Supporting Information

Highly Rigid Labdane-Type Diterpenoids from a Chinese Liverwort and Light-driven Structure Diversification

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Author Contributions

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List of Supporting Information

General experimental procedures

NMR spectra were recorded on a Bruker AV 400 spectrometer in $CDCl_3$, CD_3OD or pyridine-d_5 with TMS as internal standard. HRESIMS were carried out on a LTQ-Orbitrap XL. Optical rotations were measured on a GYROMAT-HP polarimeter. UV data were recorded using a Shimadzu UV-2450 spectrophotometer. CD spectra were obtained on a Chirascan spectropolarimeter. IR spectra were made on a Thermo Nicolet NEXUS 470 FT-IR spectrometer with KBr discs. H. HPLC was carried out on an Agilent 1200 series instrument with Eclipse XDB-C_{18} 5 μm columns (4.6 × 250 mm and 9.4 × 250 mm). All solvents used were of analytical grade. Silica gel (200–300 mesh; Qingdao Haiyang Chemical Co. Ltd., Qingdao, P. R. China), Sephadex LH-20 (25–100 μm; Pharmacia Biotek, Denmark), reversed–phase C_{18} silica gel (150–200 mesh, Merck) and MCI gel (CHP20P, 75–150 μm, Mitsubishi Chemical Industries Ltd.) were used for column chromatography. Pre-coated silica gel GF_{254} plates (Qingdao Haiyang Chemical Co. Ltd.) were used for TLC. Spots of TLC were visualized within iodine vapor or by spraying with H_2SO_4–EtOH (1:9, v/v) followed by heating.

Plant Material

Whole plants of *H. mnioides* were collected from Mount Fanjing, Guizhou Province, P. R. China，in May 2014 and identified by Prof. Yuanxin Xiong (College of Life Sciences, Guizhou University). A voucher specimen (No. 20140518001) has been deposited at the Department of Natural Products Chemistry, School of Pharmaceutical Sciences, Shandong University, P. R. China.

Extraction and isolation

The fresh plant material of *H. mnioides* (1.4 kg) was extracted with 95% EtOH at room temperature (3 × 1.5 L, each for one week). The obtained crude extract (22.42 g) was separated by MCI gel column chromatography (MeOH/H_2O, 3:7 to 1:0) to give five fractions A–E. Fraction B (3.83 g) was chromatographed using a silica gel column [200−300 mesh, petroleum ether (60−90 °C)/acetone, 200:1 to 0:1] to give subfractions B1−B7. Fraction B2 (114 mg) was applied to an RP-18 silica gel column (MeOH/H_2O, 4:6 to 9:1), followed by HPLC (MeOH/H_2O, 50:50, 1.8 mL/min) to yield **2** (15.35 mg, t_R = 47.5 min). Fraction B3 (303mg) was purified using HPLC (MeOH/H_2O, 65:35, 1.8 mL/min) after recrystallization to yield **1** (5.7 mg, t_R = 13.9 min) and **5** (74.06 mg, t_R = 19.7 min), Fraction B6 (649mg) was applied to an RP-18 silica gel column (MeOH/H_2O, 4:6 to 9:1) to obtain subfractions B6-1 and B6-2. Subfraction B6-1 (403 mg) was purified using HPLC (MeOH/H_2O, 50:50, 1.8 mL/min) to yield **3** (72.2 mg, t_R = 33.1min) and **4** (40.9 mg, t_R = 34.5 min). Subfraction B6-2 (79 mg) was purified using HPLC (CH_3CN/H_2O, 40:60, 1.8 mL/min) to yield **6** (20.1 mg, t_R = 45.9 min).

Characteristic data for compounds 1−3.

Compound 1: colorless crystals (EtOH); mp 188−189°C; $[\alpha]^{20}_D$ +36.4 (*c* 0.1 CH_3CN); UV (CH_3CN) λ_{max} (log ε) 219 (3.56) nm; CD (CH_3CN): 243($\Delta\varepsilon$ +2.03), 210 ($\Delta\varepsilon$ −1.70) nm; IR ν_{max} 3435, 2958, 2931, 2861, 1732, 1289, 1123, 1072,744 cm^{-1}; HRESIMS at *m*/*z* 373.1653 $[M + H]^+$ (calcd for $C_{21}H_{25}O_6$, 373.1646).

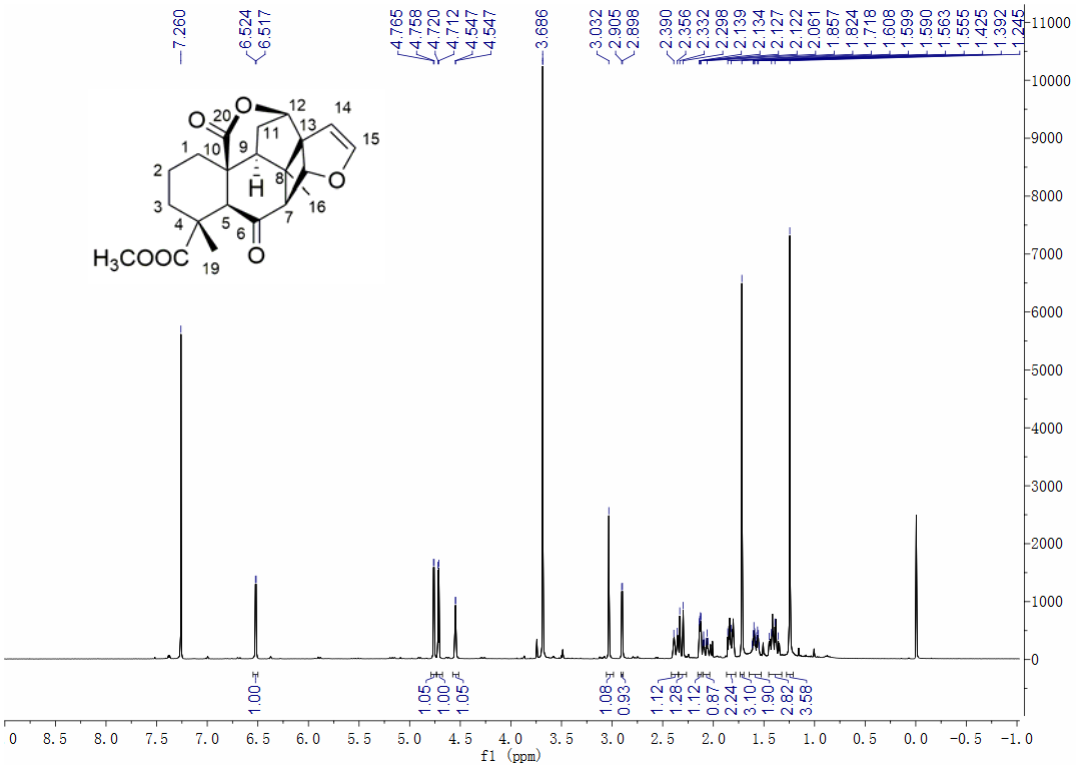

Figure S1. ^{1}H NMR spectrum (400 MHz) of **1** in $CDCl_3$.

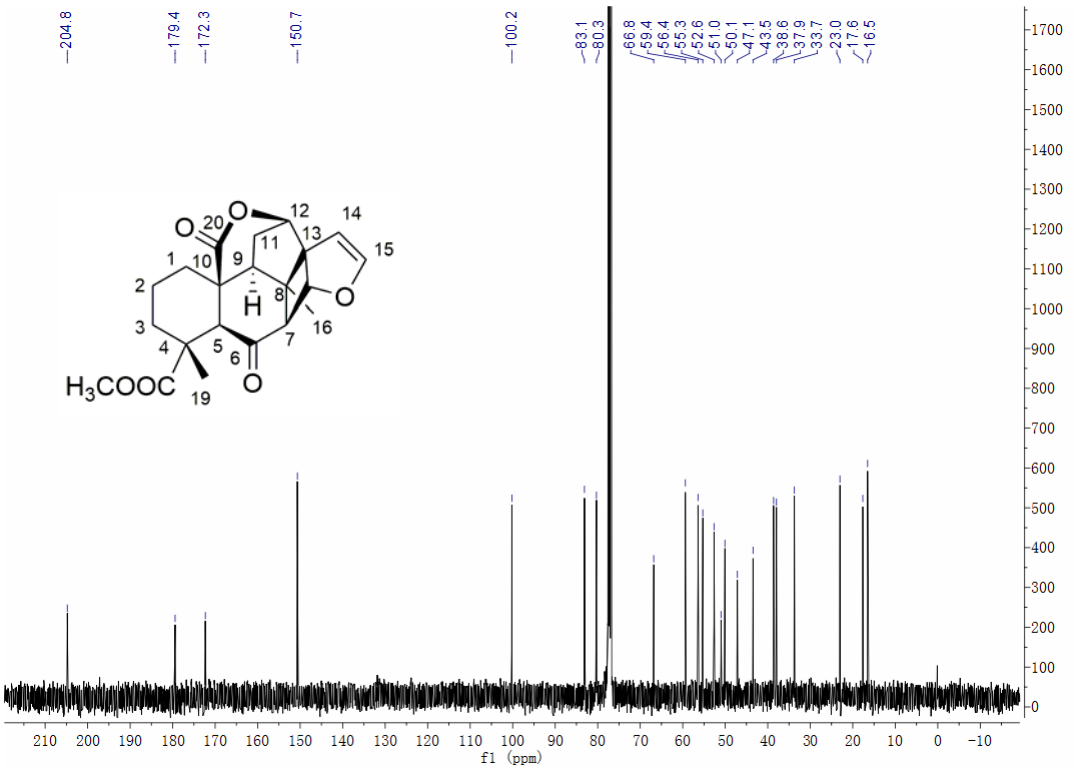

Figure S2. ^{13}C NMR spectrum (100 MHz) of **1** in $CDCl_3$.

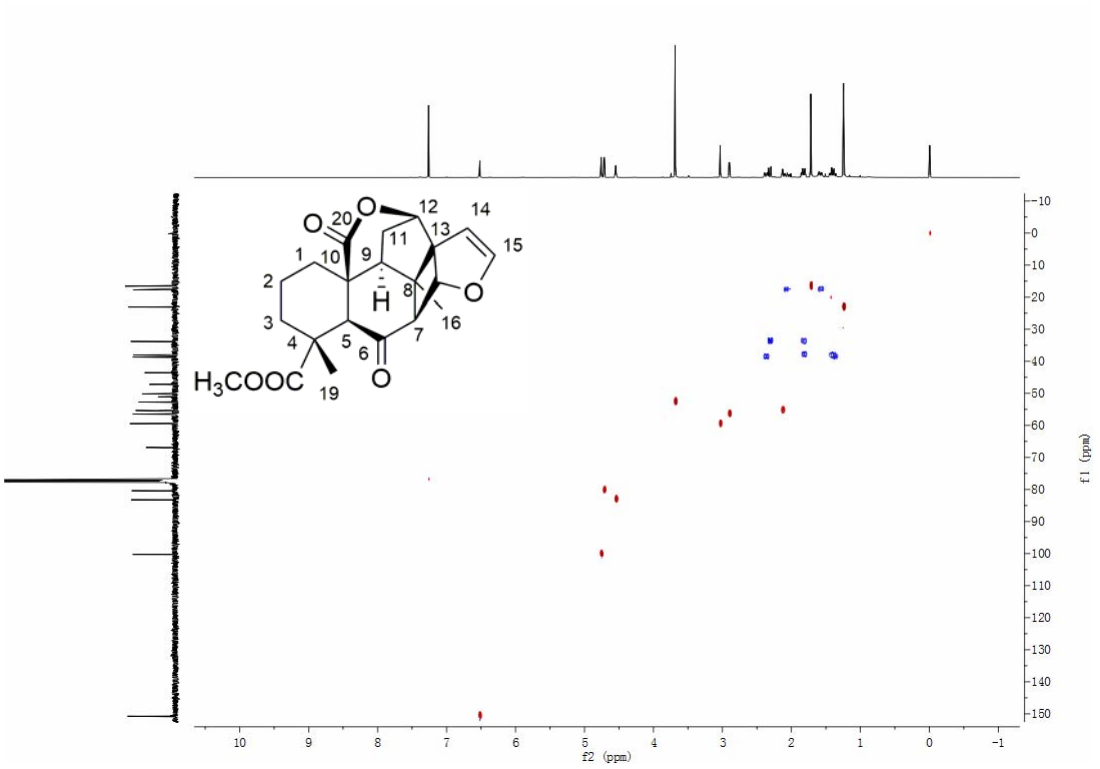

Figure S3. HSQC spectrum (400 MHz) of **1** in $CDCl_3$.

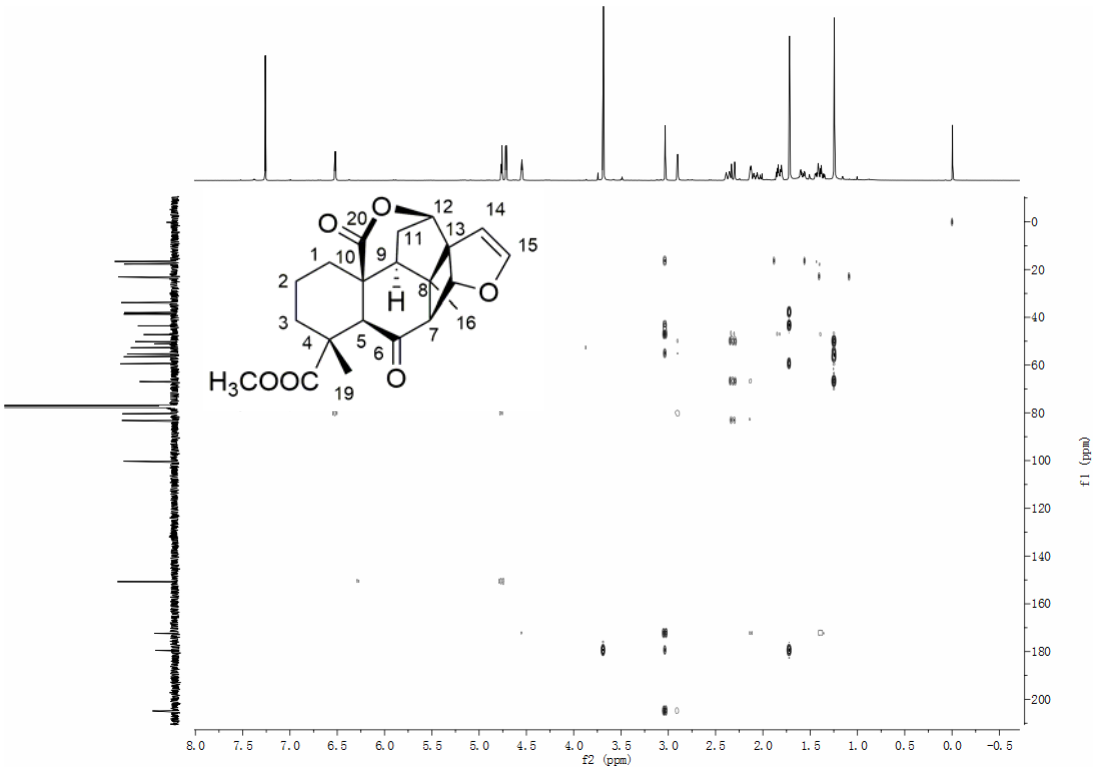

Figure S4. HMBC spectrum (400 MHz) of **1** in $CDCl_3$.

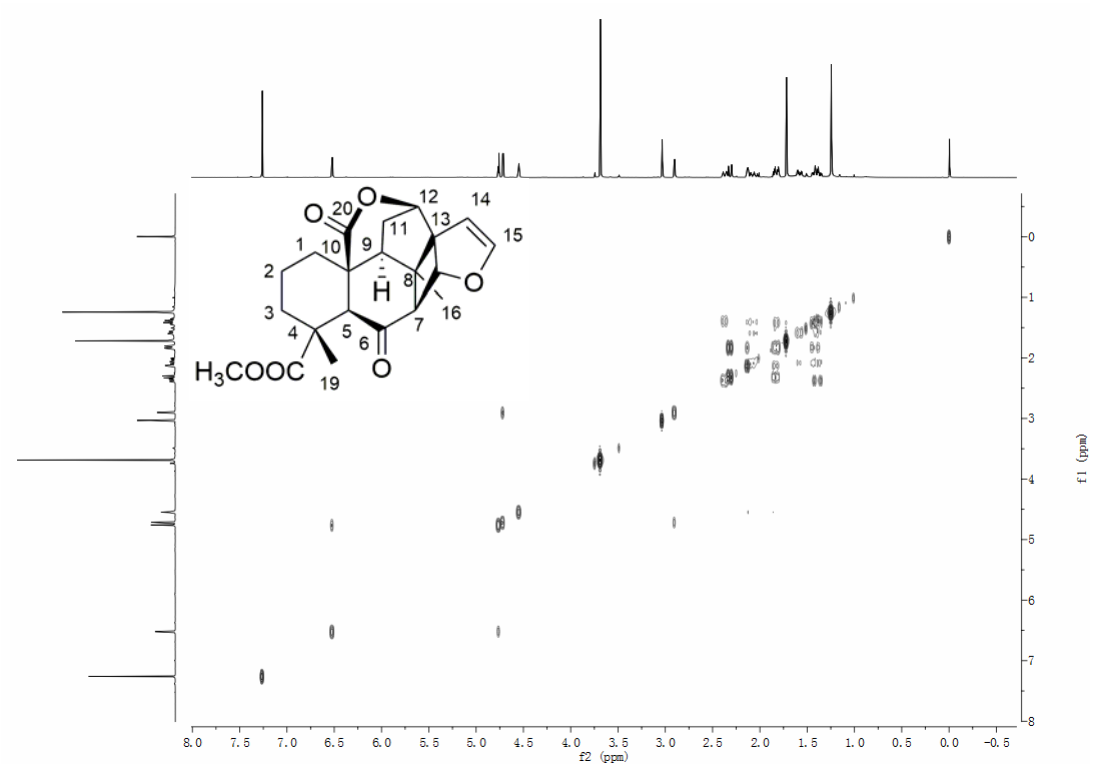

Figure S5. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1** in $CDCl_3$.

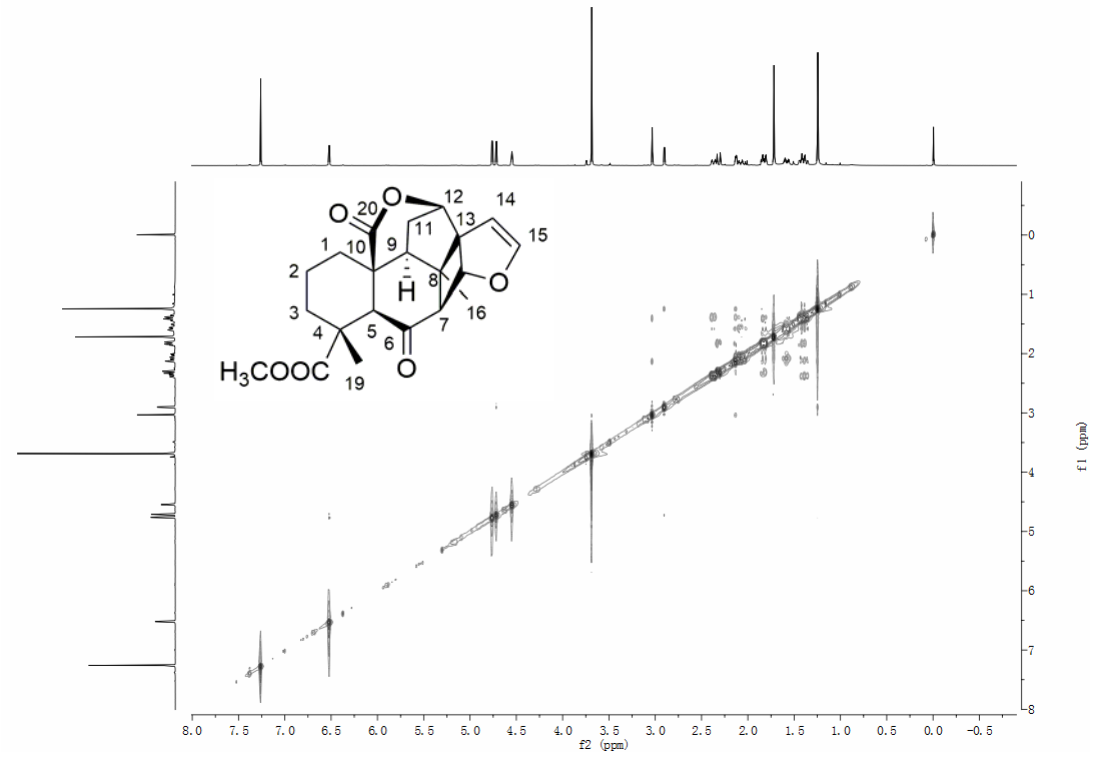

Figure S6. NOESY spectrum (400MHz) of **1** in $CDCl_3$.

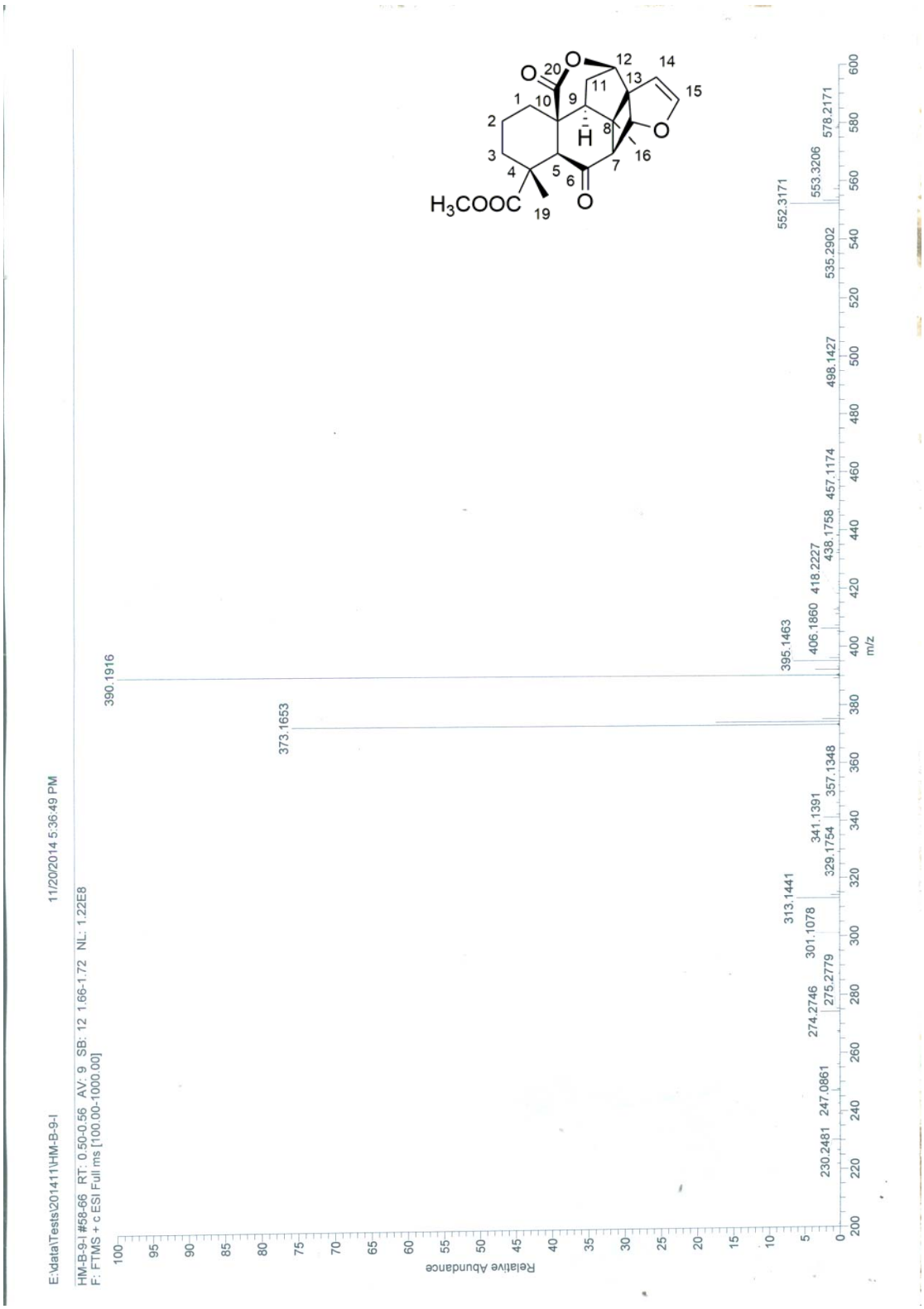

Figure S7. HRESIMS spectrum of **1**.

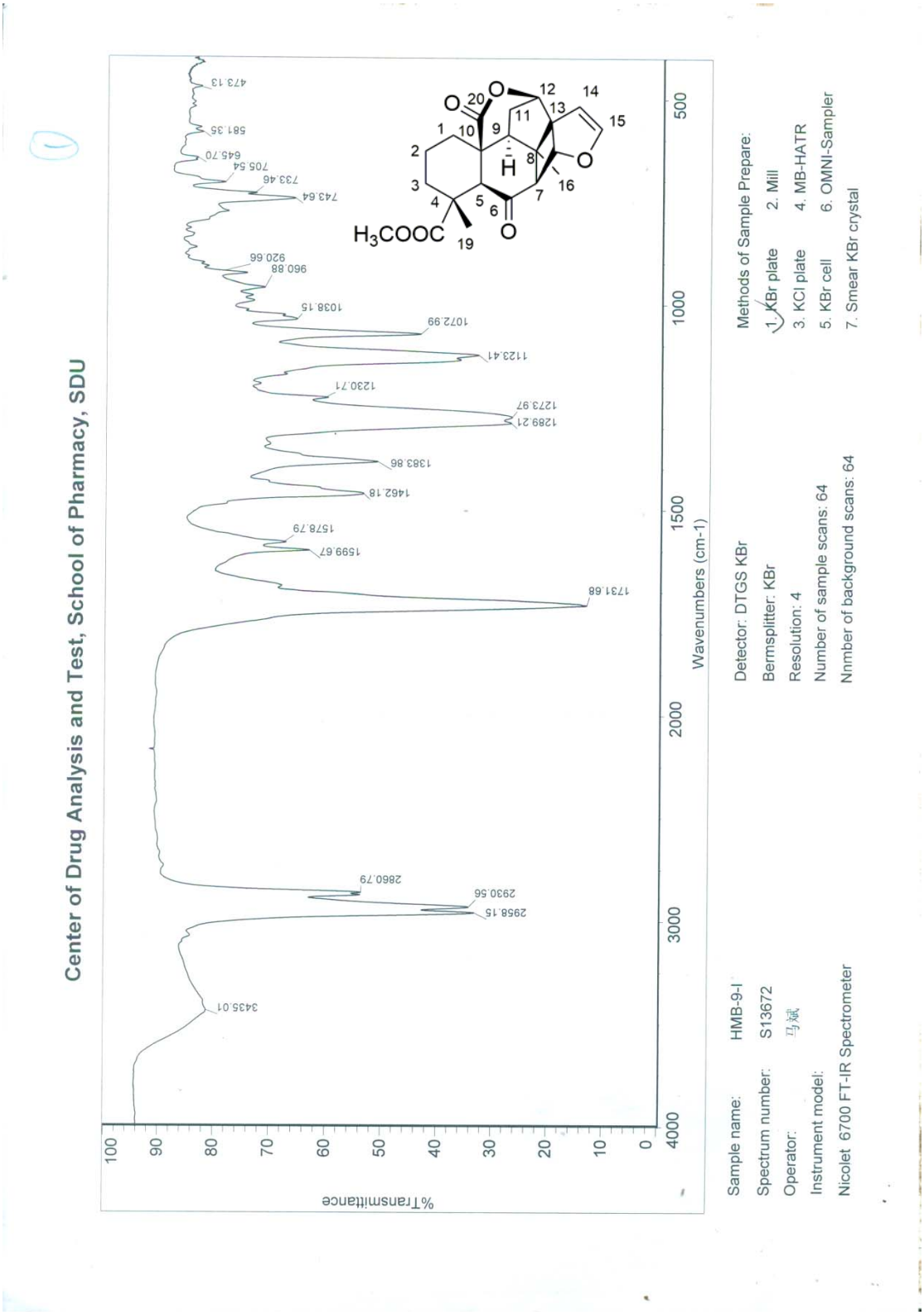

Figure S8. IR (KBr disc) spectrum of **1**.

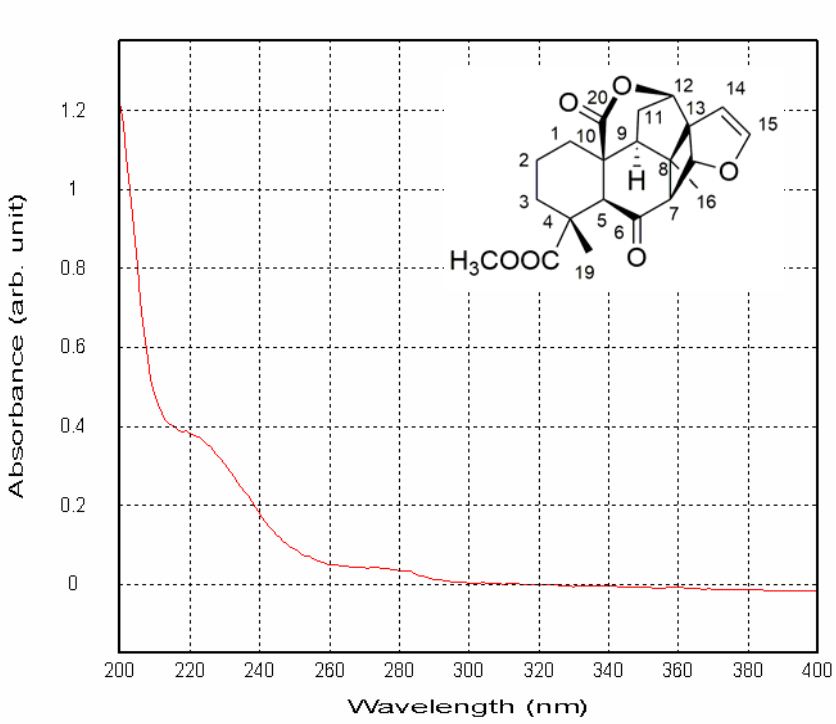

Figure S9. UV spectrum of **1**.

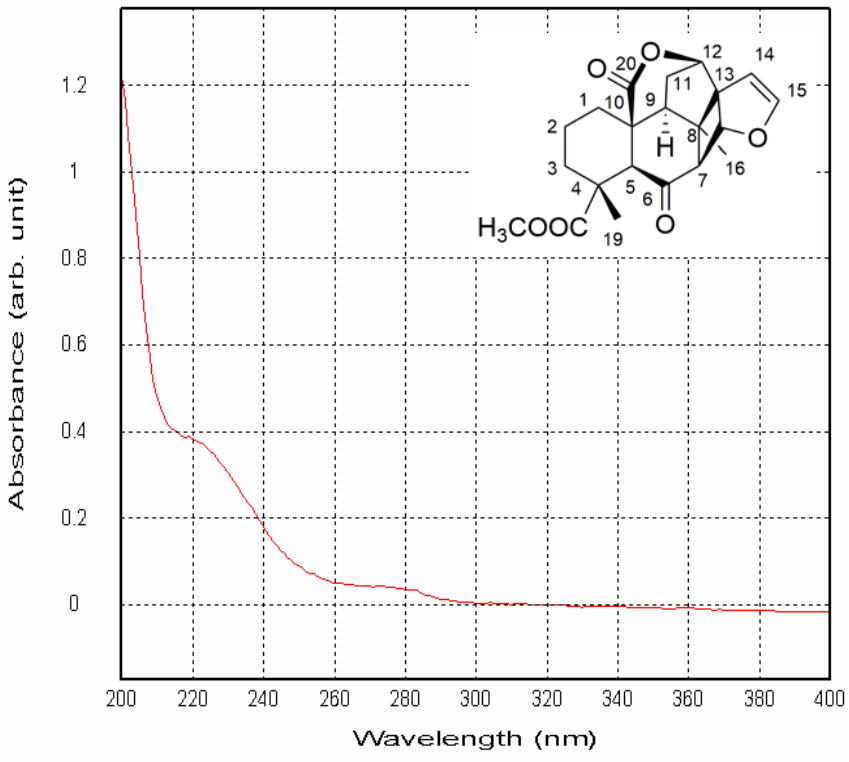

Figure S10. CD spectrum of **1**.

Compound 2: colorless crystals (EtOH); mp 184−186°C; $[\alpha]^{20}_{D}$ −39.2 (*c* 0.1 CH_3CN); UV (CH_3CN) λ_{max} (log ε) 211 (3.77) nm; CD (CH_3CN): 311 ($\Delta\varepsilon$ −1.56), 242($\Delta\varepsilon$ +7.35) nm; IR ν_{max} 3443, 2957, 2928, 1733, 1703, 1384, 1138, 1025,720 cm^{-1}; HRESIMS at *m/z* 329.1752 $[M + H]^+$ (calcd for $C_{20}H_{25}O_4$, 329.1747).

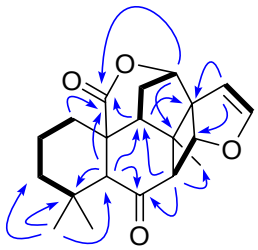

Figure S11. Selected HMBC (H→C) and ^1H–^1H COSY (H—H) correlations of **2**.

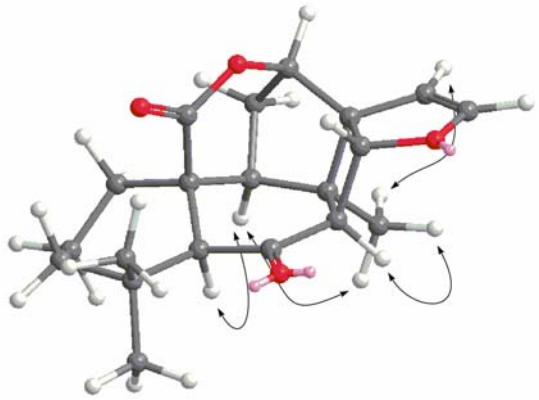

Figure S12. Selected NOESY correlations (H↔H) of **2**.

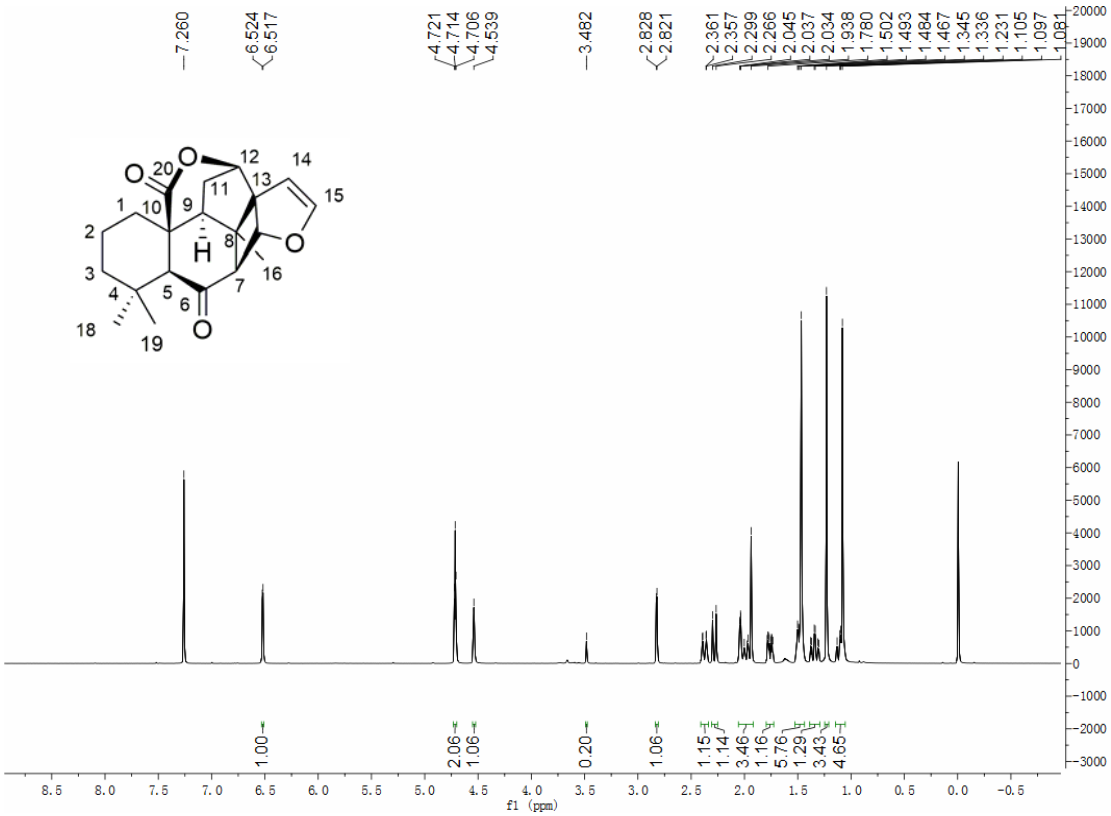

Figure S13. ^{1}H NMR spectrum (400MHz) of **2** in $CDCl_3$.

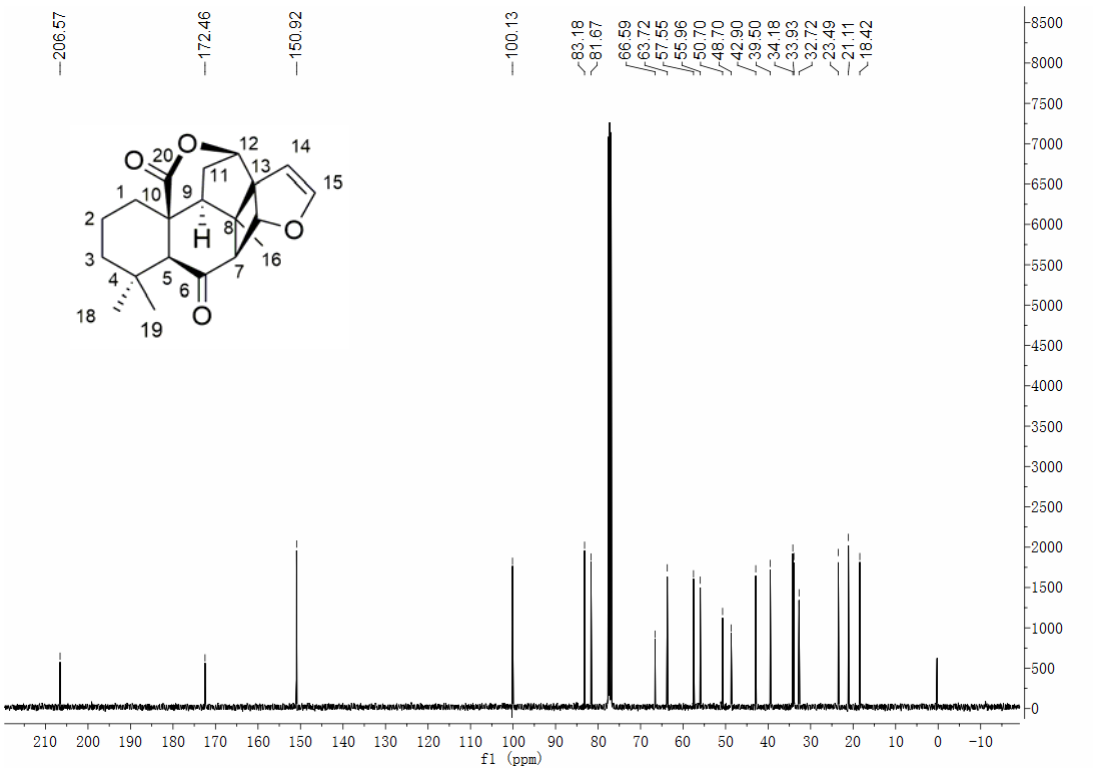

Figure S14. ^{13}C NMR spectrum (100 MHz) of **2** in $CDCl_3$.

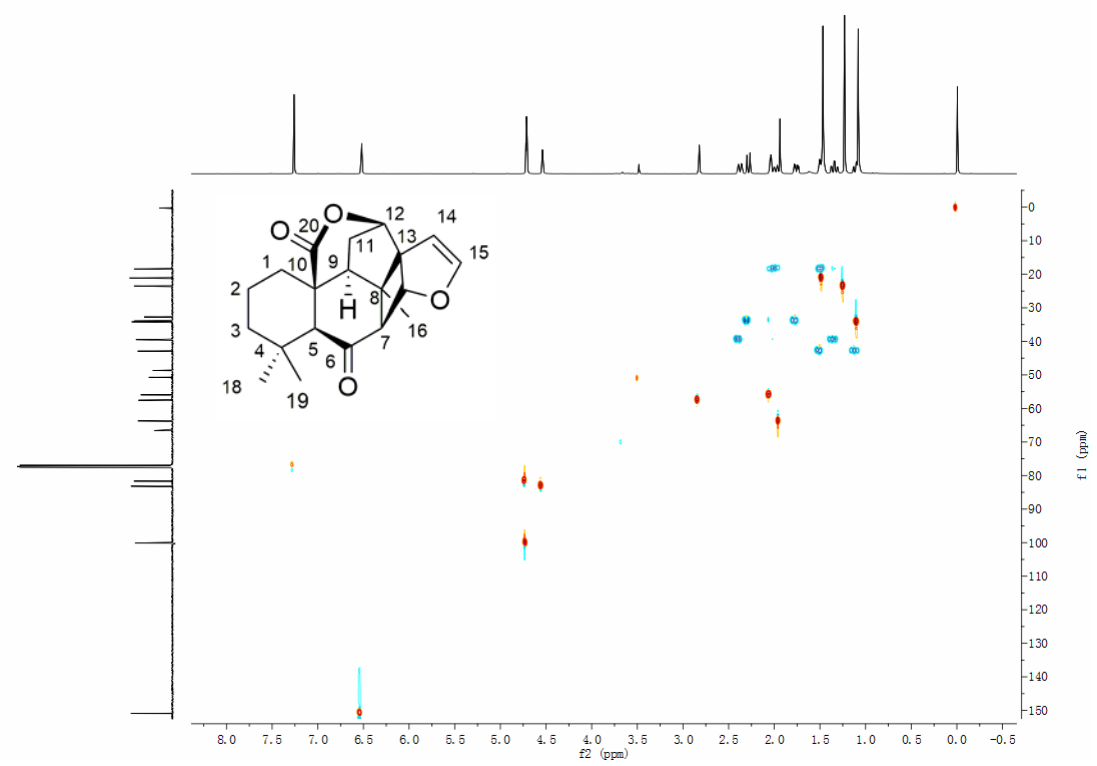

Figure S15. HSQC spectrum (400 MHz) of **2** in $CDCl_3$.

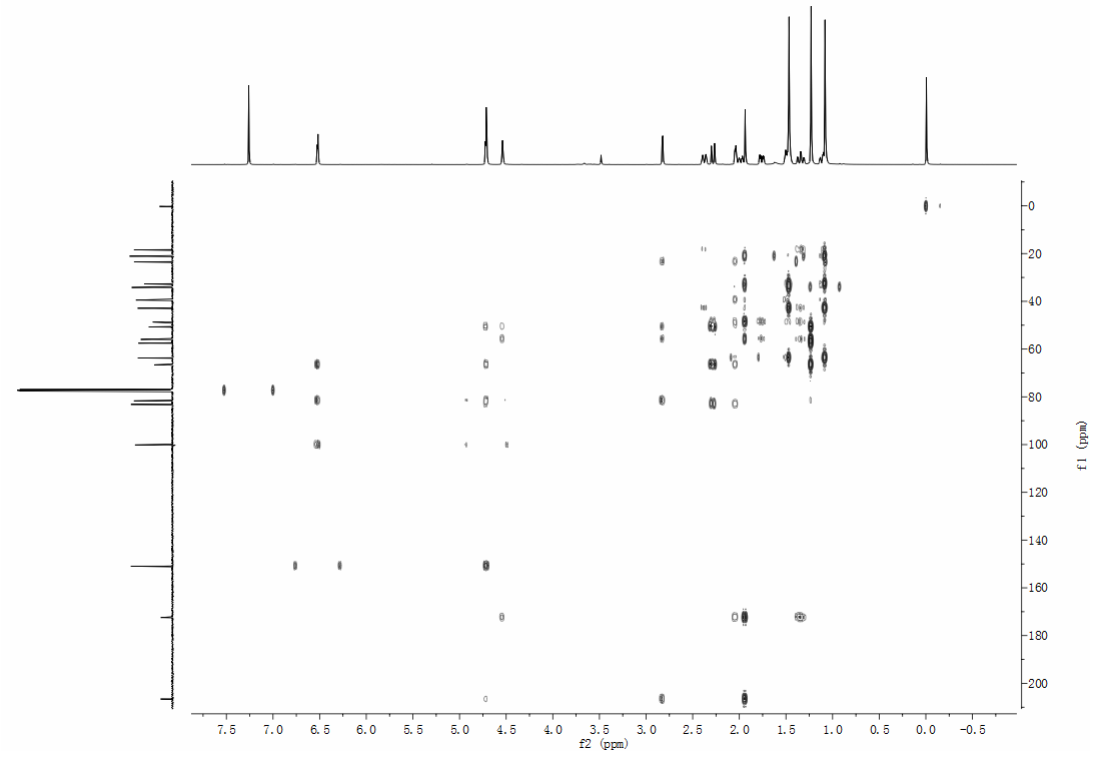

Figure S16. HMBC spectrum (400 MHz) of **2** in $CDCl_3$.

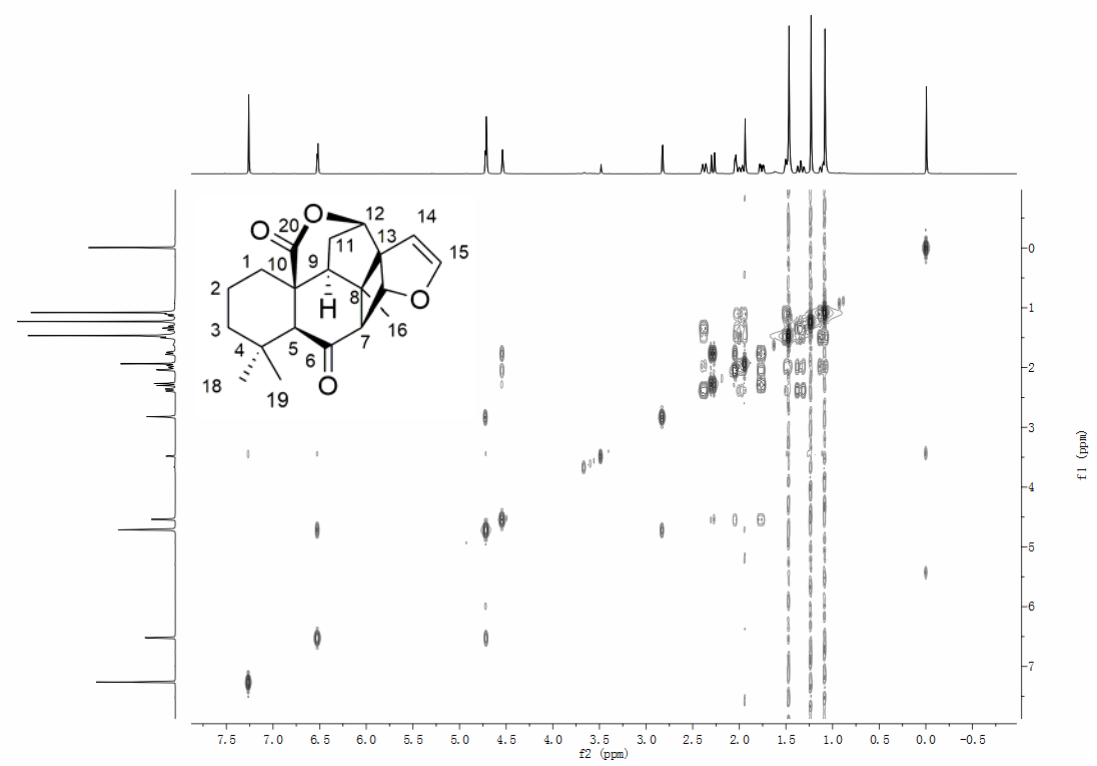

Figure S17. ^{1}H-^{1}H COSY spectrum (400 MHz) of **2** in $CDCl_3$.

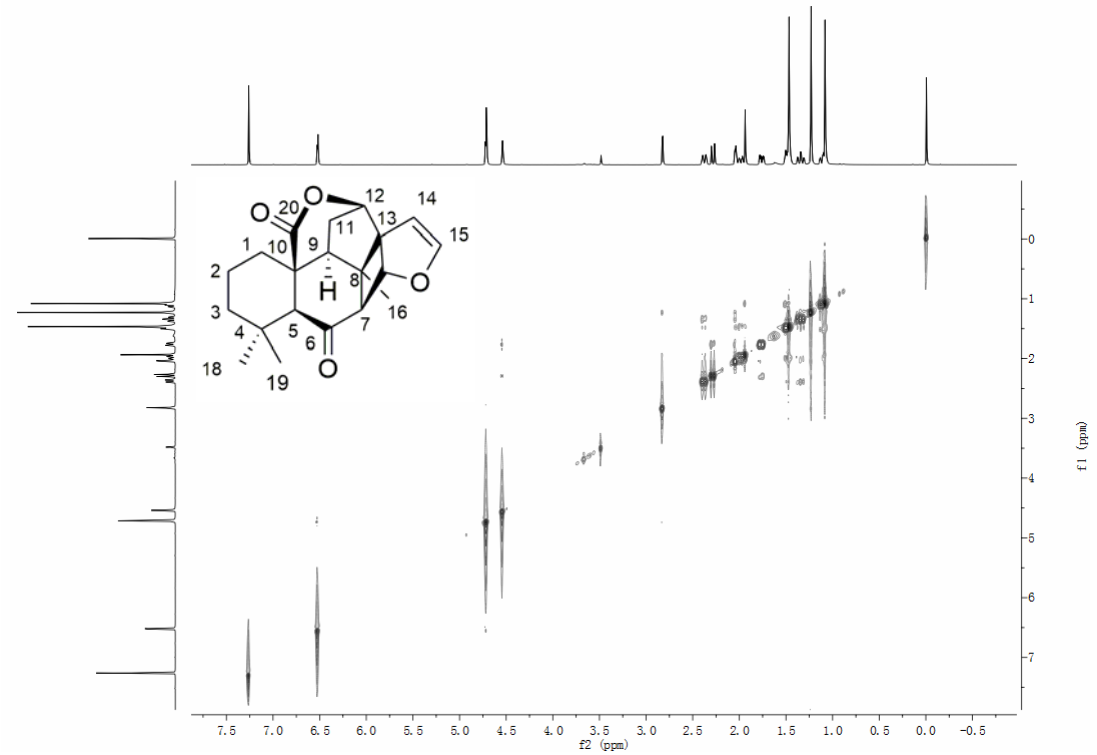

Figure S18. NOESY spectrum (400 MHz) of **2** in $CDCl_3$.

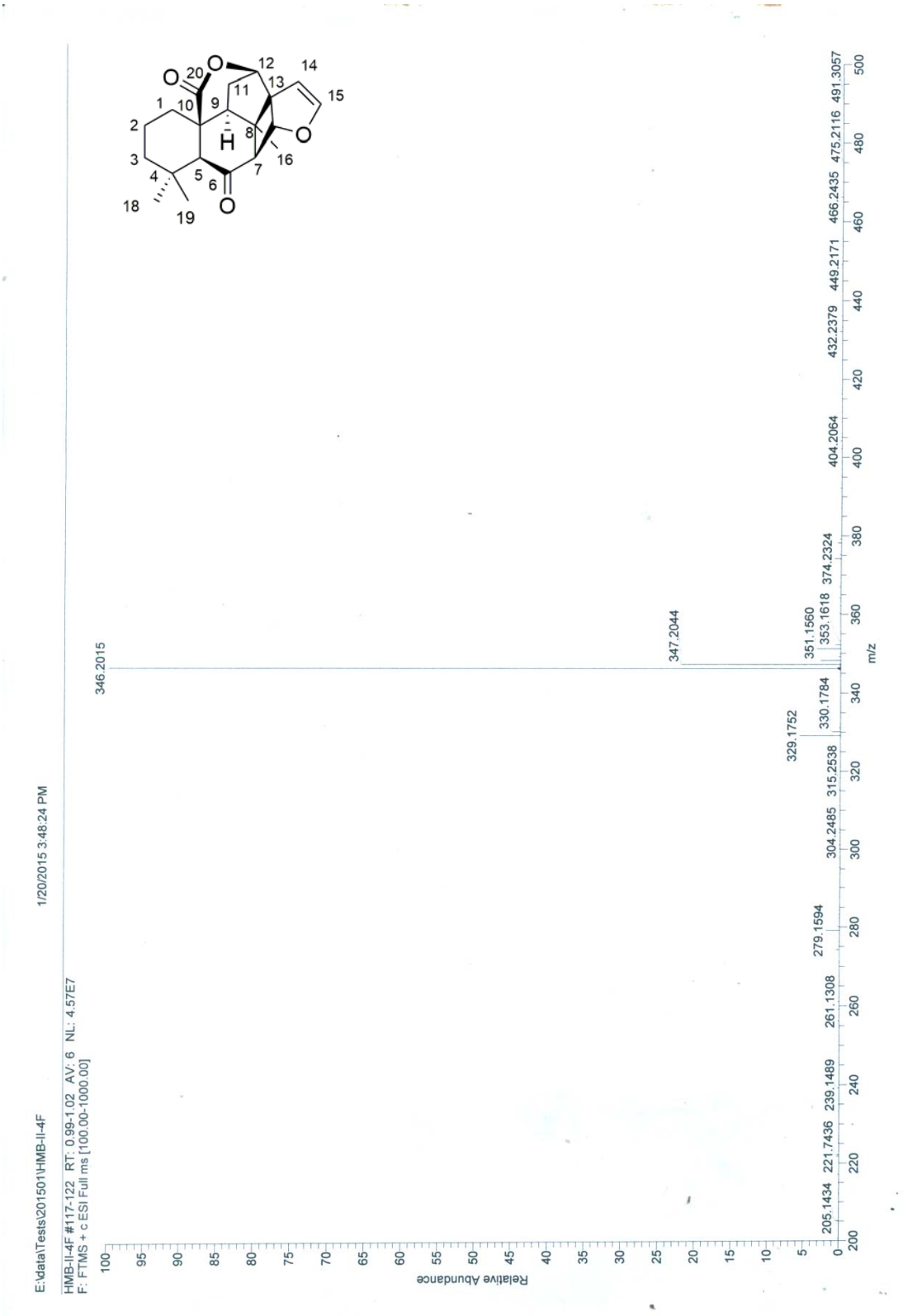

Figure S19. HRESIMS spectrum of **2**.

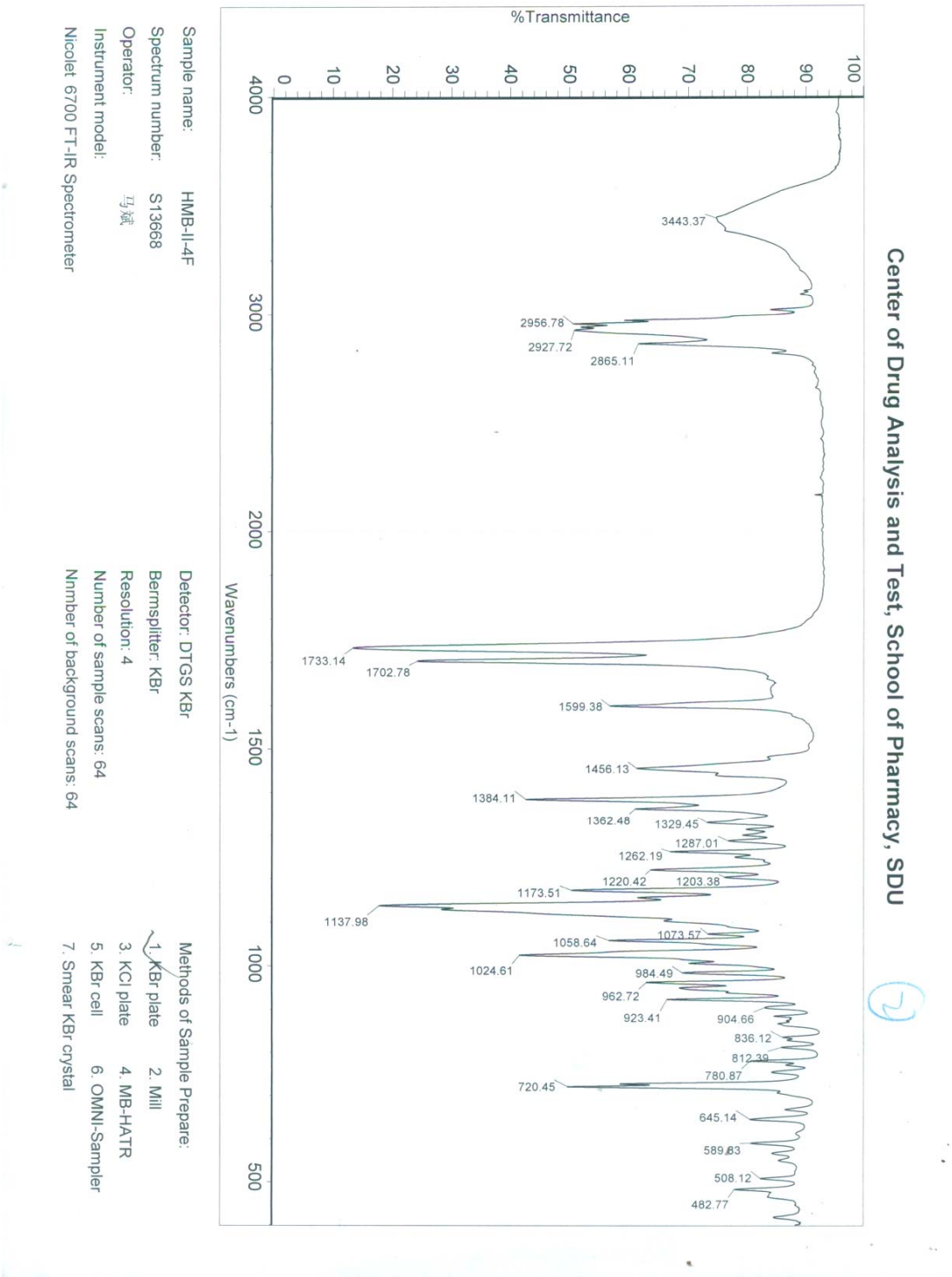

Figure S20. IR (KBr disc) spectrum of **2**.

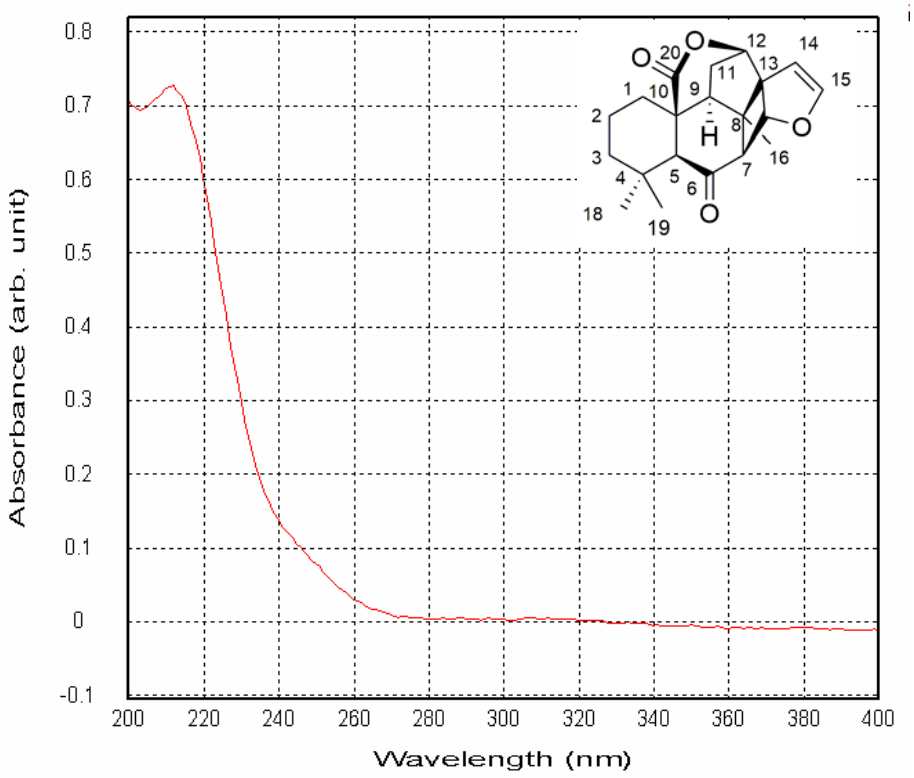

Figure S21. UV spectrum of **2**.

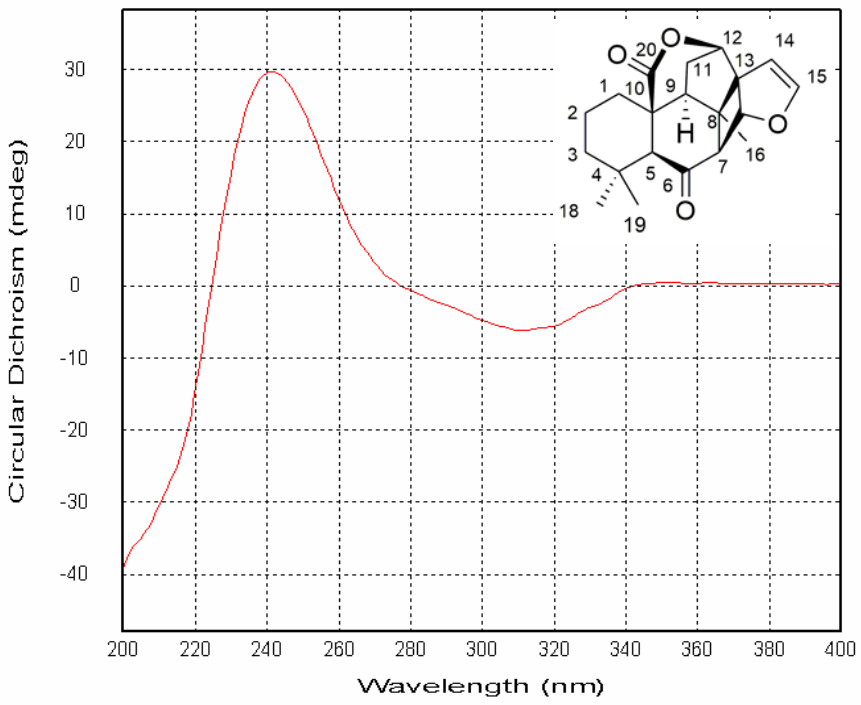

Figure S22. CD spectrum of **2**.

Compound 3: colorless crystals (MeOH); mp 160−162°C; $[\alpha]^{20}_{D}$ +36.4 (*c* 0.1 CH_3CN); UV (CH_3CN) λ_{max} (log ε) 217 (3.96) nm; CD (CH_3CN): 262 ($\Delta\varepsilon$ +0.23), 207($\Delta\varepsilon$ −1.98) nm; IR ν_{max} 3468, 2958, 1748, 1694, 1670, 1278, 1289, 1153, 1086, 1026, 876, 601 cm^{-1};HRESIMS at *m*/*z* 389.1597 $[M + H]^+$ (calcd for $C_{21}H_{25}O_7$, 389.1595).

3 had the molecular formula of $C_{21}H_{24}O_7$, with ten degrees of unsaturation, as established by HRESIMS and ^{13}C NMR data Analysis of its ^1H and ^{13}C NMR data (Table S5). revealed that the structure of **3** was closely related to haplomitrenonolides C (**6**),[1] with the exception that one methine (δ_H 2.99; δ_C 49.4) in **6** was placed with the oxygened carbon (δ_C 74.1) in **3** and this hydroxyl group was located at C-9 supported by the HMBC correlations from H-5 (δ_H 3.74), H-7 (δ_H 5.70) and H_3-17 (δ_H 1.75) to C-9. Thus, the structure of **3** was determined as that shown.

Table S1. ^{1}H and ^{13}C NMR data of 3.[a]

position	δ_C	δ_H
1	27.1 t	2.17 m 2H
2	18.5 t	1.74 m 2H
3α	37.9 t	1.55 m
3β		1.72 m
4	43.6 s	
5	49.0 d	3.74 s
6	194.9 s	
7	129.8 d	5.70 m
8	155.6 s	
9	74.1 s	
10	55.3 s	
11α	33.4 t	2.68 dd (14.8, 9.2)
11β		2.60 dd (14.8, 5.2)
12	69.9 d	5.71 m
13	126.7 s	
14	108.5 d	6.36 br s
15	144.3d	7.44 t (2.0)
16	139.2 d	7.40 br s
17	19.7 d	1.75 d (1.2)
18	179.9 s	
19	18.0 q	1.59 s 3H
20	172.7 s	
COOCH3	52.8 q	3.73 s 3H

[a] Recorded in $CDCl_3$ at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR). δ in ppm. J in Hz. ^{13}C multiplicities were determined by HSQC experiment.

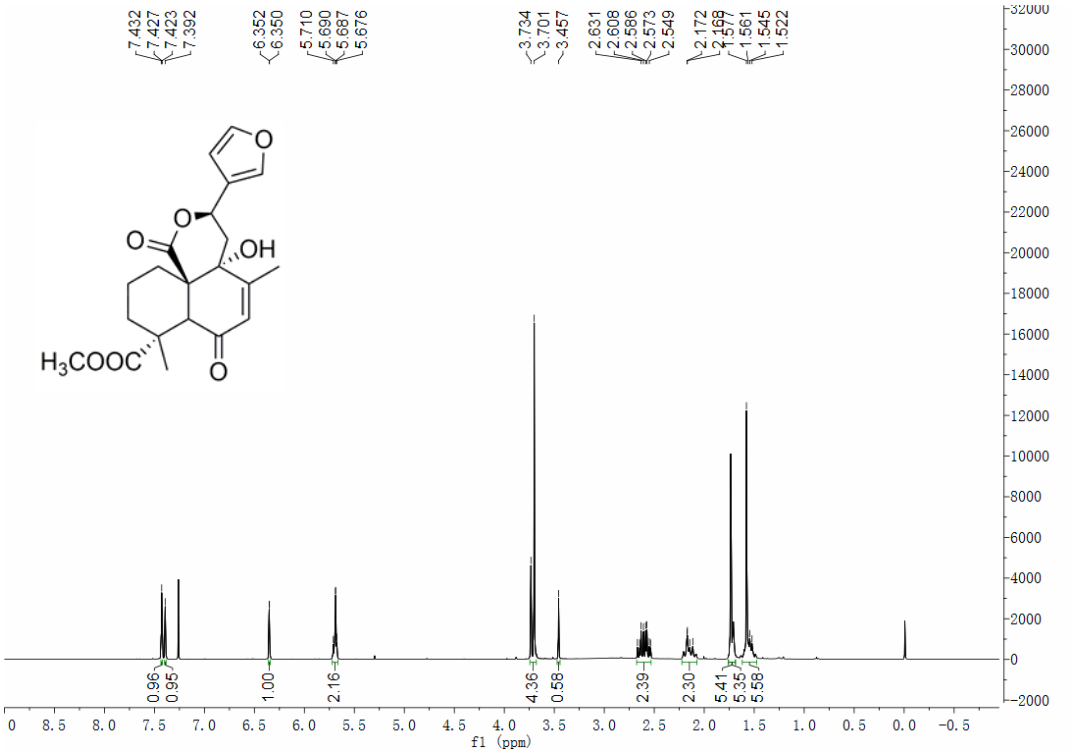

Figure S23. ^{1}H NMR spectrum (400 MHz) of **3** in $CDCl_3$.

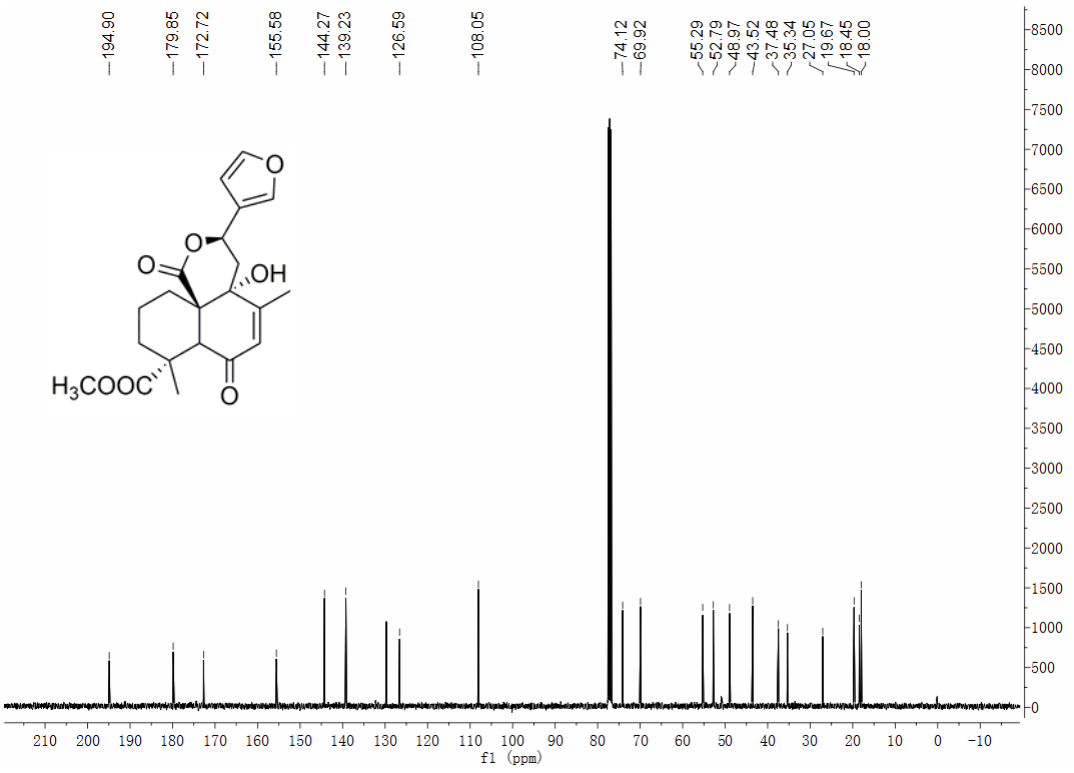

Figure S24. ^{13}C NMR spectrum (100 MHz) of **3** in $CDCl_3$.

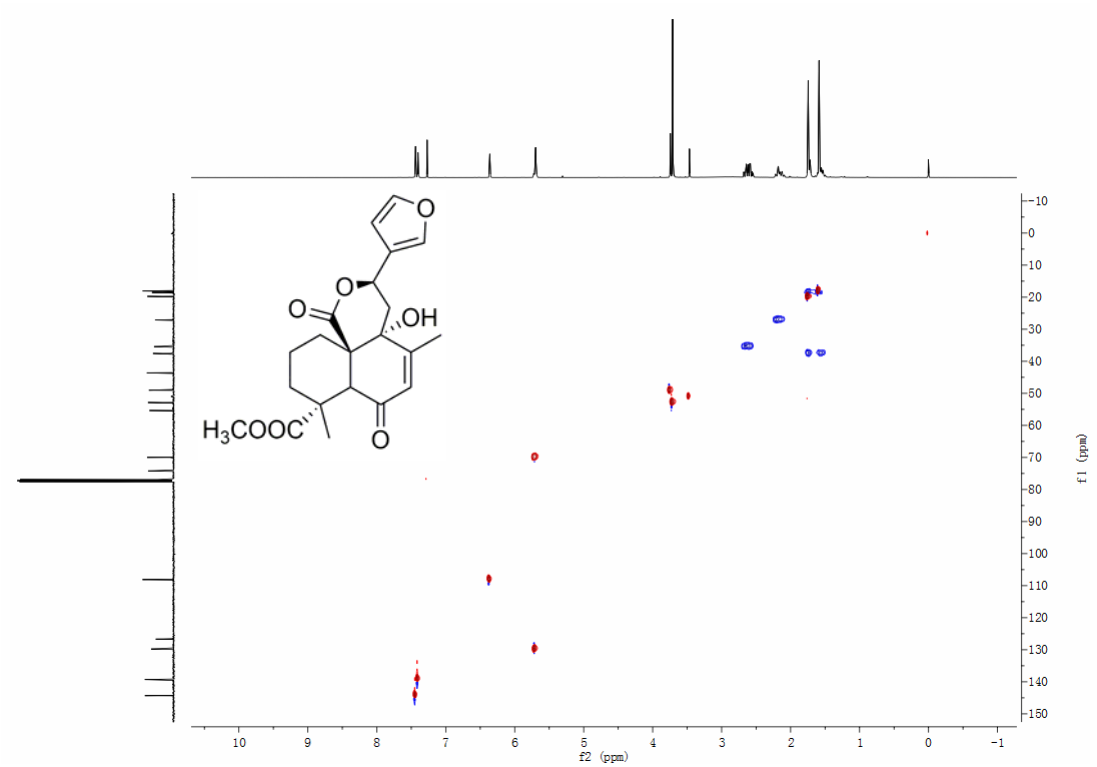

Figure S25. HSQC spectrum (400 MHz) of **3** in $CDCl_3$.

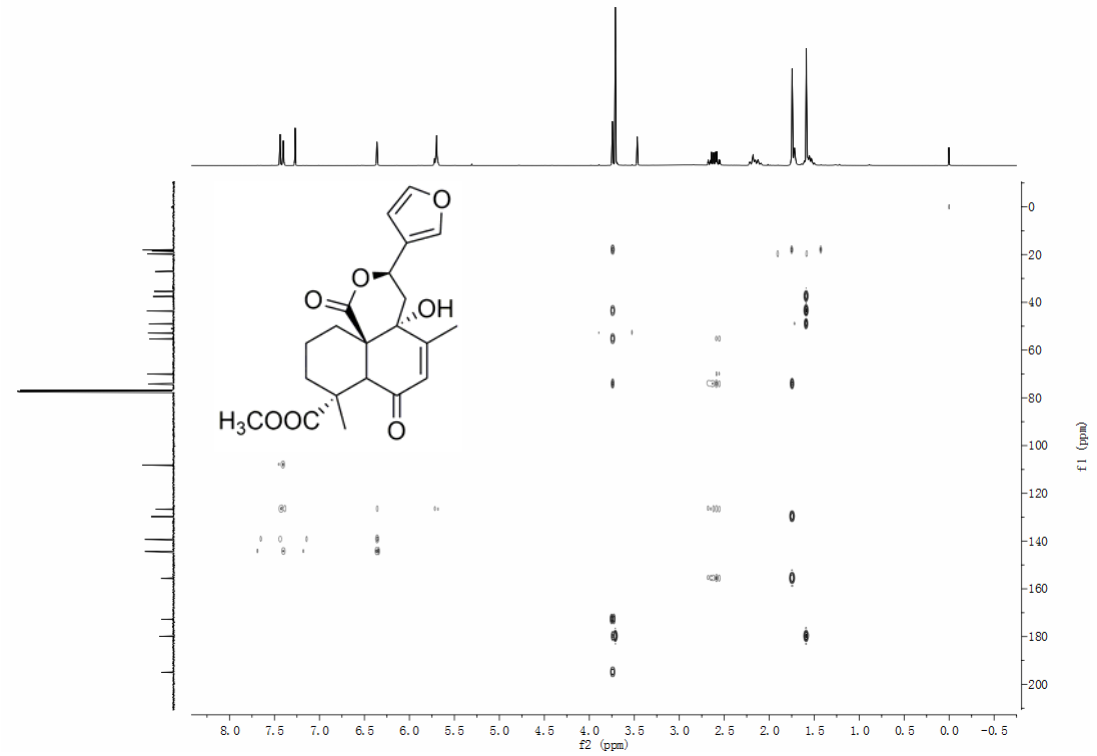

Figure S36. HMBC spectrum (400 MHz) of **3** in $CDCl_3$.

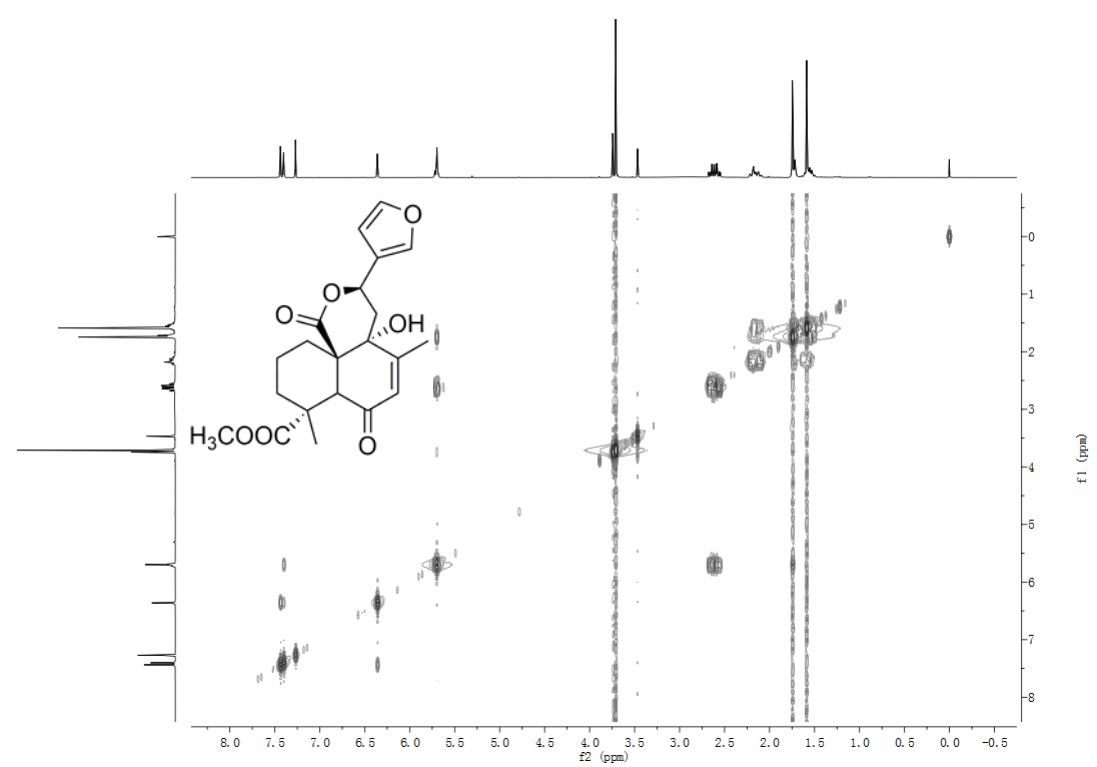

Figure S27. ^{1}H-^{1}H COSY spectrum (600 MHz) of **3** in $CDCl_3$.

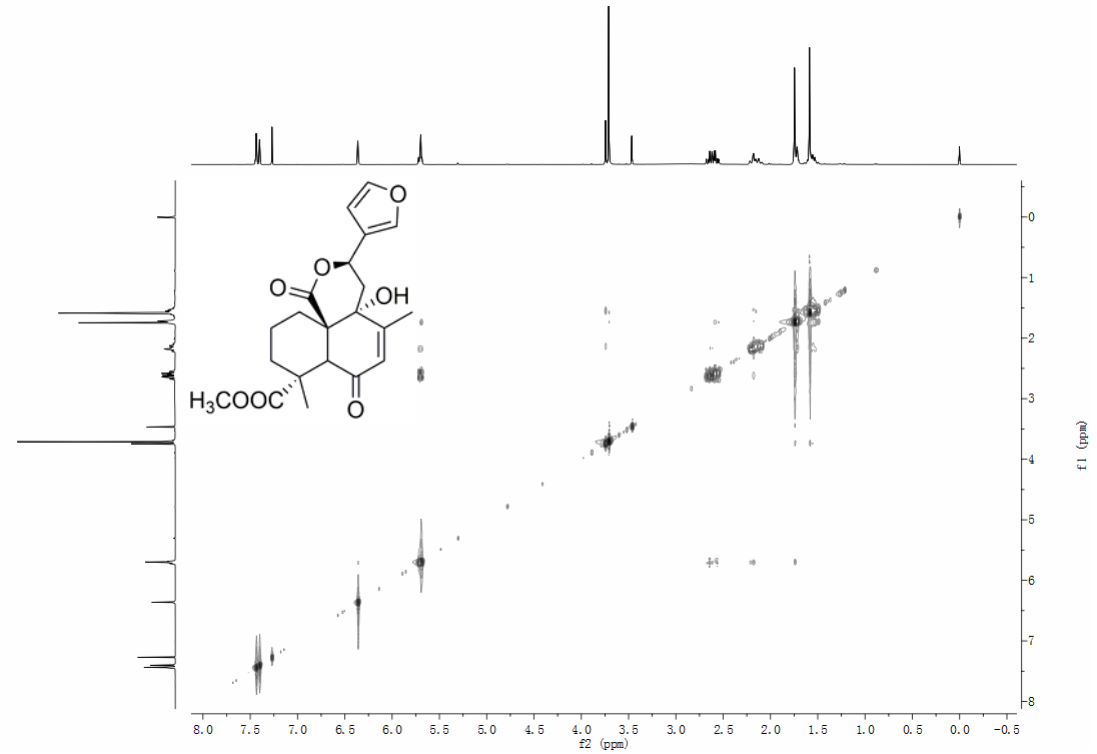

Figure S28. NOESY spectrum (400 MHz) of **3** in $CDCl_3$.

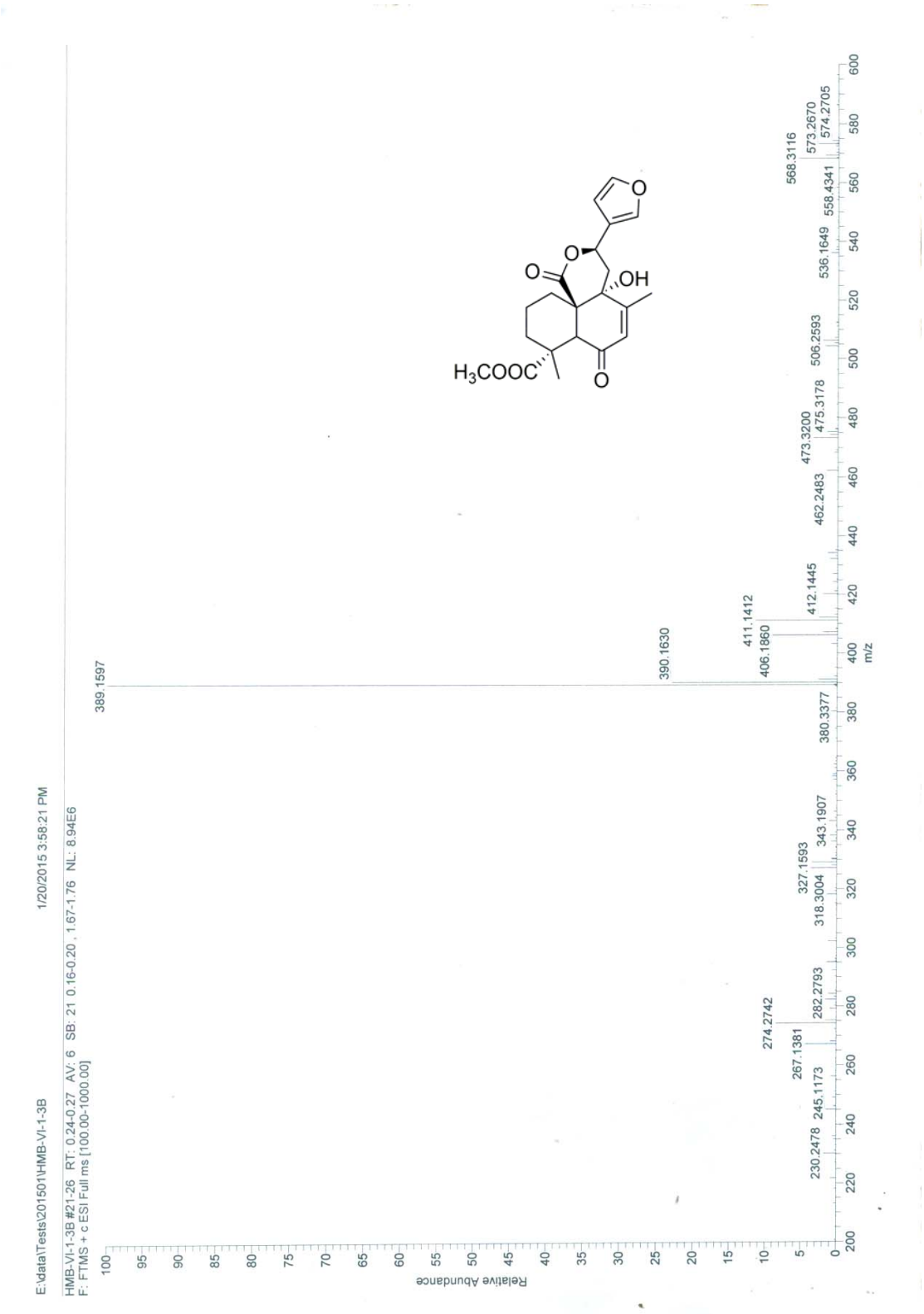

Figure S29. HRESIMS spectrum of **3**.

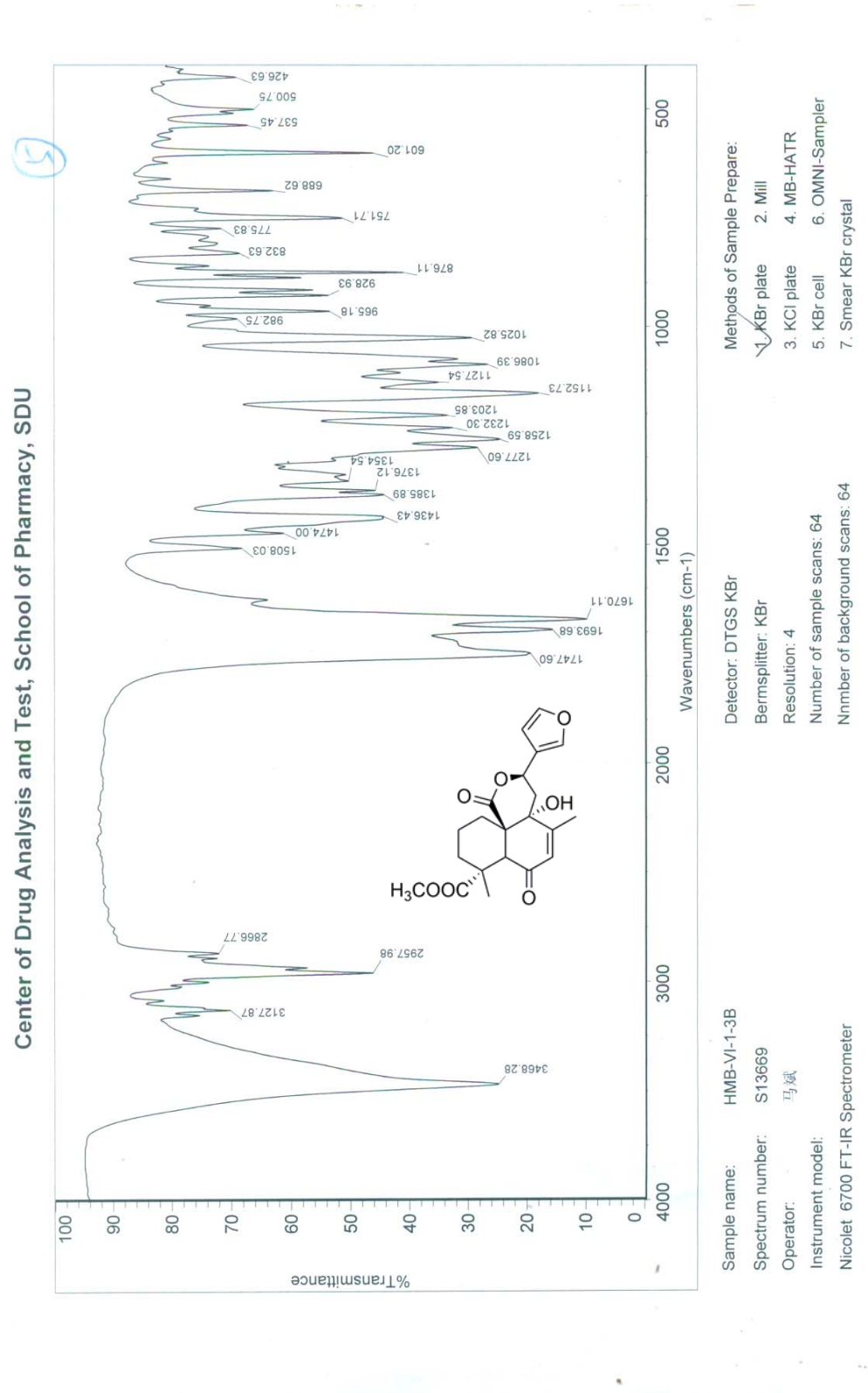

Figure S30. IR (KBr disc) spectrum of **3**.

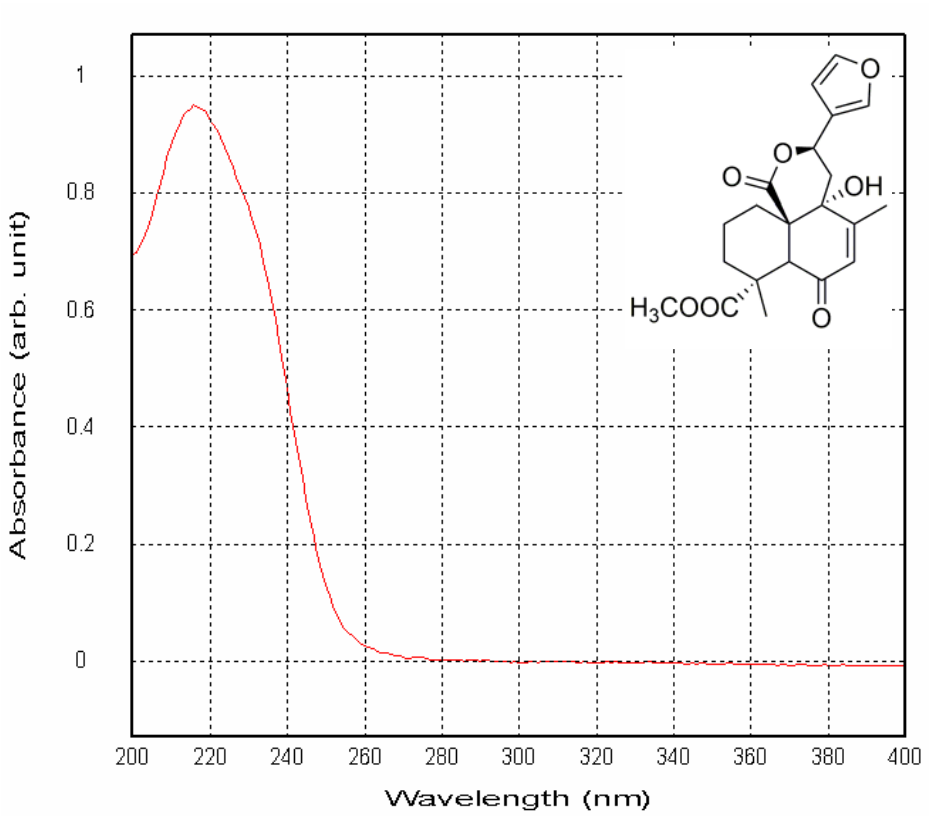

Figure S31. UV spectrum of **3**.

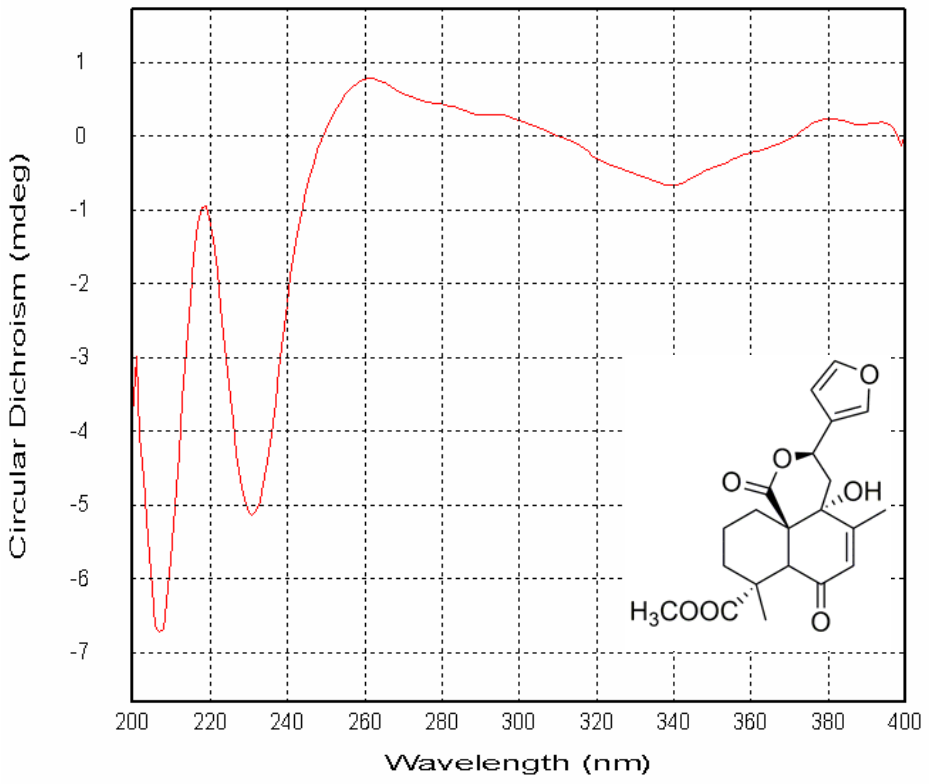

Figure S32. CD spectrum of **3**.

HPLC analysis for the plant material and light-driven transformation *in vivo*.

The composition of liverwort *Haplomitrium mnioides* (Lindb.) R. M. Schust. was analyzed to determine the presence of compounds **1**–**6** in nature. The methanol solution of crude extract (mg/mL, 20μL) was analyzed by HPLC (0–50min, MeOH/H_2O, 50:50 to 100:0, 0.8 mL/min). Pure compounds were used as references of retention times (Figure S33).

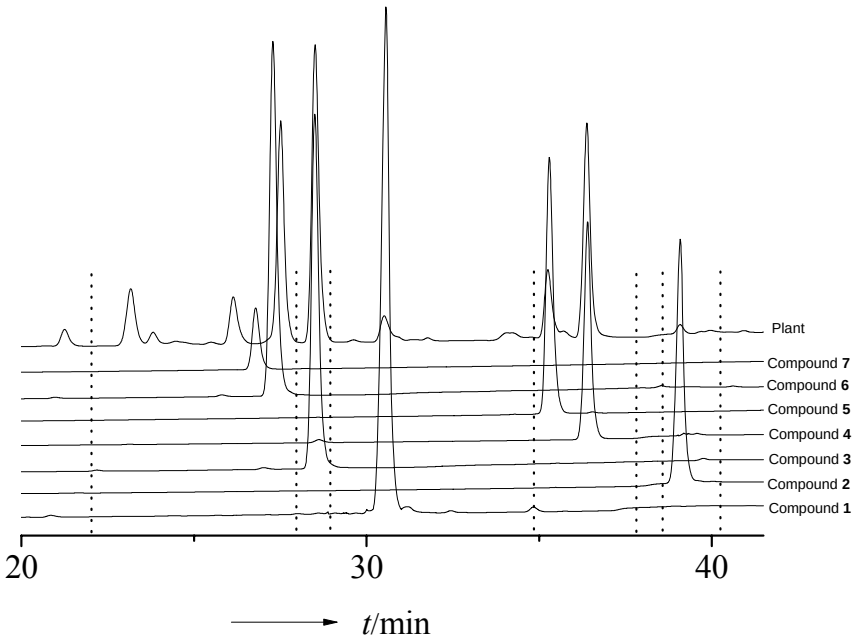

Figure S33. HPLC analysis for the liverwort *H. mnioides*

HPLC profiles were also used to show the light-driven transformation *in vivo*. The liverwort *H. mnioides* was cultivated in two small pots, positioned in shadow, and continuously exposed to daylight, respectively. The plants were picked at random after 24h, followed by freezedrying and extracted using methanol with ultrasound. The two samples with same concentration were detected by analytical HPLC (0-5min, 45% MeOH; 5-35min, 45%-65% MeOH; 35-40min 65% MeOH; 40-60min,

65%-100% MeOH). The HPLC profiles showed that elongation of exposure time to daylight led to the slightly increase of the ratio of compound **1** to its precursor compound **6** which was also been supported by the peak area of compounds **2** and **4** (Figure S34)

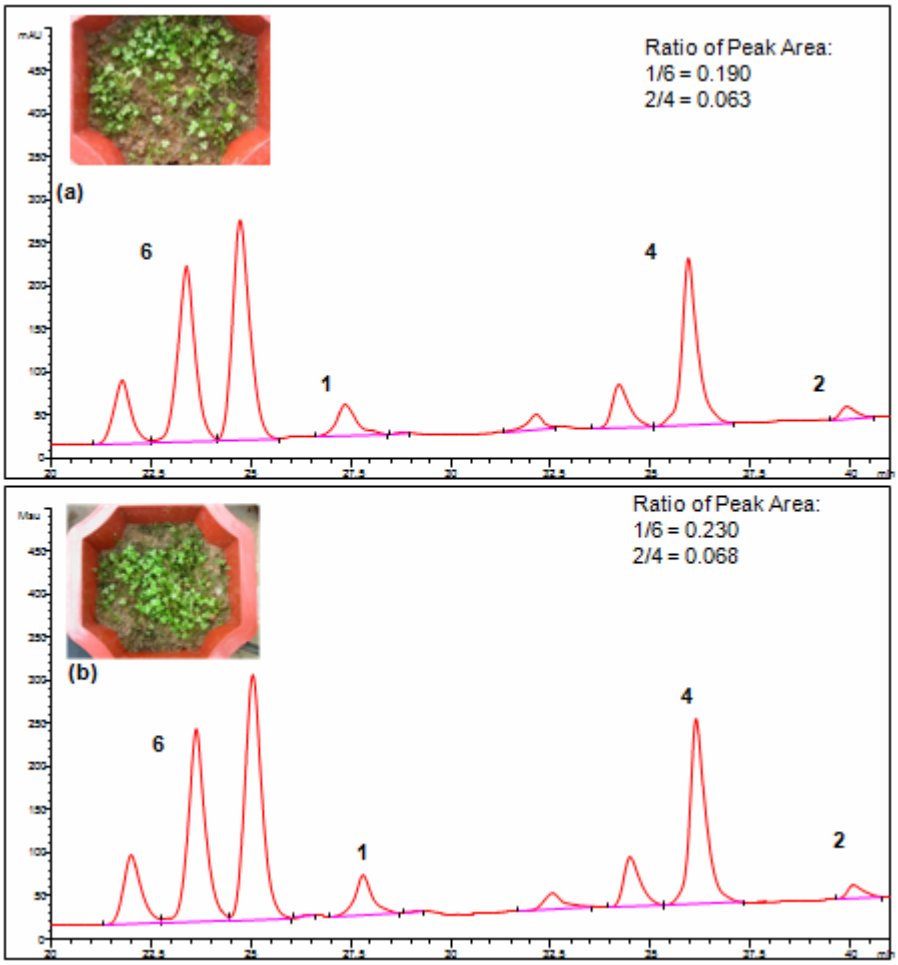

Figure S34. HPLC profiles for a) liverwort positioned in shadow, b) exposed to daylight.

HPLC analysis for the photochemistry reactions of 6, 4 and 3.

Each 1 mg of **6**, **4** or **3** was added to test tube to perform the photoinduced reaction. Start material was dissolved in 2 ml of anhydrous acetonitrile and the dissolved oxygen in the solution was removed by bubbling with nitrogen for 30 min. The

solution was irradiated (RPR-2537A Lamps, 400 W, 254nm) at room temperature under a nitrogen atmosphere and detected at various time points. The light intensity was about 2 mW/cm^2. Analytical HPLC (MeOH/H_2O, 45:55 for **6**; CH_3CN/H_2O, 50:50 for **4**; MeOH/H_2O, 45:55 for **3**) was used to analyze the changes of compounds. The flow rate was 0.8 mL/min. Samples (10 μL for **6**, 20 μL for **4** and **3**) were injected directly at various time points. Pure compounds **1**–**4**, **6** we isolated from this liverwort were used to compare their retention times with those of compounds in reaction solution and plant (Figure S35–S36).

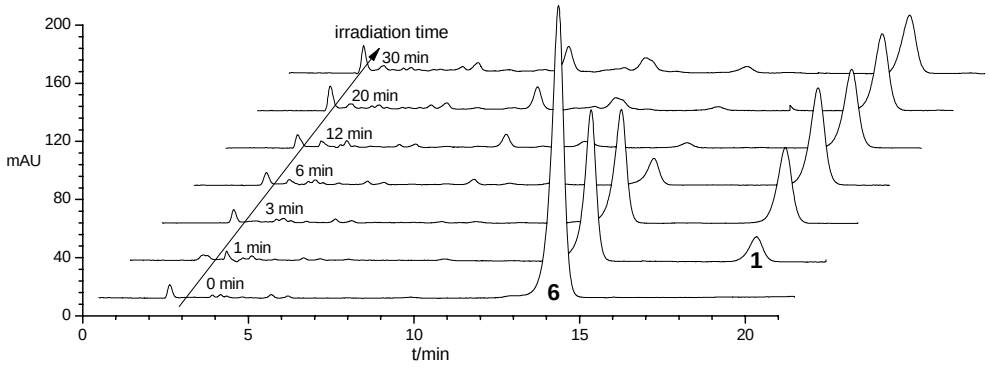

Figure S35. HPLC chromatograms (λdetection = 210 nm) as a function of irradiation time obtained for the irradiation of compound **6** in nitrogen-saturated acetonitrile solution (λexcitation = 254 nm)

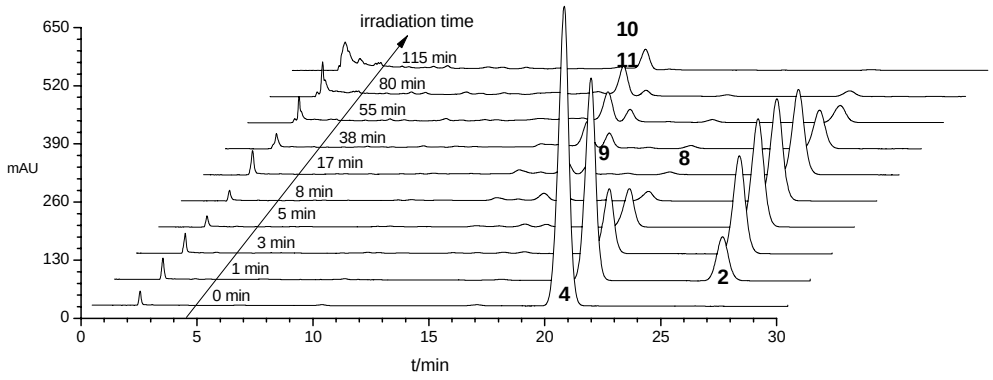

Figure S36. HPLC chromatograms (λdetection = 210 nm) as a function of irradiation time obtained for the irradiation of compound **4** in nitrogen-saturated acetonitrile solution (λexcitation = 254 nm)

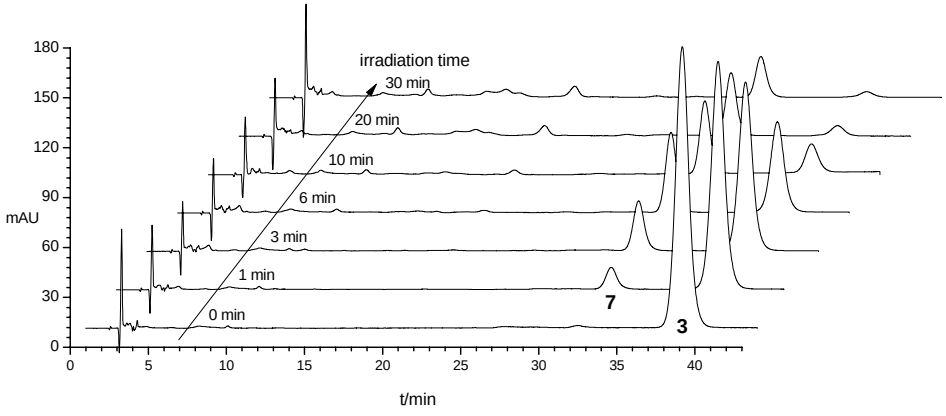

Figure S37. HPLC chromatograms (λdetection = 210 nm) as a function of irradiation time obtained for the irradiation of compound **3** in nitrogen-saturated acetonitrile solution (λexcitation = 254 nm)

UV analysis for the photochemistry reactions of 6, 4 and 3

0.035 mg compound **6**, **4** or **3** was dissolved in 3.5 ml of anhydrous acetonitrile. The solution in a quartz cell (1 cm optical pathlength) was deoxygenated by nitrogen bubbling for 20 min prior to irradiation. Then the cell was closed using a septum. The solution was irradiated (RPR-2537A Lamps, 400 W) at 35 °C and the light intensity was about 2 mW/cm^2. UV absorption spectroscopy was measured at various time points (0, 1, 2, 3, 4, 6, 8, 10, 15, 20, 30, 60min).

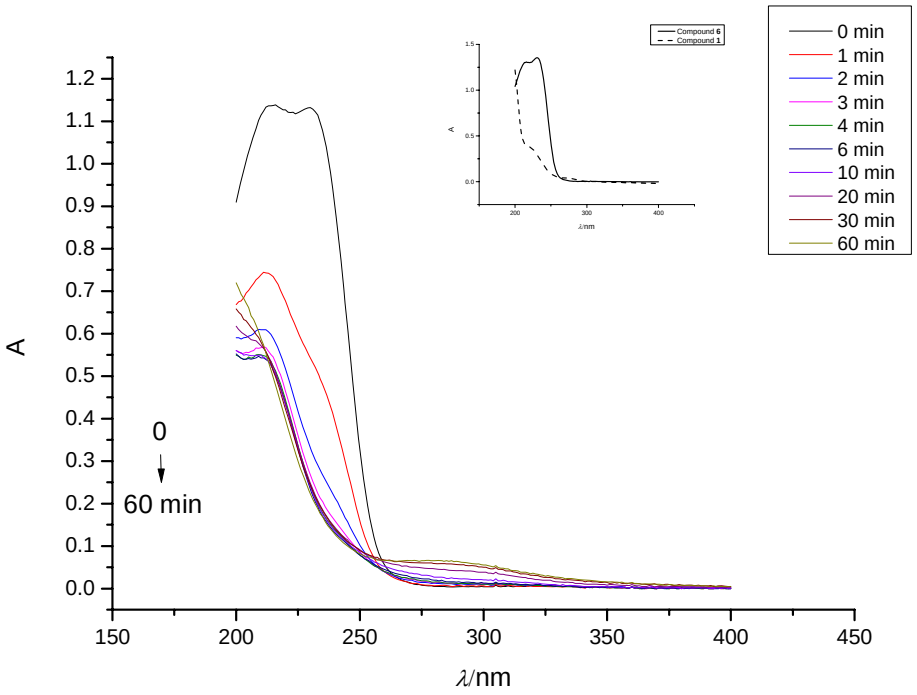

Figure S38. Changes in the UV absorption spectra of nitrogen-saturated acetonitrile solution for compound **6** irradiated by 254 nm light.

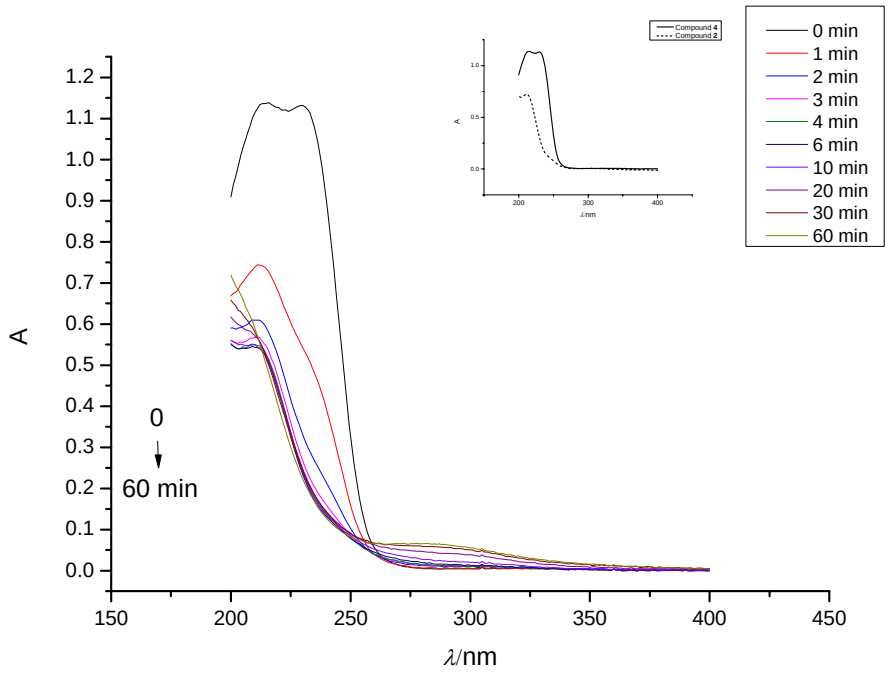

Figure S39. Changes in the UV absorption spectra of nitrogen-saturated acetonitrile solution for compound **4** irradiated by 254 nm light.

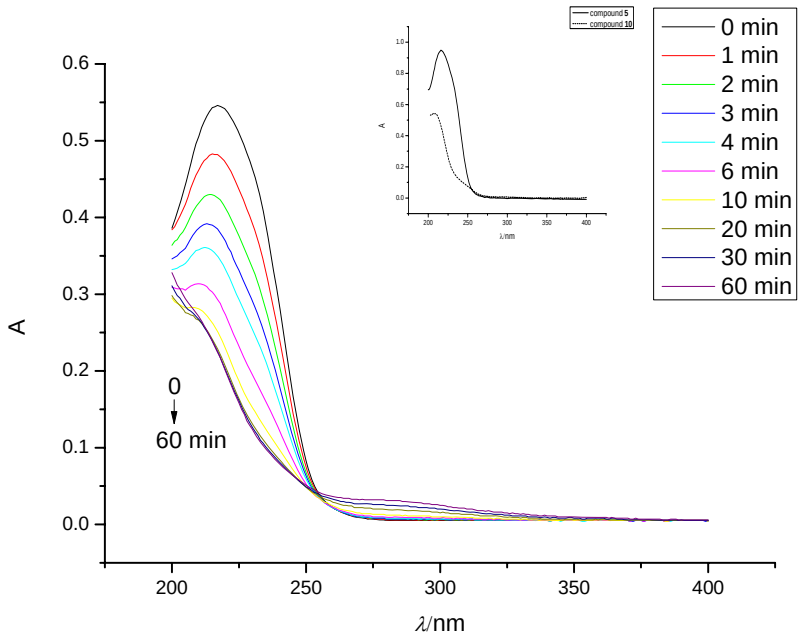

Figure S40. Changes in the UV absorption spectra of nitrogen-saturated acetonitrile solution for compound **3** irradiated by 254 nm light.

Amplified photochemical reaction of 3 and the structure elucidation of 7

Compound **3** (20.29mg) was irradiated using the aforementioned method for 8 min, followed by the semipreparative HPLC to provide **7** (6.57mg, 33% yield).

Compound **7**: White, amorphous powder; $[\alpha]^{20}_{D}$ −1.6 (*c* 0.1 CH_3CN); UV (MeOH) λ_{max} (log ε) 207 (3.79) nm; ECD (MeOH): 303($\Delta\varepsilon$ −9.06) , 247($\Delta\varepsilon$ +7.71)nm; IR ν_{max} 3481, 2926, 1738, 1717, 1696, 1384, 1268, 1238, 1141, 1130, 1117, 1029, 918 cm^{-1}; for ^1H and ^{13}C NMR data, see Tables 1 and 2; HRESIMS at *m*/*z* 389.1597 $[M + H]^+$ (calcd for $C_{21}H_{25}O_7$, 389.1595).

7 had the molecular formula of $C_{21}H_{24}O_7$, with ten degrees of unsaturation, as established by HRESIMS and ^{13}C NMR data Analysis of its ^1H and ^{13}C NMR data (Table S2) revealed that the structure of **7** was closely related to compound **1**, with the exception that one methine (δ_H 2.64; δ_C 55.3) in **1** was placed with the oxygened carbon (δ_C 79.2) in **7** and this hydroxyl group was located at C-9 supported by the HMBC correlations from H-5 (δ_H 3.85), H-7 (δ_H 2.86) and H_3-17 (δ_H 1.23) to C-9. Thus, the structure of **7** was determined as that shown.

Table S2. ^{1}H and ^{13}C NMR data of 7.[a]

position	δ_C	δ_H
1α	39.1 t	1.90 m
1β		2.41 td (13.6, 4.0)
2α	17.1 t	1.65 m
2β		1.99 m
3α	37.3 t	1.45 td (13.2, 3.2)
3β		1.80 m
4	43.4 s	
5	52.0 d	3.86 s
6	204.7 s	
7	57.1 d	2.86 d (3.2)
8	50.7 s	
9	79.2 s	
10	52.7 s	
11α	29.6 t	2.45 d (12.8)
11β		1.95 m
12	78.4 d	4.73 d (3.2)
13	67.5 s	
14	100.4 d	4.80 m
15	150.8 d	6.54 d (2.8)
16	80.1 d	4.80 m
17	18.7 q	1.23 s 3H
18	179.7 s	
19	17.2 q	1.77 s 3H
20	172.8 s	
OCH_3	52.8	3.70 s 3H

[a] Recorded in $CDCl_3$ at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR). δ in ppm. J in Hz. ^{13}C multiplicities were determined by HSQC experiment.

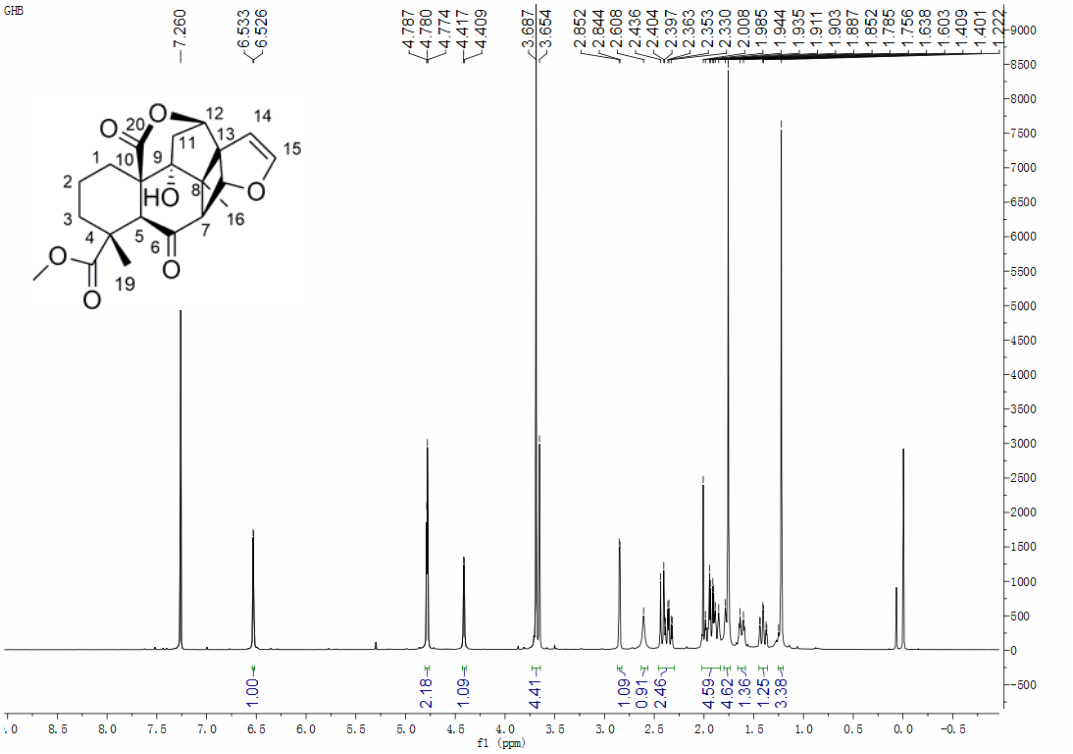

Figure S41. ^{1}H NMR spectrum (400 MHz) of **7** in $CDCl_3$.

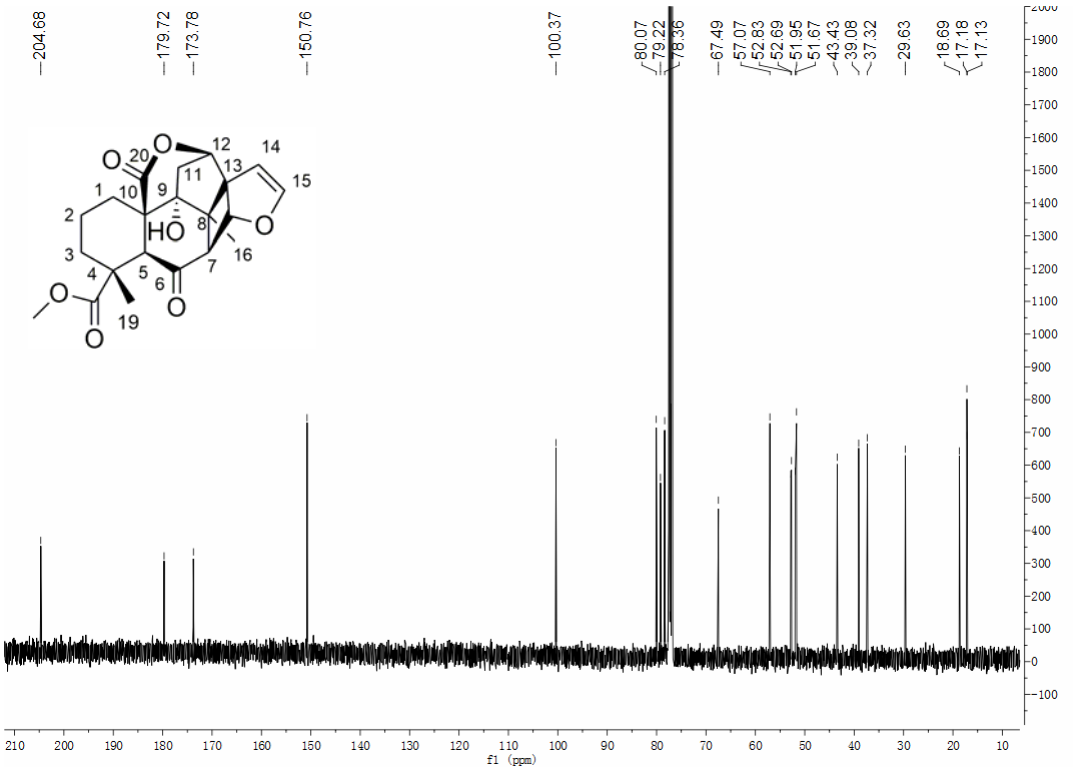

Figure S42. ^{13}C NMR spectrum (100 MHz) of **7** in $CDCl_3$.

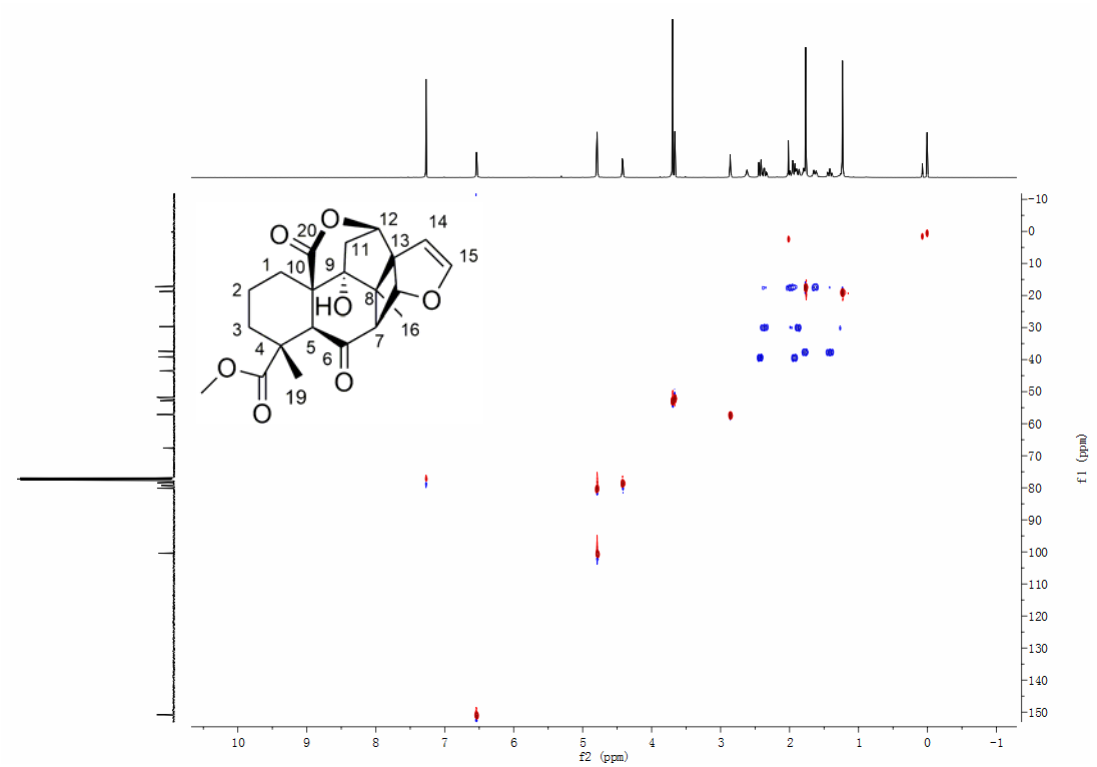

Figure S43. HSQC spectrum (400 MHz) of **7** in $CDCl_3$.

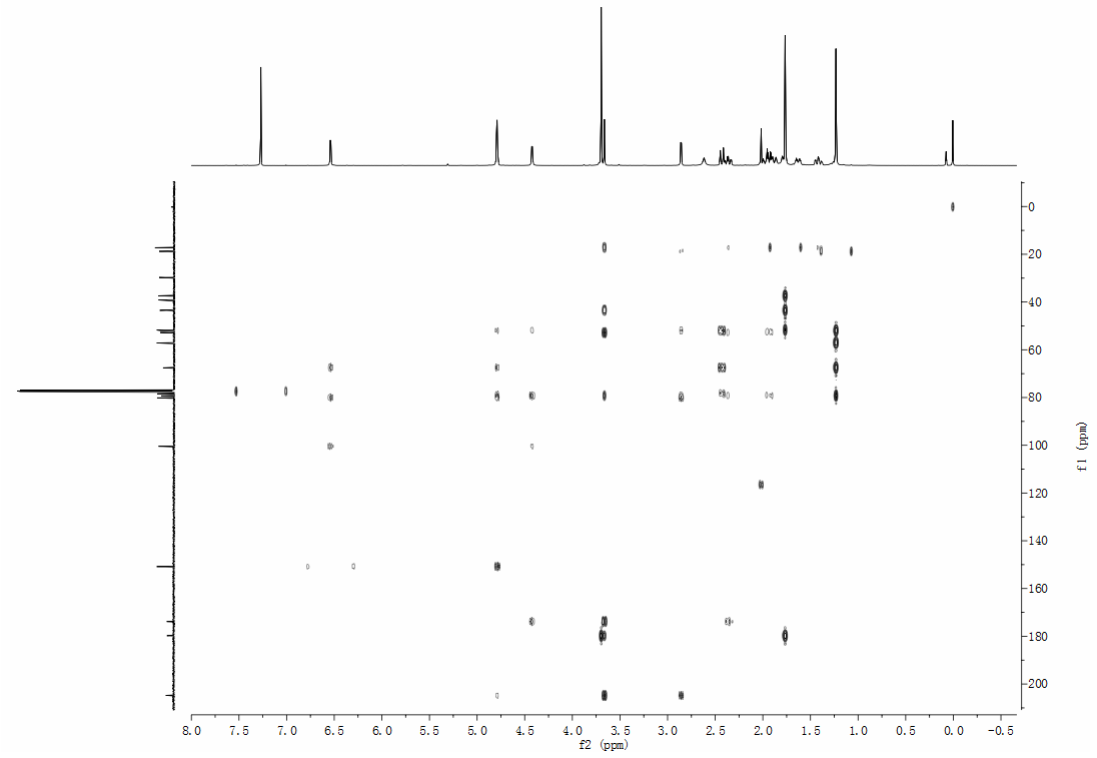

Figure S44. HMBC spectrum (400 MHz) of **7** in $CDCl_3$.

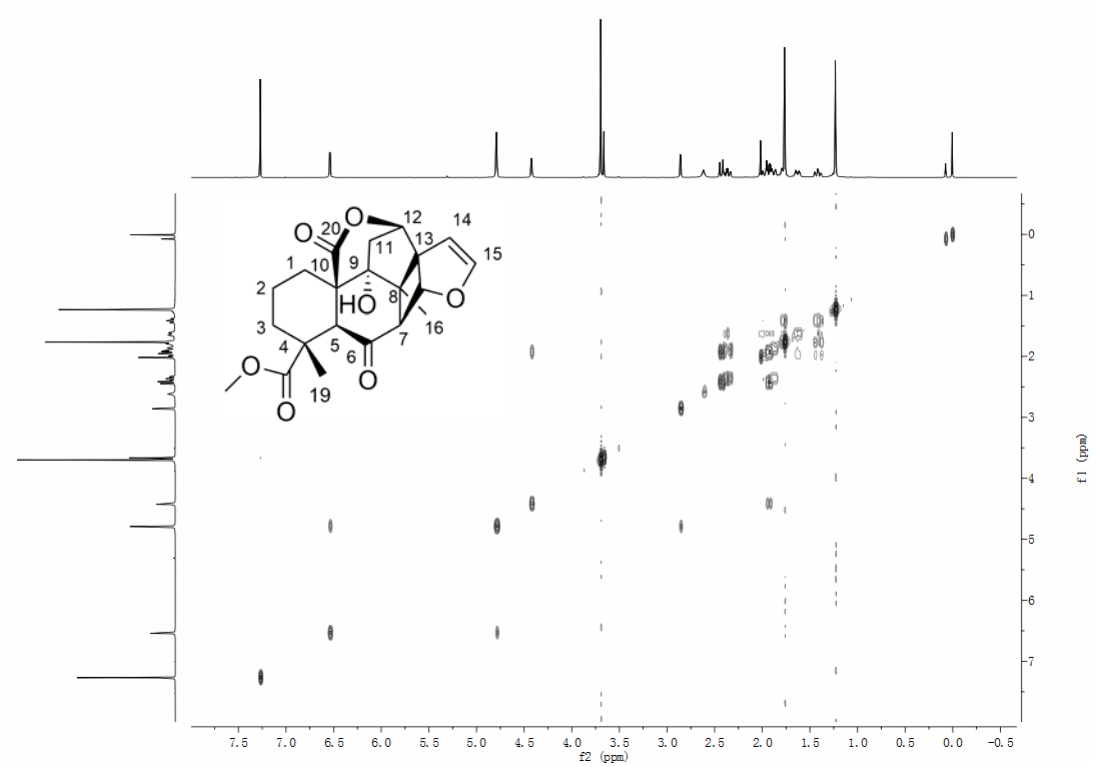

Figure S45. ^{1}H-^{1}H COSY spectrum (400 MHz) of **7** in $CDCl_3$.

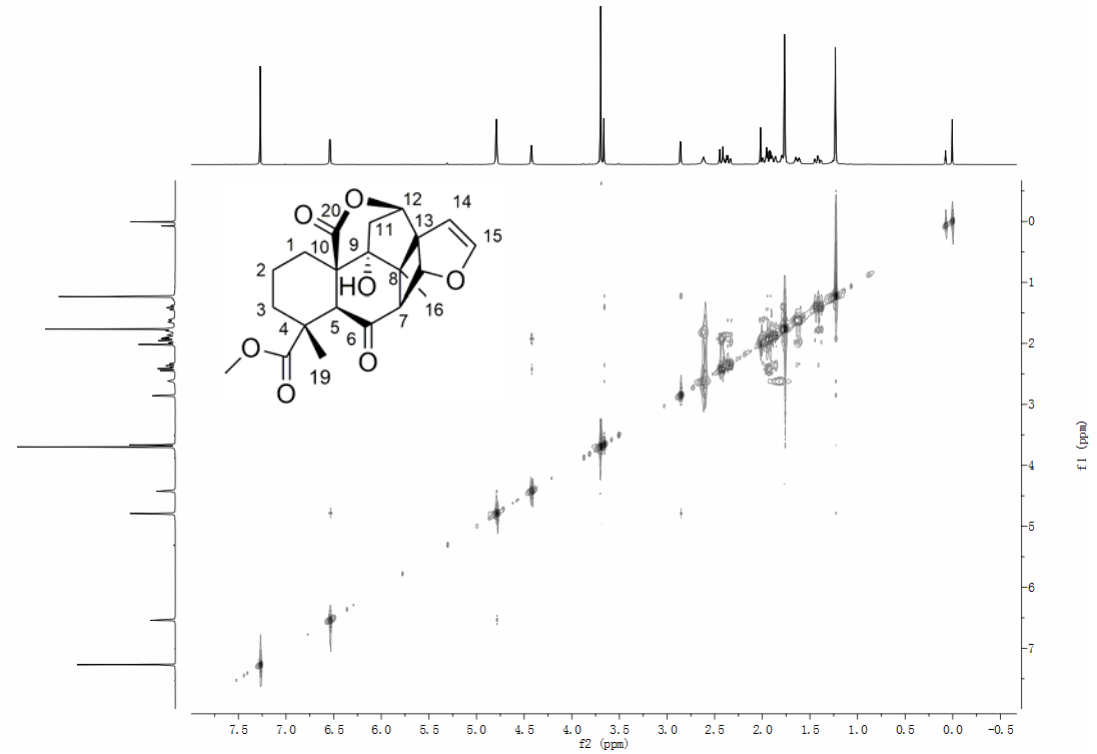

Figure S46. NOESY spectrum (400 MHz) of **7** in $CDCl_3$.

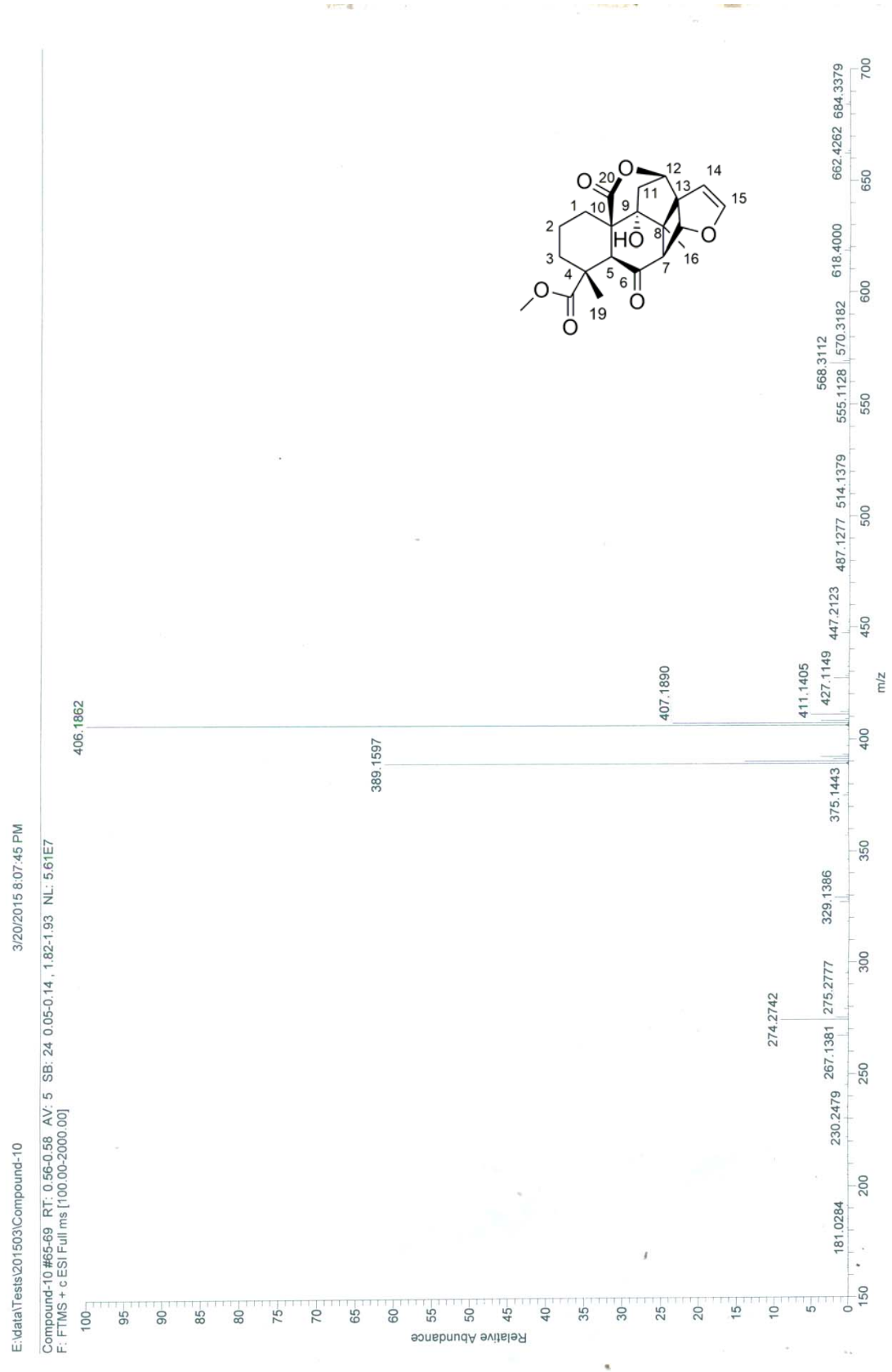

Figure S47. HRESIMS spectrum of **7**.

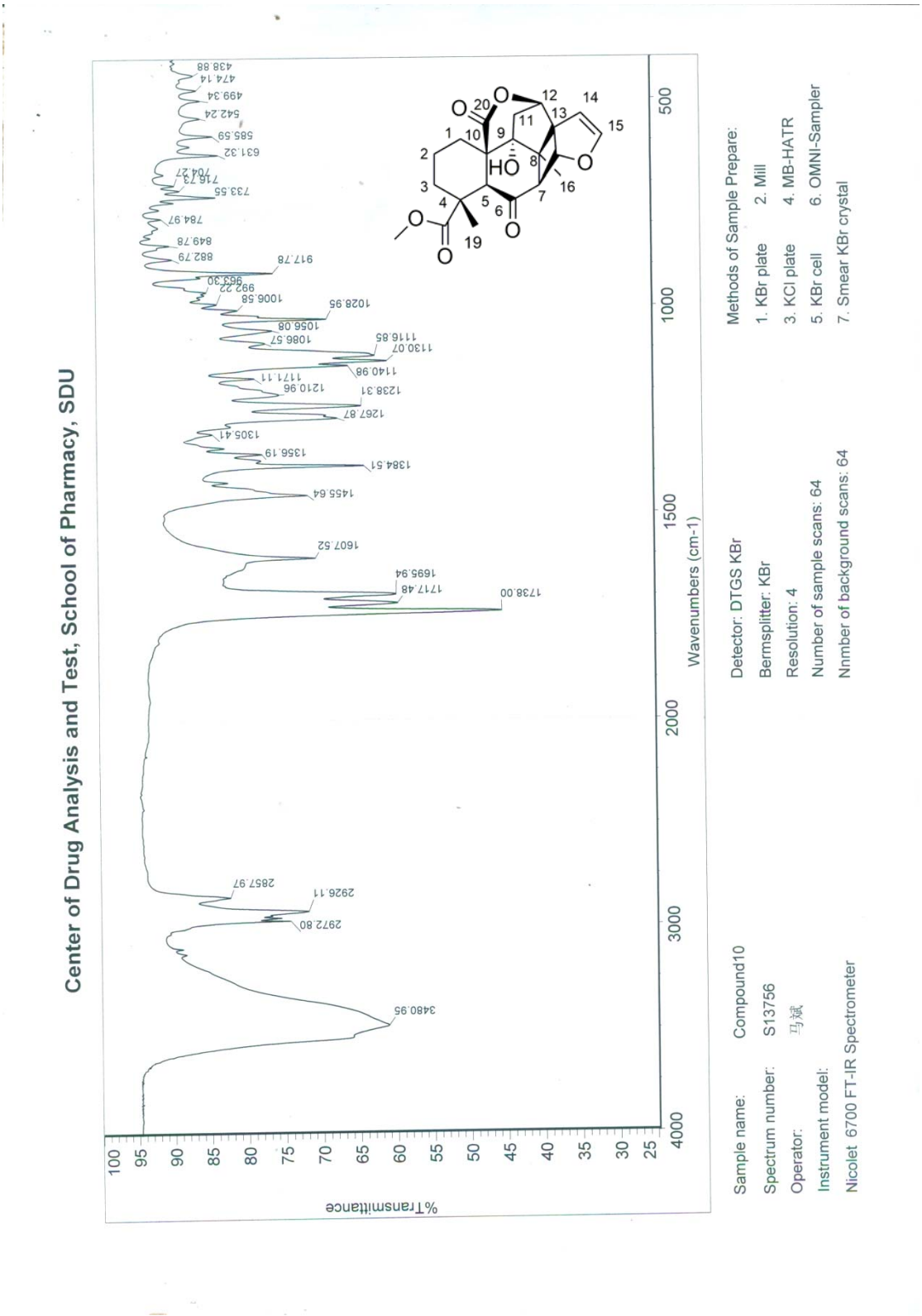

Figure S48. IR (KBr disc) spectrum of **7**.

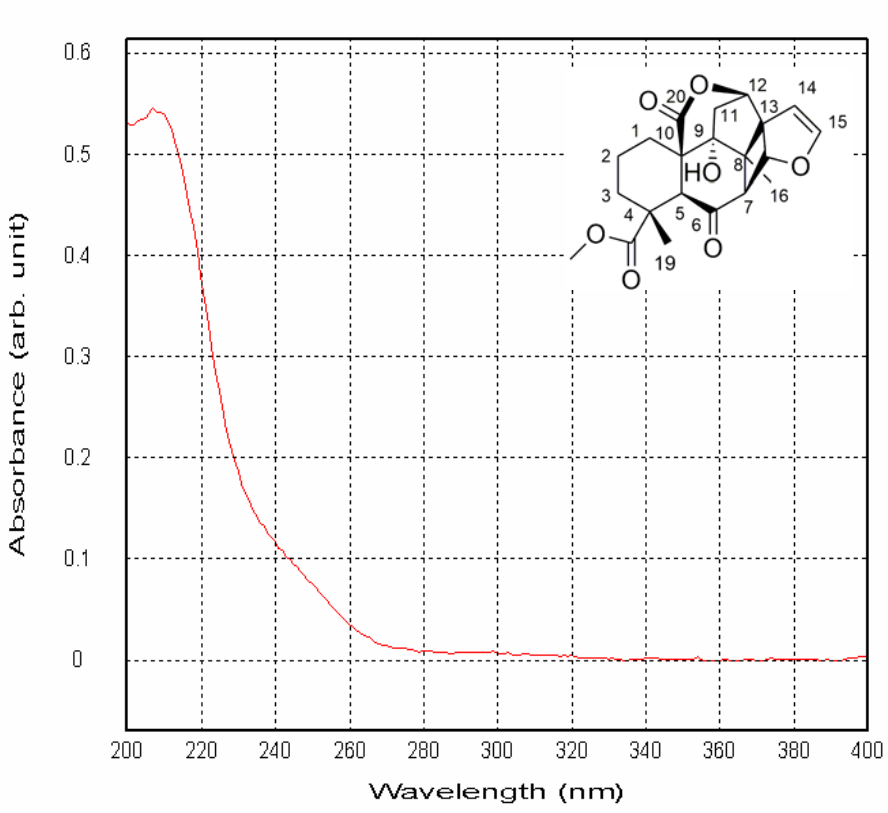

Figure S49. UV spectrum of **7**.

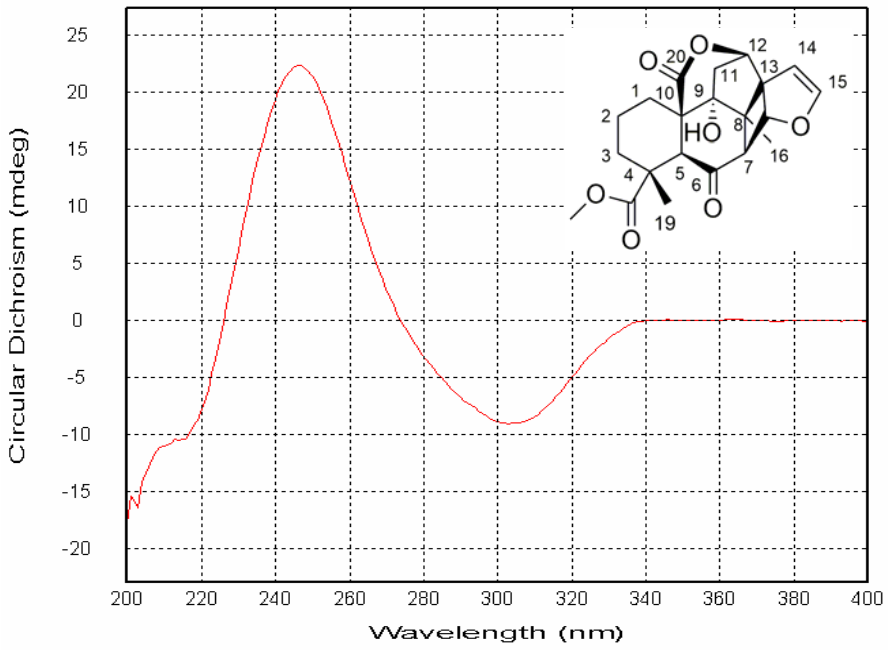

Figure S50. CD spectrum of **7**.

Amplified photochemical reaction of 4 and the structure elucidation of 8–11.

Amplified reaction of **4** (40.26 mg) was performed until the start material was consumed (50min), followed by the isolation of **2** (2.40mg), compounds **8** (1.74mg), **9** (3.26mg), **10** (2.55mg) and **11** (1.9mg) were obtained.

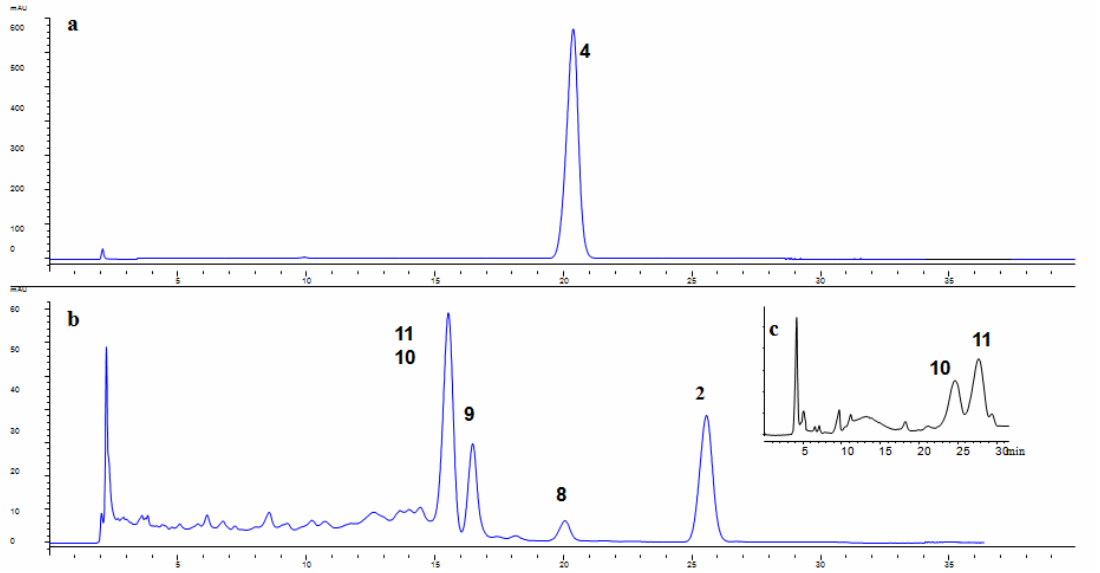

Figure S51. HPLC trace ($\lambda_{detection}$ = 210 nm) for the (a) compound **4**; (b) irradiation of compound **4** in N_2-saturated CH_3CN solution ($\lambda_{excitation}$ = 254 nm) at room temperature for 55min; (c) purification of **10** and **11**.

Compound 8: White, amorphous powder; $[\alpha]^{20}_D$ −45.5 (*c* 0.1 CH_3CN); UV (MeOH) λ_{max} (log ε) 200 (3.89) nm; CD (MeOH): 253($\Delta\varepsilon$ +0.06), 209($\Delta\varepsilon$ −2.25) nm; IR ν_{max} 3431, 2925, 1735, 1384, 1141, 1049, 1025, 875, 602 cm^{-1}; HRESIMS at *m*/*z* 346.2013 $[M + NH_4]^+$ (calcd for $C_{20}H_{28}O_4N_1$, 346.2013).

Table S3. ^{1}H and ^{13}C NMR data of 8.[a]

position	δ	δ
1α	39.5 t	1.49 m
1β		2.37 m
2α	18.1 t	1.53 m
2β		1.88 dt (13.2, 2.8)
3α	43.1 t	1.16 m
3β		1.55 m
4	32.9 s	
5	64.8 d	2.05 s
6	205.9 s	
7	47.3 d	2.90 s
8	43.2 s	
9	58.6 d	2.28 m
10	47.8 s	
11α	34.2 t	2.58 d (13.2)
11β		2.03 m
12	77.6 d	4.64 br s
13	50.5 s	
14	38.1 d	2.54 dd (5.6, 4.4)
15	198.2 d	9.90 d (4.4)
16	21.8 d	1.79 d (5.6)
17	23.8 q	1.13 s 3H
18	34.6 q	1.19 s 3H
19	21.2 q	1.46 s 3H
20	173.8 s	

[a] Recorded in $CDCl_3$ at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR). δ in ppm. J in Hz. ^{13}C multiplicities were determined by HSQC experiment.

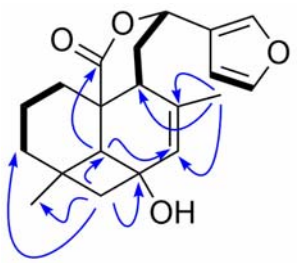

Figure S52. Selected HMBC (H→C) and ^{1}H-^{1}H COSY (H—H) correlations of **8**

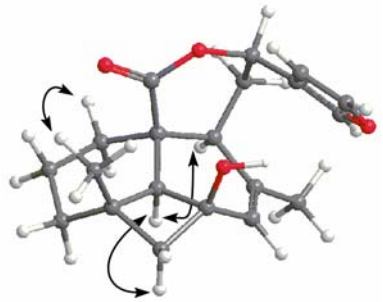

Figure S53. Selected NOESY correlations (H↔H) of **8**

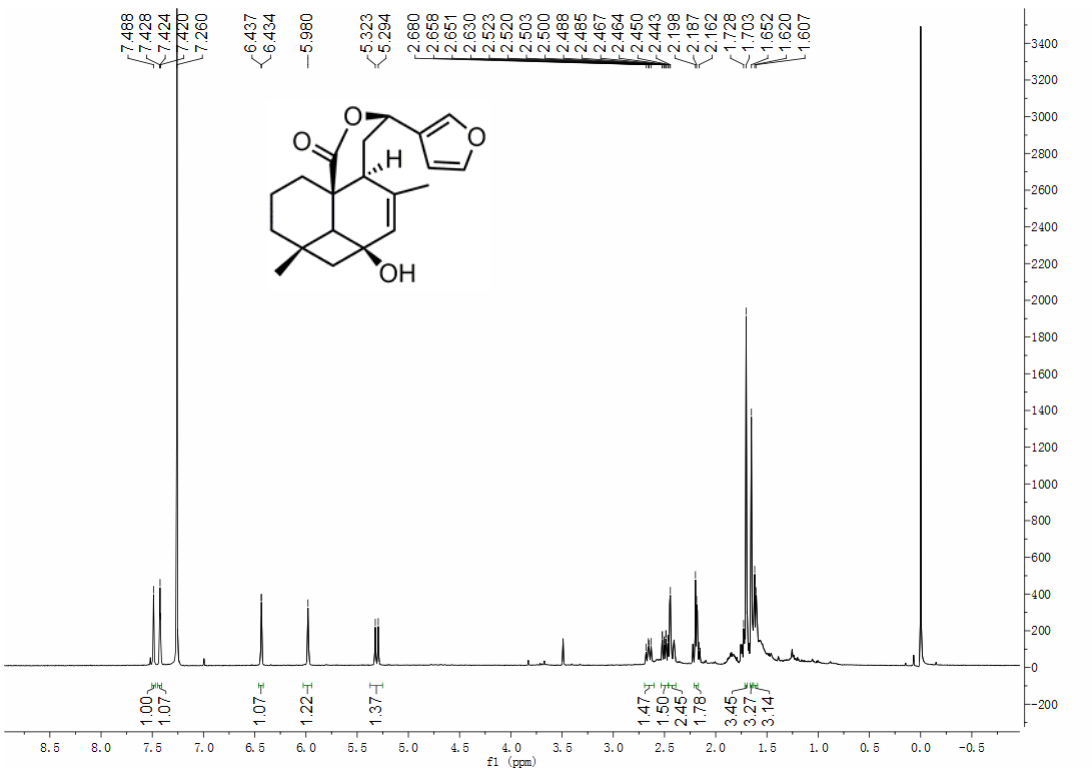

Figure S54. ^{1}H NMR spectrum (400 MHz) of **8** in $CDCl_3$.

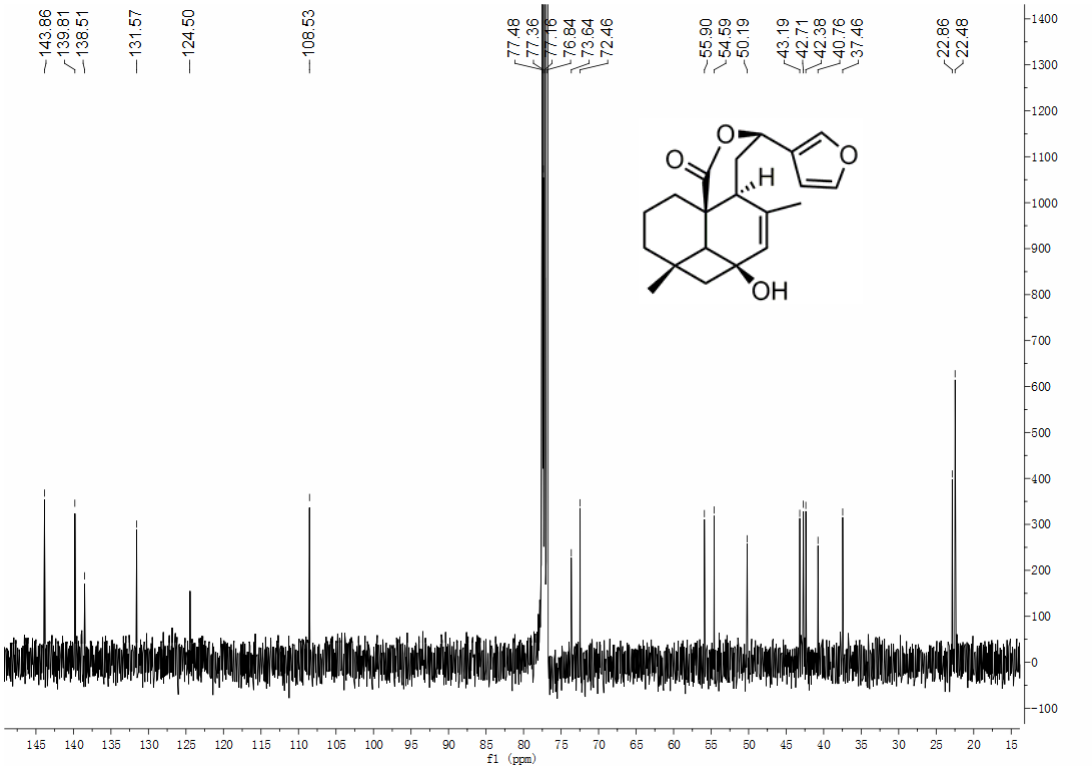

Figure S55. ^{13}C NMR spectrum (100 MHz) of **8** in $CDCl_3$.

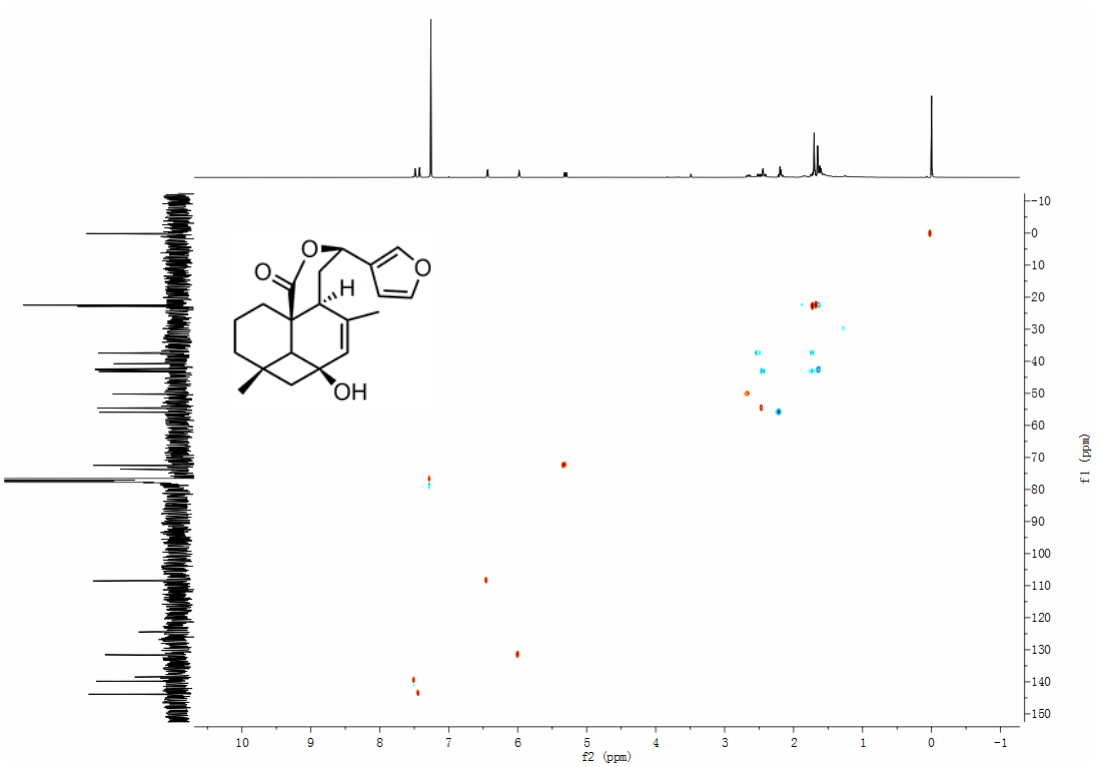

Figure S56. HSQC spectrum (400 MHz) of **8** in $CDCl_3$.

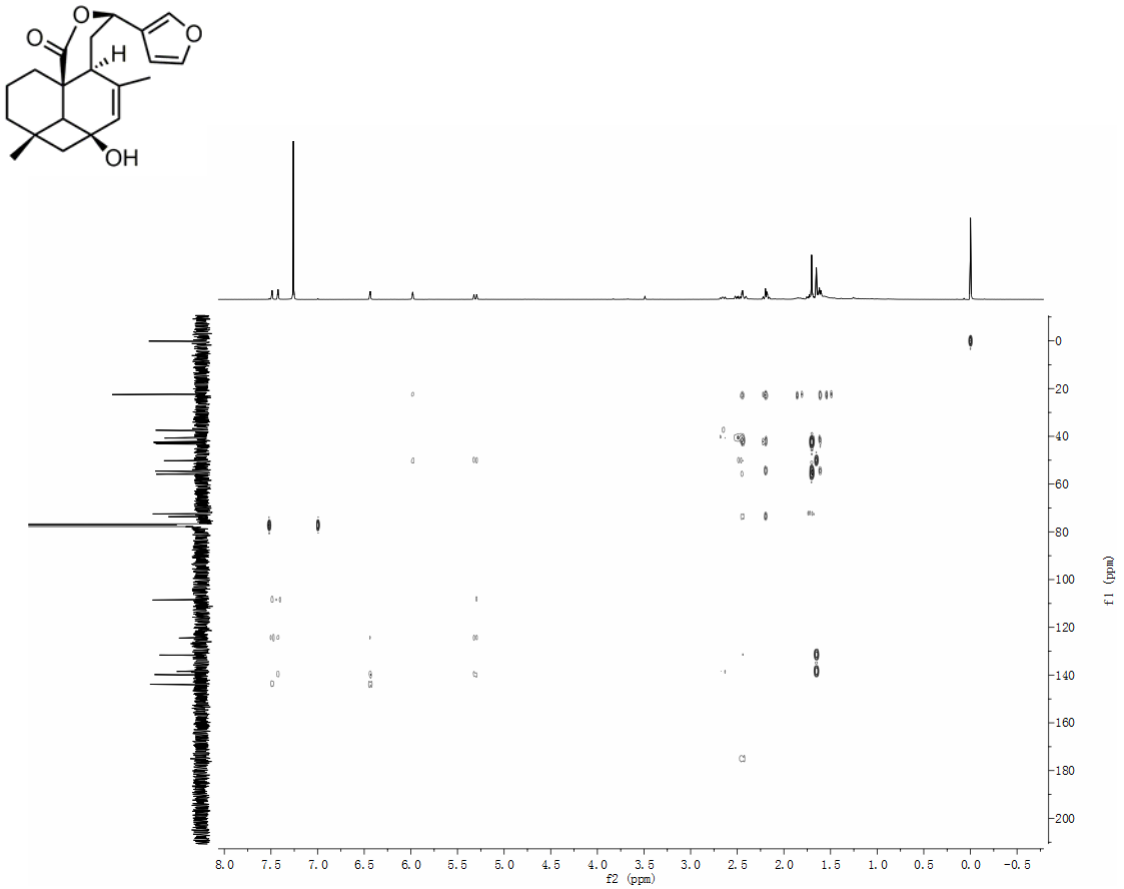

Figure S57. HMBC spectrum (400 MHz) of **8** in $CDCl_3$.

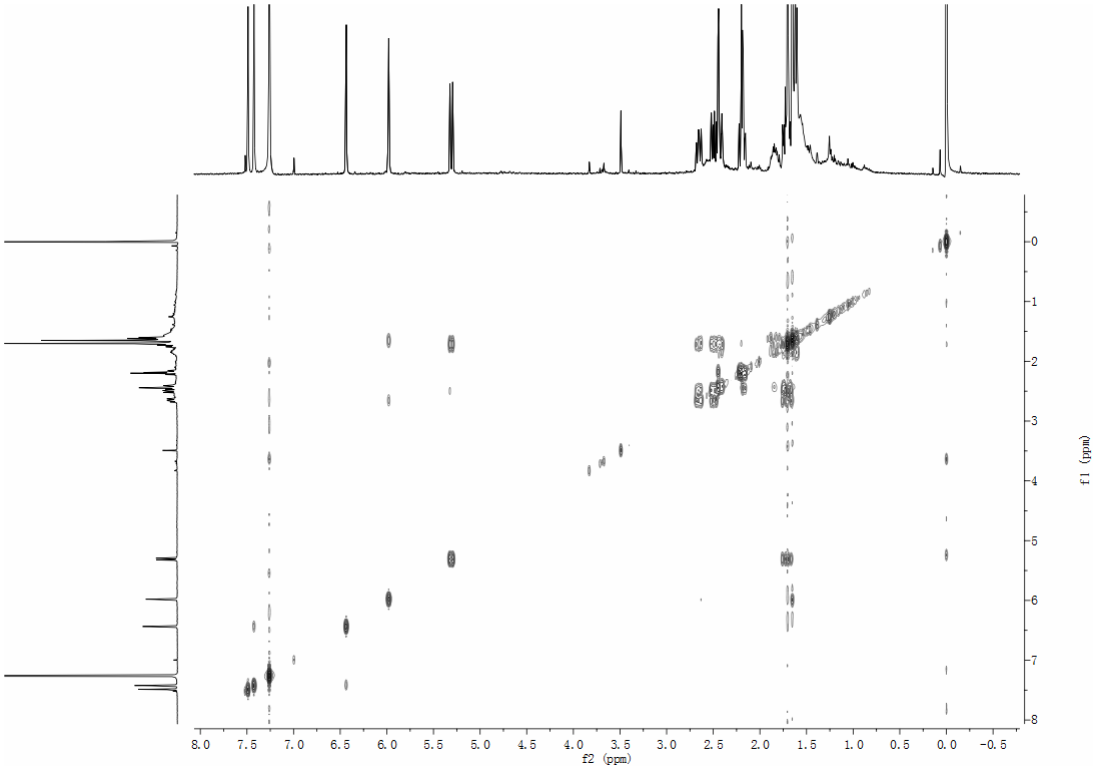

Figure S58. ^{1}H-^{1}H COSY spectrum (400 MHz) of **8** in $CDCl_3$.

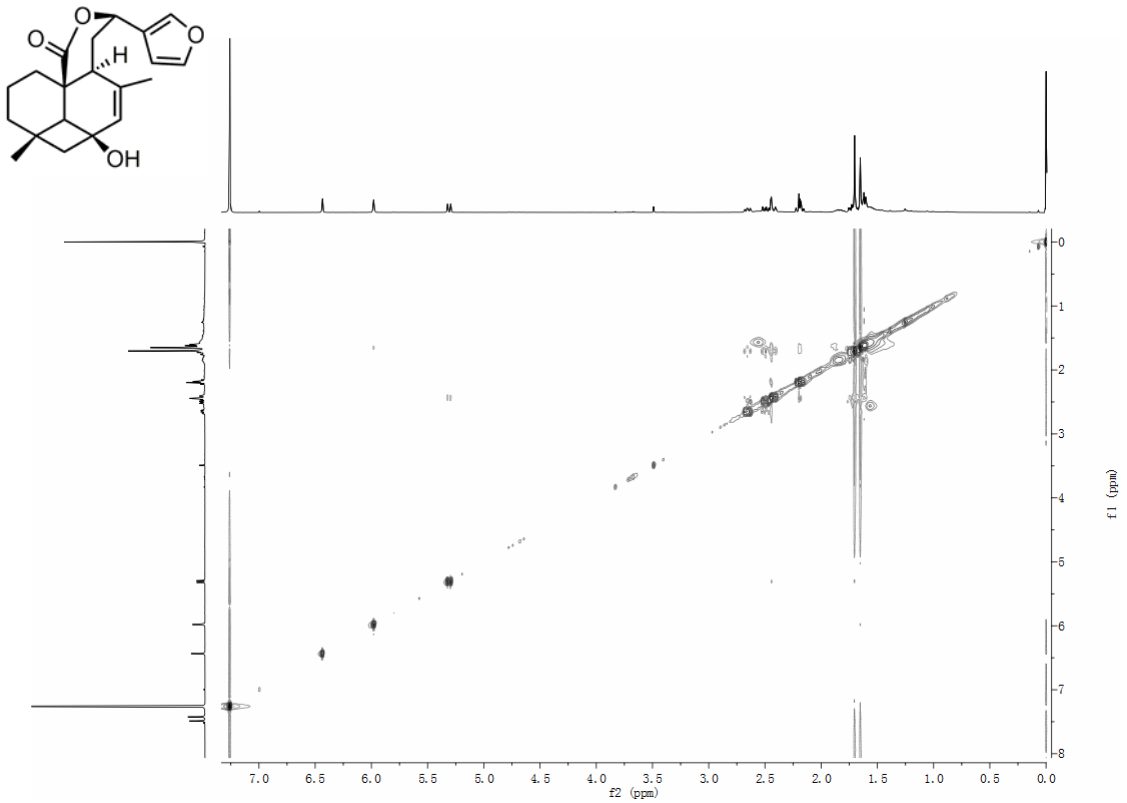

Figure S59. NOESY spectrum (400 MHz) of **8** in $CDCl_3$.

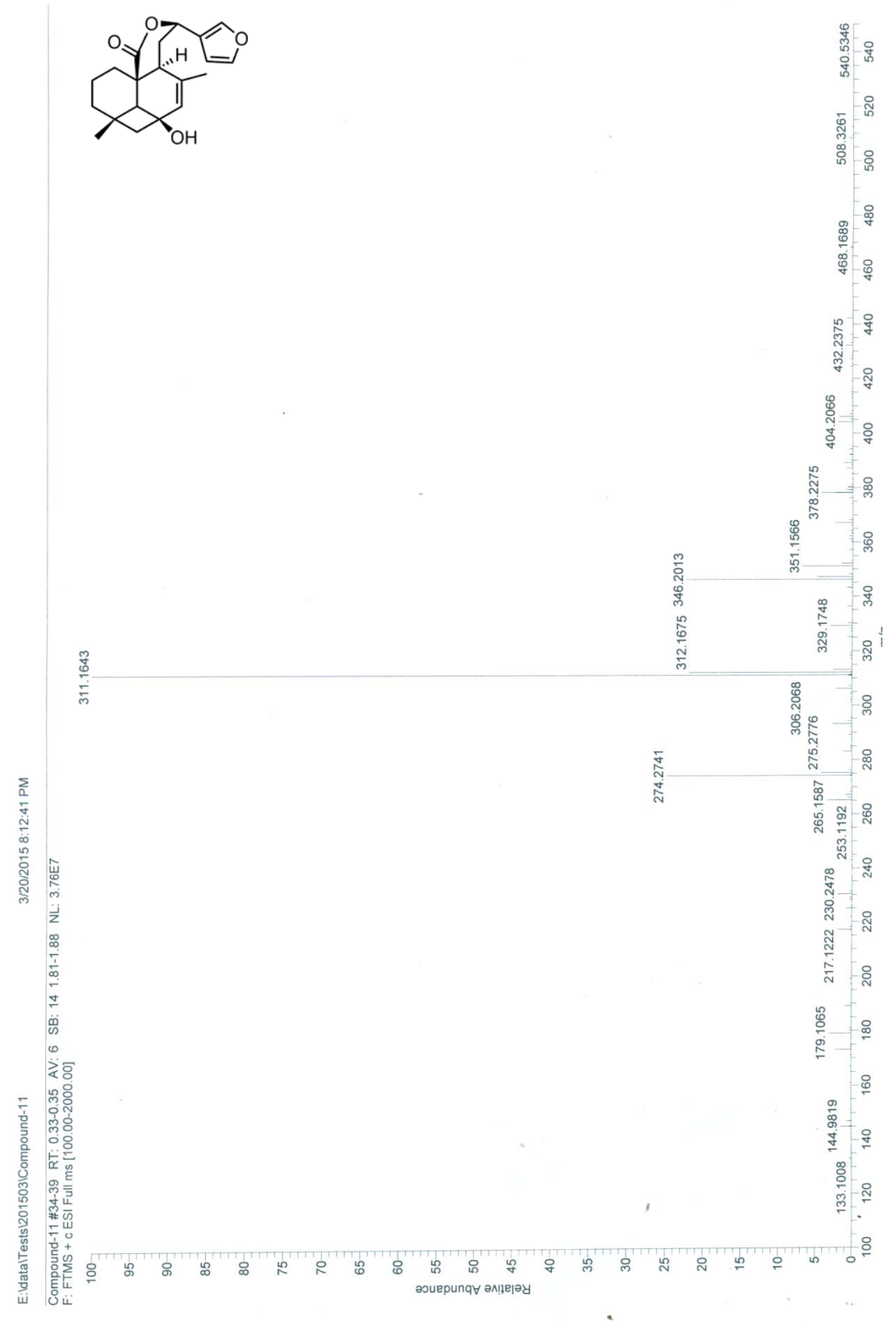

Figure S60. HRESIMS spectrum of **8**.

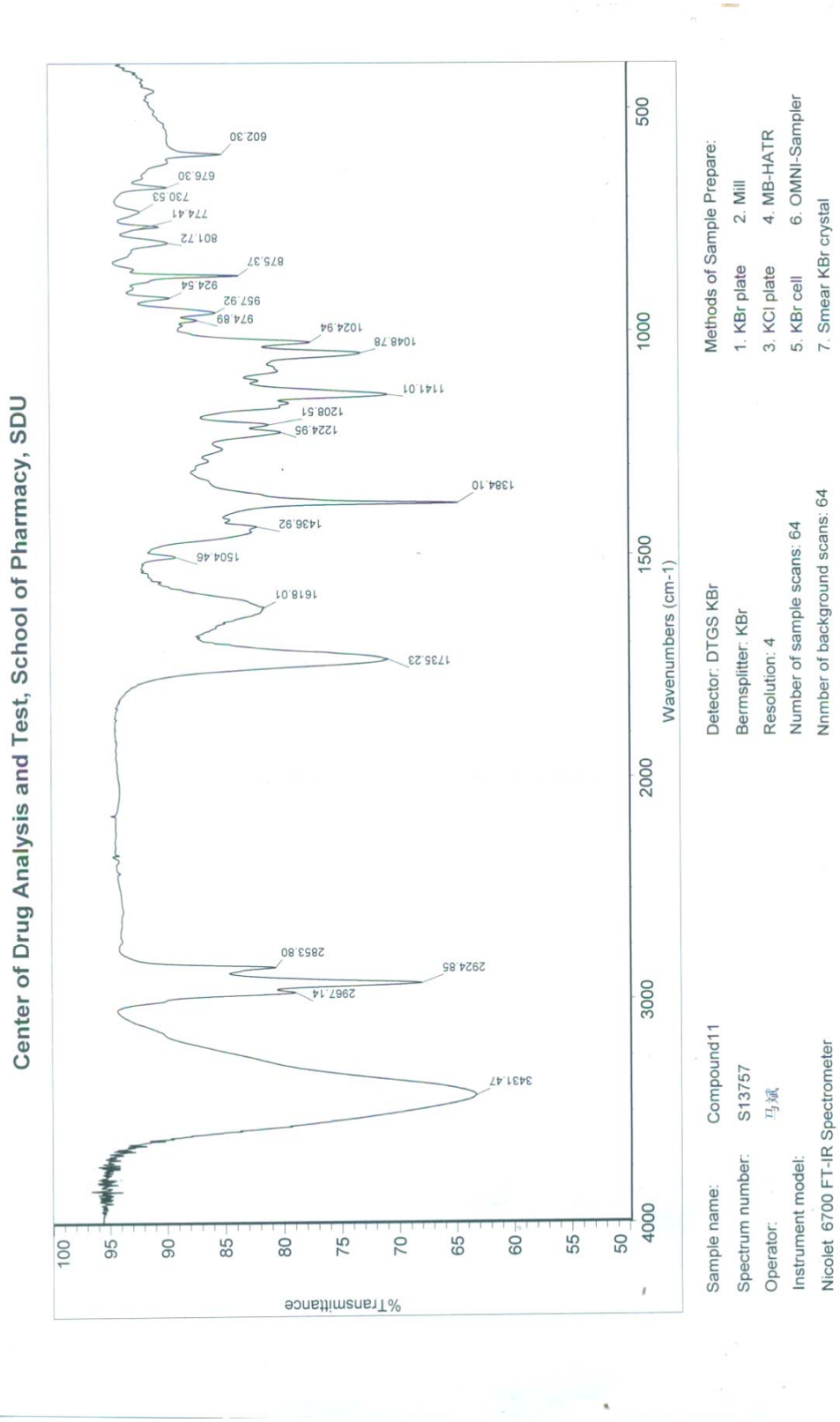

Figure S61. IR (KBr disc) spectrum of **8**.

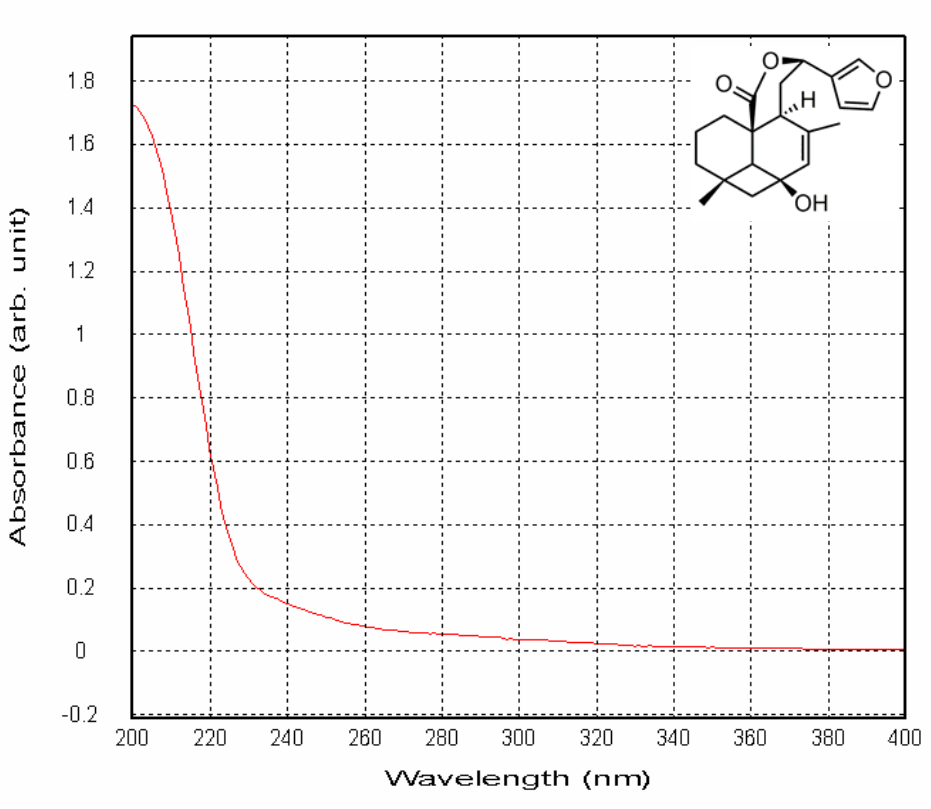

Figure S62. UV spectrum of **8**.

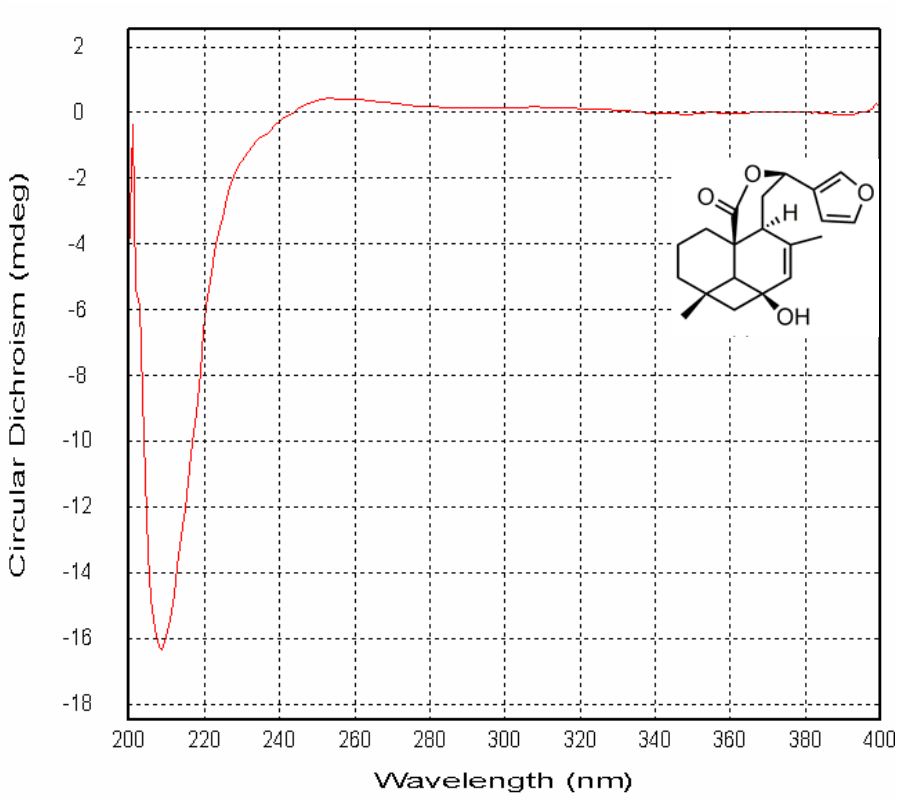

Figure S63. CD spectrum of **8**.

Compound 9: colorless crystals (EtOH); mp 192−194°C; $[\alpha]^{20}_{D}$ +18.5 (*c* 0.1 CH_3CN); UV (MeOH) λ_{max} (log ε) 217 (4.00) nm; ECD (MeOH): 308($\Delta\varepsilon$ −0.19), 228($\Delta\varepsilon$+12.80) nm; IR ν_{max} 3563, 2945, 1734, 1603, 1384, 1129, 1096, 1053, 1022, 999, 735 cm^{-1}; HRESIMS at *m*/*z* 346.2014 $[M + NH_4]^+$ (calcd for $C_{20}H_{28}O_4N_1$, 346.2013).

Table S4. ^{1}H and ^{13}C NMR data of 9.[a]

position	δ_C	δ_H
1α	29.4 t	1.49 td (14.0, 4.4)
1β		2.46 m
2α	18.6 t	1.64 m
2β		1.79 m
3α	38.7 t	1.55 m
3β		1.76 m
4	38.8 s	
5	57.5 d	1.66 d (2.4)
6	73.2 s	
7	56.4 d	2.70 d (2.4)
8	53.2 s	
9	53.2 d	2.04 dd (5.2, 2.4)
10	40.5 s	
11α	33.0 t	1.84 d (13.2)
11β		1.60 m
12	86.3 d	4.76 br s
13	63.0 s	
14	100.6 d	4.59 d (2.4)
15	150.4 d	6.53 d (2.4)
16	80.7 d	5.43 d (2.4)
17	26.8 q	1.20 s 3H
18	62.3 t	2.18 m 2H
19	24.1 q	1.58 s 3H
20	175.2 s	

[a] Recorded in $CDCl_3$ at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR). δ in ppm. *J* in Hz. ^{13}C multiplicities were determined by HSQC experiment.

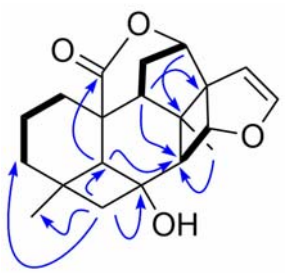

Figure S64 Selected HMBC (H→C) and ^{1}H-^{1}H COSY (H—H) correlations of **9**

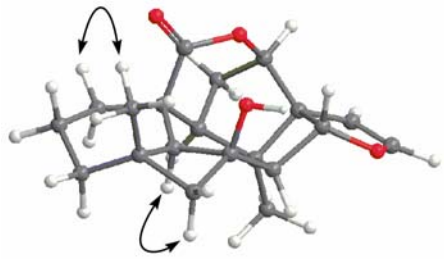

Figure S65. Selected NOESY correlations (H↔H) of **9**

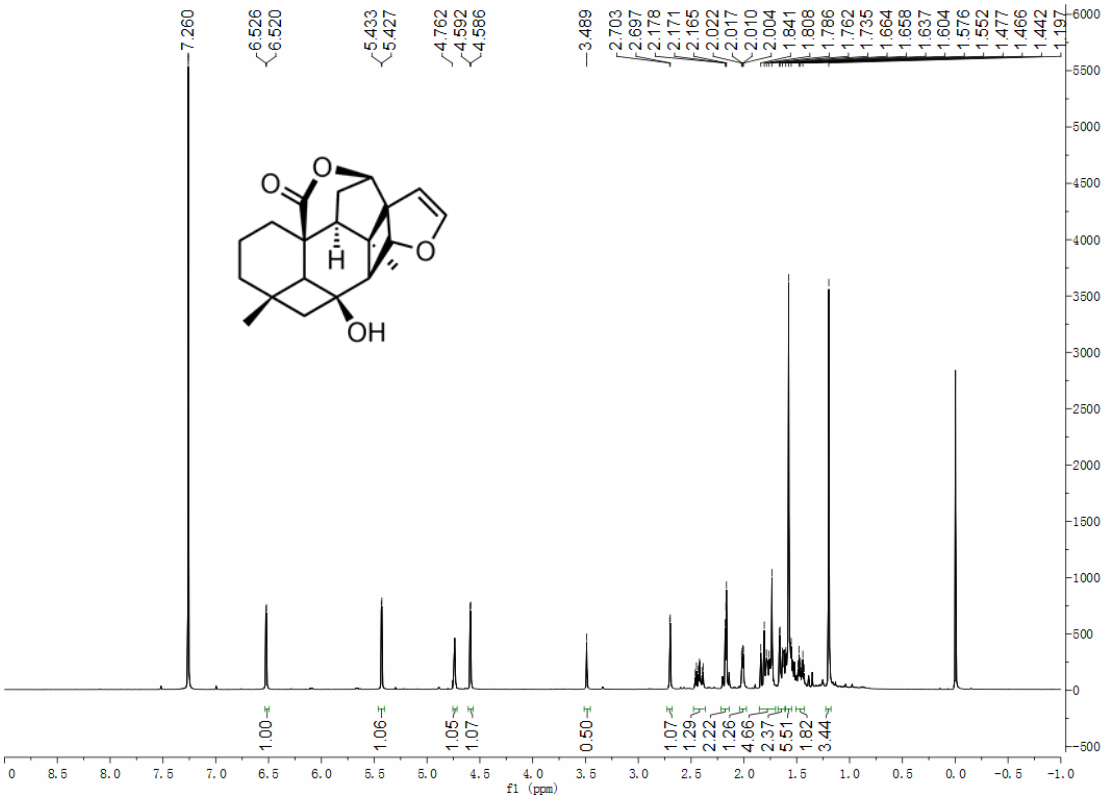

Figure S66. ^{1}H NMR spectrum (400 MHz) of **9** in $CDCl_3$.

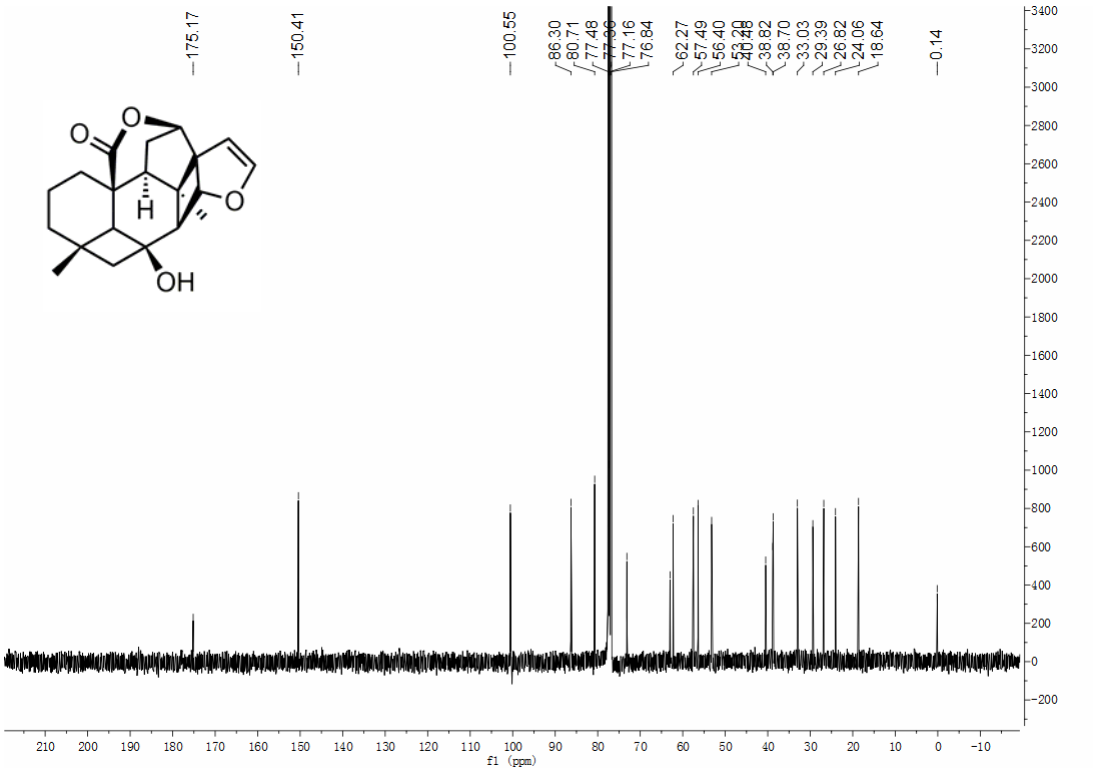

Figure S67. ^{13}C NMR spectrum (100 MHz) of **9** in $CDCl_3$.

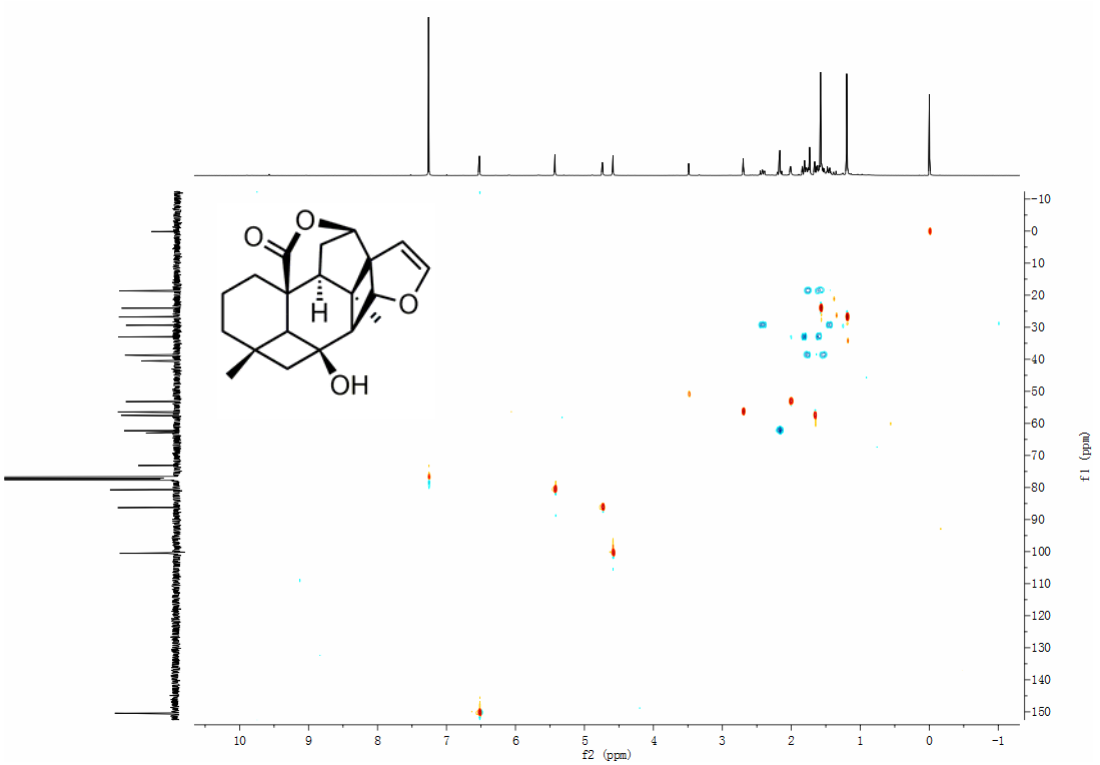

Figure S68. HSQC spectrum (400 MHz) of **9** in $CDCl_3$.

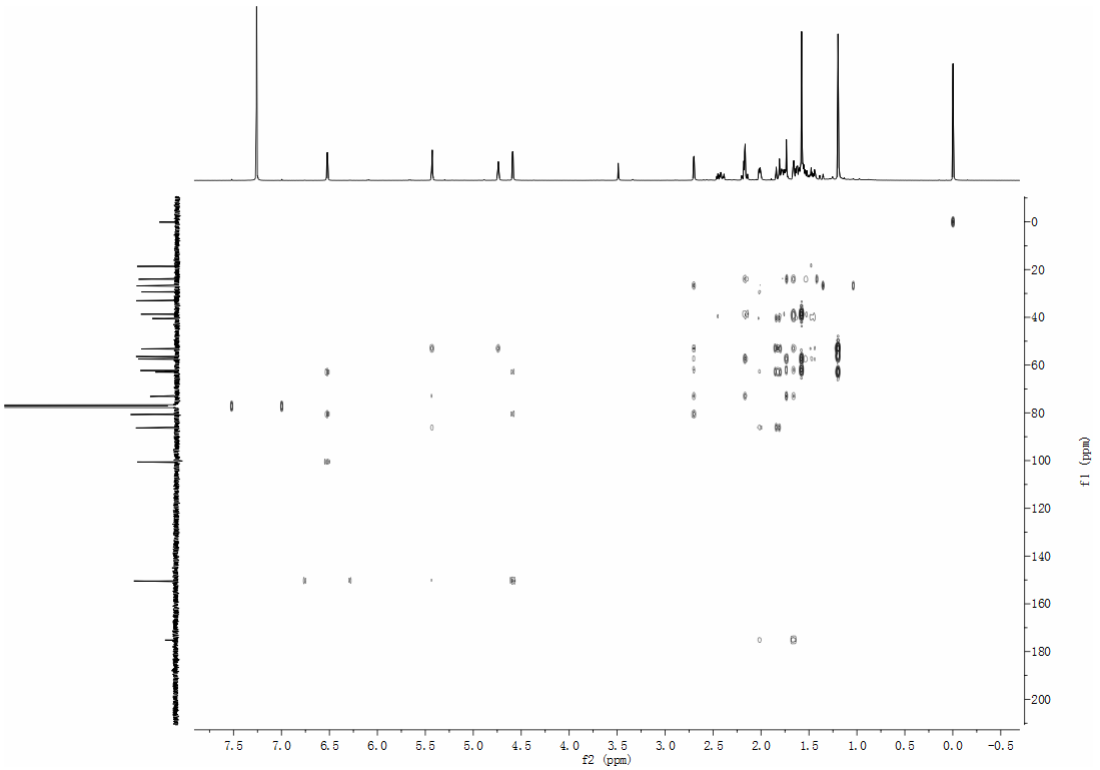

Figure S69. HMBC spectrum (400 MHz) of **9** in $CDCl_3$.

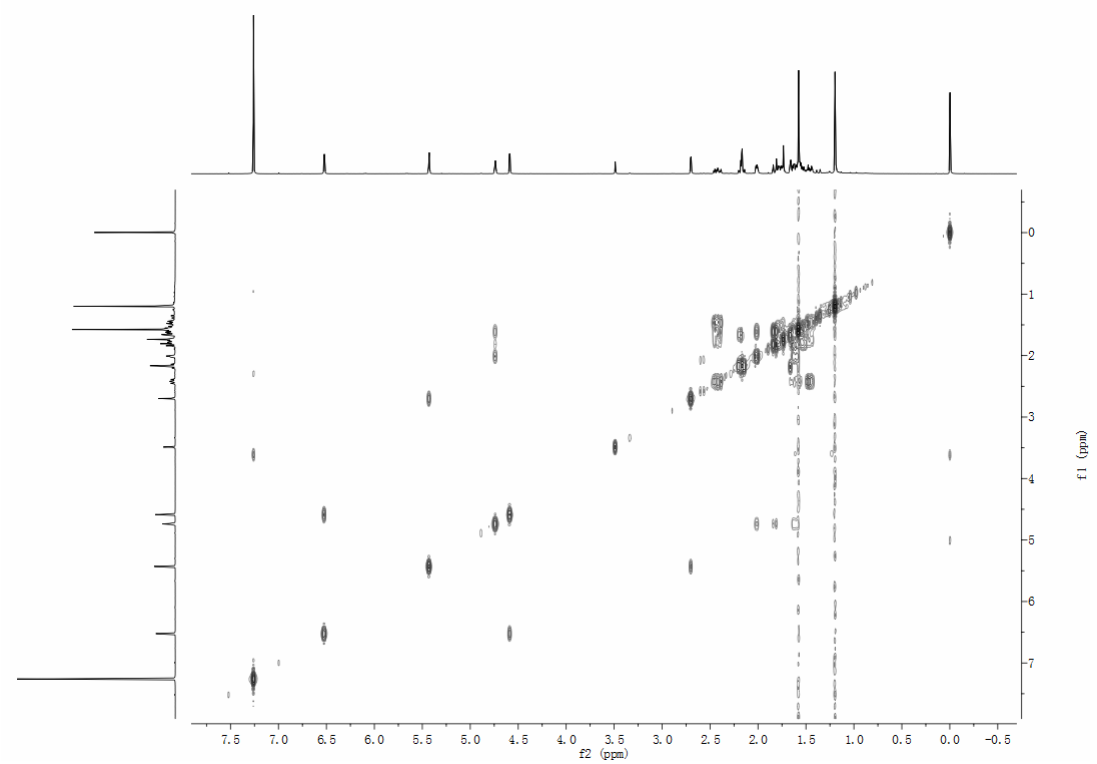

Figure S70. ^{1}H-^{1}H COSY spectrum (400 MHz) of **9** in $CDCl_3$.

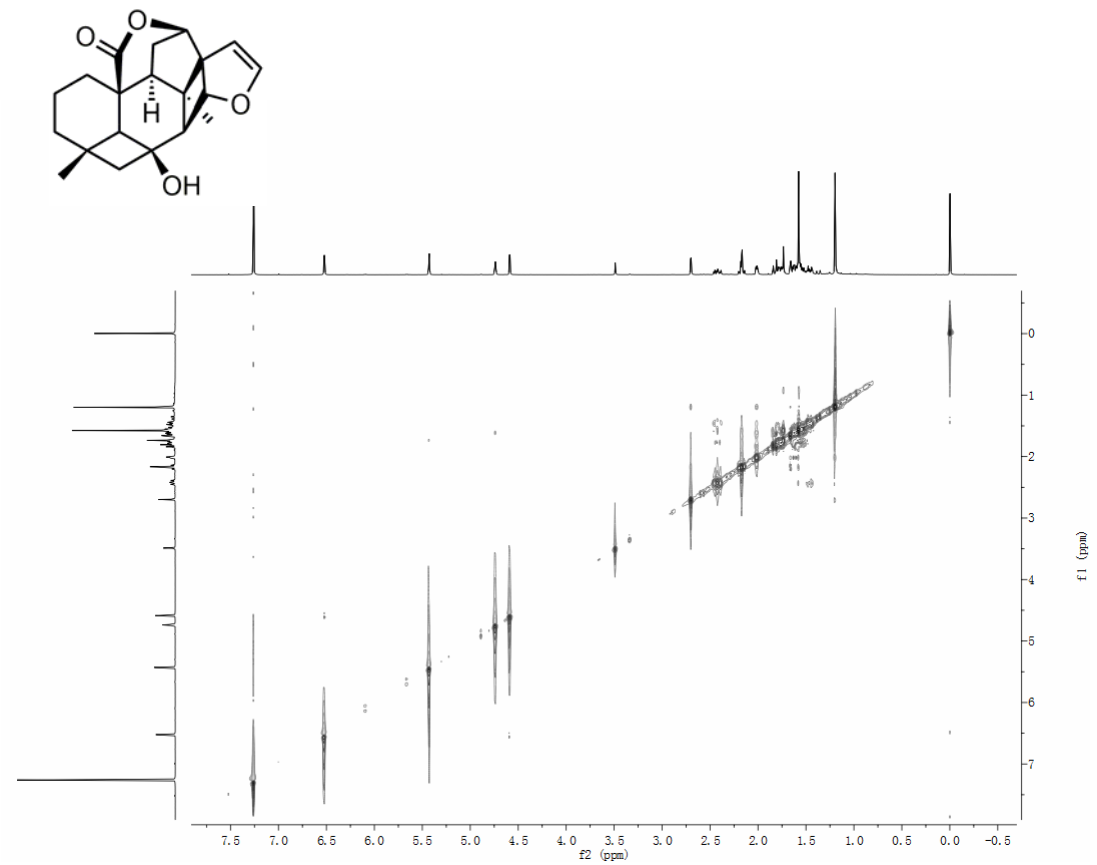

Figure S71. NOESY spectrum (400 MHz) of **9** in $CDCl_3$.

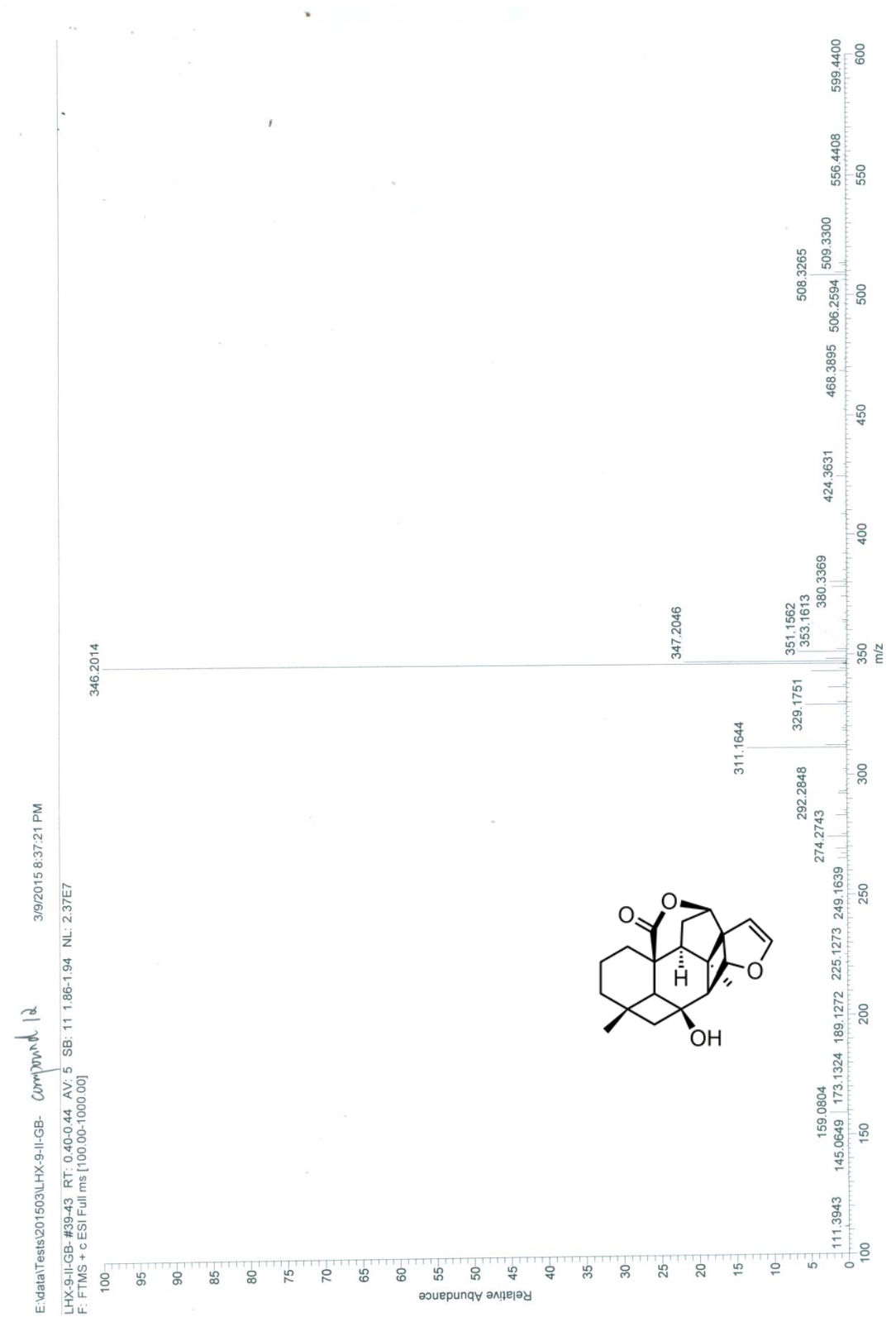

Figure S72. HRESIMS spectrum of **9**.

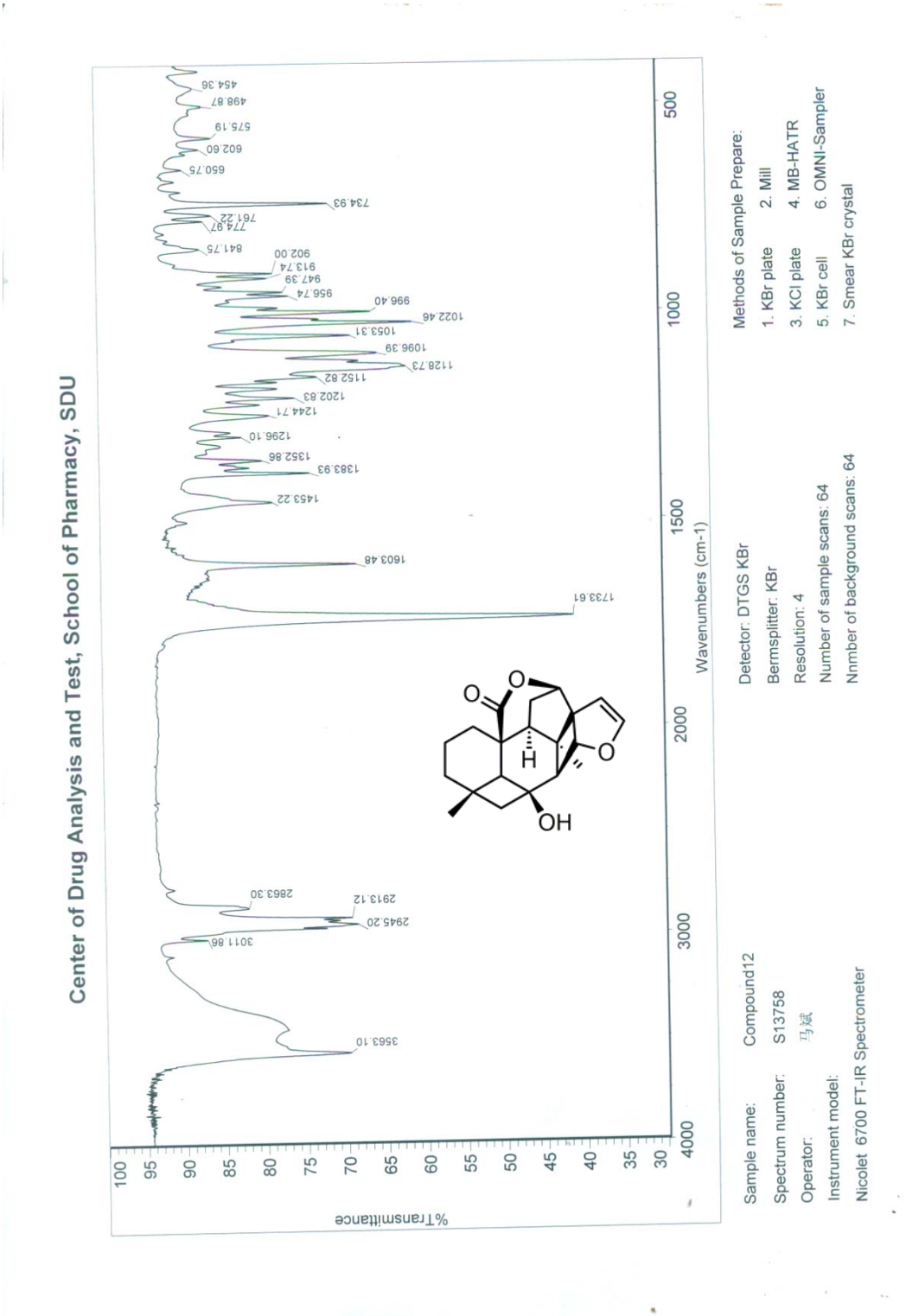

Figure S73. IR (KBr disc) spectrum of **9**.

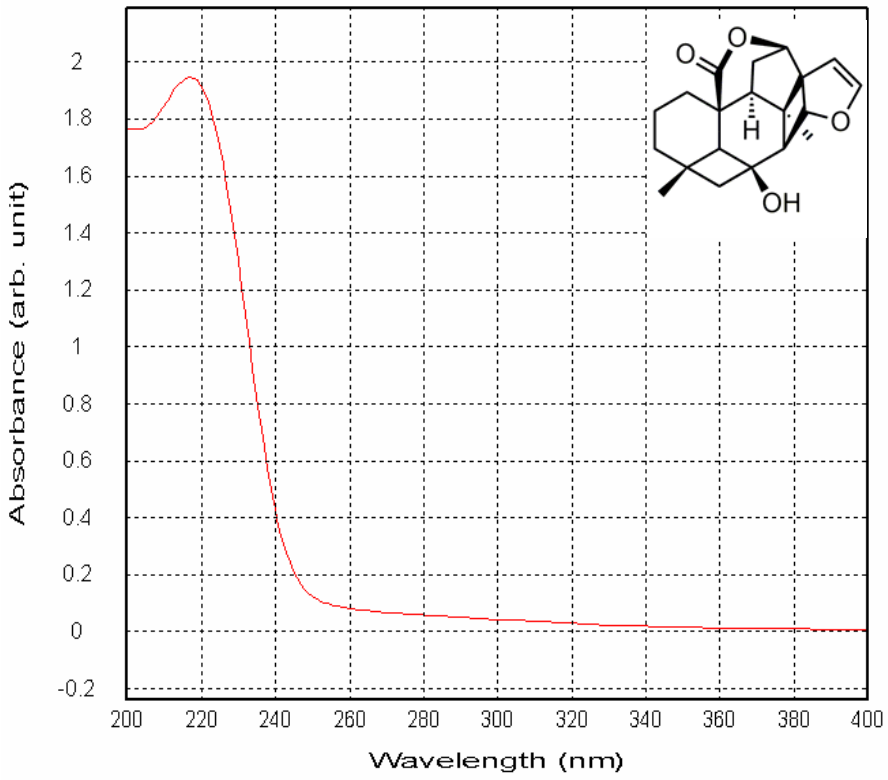

Figure S74. UV spectrum of **9**.

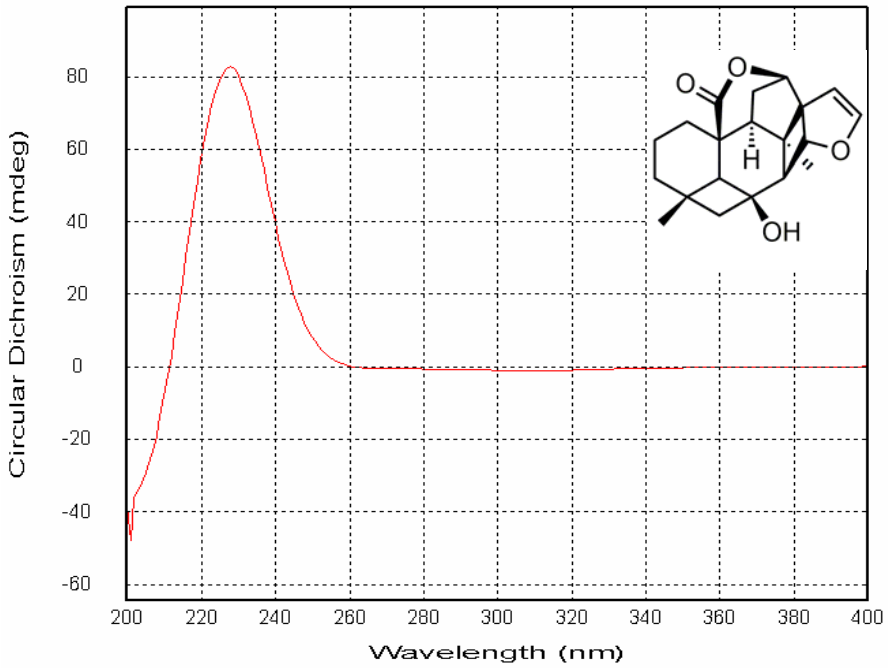

Figure S75. CD spectrum of **9**

Compound 10: White, amorphous powder; $[\alpha]^{20}_{D}$ −63.8 (*c* 0.1 CH3CN); UV (MeOH) λ_{max} (log ε) 200(3.56), 249(2.98) nm; ECD (MeOH): 271($\Delta\varepsilon$ +0.20), 234($\Delta\varepsilon$ −1.88)nm; IR ν_{max} 3431, 2926, 1738, 1706, 1384, 1122, 1092, 1063, 1021, 722 cm^{-1}; HRESIMS at *m*/*z* 346.2013 $[M + NH_4]^+$ (calcd for $C_{20}H_{28}O_4N_1$, 346.2013).

Compound 11: White, amorphous powder; $[\alpha]^{20}_{D}$ −21.5 (*c* 0.1 CH3CN); UV (MeOH) λ_{max} (log ε) 200 (3.94) nm; ECD (MeOH): 267($\Delta\varepsilon$ +0.37), 236($\Delta\varepsilon$ −0.90)nm; IR ν_{max} 3432, 2925, 2854, 1709, 1631, 1384, 1262, 1121, 1094, 1063, 1021, 803 cm^{-1}; HRESIMS at *m*/*z* 346.2016 $[M + NH_4]^+$ (calcd for $C_{20}H_{28}O_4N_1$, 346.2013).

Table S5. ^{1}H and ^{13}C NMR data of 10 and 11.[a]

position	δ_C	δ_H	δ_C	δ_H
1α	39.5 t	1.49 m	39.4 t	1.44 m
1β		2.37 m		2.42 m
2α	18.1 t	1.53 m	18.1 t	1.53 m
2β		1.88 dt (13.2, 2.8)		1.90 m
3α	43.1 t	1.16 m	43.1 t	1.19 m
3β		1.55 m		1.55 m
4	32.9 s		32.8 s	
5	64.8 d	2.05 s	64.5 d	2.01 s
6	205.9 s		205.5 s	
7	47.3 d	2.90 s	49.6 d	2.28 s
8	43.2 s		44.2 s	
9	58.6 d	2.28 m	56.0 d	2.28 m
10	47.8 s		47.7 s	
11α	34.2 t	2.58 d (13.2)	34.9 t	2.64 d (13.6)
11β		2.03 m		2.00 m
12	77.6 d	4.64 br s	75.7 d	4.74 br s
13	50.5 s		47.5 s	
14	38.1 d	2.54 dd (5.6, 4.4)	40.7 d	2.59 dd (6.4, 1.2)
15	198.2 d	9.90 d (4.4)	196.5 d	9.04 d (6.4)
16	21.8 d	1.79 d (5.6)	21.3 d	1.92 br s
17	23.8 q	1.13 s 3H	19.5 q	0.98 s 3H
18	34.6 q	1.19 s 3H	34.5 q	1.16 s 3H
19	21.2 q	1.46 s 3H	21.4 q	1.48 s 3H
20	173.8 s		173.7 s	

[a] Recorded in $CDCl_3$ at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR). δ in ppm. J in Hz. ^{13}C multiplicities were determined by HSQC experiment.

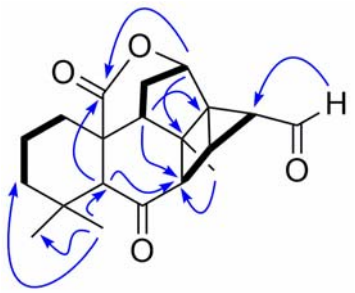

Figure S76. Selected HMBC (H→C) and ^{1}H-^{1}H COSY (H—H) correlations of **10** and **11**

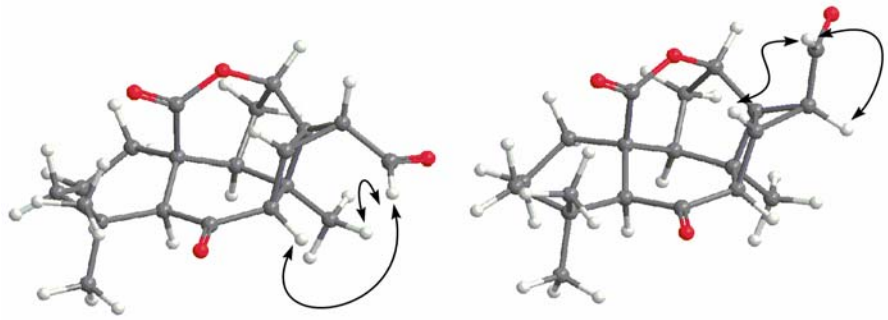

Figure S77. Selected NOESY correlations (H↔H) of **10** and **11**.

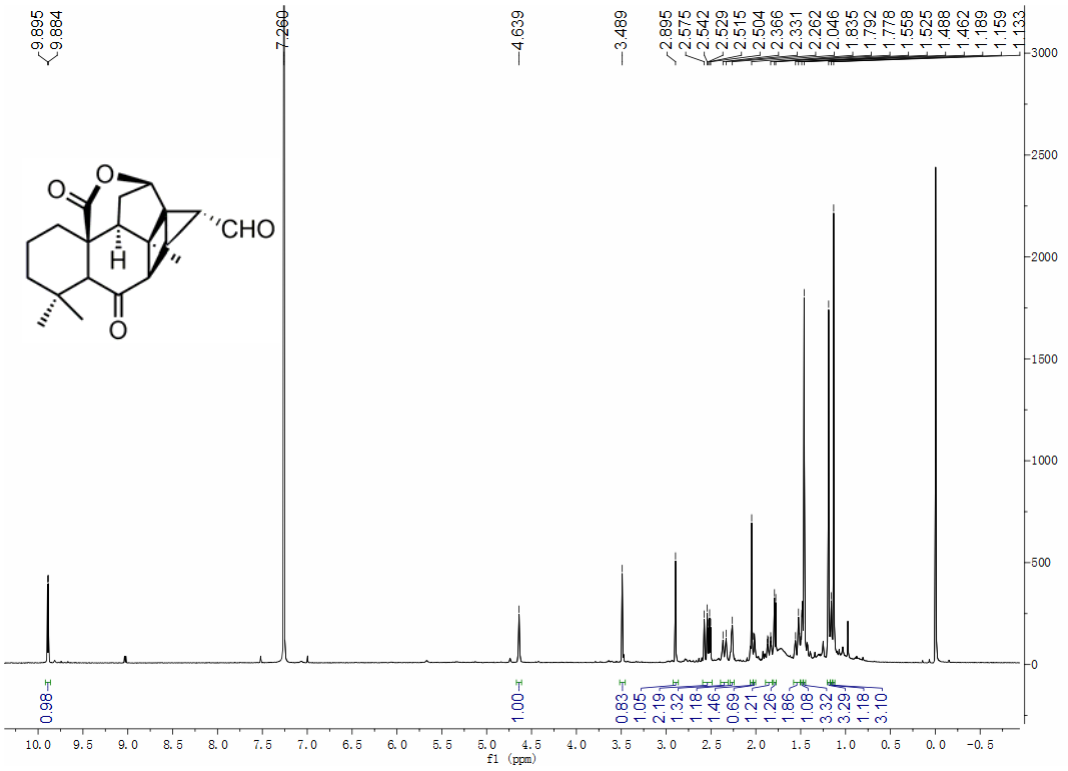

Figure S78. ^{1}H NMR spectrum (400 MHz) of **10** in $CDCl_3$.

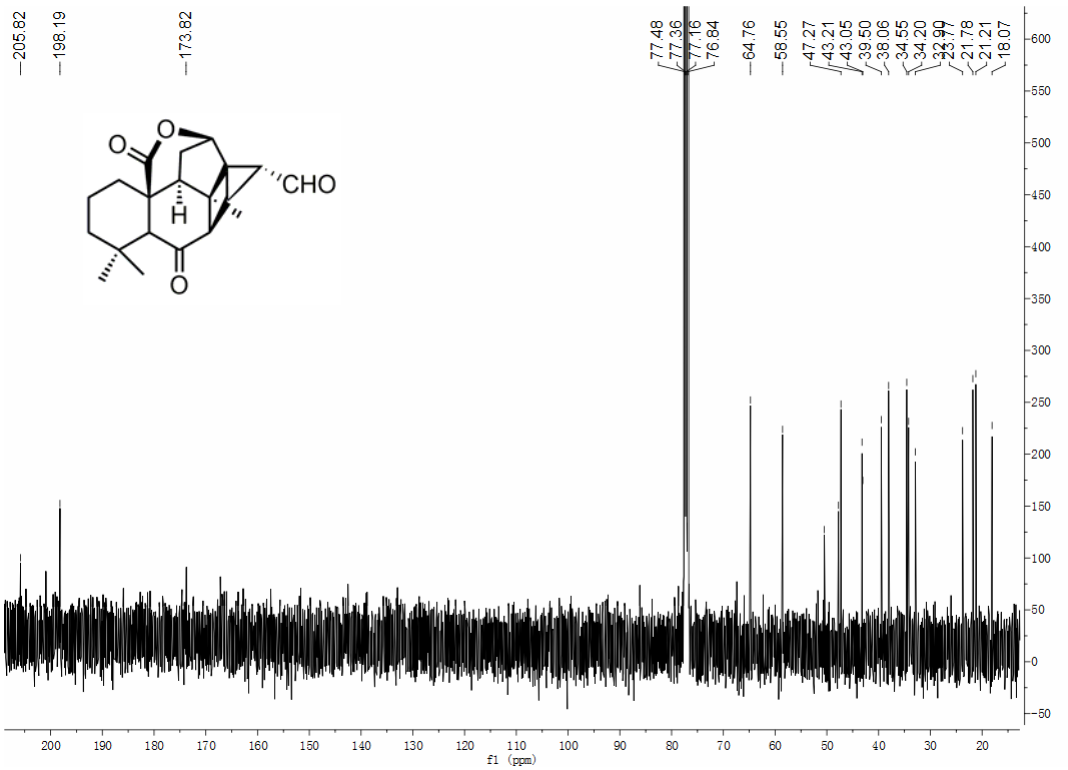

Figure S79. ^{13}C NMR spectrum (100 MHz) of **10** in $CDCl_3$.

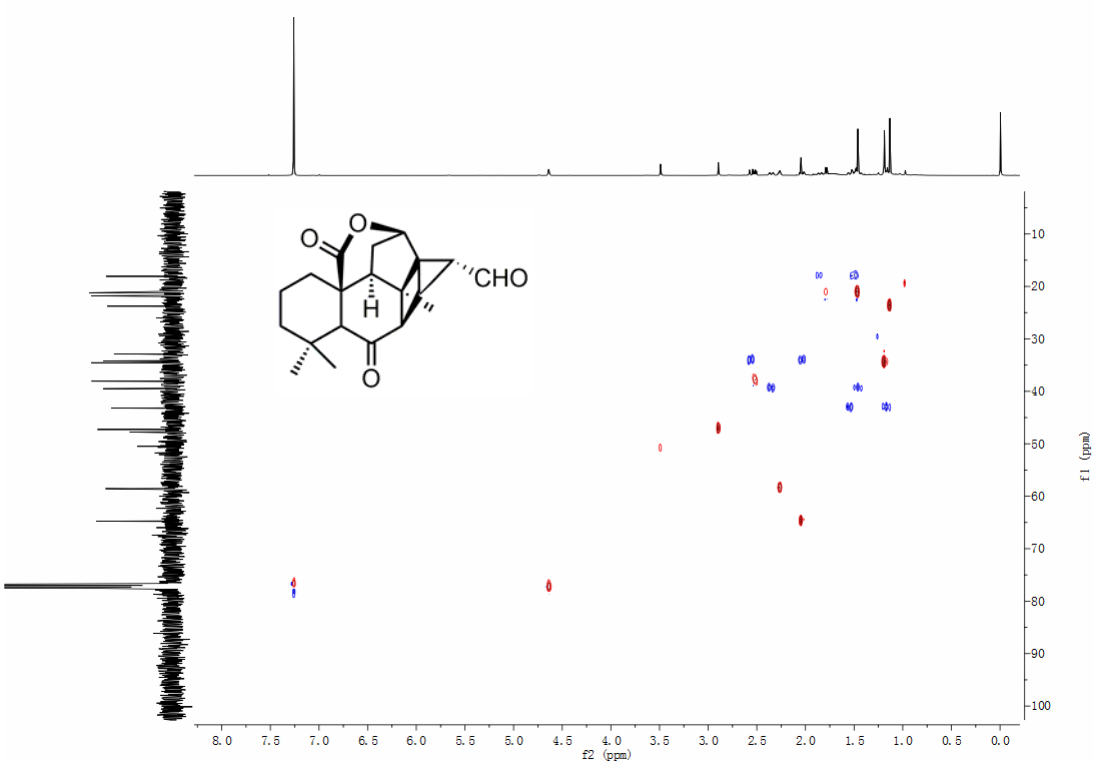

Figure S80. HSQC spectrum (400 MHz) of **10** in $CDCl_3$.

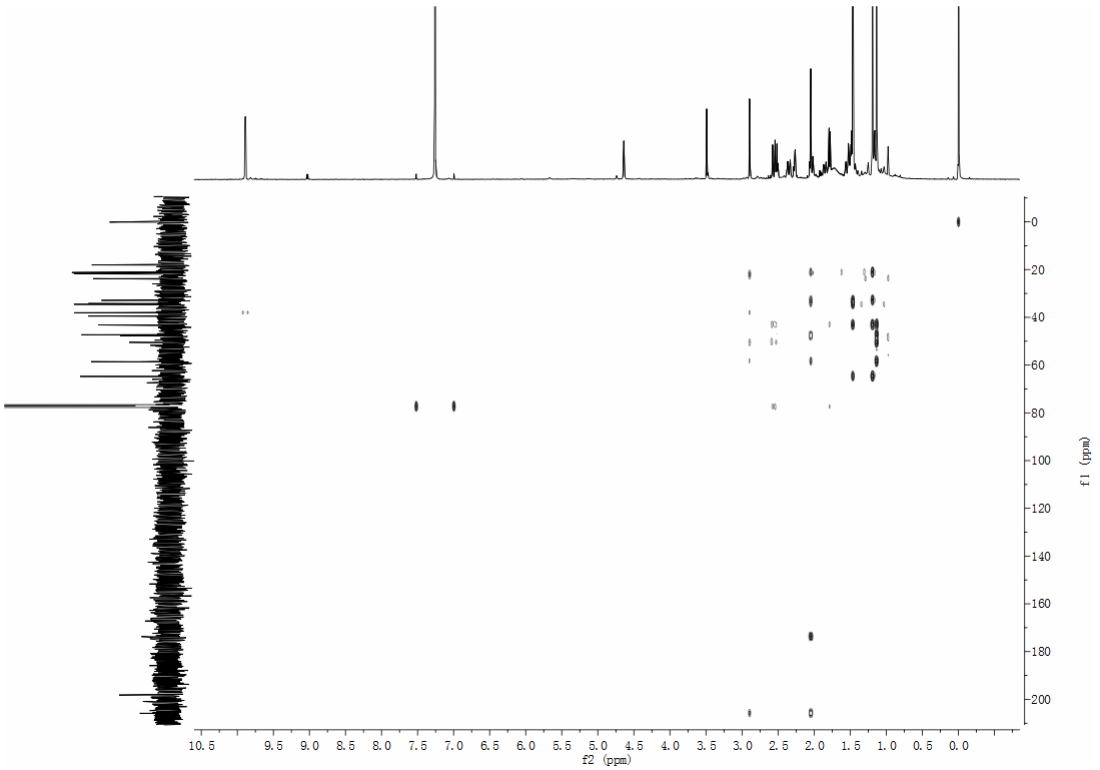

Figure S81. HMBC spectrum (400 MHz) of **10** in $CDCl_3$.

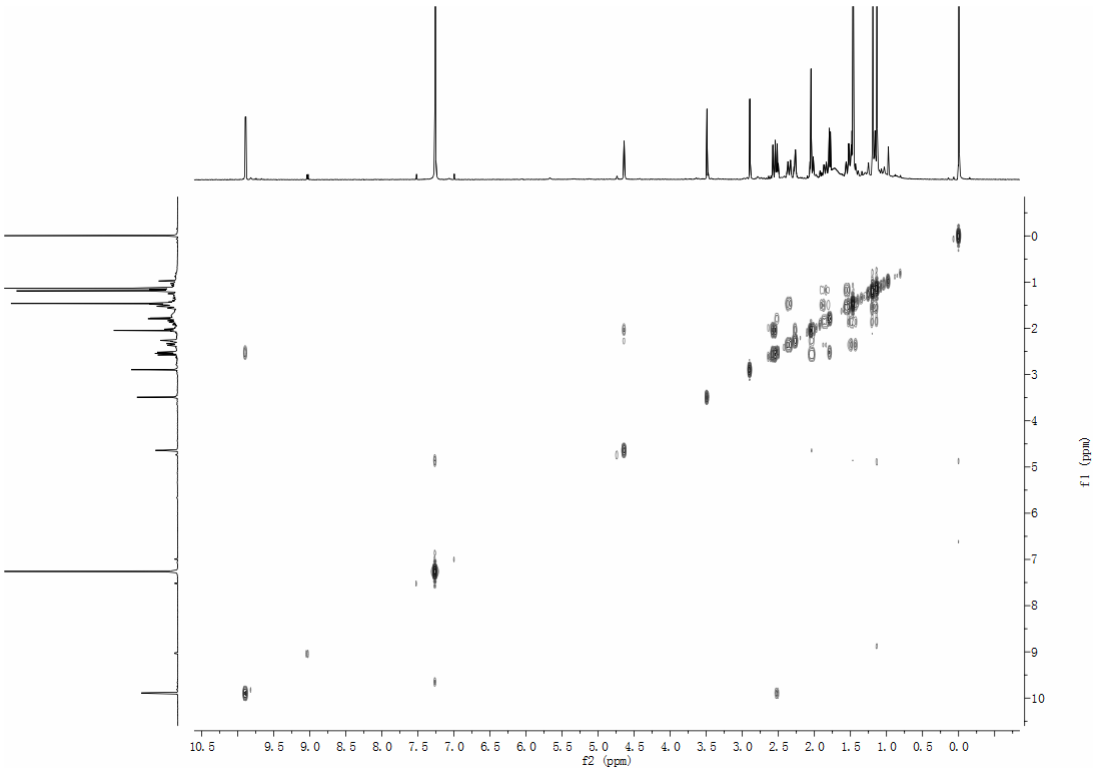

Figure S82. ^{1}H-^{1}H COSY spectrum (400 MHz) of **10** in $CDCl_3$.

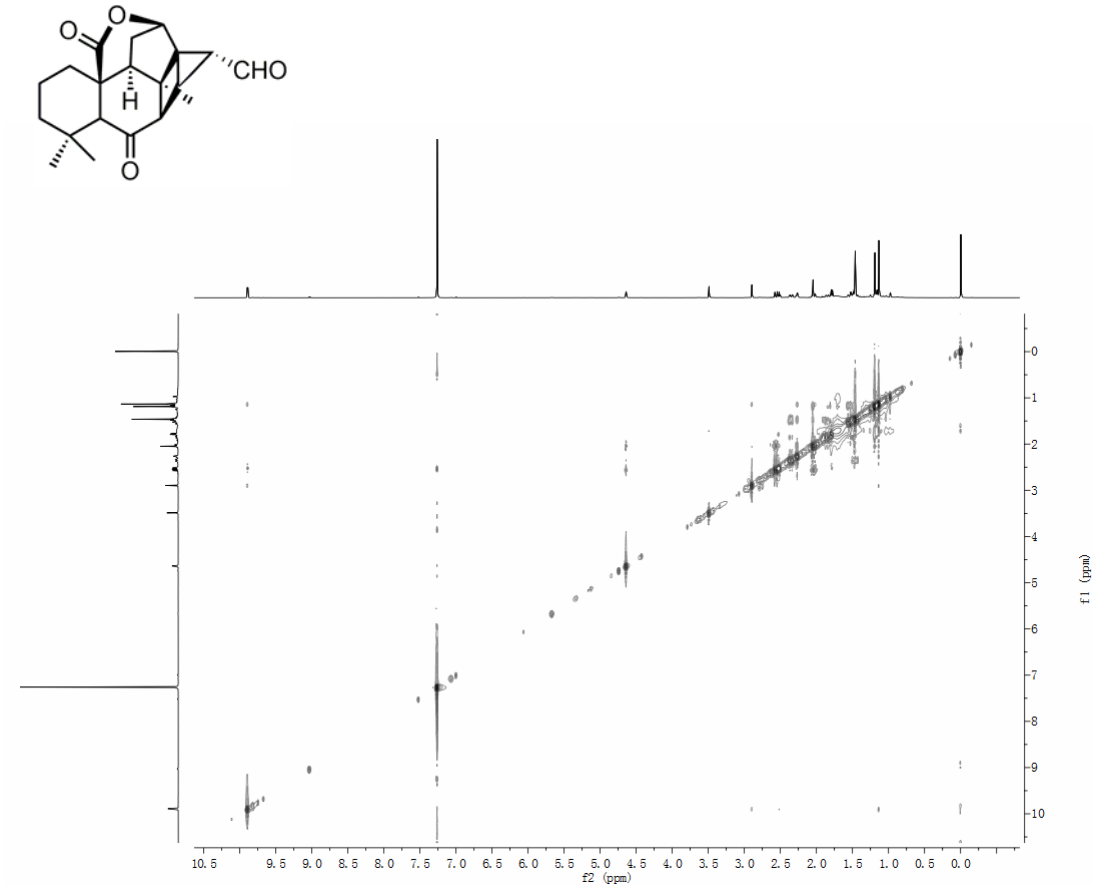

Figure S83. NOESY spectrum (400 MHz) of **10** in $CDCl_3$.

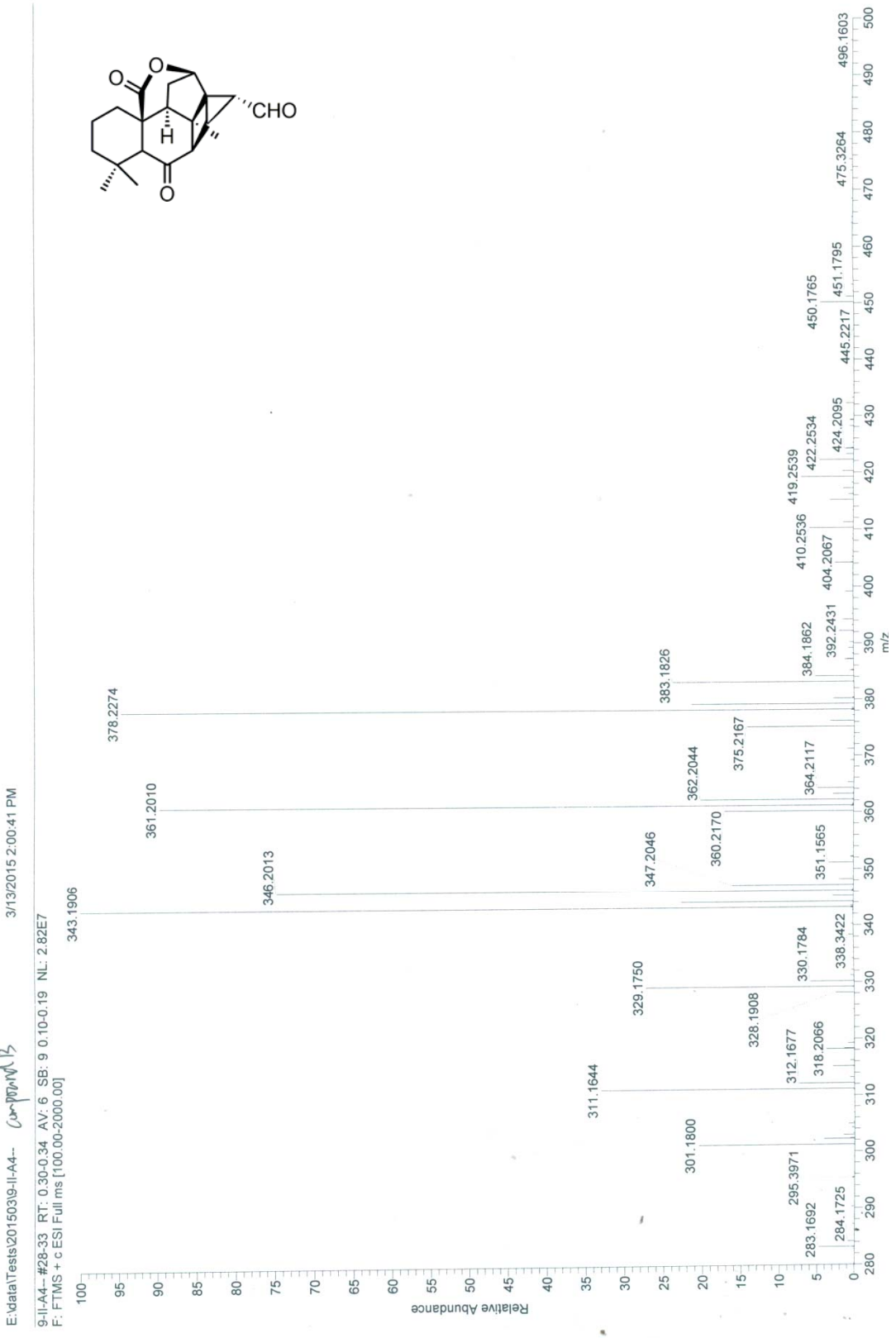

Figure S84. HRESIMS spectrum of **10**.

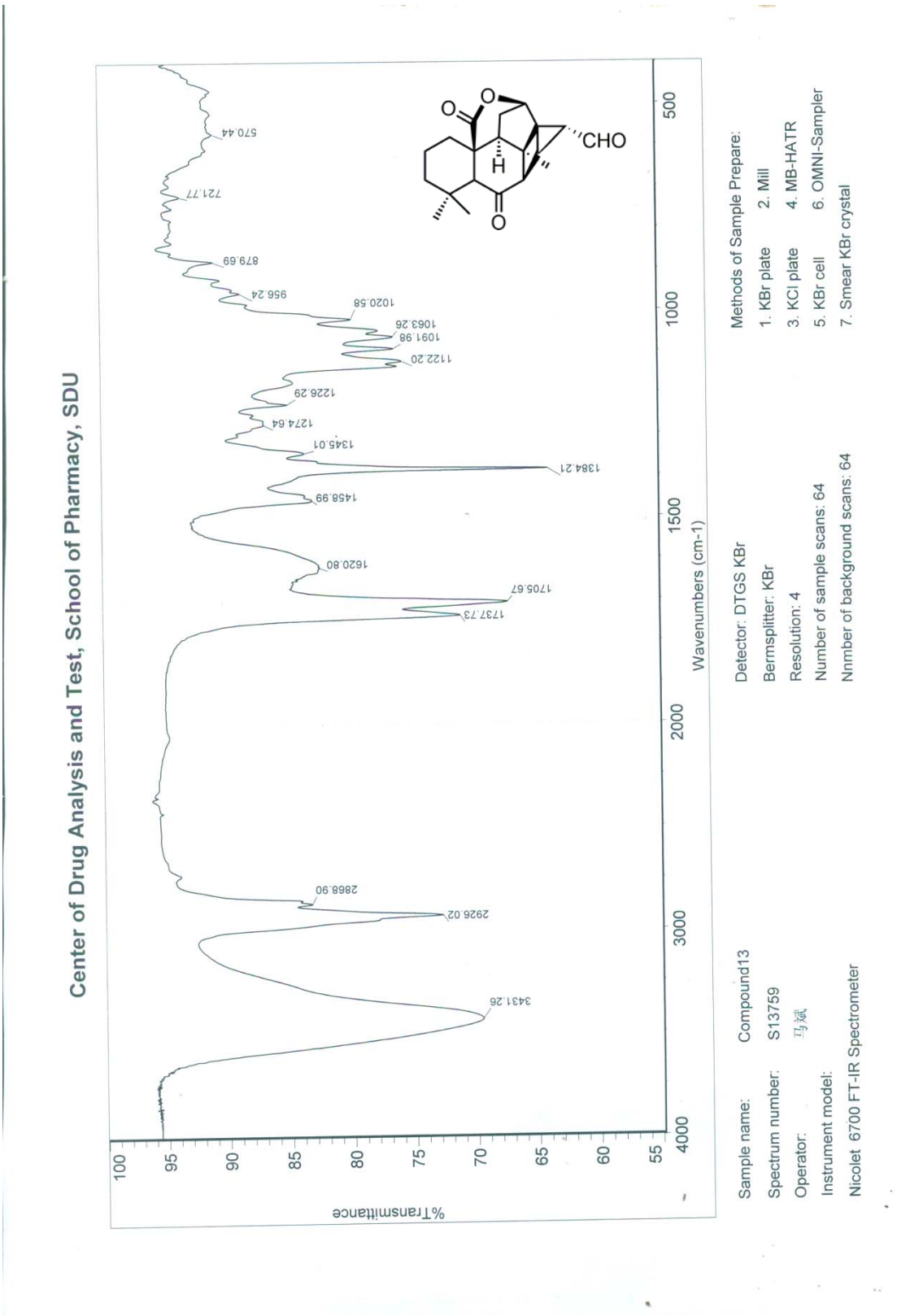

Figure S85. IR (KBr disc) spectrum of **10**.

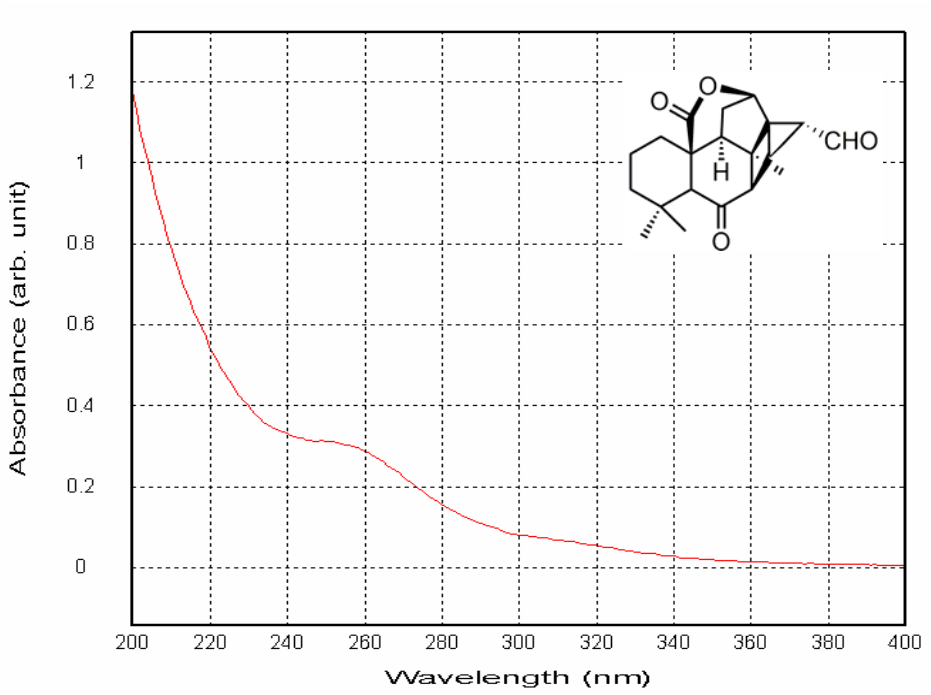

Figure S86. UV spectrum of **10**.

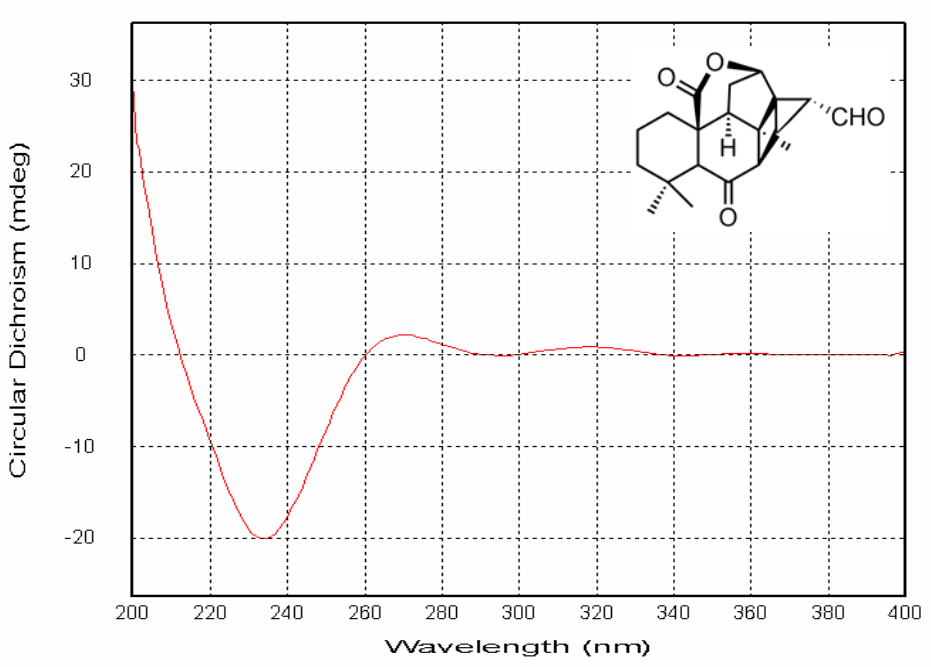

Figure S87. CD spectrum of **10**

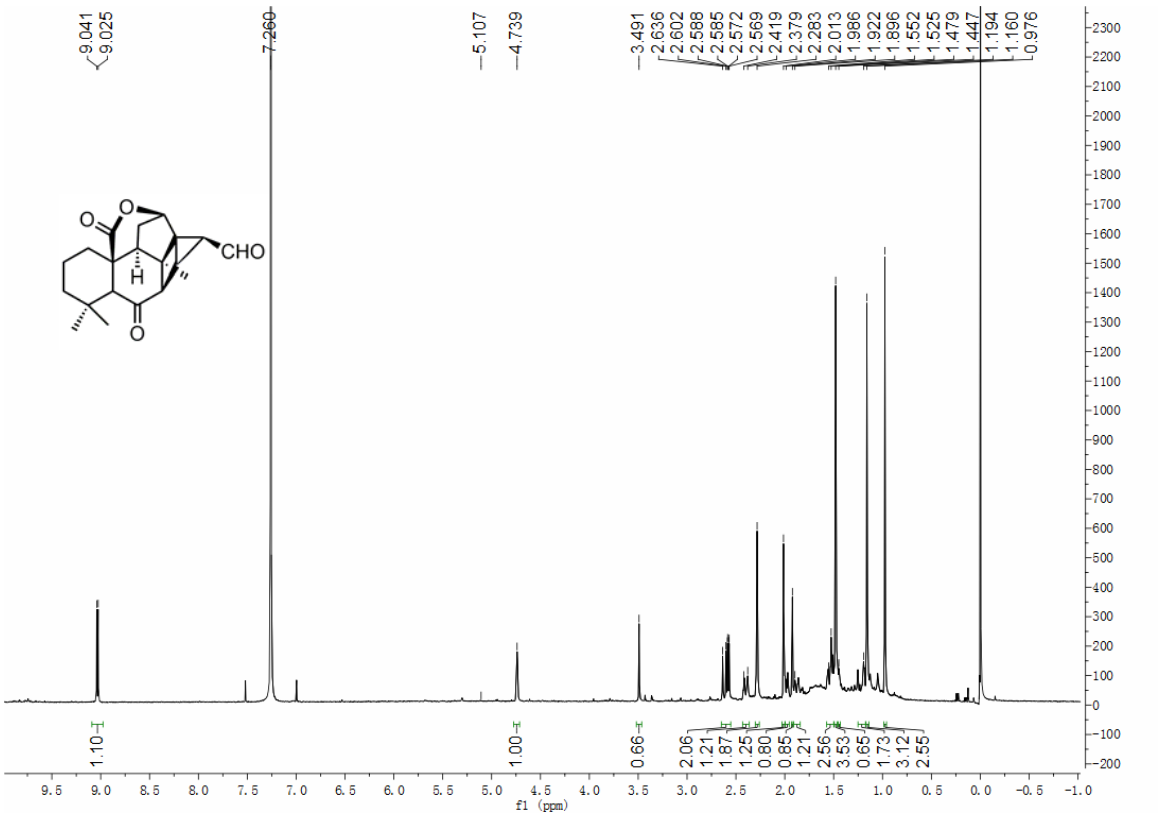

Figure S88. ^{1}H NMR spectrum (400 MHz) of **11** in $CDCl_3$.

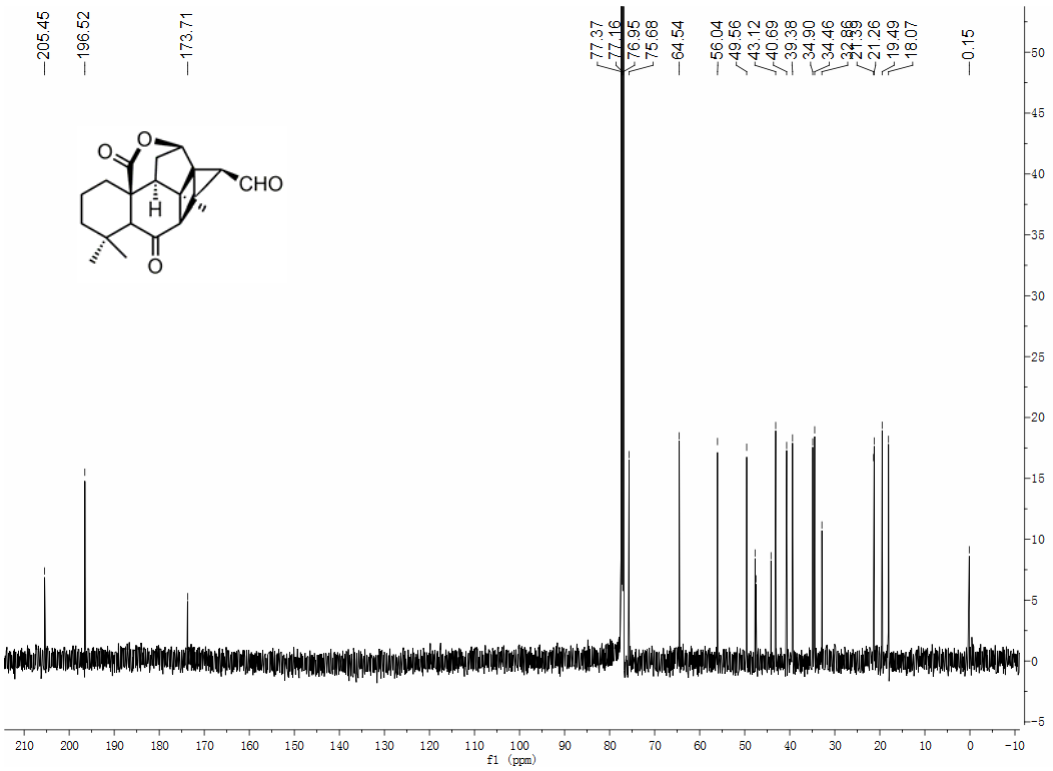

Figure S89. ^{13}C NMR spectrum (100 MHz) of **11** in $CDCl_3$.

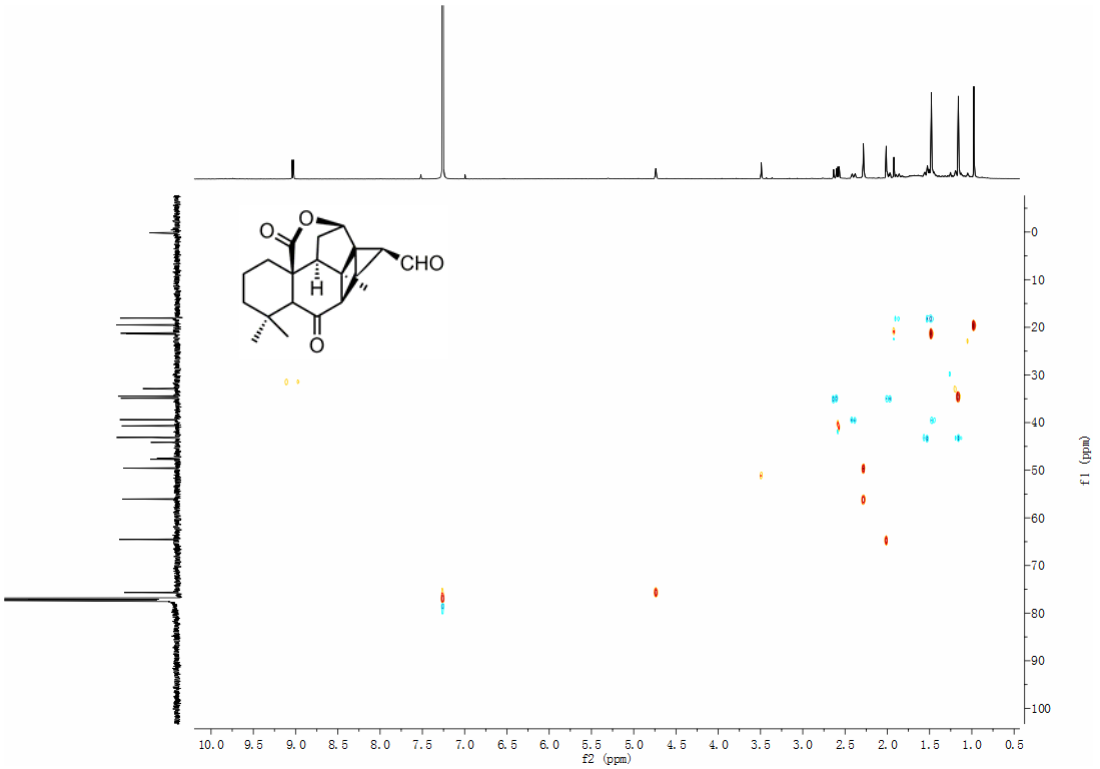

Figure S90. HSQC spectrum (400 MHz) of **11** in $CDCl_3$.

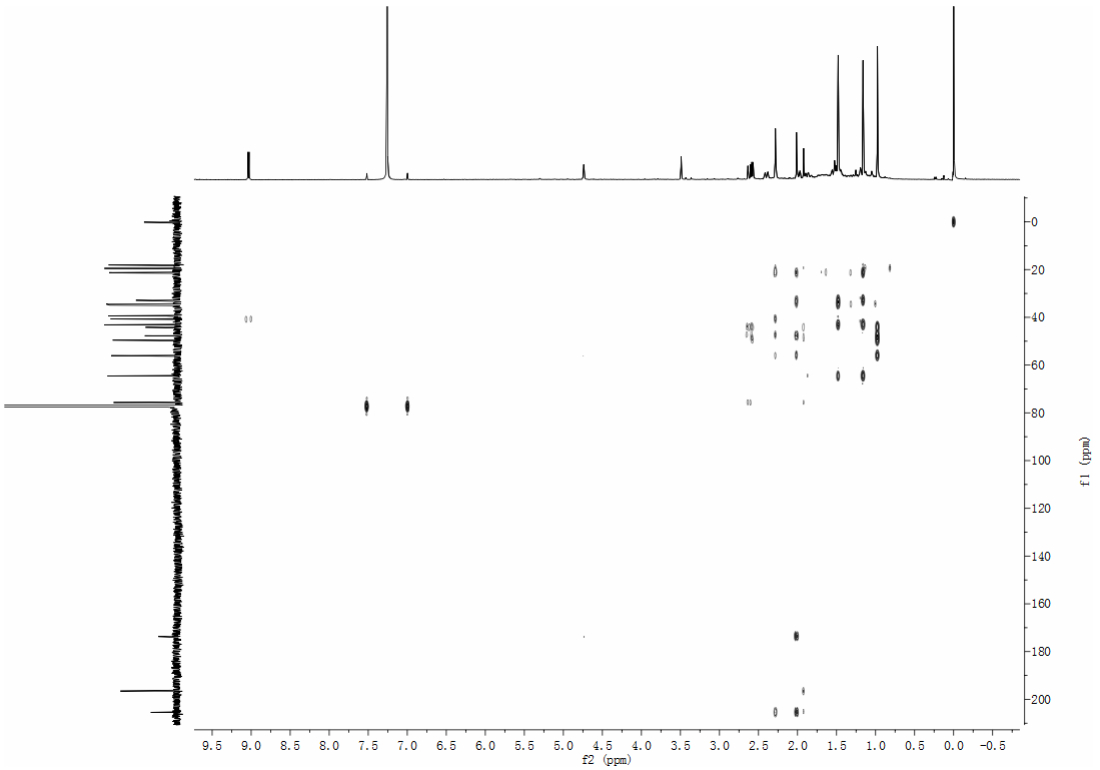

Figure S91. HMBC spectrum (400 MHz) of **11** in $CDCl_3$.

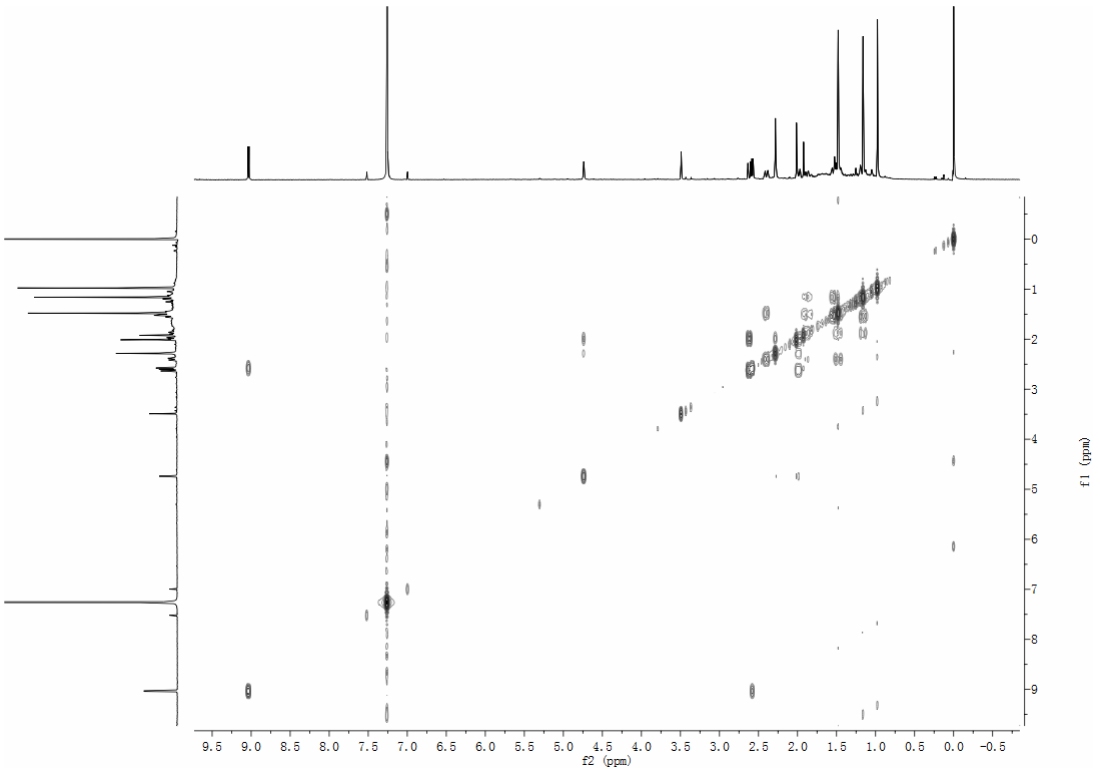

Figure S92. ^{1}H-^{1}H COSY spectrum (400 MHz) of **11** in $CDCl_3$.

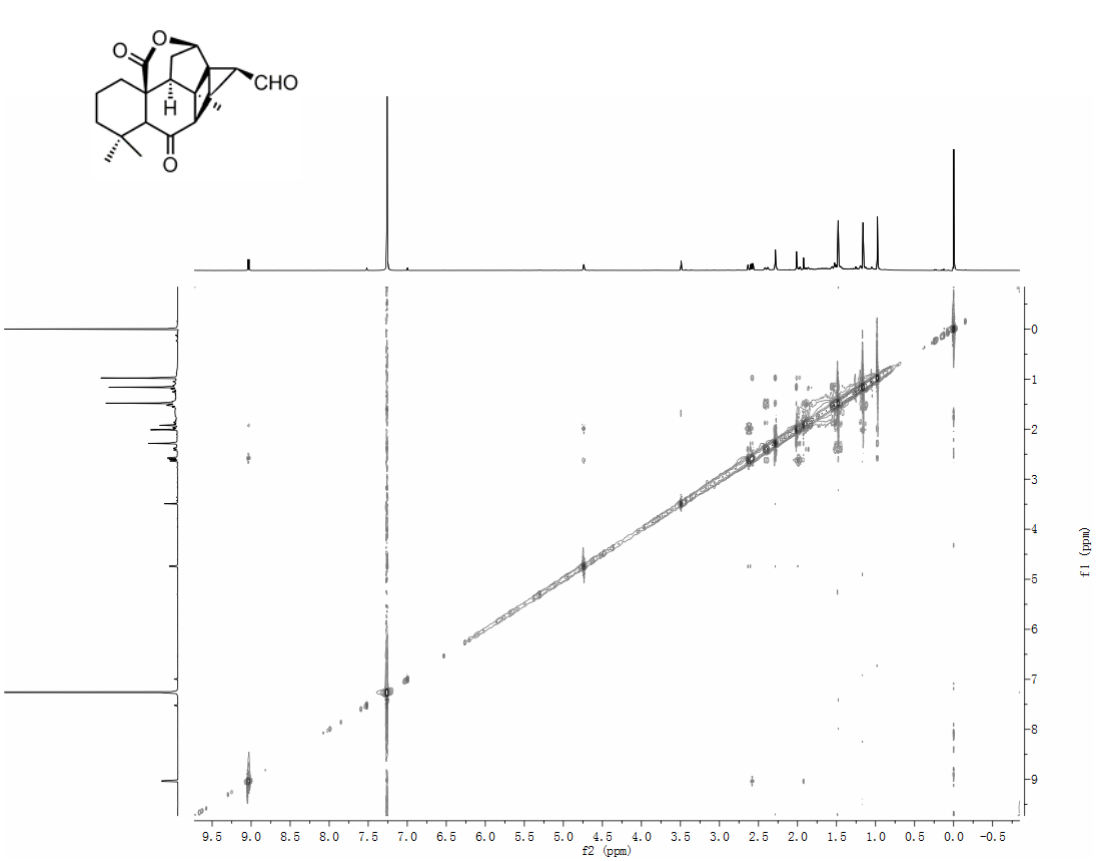

Figure S93. NOESY spectrum (400 MHz) of **11** in $CDCl_3$.

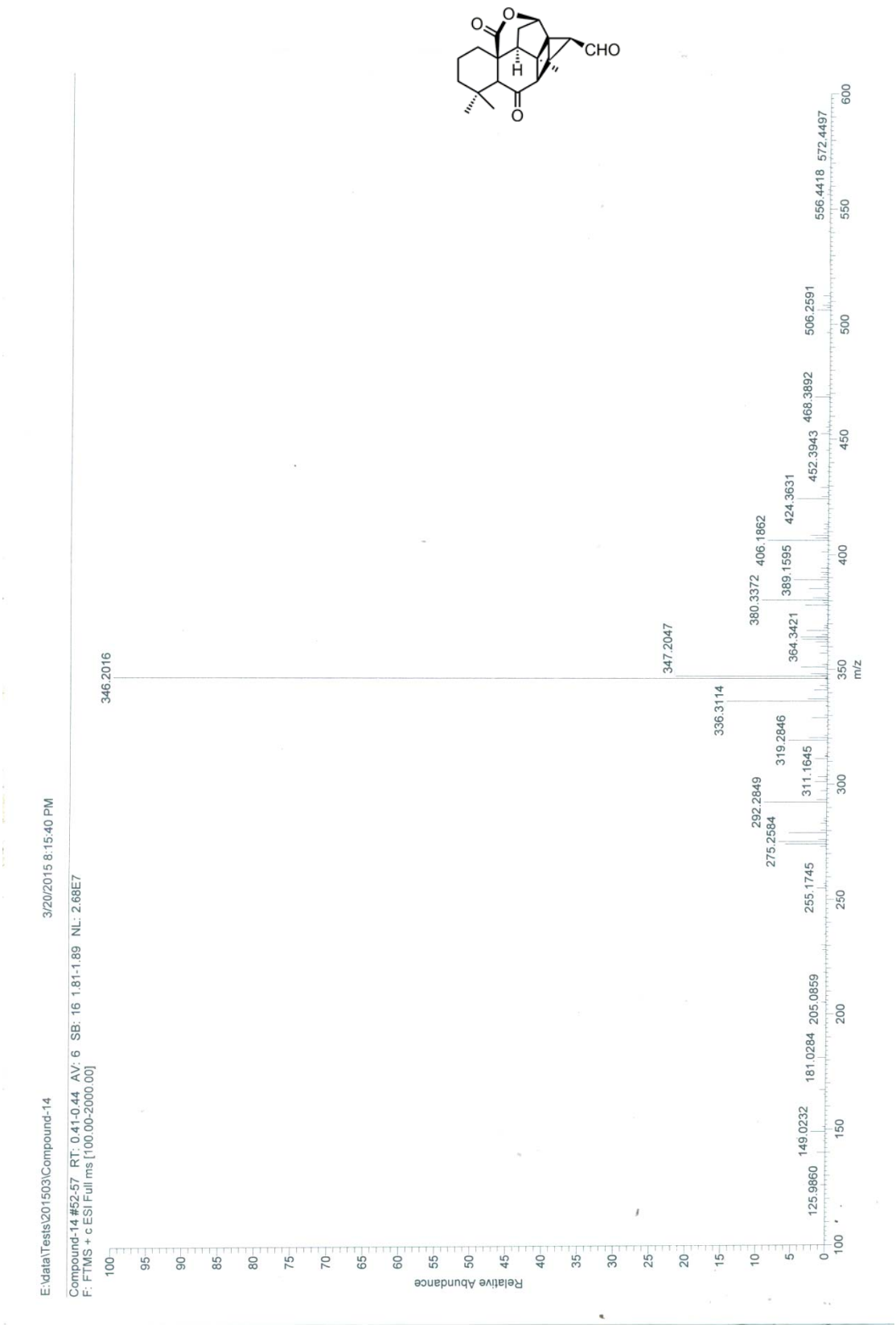

Figure S94. HRESIMS spectrum of **11**.

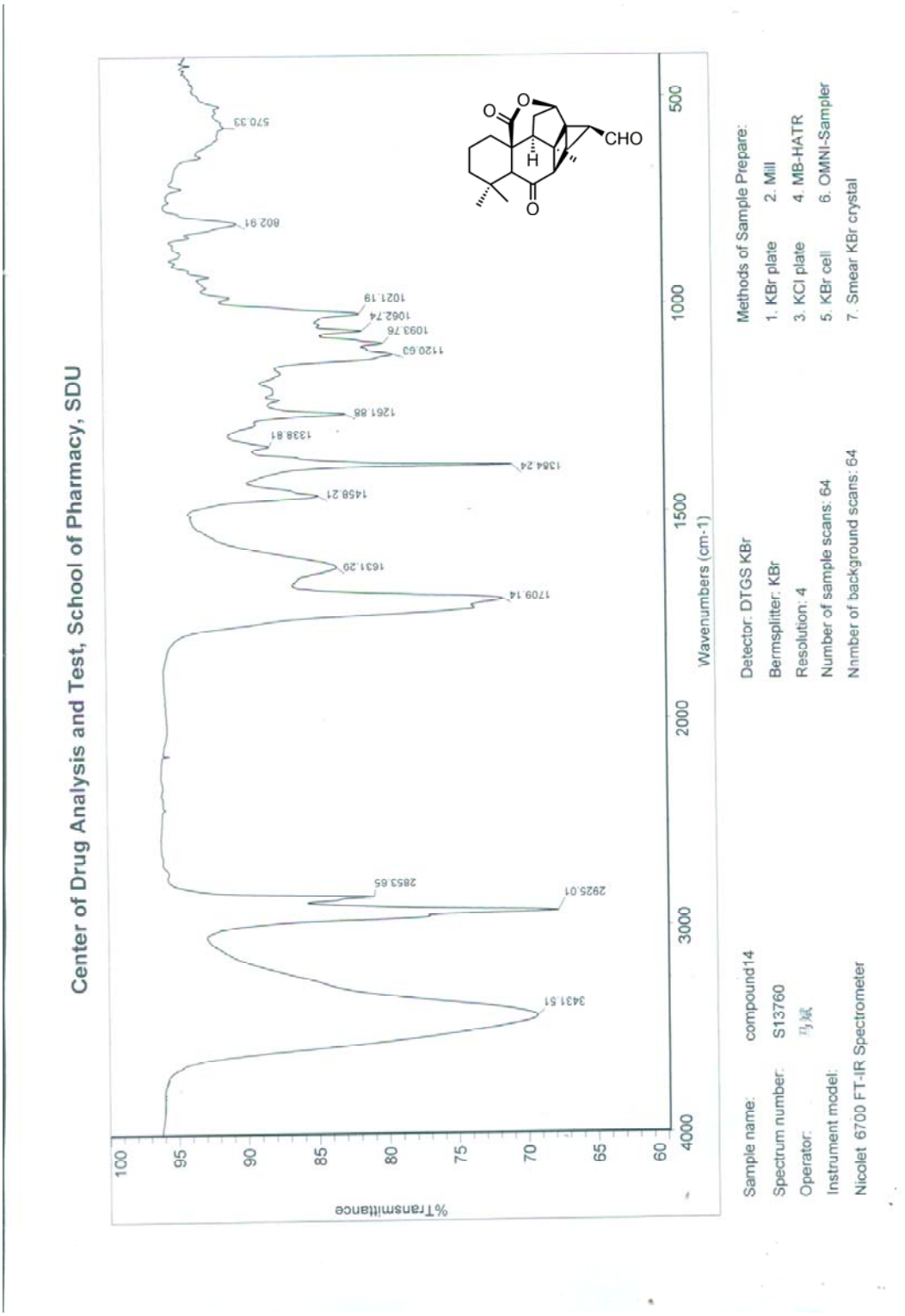

Figure S95. IR (KBr disc) spectrum of **11**.

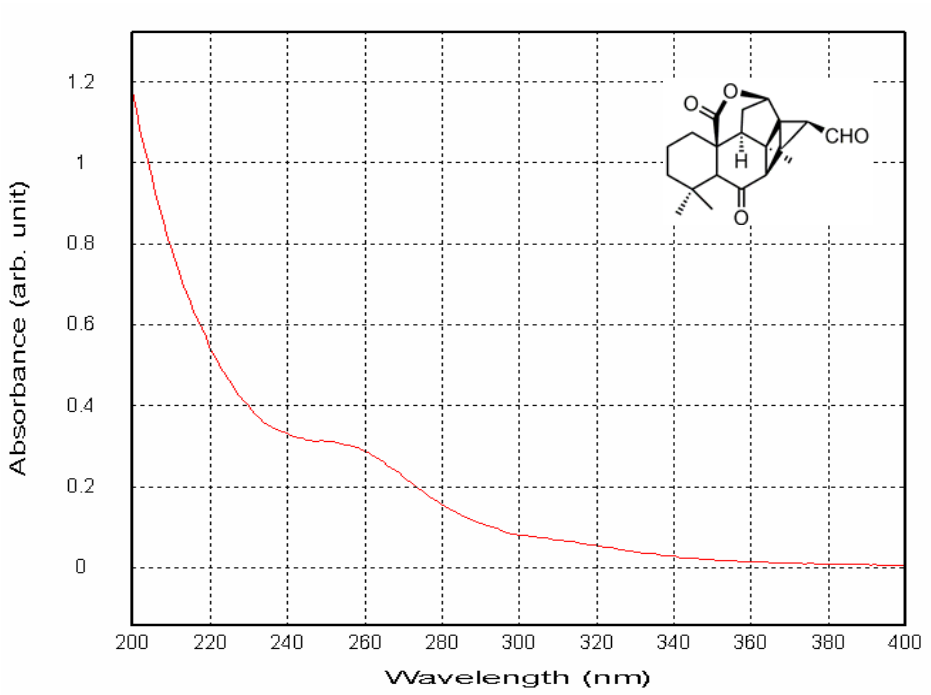

Figure S96. UV spectrum of **11**.

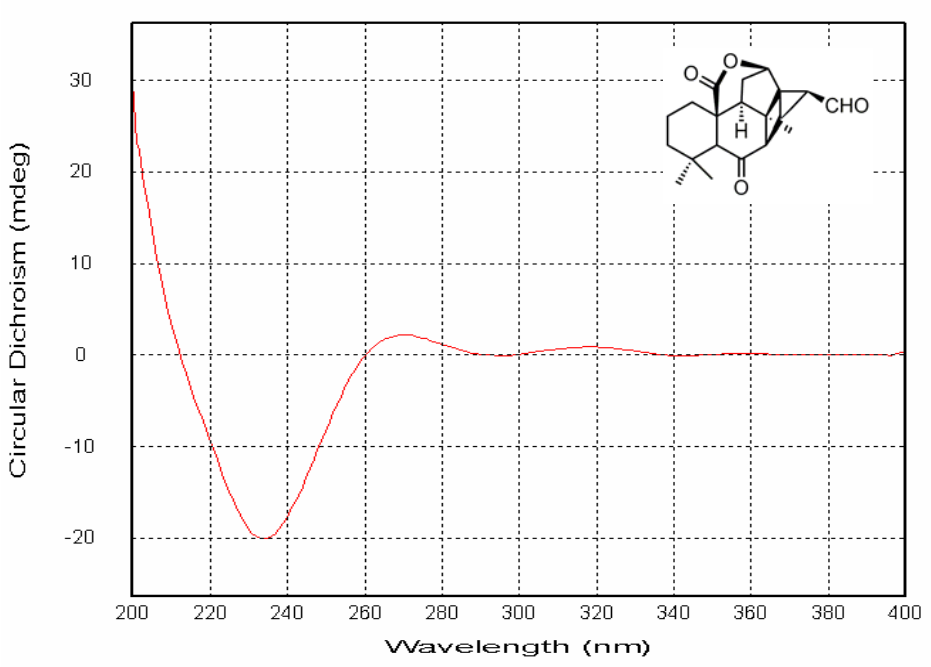

Figure S97. CD spectrum of **11**

Characteristic data for compounds 4–6

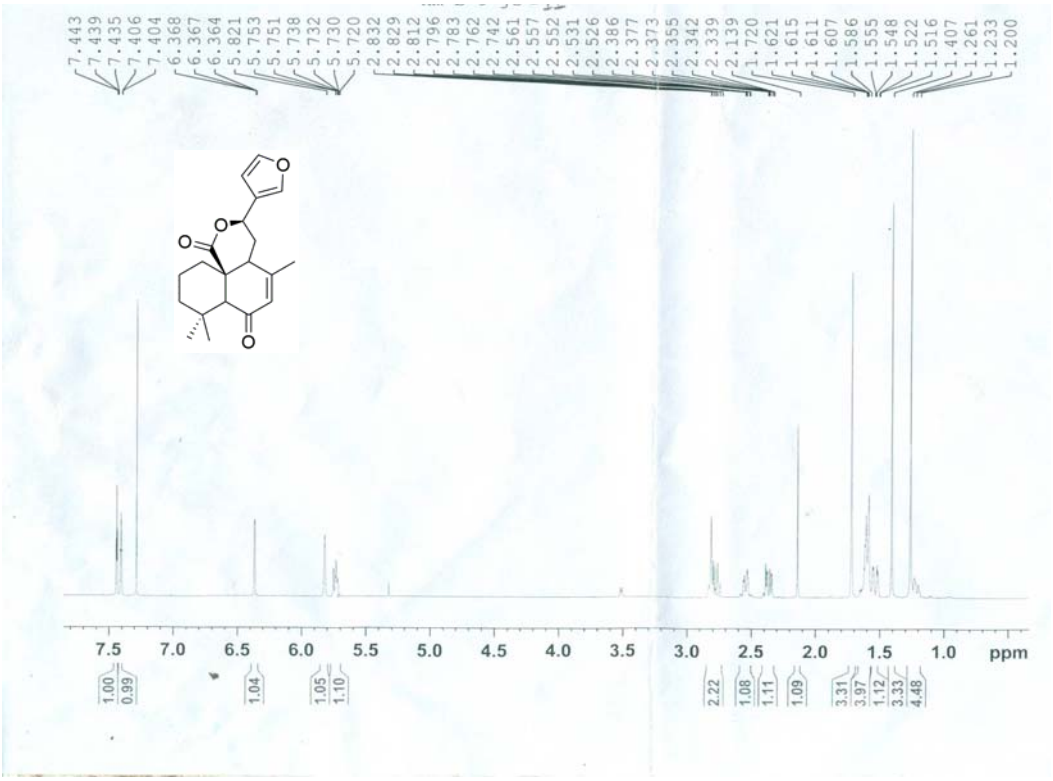

Figure S98. ^{1}H NMR spectrum (400 MHz) of **4** in $CDCl_3$.

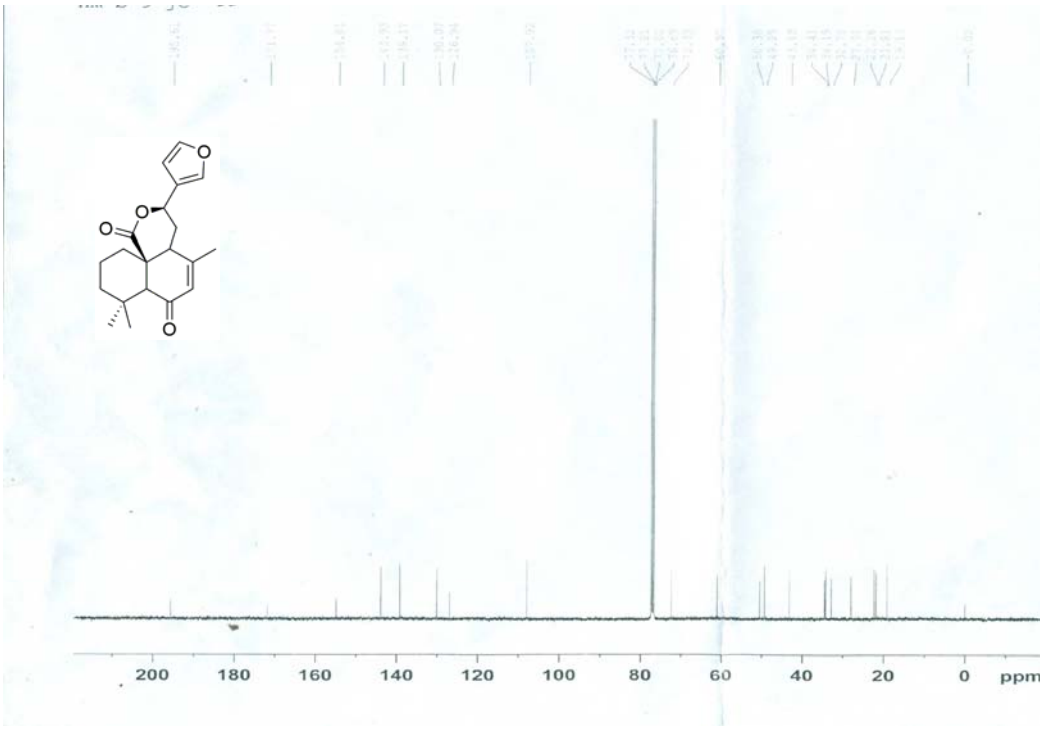

Figure S99. ^{13}C NMR spectrum (100 MHz) of **4** in $CDCl_3$.

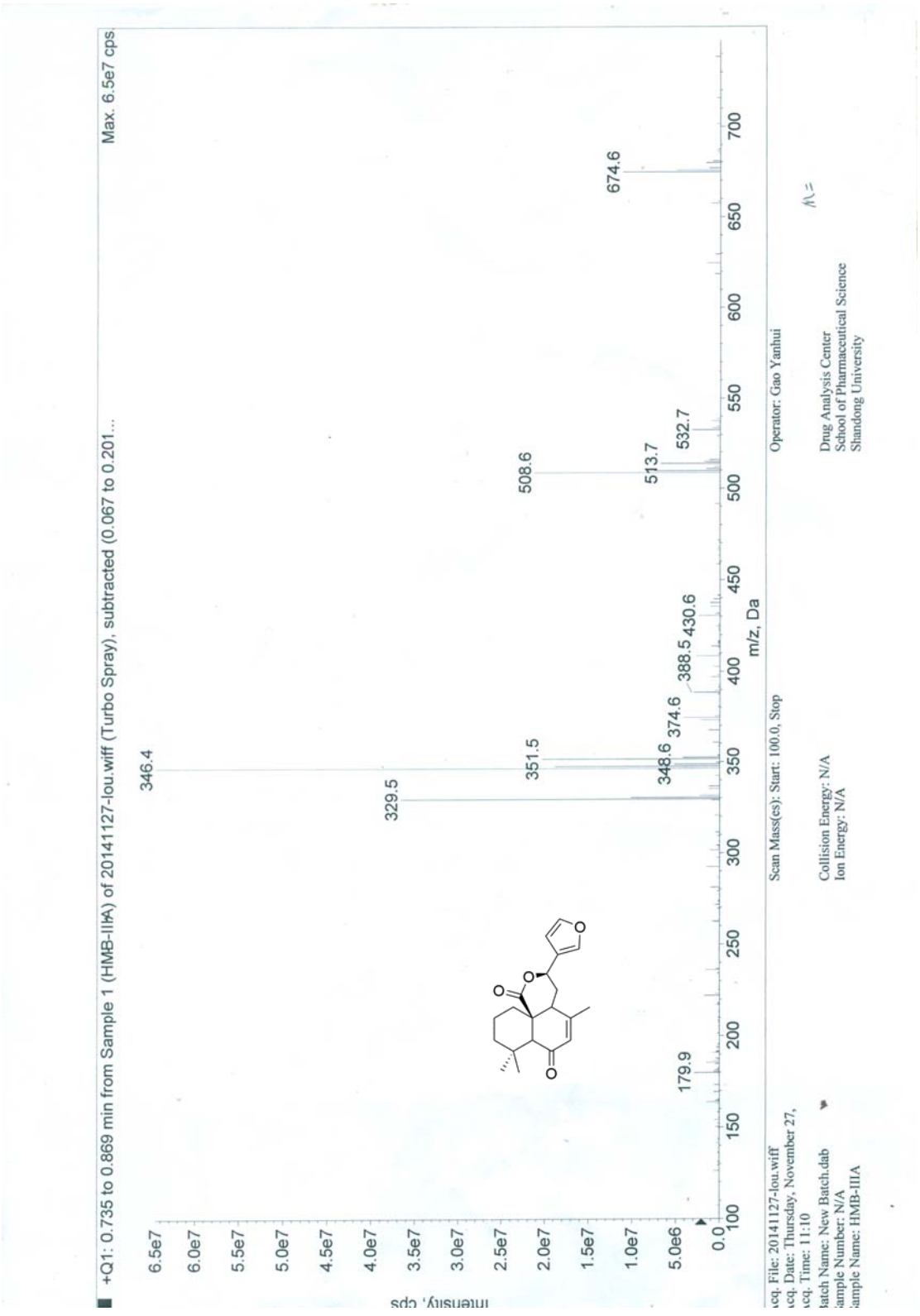

Figure S100. HRESIMS spectrum of **4**.

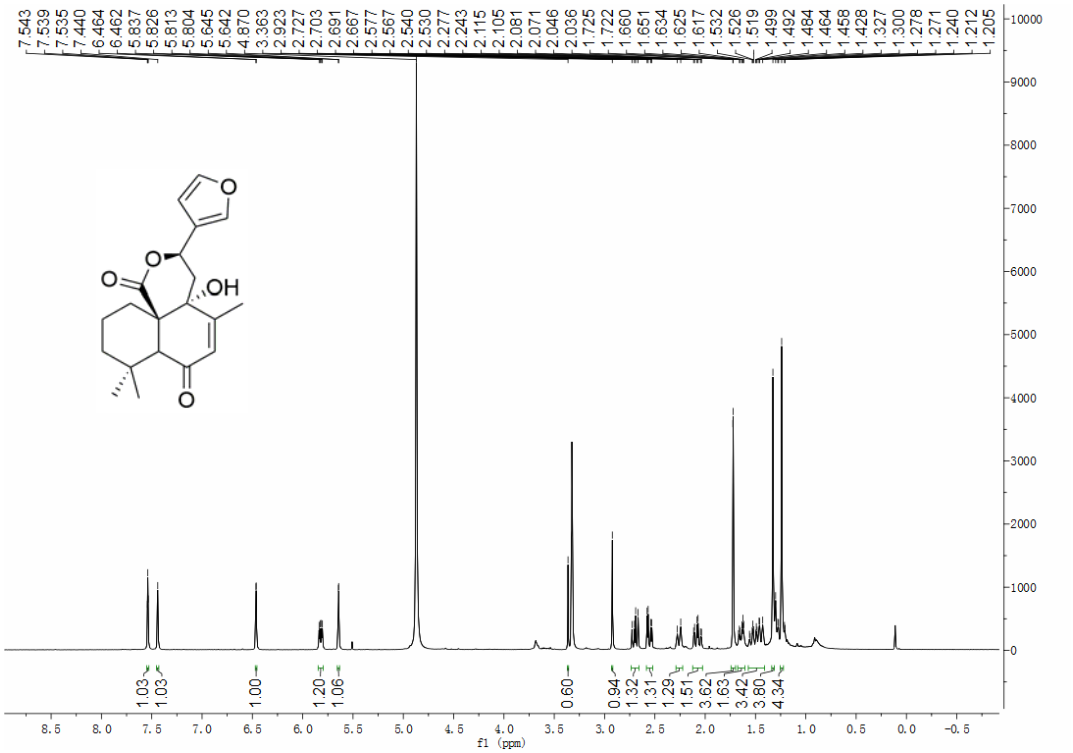

Figure S101. ^{1}H NMR spectrum (400 MHz) of **5** in CD_3OD.

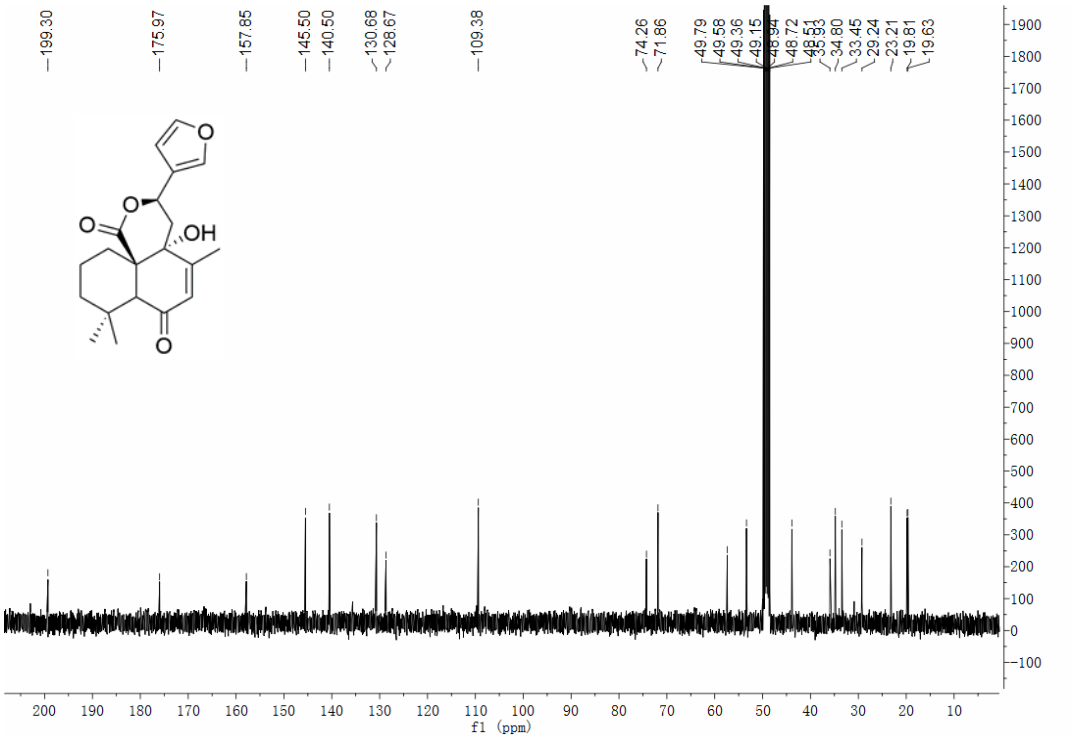

Figure S102. ^{13}C NMR spectrum (100 MHz) of **5** in CD_3OD.

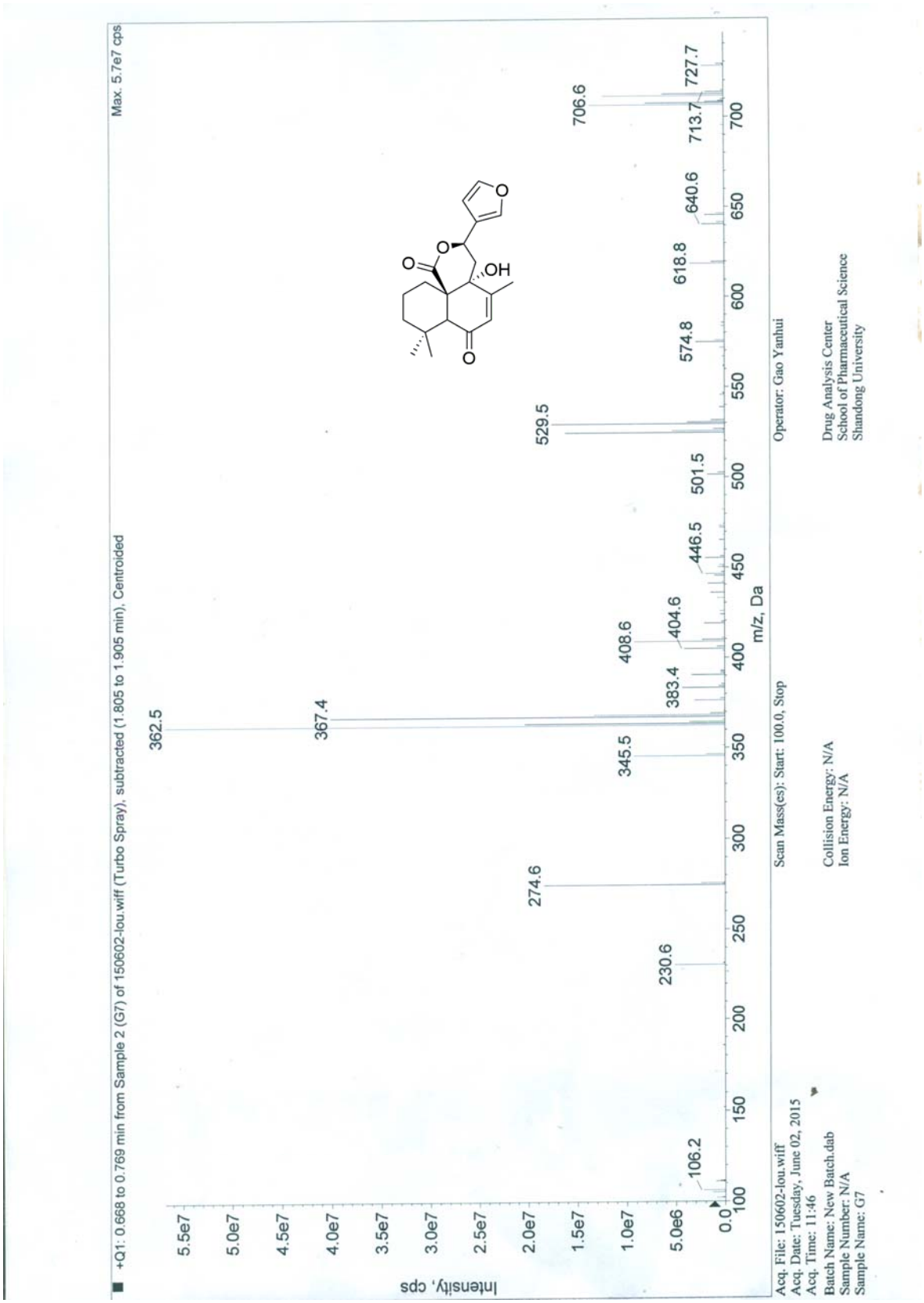

Figure S103. HRESIMS spectrum of **5**.

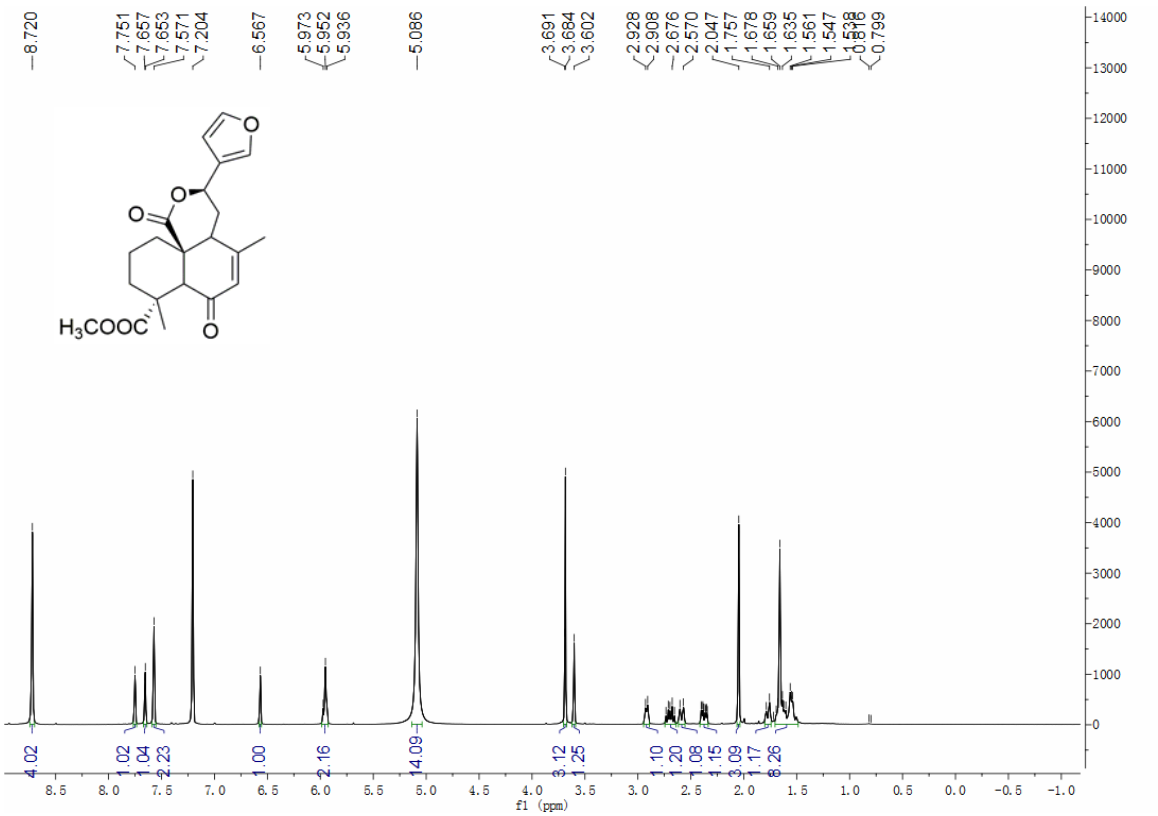

Figure S104. ^{1}H NMR spectrum (400 MHz) of **6** in pyridine-d_5.

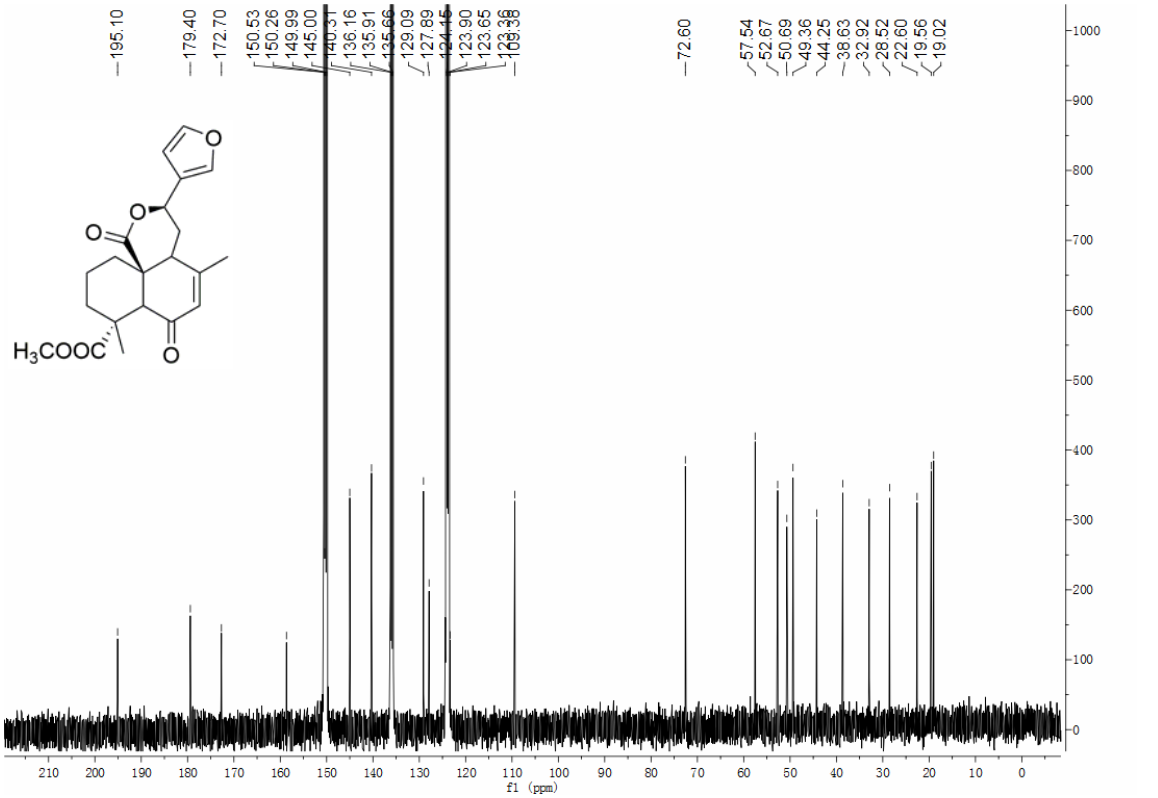

Figure S105. ^{13}C NMR spectrum (100 MHz) of **6** in pyridine-d_5.

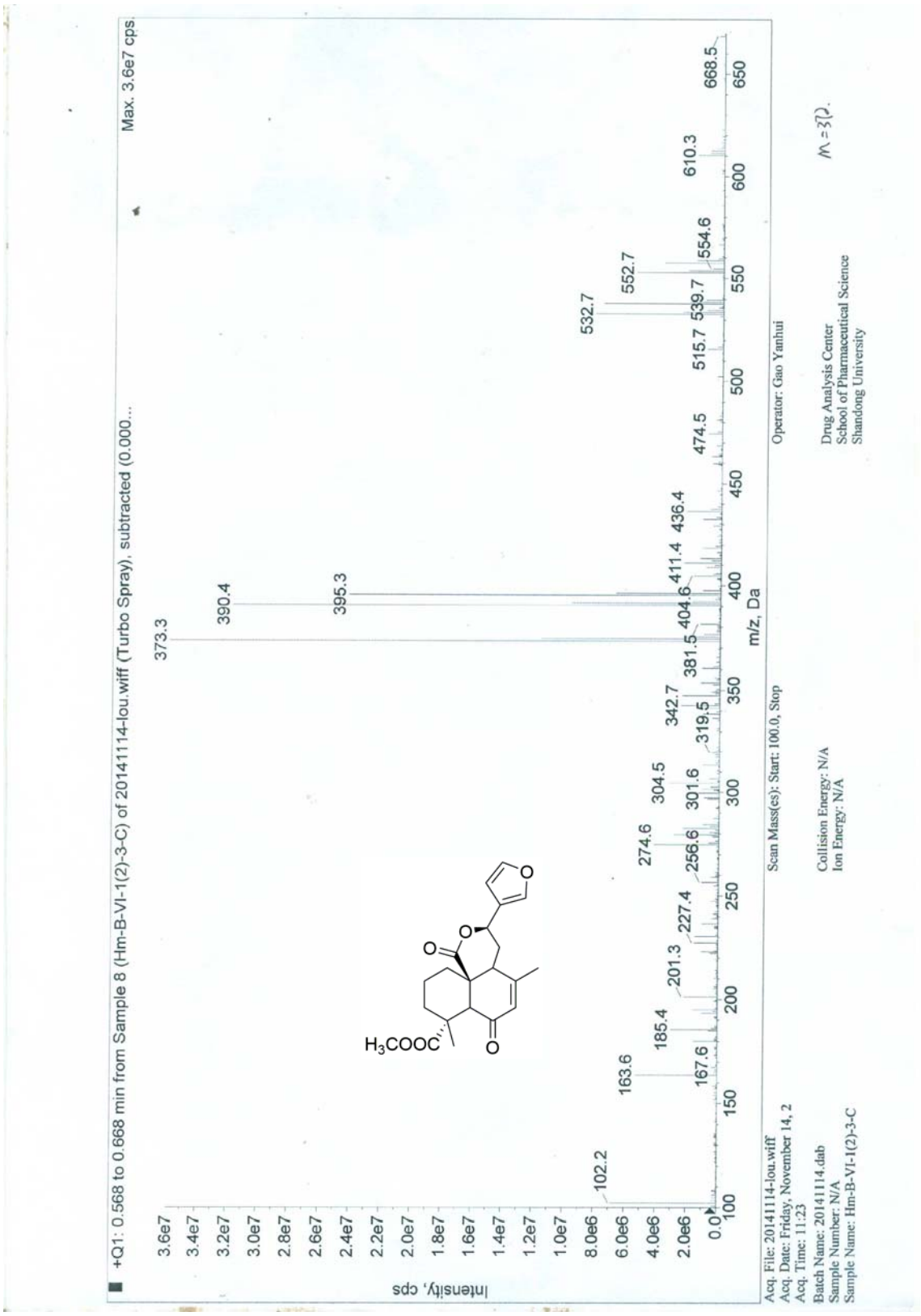

Figure S106. HRESIMS spectrum of **6**.

X-ray Crystal data of 1and 9.

Single crystals suitable for X-ray analysis were obtained by recrystallization from EtOH. All measurements were made on a Bruker APEX DUO diffractometer employing APEX Ⅱ CCD using Cu Kα radiation. Cell refinement and data reduction: APEX Ⅱ SoftwareSuite.[2] Program used to refine structure: SHELXL-97;[3] refinement on F^2, full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions and refined as riding atoms with the relative isotropic parameters. Details of crystallographic data (excluding structure factors) for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number, CCDC 1059512 for **1** and CCDC 1059598 for **9**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: C44 1223 336033 or e-mail: deposit@ccdc.cam.ac.Uk].

Crystal data of **1**: $C_{21}H_{24}O_6$, M = 372.40, monoclinic, a = 6.4773(5) Å, b=12.3883(9) Å, c=22.3542(18) Å, V= 1793.8(2) Å^3, T = 293(2) K, space group $P2_1$, Z = 4, μ(Cu Kα) = 0.831mm^{-1}, Reflections collected / unique: 3678 / 2688 [R(int) = 0.0267], GoF= 1.022, Flack parameter: 0.0 (4)

Crystal data of **9**: $C_{20}H_{24}O_4$, M = 328.39, monoclinic, a = 6.5413(5) Å, b=9.9608(7) Å, c=12.0867(7) Å, V= 787.23(9) Å^3, T = 293(2) K, space group $P2_1$, Z = 2, μ(Cu Kα) = 0.770mm^{-1}, Reflections collected / unique: 2619 / 1914[R(int) = 0.0295], GoF= 1.013, Flack parameter: 0.0 (4).

Allelopathic activity on root elongation of seeds of *A. thaliana* of compounds 2 and 4

Seeds of A. thaliana were surface sterilized using 5% NaOCl for 5 min, followed by washes with sterile distilled H_2O for five times. Compounds **2** and **4** were dissolved in DMSO to concentration of 32 mg/ml. Then, different volumes (2, 4, 8 and 16 μL) of each solution were added to 8 ml 1/2 MS medium supplemented with 0.8% (w/v) agar to obtain plates with different concentrations of compounds (8, 16, 32 and 64 μg/ml). To eliminate the effect of DMSO on the growth of *A. thaliana*, plates with DMSO (the concentration of DMSO was equivalent to plates with compounds of 8, 16, 32 and 64 μg/ml) were used as blank control. Ten seeds were distributed on each Petri dish (10.0 cm diameter) as described before. Three replicates were done for each concentration. The Petri dishes were placed in a growth chamber at 23 ± 1℃ under 16 h of light and 8 h of darkness. The lengths of seedling roots were measured after eight days.

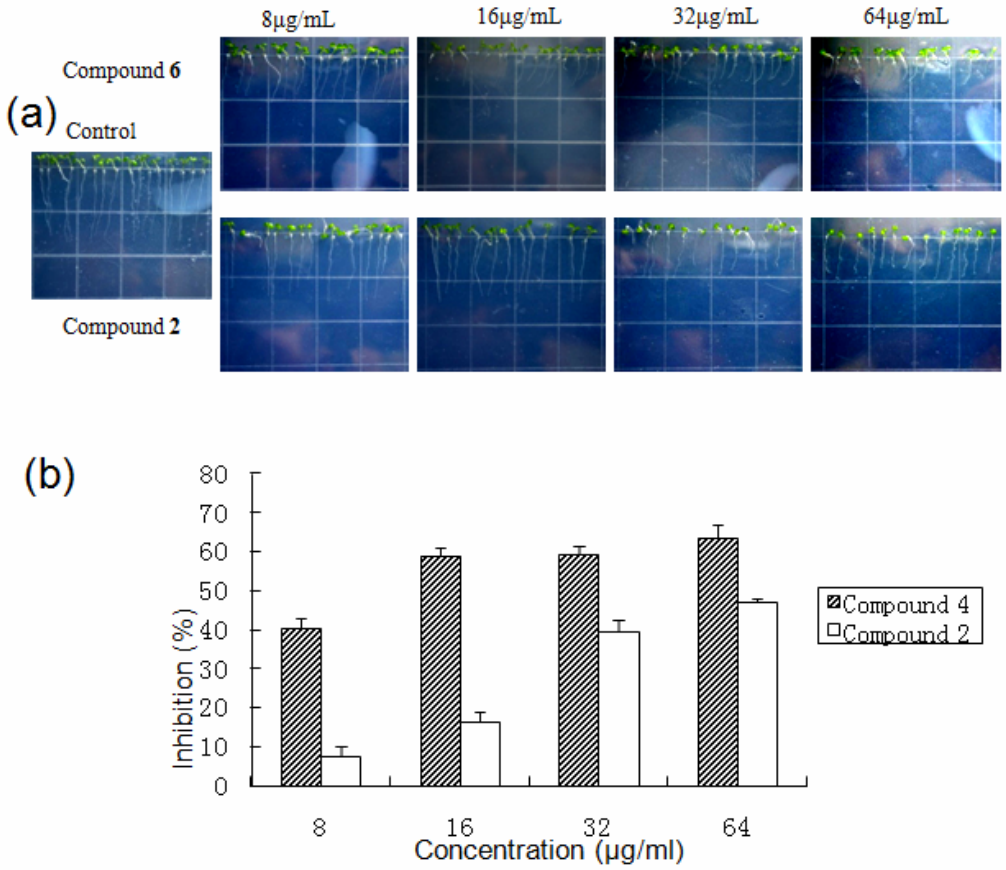

Figure S107 (a) The root elongation of *A. thaliana* on Petri dishes with different concentrations of control and compound: 8, 16, 32, and 64 μg/ml. (b) The inhibition of different concentrations of compounds **2** and **4** on *A. thaliana* root growth.
The percentage inhibition of different concentrations of these two compounds on *A. thaliana* root growth was calculated by the equation.[4]

References

[1] Y. Asakawa, M. Toyota, T. Masuya, *Phytochemistry*, **1990**, 29, 585.

[2] *APEX II Users Manual*; Bruker AXS Inc., **2005.**

[3] Sheldrick, G. M. *SHELXTL, v. 5, Reference Manual*; Siemens Energy and Automation, Inc., **1997**.

[4] P. Fan, K. Hostettmann, H. Lou, *Chemoecology* **2010**, *20*, 223.