Electronic Supplementary Information

Taiwanoids A-D, four dimeric diterpenoids featuring tetracyclic [7. $7^{5,9}$. 4. $0^{5,10}$. $0^{8,9}$] octodecane from *Taiwania cryptomerioides*†

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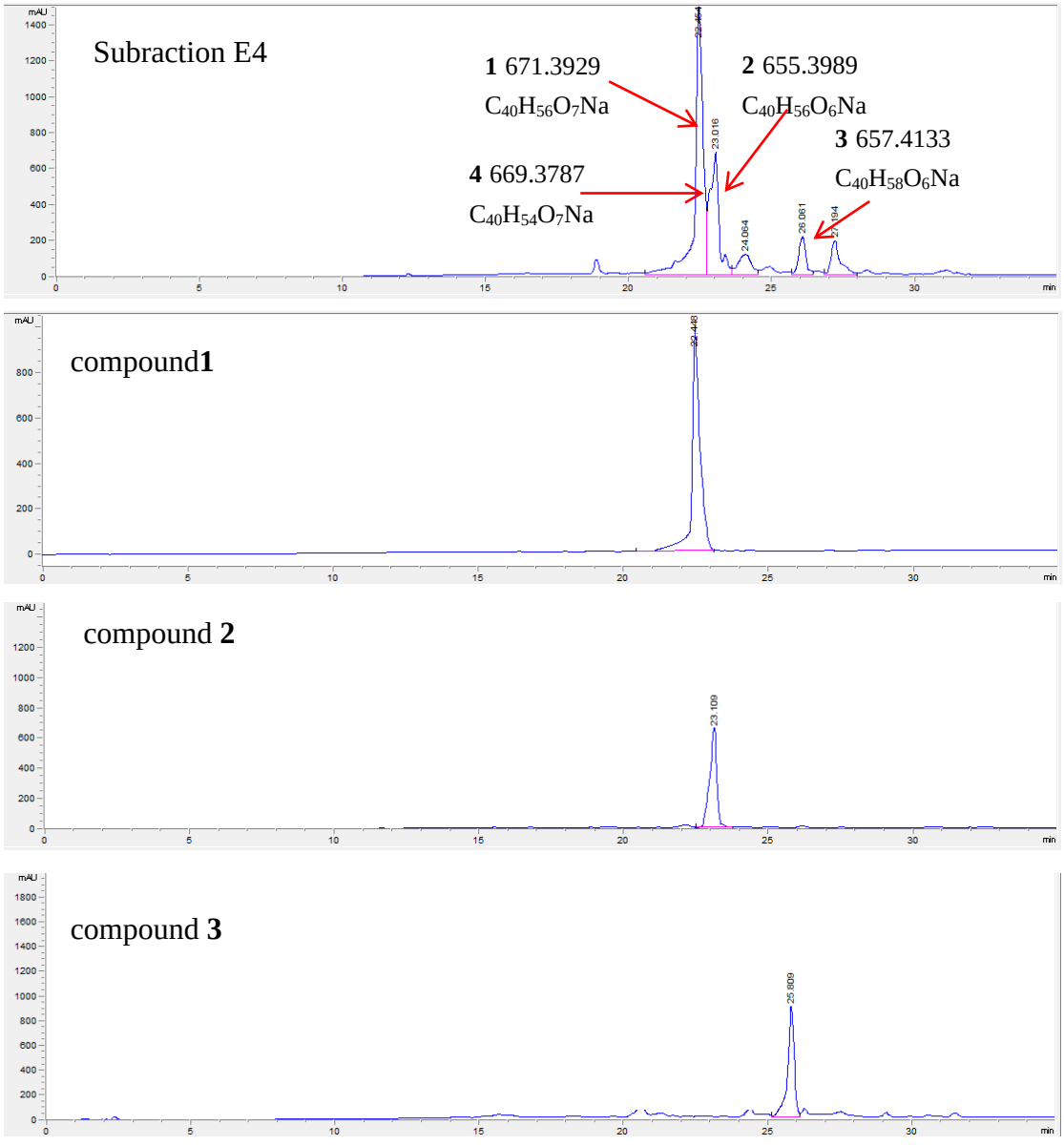
The LC-MS analysis-guided the subfraction E4 of the leaves of *Taiwania Cryptomerioides*

The dried and powdered leaves of *Taiwania cryptomerioides* (11.0 kg) were refluxed with 95% (v/v) EtOH under reflux to afford the crude extract (1.8 kg), which was solved in hot water and then partitioned into ethyl acetate part (600 g). The ethyl acetate extract was subjected on silica gel column chromatography (step with gradient PE/EtOAc 100:0 to 0:100) to afford 6 fractions (Fr.A–Fr.F). Fr.E (30 g) was separated by the ODS column eluted with MeOH/H_2O (4:6 to 1:0) to get subfractions E1-E6. Subfraction E4 was analysed by LC-MS (0-10 min: 40-80 MeOH/H_2O, 10-20 min 80-90 MeOH/H_2O, 20-30 min 90-100 MeOH/H_2O, 30-35 min 100-100 MeOH, 1 mL/min) and the results were showed in the Figure S1. The HPLC analysis of four pure compounds (**1**-**4**) was agreement with the result of LC-MS.



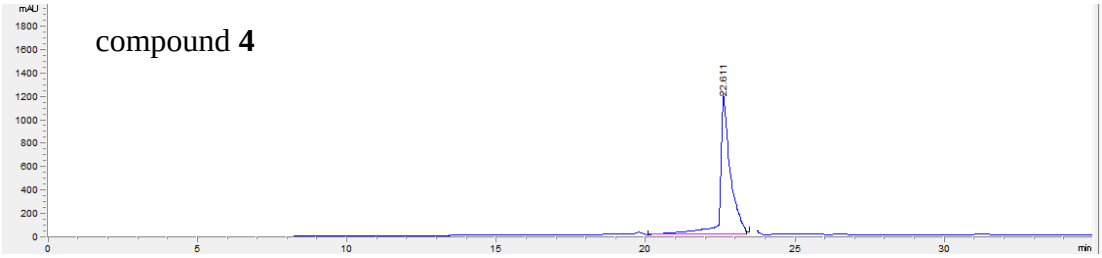


Fig. S1 The HPLC-MS analysis of subfraction E4 and HPLC analysis of pure compounds **1**-**4**.

Synthesis of 1a from 1

The substrate of compound **1** (20.0 mg, 0.031 mmol) was dissolved in CH_2Cl_2 (1 mL), then added the EDCI (17.8 mg, 0.093 mmol), DMAP (18.0 mg, 0.155 mmol) and MeOH (15 μL) in it. The reaction process was kept at room temperature and stirring all the process. After 12 h, very few substrate could not monitored by the TLC. The aim product (**1a**, 14.0 mg, 70%) was afforded by the pre-HPLC with MeOH-H_2O (92:8).

Fig. S2 Chemical conversion from **1** to **1a**.

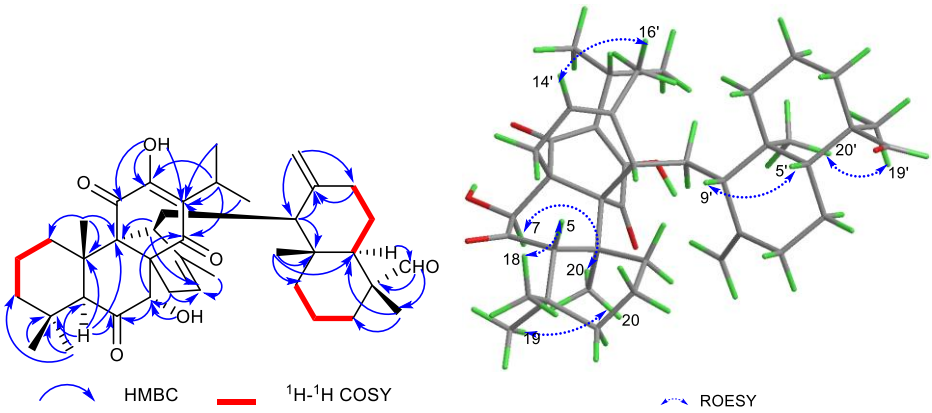


Fig. S3 Key HMBC, ^{1}H-^{1}H COSY and ROESY correlations for compound **2**.

Synthesis of 1 from 2

The substrate of compound **2** (15.0 mg, 0.0 23 mmol) was dissolved in CH_2Cl_2 (0.5 mL) and added 6 M HNO_3 (2.0 mL) in it. The reaction was kept under room temperature and stirred for 6 h. Compound **1** (12.0 mg, 80%) was detected by HPLC and purified by HPLC with MeOH/H_2O (85:15).

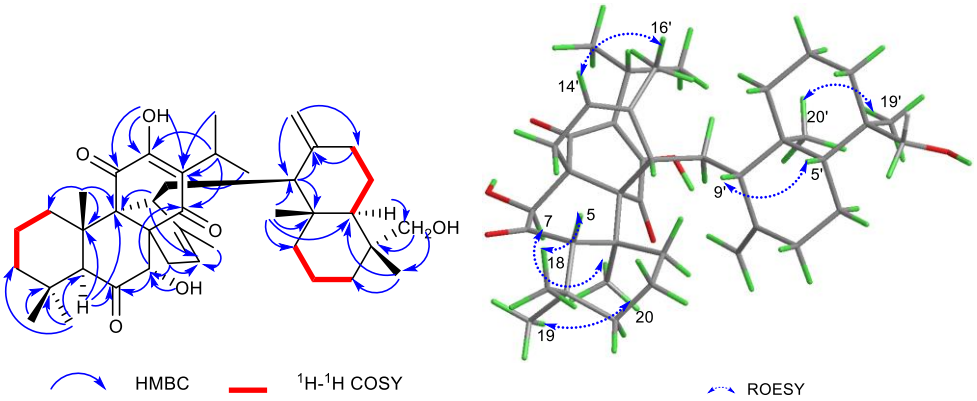


Fig. S4 Key HMBC, ^{1}H-^{1}H COSY and ROESY correlations for compound **3**.

Synthesis of 3 from 1

Compound **1** (20.0 mg, 0.031 mmol) was dissolved in 2.0 mL anhydrous THF, and stirred at 0 ℃ for 10 min, and then 1.0 M borane-tetrahydrofuran (1.0 mL) was added dropwise. After addition, the reaction solution was stirred at room temperature. Afterwards, 5 mL of methanol was added to the solution to stop the reaction. After vacuum concentration, the reaction solution added 3.0 mL H_2O and extracted with EtOAc for 3.0 mL × 3. Finally, compound **3** (10.0 mg, 50%) was obtained by HPLC with MeOH/H_2O (90:10).

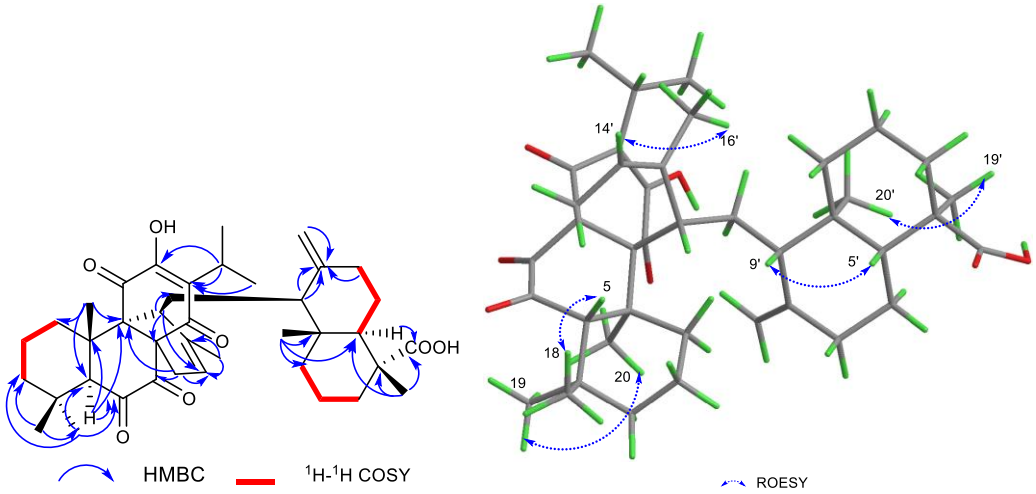


Fig. S5 Key HMBC, ^{1}H-^{1}H COSY and ROESY correlations for compound **4**.

Synthesis of 4 from 1

Compound **1** (20.0 mg, 0.031 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and added $CuSO_4$ (160.0 mg, 1.0 mmol) in it. After **1** was irradiated at 365 nm for 12 h, **4** (5.6 mg) was obtained in 28% yield. Without UV irradiating or Lewis acid, the conversion from **1** into **4** could not occur.

The X-ray crystallographic analysis of 1a.

Colorless needle crystals of **1a** were afforded from the MeOH/CH_2Cl_2 (3:1). A suitable crystal was selected and subjected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173.0 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table S1 The ^{1}H NMR and ^{13}C NMR data of compounds **1-3** in the $CDCl_3$ (*J* in Hz)

NO.	**1**		**2**		**3**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	2.28 (1H, m), 1.68 (1H, m)	37.4	2.19 (1H, m) *	37.5	2.18 (1H, m), *	37.5
2	1.62 (1H, m), 1.56 (1H, m)	17.9	1.64 (1H, m), 1.53 (1H, m)	17.8	1.68 (1H, m), 1.52 (1H, m)	18.9
3	1.48 (1H, m), 1.17 (1H, m)	42.9	1.40 (1H, m), 1.18 (1H, m)	42.6	1.42 (1H, m), 1.16 (1H, m)	42.6
4	-	34.5	-	34.5	-	34.5
5	3.05 (1H, s)	58.5	3.05 (1H, s)	58.5	3.06 (1H, s)	58.5
6	-	210.3	-	210.3	-	210.4
7	4.67 (1H, s)	76.6	4.68 (1H, s), 3.67 (OH, s)	76.6	4.67 (1H, s)	76.6
8	-	53.7	-	53.7	-	53.7
9	-	61.3	-	61.3	-	61.4
10	-	42.6	-	42.9	-	42.9
11	-	199.2	-	199.1	-	199.2
12	-	152.8	7.15 (OH, s)	152.7	7.17 (OH, s)	151.7
13	-	132.1	-	132.1	-	132.0
14	-	196.6	-	196.6	-	196.5
15	3.17 (1H, sept, 7.0)	26.9	3.19(1H, sept, 7.1)	27.1	3.18 (1H, sept, 7.0)	27.2
16	1.23 (3H, d, 7.0)	20.5	1.30 (3H, d, 7.1)	20.6	1.29 (3H, d, 7.0)	20.5
17	1.28 (3H, d, 7.0)	18.9	1.25 (3H, d, 7.1)	27.2	1.25 (3H, d, 7.0)	18.9
18	1.18 (3H, s)	35.4	1.19 (3H, s)	35.5	1.19 (3H, s)	35.5
19	1.02 (3H, s)	22.5	1.02 (3H, s)	22.5	1.02 (3H, s)	22.5
20	1.03 (3H, s)	27.2	1.04 (3H, s)	27.2	3.20 (1H, sept, 7.0)	27.2
1′	1.98 (1H, m), *	37.6	1.93 (1H, m), 1.58 (1H, m)	37.6	2.32(1H, m),1.93(1H, m)	38.1
2′	1.54 (1H, m), *	18.5	1.56 (1H, m), *	17.9	1.65 (1H, m), *	18.0
3′	2.16 (1H, m), *	37.1	2.15 (1H, m), *	32.5	2.18 (1H, m), *	38.1
4′	-	47.6	-	50.0	-	35.4
5′	1.80 (1H, m)	49.9	1.52 (1H, m)	47.9	1.58 (1H, m)	48.7
6′	1.35 (1H, m), *	27.9	1.56 (1H, m), *	27.9	1.62 (1H, m), *	24.3

7′	2.28 (1H, m), 1.94 (1H, m)	37.9	2.30 (1H, m)*	37.8	1.93 (1H, m)	38.2
8′	-	147.3	-	147.0	-	147.7
9′	1.66 (1H, m)	52.8	1.58 (1H, m)	52.6	1.50 (1H, m)	52.8
10′	-	38.9	-	38.5	-	39.6
11′	2.12 (1H, m), *	27.1	1.96 (1H, m),*	26.8	2.16 (1H, m), *	28.1
12′	3.10 (1H, dd, 2.6, 11.0)	44.8	3.12 (1H, dd, 3.1, 11.8)	44.8	3.12 (1H, dd, 2.8, 11.7)	44.8
13′	-	135.9	-	135.9	-	136.0
14′	5.59 (1H, d, 5.6)	125.2	5.62 (1H, d, 5.8)	125.3	5.59 (1H, d, 4.8)	125.1
15′	3.52 (1H, m), 1.66 (1H, m)	24.6	3.54 (1H, m), 1.67 (1H, m)	24.6	3.52 (1H, m), 1.60 (1H, m)	24.6
16′	1.81 (3H, s)	24.3	1.83 (3H, s)	24.4	1.81 (3H, s)	24.4
17′	4.84 (1H, s), 4.32 (1H, s)	108.6	4.89 (1H, s), 4.36 (1H, s)	109.0	4.85 (1H, s), 4.32 (1H, s)	108.0
18′	-	185.2	9.19 (1H, s)	206.6	3.38 (1H, d,10.9), 3.05 (1H, d, 10.9)	72.1
19′	1.06 (3H, s)	16.3	0.98 (3H, s)	14.3	0.67 (3H, s)	17.7
20′	0.43 (3H, s)	14.6	0.47 (3H, s)	14.6	0.46 (3H, s)	14.9

Table S2 The ^{1}H NMR and ^{13}C NMR data of compounds **4** and **1a** in the $CDCl_3$ (*J* in Hz)

NO.	**4**		**1a**	
	δ_H	δ_C	δ_H	δ_C
1	2.22 (1H, m), 1.68 (1H, m)	35.8	2.28 (1H, m), 1.65 (1H, m)	37.5
2	1.60 (1H, m), 1.55 (1H, m)	17.8	1.63 (1H, m), 1.58 (1H, m)	17.9
3	1.45 (1H, m), 1.15 (1H, m)	42.5	1.47 (1H, m), 1.16 (1H, m)	42.9
4	-	34.2	-	34.5
5	3.44 (1H, s)	60.6	3.06 (1H, s)	58.5
6	-	195.6	-	210.3
7	-	194.2	4.67 (1H, s)	76.6
8	-	59.3	-	53.7
9	-	63.3	-	61.4
10	-	43.2	-	42.6
11	-	198.1	-	199.2
12	7.13 (OH, s)	153.5	-	152.7
13	-	134.4	-	132.0
14	-	194.4	-	196.5
15	3.24 (1H, overlap)	27.2	3.18 (1H, sept, 7.1)	27.0
16	1.31 (3H, d, 7.1)	20.3	1.29 (3H, d, 7.1)	20.5
17	1.30 (3H, d, 7.1)	18.9	1.24 (3H, d, 7.1)	18.9
18	1.14 (3H, s)	34.8	1.19 (3H, s)	35.5
19	1.08 (3H, s)	22.2	1.02 (3H, s)	22.5
20	0.88 (3H, s)	23.8	1.03 (3H, s)	27.2
1′	1.96 (1H ,m), 0.81 (1H, m)	37.7	1.68 (1H, m), 1.49 (1H, m)	37.6
2′	1.56 (1H, m), *	18.5	1.49 (1H, m), *	18.6
3′	1.68 (1H, m), 1.60 (1H, m)	37.1	2.18 (1H, m), *	37.1
4′	-	47.5	-	47.9
5′	1.80 (1H, m)	49.8	1.79 (1H, dd, 12.6, 2.6)	50.3
6′	1.18 (1H, m), *	26.9	1.32 (1H, m), *	27.9
7′	2.31 (1H, m), *	37.8	2.28 (1H, m), 1.93 (1H, m)	37.9

8′	-	147.0	-	147.4
9′	1.54 (1H, m)	52.7	1.66 (1H, m)	52.7
10′	-	38.9	-	39.1
11′	0.98 (1H, m), 0.81 (1H, m)	27.9	0.95 (1H, m), 0.88 (1H, m)	27.1
12′	3.24 (1H, dd, overlap)	43.1	3.11 (1H, dd,11.8, 2.9)	44.8
13′	-	138.6	-	140.0
14′	5.67 (1H, d, 6.0)	121.8	5.61 (1H, d, 6.0)	125.2
15′	3.88 (1H, m), 1.80 (1H, m)	25.6	3.52 (1H, m), 1.63 (1H, m)	24.6
16′	1.91 (3H, s)	24.7	1.82 (3H, s)	24.4
17′	4.88 (1H, s), 4.33 (1H, s)	108.8	4.84 (1H, s), 4.32 (1H, s)	108.5
18′	-	185.0	-	179.5
19′	1.08 (3H, s)	16.4	1.07 (3H, s)	16.6
20′	0.44 (3H, s)	14.6	0.44 (3H, s)	14.6
21′	-	-	3.64 (3H, s)	52.1

* The one or two proton signals were to weak to be assigned according to the 2D NMR in Table S1 and S2.

Table S3 The ^{1}H NMR compounds **5-10** in the $CDCl_3$ (*J* in Hz)

NO.	**5**	**6**	**7**	**8**	**9**	**10**
	δ_H	δ_H	δ_H	δ_H	δ_H	δ_H
1	2.69 (1H, m)	2.88 (1H,m)	2.59 (1H, m)	2.05 (1H, m), *	2.05 (1H, m), *	2.08 (1H, m), *
	1.15 (1H, m)	1.50 (1H,m)	1.16 (1H, m)			
2	1.20-1.30 (2H, m)	1.19-1.32 (2H, m)	1.25 (2H, m)	1.56-1.63 (2H, m)	1.56-1.60 (2H, m)	1.58-1.62 (2H, m)
3	1.55-1.65 (2H, m)	1.55-1.65 (2H, m)	1.56-1.63 (2H, m)	2.12 (1H, m), *	2.15 (1H, m), *	2.16 (1H, m), *
4	-	-	-	-	-	-
5	1.55 (1H, m)	1.56 (1H, m)	1.50 (1H, m)	1.46 (1H, m)	1.47 (1H, m)	1.39 (1H, m)
6	1.96 (1H, m),	6.47 (1H, dd, 3.2, 9.8)	4.44 (1H, br s)	1.86 (1H, m)	1.84 (1H, m)	1.83 (1H, m)
	1.45 (1H, m)			1.18 (1H, m)	1.14 (1H, m)	1.21 (1H, m)
7	4.73 (1H, m),	6.81 (1H, dd, 3.2, 9.8)	4.51 (1H, br s)	2.08 (2H, m)	2.05 (2H, m)	2.13 (2H, m)
	3.04 (OH, s)					
8	-	-	-	-	-	-
9	-	-	-	1.86 (1H, m)	1.87 (1H, m)	1.87 (1H, m)
10	-	-	-	-	-	-
11	-	-	-	2.35 (1H, m)	2.40 (1H, m)	2.35 (1H, m)
				2.15 (1H, m)	2.15 (1H, m)	2.10 (1H, m)
12	-	7.33 (OH, s)	7.32 (OH, s)	5.41 (1H, t, 6.5)	5.41 (1H, t, 6.5)	5.41 (1H, t, 6.5)
13	-	-	-	-	-	-
14	-	-	-	6.35 (1H, dd, 10.7, 17.4)	6.33 (1H, dd, 10.7, 17.4)	6.33(1H, dd, 10.7, 17..4)
15	3.16 (1H, sept, 7.0)	3.17 (1H, sept,7.0)	3.16 (1H, sept, 7.0)	5.05 (1H, d, 17.4)	5.05 (1H, d, 17.4)	5.05 (1H, d, 17.4)
				4.89 (1H, d, 10.7)	4.89 (1H, d, 10.7)	4.88 (1H, d, 10.7)
16	1.21 (3H, d, 7.0)	1.22 (3H, d, 7.0)	1.21 (3H, d. 7.0)	1.76 (3H, s)	1.76 (3H, s)	1.75 (3H, s)
17	1.22 (3H, d, 7.0)	1.23 (3H, d, 7.0)	1.22 (3H, d, 7.0)	4.83 (3H, br s)	4.85 (1H, br s)	4.82 (1H, br s)
				4.49 (3H, br s)	4.50 (1H, br s)	4.46 (1H, br s)

18	0.90 (3H, s)	0.98 (3H, s)	1.04 (3H, s)	-	9.24 (1H, s)	3.42 (1H, d, 10.9) 3.12 (1H, d, 10.9)
19	0.98 (3H, s)	1.02 (3H, s)	1.25 (3H, s)	1.17 (3H, s)	1.06 (3H, s)	1.25 (3H, s)
20	1.22 (3H, s)	1.03 (3H, s)	1.60 (3H, s)	0.77 (3H, s)	0.79 (3H, s)	0.77 (3H, s)

Table S4 The ^{1}H NMR compounds **5-10** in the $CDCl_3$ (*J* in Hz)

NO.	**5**	**6**	**7**	**8**	**9**	**10**
	δ_C	δ_C	δ_C	δ_C	δ_C	δ_C
1	35.7	35.3	38.6	38.3	38.4	38.1
2	18.8	18.8	19.2	18.6	17.9	18.8
3	41.0	40.7	42.4	37.7	37.7	37.9
4	39.1	33.4	33.9	47.7	47.7	39.5
5	45.7	52.4	49.6	57.2	57.1	57.2
6	25.7	139.8	69.5	26.8	26.7	24.1
7	63.2	121.2	69.3	37.2	32.5	35.5
8	143.1	138.6	141.1	147.9	147.7	148.4
9	147.8	140.7	147.7	49.5	50.2	48.5
10	33.0	39.4	38.7	38.9	38.6	38.8
11	183.8	183.6	183.6	23.0	23.2	23.3
12	151.1	151.3	151.3	133.7	133.9	134.2
13	124.1	122.7	124.4	133.6	133.7	133.5
14	189.0	186.2	189.3	141.7	141.7	141.8
15	23.9	24.2	24.4	110.1	110.3	109.9
16	19.7	20.0	20.0	16.5	17.9	17.8
17	19.8	20.2	21.8	108.3	108.8	107.8
18	33.1	32.8	33.7	185.8	206.7	72.2
19	21.7	23.0	24.1	14.8	14.5	15.1
20	18.3	15.3	19.9	12.0	12.1	12.0

Table S5 Crystal data and structure refinement for compound **1a**

Empirical formula	$C_{41}H_{58}O_7$
Formula weight	662.87
Temperature/K	173.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.9237(4)
b/Å	15.5472(4)
c/Å	39.6257(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7961.9(4)
Z	8
ρ_{calc}g/cm^3	1.106
μ/mm^{-1}	0.588
F(000)	2880.0
Crystal size/mm^3	0.28 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.106 to 148.98
Index ranges	-16 ≤ h ≤ 15, -19 ≤ k ≤ 19, -49 ≤ l ≤ 49
Reflections collected	128664
Independent reflections	16273 [R_{int} = 0.0827, R_{sigma} = 0.0358]
Data/restraints/parameters	16273/43/897
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1118
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.1185
Largest diff. peak/hole / e Å^{-3}	0.18/-0.21
Flack parameter	0.08(6)

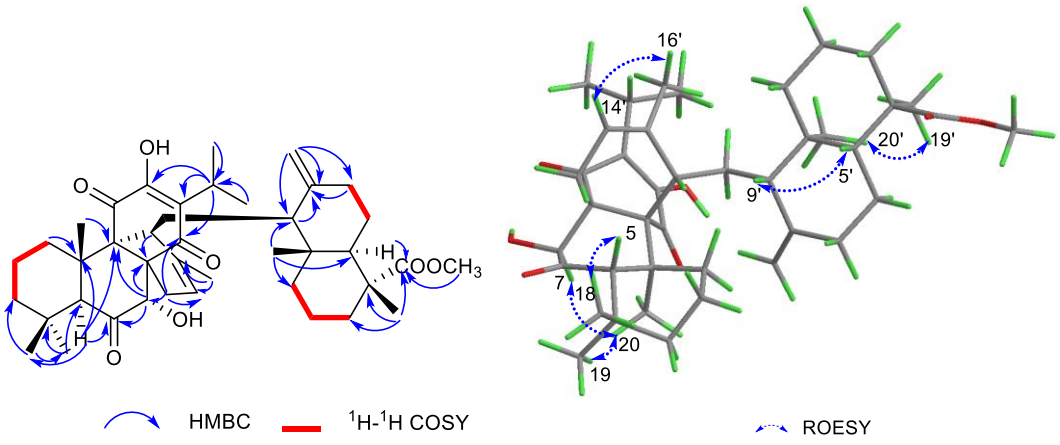
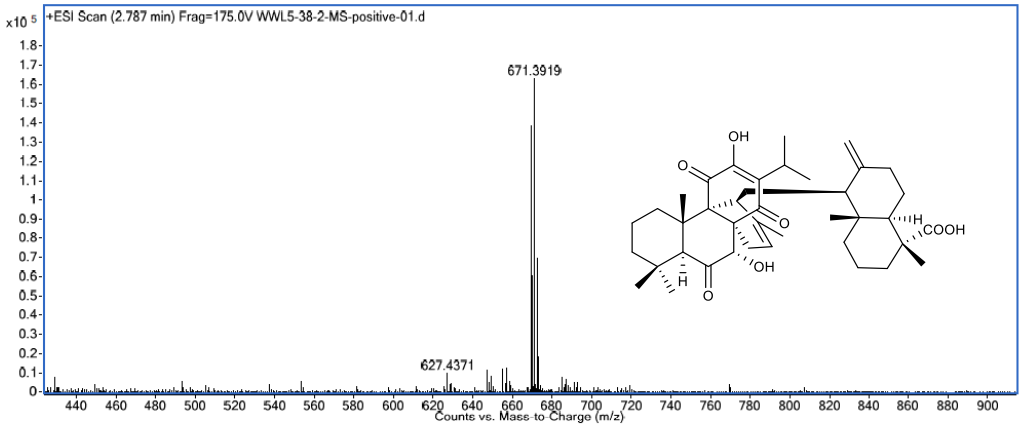


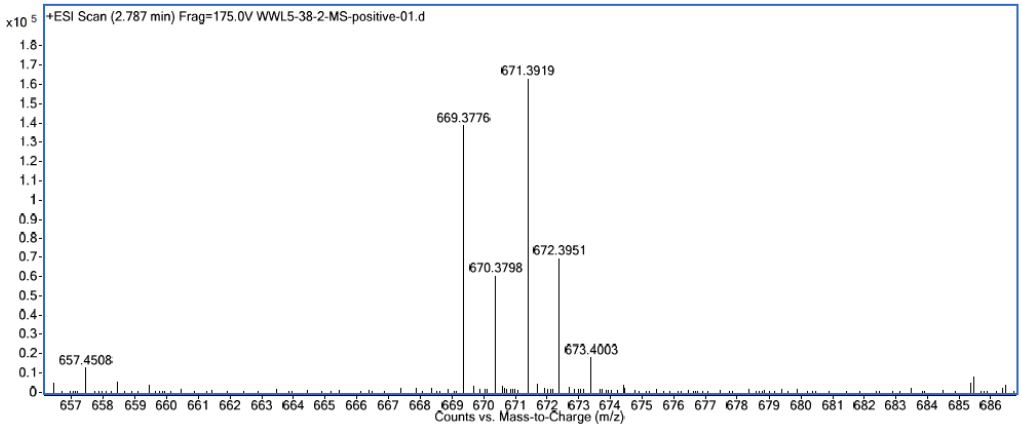
Fig. S6 Key HMBC, ^{1}H-^{1}H COSY and ROESY correlations for compound **1a**.

TCM-CPU HR-ESI-MS Display Report

Sample Name: WWL5-38-2 **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 12/25/2017 **Operator:** Administrator





Elemental Composition Calculator

Target m/z:	671.3919	**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**	
C40H56NaO7		671.3918		-0.17	

Fig. S7 The HRESIMS spectrum of compound **1** in MeOH.

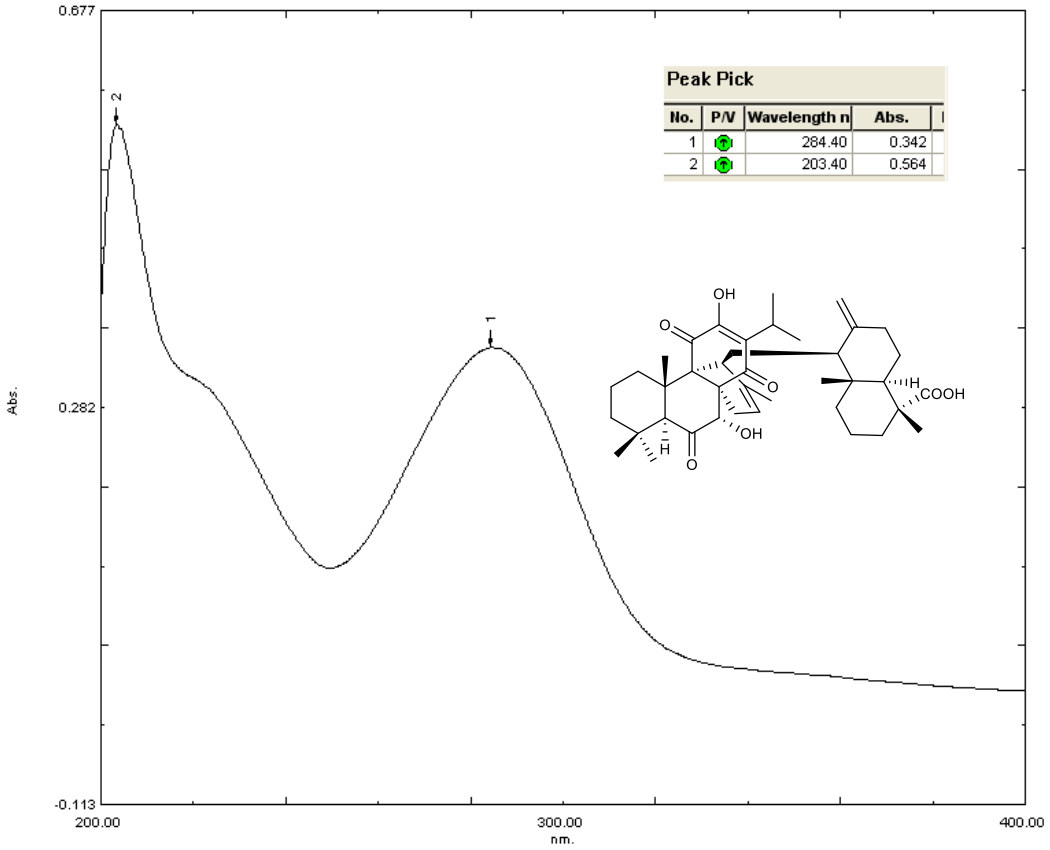


Fig. S8 The UV spectrum of compound **1** in MeOH.

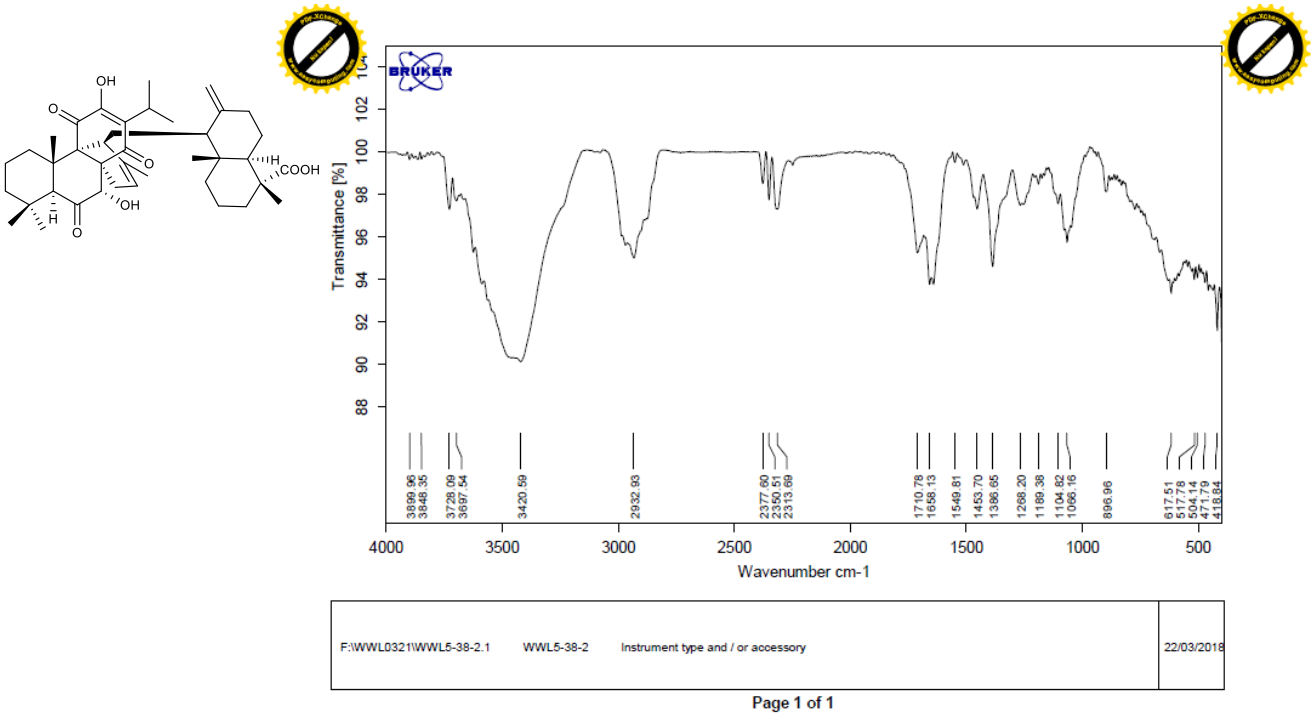


Fig. S9 The IR spectrum of compound **1** in KBr.

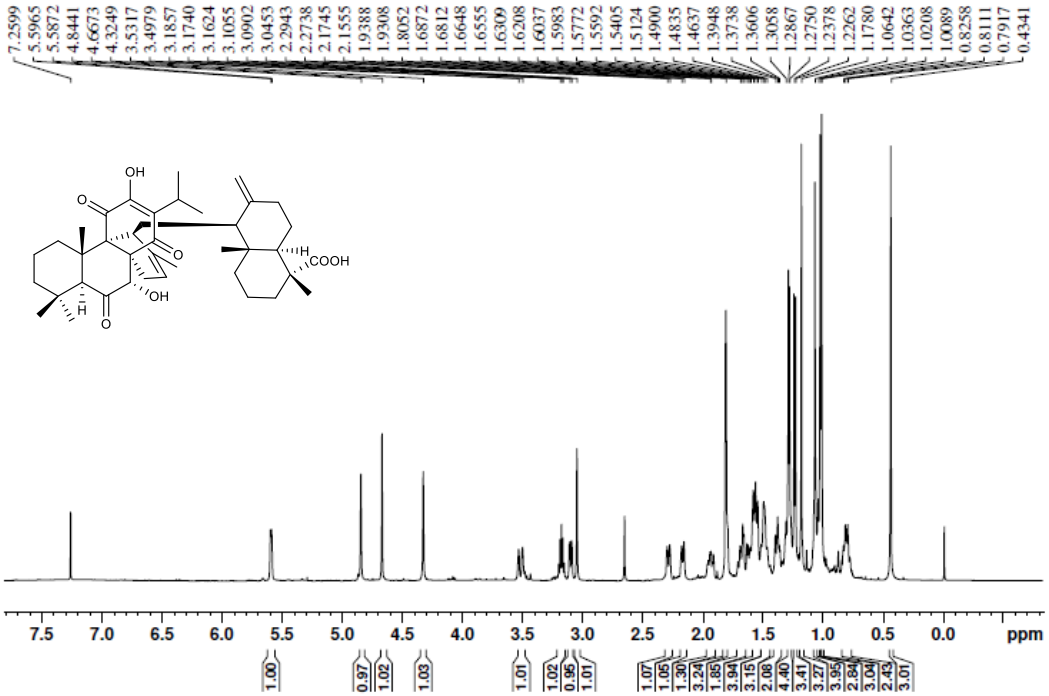


Fig. S10 The ^{1}H NMR spectrum of compound **1** in $CDCl_3$。

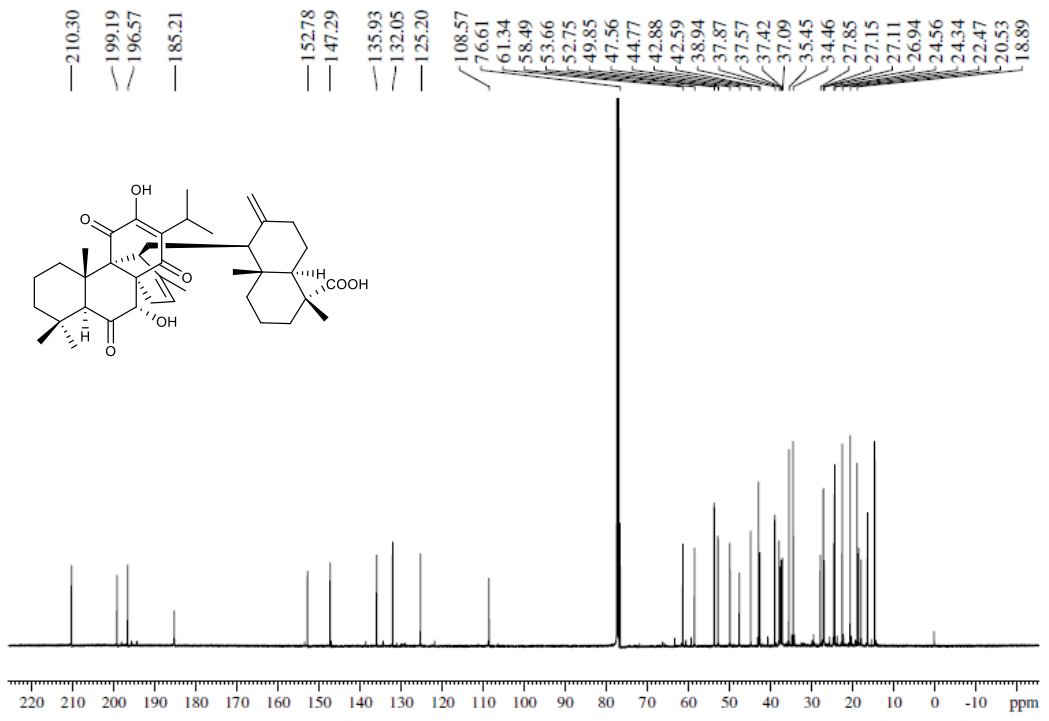


Fig. S11 The ^{13}C NMR spectrum of compound **1** in $CDCl_3$。

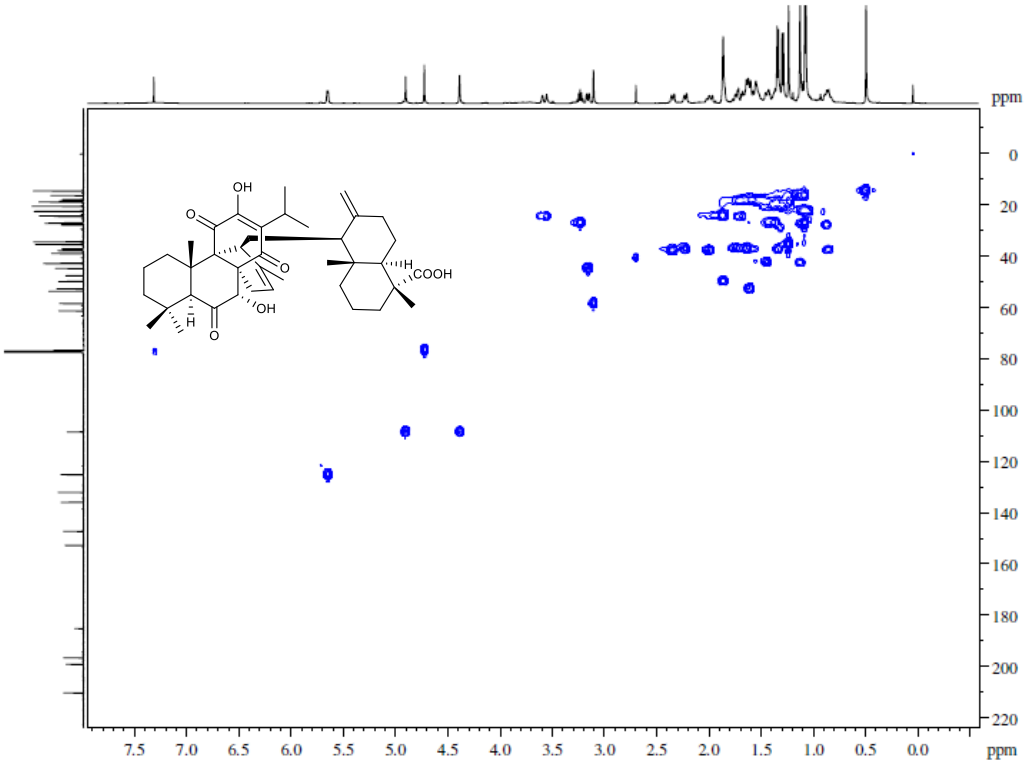


Fig. S12 The HSQC spectrum of compound **1** in $CDCl_3$。

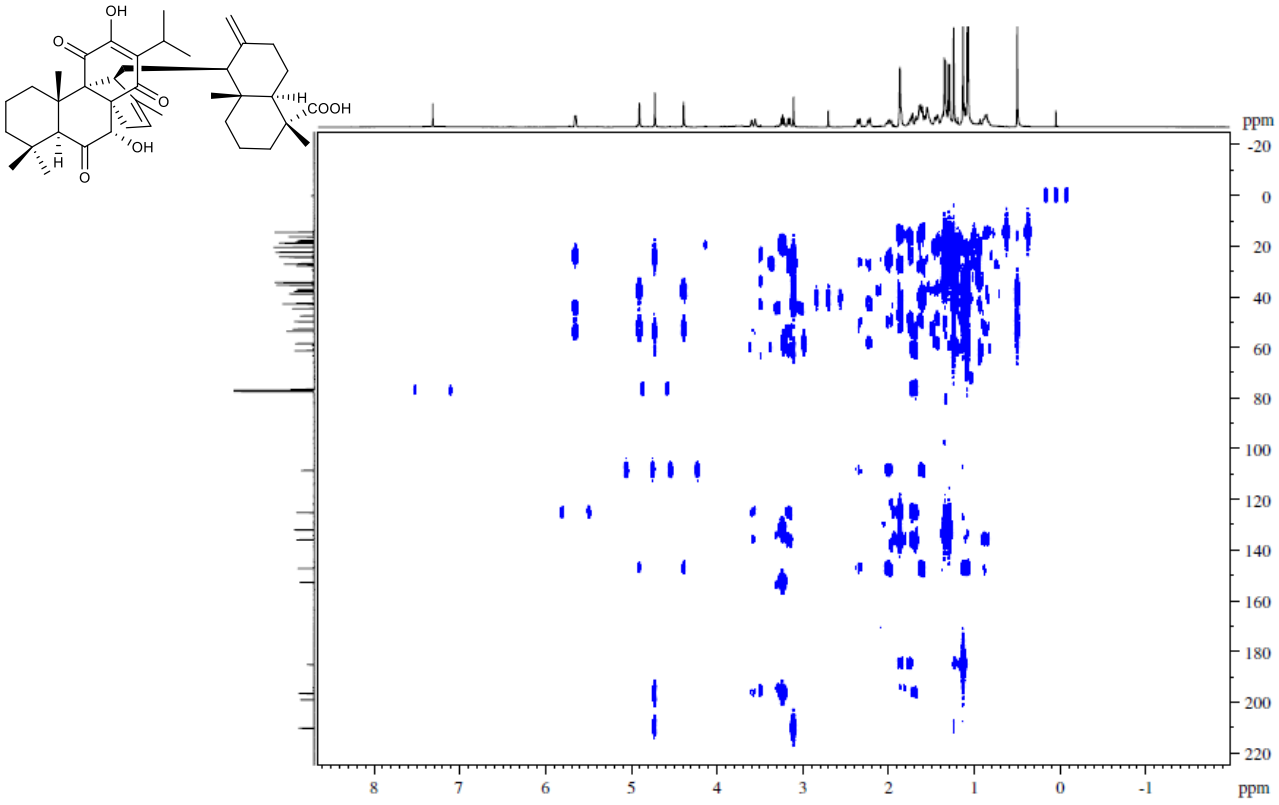


Fig. S13 The HMBC spectrum of compound **1** in $CDCl_3$。

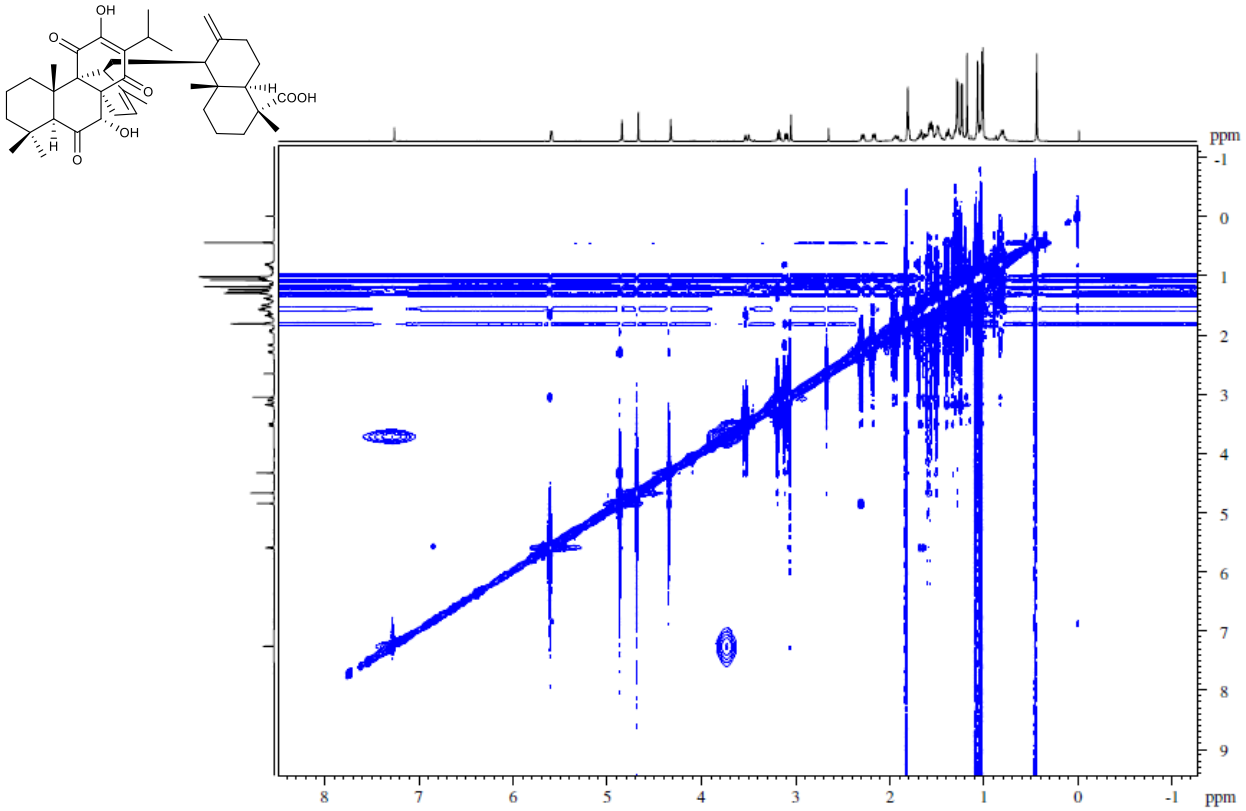
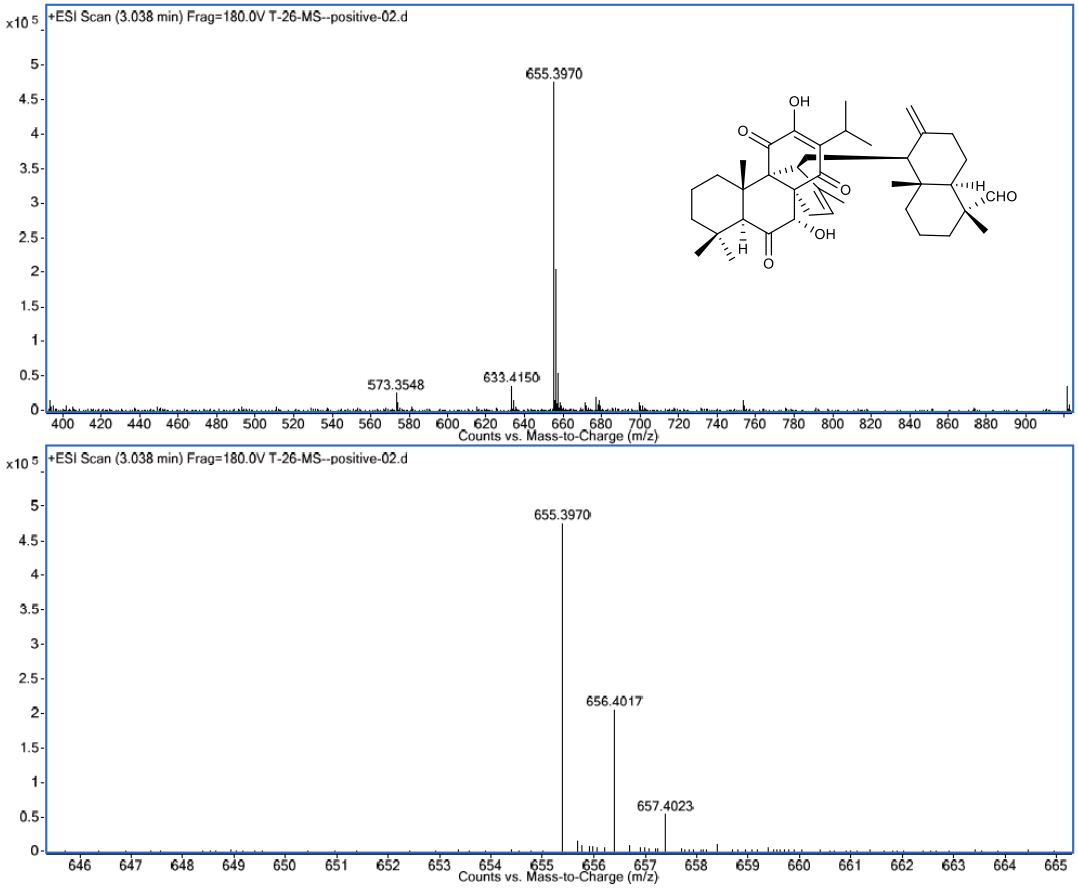


Fig. S14 The ROESY spectrum of compound **1** in $CDCl_3$.

TCM-CPU HR-ESI-MS Display Report

Sample Name: T-26 **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 01/29/2018 **Operator:** Administrator



Elemental Composition Calculator

Target m/z:	655.3970	**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**	
C40H56NaO6		655.3969		-0.08	

Fig. S15 The HRESIMS spectrum of compound **2** in MeOH.

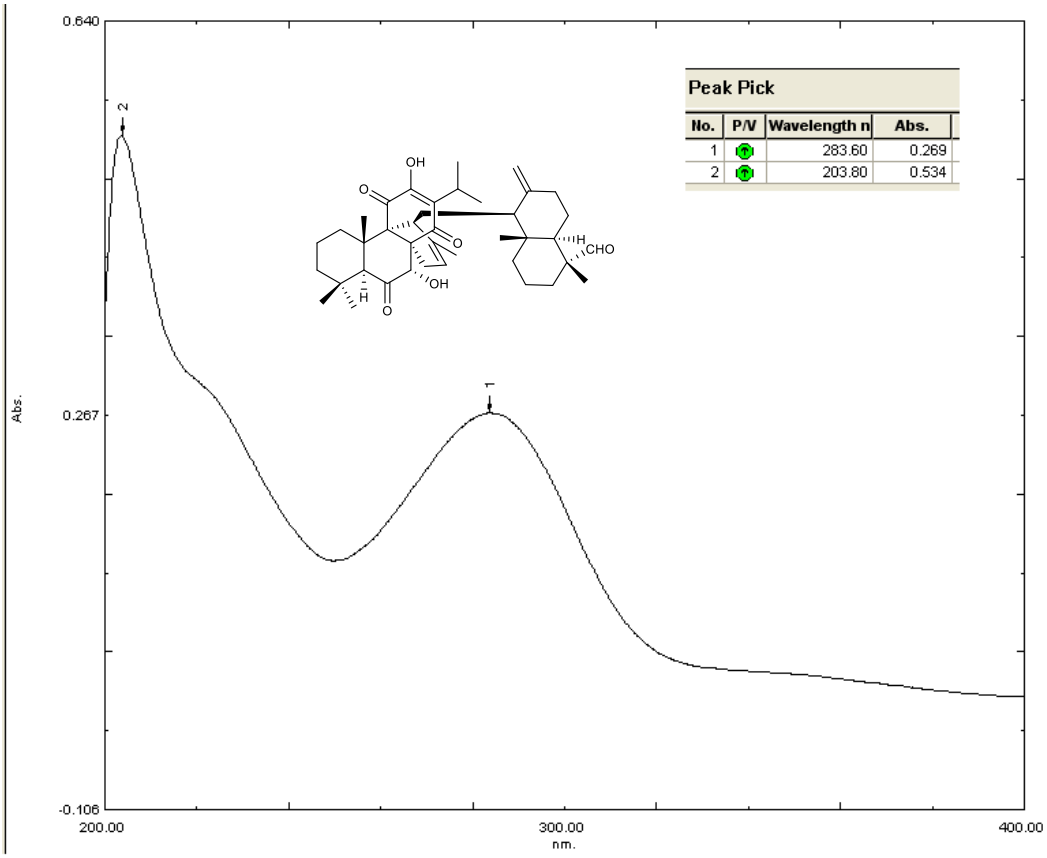


Fig. S16 The UV spectrum of compound **2** in MeOH.

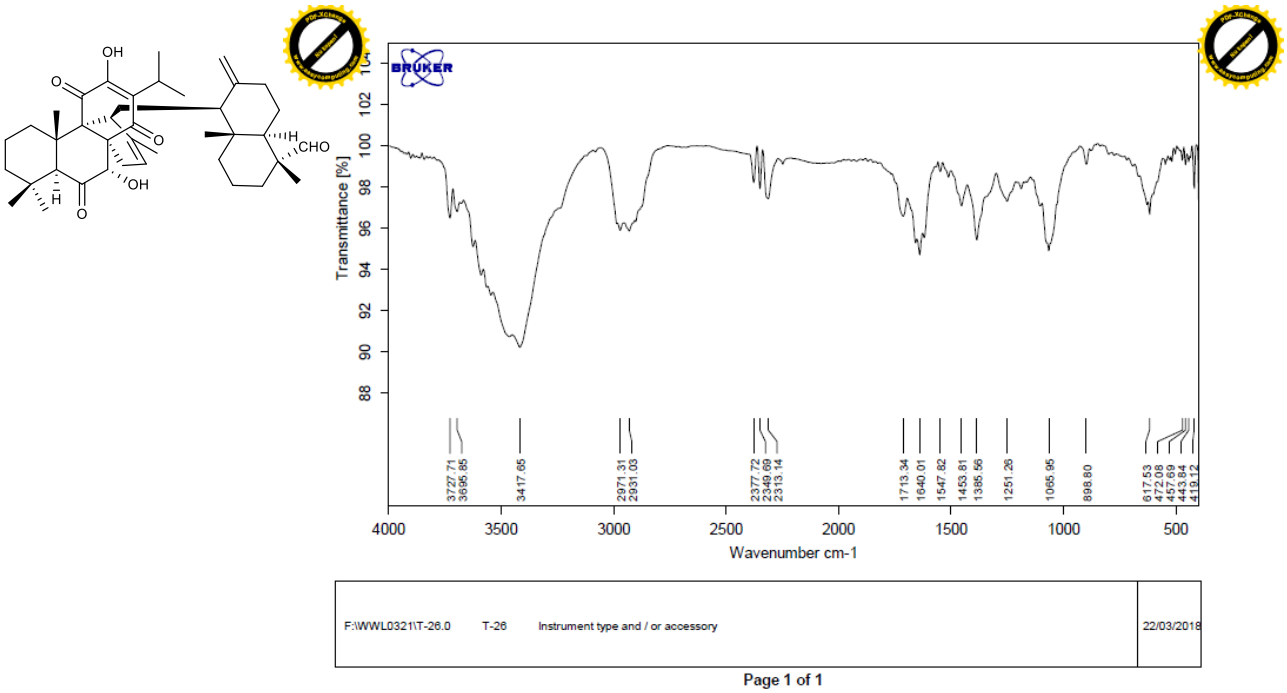


Fig. S17 The IR spectrum of compound **2** in KBr.

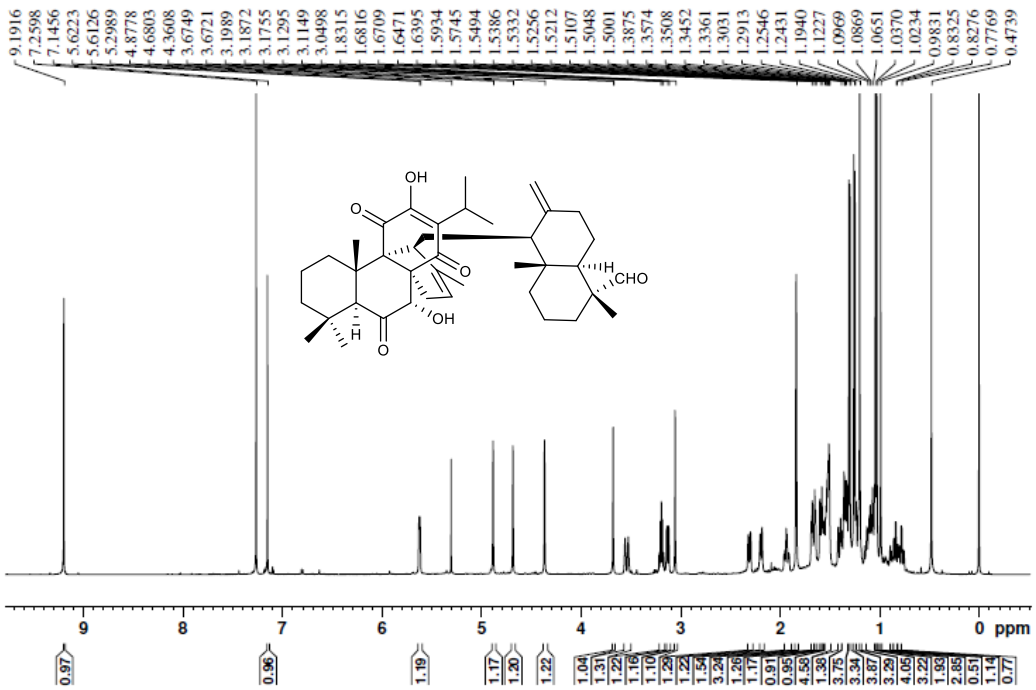


Fig. S18 The ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

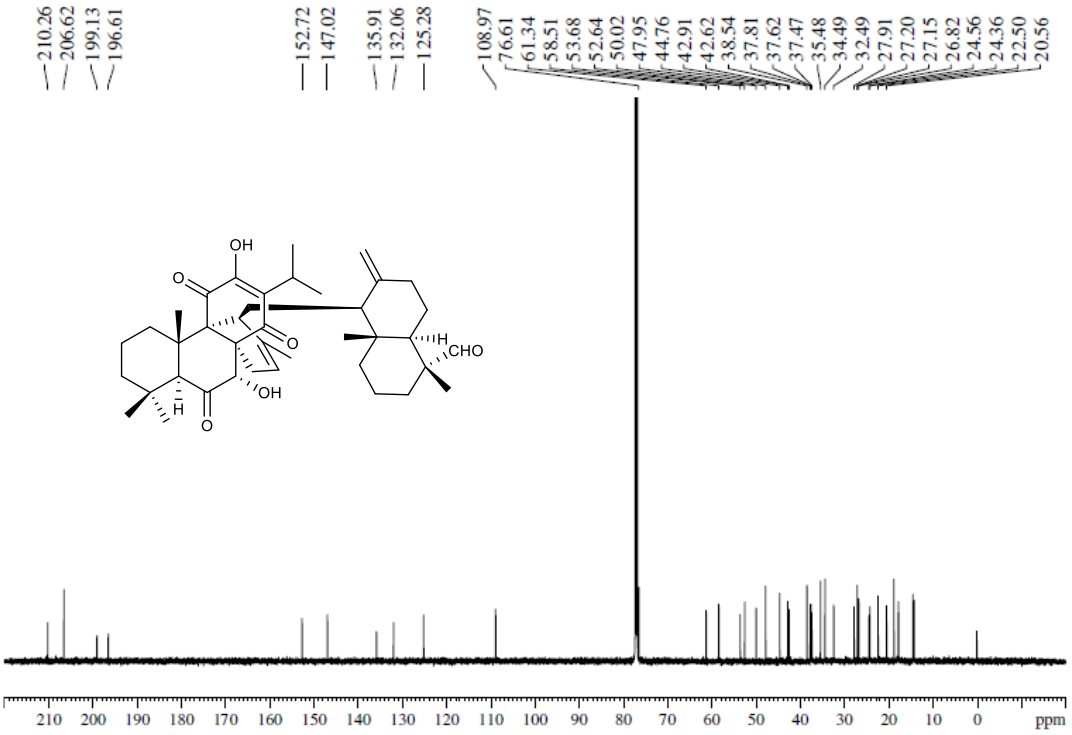


Fig. S19 The ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

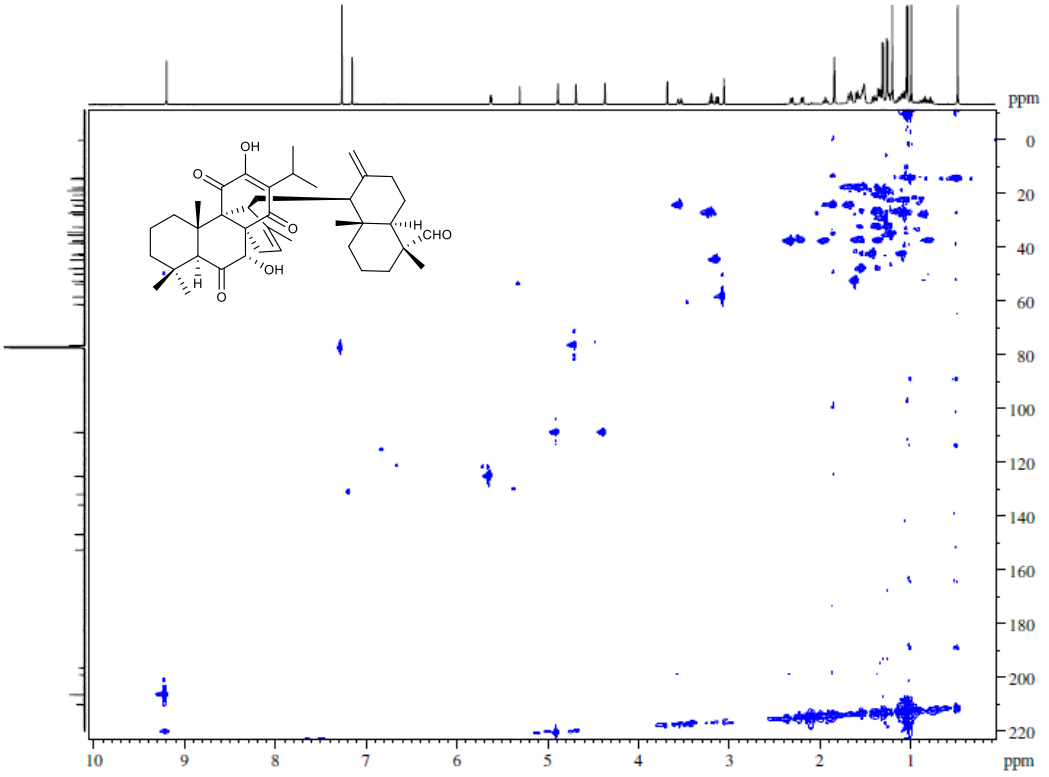


Fig. S20 The HSQC spectrum of compound **2** in $CDCl_3$.

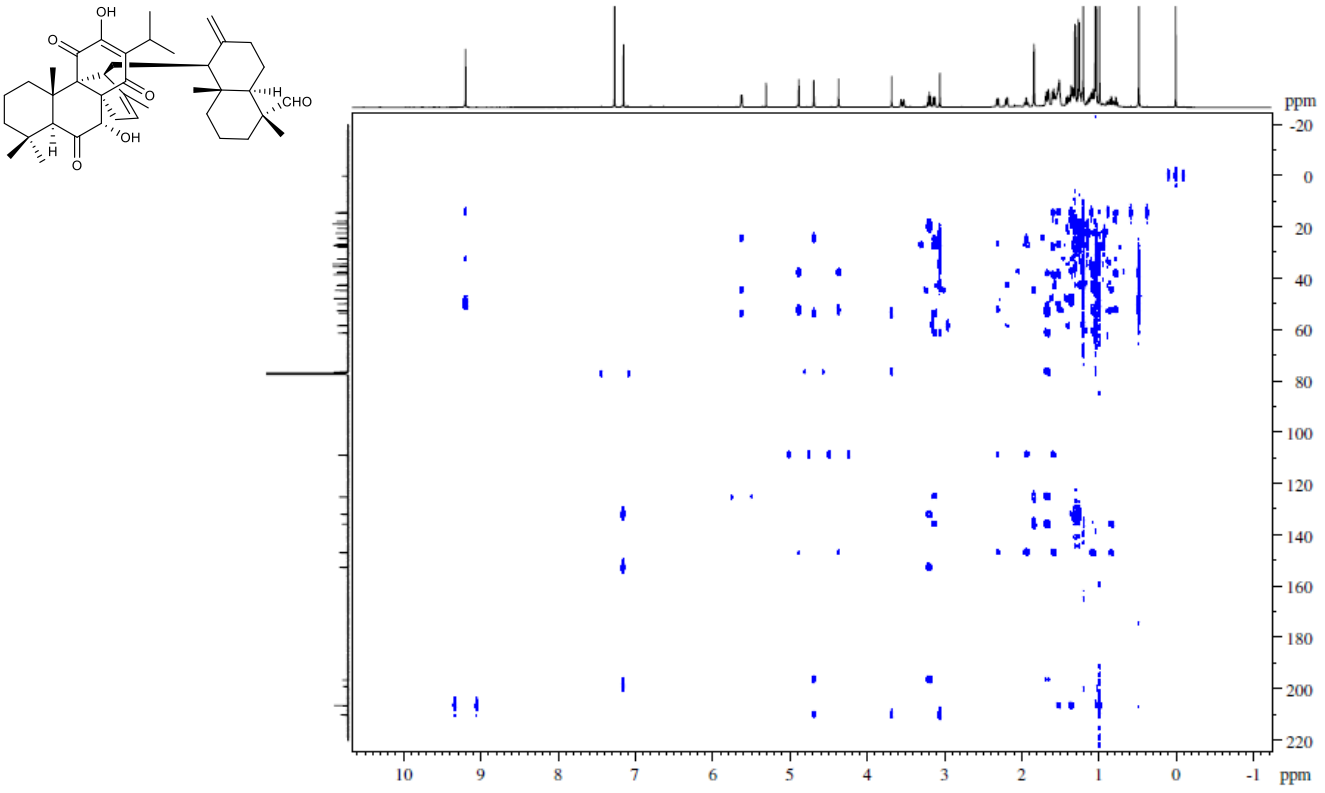


Fig. S21 The HMBC spectrum of compound **2** in $CDCl_3$.

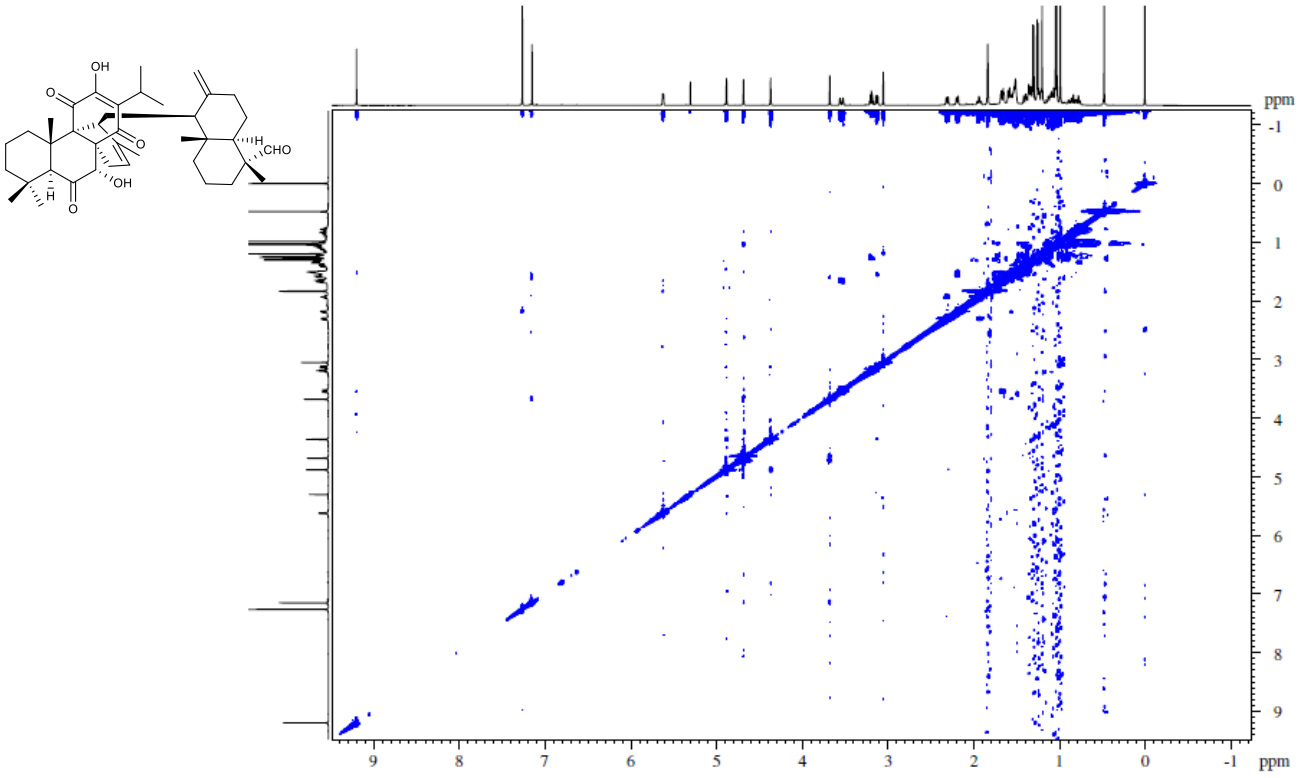
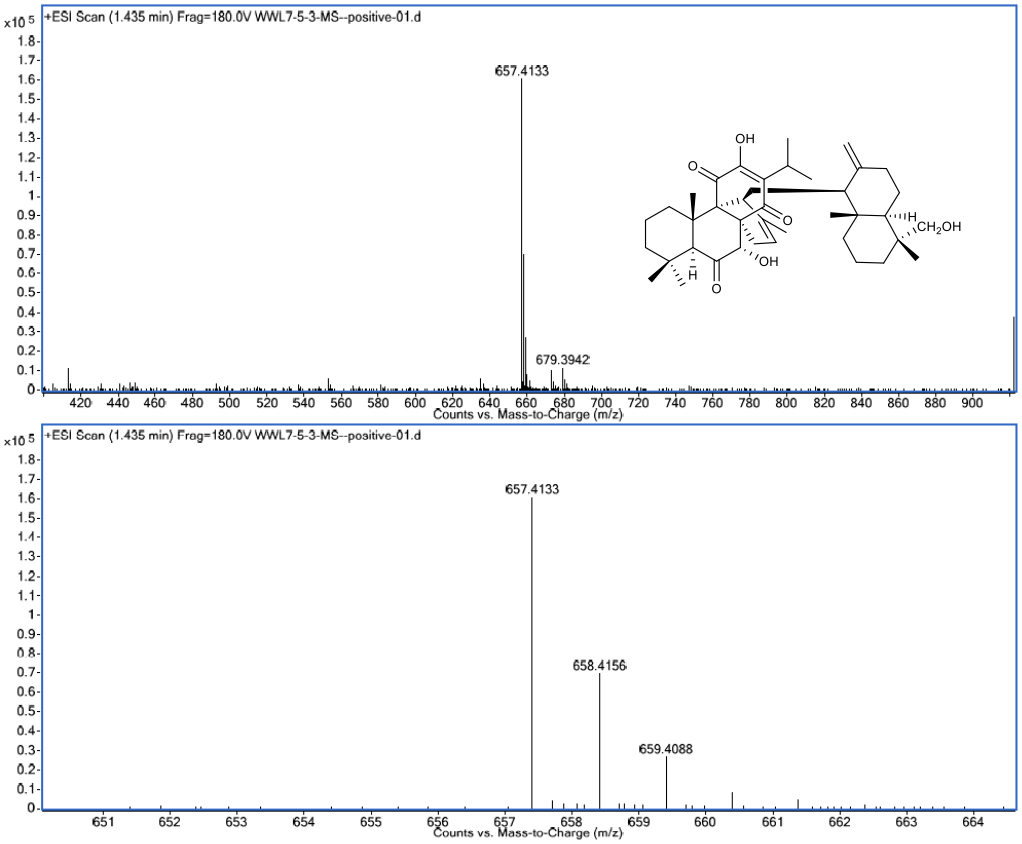


Fig. S22 The ROESY spectrum of compound **2** in $CDCl_3$.

TCM-CPU HR-ESI-MS Display Report

Sample Name: WWL7-5-2 **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 01/29/2018 **Operator:** Administrator



Elemental Composition Calculator

Target m/z:	657.4133	**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**	
C40H58NaO6		657.4126		-1.15	

Fig. S23 The HRESIMS spectrum of compound **3** in MeOH.

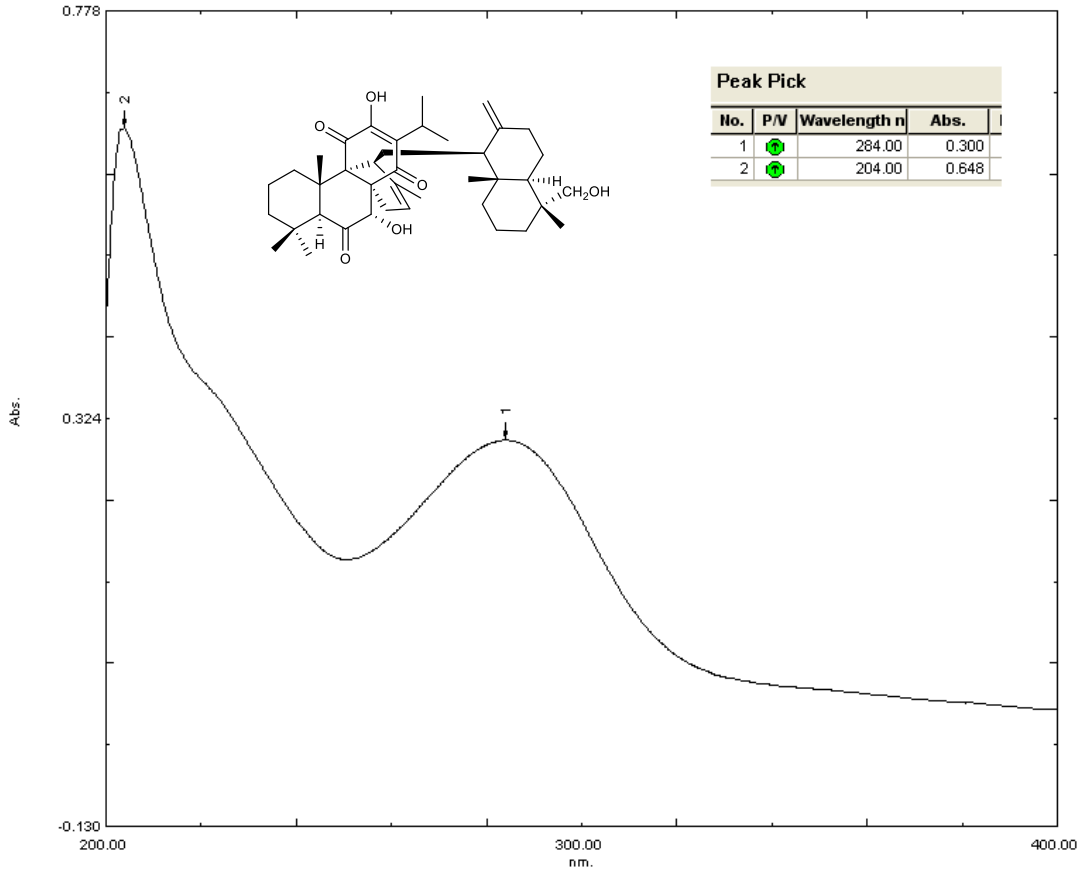


Fig. S24 The UV spectrum of compound **3** in MeOH.

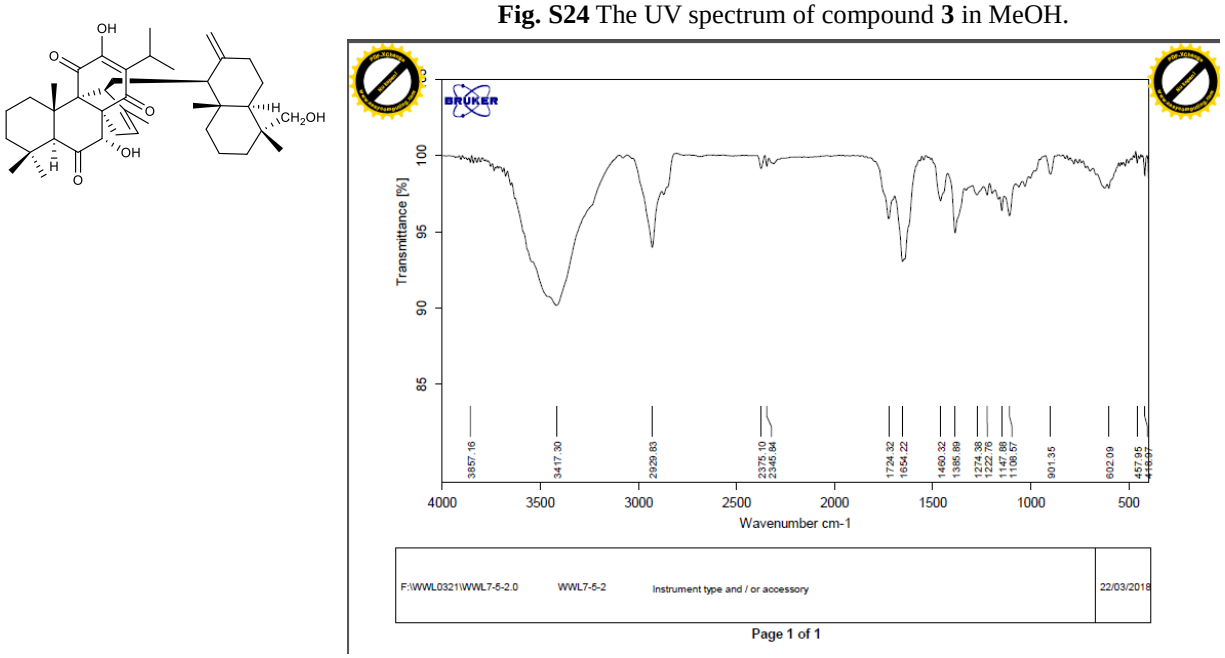


Fig. S25 The IR spectrum of compound **3** in KBr.

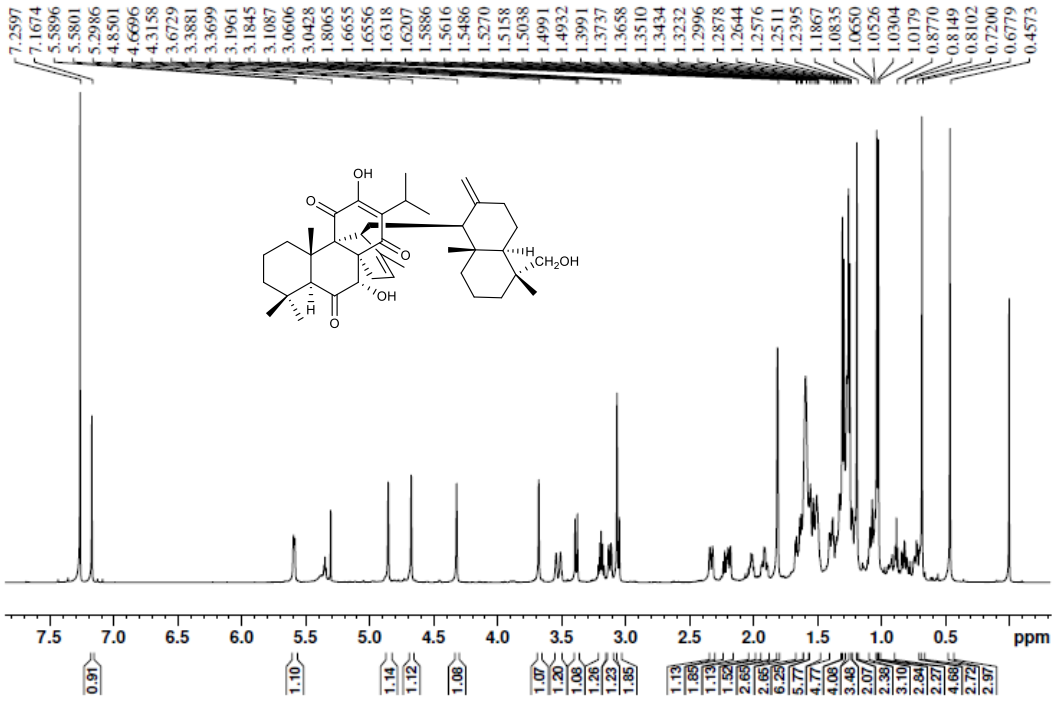


Fig. S26 The ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

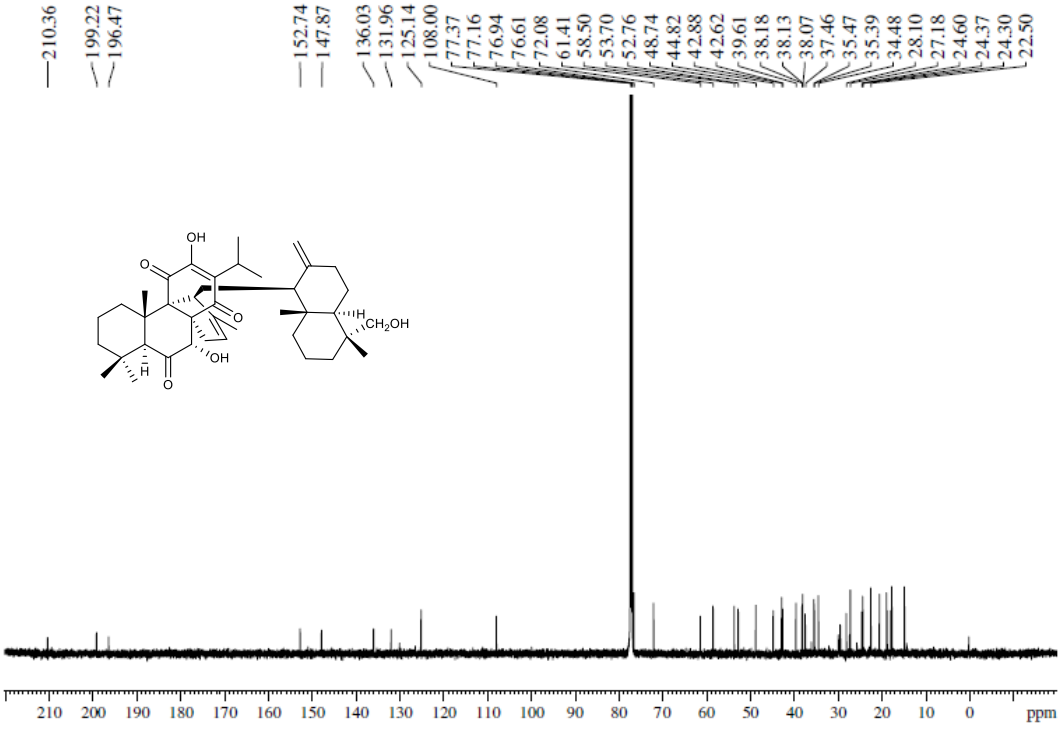


Fig. S37 The ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

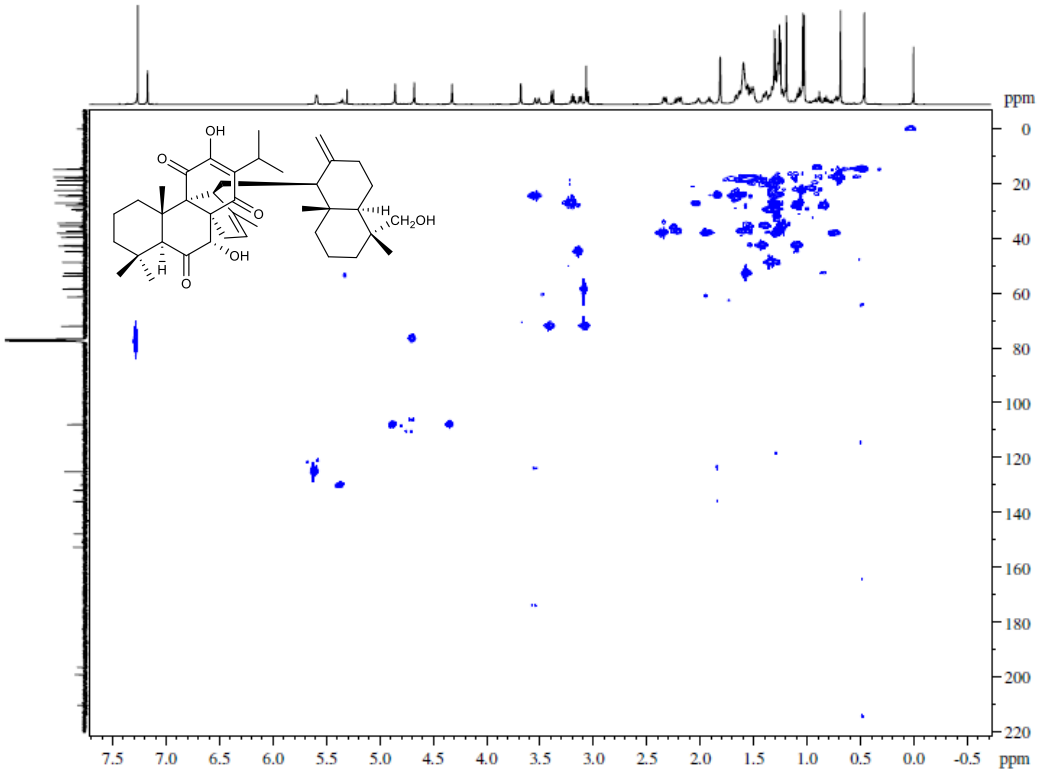


Fig. S28 The HSQC spectrum of compound **3** in $CDCl_3$.

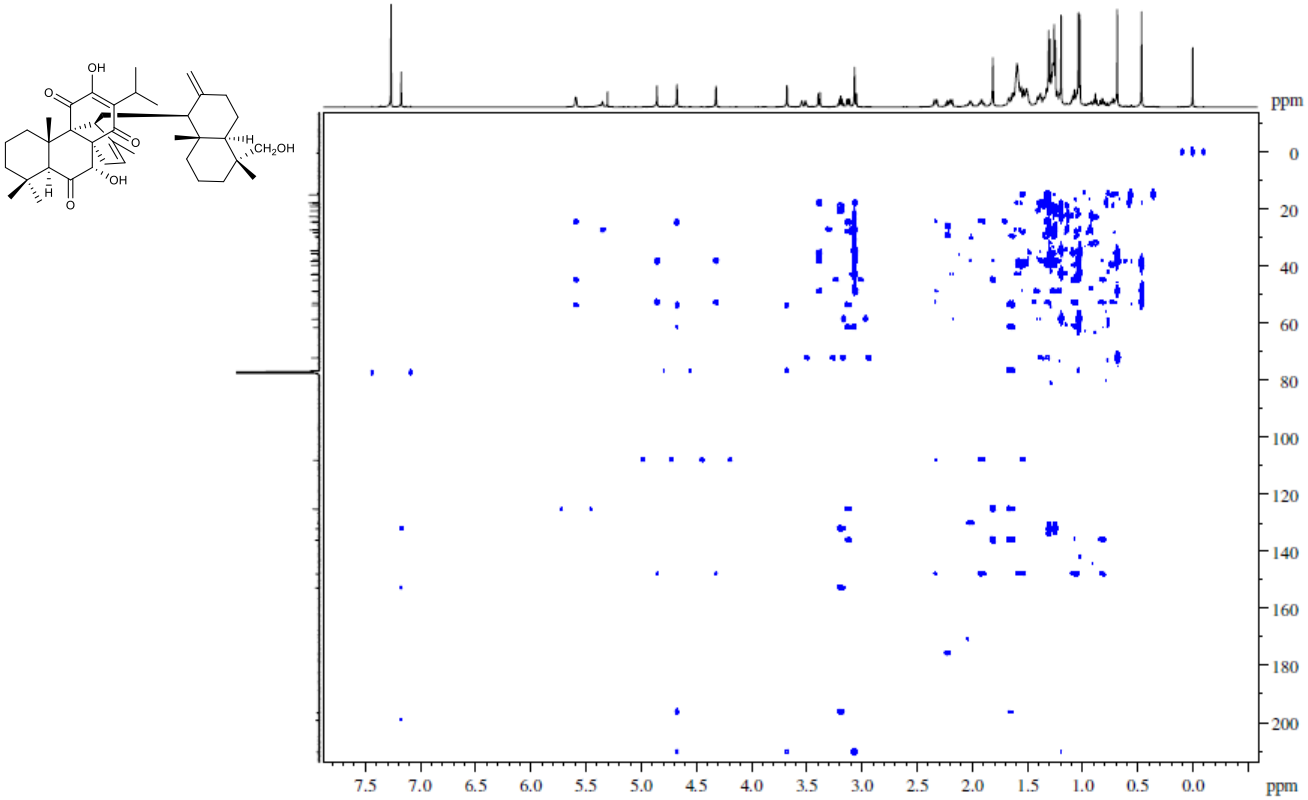


Fig. S29 The HMBC spectrum of compound **3** in $CDCl_3$.

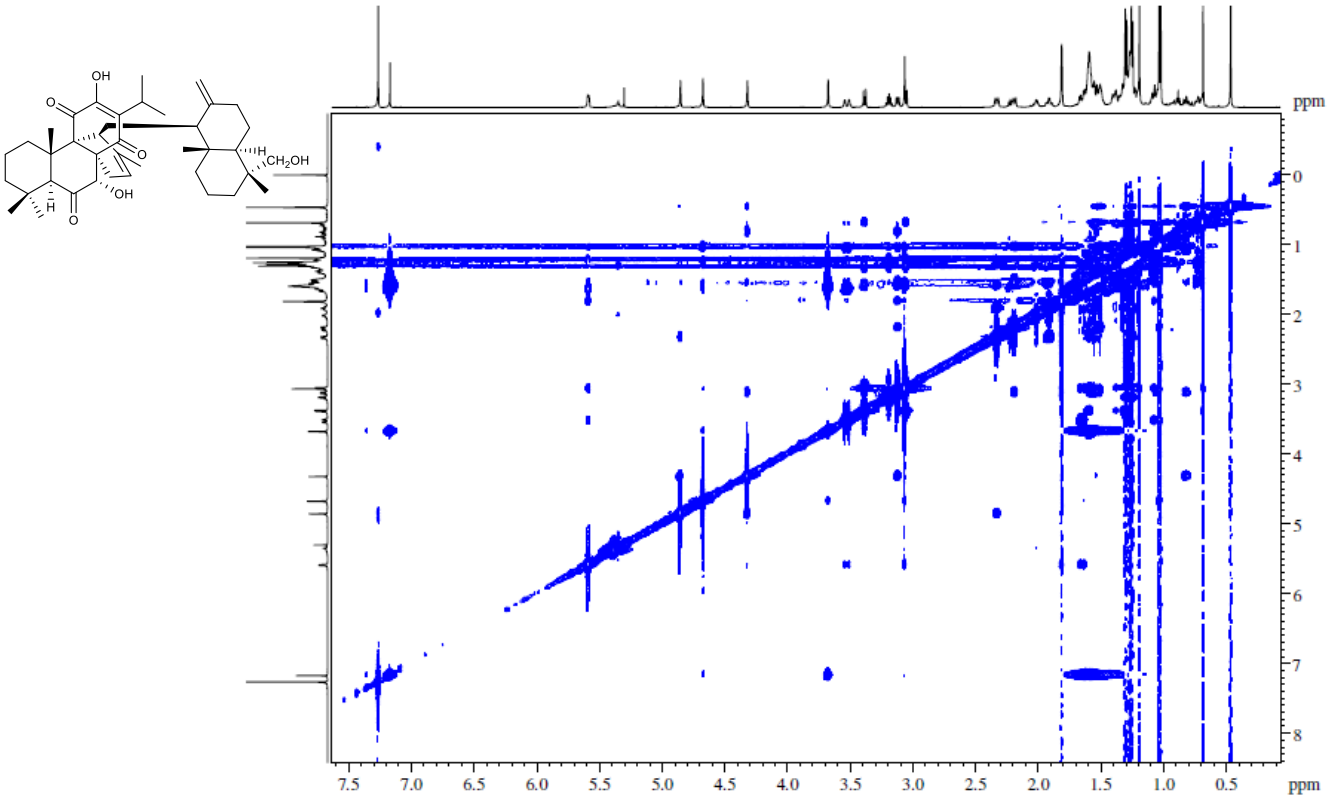
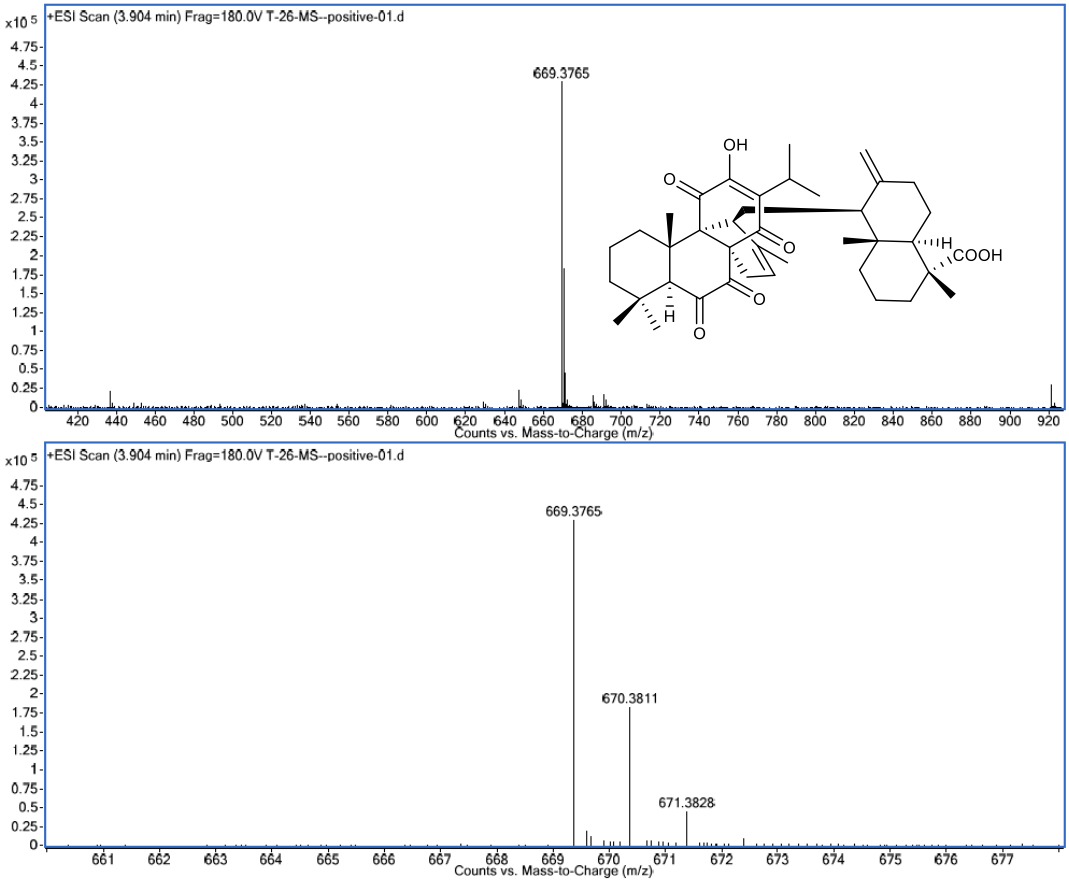


Fig. S30 The ROESY spectrum of compound **3** in $CDCl_3$.

TCM-CPU HR-ESI-MS Display Report

Sample Name: WWL7-5-3 **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 01/29/2018 **Operator:** Administrator



Elemental Composition Calculator

Target m/z:	669.3765	**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**	
C40H54NaO7		669.3762		-0.43	

Fig. S31 The HRESIMS spectrum of compound **4** in MeOH.

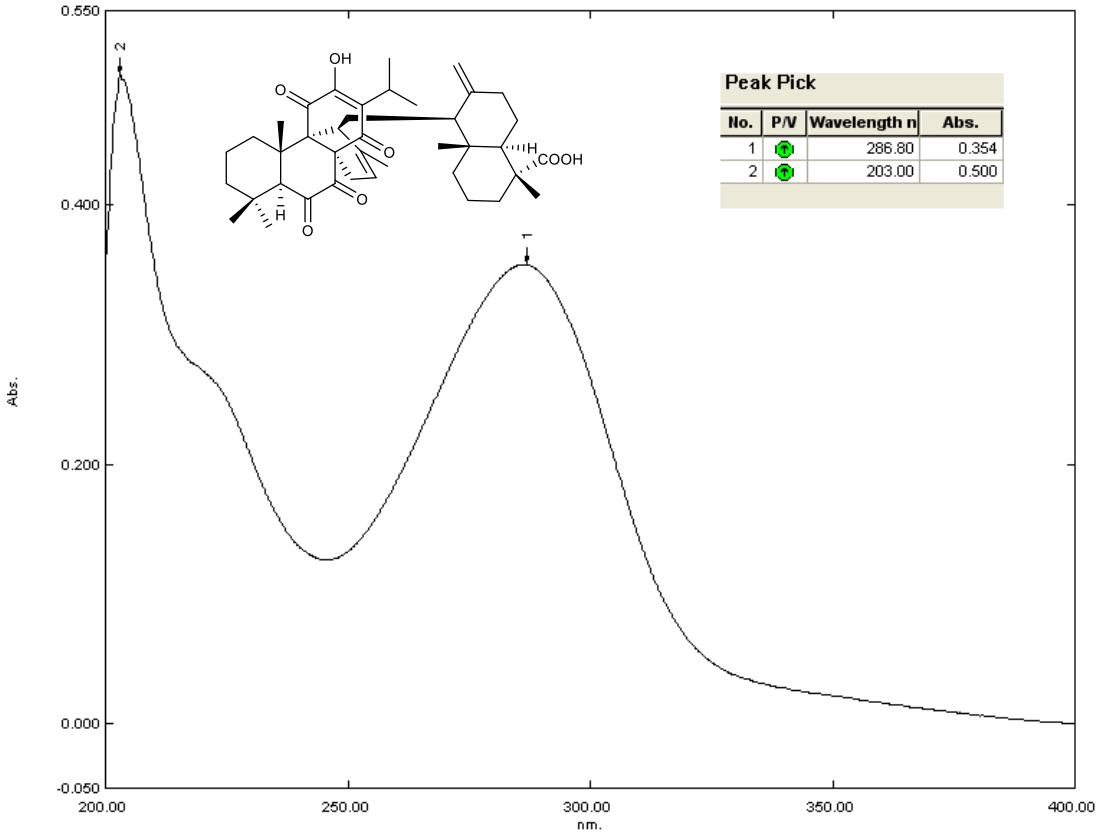


Fig. S30 The UV spectrum of compound **4** in MeOH.

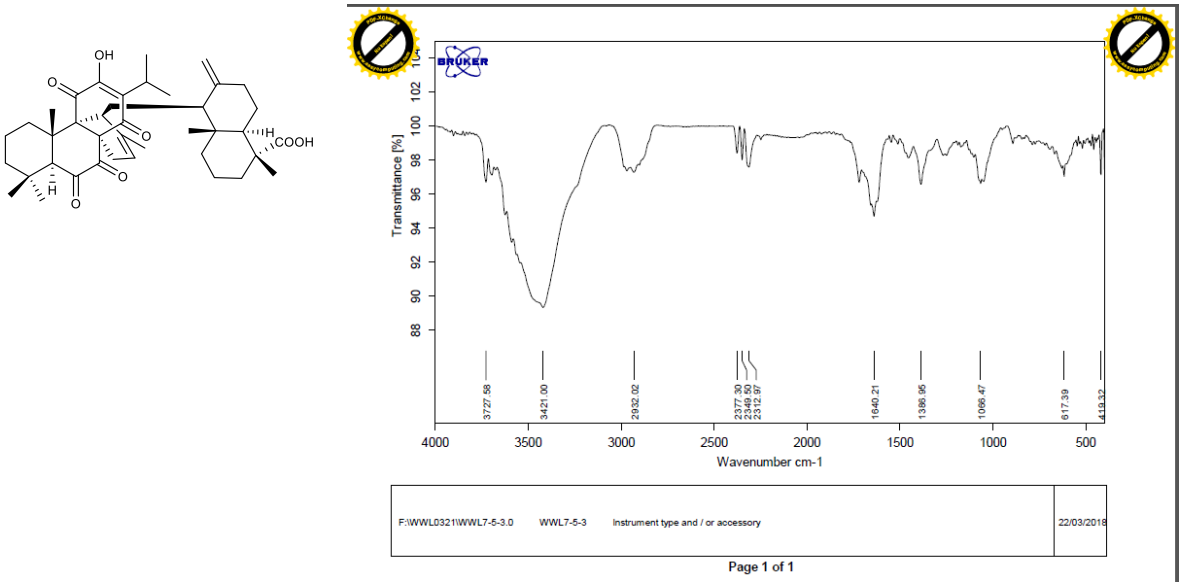


Fig. S33 The IR spectrum of compound **4** in KBr.

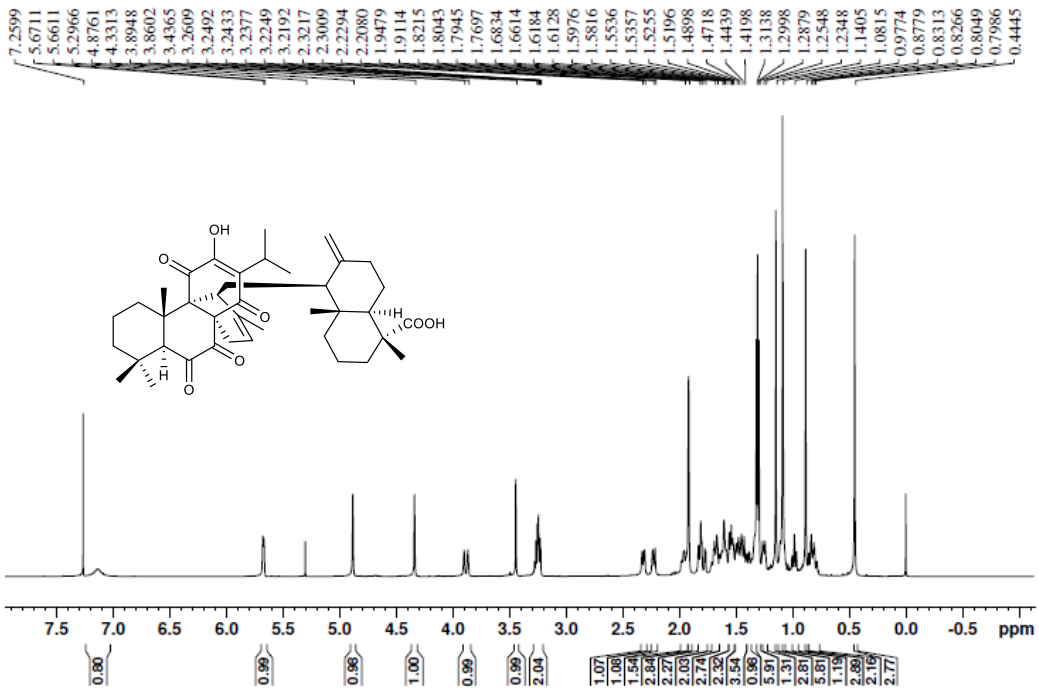


Fig. S34 The ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

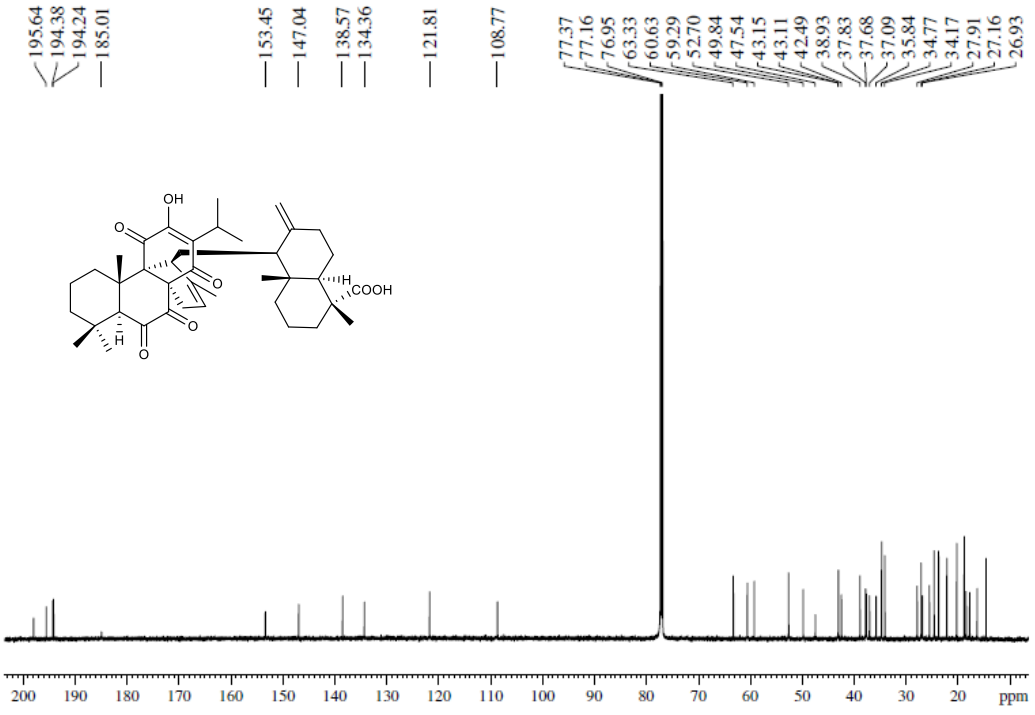


Fig. S35 The ^{1}C NMR spectrum of compound **4** in $CDCl_3$.

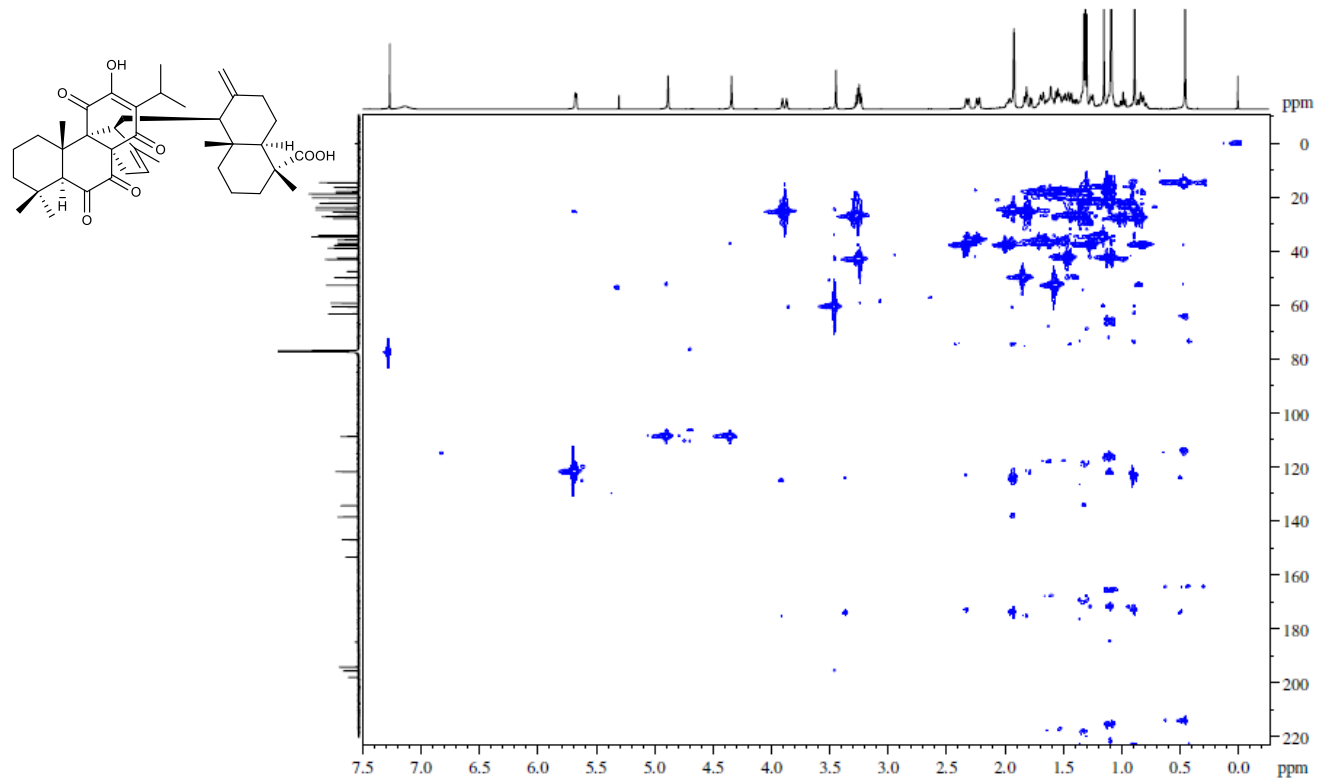


Fig. S36 The HSQC spectrum of compound **4** in $CDCl_3$.

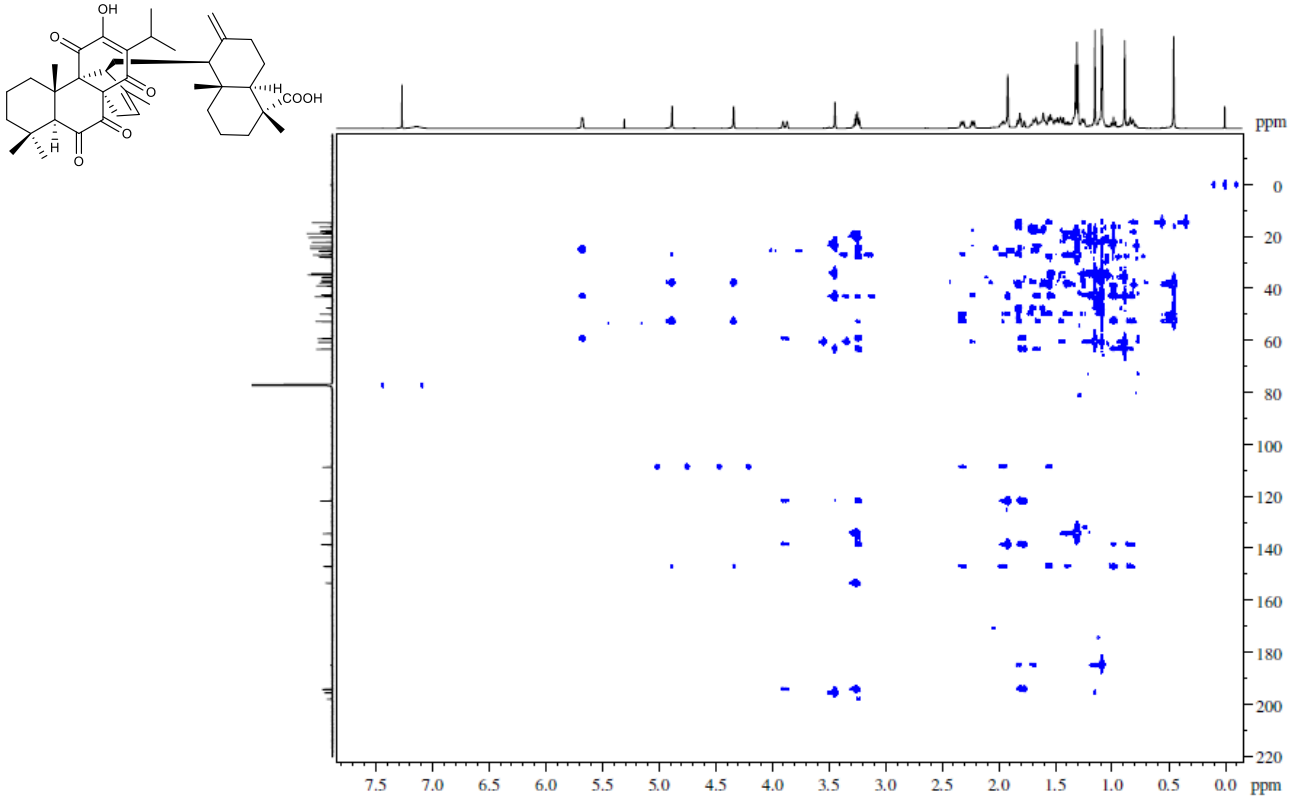


Fig. S37 The HMBC spectrum of compound **4** in $CDCl_3$.

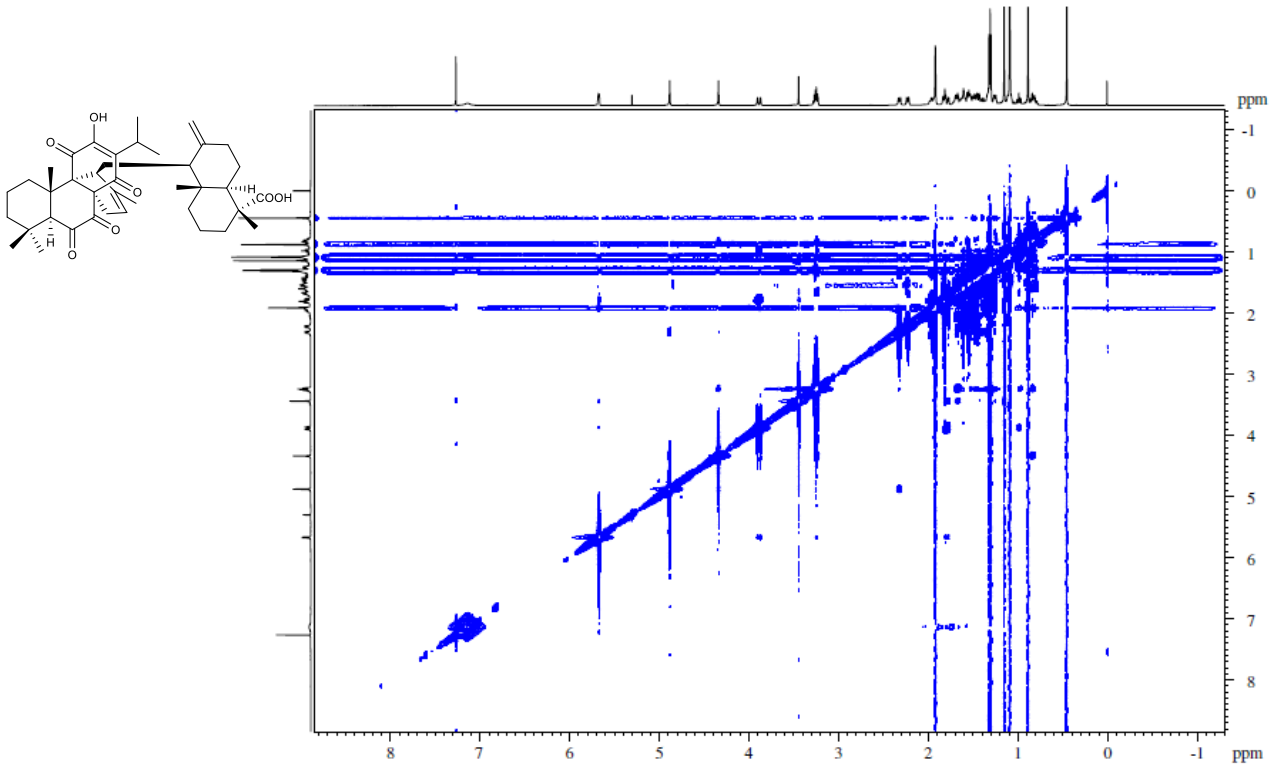
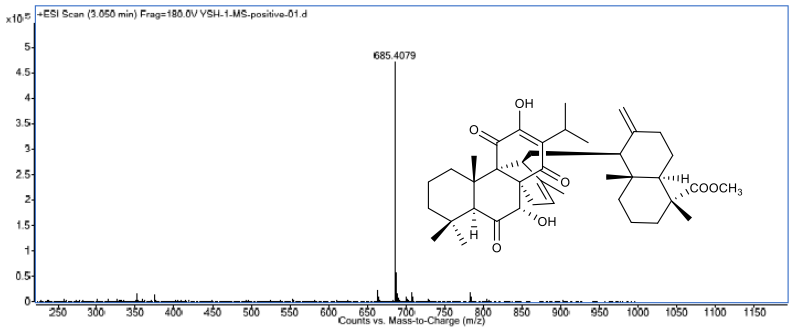


Fig. S38 The ROESY spectrum of compound **4** in $CDCl_3$.

TCM-CPU HR-ESI-MS Display Report

Sample Name: YSH-1 **Instrument:** Agilent 6520B Q-TOF

Acq. Date: 04/16/2018 **Operator:** Administrator



Elemental Composition Calculator

Target m/z:	685.4079	**Result type:**	Positive ions	**Species:**	$[M+Na]^+$
Elements:		C (0-80); H (0-120); O (0-30); N (0-5); Na (0-5) ;			
Ion Formula		**Calculated m/z**		**PPM Error**	
C41H58NaO7		685.4075		-0.67	

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Fig. S39 The HRESIMS spectrum of compound **1a** in MeOH

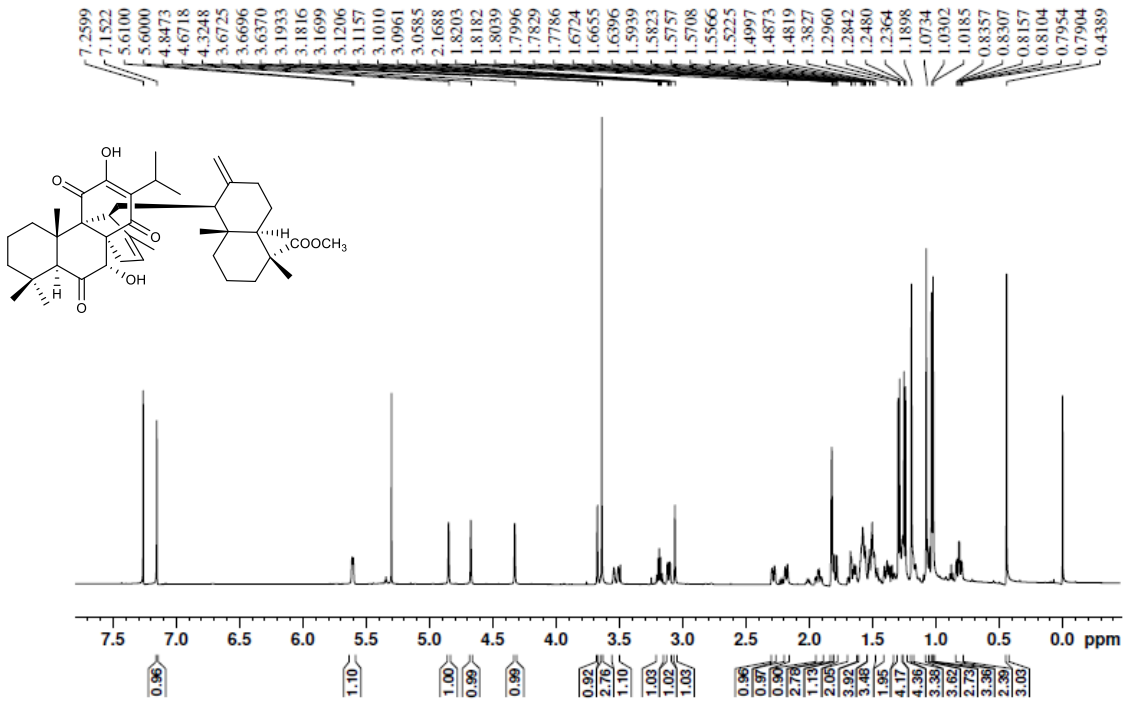

Fig. S40 The ^{1}H NMR spectrum of compound **1a** in $CDCl_3$.

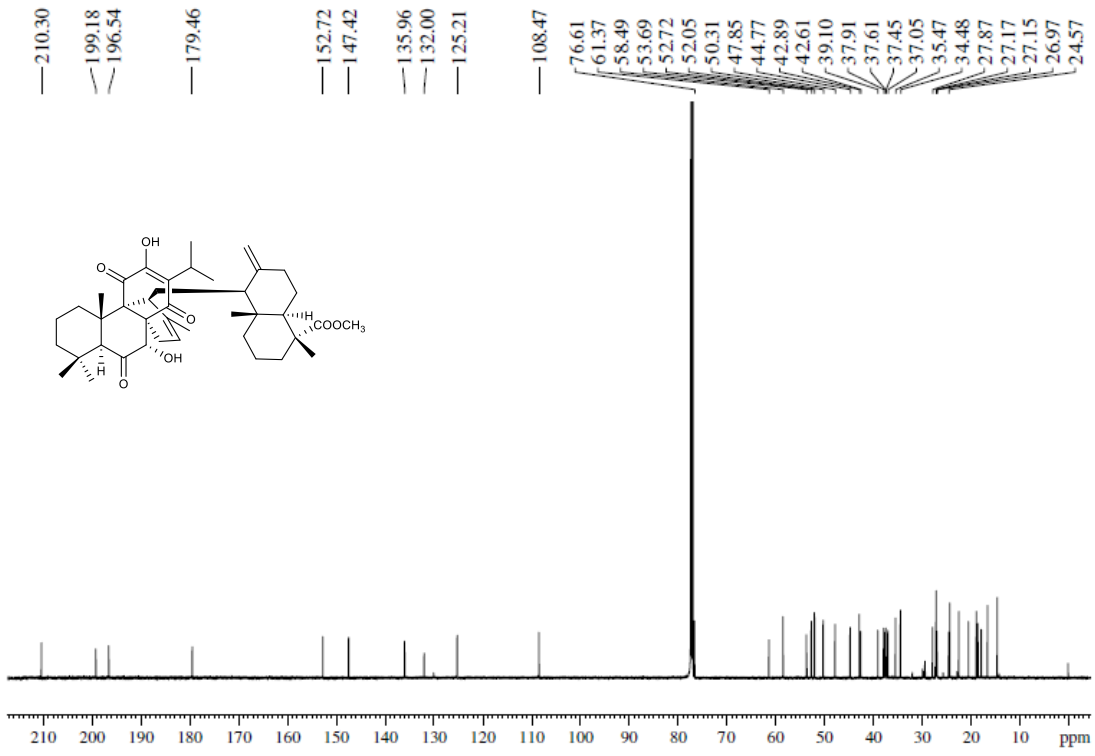

Fig. S41 The ^{13}C NMR spectrum of compound **1a** in $CDCl_3$.

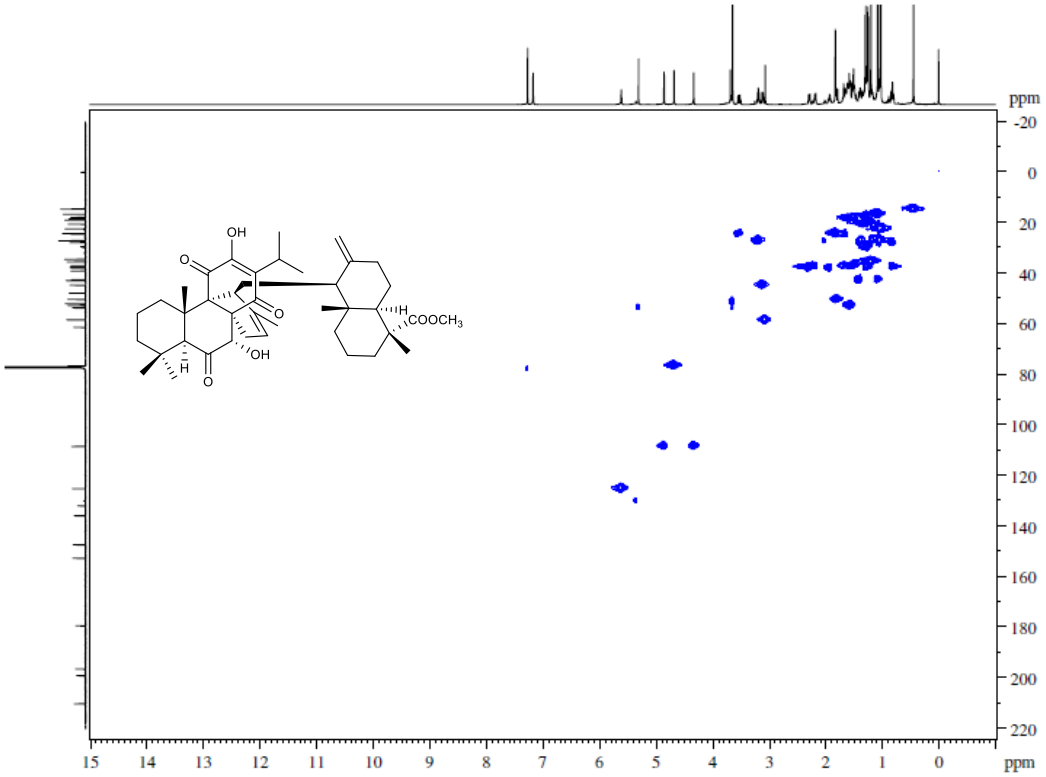

Fig. S42 The HSQC spectrum of compound **1a** in $CDCl_3$.

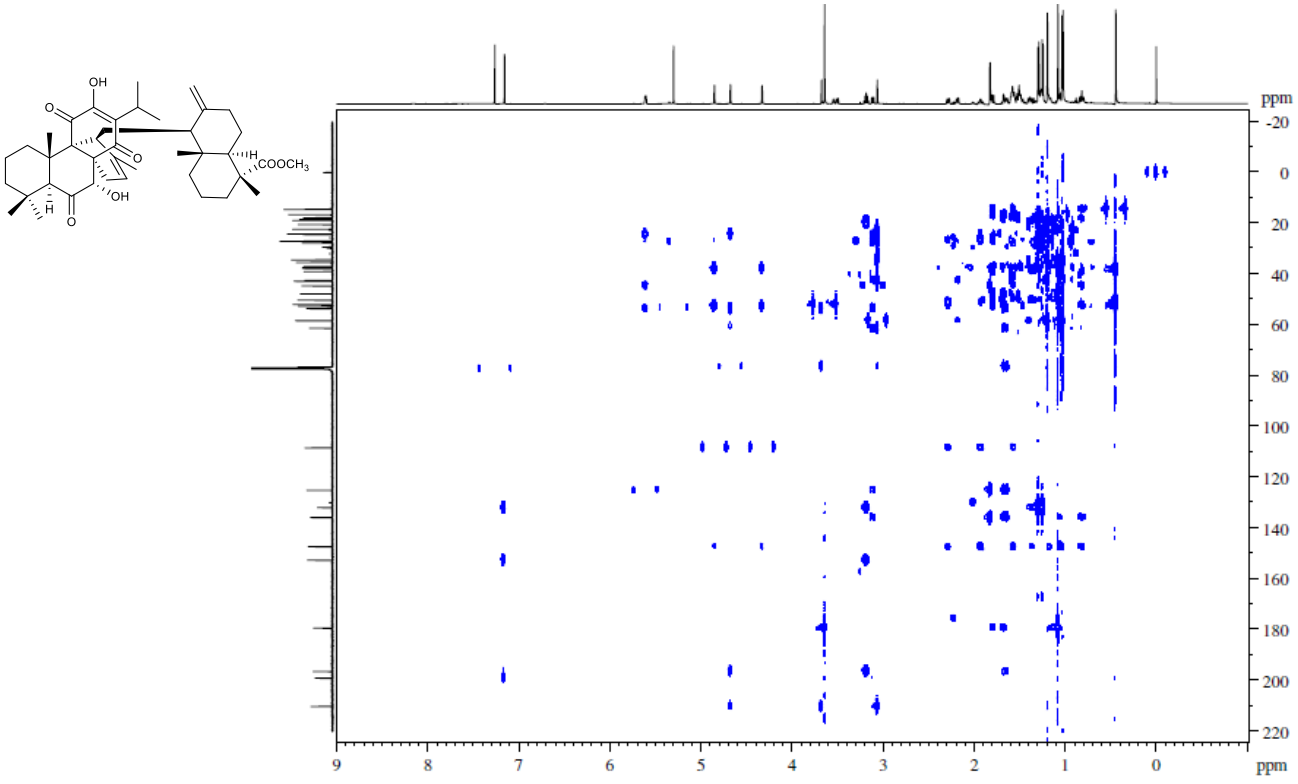

Fig. S43 The HMBC spectrum of compound **1a** in $CDCl_3$.

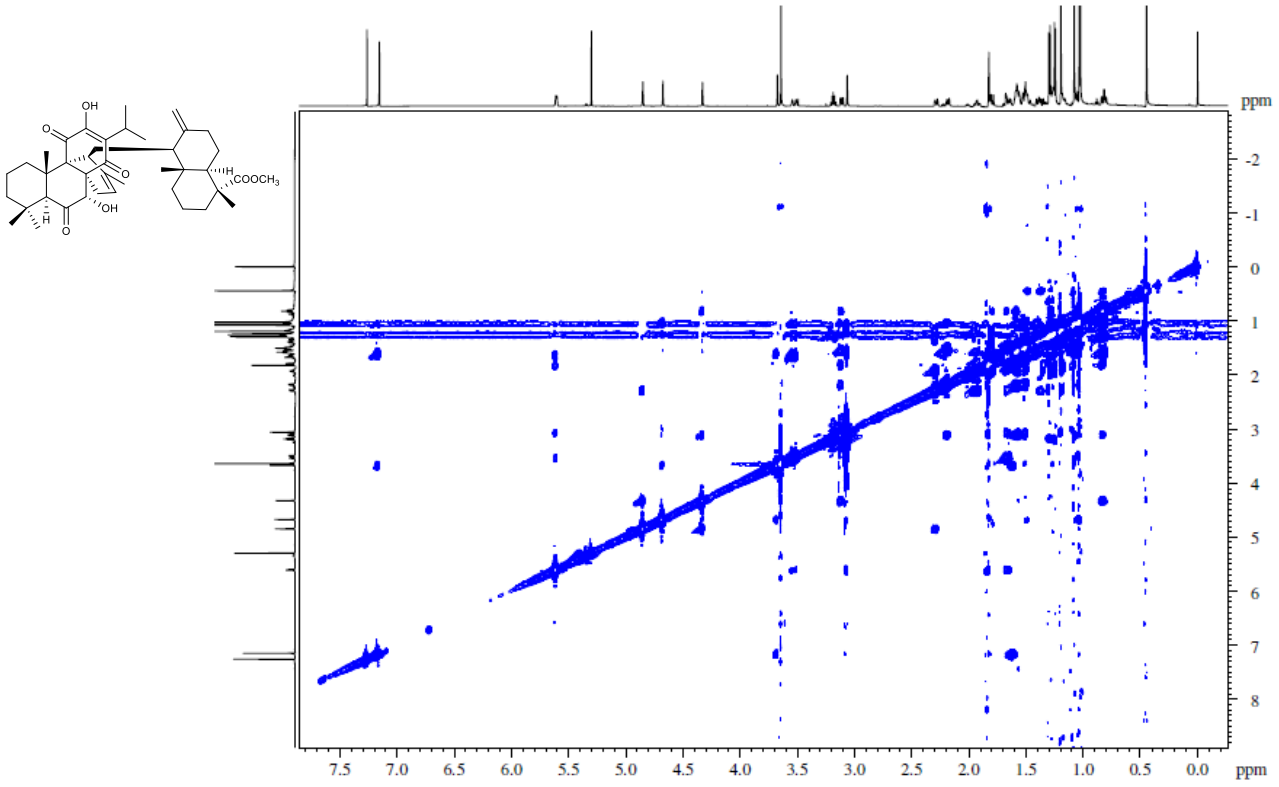

Fig. S44 The ROESY spectrum of compound **1a** in $CDCl_3$

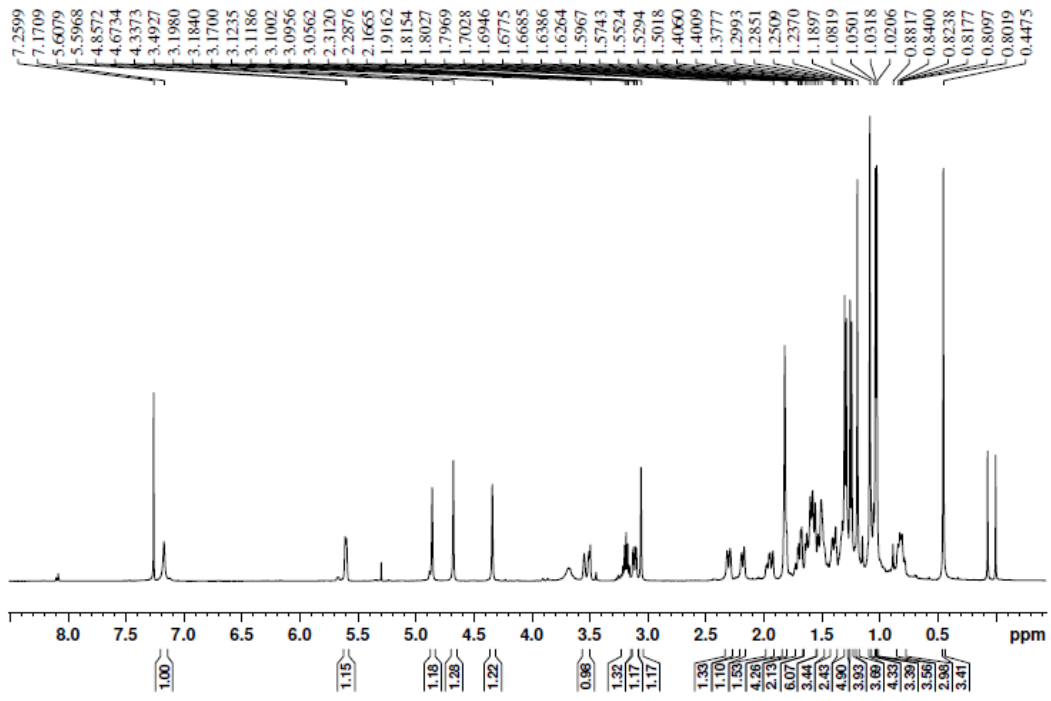

Fig. S45 The ^1H NMR spectrum of compound **1** (being oxidated from **2**) in $CDCl_3$.

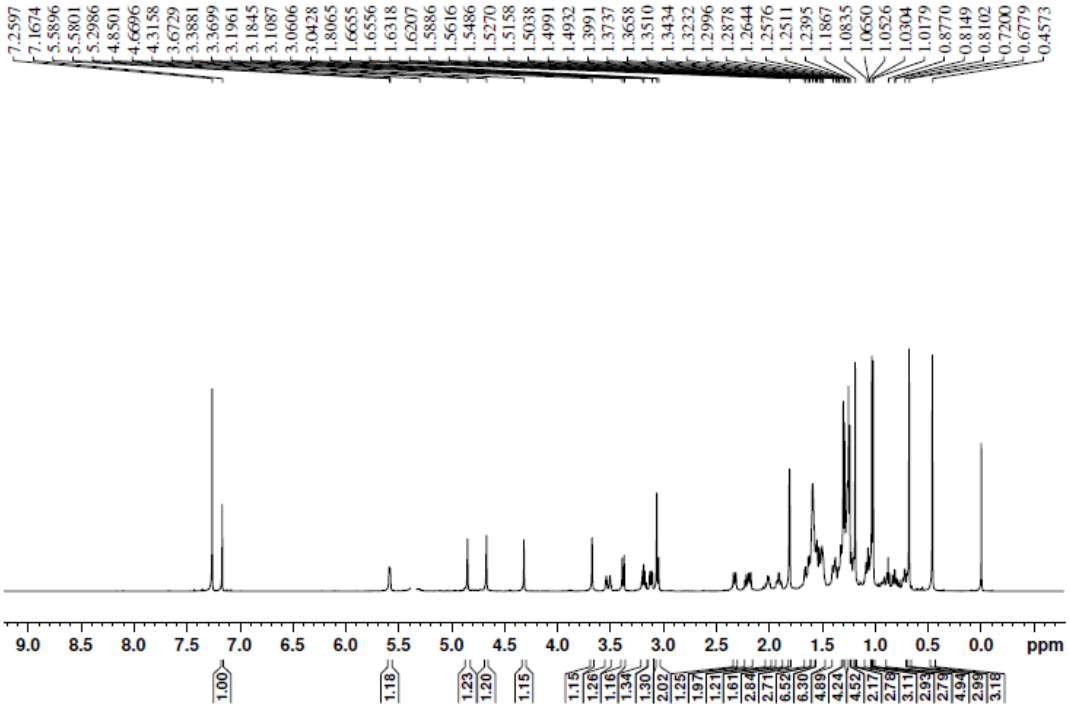

Fig. S46 The ^{1}H NMR spectrum of compound **3** (being convered from **1**) in $CDCl_3$.

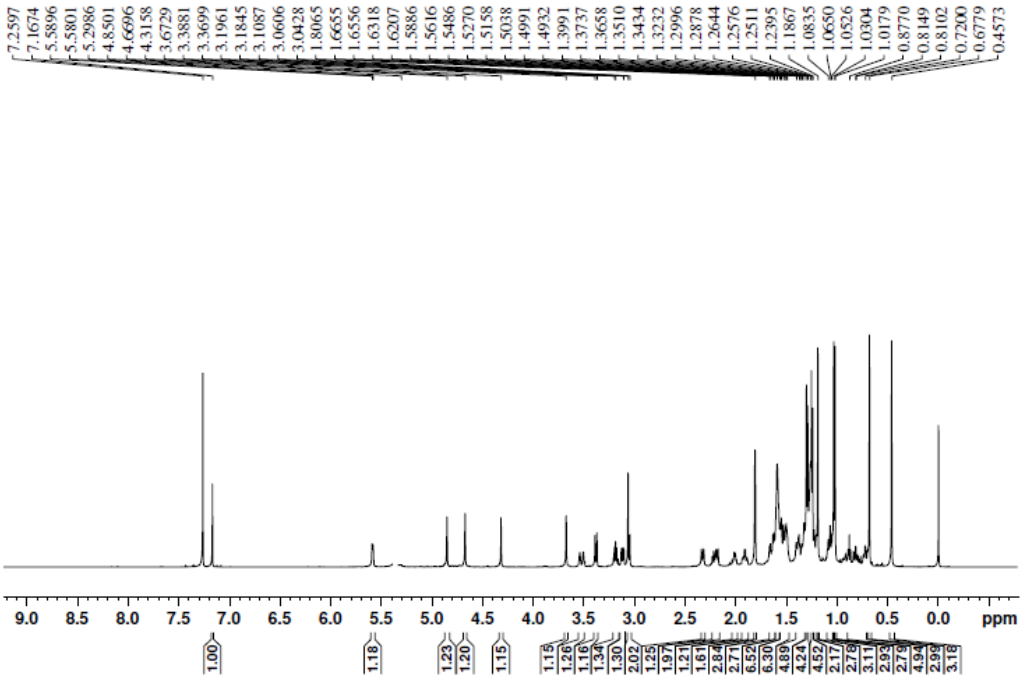

Fig. S47 The ^{1}H NMR spectrum of compound **4** (being convered from **1**) in $CDCl_3$.