Iridal-type Triterpenoids with a Cyclopentane Unit from the Rhizomes of *Belamcanda chinensis*

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S1. In vitro Bioassays.

S1-1. Cytotoxic assay. Cytotoxic activities of compounds **1-10** (except for **5**) against HCT-116, HepG2, BGC-823, A549 and MCF-7 cells were measured by using the MTT method. Briefly, test cells in culture medium 100 μL were seeded in each well of 96-well plates (Falcon, CA). Cells were treated in triplicate with 10 μL of grade concentrations 0.1, 1, 10 μM of the compounds at 37 °C. After 72 h, a 20 μL aliquot of MTT solution (5 mg/mL) was added to the wells. The cultures were incubated for another 4 h, and then 100 μL of "triplex solution" (10% SDS/5% isobutanol/10 mM HCl) was added. The plates were incubated at 37 °C in 5% CO_2 overnight. The OD values were measured at 570 nm by a plate reader (VERSA Max, Molecular Devices, Sunnyvale, CA). Average values determined from triplicate readings were used for the inhibitory rate calculation by the formula: $(OD_{control\ well} - OD_{treated\ well})/OD_{control\ well} - OD_{blank\ well} \times 100\%$. The IC_{50} was calculated using Logistic regression from three independent tests. Paclitaxel was used as the positive control with IC_{50} values of 0.2, 10.69, 2.08, 2.68, 19 *n*M, respectively. [1]

S1-2. NO Production Bioassay. Compounds **1-10** (except **5**) were tested for their inhibitory effect on LPS-induced NO production in the BV2 cell line. The BV2 cells were plated in a 96-well plate and pretreated with the compounds for 24 h followed by an additional 24 h of LPS (0.3 μg/mL) exposure. The Griess reaction was used to determine the nitrite content in the culture supernatant. $NaNO_2$ served as a standard to assess the NO^{2-} concentration. The OD values were recorded at 550 nm. Curcumin was used as the positive control. Cell viability was measured by an MTT assay.[2]

S1-3. PTP1B activity assay for compounds 1-4, 6-10.

Recombinant human GST-PTP1B protein was over expressed by hGST-PTP1B-BL21E. *coli* and purified by GST affinity chromatography. The reagent pNPP was used as substrate for the measurement of PTP1B activity. Compounds **1-4**, **6-10** (10 μM) and positive control CC06240 (10 μM) were pre-incubated with the enzyme at room temperature for 5 min. Assay was performed in final volume of 100 μL in the active system containing 50 Mm HEPES, 5 mM DTT, 150 mM NaCl, 2 mM EDTA, and 2 mM pNPP (pH 7.0), incubated at 30 °C for 10 min, stopped by addition of 50 μL 3 M NaOH. Then, the absorbance was determined at 405 nm wavelength. The similar system without GST-PTP1B protein was used as blank. Each concentration of the compounds was tested in three parallels.[3]

(1) a) Ni, G.; Shi, G. R.; Li, J. Y.; Yu, D. Q. *RSC Adv.* **2017**, *7*, 20160–20166. b) Ni, G.; Li, J. Y.; Mai, Z. P.; Yu, D. Q. *Tetrahedron Lett*. **2018**, *59*, 151–155. c) Ni, G.; Li, J. Y. *Org. Biomol. Chem.* **2018**, *16*, 3754–3759. d) Li, J. Y.; Ni, G.; Liu, Y. F.; Li, L.; Mai, Z. P.; Wang, R. Z.; Yu, D. Q. *Bioorg. Chem*. **2019**, *83*, 20–28.

(2) Zhang, C. L.; Hao, Z. Y.; Liu, Y. F.; Wang, Y.; Shi, G. R.; Jiang, Z. B. *J. Nat. Prod.* **2017**, *80*, 156–161.

(3) Li, C.; Li, C. J.; Ma, J.; Chen, F. Y.; Li, L.; Wang, X. L.; Ye, F.; Zhang, D. M. *Org. Lett.* **2018**, *20*, 3682-3686.

S2. X-ray crystallographic analysis of Polycycloiridal K (1).

Polycycloiridal K (**1**) was obtained as colorless needles from MeOH with the molecular formula $C_{30}H_{44}O_5$. Single crystals of $C_{30}H_{44}O_5$ were recrystallized from MeOH mounted in inert oil and transferred to the cold gas stream of the diffractometer. Crystal structure determination of crystal

Data. $C_{30}H_{44}O_5$, M =484.65,monoclinic, a =9.66986(17) Å, b =11.22826(19) Å, c =12.9048(2) Å, β =104.7740(18)°, U = 1354.82(4) Å^3,T = 109.5(8), space group $P2_1$ (no. 4), Z = 2, μ (Cu Kα) = 0.627, 9127 reflections measured, 5087 unique (R_{int} = 0.0266) which were used in all calculations. The final $wR(F_2)$ was 0.1035 (all data).

Table 1: Crystal data and structure refinement for compound 1.

Identification code	Compound 1
Empirical formula	$C_{30}H_{44}O_5$
Formula weight	484.65
Temperature / K	109.5(8)
Crystal system	monoclinic
Space group	$P2_1$
a / Å, b / Å, c / Å	9.66986(17), 11.22826(19), 12.9048(2)
α/°, β/°, γ/°	90.00, 104.7740(18), 90.00
Volume / Å^3	1354.82(4)
Z	2
ρ_{calc} / mg mm^{-3}	1.188
μ / mm^{-1}	0.627
F(000)	528
Crystal size / mm^3	0.28 × 0.25 × 0.12
2Θ range for data collection	10.28 to 141.94°
Index ranges	-11 ≤ h ≤ 8, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	9127
Independent reflections	5087[R(int) = 0.0266 (inf-0.9Å)]
Data/restraints/parameters	5087/1/323
Goodness-of-fit on F^2	1.038
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0389, wR_2 = 0.1020
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.1035
Largest diff. peak/hole / e Å^{-3}	0.275/-0.197
Flack Parameters	0.05(15)
Completeness	0.9984

S-3. ECD Calculations.

The theoretical calculations of compounds **1** and **5** were carried out using Gaussian 09. Conformational analysis was initially performed using Discovery Studio 3.5 Client. The conformers were optimized at B3LYP/6-31G(d) level. Room-temperature equilibrium populations were calculated according to Boltzmann distribution law. The theoretical calculation of ECD were performed using TDDFT at B3LYP/6-311++G(2d,p) level in MeOH with PCM. The ECD spectra of compounds **1** and **5** were obtained by weighing the Boltzmann distribution rate of each geometric conformation. The ECD spectrum is simulated by overlapping Gaussian functions for each transition according to

$$\Delta\varepsilon(E) = \frac{1}{2.297 \times 10^{-39}} \times \frac{1}{\sqrt{2\pi\sigma}} \sum_{i}^{A} \Delta E_i R_i e^{-[(E-E_i)/(2\sigma)]^2}$$

Where σ represents the width of the band at 1/e height, and ΔE_i and R_i are the excitation energies and rotational strengths for transition i, respectively. $\sigma = 0.20$ eV and R^{velocity} have been used in this work.[4]

(4) (*a*) Z. X. Hu, Y. M. Shi, W. G. Wang, J. W. Tang, M. Zhou, X. Du, Y. Z. Zhang, J. X. Pu, and H. D. Sun, *Org. Lett.*, 2016, **18**, 2284−2287. (*b*) Y. M. Shi, S. L. Cai, X. N. M. Liu, S. Z. Shang, X. Du, W. L. Xiao, J. X. Pu, and H. D. Sun, *Org. Lett.*, 2016, **18**, 100−103.

S4. LC-MS analysis of compounds 6, 7, and 10 in the crude extract.

The dried and powdered rhizomes of *Belamcanda chinensis* (60 g) were extracted in acetone at room temperature with ultrasonic. The crude extract was concentrated under vacuum to obtain residues (1.5 g). The residues (1.5 g) were diluted to 2.0 mL with methanol, and then analyzed using a Thermo SCIENTIFIC Q EXACTIVE Focus LC-MS (gradient: MeCN-H_2O 0-20 min, 40-75%; 20-30 min, 75-100%, 1.0 mL/min, YMC-Pack ODS-A column, 250 × 4.6 mm, 5 μm, Kyoto, Japan).

Figure S1. The UV spectrum of compound **1** in CH_3OH.

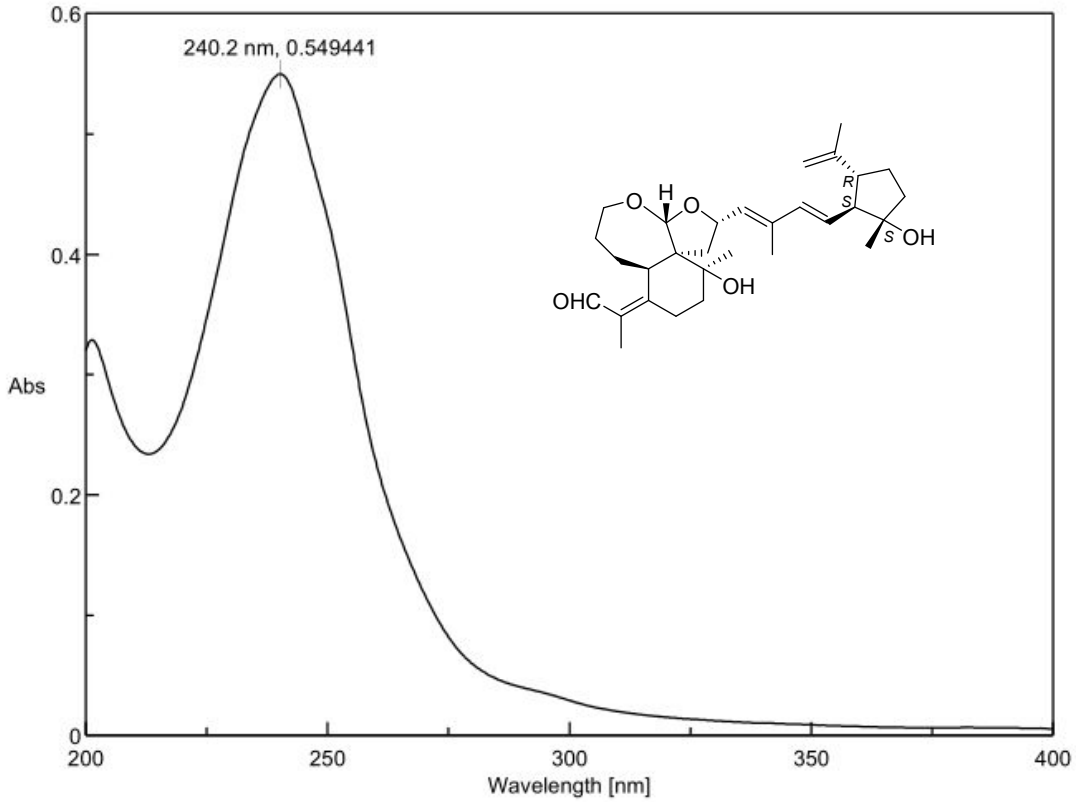


Figure S2. The IR spectrum of compound **1** in CH_3OH.

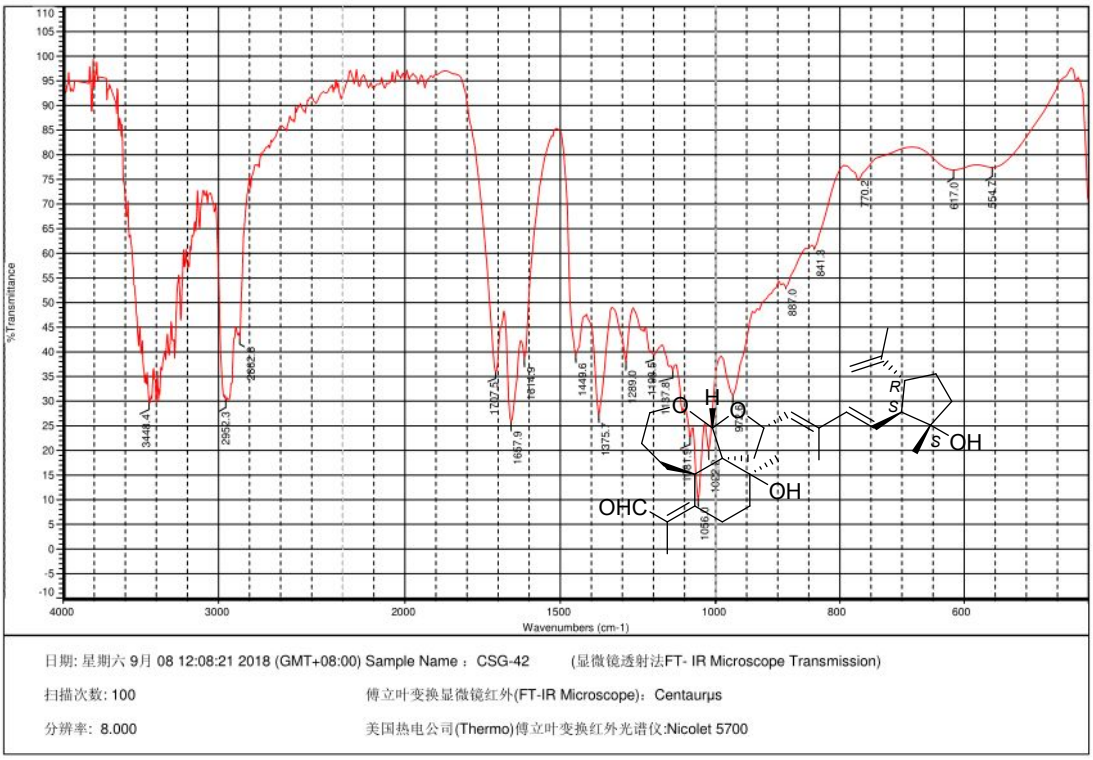
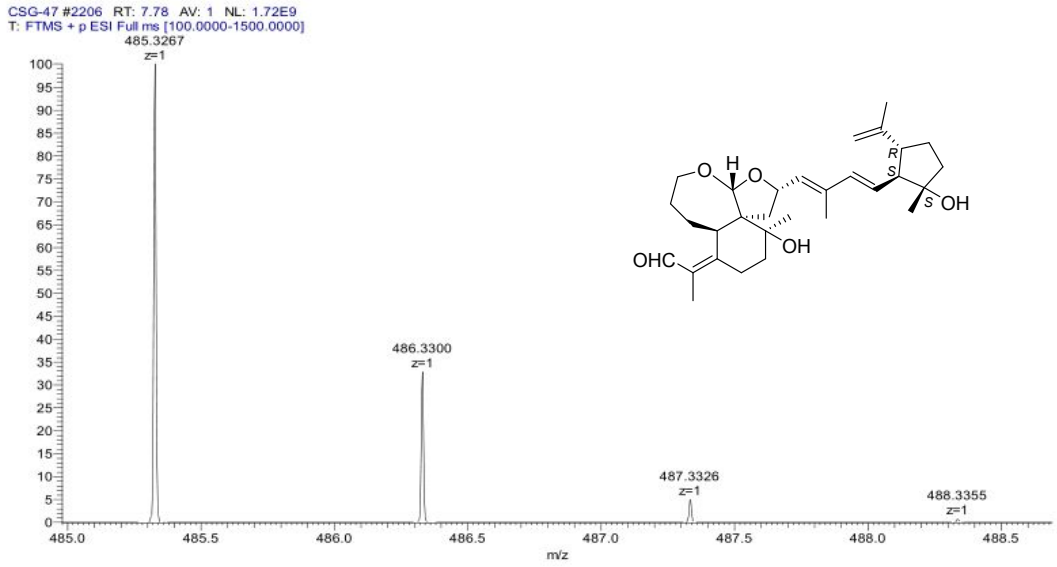


Figure S3. The HRESIMS of compound **1**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
485.3267	485.3262	1.11	8.5	C30 H45 O5	M+H

Figure S4. The CD spectrum of compound **1** in CH_3OH.

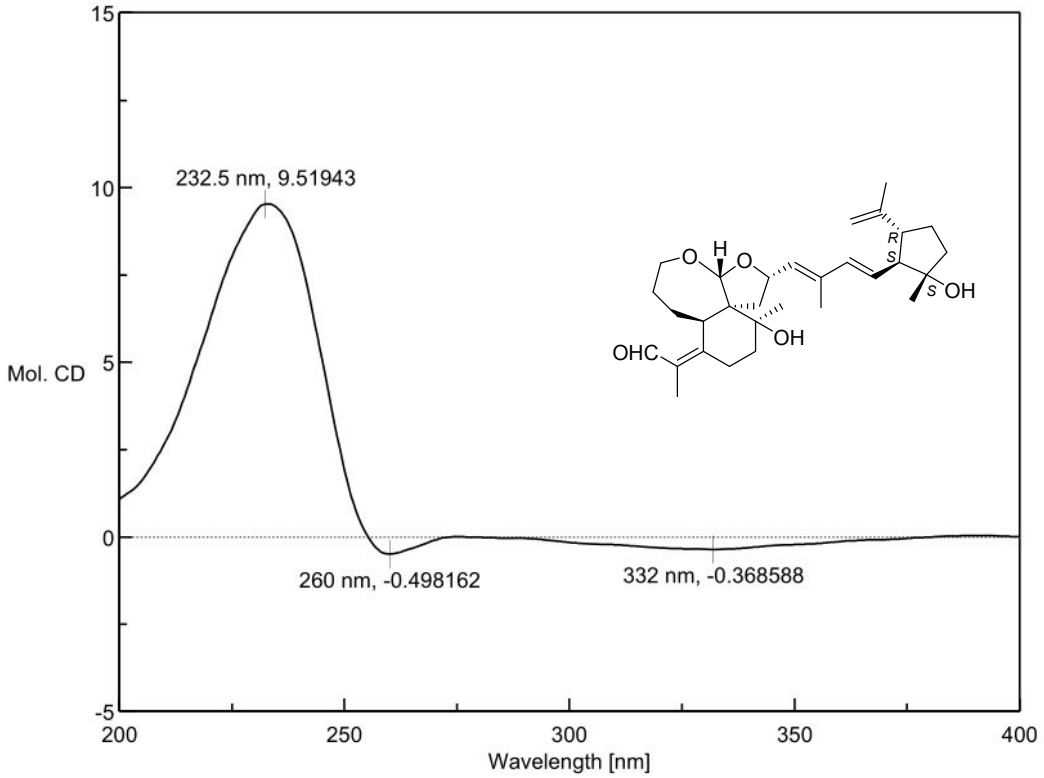


Figure S5. The [1]H NMR spectrum of compound **1** in DMSO-d_6.(600 MHz)

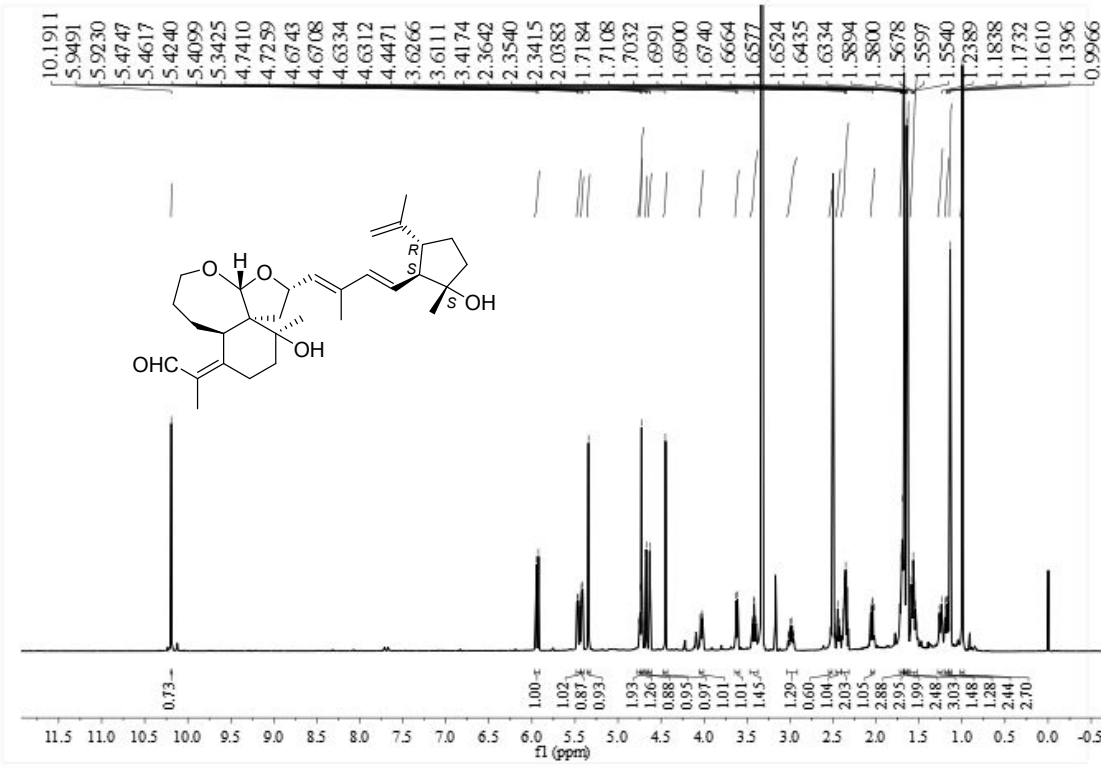


Figure S6.The [13]C NMR spectrum of compound **1** in DMSO-d_6.(150 MHz)

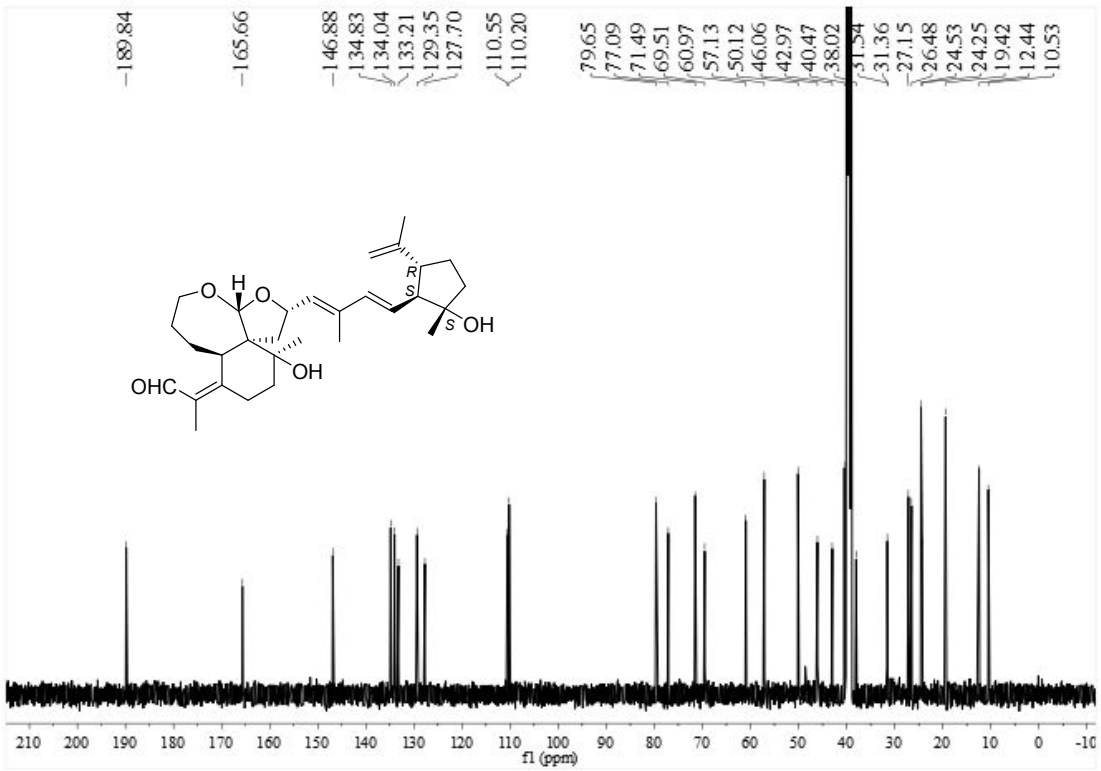


Figure S7.The HSQC spectrum of compound **1** in DMSO-d_6.(600 MHz)

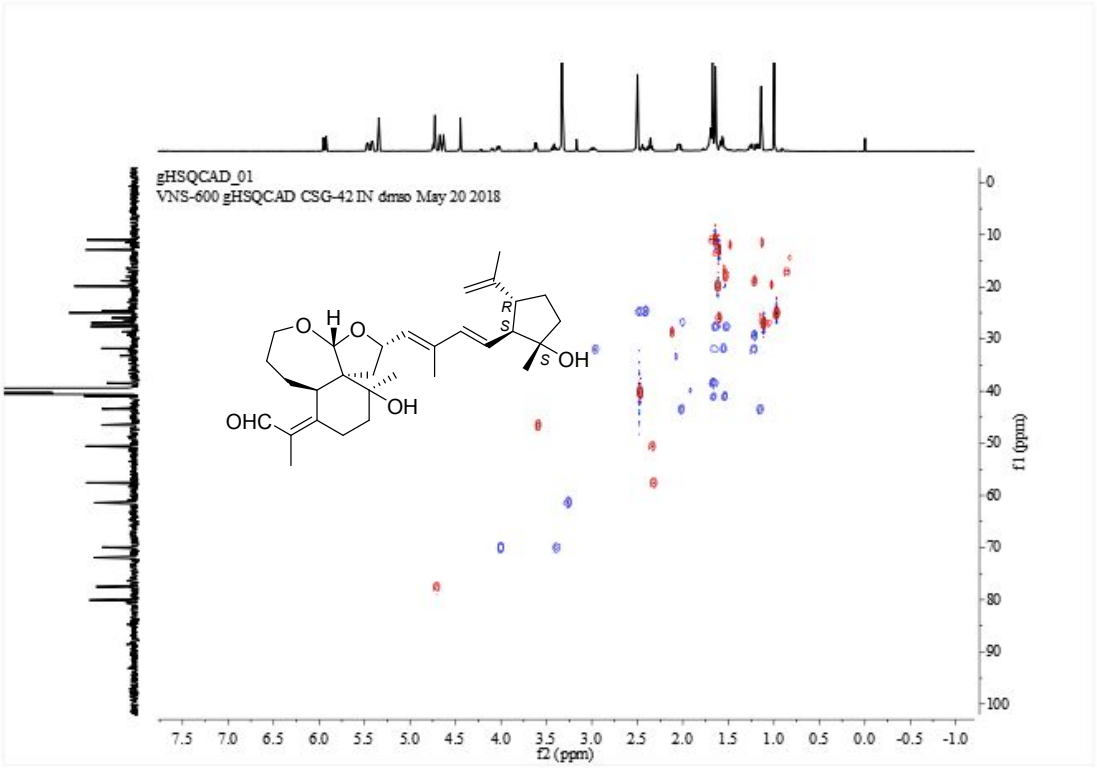


Figure S8.The HMBC spectrum of compound **1** in DMSO-d_6.(600 MHz)

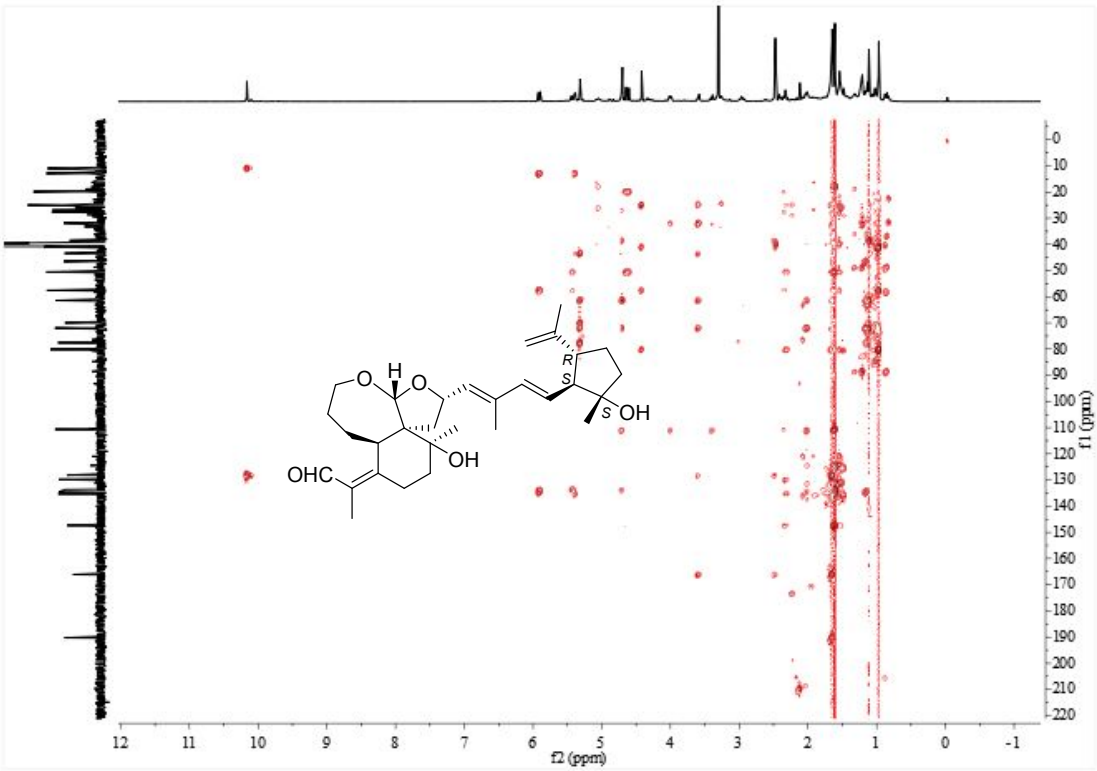


Figure S9.The NOESY spectrum of compound **1** in DMSO-d_6.(600 MHz)

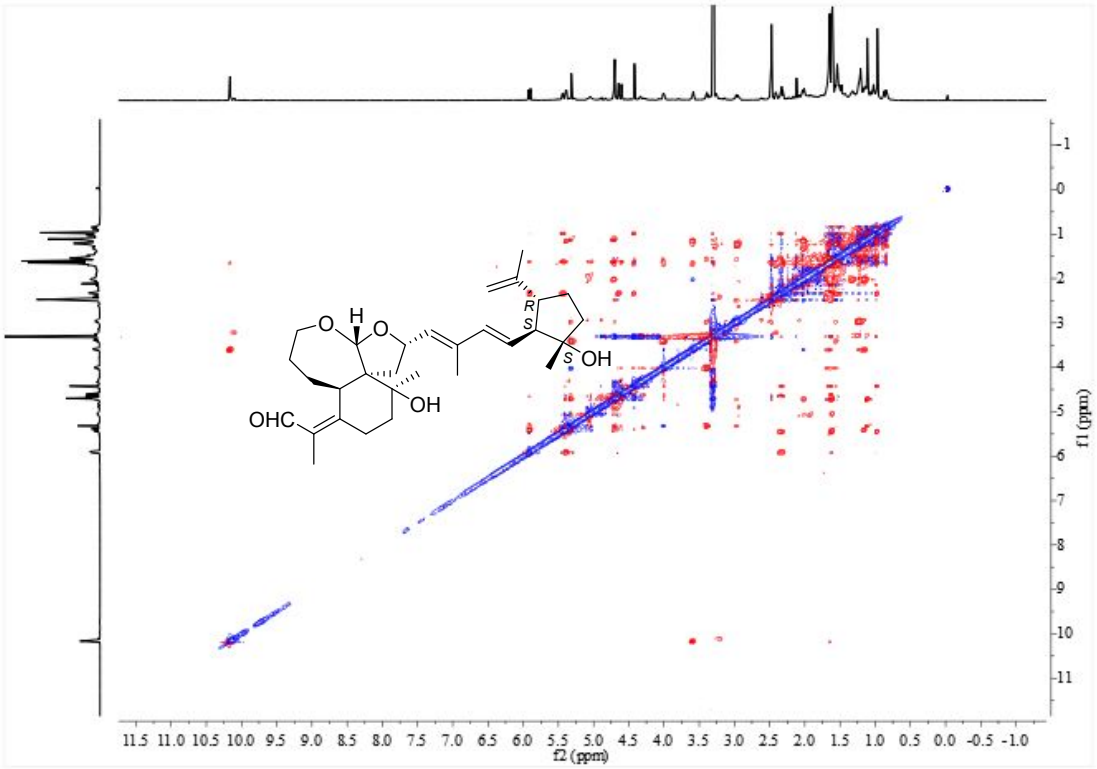
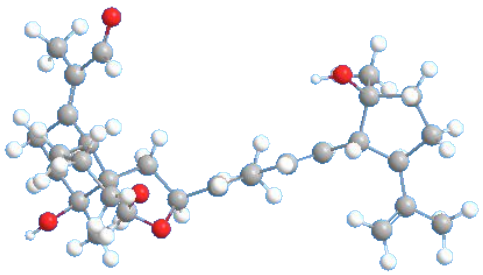
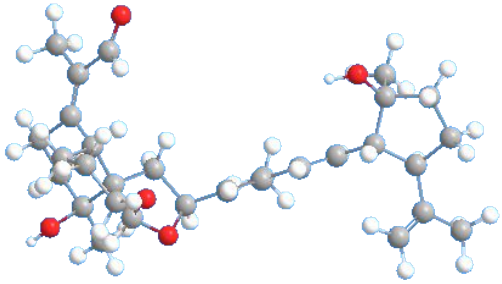


Figure S10. The 3D conformers of compound **1** obtained by optimization at B3LYP/6-3G(d) level in MeOH.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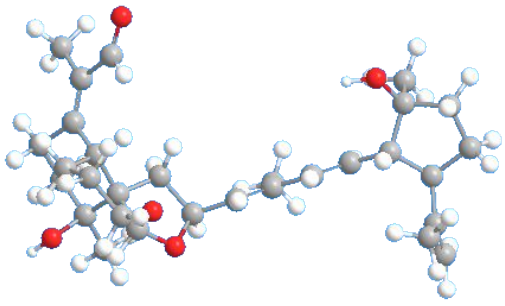
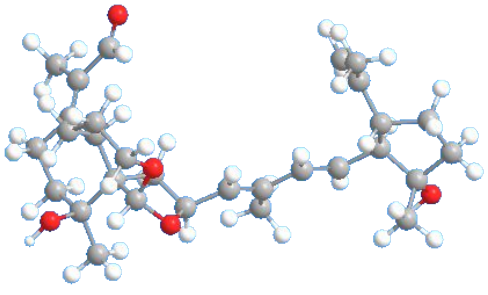
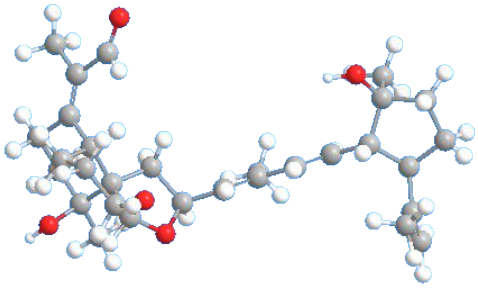
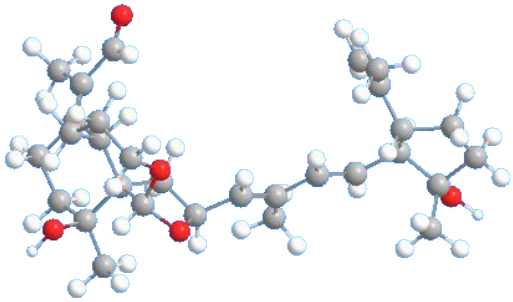
	
C3 (9.46%)	C4 (7.66%)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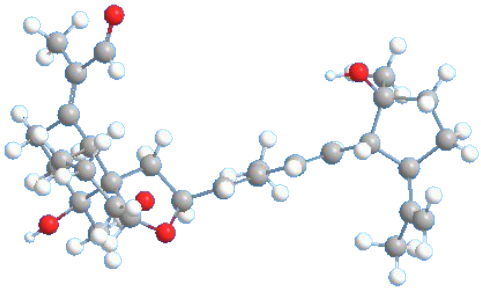	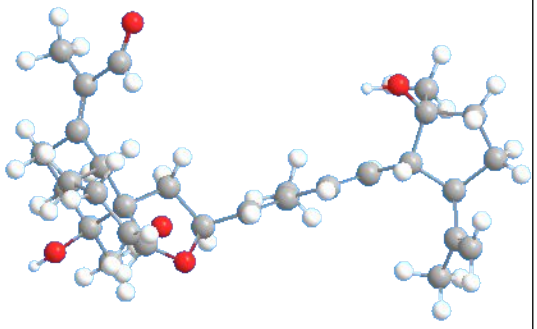
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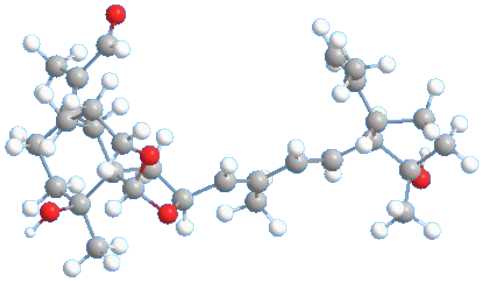	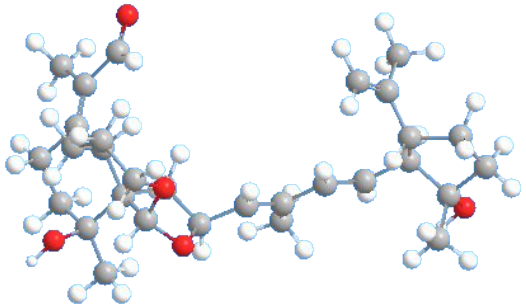
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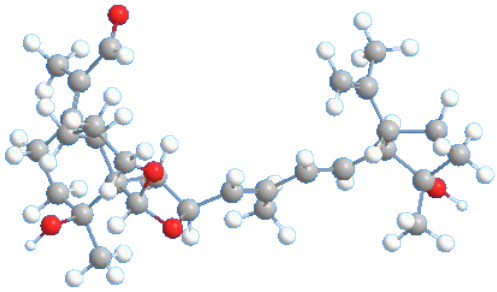
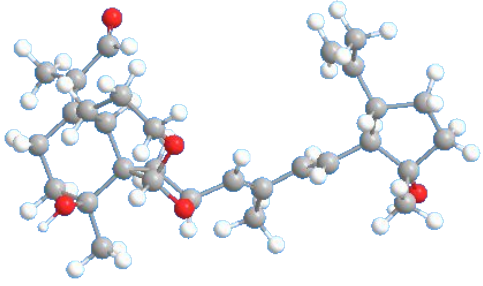
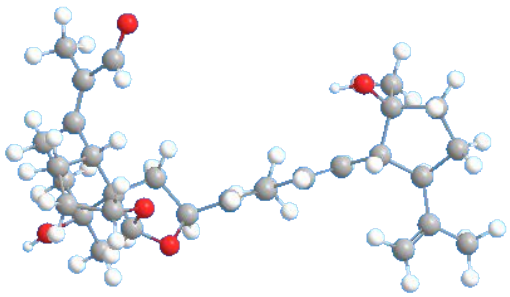
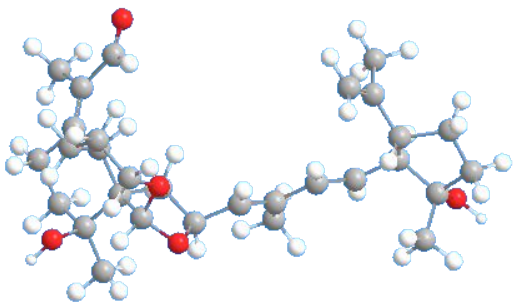
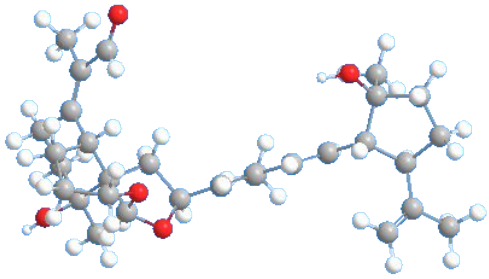
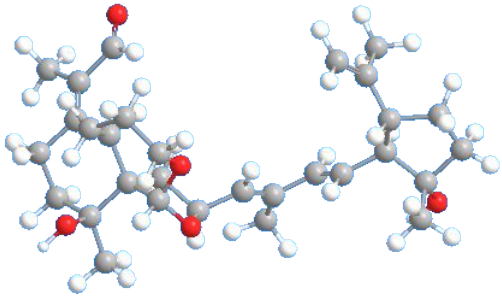
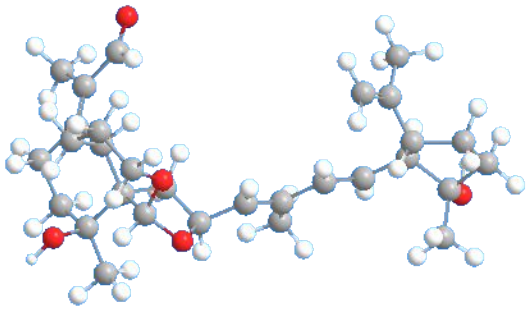
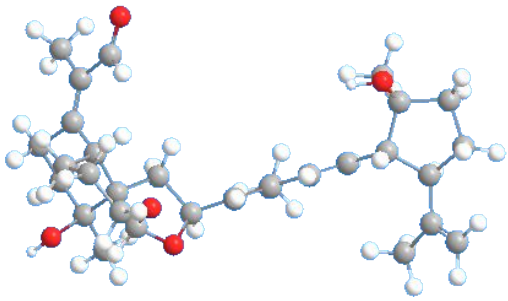
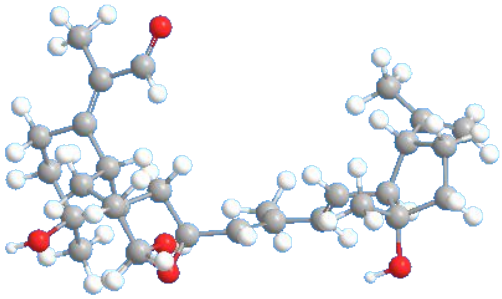
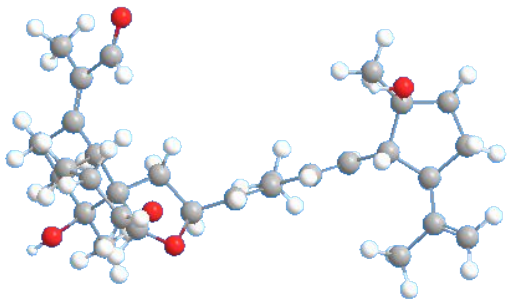
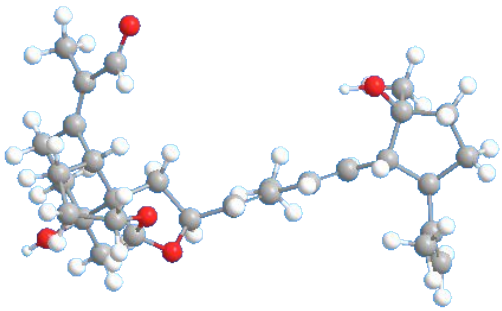
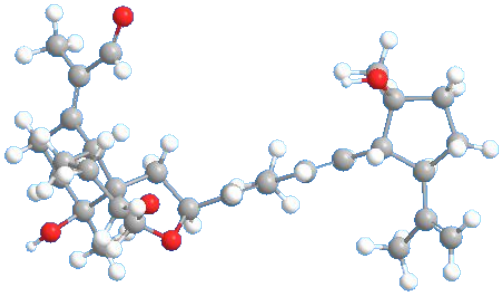
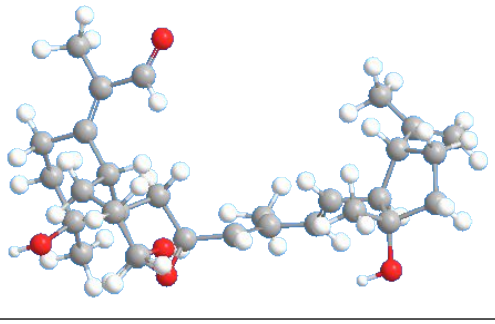
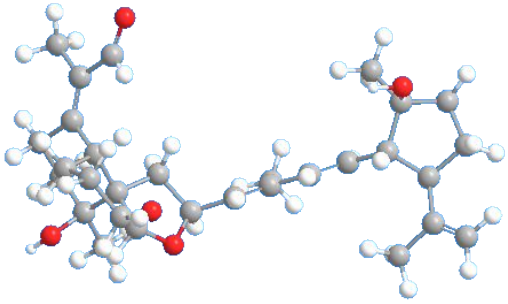
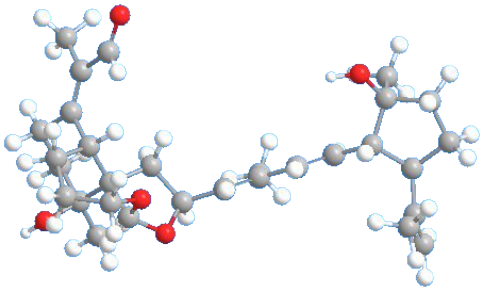
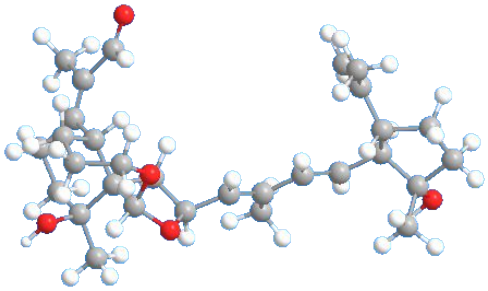
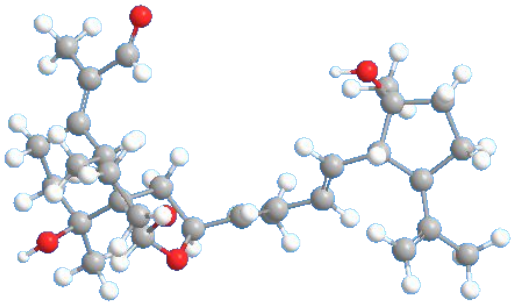
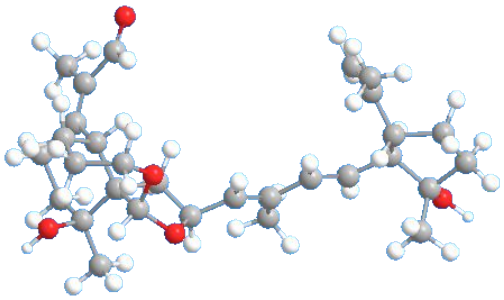
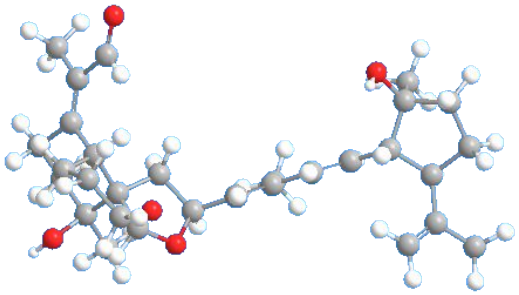
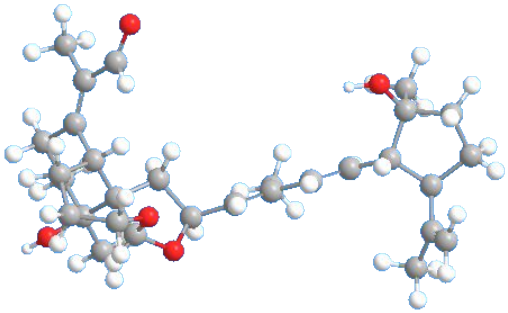
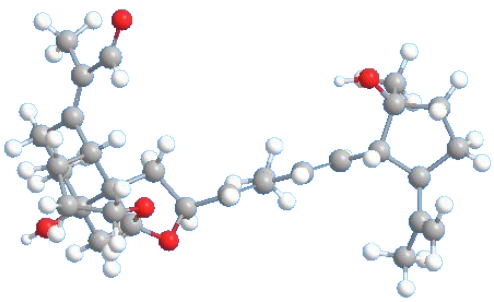
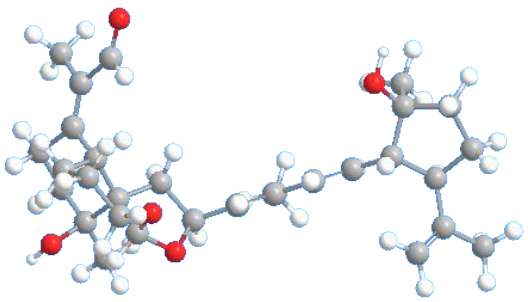
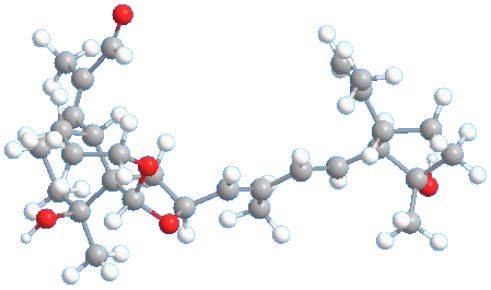
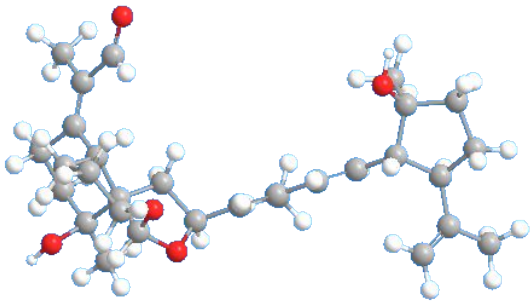
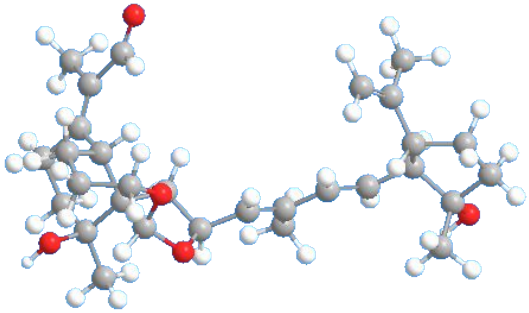
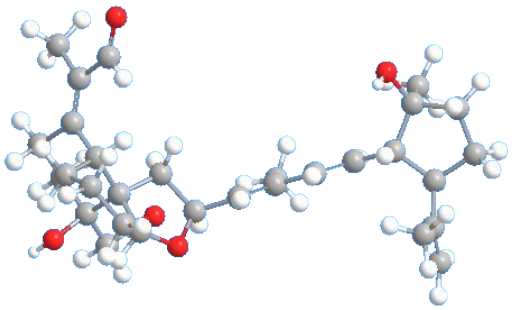
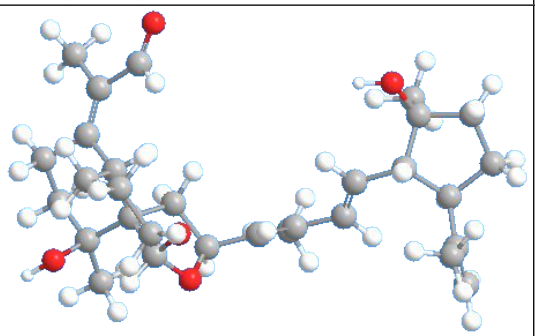
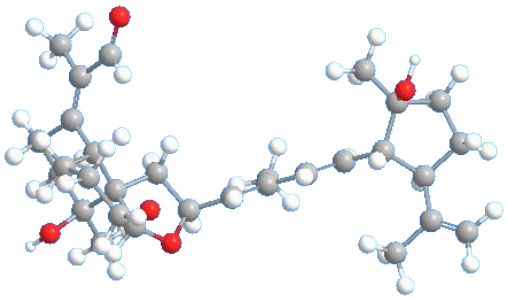
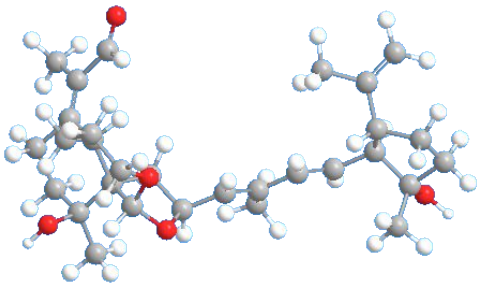
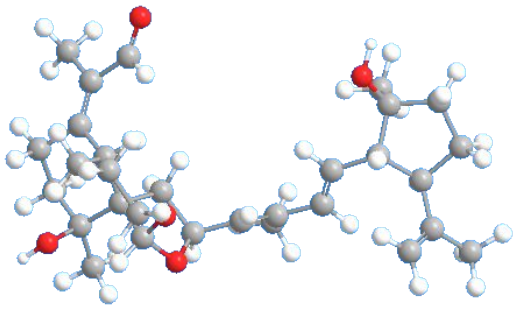
	
C11 (2.14%)	C12 (1.97%)
	

C13 (1.89%)	C14 (1.82%)
	
C15 (1.22%)	C16 (1.10%)
	
C17 (1.00%)	C18 (1.00%)
	
C19 (0.95%)	C20 (0.76%)
	
C21 (0.76%)	C22 (0.75%)

	
C23 (0.68%)	C24 (0.66%)
	
C25 (0.65%)	C26 (0.49%)
	
C27 (0.43%)	C28 (0.43%)
	
C29 (0.33%)	C30 (0.32%)
	

C31 (0.31%)	C32 (0.27%)
	
C33 (7.69%)	C34 (0.26%)
	
C35 (0.24%)	C36 (0.23%)
	
C37 (0.19%)	C38 (0.19%)
	
C39 (0.18%)	C40 (0.17%)

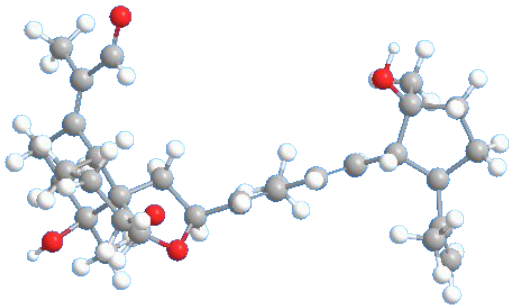
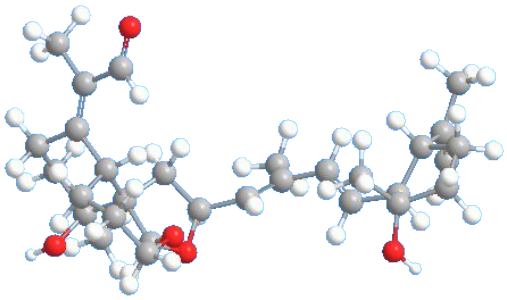
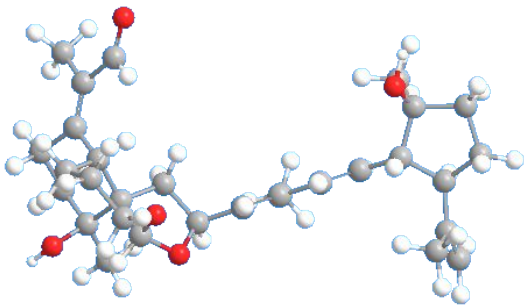
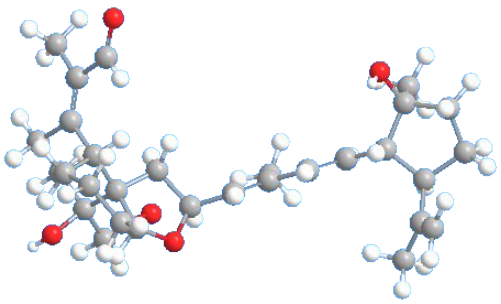
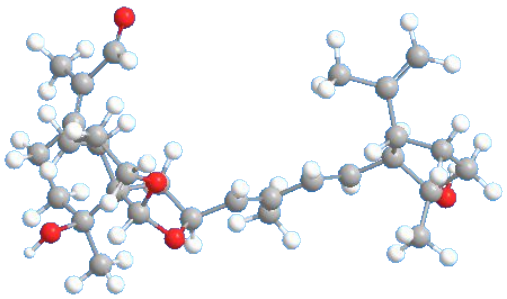
	
C41 (0.16%)	C42 (0.14%)
	
C43 (0.13%)	C44 (0.13%)
	
C45 (0.12%)	

Figure S11. The UV spectrum of compound **2** in CH_3OH.

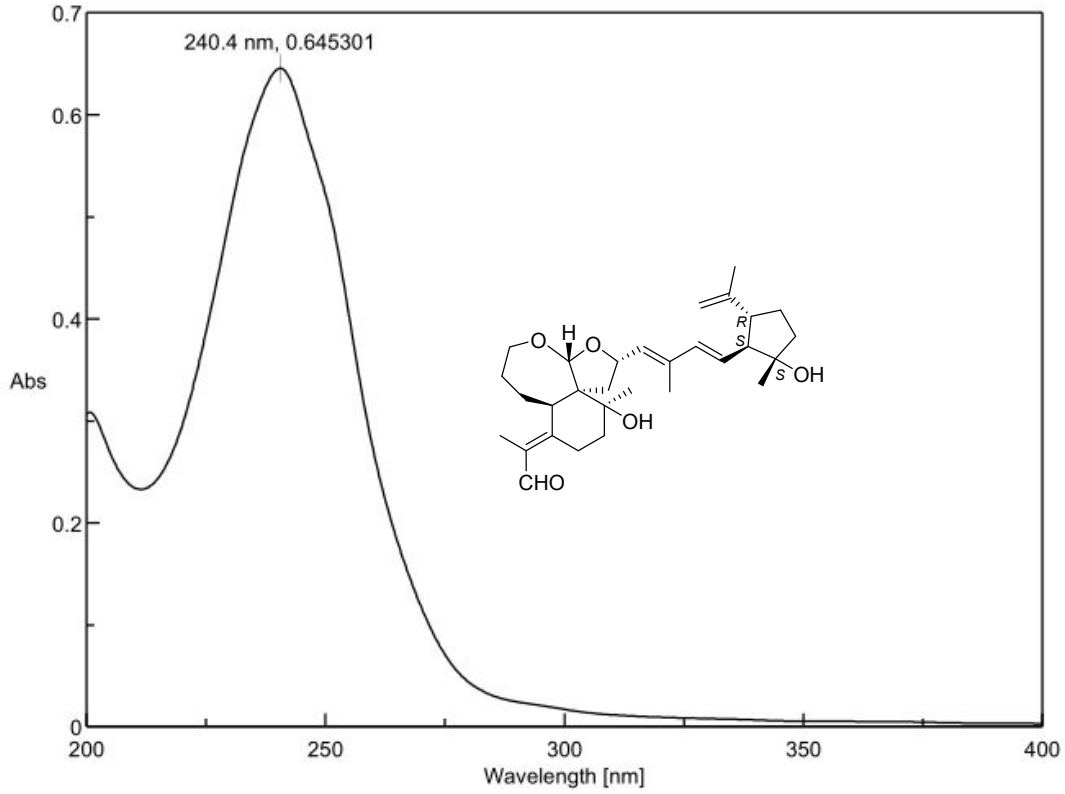


Figure S12. The IR spectrum of compound **2** in CH_3OH.

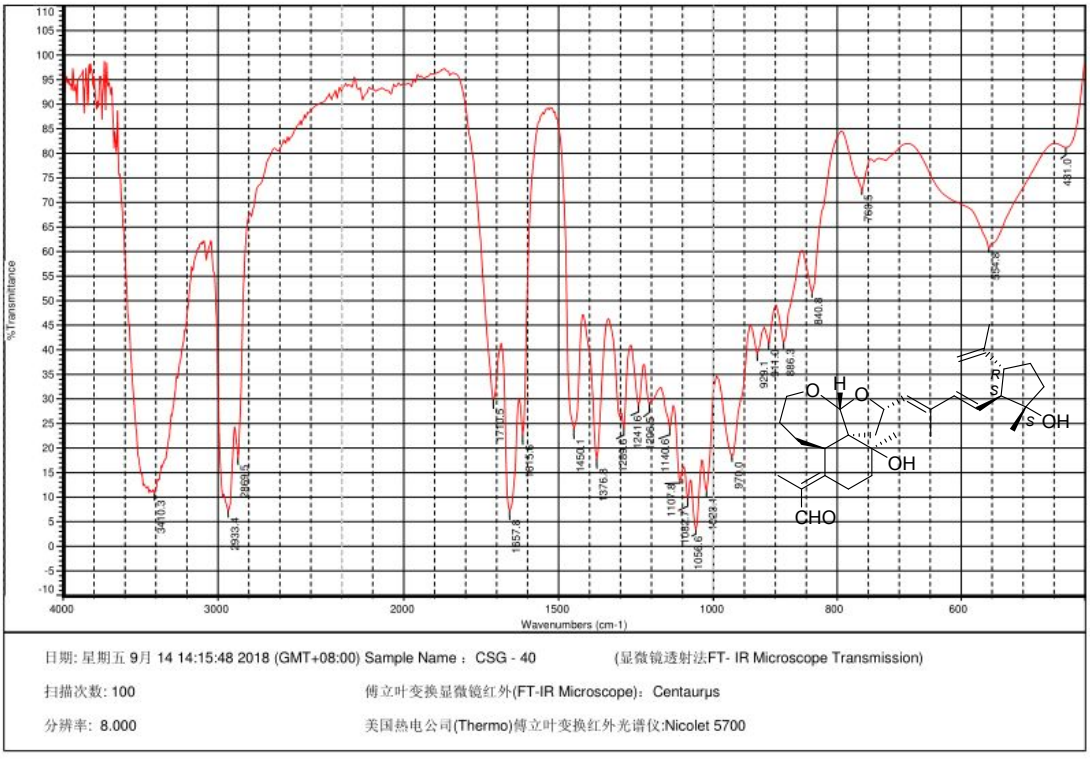
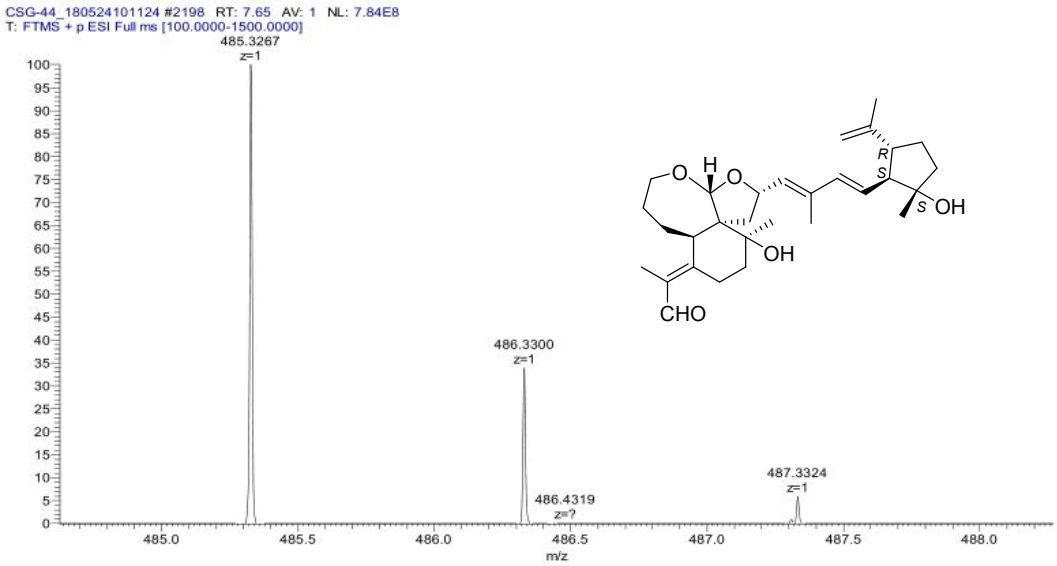


Figure S13. The HRESIMS of compound **2**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
485.3267	485.3262	1.17	8.5	C30 H45 O5	M+H

Figure S14. The CD spectrum of compound **2** in CH_3OH.

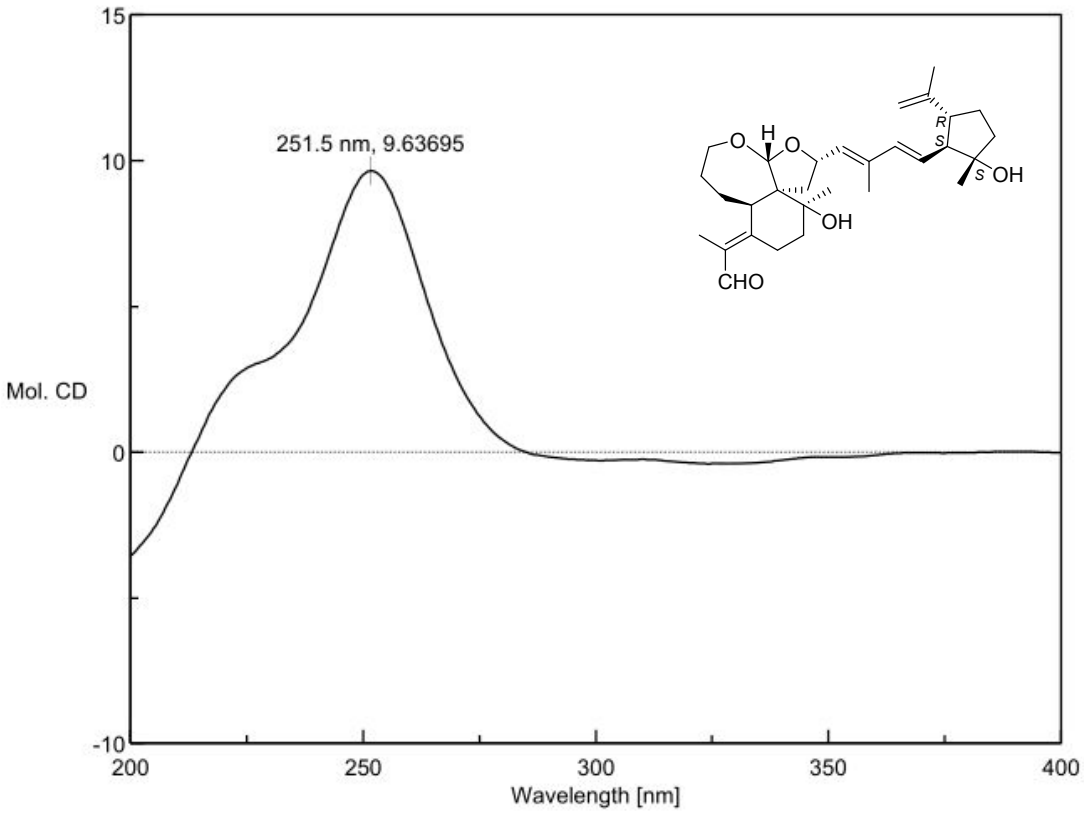


Figure S15. The [1]H NMR spectrum of compound **2** in DMSO-d_6.(600 MHz)

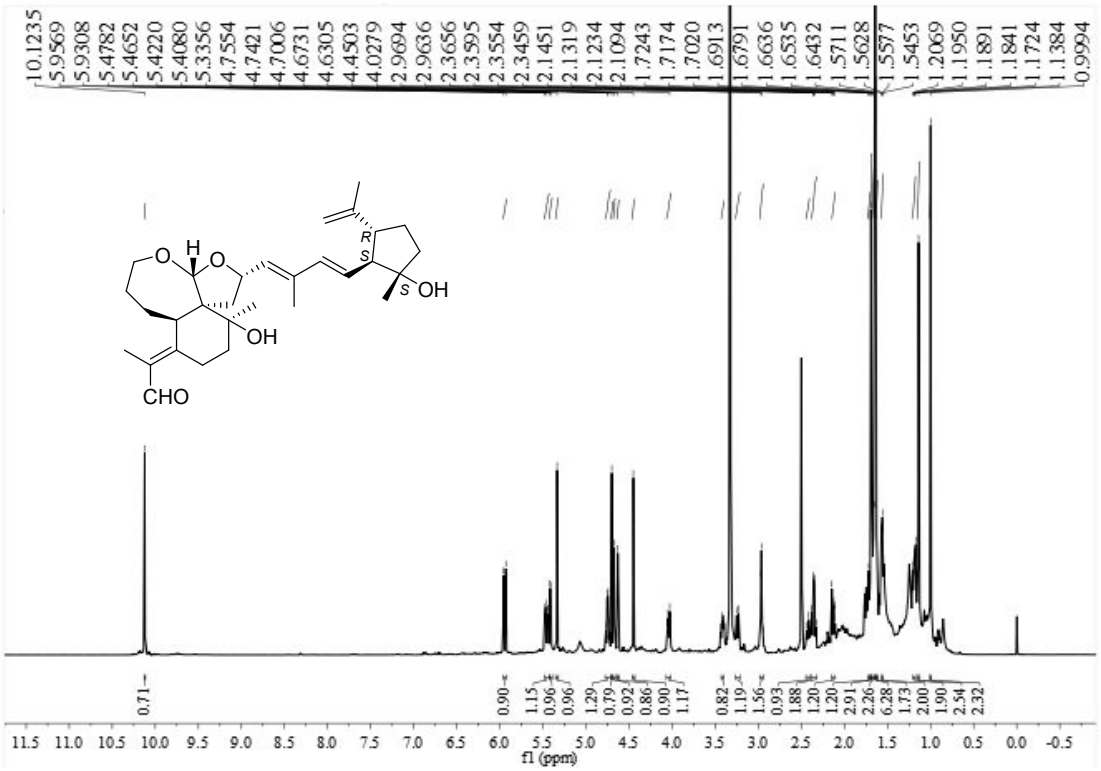


Figure S16.The [13]C NMR spectrum of compound **2** in DMSO-d_6.(150 MHz)

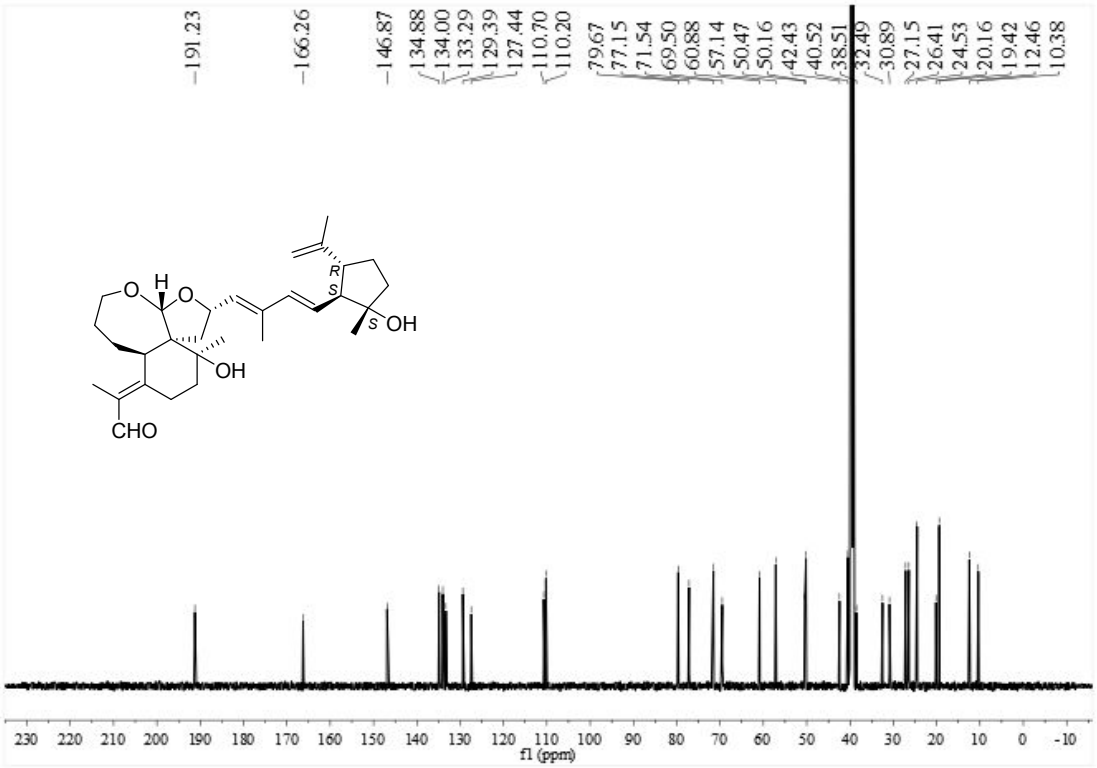


Figure S17. The HSQC spectrum of compound **2** in DMSO-d_6.(600 MHz)

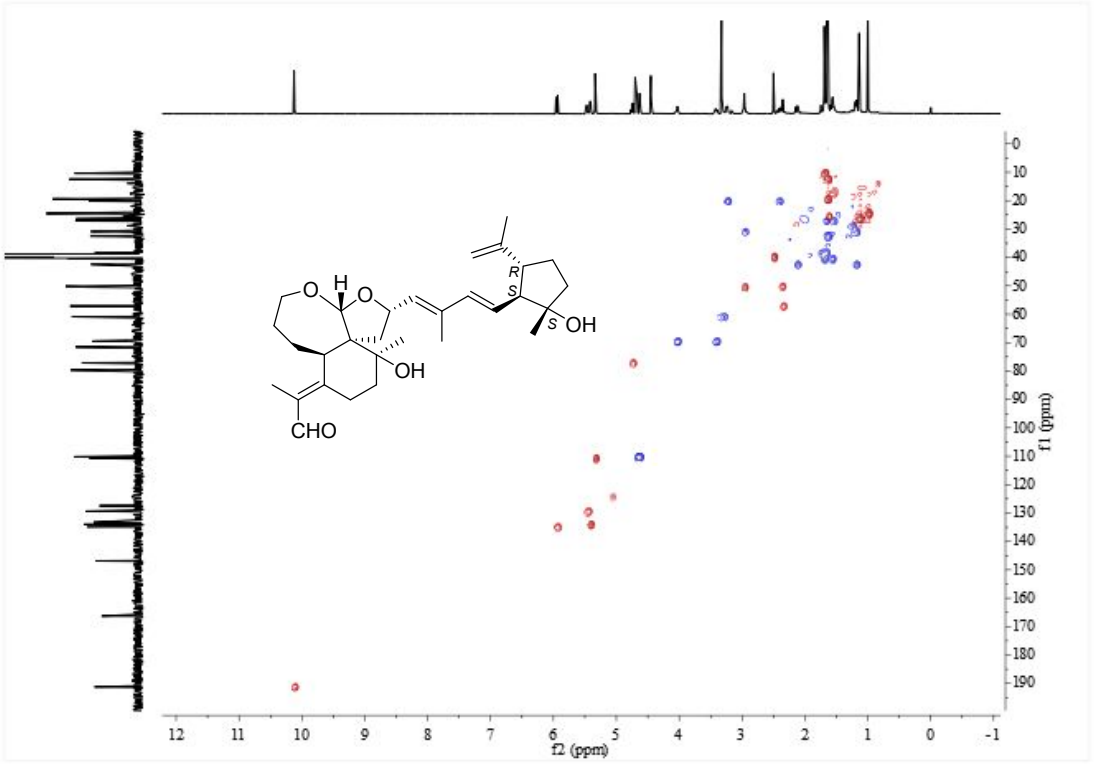


Figure S18. The HMBC spectrum of compound **2** in DMSO-d_6.(600 MHz)

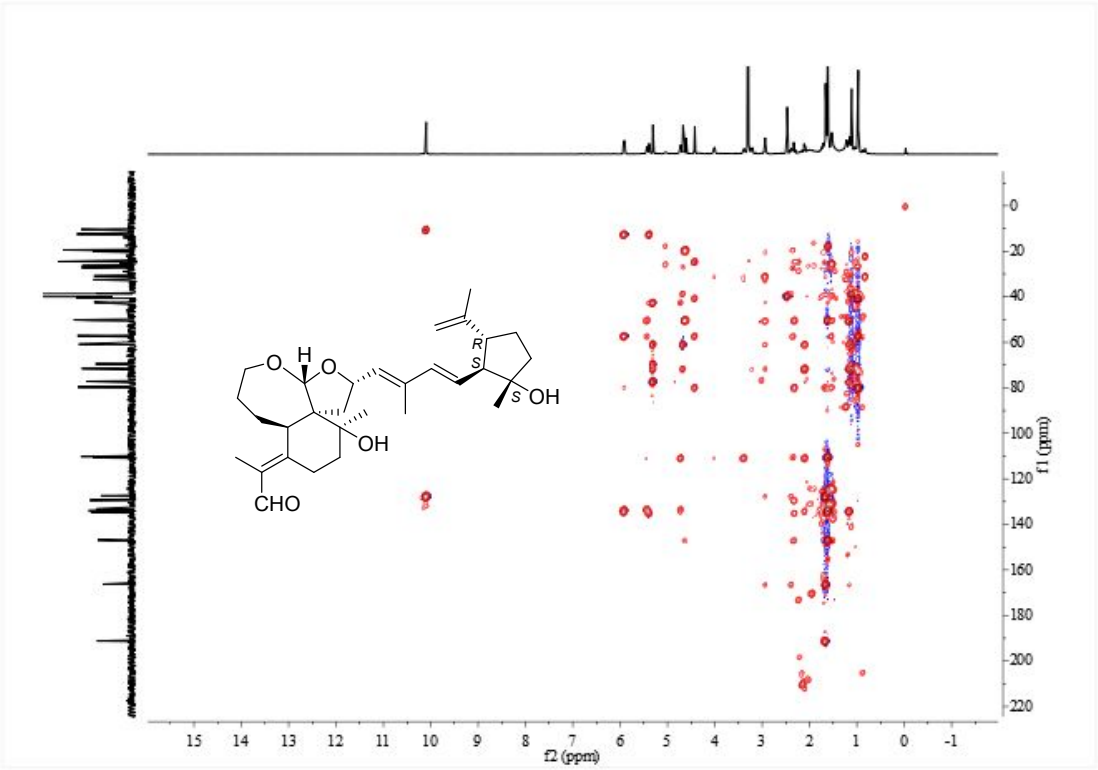


Figure S19. The NOESY spectrum of compound **2** in DMSO-d_6.(600 MHz)

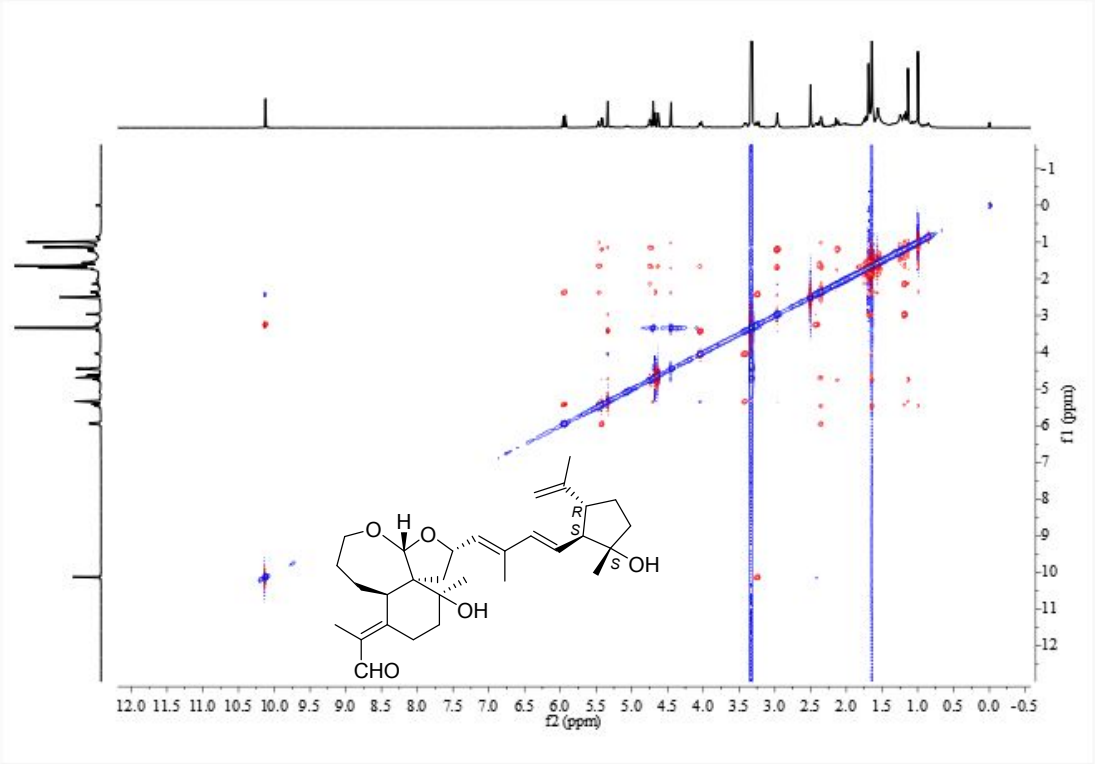


Figure S20. The UV spectrum of compound **3** in CH_3OH.

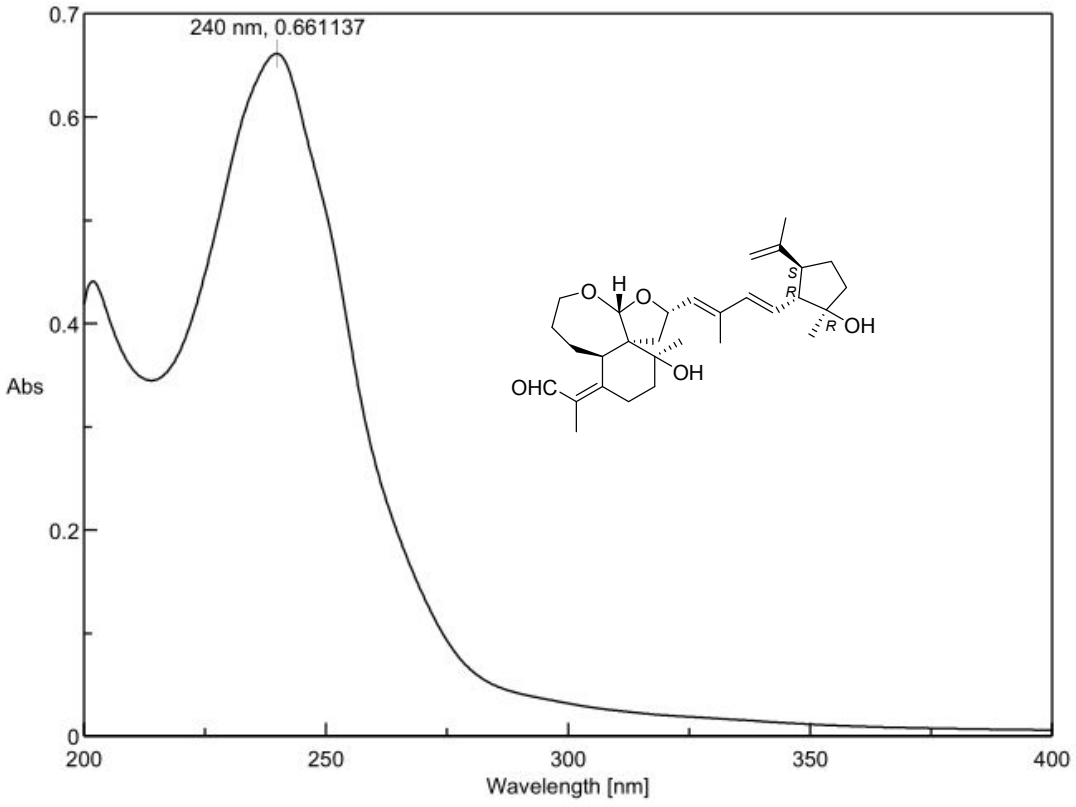


Figure S21. The IR spectrum of compound **3** in CH_3OH.

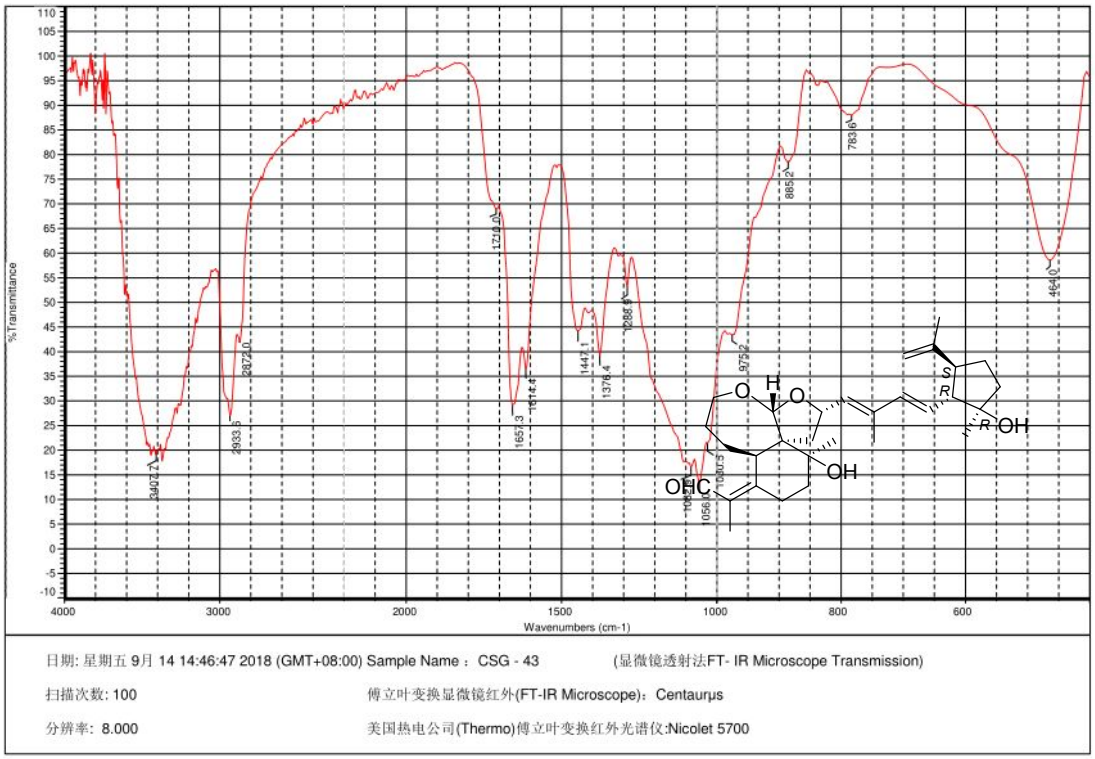
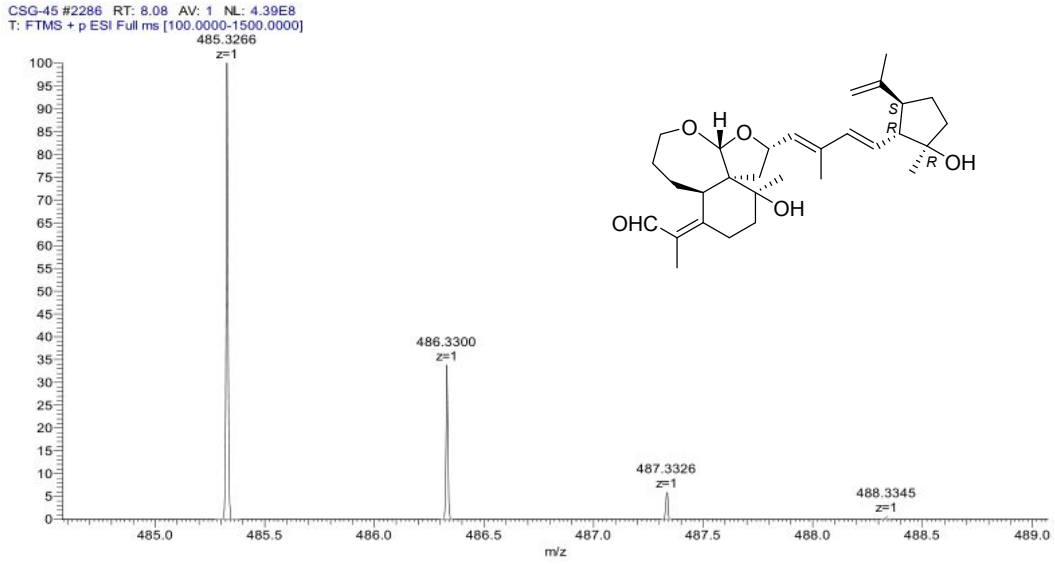


Figure S22. The HRESIMS of compound **3**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
485.3266	485.3262	0.93	8.5	C30 H45 O5	M+H

Figure S23.The CD spectrum of compound **3** in CH_3OH.

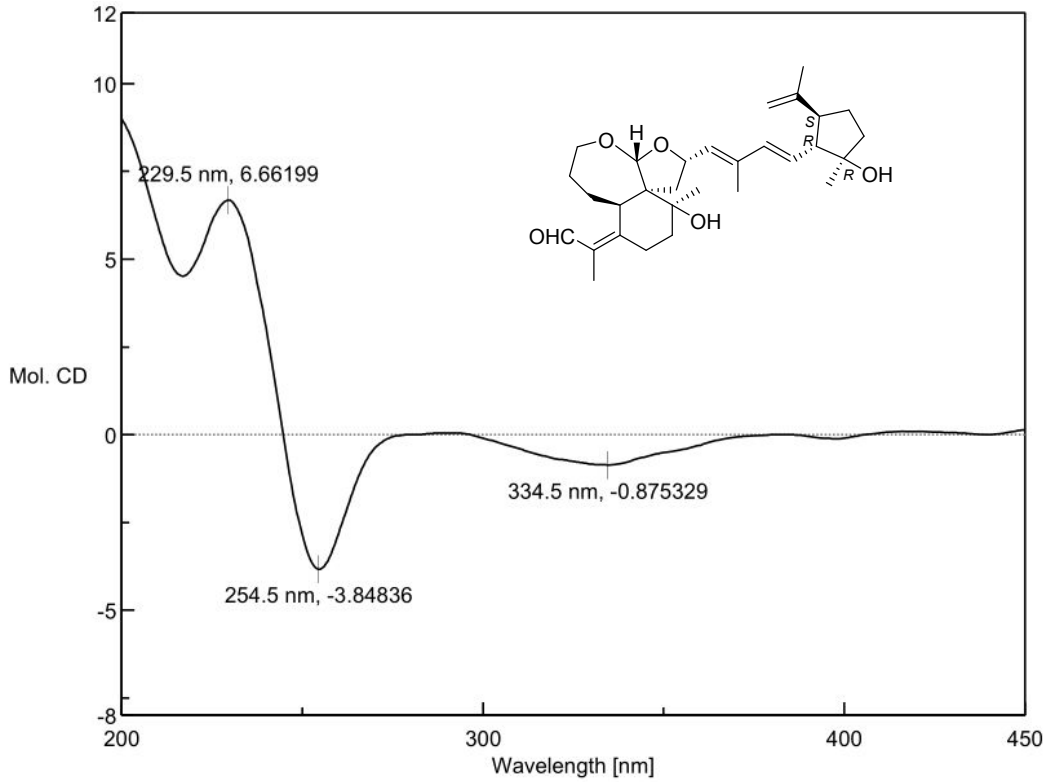


Figure S24. The ^{1}H NMR spectrum of compound **3** in DMSO-d_6. (600 MHz)

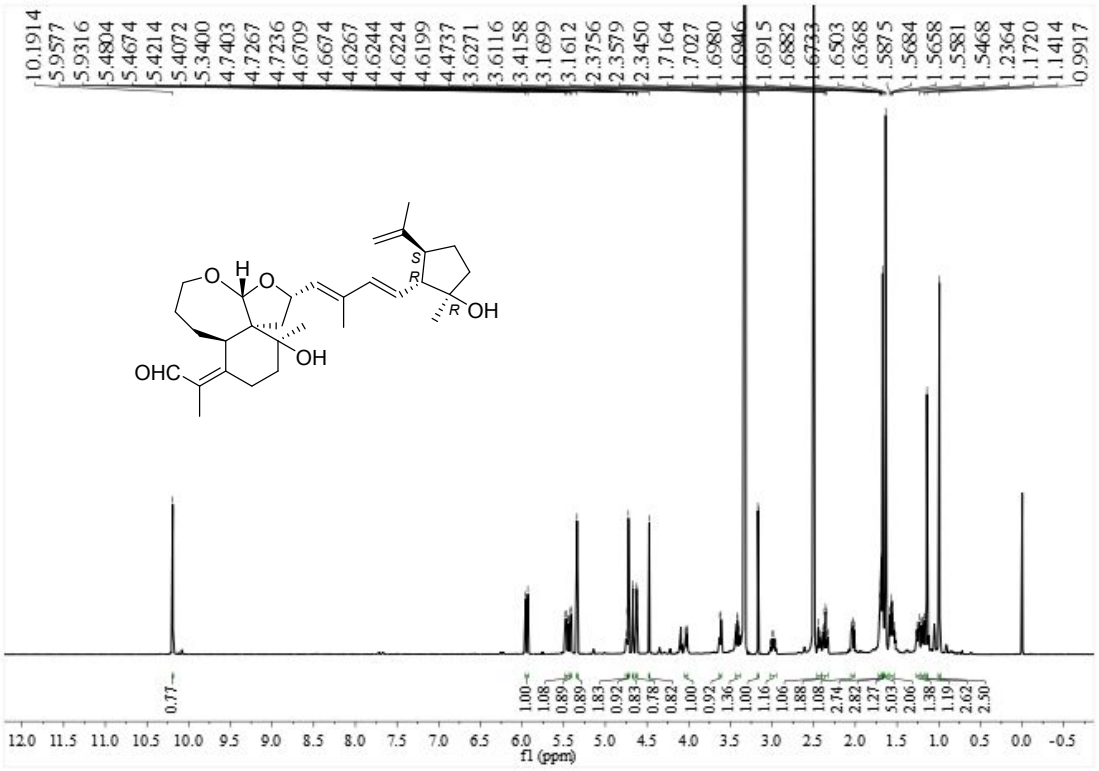


Figure S25. The ^{13}C NMR spectrum of compound **3** in DMSO-d_6. (150 MHz)

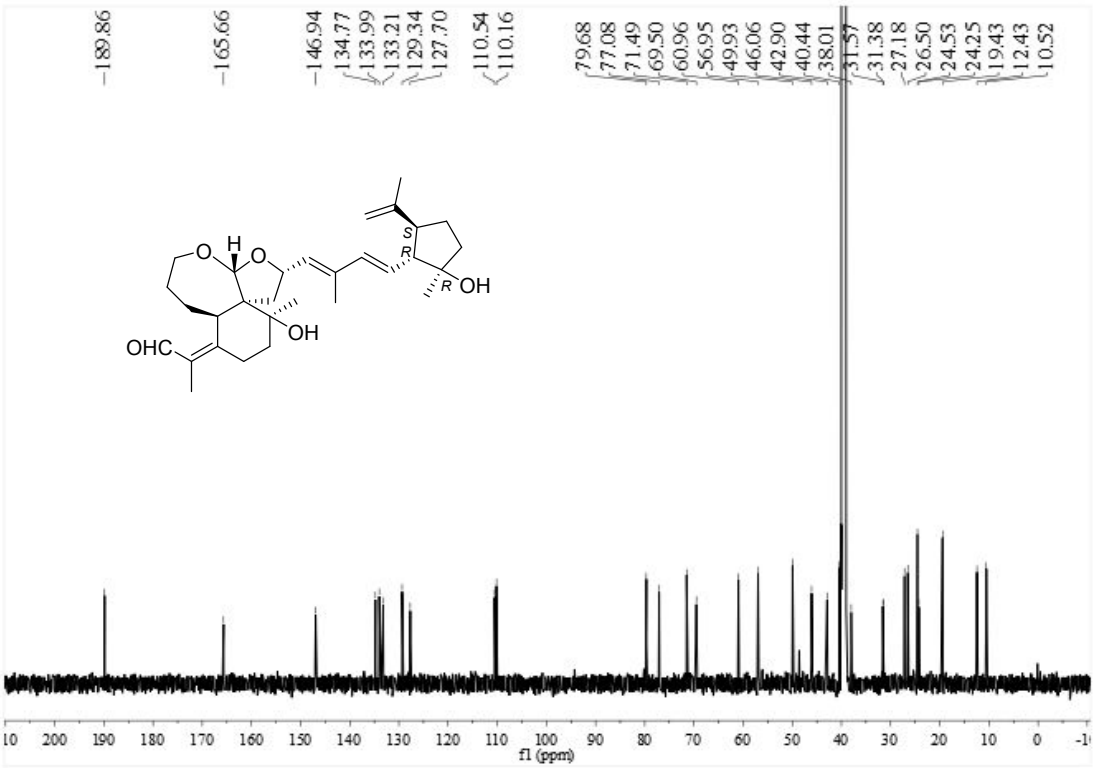


Figure S26. The HSQC spectrum of compound **3** in DMSO-d_6.(600 MHz)

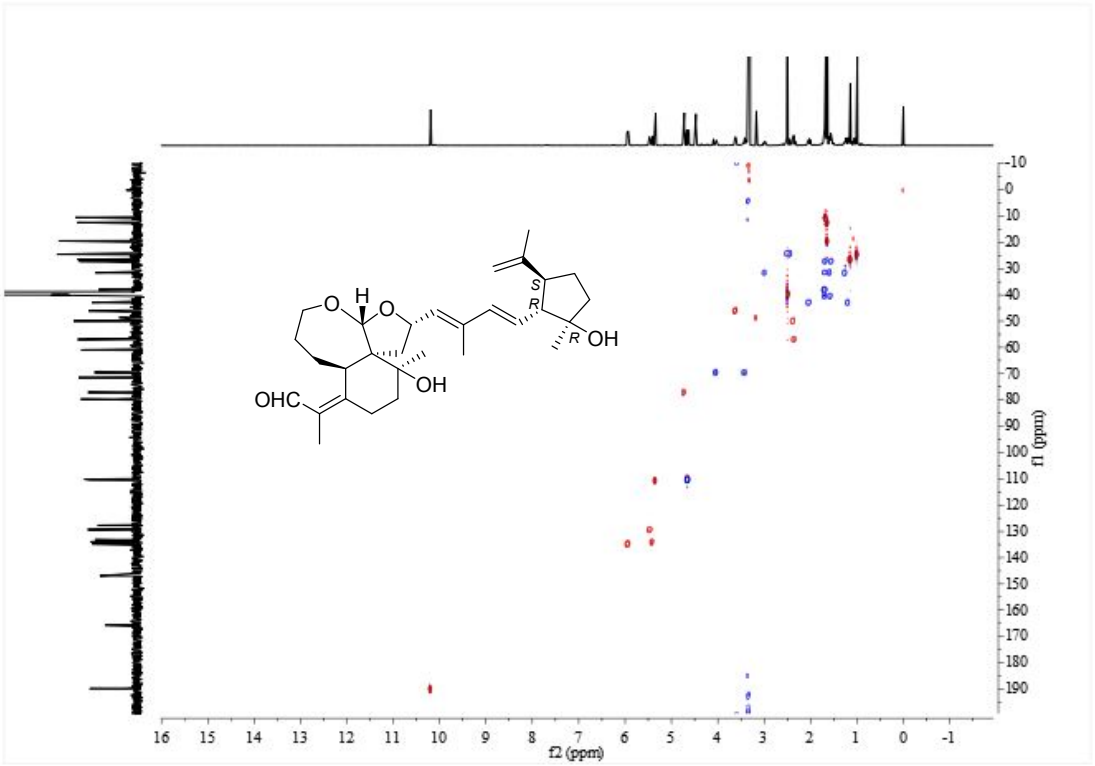


Figure S27. The HMBC spectrum of compound **3** in DMSO-d_6.(600 MHz)

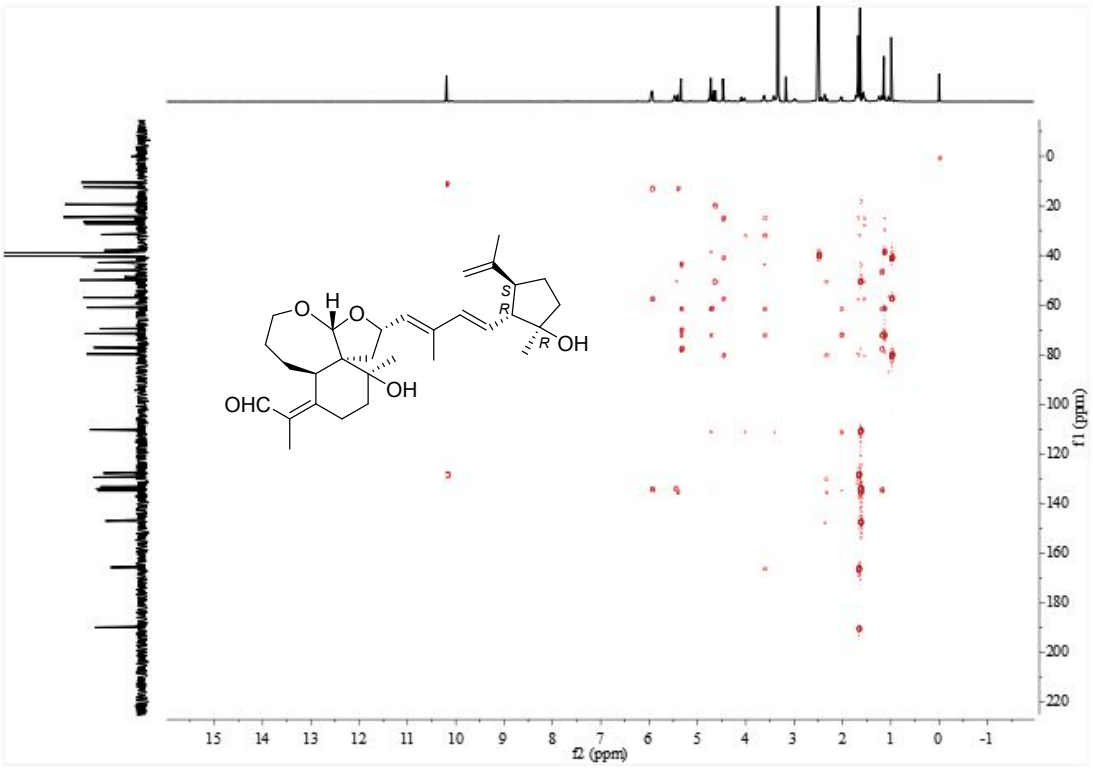


Figure S28. The NOESY spectrum of compound **3** in DMSO-d_6.(600 MHz)

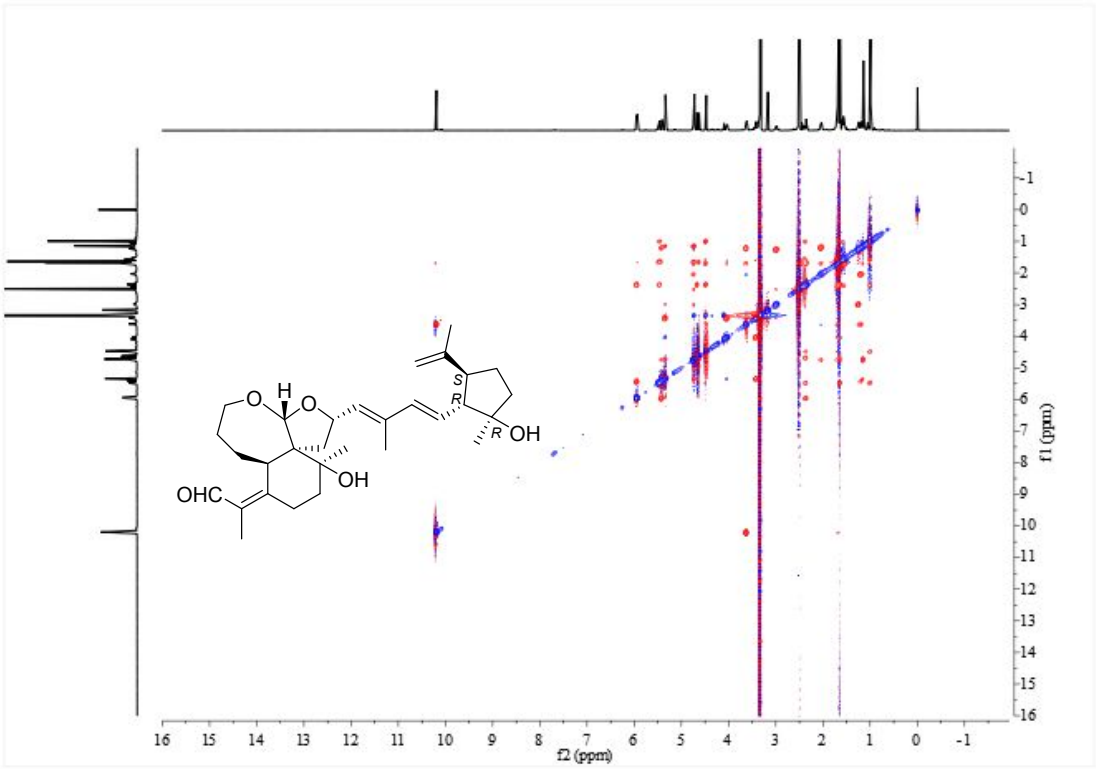


Figure S29. The UV spectrum of compound **4** in CH_3OH.

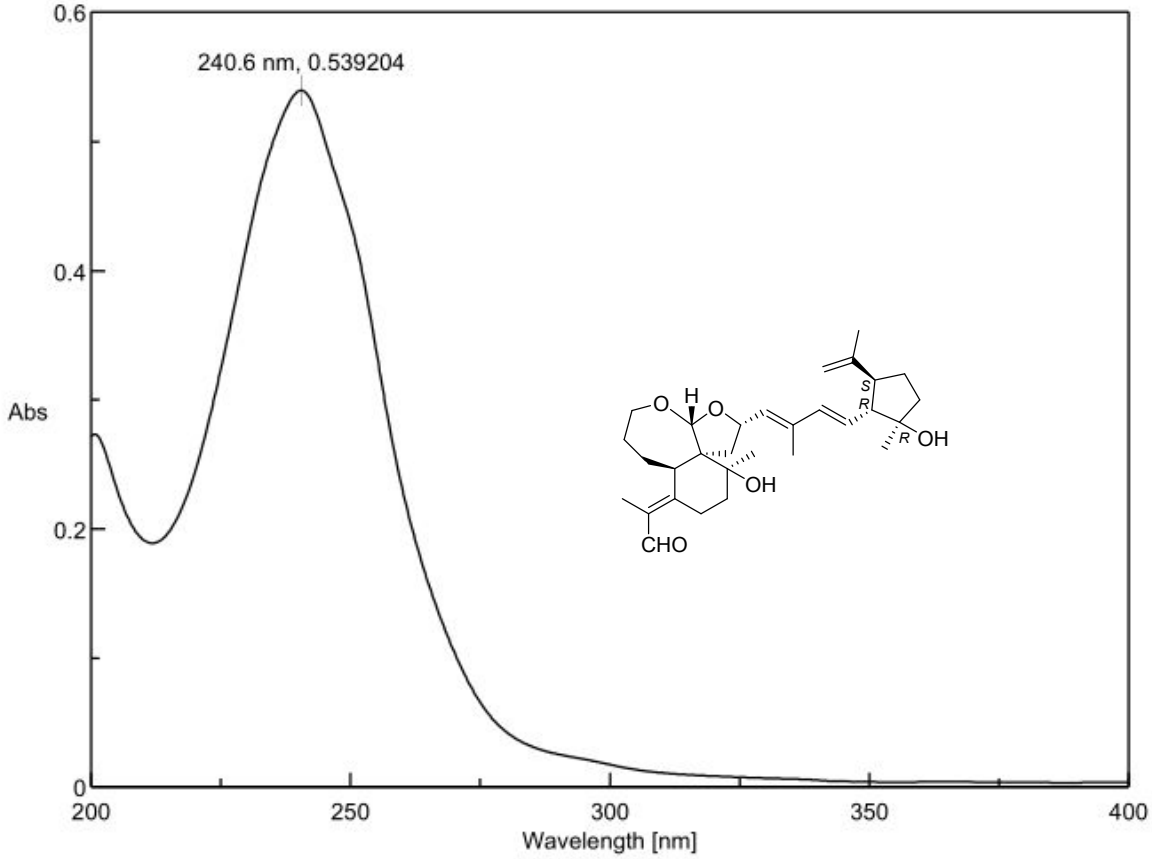


Figure S30. The IR spectrum of compound **4** in CH_3OH.

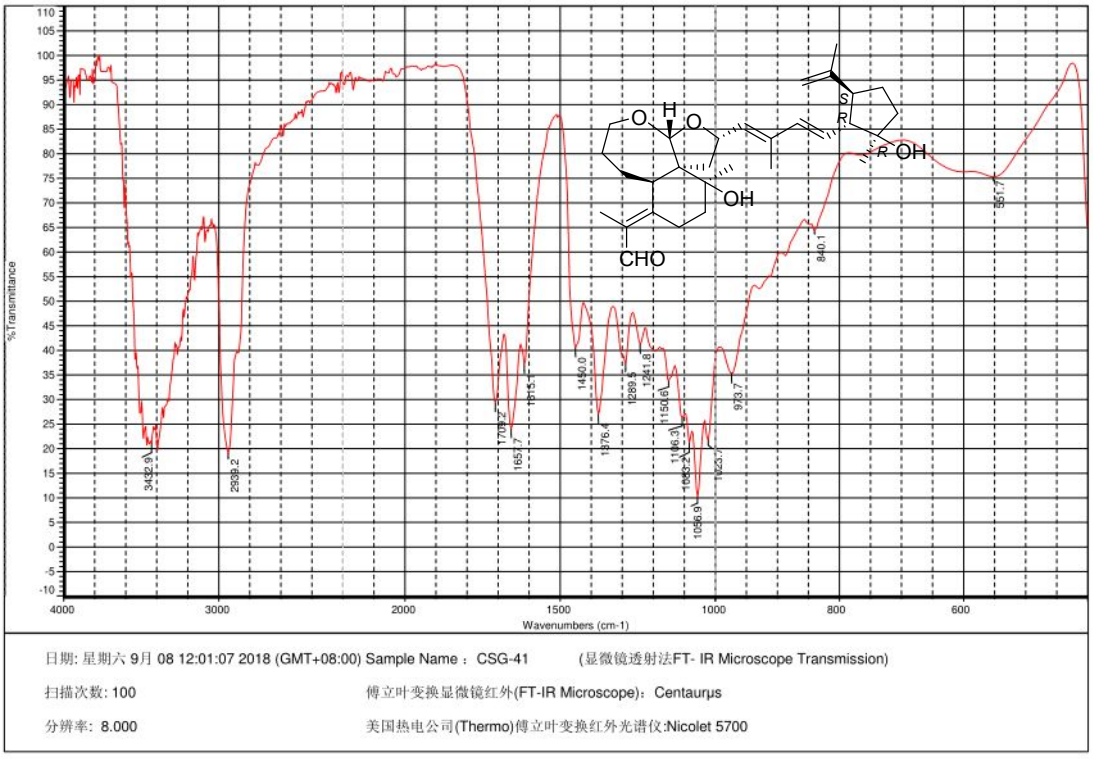
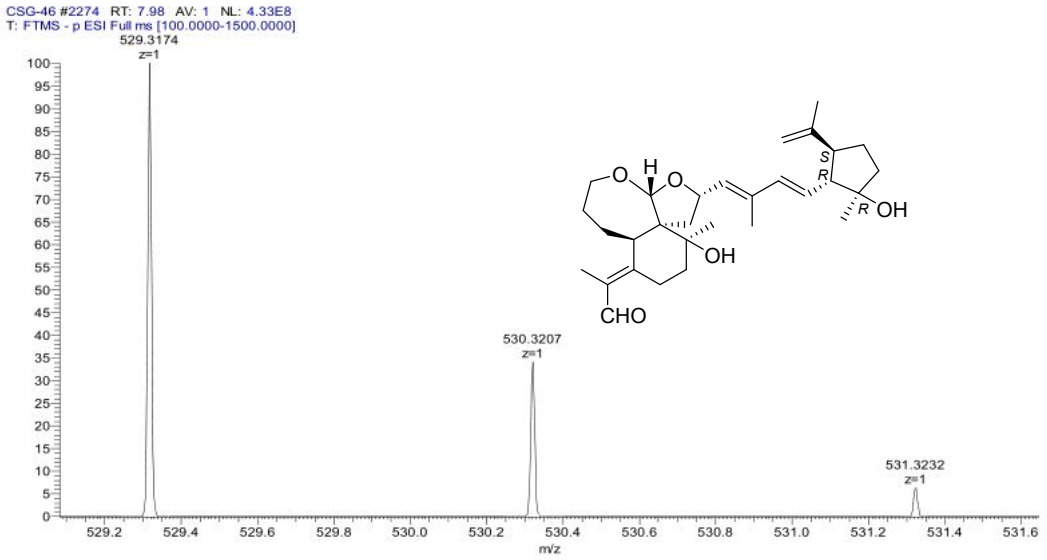


Figure S31. The HRESIMS of compound **4**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
529.31740	529.31710	0.57	9.5	C31 H45 O7	M+HCOO

Figure S32. The CD spectrum of compound **4** in CH_3OH.

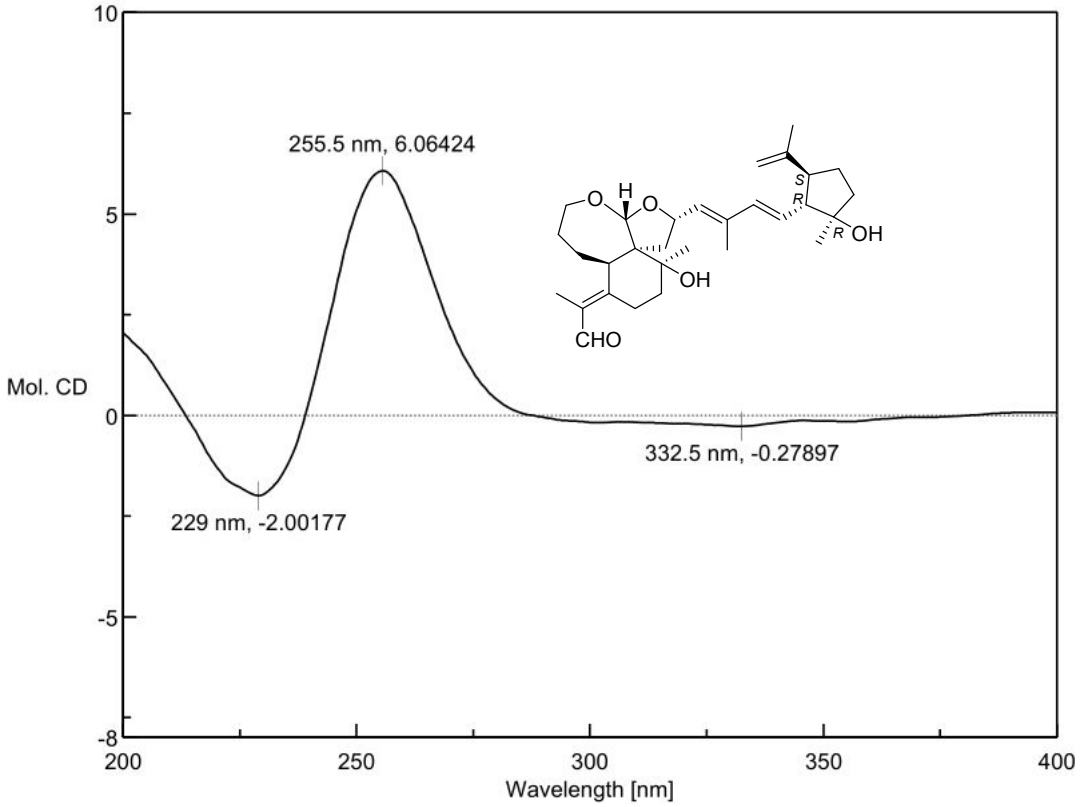


Figure S33. The ^{1}H NMR spectrum of compound **4** in DMSO-d_6.(600 MHz)

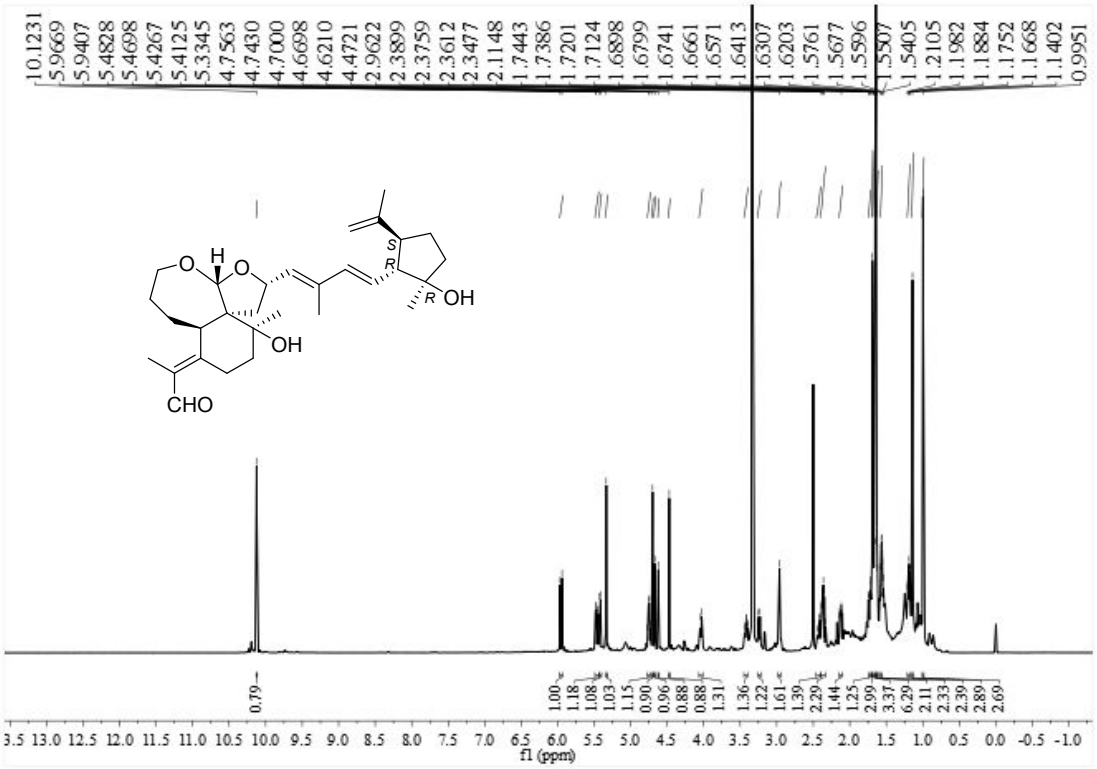


Figure S34. The ^{13}C NMR spectrum of compound **4** in DMSO-d_6.(150 MHz)

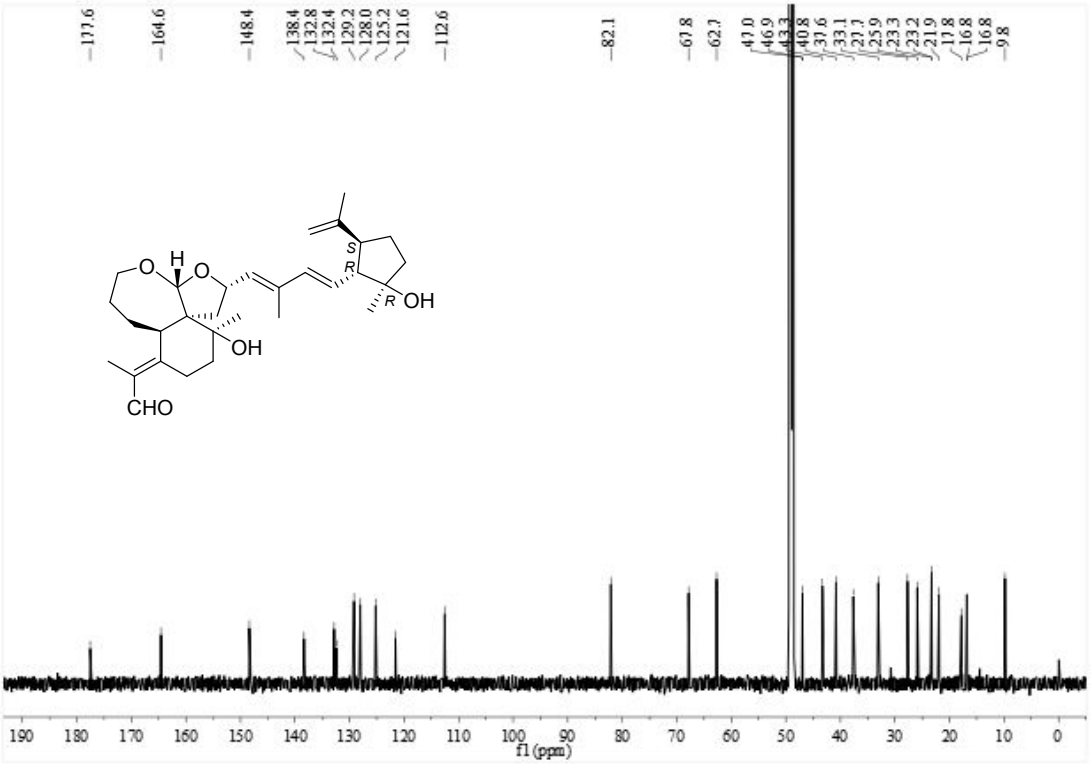


Figure S35. The HSQC spectrum of compound **4** in DMSO-d_6.(600 MHz)

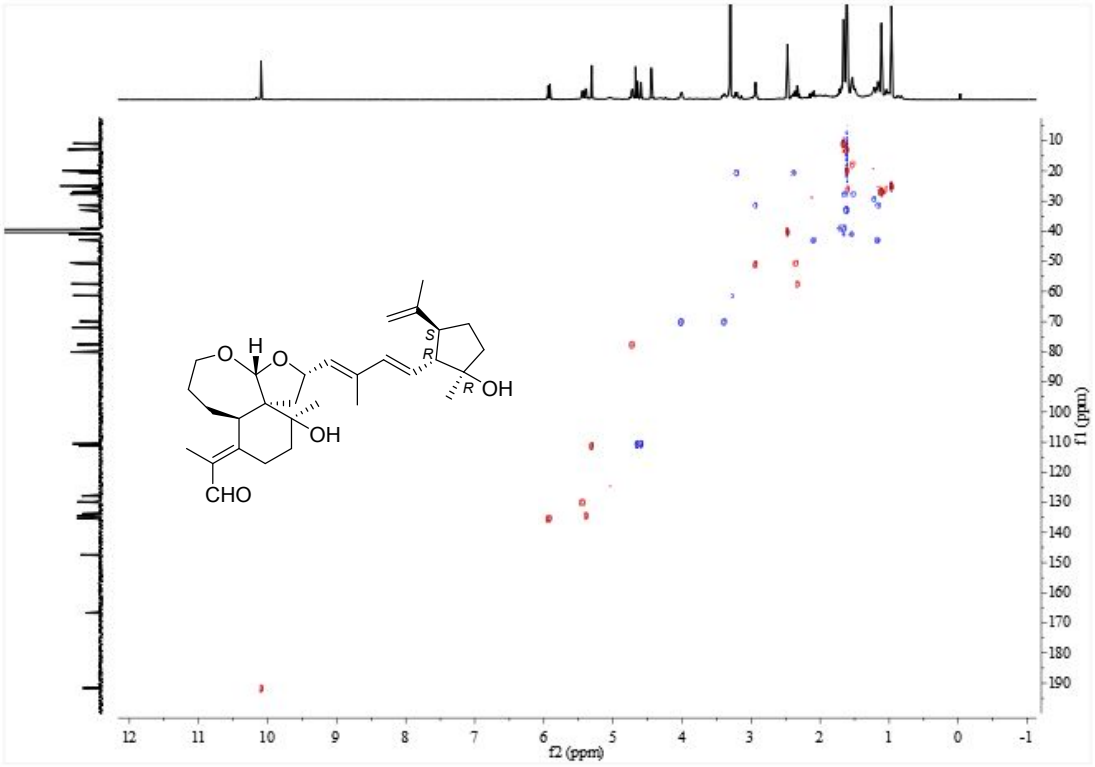


Figure S36. The HMBC spectrum of compound **4** in DMSO-d_6. (600 MHz)

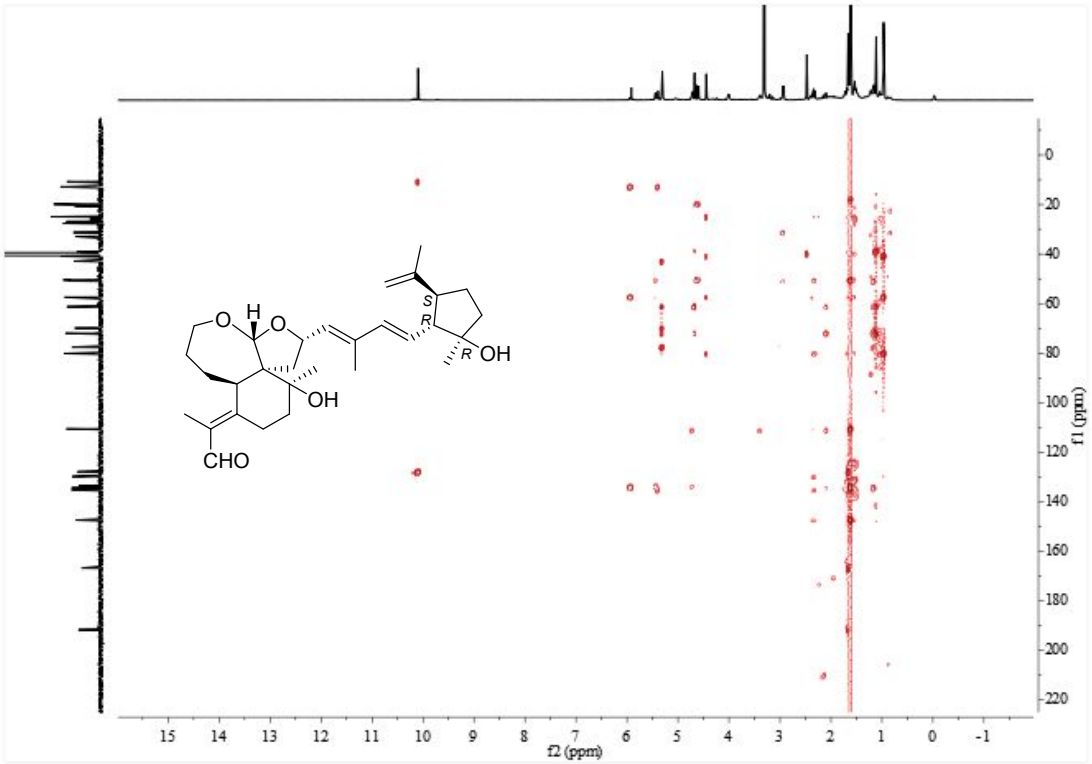


Figure S37. The NOESY spectrum of compound **4** in DMSO-d_6. (600 MHz)

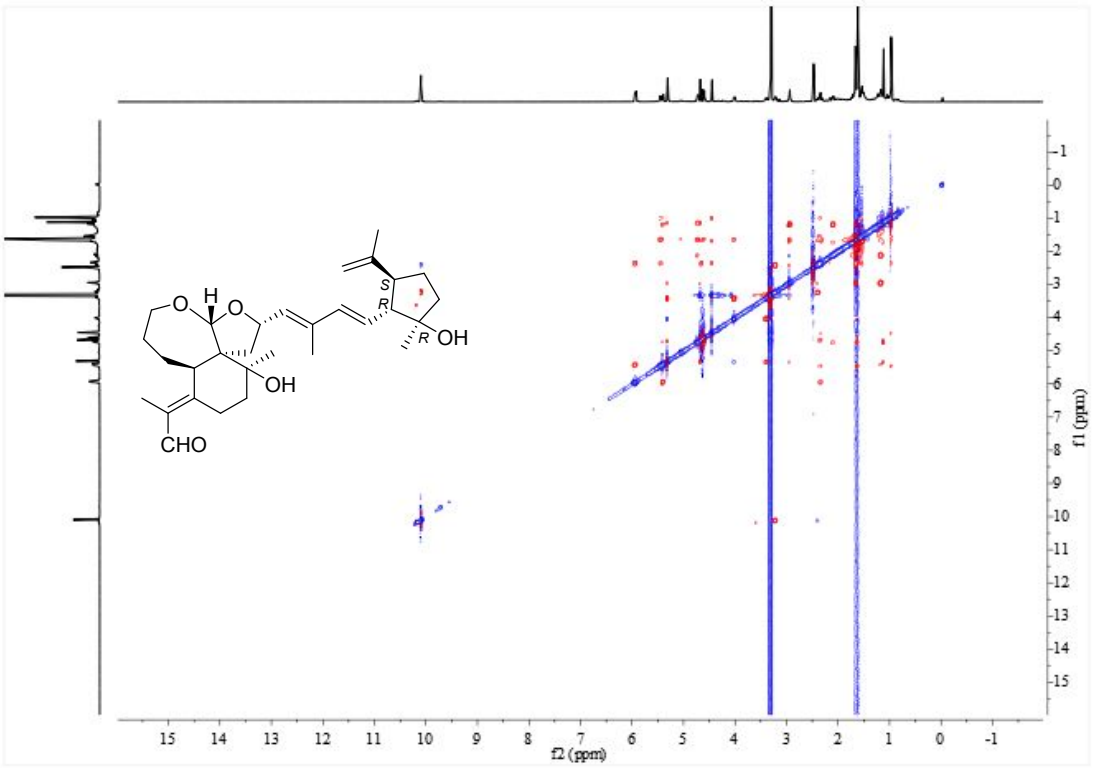


Figure S38. The UV spectrum of compound **5** in CH_3OH.

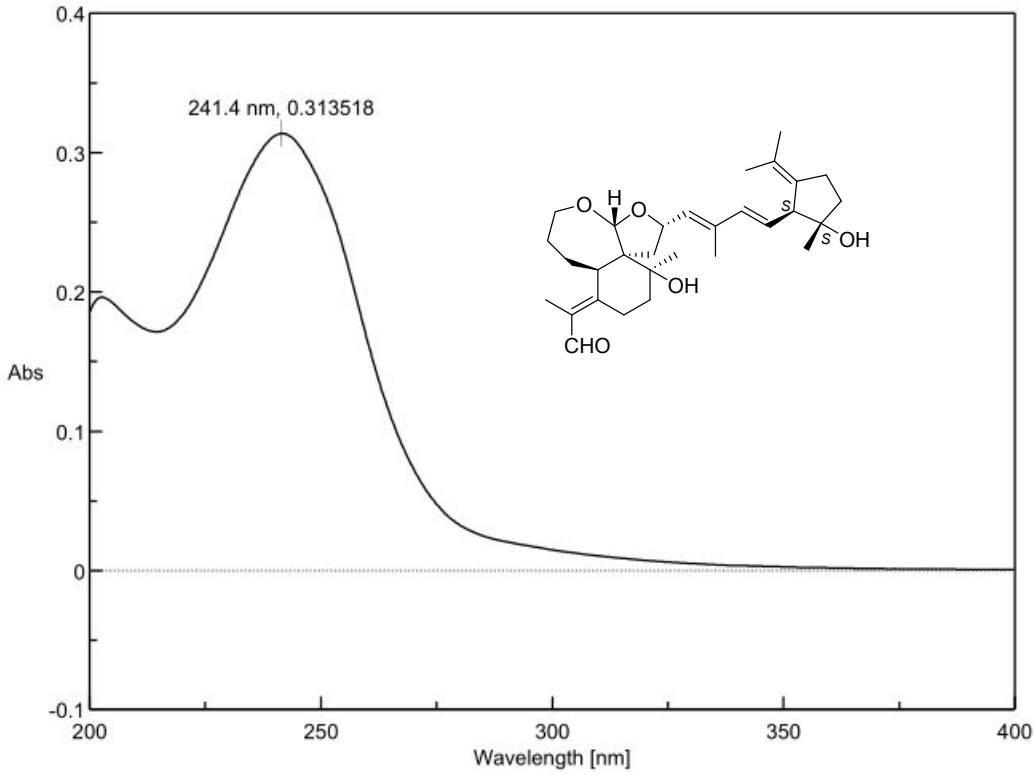


Figure S39. The IR spectrum of compound **5** in CH_3OH.

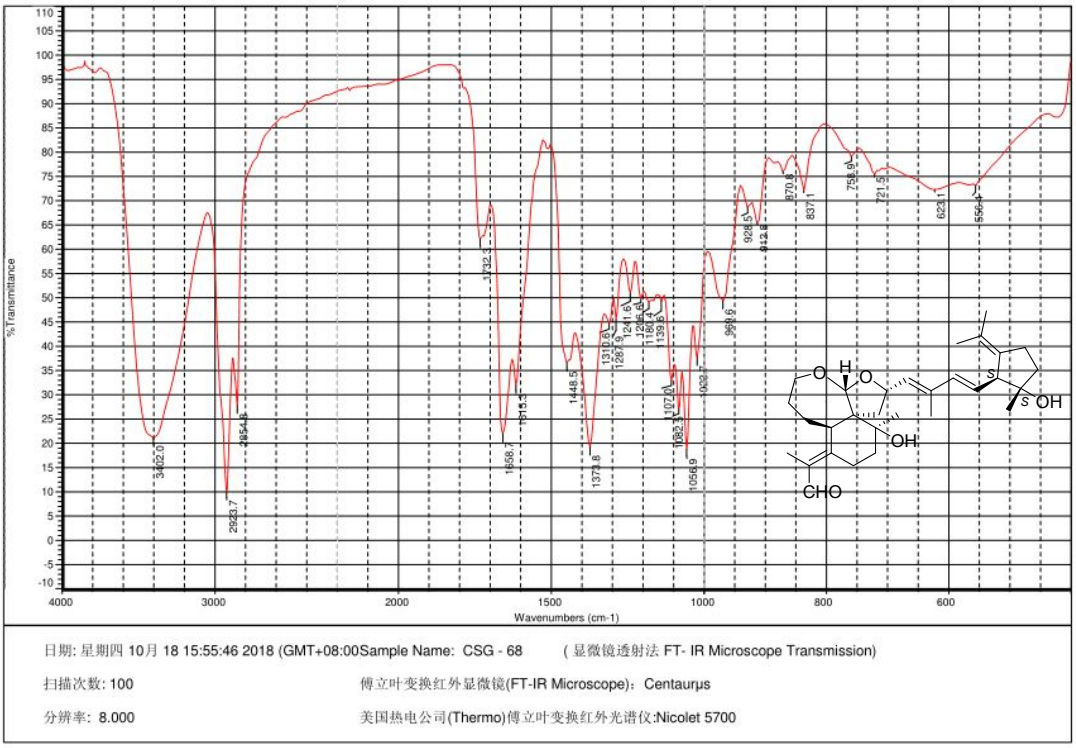
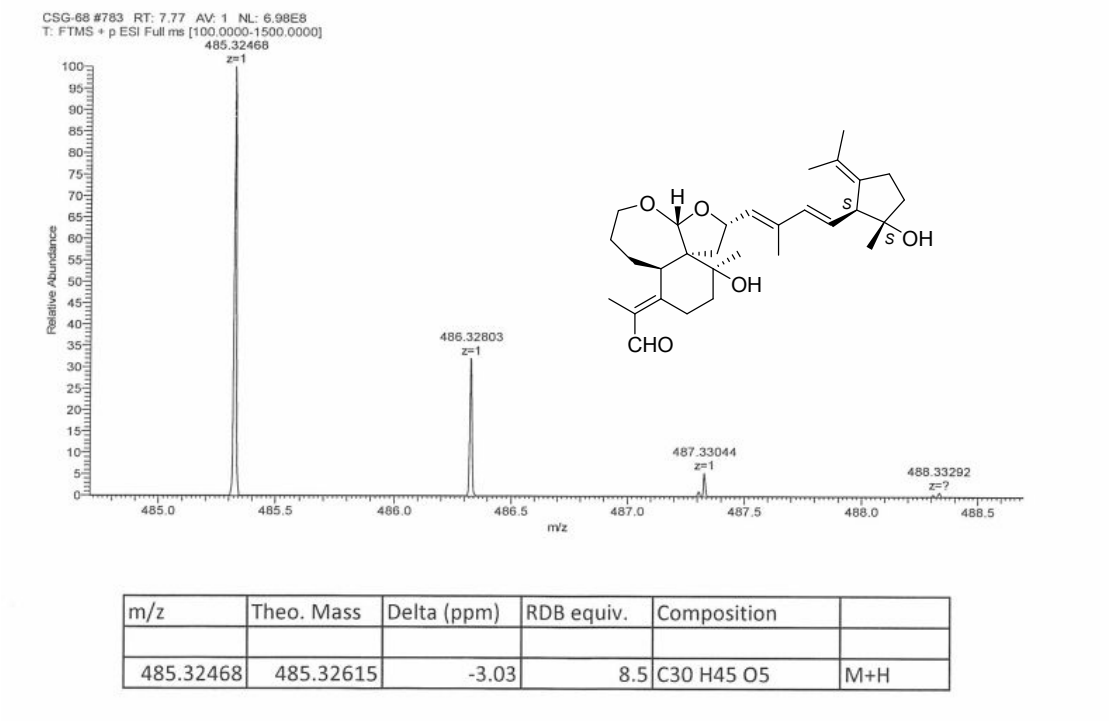


Figure S40. The HRESIMS of compound **5**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
485.32468	485.32615	-3.03	8.5	C30 H45 O5	M+H

Figure S41. The CD spectrum of compound **5** in CH_3OH.

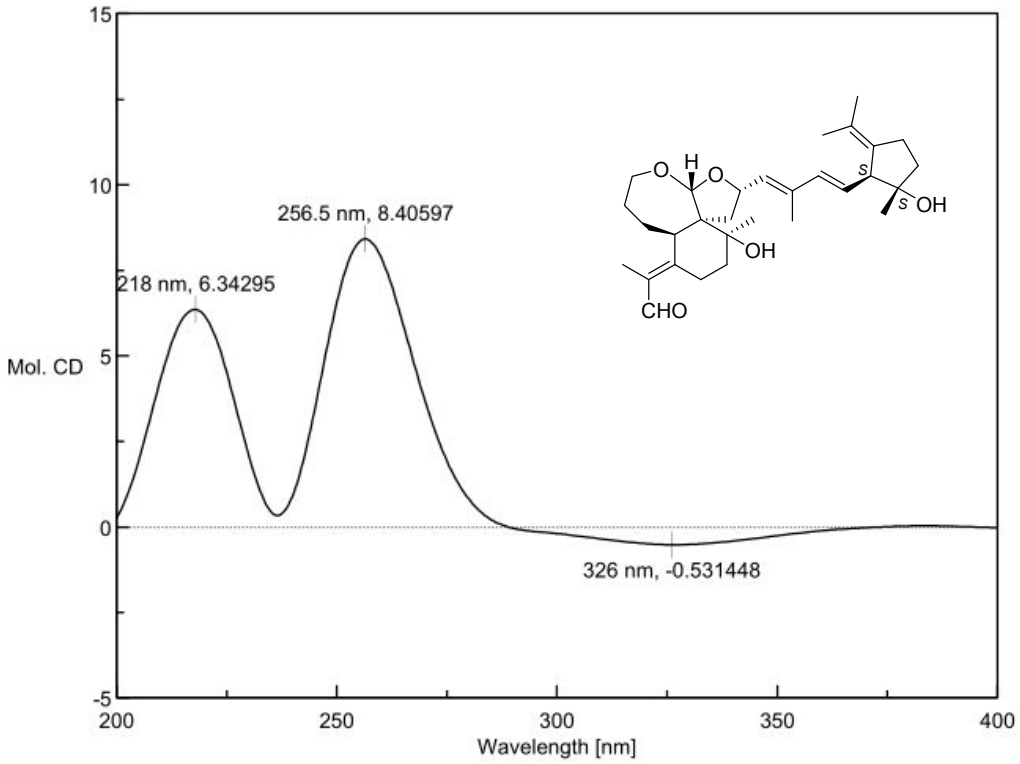


Figure S42. The ^{1}H NMR spectrum of compound **5** in DMSO-d_6.(600 MHz)

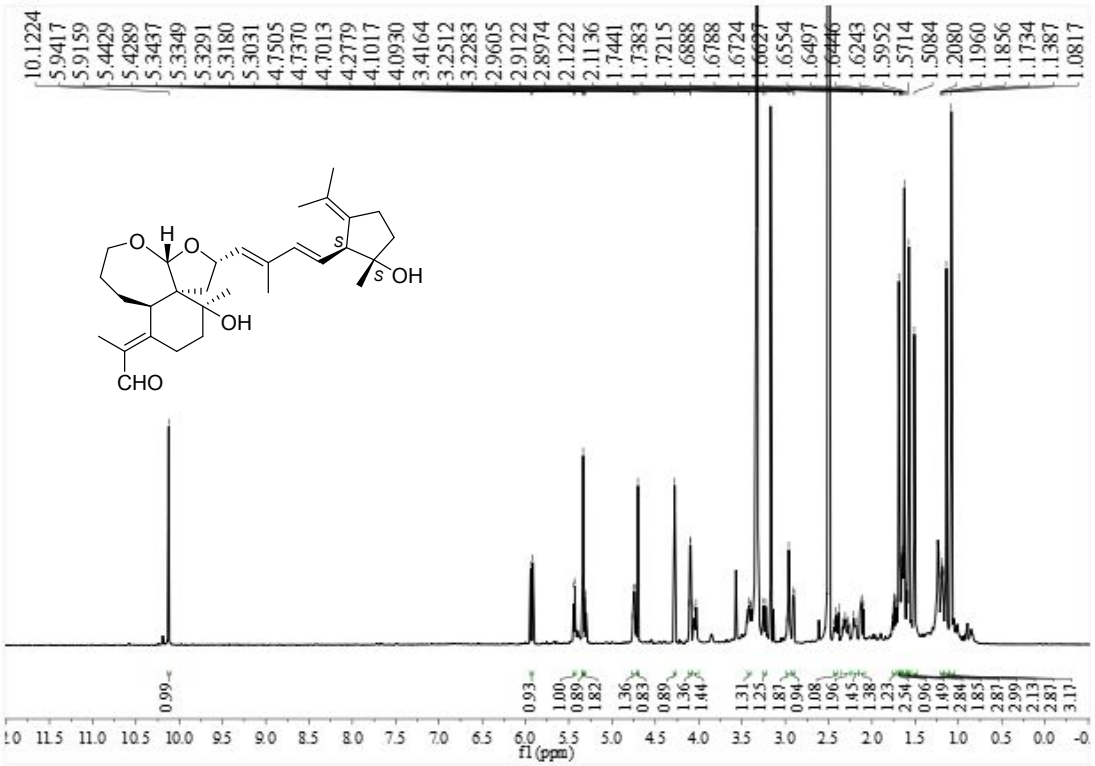


Figure S43. The ^{13}C NMR spectrum of compound **5** in DMSO-d_6. (150 MHz)

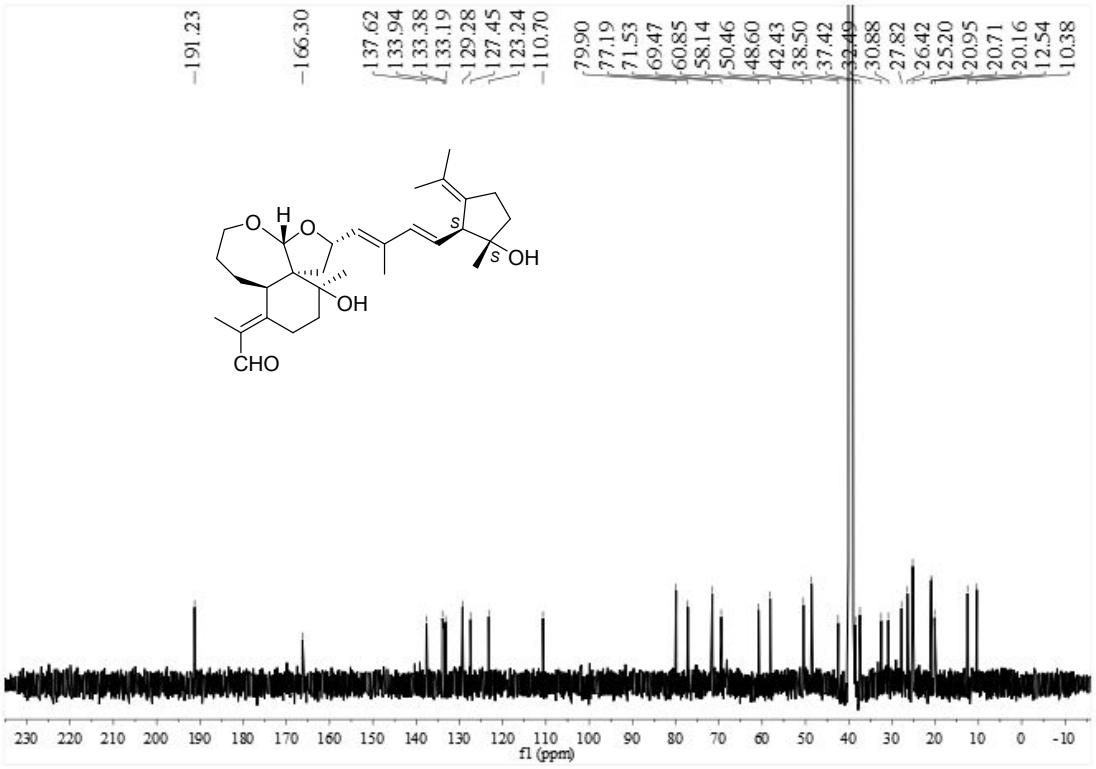


Figure S44. The ^{1}H–^{1}H COSY spectrum of compound **5** in DMSO-d_6.(600 MHz)

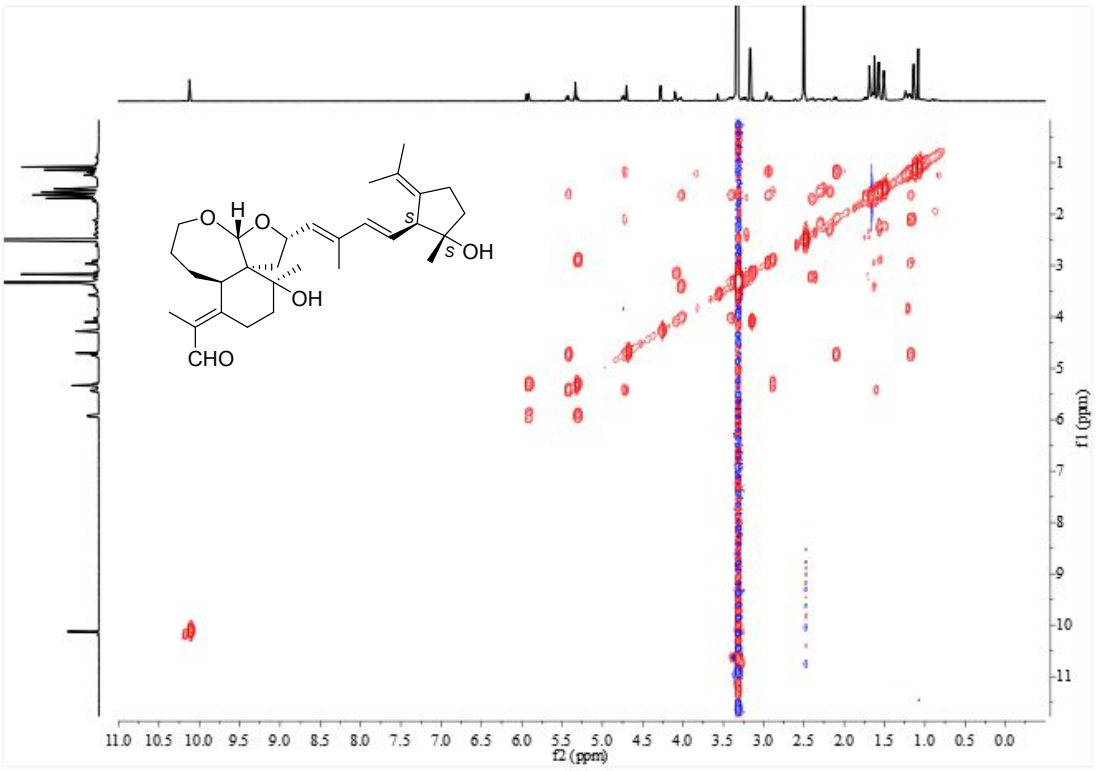


Figure S45. The HSQC spectrum of compound **5** in DMSO-d_6.(600 MHz)

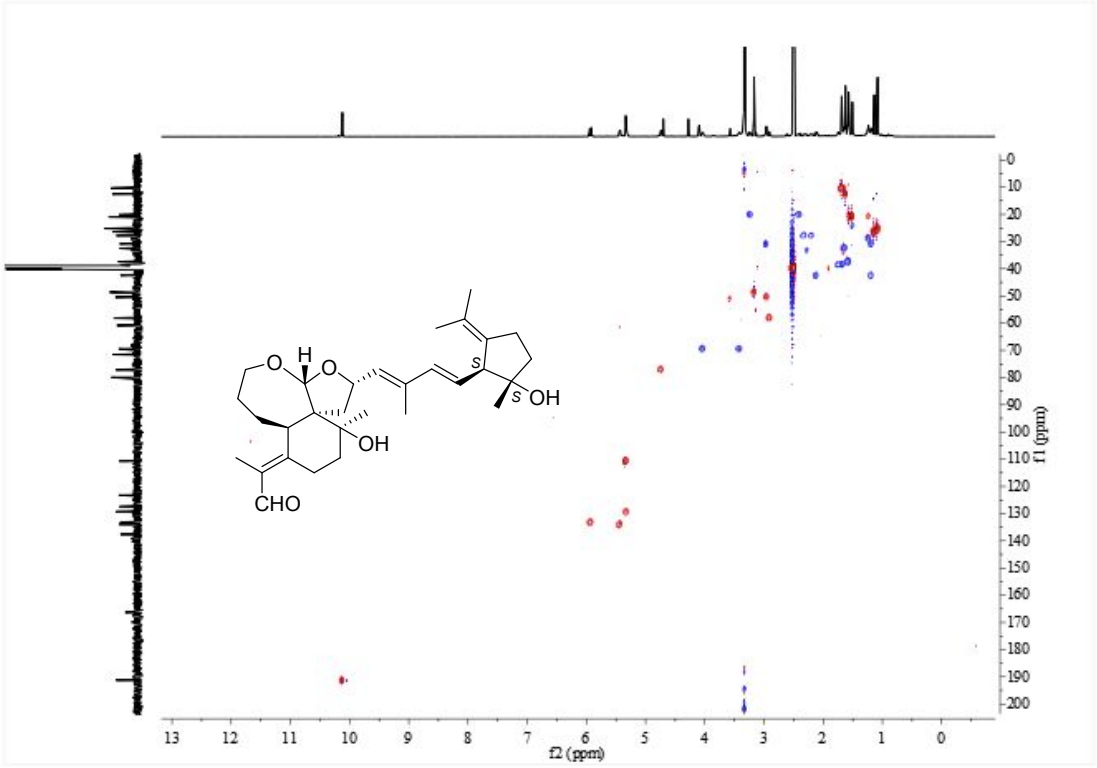


Figure S46. The HMBC spectrum of compound **5** in DMSO-d_6.(600 MHz)

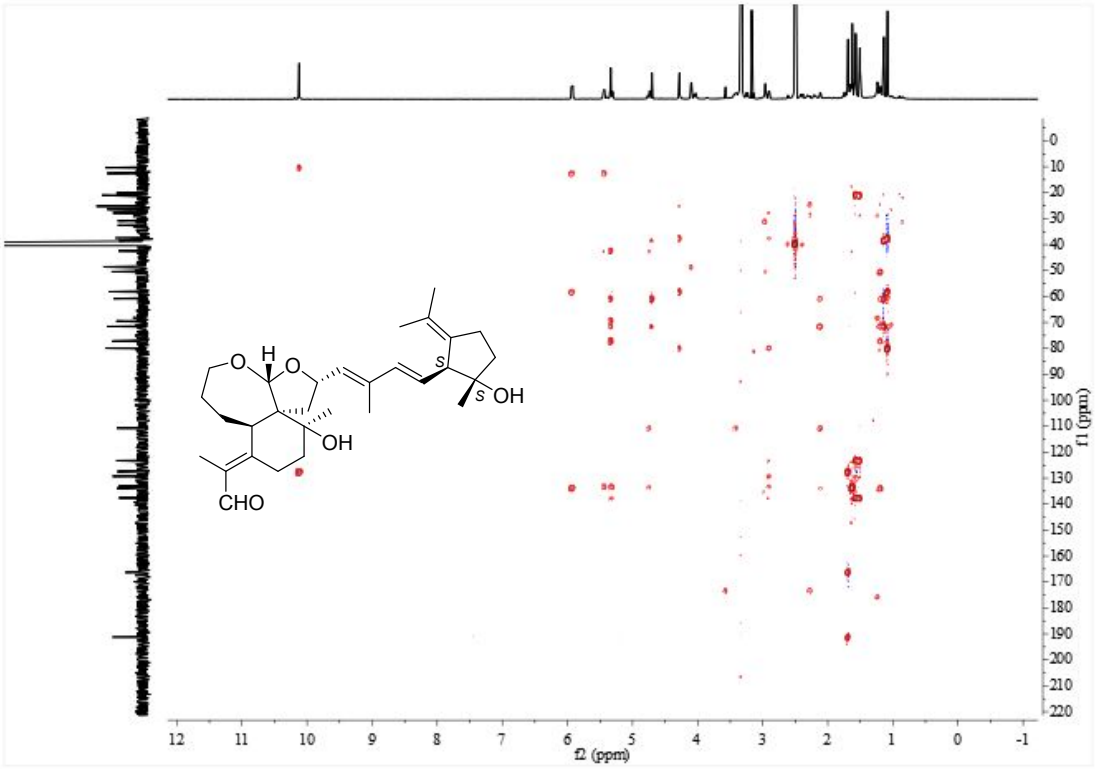


Figure S47. The NOESY spectrum of compound **5** in DMSO-d_6.(600 MHz)

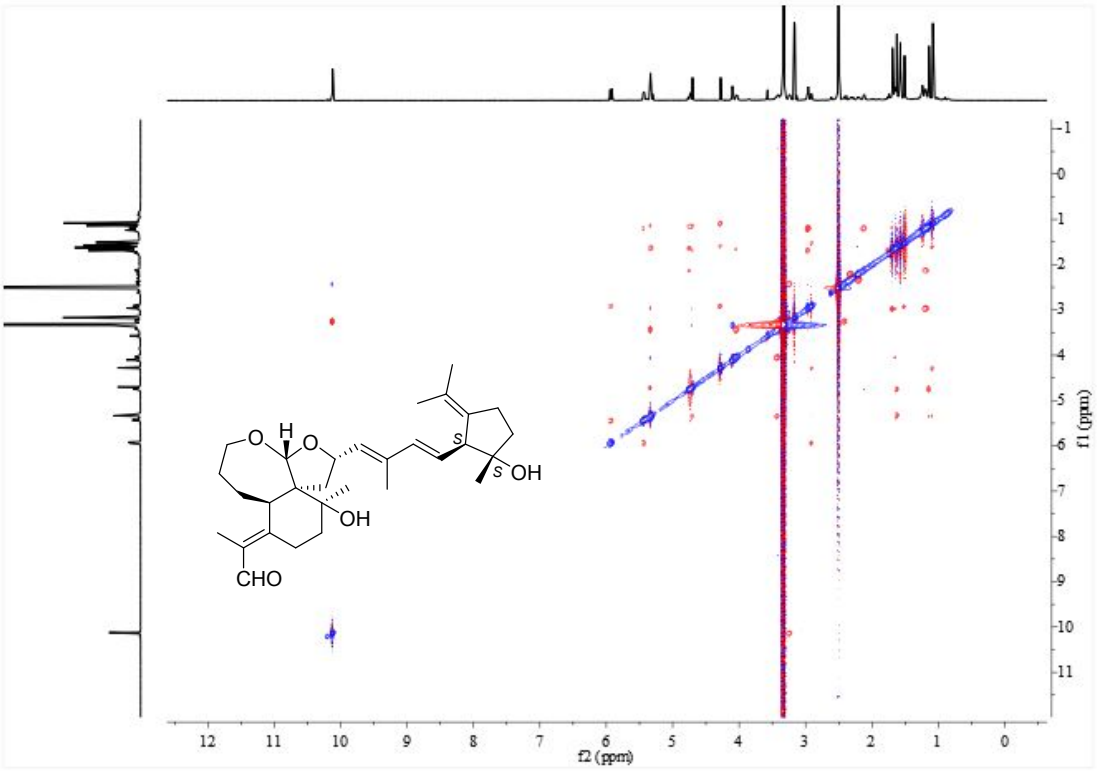
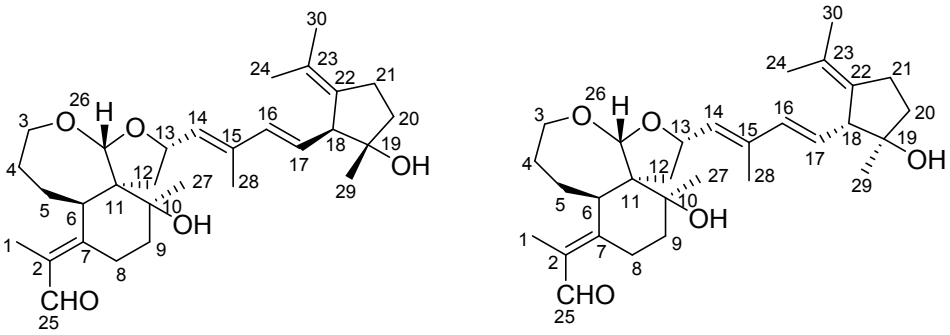
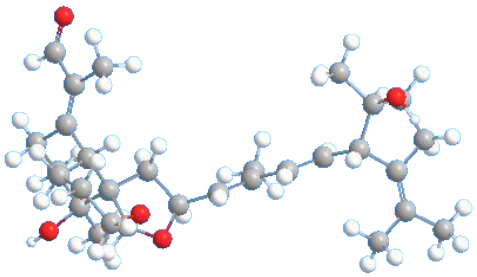
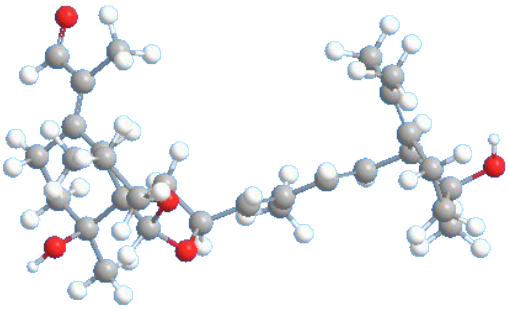
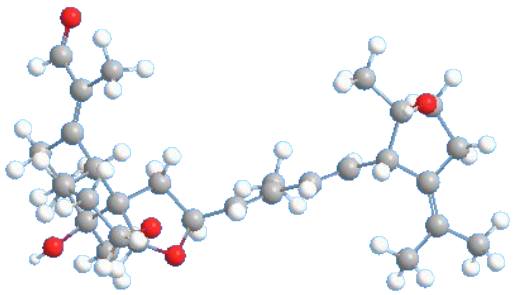
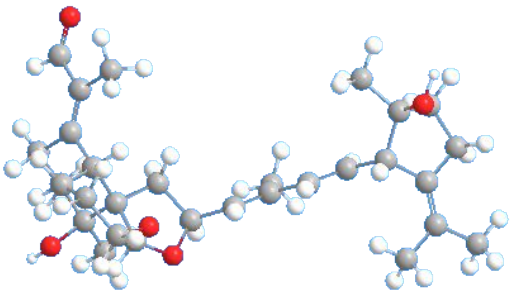
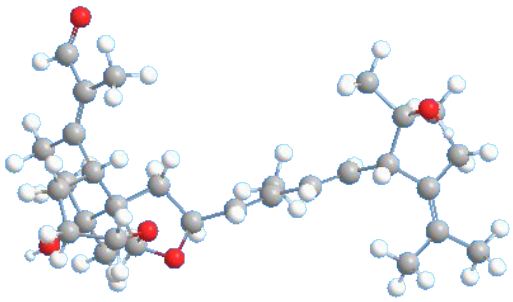
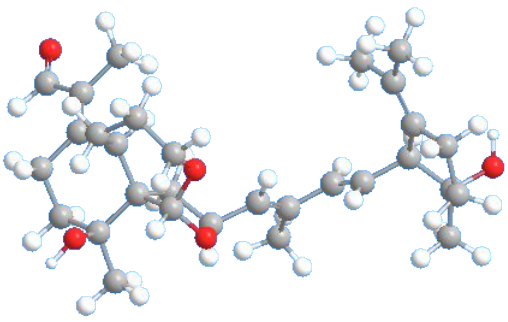


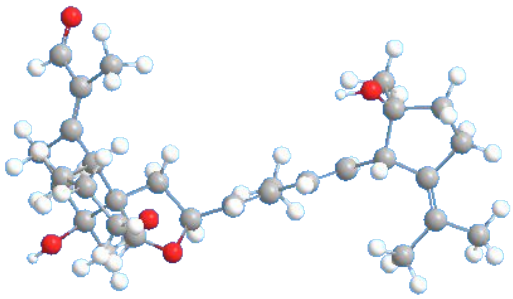
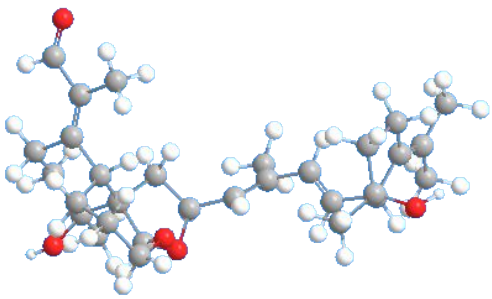
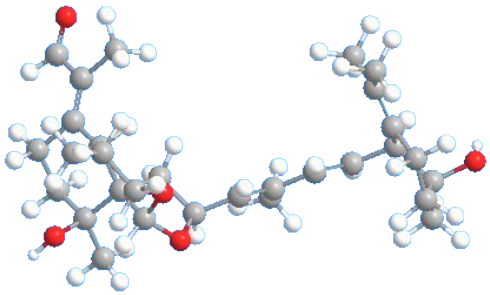
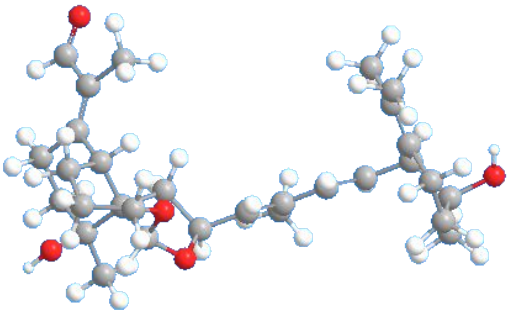
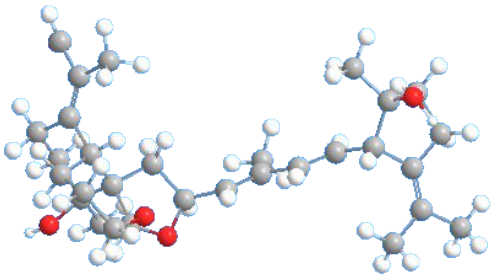
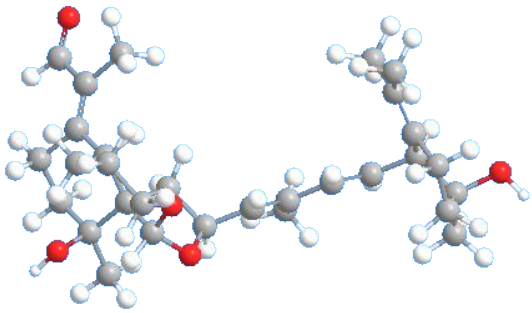
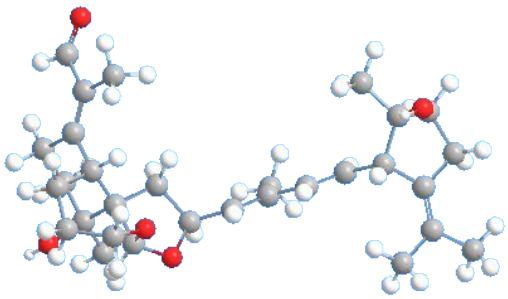
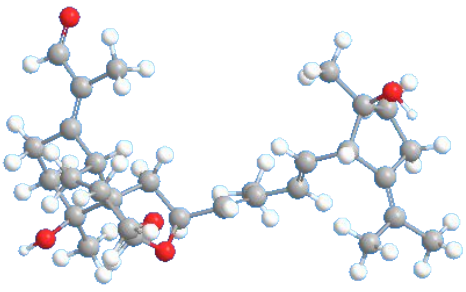
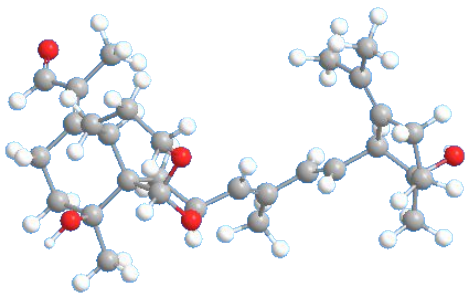
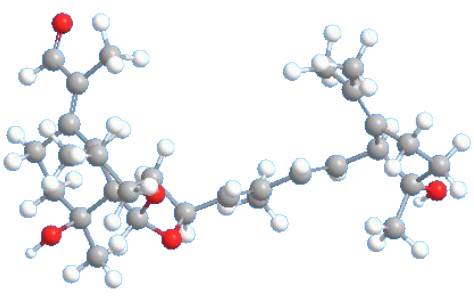
Figure S48. Two possible stereoisomers of compound **5**.



5a **5b**

Figure S49. The 3D conformers of compound **5a** obtained by optimization at B3LYP/6-31G(d) level in MeOH.

	
C1 (36.81%)	C2 (13.92%)
	
C3 (10.31%)	C4 (9.85%)
	
C5 (4.06%)	C6 (4.02%)

	
C7 (2.93%)	C8 (2.77%)
	
C9 (2.54%)	C10 (2.31%)
	
C11 (1.86%)	C12 (1.46%)
	
C13 (1.12%)	C14 (1.06%)
	

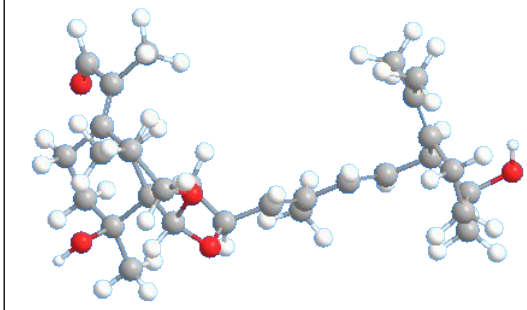
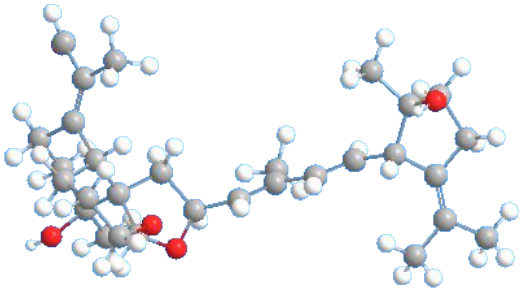
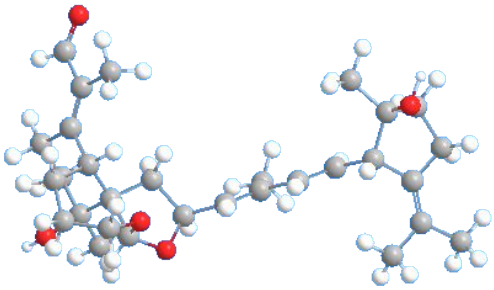
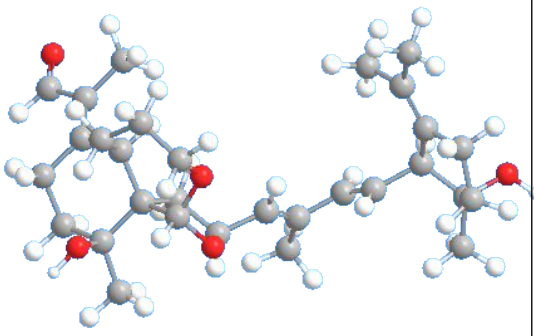
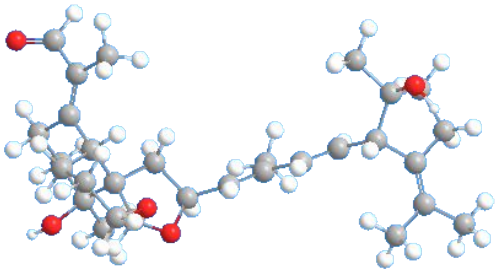
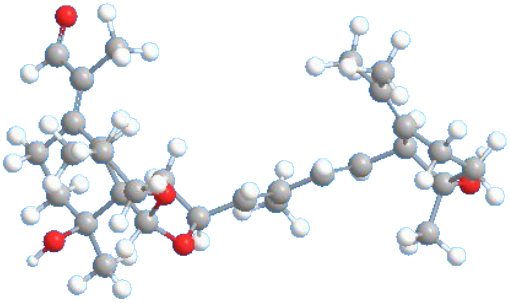
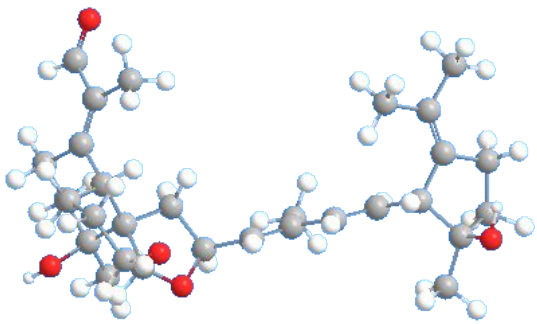
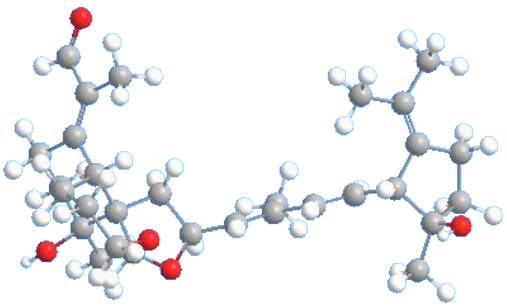
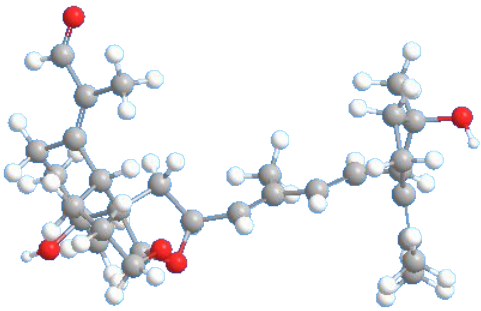
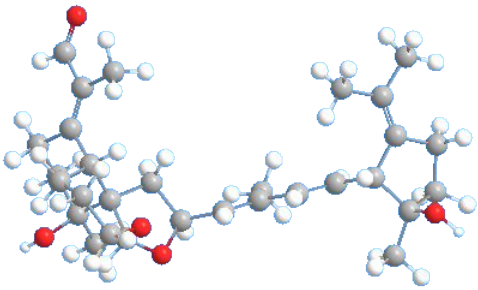
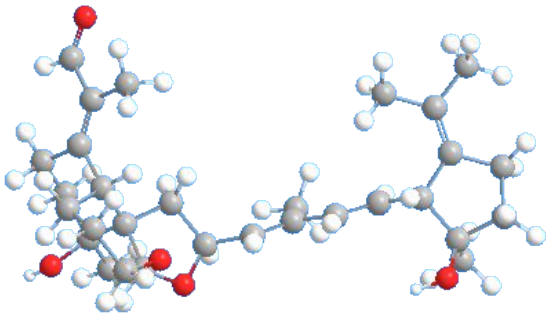
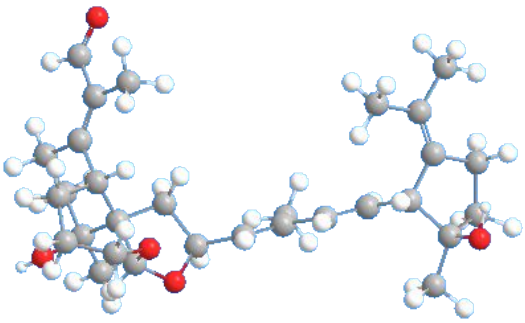
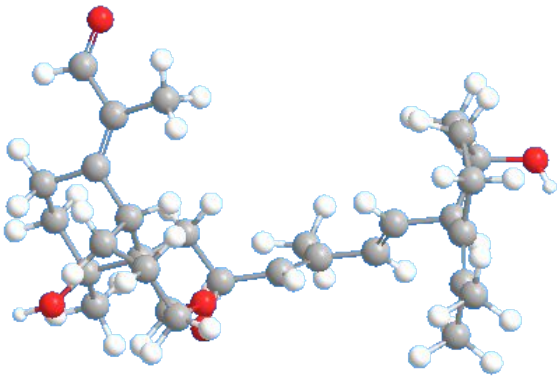
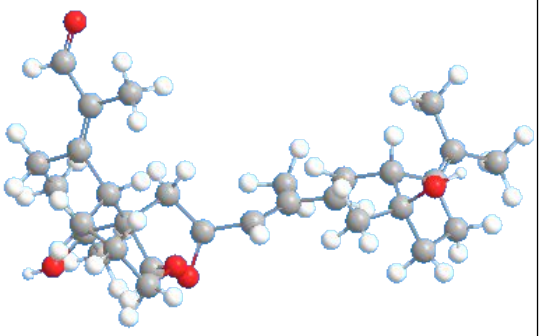
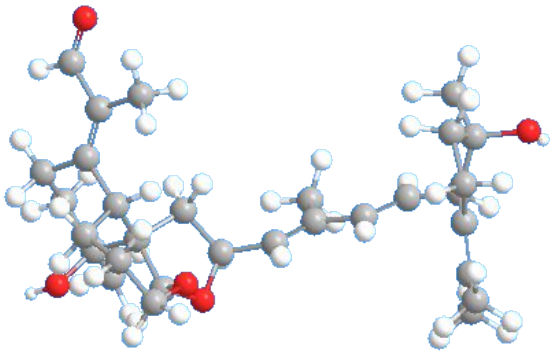
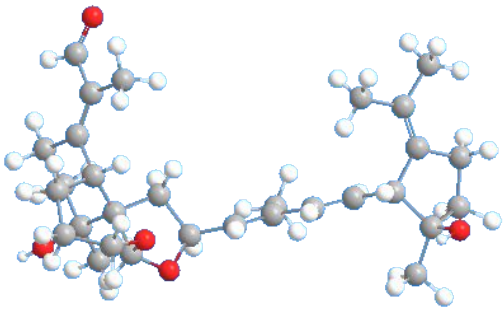
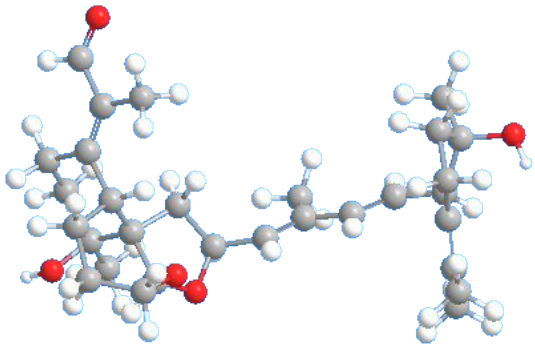
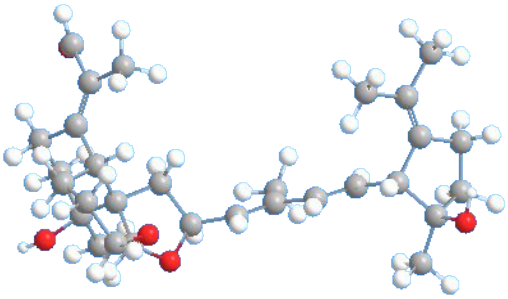
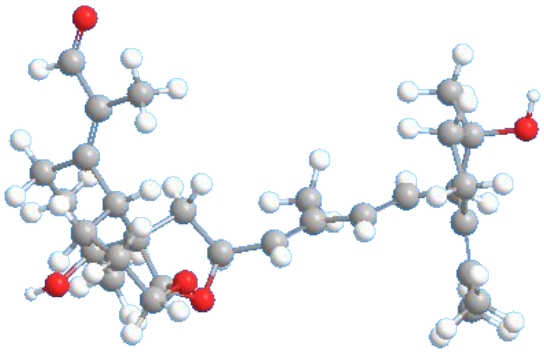
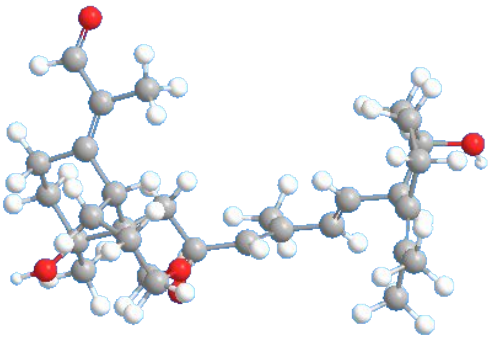
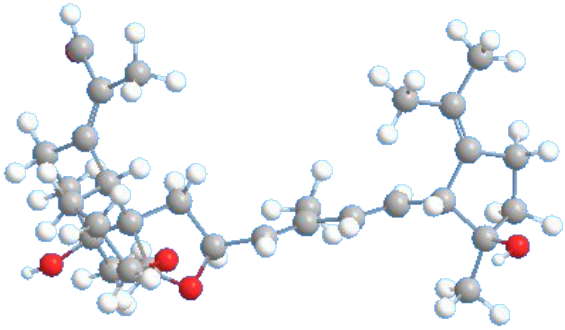
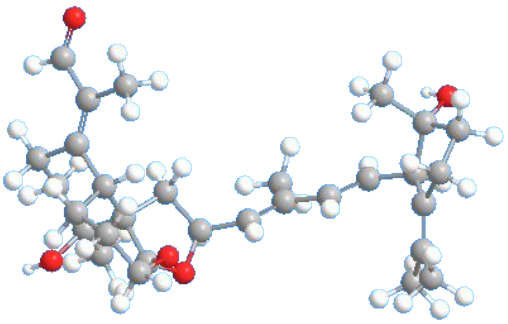
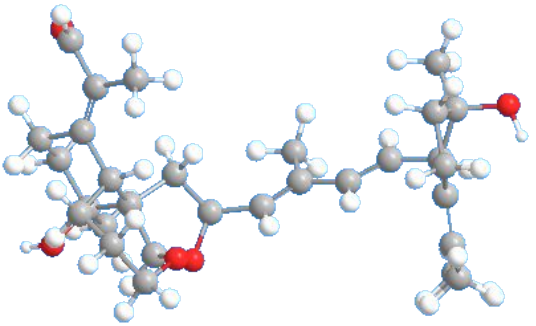
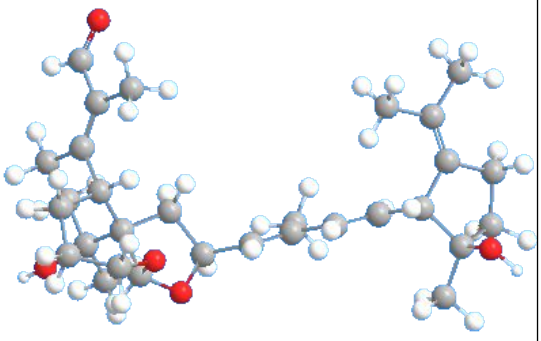
C15 (1.00%)	C16 (0.84%)
	
C17 (0.49%)	C18 (0.46%)
	
C19 (0.35%)	C20 (0.33%)
	
C21 (0.32%)	C22 (0.25%)

Figure S50. The 3D conformers of compound **5b** obtained by optimization at B3LYP/6-31G(d) level in MeOH.

	
C1 (37.79%)	C2 (15.66%)

	
C3 (10.63%)	C4 (8.98%)
	
C5 (4.31%)	C6 (4.31%)
	
C7 (3.07%)	C8 (2.88%)
	
C9 (2.79%)	C10 (1.62%)

	
C11 (1.27%)	C12 (1.26%)
	
C13 (1.05%)	C14 (0.88%)
	
C15 (0.73%)	C16 (0.57%)
	
C17 (0.35%)	C18 (0.32%)

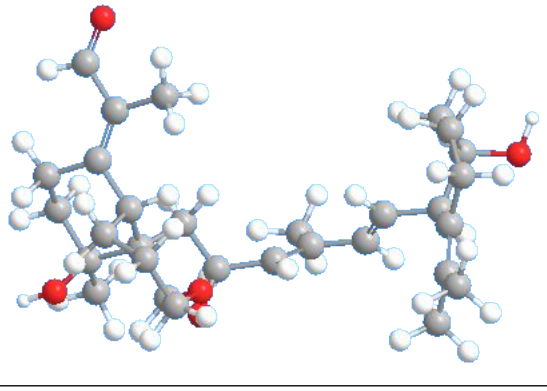
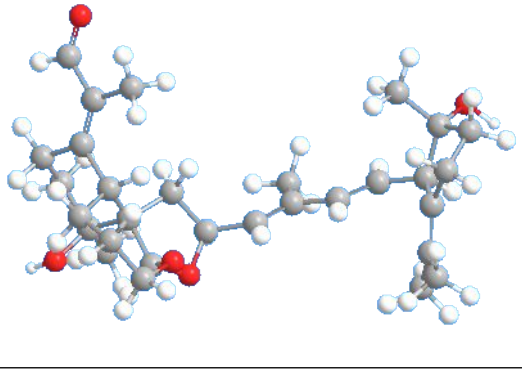
	
C19 (0.29%)	C20 (0.21%)

Figure S51. The UV spectrum of compound **6** in CH_3OH.

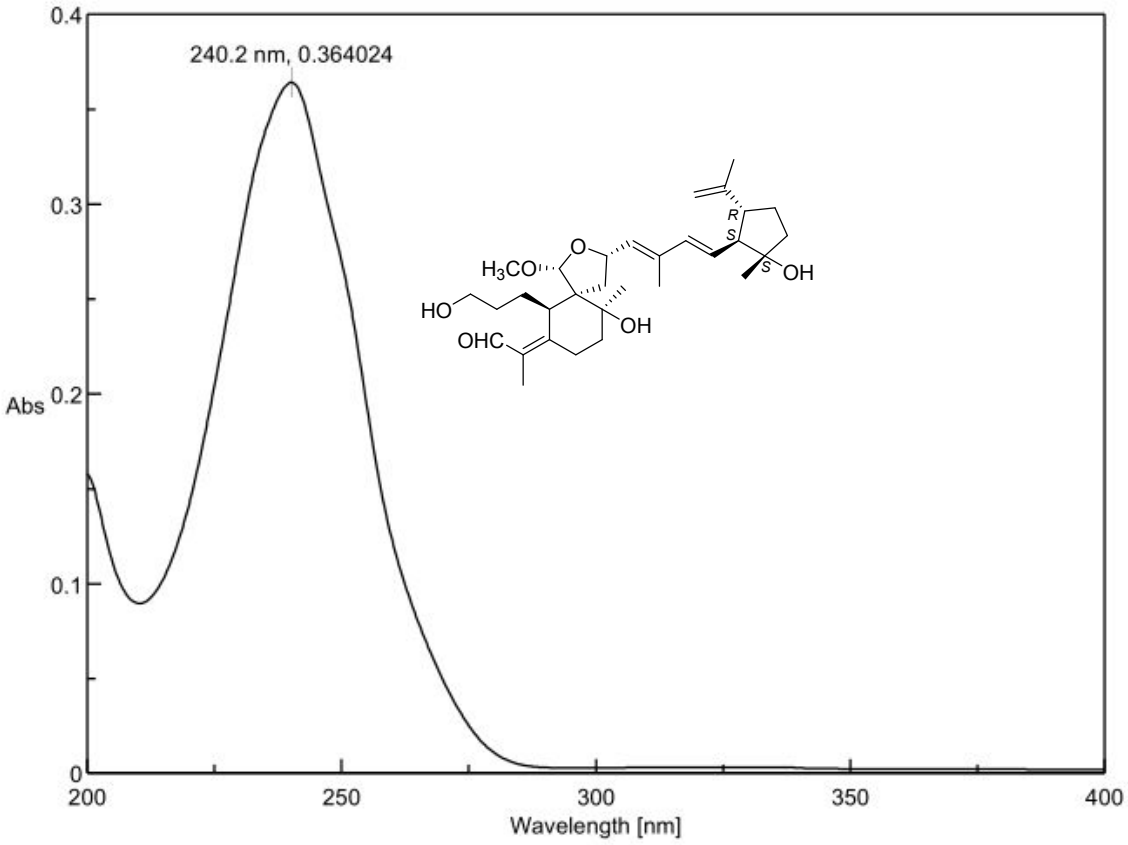


Figure S52. The IR spectrum of compound **6** in CH_3OH.

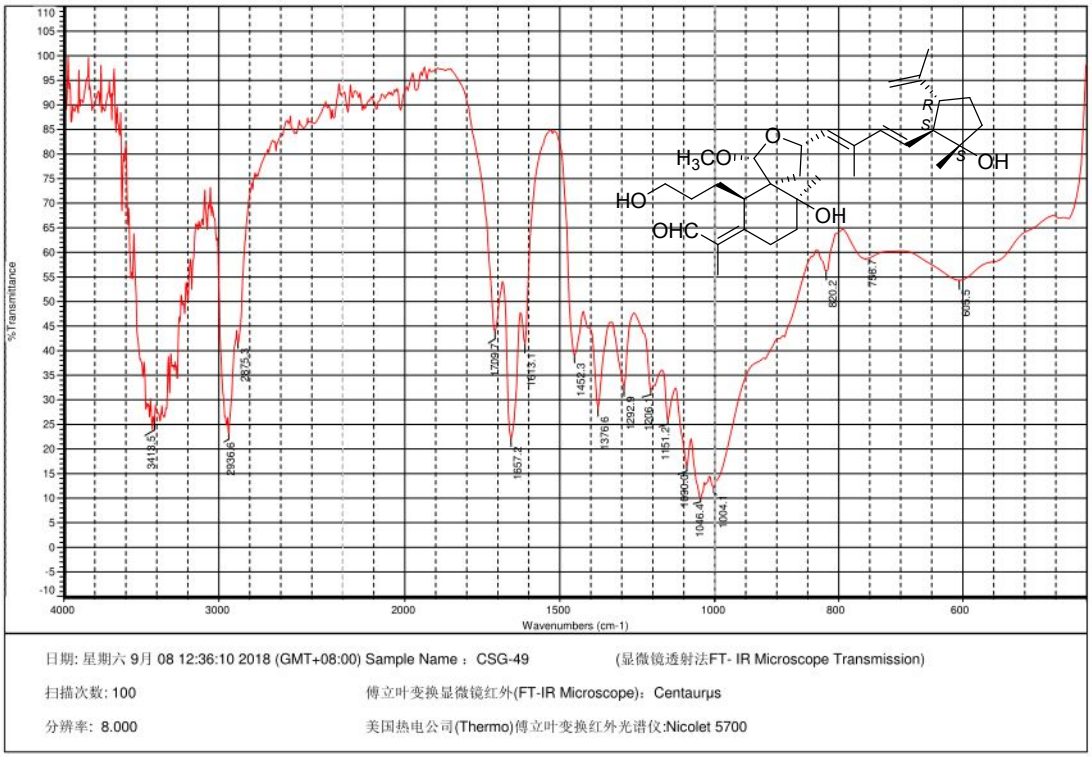
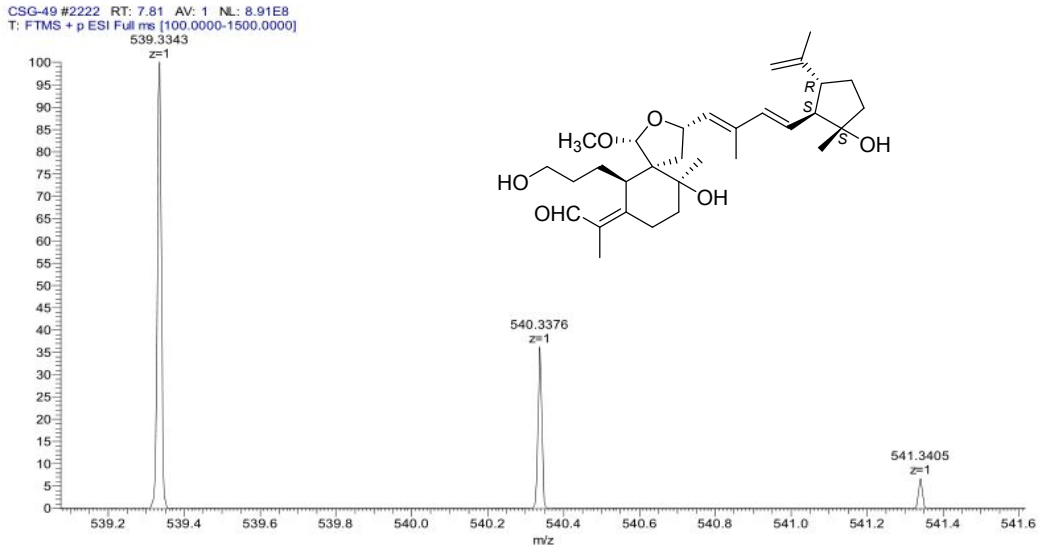


Figure S53. The HRESIMS of compound **6**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
539.3343	539.3343	-0.04	7.5	C31 H48 O6 Na	M+Na

Figure S54. The CD spectrum of compound **6** in CH_3OH.

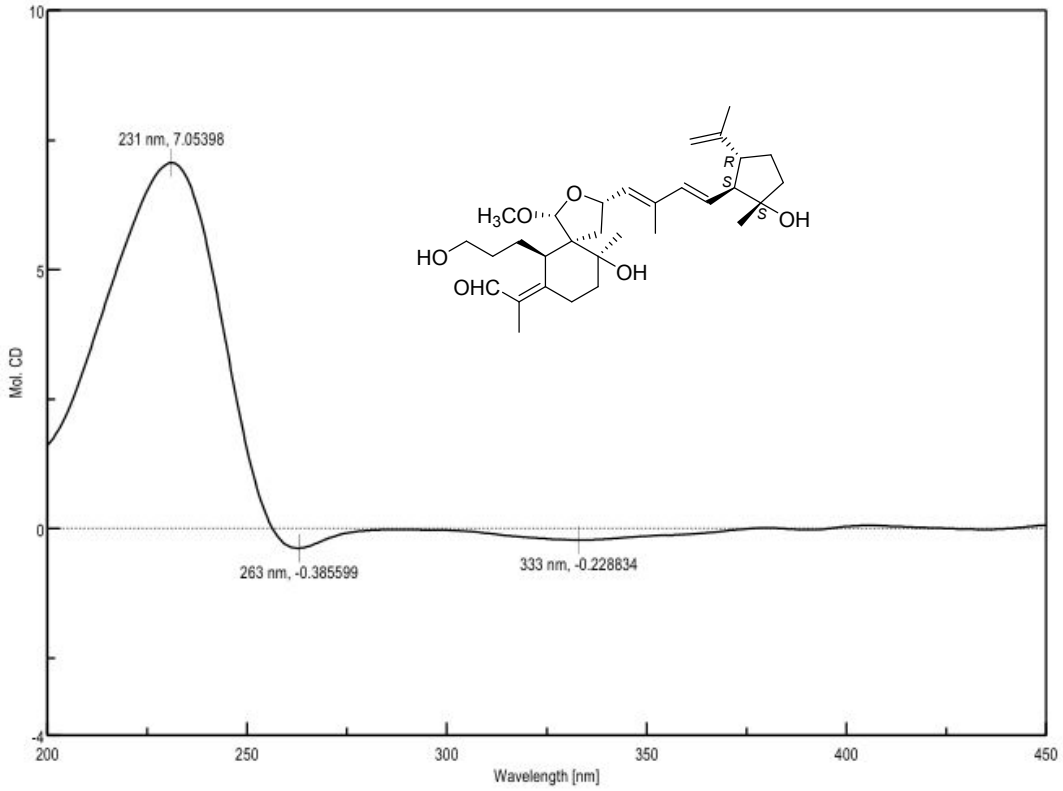


Figure S55. The ^{1}H NMR spectrum of compound **6** in DMSO-d_6.(600 MHz)

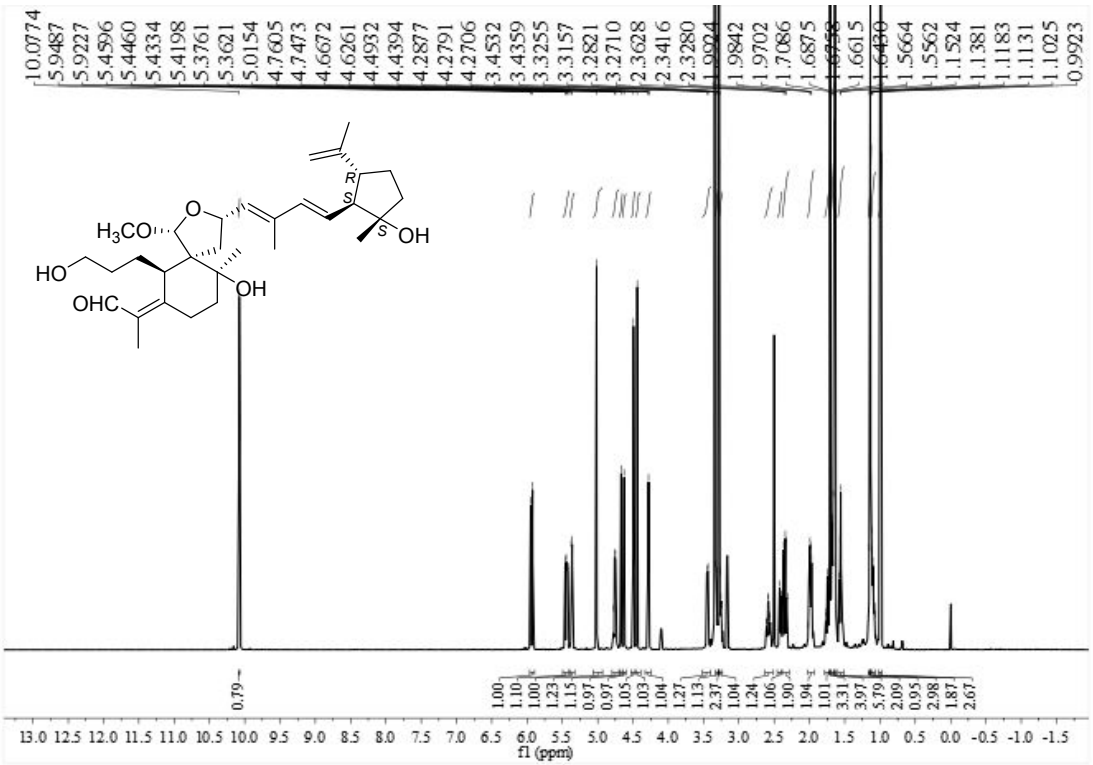


Figure S56. The ^{13}C NMR spectrum of compound **6** in DMSO-d_6.(150 MHz)

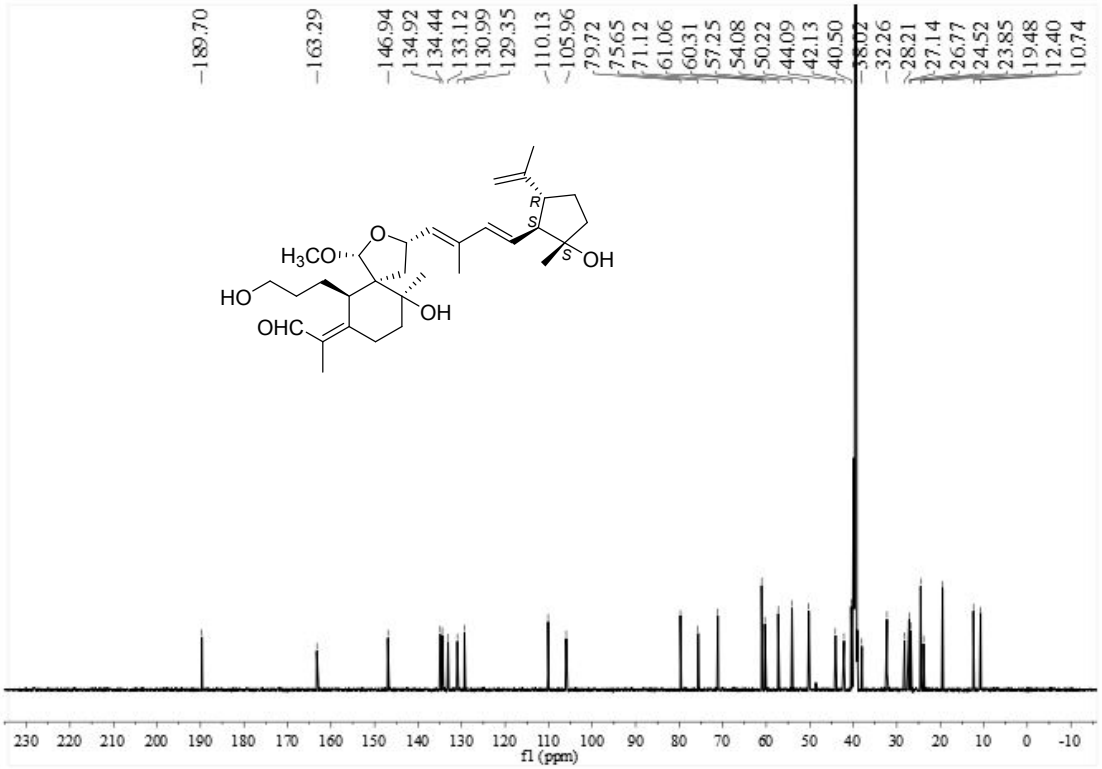


Figure S57. The HSQC spectrum of compound **6** in DMSO-d_6.(600 MHz)

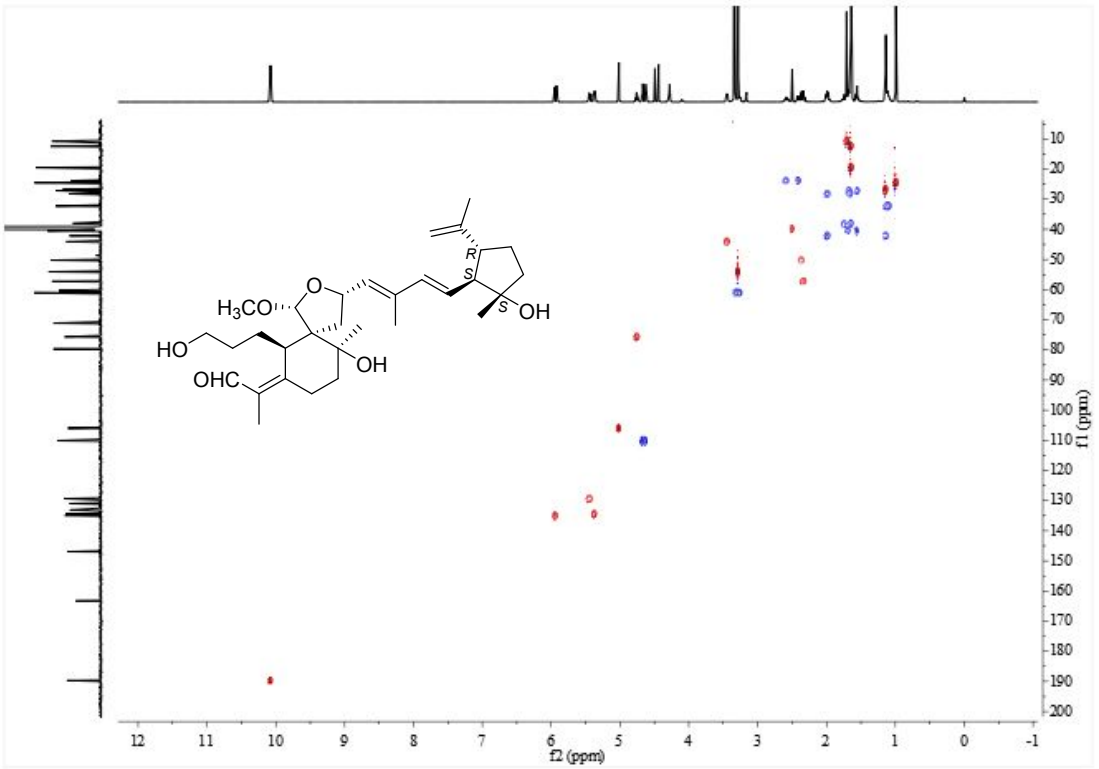


Figure S58. The HMBC spectrum of compound **6** in DMSO-d_6.(600 MHz)

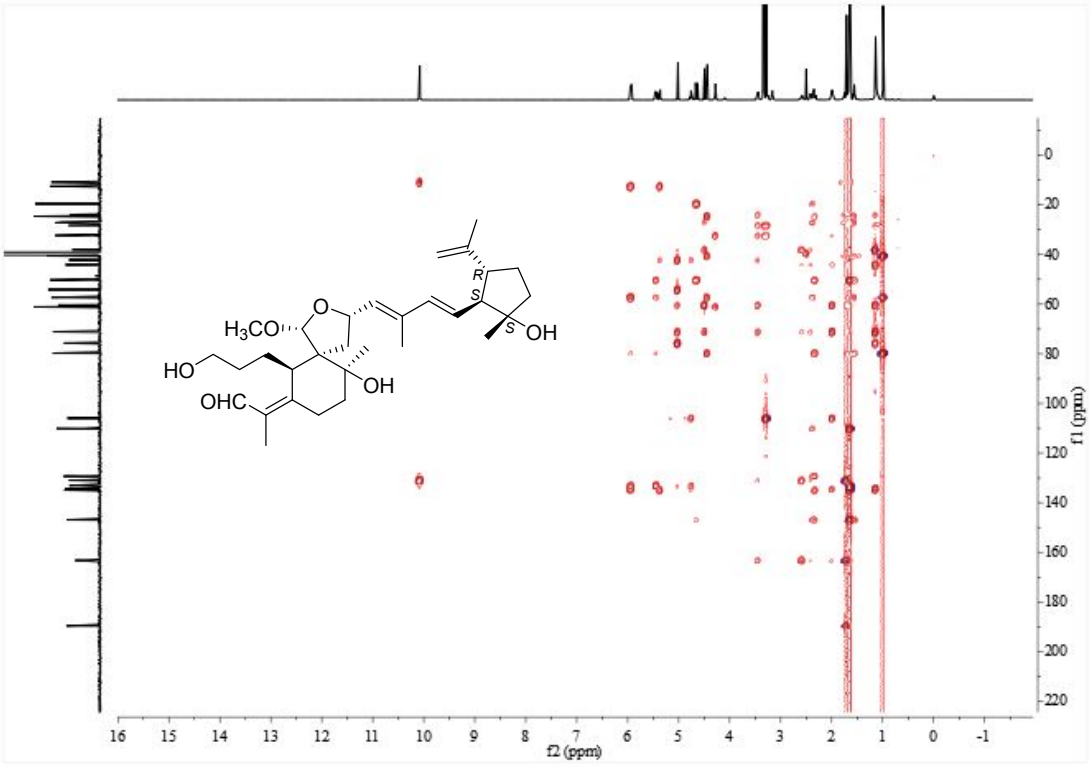


Figure S59. The NOESY spectrum of compound **6** in DMSO-d_6.(600 MHz)

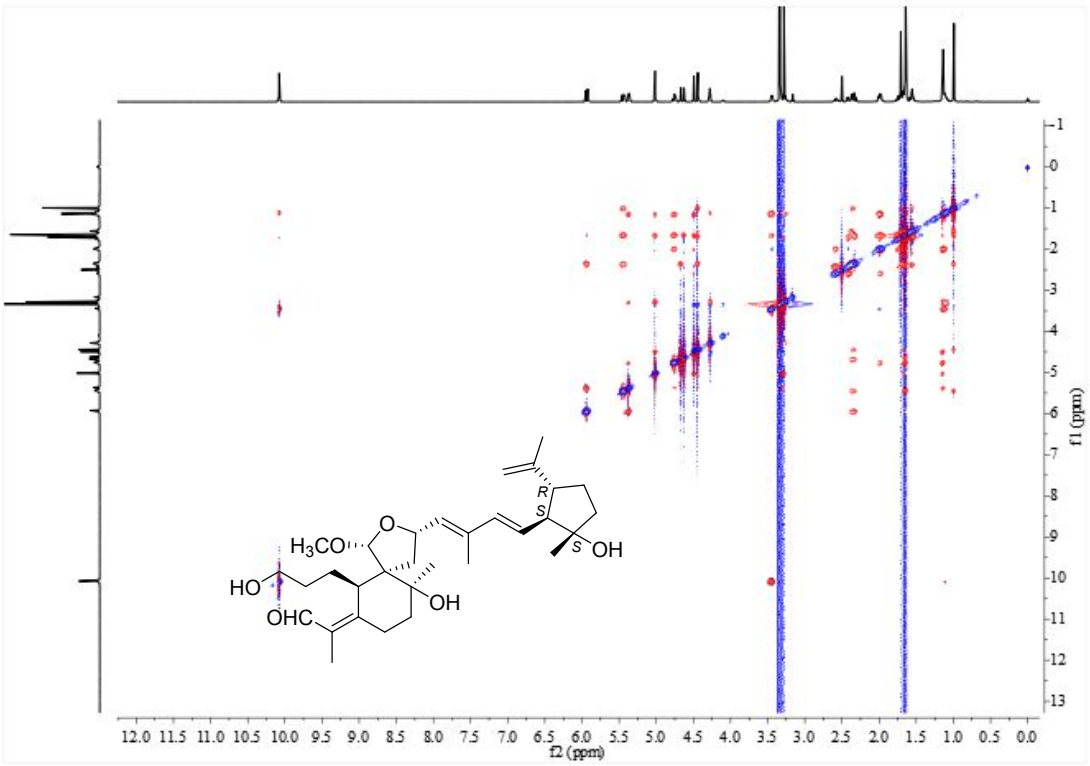


Figure S60. The UV spectrum of compound **7** in CH_3OH.

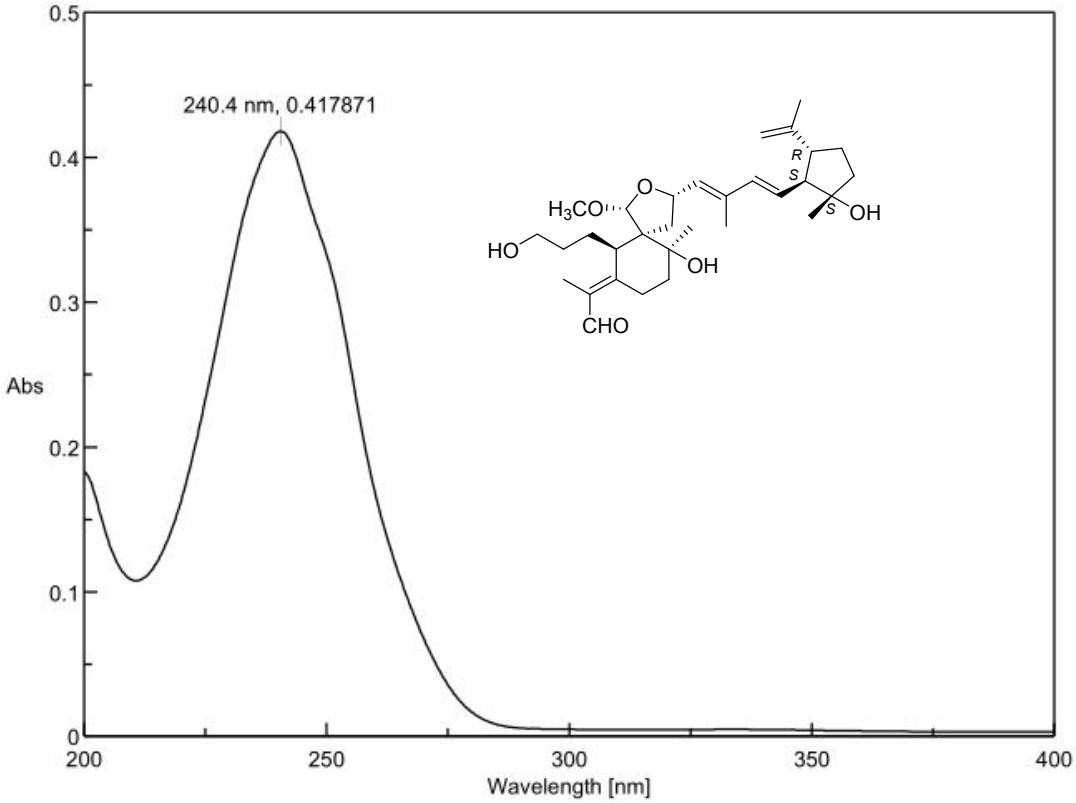


Figure S61. The IR spectrum of compound **7** in CH_3OH.

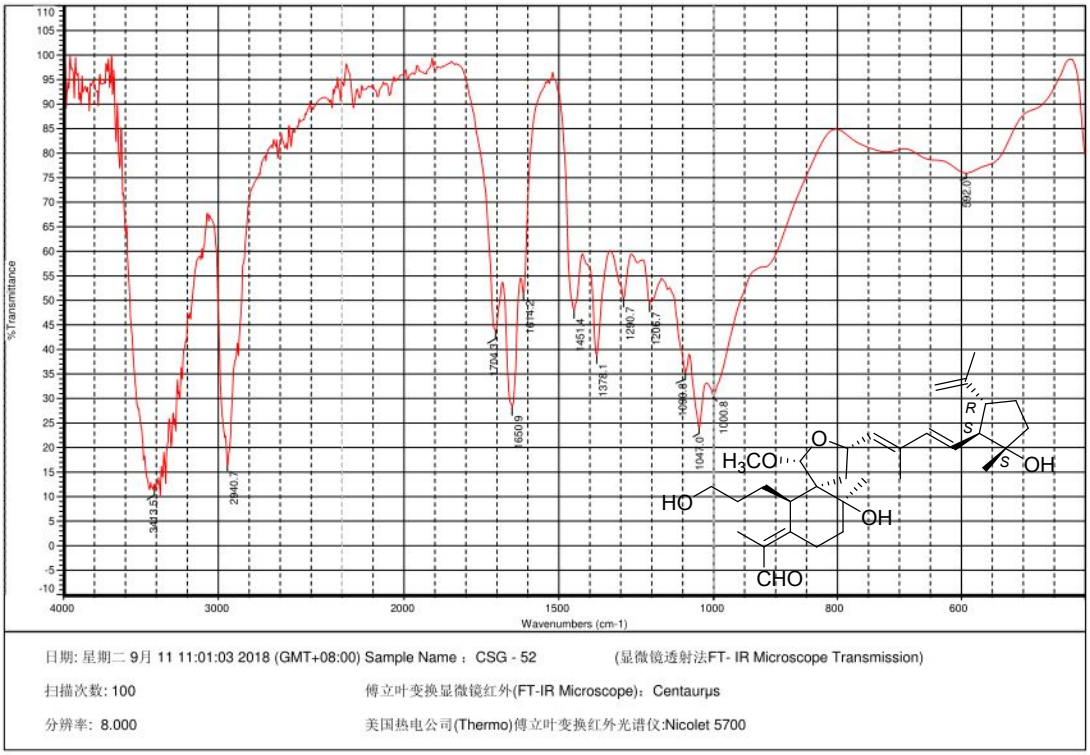
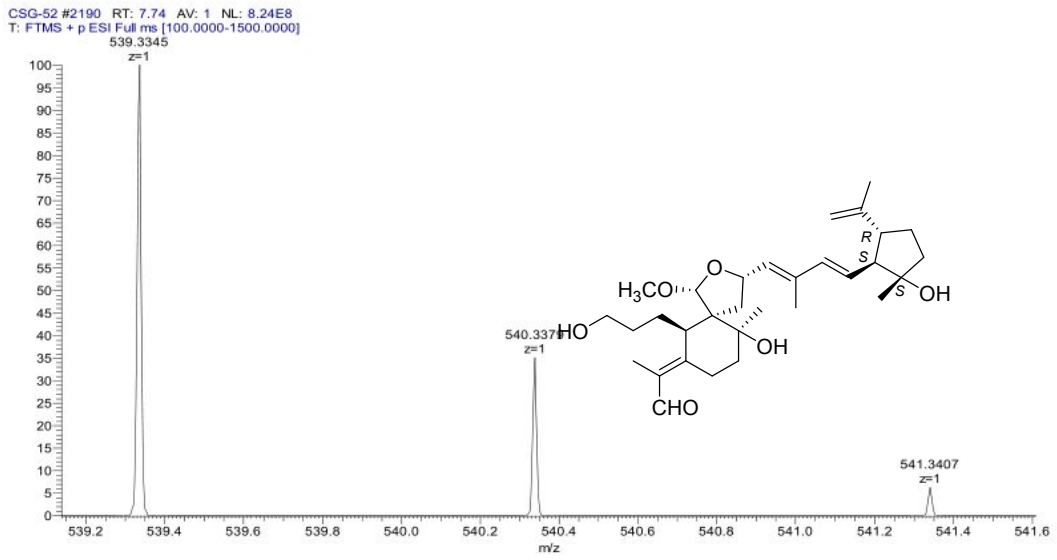


Figure S62. The HRESIMS of compound **7**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
539.3345	539.3343	0.3	7.5	C31 H48 O6 Na	M+Na

Figure S63. The CD spectrum of compound **7** in CH_3OH.

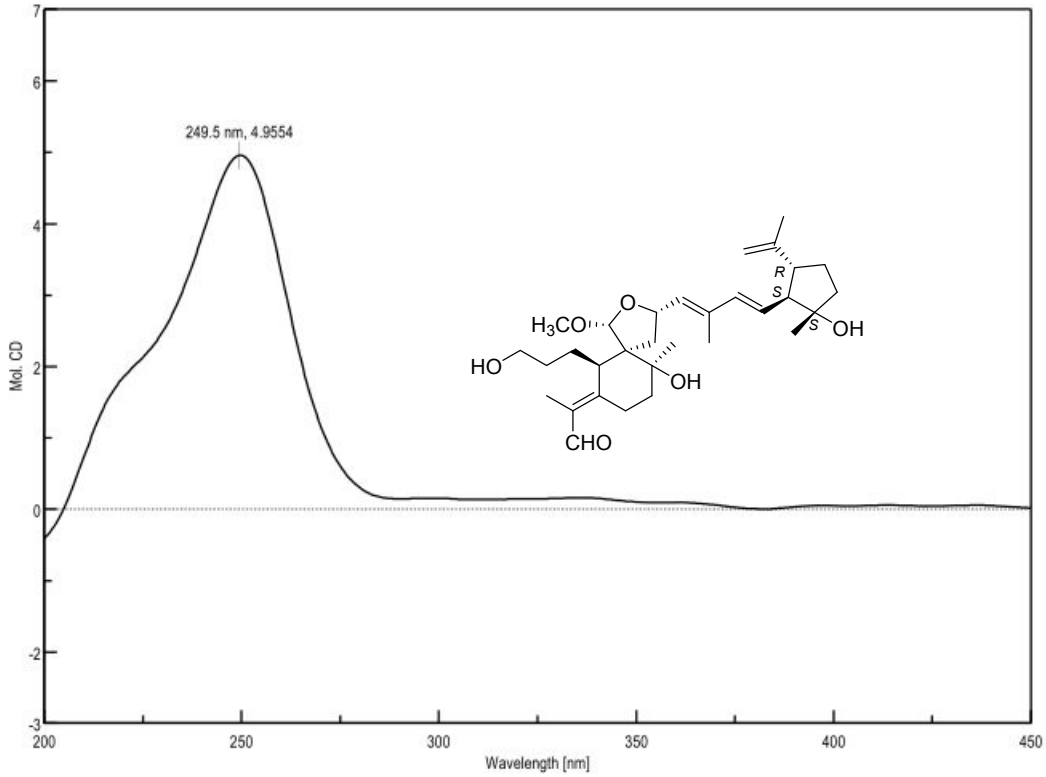


Figure S64.The ^{1}H NMR spectrum of compound **7** in DMSO-d_6.(600 MHz)

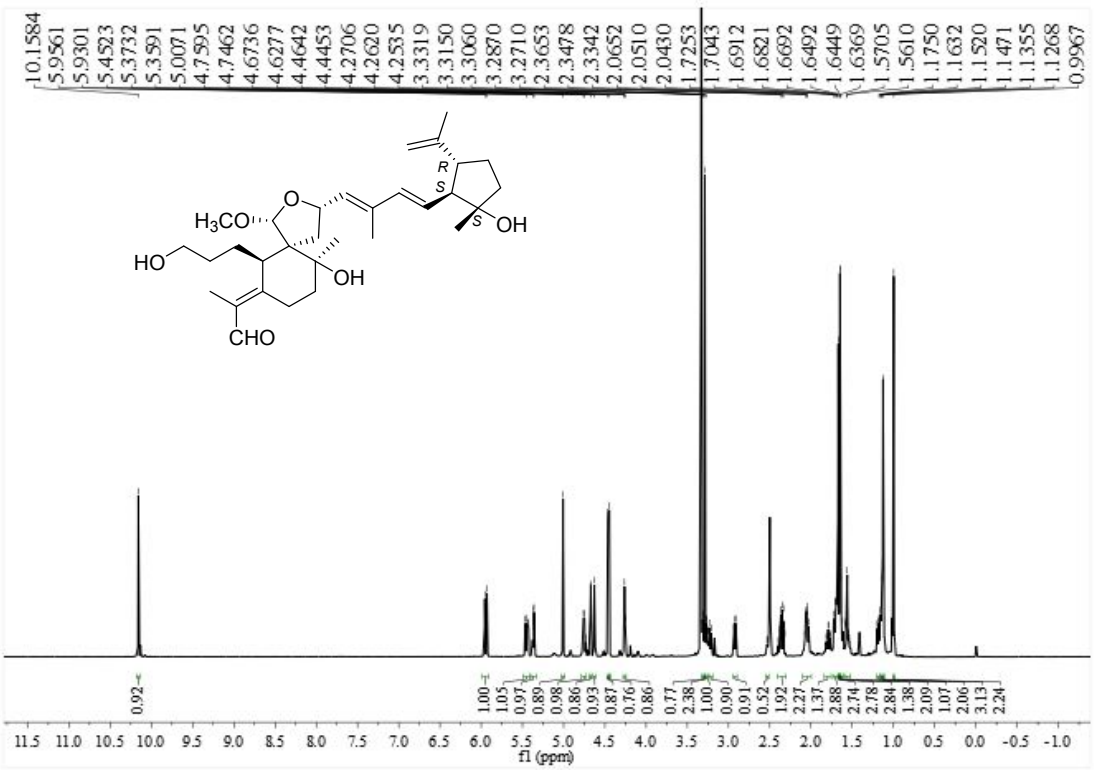


Figure S65.The ^{13}C NMR spectrum of compound **7** in DMSO-d_6.(150 MHz)

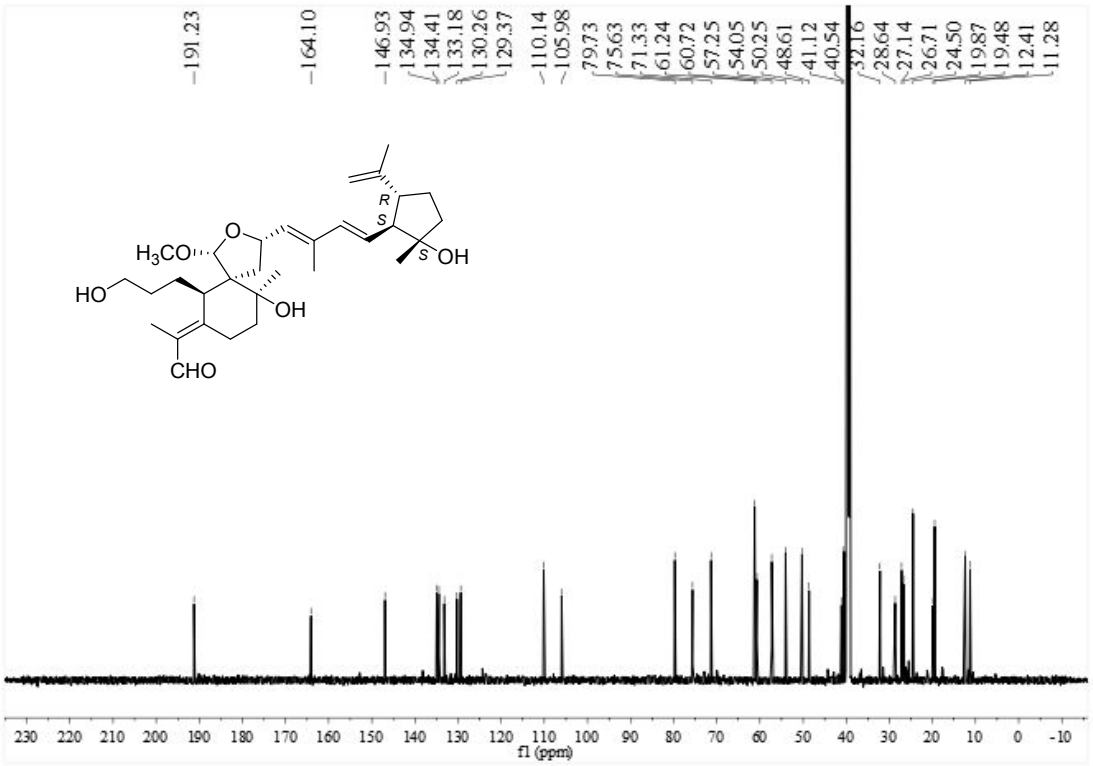


Figure S66.The HSQC spectrum of compound **7** in DMSO-d_6.(600 MHz)

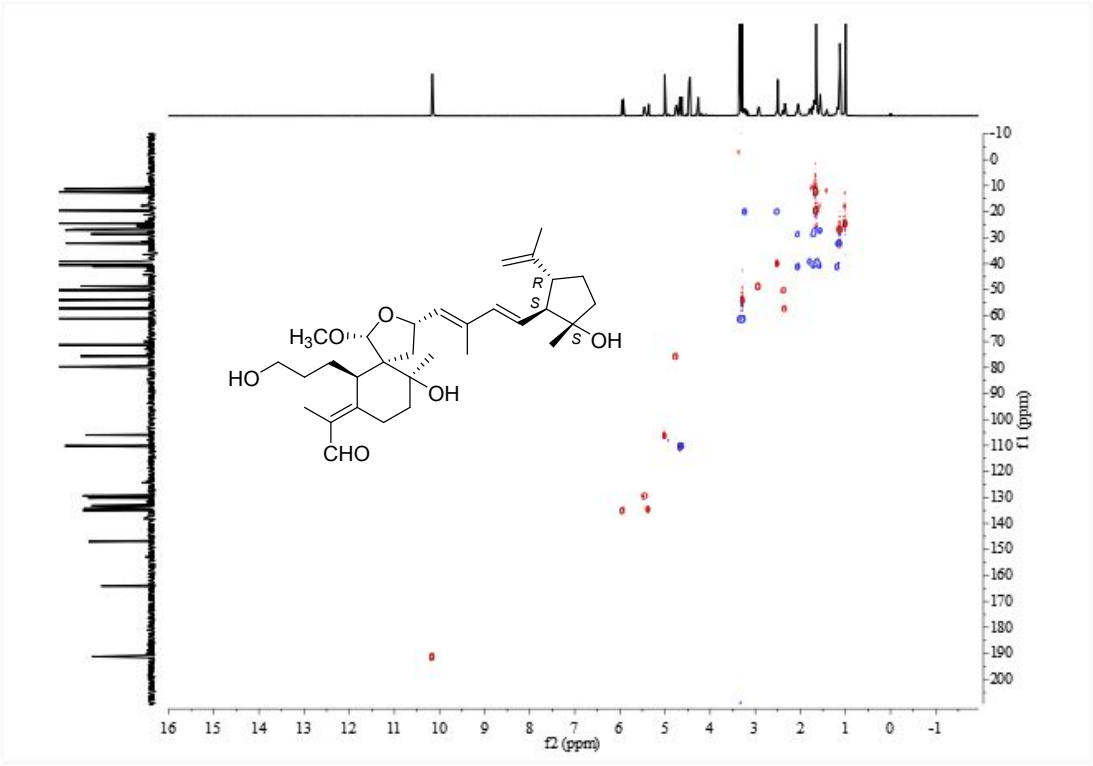


Figure S67.The HMBC spectrum of compound **7** in DMSO-d_6.(600 MHz)

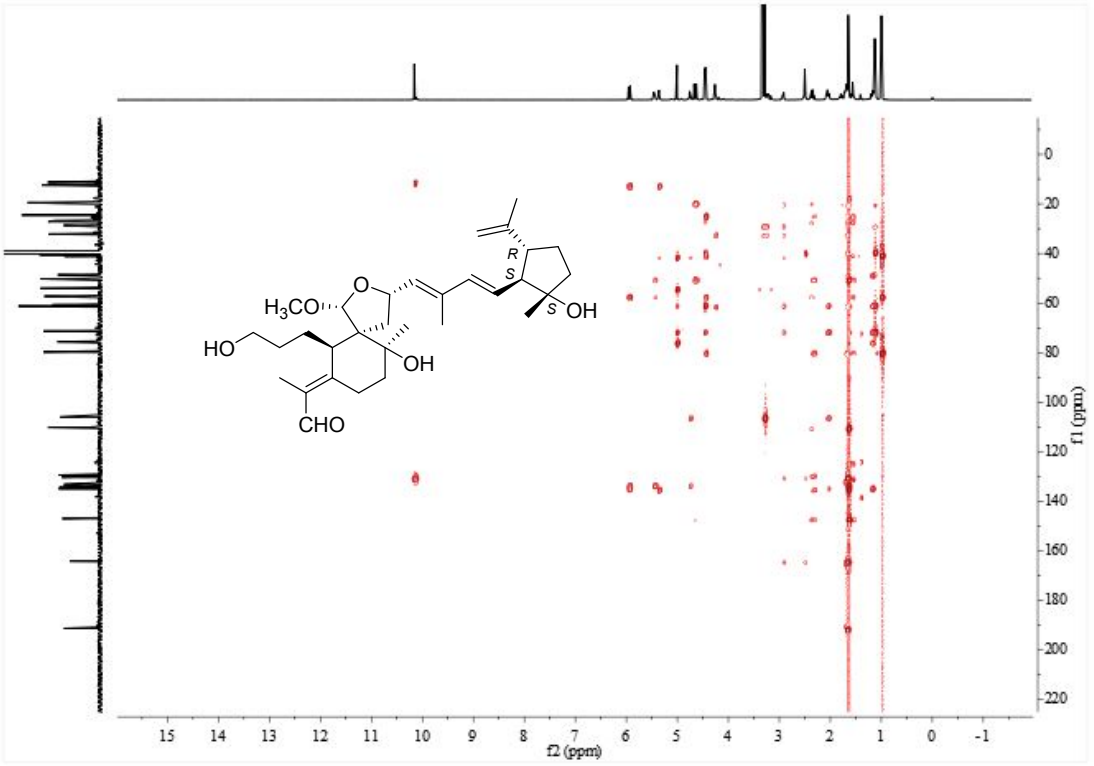


Figure S68.The NOESY spectrum of compound **7** in DMSO-d_6.(600 MHz)

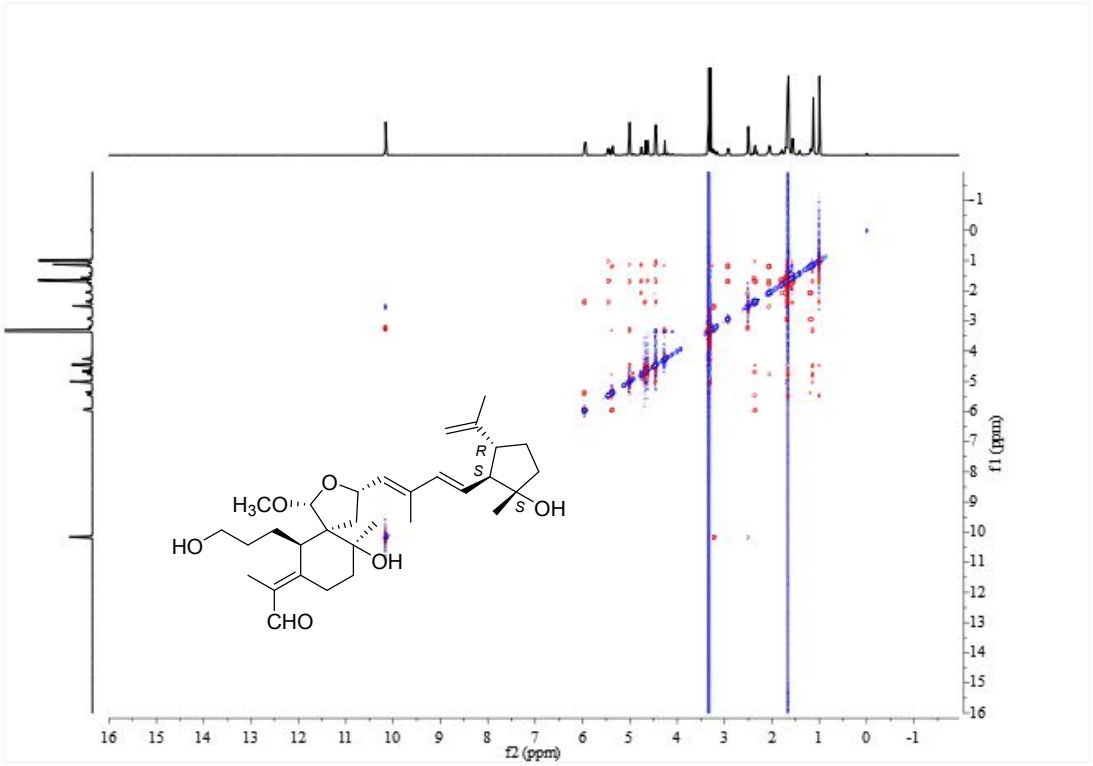


Figure S69. The UV spectrum of compound **8** in CH_3OH.

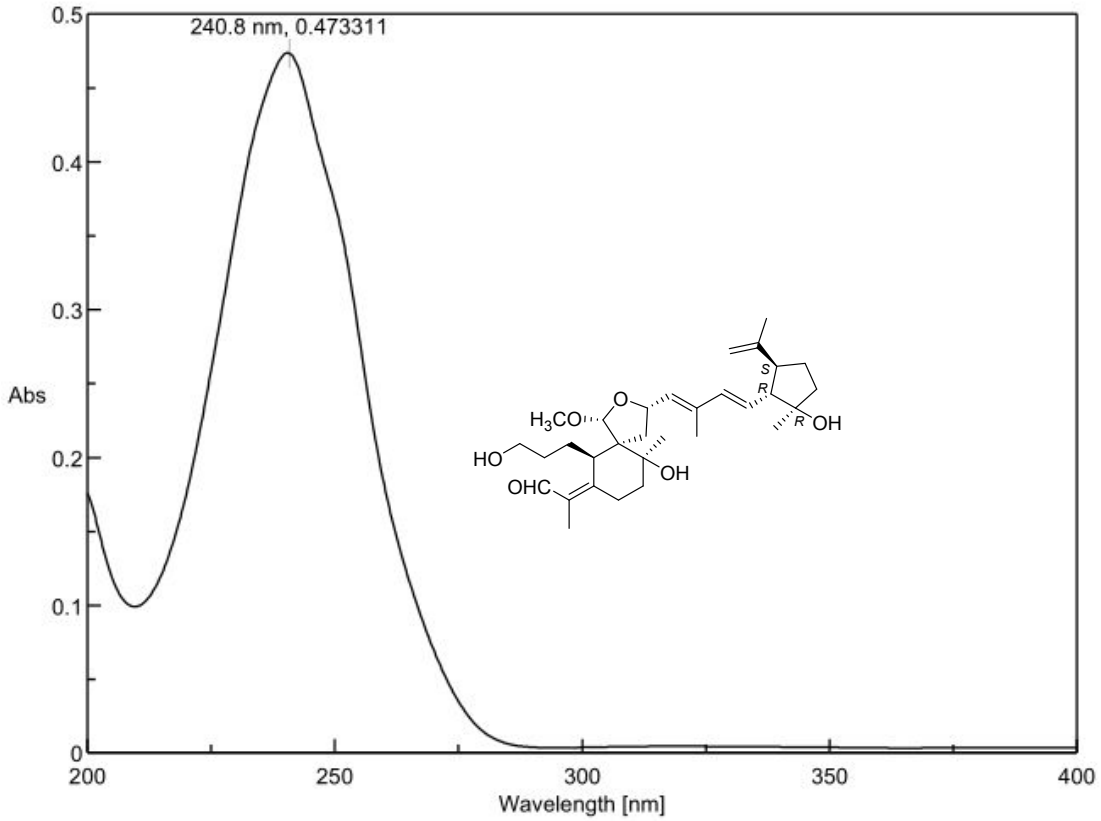


Figure S70. The IR spectrum of compound **8** in CH_3OH.

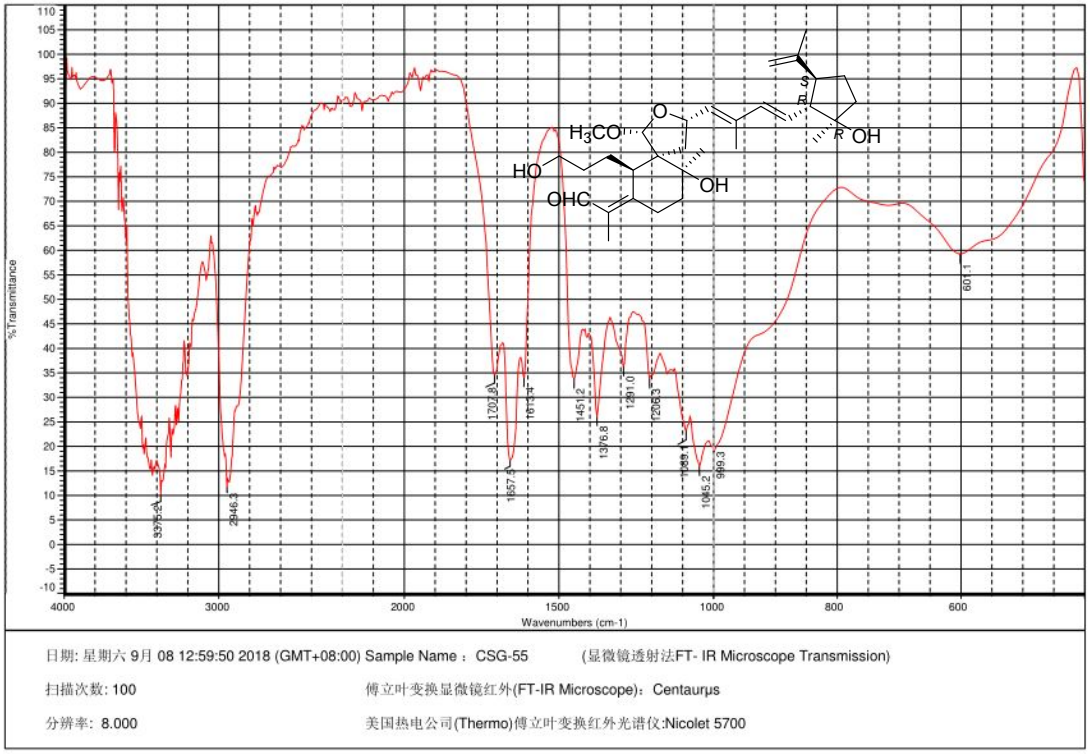
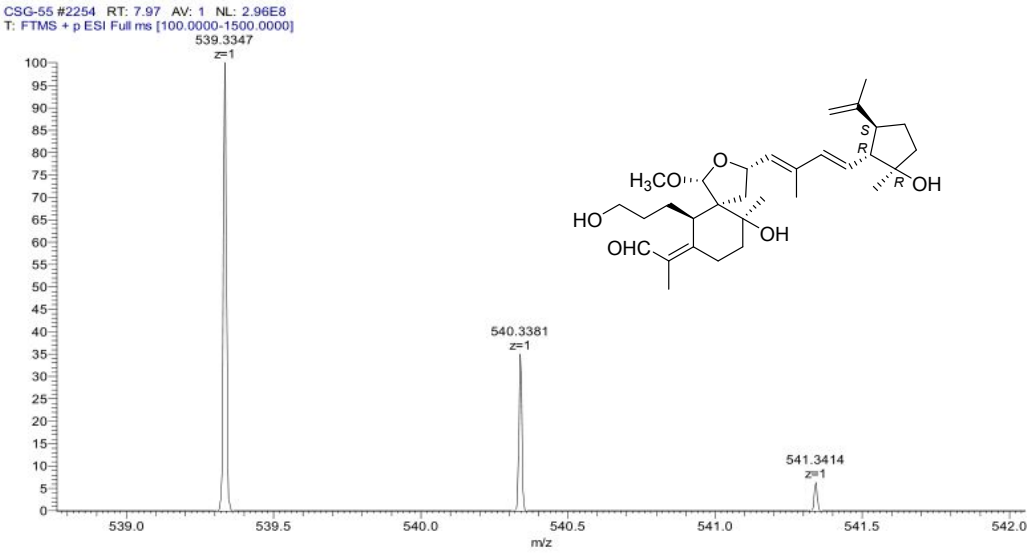


Figure S71. The HRESIMS of compound **8**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
539.3347	539.3343	0.65	7.5	C31 H48 O6 Na	M+Na

Figure S72. The CD spectrum of compound **8** in CH_3OH.

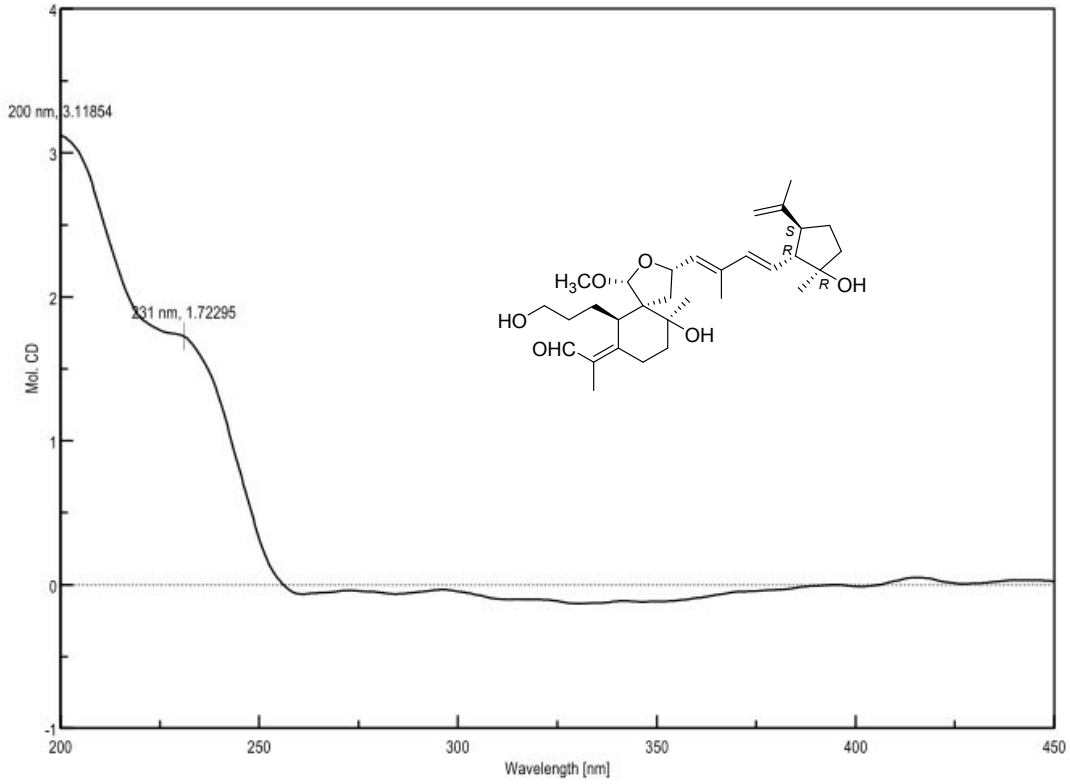


Figure S73.The ^1H NMR spectrum of compound **8** in DMSO-d_6.(600 MHz)

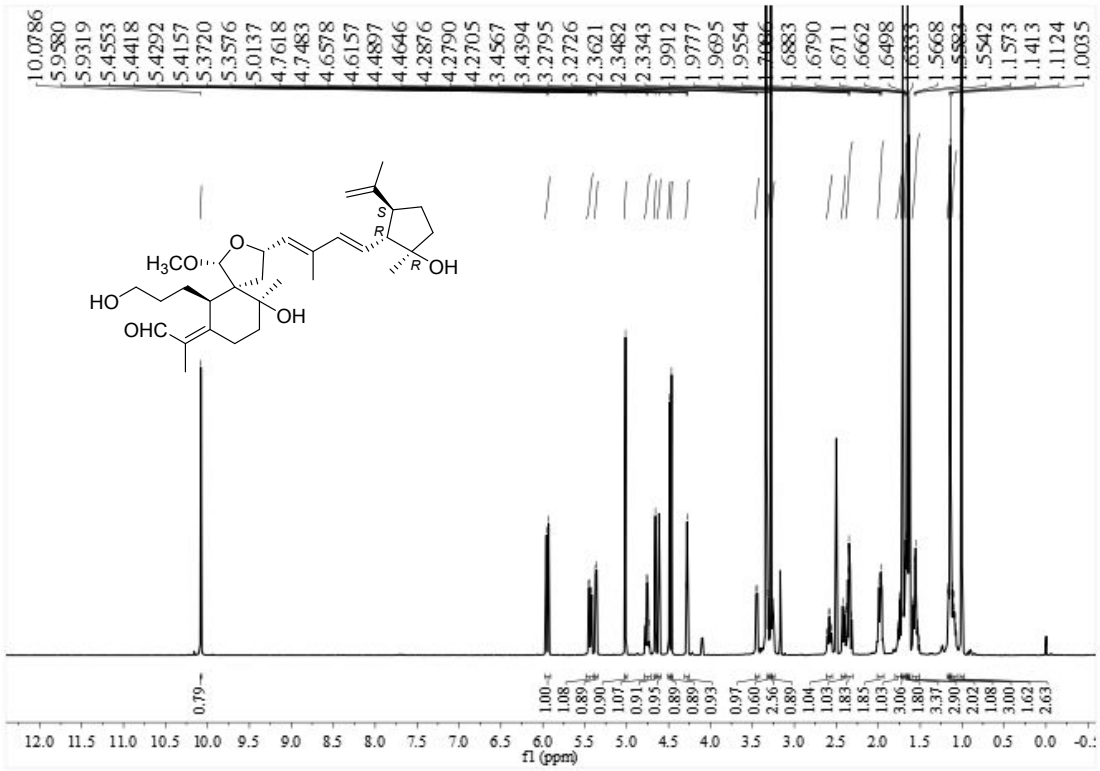


Figure S74.The ^{13}C NMR spectrum of compound **8** in DMSO-d_6.(150 MHz)

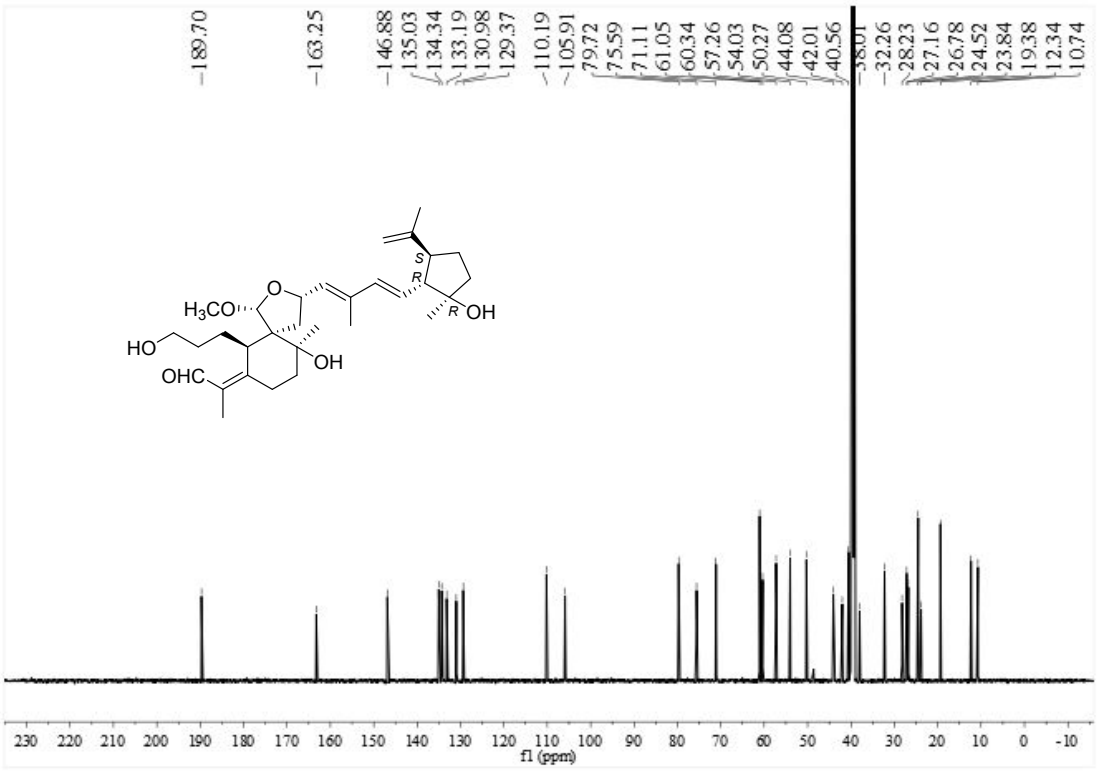


Figure S75.The HSQC spectrum of compound **8** in DMSO-d_6.(600 MHz)

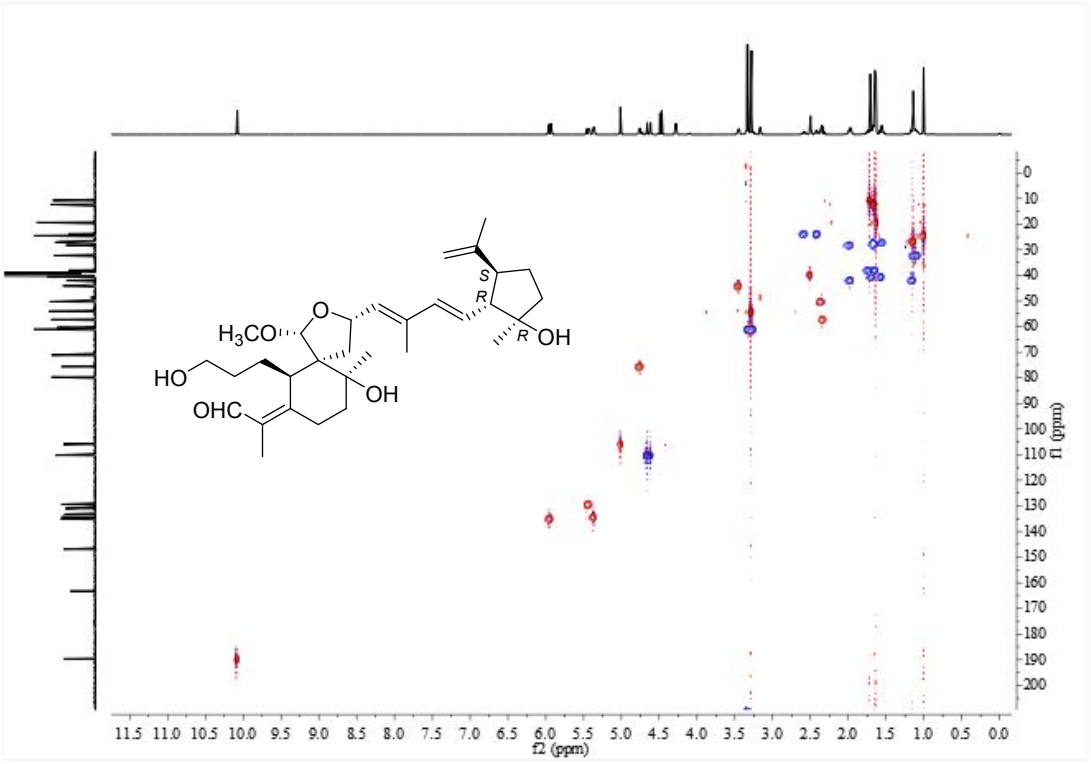


Figure S76.The HMBC spectrum of compound **8** in DMSO-d_6.(600 MHz)

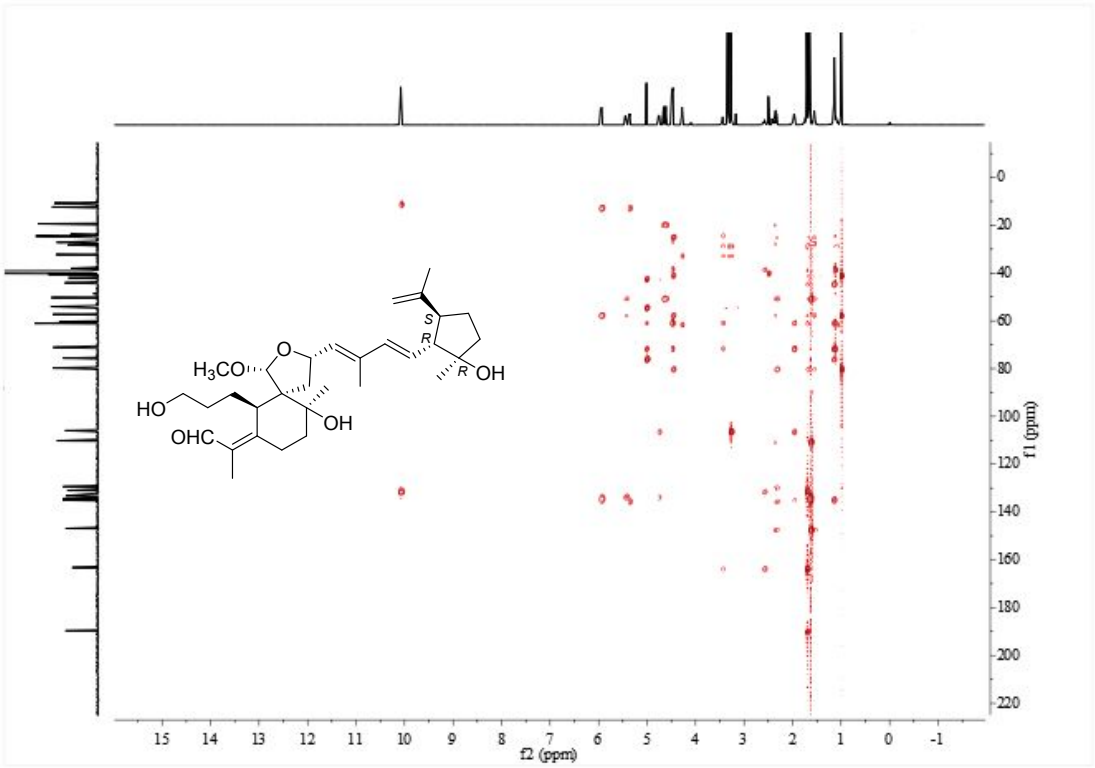


Figure S77.The NOESY spectrum of compound **8** in DMSO-d_6.(600 MHz)

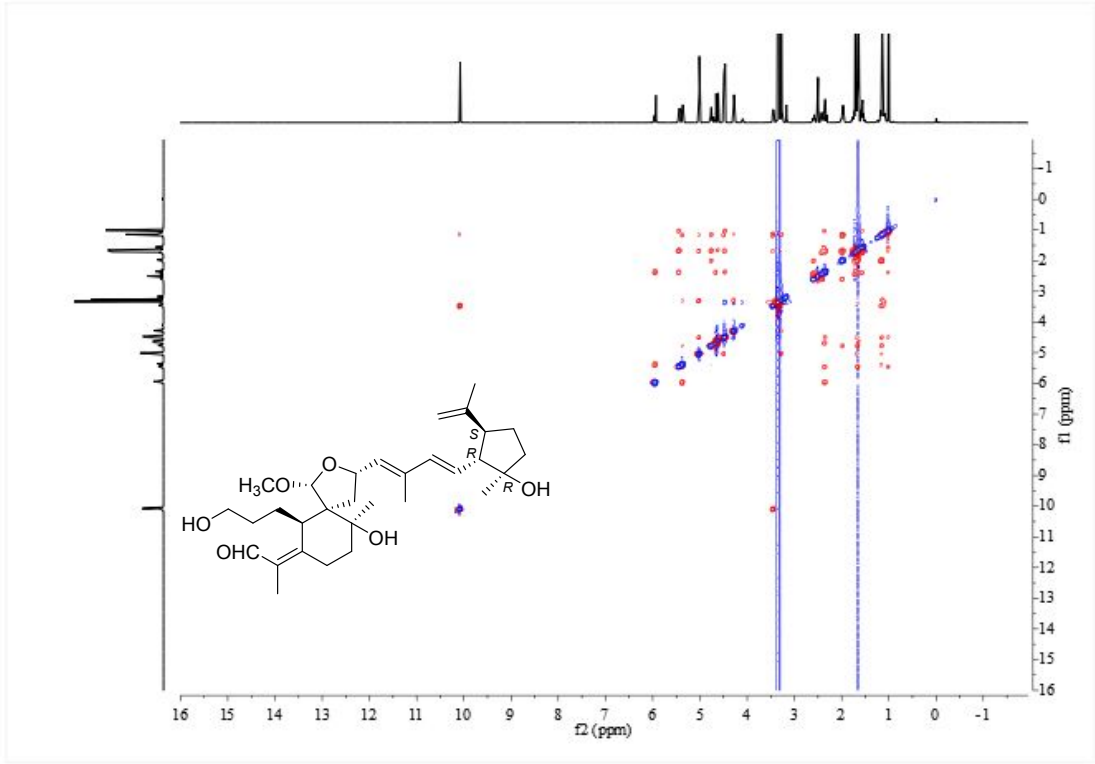


Figure S78. The UV spectrum of compound **9** in CH_3OH.

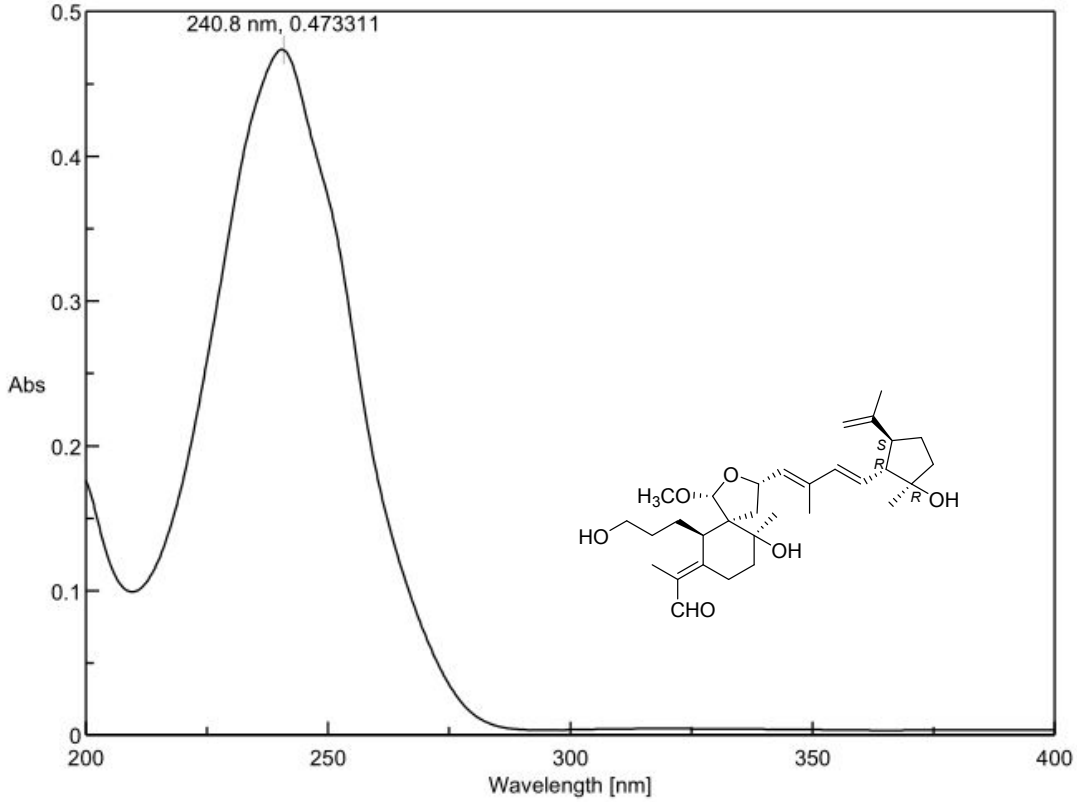


Figure S79. The IR spectrum of compound **9** in CH_3OH.

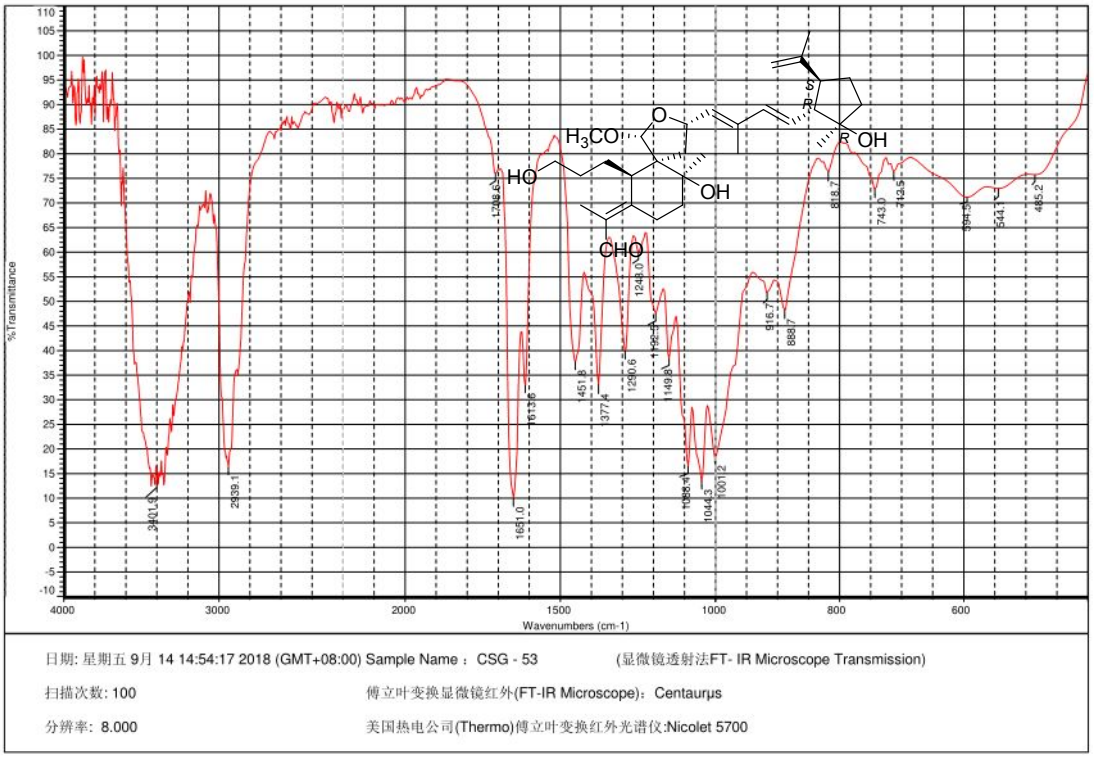
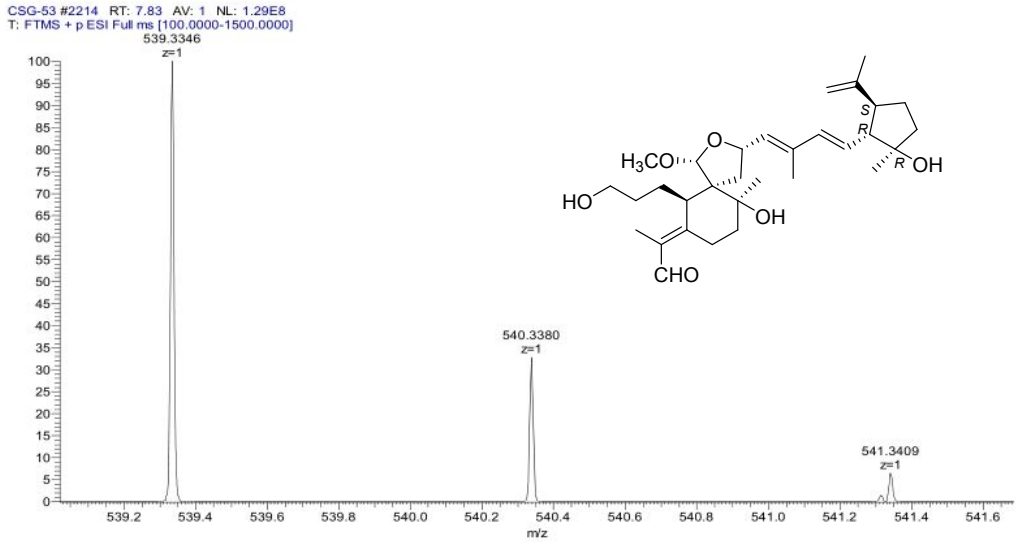


Figure S80. The HRESIMS of compound **9**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
539.3346	539.3343	0.52	7.5	C31 H48 O6 Na	M+Na

Figure S81. The CD spectrum of compound **9** in CH_3OH.

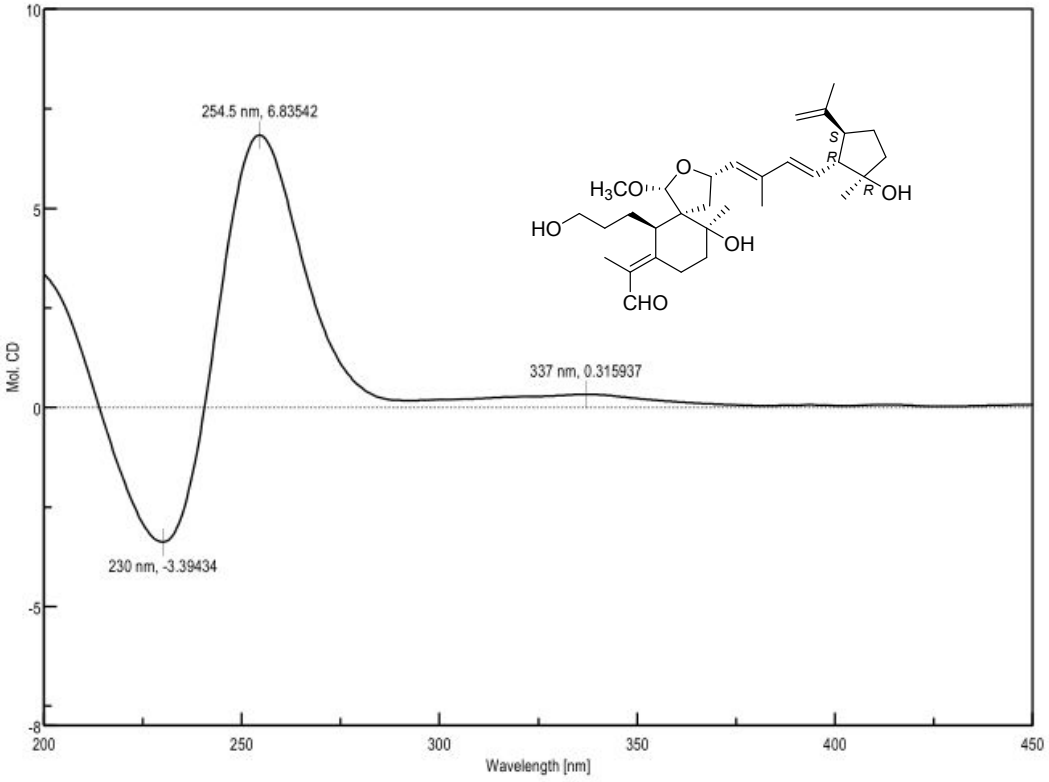


Figure S82.The ^{1}H NMR spectrum of compound **9** in DMSO-d_6.(600 MHz)

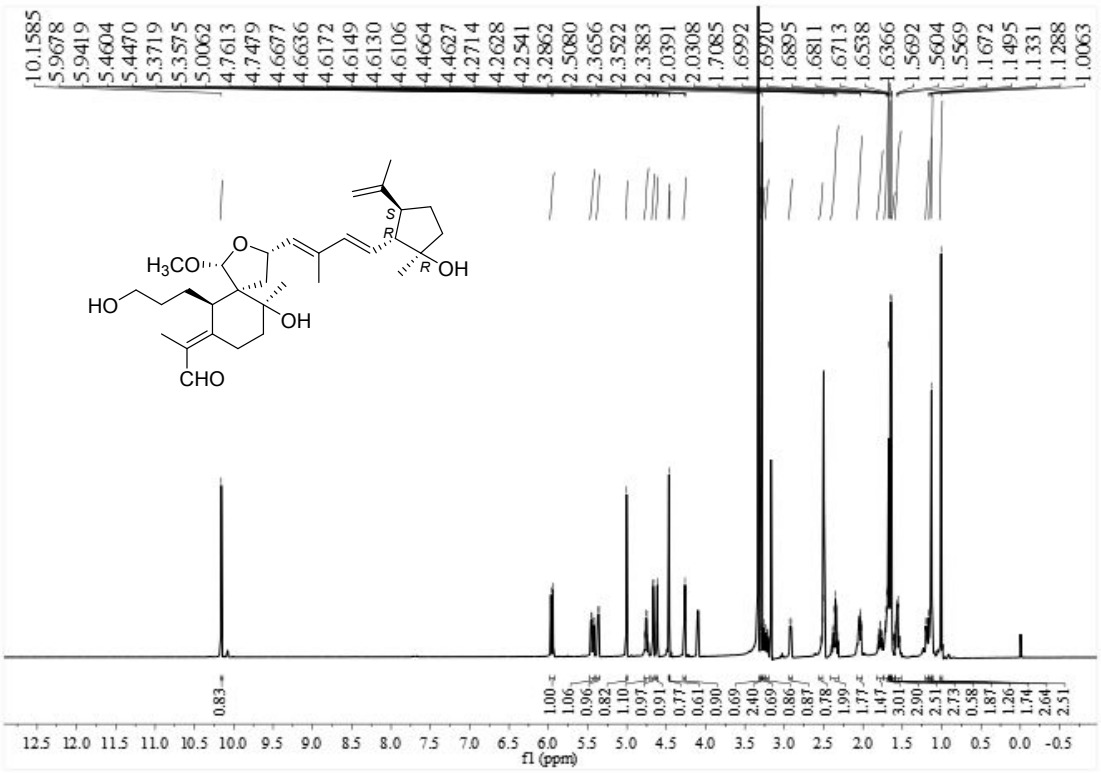


Figure S83.The ^{13}C NMR spectrum of compound **9** in DMSO-d_6.(150 MHz)

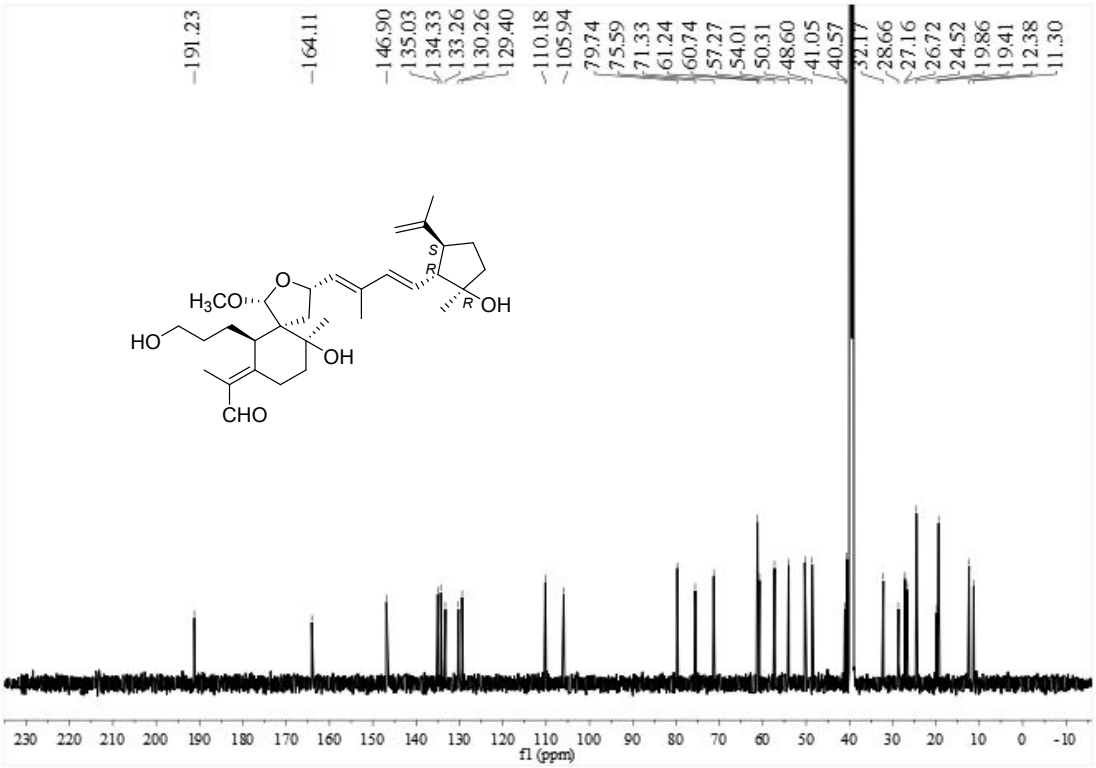


Figure S84.The HSQC spectrum of compound **9** in DMSO-d_6.(600 MHz)

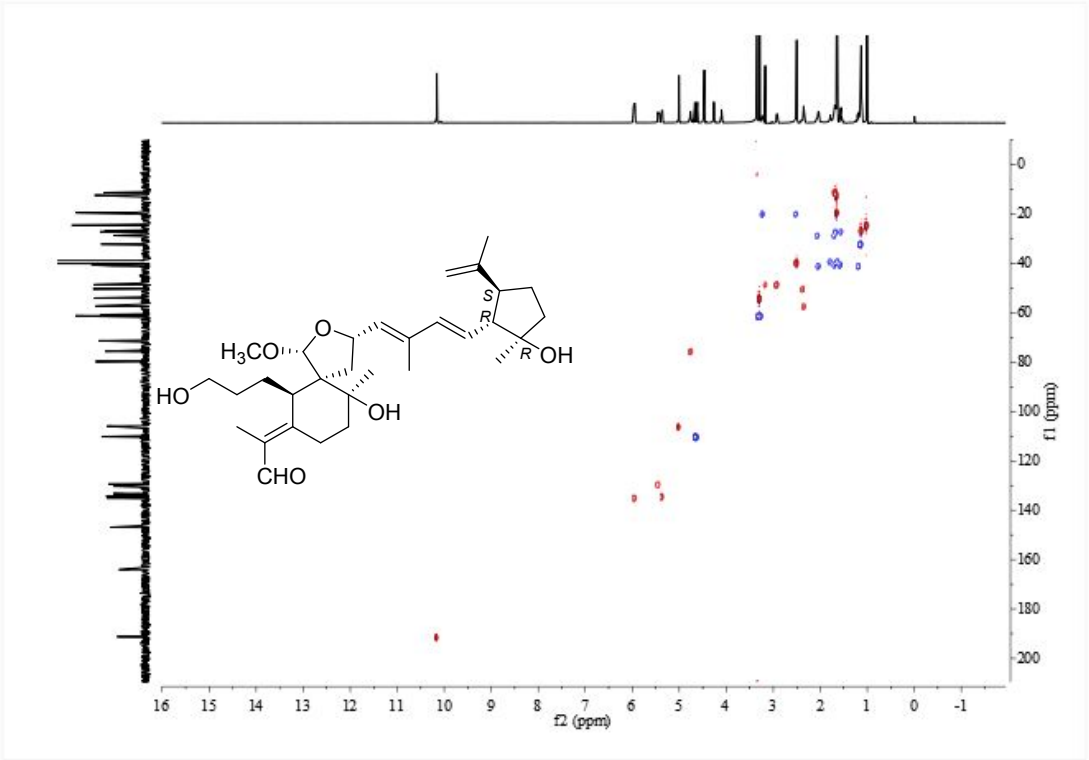


Figure S85.The HMBC spectrum of compound **9** in DMSO-d_6.(600 MHz)

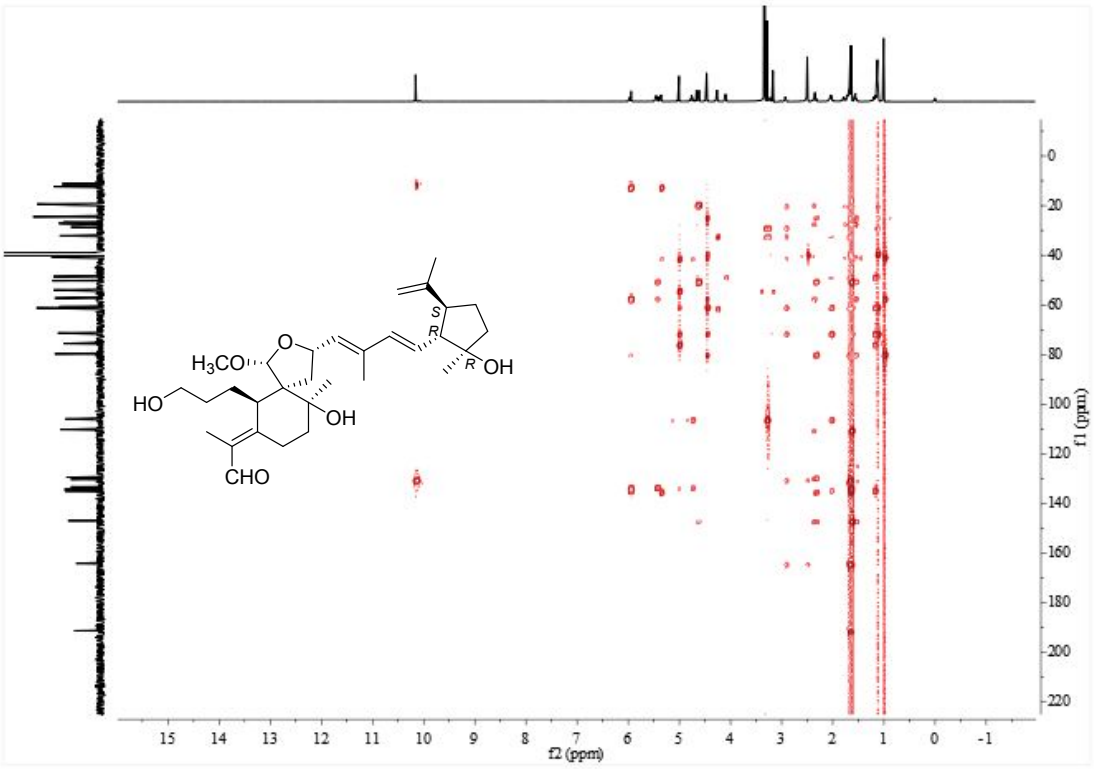


Figure S86.The NOESY spectrum of compound **9** in DMSO-d_6.(600 MHz)

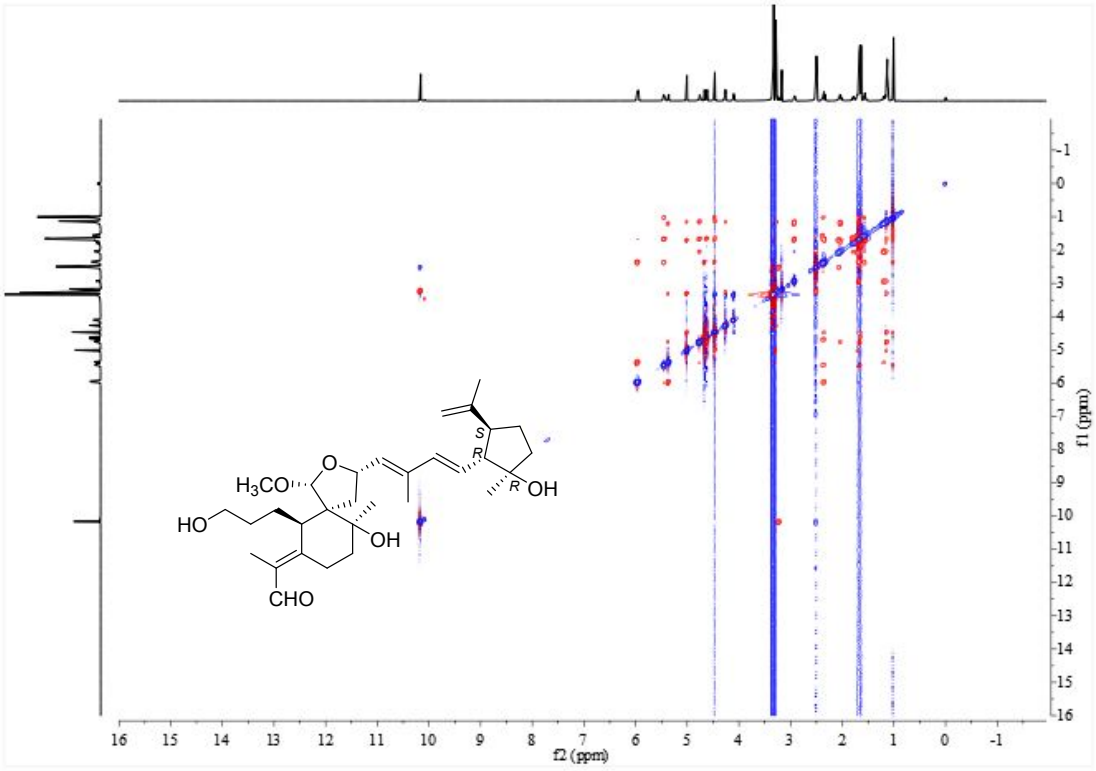


Figure S87. The UV spectrum of compound **10** in CH_3OH.

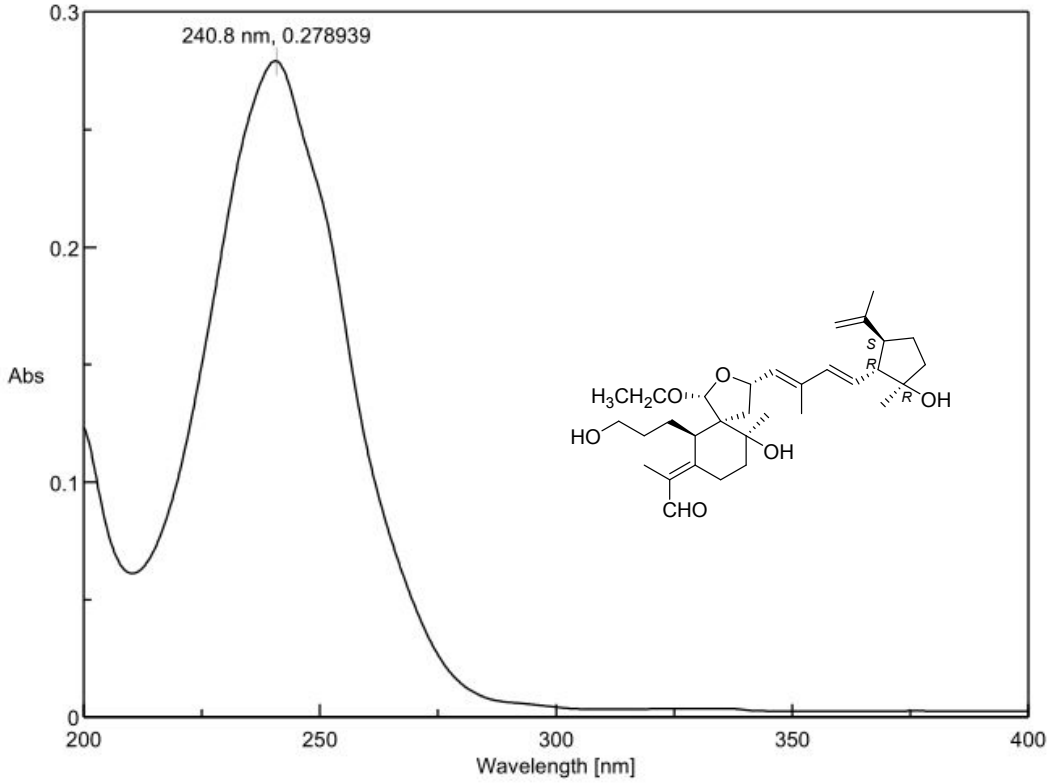


Figure S88. The IR spectrum of compound **10** in CH_3OH.

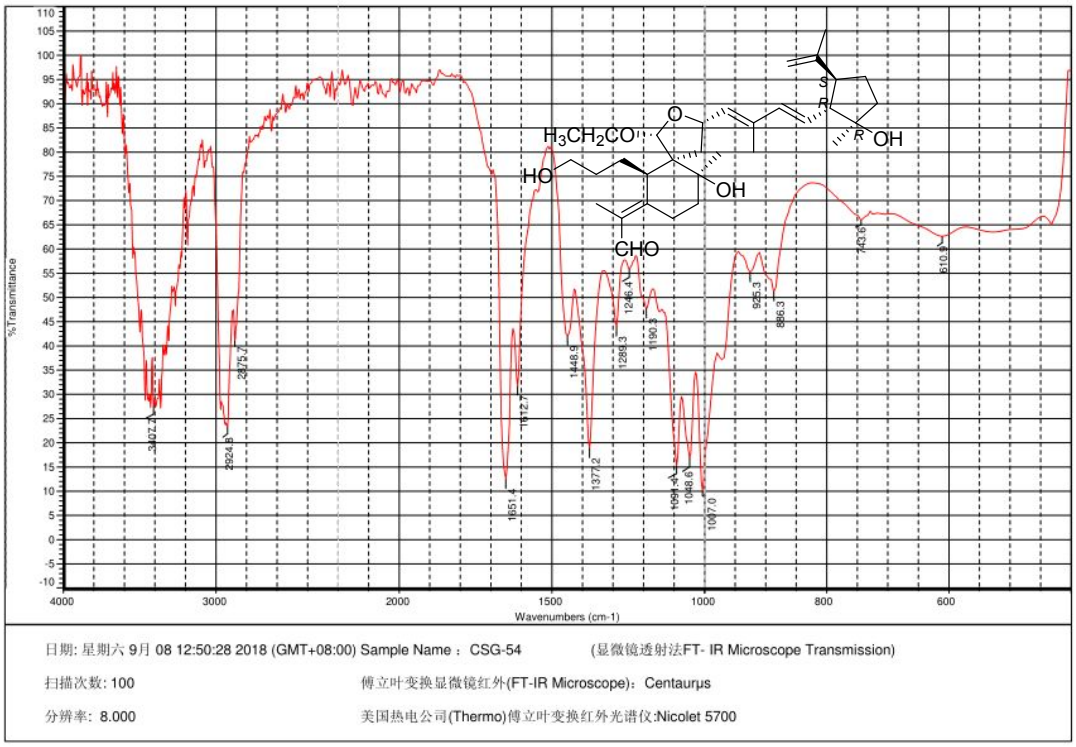
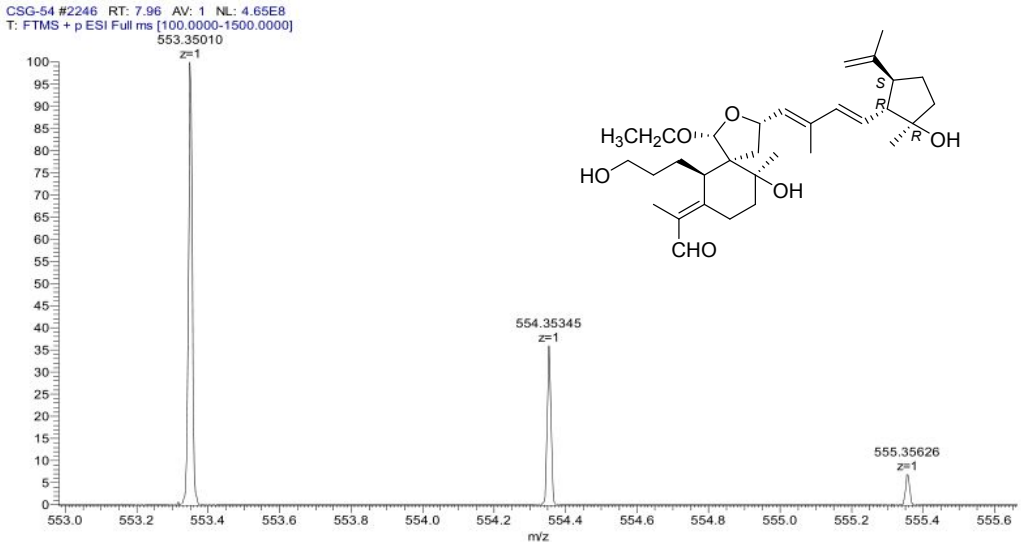


Figure S89. The HRESIMS of compound **10**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
553.3501	553.3500	0.25	7.5	C32 H50 O6 Na	M+Na

Figure S90. The CD spectrum of compound **10** in CH_3OH.

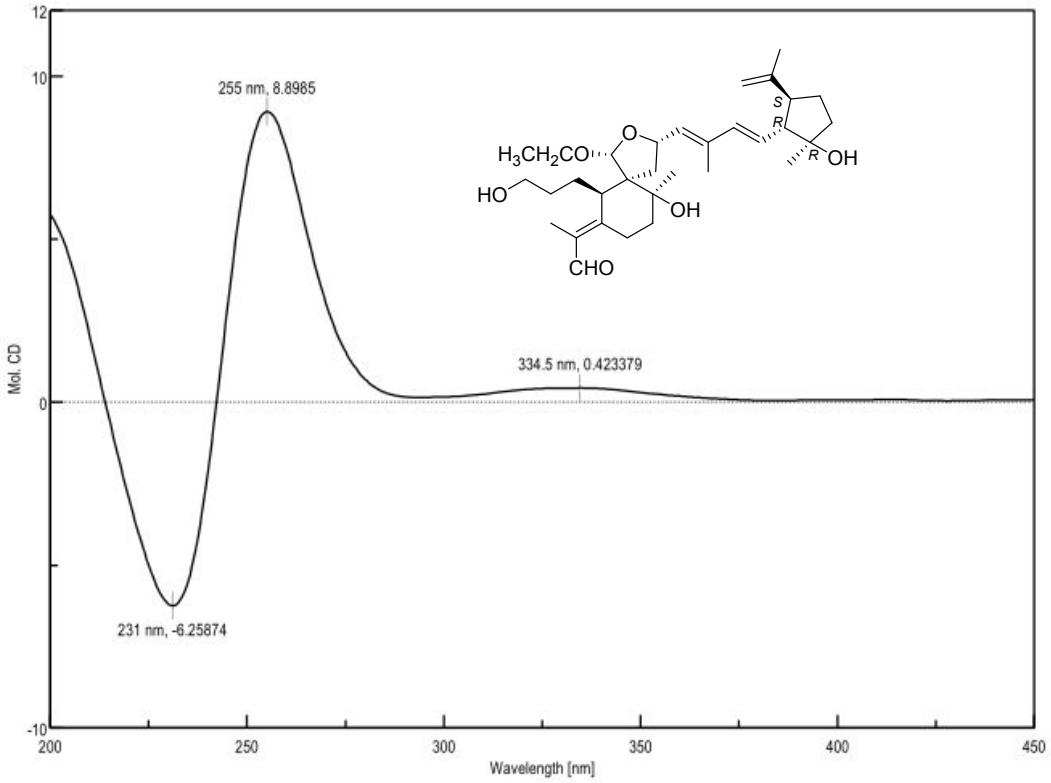


Figure S91.The ^{1}H NMR spectrum of compound **10** in DMSO-d_6.(600 MHz)

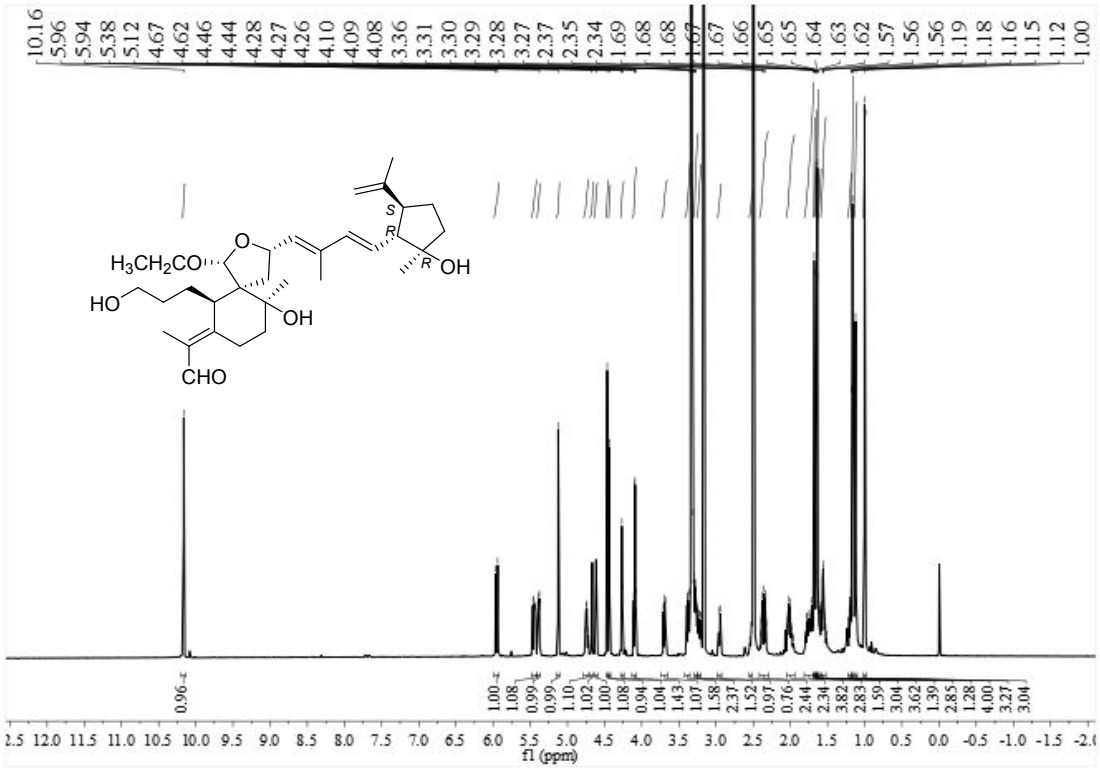


Figure S92.The ^{13}C NMR spectrum of compound **10** in DMSO-d_6.(150 MHz)

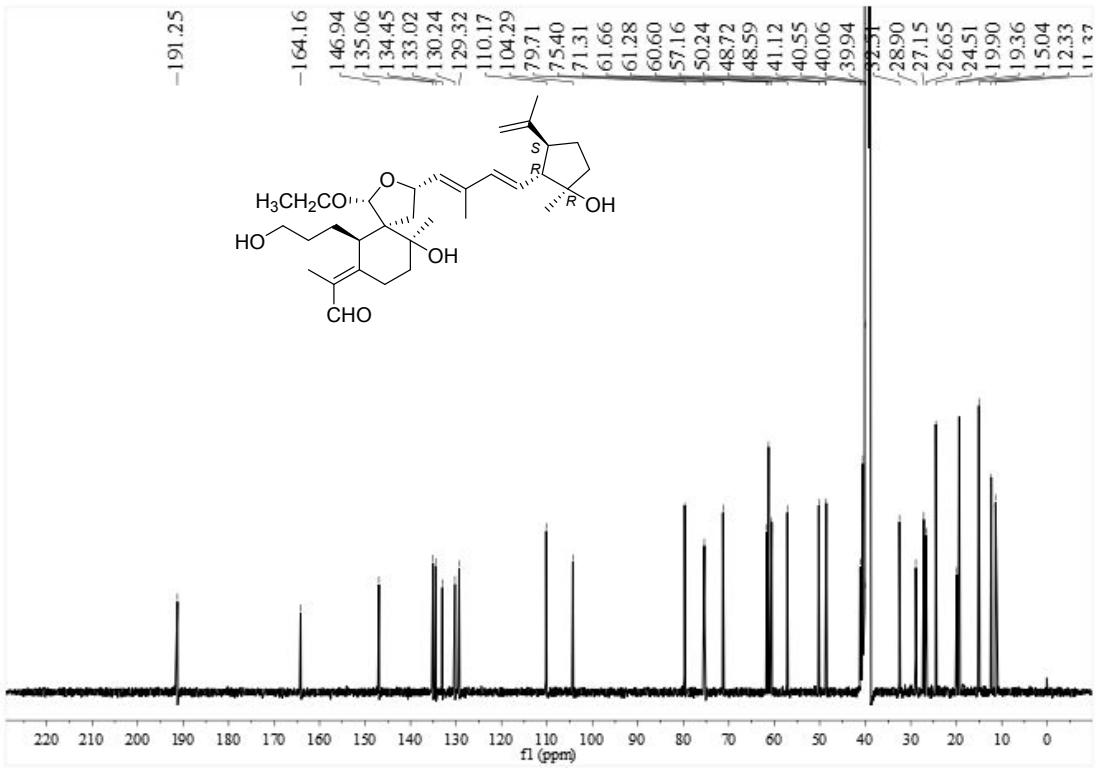


Figure S93.The HSQC spectrum of compound **10** in DMSO-d_6.(600 MHz)

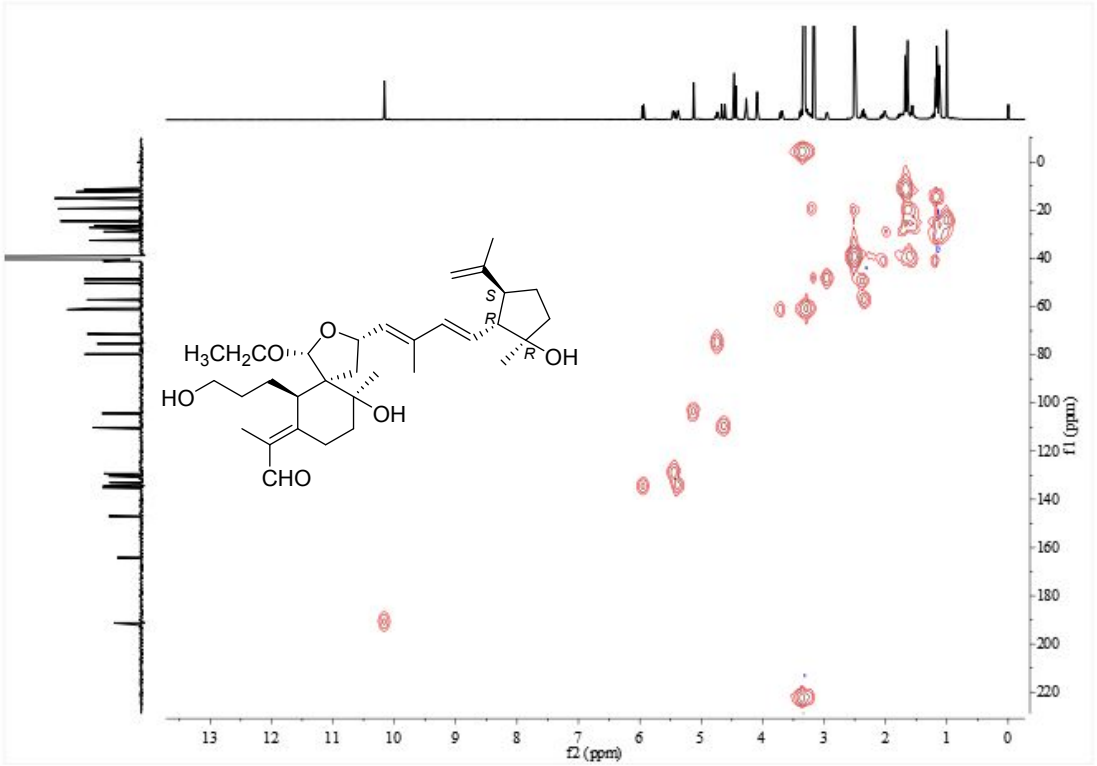


Figure S94.The HMBC spectrum of compound **10** in DMSO-d_6.(600 MHz)

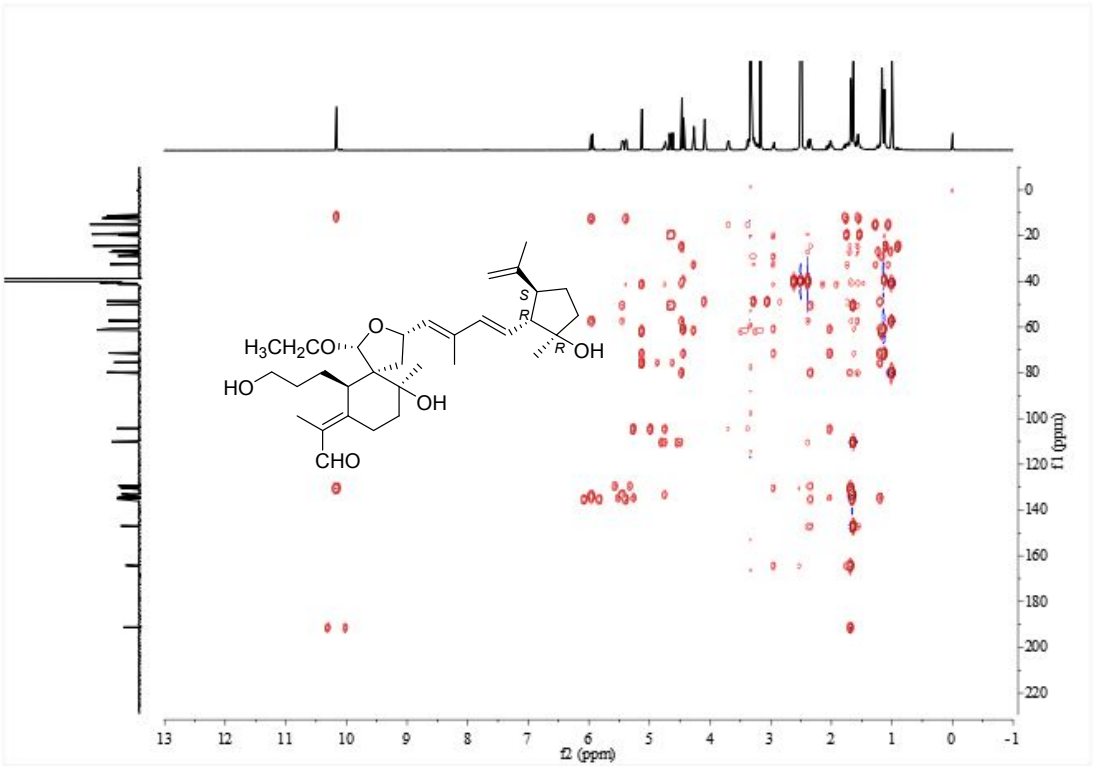


Figure S95.The NOESY spectrum of compound **10** in DMSO-d_6.(600 MHz)

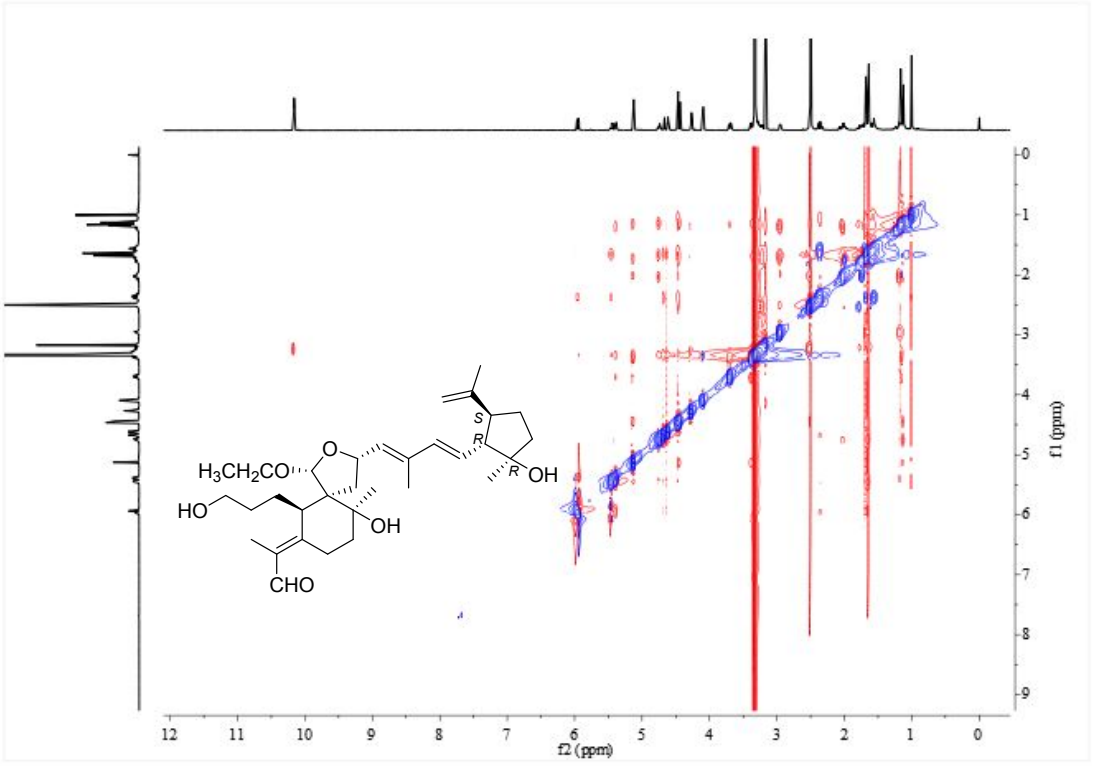
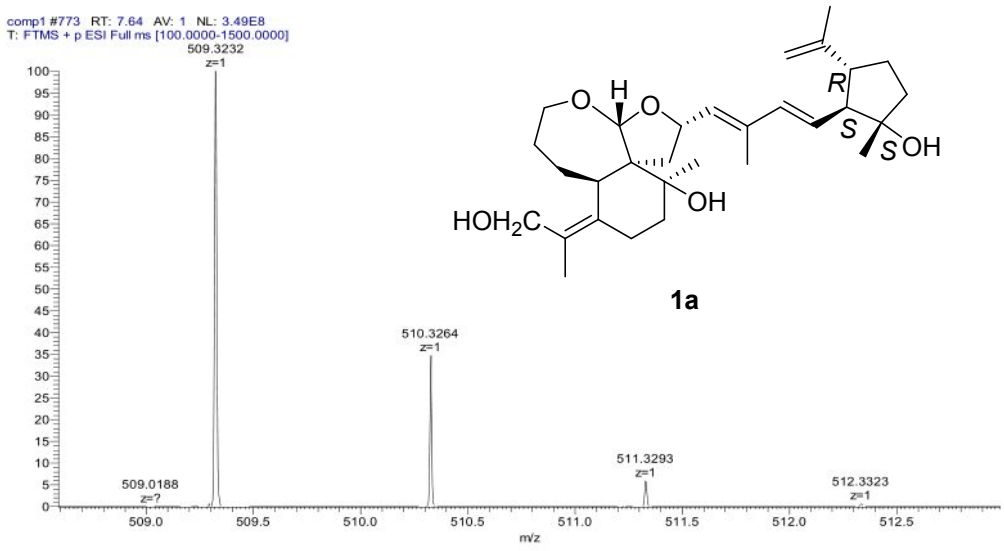
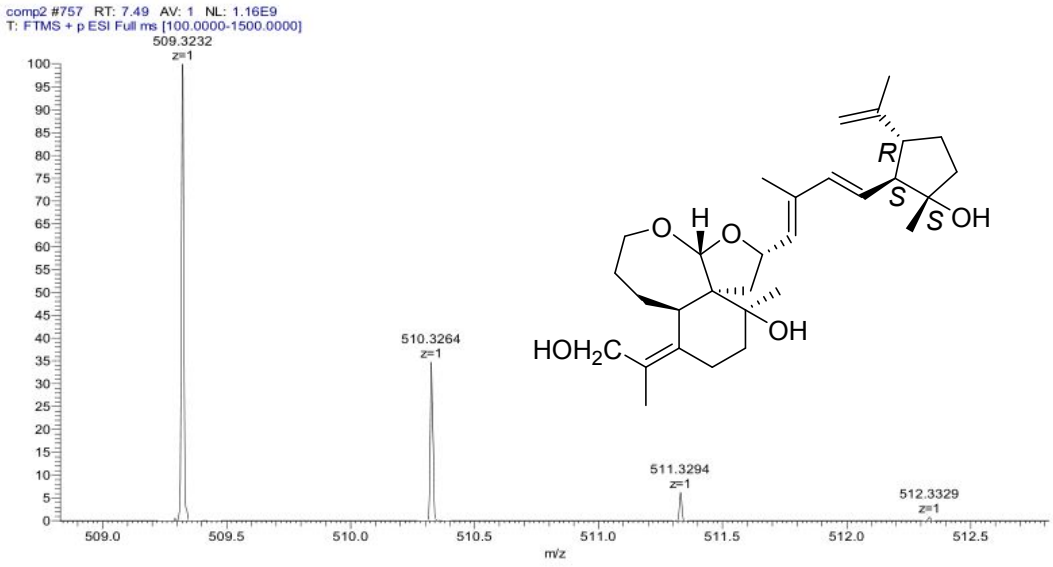


Figure S96. The HRESIMS of compound **1a**.



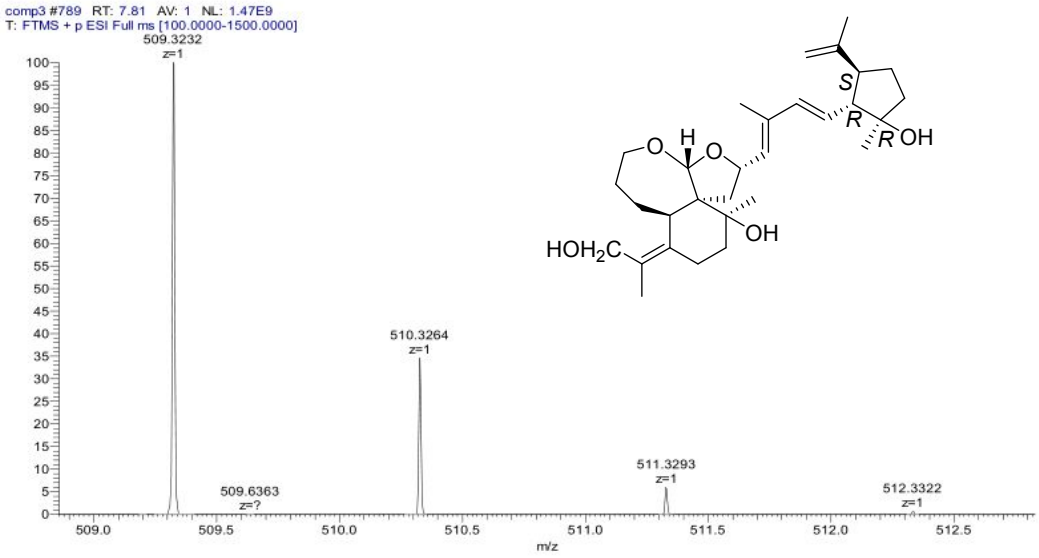
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
509.32320	509.32370	-1.11	7.5	C30 H46 O5 Na	M+Na

Figure S97. The HRESIMS of compound **2a**.



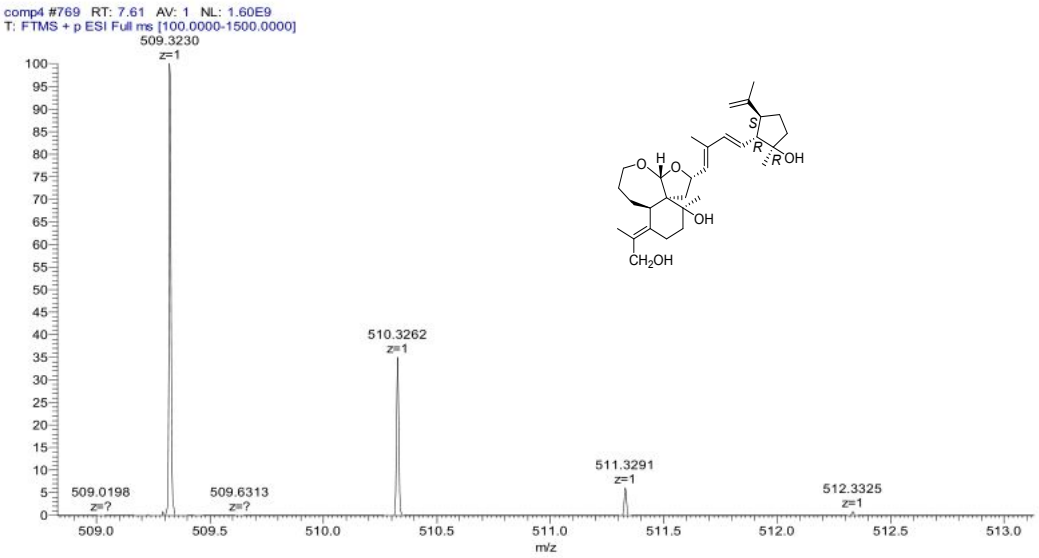
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
509.32320	509.32370	-1.05	7.5	C30 H46 O5 Na	M+Na

Figure S98. The HRESIMS of compound **3a**.



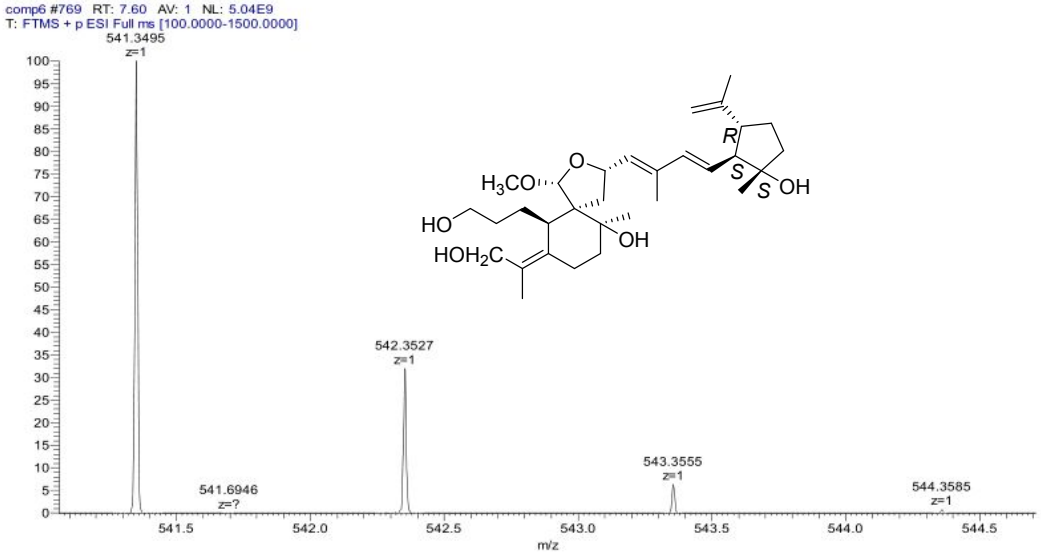
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
509.32320	509.32370	-1.11	7.5	C30 H46 O5 Na	M+Na

Figure S99. The HRESIMS of compound **4a**.



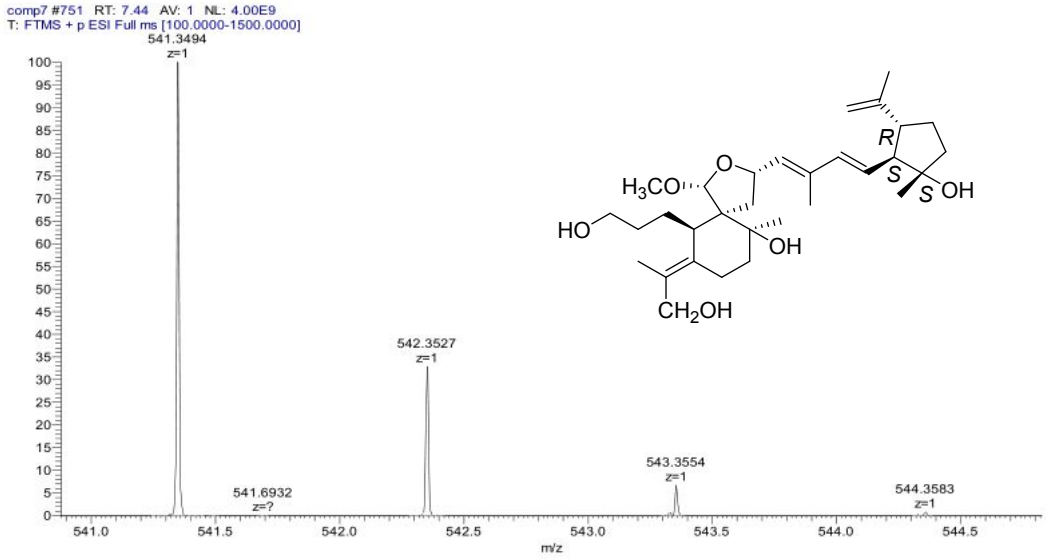
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
509.32300	509.32370	-1.41	7.5	C30 H46 O5 Na	M+Na

Figure S100. The HRESIMS of compound **6a.**



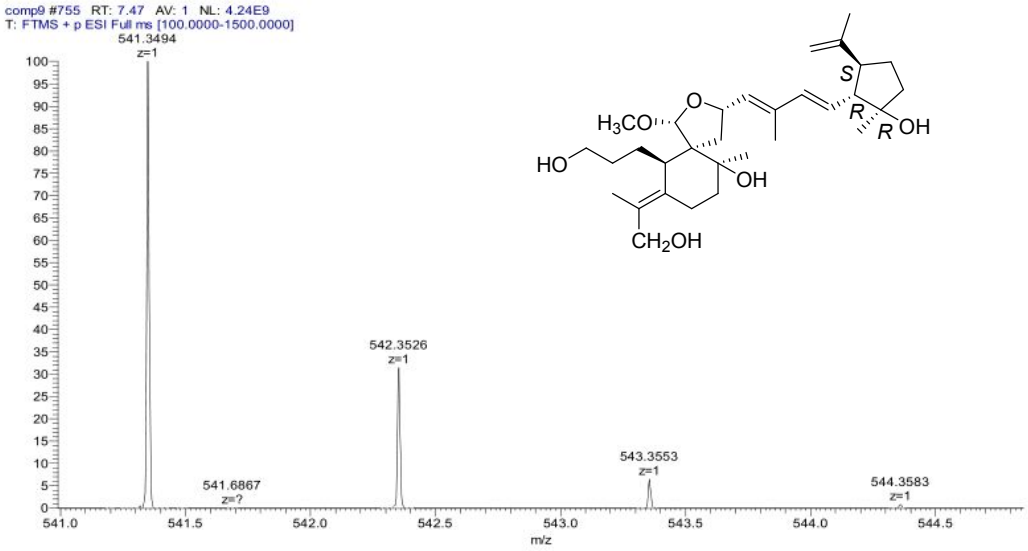
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
541.34949	541.34996	-0.87	6.5	C31 H50 O6 Na	M+Na

Figure S101. The HRESIMS of compound **7a**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
541.34940	541.35000	-0.98	6.5	C31 H50 O6 Na	M+Na

Figure S102. The HRESIMS of compound **9a**.



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
541.34940	541.35000	-1.09	6.5	C31 H50 O6 Na	M+Na

Figure S103. The CD spectrum of compound **1a** in MeOH.

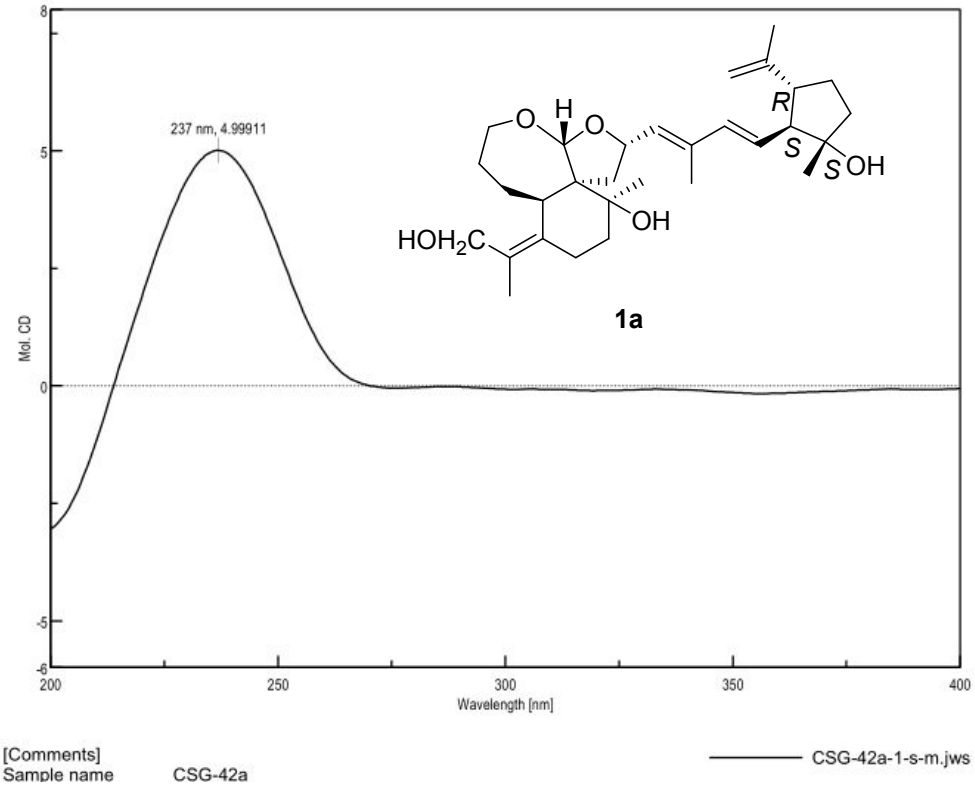


Figure S104. The CD spectrum of compound **2a** in MeOH.

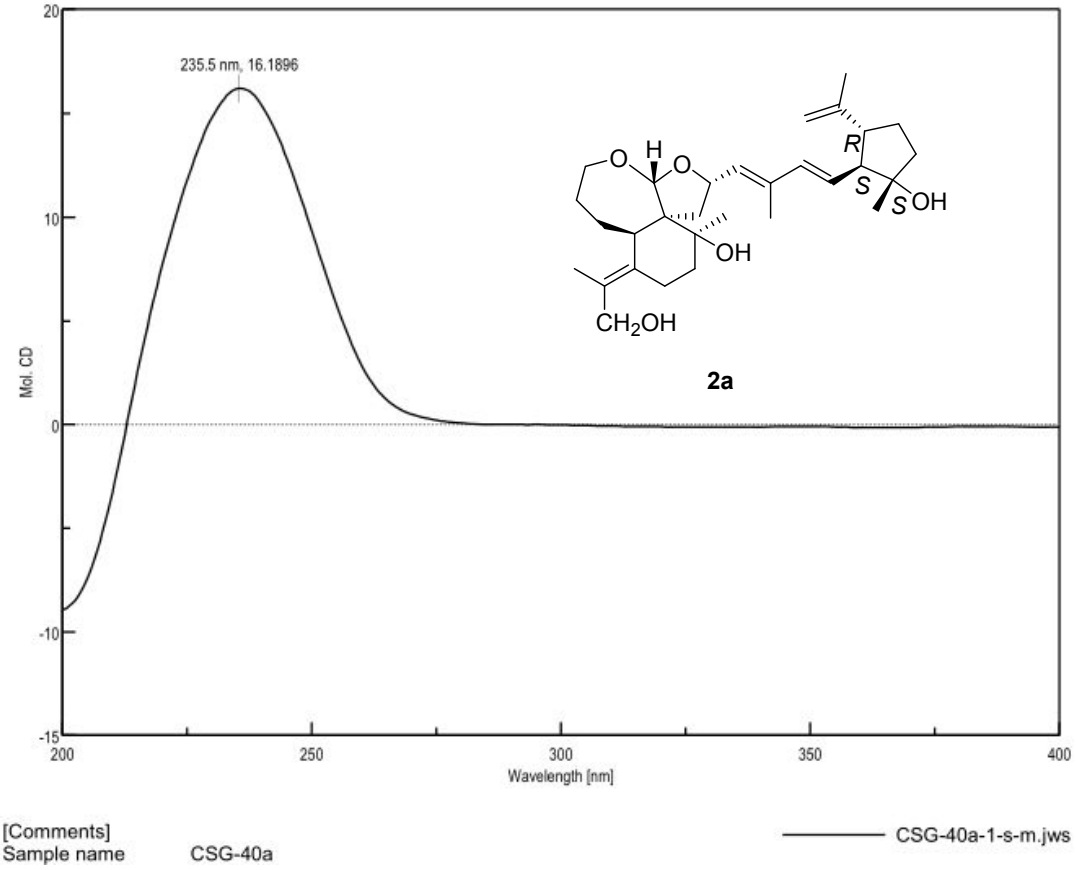


Figure S105. The CD spectrum of compound **6a** in MeOH.

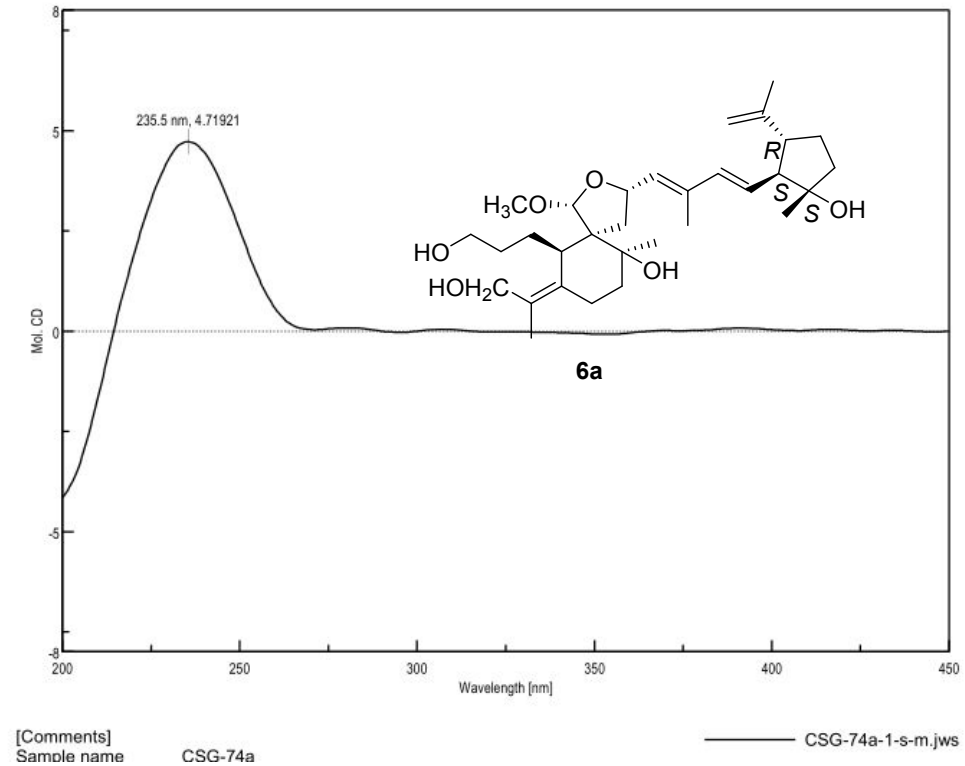


Figure S106. The CD spectrum of compound **7a** in MeOH.

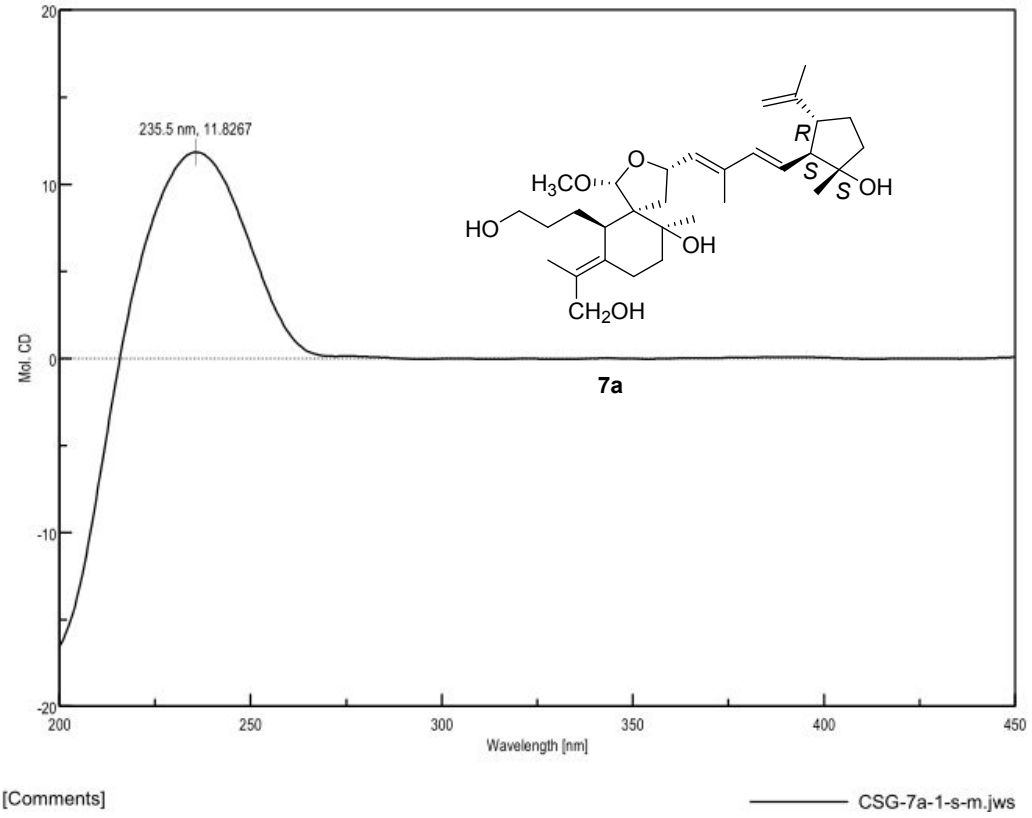


Figure S107. The CD spectrum of compound **3a** in MeOH.

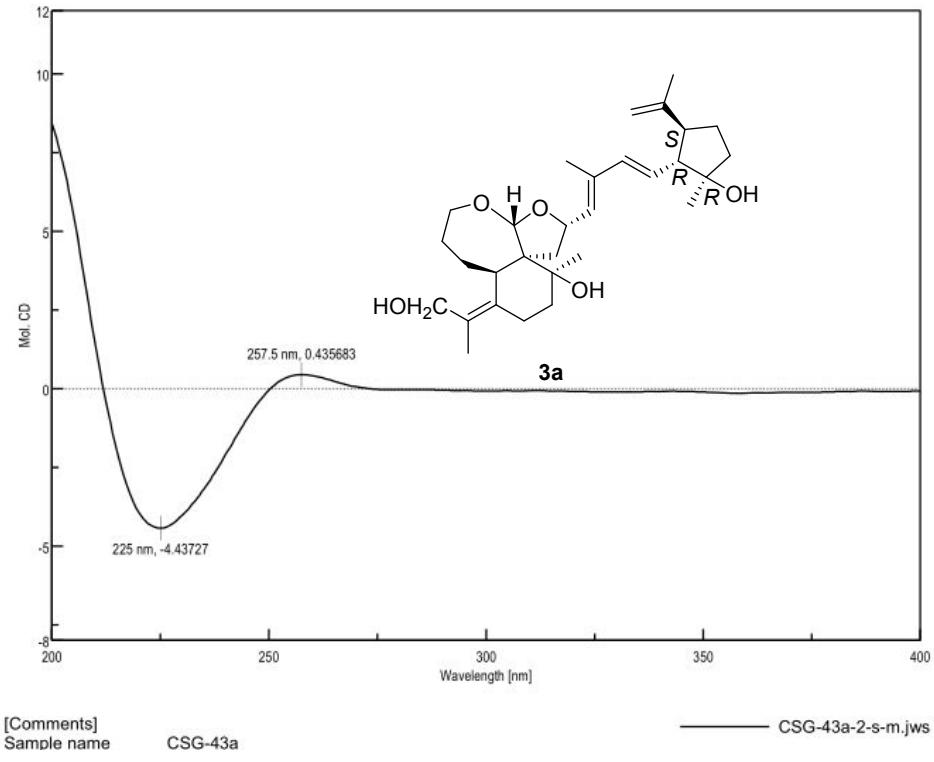


Figure S108. The CD spectrum of compound **4a** in MeOH.

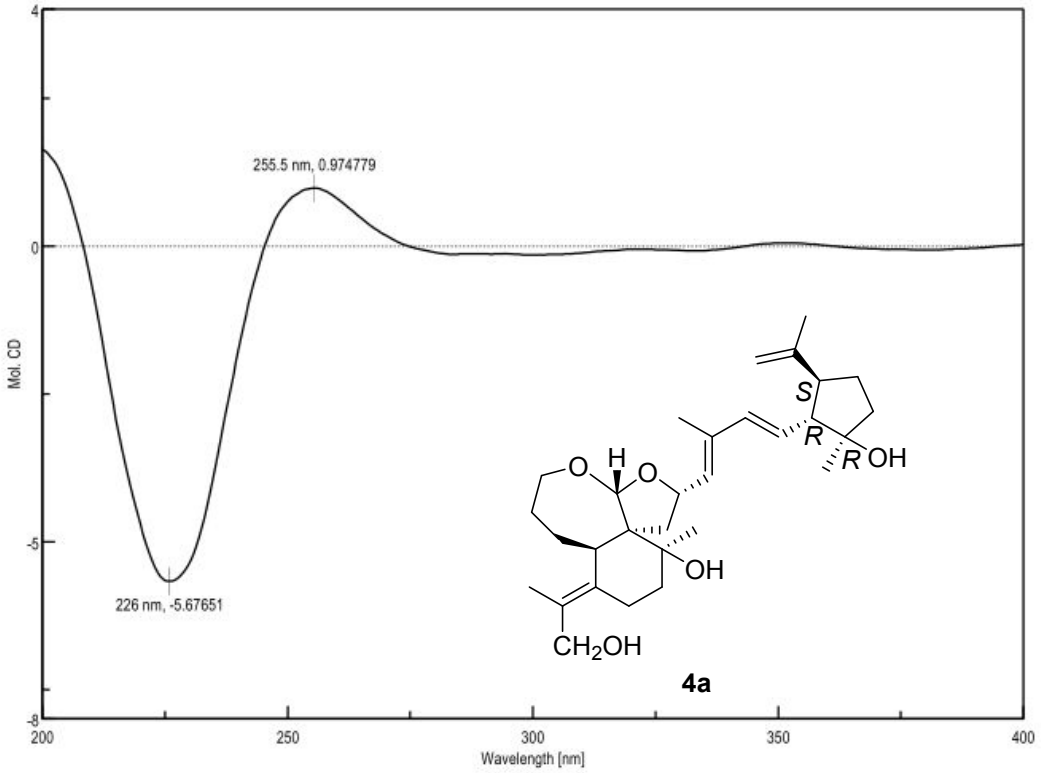


Figure S109. The CD spectrum of compound **9a** in MeOH.

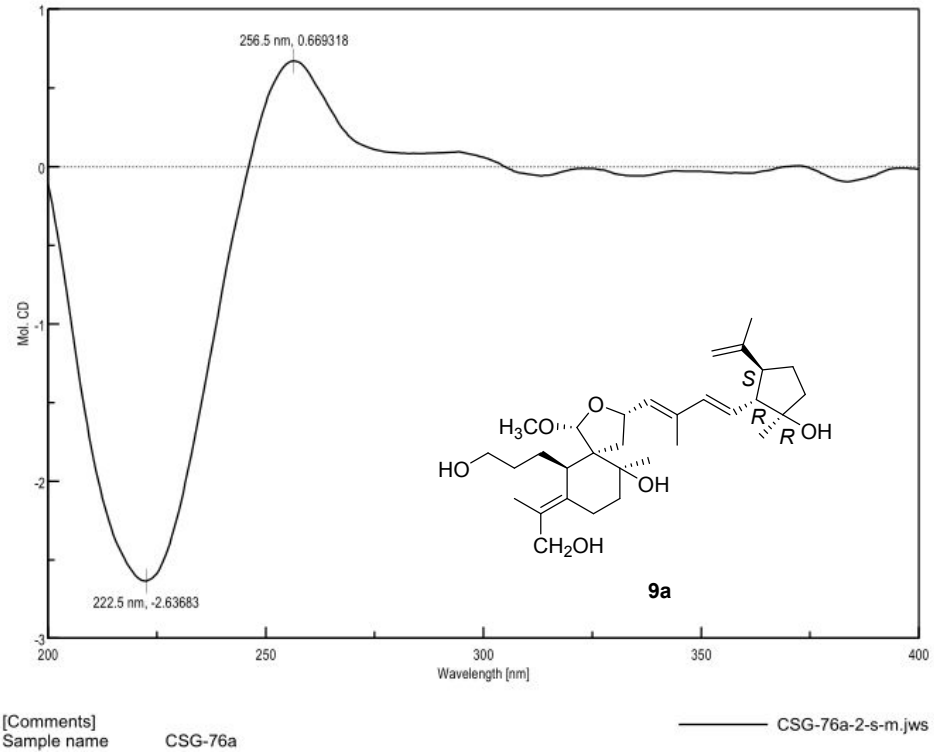


Figure S110. TIC and PDA spectra of compound **6** in LC-MS.

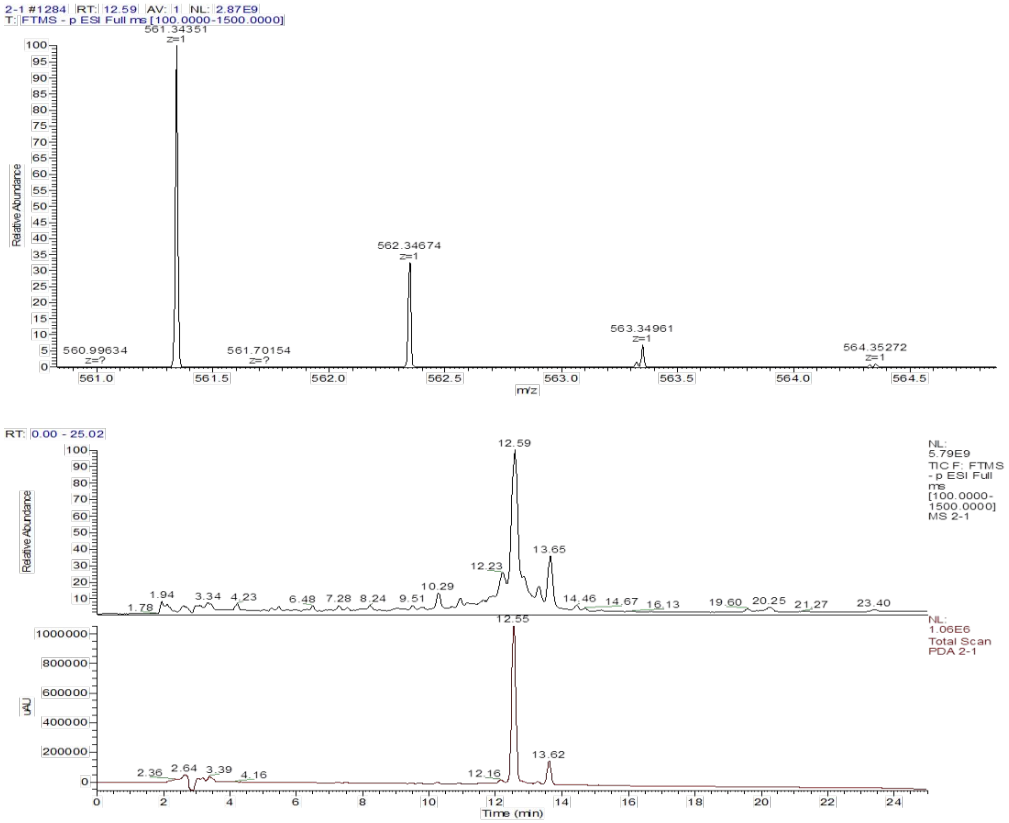


Figure S111. TIC and PDA spectra of compound **7** in LC-MS.

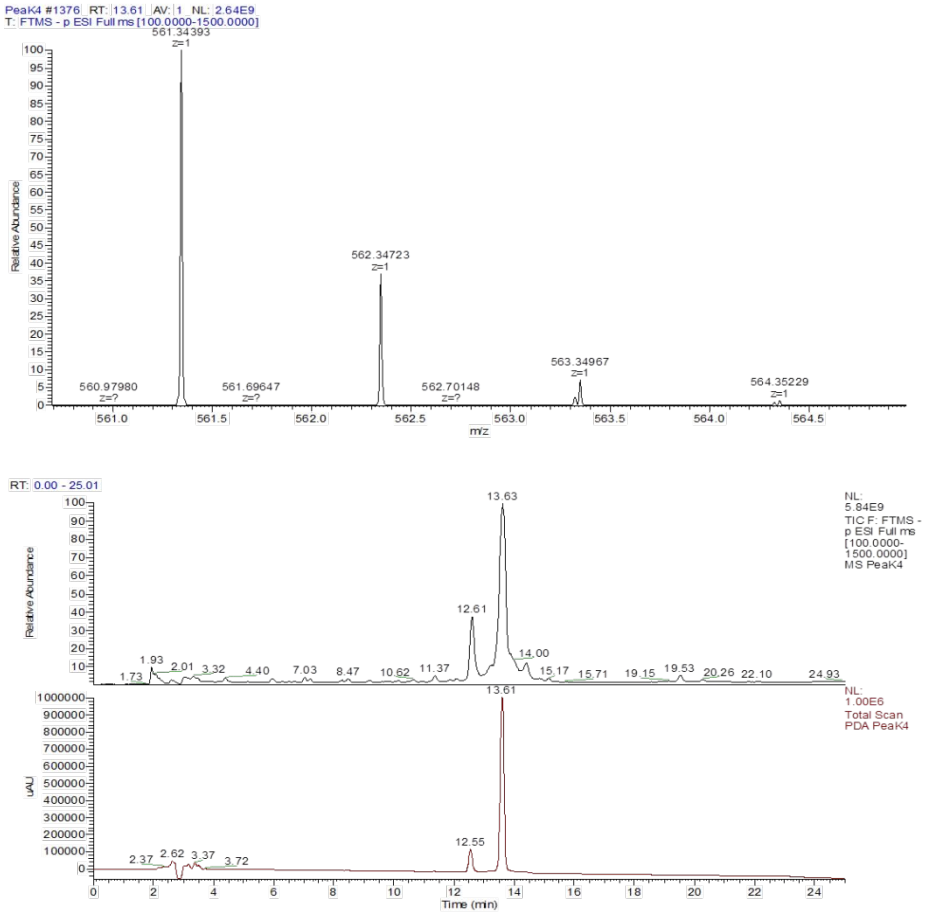


Figure S112. TIC and PDA spectra of compound **10** in LC-MS.

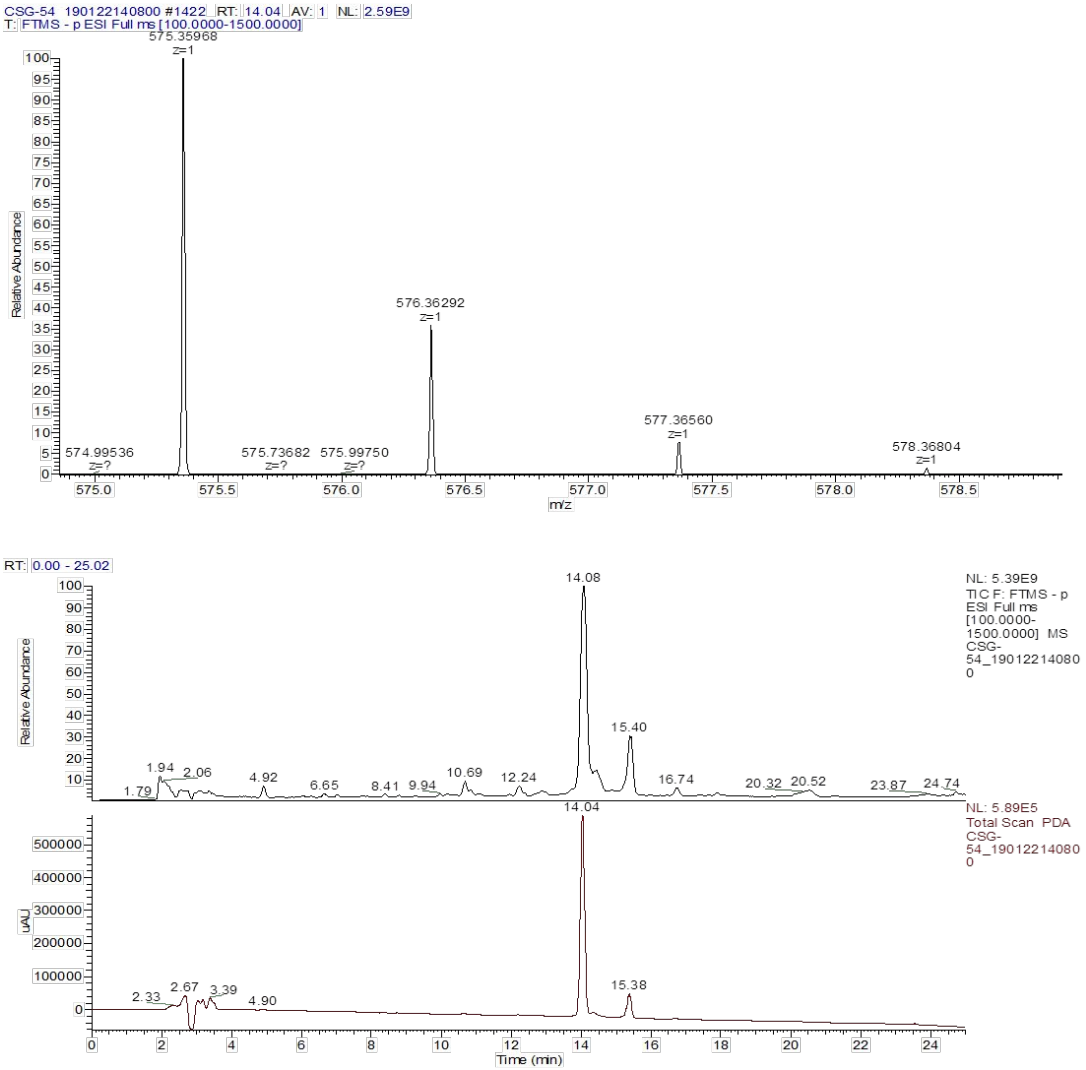
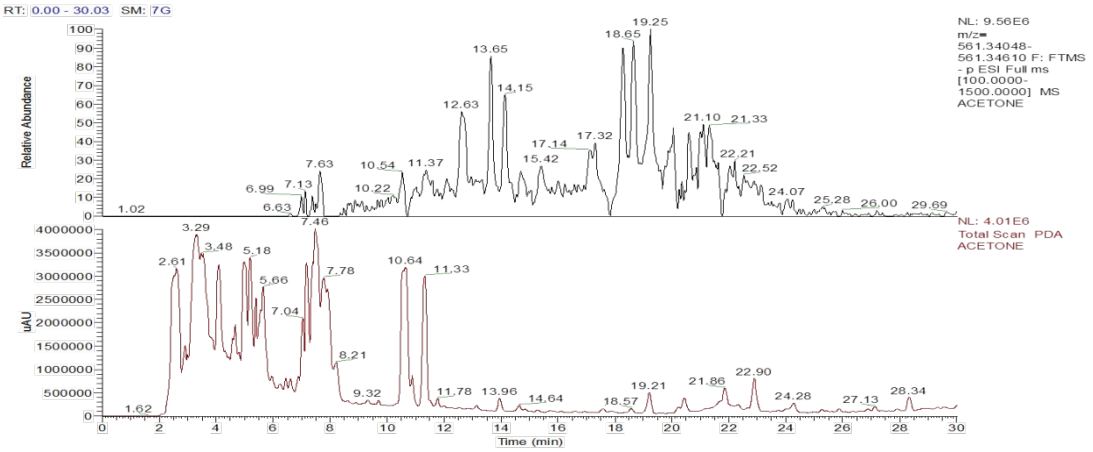
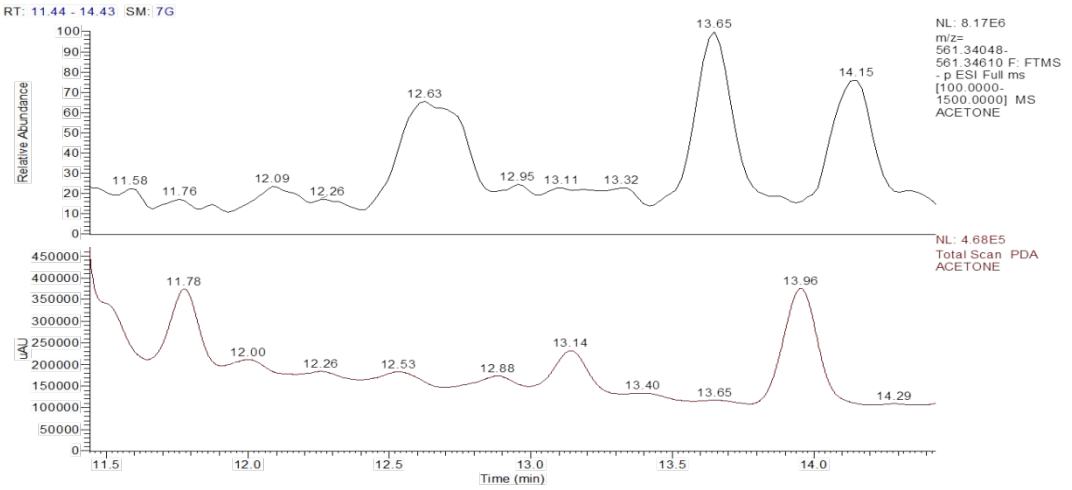
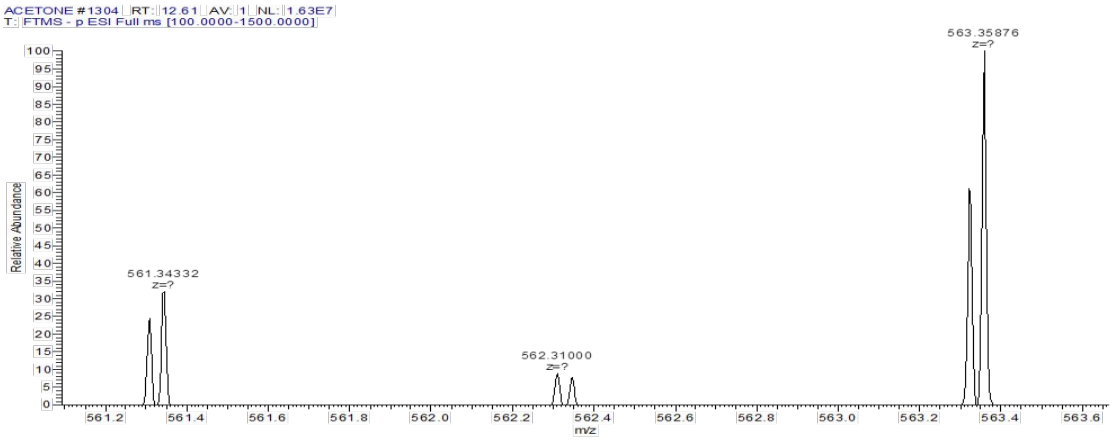


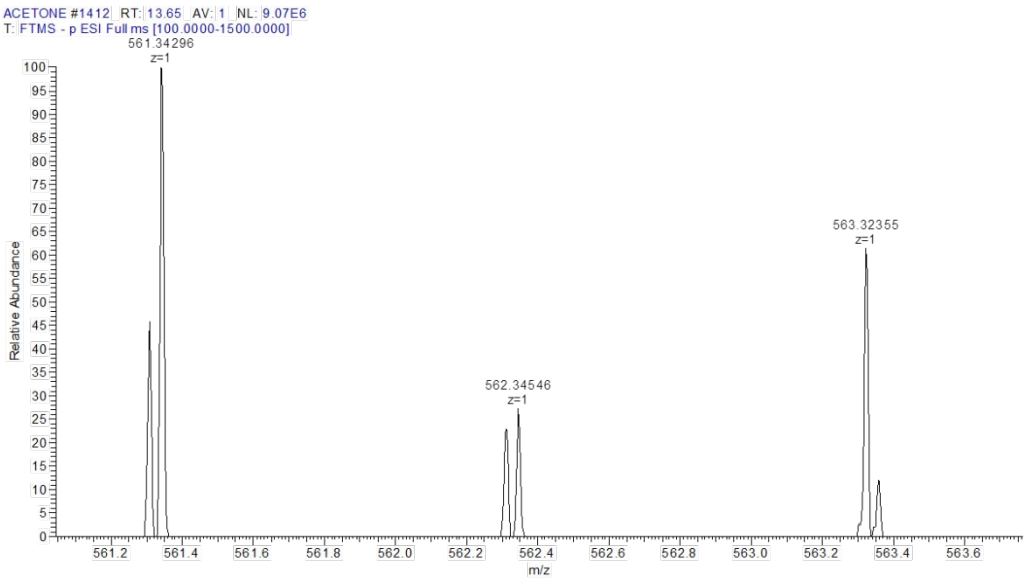
Figure S113. EIC and PDA spectra of compounds **6** and **7** in the total acetone extract in LC-MS.







m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
561.34332	561.34329	0.05	8.5	C32 H49 O8	M+HCOO



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
561.34296	561.34329	-0.59	8.5	C32 H49 O8	M+HCOO

Figure S114. EIC and PDA spectra of compound **10** in the total acetone extract in LC-MS.