

Supporting information

Pimarane Diterpenoids from the Seeds of *Caesalpinia minax* as PTP1B Inhibitors and Insulin Sensitizers

Yunshao Xu ^{1,†}, Zheling Feng ^{1,†}, Tian Zhang ¹, Peng Lv ¹, Jun Cao ¹, Dan Li ², Cheng Peng ² and Ligen Lin ^{1,2,*}

¹ State Key Laboratory of Quality Research in Chinese Medicine, Institute of Chinese Medical Sciences, University of Macau, Macao SAR 999078, China; mb75820@um.edu.mo (Y.X.); yb77508@um.edu.mo (Z.F.); yb67520@um.edu.mo (T.Z.); yb87503@um.edu.mo (P.L.); yb97509@um.edu.mo (J.C.)

² State Key Laboratory of Southwestern Characteristic Chinese Medicine Resources, School of Pharmacy, Chengdu University of Traditional Chinese Medicine, Chengdu 610075, China; lidan@cdutcm.edu.cn (D.L.); pengchengchengdu@126.com (C.P.)

* Correspondence: ligenl@um.edu.mo; Tel.: +853-8822-8041

[†] These authors contributed equally to this work.

Received: 15 September 2020; Accepted: 12 October 2020; Published: 13 October 2020

Fig. S1. ^1H NMR (600 MHz, CDCl_3) spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S2. ^{13}C NMR (150MHz, CDCl_3) spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S3. DEPT-135 spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S4. HSQC spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S5. HMBC spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S6. ROESY spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S7. IR spectrum (KBr disc) of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S8. HR-ESIMS spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**) in CH_3OH .

Fig. S9. ECD spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**) in CH_3OH .

Fig. S10. UV spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**) in CH_3OH .

Fig. S11. Preparative HPLC chromatogram for 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

Fig. S12. ^1H NMR (600 MHz, CDCl_3) spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).

Fig. S13. ^{13}C NMR (150 MHz, CDCl_3) spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).

Fig. S14. DEPT-135 spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).

Fig. S15. HMBC spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).

Fig. S16. ROESY spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).

Fig. S17. IR spectrum (KBr disc) of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).

Fig. S18. HR-ESIMS spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**) in CH₃OH.

Fig. S19. ECD spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**) in CH₃OH.

Fig. S20. UV spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**) in CH₃OH.

Fig. S21. Preparative HPLC chromatogram for 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).

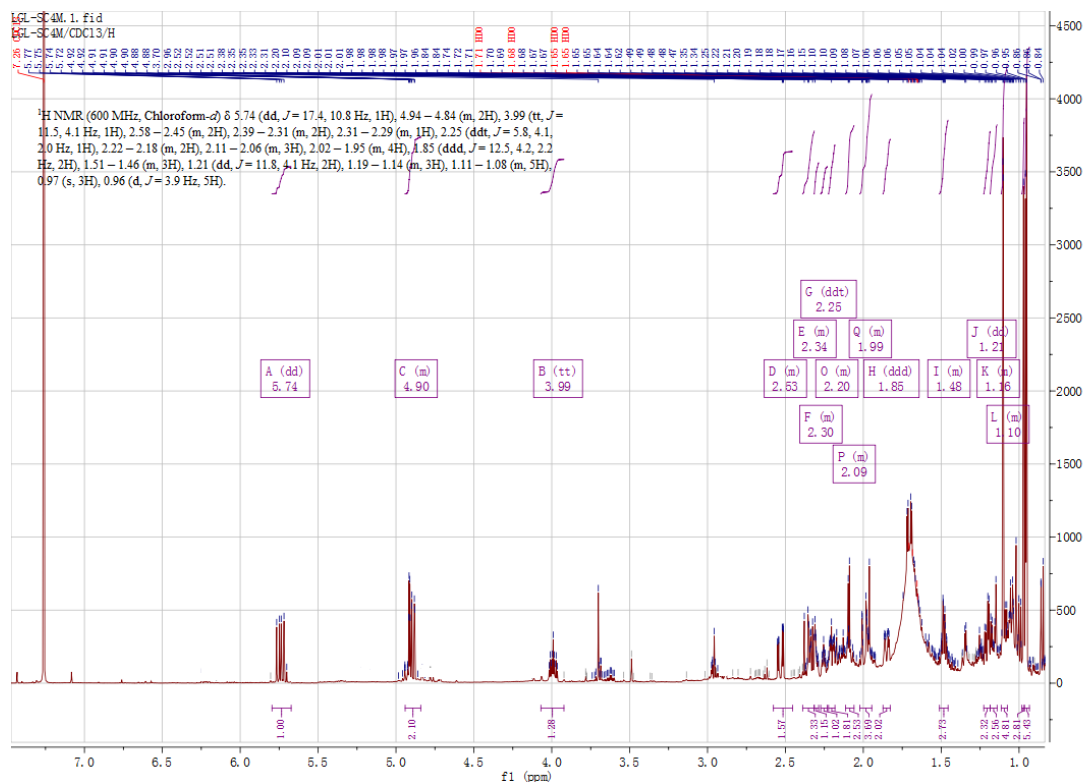


Fig. S1. ¹H NMR (600 MHz, CDCl₃) spectrum of 2α-hydroxy-7-oxo-pimara-8(9),15-diene (1).

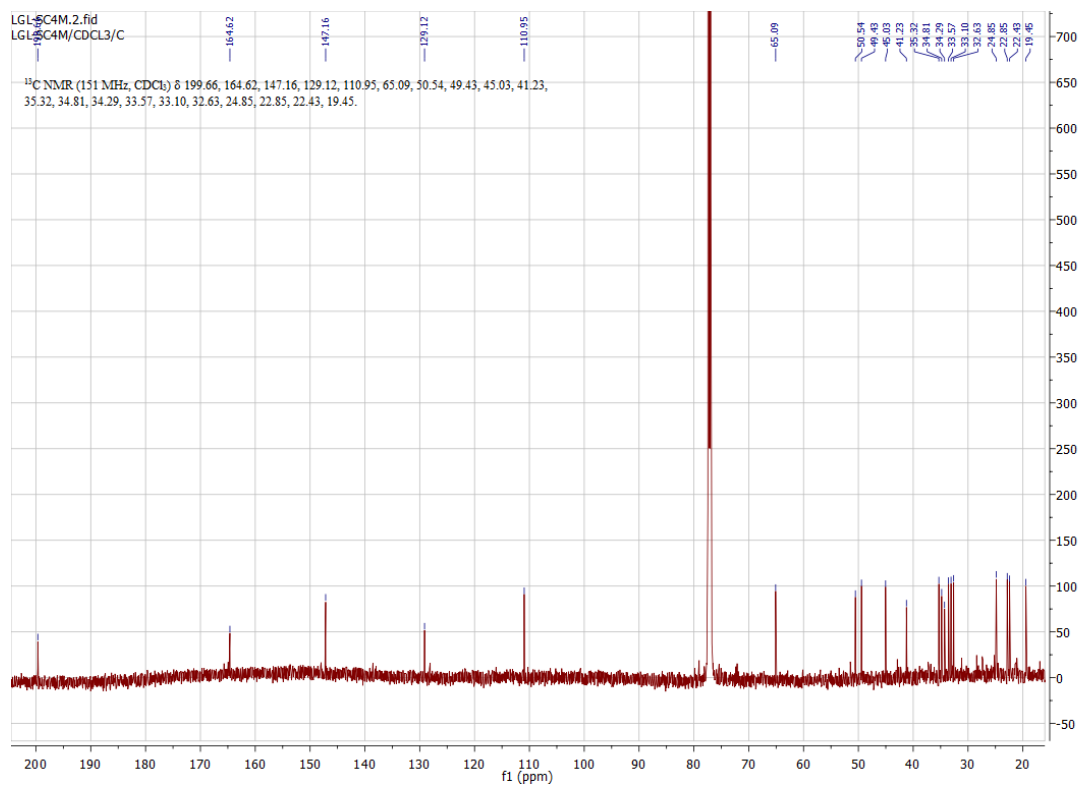


Fig. S2. ¹³C NMR (150MHz, CDCl₃) spectrum of 2α-hydroxy-7-oxo-pimara-8(9),15-diene (1).

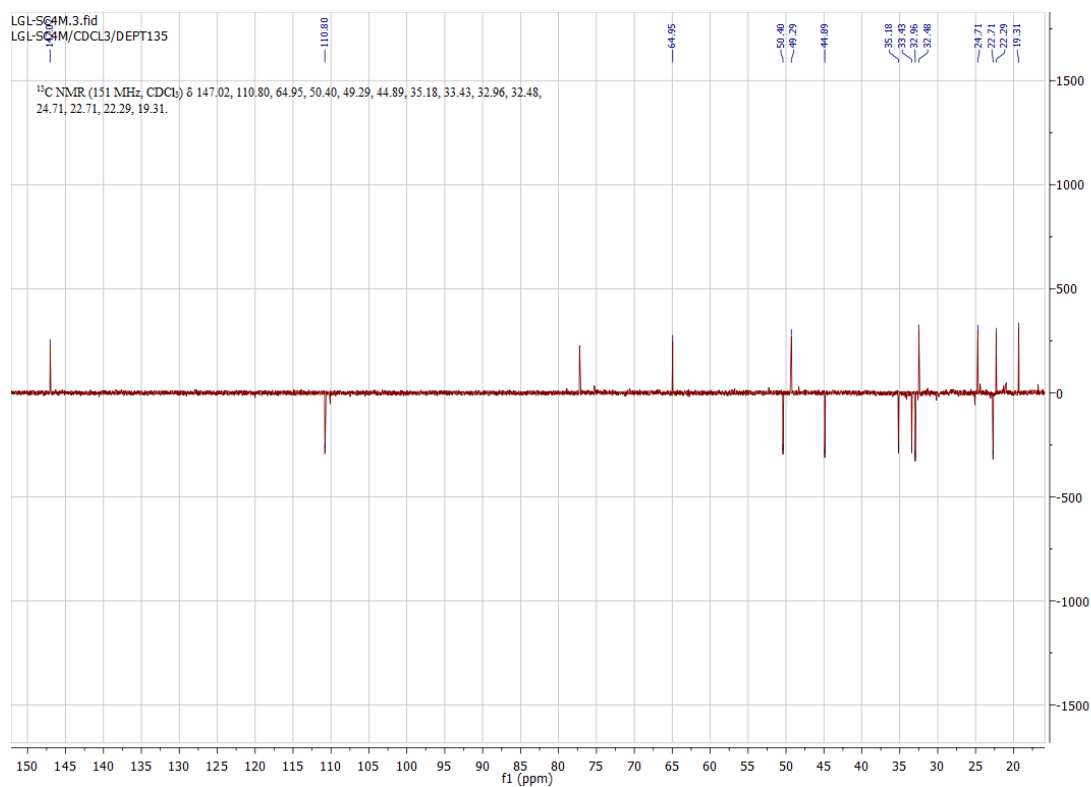


Fig. S3. DEPT-135 spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (1).

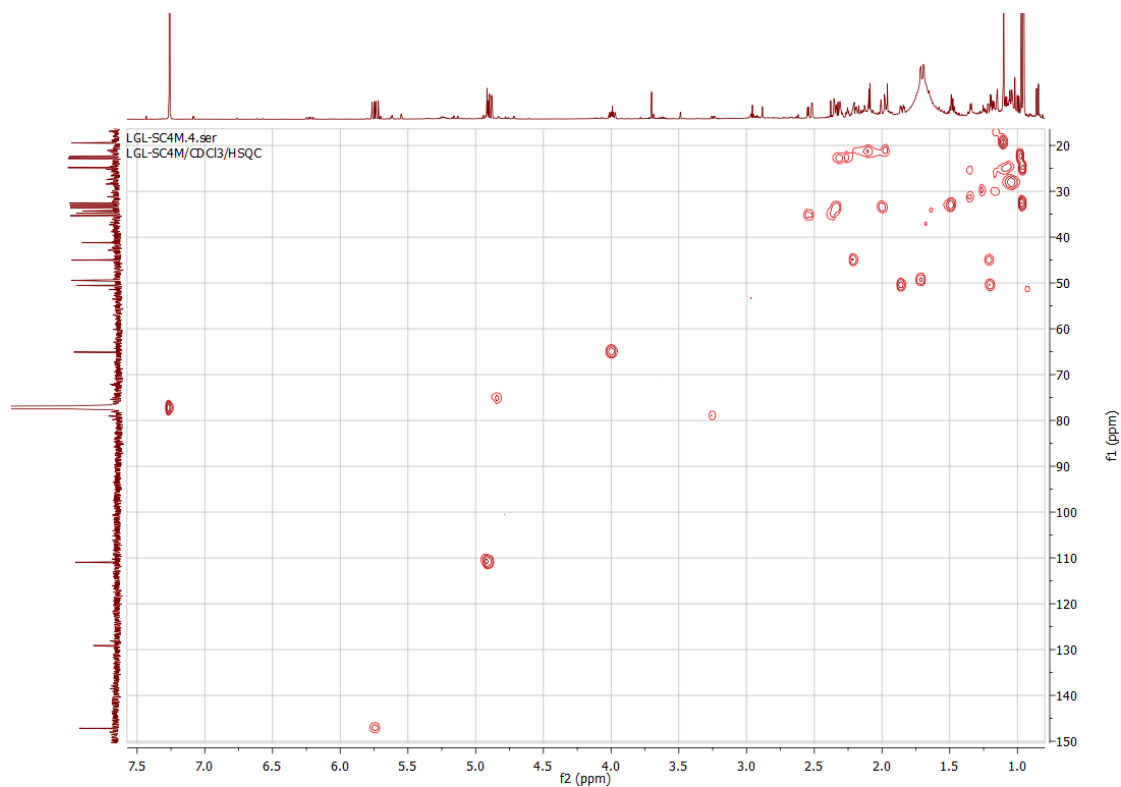


Fig. S4. HSQC spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (1).

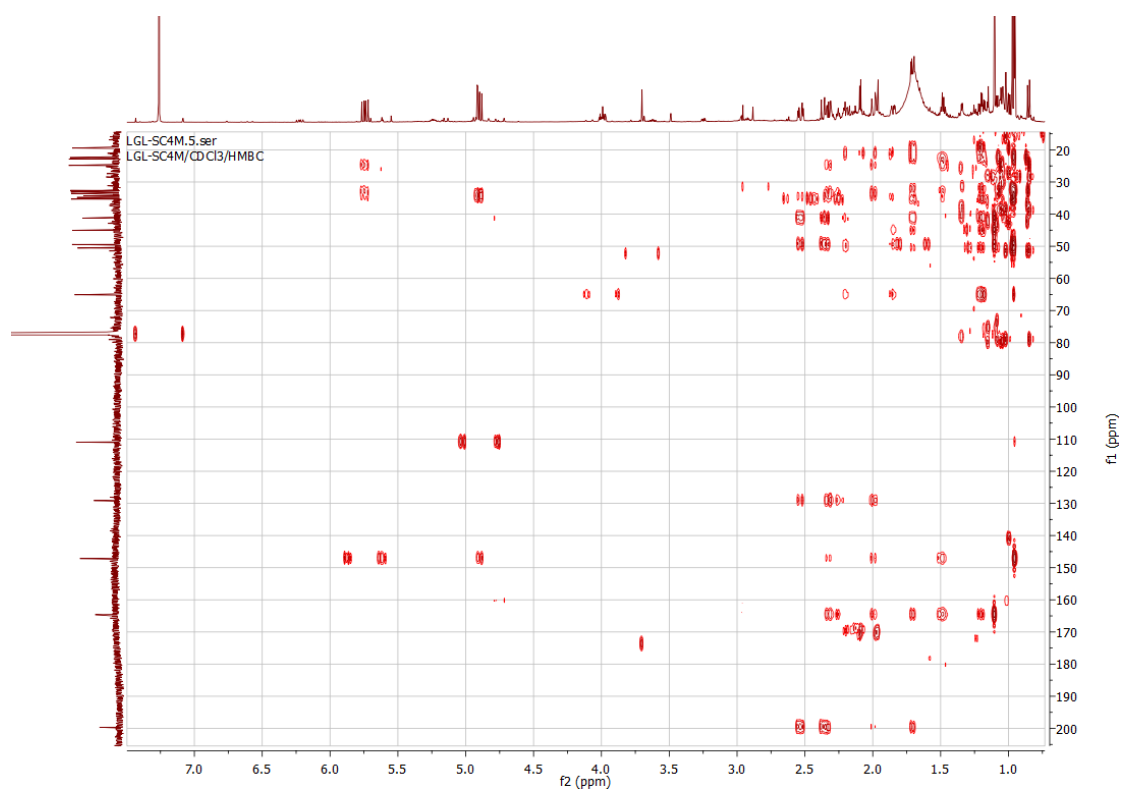


Fig. S5. HMBC spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

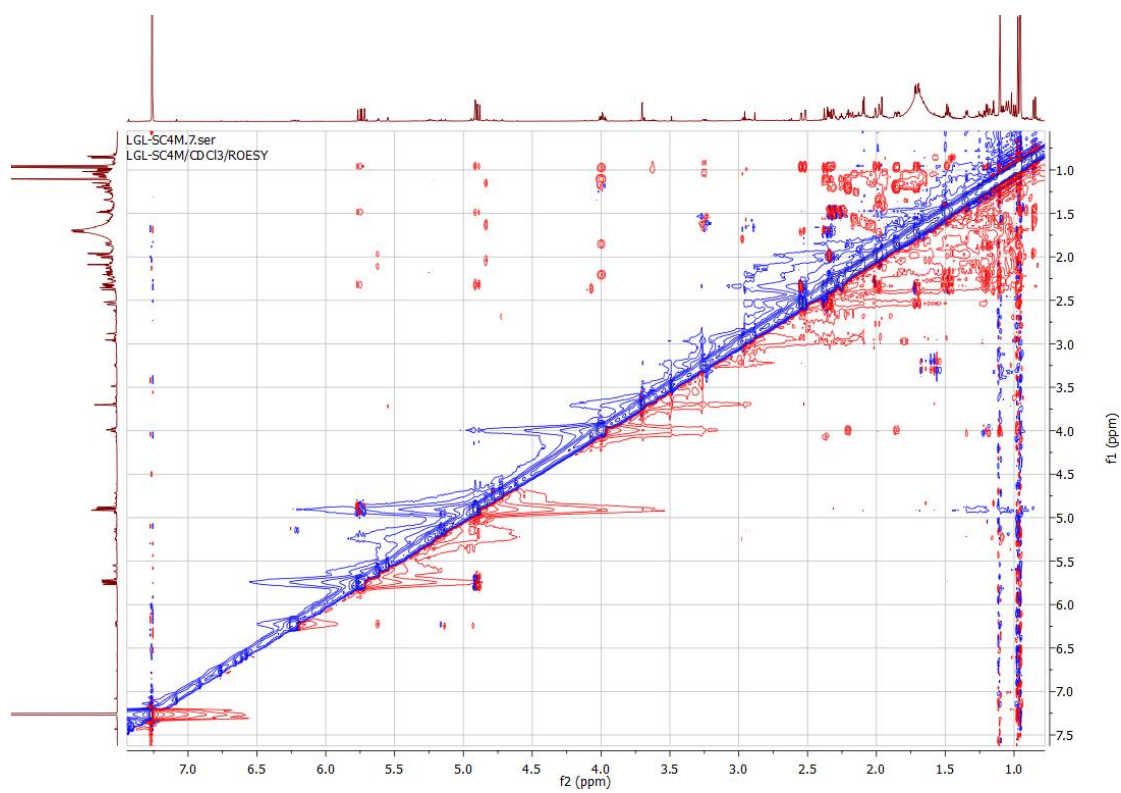


Fig. S6. ROESY spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**).

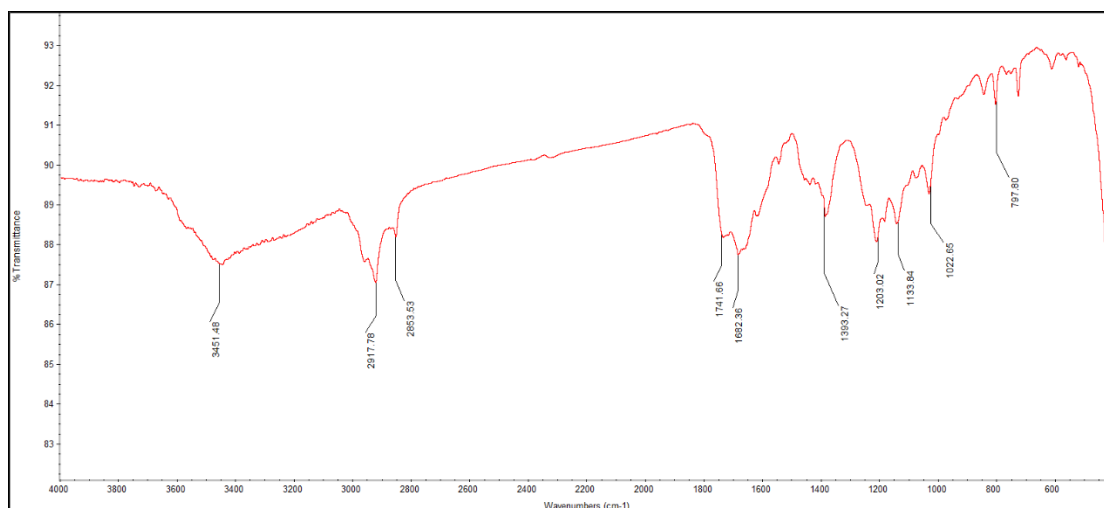


Fig. S7. IR spectrum (KBr disc) of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (1).

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

109 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
303.2326	303.2324	0.2	0.7	5.5	C ₂₀ H ₃₁ O ₂	215.7	n/a	n/a	20	31	2	

SC4M-pos
20200110-25 241 (1.226)

1: TOF MS ES+
2.87e+004

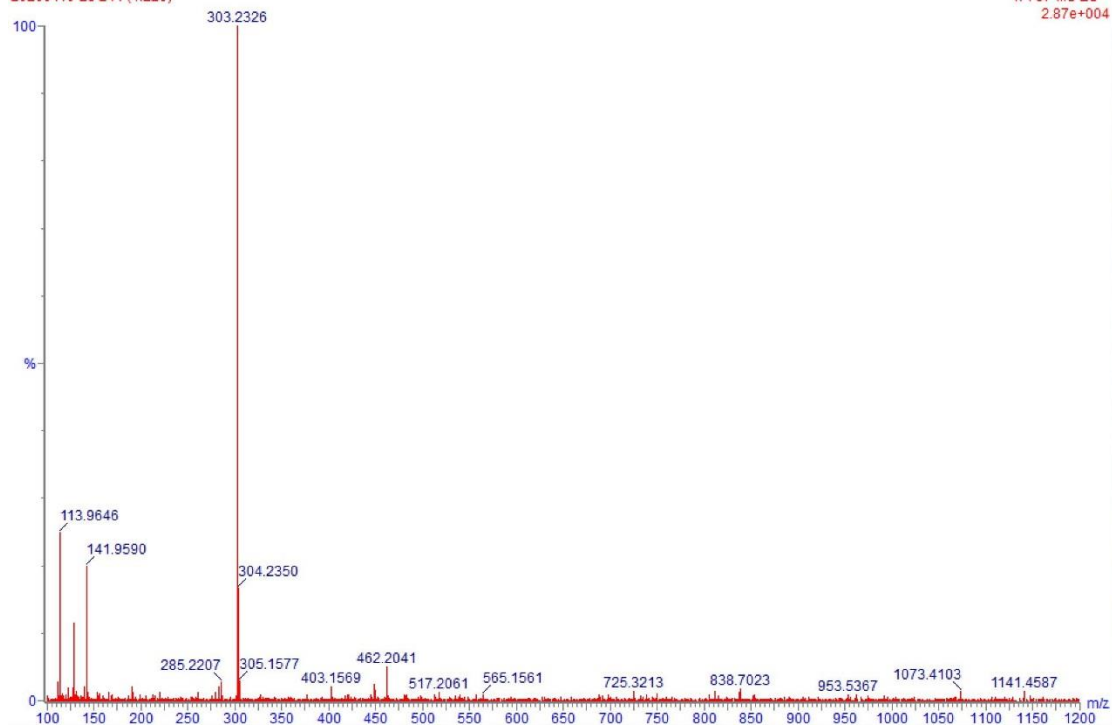


Fig. S8. HR-ESIMS spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (1) in CH₃OH.

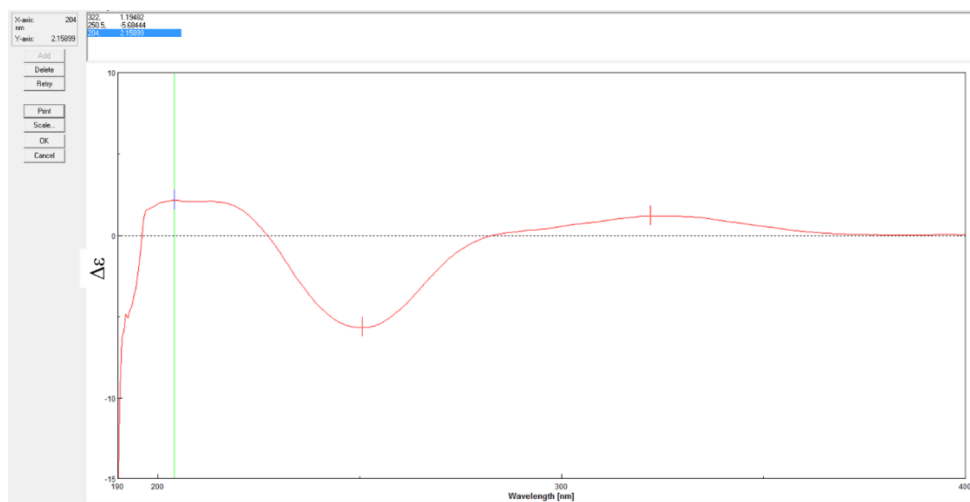
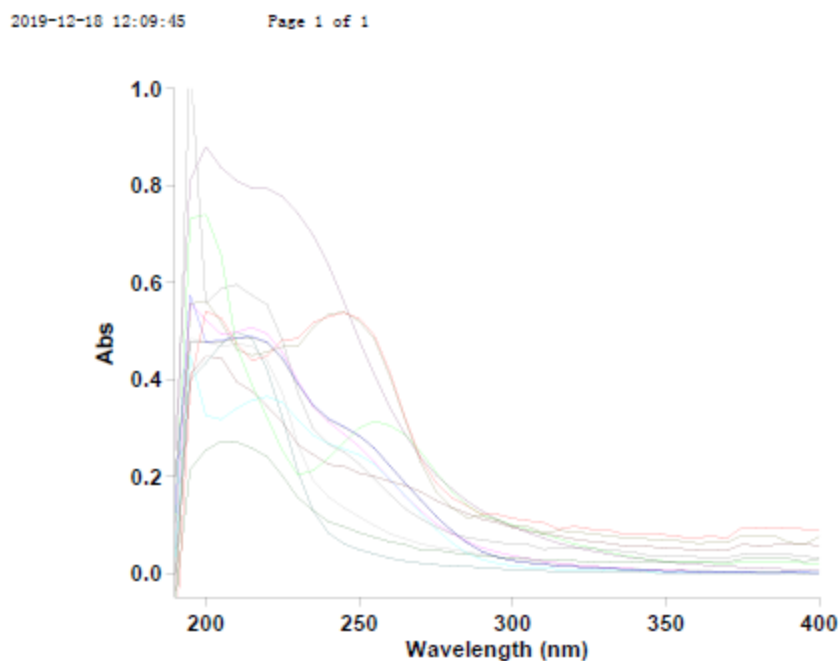


Fig. S9. ECD spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**) in CH₃OH.



Scan Analysis Report

Report Time : 星期三 18 十二月 12:09:34 PM 2019
 Method:
 Batch: D:\data\royang\SC4M.DSW
 Software version: 3.00(339)
 Operator:

Sample Name: SC4M

Collection Time 2019-12-18 12:09:37

Peak Table
 Peak Style
 Peak Threshold
 Range

Peaks
 0.0100
 400.0nm to 190.0nm

Wavelength (nm)	Abs
245.0	0.538
200.0	0.541

Fig. S10. UV spectrum of 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (**1**) in CH₃OH.

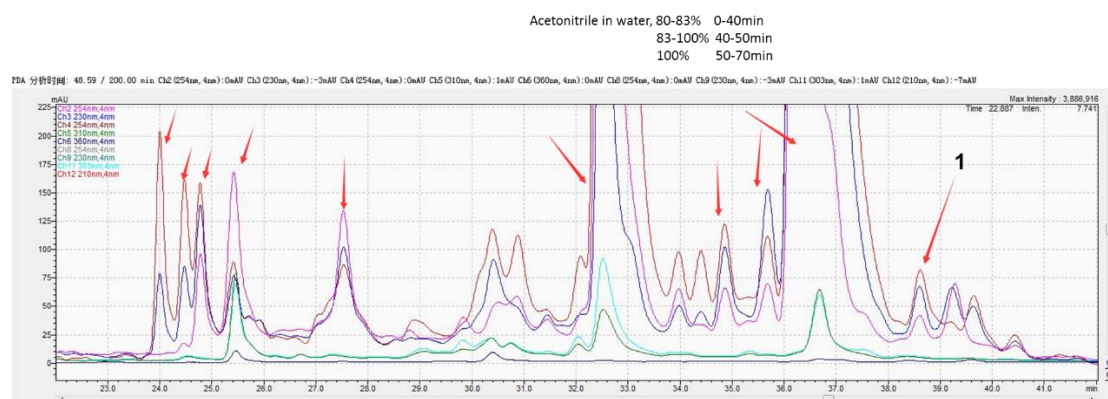


Fig. S11. Preparative HPLC chromatogram for 2 α -hydroxy-7-oxo-pimara-8(9),15-diene (1).

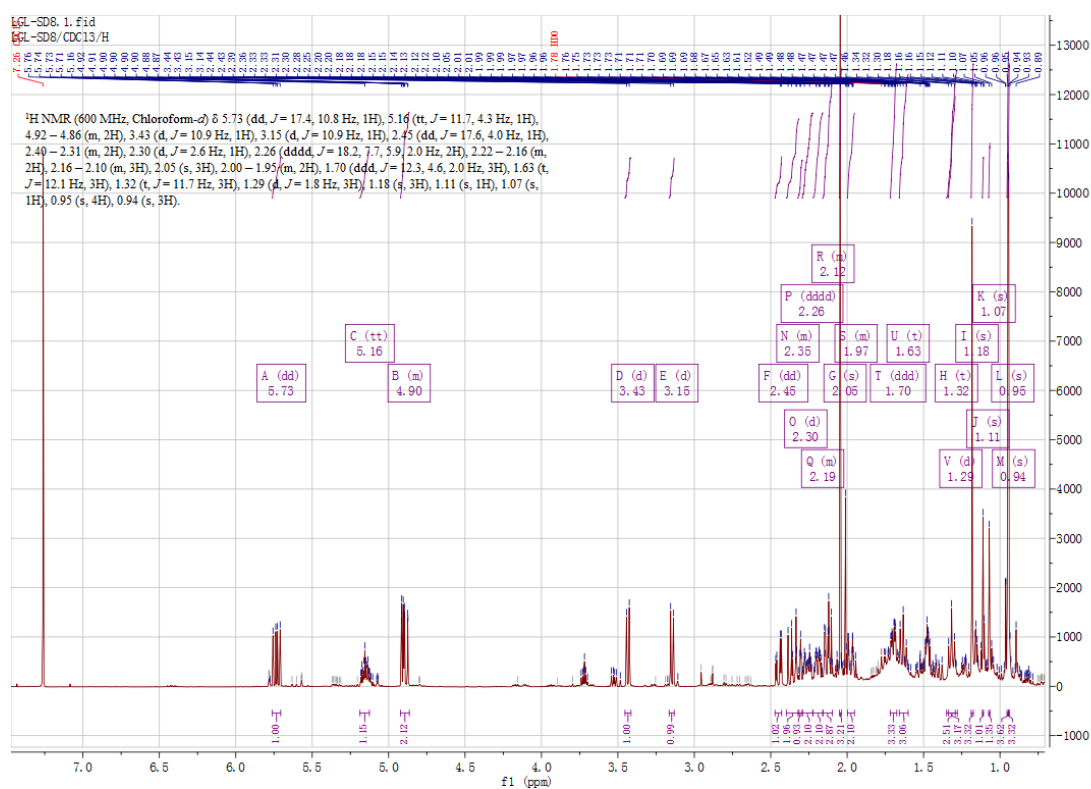


Fig. S12. ¹H NMR (600 MHz, CDCl₃) spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (2).

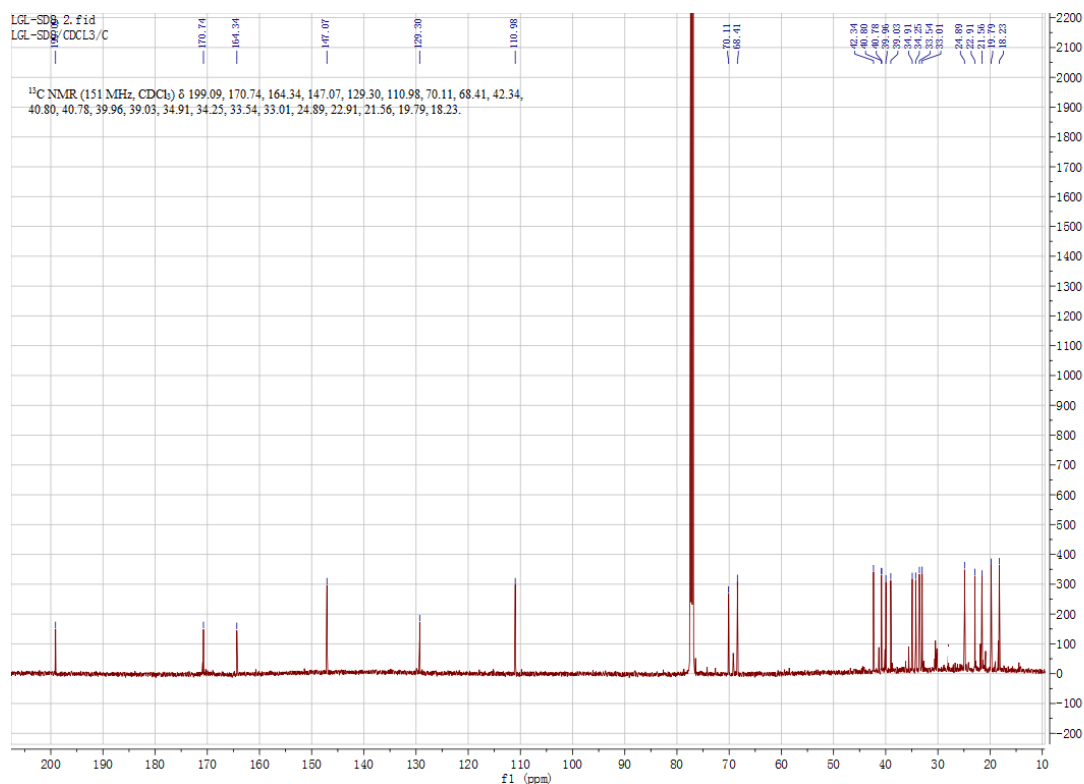


Fig. S13. ¹³C NMR (151 MHz, CDCl₃) spectrum of 19-hydroxy-2α-acetoxy-7-oxo-pimara-8(9),15-diene (2).

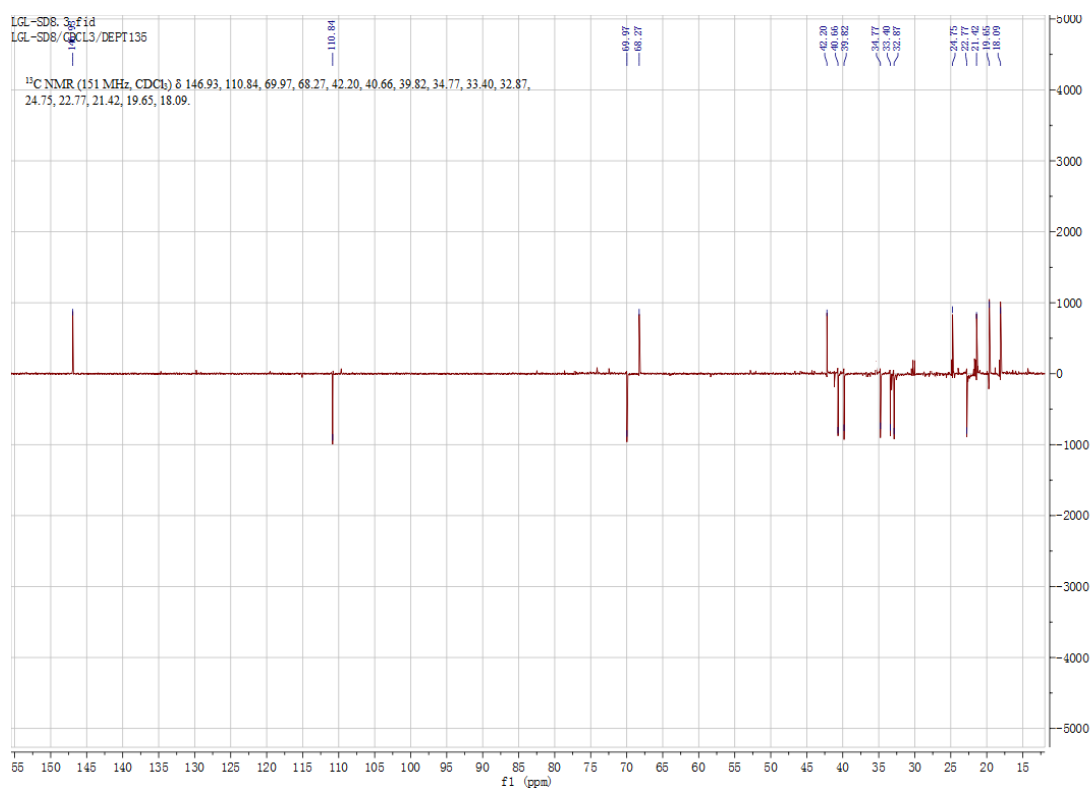


Fig. S14. DEPT-135 spectrum of 19-hydroxy-2α-acetoxy-7-oxo-pimara-8(9),15-diene (2).

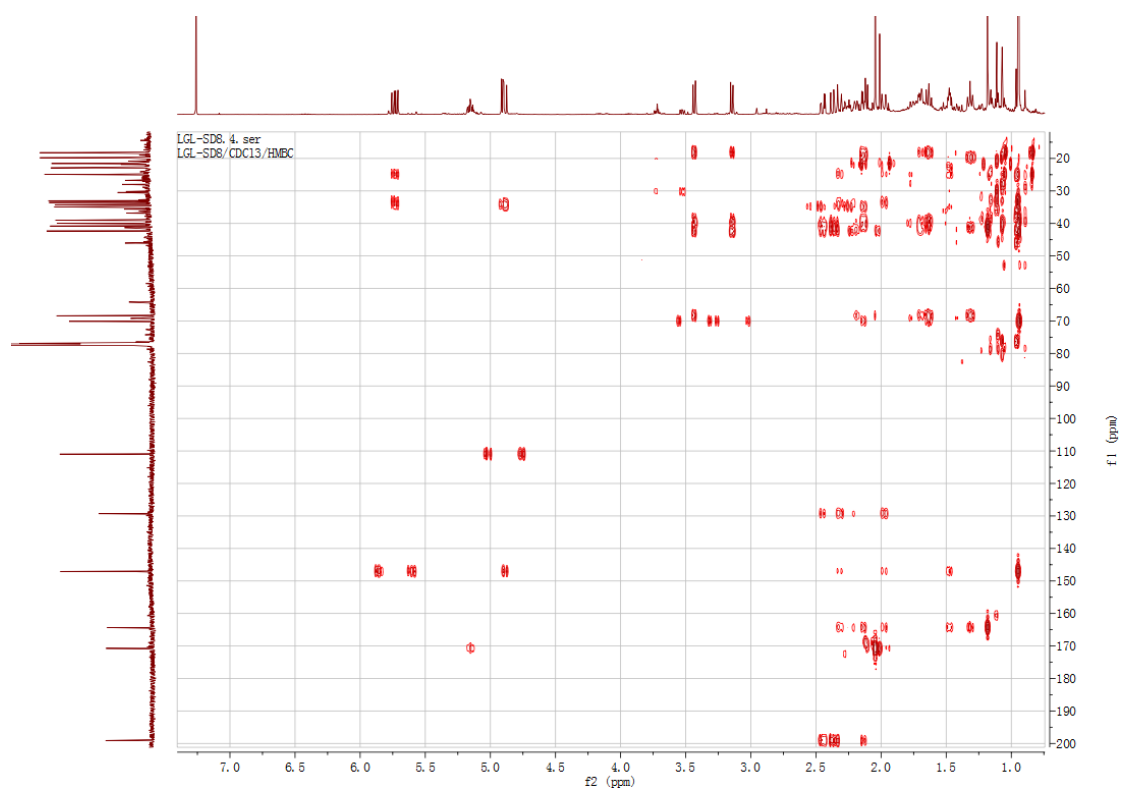


Fig. S15. HMBC spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (2).

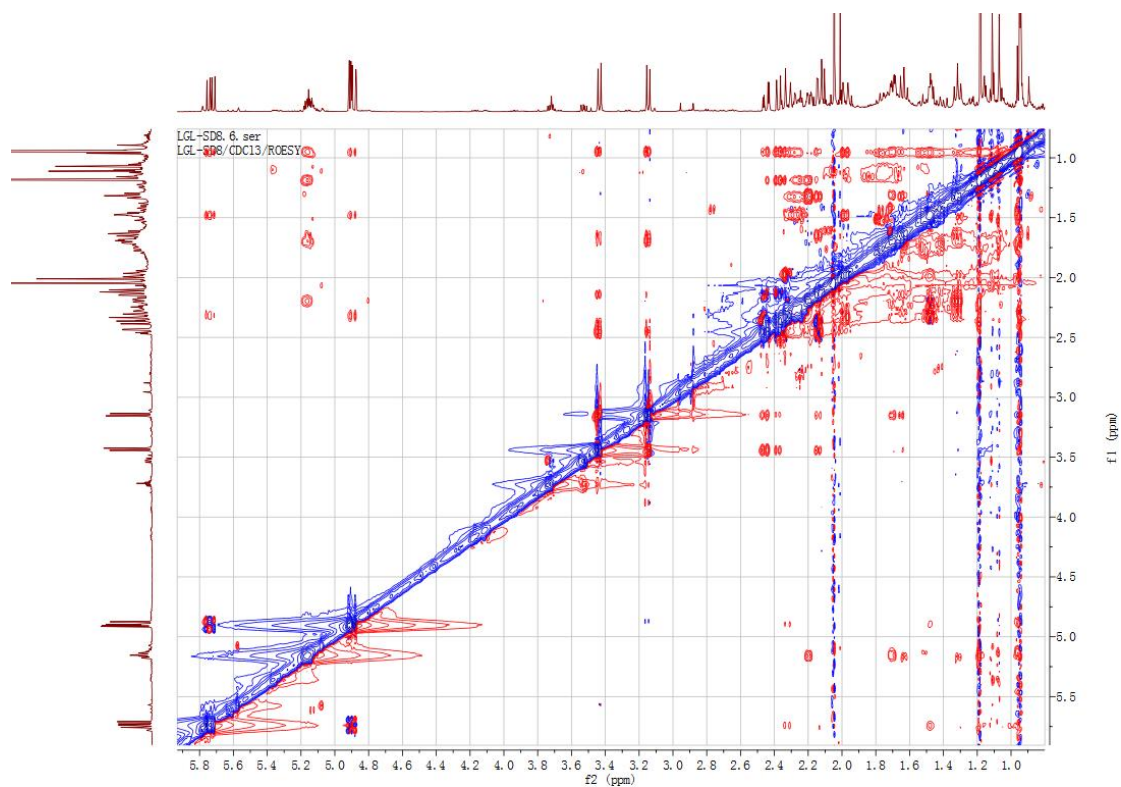


Fig. S16. ROESY spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (2).

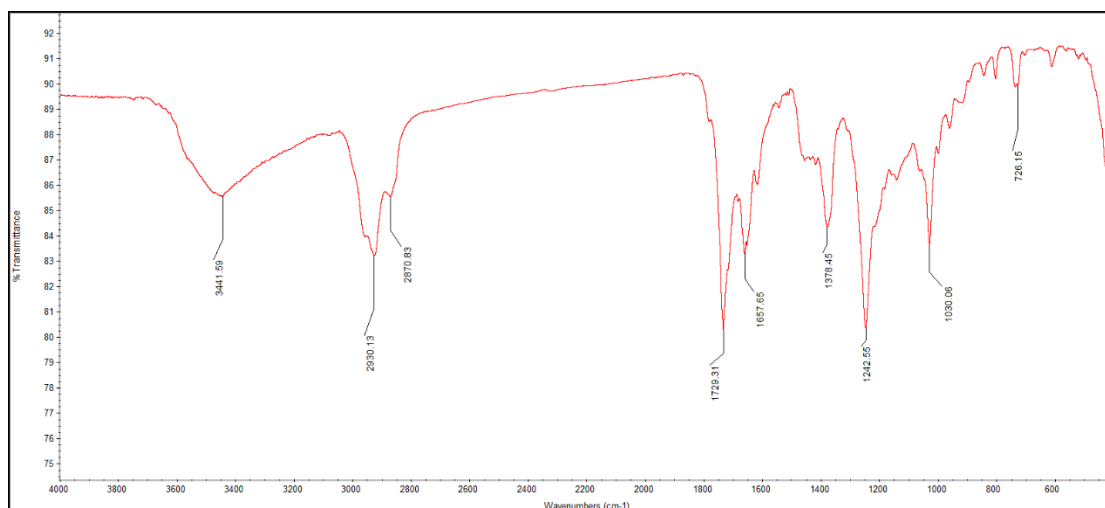


Fig. S17. IR spectrum (KBr disc) of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (2).

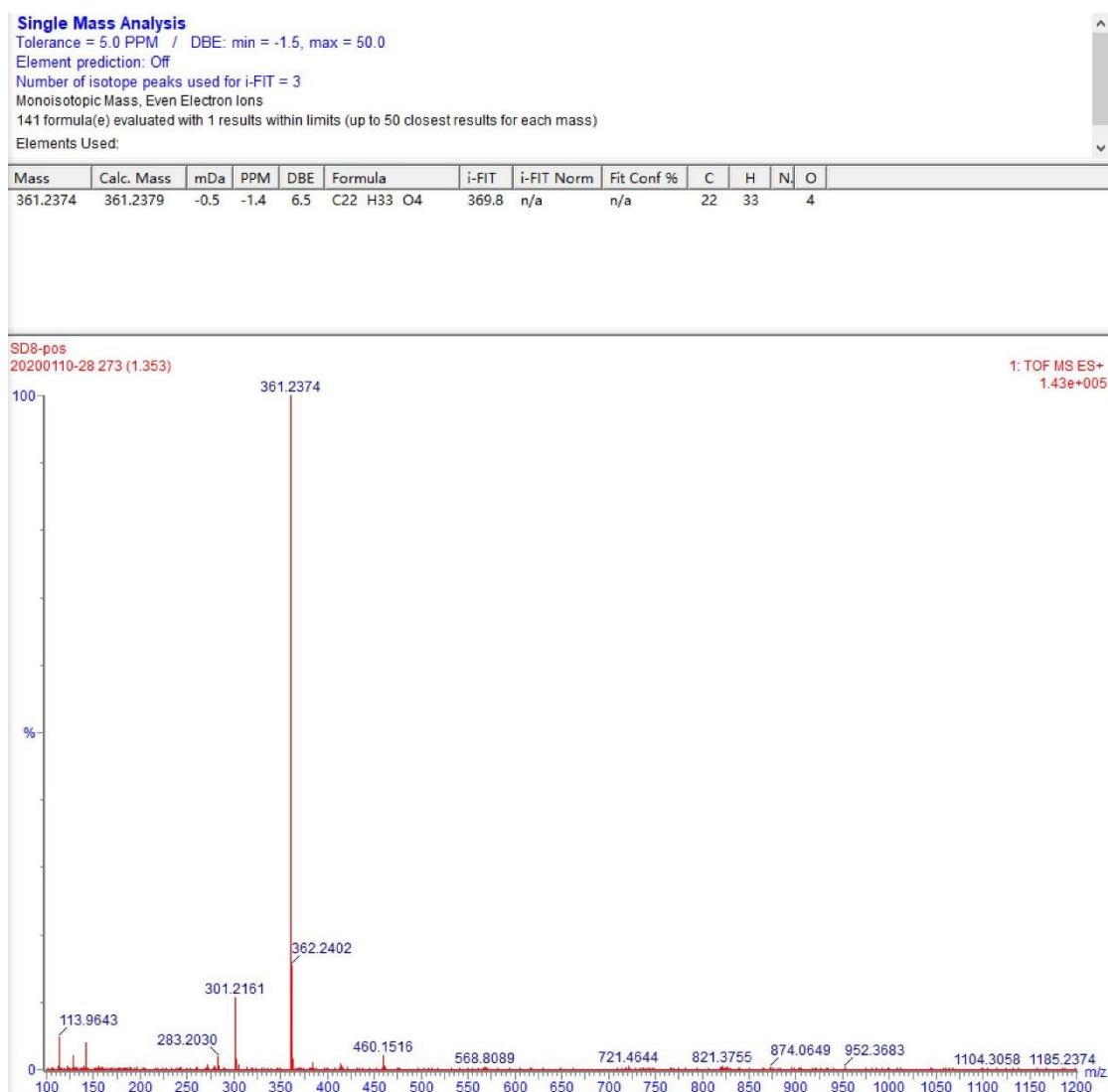


Fig. S18. HR-ESIMS spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (2) in CH₃OH.

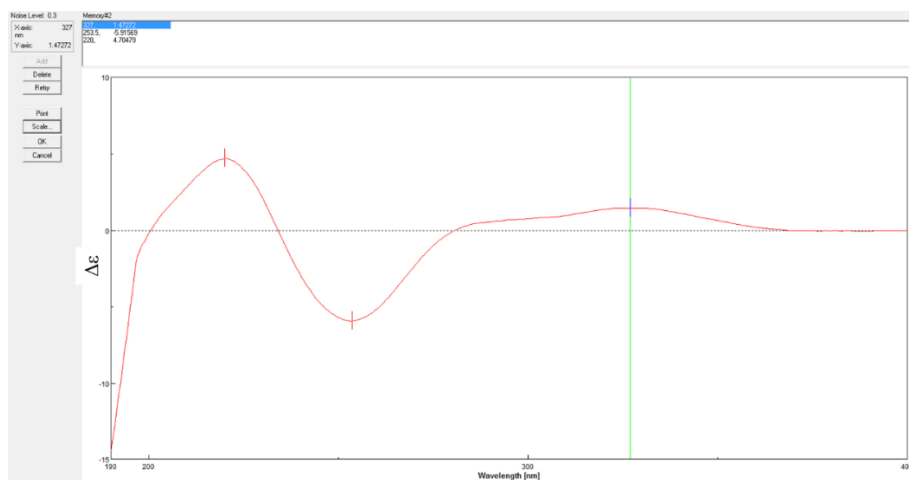
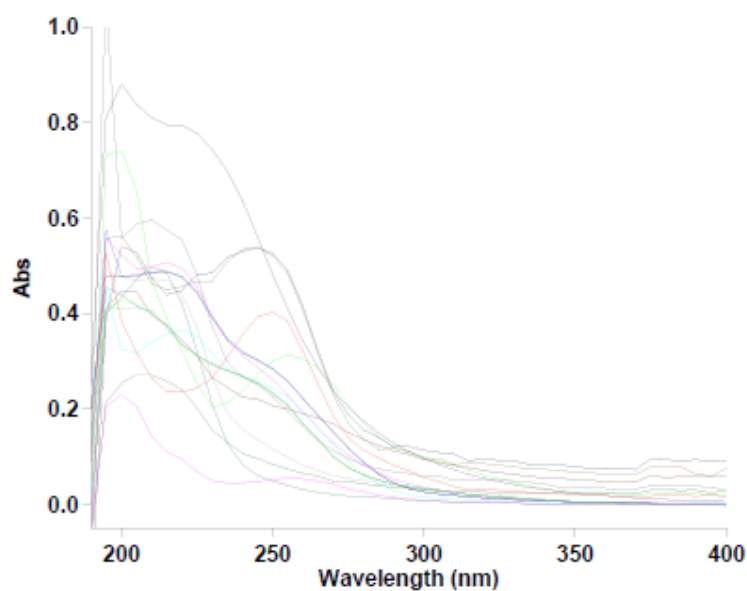


Fig. S19. ECD spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**) in CH₃OH.

2019-12-18 12:16:58

Page 1 of 1



Scan Analysis Report

Report Time : 星期三 18 十二月 12:16:49 PM 2019
 Method:
 Batch: D:\data\ycyang\SD8.DSW
 Software version: 3.00(338)
 Operator:

Sample Name: SD8

Collection Time 2019-12-18 12:16:51

Peak Table
 Peak Style Peak
 Peak Threshold 0.0100
 Range 400.0nm to 190.0nm

Wavelength (nm)	Abs
250.1	0.402
194.9	0.527

Fig. S20. UV spectrum of 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**) in CH₃OH.

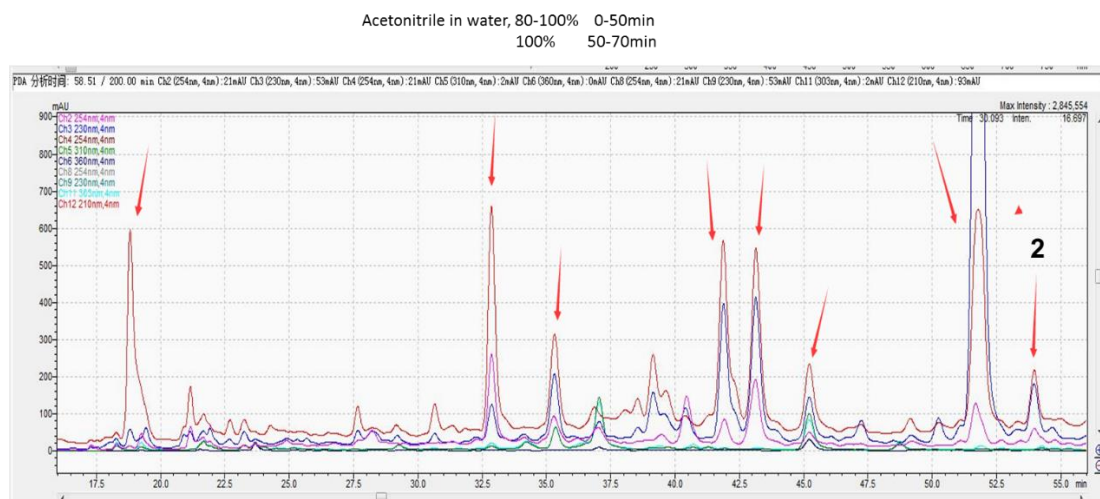


Fig. S21. Preparative HPLC chromatogram for 19-hydroxy-2 α -acetoxy-7-oxo-pimara-8(9),15-diene (**2**).