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

Asymmetric [3+2] Annulation of N-protected Isatins with But-3-yn-2-one Catalyzed by DIOP: Facile Creation of Enantioenriched Spiro[furan-2,3'-indoline]-2',4(5H)-dione

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

Cat. 1, **Cat. 2**, **Cat. 4**, **Cat. 5**, **Cat. 7**, **Cat. 8**, **Cat. 9**, **Cat. 11**, **Cat. 12**, **Cat. 13** were purchased from J&K Chemical Ltd. and used directly without further purification. **Cat. 3**,[1] **Cat. 6**,[2] **Cat. 10**,[3] were prepared according to the previously reported procedures.

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2. General procedure for Cat. 13-catalyzed [3+2] annulation of N-protected isatins 1 with but-3-yn-2-one: N-protected isatin **1** (0.1 mmol), but-3-yn-2-one **2** (0.15 mmol), **Cat. 13** (0.02 mmol), and Et_2O (0.5 mL) were added into a Schlenk tube. The reaction mixture was stirred at -20 ^oC for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/EA = 10/1~5/1).

The reactions were initially carried out on a 0.1 mmol scale with 20 mol% chiral phosphine catalysts under Ar in THF (0.5 mL) at room temperature for 24 h and the ratio of **1a**/**2** was 1.0/1.5 (Figure S1). First, chiral bidentate phosphine catalysts **Cat. 1**, **Cat. 4**, **Cat. 5**, **Cat. 7**, **Cat. 8**, **Cat. 12** were tested in this asymmetric [3+2] cycloaddition of **1a** with **2**. We found that **Cat. 1** led to the formation of the desired products **3a** in moderate yield along with 6% ee value and **Cat. 4**, **Cat. 5**, **Cat. 7**, **Cat. 8**, **Cat. 12** had no catalytic activity in this reaction. Using monodentate chiral phosphine such as the eight-membered spirocyclic phosphine **Cat. 2** as the catalyst, the reaction also nearly could not proceed. We then turned to test some bifunctional phosphine catalysts involving some substitutes, such as OH group, NH group, which could provide good opportunity to form a hydrogen bond. Chiral binaphthyl-derived bifunctional thiourea-phosphine catalysts **Cat. 6**, **Cat. 9** and **Cat. 11** did not promote the reaction either. L-valine-derived bifunctional thiourea-phosphine **Cat. 10** was also examined, but giving the desired product in 13% ee value. Subsequently, D-threonine-L-tert-leucine-derived bifunctional phosphine **Cat. 3** developed by Lu's group[3] was examined, giving **3a** in 52% yield and 20% ee within 24 h. Gratifyingly, we found that **Cat. 13** (named as DIOP) was the most effective catalyst in this reaction, giving **3a** in 84% yield and 43% ee within 24 h.

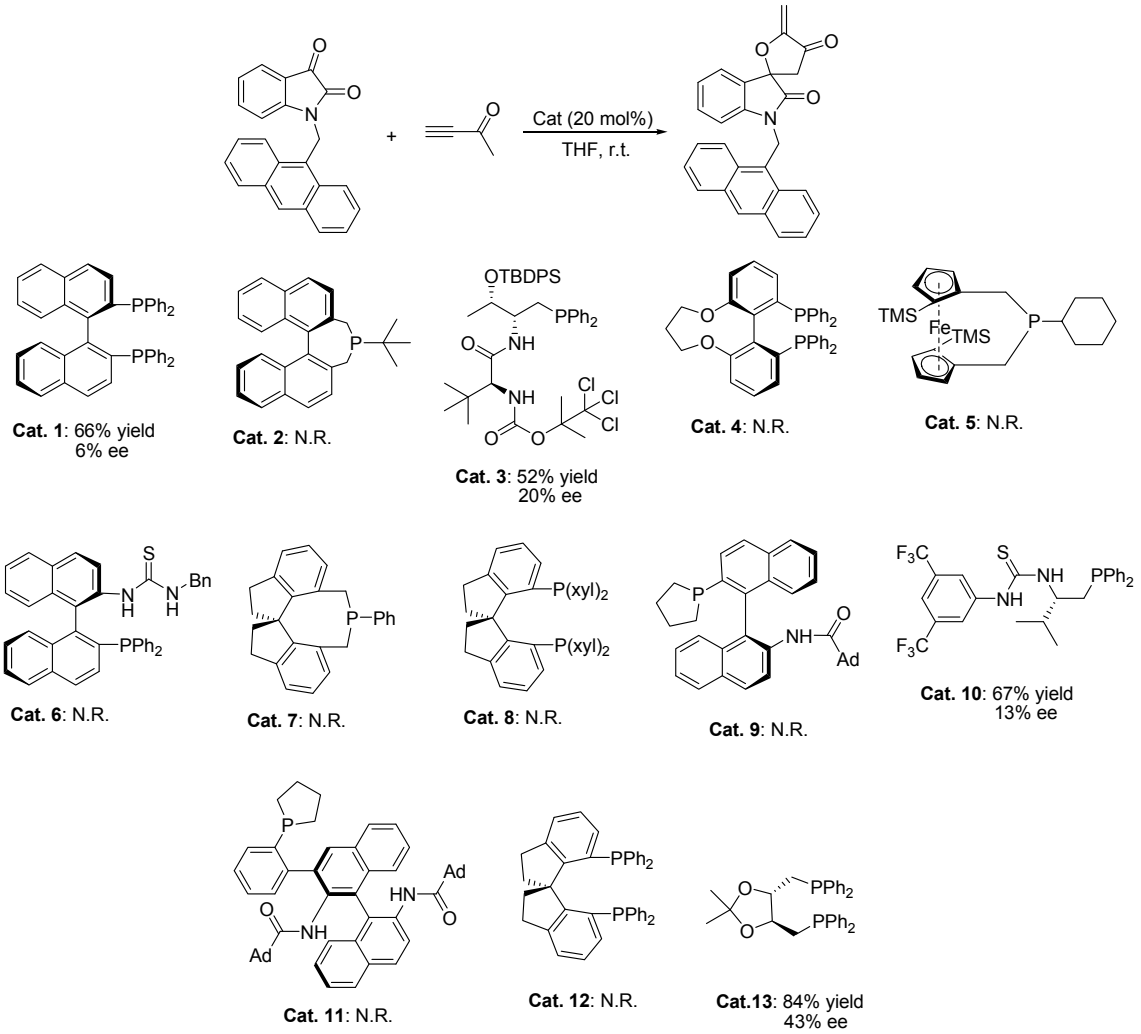

Figure SI-1. Screening of Chiral Phosphine Catalysts for the Asymmetric [3+2] Cycloaddition.

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3. References

1. (a) Y.-L. Yang, C.-K. Pei, M. Shi, *Org. Biomol. Chem.* **2011**, *9*, 3349. (b) Y.-L. Shi, M. Shi, *Adv. Synth. Catal.* **2007**, *349*, 2129. (c) H.-P. Deng, Y. Wei, M. Shi, *Eur. J. Org. Chem.* **2011**, 1956.

2. J.-J. Gong, K. Yuan, X.-Y. Wu, *Tetrahedron: Asymmetry* **2009**, *20*, 2117.

3. X. Han, Y. Wang, F. Zhong, Y. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 1726.

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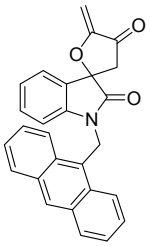
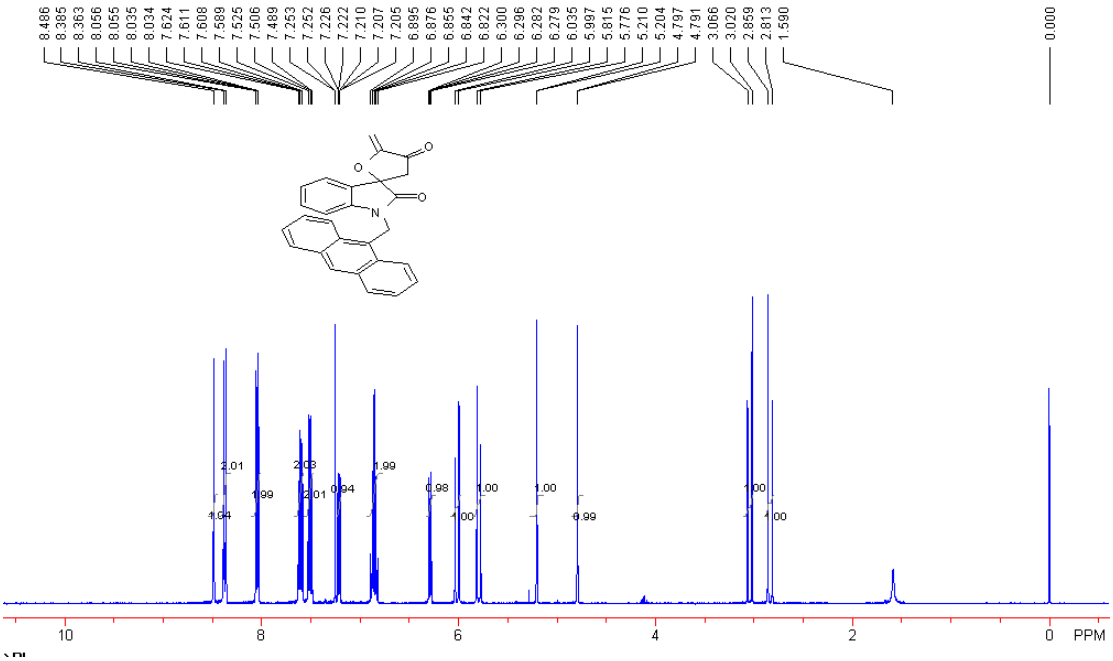
4. Characterization and spectra charts containing HPLC traces for products.



1'-(anthracen-9-ylmethyl)-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3a). 28 mg, 67% yield. mp. 299-301 ^{o}C (the racemate of compound **3a**. mp. 295-300 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.83 (d, 1H, J = 18.4 Hz, CH_2), 3.04 (d, 1H, J = 18.4 Hz, CH_2), 4.79 (d, 1H, J = 2.4 Hz, =CH_2), 5.21 (d, 1H, J = 2.4 Hz, =CH_2), 5.79 (d, 1H, J = 15.6 Hz, CH_2), 6.01 (d, 1H, J = 15.6 Hz, CH_2), 6.28-6.30 (m, 1H, ArH), 6.82-6.90 (m, 2H, ArH), 7.21-7.23 (m, 1H, ArH), 7.49-7.53 (m, 2H, ArH), 7.59-7.62 (m, 2H, ArH), 8.04 (d, 2H, J = 8.4 Hz, ArH), 8.37 (d, 2H, J = 8.4 Hz, ArH), 8.49 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 37.7, 43.0, 80.0, 90.0, 111.0, 123.3, 123.8, 124.9, 125.2, 126.0, 126.5, 127.1, 129.2, 129.7, 130.8, 131.0, 131.3, 143.2, 152.7, 174.2, 196.2; IR (CH_2Cl_2): ν 2925, 2854, 1772, 1721, 1641, 1614, 1525, 1486, 1468, 1365, 1269, 1200, 1170, 1065, 981, 891, 784, 736, 704 cm^{-1}; MS (%) (ESI) *m/z* 428.1 $[M + Na]^+$ (100); HRMS (ESI) Calcd. for $C_{27}H_{19}NNaO_3$ $[M + Na]^+$ requires 428.1257, Found: 428.1276. $[\alpha]^{20}_D$ = -52.5 (c 0.5, CH_2Cl_2, 82% ee). Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 230 nm, t_{minor} = 22.19 min, t_{major} = 32.85min).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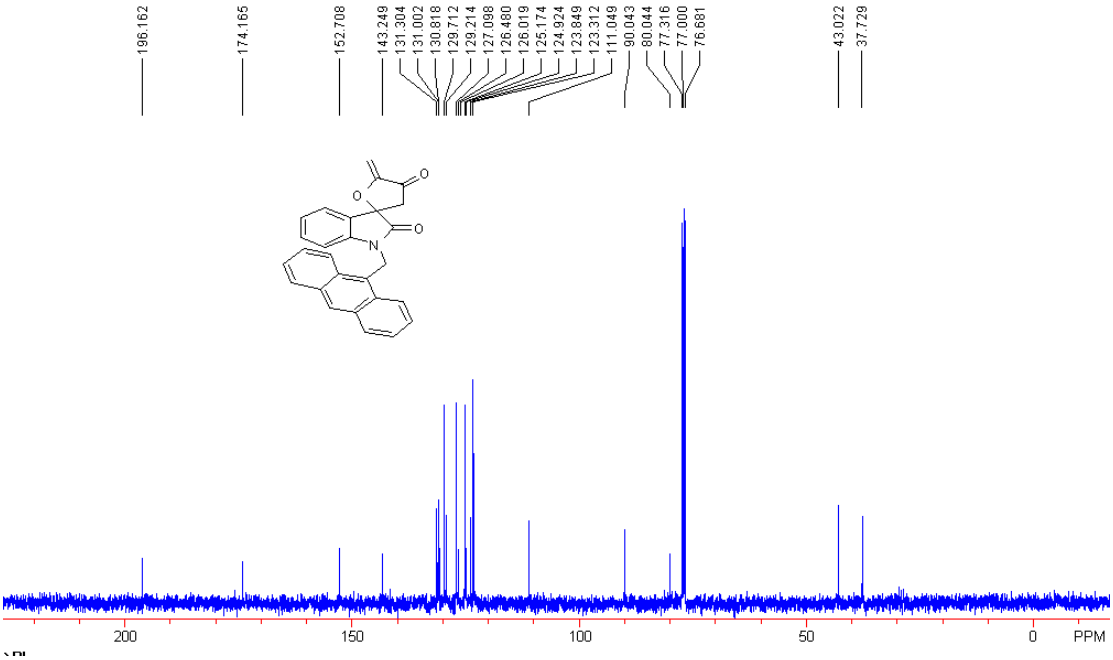
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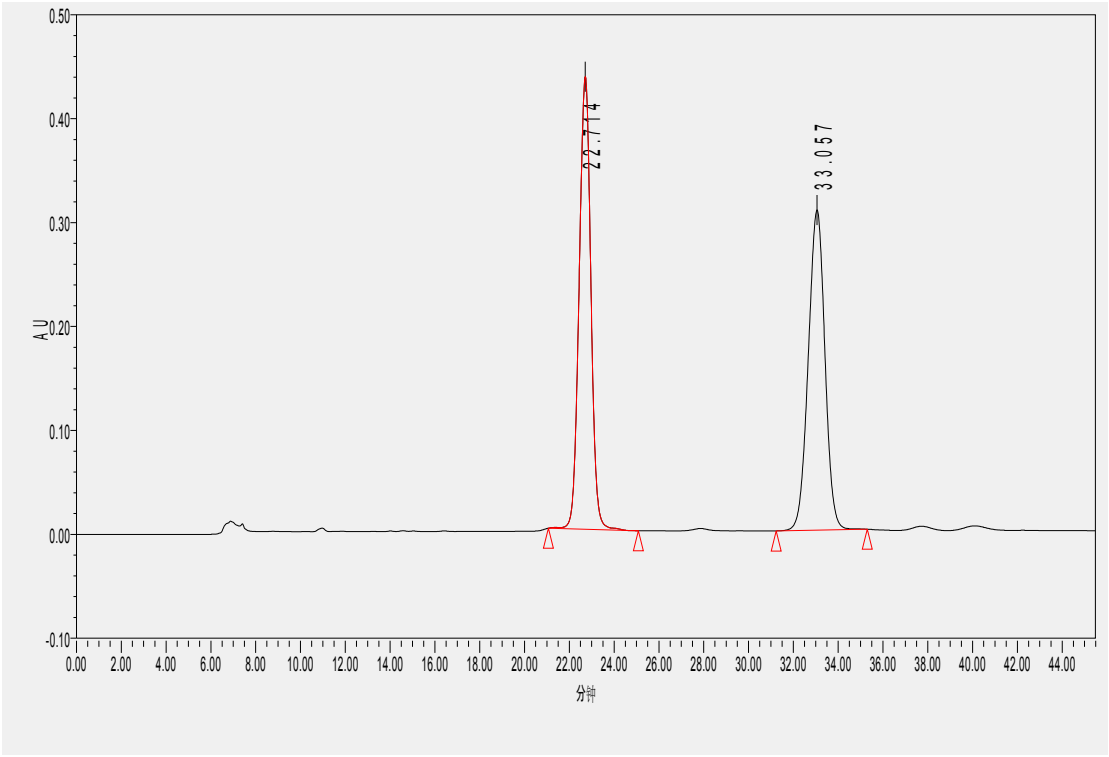

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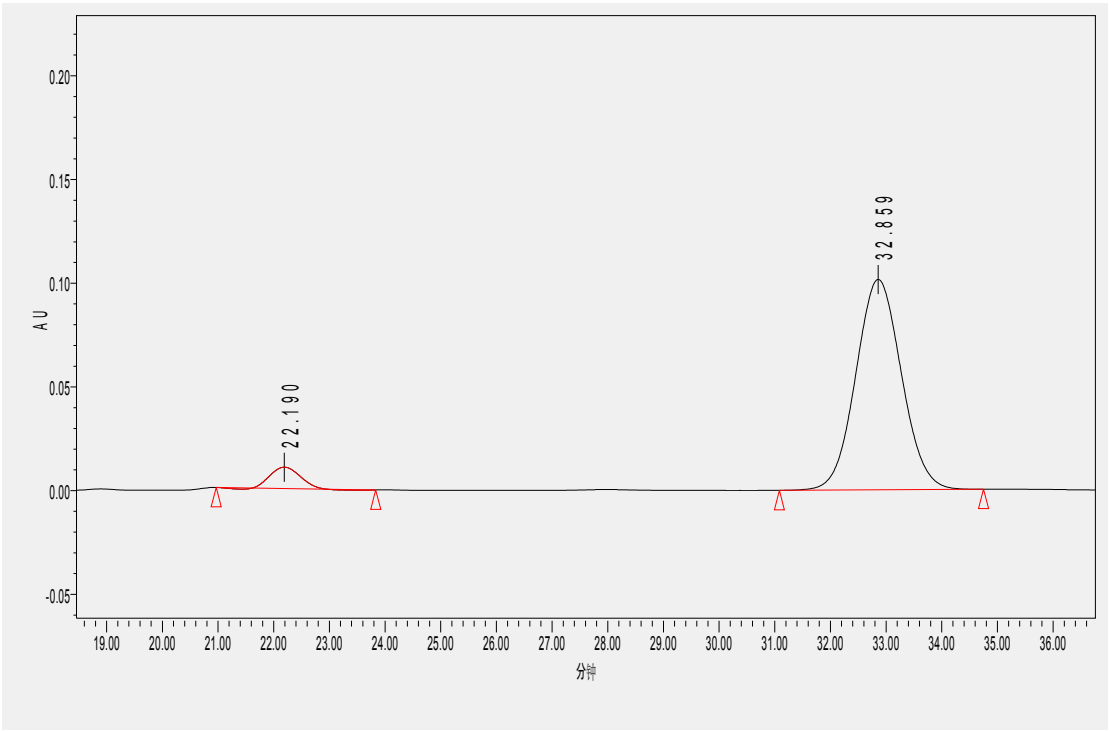

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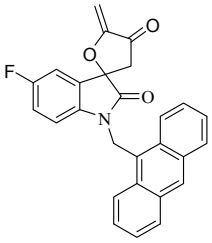
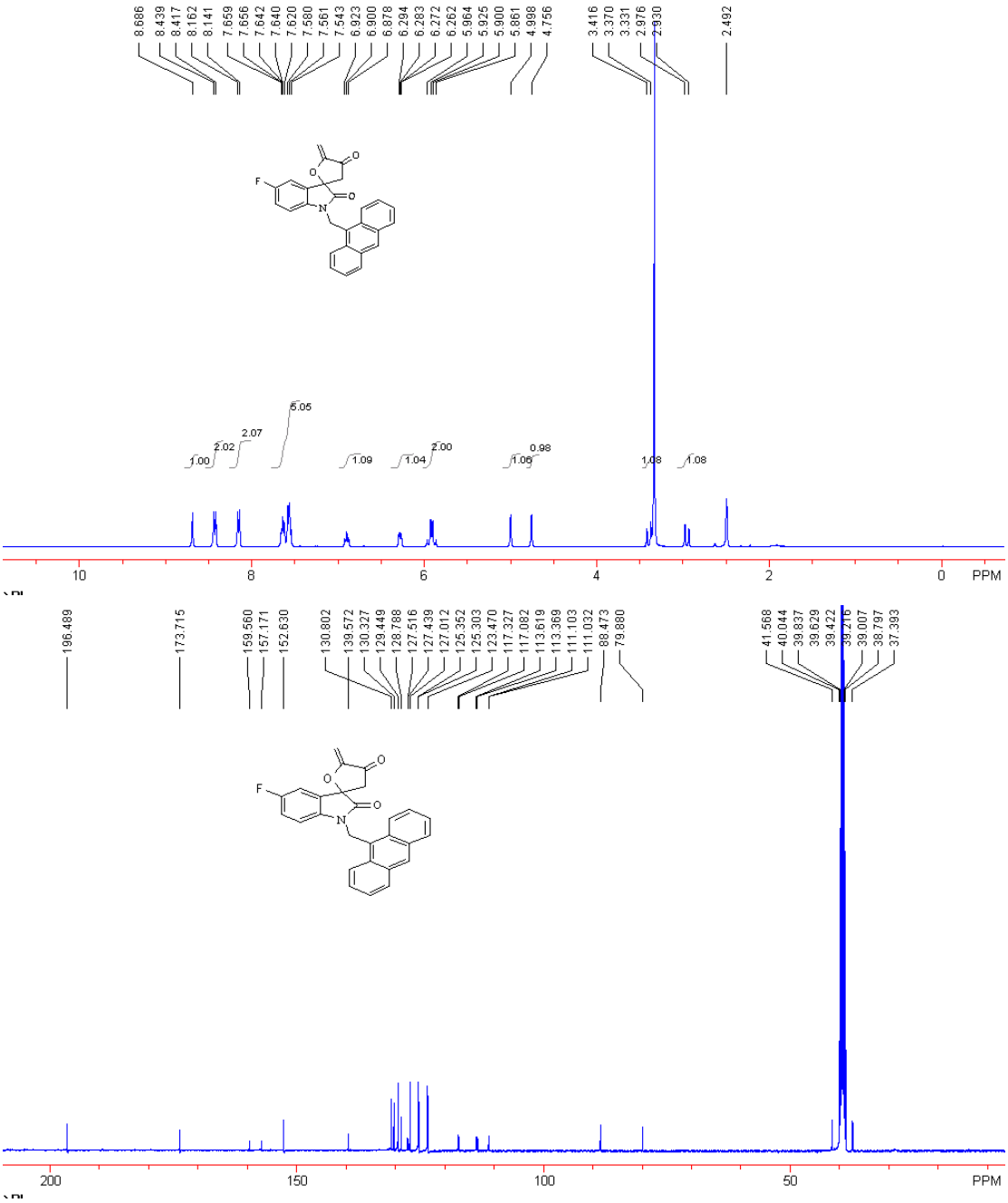


1'-(anthracen-9-ylmethyl)-5'-fluoro-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dion e (3b). 20 mg, 46% yield. mp. 305-308 ^{o}C (the racemate of **3b**. mp. 307-309 ^{o}C); ^{1}H NMR (d_6-DMSO, 400 MHz, TMS) δ 2.95 (d, 1H, J = 18.4 Hz, CH_2), 3.39 (d, 1H, J = 18.4 Hz, CH_2), 4.76 (s 1H, =CH_2), 5.00 (s, 1H, =CH_2), 5.88 (d, 1H, J = 16.0 Hz, CH_2), 5.94 (d, 1H, J = 16.0 Hz, CH_2), 6.26-6.29 (m, 1H, ArH), 6.88-6.92 (m, 1H, ArH), 7.54-7.66 (m, 5H, ArH), 8.15 (d, 2H, J = 8.4 Hz, ArH), 8.42 (d, 2H, J = 8.4 Hz, ArH), 8.69 (s, 1H, ArH); ^{13}C NMR (d_6-DMSO, 100 MHz, TMS) δ 37.4, 41.6, 79.9, 88.5, 111.1 (d, J = 7.1 Hz), 113.4 (d, J = 35.1 Hz), 117.1 (d, J = 24.5 Hz), 123.5, 125.3 (d, J = 4.9 Hz), 127.0, 127.4 (d, J = 7.7 Hz), 128.8, 129.4, 130.3, 130.8, 139.6, 152.6, 158.0 (d, J = 238.9 Hz), 173.7, 196.5; ^{19}F NMR (d_6-DMSO, 282 MHz, $CFCl_3$) δ -118.3; IR (CH_2Cl_2): ν 2946, 2920, 2835, 1744, 1716, 1480, 1446, 1291, 1160, 775 cm^{-1}; MS (MALDI/DHB) m/z (%): 423.1 $[M]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{27}H_{18}FNNaO_3$ $[M + Na]^+$ requires 446.1163, Found: 446.1156. $[\alpha]^{20}_D$ = -37.6 (c 0.5, CH_2Cl_2, 69% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 43.35 min, t_{major} = 47.85 min).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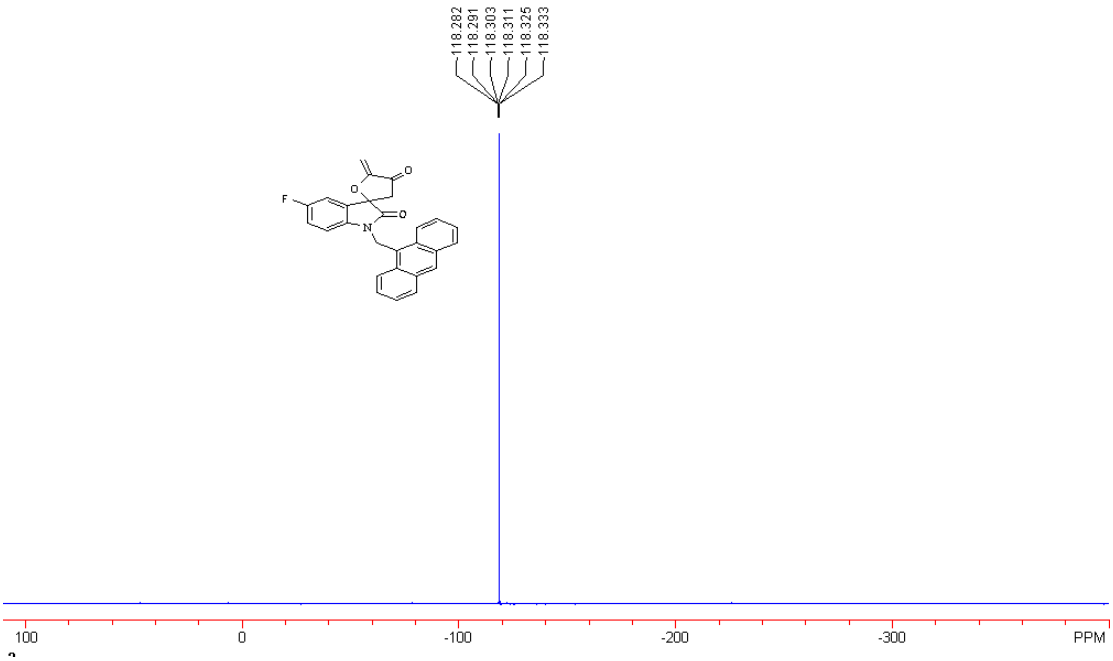

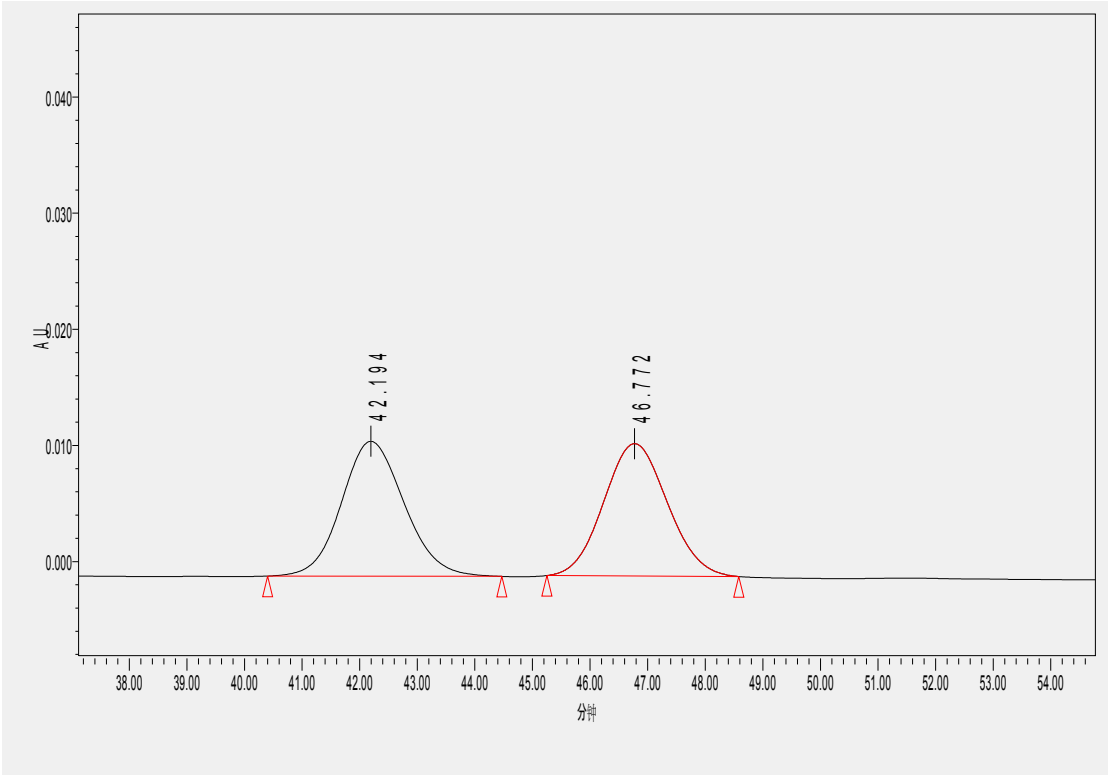

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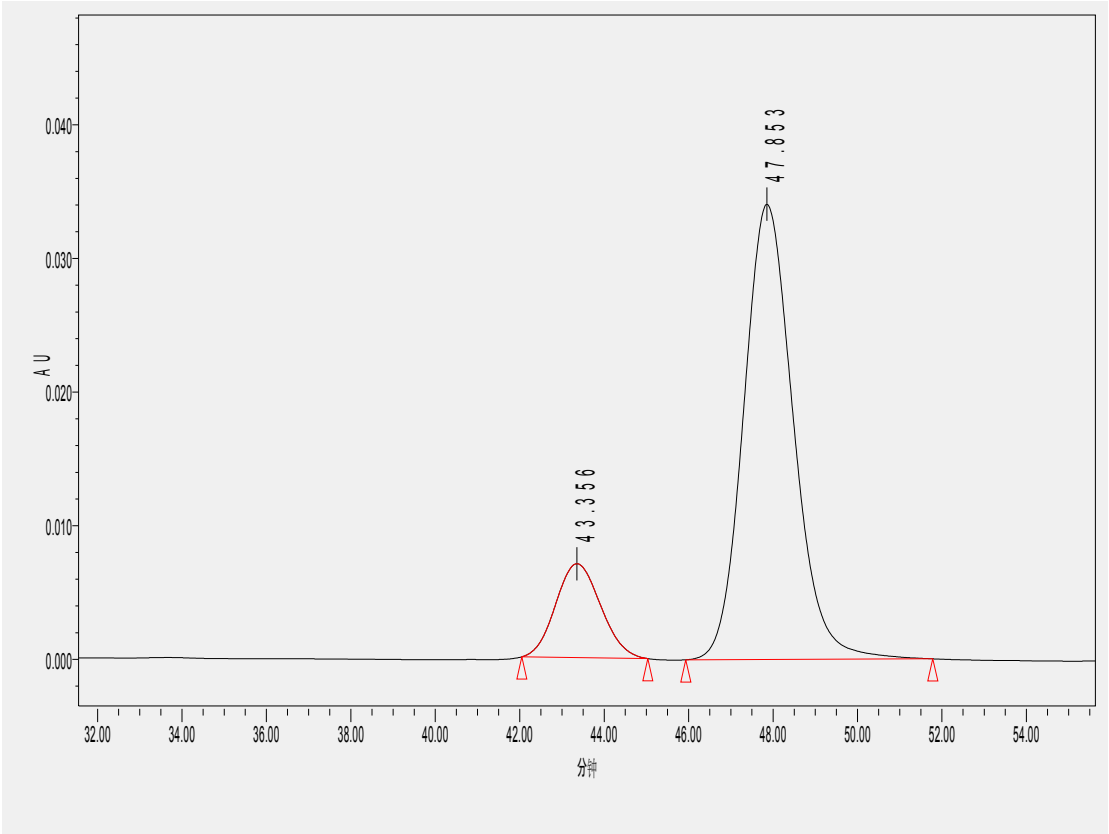

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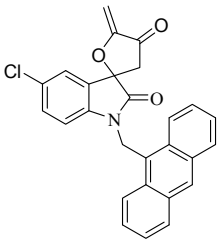
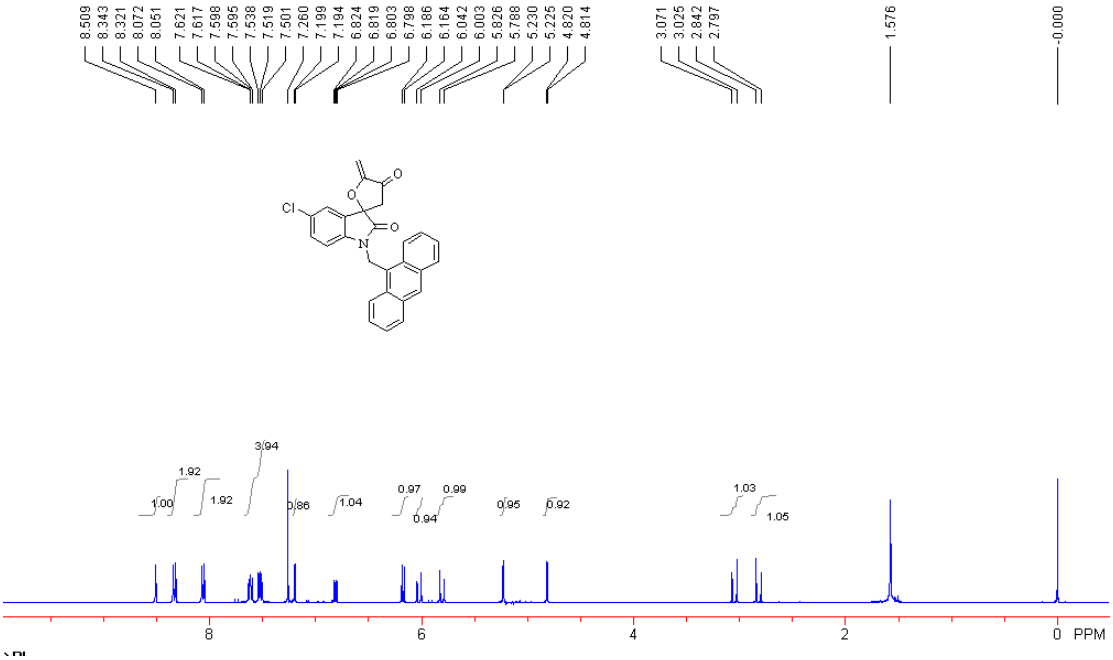
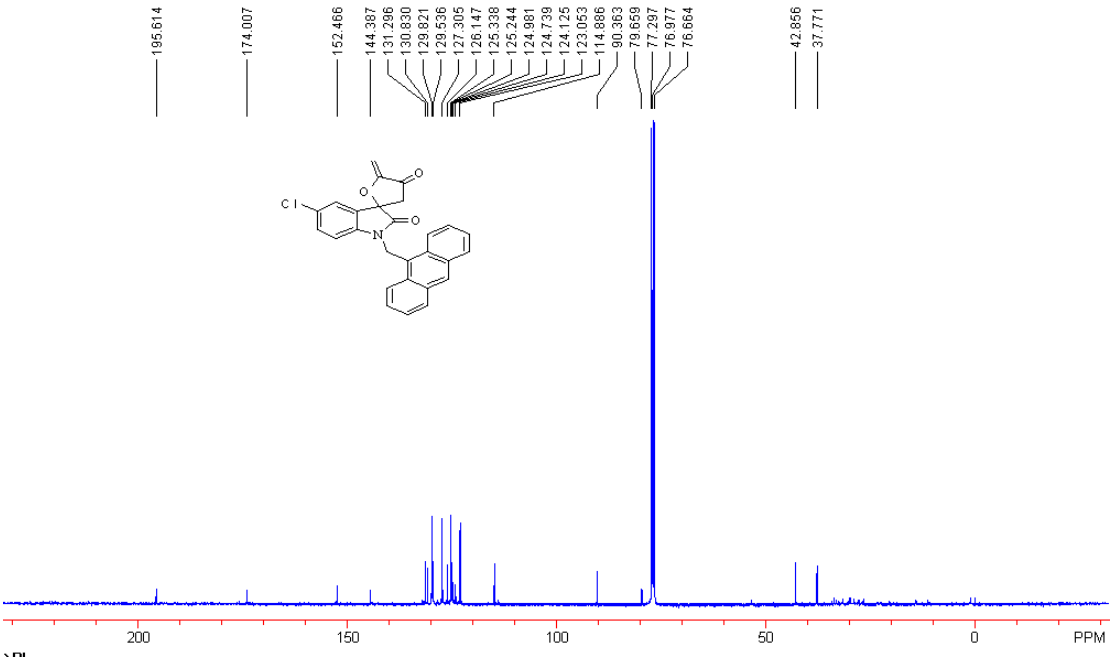
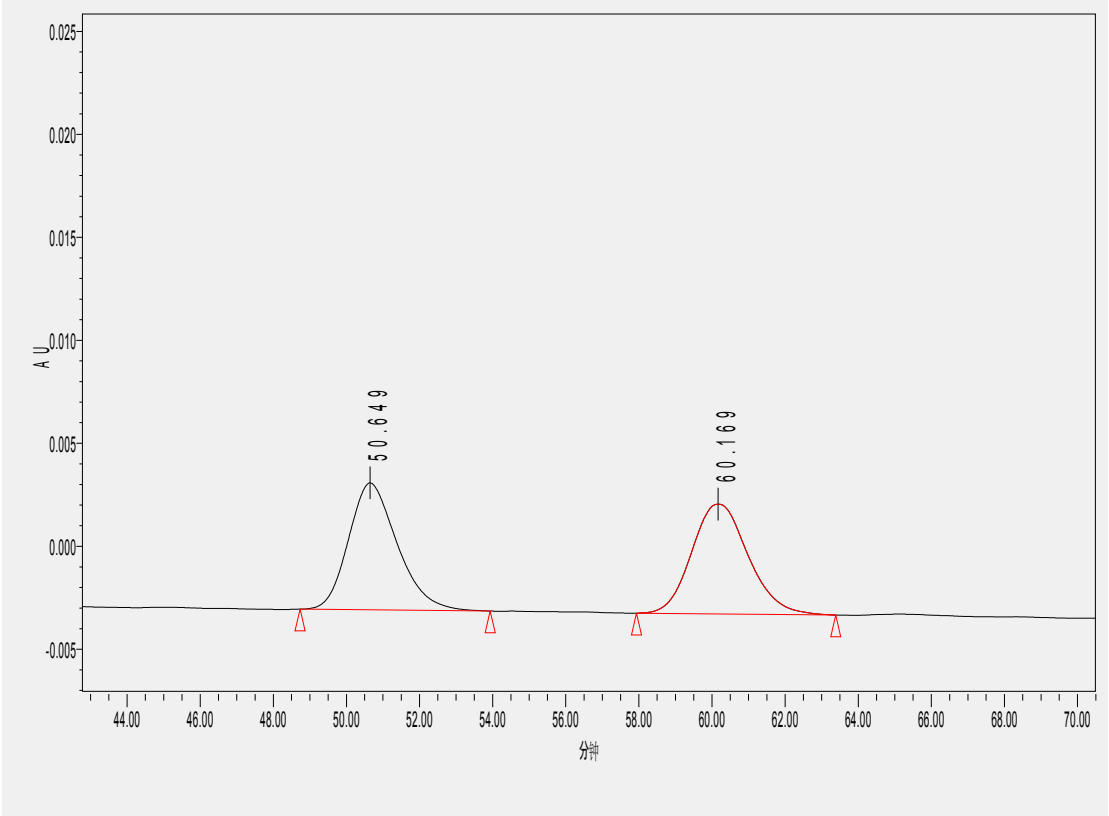


1'-(anthracen-9-ylmethyl)-5'-chloro-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3c). 20 mg, 45% yield. mp. 309-311 °C (the racemate of **3c**. mp. 313-315 °C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.82 (d, 1H, J = 18.0 Hz, CH_2), 3.05 (d, 1H, J = 18.0 Hz, CH_2), 4.82 (d, 1H, J = 2.4 Hz, =CH_2), 5.23 (d, 1H, J = 2.4 Hz, =CH_2), 5.80 (d, 1H, J = 15.2 Hz, CH_2), 6.02 (d, 1H, J = 15.2 Hz, CH_2), 6.17 (d, 1H, J = 8.8 Hz, ArH), 6.80 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.8 Hz, ArH), 7.19 (d, 1H, J = 2.0 Hz, ArH), 7.50-7.62 (m, 4H, ArH), 8.06 (d, 2H, J = 8.8 Hz, ArH), 8.33 (d, 2H, J = 8.8

Hz, ArH), 8.51 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 37.8, 42.9, 79.7, 90.4, 114.9, 123.1, 124.1, 124.7, 125.0, 125.2, 125.3, 126.1, 127.3, 129.5, 129.8, 130.8, 131.3, 144.4, 152.5, 174.0, 195.6; IR (CH_2Cl_2): ν 2957, 2924, 2853, 1748, 1652, 1489, 1456, 1281, 1249, 772, 755 cm^{-1}; MS (MALDI/DHB) m/z (%): 462.0 $[M + Na]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{27}H_{18}ClNNaO_3$ $[M + Na]^+$ requires 462.0867, Found: 462.0881. $[\alpha]^{20}_D$ = -27.7 (c 0.5, CH_2Cl_2, 77% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 50/50, 0.5 mL/min, 230 nm, t_{minor} = 49.35 min, t_{major} = 58.73 min).







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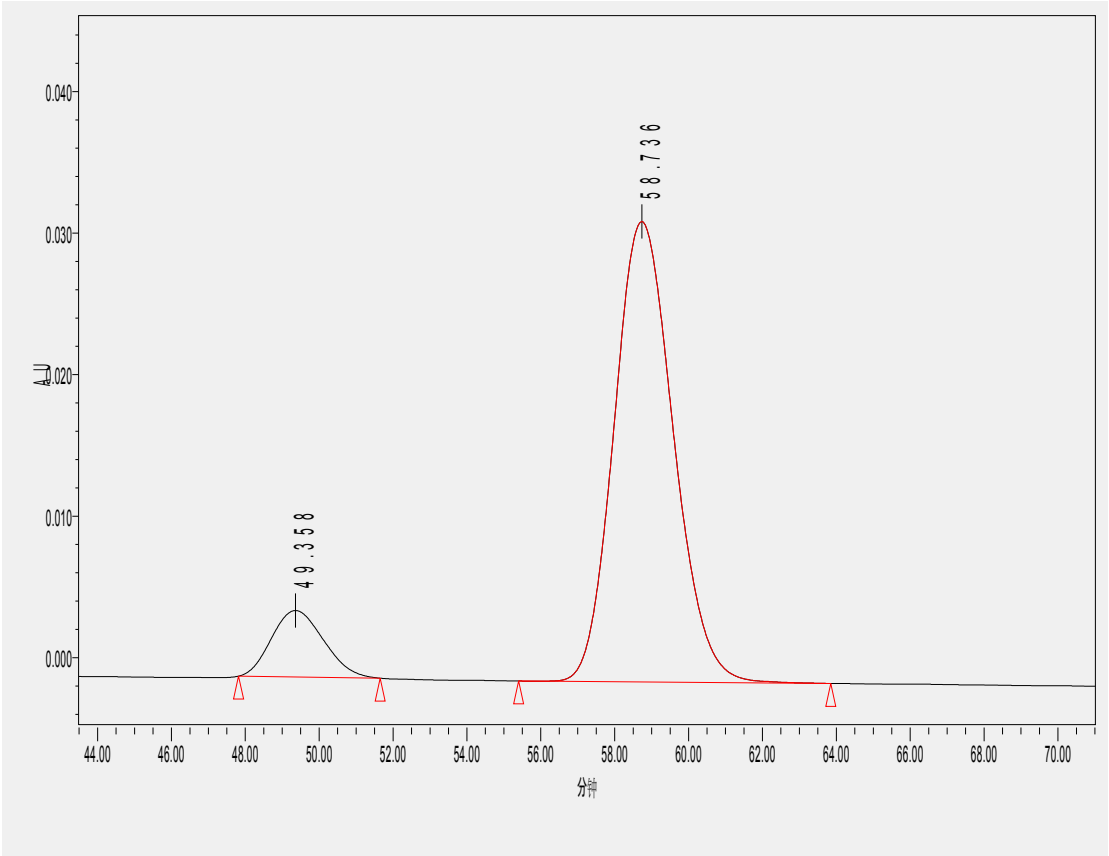

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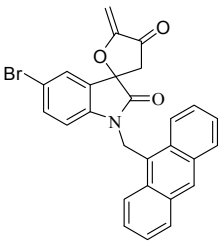
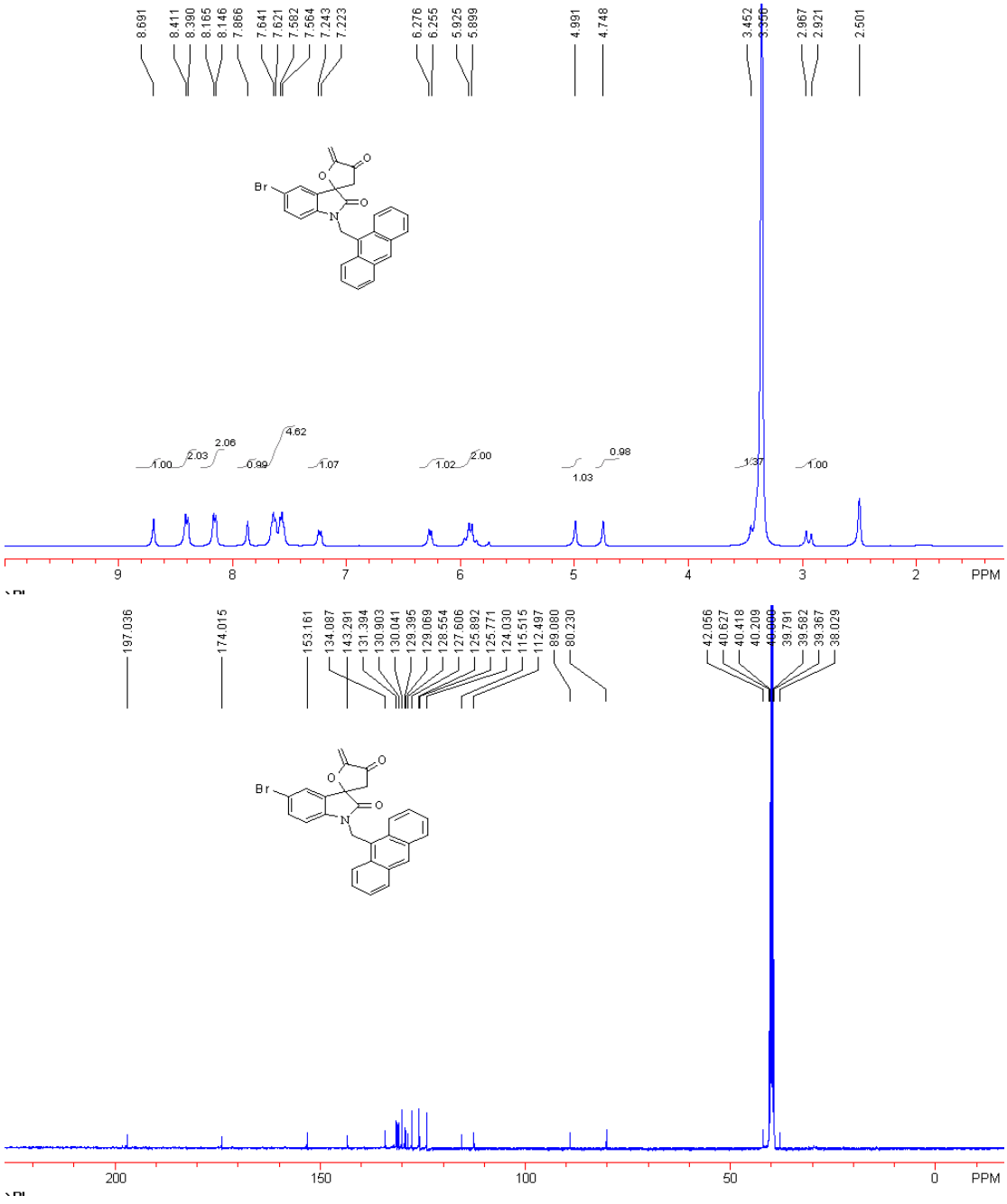
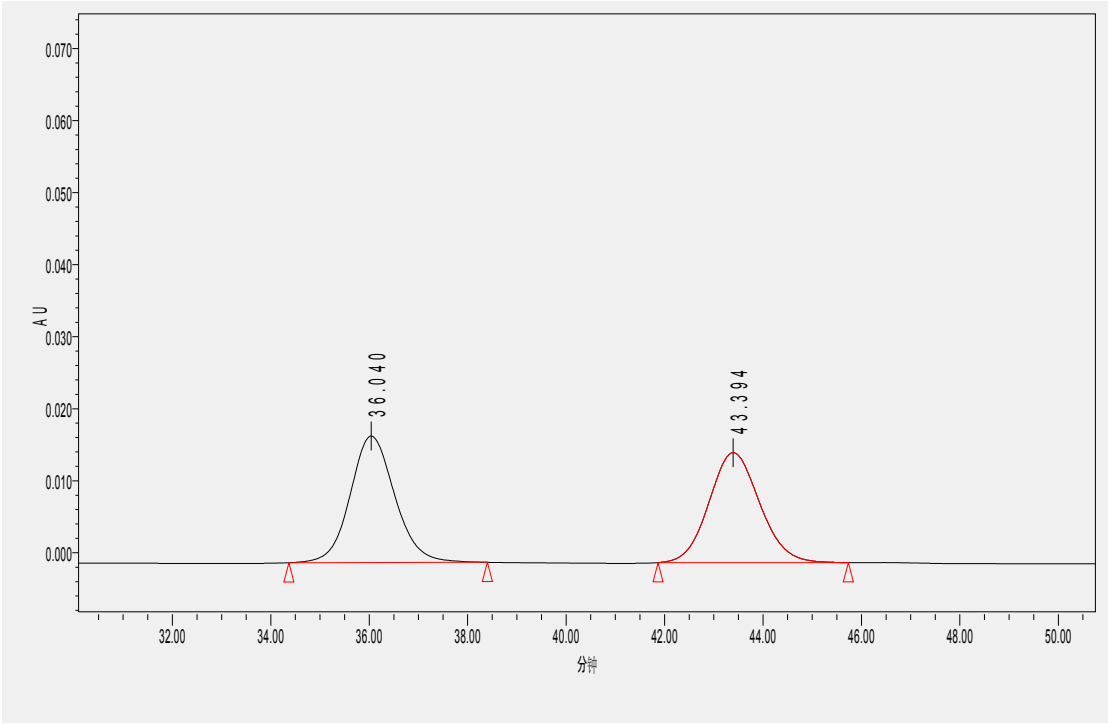


1'-(anthracen-9-ylmethyl)-5'-bromo-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3d). 23 mg, 47% yield. mp. 310-311 °C (the racemate of **3d**. mp. 315-316 °C); ^{1}H NMR (d_6-DMSO, 400 MHz, TMS) δ 2.94 (d, 1H, J = 18.4 Hz, CH_2), 3.45 (d, 1H, J = 18.4 Hz, CH_2), 4.78 (s, 1H, =CH_2), 4.99 (s, 1H, =CH_2), 5.90-5.93 (m, 2H, CH_2), 6.26 (d, 1H, J = 8.0 Hz, Ar), 7.23 (d, 1H, J = 8.0 Hz, ArH), 7.56-7.64 (m, 4H, ArH), 7.87 (s, 1H, ArH), 8.15 (d, 2H, J = 8.0 Hz, ArH), 8.40 (d, 2H, J = 8.0 Hz, ArH), 8.69 (s, 1H, ArH); ^{13}C NMR (d_6-DMSO, 100 MHz, TMS) δ 38.0,

42.1, 80.2, 89.1, 112.5, 115.5, 124.0, 125.8, 125.9, 127.6, 128.6, 129.1, 129.4, 130.0, 130.9, 131.4, 134.1, 143.3, 153.2, 174.0, 197.0; IR (CH_2Cl_2): ν 2957, 2920, 2851, 1748, 1717, 1480, 1451, 1277, 1249, 772, 755 cm^{-1}; MS (MALDI/DHB) m/z (%): 483.2 $[M]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{27}H_{18}BrNNaO_3$ $[M + Na]^+$ requires 506.0362, Found: 506.0355. $[\alpha]^{20}_D$ = -45.0 (c 0.5, CH_2Cl_2, 80% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 36.67 min, t_{major} = 44.06 min).





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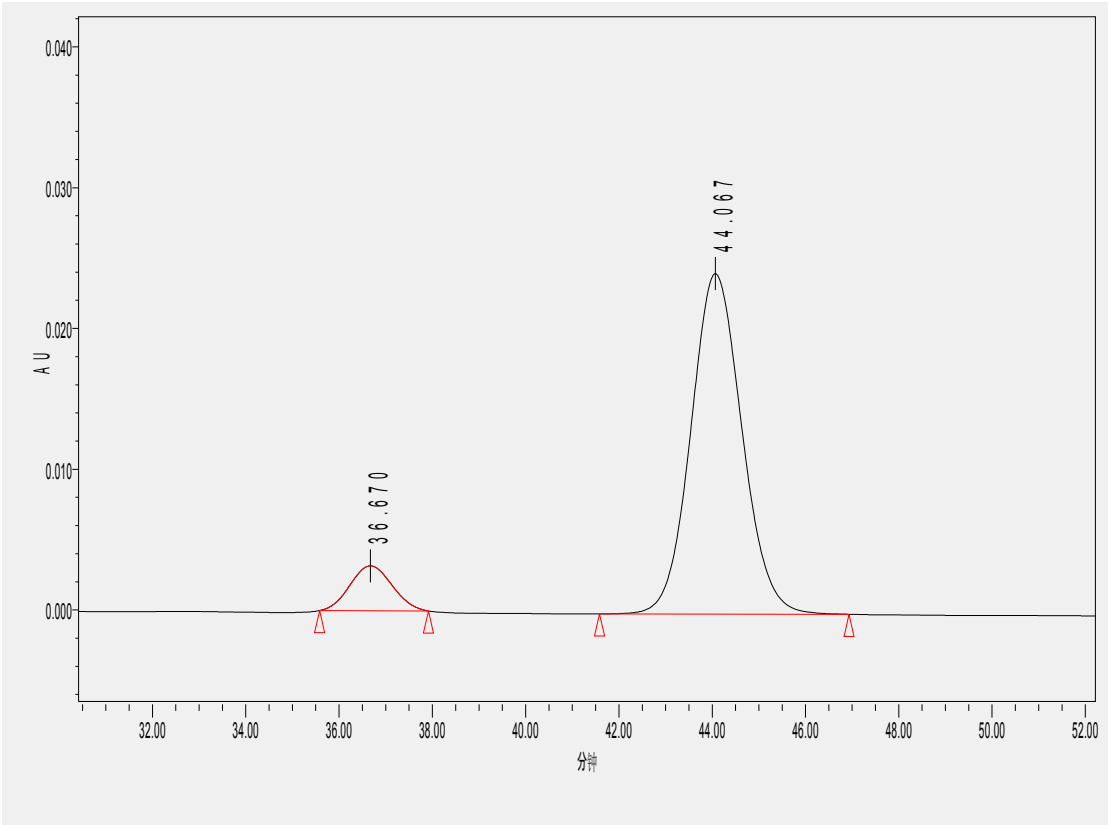

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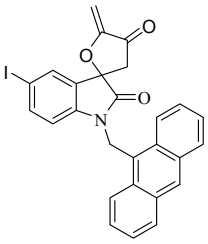
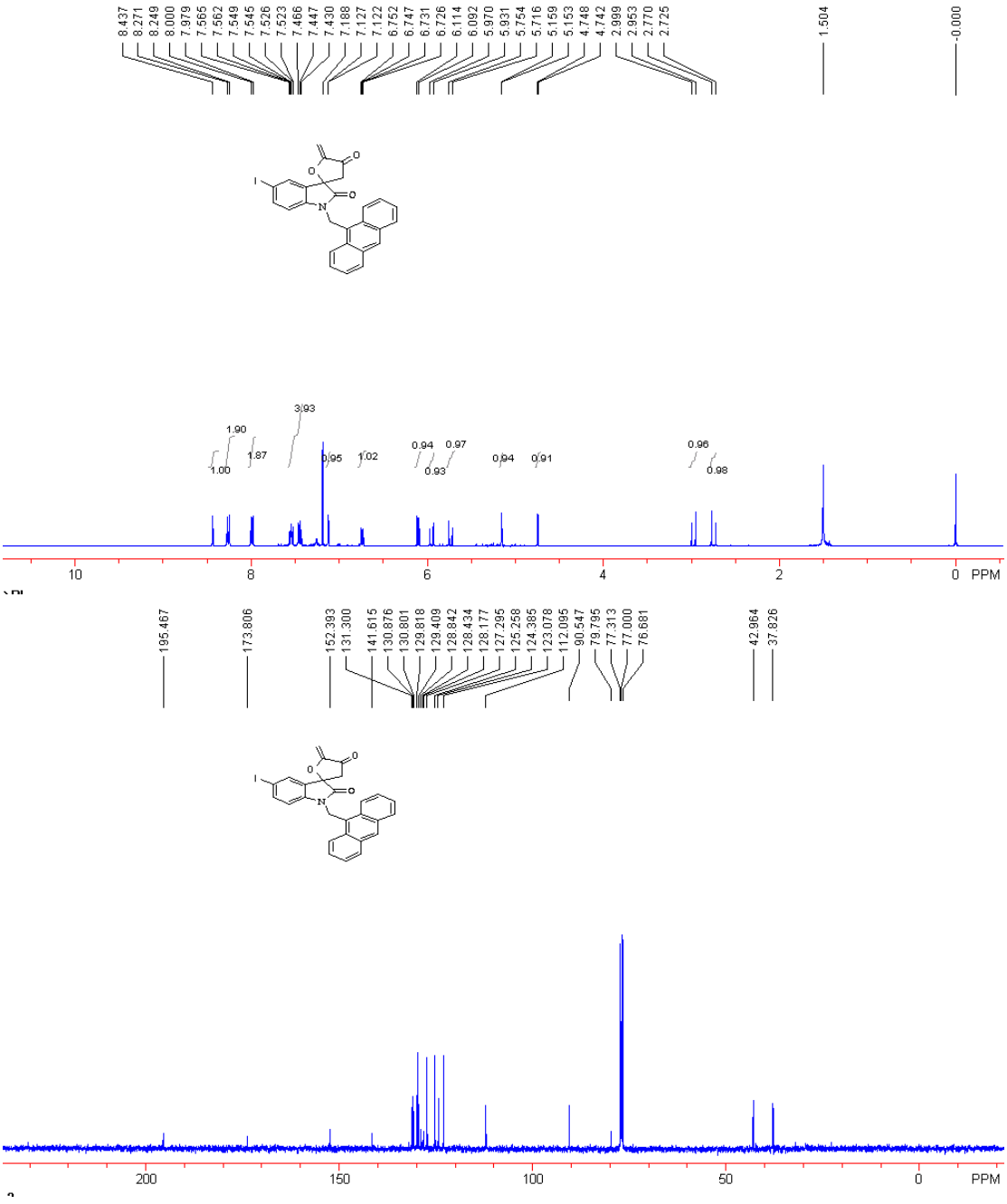


1'-(anthracen-9-ylmethyl)-5'-iodo-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3e). 22 mg, 40% yield. mp. 330-331 ^{o}C (the racemate of **3e**. mp. 335-336 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.74 (d, 1H, J = 18.0 Hz, CH_2), 2.97 (d, 1H, J = 18.0 Hz, CH_2), 4.74 (d, 1H, J = 2.4 Hz, =CH_2), 5.15 (d, 1H, J = 2.4 Hz, =CH_2), 5.73 (d, 1H, J = 15.2 Hz, CH_2), 5.75 (d, 1H, J = 15.2 Hz, CH_2), 6.10 (d, 1H, J = 8.4 Hz, ArH), 6.74 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.4 Hz, ArH), 7.12 (d, 1H, J = 2.0 Hz, ArH), 7.43-7.57 (m, 4H, ArH), 7.98 (d, 2H, J = 8.4 Hz, ArH), 8.26 (d, 2H, J = 8.4 Hz, ArH), 8.44 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 37.8, 43.0, 79.8, 90.5, 112.1, 123.1, 124.4, 125.3, 127.3, 128.2, 128.4, 128.8, 129.4, 129.8, 130.8, 130.9, 131.3, 141.6, 152.4, 173.8, 195.5; IR (CH_2Cl_2): ν 2923, 2851, 1748, 1713, 1412, 1400, 1277, 1249, 776, 755 cm^{-1}; MS (MALDI/DHB) m/z (%): 531.0 $[M]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{27}H_{18}INNaO_3$ $[M + Na]^+$ requires 554.0224, Found: 554.0211. $[\alpha]^{20}_D$ = -34.2 (c 0.2, CH_2Cl_2, 66% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 34.51min, t_{major} = 46.38 min).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7.430
7.188
7.127
7.122
6.752
6.747
6.731
6.726
6.114
6.092
5.970
5.931
5.754
5.716
5.159
5.153
4.748
4.742
2.999
2.953
2.770
2.725
1.504
-0.000
3.93
1.90
1.87
1.00
0.95
1.02
0.94
0.97
0.93
0.94
0.91
0.96
0.98
10
8
6
4
2
0 PPM
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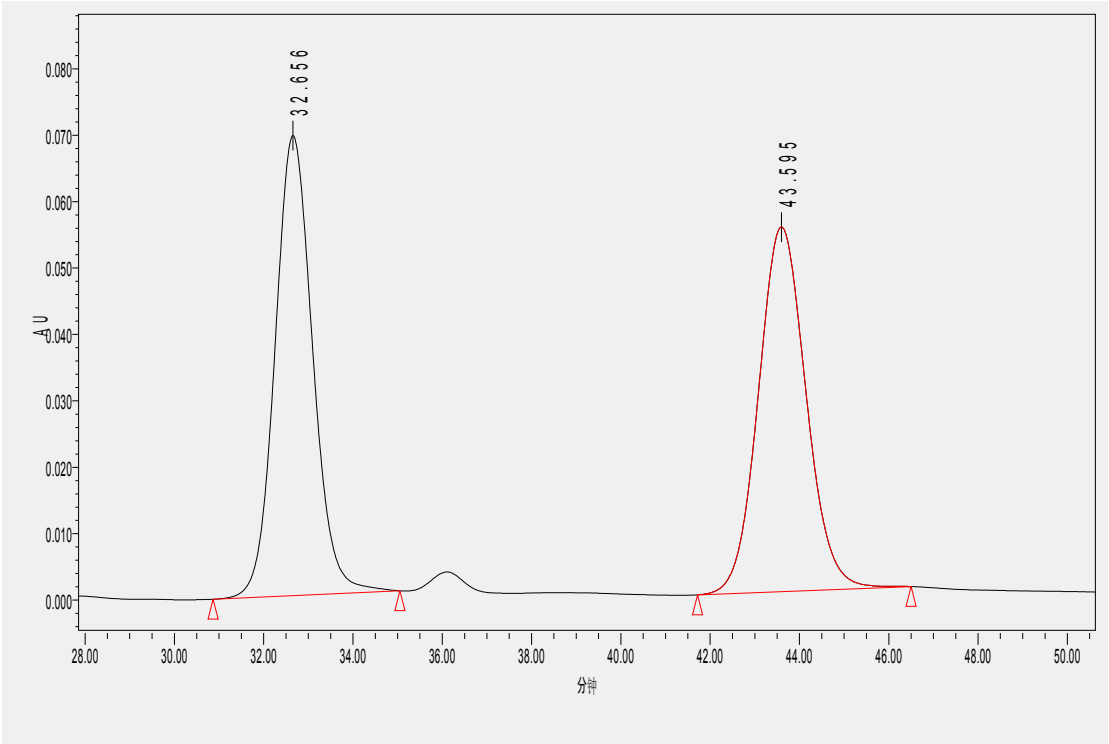
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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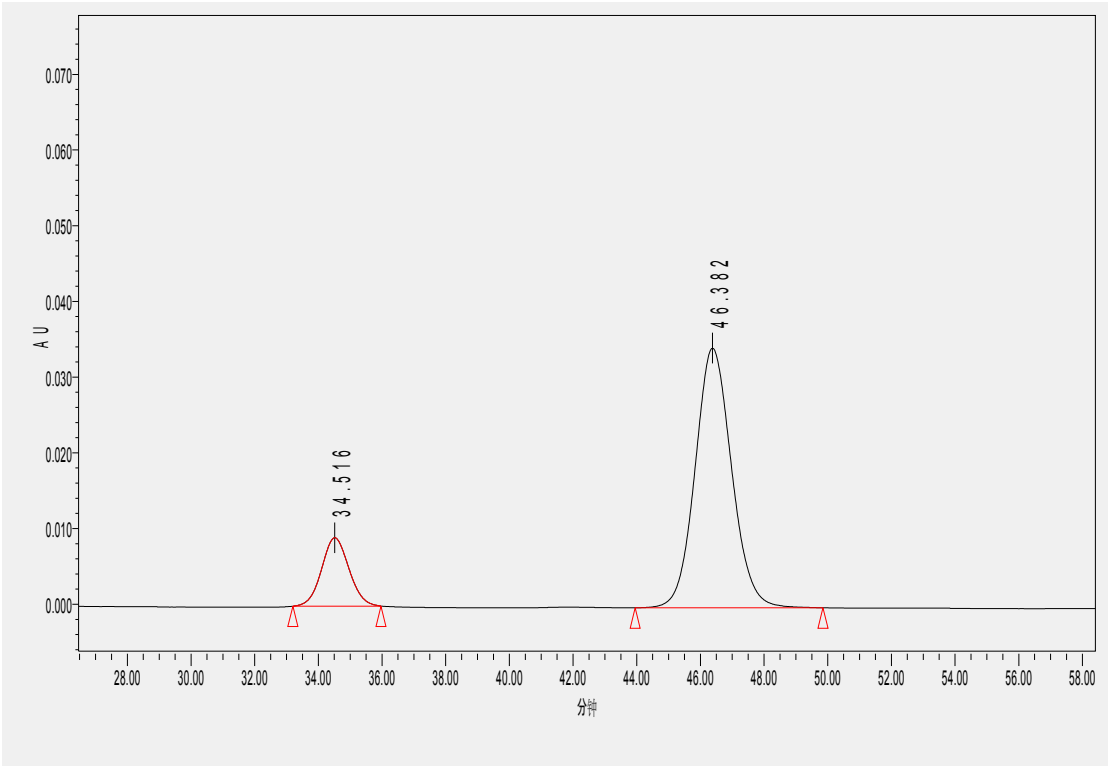

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	34.516	538702	16.46	9028
2	2	46.382	2733228	83.54	34322

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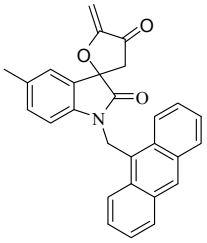
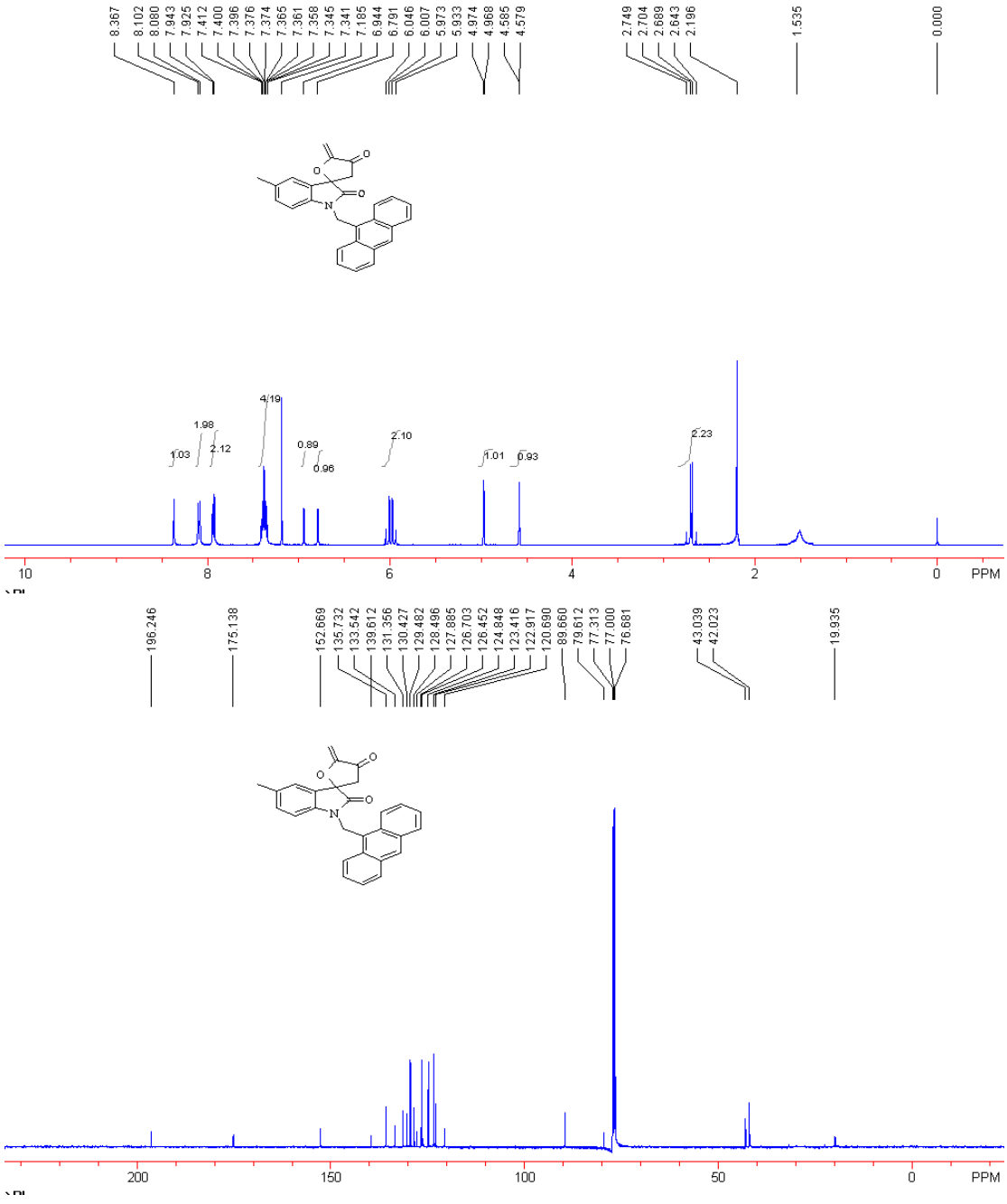


1'-(anthracen-9-ylmethyl)-5'-methyl-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3f). 37 mg, 85% yield. mp. 301-302 ^{o}C (the racemate of **3f**. mp. 305-307 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.20 (s, 3H, CH_3), 2.66 (d, 1H, J = 18.0 Hz, CH_2), 2.72 (d, 1H, J = 18.0 Hz, CH_2), 4.58 (d, 1H, J = 2.4 Hz, =CH_2), 4.97 (d, 1H, J = 2.4 Hz, =CH_2), 5.95 (d, 1H, J = 16.0 Hz, CH_2), 6.02 (d, 1H, J = 16.0 Hz, CH_2), 6.79 (s, 1H, ArH), 6.94 (s, 1H, ArH), 7.19 (s, 1H, Ar), 7.34-7.41 (m, 4H, ArH), 7.93 (d, 2H, J = 8.0 Hz, ArH), 8.09 (d, 2H, J = 8.0 Hz, ArH), 8.37 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.9, 42.0, 43.0, 79.6, 89.7, 120.7, 122.9, 123.4, 124.8, 126.5 126.7 127.9, 128.5 129.5, 130.4 131.4 133.5, 135.7, 139.6, 152.7, 175.1, 196.2; IR (CH_2Cl_2): ν 2952, 2923, 2845, 1748, 1713, 1412, 1409, 1270, 1249, 776, 757 cm^{-1}; MS (MALDI/DHB) m/z (%): 419.1 $[M]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{28}H_{21}NNaO_3$ $[M + Na]^+$ requires 442.1414, Found: 442.1421. $[\alpha]^{20}_D$ = -51.9 (c 0.5, CH_2Cl_2, 68% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 230 nm, t_{minor} = 24.08 min, t_{major} = 35.72min).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2.704
2.689
2.643
2.196
1.535
0.000
O
O
O
N
4.19
1.98
1.03
2.12
0.89
0.96
2.10
1.01
0.93
2.23
10
8
6
4
2
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50
0
PPM

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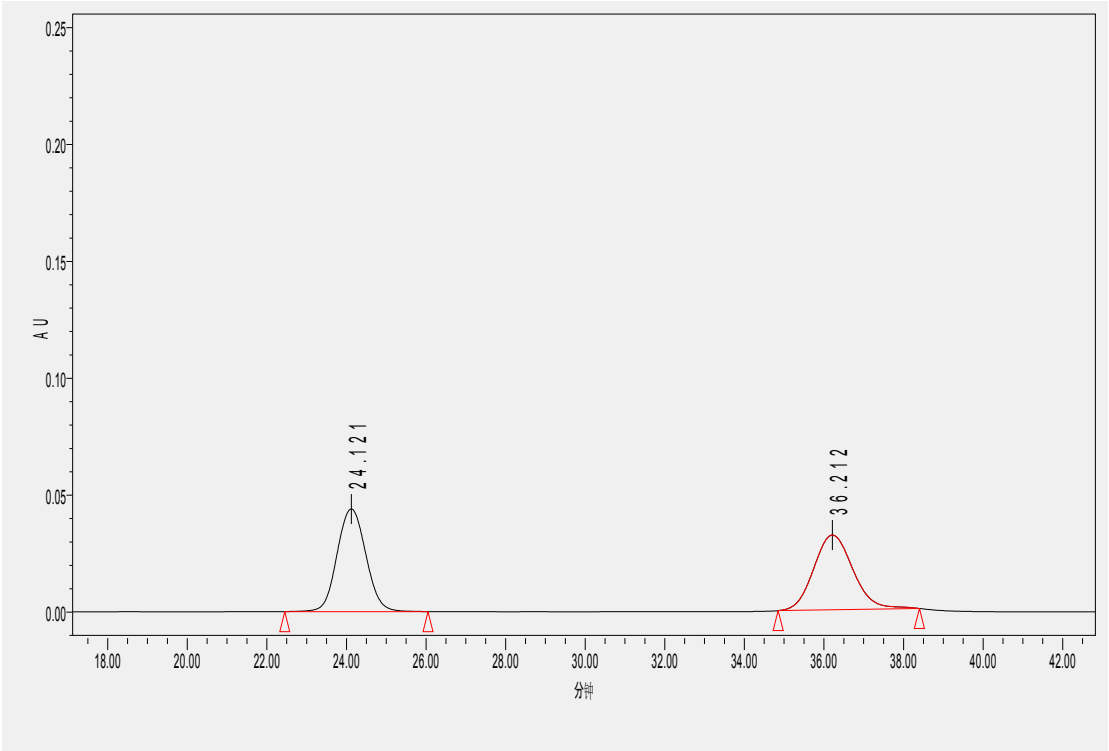

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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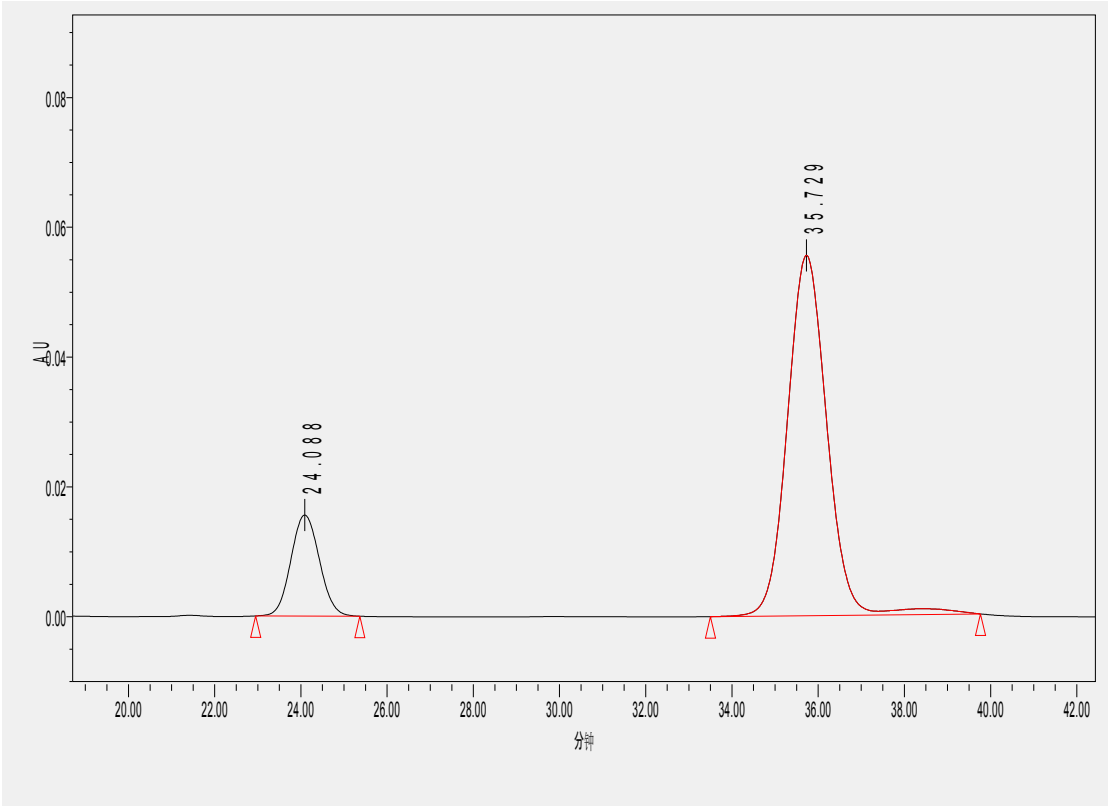

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight

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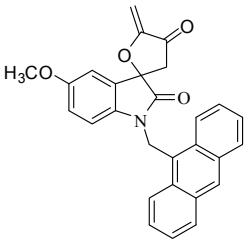
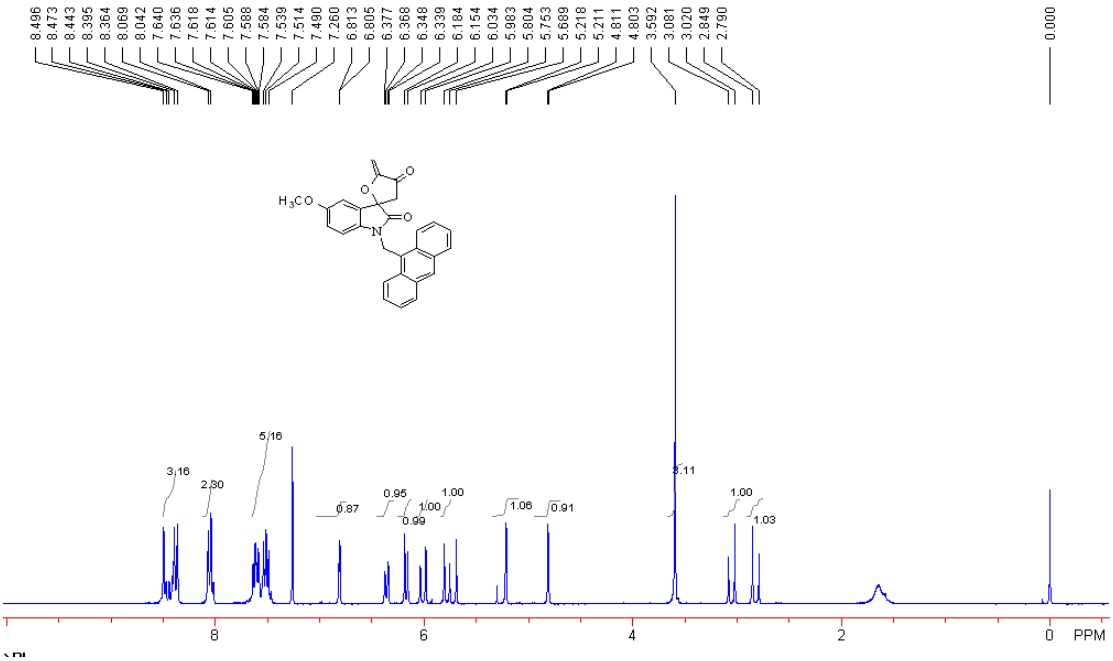


1'-(anthracen-9-ylmethyl)-5'-methoxy-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-di one (3g). 29 mg, 64% yield. mp. 305-307 ^{o}C (the racemate of **3g**. mp. 310-312 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.80 (d, 1H, J = 18.0 Hz, CH_2), 3.05 (d, 1H, J = 18.0 Hz, CH_2), 3.59 (s, 3H, CH_3), 4.81 (d, 1H, J = 2.4 Hz, =CH_2), 5.21 (d, 1H, J = 2.4 Hz, =CH_2), 5.78 (d, 1H, J = 15.0 Hz, CH_2), 6.01 (d, 1H, J = 15.0 Hz, CH_2), 6.17 (d, 1H, J = 8.4 Hz, ArH), 6.35 (dd, 1H, J_1 = 2.4 Hz, J_2 = 8.4 Hz, ArH), 6.81 (d, 1H, J = 2.4 Hz, ArH), 7.49-7.64 (m, 4H, ArH), 8.04-8.07 (m, 2H, ArH), 8.36-8.50 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 37.7, 43.2, 55.6, 80.3, 90.1, 110.9, 111.7, 115.3, 123.3, 123.9, 125.2, 126.5, 127.1, 129.2, 129.7, 130.8, 131.3, 136.3, 152.7, 156.2, 173.9, 196.1; IR (CH_2Cl_2): ν 2957, 2923, 2852, 1749, 1639, 1450, 1423, 1281, 1249, 779, 755 cm^{-1}; MS (MALDI/DHB) m/z (%): 436.1 $[M + H]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{28}H_{21}NNaO_4$ $[M + Na]^+$ requires 458.1362, Found: 458.1379. $[\alpha]^{20}_D$ = -47.6 (c 0.4, CH_2Cl_2, 84% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 48.53 min, t_{major} = 64.07 min).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6.184
6.154
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5.804
5.753
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5.218
5.211
4.811
4.803
3.592
3.081
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O
O
N
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0.87
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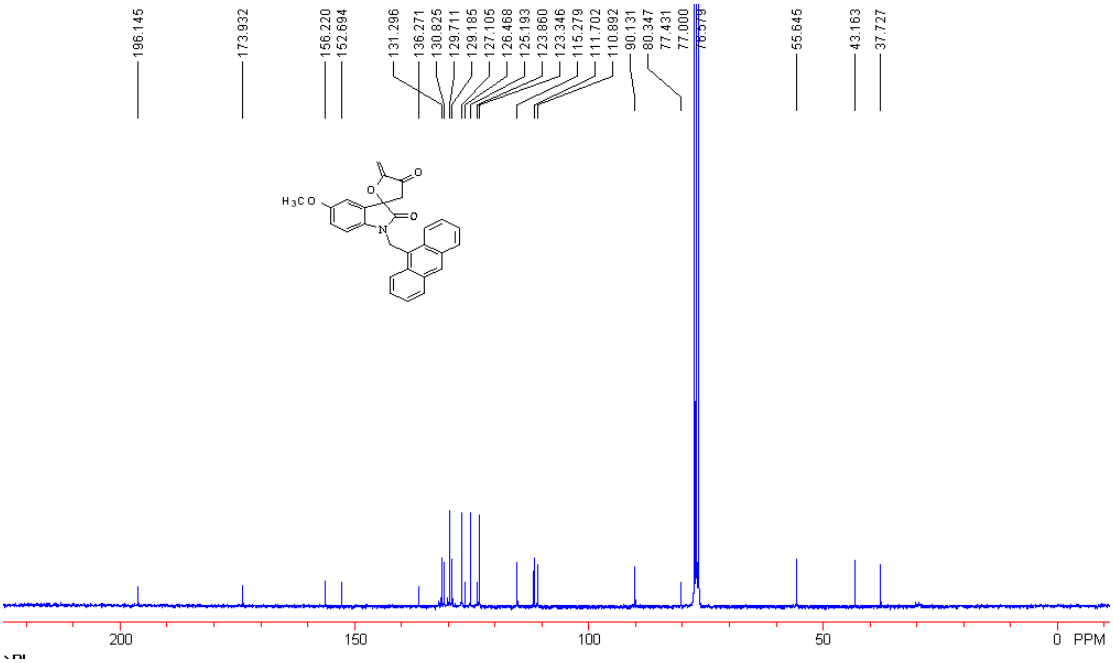
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111.702
110.892
90.131
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77.431
77.000
76.579
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H3CO
O
O
O
N
200
150
100
50
0
PPM

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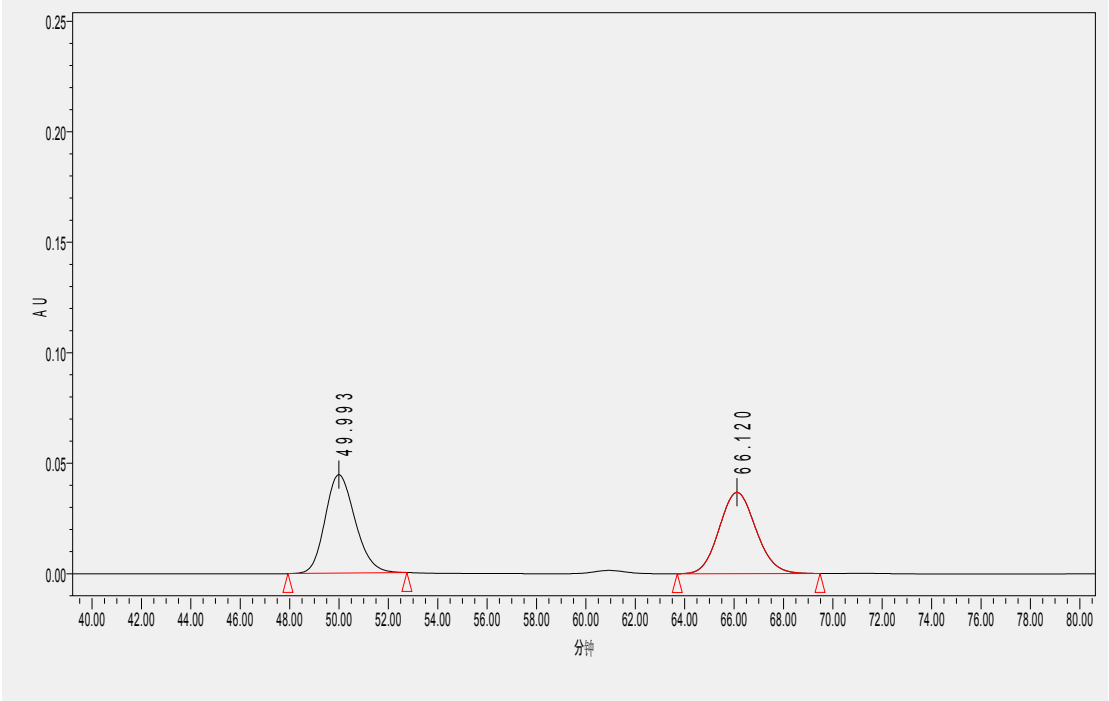

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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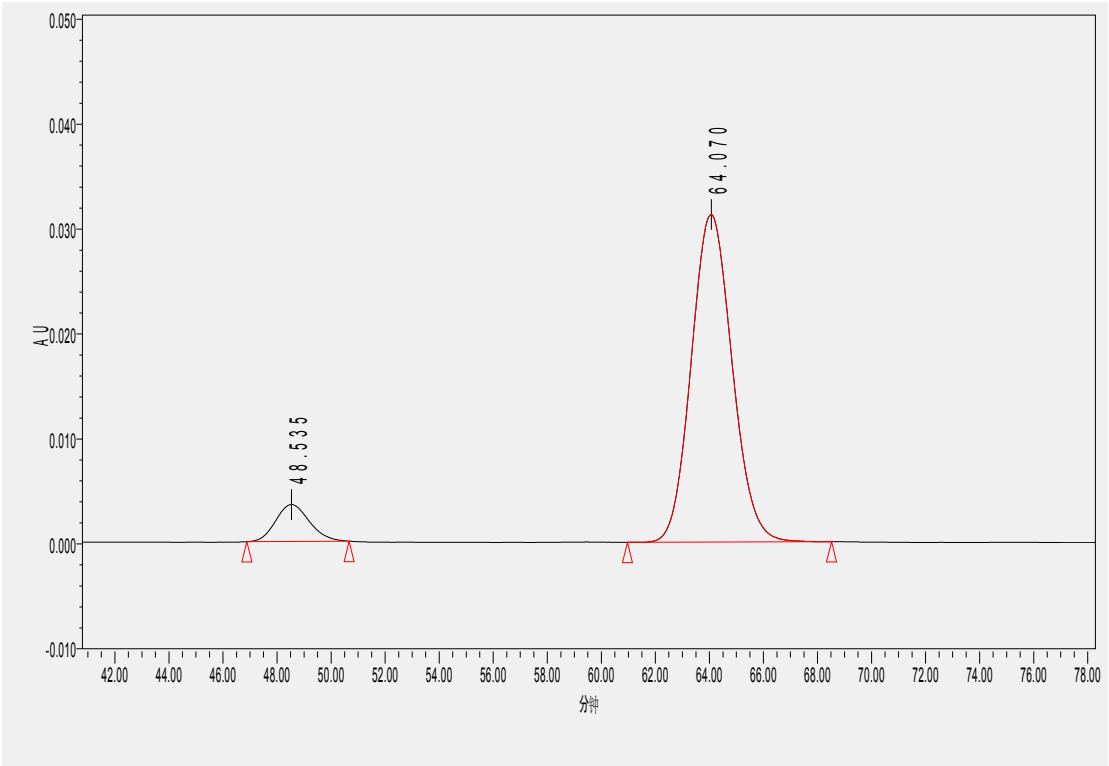

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	48.535	305175	8.52	3524
2	2	64.070	3277179	91.48	31210

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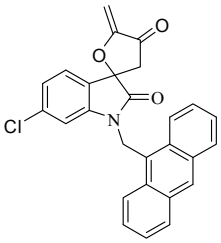

1'-(anthracen-9-ylmethyl)-6'-chloro-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3h). 27 mg, 60% yield. mp. 315-317 ^{o}C (the racemate of **3h**. mp. 319-320 ^{o}C); ^{1}H NMR (d_6-DMSO, 400 MHz, TMS) δ 2.93 (d, 1H, J = 18.4 Hz, CH_2), 3.42 (d, 1H, J = 18.4 Hz, CH_2), 4.74 (s, 1H, =CH_2), 4.98 (s, 1H, =CH_2), 5.89-5.92 (m, 2H, CH_2), 6.25 (d, 1H, J = 8.0 Hz, Ar), 7.22 (d, 1H, J = 8.0 Hz, ArH), 7.54-7.65 (m, 4H, ArH), 7.86 (s, 1H, ArH), 8.14 (d, 2H, J = 8.0 Hz, ArH), 8.39 (d, 2H, J = 8.0 Hz, ArH), 8.68 (s, 1H, ArH); ^{13}C NMR (d_6-DMSO, 100 MHz, TMS) δ 37.4, 41.5, 79.6, 88.5, 111.9, 114.9, 123.4, 125.2, 125.3, 127.0, 128.0, 128.5, 128.8, 129.4, 130.3, 130.8, 133.5, 142.7, 152.6, 173.4, 196.4; IR (CH_2Cl_2): ν 2952, 2923, 2851, 1712, 1638, 1490, 1172, 1041, 755 cm^{-1}; MS (MALDI/DHB) m/z (%): 439.1 $[M]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{27}H_{18}ClNNaO_3$ $[M + Na]^+$ requires 462.0867, Found: 462.0851. $[\alpha]^{20}_D$ = -39.6 (c 0.4, CH_2Cl_2, 82% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 22.31 min, t_{major} = 34.17min).

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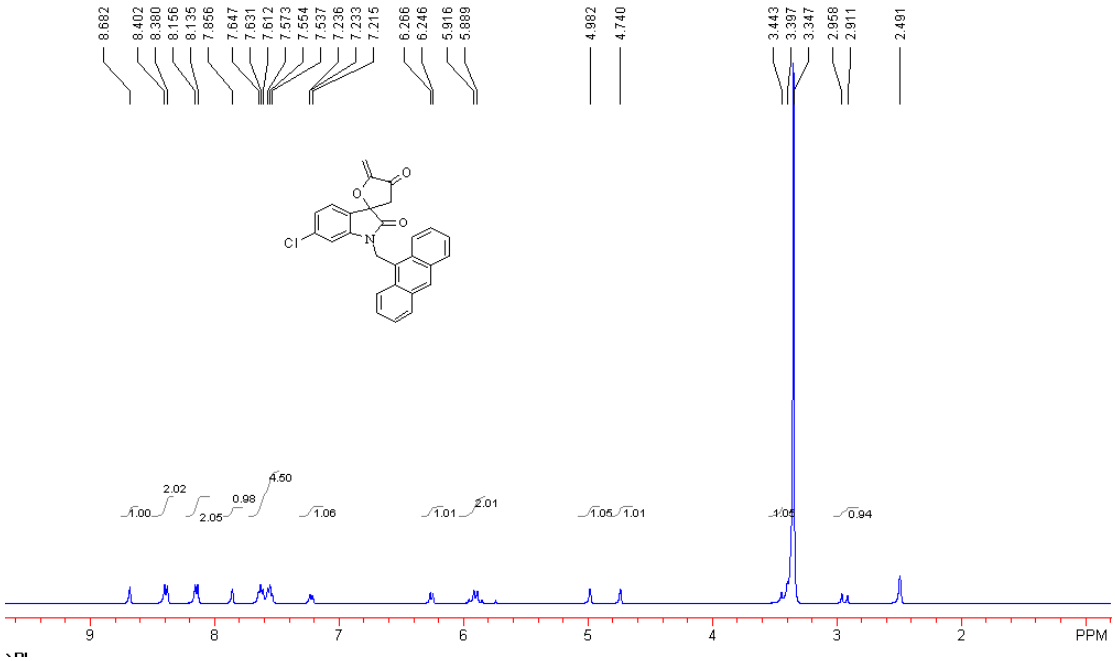

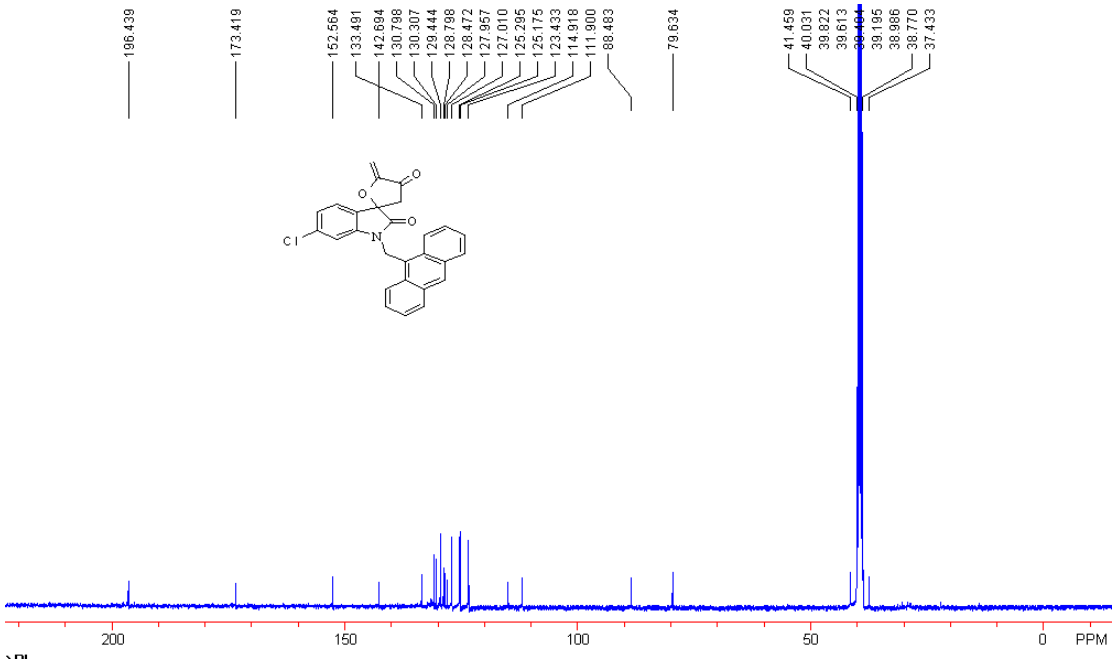

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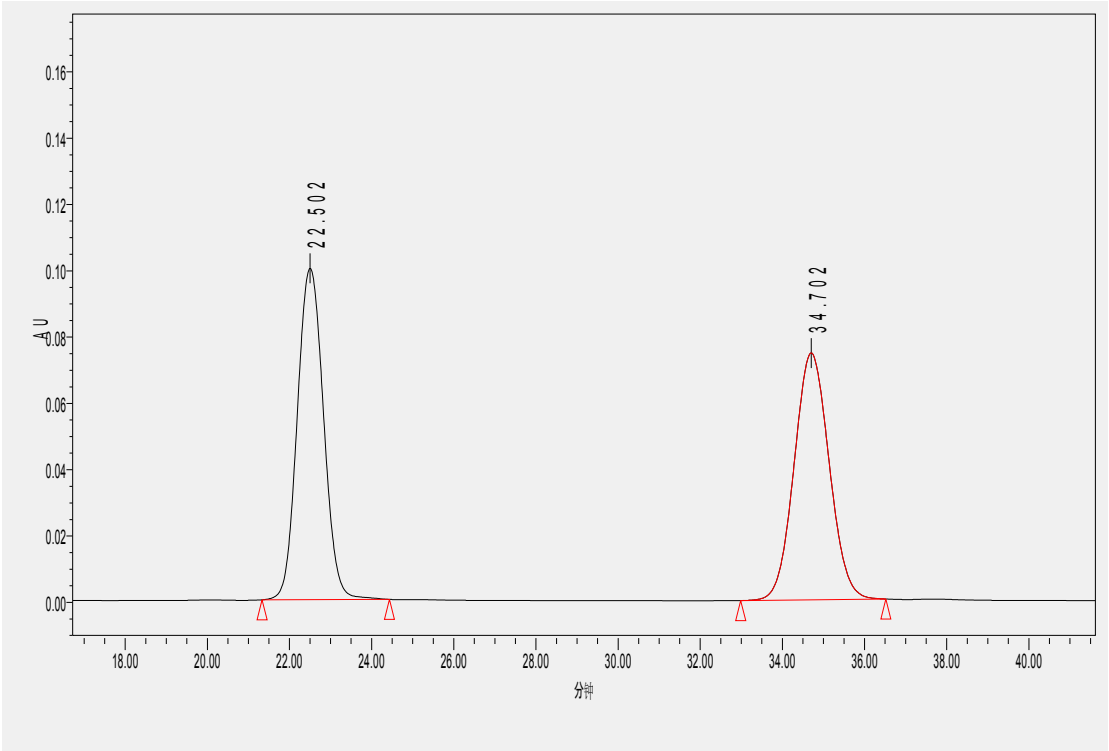

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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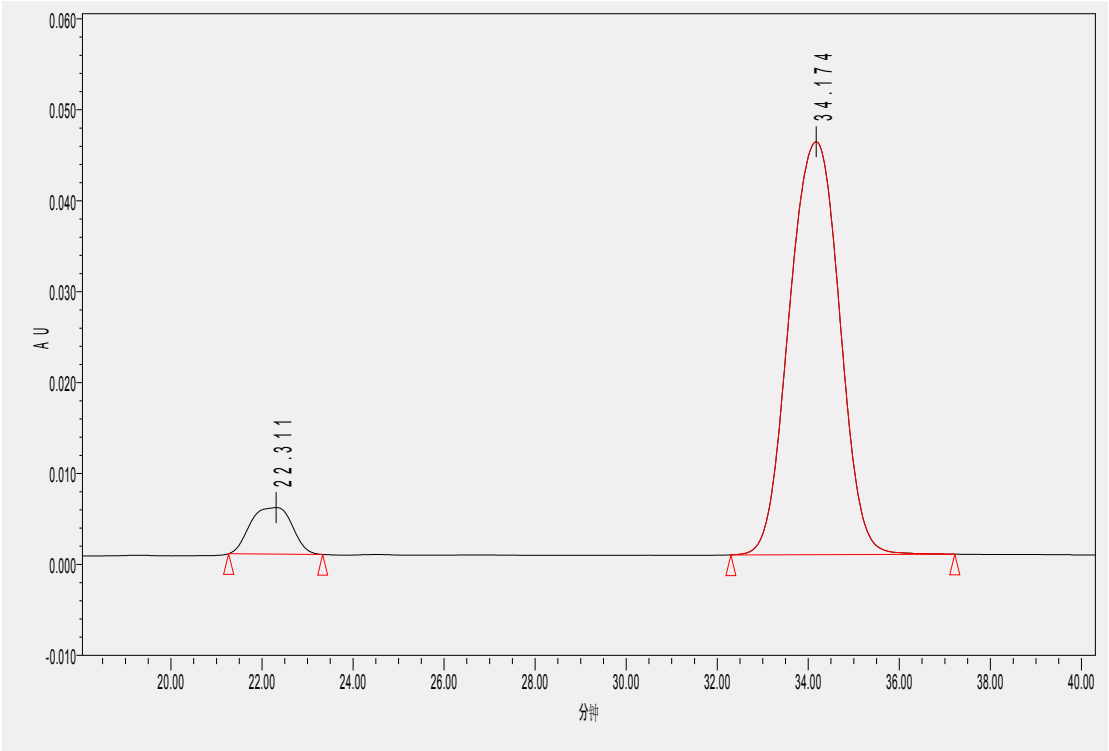

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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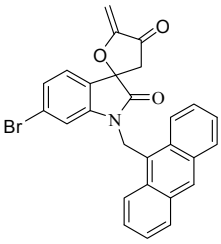
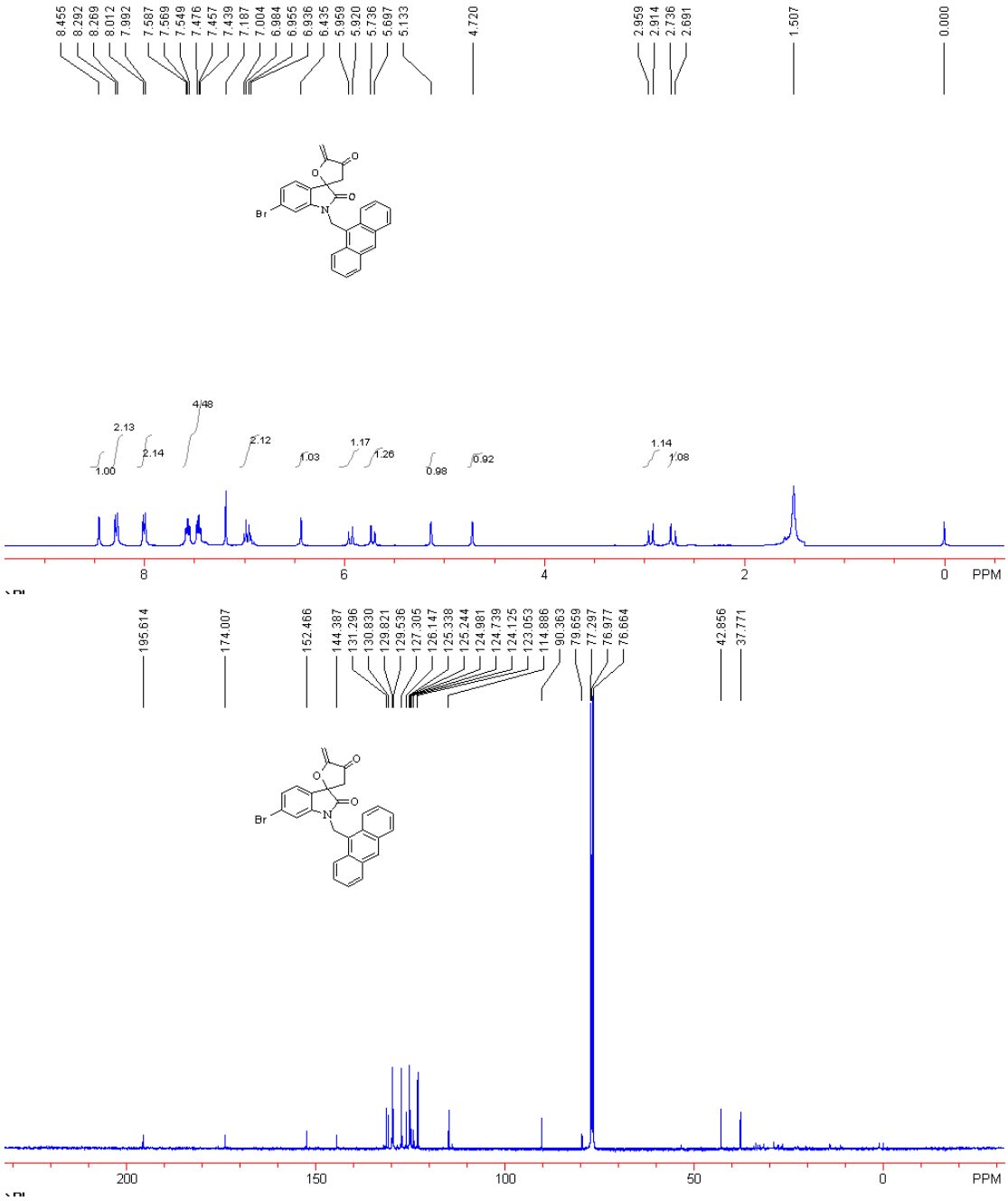


1'-(anthracen-9-ylmethyl)-6'-bromo-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dio ne (3i). 29 mg, 58% yield. mp. 321-323 ^{o}C (the racemate of **3i**. mp. 325-327 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.71 (d, 1H, J = 18.0 Hz, CH_2), 2.93 (d, 1H, J = 18.0 Hz, CH_2), 4.72 (s, 1H, =CH_2), 5.13 (s, 1H, =CH_2), 5.71 (d, 1H, J = 15.6 Hz, CH_2), 5.94 (d, 1H, J = 15.6 Hz, CH_2), 6.44 (s, 1H, ArH), 6.94-7.00 (m, 2H, ArH), 7.44-7.59 (m, 4H, ArH), 8.00 (d, 2H, J = 8.0 Hz, ArH), 8.28 (d, 2H, J = 8.0 Hz, ArH), 8.46 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 37.8, 42.9, 79.7, 90.4, 114.9, 123.1, 124.1, 124.7, 125.0, 125.2, 125.3, 126.1, 127.3, 129.5, 129.8, 130.8, 131.3, 144.4, 152.5, 174.0, 195.6; IR (CH_2Cl_2): ν 2923, 2851, 1748, 1713, 1412, 1400, 1277, 1249, 776, 755 cm^{-1}; MS (MALDI/DHB) m/z (%): 483.0 $[M]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{27}H_{18}BrNNaO_3$ $[M + Na]^+$ requires 506.0362, Found: 506.0376. $[\alpha]^{20}_D$ = -34.1 (c 0.4, CH_2Cl_2, 81% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 23.30 min, t_{major} = 37.02 min).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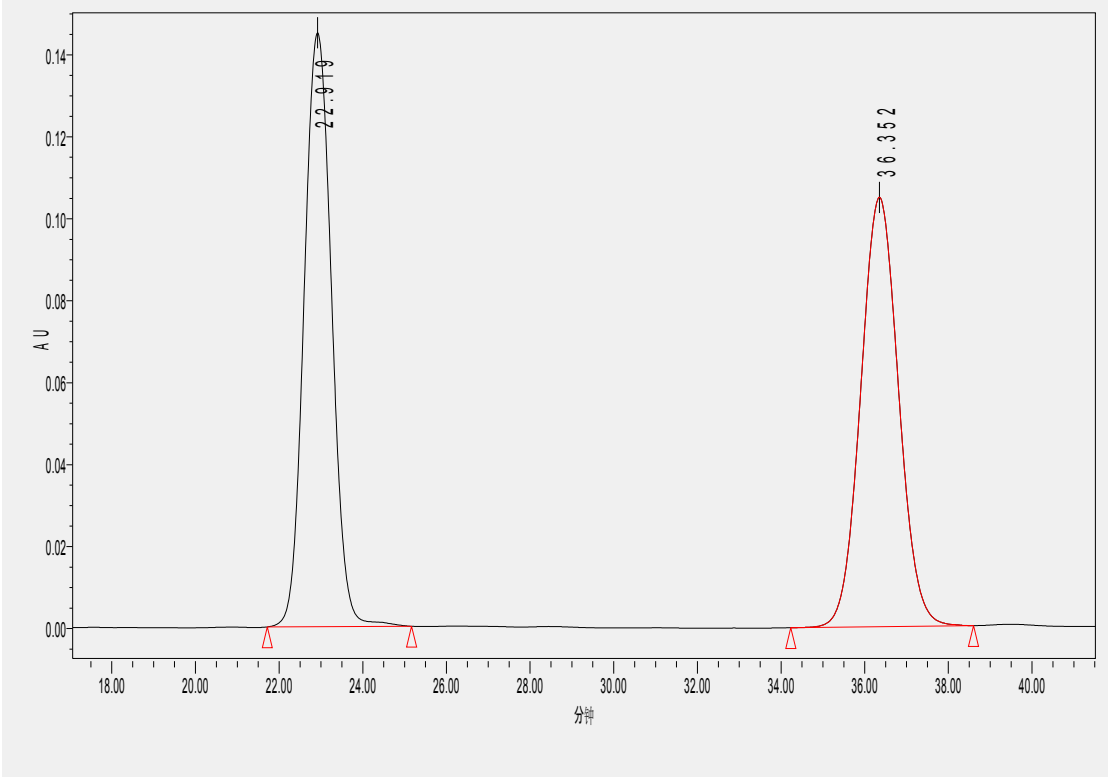

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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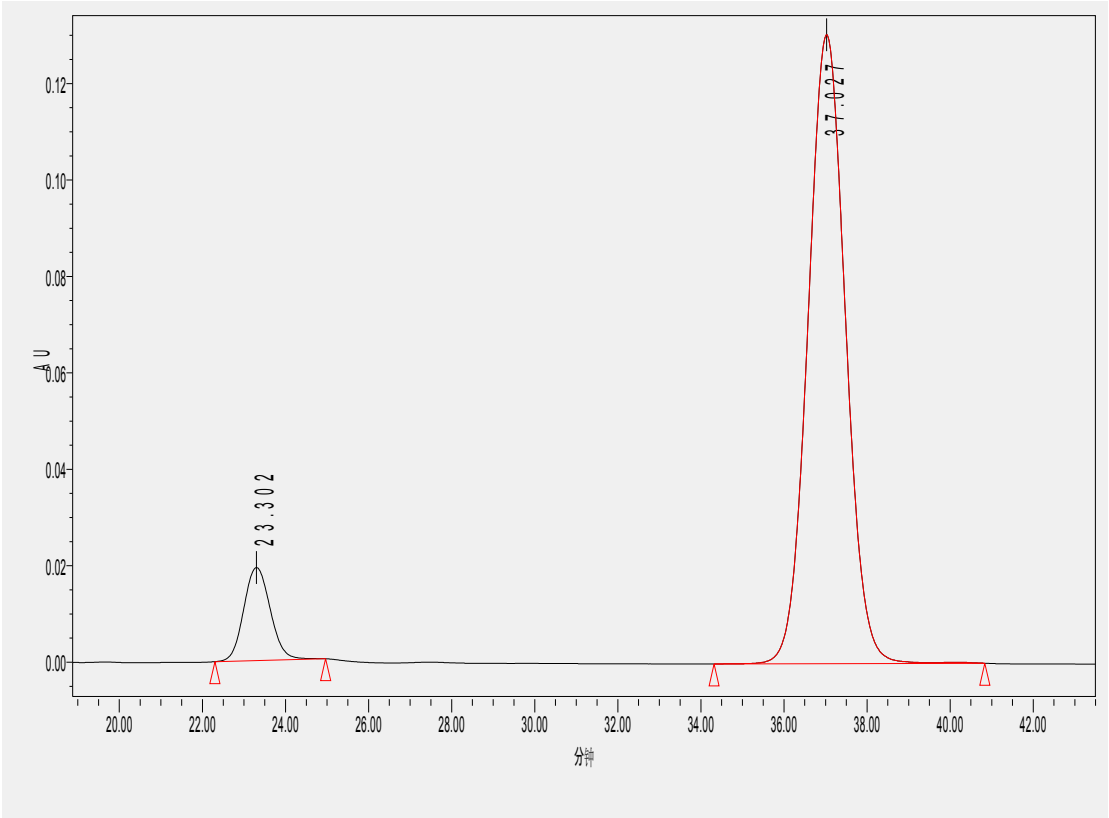
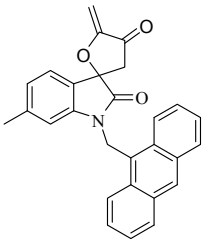
2	2	36.352	6594155	49.95	104802

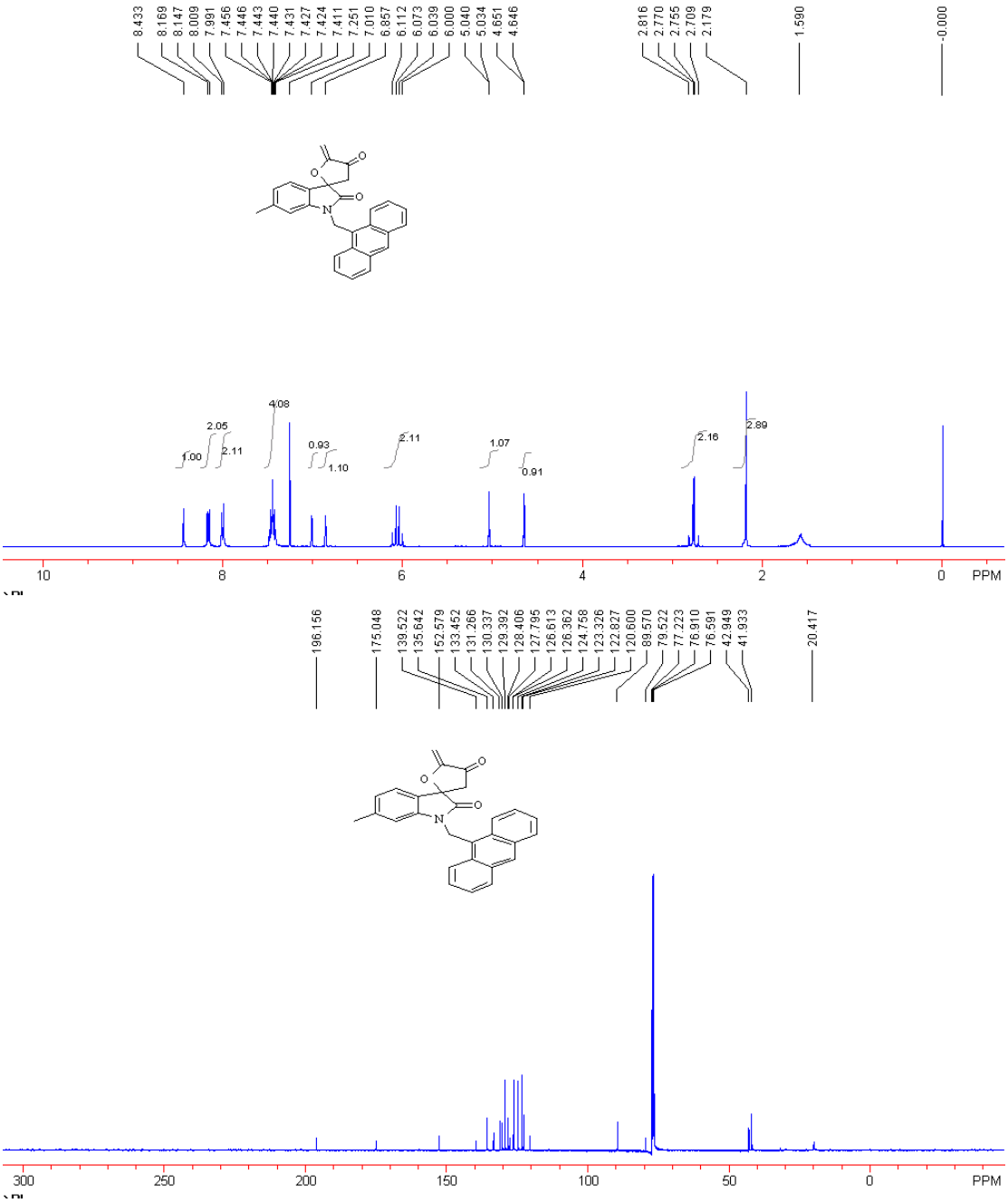


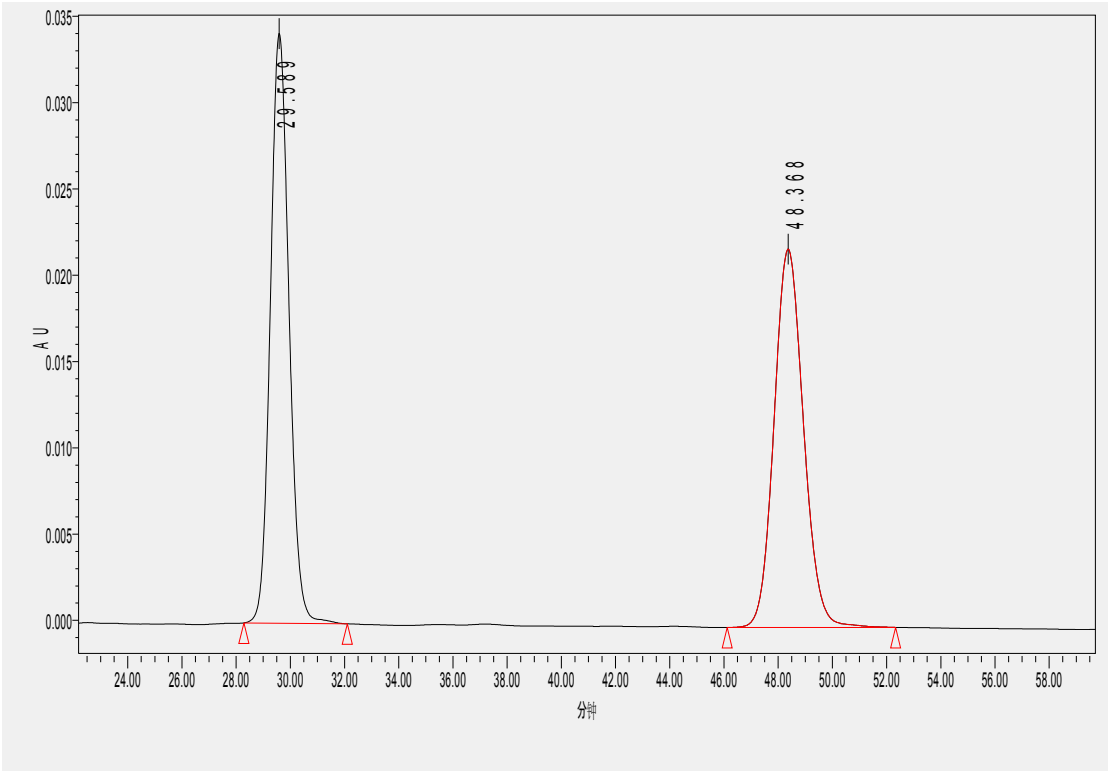
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight

1	1	23.302	855774	9.46	19289
2	2	37.027	8186120	90.54	130448



1'-(anthracen-9-ylmethyl)-6'-methyl-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3j). 27 mg, 62% yield. mp. 305-306 ^{o}C (the racemate of **3j**. mp. 309-311 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.18 (s, 3H, CH_3), 2.73 (d, 1H, J = 18.4 Hz, CH_2), 2.79 (d, 1H, J = 18.4 Hz, CH_2), 4.65 (d, 1H, J = 2.0 Hz, =CH_2), 5.04 (d, 1H, J = 2.0 Hz, =CH_2), 6.02 (d, 1H, J = 15.6 Hz, CH_2), 6.09 (d, 1H, J = 15.6 Hz, CH_2), 6.86 (s, 1H, ArH), 7.01 (s, 1H, ArH), 7.23 (s, 1H, Ar), 7.41-7.46 (m, 4H, ArH), 8.00 (d, 2H, J = 8.0 Hz, ArH), 8.16 (d, 2H, J = 8.0 Hz, ArH), 8.43 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.4, 41.9, 42.9, 79.5, 89.6, 120.6, 122.8, 123.3, 124.8, 126.4, 126.6, 127.8, 128.4 129.4, 130.3, 131.3, 133.5, 135.6, 139.5, 152.6, 175.0, 196.2; IR (CH_2Cl_2): ν 2962, 2923, 2845, 1749, 1713, 1412, 1409, 1270, 1212, 776, 757 cm^{-1}; MS (MALDI/DHB) m/z (%): 419.1 $[M]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{28}H_{21}NNaO_3$ $[M + Na]^+$ requires 442.1414, Found: 442.1423. $[\alpha]^{20}_D$ = -37.6 (c 0.4, CH_2Cl_2, 77% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 80/20, 0.5 mL/min, 230 nm, t_{minor} = 29.28 min, t_{major} = 47.46min).


8.433
8.169
8.147
8.009
7.991
7.456
7.446
7.443
7.440
7.431
7.427
7.424
7.411
7.251
7.010
6.857
6.112
6.073
6.039
6.000
5.040
5.034
4.651
4.646
2.816
2.770
2.755
2.709
2.179
1.590
-0.000
4.08
2.05
2.11
1.00
0.93
1.10
2.11
1.07
0.91
2.16
2.89
10
8
6
4
2
0
PPM
196.156
175.048
139.522
135.642
152.579
133.452
131.266
130.337
129.392
128.406
127.795
126.613
126.362
124.758
123.326
122.827
120.600
89.570
79.522
77.223
76.910
76.591
42.949
41.933
20.417
300
250
200
150
100
50
0
PPM



No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
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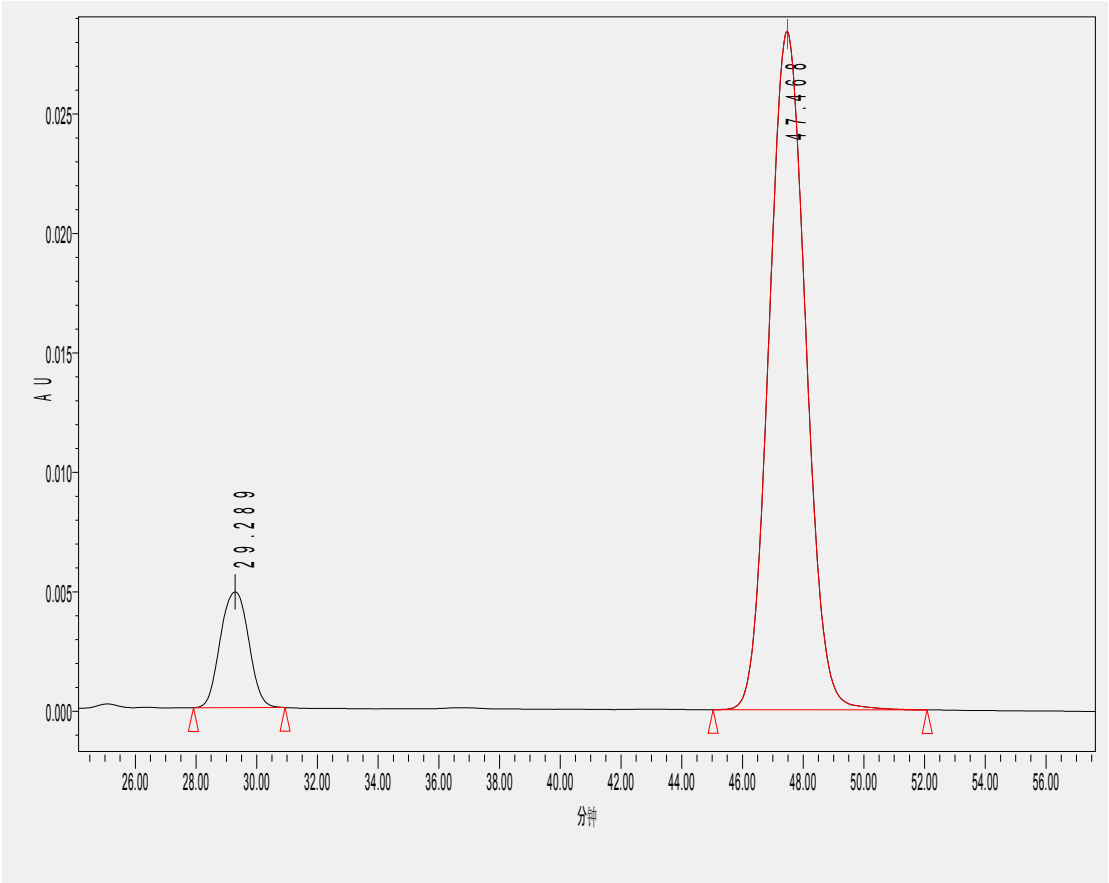
2	2	48.368	1651376	50.21	21920



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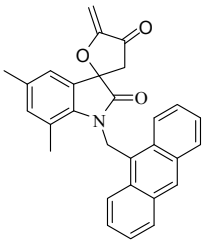
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	29.289	315152	11.65	4844
2	2	47.468	2390698	88.35	28397



1'-(anthracen-9-ylmethyl)-5',7'-dimethyl-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3k). 32 mg, 71% yield. mp. 313-315 ^{o}C (the racemate of **3k**. mp. 319-321 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.18 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.74 (d, 1H, J = 18.4 Hz, CH_2), 2.80 (d, 1H, J = 18.4 Hz, CH_2), 4.65 (d, 1H, J = 2.4 Hz, =CH_2), 5.04 (d, 1H, J = 2.4 Hz, =CH_2), 6.02 (d, 1H, J = 16.0 Hz, CH_2), 6.09 (d, 1H, J = 16.0 Hz, CH_2), 6.86 (s, 1H, ArH), 7.02 (s, 1H, ArH), 7.41-7.49 (m, 4H, ArH), 7.99-8.02 (m, 2H, ArH), 8.16 (d, 2H, J = 8.8 Hz, ArH), 8.44 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.2, 24.9, 37.3, 38.3, 74.8, 84.9, 115.9, 118.2, 118.7, 120.1, 121.7, 123.1, 123.7, 124.7, 125.7, 126.6, 128.8, 131.0, 134.8, 147.9, 170.4, 191.5; IR (CH_2Cl_2): ν 2952, 2920, 2851, 1748, 1713, 1412, 1409, 1255, 1212, 776, 757 cm^{-1}; MS (MALDI/DHB) m/z (%): 456.1 $[M + Na]^+$ (100); MS (MALDI/DHB) Calcd. for $C_{29}H_{23}NNaO_3$ $[M + Na]^+$ requires 456.1570, Found: 456.1562. $[\alpha]^{20}_D$ = -45.1 (c 0.4, CH_2Cl_2, 90% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 60/40, 0.5 mL/min, 230 nm, t_{minor} = 24.67 min, t_{major} = 36.25 min).

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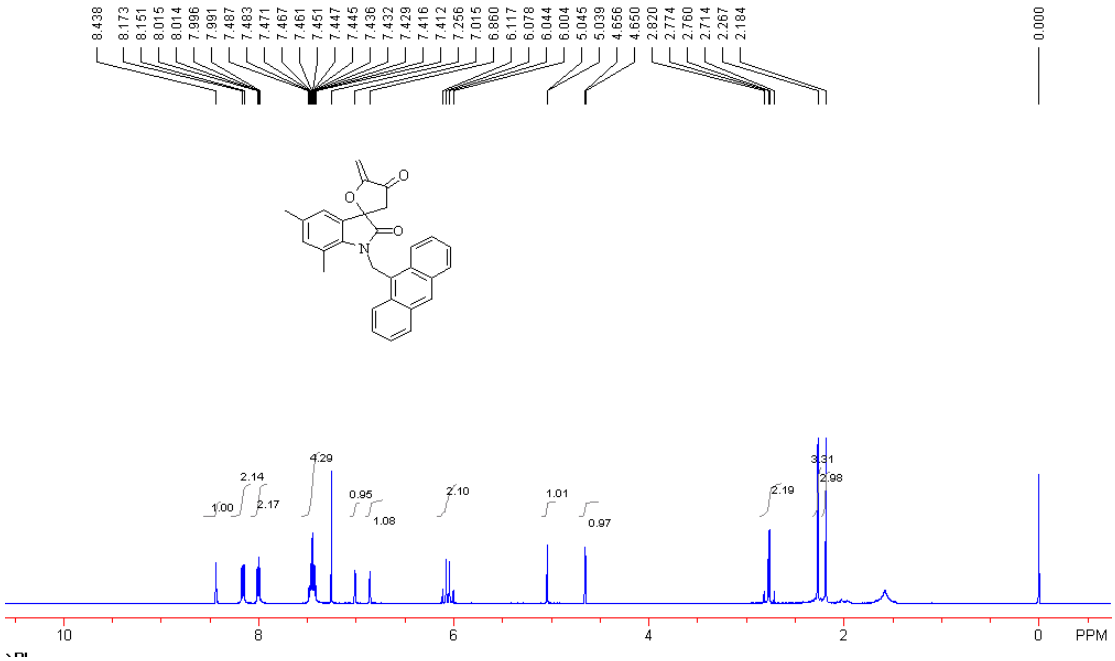
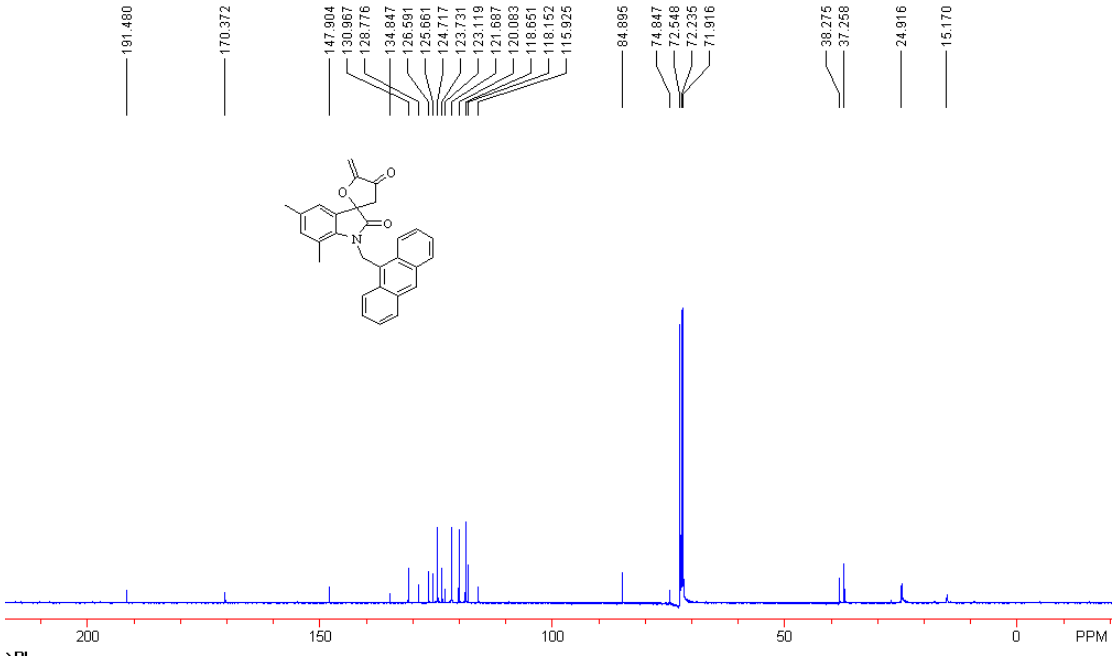
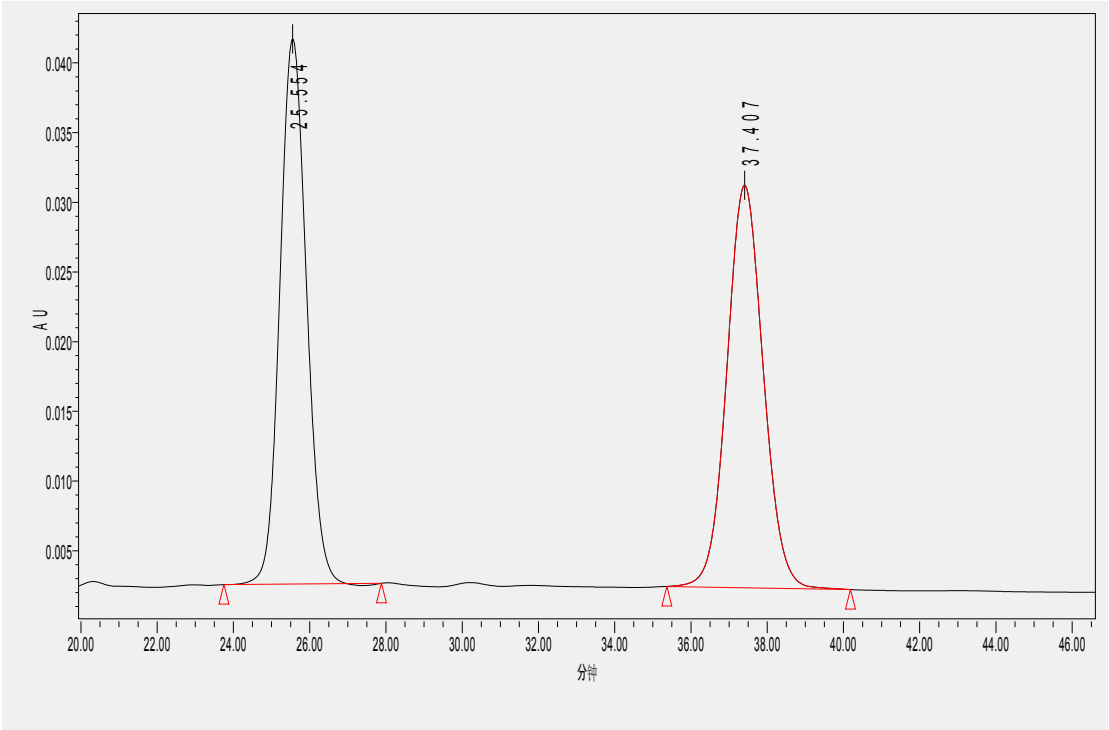
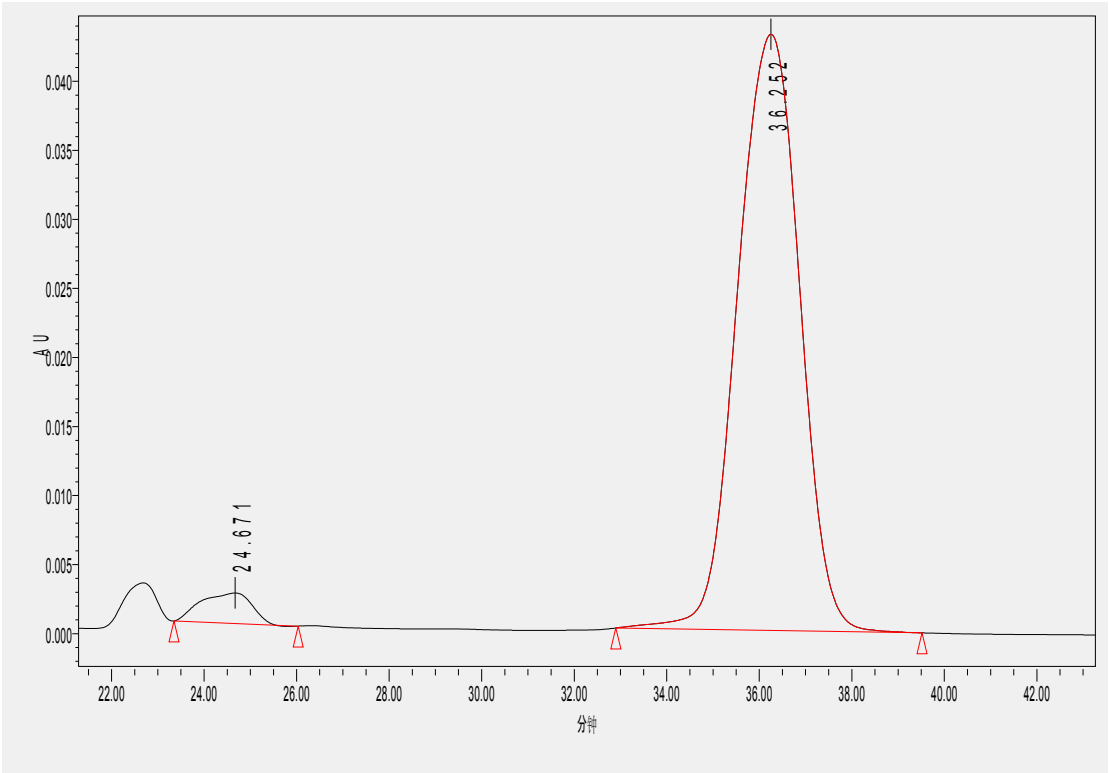


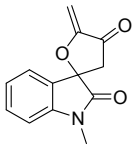




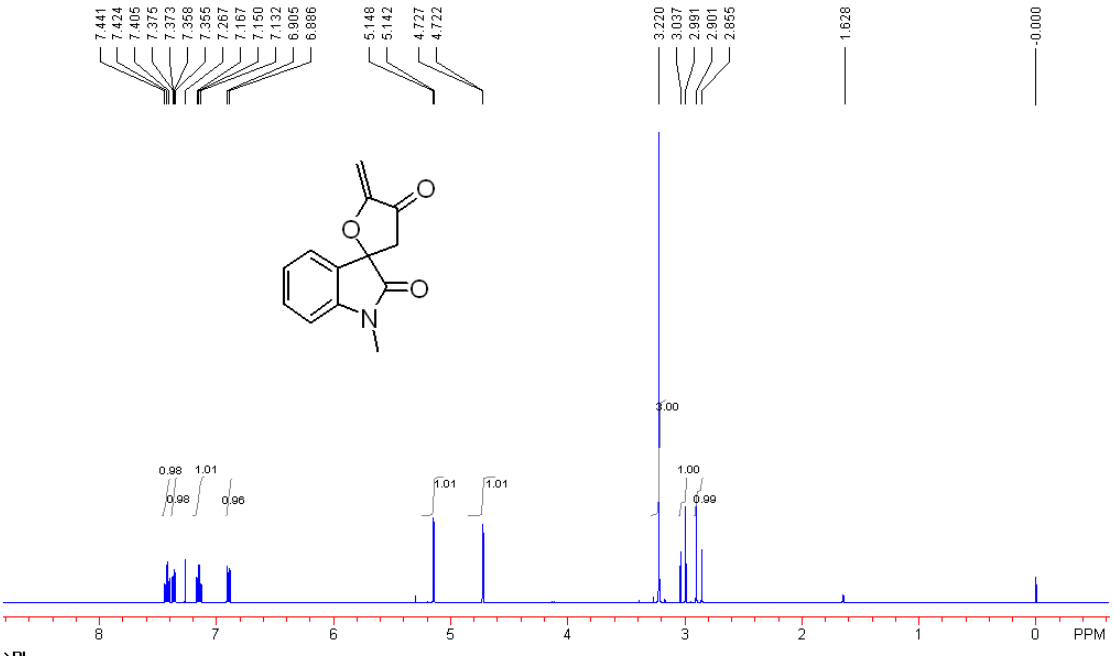
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	25.554	1899641	49.75	39123
2	2	37.407	1918617	50.25	28882

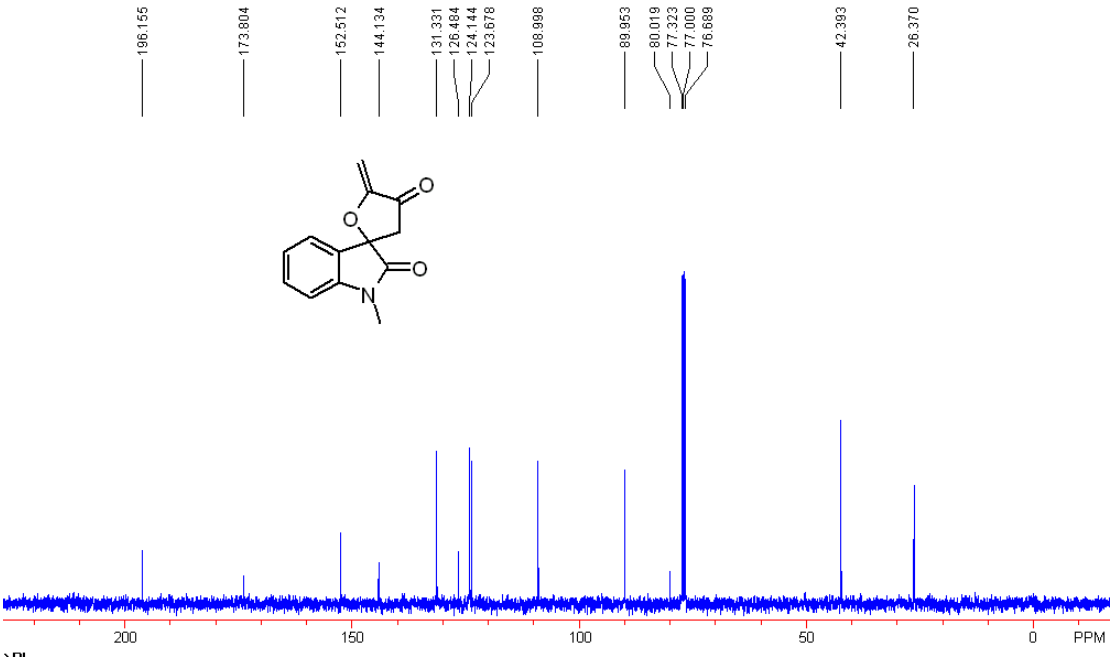


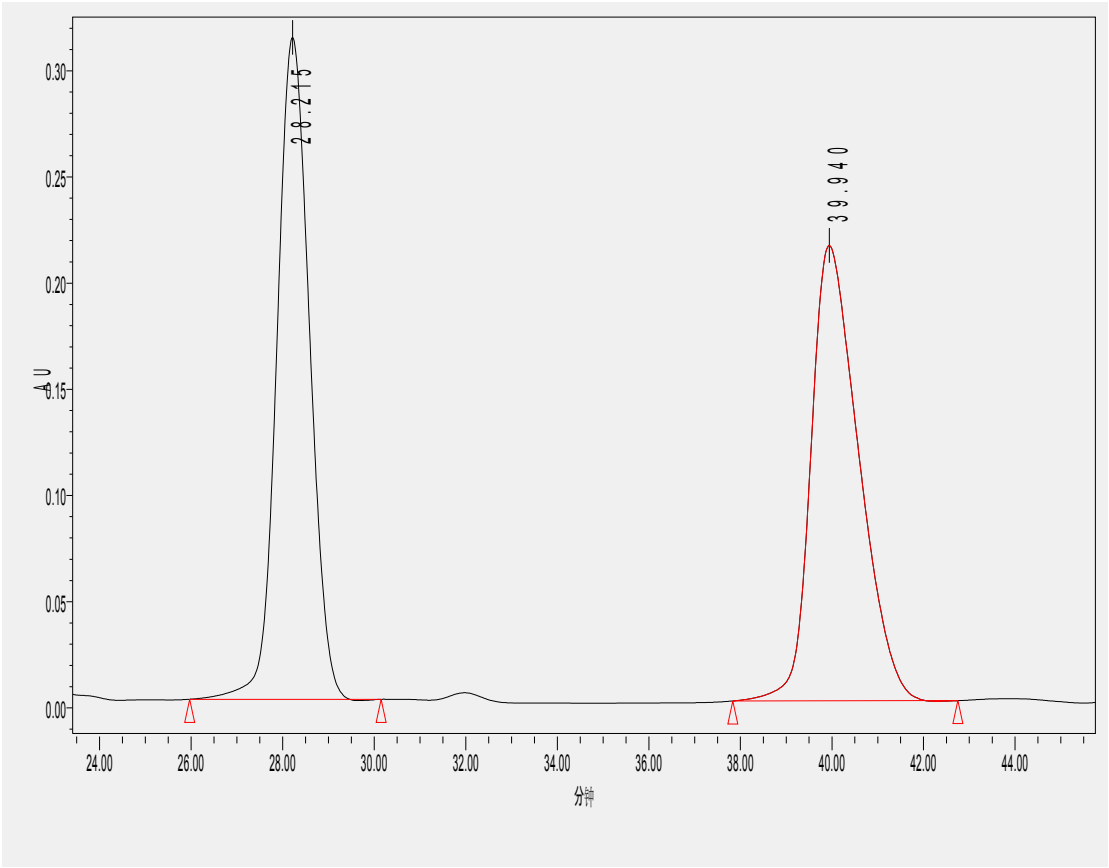
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	24.671	169495	4.04	2212
2	2	36.252	4027578	95.96	43177



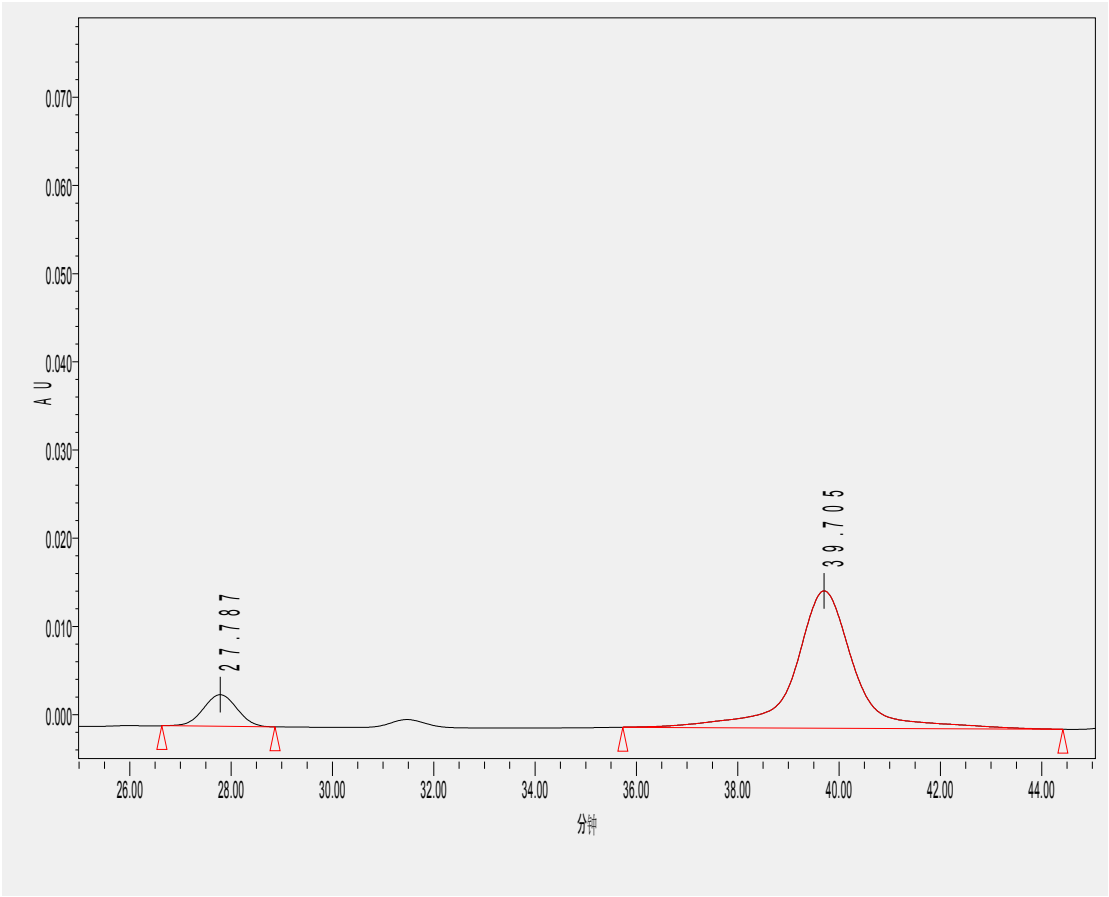
1'-methyl-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3l). 15 mg, 59% yield. mp. 270-272 ^{o}C (the racemate of **3l**. mp. 275-280 ^{o}C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.88 (d, 1H, J = 18.4 Hz, CH_2), 3.01 (d, 1H, J = 18.4 Hz, CH_2), 3.12 (s, 3H, CH_3), 4.72 (d, 1H, J = 2.0 Hz, =CH_2), 5.14 (d, 1H, J = 2.0 Hz, =CH_2), 6.89 (d, 1H, J = 7.6 Hz, ArH), 7.13-7.17 (m, 1H, ArH), 7.36 (d, 1H, J = 7.6 Hz, ArH), 7.41-7.44 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 26.4, 42.4, 80.0, 90.0, 109.0, 123.7, 124.1, 126.5, 131.3, 144.1, 152.5, 173.8, 196.2; IR (CH_2Cl_2): ν 2926, 2855, 1727, 1616, 1495, 1471, 1377, 1354, 1311, 1273, 1123, 1098, 996, 752 cm^{-1}; MS (ESI) m/z (%): 229.9 $[M]^+$ (100); MS (ESI) Calcd. for $C_{13}H_{11}NNaO_3$ $[M + Na]^+$ requires 252.0631, Found: 252.0630. $[\alpha]^{20}_D$ = -41.5 (c 0.4, CH_2Cl_2, 76% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 50/50, 0.5 mL/min, 230 nm, t_{minor} = 27.78 min, t_{major} = 39.70 min).



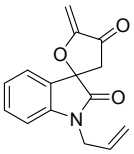




No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	28.215	15510751	49.89	311691
2	2	39.940	15576269	50.11	214443

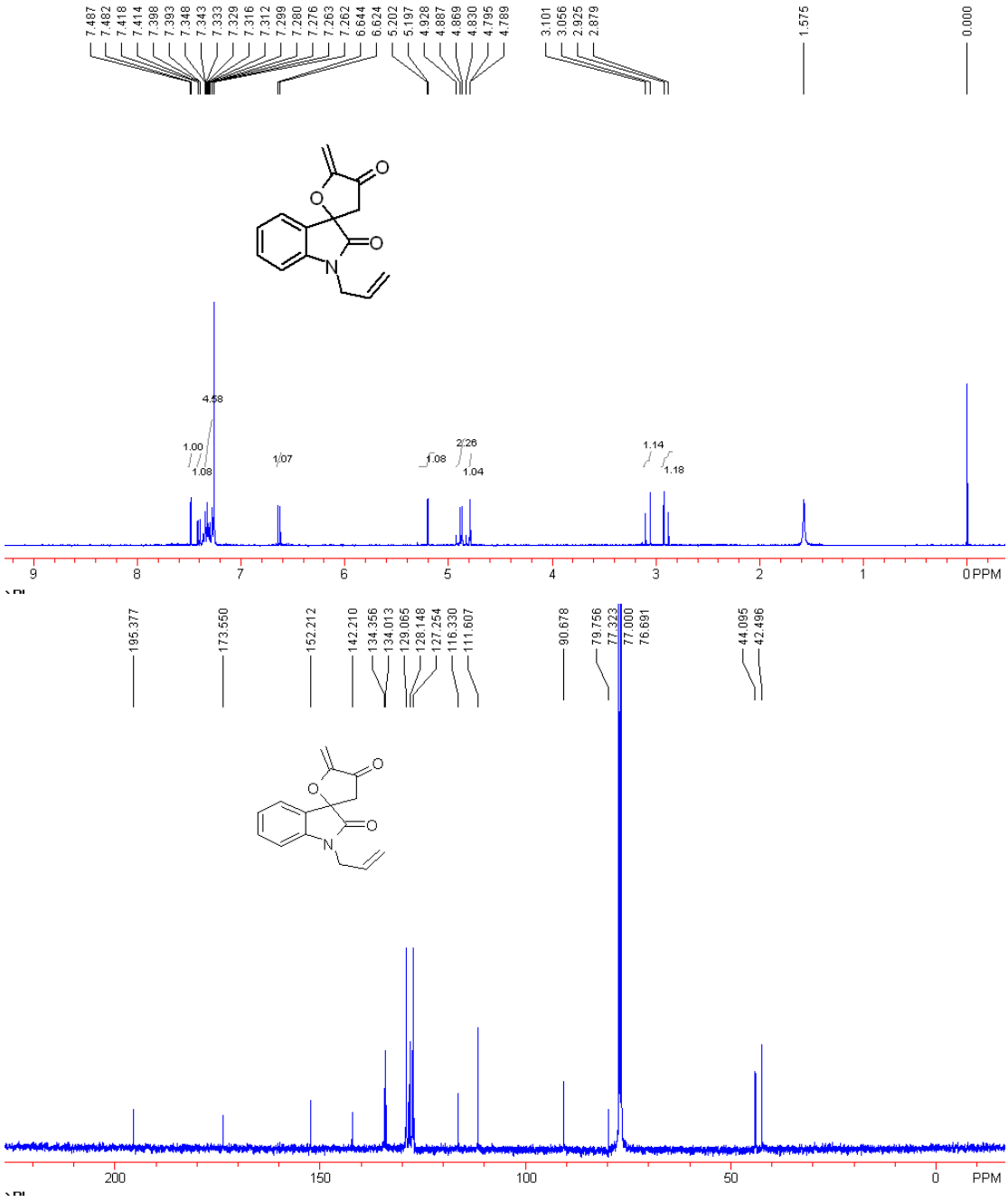


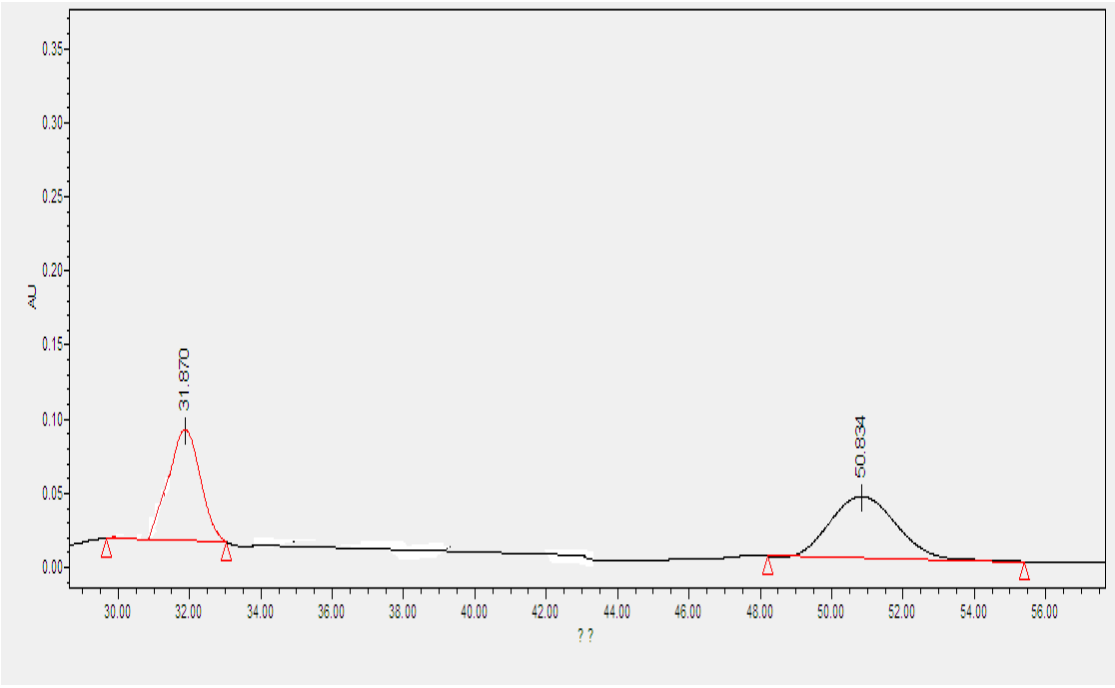
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	27.787	166402	11.58	3589
2	2	39.705	1270280	88.42	15573



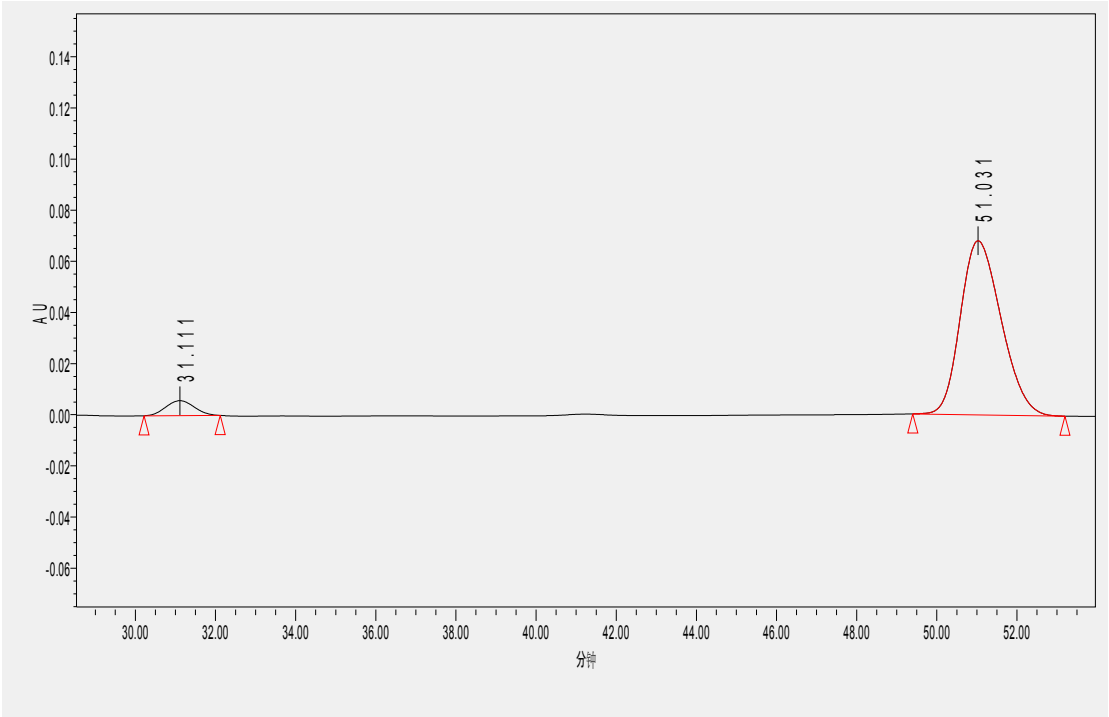
1'-allyl-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3m). 14 mg, 55% yield. mp. 270-271 °C (the racemate of **3m**. mp. 275-277 °C); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.89 (d, 1H, J = 18.4 Hz, CH_2), 3.07 (d, 1H, J = 18.4 Hz, CH_2), 4.79 (d, 1H, J = 2.4 Hz, =CH_2), 4.84 (d, 1H, J = 15.6 Hz, CH_2), 4.90 (d, 1H, J = 15.6 Hz, CH_2), 5.20 (d, 1H, J = 2.4 Hz, =CH_2), 6.63 (d, 1H, J = 8.0 Hz, =CH), 7.26-7.35 (m, 4H, ArH), 7.40 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.0 Hz, =CH_2), 7.48 (d, 1H, J = 2.0 Hz, =CH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 42.5, 44.1, 79.8, 90.7, 111.6, 116.3, 127.3, 128.1, 129.1, 134.0, 134.4, 142.2, 152.2, 173.6, 195.4; IR (CH_2Cl_2): ν 2955, 2923,

2852, 1772, 1726, 1615, 1489, 1468, 1436, 1375, 1310, 1268, 1189, 1106, 993, 931, 755, 740, 703 cm^{-1}; MS (%) (EI) *m/z* 255 (M^+, 7.3), 185 (63.3), 91 (100), 71 (42.0), 56 (78.2), 43 (83.1). HRMS (EI) Calcd. for $C_{15}H_{13}NO_3$ requires 255.0895, Found: 255.0891. $[\alpha]^{20}_D$ = -28.2 (c 0.4, CH_2Cl_2, 75% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 230 nm, t_{minor} = 31.11 min, t_{major} = 51.03 min).

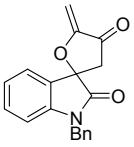




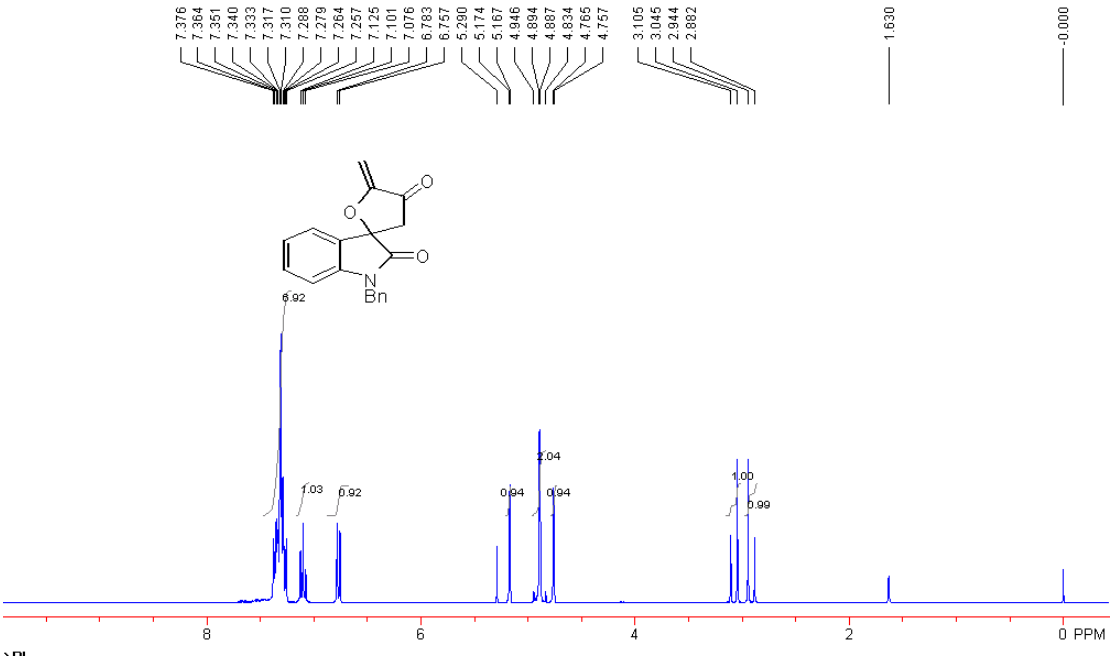
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	31.870	5476595	50.44	74750
2	2	50.834	5381699	49.56	41600

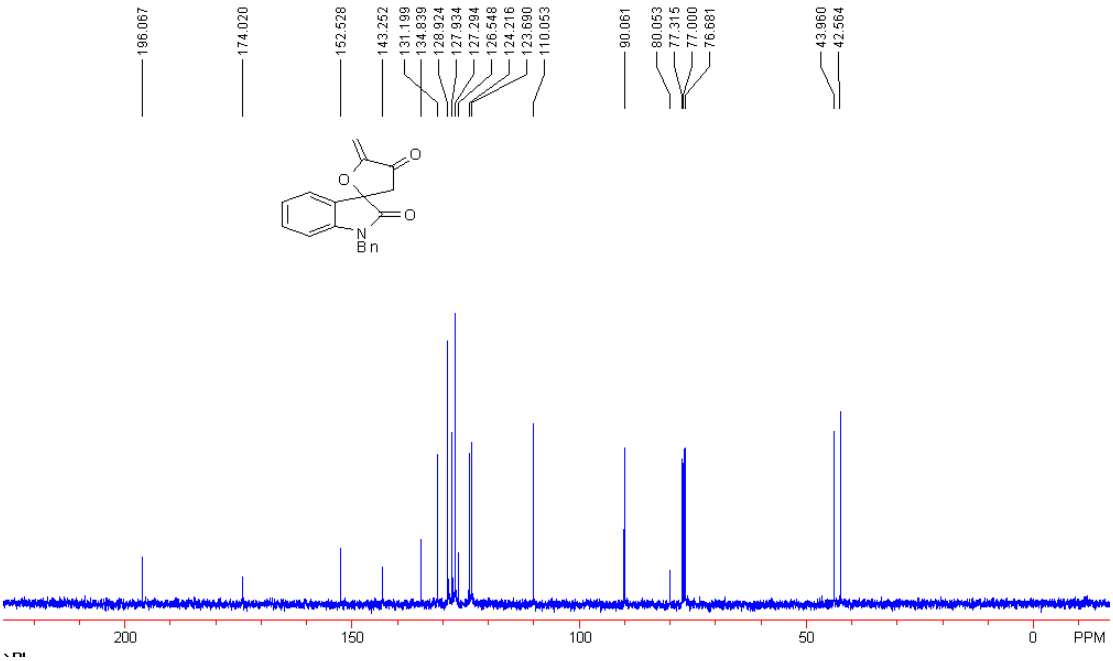


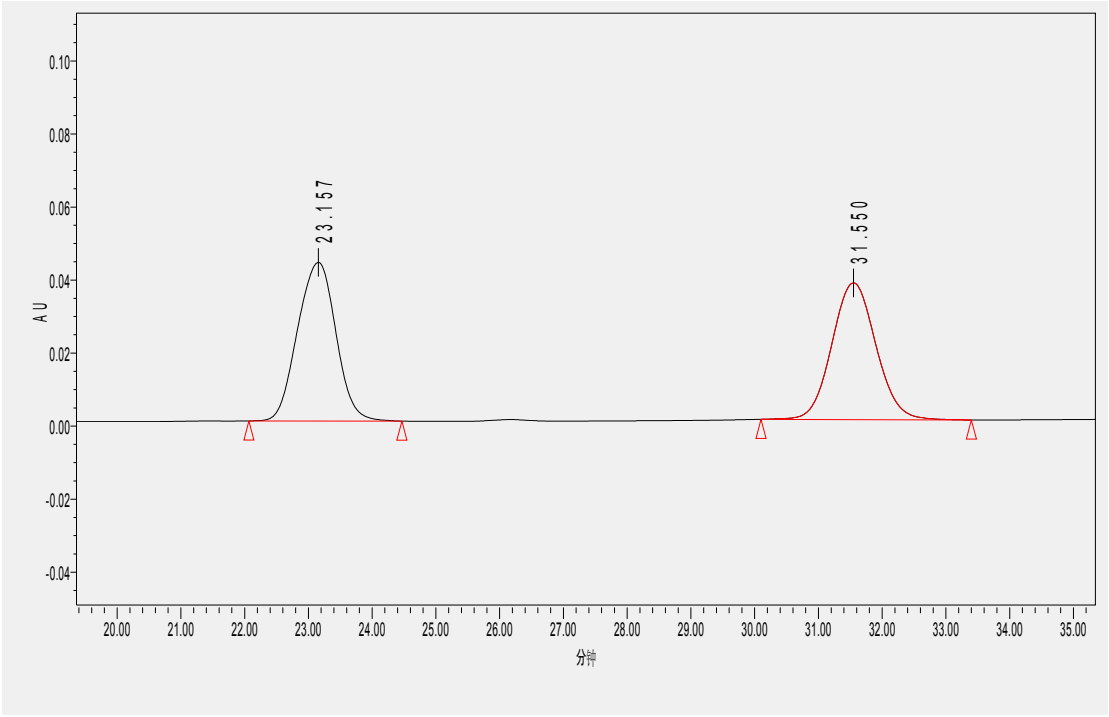
No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	31.111	288835	5.66	5834
2	2	51.031	4810282	94.34	68090



1'-benzyl-5-methylene-3H-spiro[furan-2,3'-indoline]-2',4(5H)-dione (3n). 19 mg, 62% yield. mp. 282-283 °C (the racemate of **3n**. mp. 285-289 °C); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.91 (d, 1H, J = 18.6 Hz, CH_2), 3.07 (d, 1H, J = 18.6 Hz, CH_2), 4.76 (d, 1H, J = 2.4 Hz, =CH_2), 4.85 (d, 1H, J = 15.6 Hz, CH_2), 4.92 (d, 1H, J = 15.6 Hz, CH_2), 5.17 (d, 1H, J = 2.4 Hz, =CH_2), 6.76 (d, 1H, J = 7.2 Hz, ArH), 7.08-7.13 (m, 1H, ArH), 7.26-7.38 (m, 6H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 42.6, 44.0, 80.1, 90.1, 110.1, 123.7, 124.2, 126.5, 127.3, 127.9, 128.9, 131.2, 134.8, 143.3, 152.5, 174.0, 196.1; IR (CH_2Cl_2): ν 2950, 2918, 2872, 1733, 1635, 1602, 1496, 1456, 1377, 1356, 1234, 1222, 1185, 1164, 1112, 1030, 790, 740, 645 cm^{-1}; MS (%) (ESI) *m/z* 306.1 $[M + H]^+$ (100); HRMS (ESI) Calcd. for $C_{19}H_{16}NO_3$ $[M + H]^+$ requires 306.1125, Found: 306.1131. $[\alpha]^{20}_D$ = -23.5 (c 1.0, CH_2Cl_2, 67% ee) Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column (*n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 230 nm, t_{minor} = 20.94 min, t_{major} = 27.10 min).







No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	23.157	1813610	50.21	43430
2	2	31.550	1798772	49.79	37443

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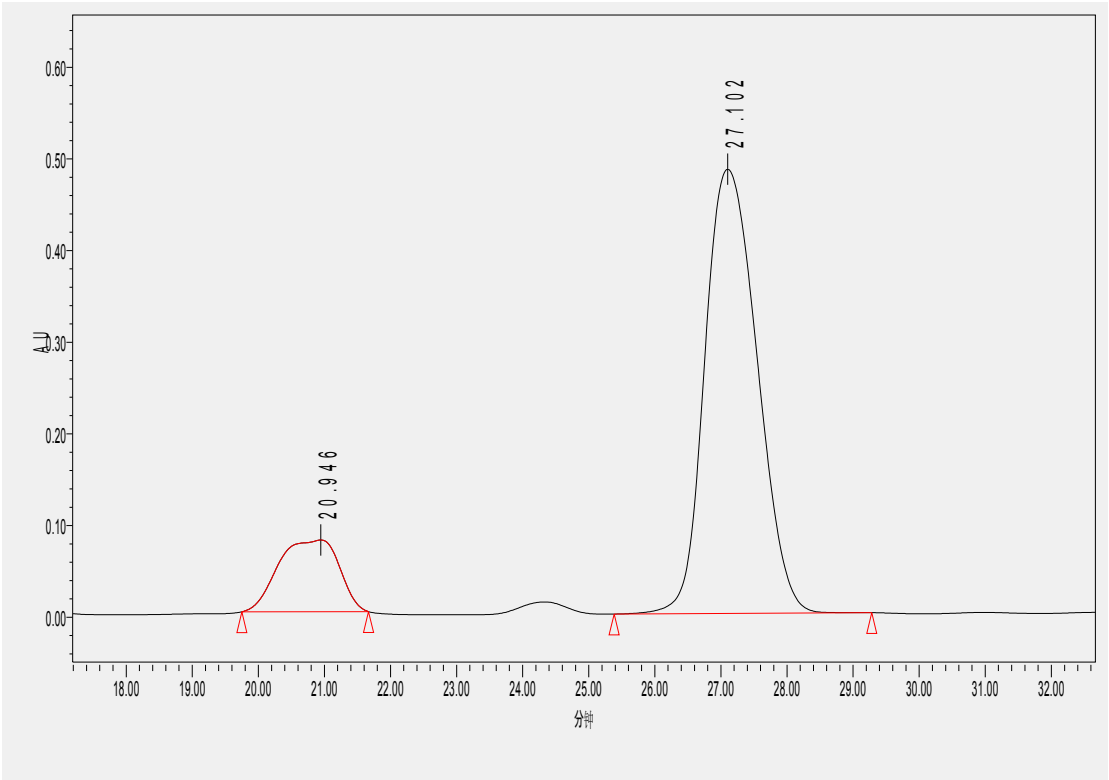

No.	PeakNo	R. Time	PeakArea	PerCent	PeakHeight
1	1	20.946	4985804	15.75	78236
2	2	27.102	26677971	84.25	484711