Supporting Information:

An Organocatalytic Asymmetric Sequential Allylic Alkylation/Cyclization of Morita-Baylis-Hillman Carbonates and 3-Hydroxyoxindoles

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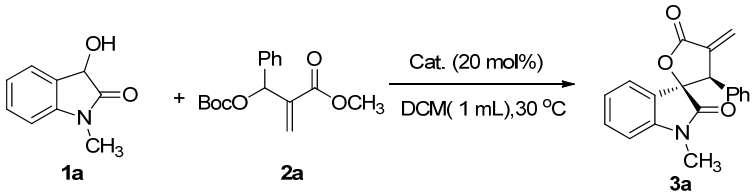
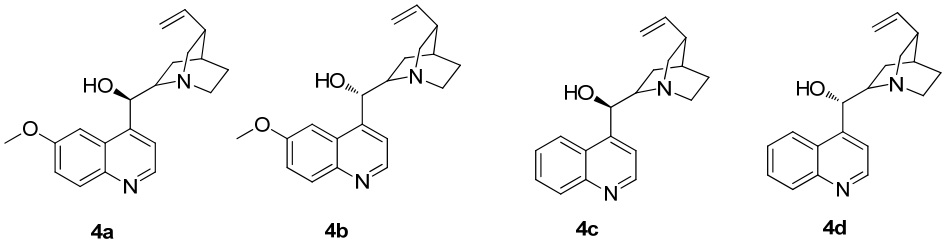
1. General methods

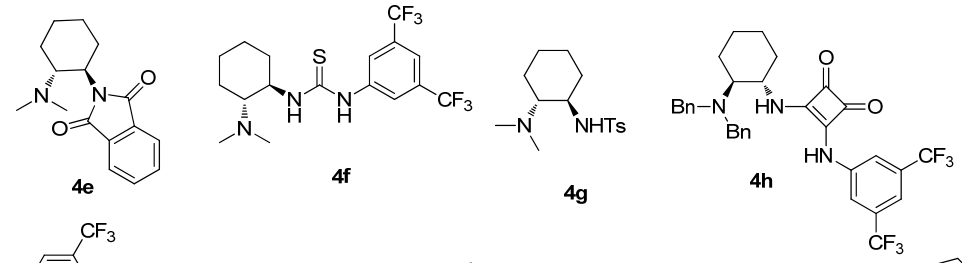
Commercial grade solvent was dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. Highresolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. Enantiomeric excess was determined by HPLC analysis on chiralpak AD-H, or IC columns. Optical rotations are reported as follows: $[\alpha]^{20}_{D}$ (C in g/100 mL, $CHCl_3$).

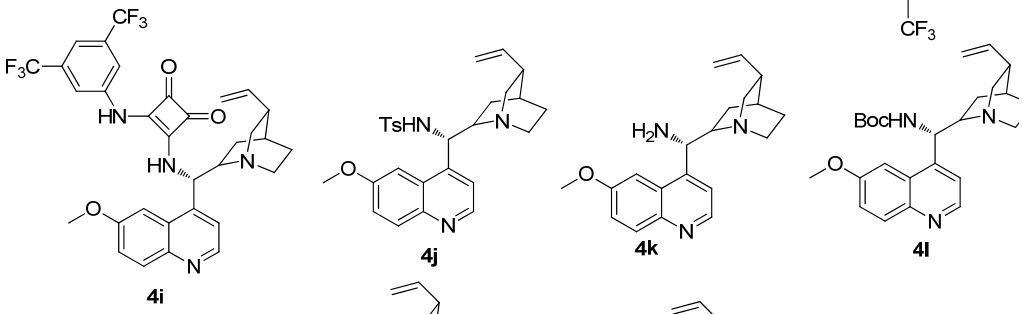
2. Optimization studies

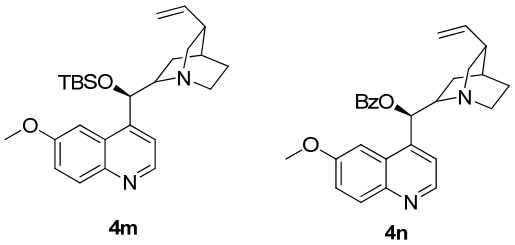
Table S1: Screening of catalysts[a]







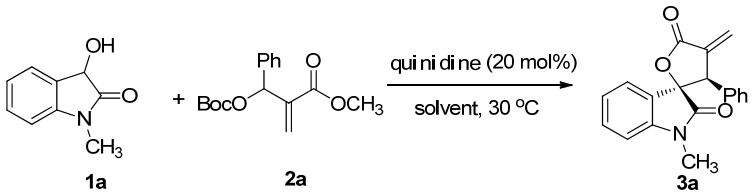




entry	cat.	time(h)	yield(%)[b]	Ee (%)[c]
1	**4a**	15.5	22	61[e]
2	**4b**	15.5	17	81
3	**4c**	19.5	20	72
4	**4d**	15.5	48	29[e]
5[d]	**4f**	24	--	--
6[d]	**4g**	24	--	--
7[d]	**4h**	24	--	--
8[d]	**4i**	24	--	--
9[d]	**4j**	24	--	--
10[d]	**4k**	24	--	--
11[d]	**4l**	24	--	--
12[d]	**4m**	24	--	--
13[d]	**4n**	24	--	--

(a) Unless otherwise specified, the reaction was conducted on a scale of 0.20 mmol **1a** and 1.1 equiv. **2a** in the presence of 20 mol% catalyst in 1.0 mL dichloromethane at 30 °C. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column. (d) The reaction did not work. (e) Contrary configuration.

Table S2 Screening of solvents[a]

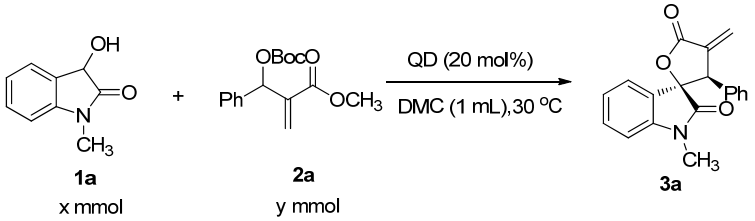


1a **2a** **3a**

entry	solvent	time(h)	yield(%)[b]	ee(%)[c]
1	DCM	15.5	17	81
2	$CHCl_3$	24	12	85
3	CCl_4	24	3	83
4	1,2-DCE	24	11	81
5	CH_3Cl_3	24	5	80
6	cyclohexane	24	9	85
7	CH_3CN	13	11	67
8	ethyl acetate	16	17	83
9	butyl acetate	16	21	82
10	DMC	16	35	85
11	DEC	16	20	84
12	toluene	14	7	81
13	mesitylene	41	10	82
14	THF	20	25	74
15	DME	14	25	82
16	*i*-PrOH	14	49	83

(a) Unless otherwise specified, the reaction was conducted on a scale of 0.20 mmol **1a** and 1.1 equiv. **2a** in the presence of 20 mol% catalyst in 1.0 mL solvent at 30 °C. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column.

Table S3: Screening of substrate ratios[a]



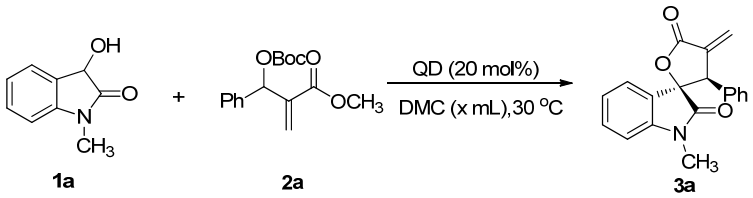
1a x mmol **2a** y mmol **3a**

entry	x	y	ratio	time(h)	yield(%)[b]	ee(%)[c]
1	0.2	0.2	1：1	14	27	84
2	0.2	0.3	1：1.5	14	40	84
3	0.2	0.4	1：2	14	46	84

4	0.2	0.5	1：2.5	14	50	84
5	0.2	0.6	1：3	14	58	84
6	0.22	0.2	1.1:1	24	30	85
7	0.3	0.2	1.5:1	24	28	85
8	0.4	0.2	2.0:1	38	26	86
9	0.5	0.2	2.5:1	38	30	86
10	0.6	0.2	3:1	38	31	86

(a) Unless otherwise specified, the reaction was conducted with the substrate ratio outlined in the table in the presence of 20 mol% catalyst in 1.0 mL DMC at 30 °C. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column.

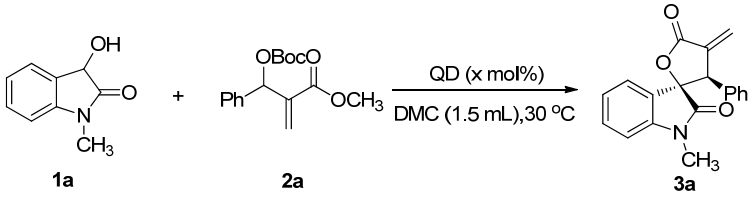
Table S4: Screening of concentrations[a]



entry	x	time(h)	yield(%)[b]	ee(%)[c]
1	0.5	13	52	83
2	1.0	13	62	84
3	1.5	13	63	84
4	2.0	13	52	84
5	2.5	13	51	84

(a) Unless otherwise specified, the reaction was conducted on a scale of 0.20 mmol **1a** and 3.0 equiv. **2a** in the presence of 20 mol% catalyst in x mL DMC at 30 °C. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column.

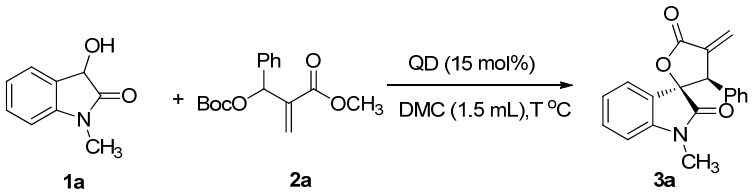
Table S5: Screening of catalyst loadings[a]



entry	x	time(h)	yield(%)[b]	ee(%)[c]
1	2	62	10	82
2	5	62	19	82
3	10	62	26	84
4	15	14	48	85
5	20	14	51	84

(a) Unless otherwise specified, the reaction was conducted on a scale of 0.20 mmol **1a** and 3.0 equiv. **2a** in the presence of x mol% catalyst in 1.5 mL DMC at 30 °C. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column.

Table S6: Screening of temperatures[a]

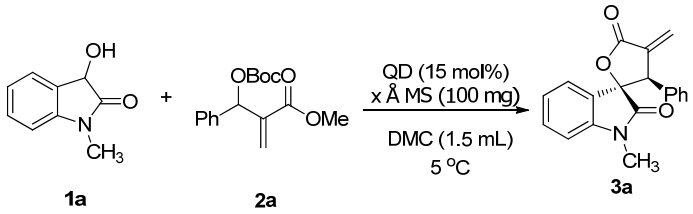


1a 2a 3a

entry	T	time(h)	yield(%)[b]	ee(%)[c]
1	30	14	48	85
2	20	60	40	85
3	5	89	46	89

(a) Unless otherwise specified, the reaction was conducted on a scale of 0.20 mmol **1a** and 3.0 equiv. **2a** in the presence of 15 mol% catalyst in 1.5 mL DMC at the specified temperature. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column.

Table S7: Screening of molecular sieves [a]

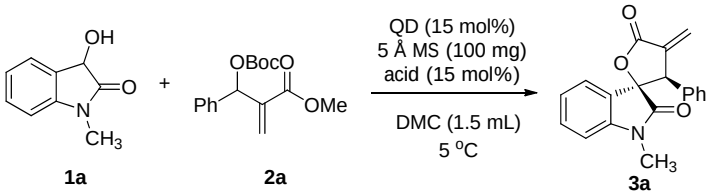


1a 2a 3a

entry	x	time(h)	yield(%)[b]	ee(%)[c]
1	3	69	59	87
2	4	69	51	88
3	5	69	53	89

(a) Unless otherwise specified, the reaction was conducted on a scale of 0.20 mmol **1a** and 3.0 equiv. **2a** with molecular sieve (100 mg) as an additive in the presence of 15 mol% catalyst in 1.5 mL DMC at 5 °C. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column.

Table S8: Acid additive screening[a]



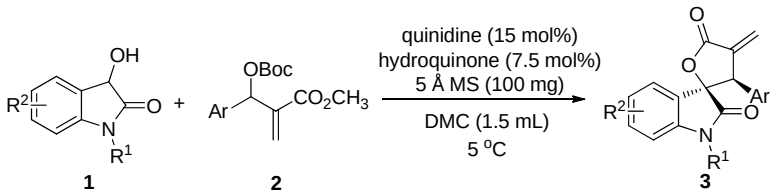
1a 2a 3a

entry	acid	time(h)	yield(%)[b]	ee(%)[c]
1	$PhCO_2H$	41	NR	NR
2[d]	hydroquinone	41	64	89
3[d]	(R)-BINOL	41	60	90
4[d]	(S)-BINOL	41	53	90
5	2,4-di-*tert*-butylphenol	41	57	89
6	2,6-di-*tert*-butylphenol	24	23	87

(a)Unless otherwise specified, the reaction was conducted on a scale of 0.20 mmol **1a** and 3.0

equiv. **2a** with 100 mg 5 Å MS and 15mol% acid as additives in the presence of 15 mol% catalyst in 1.5 mL DMC at 5 °C. All reactions afforded **3a** as a single diastereomer. (b) Isolated yield. (c) Determined by HPLC with a Chiralpak-AD column. (d) 7.5 mol% acid was added.

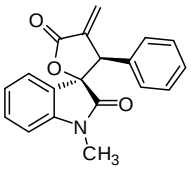
3. Genaral procedures for the synthesis of compounds **3**.



Quinidine (15 mol %), hydroquinone (7.5 mol %) and 5 Å MS (100 mg) were added to a solution of **1** (0.2 mmol) and **2** (0.6 mmol) in DMC (1.5 mL). Then, the mixture was cooled to 5 °C. After stirred for the indicated time, the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding products **3**.

4. Characterization of compounds **3**.

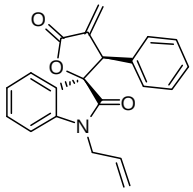
(*2R,3R*)-1'-methyl-4-methylene-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3a)



Reaction time: 41 h; Light yellow solid, $[a]_D^{20}$= +46.2 (*c* 0.88, $CHCl_3$), 64% yield, > 20:1 dr, 89% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 14.6 min, t_{minor} = 12.3 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.55 (d, *J*= 9 Hz, 1H), 7.37 (t, *J*= 3 Hz, 1H), 7.22-7.17 (m, 4H), 6.99 (d, *J*= 6 Hz, 2H), 6.65 (d, *J*= 6 Hz, 1H), 6.58 (d, *J*= 3 Hz, 1H), 5.64 (d, *J*= 3 Hz, 1H), 4.51 (t, *J*= 3 Hz, 1H), 2.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 169.2, 144.4, 136.0, 131.6, 131.3, 129.2, 128.4, 124.5, 124.2, 123.4, 123.2, 108.6, 85.3, 56.0, 25.8; HRMS (EI) Calcd. for C19H15NO3 $[M]^+$: 305.1052, Found: 305.1053.

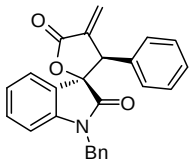
(2*R*,3*R*)-1'-allyl-4-methylene-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3b)

Reaction time: 44 h; Yellow solid, $[a]_D^{20}$= +27.5 (*c* 0.48, $CHCl_3$), 52% yield, > 20:1 dr, 87% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 13.3 min, t_{minor} = 11.0 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.56(d, *J*= 6 Hz, 1H), 7.37-7.31 (m, 1H), 7.24-7.17 (m, 4H), 7.01 (d, *J*= 6 Hz, 2H), 6.61 (t, *J*= 6 Hz, 2H), 5.67 (d, *J*= 3 Hz, 1H), 5.24-5.12 (m, 1H), 4.80



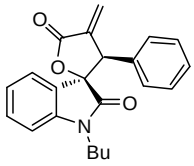
(d, *J*= 12 Hz, 1H), 4.55 (t, *J*= 3 Hz, 1H), 4.33-4.21 (m, 2H), 3.73-3.64 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 169.2, 143.7, 135.9, 131.6, 131.2, 129.9, 129.4, 128.8, 126.1, 124.4, 124.2, 123.4, 123.3, 116.8, 109.5, 85.2, 55.9, 42.0; HRMS (EI) Calcd. for C21H17NO3 $[M]^+$: 331.1208, Found: 331.1209.

(2*R*,3*R*)-1'-benzyl-4-methylene-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3c)



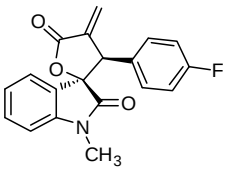
Reaction time: 44 h; Yellow solid, $[a]_D^{20}$= +27.5 (*c* 0.36, $CHCl_3$), 45% yield, > 20:1 dr, 88% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 20.2 min, t_{minor} = 19.0 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.57 (d, *J*= 9 Hz, 1H), 7.38-7.33 (m, 1H), 7.28-7.04 (m, 9H), 6.64 (d, *J*= 3 Hz, 1H), 6.42 (d, *J*= 9 Hz, 1H), 6.38 (d, *J*= 6 Hz, 2H), 5.71 (d, *J*=3 Hz, 1H), 5.01 (d, *J*= 15 Hz, 1H), 4.63 (t, *J*= 3 Hz, 1H), 4.25 (d, *J*= 15 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 169.2, 143.7, 136.1, 131.8, 131.3, 130.9, 129.7, 129.2, 128.9, 128.6, 128.6, 128.4, 127.3, 126.3, 124.4, 124.3, 123.5, 123.4, 109.9, 85.1, 55.6, 43.7; HRMS (EI) Calcd. for C25H19NO3 $[M]^+$: 381.1365, Found: 381.1363.

(2*R*,3*R*)-1'-butyl-4-methylene-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3d)



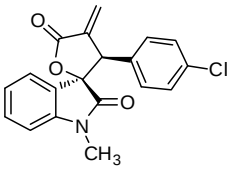
Reaction time: 44 h; Light yellow solid, $[a]_D^{20}$= +40.0 (*c* 0.25, $CHCl_3$), 38% yield, >20:1 dr, 86% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 9.8 min, t_{minor} = 8.3 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.55 (d, *J*= 9 Hz, 1H), 7.36 (dd, *J*= 6 Hz, 1H), 7.22 (d, *J*= 6 Hz, 2H), 7.17 (d, *J*= 6 Hz, 2H), 7.00 (d, *J*= 6 Hz, 2H), 6.67 (d, *J*= 6 Hz, 1H), 6.61 (d, *J*= 3 Hz, 1H), 5.68 (d, *J*= 3 Hz, 1H), 4.53 (t, *J*= 3 Hz, 1H), 3.52-3.50 (m, 1H), 3.13-3.08 (m, 1H), 0.92-0.80 (m, 4H), 0.72 (t, J= 6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 169.2, 144.2, 136.1, 131.8, 131.3, 129.4, 128.8, 124.7, 124.4, 123.3, 123.2, 123.1, 108.8, 85.0, 55.8, 39.7, 28.9, 19.6, 13.6; HRMS (EI) Calcd. for C22H21NO3 $[M]^+$: 347.1521, Found: 347.1523.

(2*R*,3*R*)-3-(4-fluorophenyl)-1'-methyl-4-methylene-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3e)



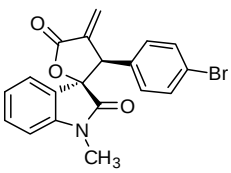
Reaction time: 41 h; Colorless solid, $[a]_D^{20}$= +42.4 (*c* 0.37, $CHCl_3$), 85% yield, > 20:1 dr, 92% ee; HPLC: Chiralcel IC column, hexane/*i*-PrOH = 50/50, flow rate 0.7 mL/min, UV detection at 254 nm, t_{major} = 24.7 min, t_{minor} = 34.0 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.54 (d, *J* = 9 Hz, 1H), 7.39 (t, *J* = 6 Hz, 1H), 7.20 (t, *J*= 6 Hz, 1H),7.01-6.97 (m, 2H), 6.88 (t, *J*= 9 Hz, 2H), 6.68 (d, *J*= 6 Hz, 1H), 6.59 (d, *J*= 6 Hz, 1H), 5.62 (d, *J*= 3 Hz, 1H), 4.50 (t, *J*= 3 Hz, 1H), 2.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 168.9, 162.7 (d, *J*= 246 Hz, 1C), 144.4, 136.2, 131.5, 131.1, 131.0, 127.5, 127.4, 124.2, 123.4 (d, *J*= 23.9 Hz, 1C), 115.5 (d, *J*= 21.4 Hz, 1C), 108.6, 85.0, 55.2, 25.9; HRMS (EI) Calcd. for C19H14FNO3 $[M]^+$: 323.0958, Found: 323.0965.

(2*R*,3*R*)-3-(4-chlorophenyl)-1'-methyl-4-methylene-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3f)



Reaction time: 34 h; White solid, $[a]_D^{20}$= -2.2 (*c* 0.58, $CHCl_3$), 51% yield, >20:1 dr, 85% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 11.4 min, t_{minor} = 12.0 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.53 (d, *J*= 6 Hz, 1H), 7.39 (t, *J*= 6 Hz, 1H), 7.22-7.16 (m, 3H), 6.95 (d, *J*= 6 Hz, 2H), 6.68 (d, *J*= 9 Hz, 1H), 6.58 (d, *J*= 3 Hz, 1H), 5.60 (d, *J*= 3 Hz, 1H), 4.49 (t, *J*= 3 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 168.8, 144.4, 135.9, 134.5, 131.5, 130.6, 130.3, 128.7, 126.3, 124.2, 123.5, 123.3, 108.8, 84.9, 55.2, 26.0; HRMS (EI) Calcd. for C19H14ClNO3 $[M]^+$: 339.0662, Found: 339.0654.

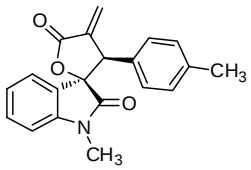
(2*R*,3*R*)-3-(4-bromophenyl)-1'-methyl-4-methylene-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3g)



Reaction time: 34 h; White solid, $[a]_D^{20}$= -17.1 (*c* 0.61, $CHCl_3$), 52% yield, >20:1 dr, 84% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 11.8 min, t_{minor} = 12.7 min; ^{1}H NMR (300 MHz, $CDCl_3$),

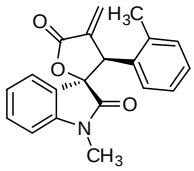
δ 7.53 (d, *J*= 9 Hz, 1H), 7.39-7.31 (m, 3H), 7.19 (t, *J*= 6 Hz, 1H), 6.89 (d, *J*= 9 Hz, 2H), 6.69 (d, *J*= 6 Hz, 1H), 6.58 (d, *J*= 6 Hz, 1H), 5.60 (d, *J*= 3 Hz, 1H), 4.47 (d, *J*= 3 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 168.7, 144.3, 135.9, 131.7, 131.5, 131.0, 130.9, 128.3, 124.2, 123.5, 123.2, 122.7, 108.8, 84.8, 55.1, 26.0; HRMS (EI) Calcd. for C19H14BrNO3 $[M]^+$: 383.0157, Found: 383.0167.

(2*R*,3*R*)-1'-methyl-4-methylene-3-(p-tolyl)-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3h)



Reaction time: 41 h; White solid, $[a]_D^{20}$= +20.7 (*c* 0.42, $CHCl_3$), 59% yield, >20:1 dr, 89% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 10.0 min, t_{minor} = 11.6 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.53 (d, *J*= 6 Hz, 1H), 7.37 (t, *J*= 7.5 Hz, 1H), 7.19 (t, *J*= 7.5 Hz, 1H), 6.99 (d, *J*= 6 Hz, 2H), 6.88 (d, *J*= 6 Hz, 2H), 6.66 (d, *J*= 6 Hz, 1H), 6.57 (d, *J*= 3 Hz, 1H), 5.62 (d, *J*= 3 Hz, 1H), 4.48 (t, *J*= 3 Hz, 1H), 2.81 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 169.3, 144.5, 138.2, 136.3, 131.2, 129.2, 129.1, 128.5, 124.6, 124.2, 123.4, 123.0, 108.6, 85.3, 55.6, 25.9, 21.0; HRMS (EI) Calcd. for C20H17NO3 $[M]^+$: 319.1208, Found: 319.1210.

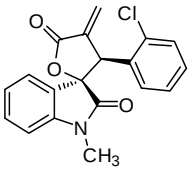
(2*R*,3*R*)-1'-methyl-4-methylene-3-(o-tolyl)-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3i)



Reaction time: 20 h; White solid, $[a]_D^{20}$= +71.8 (*c* 0.13, $CHCl_3$), 58% yield, >20:1 dr, 90% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 11.5 min, t_{minor} = 10.9min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.55 (d, *J*= 9 Hz, 1H), 7.44-7.34 (m, 2H), 7.18-7.11 (m, 3H), 6.97 (d, *J*= 6 Hz, 1H), 6.67 (d, *J*= 6 Hz, 1H), 6.55 (d, *J*=3 Hz, 1H), 5.51 (d, *J*=3 Hz, 1H), 4.89 (t, *J*= 3 Hz, 1H), 2.83 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 169.3, 144.3, 137.7, 137.6, 131.3, 130.6, 130.2, 129.7, 128.1, 125.0, 124.6, 124.0, 123.3, 123.2, 108.7, 85.4, 51.2, 26.0, 19.3; HRMS (EI) Calcd. for C20H17NO3 $[M]^+$: 319.1208, Found: 319.1210.

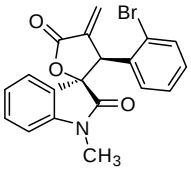
(2*R*,3*S*)-3-(2-chlorophenyl)-1'-methyl-4-methylene-3H-spiro[furan-2,3'-indoline]-

2',5(4H)-dione (3j)



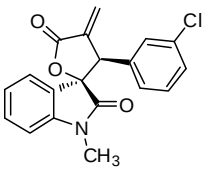
Reaction time: 18 h; Red solid, $[a]_D^{20}$= +87.0 (*c* 0.28, $CHCl_3$), 29% yield, >20:1 dr, 92% ee; HPLC: Chiralcel IC column, hexane/*i*-PrOH = 50/50, flow rate 0.7 mL/min, UV detection at 254 nm, t_{major} = 28.0 min, t_{minor} = 39.7 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.57 (d, *J*= 6 Hz, 1H), 7.52 (d, *J*= 6 Hz, 1H), 7.40-7.34 (m, 1H), 7.25-7.13 (m, 4H), 6.69 (d, *J*= 6 Hz, 1H), 6.57 (d, *J*= 3 Hz, 1H), 5.50 (d, *J*= 3 Hz, 1H), 5.29 (t, *J*= 3 Hz, 1H), 2.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 168.8, 144.1, 137.0, 135.3, 131.3, 130.5, 129.6, 129.4, 128.8, 127.0, 125.5, 124.3, 123.3, 123.3, 108.6, 84.9, 50.4, 26.0; HRMS (EI) Calcd. for C19H14ClNO3 $[M]^+$: 339.0662, Found: 339.0669.

(2*R*,3*S*)-3-(2-bromophenyl)-1'-methyl-4-methylene-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3k)



Reaction time: 18 h; Light yellow solid, $[a]_D^{20}$= +120.0 (*c* 0.17, $CHCl_3$), 25% yield, >20:1 dr, 94% ee; HPLC: Chiralcel IC column, hexane/*i*-PrOH = 50/50, flow rate 0.7 mL/min, UV detection at 254 nm, t_{major} = 29.6 min, t_{minor} = 42.1 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.59 (d, *J*= 6 Hz, 1H), 7.51 (d, *J*= 6 Hz, 1H), 7.42-7.28 (m, 3H), 7.13 (t, *J*= 9 Hz, 2H), 6.69 (d, *J*= 6 Hz, 1H), 6.56 (d, *J*= 3 Hz, 1H), 5.49 (d, *J*= 3 Hz, 1H), 5.30 (t, *J*= 3 Hz, 1H), 2.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 168.7, 144.2, 137.3, 133.0, 132.9, 131.6, 131.3, 129.9, 128.8, 126.0, 125.9, 124.2, 123.4, 123.3, 108.6, 85.0, 53.0, 26.1; HRMS (EI) Calcd. for C19H14BrNO3 $[M]^+$: 383.0157, Found: 383.0165.

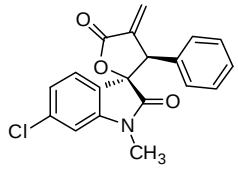
(2*R*,3*R*)-3-(3-chlorophenyl)-1'-methyl-4-methylene-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3l)



Reaction time: 34 h; White solid, $[a]_D^{20}$= +32.0 (*c* 0.29, $CHCl_3$), 67% yield, >20:1 dr, 83% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 24.6 min, t_{minor} = 13.9 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.53 (d, *J*= 6 Hz, 1H), 7.39 (t, *J*= 6 Hz, 1H), 7.24-7.15 (m, 3H), 6.95 (t, *J*= 9 Hz, 2H), 6.69 (d, *J*= 6 Hz, 1H), 6.60 (d, *J*= 3 Hz, 1H), 5.64 (d, *J*= 3 Hz, 1H), 4.47 (d, *J*= 3 Hz, 1H),

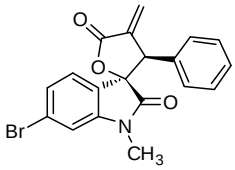
2.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 168.7, 144.4, 135.7, 134.3, 133.9, 131.6, 129.8, 129.4, 128.8, 127.5, 124.2, 123.6, 123.5, 108.8, 84.9, 55.4, 26.0; HRMS (EI) Calcd. for C19H14ClNO3 $[M]^+$: 339.0662, Found: 339.0662.

(2*R*,3*R*)-6'-chloro-1'-methyl-4-methylene-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3m)



Reaction time: 24 h; Light yellow solid, $[a]_D^{20}$= -2.0 (*c* 0.13, $CHCl_3$), 68% yield, >20:1 dr, 60% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 13.3 min, t_{minor} = 11.3 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.47 (d, *J*= 6 Hz, 1H), 7.24-7.17 (m, 4H), 7.00 (d, *J*= 6 Hz, 2H), 6.66 (s, 1H), 6.61 (d, *J*= 3 Hz, 1H), 5.67 (d, *J*= 3 Hz, 1H), 4.48 (t, *J*= 3 Hz, 1H), 2.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 168.9, 145.6, 137.3, 135.6, 131.3, 129.2, 128.8, 128.7, 128.6, 125.2, 123.7, 123.3, 109.5, 84.7, 55.9, 26.0; HRMS (EI) Calcd. for C19H14ClNO3 $[M]^+$: 339.0662, Found: 339.0655.

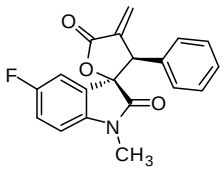
(2*R*,3*R*)-6'-bromo-1'-methyl-4-methylene-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3n)



Reaction time: 44 h; White solid, $[a]_D^{20}$= -2.0 (*c* 0.16, $CHCl_3$), 62% yield, >20:1 dr, 86% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 13.3 min, t_{minor} = 11.3 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.41 (d, *J*= 6 Hz, 1H), 7.34 (dd, *J*= 1.5 Hz, 1H), 7.26-7.21 (m, 3H), 7.00 (dd, *J*= 1.5 Hz, 2H), 6.81 (d, *J*= 1.5 Hz, 1H), 6.60 (d, *J*= 3 Hz, 1H), 5.66 (d, *J*= 3 Hz, 1H), 4.48 (t, *J*= 3 Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 168.9, 145.7, 135.6, 131.3, 129.2, 128.7, 128.6, 126.3, 125.5, 125.2, 123.6, 123.4, 112.2, 84.8, 55.9, 26.0; HRMS (EI) Calcd. for C19H14BrNO3 $[M]^+$: 383.0157, Found: 383.0161.

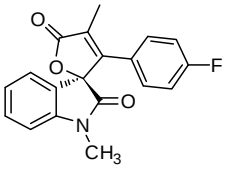
(2*R*,3*R*)-5'-fluoro-1'-methyl-4-methylene-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (3o)

Reaction time: 44 h; White solid, $[a]_D^{20}$= +1.2 (*c* 0.32, $CHCl_3$), 41% yield, >20:1 dr, 86% ee; HPLC: Chiralcel AD-H column, hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, UV detection at 254 nm, t_{major} = 15.7 min, t_{minor} = 13.1 min; ^{1}H NMR (300 MHz,



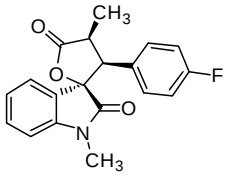
$CDCl_3$), δ 7.32-7.18 (m, 4H), 7.12-7.00 (m, 3H), 6.60 (d, *J*= 3 Hz, 1H), 6.57 (s, 1H), 5.66 (d, *J*= 3 Hz, 1H), 4.47 (s, 1H), 2.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 168.7, 159.3 (d, *J*= 241.7 Hz, 1C), 140.3, 135.5, 131.2, 129.1, 128.6, 128.5, 123.6, 123.5, 117.6 (d, *J*= 23.4 Hz, 1C), 112.3 (d, *J*= 25.1 Hz, 1C), 109.3 (d, *J*= 7.8 Hz, 1C), 85.0, 56.0, 25.9; HRMS (EI) Calcd. for C19H14FNO3 $[M]^+$: 323.0958, Found: 323.0963.

(*R*)-3-(4-fluorophenyl)-1',4-dimethyl-5H-spiro[furan-2,3'-indoline]-2',5-dione 4



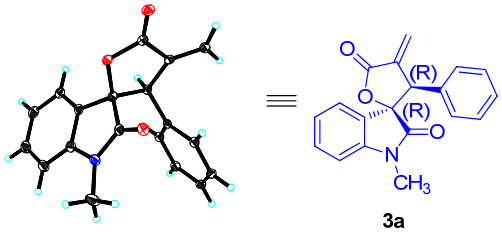
White solid, 41% yield, 84% ee; HPLC: Chiralcel IC column, hexane/*i*-PrOH = 50/50, flow rate 0.7 mL/min, UV detection at 254 nm, t_{major} = 29.6 min, t_{minor} = 42.1 min; ^1H NMR (300 MHz, $CDCl_3$), δ 7.39 (t, *J*= 6 Hz, 1H), 7.19 (d, *J*= 6 Hz, 1H), 7.10 (t, *J*= 6 Hz, 1H), 6.94 (d, *J*= 6 Hz, 4H), 6.85 (d, *J*= 6 Hz, 1H), 3.17 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 170.3, 163.2 (d, *J*= 249.6 Hz, 1C), 154.7, 144.4, 131.7, 129.6, 129.5, 127.4, 126.0, 124.2 (d, *J*= 69.5 Hz, 1C), 123.0, 116.1 (d, *J*= 21.6 Hz, 1C), 109.2, 86.2, 26,8, 10.3; HRMS (ESI) Calcd. for C19H14FNNaO3 $[M+Na]^+$: 346.0850, Found: 346.0843.

(2*R*,3*S*,4*S*)-3-(4-fluorophenyl)-1',4-dimethyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione 5



White solid, 38% yield, >99:1 dr; ^1H NMR (300 MHz, $CDCl_3$), δ 7.50 (d, *J*= 6 Hz, 1H), 7.37 (t, *J*= 6 Hz, 1H), 7.19 (t, *J*= 6 Hz, 1H), 6.93-6.83 (m, 4H), 6.67 (d, *J*= 9 Hz, 1H), 3.97-3.86 (m, 1H), 3.58 (d, *J*= 12 Hz, 1H), 2.84 (s, 3H), 1.26 (d, *J*= 6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 172.5, 162.5 (d, *J*= 246.1 Hz, 1C), 144.2, 131.3, 129.5 (d, *J*= 8.1 Hz, 1C), 127.4, 127.4, 124.7, 124.0, 123.5, 115.5 (d, *J*= 21.3 Hz, 1C), 108.6, 58.0, 37.3, 25.8, 13.4; HRMS (ESI) Calcd. for C19H16FNNaO3 $[M+Na]^+$: 348.1006, Found: 348.1001.

5. Crystal data for **3a** and **3g**

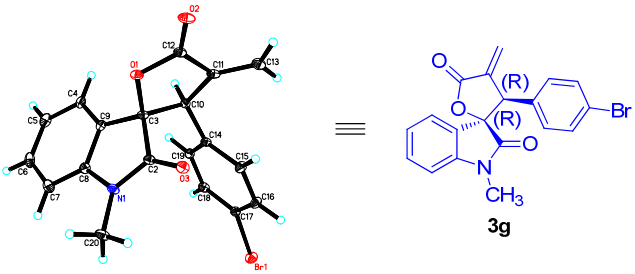


3a

Crystal data and structure refinement for **3a:** (CDCC number: CCDC 957865)

Identification code	**3a**
Empirical formula	C19 H15 N O3
Formula weight	305.32
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 10.3062(5) A alpha = 90 deg. b = 10.6362(6) A beta = 94.7880(10) deg. c = 14.2809(7) A gamma = 90 deg.
Volume	1559.99(14) A^3
Z, Calculated density	4, 1.300 Mg/m^3
Absorption coefficient	0.719 mm^-1
F(000)	640
Crystal size	1.50 x 0.27 x 0.18 mm
Theta range for data collection	3.11 to 69.21 deg.
Limiting indices	-12<=h<=12, -12<=k<=10, -17<=l<=17
Reflections collected / unique	12565 / 4420 [R(int) = 0.0402]
Completeness to theta = 69.21	92.2 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.8815 and 0.4120
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4420 / 1 / 418
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0769
R indices (all data)	R1 = 0.0292, wR2 = 0.0770
Absolute structure parameter	0.02(12)
Extinction coefficient	0.0080(5)
Largest diff. peak and hole	0.183 and -0.174 e.A^-3

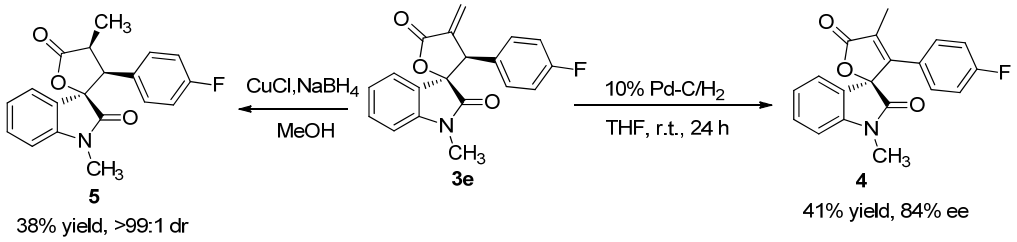


Crystal data and structure refinement for **3g:** (CDCC number: CCDC 929297)

Identification code	**3g**
Empirical formula	C19 H14 Br N O3
Formula weight	384.22
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 6.6858(12) A alpha = 90 deg. b = 13.781(2) A beta = 90 deg.

	c = 17.545(3) A gamma = 90 deg.
Volume	1616.5(5) A^3
Z, Calculated density	4, 1.579 Mg/m^3
Absorption coefficient	2.560 mm^-1
F(000)	776
Crystal size	0.60 x 0.50 x 0.04 mm
Theta range for data collection	1.88 to 30.09 deg.
Limiting indices	-9<=h<=9, -19<=k<=18, -24<=l<=24
Reflections collected / unique	15983 / 4490 [R(int) = 0.0487]
Completeness to theta = 30.09	96.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9045 and 0.3089
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4490 / 0 / 218
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0868
R indices (all data)	R1 = 0.0497, wR2 = 0.0938
Absolute structure parameter	0.030(9)
Largest diff. peak and hole	0.742 and -0.862 e.A^-3

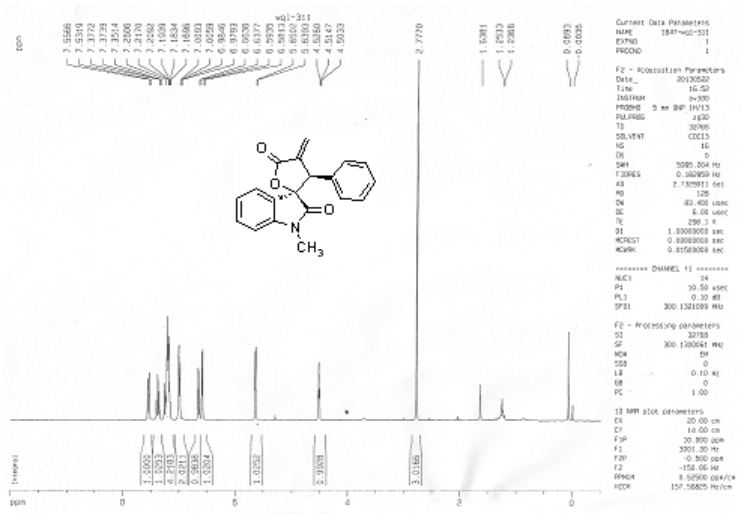
6. Synthesis of **4** and **5**

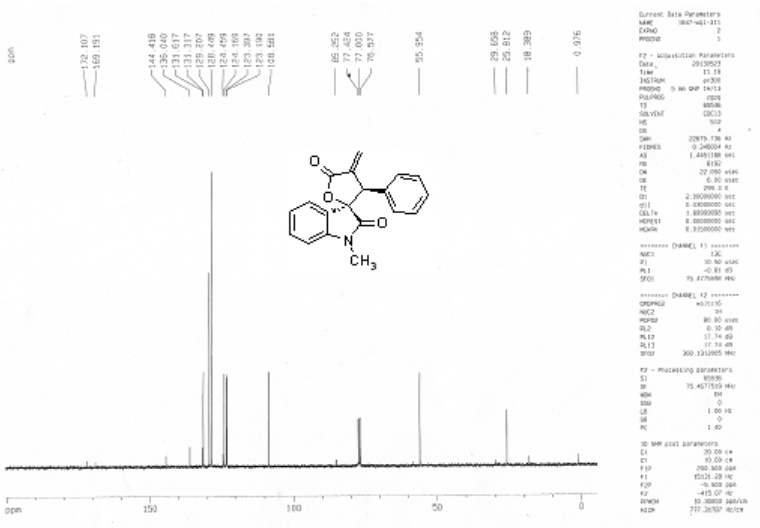


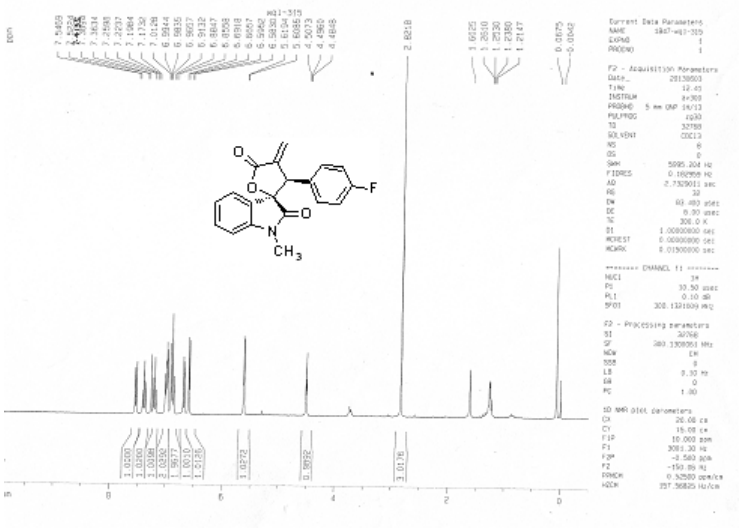
Typical Procedure for synthesis of **4**: To a solution of compound **3e** (0.1 g) in THF (9 mL) was added Pd/C (10 mg, 10% by weight on activated carbon). Hydrogenation was carried out under hydrogen atmosphere at room temperature and atmospheric pressure 12 h. Then, the reaction mixture was filtered and the filtrate was concentrated in vacuo. Purification of the residue by flash column chromatography afford the desired product **4** (41% yield, 84% ee).

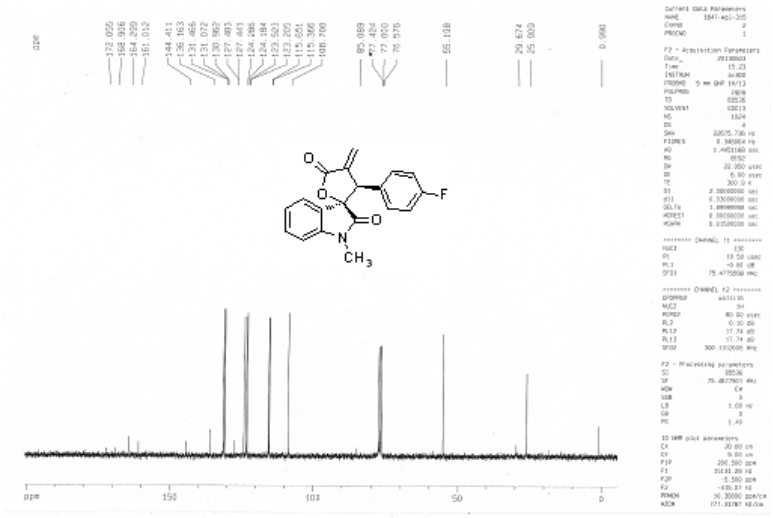
Typical Procedure for synthesis of **5**: To a solution of compound **3e** (56.4 mg) and CuCl (11.8 mg) in MeOH (1 mL) was added $NaBH_4$ (20.6 mg). The reaction was stirred at room temperature for 0.5 h. Then, water (1 mL) was added and the reaction mixture was acidized to pH 4-5 by HCl and extracted with CH_2Cl_2. Organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by flash column chromatography on silica gel to give the product **5** (38 % yield, >99:1 dr).

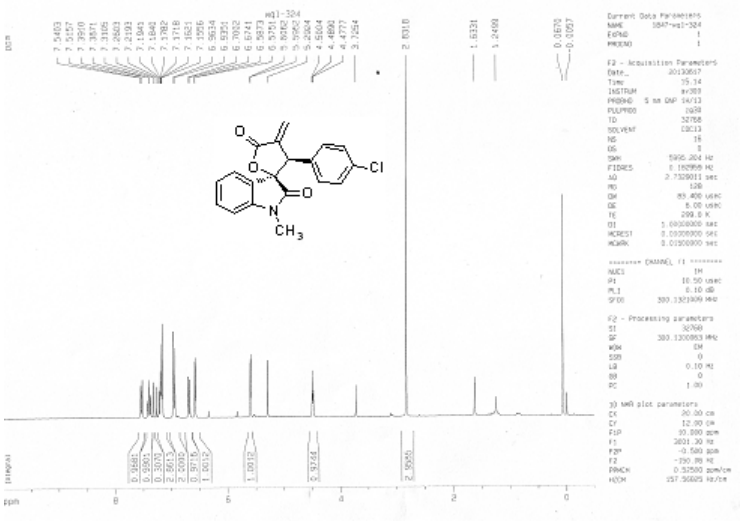
7. Selected ^{1}H NMR and ^{13}C NMR spectra

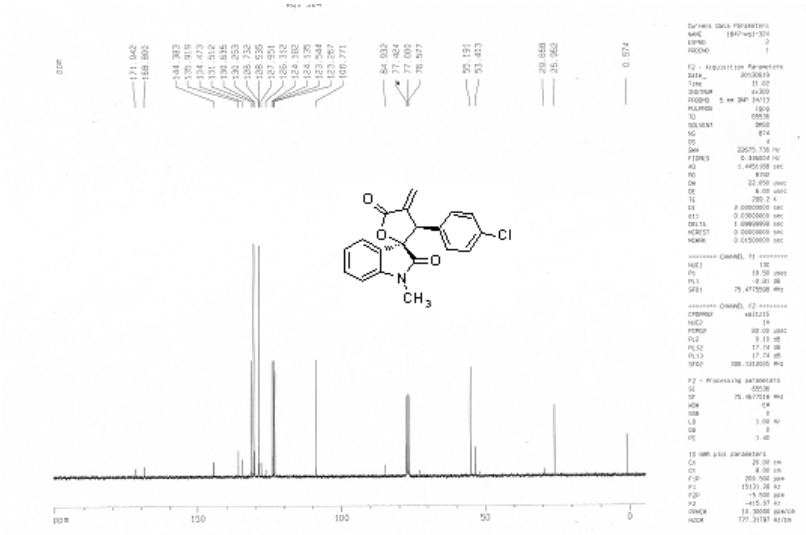


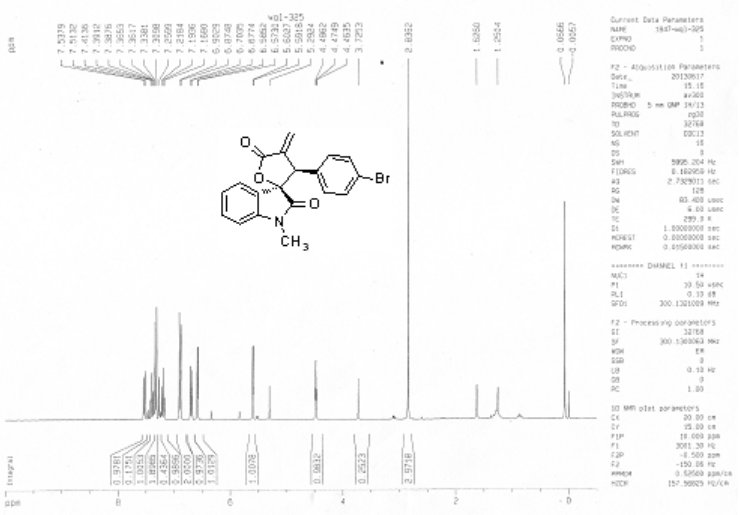


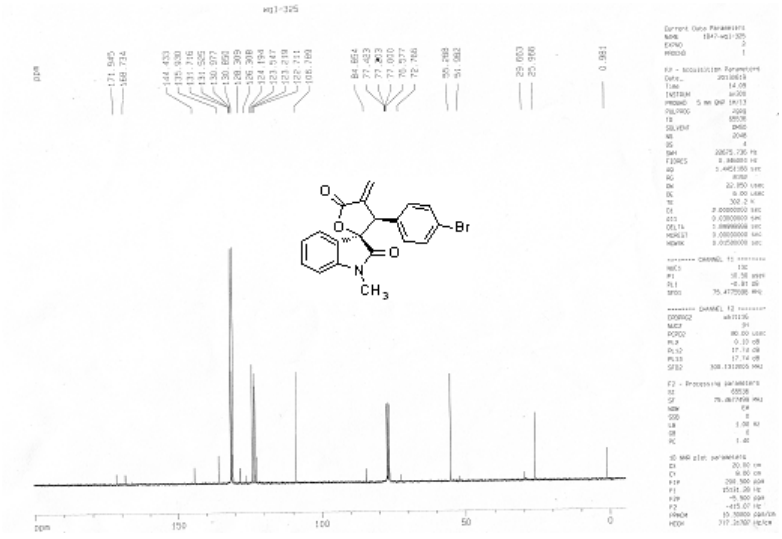


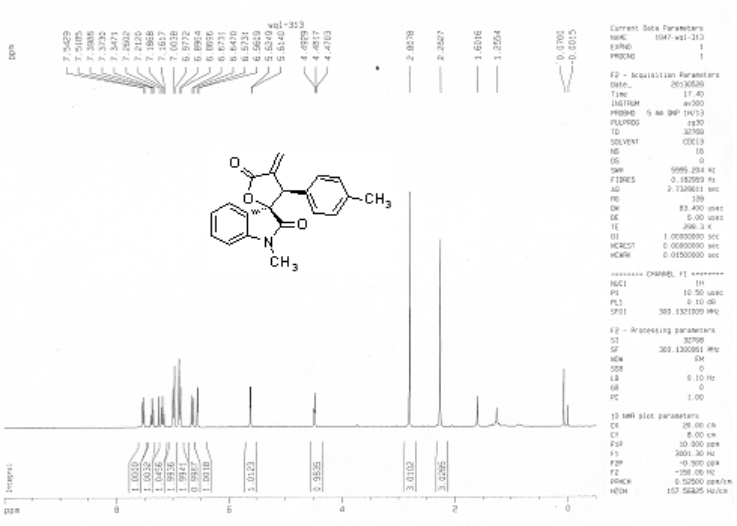


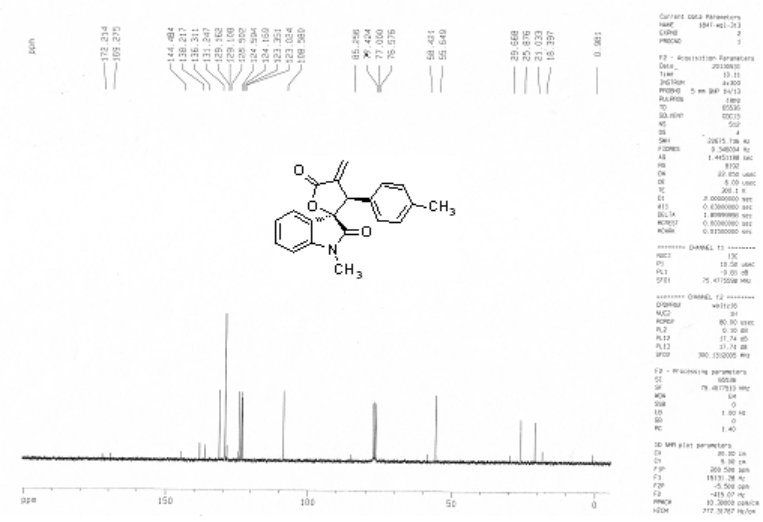


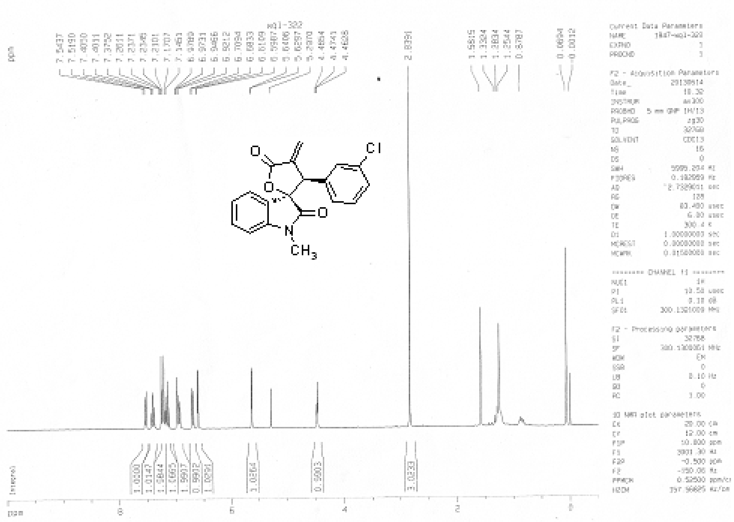


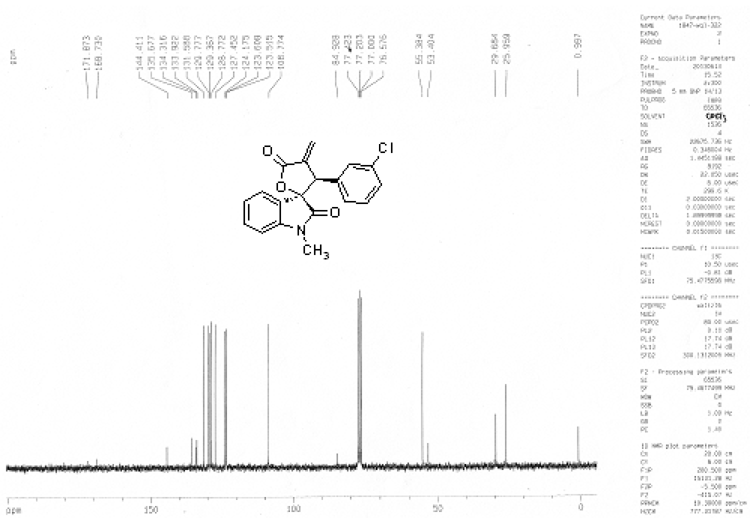


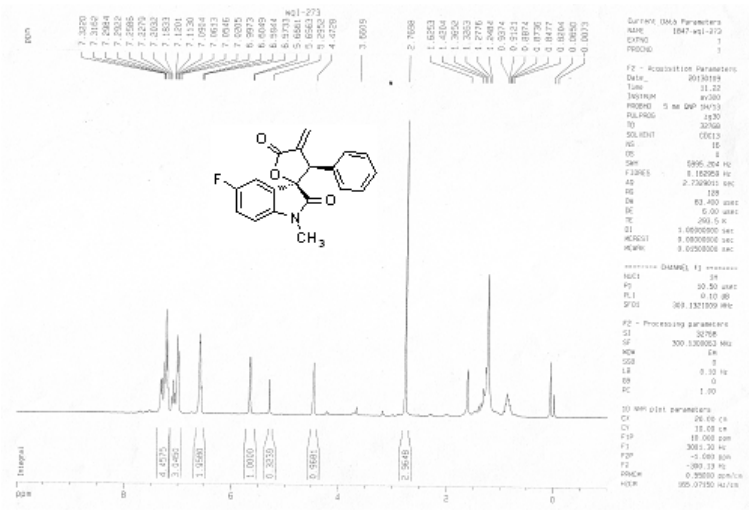


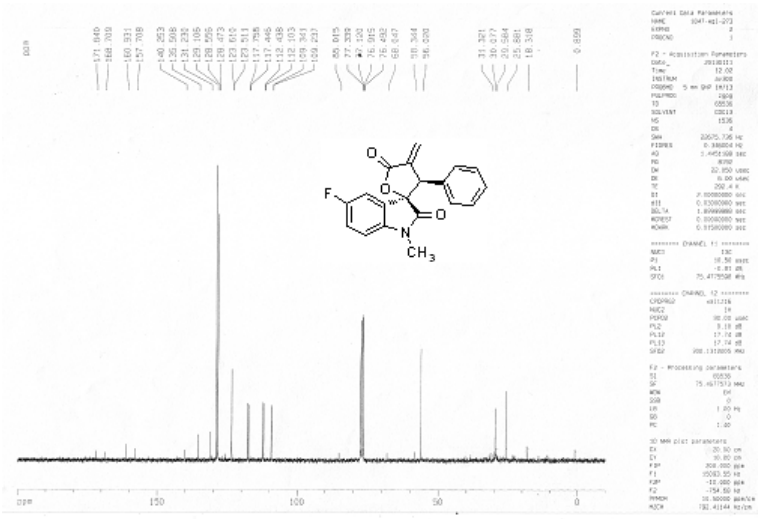


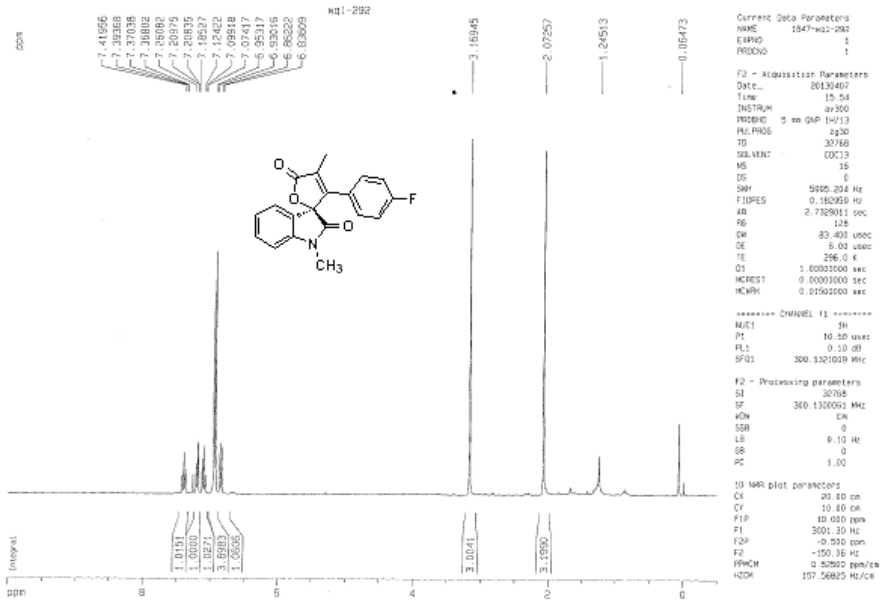








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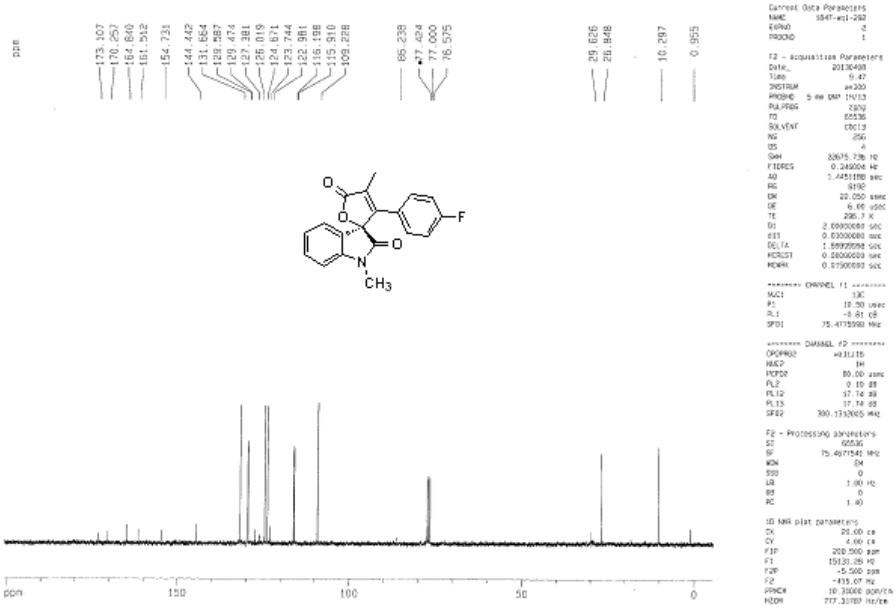
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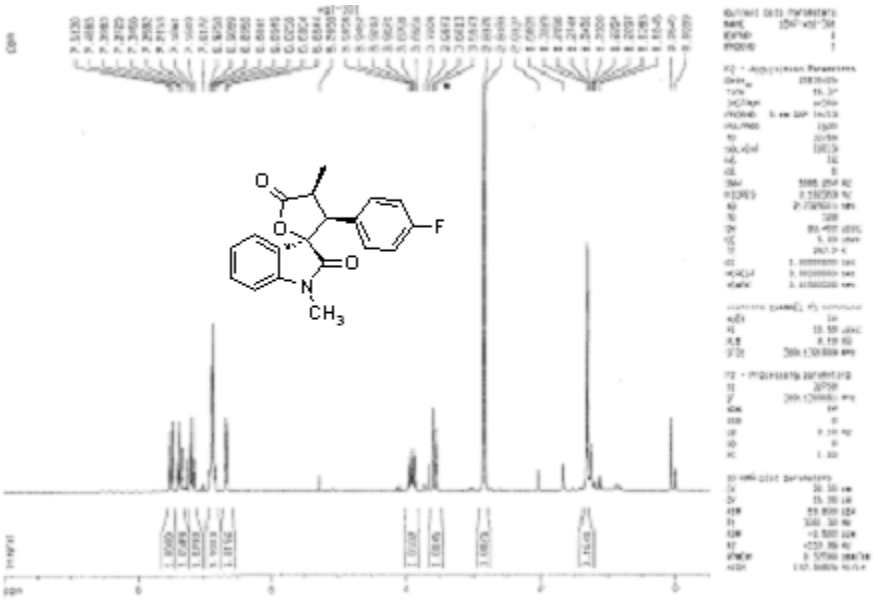
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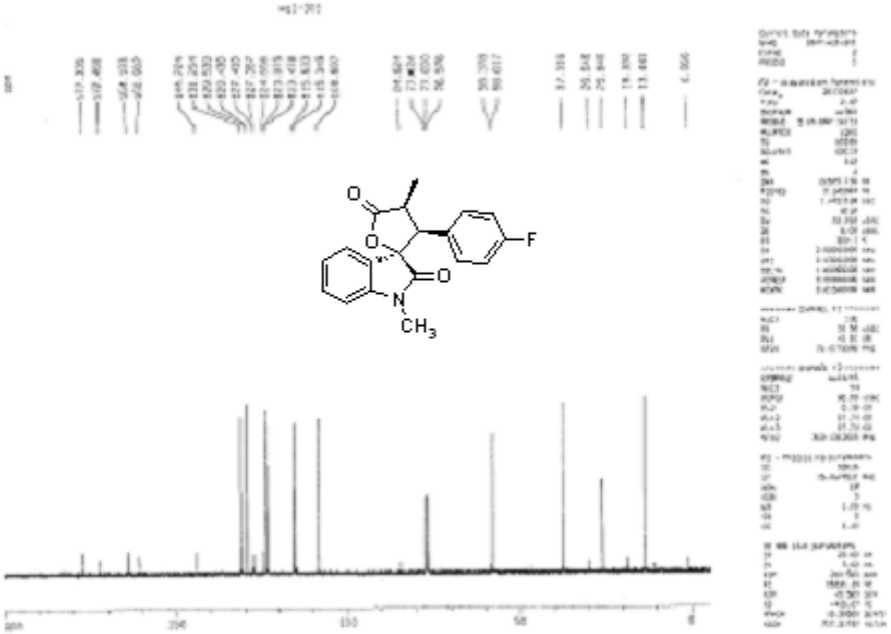
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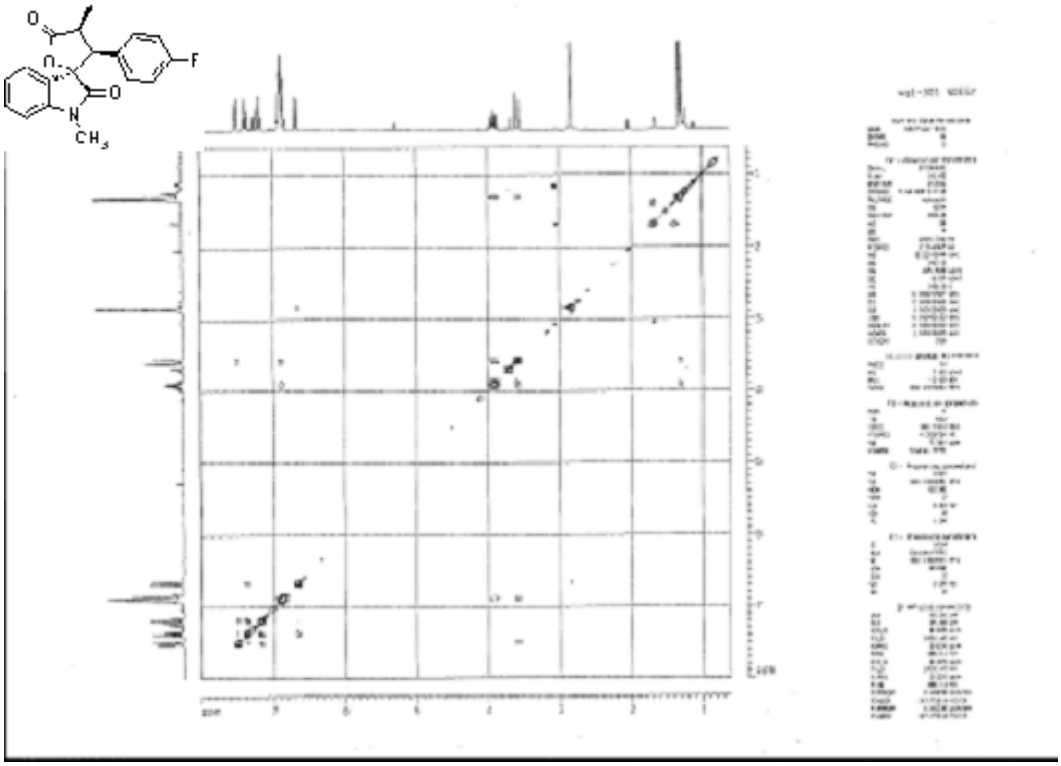
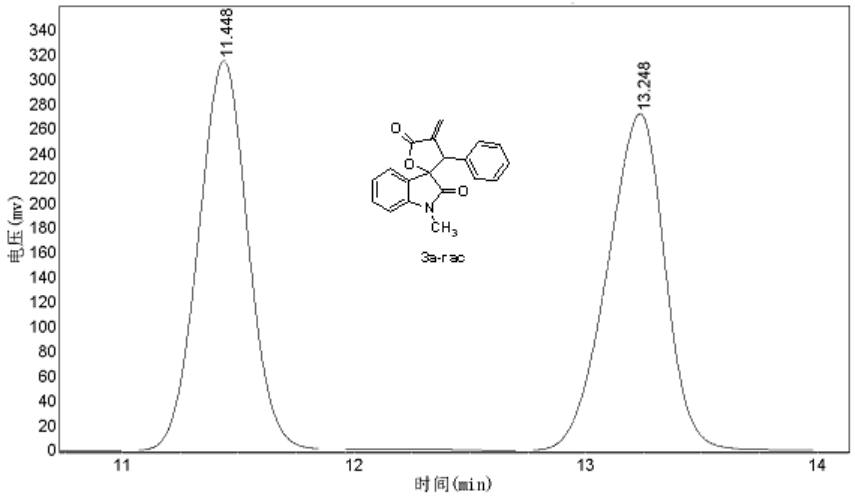
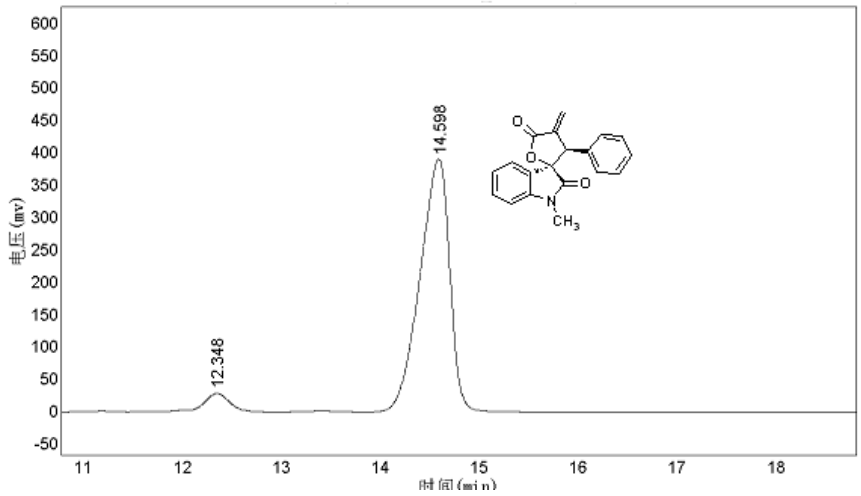


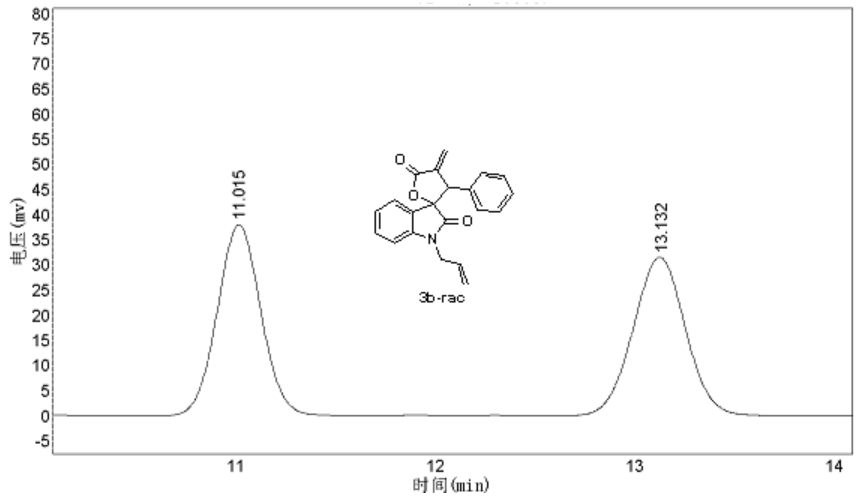
8. HPLC chromatograms



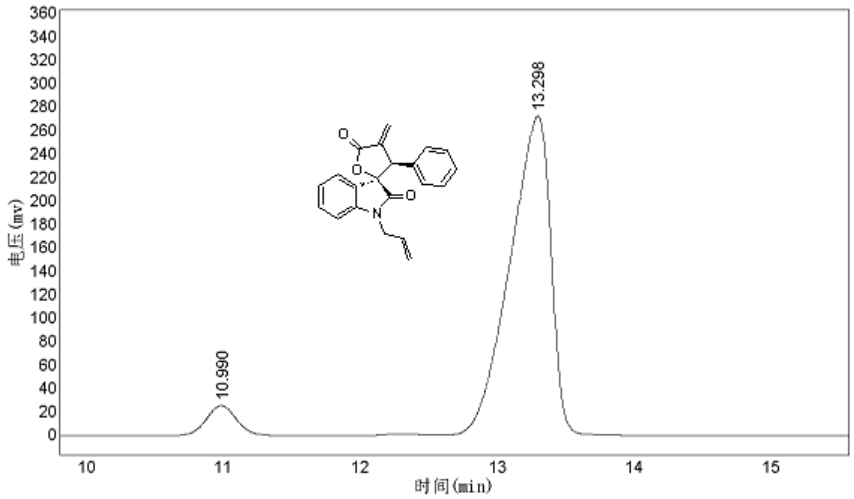
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.437	315088.719	4671135.500	49.7062
	13.233	272615.844	4726349.000	50.2938
Total		587704.563	9397484.500	100.0000



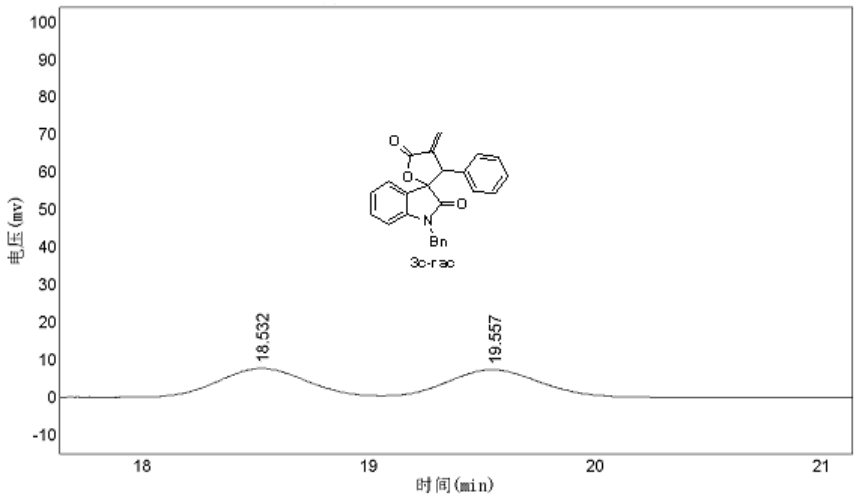
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.973	33235.953	549802.125	5.5871
	14.098	469699.250	9290689.000	94.4129
Total		502935.203	9840491.125	100.0000



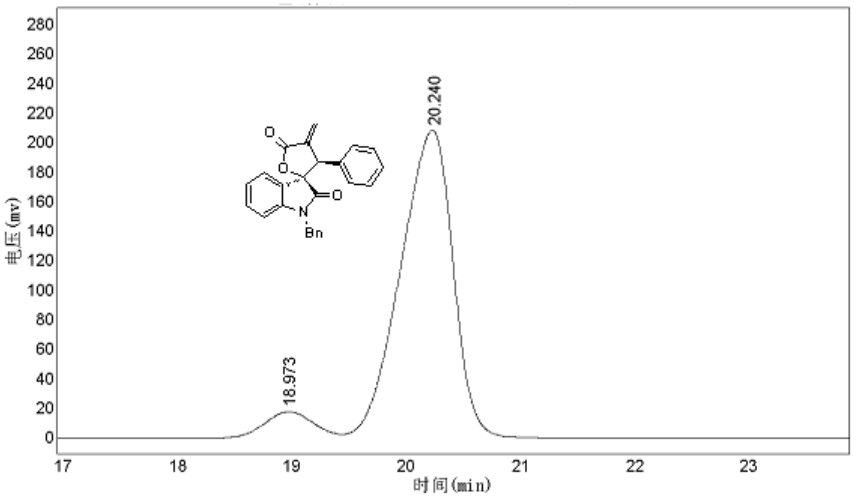
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.015	37957.766	577435.938	50.0903
	13.132	31473.609	575353.063	49.9097
Total		69431.375	1152789.000	100.0000



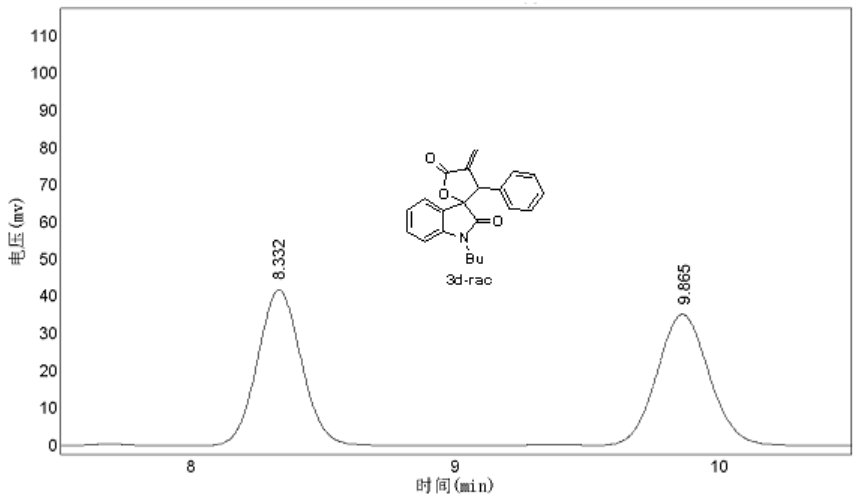
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	10.990	25378.072	385763.094	6.3968
	13.298	272046.344	5644839.500	93.6032
Total		297424.416	6030602.594	100.0000



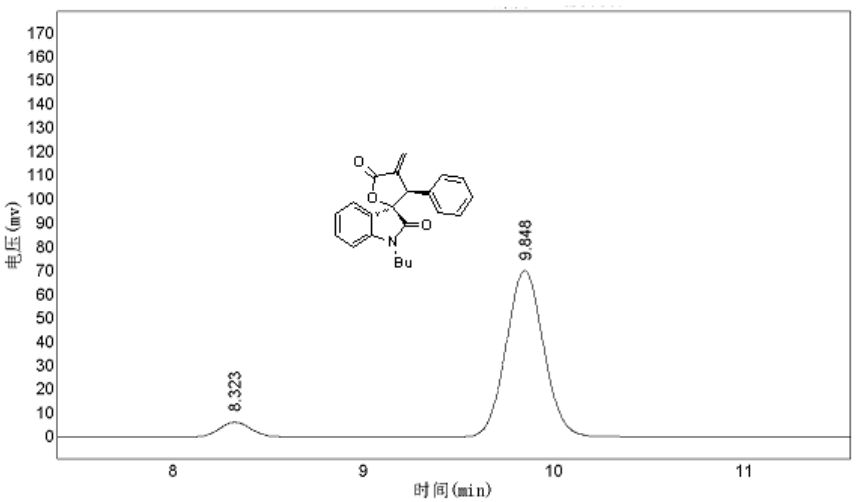
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	18.532	7479.294	198470.797	50.2540
	19.557	7115.297	196464.906	49.7460
Total		14594.591	394935.703	100.0000



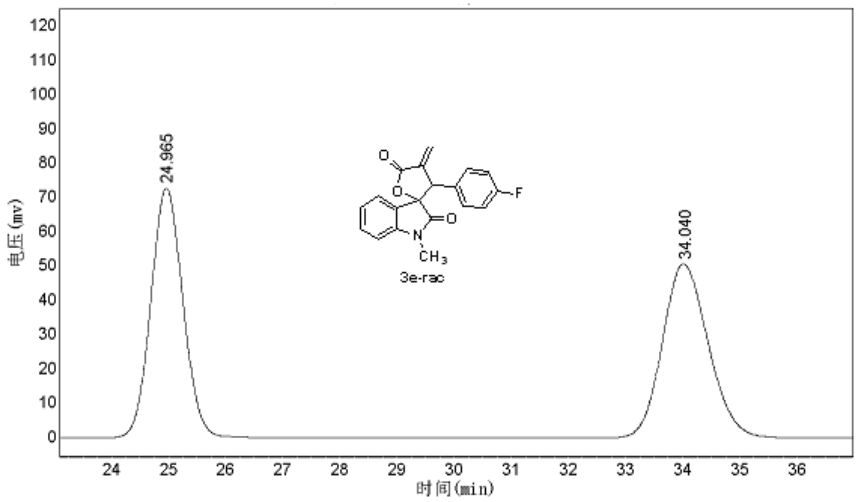
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	18.973	16154.353	432933.000	6.2240
	20.240	206777.703	6522970.500	93.7760
Total		222932.066	6955903.500	100.0000



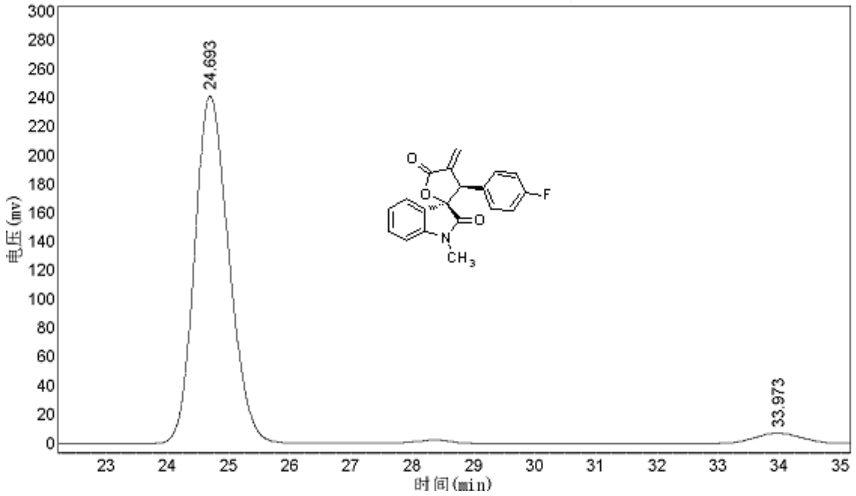
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	8.332	41685.160	479883.250	49.9972
	9.865	35120.695	479937.906	50.0028
Total		76805.855	959821.156	100.0000



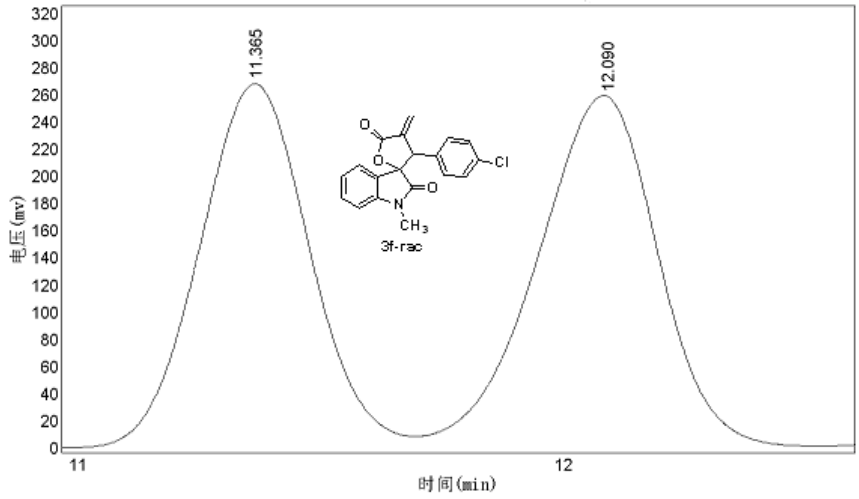
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	8.323	6301.765	72133.047	7.0084
	9.848	69946.266	957102.125	92.9916
Total		76248.030	1029235.172	100.0000



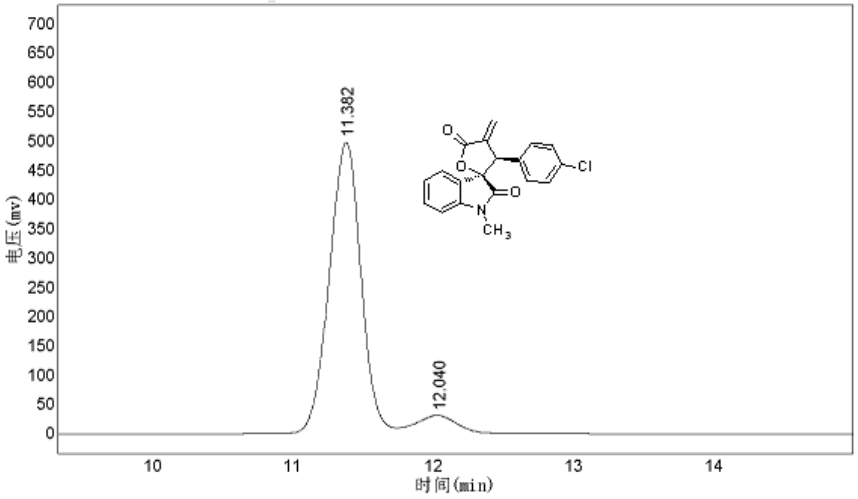
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	24.965	72658.953	2816216.000	49.8285
	34.040	50750.000	2835599.000	50.1715
Total		123408.953	5651815.000	100.0000



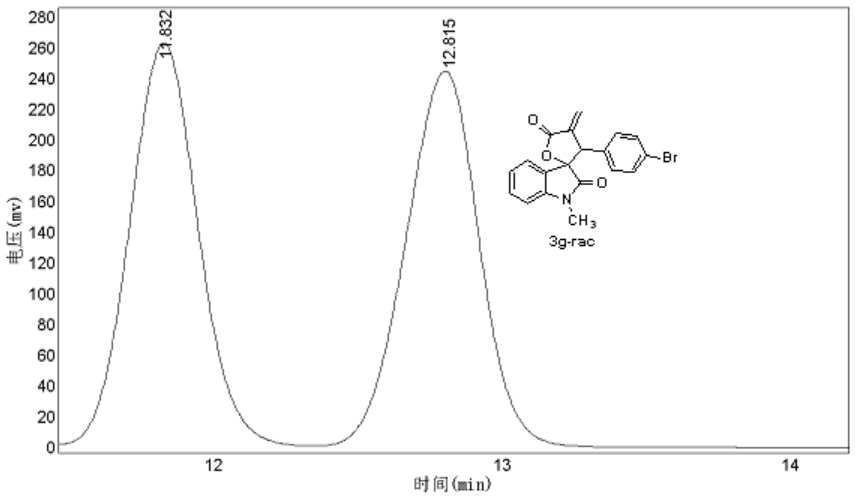
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	24.693	241457.047	9375720.000	96.0392
	33.973	7178.844	386664.438	3.9608
Total		248635.891	9762384.438	100.0000



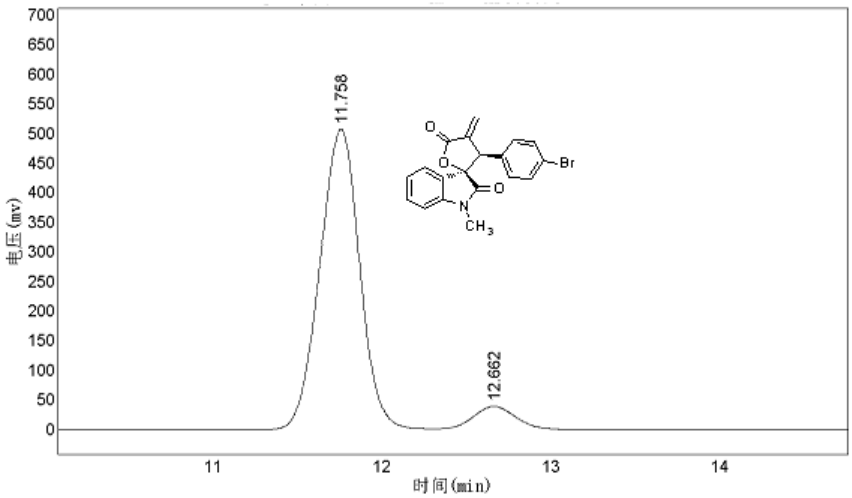
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.363	263482.719	4023938.000	48.5445
	12.082	254347.516	4265243.500	51.4555
Total		517830.234	8289181.500	100.0000



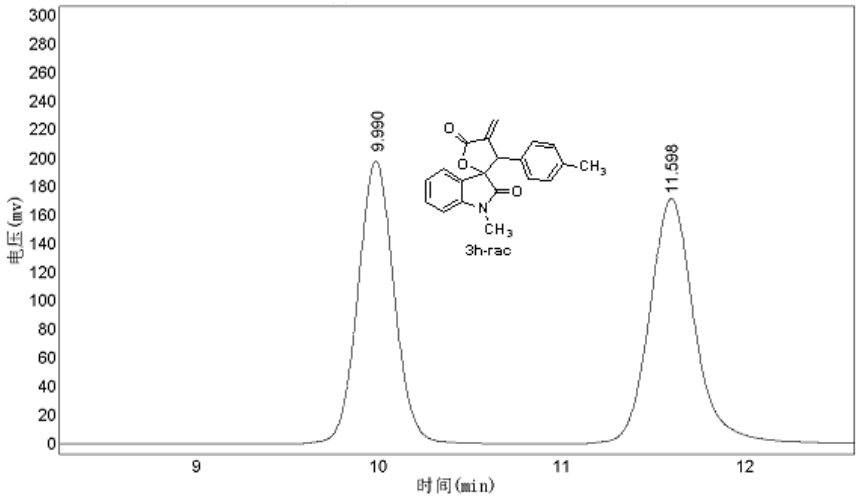
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.382	497336.656	7798620.000	92.4263
	12.040	31045.982	639044.125	7.5737
Total		528382.639	8437664.125	100.0000



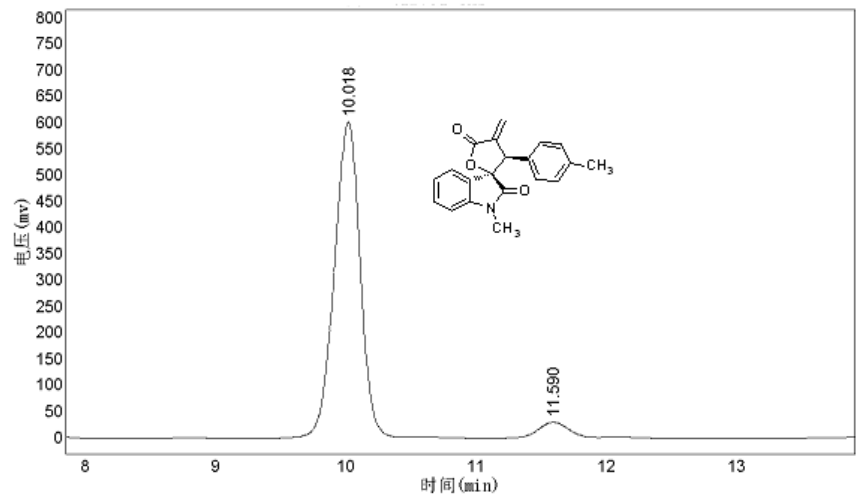
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.827	263552.344	4389133.500	50.0488
	12.802	245136.750	4380580.000	49.9512
Total		508689.094	8769713.500	100.0000



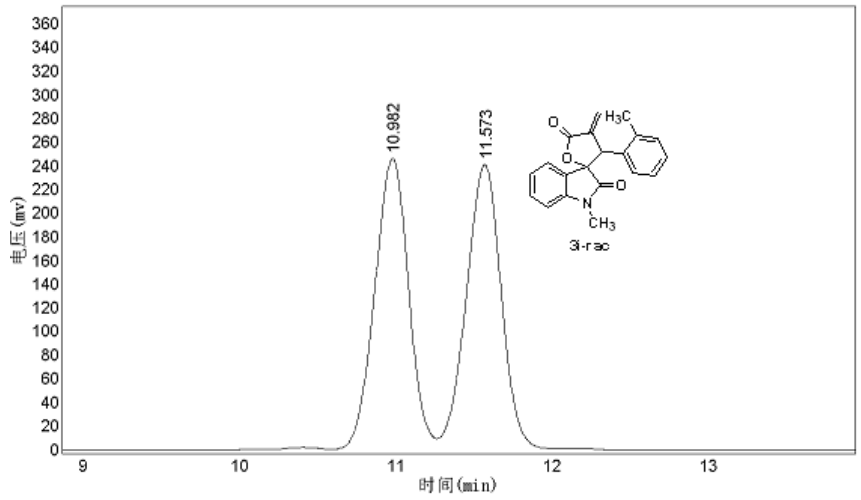
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.758	507594.313	8326933.500	92.0818
	12.662	39416.066	716037.938	7.9182
Total		547010.379	9042971.438	100.0000



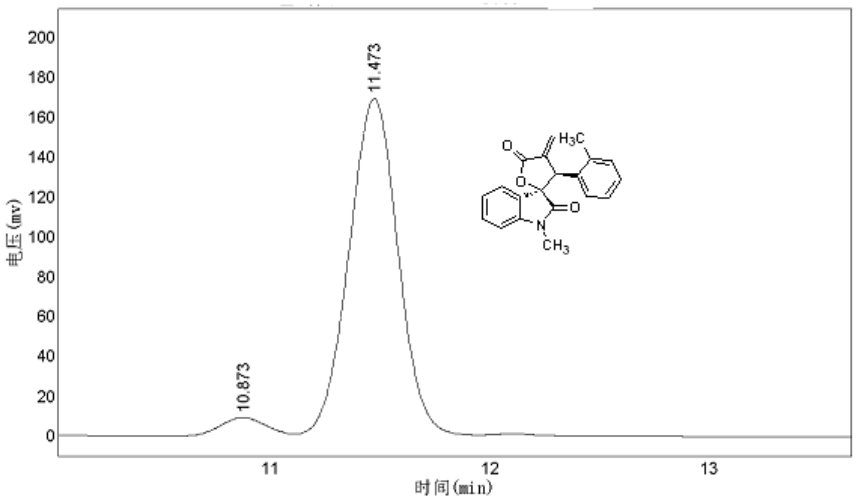
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	9.983	198000.469	2711347.500	48.3141
	11.598	171340.484	2900574.500	51.6859
Total		369340.953	5611922.000	100.0000



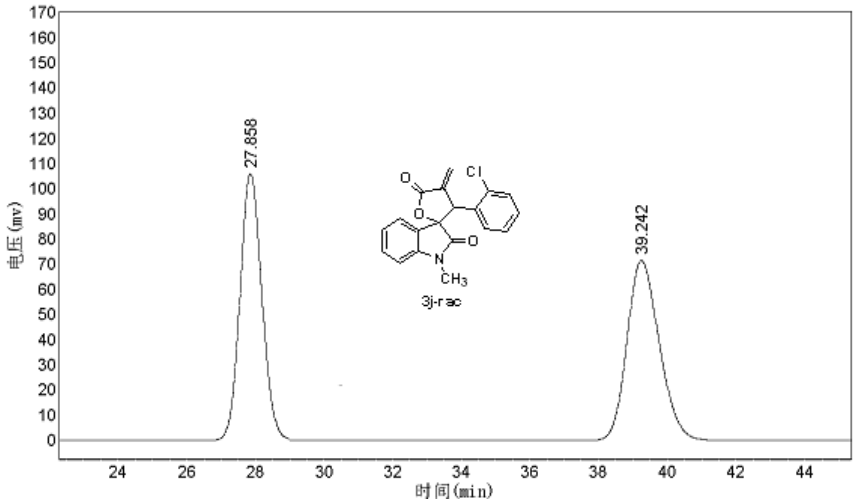
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	10.018	600581.563	8225243.500	94.4443
	11.590	30134.412	483854.531	5.5557
Total		630715.975	8709098.031	100.0000



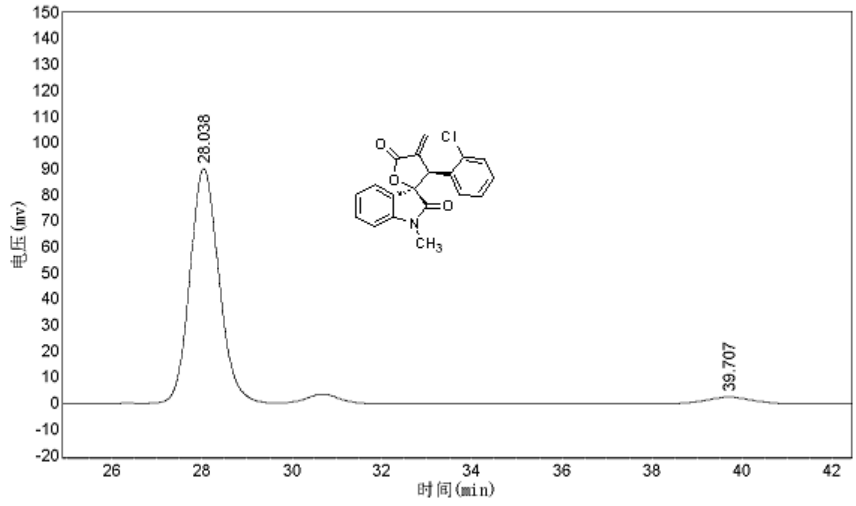
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	10.978	245978.125	3691413.000	49.7779
	11.568	240377.016	3724356.250	50.2221
Total		486355.141	7415769.250	100.0000



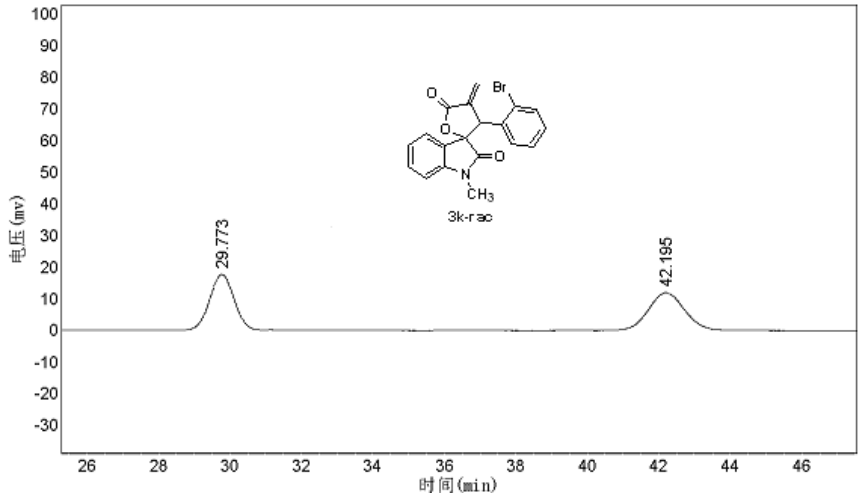
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	10.873	9245.301	133274.453	4.8407
	11.473	168831.156	2619950.250	95.1593
Total		178076.457	2753224.703	100.0000



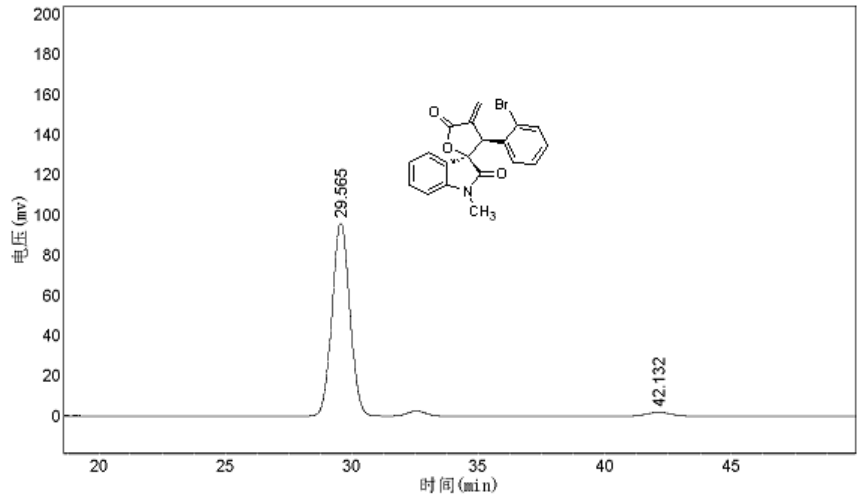
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	27.858	105887.945	4663323.000	49.8945
	39.242	71502.016	4683042.500	50.1055
Total		177389.961	9346365.500	100.0000



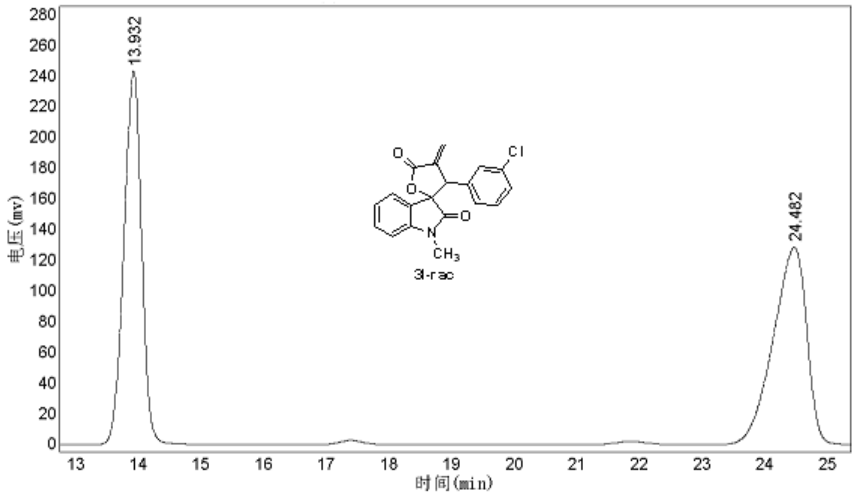
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	28.038	89745.000	4007469.750	96.2162
	39.707	2415.948	157597.094	3.7838
Total		92160.948	4165066.844	100.0000



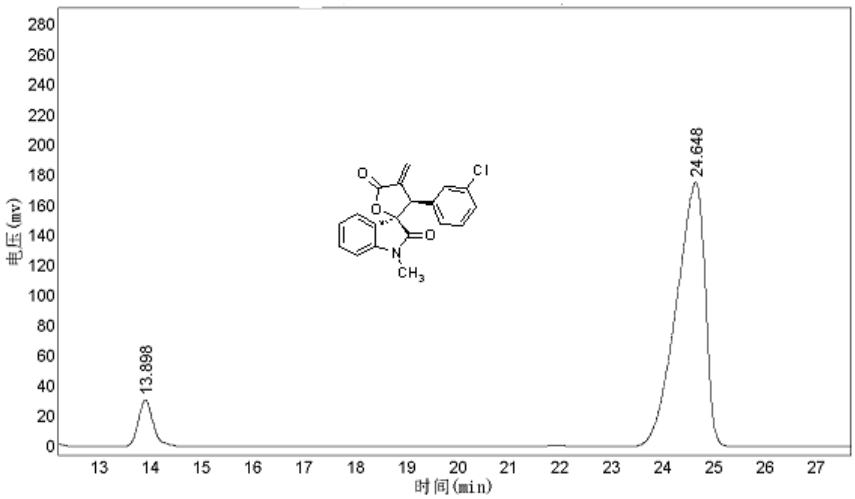
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	29.773	17587.975	826573.000	49.5655
	42.195	11949.759	841063.938	50.4345
Total		29537.733	1667636.938	100.0000



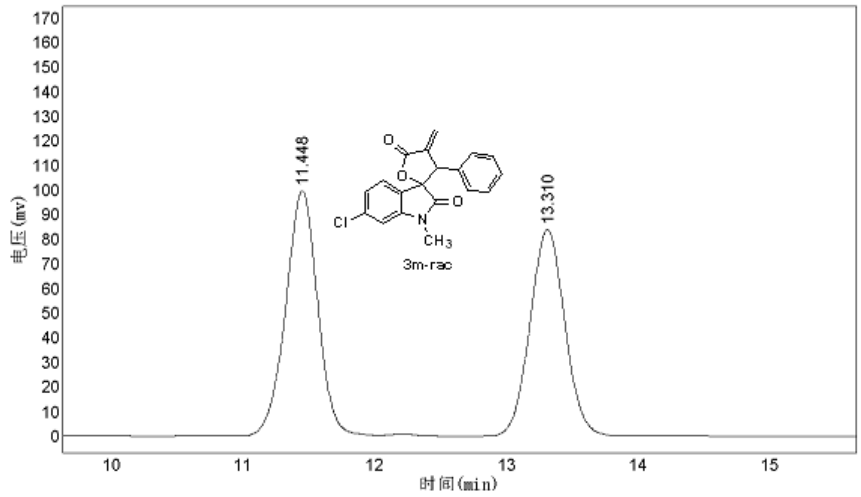
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	29.565	95969.883	4687834.000	97.1602
	42.132	2014.964	137017.203	2.8398
Total		97984.847	4824851.203	100.0000



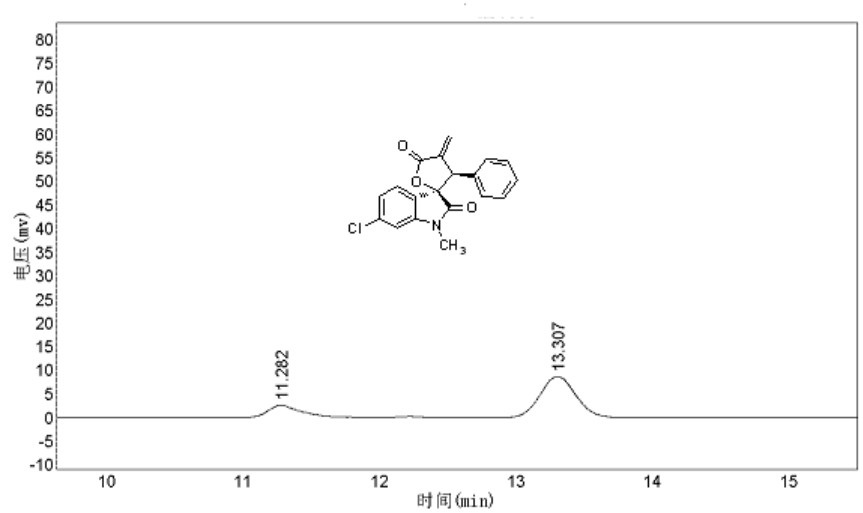
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	13.923	243525.594	4775505.000	50.0029
	24.468	128535.133	4774950.500	49.9971
Total		372060.727	9550455.500	100.0000



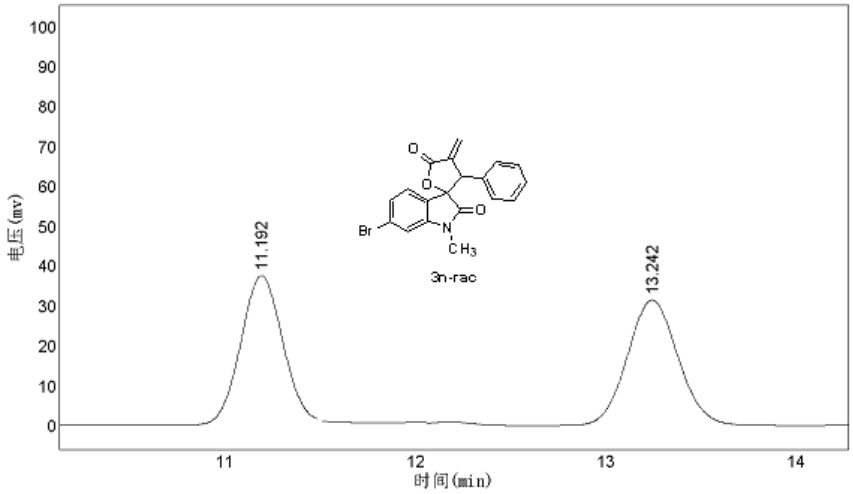
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	13.898	30938.406	626019.625	8.3600
	24.648	175552.719	6862243.000	91.6400
Total		206491.125	7488262.625	100.0000



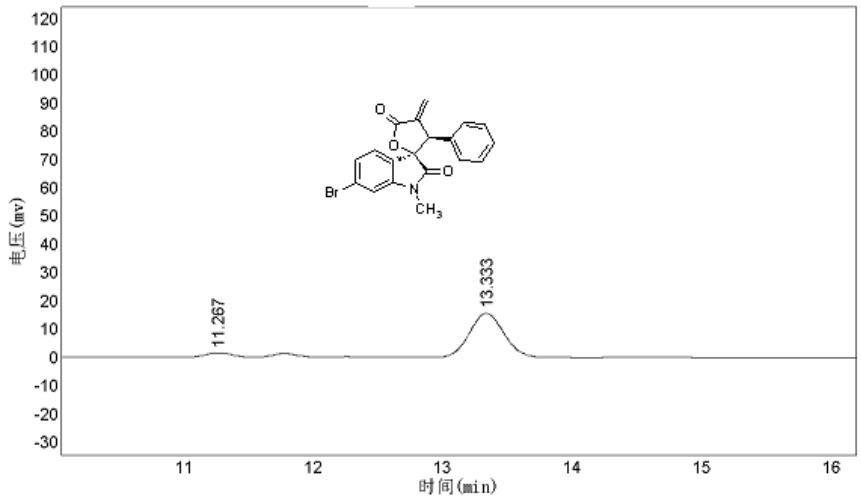
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.448	99608.977	1683634.500	52.1713
	13.310	83882.891	1543496.125	47.8287
Total		183491.867	3227130.625	100.0000



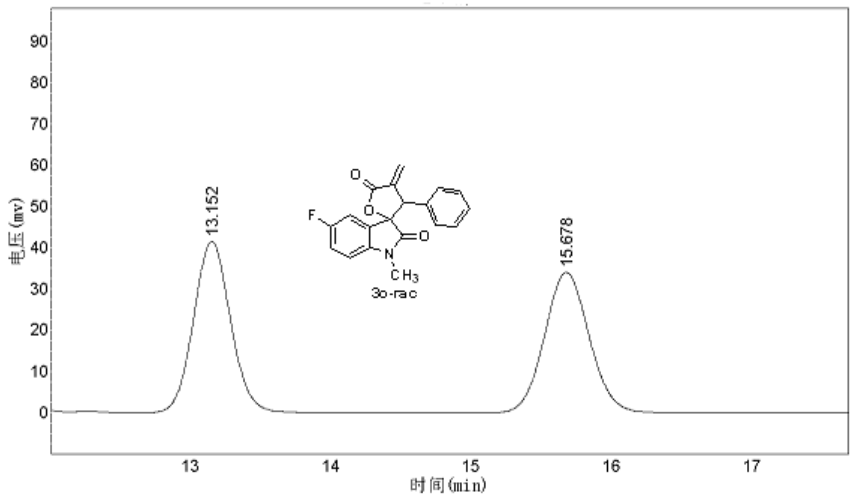
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.282	2488.532	40366.199	20.0572
	13.307	8758.616	160888.797	79.9428
Total		11247.148	201254.996	100.0000



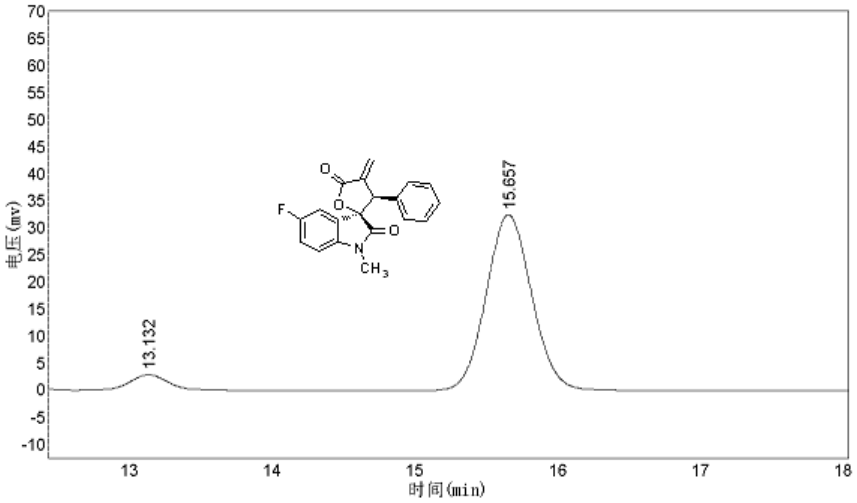
Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.192	37535.516	582728.063	49.8892
	13.242	31457.598	585316.313	50.1108
Total		68993.113	1168044.375	100.0000



Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	11.267	1492.625	21262.000	6.8362
	13.333	15627.075	289756.750	93.1638
Total		17119.700	311018.750	100.0000



Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	13.152	41501.289	760755.563	50.2785
	15.678	34021.707	752326.625	49.7215
Total		75522.996	1513082.188	100.0000



Peak	RT (min)	Height (mV*sec)	Area(mv)	Area (%)
	13.132	2868.000	53115.602	6.8724
	15.657	32487.039	719768.188	93.1276
Total		35355.039	772883.789	100.0000