Supporting information for

Antroalbocin A, an Antibacterial Sesquiterpenoid from Higher Fungus *Antrodiella albocinnamomea*

Wei Li[⊥], Juan He[⊥], Tao Feng[*], Hui-Xiang Yang, Hong-Lian Ai, Zheng-Hui Li[*], and Ji-Kai Liu[*]

School of Pharmaceutical Sciences, South-Central University for Nationalities, Wuhan 430074, China

∗Correspondence author: tfeng@mail.scuec.edu.cn (T. Feng); 2015051@mail.scuec.edu.cn (Z. H. Li); jkliu@mail.kib.ac.cn (J.-K. Liu)

List of Supporting Information

1. Experimental Section

1.1 General experimental procedures. Melting points were obtained on an X-4 micro melting point apparatus. Optical rotations were measured with a Rudoph AUTOPOL IV polarimeter. UV data were afforded with a UH5300 UV-VIS Double Beam Spectrophotometer. IR spectra were obtained with a Shimadzu Fourier Transform Infrared Spectrometer using KBr pellets. 1D and 2D spectra were run on a Bruker Avance III 600 MHz spectrometer with TMS as an internal standard. Chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Mass spectra were recorded on a Thermo Scientific Q Exactive Orbitrap MS system. Column chromatography (CC) was performed on silica gel (200-300 mesh, Qingdao Marine Chemical Ltd., Qingdao, People's Republic of China), RP-18 gel (20–45 μm, Fuji Silysia Chemical Ltd., Japan), and Sephadex LH-20 (Pharmacia Fine Chemical Co., Ltd., Sweden). Preparative High Performance Liquid Chromatography (prep-HPLC) was performed on an Agilent 1260 liquid chromatography system equipped with a Zorbax SB-C18 column (Agilent, 5 μm, 9.4 mm × 150 mm) and a DAD detector. Fractions were monitored by TLC (GF 254, Qingdao Haiyang Chemical Co., Ltd. Qingdao, China), and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in EtOH.

1.2 Fungi material .The fungus *A. albocinnamomea* was collected at Changbai Moutain, Northeast of China in 1997 and were identified by Prof. Yu-Cheng Dai (Beijing Forestry University). The strain is deposited at South-Central University for Nationalities, China (No. CGBWSHF00182.1).

1.3 Fermentation, extraction, and isolation. The culture medium consisted of glucose 5%; peptone 0.15%; yeast extract 0.5%; KH_2PO_4 0.05%; and $MgSO_4$ 0.05% in liter of deionized water (pH 6.5 before autoclaving). The fungus was grown in Erlenmeyer flasks (500 with 300 mL of medium). Fermentation was carried out in a rotary shaker at 28 °C and 160 rpm for 20 days.

The fermentation broth (60 L) was concentrated to 10 L and extracted with EtOAc five times, The extract (50 g) was subjected to CC on silica gel (19 × 30 cm, $CHCl_3$/methanol, step gradient elution 70:1, 50:1, 30:1, 10:1, 5:1, 2:1, 0:1) to obtain six fractions Fr-1–Fr-6. Fr-2 (3 g) was subjected to CC on silica gel (4 × 15 cm, petroleum ether/EtOAc, step gradient elution 15:1, 10:1, 5:1, 2:1, then 1:1) to furnish subfractions 2a-2d. Fr 2b (24.4 mg) was purified by preparative HPLC using reverse phase column (MeCN/H_2O, v/v, isocratic elution of 28:72, over 25 min; flow rate 4 mL/min) to obtain antroalbocin A (**1**) (2.0 mg, rt = 24.0 min). The structures of compound **1** was elucidated on the basis of extensive spectroscopic data. The NMR data for **1** were given in Table S1.

Table S1. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR data for antroalbocin A (**1**) (Methanol-d_4, δ in ppm, J in Hz).

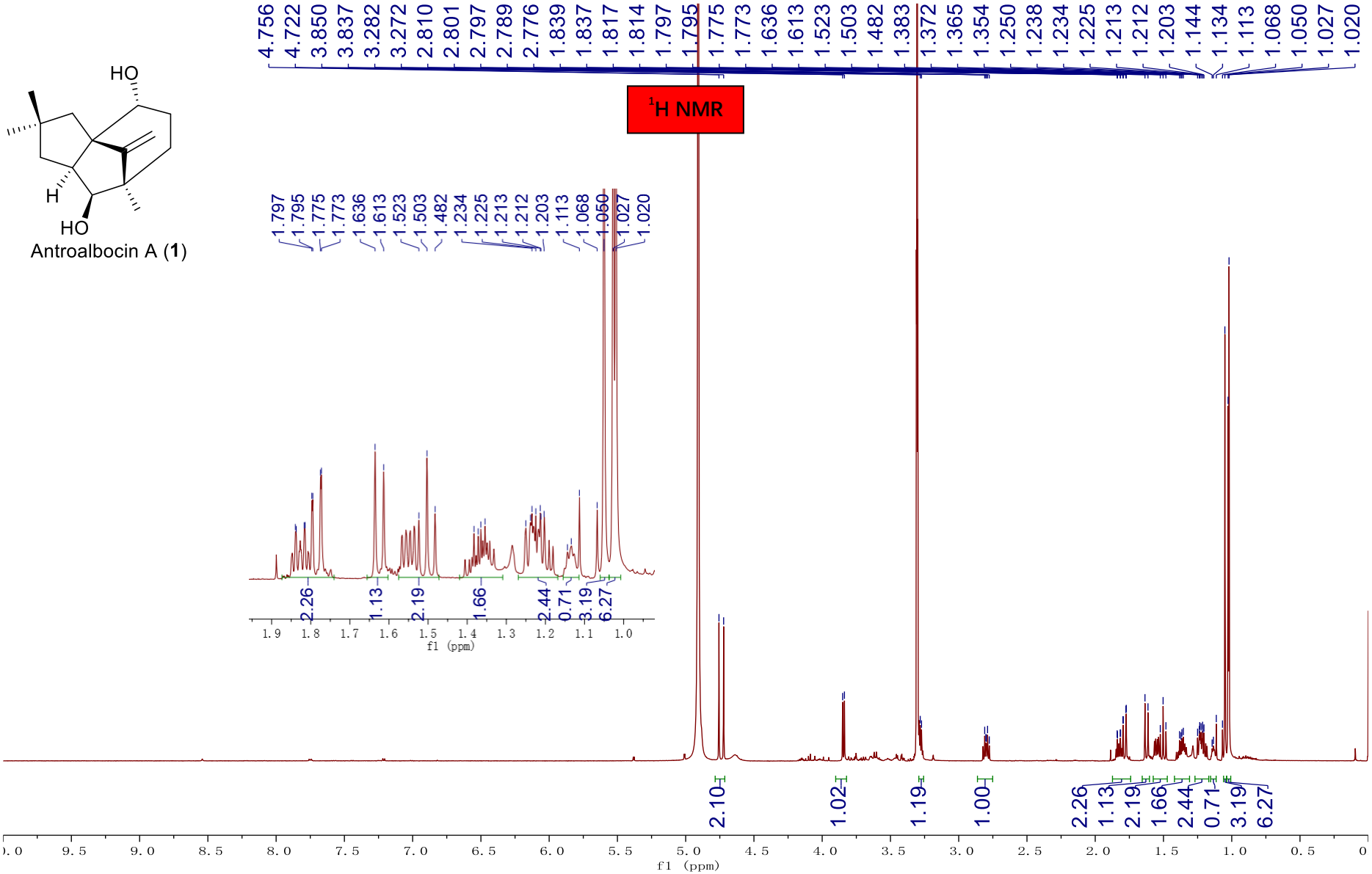
No.	δ_H	δ_C
1		40.7 (s)
2α	1.24, m	41.6 (t)
2β	1.49, dd (13.4, 12.5)	
3	2.80, dt (12.5, 7.3)	48.1 (d)
4	3.84, d (7.3)	77.2 (d)
5		50.5 (s)
6α	1.54, m	40.4 (t)
6β	1.20, m	
7α	1.36, m	30.3 (t)
7β	1.83, m	
8	3.28, dd (10.8, 5.1)	75.8 (d)
9		65.2 (s)
10α	1.78, d (13.2)	43.4 (t)
10β	1.62, d (13.2)	
11		163.7 (s)
12	1.03, s	29.2 (q)
13	1.05, s	31.7 (q)
14	1.02, s	18.8 (q)
15	4.75, s; 4.72, s	101.4 (t)

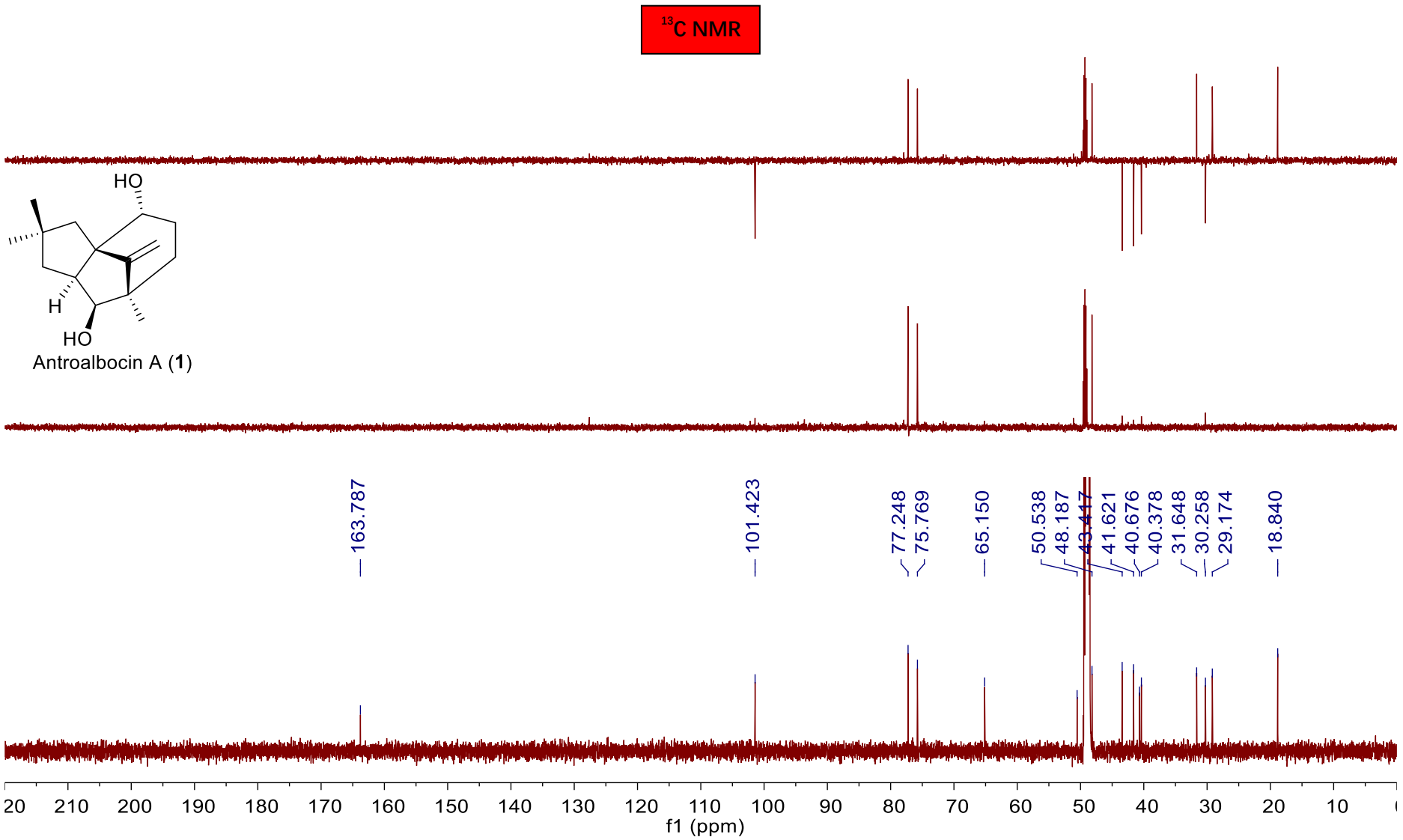
*Physical data for antroalbocin A (**1**)* : colorless crystals (MeOH); mp: 114-116 °C; $[\alpha]^{26}_D$ -3.17 (*c* 0.2, MeOH). UV (MeOH) λ_{max} nm (log ε): 205 (3.23). IR (KBr) ν_{max} cm^{-1}: 3390, 2947, 2835, 1653, 1450, 1417, 1031. For ^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectroscopic data, see Table S1. HR-EI-MS *m/z*: 237.18498 $[M + H]^+$ (calcd for $C_{15}H_{25}O_2$, 237.18491).

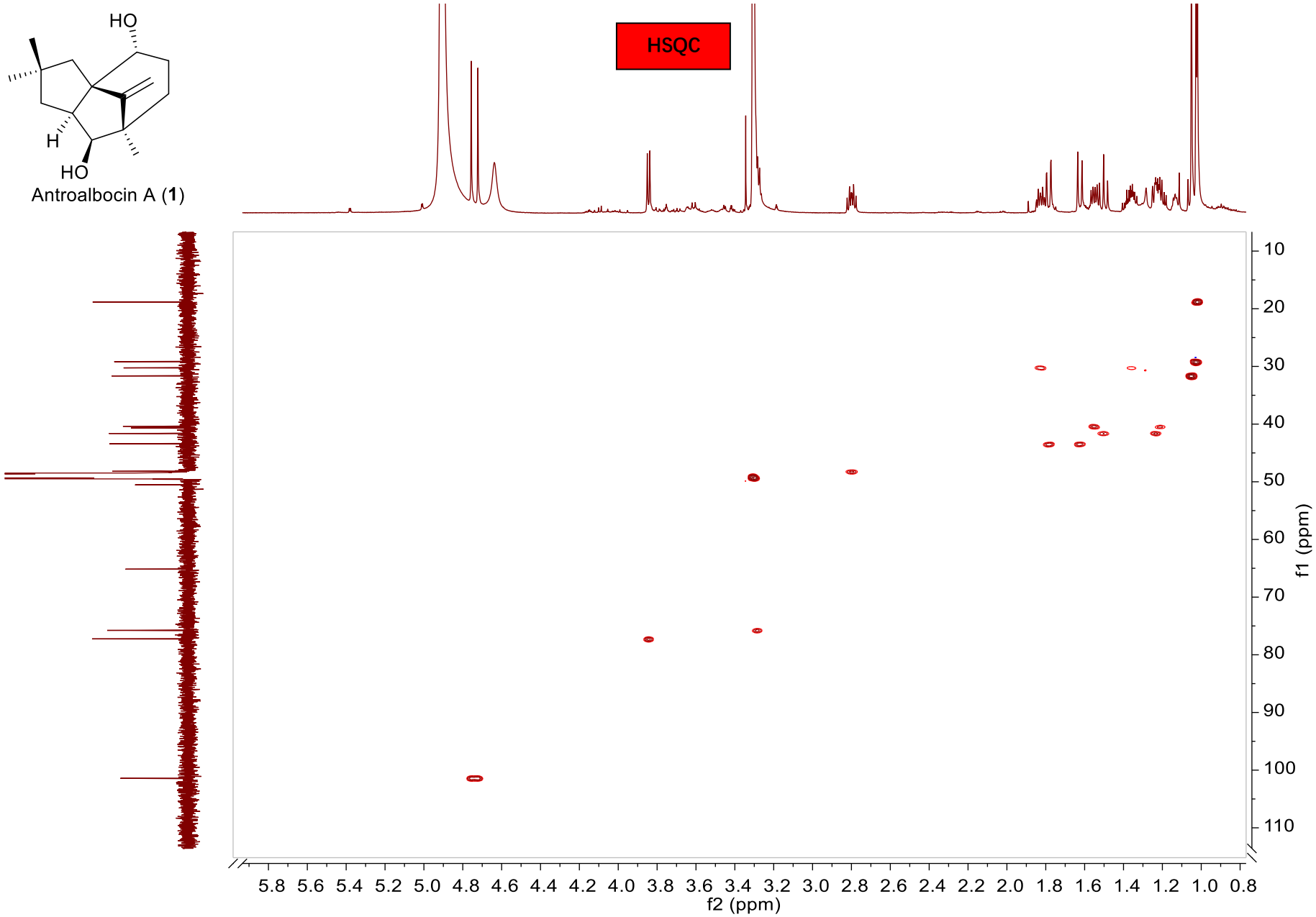
*Crystal date for antroalbocin A (**1**)*: $C_{15}H_{25}O_2$, M = 236.34. a = 12.3156(3) Å, b = 13.7051(4) Å, c = 16.2557(5) Å, α = 90°, β = 99.4850(10)°, γ = 90°, V = 2706.23(13) Å3, T = 150(2) K, space group *P 1 21 1*, Z = 8, μ(CuKα) = 0.583 mm^{-1}, 66801 reflections measured, 11595 independent reflections (R_{int} = 0.0445). The final R_1 values were 0.0372 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0884 ($I > 2\sigma(I)$). The final R_1 values were 0.0445 (all data). The final $wR(F^2)$ values were 0.0943 (all data). The goodness of fit on F^2 was 1.045. Flack parameter = -0.11(6). CCDC: 1876453 (www.ccdc.cam.ac.uk).

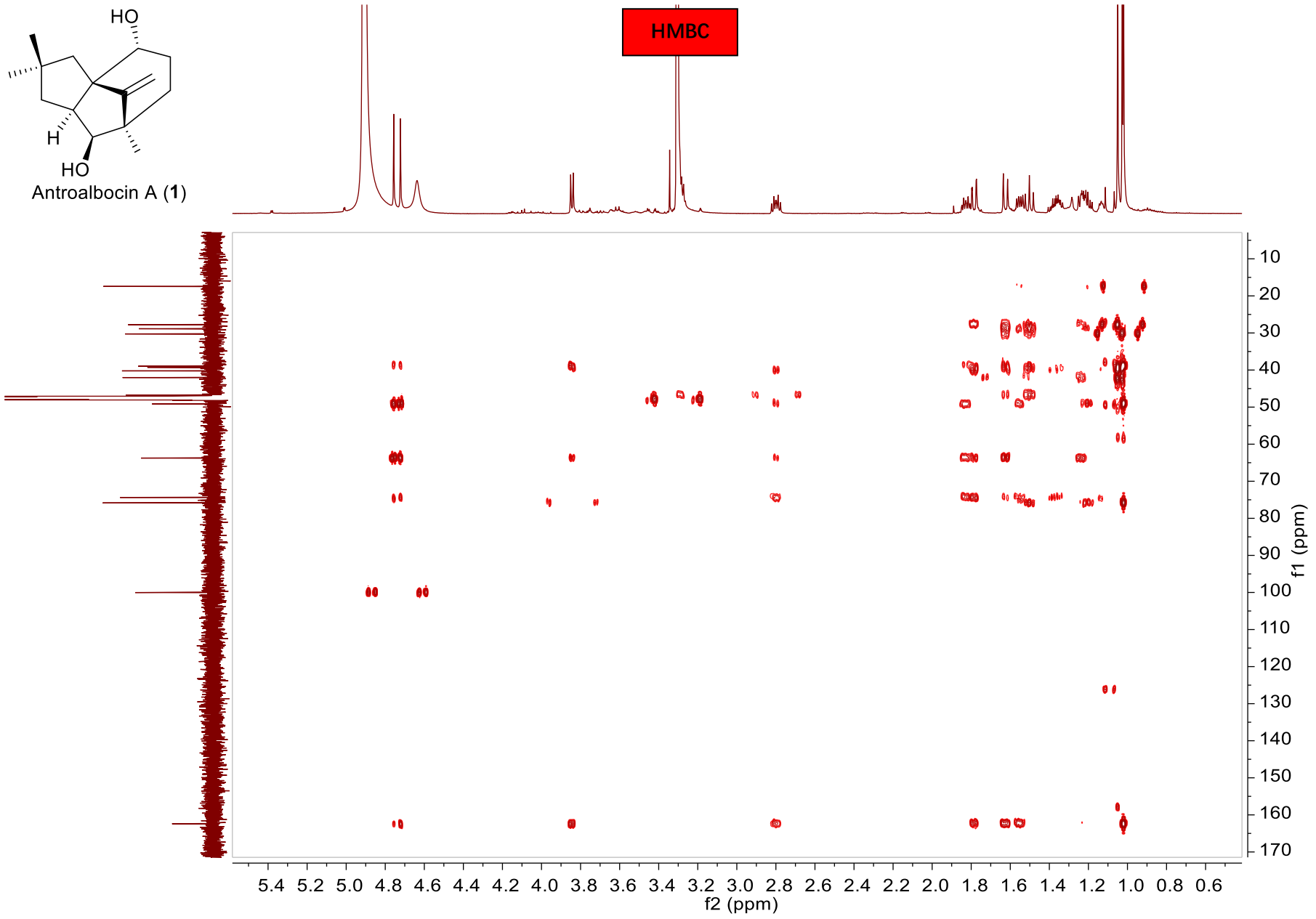
1.4. Antibacterial assay. Compound **1** was subjected to minimal inhibitory concentration (MIC) tests against two species of bacteria (*Staphylococcus aureus, Mycobacterium tuberculosis*) on the PDA medium using a twofold serial dilution in the microplate wells over the range of 2.5–320 μg/mL. To this end, into each well of 96 well plate was placed 80 μL of PDA along with a 20 μL volume of an aqueous test sample solution. The test solutions held different concentrations of the sample being tested. The control well held 80-μL PDA and 20 μL of sterile water. Then, agar plugs (1 mm^3) with fresh phytopathogens were inoculated into each well. Observations of the plates were made after 24 h of incubation at 26 °C in order to acquire the MICs with no growth in the well taken as that value. Three replicates were maintained to confirm the antifungal activity. Rifampicin was used as the positive control [MIC < 2.5 μg/mL (3.0 μM)], while a disk containing only DMSO was used as the negative control.

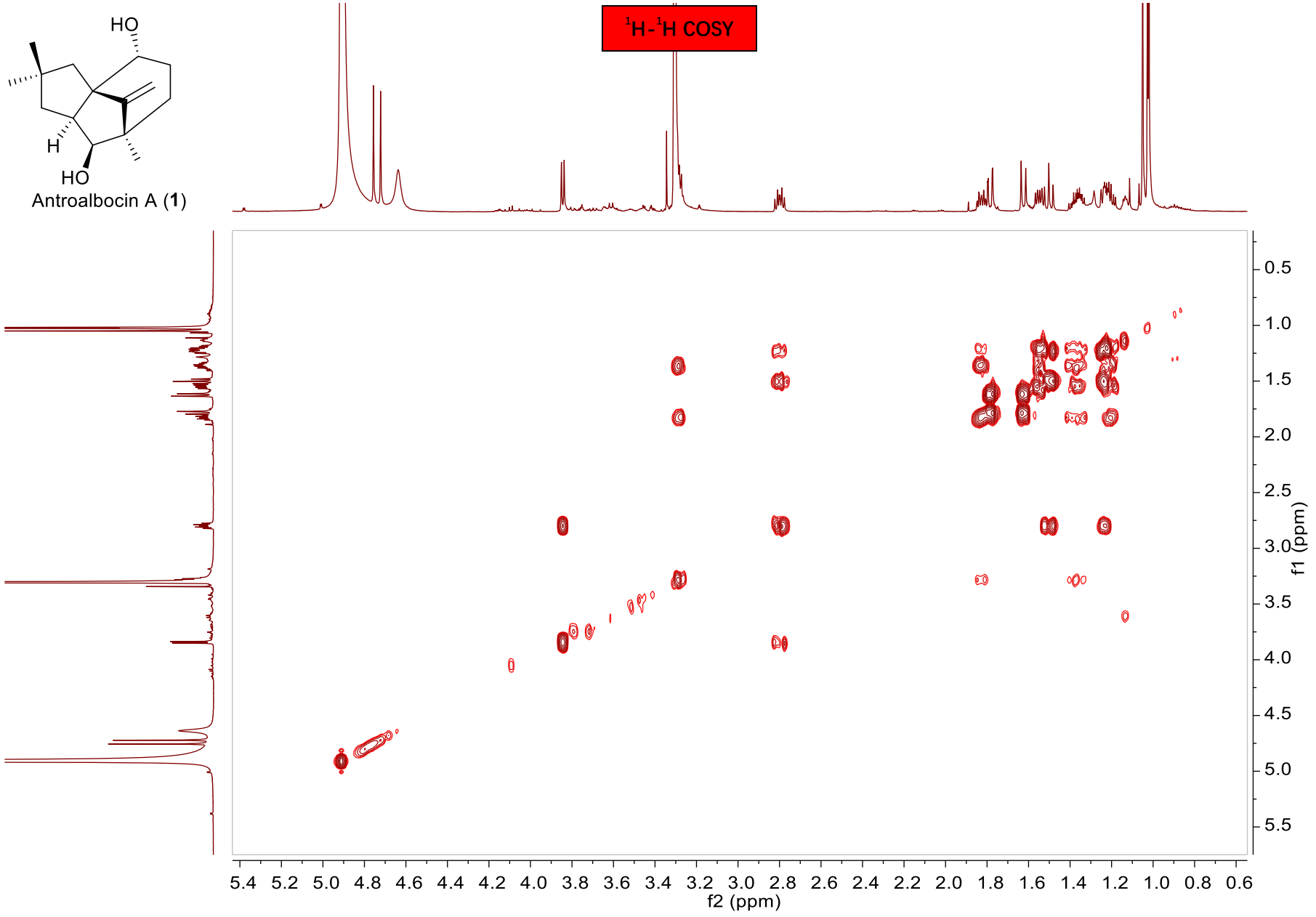
2. NMR spectra and MS for antroalbocin A (1)

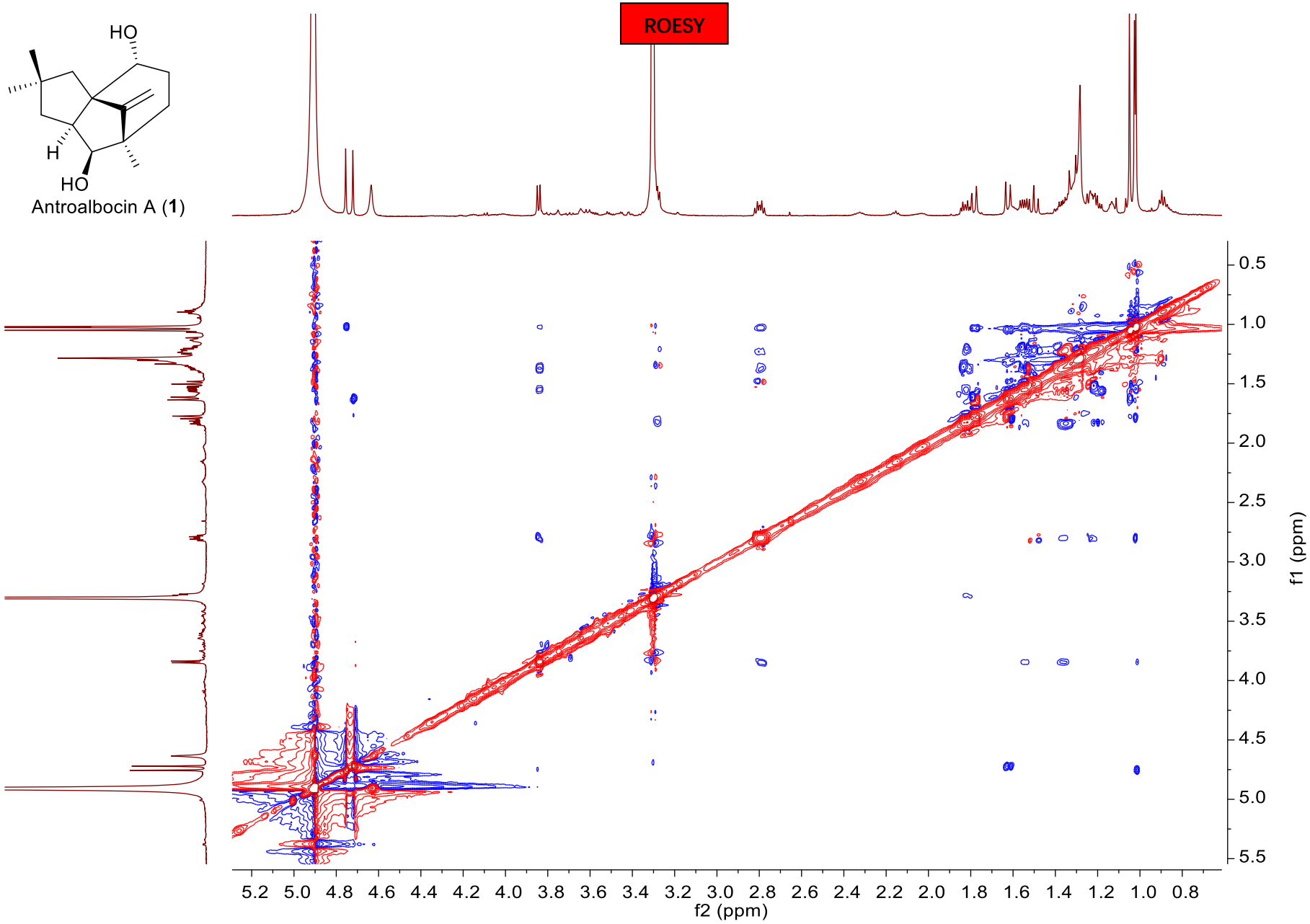


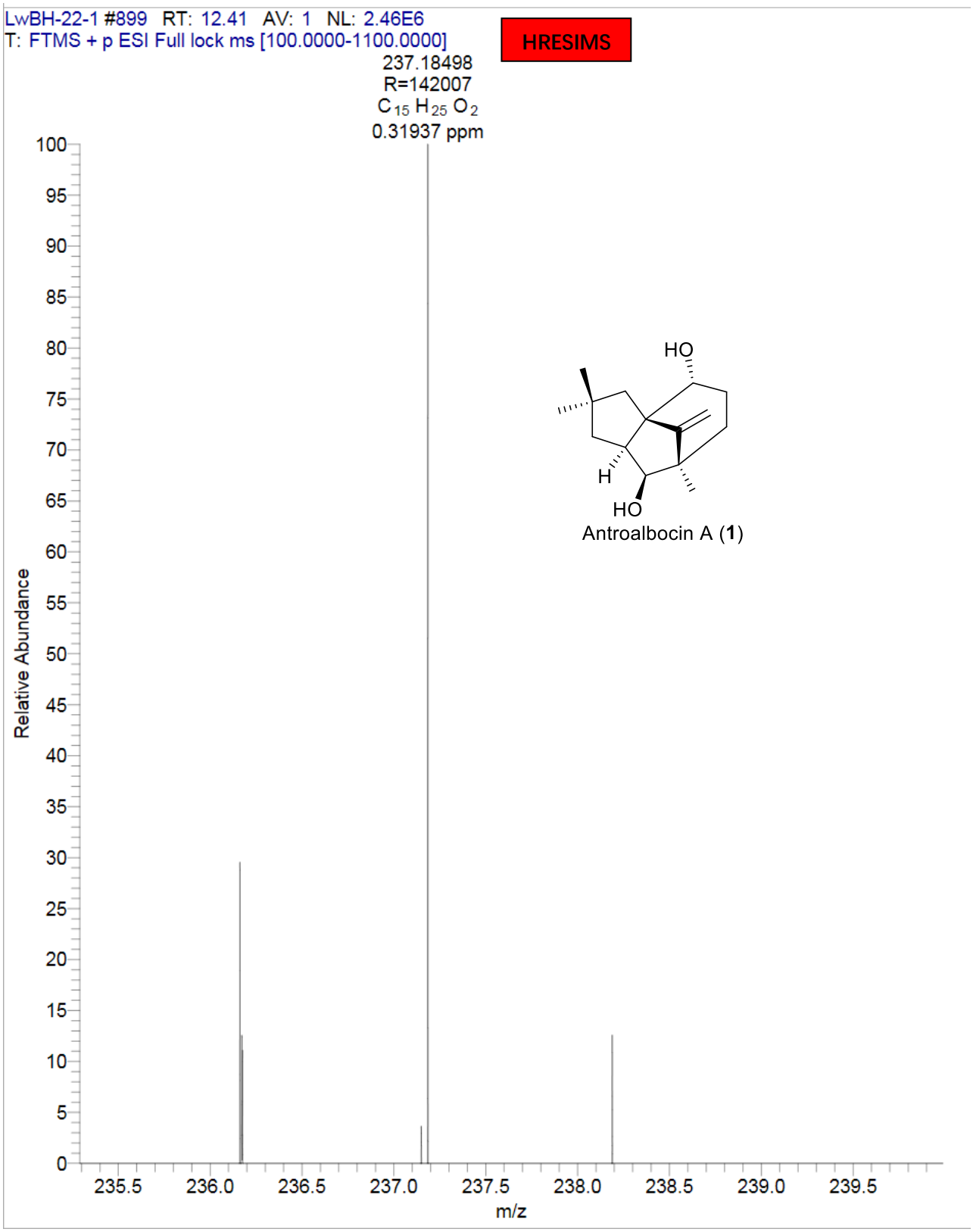

^{13}C NMR
HO
H
HO
Antroalbocin A (1)
163.787
101.423
77.248
75.769
65.150
50.538
48.187
43.417
41.621
40.676
40.378
31.648
30.258
29.174
18.840
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


HO
H
HO
Antroalbocin A (1)
HSQC
f1 (ppm)
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8


HO
H
HO
Antroalbocin A (1)
HMBC
f2 (ppm)
f1 (ppm)


HO
H
HO
Antroalbocin A (1)
^{1}H-^{1}H COSY
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f2 (ppm)
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)


HO
H
HO
Antroalbocin A (1)
ROESY
f2 (ppm)
f1 (ppm)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T: FTMS + p ESI Full lock ms [100.0000-1100.0000]
HRESIMS
237.18498
R=142007
C15 H25 O2
0.31937 ppm
HO
H
HO
Antroalbocin A (1)
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
235.5
236.0
236.5
237.0
237.5
238.0
238.5
239.0
239.5