Supporting Information

Bistachybotrysins L–V, Bioactive Phenylspirodrimane Dimers from the Fungus *Stachybotrys chartarum*

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1. Bioactivity data for compounds 1−11

Table S1. Cytotoxicity of compounds **1–4** and **6−11**

Compounds	Cytotoxicity IC_{50} (μM)				
	HCT116	NCI-H460	BGC823	Daoy	HepG2
1	10.6	13.5	22.3	>50.0	18.9
2	2.5	3.5	1.8	2.4	2.2
3	64.5	8.3	12.5	61.4	56.1
4	18.8	11.5	20.5	10.7	20.1
6	18.5	8.8	55.4	17.3	14.1
7	8.5	8.2	17.8	13.1	9.3
8	8.0	11.7	8.7	11.8	6.0
9	>50	>50	>50	>50	>50
10	9.7	10.1	9.8	8.1	9.4
11	15.0	10.9	23.9	27.7	12.9
paclitaxel[a]	0.0038	0.0004	0.0020	0.0002	0.0102

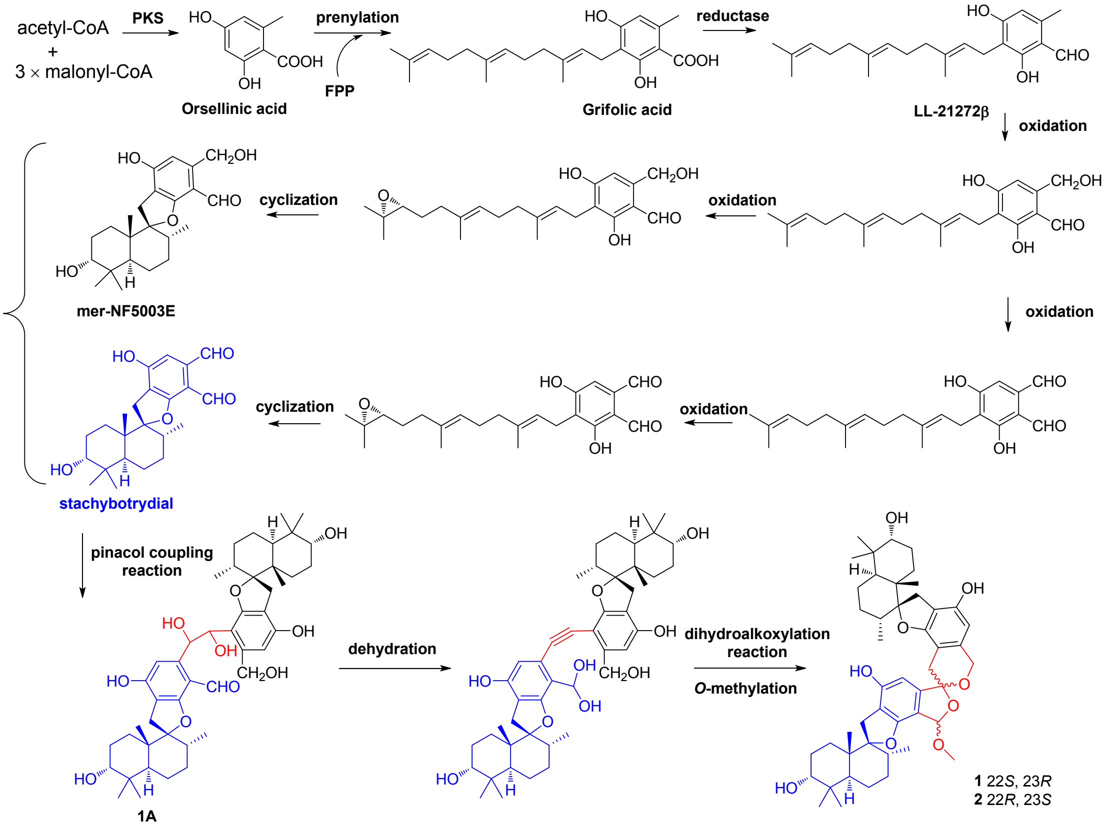
[a] Positive control

Table S2. Neuroprotective and anti-inflammatory activities of **1–10** (10 μM)

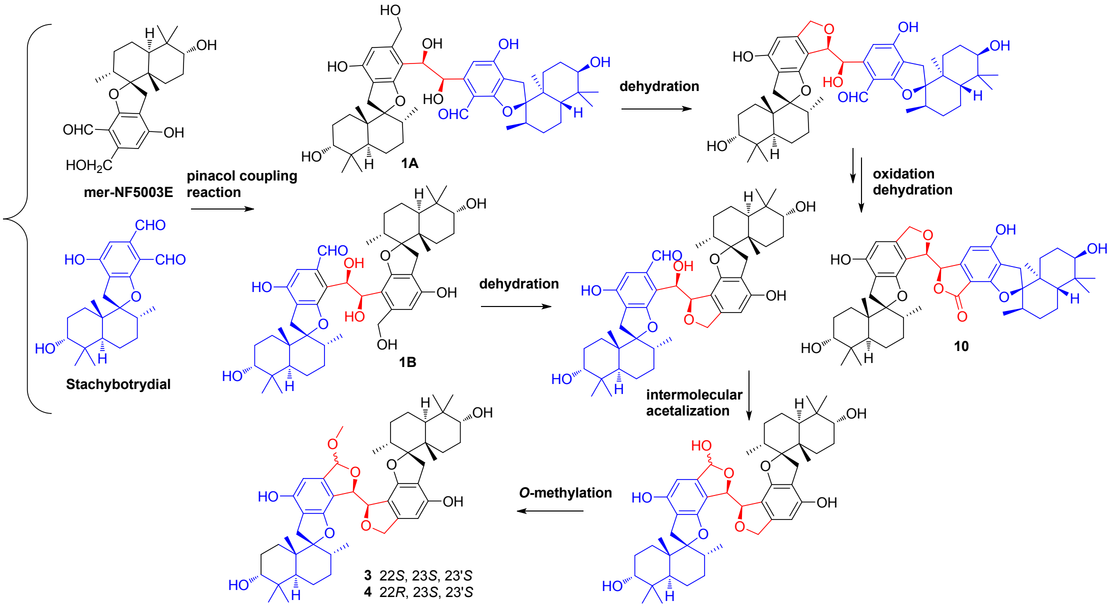
Compounds	Neuroprotective	Anti-inflammatory activity
	Increased cell viability (%)	Inhibitory rate on NO production
1	0.15	5.31
2	17.4	26.3
3	17.6	0.0
4	8.4	0.0
5	-	12.9
6	-	10.1
7	-	0.0
8	6.5	54.2
9	17.4	0.0
10	9.3	0.0
Resveratrol[a]	16.1	
Curcumin[a]		67.6

[a] Positive control; − Not tested

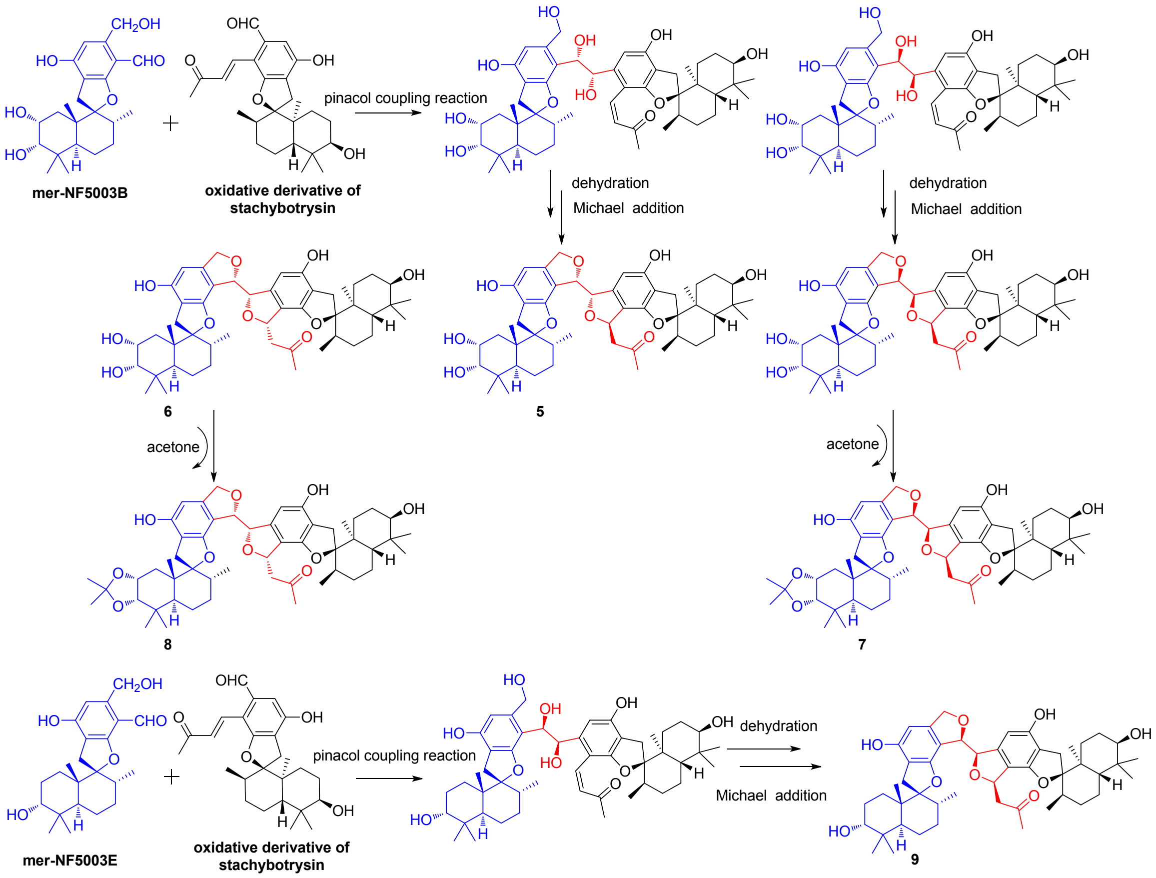
2. Proposed biosynthetic pathway of compounds 1−11



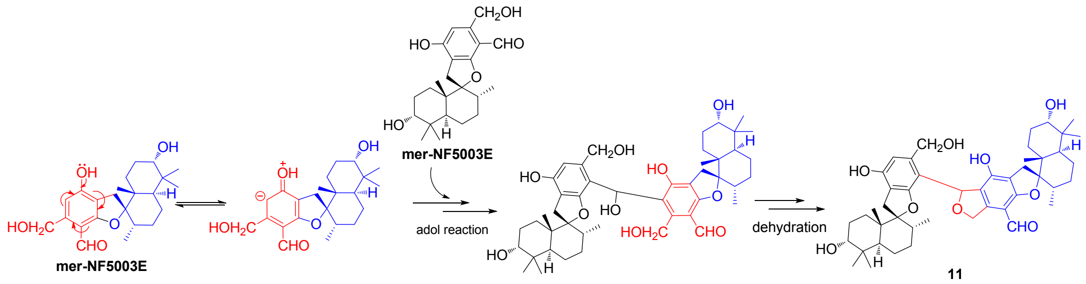
Scheme S1. A plausible biogenetic pathway of compounds **1** and **2**



Scheme S2. A plausible biogenetic pathway of compounds **3**, **4**, and **10**



Scheme S3. A plausible biogenetic pathway of compounds **5−9**



Scheme S4. A plausible biogenetic pathway of compound **11**

3. X-ray crystallographic analysis of compound 1

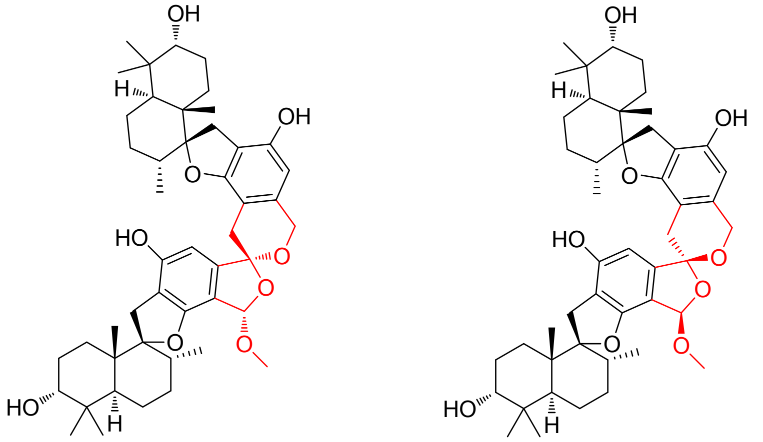
Bistachybotrysin L (**1**) was colorless crystals obtained from MeOH. Crystal structure determination of crystal data $C_{47}H_{64}O_9$, M = 772.98, monoclinic, a = 16.435(10) Å, b = 7.706 (5) Å, c = 38.384(17) Å, U = 4852.4 (5) Å^3, T = 111.2 (3), space group I_2 (no. 5), Z = 4, μ (Cu Kα) = 0.792, 23993 reflections measured, 8941 unique (Rint = 0.0827) which were used in all calculations. The final wR (F2) was 0.1680 (all data). Crystallographic data (excluding structure factor tables) for **1** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC 1899542). Copies of the data can be obtained free of charge by application to CCDC, 12, Union Road, Cambridge CB21EZ, UK [Fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

Table S3. Crystal data and structure refinement for bistachybotrysin L

Identification code	bistachybotrysin L
Empirical formula	$C_{47}H_{64}O_9$
Formula weight	772.98
Temperature / K	111.2(3)
Crystal system	monoclinic
Space group	I_2
a / Å, b / Å, c / Å	16.4353(10), 7.7055(5), 38.3838(17)
α/°, β/°, γ/°	90.00, 93.400(5), 90.00
Volume / Å^3	4852.4(5)
Z	4
ρ_{calc} / mg mm^{-3}	1.058
μ / mm^{-1}	0.577
F(000)	1672
Crystal size / mm^3	0.30 × 0.12 × 0.07
2Θ range for data collection	5.98 to 143.62°
Index ranges	$-20 \le h \le 20$, $-9 \le k \le 9$, $-47 \le l \le 45$
Reflections collected	23993
Independent reflections	8941[R(int) = 0.0827 (inf-0.9Å)]
Data/restraints/parameters	8941/1/518
Goodness-of-fit on F^2	0.997
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	$R_1 = 0.0621$, $wR_2 = 0.1592$
Final R indexes [all data]	$R_1 = 0.0711$, $wR_2 = 0.1680$
Largest diff. peak/hole / e Å^{-3}	0.185/-0.231
Flack Parameters	0.0(2)
Completeness	0.9994

4. ECD calculations of compounds 2, 3, 5, 10, and 11

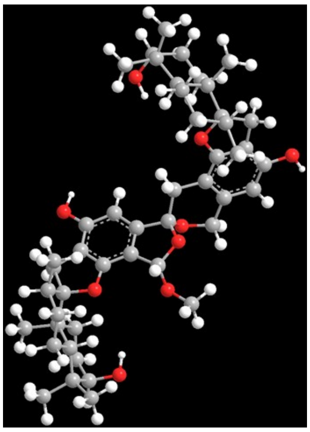
ECD calculation of 2. Conformational analysis of the **2a** and **2b** (Figure S1) were carried out via Monte Carlo searching with the MMFF94s molecular mechanics force field using the spartan 14 software.[1] 7 of **2a** (Figure S2) and 5 of **2b** (Figure S3) geometries having relative energies within 2 kcal/mol were optimized using DFT at the B3LYP/6-31G (d') level in vacuum with the Gaussian 09 program, respectively.[2] Those stable conformers with their Boltzmann distribution (>1%) also were carried out at the TDDFT CAM-B3LYP/6-31G (d') level in the methanol for ECD computation. Boltzmann statistics were performed for ECD simulations with a standard deviation of σ 0.3 eV. The final ECD spectra of **2a** and **2b** were obtained according to the Boltzmann distribution (Table S4 and S5) theory and their relative Gibbs free energy (ΔG), respectively.



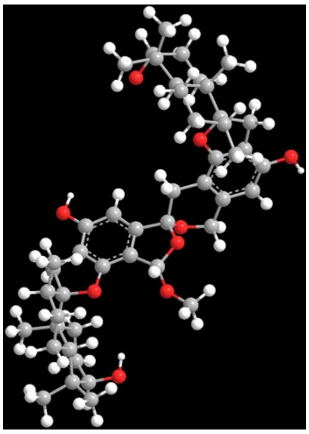
2a: 3*R*, 5*S*, 8*R*, 9*R*, 10*S*, 22*R*, 23*S*, 3'*R*, 5'*S*, 8'*R*, 9'*R*, 10'*S*

2b: 3*R*, 5*S*, 8*R*, 9*R*, 10*S*, 22*S*, 23*R*, 3'*R*, 5'*S*, 8'*R*, 9'*R*, 10'*S*

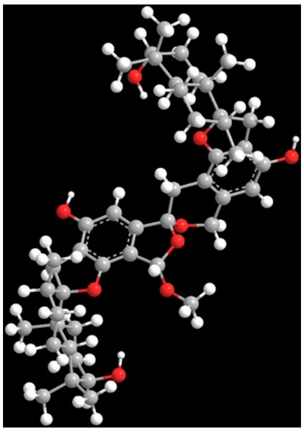
Figure S1. The structures of **2a** and **2b**



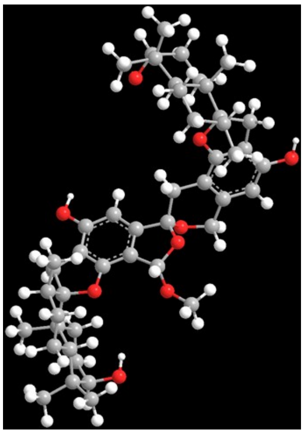
2a-C1



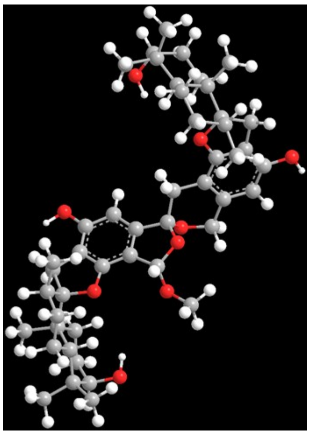
2a-C2



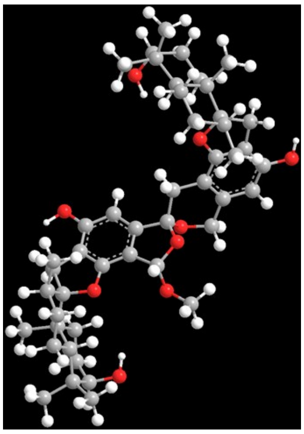
2a-C3



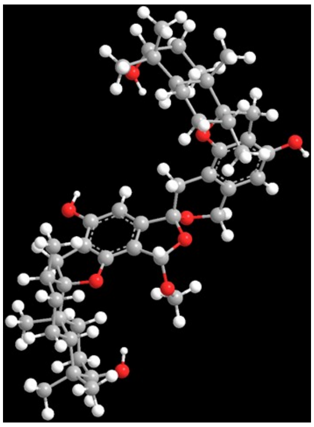
2a-C4



2a-C5

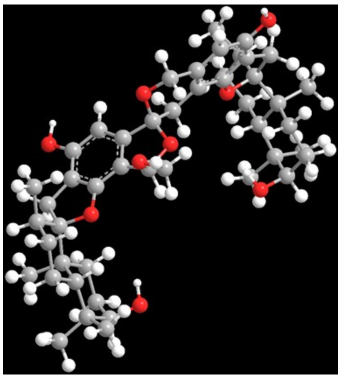


2a-C6

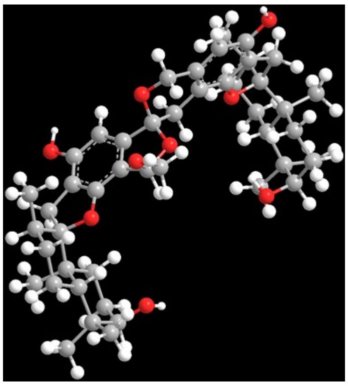


2a-C7

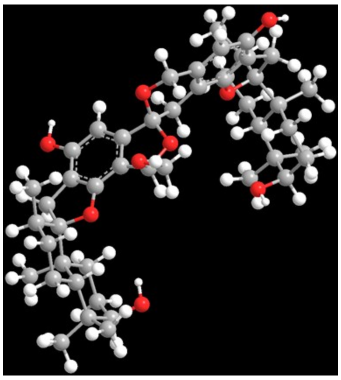
Figure S2. B3LYP/6-31G (d') optimized 7 conformers of **2a** and their relative energies (ΔG ≦ 2 Kcal/mol)



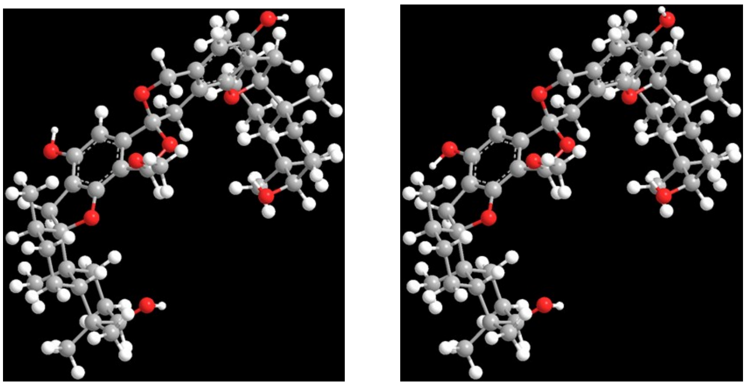
2b-C1



2b-C2



2b-C3



2b-C4 **2b-C5**

Figure S3. B3LYP/6-31G (d') optimized 5 conformers of **2b** and their relative energies (ΔG ≦ 2 Kcal/mol)

Table S4. Free energies (Δ*G*), and Boltzmann distribution abundances of conformers of **2a.**

Conf.	B3LYP/6-31 G (d') Gibbs free energy (298.15 K)		
	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
2a-C1	-2505.552141	0.0000	0.422
2a-C2	-2505.551786	0.2230	0.290
2a-C3	-2505.550523	1.0150	0.076
2a-C4	-2505.550279	1.1680	0.059
2a-C5	-2505.550678	0.9180	0.090
2a-C6	-2505.549081	1.9200	0.016
2a-C7	-2505.550069	1.3000	0.047

Table S5. Free energies (Δ*G*), and Boltzmann distribution abundances of conformers of **2b.**

Conf.	B3LYP/6-31 G (d') Gibbs free energy (298.15 K)		
	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
2b-C1	-2505.54943	0.233	0.283
2b-C2	-2505.549801	0.000	0.419
2b-C3	-2505.54875	0.660	0.138
2b-C4	-2505.548147	1.038	0.073
2b-C5	-2505.54832	0.929	0.087

ECD calculations of 3 and 5. Based on the NOE difference spectral analysis and by comparison with our reported stachybotrysins A–G[3] and bistachybotrysins A–C,[4] the absolute configuration of two phenylspirodrimane units was assigned to be 3*R*, 5*S*, 8*R*, 9*R*, 10*S*, 3′*R*, 5′*S*, 8′*R*, 9′*R*, and 10′*S* in **3**, and to be 2*R*, 3*S*, 5*S*, 8*R*, 9*R*, 10*S*, 3′*R*, 5′*S*, 8′*R*, 9′*R*, and 10′*S* in **5**, and additionally the linkage segment in **3** had a *syn*-orientation of H_3-24, H-23 and H-23′, and in **5** it showed a *syn*-orientation of H-23, H-

22′ and H_2-24′. So two stereoisomers exited for **3**, (3*R*, 5*S*, 8*R*, 9*R*, 10*S*, 22*R*, 23*R*, 23′*R*, 3′*R*, 5′*S*, 8′*R*, 9′*R*, 10′*S*)-**3a** and (3*R*, 5*S*, 8*R*, 9*R*, 10*S*, 22*S*, 23*S*, 23′*S*, 3′*R*, 5′*S*, 8′*R*, 9′*R*, 10′*S*)-**3b**; and two stereoisomers exited for **5**, (2*R*, 3*S*, 5*S*, 8*R*, 9*R*, 10*S*, 23*R*, 22′*R*, 23′*S*, 3′*R*, 5′*S*, 8′*R*, 9′*R*, 10′*S*)-**5a** and (2*R*, 3*S*, 5*S*, 8*R*, 9*R*, 10*S*, 23*S*, 22′*S*, 23′*R*, 3′*R*, 5′*S*, 8′*R*, 9′*R*, 10′*S*)-**5b**. The resultant conformers were further optimized and checked as the true minima of potential energy surface by the density functional theory method at the B3LYP/6-31G(d) level, and 100 lowest electronic transitions were calculated. ECD spectra of different conformers were simulated using a Gaussian function with a half-band width of 0.3 eV. The overall theoretical ECD spectra were given on the basis of the Boltzmann weighting of each conformers. The theoretically calculated ECD spectra were compared with the experimental ECD curves, resulting in the assignment of the absolute configuration of **3** and **5**.

ECD calculations of 10 and **11**. The theoretical calculations were carried out using Gaussian 09.[5] At first, conformers were optimized at PM6 using semi-empirical theory method and subsequent Hartree-Fock calculations, which resulted in only one remaining conformer for each configuration. Compounds **10** and **11** were finally optimized at B3LYP/6-311G(d,p) in methanol using the IEFPCM model. Vibrational frequency analysis confirmed the stable structures. Under the same condition, the ECD calculation was conducted using Time-dependent Density functional theory (TD-DFT). Rotatory strengths for a total of 30 excited states were calculated. The ECD spectrum was simulated in SpecDis[6] by overlapping Gaussian functions for each transition according to (eq. 1).

$$\Delta\varepsilon(E) = \frac{1}{2.297\times10^{-39}} \times \frac{1}{\sqrt{2\pi\sigma}} \sum_{i}^{A} \Delta E_i R_i e^{-\left(\frac{E-E_i}{2\sigma}\right)^2}$$

where σ represents the width of the band at 1/*e* height, and ΔE_i and R_i are the excitation energies and rotatory strengths for transition *i*, respectively. Parameters of σ were set 0.28, 0.16, and 0.40 eV, and UV-shift values were -2, 10, and 40 nm for compounds **10** and **11**, respectively.

(1) Spartan 14, Wavefunction, Inc.: Irvine, CA.

(2) Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, Revision C.01; Gaussian, Inc., Wallingford CT, 2010.

(3) Zhao J, Feng J, Tan Z, Liu J, Zhao J, Chen R, et al. *J. Nat. Prod.* **2017**, *80*, 1819–1826.

(4) Zhao J, Feng J, Tan Z, Liu J, Zhang M, Chen R, et al. *Bioorg. Med. Chem. Lett.* **2018**, *28*, 355–359.

(5) Gaussian R A. 1.; MJ Frisch.; GW Trucks.; HB Schlegel.; et al., Gaussian. Inc., Wallingford CT, **2009**, *121*, 150–166.

(6) Bruhn T.; Schaumlöffel A.; Hemberger Y.; et al. *J. Chirality*. **2013**, *25*, 243–249.

5. NMR, HR-ESI-MS, IR, UV, and ECD spectra of compounds 1–11

Figure S4. ^{1}H NMR spectrum of compound **1** in DMSO-d_6 at 600 MHz

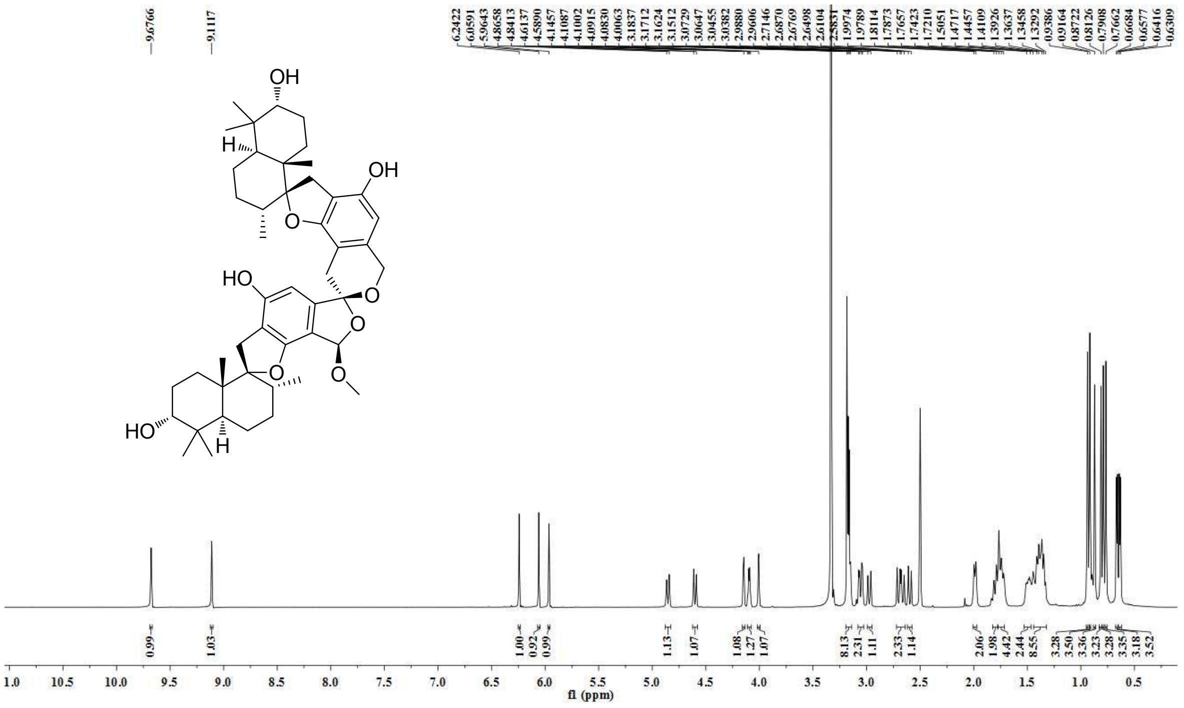


Figure S5. ^{13}C NMR spectrum of compound **1** in DMSO-d_6 at 150 MHz

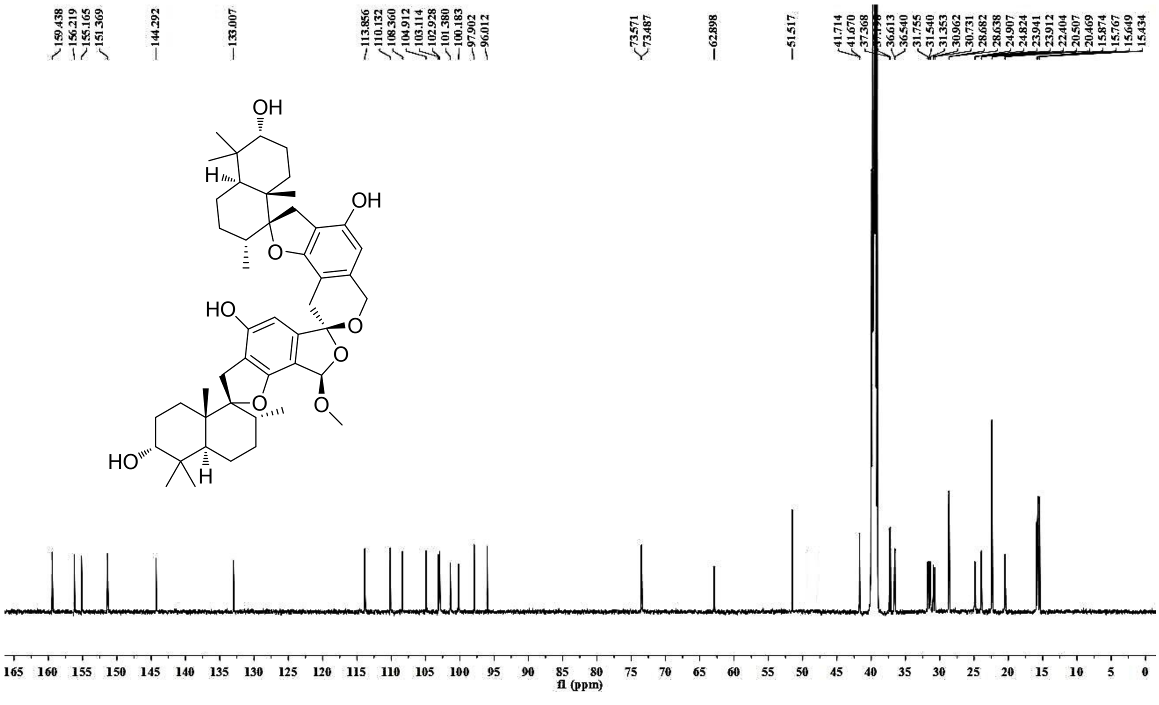


Figure S6. DEPT spectrum of compound **1** in DMSO-*d*$_6$ at 150 MHz

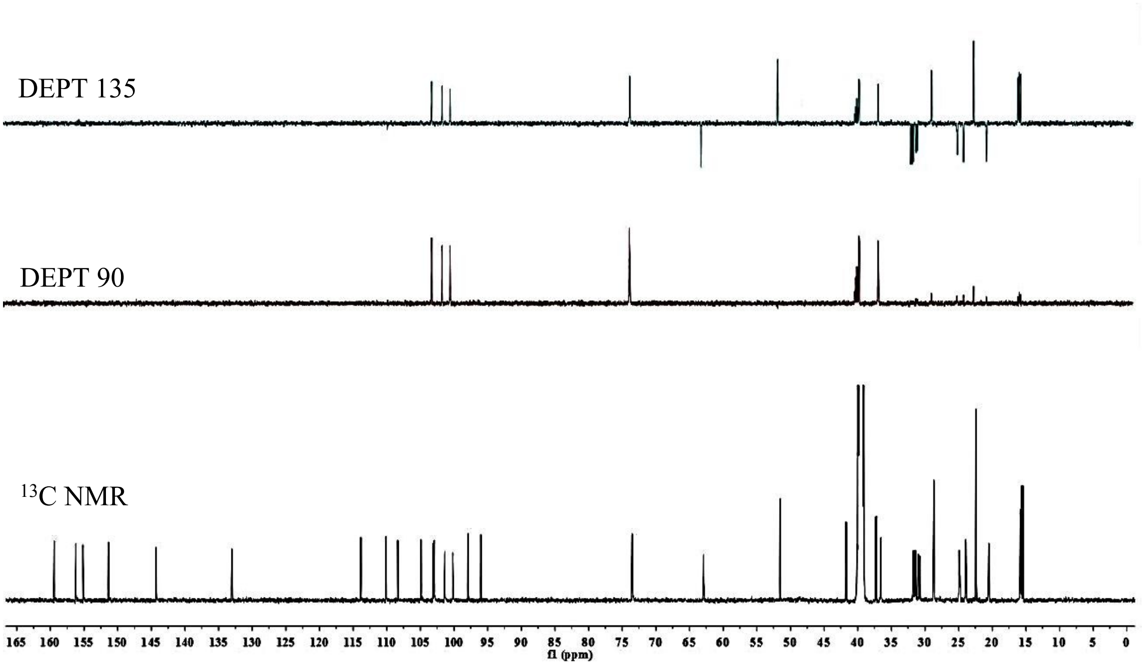


Figure S7. ^{1}H–^{1}H COSY spectrum of compound **1** in DMSO-*d*$_6$

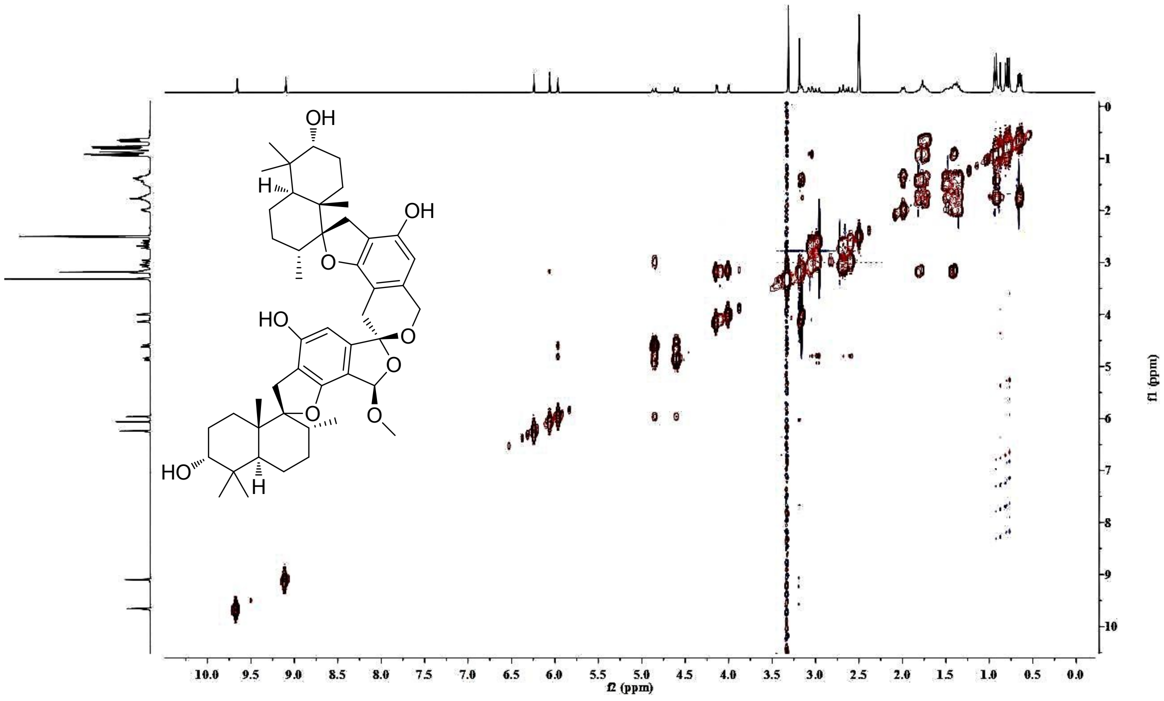


Figure S8. HSQC spectrum of compound **1** in DMSO-d_6

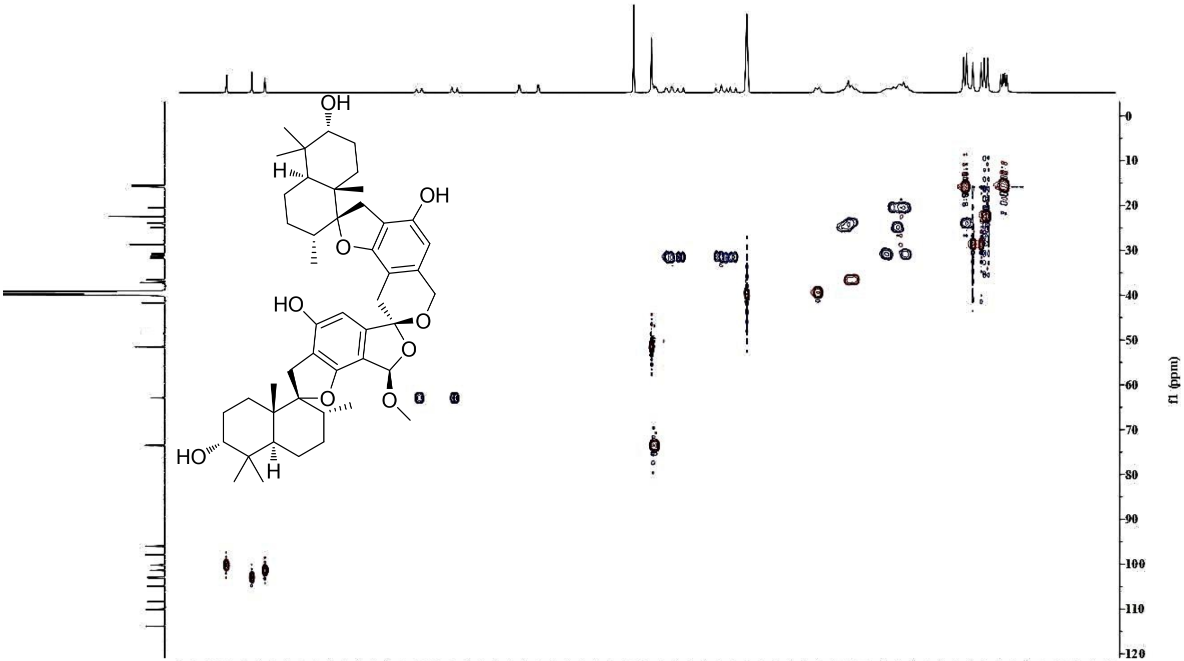


Figure S9. HMBC spectrum of compound **1** in DMSO-d_6

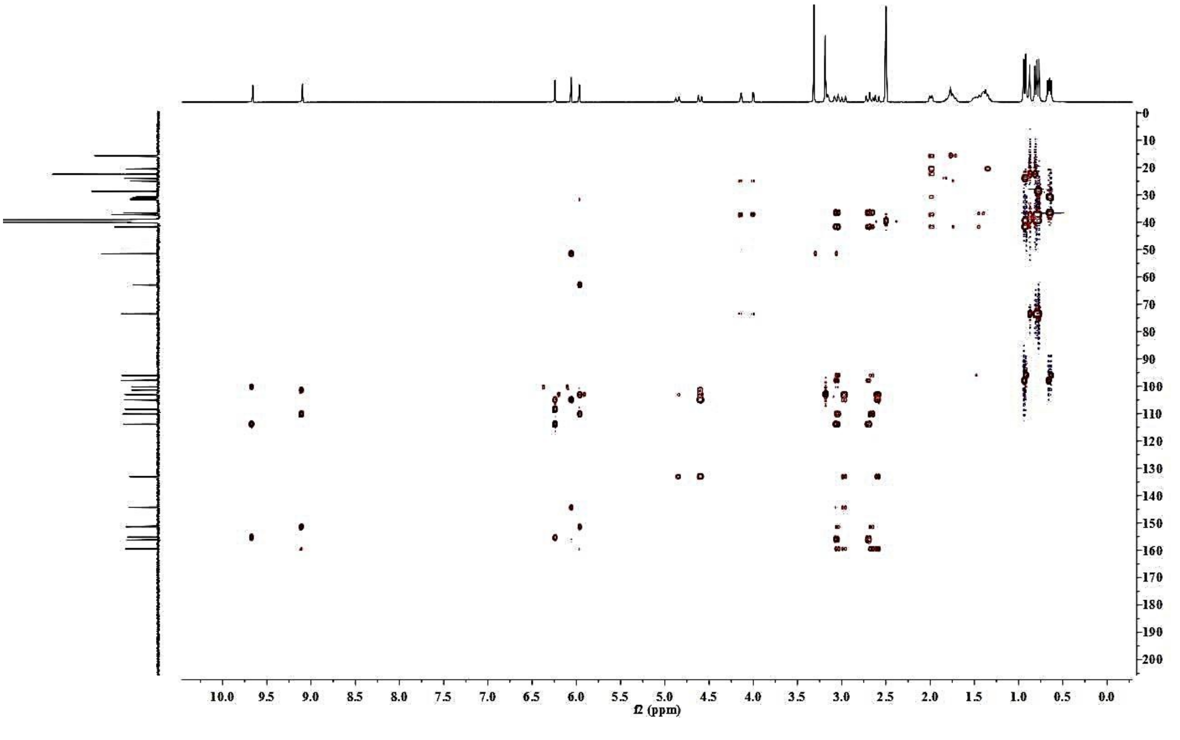


Figure S10. NOE difference spectrum of compound **1** in DMSO-d_6

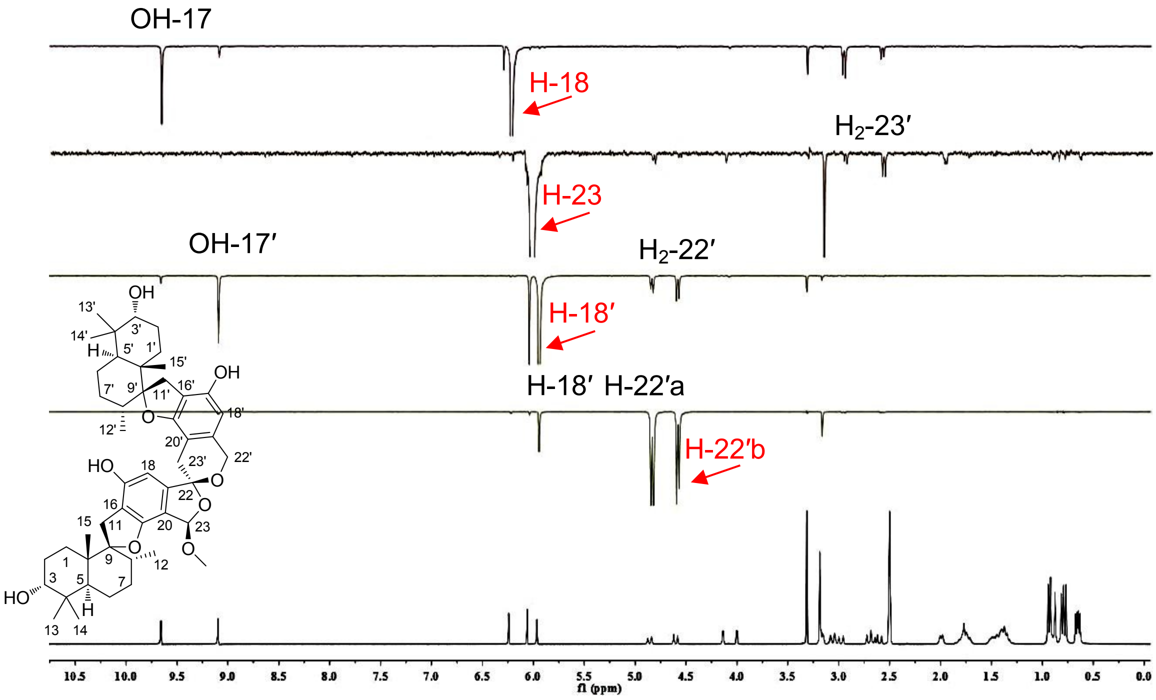


Figure S10. NOE difference spectrum of compound **1** in DMSO-d_6 (continued)

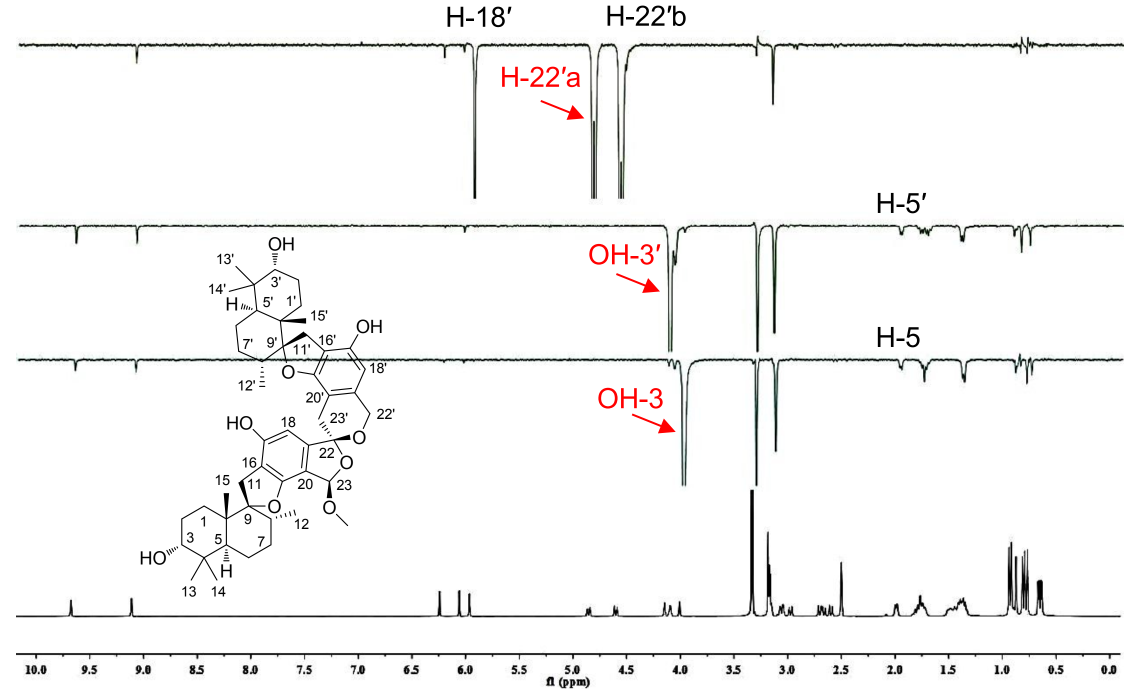


Figure S10. NOE difference spectrum of compound **1** in DMSO-d_6 (continued)

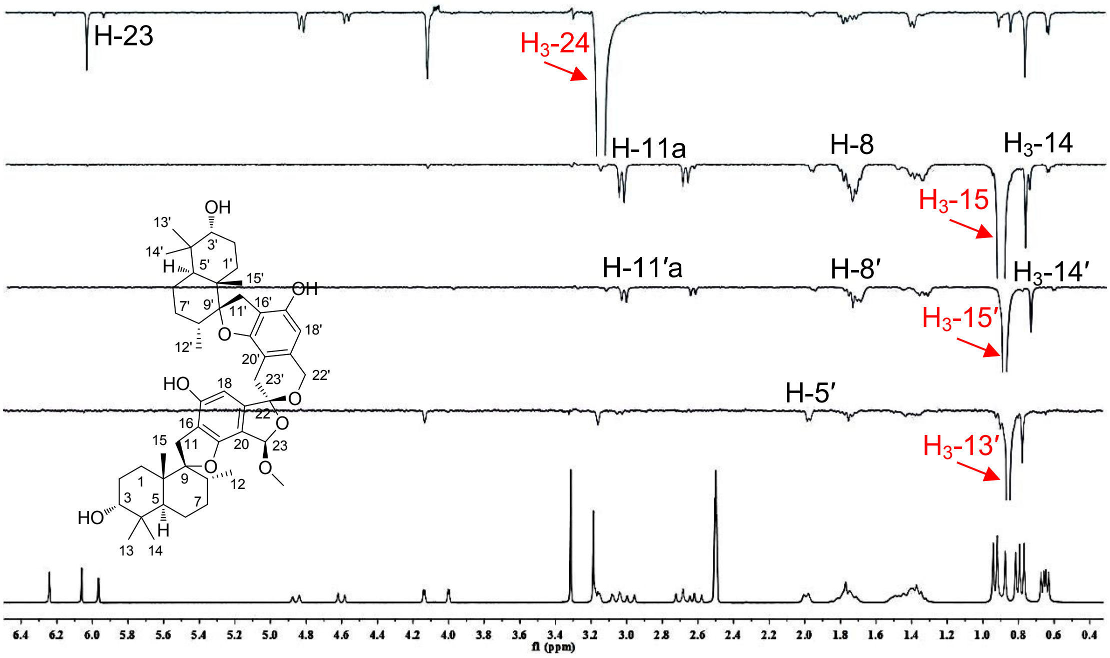


Figure S10. NOE difference spectrum of compound **1** in DMSO-d_6(continued)

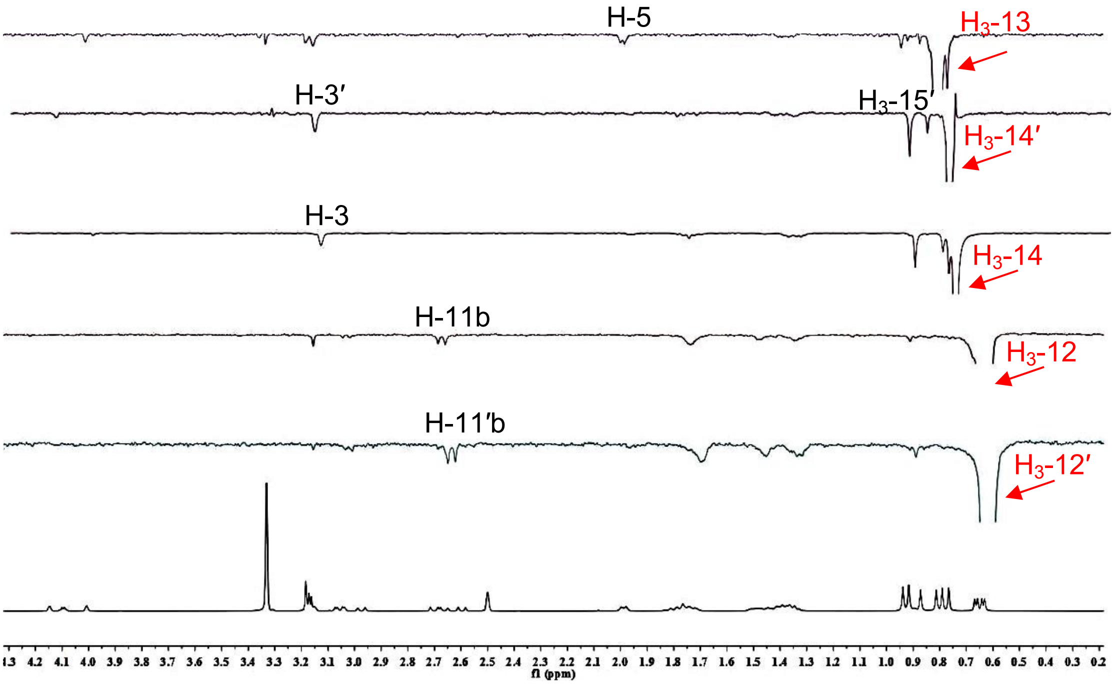


Figure S11. HR-ESI-MS spectrum of compound **1**

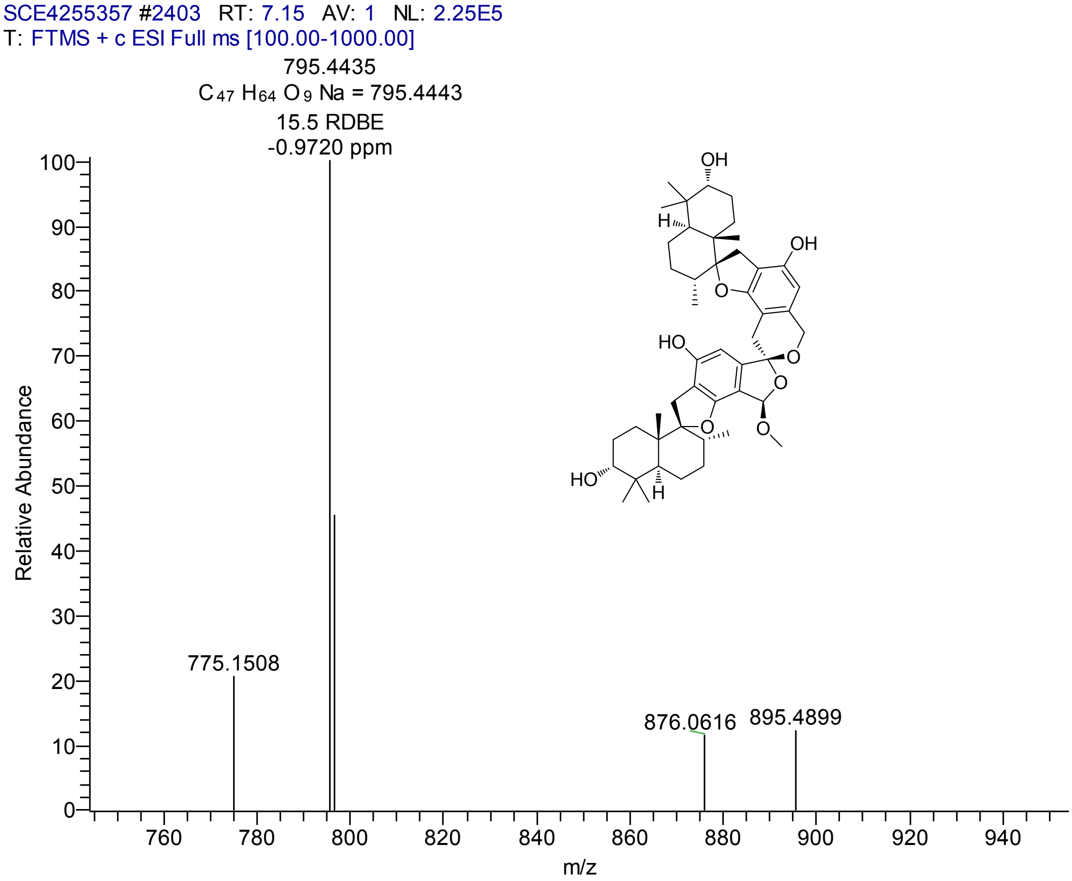
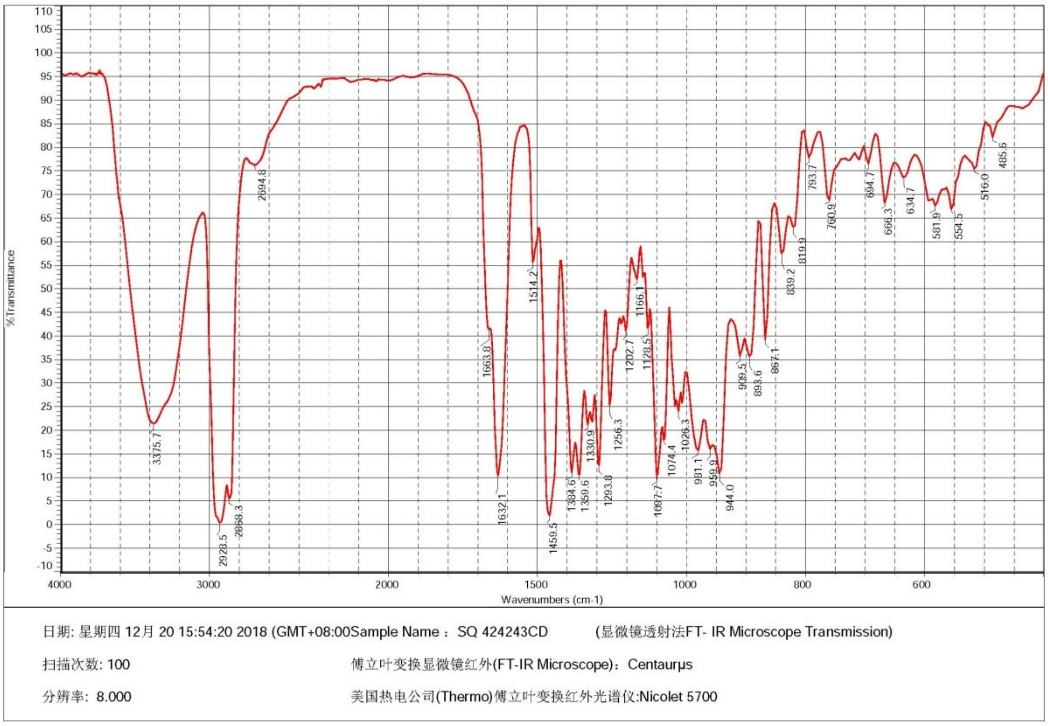


Figure S12. IR spectrum of compound **1**



日期: 星期四 12月 20 15:54:20 2018 (GMT+08:00Sample Name： SQ 424243CD (显微镜透射法FT- IR Microscope Transmission)

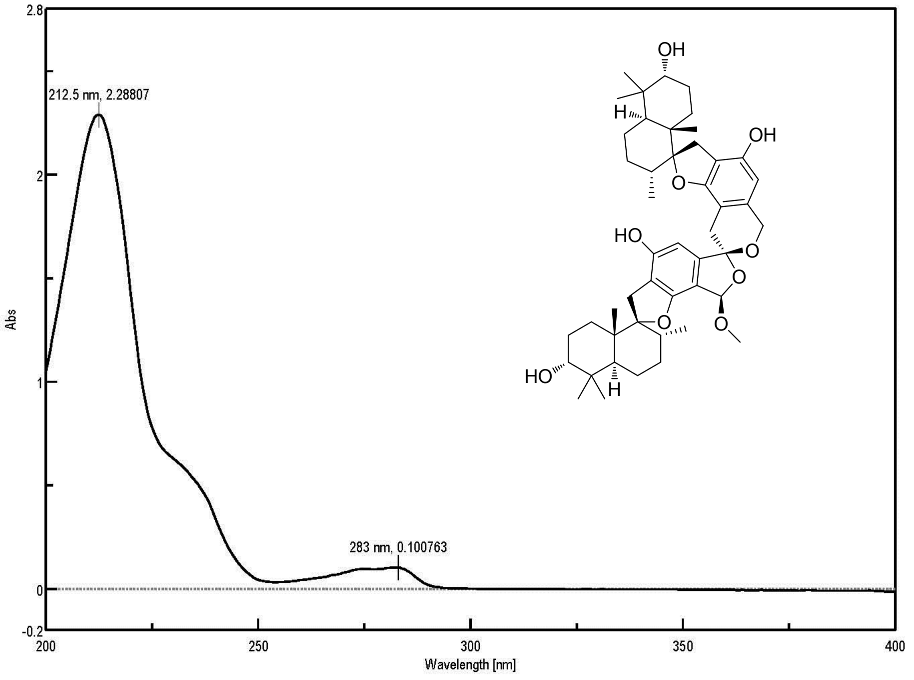
扫描次数: 100

傅立叶变换显微镜红外(FT-IR Microscope)：Centaurμs

分辨率: 8.000

美国热电公司(Thermo)傅立叶变换红外光谱仪:Nicolet 5700

Figure S13. UV spectrum of compound **1**



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Start Mode	Immediately
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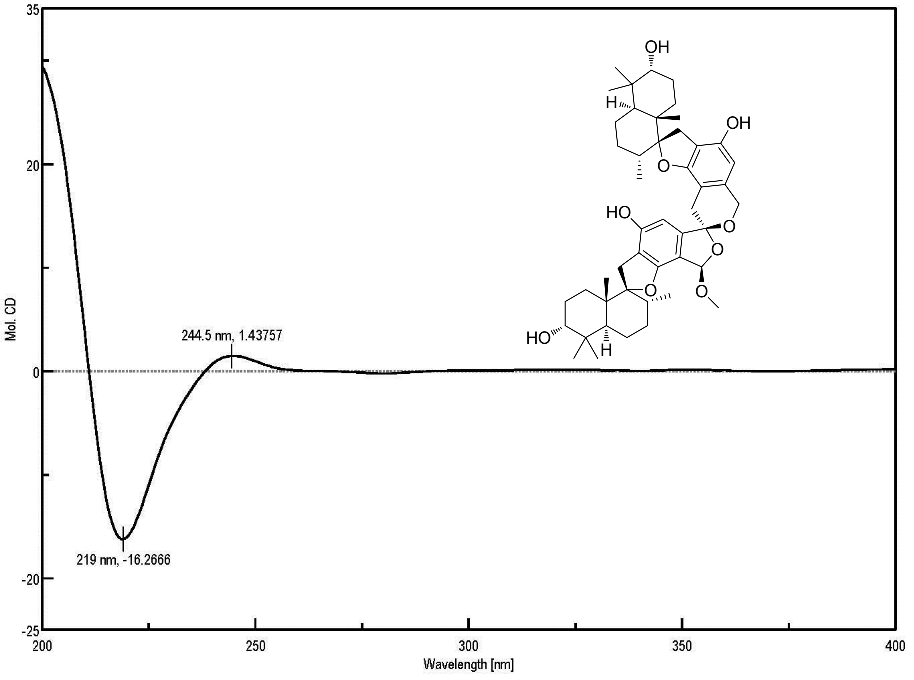
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.2 (w/v)%

Figure S14. ECD spectrum of compound **1**



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Model Name	J-815
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D.I.T.	1 sec
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Start Mode	Immediately
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Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.2 (w/v)%

Figure S15. ^{1}H NMR spectrum of compound **2** in DMSO-d_6 at 600 MHz

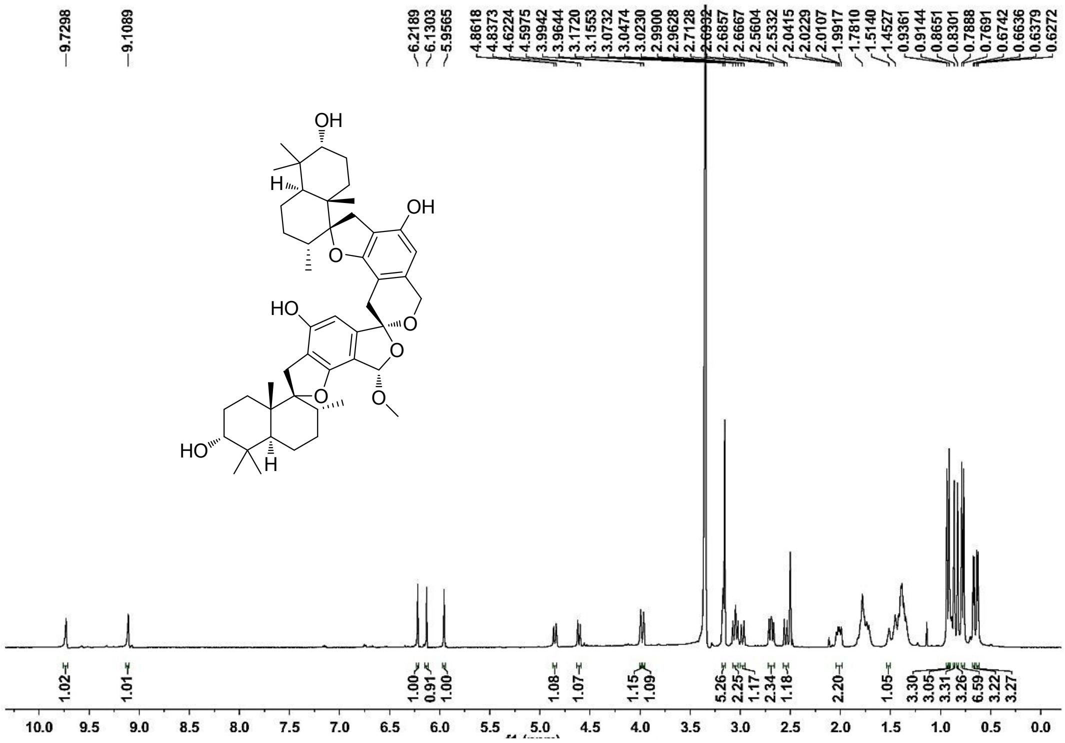


Figure S16. ^{13}C NMR spectrum of compound **2** in DMSO-d_6 at 150 MHz

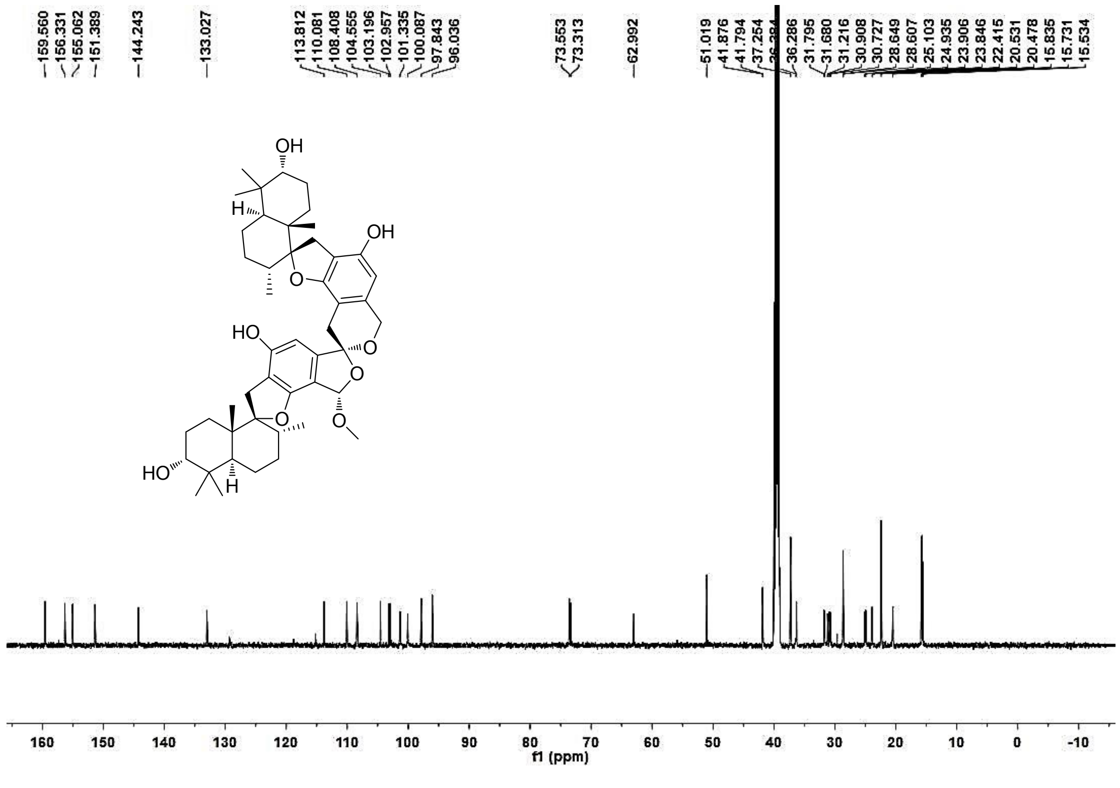


Figure S17. DEPT spectrum of compound **2** in DMSO-d_6 at 150 MHz

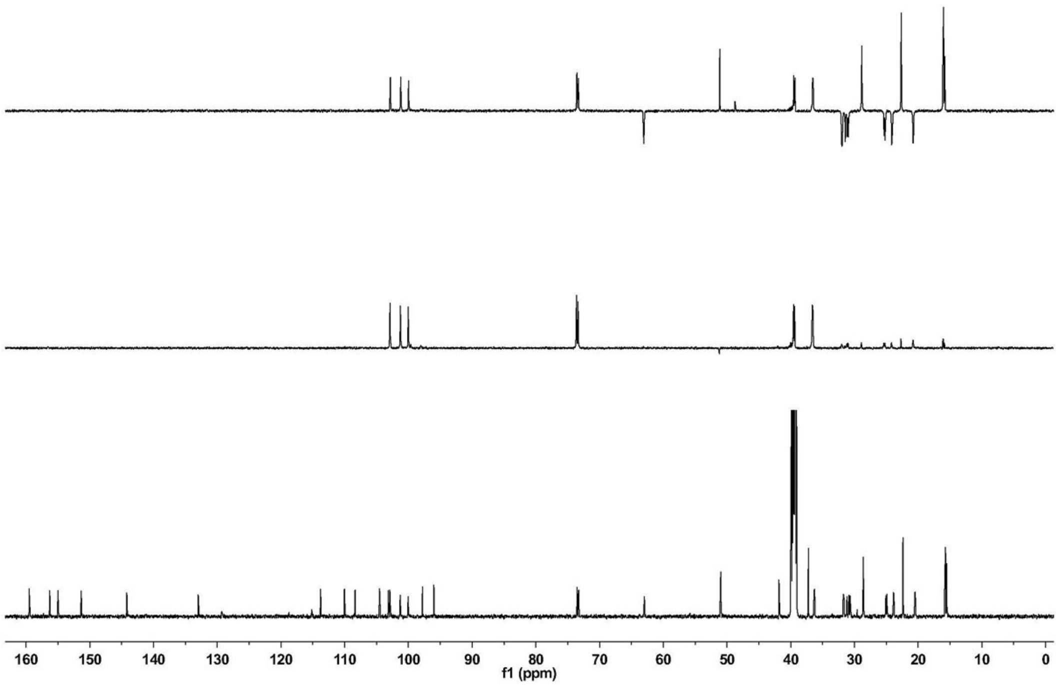


Figure S18. ^{1}H–^{1}H COSY spectrum of compound **2** in DMSO-d_6

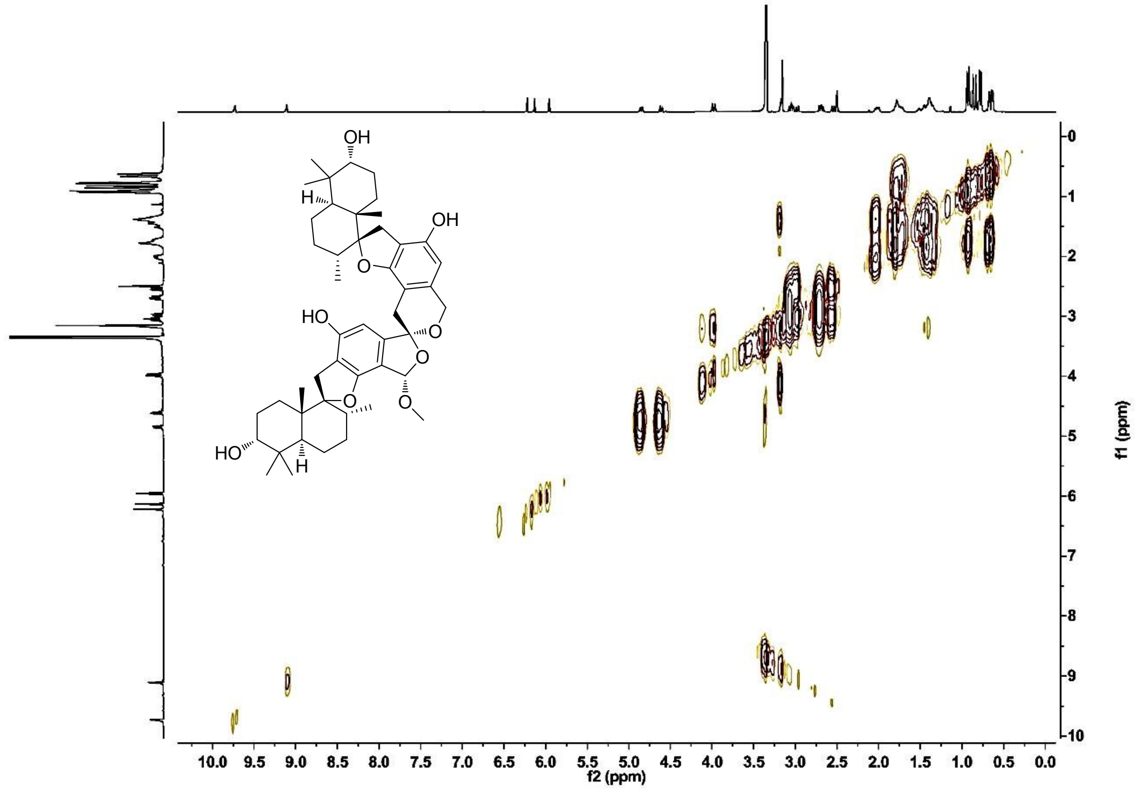


Figure S19. HSQC spectrum of compound **2** in DMSO-d_6

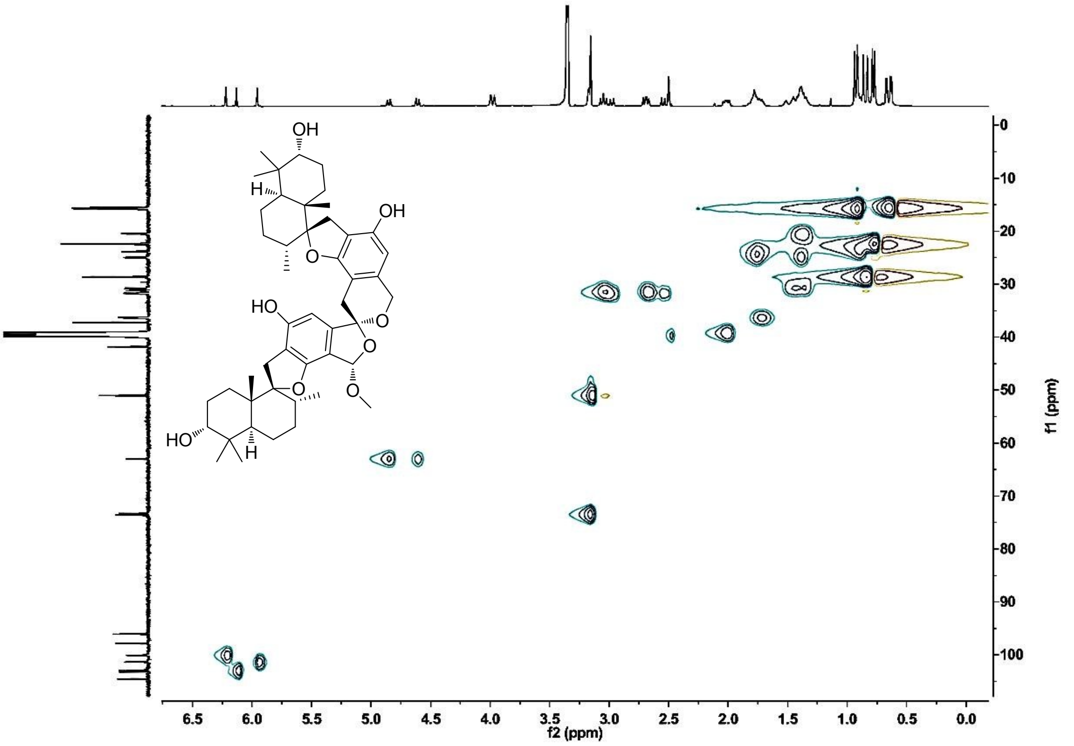


Figure S20. HMBC spectrum of compound **2** in DMSO-d_6

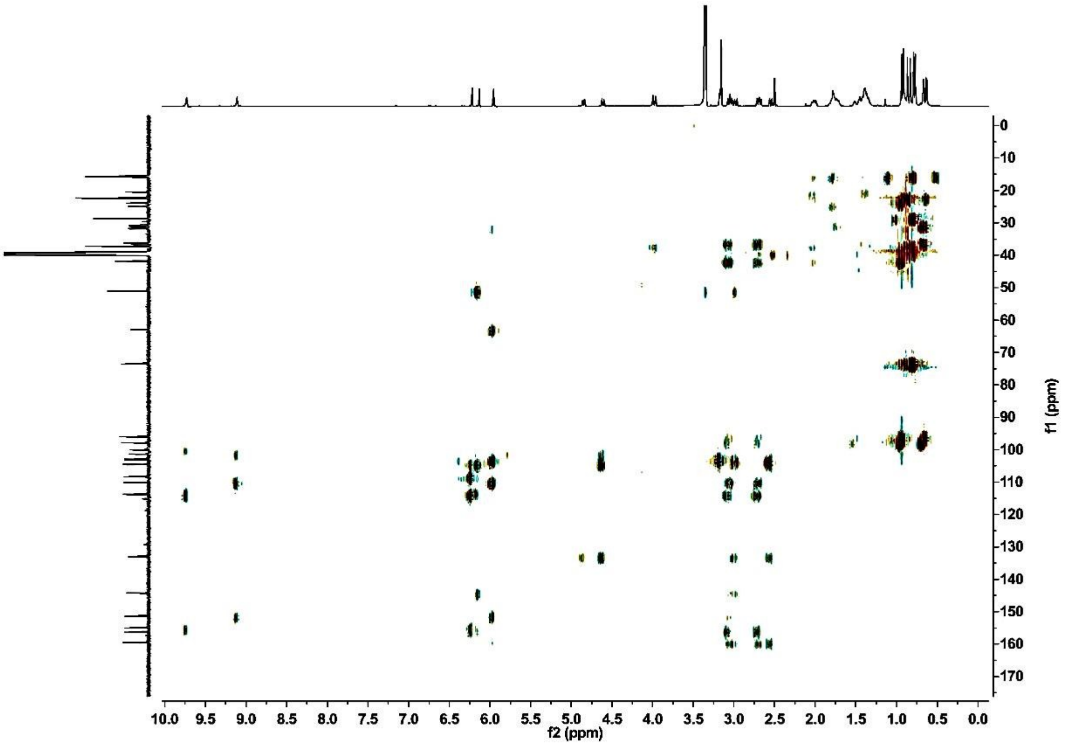


Figure S21. NOE difference spectrum of compound **2** in DMSO-d_6

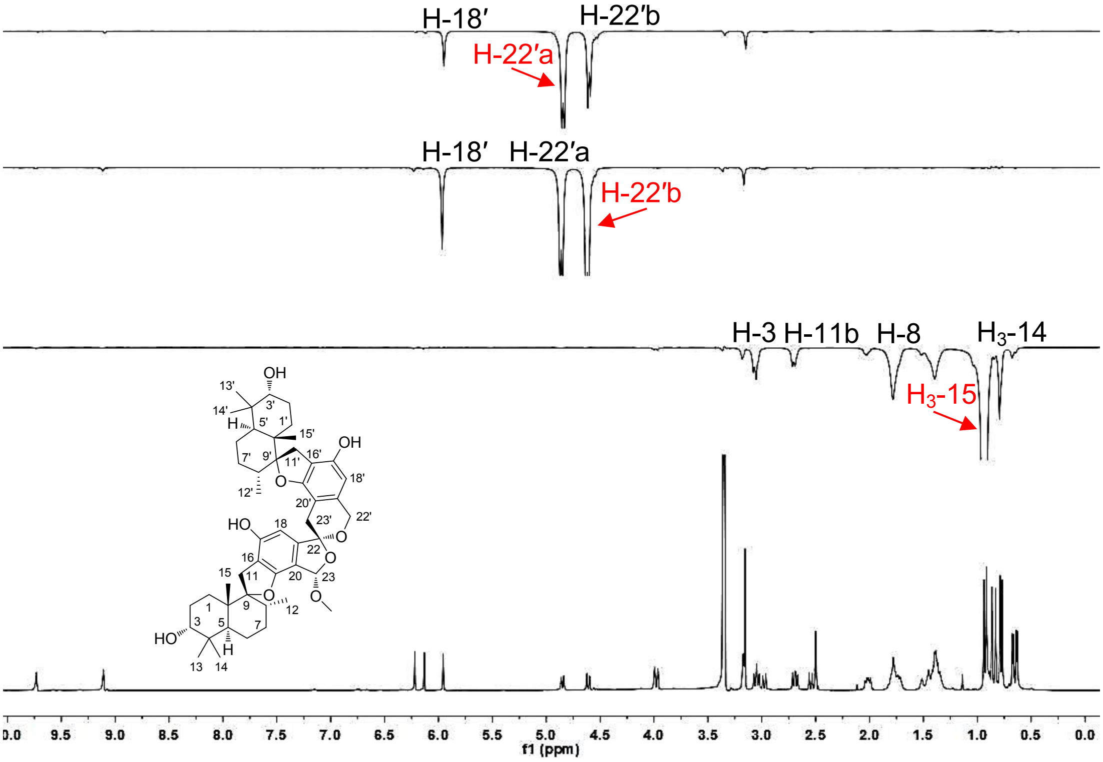


Figure S21. NOE difference spectrum of compound **2** in DMSO-d_6(continued)

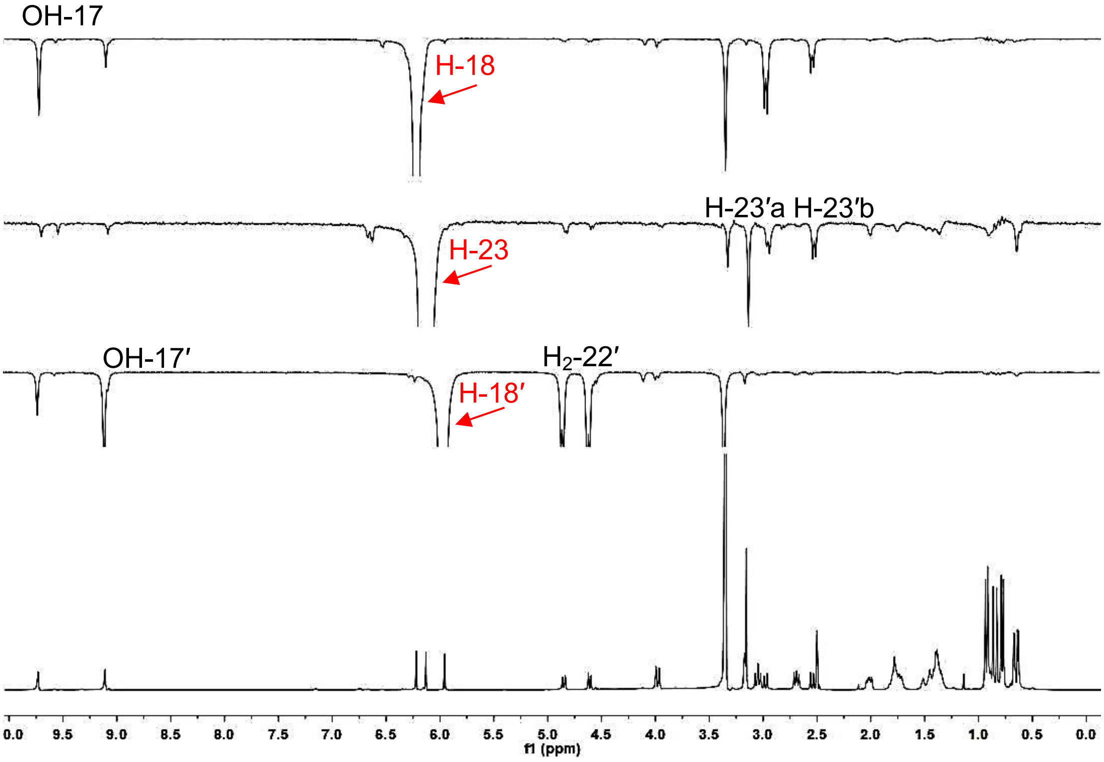


Figure S22. HR-ESI-MS spectrum of compound **2**

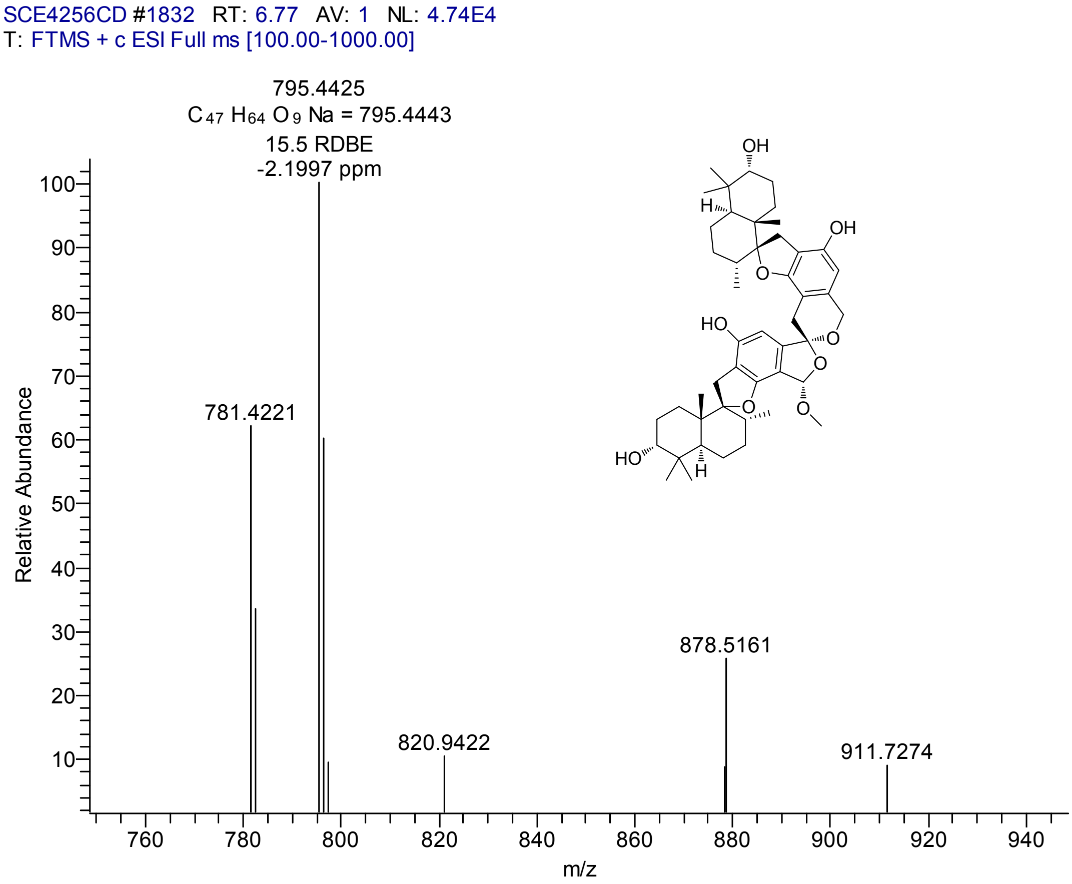
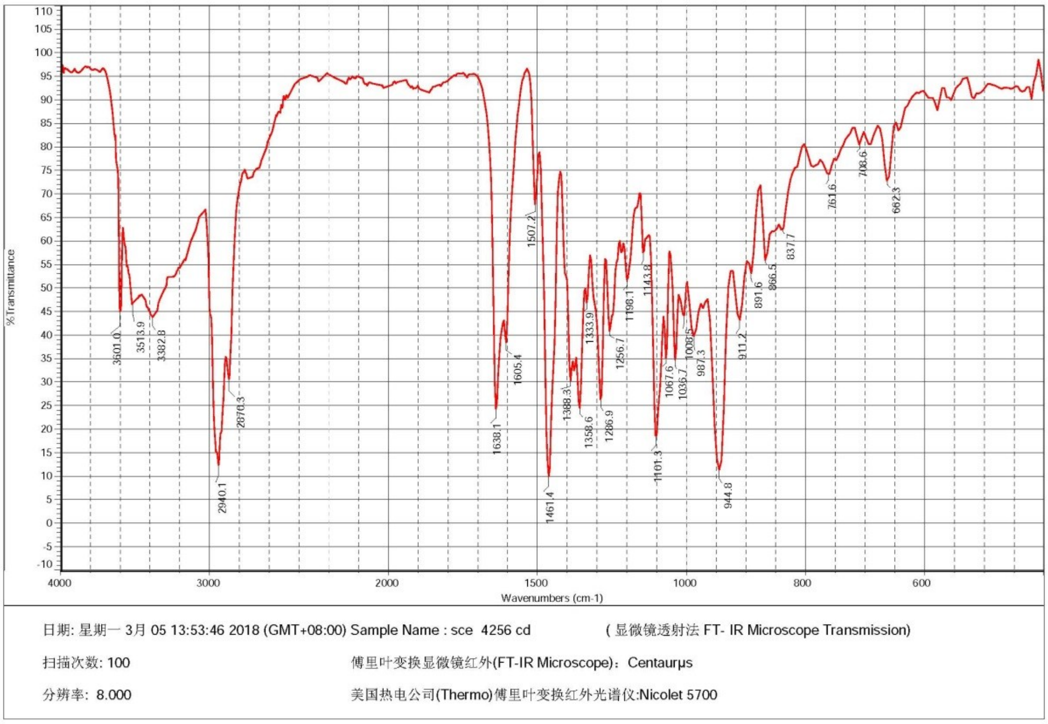


Figure S23. IR spectrum of compound **2**

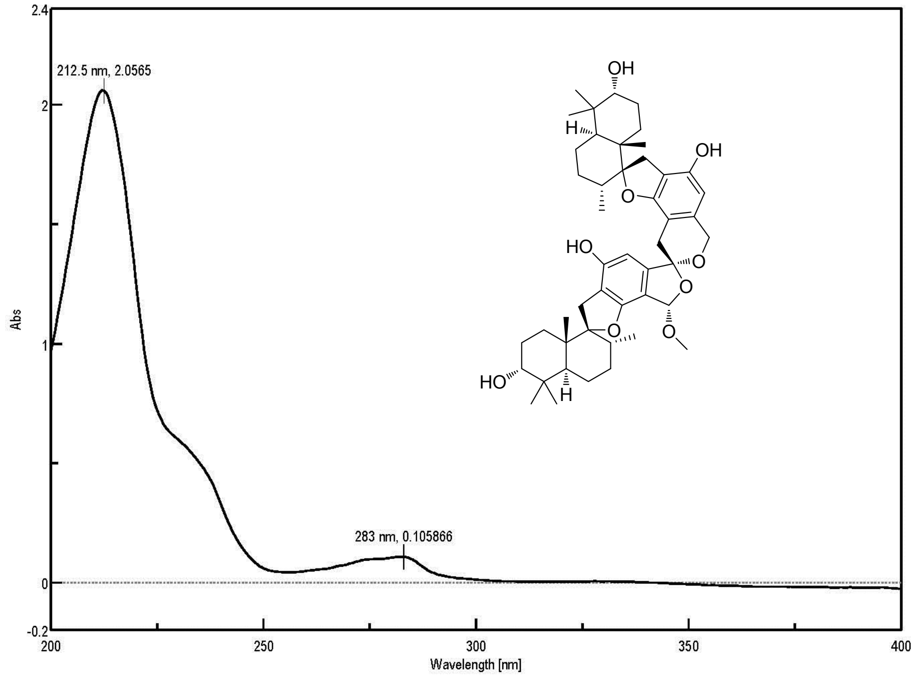


日期: 星期一 3月 05 13:53:46 2018 (GMT+08:00) Sample Name : sce 4256 cd (显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100 傅里叶变换显微镜红外(FT-IR Microscope)：Centaurμs

分辨率: 8.000 美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

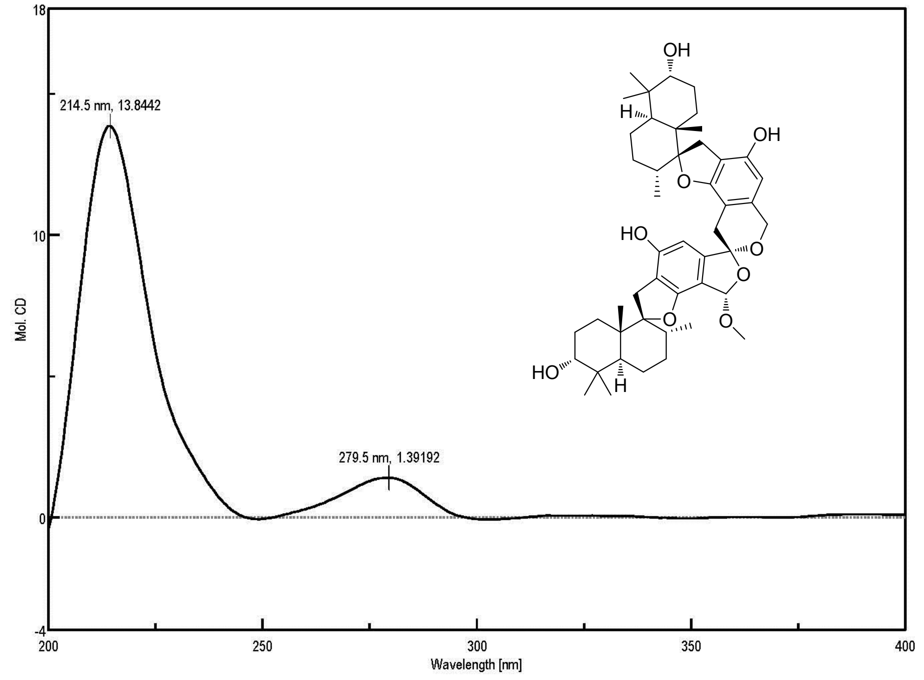
Figure S24. UV spectrum of compound **2**



[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2018/10/12 10:55
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.3 (w/v)%

Figure S25. ECD spectrum of compound **2**



[Measurement Information]	
Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2018/10/12 10:55
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.3 (w/v)%

Figure S26. ^{1}H NMR spectrum of compound **3** in acetone-d_6 at 500 MHz

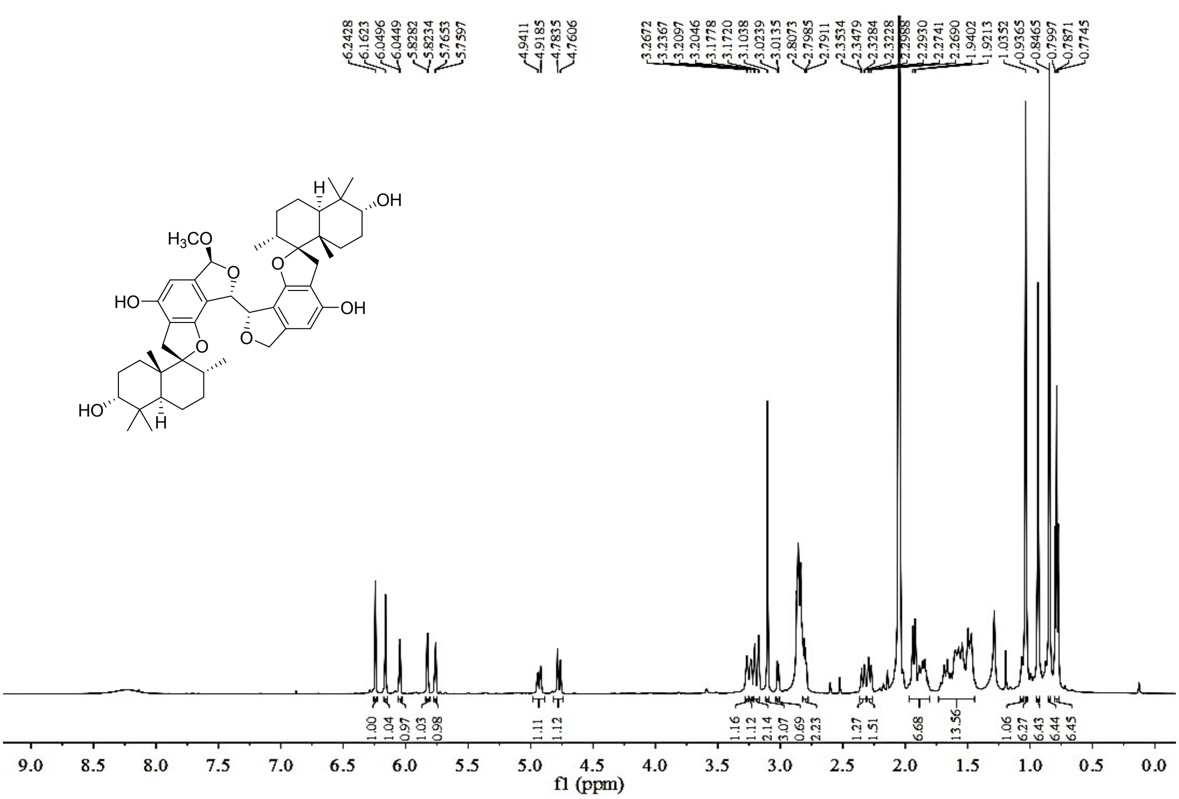


Figure S27. ^{13}C NMR spectrum of compound **3** in acetone-d_6 at 125 MHz

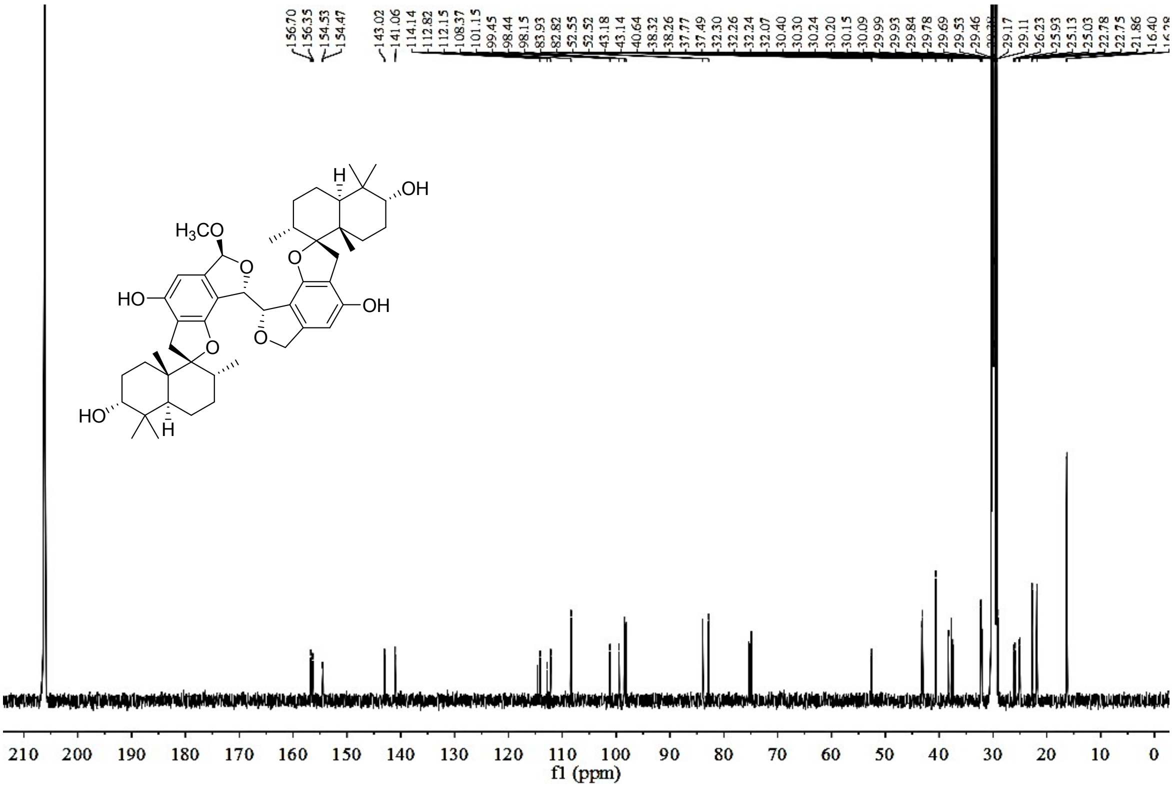


Figure S28. DEPT spectrum of compound **3** in acetone-d_6 at 125 MHz

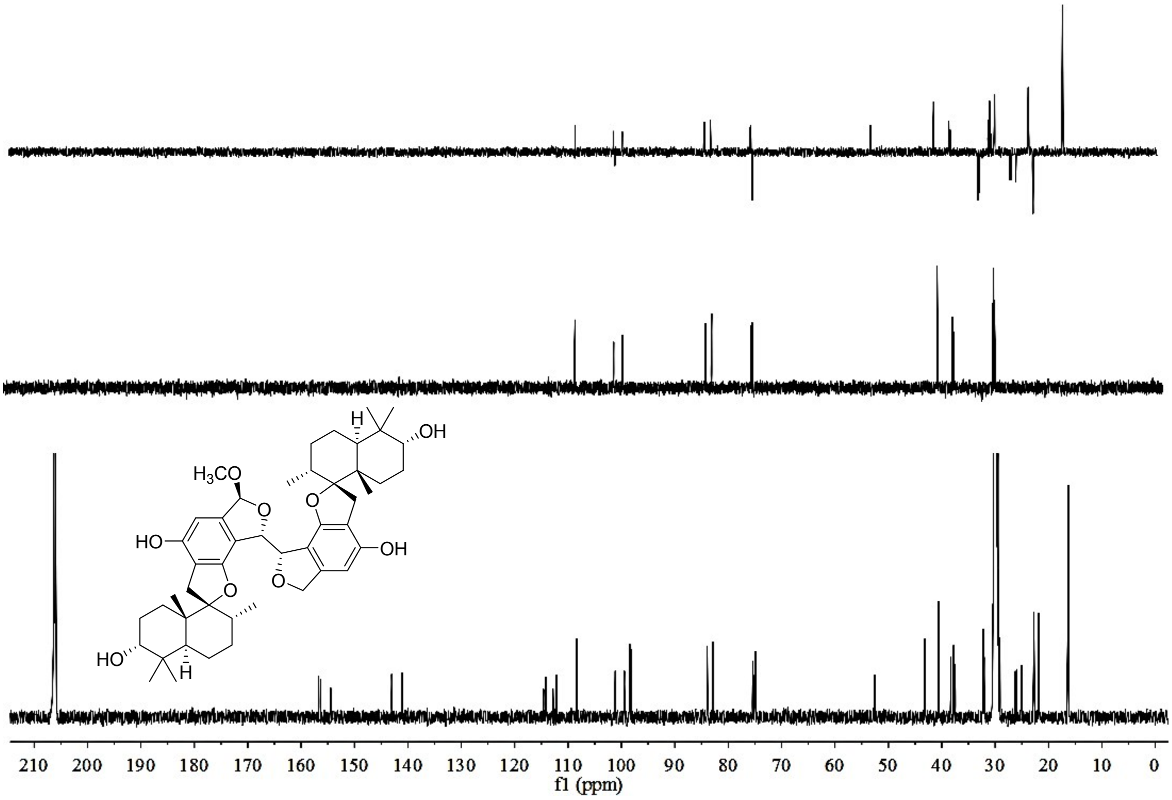


Figure S29. ^{1}H−^{1}H COSY spectrum of compound **3** in acetone-d_6

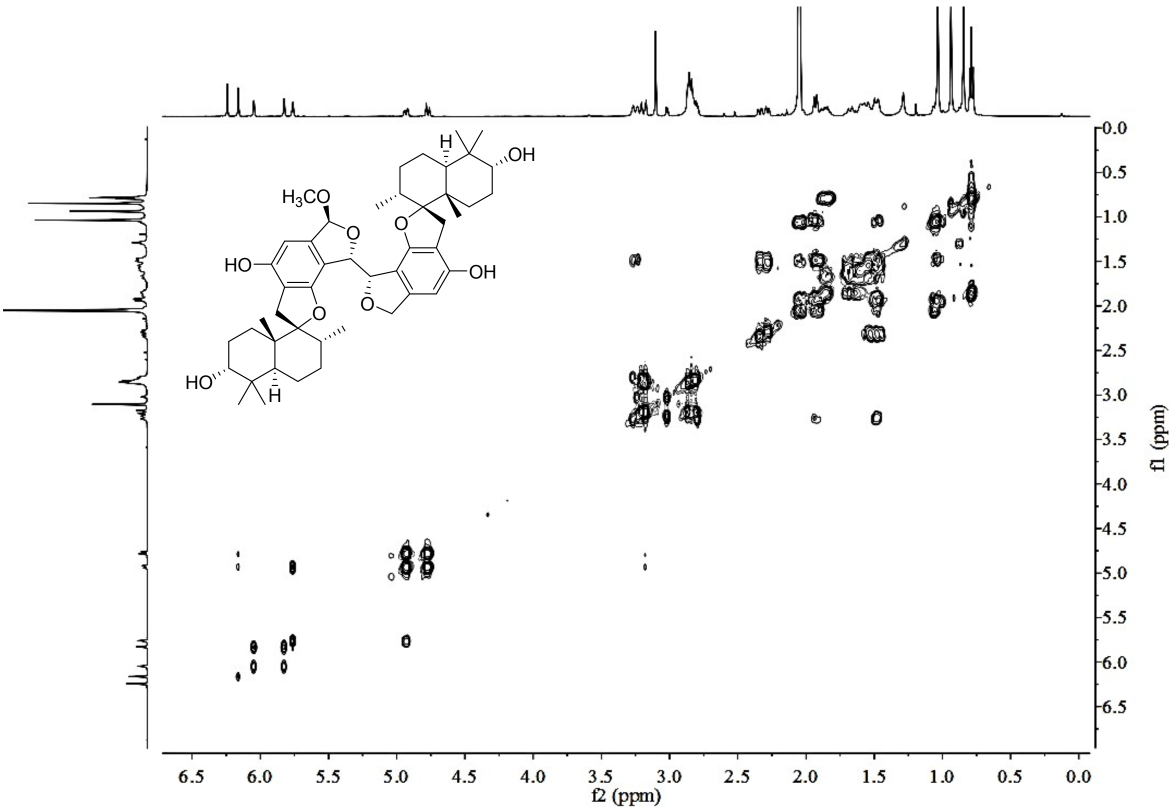


Figure S30. HSQC spectrum of compound **3** in acetone-d_6

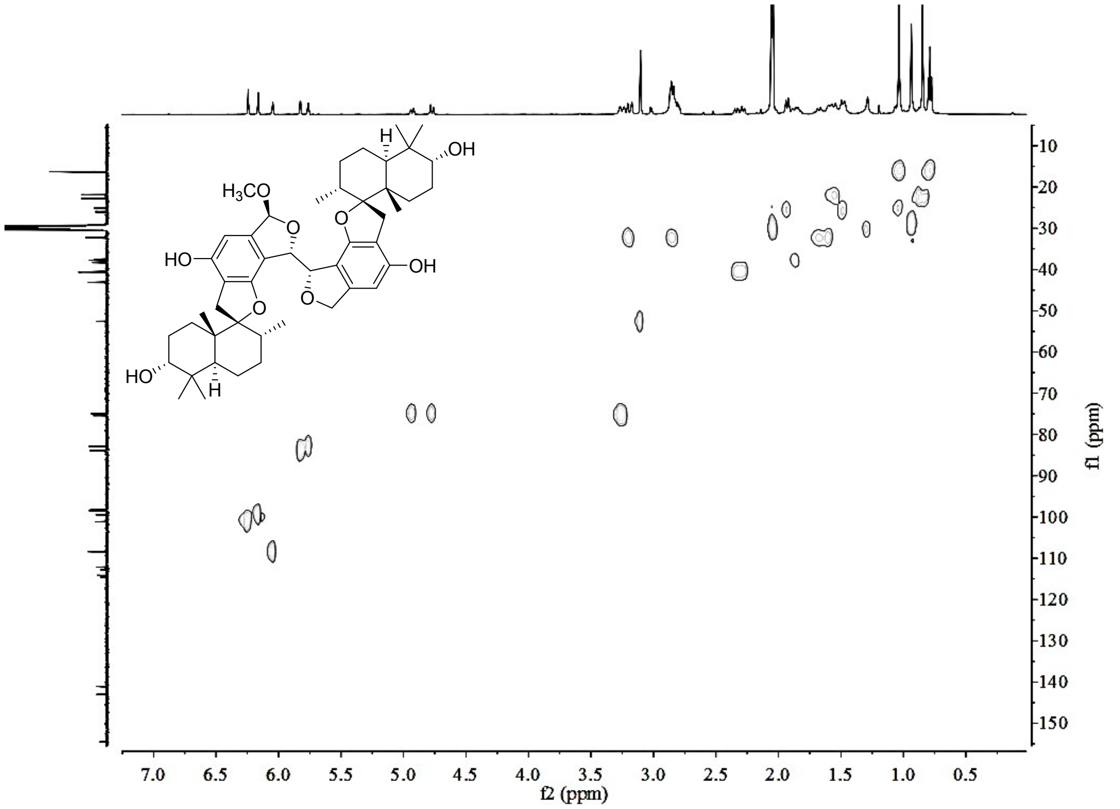


Figure S31. HMBC spectrum of compound **3** in acetone-d_6

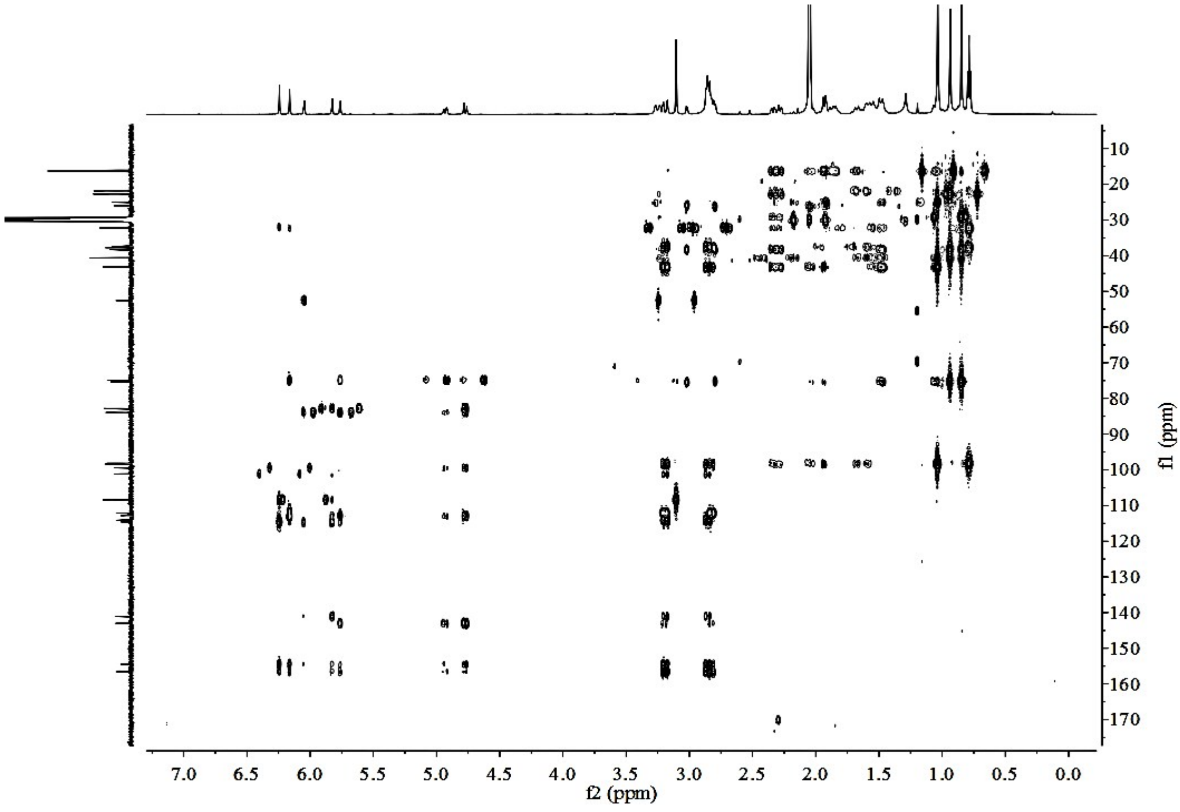


Figure S32. NOE difference spectrum of compound **3** in acetone-d_6

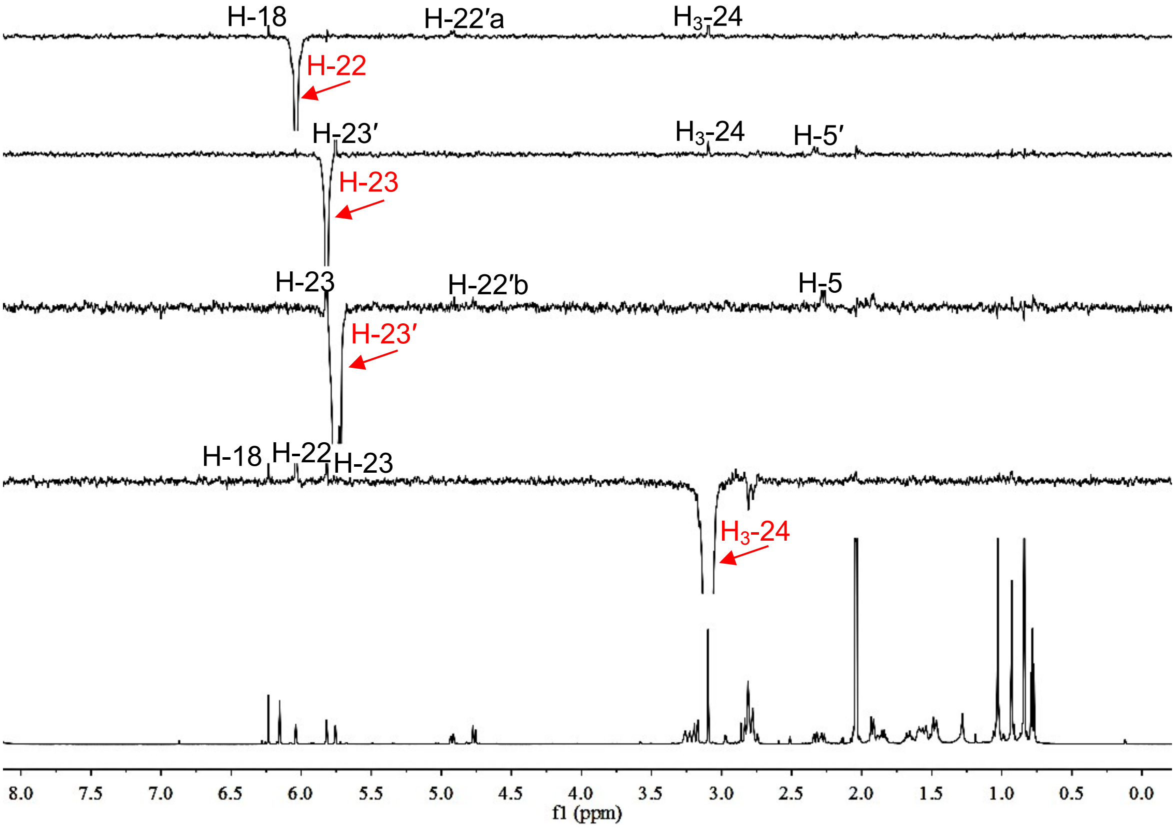


Figure S32. NOE difference spectrum of compound **3** in acetone-d_6 (continued)

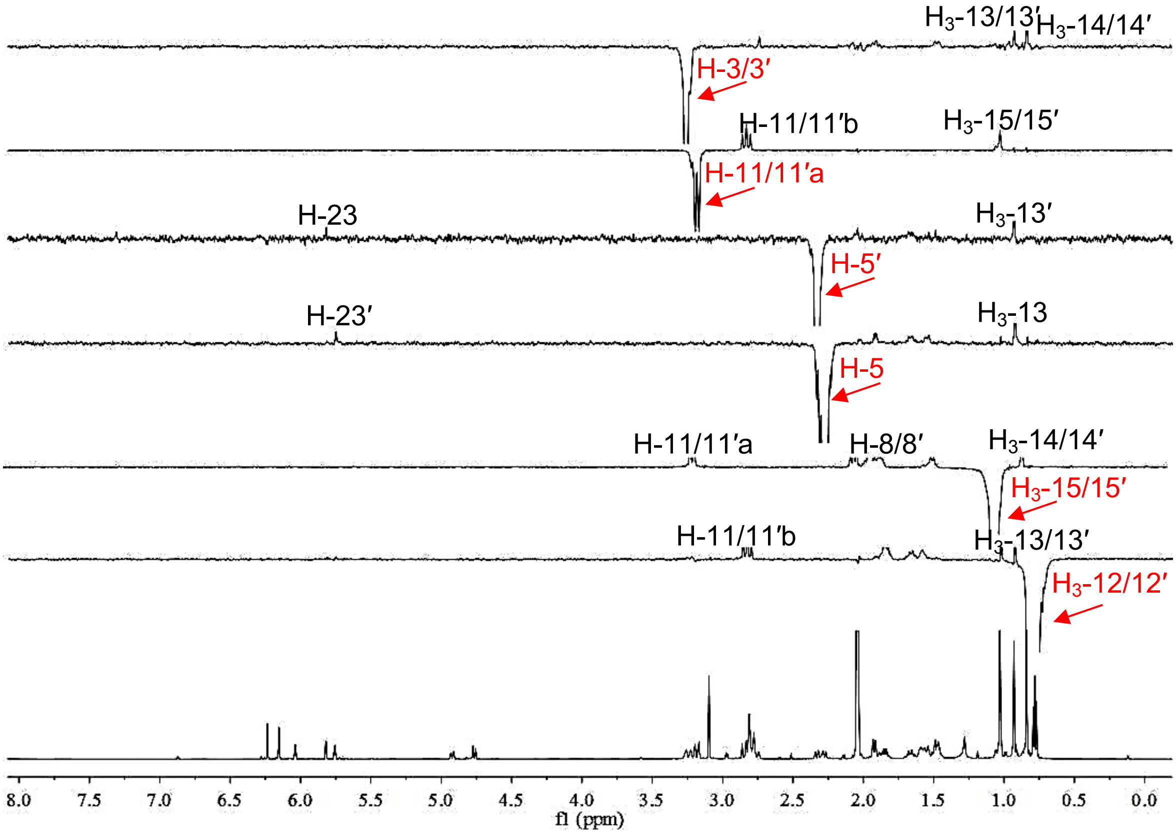


Figure S33. HR-ESI-MS spectrum of compound **3**

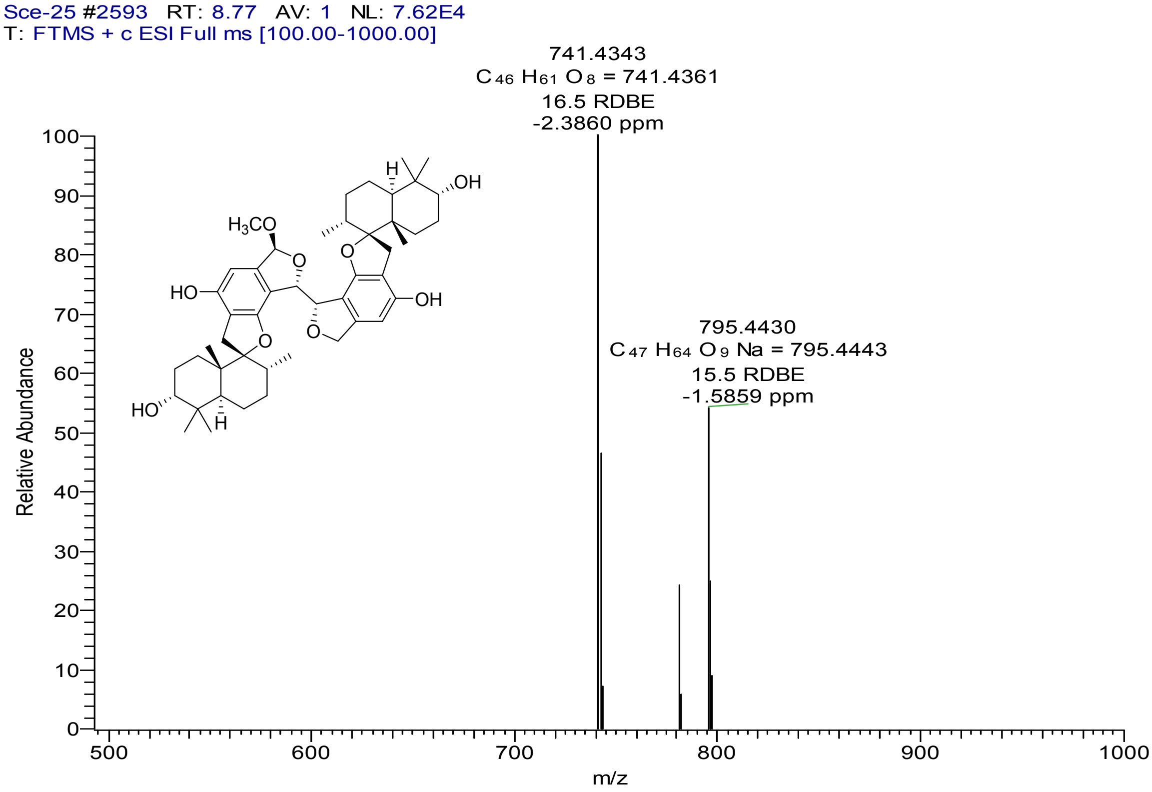
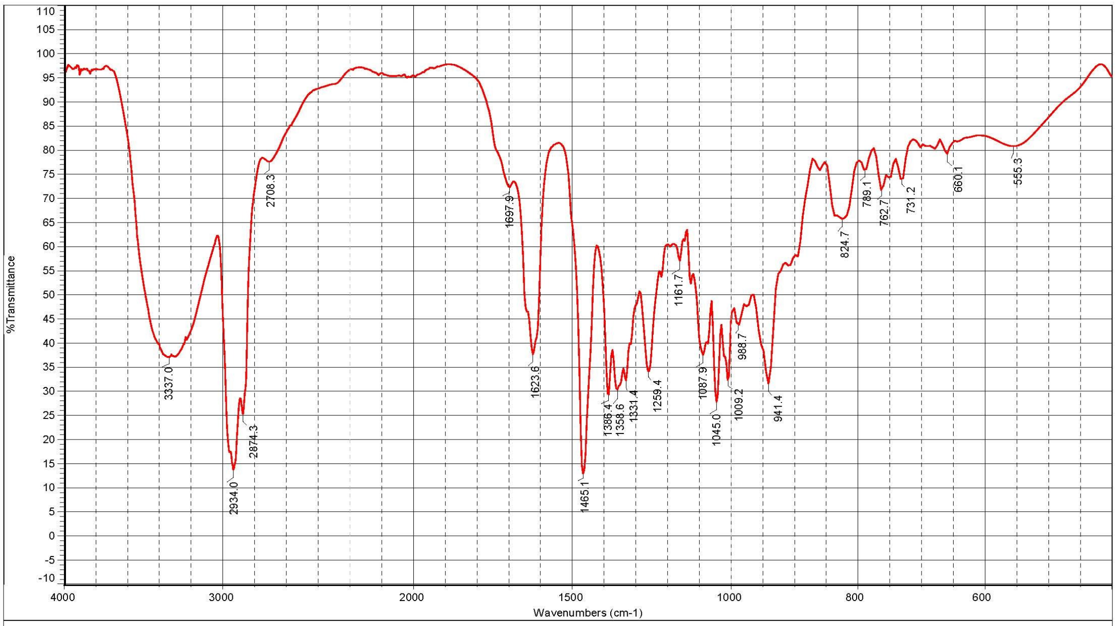


Figure S34. IR spectrum of compound **3**

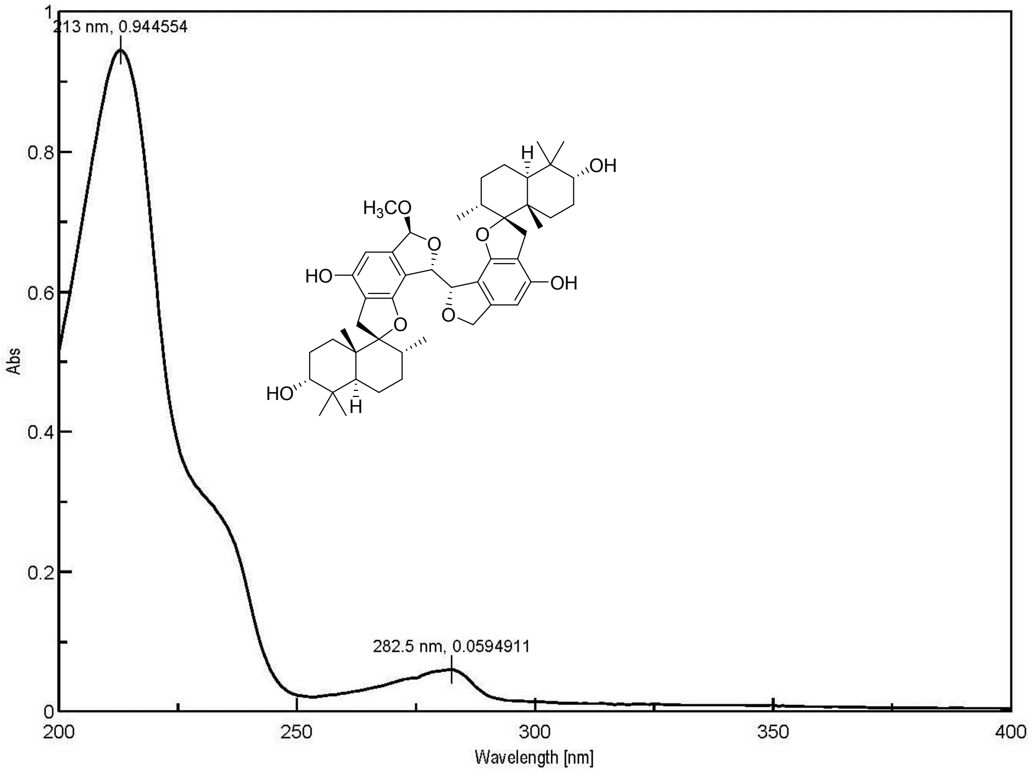


日期: 星期四 12月 29 10:33:34 2016 (GMT+08:00Sample Name：Sce - 25　　(显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100　　傅里叶变换红外显微镜(FT-IR Microscope)：Centaurμs

分辨率: 8.000　　美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

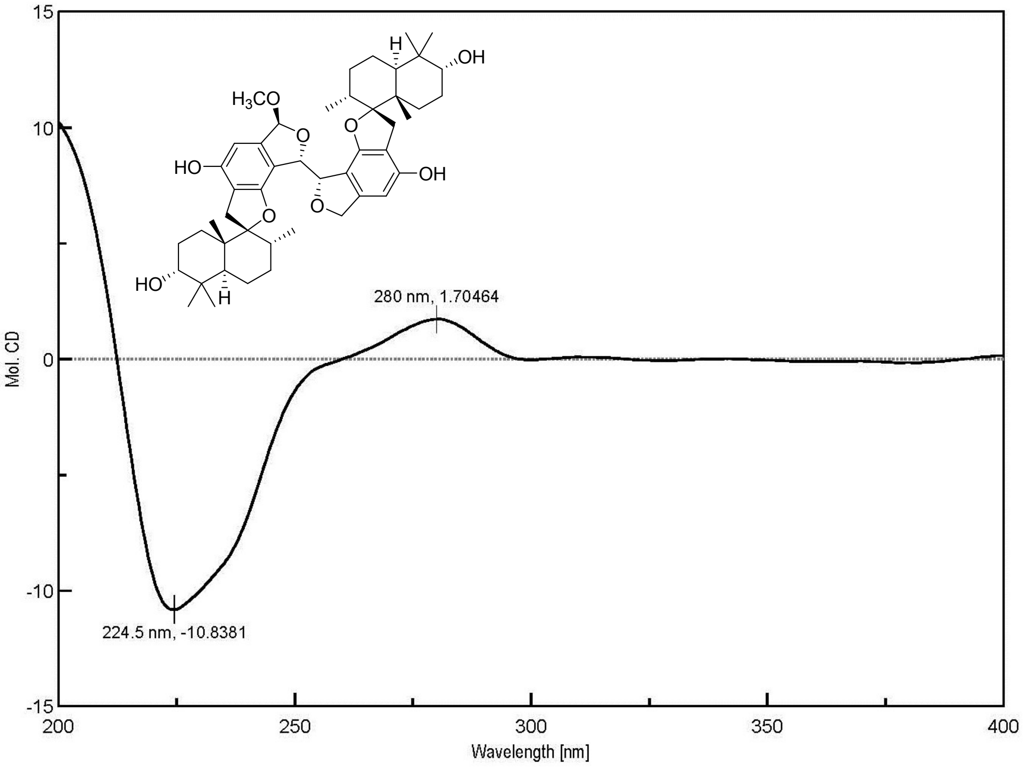
Figure S35. UV spectrum of compound **3**



[Measurement Information]

Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 16:59
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S36. ECD spectrum of compound **3**



[Measurement Information]

Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 16:59
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S37. ^{1}H NMR spectrum of compound **4** in acetone-d_6 at 600 MHz

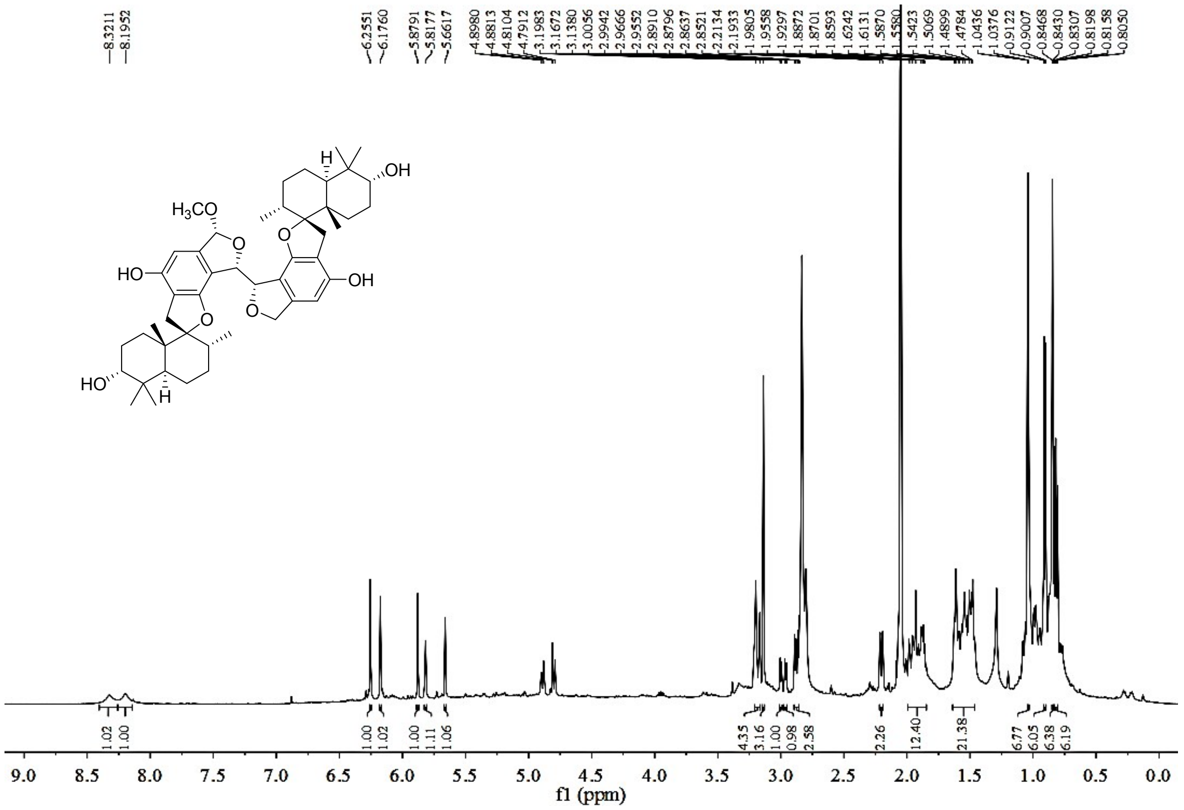


Figure S38. ^{13}C NMR spectrum of compound **4** in acetone-d_6 at 150 MHz

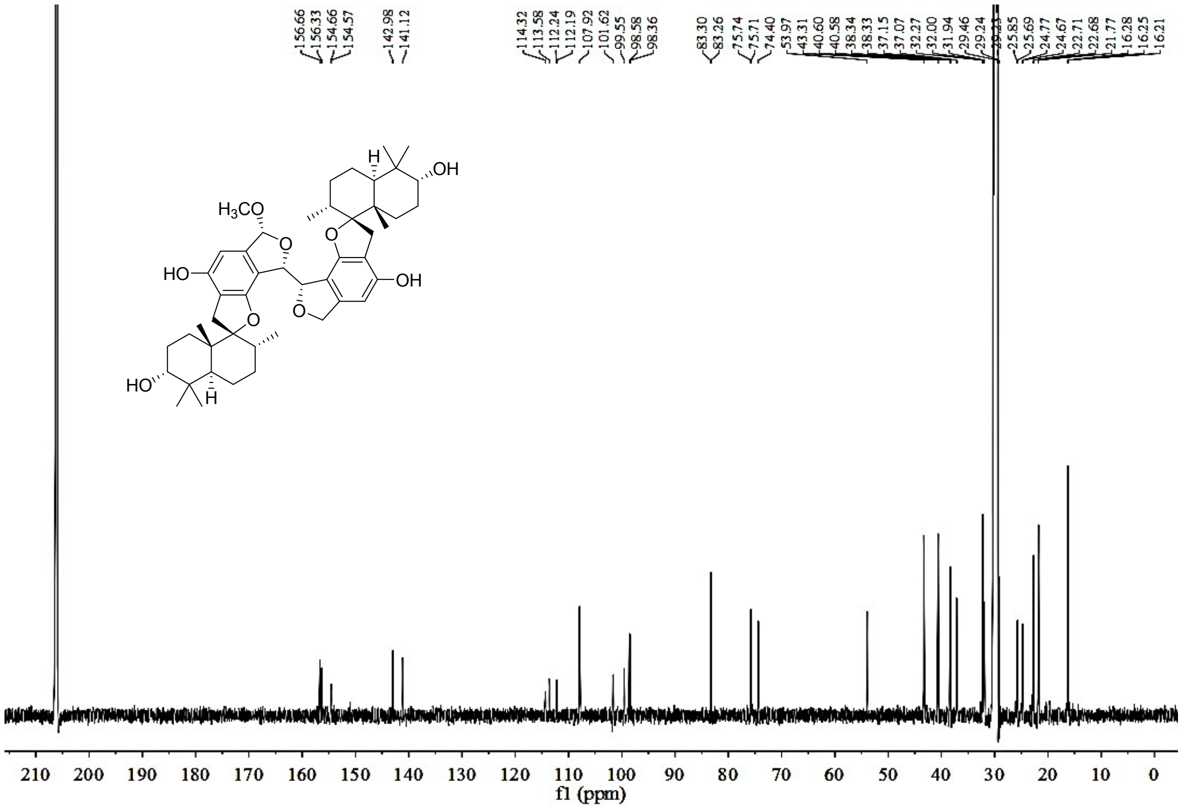


Figure S39. DEPT spectrum of compound **4** in acetone-d_6 at 150 MHz

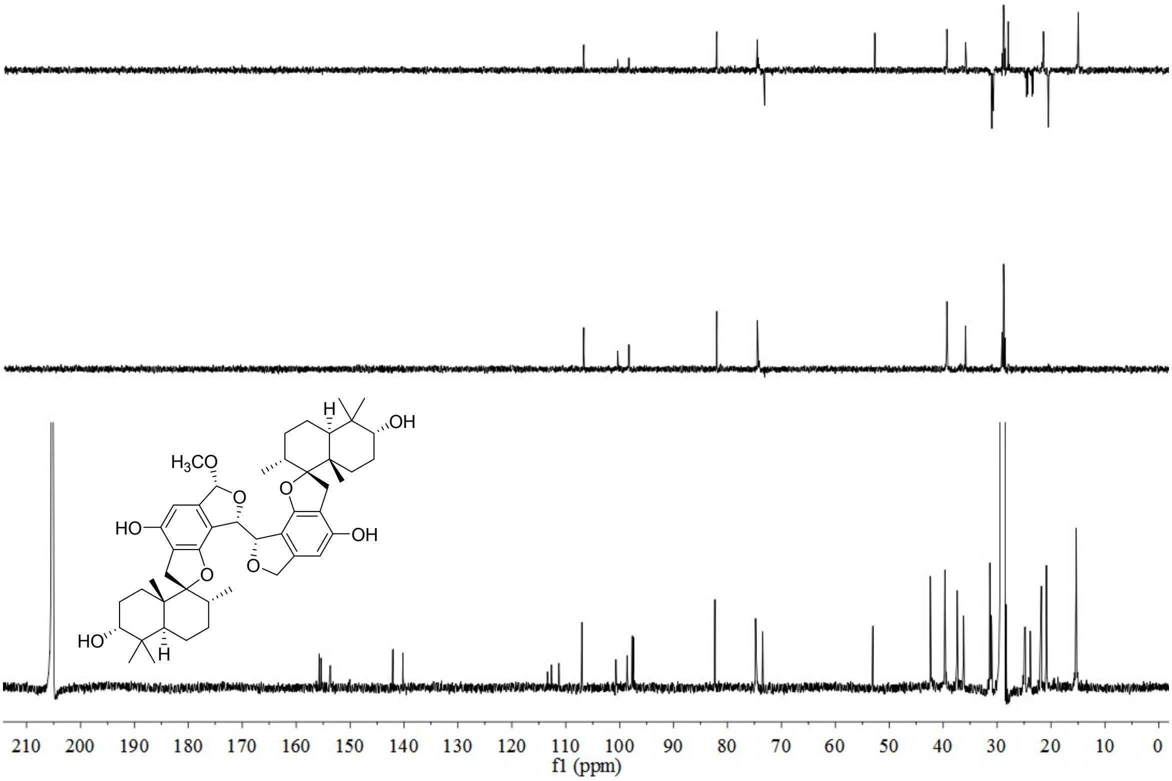


Figure S40. ^1H–^1H COSY spectrum of compound **4** in acetone-d_6

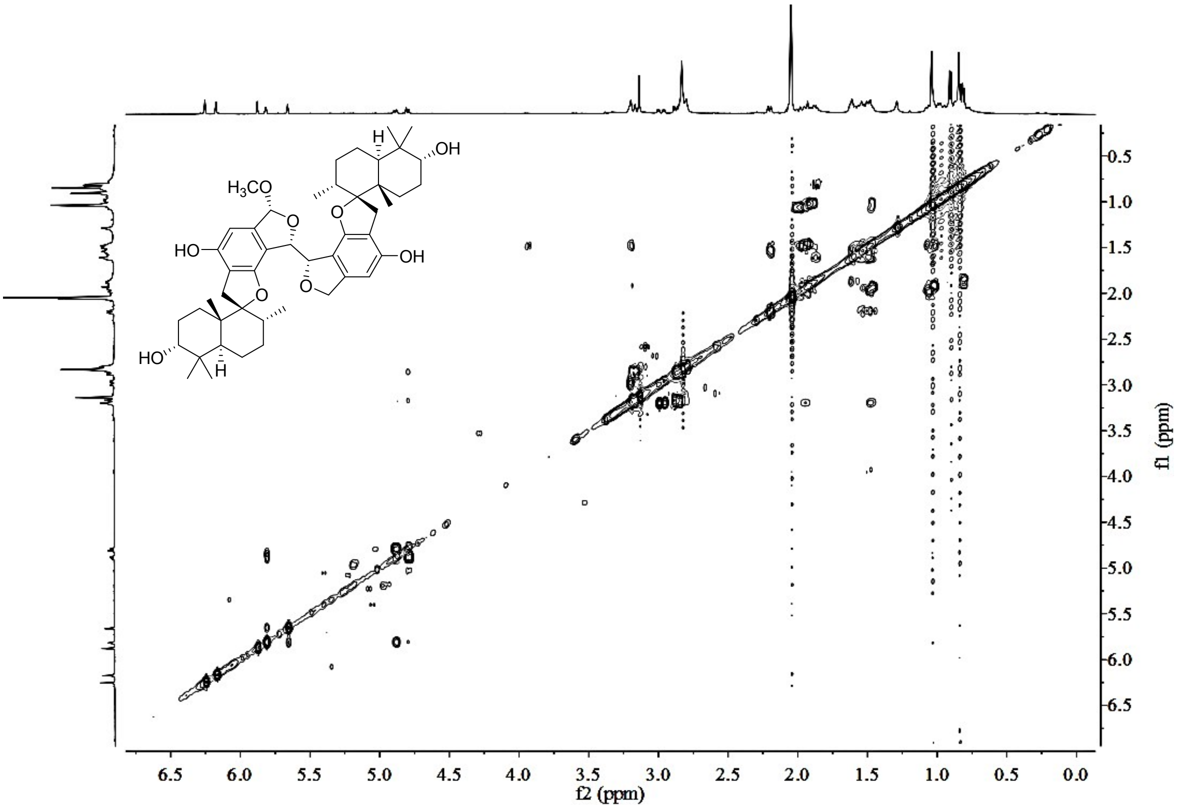


Figure S41. HSQC spectrum of compound **4** in acetone-d_6

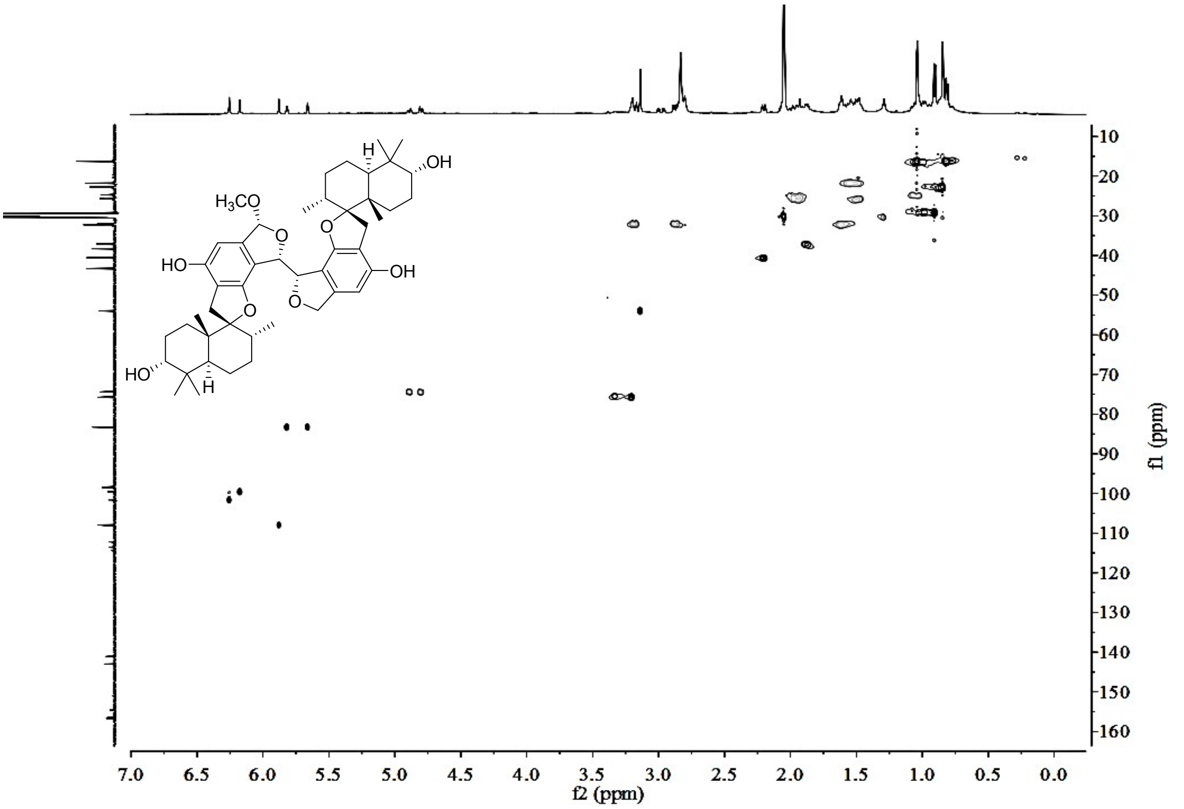


Figure S42. HMBC spectrum of compound **4** in acetone-d_6

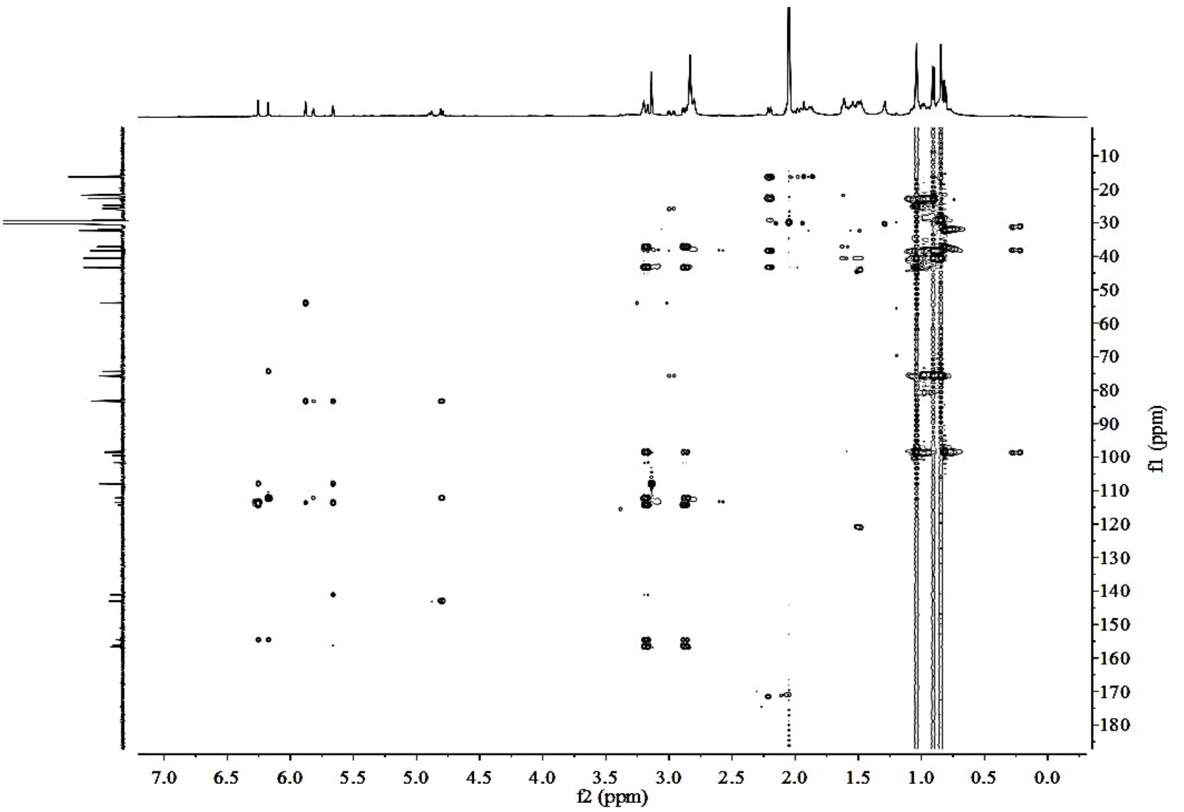


Figure S43. NOE difference spectrum of compound **4** in acetone-d_6

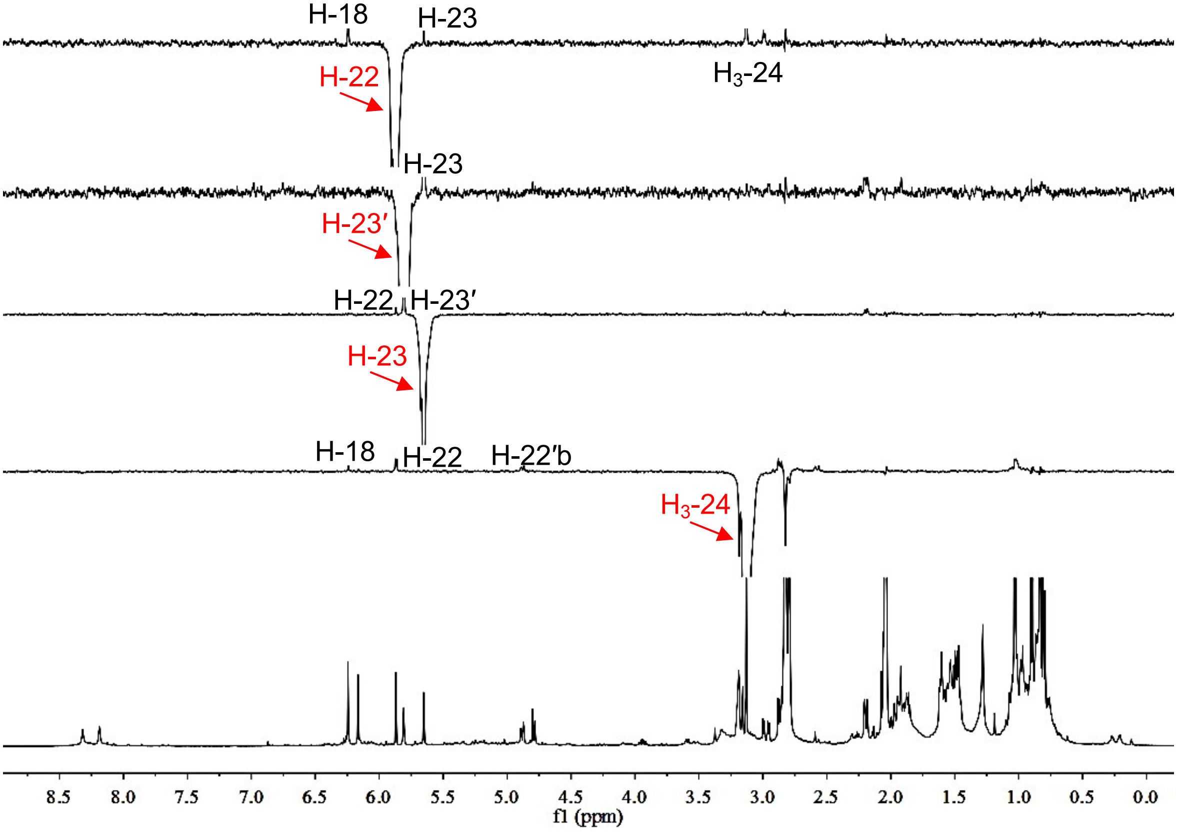


Figure S43. NOE difference spectrum of compound **4** in acetone-d_6 (continued)

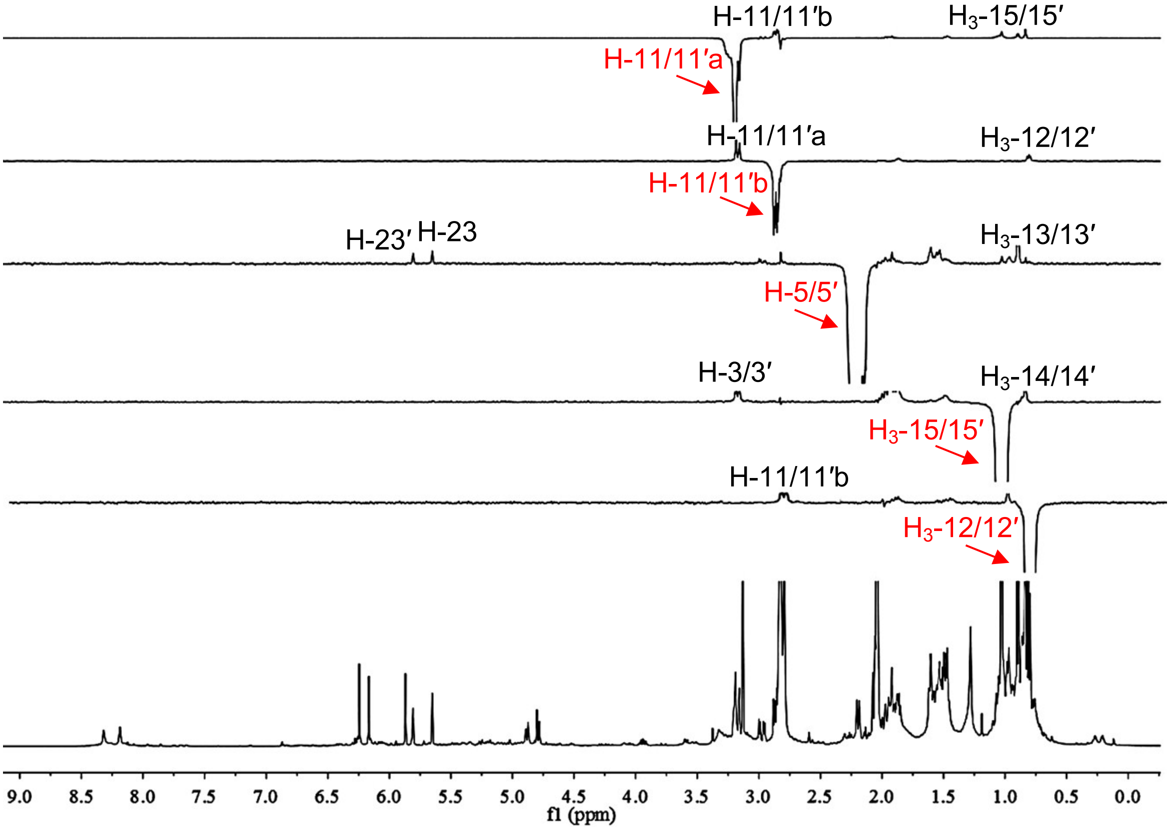


Figure S44. HR-ESI-MS spectrum of compound **4**

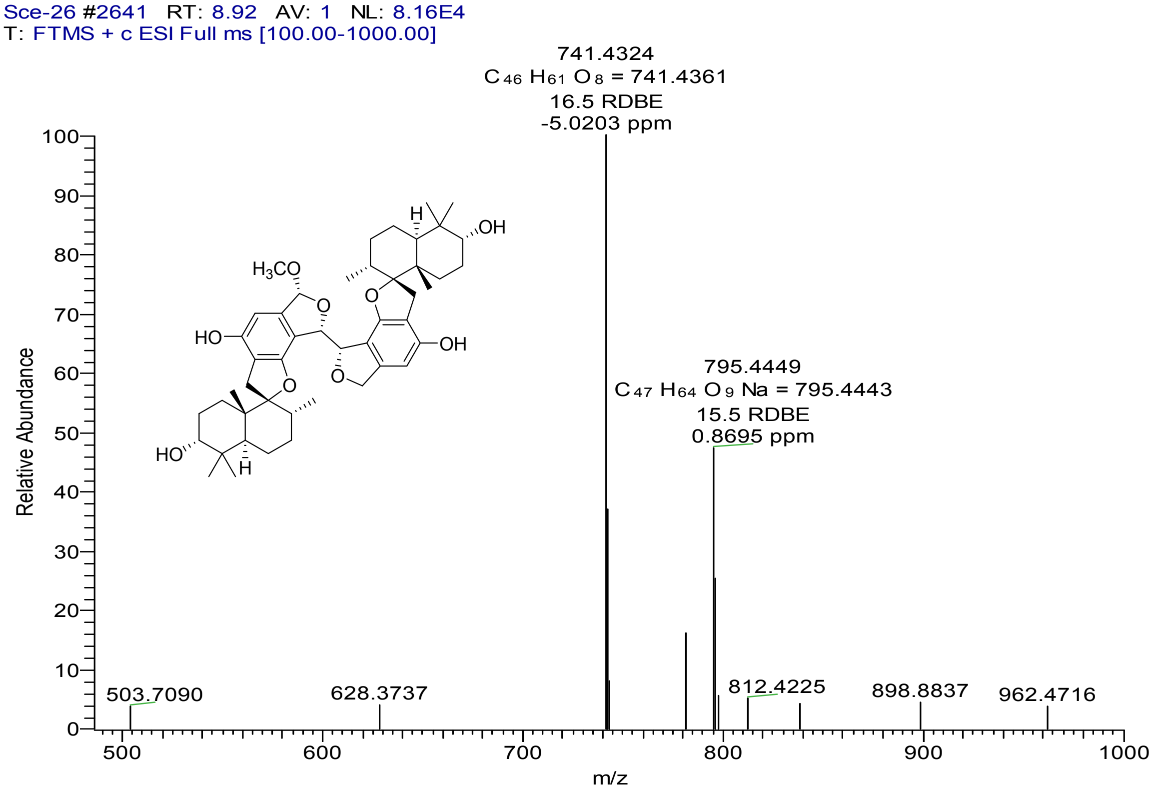
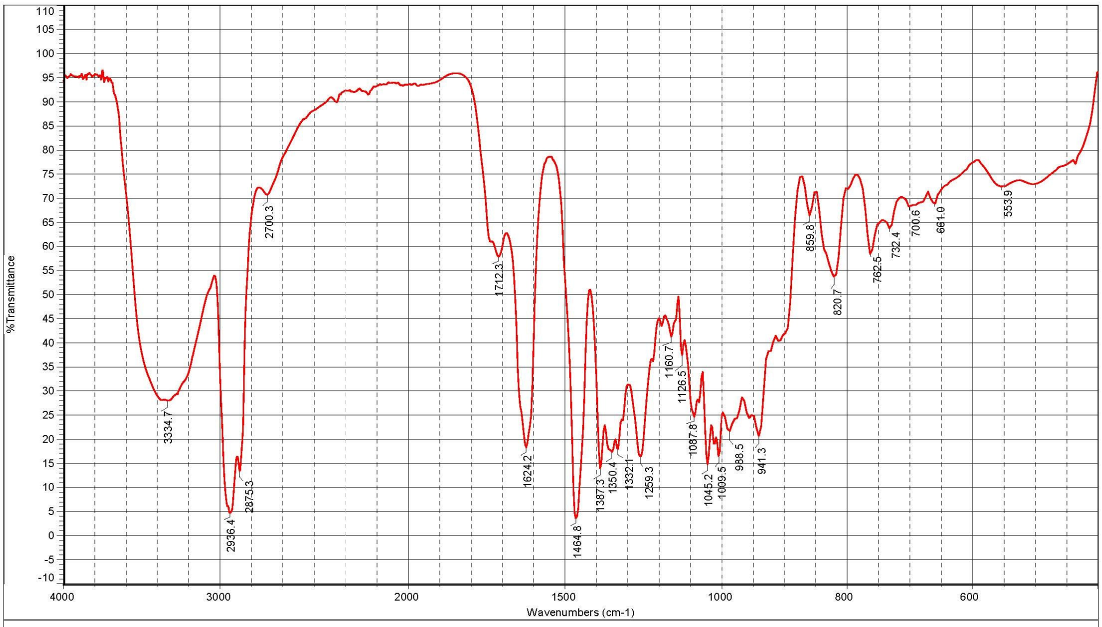


Figure S45. IR spectrum of compound **4**

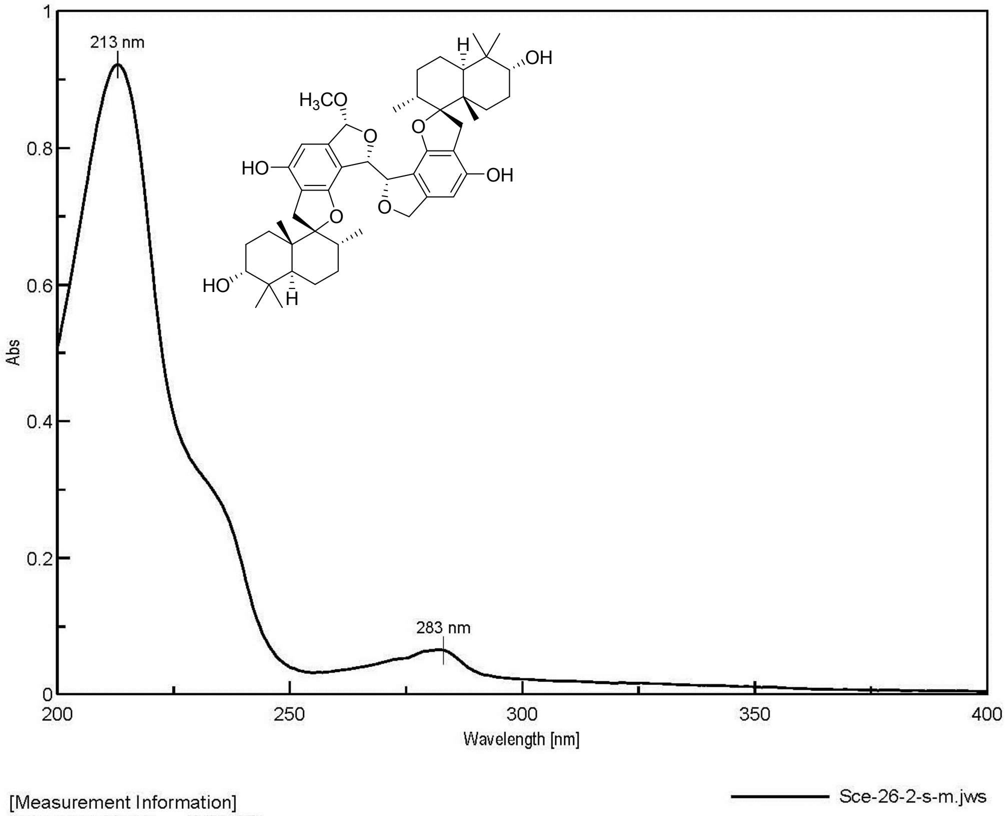


日期: 星期四 12月 29 10:53:57 2016 (GMT+08:00Sample Name： Sce - 26　(显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100　傅里叶变换红外显微镜(FT-IR Microscope)：Centaurμs

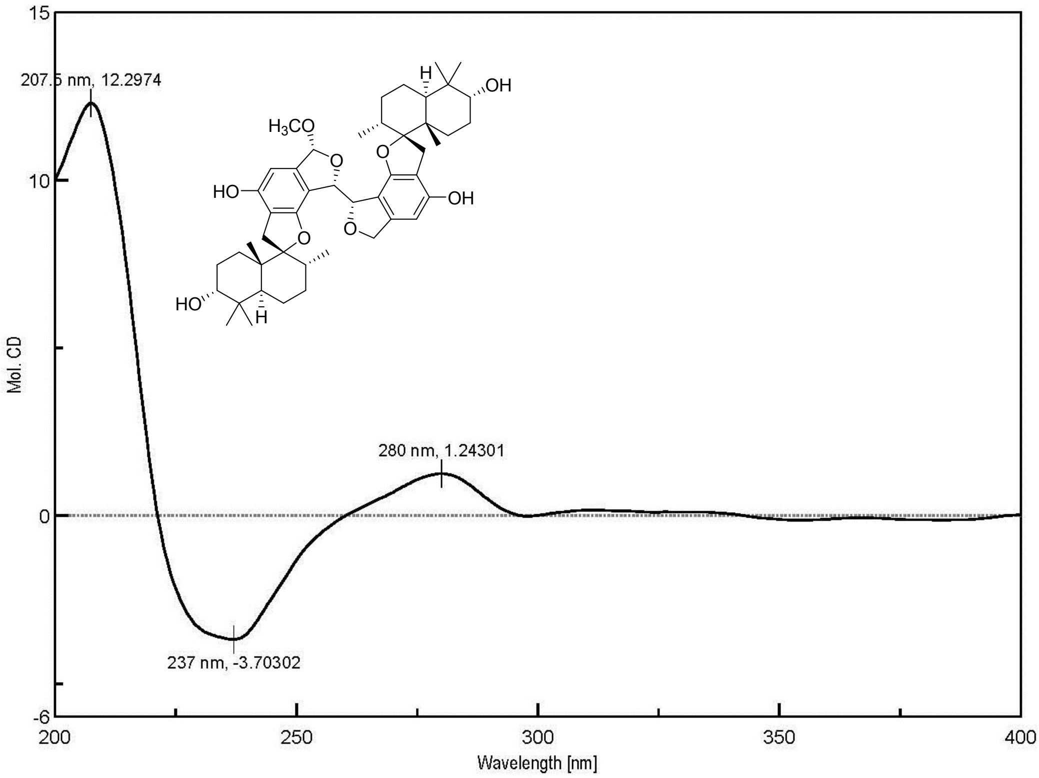
分辨率: 8.000　美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S46. UV spectrum of compound **4**



[Measurement Information]	
Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 17:12
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S47. ECD spectrum of compound **4**



Sce-26-2-s-m.jws

[Measurement Information]

Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 17:12
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S48. ^{1}H NMR spectrum of compound **5** in acetone-d_6 at 600 MHz

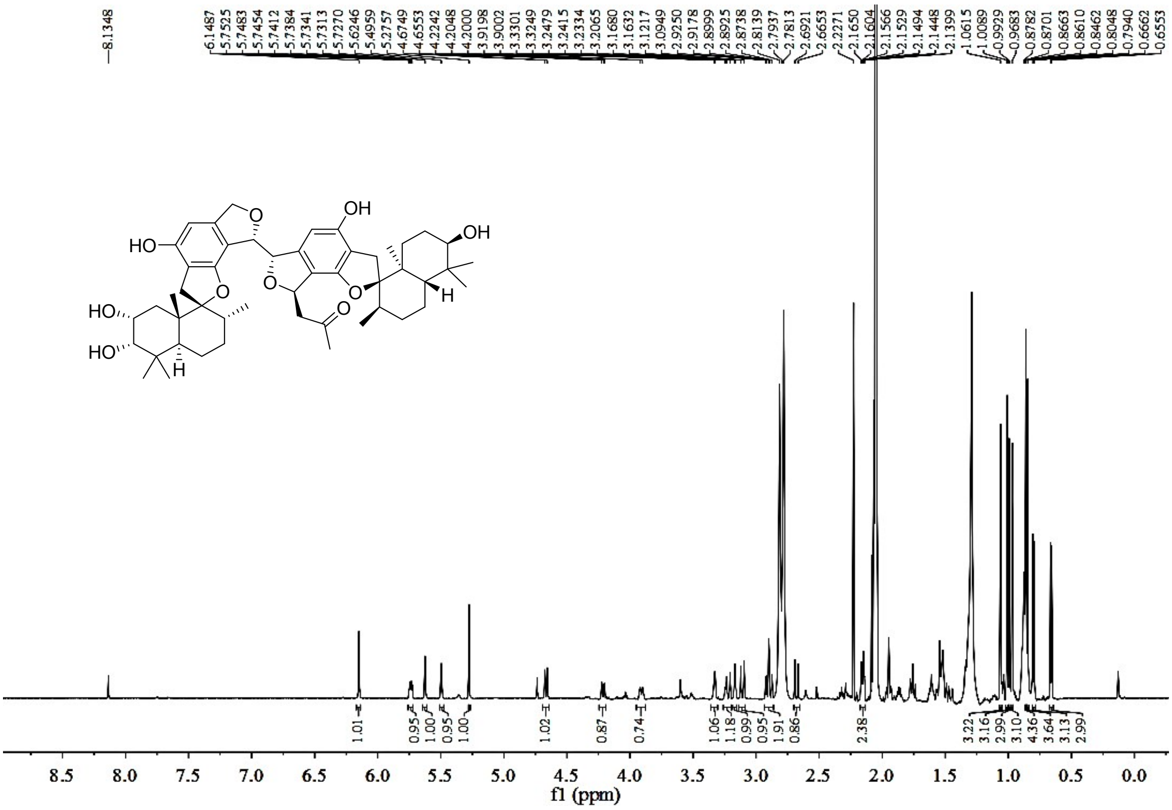


Figure S49. ^{13}C NMR spectrum of compound **5** in acetone-d_6 at 150 MHz

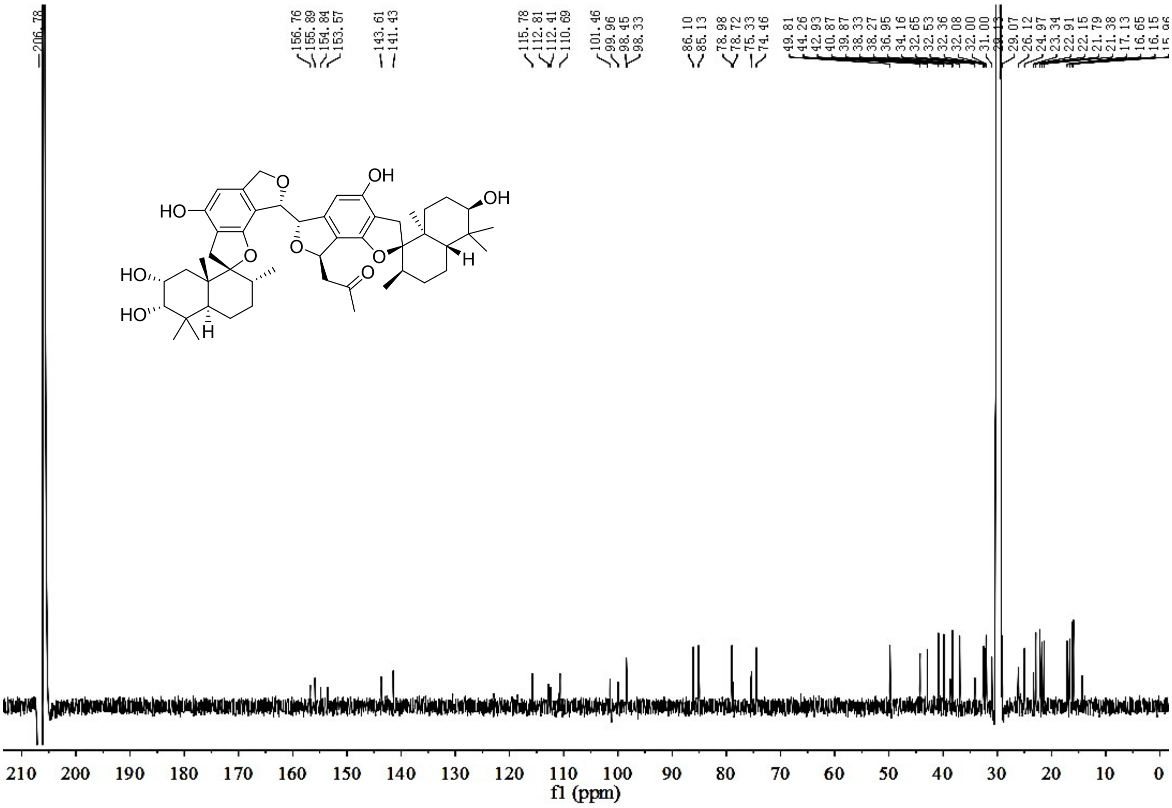


Figure S50. DEPT spectrum of compound **5** in acetone-d_6 at 150 MHz

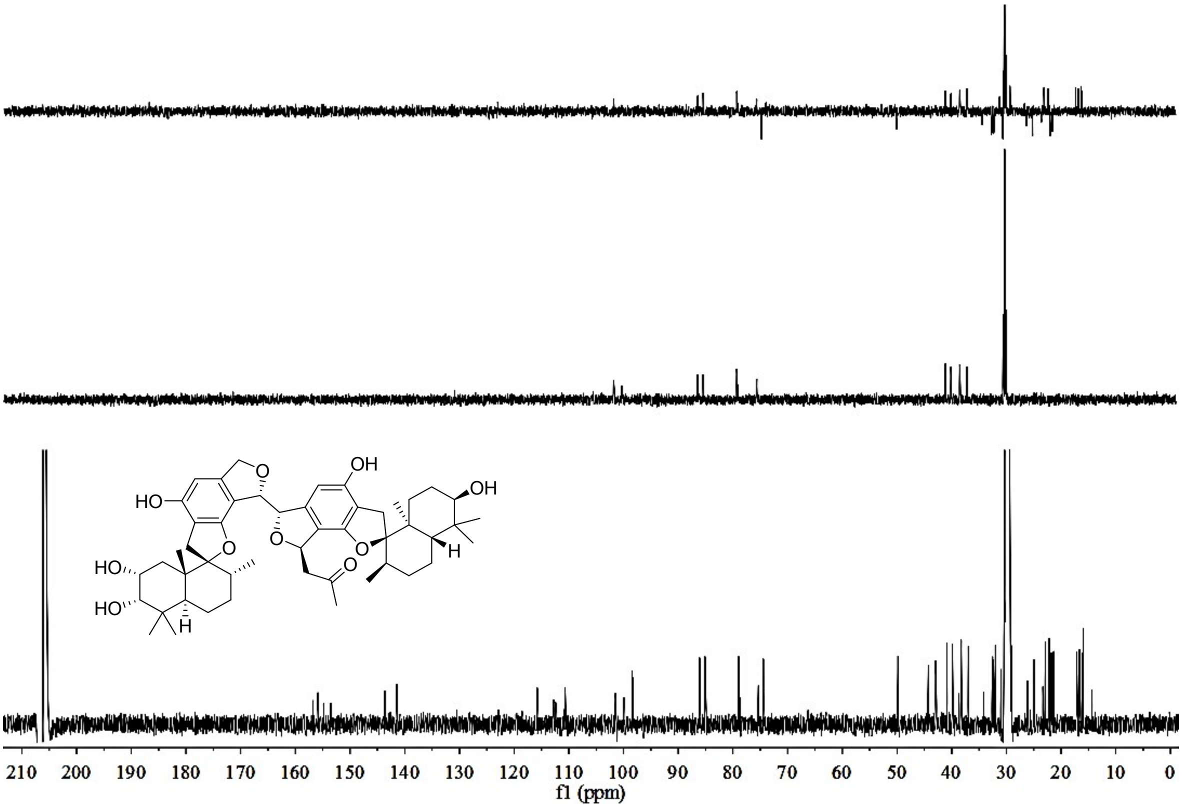


Figure S51. ^{1}H−^{1}H COSY spectrum of compound **5** in acetone-d_6

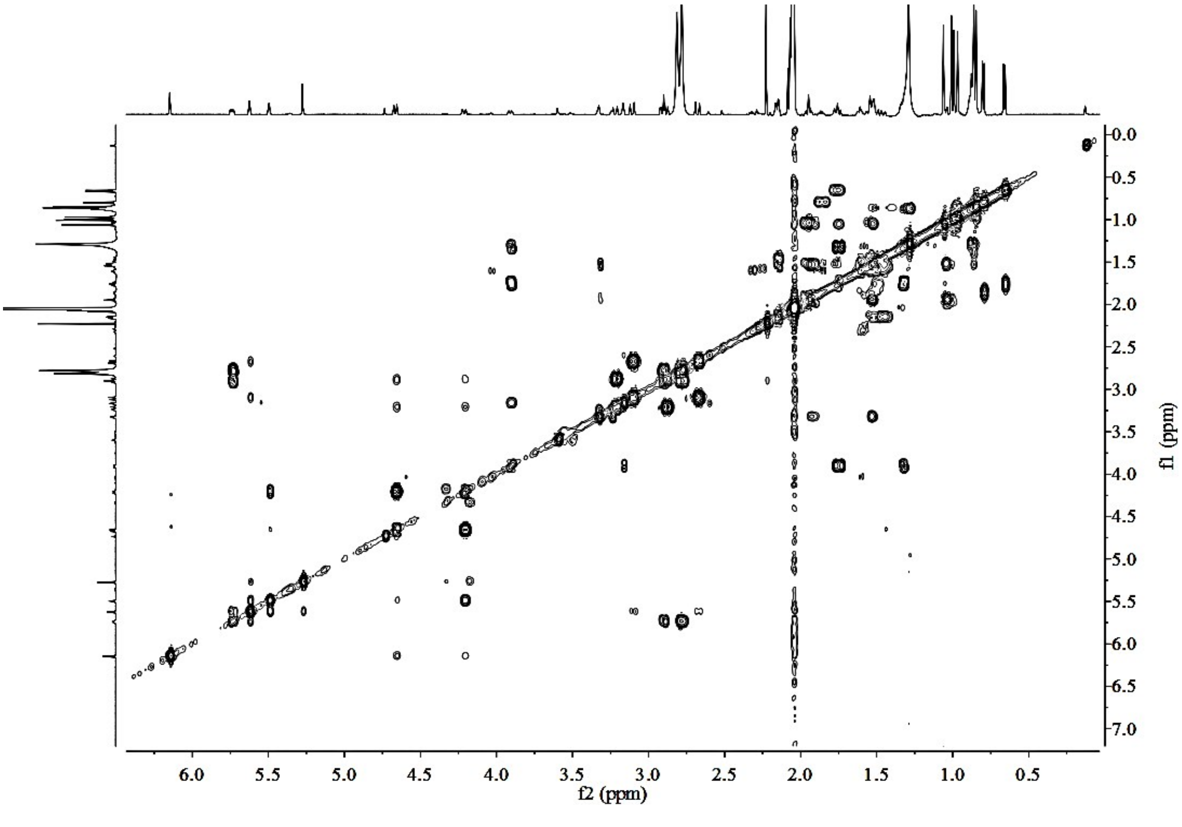


Figure S51. Enlarged ^{1}H–^{1}H COSY spectrum of compound **5** in acetone-d_6

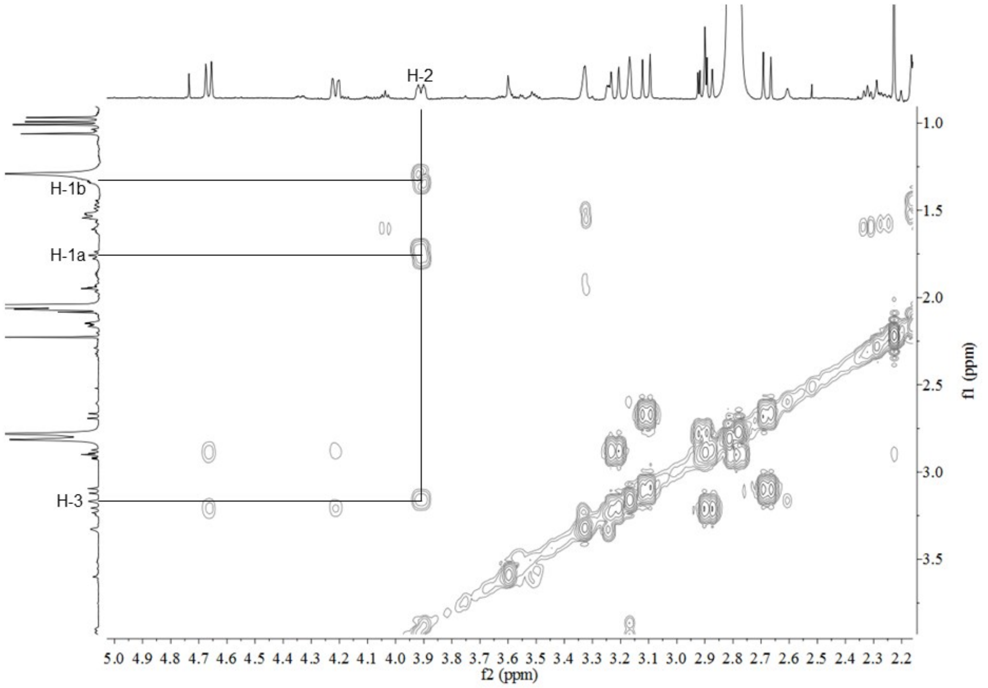


Figure S52. HSQC spectrum of compound **5** in acetone-d_6

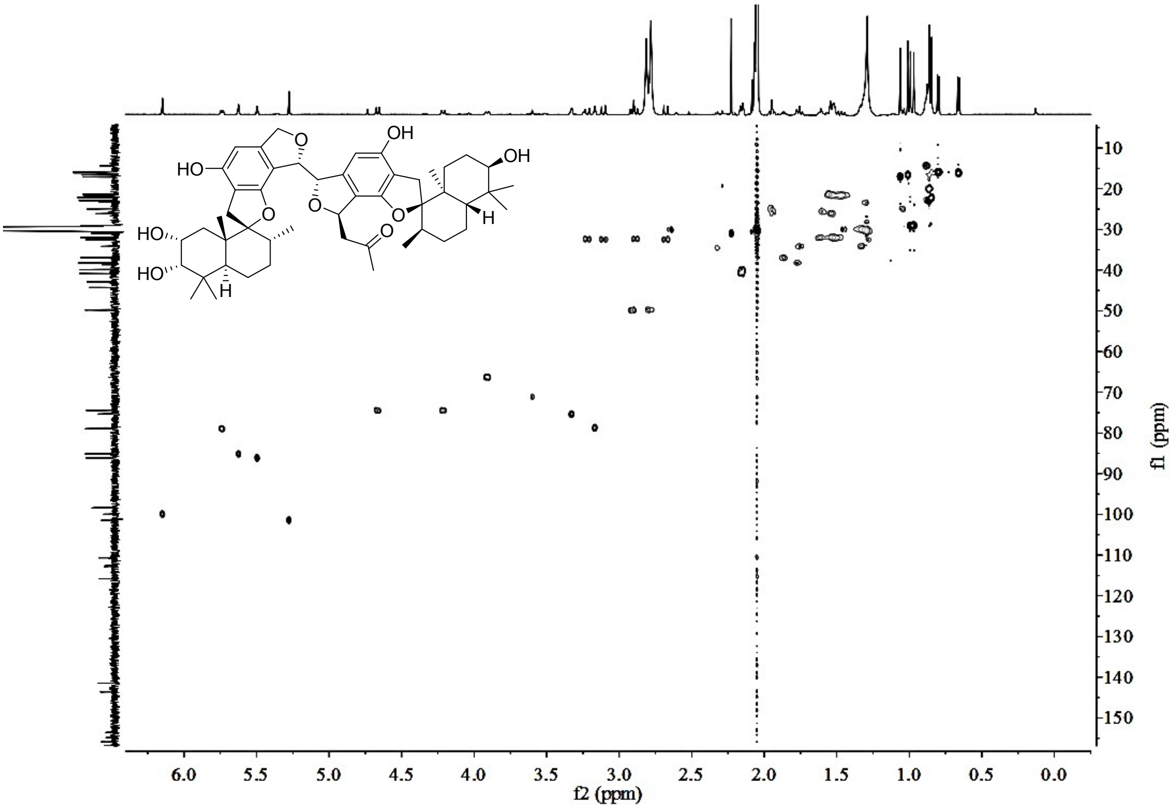


Figure S53. HMBC spectrum of compound **5** in acetone-d_6

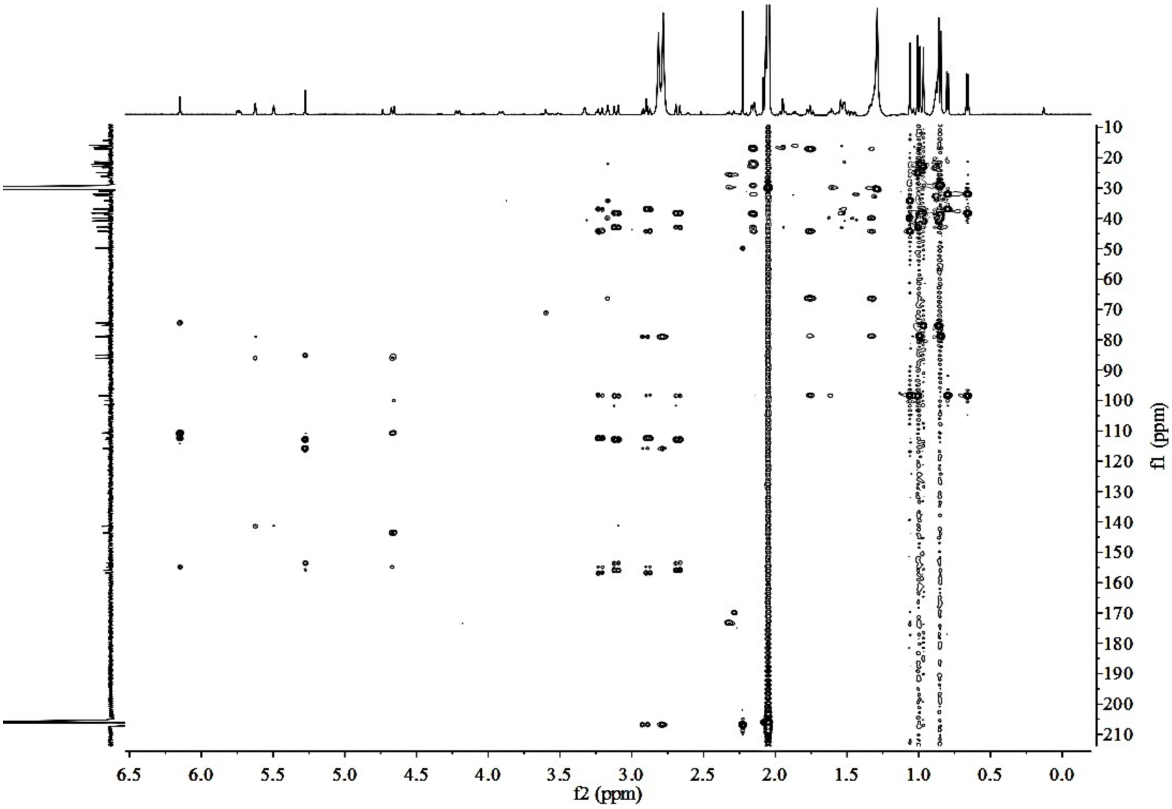


Figure S53. Enlarged HMBC spectrum of compound **5** in acetone-d_6

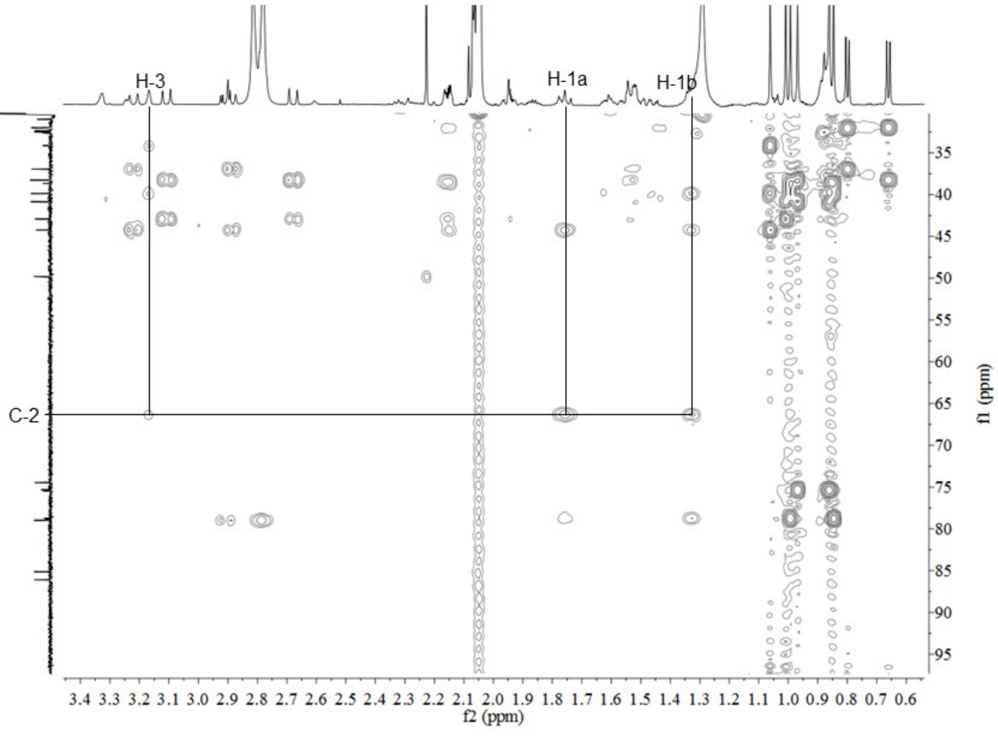


Figure S54. NOE difference spectrum of compound **5** in acetone-d_6

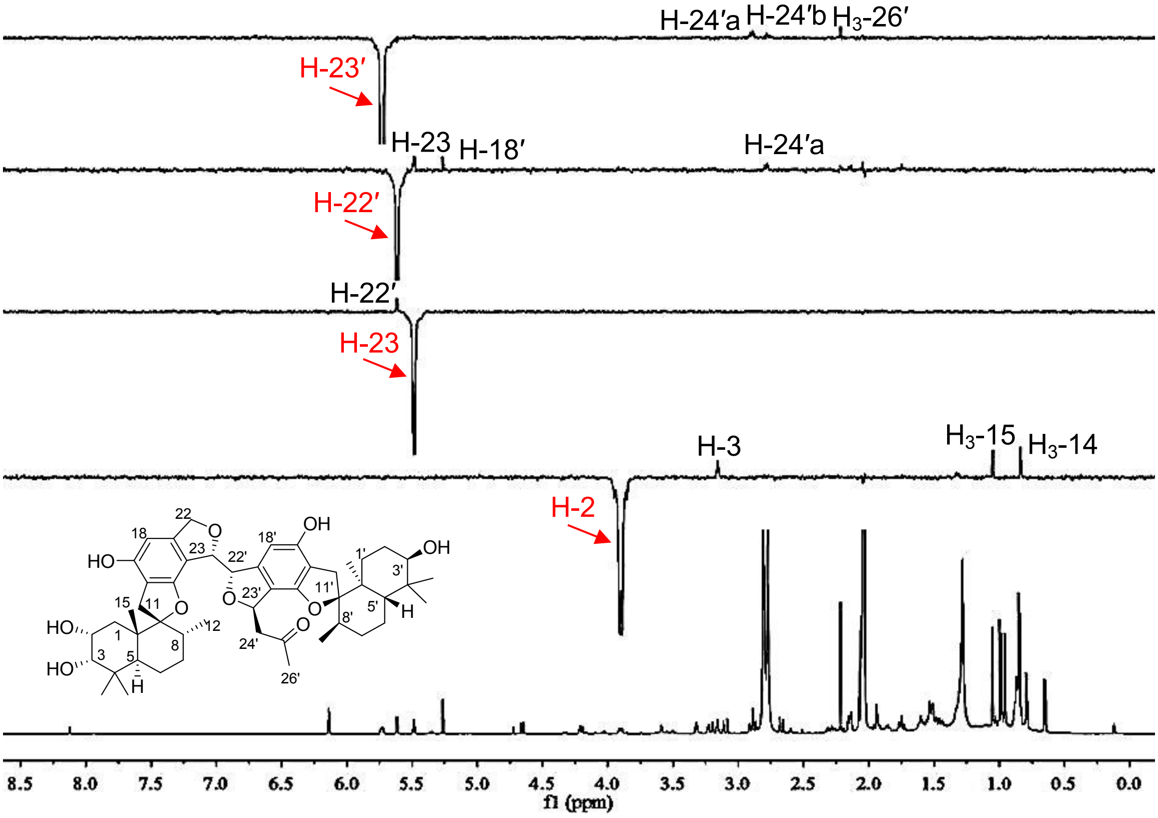


Figure S54. NOE difference spectrum of compound **5** in acetone-d_6 (continued)

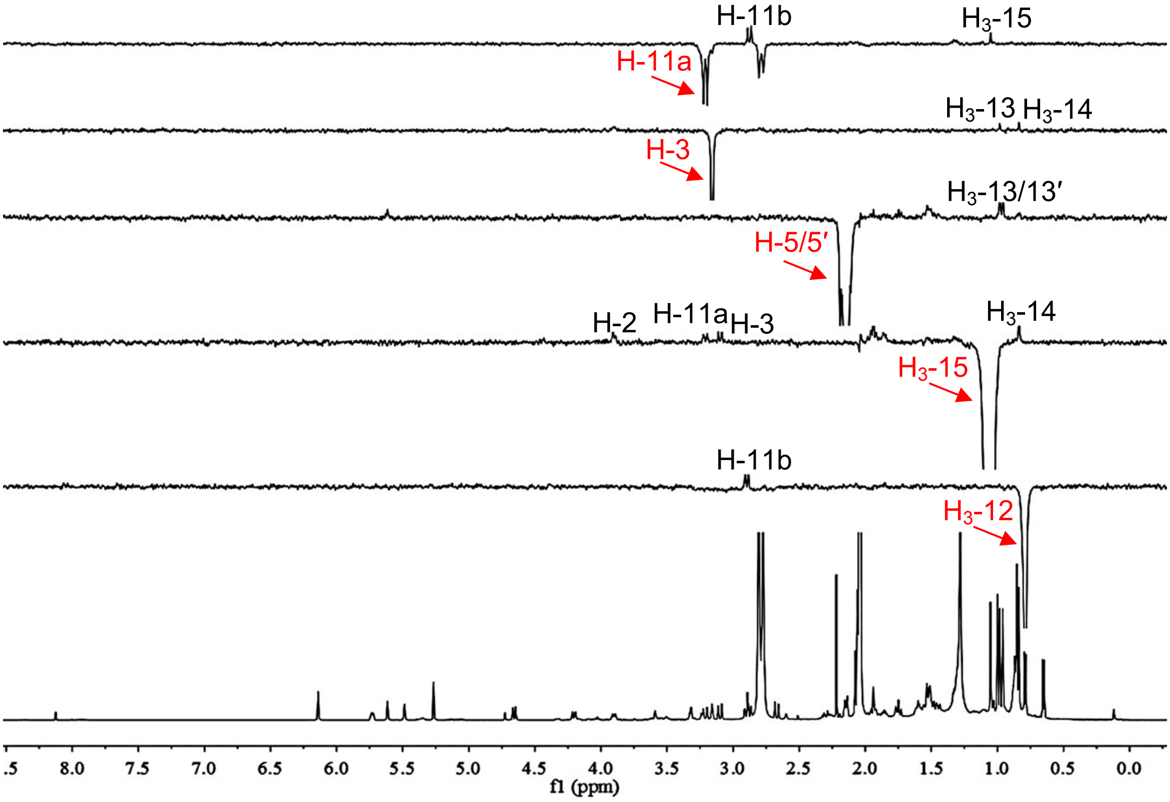


Figure S54. NOE difference spectrum of compound **5** in acetone-d_6 (continued)

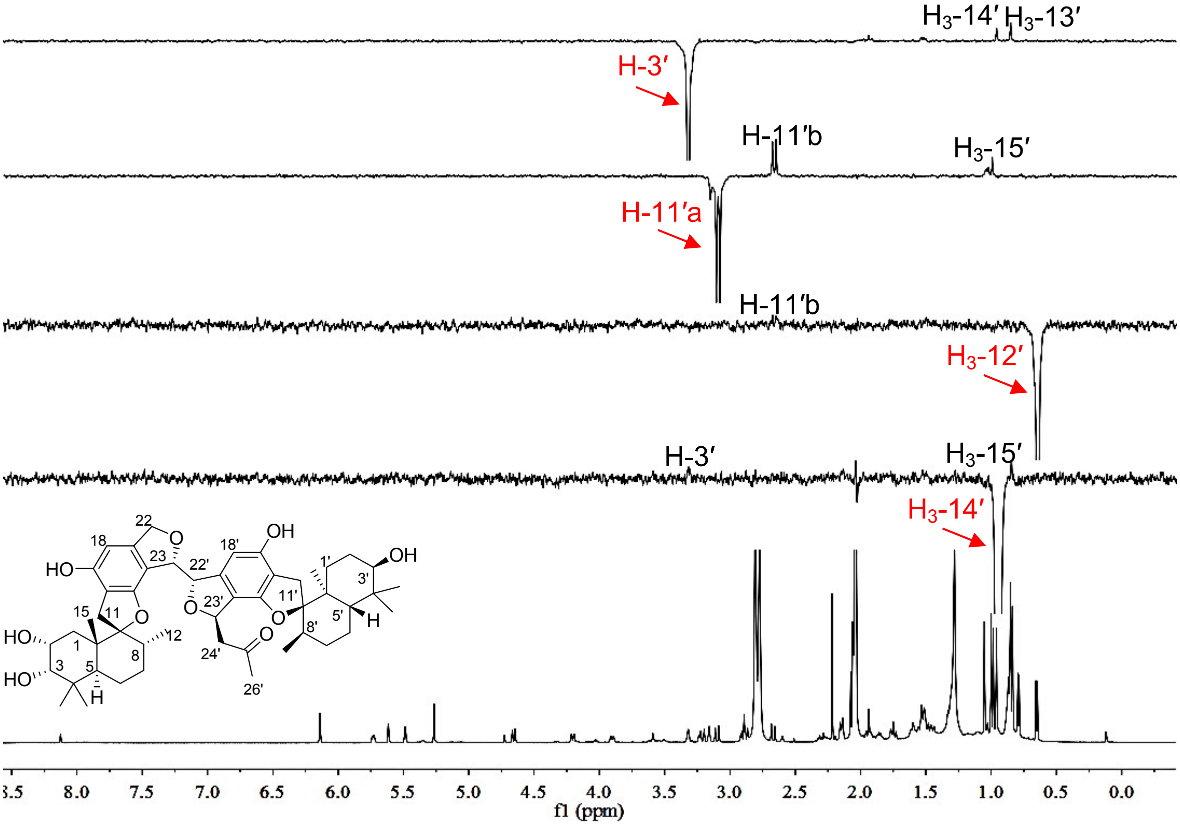


Figure S55. HR-ESI-MS spectrum of compound **5**

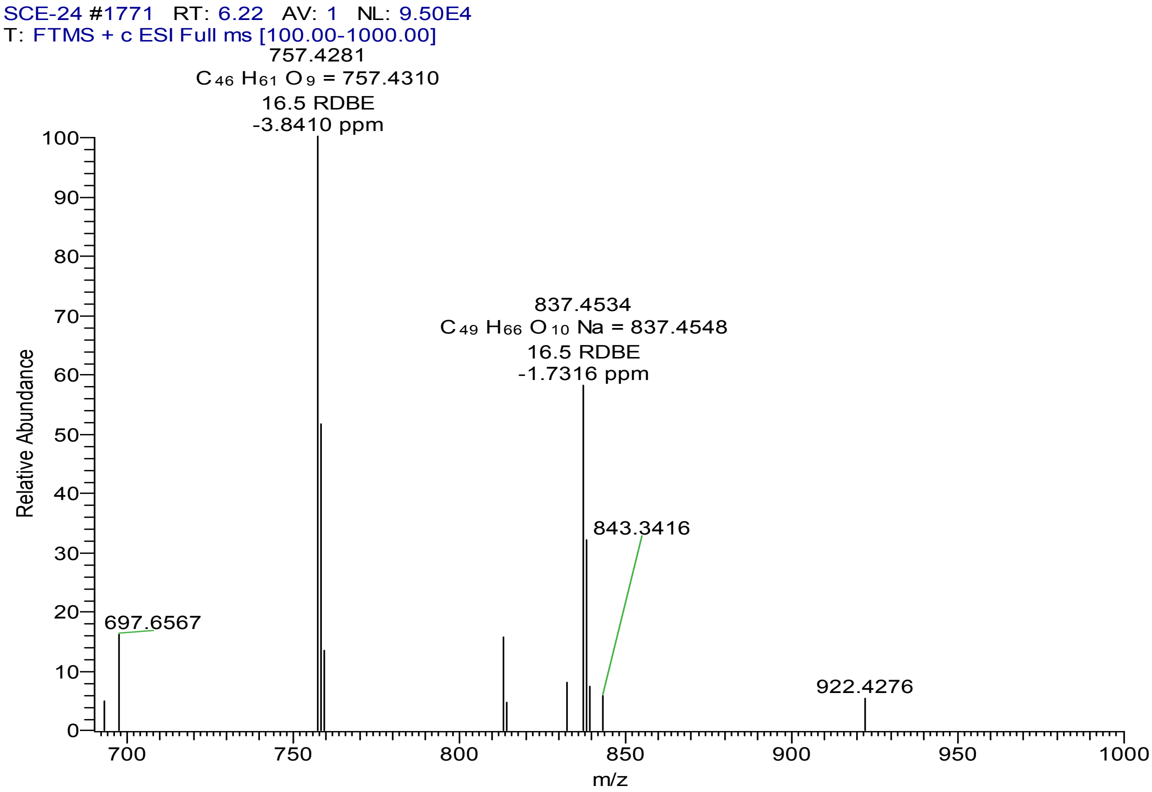
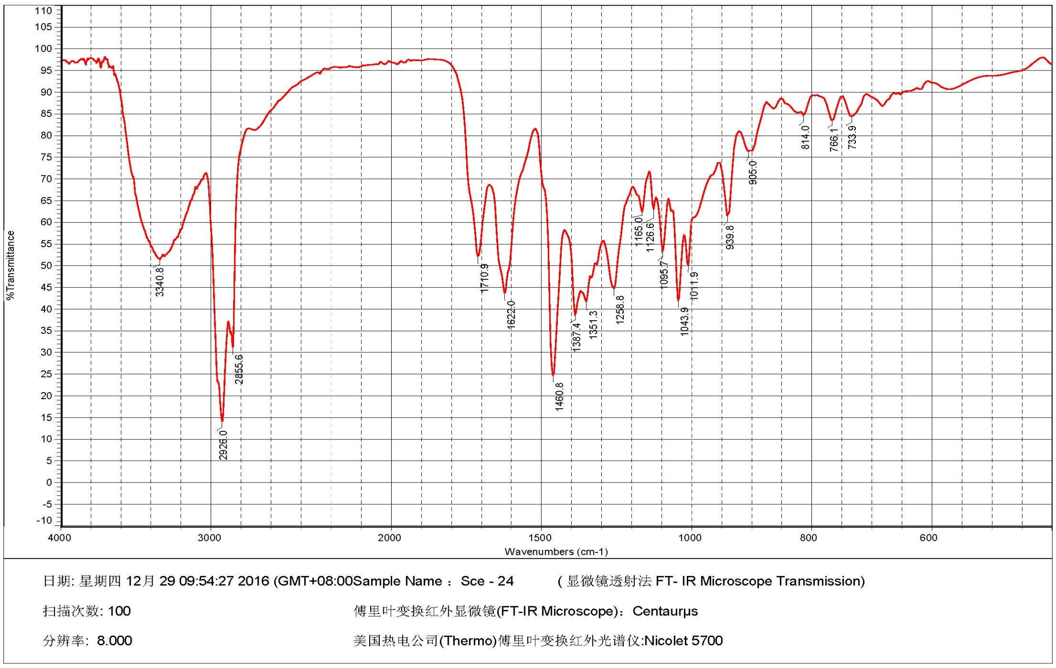


Figure S56. IR spectrum of compound **5**



日期: 星期四 12月 29 09:54:27 2016 (GMT+08:00Sample Name : Sce - 24 (显微镜透射法 FT- IR Microscope Transmission)

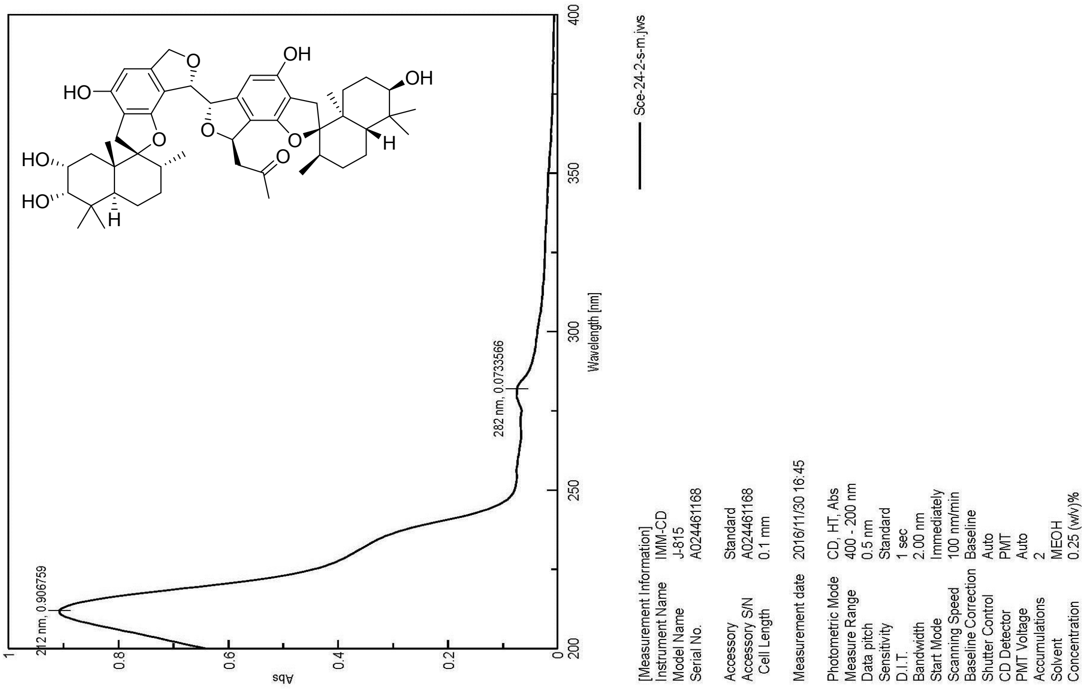
扫描次数: 100

傅里叶变换红外显微镜(FT-IR Microscope)：Centaurμs

分辨率: 8.000

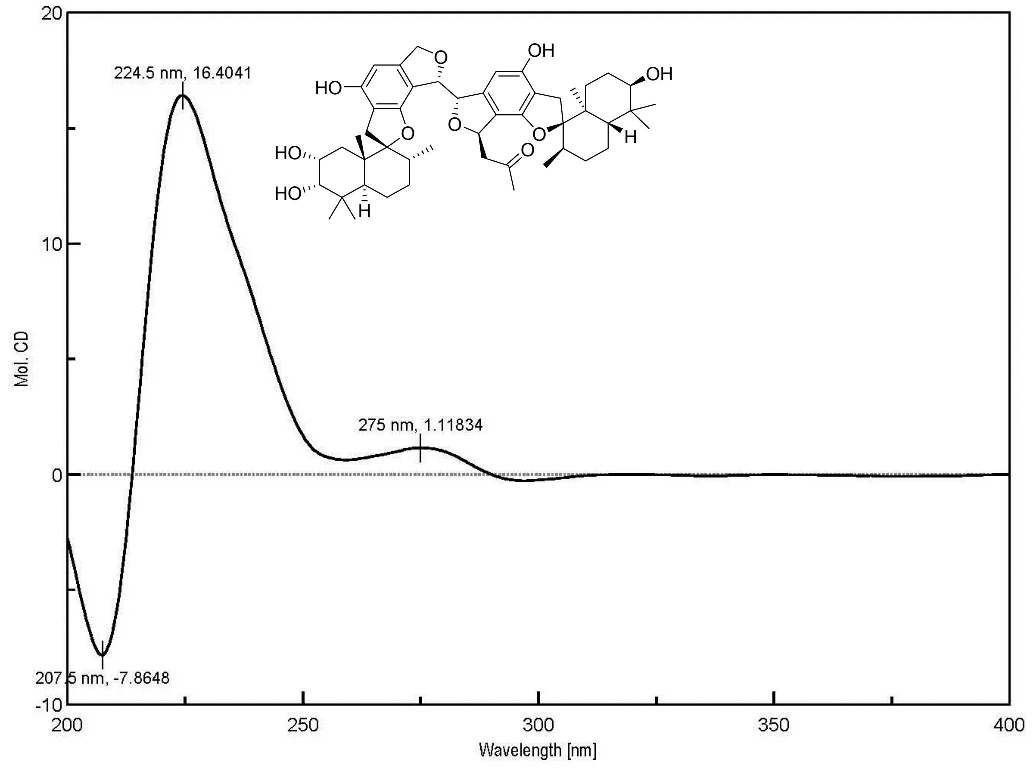
美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S57. UV spectrum of compound **5**



[Measurement Information]	
Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 16:45
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.25 (w/v)%

Figure S58. ECD spectrum of compound **5**



Sce-24-2-s-m.jws

[Measurement Information]

Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 16:45
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.25 (w/v)%

Figure S59. ^{1}H NMR spectrum of compound **6** in acetone-d_6 at 600 MHz

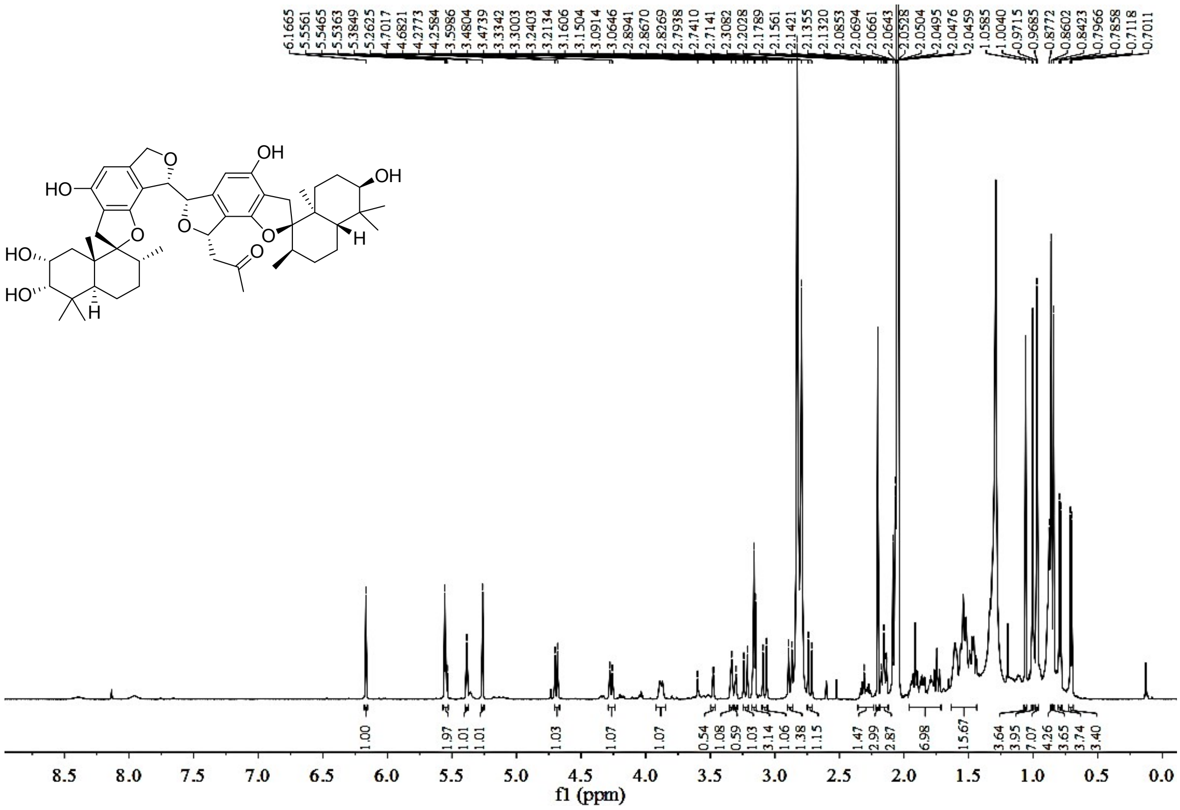


Figure S60. ^{13}C NMR spectrum of compound **6** in acetone-d_6 at 150 MHz

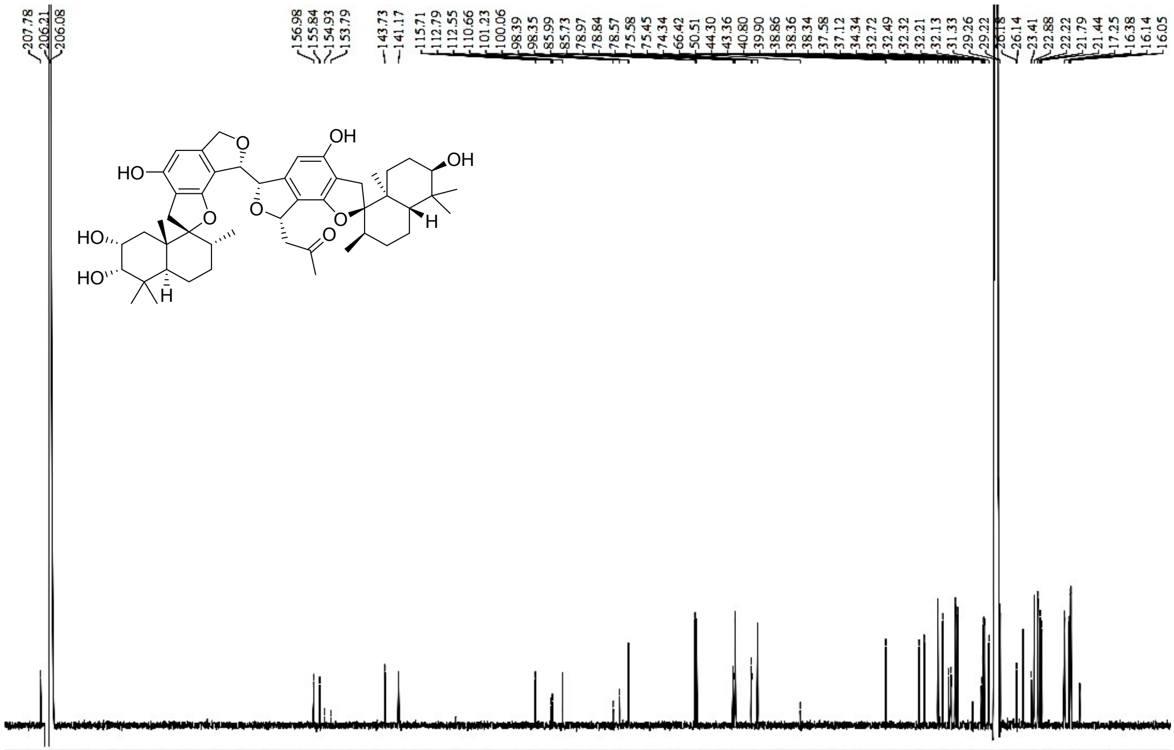


Figure S61. DEPT spectrum of compound **6** in acetone-d_6 at 150 MHz

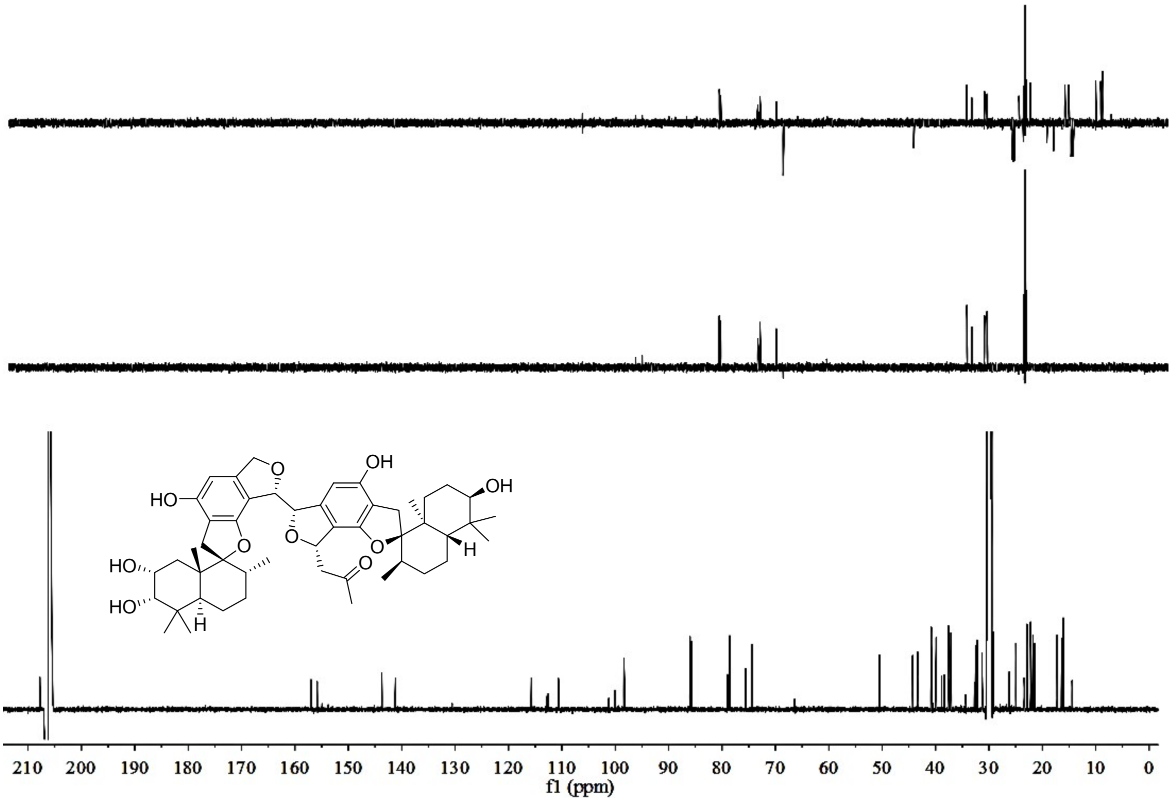


Figure S62. $^1H-^1H$ COSY spectrum of compound **6** in acetone-d_6

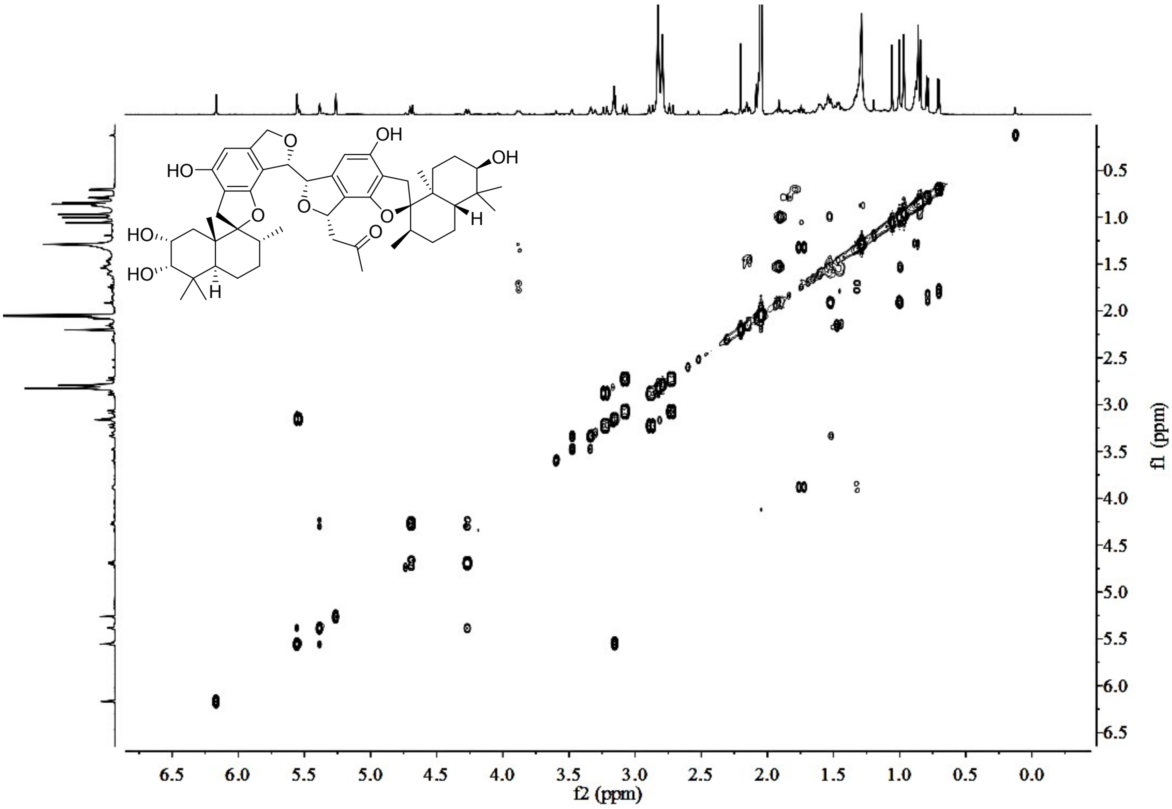


Figure S62. Enlarged ^{1}H–^{1}H COSY spectrum of compound **6** in acetone-d_6

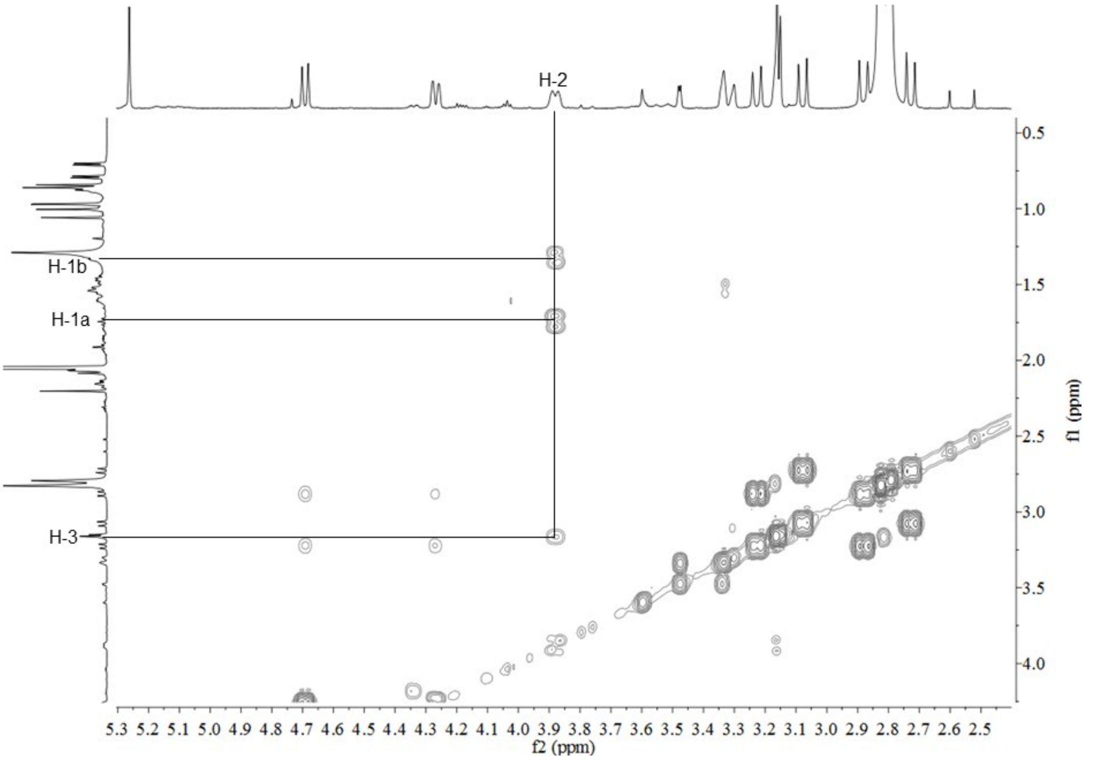


Figure S63. HSQC spectrum of compound **6** in acetone-d_6

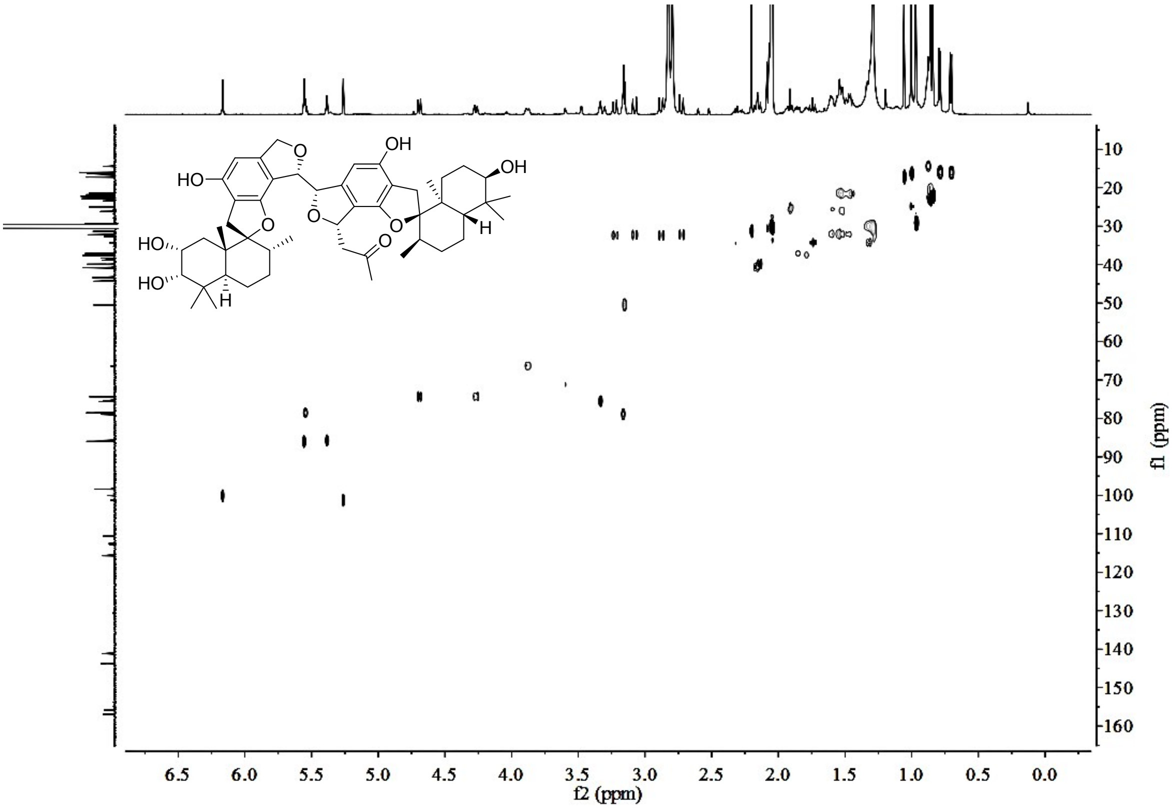


Figure S64. HMBC spectrum of compound **6** in acetone-d_6

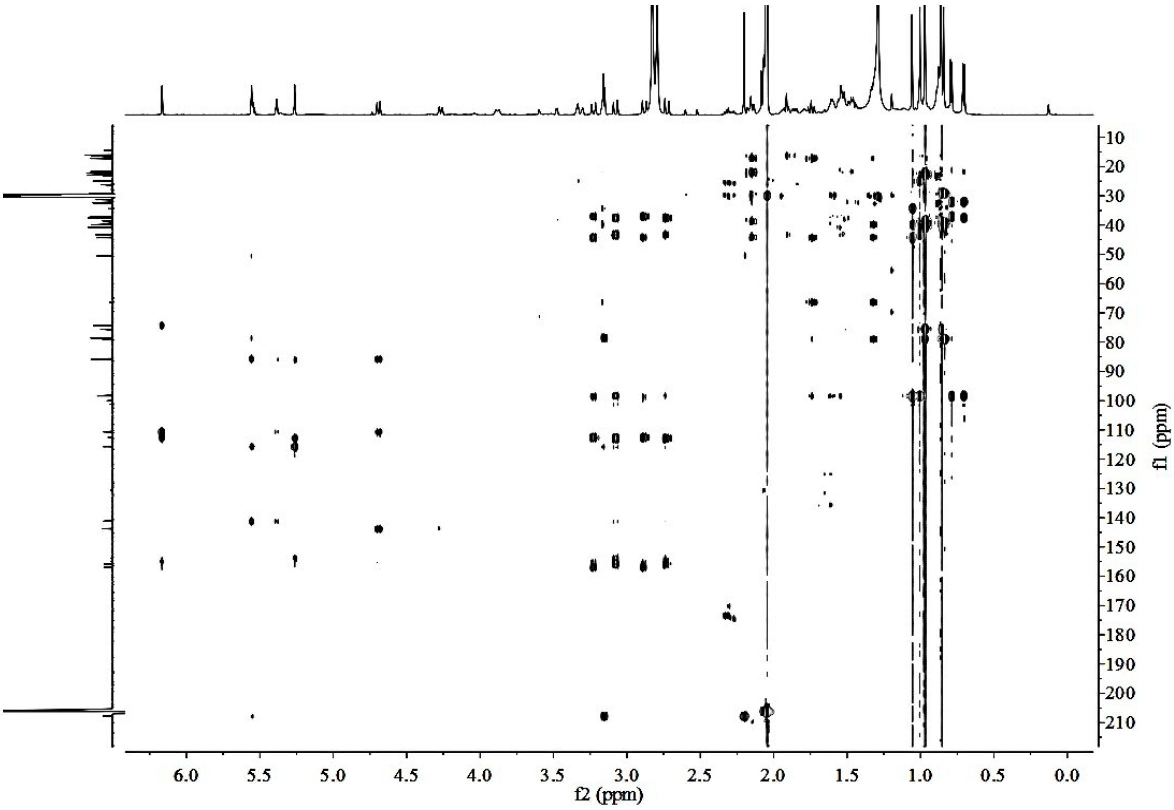


Figure S64. Enlarged HMBC spectrum of compound **6** in acetone-d_6

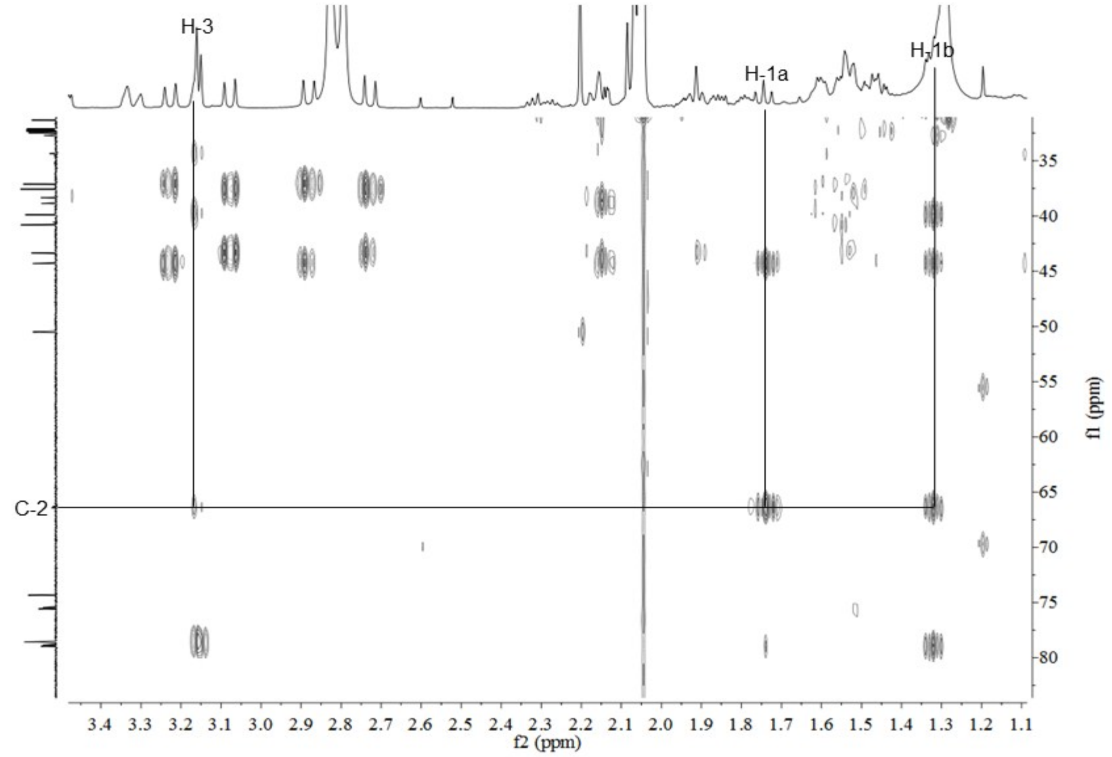


Figure S64. Enlarged HMBC spectrum of compound **6** in acetone-*d*$_6$

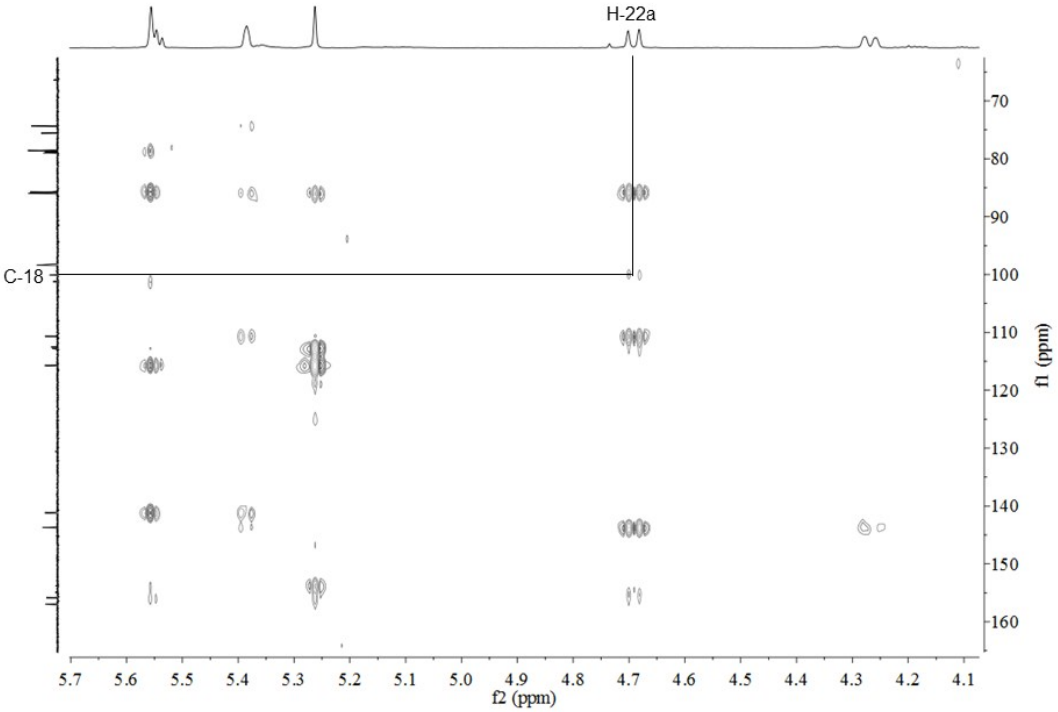


Figure S65. NOE difference spectrum of compound **6** in acetone-*d*$_6$

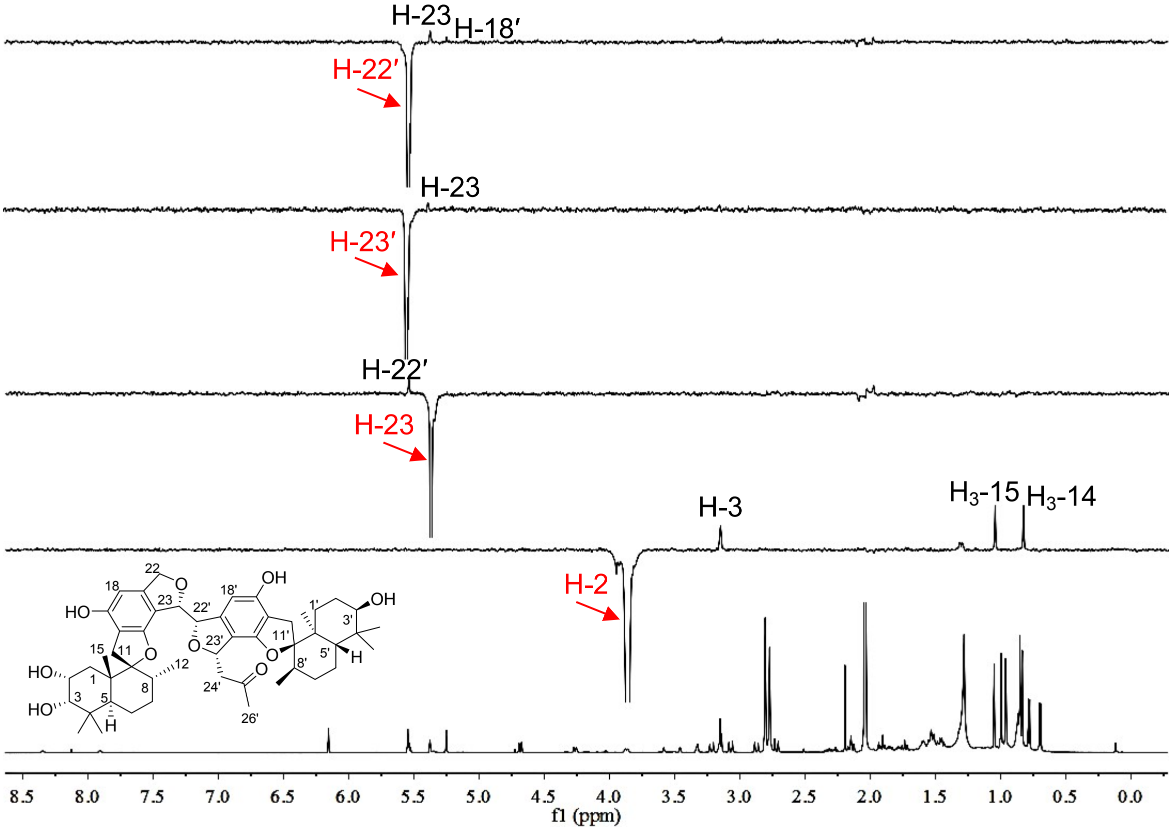


Figure S65. NOE difference spectrum of compound **6** in acetone-d_6 (continued)

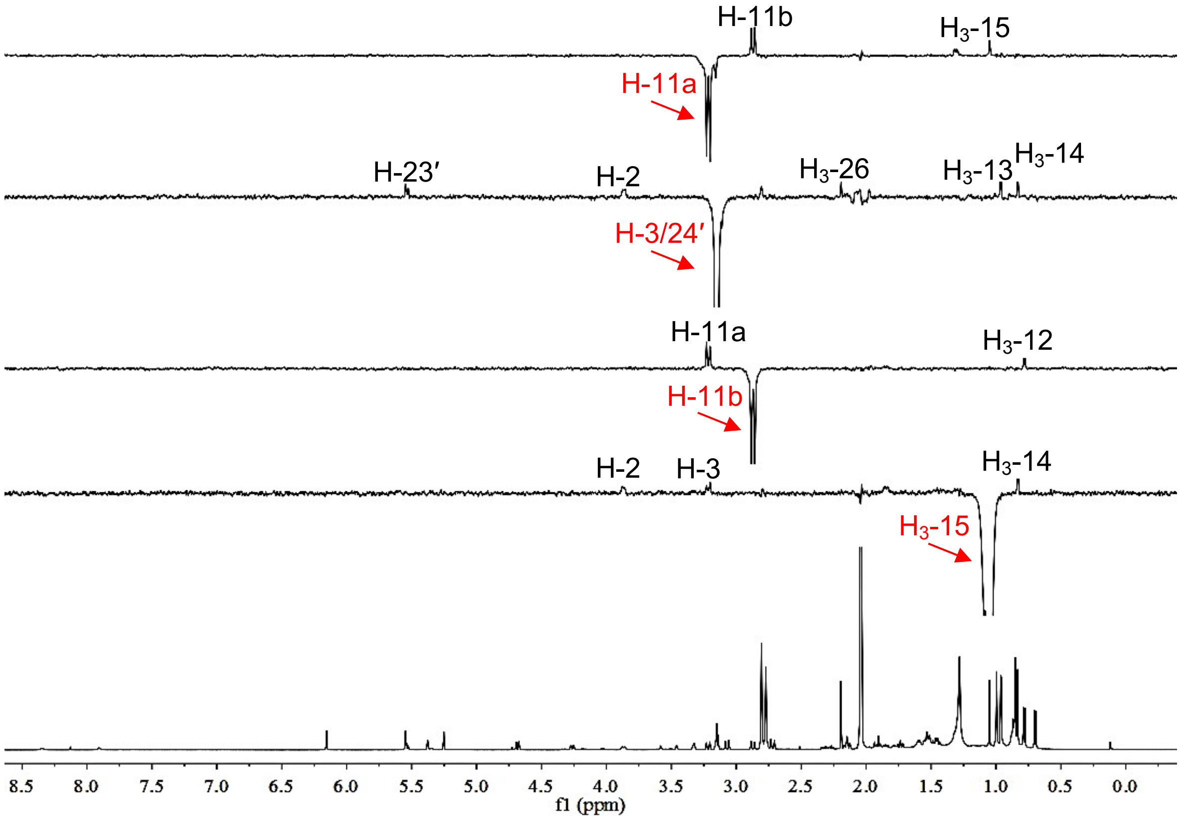


Figure S65. NOE difference spectrum of compound **6** in acetone-d_6 (continued)

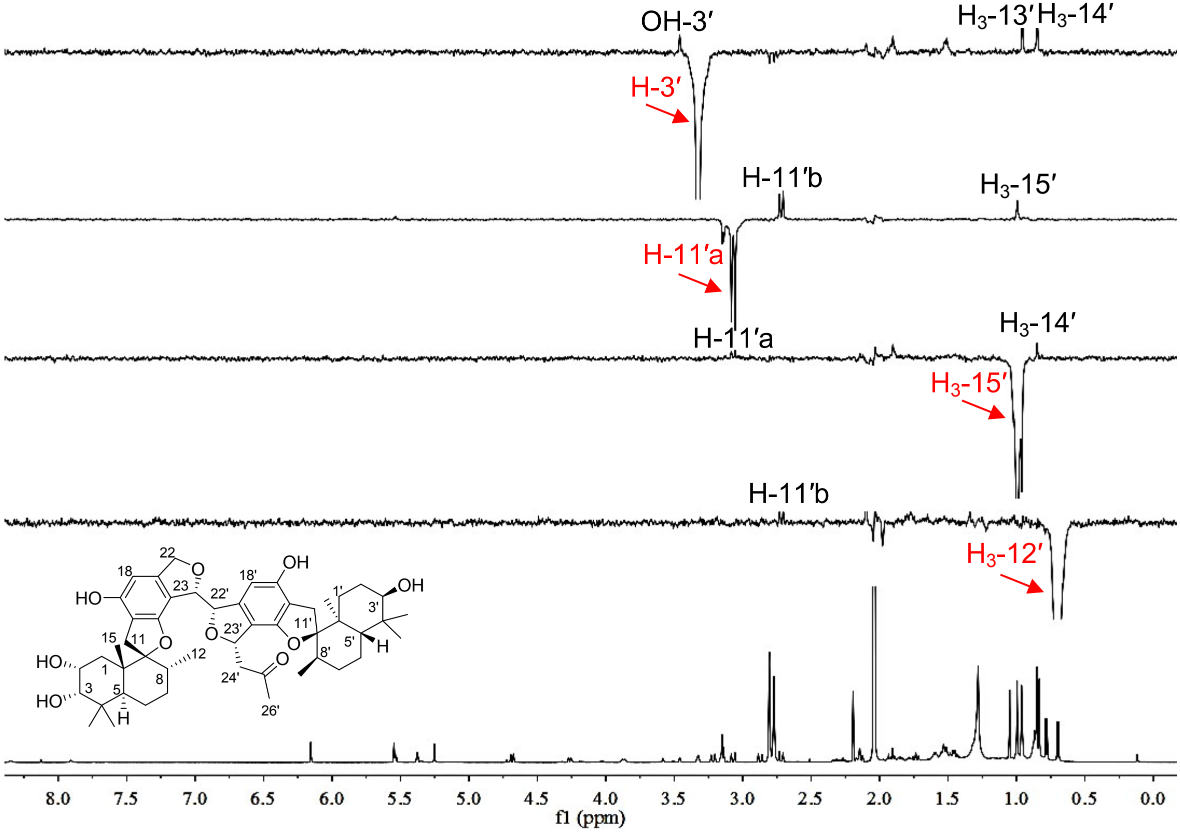


Figure S66. HR-ESI-MS spectrum of compound **6**

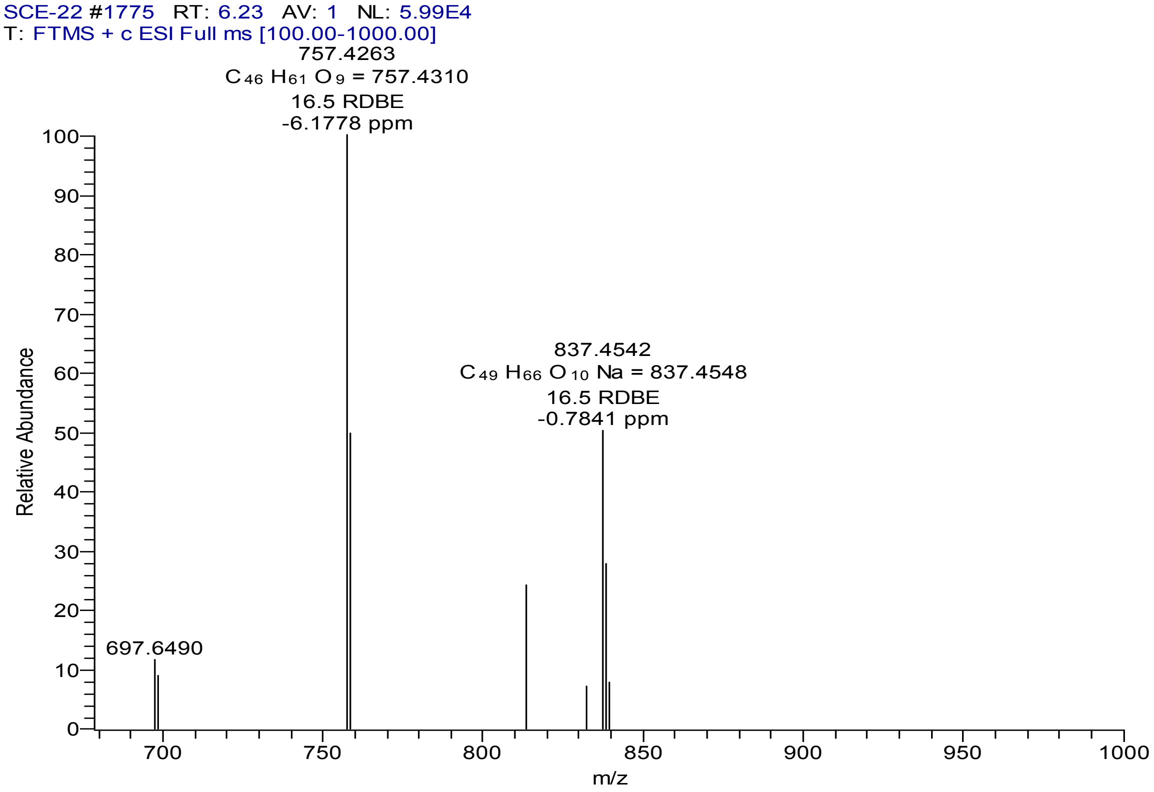
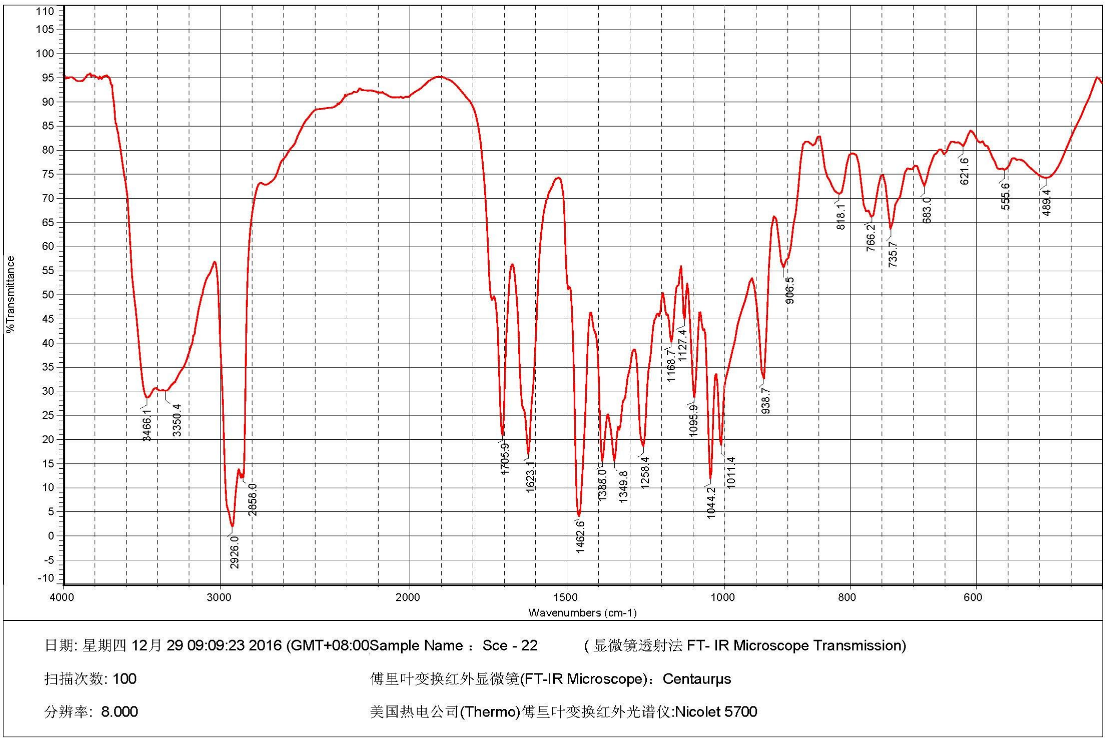


Figure S67. IR spectrum of compound **6**

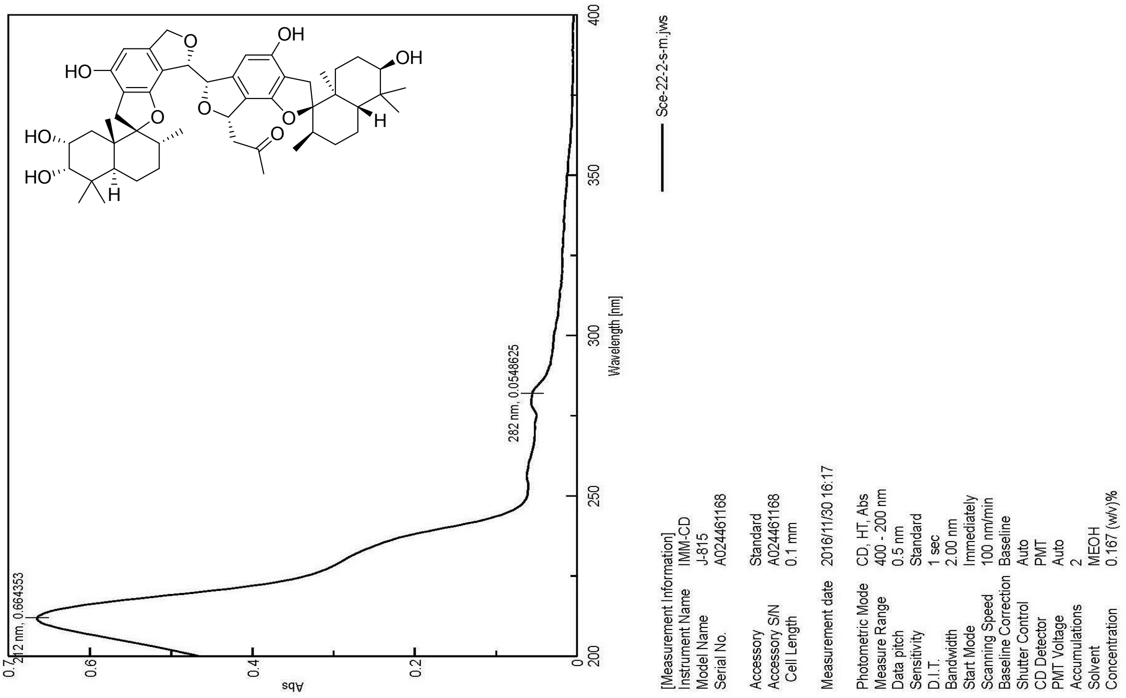


日期: 星期四 12月 29 09:09:23 2016 (GMT+08:00Sample Name： Sce - 22 （显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100 傅里叶变换红外显微镜(FT-IR Microscope)：Centaurμs

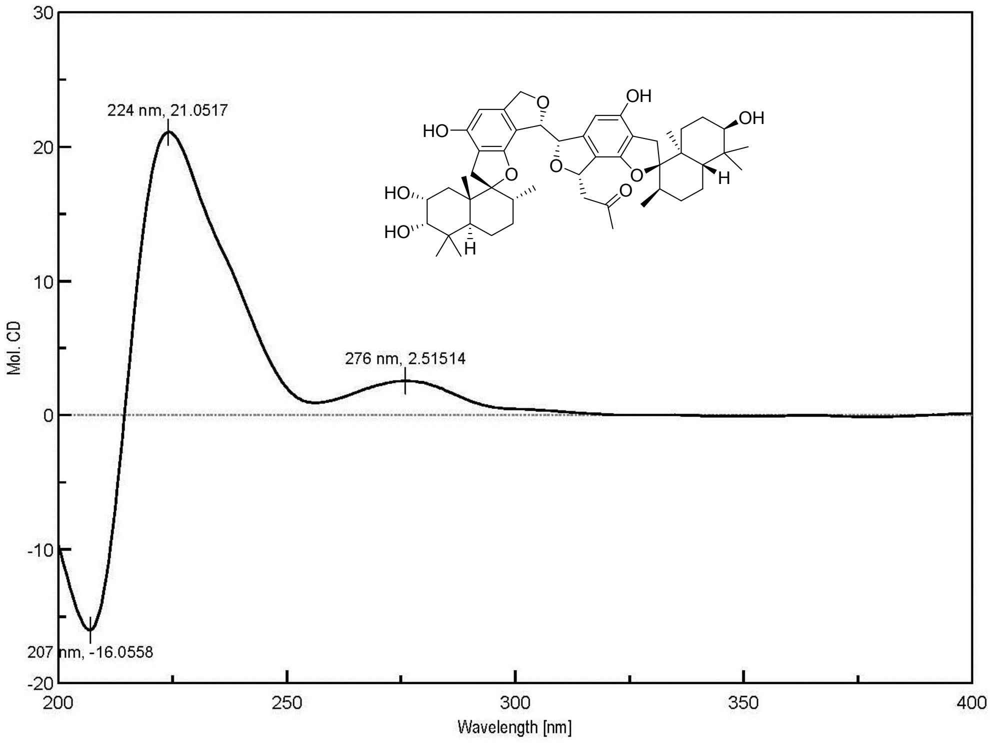
分辨率: 8.000 美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S68. UV spectrum of compound **6**



[Measurement Information]	
Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 16:17
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S69. ECD spectrum of compound **6**



[Measurement Information]

Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 16:17
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S70. ^{1}H NMR spectrum of compound **7** in acetone-d_6 at 600 MHz

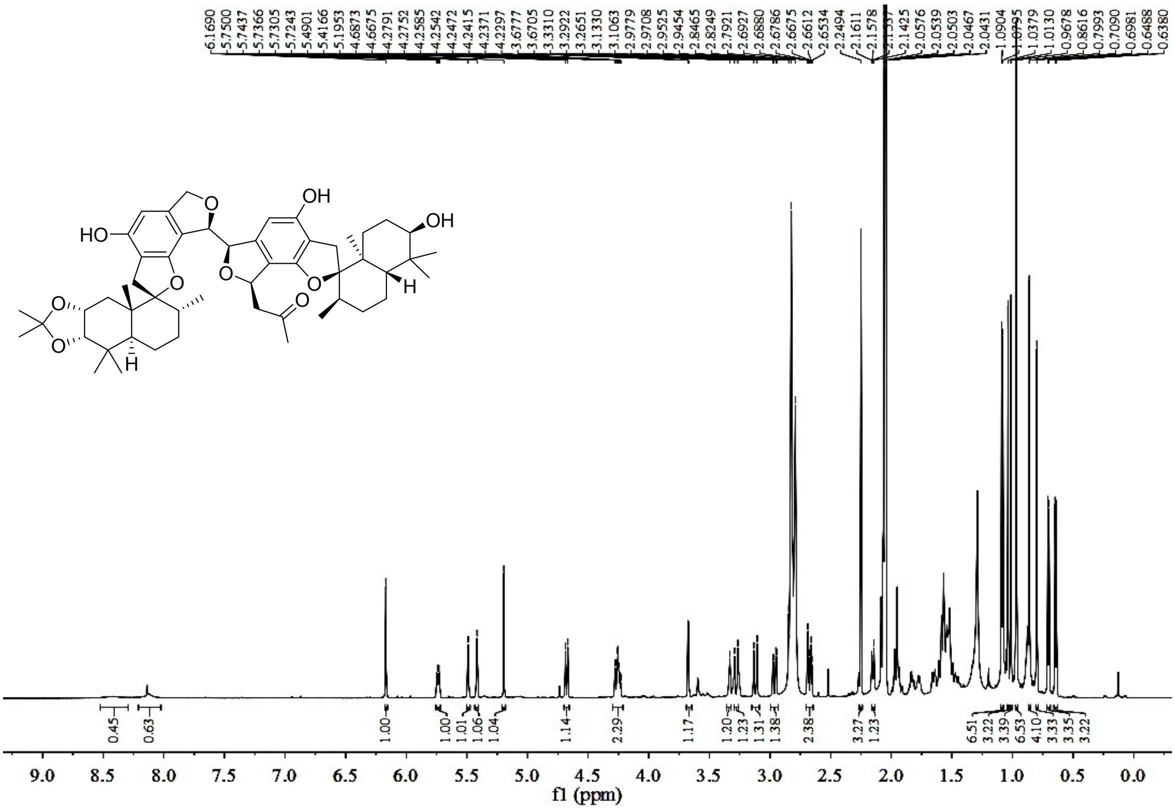


Figure S71. ^{13}C NMR spectrum of compound **7** in acetone-d_6 at 150 MHz

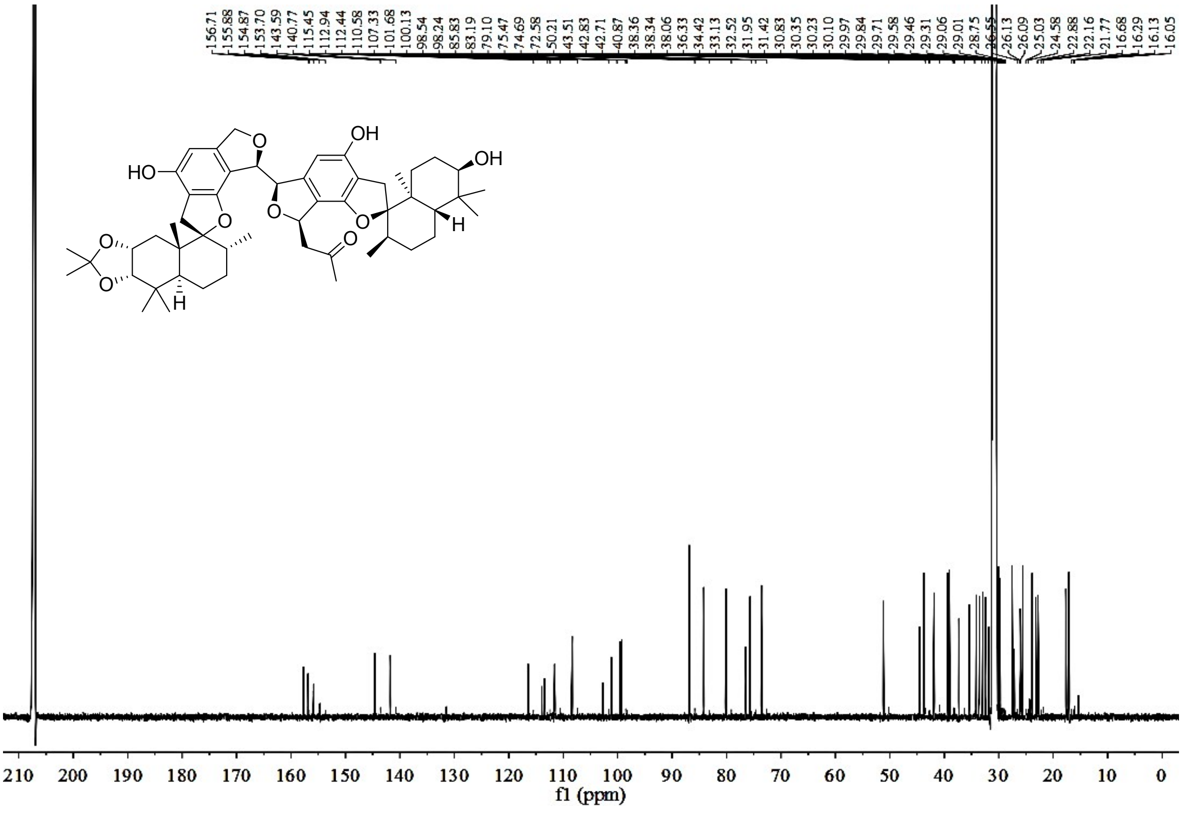


Figure S72. DEPT spectrum of compound **7** in acetone-d_6 at 150 MHz

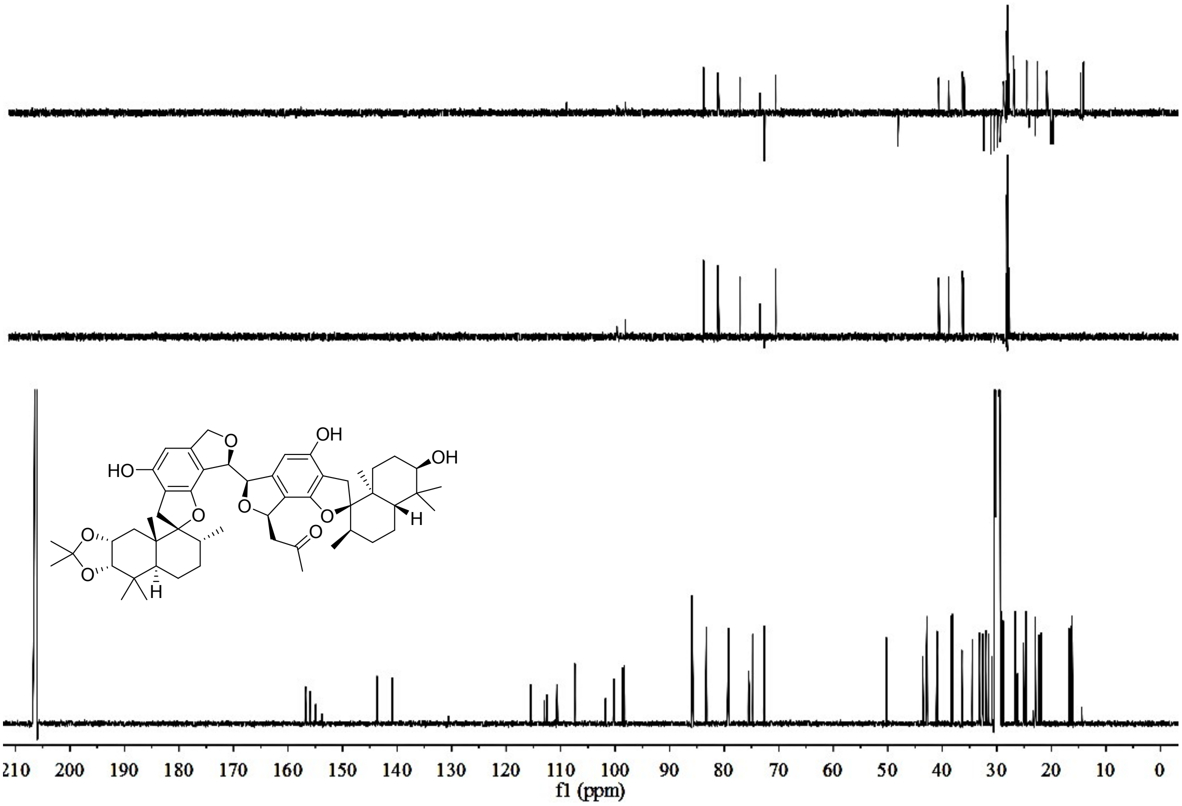


Figure S73. ^{1}H–^{1}H COSY spectrum of compound **7** in acetone-d_6

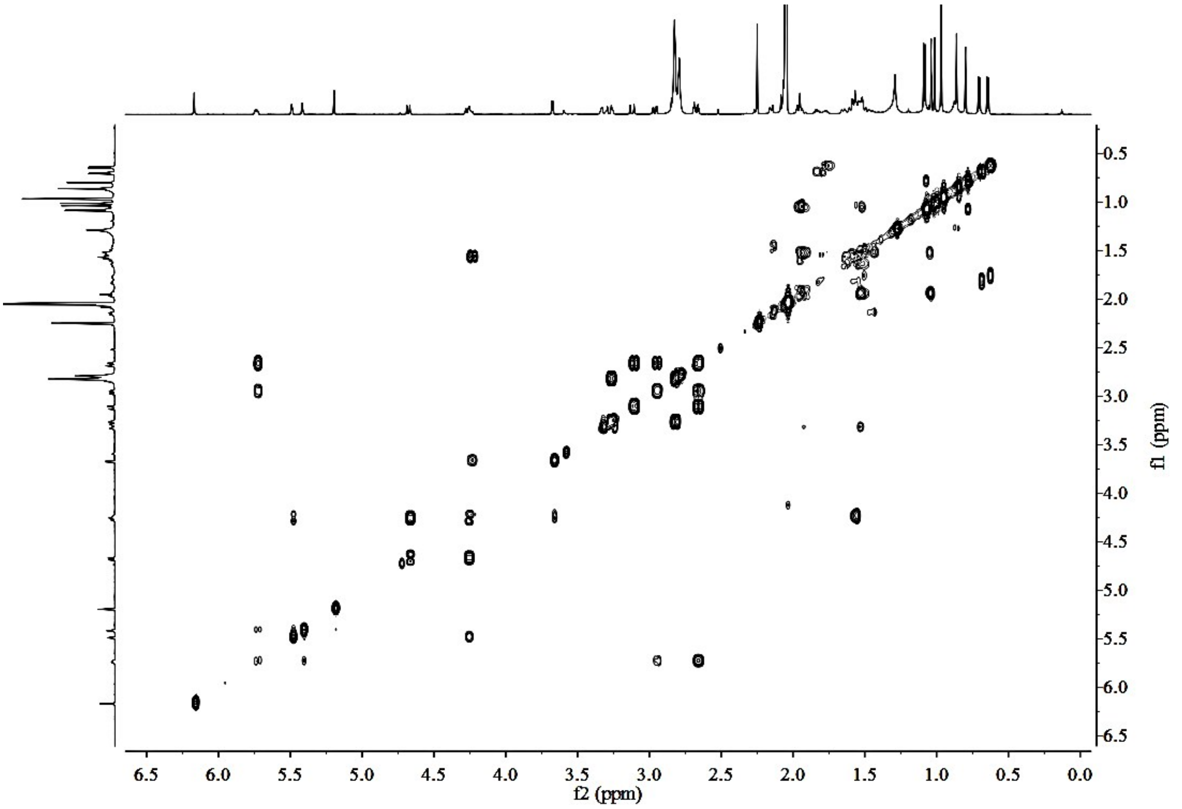


Figure S74. HSQC spectrum of compound **7** in acetone-d_6

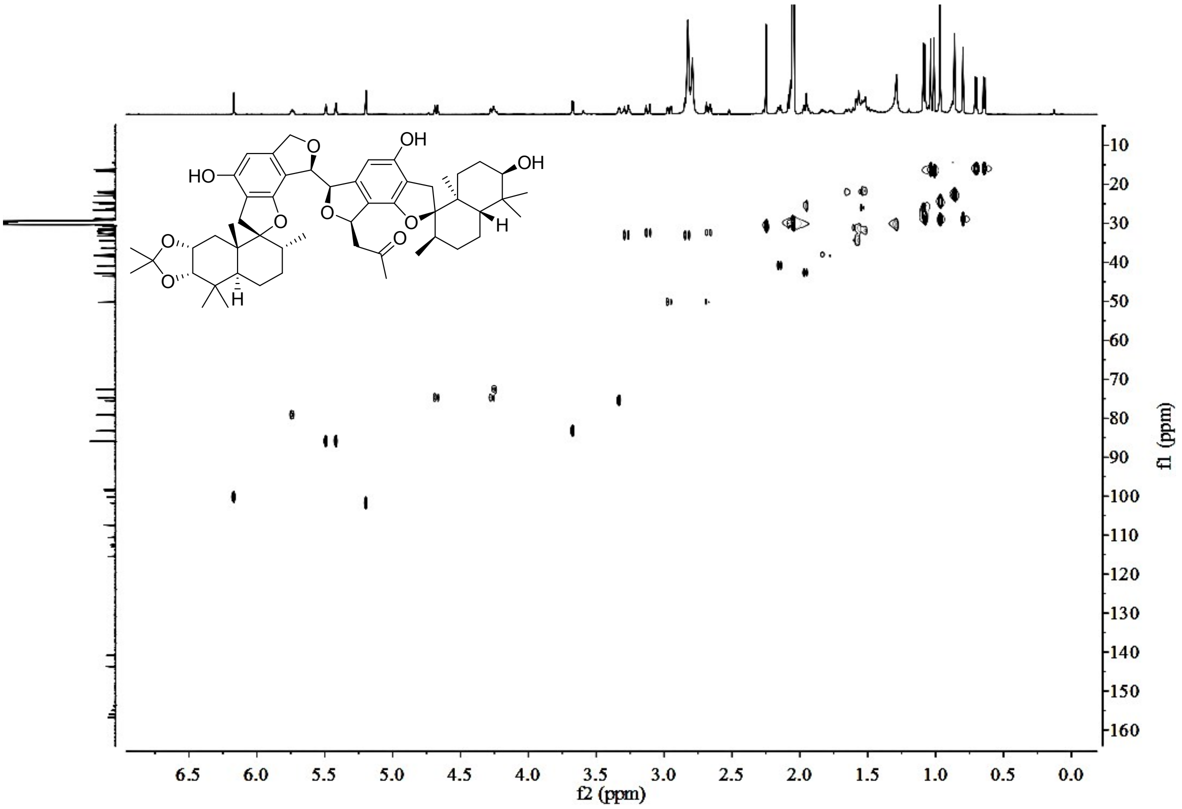


Figure S75. HMBC spectrum of compound **7** in acetone-d_6

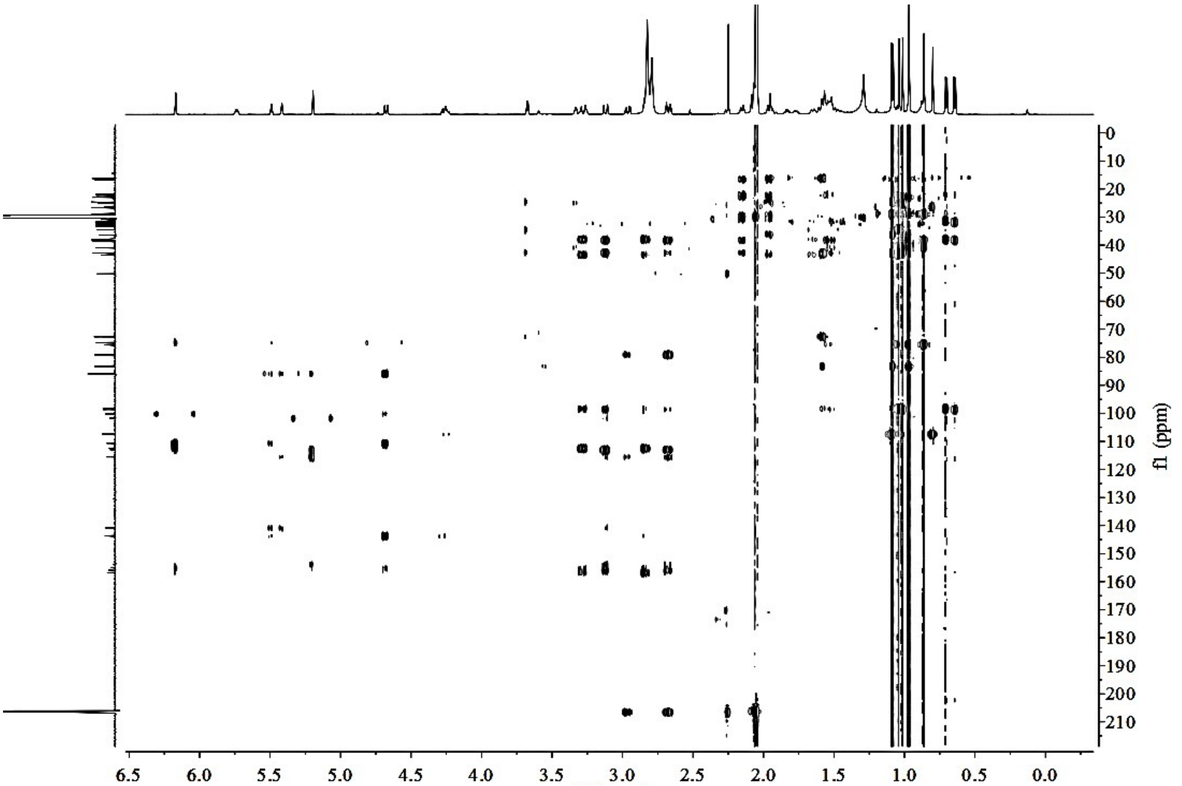


Figure S76. NOE difference spectrum of compound **7** in acetone-d_6

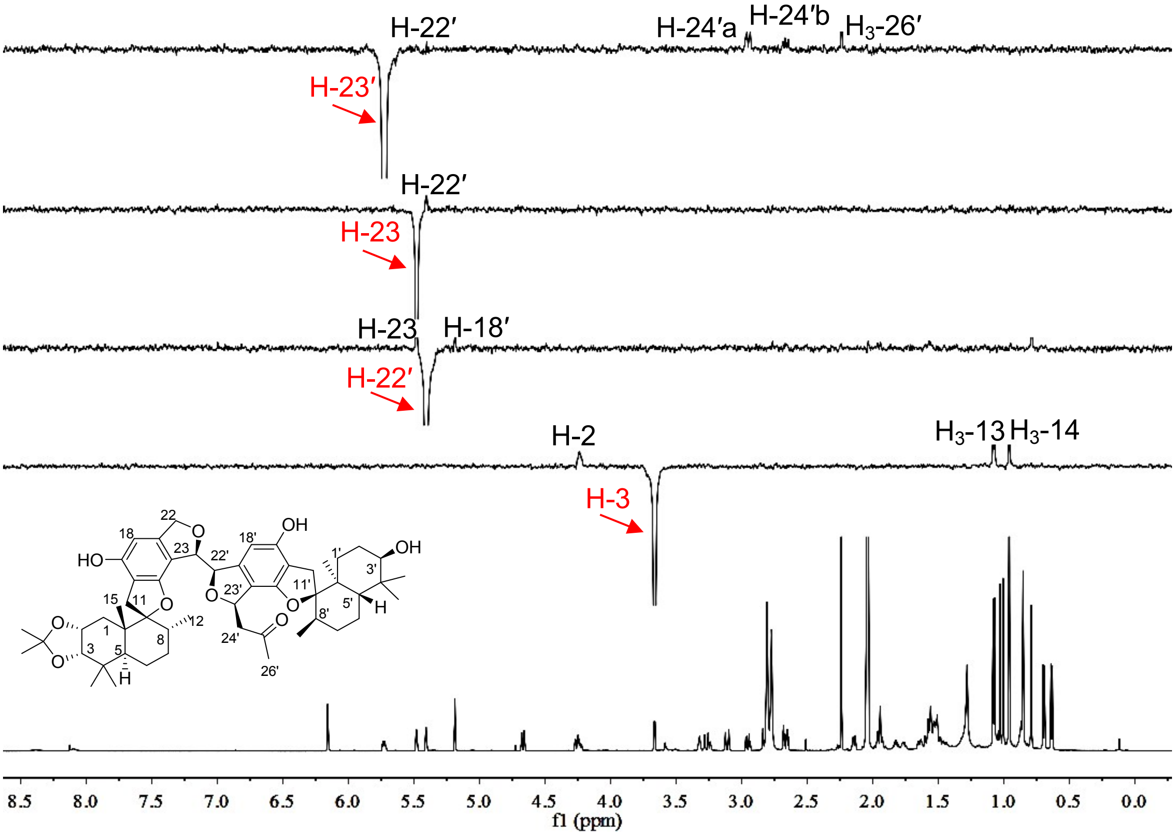


Figure S76. NOE difference spectrum of compound **7** in acetone-d_6 (continued)

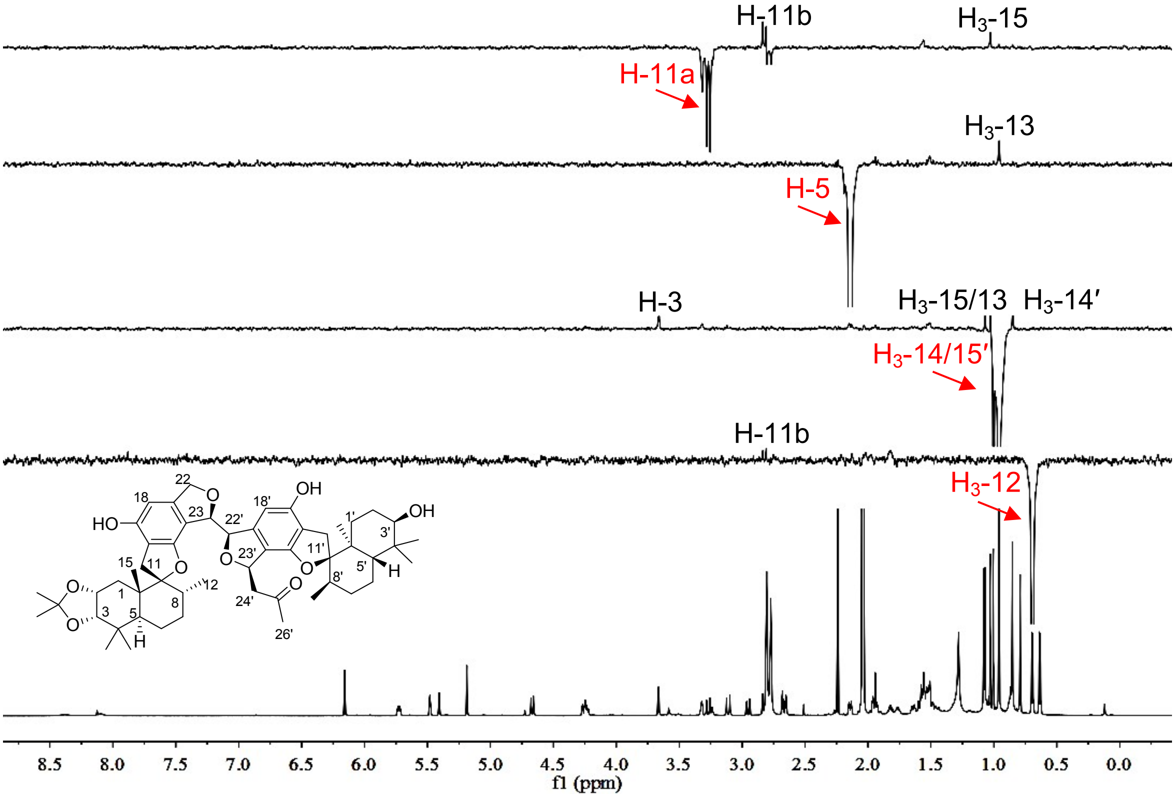


Figure S76. NOE difference spectrum of compound **7** in acetone-d_6 (continued)

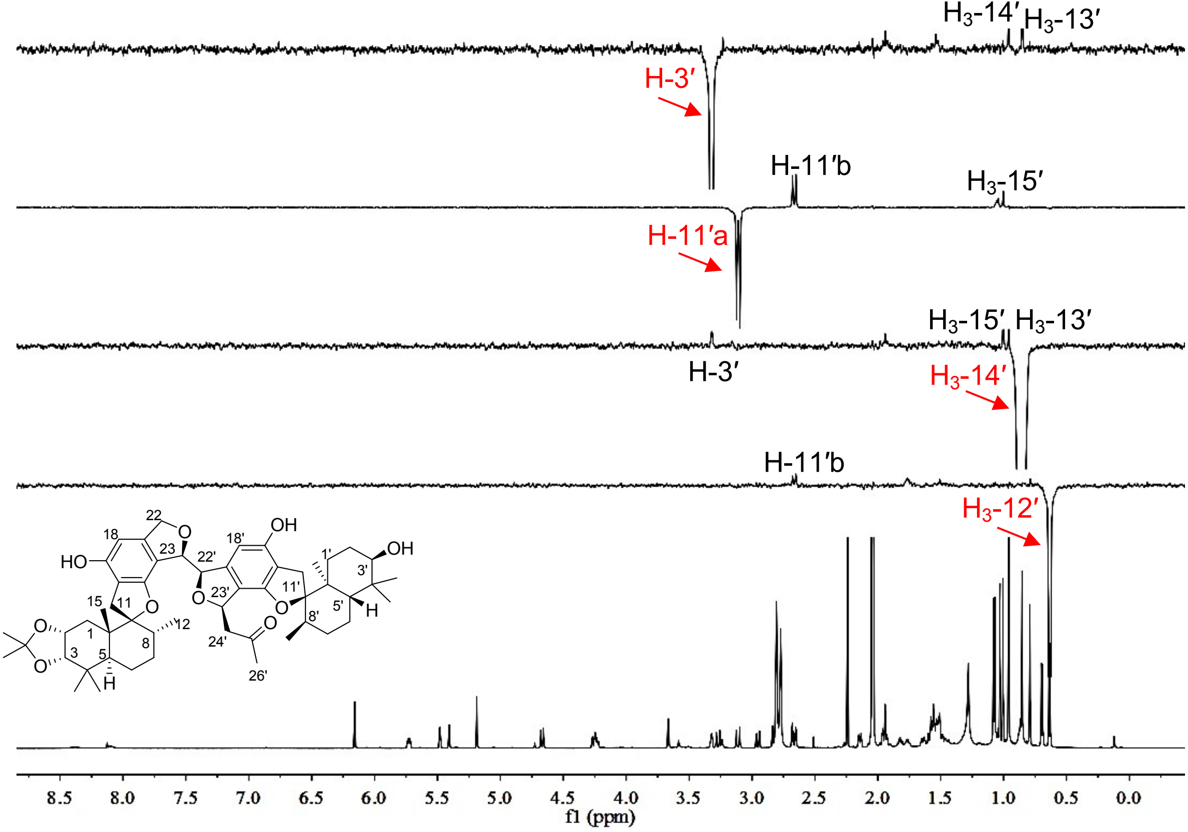


Figure S77. HR-ESI-MS spectrum of compound **7**

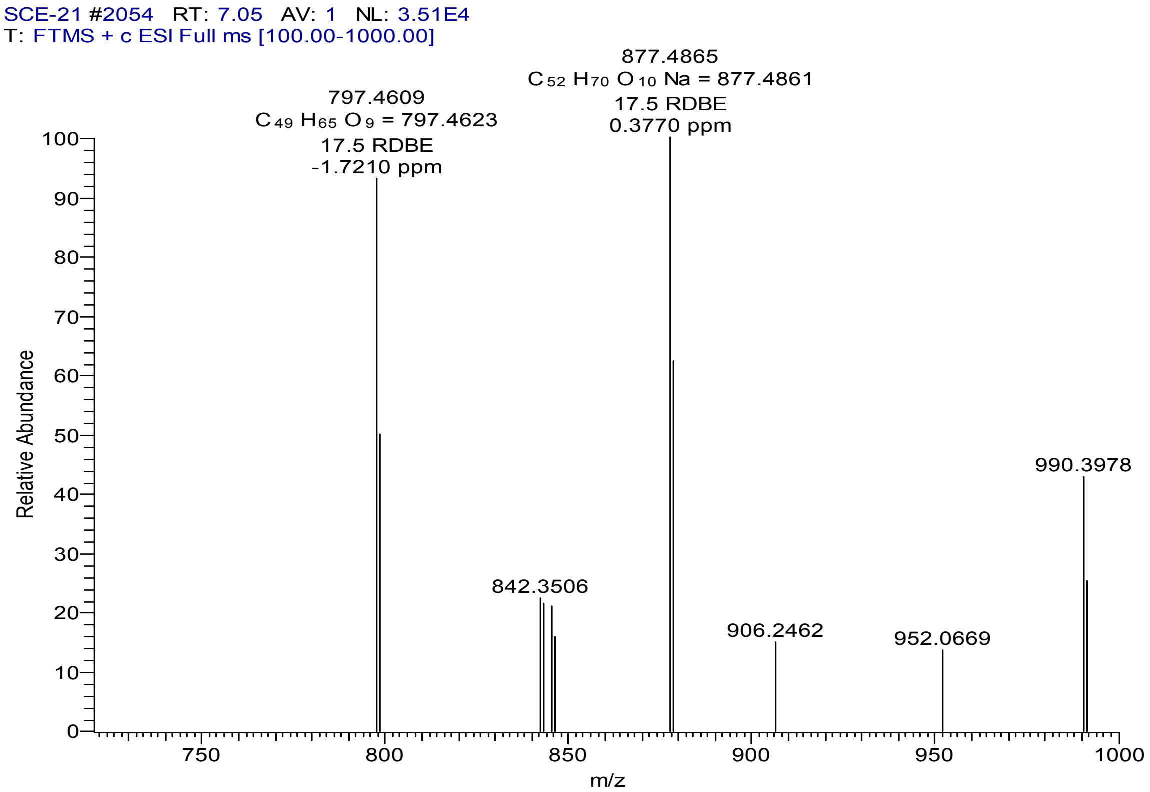
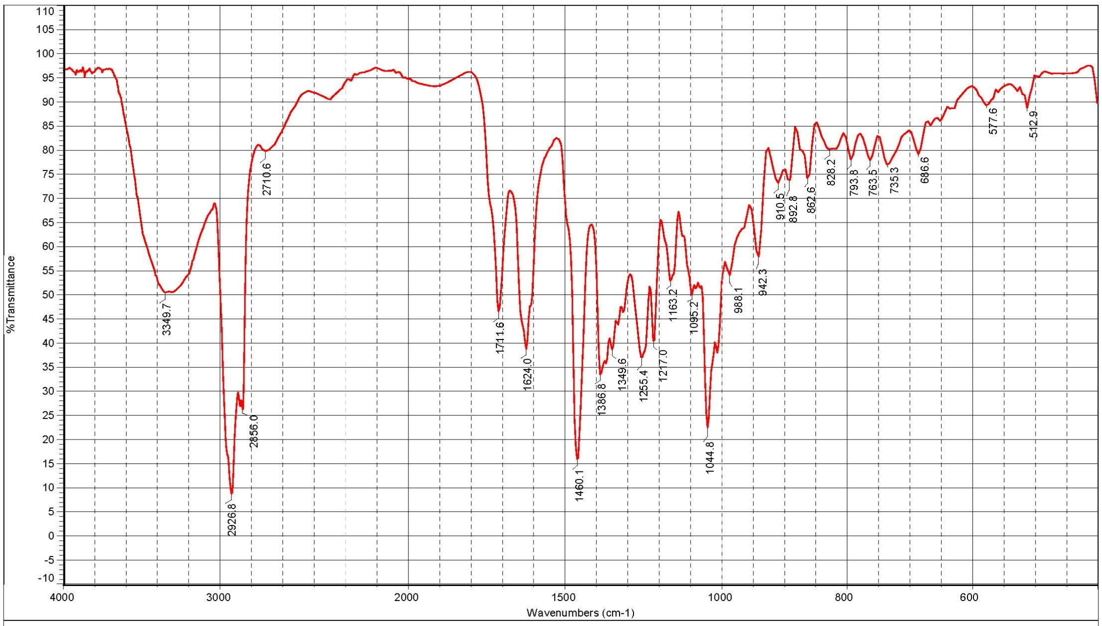


Figure S78. IR spectrum of compound **7**

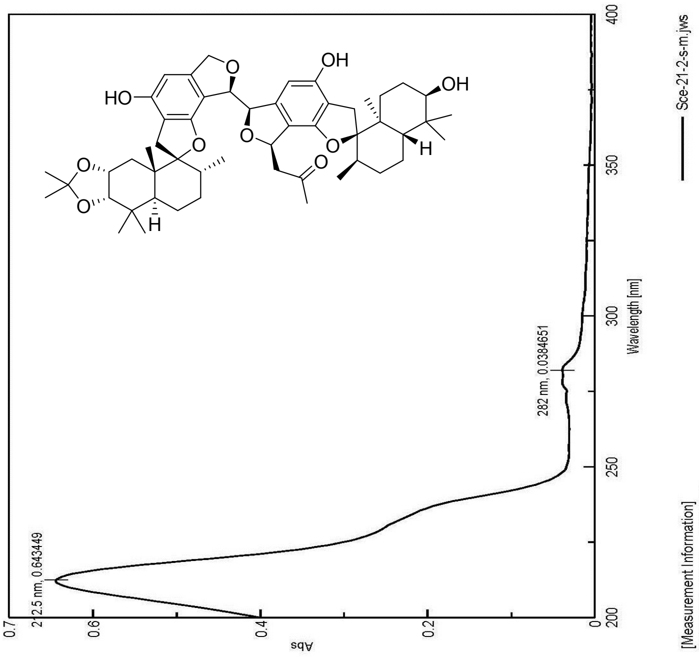


日期: 星期四 12月 29 08:46:52 2016 (GMT+08:00Sample Name： Sce - 21 （显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100 傅里叶变换红外显微镜(FT-IR Microscope)：Centaurμs

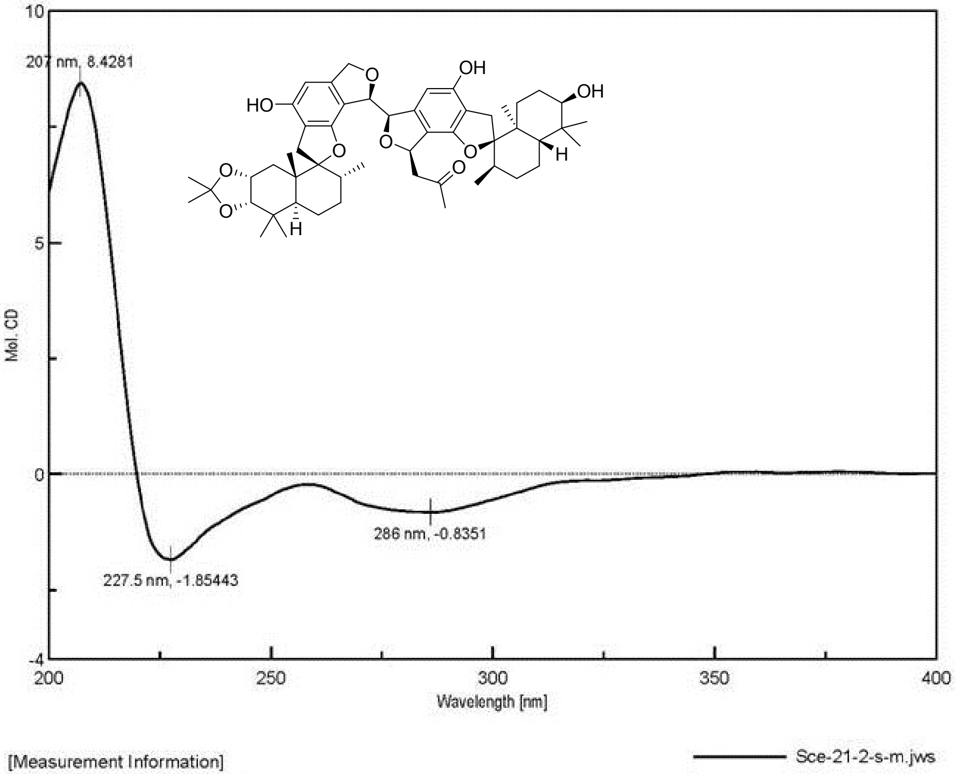
分辨率: 8.000 美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S79. UV spectrum of compound **7**



[Measurement Information]	
Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 16:02
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S80. ECD spectrum of compound **7**



[Measurement Information]

Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/9/22 15:26
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.183 (w/v)%

Figure S81. ^{1}H NMR spectrum of compound **8** in acetone-d_6 at 600 MHz

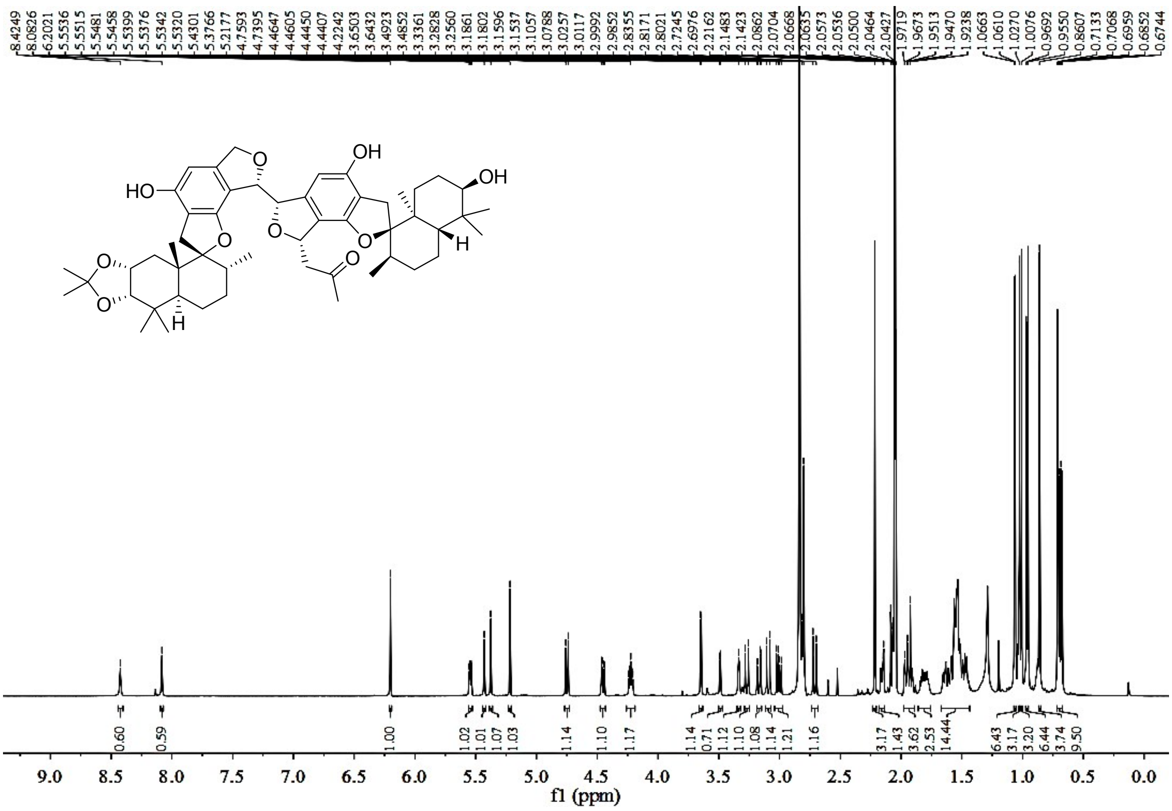


Figure S82. ^{13}C NMR spectrum of compound **8** in acetone-d_6 at 150 MHz

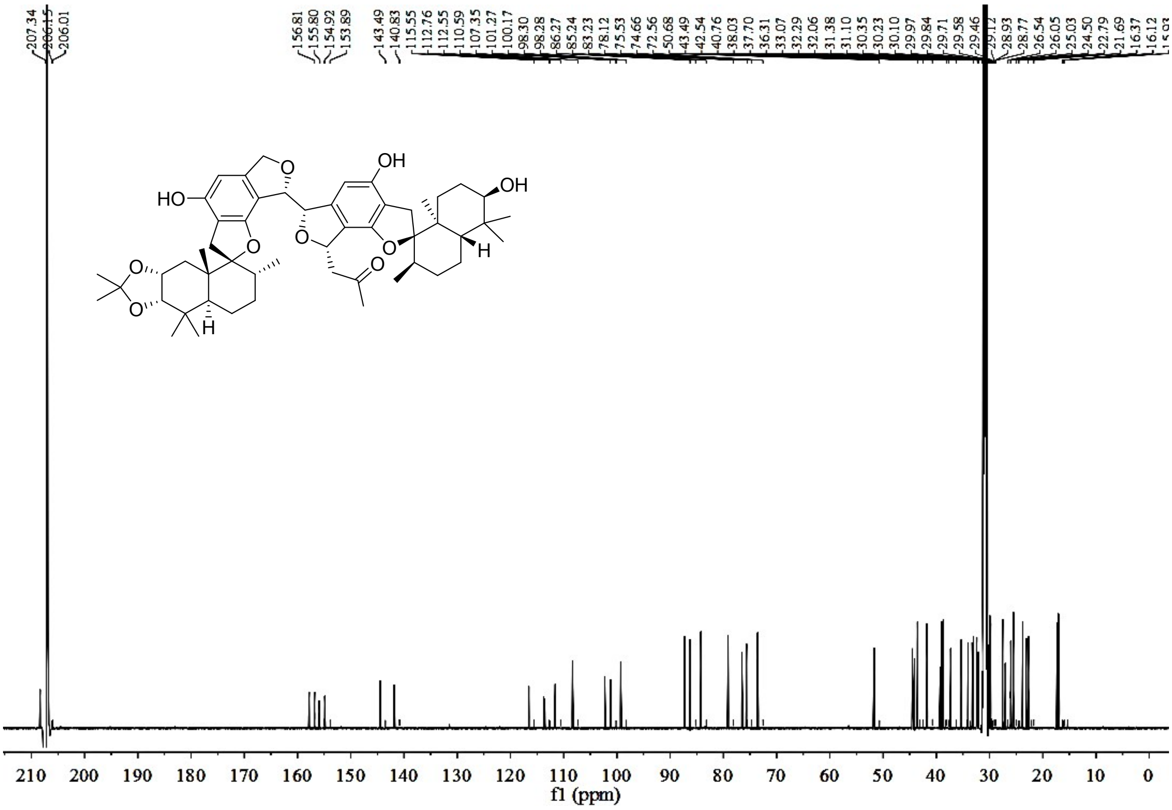


Figure S83. DEPT spectrum of compound **8** in acetone-d_6 at 150 MHz

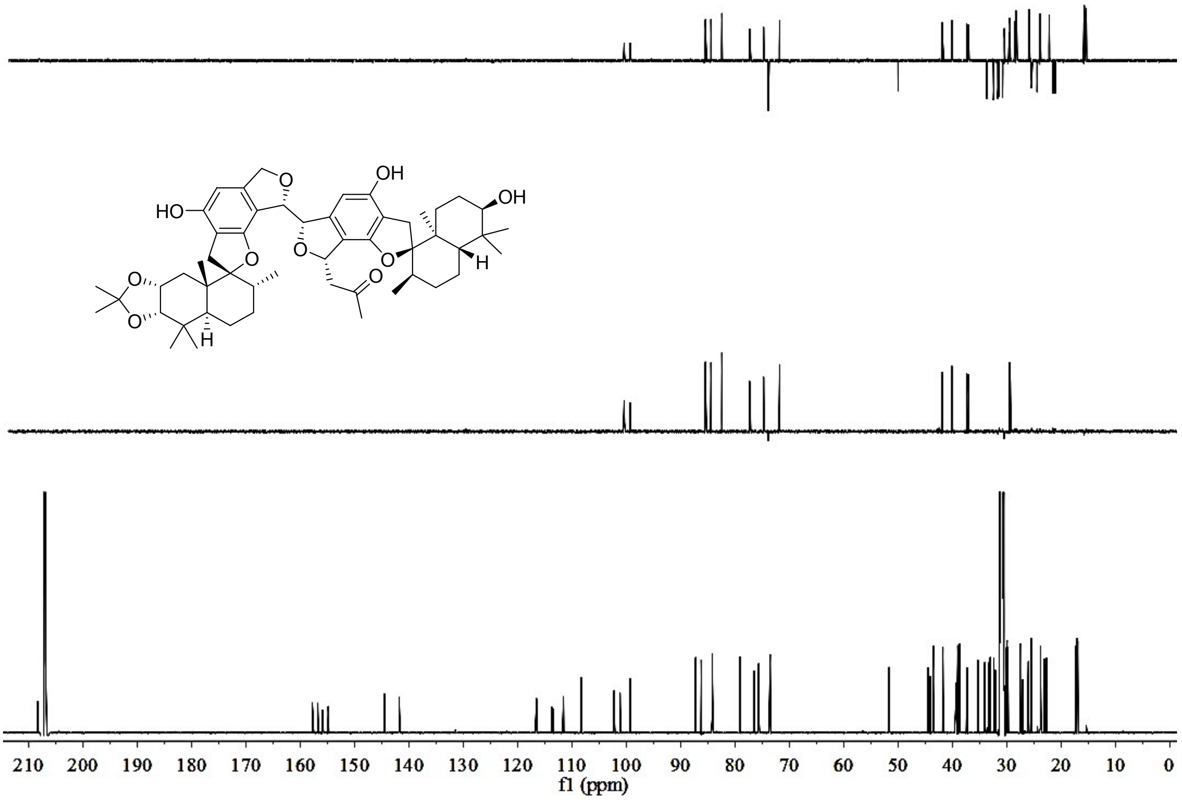


Figure S84. ^{1}H–^{1}H COSY spectrum of compound **8** in acetone-d_6

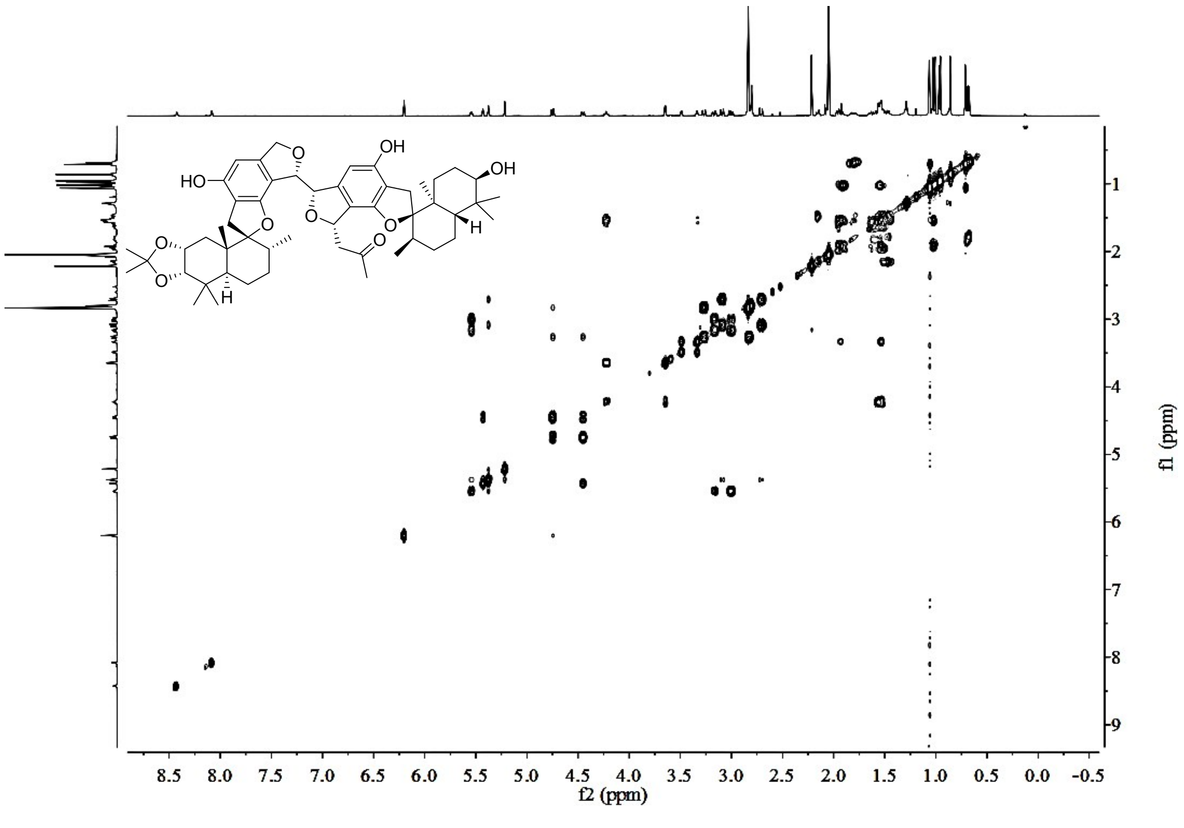


Figure S85. HSQC spectrum of compound **8** in acetone-d_6

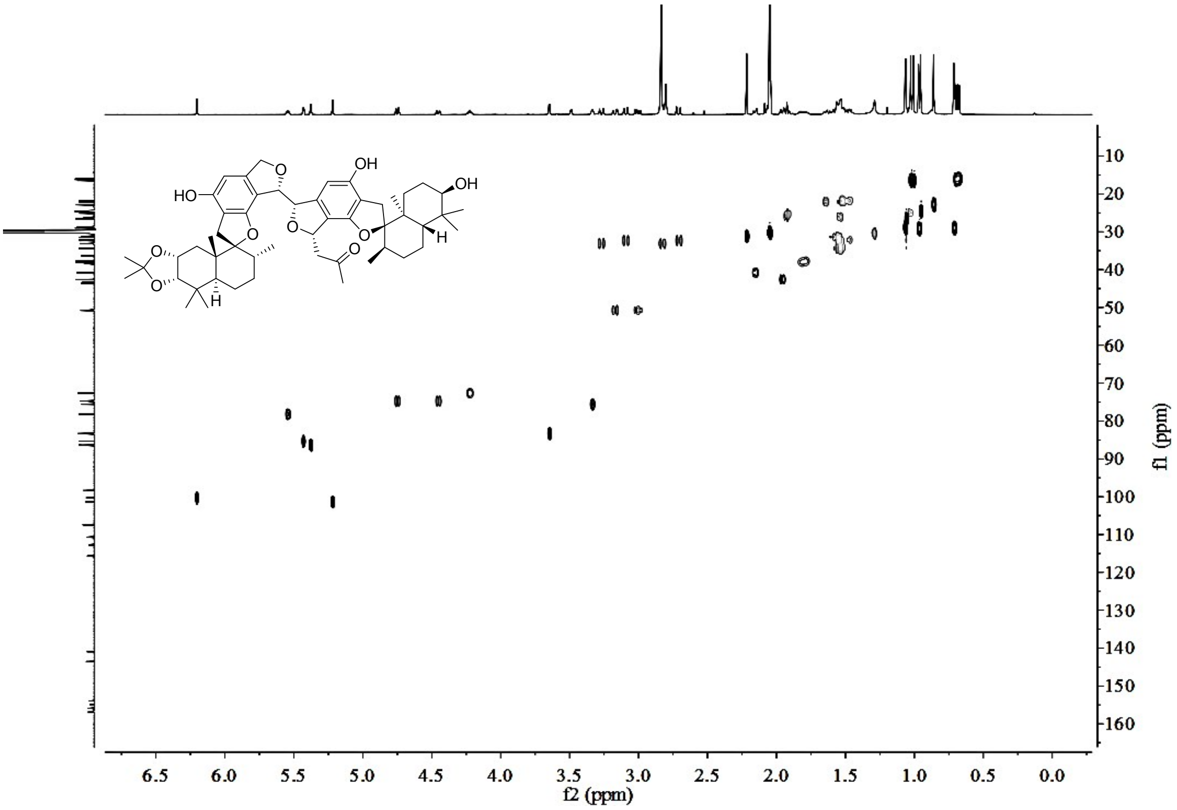


Figure S86. HMBC spectrum of compound **8** in acetone-d_6

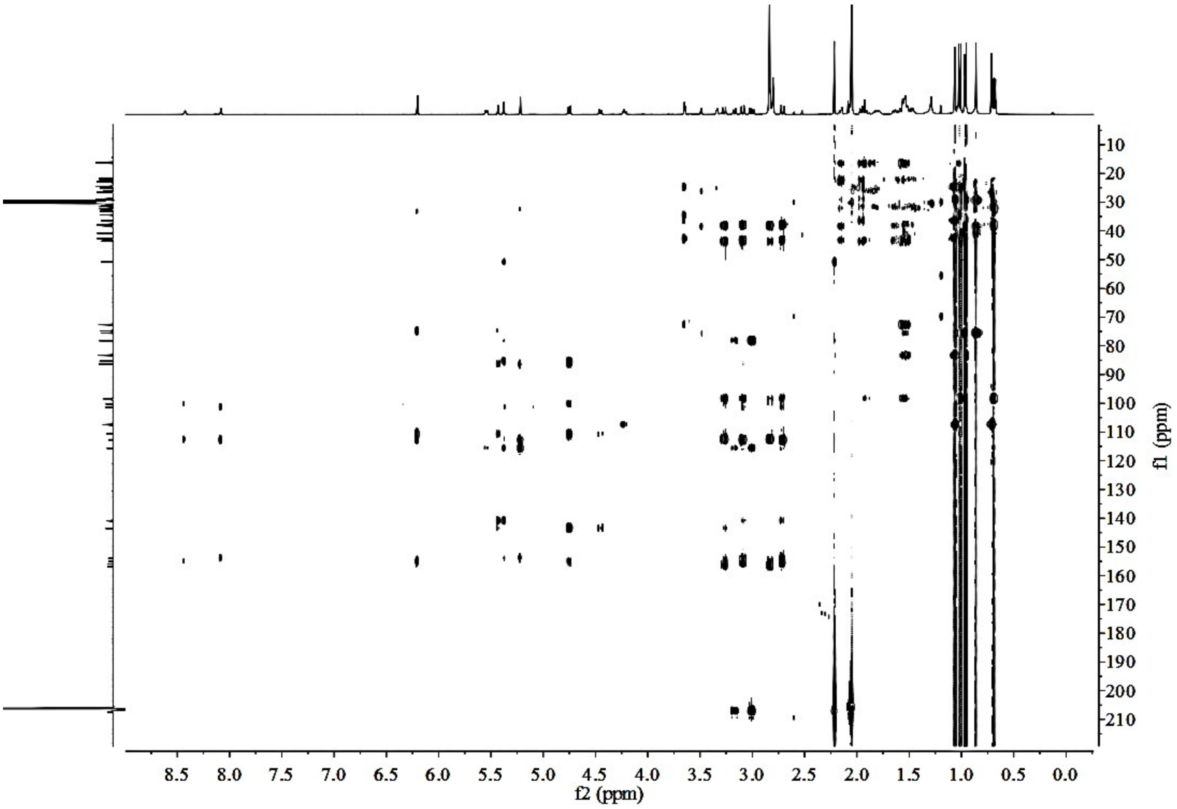


Figure S87. NOE difference spectrum of compound **8** in acetone-*d*$_6$

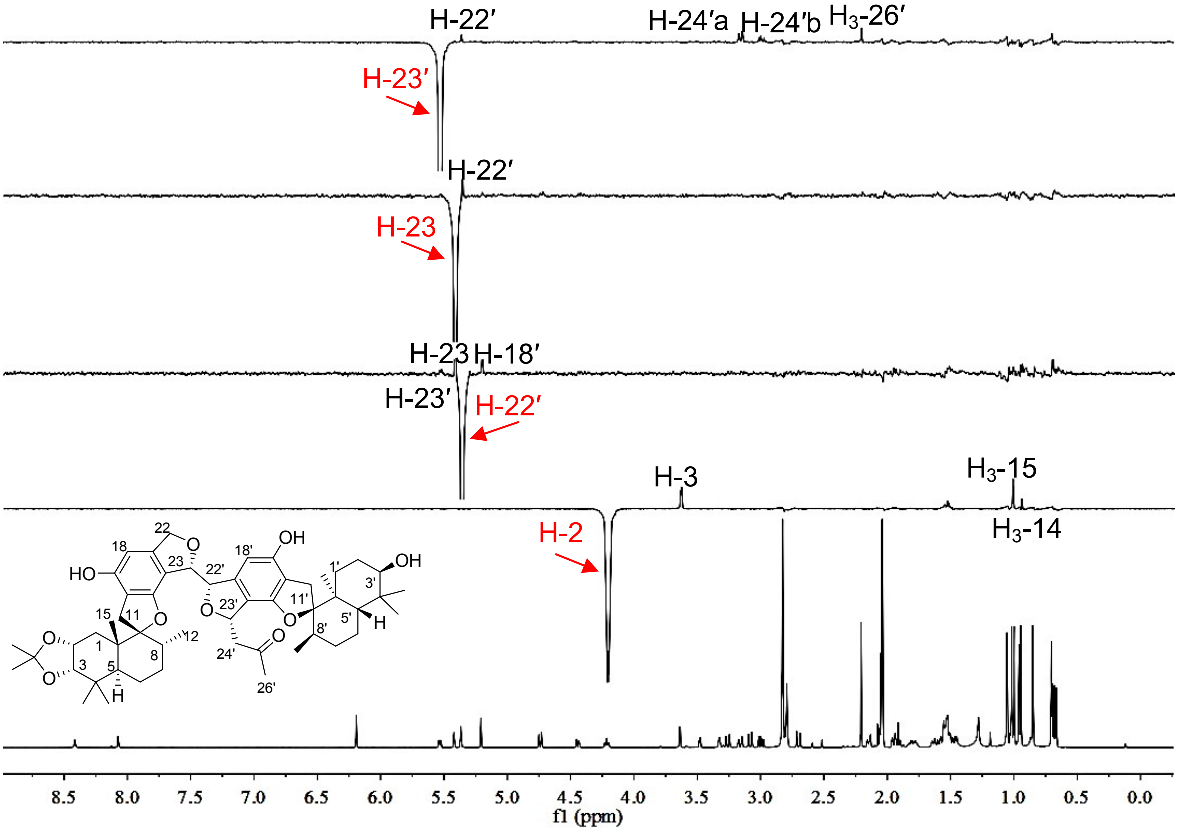


Figure S87. NOE difference spectrum of compound **8** in acetone-*d*$_6$ (continued)

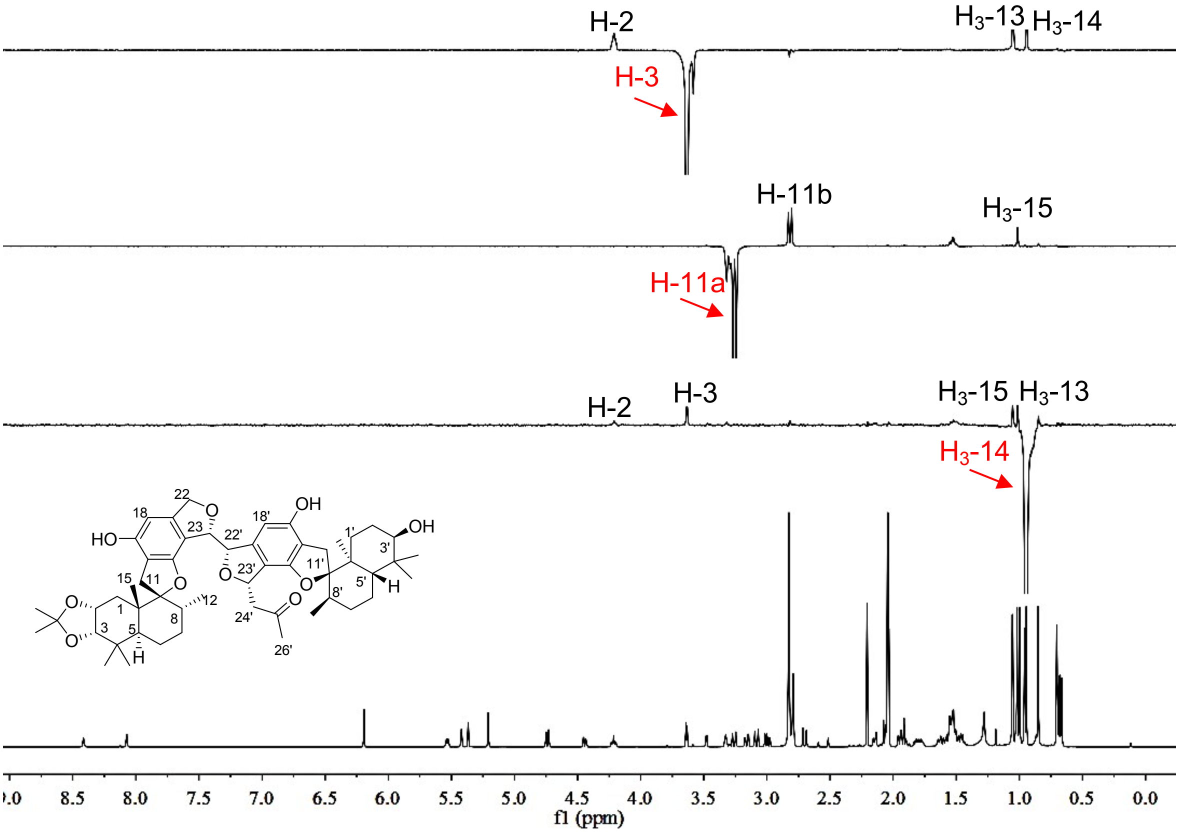


Figure S87. NOE difference spectrum of compound **8** in acetone-d_6 (continued)

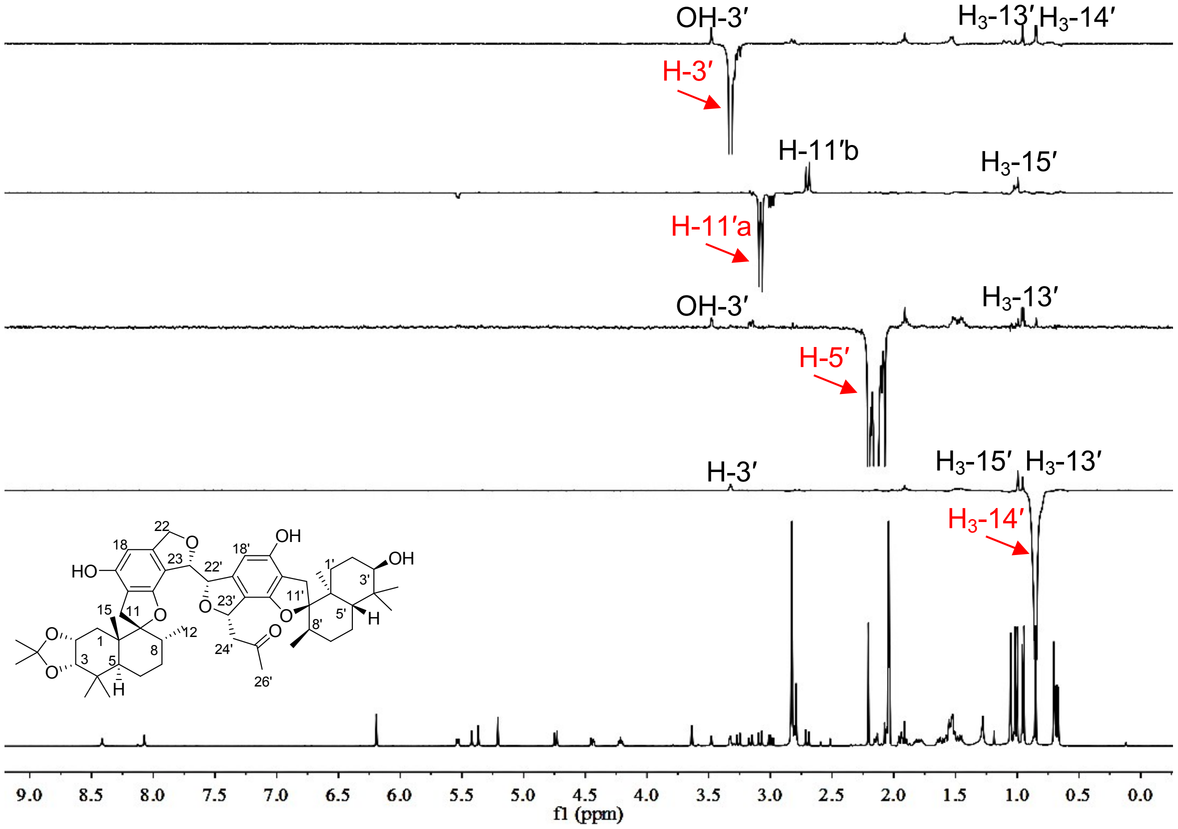


Figure S88. HR-ESI-MS spectrum of compound **8**

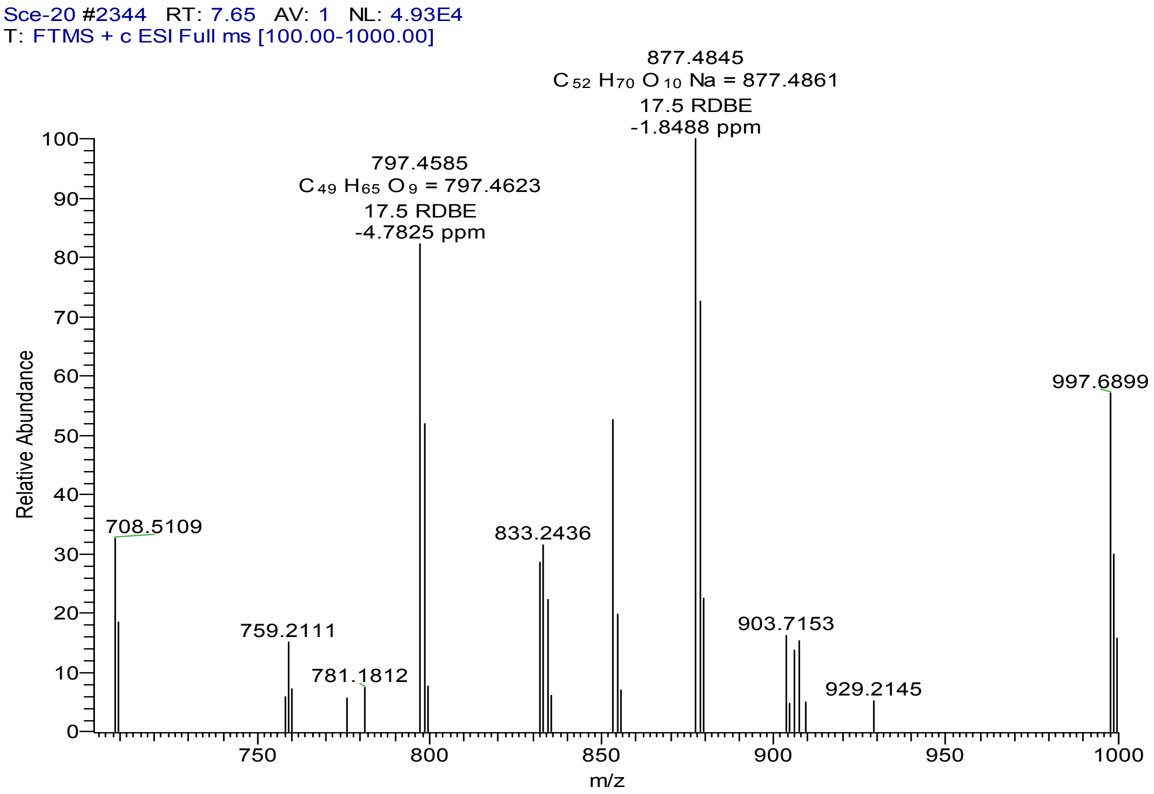
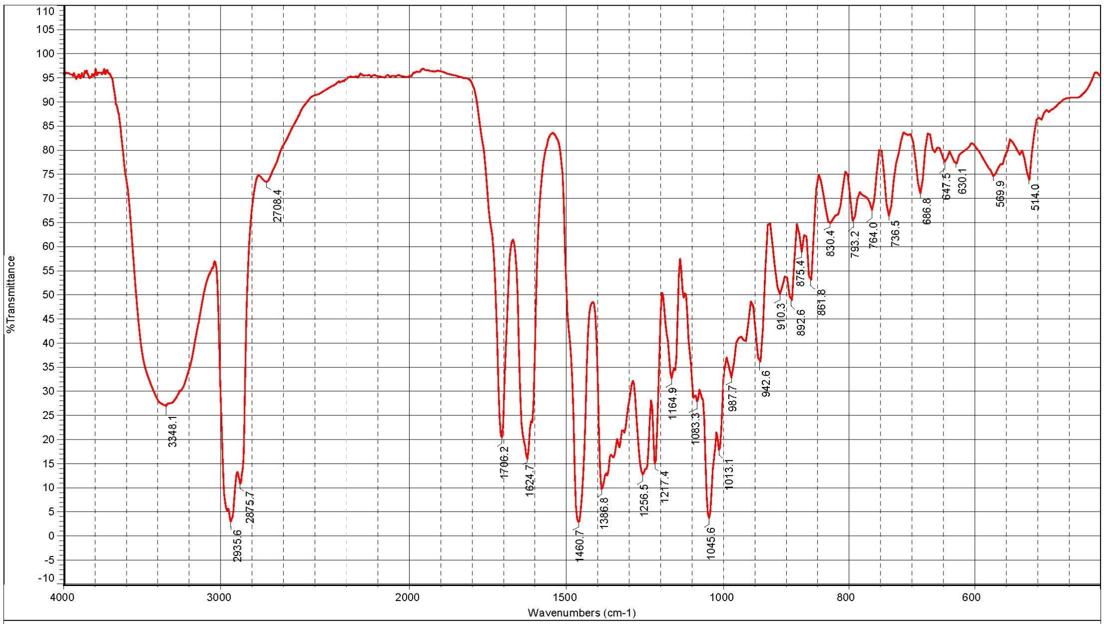


Figure S89. IR spectrum of compound **8**

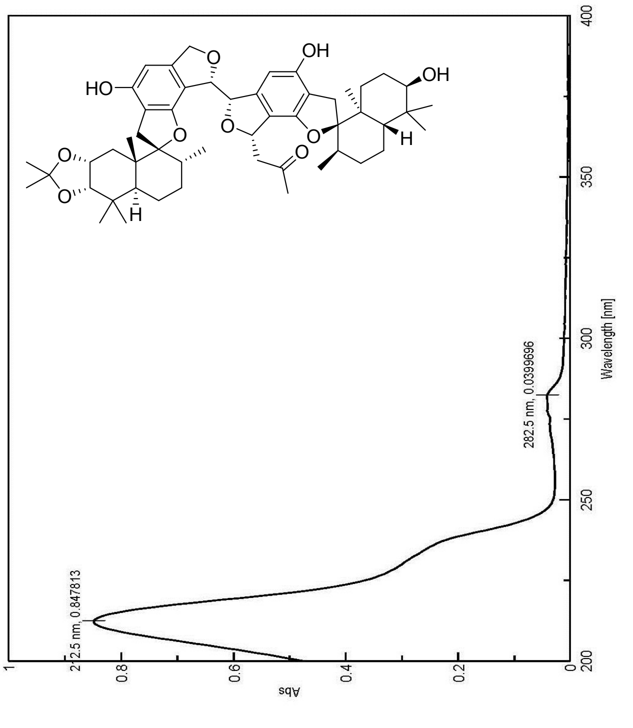


日期: 星期四 12月 29 08:37:51 2016 (GMT+08:00Sample Name ： Sce - 20　(显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100　傅里叶变换红外显微镜(FT-IR Microscope)：Centaurμs

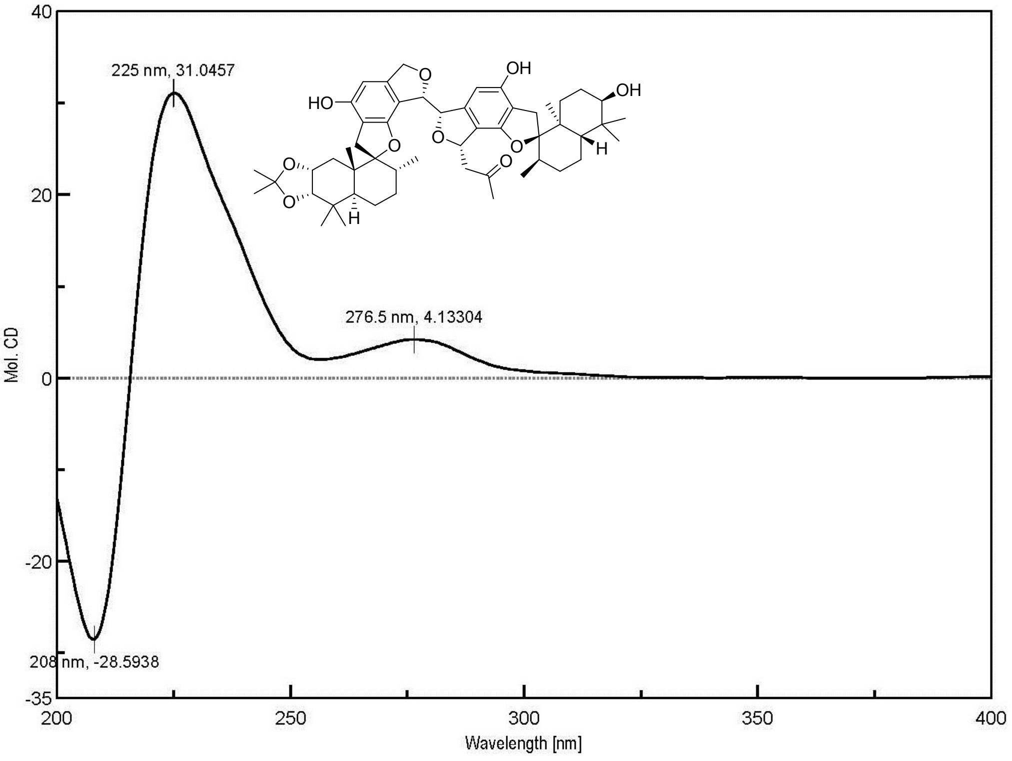
分辨率: 8.000　美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S90. UV spectrum of compound **8**



[Measurement Information]	
Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 15:40
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S91. ECD spectrum of compound **8**



[Measurement Information]

Instrument Name	IMM-CD
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	0.1 mm
Measurement date	2016/11/30 15:40
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	2.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.167 (w/v)%

Figure S92. ^{1}H NMR spectrum of compound **9** in acetone-d_6 at 600 MHz

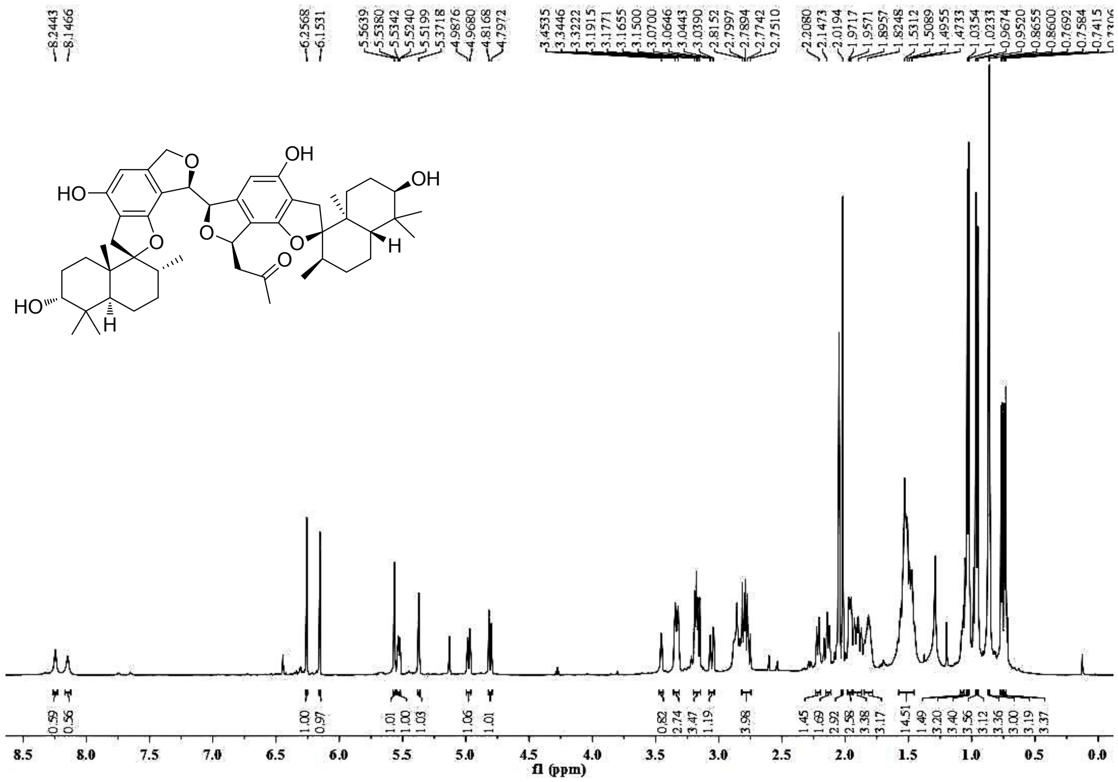


Figure S93. ^{13}C NMR spectrum of compound **9** in acetone-d_6 at 150 MHz

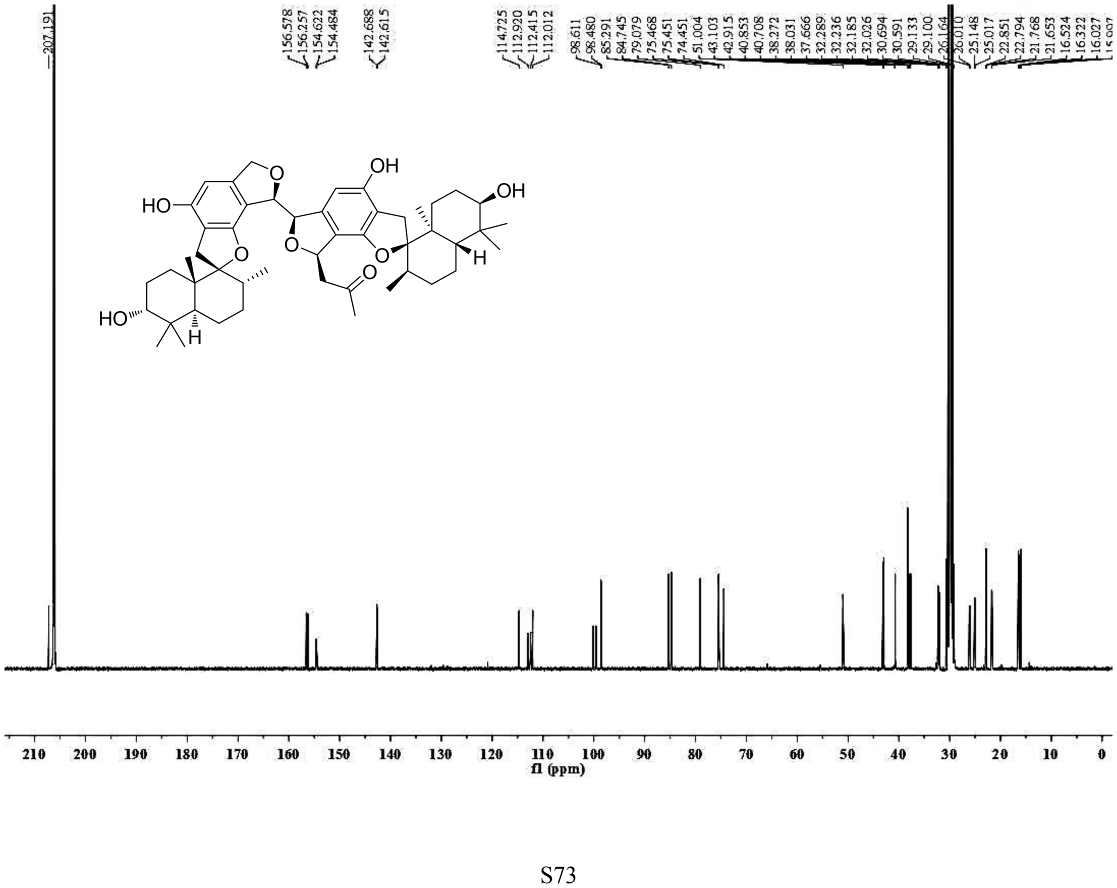


Figure S94. DEPT spectrum of compound **9** in acetone-d_6 at 150 MHz

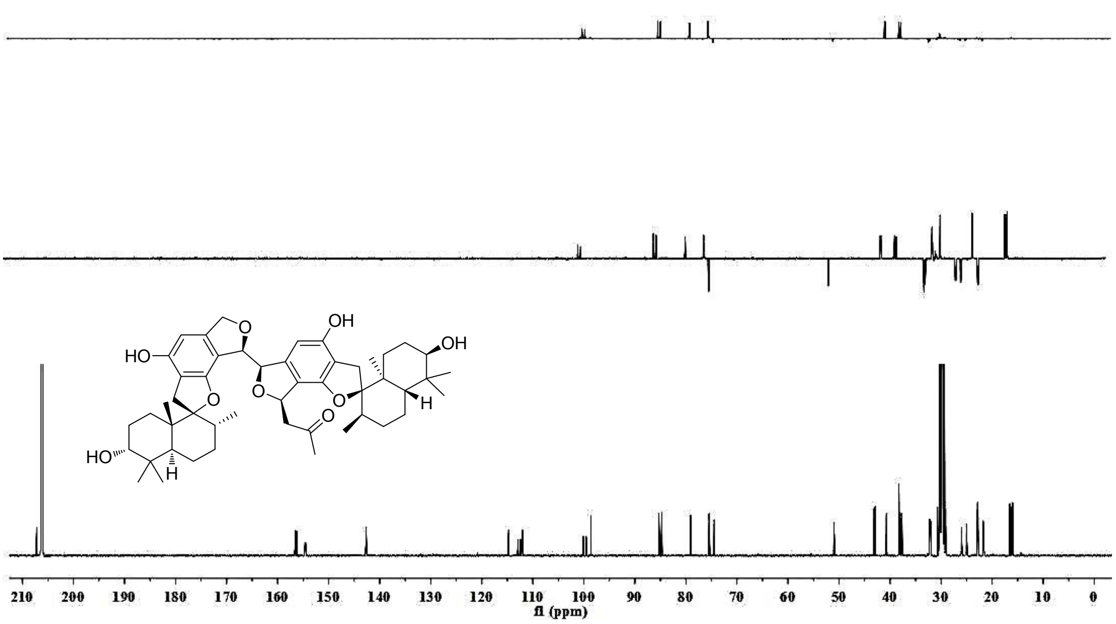


Figure S95. ^{1}H–^{1}H COSY spectrum of compound **9** in acetone-d_6

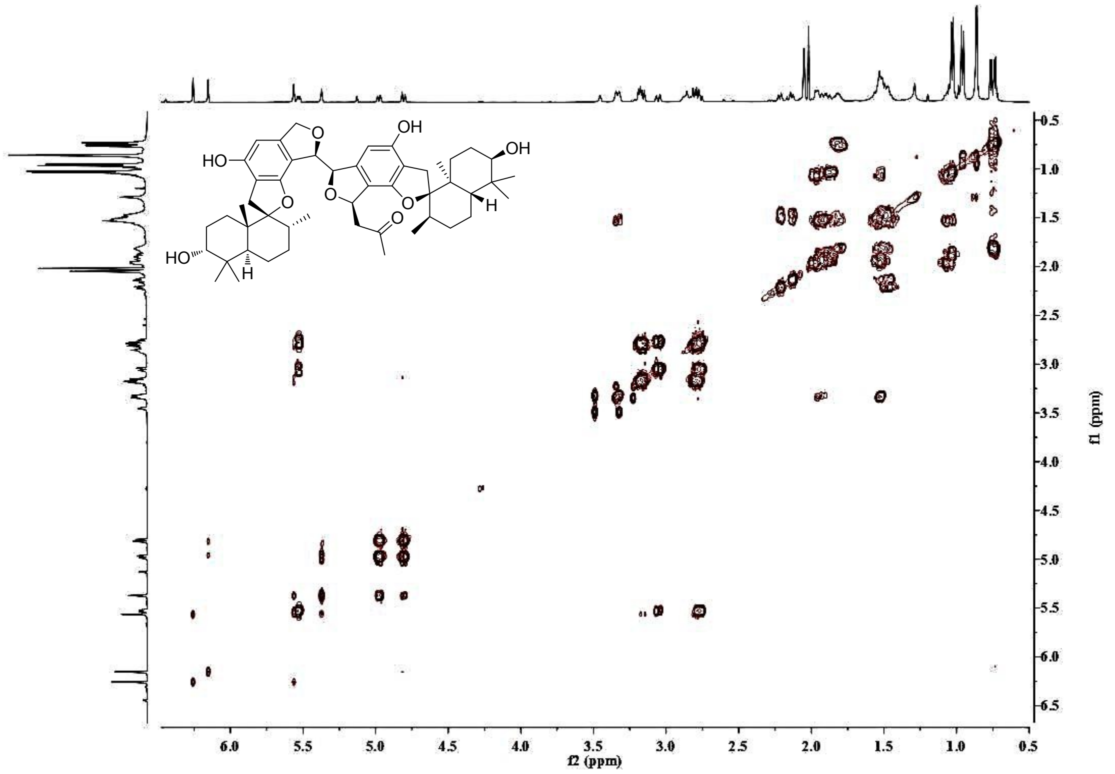


Figure S96. HSQC spectrum of compound **9** in acetone-d_6

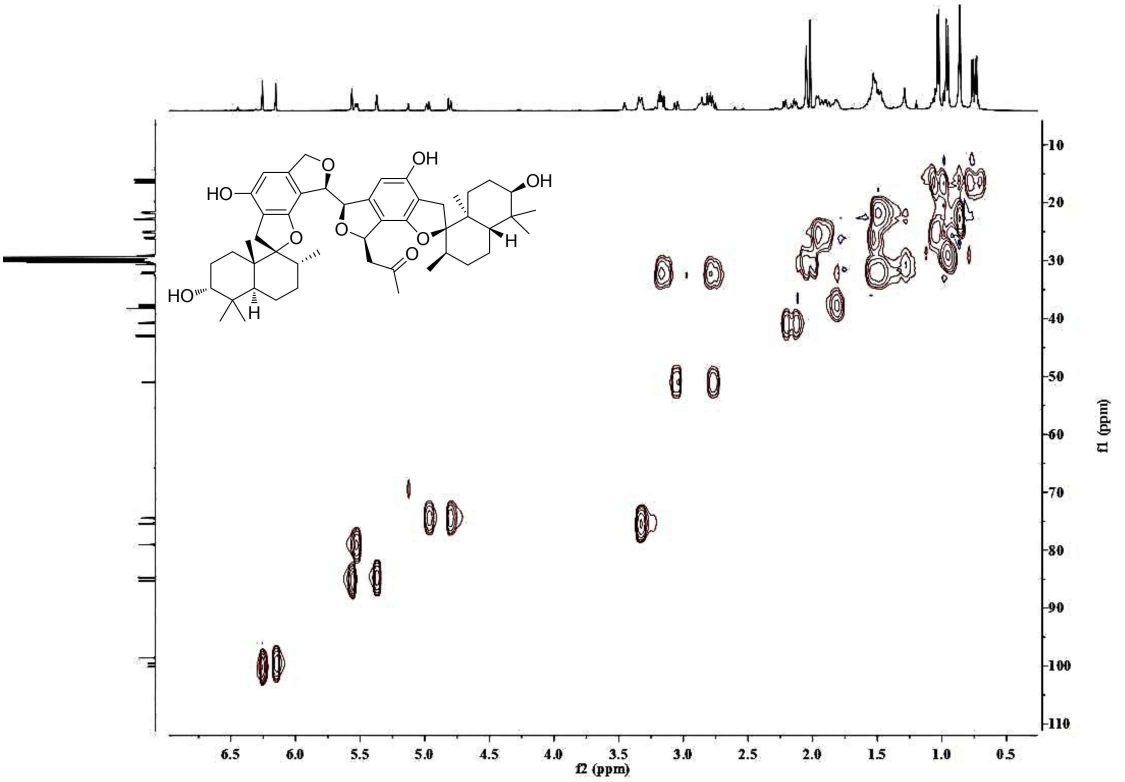


Figure S97. HMBC spectrum of compound **9** in acetone-d_6

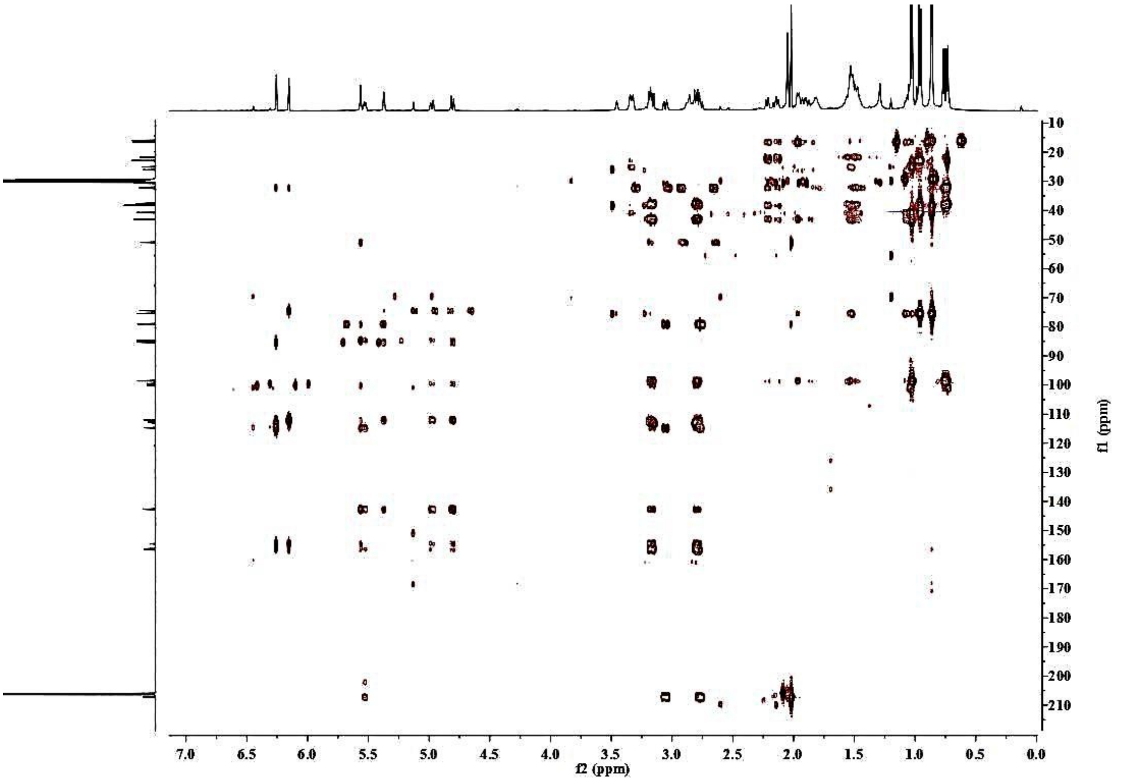


Figure S98. 1D NOE spectrum of compound **9** in acetone-d_6

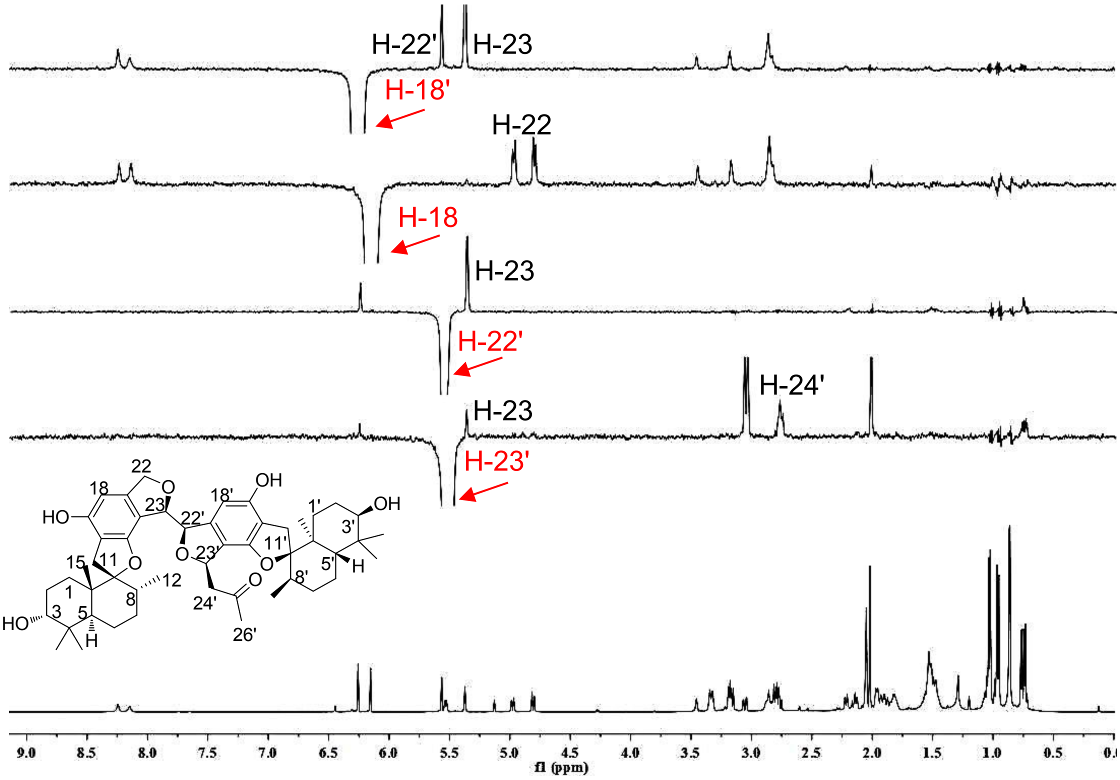


Figure S98. 1D NOE spectrum of compound **9** in acetone-d_6 (continued)

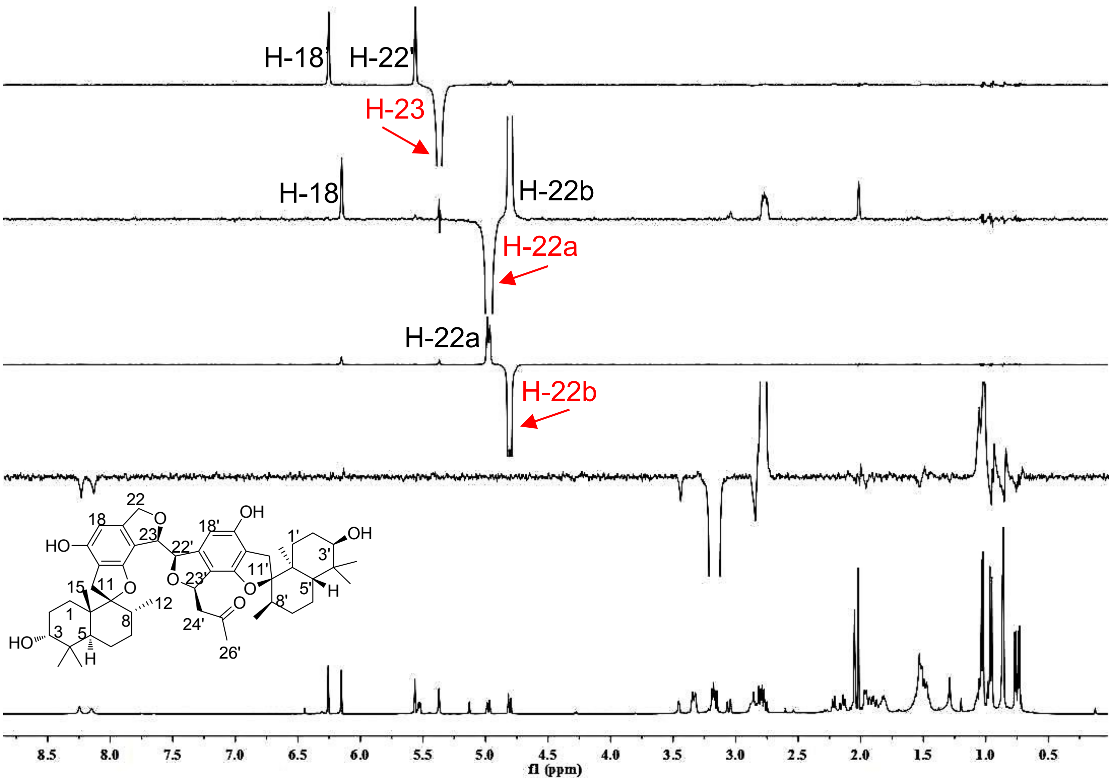


Figure S99. 2D NOE spectrum of compound **9** in acetone-d_6

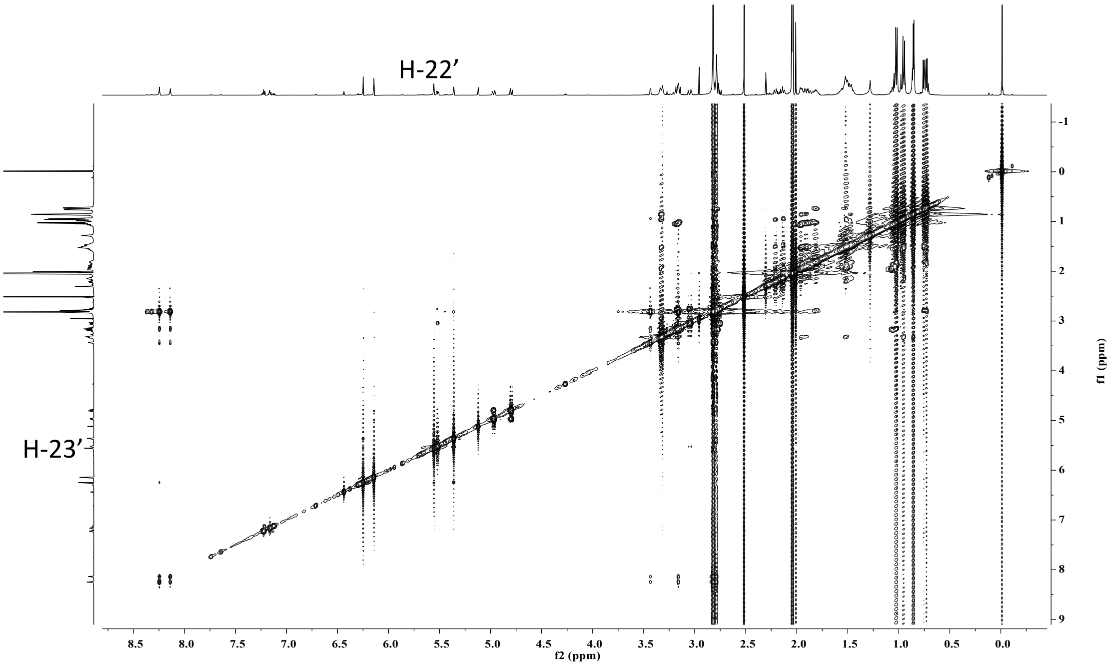


Figure S100. HR-ESI-MS spectrum of compound **9**

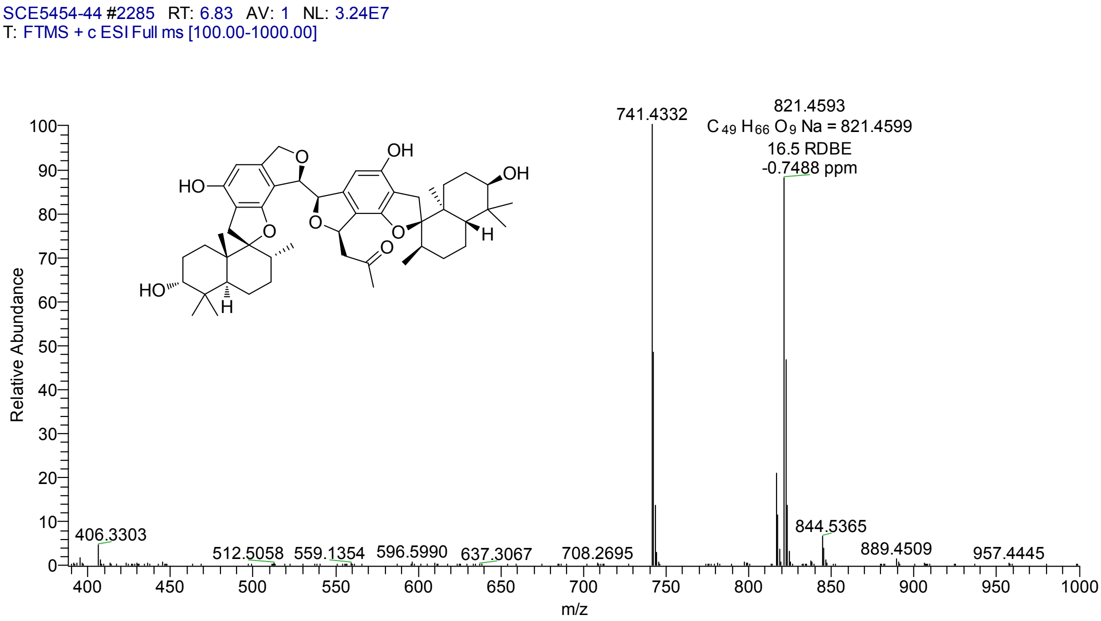
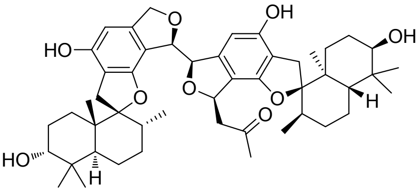
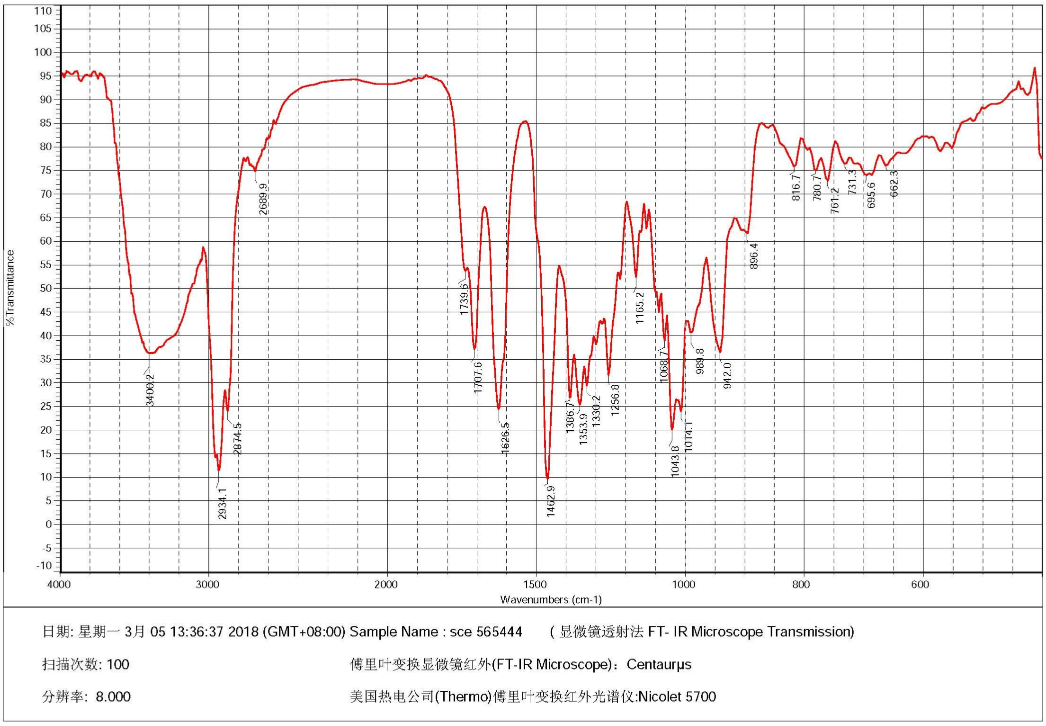


Figure S101. IR spectrum of compound **9**



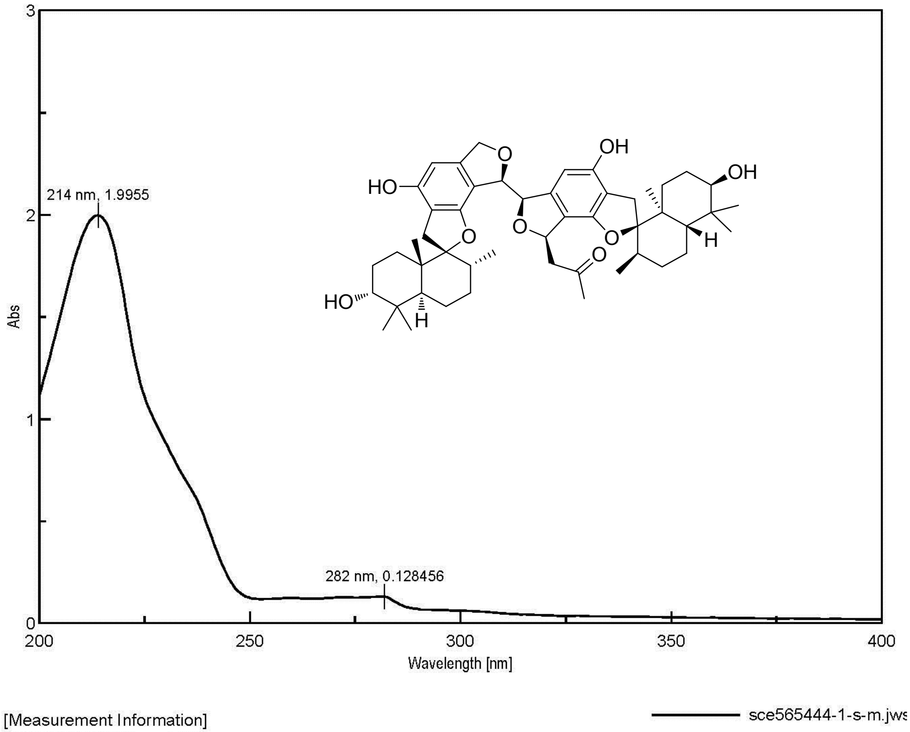


日期: 星期一 3月 05 13:36:37 2018 (GMT+08:00) Sample Name : sce 565444 (显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100 傅里叶变换显微镜红外(FT-IR Microscope)：Centaurμs

分辨率: 8.000 美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

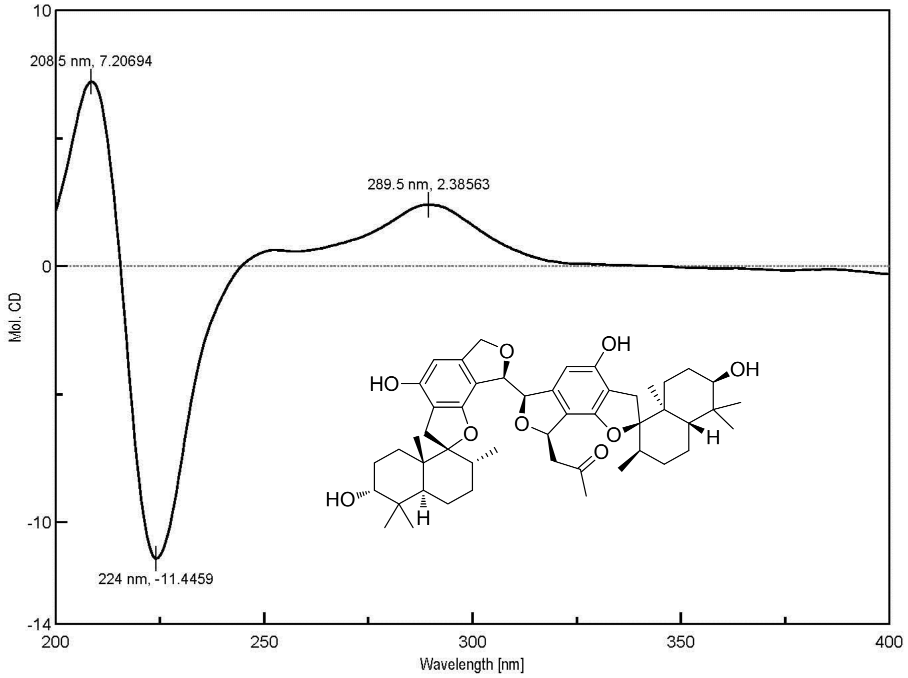
Figure S102. UV spectrum of compound **9**



[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2017/7/5 10:40
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.2 (w/v)%

Figure S103. ECD spectrum of compound **9**



[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2017/7/5 10:40
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.2 (w/v)%

Figure S104. ^{1}H NMR spectrum of compound **10** in acetone-d_6 at 600 MHz

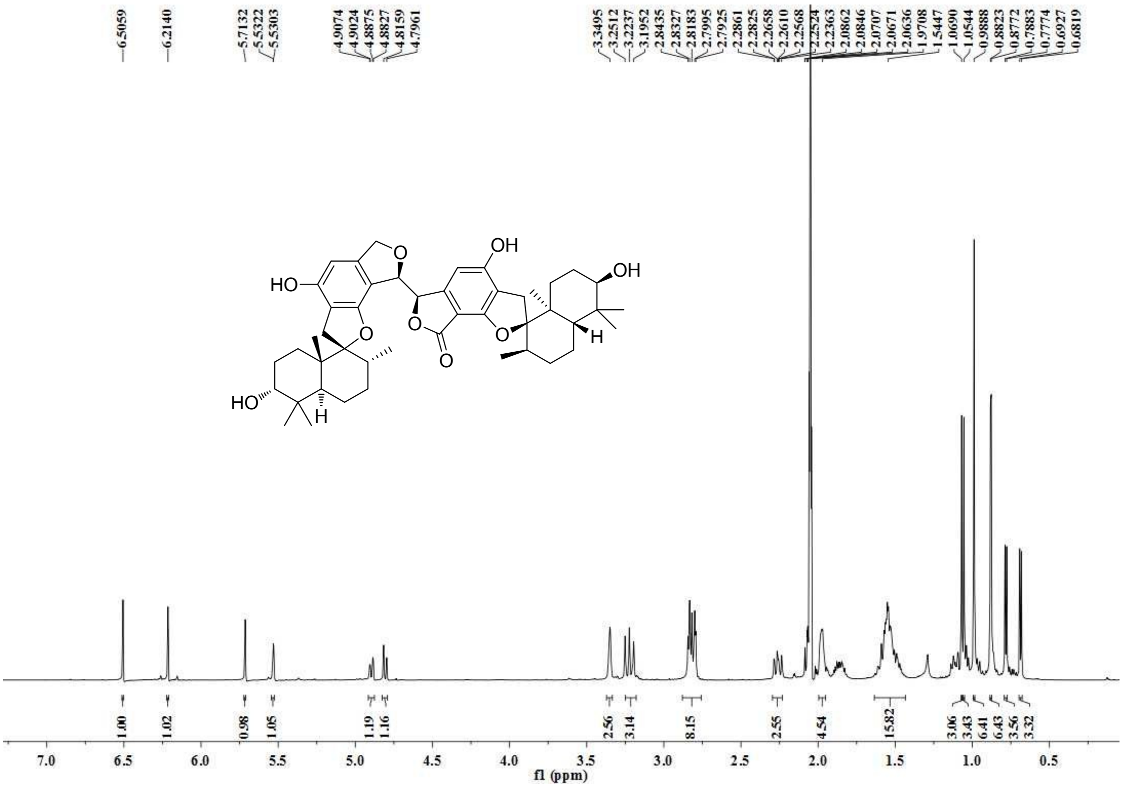


Figure S105. ^{13}C NMR spectrum of compound **10** in acetone-d_6 at 150 MHz

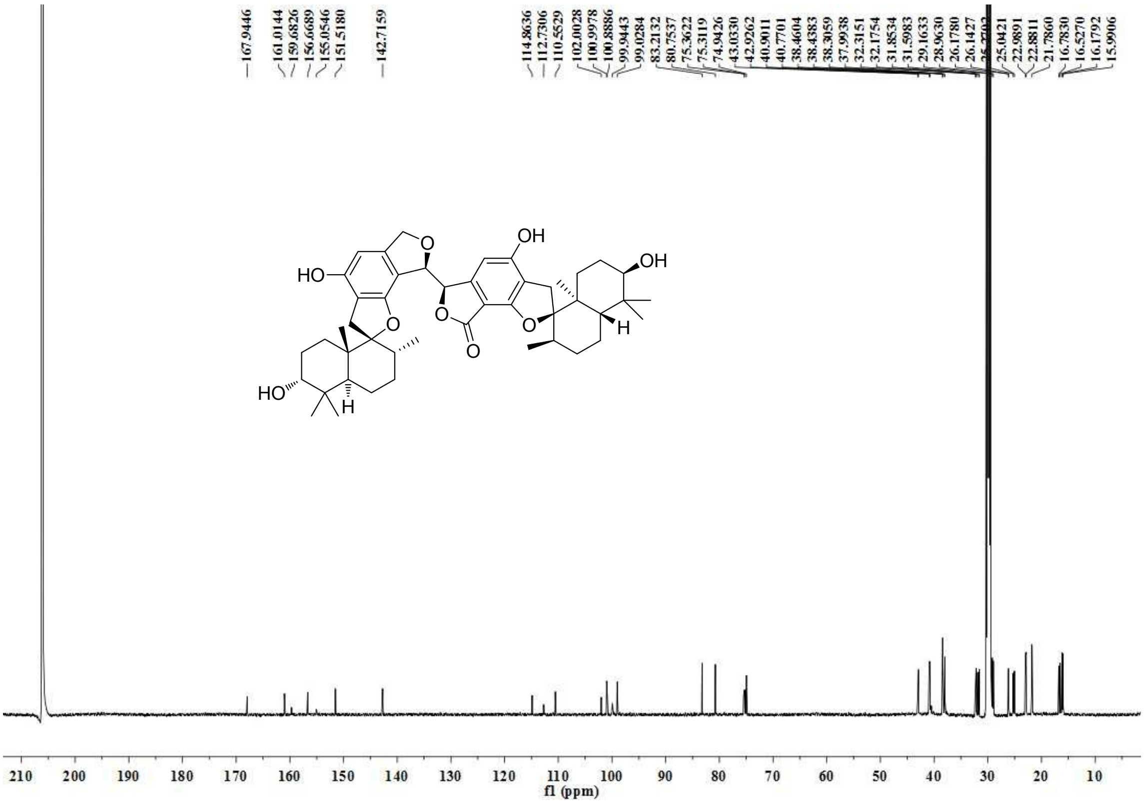


Figure S106. DEPT spectrum of compound **10** in acetone-d_6 at 150 MHz

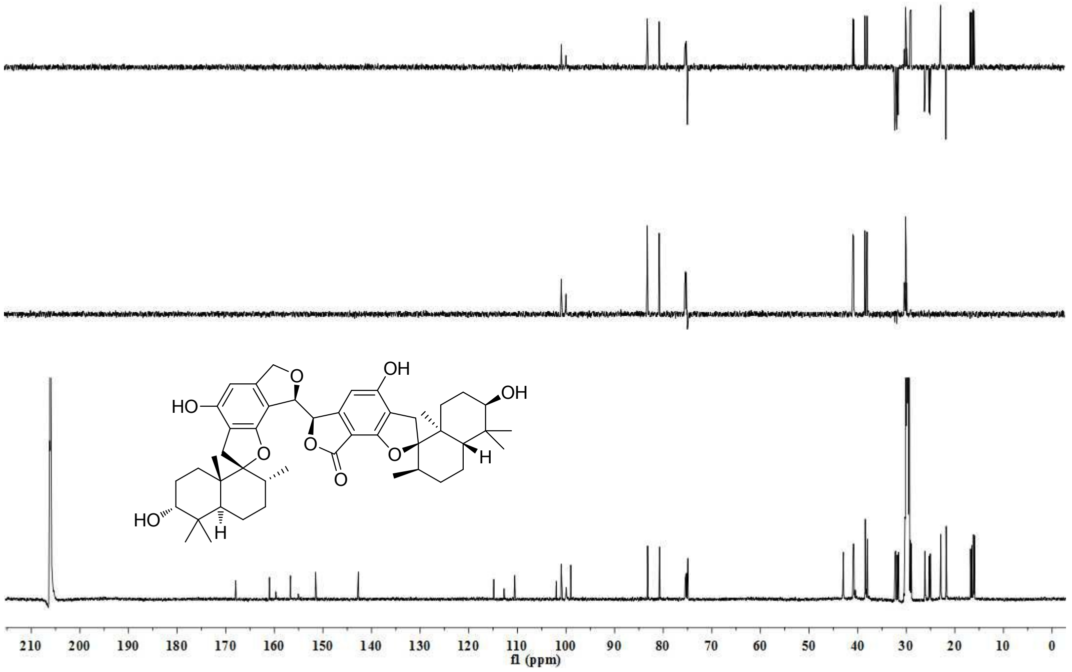


Figure S107. ^{1}H–^{1}H COSY spectrum of compound **10** in acetone-d_6

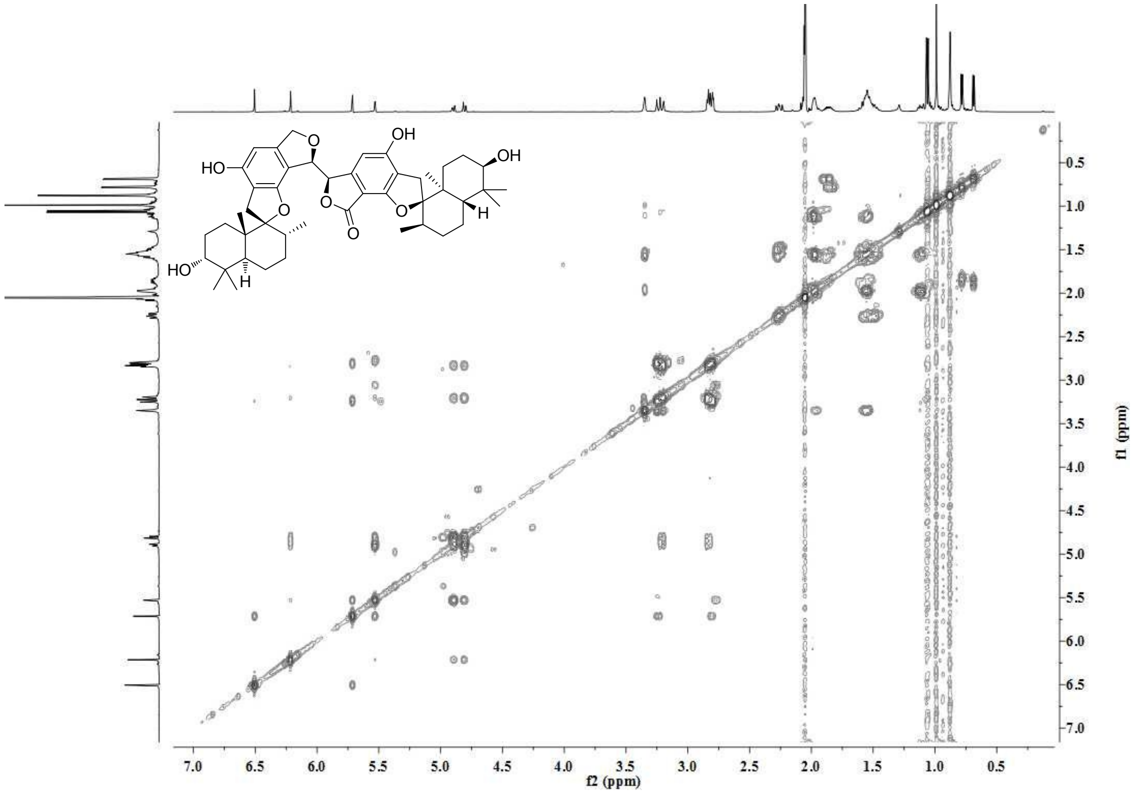


Figure S108. HSQC spectrum of compound **10** in acetone-d_6

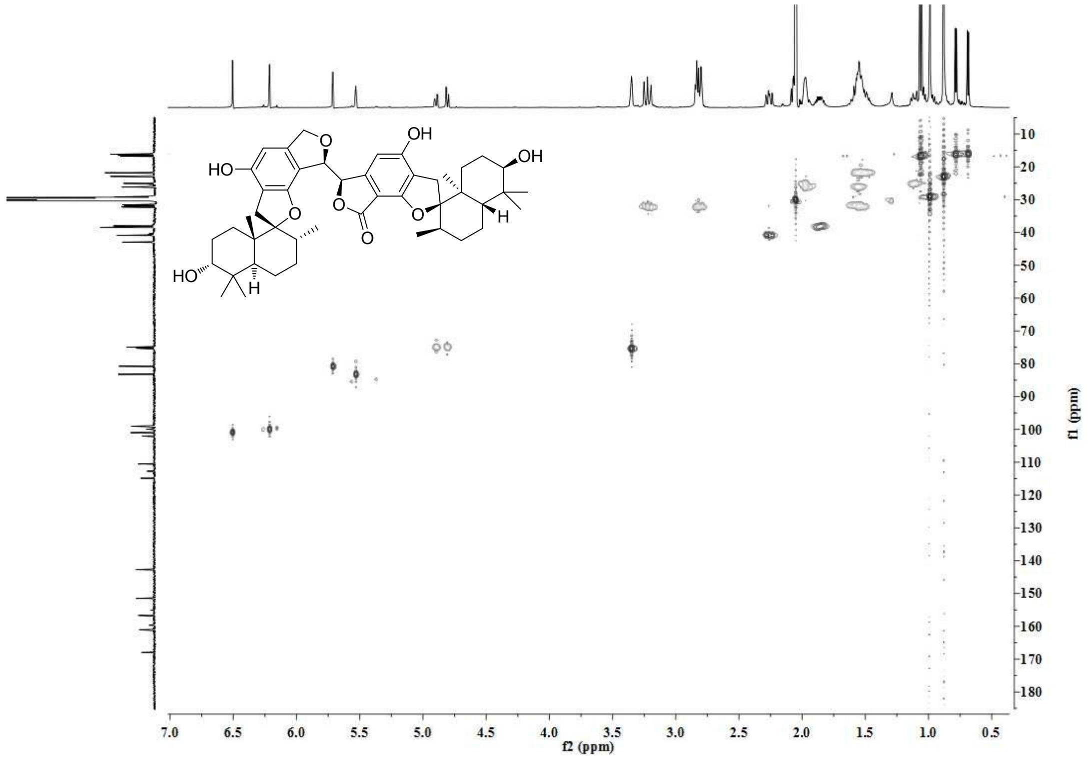


Figure S109. HMBC spectrum of compound **10** in acetone-d_6

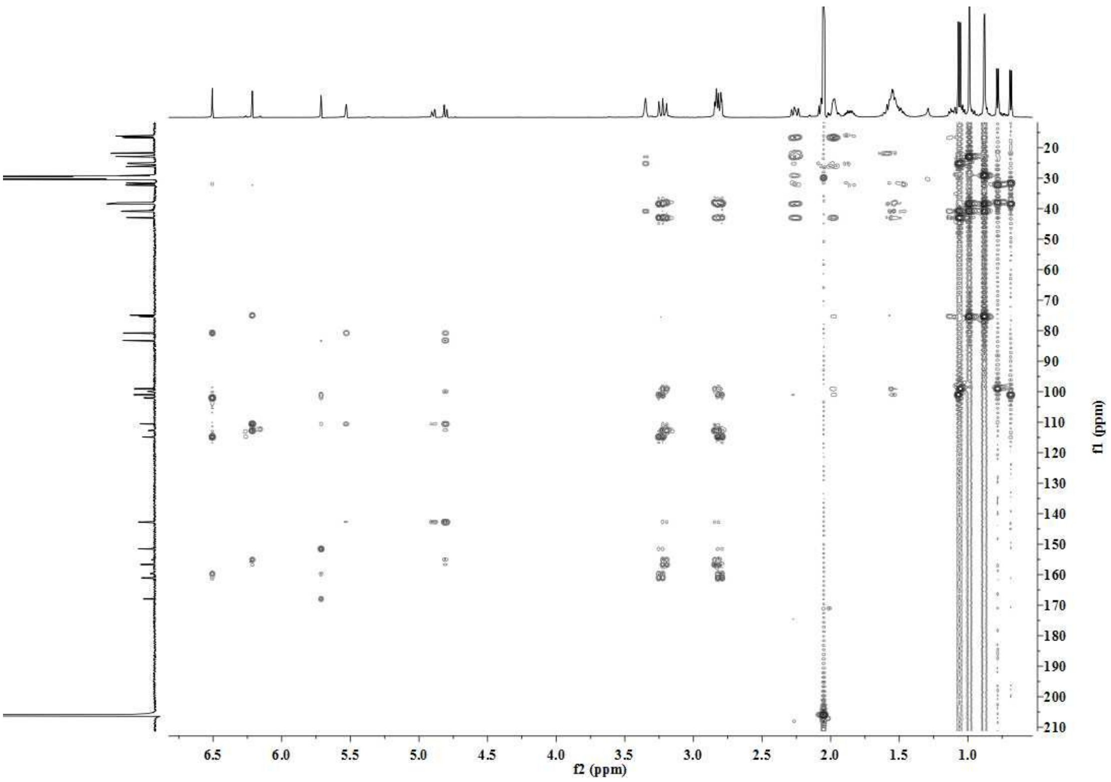


Figure S109. Enlarged HMBC spectrum of compound **10** in acetone-d_6

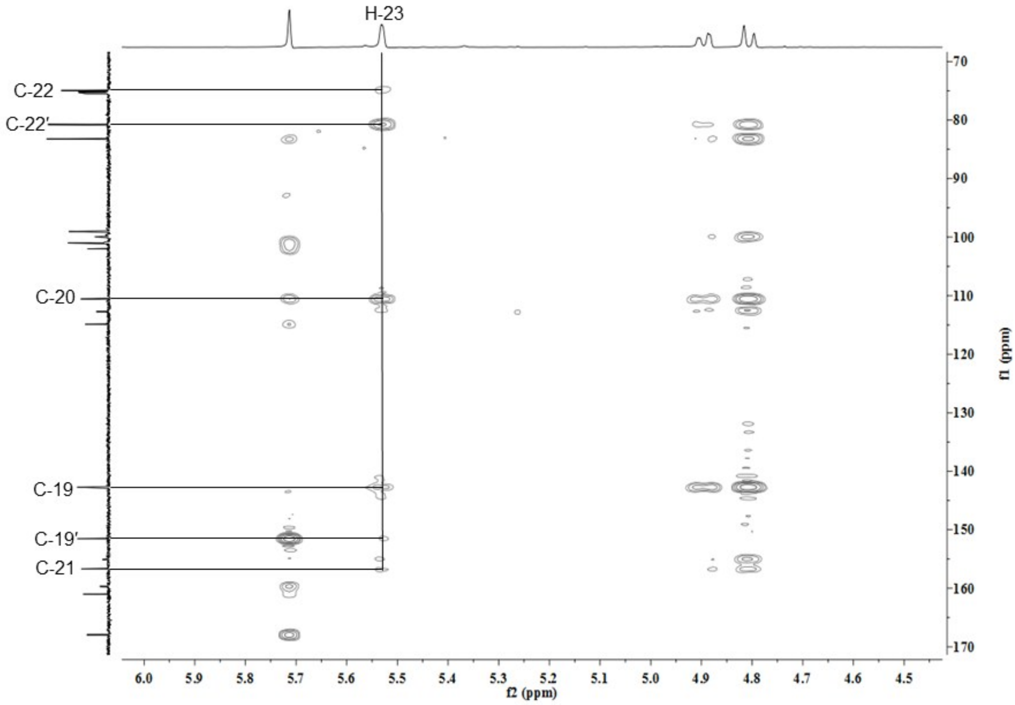


Figure S110. 1D NOE spectrum of compound **10** in acetone-d_6

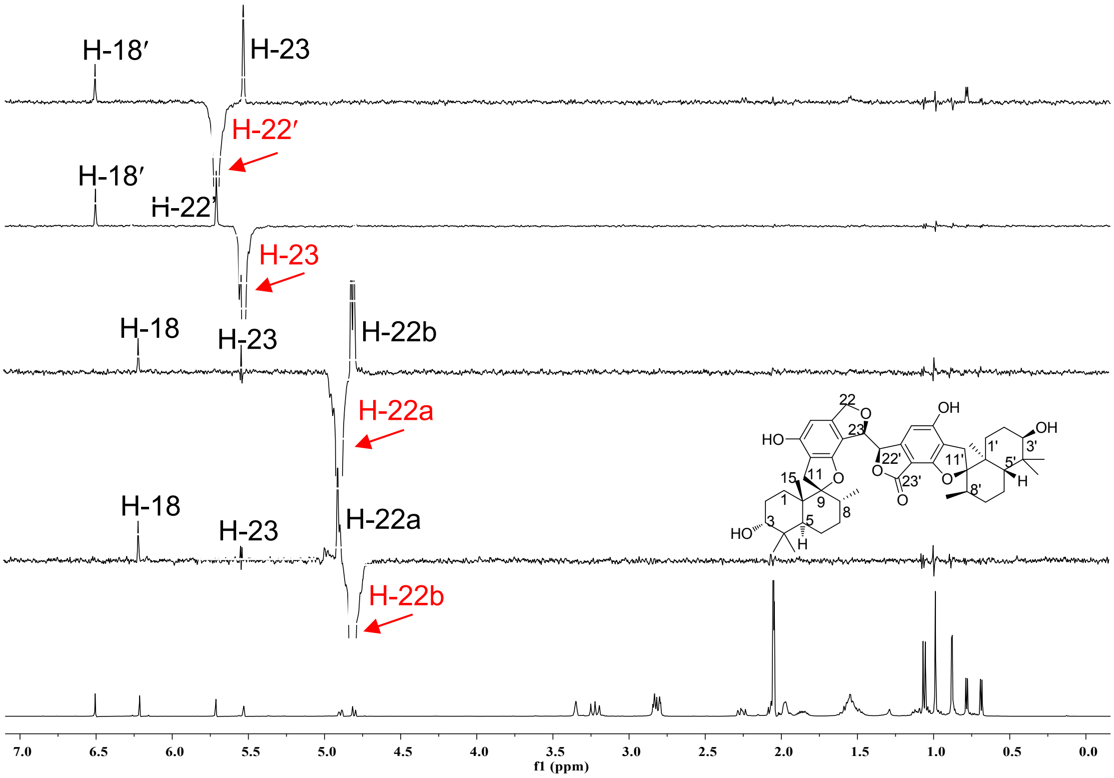


Figure S110. 1D NOE spectrum of compound **10** in acetone-*d*$_6$ (continued)

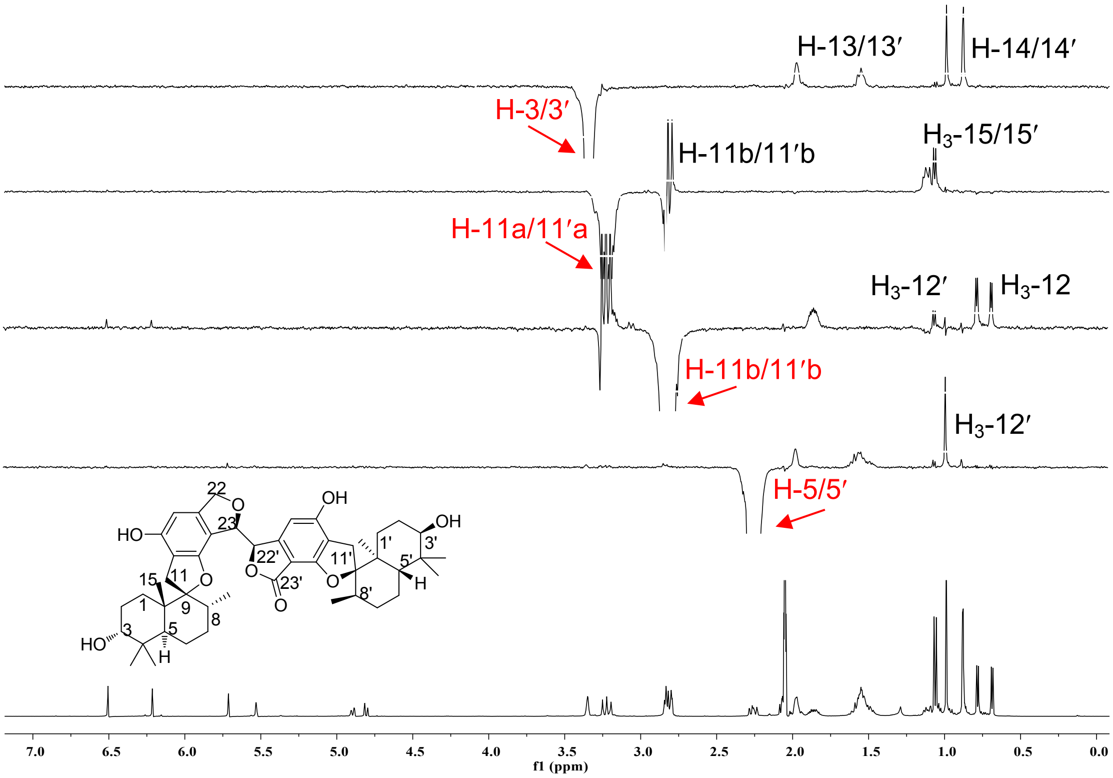


Figure S111. HR-ESI-MS spectrum of compound **10**

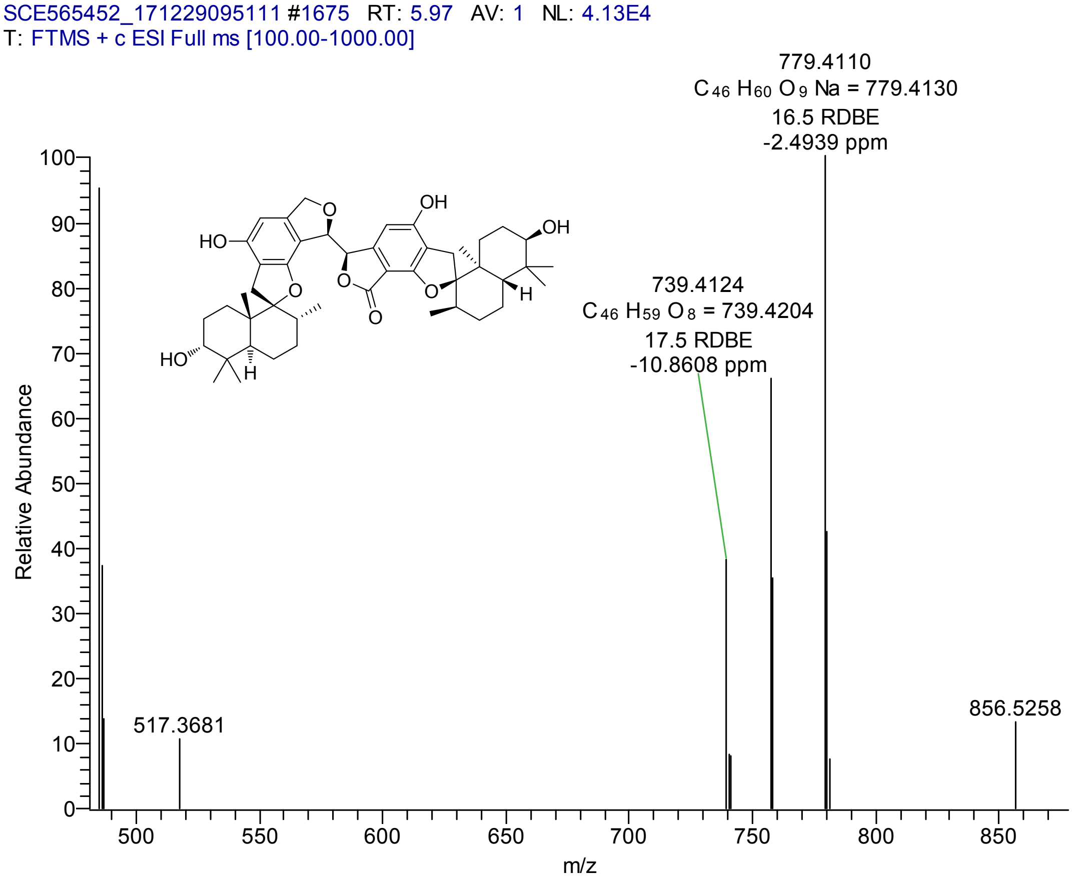
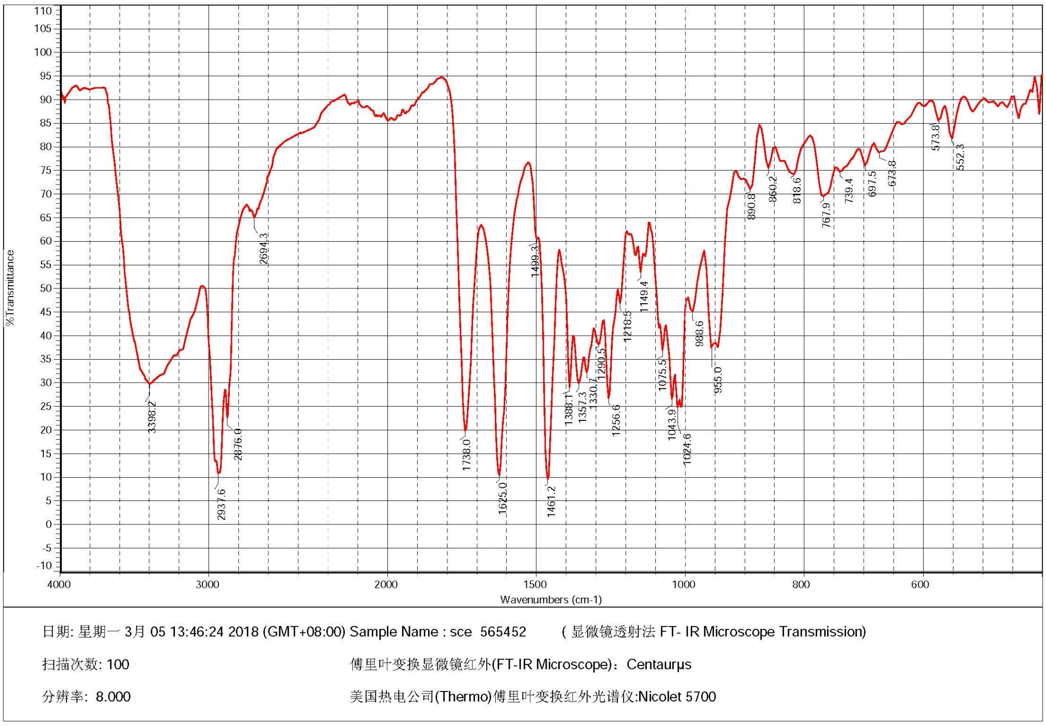

SCE565452_171229095111 #1675 RT: 5.97 AV: 1 NL: 4.13E4
T: FTMS + c ESI Full ms [100.00-1000.00]

Figure S112. IR spectrum of compound **10**

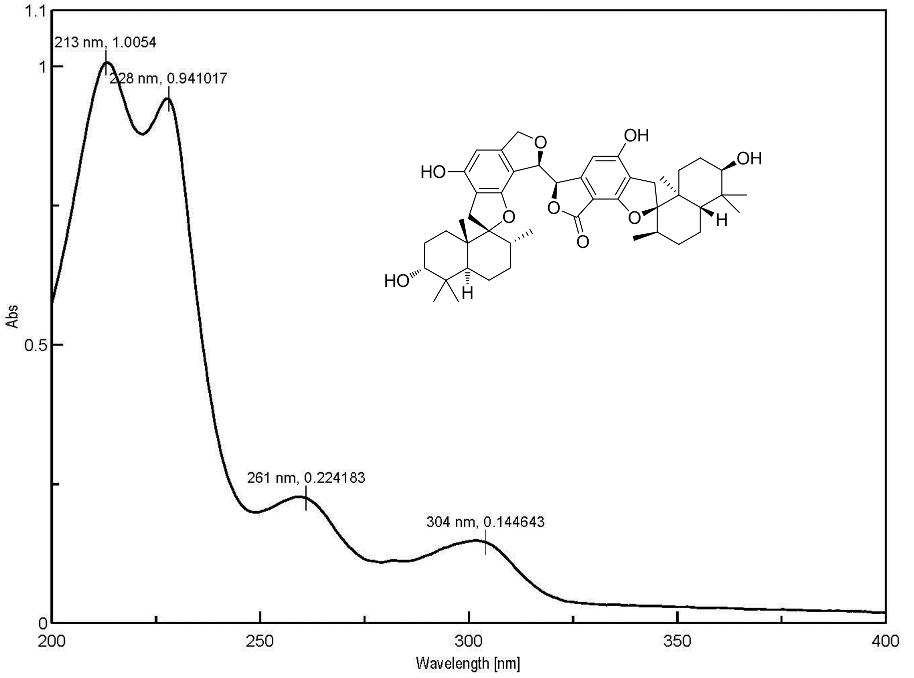


日期: 星期一 3月 05 13:46:24 2018 (GMT+08:00) Sample Name : sce 565452 (显微镜透射法 FT- IR Microscope Transmission)

扫描次数: 100 傅里叶变换显微镜红外(FT-IR Microscope)：Centaurμs

分辨率: 8.000 美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

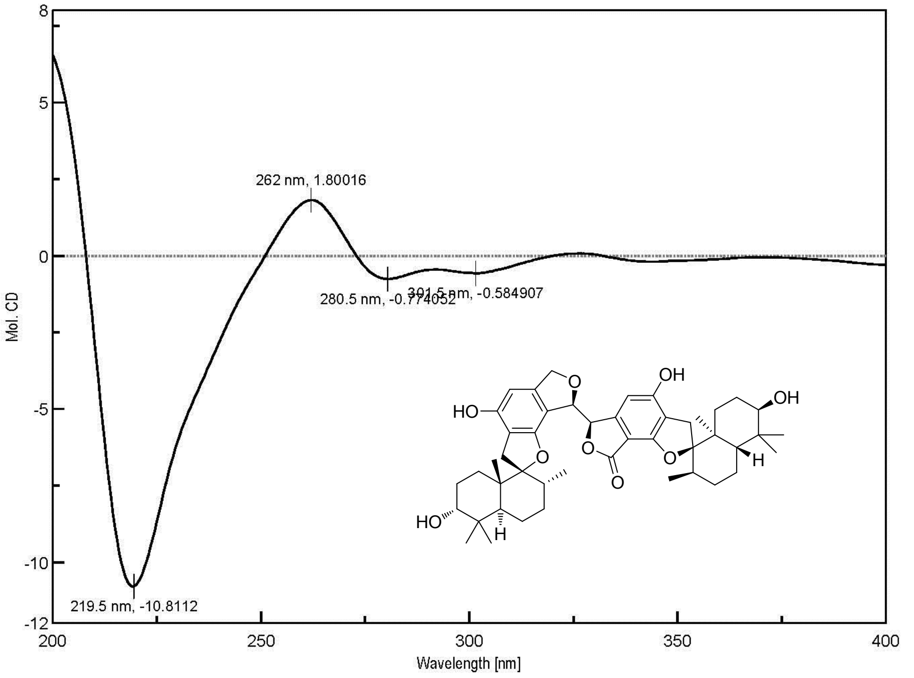
Figure S113. UV spectrum of compound **10**



[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2017/7/5 10:49
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.2 (w/v)%

Figure S114. ECD spectrum of compound **10**



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[Measurement Information]
Instrument Name     J-815
Model Name          J-815
Serial No.          A024461168

Accessory           Standard
Accessory S/N       A024461168
  Cell Length       1 mm

Measurement date    2017/7/5 10:49

Photometric Mode    CD, HT, Abs
Measure Range       400 - 200 nm
Data pitch          0.5 nm
Sensitivity         Standard
D.I.T.              1 sec
Bandwidth           1.00 nm
Start Mode          Immediately
Scanning Speed      100 nm/min
Baseline Correction Baseline
Shutter Control     Auto
CD Detector         PMT
PMT Voltage         Auto
Accumulations       2
Solvent             MEOH
Concentration       0.2 (w/v)%
```

Figure S115. ^{1}H NMR spectrum of compound **11** in acetone-d_6 at 600 MHz

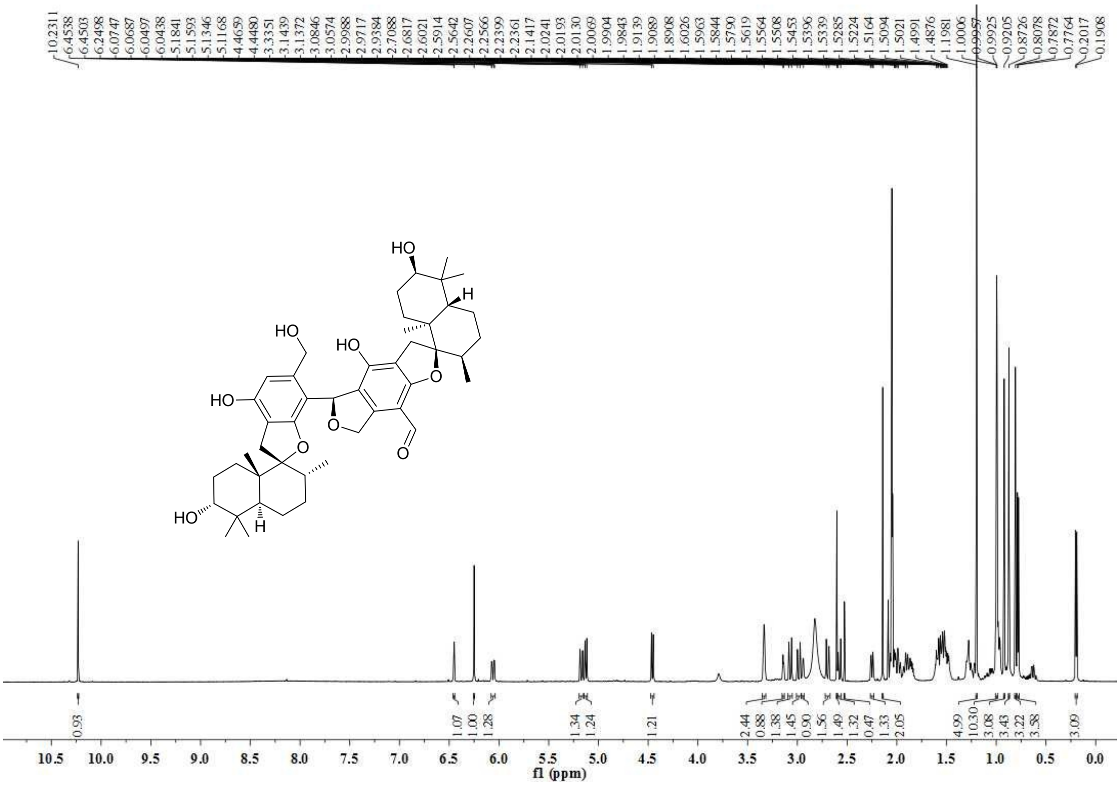


Figure S116. ^{13}C NMR spectrum of compound **11** in acetone-d_6 at 150 MHz

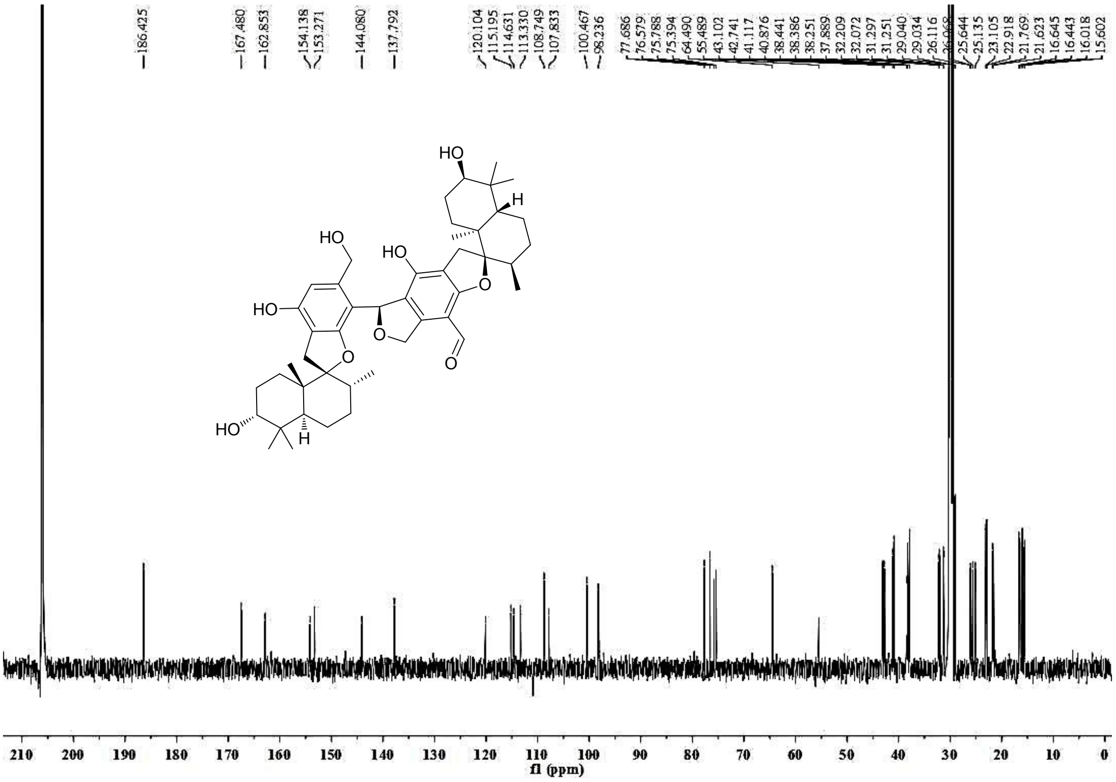


Figure S117. DEPT spectrum of compound **11** in acetone-d_6 at 150 MHz

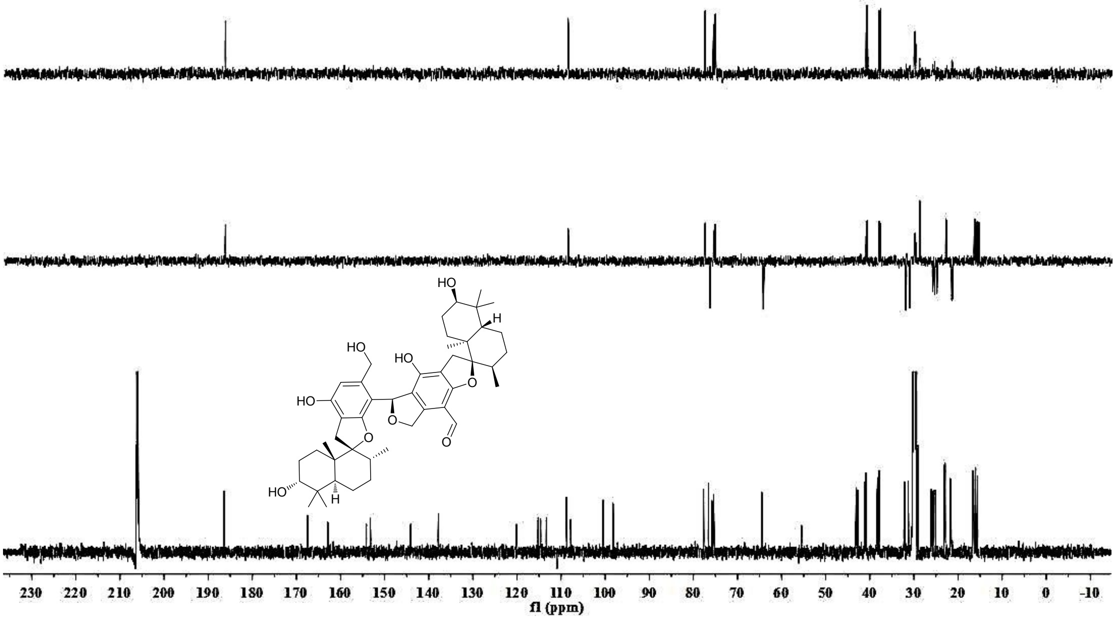


Figure S118. ^{1}H–^{1}H COSY spectrum of compound **11** in acetone-d_6

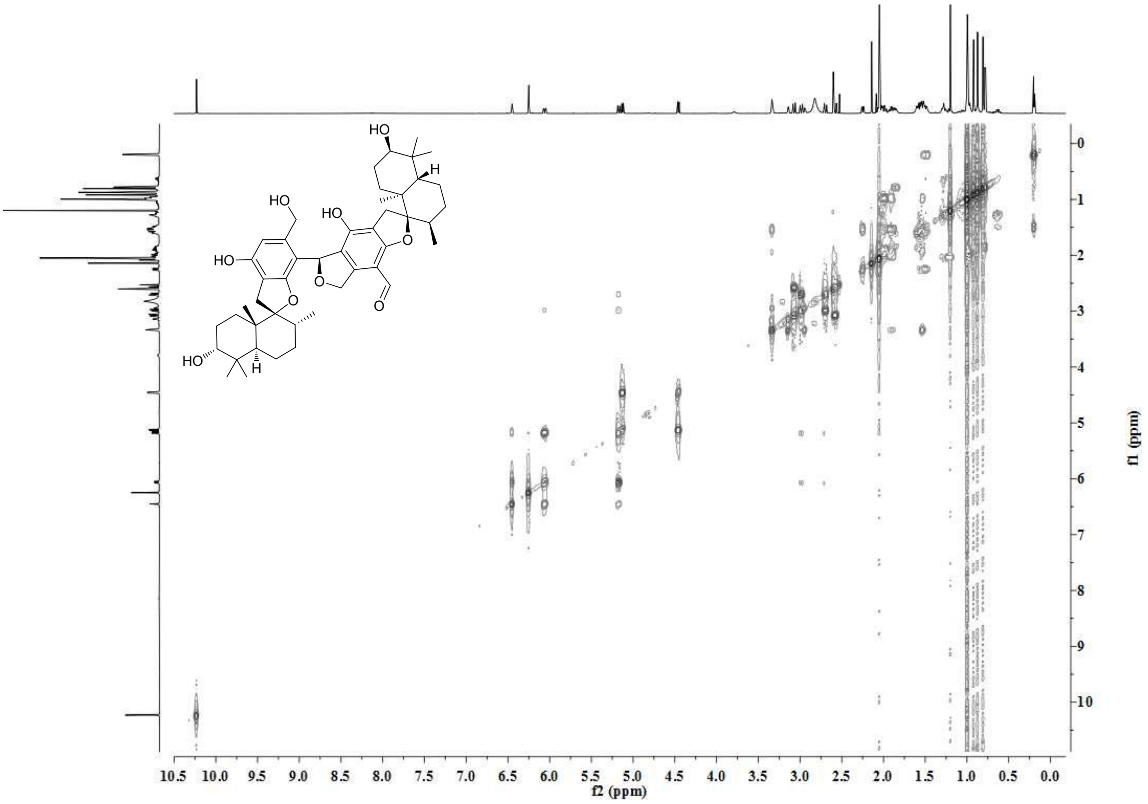


Figure S119. HSQC spectrum of compound **11** in acetone-d_6

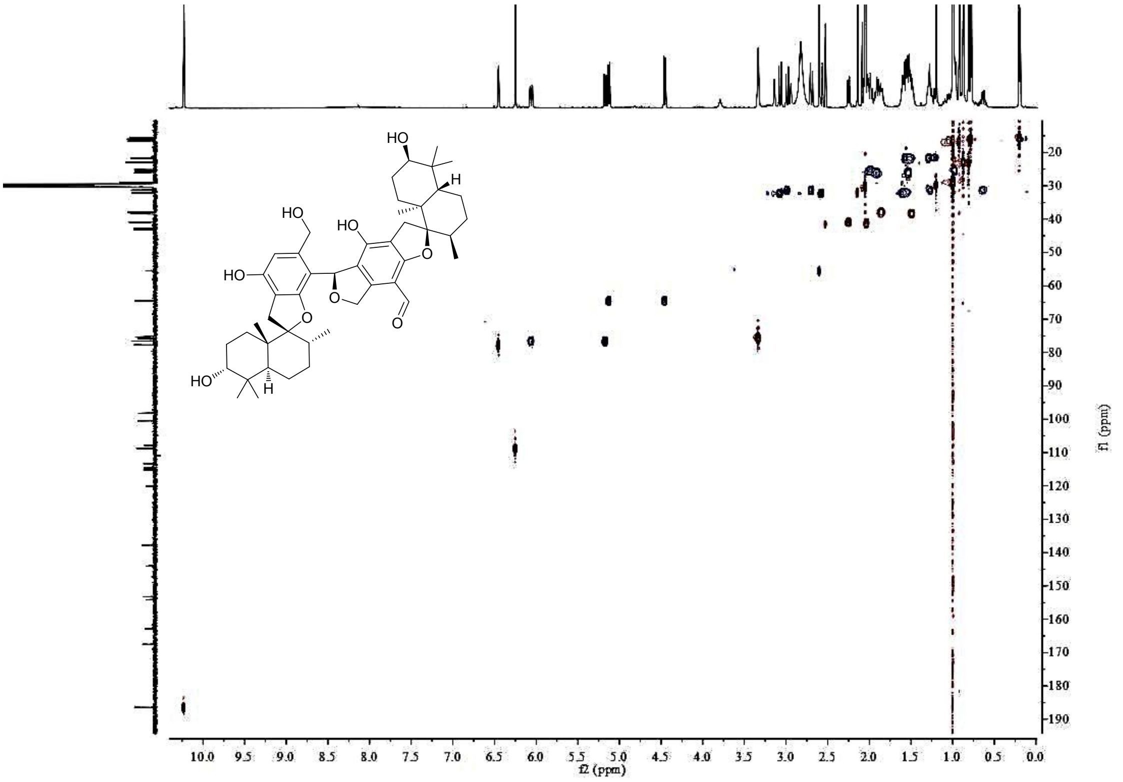


Figure S120. HMBC spectrum of compound **11** in acetone-d_6

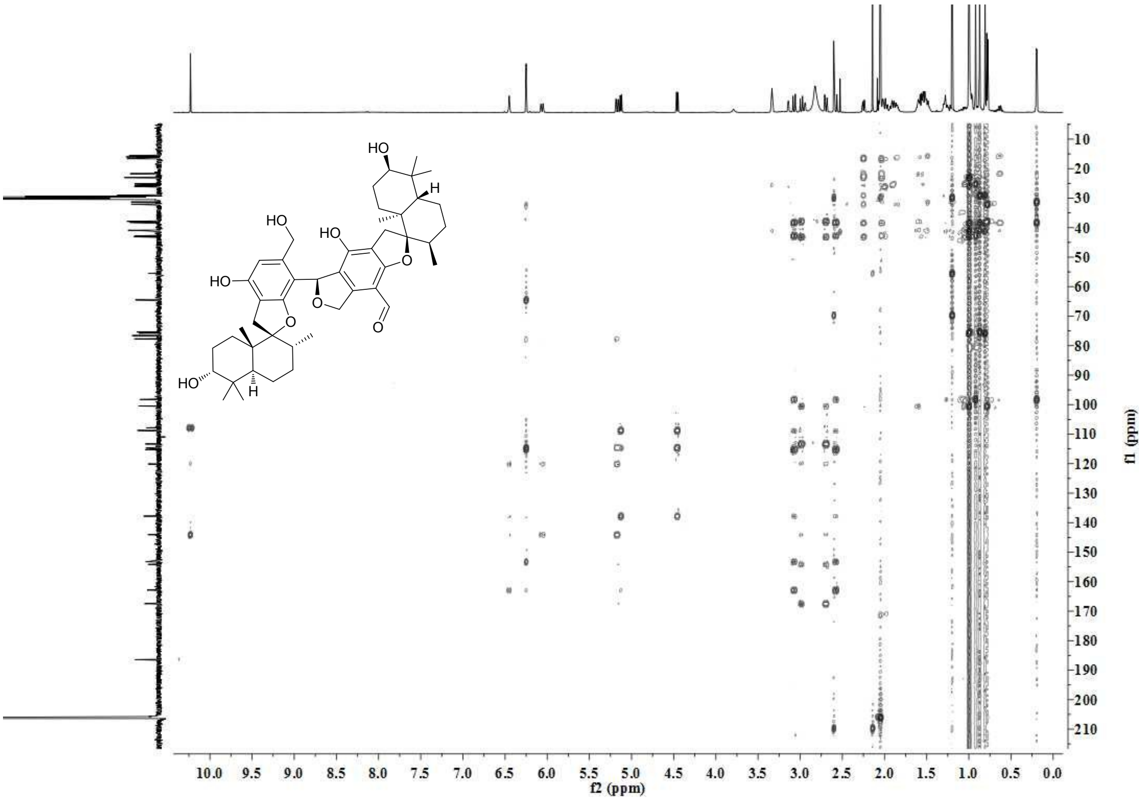


Figure S121. NOE difference spectrum of compound **11** in acetone-d_6

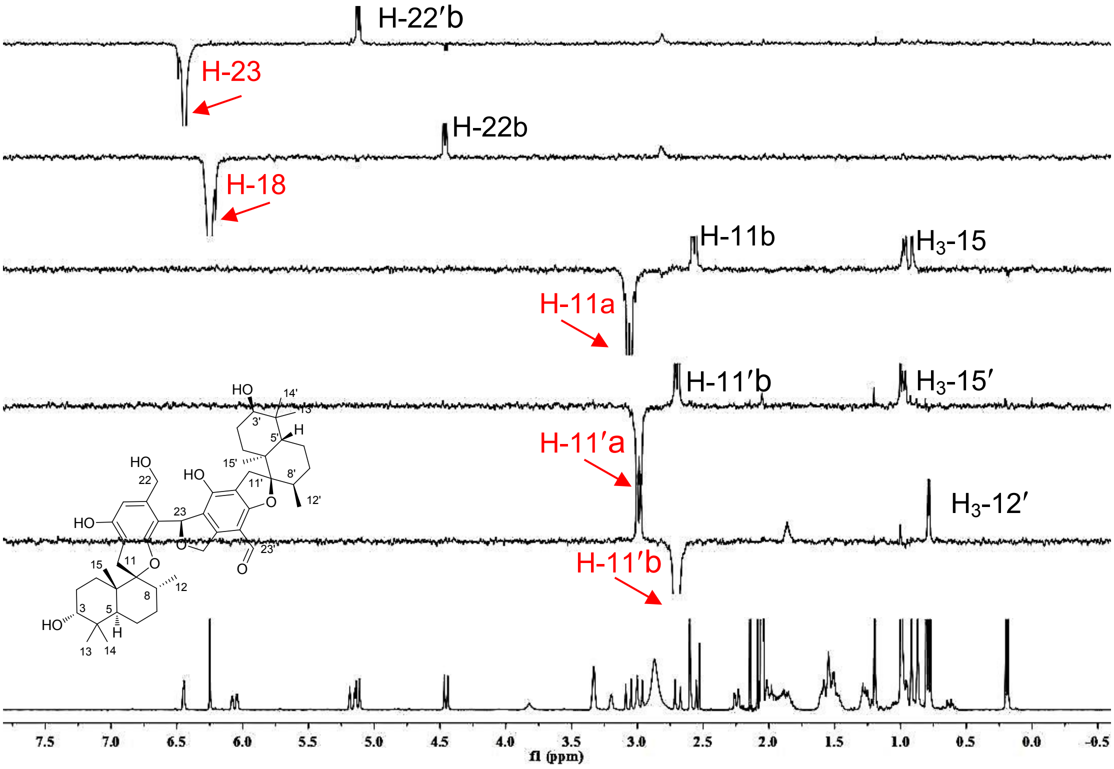


Figure S121. NOE difference spectrum of compound **11** in acetone-d_6

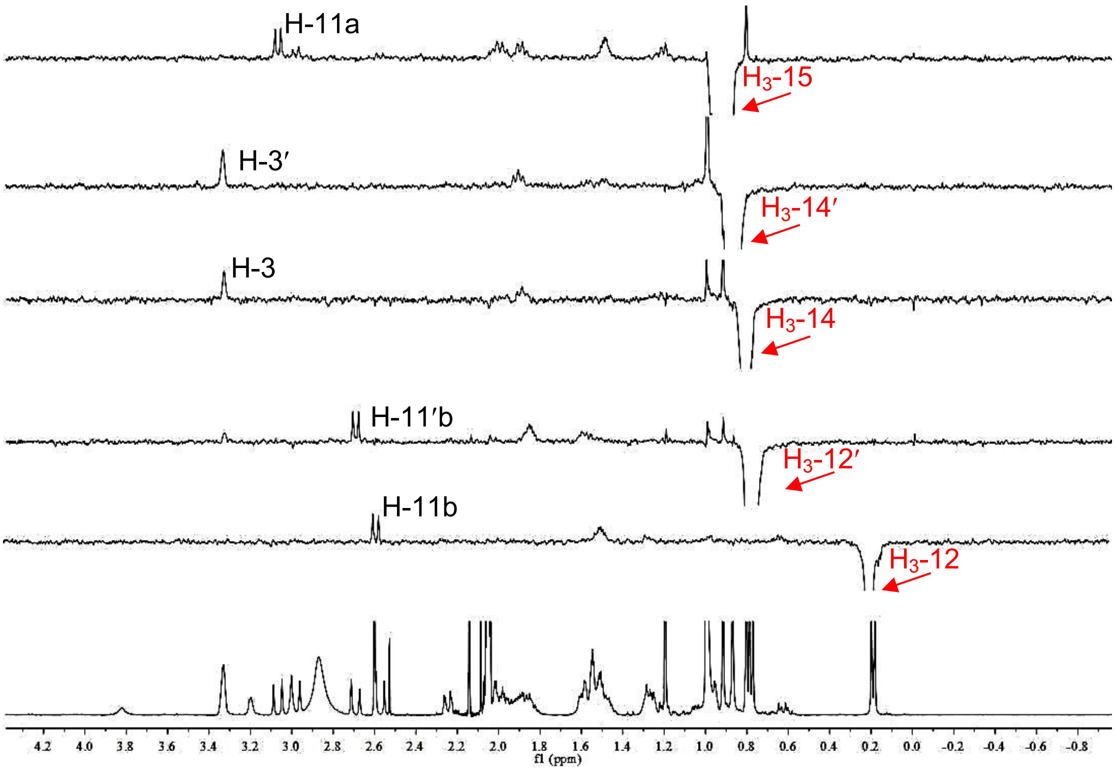


Figure S122. HR-ESI-MS spectrum of compound **11**

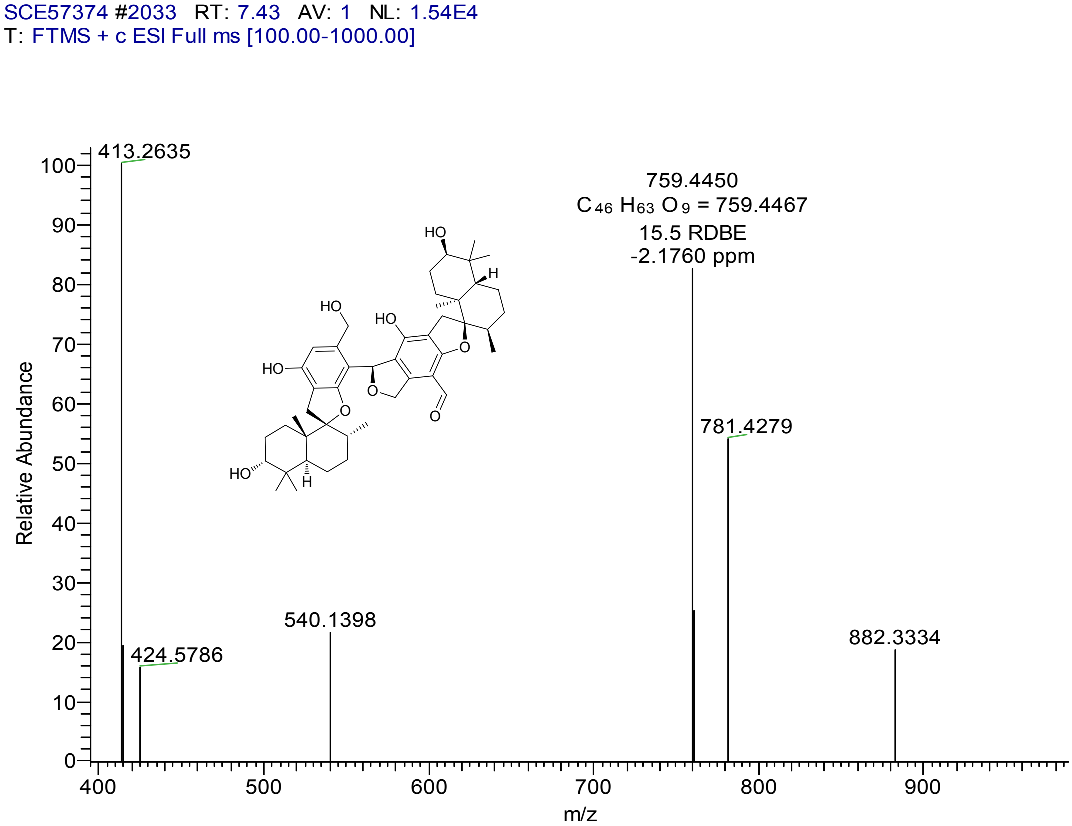
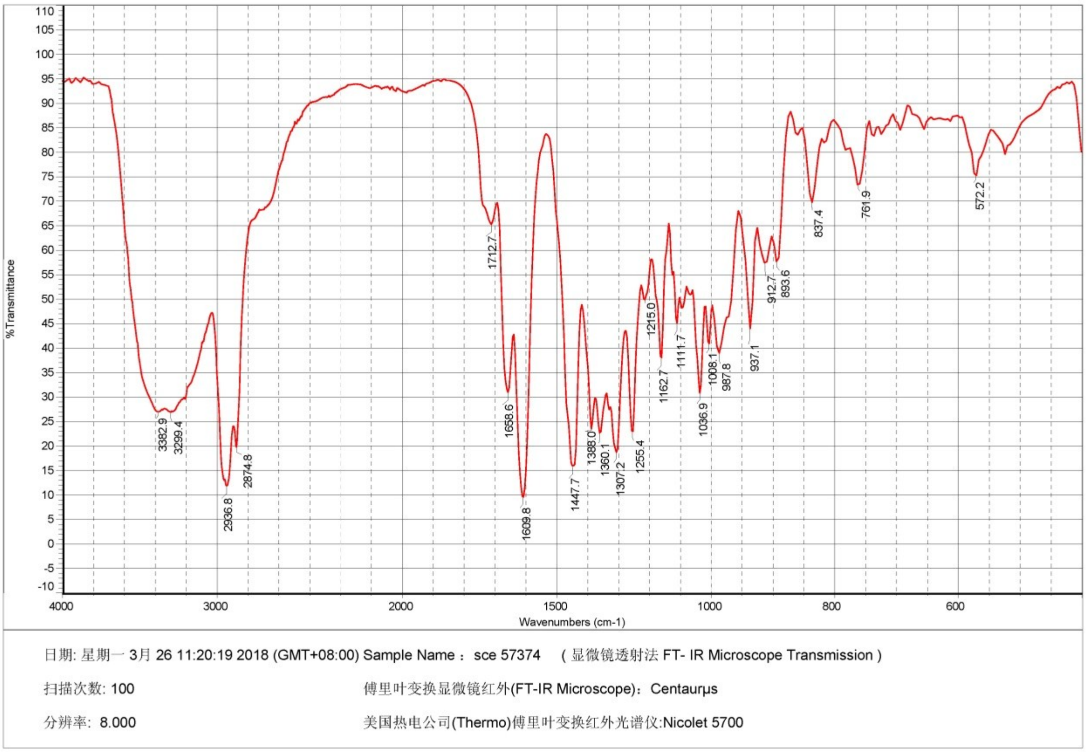

SCE57374 #2033 RT: 7.43 AV: 1 NL: 1.54E4
T: FTMS + c ESI Full ms [100.00-1000.00]

Figure S123. IR spectrum of compound **11**


日期: 星期一 3月 26 11:20:19 2018 (GMT+08:00) Sample Name： sce 57374 （显微镜透射法 FT- IR Microscope Transmission）

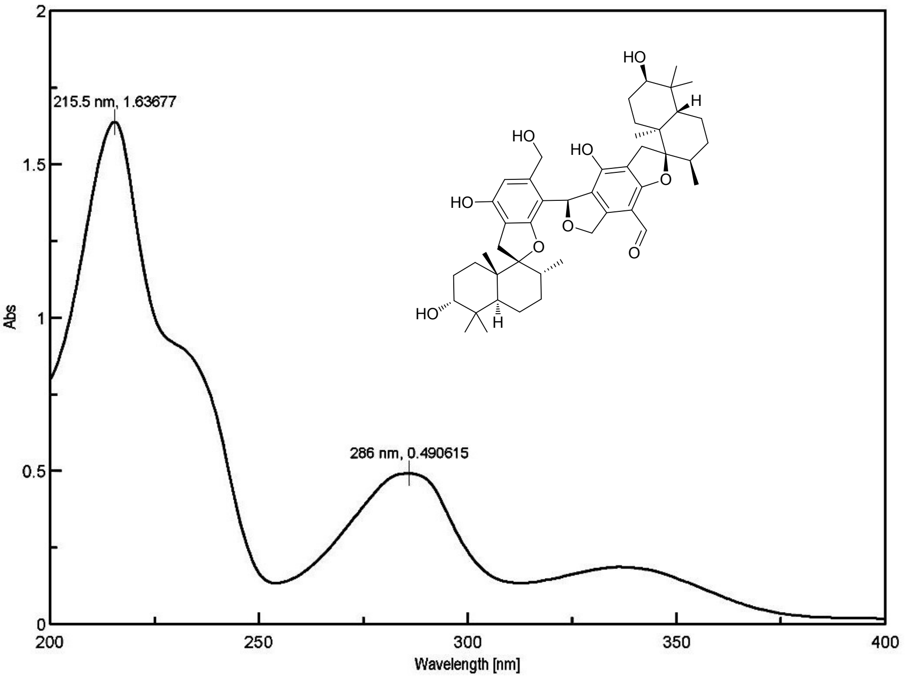
扫描次数: 100

傅里叶变换显微镜红外(FT-IR Microscope)：Centaurμs

分辨率: 8.000

美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

Figure S124. UV spectrum of compound **11**



sce57374-1-s-m.jws

[Measurement Information]

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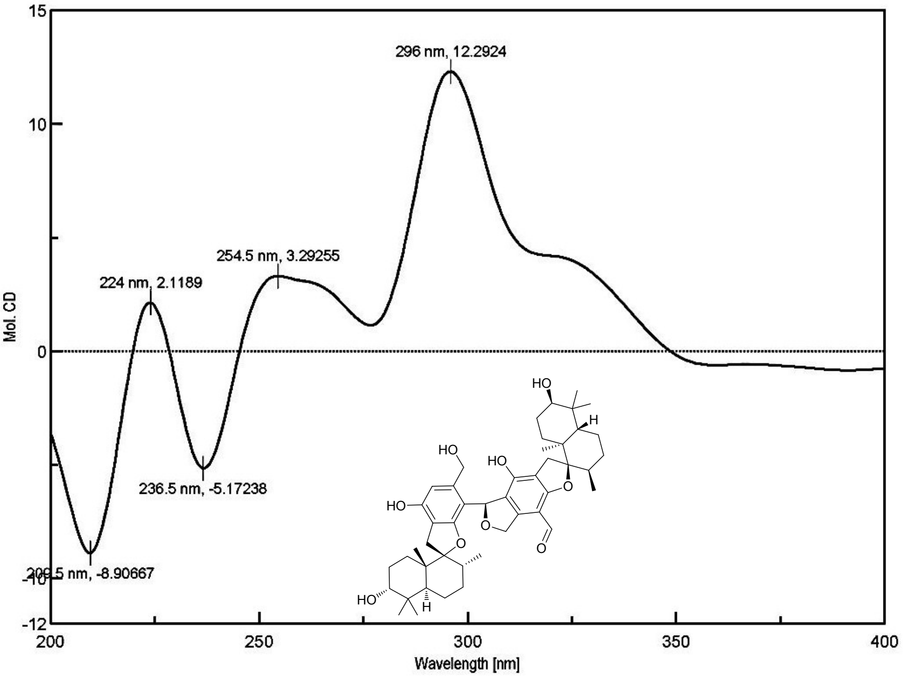
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2017/9/18 9:51
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.25 (w/v)%

Figure S125. ECD spectrum of compound **11**



[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2017/9/18 9:51
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	0.5 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.25 (w/v)%