

## Supporting Information

Amphidinolide Y, a Novel 17-Membered Macrolide from Dinoflagellate *Amphidinium* sp.; Plausible Biogenetic Precursor of Amphidinolide X

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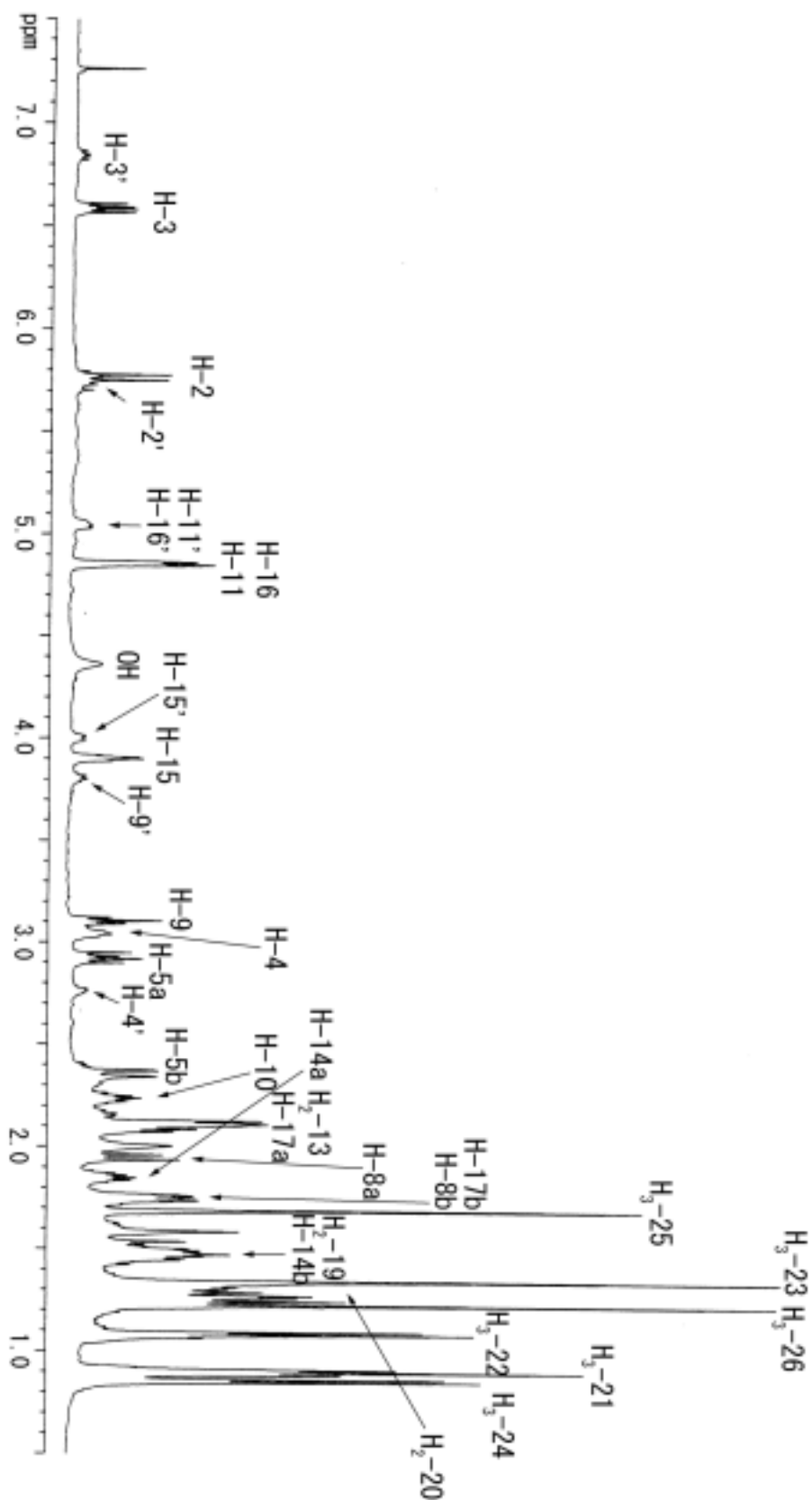
**General Methods.** NMR spectra except 2D DEPT C–C LR Relay spectrum were recorded on a 600 MHz spectrometer using 2.5 mm micro cells for CDCl<sub>3</sub> (Shigemi Co., Ltd.). Positive mode ESIMS spectra were measured at -80 V as a focus voltage using a sample dissolved in MeOH with flow rate of 200 μL/min. Positive mode FABMS spectra were obtained using nitrobenzyl alcohol as a matrix.

Table S1. Isotope Incorporation Results Based on  $^{13}\text{C}$  NMR Data of Amphidinolide Y (**1**) in  $\text{CDCl}_3$ .

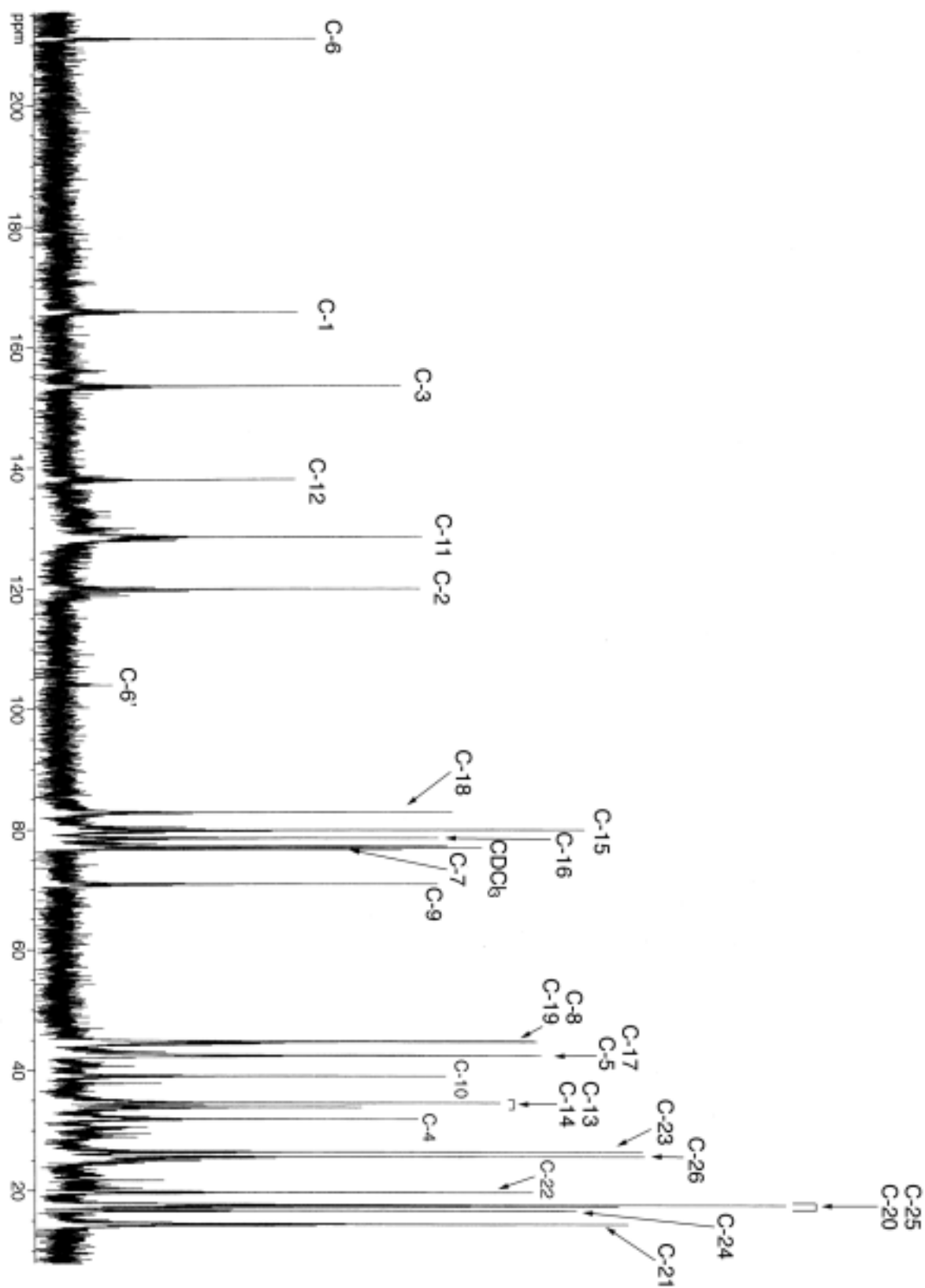
Positn.	[1- $^{13}\text{C}$ ]- acetate <sup>a</sup>	[2- $^{13}\text{C}$ ]- acetate <sup>a</sup>	Assignment c or m <sup>b</sup>
1	3.56	1.22	c
2	0.87	1.98	m
3	1	3.12	m
4	3.94	1	c
5	1.26	2.73	m
6	0.69	1.81	m
7	<sup>c,d</sup>	1.82 <sup>d</sup>	m
8	4.14	1.33	c
9	0.93	2.53	m
10	3.93	0.98	c
11	0.60	2.00	m
12	<sup>c,d</sup>	1.68 <sup>d</sup>	m
13	3.86	1.36	c
14	0.84	2.47	m
15	3.62	1.23	c
16	0.93	2.91	m
17	1.41	2.32	m
18	3.96	0.87	c
19	1.00	2.79	m
20	3.74	1.16	c
21	0.84	3.02	m
22	0.65	2.44	m
23	1.10	3.10	m
24	1.15	3.09	m
25	1.21	2.90	m
26	0.84	2.42	m

<sup>a</sup>Intensity ratios of each peak in the labeled **1** divided by that of the corresponding signal in the unlabeled **1**, respectively, normalized to give a ratio of 1 for unenriched peak (C-3 for [1- $^{13}\text{C}$ ]-acetate labeling and C-4 for [2- $^{13}\text{C}$ ]-acetate labeling). <sup>b</sup>denotes the carbon derived from C-1 of acetate, while m indicates the carbon derived from C-2 of acetate. <sup>c</sup>not observed. <sup>d</sup>in  $\text{C}_6\text{D}_6$ .

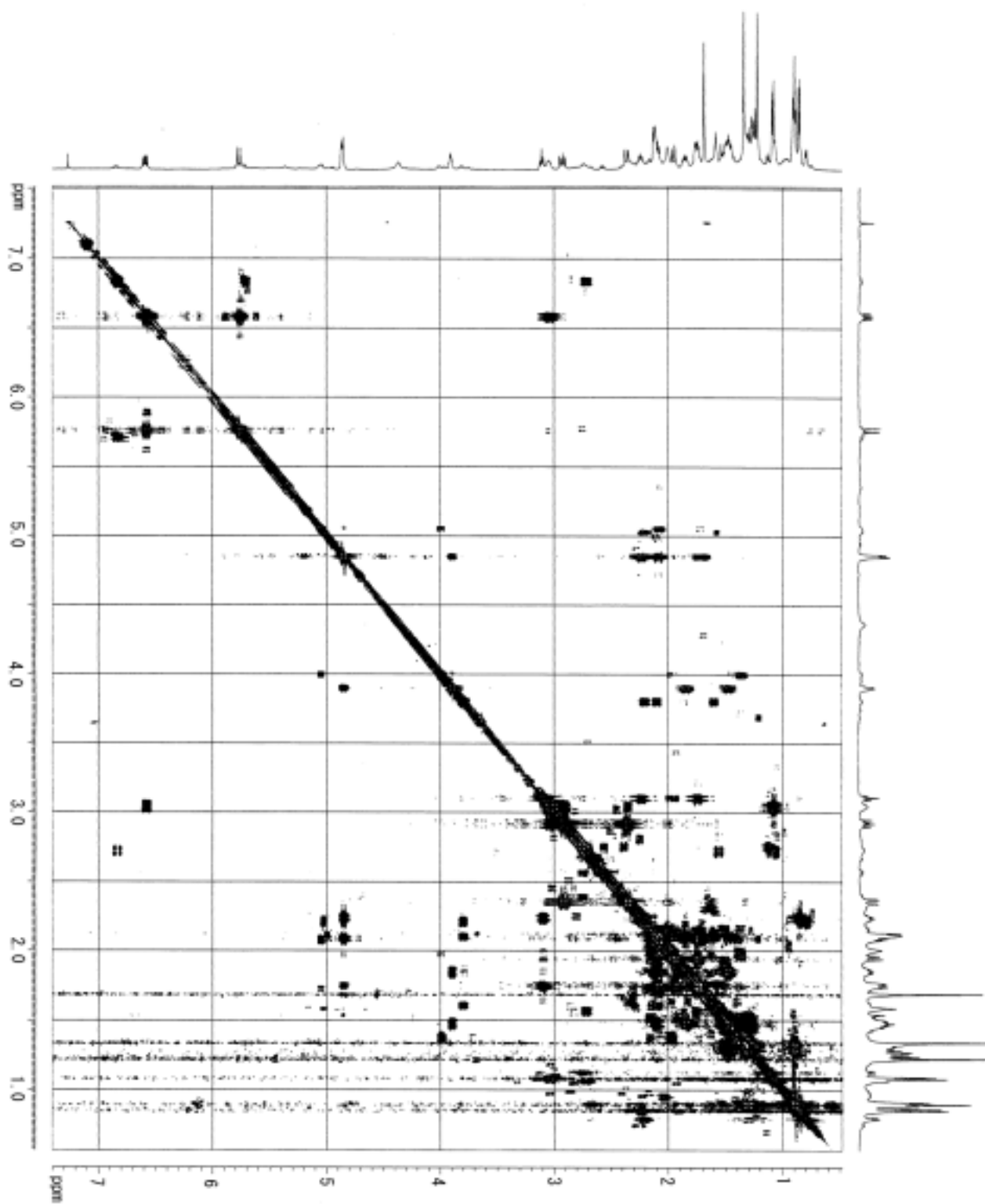
**Figure S1.**  $^1\text{H}$  NMR spectrum of amphidinolide Y (**1**, 1 mg/40  $\mu\text{L}$ ) in  $\text{CDCl}_3$ .



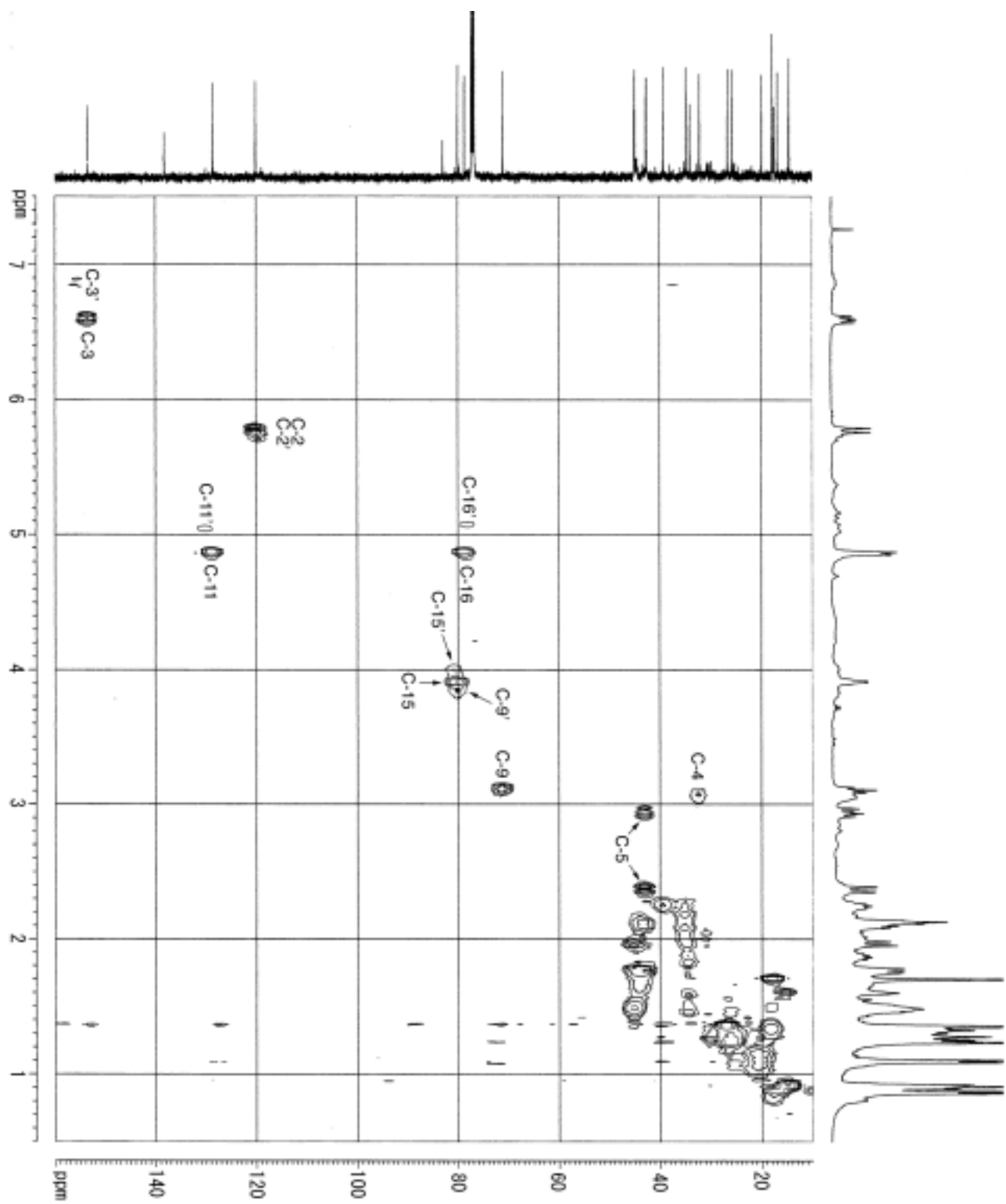
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of  $^{13}\text{C}$ -labeled amphidinolide Y (**1**) in  $\text{CDCl}_3$ .



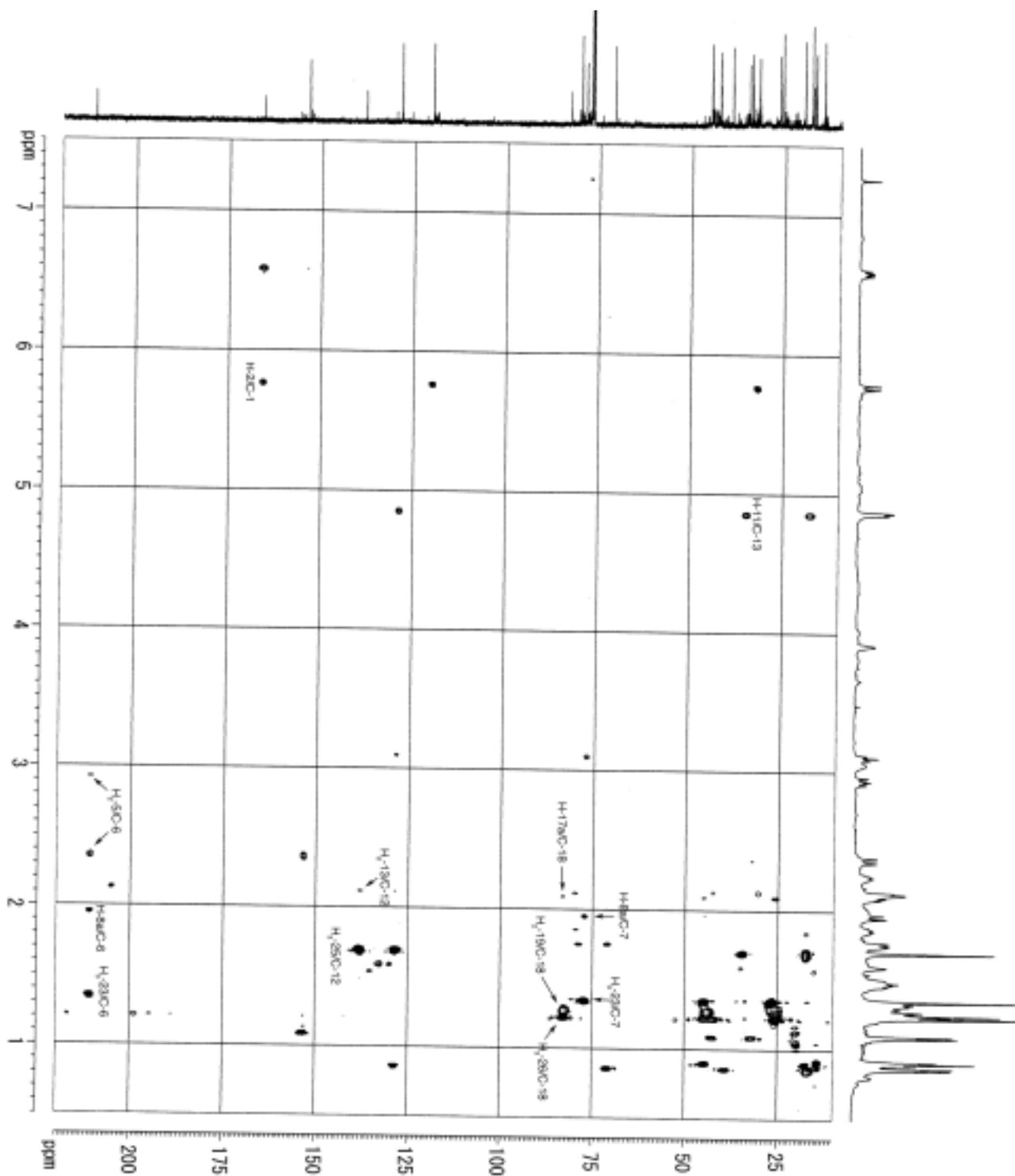
**Figure S3.** DQF COSY spectrum of amphidinolide Y (**1**) in  $\text{CDCl}_3$ .



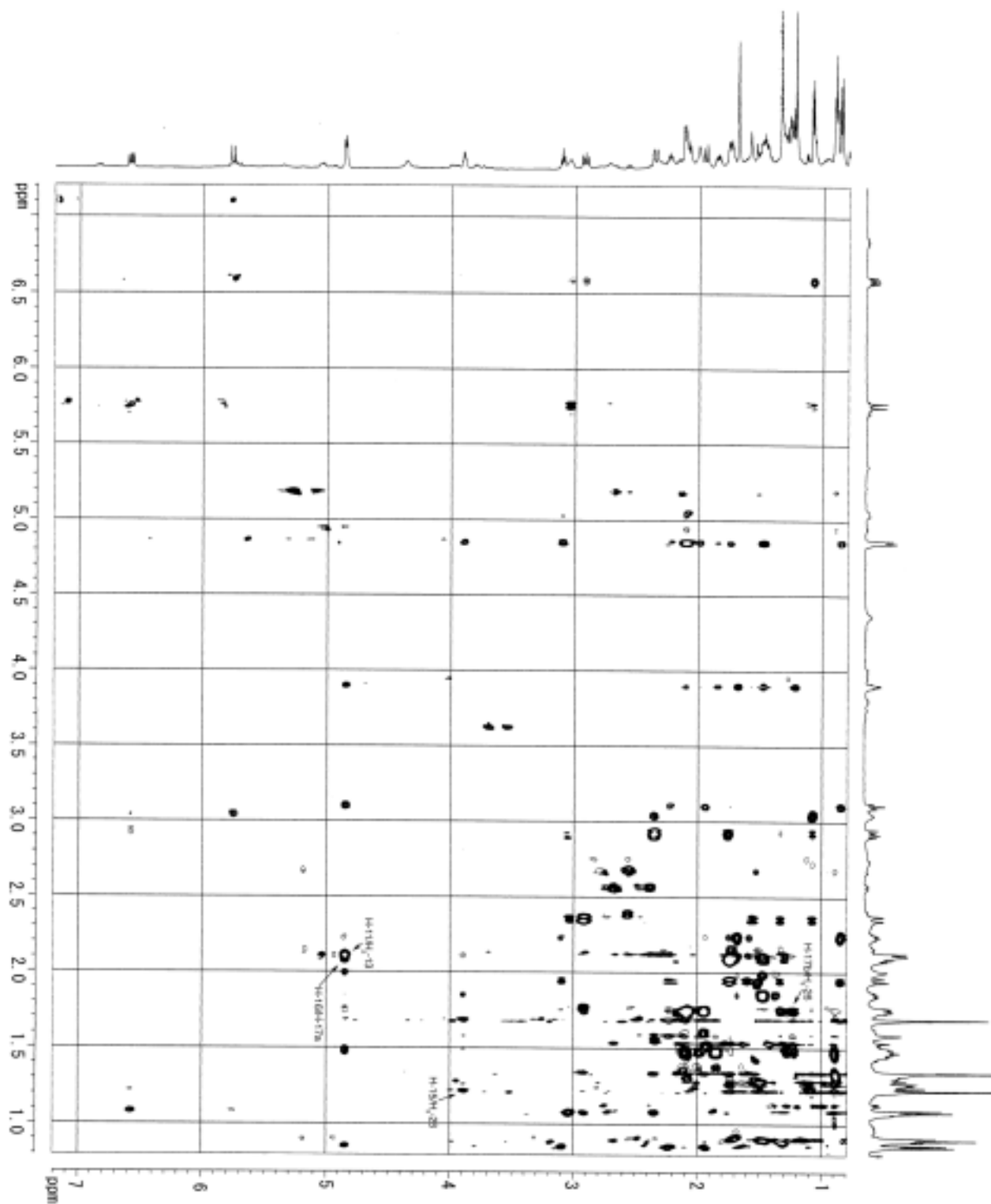
**Figure S4.** HMQC spectrum of amphidinolide Y (**1**) in CDCl<sub>3</sub>.



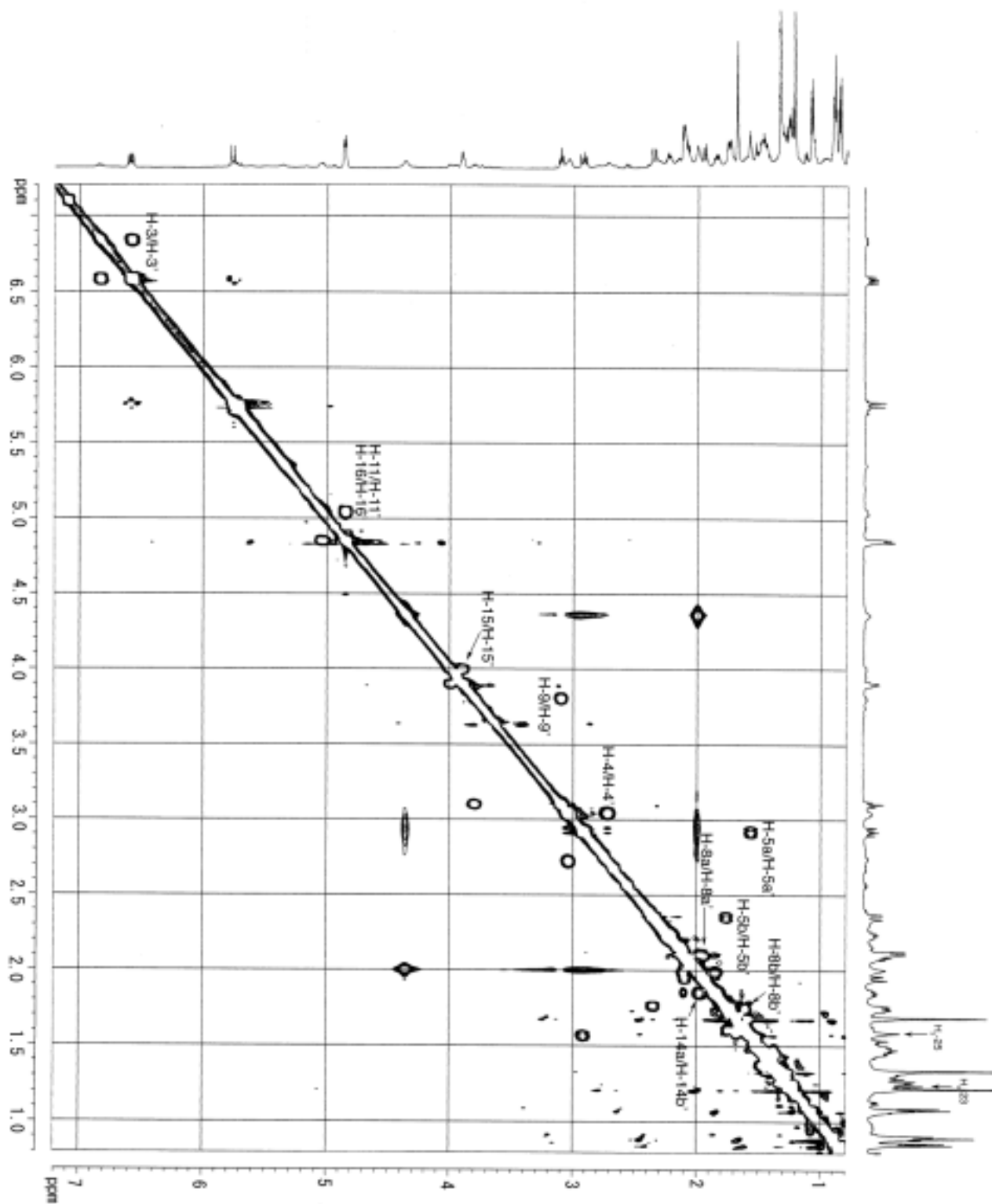
**Figure S5.** HMBC spectrum of amphidinolide Y (**1**) in  $\text{CDCl}_3$ .



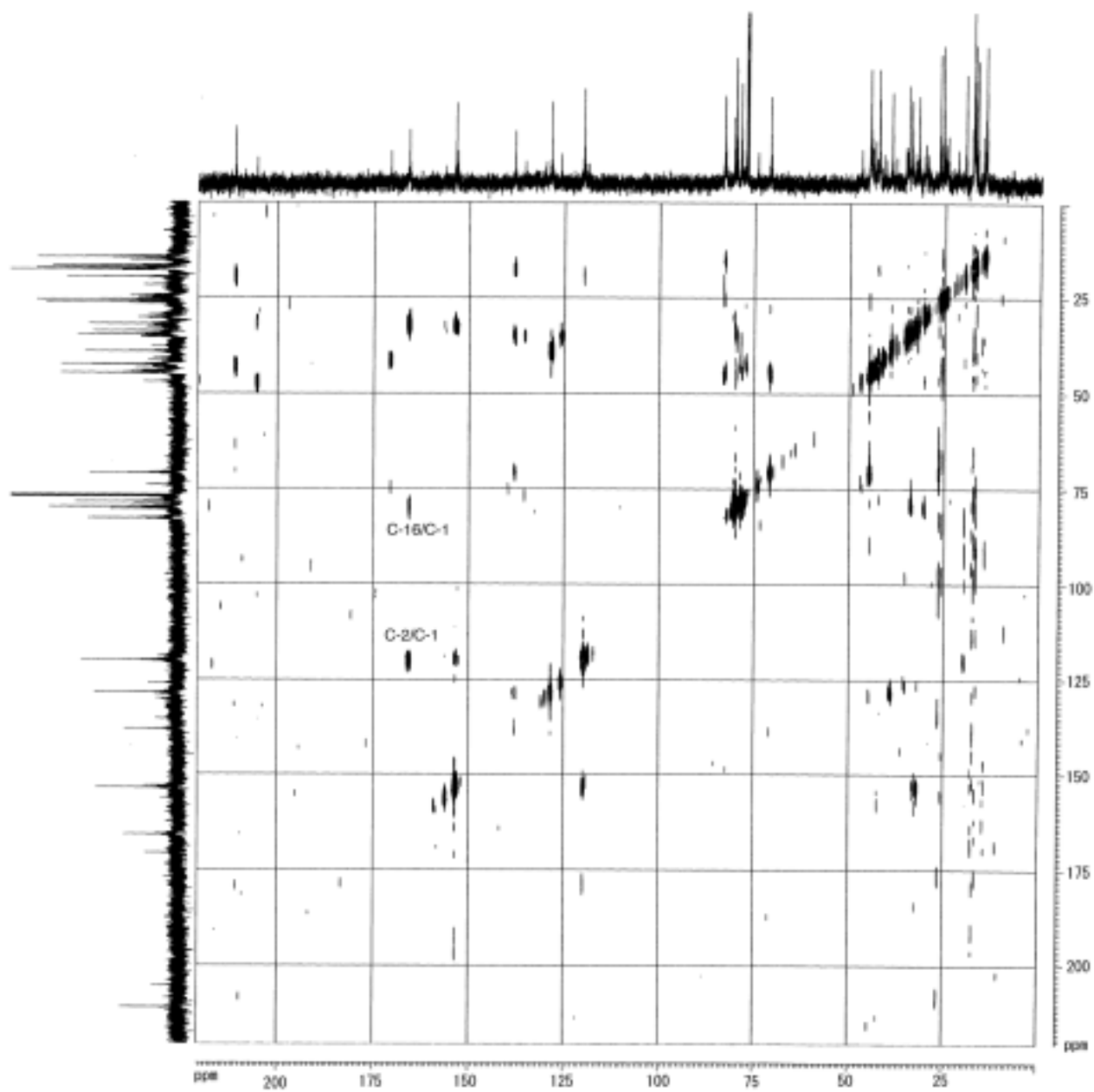
**Figure S6.** NOESY spectrum (positive) of amphidinolide Y (**1**) in CDCl<sub>3</sub>.



**Figure S7.** NOESY spectrum (negative) of amphidinolide Y (**1**) in  $\text{CDCl}_3$ .



**Figure S8.** 2D DEPT C–C LR Relay spectrum (500 MHz) of  $^{13}\text{C}$ -labeled amphidinolide Y (**1**) in  $\text{CDCl}_3$ .



**Figure S9.**  $^1\text{H}$  NMR spectra of amphidinolide X (**2**, red) derived from amphidinolide Y (**1**) and natural specimen (black) in  $\text{CDCl}_3$ .

