Supporting Information

Asperones A-E, Five Dimeric Polyketides with New Carbon Skeletons from the Fungus *Aspergillus* sp. AWG 1-15

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1. Experimental details

1.1 General experiment procedures.

Optical rotations were determined with a JASCO P-1020 polarimeter. UV spectra were performed on a Shimadzu UV-2450 spectrophotometer. ECD spectrum was measured on a JASCO 810 spectropolarimeter. NMR spectra were obtained with a Bruker AV-600 and AV-500 spectrometer. Chemical shifts are stated relative to TMS and are expressed as δ (ppm) with coupling constants in Hz. ESI and HRESI mass spectra were recorded on an Agilent 1100 series LC-MSD-Trap-SL mass analyzer and an Agilent 6520B Q-TOF mass instrument, respectively. Column chromatography was performed on silica gel (100-200, and 200-300 mesh, Qingdao Marine Chemical Inc., Qingdao, China), ODS (40-63 μm, FuJi, Japan), Sephadex LH-20 (Pharmacia, Sweden). Preparative HPLC was carried out using an SHMADZU LC-6AD series instrument with a Shim-park RP-C_{18} column (20×200 mm) and a SHMADZU SPD-20A detector. GF254 plates (Qingdao Marine Chemical Inc., Qingdao, China) were used for TLC. Fractions were monitored by TLC, and the spots were visualized by heating the silica gel plates after spraying with 10% H_2SO_4 in EtOH.

1.2 Fungal material.

The fungus was obtained from the intestine of centipede by plate coating method, which was collected from the campus of China Pharmaceutical University, Nanjing, Jiangsu, People's Republic of China, in April 2013. The isolated strain was identified as *Aspergillus* sp. on the basis of the morphological method and reinforced by 18S rDNA and internal transcribed spacer (ITS) sequences with 99% identity to the known Aspergillus sp. (GenBank accession no. E9J41N5Z013).

1.3 Fermentation and isolation.

The strain was cultured on potato dextrose agar (PDA) at 28 °C for 7 days. Then two pieces of the agar (about 1.0 cm3) were added to an Erlenmeyer flask (500 mL) with 200 mL of potato dextrose liquid medium, and the flask was incubated on a rotary shaker at 28 °C and 150 rpm for 5 days to prepare seed culture. Solid fermentation was carried out in 80 Erlenmeyer flasks (2L), previously sterilized by autoclaving, each containing 400 g rice, 0.4g $CuSO_4$•$5H_20$, and 400 mL distilled water. All flasks were incubated at 28 °C for 40 days. The solid cultures were extracted with EtOAc three times at room temperature. The solvent was removed under reduced pressure to yield 450 g crude extract. The crude extract (450 g) was subjected to silica gel column chromatography (CC) eluting with a mixture of petroleum ether (60-90 °C) and EtOAc (50:1 to 0:1) with increasing polarity to yield eight fractions A1-A12, based on TLC.

Fr. A4 (120.0 g) was fractionated with repeated CC on a silica gel eluting with petroleum ether (60-90 °C) and EtOAc (10:1 to 0:1) with increasing polarity to yield seven subfractions A4.1-A4.7, based on TLC. Fr. A4.5 (27.5 g) was further fractionated with MCI eluting with MeOH and H_2O (30:70 to 100:0) to give twenty-three subfractions A4.5.1-A4.5.21. Fr. A4.5.10 (170.0 mg) was separated by preparative HPLC with MeOH-H_2O (65:35) to yield compound **1** (48.0 mg). Fr. A4.5.15 (97.5 mg) was separated by preparative HPLC with MeOH-H_2O (70:30) to yield compound **2** (24.8 mg). Fr. A2 (80.0 g) was fractionated with repeated CC on a silica gel eluting with petroleum ether (60-90 °C) and EtOAc (10:1 to 1:1) with increasing polarity to yield seven subfractions A2.1-A2.13, based on TLC. Fr. A2.5 (13.5 g) was further fractionated with ODS

eluting with MeOH and H_2O(30:70 to 100:0) to give twenty-three subfractions A2.5.1-A2.5.23. A2.5.20 (27.5 mg) was separated by preparative HPLC with CH_3CN-H_2O (65:35) to yield compound **3** (10.5 mg). A2.5.17 (34.5 mg) was separated by preparative HPLC with MeOH-H_2O (80:20) to yield compound **4** (3.4 mg) and compound **5** (4.1 mg).

Compound 1 : colorless oil; [α]25 D +49 (*c* 0.1, MeOH); UV (MeOH) (log ε) λ_{max} 233 (3.72), 280 (3.45) nm; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 211 (- 0.18), 223 (+0.25), 248 (+1.87), 271 (+2.11), 302 (-2.23) nm; HR-ESI-MS *m/z* 495.1990 $[M + Na]^+$ (calcd for $C_{26}H_{32}O_8Na$ 495.1995); ^1H NMR and ^{13}C NMR data, see Table S1.

Compound 1A: colorless needle; HR-ESI-MS *m/z* 523.2304 $[M + Na]^+$ (calcd for $C_{28}H_{36}O_8Na$ 523.2308); ^1H NMR and ^{13}C NMR data, see Table S1.

Compound 2: colorless oil; [α]25 D +48 (*c* 0.1, MeOH); UV (MeOH) (log ε) λmax 231 (3.67), 283 (3.42) nm; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 207 (-1.85), 228 (+0.05), 245 (+2.16), 266 (-1.13), 296 (+0.54), 328 (-0.54) nm; HR-ESI-MS *m/z* 495.1988 $[M + Na]^+$ (calcd for $C_{26}H_{32}O_8Na$ 495.1995); ^1H NMR and ^{13}C NMR data, see Table S2.

Compound 2A: colorless needle; HR-ESI-MS *m/z* 523.2307 $[M + Na]^+$ (calcd for $C_{28}H_{36}O_7Na$ 523.2308); ^1H NMR and ^{13}C NMR data, see Table S2.

Compound 3: white amorphous powders; [α]25 D +126 (*c* 0.1, MeOH); UV (MeOH) (log ε) λ_{max} 231 (3.59) nm; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 211 (+1.54), 245 (-0.70), 267 (-0.10), 320 (+0.08) nm; HR-ESI-MS *m/z* 393.2034 $[M + Na]^+$ (calcd for $C_{23}H_{30}O_4Na$ 393.2042); ^1H NMR and ^{13}C NMR data, see Table S3.

Compound 4: colorless oil; [α]25 D -15 (*c* 0.1, MeOH); UV (MeOH) (log ε) λmax 231 (3.63) nm; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 212 (+1.48), 239 (-0.94), 301 (-0.41), 344 (+0.13) nm; HR-ESI-MS *m/z* 393.2037 $[M + Na]^+$ (calcd for $C_{23}H_{30}O_4Na$ 393.2042); ^1H NMR and ^{13}C NMR data, see Table S4.

Compound 5: colorless oil; [α]25 D -111 (*c* 0.1, MeOH); UV (MeOH) (log ε) λmax 245 (3.64), nm; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 223 (-0.81), 310 (+0.35), 341 (-0.06) nm; HR-ESI-MS *m/z* 395.2190 $[M + Na]^+$ (calcd for $C_{23}H_{32}O_4Na$ 395.2198); ^1H NMR and ^{13}C NMR data, see Table S5.

1.4 X-ray crystallographic analysis

1.4.1 Compound **1A**

Colorless needle crystals of **1A** were obtained from MeOH/H_2O (10:1). Crystallographic data for **1A** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CDCC 1573433). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. [fax (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk]. Some details as follows:

Computing details: Cell refinement: SAINT v8.34A (Bruker, 2013); data reduction: SAINT v8.34A (Bruker, 2013); program(s) used to solve structure: ShelXT (Sheldrick, 2015); program(s) used to refine structure: SHELXL (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov et al., 2009); software used to prepare material for publication: Olex2 (Dolomanov et al., 2009).

$C_{28}H_{36}O_8 \cdot H_2O$	D_x = 1.224 Mg m^{-3}
M_r = 518.58	Cu *K*a radiation, l = 1.54178 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 9961 reflections
a = 8.3949 (9) Å	q = 3.5–71.0°
b = 15.0525 (16) Å	m = 0.75 mm^{-1}
c = 22.267 (2) Å	*T* = 173 K
V = 2813.7 (5) Å^3	Block, colourless
Z = 4	0.28 × 0.15 × 0.12 mm
F(000) = 1112	
Bruker APEX-II CCD	5086 reflections with *I* > 2s(*I*)
diffractometer	
f and w scans	R_{int} = 0.043
Absorption correction: multi-scan *SADABS2014*/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.0899 before and 0.0582 after correction. The Ratio of minimum to maximum transmission is 0.8970. The l/2 correction factor is 0.00150.	q_{max} = 71.0°, q_{min} = 3.5°
T_{min} = 0.676, T_{max} = 0.753	*h* = -9®9
33212 measured reflections	*k* = -18®18
5259 independent reflections	*l* = -26®26
Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2s(F^2)]$ = 0.033	$w = 1/[s^2(F_o^2) + (0.052P)^2 + 0.3603P]$
	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.087	$(D/s)_{max}$ < 0.001
S = 1.05	Dñ$_{max}$ = 0.16 e Å^{-3}
5259 reflections	Dñ$_{min}$ = -0.16 e Å^{-3}
346 parameters	Absolute structure: Flack x determined using 2129 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
0 restraints	Flack parameter: -0.02 (4)

1.4.2 Compound **2A**

Colorless needle crystals of **2A** were obtained from MeOH/H_2O (10:1). Crystallographic data for **2A** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CDCC 1548345). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre,

12, Union Road, Cambridge CB2 1EZ, U.K. [fax (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk]. Some details as follows:

Identification code	cu_dm17260_0m
Empirical formula	C28 H36 O8
Formula weight	500.57
Temperature	273(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P 1
Unit cell dimensions	a = 13.9860(8) Å; a= 98.119(3)°.
	b = 14.0190(8) Å; b= 91.053(3)°.
	c = 28.0285(13) Å; g = 90.157(3)°.
Volume	5439.5(5) Å3
Z	8
Density (calculated)	1.222 Mg/m3
Absorption coefficient	0.731 mm-1
F(000)	2144
Crystal size	0.200 x 0.160 x 0.130 mm3
Theta range for data collection	3.160 to 66.500°.
Index ranges	-16<=h<=15, -16<=k<=16, -33<=l<=32
Reflections collected	43801
Independent reflections	24086 [R(int) = 0.0623]
Completeness to theta = 67.679°	92.80%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.4450
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	24086 / 763 / 2665
Goodness-of-fit on F2	1.147
Final R indices [I>2sigma(I)]	R1 = 0.1102, wR2 = 0.2928
R indices (all data)	R1 = 0.1592, wR2 = 0.3537
Absolute structure parameter	0.0(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.802 and -0.451 e.Å-3

1.5 Synthesis of 1A from 1.

The substrate of **1** (10.0 mg) was dissolved in toluene/methanol (4:1, 1.0 mL), and the solution was treated with TMS-diazomethane (2mol/L in n-hexane, 75.0μL) for 30 min. The solvent and the volatile reagent were removed under a reduced pressure. The residue was isolated by HPLC with MeOH-H_2O (70:30) to yield compound **1A** (9.2 mg).

1.6 Synthesis of 2A from 2.

The substrate of **1** (8.0 mg) was dissolved in toluene/methanol (4:1, 1.0 mL), and the solution

was treated with TMS-diazomethane (2mol/L in n-hexane, 85.0μL) for 30 min. The solvent and the volatile reagent were removed under a reduced pressure. The residue was isolated by HPLC with MeOH-H_2O (75:25) to yield compound **2A** (7.1 mg).

1.7 Computational Section

The calculation of ECD have been an important method in determining the absolute configurations of natural chiral compounds. Systematic conformation analyses for compound **2** were applied via Confab using the MMFF94 force field calculation. Conformers with Boltzmann distribution (Table S6 and Figure S63) over 1% were chosen as the beginning for ECD calculations and only one conformer was chosen for compound **2**. The further re-optimized was achieved by DFT calculations at the B3LYP/6-31+G (d, p) level. ECD computations were performed by means of the TD-SCF method under B3LYP/6-311+G (d, 2p) level with-12 nm UV correction ($\sigma = 0.25$) for compound **2**.

For the rigid structures of **3**-**5**, these geometries generated based on NMR data were optimized using MM2. The corresponding minimum geometries were further re-optimized by DFT calculations at the B3LYP/6-31+G (d, p) level. ECD computations were performed by means of the TD-SCF method under B3LYP/6-311+G (d, 2p) level with -16 nm UV correction ($\sigma = 0.30$) for compound **3**, -16 nm UV correction ($\sigma = 0.27$) for compound **4**, and -30 nm UV correction ($\sigma = 0.30$) for compound **5**.

1.8 Biological activity

1.8.1 NO production bioassay

The RAW264.7 cell line was purchased from the Chinese Academic of Sciences. The cells were cultured in DMEM containing 10% FBS with penicillin (100 U/mL) and streptomycin (100 U/mL) at 37 ºC in a humidified atmosphere with 5% CO_2. The cells were allowed to grow in 96-well plates with 1 × 105 cells/ well to treat test compounds. After being incubated for 2 h, the cells were treated with 100 ng/mL of LPS for 18 h. Nitrite in culture media was measured to assess NO production using Griess reagent. The absorbance at 540nm was measured on a microplate reader. N-monomethyl-L-arginine was used as the positive control. Cytotoxicity was determined by the MTT method, after 48 h incubation with test compounds. All the experiments were performed in three independent replicates. NG-Monomethyl-L-arginine (L-NMMA) as positive control, IC_{50} = 41.9 μM.

1.8.2 Antimicrobial assay

Broth microdilution method was used for determining the MIC of a pure compound according to the antimicrobial susceptibility testing standards of National Center for Clinical Laboratory Standards (NCCLS). The assays were carried out using sterile 96-well microtiter plates in triplicate. The test samples were first dissolved in DMSO, then the solutions were diluted with broth by a serial 2-fold method (DMSO < 1%). Fluconazole was used as the positive control for antifungal, amoxicillin for Gram-positive bacteria, and streptomycin for Gram-negative bacteria assays. Control wells were only incubated with medium to ensure the sterility. MIC value was defined as the drug concentration that caused 50% reduction of the microbial growth, which was obtained by the optical density measurement after incubation for 24 h.

2. Tables

Table S1. NMR data of Compounds **1** and **1A**

	1 [a]			**1A** [b]		
no.	δ_H	δ_C	HMBC（H → C）	δ_H	δ_C	HMBC（H → C）
1		57.3			57.2	
2		200.2			200.9	
3	3.78, d (7.2)	65.3	1, 2, 4, 5, 7'	3.69, d (7.4)	67.7	1, 2, 4, 5, 7'
4		191.1			191.3	
5		147.4			152.3	
6		142.1			156.8	
7	2.70, brs	42.3	1, 5, 6, 8, 10	2.73, brs	43.2	
8	4.25, brs	69.6		4.13,dq (9.2,6.1)	70.0	
9	1.20, d (5.7)	22.2	7, 8	1.25, d (6.1)	22.5	7, 8
10	1.40, d (7.2)	15.9	6, 7, 8	1.35, d (7.0)	17.4	6, 7, 8
11	1.26, s	13.8	1, 2, 6, 7'	1.29, s	13.7	1, 2, 6, 7'
2'		93.6			92.0	
3'		203.4			197.6	
4'		108.3			109.5	
5'		195.6			194.0	
6'		162.0			163.4	
7'	4.29, brs	51.5		4.26, brs	51.4	
8'	2.95, m	33.1	3, 4, 5', 7',9'	2.91, m	33.1	3, 4, 5', 7',9'
9'	1.05, d (7.2)	18.3	3, 7', 8'	1.13, d (7.2)	18.3	3, 4, 5', 7',9'
10'	1.58, s	22.0	2', 3', 11'	1.51, s	22.4	2', 3', 11'
11'	5.47, d (15.4)	123.0	2', 3', 10', 12', 13', 14'	5.47, d (15.5)	124.8	2', 3', 10', 12', 13', 14'
12'	6.24,dd (15.4, 10.1)	134.1	2', 11', 13', 14'	6.20,dd (15.5, 10.3)	132.7	2', 11', 13', 14'
13'	5.98, dd (15.4, 10.1)	127.2	11', 12', 14', 15'	5.96, dd (15.5, 10.3)	127.6	11', 12', 14', 15'
14'	5.89, dt (15.4, 6.3)	141.7	12', 13', 15', 16'	5.83, dt (15.5, 6.4)	140.5	12', 13', 15', 16'
15'	2.11, m	25.8	13', 14', 16'	2.10, m	25.8	13', 14', 16'
16'	1.00, t (7.5)	13.2	14', 15'	0.99, t (7.5)	13.3	14', 15'
5'-OCH_3				3.84, s	59.6	5
6'-OCH_3				3.85, s	52.1	6'

[a] ^1H (500 MHz) and ^{13}C (125 MHz) NMR Data of **1** in $CDCl_3$; [b] ^1H (600 MHz) and ^{13}C (150 MHz) NMR Data of **1** in $CDCl_3$.

Table S2. NMR data of Compounds **2** and **2A**

	2 [a]			**2A** [b]		
no.	δ_H	δ_C	HMBC（H → C）	δ_H	δ_C	HMBC（H → C）
1		58.0			57.6	
2		201.1			202.0	
3	3.79, d (7.7)	64.7	1, 2, 4, 5, 7'	3.68, d (7.7)	67.5	1, 2, 4, 5, 7'
4		191.1			191.6	
5		146.9			152.0	
6		141.2			154.7	
7	2.44, dq (12.3,7.0)	44.2	1, 5, 6, 8, 9, 10	2.47, dq (9.3,7.0)	44.8	1, 5, 6, 8, 9, 10
8	4.31,dq (12.3,6.4)	68.3	6, 7, 9, 10	4.13,dq (11.6,6.1)	69.4	7, 10
9	1.35, d (6.4)	22.7	7, 8	1.37, d (6.1)	23.2	7, 8
10	1.18, d (7.0)	15.5	6, 7, 8	1.14, d (6.8)	16.7	6, 7, 8
11	1.14, s	12.8	1, 2, 6, 7'	1.13, s	12.6	1, 2, 6, 7'
2'		94.0			92.6	
3'		203.4			197.5	
4'		108.1			109.4	
5'		196.2			194.6	
6'		162.4			164.2	
7'	4.46, (d, 4.7)	48.8	1, 2, 6, 5', 8', 9'	4.32, (d, 4.8)	48.7	1, 2, 6, 5', 8', 9'
8'	3.08, m	31.9	1, 3, 4, 5', 7', 9'	3.03, m	31.6	1, 3, 4, 5', 7', 9'
9'	1.05, d (7.3)	18.0	3, 7', 8'	1.12, d (7.2)	18.1	3, 7', 8'
10'	1.61, s	22.9	2', 3', 11'	1.51, s	23.2	2', 3', 11'
11'	5.46, d (15.4)	122.3	2', 3', 10', 12', 13', 14'	5.46, d (15.5)	124.3	2', 3', 10', 12', 13', 14'
12'	6.24,dd (15.4, 8.6)	134.1	2', 11', 13', 14'	6.21,dd (15.5, 9.9	132.9	2', 11', 13', 14'
13'	5.97, overlap	127.1	11', 12', 14', 15'	5.93, overlap	127.4	11', 12', 14', 15'
14'	5.96, overlap	141.8	12', 13', 15', 16'	5.91, overlap	140.5	12', 13', 15', 16'
15'	2.12, m	25.8	13', 14', 16'	2.11, m	25.8	13', 14', 16'
16'	1.02, t (7.5)	13.2	14', 15'	1.00, t (7.4)	13.3	14', 15'
5'-OCH_3				3.83, s	59.2	
6'-OCH_3				3.87, s	52.5	

[a] ^1H (500 MHz) and ^{13}C (125 MHz) NMR Data of **2** in $CDCl_3$; [b] ^1H (600 MHz) and ^{13}C (150 MHz) NMR Data of **2A** in $CDCl_3$.

Table S3. NMR data of Compound **3**

	3		
no.	δ_H	δ_C	HMBC (H → C)
1		149.5	
2		137.3	
3		197.4	
4		63.7	
5		205.8	
6	3.25, s	66.5	1, 2, 4, 5, 9, 4', 5', 6'
7	1.30, s	13.8	3, 4, 5, 7'
8	1.84, s	12.4	1, 2, 3
9	2.09, s	22.7	1, 2, 6
2'		83.2	
3'		213.0	
4'	2.43, d (17.5), a	45.8	6, 2', 3', 5', 6'
	2.69, d (17.5), b		6, 2', 3', 5', 6'
5'		82.4	
6'	1.64, t (13.7), a	39.4	4, 6, 4', 5', 7', 8'
	1.79, dd (13.7, 4.2), b		4, 6, 4', 5', 7', 8'
7'	2.26, m	37.3	3, 4, 5, 7, 5', 6', 8'
8'	0.92, d (6.8)	15.6	4, 6', 7'
9'	1.41, s	26.0	2', 3', 10'
10'	5.52, d (15.4)	130.9	2', 3', 9',11', 12'
11'	6.23, dd (15.4, 10.5)	130.4	2', 10', 12', 13'
12'	5.95, dd (15.4, 10.5)	128.0	10', 11', 13', 14'
13'	5.75, dt (15.4, 6.6)	138.5	11', 12', 14', 15'
14'	2.09, overlap	25.8	12', 13', 15'
15'	0.98, t (7.5)	13.5	13', 14'

^1H (600 MHz) and ^{13}C (150 MHz) NMR Data of **3** in $CDCl_3$.

Table S4. NMR data of Compound **4**

	4		HMBC (H → C)
no.		δ_C	
1		152.2	
2		135.8	
3		196.5	
4		63.9	
5		206.3	
6	3.40, s	67.3	1, 2, 4, 5, 9, 4', 5', 6'
7	1.23, s	13.8	3, 4, 5, 7'
8	1.92, s	12.2	1, 2, 3
9	2.26, s	23.5	1, 2, 6
2'		83.7	
3'		212.1	
4'	2.74, d (18.0), a	44.2	6, 2', 3', 5', 6'
	2.46, d (18.0), b		6, 2', 3', 5', 6'
5'		81.1	
6'	1.59, m, a	41.1	4, 6, 4', 5', 7', 8'
	1.85, t (13.7), b		4, 6, 4', 5', 7', 8'
7'	1.42, m	38.1	3, 4, 5, 7, 5', 6', 8'
8'	0.95, d (6.8)	16.0	4, 6', 7'
9'	1.35, s	25.0	2', 3', 10'
10'	5.52, d (15.4)	130.5	2', 3', 9',11', 12'
11'	6.27, dd (15.4, 10.4)	131.1	2', 10', 12', 13'
12'	6.00, dd (15.4, 10.4)	127.9	10', 11', 13', 14'
13'	5.81, dt (15.4, 6.6)	139.1	11', 12', 14', 15'
14'	2.12, m	25.9	12', 13', 15'
15'	1.02, t (7.4)	13.5	13', 14'

^{1}H (600 MHz) and ^{13}C (150 MHz) NMR Data of **4** in $CDCl_3$.

Table S5. NMR data of Compound **5**

	5		
no.	δ_H	δ_C	HMBC (H → C)
1		155.0	
2		134.6	
3		200.0	
4		50.1	
5	3.96, brs	76.0	1, 3, 4, 6, 7, 5', 7'
6	2.85, overlap	55.9	1, 2, 4, 5, 9, 4', 5', 6'
7	1.15, s	18.1	3, 4, 5, 7'
8	1.83, s	11.7	1, 2, 3
9	2.23, s	24.5	1, 2, 6
2'		81.3	
3'		215.7	
4'	2.86, overlap	47.6	6, 2', 3', 5', 6'
5'		79.3	
6'	1.41, m, a	41.3	4, 6, 4', 5', 7', 8'
	1.47, t (13.5), b		4, 6, 4', 5', 7', 8'
7'	1.83, overlap	30.8	3, 4, 5, 7, 5', 6', 8'
8'	0.80, d (6.7)	15.9	4, 6', 7'
9'	1.30, s	25.1	2', 3', 10'
10'	5.51, d (15.4)	132.3	2', 3', 9',11', 12'
11'	6.34, dd (15.4, 10.6)	130.2	2', 10', 12', 13'
12'	6.01, dd (15.4, 10.6)	128.3	10', 11', 13', 14'
13'	5.78, dt (15.4, 6.7)	138.0	11', 12', 14', 15'
14'	2.11, m	25.8	12', 13', 15'
15'	1.01, t (7.6)	13.5	13', 14'

^{1}H (600 MHz) and ^{13}C (150 MHz) NMR Data of **1** in $CDCl_3$.

Table S6. Energies of the conformers with Boltzmann distribution over 1% of compound **2**

No.	Energie(kcal/mol)	%
1	108.7379	99.8
2	112.6166	0.14
3	113.3952	0.04
4	113.9977	0.01
5	114.8257	0
6	115.7153	0
7	115.8021	0
8	115.9644	0

3. Figures

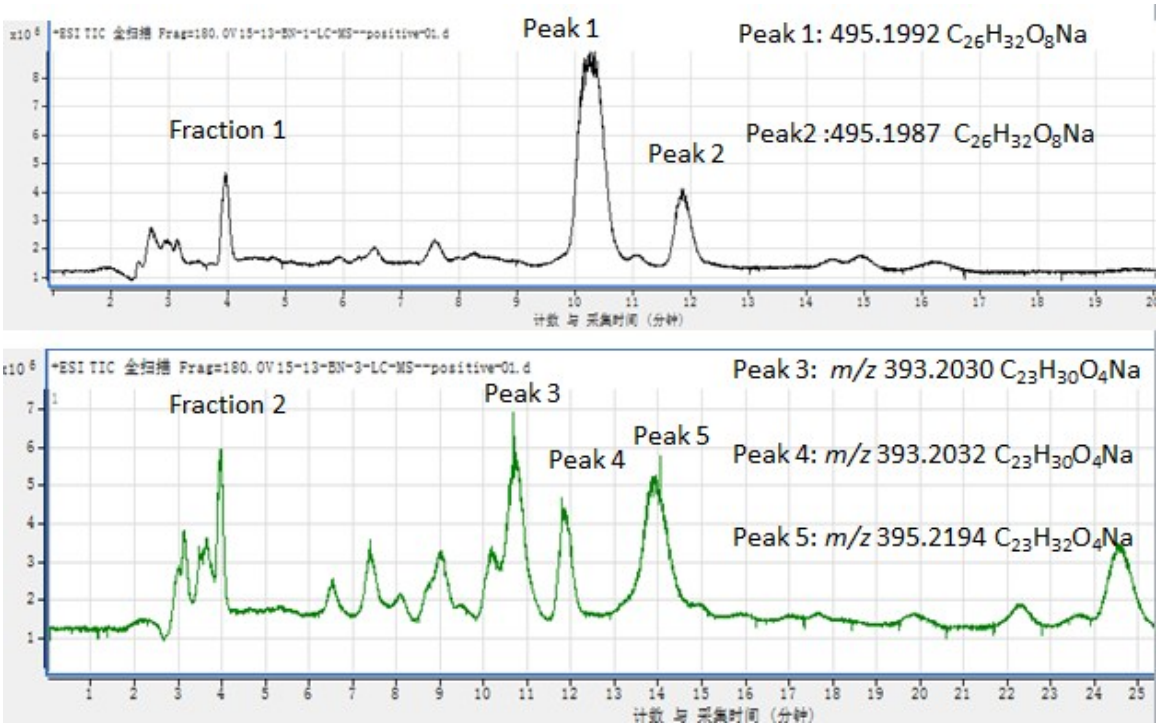


Figure S1. HPLC-ESI-MS spectrum of Fraction 1 and 2 .

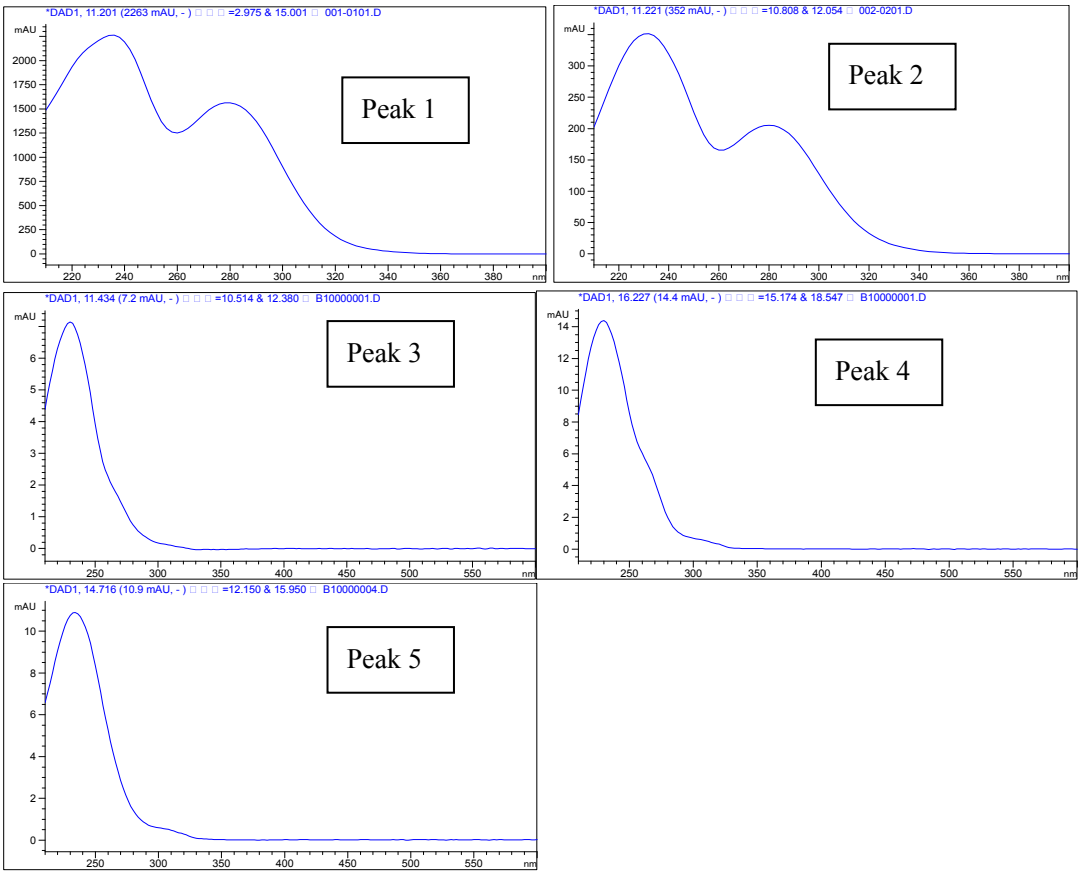


Figure S2. UV spectrum of peaks in Fractions 1 and 2 .

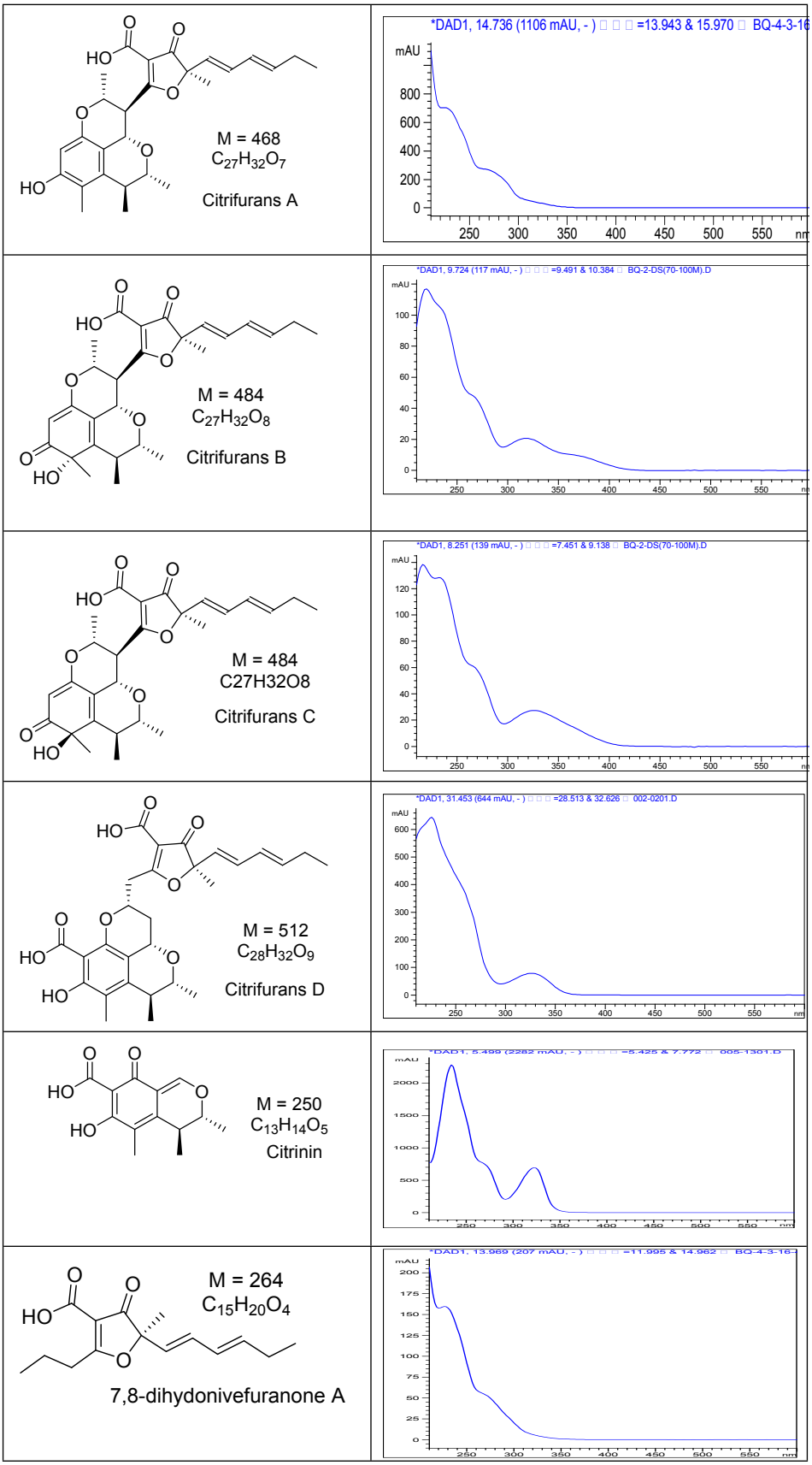


Figure S3. The structures and UV data of isolated compounds.

For compound of 1

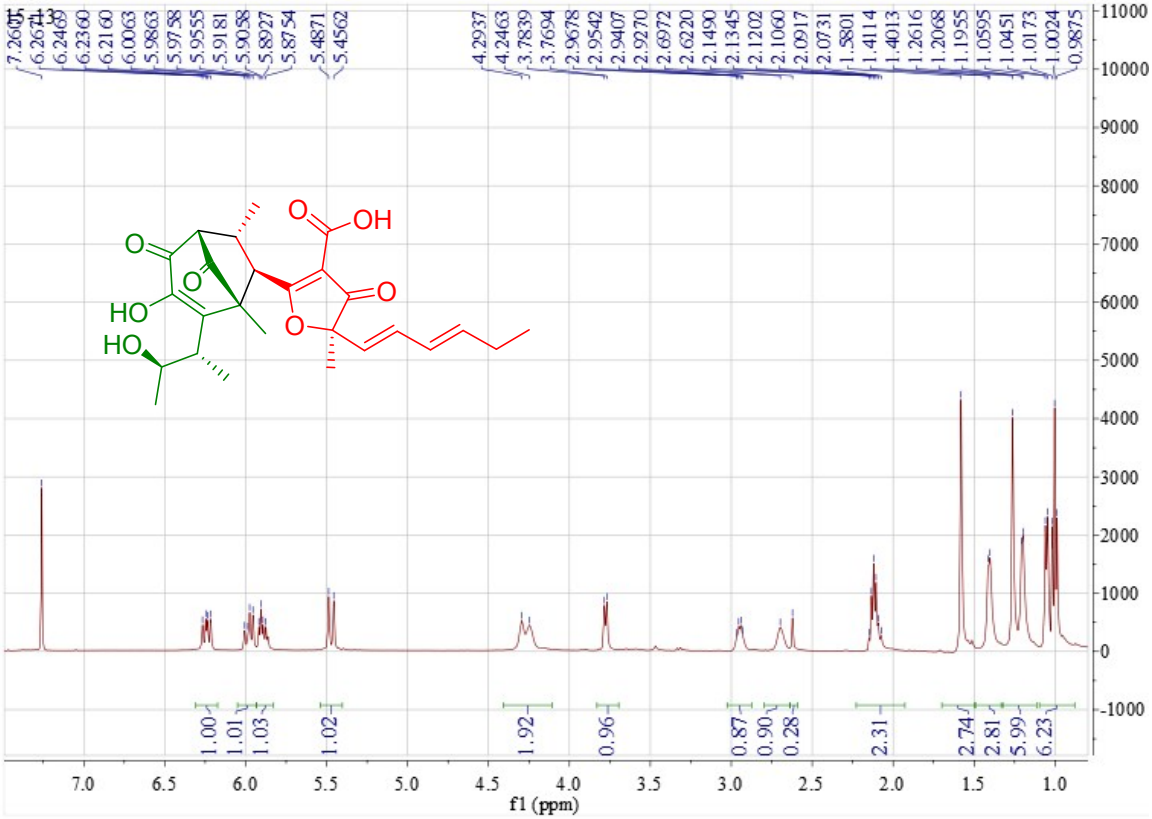


Figure S4. ^{1}H NMR spectrum of Compound **1** (500 MHz, $CDCl_3$)

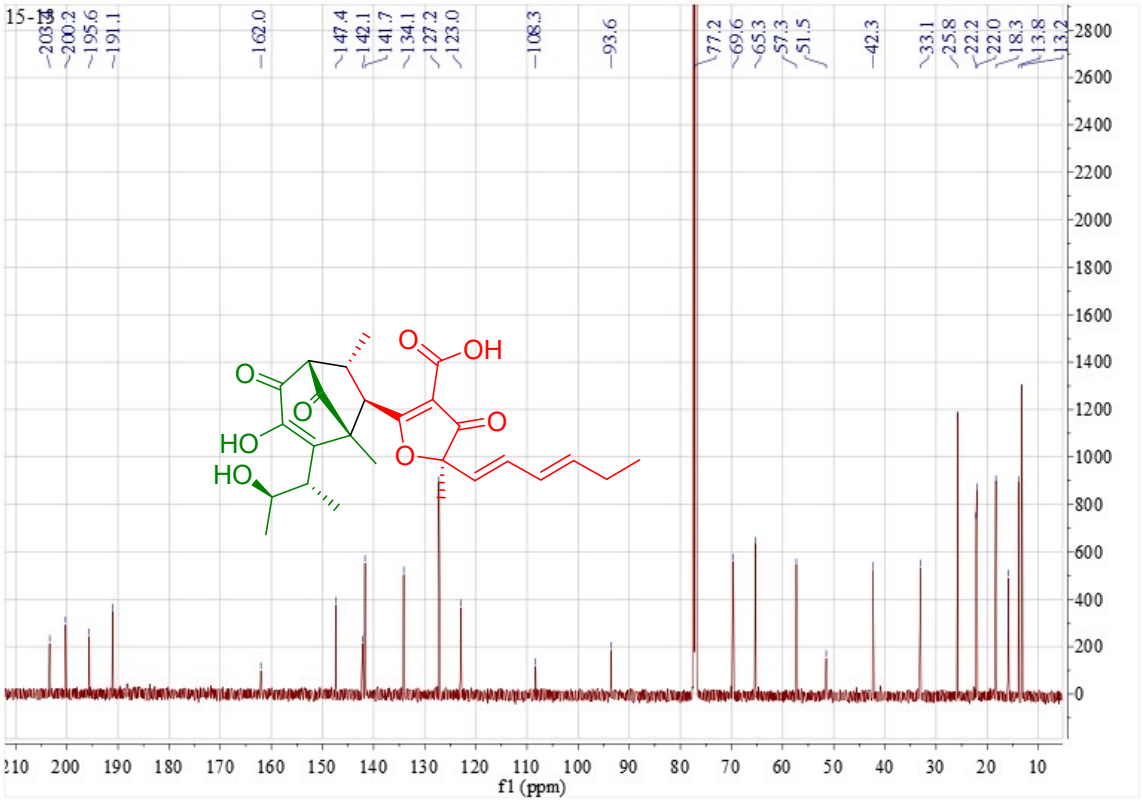


Figure S5. ^{13}C NMR spectrum of Compound **1** (125 MHz, $CDCl_3$)

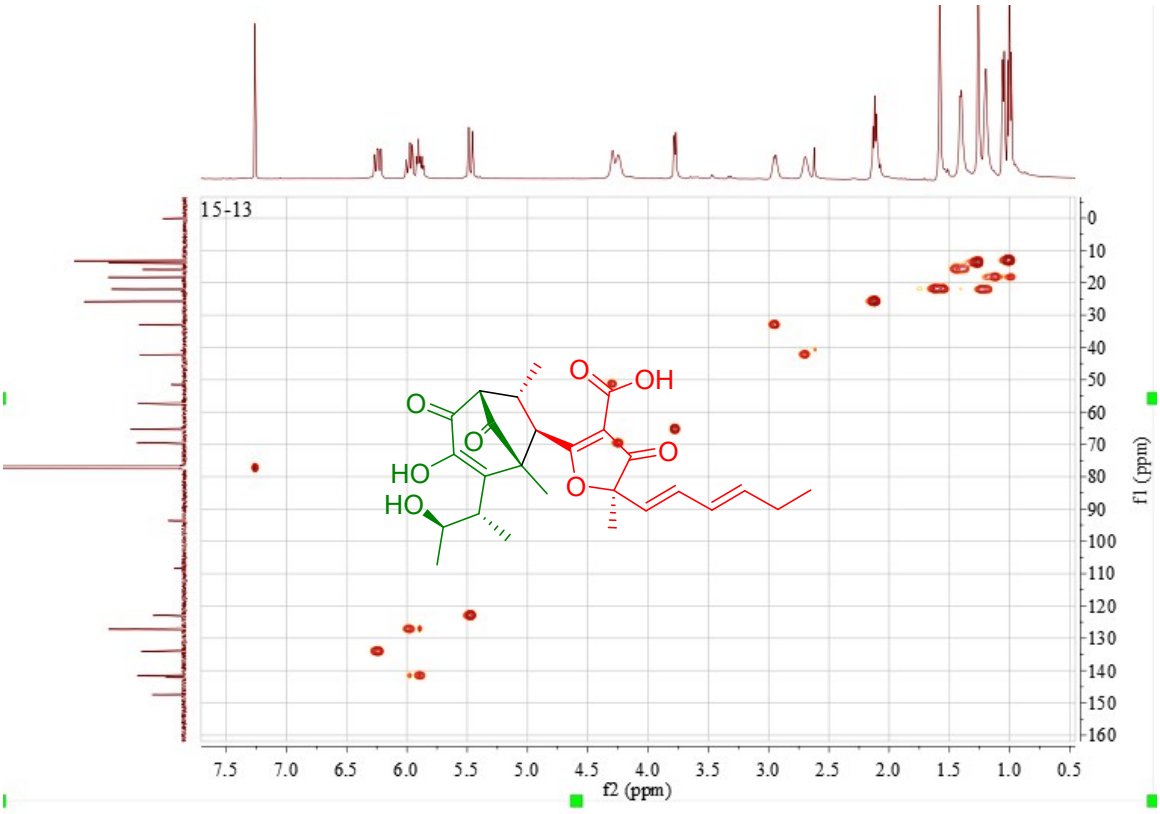


Figure S6. HSQC spectrum of Compound **1** (500 MHz, $CDCl_3$)

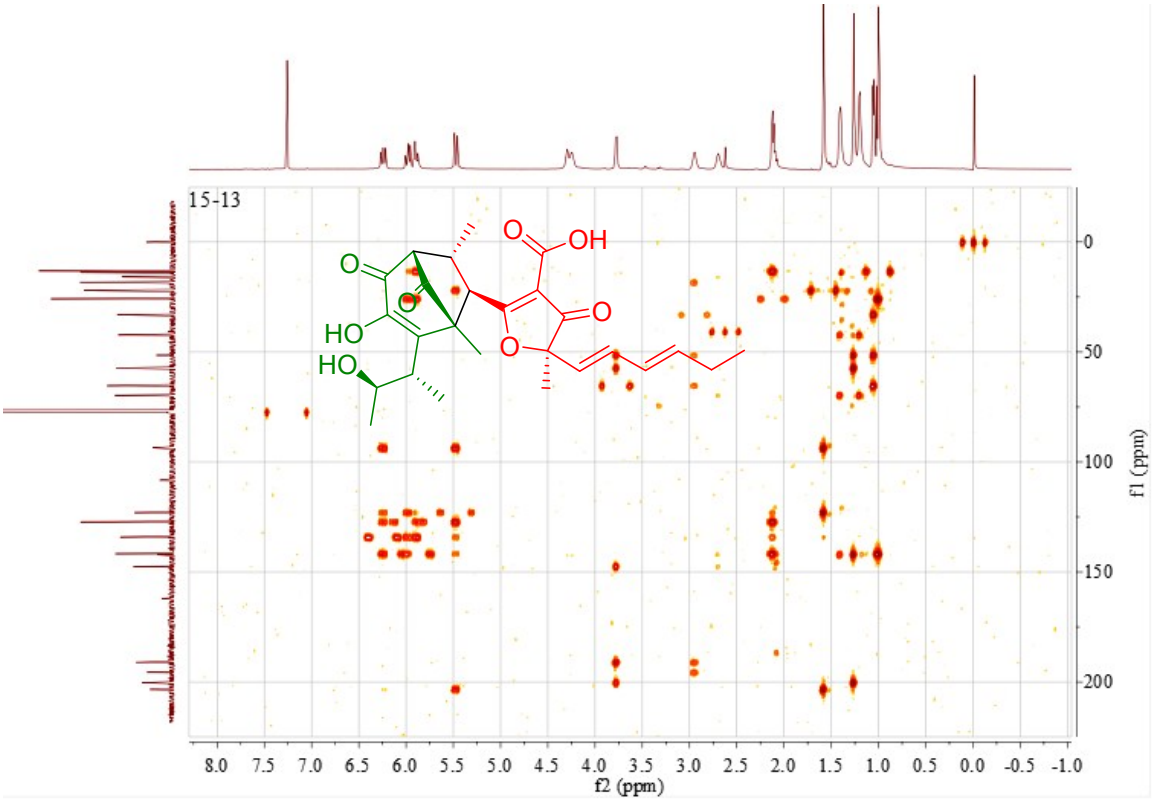


Figure S7. HMBC spectrum of Compound **1** (500 MHz, $CDCl_3$)

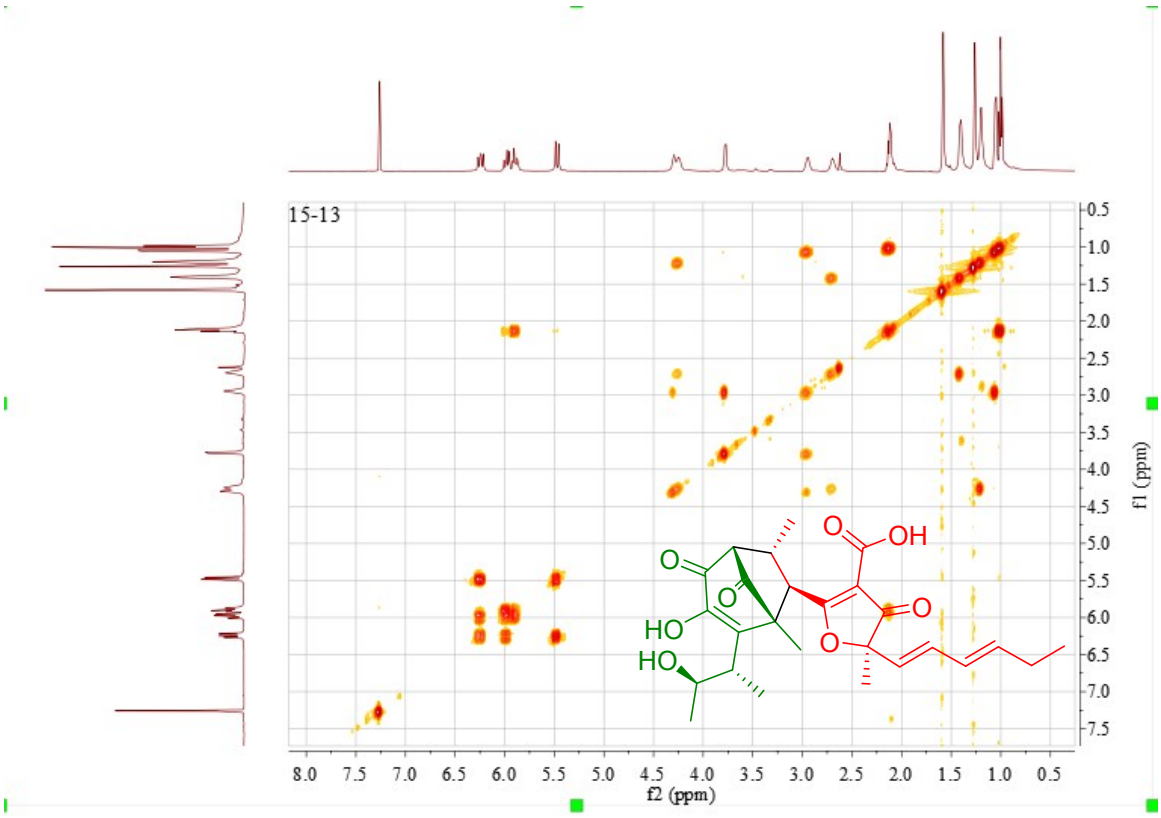


Figure S8. ^{1}H-^{1}H COSY spectrum of Compound **1** (500 MHz, $CDCl_3$)

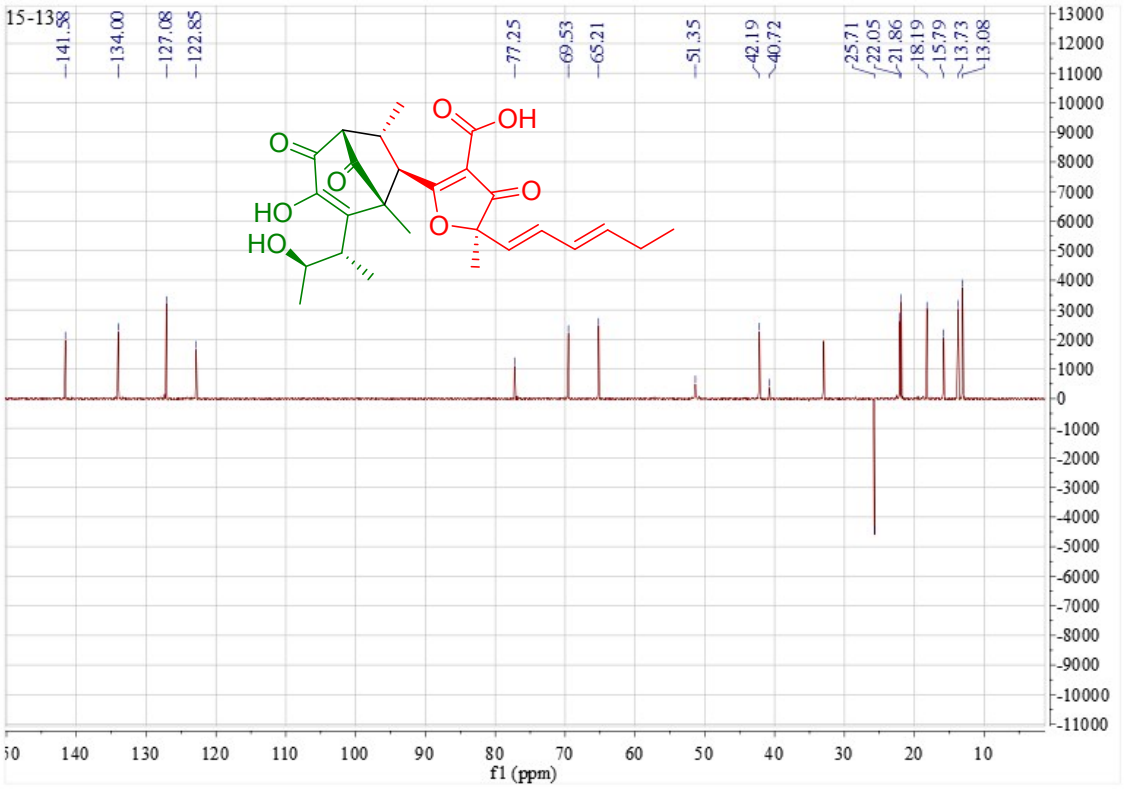


Figure S9. DEPT135 spectrum of Compound **1** (125 MHz, $CDCl_3$)

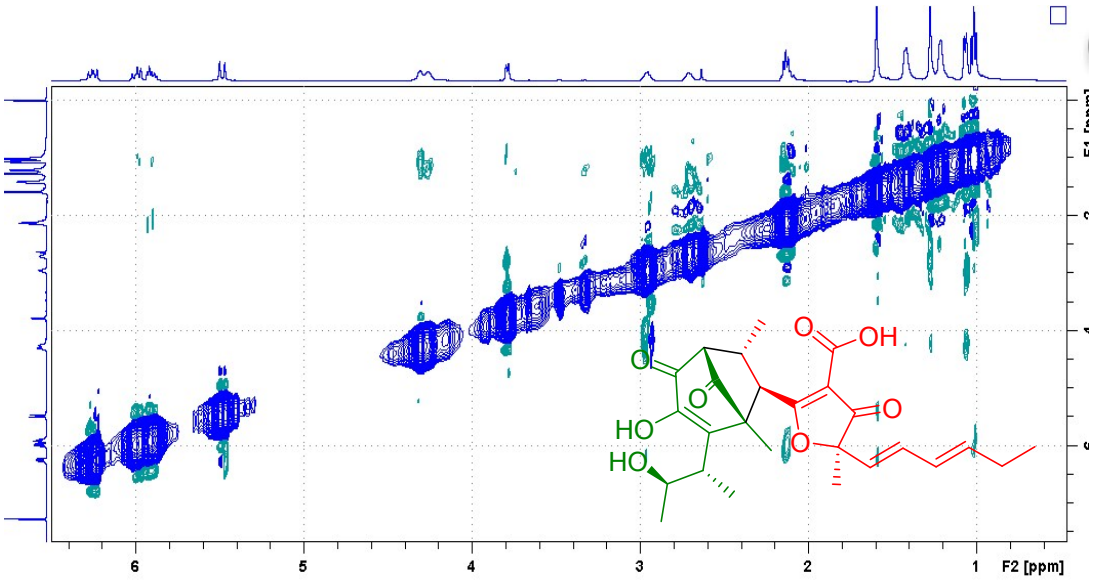
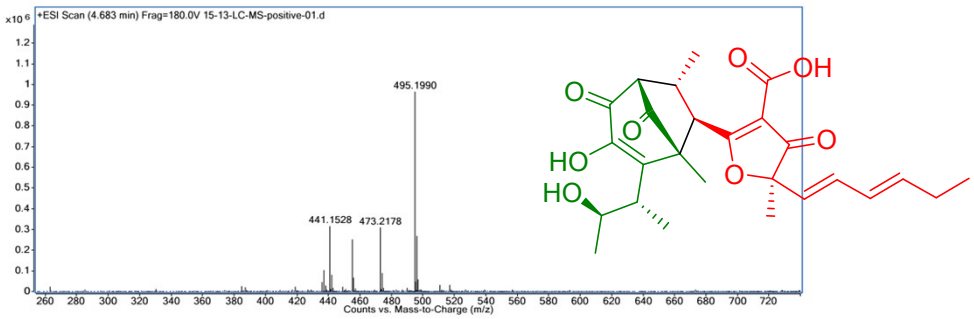
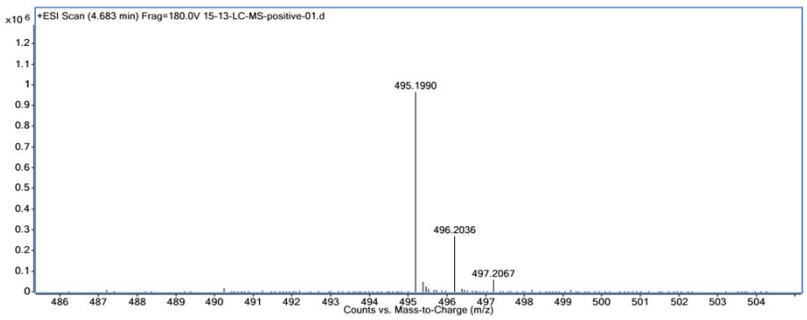


Figure S10 ROESY spectrum of Compound **1** (500 MHz, $CDCl_3$)

TCM-CPU HR-ESI-MS Display Report

Sample Name:	15-13	**Instrument:**	Agilent 6520B Q-TOF
Acq. Date:	09/05/2017	**Operator:**	Administrator





Elemental Composition Calculator

Target m/z:	495.1990	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C26H32NaO8		495.1989		-0.08	

Agilent Technologies

Figure S11. HRESIMS spectrum of Compound **1**

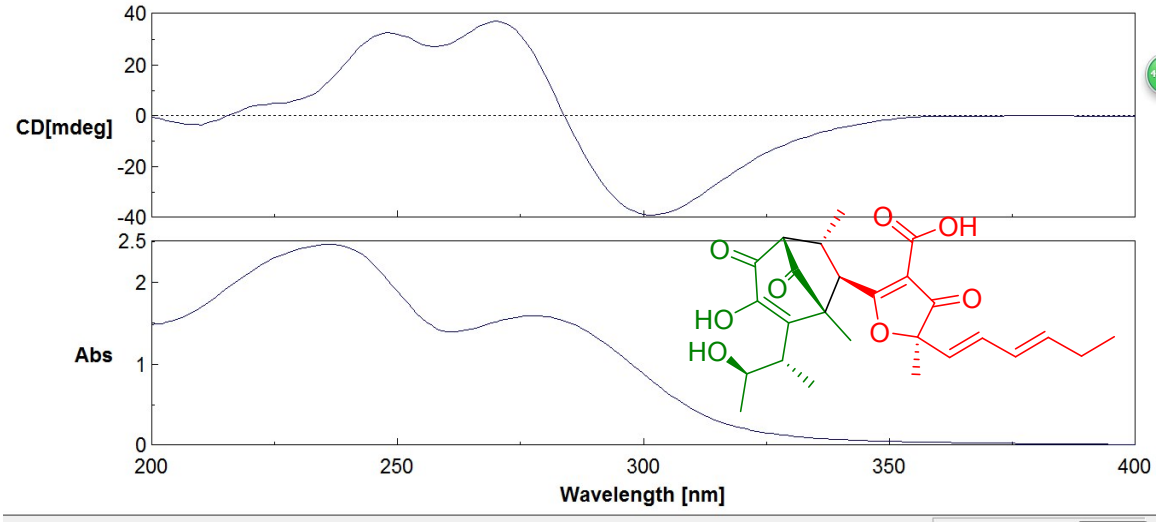


Figure S12. ECD spectrum of Compound **1**

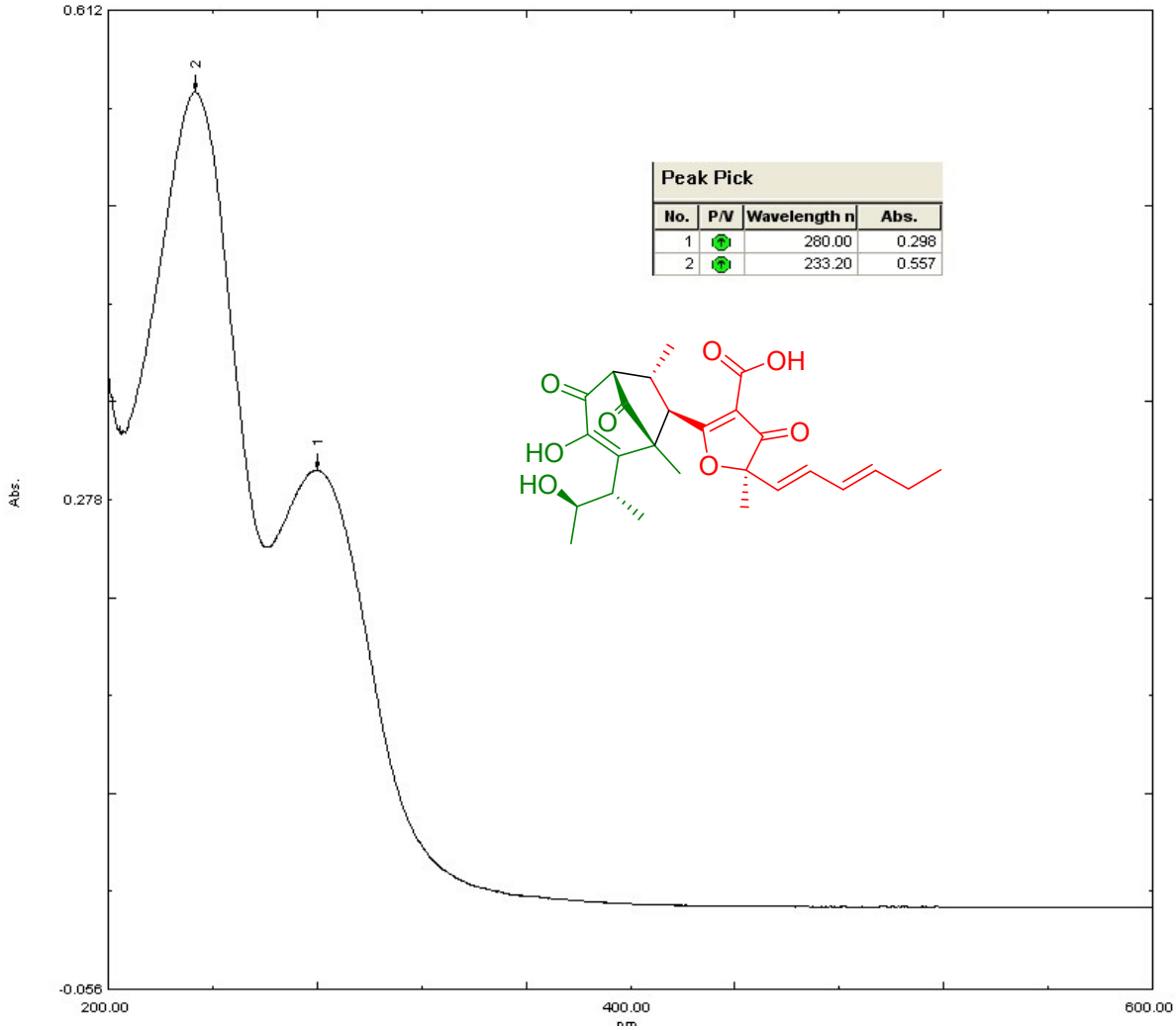


Figure S13. UV spectrum of Compound **1**

For compound of 1A

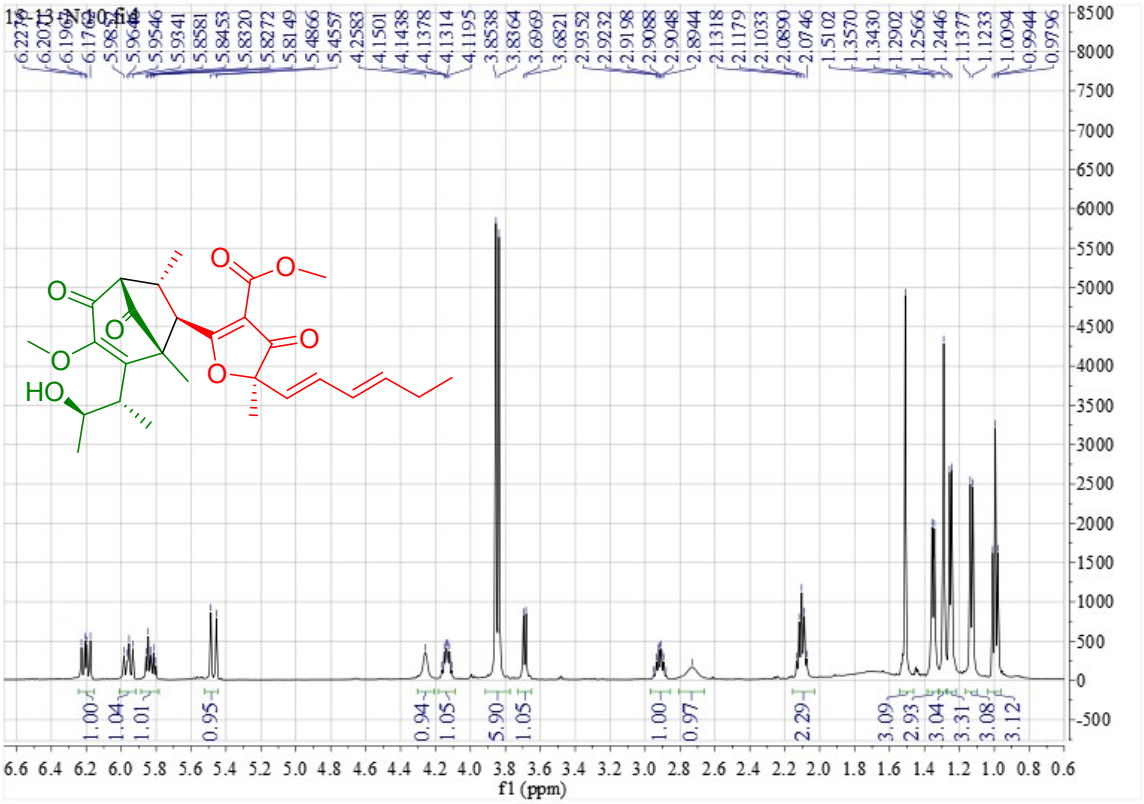


Figure S14. ^{1}H NMR spectrum of Compound **1A** (600 MHz, $CDCl_3$)

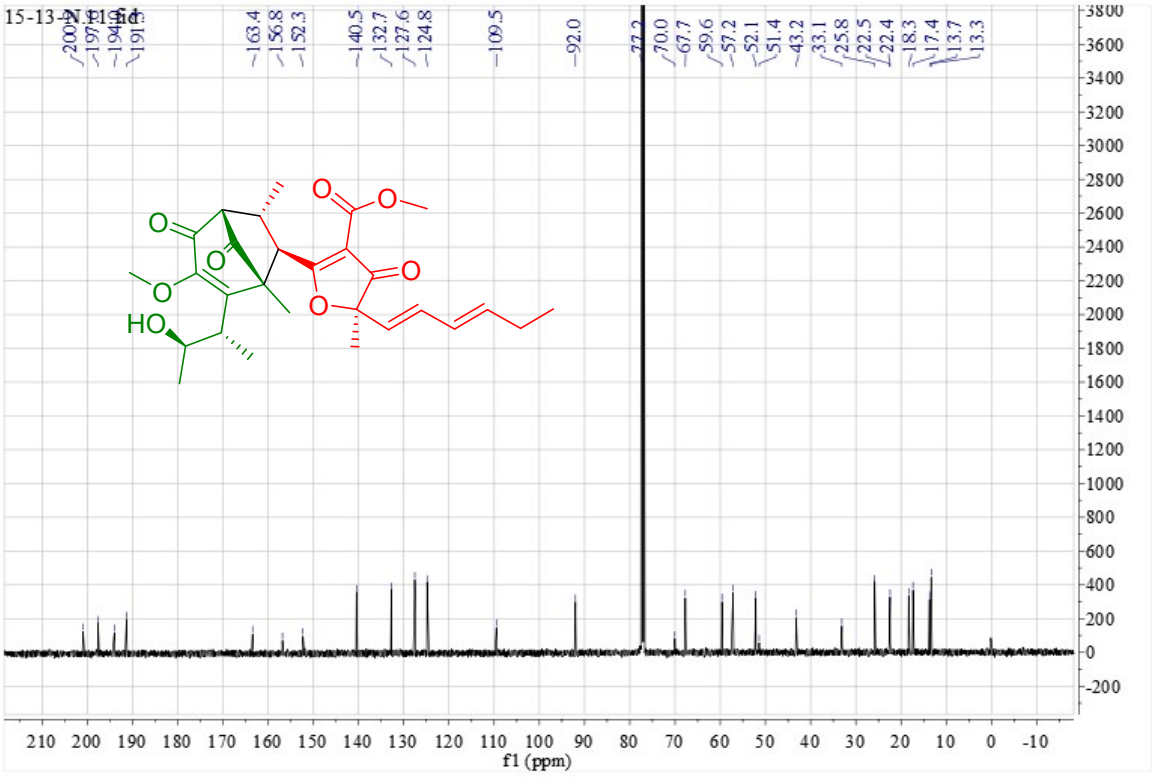


Figure S15. ^{13}C NMR spectrum of Compound **1A** (150 MHz, $CDCl_3$)

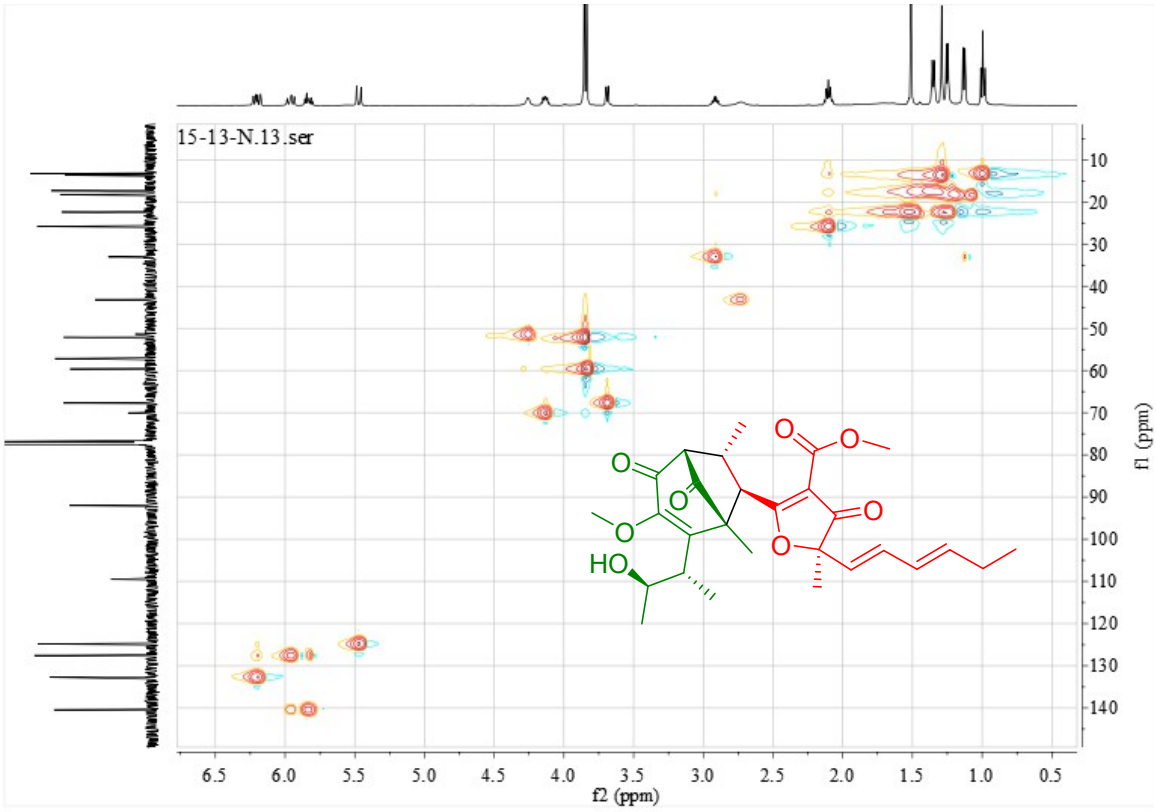


Figure S16. HSQC spectrum of Compound **1A** (600 MHz, $CDCl_3$)

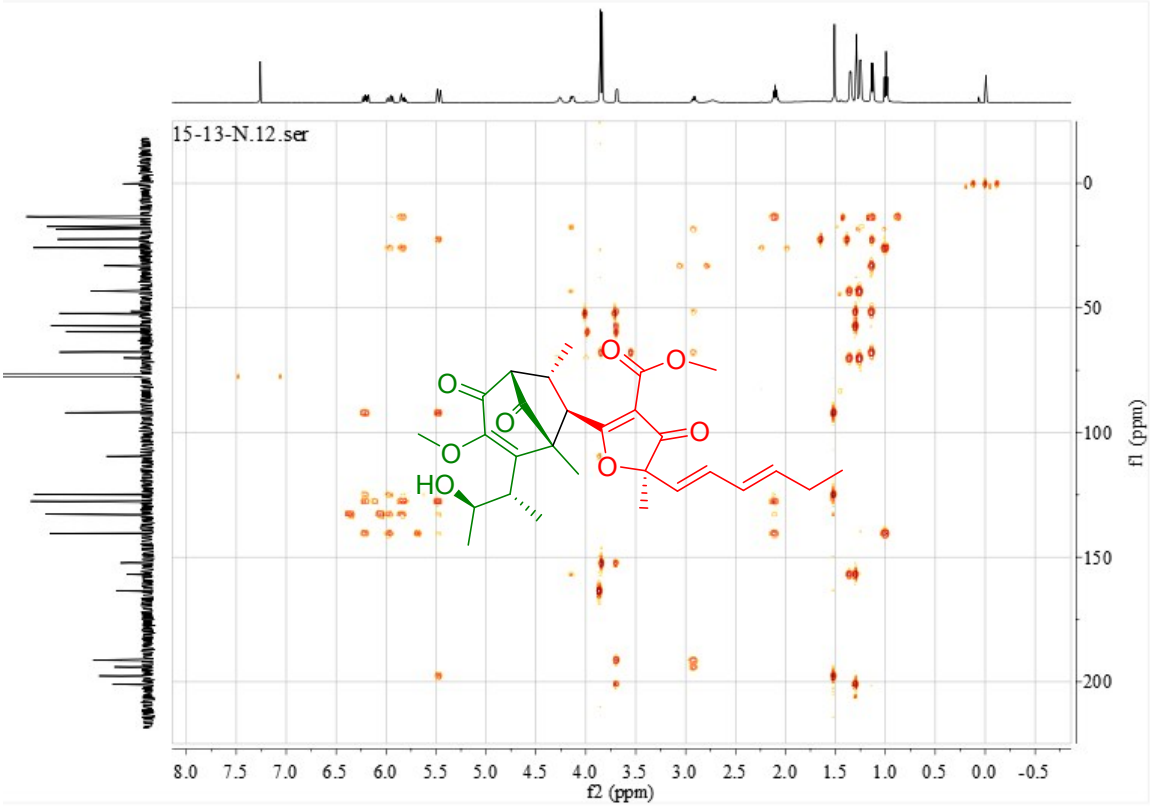


Figure S17. HMBC spectrum of Compound **1A** (600 MHz, $CDCl_3$)

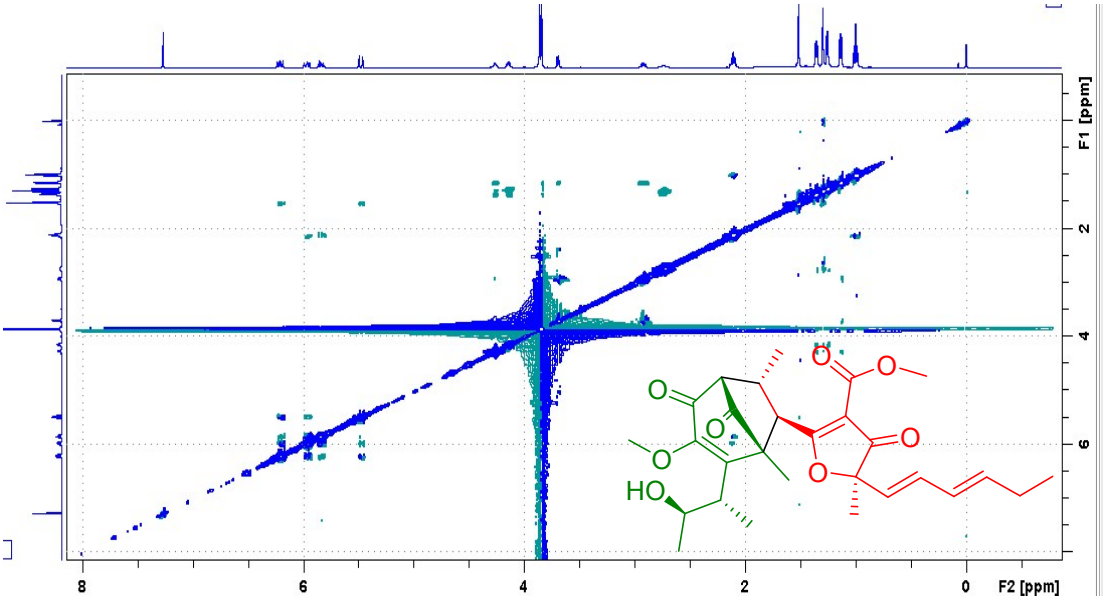
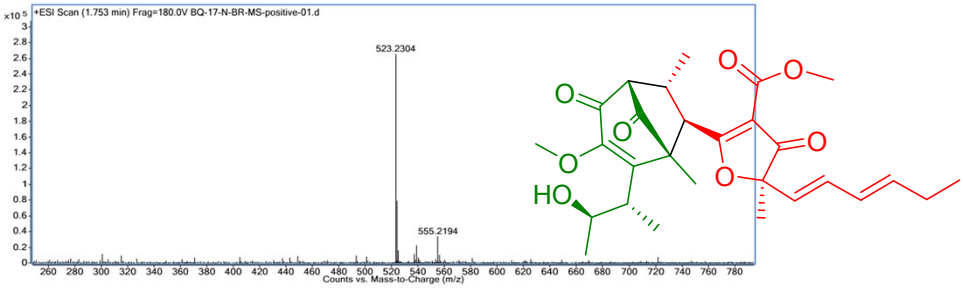


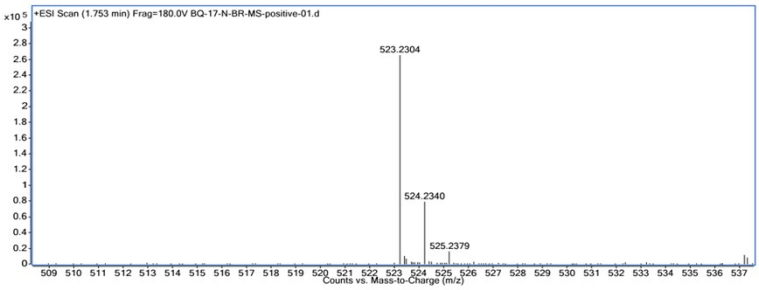
Figure S18. ROESY spectrum of Compound **1A** (600 MHz, $CDCl_3$)

TCM-CPU HR-ESI-MS Display Report

Sample Name: 15-13-N **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 09/05/2017 **Operator:** Administrator





Elemental Composition Calculator

Target m/z:	523.2304	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
$C_{28}H_{36}NaO_8$		523.2302		-0.36	

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Figure S19. HRESIMS spectrum of Compound **1A**

For compound of 2

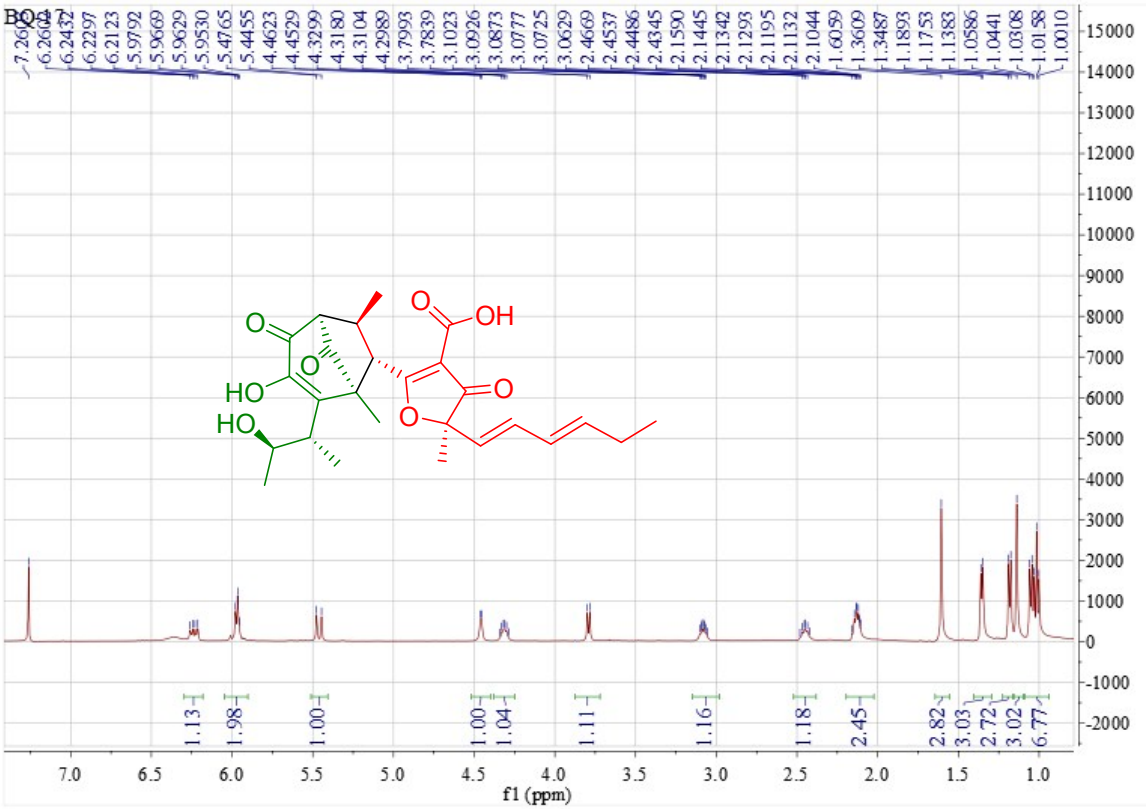


Figure S20. ^{1}H NMR spectrum of Compound **2** (500 MHz, $CDCl_3$)

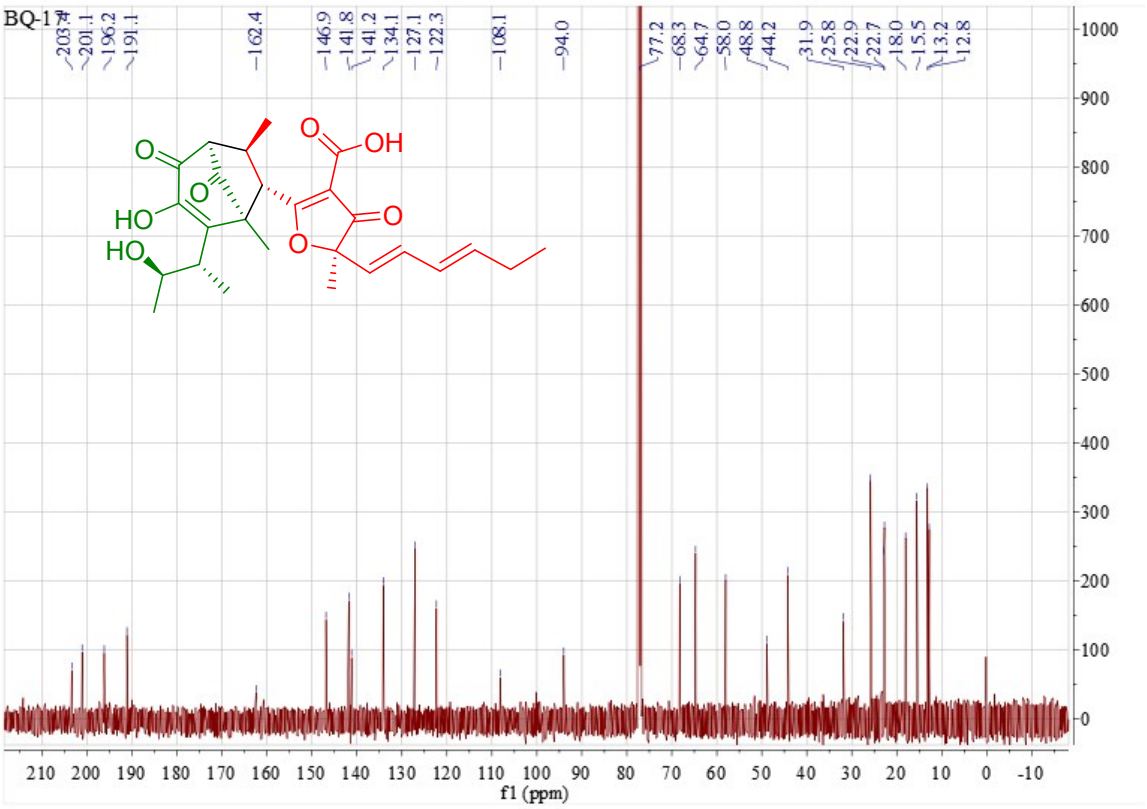


Figure S21. ^{13}C NMR spectrum of Compound **2** (125 MHz, $CDCl_3$)

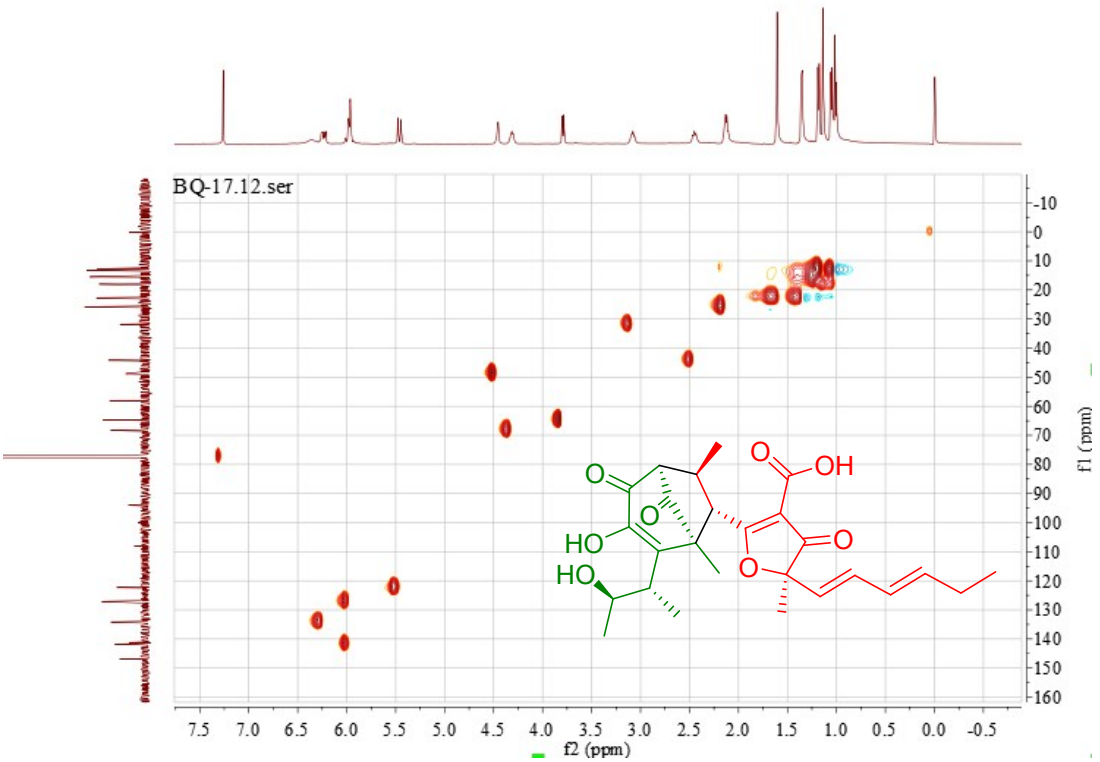


Figure S22. HSQC spectrum of Compound **2** (500 MHz, $CDCl_3$)

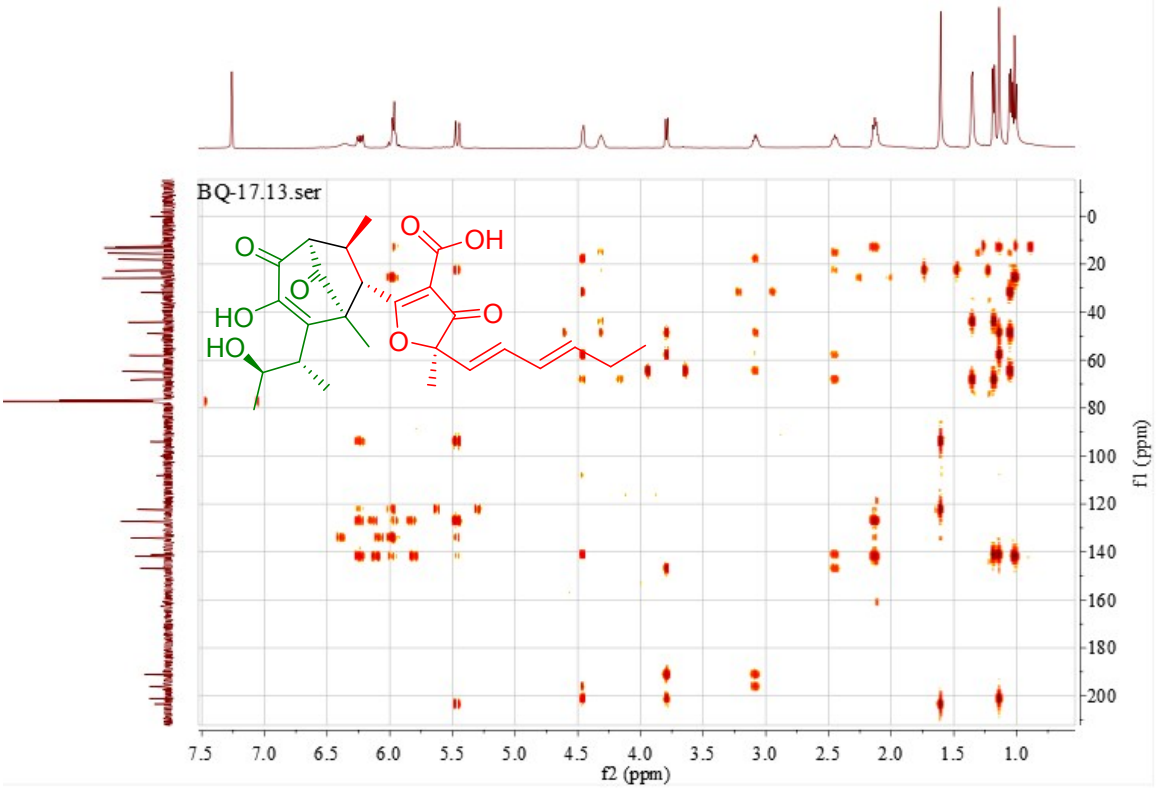


Figure S23. HMBC spectrum of Compound **2** (500 MHz, $CDCl_3$)

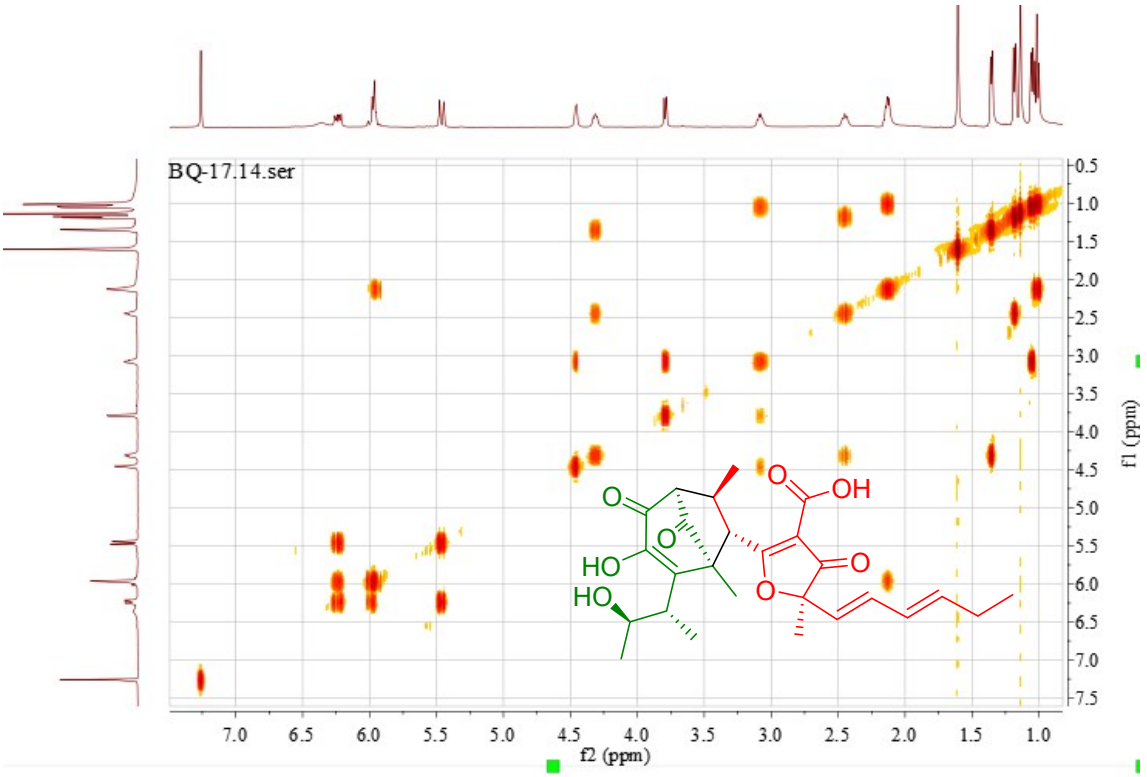


Figure S24. ^{1}H-^{1}H COSY spectrum of Compound **2** (500 MHz, $CDCl_3$)

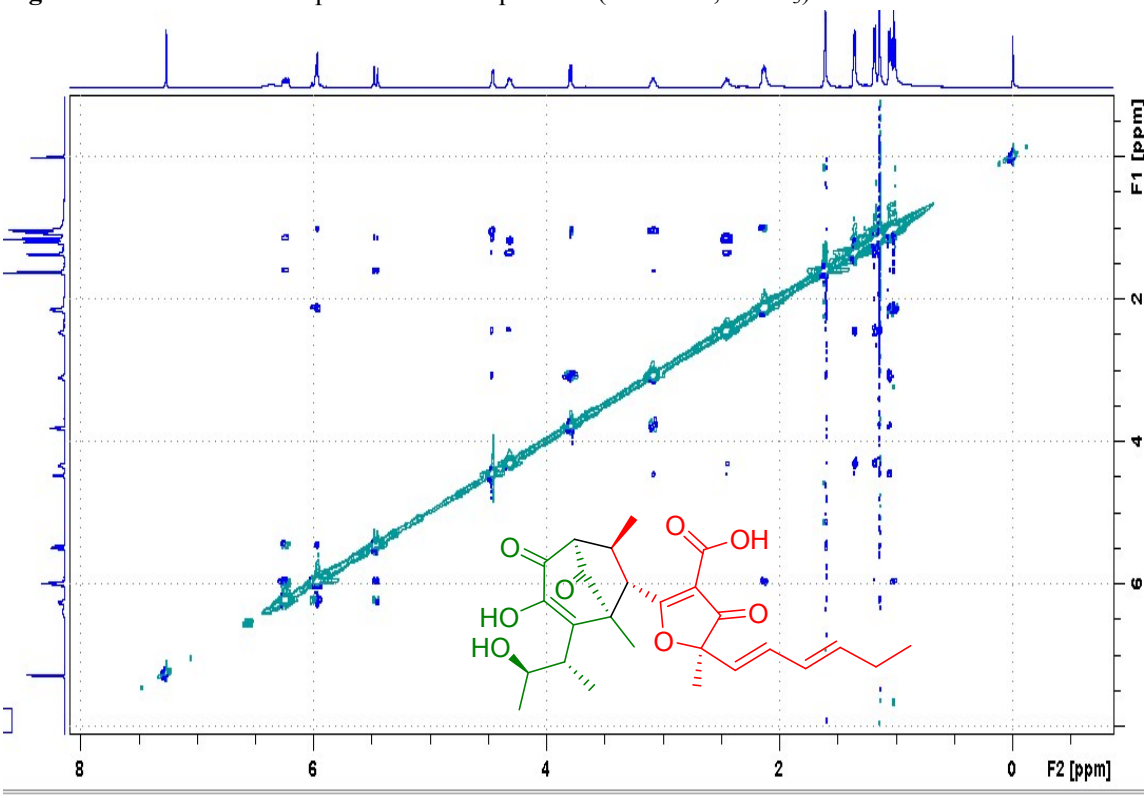


Figure S25. ROESY spectrum of Compound **2** (500 MHz, $CDCl_3$)

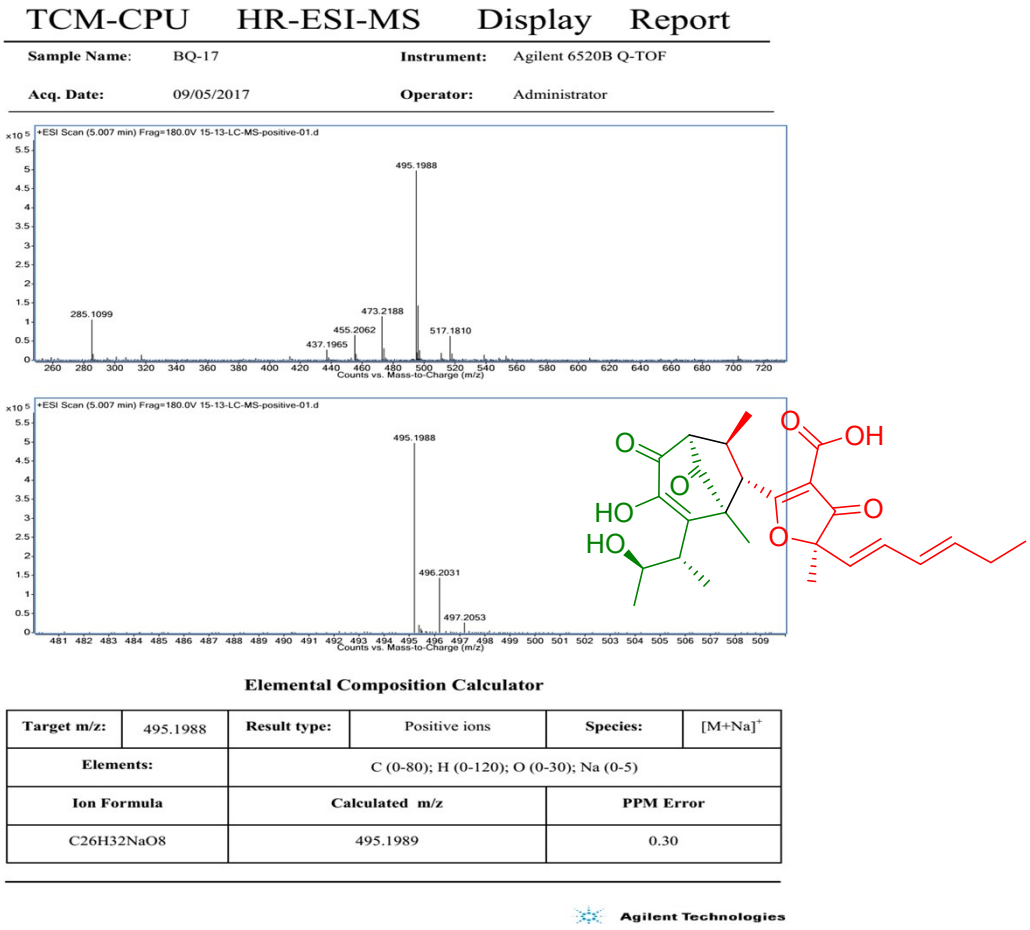


Figure S26. HRESIMS spectrum of Compound **2**

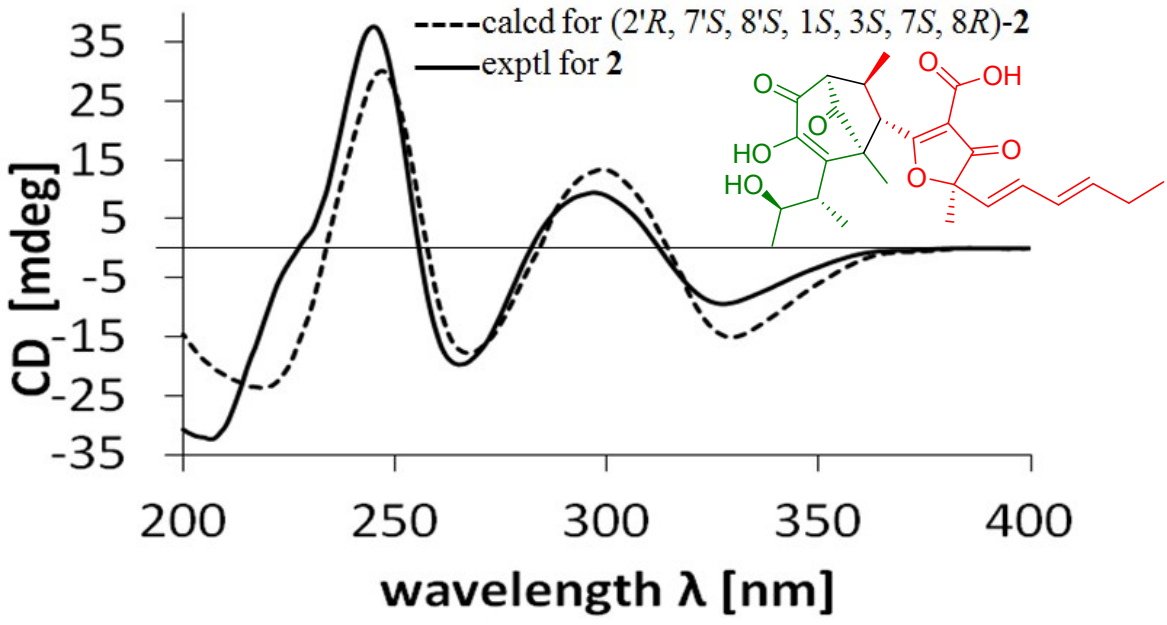


Figure S27. Calculated and experimental ECD spectra of Compound **2**.

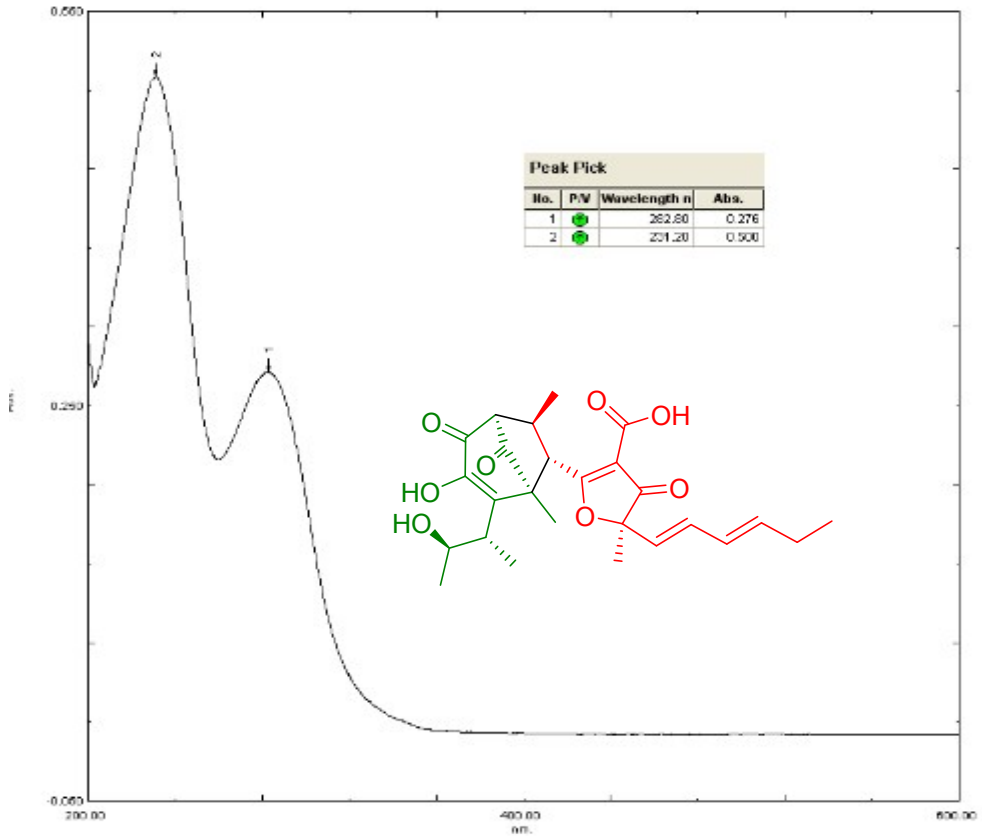


Figure S28.UV spectrum of Compound **2**

For compound of 2A

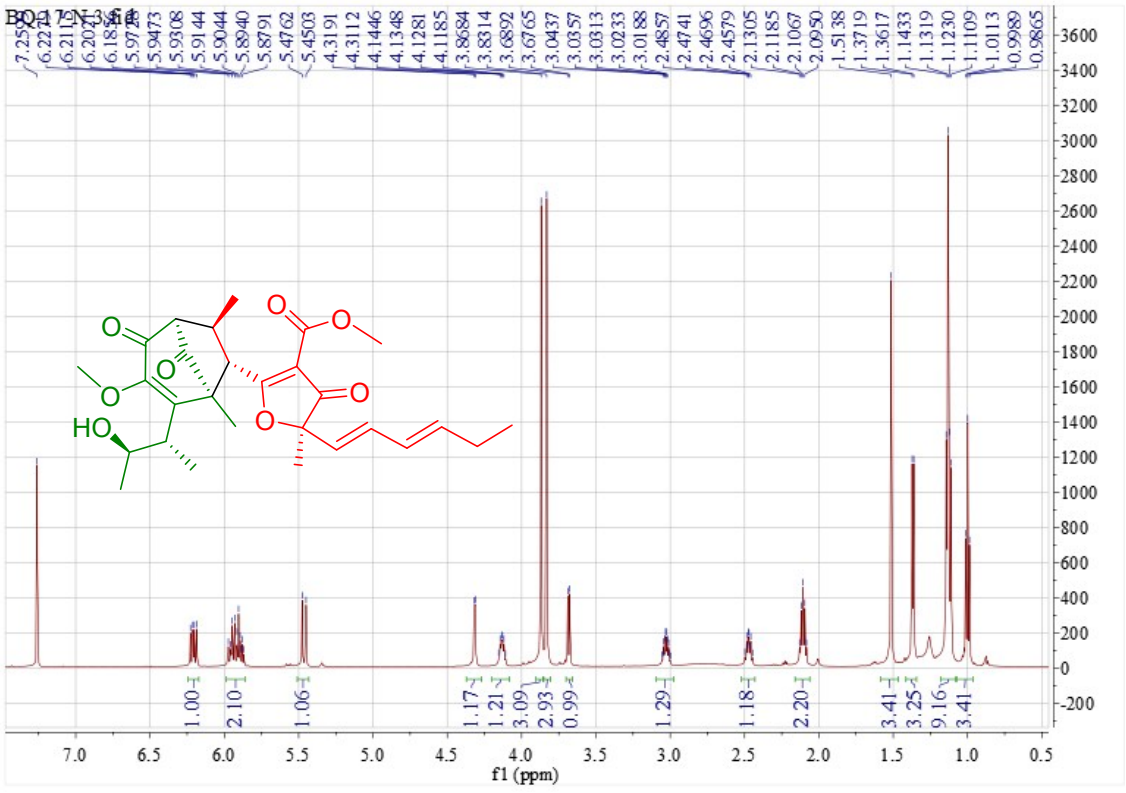


Figure S29. ^{1}H NMR spectrum of Compound **2A** (600 MHz, $CDCl_3$)

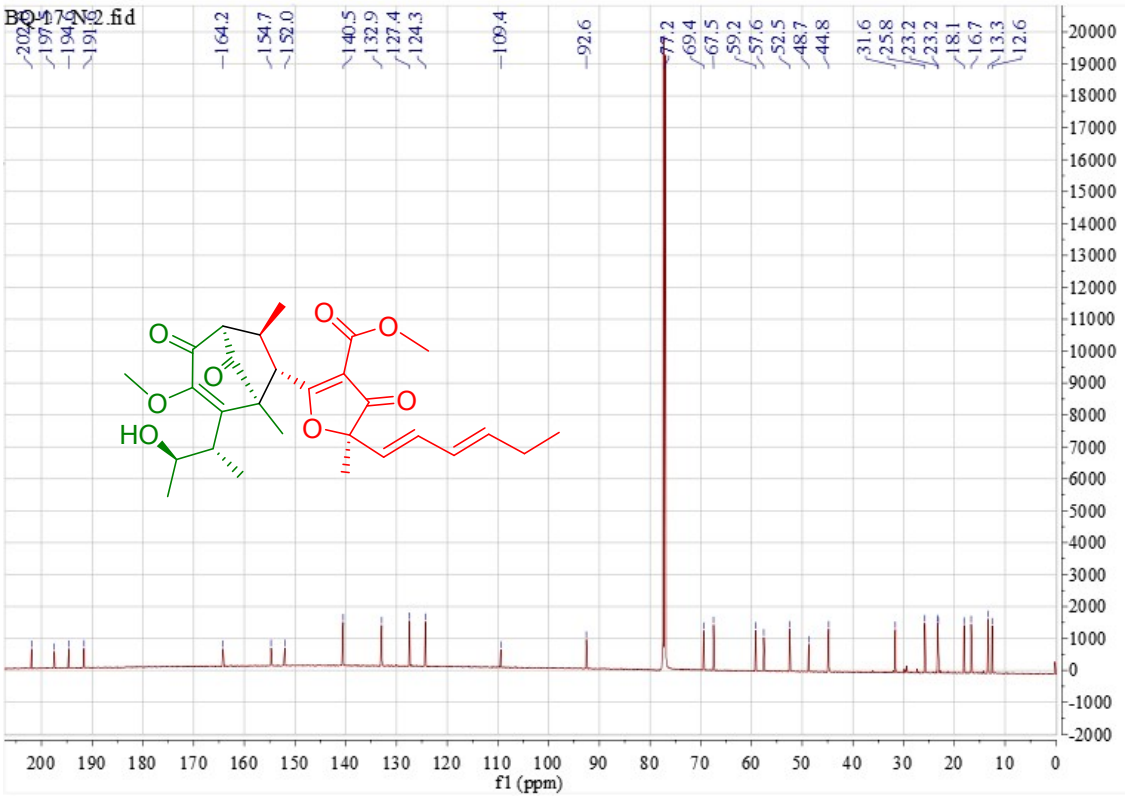


Figure S30. ^{13}C NMR spectrum of Compound **2A** (600 MHz, $CDCl_3$)

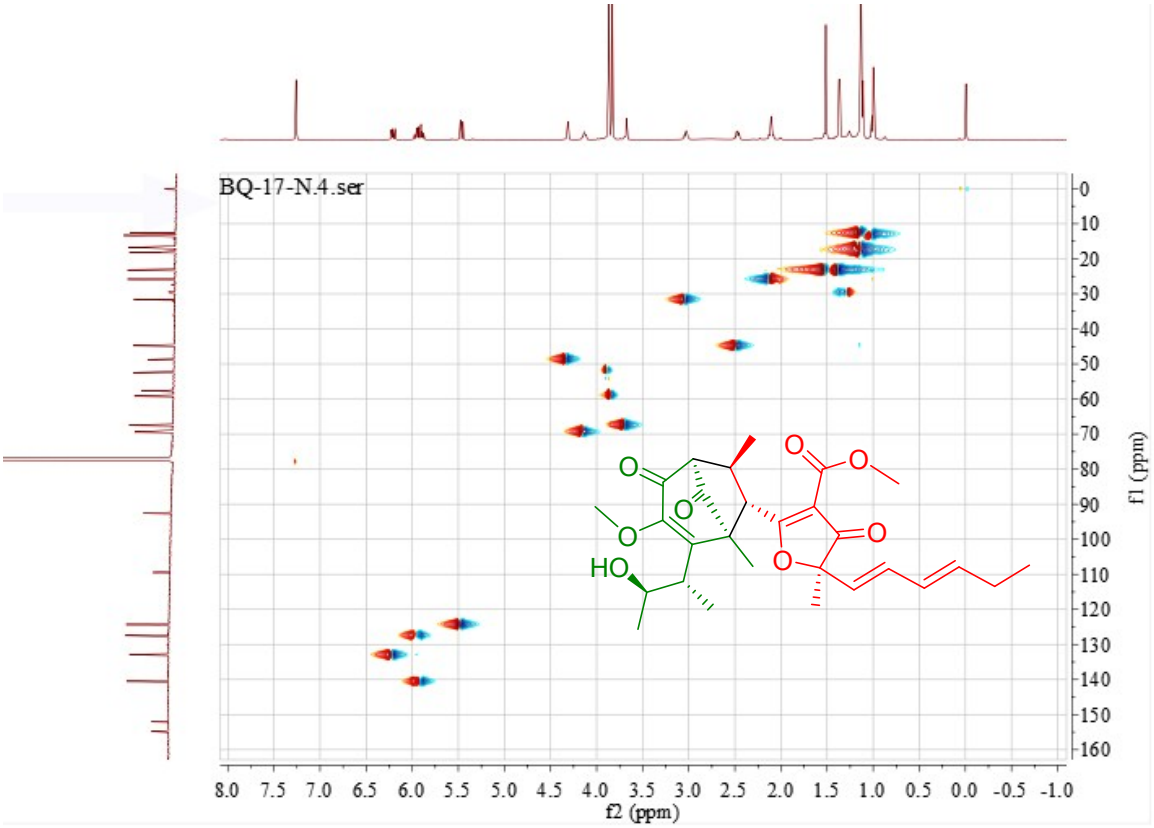


Figure S31. HSQC spectrum of Compound **2A** (600 MHz, $CDCl_3$)

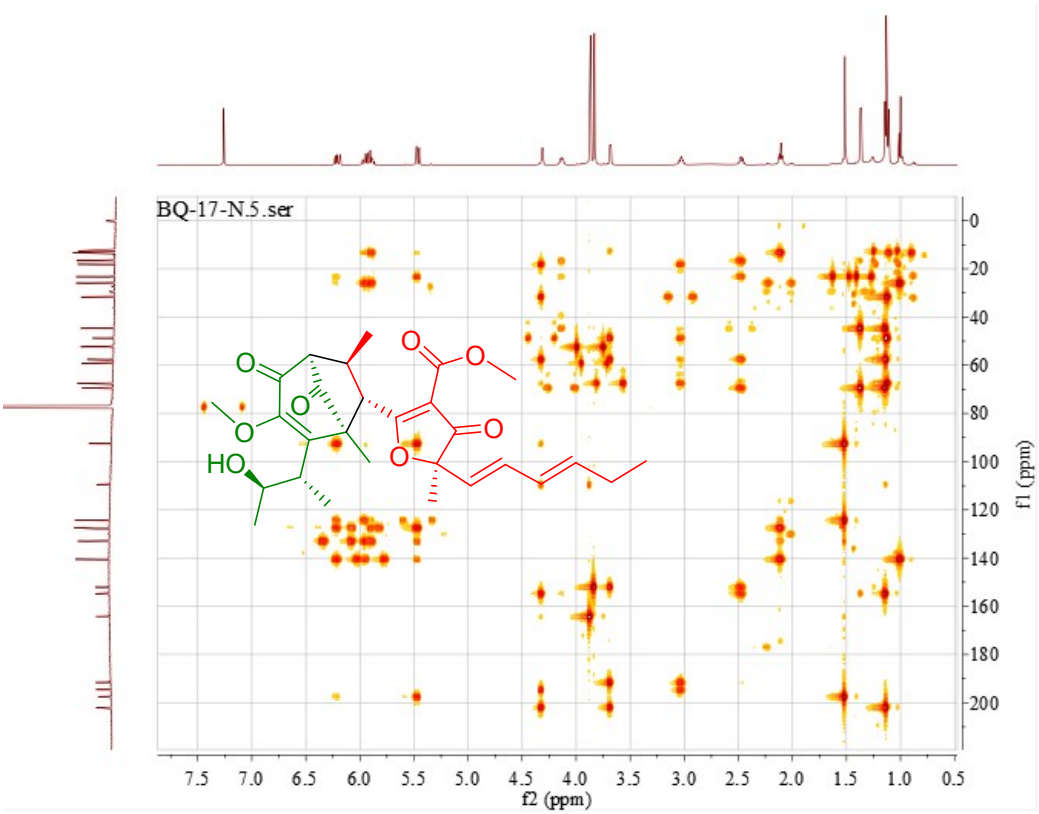


Figure S32. HMBC spectrum of Compound **2A** (600 MHz, $CDCl_3$)

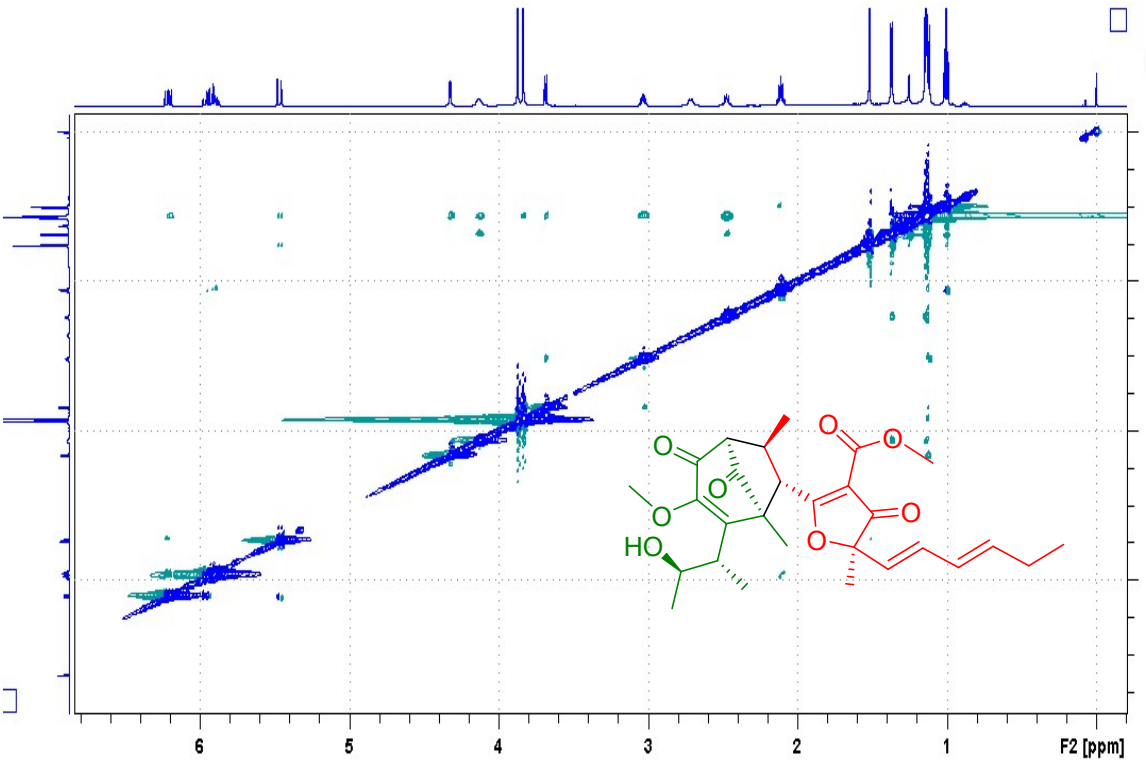
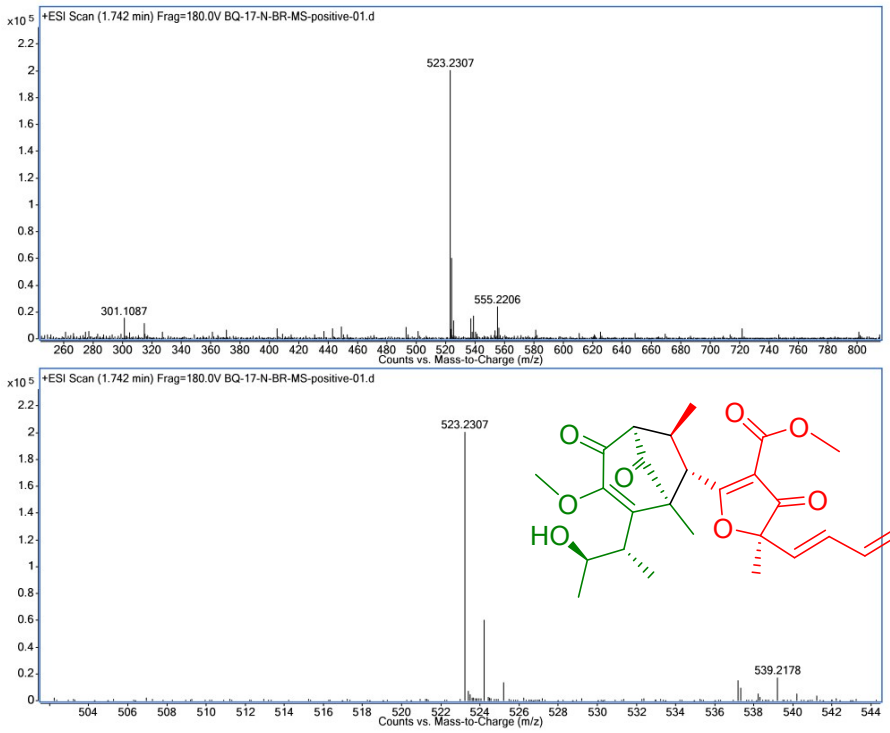


Figure S33 ROESY spectrum of Compound **2A** (600 MHz, $CDCl_3$)

TCM-CPU HR-ESI-MS Display Report

Sample Name: BQ-17-N-BR **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 04/04/2017 **Operator:** Administrator

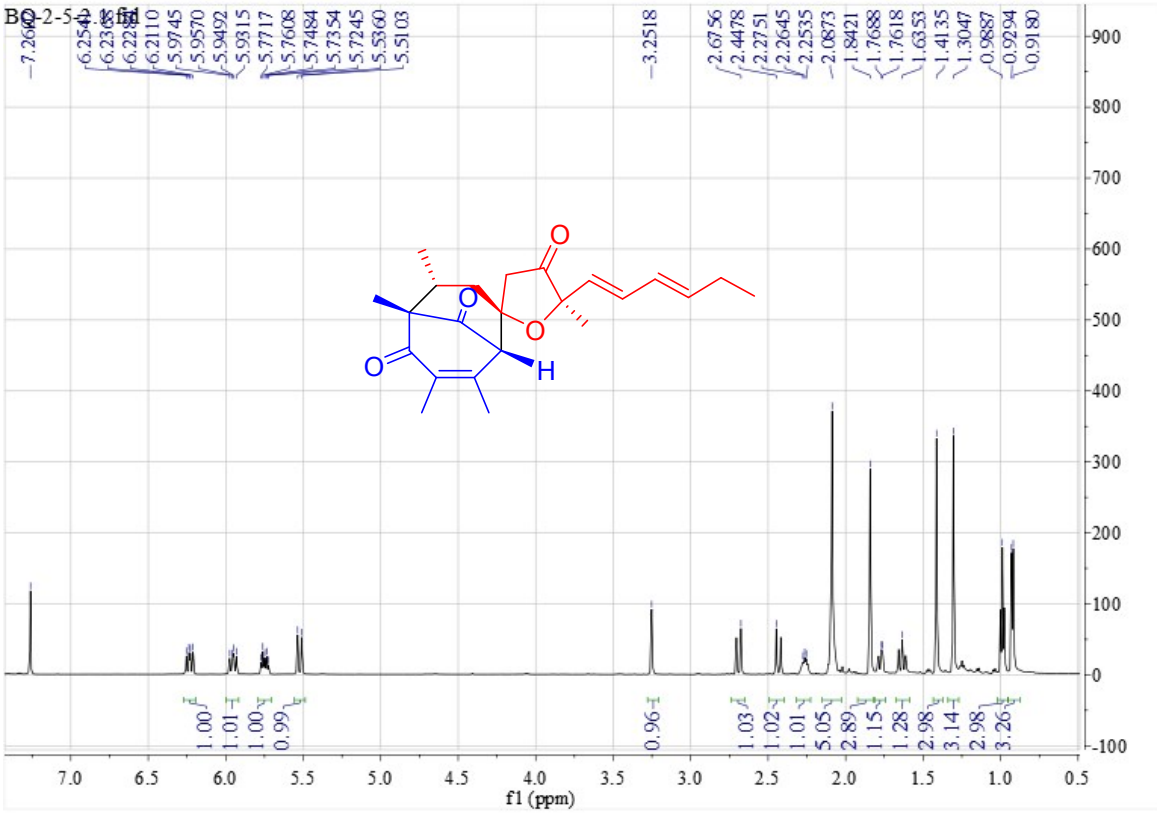


Elemental Composition Calculator

Target m/z:	523.2307	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C28H36NaO8		523.2302		-0.96	

Agilent Technologies

Figure S34. HRESIMS spectrum of Compound **2A**



、 **Figure S35**. ^{1}H NMR spectrum of Compound **3** (600 MHz, $CDCl_3$)

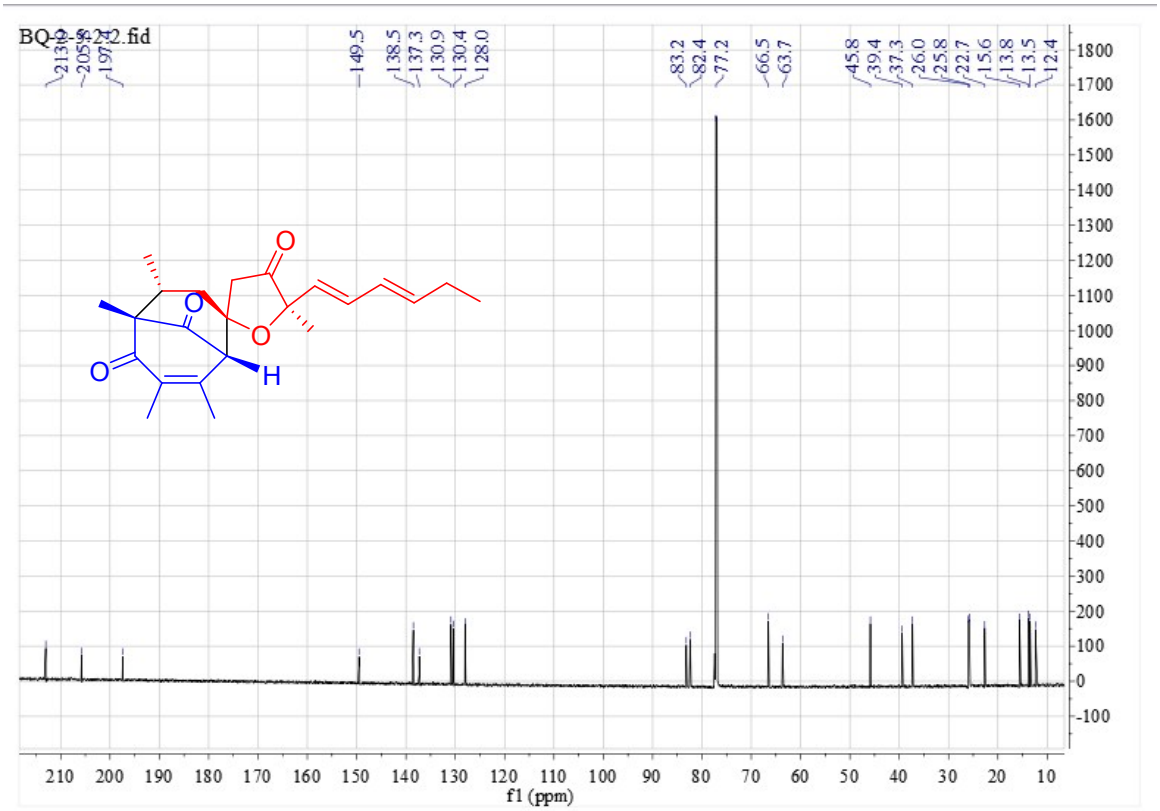


Figure S36. ^{13}C NMR spectrum of Compound**3** (125 MHz, $CDCl_3$)

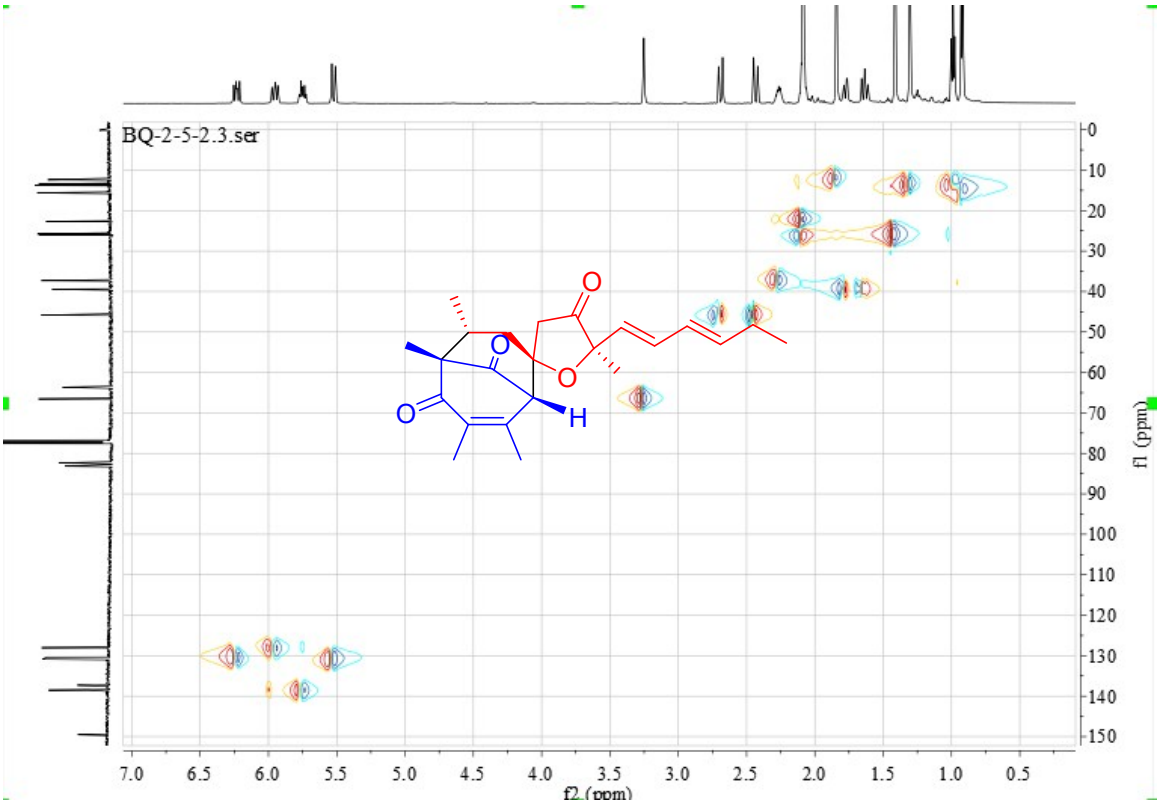


Figure S37. HSQC spectrum of Compound **3** (600 MHz, $CDCl_3$)

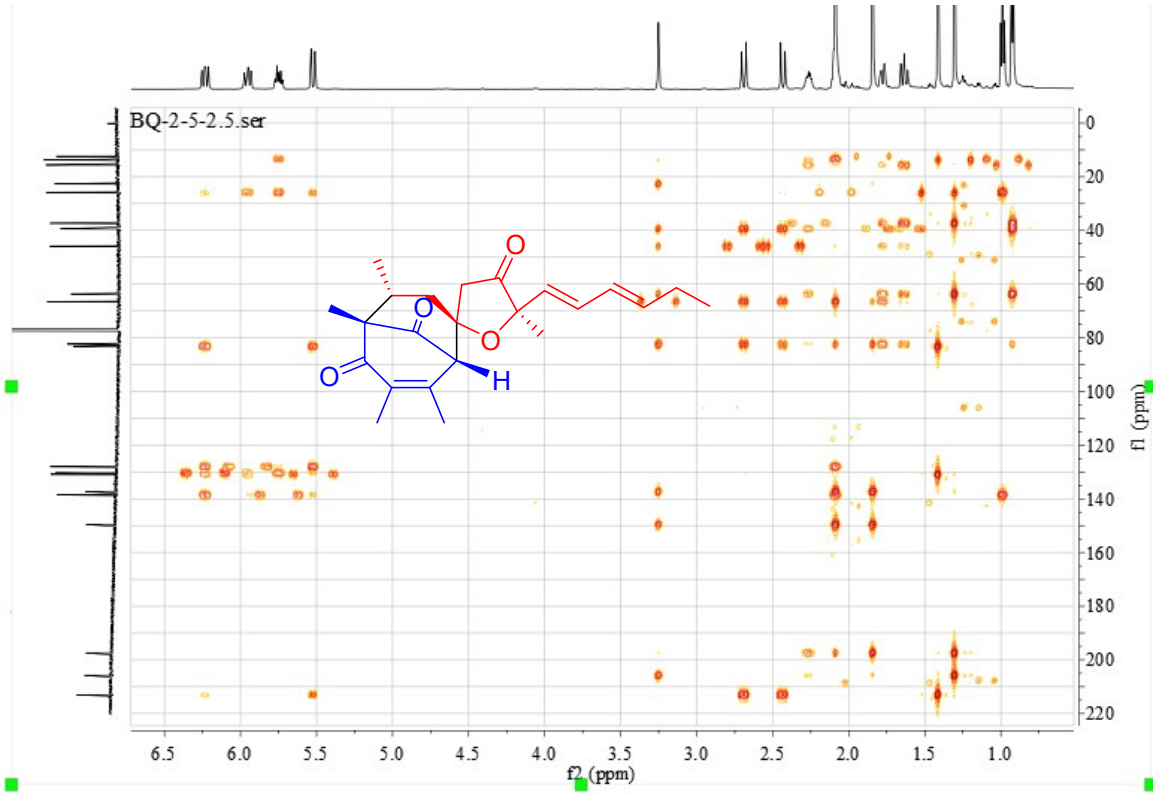


Figure S38. HMBC spectrum of Compound **3** (600 MHz, $CDCl_3$)

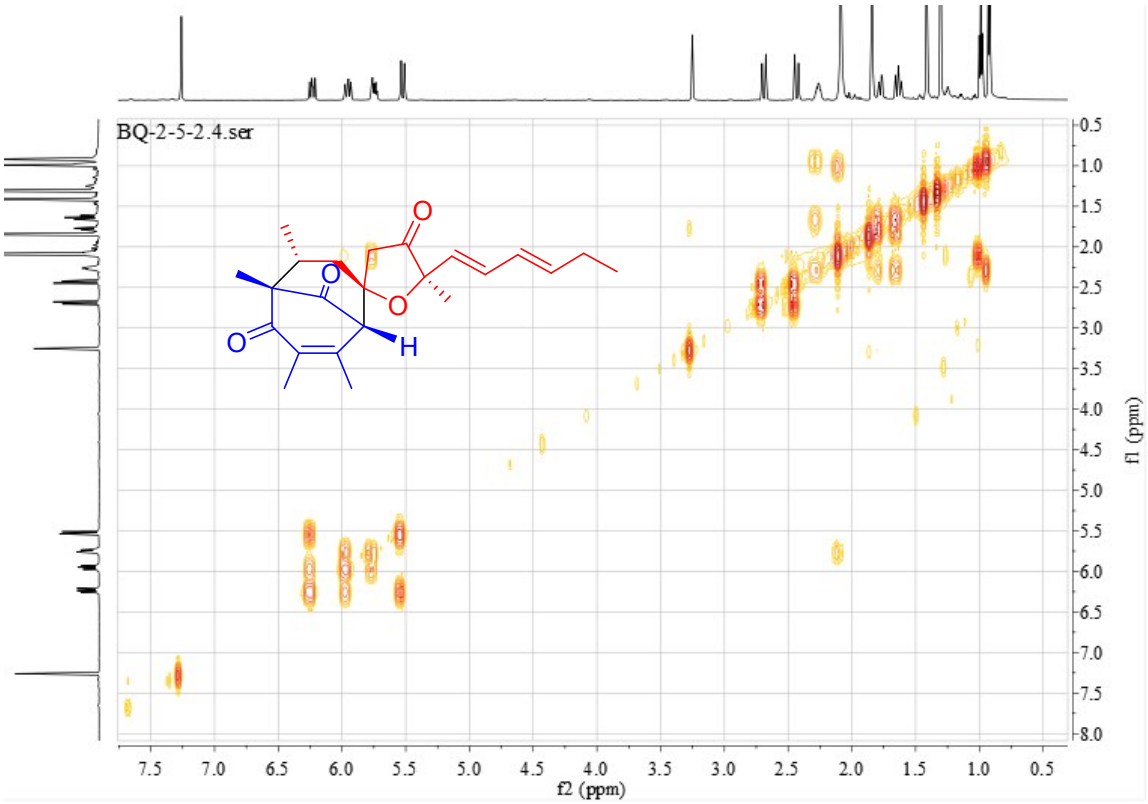


Figure S39. ^{1}H-^{1}H COSY spectrum of Compound **3** (600 MHz, $CDCl_3$)

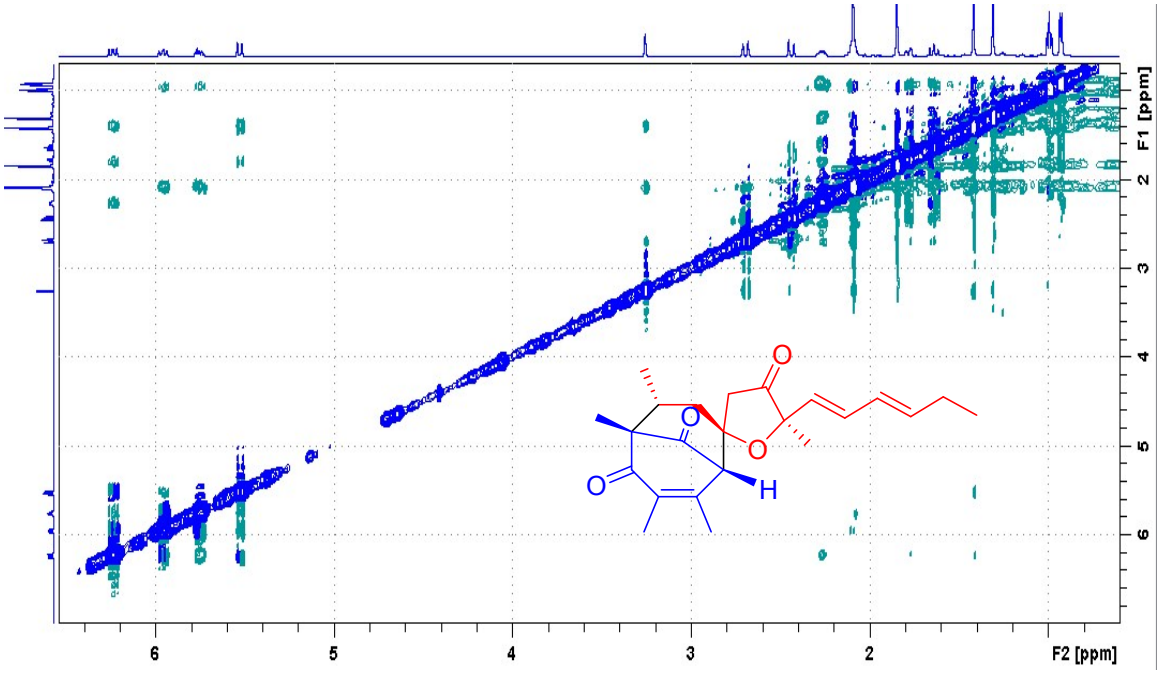
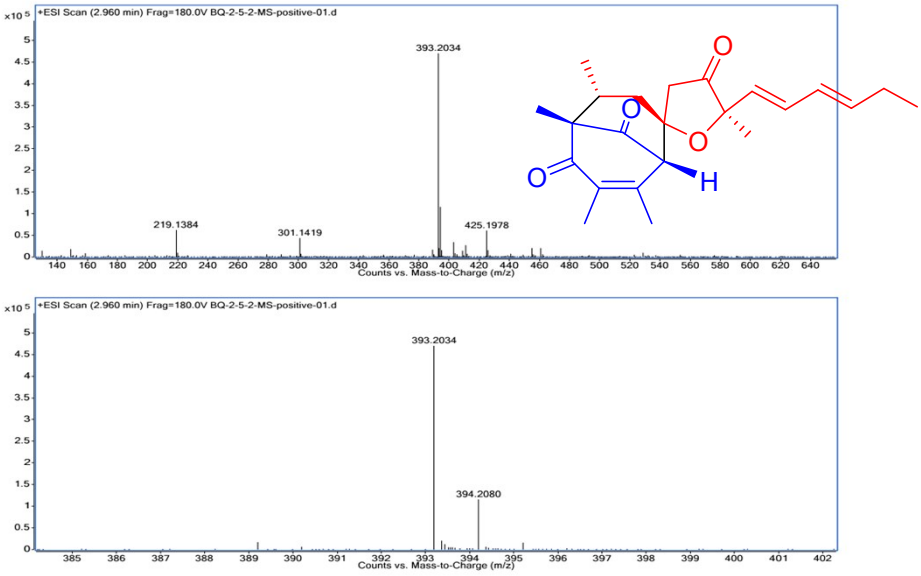


Figure S40. ROESY spectrum of Compound **3** (600 MHz, $CDCl_3$)

TCM-CPU HR-ESI-MS Display Report

Sample Name:	BQ-2-5-2	**Instrument:**	Agilent 6520B Q-TOF
Acq. Date:	09/05/2017	**Operator:**	Administrator



Elemental Composition Calculator

Target m/z:	393.2034	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C23H30NaO4		393.2036		0.60	

Agilent Technologies

Figure S41. HRESIMS spectrum of Compound **3**

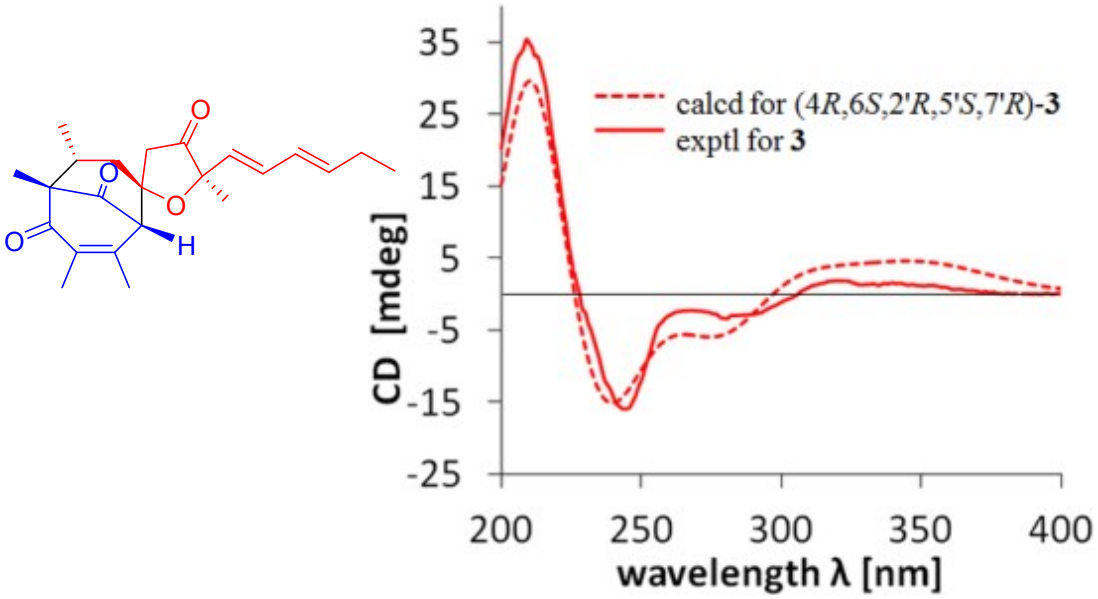


Figure S42. Calculated and experimental ECD spectra of Compound **3**

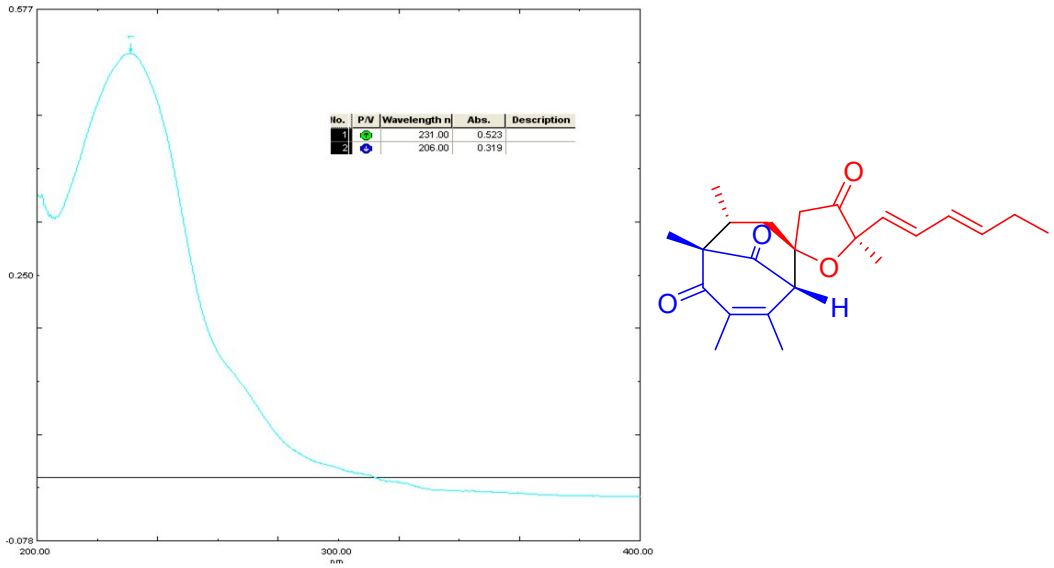


Figure S43. UV spectrum of Compound **3**

For compound of 4

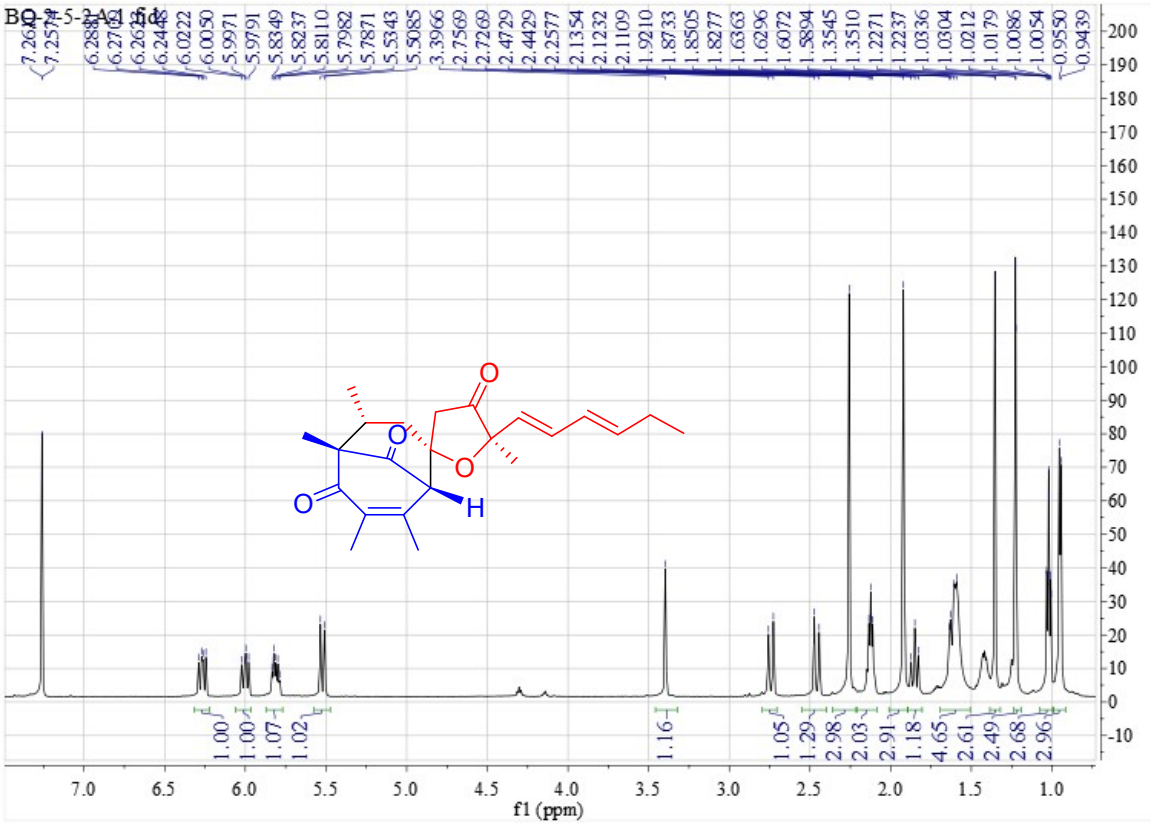


Figure S44. ^{1}H NMR spectrum of Compound **4** (600 MHz, $CDCl_3$)

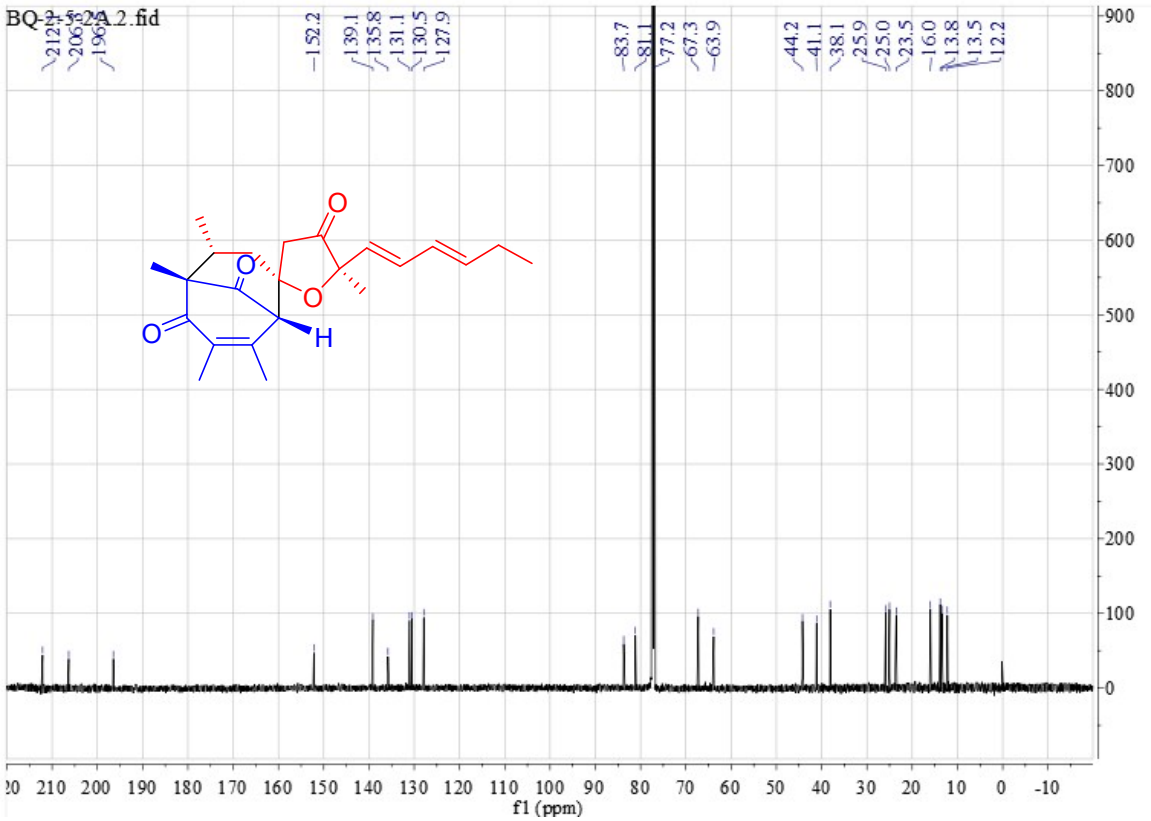


Figure S45. ^{13}C NMR spectrum of Compound **4** (150 MHz, $CDCl_3$)

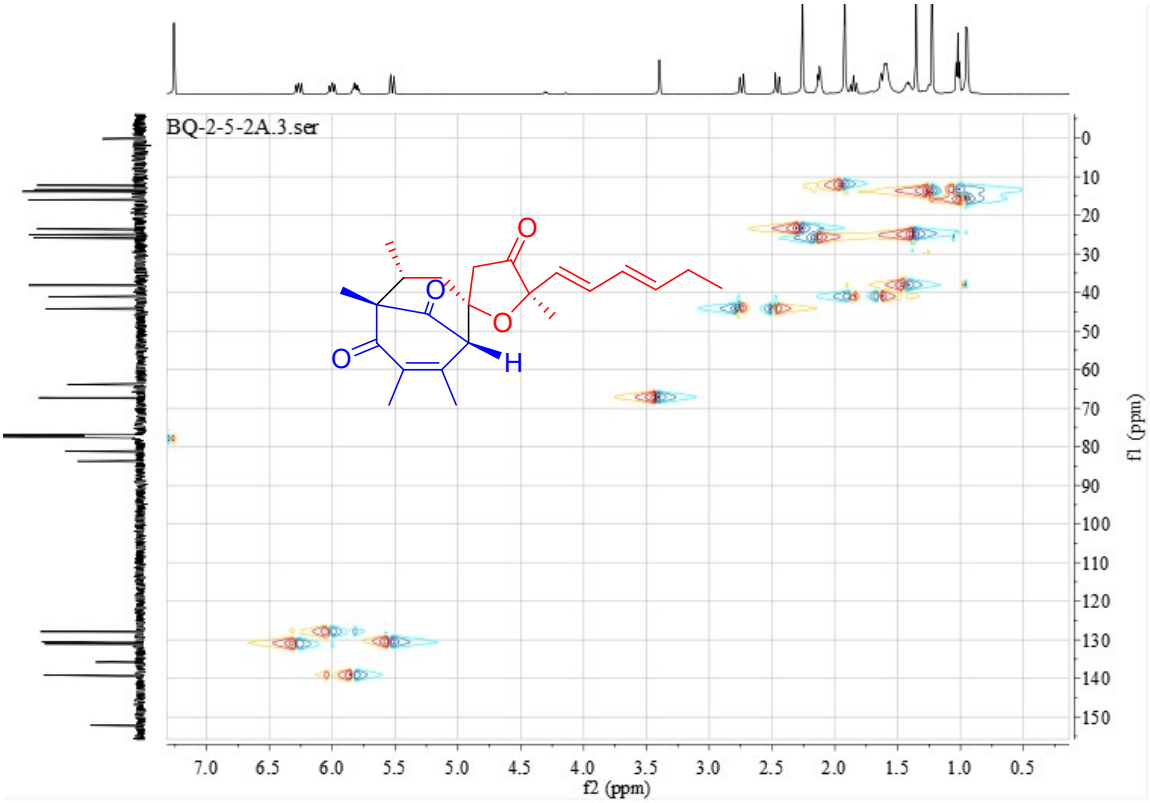


Figure S46. HSQC spectrum of Compound **4** (600 MHz, $CDCl_3$)

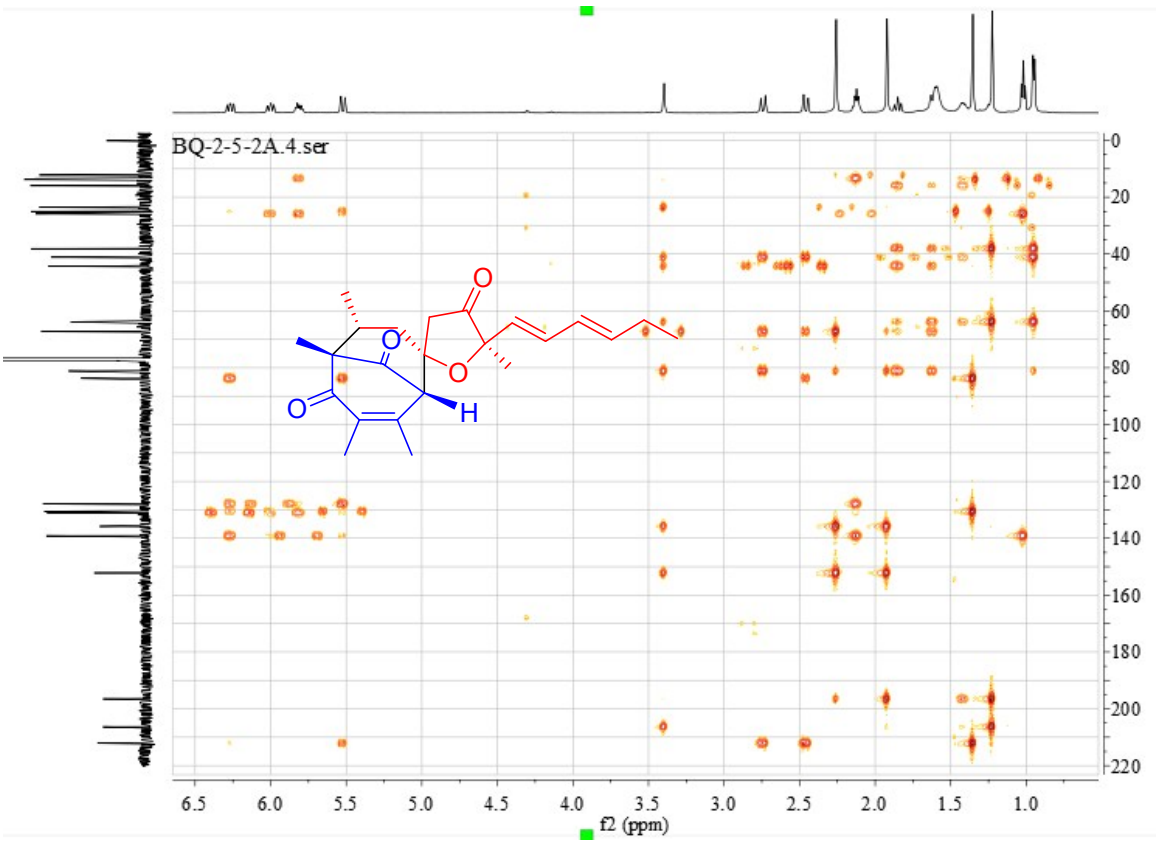


Figure S47. HMBC spectrum of Compound **4**(600 MHz, $CDCl_3$)

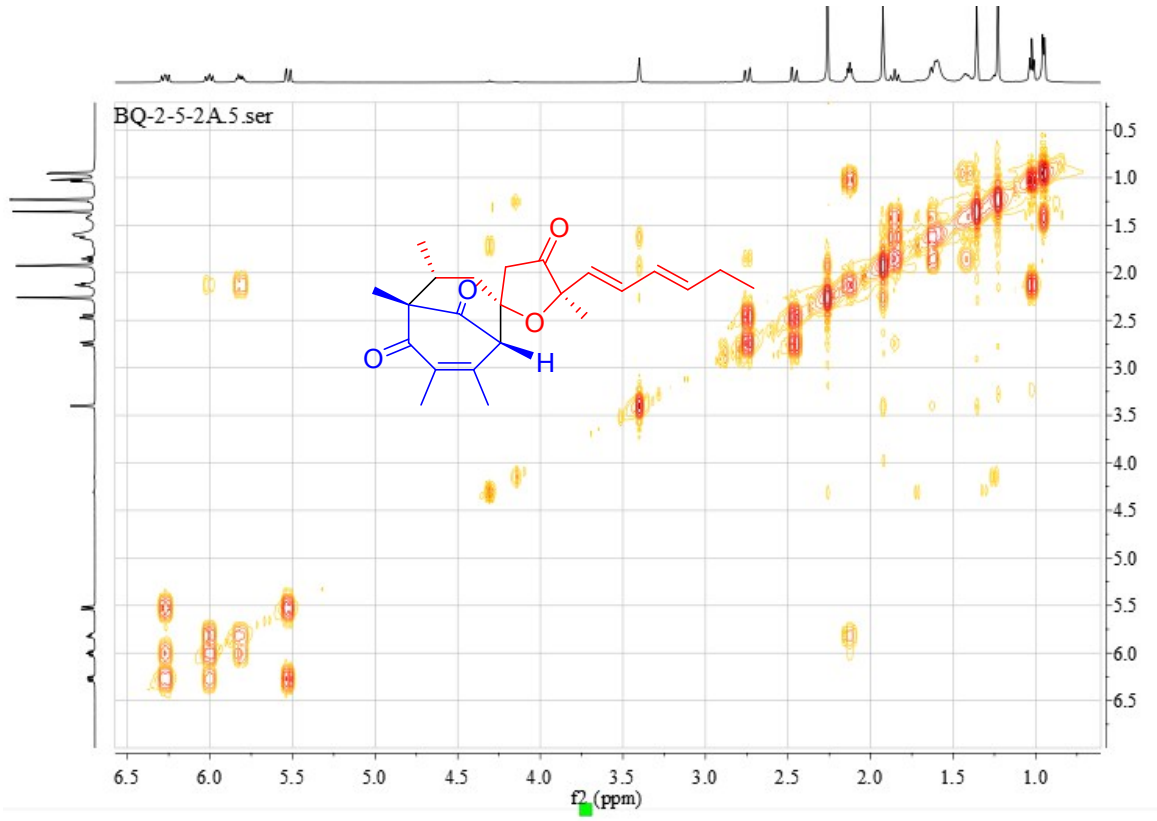


Figure S48. ^1H-^1H COSY spectrum of Compound **4** (600 MHz, $CDCl_3$)

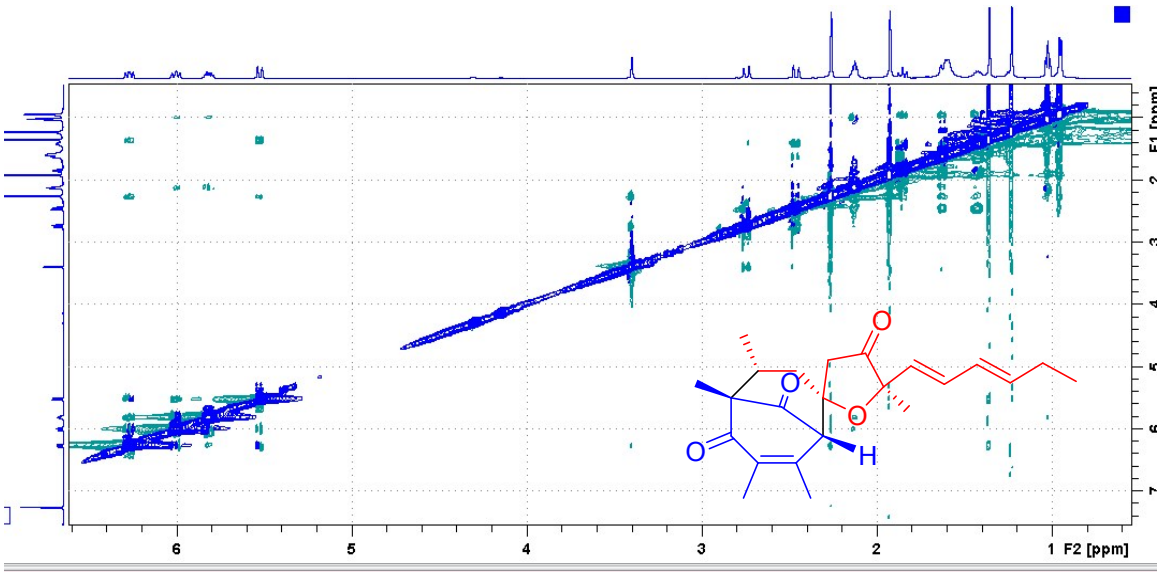
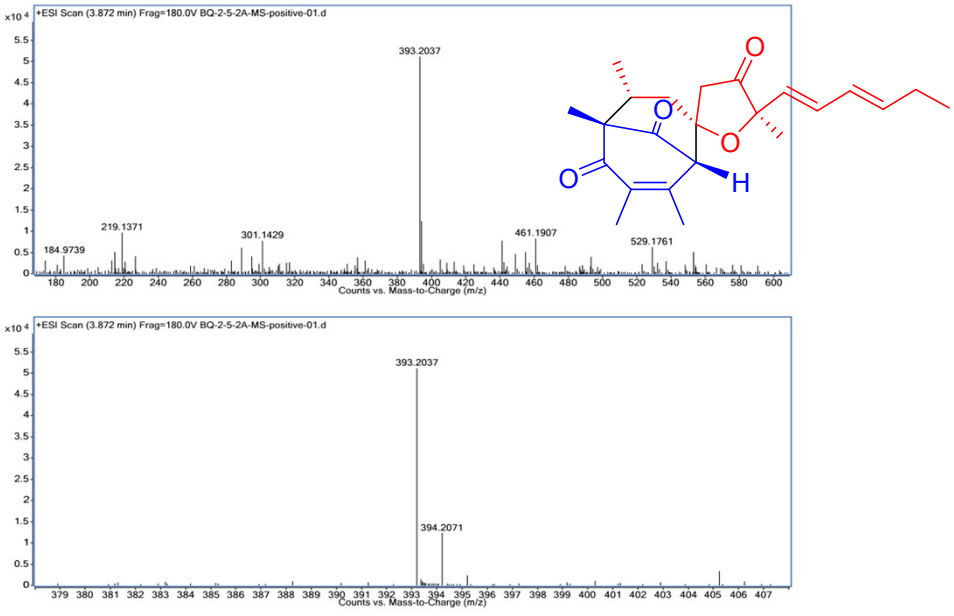


Figure S49. ROESY spectrum of Compound **4**(600 MHz, $CDCl_3$)

TCM-CPU HR-ESI-MS Display Report

Sample Name:	BQ-2-5-2A	**Instrument:**	Agilent 6520B Q-TOF
Acq. Date:	09/05/2017	**Operator:**	Administrator



Elemental Composition Calculator

Target m/z:	393.2037	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C23H30NaO4		393.2036		-0.21	

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Figure S50. HRESIMS spectrum of Compound **4**

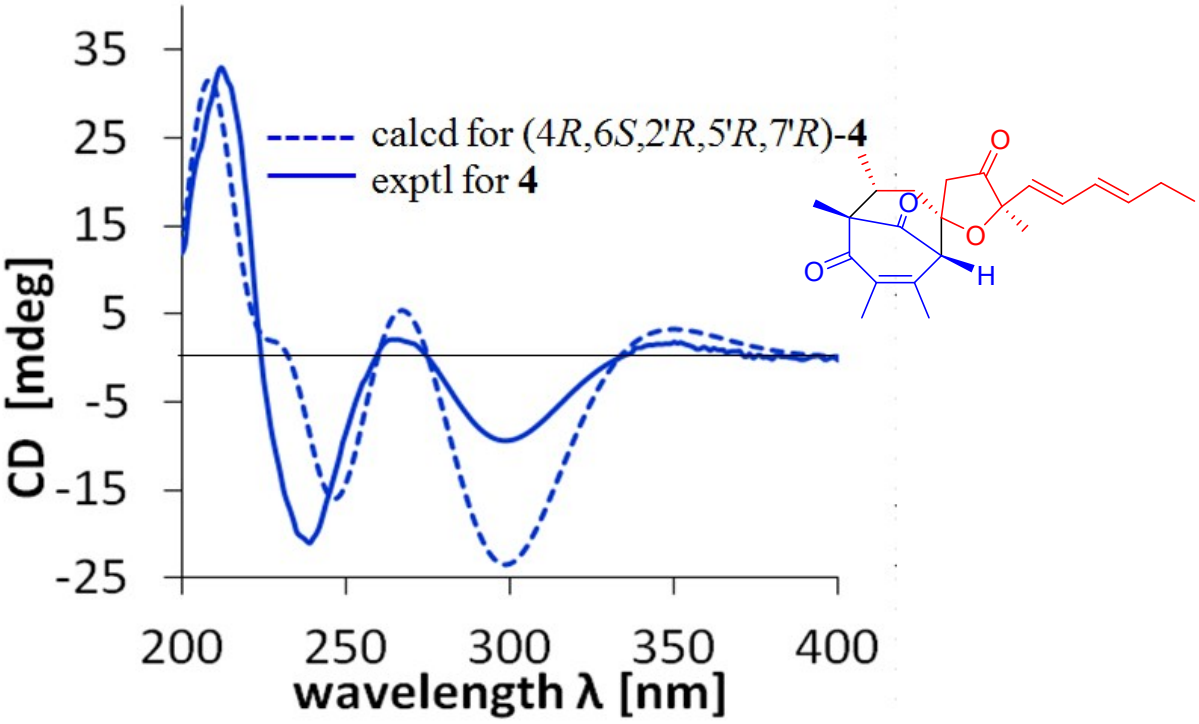


Figure S51 Calculated and experimental ECD spectra of Compound **4**

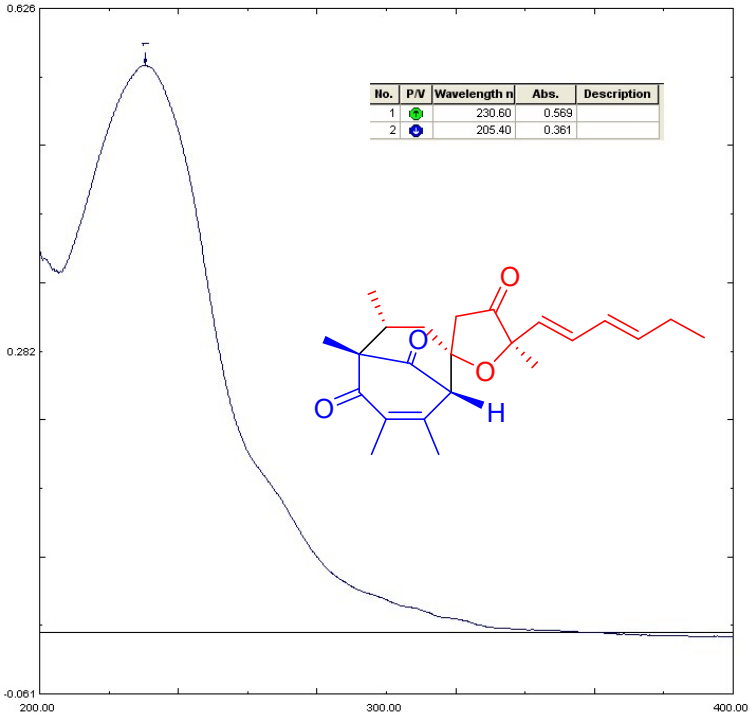


Figure S52 UV spectrum of Compound **4**

For compound of 5

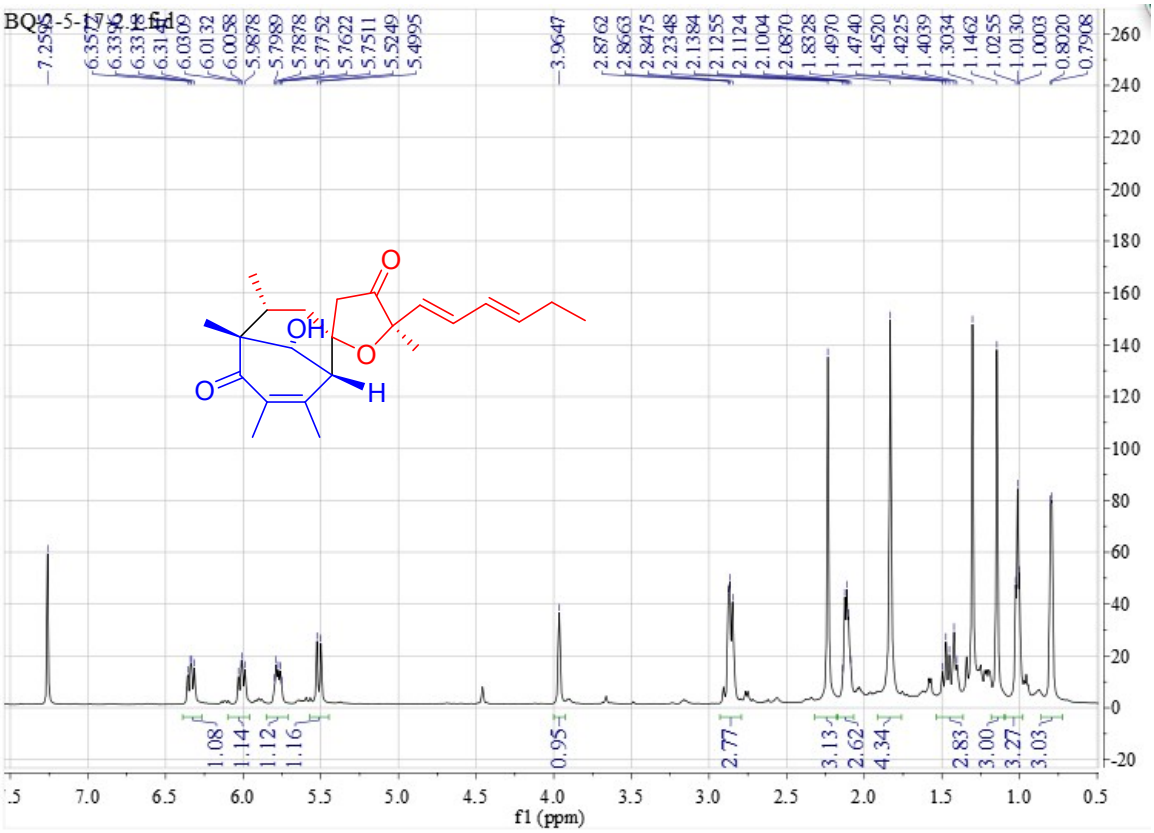


Figure S53. ^{1}H NMR spectrum of Compound **5** (600 MHz, $CDCl_3$)

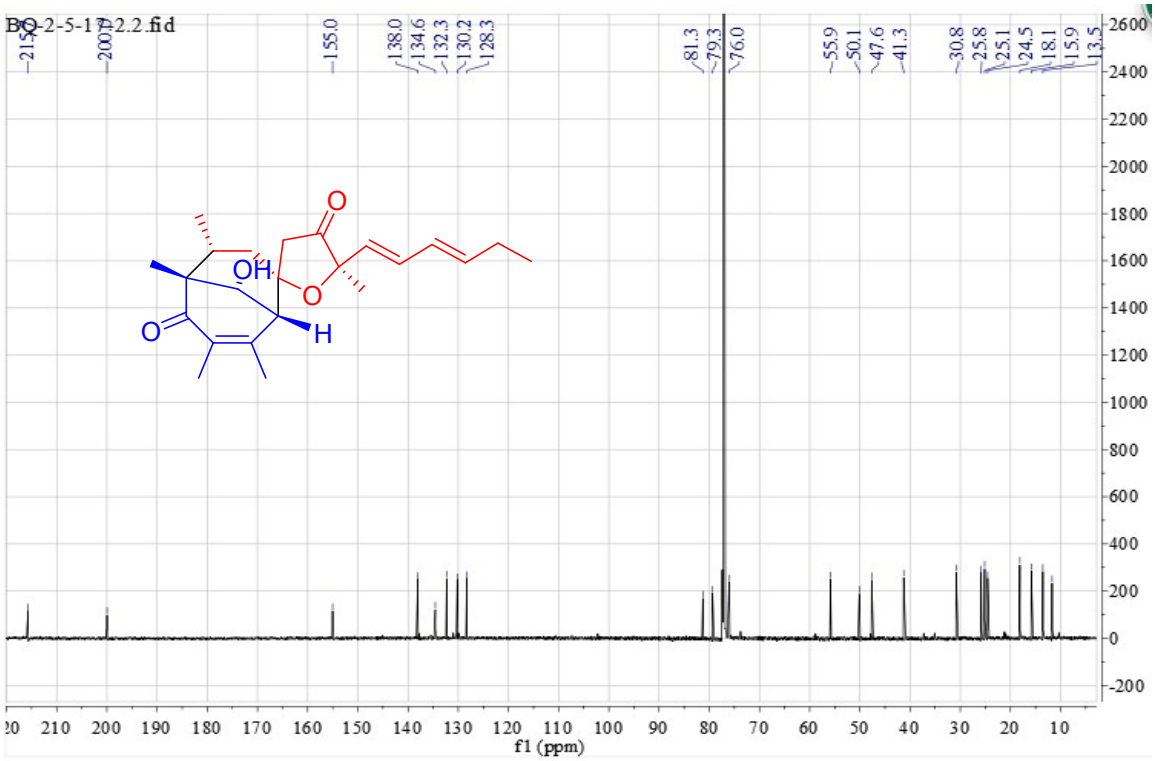


Figure S54. ^{13}C NMR spectrum of Compound **5** (150 MHz, $CDCl_3$)

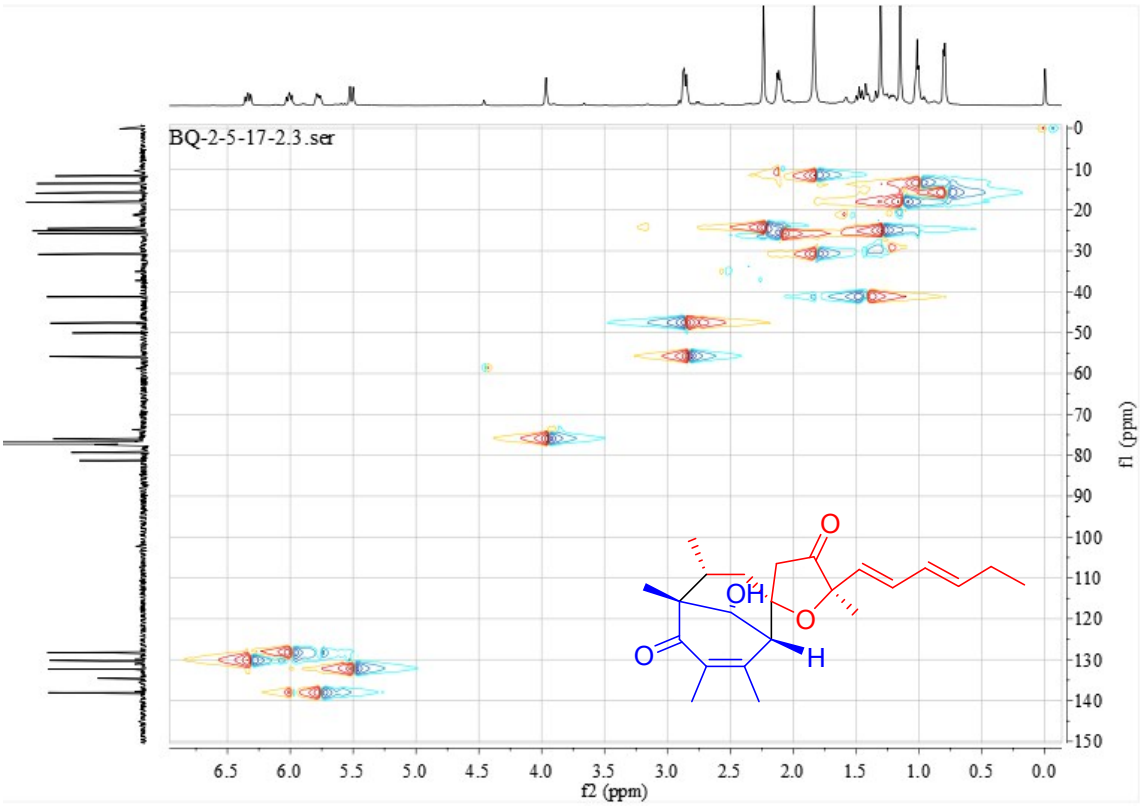


Figure S55. HSQC spectrum of Compound **5** (600 MHz, $CDCl_3$)

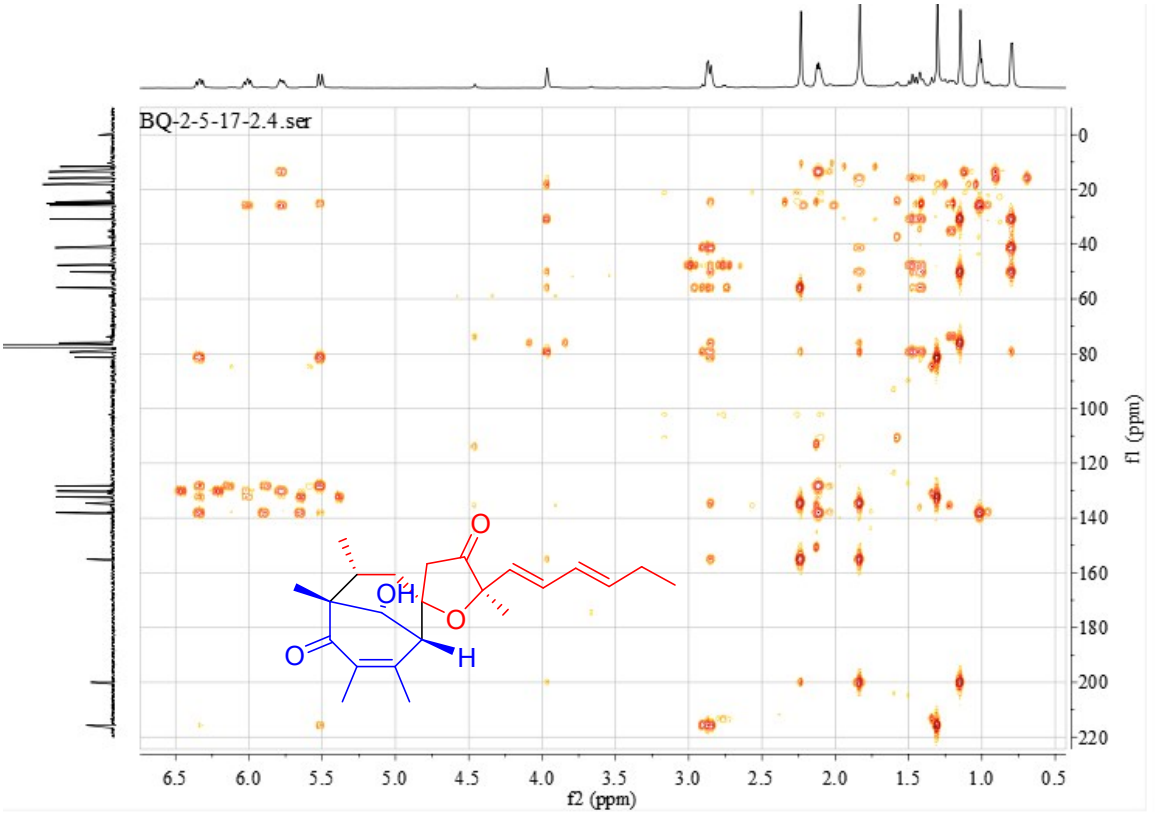


Figure S56. HMBC spectrum of Compound **5** (600 MHz, $CDCl_3$)

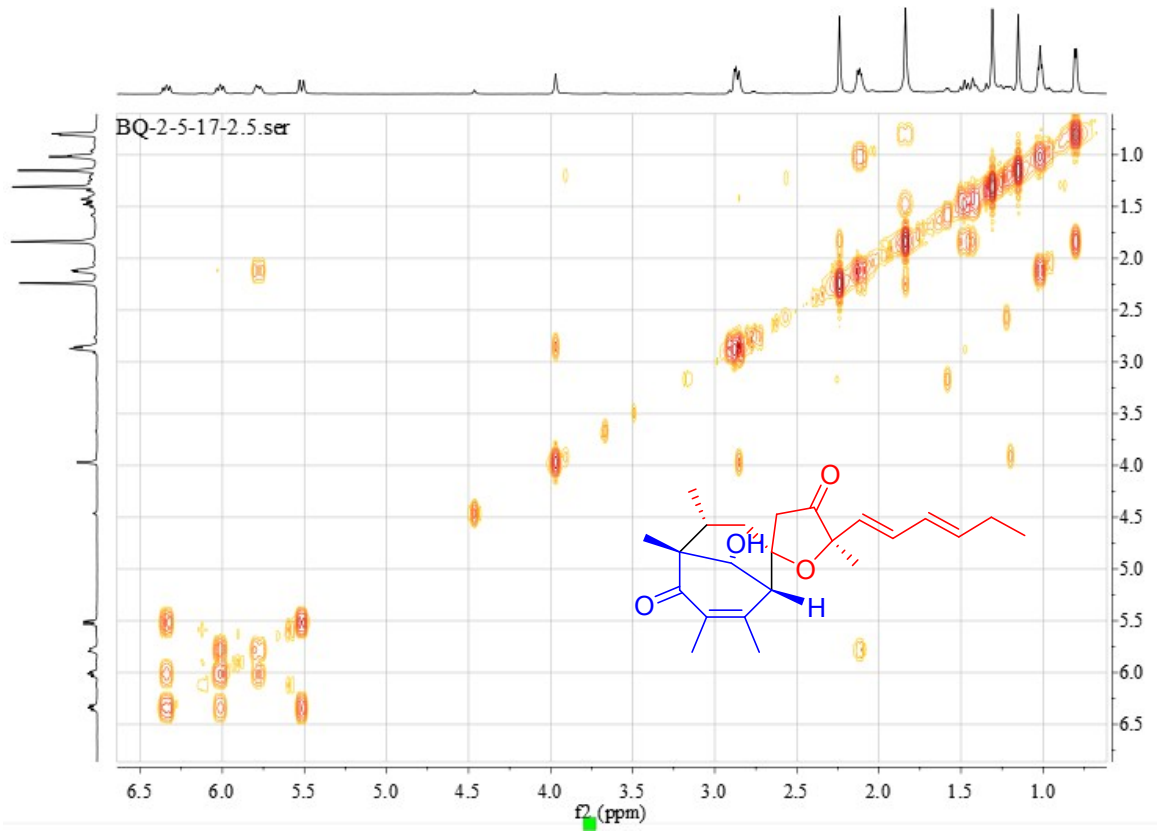


Figure S57. ^{1}H-^{1}H COSY spectrum of Compound **5** (600 MHz, $CDCl_3$)

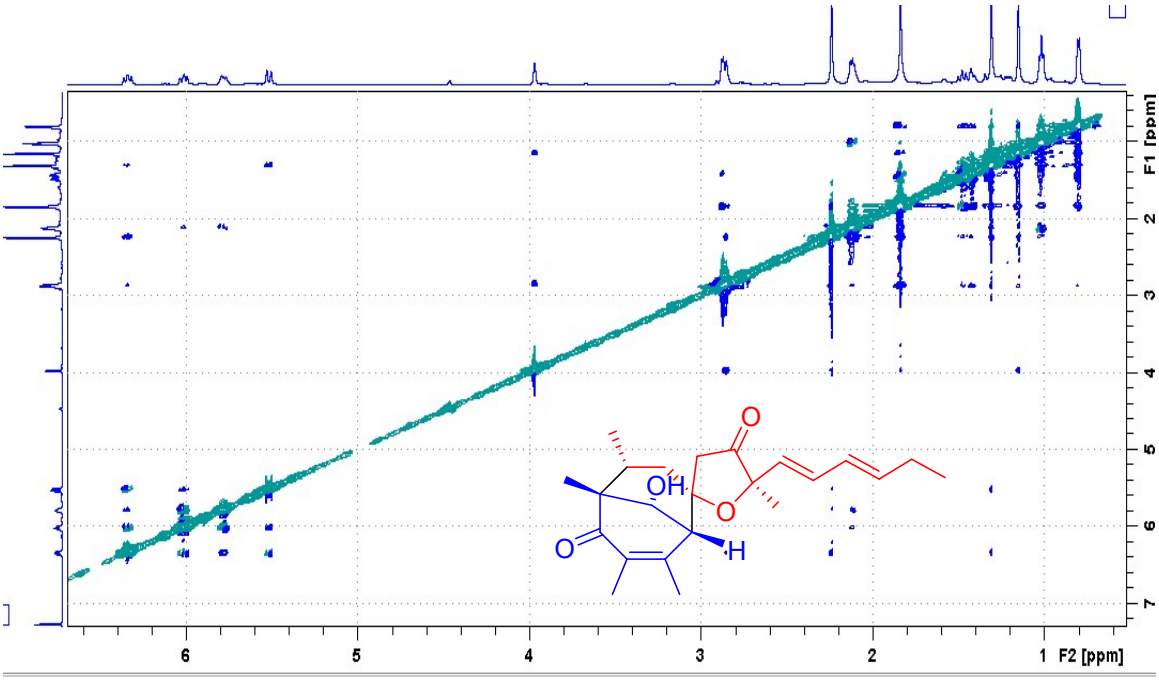


Figure S58. ROESY spectrum of Compound **5** (600 MHz, $CDCl_3$)

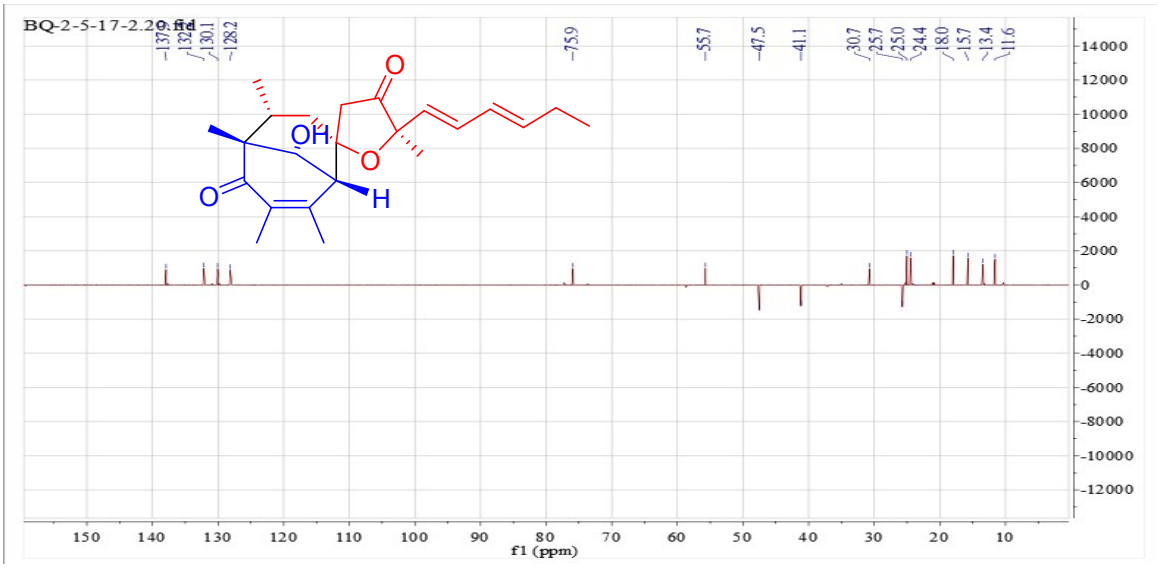
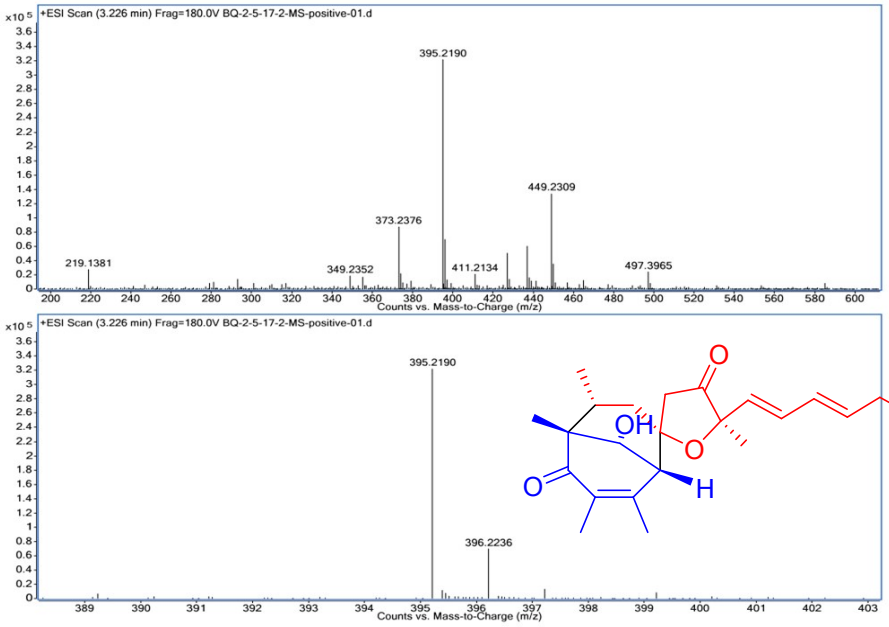


Figure S59. DEPT135 spectrum of Compound **5** (150 MHz, $CDCl_3$)

TCM-CPU HR-ESI-MS Display Report

Sample Name: BQ-2-5-17-2 **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 04/11/2017 **Operator:** Administrator



Elemental Composition Calculator

Target m/z:	395.2190	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); Na (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C23H32NaO4		395.2193		0.69	

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Figure S60. HRESIMS spectrum of Compound **5**

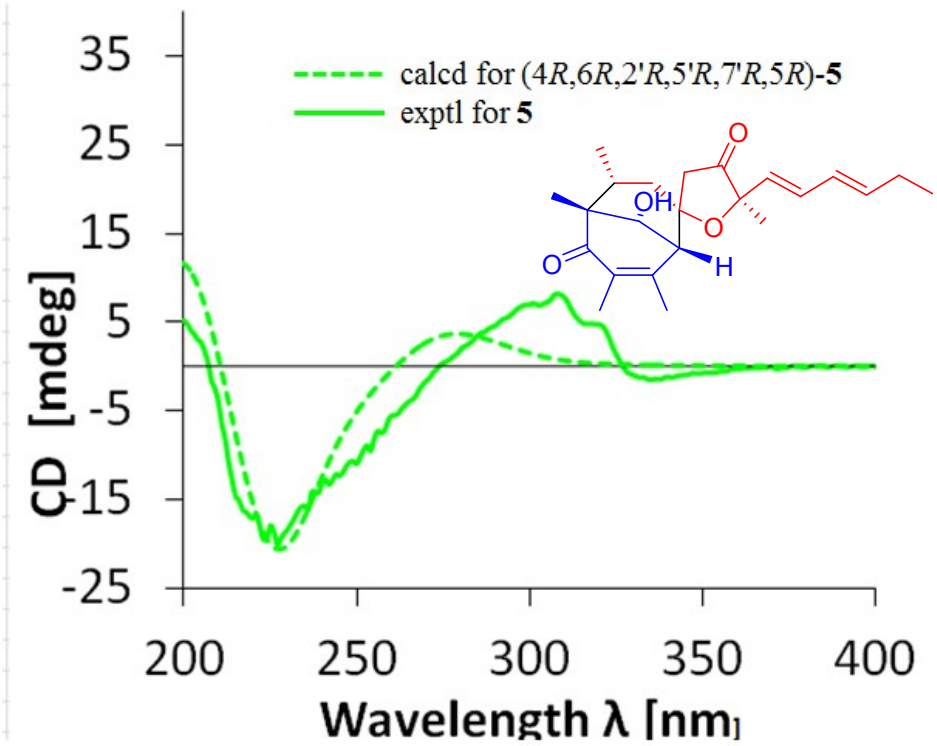

Figure S61. Calculated and experimental ECD spectra of Compound **5**

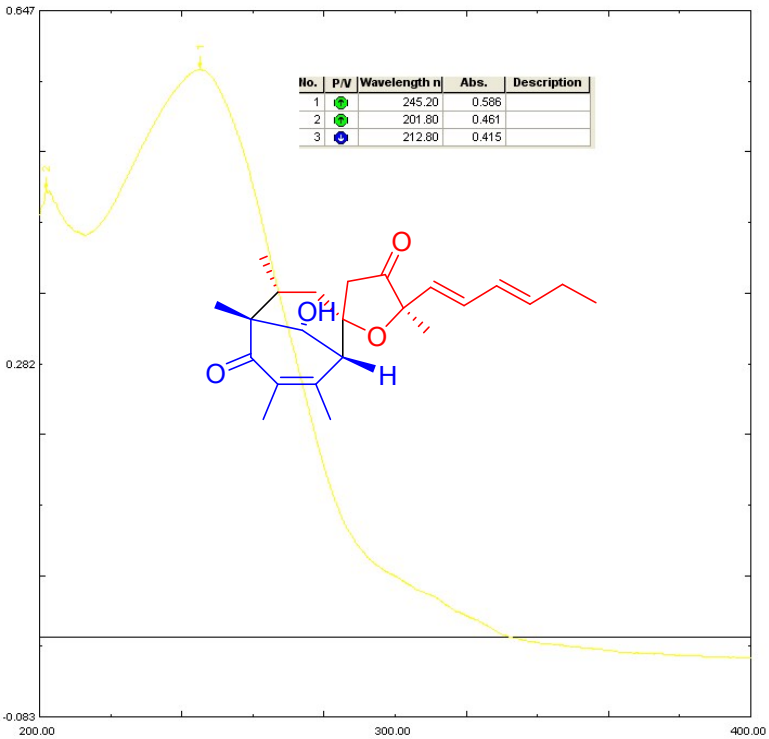

Figure S62. UV spectrum of Compound **5**

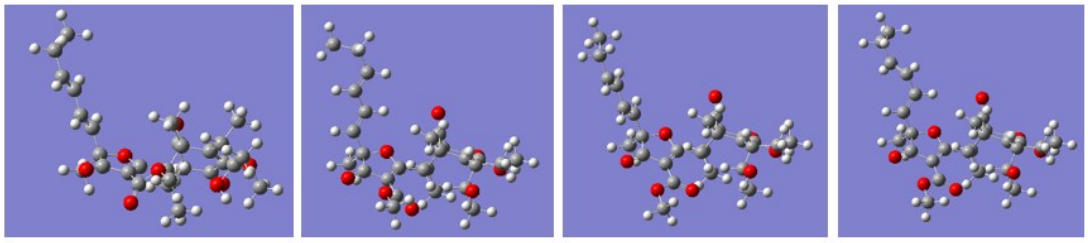

Figure S63. The low-energy conformers of **2**.