Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting information

Chiral Phosphine-Catalyzed Asymmetric Allylic Alkylation of 3-Substituted Benzofunan-2(3H)-ones or Oxindoles with Morita-Baylis-Hillman Carbonates

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Contents:

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1. General Methods: ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz or 300 and 75 MHz by VARIAN, respectively. Low- and high-resolution mass spectra were recorded by EI, ESI or MALDI 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.

Chiral phosphine catalysts **LB1-LB5** were synthesized according to our previous works.[1] All MBH carbonates **2a-2h**,[2] 3-substituted benzofunan-2(3H)-ones **1a-1d**[3] and 3-substituted oxindoles **4a-4e**[4] were prepared according to the previously reported procedures.

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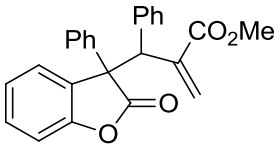
2. General procedure for the synthesis of 3 (using 3a as an example)

To a mixture of **1a** (0.10 mmol, 21.0 mg), **2a** (0.20 mmol, 58.0 mg) and **LB1** (10.0 mg, 0.02 mmol) was added 1.0 mL of toluene at 0 ^{o}C. The reaction solution was monitored by TLC. After the reaction complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/10) to give the target product **3a**.

3. General procedure for the synthesis of 5 (using 5a as an example)

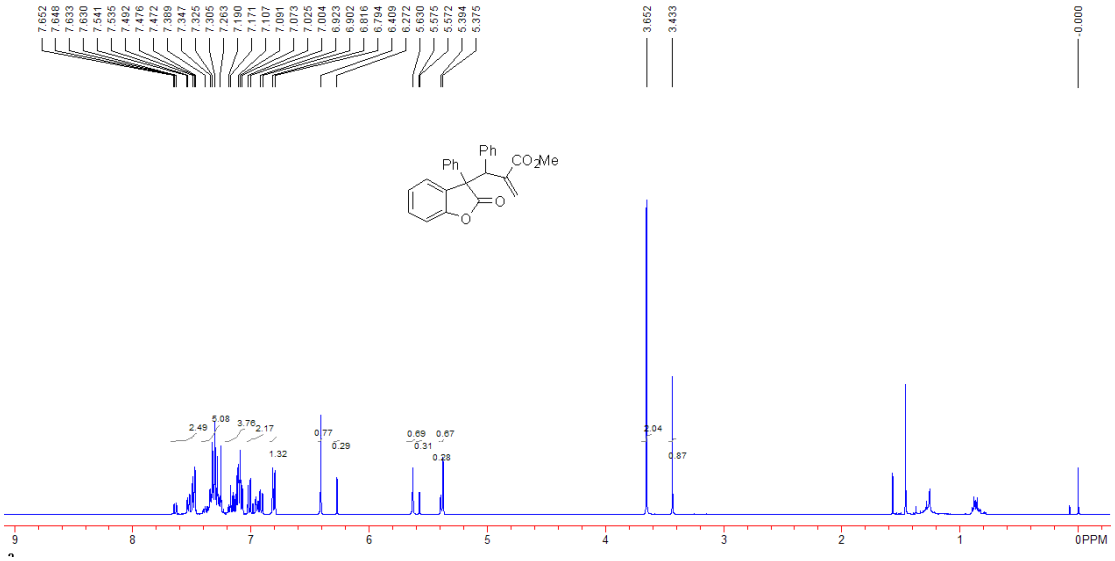
To a mixture of **4a** (0.10 mmol, 31.0 mg), **2e** (0.20 mmol, 67.0 mg) and **LB1** (10.0 mg, 0.02 mmol) was added 1.0 mL of toluene at roomtempreture. The reaction solution was monitored by TLC. After the reaction complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/10) to give the target product **5a**.

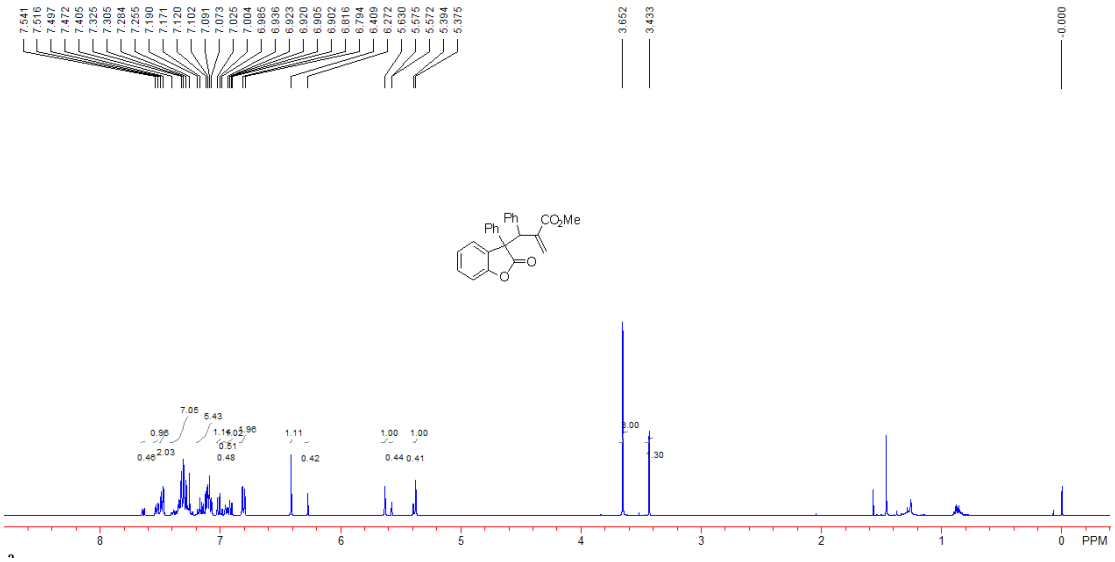
4. Characterization and spectra charts containing HPLC traces for products 3a-q.



Methyl 2-((2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methyl)acrylate **3a**

A white solid, this is a known compound,[5] 95% yield, 36 mg (*syn*:*anti* = 67:33); $[\alpha]^{20}_{D}$ = -160.5 (c 0.5, $CHCl_3$) for 94% ee (*syn*) and 91% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 230 nm, for *syn* product t_{major} = 27.323 min, t_{minor} = 35.282 min; for *anti* product t_{major} = 33.532 min, t_{minor} = 25.773 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.43 (s, 0.99H, CH_3), 3.65 (s, 2.01H, CH_3), 5.38 (s, 0.67H, =CH_2), 5.39 (s, 0.33H, =CH_2), 5.57 (d, *J* = 1.2 Hz, 0.33H, =CH_2), 5.63 (s, 0.67H, =CH_2), 6.27 (s, 0.33H, CH), 6.41 (s, 0.67H, CH), 6.79-6.82 (m, 1H, Ar), 6.90-7.03 (m, 2H, Ar), 7.07-7.19 (m, 4H, Ar), 7.26-7.39 (m, 5H, Ar), 7.47-7.65 (m, 2H, Ar); MS (ESI) *m/z* 407.4 (M+Na$^+$, 100). HRMS (MALDI) Calcd. for $C_{25}H_{20}O_4Na$ requires (M+Na$^+$) 407.1270, Found: 407.1254.





N2000 数据工作站

1

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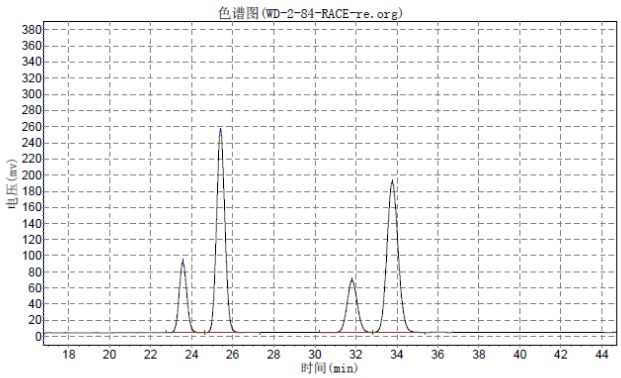
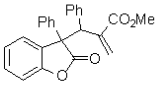
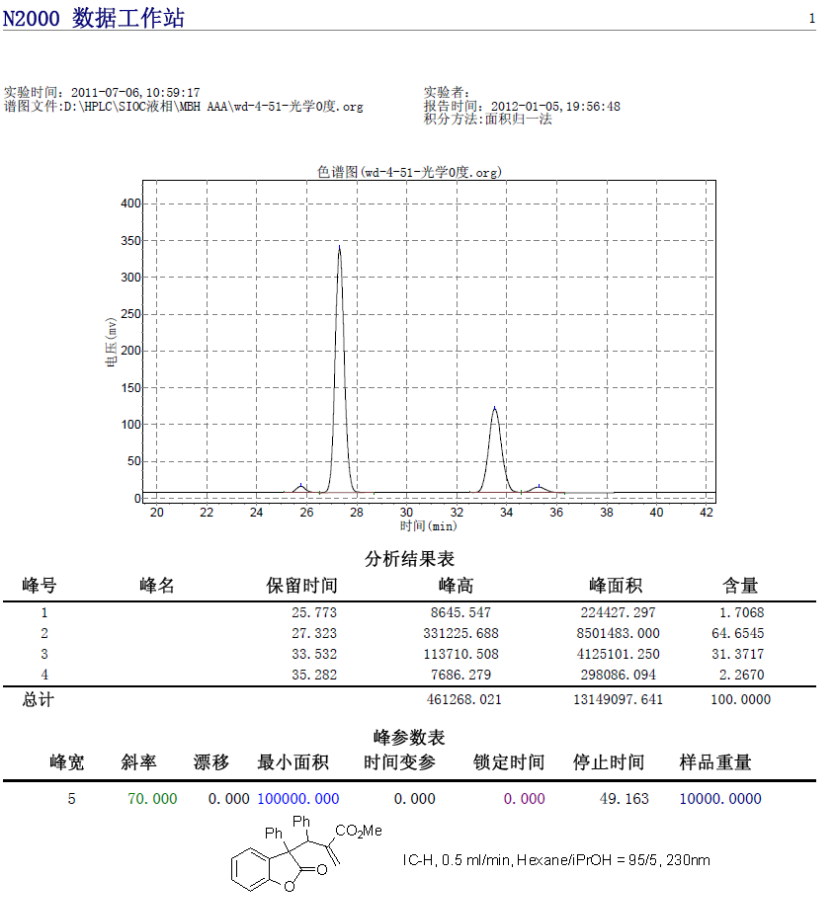


分析结果表

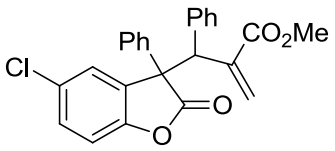
峰号	峰名	保留时间	峰高	峰面积	含量
1		23.565	86588.977	2269396.750	12.1286
2		25.432	251424.922	7079045.000	37.8334
3		31.832	64540.422	2256043.500	12.0572
4		33.798	186120.984	7106616.000	37.9807
总计			588675.305	18711101.250	100.0000



IC-H, 0.5 ml/min, Hexane/iPrOH = 95/5, 230nm



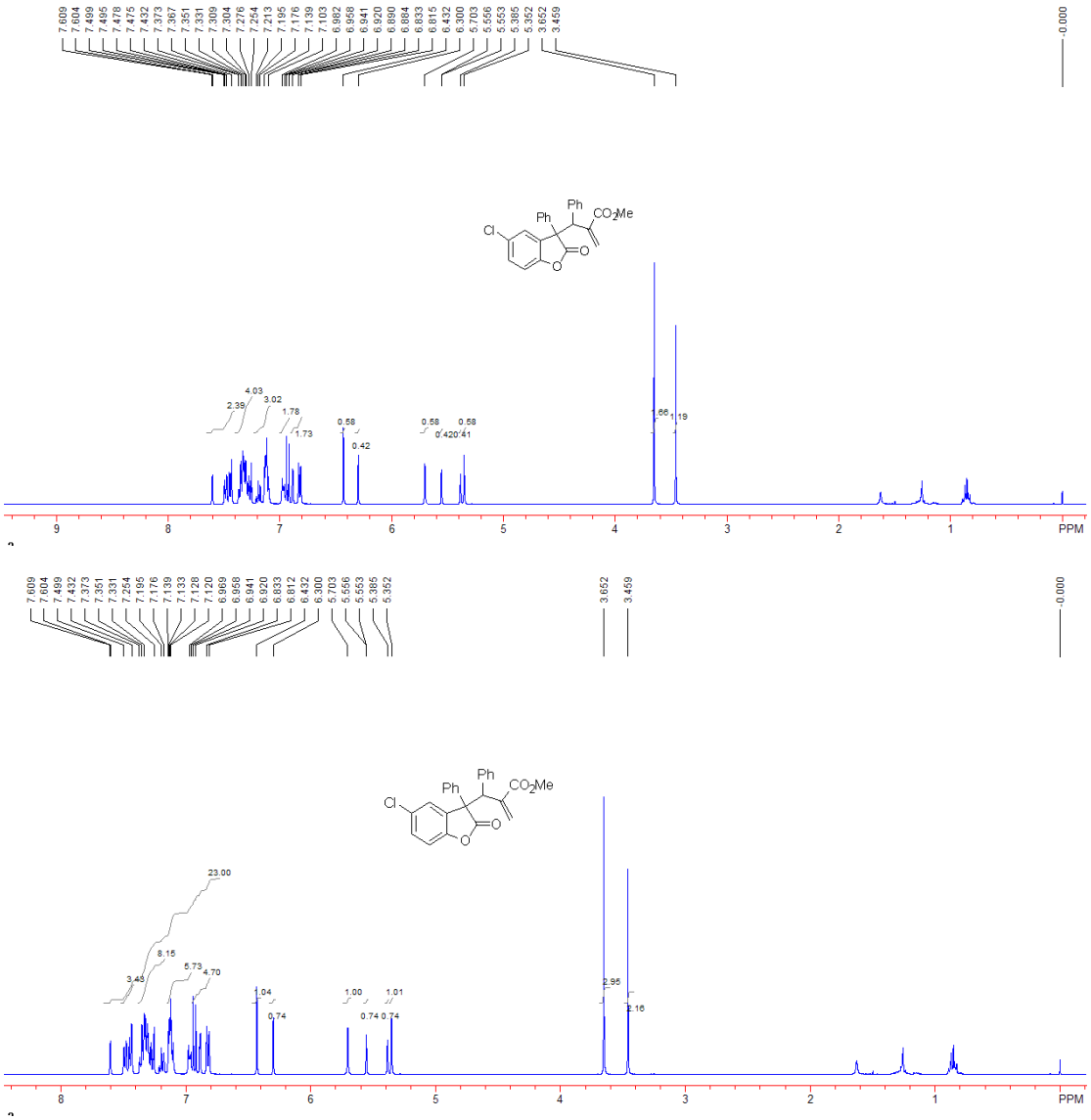
Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 230 nm, for *syn* product t_{major} = 27.323 min, t_{minor} = 35.282 min; for *anti* product t_{major} = 33.532 min, t_{minor} = 25.773 min;

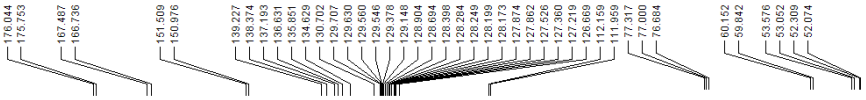


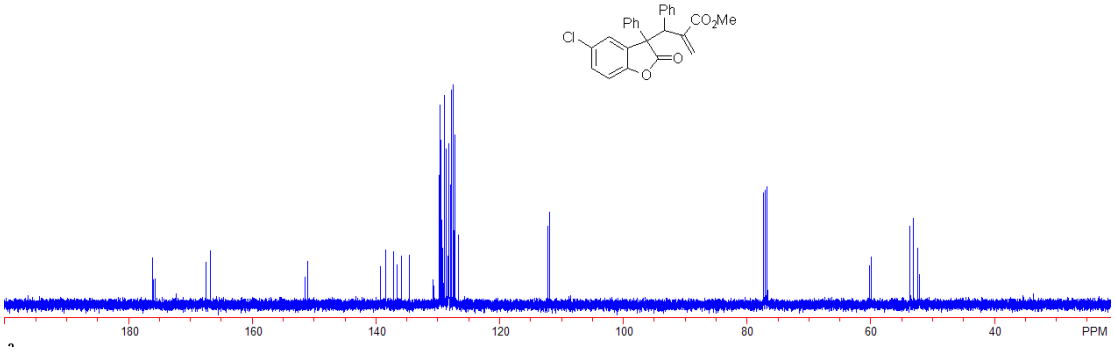
Methyl 2-((5-chloro-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methyl)acrylate **3b**

A white solid, 93% yield, 38 mg, m.p. 105-108 ^{o}C, (*syn*:*anti* = 56:44); $[\alpha]^{20}_{D}$ = -148.1 (c 1.1, $CHCl_3$) for 92% ee (*syn*) and 91% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 0.5 mL/min, 254 nm, for *syn* product t_{major} = 13.377 min, t_{minor} = 18.227 min; for *anti* product t_{major} = 14.227 min, t_{minor} = 16.927 min. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.46 (s, 1.32H, CH_3), 3.65 (s, 1.68H, CH_3), 5.35 (s, 0.56H, $=CH_2$), 5.39 (s, 0.44H, $=CH_2$), 5.55 (d, *J* = 1.2 Hz, 0.44H, $=CH_2$), 5.70 (s, 0.56H, $=CH_2$), 6.30 (s, 0.44H, CH), 6.43 (s, 0.56H, CH), 6.82-6.89 (m, 2H, Ar), 6.92-6.98 (m, 2H, Ar), 7.10-7.21 (m, 3H, Ar), 7.25-7.37 (m, 4H, Ar), 7.43-7.61 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □52.07, 52.31, 53.05, 53.58, 59.84, 60.15, 111.96, 112.16, 126.67, 127.22,

127.36, 127.53, 127.86, 127.87, 128.17, 128.20, 128.25, 128.28, 128.40, 128.69, 128.90, 129.15, 129.38, 129.55, 129.56, 129.63, 129.71, 130.70, 134.63, 135.85, 136.63, 137.19, 138.37, 139.23, 150.98, 151.51, 166.74, 167.49, 175.75, 176.04; IR (neat) ν 2949, 1805, 1718, 1466, 1262, 1132, 1065, 702 cm^{-1}; MS (ESI) *m/z* 441.4 ($M+Na^+$, 100). HRMS (ESI) Calcd. for $C_{25}H_{19}ClO_4Na$ requires ($M+Na^+$) 441.0868, Found: 441.0864.







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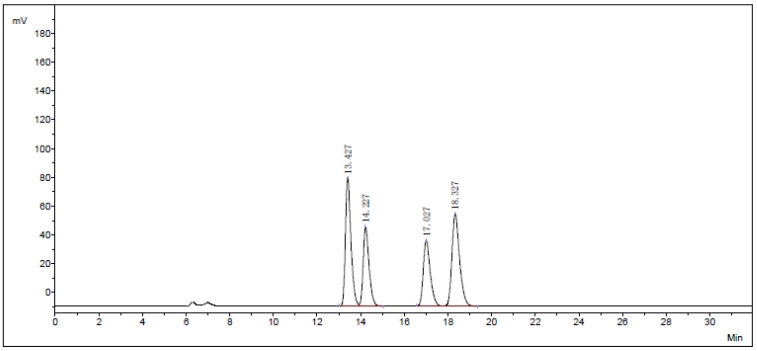

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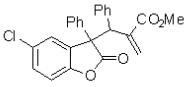
2	2	14.227	54979.2	1025046.9	19.7526
3	3	17.027	45598.9	1018930.0	19.6347
4	4	18.327	64006.5	1567151.8	30.1990
Total			253684.7	5189424.7	100.0000



AD-H, 0.5 ml/min, Hexane/iPrOH = 95/5, 254nm

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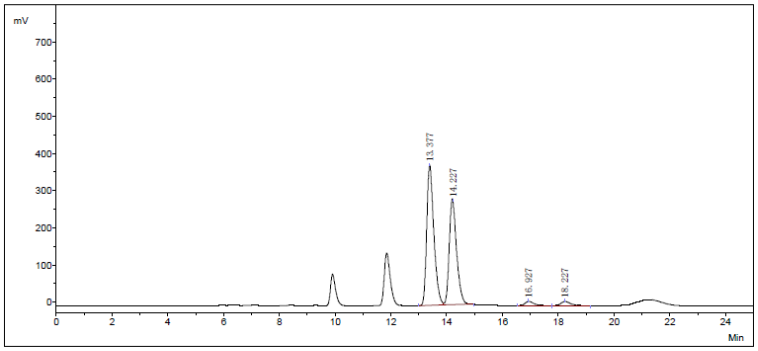
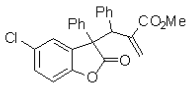
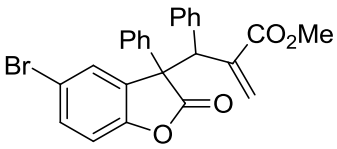


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	13.377	374836.0	6632590.6	53.7063
2	2	14.227	277739.9	5195300.8	42.0681
3	3	16.927	11455.0	251025.2	2.0326
4	4	18.227	11233.7	270836.6	2.1931
Total			675264.5	12349753.2	100.0000



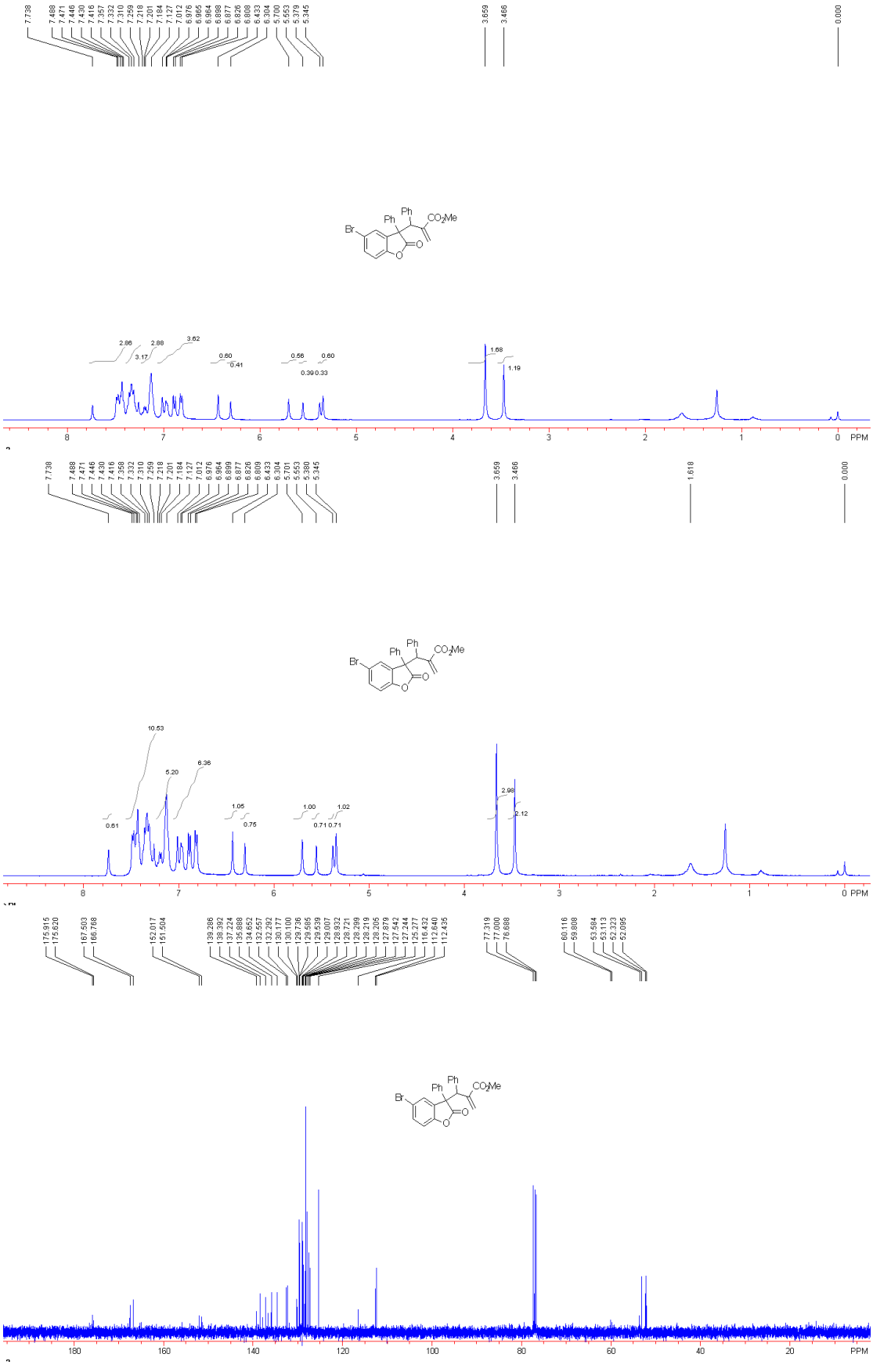
AD-H, 0.5 ml/min, Hexane/iPrOH = 95/5, 254nm



Methyl 2-((5-bromo-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methyl)acrylate **3c**

A white solid, 90% yield, 41 mg, m.p. 94-95 ^{o}C, (*syn*:*anti* = 71:29); $[\alpha]^{20}_{D}$ = -172.7 (c 0.6, $CHCl_3$) for 97% ee (*syn*) and 92% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 98/2, 0.7 mL/min, 230 nm, for *syn* product t_{major} = 19.027 min, t_{minor} = 23.527 min; for *anti* product t_{major} = 21.727 min, t_{minor} = 16.977 min. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.47 (s, 0.87H, CH_3), 3.66 (s, 2.13H, CH_3), 5.35 (s, 0.71H, =CH_2), 5.38 (s, 0.29H, =CH_2), 5.55 (s, 0.29H, =CH_2), 5.70 (s, 0.71H, =CH_2), 6.30 (s, 0.29H, CH), 6.43 (s, 0.71H, CH), 6.81-7.01 (m, 4H, Ar), 7.13-7.22 (m, 3H, Ar), 7.31-7.36 (m, 3H, Ar), 7.42-7.74 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □52.10, 52.32, 53.11, 53.58, 59.81, 60.12, 112.44, 112.64, 116.43, 125.28, 127.24, 127.54, 127.88, 128.21, 128.22, 128.30, 128.72, 128.93, 129.01, 129.54, 129.59, 129.74, 130.10, 130.18, 132.29, 132.56, 134.65, 135.89, 137.22, 138.39, 139.29, 151.50, 152.02, 166.77, 167.50, 175.62, 175.92; IR (neat) ν

2916, 1806, 1719, 1466, 1234, 1135, 1065, 701 cm^{-1}; MS (ESI) *m/z* 485.3 ($M+Na^+$, 100). HRMS (ESI) Calcd. for $C_{25}H_{19}BrO_4Na$ requires ($M+Na^+$) 485.0366, Found: 485.0359.



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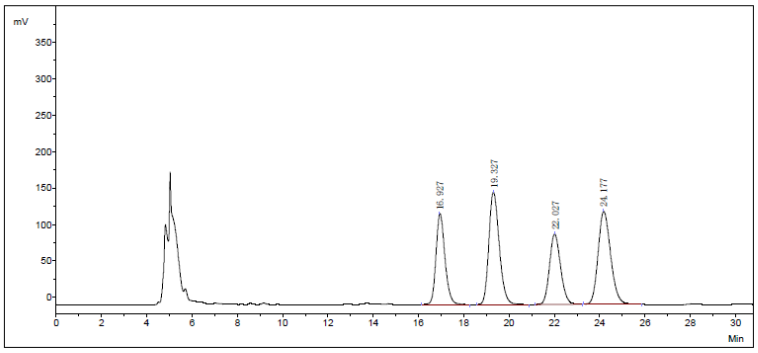

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3	3	22.027	96401.4	3267880.7	19.8157
4	4	24.177	127228.1	4888389.3	29.6421
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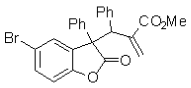

IC-H, 0.7 ml/min, Hexane/iPrOH = 98/2, 230nm

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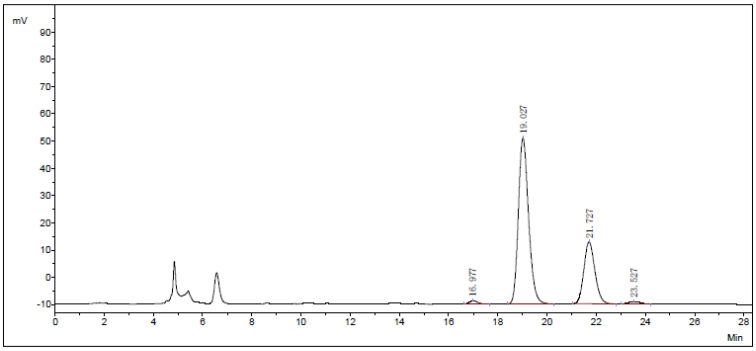

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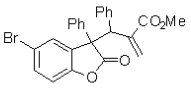
1	1	16.977	1182.3	29229.5	1.1621
2	2	19.027	60933.8	1752194.2	69.6627
3	3	21.727	22674.7	707999.2	28.1482
4	4	23.527	795.5	25832.0	1.0270
Total			85586.3	2515254.9	100.0000



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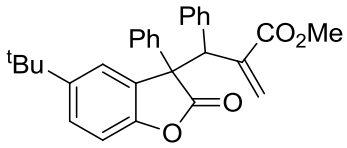
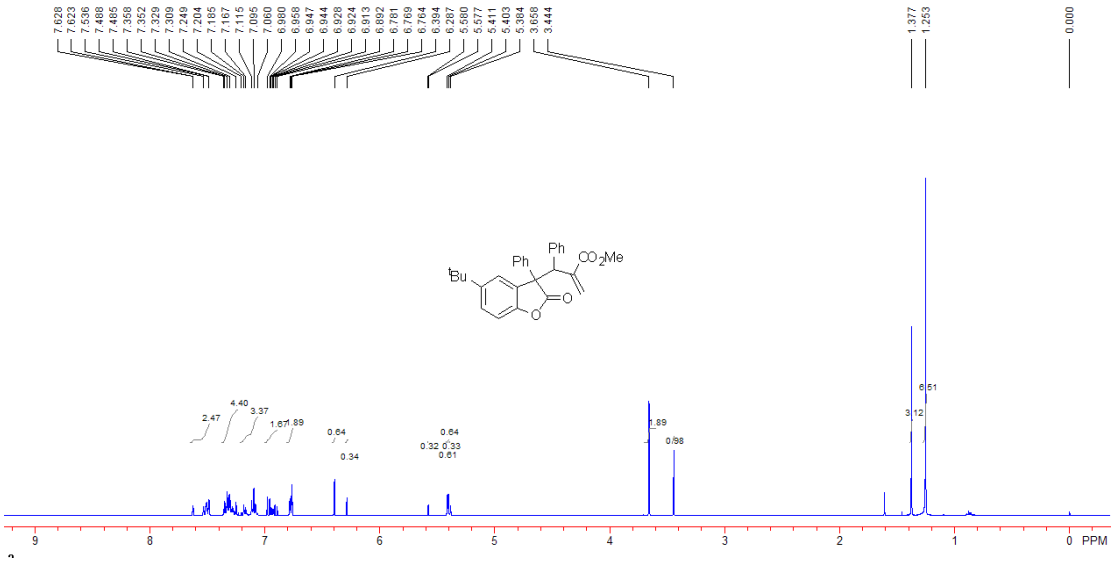
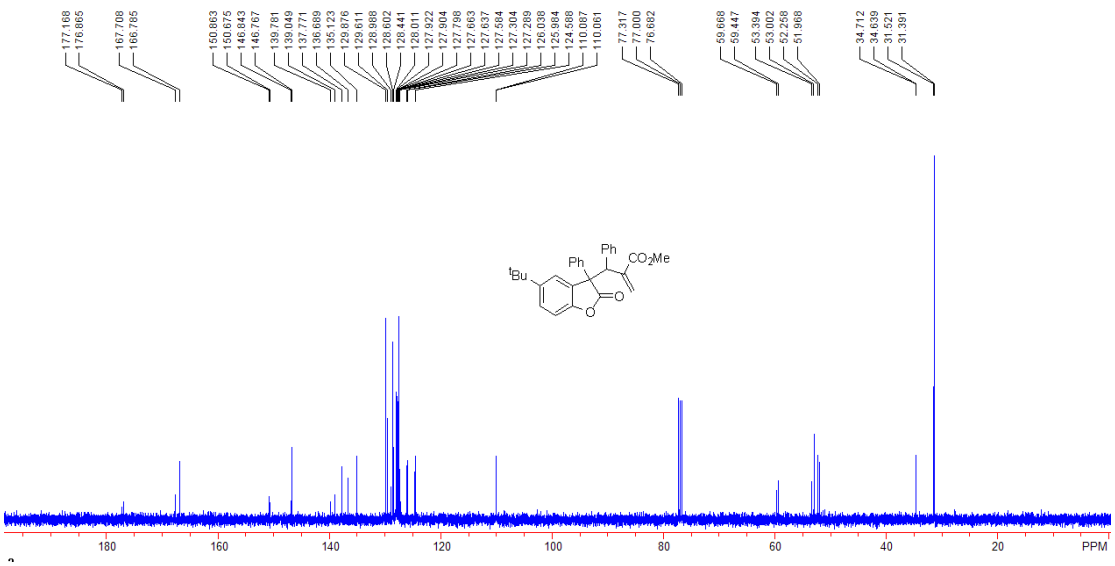


Methyl 2-((5-(tert-butyl)-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methyl)acrylate

3d

A colorless oil, 91% yield, 40 mg (*syn*:*anti* = 63:37); $[\alpha]^{20}_{D}$ = -134.6 (c 2.0, $CHCl_3$) for 90% ee (*syn*) and 88% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 93/7, 0.5 mL/min, 230 nm, for *syn* product t_{major} = 19.627 min, t_{minor} = 26.327 min; for *anti* product t_{major} = 18.077 min, t_{minor} = 15.177 min. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (s, 5.67H, ^{t}Bu), 1.38 (s, 3.33H, ^{t}Bu), 3.44 (s, 1.11H, CH_3), 3.66 (s, 1.89H, CH_3), 5.38 (s, 0.37H, =CH_2), 5.40 (s, 0.63H, =CH_2), 5.41 (s, 0.67H, =CH_2), 5.58 (d, *J* = 1.2 Hz, 0.33H, =CH_2), 6.29 (s, 0.33H, CH), 6.39 (s, 0.67H, CH), 6.76-6.78 (m, 2H, Ar), 6.89-6.98 (m, 2H, Ar), 7.06-7.20 (m, 3H, Ar), 7.25-7.36 (m, 4H, Ar), 7.49-7.63 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □31.39, 31.52, 34.64, 34.71, 51.97, 52.26, 53.00, 53.39, 59.45, 59.67, 110.06, 110.09, 124.59, 125.98, 126.04, 127.29, 127.30, 127.58, 127.64, 127.66, 127.80, 127.90, 127.92, 128.01, 128.44, 128.60, 128.99, 129.61, 129.88, 135.12, 136.69, 137.77, 139.05, 139.78, 146.77, 146.84, 150.68, 150.86, 166.79, 167.71, 176.87, 177.17; IR (neat) ν 2957, 1801, 1720, 1488, 1264, 1145, 1065, 704, 702 cm^{-1}; MS (ESI) *m/z* 463.5 (M+Na^{+}, 100). HRMS (ESI) Calcd. for $C_{29}H_{28}O_4Na$ requires (M+Na^{+}) 463.1889, Found: 463.1880.





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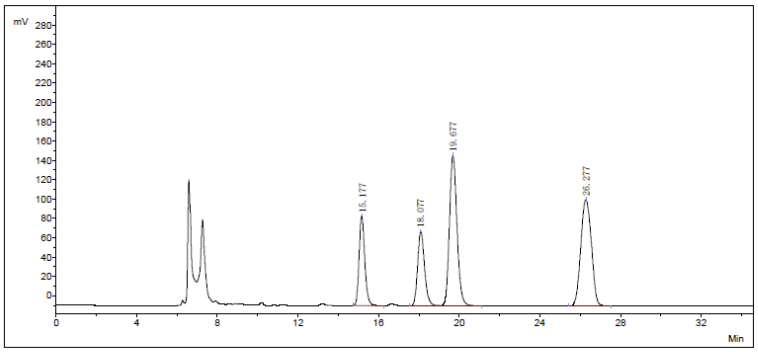

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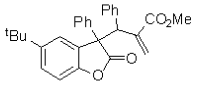
3	3	19.677	155688.8	4063108.5	34.7145
4	4	26.277	110060.1	4001874.8	34.1914
Total			434452.1	11704344.5	100.0000



IC-H, 0.5 ml/min, Hexane/iPrOH = 93/7, 230nm

HPLC REPORT

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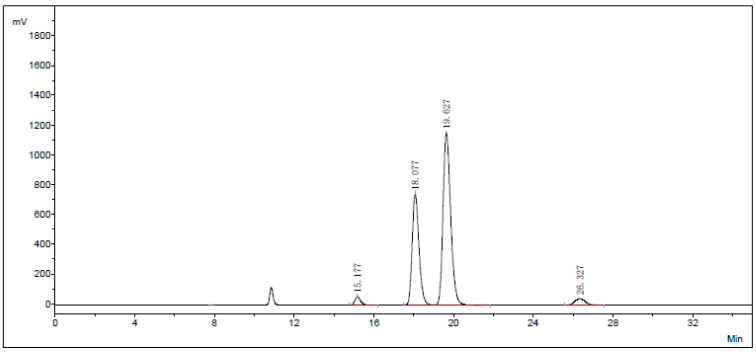
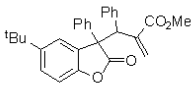
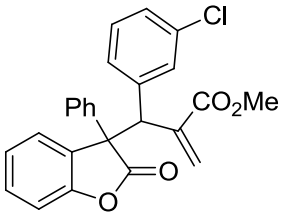
Date:2011-08-25
Time:09:22
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.177	55901.6	1077948.5	2.1038
2	2	18.077	745865.7	17662768.1	34.4717
3	3	19.627	1154194.5	30911146.0	60.3280
4	4	26.327	43733.9	1586605.2	3.0965
Total			1999695.7	51238467.8	100.0000



IC-H, 0.5 ml/min, Hexane/iPrOH = 93/7, 230nm



Methyl 2-((3-chlorophenyl)(2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)acrylate **3e**

A white solid, this is a know compound,[5] 99% yield, 41 mg (*syn*:*anti* = 56:44); $[\alpha]^{20}_{D}$ = -189.6 (c 2.2, $CHCl_3$) for 94% ee (*syn*) and 90% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel REGIS-H column, Hexane/^{i}PrOH = 100/0.5, 0.5 mL/min, 230 nm, for *syn* product t_{major} = 93.710 min, t_{minor} = 68.245 min; for *anti* product t_{major} = 71.377 min, t_{minor} = 86.127 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.46 (s, 1.32H, CH_3), 3.67 (s, 1.68H, CH_3), 5.33 (s, 0.63H, $=CH_2$), 5.37 (s, 0.37H, $=CH_2$), 5.58 (s, 0.40H, $=CH_2$), 5.60 (s, 0.60H, $=CH_2$), 6.31 (s, 0.36H, CH), 6.44 (s, 0.64H, CH), 6.67-6.74 (m, 1H, Ar), 6.90 (d, *J* = 6.8 Hz, 1H, Ar), 7.01-7.18 (m, 4H, Ar), 7.27-7.39 (m, 5H, Ar), 7.47-7.51 (m, 2H, Ar).

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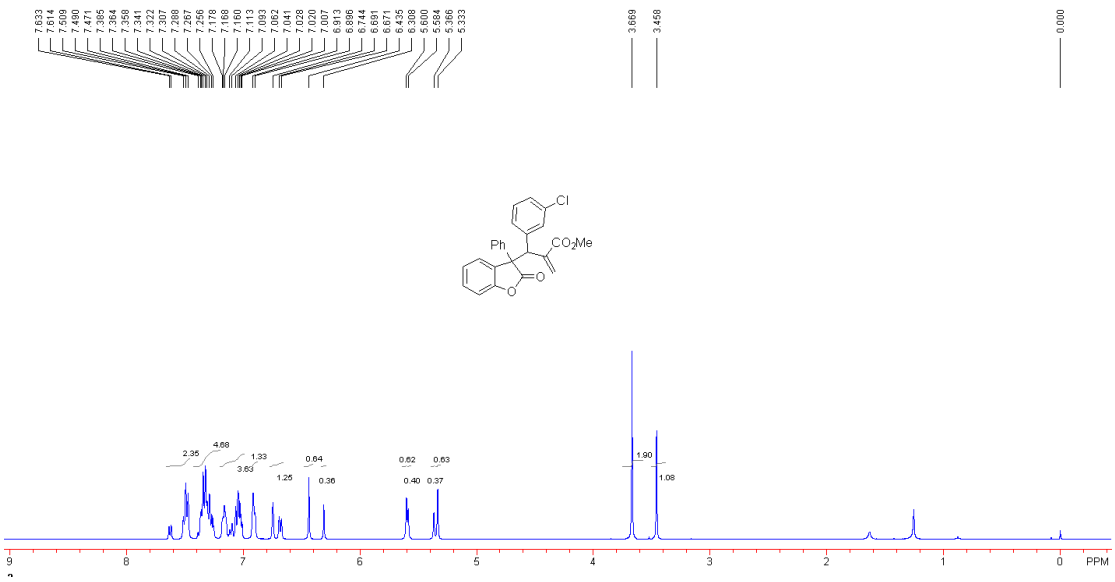
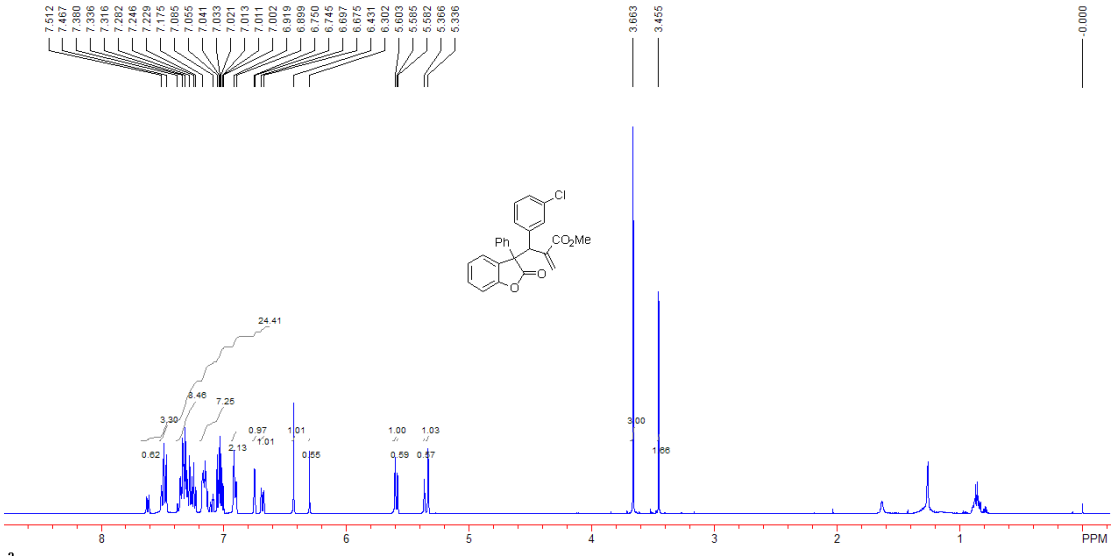
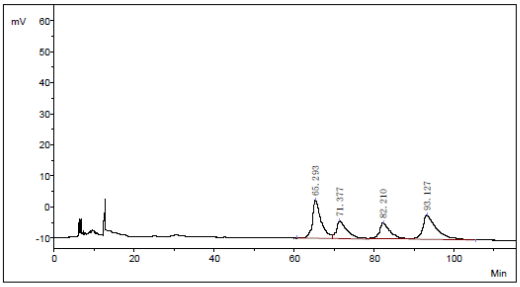


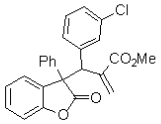


HPLC REPORT

Sample Name:WD-4-84-REGIS-100+0.5-0.5.che
Date:2011-09-07
Time:12:09
Method:
Column:
Flow Rate:
Wave Length:
Mobile Phase:



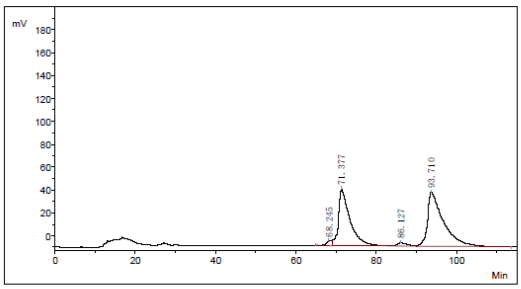
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	65.293	12397.5	1872218.9	32.5371
2	2	Unknown	71.377	5610.4	1052225.9	18.2865
3	3	Unknown	82.210	5115.8	980482.7	17.0397
4	4	Unknown	93.127	7825.4	1849184.9	32.1368
Total				30949.2	5754112.4	100.0000



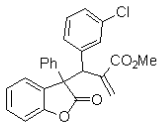
REGIS, 0.5 ml/min, Hexane/iPrOH = 100/0.5, 230nm

HPLC REPORT

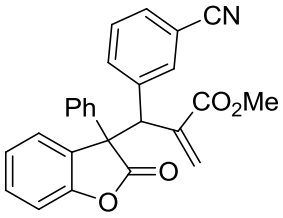
Sample Name:WD-4-80.che
Date:2011-09-08
Time:08:04
Method:
Column:
Flow Rate:
Wave Length:
Mobile Phase:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	68.245	4141.1	376997.5	1.6046
2	2	Unknown	71.377	49499.3	9791626.4	41.6757
3	3	Unknown	86.127	2778.3	506412.8	2.1554
4	4	Unknown	93.710	46967.7	12819777.9	54.5643
Total				103386.4	23494814.6	100.0000

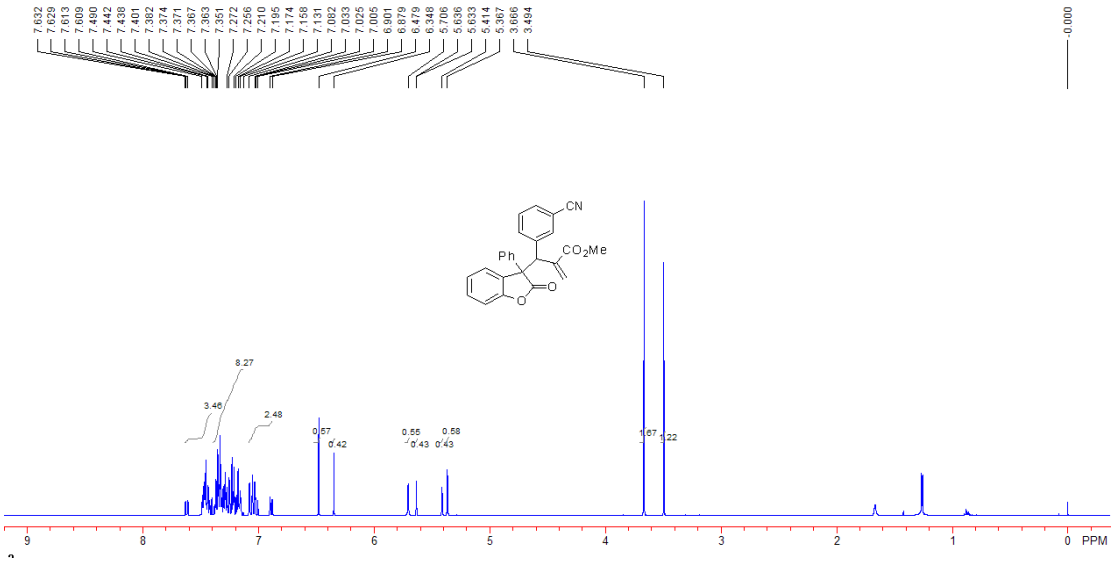


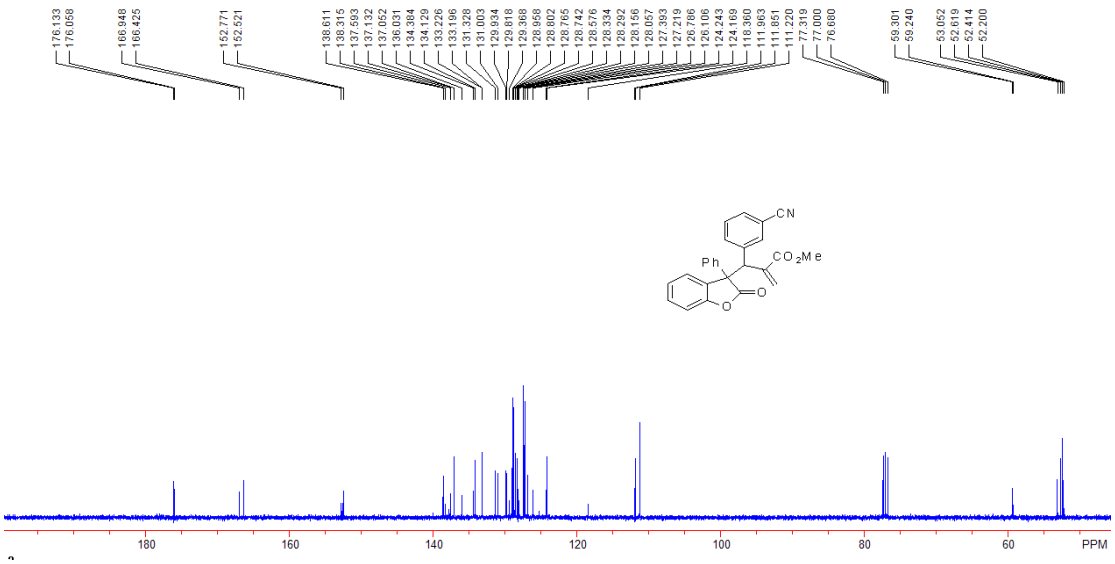
REGIS, 0.5 ml/min, Hexane/iPrOH = 100/0.5, 230nm



Methyl 2-((3-cyanophenyl)(2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)acrylate **3f**

A white solid, 84% yield, 34 mg, m.p. 124-126 ^{o}C, (*syn*:*anti* = 56:44); $[\alpha]^{20}_{D}$ = -254.8 (c 1.8, $CHCl_3$) for 90% ee (*syn*) and 88% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 93/7, 0.5 mL/min, 230 nm, for *syn* product t_{major} = 55.027 min, t_{minor} = 61.327 min; for *anti* product t_{major} = 45.677 min, t_{minor} = 50.477 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.49 (s, 1.32H, CH_3), 3.67 (s, 1.68H, CH_3), 5.37 (s, 0.56H, $=CH_2$), 5.41 (s, 0.44H, $=CH_2$), 5.63 (d, *J* = 1.2 Hz, 0.44H, $=CH_2$), 5.71 (s, 0.56H, $=CH_2$), 6.35 (s, 0.44H, CH), 6.48 (s, 0.56H, CH), 6.88-7.08 (m, 2H, Ar), 7.13-7.38 (m, 8H, Ar), 7.40-7.63 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.20, 52.41, 52.62, 53.05, 59.24, 59.30, 111.22, 111.85, 111.96, 118.36, 124.17, 124.24, 126.11, 126.79, 127.22, 127.39, 128.06, 128.16, 128.29, 128.33, 128.58, 128.74, 128.77, 128.80, 128.96, 129.37, 129.82, 129.93, 131.00, 131.33, 133.20, 133.23, 134.13, 134.38, 136.03, 137.05, 137.13, 137.59, 138.32, 138.61, 152.52, 152.77, 166.43, 166.95, 176.06, 176.13; IR (neat) ν 2952, 2230, 1800, 1719, 1462, 1271, 1066, 753, 699 cm^{-1}; MS (ESI) *m/z* 432.3 (M+Na^{+}, 100). HRMS (ESI) Calcd. for $C_{26}H_{19}NO_4Na$ requires (M+Na^{+}) 432.1216, Found: 432.1206.





HPLC REPORT

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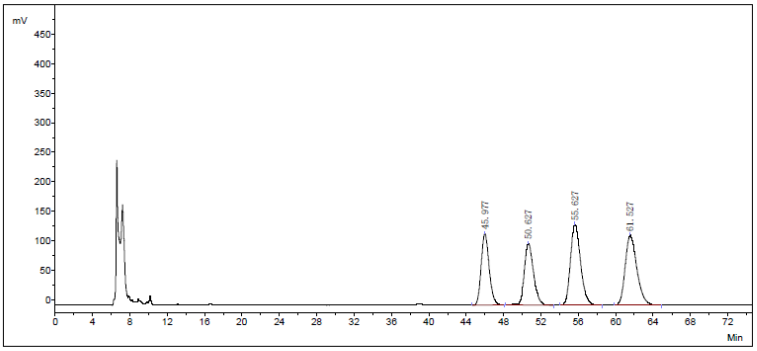
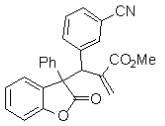
Date:2011-08-25
Time:10:30
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



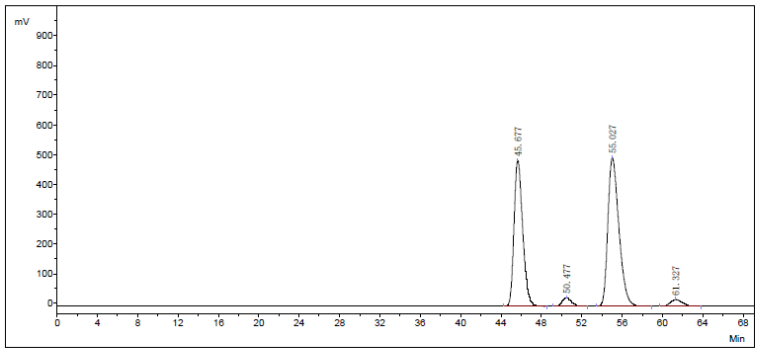
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	45.977	121196.9	7184814.3	20.4908
2	2	50.627	104886.5	7200155.6	20.5346
3	3	55.627	137349.5	10356109.6	29.5352
4	4	61.527	118658.8	10322494.6	29.4394
Total			482091.6	35063574.1	100.0000



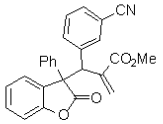
IC-H, 0.5 ml/min, Hexane/iPrOH = 93/7, 230nm

HPLC REPORT

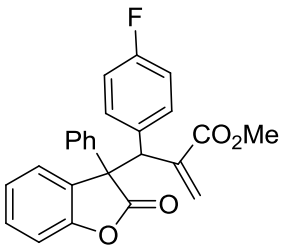
Sample Name:wd-4-87.che
Date:2011-08-25
Time:11:47
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	45.677	490629.7	29350434.7	41.2325
2	2	50.477	28455.6	1880540.9	2.6418
3	3	55.027	498557.1	38037851.3	53.4368
4	4	61.327	22560.2	1914022.8	2.6889
Total			1040202.6	71182849.7	100.0000



IC-H, 0.5 ml/min, Hexane/iPrOH = 93/7, 230nm



Methyl 2-((4-fluorophenyl)(2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)acrylate **3g**

A white solid, this is a known compound,[5] 93% yield, 37 mg (*syn*:*anti* = 64:36); $[\alpha]^{20}_{D}$ = -228.7 (c 1.85, $CHCl_3$) for 92% ee (*syn*) and 89% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 97/3, 0.5 mL/min, 210 nm, for *syn* product t_{major} = 17.460 min, t_{minor} = 31.167 min; for *anti* product t_{major} = 26.322 min, t_{minor} = 43.432 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.46 (s, 1.08H, CH_3), 3.66 (s, 1.92H, CH_3), 5.34 (s, 0.64H, $=CH_2$), 5.38 (s, 0.36H, $=CH_2$), 5.57 (d, J = 1.2 Hz, 0.36H, $=CH_2$), 5.65 (s, 0.64H, $=CH_2$), 6.27 (s, 0.36H, CH), 6.40 (s, 0.64H, CH), 6.76-6.80 (m, 3H, Ar), 6.92-6.96 (m, 1H, Ar), 6.99-7.16 (m, 2H, Ar), 7.23-7.35 (m, 5H, Ar), 7.46-7.51 (m, 2H, Ar); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ □-114.83, -114.69.

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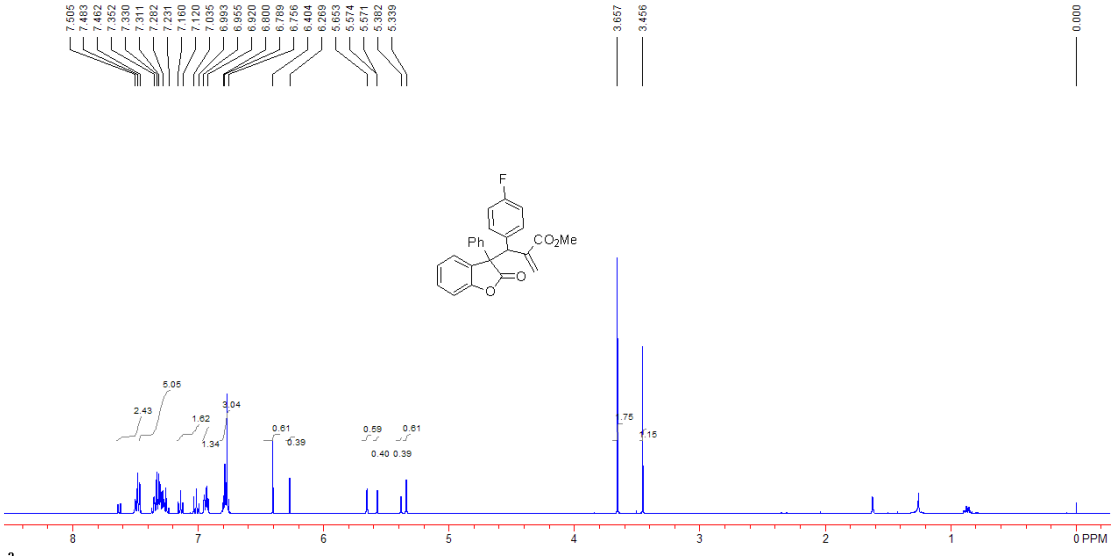
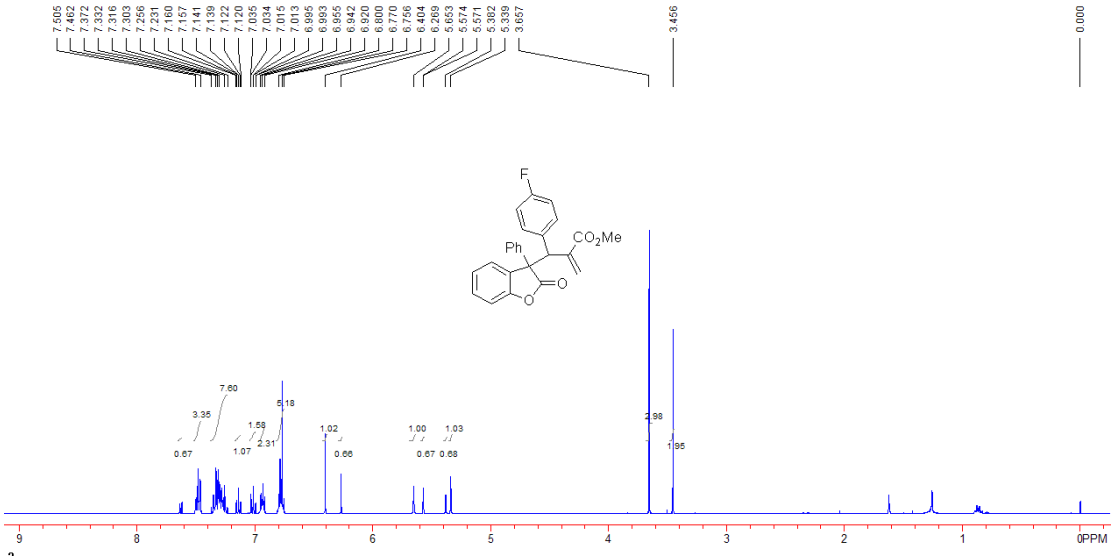
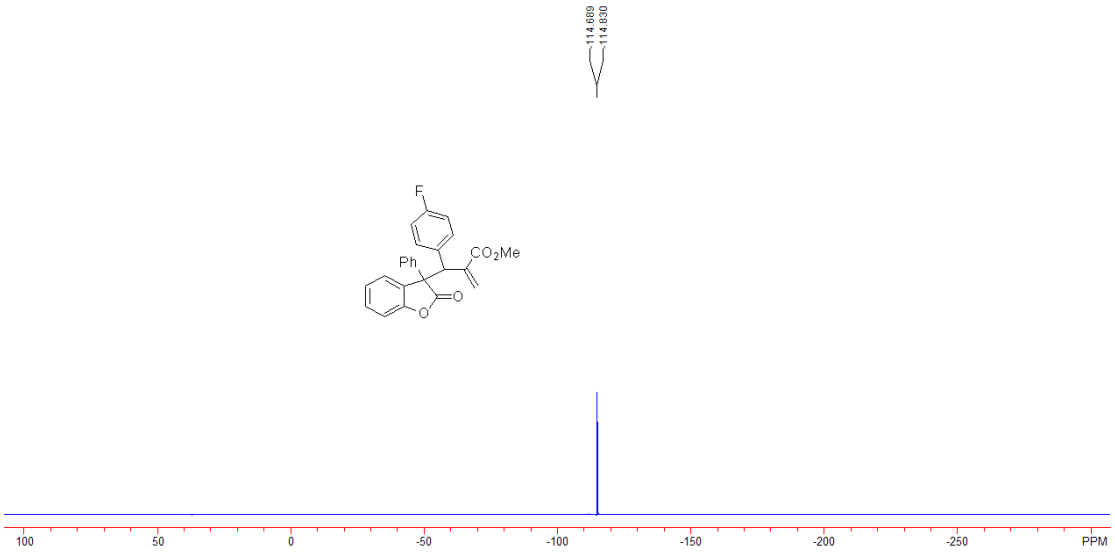
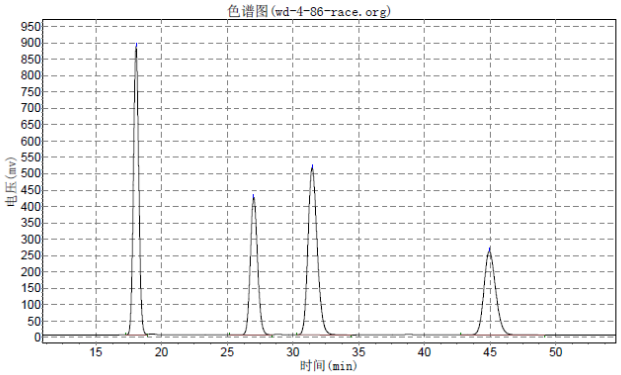






实验时间：2011-07-20,18:39:22
谱图文件:D:\HPLC\SIOC液相\MBH AAA\wd-4-86-race.org

实验者:
报告时间：2012-01-05,20:43:07
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		18.073	881430.250	24778986.000	30.4113
2		27.023	419636.563	16027287.000	19.6703
3		31.468	510919.063	24940930.000	30.6101
4		44.942	256138.547	15732261.000	19.3083
总计			2068124.422	81479464.000	100.0000

峰参数表

峰宽	斜率	漂移	最小面积	时间变参	锁定时间	停止时间	样品重量
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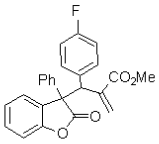
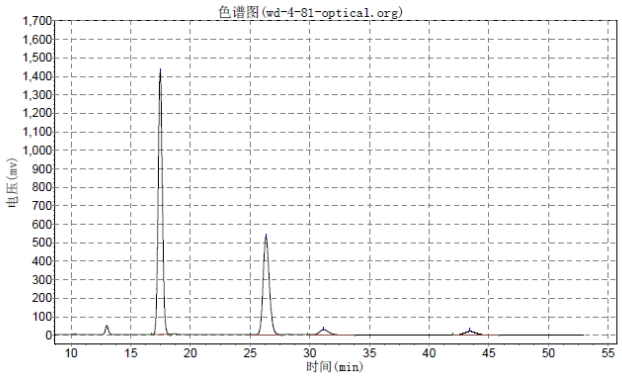


AD-H, 1.0 ml/min, Hexane/iPrOH = 97/3, 210nm

N2000 数据工作站 1

实验时间：2011-07-20,19:44:06
谱图文件:D:\HPLC\SIOC液相\MBH AAA\wd-4-81-optical.org

实验者：
报告时间：2012-01-05,20:44:02
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.460	1417212.625	34751088.000	61.5959
2		26.322	529177.625	19091314.000	33.8391
3		31.167	27199.533	1490820.000	2.6425
4		43.432	19096.063	1084653.250	1.9225
总计			1992685.846	56417875.250	100.0000

峰参数表

峰宽	斜率	漂移	最小面积	时间变参	锁定时间	停止时间	样品重量
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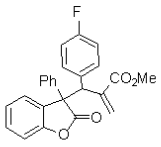
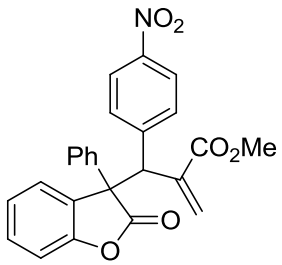


AD-H, 1.0 ml/min, Hexane/iPrOH = 97/3, 210nm

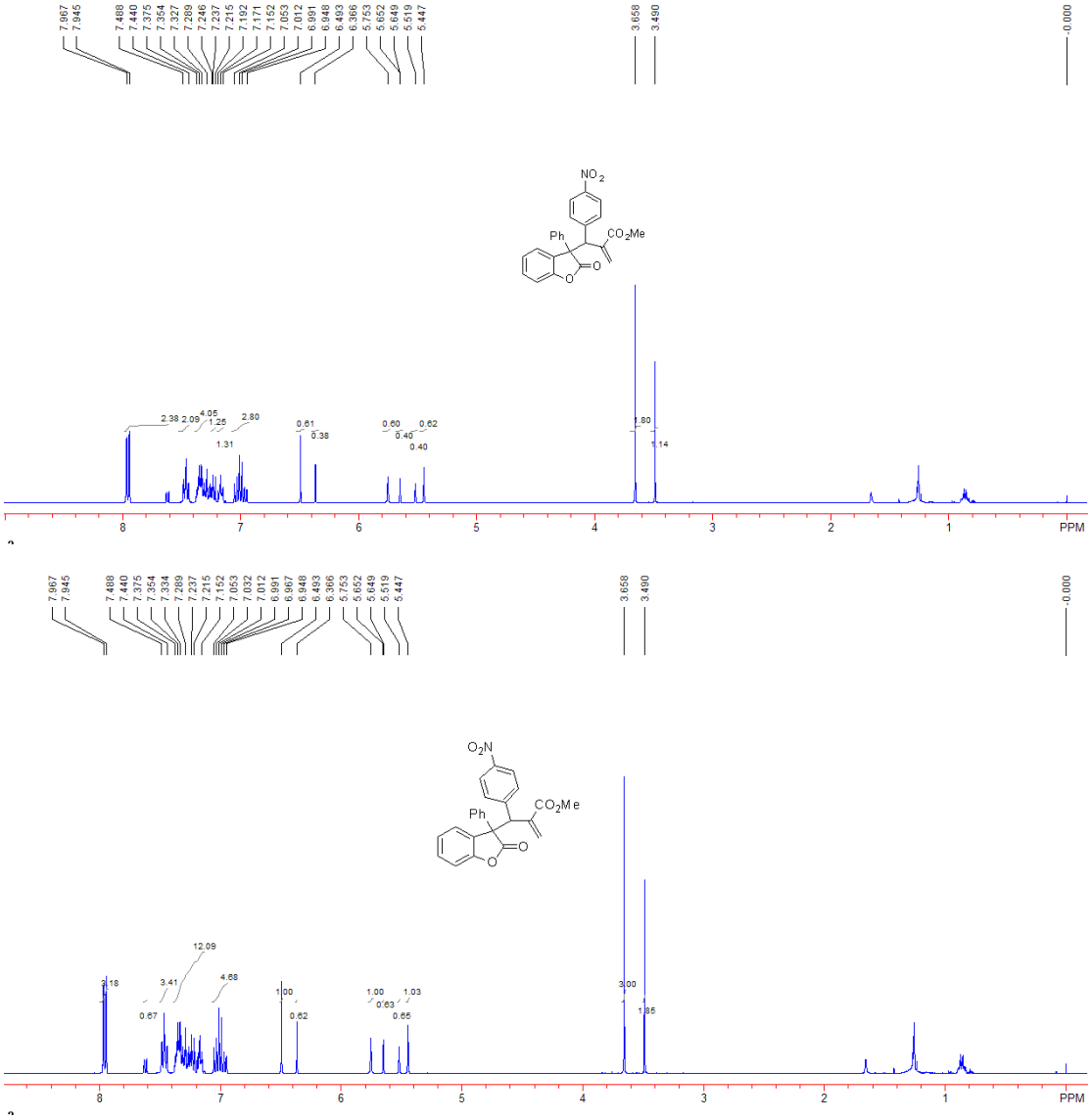
Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 97/3, 0.5 mL/min, 210 nm, for *syn* product t_{major} = 17.460 min, t_{minor} = 31.167 min; for *anti* product t_{major} = 26.322 min, t_{minor} = 43.432 min;



Methyl 2-((4-nitrophenyl)(2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)acrylate **3h**

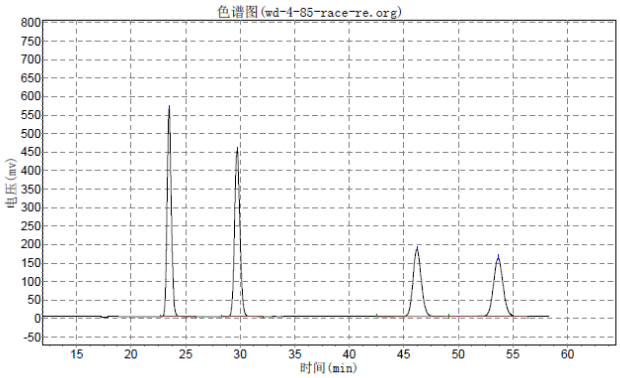
A white solid, this is a known compound,[5] 98% yield, 42 mg (*syn*:*anti* = 58:42); $[\alpha]^{20}_{D}$ = -171.4 (c 2.8, $CHCl_3$) for 95% ee (syn) and 92% ee (anti); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, 210 nm, for *syn* product t_{major} = 22.917 min, t_{minor} = 28.935 min; for *anti* product t_{major} = 51.235 min, t_{minor} = 44.657 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.49 (s, 1.26H, CH_3), 3.66 (s, 1.74H, CH_3), 5.45 (s, 0.58H, =CH_2), 5.52 (s, 0.42H, =CH_2), 5.65 (d, *J* = 1.2 Hz, 0.42H,

=CH_2), 5.75 (s, 0.58H, =CH_2), 6.37 (s, 0.42H, CH), 6.49 (s, 0.58H, CH), 6.95-7.05 (m, 3H, Ar), 7.15-7.19 (m, 1H, Ar), 7.22-7.25 (m, 1H, Ar), 7.29-7.38 (m, 4H, Ar), 7.44-7.49 (m, 2H, Ar), 7.95-7.97 (m, 2H, Ar).



实验时间：2011-07-21,17:25:06
谱图文件:D:\HPLC\SIOC液相\MBH AAA\wd-4-85-race-re.org

实验者：
报告时间：2012-01-05,20:37:29
积分方法:面积归一法

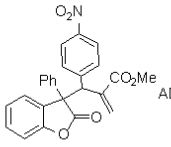


分析结果表

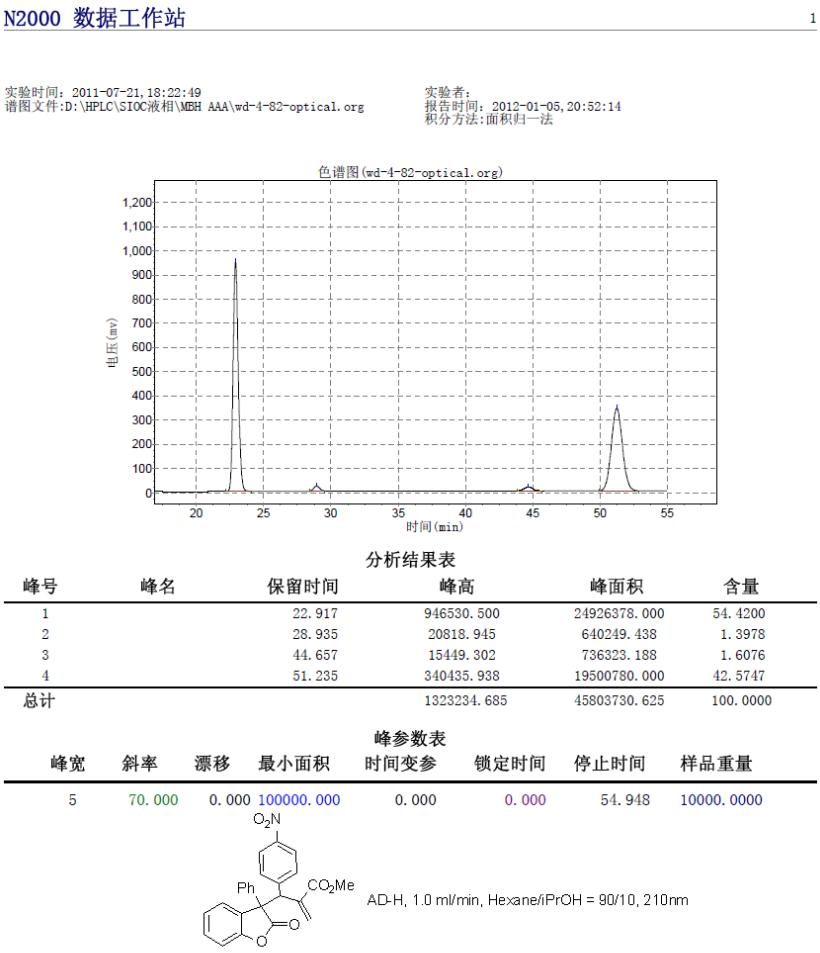
峰号	峰名	保留时间	峰高	峰面积	含量
1		23.488	562525.188	15296004.000	30.8059
2		29.725	449054.969	15251658.000	30.7166
3		46.202	181389.391	9631626.000	19.3979
4		53.648	156549.188	9473547.000	19.0796
总计			1349518.734	49652835.000	100.0000

峰参数表

峰宽	斜率	漂移	最小面积	时间变参	锁定时间	停止时间	样品重量
5	70.000	0.000	1000000.000	0.000	0.000	58.270	10000.0000



AD-H, 1.0 ml/min, Hexane/iPrOH = 90/10, 210nm


N2000 数据工作站 1

实验时间：2011-07-21,18:22:49
谱图文件:D:\HPLC\SIOC液相\MEH AAA\wd-4-82-optical.org
实验者:
报告时间：2012-01-05,20:52:14
积分方法:面积归一法

色谱图(wd-4-82-optical.org)

电压(mv)

时间(min)

分析结果表

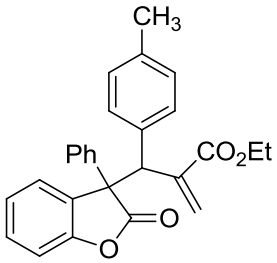
峰号	峰名	保留时间	峰高	峰面积	含量
1		22.917	946530.500	24926378.000	54.4200
2		28.935	20818.945	640249.438	1.3978
3		44.657	15449.302	736323.188	1.6076
4		51.235	340435.938	19500780.000	42.5747
总计			1323234.685	45803730.625	100.0000

峰参数表

峰宽	斜率	漂移	最小面积	时间变参	锁定时间	停止时间	样品重量
5	70.000	0.000	100000.000	0.000	0.000	54.948	10000.0000

AD-H, 1.0 ml/min, Hexane/iPrOH = 90/10, 210nm

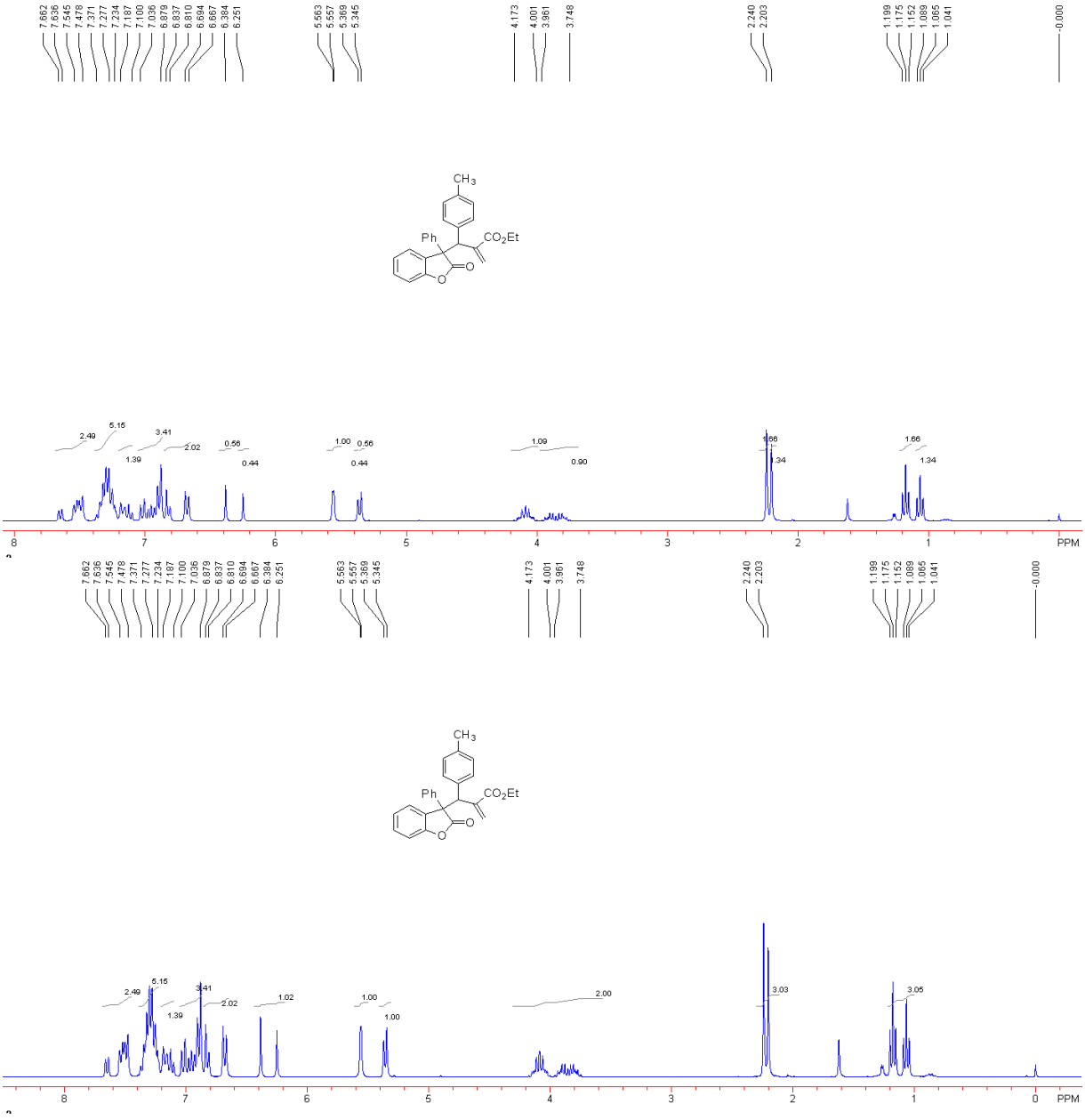
Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, 210 nm, for *syn* product t_{major} = 22.917 min, t_{minor} = 28.935 min; for *anti* product t_{major} = 51.235 min, t_{minor} = 44.657 min

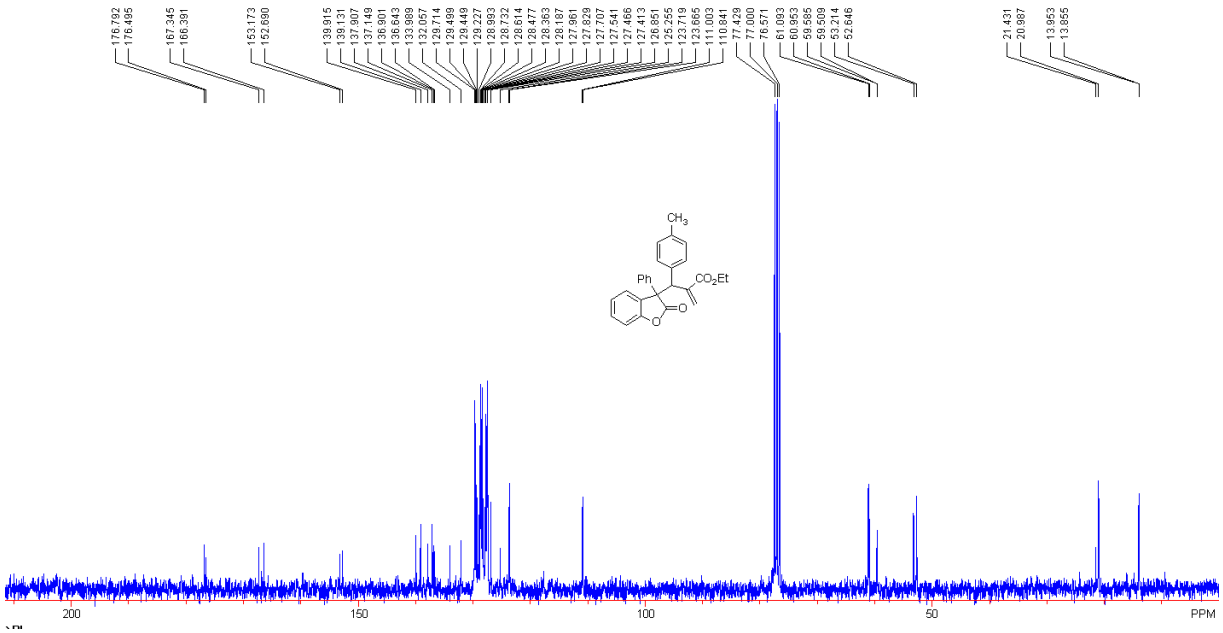


Ethyl 2-((2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)(p-tolyl)methyl)acrylate **3i**

A colorless oil, 85% yield, 35 mg (*syn*:*anti* = 56:44); $[\alpha]^{20}_{D}$ = -187.7 (c 1.2, $CHCl_3$) for 95% ee (*syn*) and 92% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 98/2, 1.0 mL/min, 210 nm, for *syn* product t_{major} = 14.540 min, t_{minor} = 29.405 min; for *anti* product t_{major} = 33.103 min, t_{minor} = 42.455 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.07 (t, *J* = 9.6 Hz, 1.32H, CH_3), 1.18 (t, *J* = 9.6 Hz, 1.68H, CH_3), 2.20 (s, 1.32H, CH_3), 2.24 (s, 1.68H, CH_3), 3.75-3.96 (m, 0.88H, CH_2), 4.00-4.17 (m, 1.12H,

CH_2), 5.35 (s, 0.56H, $=CH_2$), 5.37 (s, 0.44H, $=CH_2$), 5.55 (s, 0.44H, $=CH_2$), 5.56 (s, 0.56H, $=CH_2$), 6.25 (s, 0.44H, CH), 6.38 (s, 0.56H, CH), 6.67-6.84 (m, 2H, Ar), 6.88-7.04 (m, 3H, Ar), 7.23-7.37 (m, 5H, Ar), 7.48-7.66 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ□ 13.86, 13.95, 20.99, 21.43, 52.65, 53.21, 59.51, 59.59, 60.95, 61.09, 110.84, 111.00, 123.67, 123.72, 125.26, 126.85, 127.41, 127.47, 127.54, 127.71, 127.83, 127.96, 128.19, 128.36, 128.48, 128.61, 128.73, 128.99, 129.23, 129.45, 129.50, 129.71, 132.06, 133.99, 136.64, 136.90, 137.15, 137.91, 139.13, 139.92, 152.69, 153.17, 166.39, 167.35, 176.50, 176.79; IR (neat) ν 2980, 1796, 1712, 1460, 1232, 1127, 1061, 734, 696 cm^{-1}; MS (ESI) *m/z* 413.1 ($M+H^+$, 100). HRMS (ESI) Calcd. for $C_{27}H_{25}O_4$ requires ($M+H^+$) 413.1675, Found: 413.1738.





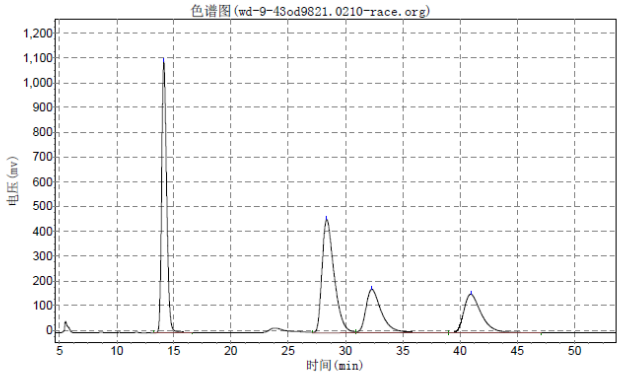
N2000 数据工作站 1

实验时间：2012-03-31,19:28:33
谱图文件:I:\SIOC液相\MEH AAA\wd-9-43od9821.0210-race.org

实验者:
报告时间：2012-04-03,14:43:00
积分方法:面积归一法

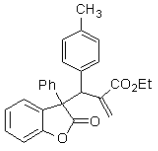
使用仪器类型:气相色谱　　检测器:FID　　进样器:分流

柱温:程序升温

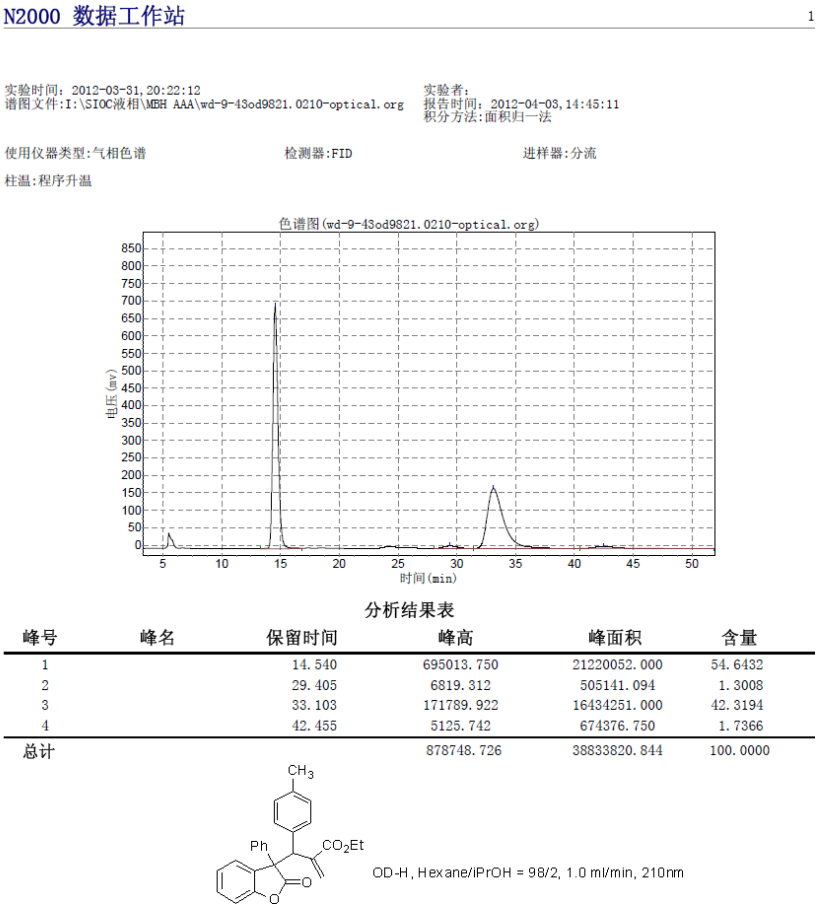


分析结果表

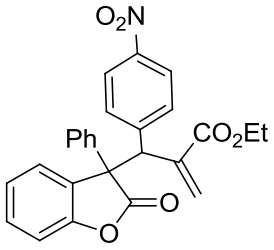
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.127	1095313.500	33259882.000	33.2720
2		28.345	458065.438	33680548.000	33.6929
3		32.285	175899.250	16685321.000	16.6914
4		40.923	155865.781	16337720.000	16.3437
总计			1885143.969	99963471.000	100.0000



OD-H, Hexane/iPrOH = 98/2, 1.0 ml/min, 210nm



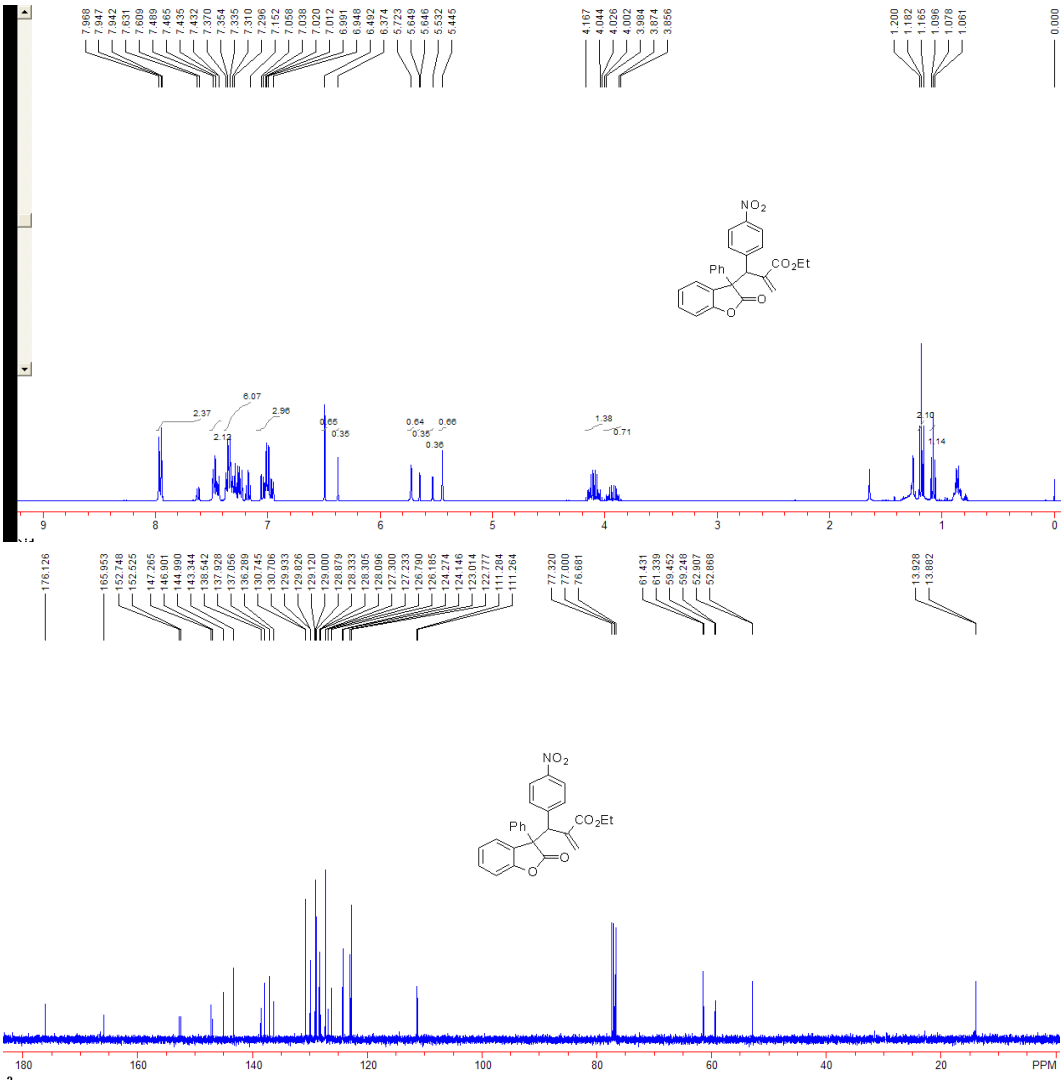
Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 98/2, 1.0 mL/min, 210 nm, for *syn* product t_{major} = 14.540 min, t_{minor} = 29.405 min; for *anti* product t_{major} = 33.103 min, t_{minor} = 42.455 min



Ethyl 2-((4-nitrophenyl)(2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)acrylate **3j**

A yellowish solid, 95% yield, 42 mg, m.p. 65-67 ^{o}C, (*syn*:*anti* = 55:45); $[\alpha]^{20}_{D}$ = -229.1 (c 2.0, $CHCl_3$) for 93% (*syn*) and 88% (*anti*) ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 0.8 mL/min, 230 nm, for *syn* product t_{major} = 15.727 min, t_{minor} = 19.227 min; for *anti* product t_{major} = 34.527 min, t_{minor} = 31.077 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.08 (t, *J* = 6.8 Hz, 1.35H, CH_3), 1.18 (t, *J* = 6.8 Hz, 1.65H, CH_3), 3.86-4.00 (m, 0.90H, CH_2), 4.03-4.17 (m, 1.10H, CH_2), 5.45 (s, 0.55H, =CH_2), 5.53 (s, 0.45H, =CH_2), 5.65 (d, *J* = 1.2 Hz, 0.45H, =CH_2), 5.72 (s, 0.55H, =CH_2), 6.37 (s, 0.45H, CH),

6.49 (s, 0.55H, CH), 6.95-7.06 (m, 3H, Ar), 7.15-7.37 (m, 6H, Ar), 7.43-7.49 (m, 2H, Ar), 7.61-7.97 (m, 2H,Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.88, 13.93, 52.87, 52.91, 59.25, 59.45, 61.34, 61.43, 111.26, 111.28, 122.78, 123.01, 124.15, 124.27, 126.19, 126.79, 127.23, 127.30, 128.10, 128.31, 128.33, 128.88, 129.00, 129.12, 129.83, 129.93, 130.71, 130.75, 136.29, 137.06, 137.93, 138.54, 143.34, 144.99, 146.90, 147.27, 152.53, 152.75, 165.95, 176.13; IR (neat) ν 2981, 1800, 1716, 1597, 1521, 1347, 1065, 757, 699 cm^{-1}; MS (ESI) *m/z* 466.4 (M+Na$^+$, 100). HRMS (ESI) Calcd. for $C_{26}H_{21}NO_6Na$ requires (M+Na$^+$) 466.1268, Found: 466.1261.



HPLC REPORT

Sample Name:wd-4-95-A-rac ad250 95 0.8.che
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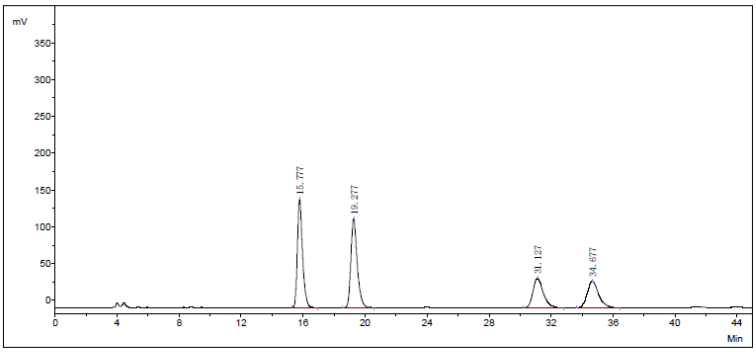
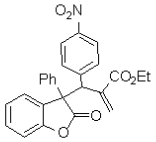
Time:12:30
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.777	146972.8	3380264.2	32.3040
2	2	19.277	120208.5	3393885.9	32.4341
3	3	31.127	39912.9	1839532.1	17.5797
4	4	34.677	35955.1	1850246.1	17.6821
Total			343049.3	10463928.3	100.0000



AD-H, 0.8 ml/min, Hexane/iPrOH = 95/5, 230nm

HPLC REPORT

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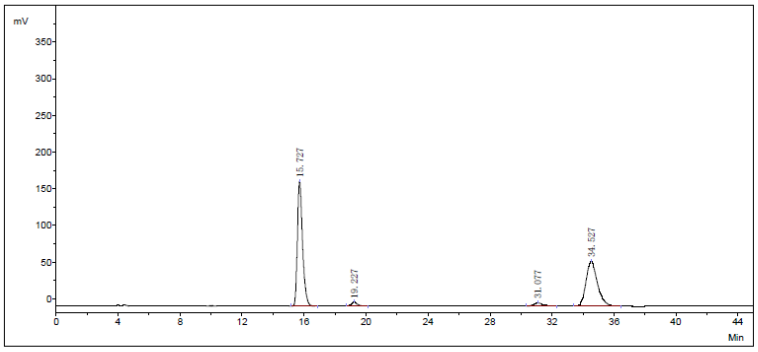
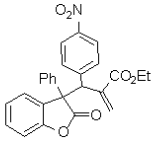
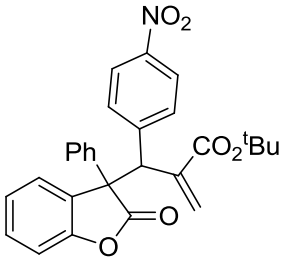
Time:13:39
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.727	169650.8	3919545.2	52.9898
2	2	19.227	5306.2	145880.2	1.9722
3	3	31.077	4488.4	200468.8	2.7102
4	4	34.527	61063.8	3130898.5	42.3278
Total			240509.2	7396792.7	100.0000

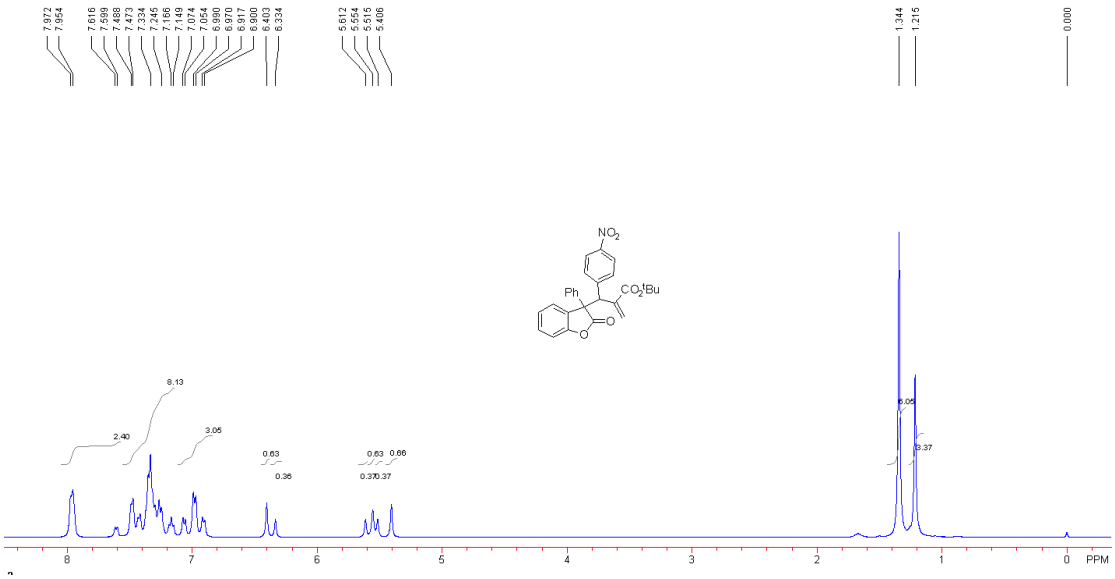


AD-H, 0.8 ml/min, Hexane/iPrOH = 95/5, 230nm



Tert-butyl 2-((4-nitrophenyl)(2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)acrylate **3k**

A white solid, 87% yield, 41 mg, m.p. 147-149 ^{o}C, (*syn*:*anti* = 54:46); $[\alpha]^{20}_{D}$ = -119.7 (c 1.8, $CHCl_3$) for 91% ee (*syn*) and 85% ee (*anti*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 93/7, 0.5 mL/min, 230 nm, for *syn* product t_{major} = 17.477 min, t_{minor} = 14.977 min; for *anti* product t_{major} = 19.777 min, t_{minor} = 16.177 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (s, 4.14H, ^{t}Bu), 1.34 (s, 4.86H, ^{t}Bu), 5.41 (s, 0.54H, =CH_2), 5.52 (s, 0.46H, =CH_2), 5.55 (s, 0.54H, =CH_2), 5.61 (s, 0.46H, =CH_2), 6.33 (s, 0.46H, CH), 6.40 (s, 0.54H, CH), 6.90-7.07 (m, 3H, Ar), 7.15-7.49 (m, 8H, Ar), 7.96 (d, *J* = 7.2 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ □27.64, 27.78, 52.41, 52.79, 59.00, 59.71, 81.69, 81.77, 111.18, 111.27, 122.68, 122.90, 124.04, 124.29, 126.33, 126.83, 127.16, 127.31, 127.85, 128.13, 128.25, 128.32, 128.45, 128.93, 129.77, 129.87, 130.66, 130.73, 136.58, 137.04, 139.21, 139.50, 143.72, 145.52, 146.72, 147.14, 152.58, 152.69, 165.00, 165.51, 176.10, 176.29; IR (neat) ν 2978, 1801, 1709, 1604, 1524, 1347, 1146, 1065, 757 cm^{-1}; MS (ESI) *m/z* 494.5 (M+Na^{+}, 100). HRMS (MALDI) Calcd. for $C_{28}H_{25}NO_6Na$ requires (M+Na^{+}) 494.1579, Found: 494.1574.



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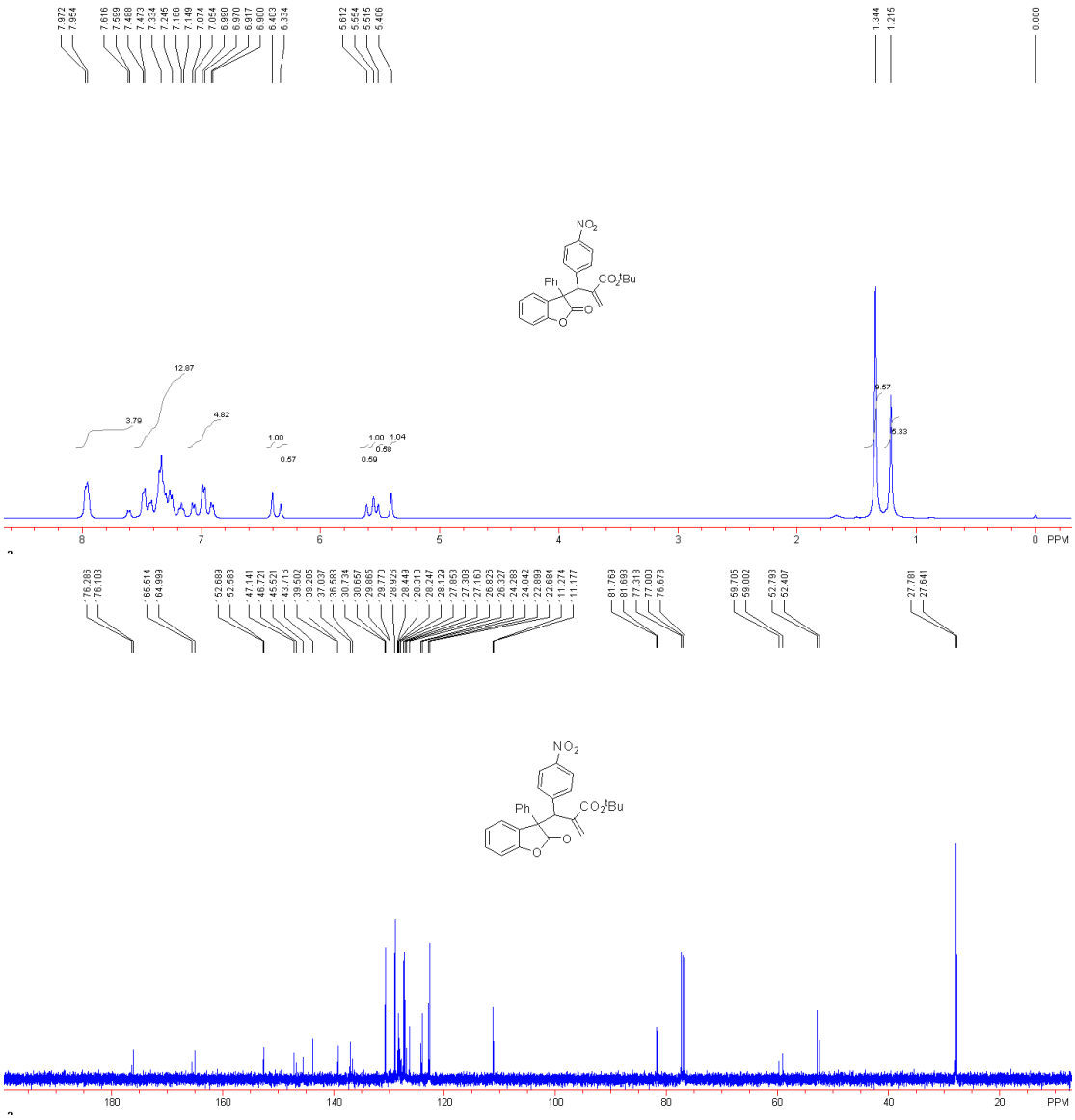

HPLC REPORT

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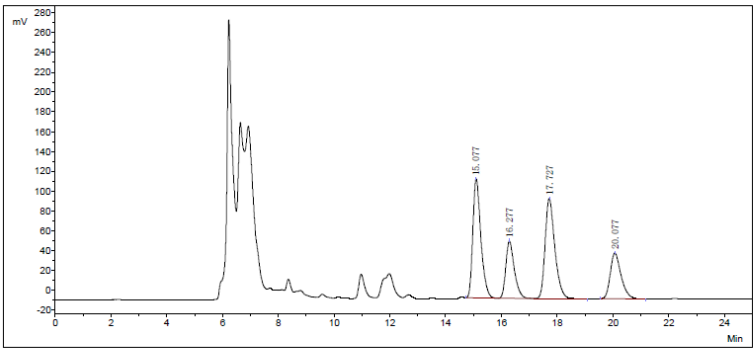
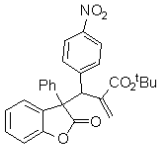
Time:06:55
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.077	119233.2	2407450.9	32.9141
2	2	16.277	57693.0	1230426.5	16.8221
3	3	17.727	100400.0	2432569.9	33.2575
4	4	20.077	46115.0	1243896.3	17.0063
Total			323441.2	7314343.6	100.0000



AD-H, 0.5 ml/min, Hexane/iPrOH = 93/7, 230nm

HPLC REPORT

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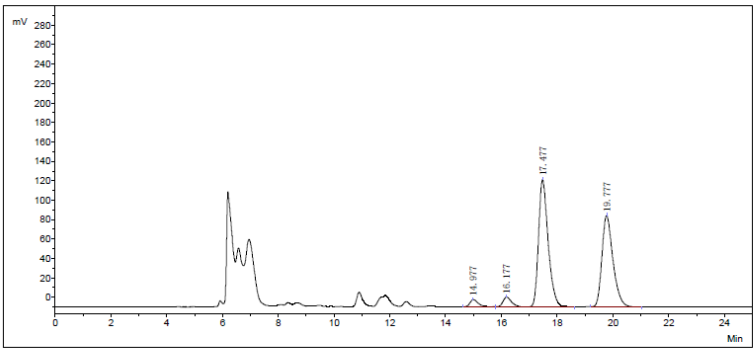
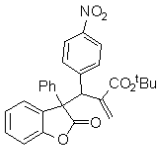
Time:07:42
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	14.977	7345.7	151133.6	2.4949
2	2	16.177	10002.3	211709.0	3.4948
3	3	17.477	130668.9	3118097.1	51.4728
4	4	19.777	93824.7	2576822.2	42.5375
Total			241841.6	6057761.9	100.0000



AD-H, 0.5 ml/min, Hexane/iPrOH = 93/7, 230nm

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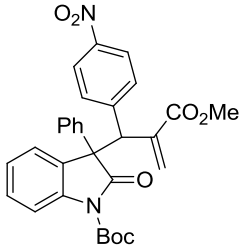
5. Characterization and spectra charts containing HPLC traces for products 5a-k.



Tert-butyl

3-(2-(methoxycarbonyl)-1-(4-nitrophenyl)allyl)-2-oxo-3-phenylindoline-1-carboxylate **5a**

A white solid, 91% yield, 48 mg, m.p. 90-92 ^{o}C, (*anti:syn* = 67:33); $[\alpha]^{20}_{D}$ = -200.0 (c 0.1, $CHCl_3$) for 98% ee (*anti*) and 89% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 230 nm, for *anti* product t_{major} = 7.057 min, t_{minor} = 8.517 min; for *syn* product t_{major} = 9.900 min, t_{minor} = 17.785 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.56 (s, 9.00H, for *syn* and *anti*, Boc), 3.48 (s, 0.99H, CH_3), 3.64 (s, 2.01H, CH_3), 5.40 (s, 0.67H, $=CH_2$), 5.53 (s, 0.33H, $=CH_2$), 5.59 (s, 0.33H, $=CH_2$), 5.97 (s, 0.67H, $=CH_2$), 6.32 (s, 0.33H, CH), 6.49 (s, 0.67H, CH), 6.99 (d, *J* = 8.8 Hz, 2H, Ar), 7.13-7.21 (m, 1H, Ar), 7.25-7.35 (m, 5H, Ar), 7.39-7.44 (m, 2H, Ar), 7.60-7.66 (m, 1H, Ar), 7.91 (d, *J* = 8.8 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.88, 28.03, 52.15, 52.31, 53.17, 53.26, 60.15, 60.28, 84.76, 115.05, 115.19, 122.54, 122.72, 124.17, 124.27, 125.53, 126.60, 127.57, 127.80, 127.86, 127.96, 128.60, 128.80, 128.95, 129.03, 129.20, 130.70, 130.82, 136.95, 137.36, 137.99, 138.74, 138.94, 139.60, 143.88, 145.37, 146.75, 147.09, 148.40, 166.75, 167.25, 175.19, 175.43; IR (neat) ν 2982, 1793, 1762, 1719, 1604, 1522, 1251, 1147, 738 cm^{-1}; MS (ESI) *m/z* 551.4 (M+Na^{+}, 100). HRMS (ESI) Calcd. for $C_{30}H_{28}N_2O_7Na$ requires (M+Na^{+}) 551.1797, Found: 551.1789.

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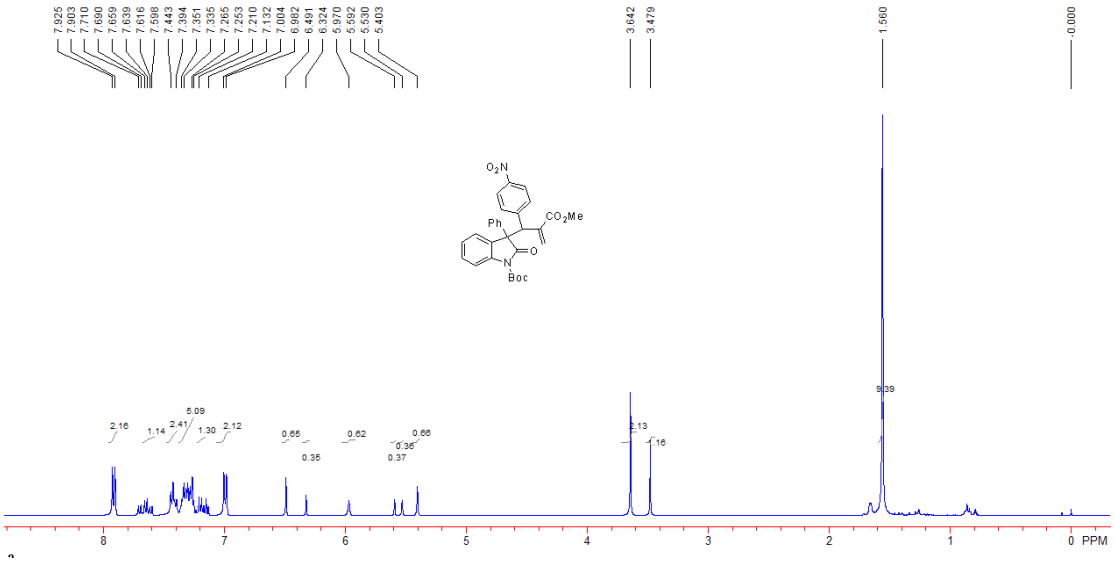

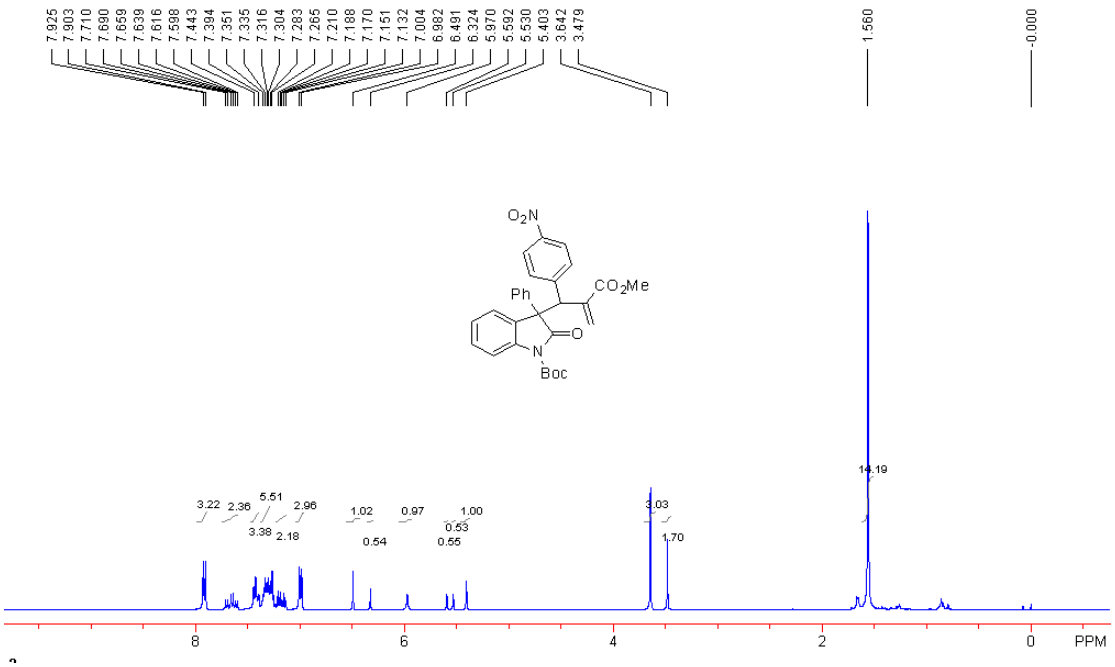

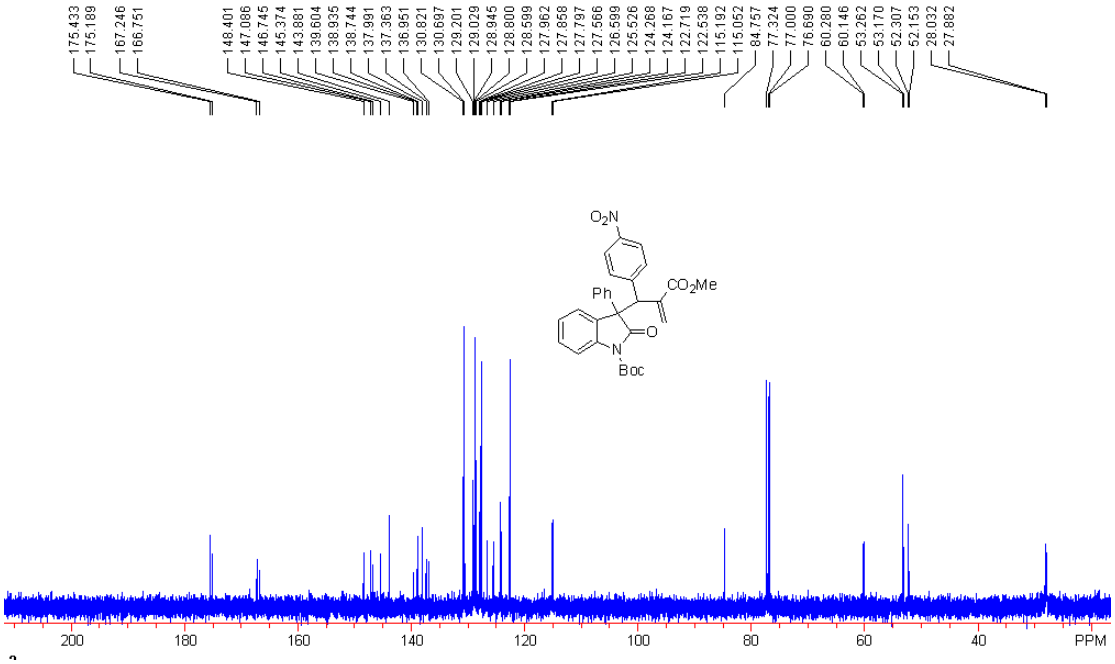

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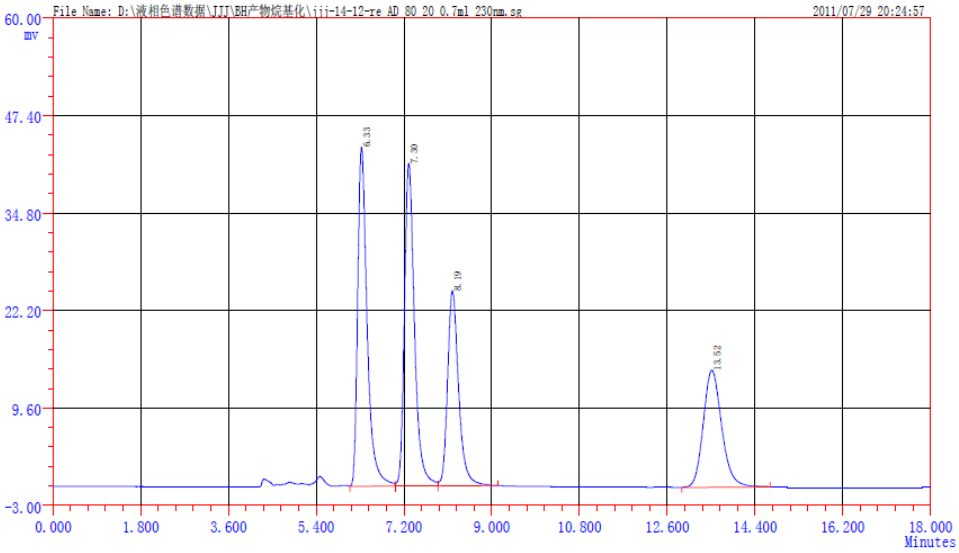

ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.330	43879	591218.0	29.7703	1.55	4399
2		7.300	41730	597751.8	30.0993	1.35	5176
3		8.193	25220	398571.2	20.0697	1.31	5357
4		13.518	15113	398392.5	20.0607	1.18	5241
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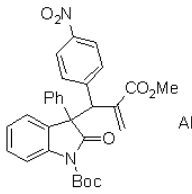
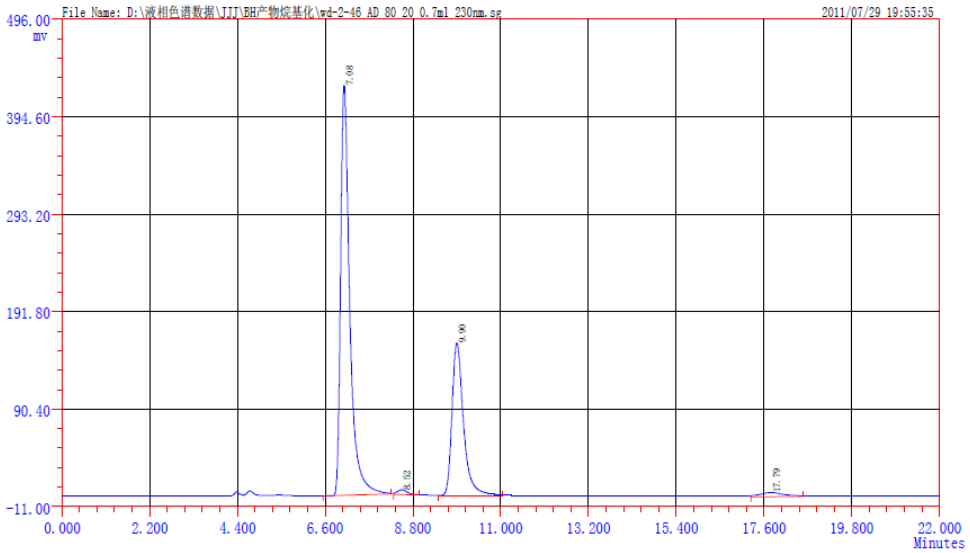
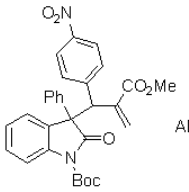


AD-H, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 230nm

WH-500 色 谱 分 析 报 告

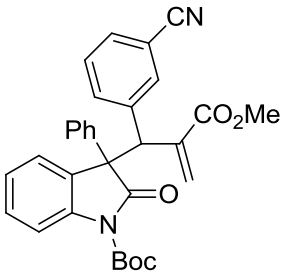


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		7.075	426652	6854901.0	66.1395	1.69	3865
2		8.517	4970	86037.4	0.8301	1.20	4824
3		9.900	159276	3240683.8	31.2677	1.45	4719
4		17.785	4340	182689.9	1.7627	1.27	3558
Σ:			595238	10364312.3	100.0000		



AD-H, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 254nm

Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 230 nm, for *anti* product t_{major} = 7.057 min, t_{minor} = 8.517 min; for *syn* product t_{major} = 9.900 min, t_{minor} = 17.785 min

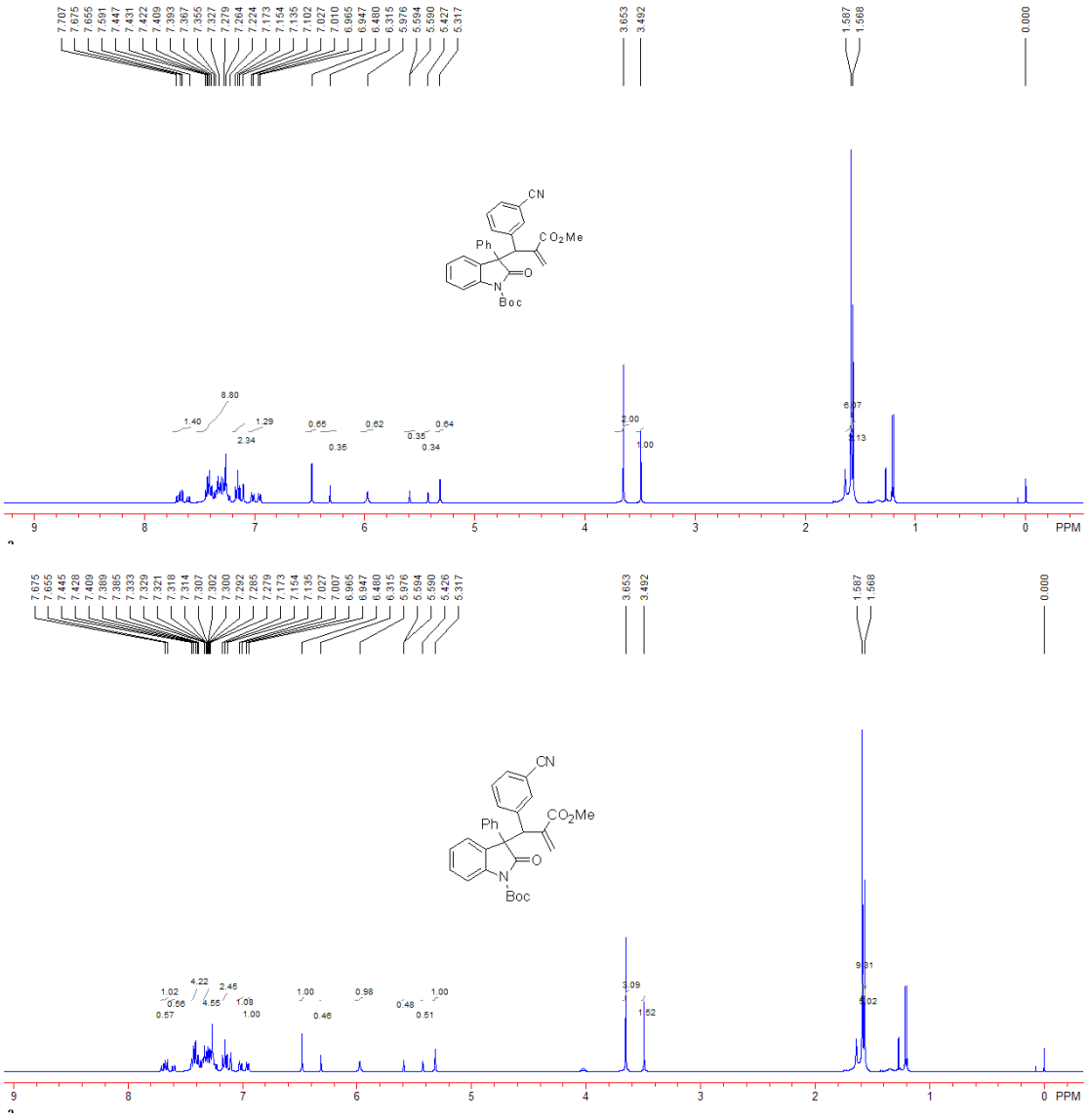


Tert-butyl

3-(1-(3-cyanophenyl)-2-(methoxycarbonyl)allyl)-2-oxo-3-phenylindoline-1-carboxylate **5b**

A white solid, this is a known compound.[6] 86% yield, 43 mg (*anti*:*syn* = 62:38); $[\alpha]^{20}_{D}$ = -98.0 (c 0.15, $CHCl_3$) for 94% ee (anti) and 80% ee (syn); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 5.607 min, t_{minor} = 6.290 min; for *syn* product t_{major} = 7.147 min, t_{minor} = 8.542

min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.57 (s, 3.42H, Boc), 1.59 (s, 5.58H, Boc), 3.49 (s, 1.14H, CH_3), 3.65 (s, 1.86H, CH_3), 5.32 (s, 0.62H, $=CH_2$), 5.43 (s, 0.38H, $=CH_2$), 5.59 (d, *J* = 1.6 Hz, 0.38H, $=CH_2$), 5.98 (s, 0.62H, $=CH_2$), 6.32 (s, 0.38H, CH), 6.48 (s, 0.62H, CH), 6.95-7.03 (m, 1H, Ar), 7.10-7.17 (m, 2H, Ar), 7.22-7.45 (m, 9H, Ar), 7.59-7.71 (m, 1H, Ar).



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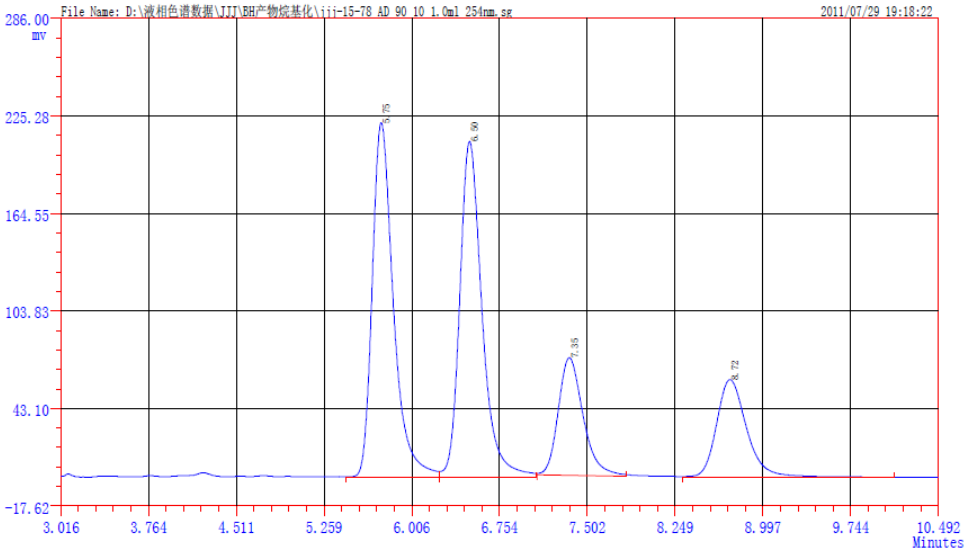
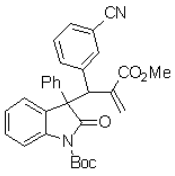
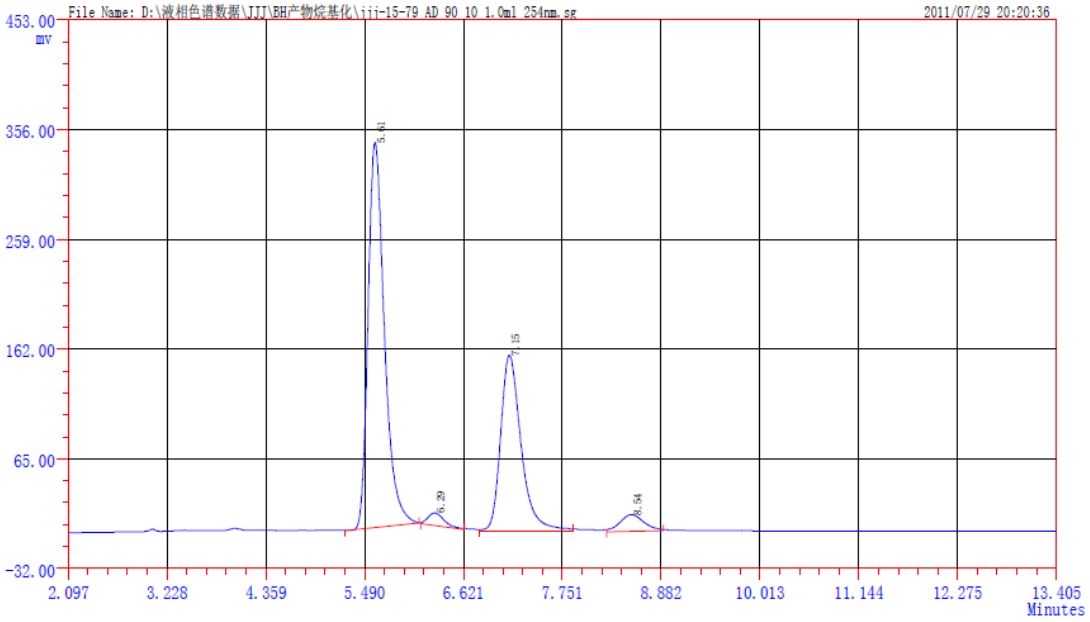


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		5.745	220907	2767386.9	35.9667	1.43	4192
2		6.498	209149	2765598.6	35.9434	1.30	4814
3		7.348	73159	1077072.4	13.9983	1.26	4965
4		8.717	60817	1084248.5	14.0916	1.26	4765
	Σ:		564032	7694306.3	100.0000		



AD-H, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254nm

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		5.607	340419	4435880.2	60.1622	1.45	3690
2		6.290	11063	143806.5	1.9504	1.04	4667
3		7.147	154922	2509030.1	34.0290	1.36	3881
4		8.542	14799	284484.0	3.8584	1.15	3935
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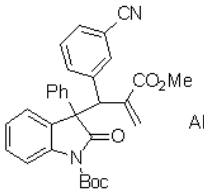
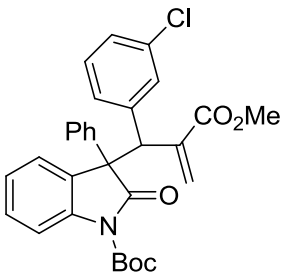


AD-H, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254nm

Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 5.607 min, t_{minor} = 6.290 min; for *syn* product t_{major} = 7.147 min, t_{minor} = 8.542 min

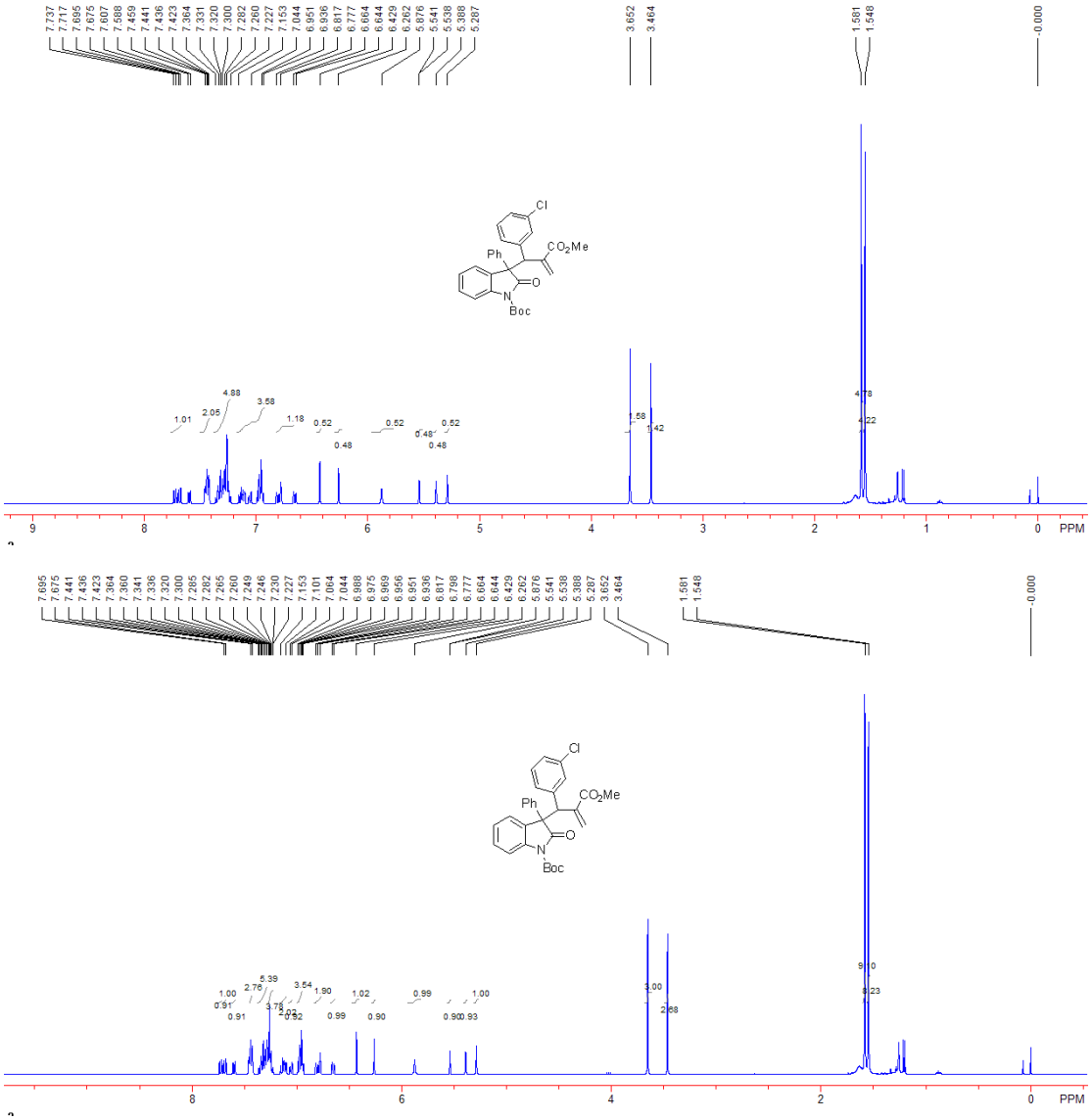


Tert-butyl

3-(1-(3-chlorophenyl)-2-(methoxycarbonyl)allyl)-2-oxo-3-phenylindoline-1-carboxylate **5c**

A white solid, this is a known compound.[6] 93% yield, 48 mg (*anti*:*syn* = 51:49); $[\alpha]^{20}_{D}$ = -254.6 (c 1.85, $CHCl_3$) for 92% ee (*anti*) and 87% ee (*syn*); Enantiomeric excess was

determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254 nm, for *anti* product t_{major} = 4.915 min, t_{minor} = 14.830 min; for *syn* product t_{major} = 5.487 min, t_{minor} = 16.798 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.55 (s, 4.41H, Boc), 1.58 (s, 4.78H, Boc), 3.46 (s, 1.47H, CH_3), 3.65 (s, 1.53H, CH_3), 5.29 (s, 0.51H, $=CH_2$), 5.39 (s, 0.49H, $=CH_2$), 5.54 (d, J = 1.2 Hz, 0.49H, $=CH_2$), 5.88 (s, 0.51H, $=CH_2$), 6.26 (s, 0.49H, CH), 6.43 (s, 0.51H, CH), 6.64-6.82 (m, 1H, Ar), 6.94-7.15 (m, 4H, Ar), 7.23-7.36 (m, 5H, Ar), 7.42-7.46 (m, 2H, Ar), 7.59-7.74 (m, 1H, Ar).



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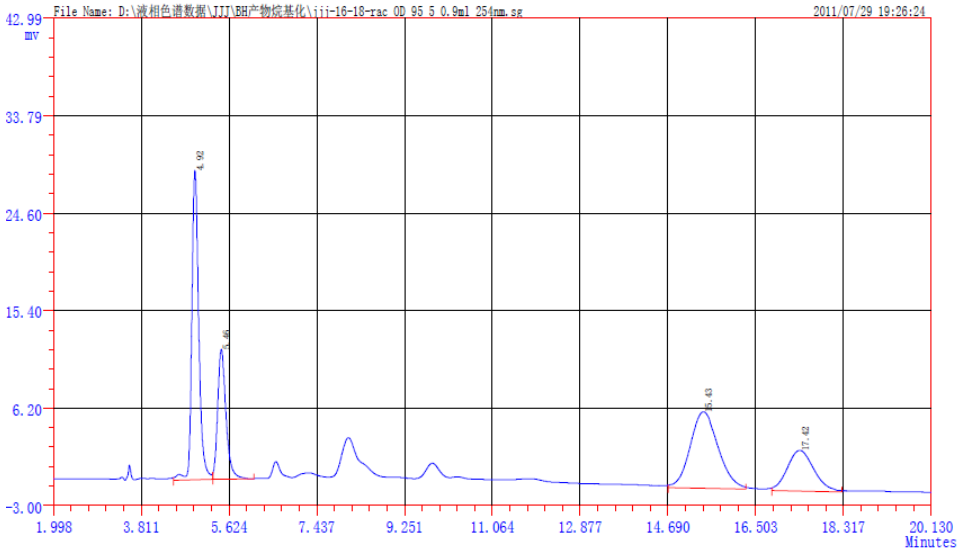
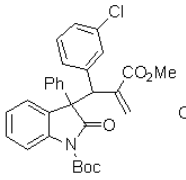


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		4.918	29217	291127.9	33.2162	1.29	4856
2		5.463	12295	147254.9	16.8011	1.28	4147
3		15.427	7206	290159.4	33.1057	1.06	2925
4		17.422	3850	147920.2	16.8770	1.11	4098
	Σ:		52568	876462.6	100.0000		



OD-H, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254nm

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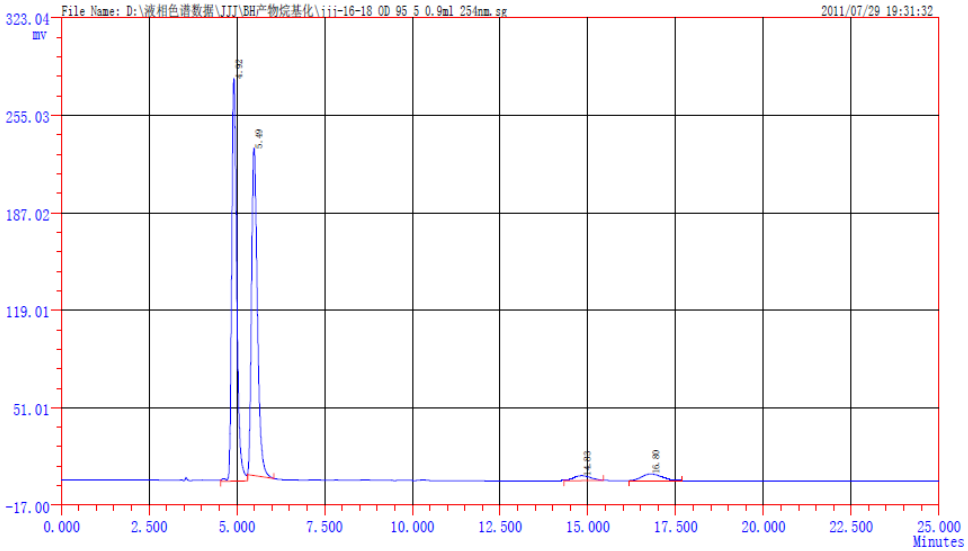
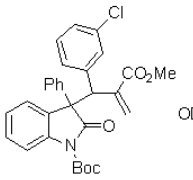
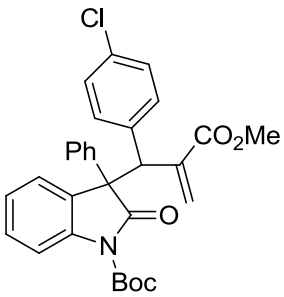


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		4.915	280984	2784728.2	48.5168	1.35	4902
2		5.487	228500	2648240.0	46.1388	1.36	4467
3		14.830	3432	120264.1	2.0953	1.13	3570
4		16.798	4664	186489.8	3.2491	1.19	3518
Σ:			517580	5739722.2	100.0000		



OD-H, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254nm

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254 nm, for *anti* product t_{major} = 4.915 min, t_{minor} = 14.830 min; for *syn* product t_{major} = 5.487 min, t_{minor} = 16.798 min

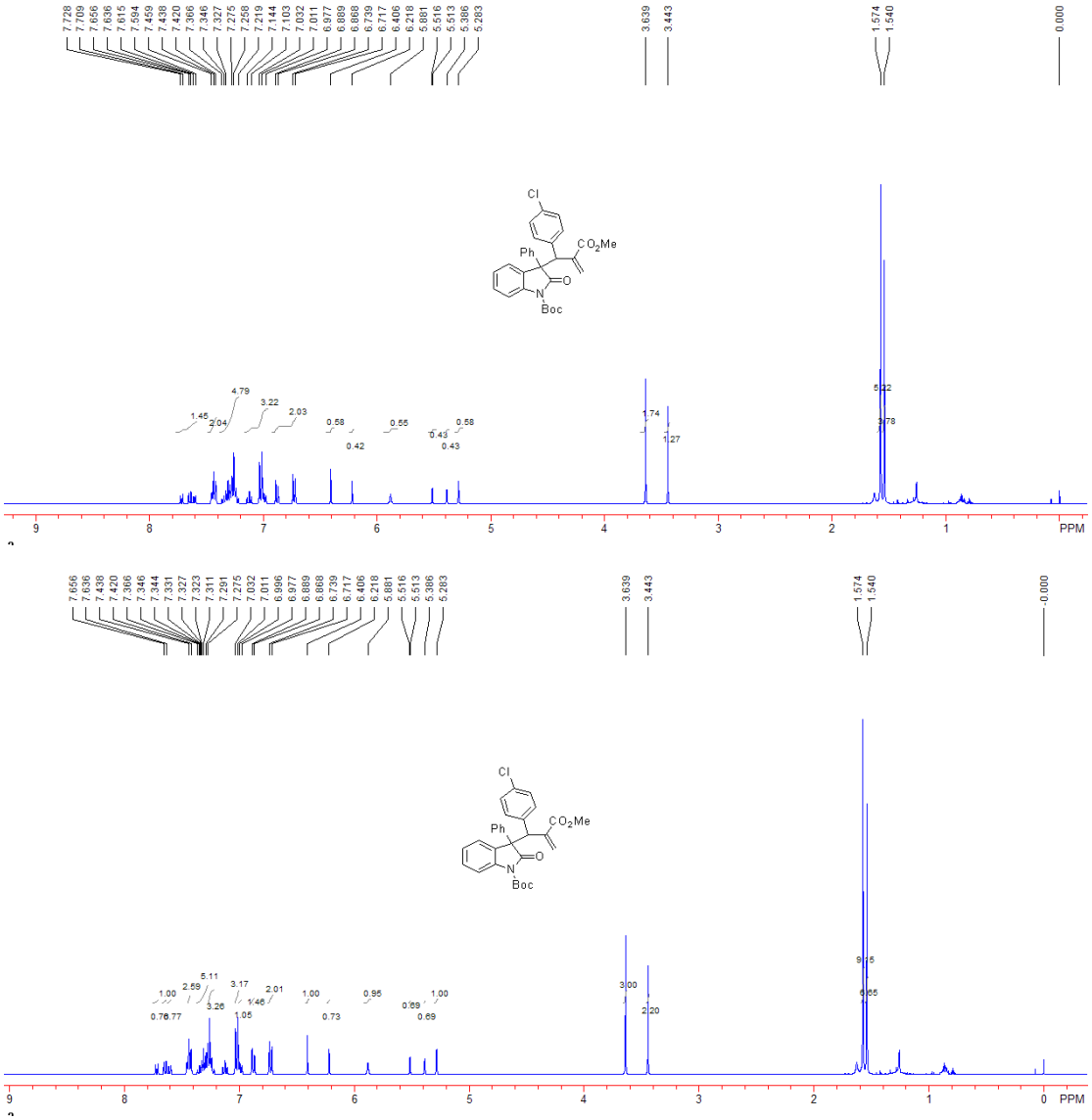


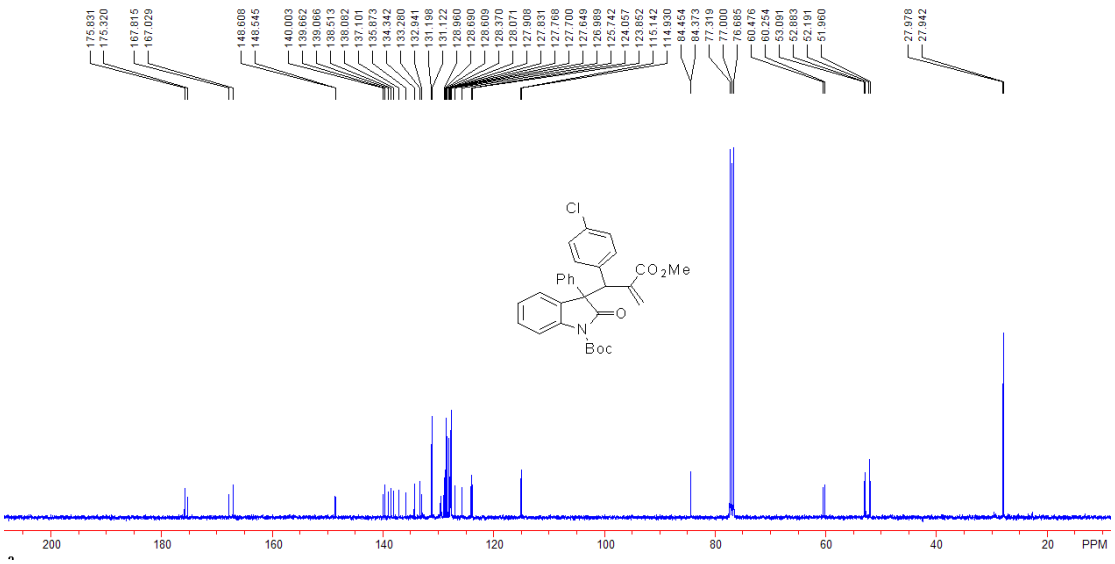
Tert-butyl

3-(1-(4-chlorophenyl)-2-(methoxycarbonyl)allyl)-2-oxo-3-phenylindoline-1-carboxylate **5d**

A white solid, this is a known compound.[6] 92% yield, 47 mg, m.p. 134-136 ^{o}C, (*anti*:*syn* = 59:41); $[\alpha]^{20}_{D}$ = -203.0 (c 0.1, $CHCl_3$) for 93% ee (*anti*) and 88% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 230 nm, for *anti* product t_{major} = 6.652 min, t_{minor} = 7.385 min; for *syn* product t_{major} =

7.985 min, t_{minor} = 13.052 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.54 (s, 3.69H, Boc), 1.57 (s, 5.31H, Boc), 3.44 (s, 1.23H, CH_3), 3.64 (s, 1.77H, CH_3), 5.28 (s, 0.59H, $=CH_2$), 5.39 (s, 0.41H, $=CH_2$), 5.51 (d, J = 1.2 Hz, 0.41H, $=CH_2$), 5.88 (s, 0.59H, $=CH_2$), 6.22 (s, 0.41H, CH), 6.41 (s, 0.59H, CH), 6.72-6.89 (m, 2H, Ar), 6.98-7.14 (m, 3H, Ar), 7.22-7.37 (m, 5H, Ar), 7.42-7.46 (m, 2H, Ar), 7.59-7.73 (m, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.94, 27.98, 51.96, 52.19, 52.88, 53.09, 60.25, 60.48, 84.37, 84.45, 114.93, 115.14, 123.85, 124.06, 125.74, 126.99, 127.65, 127.70, 127.77, 127.83, 127.91, 128.07, 128.37, 128.61, 128.69, 128.96, 131.12, 131.20, 132.94, 133.28, 134.34, 135.87, 137.10, 138.08, 138.51, 139.07, 139.66, 140.00, 148.55, 148.61, 167.03, 167.82, 175.32, 175.83; IR (neat) ν 2927, 1793, 1762, 1735, 1491, 1368, 1287, 1148, 738 cm^{-1}; MS (ESI) *m/z* 494.5 (M+Na^{+}, 100). HRMS (ESI) Calcd. for $C_{30}H_{28}ClNO_5Na$ requires (M+Na^{+}) 540.1563, Found: 540.1548.

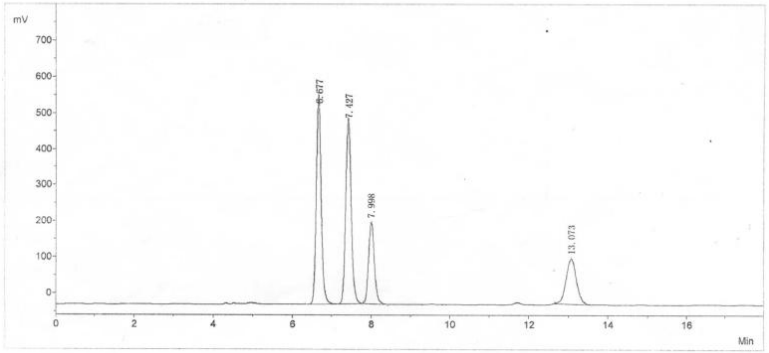




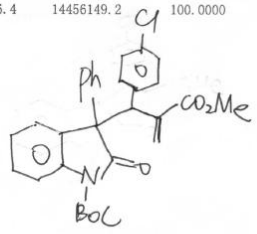
HPLC REPORT

Sample Name:jj-16-19-rac ad250 90.che
Time:14:03
column: AD-H(DP)
Velocity: 0.7

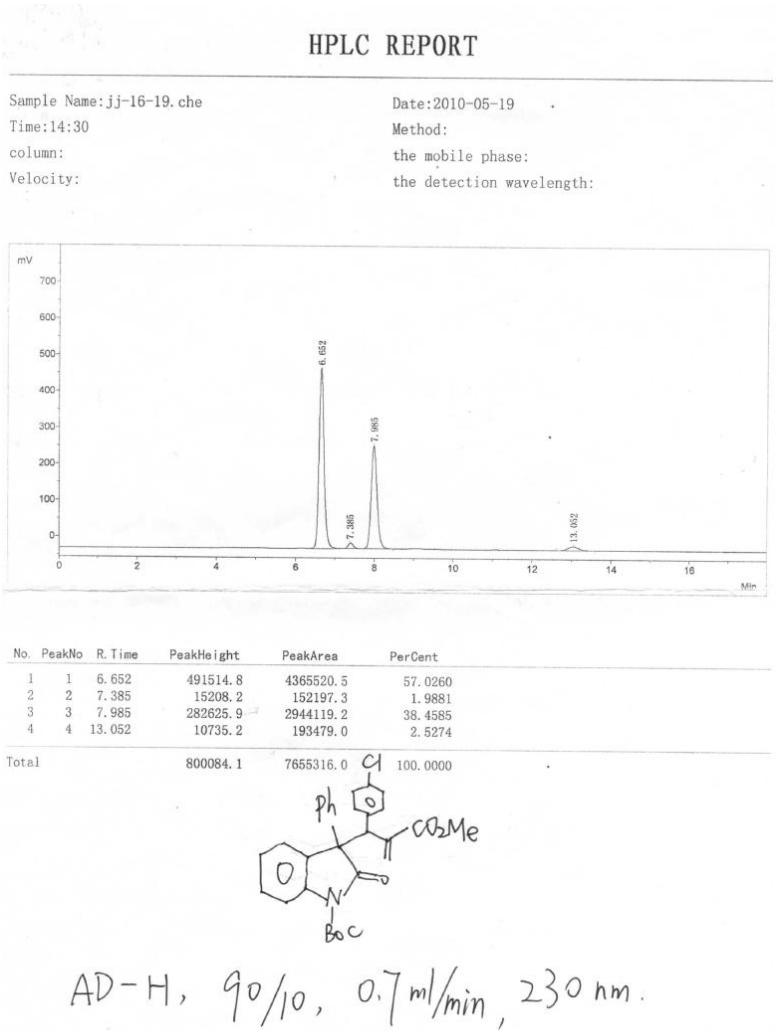
Date:2010-05-19
Method:
the mobile phase: 9:1
the detection wavelength: 230

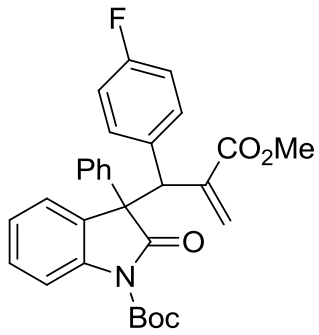


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	6.677	543457.5	4999209.2	34.5819
2	2	7.427	502362.5	4954883.8	34.2753
3	3	7.998	224095.2	2272195.6	15.7178
4	4	13.073	124201.2	2229860.6	15.4250
Total			1394116.4	14456149.2	100.0000



AD-H, 90/10, 0.7 ml/min, 230nm.



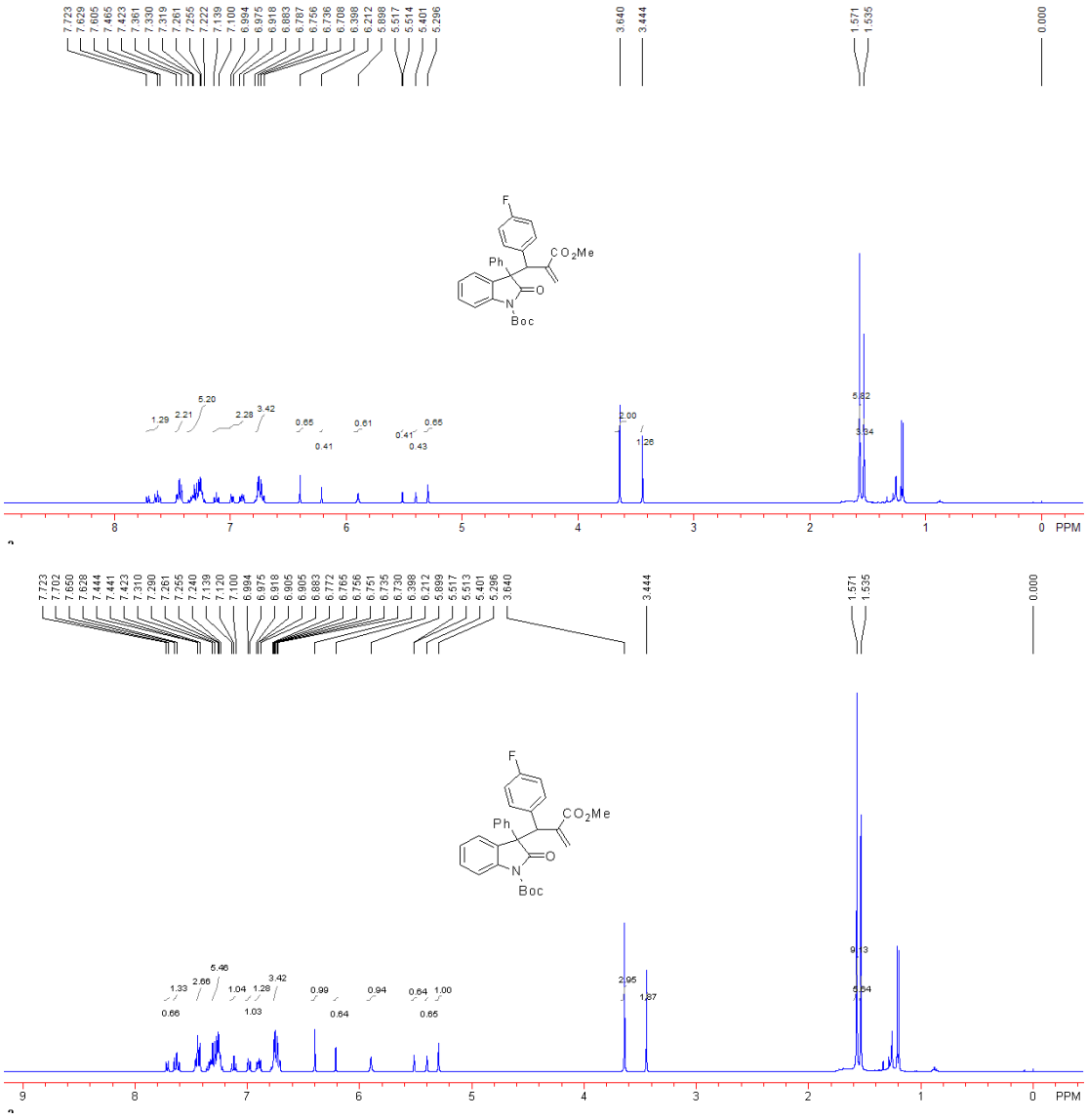


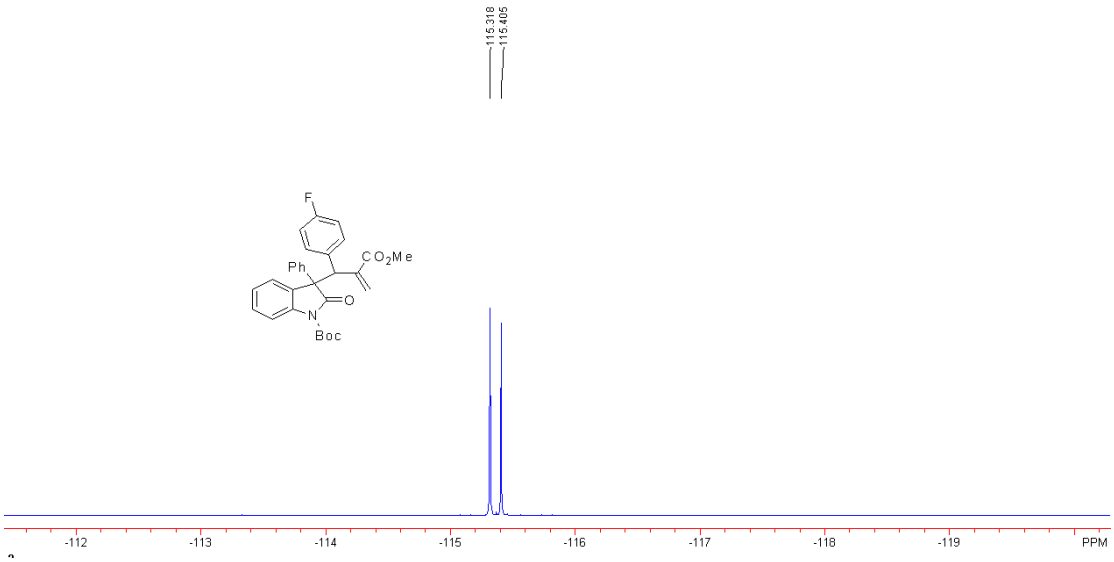
Tert-butyl

3-(1-(4-fluorophenyl)-2-(methoxycarbonyl)allyl)-2-oxo-3-phenylindoline-1-carboxylate **5e**

A white solid, this is a known compound.[6] 86% yield, 43 mg (*anti*:*syn* = 58:42); $[\alpha]^{20}_{D}$ = -236.0 (c 1.9, $CHCl_3$) for 93% ee (*anti*) and 85% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 99/1, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 6.793 min, t_{minor} = 35.273 min; for *syn* product t_{major} = 8.958 min, t_{minor} = 52.310 min; ^{1}H NMR (400MHz, $CDCl_3$, TMS) δ 1.54 (s, 3.78H, Boc), 1.57 (s, 5.22H,

Boc), 3.44 (s, 1.26H, CH_3), 3.64 (s, 1.74H, CH_3), 5.30 (s, 0.58H, $=CH_2$), 5.40 (s, 0.42H, $=CH_2$), 5.52 (d, J = 1.2 Hz, 0.42H, $=CH_2$), 5.90 (s, 0.58H, $=CH_2$), 6.21 (s, 0.42H, CH), 6.40 (s, 0.58H, CH), 6.71-6.79 (m, 3H, Ar), 6.88-7.14 (m, 2H, Ar), 7.22-7.36 (m, 5H, Ar), 7.42-7.47 (m, 2H, Ar), 7.61-7.72 (m, 1H, Ar).





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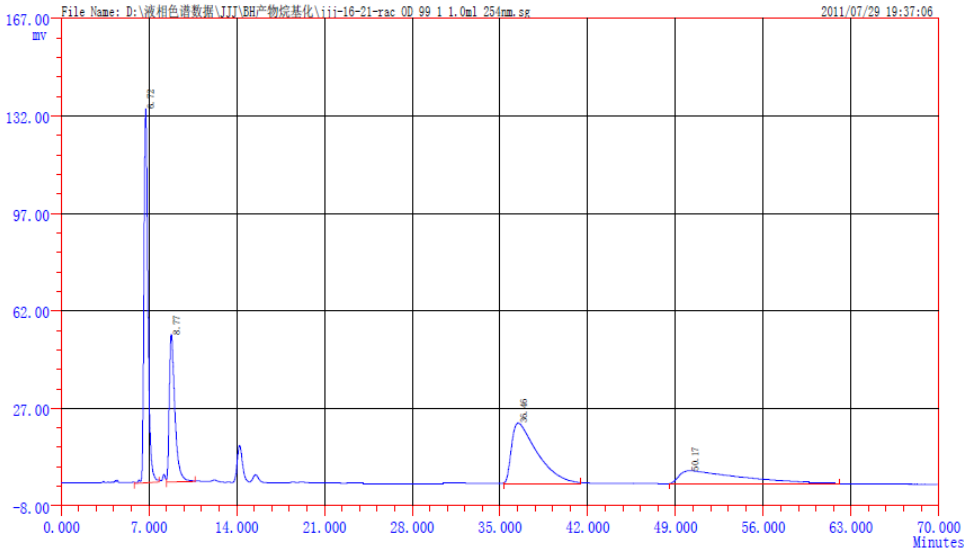
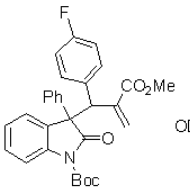


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.723	134396	3001215.1	32.0112	1.38	1807
2		8.773	52925	1636236.2	17.4522	1.80	1605
3		36.460	21603	3069048.0	32.7347	2.55	1313
4		50.167	4729	1669010.6	17.8018	4.42	403
	Σ:		213653	9375509.9	100.0000		



OD-H, Hexane/^{i}PrOH = 99/1, 1.0 mL/min, 254nm

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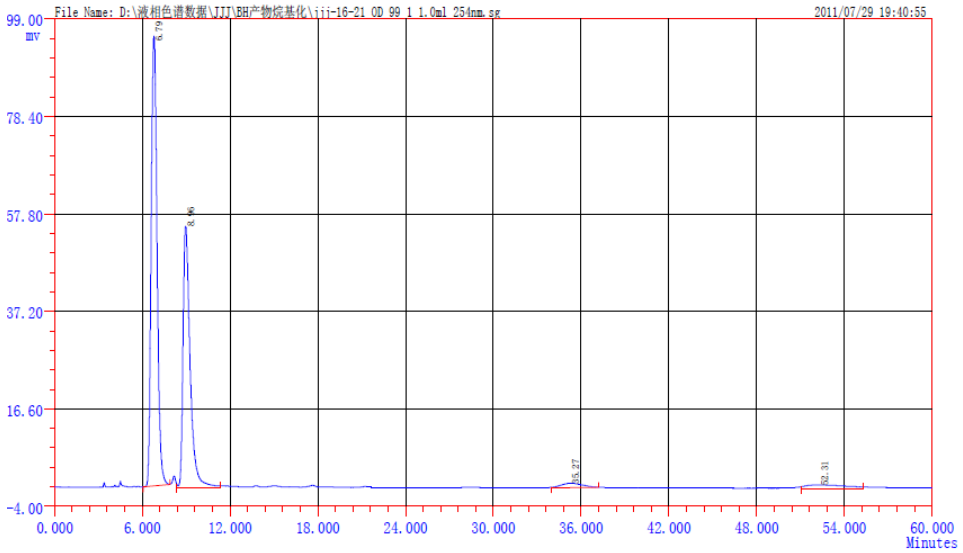
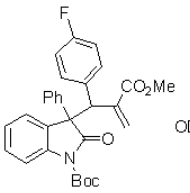
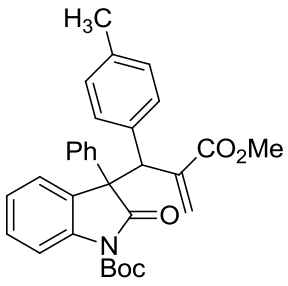


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.793	95021	2667696.1	56.0877	1.19	1167
2		8.958	55152	1849147.4	38.8779	1.66	1423
3		35.273	905	94013.3	1.9766	1.24	2298
4		52.310	742	145435.8	3.0578	1.70	1420
Σ:			151820	4756292.5	100.0000		



OD-H, Hexane/^{i}PrOH = 99/1, 1.0 mL/min, 254nm

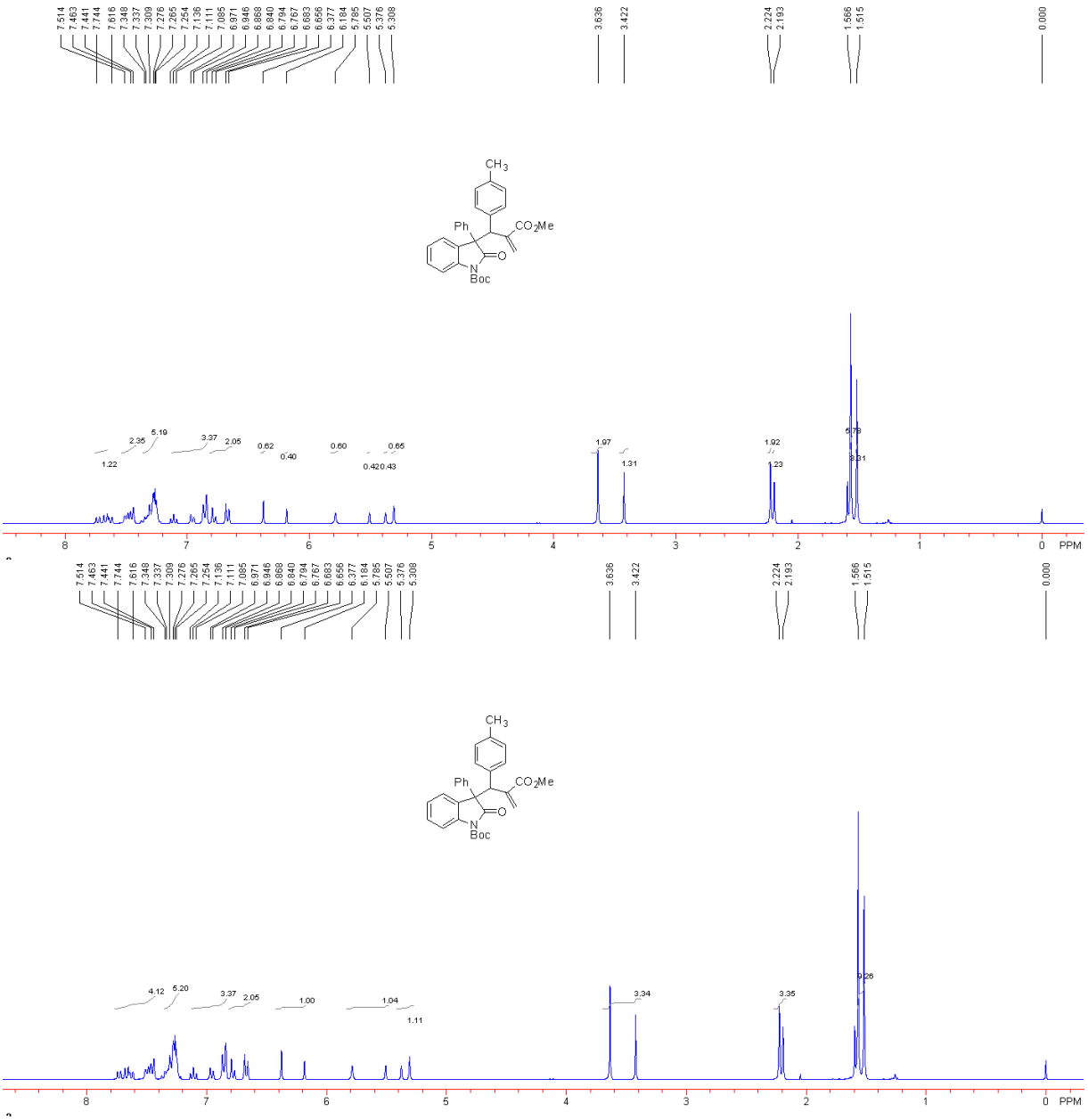
Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 99/1, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 6.793 min, t_{minor} = 35.273 min; for *syn* product t_{major} = 8.958 min, t_{minor} = 52.310 min

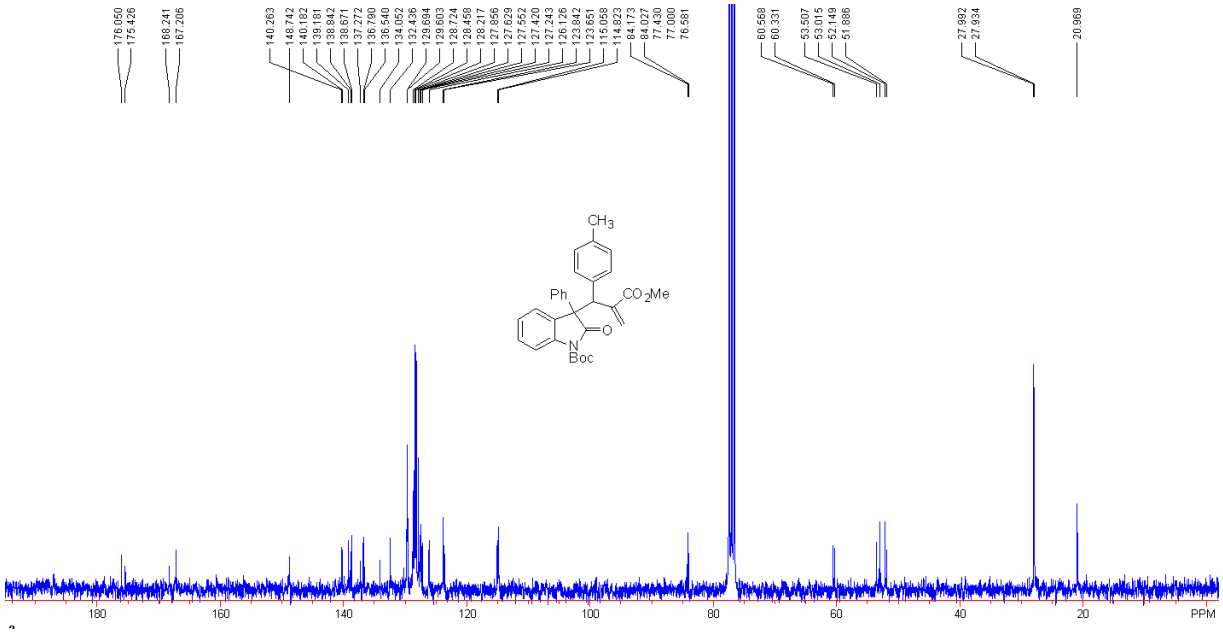


Tert-butyl 3-(2-(methoxycarbonyl)-1-(p-tolyl)allyl)-2-oxo-3-phenylindoline-1-carboxylate **5f**

A white solid, 81% yield, 39 mg, m.p. 82-84 ^{o}C, (*anti*:*syn* = 60:40); $[\alpha]^{20}_{D}$ = -89.5 (c 1.2, $CHCl_3$) for 95% ee (*anti*) and 91% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, for *anti* product t_{major} = 11.627 min, t_{minor} = 25.043 min; for *syn* product t_{major} = 15.877 min, t_{minor} = 22.543 min; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.52 (s, 3.60H, Boc), 1.57 (s, 5.40H, Boc), 2.19 (s,

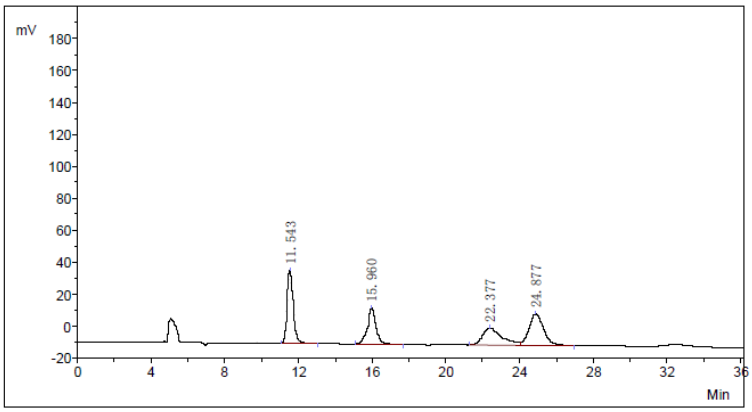
1.20H, CH_3), 2.22 (s, 1.80H, CH_3), 3.42 (s, 1.20H, CH_3), 3.64 (s, 1.80H, CH_3), 5.31 (s, 0.60H, $=CH_2$), 5.38 (s, 0.40H, $=CH_2$), 5.51 (s, 0.40H, $=CH_2$), 5.79 (s, 0.60H, $=CH_2$), 6.18 (s, 0.37H, CH), 6.38 (s, 0.63H, CH), 6.66-6.79 (m, 2H, Ar), 6.84-7.14 (m, 3H, Ar), 7.25-7.34 (m, 5H, Ar), 7.35-7.51 (m, 2H, Ar), 7.62-7.74 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.97, 27.93, 27.99, 51.89, 52.15, 53.02, 53.51, 60.33, 60.57, 84.03, 84.17, 114.82, 115.06, 123.65, 123.84, 126.13, 127.24, 127.42, 127.55, 127.63, 127.86, 128.22, 128.46, 128.72, 129.60, 129.69, 132.44, 134.05, 136.54, 136.79, 137.27, 138.67, 138.84, 139.18, 140.18, 140.26, 148.74, 167.21, 168.24, 175.43, 176.05; IR (neat) ν 2981, 1759, 1724, 1463, 1345, 1287, 1146, 1098, 734, 697 cm^{-1}; MS (ESI) *m/z* 520.2 ($M+Na^+$, 100). HRMS (ESI) Calcd. for $C_{31}H_{31}O_5Na$ requires ($M+Na^+$) 520.2202, Found: 520.2086.



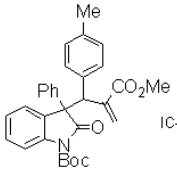


HPLC REPORT

Sample Name:wd-9-85-rac-ic-9-1-0.7-214.che
Date:2012-04-05
Time:09:41
Method:
Column:
Flow Rate:
Wave Length:
Mobile Phase:



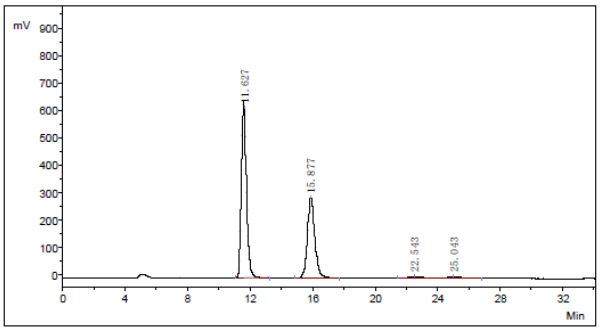
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	11.543	45343.0	1064361.9	29.1625
2	2	Unknown	15.960	22489.6	733796.2	20.1053
3	3	Unknown	22.377	10783.5	781395.6	21.4095
4	4	Unknown	24.877	19691.6	1070208.9	29.3227
Total				98307.7	3649762.6	100.0000



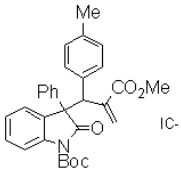
IC-H, Hexane/iPrOH = 90/10, 0.7 ml/min, 214 nm

HPLC REPORT

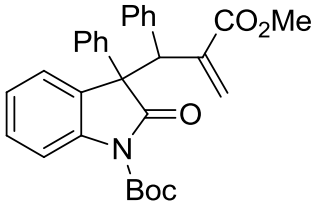
Sample Name:wd-9-85-chiral.che Date:2012-04-05
Time:10:18 Method:
Column: Flow Rate:
Wave Length: Mobile Phase:



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	11.627	618571.0	14727940.9	58.7947
2	2	Unknown	15.877	291572.9	9527367.0	38.0337
3	3	Unknown	22.543	5898.0	425616.2	1.6991
4	4	Unknown	25.043	6737.6	368857.5	1.4725
Total				922779.3	25049781.6	100.0000



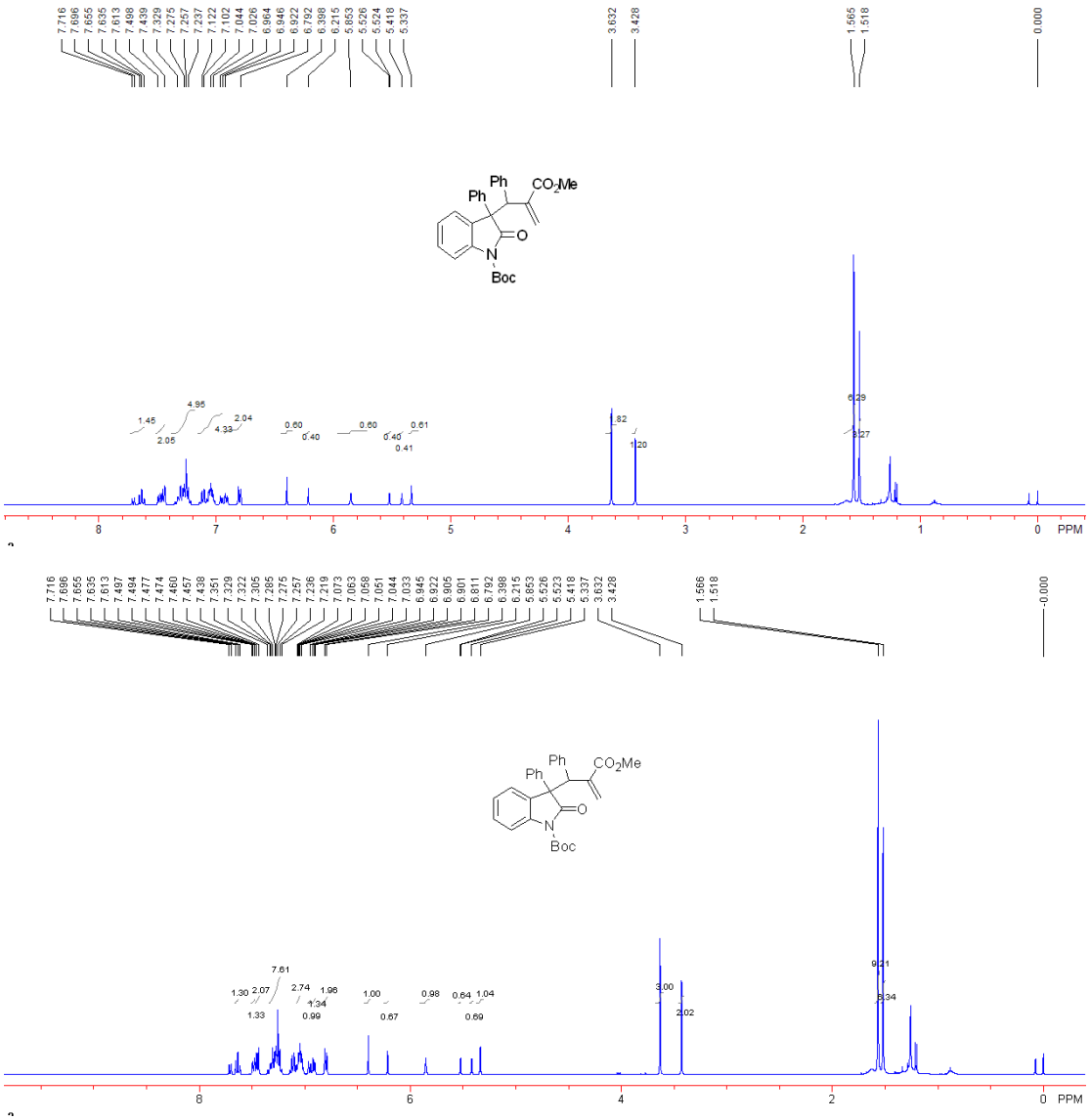
IC-H, Hexane/iPrOH = 90/10, 0.7 ml/min, 214 nm



Tert-butyl 3-(2-(methoxycarbonyl)-1-phenylallyl)-2-oxo-3-phenylindoline-1-carboxylate **5g**

A white solid, this is a known compound.[6] 89% yield, 42 mg (*anti*:*syn* = 57:43); $[\alpha]^{20}_{D}$ = -196.0 (c 0.1, $CHCl_3$) for 93% ee (*anti*) and 89% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254 nm, for *anti* product t_{major} = 6.295 min, t_{minor} = 12.578 min; for *syn* product t_{major} = 8.940 min, t_{minor} = 18.340 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.52 (s, 3.87H, Boc), 1.57 (s, 5.13H, Boc), 3.43 (s, 1.29H, CH_3), 3.63 (s, 1.71H, CH_3), 5.34 (s, 0.57H, $=CH_2$), 5.42 (s, 0.43H, $=CH_2$), 5.53 (d, *J* = 0.8 Hz, 0.43H, $=CH_2$), 5.85 (s, 0.57H, $=CH_2$), 6.22 (s, 0.43H, CH), 6.40 (s,

0.57H, CH), 6.79-6.92 (m, 2H, Ar), 6.95-7.12 (m, 4H, Ar), 7.24-7.33 (m, 5H, Ar), 7.44-7.50 (m, 2H, Ar), 7.61-7.72 (m, 1H, Ar).



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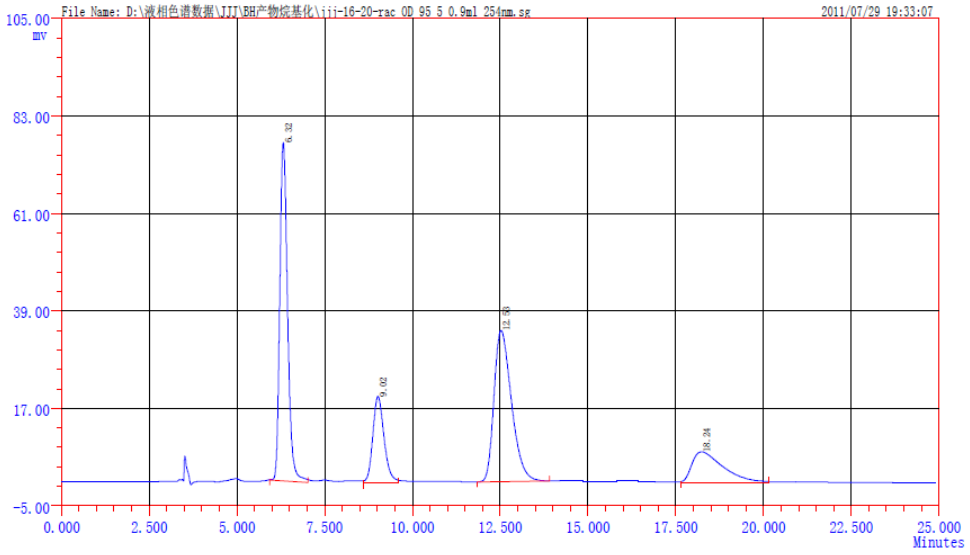
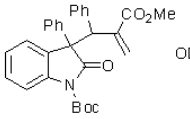


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.320	76344	1179214.7	36.5696	1.23	3337
2		9.017	19584	441699.6	13.6979	1.24	3185
3		12.525	34142	1179442.9	36.5767	1.41	2620
4		18.242	6926	424217.5	13.1558	2.04	1768
	Σ:		136996	3224574.6	100.0000		



OD-H, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254nm

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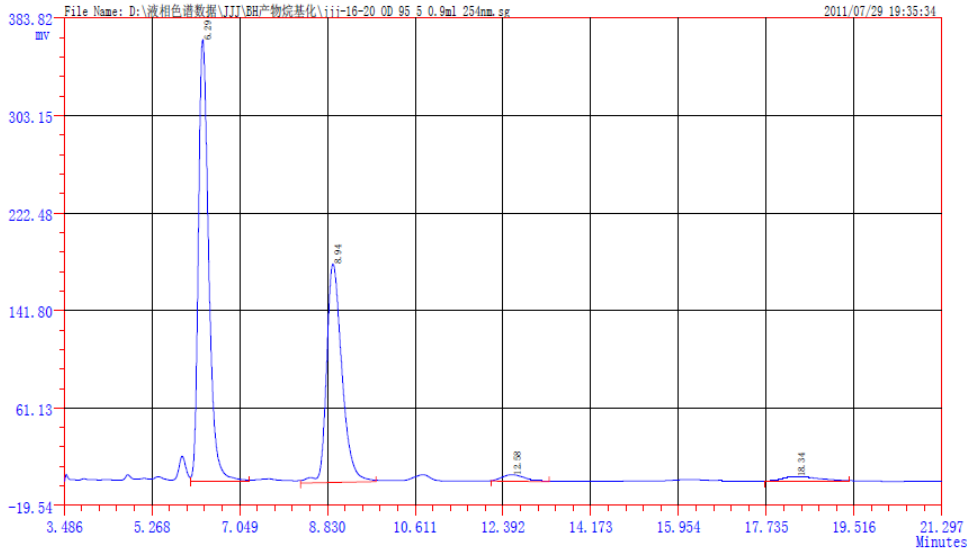
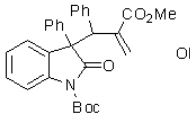
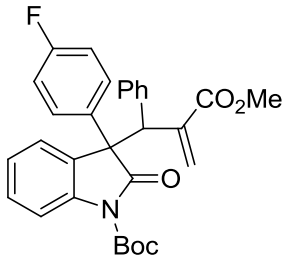


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.295	365651	5316050.0	55.0017	1.38	3737
2		8.940	180774	3936893.5	40.7325	1.39	3359
3		12.578	5394	181858.0	1.8816	1.26	2774
4		18.340	4067	230448.4	2.3843	1.35	2088
Σ:			555886	9665249.8	100.0000		



OD-H, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254nm

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254 nm, for *anti* product t_{major} = 6.295 min, t_{minor} = 12.578 min; for *syn* product t_{major} = 8.940 min, t_{minor} = 18.340 min

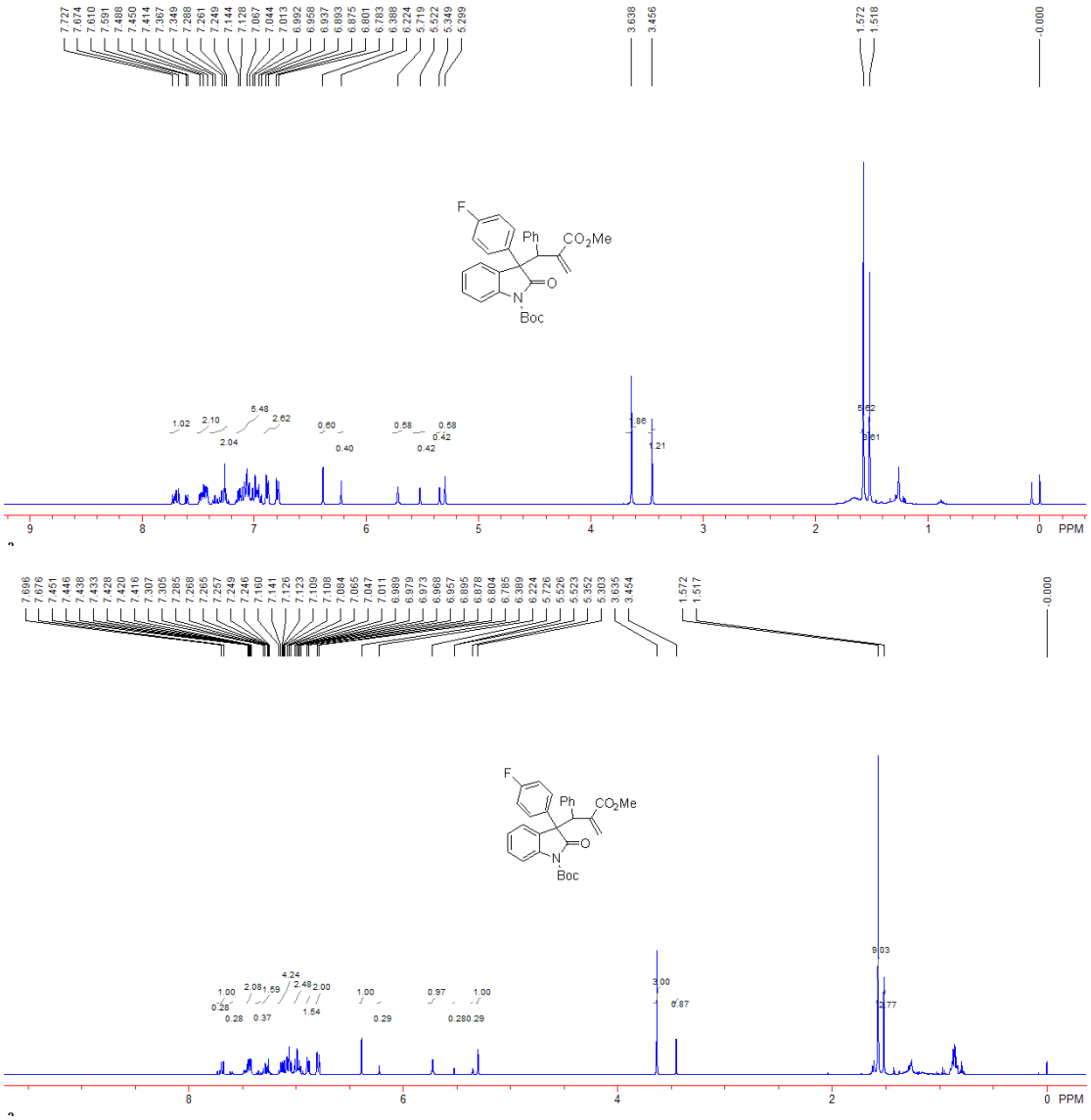


Tert-butyl

3-(4-fluorophenyl)-3-(2-(methoxycarbonyl)-1-phenylallyl)-2-oxoindoline-1-carboxylate **5h**

A white solid, this is a known compound.[6] 82% yield, 41 mg (*anti*:*syn* = 60:40); $[\alpha]^{20}_{D}$ = -147.7 (c 1.1, $CHCl_3$) for 92% ee (*anti*) and 89% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 5.468 min, t_{minor} = 7.813 min; for *syn* product t_{major} = 5.998 min,

t_{minor} = 8.328 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.52 (s, 3.38H, Boc), 1.57 (s, 5.62H, Boc), 3.46 (s, 1.20H, CH_3), 3.64 (s, 1.80H, CH_3), 5.30 (s, 0.60H, $=CH_2$), 5.35 (s, 0.40H, $=CH_2$), 5.52 (s, 0.40H, $=CH_2$), 5.72 (s, 0.60H, $=CH_2$), 6.22 (s, 0.40H, CH), 6.39 (s, 0.60H, CH), 6.78-6.89 (m, 3H, Ar), 6.94-7.14 (m, 5H, Ar), 7.25-7.37 (m, 2H, Ar), 7.41-7.49 (m, 2H, Ar), 7.59-7.73 (m, 1H, Ar).



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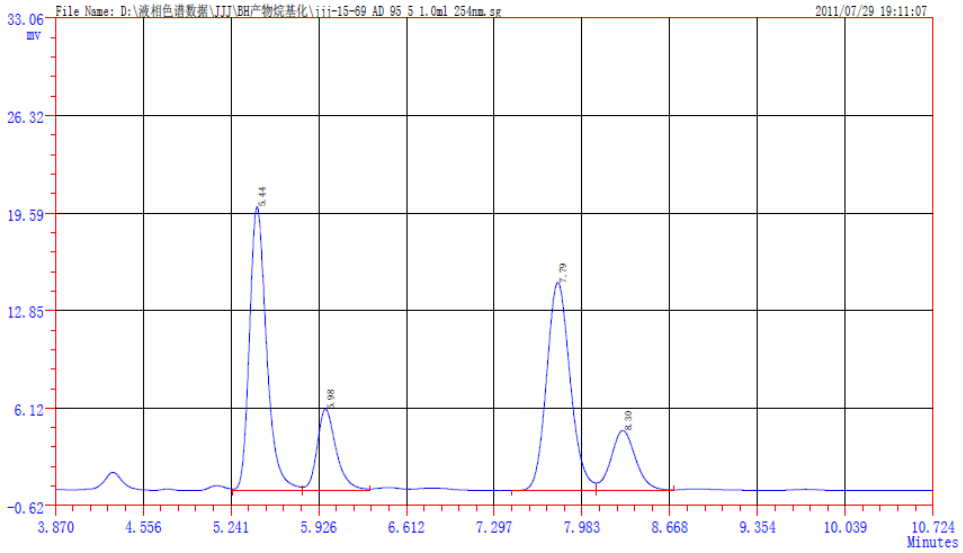
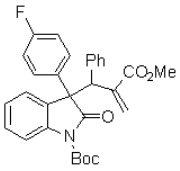
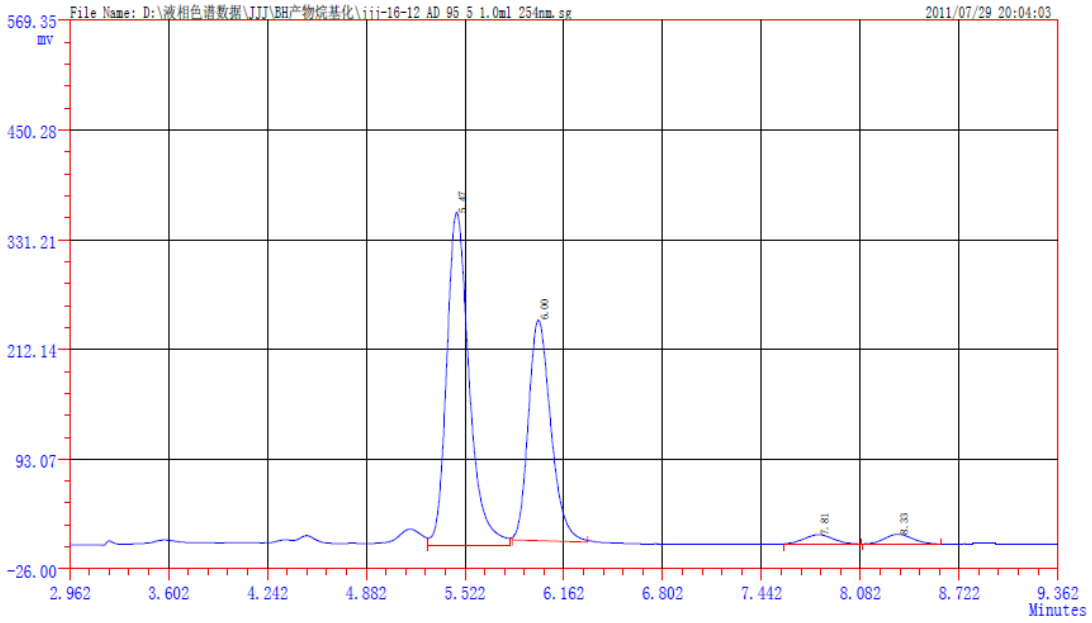


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		5.443	19629	182816.7	37.8243	1.32	6808
2		5.978	5647	59227.4	12.2540	1.27	6476
3		7.793	14395	185007.4	38.2775	1.17	7329
4		8.302	4170	56280.5	11.6443	1.14	7541
	Σ:		43841	483331.9	100.0000		

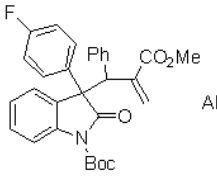


AD-H, Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254nm

WH-500 色 谱 分 析 报 告

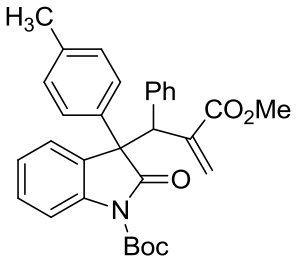


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		5.468	361279	3655820.7	57.3072	1.31	5820
2		5.998	239439	2425689.4	38.0241	1.23	6987
3		7.813	10632	150569.4	2.3603	1.10	6067
4		8.328	11033	147263.5	2.3084	1.07	7760
Σ:			622383	6379343.1	100.0000		



AD-H, Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254nm

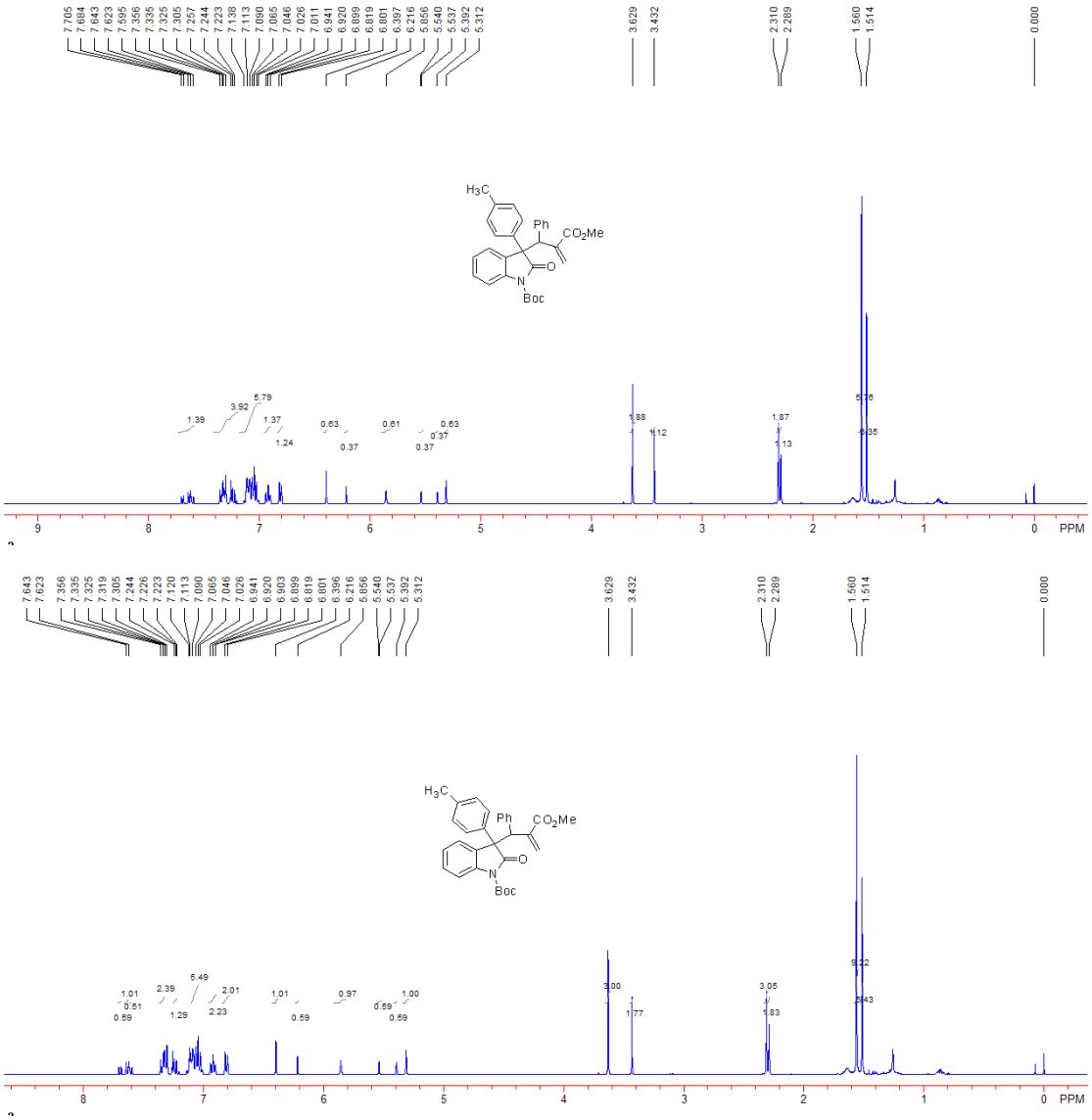
Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 5.468 min, t_{minor} = 7.813 min; for *syn* product t_{major} = 5.998 min, t_{minor} = 8.328 min



Tert-butyl 3-(2-(methoxycarbonyl)-1-phenylallyl)-2-oxo-3-(p-tolyl)indoline-1-carboxylate **5i**

A white solid, this is a known compound.[6] 76% yield, 38 mg (*anti*:*syn* = 61:39); $[\alpha]^{20}_{D}$ = -177.8 (c 1.85, $CHCl_3$) for 92% ee (*anti*) and 88% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 0.8 mL/min, 254

nm, for *anti* product t_{major} = 6.902 min, t_{minor} = 8.437 min; for *syn* product t_{major} = 7.322 min, t_{minor} = 18.025 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.51 (s, 3.51H, Boc), 1.56 (s, 5.49H, Boc), 2.29 (s, 1.13H, CH_3), 2.31 (s, 1.87H, CH_3), 3.43 (s, 1.17H, CH_3), 3.63 (s, 1.83H, CH_3), 5.31 (s, 0.61H, $=CH_2$), 5.39 (s, 0.39H, $=CH_2$), 5.54 (d, *J* = 1.2 Hz, 0.39H, $=CH_2$), 5.86 (s, 0.61H, $=CH_2$), 6.22 (s, 0.39H, CH), 6.40 (s, 0.61H, CH), 6.81 (d, *J* = 7.2 Hz, 1H, Ar), 6.92 (t, *J* = 8.4 Hz, 1H, Ar), 7.01-7.14 (m, 6H, Ar), 7.22-7.36 (m, 4H, Ar), 7.60-7.71 (m, 1H, Ar).



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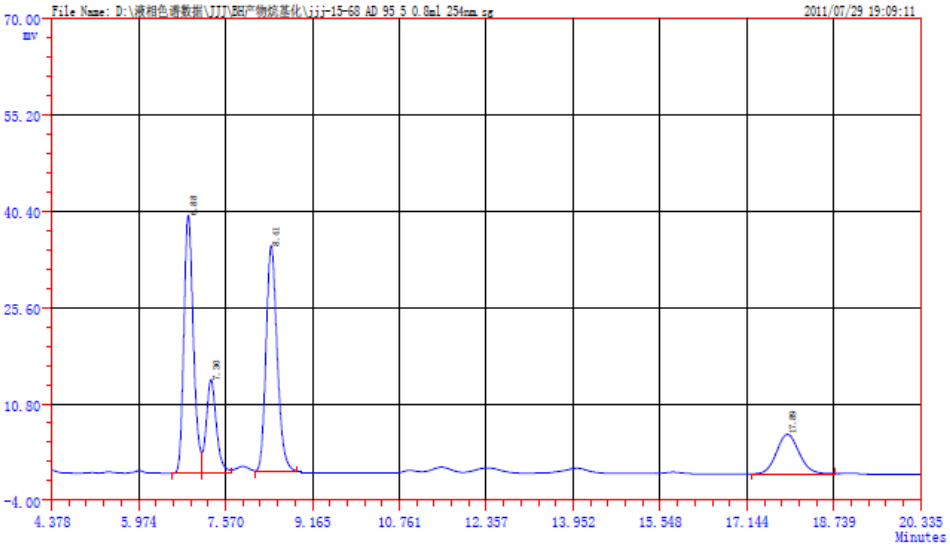
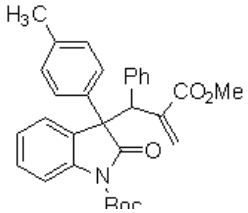
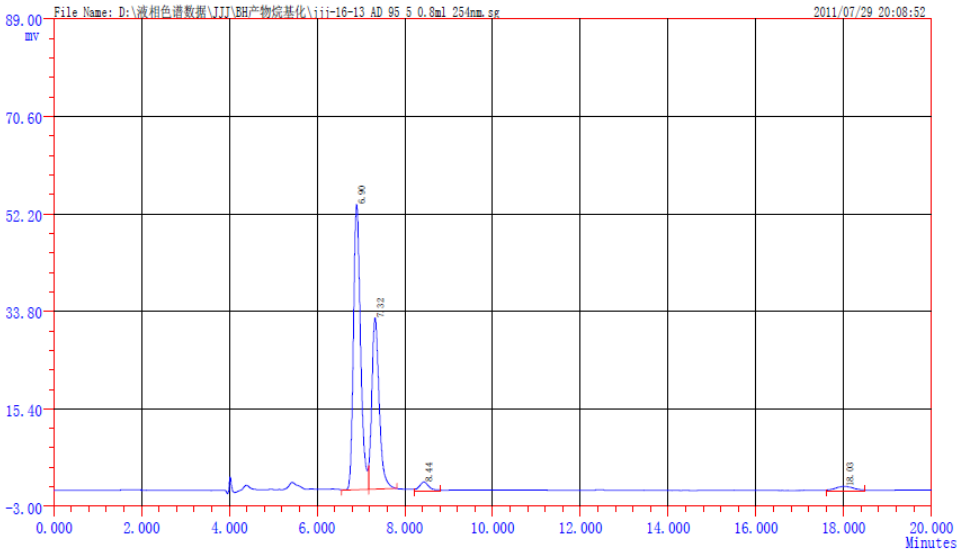


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.882	39545	479921.8	35.9022	1.23	6408
2		7.300	14356	186815.4	13.9754	1.34	6272
3		8.405	34694	497650.4	37.2285	1.21	6843
4		17.888	6030	172358.4	12.8939	1.10	7806
Σ:			94625	1336745.9	100.0000		

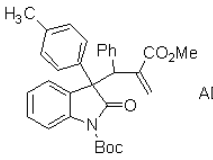


AD-H, Hexane/^{i}PrOH = 95/5, 0.8 mL/min, 254nm

WH-500 色 谱 分 析 报 告

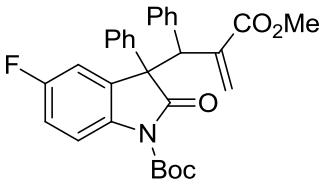


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.902	53925	609277.0	58.6916	1.38	7437
2		7.322	32395	378913.2	36.5007	1.42	7809
3		8.437	1672	25909.0	2.4958	1.33	5908
4		18.025	826	23999.8	2.3119	1.04	7670
Σ:			88818	1038099.1	100.0000		



AD-H, Hexane/^{i}PrOH = 95/5, 0.8 mL/min, 254nm

Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 0.8 mL/min, 254 nm, for *anti* product t_{major} = 6.902 min, t_{minor} = 8.437 min; for *syn* product t_{major} = 7.322 min, t_{minor} = 18.025 min

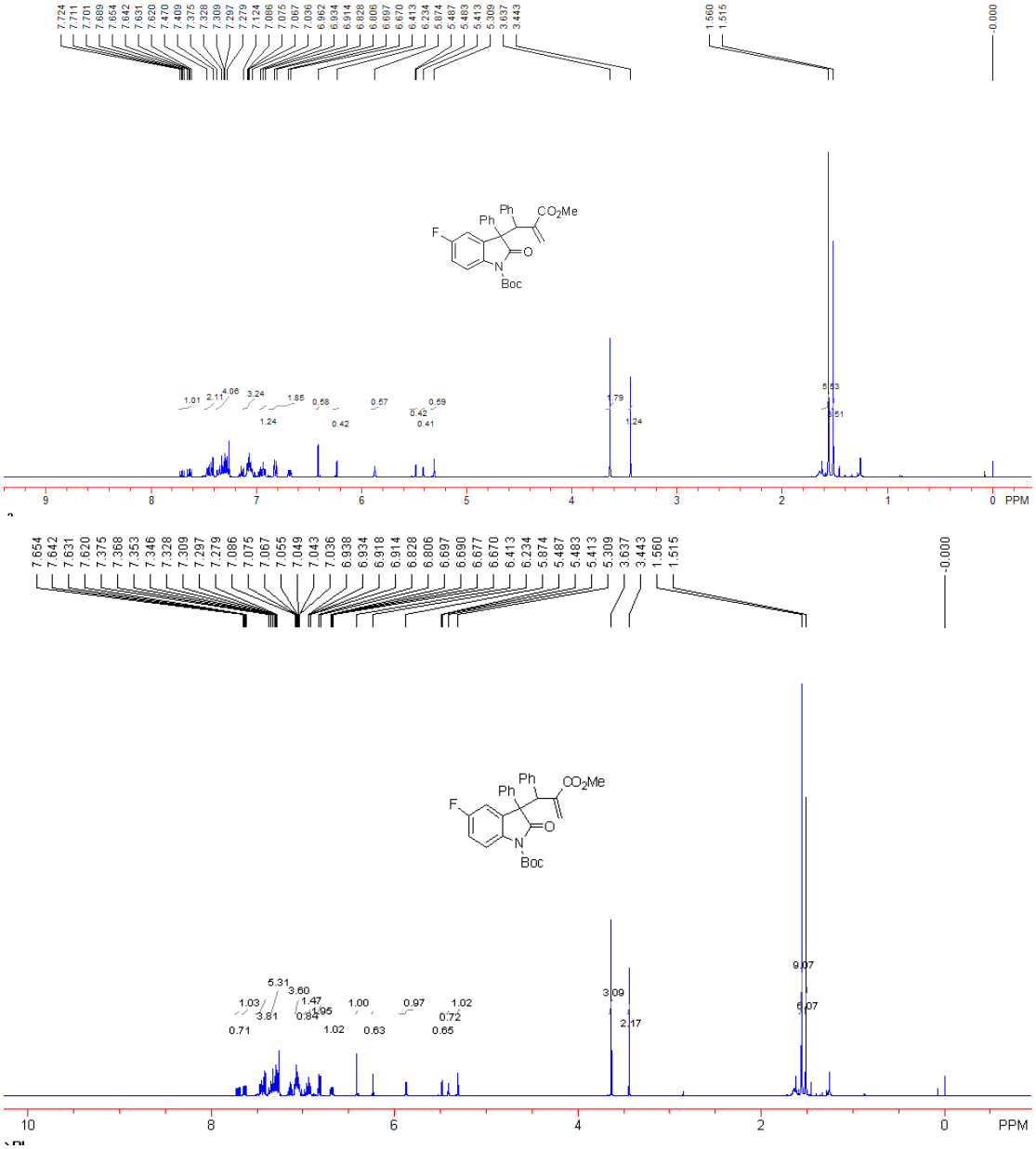


Tert-butyl

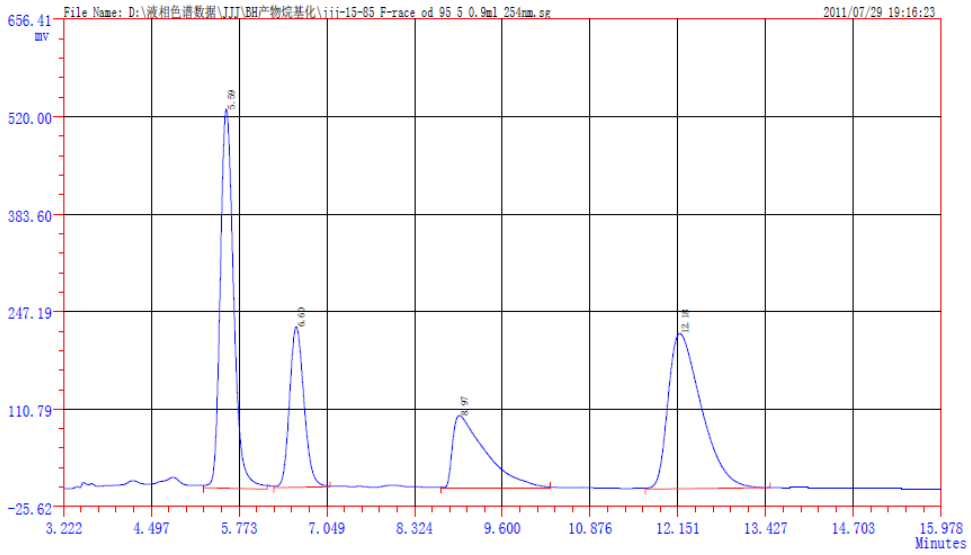
5-fluoro-3-(2-(methoxycarbonyl)-1-phenylallyl)-2-oxo-3-phenylindoline-1-carboxylate **5j**

A white solid, this is a known compound.[6] 82% yield, 41 mg (*anti*:*syn* = 56:44); $[\alpha]^{20}_{D}$ = -155.0 (c 0.25, $CHCl_3$) for 97% ee (*anti*) and 84% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254 nm, for *anti* product t_{major} = 5.585 min, t_{minor} = 12.665 min; for *syn* product t_{major} = 6.605 min, t_{minor} = 9.740 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.52 (s, 3.96H, Boc), 1.56 (s, 5.04H, Boc), 3.44 (s, 1.32H, CH_3), 3.64 (s, 1.68H, CH_3), 5.31 (s, 0.56H, $=CH_2$), 5.41 (s, 0.44H,

=CH_2), 5.49 (d, *J* = 1.6 Hz, 0.44H, =CH_2), 5.87 (s, 0.56H, =CH_2), 6.23 (s, 0.44H, CH), 6.41 (s, 0.56H, CH), 6.67-6.83 (m, 2H, Ar), 6.91-6.96 (m, 1H, Ar), 7.04-7.12 (m, 3H, Ar), 7.28-7.38 (m, 4H, Ar), 7.41-7.47 (m, 2H, Ar), 7.62-7.72 (m, 1H, Ar).



WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		5.587	530705	7208392.5	34.0744	1.24	3372
2		6.603	224695	3289147.0	15.5480	1.18	4056
3		8.973	101129	3376935.5	15.9629	3.60	1439
4		12.183	217090	7280374.5	34.4147	1.67	2630
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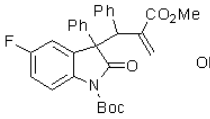
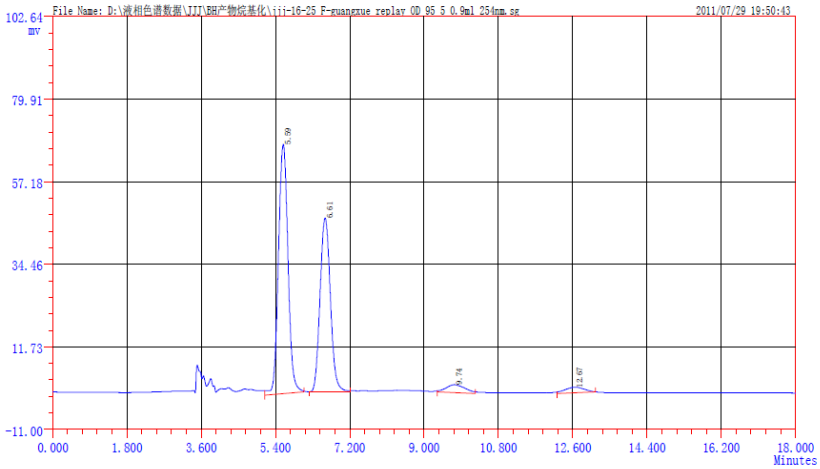
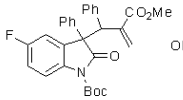


OD-H, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254nm

WH-500 色 谱 分 析 报 告

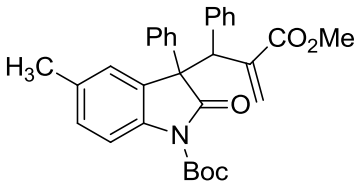


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		5.585	68599	1108391.1	53.6901	1.09	2381
2		6.605	47884	834428.4	40.4194	1.09	2863
3		9.740	2198	71164.9	3.4472	1.09	1804
4		12.665	1519	50439.9	2.4433	1.05	2899
Σ:			120200	2064424.3	100.0000		



OD-H, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254nm

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 95/5, 0.9 mL/min, 254 nm, for *anti* product t_{major} = 5.585 min, t_{minor} = 12.665 min; for *syn* product t_{major} = 6.605 min, t_{minor} = 9.740 min

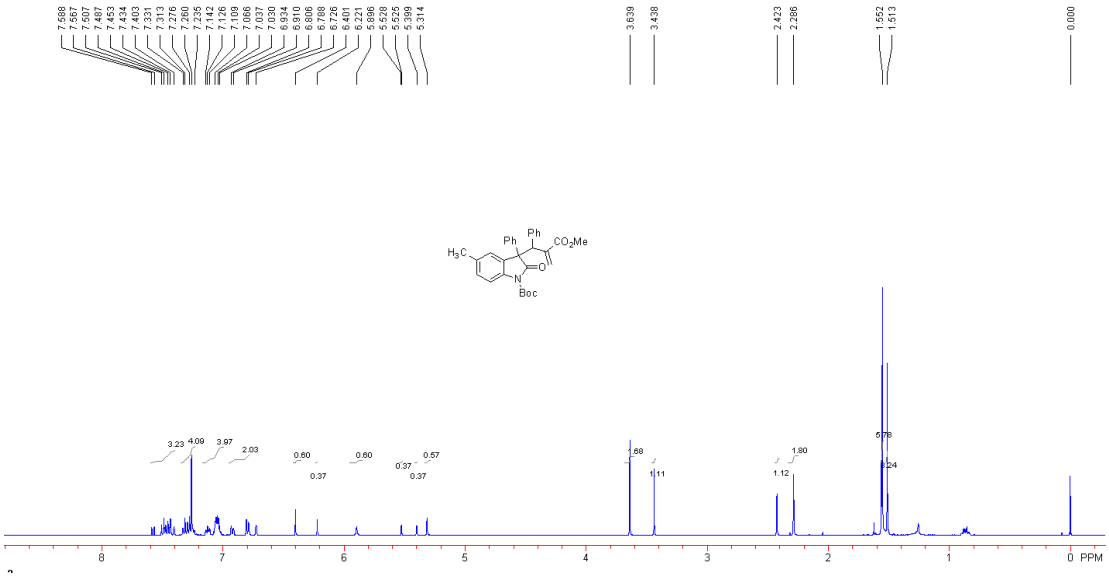


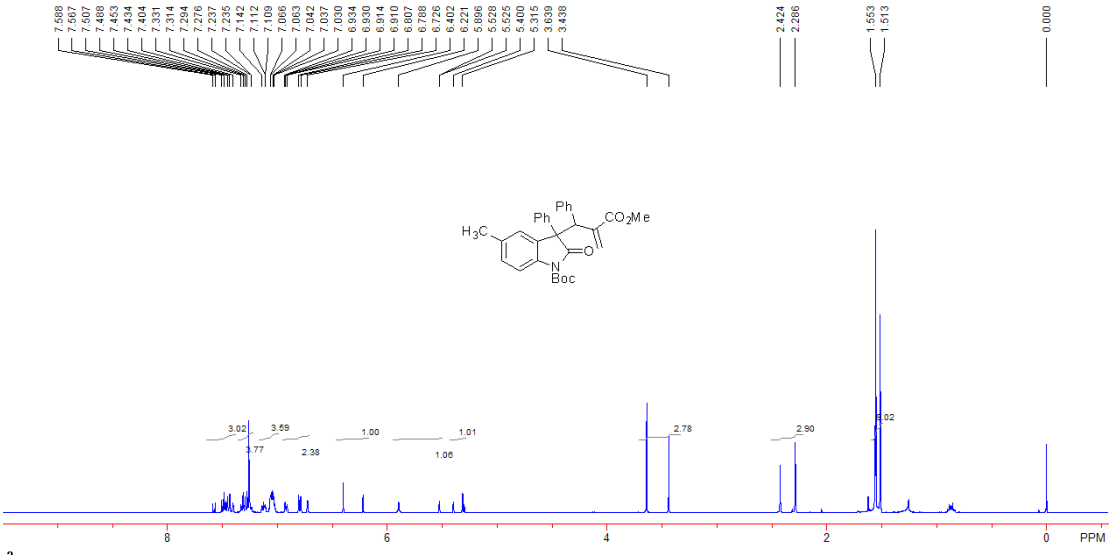
Tert-butyl

3-(2-(methoxycarbonyl)-1-phenylallyl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate

5k

A colorless oil, this is a known compound.[6] 78% yield, 38 mg (*anti*:*syn* = 64:36); $[\alpha]^{20}_{D}$ = -32.7 (c 0.25, $CHCl_3$) for 96% ee (*anti*) and 94% ee (*syn*); Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 7.887 min, t_{minor} = 11.732 min; for *syn* product t_{major} = 9.095 min, t_{minor} = 13.745 min; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.51 (s, 3.24H, Boc), 1.55 (s, 5.78H, Boc), 2.29 (s, 1.92H, CH_3), 2.42 (s, 1.08H, CH_3), 3.44 (s, 1.08H, CH_3), 3.64 (s, 1.92H, CH_3), 5.31 (s, 0.64H, =CH_2), 5.40 (s, 0.36H, =CH_2), 5.53 (d, *J* = 1.2 Hz, 0.36H, =CH_2), 5.90 (s, 0.64H, =CH_2), 6.22 (s, 0.36H, CH), 6.40 (s, 0.64H, CH), 6.73-6.93 (m, 2H, Ar), 7.03-7.14 (m, 4H, Ar), 7.24-7.33 (m, 4H, Ar), 7.40-7.59 (m, 3H, Ar).





N2000 数据工作站 1

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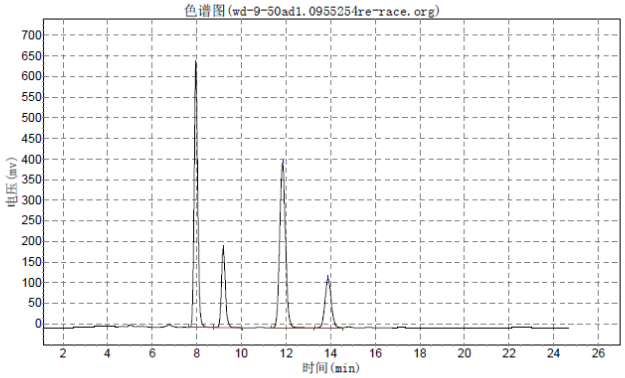
实验者：
报告时间：2012-04-05,20:30:25
积分方法:面积归一法

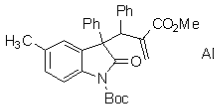
使用仪器类型:气相色谱　　检测器:FID　　进样器:分流

柱温:程序升温



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.957	640804.813	7119955.500	37.3500
2		9.182	190706.297	2364060.500	12.4014
3		11.848	399607.531	7257721.000	38.0727
4		13.882	118504.047	2321050.000	12.1758
总计			1349622.688	19062787.000	100.0000



AD-H, Hexane/iPrOH = 95/5, 1.0 ml/min, 254 nm

N2000 数据工作站 1

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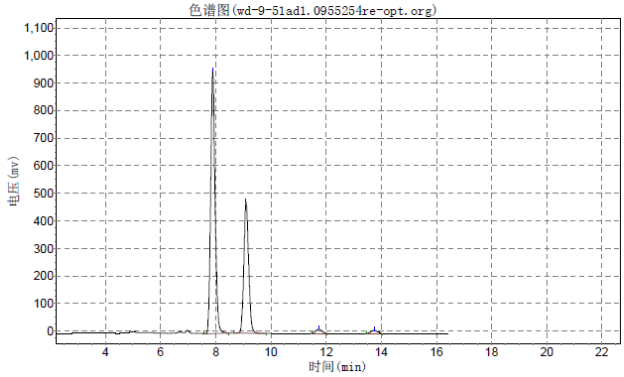
实验者:
报告时间：2012-04-05, 20:35:46
积分方法:面积归一法

使用仪器类型:气相色谱　　检测器:FID　　进样器:分流

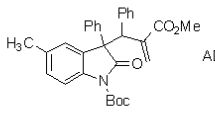
柱温:程序升温

色谱图(wd-9-51ad1.0955254re-opt.org)



分析结果表

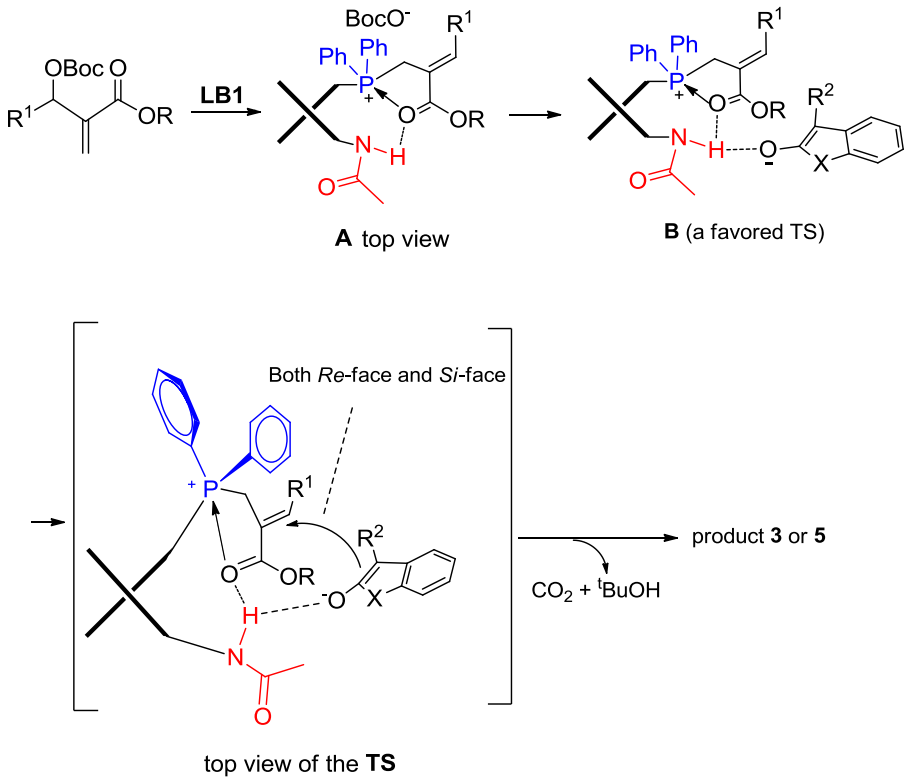
峰号	峰名	保留时间	峰高	峰面积	含量
1		7.887	952219.063	10546484.000	63.0347
2		9.095	474828.375	5753848.000	34.3898
3		11.732	14787.407	238885.078	1.4278
4		13.745	11075.888	192029.906	1.1477
总计			1452910.732	16731246.984	100.0000



AD-H, Hexane/iPrOH = 95/5, 1.0 ml/min, 254 nm

Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254 nm, for *anti* product t_{major} = 7.887 min, t_{minor} = 11.732 min; for *syn* product t_{major} = 9.095 min, t_{minor} = 13.745 min

6. A plausible reaction mechanism



Scheme SI-1

A plausible mechanism for this asymmetric reaction is outlined in Scheme SI-1. As proposed by Krische,[7] the treatment of MBH carbonate with **LB1** produces an electrophile-nucleophile ion pair **A** stabilized by an intramolecular H-bonding, which reacts with the 3-substituted benzofunan or oxindole anion generated from $BocO^-$ and 3-substituted benzofunan or oxindole to give intermediate **B**. Intermediate **B** is favored through intermolecular hydrogen-bonding, providing the addition product **3** or **5** from both Re-face or Si-face attacking via the transition state **TS** shown in Scheme SI-1.

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7. References

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