

Supporting Information

Iriomoteolide-3a, a Cytotoxic 15-Membered Macrolide from a Marine Dinoflagellate *Amphidinium* Species

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Table S1. ^1H and ^{13}C NMR Data of Iriomoteolide-3a (**1**) in CDCl_3 .

position	^{13}C	^1H
1	172.6 C	
2	37.7 CH_2	2.38 dd, 2.4, 14.0 1.98 dd, 7.8, 14.0
3	29.8 CH	2.10 m
4	36.0 CH_2	2.32 ddd, 4.0, 10.0, 13.8 1.82 ddd, 4.0, 8.9, 13.8
5	133.2 CH	5.77 ddd, 4.0, 10.0, 16.3
6	131.3 CH	5.40 m
7	76.7 ^a CH	3.965 m ^b
8	76.6 ^a CH	3.955 m ^b
9	135.8 CH	5.79 m
10	132.5 CH	5.25 dd, 9.8, 15.5
11	59.0 CH	3.00 dd, 2.3, 9.8
12	57.7 CH	2.90 dt, 9.8, 2.3
13	34.3 CH_2	2.26 dt, 14.0, 2.3 1.48 ddd, 9.8, 10.4, 14.0
14	72.7 CH	5.11 ddd, 2.3, 3.4, 10.4
15	70.8 CH	3.60 br dt, 10.0, 3.6
16	40.6 CH_2	1.39 ddd, 4.0, 10.0, 13.9 1.27 ddd, 3.6, 10.7, 13.9
17	33.3 CH	2.35 m
18	135.3 CH	5.20 dd, 8.5, 15.5
19	128.6 CH	5.45 m

20	35.4	CH ₂	2.66 ^c	m
21	129.5	CH	5.38	m
22	125.6	CH	5.40	m
23	17.8	CH ₃	1.64 ^d	d, 6.6
24	20.7	CH ₃	1.01 ^d	d, 6.6
25	21.6	CH ₃	1.01 ^d	d, 6.6

^aThese signals were interchangeable. ^bAlthough these signals were overlapped with each other, $J(\text{H-6/H-7})$, $J(\text{H-7/H-8})$, and $J(\text{H-8/H-9})$ values were approximately 8.6 Hz. ^c2H. ^d3H.

General Methods.

NMR data in CDCl₃ (99.96% deuteration degree) were obtained using 2.5 mm micro cells for CDCl₃, and measured on a 600 MHz spectrometer equipped with 2.5 mm inverse probe or 500 MHz spectrometer equipped with 2.5 mm dual probe. For the phase-sensitive HMBC spectrum, the mixing time Δ was set to 60 msec. Positive- and negative-mode ESIMS spectra were measured at -80 V as a focus voltage using a sample dissolved in MeOH with flow rate of 200 μ L/min. NMR simulations were carried out using NMRPEAK.exe program by Dr. H. Nakamura.

Figure S1. ^1H NMR spectrum of iriomoteolide-3a (**1**) in CDCl_3 .

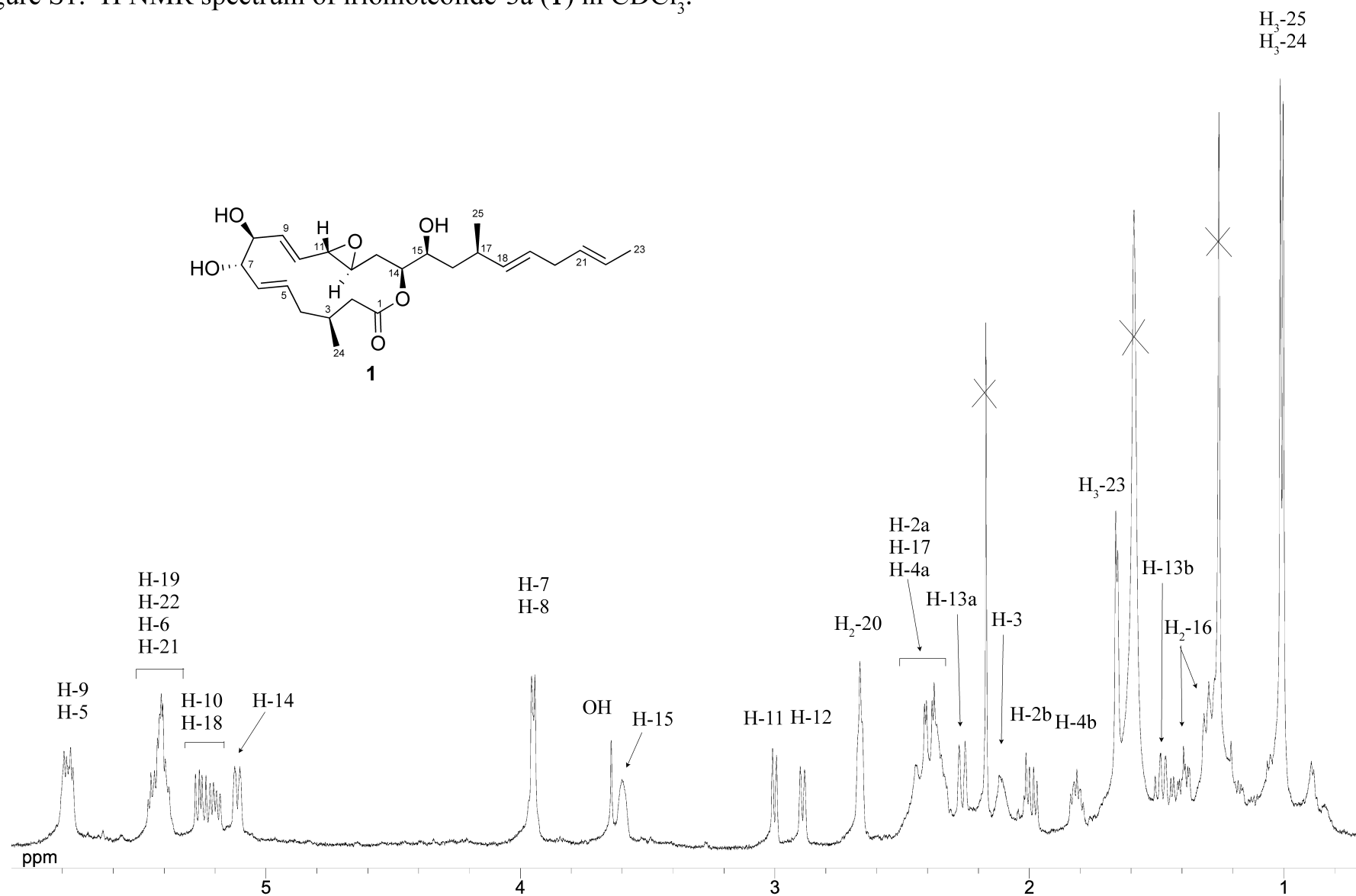


Figure S2. ^{13}C NMR spectrum of iriomoteolide-3a (1) in CDCl_3 .

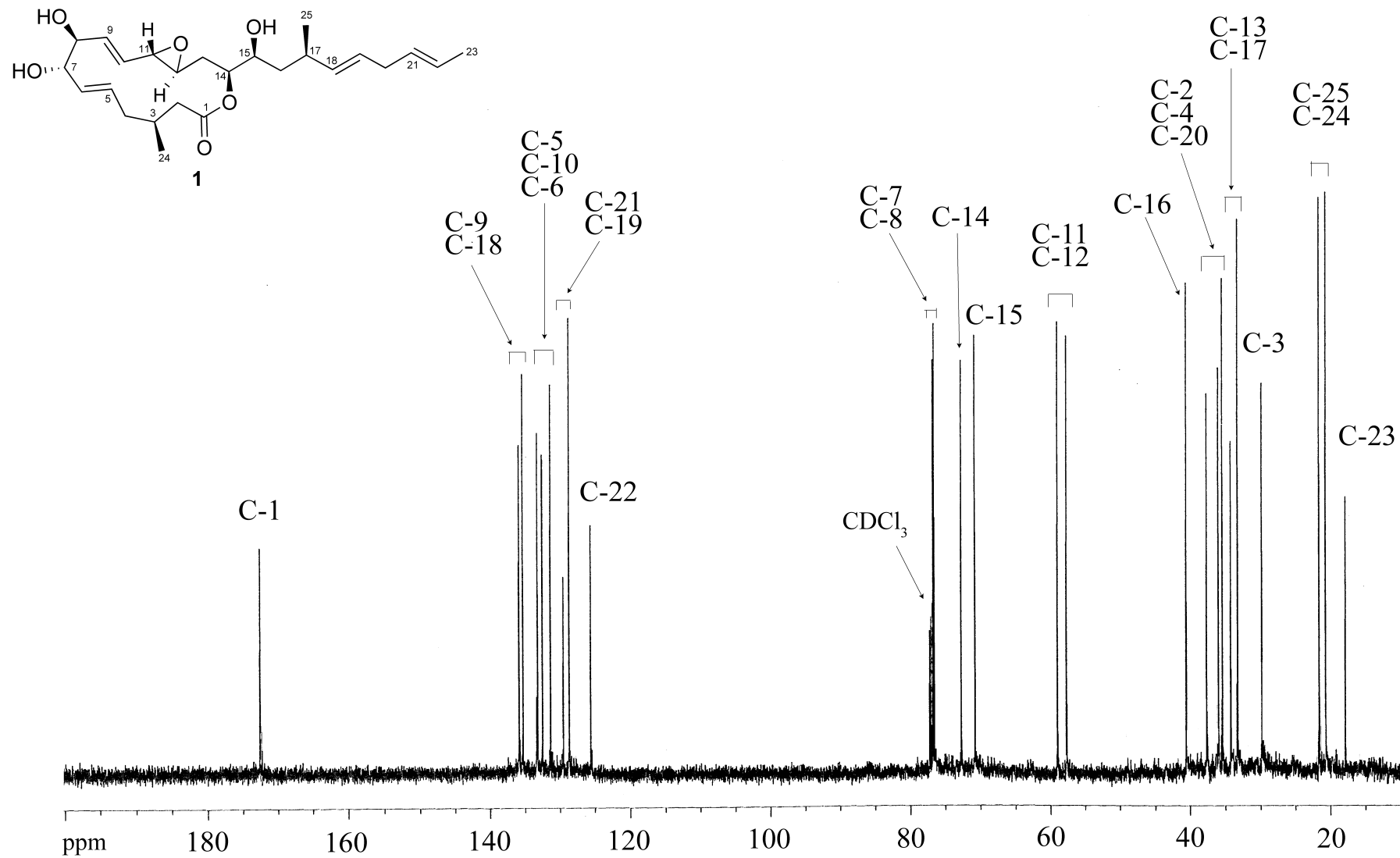


Figure S3. ^1H - ^1H COSY spectrum of iriomoteolide-3a (1) in CDCl_3 .

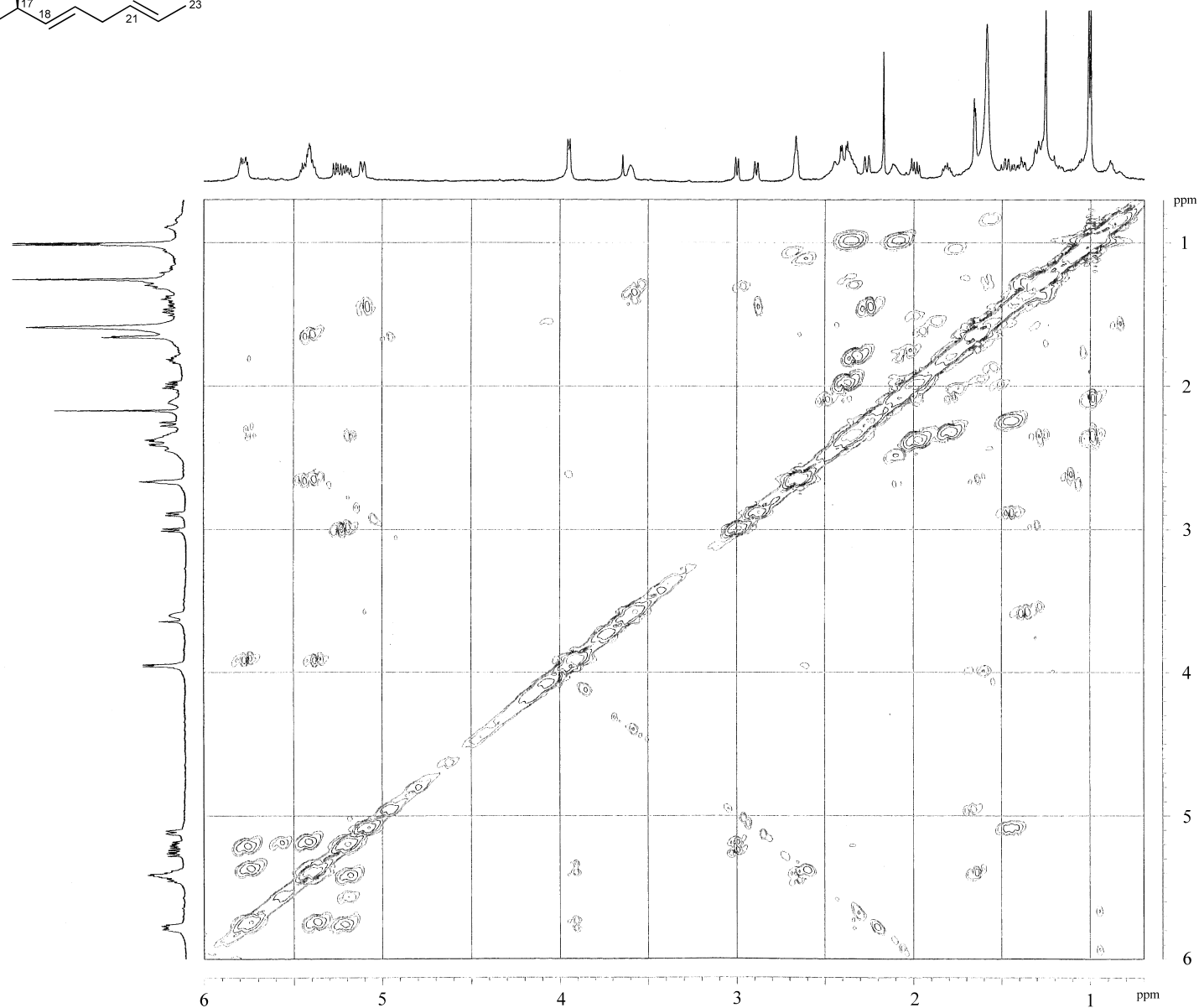
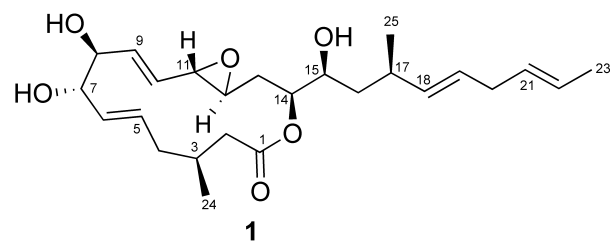


Figure S4. TOCSY spectrum of iriomoteolide-3a (1) in CDCl_3 .

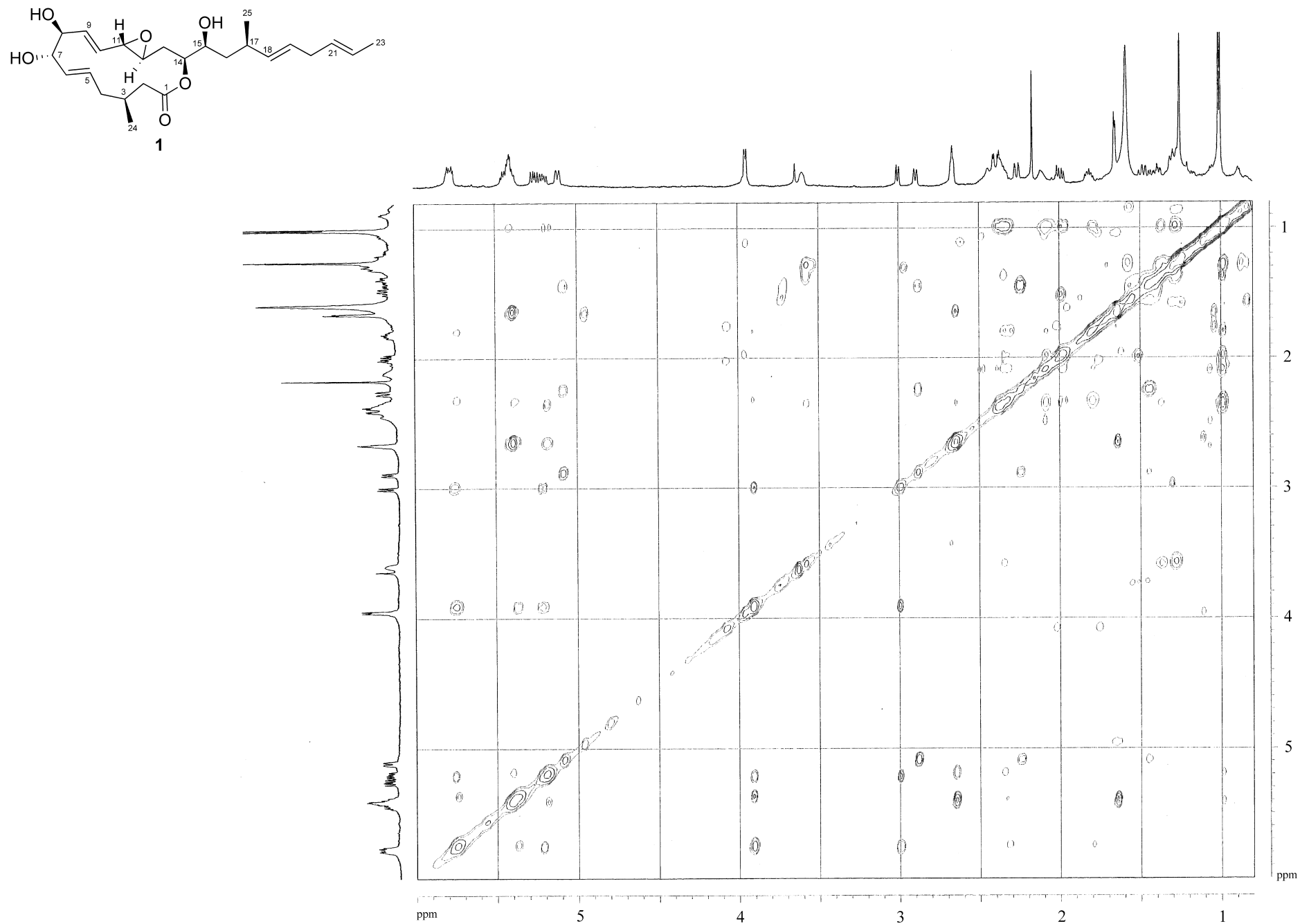


Figure S5. HMQC spectrum of iriomoteolide-3a (1) in CDCl₃.

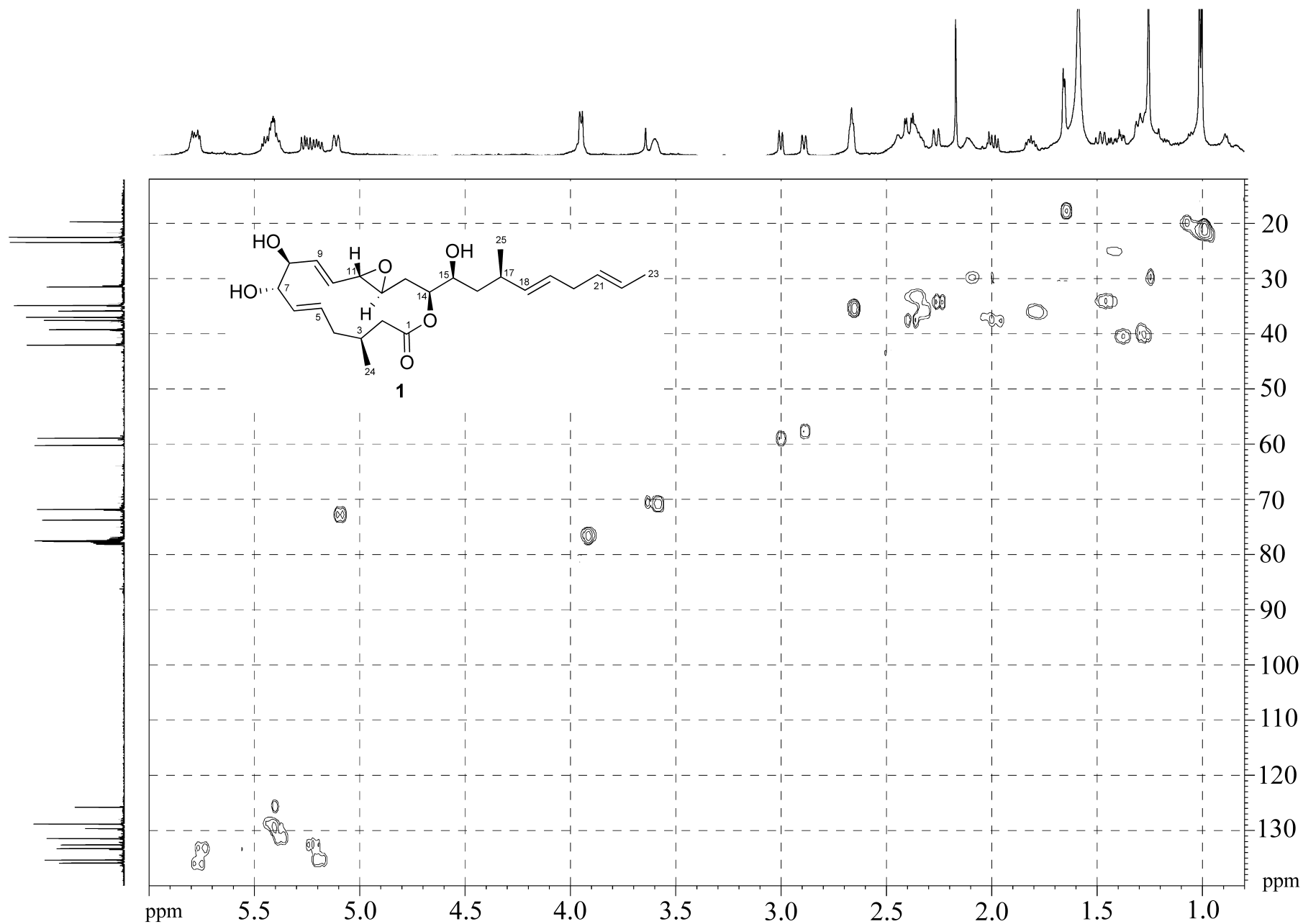


Figure S6. Phase-sensitive HMBC spectrum of iriomoteolide-3a (1) in CDCl_3 .

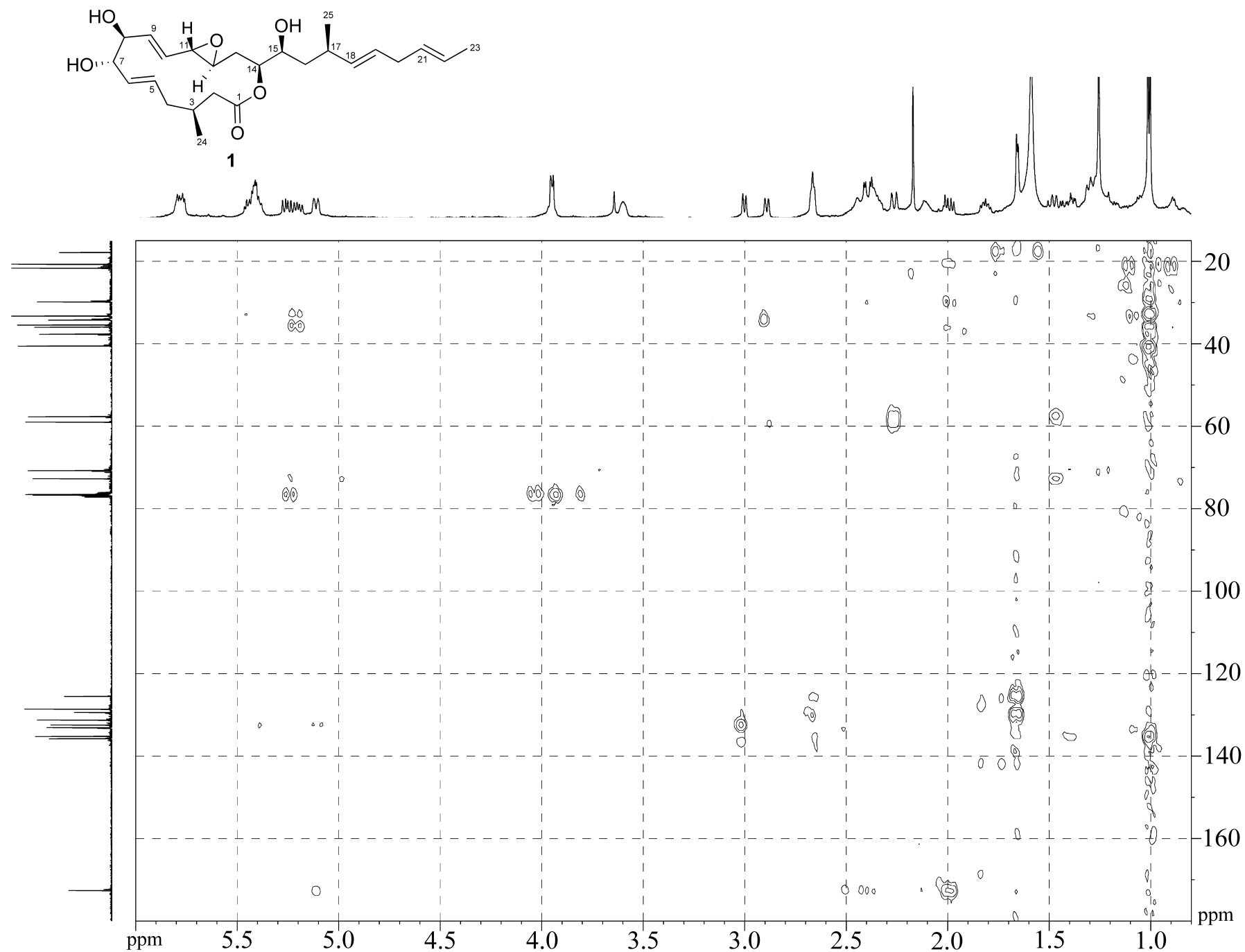


Figure S7. NOESY spectrum of iriomoteolide-3a (1) in CDCl₃.

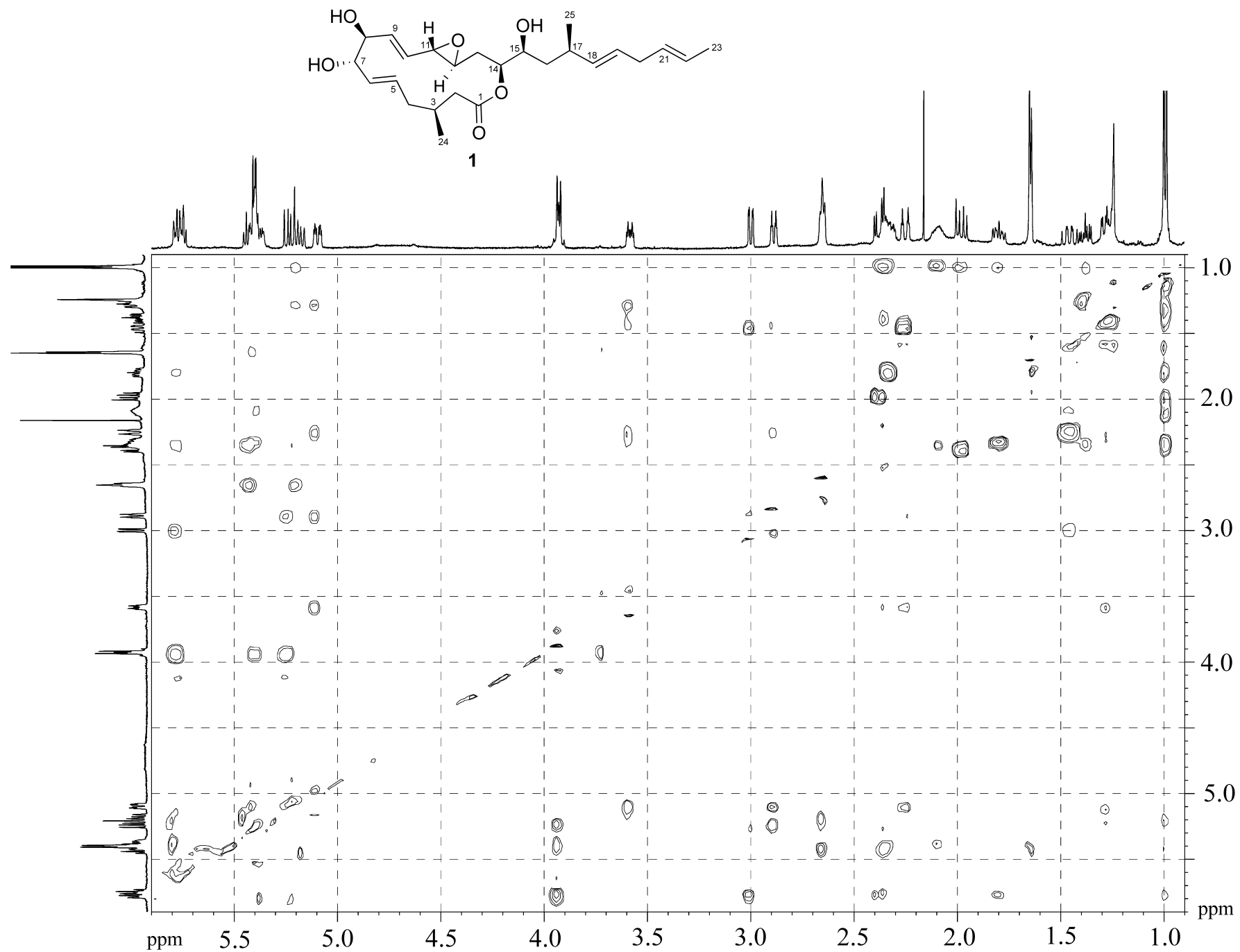


Figure S8. ^1H NMR spectrum of 7,8-*O*-isopropylidene derivative (2) of iriomoteolide-3a (1) in CDCl_3 .

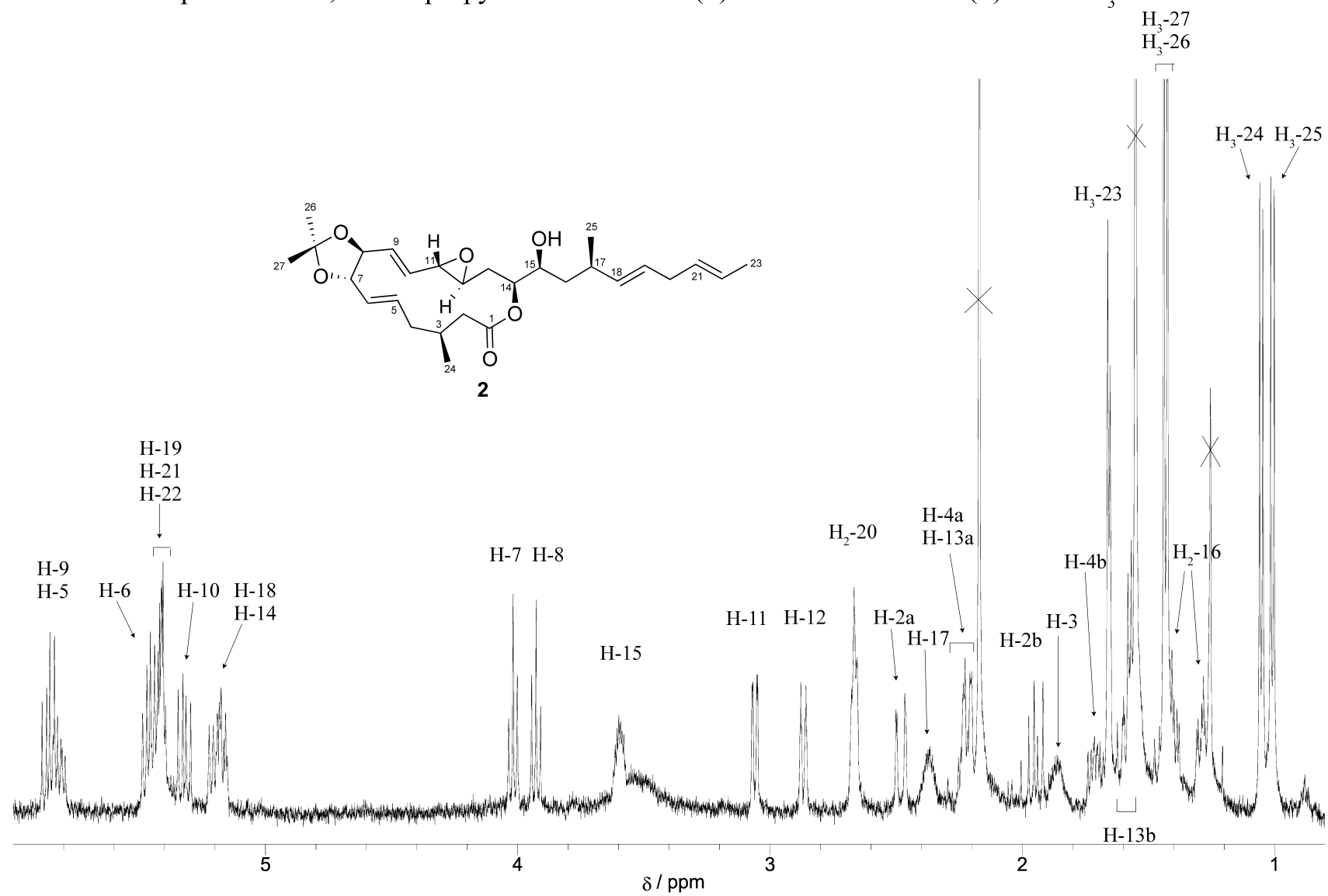


Figure S9. ^1H - ^1H COSY spectrum of 7,8-*O*-isopropylidene derivative (2) of iriomoteolide-3a (1) in CDCl_3 .

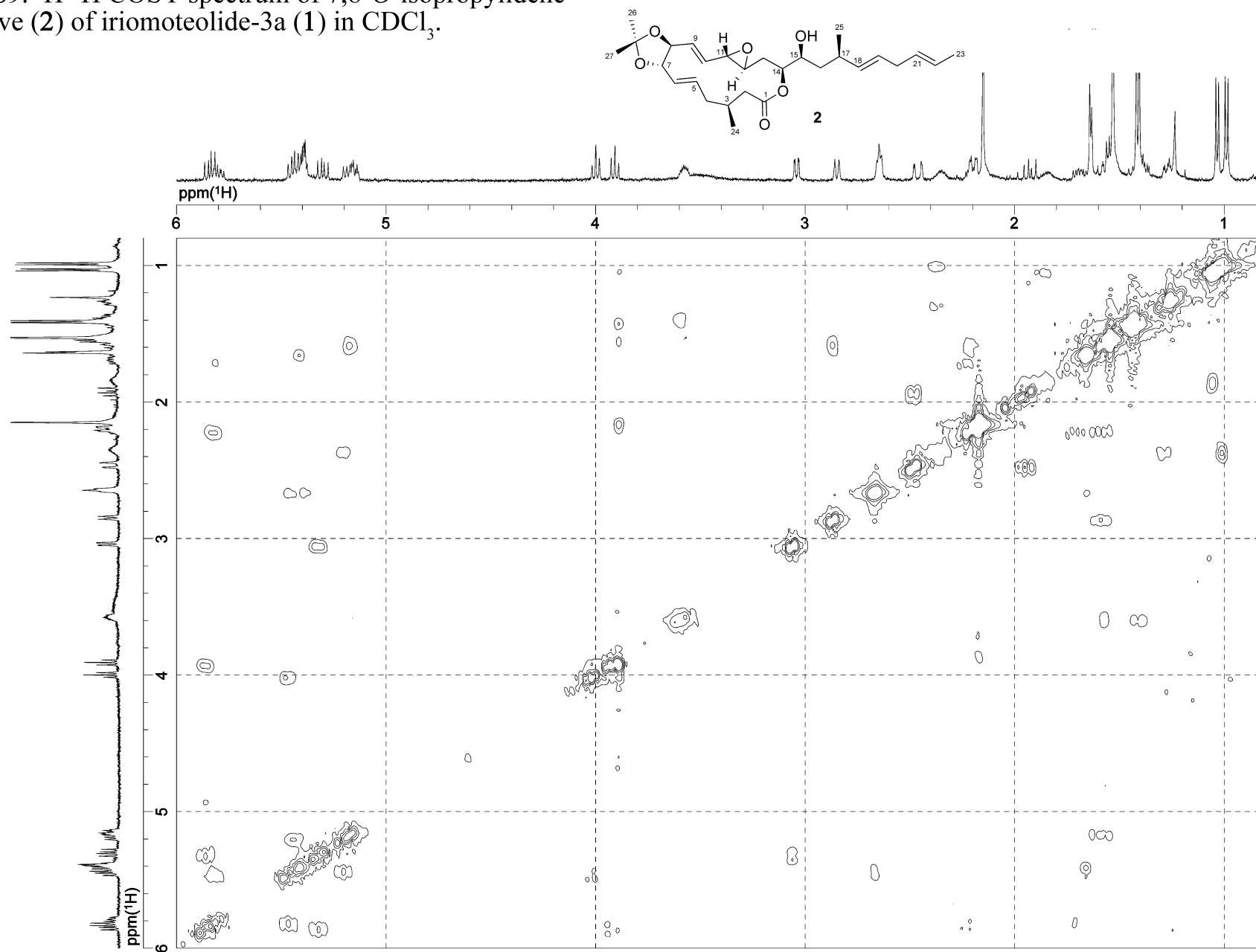


Figure S10. NOESY spectrum of 7,8-*O*-isopropylidene derivative (2) of iriomoteolide-3a (1) in CDCl₃.

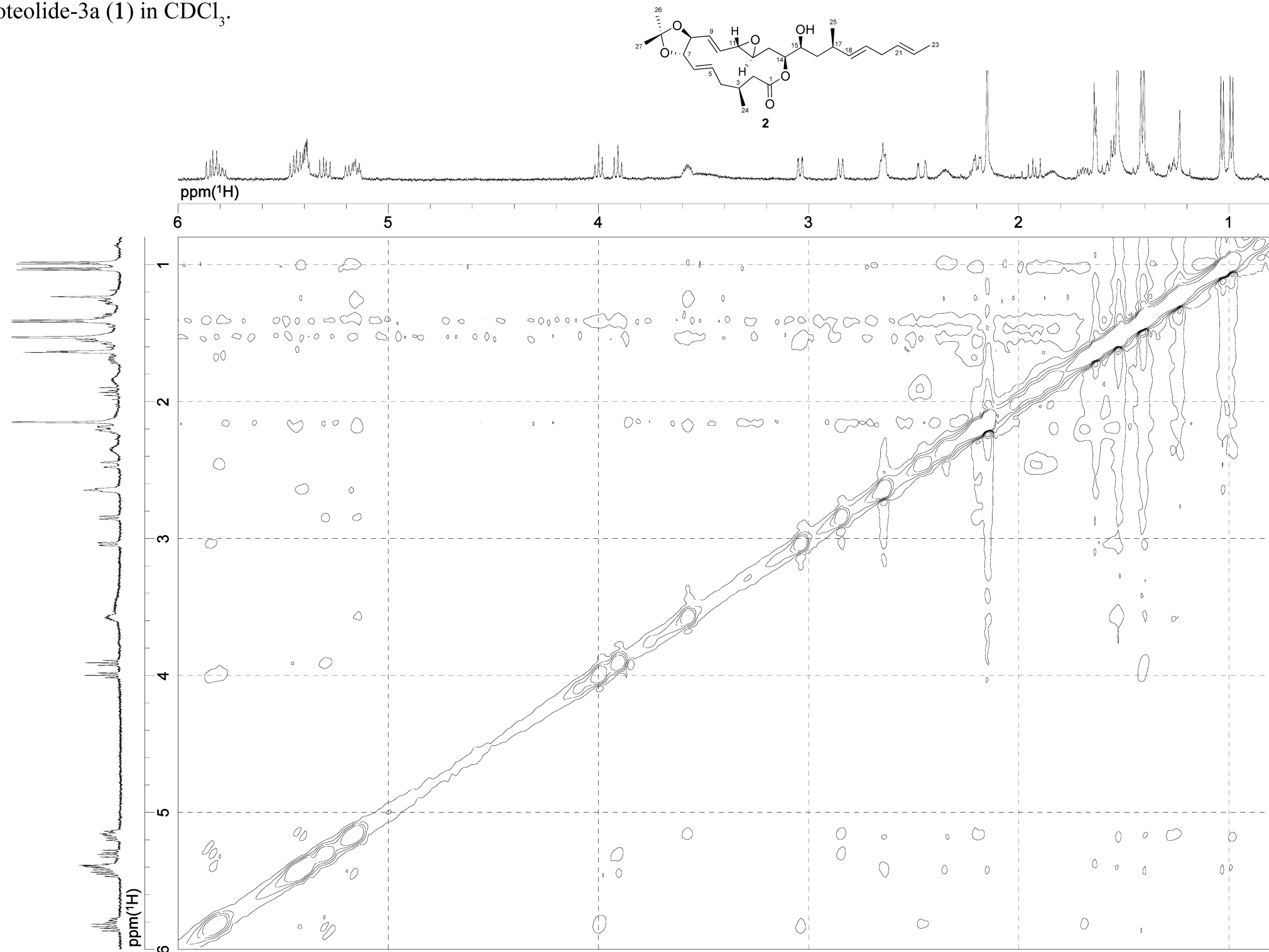


Figure S11. ^1H NMR spectrum of 7,8,15-(*S*)-MTPA ester (**3a**) of iriomotelide-3a (**1**) in CDCl_3 .

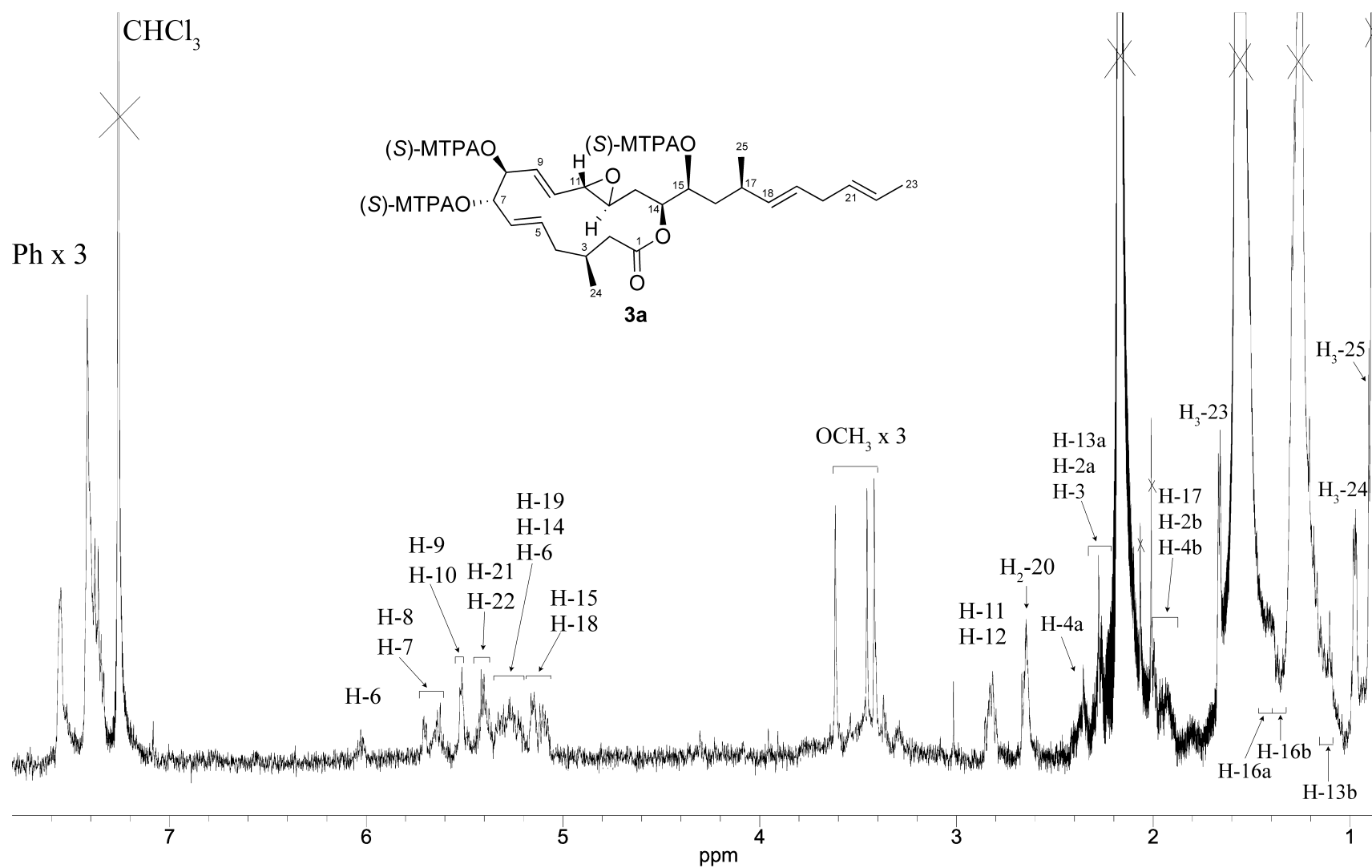


Figure S12. ^1H NMR spectrum of 7,8,15-(*R*)-MTPA ester (**3b**) of iriomoteolide-3a (**1**) in CDCl_3 .

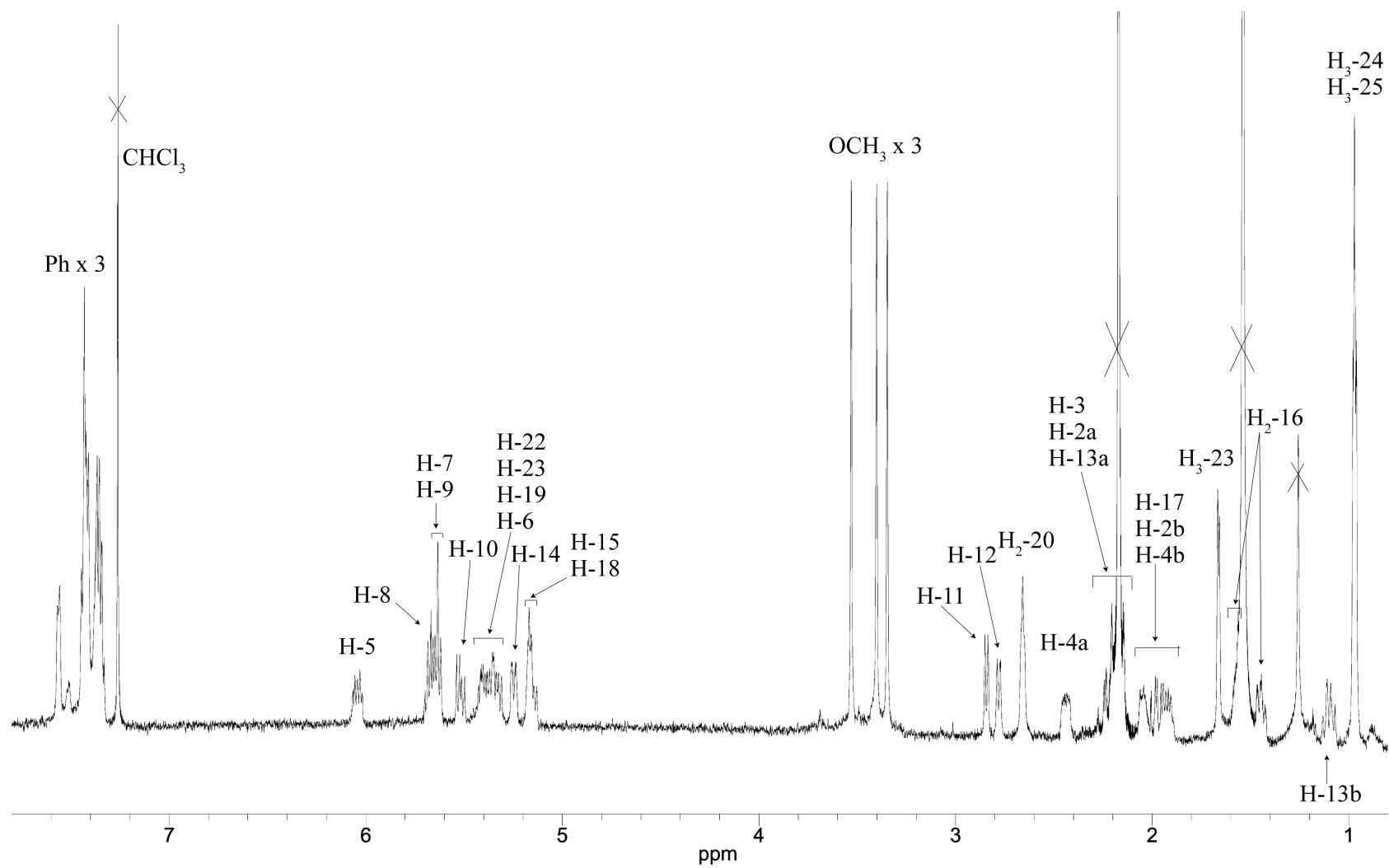


Figure S13. ^1H NMR signals for H-7 and H-8 a) of natural iriomoteolide-3a (1) and b) simulated by NMRPEAK.exe program.

