Highly efficient asymmetric synthesis of α, β-epoxy esters via one-pot organocatalytic epoxidation and oxidative esterification

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(A) General details

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in ppm relative to residual solvent signals (CDCl3, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.16 ppm for ^{13}C NMR), Coupling constants are reported in Hertz (abbreviated for Hz). The following abbreviations are used to designate chemical shift mutiplicities: s= singlet, d= doublet, m= multiplet, br=broad. High-resolution mass spectra were obtained with Shimadazu LCMS-IT-TOF mass spectrometer. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Perkin-Elmer 341 digital polarimeter and are reported as follows: $[\alpha]_D^{20}$ (*c* in gram per 100 mL of solvent). The flash column chromatography was carried out over silica gel (230–400 mesh), purchased from Qingdao Haiyang Chemical Co., Ltd. Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected. TLC analysis was performed on precoated silica gel GF_{254} slides, and visualised by either UV irradiation or I_2 staining. Infrared (IR) spectra were recorded on a Bruker Tensor 37 spectrophotometer. Data are represented as frequency of absorption (cm^{-1}). Unless otherwise stated, all reagents were obtained from commercial sources and used as received. The solvents were used as commercial anhydrous grade without further purification. Enantiomeric excesses were determined by HPLC using a Daicel Chiralcel AD-H or OD-H column (4.6 mm × 25 cm) and eluting with *n*-hexane/*i*-PrOH solution.

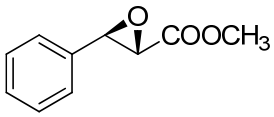
(B) General experimental procedure for the synthesis of α, β-epoxy esters and (-)-clausenamide

Asymmetric synthesis of α, β-epoxy esters

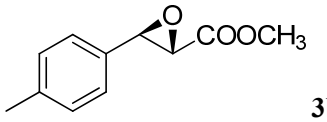
To a solution of a α, β-unsaturated aldehydes (0.5 mmol) in CH_2Cl_2 (0.5 mL) was added catalyst **6** (18 mg, 0.05 mmol, 10 mol %) and H_2O_2 (30 wt % in H_2O, 68 mg, 0.6 mmol, 1.2 equiv.) at room temperature. After the reaction mixture was stirred for 2h, CH_3OH (1 mL), NBS (116 mg, 0.65 mmol, 1.3 eq) and Na_2CO_3 (69 mg, 0.65 mmol, 1.3 eq) were added. The mixture was stirred for another 3h. Then it was concentrated under vacuum and purified by flash column chromatography.

The racemic α, β-epoxy esters were obtained by mixing equal amounts of **3** and ent-3 independently obtained by using catalyst 6 and its enatiomer.

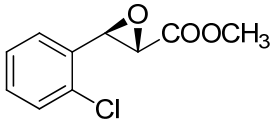
(-)-clausenamide was synthesized from **3a** according to literature method.[1]



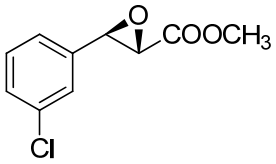
3a,[2] pale yellow oil, 72% yield (ethyl acetate / petrol ether = 1/15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 3H), 7.30 –7.28 (m, 2H), 4.10 (d, *J* = 1.6 Hz, 1H), 3.83 (s, 3H), 3.52 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.72, 134.99, 129.11, 128.76, 125.90, 58.07, 56.73, 52.68. $[\alpha]_D^{20}$ = + 157.1 (c = 1.3, $CHCl_3$); The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 220 nm, 0.8 mL/min); t_R (major enantiomer) = 18.4 min, t_R (minor enantiomer) = 19.7 min, 95% ee.



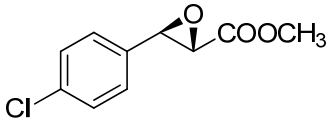
3b,[2] colorless oil, 54% yield (ethyl acetate / petrol ether = 1/15).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17(s, 4H), 4.06 (d, *J* = 1.7 Hz, 1H), 3.81(s, 3H), 3.50 (d, *J* = 1.7 Hz, 1H), 2.34(s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 168.83, 139.04, 131.95, 129.42, 125.86, 58.08, 56.64, 52.59, 21.27; $[\alpha]_D^{20}$ = +165.5 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 220 nm, 0.8 mL/min); t_R (major enantiomer) = 7.8 min, t_R (minor enantiomer) = 8.6 min, 96% ee.



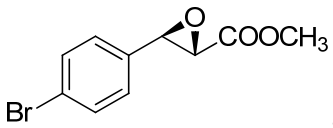
3c, colorless oil, 55% yield (ethyl acetate / petrol ether = 1/15).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38– 7.24 (m, 4H),, 4.43 (d, *J* = 1.4 Hz, 1H), 3.85 (s, 3H), 3.39 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.44, 133.60, 133.20, 129.88, 129.47, 127.27, 126.11, 56.08, 55.65, 52.84; IR (KBr) ν/cm^{-1}: 1755, 1481, 1442, 1292, 1243, 1211, 1053, 760; $[\alpha]_D^{20}$ = +44.5 (c = 0.9, $CHCl_3$); HRMS (ESI) calcd for $C_{10}H_9ClNaO_3$ $(M + Na)^+$: 235.0132, found: 235.0137. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 220 nm, 0.8 mL/min); t_R (minor enantiomer) = 6.6 min, t_R (major enantiomer) = 8.2 min, 97% ee.



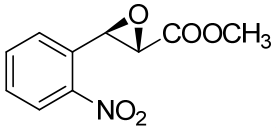
3d, pale yellow oil, 71% yield (ethyl acetate / petrol ether = 1/15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32– 7.28 (m, 3H), 7.20-7.18 (m, 1H), 4.08(s, 1H), 3.83 (s, 3H), 3.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.35, 137.19, 134.97, 130.12, 129.33, 125.95, 124.19, 57.29, 56.70, 52.82; IR (KBr) ν/cm^{-1}: 3029, 2960, 1752, 1460, 1416, 1341, 1213, 1180, 993, 878; $[\alpha]_D^{20}$ = +145.7 (c = 1.0, $CHCl_3$); HRMS (ESI) calcd for $C_{10}H_9ClNaO_3$ $(M + Na)^+$: 235.0132, found: 235.0131. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 220 nm, 0.8 mL/min); t_R (minor enantiomer) = 8.5 min, t_R (major enantiomer) = 10.5 min, 93% ee.



3e,[2,3] colorless oil, 62% yield (ethyl acetate / petrol ether = 1/15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.07 (d, *J* = 1.7 Hz, 1H), 3.82 (s, 3H), 3.47 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.45, 135.10, 133.62, 129.08, 127.28, 57.44, 56.74, 52.77; $[\alpha]_D^{20}$ = +150.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 227 nm, 0.8 mL/min); t_R (minor enantiomer) = 8.6 min, t_R (major enantiomer) = 9.7 min, 96% ee.

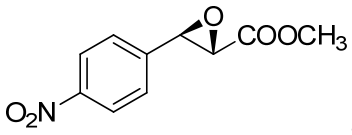


3f,[3] white solid, 69% yield (ethyl acetate / petrol ether = 1/15). mp: 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.07 (d, *J* = 1.6 Hz, 1H), 3.83 (s, 3H), 3.46 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.45, 134.14, 132.03, 127.57, 123.22, 57.52, 56.72, 52.82; $[\alpha]_D^{20}$ = +127.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 230 nm, 0.8 mL/min); t_R (minor enantiomer) = 8.6 min, t_R (major enantiomer) = 10.5 min, 96% ee.

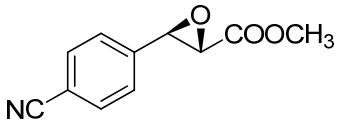


3g, white solid, 67% yield (ethyl acetate / petrol ether = 1/15). mp: 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.52 (m, 3H), 4.70 (s, 1H), 3.88 (s, 3H), 3.39 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.13, 134.66, 132.23, 129.58, 127.44, 125.07, 56.35, 55.83, 53.02; IR (KBr) ν/cm^{-1}: 2961, 1755, 1745, 1578, 1526, 1443, 1347, 1210, 907; $[\alpha]_D^{20}$ = +149.5 (c = 1.0, $CHCl_3$); HRMS (ESI) calcd for $C_{10}H_9NNaO_5$ $(M + Na)^+$: 246.0373, found: 246.0380. The enantiomeric excess was determined by HPLC with a Chiralcel

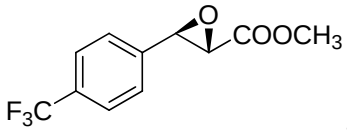
AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 254 nm, 0.8 mL/min); t_R (minor enantiomer) = 13.2 min, t_R (major enantiomer) = 45.2 min, 97% ee.



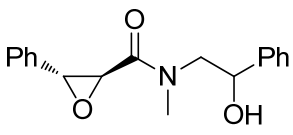
3h,[4] white solid, 63% yield (ethyl acetate / petrol ether = 1/5). mp: 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 4.22 (d, *J* = 1.5 Hz, 1H), 3.86 (s, 3H), 3.50 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.88, 148.51, 142.28, 126.81, 124.13, 56.98, 56.90, 53.02; $[\alpha]_D^{20}$ = +151.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 254 nm, 0.8 mL/min); t_R (minor enantiomer) = 20.2 min, t_R (major enantiomer) = 22.6 min, 99% ee.



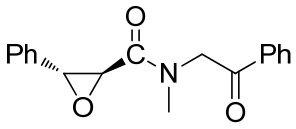
3i, white solid, 73% yield (ethyl acetate / petrol ether = 1/15). mp: 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 4.15 (d, *J* = 1.5 Hz, 1H), 3.83 (s, 3H), 3.46 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.91, 140.36, 132.61, 126.58, 118.38, 112.96, 57.03, 56.87, 52.92; IR (KBr) ν/cm^{-1}: 2228, 1754, 1611, 1446, 1345, 1214, 992, 846, 810; $[\alpha]_D^{20}$ = +152.6 (c = 1.0, $CHCl_3$); HRMS (ESI) calcd for $C_{11}H_8NO_3$ (M - H)$^-$: 202.0524, found:202.0510. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 230 nm, 0.8 mL/min); t_R (minor enantiomer) = 18.6 min, t_R (major enantiomer) = 20.7 min, 95% ee.



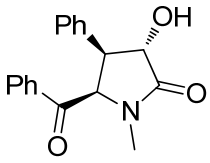
3j,[2] white solid, 63% yield (ethyl acetate / petrol ether = 1/15). mp: 52-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 4.17 (d, *J* = 1.6 Hz, 1H), 3.85 (s, 3H), 3.50 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.23, 139.14, 131.82 – 130.88 (m),126.27, 125.83 (q, *J* = 3.7 Hz), 125.34, 122.64, 57.26, 56.83, 52.87; $[\alpha]_D^{20}$ = +123.9 (c = 0.9, $CHCl_3$); The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 230 nm, 0.8 mL/min); t_R (minor enantiomer) = 8.8 min, t_R (major enantiomer) = 9.2 min, 96% ee.



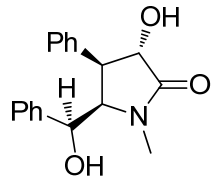
7a,[1] white solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 10H), 5.05 – 4.91 (m, 1H), 4.08 – 4.03 (m, 1H), 3.83 – 3.44 (m, 4H), 3.07, 2.98 (2s, 3H).



7b,[1] pale yellow oil, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.18 (m, 10H), 5.01 – 4.76 (m, 2H), 4.10, 4.00 (2d, *J* = 1.7 Hz, 1H), 3.78, 3.48 (2d, *J* = 1.8 Hz, 1H), 3.18, 3.05 (2s, 3H).



7c,[1] white solid, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.12 – 6.98 (m, 5H), 5.39 (d, *J* = 8.9 Hz, 1H), 4.91 (d, *J* = 9.8 Hz, 1H), 3.86 (t, *J* = 9.3 Hz, 1H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.41, 175.19, 136.46, 134.31, 133.62, 128.69, 128.65, 128.46, 128.26, 127.98, 72.04, 65.08, 51.52, 29.73.



. **7d**, white solid, 28% overall yield (CH_3OH /CH_2Cl_2 = 1/10). mp: 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 8H), 6.80 (d, *J* = 7.2 Hz, 2H), 4.81 (d, *J* = 3.9 Hz, 1H), 4.22 (dd, *J* = 8.3, 3.9 Hz, 1H), 4.05 (d, *J* = 10.9 Hz, 1H), 3.74 (dd, *J* = 10.6, 8.5 Hz, 1H), 2.97 (s, 3H), 2.37 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.20, 139.24, 135.04, 128.82, 128.50, 128.42, 127.55, 127.37, 74.06, 69.46, 66.38, 50.39, 31.59; IR (KBr) ν/cm^{-1}: 2957, 1743, 1557, 1438, 1368, 1293, 1121; $[\alpha]_D^{20}$ = -128.0 (c = 1.0, CH_3OH); HRMS (ESI) calcd for $C_{18}H_{20}NO_3$ $(M + H)^+$: 298.1438, found: 298.1436. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (4.6 mm × 25 cm) (*n*-hexane/*i*-PrOH = 90/10, λ = 220 nm, 0.8 mL/min); t_R (minor enantiomer) =41.1 min, t_R (major enantiomer) = 49.7 min, >99% ee.

References

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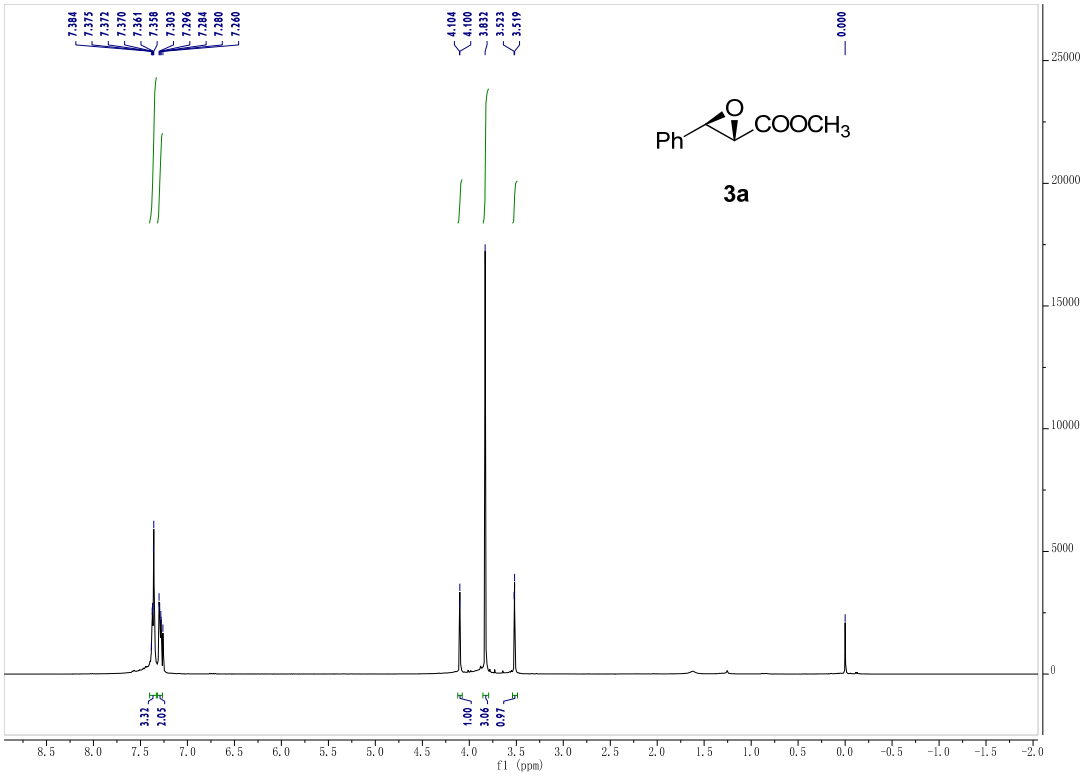
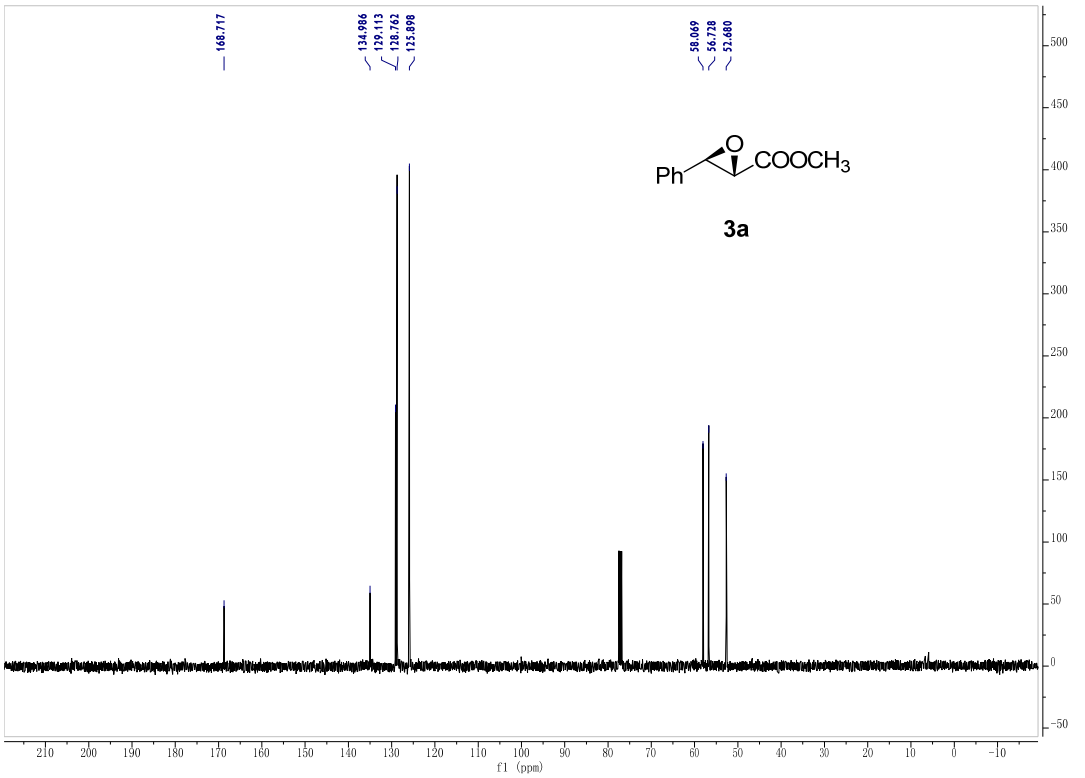
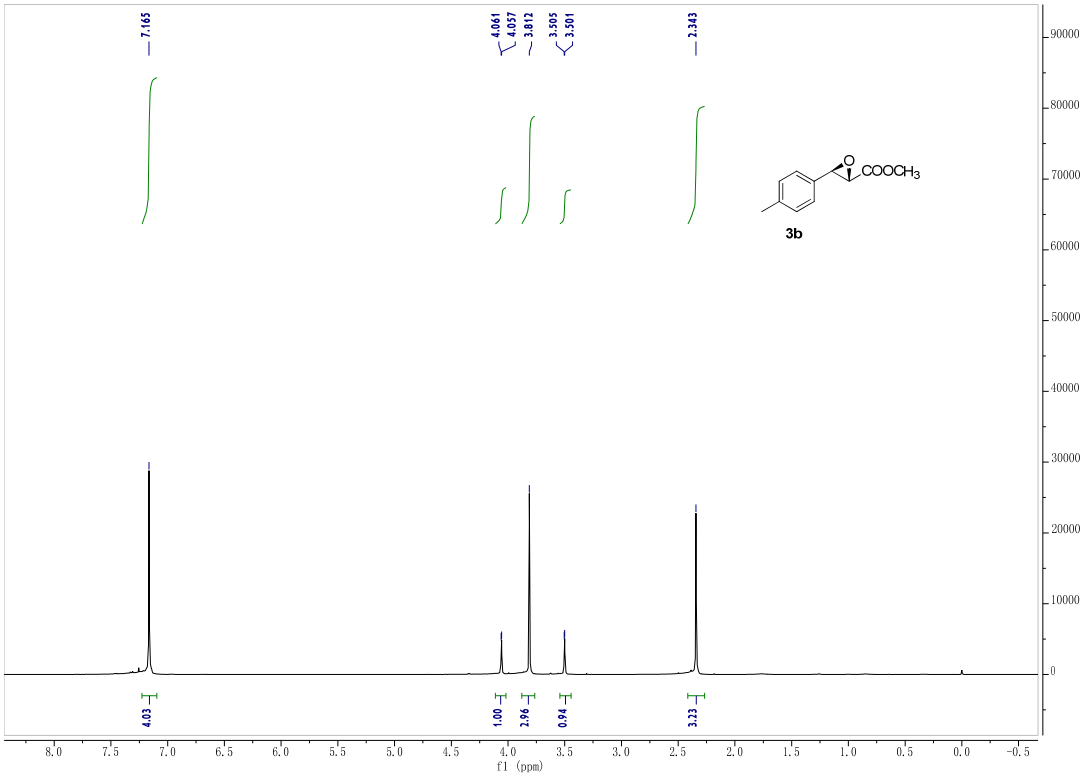
(C) NMR spectra of α, β-epoxy esters and (-)-clausenamide



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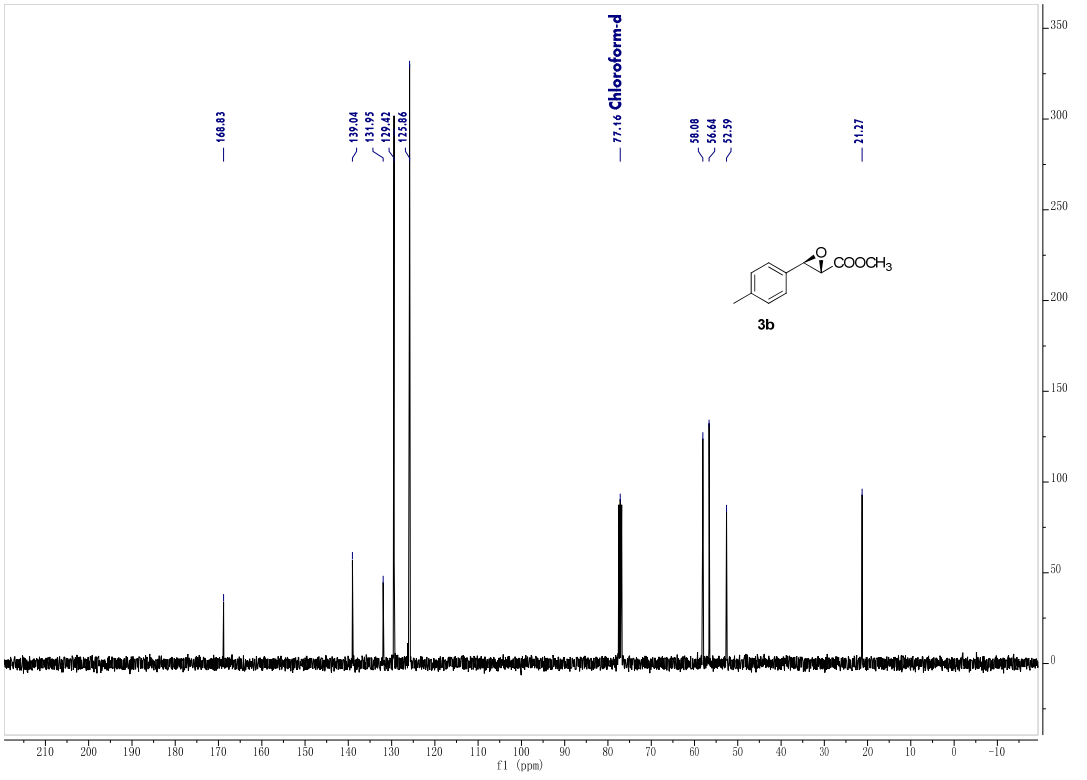
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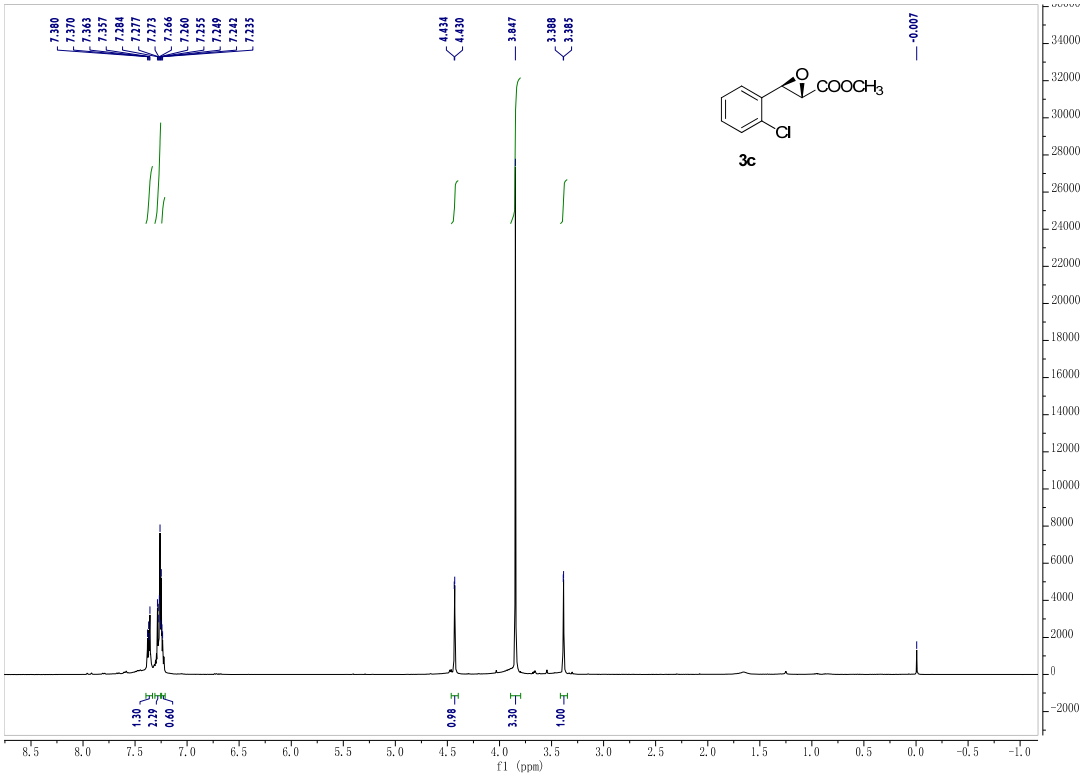
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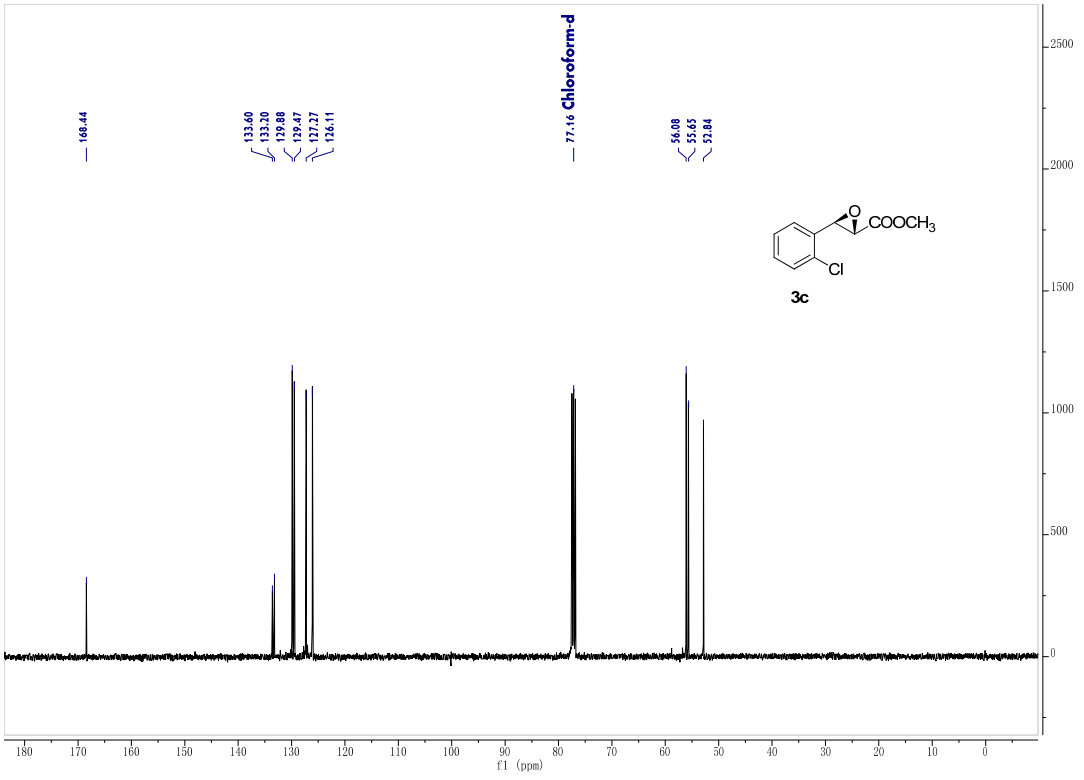
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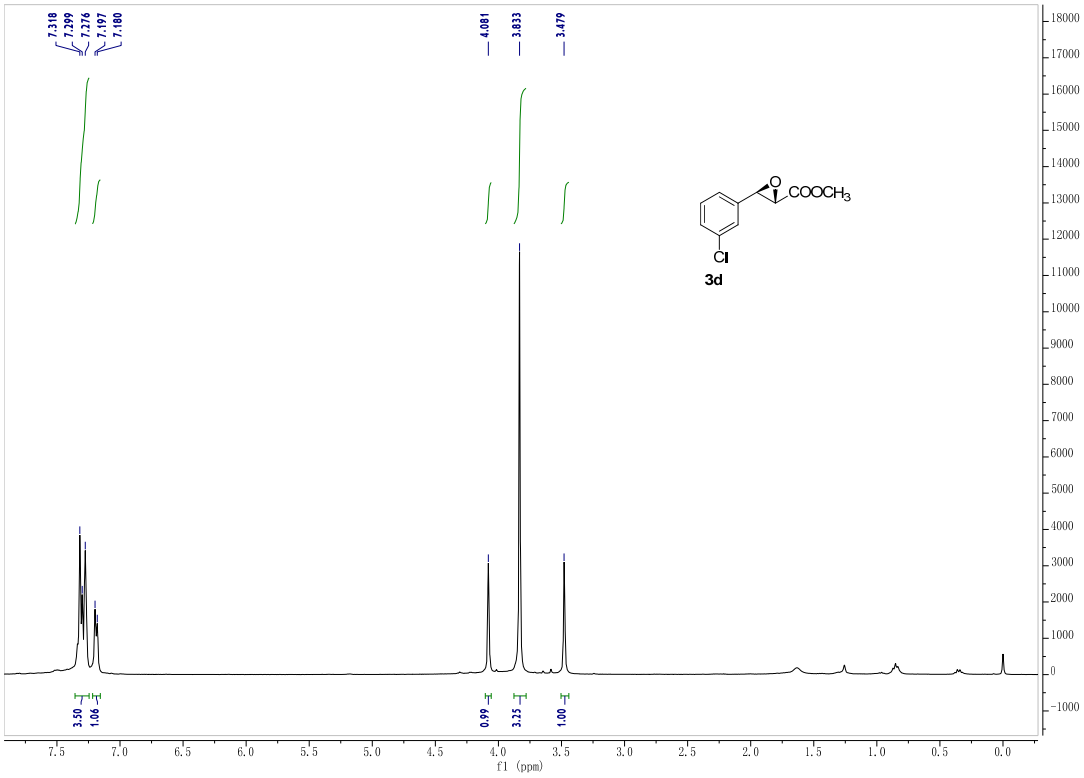
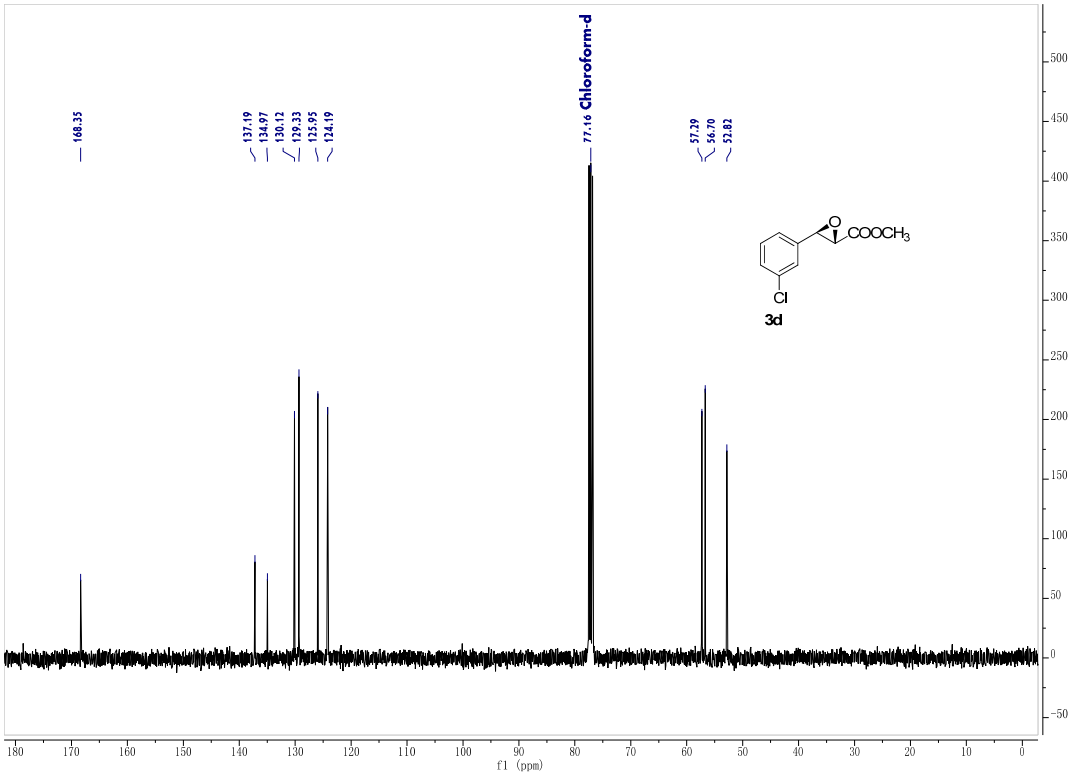
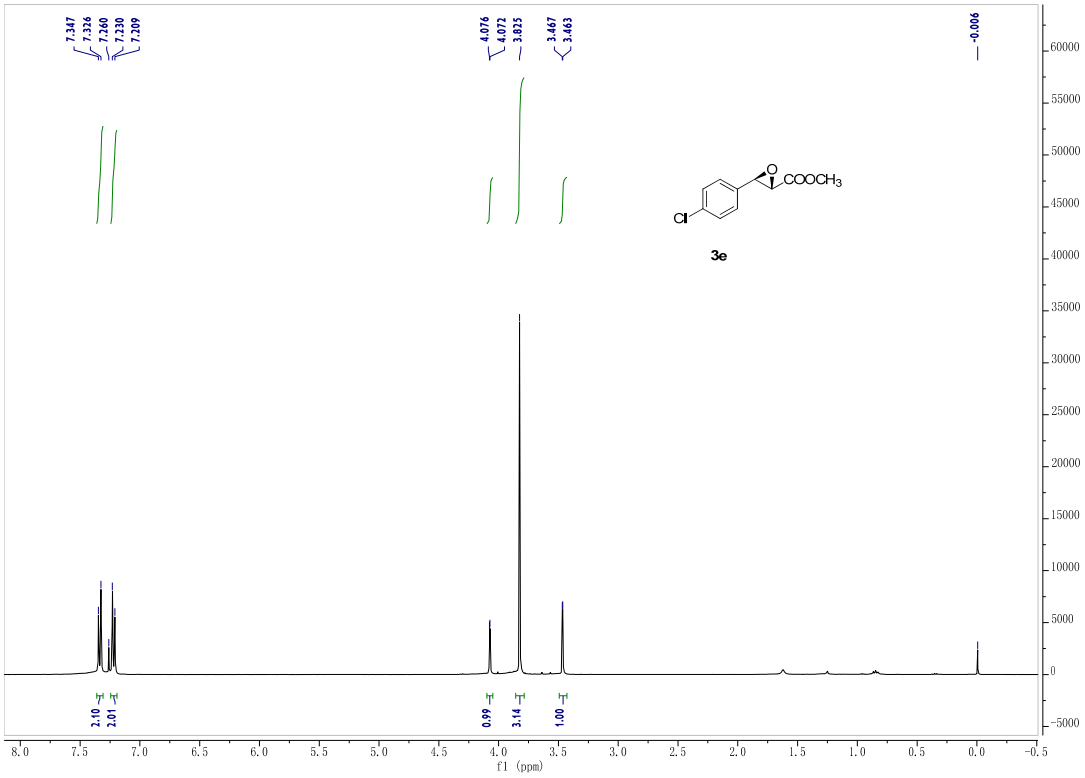
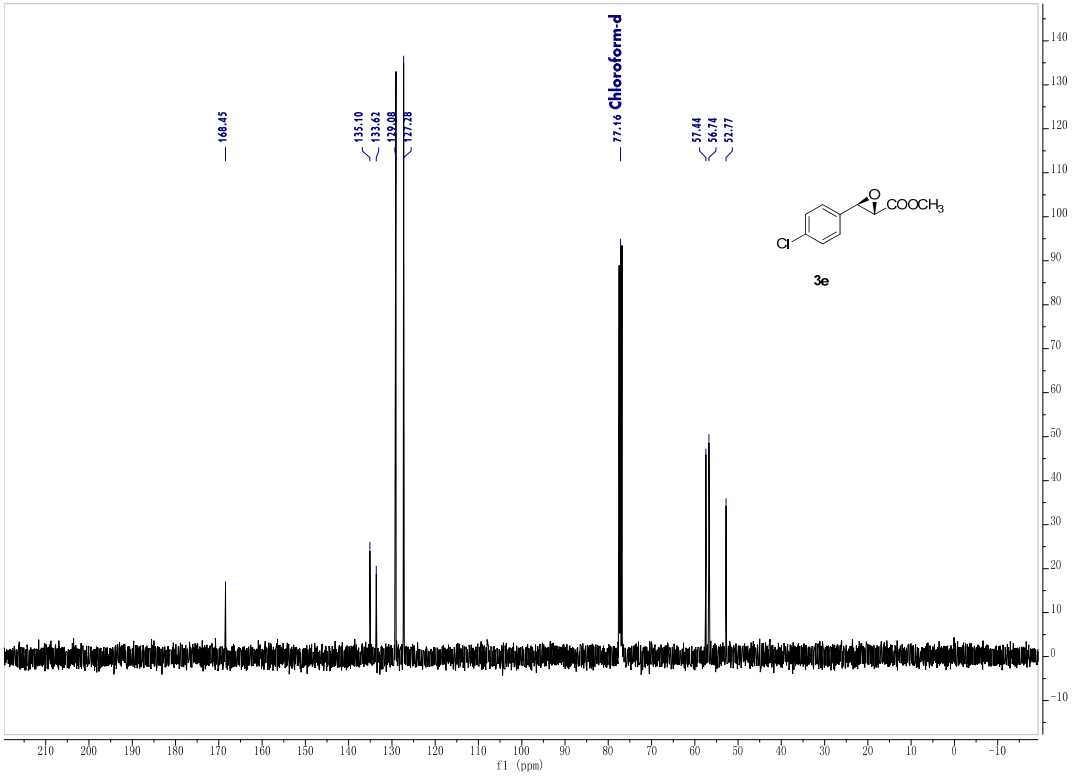
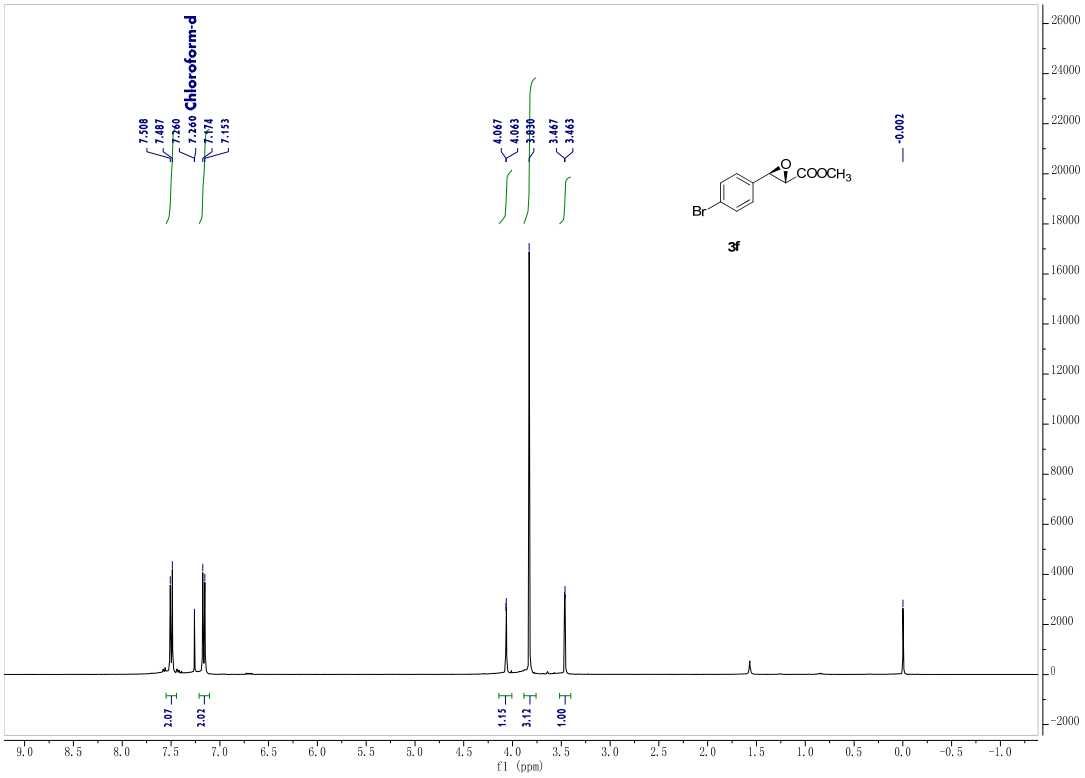
3c
f1 (ppm)

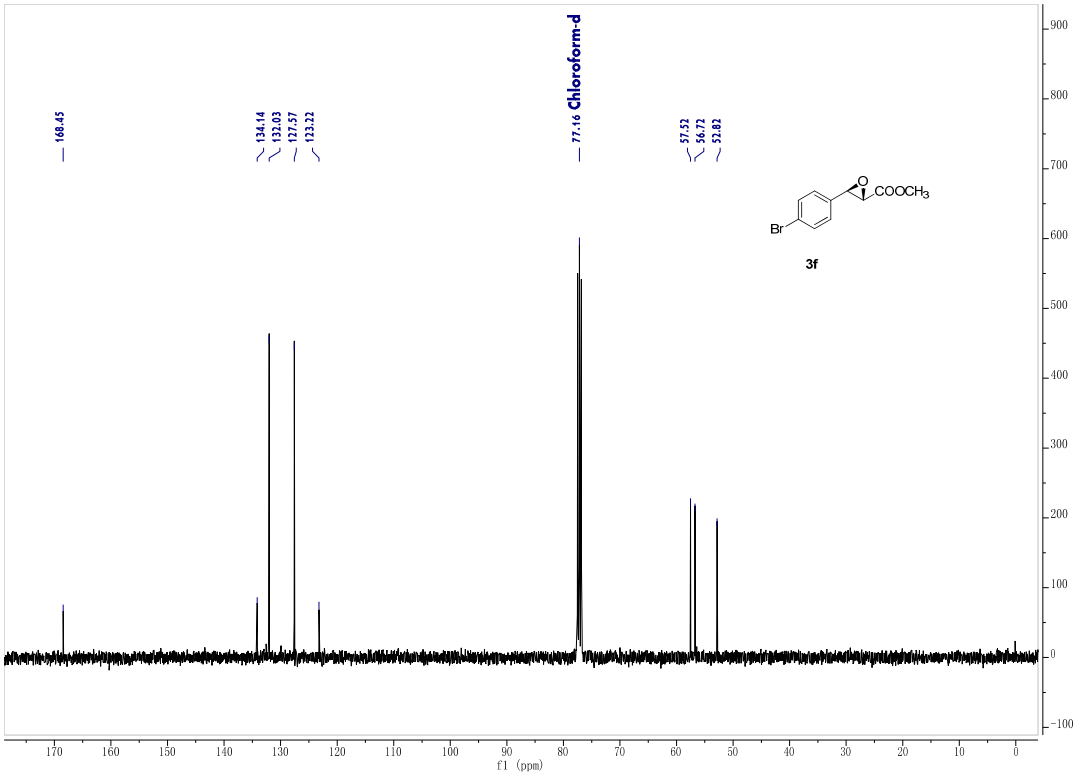

7.318
7.299
7.276
7.197
7.180
4.081
3.833
3.479
3.50
1.06
0.99
3.25
1.00
f1 (ppm)
3d

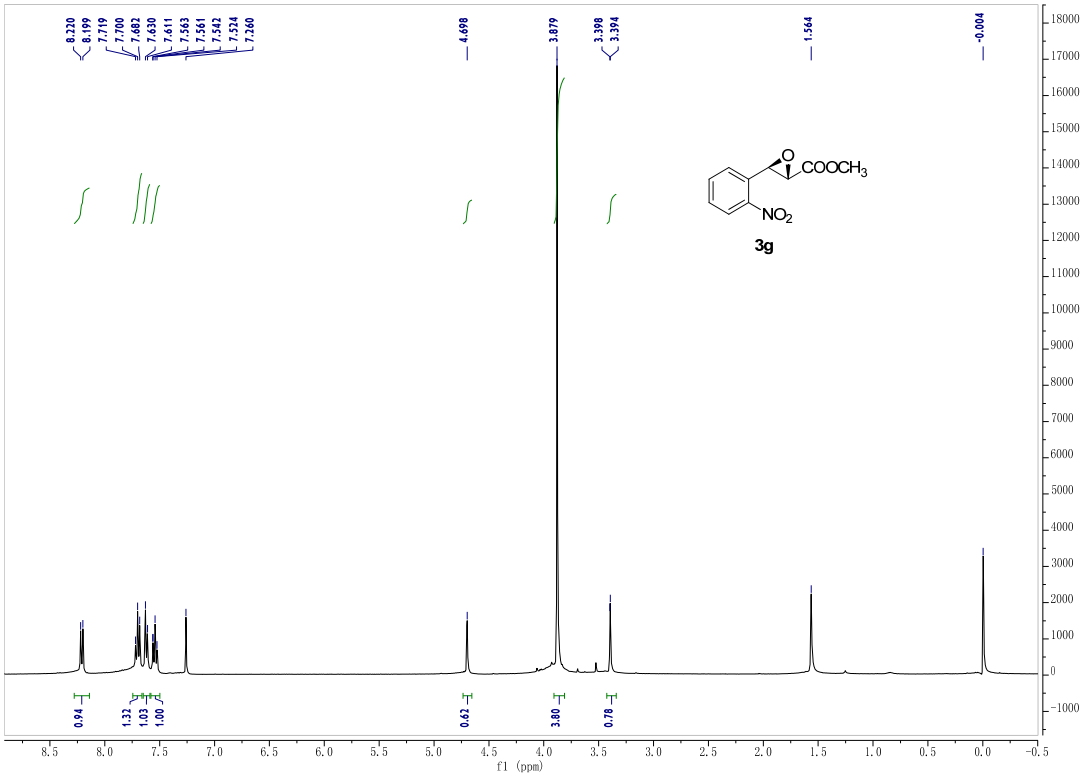

168.35
137.19
134.97
130.12
129.33
125.95
124.19
77.16 Chloroform-d
57.29
56.70
51.82
f1 (ppm)
3d

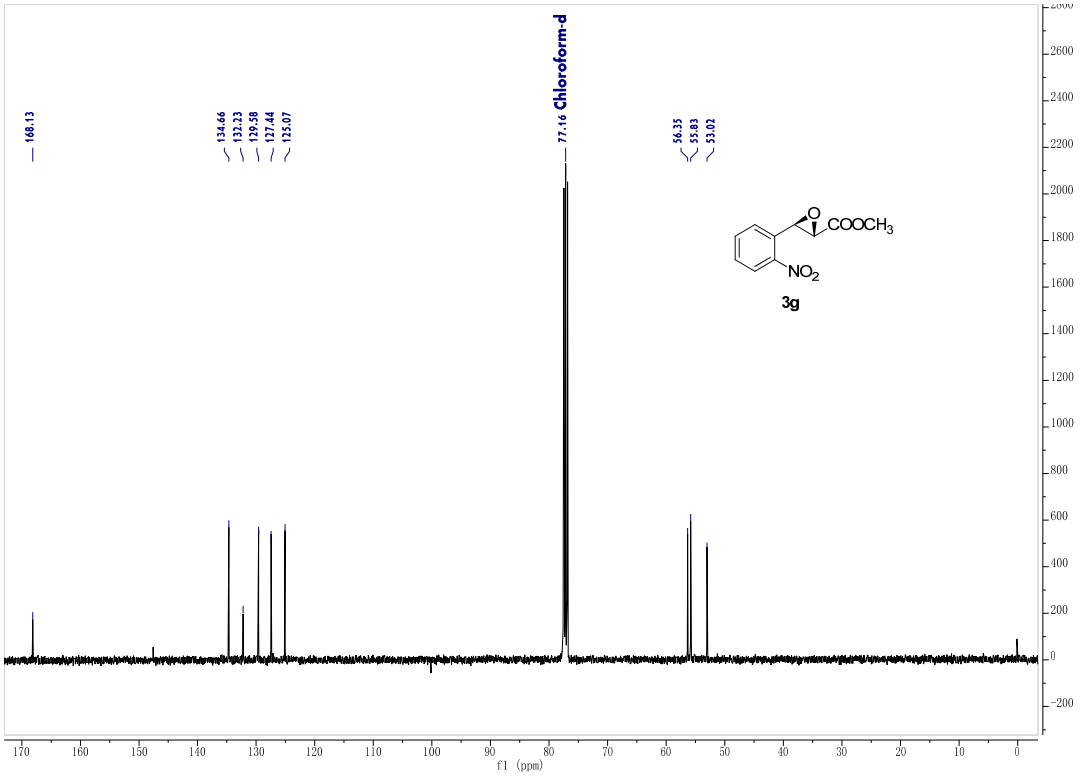

7.347
7.326
7.260
7.230
7.209
4.076
4.072
3.825
3.467
3.463
-0.006
COOCH3
Cl
3e
2.10
2.01
0.99
3.14
1.00
f1 (ppm)

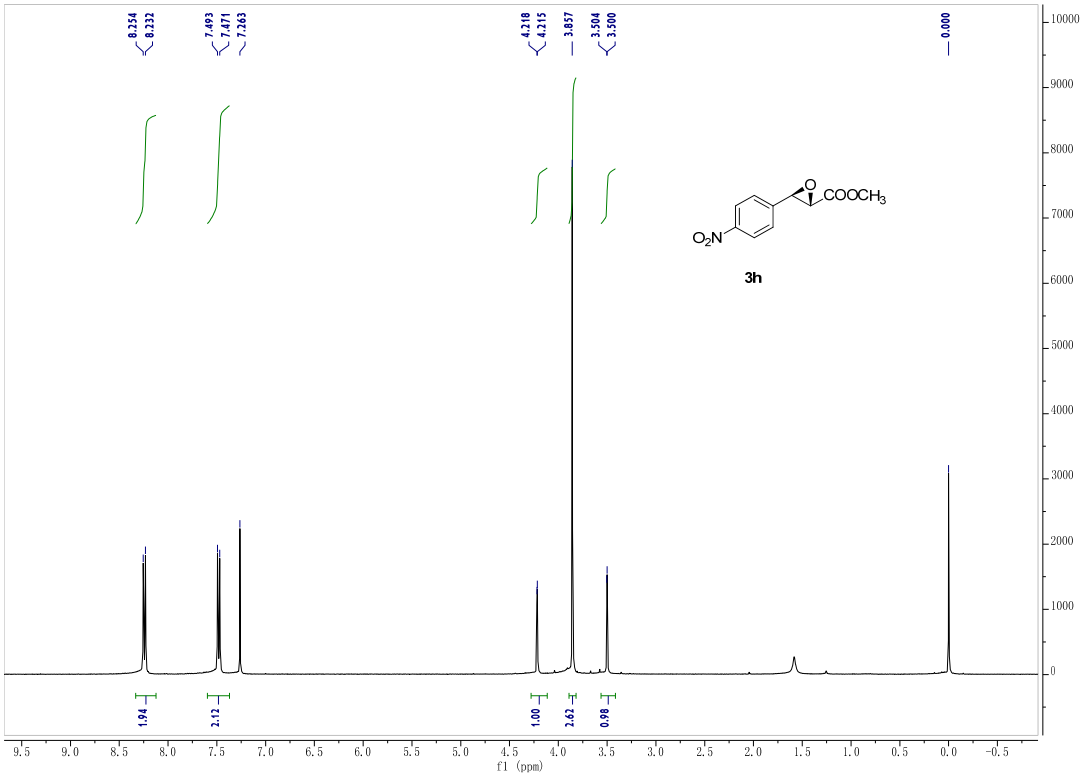

168.45
135.10
133.62
129.08
127.28
77.16 Chloroform-d
57.44
56.74
53.77
COOCH3
Cl
3e
f1 (ppm)

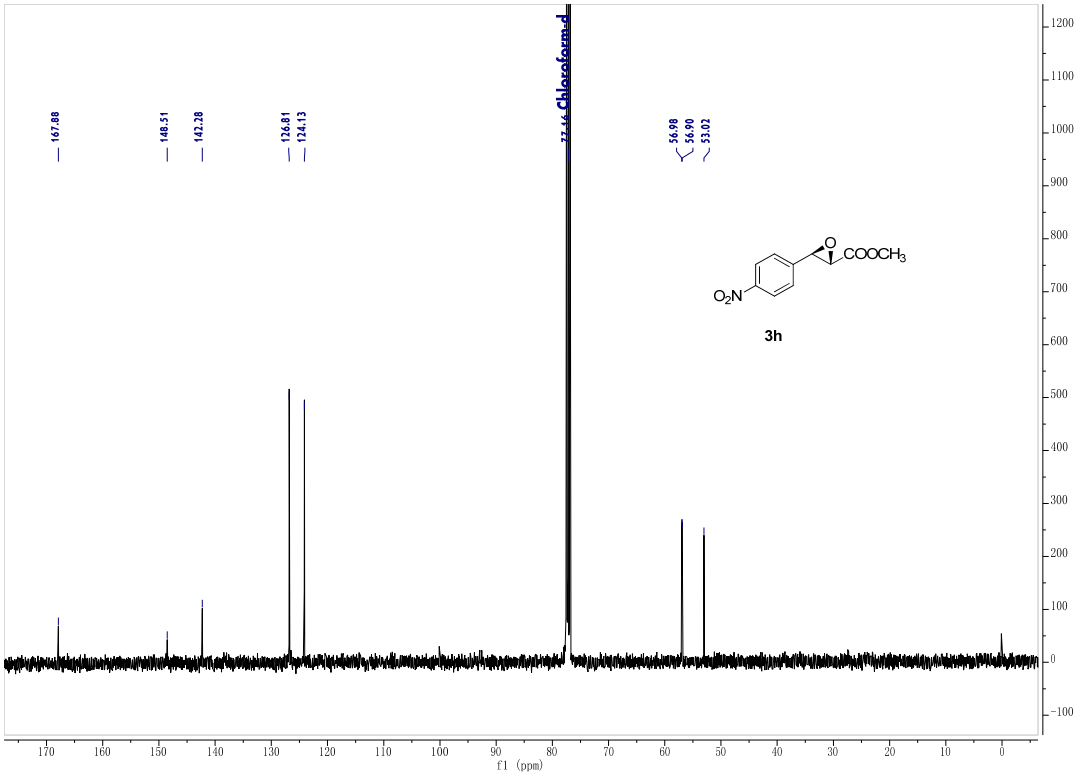

7.508
7.487
Chloroform-d
7.260
7.174
7.153
4.067
4.063
3.830
3.467
3.463
-0.002
COOCH3
Br
3f
2.07
2.02
1.15
3.12
1.00
f1 (ppm)

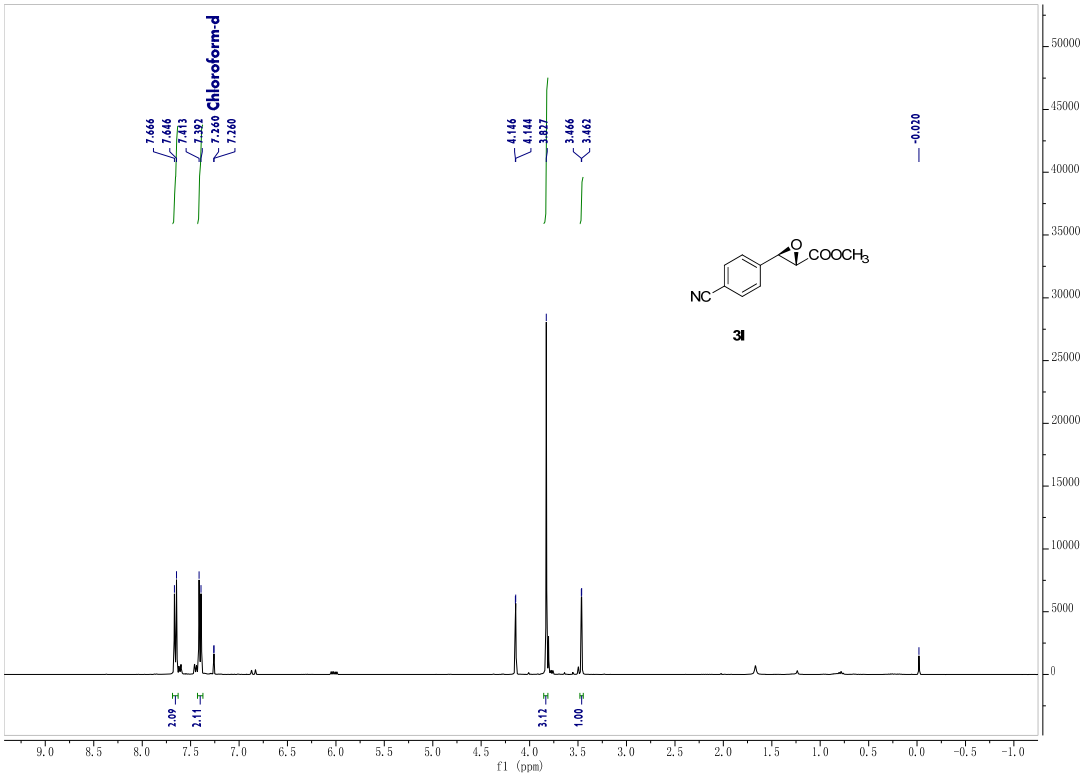

168.45
134.14
132.03
127.57
123.22
Chloroform-d
77.16
57.52
56.72
52.82
COOCH3
Br
3f
f1 (ppm)

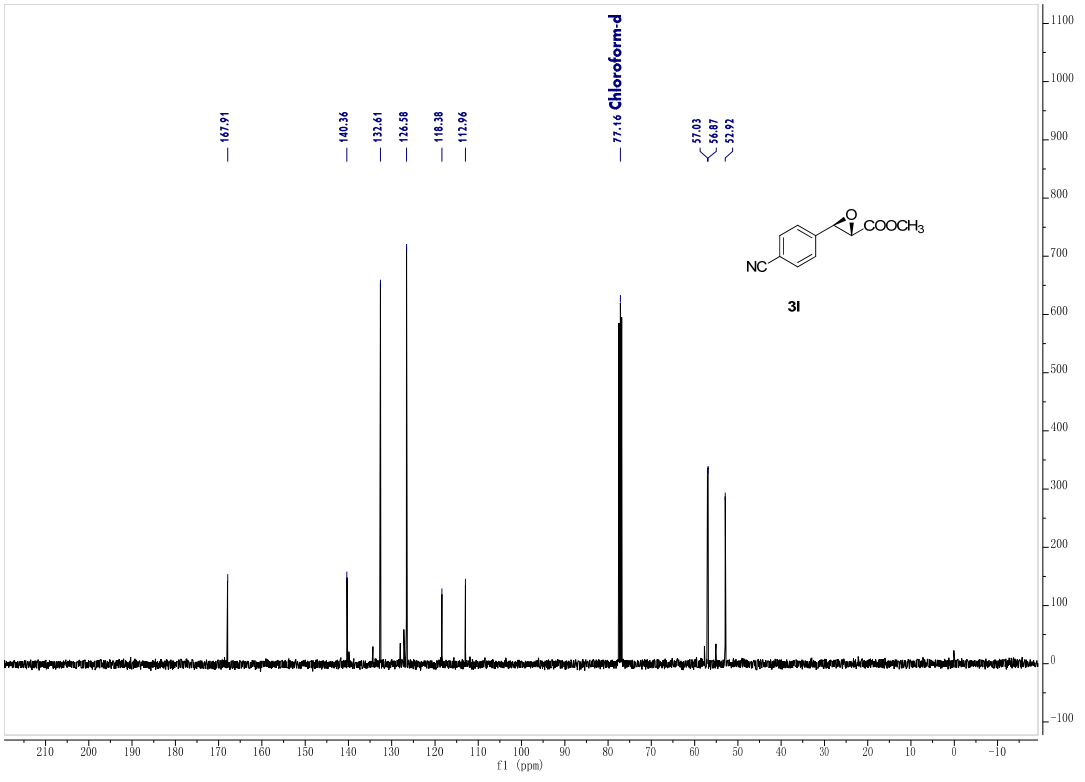

8.220
8.199
7.719
7.700
7.682
7.630
7.611
7.563
7.561
7.542
7.524
7.260
4.698
3.879
3.398
3.394
1.564
-0.004
0.94
1.32
1.03
1.00
0.62
3.80
0.78
f1 (ppm)
COOCH3
NO2
3g

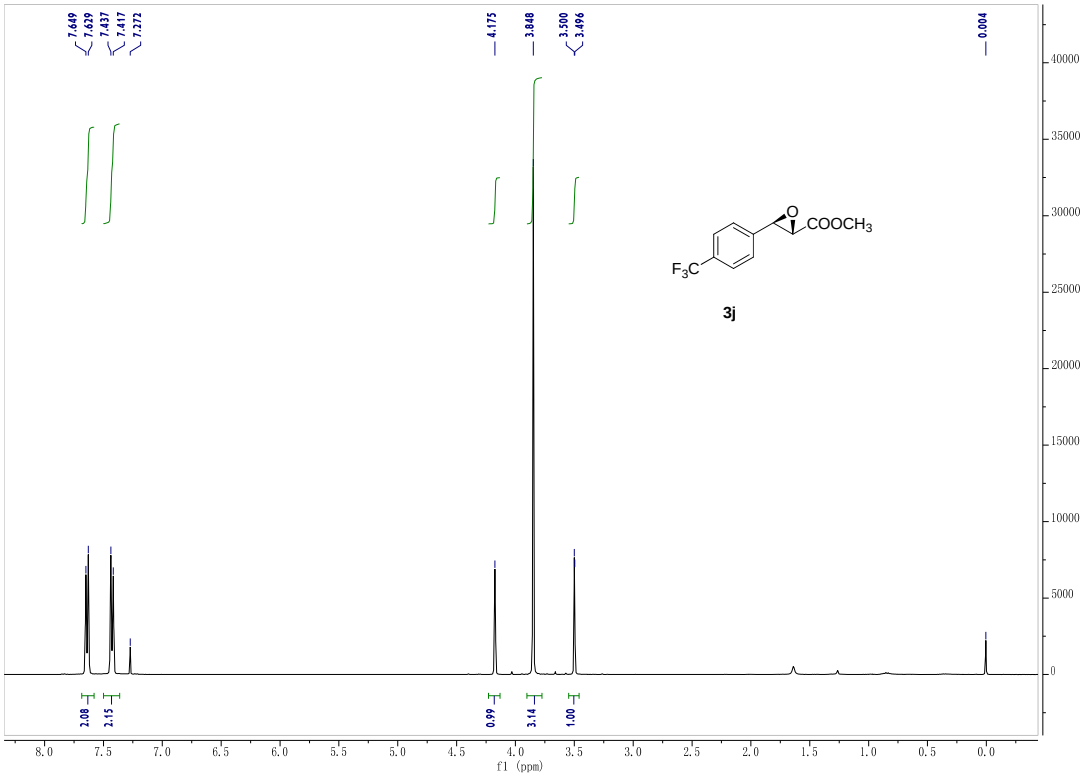

168.13
134.66
132.23
129.58
127.44
125.07
77.16 Chloroform-d
56.35
55.83
53.02
f1 (ppm)
COOCH3
NO2
3g

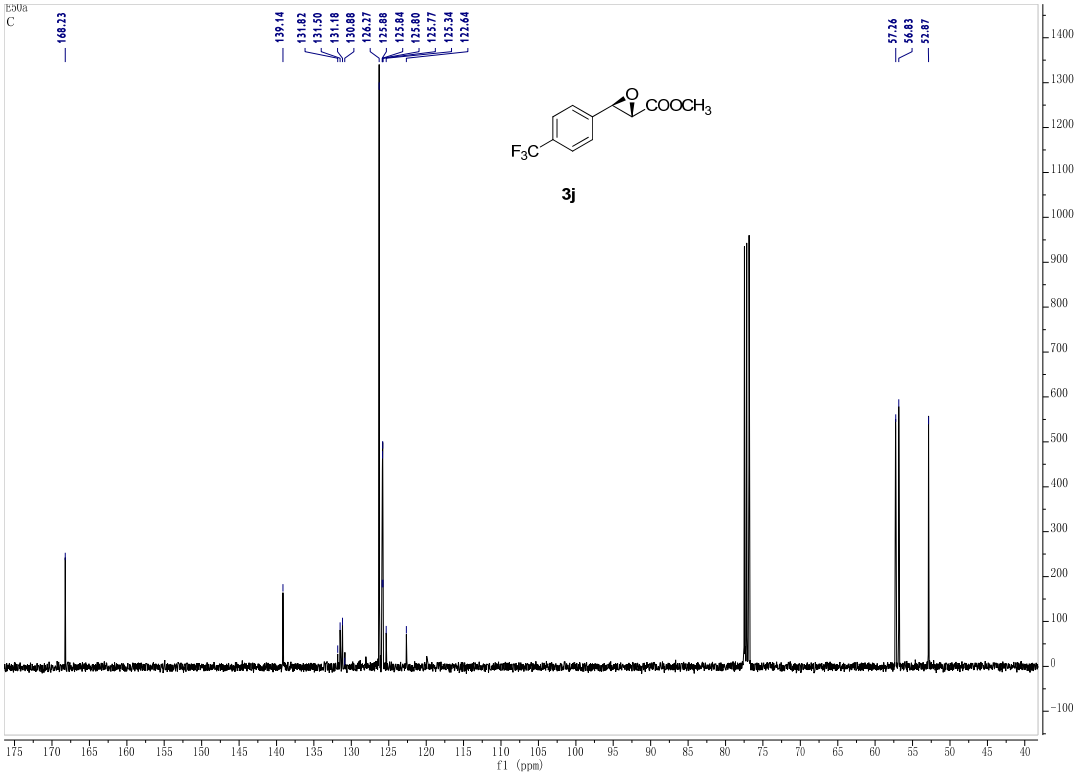

8.354
8.332
7.493
7.471
7.263
4.218
4.215
3.857
3.504
3.500
0.000
1.94
2.12
1.00
2.62
0.98
f1 (ppm)
3h

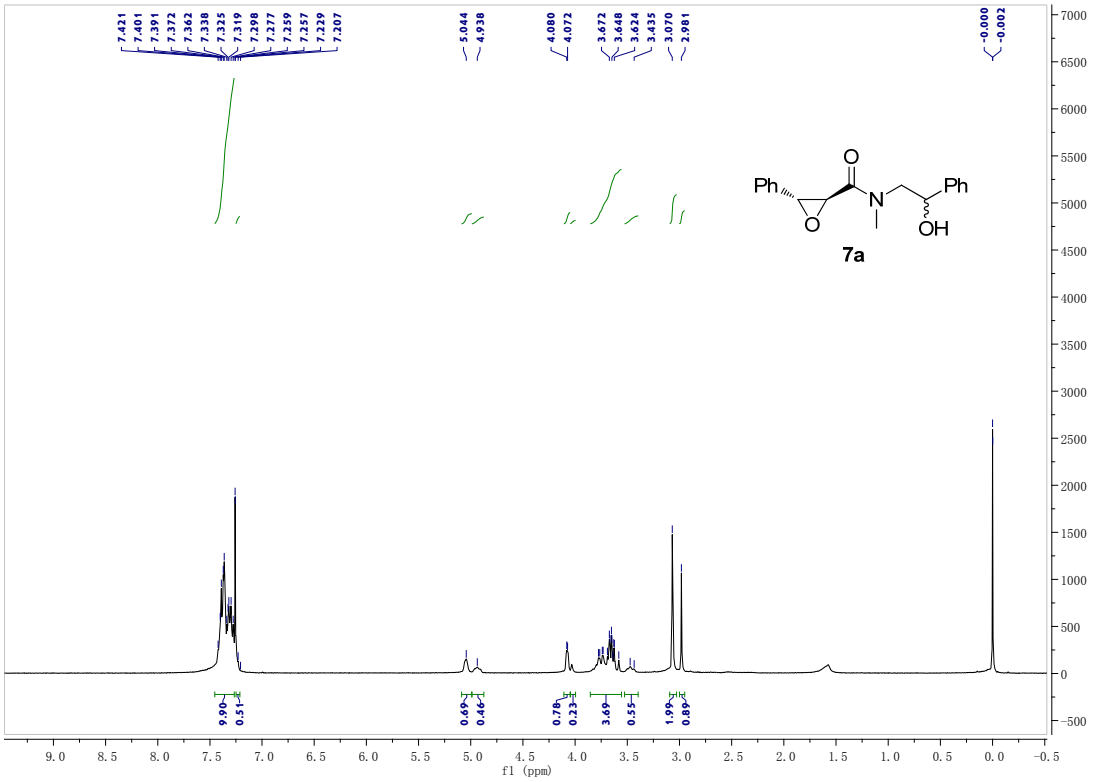

167.88
148.51
142.28
126.81
124.13
77.16 Chloroform-d
56.98
56.90
53.02
f1 (ppm)
3h

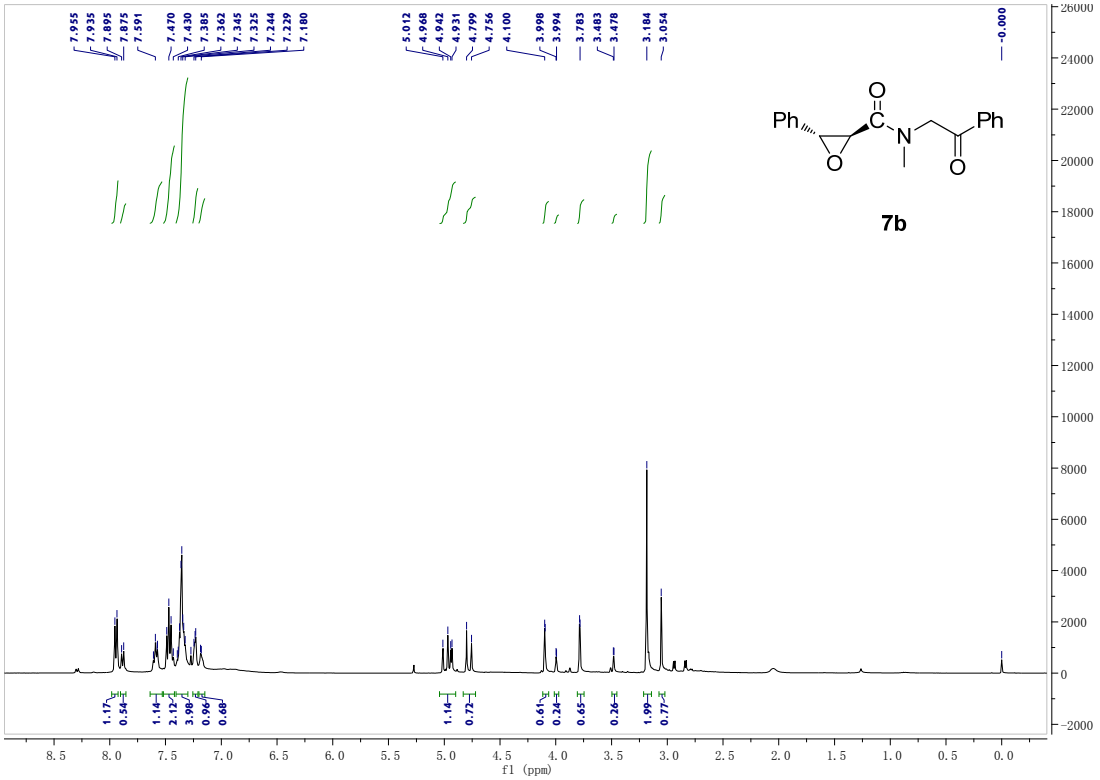

7.666
7.646
7.413
7.392
Chloroform-d
7.260
7.260
4.146
4.144
3.827
3.466
3.462
-0.020
O
COOCH3
NC
3l
2.09
2.11
3.12
1.00
f1 (ppm)

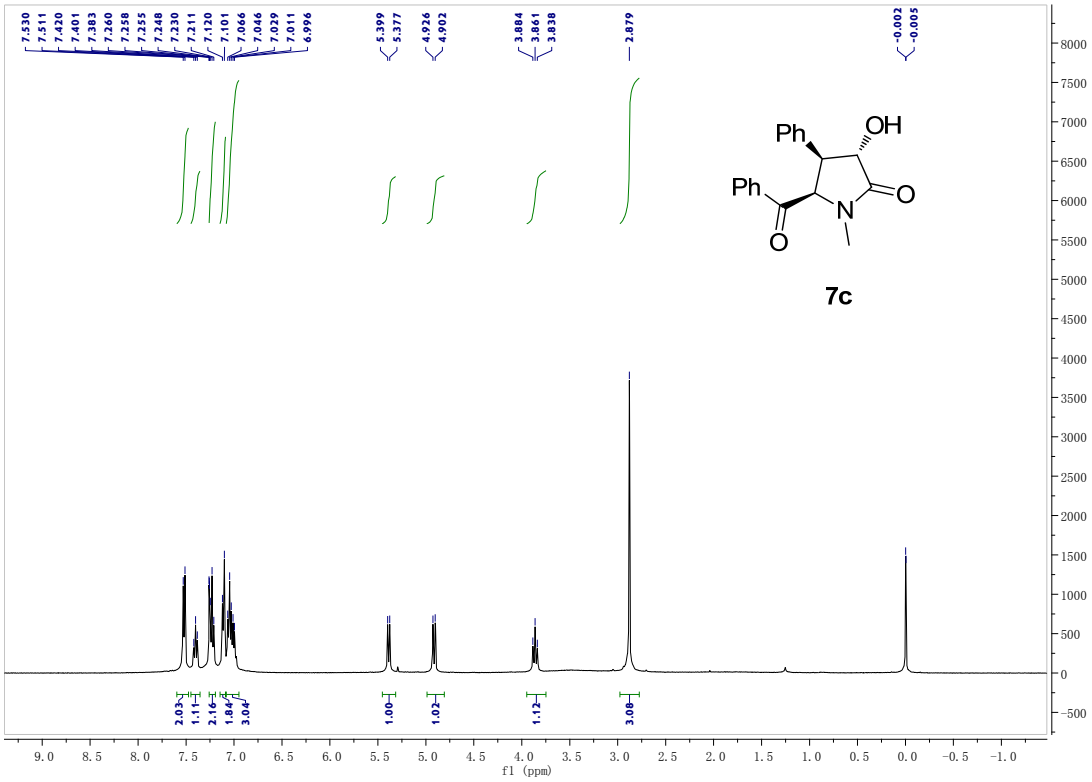

167.91
140.36
132.61
126.58
118.38
112.96
Chloroform-d
77.16
57.03
56.87
53.92
O
COOCH3
NC
3l
f1 (ppm)


7.649
7.629
7.437
7.417
7.272
4.175
3.848
3.500
3.496
0.004
2.08
2.15
0.99
3.14
1.00
f1 (ppm)
COOCH3
F3C
3j

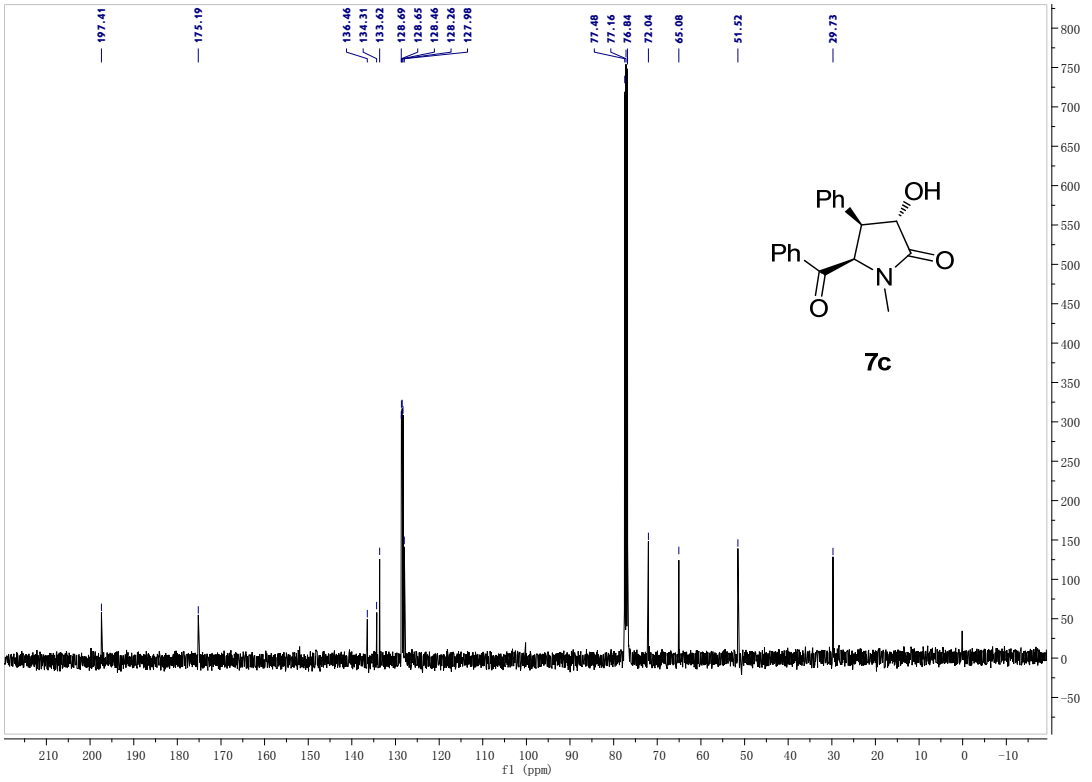

168.23
139.14
131.82
131.50
131.18
130.88
126.27
125.88
125.84
125.80
125.77
125.34
122.64
57.26
56.83
52.87
f1 (ppm)
COOCH3
F3C
3j


7.421
7.401
7.391
7.372
7.362
7.338
7.325
7.319
7.298
7.277
7.259
7.257
7.229
7.207
5.044
4.938
4.080
4.072
3.672
3.648
3.624
3.435
3.070
2.981
-0.000
-0.002
Ph
O
N
Ph
OH
O
7a
f1 (ppm)

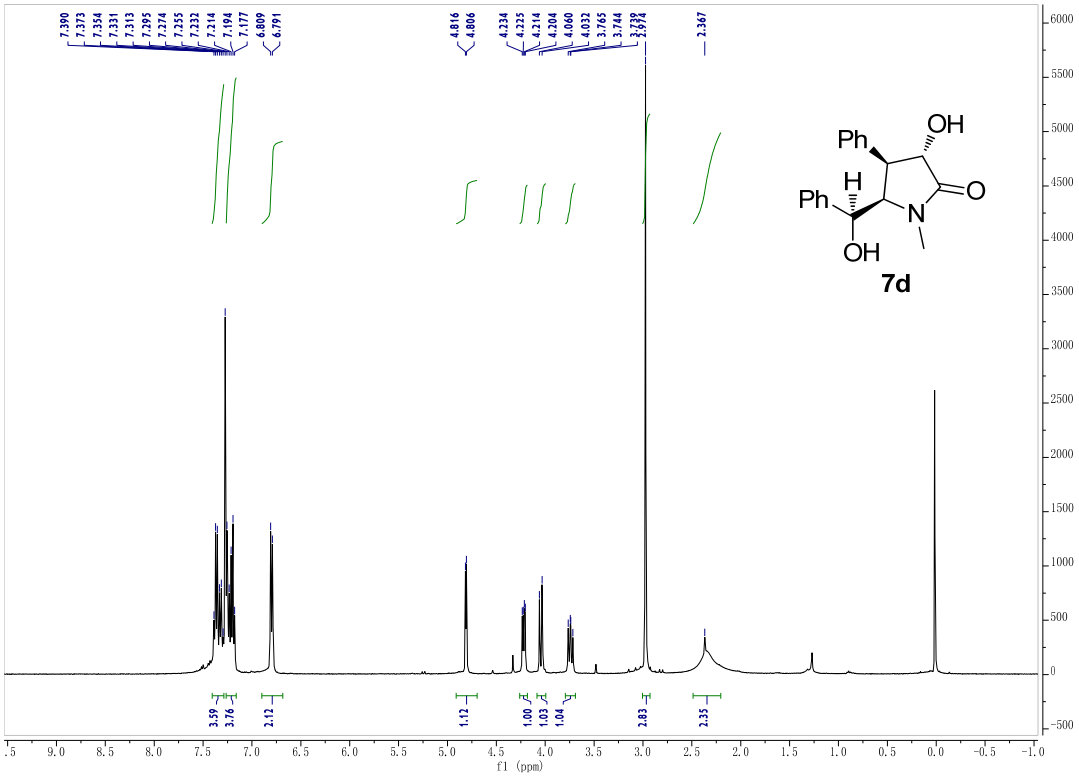

7.955
7.935
7.895
7.875
7.591
7.470
7.430
7.385
7.362
7.345
7.335
7.244
7.229
7.180
5.012
4.968
4.942
4.931
4.799
4.756
4.100
3.998
3.994
3.783
3.483
3.478
3.184
3.054
-0.000
Ph
O
C
N
Ph
O
O
7b
f1 (ppm)

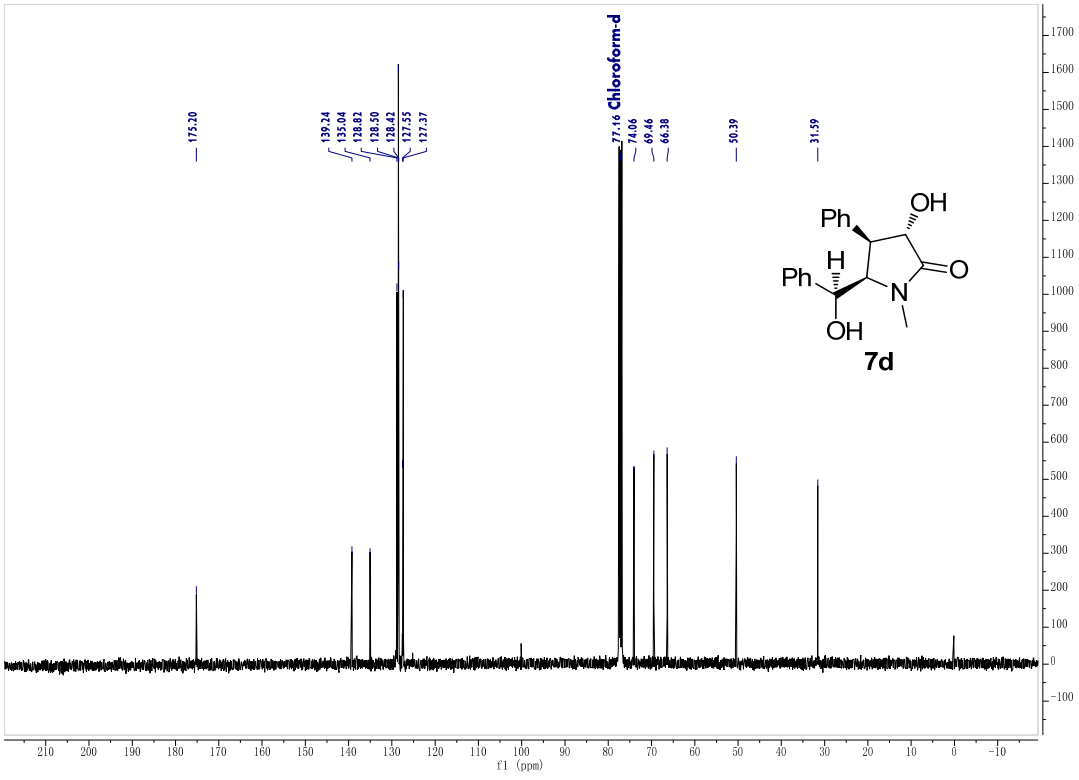

7.530
7.511
7.420
7.401
7.383
7.260
7.258
7.255
7.248
7.230
7.211
7.120
7.101
7.066
7.046
7.029
7.011
6.996
5.399
5.377
4.926
4.902
3.884
3.861
3.838
2.879
-0.002
-0.005
Ph
OH
Ph
O
N
O
2.03
1.11
2.16
1.84
3.04
1.00
1.02
1.12
3.00
f1 (ppm)

7c

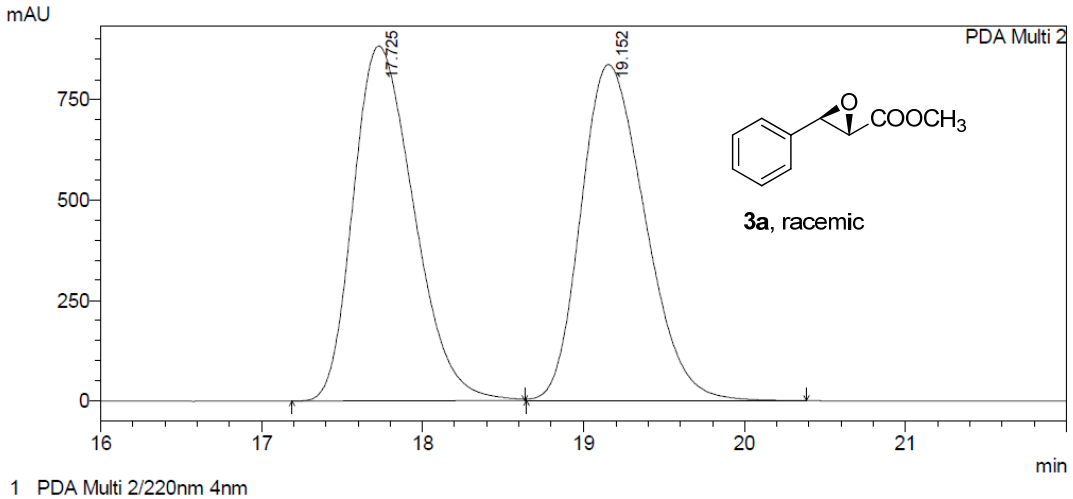

197.41
175.19
136.46
134.31
133.62
128.69
128.65
128.46
128.26
127.98
77.48
77.16
76.84
72.04
65.08
51.52
29.73
Ph
OH
Ph
O
N
O
f1 (ppm)

7c


7.390
7.373
7.354
7.331
7.313
7.295
7.274
7.255
7.232
7.214
7.194
7.177
6.809
6.791
4.816
4.806
4.234
4.225
4.214
4.204
4.060
4.032
3.765
3.744
2.367
OH
Ph
H
Ph
N
O
OH
7d
3.59
3.76
2.12
1.12
1.00
1.03
1.04
2.83
2.35
f1 (ppm)


175.20
139.24
135.04
128.82
128.50
128.42
127.55
127.37
77.16 Chloroform-d
74.06
69.46
66.38
50.39
31.59
OH
Ph
H
Ph
N
O
OH
7d
f1 (ppm)

(D) HPLC chromatogram of α, β-epoxy esters and (-)-clausenamide

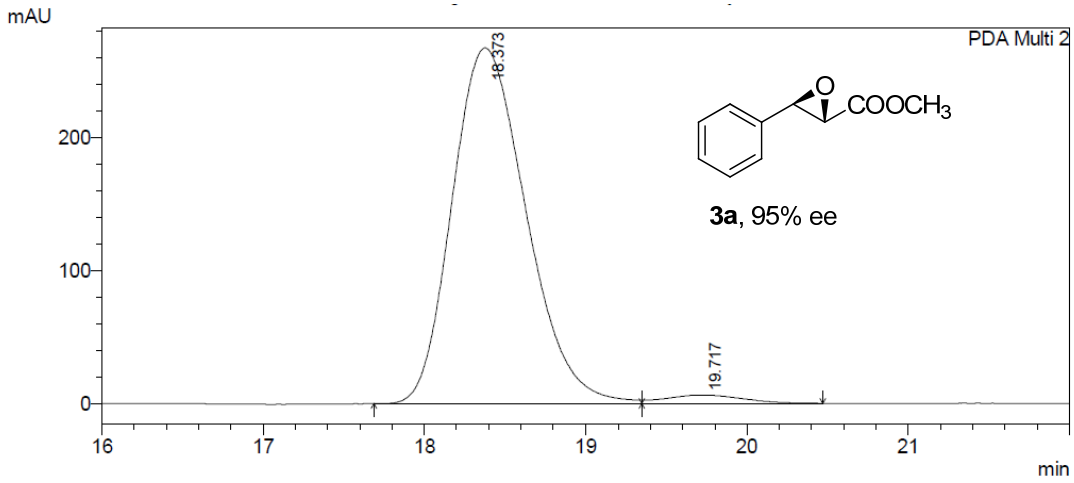


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.725	23136327	883846	50.003	51.392
2	19.152	23133938	835962	49.997	48.608
Total		46270265	1719808	100.000	100.000

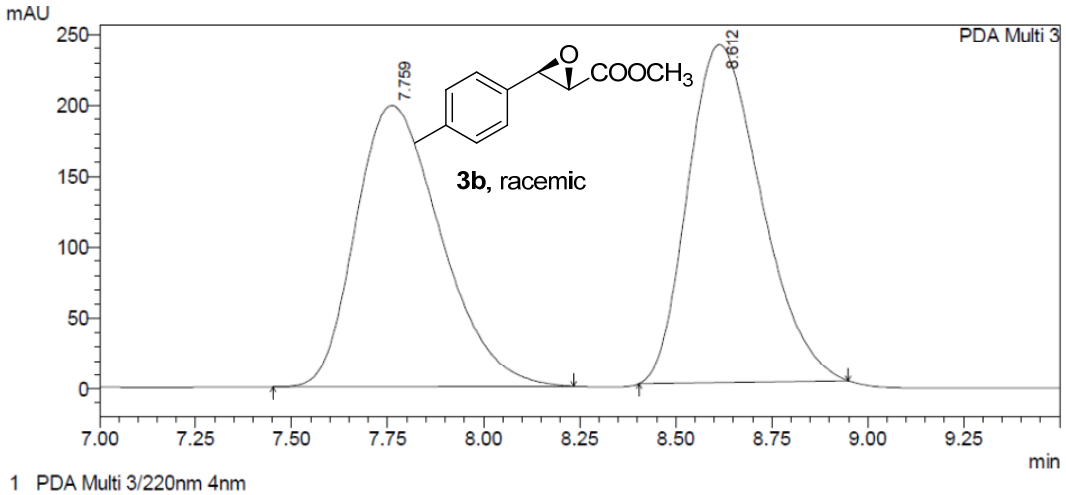


1 PDA Multi 2/220nm 4nm

PeakTable

PDA Ch2 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.373	8528748	267388	97.563	97.661
2	19.717	212996	6403	2.437	2.339
Total		8741744	273792	100.000	100.000

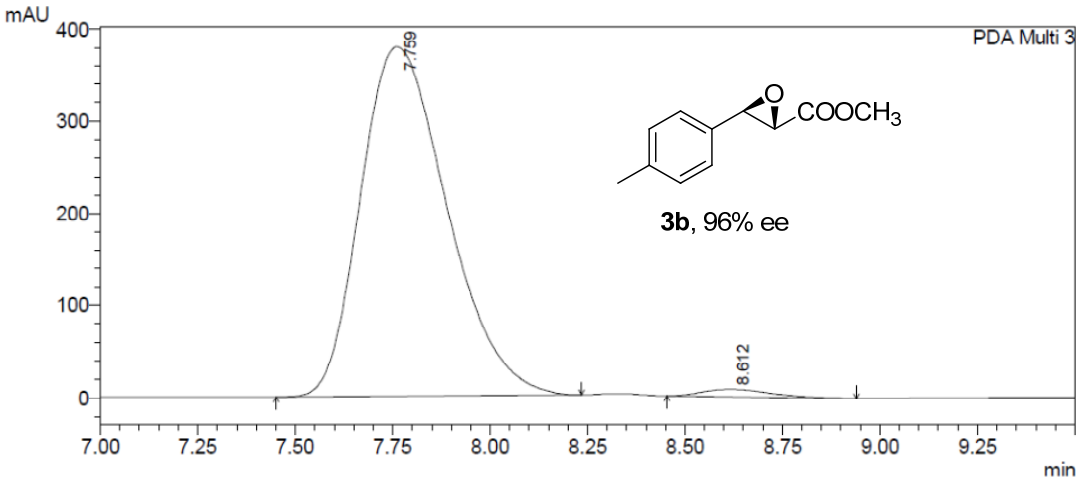


1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.759	3058813	198245	49.072	45.464
2	8.612	3174463	237802	50.928	54.536
Total		6233276	436047	100.000	100.000

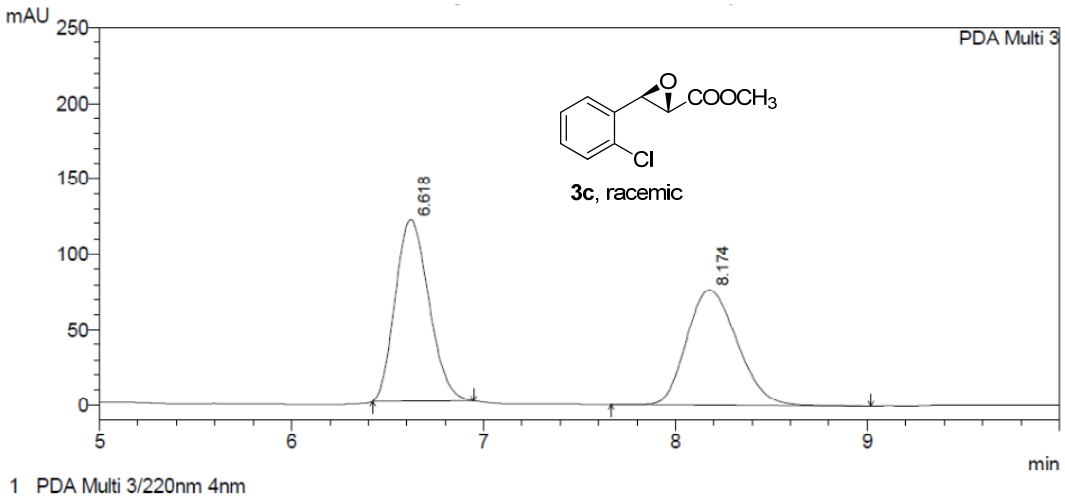


1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.759	5835115	379186	98.336	97.926
2	8.612	98729	8033	1.664	2.074
Total		5933844	387219	100.000	100.000

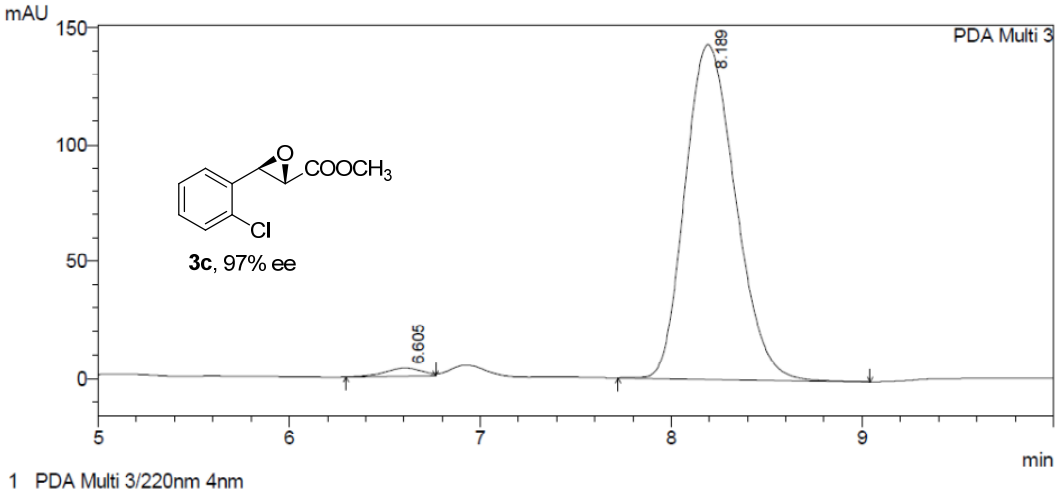


1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.618	1461381	119496	51.161	61.078
2	8.174	1395045	76150	48.839	38.922
Total		2856426	195646	100.000	100.000

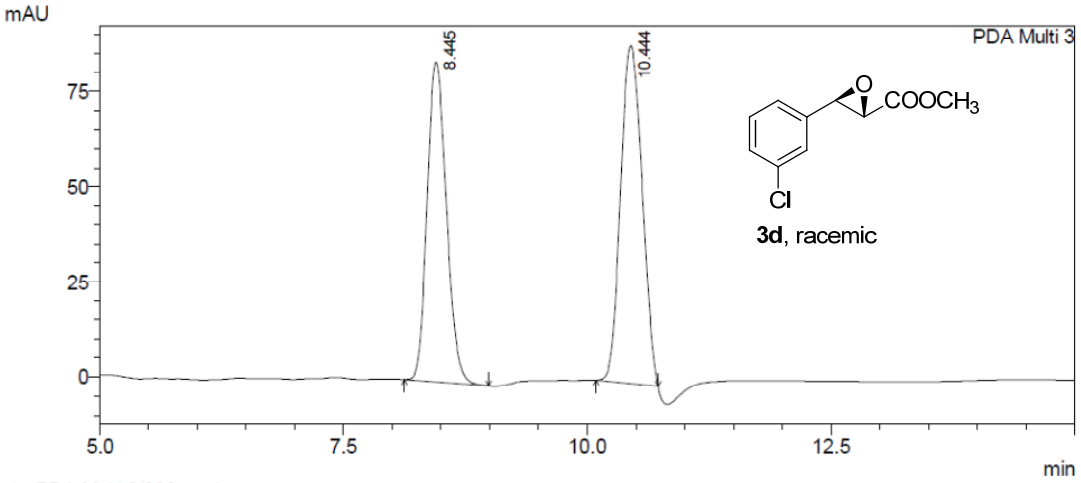


1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.605	45436	3367	1.698	2.300
2	8.189	2630243	143040	98.302	97.700
Total		2675679	146407	100.000	100.000

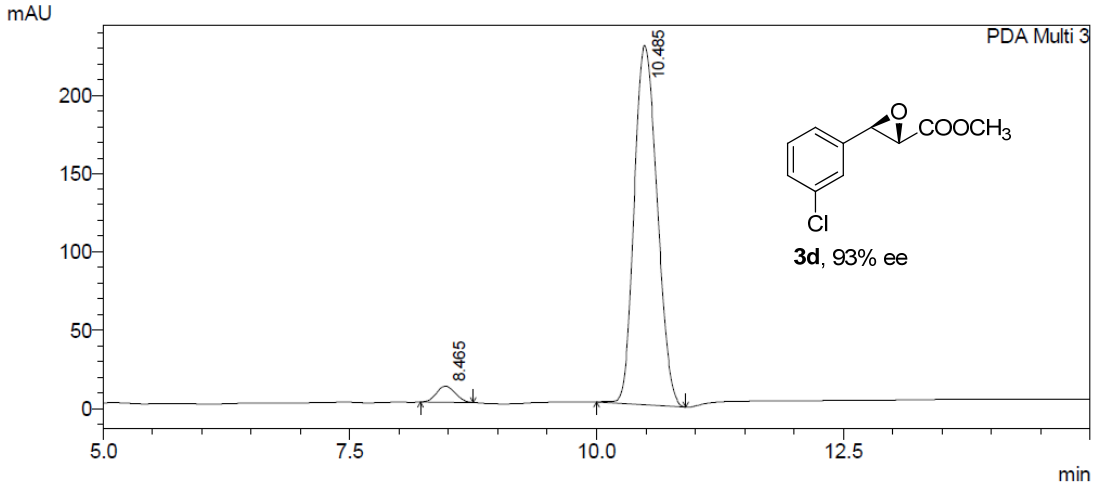


1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.445	1156249	83991	45.842	48.604
2	10.444	1365976	88816	54.158	51.396
Total		2522225	172807	100.000	100.000

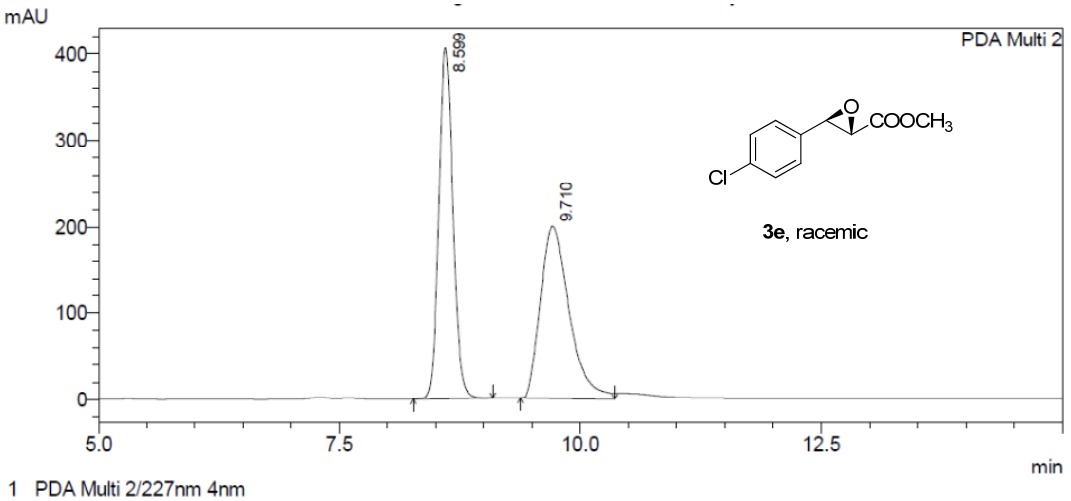


1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.465	137292	10250	3.562	4.279
2	10.485	3716942	229263	96.438	95.721
Total		3854234	239513	100.000	100.000

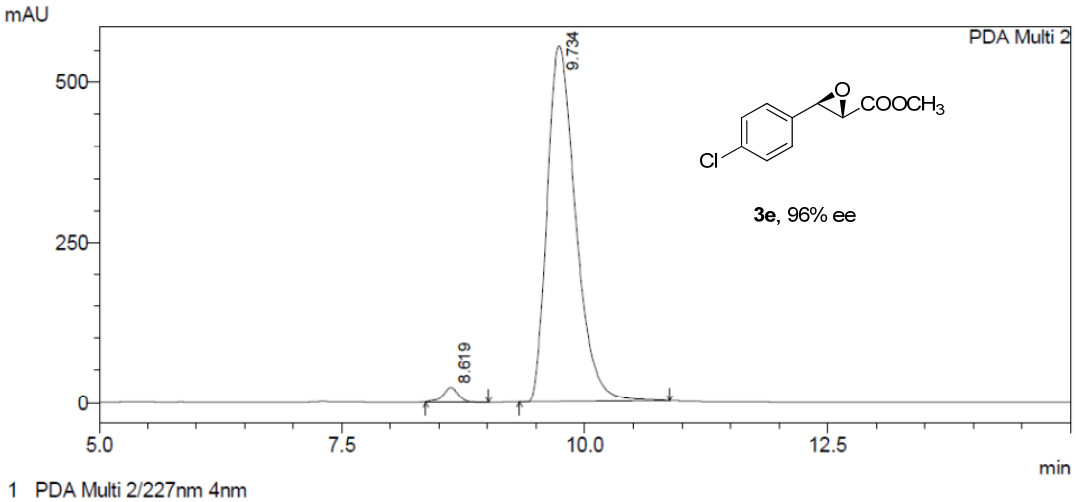


1 PDA Multi 2/227nm 4nm

PeakTable

PDA Ch2 227nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.599	4134695	405410	50.010	67.062
2	9.710	4133033	199117	49.990	32.938
Total		8267727	604527	100.000	100.000

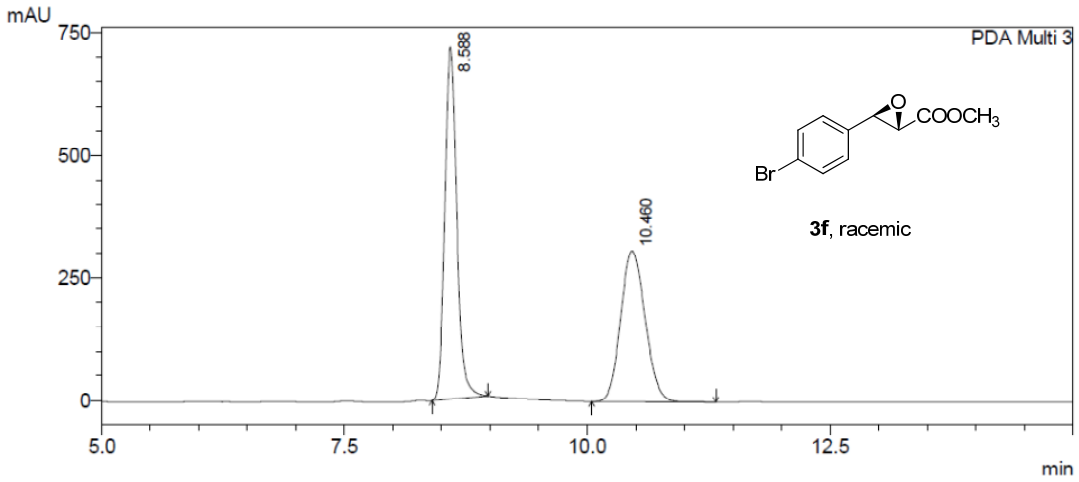


1 PDA Multi 2/227nm 4nm

PeakTable

PDA Ch2 227nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.619	256170	22923	2.209	3.961
2	9.734	11342250	555861	97.791	96.039
Total		11598420	578784	100.000	100.000

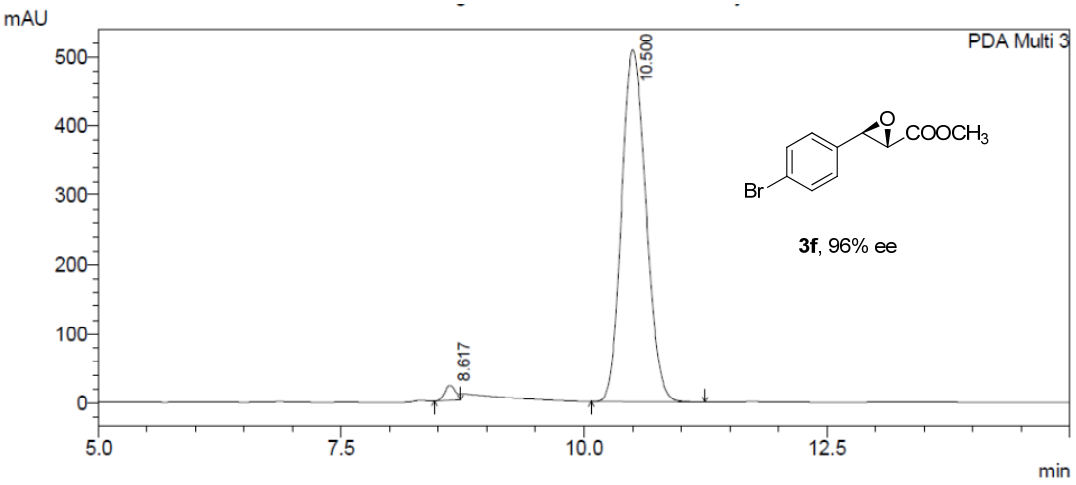


1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.588	6157647	717897	53.408	70.045
2	10.460	5371791	307010	46.592	29.955
Total		11529438	1024907	100.000	100.000

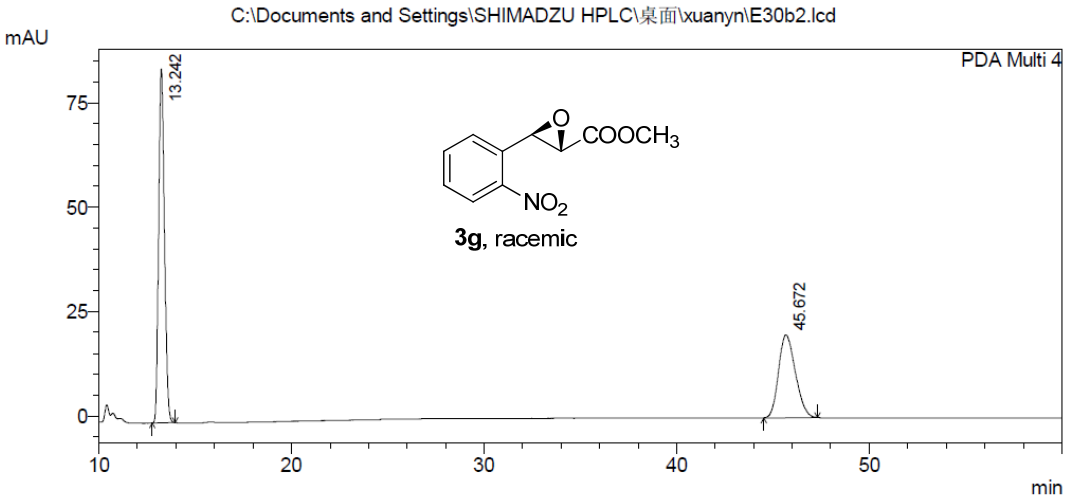


1 PDA Multi 3/230nm 4nm

PeakTable

PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.617	176419	21881	1.945	4.125
2	10.500	8892830	508538	98.055	95.875
Total		9069249	530419	100.000	100.000

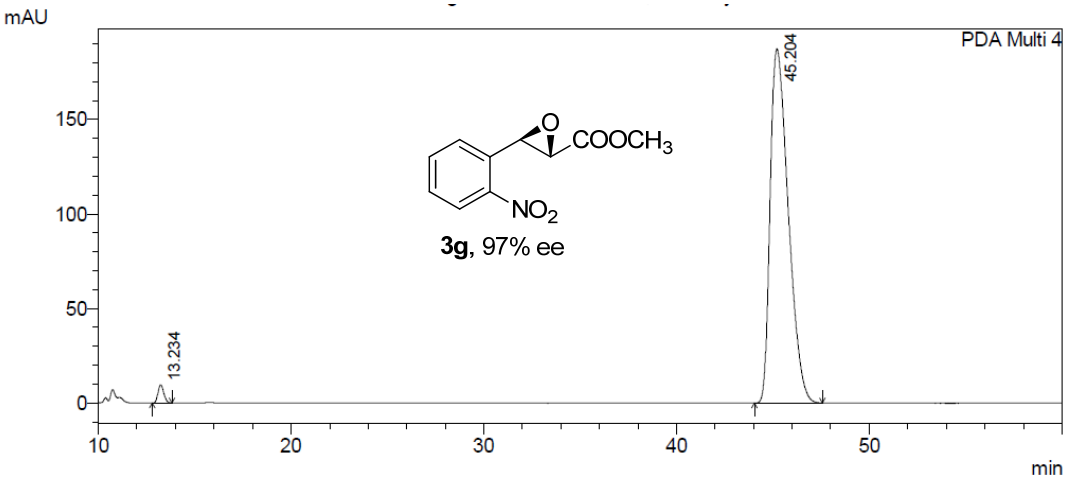


1 PDA Multi 4/254nm 4nm

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.242	1576428	84692	52.808	80.999
2	45.672	1408762	19867	47.192	19.001
Total		2985190	104559	100.000	100.000

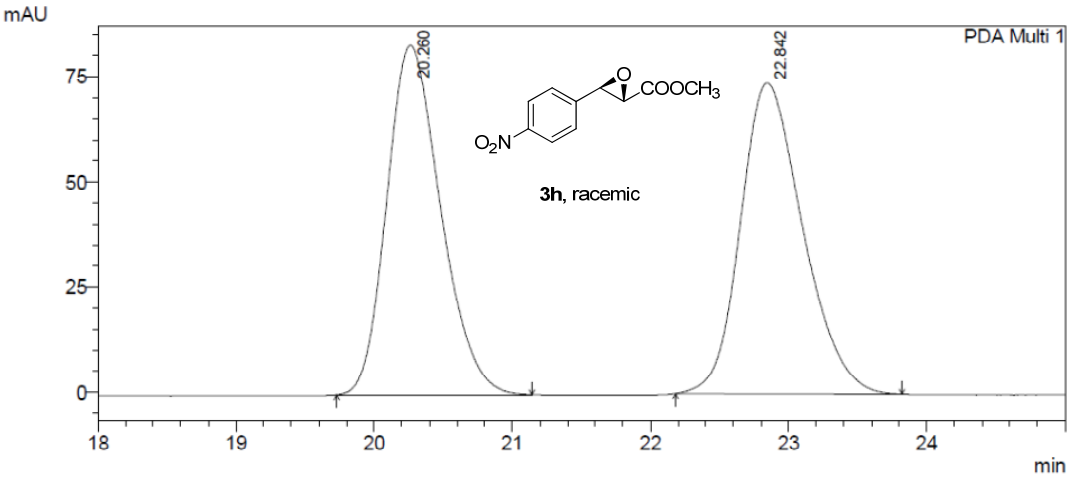


1 PDA Multi 4/254nm 4nm

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.234	201719	9610	1.617	4.878
2	45.204	12274328	187406	98.383	95.122
Total		12476047	197016	100.000	100.000

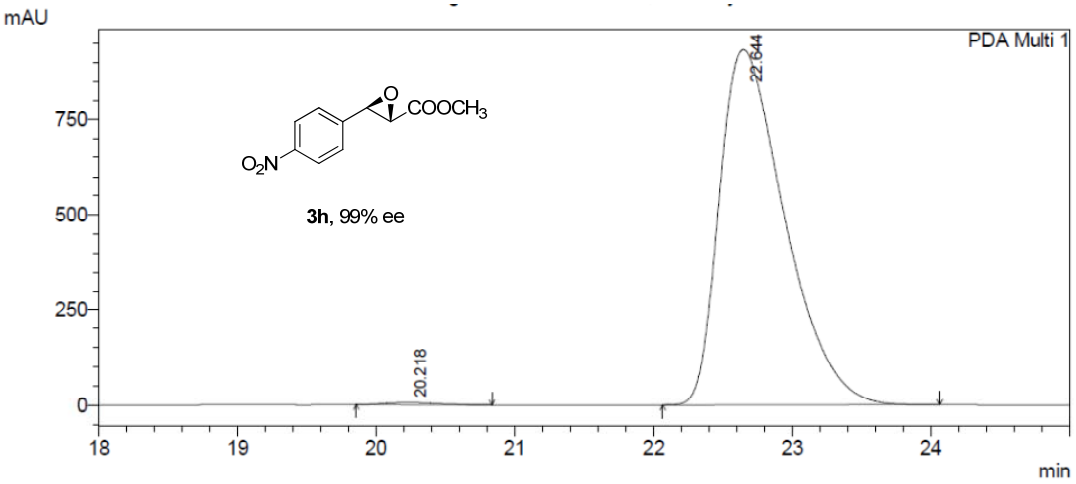


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.260	2255165	82972	49.306	52.928
2	22.842	2318652	73792	50.694	47.072
Total		4573817	156764	100.000	100.000

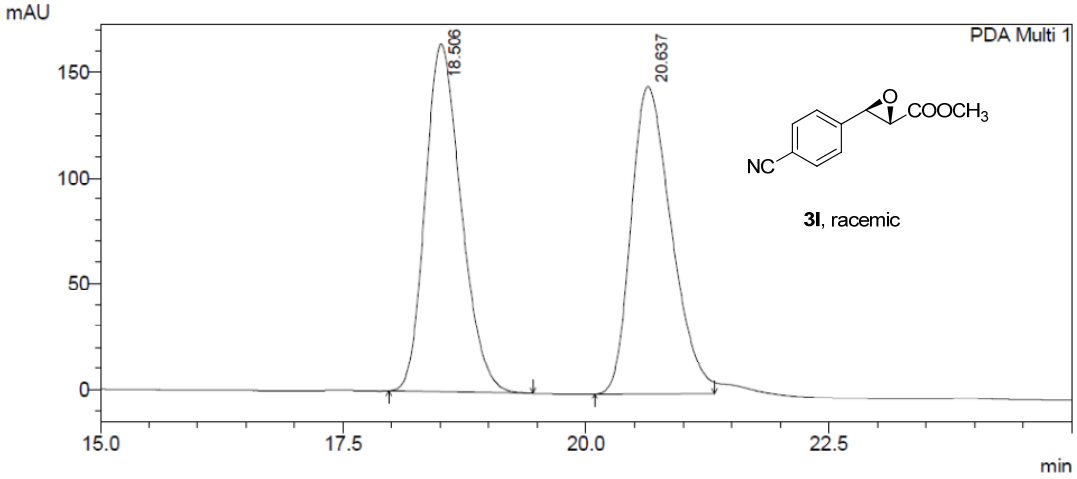


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.218	156589	6137	0.509	0.653
2	22.644	30608039	934070	99.491	99.347
Total		30764627	940208	100.000	100.000

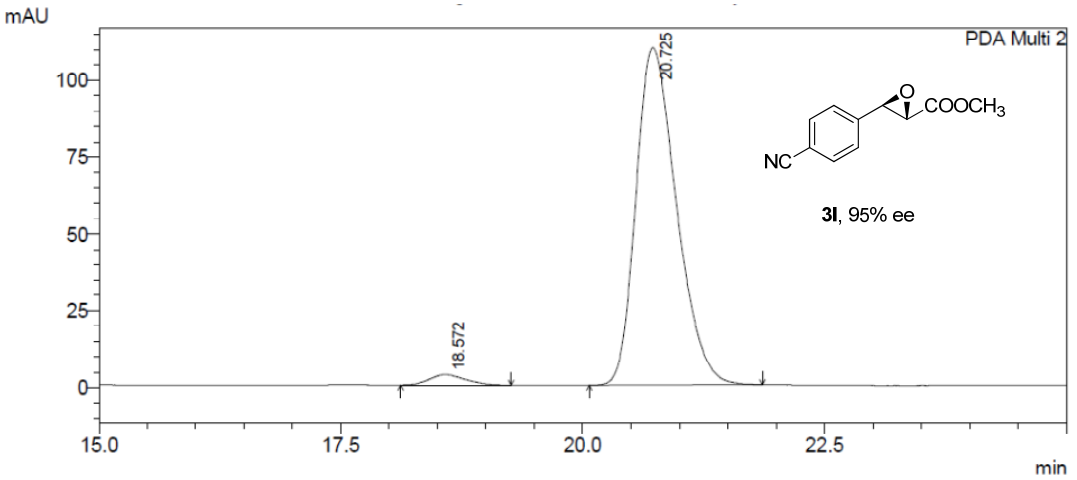


1 PDA Multi 1/230nm 4nm

PeakTable

PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.506	4222648	163882	50.248	53.052
2	20.637	4180928	145027	49.752	46.948
Total		8403576	308909	100.000	100.000

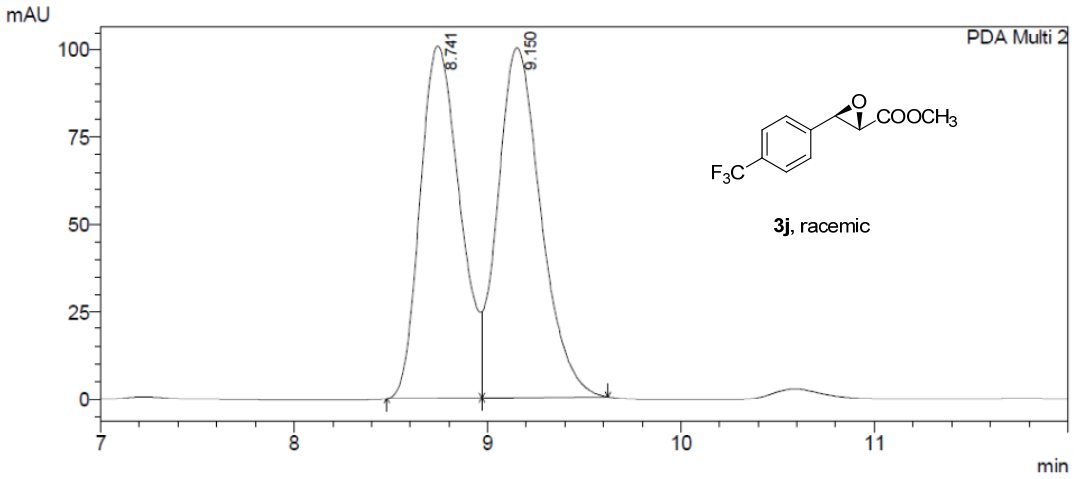


1 PDA Multi 2/230nm 4nm

PeakTable

PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.572	85537	3319	2.607	2.938
2	20.725	3195414	109655	97.393	97.062
Total		3280951	112974	100.000	100.000

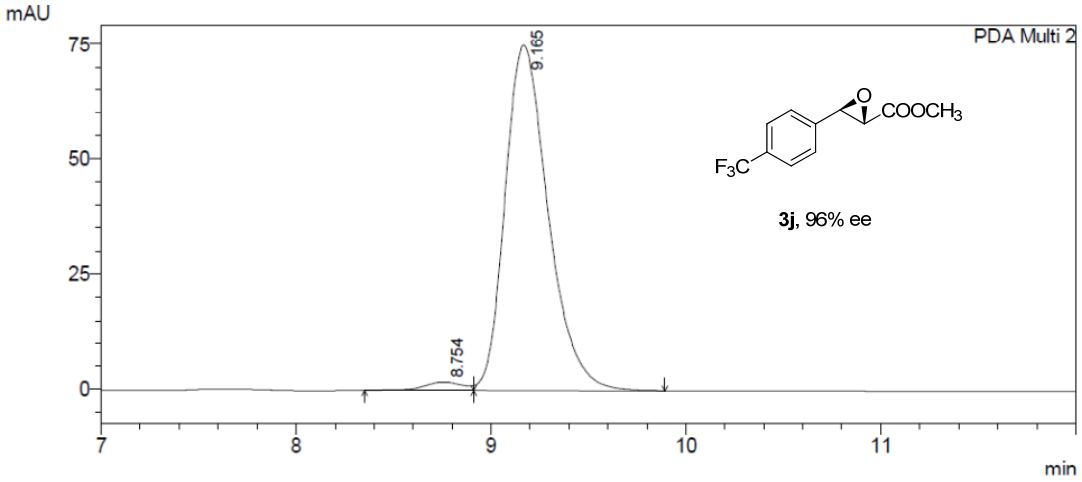


1 PDA Multi 2/230nm 4nm

PeakTable

PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.741	1441902	100625	48.148	50.143
2	9.150	1552822	100052	51.852	49.857
Total		2994725	200677	100.000	100.000

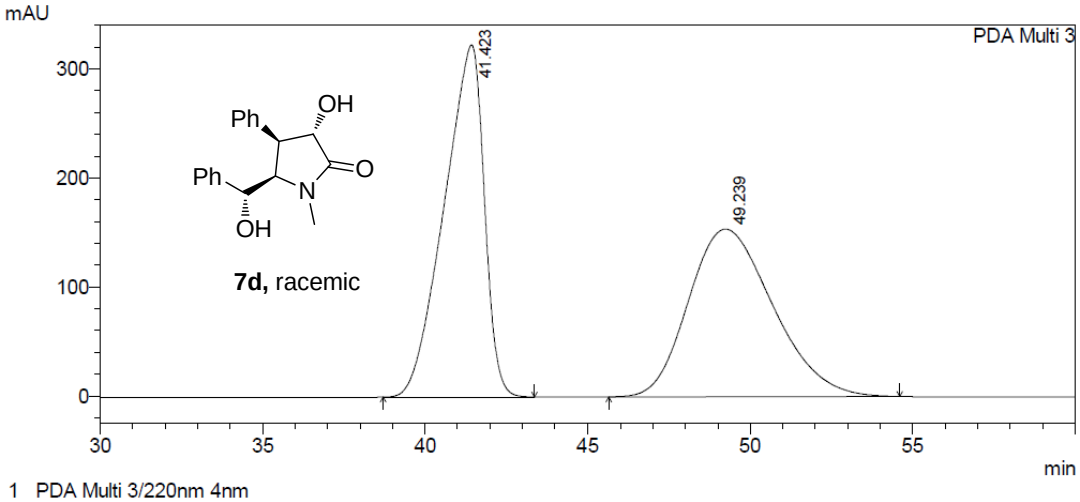


1 PDA Multi 2/230nm 4nm

PeakTable

PDA Ch2 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.754	26182	1782	2.210	2.317
2	9.165	1158729	75129	97.790	97.683
Total		1184911	76911	100.000	100.000

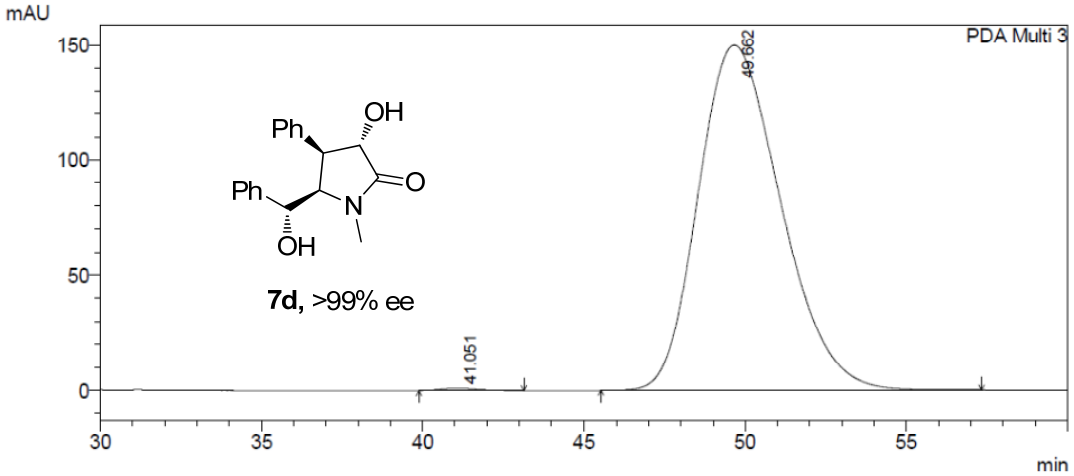


1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.423	27750441	323146	49.945	67.739
2	49.239	27811814	153902	50.055	32.261
Total		55562255	477049	100.000	100.000



1 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.051	72164	969	0.271	0.644
2	49.662	26593262	149539	99.729	99.356
Total		26665427	150507	100.000	100.000