, 214 nm

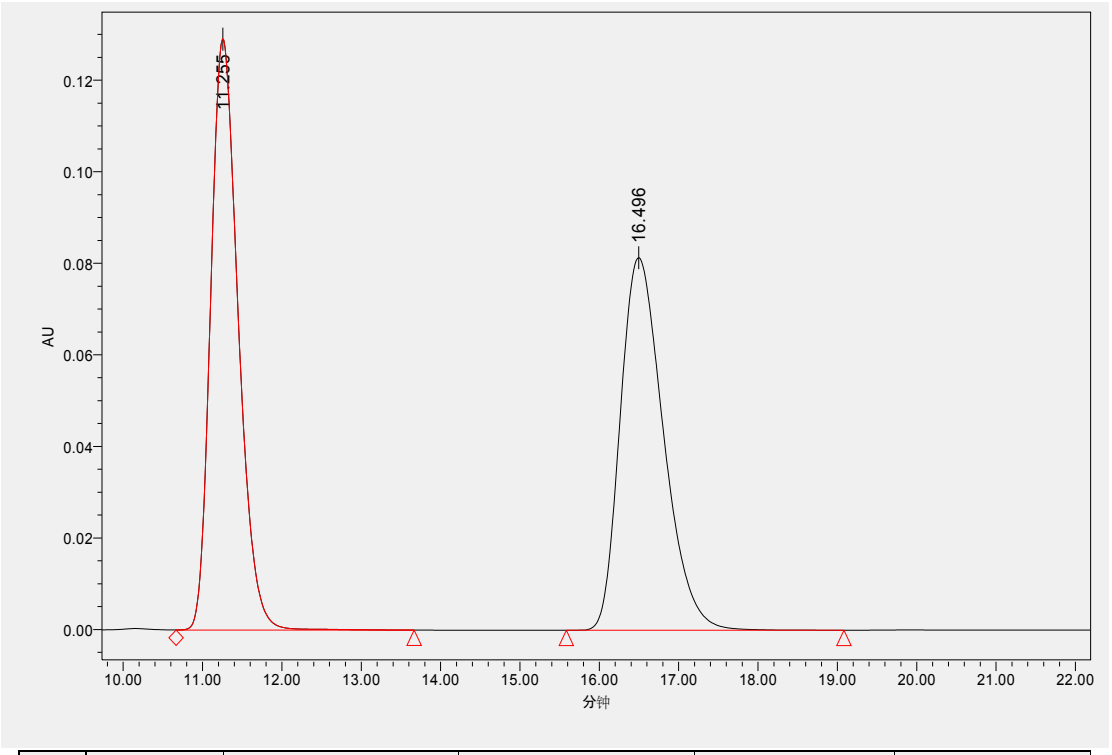


Compound 3ie. 39 mg, Yield: 94%, white solid, m.p. 100-101 ^{o}C; IR (neat): ν 3064, 2993, 2928, 2842, 1757, 1723, 1683, 1536, 1272, 1232, 1162, 1098, 1031, 906, 836, 777, 634 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87-0.96 (2H, m), 1.09-1.22 (3H, m), 1.51-1.71 (6H, m), 2.41 (3H, s), 2.92-3.10 (2H, m), 3.26-3.35 (2H, m), 3.53 (1H, ddd, *J* = 4.2, 8.4, 10.4 Hz), 4.25-4.29 (1H, m), 6.71 (1H, dd, *J* = 2.8, 4.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □25.5, 26.1, 27.6, 30.5, 35.9, 36.0, 42.7, 44.8, 51.1, 141.6, 143.2, 175.9, 179.1, 194.4; MS (EI) *m/z* (%): 275 [M^+] (18.7), 242 (12.6), 193 (40.5), 180 (100.0), 135 (21.1), 108 (16.6), 93 (22.9), 57 (20.6), 43 (51.8), 41 (19.4); HRMS (EI) Calcd. for $C_{16}H_{21}NO_3$ requires (M^+) 275.1521, Found: 275.1524; $[\alpha]^{20}_{D}$ = +75.3 (c 0.1, CH_2Cl_2, 70% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm, t_{minor} = 16.55 min, t_{major} = 11.25 min).

Compound 3m (the racemate of **3ie**). 41 mg, Yield: 99%, white solid, m.p. 119-120 ^{o}C.




194.377
179.148
175.891
143.160
141.627
77.421
77.000
76.569
51.096
44.819
42.747
35.955
35.924
30.516
27.643
26.086
25.491
O
N
O
O
200
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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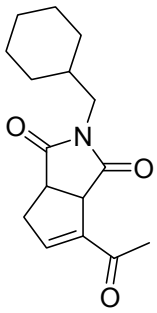
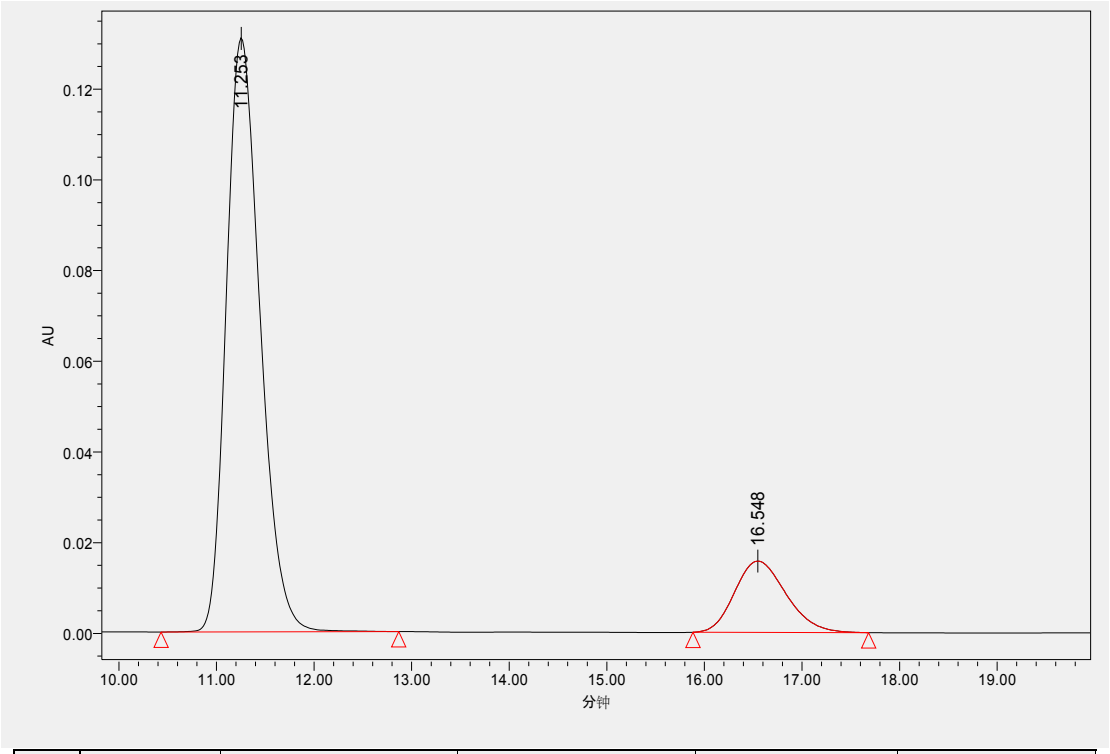
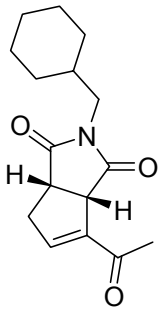


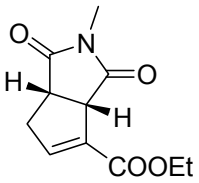
OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	11.253	3147238	85.03	130980
2	2	16.548	554081	14.97	15468

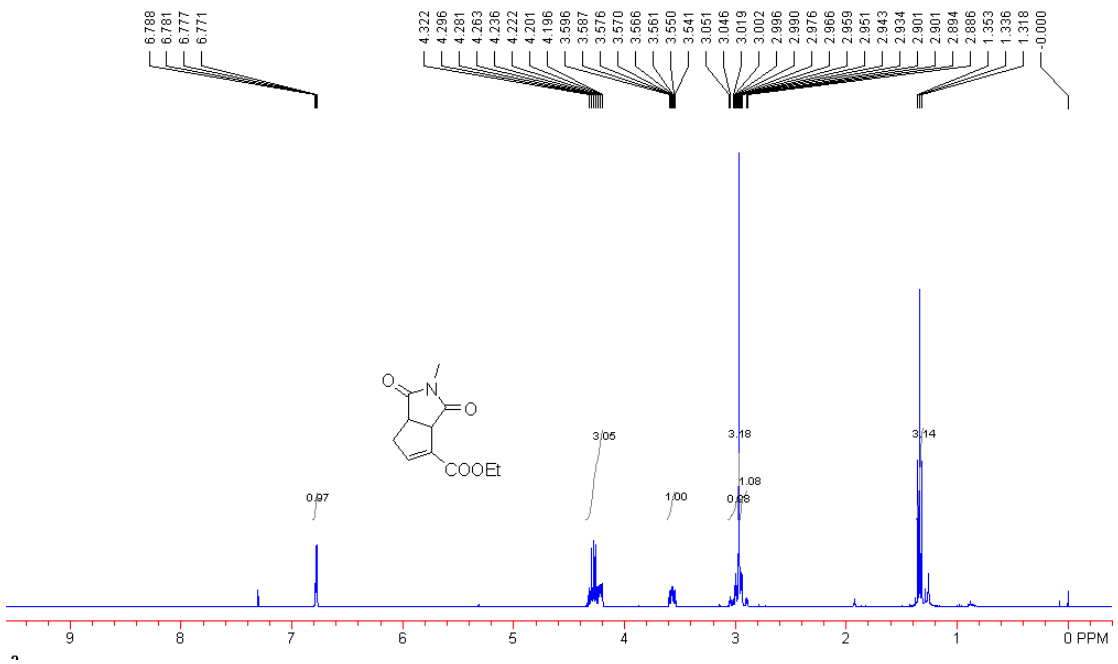


OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



Compound 3ja. 28 mg, Yield: 85%, colorless oil; IR (neat): ν 2990, 2953, 2923, 2852, 1768, 1685, 1625, 1434, 1374, 1291, 1206, 1122, 1095, 1020, 973, 819, 785, 721, 627 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (3H, t, *J* = 7.2 Hz)□, 2.89-3.05 (5H, m), 3.57 (1H, ddd, *J* = 3.6, 8.0, 10.4 Hz), 4.20-4.32 (3H, m), 6.78 (1H, dd, *J* = 2.8, 4.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.0, 24.8, 35.3, 43.0, 51.5, 60.7, 133.0, 143.6, 162.9, 175.4, 178.9; MS (EI) *m/z* (%): 223 [M^+] (85.9), 178 (54.3), 151 (24.2), 138 (100.0), 110 (34.7), 93 (55.8), 79 (79.4), 66 (66.5), 49 (11.8); HRMS (EI) Calcd. for $C_{11}H_{13}NO_4$ requires (M^+) 223.0845, Found: 223.0849; $[\alpha]^{20}_D$ = -10.7 (c 0.1, CH_2Cl_2, 80% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 230 nm, t_{minor} = 16.32 min, t_{major} = 12.28 min).

Compound 3n (the racemate of **3ja**). 33 mg, Yield: 99%, white solid, m.p. 65-66 ^{o}C.


6.788
6.781
6.777
6.771
4.322
4.296
4.281
4.263
4.236
4.222
4.201
4.196
3.596
3.587
3.576
3.570
3.566
3.561
3.550
3.541
3.051
3.046
3.019
3.002
2.996
2.990
2.976
2.966
2.959
2.951
2.943
2.934
2.901
2.901
2.894
2.886
1.353
1.336
1.318
-0.000
O
N
O
COOEt
0.97
3.05
1.00
1.08
0.98
3.18
3.14
9
8
7
6
5
4
3
2
1
0 PPM


178.854
175.362
162.932
143.618
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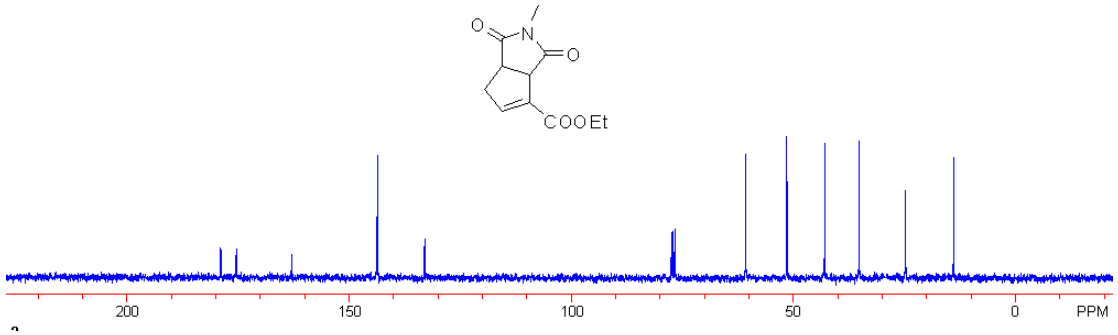
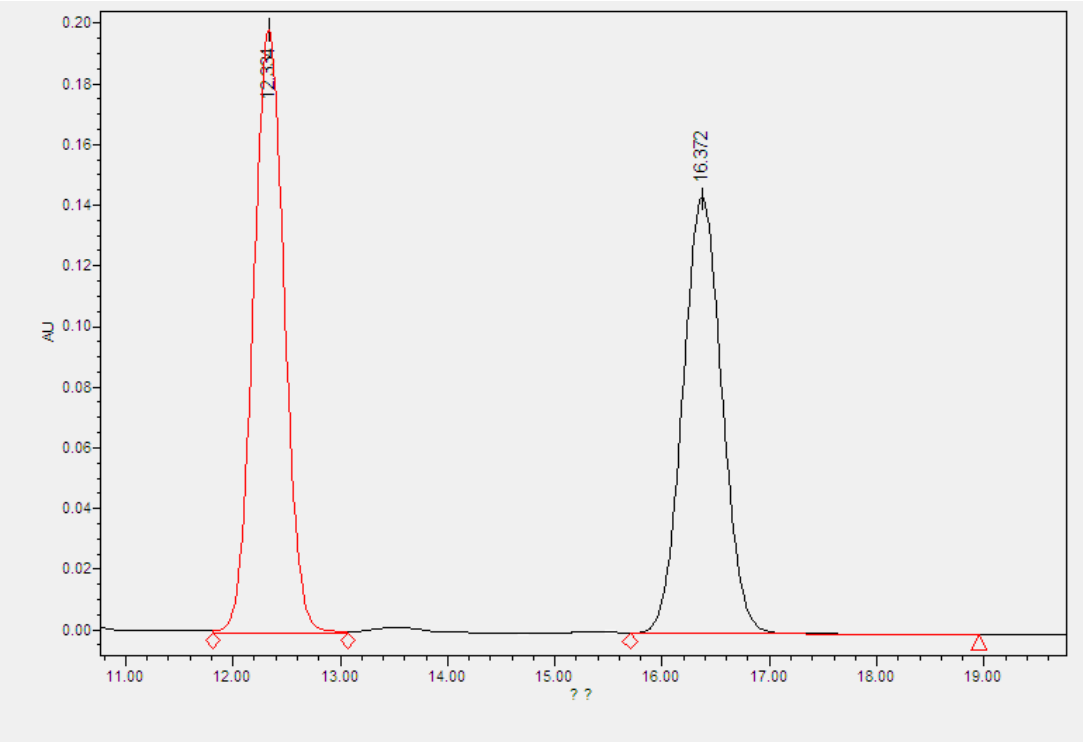
51.478
42.977
35.257
24.780
13.984


O
N
O
COOEt
200
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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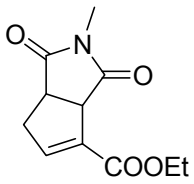
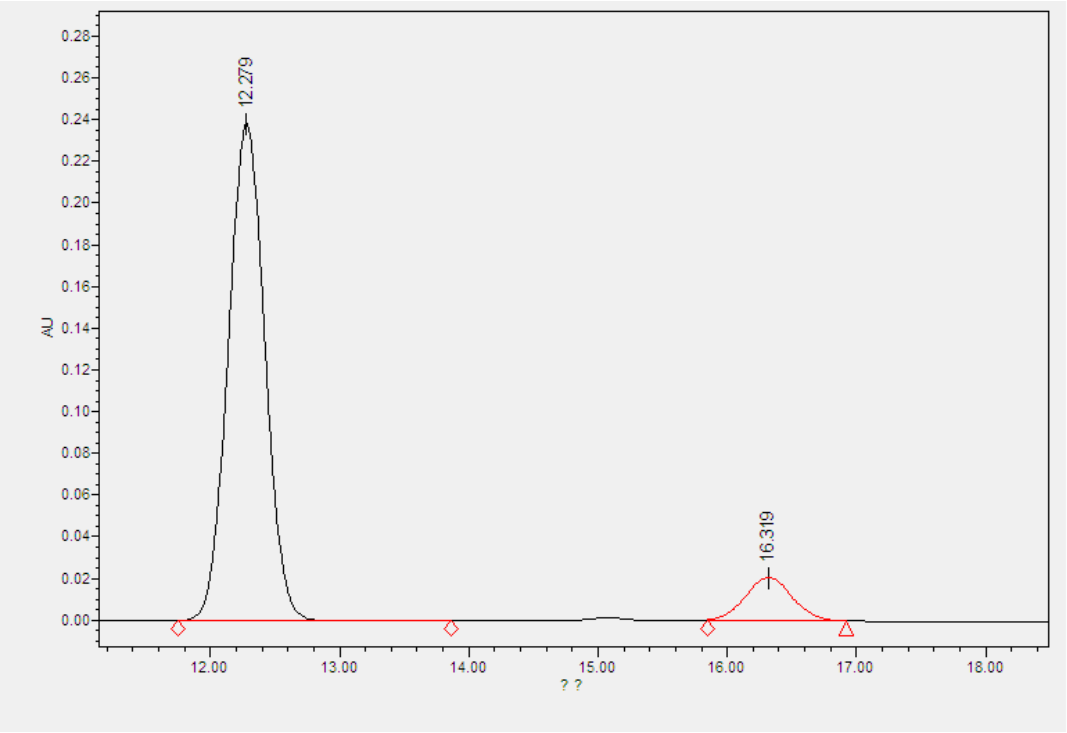
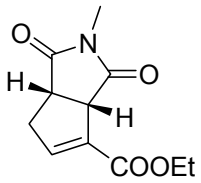
2		16.372	3670214	47.89	143787



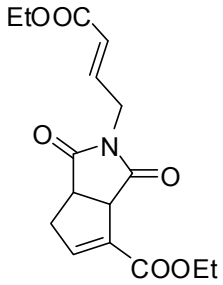
OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 230 nm



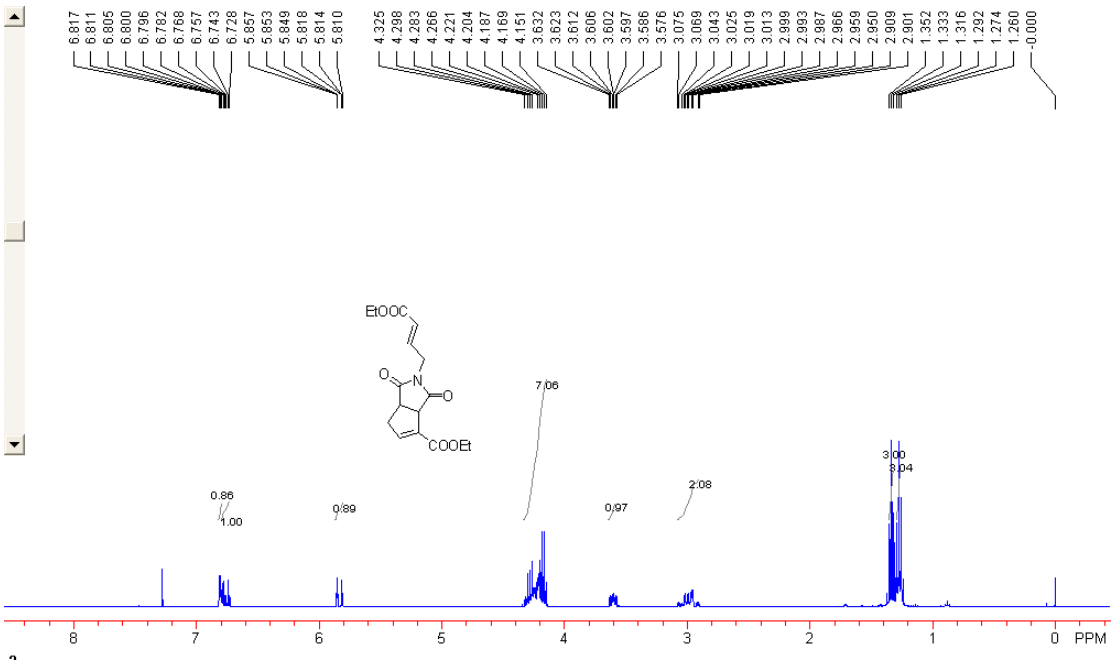
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	12.279	4752949	90.07	238713
2	2	16.319	523745	9.93	20774



OD-H, *n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 230 nm



Compound 3o. 46 mg, Yield: 96%, colorless oil; IR (neat): ν 2991, 2924, 2854, 1777, 1703, 1417, 1390, 1272, 1172, 1092, 1037, 906, 858, 731, 620 □cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.27 (3H, t, *J* = 7.2 Hz)□, 1.33 (3H, t, *J* = 7.2 Hz)□, 2.90-3.08 (2H, m), 3.60 (1H, ddd, *J* = 3.6, 8.0, 10.4 Hz), 4.15-4.33 (7H, m), 5.83 (1H, dt, *J* = 1.6, 15.6 Hz), 6.76 (1H, dt, *J* = 6.0, 15.6 Hz), 6.81 (1H, dd, *J* = 2.0, 4.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.5, 39.0, 43.2, 51.6, 60.6, 61.0, 123.8, 133.1, 139.4, 143.9, 162.9, 165.4, 174.5, 178.0; MS (EI) *m/z* (%): 321 [M^+] (12.8), 275 (99.5), 247 (38.5), 201 (16.7), 165 (100.0), 138 (23.9), 119 (28.0), 93 (38.3), 79 (24.2), 43 (10.6); HRMS (EI) Calcd. for $C_{16}H_{19}NO_6$ requires (M^+) 321.1212, Found: 321.1208.


6.817
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6.796
6.782
6.768
6.757
6.743
6.728
5.857
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5.818
5.814
5.810
4.325
4.298
4.283
4.266
4.221
4.204
4.187
4.169
4.151
3.632
3.623
3.612
3.606
3.602
3.597
3.586
3.576
3.075
3.069
3.043
3.025
3.019
3.013
2.999
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2.987
2.966
2.959
2.950
2.909
2.901
1.352
1.333
1.316
1.292
1.274
1.260
-0.000
EtOOC
O
N
O
COOEt
7.06
3.00
3.04
2.08
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0.89
0.86
1.00
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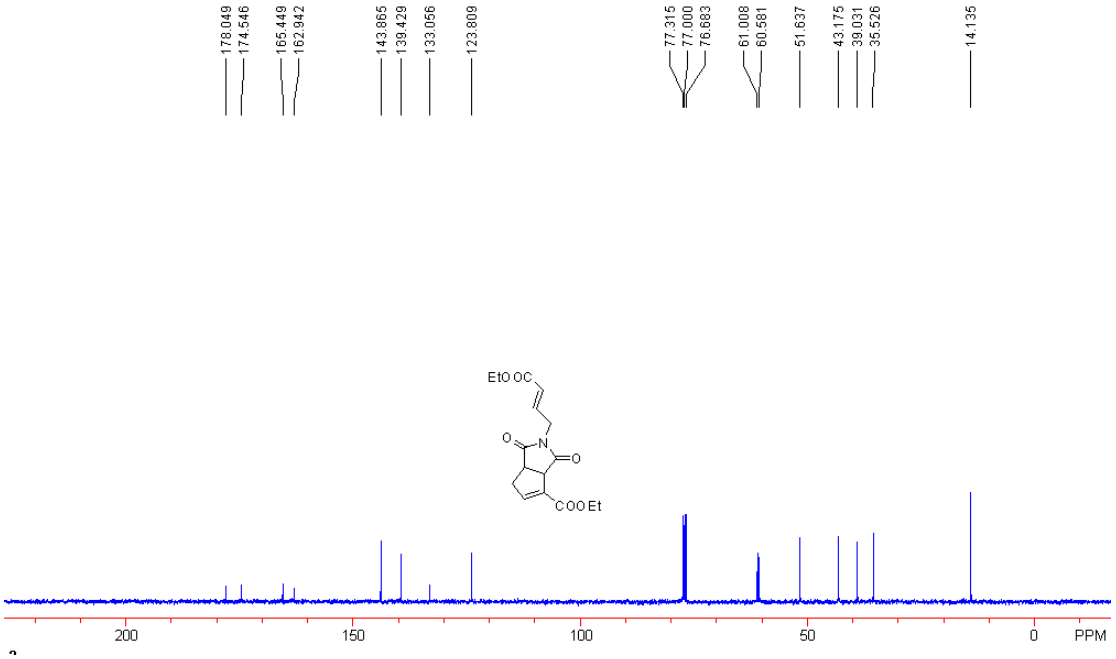
6
5
4
3
2
1
0
PPM


178.049
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139.429
133.056
123.809
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77.000
76.683
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60.581
51.637
43.175
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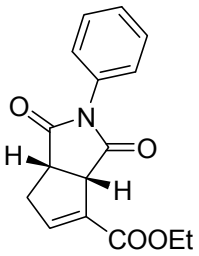
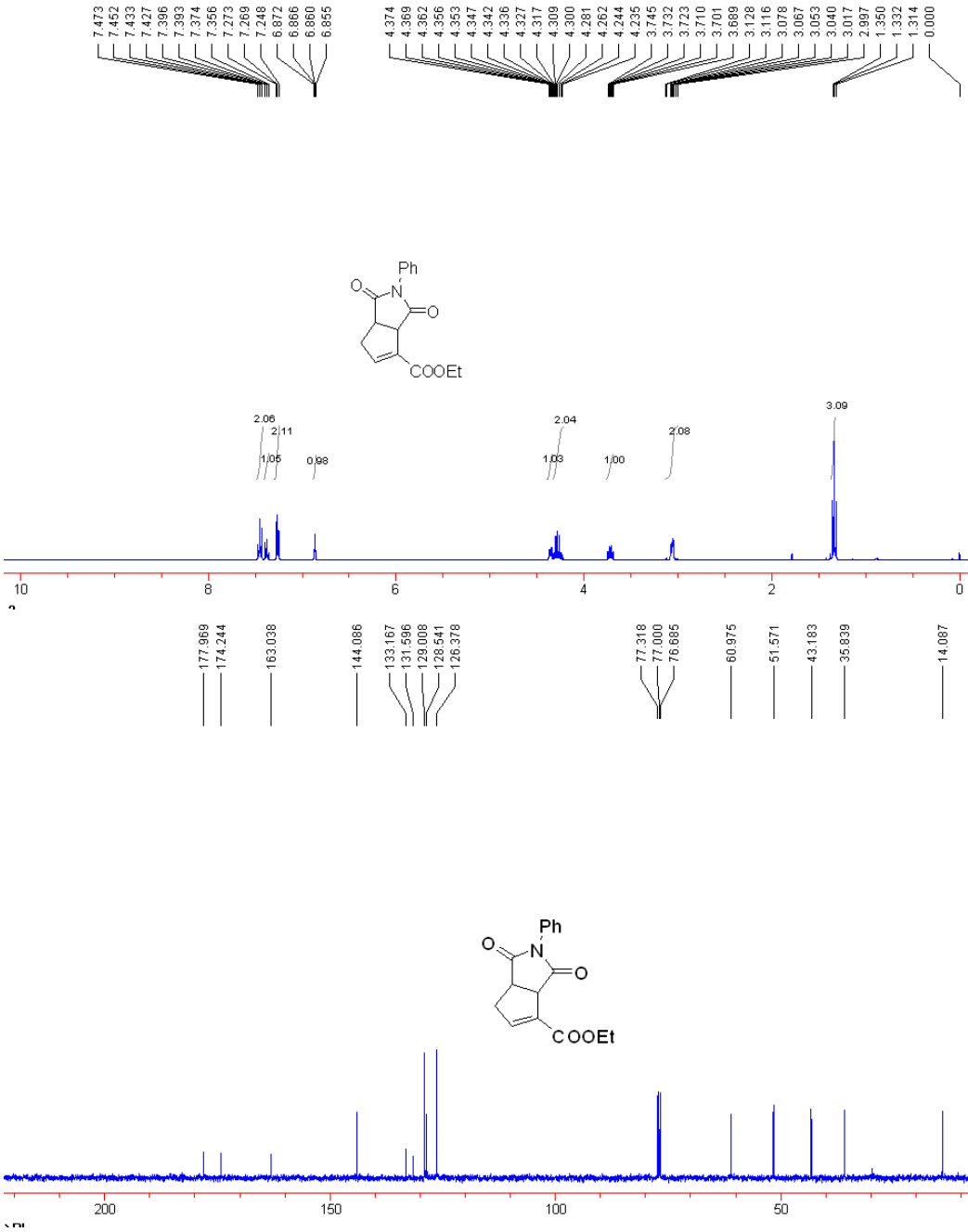
35.526
14.135
EtO OC
O
N
O
COO Et
200
150
100
50
0
PPM



Compound 3la. 32 mg, Yield: 76%, white solid, m.p. 105-106 ^{o}C; IR (neat): ν 2923, 2851, 1704, 1635, 1595, 1495, 1459, 1379, 1272, 1192, 1150, 1092, 1038, 916, 841, 760, 626 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 7.2 Hz)□, 3.00-3.13 (2H, m), 3.72 (1H, td, *J* = 5.2, 8.8 Hz), 4.24-4.33 (2H, m), 4.34-4.37 (1H, m), 6.86 (1H, dd, *J* = 2.4, 4.8 Hz), 7.25-7.27 (2H, m), 7.36-7.40 (1H, m), 7.43-7.47 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.8, 43.2, 51.6, 61.0, 126.4, 128.5, 129.0, 131.6, 133.2, 144.1, 163.0, 174.2, 178.0; MS (EI) *m/z* (%): 635 [M^+] (7.6), 285 (100.0), 240 (9.3), 138 (89.0), 119 (25.3), 110 (27.1), 93 (23.4), 79 (44.4), 66 (50.7), 49 (7.2); HRMS (EI) Calcd. for $C_{16}H_{15}NO_4$ requires (M^+) 285.1001, Found: 285.1000; $[\alpha]^{20}_{D}$ = -23.0 (c 0.1, CH_2Cl_2, 68% ee). Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm, t_{minor} = 25.30 min, t_{major} = 17.87 min).

Compound 3p (the racemate of **3la**). 41 mg, Yield: 96%, white solid, m.p. 98-99 ^{o}C.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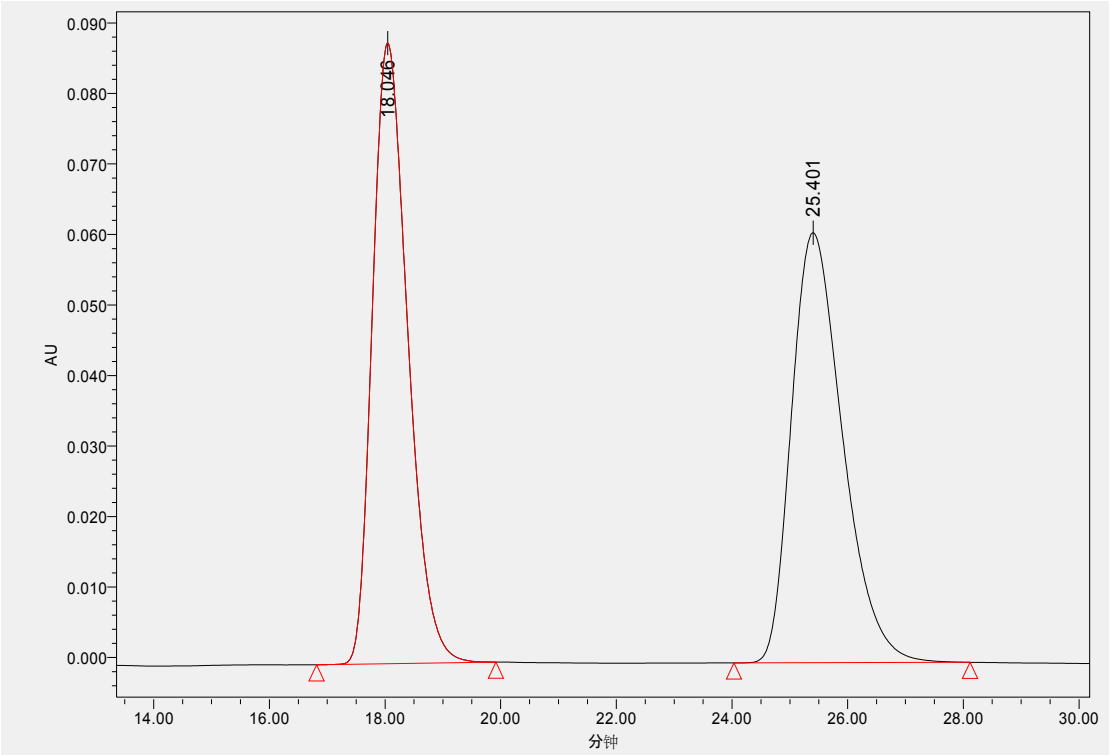
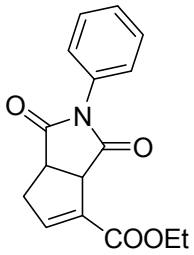
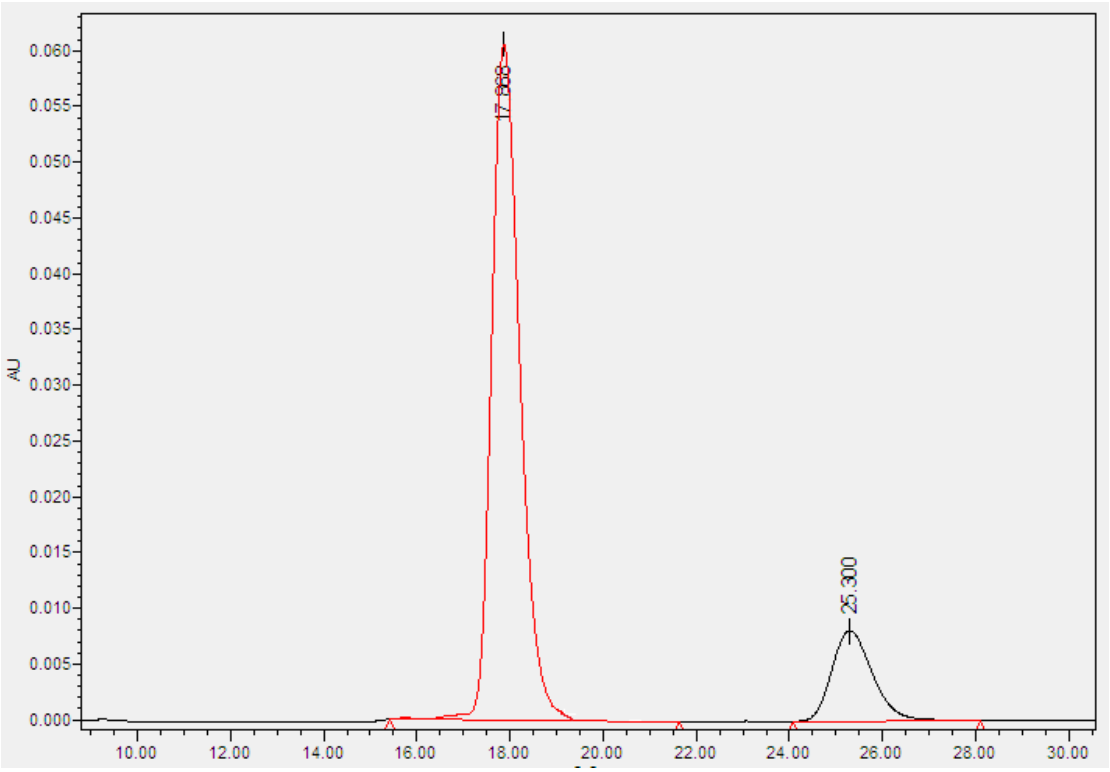
6.860
6.855
4.374
4.369
4.362
4.356
4.353
4.347
4.342
4.336
4.327
4.317
4.309
4.300
4.281
4.262
4.244
4.235
3.745
3.732
3.723
3.710
3.701
3.689
3.128
3.116
3.078
3.067
3.053
3.040
3.017
2.997
1.350
1.332
1.314
0.000
Ph
O
N
O
COOEt
2.06
2.11
1.05
0.98
2.04
1.03
1.00
2.08
3.09
10
8
6
4
2
0
PPM
177.969
174.244
163.038
144.086
133.167
131.596
129.008
128.541
126.378
77.318
77.000
76.685
60.975
51.571
43.183
35.839
14.087
Ph
O
N
O
COOEt
200
150
100
50
PPM



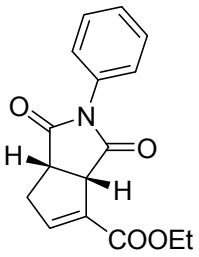
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	18.046	3740972	49.96	88038
2	2	25.401	3746755	50.04	60972



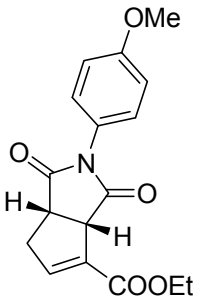
IC-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	17.868	2474192	84.12	60103
2	2	25.300	466928	15.88	8009

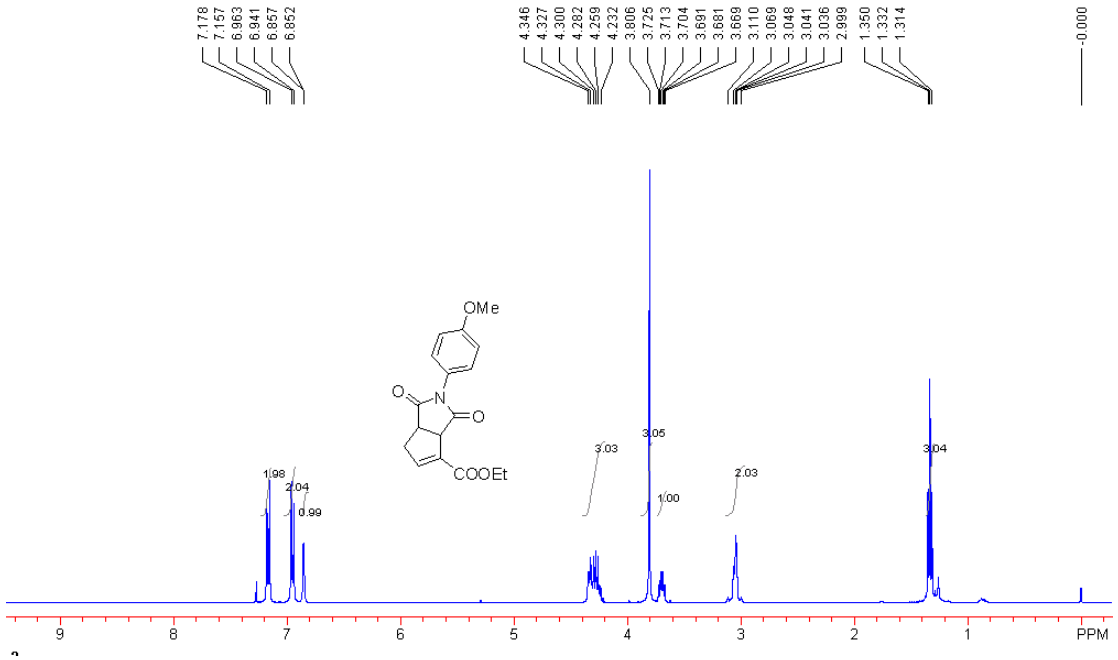


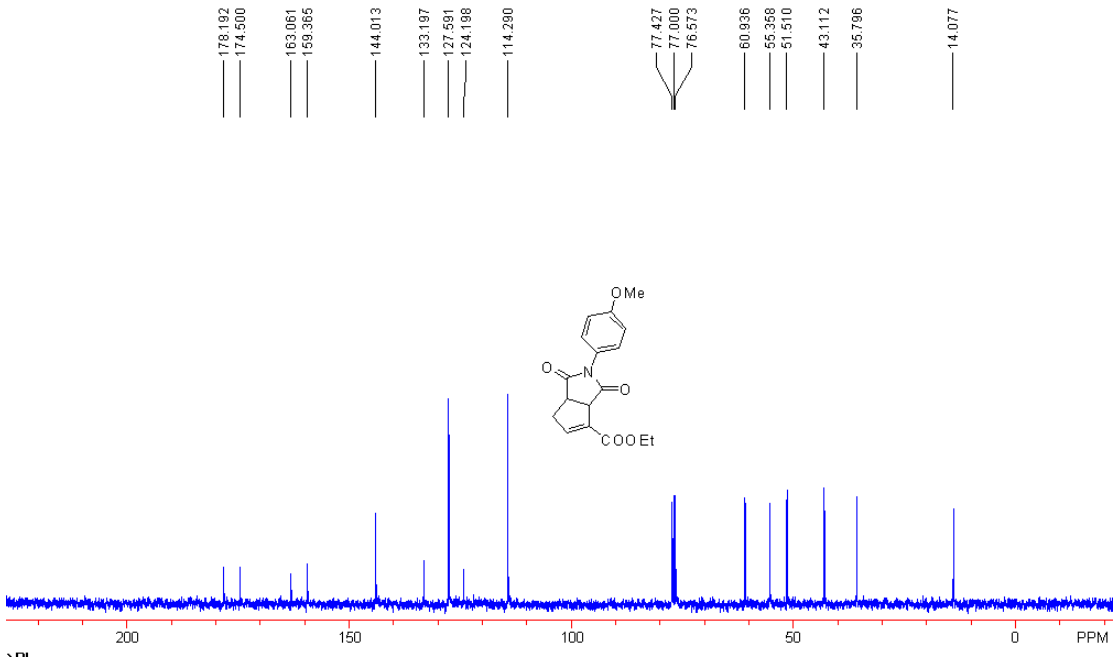
IC-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm

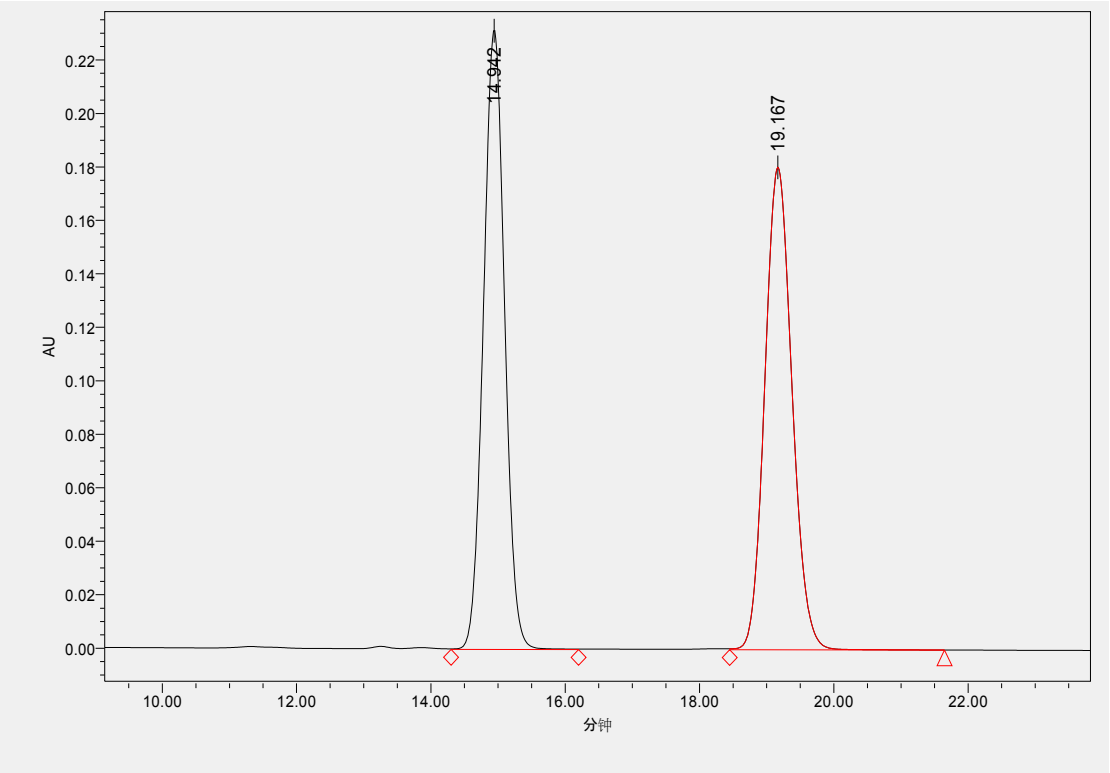


Compound 3ma. 41 mg, Yield: 87%, white solid, m.p. 128-129 ^{o}C; IR (neat): ν 3067, 2926, 2842, 1779, 1708, 1631, 1512, 1384, 1249, 1185, 1093, 1031, 914, 830, 731, 616 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 7.2 Hz)□, 3.00-3.11 (2H, m), 3.70 (1H, td, *J* = 4.8, 8.4 Hz), 3.81 (3H, s), 4.23-4.35 (3H, m), 6.85 (1H, dd, *J* = 2.4, 4.4 Hz), 6.95 (2H, d, *J* = 8.8 Hz), 7.17 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □14.1, 35.8, 43.1, 51.5, 55.4, 60.9, 114.3, 124.2, 127.6, 133.2, 144.0, 159.4, 163.1, 174.5, 178.2; MS (EI) *m/z* (%): 315 [M^+] (100.0), 270 (4.2), 149 (60.6), 134 (11.2), 106 (5.6), 84 (10.8), 79 (5.4), 65 (8.3), 49 (10.5); HRMS (EI) Calcd. for $C_{17}H_{17}NO_5$ requires (M^+) 315.1107, Found: 315.1112; $[\alpha]^{20}_{D}$ = -12.3 (c 0.1, CH_2Cl_2, 64% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm, t_{minor} = 19.10 min, t_{major} = 14.85 min).

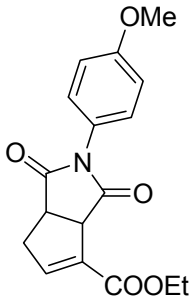
Compound 3q (the racemate of **3ma**). 47 mg, Yield: 99%, white solid, m.p. 133-134 ^{o}C.


7.178
7.157
6.963
6.941
6.857
6.852
4.346
4.327
4.300
4.282
4.259
4.232
3.806
3.725
3.713
3.704
3.691
3.681
3.669
3.110
3.069
3.048
3.041
3.036
2.999
1.350
1.332
1.314
-0.000
OMe
COOEt
1.98
2.04
0.99
3.03
3.05
1.00
2.03
3.04
PPM

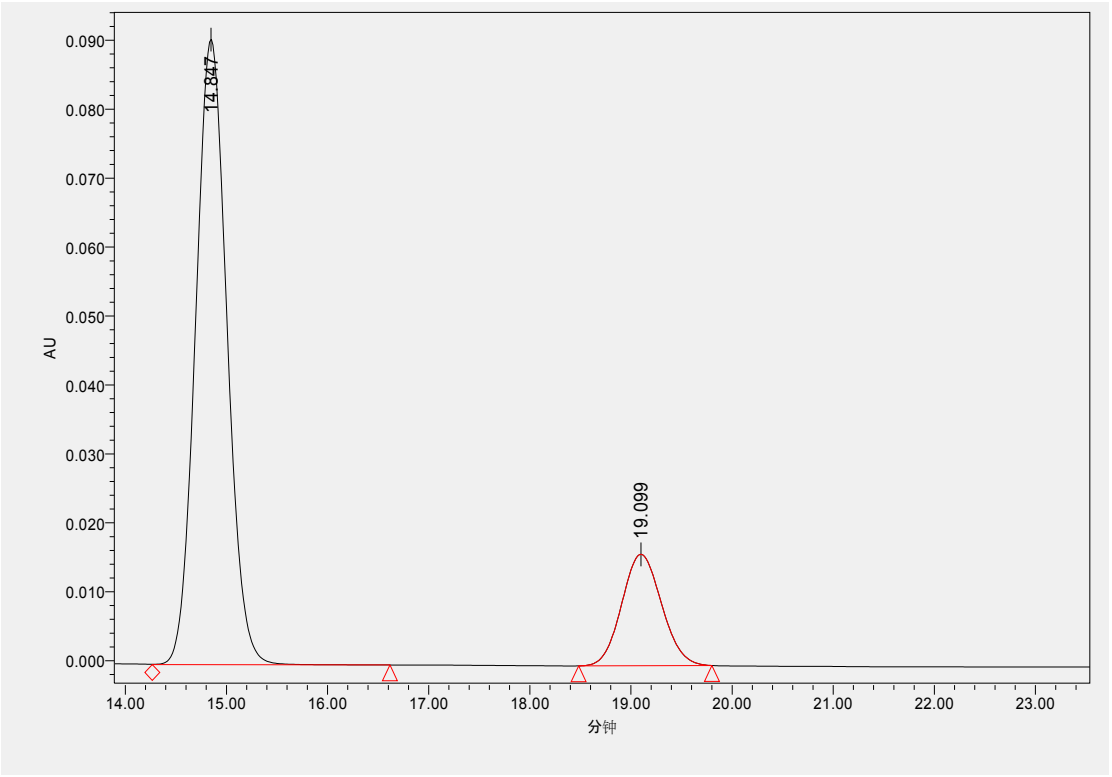

178.192
174.500
163.061
159.365
144.013
133.197
127.591
124.198
114.290
77.427
77.000
76.573
60.936
55.358
51.510
43.112
35.796
14.077
OMe
COOEt
200
150
100
50
0
PPM



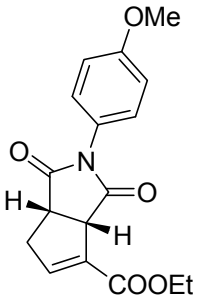
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	14.942	5082461	50.04	231722
2	2	19.167	5073621	49.96	180451



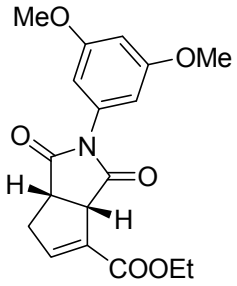
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	14.847	1951629	81.95	90721
2	2	19.099	441680	18.05	16140

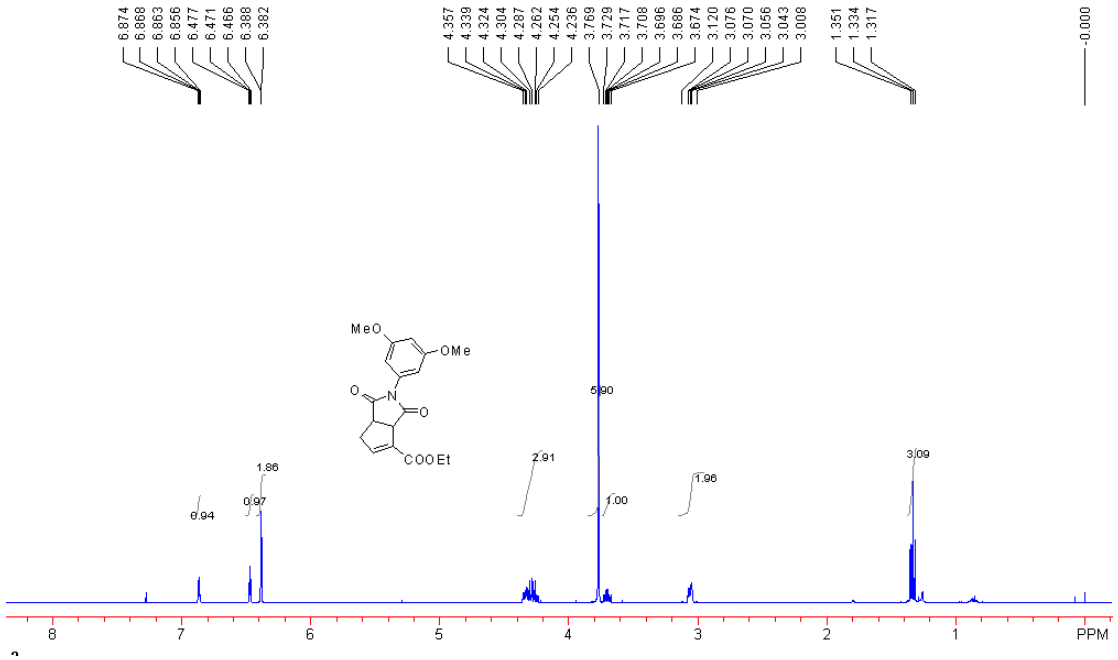


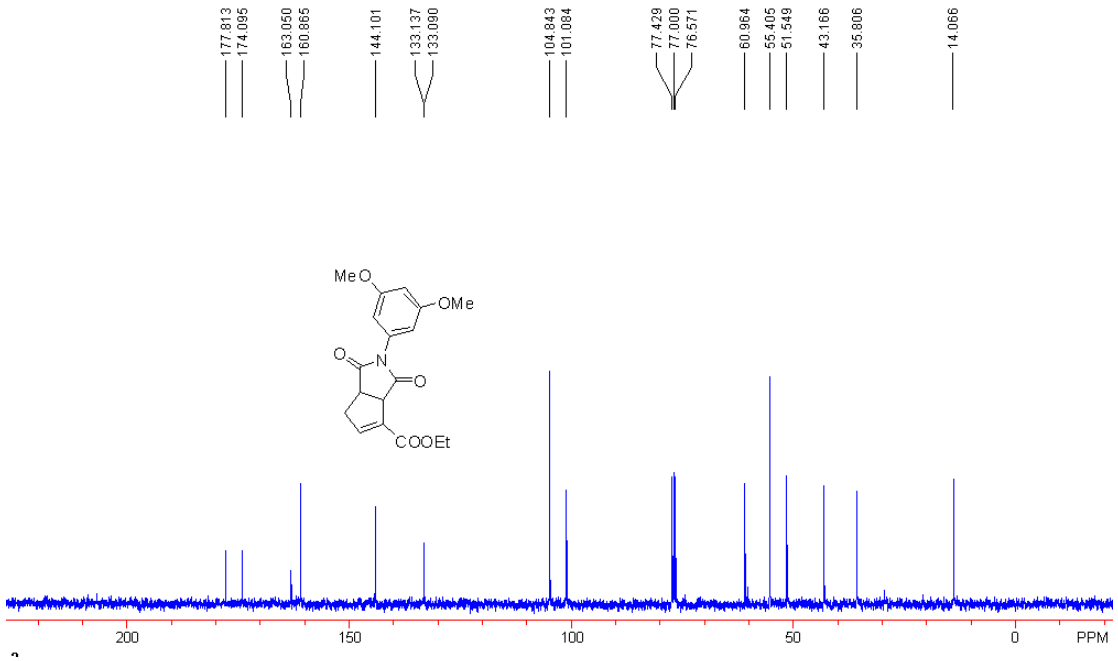
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm

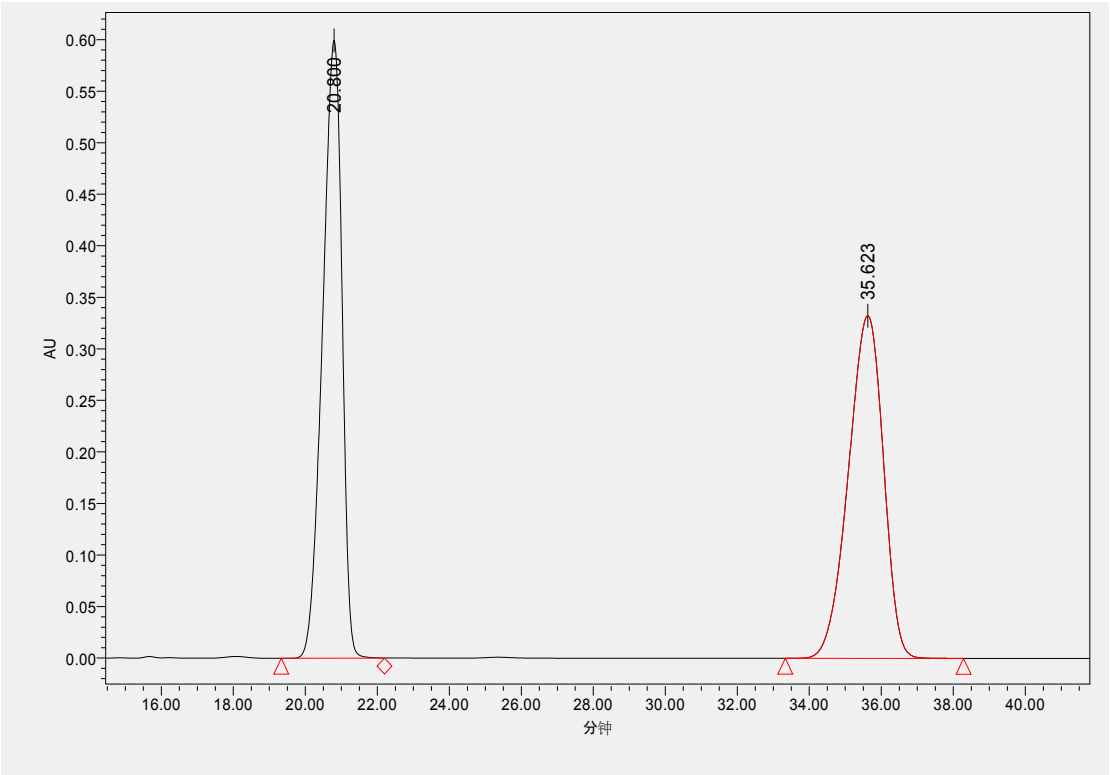


Compound 3na. 43 mg, Yield: 83%, white solid, m.p. 58-59 ^{o}C; IR (neat): ν 3099, 2927, 2849, 2841, 1782, 1709, 1597, 1474, 1334, 1286, 1203, 1154, 1094, 1058, 921, 825, 731, 641 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 6.8 Hz)□, 3.01-3.12 (2H, m), 3.70 (1H, td, *J* = 4.8, 8.4 Hz), 3.77 (6H, s), 4.24-4.36 (3H, m), 6.39 (2H, d, *J* = 2.4 Hz), 6.47 (1H, t, *J* = 2.4 Hz), 6.87 (1H, dd, *J* = 2.4, 4.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □14.1, 35.8, 43.2, 51.5, 55.4, 61.0, 101.1, 104.8, 133.0, 133.1, 144.1, 160.9, 163.1, 174.1, 177.8; MS (EI) *m/z* (%): 345 [M^+] (100.0), 299 (11.3), 273 (6.3), 179 (62.9), 150 (12.7), 138 (9.0), 93 (14.8), 79 (10.0), 65 (13.6); HRMS (EI) Calcd. for $C_{18}H_{19}NO_6$ requires (M^+) 345.1212, Found: 345.1218; $[\alpha]^{20}_{D}$ = -17.0 (c 0.1, CH_2Cl_2, 61% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm, t_{minor} = 35.49 min, t_{major} = 20.46 min).

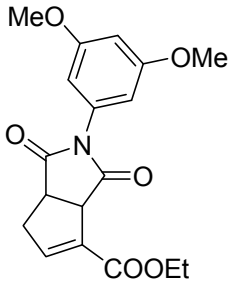
Compound 3r (the racemate of **3na**). 51 mg, Yield: 99%, colorless oil.


6.874
6.868
6.863
6.856
6.477
6.471
6.466
6.388
6.382
4.357
4.339
4.324
4.304
4.287
4.262
4.254
4.236
3.769
3.729
3.717
3.708
3.696
3.686
3.674
3.120
3.076
3.070
3.056
3.043
3.008
1.351
1.334
1.317
-0.000
MeO
OMe
O
N
O
COOEt
0.94
1.86
0.97
2.91
5.90
1.00
1.96
3.09
8
7
6
5
4
3
2
1
PPM

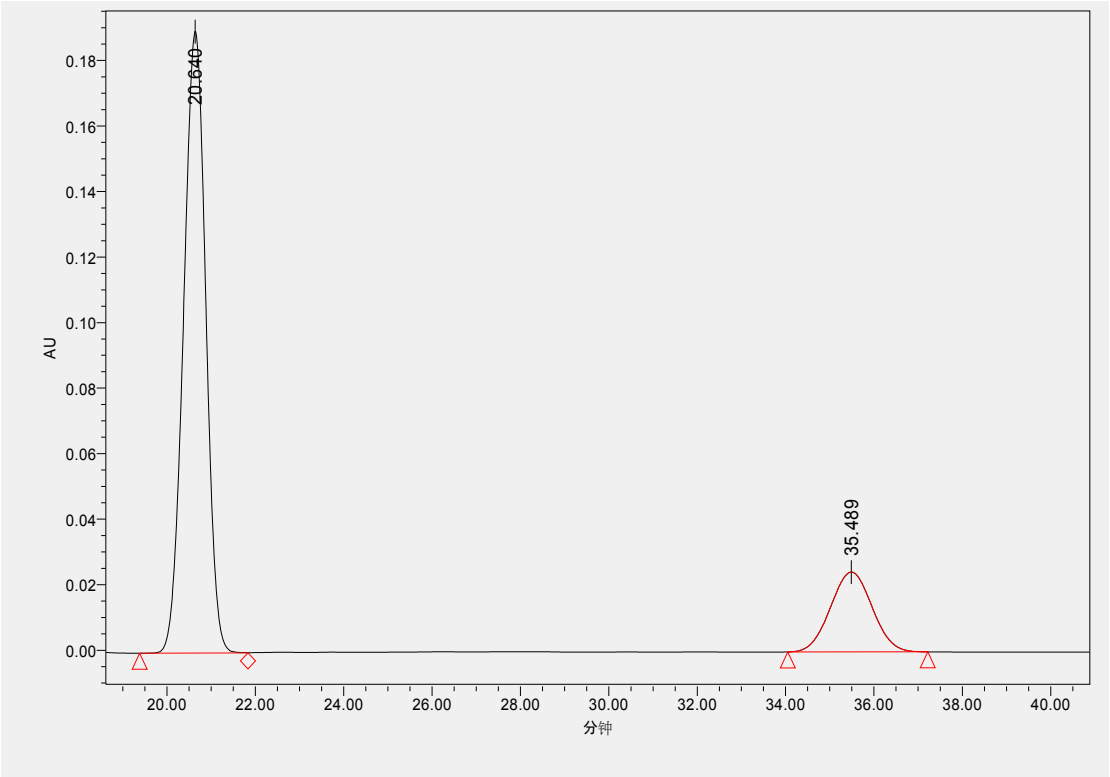

177.813
174.095
163.050
160.865
144.101
133.137
133.090
104.843
101.084
77.429
77.000
76.571
60.964
55.405
51.549
43.166
35.806
14.066
MeO
OMe
O
N
O
COOEt
200
150
100
50
0
PPM



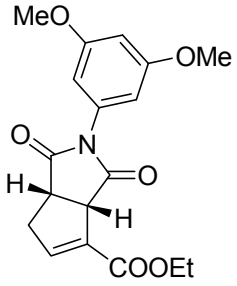
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	20.800	22423104	49.95	599454
2	2	35.623	22466326	50.05	332533



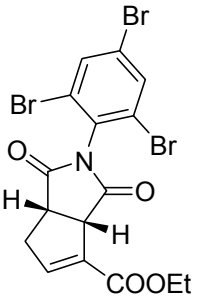
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	20.640	6615181	80.53	189822
2	2	35.489	1598974	19.47	24370

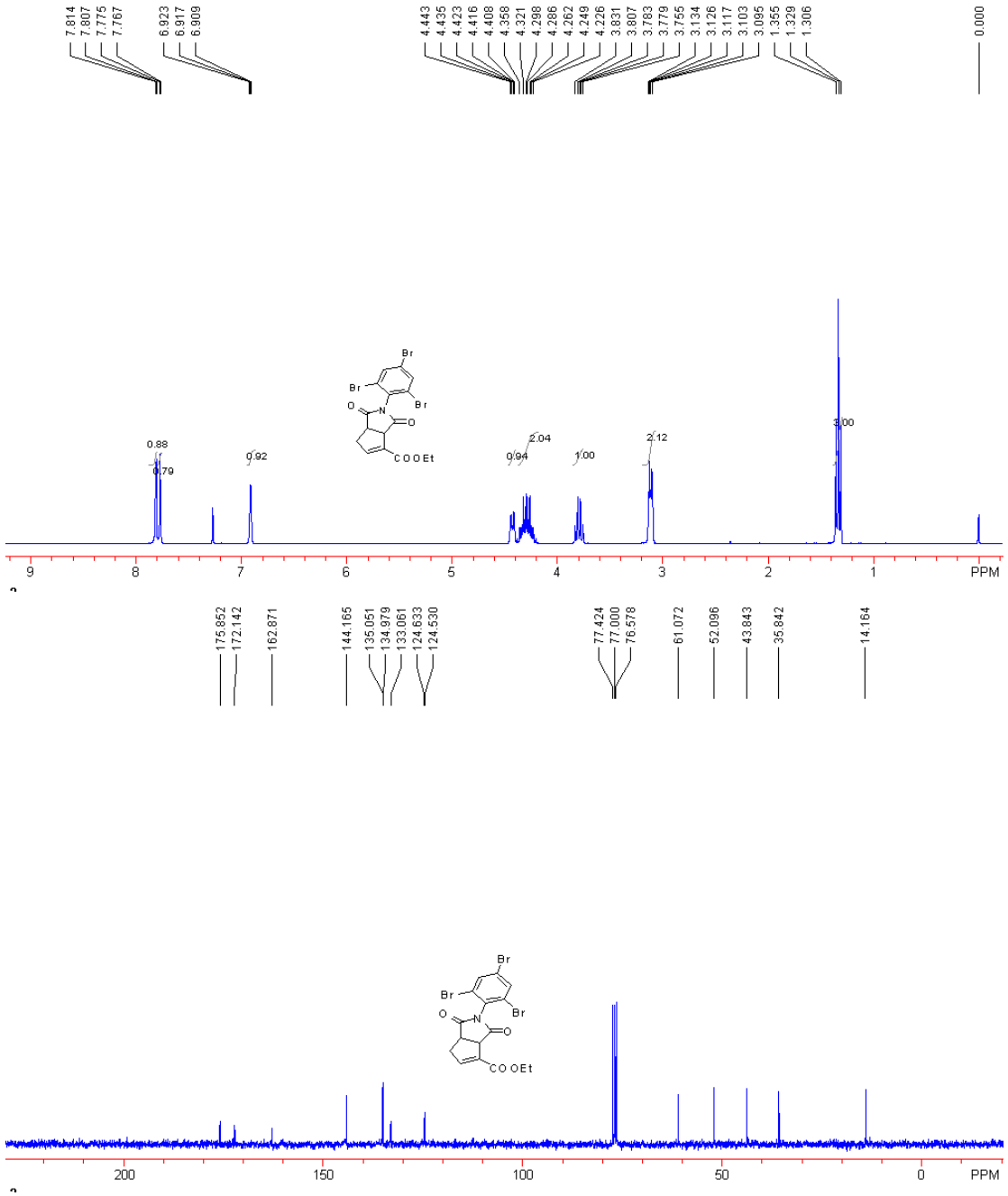


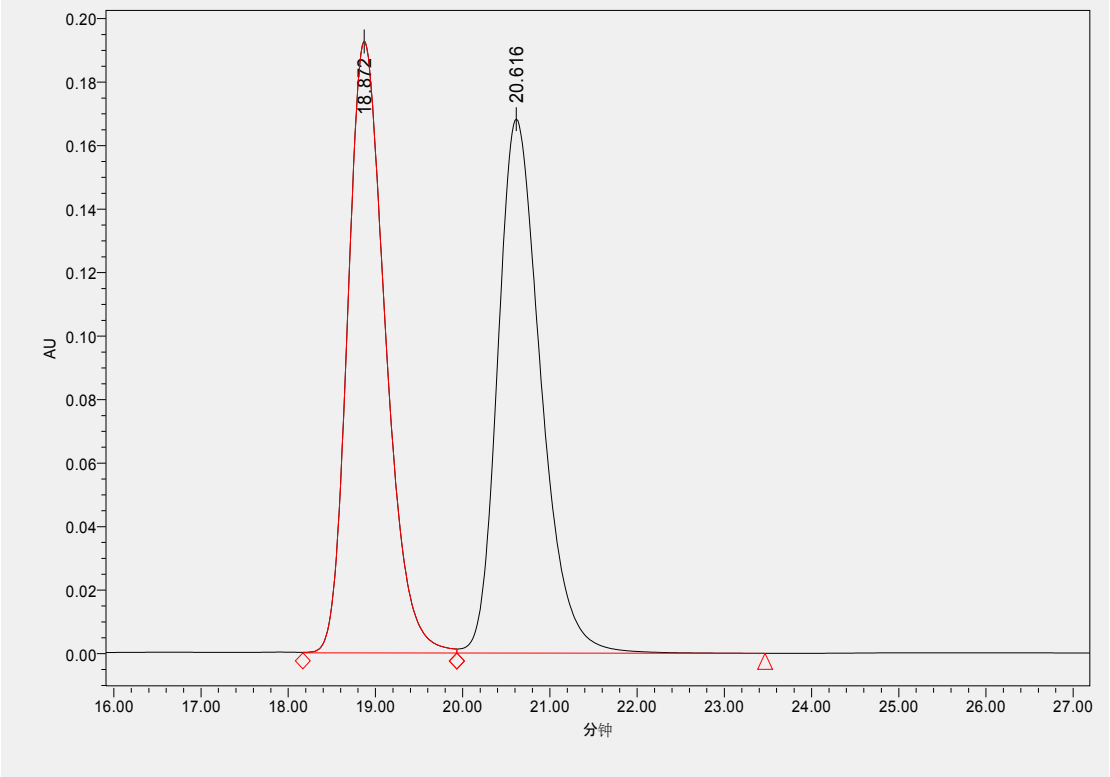
AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.6 mL/min, 214 nm



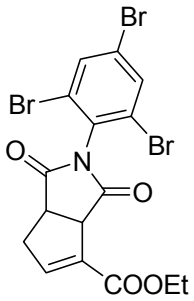
Compound 3oa. 64 mg, Yield: 83%, colorless oil; ν 3071, 2984, 2901, 1706, 1683, 1544, 1455, 1363, 1274, 1171, 1082, 1029, 924, 867, 749, 650 □cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.33 (3H, t, *J* = 7.2 Hz)□, 3.10-3.13 (2H, m), 3.76-3.83 (1H, m), 4.23-4.36 (2H, m), 4.41-4.44 (1H, m), 6.91 (1H, dd, *J* = 1.8, 4.2 Hz), 7.77 (1H, d, *J* = 3.2 Hz), 7.81 (1H, d, *J* = 3.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □14.2, 35.8, 43.8, 52.1, 61.1, 124.5, 124.6, 133.1, 135.0, 135.1, 144.2, 162.9, 172.1, 175.9; MS (EI) *m/z* (%): 519 [M^+] (1.9), 442 (55.9), 287 (12.9), 242 (13.3), 155 (13.1), 138 (78.0), 99 (28.1), 71 (64.7), 57 (100.0), 43 (59.1), 41 (22.4); HRMS (EI) Calcd. for $C_{16}H_{12}NO_4Br_3$ requires (M^+) 518.8316, Found: 518.8320; $[\alpha]^{20}_D$ = +4.4 (c 0.4, CH_2Cl_2, 38% ee). Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 230 nm, t_{minor} = 10.71 min, t_{major} = 20.39 min).

Compound 3s (the racemate of **3oa**). 74 mg, Yield: 95%, colorless oil.

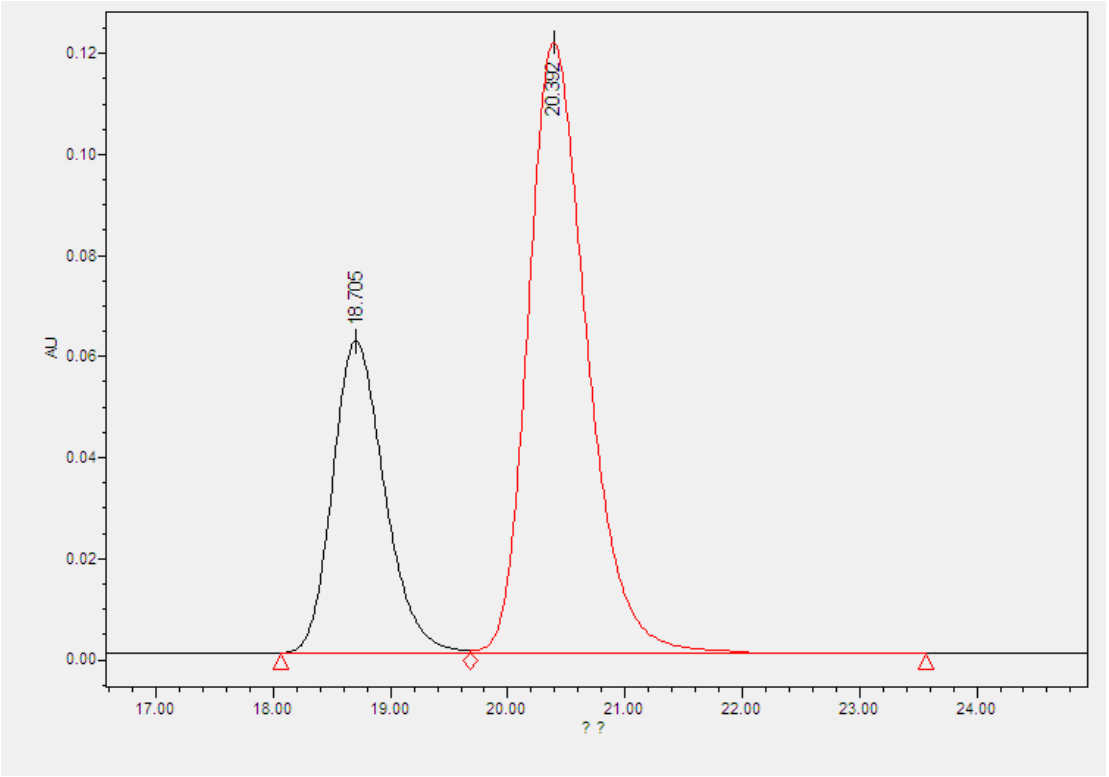

7.814
7.807
7.775
7.767
6.923
6.917
6.909
4.443
4.435
4.423
4.416
4.408
4.358
4.321
4.298
4.286
4.262
4.249
4.226
3.831
3.807
3.783
3.779
3.755
3.134
3.126
3.117
3.103
3.095
1.355
1.329
1.306
0.000
Br
Br
Br
O
N
O
COOEt
0.88
0.79
0.92
2.04
0.94
1.00
2.12
3.00
9
8
7
6
5
4
3
2
1
PPM
175.852
172.142
162.871
144.165
135.051
134.979
133.061
124.633
124.530
77.424
77.000
76.578
61.072
52.096
43.843
35.842
14.164
200
150
100
50
0
PPM



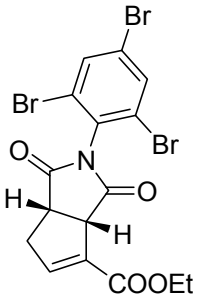
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	18.872	5791902	50.10	192777
2	2	20.616	5769117	49.90	168203



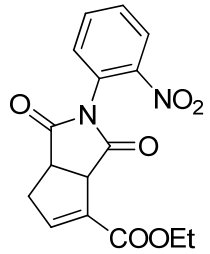
IC-H, *n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 230 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	18.705	1900173	30.98	61882
2	2	20.392	4232900	69.02	120872

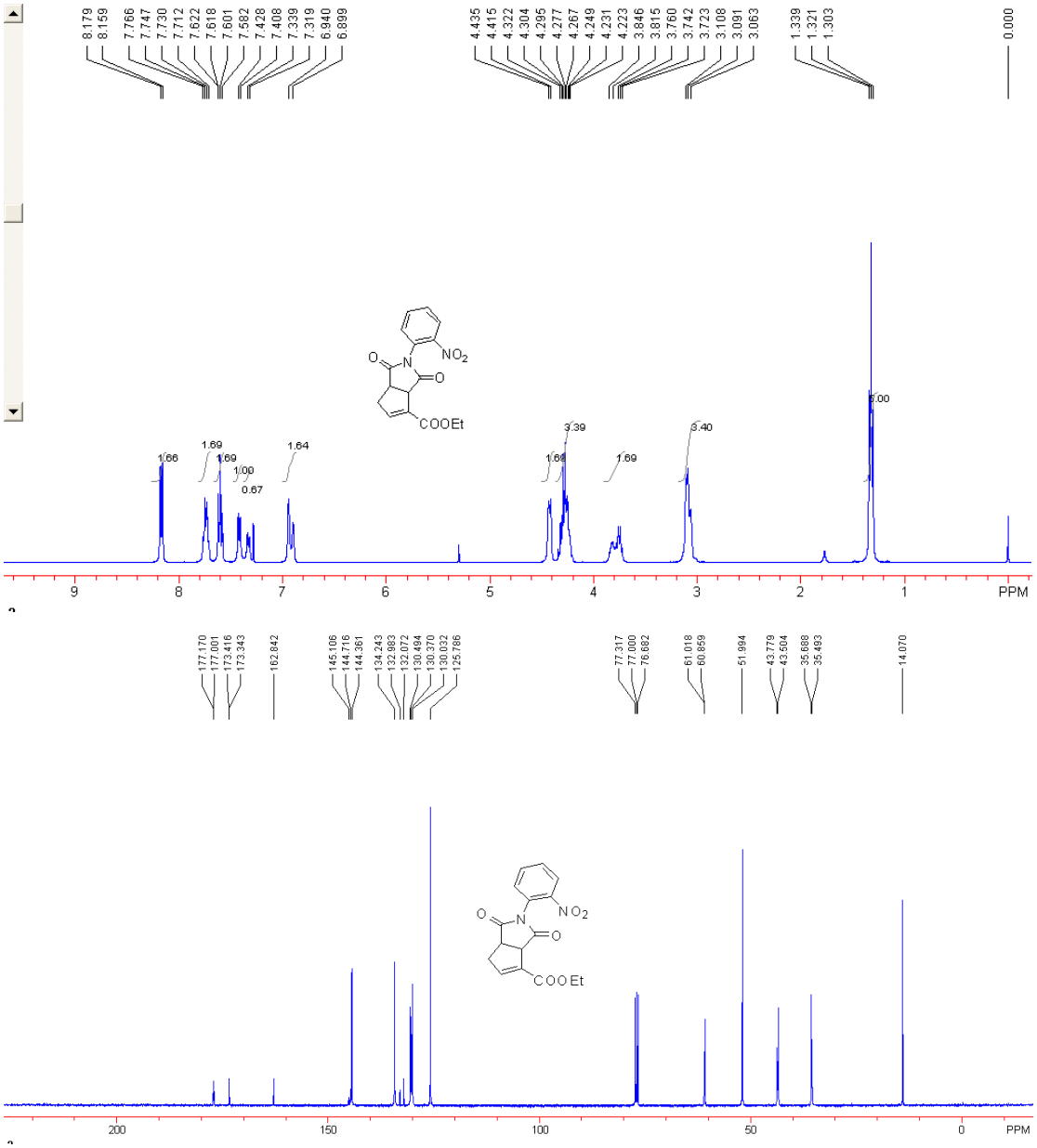


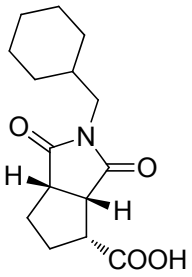
IC-H, *n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 230 nm



Compound 3t. 45 mg, Yield: 90%, white solid, m.p. 168-169 ^{o}C; IR (neat): ν 2976, 2923, 2851, 1778, 1710, 1628, 1435, 1381, 1292, 1202, 1091, 969, 861, 788, 724, 655 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.32 (3H+2H, t, *J* = 7.2 Hz)□, 3.06-3.11 (2H+1.3H, m), 3.72-3.85 (1H+0.67H, m), 4.22-4.36 (2H+1.3H, m), 4.42-4.44 (1H+0.67H, m), 6.90-6.94 (1H+0.67H, m), 7.33 (0.67H, d, *J* = 8.0 Hz), 7.42 (1H, d, *J* = 8.0 Hz), 7.58-7.62 (1H+0.67H, m), 7.71-7.77 (1H+0.67H, m), 8.17 (1H+0.67H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □14.1, 35.5, 35.7, 43.5, 43.8, 52.0, 60.9, 61.0, 125.8, 130.0, 130.3, 130.5, 132.1, 133.0, 134.2, 144.4, 144.7, 145.1, 162.8, 173.3, 173.4, 177.0, 177.2; MS (EI) *m/z* (%): 330 [M^+] (19.3), 284 (100.0), 210 (6.5), 138 (29.5), 110 (13.6), 93 (17.9), 79 (24.0), 66 (22.9), 49 (6.5); HRMS (EI) Calcd. for $C_{16}H_{14}N_2O_6$ requires (M^+) 330.0852, Found: 330.0855.

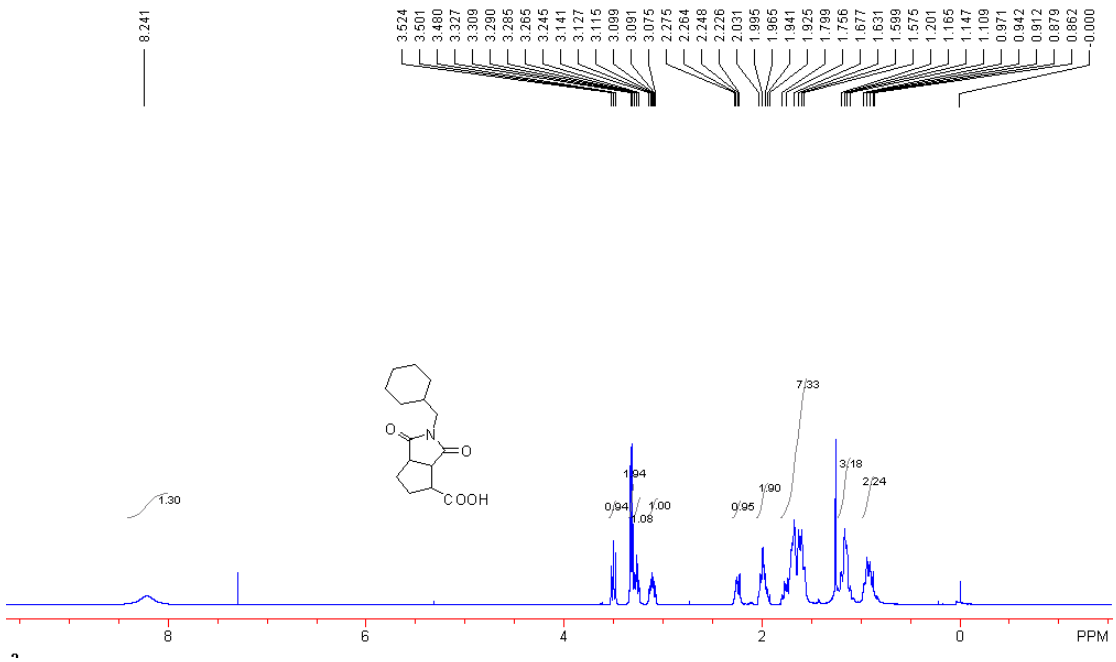
The isomers of racemic [3+2] cycloaddition product **3t** could not be separated by HPLC, thus we did not further synthesize its chiral product **3pa**.

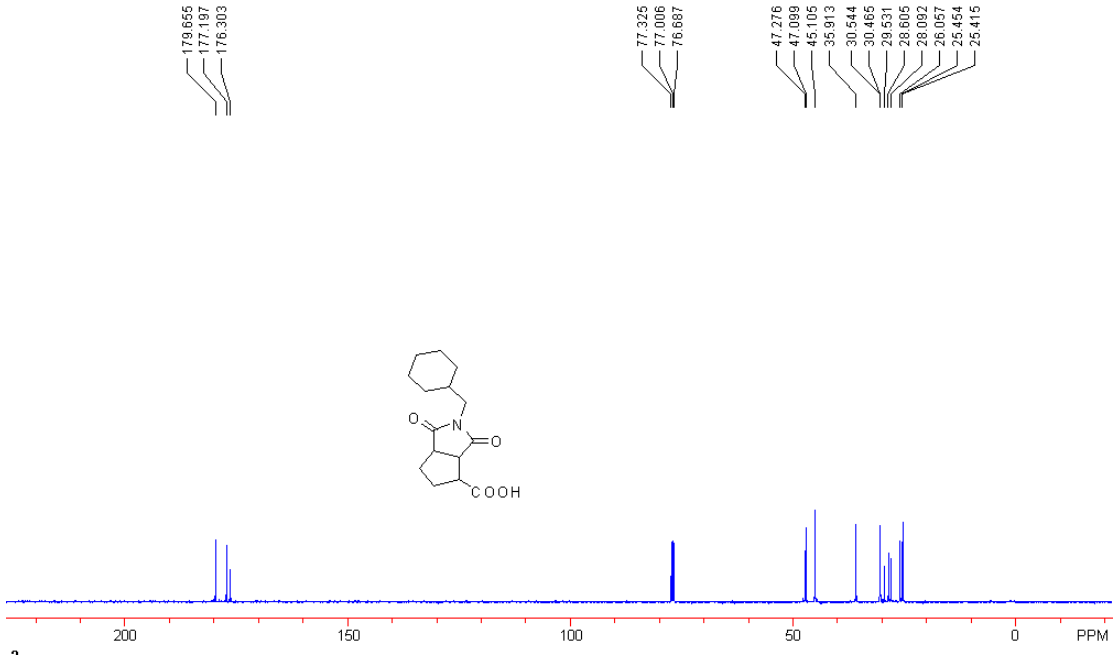

8.179
8.159
7.766
7.747
7.730
7.712
7.622
7.618
7.601
7.582
7.428
7.408
7.339
7.319
6.940
6.899
4.435
4.415
4.322
4.304
4.295
4.277
4.267
4.249
4.231
4.223
3.846
3.815
3.760
3.742
3.723
3.108
3.091
3.063
1.339
1.321
1.303
0.000
NO2
O
N
O
COOEt
1.66
1.69
1.69
1.00
0.67
1.64
3.39
1.66
1.69
3.40
2.00
9
8
7
6
5
4
3
2
1
PPM
177.170
177.001
173.416
173.343
162.842
145.106
144.716
144.361
134.243
132.983
132.072
130.494
130.370
130.032
125.786
77.317
77.000
76.682
61.018
60.859
51.994
43.779
43.504
35.688
35.493
14.070
200
150
100
50
0
PPM



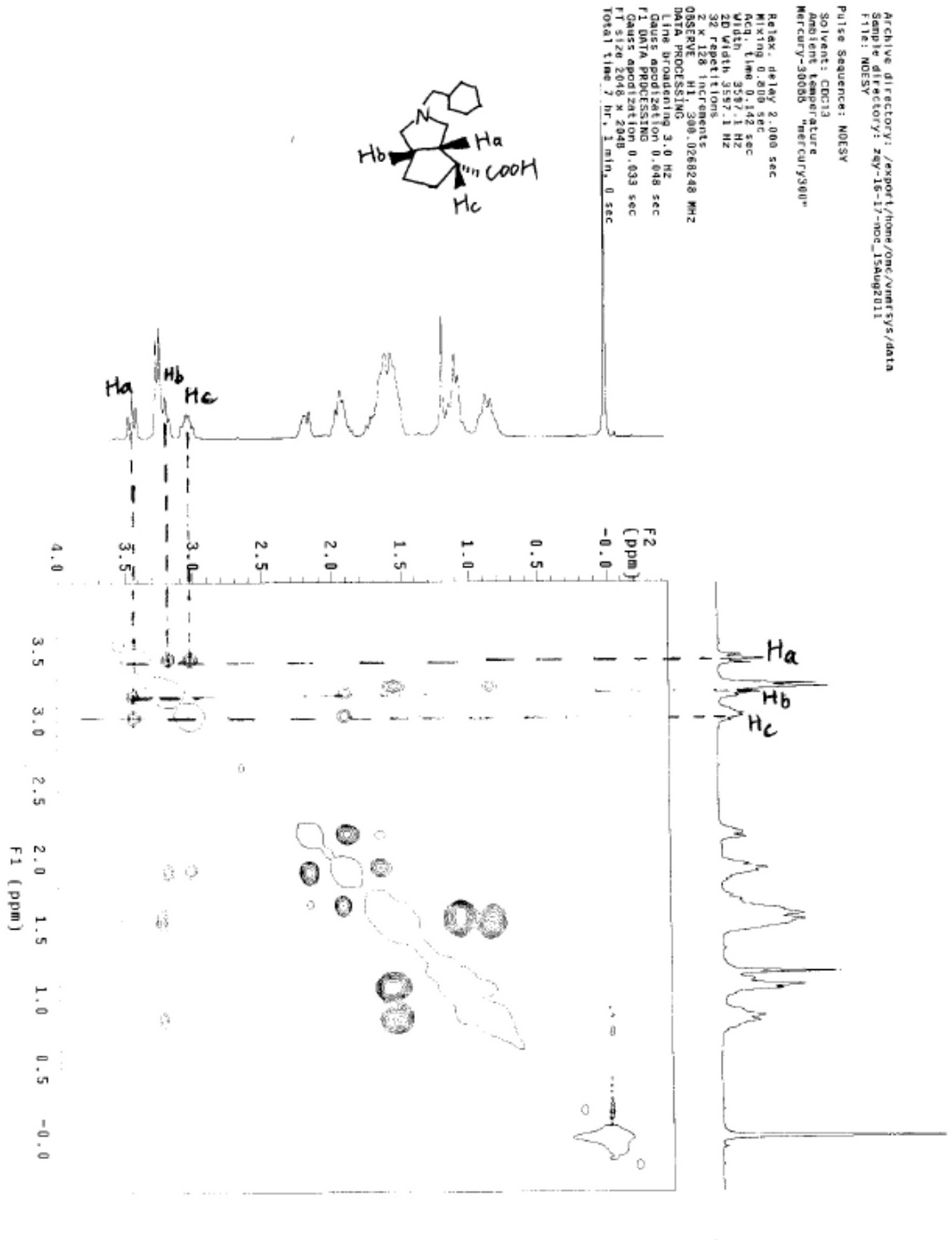
Compound 4. 41 mg, Yield: >99%, white solid, m.p. 147-148 ^{o}C; IR (neat): ν 3374, 2993, 2948, 2831, 1757, 1693, 1526, 1283, 1262, 1142, 1091, 1044, 906, 826, 777, 634 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86-0.97 (2H, m), 1.11-1.20 (3H, m), 1.58-1.80 (7H, m), 1.93-2.03 (2H, m), 2.23-2.28 (1H, m), 3.08-3.14 (1H, m), 3.25-3.29 (1H, m), 3.32 (2H, d, *J* = 7.2 Hz), 3.50 (1H, t, *J* = 8.4 Hz), 8.24 (1H, bs); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □25.4, 25.5, 26.1, 28.1, 28.6, 29.5, 30.4, 30.5, 35.9, 45.1, 47.1, 47.3, 176.3, 177.2, 179.7; MS (EI) *m/z* (%): 279 [M^+] (5.2), 197 (34.6), 184 (62.4), 179 (65.4), 166 (100.0), 151 (25.2), 95 (31.5), 67 (91.5), 55 (29.4), 41 (32.4); HRMS (EI) Calcd. for $C_{15}H_{21}NO_4$ requires (M^+) 279.1471, Found: 279.1473; $[\alpha]^{20}_{D}$ = +40.0 (c 0.2, CH_2Cl_2, for a 87% ee sample).

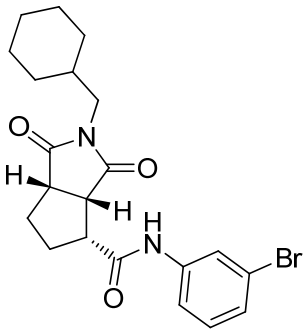
Compound race-4. 41 mg, Yield: >99%, white solid, m.p. 158-159 ^{o}C.


8.241
3.524
3.501
3.480
3.327
3.309
3.290
3.285
3.265
3.245
3.141
3.127
3.115
3.099
3.091
3.075
2.275
2.264
2.248
2.226
2.031
1.995
1.965
1.941
1.925
1.799
1.756
1.677
1.631
1.599
1.575
1.201
1.165
1.147
1.109
0.971
0.942
0.912
0.879
0.862
0.000
O
N
O
COOH
1.30
0.94
1.94
1.00
1.08
0.95
1.90
7.33
3.18
2.24
8
6
4
2
0
PPM


179.655
177.197
176.303
77.325
77.006
76.687
47.276
47.099
45.105
35.913
30.544
30.465
29.531
28.605
28.092
26.057
25.454
25.415
O
N
O
COOH
200
150
100
50
0
PPM

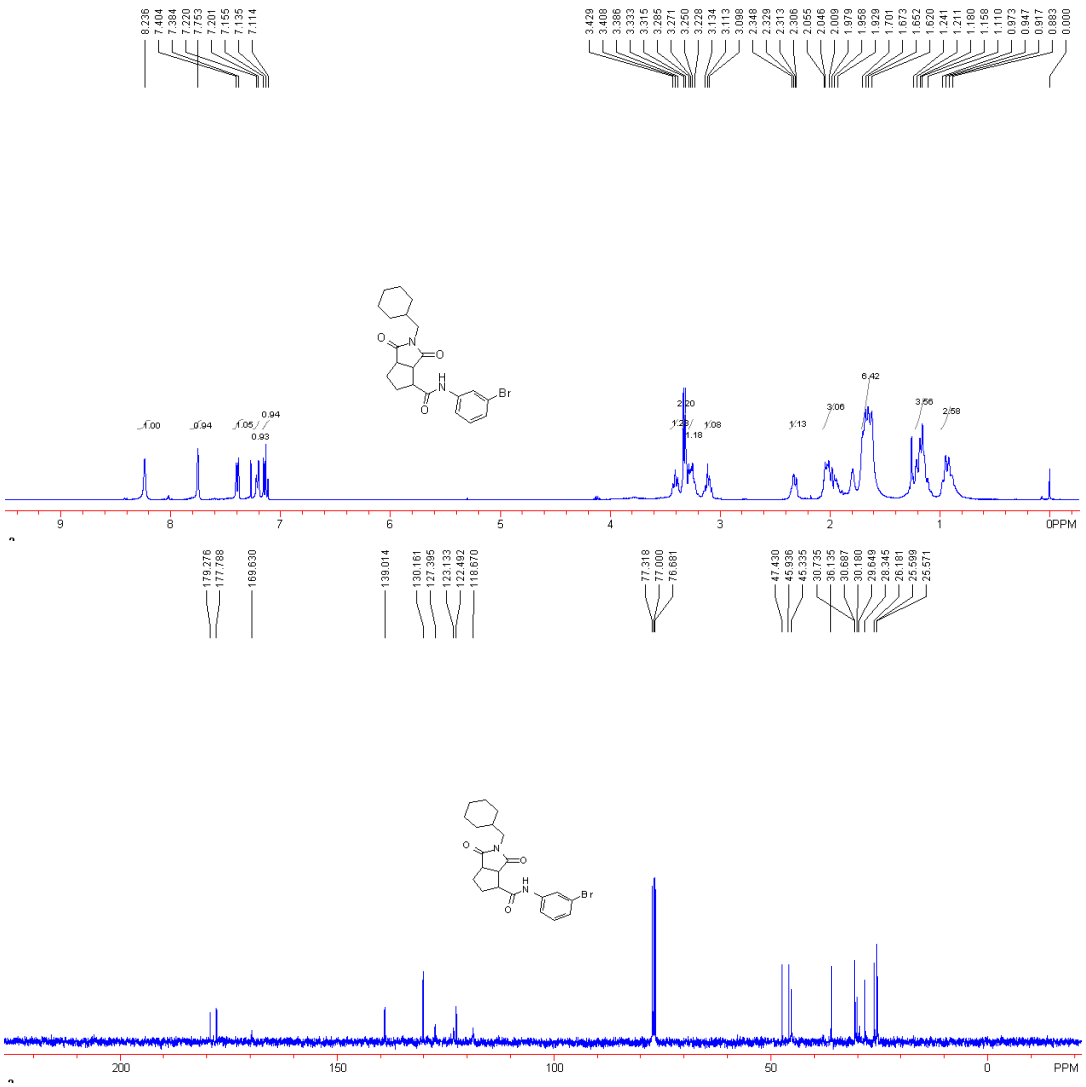
NOESY spectrum of Compound 4

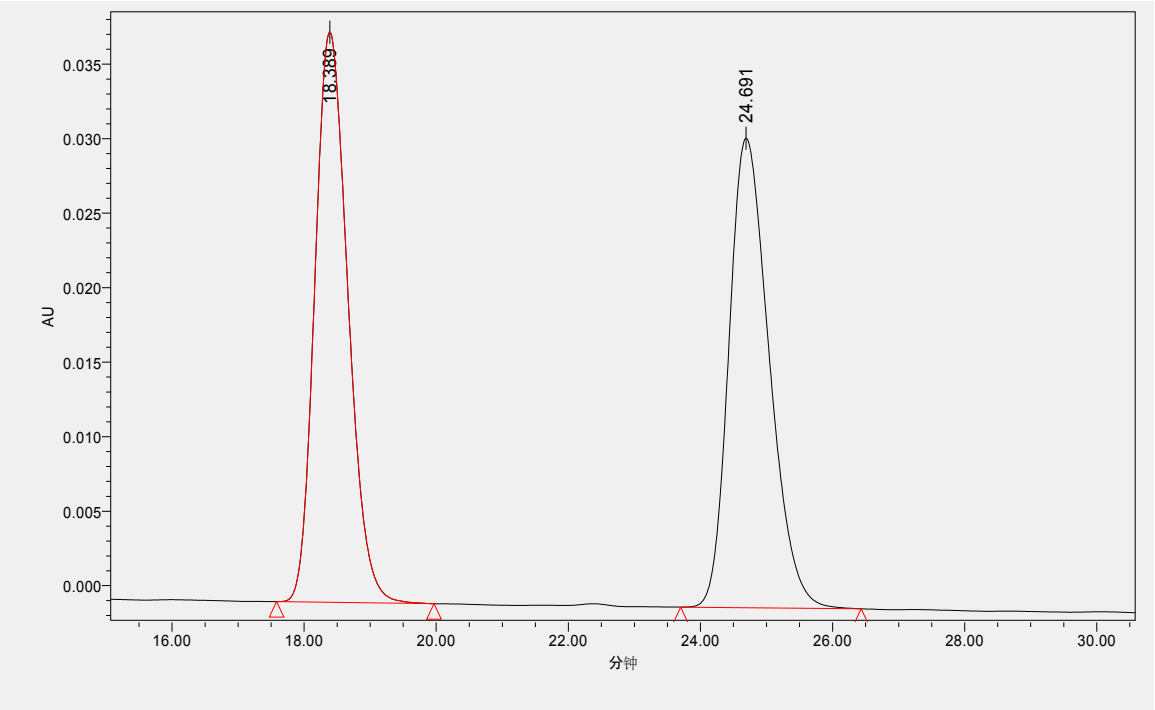




Compound 5. 49 mg, Yield: 76%, white solid, m.p. 207-208 ^{o}C; IR (neat): ν 3414, 2987, 2928, 2841, 1747, 1702, 1693, 14796, 1382, 1255, 1162, 1091, 1031, 907, 829, 779, 636 □cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88-0.97 (2H, m), 1.11-1.24 (3H, m), 1.62-1.70 (6H, m), 1.93-2.06 (3H, m), 2.31-2.35 (1H, m), 3.10-3.13 (1H, m), 3.23-3.29 (1H, m), 3.32 (2H, d, *J* = 7.2 Hz), 3.41 (1H, t, *J* = 8.4 Hz), 7.14 (1H, t, *J* = 8.0 Hz), 7.21 (1H, d, *J* = 8.0 Hz), 7.39 (1H, d, *J* = 8.0 Hz), 7.75 (1H, s), 8.24 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □25.5, 25.6, 26.2, 28.3, 29.6, 30.2, 30.6, 30.7, 36.1, 45.3, 45.9, 47.4, 118.7, 122.5, 123.1, 127.4, 130.2, 139.0, 169.6, 177.8, 179.3; MS (EI) *m/z* (%): 432 [M^+] (15.9), 262 (34.4), 171 (14.0), 95 (20.4), 67 (100.0), 55 (15.3), 41 (11.2); HRMS (EI) Calcd. for $C_{21}H_{25}N_2O_3Br$ requires (M^+) 432.1049, Found: 432.1052; $[\alpha]^{20}_{D}$ = +21.5 (c 0.6, CH_2Cl_2, 87% ee). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 214 nm, t_{minor} = 18.82 min, t_{major} = 25.05 min).

Compound race-5. 49 mg, Yield: 76%, white solid, m.p. 198-199 ^{o}C.


8.236
7.404
7.384
7.220
7.753
7.201
7.155
7.135
7.114
3.429
3.408
3.386
3.333
3.315
3.285
3.271
3.250
3.228
3.134
3.113
3.098
2.348
2.329
2.313
2.095
2.055
2.046
2.009
1.979
1.958
1.929
1.701
1.673
1.652
1.620
1.241
1.211
1.180
1.158
1.110
0.973
0.947
0.917
0.883
0.000
Br
1.00
0.94
1.05
0.94
0.93
2.20
1.23
1.18
1.08
1.13
3.06
6.42
3.56
2.58
9
8
7
6
5
4
3
2
1
0PPM
179.276
177.768
169.630
139.014
130.161
127.395
123.133
122.492
118.670
77.318
77.000
76.681
47.430
45.936
45.335
36.135
30.735
30.687
30.180
29.649
28.345
26.181
25.599
25.571
Br
200
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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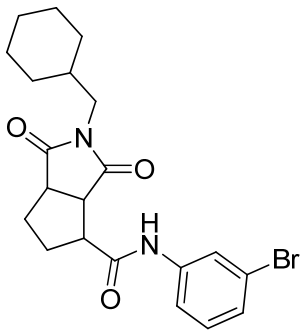
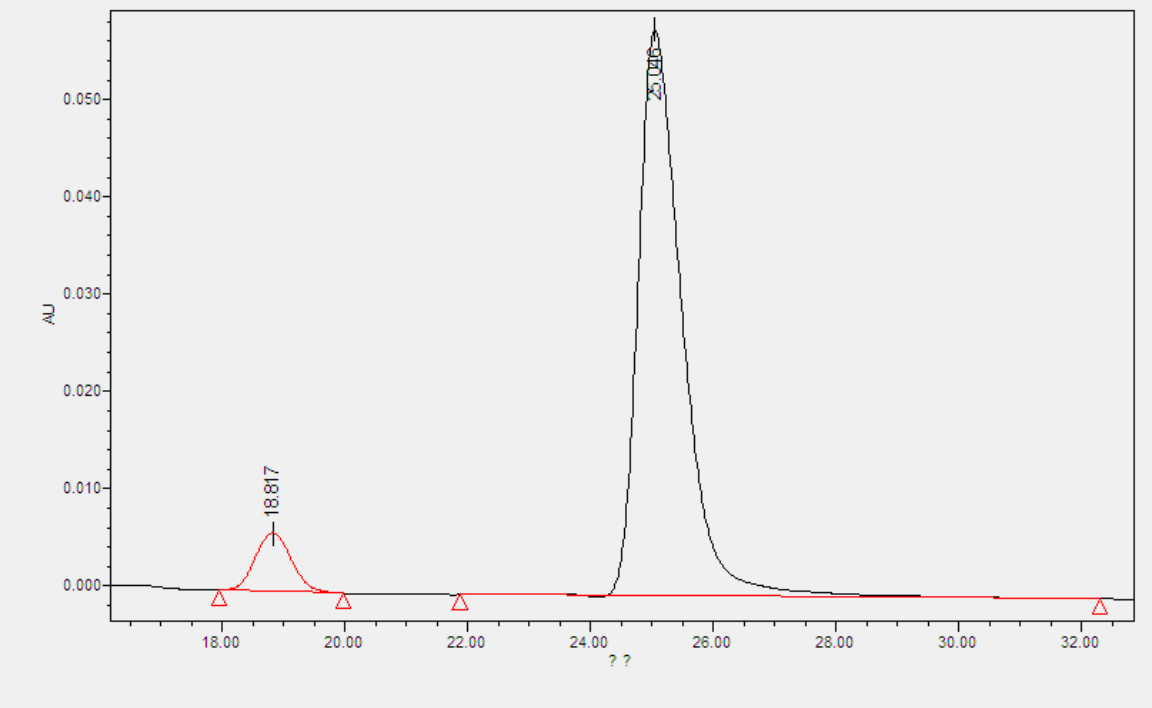
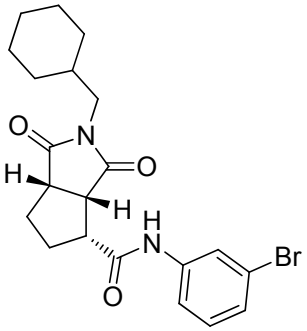
2	2	24.691	1332909	50.04	31522



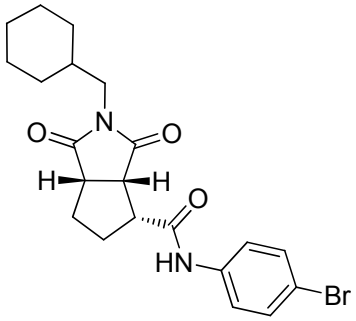
AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 214 nm



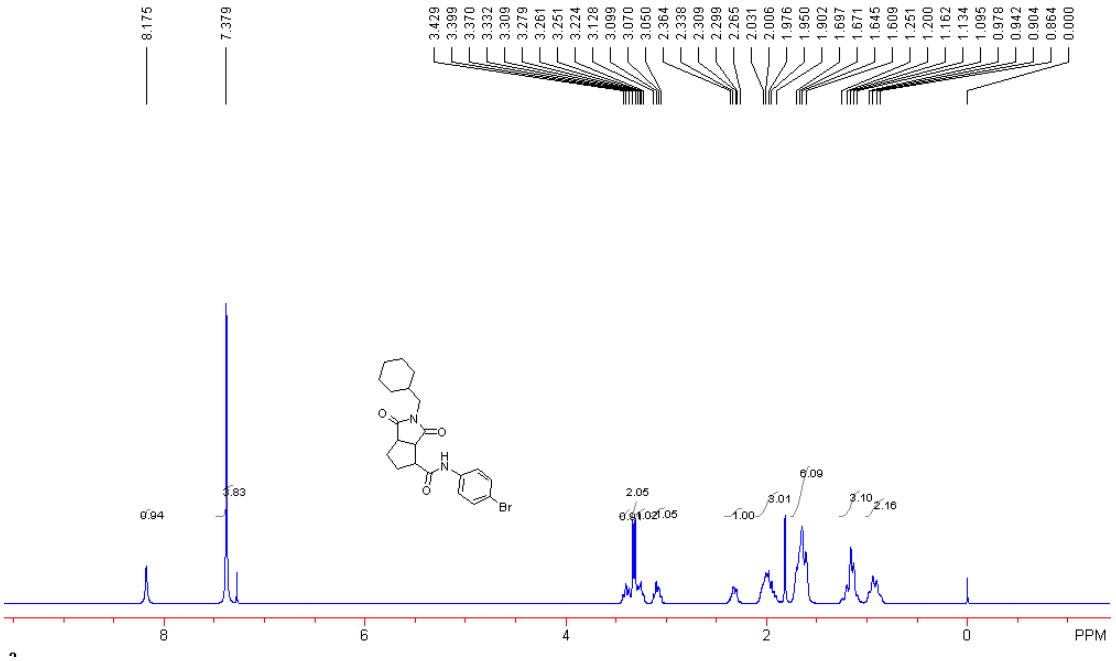
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	18.817	206157	6.54	5542
2	2	25.046	2947394	93.46	58179



AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, 214 nm



Compound 8. 46 mg, Yield: 71%, white solid, m.p. 198-199 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.86-0.98 (2H, m), 1.10-1.25 (3H, m), 1.61-1.70 (6H, m), 1.90-2.03 (3H, m), 2.27-2.36 (1H, m), 3.05-3.13 (1H, m), 3.22-3.28 (1H, m), 3.32 (2H, d, *J* = 6.9 Hz), 3.40 (1H, t, *J* = 8.7 Hz), 7.38 (4H, s), 8.18 (1H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □25.5, 26.1, 28.3, 30.1, 30.6, 30.7, 36.1, 45.3, 45.9, 47.4, 49.6, 117.0, 121.8, 131.8, 136.7, 169.5, 177.8, 179.3; $[\alpha]^{20}_{D}$ = +11.3 (c 1.1, CH_2Cl_2, for a 87% ee sample).


8.175
7.379
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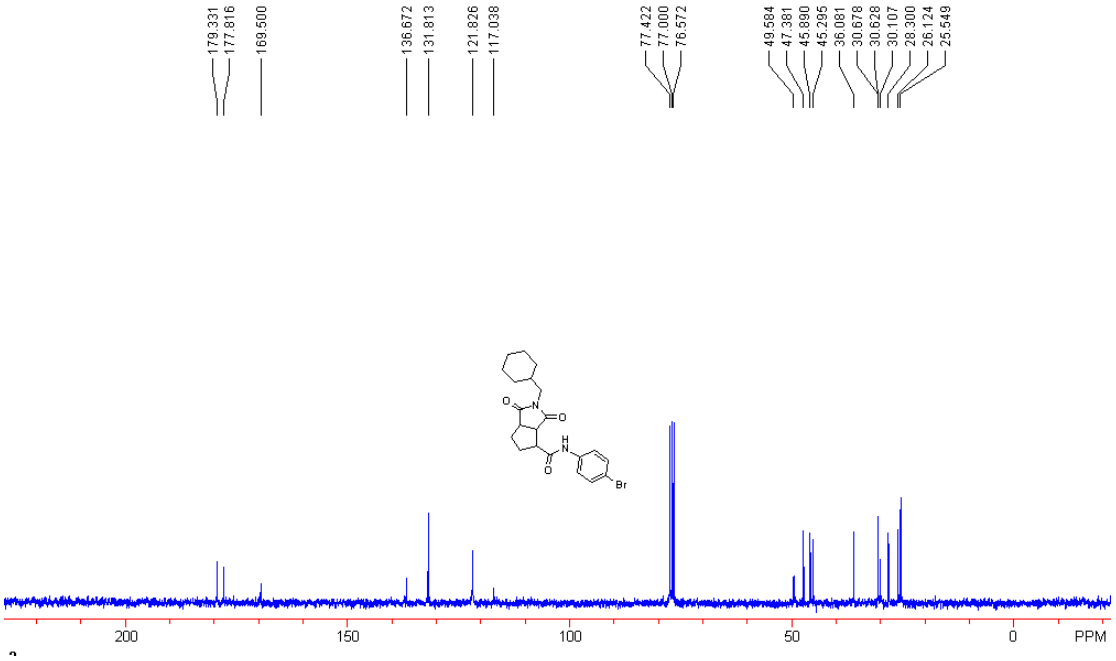
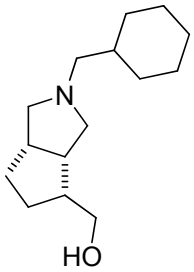
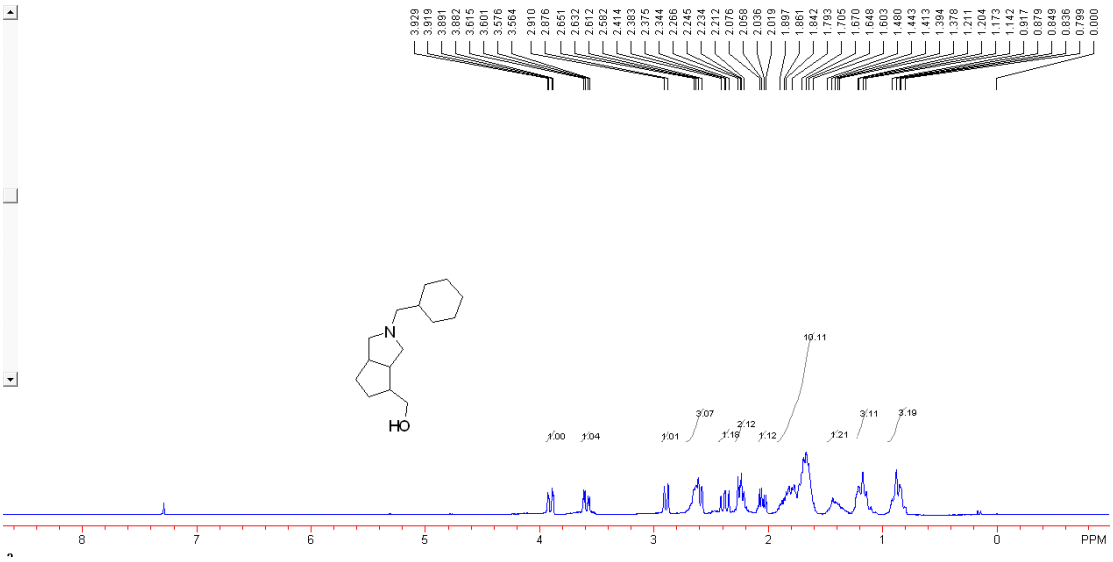
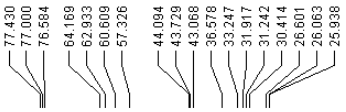
3.399
3.370
3.332
3.309
3.279
3.261
3.251
3.224
3.128
3.099
3.070
3.050
2.364
2.338
2.309
2.299
2.265
2.031
2.006
1.976
1.950
1.902
1.697
1.671
1.645
1.609
1.251
1.200
1.162
1.134
1.095
0.978
0.942
0.904
0.864
0.000
0.94
3.83
2.05
0.91
1.02
1.05
1.00
3.01
6.09
3.10
2.16
Br
8
6
4
2
0
PPM


179.331
177.816
169.500
136.672
131.813
121.826
117.038
77.422
77.000
76.572
49.584
47.381
45.890
45.295
36.081
30.678
30.628
30.107
28.300
26.124
25.549
Br
200
150
100
50
0
PPM



Compound 6. 24 mg, Yield: 99%, colorless oil; IR (neat): ν 3345, 2984, 2931, 2856, 1489, 1243, 1259, 1102, 1073, 1011, 899, 835, 755, 634 □cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.80-0.92 (3H, m), 1.14-1.21 (3H, m), 1.38-1.48 (1H, m), 1.60-1.90 (10H, m), 2.05 (1H, dd, *J* = 5.1, 11.7 Hz), 2.21-2.27 (2H, m), 2.38 (1H, dd, *J* = 9.3, 11.7 Hz), 2.58-2.65 (3H, m), 2.89 (1H, d, *J* = 10.2 Hz), 3.59 (1H, dd, *J* = 3.9, 11.1 Hz), 3.90 (1H, dd, *J* = 2.7, 11.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ □25.9, 26.1, 26.6, 30.4, 31.2, 31.9, 33.2, 36.6, 43.1, 43.7, 44.1, 57.3, 60.6, 62.9, 64.2; MS (EI) *m/z* (%): 237 [M^+] (2.5), 155 (10.2), 154 (100.0), 124 (6.9), 95 (4.4), 57 (5.9), 55 (11.4), 41 (12.1); HRMS (EI) Calcd. for $C_{15}H_{27}NO$ requires (M^+) 237.2093, Found: 237.2094; $[\alpha]^{20}_D$ = +11.2 (c 0.4, CH_2Cl_2, 87% ee). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-PrOH = 98/02, 0.7 mL/min, 214 nm, t_{minor} = 12.16 min, t_{major} =11.34 min).


3.929
3.919
3.891
3.882
3.615
3.601
3.576
3.564
2.910
2.876
2.651
2.632
2.612
2.582
2.414
2.383
2.375
2.344
2.266
2.245
2.234
2.212
2.076
2.058
2.036
2.019
1.897
1.861
1.842
1.793
1.705
1.670
1.648
1.603
1.480
1.443
1.413
1.394
1.378
1.211
1.204
1.173
1.142
0.917
0.879
0.849
0.836
0.799
0.000
N
HO
19.11
3.07
2.12
1.18
1.12
1.00
1.04
1.01
1.21
3.11
3.19
8
7
6
5
4
3
2
1
0
PPM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76.584
64.169
62.933
60.609
57.326
44.094
43.729
43.068
36.578
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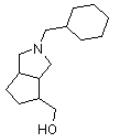
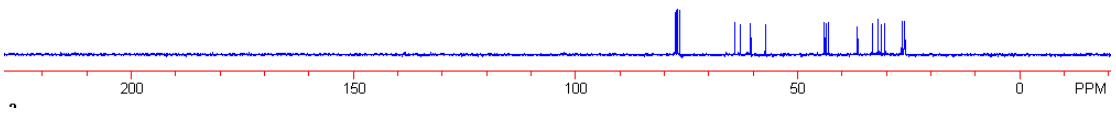
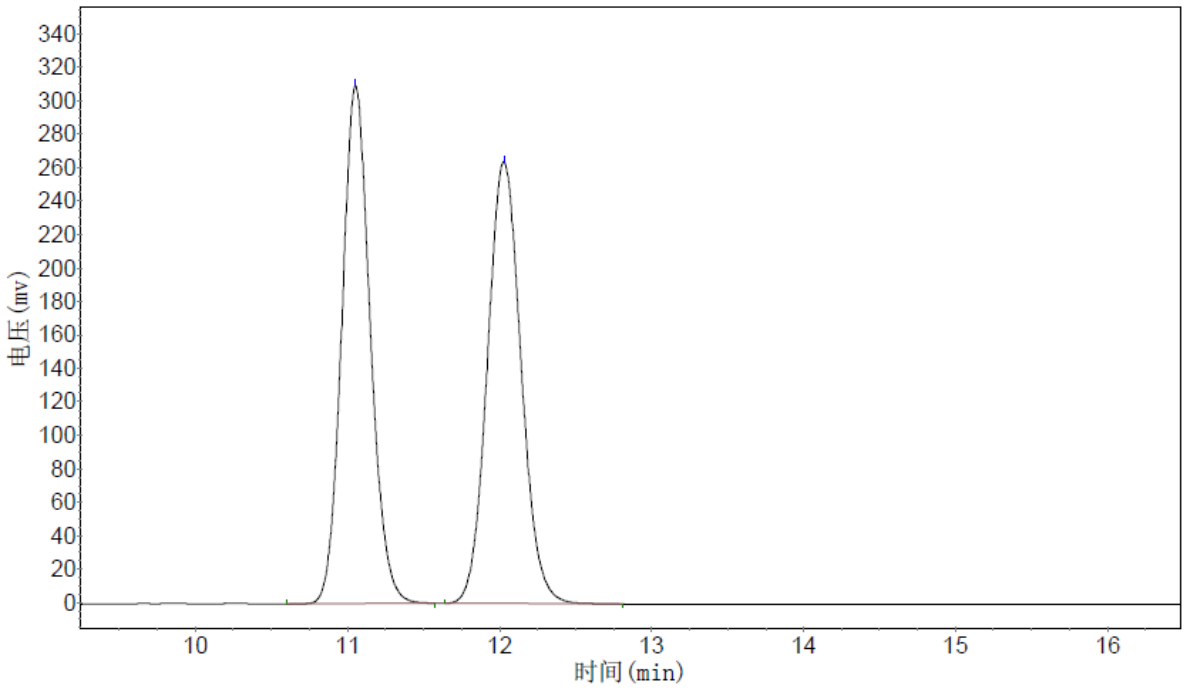
31.917
31.242
30.414
26.601
26.063
25.938


N
HO


200
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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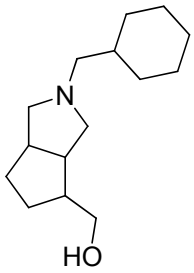
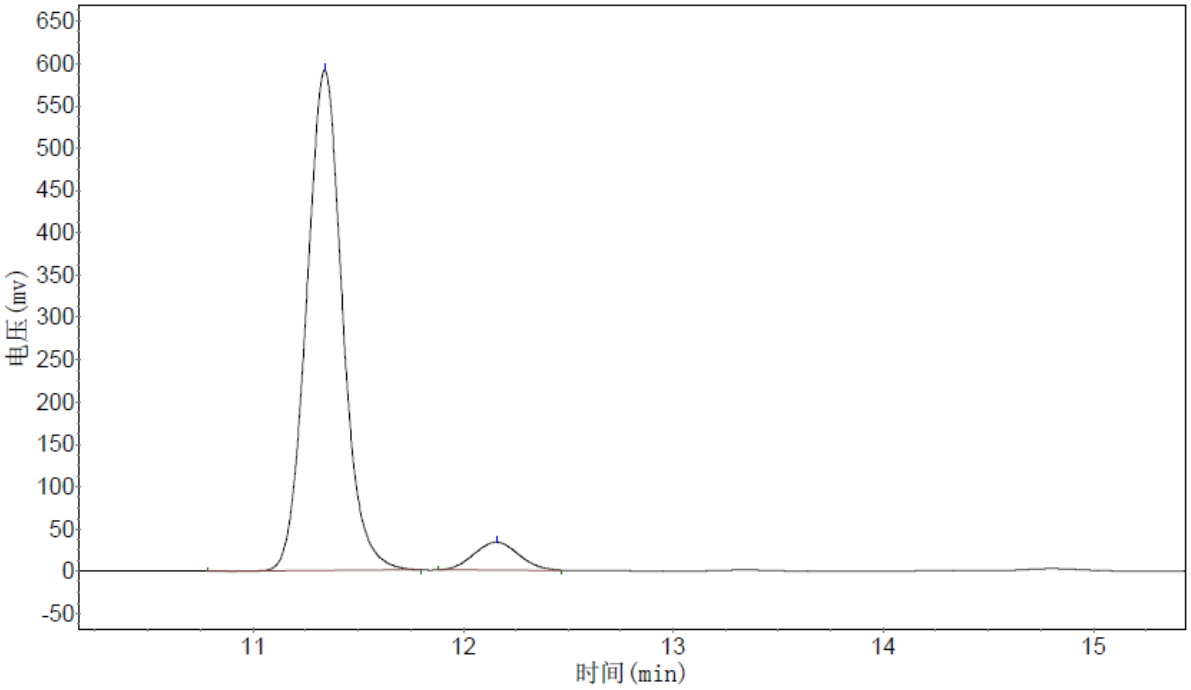


OD-H, *n*-hexane/*i*-PrOH = 98/02, 0.7 mL/min, 214 nm



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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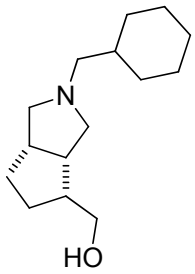
2	2	12.158	487004	6.50	32771



OD-H, *n*-hexane/*i*-PrOH = 98/02, 0.7 mL/min, 214 nm