Supporting Information

Rec. Nat. Prod. **17:3 (2023) 566-570**

Two New Sesquiterpenoids from *Kalimeris shimada*

Yun-Peng Sun[1], Yu-Fei Huang[1], Yang Yu[1], Jai-Sing Yang[2], Jin-Song Liu[1*] and Guo-Kai Wang[1,3*]

[1] School of Pharmacy, Anhui University of Chinese Medicine, Hefei 230012, P.R. China

[2] Department of Medical Research, China Medical University Hospital, China Medical University, Taichung, Taiwan

[3] Anhui Province Key Laboratory of Research & Development of Chinese Medicine, Hefei 230012, P.R. China

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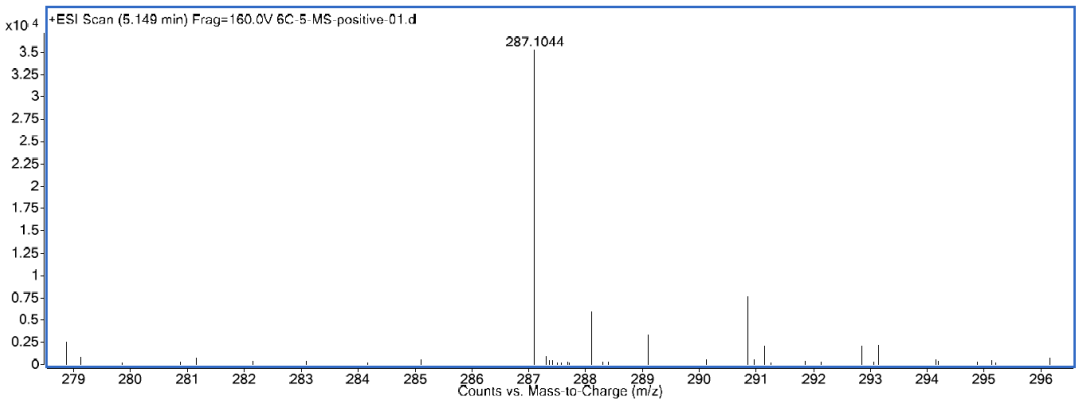


Elemental Composition Calculator

Target m/z:	287.1044	**Result type:**	Positive ions	**Species:**	$[M+K]^+$
Elements:		C (0-80); H (0-120); O (0-30); K (0-5)			
Ion Formula		**Calculated m/z**		**PPM Error**	
C15H20KO3		287.1044		-0.16	

Figure S1: HR-ESI-MS spectrum of **1** (kalshinoid G)

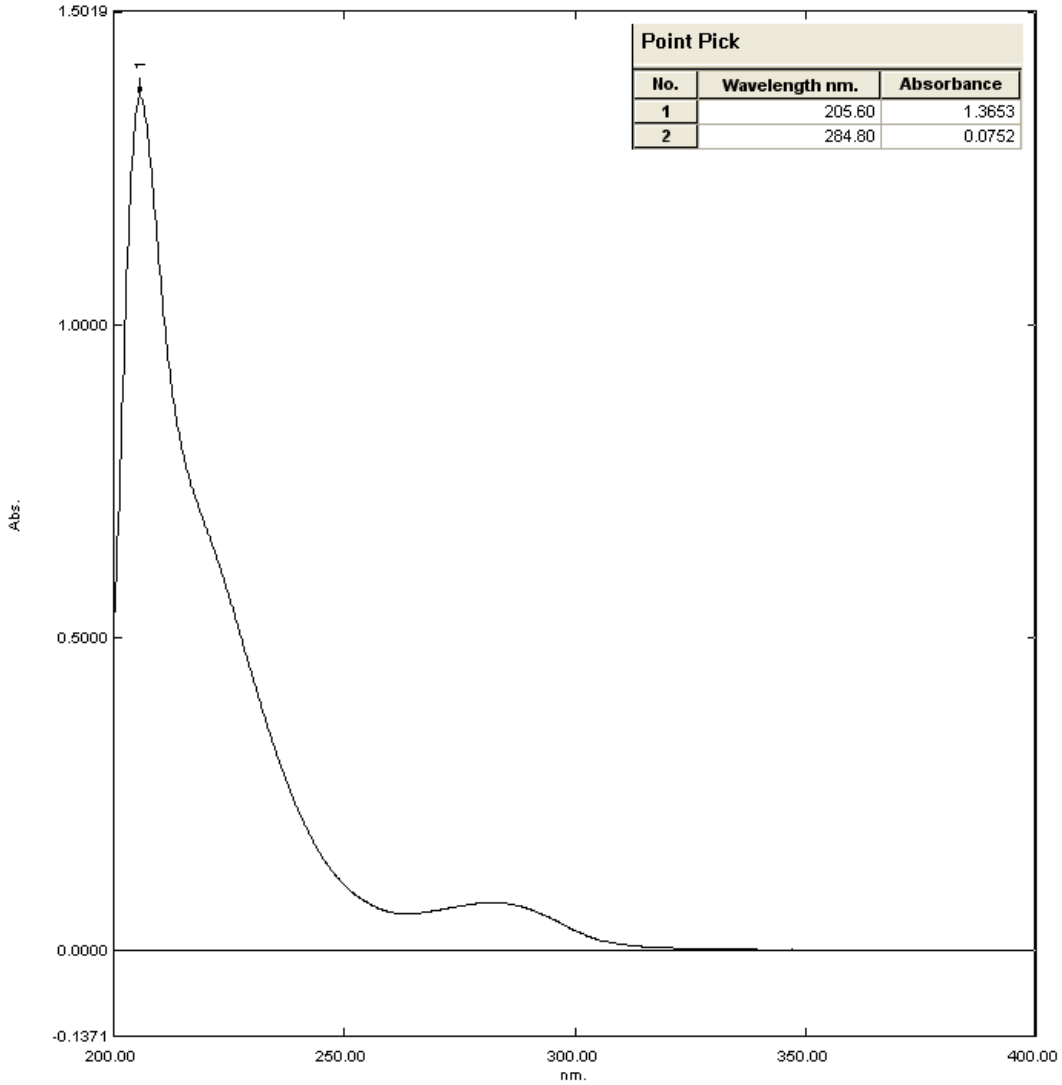


Figure S2: UV spectrum of **1**

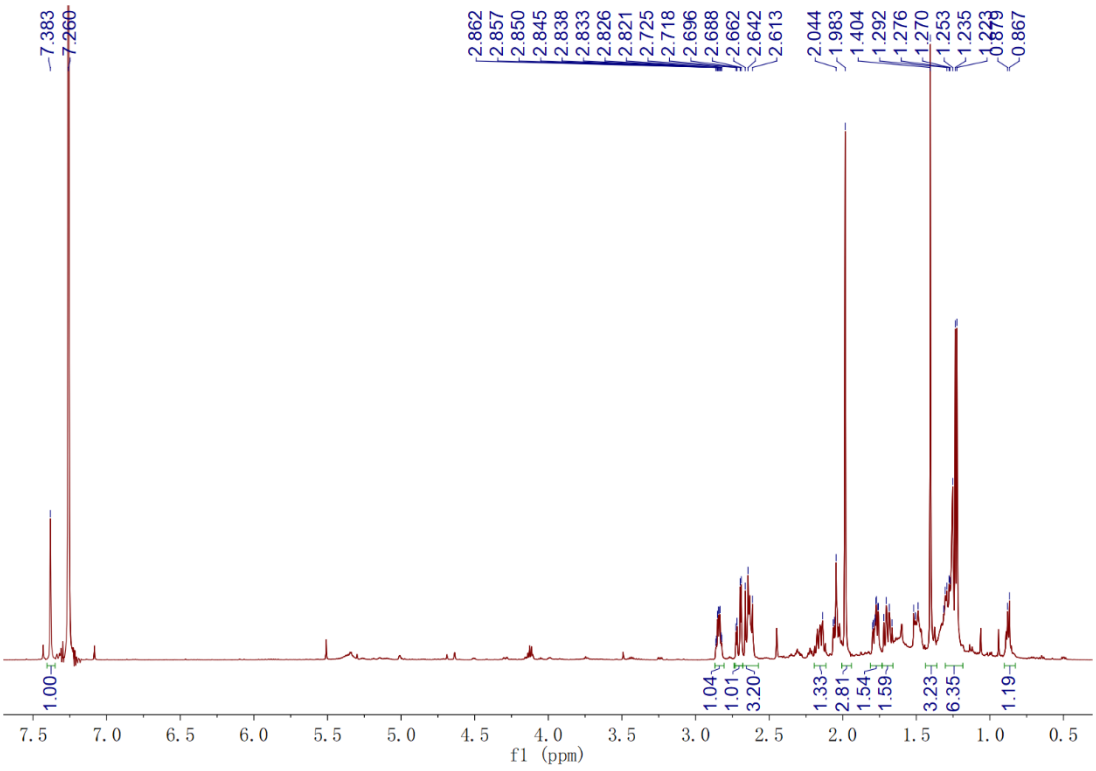


Figure S3: ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **1** (kalshinoid G)

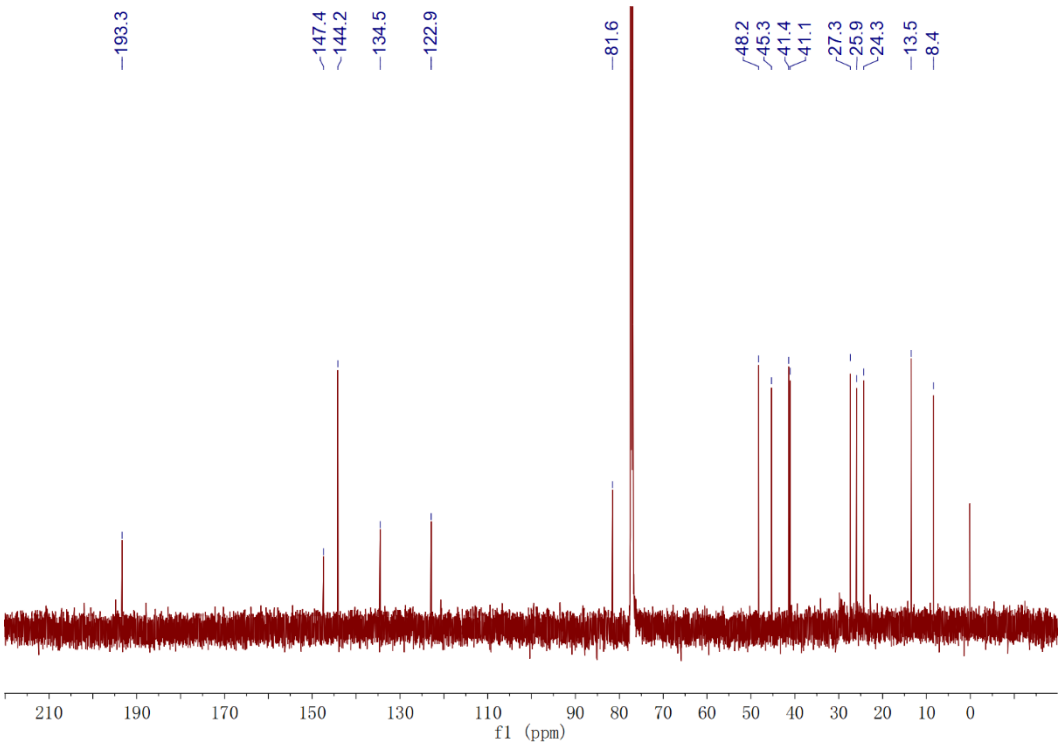


Figure S4: ^{13}C-NMR (150 MHz, $CDCl_3$) spectrum of **1** (kalshinoid G)

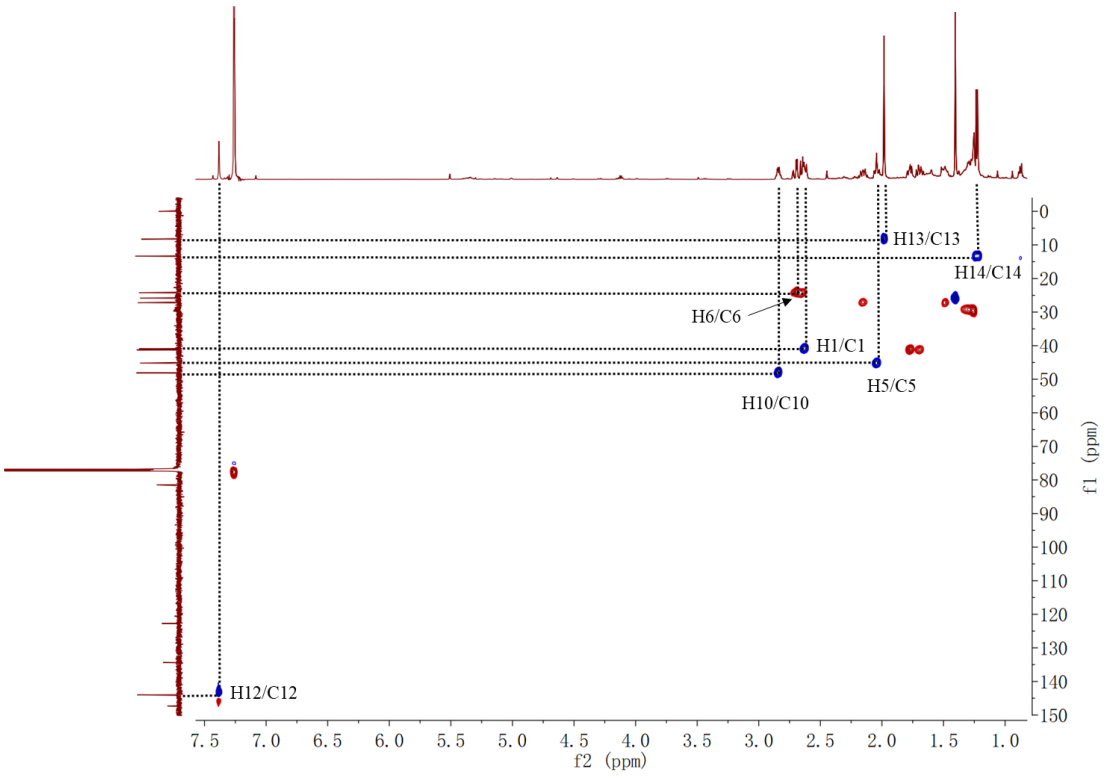


Figure S5: HSQC spectrum of **1** (kalshinoid G)

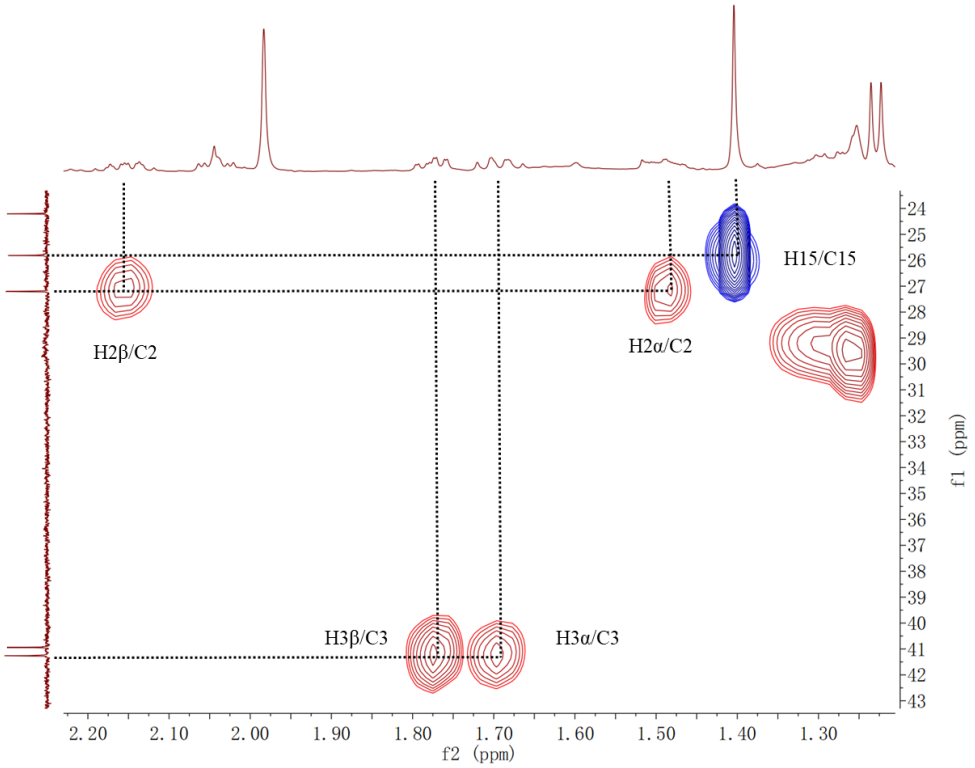


Figure S6: HSQC spectrum of **1** (kalshinoid G) (From δ_C24 ppm to δ_C 43 ppm)

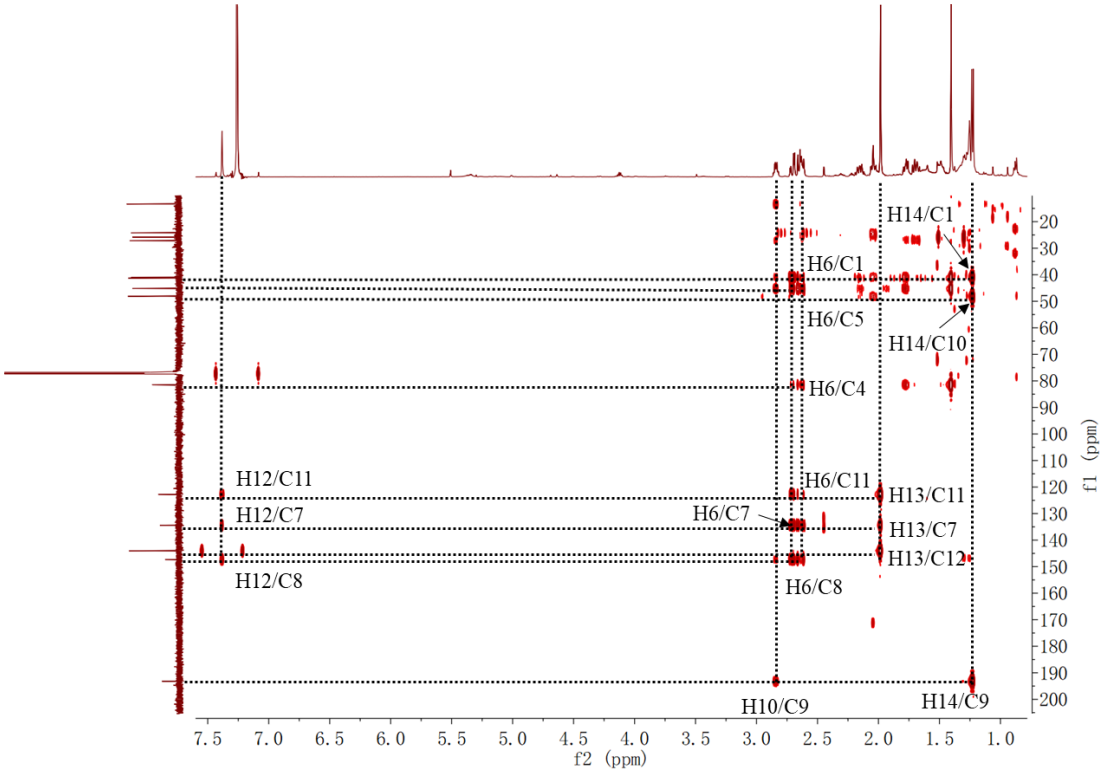


Figure S7: HMBC spectrum of **1** (kalshinoid G)

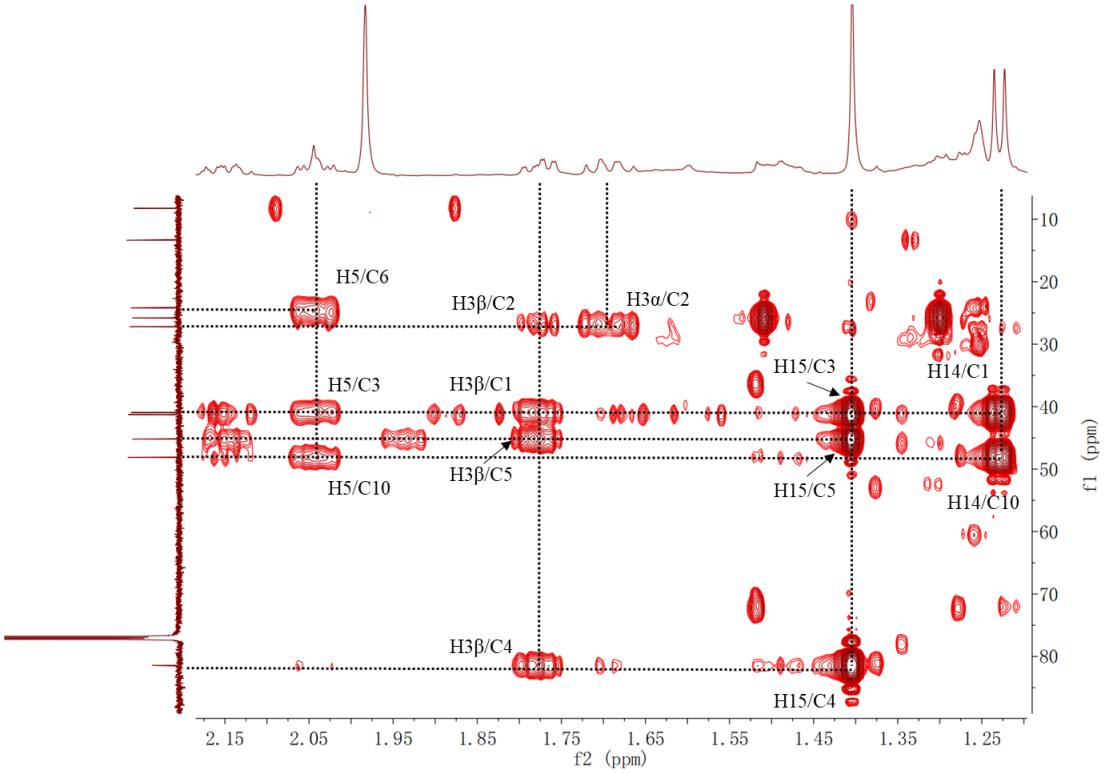


Figure S8: HMBC spectrum of **1** (kalshinoid G) (From δ_C5 ppm to δ_C 90 ppm)

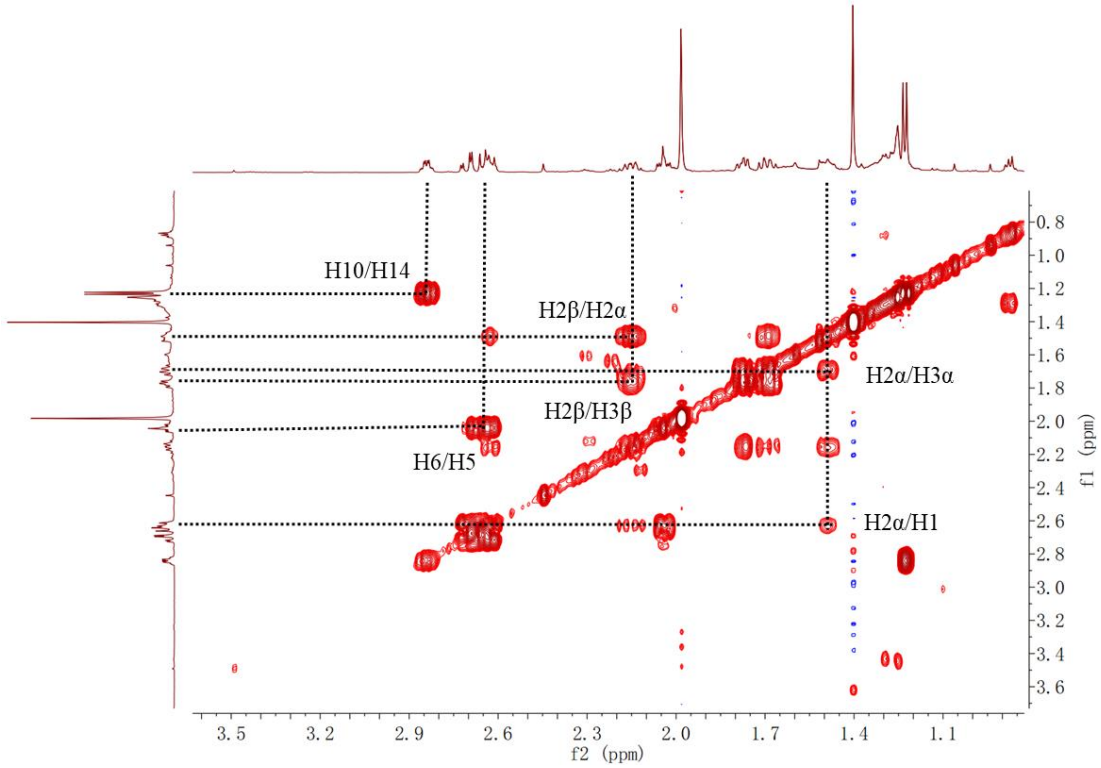


Figure S9: ^{1}H-^{1}H COSY spectrum of **1** (kalshinoid G)

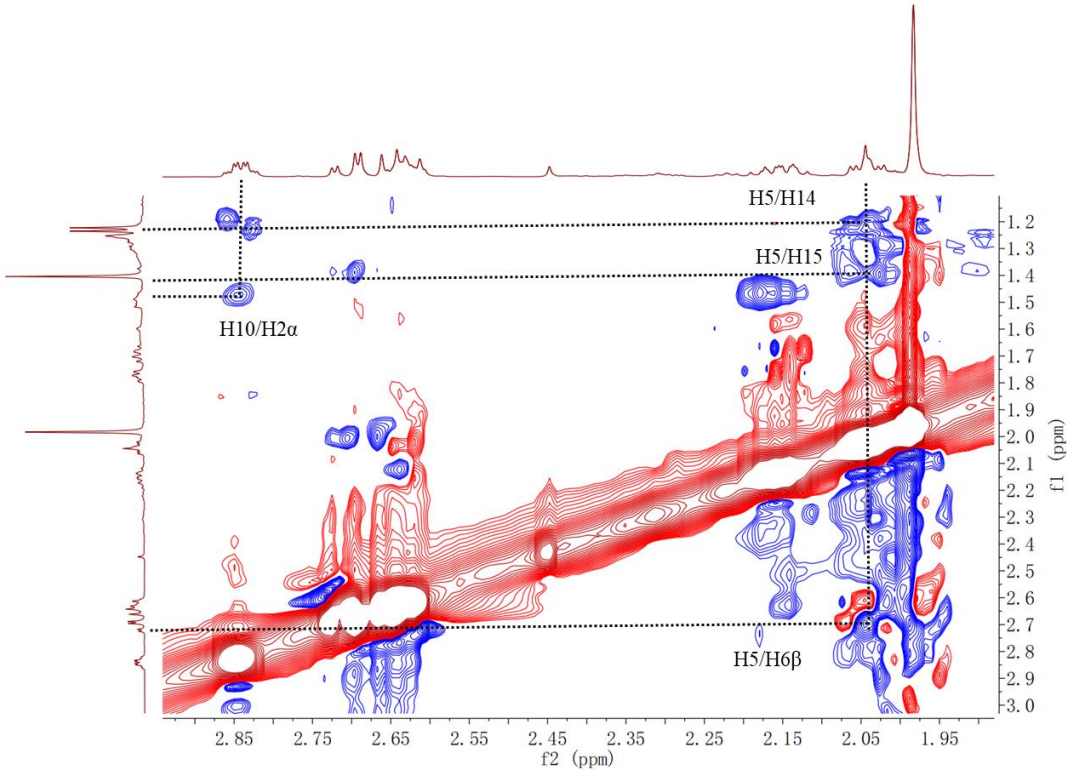


Figure S10: ROESY spectrum of **1** (kalshinoid G) (From δ_H1.9 ppm to δ_H 3.0 ppm)

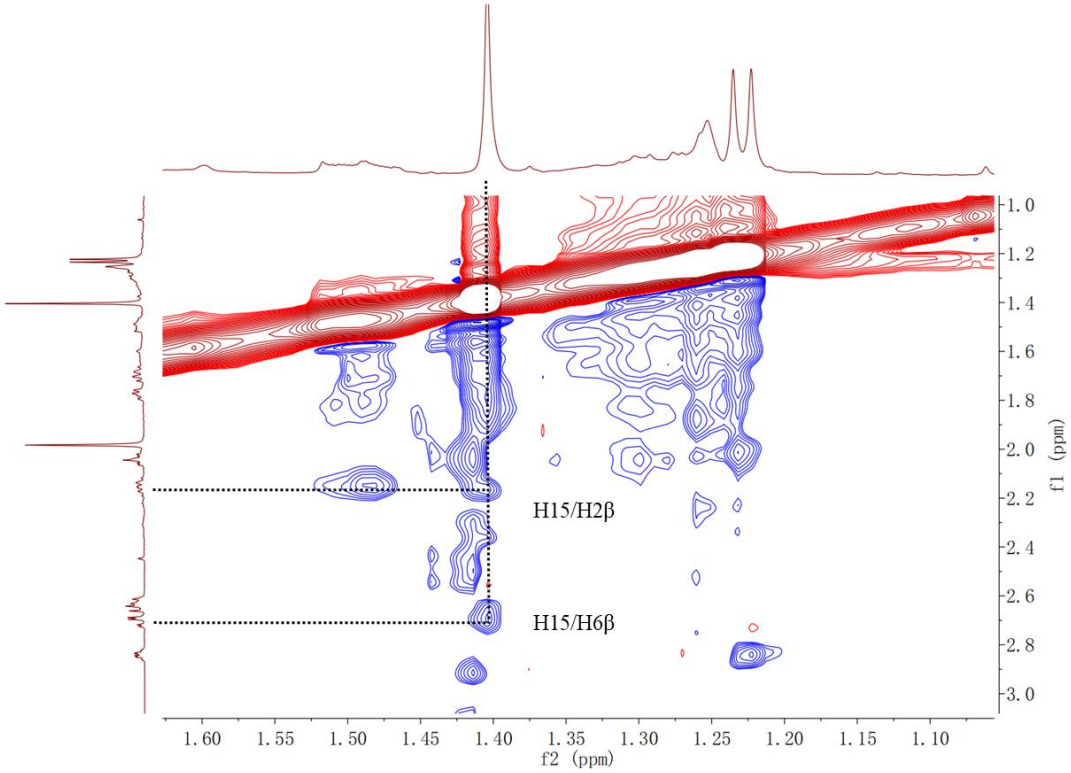


Figure S11: ROESY spectrum of **1** (kalshinoid G) (From δ_H1.0 ppm to δ_H 1.6 ppm)

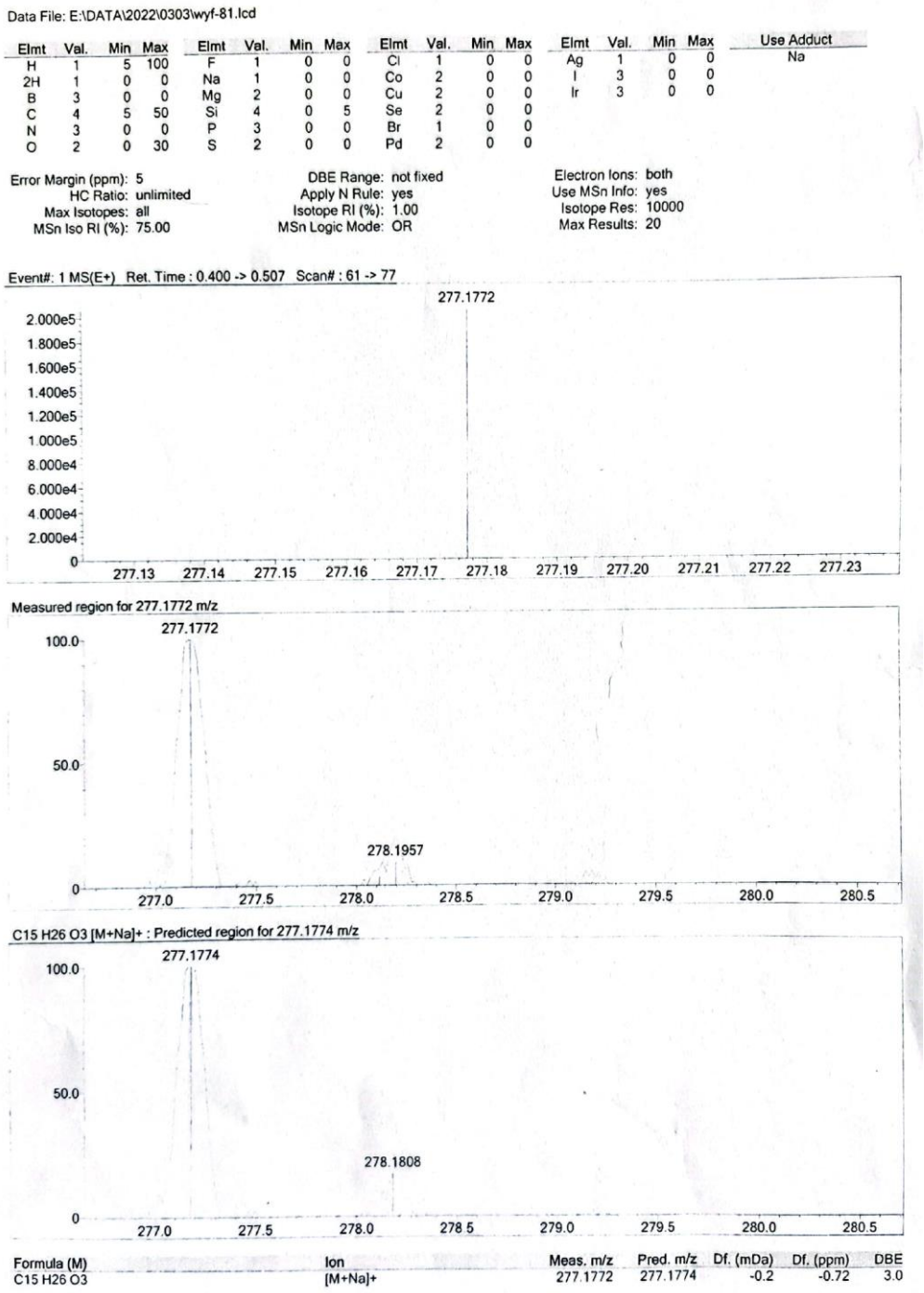


Figure S12: HR-ESI-MS spectrum of **2** (kalshinoid H)

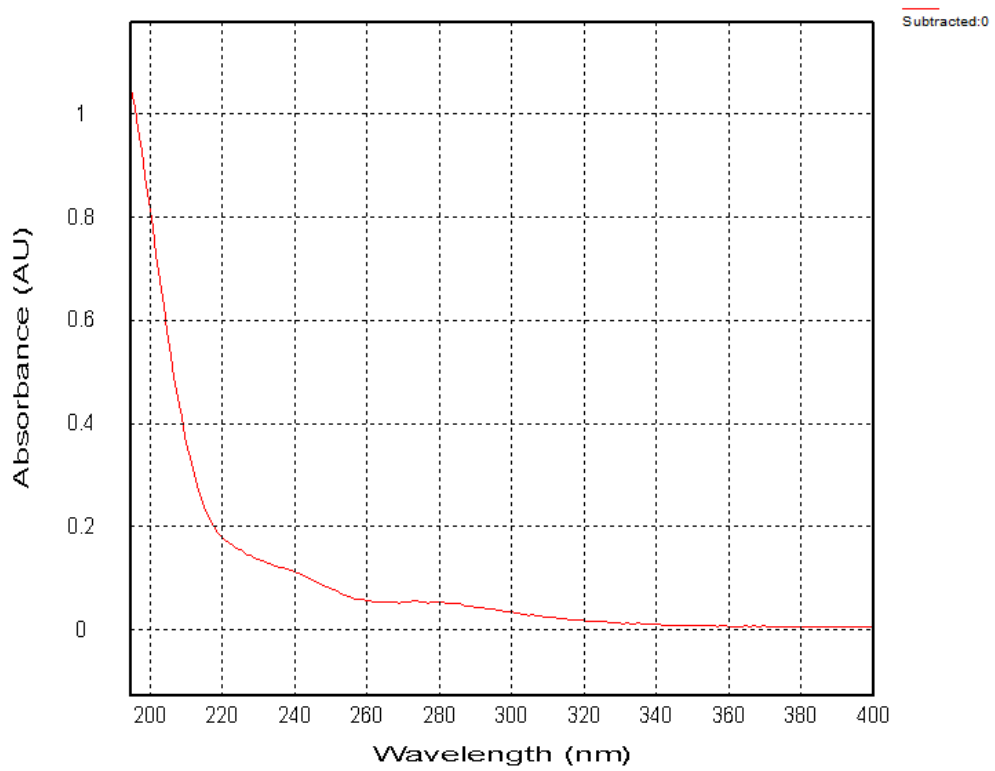


Figure S13: UV spectrum of **2**

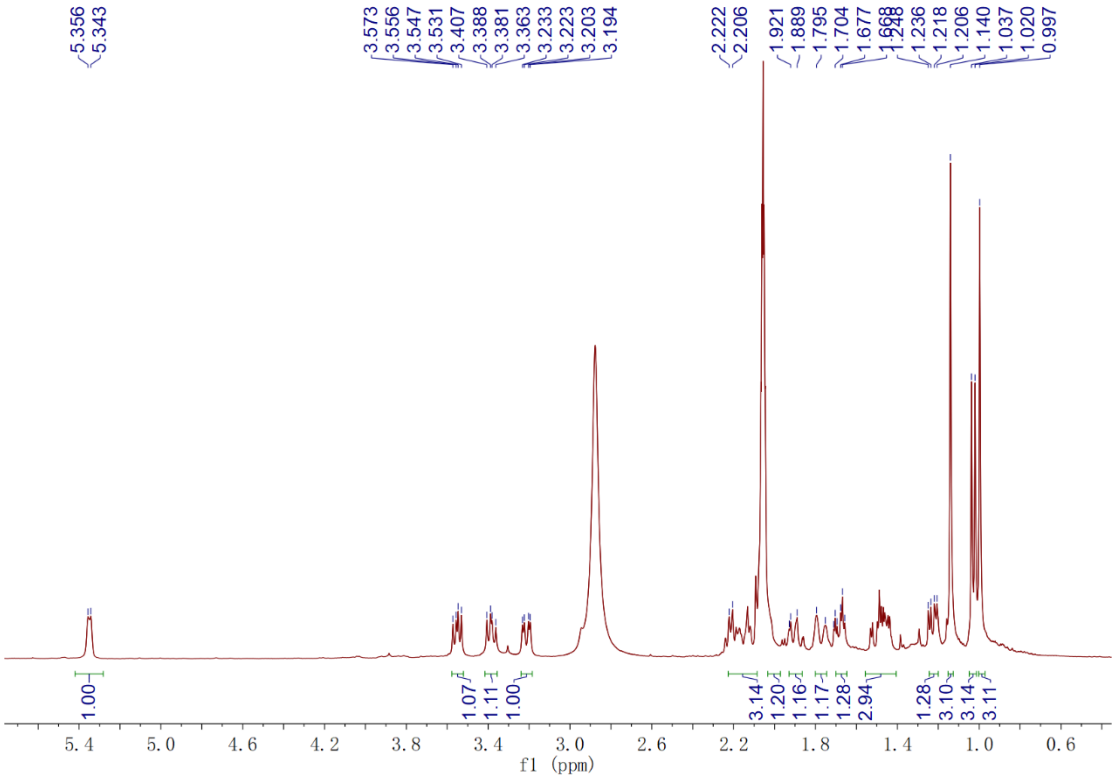


Figure S14: ^{1}H-NMR (600 MHz, Acetone-d_6) spectrum of **2** (kalshinoid H)

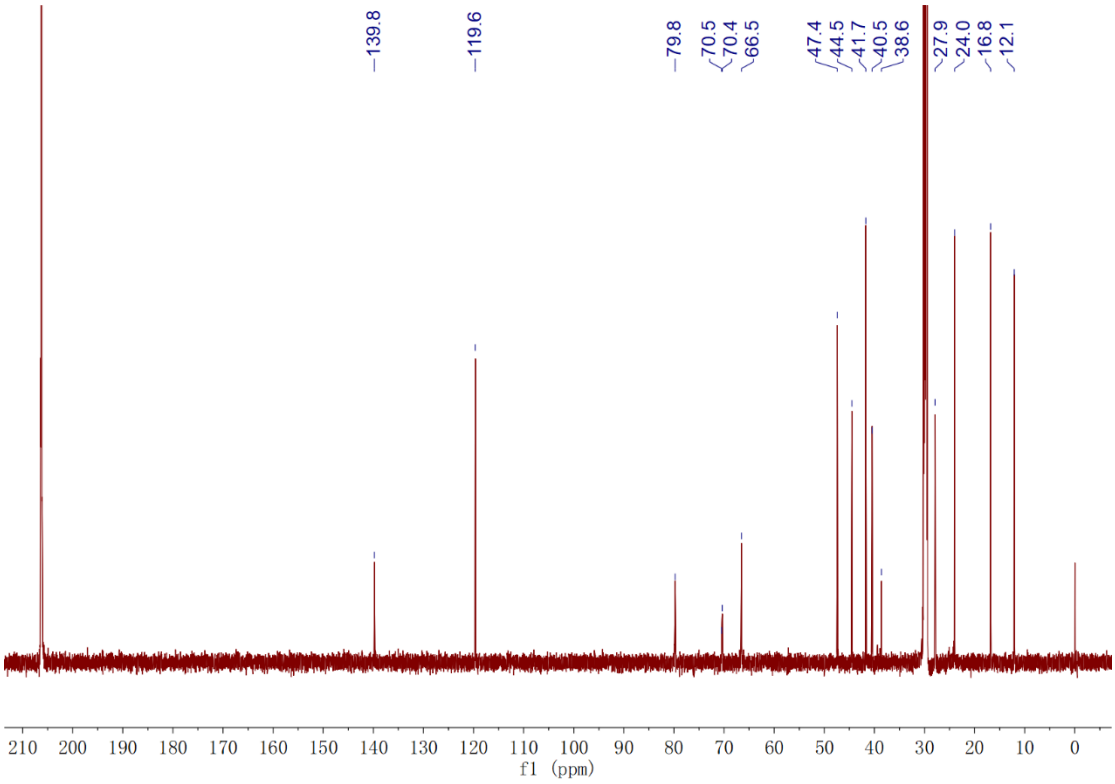


Figure S15: ^{13}C-NMR (150 MHz, Acetone-d_6) spectrum of **2** (kalshinoid H)

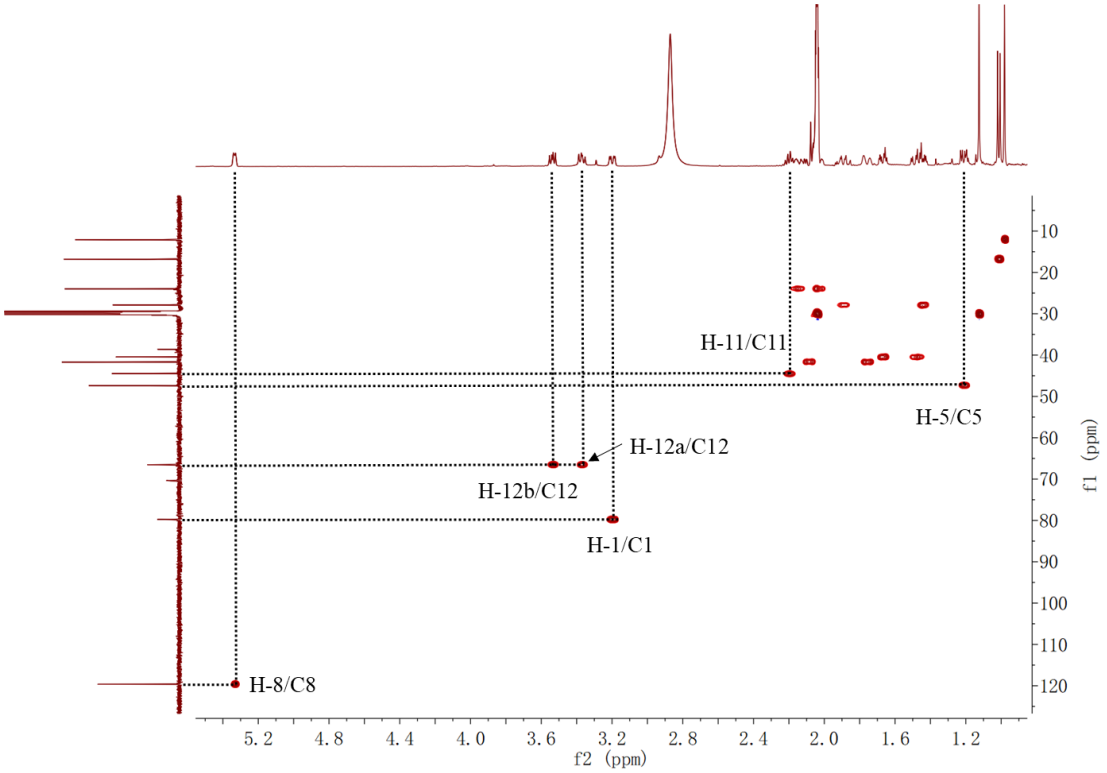


Figure S16: HSQC spectrum of **2** (kalshinoid H)

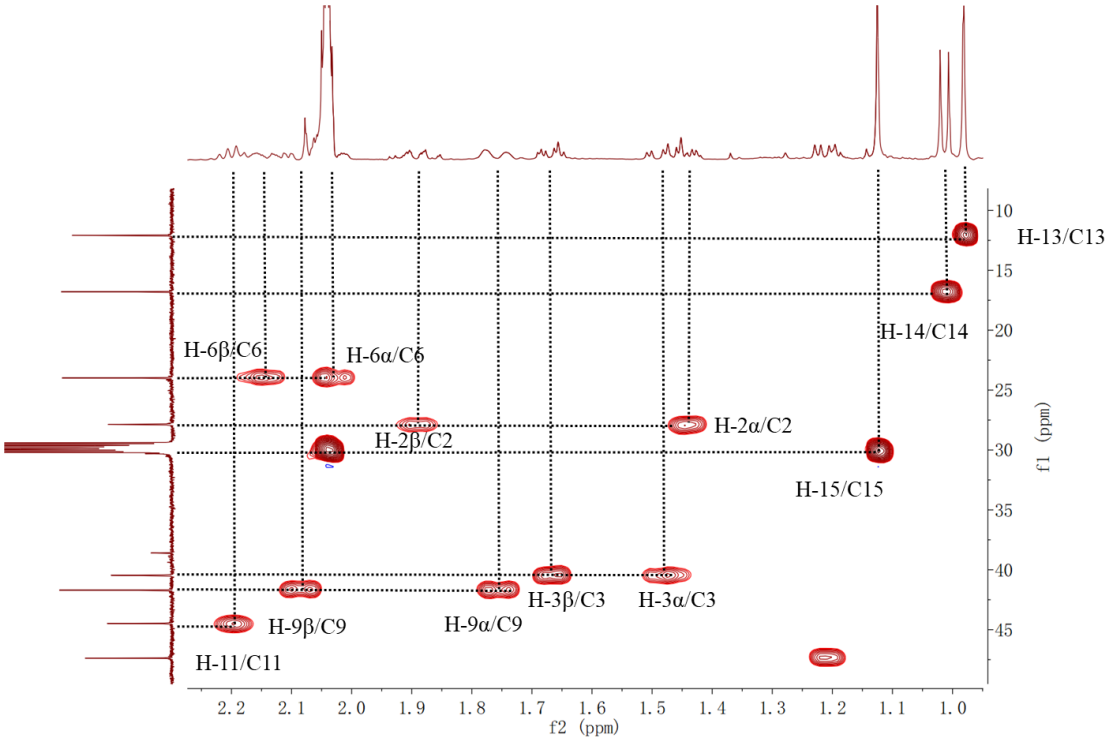


Figure S17: HSQC spectrum of **2** (kalshinoid H) (From δ_C 10 ppm to 50 ppm)

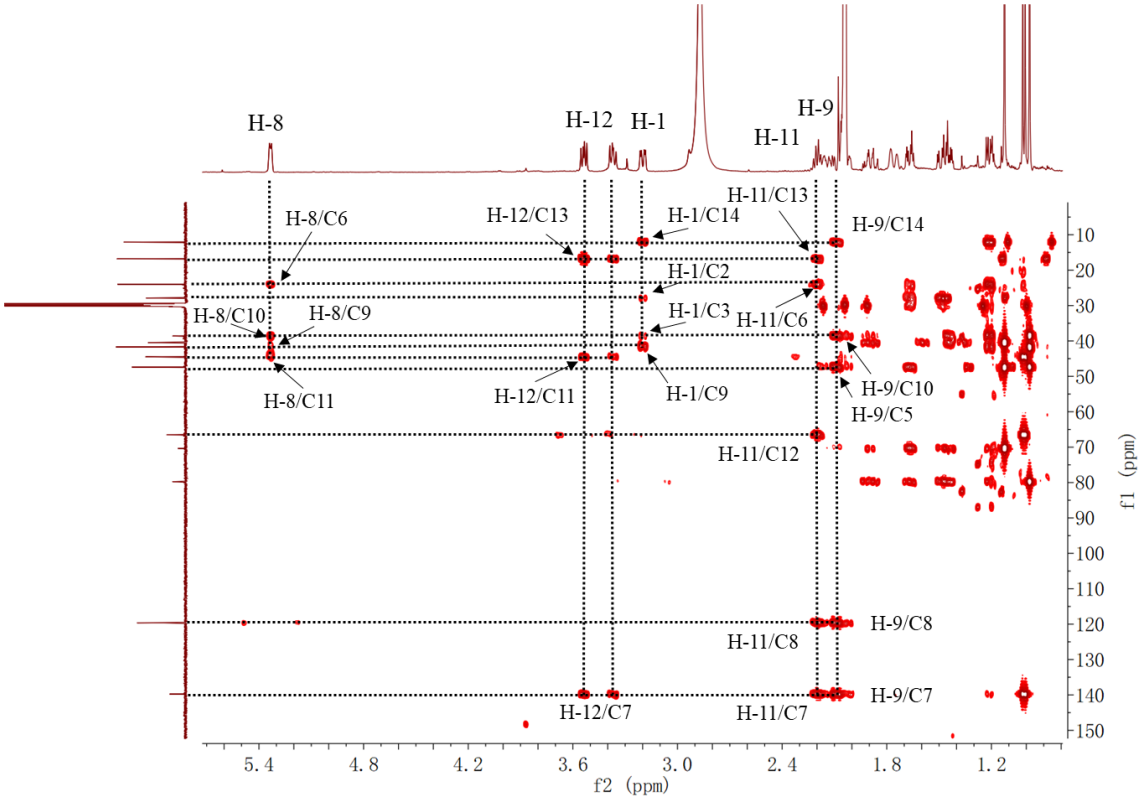


Figure S18: HMBC spectrum of **2** (kalshinoid H)

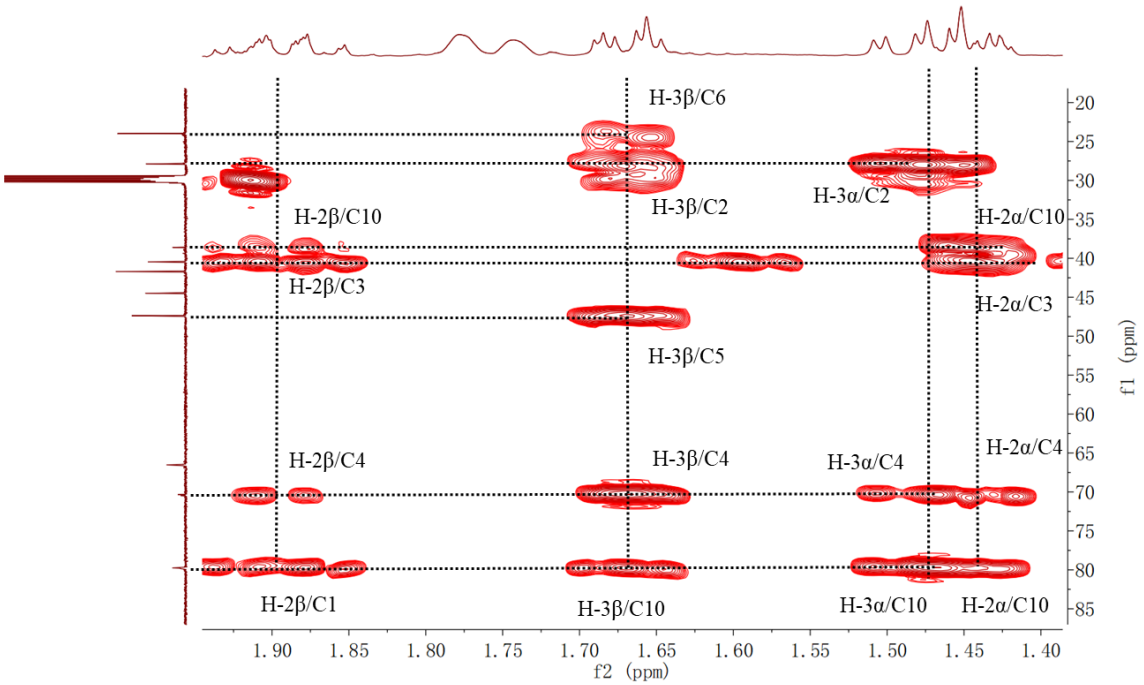


Figure S19: HMBC spectrum of **2** (kalshinoid H) (From δ_C 15 ppm to 85 ppm)

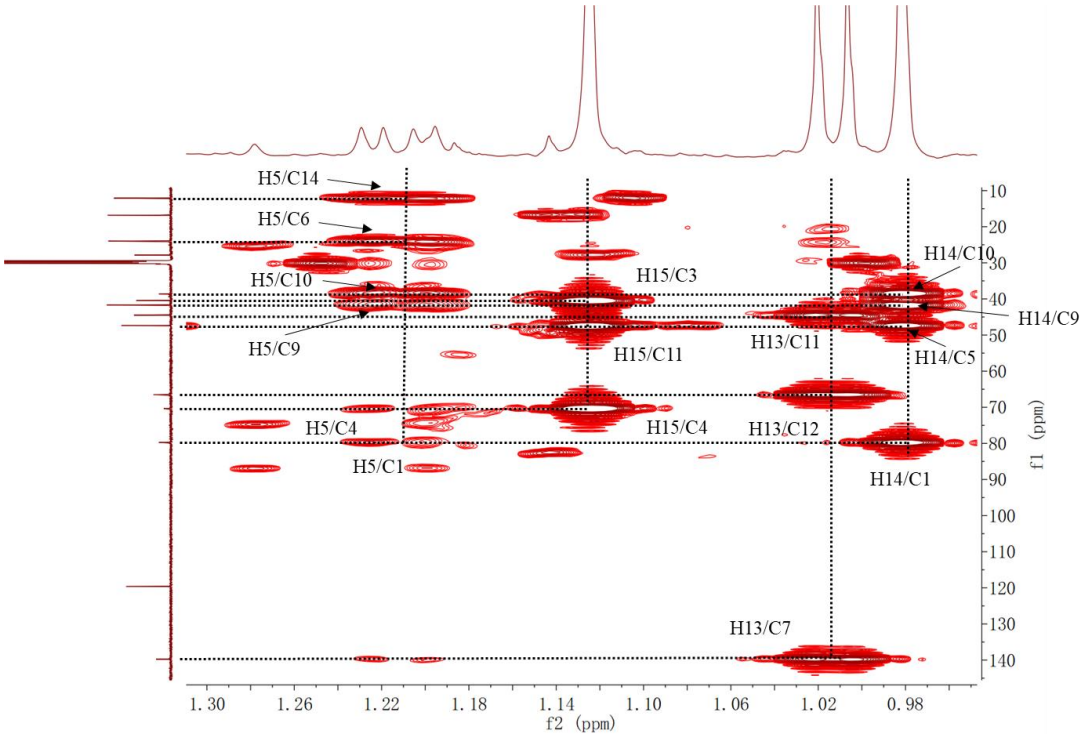


Figure S20: HMBC spectrum of **2** (kalshinoid H) (From δ_C 10 ppm to 145 ppm)

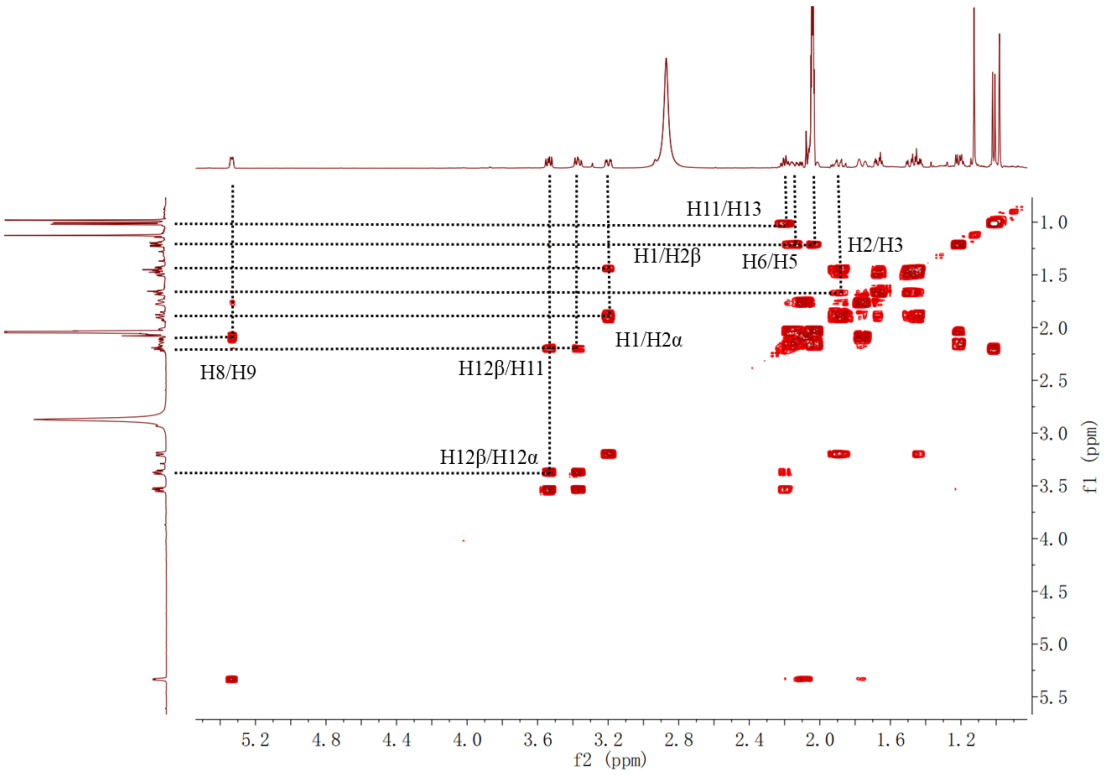


Figure S21: ^{1}H-^{1}H COSY spectrum of **2** (kalshinoid H)

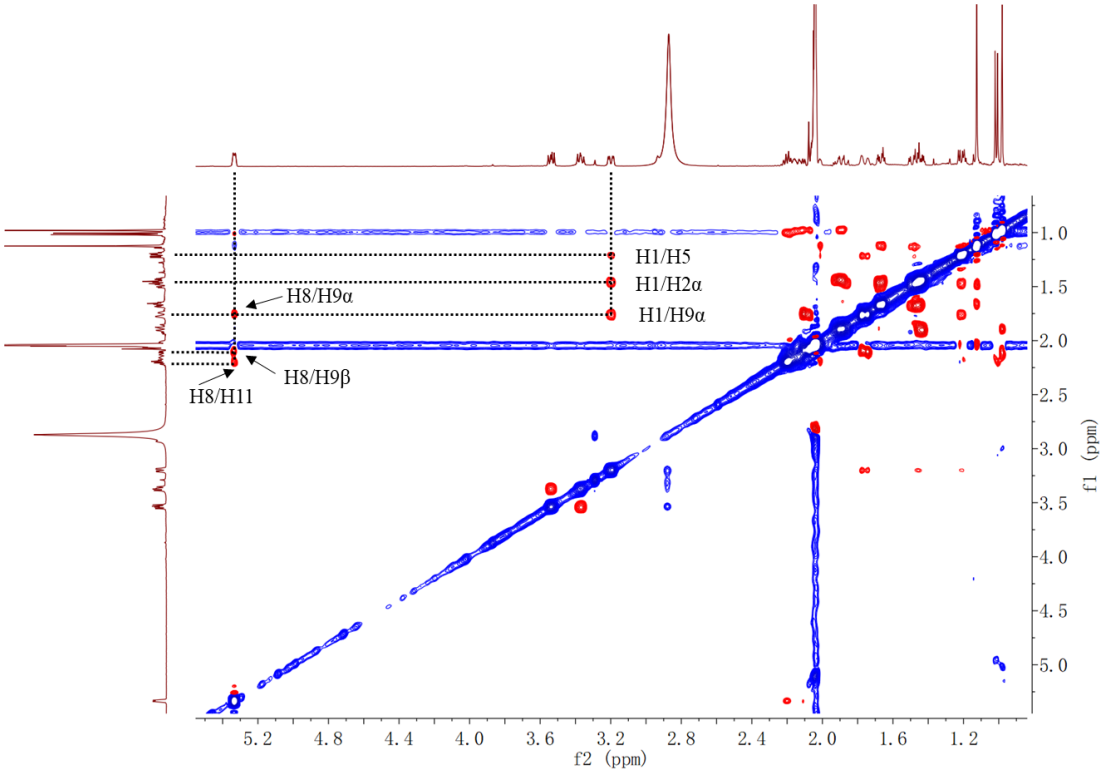


Figure S22: ROESY spectrum of **2** (kalshinoid H)

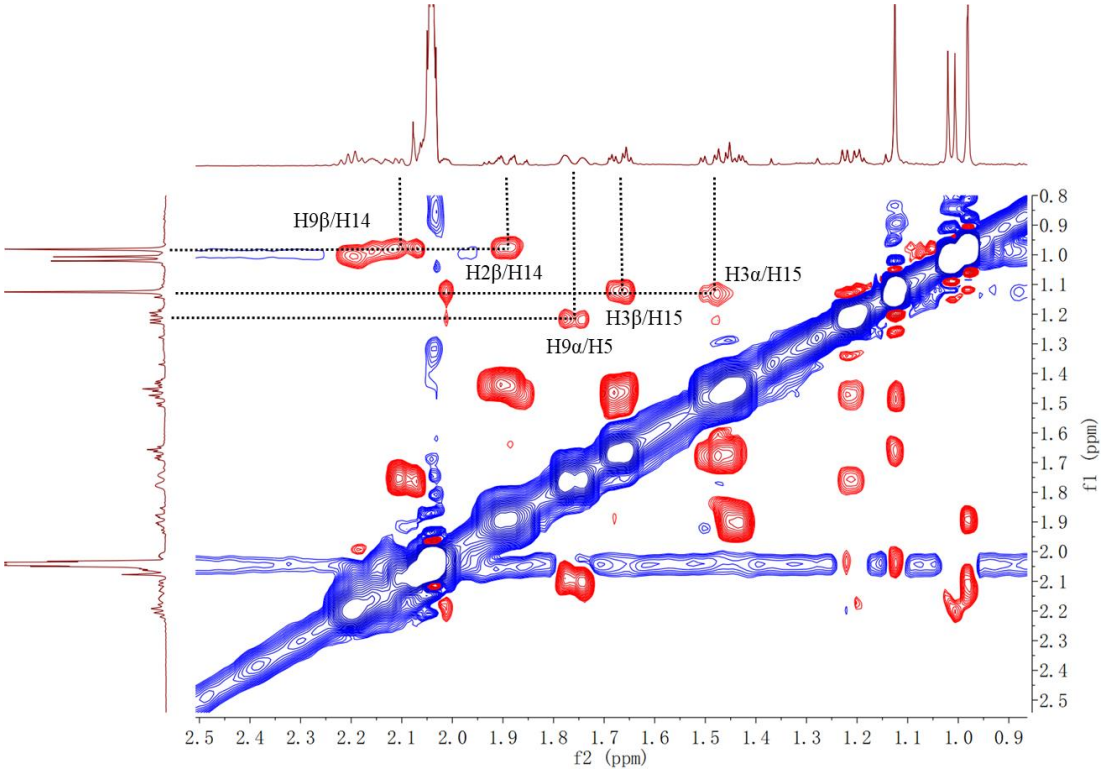


Figure S23: ROESY spectrum of **2** (kalshinoid H) (From δ_H 0.8 ppm to 2.5 ppm)

Functional	Solvent?	Basis Set	Type o
mPW1PW91	PCM	6-311+G(d,p)	Unscale

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
sDP4+ (H data)	50.00%	50.00%	-	-	-
sDP4+ (C data)	0.00%	100.00%	-	-	-
sDP4+ (all data)	0.00%	100.00%	-	-	-
uDP4+ (H data)	50.00%	50.00%	-	-	-
uDP4+ (C data)	0.00%	100.00%	-	-	-
uDP4+ (all data)	0.00%	100.00%	-	-	-
DP4+ (H data)	50.00%	50.00%	-	-	-
DP4+ (C data)	0.00%	100.00%	-	-	-
DP4+ (all data)	0.00%	100.00%	-	-	-

Functional	Solvent?	Basis Set
mPW1PW91	PCM	6-311+G(d,p)

		DP4+	0.00%	100.00%	-
Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3
C		41	49.46734138	46.71155763	
C		27.2	33.4922654	32.48127349	
C		41.4	42.38334536	46.00043225	
C		81.5	84.28539125	85.84660976	
C		45.3	59.43599918	49.87409779	
C		24.3	25.88678032	29.350518	
C	x	134.5	148.1788976	144.5973367	
C	x	147.3	158.2175355	155.3180791	
C	x	193.3	196.2345314	198.1770268	
C		48.2	55.82750043	54.97037251	
C	x	122.9	131.0940386	131.4504046	
C	x	144	150.1674479	151.9416415	
C		8.4	11.50127843	11.50354538	
C		13.5	17.29997844	16.63493215	
C		25.9	31.86819349	27.9792457	
H		2.62	2.770015722	2.770015722	
H		2.14	2.376490475	2.376490475	
H		1.48	1.517200331	1.517200331	
H		1.77	1.834719506	1.834719506	
H		1.68	1.795210523	1.795210523	
H		2.03	2.192927539	2.192927539	
H		2.65	2.921285322	2.921285322	
H		2.71	2.907358099	2.907358099	
H		2.84	2.803210519	2.803210519	
H	x	7.38	7.797839962	7.797839962	
H		1.98	2.136621608	2.136621608	
H		1.23	1.348845474	1.348845474	
H		1.4	1.441353786	1.441353786	

Figure S24 . DP4+ analyses of calculated and experimental NMR chemical shifts of **1.** Isomer 1: 1*S**-**1**; Isomer 2: 1*R**-**1**

Table S1 : Energy analyses of conformers (1*R*,4*R*,5*S*,10*R*)-**1**a-d

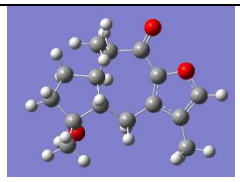
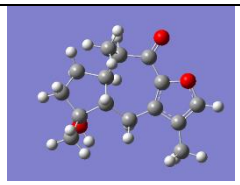
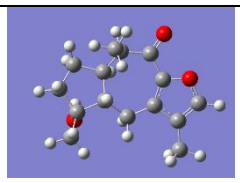
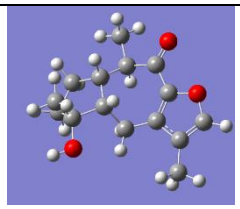
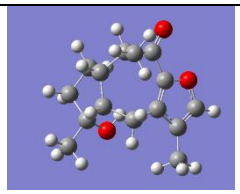
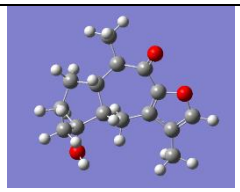
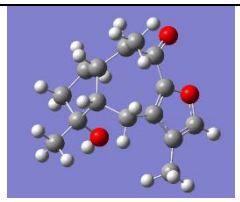
NO.	3D comformers	Free energy		
		E (Hartree)	ΔE (Kcal/mol)	Boltzmann distribution
1a		-808.4255828	0.0000	53.69%
1b		-808.4248818	0.000700923	25.55%
1c		-808.4244607	0.704122371	16.35%

Table S2 : Energy analyses of conformers (1*S*,4*R*,5*S*,10*R*)-**1**a-d

NO.	3D comformers	Free energy		
		E (Hartree)	ΔE (Kcal/mol)	Boltzmann distribution
2a		-808.4255828	0.0000	53.69%
2b		-808.4248818	0.000700923	25.55%
2c		-808.4244607	0.704122371	16.35%
2d		-808.4232252	0.002357659	4.41%

NMR Computational details of compound 1.

The initial conformational analysis of the compound **1** was executed by employing Monte Carlo searching algorithm via the MMFF94 molecular mechanics force field[1], with the aid of the SPARTAN'16 program package, leading to afford a panel of relatively favored conformations in an energy range of 3 kcal/mol above the global minimum. The force field minimum energy conformers thus obtained were subsequently optimized by applying the density functional theory (DFT) with the B3LYP/6-31G(d) level in vacuum, implemented in the Gaussian 09 software package[2]. Harmonic vibrational frequencies were also performed to confirm no imaginary frequencies of the finally optimized conformers. Gauge-Independent Atomic Orbital (GIAO) calculations of NMR chemical shifts were accomplished by DFT at the mPW1PW91/6-311+g (d, p) level in Chloroform with the PCM solvent model in Gaussian 09 software. NMR chemical shifts of TMS were calculated in the same level and used as the references. Regression analysis of calculated versus experimental NMR chemical shifts of **1** was carried out. Linear correlation coefficients (R^2) and Root-mean-square deviation (RMSD) were calculated for the evaluation of the results. After Boltzmann weighing of the predicted chemical shift of each isomers, the DP4+ parameters were calculated using the excel file provided by Ariel M. Sarotti.[3]

Measurement of NO production

NO production was quantified by measuring the accumulation of nitrite in the cell culture supernatant with Griese reagent [4]. Briefly, RAW 264.7 cells (6×10^6 cells/mL) were seeded in 96-well plates and pretreatment with compounds for 1 h before LPS (1μg/mL) stimulation. The isolated culture supernatant was mixed with Griese reagent (Beyotime Biotechnology, China). $NaNO_2$ was used to generate a standard curve, and the absorbance of the mixture was measured at 540 nm. In the experiment, monomethylarginine monoacetate (L-NMMA) was used as a positive control.

References

[1] T. A. Halgren(1999). MMFF VII. Characterization of MMFF94, MMFF94s, and other widely available force fields for conformational energies and for intermolecular-interaction energies and geometries, *J. Comput. Chem.* **20**, 730-748.

[2] M.J.Frisch, G.W.Trucks, H.B. Schlegel, G :E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, *et.al*. Gaussian 09, Rev. C 01; Gaussian, Inc., Wallingford CT, 2009.

[3] T. Bruhn, A. Schaumloffel, Y. Hemberger and G. Bringmann (2013). SpecDis: quantifying the comparison of calculated and experimental electronic circular dichroism spectra, *Chirality* **25**, 243-244.
[4] S. S. Wei, J. Chi, M. M. Zhou, R. J. Li, Y. R. Li, J. Luo and L. Y. Kong (2019). Anti-inflammatory lindenane sesquiterpeniods and dimers from *Sarcandra glabra* and its upregulating AKT/Nrf2/HO-1 signaling mechanism, *Ind. Crop. Prod.* **137**, 367–376.

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