Supporting Information

Detoxification of Plant Aromatic Abietanoids via Cleavage of the Benzene Ring into 11,12-*Seco*-diterpene Polyenes by a Specialist Insect of *Leucosceptrum canum*

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Experimental section

1.1 General experimental procedures

Column chromatography (CC) was carried out on silica gel (200–300 mesh, Qingdao Marine Chemical Factory, Qingdao, P. R. China) and Sephadex LH-20 (20–100 μm, Amersham Pharmacia Biotech, Sweden). Thin-layer chromatography (TLC) was performed on silica gel (GF_{254}, 10–40 μm, Qingdao Marine Chemical Factory). Spots were detected on TLC under UV light or by heating after spraying with 5% H_2SO_4 in EtOH (v/v). Semi-preparative HPLC was performed on an Agilent 1200 series instrument equipped with a quaternary pump, a vacuum degasser, an autosampler, a thermostated column compartment, a diode array detector, and a Zorbax SB-C_{18} column (5 μm, 9.4×250 mm, 3 mL/min). NMR experiments were carried out using a Bruker AV-800 spectrometer with TMS as internal standard. Mass spectra were obtained on a Waters AutoSpec Premier P776 spectrometer. IR spectra were recorded on a Bruker-Tensor-27 spectrometer with KBr pellets. UV spectra were measured on a Shimadzu-210A double-beam spectrophotometer. Optical rotations were obtained on a Jasco P-1020 spectropolarimeter. ECD experiments were conducted with an Agilent Applied Photophysics circular dichroism spectrometer.

1.2 Plant materials and insects

Fresh leaves of *Leucosceptrum canum* Smith (Lamiaceae) and *Nacna malachitis* larvae were collected from the Botanical Garden of Kunming Institute of Botany from early July to late August in 2017. The larvae were reared at room temperature in the laboratory and fed with fresh leaves of *L. canum*. Pupae emerged about one week later and were put into separate cages for eclosion. Metabolic excrement of the larvae was carefully picked every day and then stored at –80 °C until use. Moths of *N. malachitis* Oberthür (Noctuidae) were identified by Professor Da-Zhi Dong from Kunming Institute of Zoology, Chinese Academy of Sciences (CAS), and a voucher specimen (NM-2017-08) was kept in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, CAS.

1.3 Extraction and isolation

After about two months' collection, the metabolic excrement (9.6 g, fresh weight) from a total of 62 larvae was soaked in acetone (200 mL) at room temperature for 24 h, and the extraction was conducted for five times under the same condition. The extract was evaporated to dryness under reduced pressure and combined to yield an oily residue (0.90 g). The residue was subjected to silica gel column chromatography (CC, 2×30 cm) eluting with PE (petroleum ether)/Me_2CO stepwise-gradient system (from 10:0 to 0:10, v/v) to give five fractions (Fr.1–Fr.5). Fr.2 and Fr.3 were obtained from 10:1 and 5:1 of the elution solvents of PE /Me_2CO, respectively. Fr.2 (15 mg) was purified over Sephadex LH-20 column (1×170 cm) eluting with $CHCl_3$/MeOH (1:1, v/v), giving a more purified fraction (9.2 mg), which was then applied to semi-preparative RP-HPLC (5 μm, 9.4×250 mm, 3 mL/min) using MeOH as the mobile phase to yield compound **2** (t_R 9.2 min, 2.6 mg). Fr.3 (320 mg) was separated on Sephadex LH-20 column (1.5×170 cm) with Me_2CO as the eluent to give three sub-fractions (Fr.3-1–Fr.3-3). Fr.3-3 (60 mg) was submitted to semi-preparative RP-HPLC (5 μm, 9.4×250 mm, 3 mL/min) using MeCN-H_2O (90:10, v/v) as the mobile phase to yield compound **1** (t_R 12.0 min, 1.5 mg). UV detection was adopted for the above HPLC preparation with a diode array detector (DAD).

1.4 Compound characterization

Nacnabietanin A (**1**): Colorless oil; $[\alpha]_D^{20}$ +12 (*c* 0.06, MeOH); UV (MeOH) λ_{max} (log ε) 203 (3.47), 238 (3.14) nm; IR (KBr) ν_{max} 3430, 2926, 1719, 1657, 1459, 1461, 1383 cm^{-1}; ECD (*c* 0.004, MeOH): λ_{max} ($\Delta\varepsilon$) 198 (+6.46), 212 (–7.24), 237 (+2.29); ^1H and ^{13}C NMR data, see Table 1; HREIMS *m*/*z* 286.2299 $[M]^+$ (calcd for $C_{20}H_{30}O$, *m*/*z* 286.2297).

Nacnabietanin B (**2**): Colorless oil; $[\alpha]_D^{20}$ +7 (*c* 0.06, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 240 (3.54) nm; IR (KBr) ν_{max} 3438, 2925, 1632, 1452, 1384 cm^{-1}; ECD (*c* 0.002, $CHCl_3$): λ_{max} ($\Delta\varepsilon$) 199 (+8.31), 208 (–3.12), 236 (+0.96); ^1H and ^{13}C NMR data, see Table 1; HREIMS *m*/*z* 268.2189 $[M]^+$ (calcd for $C_{20}H_{28}$, *m*/*z* 268.2191).

Figure S1. EIMS of compound **1**

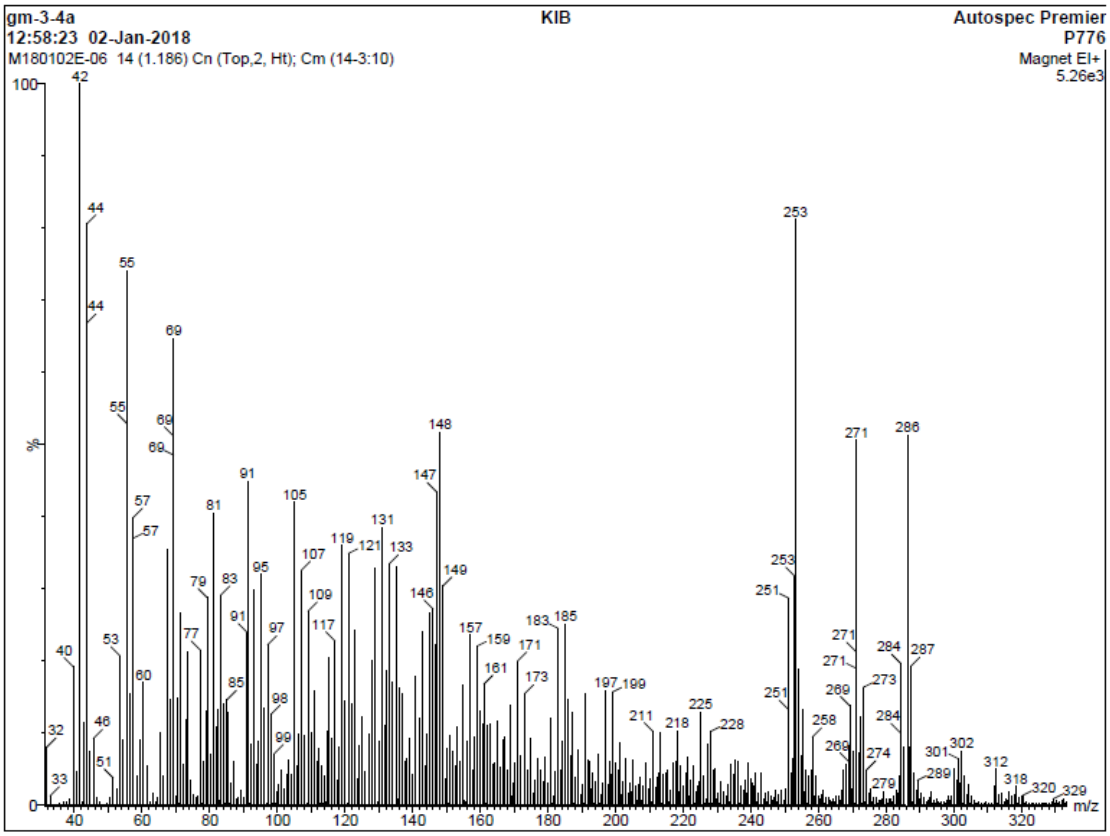

Figure S2. HREIMS of compound **1**

Elemental Composition Report **Page 1**

Single Mass Analysis
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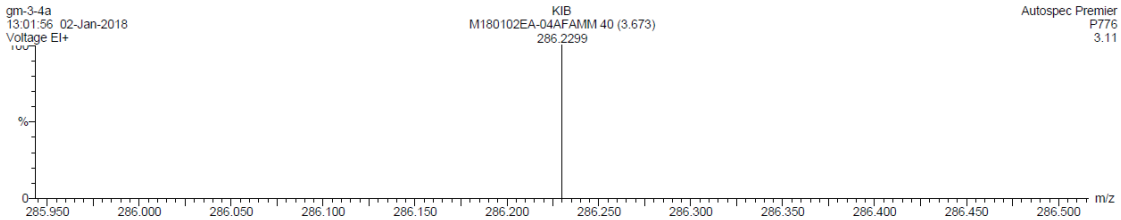
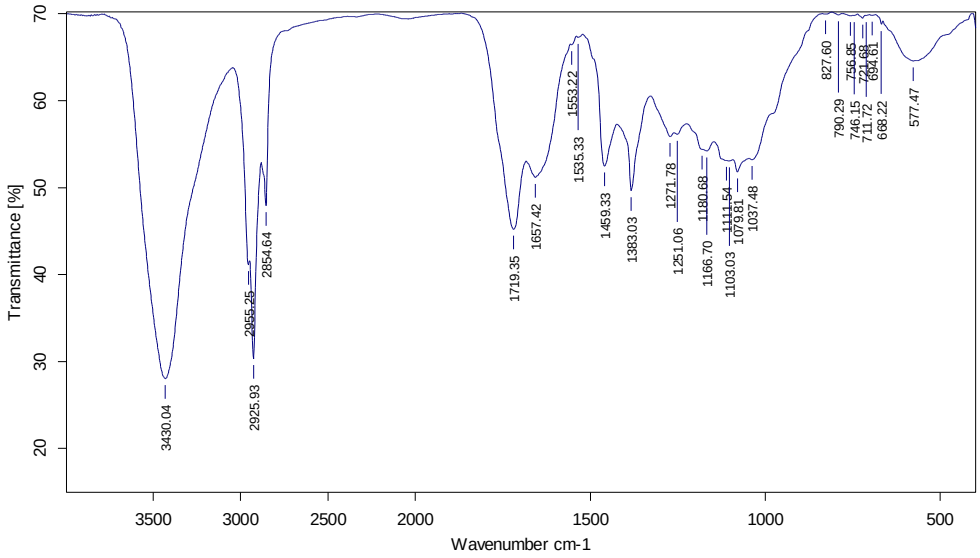
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 O: 0-2



Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
286.2299	286.2297	0.2	0.7	6.0	5546025.5	C20 H30 O

Figure S3. IR spectrum of compound **1**



Sample : glm-3-4a	Frequency Range : 399.246 - 3996.32	Measured on : 19/03/2018	
Technique : KBr	Resolution : 4	Instrument : Tensor27	Sample Scans : 16
Filename : 180319IR.23	Zerofilling : 2	Acquisition : Double Sided,For	

Figure S4. ECD spectrum of compound **1**

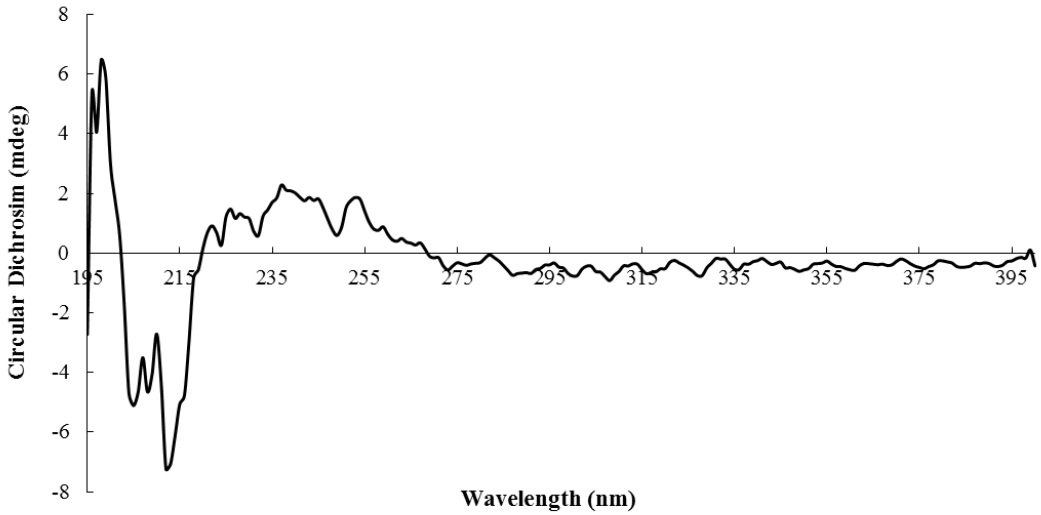


Figure S5. ^{1}H NMR spectrum of compound **1** in acetone-d_6 (800 MHz)

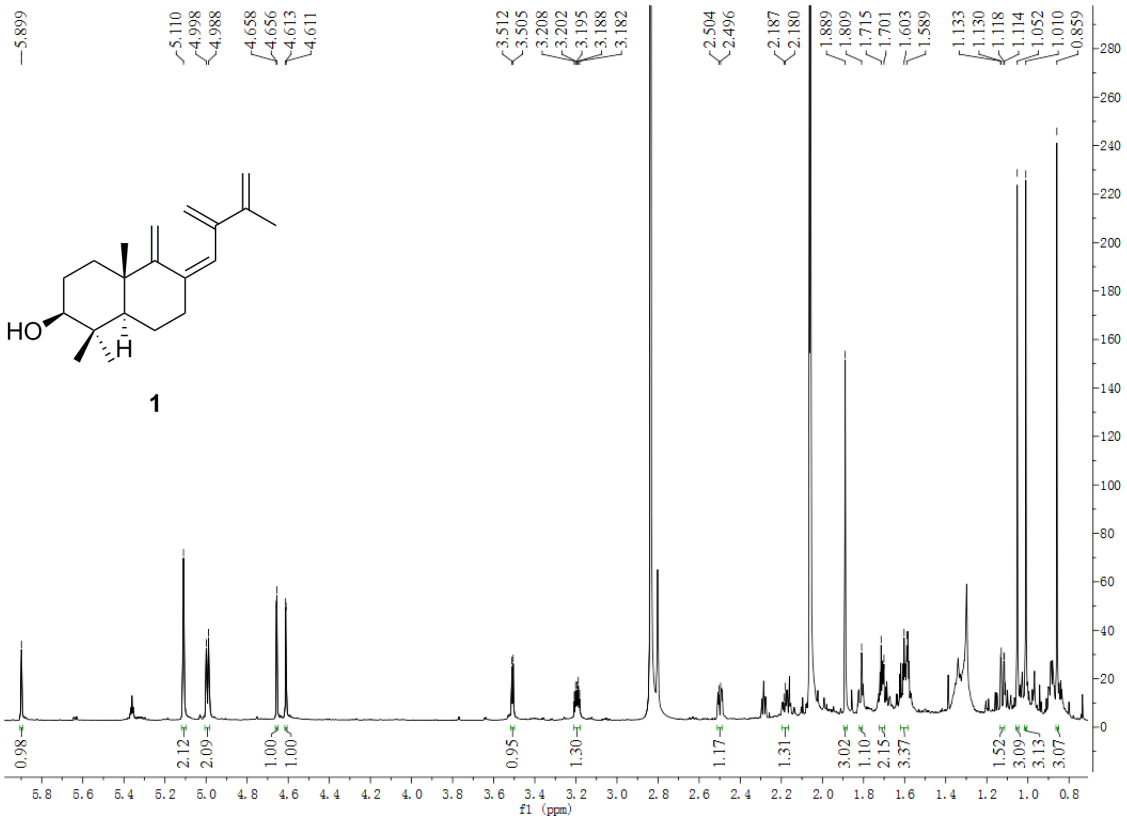


Figure S6. ^{13}C NMR (DEPT) spectrum of compound **1** in acetone-d_6 (200 MHz)

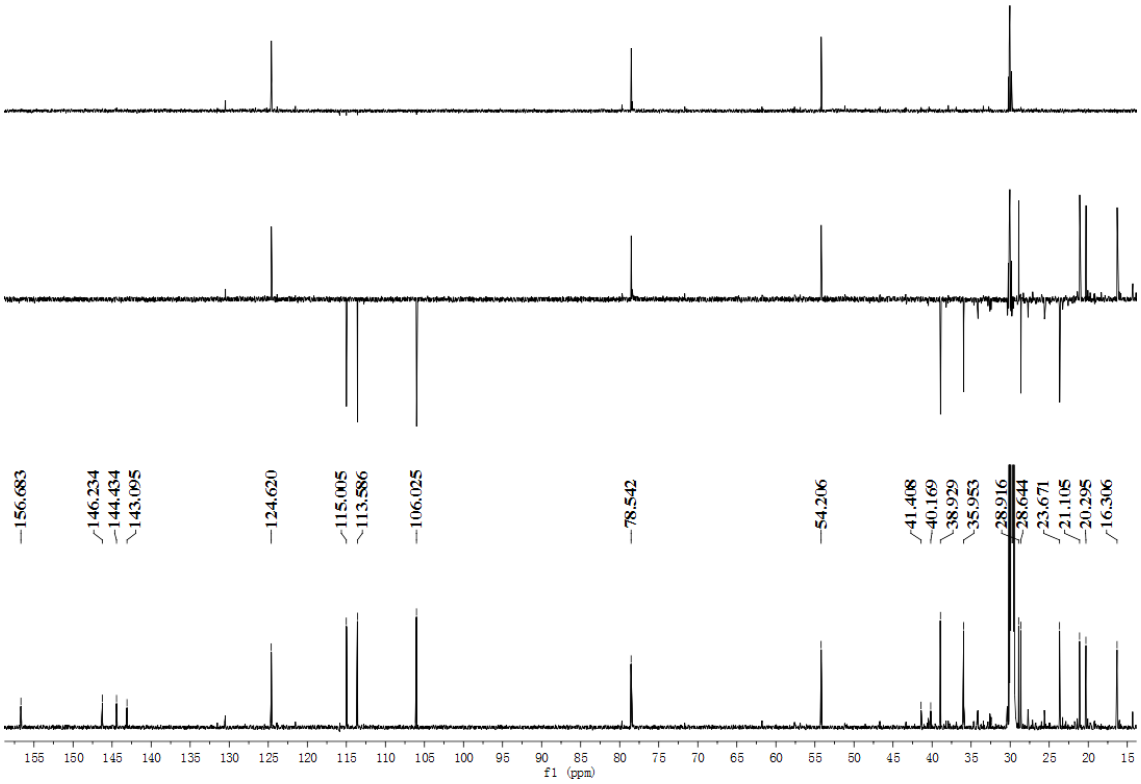


Figure S7. ^{1}H-^{1}H COSY spectrum of compound **1** in acetone-d_6

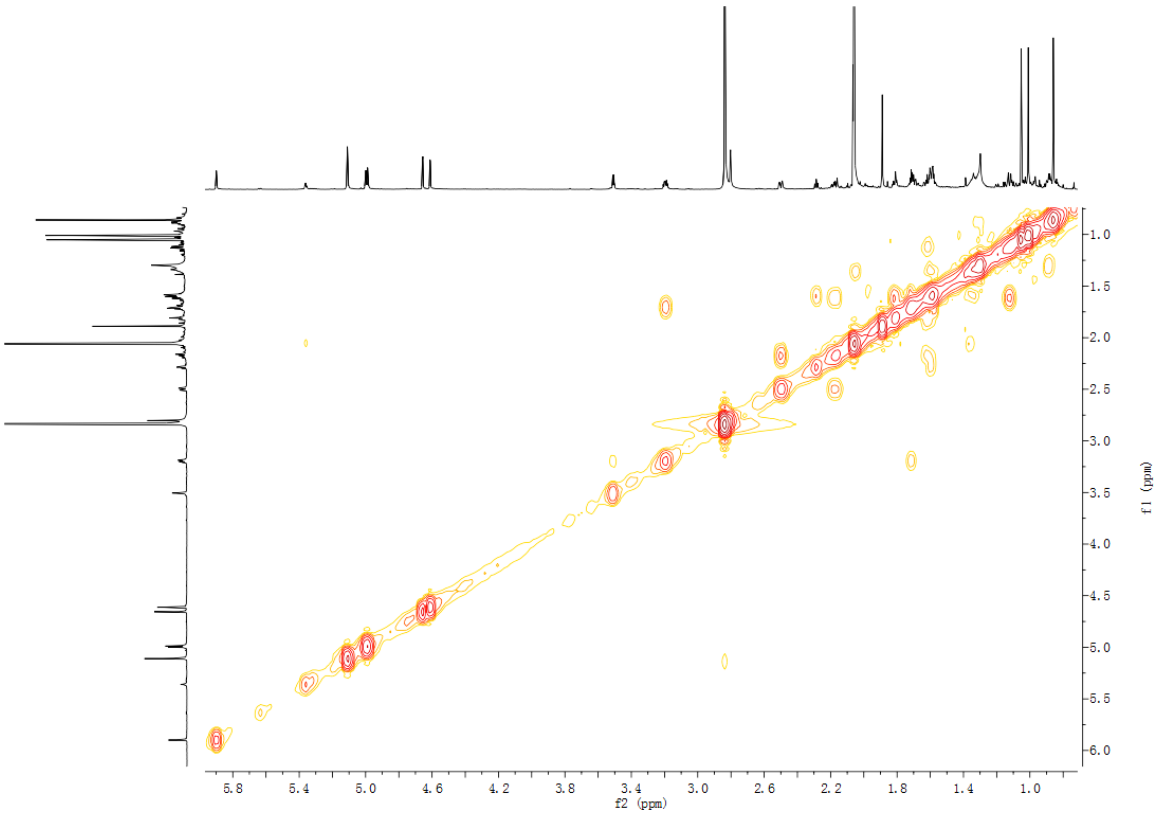


Figure S8. HSQC spectrum of compound **1** in acetone-d_6

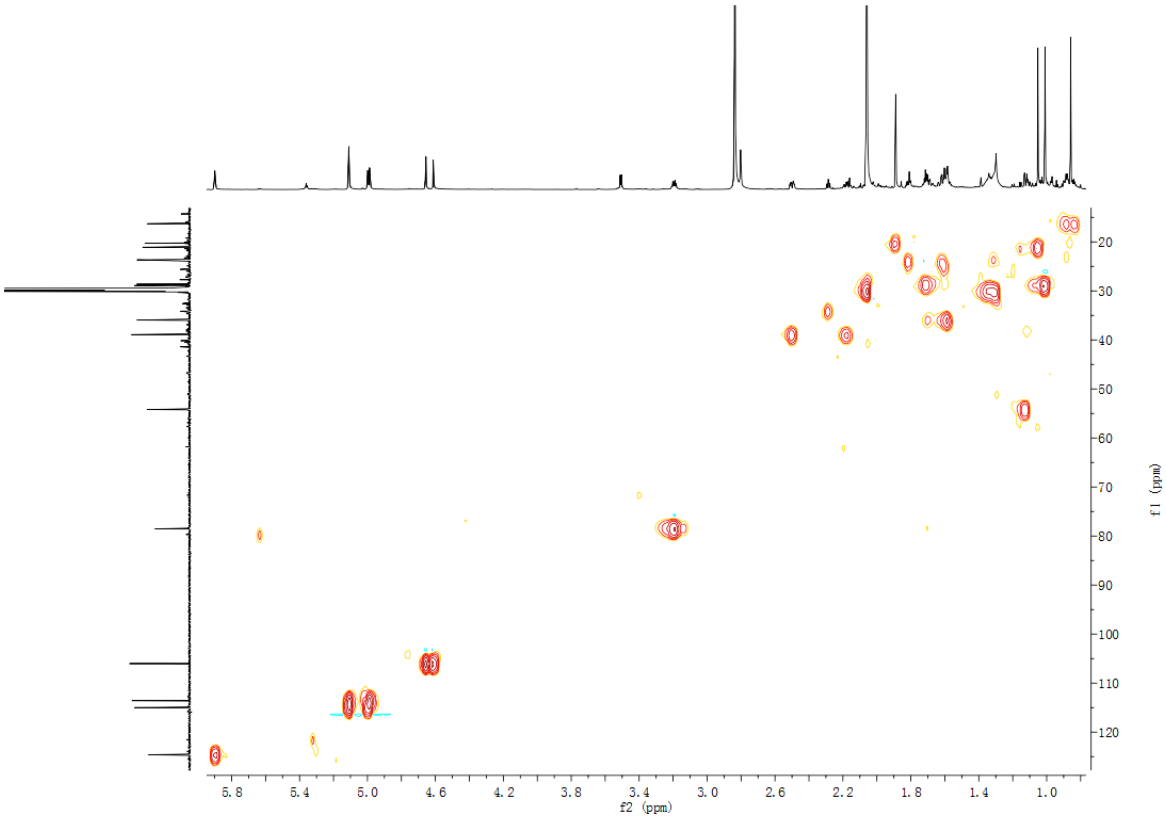


Figure S9. HMBC spectrum of compound **1** in acetone-d_6

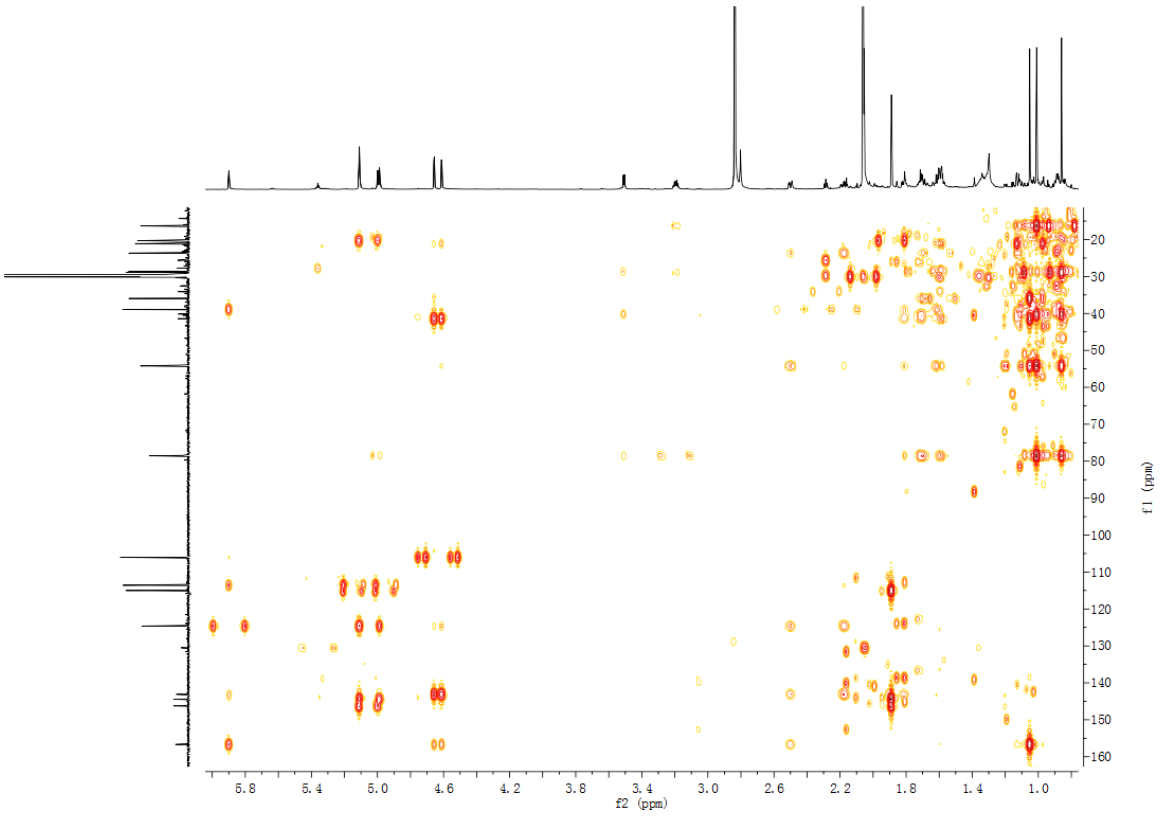


Figure S10. ROESY spectrum of compound **1** in acetone-d_6

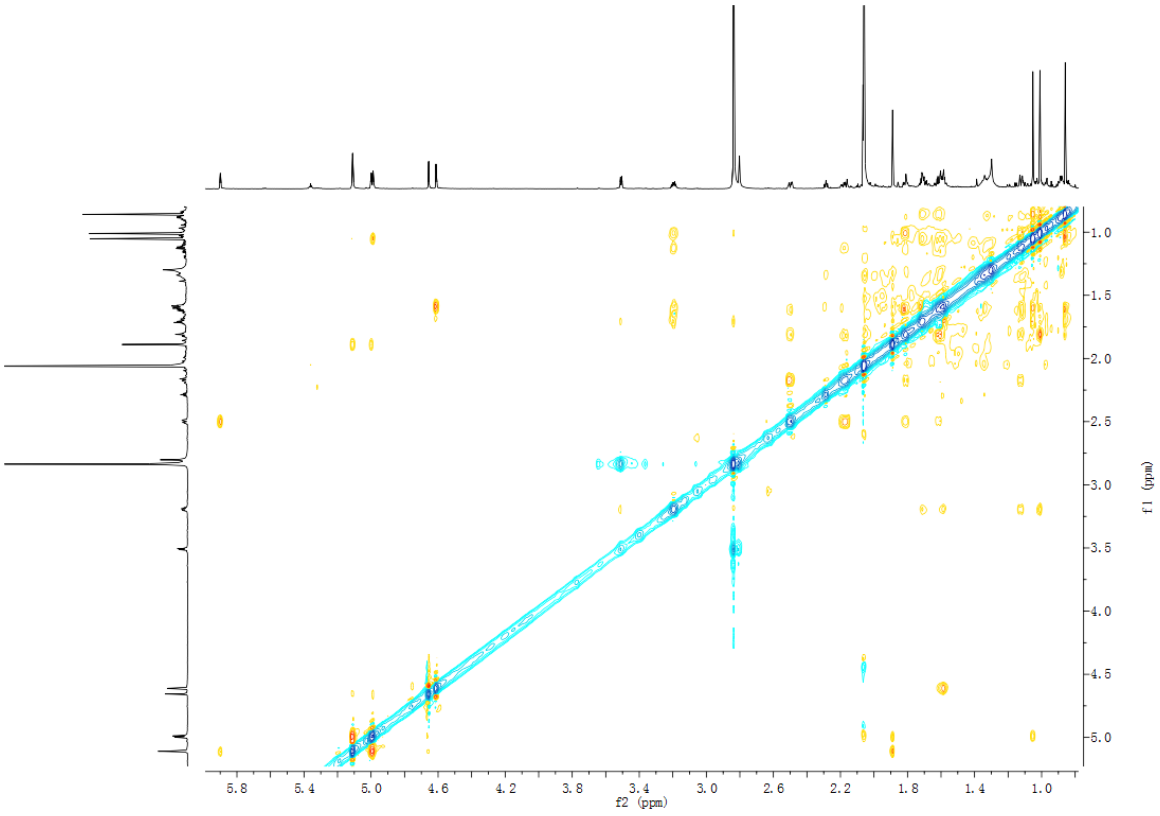


Figure S11. EIMS of compound **2**

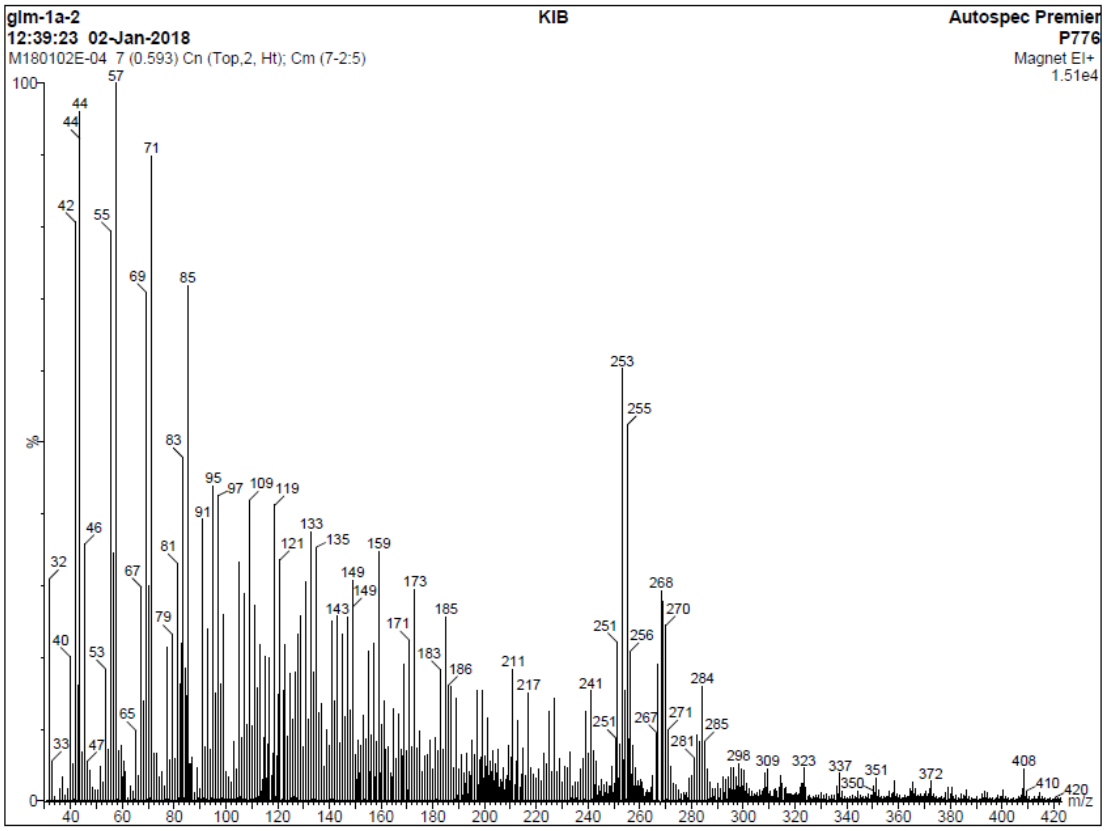
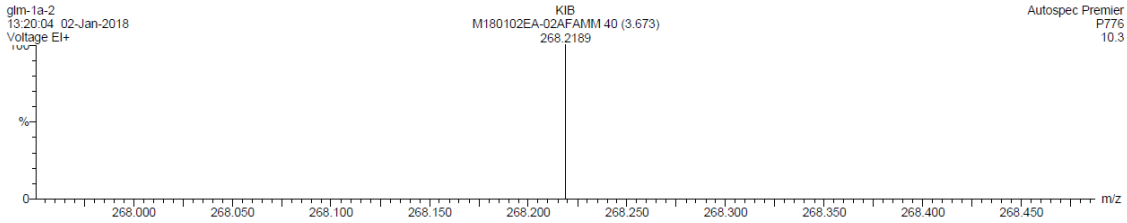


Figure S12. HREIMS of compound **2**

Elemental Composition Report **Page 1**

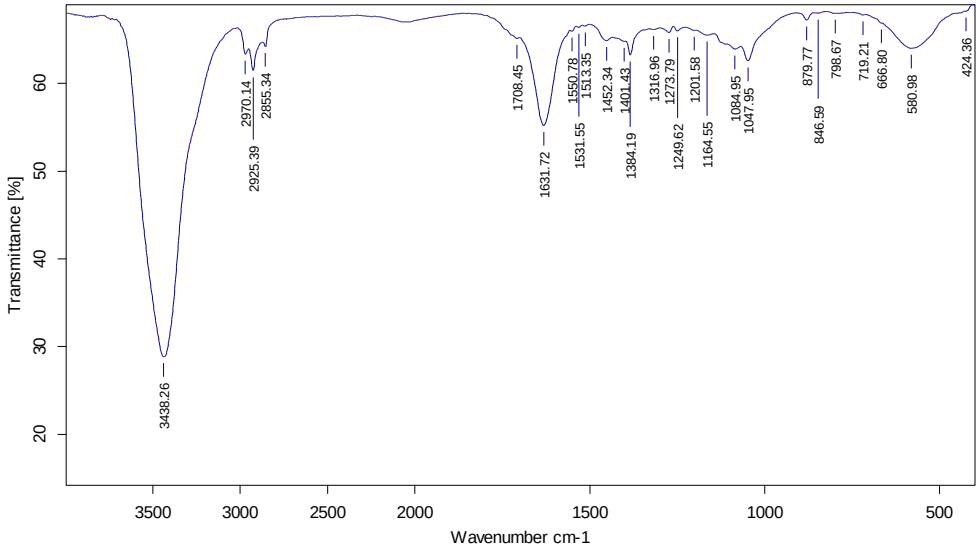
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400



Minimum:				-10.0		
Maximum:		200.0	10.0	120.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
268.2189	268.2191	-0.2	-0.7	7.0	5546026.0	C20 H28

Figure S13. IR spectrum of compound **2**



Sample : glm-1a-2	Frequency Range : 399.246 - 3996.32	Measured on : 19/03/2018	
Technique : KBr	Resolution : 4	Instrument : Tensor27	Sample Scans : 16
Filename : 180319IR.24	Zerofilling : 2	Acquisition : Double Sided,Forv	

Figure S14. ECD spectrum of compound **2**

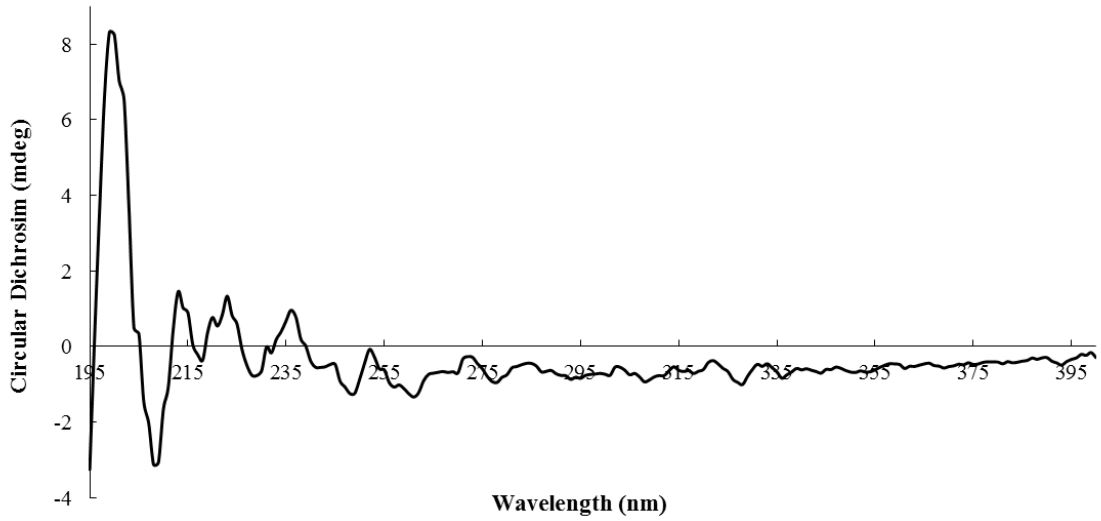


Figure S15. ^{1}H NMR spectrum of compound **2** in $CDCl_3$ (800 MHz)

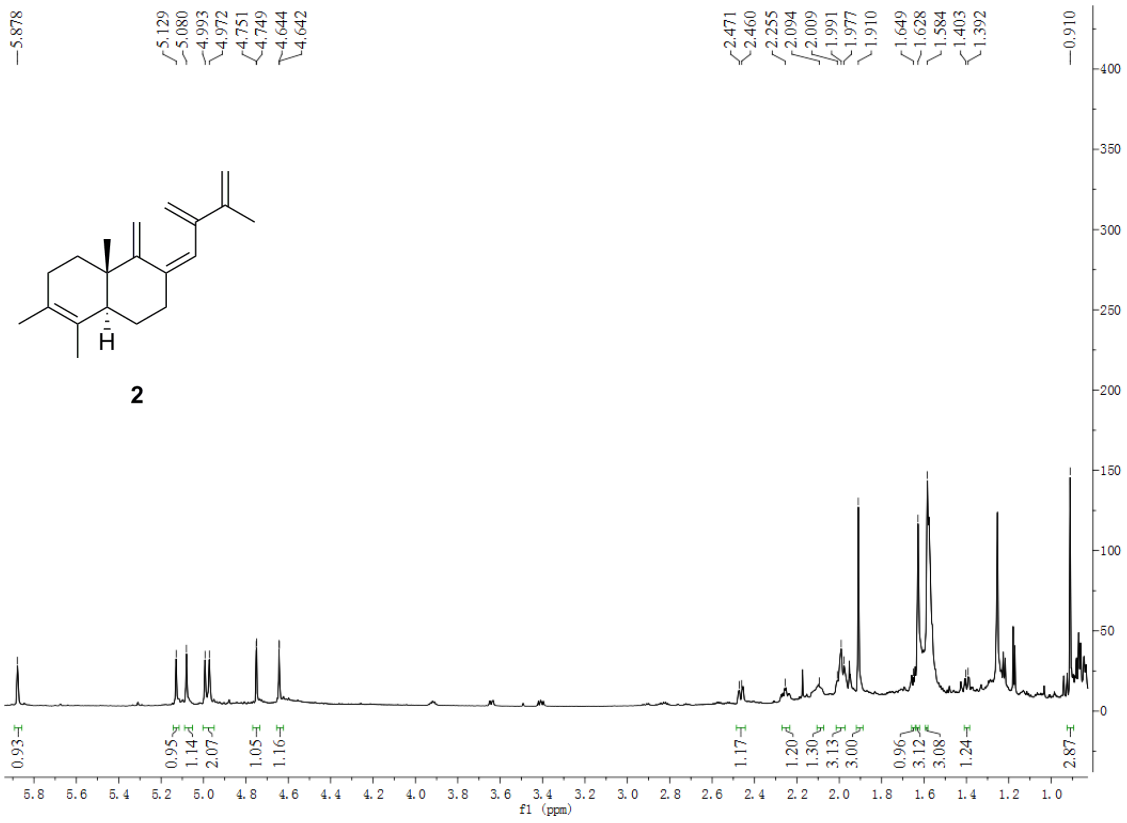


Figure S16. ^{13}C NMR (DEPT) spectrum of compound **2** in $CDCl_3$ (200 MHz)

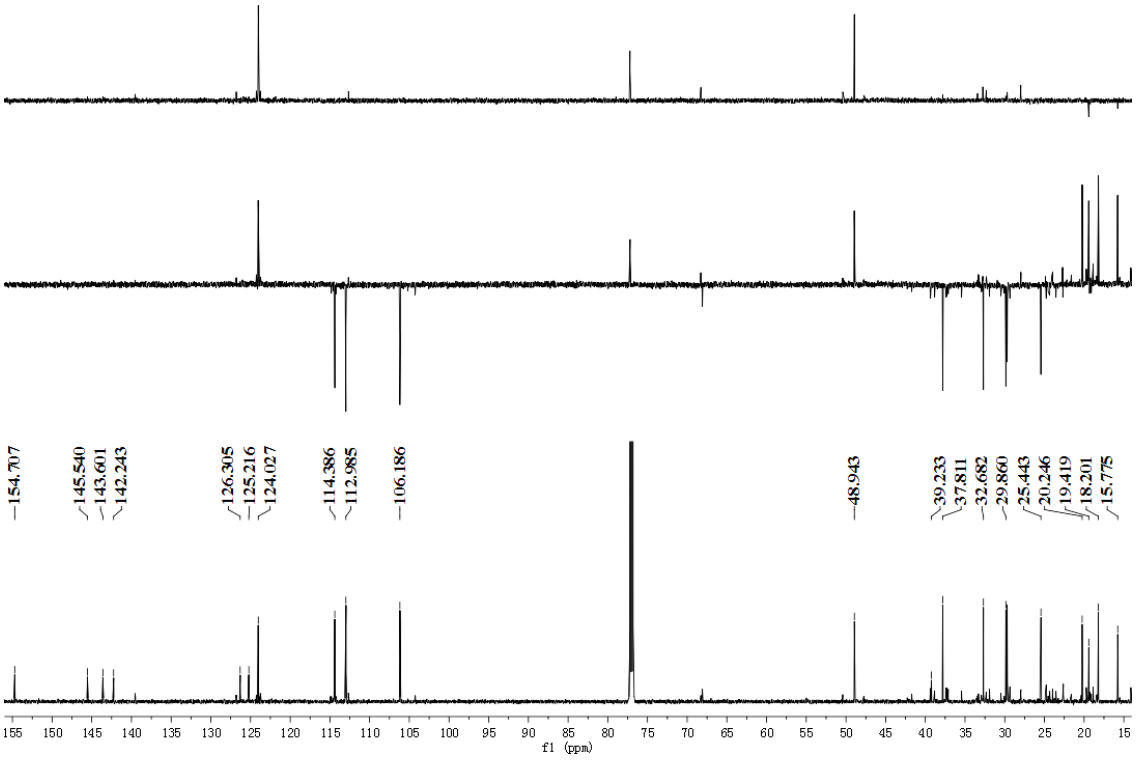


Figure S17. ^{1}H-^{1}H COSY spectrum of compound **2** in $CDCl_3$

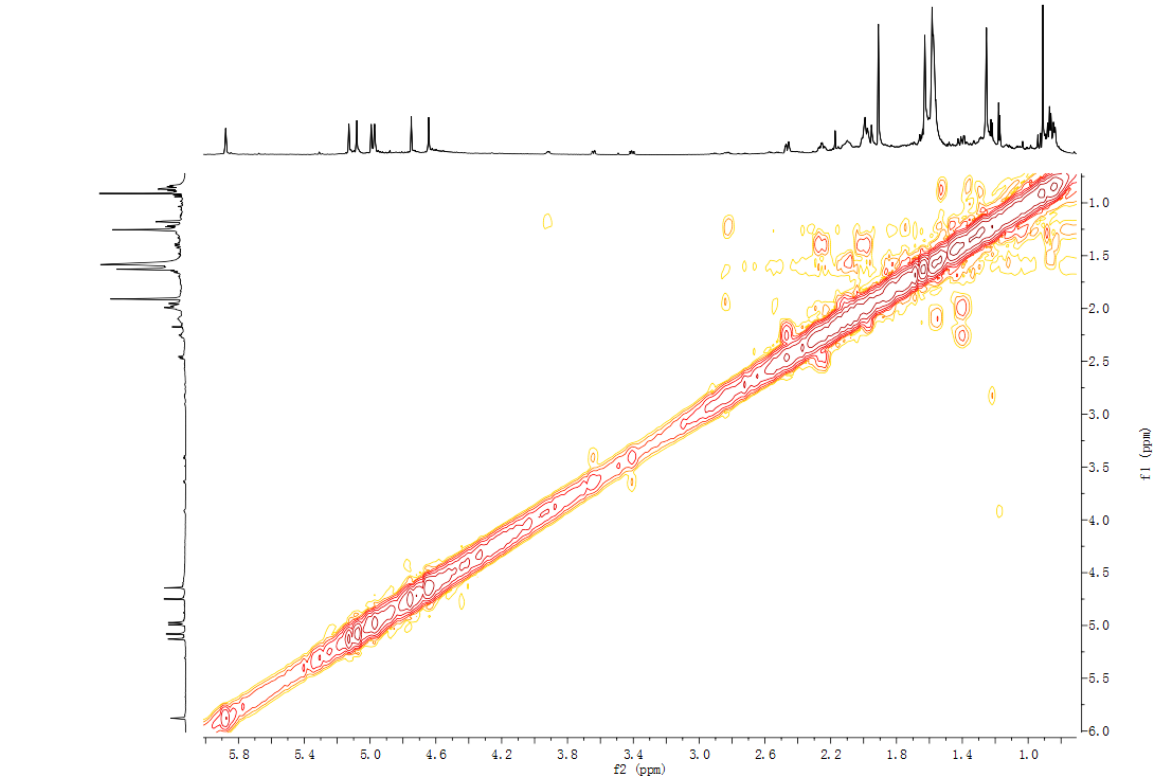


Figure S18. HSQC spectrum of compound **2** in $CDCl_3$

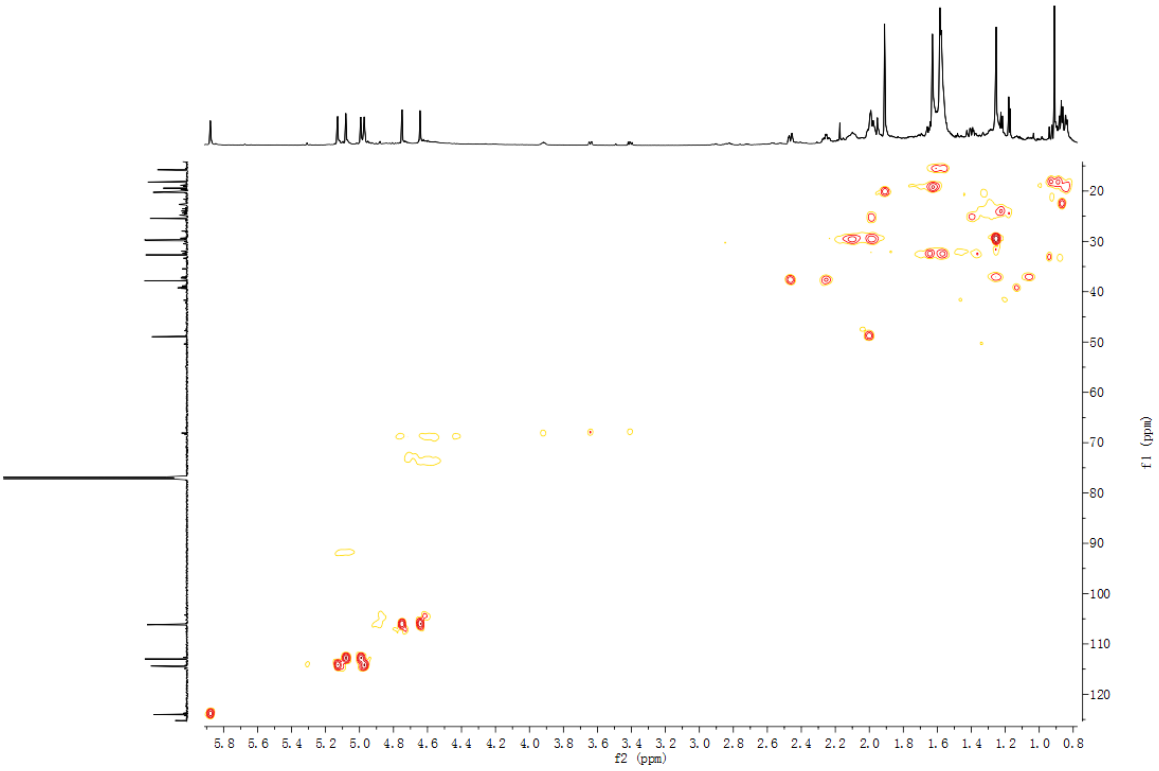


Figure S19. HMBC spectrum of compound **2** in $CDCl_3$

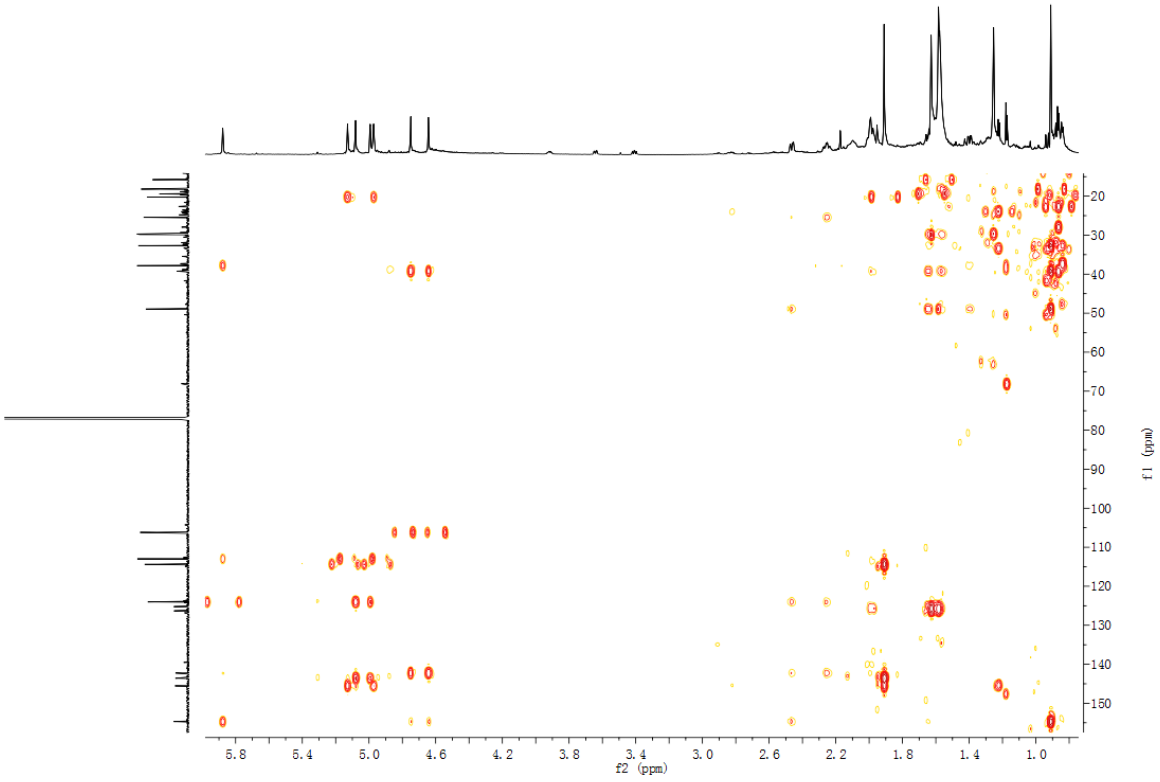


Figure S20. ROESY spectrum of compound **2** in $CDCl_3$

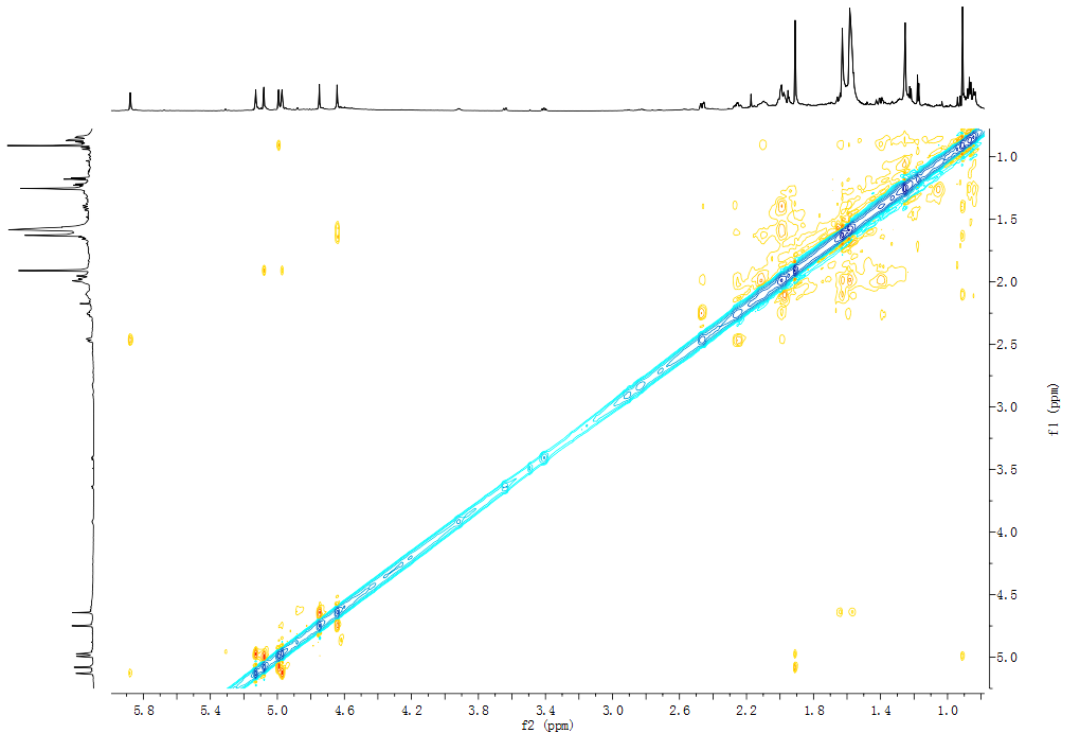
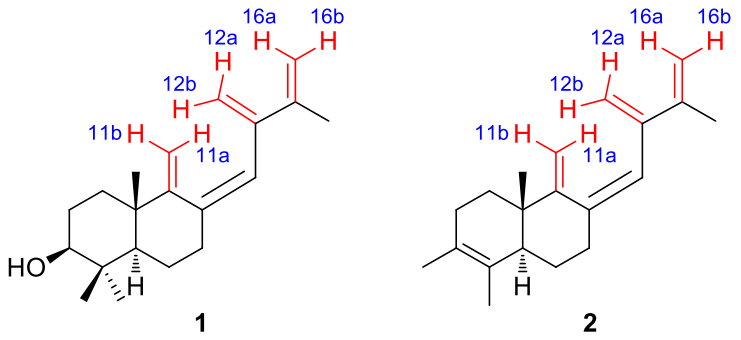


Figure S21. Assignment of the terminal olefinic protons of **1** and **2**



Note: The terminal olefinic protons of **1** and **2** were assigned by detailed ROESY analysis, including the correlations of H-11b/Me-20, H-11a/H-12b, H-16b/Me-17, and H-16a/H-12a (double bonds were shaped for better presentation).