Supporting information

Construction of Adjacent Spiro-quaternary and Tertiary Stereocenters through Phosphine-Catalyzed Asymmetric [3+2] Annulation of Allenoates with Alkylidene Azlactones

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Contents:

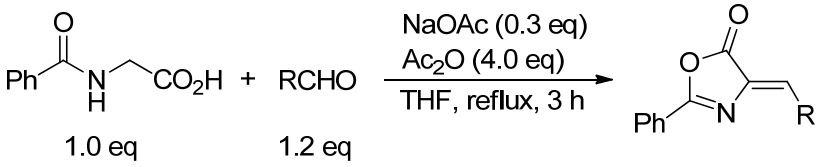
1. General Methods: ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz or 300 and 75 MHz by VARIAN, respectively. Low- and high-resolution mass spectra were recorded by EI or ESI method. The used organic solvents were dried by standard methods if it was necessary. Optical rotations were determined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

Catalysts **CP3**, **CP7**, **CP8**, **CP9**, and **CP10** were purchased from J&K Chemical Ltd. and used directly without further purification.

CP1,[1] **CP2**,[1] **CP4**,[2] **CP5**,[2] **CP6**,[3] were prepared according to the previously reported procedures.

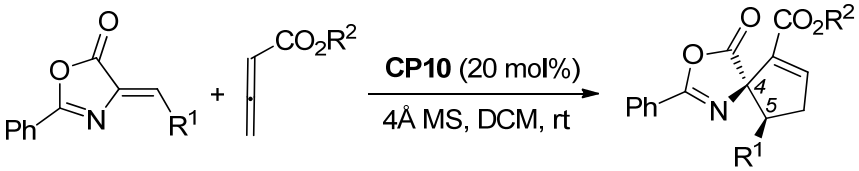
All allenoates[4] and compound **6**[5] were prepared according to the previously reported procedures.

2. General procedure for the synthesis of alkylidene azlactone 1[6]



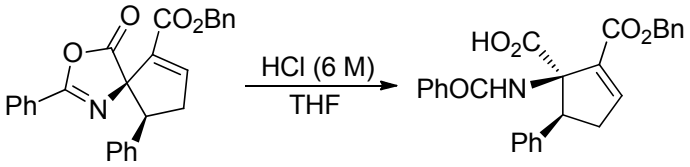
Hippuric acid (1.8 g, 10 mmol, 1.0 eq), aldehyde (12 mmol, 1.2 eq), NaOAc (0.25 g, 3 mmol, 0.3 eq) and Ac_2O (40 mmol, 4.0 mL, 4.0 eq) were dissolved in 30 mL THF, and then heated to reflux for about 3 h. The reaction mixture was cooled to room temperature. Saturate Na_2CO_3 aqueous solution was added to the reaction mixture, and extracted with DCM for 3 times. The combined organic layers were dried over Na_2SO_4. The crude product was purified by flash silica gel chromatography or recrystallization by EtOH to afford products **1a-n**.

3. General procedure for the phosphine-catalyzed [3+2] annulation of alkylidene azlactone with electron-deficient allenoate.



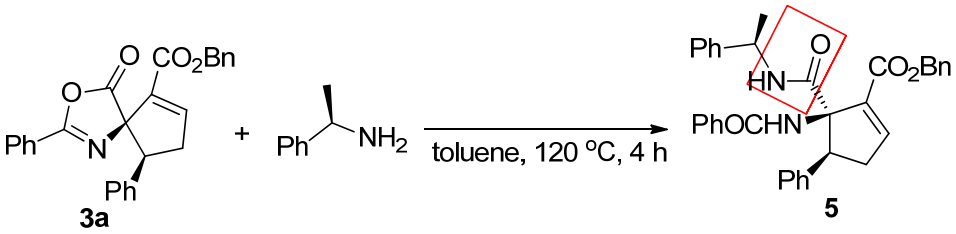
Alkylidene azlactone **1** (0.1 mmol), (R)-SITCP (0.02 mmol), 4A MS (30 mg) and anhydrous DCM (3.0 mL) were added into a Schlenk tube, then allenoate **2** (0.30 mmol) was added very slowly. The reaction mixture was stirred at room temperature for 8 h (TLC monitored) under argon atmosphere. The reaction mixture was then concentrated on a rotary evaporator under reduce pressure and the residue was subjected to purification by column chromatography (PE/AcOEt = 12/1~8/1) to afford the corresponding product **3**.

4. General procedure for the synthesis of 4



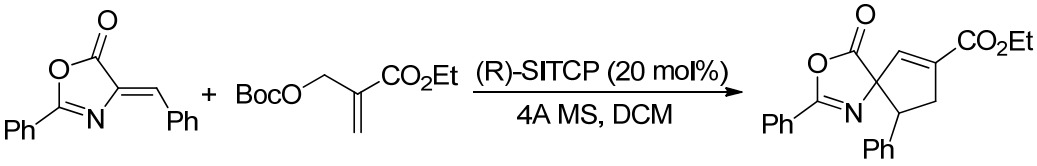
Compound **3a** was dissolved in THF (1.0 mL), then 6 M HCl (5 mL) was added. The solution was heated at 90 °C for 4 h. After cooling to room temperature, the aqueous solution was extracted with DCM and the combined organic layers were dried over Na_2SO_4. Then the crude product was purified by flash silica gel chromatography (DCM/MeOH = 9/1) to afford the product **4** as a white solid in 76% yield.

5. General procedure for the synthesis of 5



A mixture of **3a** (42 mg, 0.1 mmol) and (*R*)-(+)-1-phenylethylamine (15 μL, 0.12 mmol) in toluene (1.0 mL) was stirred at 120 °C under Ar atmosphere for 4 h. After cooling to room temperature, purification of the crude mixture by column chromatography on silica gel (PE/AcOEt = 1/2) gave peptide derivative **7** as white foam solid in 67% yield.

6. General procedure for the synthesis of 7



Alkylidene azlactone (0.1 mmol), (R)-SITCP (0.02 mmol), 4A MS (30 mg) and anhydrous DCM (3.0 mL) were added into a Schlenk tube, then allylic carbonate **5** (0.30 mmol) was added very slowly. The reaction mixture was stirred at room temperature for 24 h (TLC monitored) under argon atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/AcOEt = 12/1~8/1) to afford the product **6** as a yellowish solid in 62% yield.

7. Screening of chiral phosphines for the asymmetric [3+2] annulation

The corresponding spiro-cycloadduct **3a** was obtained in low yields and low ee values in the presence of axially chiral binaphthyl skeleton containing phosphines **CP1**-**CP3** at room temperature. Using **CP1** as the catalyst gave **3a** in 8% yield with 20% ee and the other two chiral phosphines afforded barely no product (Table SI-1, entries 1-3). Subsequently we examined several multifunctional chiral phosphines derived from natural amino acids (**CP4**-**CP6**) and some commercially available chiral phosphines (**CP7**-**CP10**). Using **CP4** or **CP7** as the chiral phosphine produced **3a** in 23% yield with >10:1 dr and 14% ee value or in 38% yield with 9:1 dr and 32% ee value (Table SI-1, entries 4 and 7). The use of **CP5**, **CP6**, and **CP8** as the catalysts gave the desired product in low yields but with no ee value (Table SI-1, entries 5, 6 and 8). Chiral phosphine **CP9** was also inefficient in this reaction (Table SI-1, entry 9). Gratefully, we found that using chiral phosphine **CP10** (R)-SITCP as the catalyst, **3a** was produced in 20% yield with 19:1 dr and 94% ee (Table SI-1, entry 10).

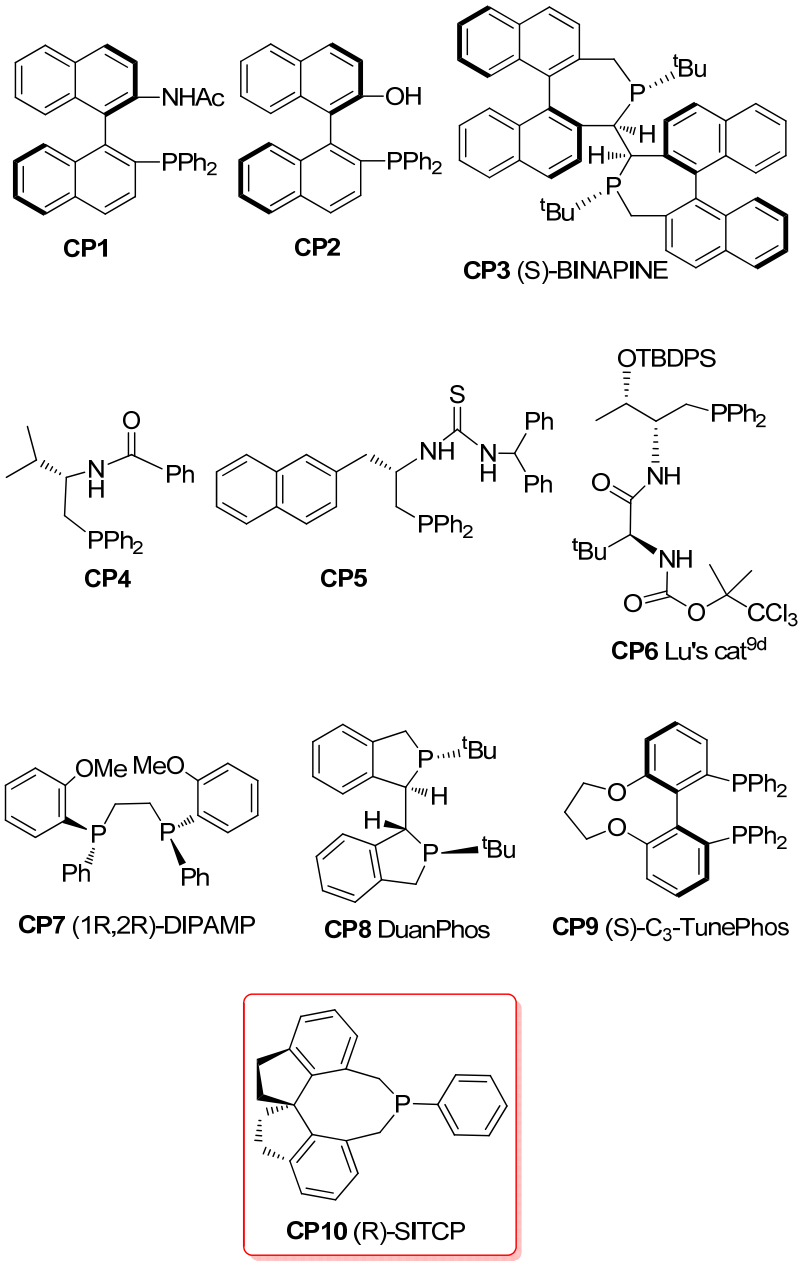
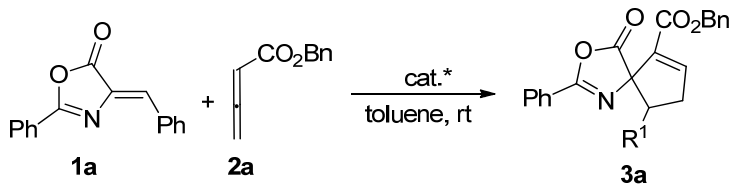


Figure SI-1. Chiral phosphines having different skeleton

Table SI-1. Screening of chiral phosphines for the asymmetric [3+2] annulation of **1a** with **2a**



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

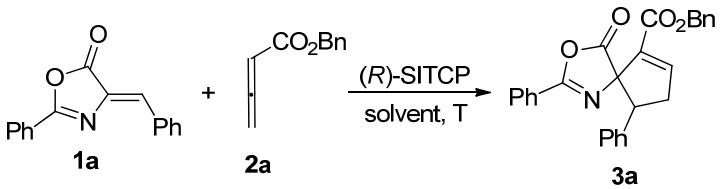
entry[a]	cat.*	yield[b] (%)	dr[c]	ee (%)[d]
1	**CP1**	8	10:1	20
2	**CP2**	trace	-	-
3	**CP3**	trace	-	-
4	**CP4**	23	>10:1	14
5	**CP5**	13	>19:1	0
6	**CP6**	42	10:1	0
7	**CP7**	38	9:1	32
8	**CP8**	38	>19:1	0
9	**CP9**	30	>19:1	18
10	**CP10**	20	>19:1	94

[a] The reactions were carried out with **1a** (0.1 mmol), **2a** (0.2 mmol), cat* (0.01 mmol) in toluene (1.0 mL) at room temperature for 8 h. [b] Isolated yield by column chromatography. [c] Diastereomeric ratios determined by ^{1}H NMR spectroscopy. [d] Determined by chiral HPLC analysis.

8. Optimization of the reaction conditions

The examination of solvent effects revealed that in dichloromethane (DCM), the desired product **3a** could be obtained in 48% yield along with 97% ee and using other solvents such as $CHCl_3$ or tetrahydrofuran (THF) gave **3a** in lower yield with excellent ee values under identical conditions (Table SI-2, entries 1-4). Lowering the reaction temperature to 0 ^oC did not improve the yield of **3a** in DCM (Table SI-2, entry 5). Increasing the reactant concentration by carrying out the reaction in 0.5 mL of DCM did not enhance the yield of **3a** either, affording **3a** in 18% yield (Table SI-2, entry 6). Increasing the catalyst loading to 20 mol% could significantly improve the yield of **3a** (Table SI-2, entry 7). Dilution of the reactant concentration by carrying out the reaction in 3.0 mL of DCM could further improve the yield of **3a** (Table SI-2, entry 8). Moreover, adding 4Å MS into the reaction system to get rid of the adventitious water afforded **3a** in 78% with 12:1 dr and 97% ee value, which served as the best reaction conditions in above reaction (Table SI-2, entry 9).

Table SI-2. Optimization of the reaction conditions

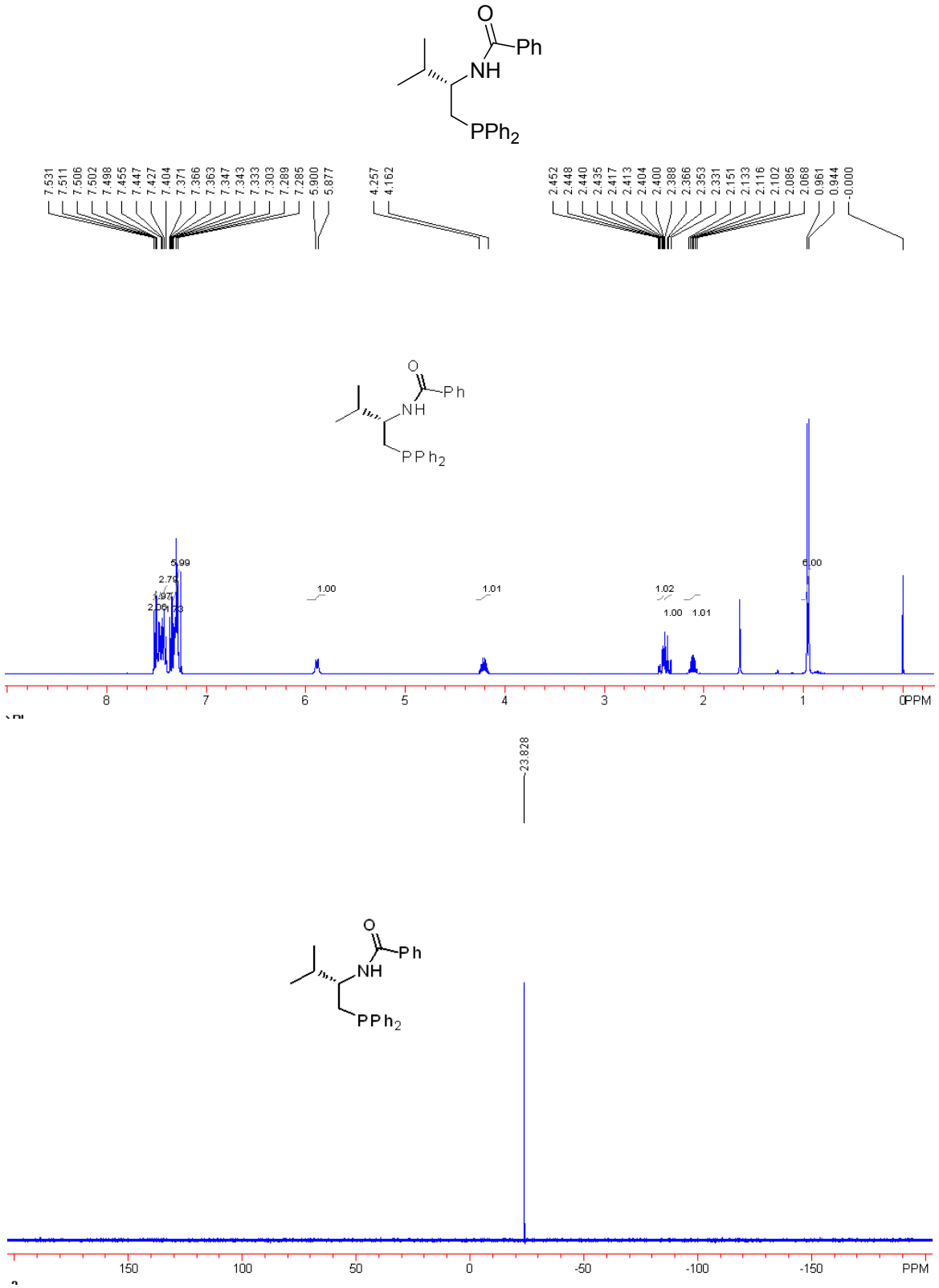


1a **2a** **3a**

entry[a]	solvent	T (^oC)	yield[b] (%)	dr[c]	ee (%)[d]
1	toluene	rt	20	>19:1	94
2	DCM	rt	48	>19:1	97
3	$CHCl_3$	rt	38	>19:1	97
4	THF	rt	45	>19:1	95
5	DCM	0	28	>19:1	95
6[e]	DCM	rt	18	>19:1	97
7[f]	DCM	rt	60	>19:1	97
8[f,g]	DCM	rt	67	>19:1	97
9[f,g,h]	DCM	rt	78	12:1	97

[a] The reactions were carried out with **1a** (0.1 mmol), **2a** (0.2 mmol), (R)-SITCP (0.01 mmol) in solvent (1.0 mL) at rt for 8 h. [b] Isolated yield by column chromatography. [c] Diastereomeric ratios determined by ^1H NMR spectroscopy. [d] Determined by chiral HPLC analysis. [e] 0.5 mL DCM was used. [f] 20 mol% (*R*)-SITCP was used. [g] 3.0 mL DCM was used. [h] 4A MS (30 mg) was used.

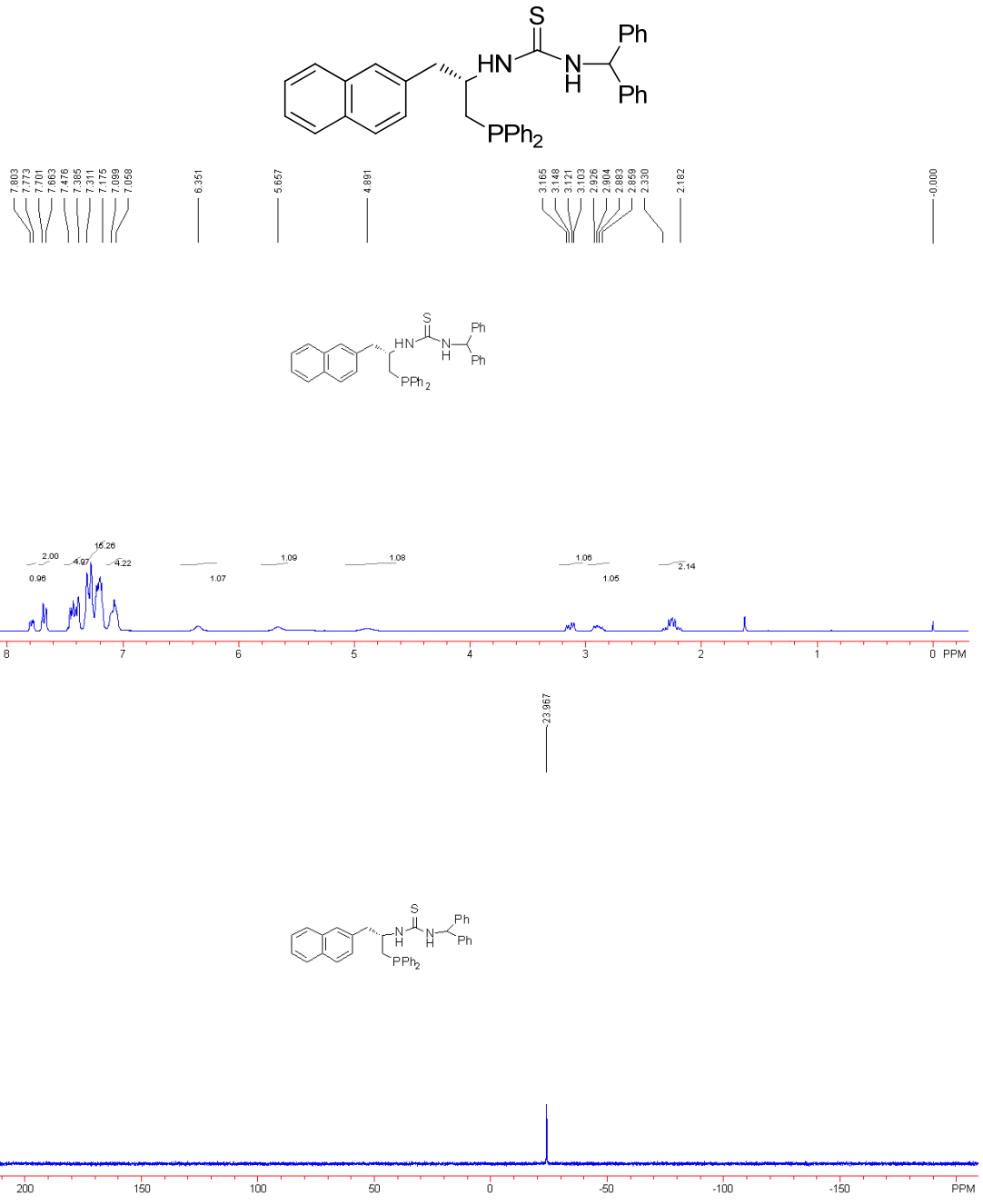
9 Characterization and spectra charts for catalysts CP4-6.



(S)-N-(1-(diphenylphosphino)-3-methylbutan-2-yl)benzamide (CP4)

A white solid, 82% yield, 114 mg, Mp: 139-140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53-7.50 (m, 2H), 7.49-7.46 (m, 2H), 7.45-7.40 (m, 3H), 7.37-7.34 (m, 2H), 7.33-7.29 (m,

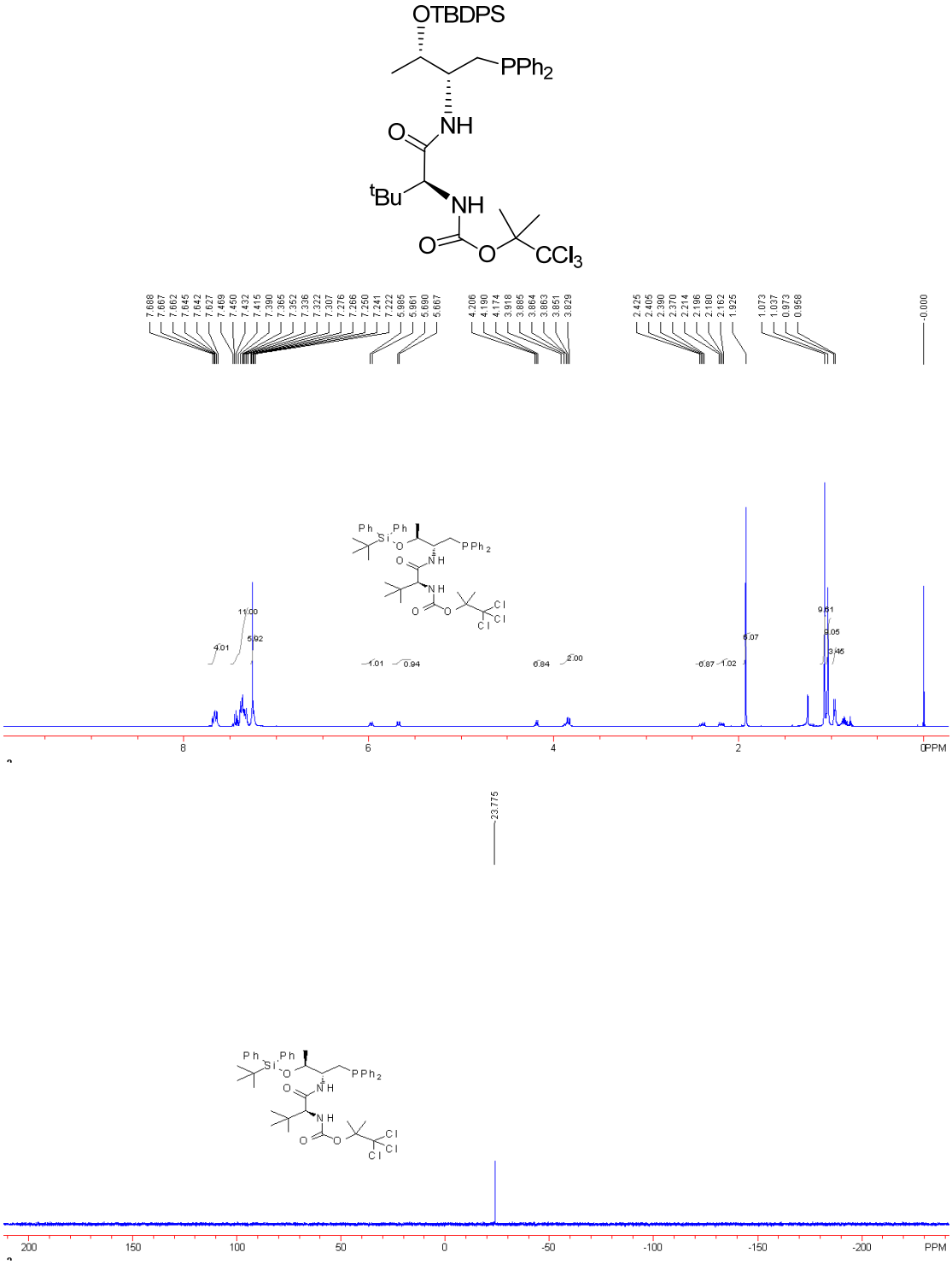
6H), 5.89 (d, J = 9.2 Hz, 3H), 4.23 (m, 1H), 2.43 (ddd, J_1 = 1.6 Hz, J_2 = 4.2 Hz, J_3 = 14.0 Hz, 1H), 2.36 (dd, J_1 = 8.8 Hz, J_2 = 14.0 Hz, 1H), 2.15-2.07 (m, 1H), 0.95 (d, J = 6.8 Hz, 6H); ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ -23.83; IR (neat) ν 3310, 2966, 1637, 1541, 740, 695 cm^{-1}; MS (ESI) *m/z* 376.0 (M^++H, 100); HRMS Calcd. for $C_{19}H_{27}N_3O_3P^{+1}$ (M^++H): 376.1804, found: 376.1785. $[\alpha]^{20}_D$ = +31 (c 0.25, $CHCl_3$).



(S)-1-benzhydryl-3-(1-(diphenylphosphino)-3-(naphthalen-2-yl)propan-2-yl)thiourea (CP5)

Colorless solid, m.p. 84-88 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.18-2.33 (m, 2H), 2.89 (dd, J_1 = 6.6 Hz, J_2 = 12.9 Hz, 1H), 3.13 (dd, J_1 = 5.1, J_2 = 12.9 Hz, 1H), 4.89 (br, 1H), 5.66

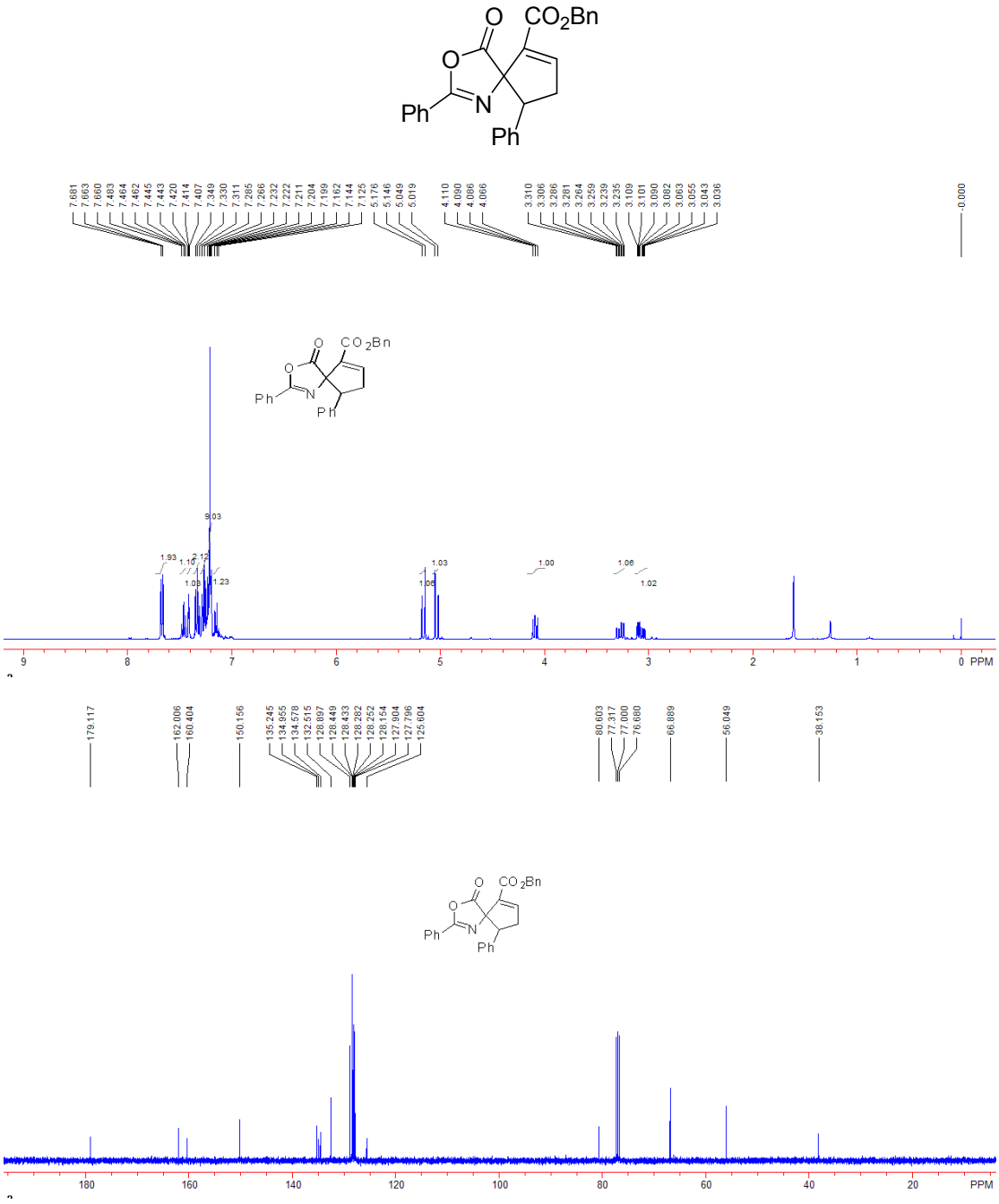
(br, 1H), 6.35 (br, 1H), 7.06-7.10 (m, 4H), 7.18-7.31 (m, 15H), 7.38-7.48 (m, 5H), 7.66-7.70 (m, 2H), 7.77-7.80 (m, 1H); ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ -23.97; IR (CH_2Cl_2): ν 3279, 3054, 2924, 2853, 1599, 1530, 1494, 1480, 1453, 1434, 1344, 1271, 1097, 1027, 814, 740, 696 cm^{-1}; MS (ESI) *m/z* (%): 595.1 (100) [M^++H]; HRMS Calcd. For $C_{39}H_{36}N_2PS^{+1}$ (M^++H) requires 595.2331, Found: 595.2340; $[\alpha]^{20}_D$ = -16.2 (c 1.0, $CHCl_3$).



This is a known compound.[3] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.97 (d, *J* = 6.0 Hz, 3H),

1.04 (s, 9H), 1.07 (s, 9H), 1.93 (s, 6H), 2.19 (dd, J_1 = 7.2 Hz, J_2 = 13.6 Hz, 1H), 2.40 (dd, J_1 = 8.0 Hz, J_2 = 13.6 Hz, 1H,), 3.83-3.92 (m, 2H), 4.19 (t, J = 6.4 Hz, 1H), 5.68 (d, J = 9.2 Hz, 1H), 5.98 (d, J = 9.6 Hz, 1H), 7.22-7.28 (m, 5H), 7.31-7.47 (m, 11H), 7.63-7.69 (m, 4H); ^{31}P NMR (161 MHz, $CDCl_3$, 85% H_3PO_4): δ -23.78.

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



Benzyl 4-oxo-2,9-diphenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3a)

A known product, pale yellow solid,[7] 78% yield, 32 mg, Mp: 119-121 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68-7.66 (m, 2H), 7.48-7.44 (m, 1H), 7.41 (t, J = 2.4 Hz, 1H), 7.35-7.31 (m, 2H), 7.29-7.20 (m, 9H), 7.16-7.13 (m, 1H), 5.16 (d, J = 12.0 Hz, 1H), 5.03 (d, J = 12.0 Hz, 1H), 4.09 (dd, J_1 = 8.0 Hz, J_2 = 9.6 Hz, 1H), 3.27 (ddd, J_1 = 2.0 Hz, J_2 = 9.6 Hz, J_3

= 18.8 Hz, 1H), 3.07 (ddd, J_1 = 2.8 Hz, J_2 = 8.0 Hz, J_3 = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 162.0, 160.4, 150.2, 135.2, 135.0, 134.6, 132.5, 128.9, 128.45, 128.43, 128.28, 128.25, 128.2, 127.9, 127.8, 125.6, 80.6, 66.9, 56.0, 38.2; $[\alpha]^{20}_D$ = +147.9 (c 0.5, $CHCl_3$) for 97% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 80/20, 0.5 mL/min, 214 nm, t_{minor} = 19.832 min, t_{major} = 21.988 min.

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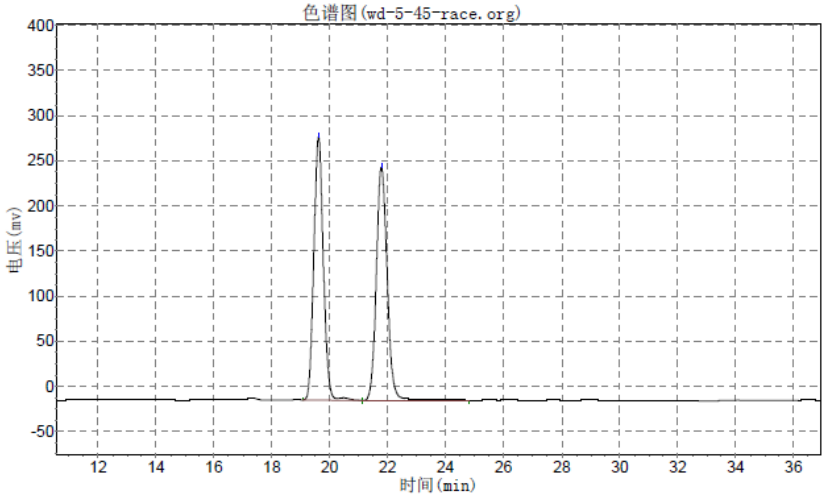

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峰参数表

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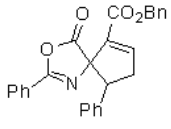

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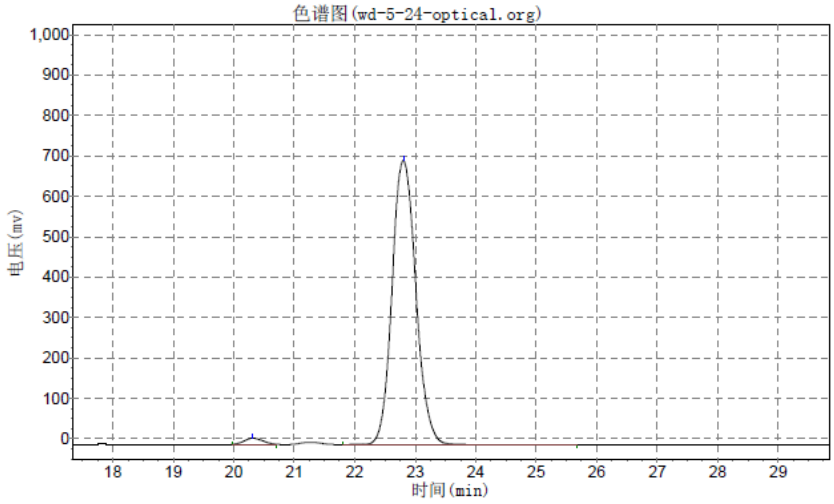

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峰参数表

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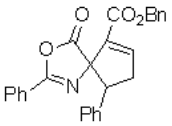

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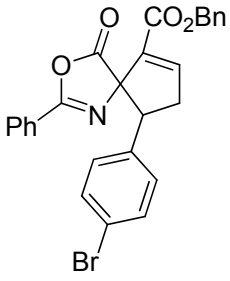

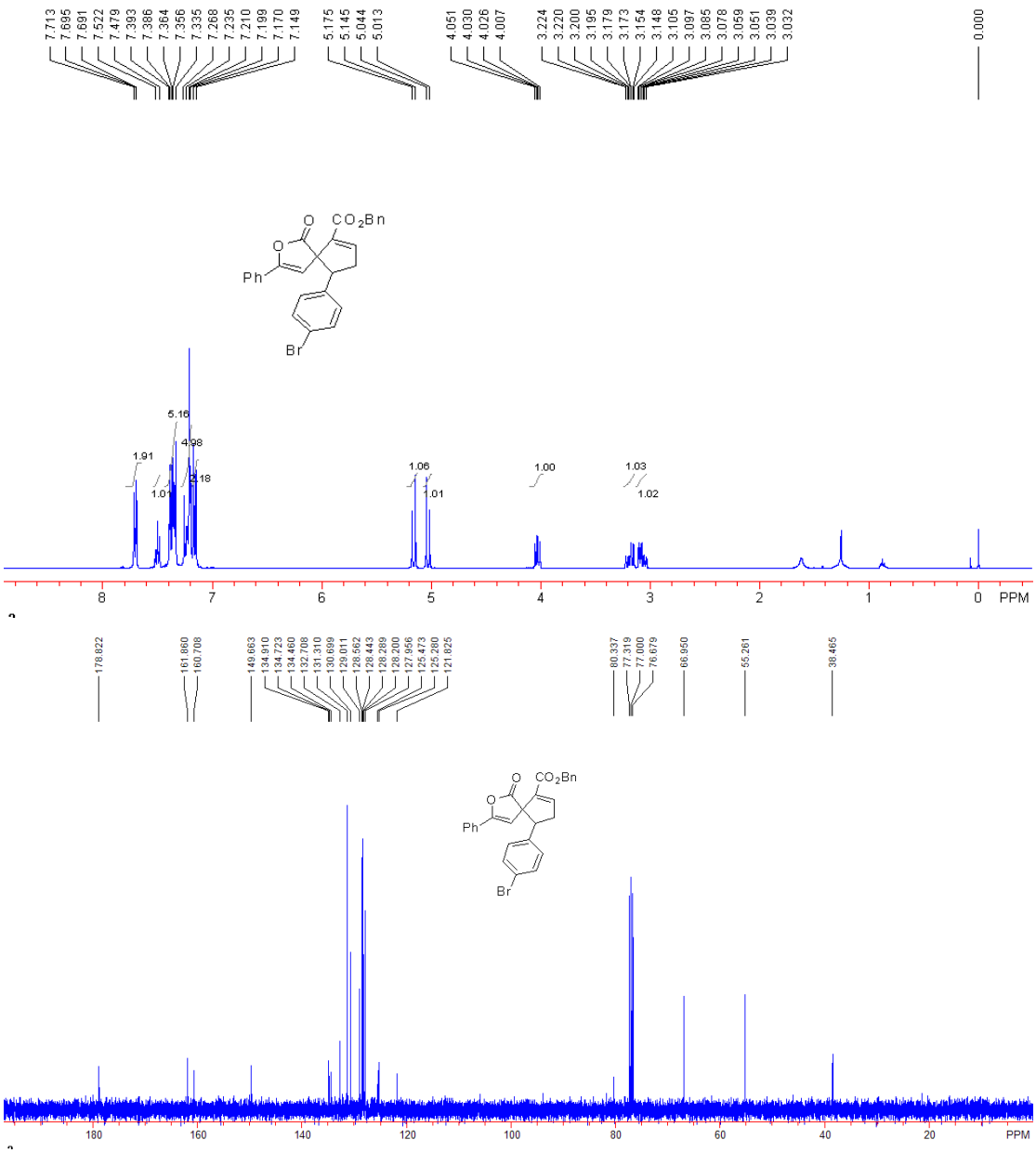

Benzyl

9-(4-bromophenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate

(3b)

A pale yellow solid, 80% yield, 37 mg, Mp: 104-105 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71-7.69 (m, 2H), 7.52-7.48 (m, 1H), 7.39-7.34 (m, 5H), 7.27-7.20 (m, 5H), 7.17-7.15 (m, 2H), 5.16 (d, J = 12.0 Hz, 1H), 5.03 (d, J = 12.0 Hz, 1H), 4.03 (dd, J_1 = 7.6 Hz, J_2 = 9.2 Hz, 1H), 3.19 (ddd, J_1 = 2.4 Hz, J_2 = 9.6 Hz, J_3 = 18.6 Hz, 1H), 3.07 (ddd, J_1 = 3.2 Hz, J_2 = 7.6 Hz, J_3 = 18.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 161.9, 160.7, 150.4, 149.7, 134.9,

134.7, 134.4, 132.7, 131.3, 130.7, 128.6, 128.5, 128.44, 128.43, 128.30, 128.29, 127.9, 125.4, 121.8, 80.3, 67.0, 55.2, 38.5; IR (neat) ν 3065, 1813, 1718, 1648, 1260, 1117, 953, 750, 695 cm^{-1}; MS (ESI) *m/z* 502.0 (M^++H, 100); HRMS Calcd. for $C_{27}H_{20}BrNO_4Na^{+1}$ (M^++Na): 524.0488, found: 524.0468. $[\alpha]^{20}_D$ = +119.8 (c 1.0, $CHCl_3$) for 96% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, hexane/^{i}PrOH = 90/10, 0.5 mL/min, 214 nm, t_{minor} = 20.377 min, t_{major} = 27.377 min.

HPLC REPORT

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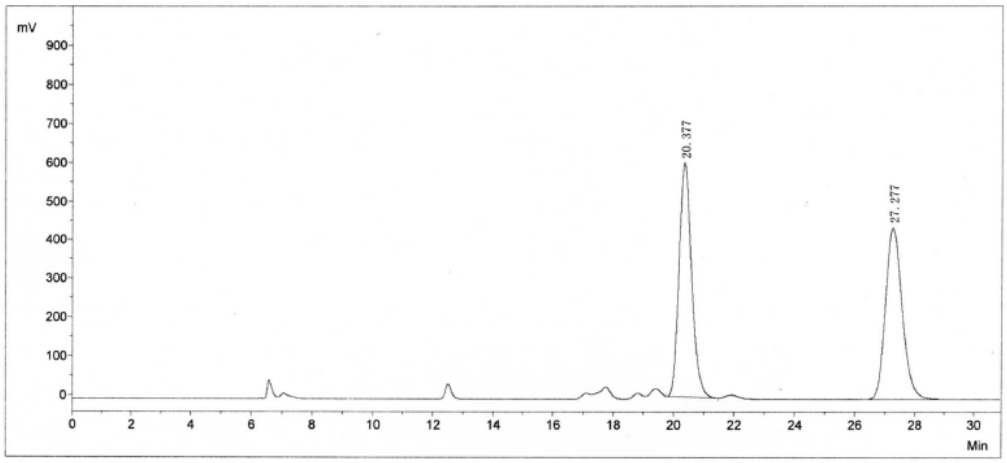

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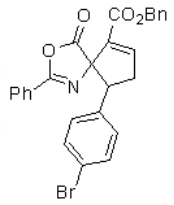
2	2	27.277	440740.4	17156615.4	49.6469
Total			1041200.9	34557290.1	100.0000

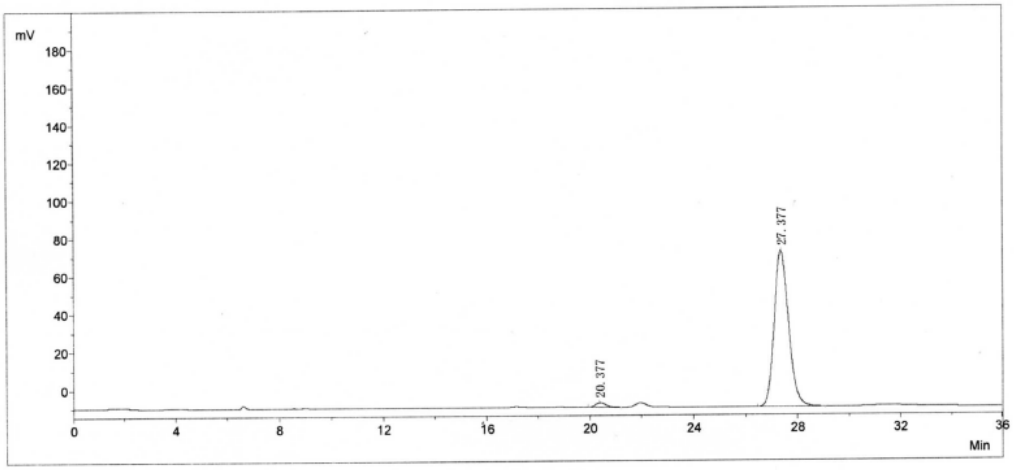


IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm.

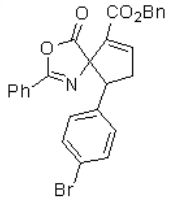
HPLC REPORT

Sample Name:wd-5-74.che
Time:10:47
column:
Velocity:

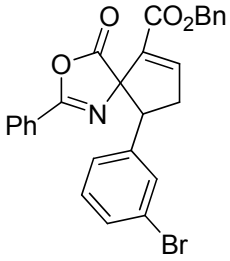
Date:2011-09-16
Method:
the mobile phase:
the detection wavelength:

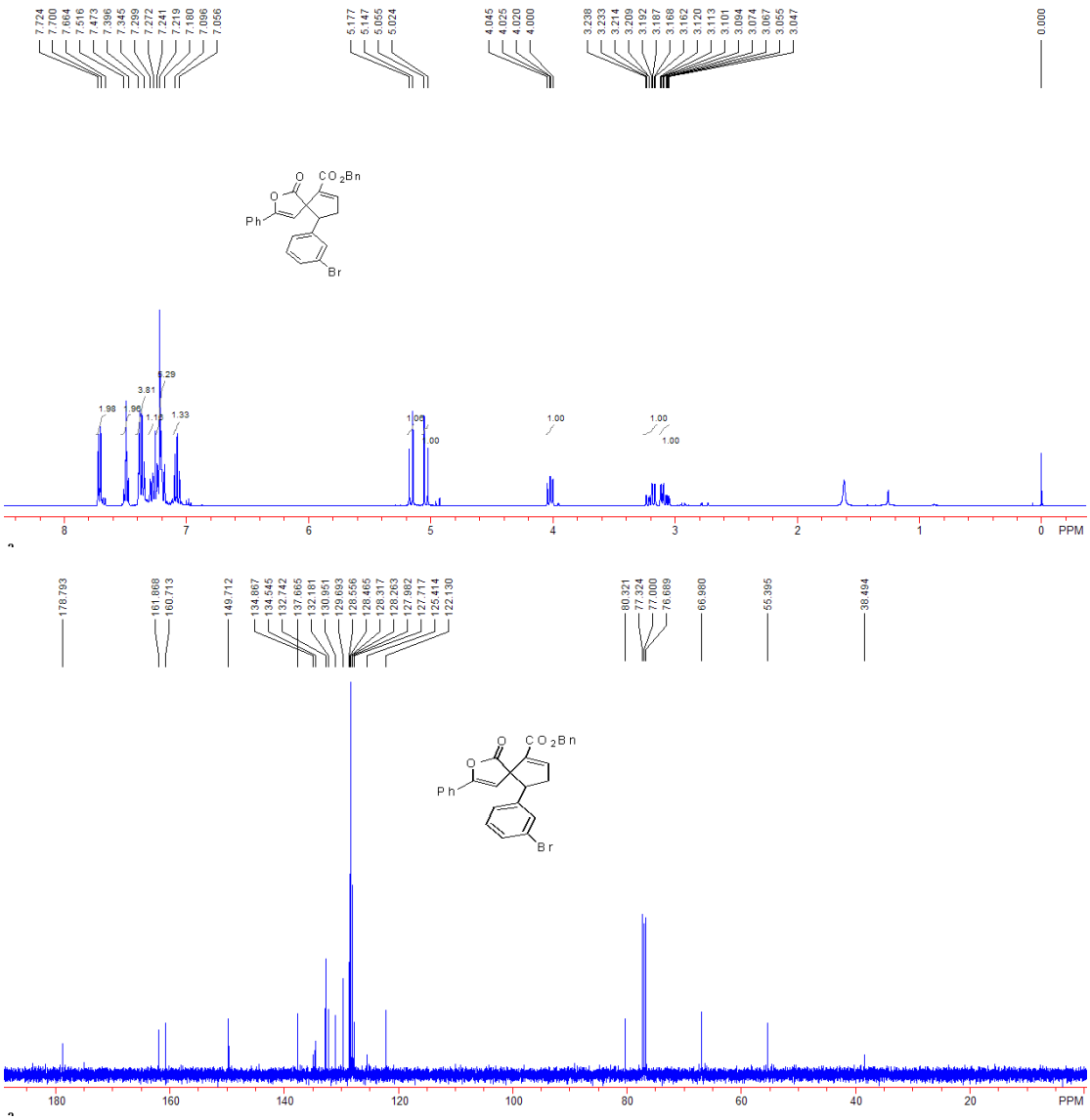


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	20.377	2297.9	66986.7	2.0753
2	2	27.377	82062.7	3160761.4	97.9247
Total			84360.6	3227748.1	100.0000



IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm.





Benzyl

9-(3-bromophenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate

(3c)

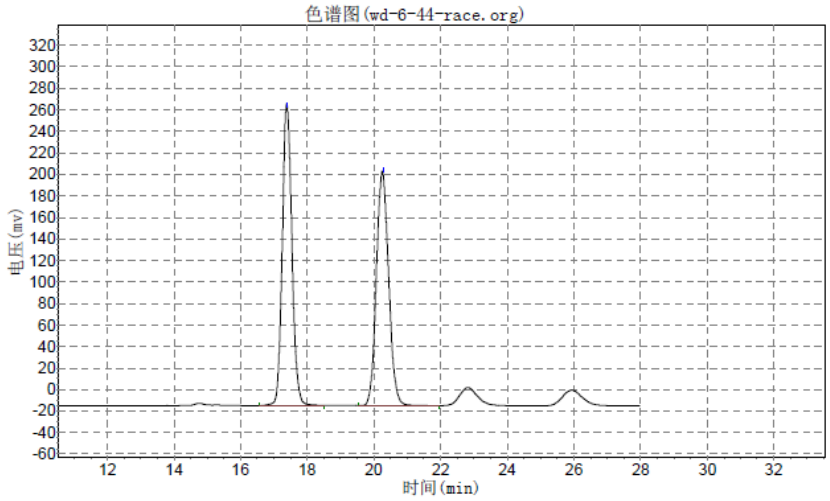
A pale yellow solid, 96% yield, 48 mg, Mp: 108-110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72-7.66 (m, 2H), 7.52-7.47 (m, 2H), 7.40-7.35 (m, 4H), 7.30-7.27 (m, 1H), 7.24-7.18 (m, 5H), 7.10-7.06 (m, 1H), 5.16 (d, J = 12.0 Hz, 1H), 5.04 (d, J = 12.0 Hz, 1H), 4.02 (dd, J_1 = 8.0 Hz, J_2 = 10.0 Hz, 1H), 3.20 (ddd, J_1 = 2.0 Hz, J_2 = 10.0 Hz, J_3 = 18.4 Hz, 1H), 3.08 (ddd, J_1 = 2.8 Hz, J_2 = 8.0 Hz, J_3 = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 161.9, 160.7, 149.7, 137.7, 134.9, 134.5, 132.7, 132.2, 131.0, 129.7, 128.6, 128.5, 128.32, 128.26, 128.0,

127.7, 125.4, 122.1, 80.3, 67.0, 55.4, 38.5; IR (neat) ν 3065, 1813, 1718, 1648, 1560, 1320, 1248, 1119, 955, 883, 692 cm^{-1}; MS (ESI) *m/z* 502.0 (M^++H, 100); HRMS Calcd. for $C_{27}H_{20}BrNO_4Na^{+1}$ (M^++Na): 524.0456, found: 524.0468. $[\alpha]^{20}_D$ = +119.4 (c 0.8, $CHCl_3$) for 95% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 90/10, 0.8 mL/min, 214 nm, t_{minor} = 17.068 min, t_{major} = 19.835 min.

N2000 数据工作站 1

实验时间：2011-10-20, 14:48:47
谱图文件:J:\SIOC液相\spiro\wd-6-44-race.org

实验者：
报告时间：2011-10-20, 20:48:29
积分方法:面积归一法

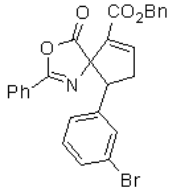


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.398	279903.719	5686112.500	50.1870
2		20.265	218167.281	5643733.500	49.8130
总计			498071.000	11329846.000	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	27.972	10000.0000

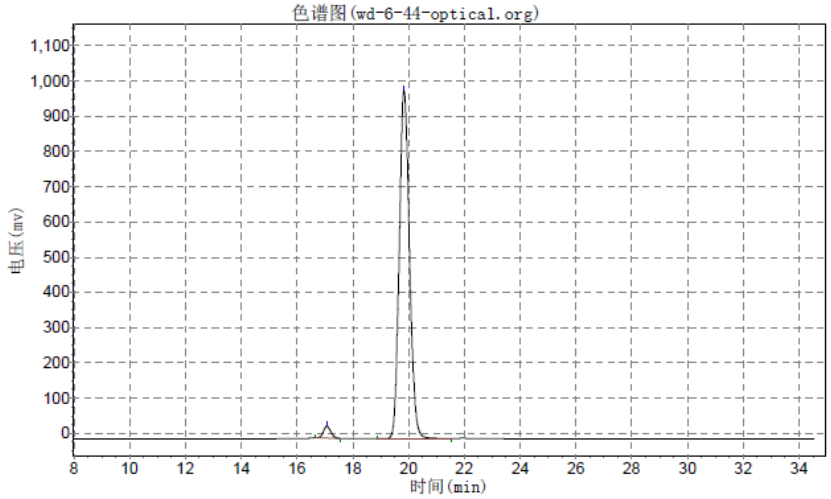


IC-H, 0.8 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.

N2000 数据工作站

实验时间：2011-10-20,15:26:04
谱图文件:J:\SIOC液相\spiro\wd-6-44-optical.org

实验者：
报告时间：2011-10-20,20:51:43
积分方法:面积归一法

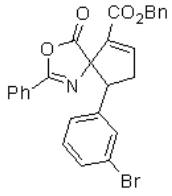


分析结果表

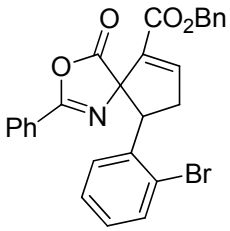
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.068	33696.328	615627.938	2.3980
2		19.835	987207.875	25056638.000	97.6020
总计			1020904.203	25672265.938	100.0000

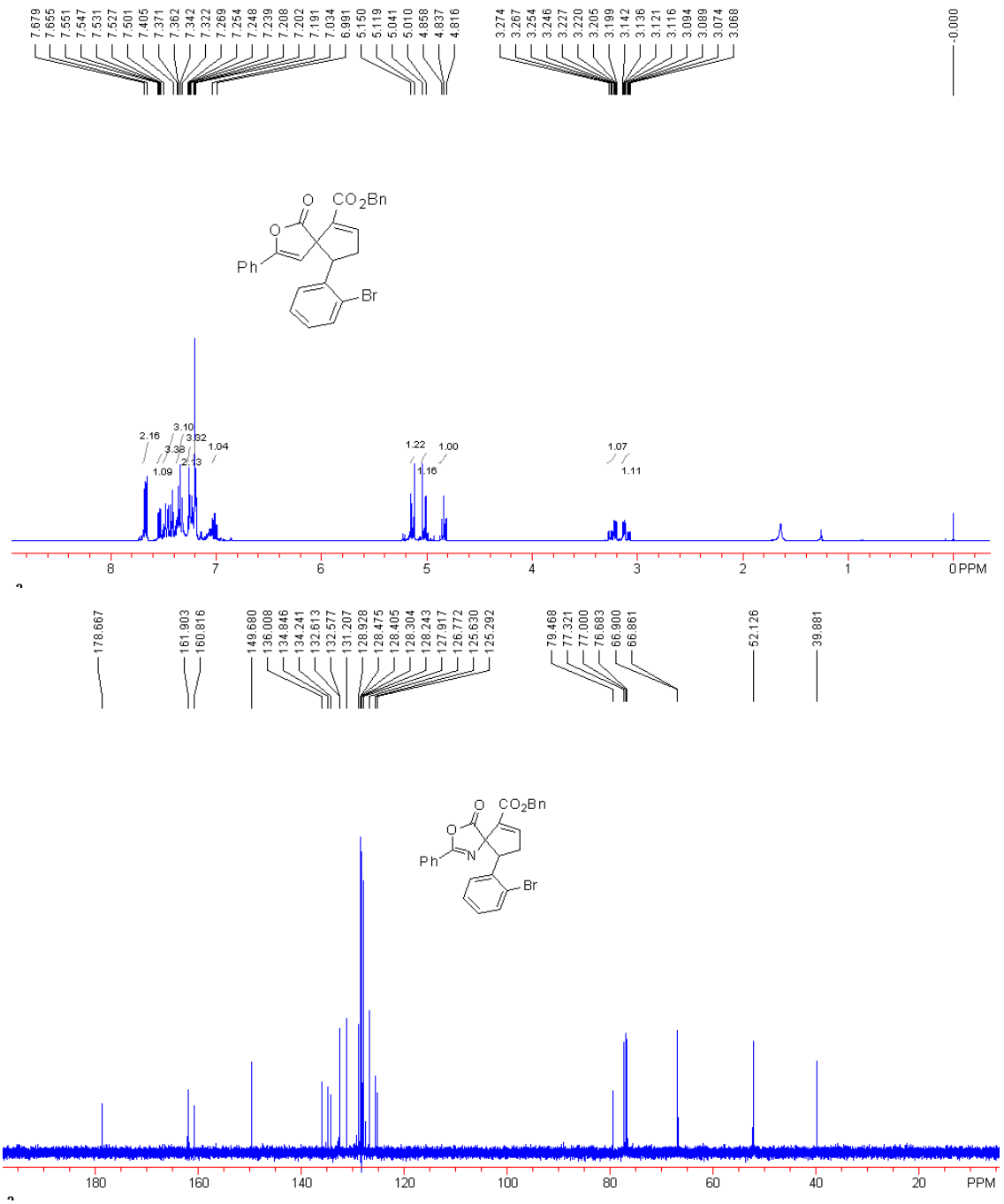
峰参数表

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	34.535	10000.0000



IC-H, 0.8 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.





Benzyl

9-(2-bromophenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate

(3d)

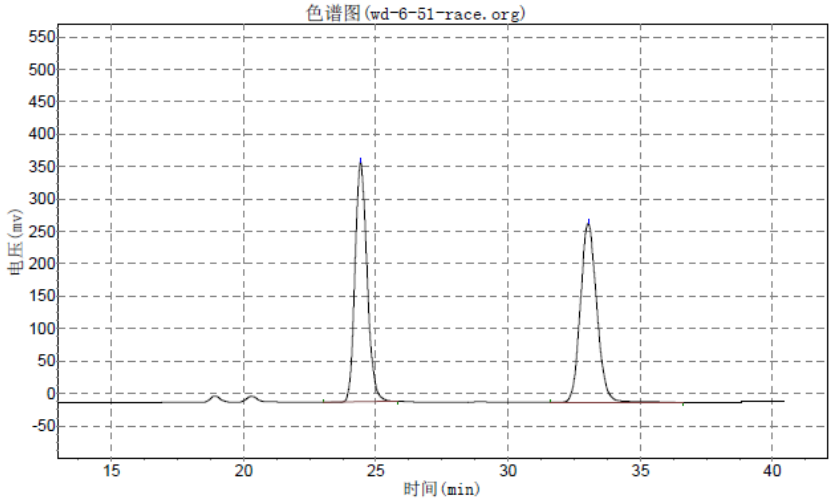
A pale yellow solid, 90% yield, 42 mg, Mp: 107-109 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68-7.66 (m, 2H), 7.55-7.53 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.50-7.41 (m, 3H), 7.37-7.32 (m, 3H), 7.27-7.24 (m, 2H), 7.21-7.19 (m, 3H), 7.03-6.99 (m, 1H), 5.13 (d, J = 12.4 Hz, 1H), 5.03 (d, J = 12.4 Hz, 1H), 4.84 (t, J = 8.4 Hz, 1H), 3.24 (ddd, J_1 = 2.8 Hz, J_2 = 8.4 Hz, J_3 =

18.8 Hz, 1H), 3.11 (ddd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, J_3 = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 161.9, 160.8, 149.7, 136.0, 134.8, 134.2, 132.61, 132.57, 131.2, 128.9, 128.5, 128.4, 128.3, 128.2, 127.9, 126.8, 125.6, 125.3, 79.5, 66.9, 52.1, 39.9; IR (neat) ν 3069, 1815, 1718, 1654, 1648, 1267, 1117, 955, 687 cm^{-1}; MS (ESI) *m/z* 502.0 (M^++H, 100); HRMS Calcd. for $C_{27}H_{20}BrNO_4Na^{+1}$ (M^++Na): 524.0447, found: 524.0468. $[\alpha]^{20}_D$ = +163.2 (c 1.7, $CHCl_3$) for 85% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, t_{minor} = 23.820 min, t_{major} = 32.312 min.

N2000 数据工作站 1

实验时间：2011-10-22,16:09:55
谱图文件:J:\SIOC液相\spiro\wd-6-51-race.org

实验者：
报告时间：2011-10-24,19:36:19
积分方法:面积归一法

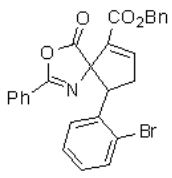


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		24.422	369927.344	11754477.000	49.7551
2		33.025	275296.125	11870184.000	50.2449
总计			645223.469	23624661.000	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	40.420	10000.0000

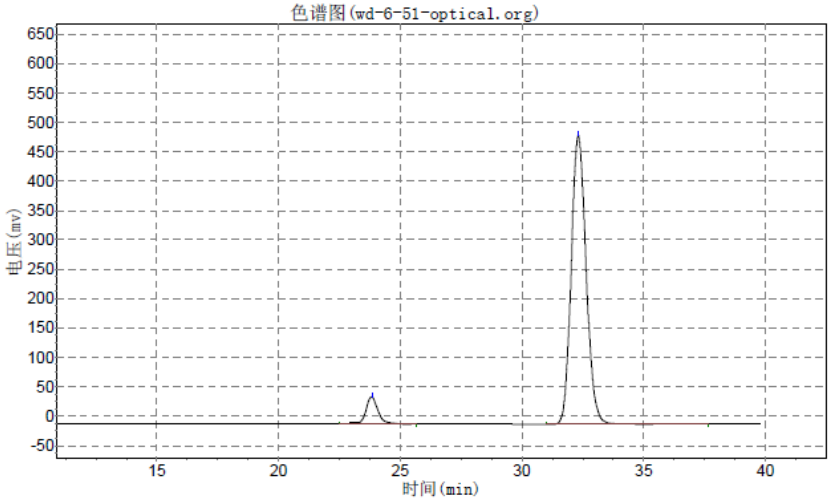


IC-H, 0.7 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm.

N2000 数据工作站 1

实验时间：2011-10-22,16:50:36
谱图文件:J:\SIOC液相\spiro\wd-6-51-optical.org

实验者：
报告时间：2011-10-24,19:40:52
积分方法:面积归一法

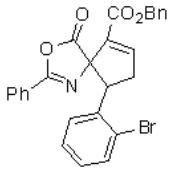


分析结果表

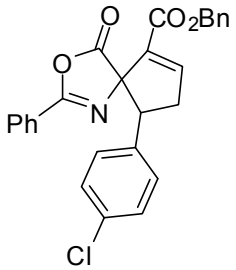
峰号	峰名	保留时间	峰高	峰面积	含量
1		23.820	46899.789	1710876.500	7.5328
2		32.312	491802.313	21001340.000	92.4672
总计			538702.102	22712216.500	100.0000

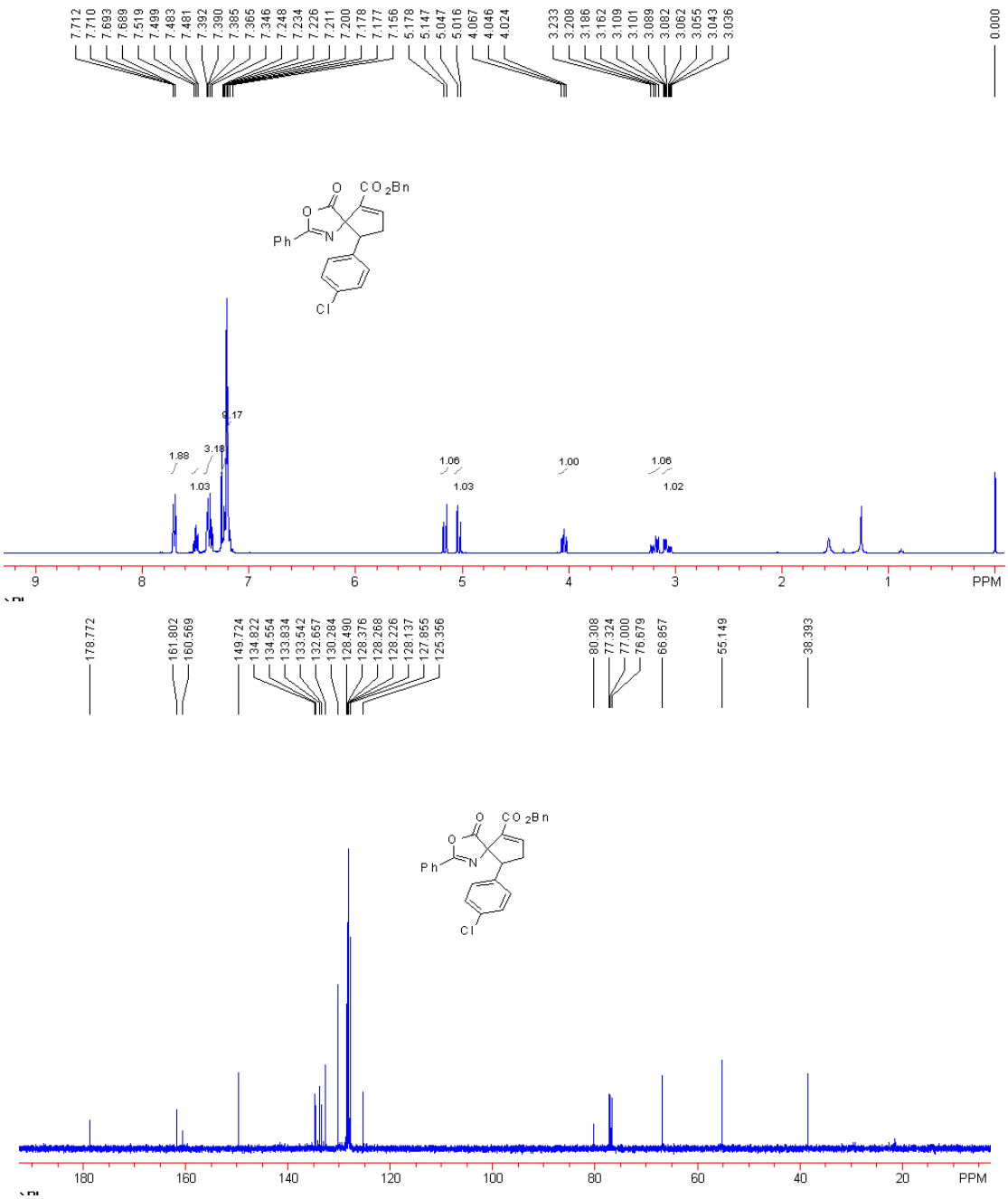
峰参数表

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	39.753	10000.0000



IC-H, 0.7 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm.





Benzyl

9-(4-chlorophenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate

(3e)

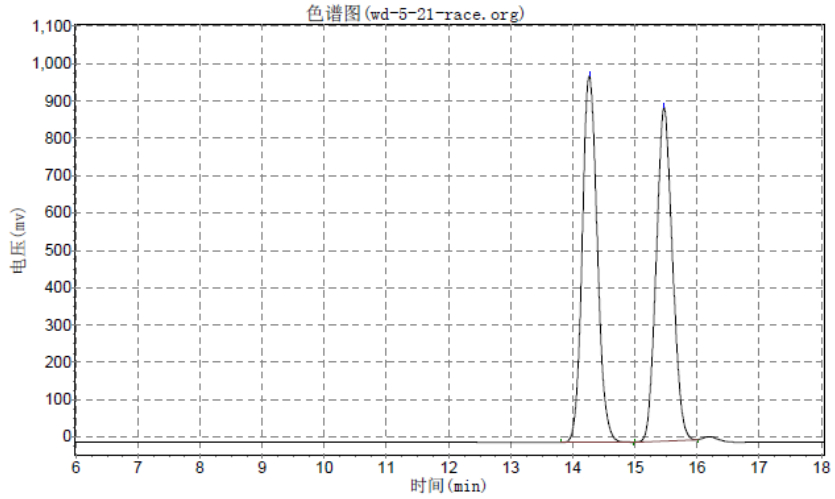
A known product, white solid,[7] 85% yield, 34 mg, Mp: 72-73 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71-7.69 (m, 2H), 7.52-7.48 (m, 1H), 7.39-7.35 (m, 3H), 7.25-7.16 (m, 9H), 5.16 (d, J = 12.4 Hz, 1H), 5.03 (d, J = 12.4 Hz, 1H), 4.05 (t, J = 8.8 Hz, 1H), 3.20 (dd, J_1 = 8.8 Hz, J_2 = 18.4 Hz, 1H), 3.07 (ddd, J_1 = 3.2 Hz, J_2 = 8.8 Hz, J_3 = 18.4 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 178.8, 161.8, 160.6, 149.7, 134.8, 134.6, 133.8, 133.5, 132.7, 130.3, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 125.4, 80.3, 66.9, 55.1, 38.4; $[\alpha]^{20}_{D}$ = +121.1 (c 1.4, $CHCl_3$) for 95% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.75 mL/min, 214 nm, t_{minor} = 14.135 min, t_{major} = 15.332 min.

N2000 数据工作站 1

实验时间：2011-09-27,16:02:39
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-21-race.org

实验者：
报告时间：2011-10-11,21:09:31
积分方法:面积归一法

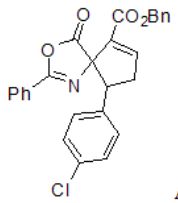


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		14.262	980517.438	16533394.000	50.5447
2		15.467	893201.688	16177028.000	49.4553
总计			1873719.125	32710422.000	100.0000

峰参数表

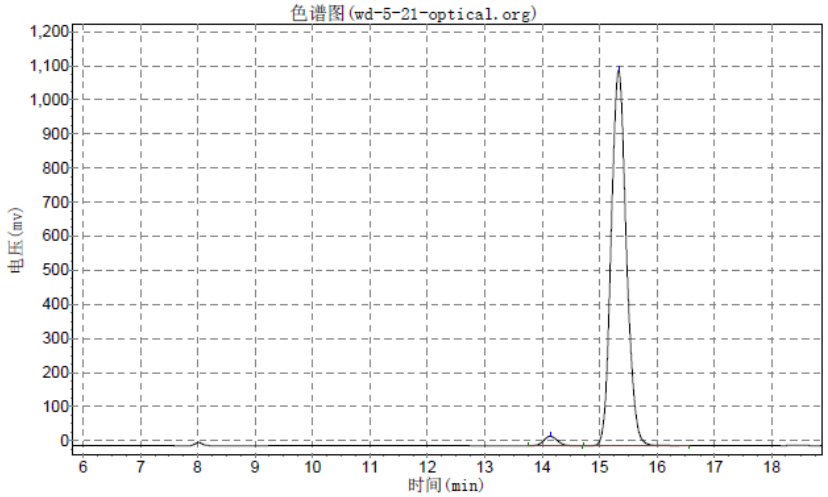
峰宽	斜率	漂移	最小面积	时间变参	锁定时间	停止时间	样品重量
5	70.000	0.000	1000000.000	0.000	0.000	37.318	10000.0000



AD-H, 0.75 ml/min, Hexane/^{i}PrOH = 80/20, 214nm.

实验时间：2011-09-27,16:55:22
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-21-optical.org

实验者：
报告时间：2011-10-11,21:04:22
积分方法:面积归一法

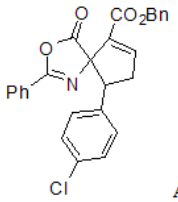


分析结果表

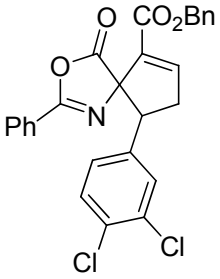
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.135	28532.049	477575.781	2.3040
2		15.332	1101017.500	20250588.000	97.6960
总计			1129549.549	20728163.781	100.0000

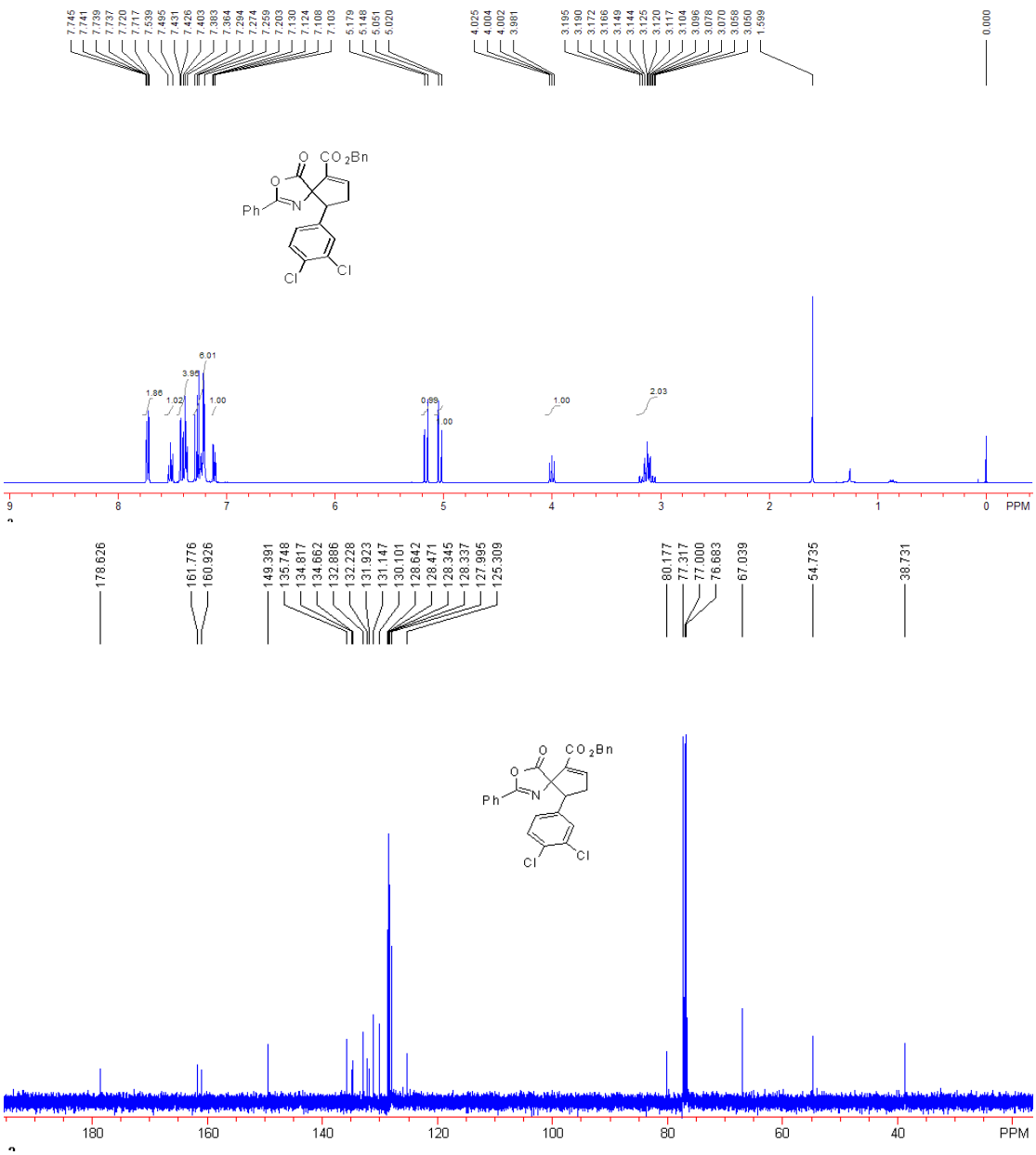
峰参数表

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	37.570	10000.0000



AD-H, 0.75 ml/min, Hexane/^{i}PrOH = 80/20, 214nm.





Benzyl

9-(3,4-dichlorophenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylat

e (3f)

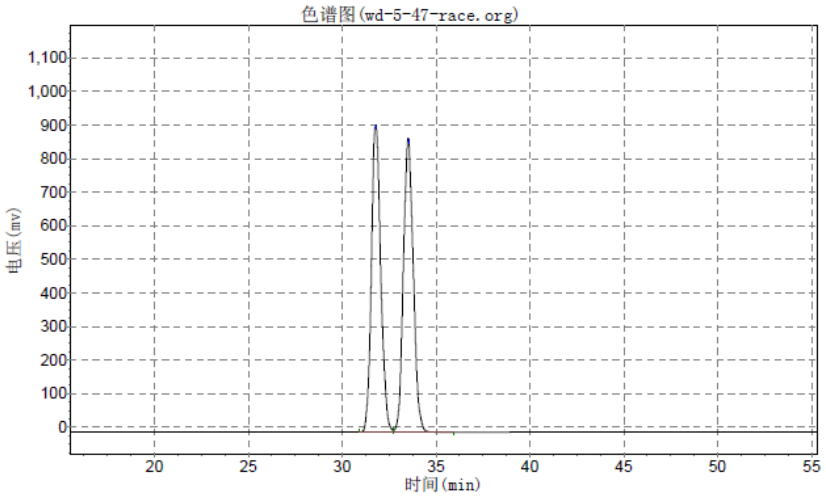
A white solid, 75% yield, 36 mg, Mp: 98-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75-7.72 (m, 2H), 7.54-7.50 (m, 1H), 7.43-7.36 (m, 4H), 7.29-7.20 (m, 6H), 7.12 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 5.16 (d, J = 12.4 Hz, 1H), 5.04 (d, J = 12.4 Hz, 1H), 4.00 (dd, J_1 = 8.4 Hz, J_2 = 9.2 Hz, 1H), 3.20-3.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 161.8, 160.9, 149.4, 135.7, 134.8, 134.7, 132.9, 132.2, 131.9, 131.1, 130.1, 128.6, 128.5, 128.35, 128.34,

128.0, 125.3, 80.2, 67.0, 54.7, 38.7; IR (neat) ν 2947, 1813, 1716, 1650, 1473, 1451, 1247, 1122, 956, 885, 695 cm^{-1}; MS (ESI) *m/z* 492.0 (M^++H, 100); HRMS Calcd. for $C_{27}H_{19}Cl_2NO_4Na^{+1}$ (M^++Na): 514.0590, found: 514.0583. $[\alpha]^{20}_D$ = +106.1 (c 0.85, $CHCl_3$) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.5 mL/min, 214 nm, t_{minor} = 31.475 min, t_{major} = 33.128 min.

N2000 数据工作站 1

实验时间：2011-09-28,19:17:22
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-47-race.org

实验者:
报告时间：2011-10-17,22:35:12
积分方法:面积归一法

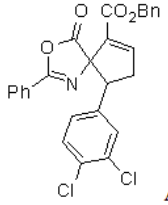


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		31.832	910691.813	31789502.000	49.7948
2		33.565	871605.313	32051542.000	50.2052
总计			1782297.125	63841044.000	100.0000

峰参数表

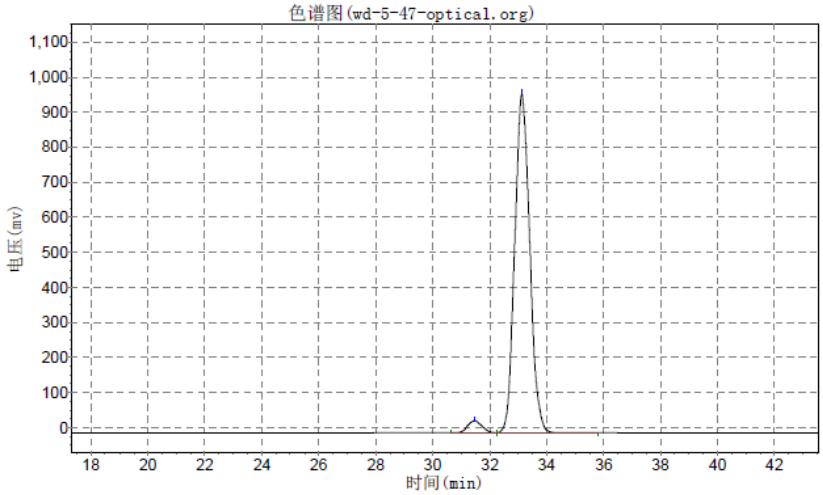
峰宽	斜率	漂移	最小面积	时间变参	锁定时间	停止时间	样品重量
5	70.000	0.000	1000000.000	0.000	0.000	90.112	10000.0000



AD-H, 0.5 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm.

实验时间：2011-09-28,20:39:12
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-47-optical.org

实验者：
报告时间：2011-10-17,22:37:06
积分方法:面积归一法

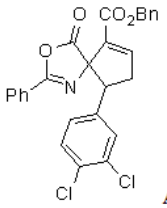


分析结果表

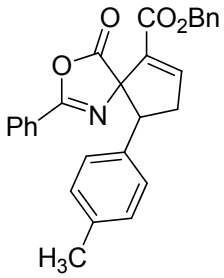
峰号	峰名	保留时间	峰高	峰面积	含量
1		31.475	35121.477	1226593.750	3.3399
2		33.128	966725.438	35498968.000	96.6601
总计			1001846.914	36725561.750	100.0000

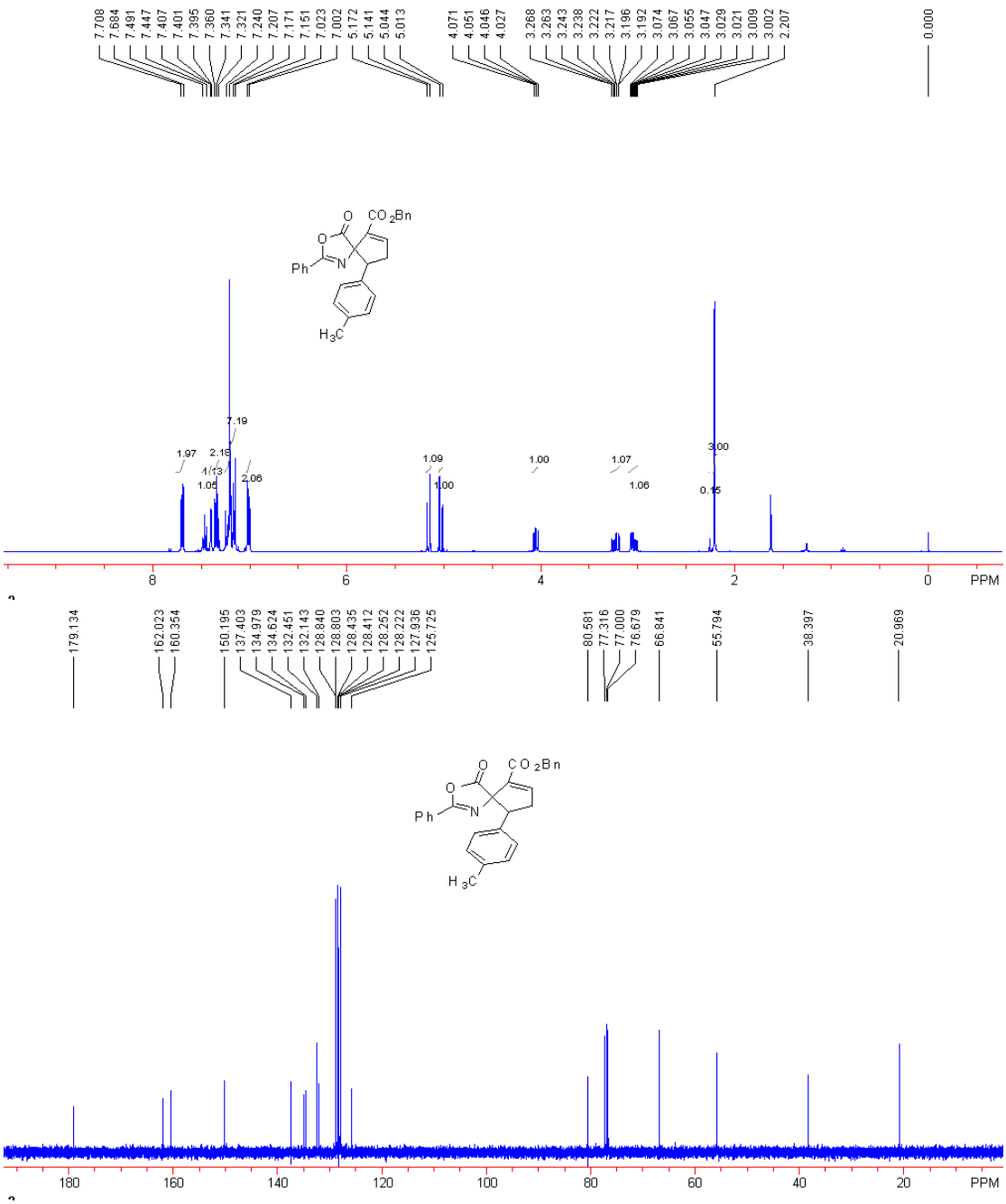
峰参数表

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	55.792	10000.0000



AD-H, 0.5 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm.





Benzyl 4-oxo-2-phenyl-9-(p-tolyl)-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3g)

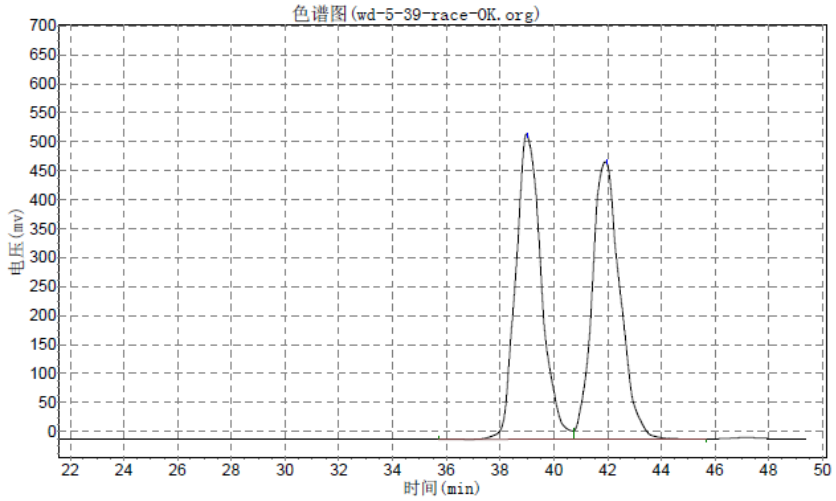
A known product, white solid,[7] 76% yield, 29 mg, Mp: 82-83 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71-7.68 (m, 2H), 7.49-7.45 (m, 1H), 7.40 (t, J = 2.4 Hz, 1H), 7.36-7.32 (m, 2H), 7.24-7.15 (m, 7H), 7.01 (d, J = 8.4 Hz, 1H), 5.16 (d, J = 12.4 Hz, 1H), 5.03 (d, J = 12.4 Hz, 1H), 4.45 (dd, J_1 = 8.0 Hz, J_2 = 10.0 Hz, 1H), 3.23 (ddd, J_1 = 2.0 Hz, J_2 = 10.0 Hz, J_3 = 18.6 Hz, 1H), 3.04 (ddd, J_1 = 2.8 Hz, J_2 = 8.0 Hz, J_3 = 18.6 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 162.0, 160.4, 150.2, 137.4, 135.0, 134.6, 132.4, 132.1, 128.84, 128.80,

128.43, 128.41, 128.3, 128.2, 127.9, 125.7, 80.6, 66.8, 55.8, 38.4, 21.0; $[\alpha]^{20}_{D}$ = +190.1 (c 1.0, $CHCl_3$) for 99% ee; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/*i*PrOH = 80/20, 0.3 mL/min, 214 nm, t_{minor} = 39.848 min, t_{major} = 42.678 min.

N2000 数据工作站 1

实验时间：2011-10-11,17:16:14
谱图文件:J:\SIOC液相\spiro\wd-5-39-race-OK.org

实验者：
报告时间：2011-10-13,17:17:29
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		39.048	525041.313	35117732.000	50.3850
2		41.982	478868.406	34581052.000	49.6150
总计			1003909.719	69698784.000	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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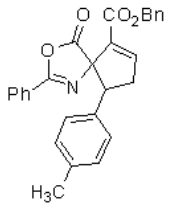
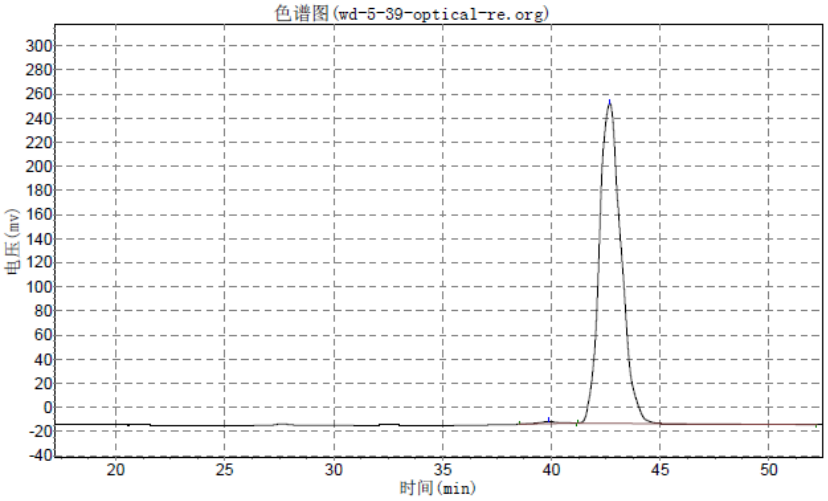


OD-H, 0.3 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.

N2000 数据工作站 1

实验时间：2011-10-11,19:07:19
谱图文件:J:\SIOC液相\spiro\wd-5-39-optical-re.org

实验者：
报告时间：2011-10-13,17:13:57
积分方法:面积归一法

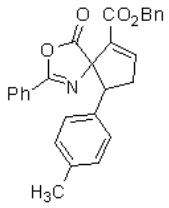


分析结果表

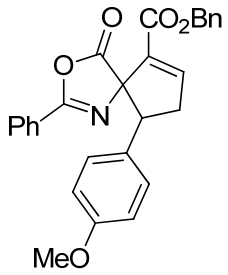
峰号	峰名	保留时间	峰高	峰面积	含量
1		39.848	1661.220	103938.484	0.5667
2		42.678	265673.469	18237150.000	99.4333
总计			267334.689	18341088.484	100.0000

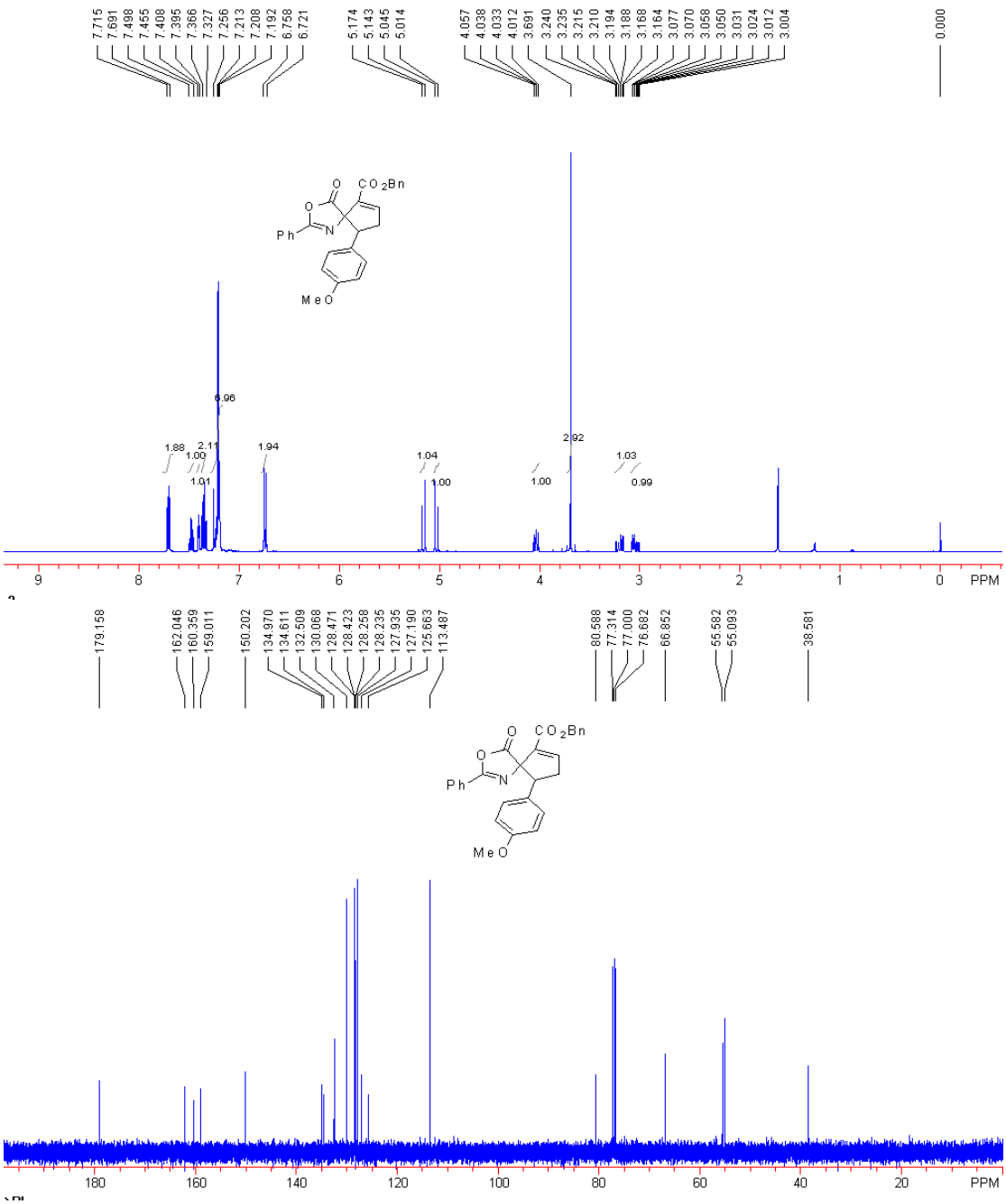
峰参数表

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	52.445	10000.0000



OD-H, 0.3 ml/min, ^{i}PrOH/Hexane = 80/20, 214 nm.





Benzyl

9-(4-methoxyphenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate

(3h)

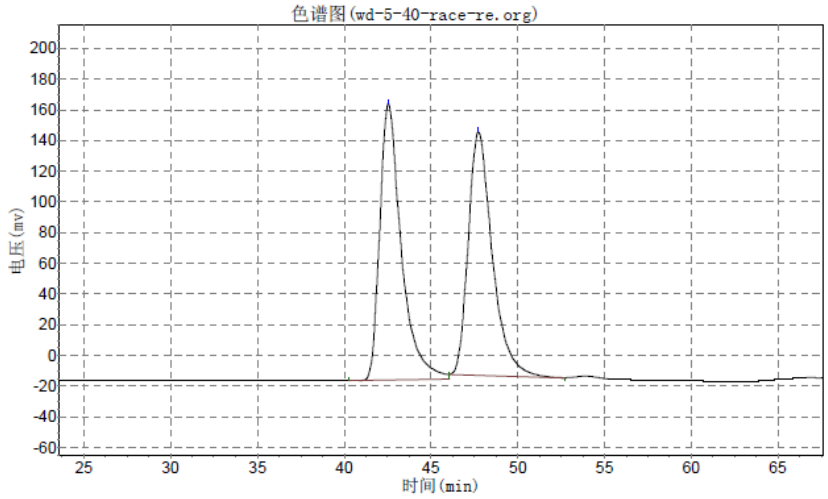
A known product, white solid,[7] 66% yield, 26 mg, Mp: 61-62 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72-7.69 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.40 (m, 1H), 7.37-7.33 (m, 2H), 7.26-7.19 (m, 7H), 6.76-6.72 (m, 2H), 5.16 (d, J = 12.4 Hz, 1H), 5.03 (d, J = 12.4 Hz, 1H), 4.04 (dd, J_1 = 8.4 Hz, J_2 = 10.4 Hz, 1H), 3.69 (s, 3H), 3.20 (ddd, J_1 = 2.0 Hz, J_2 = 10.4 Hz, J_3

= 18.8 Hz, 1H), 3.04 (ddd, J_1 = 2.8 Hz, J_2 = 8.4 Hz, J_3 = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 162.0, 160.4, 159.0, 150.2, 135.0, 134.6, 132.5, 130.1, 128.5, 128.4, 128.3, 128.2, 127.9, 127.2, 125.7, 113.5, 80.6, 66.8, 55.6, 55.1, 38.6; $[\alpha]^{20}_D$ = +160.2 (c 0.9, $CHCl_3$) for 96% ee; Enantiomeric excess was determined by HPLC with a Chiralcel PC-2, Hexane/^{i}PrOH = 80/20, 0.5 mL/min, 214 nm, t_{minor} = 42.518 min, t_{major} = 46.942 min.

N2000 数据工作站 1

实验时间：2011-10-10,18:18:16
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-40-race-re.org

实验者:
报告时间：2011-10-11,21:46:15
积分方法:面积归一法

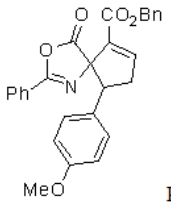


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		42.542	180170.984	15578170.000	50.4906
2		47.720	158463.750	15275447.000	49.5094
总计			338634.734	30853617.000	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	74.997	10000.0000

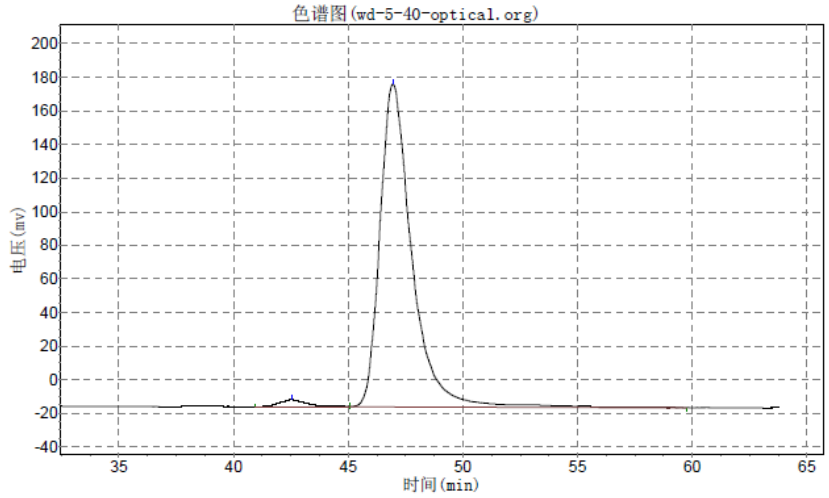


PC-2, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.

N2000 数据工作站 1

实验时间：2011-10-10,17:01:24
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-40-optical.org

实验者：
报告时间：2011-10-11,21:43:29
积分方法:面积归一法

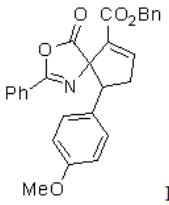


分析结果表

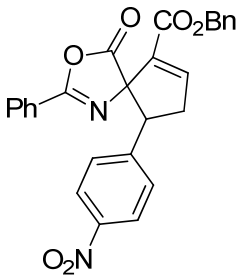
峰号	峰名	保留时间	峰高	峰面积	含量
1		42.518	4072.862	353726.125	1.8645
2		46.942	192277.344	18617488.000	98.1355
总计			196350.206	18971214.125	100.0000

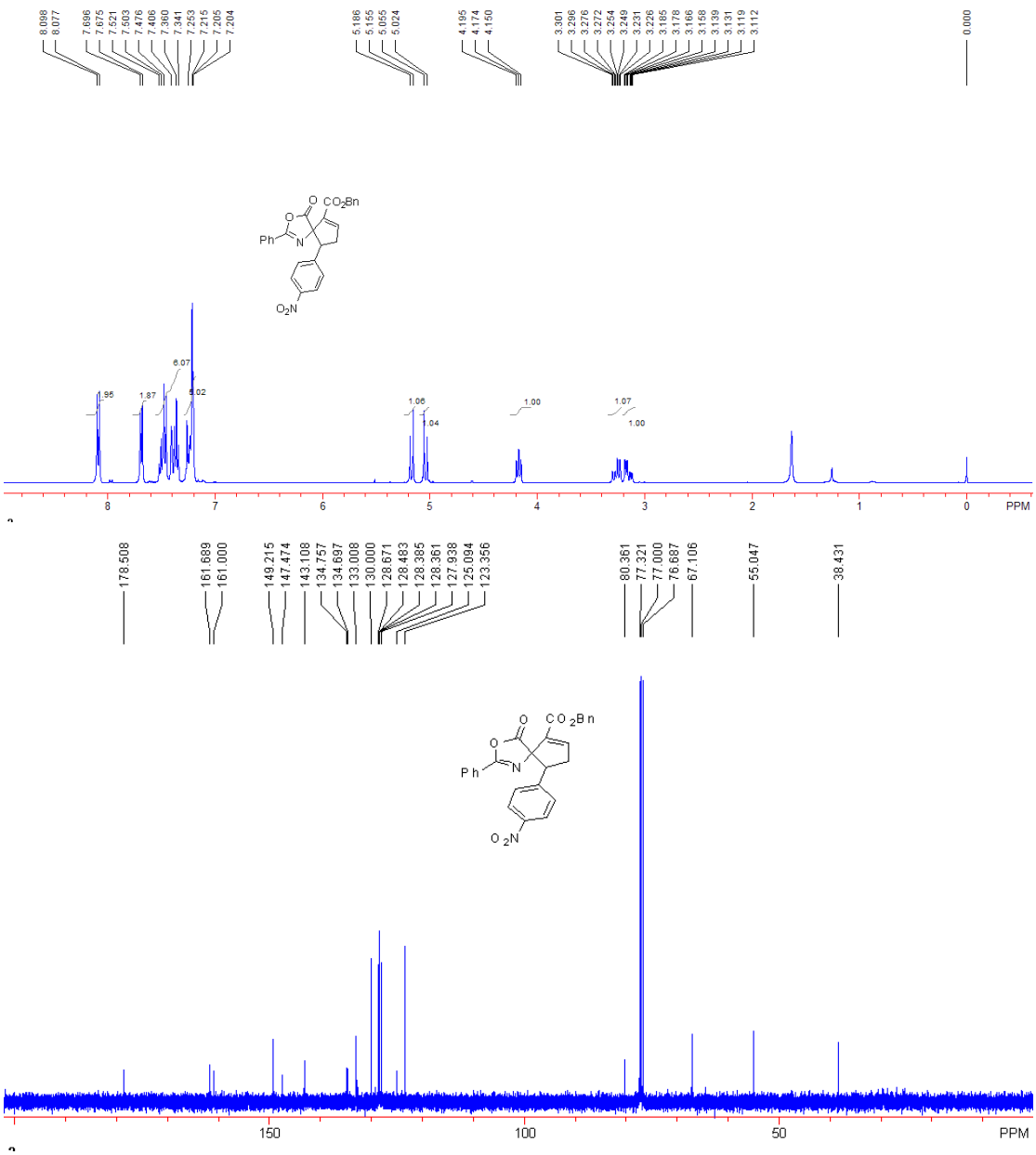
峰参数表

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	63.768	10000.0000



PC-2, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.





Benzyl

9-(4-nitrophenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3i)

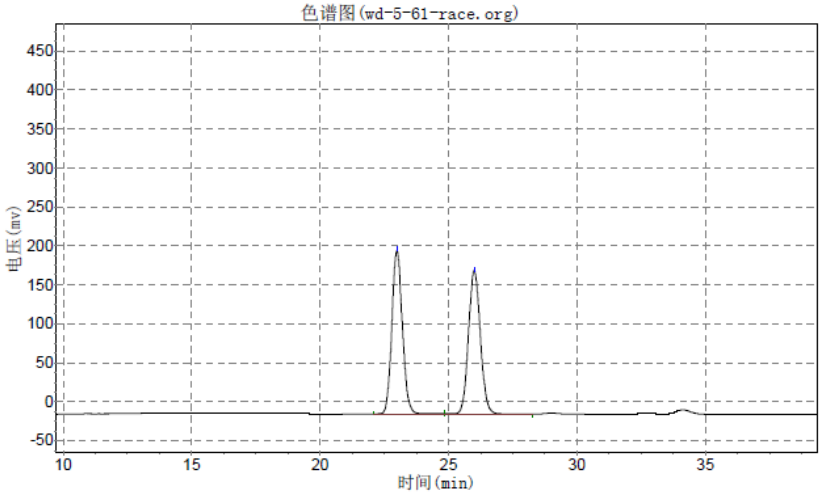
A pale yellow solid, 69% yield, 31 mg, Mp: 135-136 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.10-8.08 (m, 2H), 7.70-7.68 (m, 2H), 7.52-7.34 (m, 6H), 7.25-7.20 (m, 5H), 5.17 (d, J = 12.4 Hz, 1H), 5.04 (d, J = 12.4 Hz, 1H), 4.17 (t, J = 8.4 Hz, 1H), 3.26 (ddd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, J_3 = 18.8 Hz, 1H), 3.15 (ddd, J_1 = 2.8 Hz, J_2 = 8.4 Hz, J_3 = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 161.7, 161.0, 149.2, 147.5, 143.1, 134.8, 134.7, 133.0, 130.0, 128.7, 128.5, 128.39, 128.36, 127.9, 125.1, 123.4, 80.4, 67.1, 55.0, 38.4; IR (neat) ν 2925, 1816,

1713, 1650, 1522, 1346, 1118, 955, 700 cm^{-1}; MS (ESI) *m/z* 469.0 (M^++H, 100); HRMS Calcd. for $C_{27}H_{21}N_2O_6^{+1}$ (M^++H): 469.1400, found: 469.1394. $[\alpha]^{20}_D$ = +49.6 (c 0.75, $CHCl_3$) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.75 mL/min, 214 nm, t_{minor} = 22.893 min, t_{major} = 25.902 min.

N2000 数据工作站 1

实验时间：2011-09-29,10:09:24
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-61-race.org

实验者：
报告时间：2011-10-17,22:18:25
积分方法:面积归一法

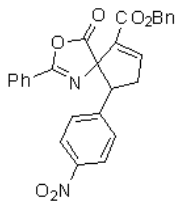


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		22.998	208385.969	5988689.000	50.1978
2		26.032	183868.938	5941497.000	49.8022
总计			392254.906	11930186.000	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	44.168	10000.0000

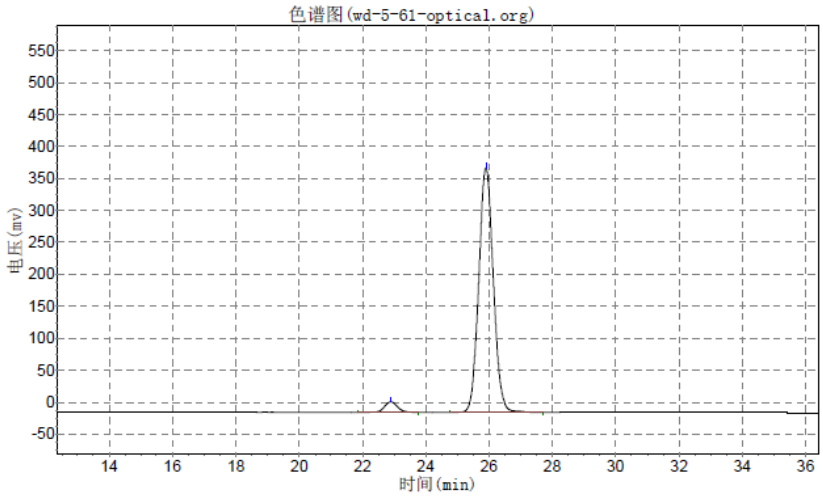


AD-H, 0.75 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.

N2000 数据工作站 1

实验时间：2011-09-29,10:51:46
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-61-optical.org

实验者：
报告时间：2011-10-17,22:21:03
积分方法:面积归一法

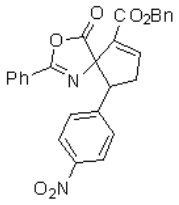


分析结果表

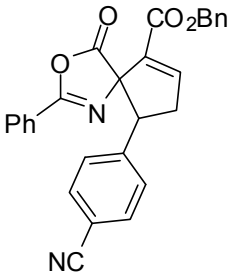
峰号	峰名	保留时间	峰高	峰面积	含量
1		22.893	16517.879	466934.719	3.6722
2		25.902	382464.969	12248398.000	96.3278
总计			398982.848	12715332.719	100.0000

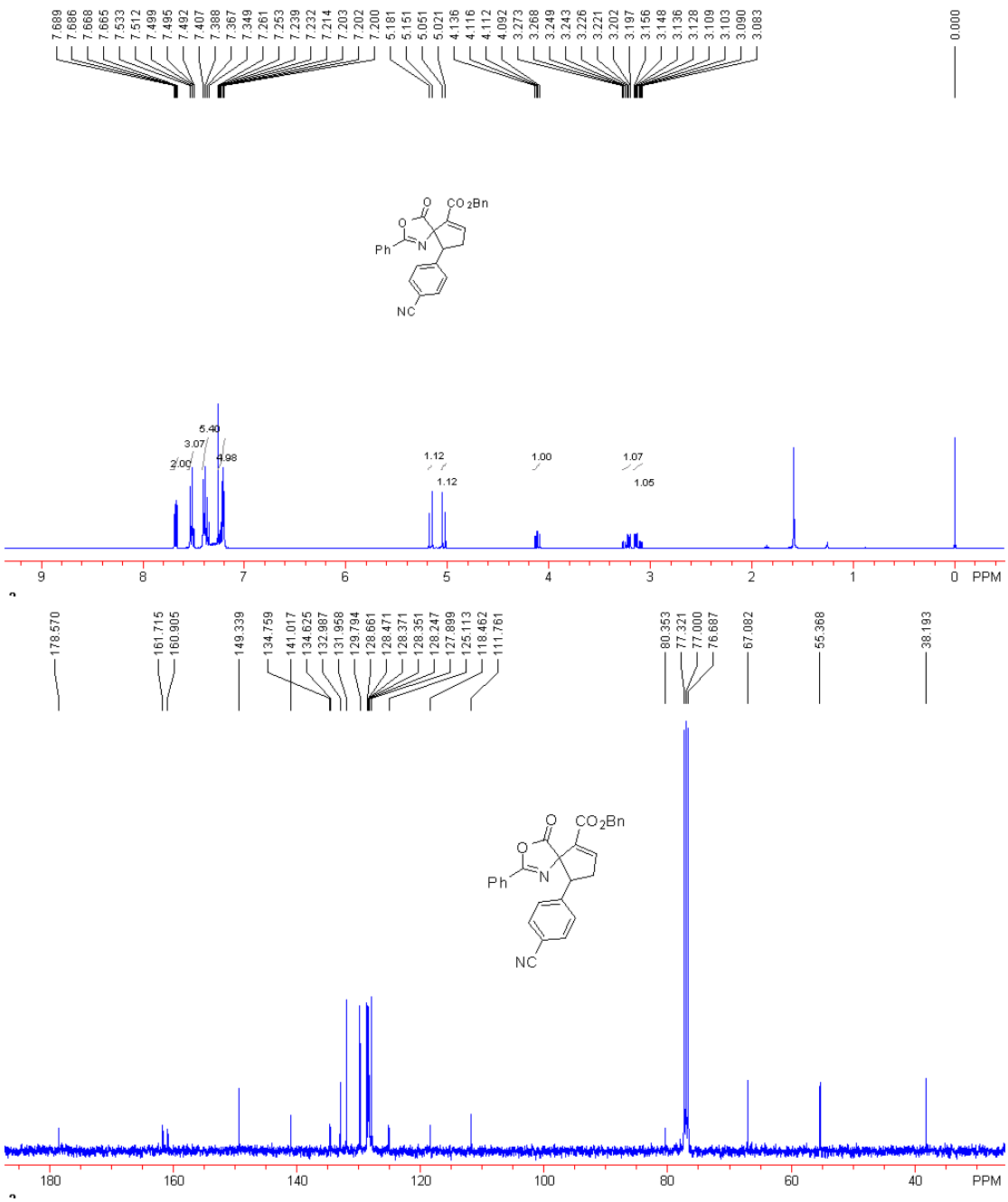
峰参数表

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	40.243	10000.0000



AD-H, 0.75 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.





Benzyl

9-(4-cyanophenyl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate

(3j)

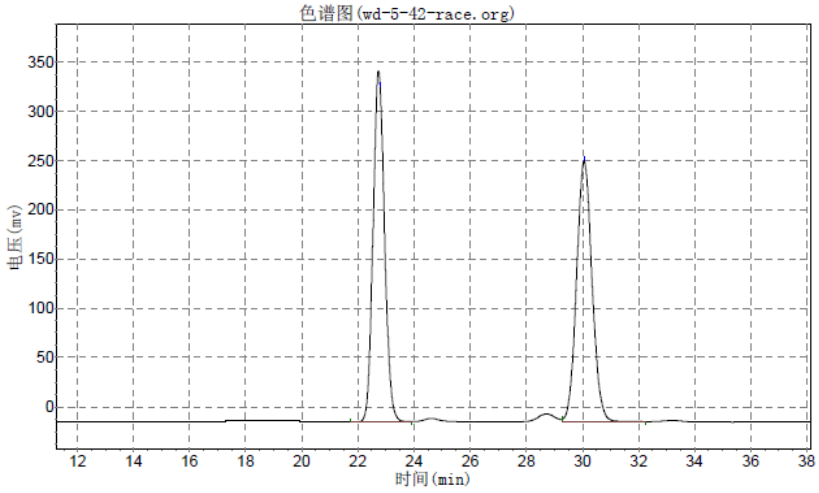
A white solid, 83% yield, 37 mg, Mp: 91-92 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69-7.67 (m, 2H), 7.53-7.49 (m, 3H), 7.41-7.35 (m, 5H), 7.25-7.20 (m, 5H), 5.17 (d, J = 12.0 Hz, 1H), 5.04 (d, J = 12.0 Hz, 1H), 4.11 (dd, J_1 = 8.0 Hz, J_2 = 9.6 Hz, 1H), 3.24 (ddd, J_1 = 2.0 Hz, J_2 = 9.6 Hz, J_3 = 18.8 Hz, 1H), 3.12 (ddd, J_1 = 3.2 Hz, J_2 = 8.0 Hz, J_3 = 18.8 Hz, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 178.6, 161.7, 160.9, 149.3, 141.0, 134.8, 134.6, 133.0, 132.0, 129.8, 128.7, 128.5, 128.37, 128.35, 128.2, 127.9, 125.1, 118.5, 111.8, 80.4, 67.1, 55.4, 38.2; IR (neat) ν 3065, 2228, 1813, 1718, 1648, 1451, 1321, 1119, 956, 695 cm^{-1}; MS (ESI) *m/z* 449.1 (M^++H, 100); HRMS Calcd. for $C_{28}H_{21}N_2O_4^{+1}$ (M^++H): 449.1509, found: 449.1496. $[\alpha]^{20}_D$ = +87.7 (c 0.75, $CHCl_3$) for 93% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, 0.75 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm, t_{minor} = 23.240 min, t_{major} = 30.775 min.

N2000 数据工作站 1

实验时间：2011-09-29,11:36:04
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-42-race.org

实验者：
报告时间：2011-10-11,21:50:47
积分方法:面积归一法

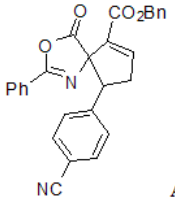


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		22.790	351659.719	10168215.000	49.7892
2		30.057	262047.734	10254333.000	50.2108
总计			613707.453	20422548.000	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	41.950	10000.0000

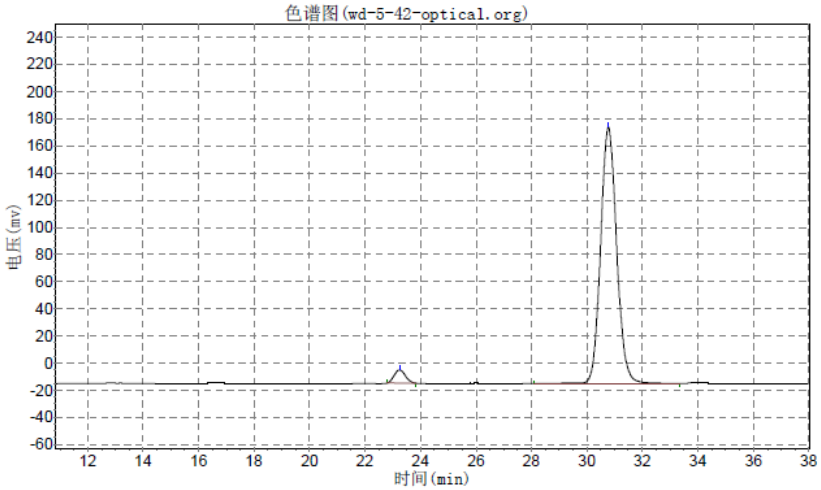


AD-H, 0.75 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.

N2000 数据工作站 1

实验时间：2011-09-29,12:15:17
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-42-optical.org

实验者：
报告时间：2011-10-11,21:53:35
积分方法:面积归一法

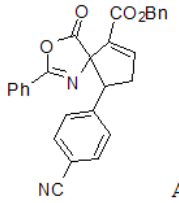


分析结果表

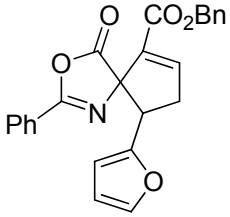
峰号	峰名	保留时间	峰高	峰面积	含量
1		23.240	9825.697	273944.906	3.4788
2		30.775	188970.641	7600833.000	96.5212
总计			198796.338	7874777.906	100.0000

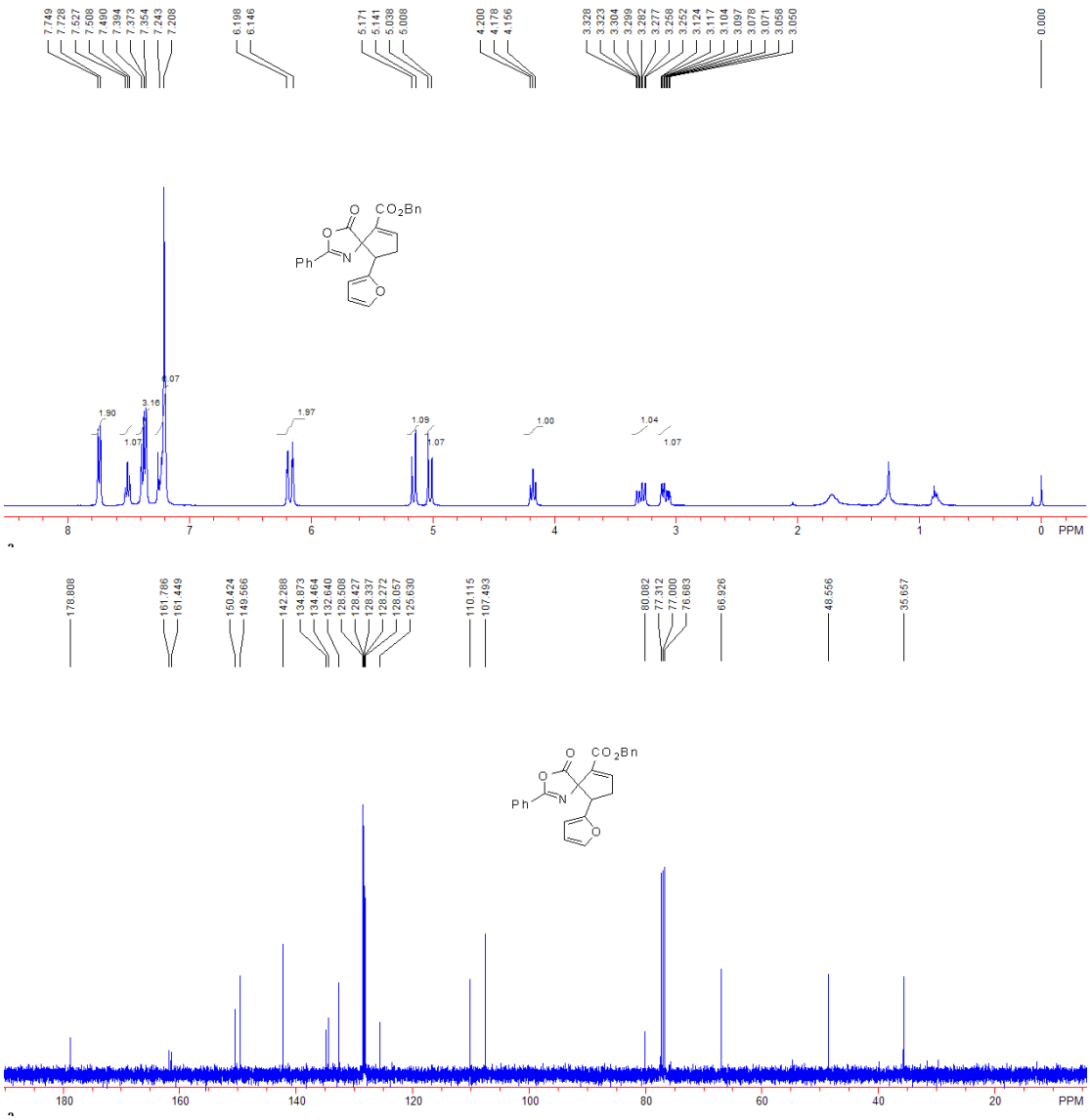
峰参数表

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	37.943	10000.0000



AD-H, 0.75 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.





Benzyl 9-(furan-2-yl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3k)

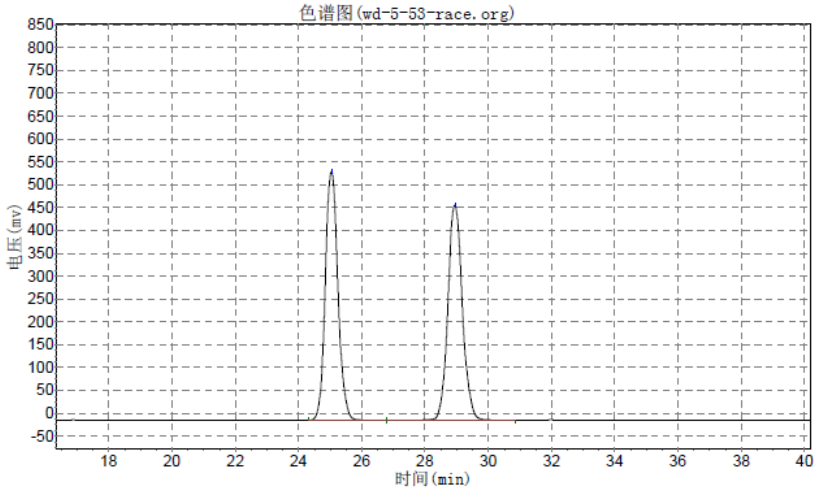
A known product, white solid,[7] 65% yield, 26 mg, Mp: 87-89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75-7.73 (m, 2H), 7.53-7.49 (m, 1H), 7.39-7.35 (m, 3H), 7.24-7.21 (m, 6H), 6.20-6.15 (m, 2H), 5.16 (d, J = 12.0 Hz, 1H), 5.02 (d, J = 12.0 Hz, 1H), 4.18 (t, J = 8.8 Hz, 1H), 3.29 (ddd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, J_3 = 18.4 Hz, 1H), 3.09 (ddd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, J_3 = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 161.8, 161.4, 150.4, 149.6, 142.3, 134.9, 134.5, 132.6, 128.5, 128.4, 128.34, 128.27, 128.1, 125.6, 110.1, 107.4, 80.1, 66.9, 48.6, 35.7; $[\alpha]^{20}_{D}$ = +33.4 (c 1.1, $CHCl_3$) for 94% ee; Enantiomeric excess was determined by

HPLC with a Chiralcel AD-H column, hexane/*i*PrOH = 80/20, 0.5 mL/min, 214 nm, t_{minor} = 25.515 min, t_{major} = 29.382 min.

N2000 数据工作站 1

实验时间：2011-09-29,16:05:12
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-53-race.org

实验者：
报告时间：2011-10-18,22:23:23
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
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2		28.965	468953.250	14931799.000	49.7511
总计			1011742.938	30012994.000	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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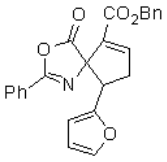
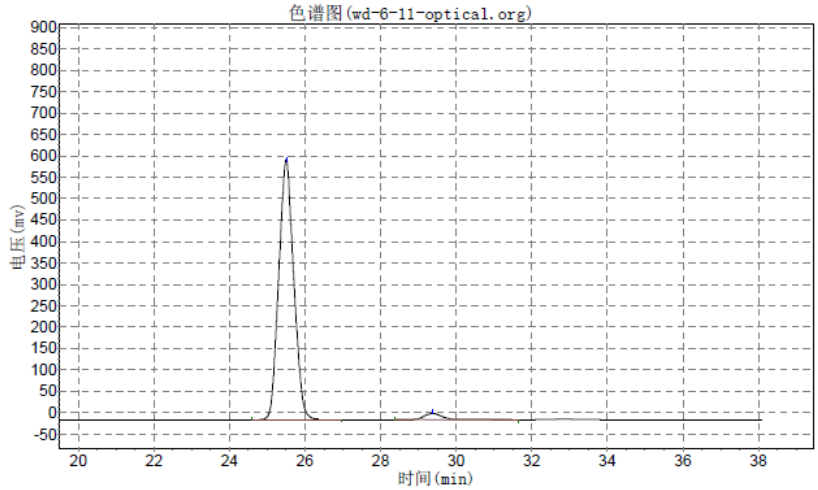


AD-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.

N2000 数据工作站 1

实验时间：2011-09-30,10:44:21
谱图文件:D:\HPLC\SIOC液相\spiro\wd-6-11-optical.org

实验者：
报告时间：2011-10-18,22:25:47
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		25.515	606466.000	16684975.000	97.2433
2		29.382	14694.490	472985.594	2.7567
总计			621160.490	17157960.594	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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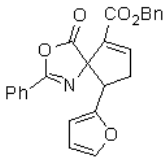
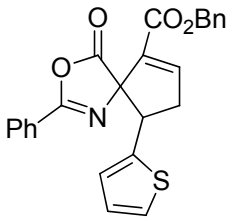
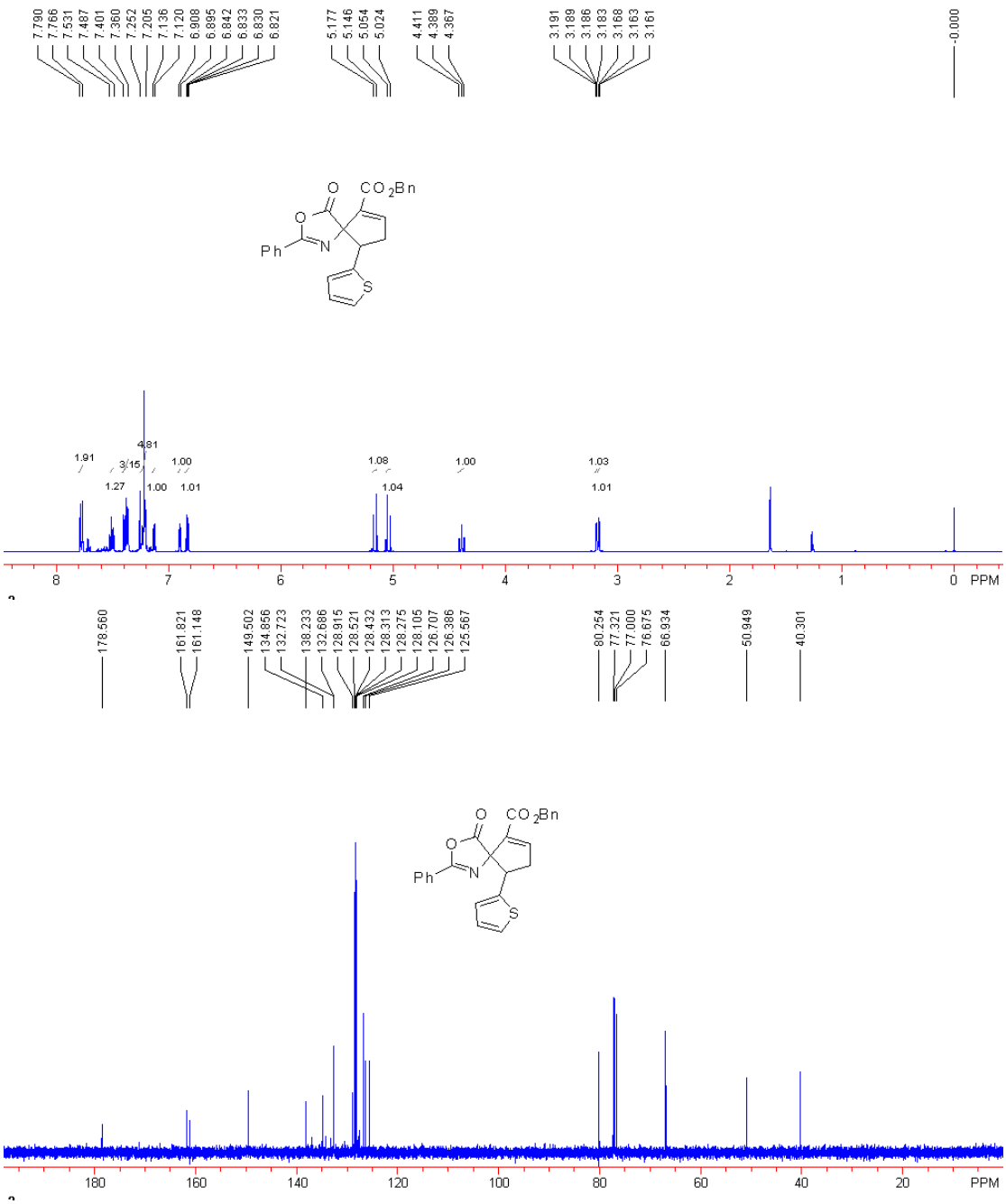


AD-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.





Benzyl

4-oxo-2-phenyl-9-(thiophen-2-yl)-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3l)

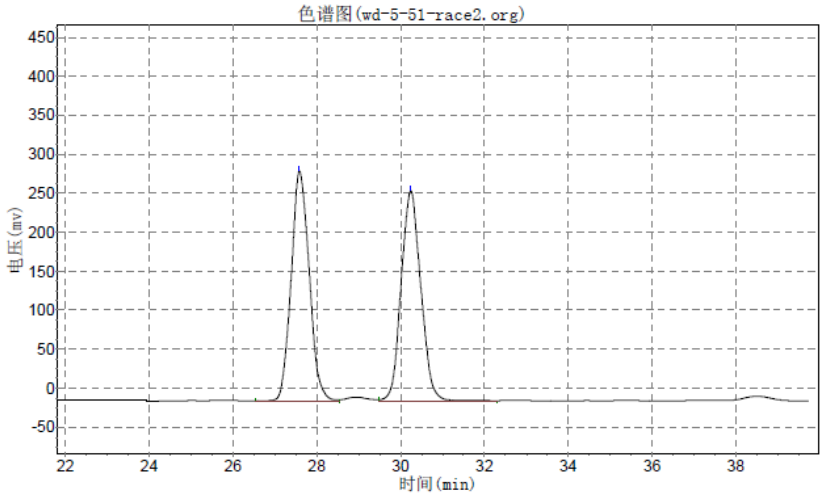
A pale yellow solid, 66% yield, 28 mg, Mp: 96-97 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.79-7.77 (m, 2H), 7.53-7.49 (m, 1H), 7.40-7.36 (m, 3H), 7.25-7.21 (m, 5H), 7.14-7.12 (m, 1H), 6.91-6.90 (m, 1H), 6.83 (dd, J_1 = 3.6 Hz, J_2 = 4.8 Hz, 1H), 5.16 (d, J = 12.4 Hz, 1H), 5.04 (d, J = 12.4 Hz, 1H), 4.39 (t, J = 8.8 Hz, 1H), 3.19-3.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 161.8, 161.1, 149.5, 138.2, 134.9, 132.72, 132.69, 128.9, 128.5, 128.4,

128.31, 128.28, 128.1, 126.7, 126.4, 125.6, 80.3, 66.9, 50.9, 40.3; IR (neat) ν 3065, 1817, 1714, 1647, 1494, 1450, 1321, 1065, 884, 695 cm^{-1}; MS (ESI) *m/z* 430.0 (M^++H, 100); HRMS Calcd. for $C_{25}H_{20}NO_4S^{+1}$ (M^++H): 430.1106, found: 430.1108. $[\alpha]^{20}_D$ = +95.0 (c 1.2, $CHCl_3$) for 94% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.5 mL/min, 214 nm, t_{minor} = 29.800 min, t_{major} = 27.128 min.

N2000 数据工作站 1

实验时间：2011-09-30,11:26:22
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-51-race2.org

实验者：
报告时间：2011-10-17,21:22:28
积分方法:面积归一法

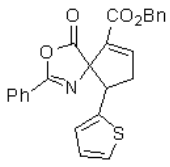


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		27.580	294600.031	8795129.000	50.2727
2		30.242	269063.625	8699725.000	49.7273
总计			563663.656	17494854.000	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	100000.000	0.000	0.000	39.725	10000.0000

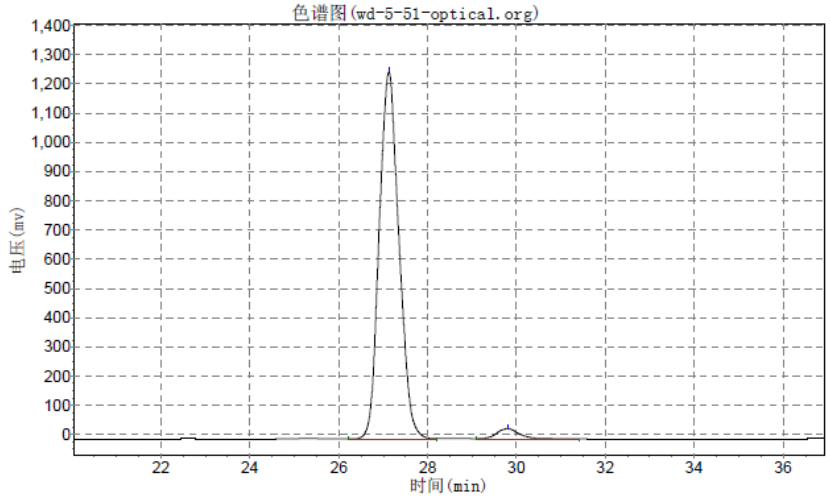


AD-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.

N2000 数据工作站 1

实验时间：2011-09-29,14:48:22
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-51-optical.org

实验者：
报告时间：2011-10-17,21:18:15
积分方法:面积归一法

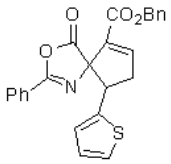


分析结果表

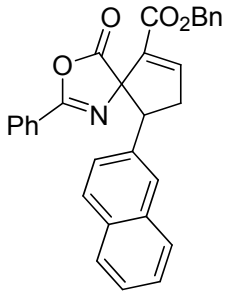
峰号	峰名	保留时间	峰高	峰面积	含量
1		27.128	1255549.875	38657296.000	96.9405
2		29.800	34461.828	1220046.250	3.0595
总计			1290011.703	39877342.250	100.0000

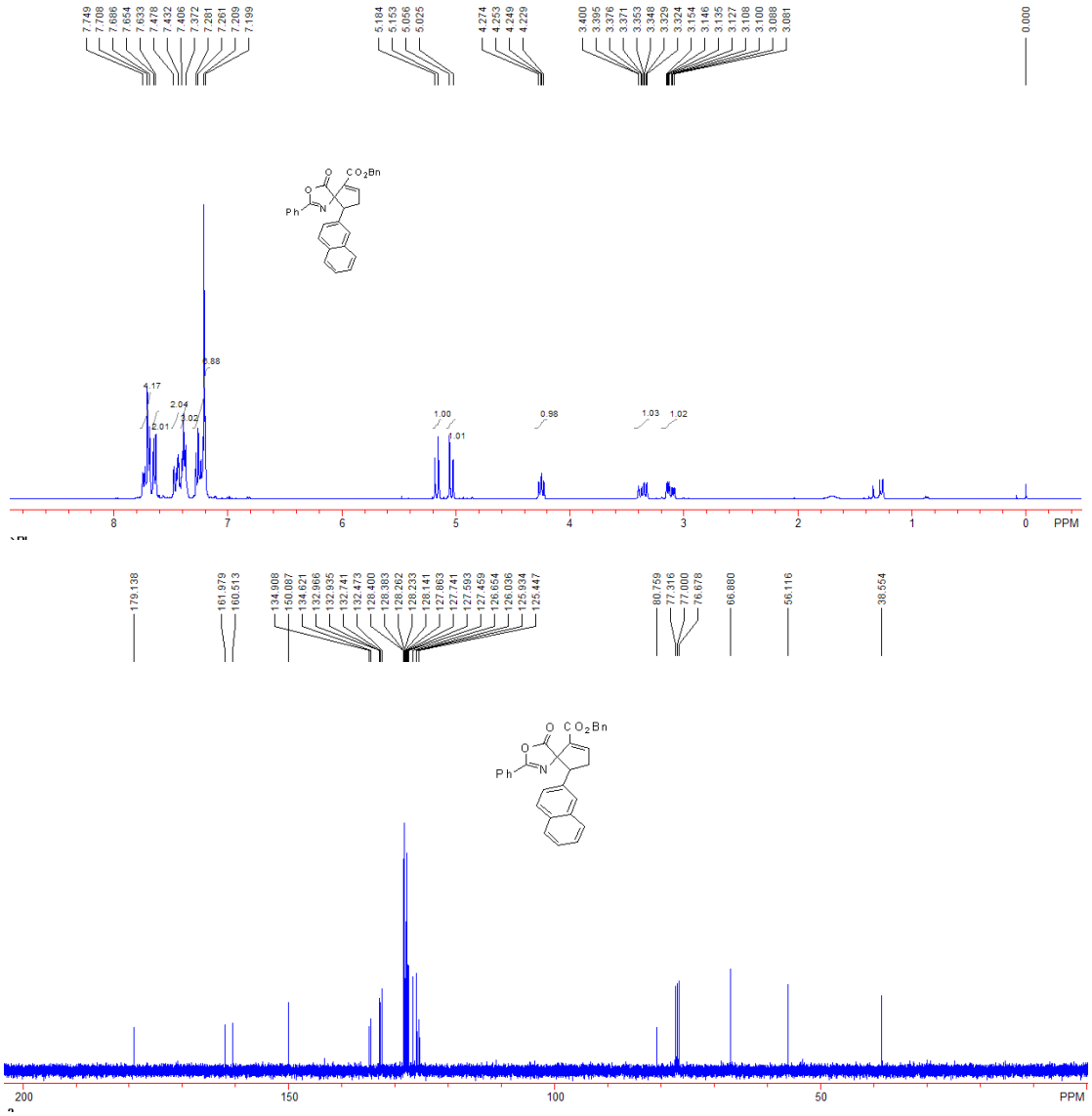
峰参数表

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
5	70.000	0.000	1000000.000	0.000	0.000	53.760	10000.0000



AD-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 214 nm.





Benzyl

9-(naphthalen-2-yl)-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate

(3m)

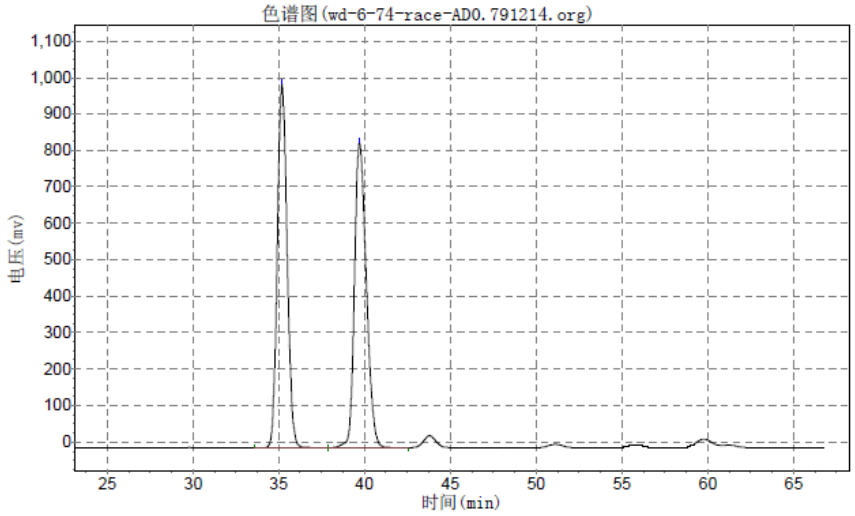
A pale yellow solid,[7] 68% yield, 29 mg, Mp: 135-137 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75-7.69 (m, 4H), 7.65-7.63 (m, 2H), 7.48-7.41 (m, 2H), 7.37-7.28 (m, 3H), 7.26-7.20 (m, 7H), 5.17 (d, J = 12.4 Hz, 1H), 5.04 (d, J = 12.4 Hz, 1H), 4.25 (dd, J_1 = 8.0 Hz, J_2 = 9.6 Hz, 1H), 3.36 (ddd, J_1 = 2.0 Hz, J_2 = 9.6 Hz, J_3 = 18.6 Hz, 1H), 3.12 (ddd, J_1 = 2.9 Hz, J_2 = 8.0 Hz, J_3 = 18.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 162.0, 160.5, 150.1, 134.9, 134.6, 133.0, 132.9, 132. 7, 132.5, 128.40, 128.38, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5,

126.7, 126.0, 125.9, 125.4, 80.8, 66.9, 56.1, 38.6; $[\alpha]^{20}_{D}$ = +8.4 (c 1.0, $CHCl_3$) for 96% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, t_{minor} = 39.822 min, t_{major} = 35.142 min.

N2000 数据工作站 1

实验时间：2011-11-03,19:25:31
谱图文件:J:\SIOC液相\spiro\wd-6-74-race-AD0.791214.org

实验者：
报告时间：2011-11-23,16:12:47
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		35.182	997187.188	39596720.000	49.7098
2		39.697	836912.188	40059004.000	50.2902
总计			1834099.375	79655724.000	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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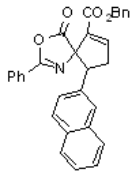
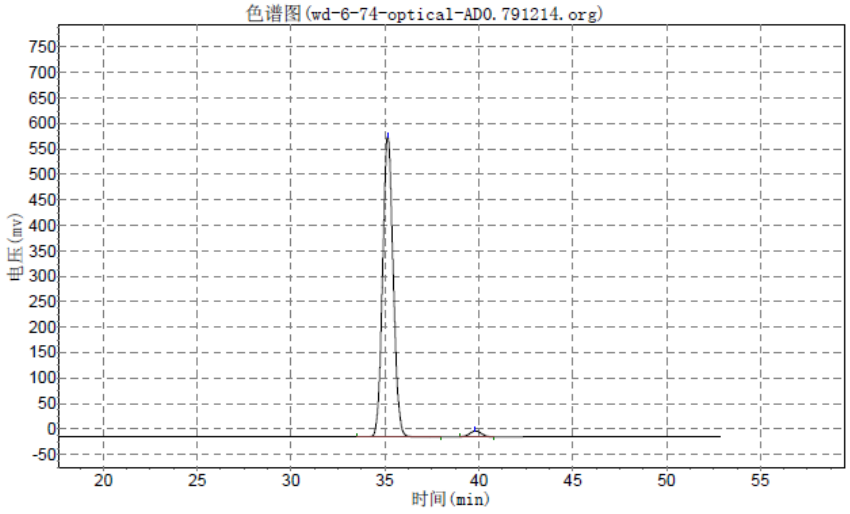


AD-H, Hexane/IPrOH = 90/10, 0.7 mL/min, 214 nm

实验时间：2011-11-03,21:24:28
谱图文件:J:\SIOC液相\spiro\wd-6-74-optical-AD0.791214.org

实验者：
报告时间：2011-11-23,16:14:23
积分方法:面积归一法

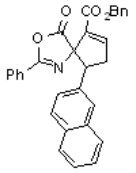


分析结果表

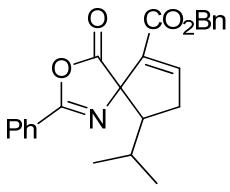
峰号	峰名	保留时间	峰高	峰面积	含量
1		35.142	589369.063	23163584.000	97.9269
2		39.822	11484.433	490358.500	2.0731
总计			600853.495	23653942.500	100.0000

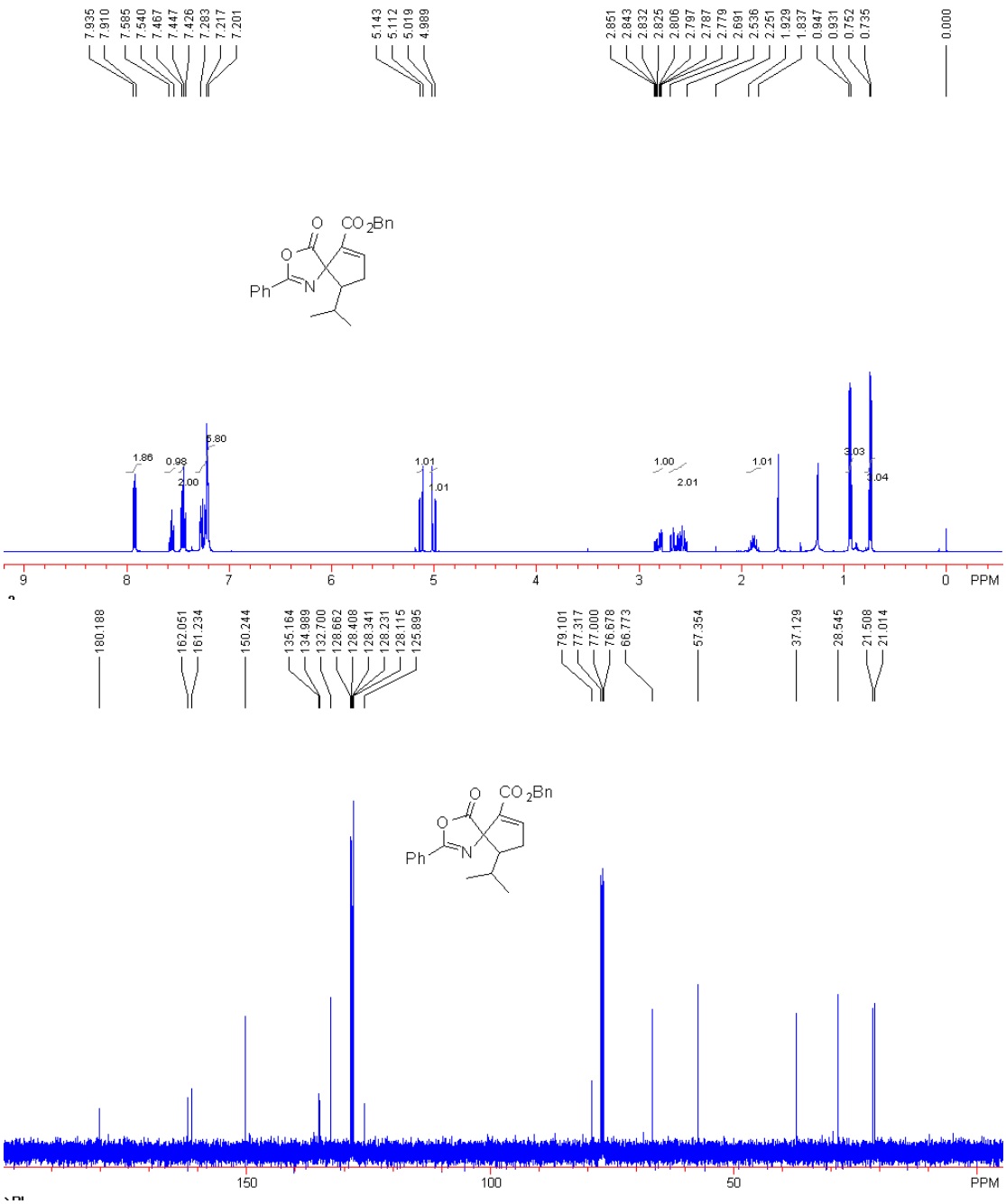
峰参数表

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	52.875	10000.0000



AD-H, Hexane/iPrOH = 90/10, 0.7 mL/min, 214 nm





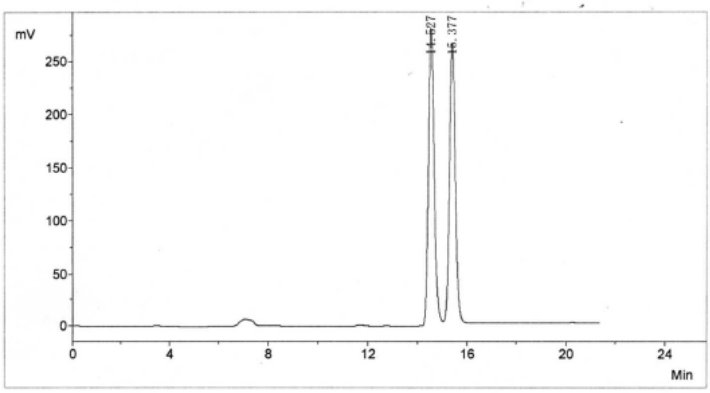
Benzyl 9-isopropyl-4-oxo-2-phenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3n)

A colorless oil, 68% yield, 26 mg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94-7.91 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.28-7.20 (m, 6H), 5.13 (d, J = 12.4 Hz, 1H), 5.00 (d, J = 12.4 Hz, 1H), 2.81 (ddd, J_1 = 3.2 Hz, J_2 = 7.6 Hz, J_3 = 18.2 Hz, 1H), 2.69-2.54 (m, 2H), 1.93-1.84 (m, 1H), 0.94 (d, J = 6.4 Hz, 3H), 0.74 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 162.1, 161.2, 150.2, 135.2, 135.0, 132.7, 128.7, 128.4, 128.3, 128.2, 128.1,

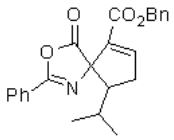
125.9, 79.1, 66.8, 57.4, 37.1, 28.5, 21.5, 21.0; IR (neat) ν 2922, 1816, 1715, 1647, 1451, 1335, 1249, 1064, 882, 697 cm^{-1}; MS (ESI) *m/z* 390.1 (M^++H, 100); HRMS Calcd. for $C_{24}H_{24}NO_4^{+1}$ (M^++H): 390.1702, found: 390.1700. $[\alpha]^{20}_D$ = +100.3 (c 1.15, $CHCl_3$) for 79% ee; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.4 mL/min, 214 nm, t_{minor} = 14.727 min, t_{major} = 15.377 min.

色谱分析报告

样品名称:　　样品文件名:WD-5-56+-AD-H820.4214.che
样品批号:　　分析者:
分析日期:2011-09-27　　分析时间:08:47



序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1		14.527	279162.1	4543119.3	48.0011
2	2		15.377	261148.1	4921489.0	51.9989
合计:				540310.1	9464608.3	100.0000

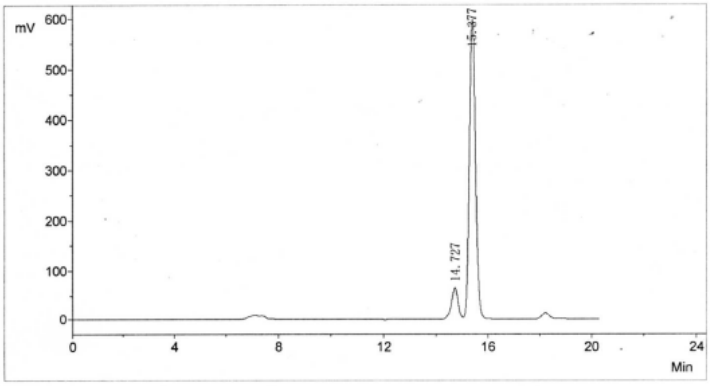


AD-H, 0.4 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm

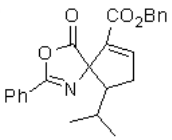
HPLC Report

Sample Name:
Operator:
Time:09:11

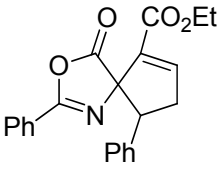
Data File:WD-5-93.che
Date:2011-09-27

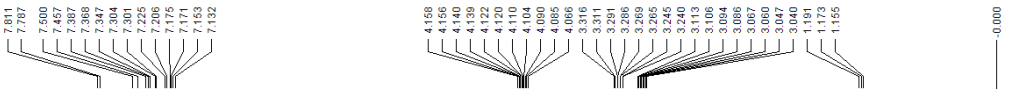


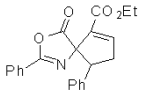
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		14.727	65580.6	1174939.1	10.5756
2	2		15.377	581774.7	9934967.0	89.4244
Total				647355.3	11109906.1	100.0000

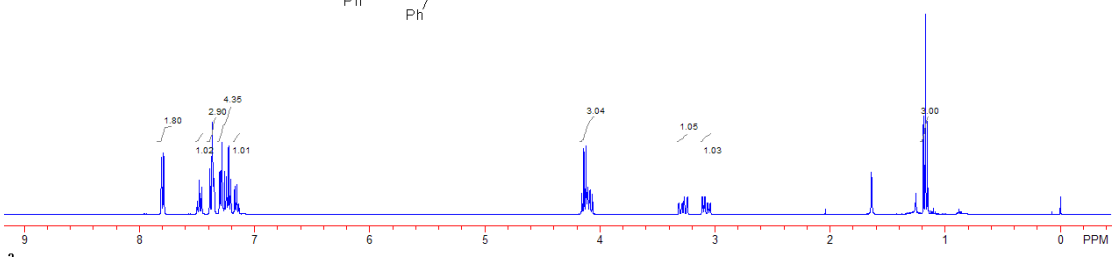


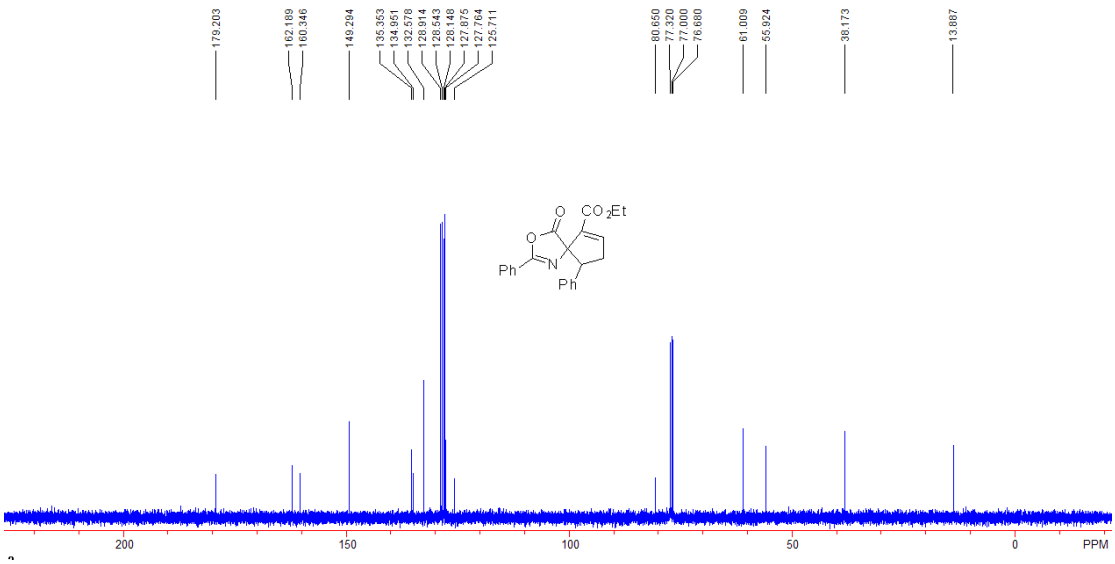
AD-H, 0.4 ml/min, Hexane/^{i}PrOH = 90/10, 214 nm.









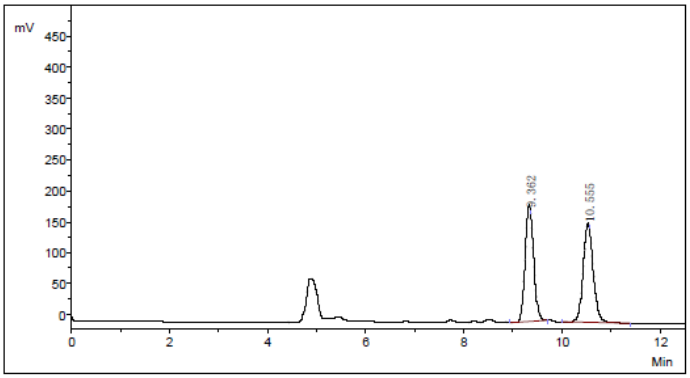


Ethyl 4-oxo-2,9-diphenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3o)

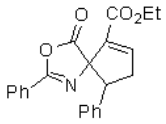
A white solid, 77% yield, 28 mg, Mp: 98-99 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81-7.79 (m, 2H), 7.50-7.46 (m, 1H), 7.39-7.35 (m, 3H), 7.30-7.14 (m, 5H), 4.16-4.07 (m, 3H), 3.28 (ddd, J_1 = 2.0 Hz, J_2 = 10.0 Hz, J_3 = 18.6 Hz, 1H), 3.08 (ddd, J_1 = 2.8 Hz, J_2 = 7.6 Hz, J_3 = 18.6 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 162.2, 160.3, 149.3, 135.4, 135.0, 132.6, 128.9, 128.5, 128.1, 127.9, 127.8, 125.7, 80.7, 61.0, 55.9, 38.2, 13.9; IR (neat) ν 2976, 1815, 1711, 1650, 1451, 1256, 1081, 954, 884, 695 cm^{-1}; MS (ESI) *m/z* 362.0 (M^++H, 100); HRMS Calcd. for $C_{22}H_{20}NO_4^{+1}$ (M^++H): 362.1388, found: 362.1387. $[\alpha]^{20}_D$ = +200.8 (c 0.4, $CHCl_3$) for 95% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 70/30, 0.5 mL/min, 214 nm, t_{minor} = 9.263 min, t_{major} = 10.460 min.

HPLC REPORT

Sample Name:WD-4-56-IC-7-3-0.5-230.che
Date:2011-09-05
Time:10:06
Method:
Column:
Flow Rate:
Wave Length:
Mobile Phase:



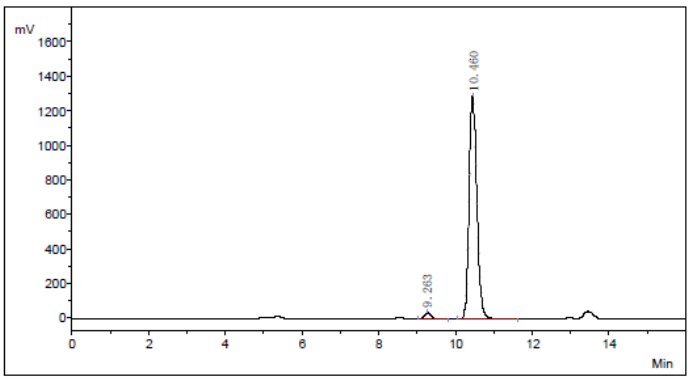
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.362	173402.1	2234823.1	49.6826
2	2	Unknown	10.555	152695.2	2263374.1	50.3174
Total				326097.2	4498197.2	100.0000



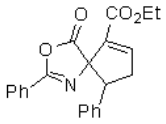
IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 70/30, 230 nm.

HPLC REPORT

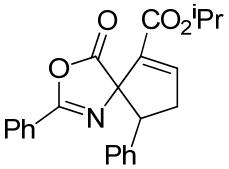
Sample Name:WD-5-48.che
Date:2011-09-05
Time:10:43
Method:
Column:
Flow Rate:
Wave Length:
Mobile Phase:

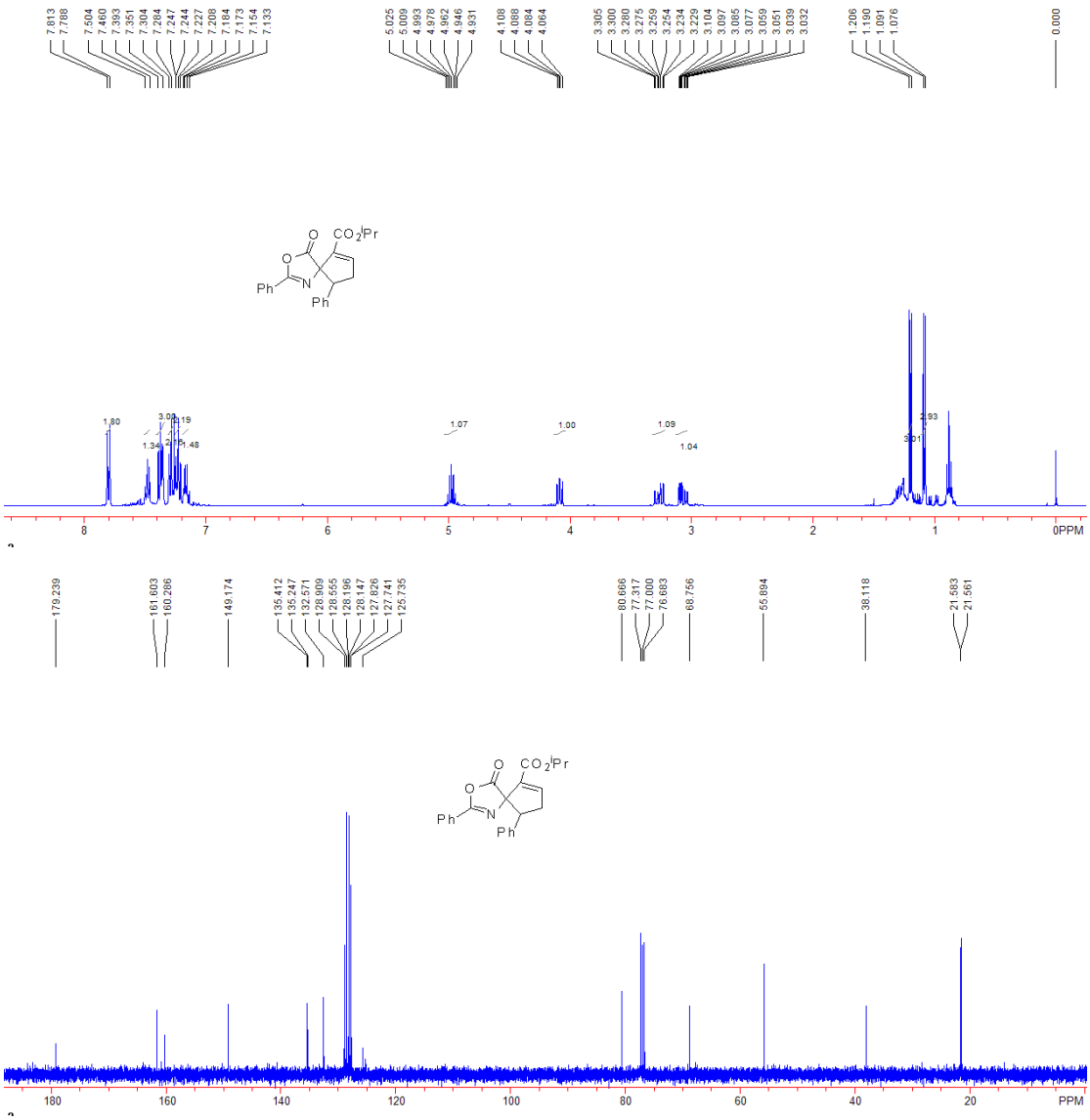


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.263	35329.9	418081.8	2.2516
2	2	Unknown	10.460	1290417.2	18149990.8	97.7484
Total				1325747.1	18568072.6	100.0000



IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 70/30, 230 nm.





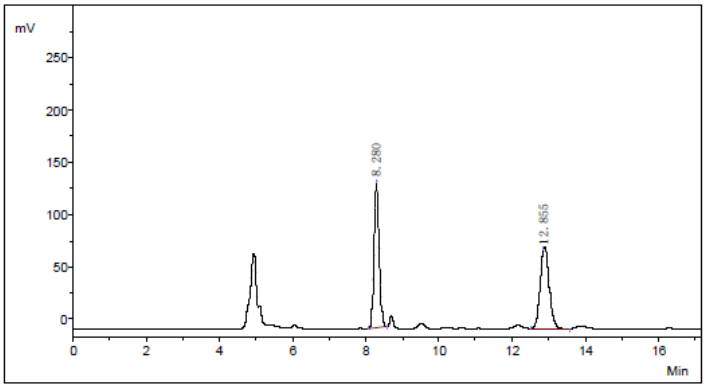
Isopropyl 4-oxo-2,9-diphenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3p)

A white solid, 91% yield, 32 mg, Mp: 130-131 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81-7.79 (m, 2H), 7.50-7.46 (m, 1H), 7.39-7.35 (m, 3H), 7.30-7.28 (m, 2H), 7.25-7.21 (m, 2H), 7.18-7.13 (m, 1H), 5.03-4.93 (m, 1H), 4.09 (dd, J_1 = 8.0 Hz, J_2 = 9.6 Hz, 1H), 3.27 (ddd, J_1 = 2.0 Hz, J_2 = 9.6 Hz, J_3 = 18.4 Hz, 1H), 3.07 (ddd, J_1 = 2.8 Hz, J_2 = 8.0 Hz, J_3 = 18.4 Hz, 1H), 1.20 (d, J = 6.4 Hz, 3H), 1.08 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 161.6, 160.3, 149.2, 135.4, 135.2, 132.6, 128.9, 128.6, 128.2, 128.1, 127.8, 127.7, 125.7, 80.7, 68.8, 55.9, 38.1, 21.58, 21.56; IR (neat) ν 2976, 1810, 1702, 1654, 1260, 1102, 945, 694 cm^{-1}; MS (ESI) *m/z* 398.3.0 (M^++Na, 100); HRMS Calcd. for $C_{23}H_{21}NO_4Na^{+1}$ (M^++Na): 398.1370,

found: 398.1363. $[\alpha]^{20}_{D}$ = +161.1 (c 0.6, $CHCl_3$) for 94% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/^{i}PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 8.252 min, t_{major} = 12.877 min.

HPLC REPORT

Sample Name:WD-5-25-IC-8-2-0.5-230.che Date:2011-09-05
Time:15:16 Method:
Column: Flow Rate:
Wave Length: Mobile Phase:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
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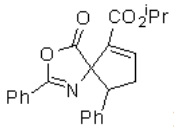
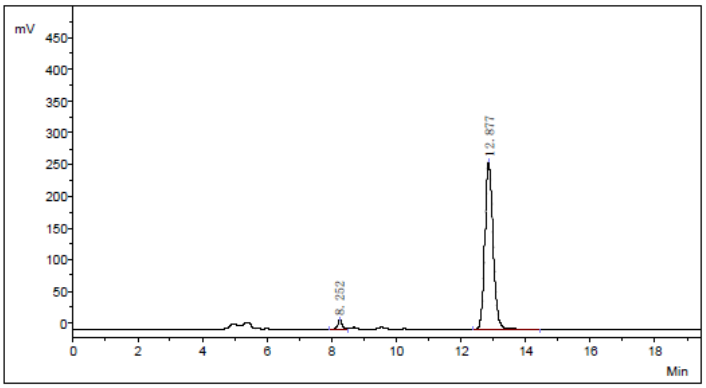
2	2	Unknown	12.855	75123.6	1340790.8	49.9607
Total				214056.4	2683691.2	100.0000



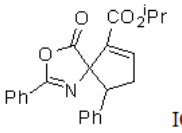
IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 230 nm

HPLC REPORT

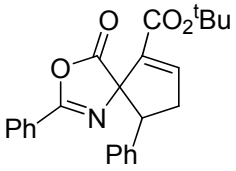
Sample Name:WD-5-50...che
Date:2011-09-05
Time:15:34
Method:
Column:
Flow Rate:
Wave Length:
Mobile Phase:

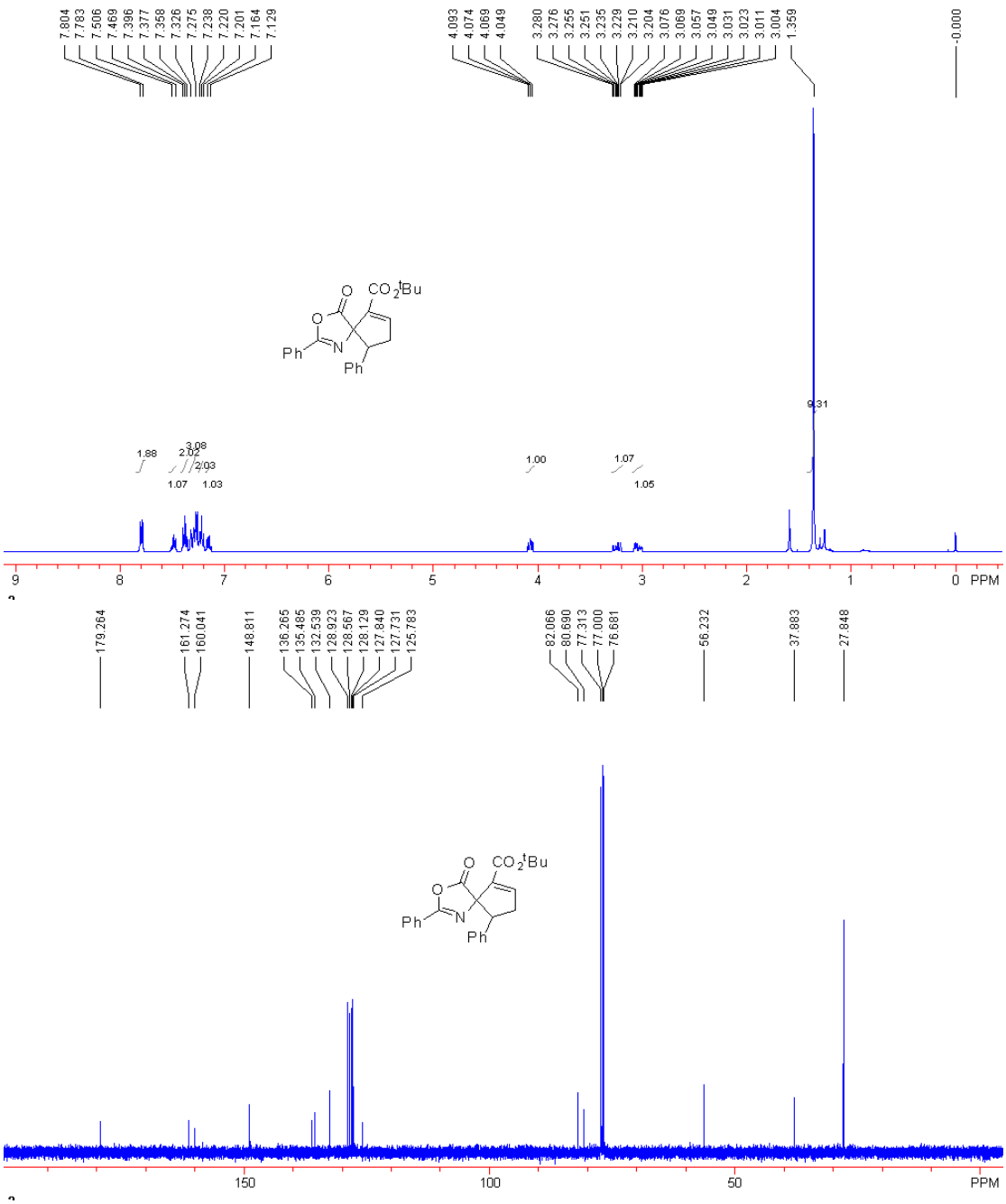


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	8.252	13720.3	131908.4	2.7683
2	2	Unknown	12.877	263212.6	4633036.7	97.2317
Total				276932.8	4764945.0	100.0000



IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 230 nm.





Tert-butyl 4-oxo-2,9-diphenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-6-carboxylate (3q)

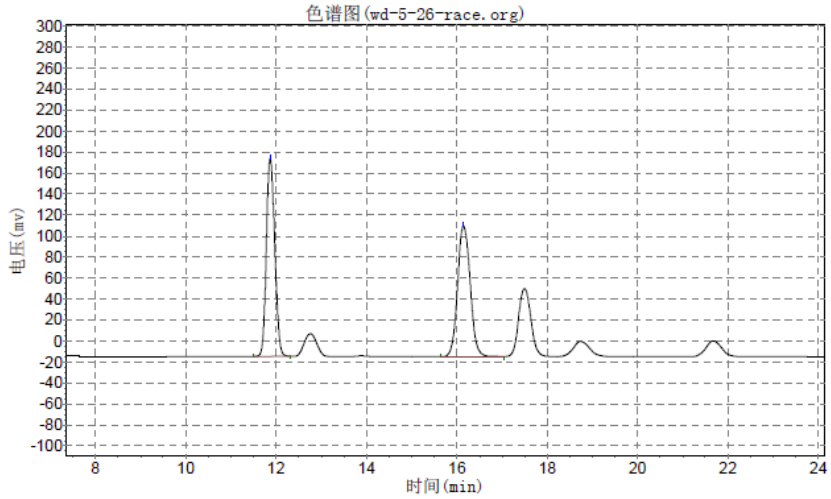
A white solid, 89% yield, 33 mg, Mp: 139-141 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80-7.78 (m, 2H), 7.51-7.47 (m, 1H), 7.40-7.36 (m, 2H), 7.33-7.28 (m, 3H), 7.24-7.20 (m, 2H), 7.16-7.13 (m, 1H), 4.07 (dd, J_1 = 8.0 Hz, J_2 = 10.0 Hz, 1H), 3.24 (ddd, J_1 = 2.4 Hz, J_2 = 10.0 Hz, J_3 = 18.4 Hz, 1H), 3.04 (ddd, J_1 = 2.8 Hz, J_2 = 8.0 Hz, J_3 = 18.4 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 161.3, 160.0, 148.8, 136.3, 135.5, 132.5, 128.9, 128.6, 128.1, 127.8, 127.7, 125.8, 82.1, 80.7, 56.2, 37.9, 27.8; IR (neat) ν 2976, 1813, 1716, 1647,

1447, 1273, 1118, 765, 688 cm^{-1}; MS (ESI) *m/z* 412.4 (M^++Na, 100); HRMS Calcd. for $C_{24}H_{23}NO_4Na^{+1}$ (M^++Na): 412.1529, found: 412.1519. $[\alpha]^{20}_D$ = +152.0 (c 0.45, $CHCl_3$) for 91% ee; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column, Hexane/*i*PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 11.663 min, t_{major} = 15.925 min.

N2000 数据工作站 1

实验时间：2011-09-27,20:38:53
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-26-race.org

实验者：
报告时间：2011-10-11,21:19:24
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		11.865	188628.188	2439719.000	50.2336
2		16.145	124530.391	2417030.000	49.7664
总计			313158.578	4856749.000	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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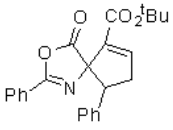
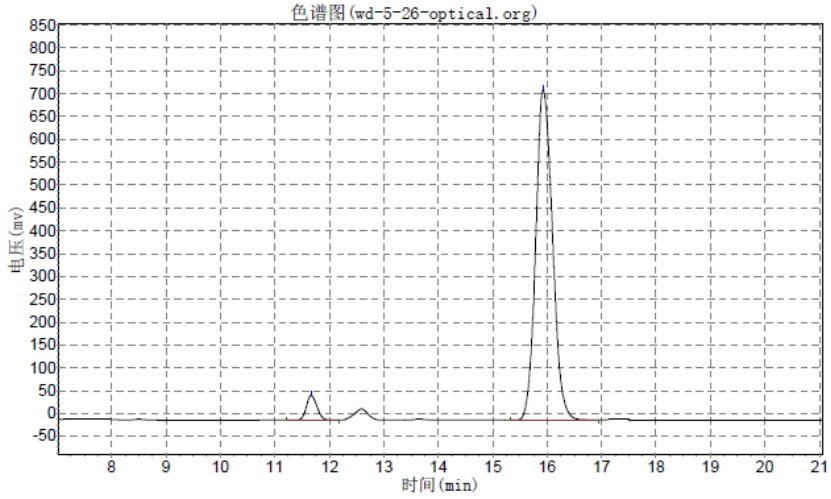


IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 230 nm.

实验时间：2011-09-27,21:14:21
谱图文件:D:\HPLC\SIOC液相\spiro\wd-5-26-optical.org

实验者：
报告时间：2011-10-11,21:28:38
积分方法:面积归一法

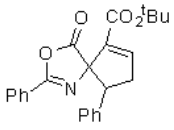


分析结果表

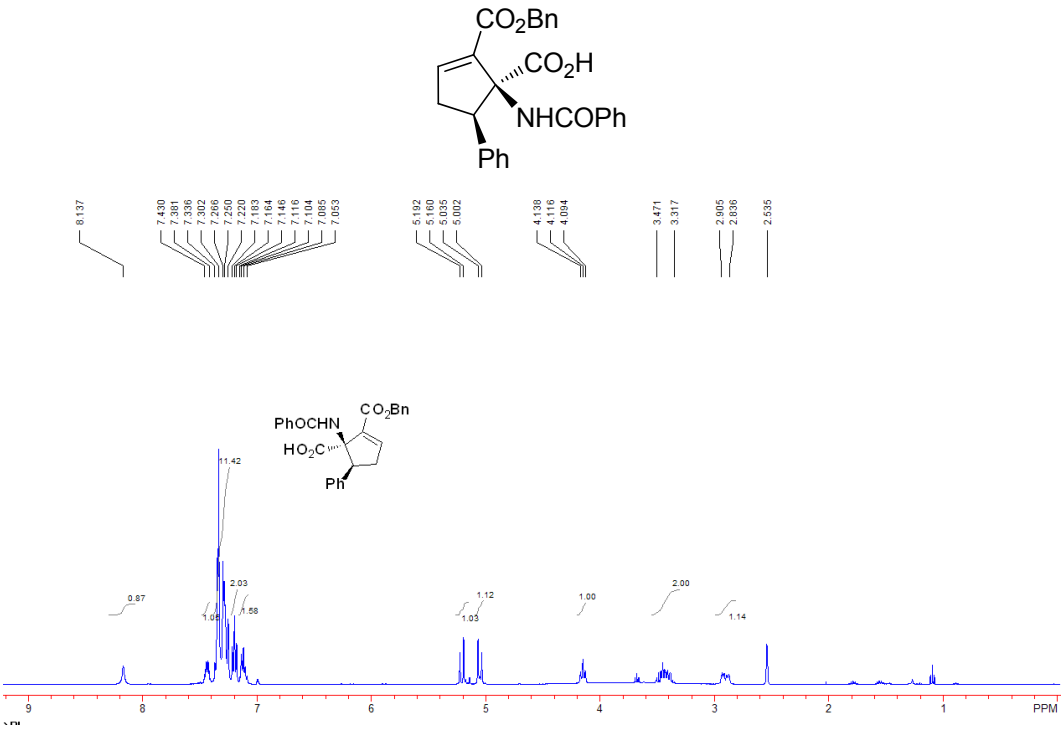
峰号	峰名	保留时间	峰高	峰面积	含量
1		11.663	54091.699	724222.125	4.4603
2		15.925	723351.375	15512844.000	95.5397
总计			777443.074	16237066.125	100.0000

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	32.578	10000.0000

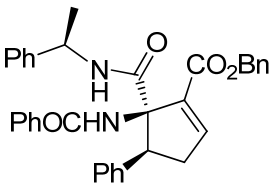


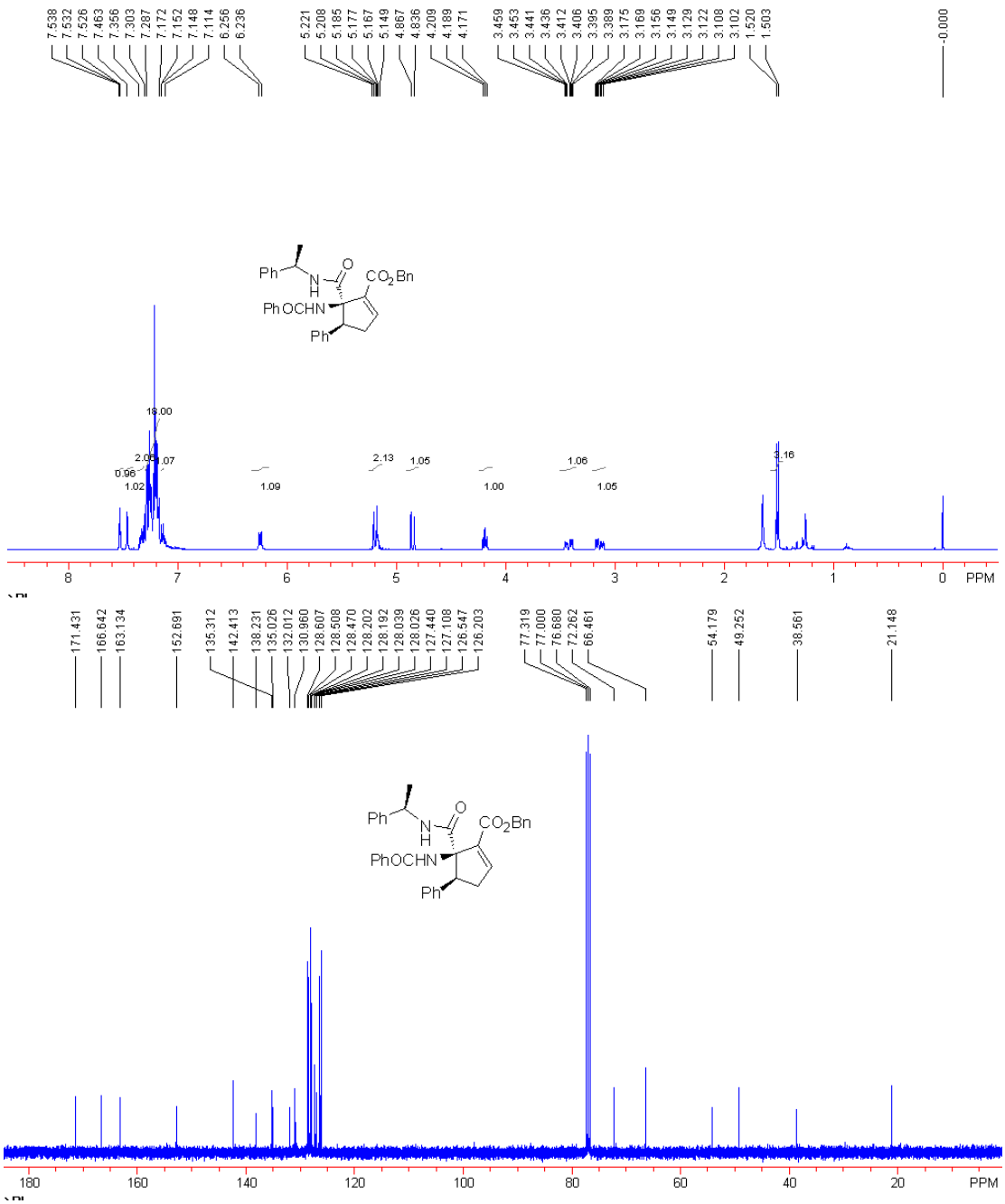
IC-H, 0.5 ml/min, Hexane/^{i}PrOH = 80/20, 230 nm.



(1S,5R)-1-Benzamido-2-((benzyloxy)carbonyl)-5-phenylcyclopent-2-enecarboxylic acid (4)

This is a known compound.[7] A white solid, 82% yield, 92 mg. ^{1}H NMR (400 MHz, D_6-DMSO, TMS) δ 8.13 (s, 1H), 7.43-7.38 (m, 1H), 7.34-7.22 (m, 11H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.12-7.05 (m, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 5.02 (d, *J* = 12.4 Hz, 1H), 4.12 (t, *J* = 8.8 Hz, 1H), 3.47-3.32 (m, 2H), 2.91-2.84 (m, 1H). $[\alpha]^{20}_D$ = +12.7 (c 0.9, $CHCl_3$)



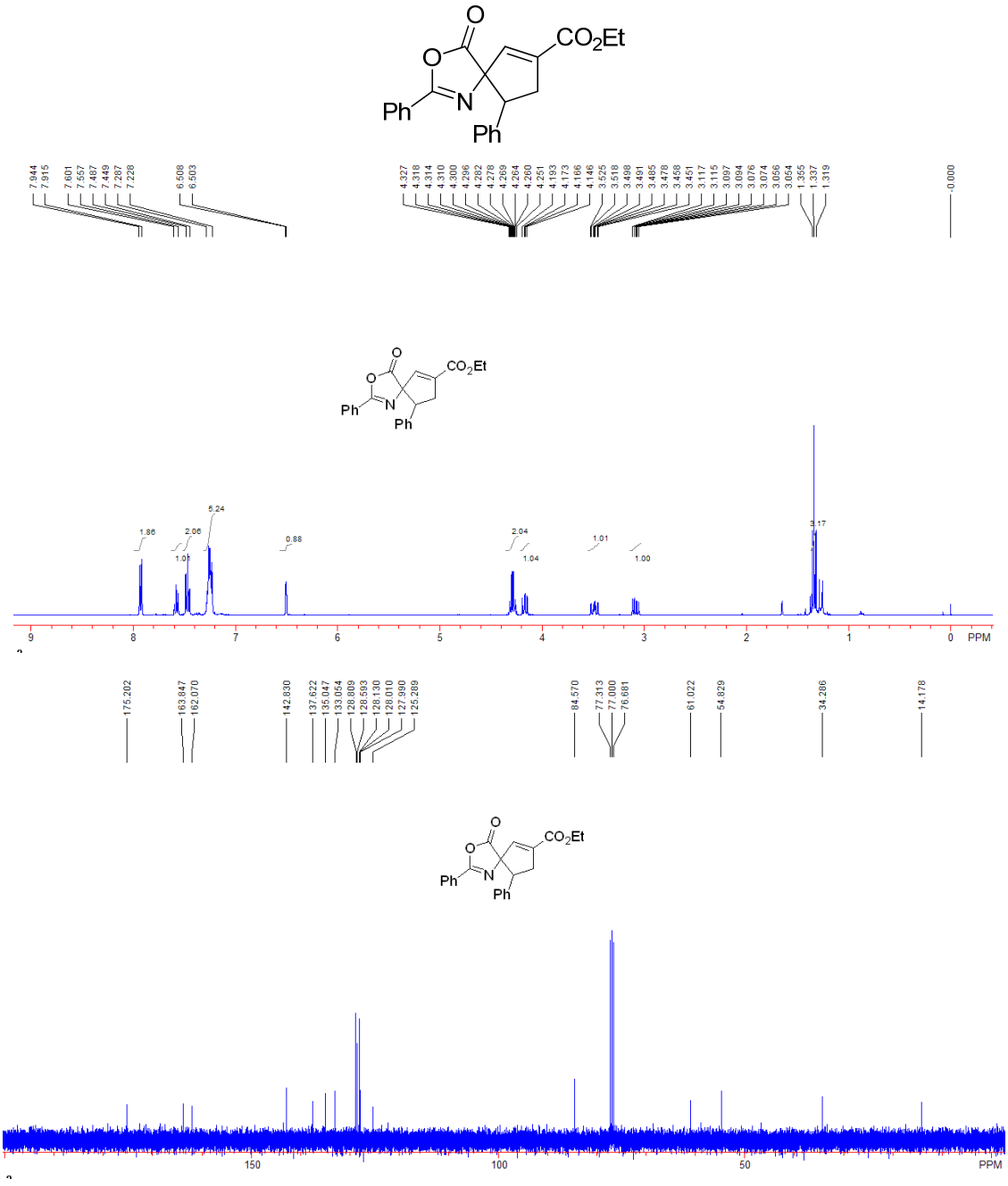


(4S,5R)-benzyl

5-benzamido-4-phenyl-5-(((R)-1-phenylethyl)carbamoyl)cyclopent-1-enecarboxylate (5)

A white solid, 63% yield, 12 mg, Mp: 72-74 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (t, J = 2.4 Hz, 1H), 7.46 (s, 1H), 7.36-7.30 (m, 2H), 7.29-7.17 (m, 18H), 7.15-7.11 (m, 1H), 6.25 (d, J = 8.0 Hz, 1H), 5.22-5.15 (m, 2H), 4.85 (d, J = 12.4 Hz, 1H), 4.19 (t, J = 8.0 Hz, 1H), 3.42 (ddd, J_1 = 2.4 Hz, J_2 = 6.8 Hz, J_3 = 18.6 Hz, 1H), 3.14 (ddd, J_1 = 2.4 Hz, J_2 = 8.0 Hz, J_3 = 18.6 Hz, 1H), 1.51 (t, J_2 = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 166.6, 163.1,

152.7, 142.4, 138.2, 135.3, 135.0, 132.0, 131.0, 128.6, 128.51, 128.47, 128.20, 128.19, 128.04, 128.03, 127.4, 127.1, 126.5, 126.2, 72.3, 66.5, 54.2, 49.3, 38.6, 21.1; IR (neat) ν 3344, 2954, 1714, 1650, 1504, 1480, 1453, 1257, 1126, 751, 698 cm^{-1}; MS (ESI) *m/z* 567.4 (M^++Na, 100); HRMS Calcd. for $C_{35}H_{32}N_2O_4Na^{+1}$ (M^++Na): 567.2260, found: 567.2254. $[\alpha]^{20}_D$ = +68.9 (c 0.5, $CHCl_3$)



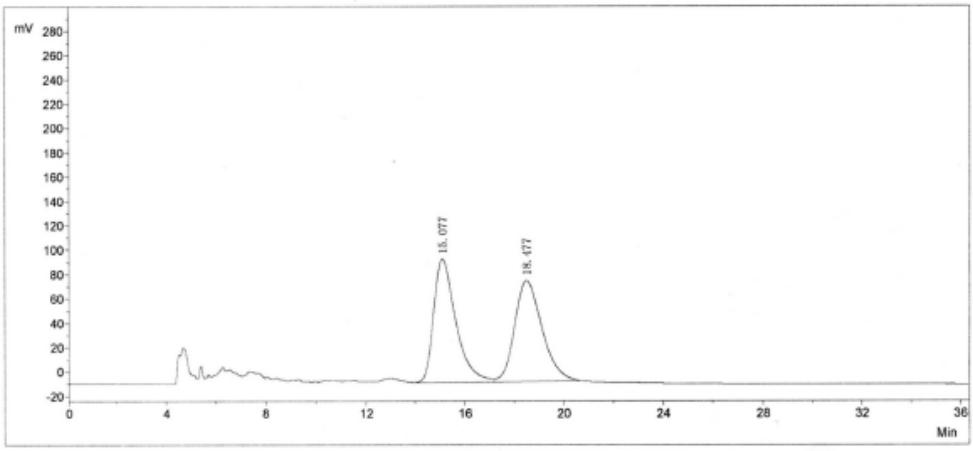
ethyl 4-oxo-2,9-diphenyl-3-oxa-1-azaspiro[4.4]nona-1,6-diene-7-carboxylate (7)

A white solid, 62% yield, 22 mg, Mp: 107-109 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.93 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 2H), 7.60-7.56 (m, 1H), 7.49-7.45 (m, 2H), 7.29-7.23 (m, 5H), 6.51 (d, J = 2.0 Hz, 1H), 4.32-4.26 (m, 2H), 4.17 (dd, J_1 = 8.0 Hz, J_2 = 10.4 Hz, 1H), 3.49 (ddd, J_1 = 2.8 Hz, J_2 = 10.4 Hz, J_3 = 16.0 Hz, 1H), 3.09 (ddd, J_1 = 0.8 Hz, J_2 = 8.0 Hz, J_3 = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 163.8, 162.1, 142.8, 137.6, 135.0, 133.1, 128.8, 128.6, 128.1, 128.01, 127.99, 125.3, 84.6, 61.0, 54.8, 34.3, 14.2; IR (neat) ν 2927, 1810, 1717, 1647, 1647, 1451, 1255, 1081, 694 cm^{-1}; MS (ESI) *m/z* 362.3 (M^++H, 100); HRMS Calcd. for $C_{22}H_{20}NO_4^{+1}$ (M^++H): 362.1389, found: 362.1387. $[\alpha]^{20}_D$ = -17 (c 0.2, $CHCl_3$) for 68% ee; Enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 214 nm, t_{minor} = 18.282 min, t_{major} = 14.857 min.

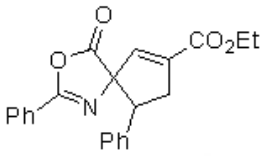
HPLC REPORT

Sample Name:wd-6-54-rac oj250 80.che
Time:06:57
column: OJ-H(15)
Velocity: a)

Date:2011-10-31
Method:
the mobile phase: 80/20
the detection wavelength: 214



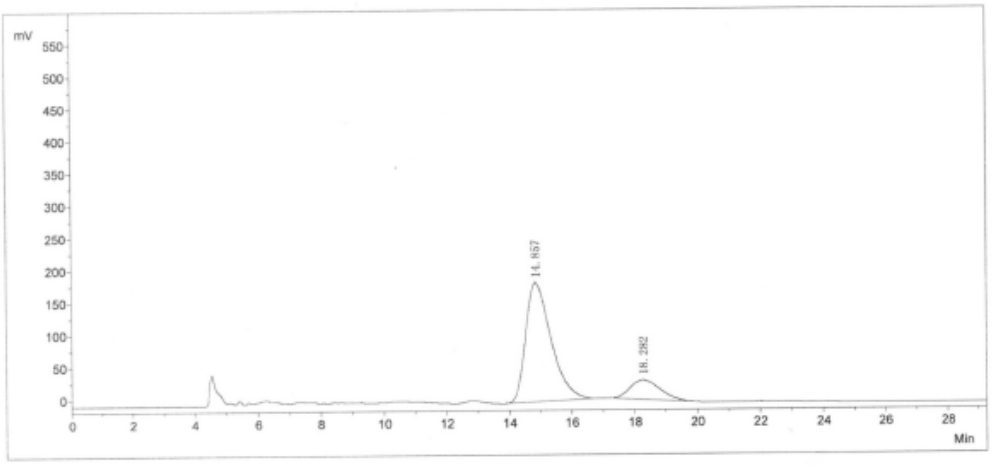
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.077	100768.3	6272414.6	49.6468
2	2	18.477	82496.5	6361654.5	50.3532
Total			183264.9	12634069.1	100.0000



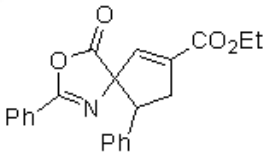
OJ-H, Hexane/^{i}PrOH = 80/20, 0.7 ml/min, 214 nm

HPLC REPORT

Sample Name:wd-6-59 oj 80.che
Date:2011-10-31
Time:07:35
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:

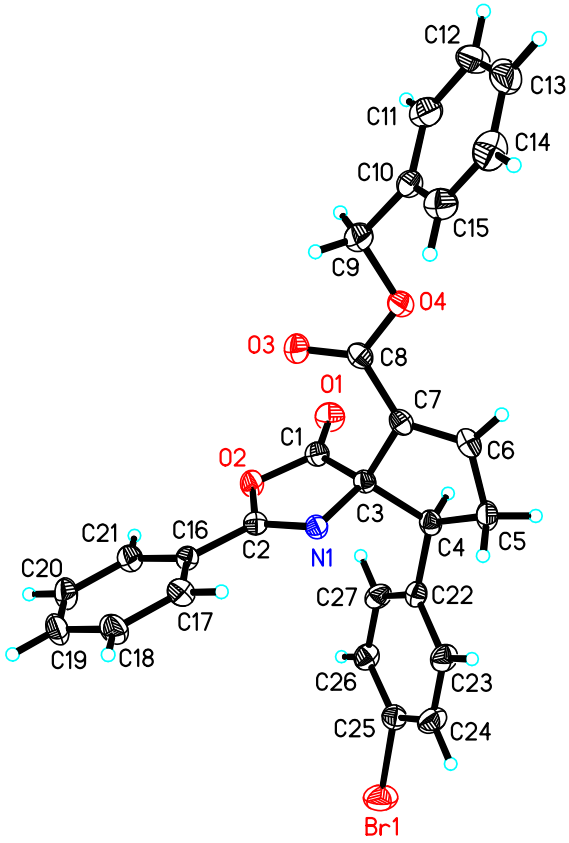


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	14.857	183571.8	10402783.9	83.8672
2	2	18.282	29881.6	2001085.8	16.1328
Total			213453.3	12403869.7	100.0000



OJ-H, Hexane/^{i}PrOH = 80/20, 0.7 ml/min, 214 nm

11. X-ray data of product **3b**



The crystal data of **3b** have been deposited in CCDC with number 853417. Empirical Formula: $C_{27}H_{20}BrNO_4$; Formula Weight: 502.35; Crystal Color, Habit: colorless; Crystal Dimensions: 0.257 x 0.069 x 0.057 mm; Crystal System: Monoclinic; Lattice Parameters: a = 13.1287(16)Å, b = 5.9348(7)Å, c = 15.3288(19)Å, $\alpha = 90^{o}$, $\beta = 111.831(2)^{o}$, $\gamma = 90^{o}$, V = 1108.7(2)Å^3; Space group: P2(1); Z = 2; D_{calc}= 1.505 g/cm^3; F_{000} = 512; Final R indices [I>2sigma(I)] R1 = 0.0349, wR2 = 0.0723.

12. References

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