

*Supporting information*

**Neophthalides A and B, two pairs of unusual phthalide analog enantiomers from *Ligusticum chuanxiong***

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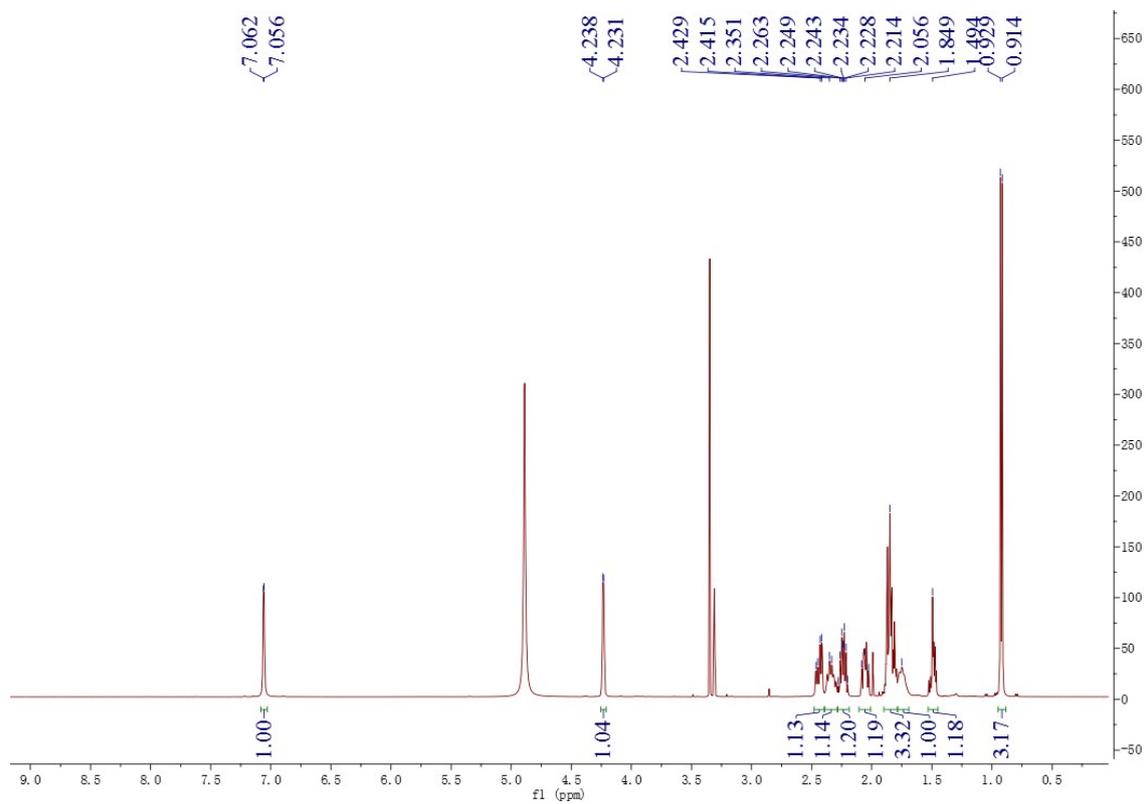
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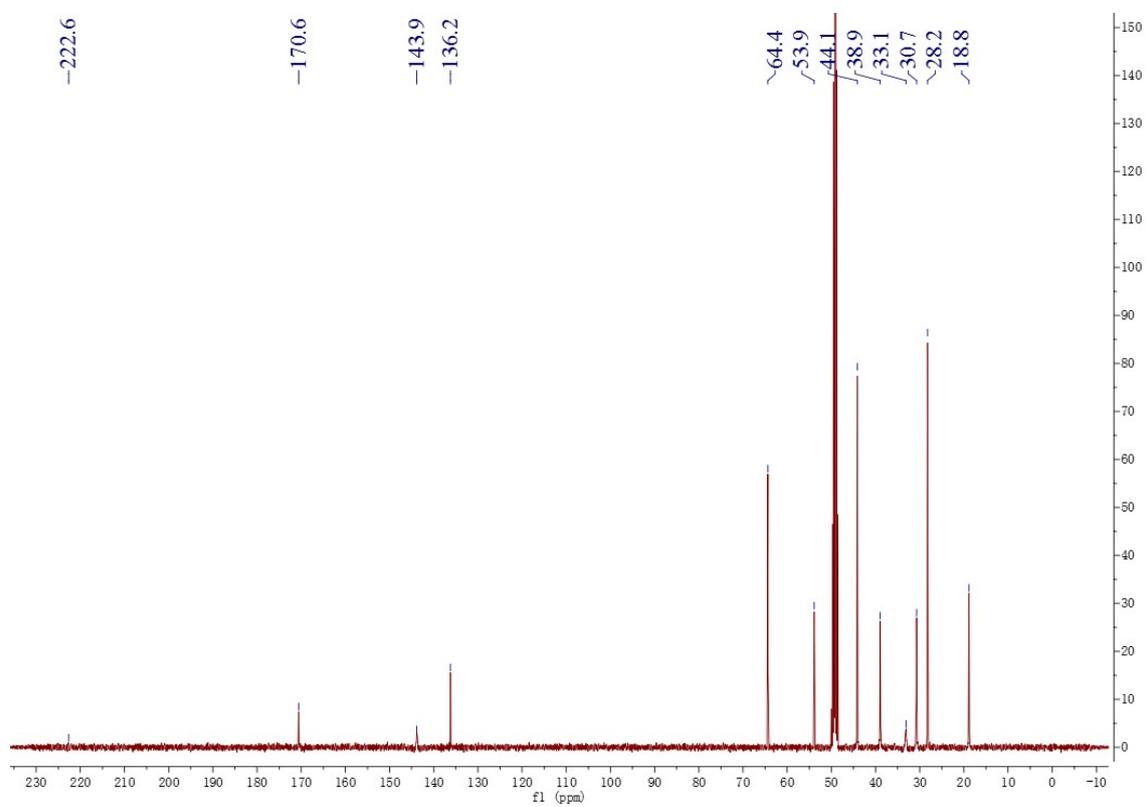
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**Figure S1.** The  $^1\text{H}$  NMR spectrum of compound **1** in methanol- $d_4$



**Figure S2.** The  $^{13}\text{C}$  NMR spectrum of compound **1** in methanol- $d_4$

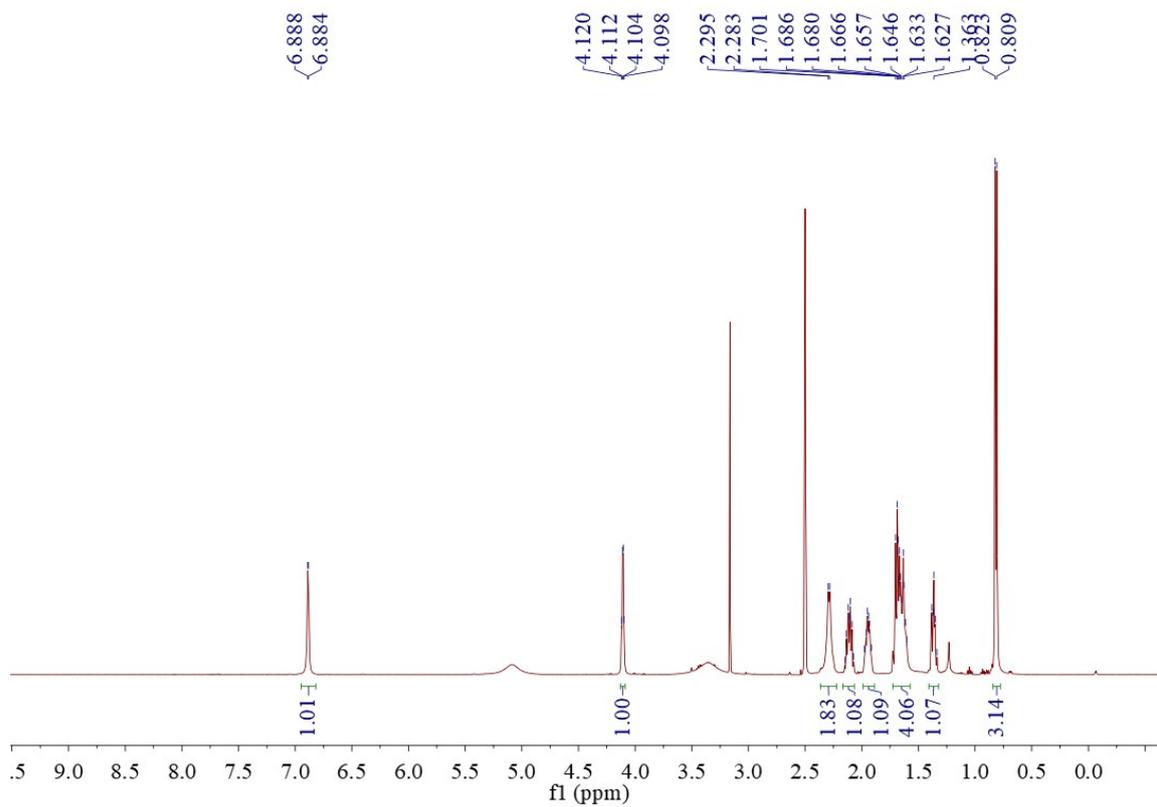


Figure S3. The <sup>1</sup>H NMR spectrum of compound **1** in DMSO-*d*<sub>6</sub>

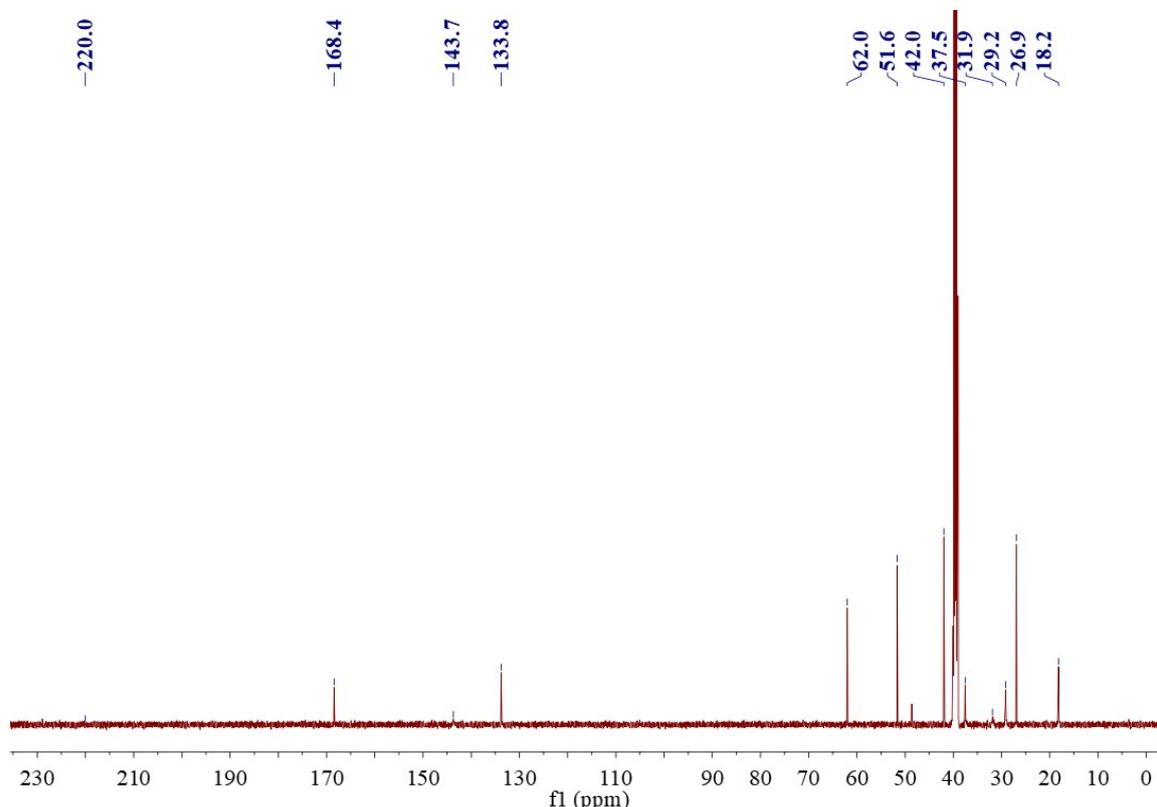
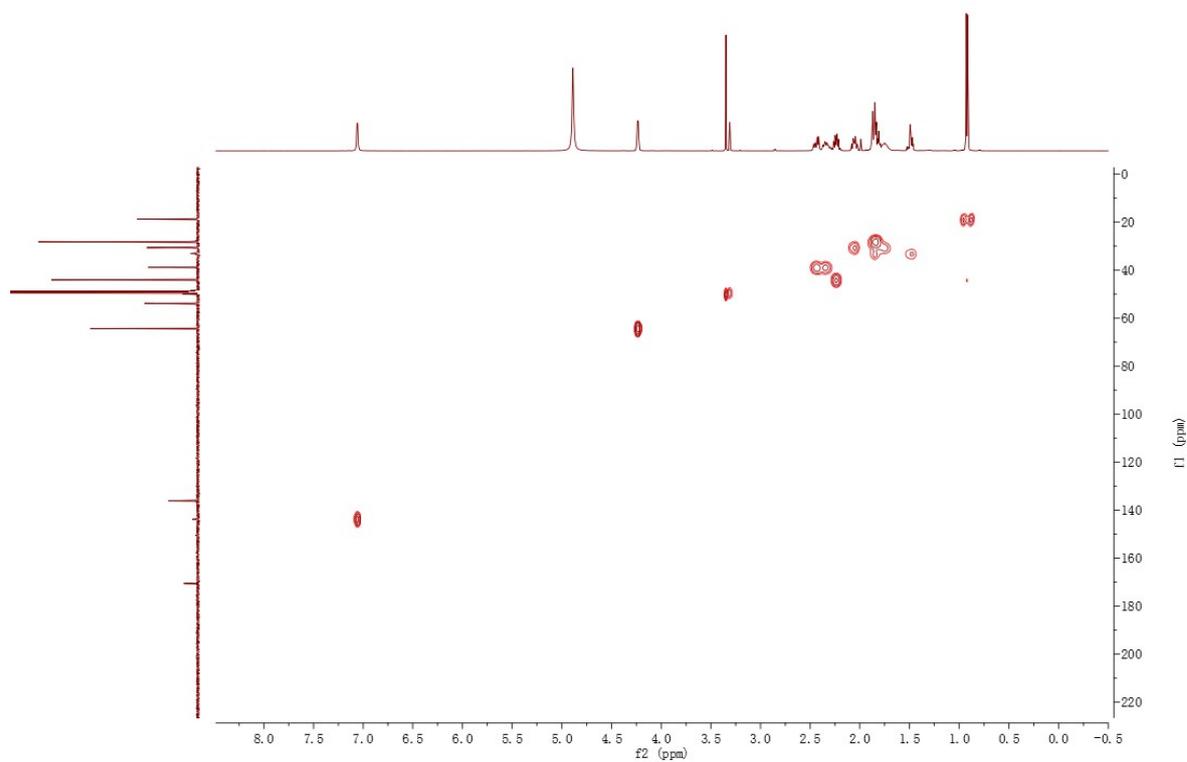
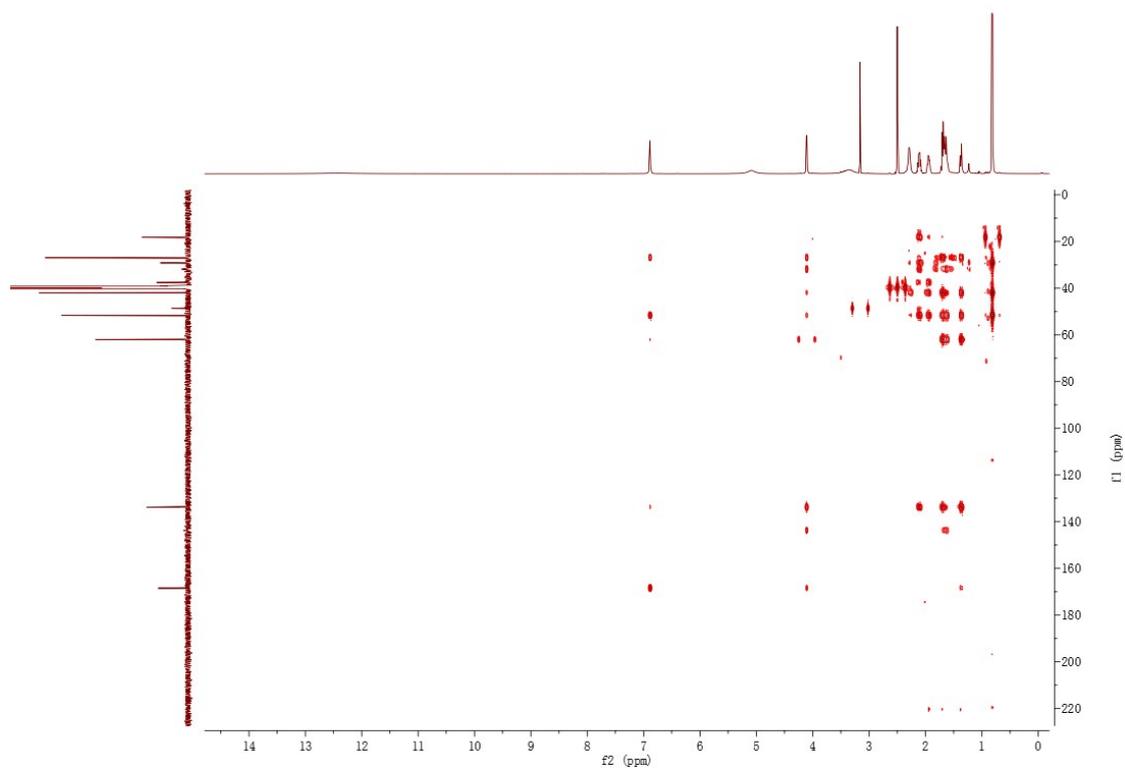


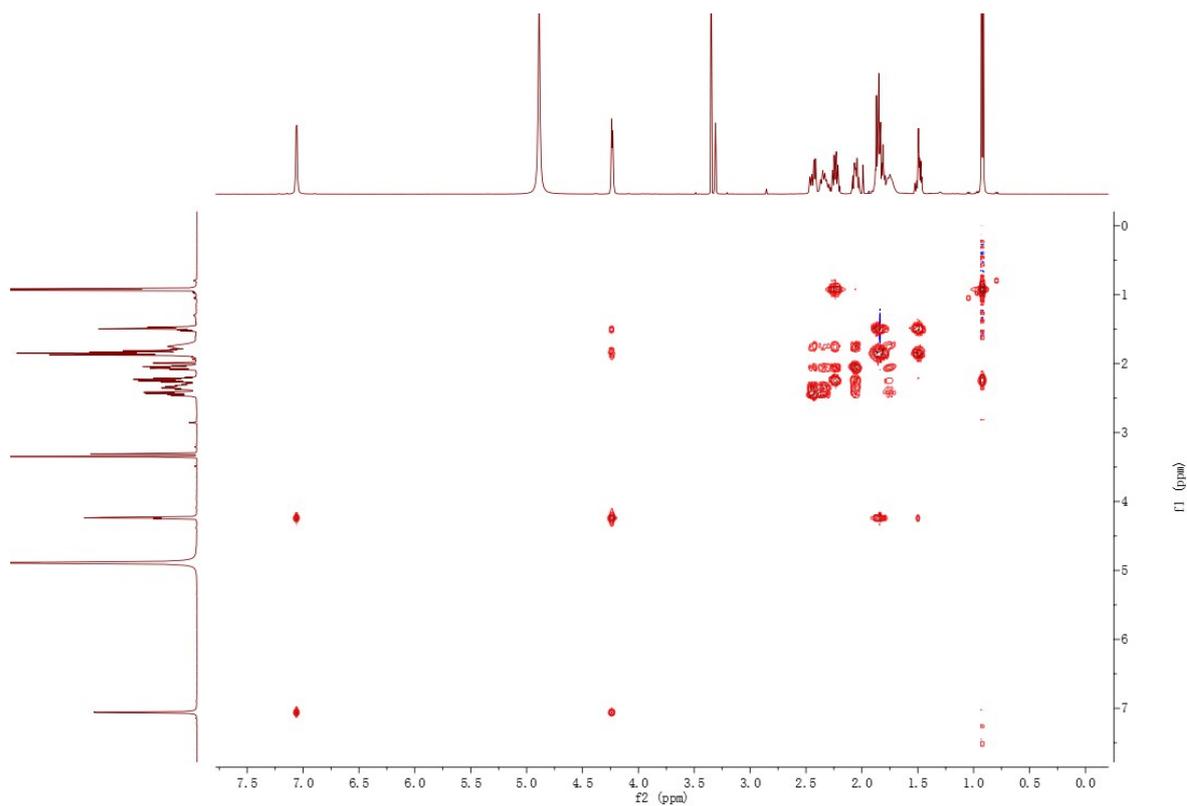
Figure S4. The <sup>13</sup>C NMR spectrum of compound **1** in DMSO-*d*<sub>6</sub>



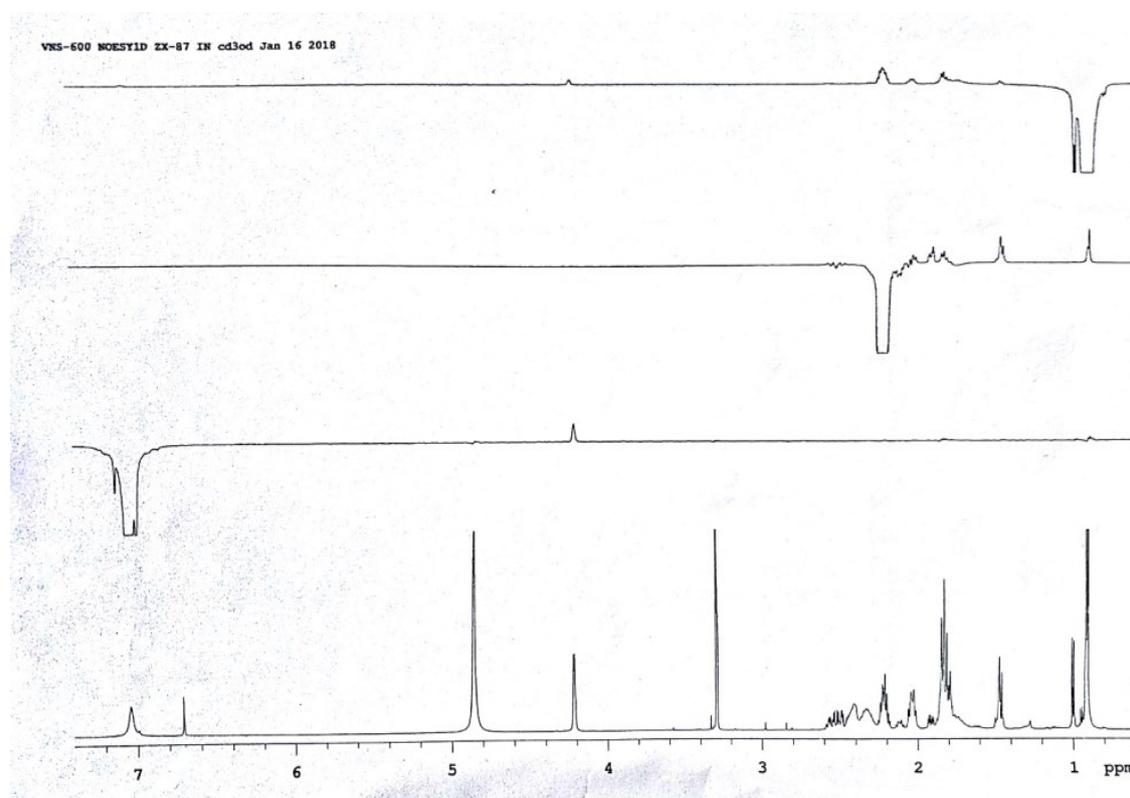
**Figure S5.** The HSQC spectrum of compound **1** in methanol- $d_4$



**Figure S6.** The HMBC spectrum of compound **1** in DMSO- $d_6$



**Figure S7.** The  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **1** in methanol- $d_4$



**Figure S8.** The 1D NOE spectrum of compound **1** in methanol- $d_4$

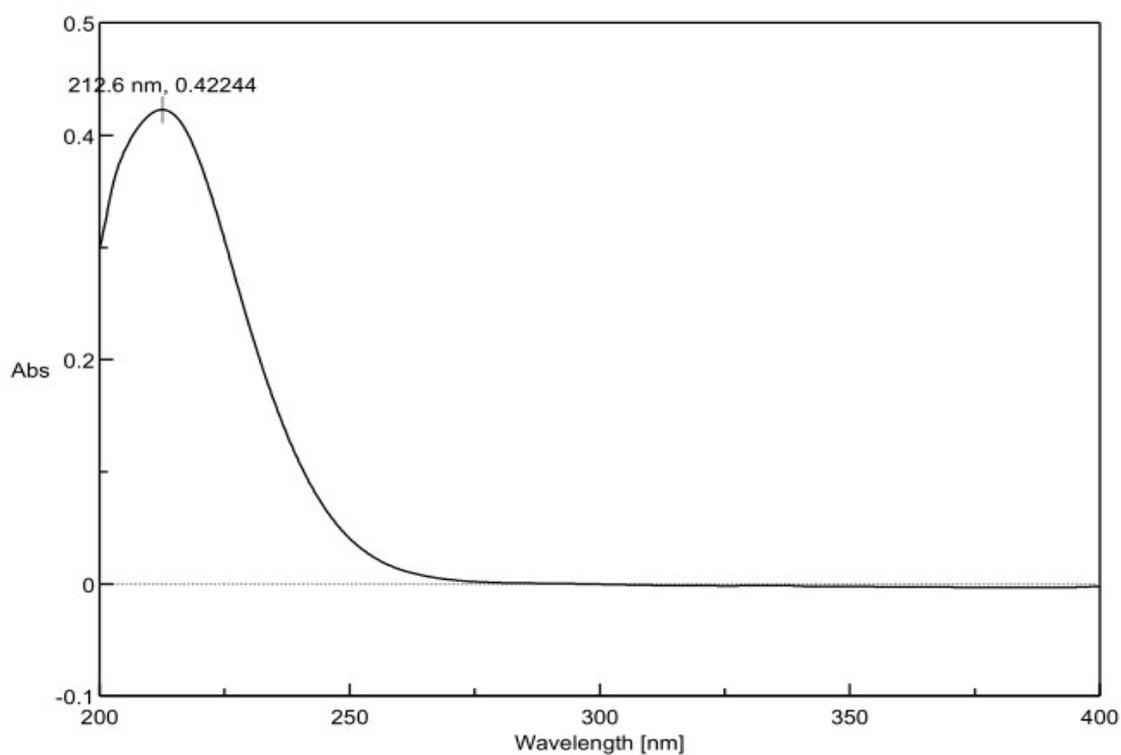


Figure S9. The UV spectrum of compound **1** in methanol

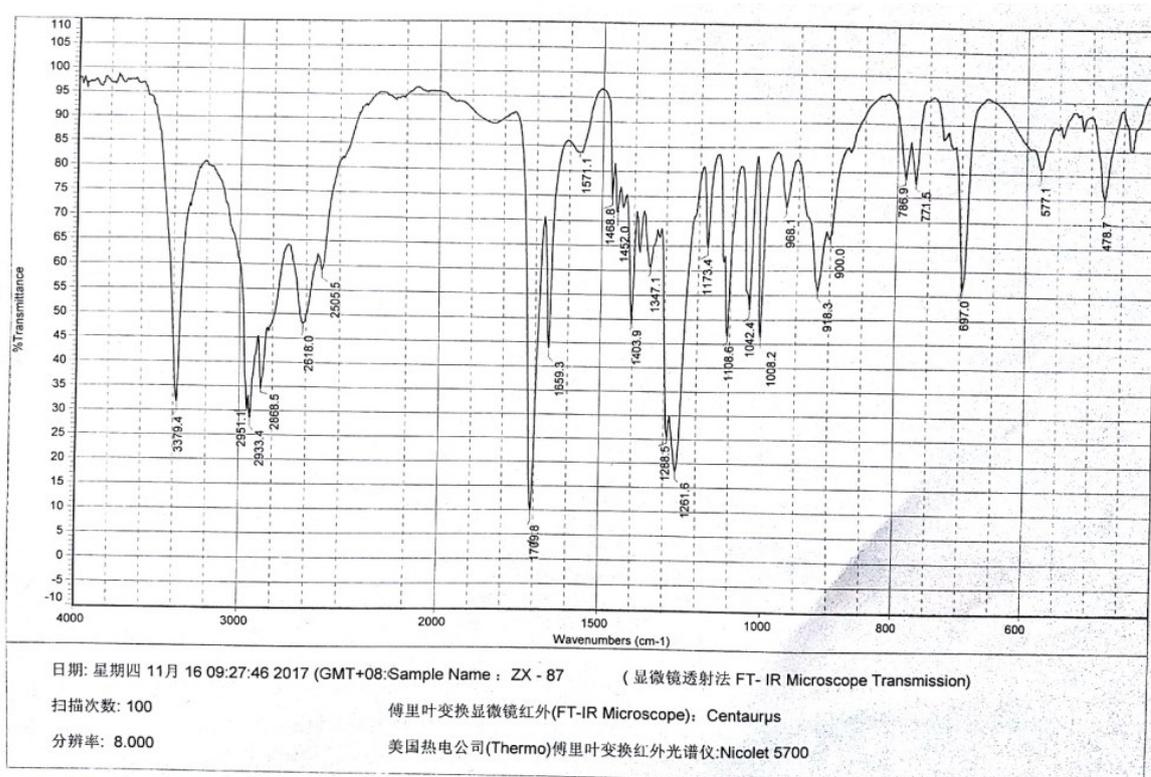
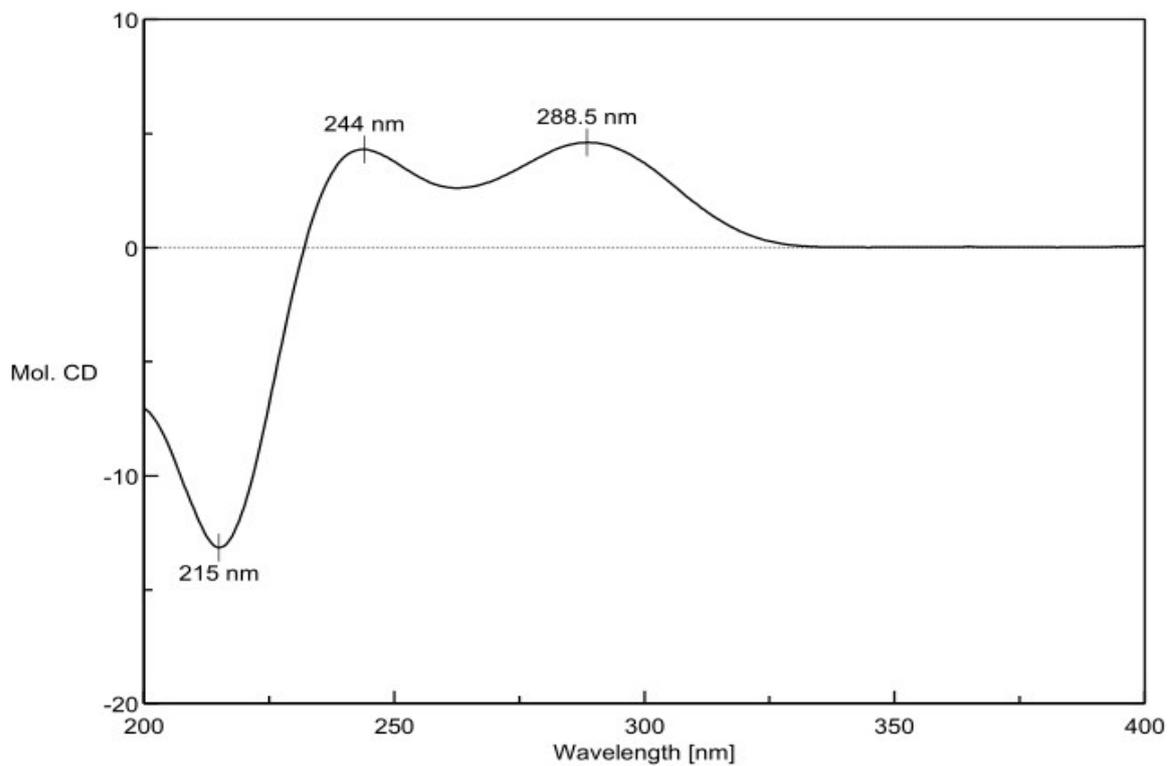
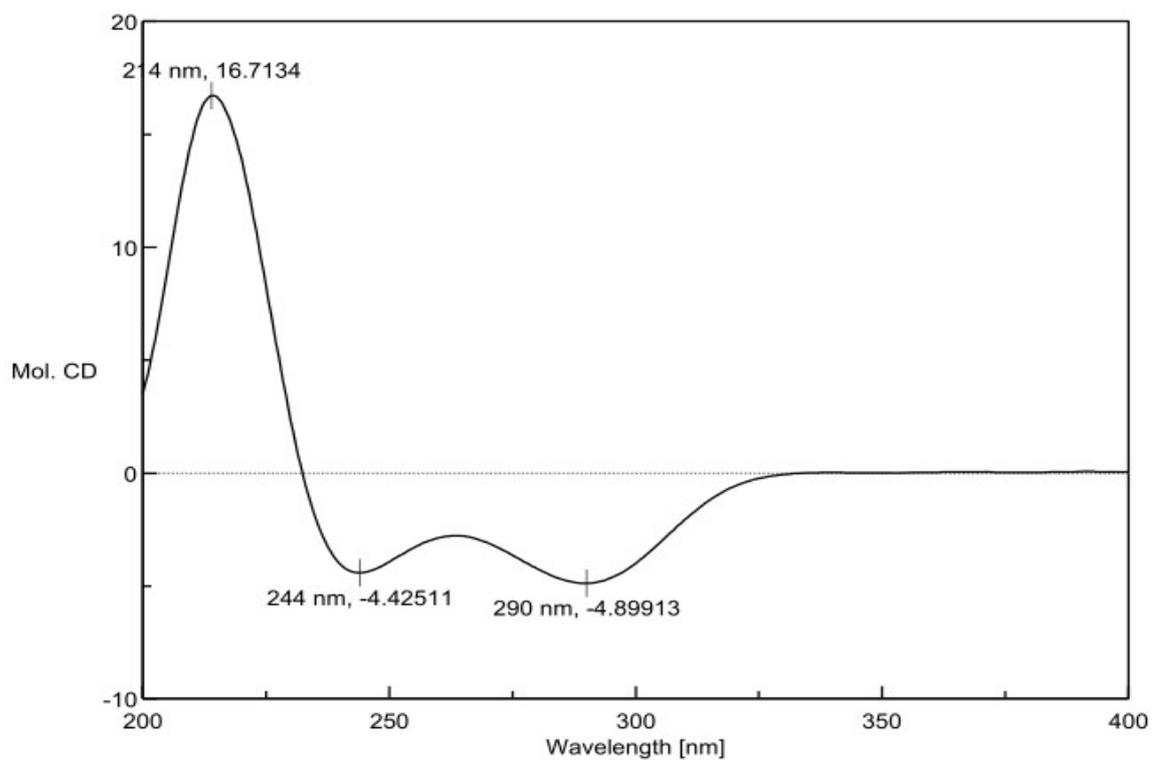


Figure S10. The IR spectrum (KBr) of compound **1**



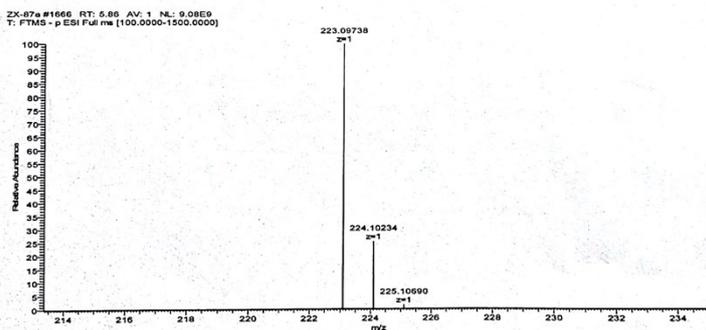
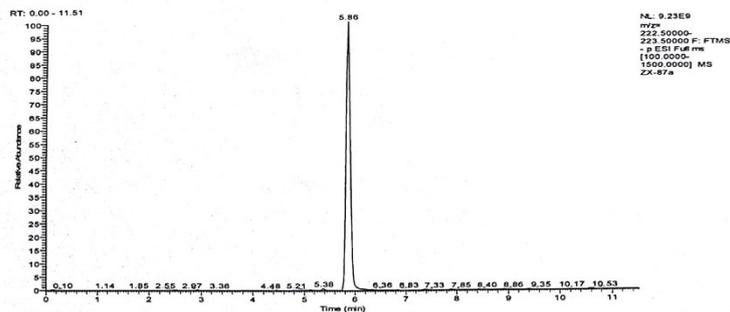
**Figure S11.** The ECD spectrum of compound **1a** in methanol



**Figure S12.** The ECD spectrum of compound **1b** in methanol

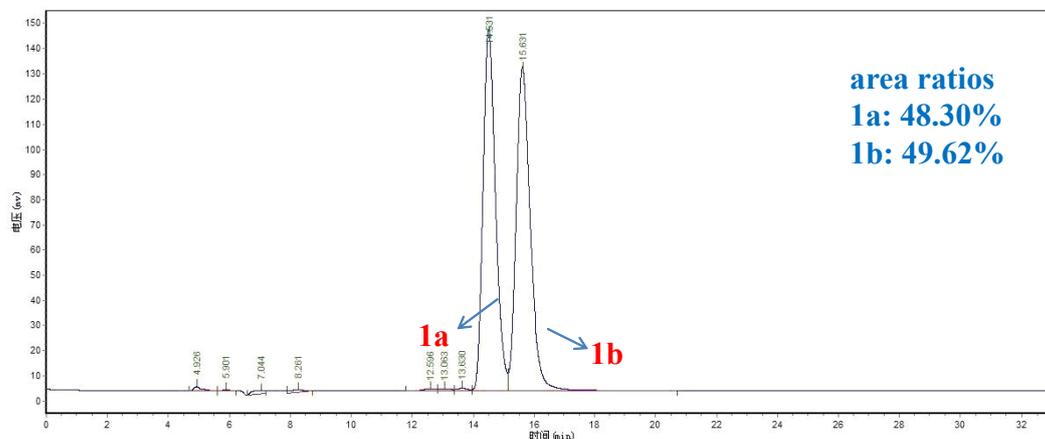
Thermo Qexactive Focus Report

compound NO. : ZX-87a  
Method : LCMS(compound)-low



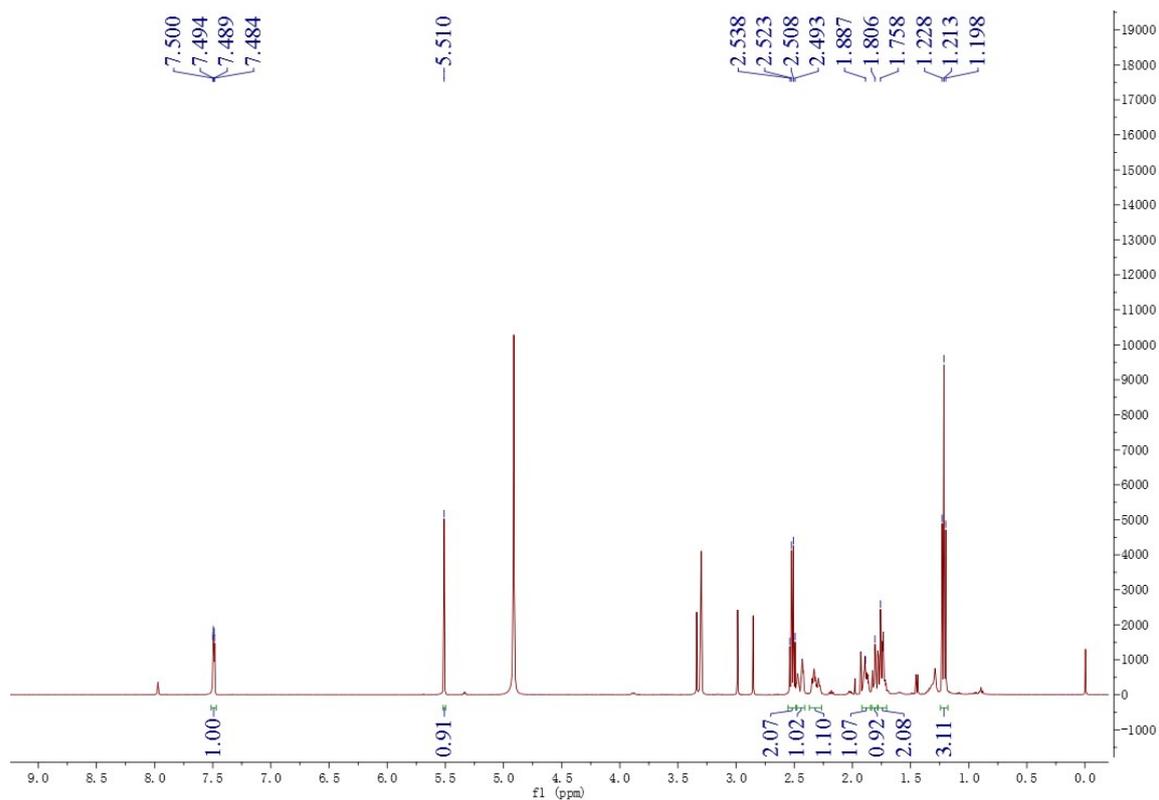
m/z	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
223.09738	223.09758	-0.2	5.5	C12 H15 O4 M-H

Figure S13. The HR-ESI-MS spectrum of compounds 1

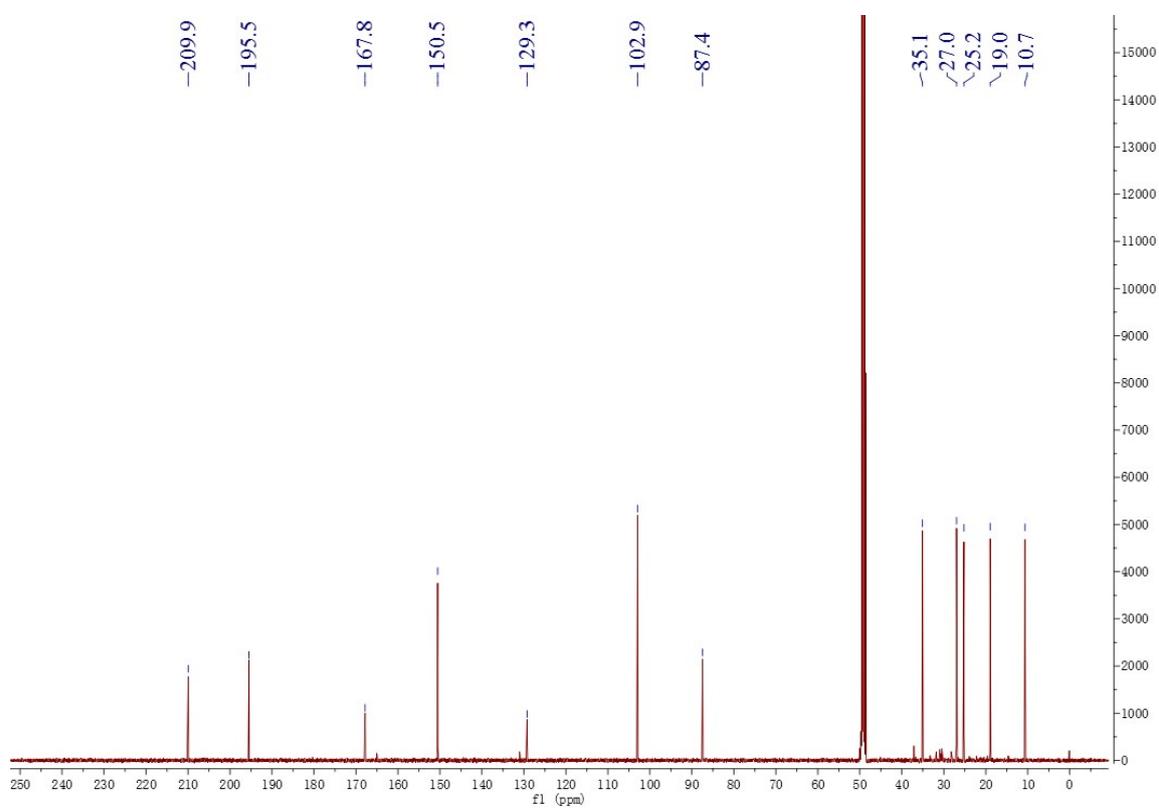


峰序号	保留时间	峰高	面积(A)	面积%	峰类型	起点	终点
1	4.926	1.582	28708.500	0.34	单峰	4.676	5.593
2	5.901	0.400	5514.200	0.07	单峰	5.601	6.201
3	7.044	1.336	43532.934	0.52	单峰	6.577	7.194
4	8.261	0.775	24847.318	0.29	重叠峰	7.877	8.711
5	12.596	0.847	23800.301	0.28	单峰	11.796	12.830
6	13.063	0.867	23295.354	0.28	重叠峰	12.830	13.363
7	13.630	0.972	25726.602	0.30	重叠峰	13.363	13.964
8	14.531	142.871	4075284.250	48.30	重叠峰	13.964	15.131
9	15.631	128.274	4186012.000	49.62	重叠峰	15.131	20.700
总面积:			8436781.458				

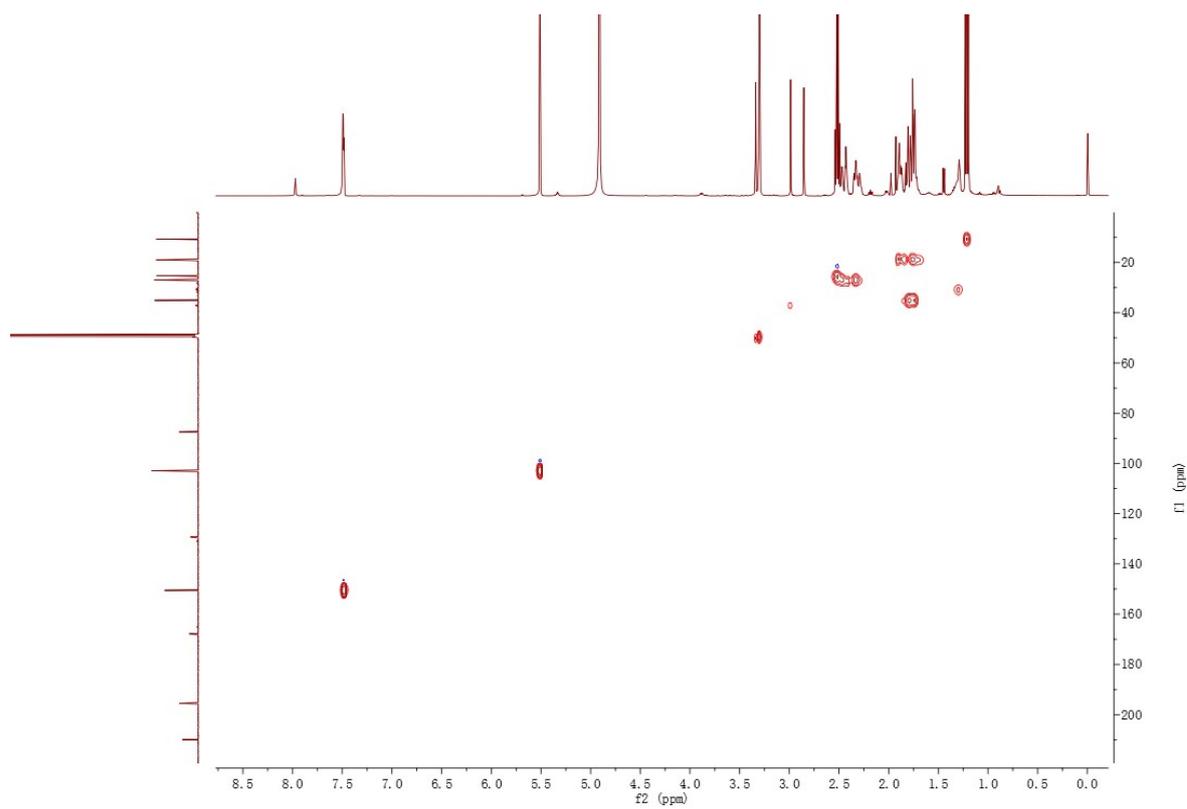
Figure S14. The Chiral separation on preparative HPLC of 1a and 1b



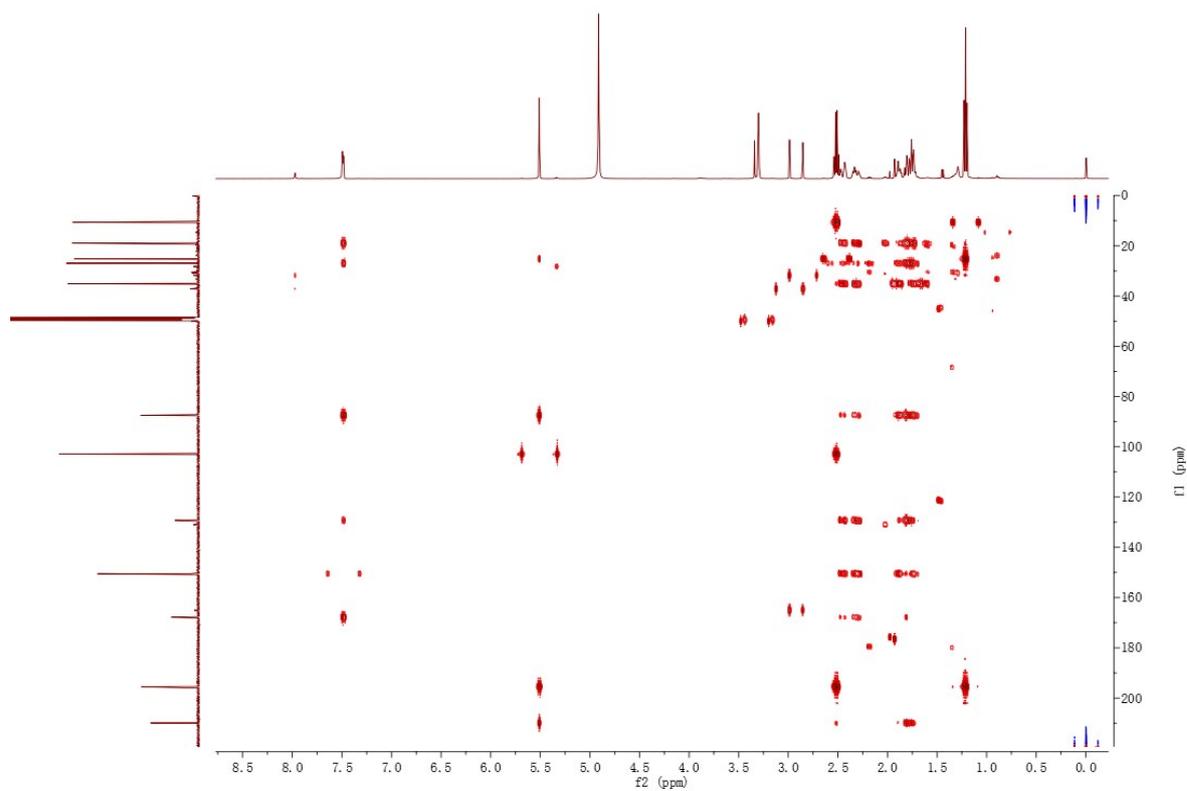
**Figure S15.** The  $^1\text{H}$  NMR spectrum of compound **2** in methanol- $d_4$



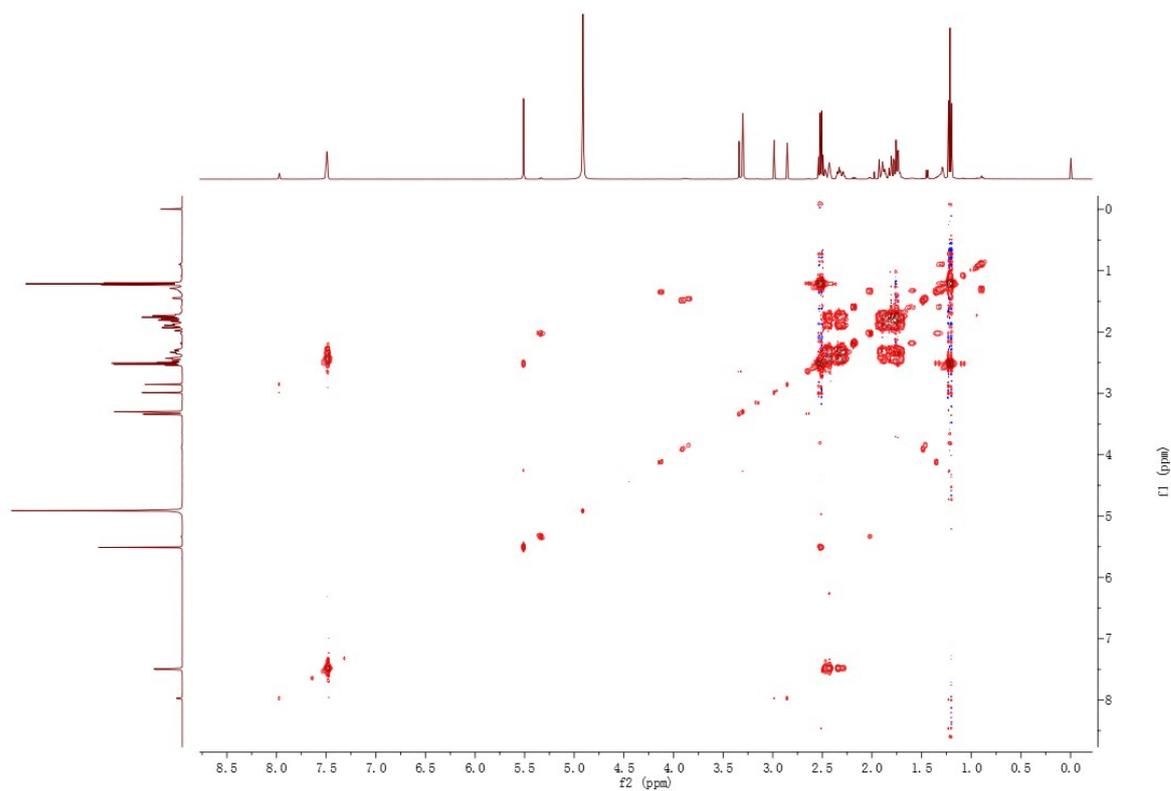
**Figure S16.** The  $^{13}\text{C}$  NMR spectrum of compound **2** in methanol- $d_4$



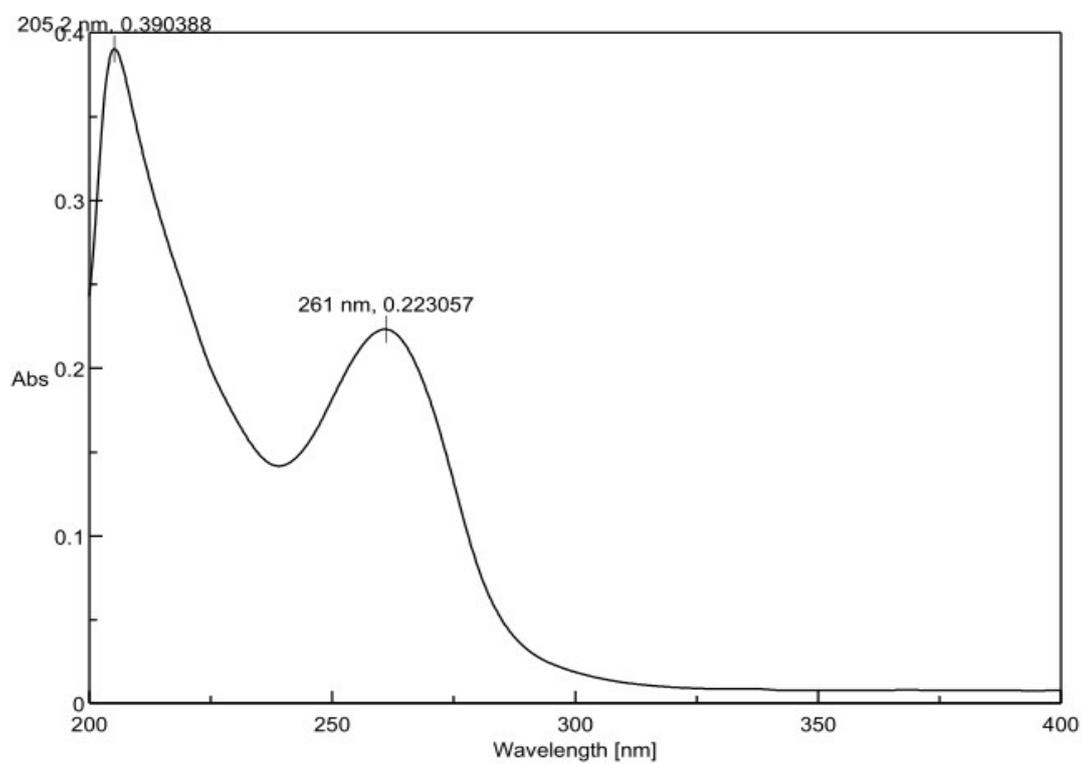
**Figure S17.** The HSQC spectrum of compound **2** in methanol- $d_4$



**Figure S18.** The HMBC spectrum of compound **2** in methanol- $d_4$



**Figure S19.** The  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **2** in methanol- $d_4$



**Figure S20.** The UV spectrum of compound **2** in methanol

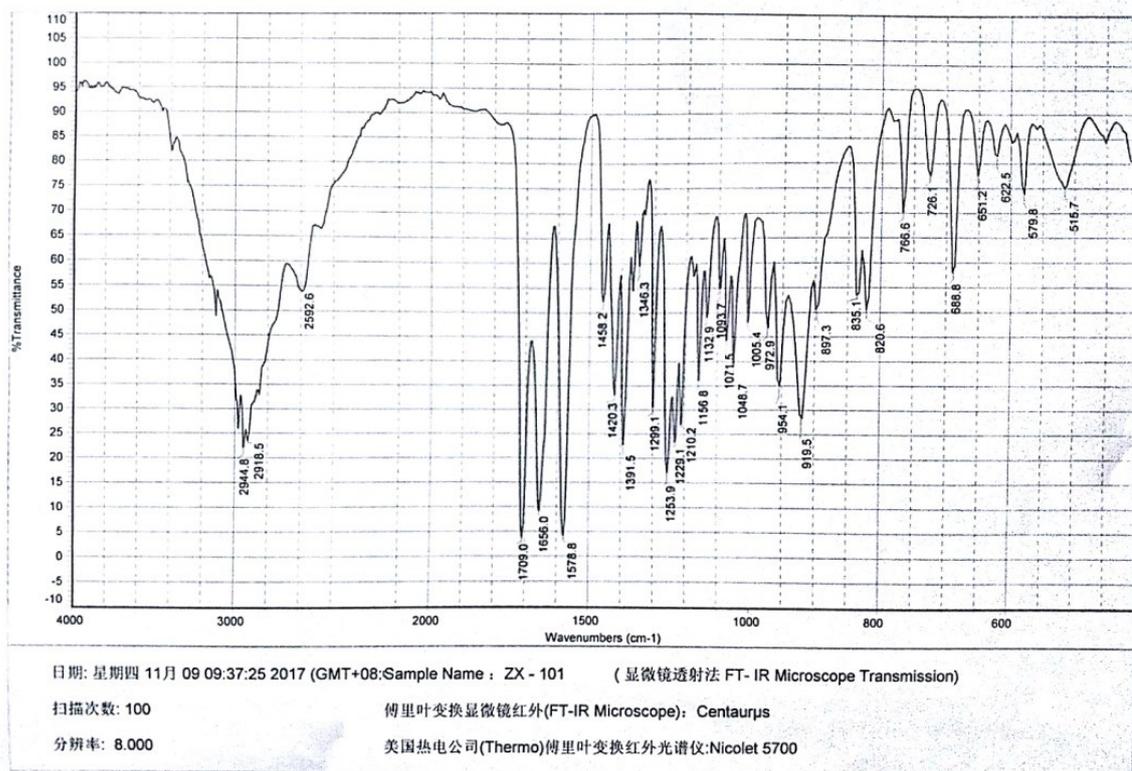


Figure S21. The IR spectrum (KBr) of compound **2**

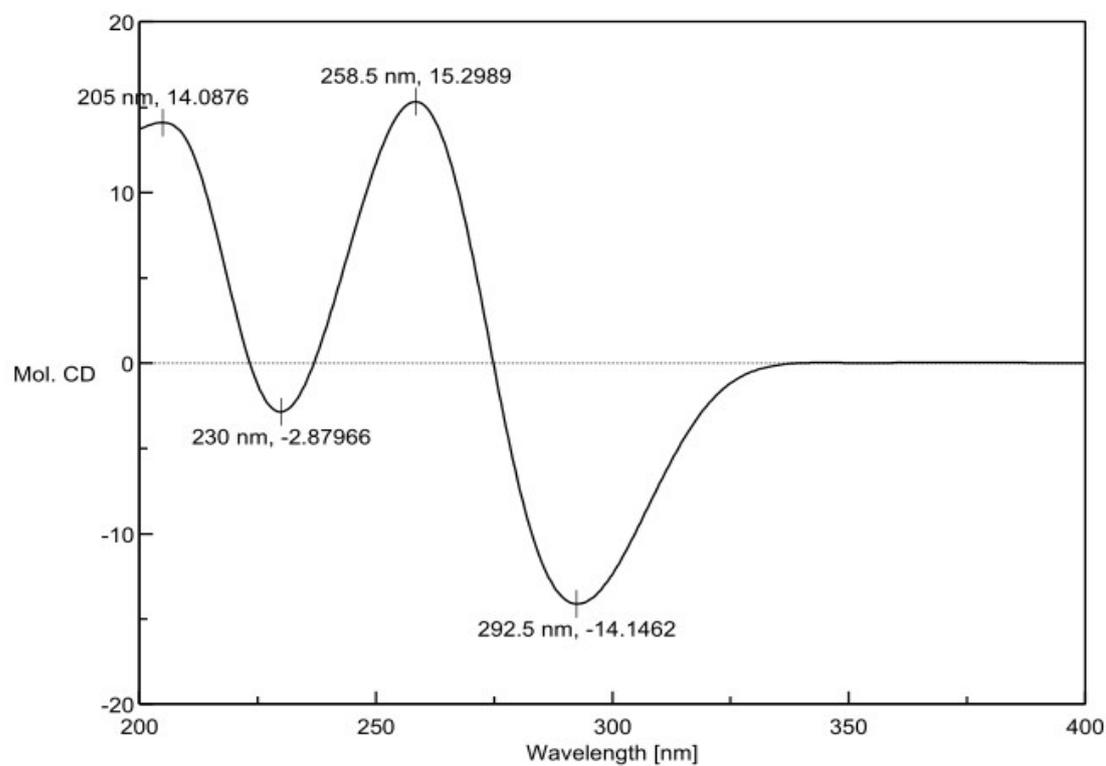
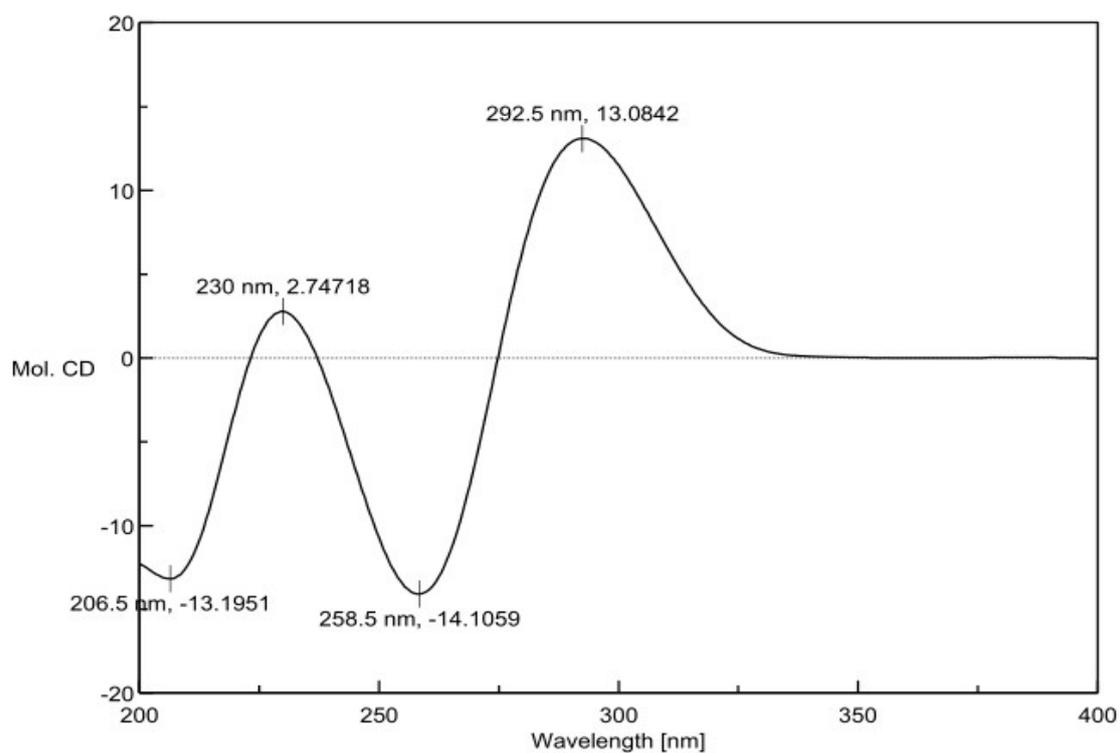
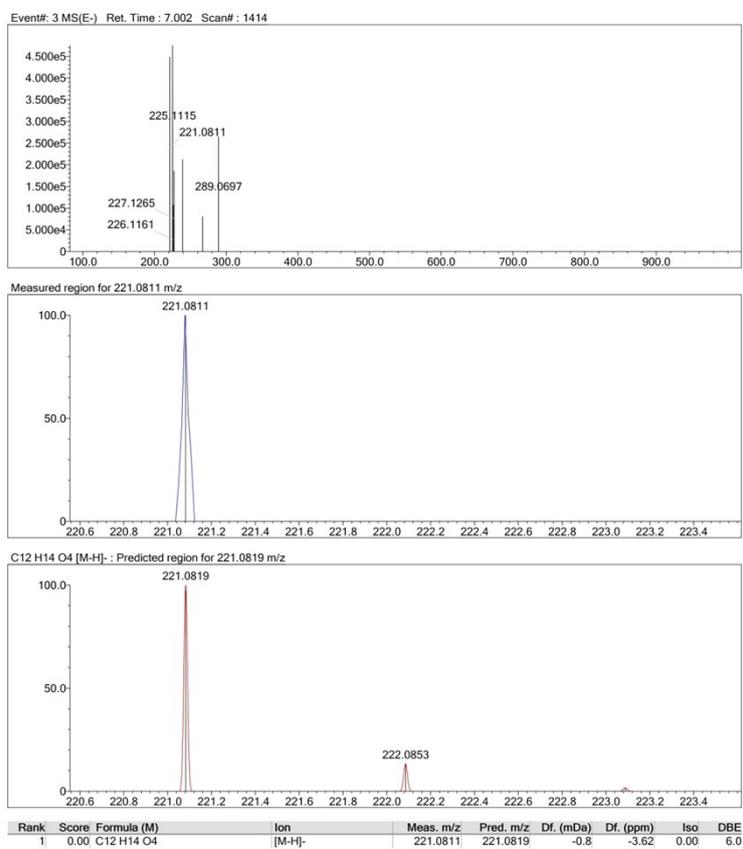


Figure S22. The ECD spectrum of compound **2a** in methanol



**Figure S23.** The ECD spectrum of compound **2b** in methanol



**Figure S24.** The HR-ESI-MS data of compound **2** (negative ion)

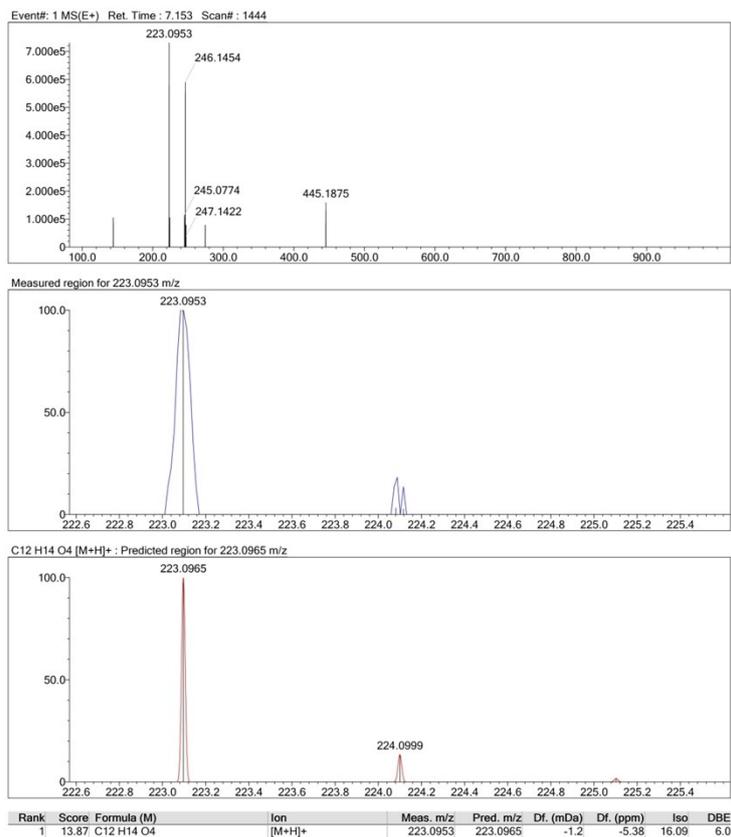


Figure S25. The HR-ESI-MS data of compound **2** (positive ion)

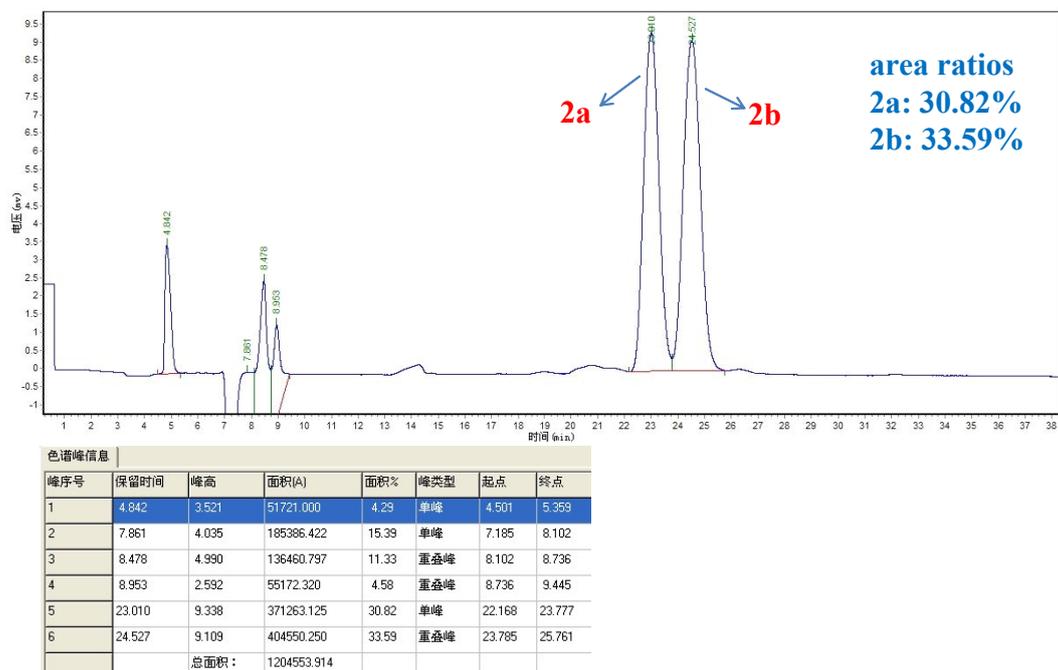
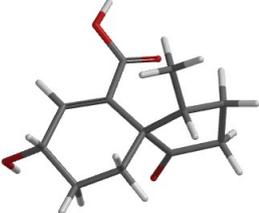
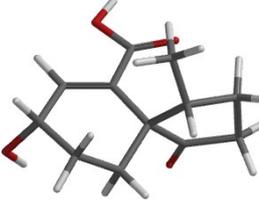
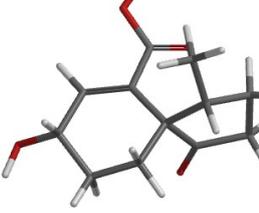
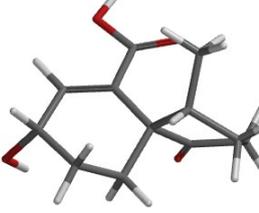
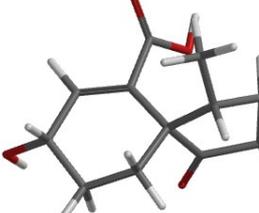
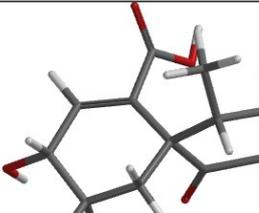
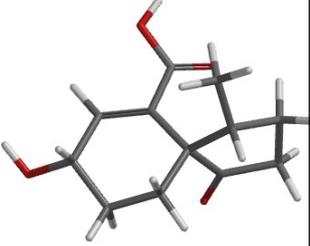


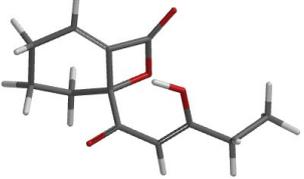
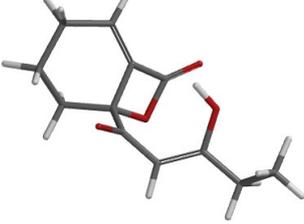
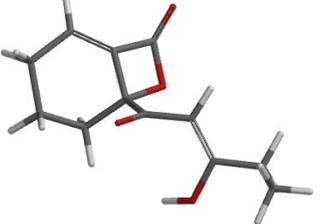
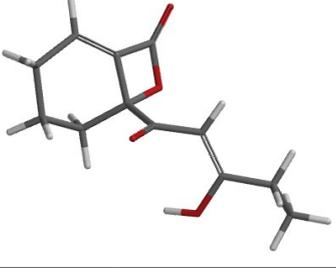
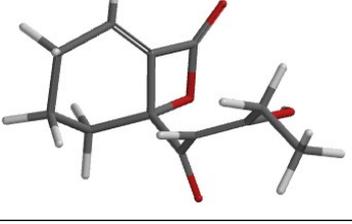
Figure S26. The Chiral separation on preparative HPLC of **2a** and **2b**

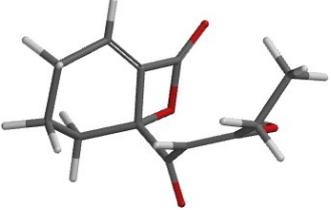
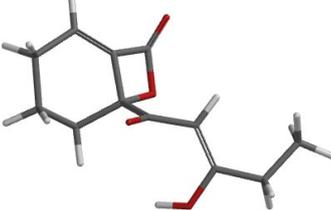
**Table S1.** Seven optimized conformations of **1a** (1*S*,2*R*,9*S*).

NO.	conformer	E (kJ/mol)	rel.E (kJ/mol)	Boltzmann Dist
1		-61.82	0.00	0.458
2		-61.00	0.82	0.329
3		-56.98	4.84	0.065
4		-56.22	5.61	0.048
5		-55.35	6.47	0.034
6		-54.72	7.11	0.026

7		-52.92	8.90	0.013
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**Table S2.** Seven optimized conformations of **2a** (2aR).

NO.	conformer	E (kJ/mol)	rel.E (kJ/mol)	Boltzmann Dist
1		392.45	0.00	0.468
2		393.92	1.47	0.259
3		396.33	3.88	0.098
4		397.13	4.68	0.071
5		398.69	6.24	0.038

6		399.57	7.12	0.026
7		399.65	7.20	0.026