Supporting Information

Palladium-Catalyzed Asymmetric [3+2] Cycloaddition to Construct 1,3-Indandione and Oxindole-Fused Spiropyrazolidine Scaffolds

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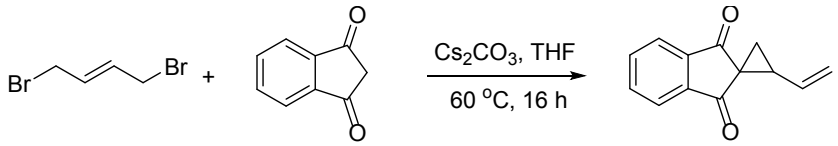
1. General remarks. MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Optical rotations were determined in a solution of $CHCl_3$ or CH_2Cl_2 at 20 ^oC by using a Perkin-Elmer-241 MC polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Infra-red spectra were measured on a spectrometer. ^1H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; ^{31}P NMR spectra were recorded for a solution in $CDCl_3$ with 85% H_3PO_4 as the external reference. *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. The optical purities of products were determined by HPLC analysis using a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak IB-3 and IF-3 columns 4.6 x 250 mm, (Daicel Chemical Ind., Ltd.)).

Ligands **L1-L5**, **L8**, **L11-L15**[1] were prepared according to the previously reported procedures.

2-Vinylspiro[cyclopropane-1,2'-indene]-1',3'-dione **1**,[2] was prepared according to the previously reported procedures.

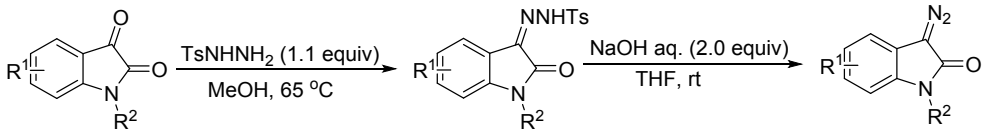
3-Diazooxindoles **2** were prepared according to the previously reported procedures.[3]

2. General procedure for the synthesis of 2-vinylspiro[cyclopropane-1,2'-indene]-1',3'-dione 1



1*H*-indene-1,3(2*H*)-dione (1.0 equiv) and 1,4-dibromobut-2-ene (1.0 equiv) were added to a round bottom flask with a magnetic stir bar under an atmosphere of argon. To this was added tetrahydrofuran (0.2 mL) and cesium carbonate (2.5 equiv). A condenser was added, and reaction mixture was then heated to 60 °C over night. After cooling down to room temperature, the reaction mixture was filtered through a celite and washed with diethyl ether. The organic phase was washed with saturated aqueous $NaHCO_3$, followed by water and brine. The solution was dried over anhydrous Na_2SO_4. After filtration over Na_2SO_4, the solvent is removed under reduced pressure. The crude product is purified by means of silica gel chromatography using petroleum ether and diethylether as an eluent. The yields have not been optimized for the synthesis of 2-vinylspiro[cyclopropane-1,2'-indene]-1',3'-dione.

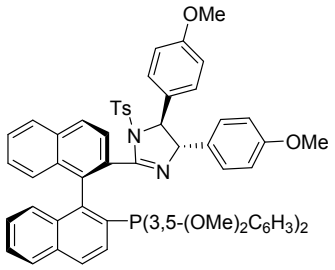
3. General procedure for the synthesis of 3-diazooxindoles 2



Isatin (5.0 mmol, 1.0 equiv) was suspended in MeOH (20 mL). The suspension was heated to 60 °C, whereupon a deep-red solution was obtained. To this hot solution was added tosylhydrazine (5.5 mmol, 1.1 equiv) in one portion. A yellow product started precipitating from the hot mixture. The reaction mixture was stirred at 60 °C for 18 h, and then allowed to reach room temperature. The corresponding tosylhydrazone was collected by filtration and was used for the next step without further purification.

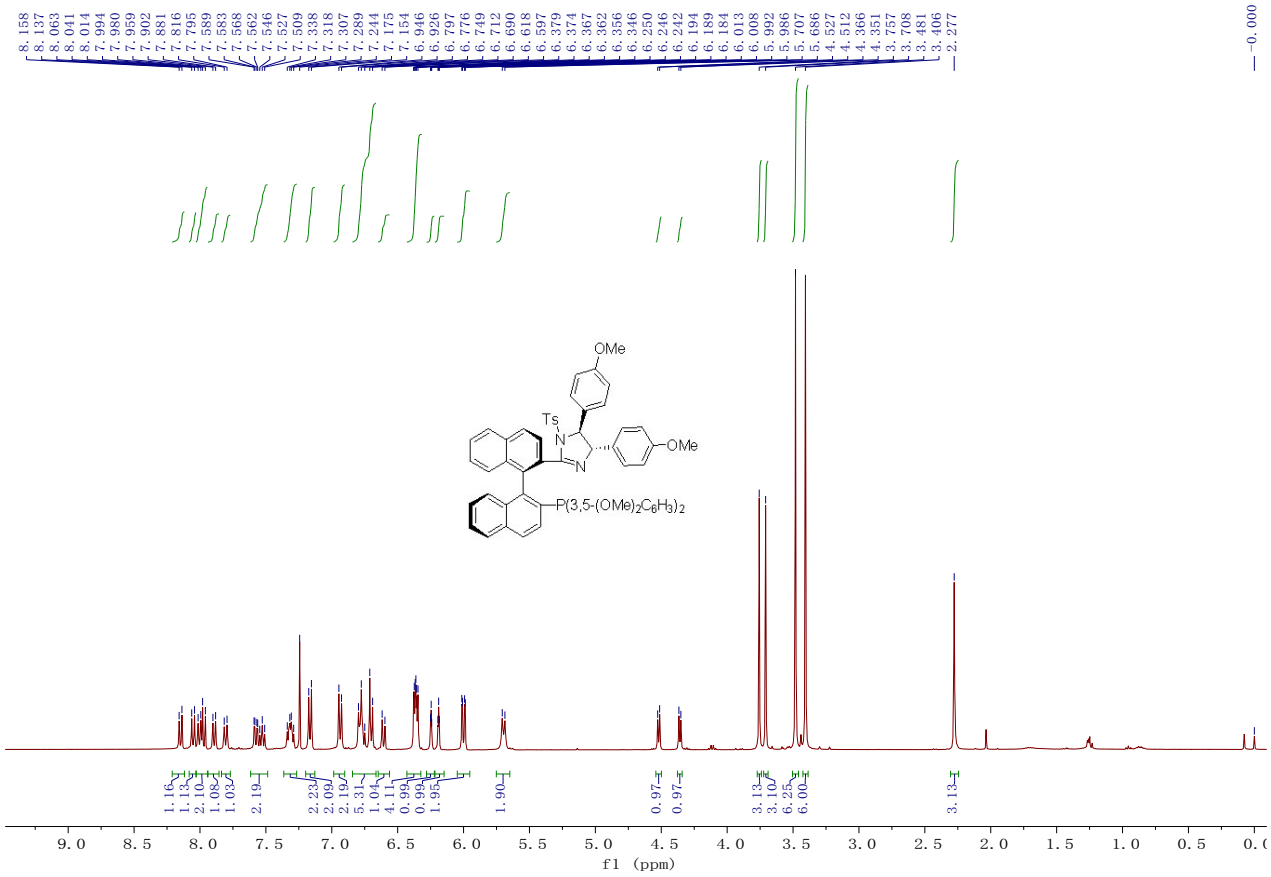
A solution of the tosylhydrazone (5.0 mmol, 1.0 equiv) in THF (20 mL) was treated with a solution of NaOH (10.0 mmol, 2.0 equiv) in H_2O (50 mL). The reaction mixture was stirred for 3 h at room temperature. EtOAc (40 mL) was added to the reaction mixture and the organic layers were separated. The aqueous layer was adjusted to pH = 7 by addition of dry-ice, and extracted with EtOAc (60 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent was evaporated in vacuo. Column chromatography (1:6 EtOAc/PE) afforded **2** as deep-orange solids.

4. Characterization and spectra charts for ligand.



(4S,5S)-2-((R)-1-(2-(bis(3,5-dimethoxyphenyl)phosphino)naphthalen-1-yl)naphthalen-2-yl)-1-tosyl-4,5-bis(4-methoxyphenyl)-4,5-dihydro-1H-imidazole L6

0.5 mmol scale, a white solid, 11% yield for three steps (86 mg). M.p.: 128-130 ^oC. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.28 (s, 3H, CH_3), 3.41 (s, 6H, CH_3), 3.48 (s, 6H, CH_3), 3.71 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 4.36 (d, *J* = 6.0 Hz, 1H, CH), 4.52 (d, *J* = 6.0 Hz, 1H, CH), 5.70 (d, *J* = 8.4 Hz, 2H, ArH), 6.00 (dd, *J* = 2.4 Hz, 8.8 Hz, 2H, ArH), 6.19 (dd, *J* = 2.0 Hz, 2.0 Hz, 1H, ArH), 6.24-6.25 (m, 1H, ArH), 6.34-6.38 (m, 4H, ArH), 6.61 (d, *J* = 8.4 Hz, 1H, ArH), 6.69-6.80 (m, 5H, ArH), 6.94 (d, *J* = 8.0 Hz, 2H, ArH), 7.16 (d, *J* = 8.4 Hz, 2H, ArH), 7.28-7.34 (m, 2H, ArH), 7.50-7.59 (m, 2H, ArH), 7.81 (d, *J* = 8.4 Hz, 1H, ArH), 7.89 (d, *J* = 8.4 Hz, 1H, ArH), 7.95-8.02 (m, 2H, ArH), 8.05 (d, *J* = 8.8 Hz, 1H, ArH), 8.15 (d, *J* = 8.4 Hz, 1H, ArH). ^{31}P NMR ($CDCl_3$, 161 MHz, 85% H_3PO_4) δ -9.31. IR (CH_2Cl_2) ν 3062, 2960, 2932, 2834, 1642, 1584, 1511, 1460, 1411, 1280, 1247, 1203, 1155, 1087, 1036, 816, 689, 665 cm^{-1}. MS (MALDI) *m/z* (%): 993.2 (100) $[M+H]^+$; HRMS (MALDI) Calcd. for $C_{60}H_{54}N_2O_8PS^{+1}(M+H)^+$ requires 993.3333, Found: 993.3327. $[\alpha]_D^{20}$ = +17.27 (c = 1.00, CH_2Cl_2).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OMe
Ts
N
N
OMe
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1.16
1.13
2.10
1.08
1.03
2.19
2.23
2.09
2.19
5.31
1.04
4.11
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0.99
1.95
1.90
0.97
0.97
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3.13
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7.0
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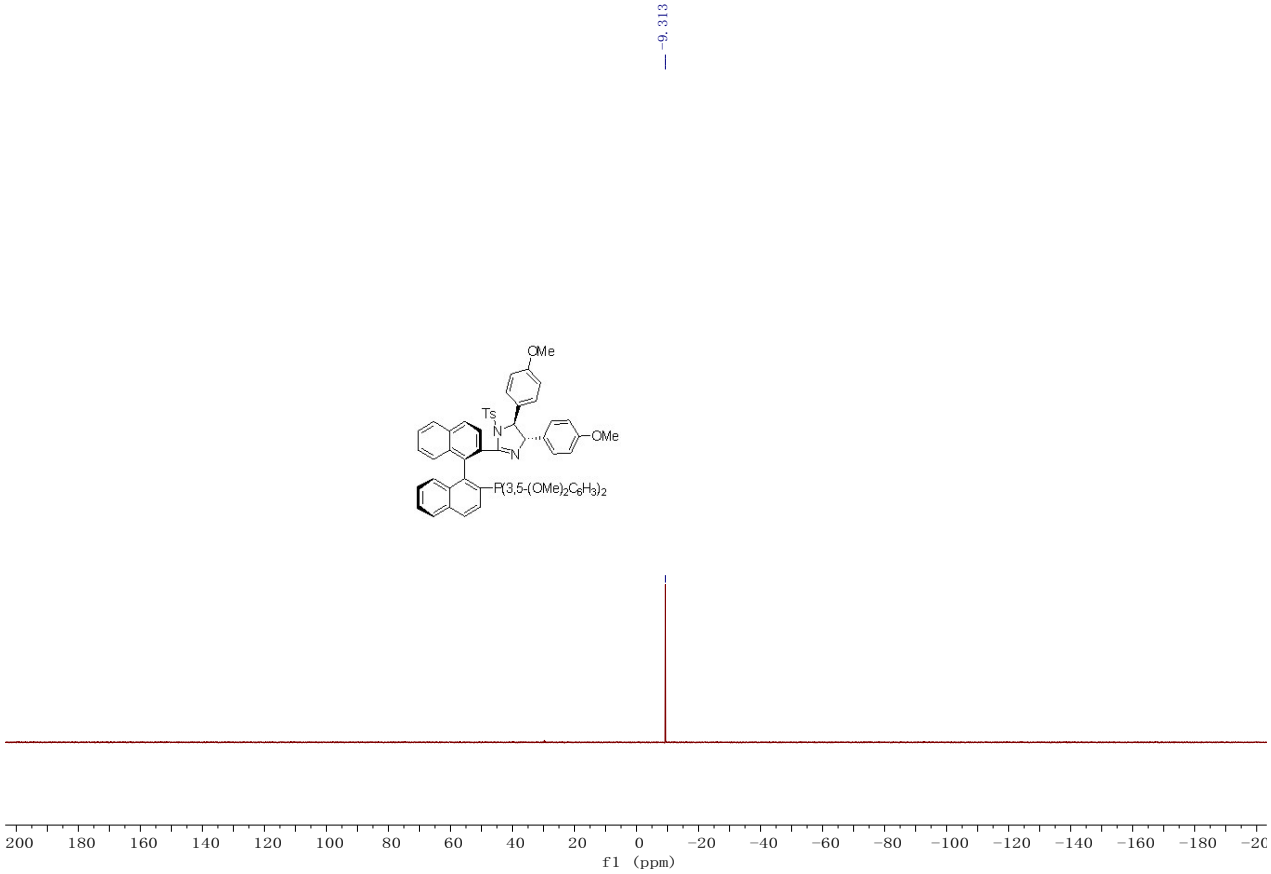
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Ts
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N
OMe
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-140
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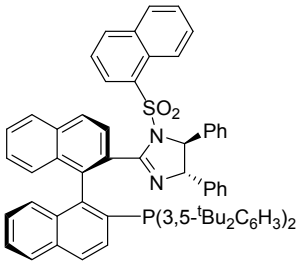
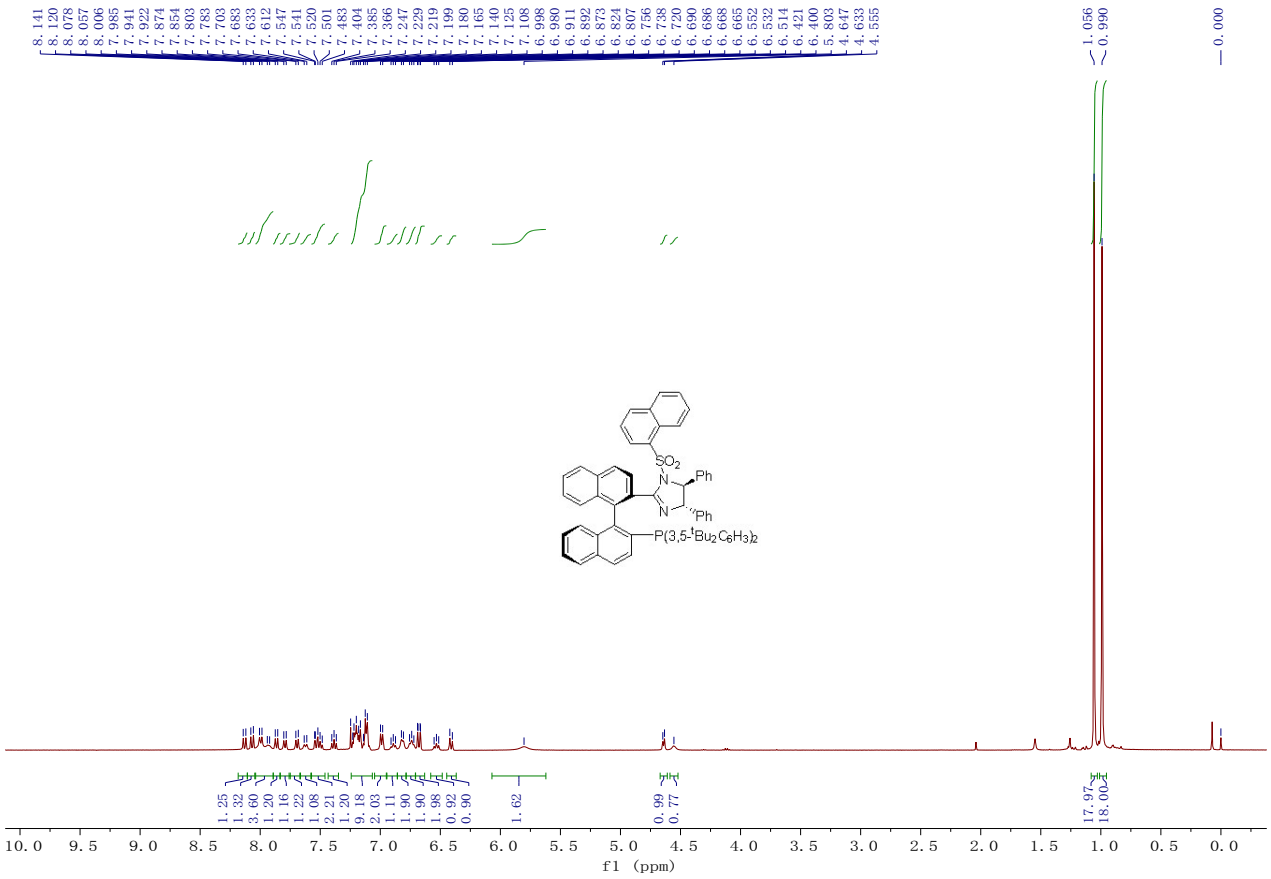
-180
-20
f1 (ppm)



(4S,5S)-2-((R)-1-(2-(bis(3,5-di-tert-butylphenyl)phosphino)naphthalen-1-yl)naphthalen-2-yl)-1-(naphthalen-1-ylsulfonyl)-4,5-diphenyl-4,5-dihydro-1H-imidazole L7

0.5 mmol scale, a white solid, 9% yield for three steps (65 mg). M.p.: 154-156 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.99 (s, 18H, $C(CH_3)_3$), 1.06 (s, 18H, $C(CH_3)_3$), 4.56 (br, 1H, CH), 4.64 (d, *J* = 5.6 Hz, 1H, CH), 5.80 (br, 2H, ArH), 6.41 (d, *J* = 8.4 Hz, 1H, ArH), 6.53 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H, ArH), 6.68 (dd, *J* = 1.2 Hz, 8.4 Hz, 2H, ArH), 6.74 (dd, *J* = 7.2 Hz, 7.2 Hz, 2H, ArH), 6.80-6.83 (m, 2H, ArH), 6.89 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 6.99 (d, *J* = 7.2 Hz, 2H, ArH), 7.10-7.25 (m, 9H, ArH), 7.39 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.48-7.55 (m, 2H, ArH), 7.62 (d, *J* = 8.4 Hz, 1H, ArH), 7.69 (d, *J* = 8.0 Hz, 1H, ArH), 7.79 (d, *J* = 8.0 Hz, 1H, ArH), 7.86 (d, *J* = 8.0 Hz, 1H, ArH), 7.92-8.01 (m, 4H, ArH), 8.07 (d, *J* = 8.4 Hz, 1H, ArH), 8.13 (d, *J* = 8.4 Hz, 1H, ArH). ^{31}P NMR ($CDCl_3$, 161 MHz, 85% H_3PO_4) δ -11.29. IR (CH_2Cl_2) ν 3061, 2961, 2867, 1644, 1589, 1476, 1362, 1337, 1248, 1134, 1165, 1024, 818, 770, 747, 697, 680 cm^{-1}. HRMS (ESI) Calcd. for $C_{73}H_{74}N_2O_2PS^{+1}(M+H)^+$ requires 1073.5203, Found: 1073.5198. $[\alpha]_D^{20}$ = -4.72 (c = 1.00, CH_2Cl_2).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7.633
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7.541
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Ph
Ph
P(3,5-tBu2C6H3)2
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3.60
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1.16
1.22
1.08
2.21
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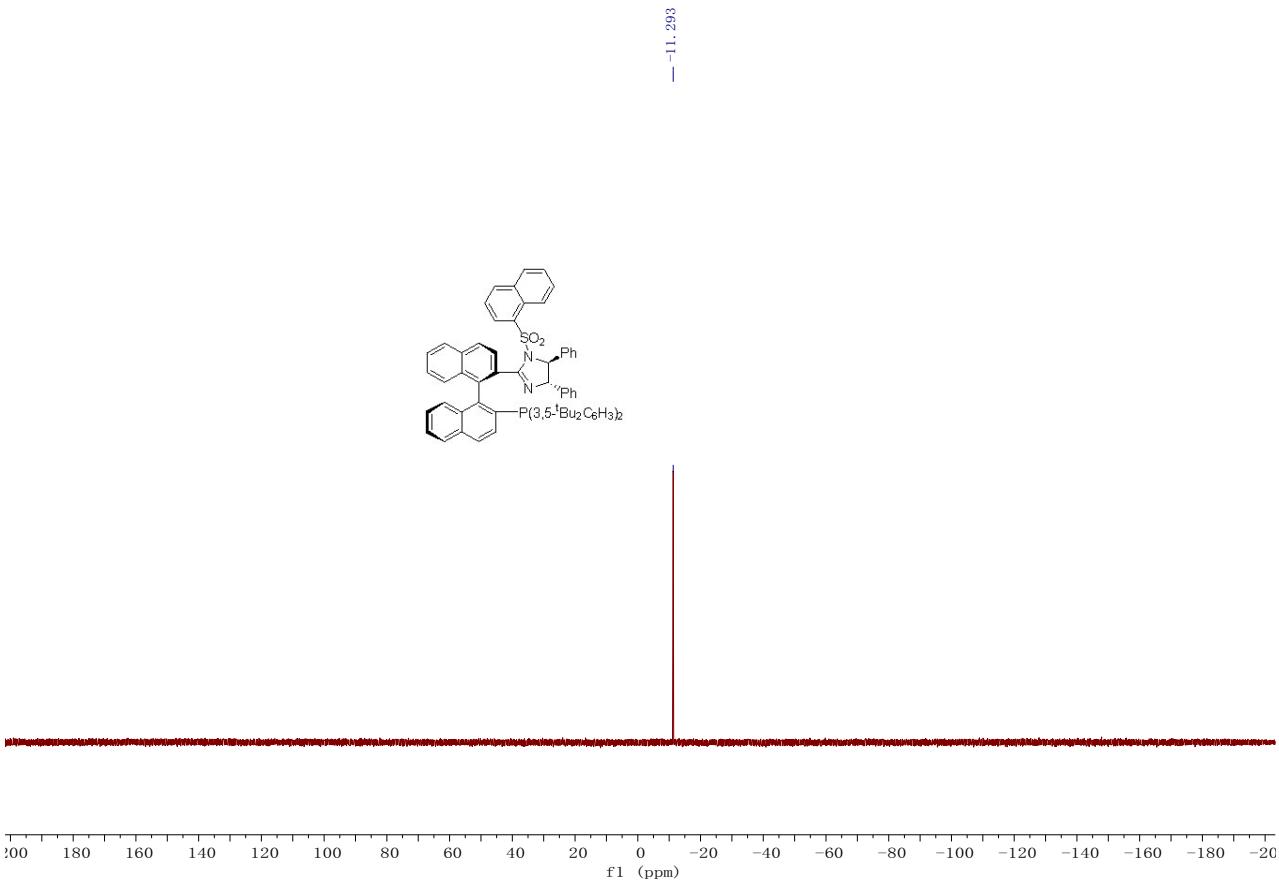
9.18
2.03
1.11
1.90
1.90
1.98
0.92
0.90
1.62
0.99
0.77
17.97
18.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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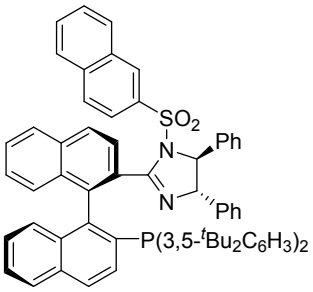
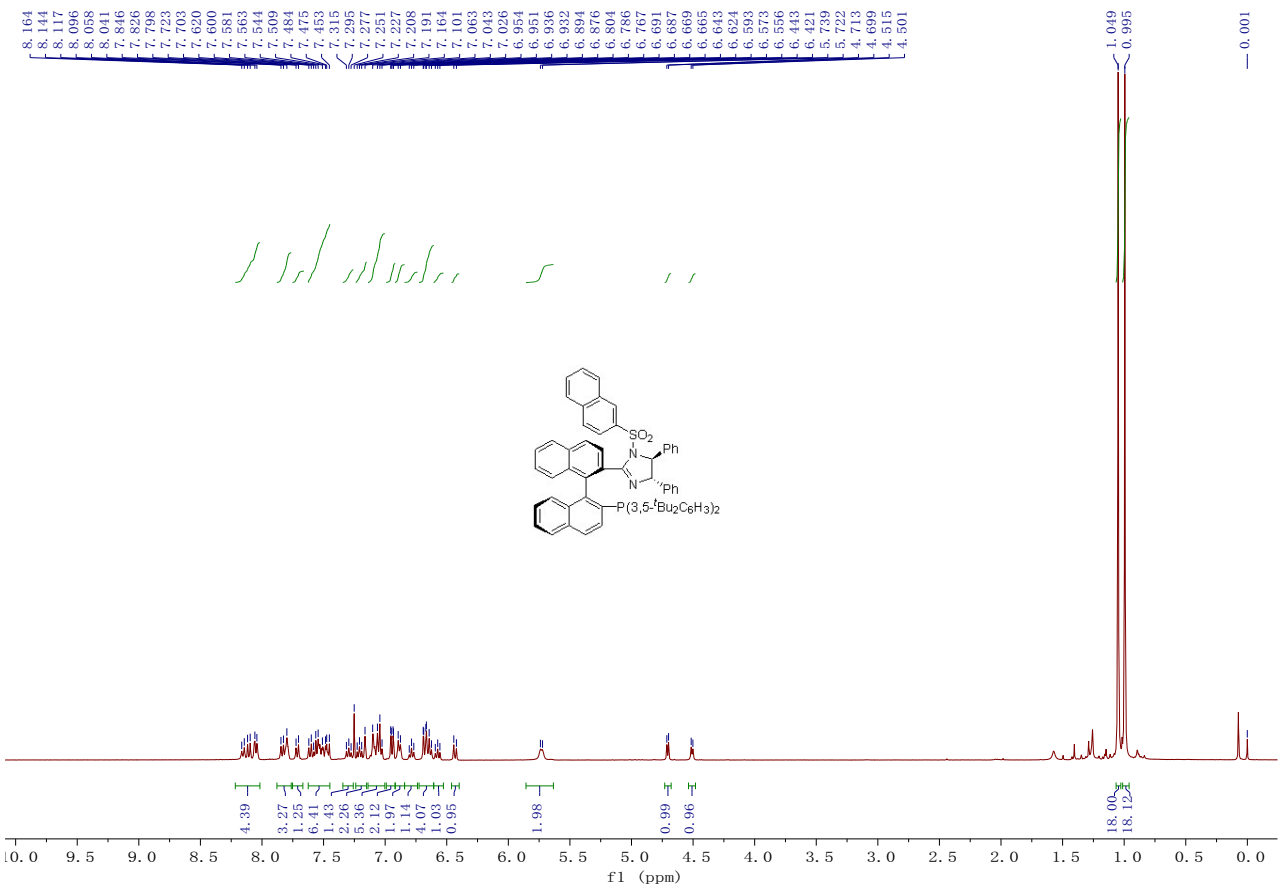


(4S,5S)-2-((R)-1-(2-(bis(3,5-di-tert-butylphenyl)phosphino)naphthalen-1-yl)naphthalen-2-yl)-1-(naphthalen-2-ylsulfonyl)-4,5-diphenyl-4,5-dihydro-1H-imidazole L9

0.5 mmol scale, a white solid, 7% yield for three steps (30 mg). M.p.: 150-153 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.00 (s, 18H, $C(CH_3)_3$), 1.05 (s, 18H, $C(CH_3)_3$), 4.51 (d, *J* = 5.6 Hz, 1H, CH), 4.71 (d, *J* = 5.6 Hz, 1H, CH), 5.73 (d, *J* = 6.8 Hz, 2H, ArH), 6.43 (d, *J* = 8.8 Hz, 1H, ArH), 6.57 (dd, *J* = 6.8 Hz, 6.8 Hz, 1H, ArH), 6.62-6.70 (m, 4H, ArH), 6.79 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 6.89 (d, *J* = 7.2 Hz, 2H, ArH), 6.94 (dd, *J* = 0.8 Hz, 7.6 Hz, 2H, ArH), 7.02-7.11 (m, 5H, ArH), 7.16-7.23 (m, 2H, ArH), 7.27-7.32 (m, 1H, ArH), 7.45-7.62 (m, 6H, ArH), 7.71 (d, *J* = 8.0 Hz, 1H, ArH), 7.79-7.85 (m, 3H, ArH), 8.04-8.17 (m, 4H, ArH). ^{31}P NMR ($CDCl_3$, 161 MHz, 85% H_3PO_4) δ -11.44. IR (CH_2Cl_2) ν 3060, 2961, 2926, 2858, 1644, 1588, 1456, 1476, 1362, 1341, 1362, 1341, 1261, 1249, 1167, 1073, 1020, 874, 817, 746, 697, 666 cm^{-1}. HRMS (ESI) Calcd. for $C_{73}H_{74}N_2O_2PS^{+1}(M+H)^+$ requires 1073.5203, Found: 1073.5201. $[\alpha]_D^{20}$ = -36.24 (c = 1.00, CH_2Cl_2).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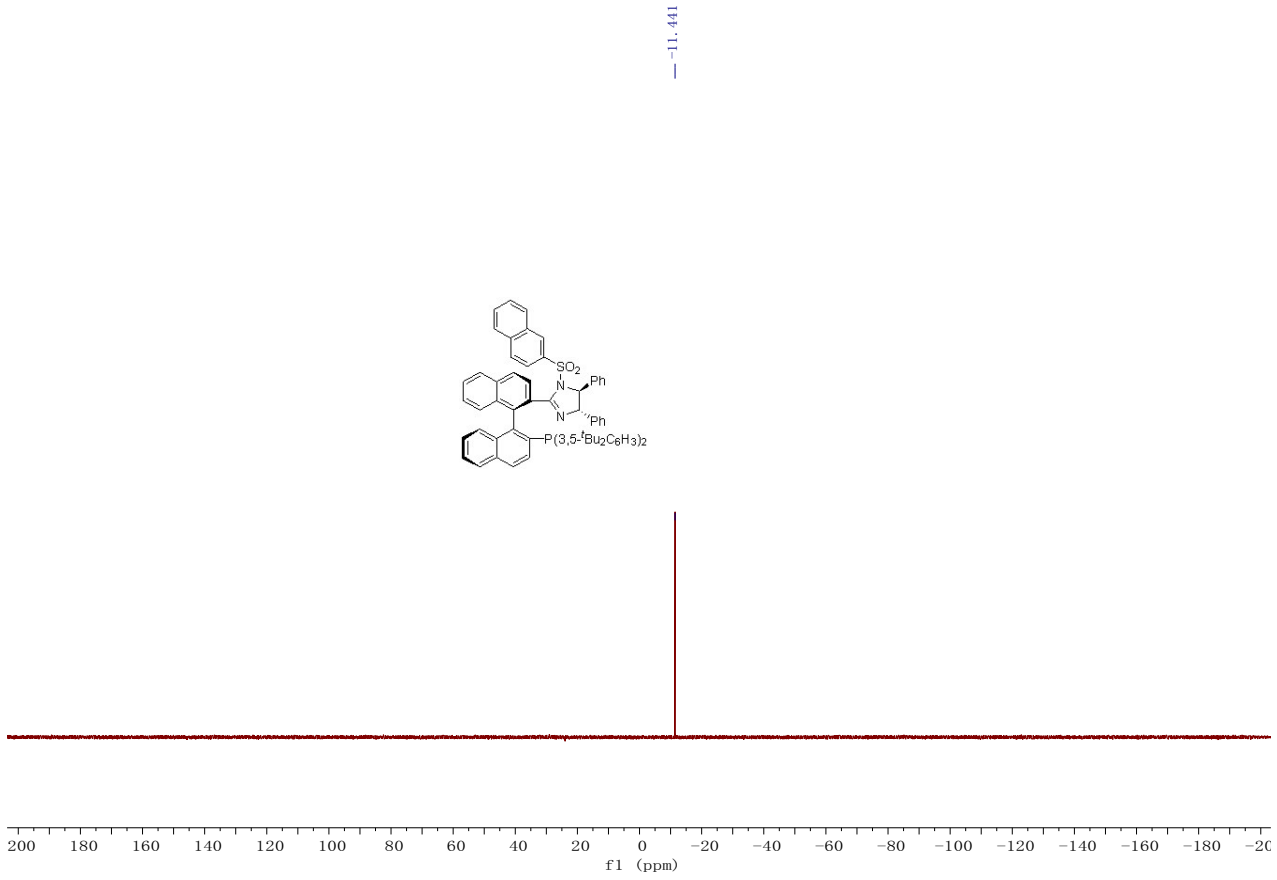
f1 (ppm)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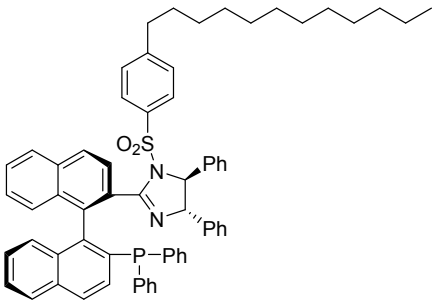
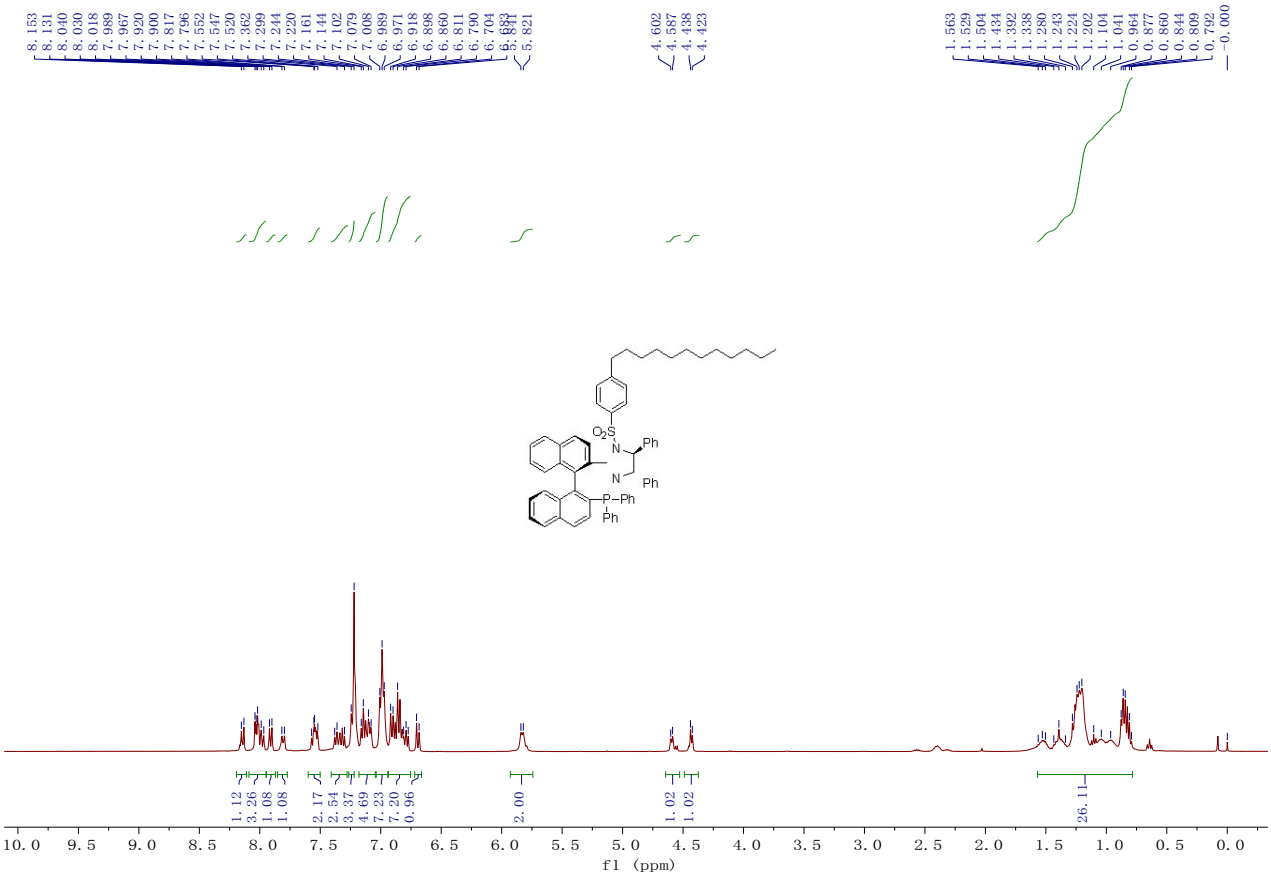


(4S,5S)-2-((R)-1-(2-(diphenyl)phosphino)naphthalen-1-yl)naphthalen-2-yl)-1-(4-dodecylphenyl)sulfonyl)-4,5-diphenyl-4,5-dihydro-1H-imidazole L10

0.5 mmol scale, a white solid, 30% yield for three steps (181 mg). M.p.: 92-95 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.79-1.57 (m, 25H, CH_2, CH_3), 4.43 (d, *J* = 6.0 Hz, 1H, CH), 4.59 (d, *J* = 6.0 Hz, 1H, CH), 5.83 (d, *J* = 8.0 Hz, 2H, ArH), 6.69 (d, *J* = 8.4 Hz, 1H, ArH), 6.77-6.92 (m, 7H, ArH), 6.97-7.01 (m, 7H, ArH), 7.07-7.17 (m, 5H, ArH), 7.22-7.25 (m, 3H, ArH), 7.29-7.39 (m, 3H, ArH), 7.52-7.58 (m, 2H, ArH), 7.81 (d, *J* = 8.4 Hz, 1H, ArH), 7.91 (d, *J* = 8.0 Hz, 1H, ArH), 7.96-8.04 (m, 3H, ArH), 8.14 (d, *J* = 8.8 Hz, 1H, ArH). ^{31}P NMR ($CDCl_3$, 161 MHz, 85% H_3PO_4) δ -14.32. IR (CH_2Cl_2) ν 3056, 2955, 2926, 2854, 1643, 1595, 1494, 1455, 1434, 1373, 1341, 1167, 1089, 1026, 958, 817, 775, 742, 696, 676 cm^{-1}. HRMS (ESI) Calcd. for $C_{65}H_{64}N_2O_2PS^{+1}(M+H)^+$ requires 967.4421, Found:967.4416. $[\alpha]_D^{20}$ = +14.84 (c = 1.00, CH_2Cl_2).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Ph
Ph
P-Ph
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7.23
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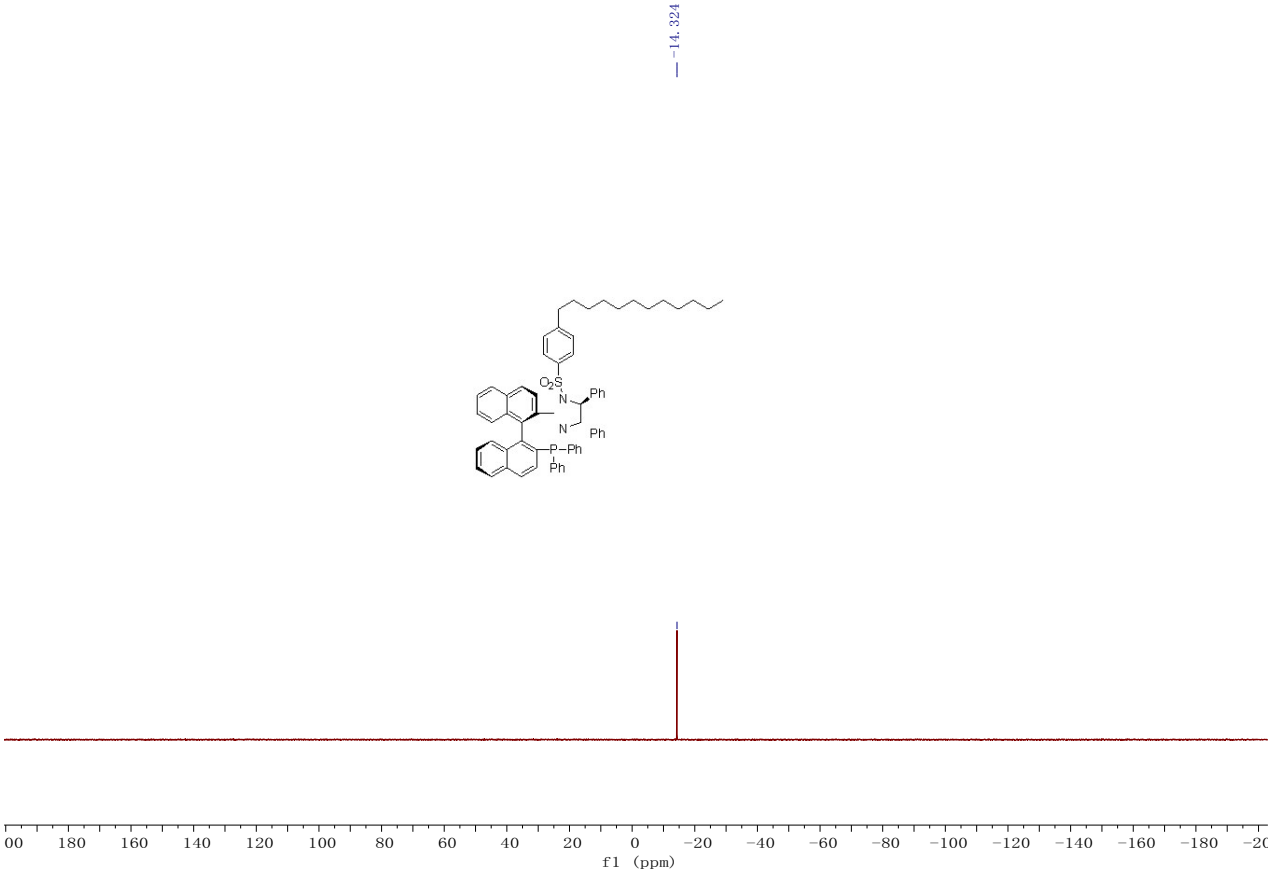
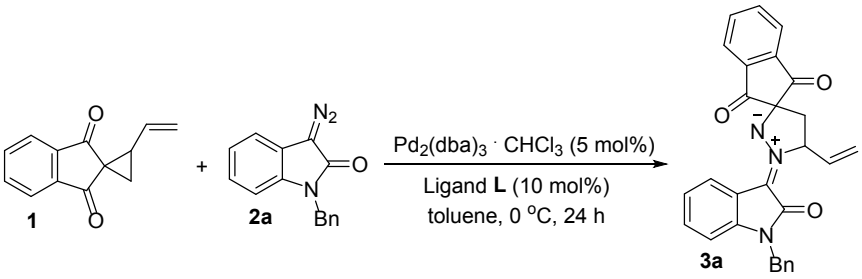
1.02
26.11
f1 (ppm)


14.324
Ph
Ph
Ph
P-Ph
f1 (ppm)

5. Screening of ligands for palladium-catalyzed asymmetric formal [3+2]-cycloaddition

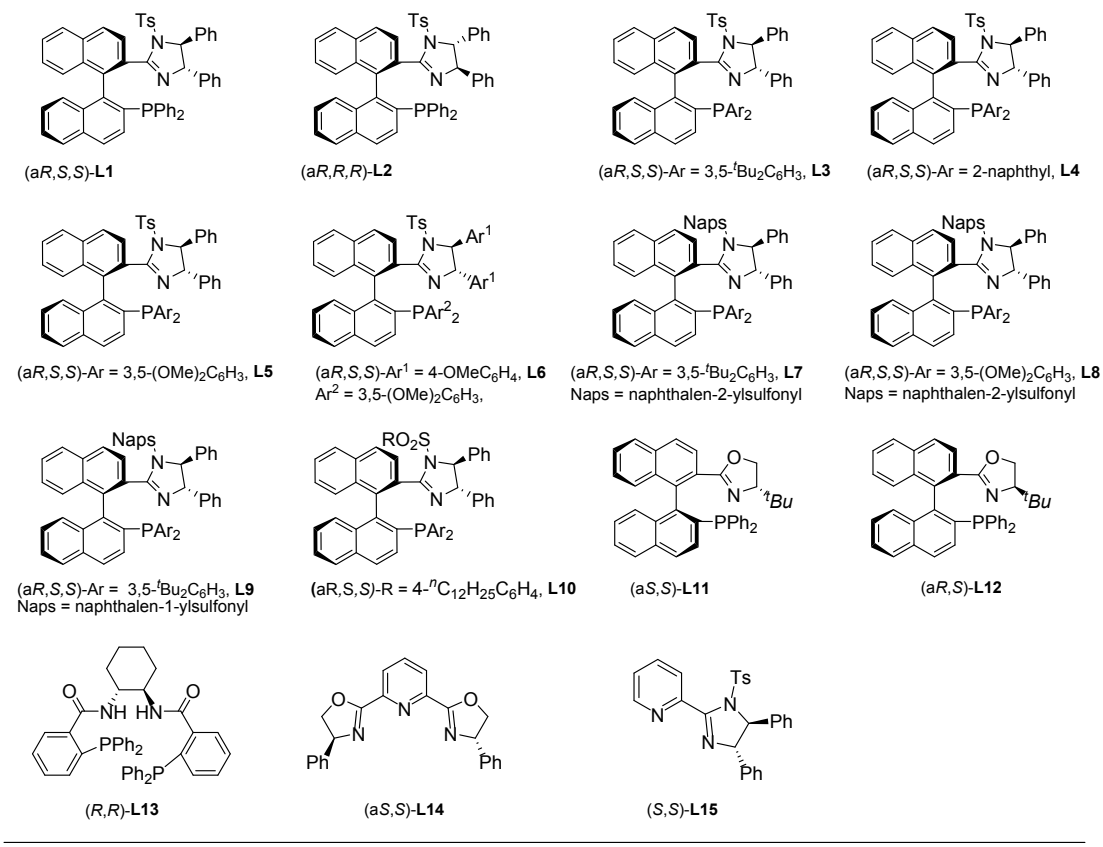
We began our investigation by exploring our previously developed catalytic system for palladium(0)-catalyzed asymmetric [3+2] cycloaddition using 3-diazooxindoles serving as dipolarophiles. 2-vinylspiro[cyclopropane-1,2'-indene]-1',3'-dione **1** and 1-benzyl-3-diazoindolin-2-one **2a** were used as the model substrates, toluene was employed as solvent in the presence of ligands **L1**-**L15** at 0 ^{o}C. The use of chiral imidazoline-phosphine type ligand (a*R,S,S*)-**L1** in the reaction furnished the desired product **3a** in 88% yield along with 48% ee (Table SI-1, entry 1), while employing ligand (a*R,R,R*)-**L2** provided the product **3a** in 47% yield with 19% ee value (Table SI-1, entry 2). Another four newly synthesized chiral imidazoline-phosphine ligands **L6**, **L7**, **L9**, and **L10** as well as **L2-L5** and **L8** were also used to screen the optimal ligand for this reaction. It was found that using **1** and **2a** as model substrates in toluene at 0 ^{o}C, chiral imidazoline-phosphine (a*R,S,S*)-**L8** was identified as the best ligand for this reaction, resulting in **3a** in 95% yield and 78% ee (Table SI-1, entry8). For comparison, we also examined the chiral phosphine-oxazoline ligands (a*S,S*)-**L11** and (a*R,S*)-**L12** in this reaction under identical conditions. However, the use of ligand **L12** gave no desired product **3a** (Table SI-1, entry 12), while the use of ligand **L11** resulted in the formation of **3a** in 88% yield but only along with 15% ee (Table SI-1, entry 11). Other ligands, such as **L13**, **L14** or **L15**, did not give the desired product **3a** (Table SI-1, entries 13-15).

Table SI-1. Screening of Ligands for Pd-Catalyzed [3+2] Cycloaddition

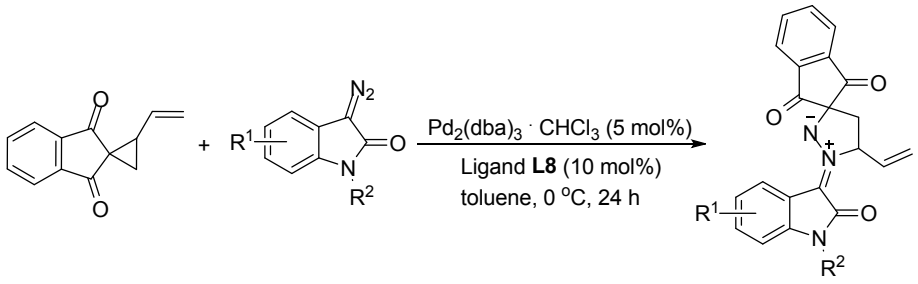


entry[a]	Ligand	yield [%][b]	ee [%][c]
1	**L1**	88	48
2	**L2**	47	19
3	**L3**	97	70
4	**L4**	84	50
5	**L5**	92	60
6	**L6**	98	71
7	**L7**	96	61
8	**L8**	95	78
9	**L9**	96	67
10	**L10**	93	26
11	**L11**	88	15
12	**L12**	trace	n. d.
13	**L13**	trace	n. d.
14	**L14**	trace	n. d.
15	**L15**	trace	n. d.

a) The reaction was conducted with **1** (0.1 mmol) and **2a** (0.15 mmol) in toluene (0.75 mL).
b) Isolated yield. c) The ee values were determined by chiral HPLC on Chiralcel IB-3.



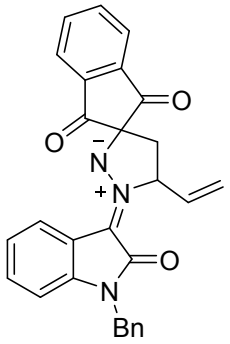
6. General procedure for palladium-catalyzed asymmetric formal [3+2]-cycloaddition of 2-vinylspiro[cyclopropane-1,2'-indene]-1',3'-dione with 3-diazooxindole in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ and chiral imidazoline-phosphine ligand L8



A solution of enantiomerically pure ligand **L8** (0.01 mmol, 10 mol %) and tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct $Pd_2(dba)_3{\cdot}CHCl_3$ (0.005 mmol, 5 mol %) in toluene (0.25 mL) was stirred at room temperature under argon atmosphere for 30 minutes. To the solution were added a solution of 2-vinylspiro[cyclopropane-1,2'-indene]-1',3'-dione **1** (0.1 mmol, 1.0 equiv) and 3-diazooxindole **2** (0.15 mmol, 1.5 equiv) in toluene (0.5 mL), and the

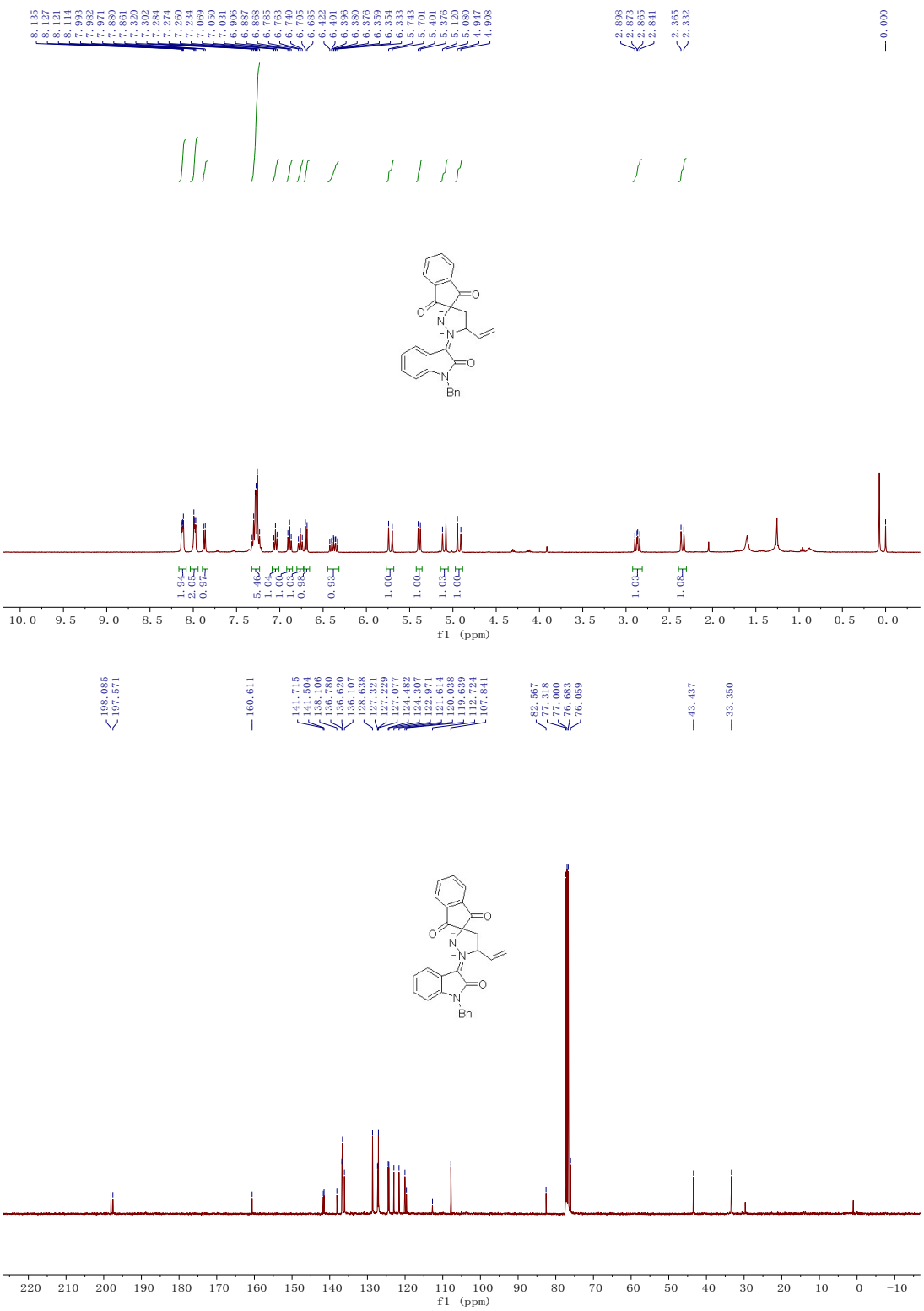
reaction mixture was stirred at 0 °C for 24 hours. After the reaction completed, the mixture was concentrated in vacuo to yield the crude product, which was purified by a flash chromatography on silica gel (eluent: PE/EtOAc = 5/1 ~ 10/1) to furnish the desired product **3** as a red solid.

7. Characterization and spectra containing HPLC traces charts for 3



(E)-1'-(1-benzyl-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3a

A red solid, 98% yield (44 mg), 78% ee. M.p.: 118-121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.35 (d, *J* = 13.2 Hz, 1H, CH_2), 2.87 (dd, *J* = 9.6 Hz, 13.2 Hz, 1H, CH_2), 4.93 (d, *J* = 15.6 Hz, 1H, CH_2), 5.10 (d, *J* = 15.6 Hz, 1H, CH_2), 5.39 (d, *J* = 10.0 Hz, 1H, =CH_2), 5.72 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.38 (ddd, *J* = 8.4 Hz, 10.0 Hz, 16.8 Hz, 1H, =CH), 6.70 (d, *J* = 8.0 Hz, 1H, ArH), 6.74-6.79 (m, 1H, CH), 6.89 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.05 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.23-7.33 (m, 5H, ArH), 7.87 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.97-8.00 (m, 2H, ArH), 8.11-8.14 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.4, 43.4, 76.1, 82.6, 107.8, 112.7, 119.6, 120.0, 121.6, 123.0, 124.3, 124.5, 127.1, 127.2, 127.3, 128.6, 136.1, 136.6, 136.8, 138.1, 141.5, 141.7, 160.6, 197.6, 198.1. IR (CH_2Cl_2) ν 2923, 2853, 1712, 1673, 1605, 1542, 1466, 1343, 1269, 1217, 1185, 1166, 759, 746, 719, 670 cm^{-1}. Ms (MALDI) m/z: 447.6 (M+H$^+$, 100); HRMS (MALDI) Calcd. for $C_{28}H_{22}N_3O_3$ (M+H$^+$), requires 448.1656, found: 448.1639.



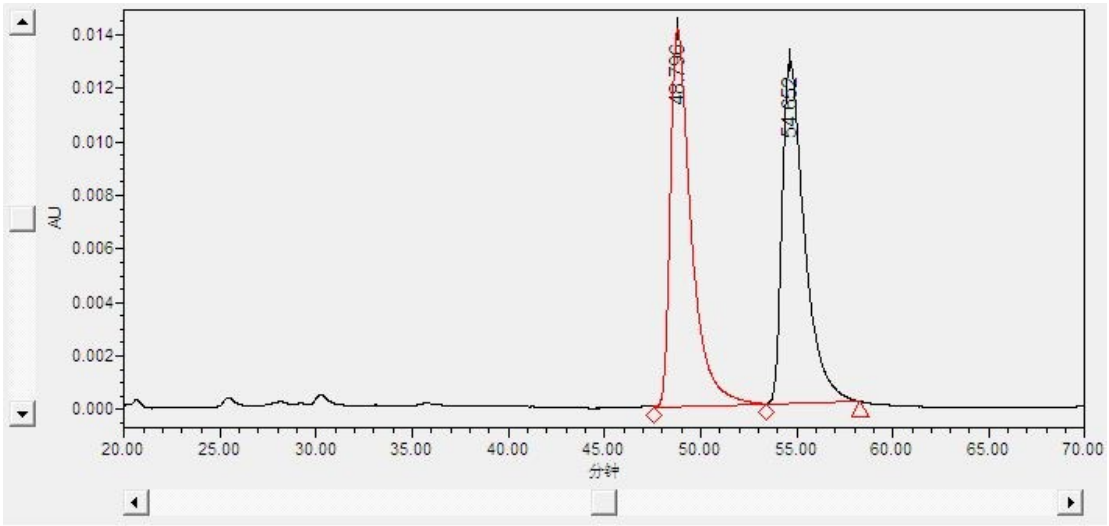
HPLC spectra:

HPLC REPORT

Sample Name: mly-20-16-a -racemic Date: ####

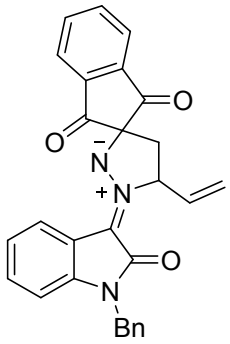
Column: IB-3 Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		48.796	1063995	50.73	14107	VV			未知				47.583	53.417
2		54.652	1033565	49.27	12807	VB			未知				53.417	58.317

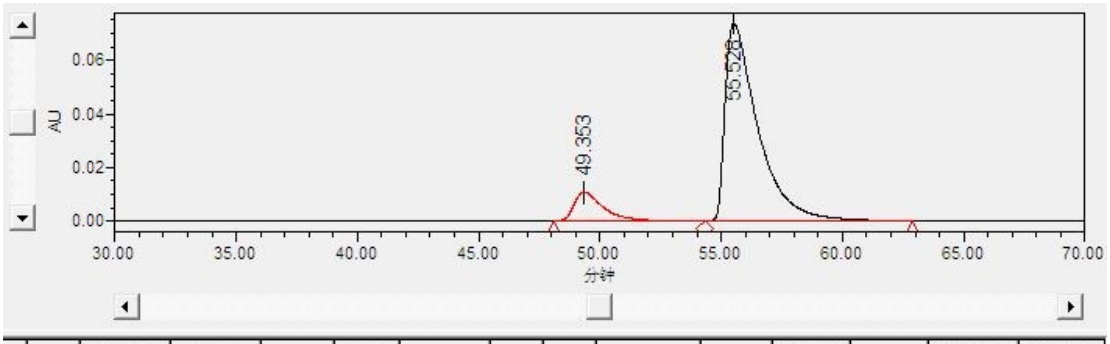
NO	R. Time	Peak Area	Percent	Peak Height
1	48.796	1063995	50.73	14107
2	54.652	1033565	49.27	12807



Chiral HPLC report: **3a**

HPLC REPORT

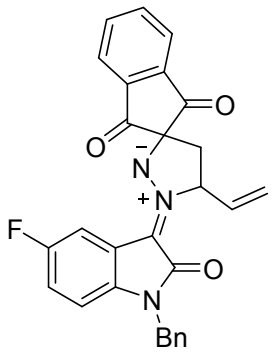
Sample Name: mly-20-16-a-chiral Date: ####
Column: IB-3 Mobile Phase: hex/ipr = 95/5
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		49.353	917055	11.64	10804	bV			未知				48.117	54.317
2		55.528	6963895	88.36	73851	Vb			未知				54.317	62.900

NO	R. Time	Peak Area	Percent	Peak Height
1	49.353	917055	11.64	10804
2	55.528	6963895	88.36	73851

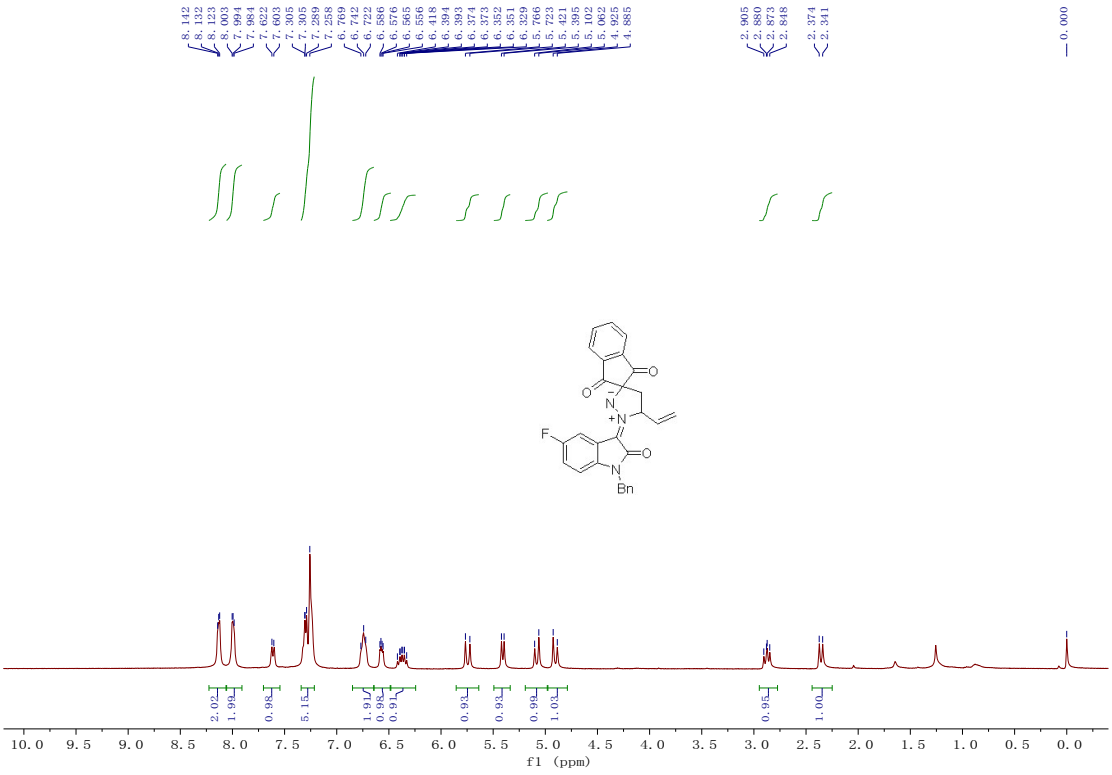
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 49.353 min, t_{major} = 55.528 min; ee = 84%. $[\alpha]_D^{20}$ = -86.3 (c = 0.460, CH_2Cl_2).

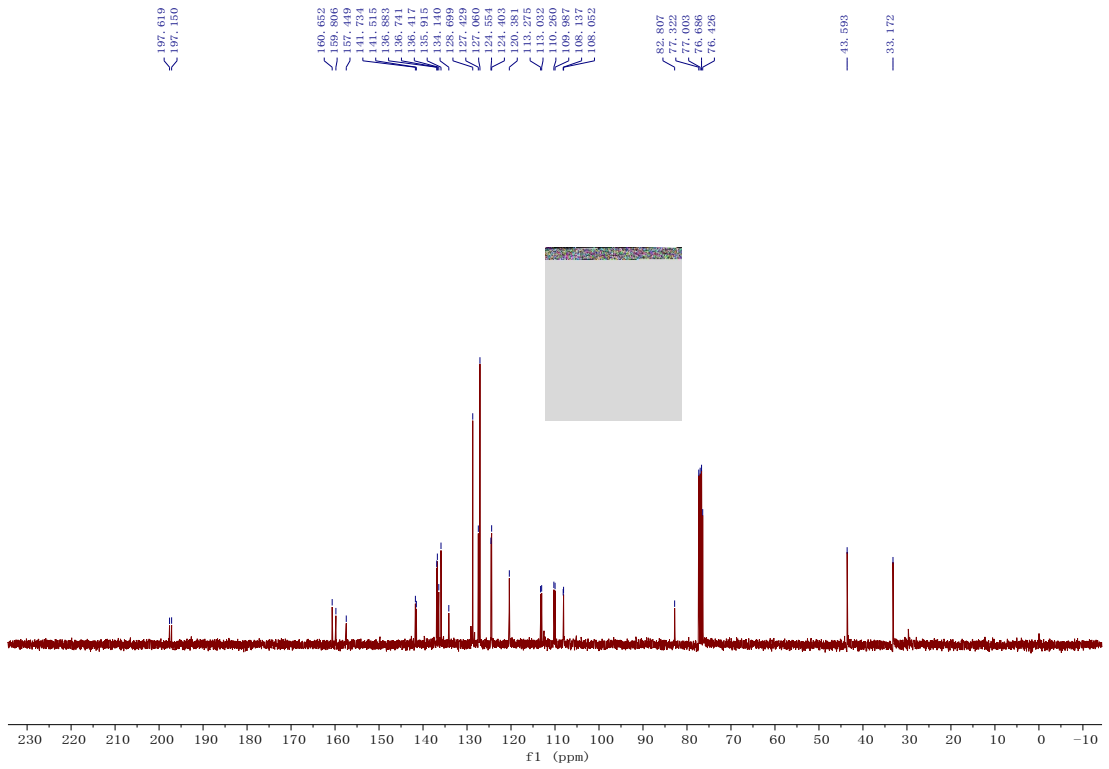


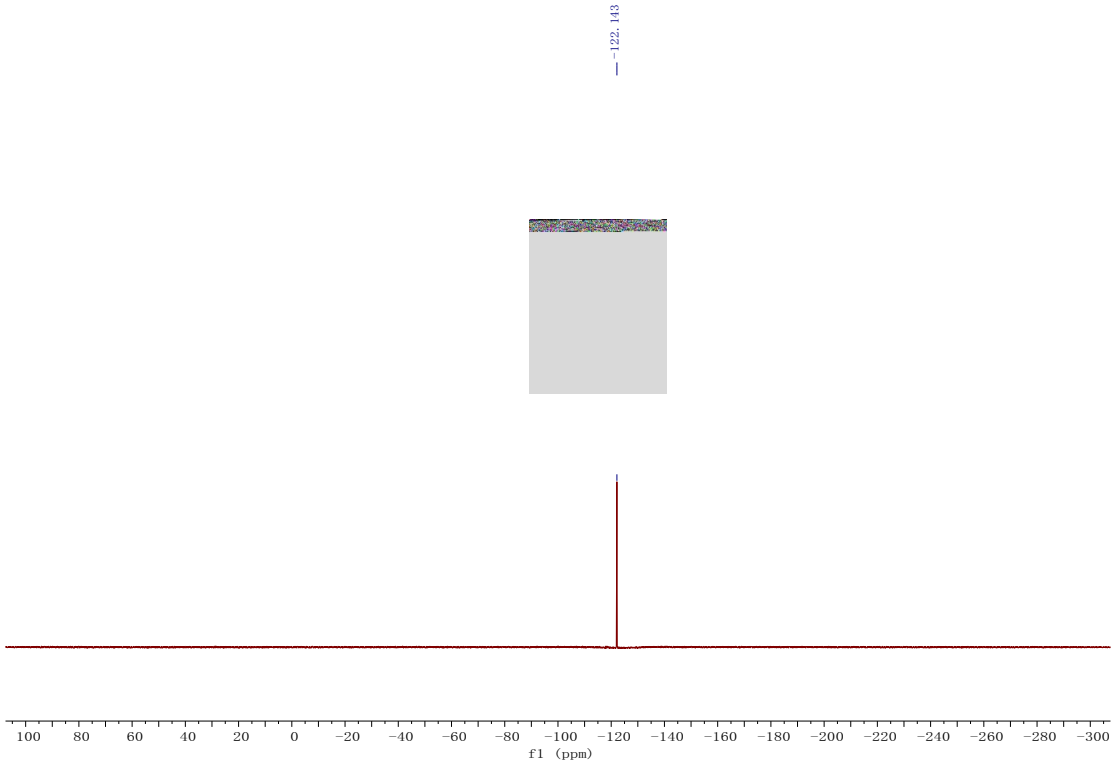
(E)-1'-(1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydros piro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3b

A red solid, 97% yield (46 mg), 64% ee. M.p.: 187-190 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.36 (d, *J* = 13.2 Hz, 1H, CH_2), 2.88 (dd, *J* = 10.0 Hz, 13.2 Hz, 1H, CH_2), 4.91 (d, *J* = 16.0 Hz, 1H, CH_2), 5.08 (d, *J* = 16.0 Hz, 1H, CH_2), 5.41 (d, *J* = 10.4 Hz, 1H, =CH_2), 5.74 (d, *J* = 17.2 Hz, 1H, =CH_2), 6.37 (ddd, *J* = 8.8 Hz, 10.4 Hz, 17.2 Hz, 1H, =CH), 6.55-6.59 (m, 1H, ArH), 6.72-6.77 (m, 2H, CH, ArH), 7.25-7.31 (m, 5H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.98-8.00 (m, 2H, ArH),

8.12-8.14 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.2, 43.6, 76.4, 82.8, 108.1 (d, J = 8.5 Hz), 110.1 (d, J = 27.3 Hz), 113.2 (d, J = 24.3 Hz), 120.4, 124.4, 124.6, 127.1, 127.4, 128.7, 134.1, 135.9, 136.4, 136.8, (d, J = 14.2 Hz), 141.5, 141.7, 158.6 (d, J = 235.7 Hz), 160.7, 197.2, 197.6. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -122.1. IR (CH_2Cl_2) ν 2923, 2854, 1712, 1673, 1541, 1472, 1326, 1288, 1204, 1151, 1111, 976, 791, 725, 716, 699 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{21}FN_3O_3$ ($M+H^+$), requires 466.1561, found: 466.1561.







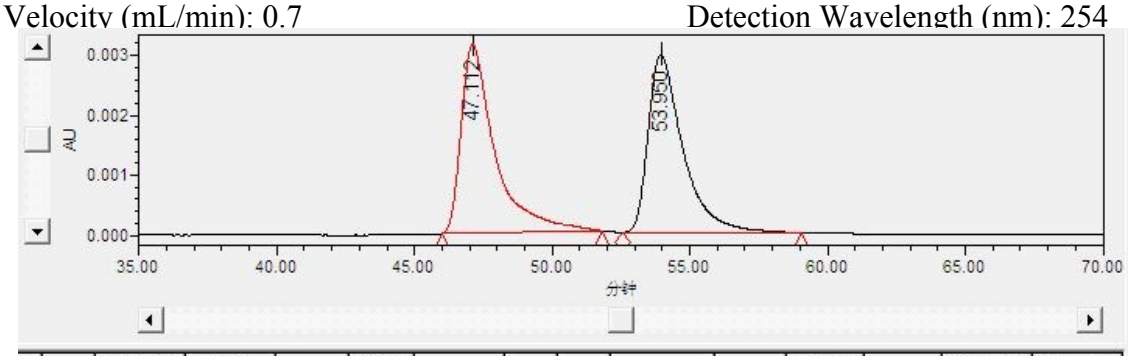
HPLC spectra:

HPLC REPORT

Sample Name: cb-1-83-a-racemic Date: ####

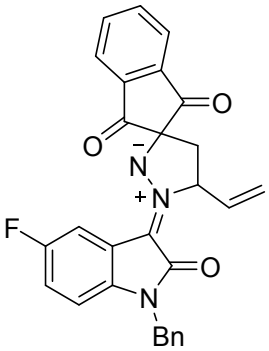
Column: IB-3 Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		47.112	269878	50.60	3144	bb			未知				46.000	51.833
2		53.950	263468	49.40	2976	VB			未知				52.550	59.067

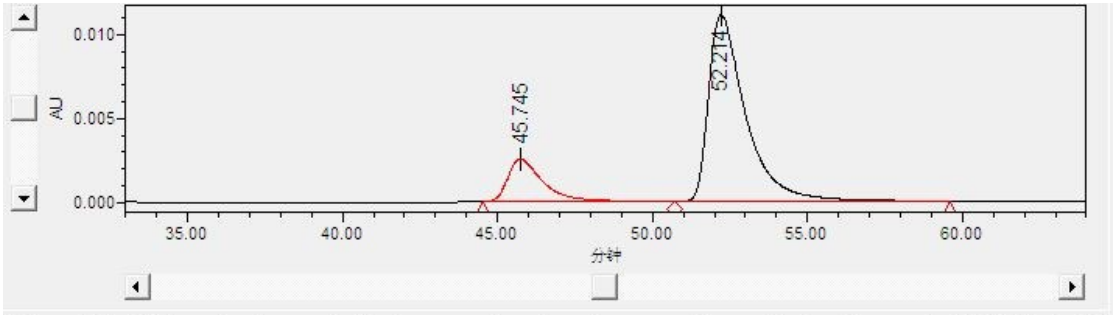
NO	R. Time	Peak Area	Percent	Peak Height
1	47.112	269878	50.60	3144
2	53.950	263468	49.40	2976



Chiral HPLC report: **3b**

HPLC REPORT

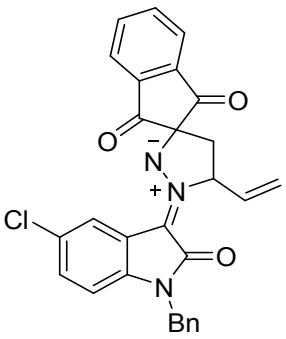
Sample Name: cb-1-83-a-chiral Date: ####
Column: IB-3 Mobile Phase: hex/ipr = 95/5
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		45.745	206701	17.99	2551	BV			未知				44.517	50.717
2		52.214	942532	82.01	11137	VB			未知				50.717	59.600

NO	R. Time	Peak Area	Percent	Peak Height
1	45.745	206701	17.99	2551
2	52.214	942532	82.01	11137

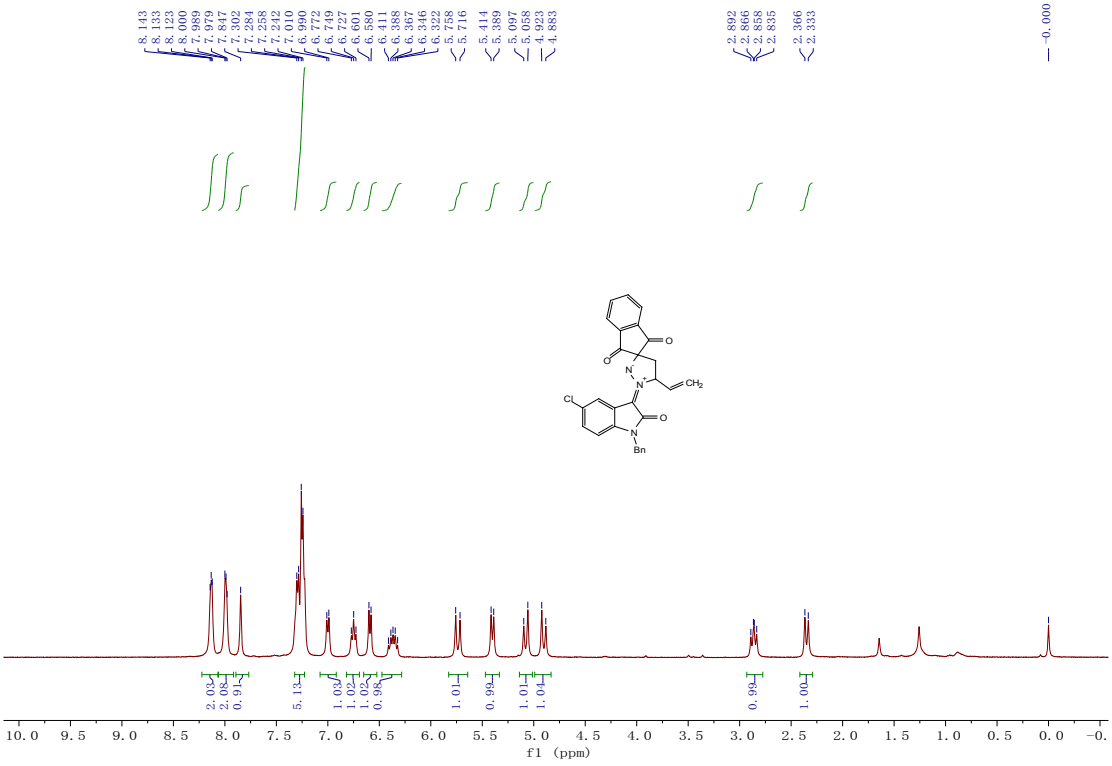
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 45.745 min, t_{major} = 52.214 min; ee = 64%. $[\alpha]_D^{20}$ = -46.2 (c = 0.700, CH_2Cl_2).

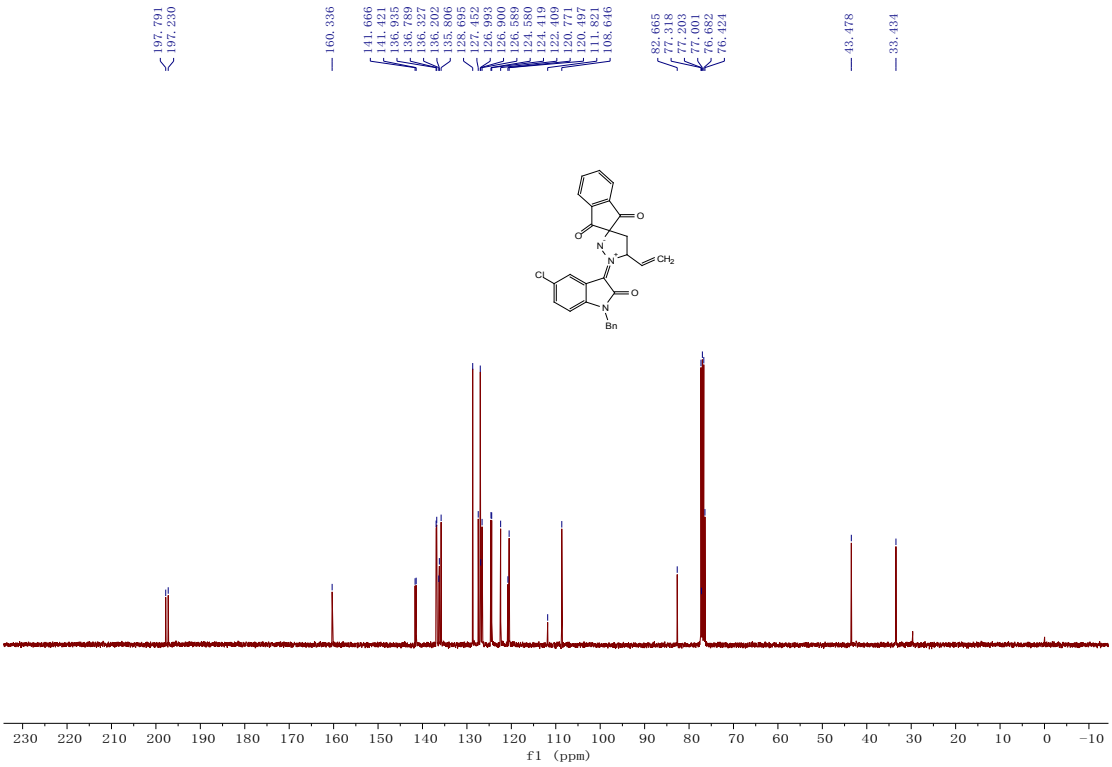


(E)-1'-(1-benzyl-5-chloro-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3c

A red solid, 92% yield (44 mg), 78% ee. M.p.: 141-144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.35 (d, *J* = 13.2 Hz, 1H, CH_2), 2.86 (dd, *J* = 9.2 Hz, 12.4 Hz, 1H, CH_2), 4.90 (d, *J* = 16.0 Hz, 1H, CH_2), 5.08 (d, *J* = 16.0 Hz, 1H, CH_2), 5.40 (d, *J* = 10.0 Hz, 1H, =CH_2), 5.74 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.32-6.42 (m, 1H, =CH), 6.59 (d, *J* = 8.4 Hz, 1H, ArH), 6.75 (dd, *J* = 9.2 Hz, 9.2 Hz, 1H, CH), 7.00 (d, *J* = 8.0 Hz, 1H, ArH), 7.24-7.31 (m, 5H, ArH), 7.85 (s, 1H, ArH), 7.97-8.00 (m, 2H, ArH), 8.12-8.15 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.4, 43.5, 76.4, 82.7, 108.6,

111.8, 120.5, 120.8, 122.4, 124.4, 124.6, 126.6, 126.9, 127.0, 127.5, 128.7, 135.8, 136.2, 136.3, 136.8, 136.9, 141.4, 141.7, 160.3, 197.2, 197.8. IR (CH_2Cl_2) ν 3028, 2924, 2854, 1710, 1672, 1496, 1465, 1287, 1262, 1163, 1120, 968, 802, 732, 697, 679 cm^{-1}. MS (MALDI) m/z: 482.1 ($M+H^+$, 100); HRMS (MALDI) Calcd. for $C_{28}H_{21}ClN_3O_3$ ($M+H^+$), requires 482.1266, found: 482.1256.



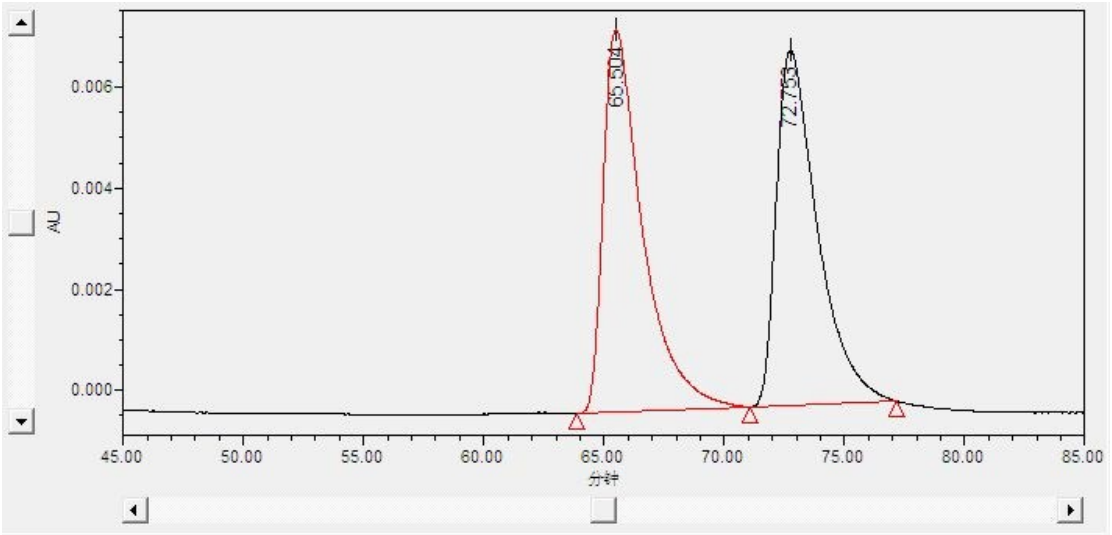


HPLC spectra:

HPLC REPORT

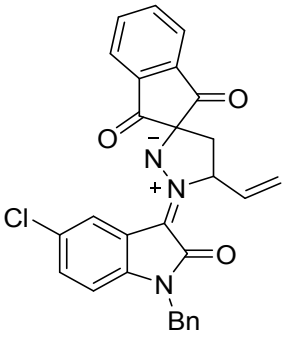
Sample Name: cb-2-3-a-racemic
Column: IB-3
Velocity (mL/min): 0.7

Date: ####
Mobile Phase: hex/ipr = 95/5
Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		65.504	867506	50.92	7566	BB			未知				63.867	71.100
2		72.753	836185	49.08	7025	BB			未知				71.100	77.183

NO	R. Time	Peak Area	Percent	Peak Height
1	65.504	867506	50.92	7566
2	72.753	836185	49.08	7025

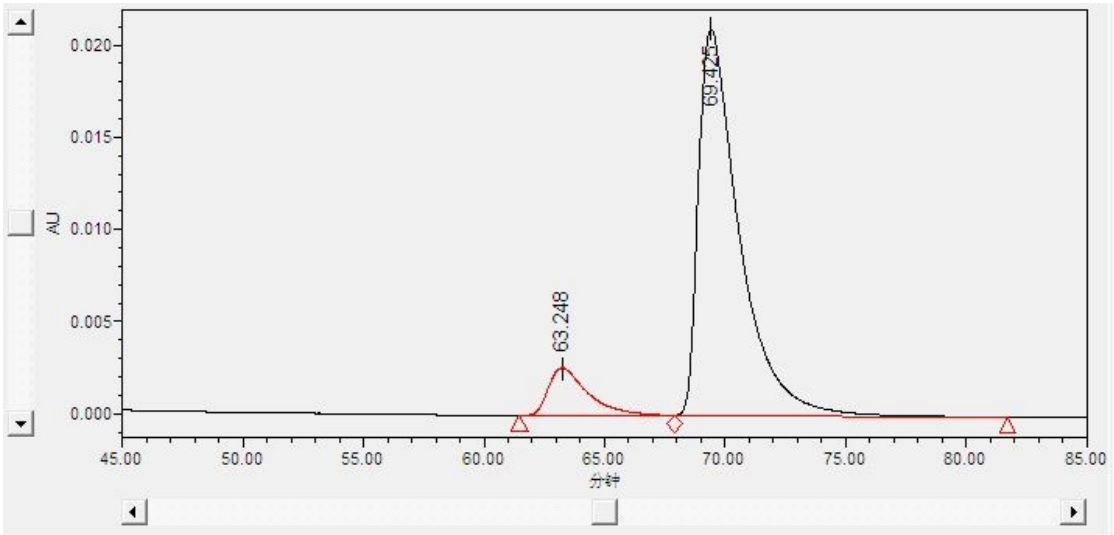


Chiral HPLC report: **3c**

HPLC REPORT

Sample Name: cb-2-3-a-chiral
Column: IB-3
Velocity (mL/min): 0.7

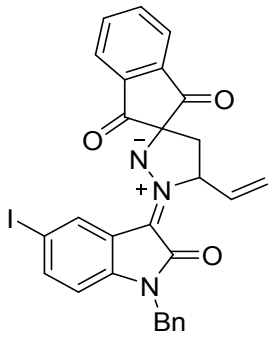
Date: ####
Mobile Phase: hex/ipr = 95/5
Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		63.248	304247	10.82	2597	BV			未知				61.483	67.900
2		69.425	2508093	89.18	20990	VB			未知				67.900	81.733

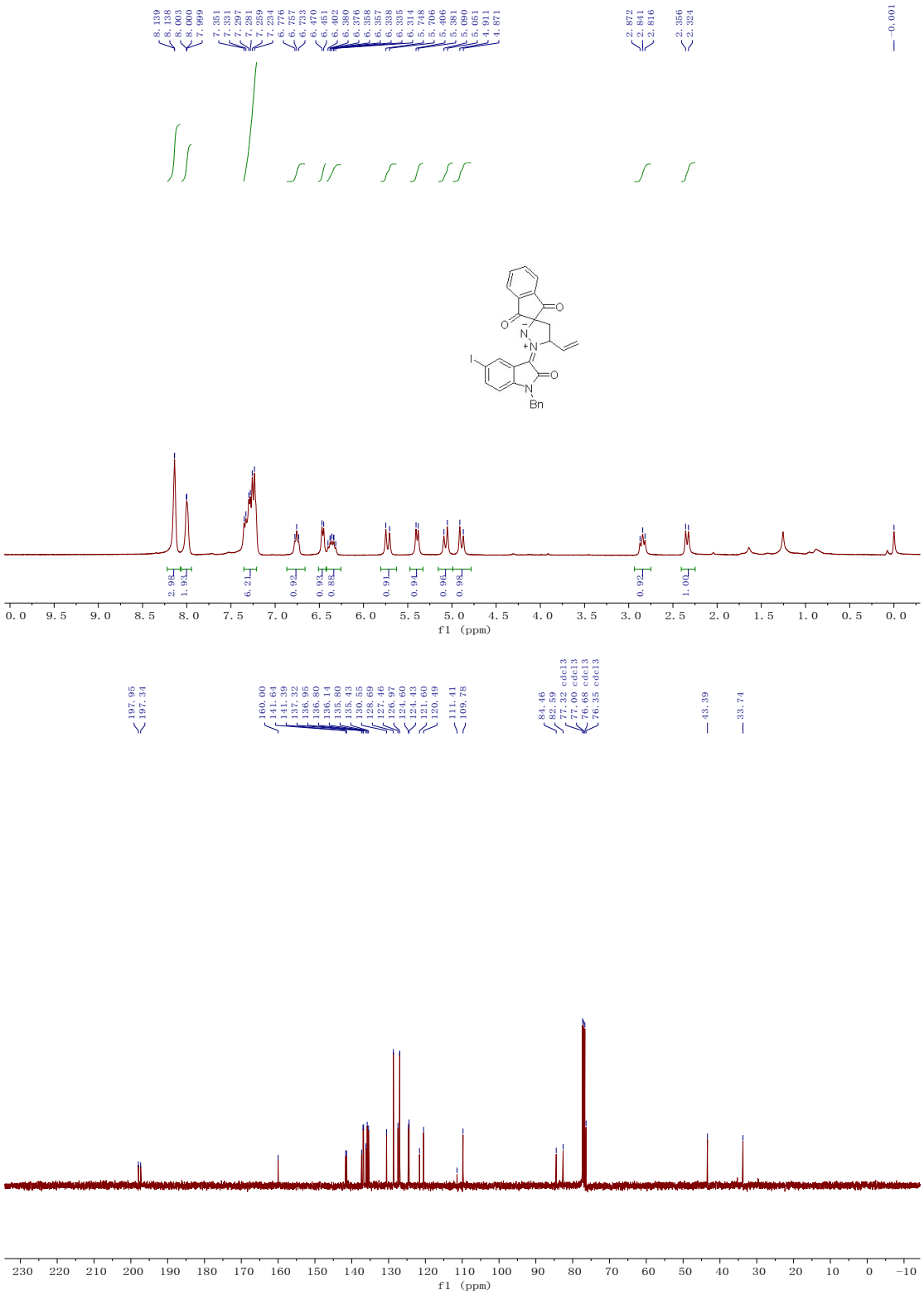
NO	R. Time	Peak Area	Percent	Peak Height
1	63.248	304247	10.82	2597
2	69.425	2508093	89.18	20990

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 63.248 min, t_{major} = 69.425 min; ee = 78%. $[\alpha]_D^{20}$ = -72.0 (c = 0.500, CH_2Cl_2).



(E)-1'-(1-benzyl-5-iodo-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3d

A red solid, 98% yield (56 mg), 82% ee. M.p.: 213-214 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (d, *J* = 12.8 Hz, 1H, CH_2), 2.84 (dd, *J* = 10.0 Hz, 12.8 Hz, 1H, CH_2), 4.89 (d, *J* = 16.0 Hz, 1H, CH_2), 5.07 (d, *J* = 16.0 Hz, 1H, CH_2), 5.39 (d, *J* = 10.0 Hz, 1H, =CH_2), 5.73 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.31-6.41 (m, 1H, =CH), 6.46 (d, *J* = 7.6 Hz, 1H, ArH), 6.76 (dd, *J* = 10.0 Hz, 10.0 Hz, 1H, CH), 7.23-7.36 (m, 6H, ArH), 7.99-8.01 (m, 2H, ArH), 8.13-8.14 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.7, 43.4, 76.4, 82.6, 84.5, 109.8, 111.4, 120.5, 121.6, 124.4, 124.6, 127.0, 127.5, 128.7, 130.6, 135.4, 135.8, 136.1, 136.8, 137.0, 137.3, 141.4, 141.6, 160.0, 197.3, 198.0. IR (CH_2Cl_2) ν 2923, 2853, 1712, 1677, 1537, 1464, 1271, 1164, 1124, 917, 786, 756, 699, 673, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{21}IN_3O_3$ ($M+H^+$), requires 574.0622, found: 574.0623.



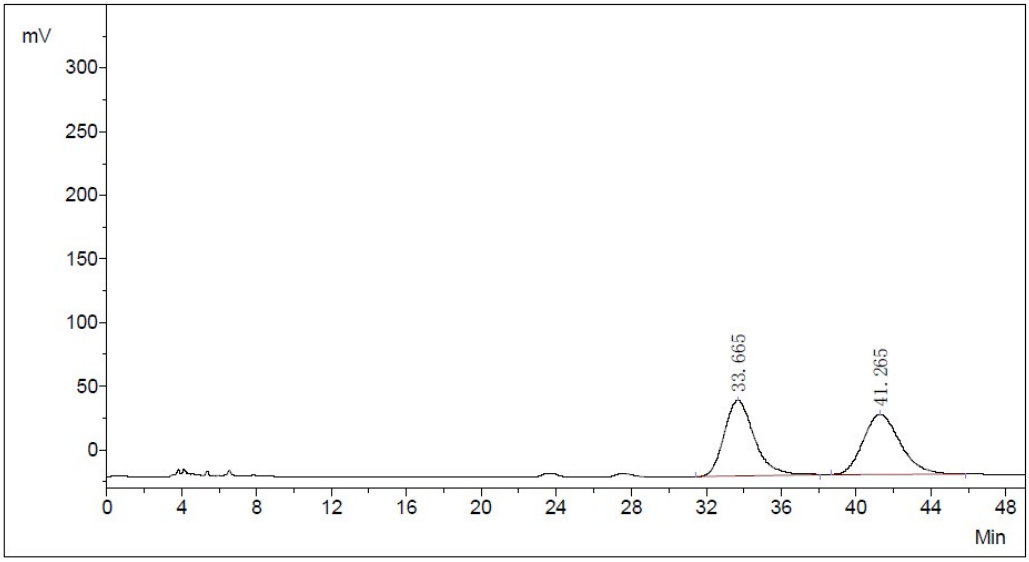
HPLC spectra:

HPLC REPORT

Sample Name: cb-1-83-3-2-racemic Date: ####

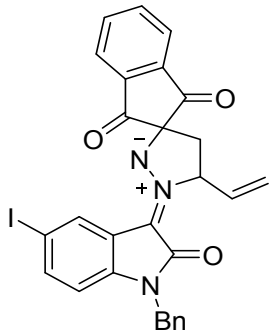
Column: od-h Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	33.665	59067.3	6614751.3	50.5396
2	2	Unknown	41.265	46912.4	6473498.0	49.4604
Total				105979.7	13088249.3	100.0000

NO	R. Time	Peak Area	Percent	Peak Height
1	33.665	6614751	50.54	59067
2	41.265	6473498	49.46	46912



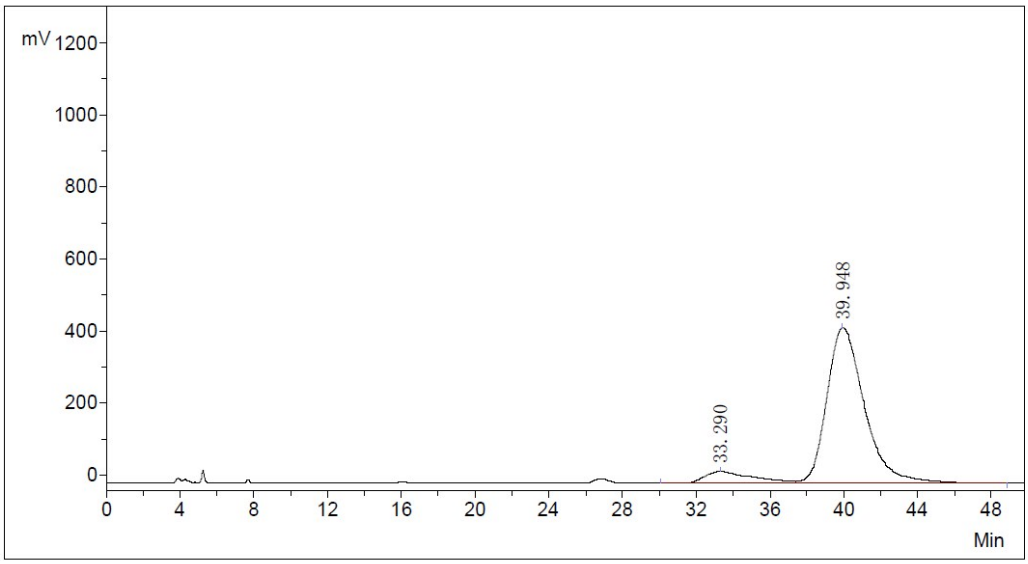
Chiral HPLC report: **3d**

HPLC REPORT

Sample Name: cb-1-83-3-1-chiral Date: ####

Column: ad-h Mobile Phase: hex/ipr = 70/30

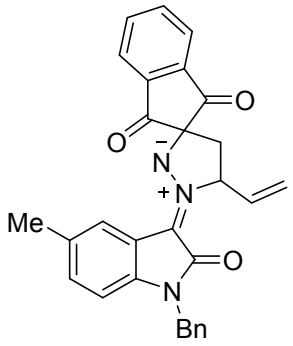
Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	33.290	32914.7	6173280.4	9.1123
2	2	Unknown	39.948	432993.7	61573224.7	90.8877
Total				465908.4	67746505.1	100.0000

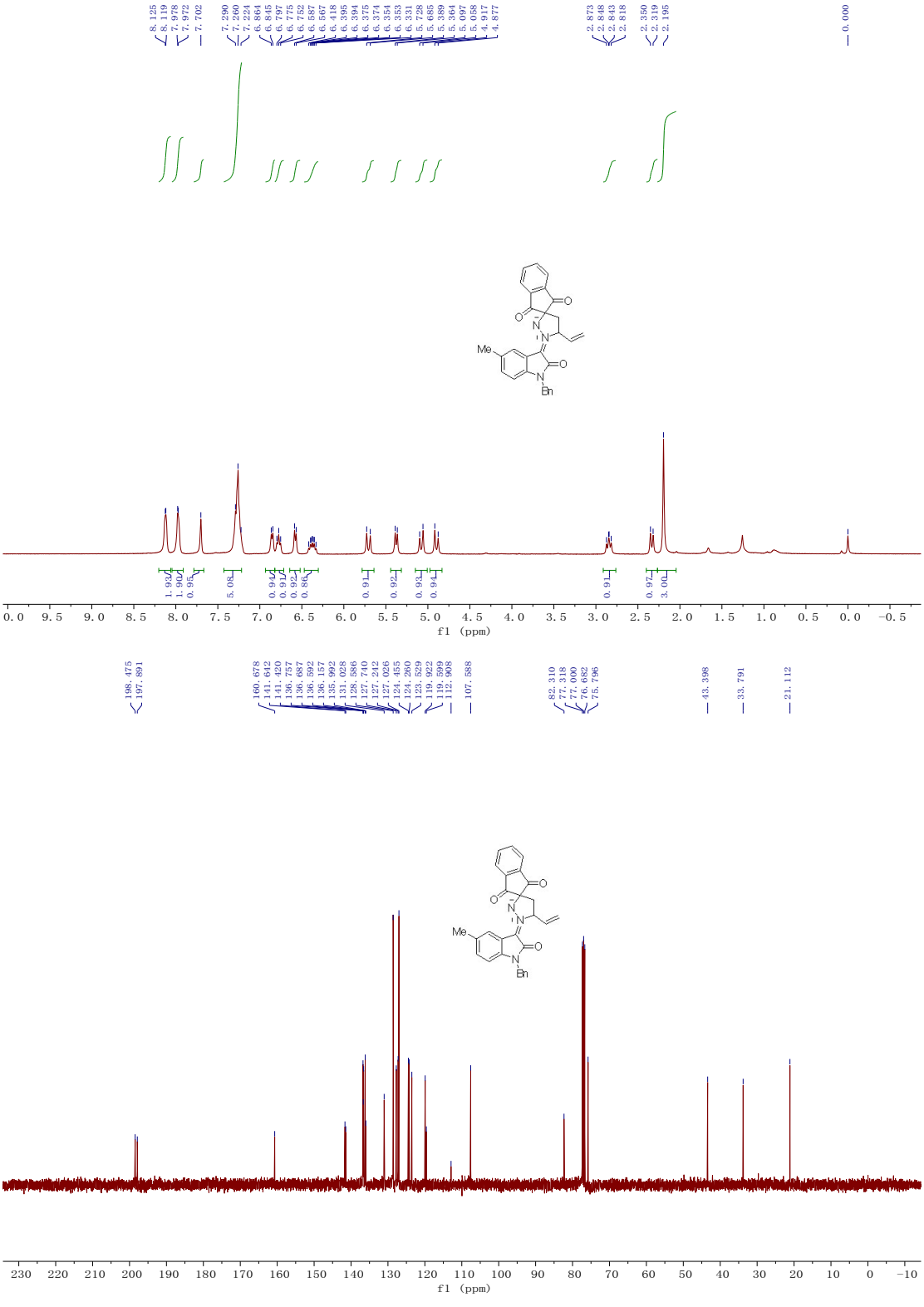
NO	R. Time	Peak Area	Percent	Peak Height
1	33.290	6173280	9.11	32915
2	39.948	61573225	90.89	432994

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak od-h column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 33.290 min, t_{major} = 39.948 min; ee = 82%. $[\alpha]_D^{20}$ = -29.2 (c = 0.380, CH_2Cl_2).



(E)-1'-(1-benzyl-5-methyl-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3e

A red solid, quantitative yield (46 mg), 69% ee. M.p.: 209-211 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.20 (s, 3H, CH_3), 2.33 (d, *J* = 12.4 Hz, 1H, CH_2), 2.84 (dd, *J* = 10.0 Hz, 12.4 Hz, 1H, CH_2), 4.90 (d, *J* = 16.0 Hz, 1H, CH_2), 5.08 (d, *J* = 16.0 Hz, 1H, CH_2), 5.38 (d, *J* = 10.0 Hz, 1H, =CH_2), 5.71 (d, *J* = 17.2 Hz, 1H, =CH_2), 6.33-6.42 (m, 1H, =CH), 6.58 (d, *J* = 8.0 Hz, 1H, ArH), 6.78 (dd, *J* = 10.0 Hz, 10.0 Hz, 1H, CH), 6.85 (d, *J* = 7.6 Hz, 1H, ArH), 7.22-7.29 (m, 5H, ArH), 7.70 (s, 1H, ArH), 7.97-7.98 (m, 2H, ArH), 8.11-8.12 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 33.8, 43.4, 75.8, 82.3, 107.6, 112.9, 119.6, 119.9, 123.5, 124.3, 124.5, 127.0, 127.2, 127.7, 128.6, 131.0, 136.0, 136.1, 136.6, 136.7, 136.8, 141.4, 141.6, 160.7, 197.9, 198.5. IR (CH_2Cl_2) ν 2964, 2923, 1709, 1668, 1538, 1496, 1353, 1266, 1190, 1164, 1124, 926, 801, 729, 715, 698 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{24}N_3O_3$ ($M+H^+$), requires 462.1812, found: 462.1807.



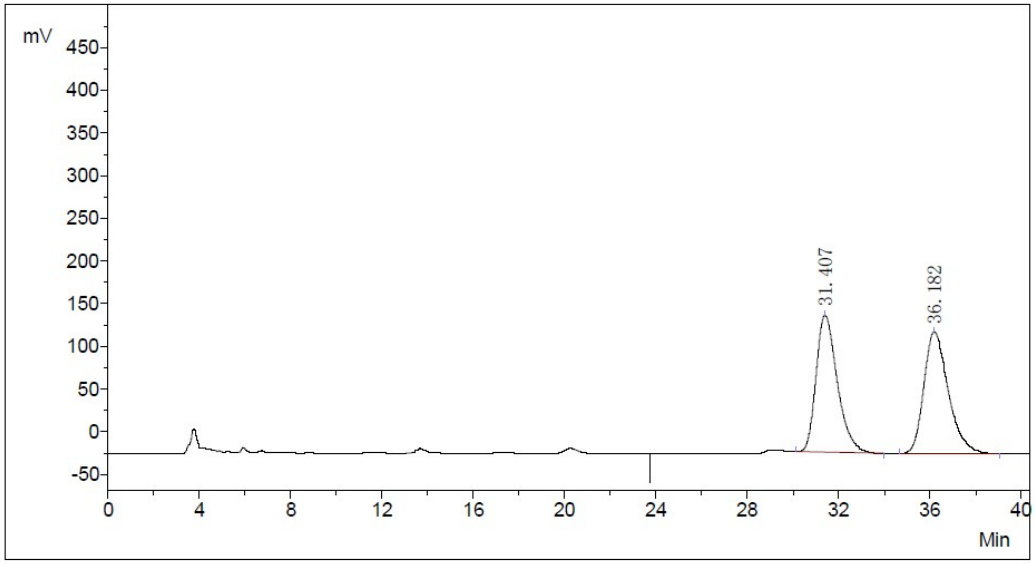
HPLC spectra:

HPLC REPORT

Sample Name: cb-1-83-2-2-racemic Date: ####

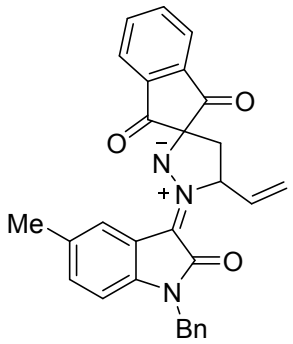
Column: ad-h Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	31.407	160358.3	10343968.6	49.6032
2	2	Unknown	36.182	141918.8	10509467.2	50.3968
Total				302277.1	20853435.8	100.0000

NO	R. Time	Peak Area	Percent	Peak Height
1	31.407	10343969	49.60	160358
2	36.182	10509467	50.40	141919



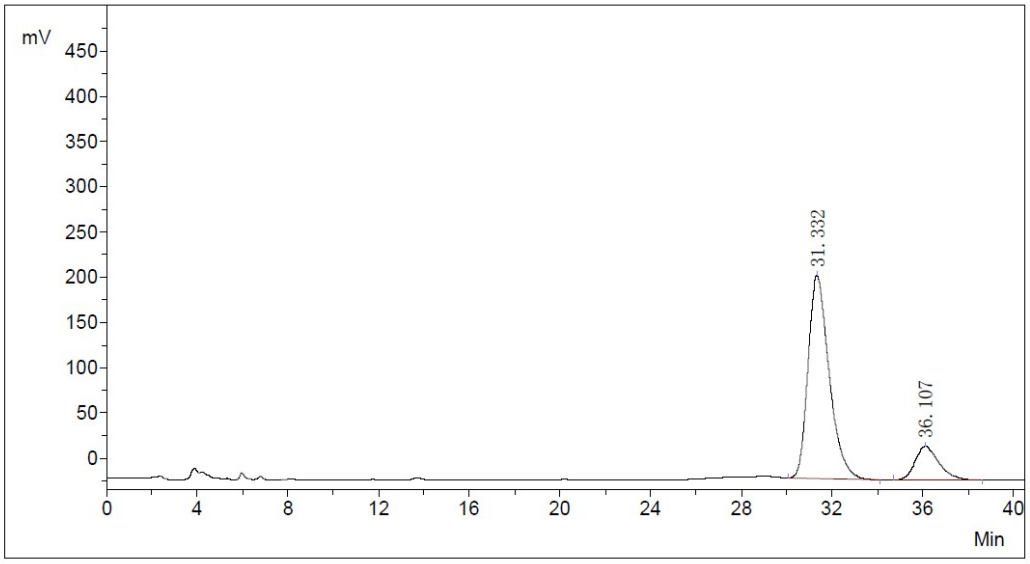
Chiral HPLC report: **3e**

HPLC REPORT

Sample Name: cb-1-83-2-1-chiral Date: ####

Column: ad-h Mobile Phase: hex/ipr = 70/30

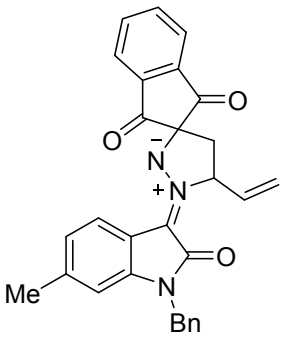
Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	31.332	223715.7	14489565.5	84.4093
2	2	Unknown	36.107	36553.3	2676268.8	15.5907
Total				260269.0	17165834.3	100.0000

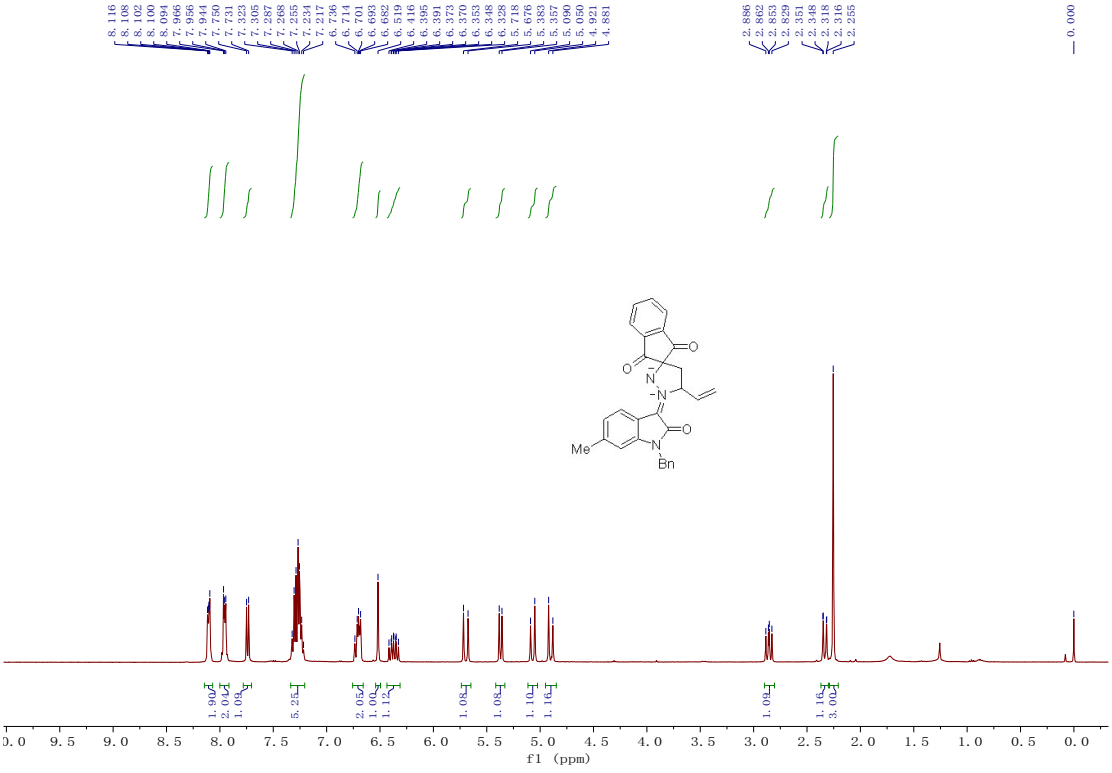
NO	R. Time	Peak Area	Percent	Peak Height
1	31.332	14489566	84.41	223716
2	36.197	2676269	15.59	36553

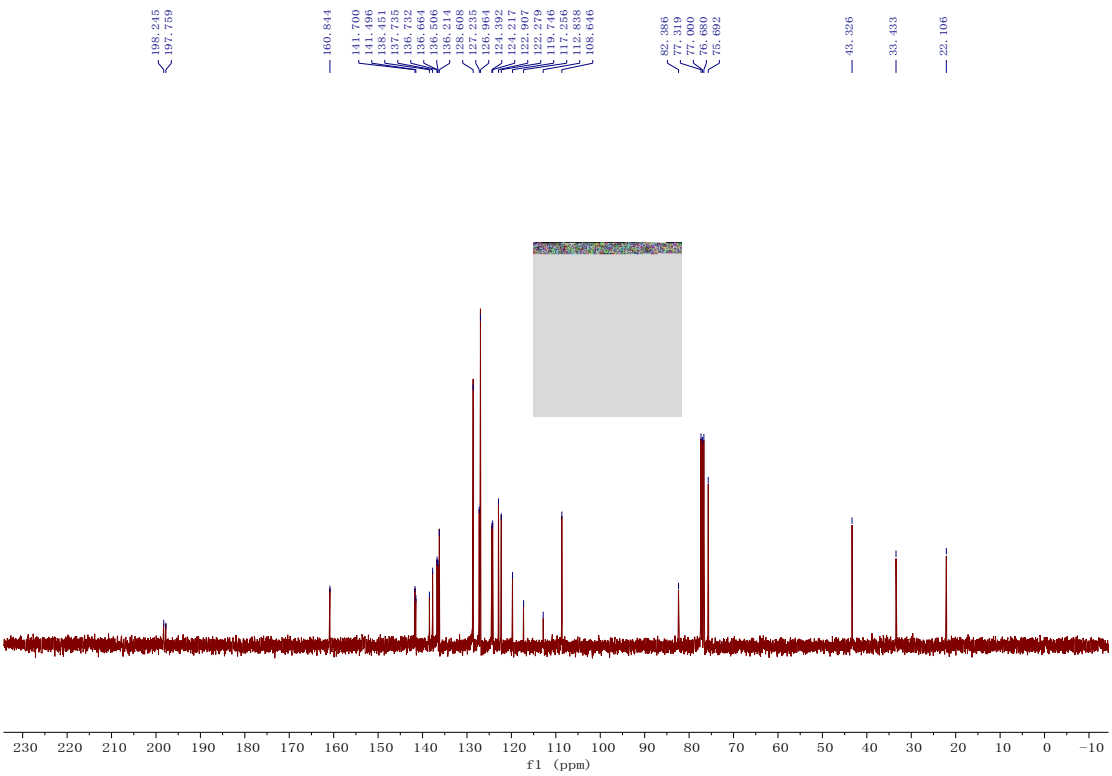
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak ad-h column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 36.197 min, t_{major} = 31.332 min; ee = 69%. $[\alpha]_D^{20}$ = -59.5 (c = 0.340, CH_2Cl_2).



(E)-1'-(1-benzyl-6-methyl-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3f

A red solid, 78% yield (36 mg), 59% ee. M.p.: 202-205 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.26 (s, 3H, CH_3), 2.33 (dd, J = 0.8 Hz, J = 13.2 Hz, 1H, CH_2), 2.86 (dd, J = 9.6 Hz, 13.2 Hz, 1H, CH_2), 4.90 (d, J = 16.0 Hz, 1H, CH_2), 5.07 (d, J = 16.0 Hz, 1H, CH_2), 5.37 (d, J = 10.4 Hz, 1H, =CH_2), 5.70 (d, J = 16.8 Hz, 1H, =CH_2), 6.37 (ddd, J = 8.0 Hz, 10.4 Hz, 16.8 Hz, 1H, =CH), 6.52 (s, 1H, ArH), 6.68-6.74 (m, 2H, CH, ArH), 7.21-7.32 (m, 5H, ArH), 7.74 (d, J = 7.6 Hz, 1H, ArH), 7.94-7.97 (m, 2H, ArH), 8.09-8.12 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 22.1, 33.4, 43.3, 75.7, 82.4, 108.6, 112.8, 117.3, 119.7, 122.3, 122.9, 124.2, 124.4, 127.0, 127.2, 128.6, 136.2, 136.5, 136.66, 136.73, 137.7, 138.5, 141.5, 141.7, 160.8, 197.8, 198.2. IR (CH_2Cl_2) ν 3085, 2923, 1709, 1670, 1586, 1541, 1454, 1381, 1329, 1268, 1215, 1158, 1141, 811, 756, 717, 699 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{24}N_3O_3$ ($M+H^+$), requires 462.1812, found: 462.1815.

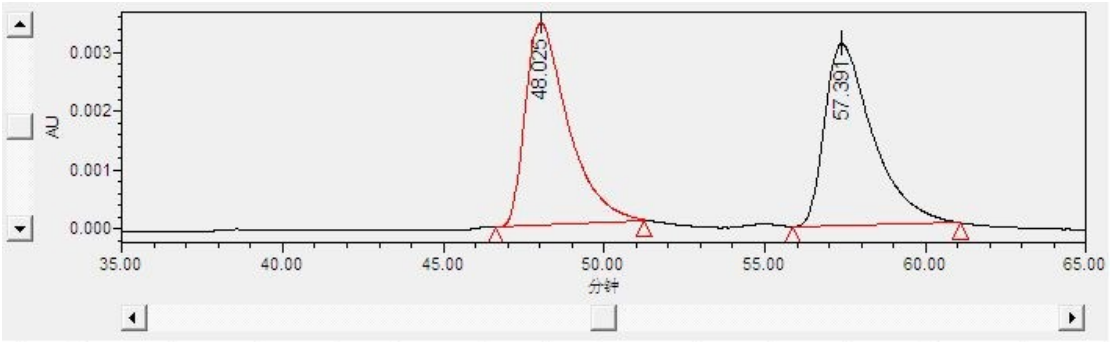




HPLC spectra:

HPLC REPORT

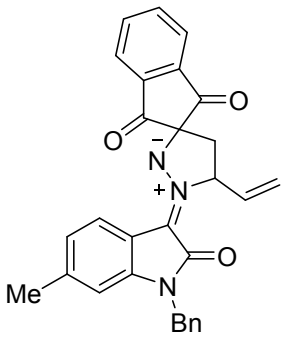
Sample Name: cb-1-91-a-racemic Date: ####
Column: IB-3 Mobile Phase: hex/ipr = 95/5
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		48.025	318997	49.79	3442	BB			未知				46.633	51.267
2		57.391	321749	50.21	3091	BB			未知				55.867	61.100

NO	R. Time	Peak Area	Percent	Peak Height
1	48.025	318997	49.79	3442

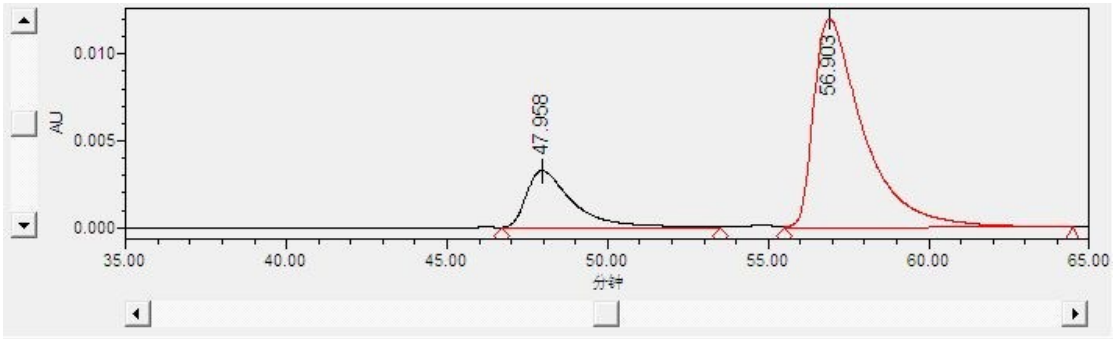
2	57.391	321749	50.21	3091



Chiral HPLC report: **3f**

HPLC REPORT

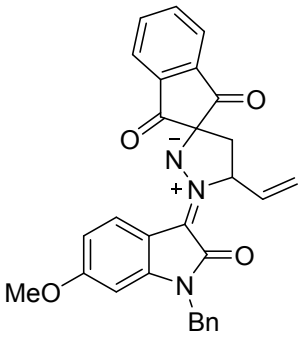
Sample Name: cb-1-91-a-chiral Date: ####
Column: IB-3 Mobile Phase: hex/ipr = 95/5
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		47.958	338374	20.74	3308	VV			未知				46.683	53.500
2		56.903	1292882	79.26	12004	VB			未知				55.483	64.467

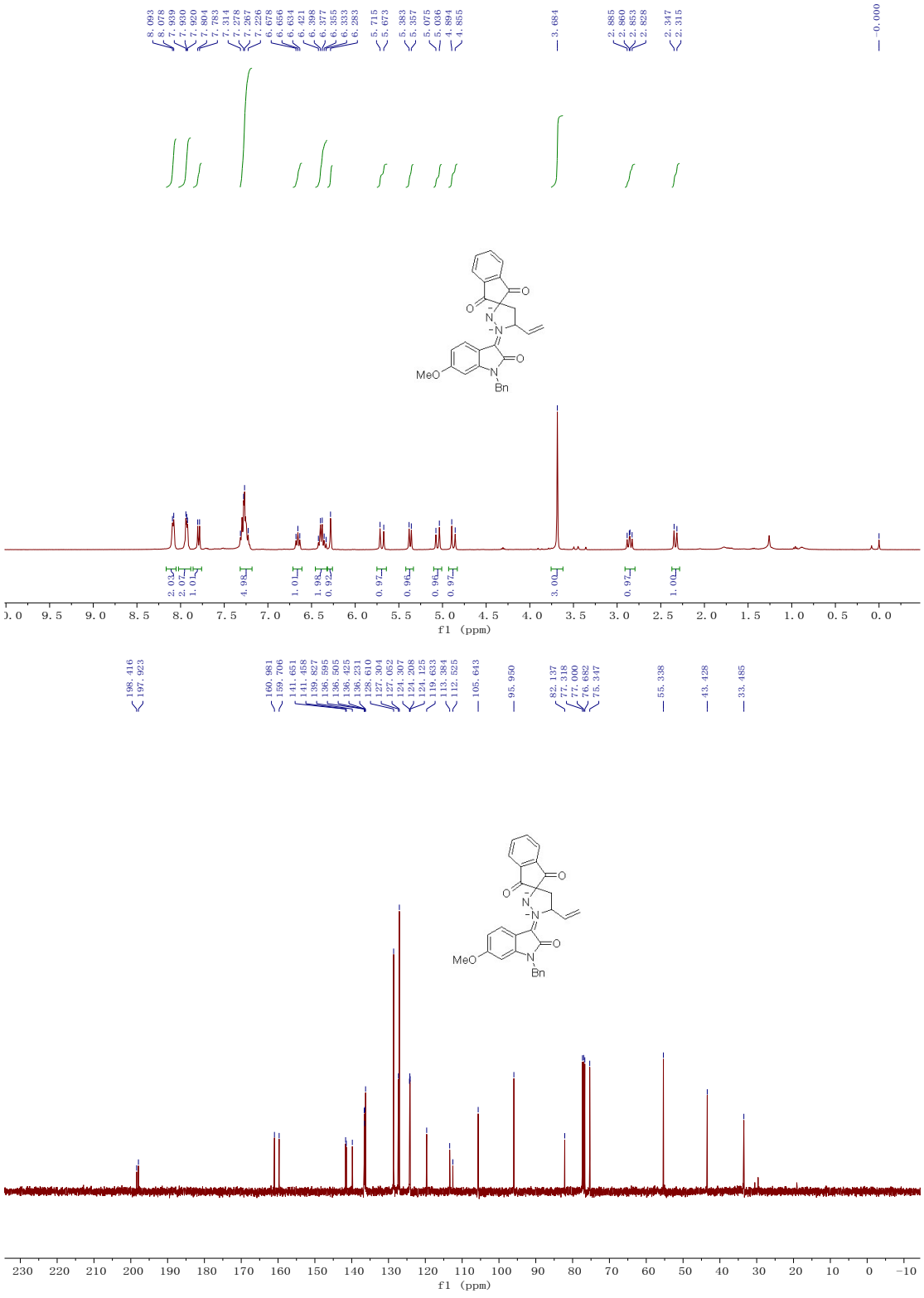
NO	R. Time	Peak Area	Percent	Peak Height
1	47.958	338374	20.74	3308
2	56.903	1292882	79.26	12004

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 47.958 min, t_{major} = 56.903 min; ee = 59%. $[\alpha]_D^{20}$ = -91.3 (c = 0.227, CH_2Cl_2).



(E)-1'-(1-benzyl-6-methoxy-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3g

A red solid, 96% yield (46 mg), 78% ee. M.p.: 191-193 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (d, *J* = 12.8 Hz, 1H, CH_2), 2.86 (dd, *J* = 10.0 Hz, 12.8 Hz, 1H, CH_2), 3.68 (s, 3H, CH_3), 4.87 (d, *J* = 15.6 Hz, 1H, CH_2), 5.06 (d, *J* = 15.6 Hz, 1H, CH_2), 5.37 (d, *J* = 10.4 Hz, 1H, =CH_2), 5.69 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.28 (s, 1H, ArH), 6.33-6.42 (m, 2H, CH, =CH), 6.66 (dd, *J* = 8.8 Hz, 8.8 Hz, 1H, ArH), 7.22-7.32 (m, 5H, ArH), 7.79 (d, *J* = 8.4 Hz, 1H, ArH), 7.92-7.94 (m, 2H, ArH), 8.07-8.09 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.5, 43.4, 55.3, 75.3, 82.1, 96.0, 105.6, 112.5, 113.4, 119.6, 124.1, 124.2, 124.3, 127.1, 127.3, 128.6, 136.2, 136.4, 136.5, 136.6, 139.8, 141.5, 141.7, 159.7, 161.0, 197.9, 198.4. IR (CH_2Cl_2) ν 2960, 2923, 1709, 1674, 1617, 1383, 1265, 1185, 1158, 1027, 963, 797, 735, 699, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{24}N_3O_4$ ($M+H^+$), requires 478.1761, found: 478.1763.



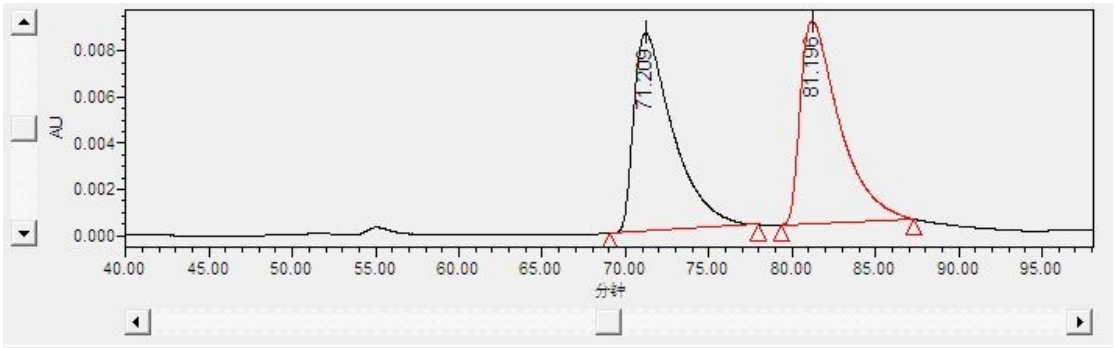
HPLC spectra:

HPLC REPORT

Sample Name: cb-1-91-b-racemic Date: ####

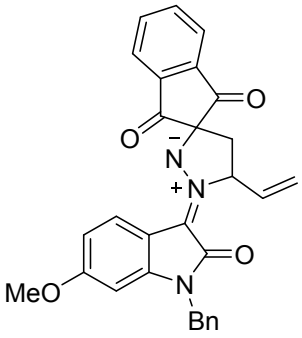
Column: IB-3 Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		71.209	1413002	49.59	8591	bb			未知				69.067	77.967
2		81.196	1436355	50.41	8790	bb			未知				79.367	87.317

NO	R. Time	Peak Area	Percent	Peak Height
1	71.209	1413002	49.59	8591
2	81.196	1436355	50.41	8790

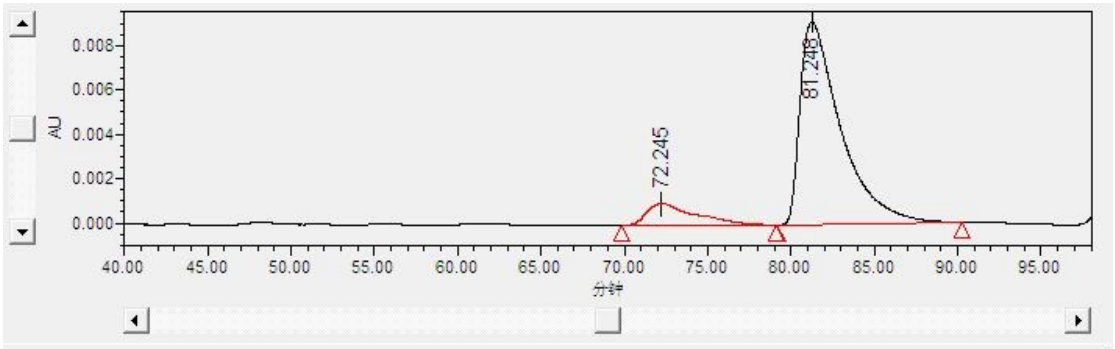


Chiral HPLC report: **3g**

HPLC REPORT

Sample Name: cb-1-91-b-chiral
Column: IB-3
Velocity (mL/min): 0.7

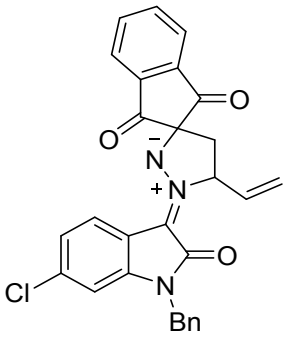
Date: ####
Mobile Phase: hex/ipr = 95/5
Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		72.245	201063	11.53	984	BB			未知				69.883	79.150
2		81.248	1543314	88.47	9135	BB			未知				79.167	90.317

NO	R. Time	Peak Area	Percent	Peak Height
1	72.245	201063	11.53	984
2	81.248	1543314	88.47	9135

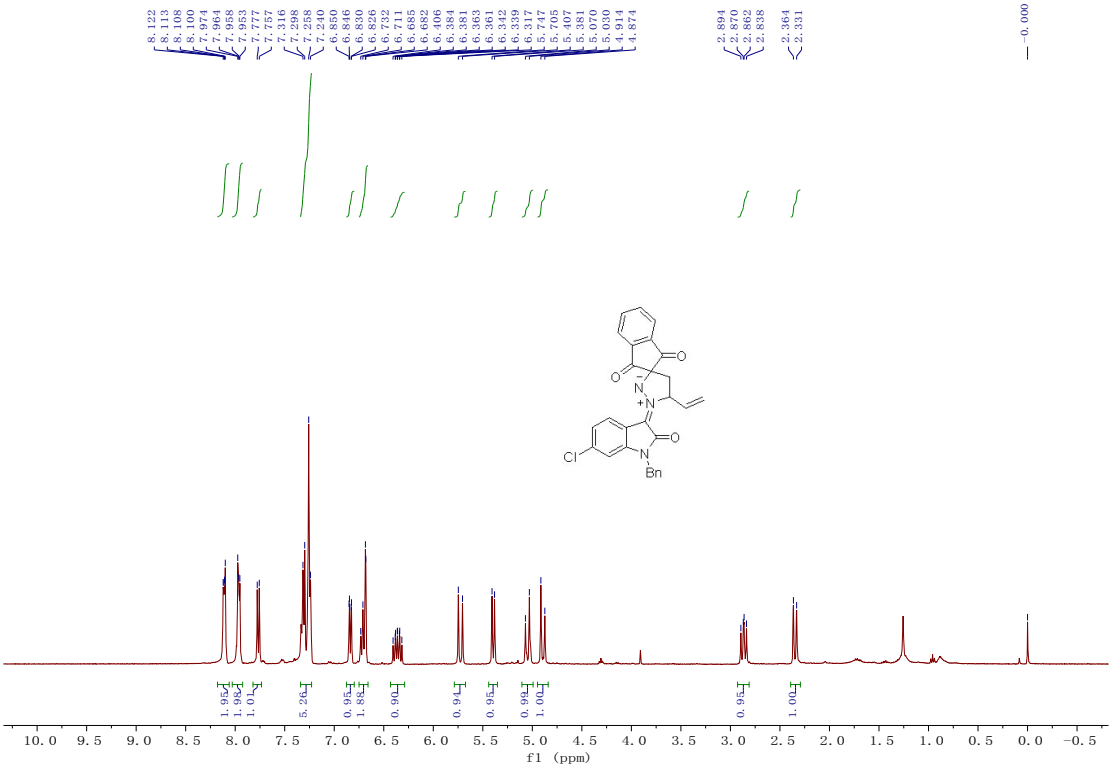
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 72.245 min, t_{major} = 81.248 min; ee = 78%. $[\alpha]_D^{20}$ = -90.3 (c = 0.325, CH_2Cl_2).

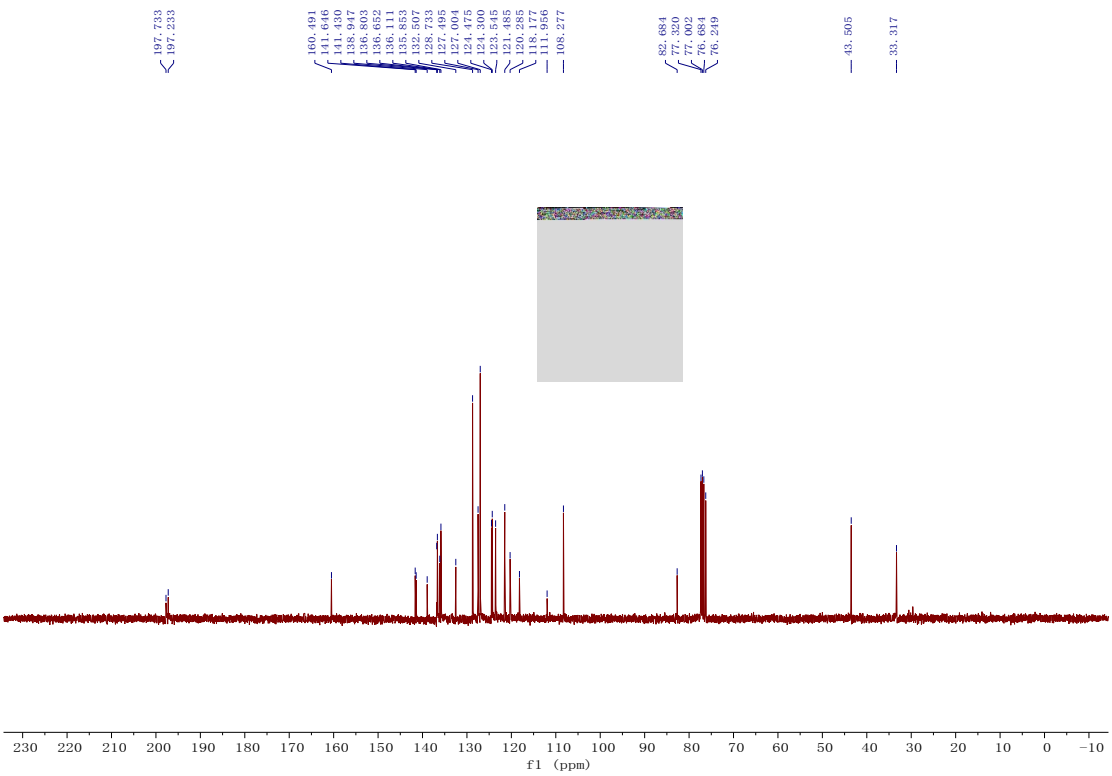


(E)-1'-(1-benzyl-6-chloro-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3h

A red solid, 96% yield (46 mg), 65% ee. M.p.: 139-140 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.35 (d, *J* = 13.2 Hz, 1H, CH_2), 2.87 (dd, *J* = 9.6 Hz, 13.2 Hz, 1H, CH_2), 4.89 (d, *J* = 16.0 Hz, 1H, CH_2), 5.05 (d, *J* = 16.0 Hz, 1H, CH_2), 5.39 (d, *J* = 10.4 Hz, 1H, =CH_2), 5.73 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.36 (ddd, *J* = 8.8 Hz, 10.4 Hz, 16.8 Hz, 1H, =CH), 6.68-6.74 (m, 2H, CH, ArH), 6.84 (dd, *J* = 1.6 Hz, 8.0 Hz, 1H, ArH), 7.24-7.32 (m, 5H, ArH), 7.77 (d, *J* = 8.0 Hz, 1H, ArH), 7.95-7.98

(m, 2H, ArH), 8.10-8.13 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.3, 43.5, 76.2, 82.7, 108.3, 112.0, 118.2, 120.3, 121.5, 123.5, 124.3, 124.5, 127.0, 127.5, 128.7, 132.5, 135.9, 136.1, 136.7, 136.8, 138.9, 141.4, 141.6, 160.5, 197.2, 197.7. IR (CH_2Cl_2) ν 2923, 2853, 1712, 1677, 1496, 1470, 1376, 1326, 1270, 1184, 1163, 1121, 963, 724, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{21}ClN_3O_3$ ($M+H^+$), requires 482.1266, found: 482.1268.

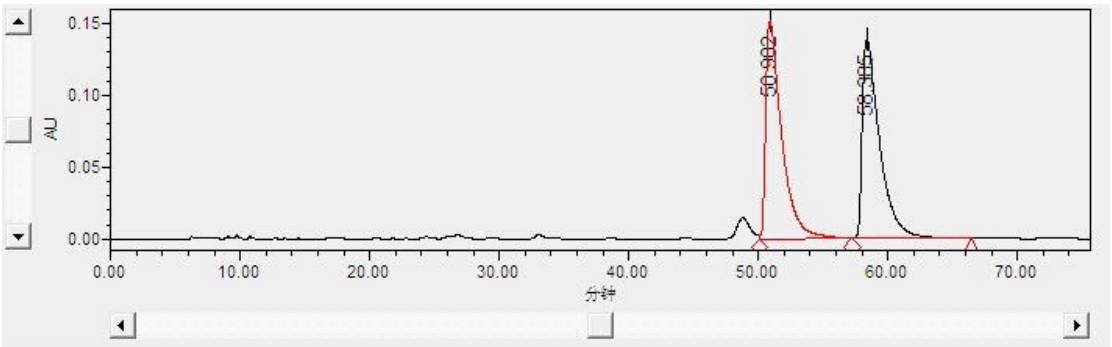




HPLC spectra:

HPLC REPORT

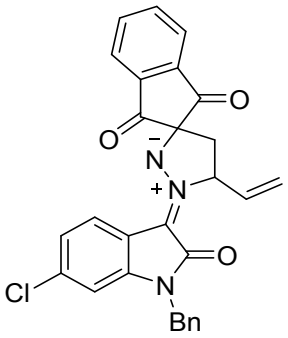
Sample Name: cb-1-91-c-racemic Date: ####
Column: IB-3 Mobile Phase: hex/ipr = 95/5
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		50.902	13110720	50.31	151976	VV			未知				50.067	57.267
2		58.385	12949911	49.69	138389	VB			未知				57.267	66.517

NO	R. Time	Peak Area	Percent	Peak Height
1	50.902	13110720	50.31	151976

2	58.385	12949911	49.69	138389



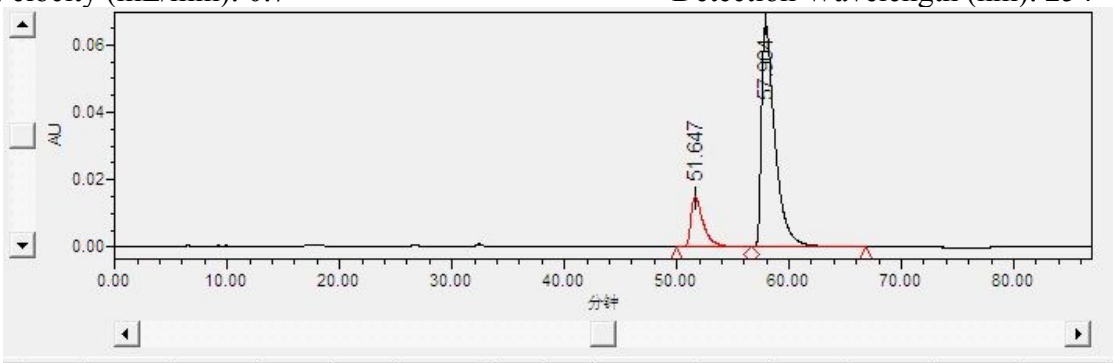
Chiral HPLC report: **3h**

HPLC REPORT

Sample Name: cb-1-91-c-chiral Date: ####

Column: IB-3 Mobile Phase: hex/ipr = 95/5

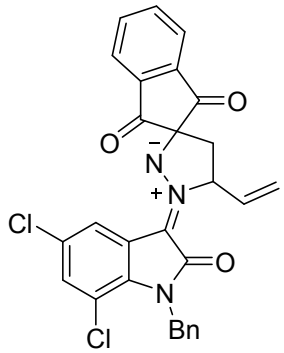
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		51.647	1165357	17.27	14963	BV			未知				49.950	56.667
2		57.904	5581849	82.73	66396	VB			未知				56.667	66.850

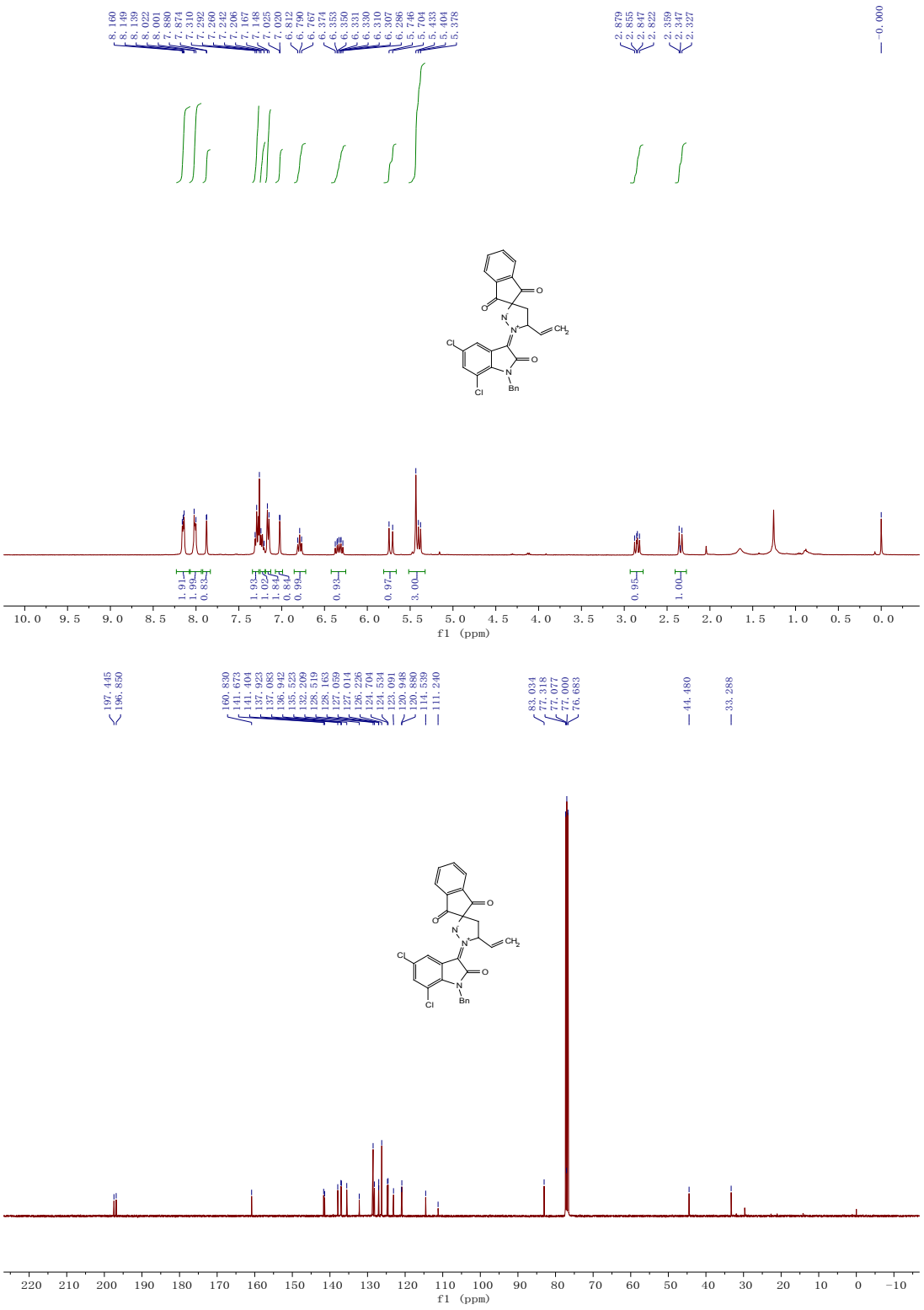
NO	R. Time	Peak Area	Percent	Peak Height
1	51.647	1165357	17.27	14963
2	57.904	5581849	82.73	66396

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 51.647 min, t_{major} = 57.904 min; ee = 65%. $[\alpha]_D^{20}$ = -83.8 (c = 0.85, CH_2Cl_2).



(E)-1'-(1-benzyl-5,7-dichloro-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3i

A red solid, 39% yield (20 mg), 75% ee. M.p.: 132-135 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (d, *J* = 12.8 Hz, 1H, CH_2), 2.85 (dd, *J* = 9.6 Hz, 12.8 Hz, 1H, CH_2), 5.37-5.44 (m, 3H, CH_2, CH_2, =CH), 5.73 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.33 (ddd, *J* = 8.4 Hz, 9.6 Hz, 18.0 Hz, 1H, =CH), 6.79 (dd, *J* = 9.6 Hz, 9.6 Hz, 1H, CH), 7.02 (d, *J* = 1.0 Hz, 1H, ArH), 7.16 (d, *J* = 7.6 Hz, 2H, ArH), 7.20-7.24 (m, 1H, ArH), 7.26-7.31 (m, 2H, ArH), 7.88 (d, *J* = 2.4 Hz, 1H, ArH), 8.00-8.03 (m, 2H, ArH), 8.13-8.16 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.3, 44.5, 77.1, 83.0, 111.2, 114.5, 120.88, 120.95, 123.1, 124.5, 124.7, 126.2, 127.0, 127.1, 128.2, 128.5, 132.2, 135.5, 136.9, 137.1, 137.9, 141.4, 141.7, 160.8, 196.9, 197.4. IR (CH_2Cl_2) ν 3065, 2925, 2854, 1711, 1674, 1532, 1449, 1316, 1217, 1179, 1126, 977, 855, 726, 664 cm^{-1}. Ms (MALDI) m/z: 516.1 (M+H^{+}, 100); HRMS (MALDI) Calcd. for $C_{28}H_{20}Cl_2N_3O_3$ (M+H^{+}), requires 516.0876, found: 516.0866.



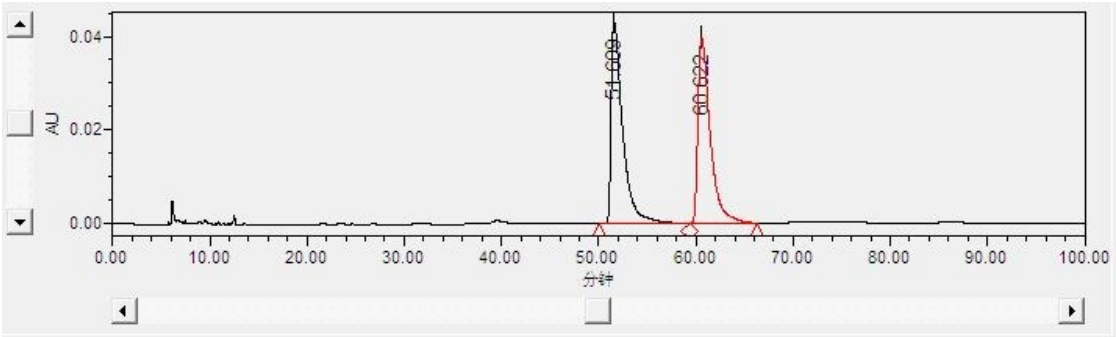
HPLC spectra:

HPLC REPORT

Sample Name: cb-1-95-a-racemic Date: ####

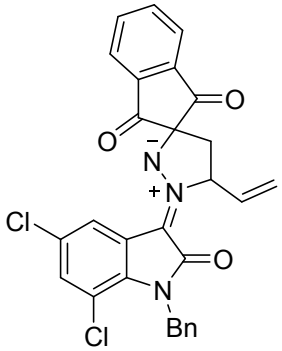
Column: IB-3 Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		51.609	3549655	50.49	43074	bV			未知				50.083	59.350
2		60.622	3480497	49.51	39675	Vb			未知				59.350	66.317

NO	R. Time	Peak Area	Percent	Peak Height
1	51.609	3549655	50.49	43074
2	60.622	3480497	49.51	39675

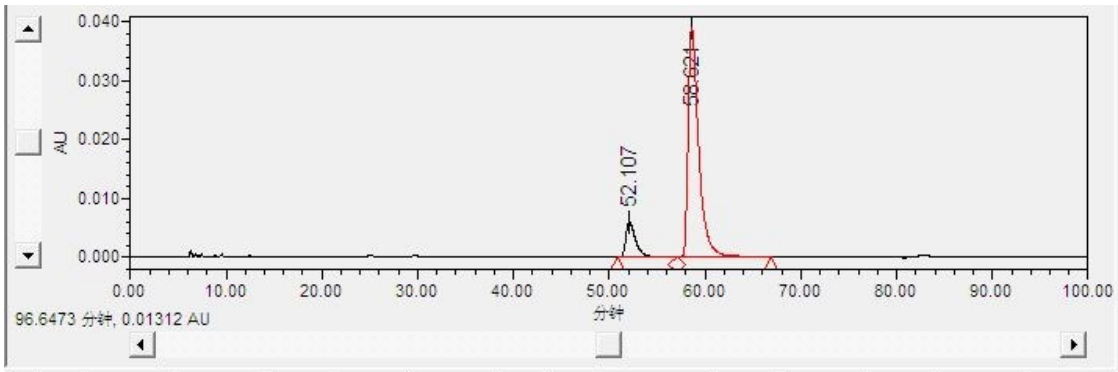


Chiral HPLC report: **3i**

HPLC REPORT

Sample Name: cb-1-95-a-chiral
Column: IB-3
Velocity (mL/min): 0.7

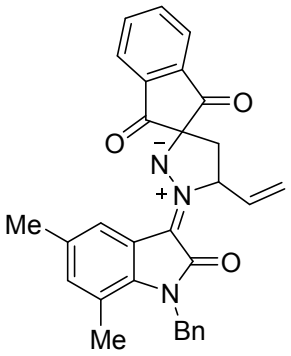
Date: ####
Mobile Phase: hex/ipr = 95/5
Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		52.107	430986	12.56	6030	BV			未知				50.850	57.050
2		58.621	2999580	87.44	38857	VB			未知				57.050	66.900

NO	R. Time	Peak Area	Percent	Peak Height
1	52.107	430986	12.56	6030
2	58.621	2999580	87.44	38857

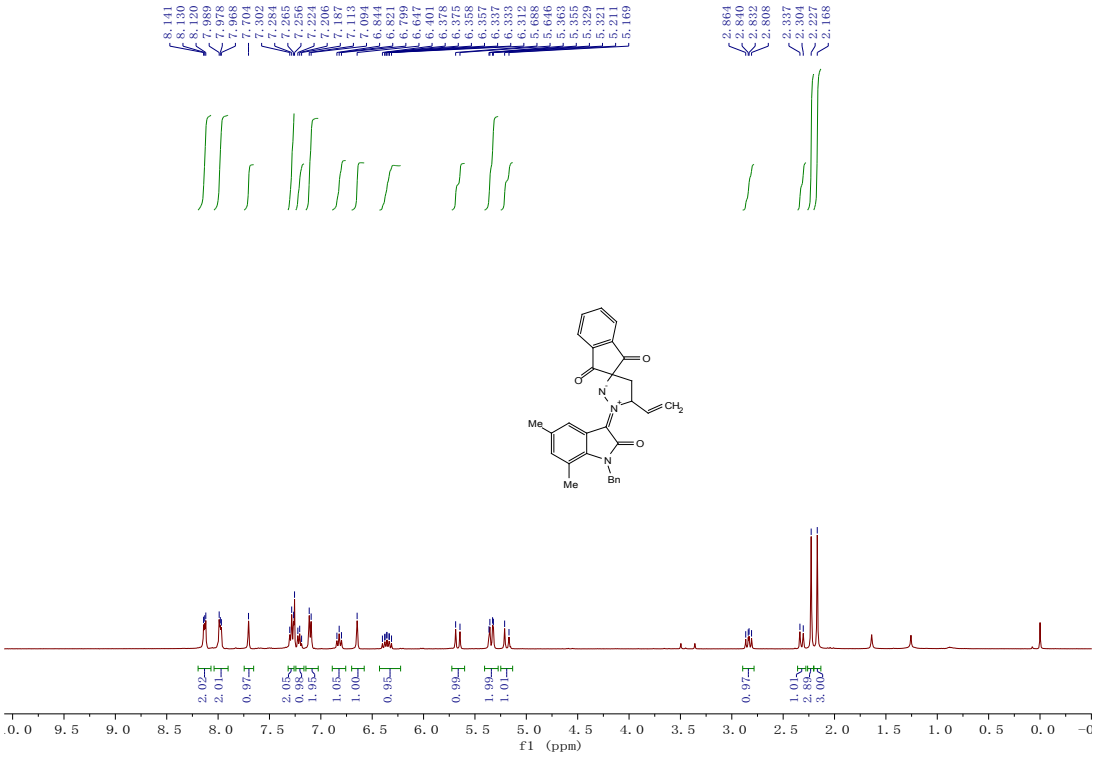
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 52.107 min, t_{major} = 58.621 min; ee = 75%. $[\alpha]_D^{20}$ = -101.4 (c = 0.40, CH_2Cl_2).

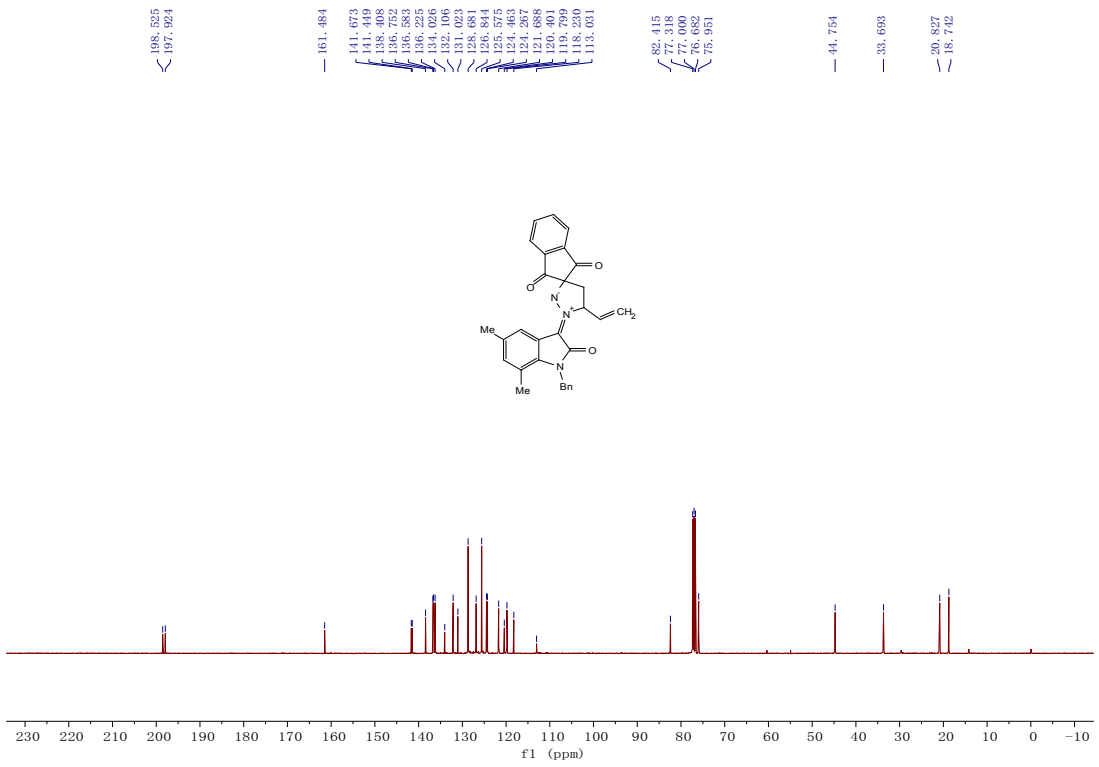


(E)-1'-(1-benzyl-5,7-dimethyl-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3j

A red solid, 80% yield (38 mg), 48% ee. M.p.: 191-193 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.17 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.32 (d, *J* = 13.2 Hz, 1H, CH_2), 2.84 (dd, *J* = 9.6 Hz, 12.8 Hz, 1H, CH_2), 5.19 (d, *J* = 16.8 Hz, 1H, CH_2), 5.32-5.37 (m, 2H, CH_2, =CH_2), 5.67 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.36 (ddd, *J* = 8.4 Hz, 9.6 Hz, 18.0 Hz, 1H, =CH), 6.65 (s, 1H, ArH), 6.82 (dd, *J* = 9.6 Hz,

9.6 Hz, 1H, CH), 7.10 (d, J = 7.6 Hz, 1H, ArH), 7.18-7.23 (m, 1H, ArH), 7.26-7.31 (m, 2H, ArH), 7.70 (s, 1H, ArH), 7.96-7.99 (m, 2H, ArH), 8.12-8.14 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.7, 20.8, 33.7, 44.8, 76.0, 82.4, 113.0, 118.2, 119.8, 120.4, 121.7, 124.3, 124.5, 125.6, 126.8, 128.7, 131.0, 132.1, 134.0, 136.2, 136.6, 136.8, 138.4, 141.4, 141.7, 161.5, 197.9, 198.5. IR (CH_2Cl_2) ν 2922, 2852, 1711, 1668, 1541, 1439, 1329, 1262, 1218, 1159, 980, 796, 732, 696 cm^{-1}. HRMS (ESI) Calcd. for $C_{30}H_{26}N_3O_3$ ($M+H^+$), requires 476.1969, found: 476.1970.





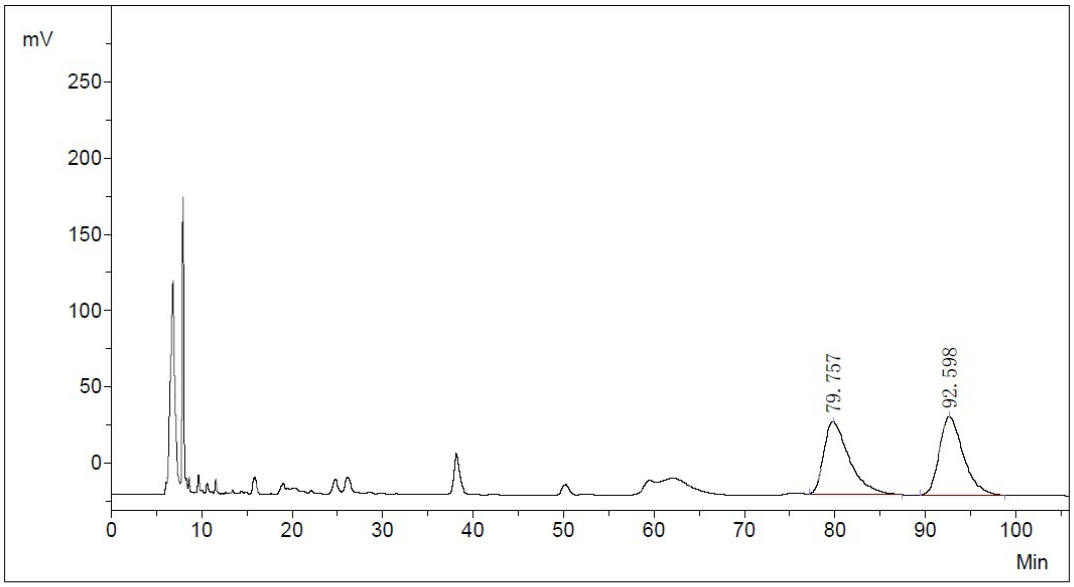
HPLC spectra:

HPLC REPORT

Sample Name: cb-1-95-b-racemic Date: ####

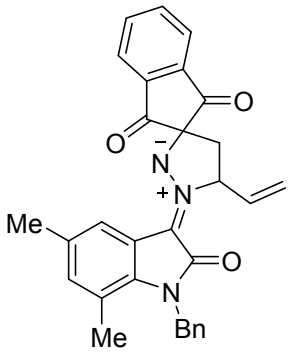
Column: id Mobile Phase: hex/ipr = 70/30

Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	79.757	47331.6	9208701.5	49.4914
2	2	Unknown	92.598	51265.0	9397980.6	50.5086
Total				98596.6	18606682.1	100.0000

NO	R. Time	Peak Area	Percent	Peak Height
1	79.757	9208702	49.49	47332
2	92.598	9397981	50.51	51265

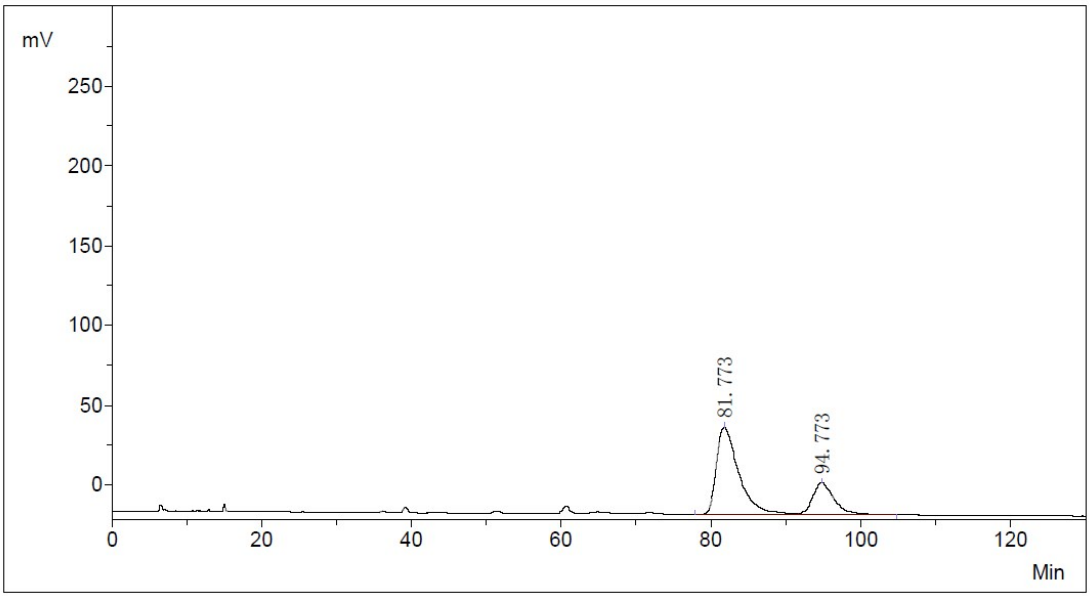


Chiral HPLC report: **3j**

HPLC REPORT

Sample Name: cb-1-95-b-chiral Date: ####
Column: id Mobile Phase: hex/ipr = 70/30

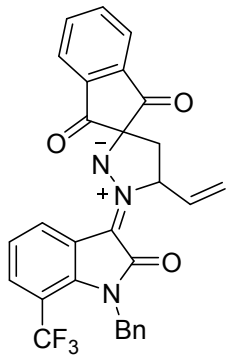
Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	81.773	55066.0	11349098.8	74.2182
2	2	Unknown	94.773	19805.0	3942436.6	25.7818
Total				74871.0	15291535.4	100.0000

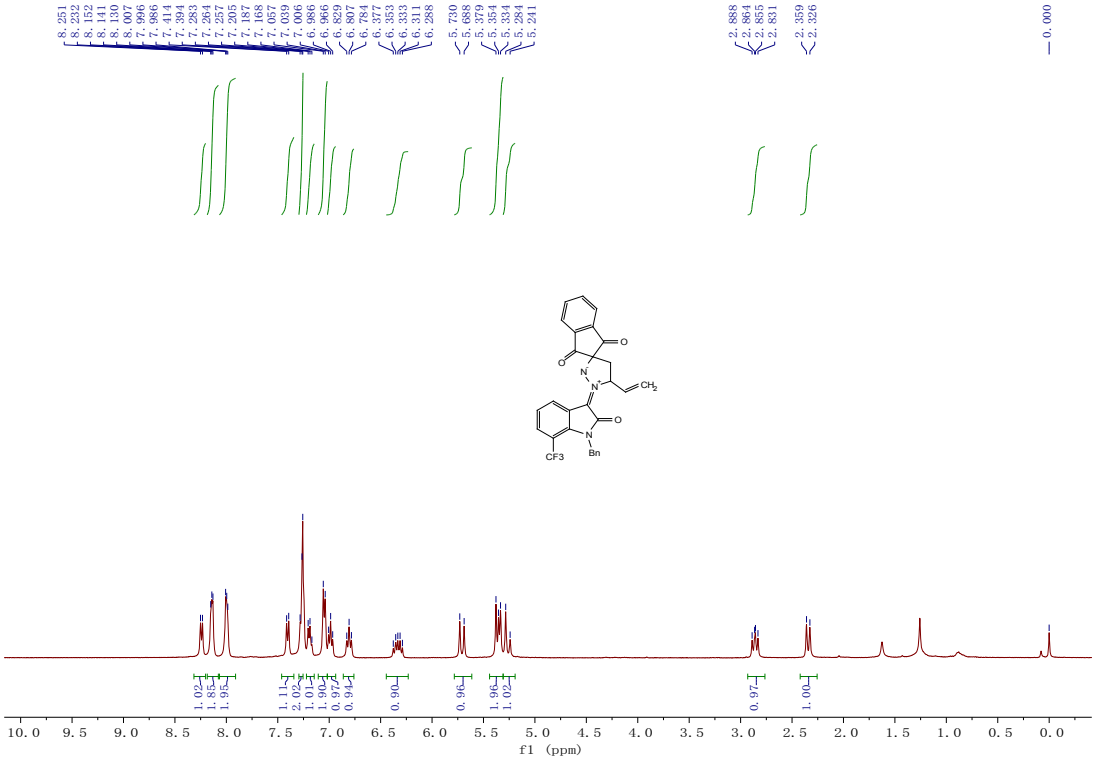
NO	R. Time	Peak Area	Percent	Peak Height
1	81.773	11349099	74.22	55066
2	94.773	19805	25.78	19805

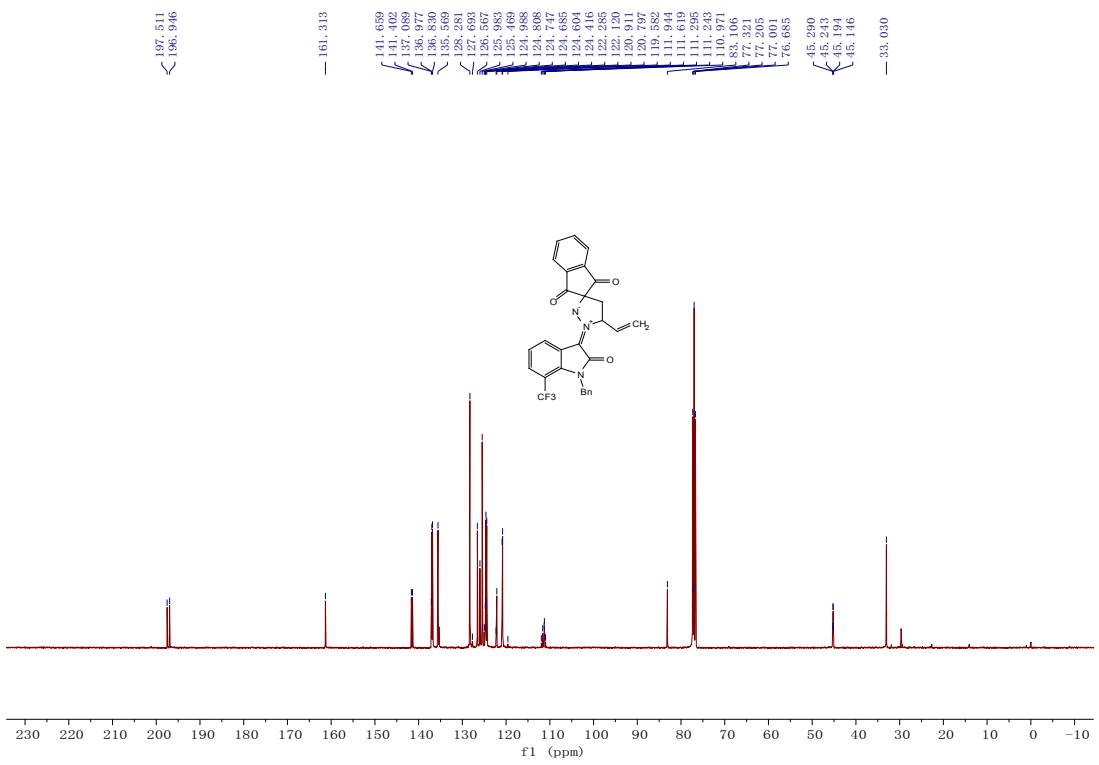
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak id column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{minor} = 94.773 min, t_{major} = 81.773 min; ee = 48%. $[\alpha]_D^{20}$ = -45.0 (c = 0.55, CH_2Cl_2).

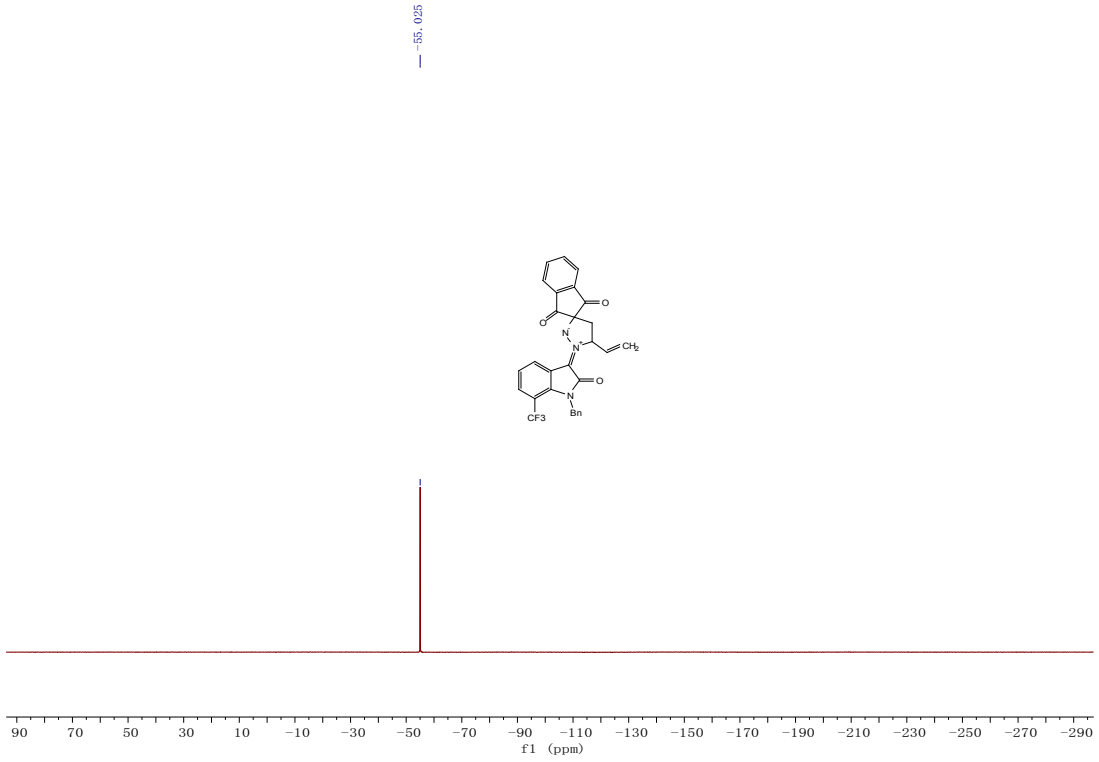


(E)-1'-(1-benzyl-2-oxo-7-(trifluoromethyl)indolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3k

A red solid, 52% yield (27 mg), 68% ee. M.p.: 126-128 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (d, *J* = 13.2 Hz, 1H, CH_2), 2.86 (dd, *J* = 9.6 Hz, 13.2 Hz, 1H, CH_2), 5.26 (d, *J* = 17.2 Hz, 1H, CH_2), 5.33-5.38 (m, 2H, CH_2, =CH_2), 5.71 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.28-6.38 (m, 1H, =CH), 6.81 (dd, *J* = 9.6 Hz, 9.6 Hz, 1H, CH), 6.99 (dd, *J* = 8.0 Hz, 8.0 Hz, 1H, ArH), 7.05 (d, *J* = 7.2 Hz, 2H, ArH), 7.16-7.21 (m, 1H, ArH), 7.25-7.29 (m, 2H, ArH), 7.40 (d, *J* = 8.0 Hz, 1H, ArH), 7.98-8.01 (m, 2H, ArH), 8.13-8.16 (m, 2H, ArH), 8.24 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.0, 45.2 (q, *J* = 4.8 Hz), 77.2, 83.1, 111.2, 111.5 (q, *J* = 32.4 Hz), 120.8, 120.9, 122.1, 122.3, 123.6, (q, *J* = 270.3 Hz), 124.4, 124.6, 124.7 (q, *J* = 6.1 Hz), 125.5, 126.0, 126.6, 128.3, 135.4, 135.6, 136.8, 137.0, 137.1, 141.4, 141.7, 161.3, 196.9, 197.5. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -55.0. IR (CH_2Cl_2) ν 3028, 2964, 2925, 1711, 1679, 1537, 1448, 1426, 1326, 1261, 1116, 1091, 1018, 795, 739, 718 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{21}F_3N_3O_3$ ($M+H^+$), requires 516.1530, found: 516.1526.







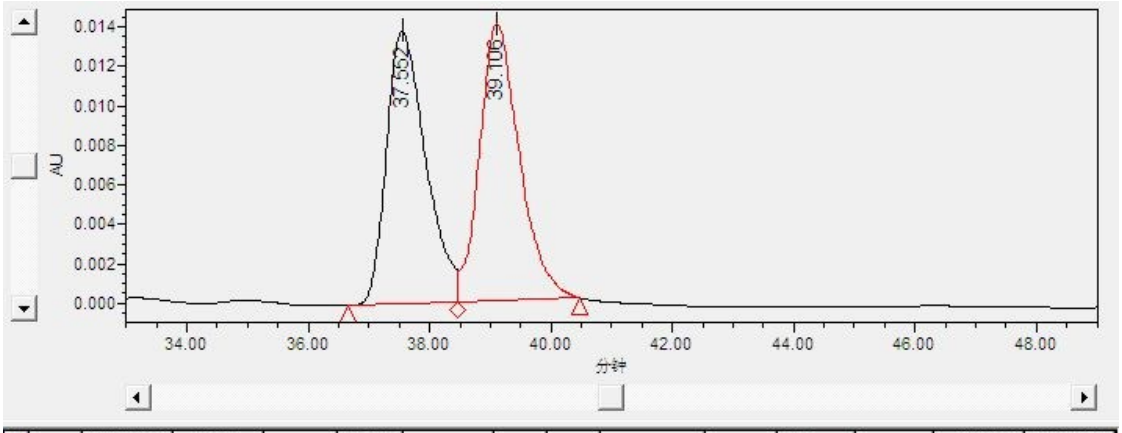
HPLC spectra:

HPLC REPORT

Sample Name: cb-1-95-c-racemic Date: ####

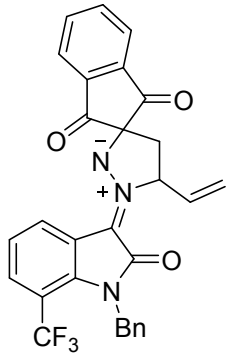
Column: IB-3 Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		37.552	621602	49.15	13840	BV			未知				36.667	38.467
2		39.106	643152	50.85	14039	Vb			未知				38.467	40.483

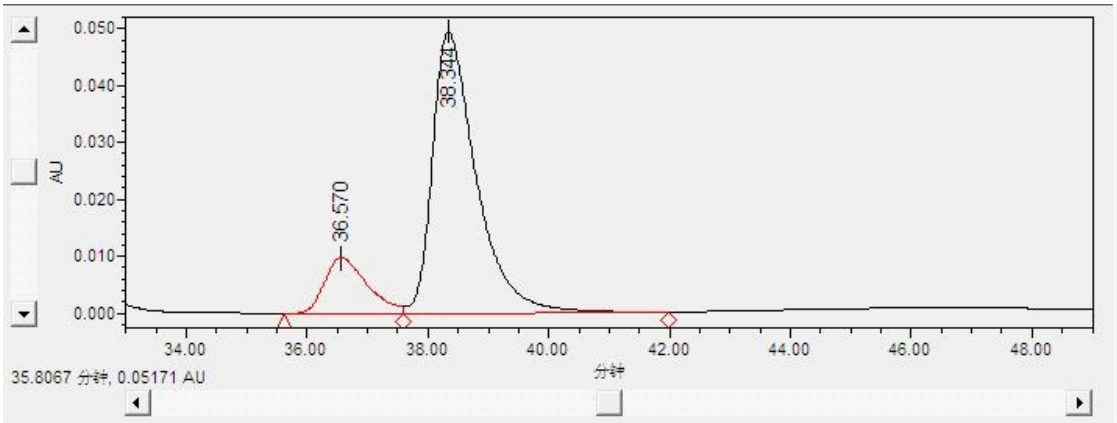
NO	R. Time	Peak Area	Percent	Peak Height
1	37.552	621602	49.15	13840
2	39.106	643152	50.85	14039



Chiral HPLC report: **3k**

HPLC REPORT

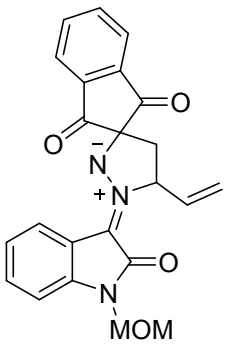
Sample Name: cb-1-95-c-chiral Date: ####
Column: IB-3 Mobile Phase: hex/ipr = 95/5
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		36.570	474083	15.98	9760	BV			未知				35.633	37.600
2		38.344	2491783	84.02	49487	VV			未知				37.600	41.983

NO	R. Time	Peak Area	Percent	Peak Height
1	36.570	474083	15.98	9760
2	38.344	2491783	84.02	49487

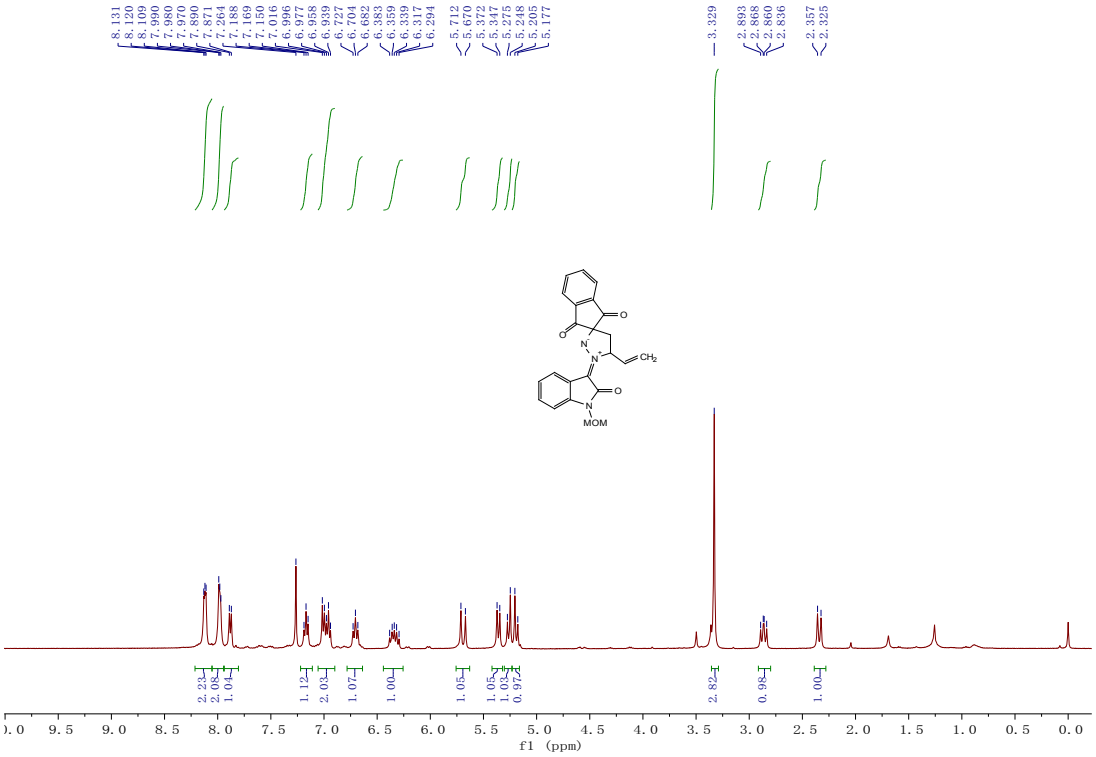
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 36.570 min, t_{major} = 38.344 min; ee = 68%. $[\alpha]_D^{20}$ = -38.7 (c = 0.950, CH_2Cl_2).

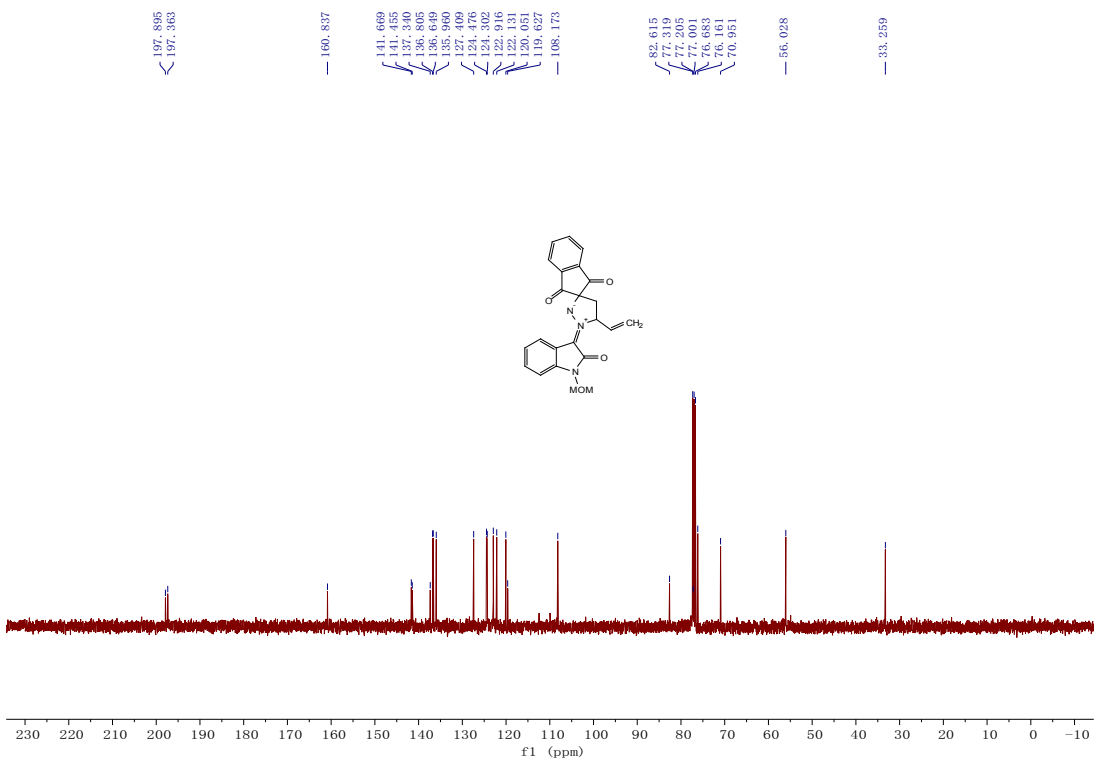


(E)-1'-(1-(methoxymethyl)-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3l

A red solid, 65% yield (26 mg), 77% ee. M.p.: 182-184 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (d, *J* = 12.8 Hz, 1H, CH_2), 2.86 (dd, *J* = 9.6 Hz, 12.8 Hz, 1H, CH_2), 3.33 (s, 3H, CH_3), 5.19 (d, *J* = 11.2 Hz, 1H, CH_2), 5.26 (d, *J* = 11.2 Hz, 1H, CH_2), 5.36 (d, *J* = 10.0 Hz, 1H, =CH_2), 5.69 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.29-6.38 (m, 1H, =CH), 6.70 (dd, *J* = 9.6 Hz, 9.6 Hz, 1H, CH), 6.93-7.02

(m, 2H, ArH), 7.17 (dd, J = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.88 (d, J = 7.6 Hz, 1H, ArH), 7.97-7.99 (m, 2H, ArH), 8.10-8.14 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.3, 56.0, 71.0, 76.2, 77.2, 82.6, 108.2, 119.6, 120.1, 122.1, 122.9, 124.3, 124.5, 127.4, 136.0, 136.6, 136.8, 137.3, 141.5, 141.7, 160.8, 197.4, 197.9. IR (CH_2Cl_2) ν 2924, 2853, 2360, 1712, 1677, 1540, 1465, 1344, 1214, 1189, 1083, 915, 761, 721, 670 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{20}N_3O_4$ ($M+H^+$), requires 402.1448, found: 402.1449.



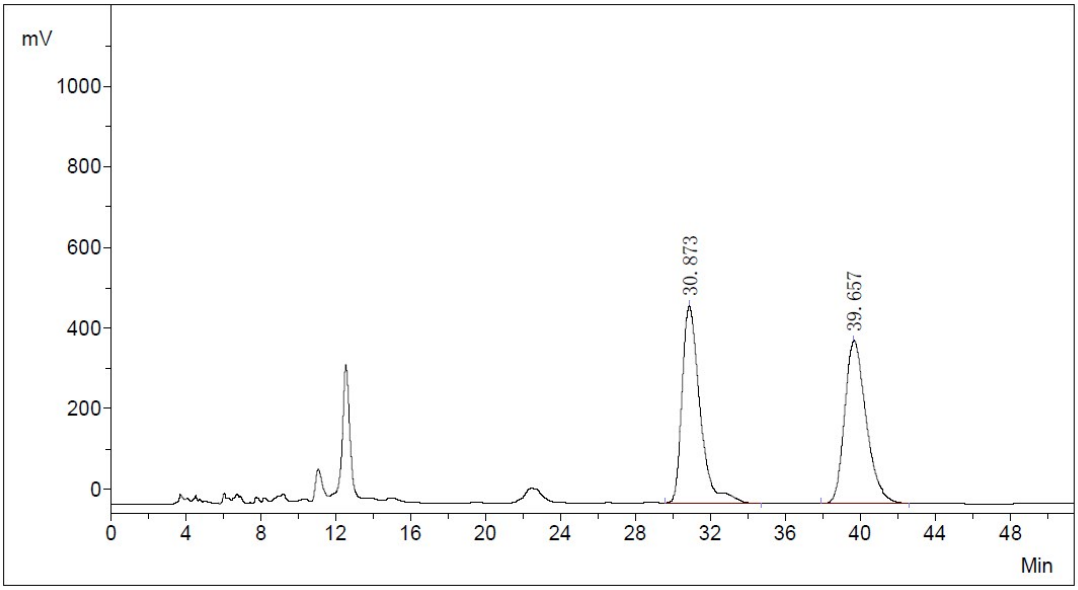


HPLC spectra:

HPLC REPORT

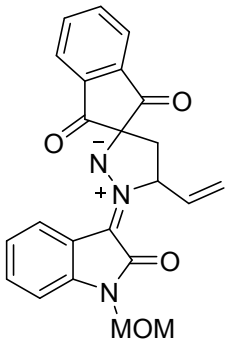
Sample Name: cb-2-3-b-racemic
Column: ad-h
Velocity (mL/min): 0.5

Date: ####
Mobile Phase: hex/ipr = 80/20
Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	30.873	490002.8	32454721.3	50.3317
2	2	Unknown	39.657	404152.1	32026965.9	49.6683
Total				894155.0	64481687.2	100.0000

NO	R. Time	Peak Area	Percent	Peak Height
1	30.873	32454721	50.33	490003
2	39.657	32026966	49.67	404152



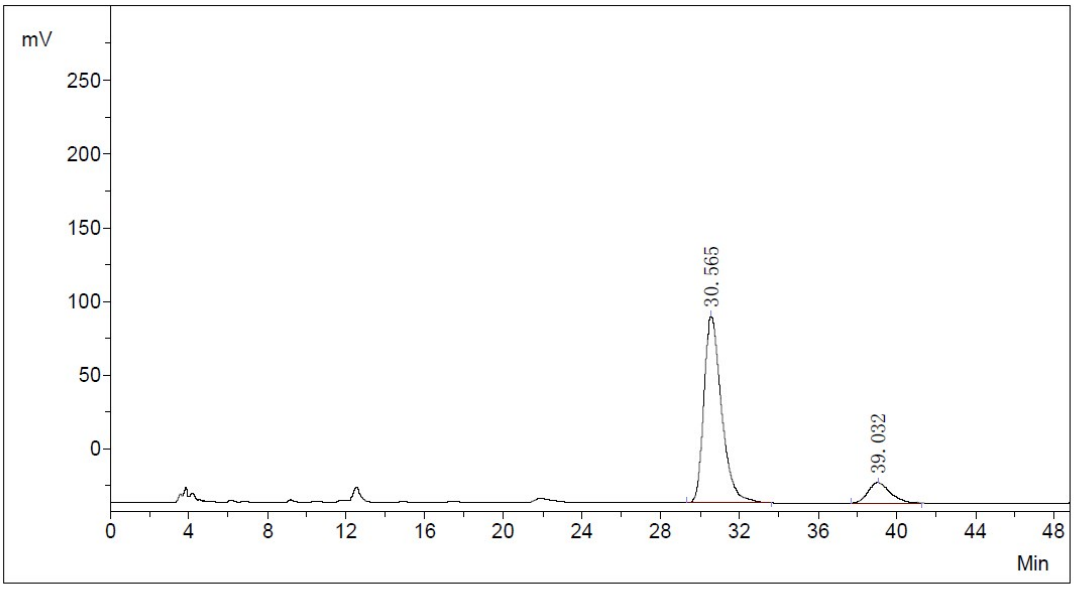
Chiral HPLC report: **3l**

HPLC REPORT

Sample Name: cb-2-3-b-chiral Date: ####

Column: ad-h Mobile Phase: hex/ipr = 80/20

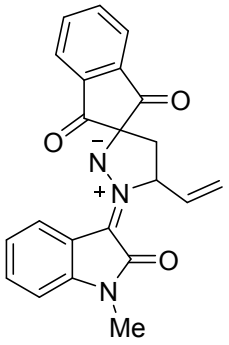
Velocity (mL/min): 0.5 Detection Wavelength (nm): 230



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	30.565	126359.0	7849555.3	88.3955
2	2	Unknown	39.032	13519.5	1030481.0	11.6045
Total				139878.4	8880036.3	100.0000

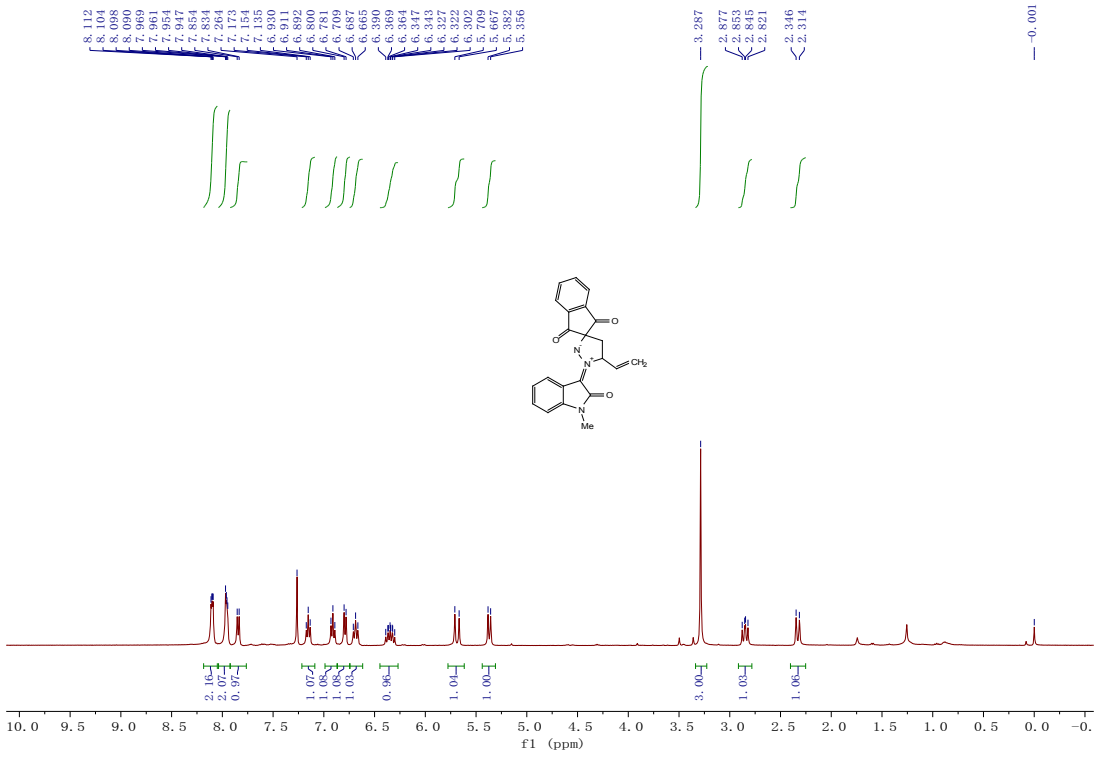
NO	R. Time	Peak Area	Percent	Peak Height
1	30.565	7849555	88.40	126359
2	39.032	10304813	11.60	13520

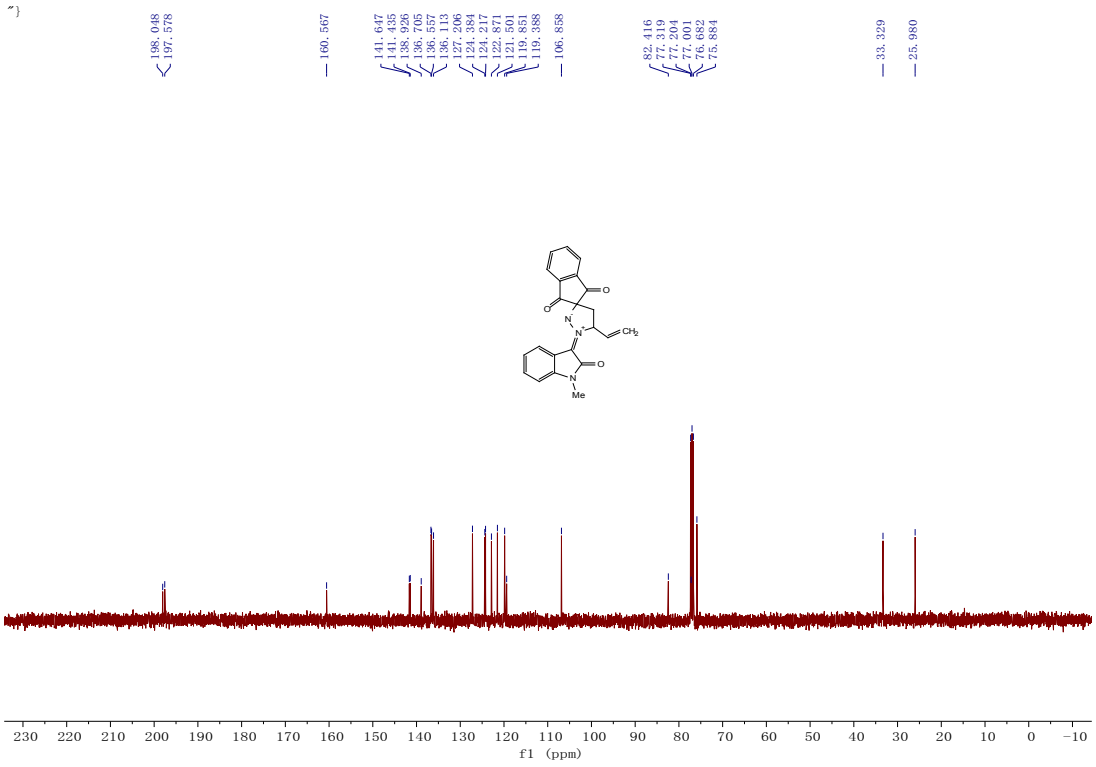
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak ad-h column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{minor} = 39.032 min, t_{major} = 30.565 min; ee = 77%. $[\alpha]_D^{20}$ = -100.4 (c = 0.575, CH_2Cl_2).



(E)-1'-(1-methyl-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro[indene-2,3'-pyrazolidin]-1'-ium-2'-ide 3m

A red solid, 81% yield (30 mg), 84% ee. M.p.: 174-175 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (d, *J* = 12.8 Hz, 1H, CH_2), 2.85 (dd, *J* = 9.6 Hz, 12.8 Hz, 1H, CH_2), 3.29 (s, 3H, CH_3), 5.37 (d, *J* = 10.4 Hz, 1H, =CH_2), 5.69 (d, *J* = 16.8 Hz, 1H, =CH_2), 6.30-6.39 (m, 1H, =CH), 6.69 (dd, *J* = 9.6 Hz, 9.6 Hz, 1H, CH), 6.79 (d, *J* = 7.6 Hz, 1H, ArH), 6.91 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.15 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.84 (d, *J* = 8.0 Hz, 1H, ArH), 7.94-7.97 (m, 2H, ArH), 8.09-8.11 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 26.0, 33.3, 75.9, 77.2, 82.4, 106.9, 119.4, 119.9, 121.5, 122.9, 124.2, 124.4, 127.2, 136.1, 136.6, 136.7, 138.9, 141.4, 141.6, 160.6, 197.6, 198.0. IR (CH_2Cl_2) ν 3057, 2955, 2925, 1709, 1668, 1538, 1469, 1353, 1212, 1022, 984, 913, 758, 736, 666 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{18}N_3O_3$ ($M+H^+$), requires 372.1343, found: 372.1343.

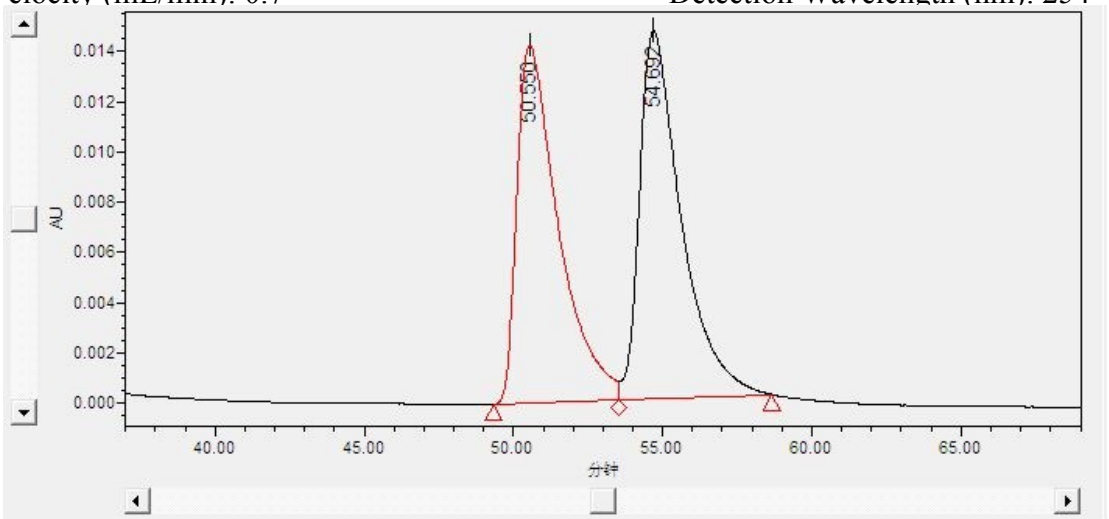




HPLC spectra:

HPLC REPORT

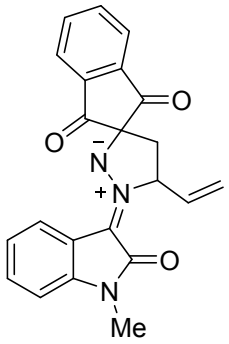
Sample Name: cb-2-3-c-racemic
Date: ####
Column: IB-3
Mobile Phase: hex/ipr = 95/5
Velocity (mL/min): 0.7
Detection Wavelength (nm): 254



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		50.550	1377973	49.14	14217	BV			未知				49.333	53.533
2		54.692	1426476	50.86	14626	VB			未知				53.533	58.667

NO	R. Time	Peak Area	Percent	Peak Height

1	50.550	1377973	49.14	14217
2	54.692	1426476	50.86	14626



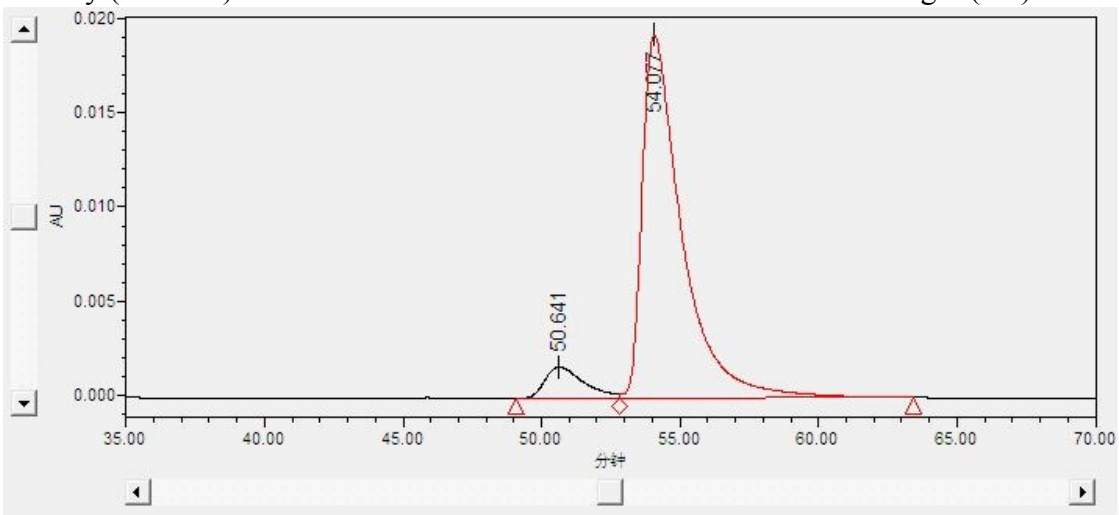
Chiral HPLC report: **3m**

HPLC REPORT

Sample Name: cb-2-3-c-chiral Date: ####

Column: IB-3 Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.7 Detection Wavelength (nm): 254

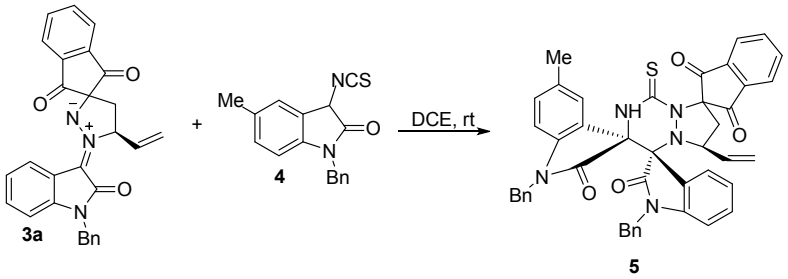


	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	相对 RT (分钟)	RT 比率	开始时间 (分钟)	结束时间 (分钟)
1		50.641	164942	7.86	1680	BV			未知				49.100	52.800
2		54.077	1934608	92.14	19281	VB			未知				52.800	63.417

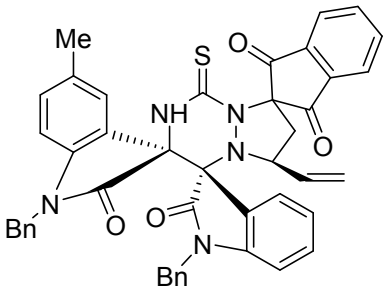
NO	R. Time	Peak Area	Percent	Peak Height
1	50.641	164942	7.86	1680
2	54.077	1934608	92.14	19281

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IB-3 column; λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 50.641 min, t_{major} = 54.077 min; ee = 84%. $[\alpha]_D^{20}$ = -113.5 (c = 0.420, CH_2Cl_2).

8. General procedure for the synthesis of 5 and their characterization and spectra charts containing HPLC traces



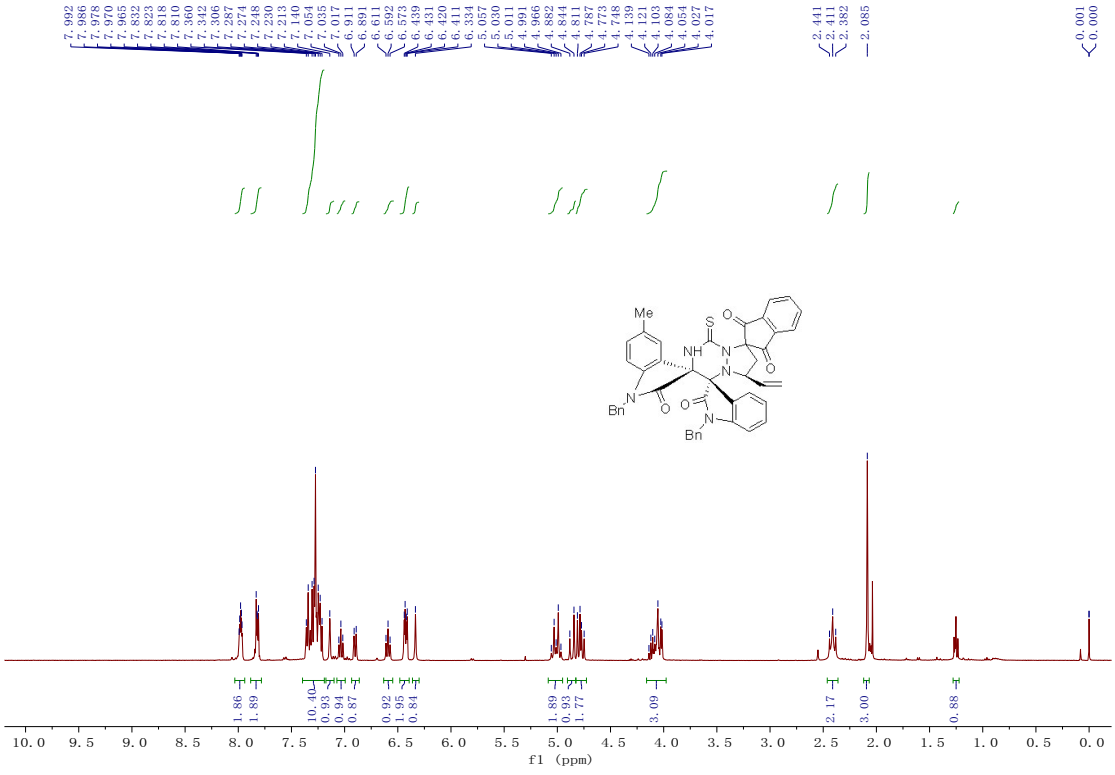
To a solution of (E)-1'-(1-benzyl-2-oxoindolin-3-ylidene)-1,3-dioxo-5'-vinyl-1,3-dihydrospiro [indene-2,3'-pyrazolidin]-1'-ium-2'-ide **3a** (1.0 equiv) and 1-benzyl-3-isothiocyanato-5-methylindolin-2-one **4** (1.5 equiv) in DCE was stirred in at room temperature for 24 hours. Then, the solvent is directly removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc = 6/1) to furnish the desired product **5** as a light yellow solid.

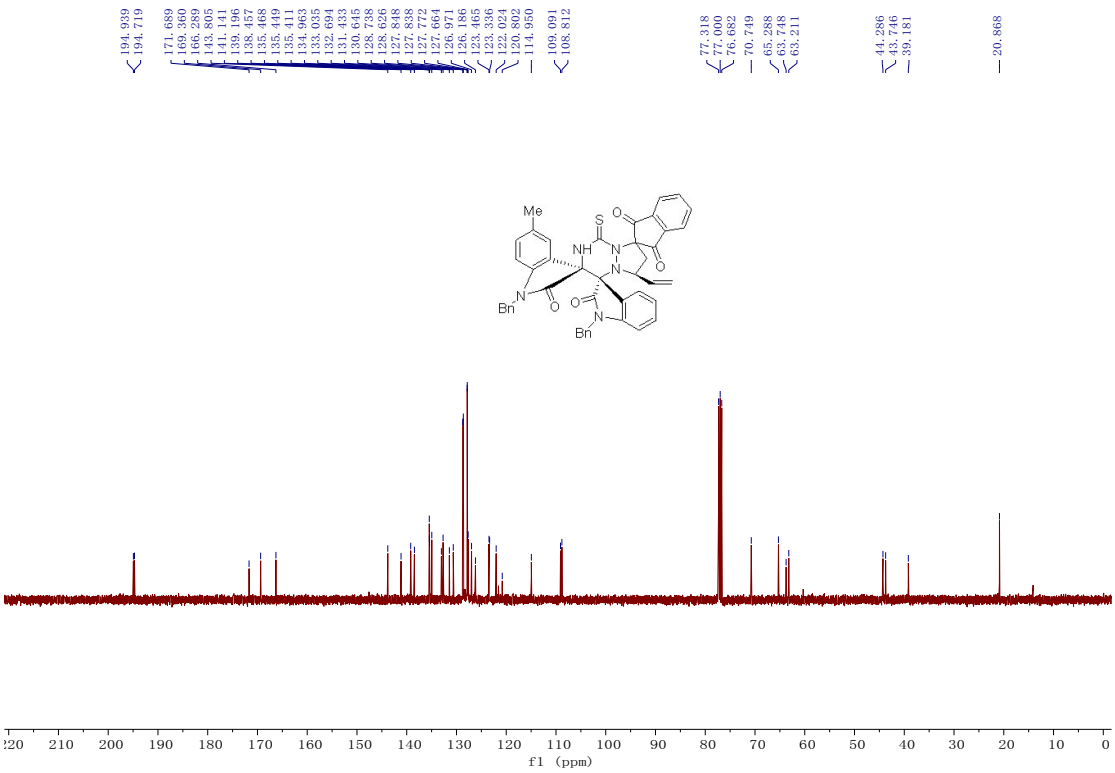


Compound 5

A light yellow solid, 76% yield (28 mg), 74% ee. M.p.: 301-302 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.09 (s, 3H, CH_3), 2.41 (dd, *J* = 12.0 Hz, 12.0 Hz, 2H, CH_2), 4.01-4.14 (m, 3H, =CH,

=CH_2), 4.77 (d, J = 15.6 Hz, 1H, CH_2), 4.79 (d, J = 15.2 Hz, 1H, CH_2), 4.86 (d, J = 15.2 Hz, 1H, CH_2), 4.96-5.06 (m, 2H, CH, CH_2), 6.33 (s, 1H, ArH), 6.41-6.44 (m, 2H, ArH), 6.59 (dd, J = 7.6 Hz, 7.6 Hz, 1H, ArH), 6.89 (d, J = 8.0 Hz, 1H, ArH), 7.04 (dd, J = 7.6 Hz, 7.6 Hz, 1H, ArH), 7.14 (s, 1H, ArH), 7.21-7.36 (m, 10H, ArH), 7.81-7.84 (m, 2H, ArH), 7.96-8.00 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.9, 39.2, 43.7, 44.3, 63.2, 63.7, 65.3, 70.7, 108.8, 109.1, 115.0, 120.8, 122.0, 123.3, 123.5, 126.2, 127.0, 127.66, 127.77, 127.84, 127.85, 128.6, 128.7, 130.6, 131.4, 132.7, 133.0, 135.0, 135.41, 135.45, 135.47, 138.5, 139.2, 141.1, 143.8, 166.3, 169.4, 171.7, 194.7, 194.9. IR (CH_2Cl_2) ν 2960, 2923, 2854, 1719, 1613, 1496, 1467, 1344, 1259, 1080, 1017, 866, 796, 732, 699 cm^{-1}. HRMS (ESI) Calcd. for $C_{45}H_{36}N_5O_4S^{+1}$(M+H)$^+$ requires 742.2483, found: 742.2481.





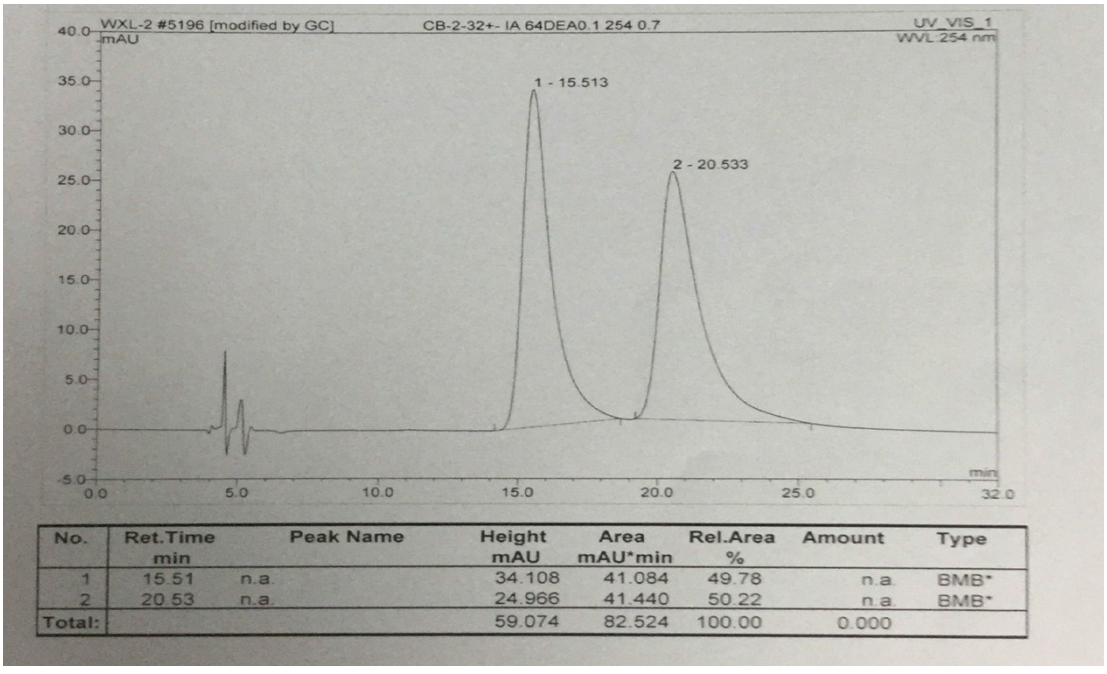
HPLC spectra:

HPLC REPORT

Sample Name: cb-2-32-racemic Date: ####

Column: IA Mobile Phase: hex/ipr = 60/40

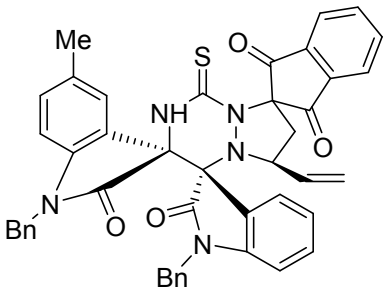
Velocity (mL/min): 0.7 Detection Wavelength (nm): 254



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.51	n.a.	34.108	41.084	49.78	n.a.	BMB*
2	20.53	n.a.	24.966	41.440	50.22	n.a.	BMB*
Total:			59.074	82.524	100.00	0.000	

NO	R. Time	Peak Area	Percent	Peak Height

1	15.51	41.084	49.78	34.108
2	20.53	41.440	50.22	24.966



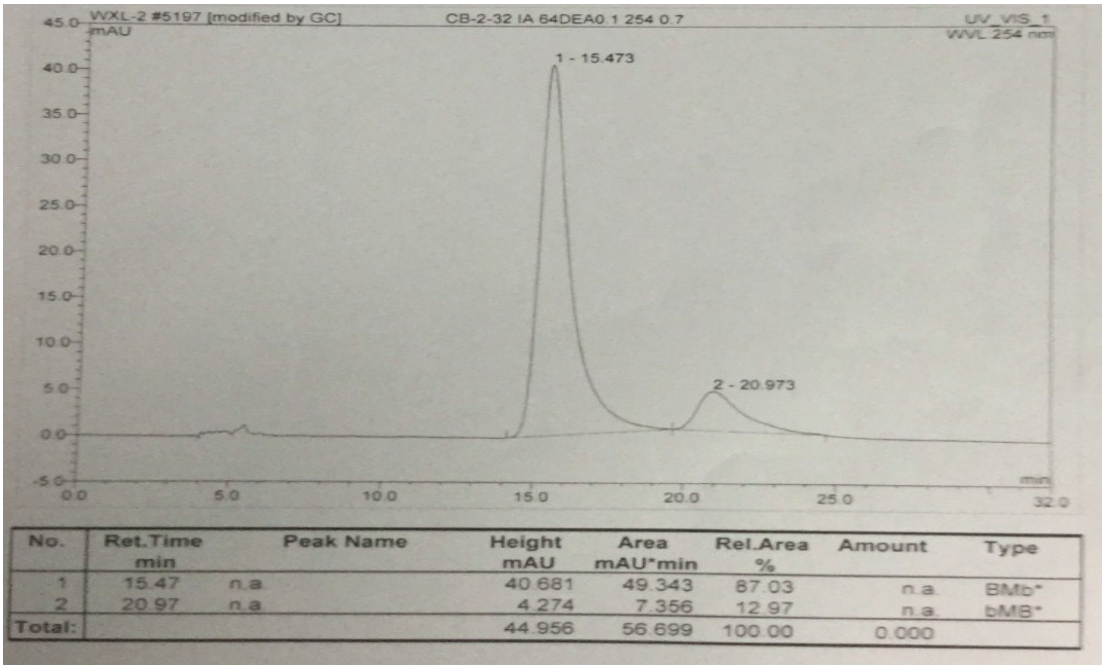
Chiral HPLC report: **3m**

HPLC REPORT

Sample Name: cb-2-32-chiral Date: ####

Column: IA Mobile Phase: hex/ipr = 60/40

Velocity (mL/min): 0.7 Detection Wavelength (nm): 254

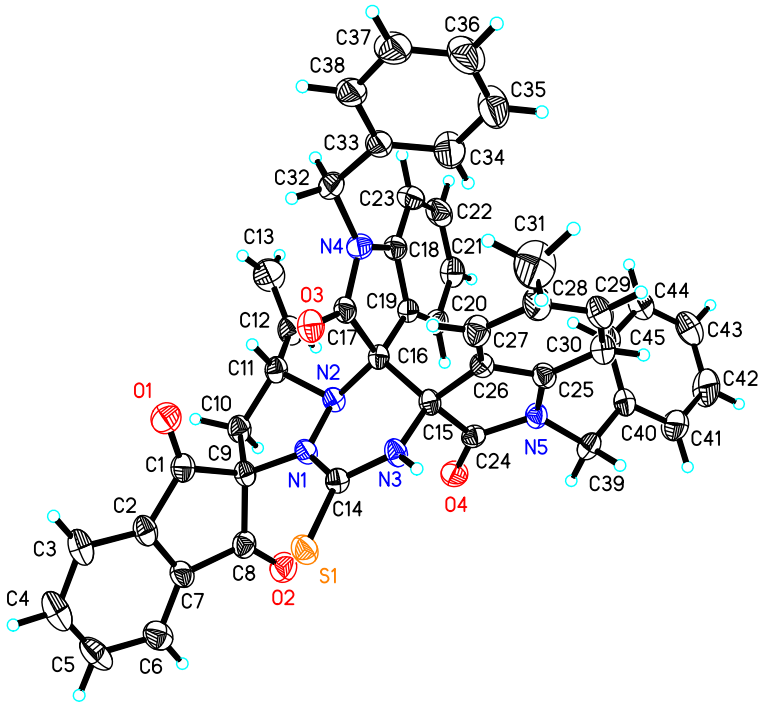


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.47 n.a.		40.681	49.343	87.03	n.a.	BMb*
2	20.97 n.a.		4.274	7.356	12.97	n.a.	bMB*
Total:			44.956	56.699	100.00	0.000	

NO	R. Time	Peak Area	Percent	Peak Height
1	15.47	49.343	87.03	40.681
2	20.97	4.274	12.97	7.356

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IA column; λ = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min; t_{minor} = 20.97 min, t_{major} = 15.47 min; ee = 74%. $[\alpha]_D^{20}$ = 103.0 (c = 1.00, CH_2Cl_2).

9. X-ray crystallographic information of compound 5



The crystal data of racemate **5** have been deposited in CCDC with number 1414548. Empirical Formula: $C_{45}H_{35}N_5O_4S$; Formula Weight: 741.84; Crystal Color, Habit: colorless, Crystal Dimensions: 0.180 x 0.150 x 0.110 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 21.457(3)Å, b = 17.435(3)Å, c = 22.102(3)Å, $\alpha = 90^o$, $\beta = 101.295(3)^o$, $\gamma = 90^o$, V = 8108(2)$Å^3$; Space group: C 2/c; Z = 8; D_{calc}= 1.215 g/cm^3; F_{000} = 3104; Final R indices [I>2sigma(I)] R1 = 0.0540, wR2 = 0.1059.

10. Experimental and results Vibrational Circular Dichroism (VCD) of products 5.

VCD and IR experimental

VCD and IR spectra were measured using a BioTools ChiralIR-2X FT-VCD spectrometer, equipped with a single photoelastic modulation and a mercury cadmium tellurium detector. About 5 mg of compound **5** was dissolved in 150 μL $CDCl_3$ and placed in a BaF_2 cell with a pathlength of 75 μm. Data were acquired at a resolution of 4 cm^{-1} for 8 h. Besides the chiral sample, the corresponding racemate was measured under the same conditions to obtain VCD baseline.

VCD and IR calculations

The assignment of absolute configuration with VCD method is based on comparisons of the experimental spectra with the theoretical curve obtained by density functional theory (DFT) calculations. Molecular model of (*R,R,R*)-**5** was built and subjected to a conformational analysis using the Monte Carlo protocol at the molecular mechanic force field MMFF94 level with Compute VOA (BioTools Inc., Jupiter, FL). Within a 5 kcal/mol window, 26 energetically distinct conformers were predicted. Geometry optimization and frequencies calculation of the conformers were then carried out using the B3LYP hybrid density functional and 6-31G (d) basis set with Gaussian 09 (Gaussian Inc., Wallingford, CT). Boltzmann-population-weighted composite VCD and IR spectra were then generated by Compute VOA. Theoretical curves for (*S,S,S*)-**5** were deduced from (*R,R,R*)-**5**. As enantiomers, their IR curves are exactly the same and VCD spectra are mirror images.

Figure SI-1 and **Figure SI-2** show the experimental and calculated VCD and IR spectra over the range of 1100-1900 cm^{-1}. A scale factor of 0.96 has been applied to the calculated frequencies to overcome a systematic overestimation of the molecular force constant values by DFT. The good agreement between the corresponding spectra of compound **5** and (*S,S,S*)-**5**, leads to an unambiguous assignment of its absolute configuration as (*S,S,S*).

Quantitative evaluation of this assignment was achieved by Compare VOA (BioTools Inc., Jupiter, FL).The related results, including the spectral similarities and enantiomeric similarity index (the difference between the VCD spectral similarity of the correct and the incorrect enantiomers, ESI) are listed in **Table SI-2**. Based on the current Compare VOA database, the

confidence level of the (*S,S,S*) assignment for compound **5** is 97%.

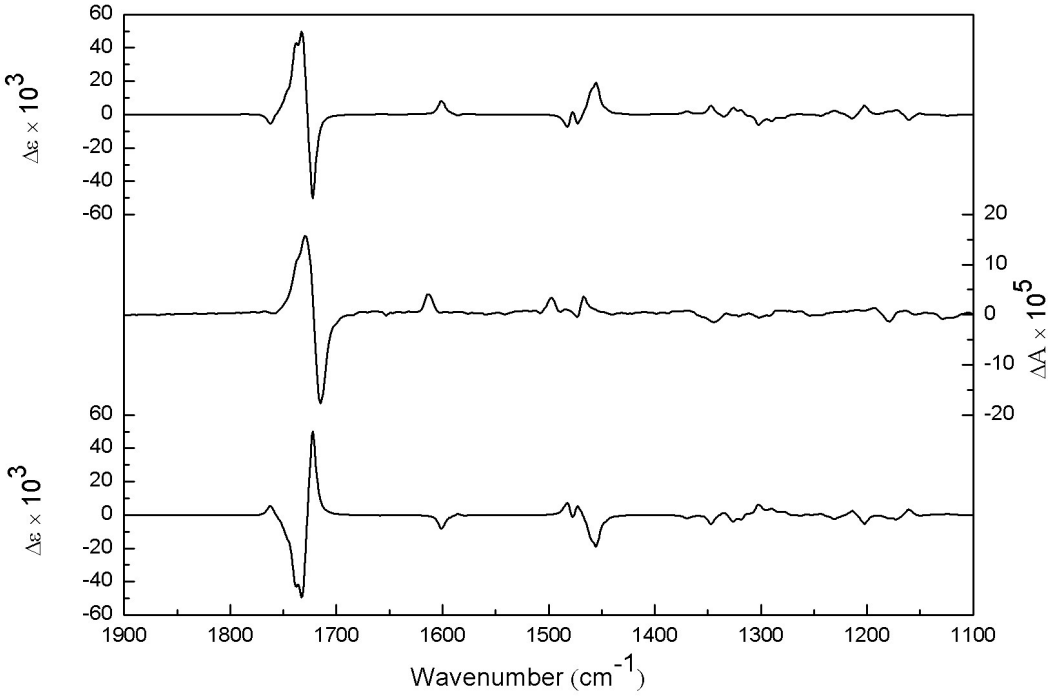


Figure SI-1. Comparison of the experimental VCD spectrum of compound **5** (center) and the calculated VCD spectra of (S,S,S)-**5** (top) and (*R,R,R*)-**5** (bottom)

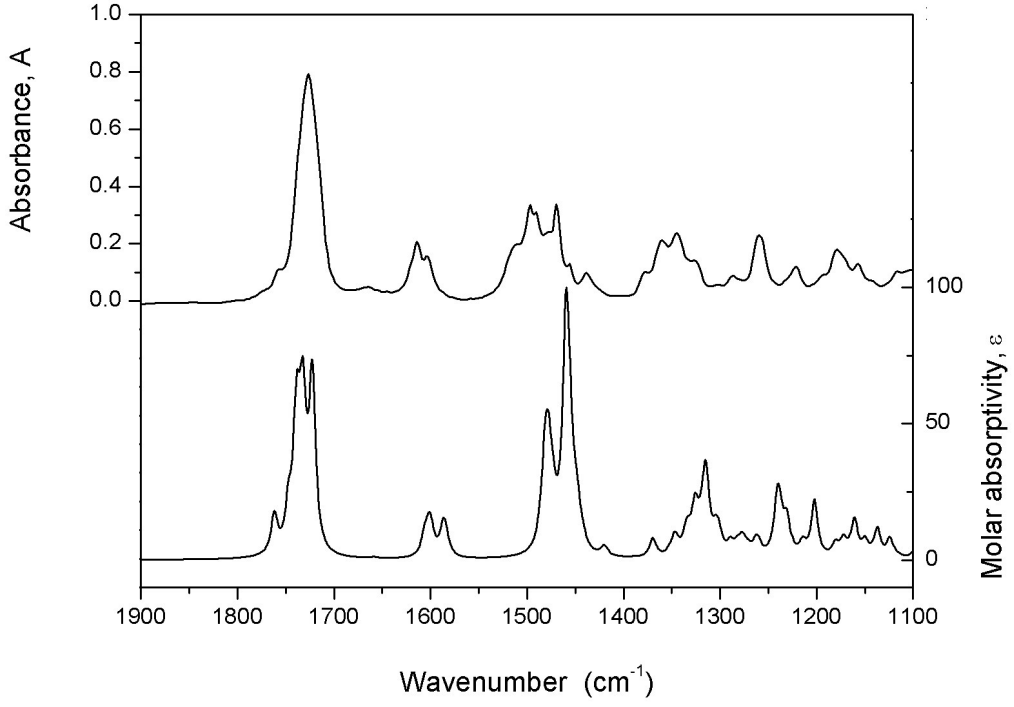


Figure SI-2. Comparison of the experimental IR spectrum of compound **5** (top) and the calculated

IR spectra for (S,S,S)-**5** and (*R,R,R*)-**5** (bottom)

Table SI-2. Evaluations for the AC assignment of compound **5**

Calculation Method	[a]S_{IR}	[b]S_E	[c]$S_{,-E}$	[d]*ESI*
DFT//B3LYP/6-31G(d)	77.8	72.0	15.6	56.4

[a] Total neighborhood similarity for IR spectra

[b] VCD spectral neighborhood similarity for the correct enantiomer

[c] VCD spectral neighborhood similarity for the incorrect enantiomer

[d] Enantiomeric similarity index

11. **References**

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