

# Supporting Information for

## Nonterpenoid C<sub>15</sub> Acetogenins from *Laurencia marilzae*

Adrián Gutiérrez-Cepeda, José J. Fernández,\* Laura V. Gil, Matías López-Rodríguez, Manuel Norte\*

and María L. Souto\*

Instituto Universitario de Bio-Orgánica “Antonio González”, Universidad de La Laguna,  
Astrofísico Francisco Sánchez 2, 38206 La Laguna, Spain

\*To whom correspondence should be addressed. Tel: +34 922318586. Fax: +34 922318571. E-mail:  
[jjfercas@ull.es](mailto:jjfercas@ull.es); [mnorte@ull.es](mailto:mnorte@ull.es); [msouto@ull.es](mailto:msouto@ull.es).

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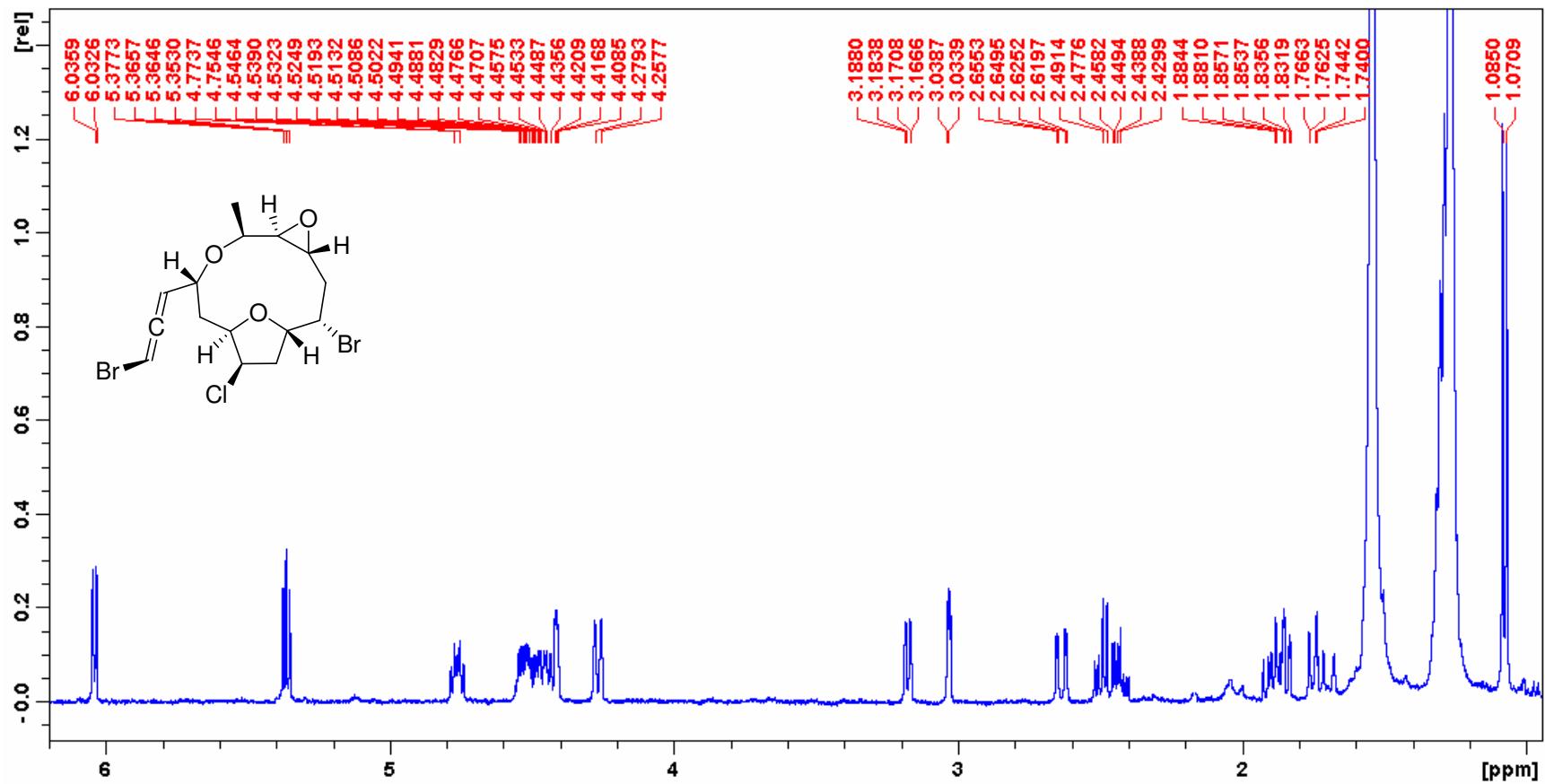
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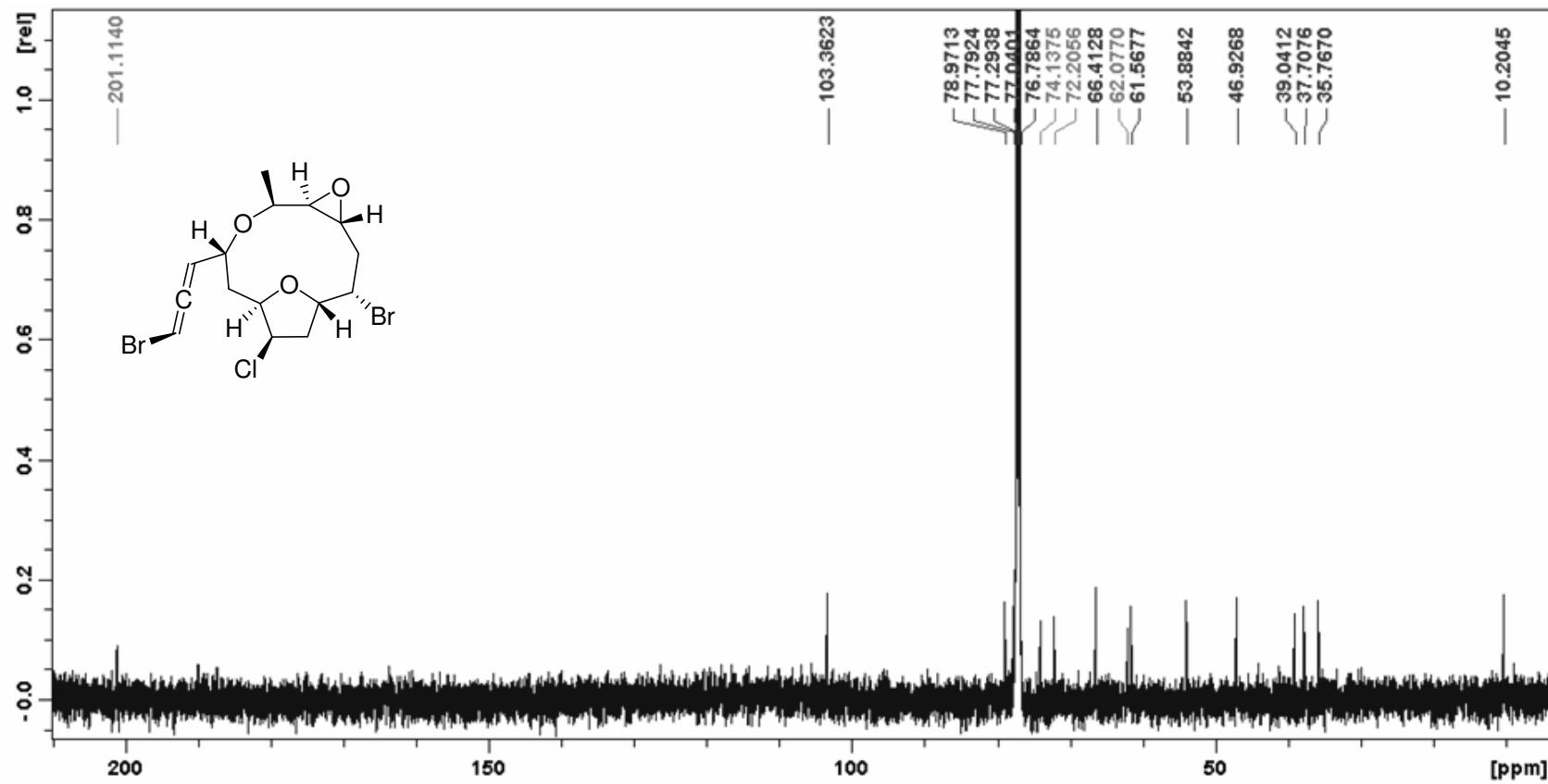
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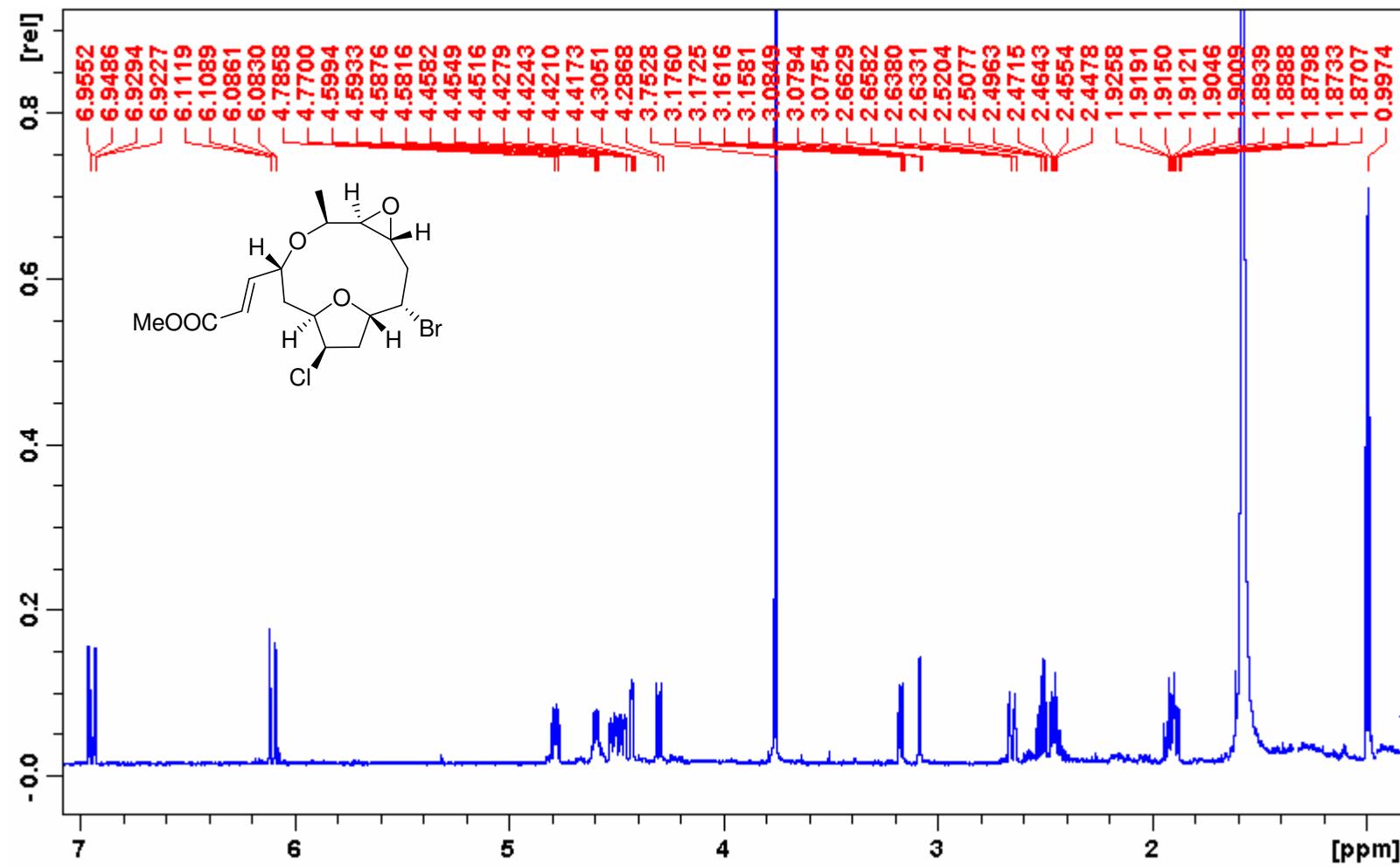
**Figure S1.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of 12-epoxy-obtusallene IV (**1**).



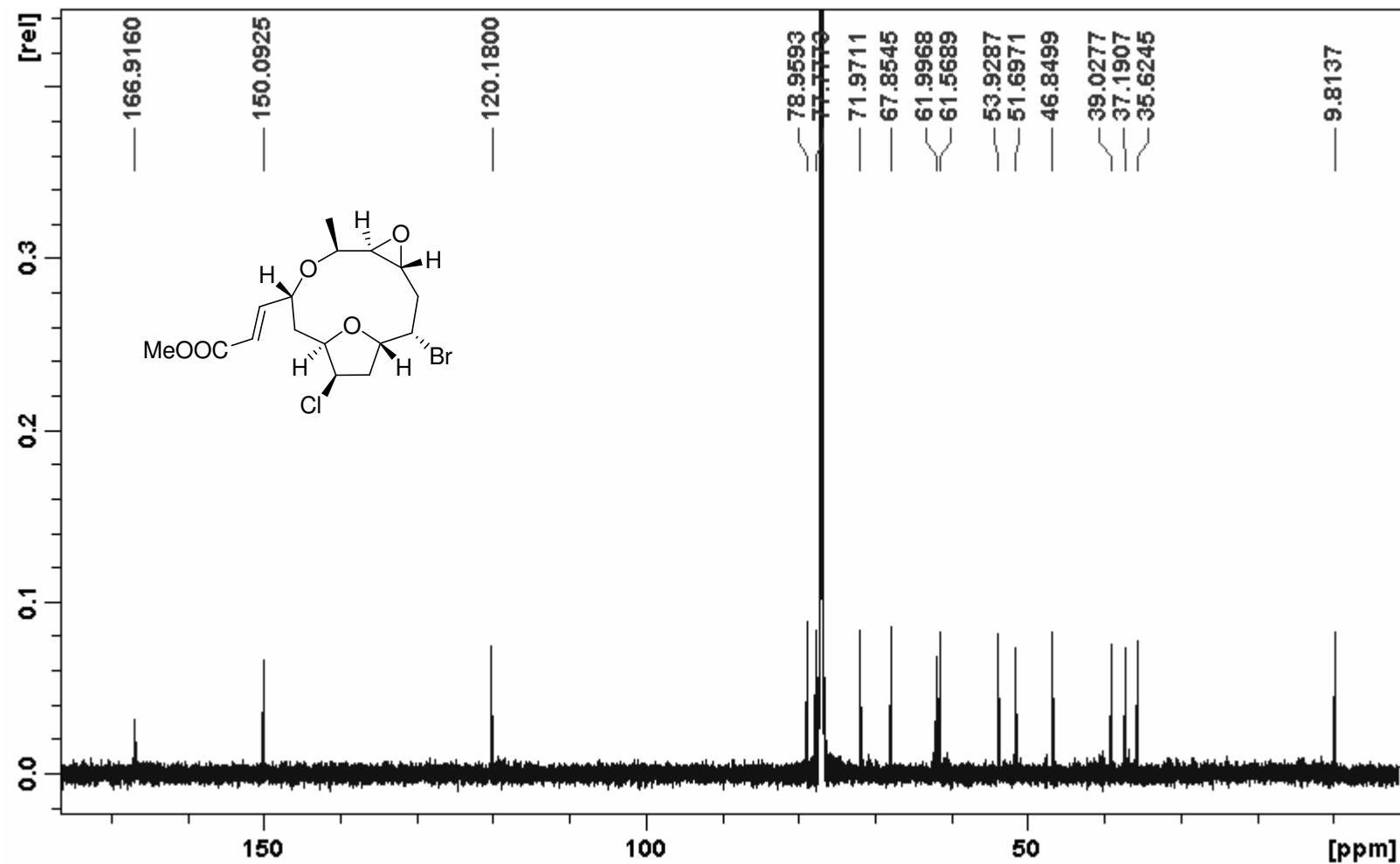
**Figure S2.**  $^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ ) of 12-epoxy-obtusallene IV (**1**).



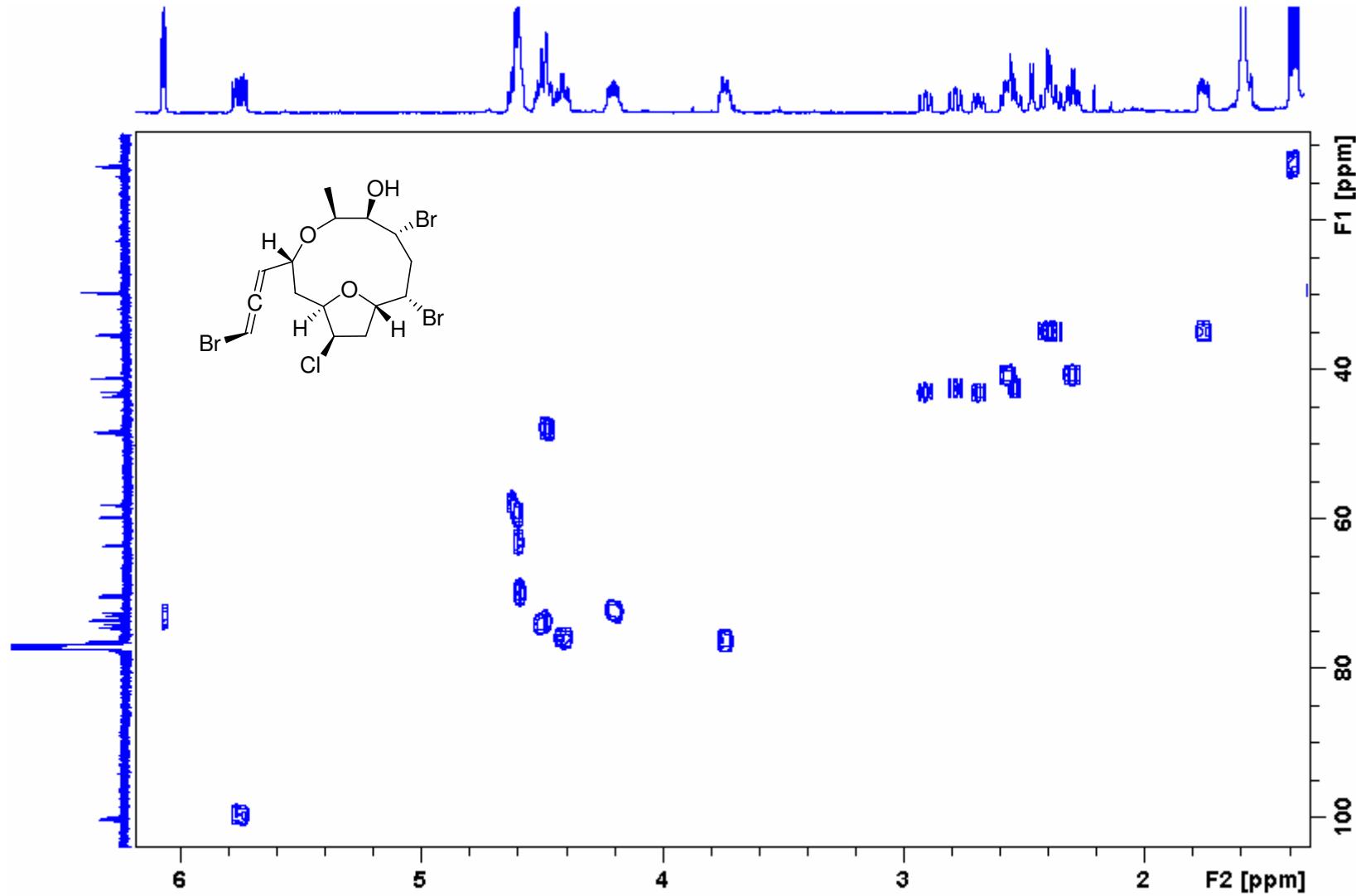
**Figure S3.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of compound 2.



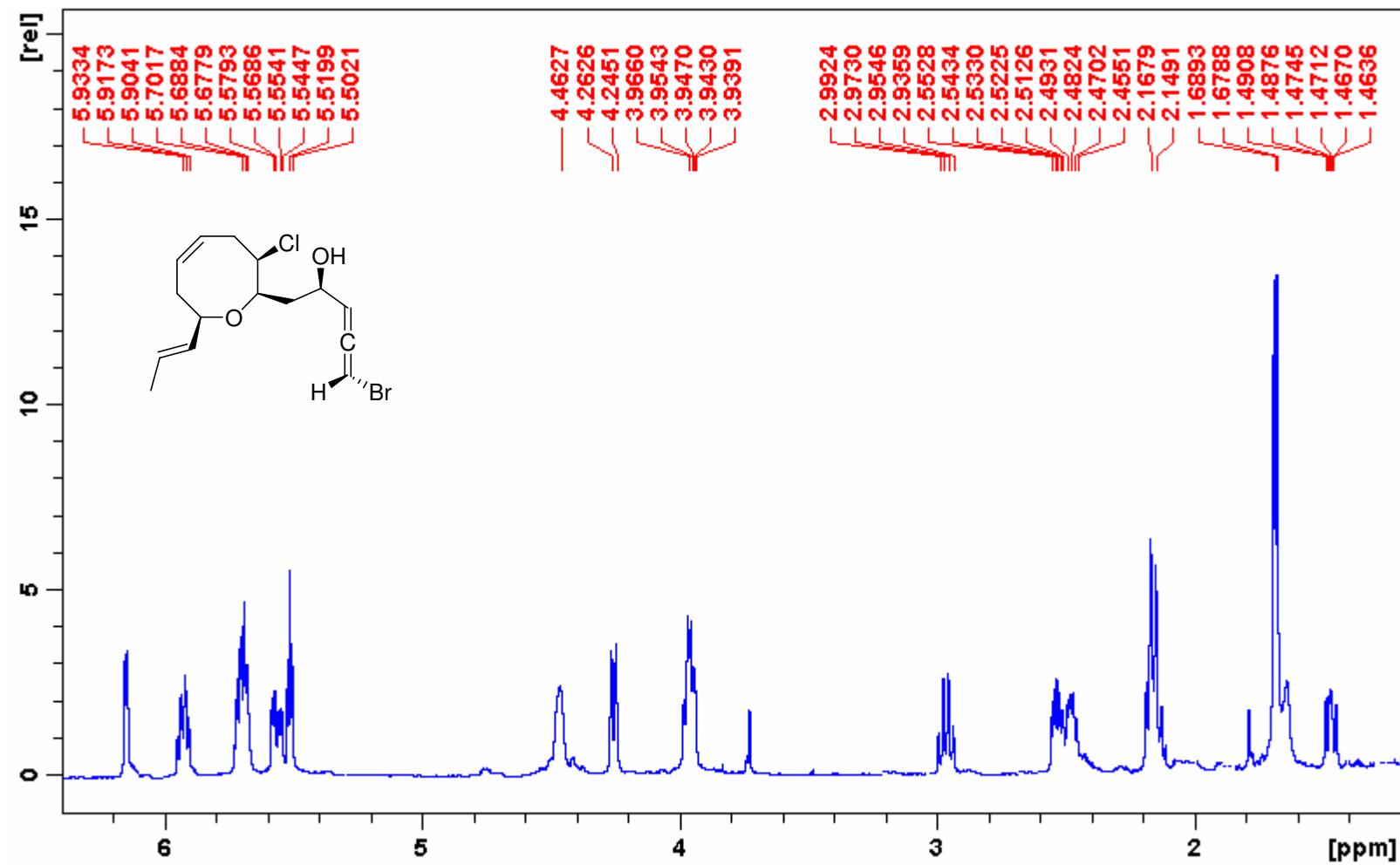
**Figure S4.**  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of compound **2**.



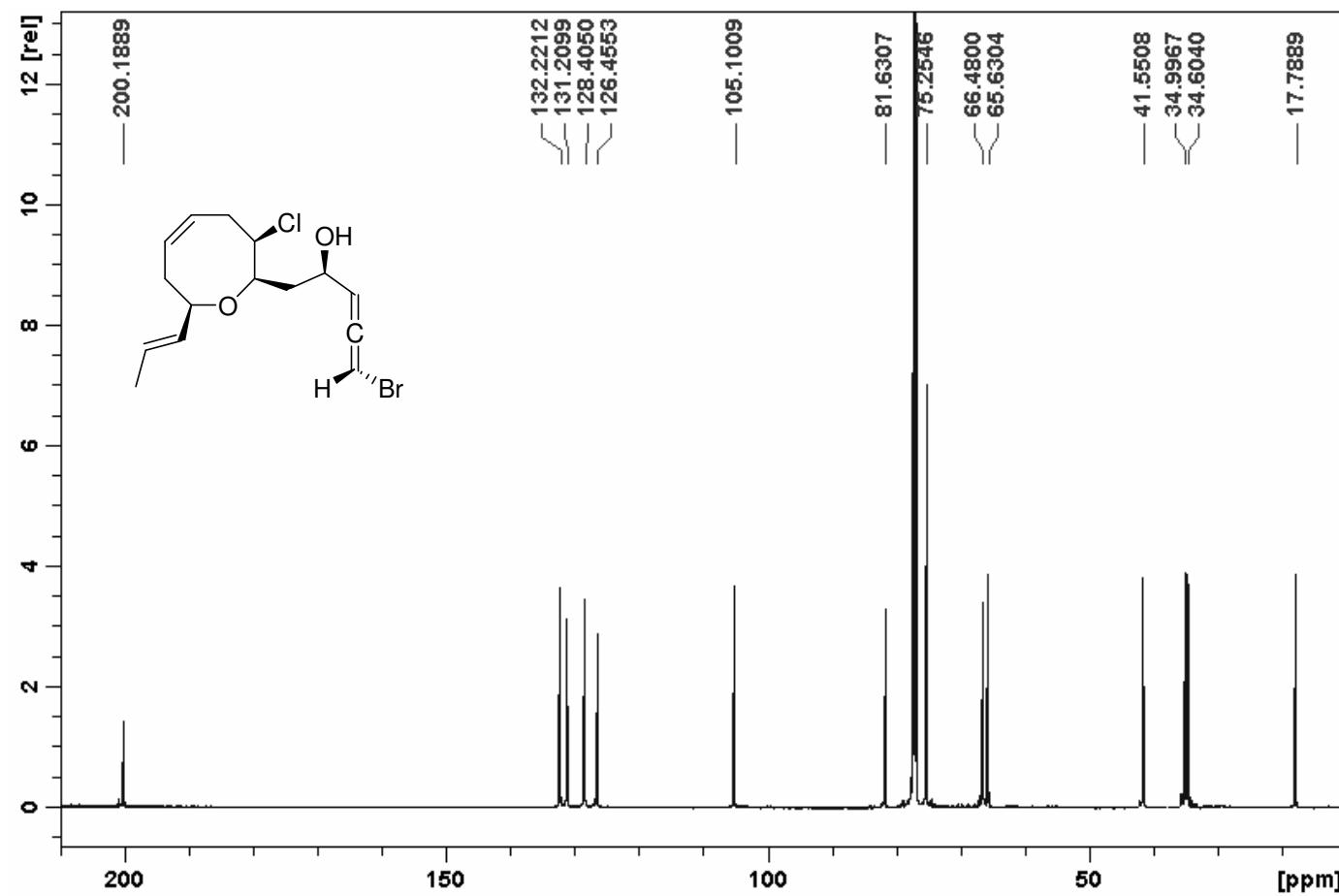
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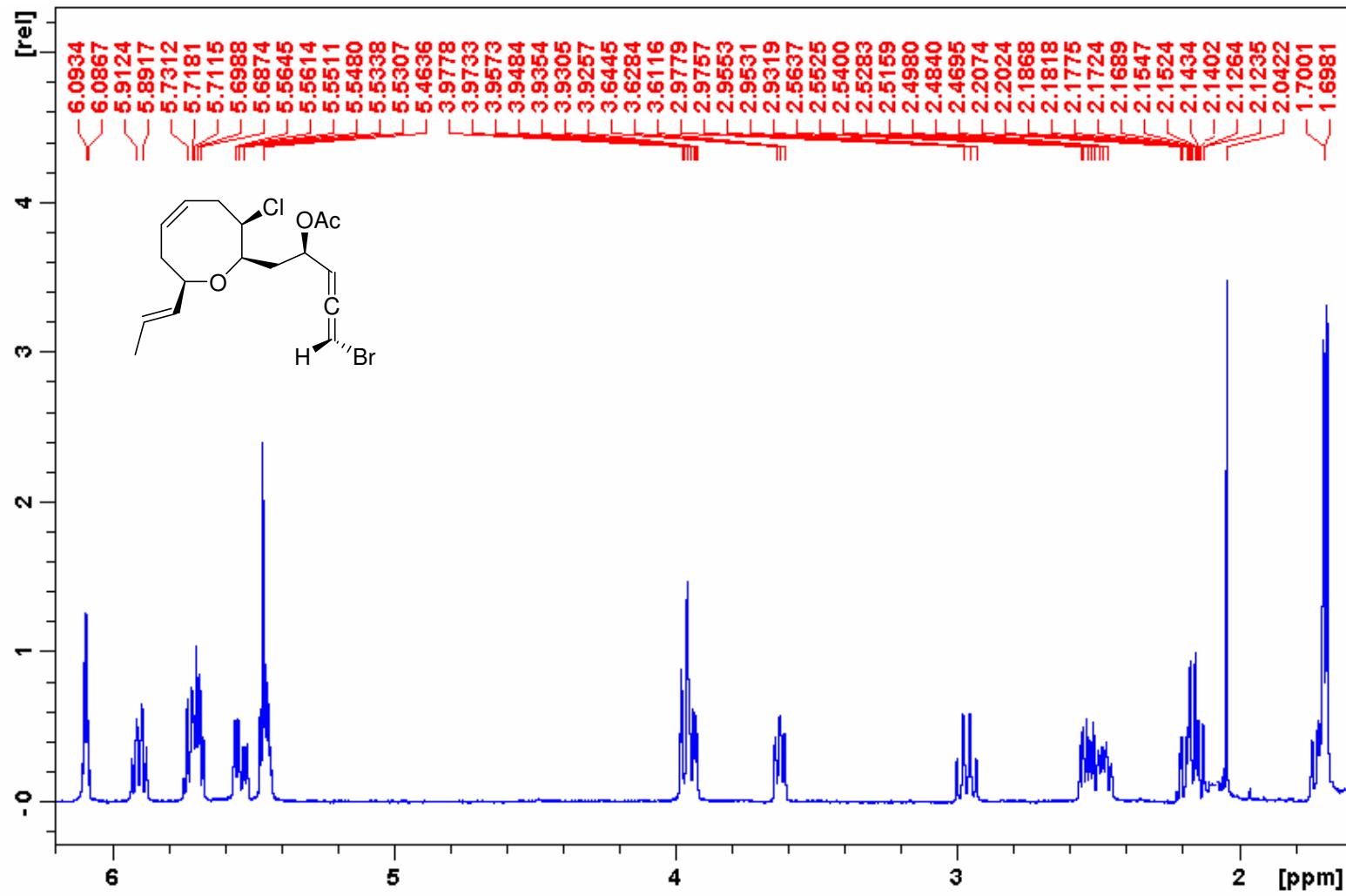
**Figure S6.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of marilzallene (**4**).



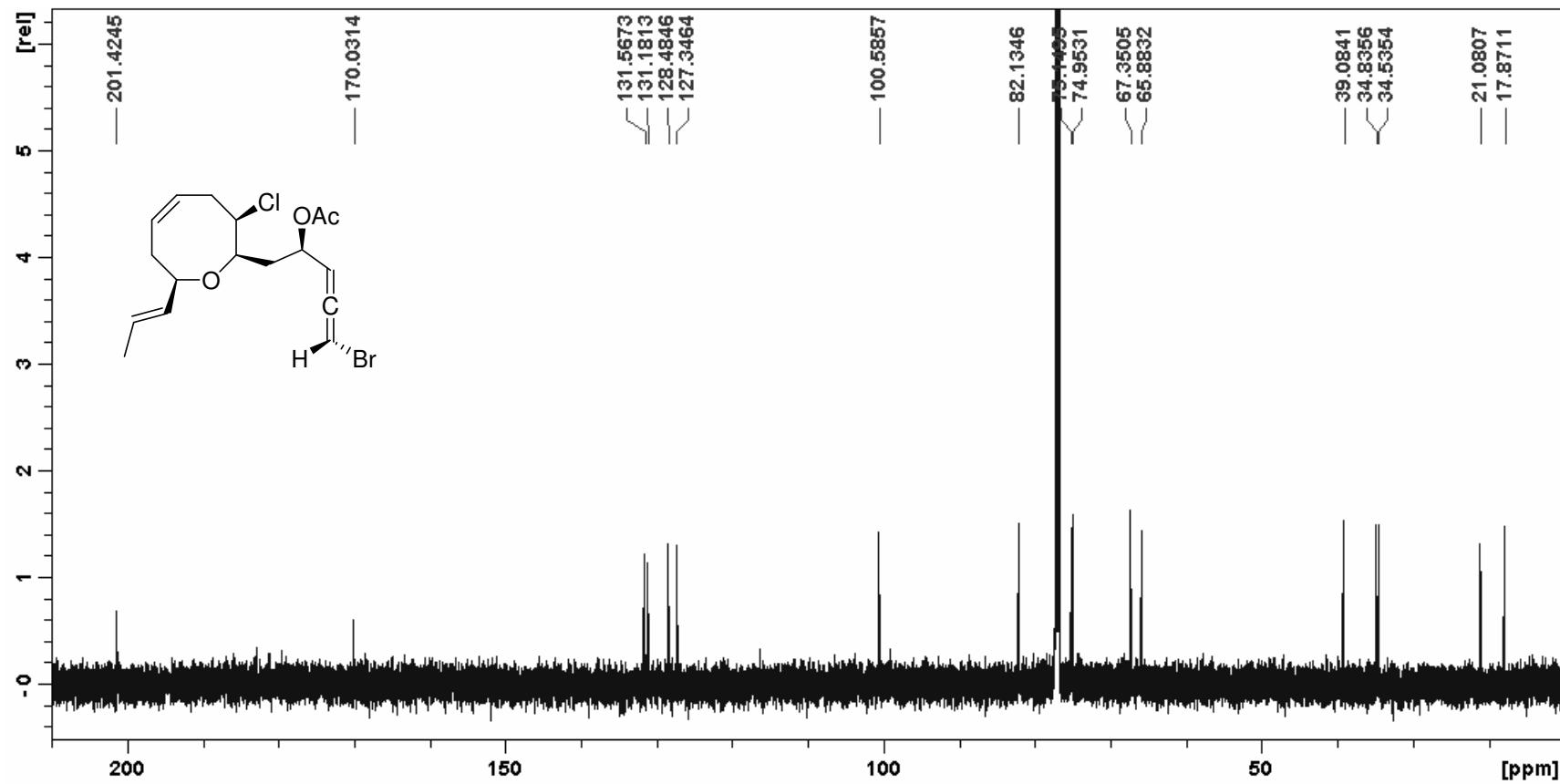
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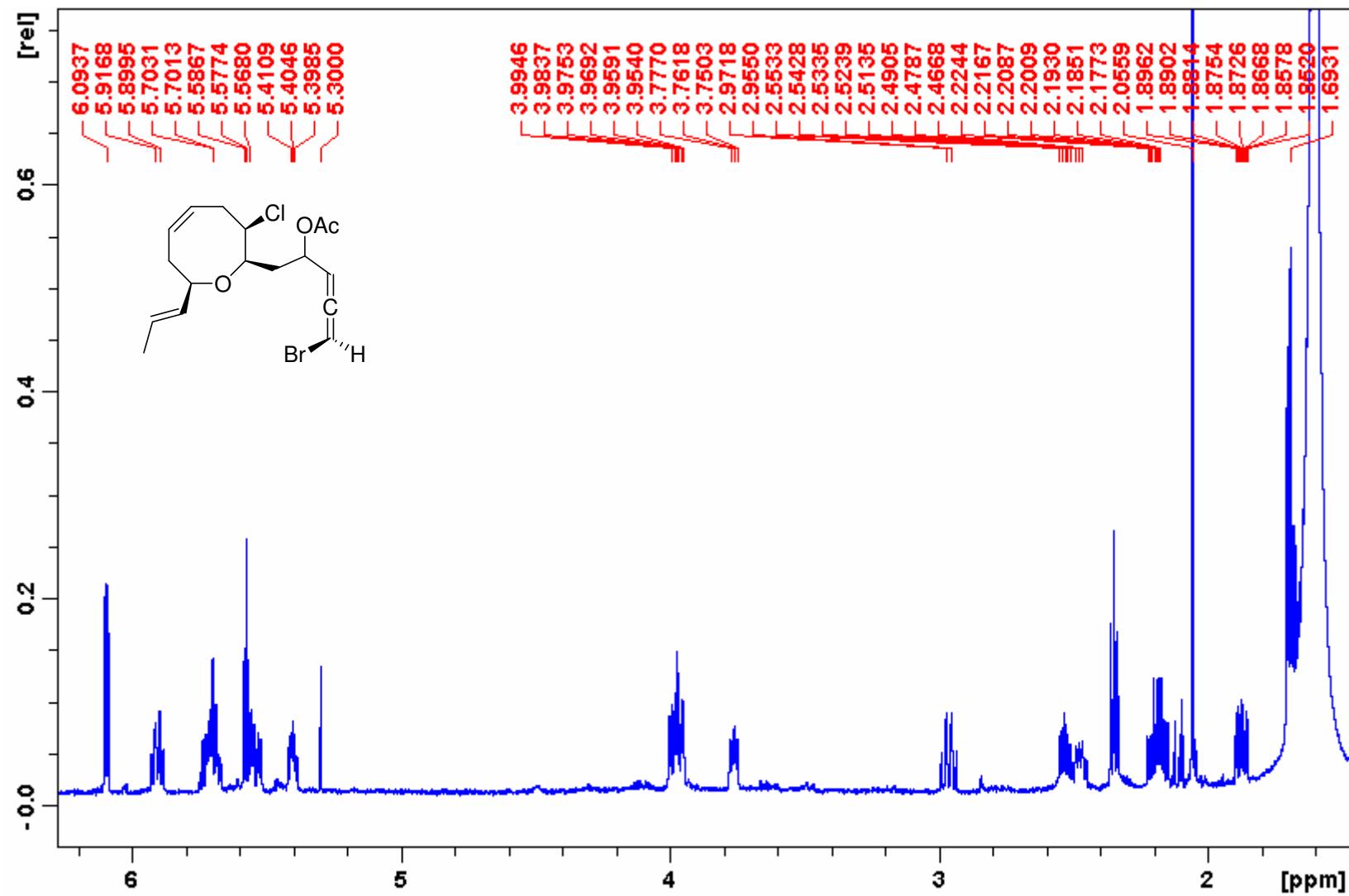
**Figure S8.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of (+)-4-acetoxy-marilzallene (**5**).



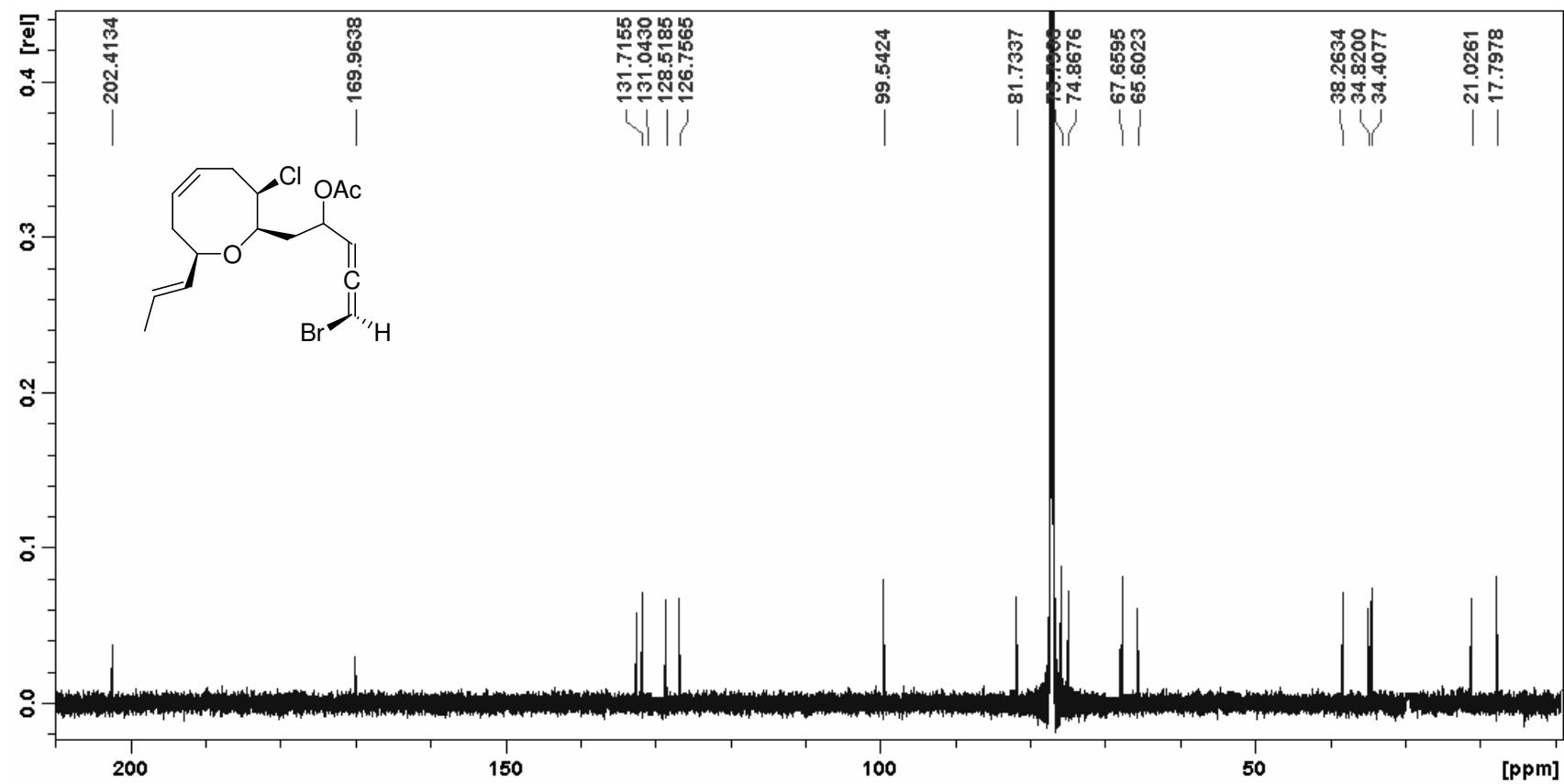
**Figure S9.**  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of (+)-4-acetoxy-marilzallene (**5**).



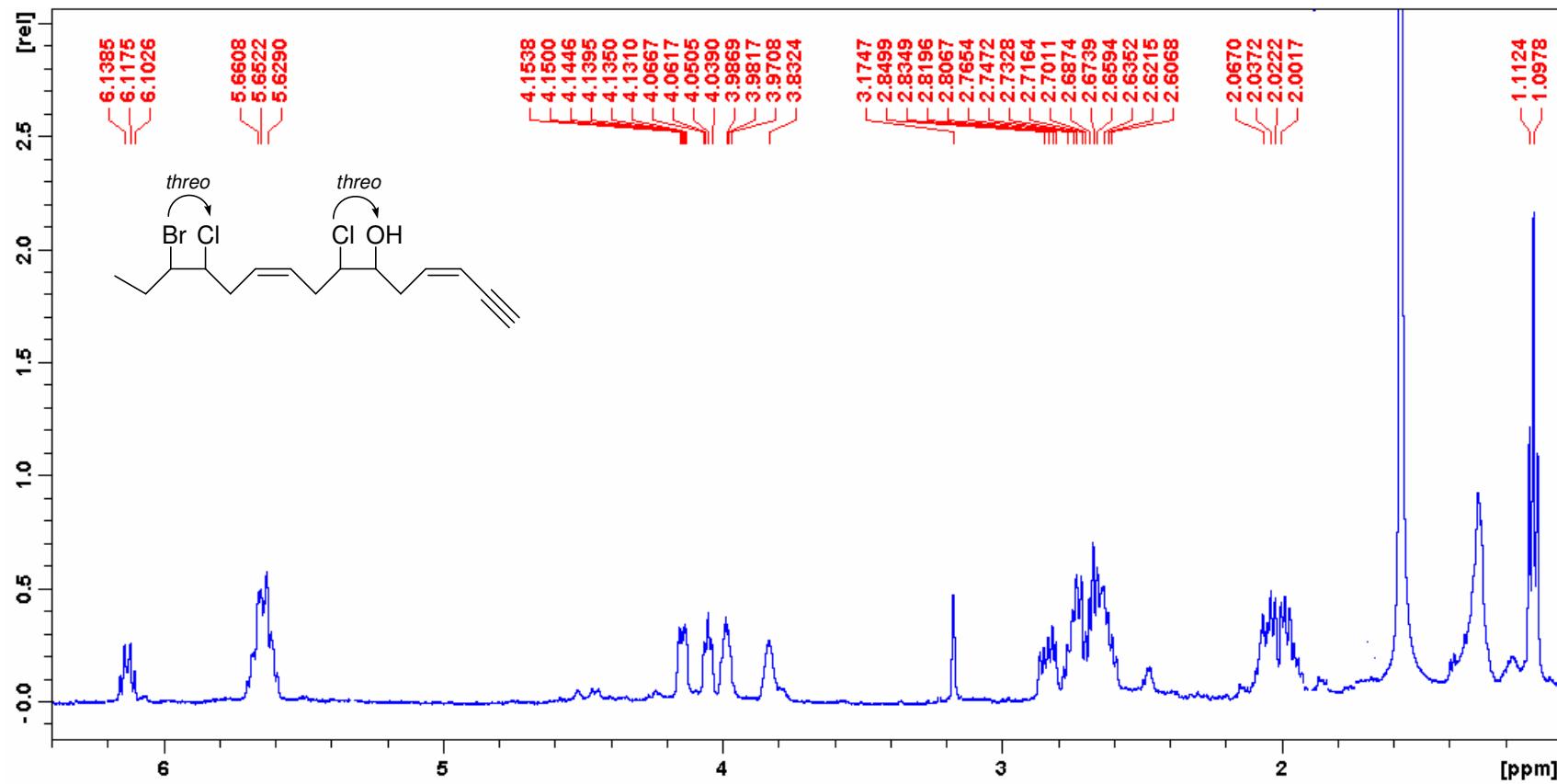
**Figure S10.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of ( $-$ )-4-acetoxy-marilzallene (**6**).



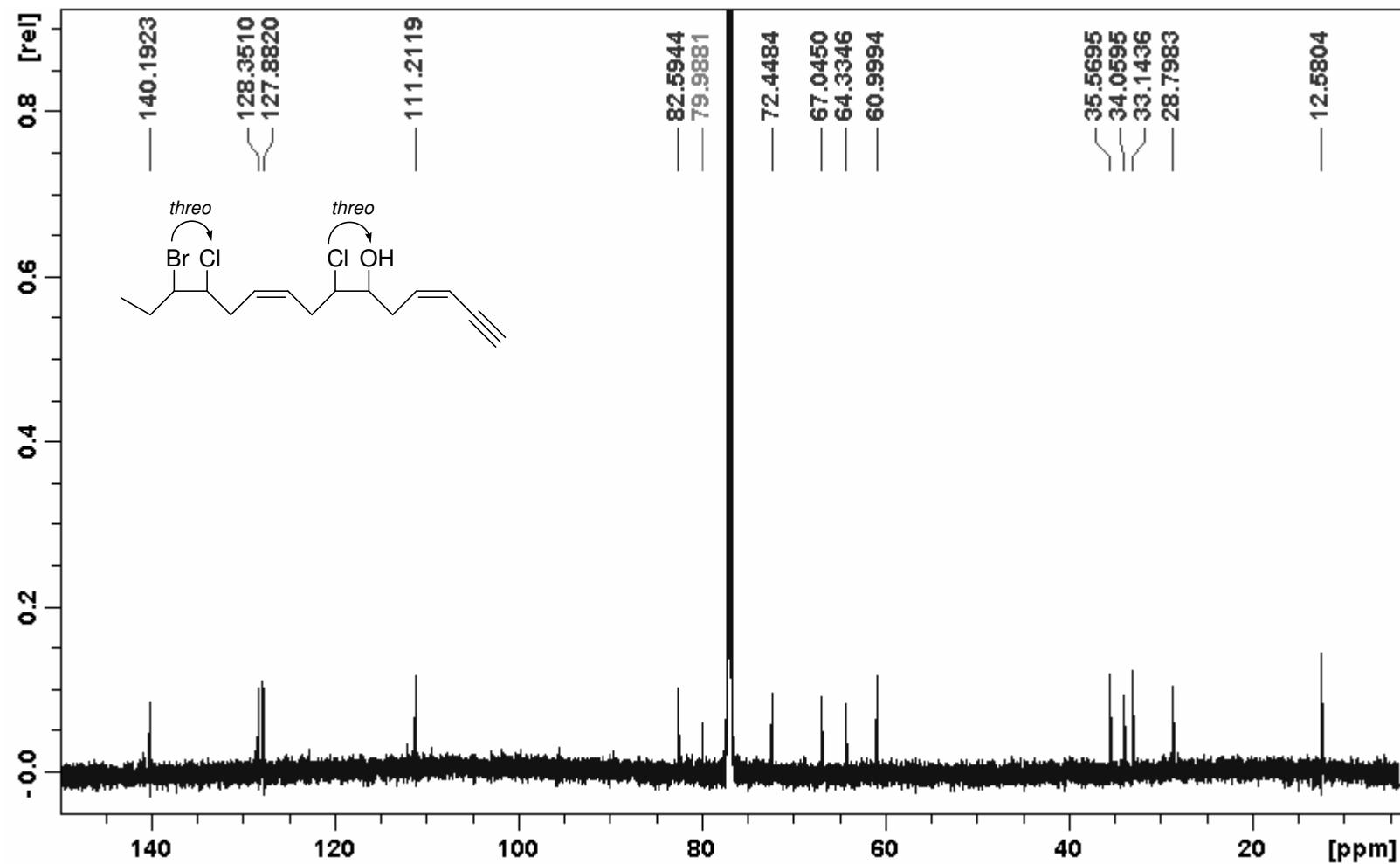
**Figure S11.**  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of ( $-$ )-4-acetoxy-marilzallene (**6**).



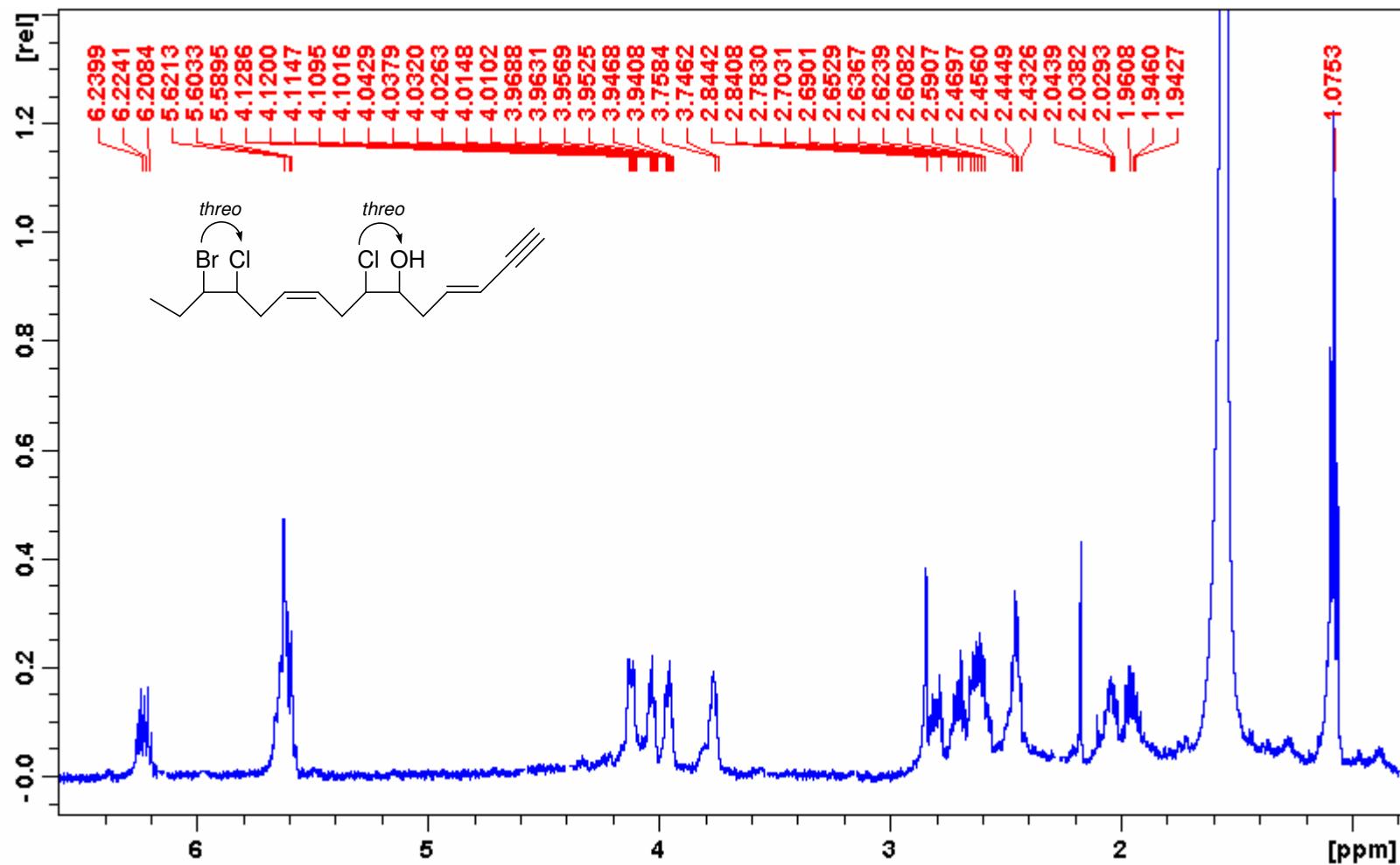
**Figure S12.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of Z-adrienyne (**7**).



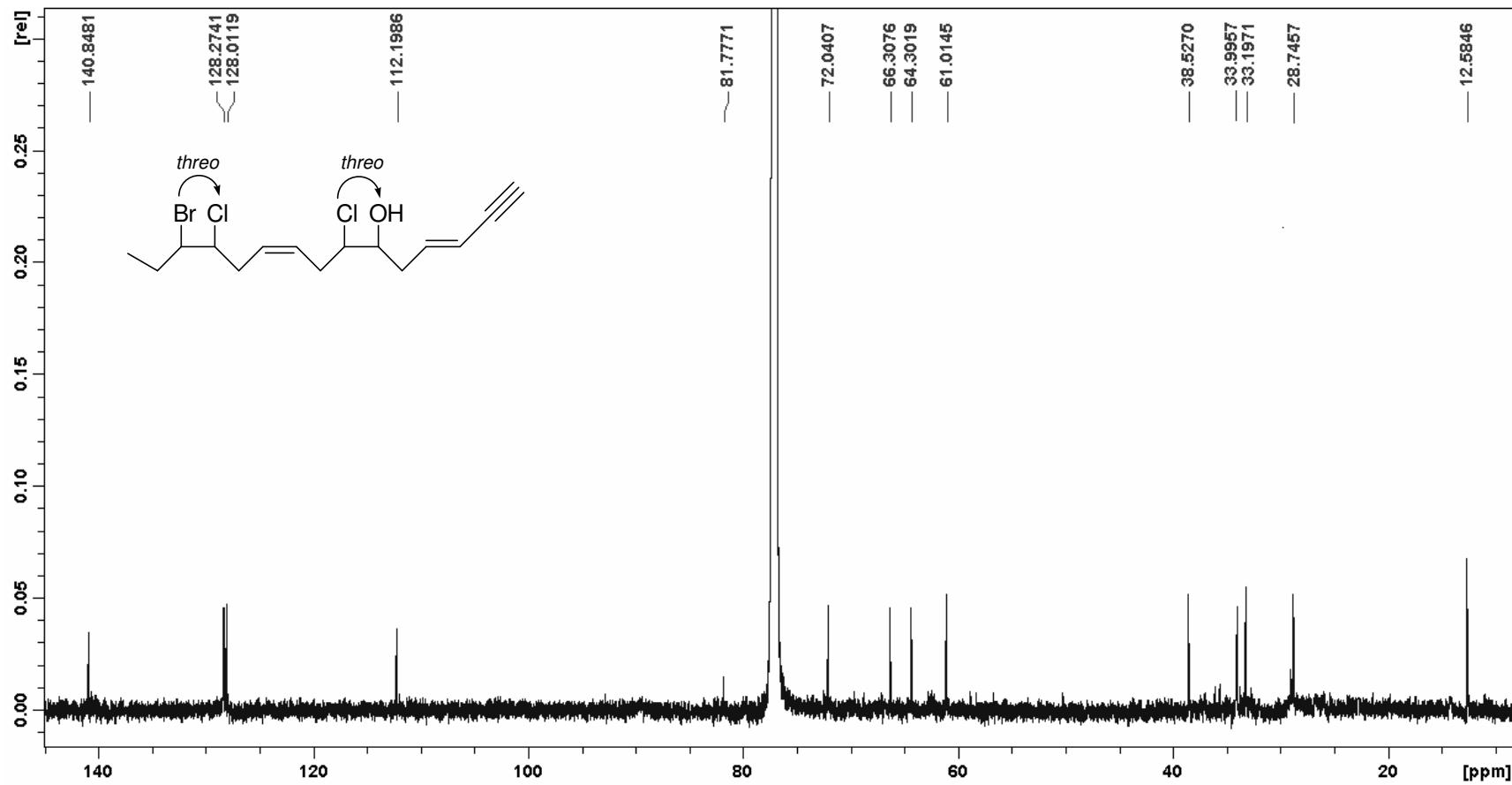
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**Table S1.** NMR Spectroscopic Data for the Observed Obtusallene X (**3**) Conformers in C<sub>6</sub>D<sub>6</sub> and CD<sub>3</sub>OD.

	3a-C <sub>6</sub> D <sub>6</sub> <sup>c</sup>		3b-C <sub>6</sub> D <sub>6</sub> <sup>c</sup>		3a-CD <sub>3</sub> OD <sup>d</sup>		3b-CD <sub>3</sub> OD	
position	δ <sub>C</sub> mult.	δ <sub>H</sub> (J in Hz)	δ <sub>C</sub>	δ <sub>H</sub> (J in Hz)	δ <sub>C</sub>	δ <sub>H</sub> (J in Hz)	δ <sub>C</sub>	δ <sub>H</sub> (J in Hz)
1	72.5, CH	5.57, br d (5.6)	[a]	[a]	72.7	6.31, br d (5.7)	[a]	[a]
2 <sup>b</sup>								
3	100.0, CH	5.22, dd (5.7, 8.8)	100.2	5.20, dd (5.6, 8.7)	100.7	5.71, dd (5.4, 5.7)	100.8	5.69, dd (5.4, 5.7)
4	69.8, CH	4.10, m	[a]	[a]	69.2	4.54, m	[a]	[a]
5	34.7, CH <sub>2</sub>	β 2.02, m α 1.19, m	[a]	[a] [a]	35.4	β 2.17, m α 1.73, ddd (3.2, 8.6, 14.5)	[a]	β 2.14, m [a]
6	75.6, CH	3.66, m	[a]	[a]	76.6	4.35, ddd (3.2, 4.0, 10.9)	[a]	4.32, ddd (3.2, 3.9, 11.0)
7	59.1, CH	3.82, br d (7.2)	59.2	3.80, br d (8.3)	60.8	4.63, m	[a]	[a]
8	40.5, CH <sub>2</sub>	α 2.00, m β 1.70, ddd (5.2, 8.9, 14.3)	[a]	[a]	40.3	α 2.64, dddd (1.9, 6.8, 8.8, 14.3) β 2.31, dddd (1.0, 3.8, 6.3, 14.3)	[a]	α 2.61, m [a]
9	73.3, CH	3.97, ddd (2.6, 5.4, 8.9)	73.7	3.95, ddd (3.3, 5.7, 9.4)	75.6	4.60, m	74.6	[a]
10	48.7, CH	4.13, m	48.4	4.09, m	48.6	4.61, m	[a]	4.58, m
11	43.4, CH <sub>2</sub>	2.47 (2H), m	43.0	2.33 (2H), m	44.2	α 2.92, ddd (1.2, 12.7, 15.6) β 2.59, ddd (2.1, 9.9, 15.6)	43.4	α 2.82, ddd (1.2, 11.7, 15.2) β 2.44, ddd (2.3, 9.7, 15.2)
12	58.5, CH	4.28, ddd (2.4, 6.2, 8.2)	63.6	4.24, ddd (2.4, 7.3, 9.5)	55.0	4.67, ddd (1.2, 4.9, 9.9)	60.8	4.62, m
13	76.3, CH	3.21, dd (4.0, 6.2)	[a]	3.24, dd (4.1, 7.3)	76.6	3.70, dd (3.3, 4.9)	[a]	3.77, dd (3.4, 4.5)
14	72.1, CH	3.66, m	72.3	3.69, m	74.3	4.17, dd (3.3, 6.7)	74.5	4.14, ddd (3.4, 6.8)
15	12.7, CH <sub>3</sub>	1.33, m	12.5	1.32, m	11.4	1.36, d (6.7)	11.1	1.34, d (6.8)

[a] Signal overlapped by the resonance of the conformer **3a**. <sup>b</sup> Signal not observed. <sup>c</sup> Data recorded at 600/150 MHz (<sup>1</sup>H/<sup>13</sup>C nuclei). <sup>d</sup> Data recorded at 500/125MHz (<sup>1</sup>H/<sup>13</sup>C nuclei).

**Table S2.** NMR Spectroscopic Data for Marilzallene (**4**) in pyridine-*d*<sub>5</sub>.

Marilzallene ( <b>4</b> ) <sup>a</sup>		
position	$\delta_{\text{C}}$ mult.	$\delta_{\text{H}}$ ( <i>J</i> in Hz)
1	74.8, CH	6.47, dd (1.8, 5.9)
2	201.1, C	
3	107.0, CH	5.81, dd (5.9, 5.9)
4	65.8, CH	4.86, dddd (1.8, 2.5, 5.9, 10.8)
5	43.1, CH <sub>2</sub>	$\beta$ 2.40, ddd (2.5, 10.4, 14.0) $\alpha$ 1.86, ddd (2.1, 10.8, 14.0)
6	76.1, CH	4.65, ddd (2.1, 2.1, 10.4)
7	68.2, CH	4.18, ddd (2.1, 4.7, 11.4)
8	35.6, CH <sub>2</sub>	$\beta$ 3.15, ddd (10.9, 11.4, 11.9) $\alpha$ 2.55, ddd (4.7, 5.5, 11.9)
9	129.2, CH	5.66, ddd (5.5, 10.1, 10.9)
10	131.8, CH	5.86, ddd (7.2, 8.5, 10.1)
11	35.7, CH <sub>2</sub>	$\beta$ 2.50, ddd (7.2, 9.3, 14.1) $\alpha$ 2.14, br dd (8.5, 14.1)
12	81.8, CH	4.27, br dd (5.6, 9.3)
13	133.7, CH	5.61, ddd (1.1, 5.6, 15.5)
14	125.7, CH	5.69, dd (6.3, 15.5)
15	18.1, CH <sub>3</sub>	1.54, dd (1.1, 6.3)

<sup>a</sup> Data recorded at 600/150 MHz (<sup>1</sup>H/<sup>13</sup>C nuclei).