

## Supporting Information

### Stereoselective Total Synthesis of (–)-Cleistenolide

Chao Cai<sup>1,2</sup>, Jun Liu<sup>1</sup>, Yuguo Du<sup>\*1,2</sup> and Robert J. Linhardt<sup>\*3</sup>

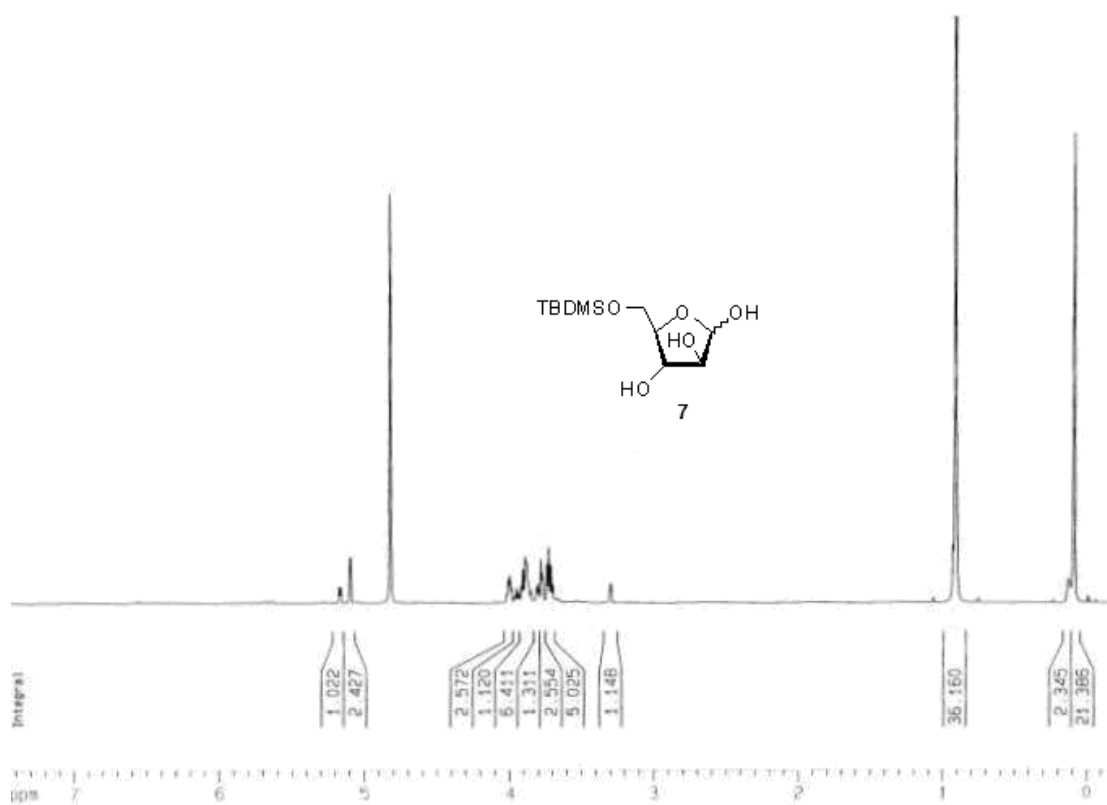
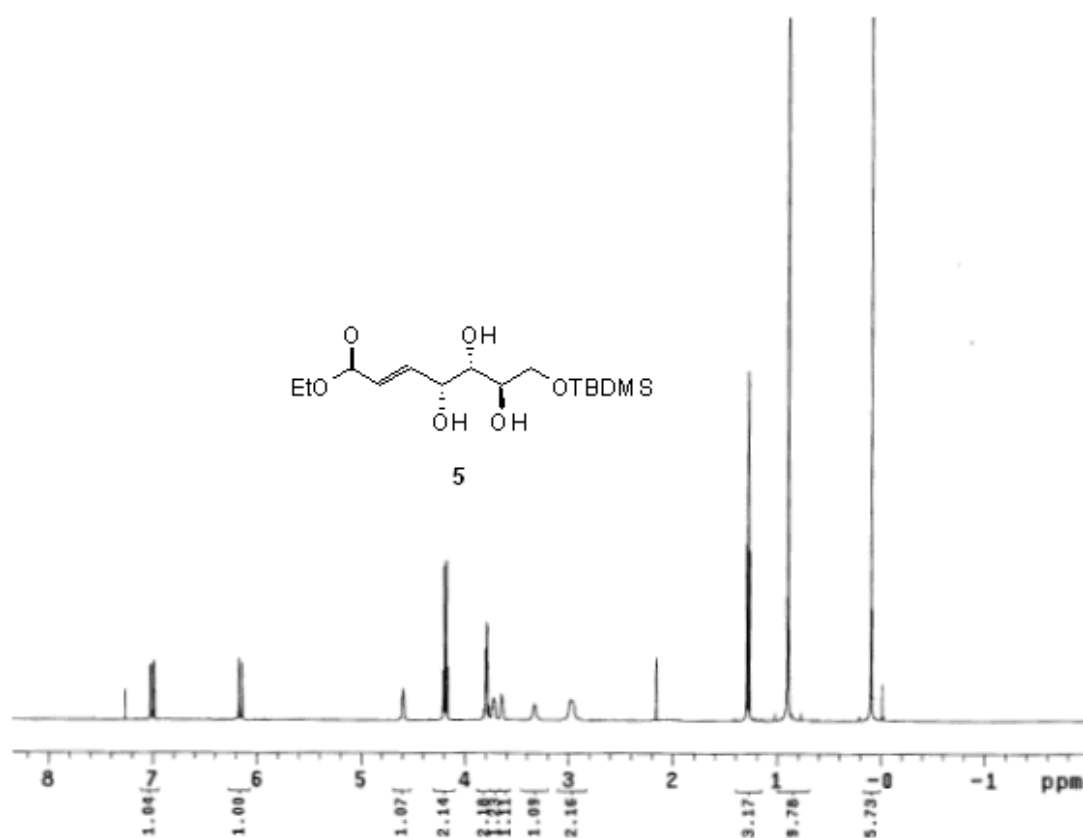
<sup>1</sup>State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China, <sup>2</sup>College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, China, and <sup>3</sup>Departments of Chemistry, Biology, and Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

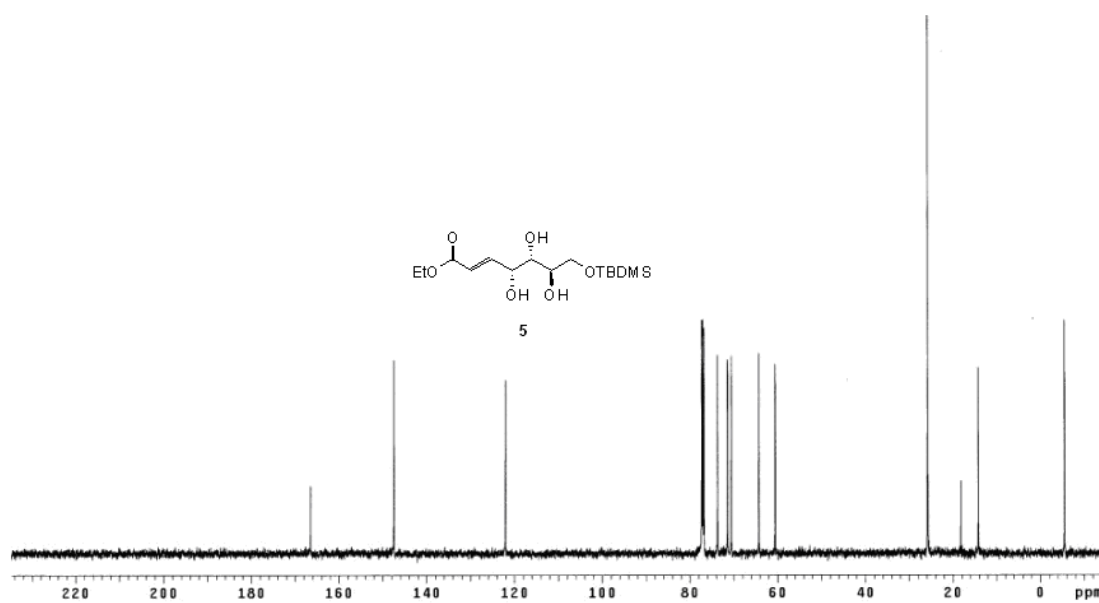
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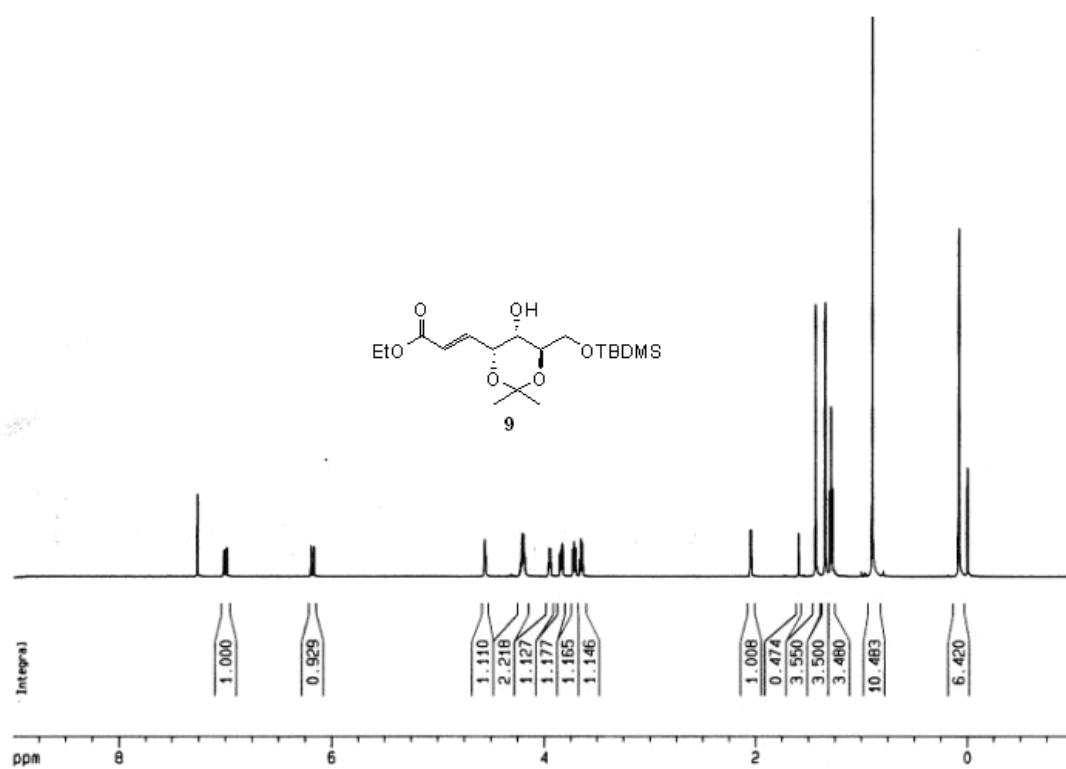
## Experimental section

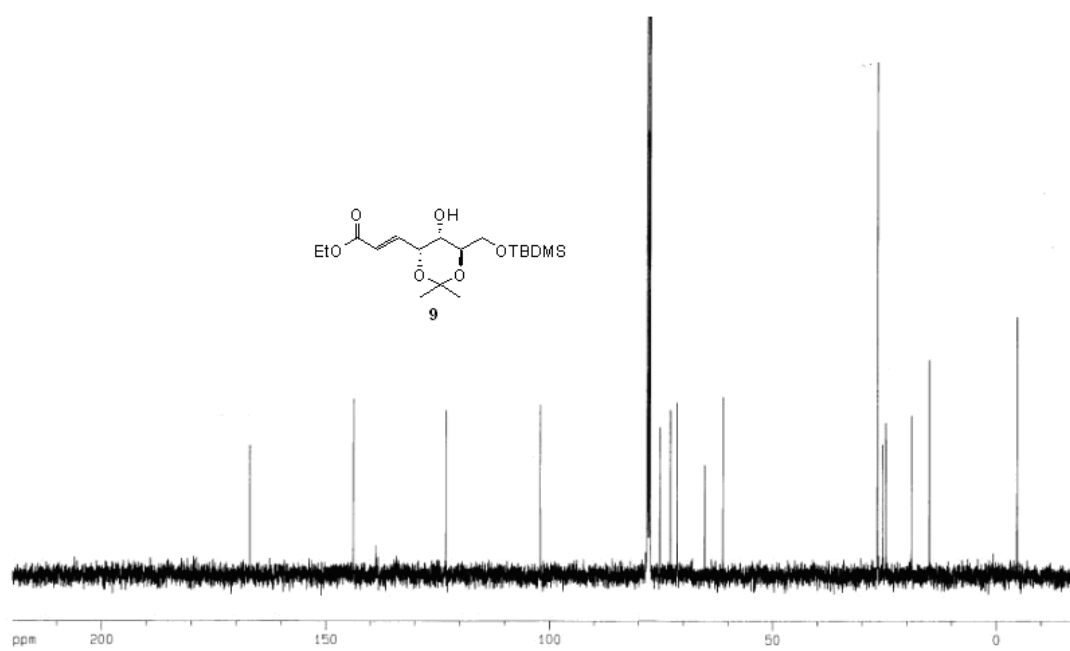
**General methods:** Optical rotations were determined at 25°C with an automatic polarimeter.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with 500 or 600 MHz spectrometer for solutions in  $\text{CDCl}_3$  or  $\text{CD}_3\text{OD}$ . Mass spectra were measured using electrospray ionization mass spectrometer (ESI-MS).

$^1\text{H}$  NMR for compound 7 $^1\text{H}$  and  $^{13}\text{C}$  NMR for compound 5

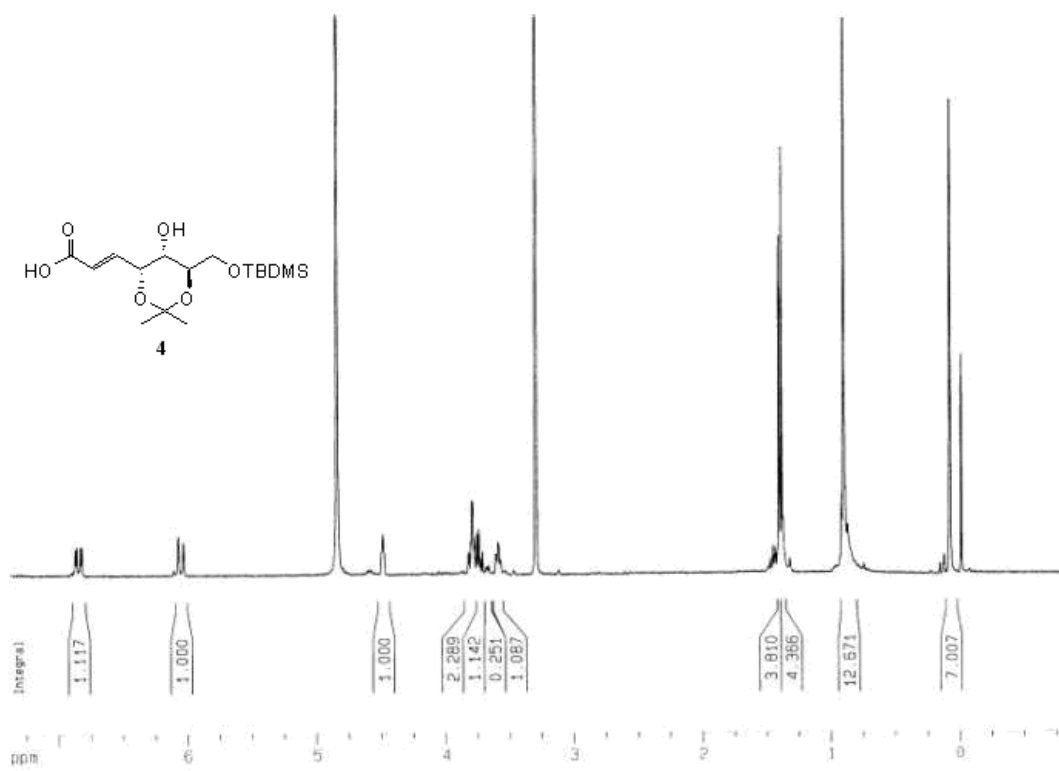


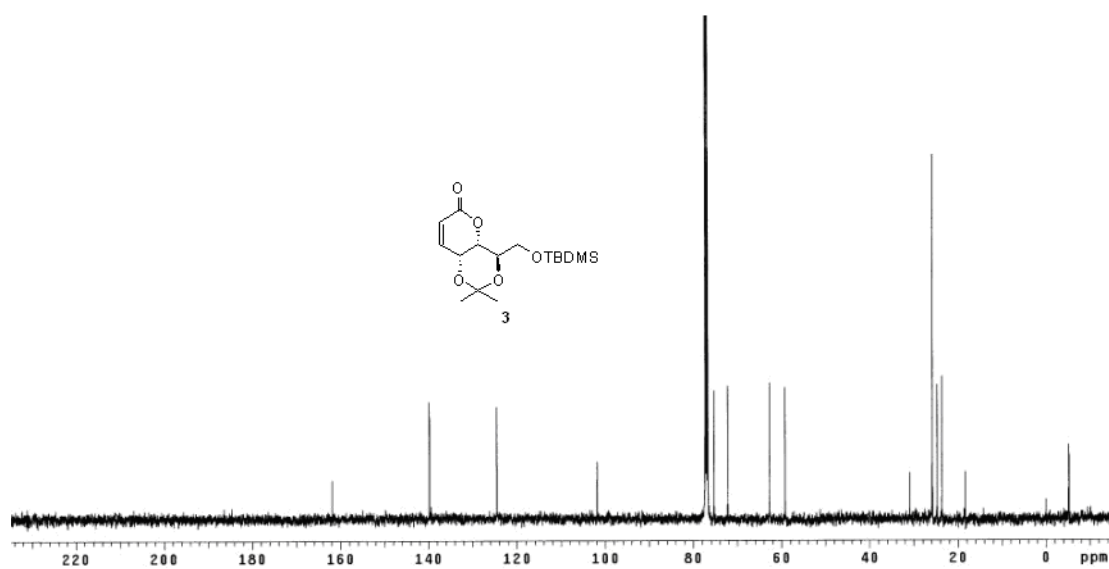
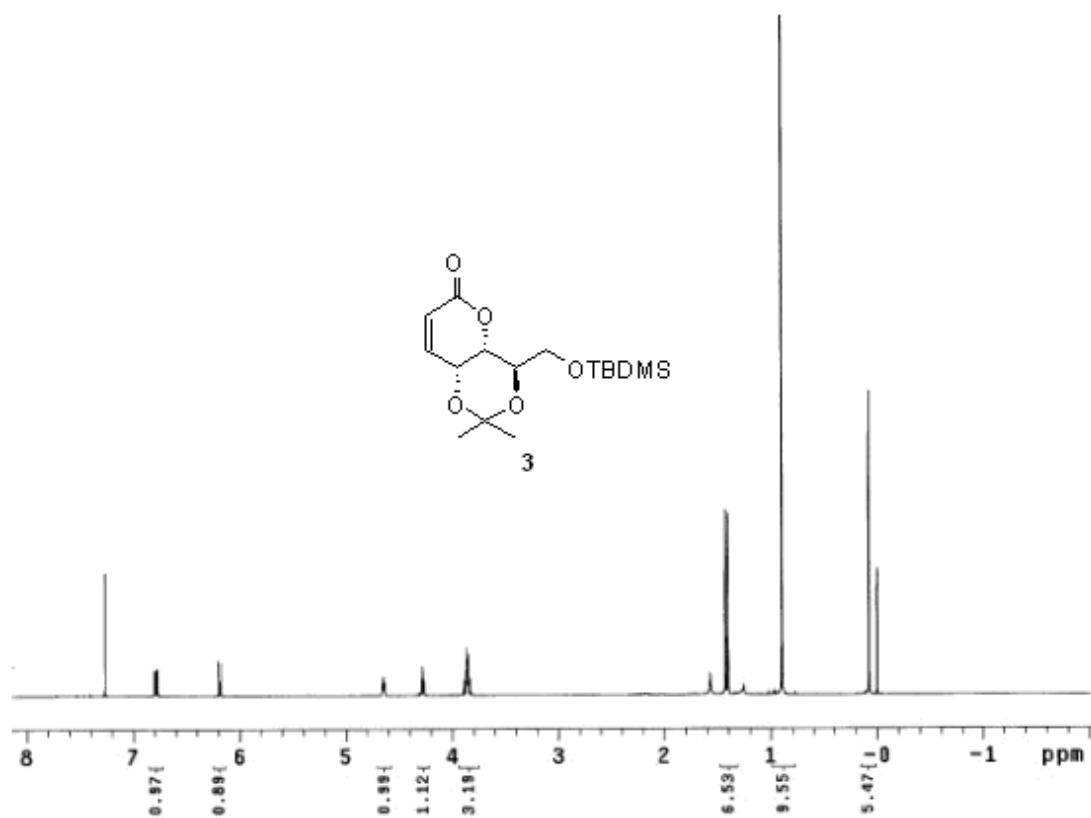
<sup>1</sup>H and <sup>13</sup>C NMR for compound **9**

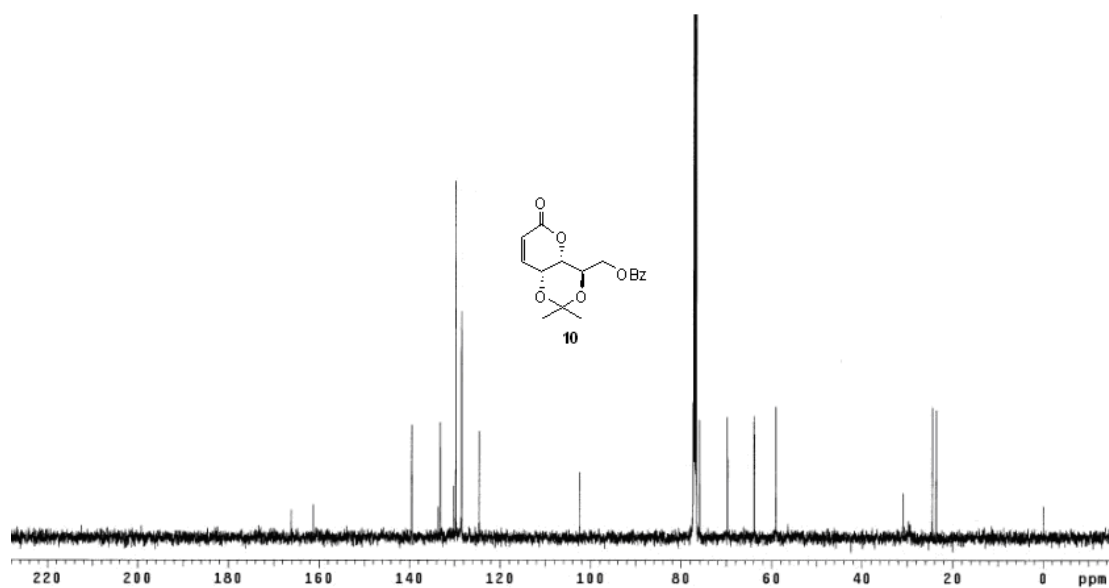
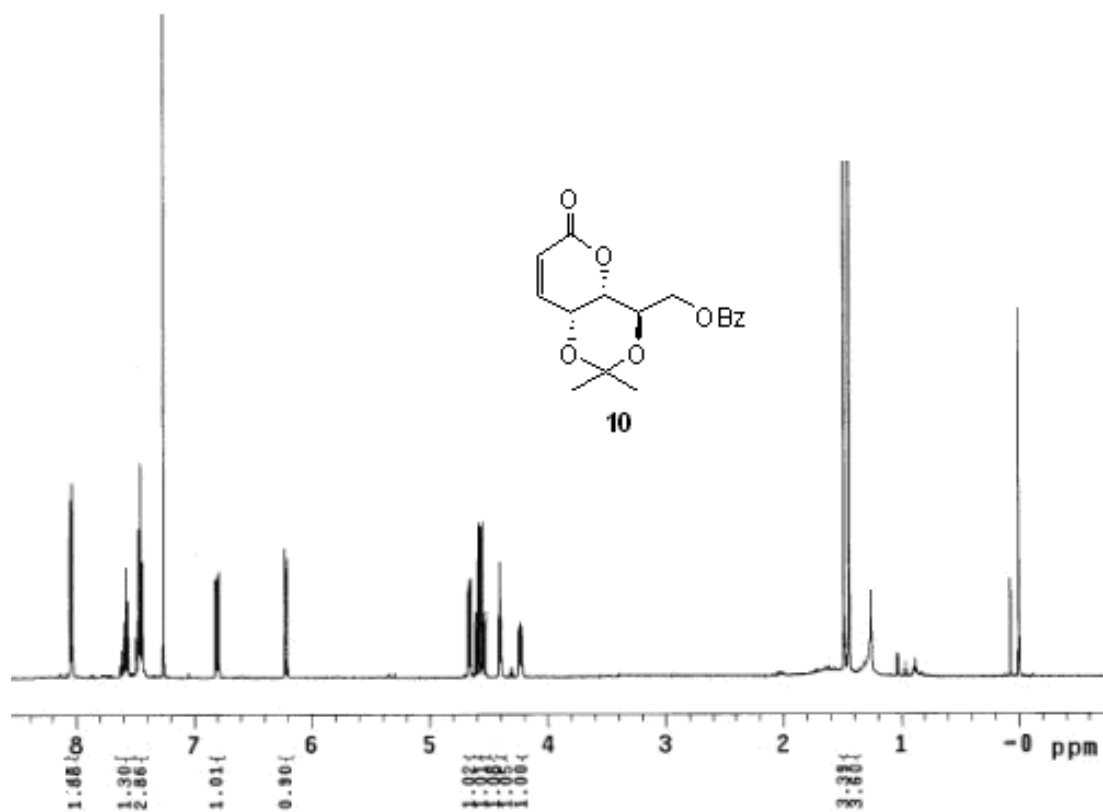


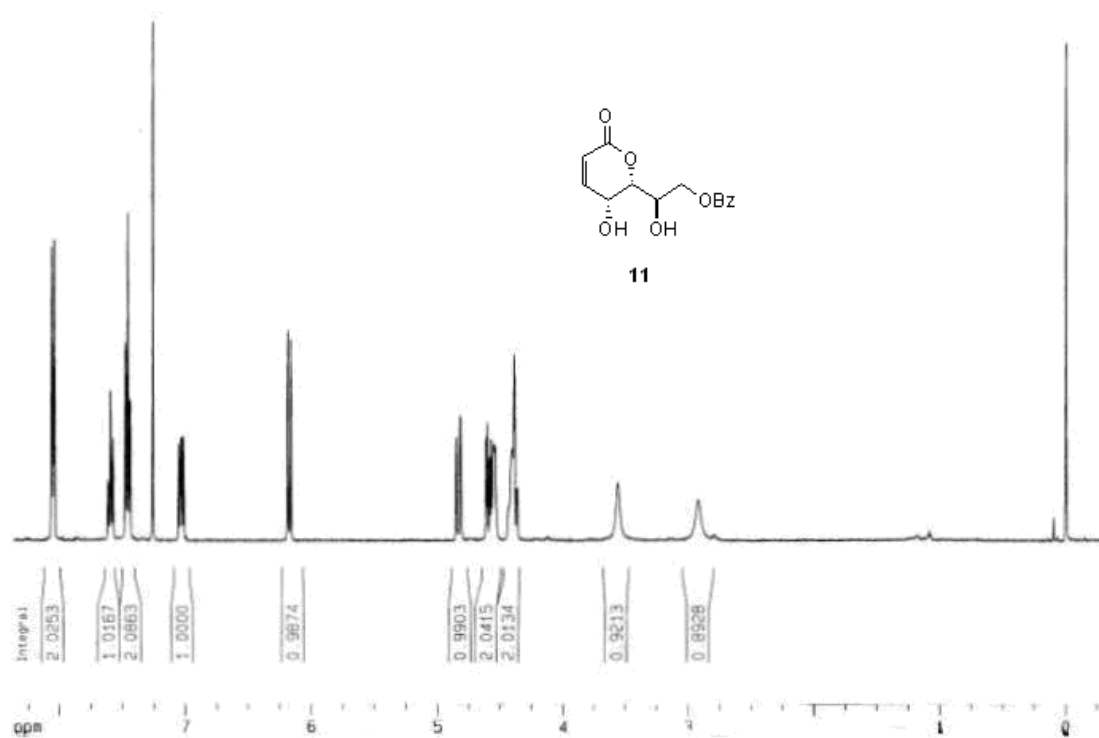
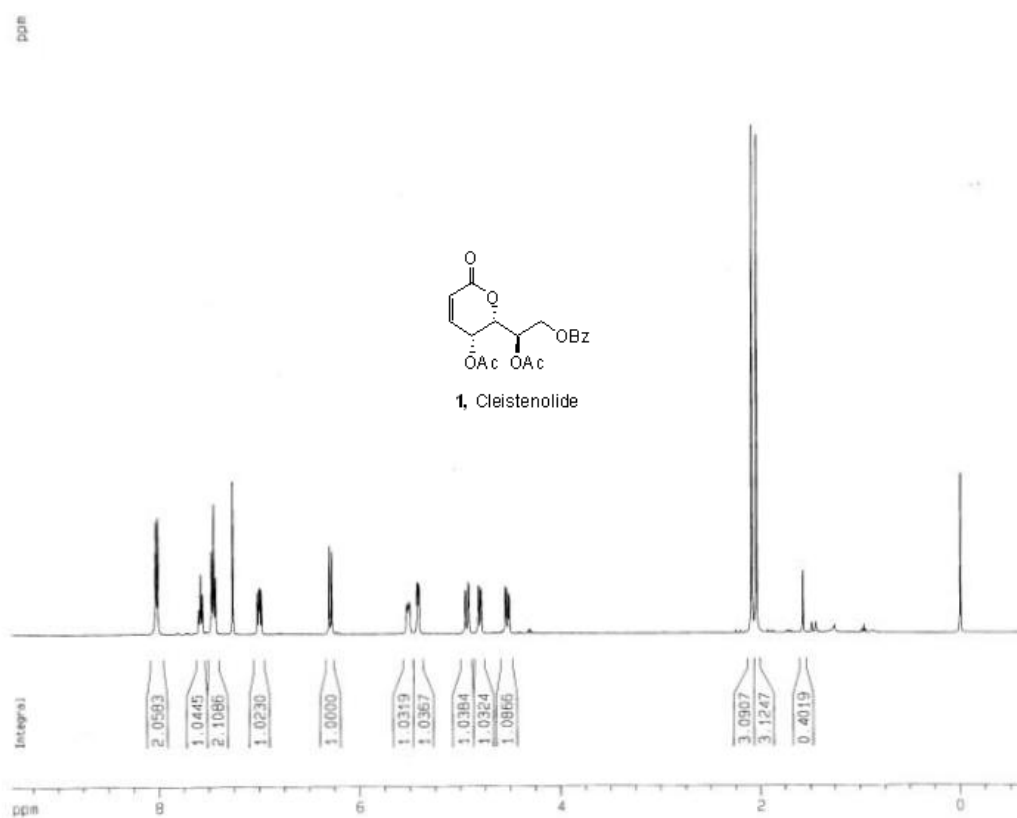


<sup>1</sup>H NMR for compound 4



$^1\text{H}$  and  $^{13}\text{C}$  NMR for compound 3

$^1\text{H}$  and  $^{13}\text{C}$  NMR for compound **10**

$^1\text{H}$  NMR for compound **11** $^1\text{H}$  and  $^{13}\text{C}$  NMR for compound Cleistenolide (**1**)



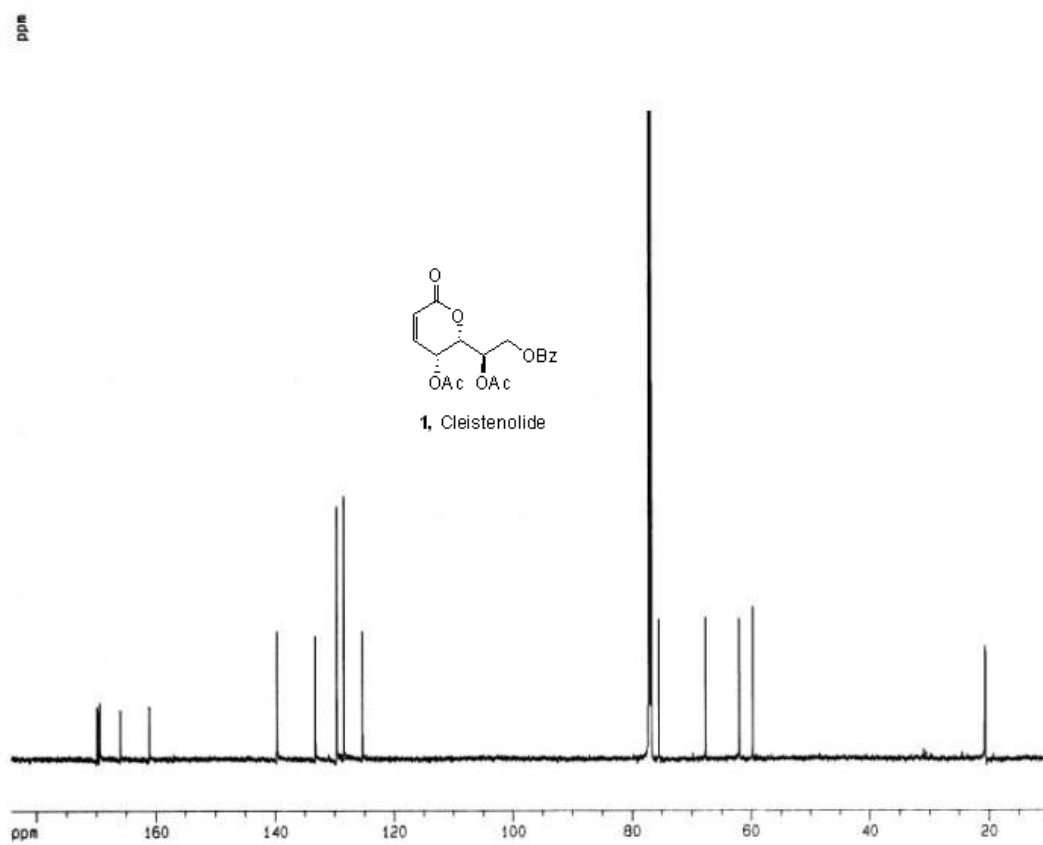


TABLE 1. Comparison of the  $^1\text{H}$  NMR data of synthetic and natural Cleistenolide

Position	Natural	Synthetic (Ref. 5)	Synthetic (our report)
2	6.30 (d, $J = 9.7$ Hz)	6.29 (d, $J = 9.7$ Hz)	6.29 (d, $J = 9.7$ Hz)
3	7.02 (dd, $J = 9.7, 6.1$ Hz)	7.00 (dd, $J = 9.7, 6.1$ Hz)	7.00 (dd, $J = 9.6, 6.1$ Hz)
4	5.42 (dd, $J = 6.1, 2.7$ Hz)	5.41 (dd, $J = 6.1, 2.6$ Hz)	5.42 (dd, $J = 6.0, 2.5$ Hz)
5	4.82 (dd, $J = 9.7, 2.7$ Hz)	4.80 (dd, $J = 9.6, 2.7$ Hz)	4.80 (dd, $J = 9.6, 2.5$ Hz)
7 Ac	2.08 (s)	2.04 (s)	2.04 (s)
8	5.53 (ddd, $J = 9.6, 4.4, 2.4$ Hz)	5.51 (ddd, $J = 9.9, 4.4, 2.4$ Hz)	5.52 (ddd, $J = 9.5, 4.0, 2.3$ Hz)
10Ac	2.13 (s)	2.08 (s)	2.09 (s)
11a	4.54 (dd, $J = 12.5, 2.4$ Hz)	4.52 (dd, $J = 12.5, 4.4$ Hz)	4.53 (dd, $J = 12.5, 4.4$ Hz)
11b	4.93 (dd, $J = 12.5, 4.4$ Hz)	4.93 (dd, $J = 12.5, 2.4$ Hz)	4.93 (dd, $J = 12.5, 2.0$ Hz)
2'	8.05 (dd, $J = 7.6, 1.9$ Hz)	8.01 (d, $J = 7.7$ Hz)	8.02 (d, $J = 7.7$ Hz)
3'	7.49 (ddd, $J = 7.7, 7.5, 1.8$ Hz)	7.44 (dd, $J = 7.7, 7.4$ Hz)	7.45 (t, $J = 7.6$ Hz)
4'	7.60 (m)	7.57 (t, $J = 7.5$ Hz)	7.57 (t, $J = 7.4$ Hz)
5'	7.49 (ddd, $J = 7.7, 7.5, 1.8$ Hz)	7.44 (dd, $J = 7.7, 7.4$ Hz)	7.45 (t, $J = 7.6$ Hz)
6'	8.05 (dd, $J = 7.6, 1.9$ Hz)	8.01 (d, $J = 7.7$ Hz)	8.02 (d, $J = 7.7$ Hz)

TABLE 2. Comparison of the  $^{13}\text{C}$  NMR data of synthetic and natural Cleistenolide

Position	Natural	Synthetic (Ref. 5)	Synthetic (our report)
5- $\underline{\text{C}}\text{H}_3\text{COO}$	20.84	20.4	20.5
7- $\underline{\text{C}}\text{H}_3\text{COO}$	21.05	20.6	20.7
C-6	60.13	59.7	59.7
C-8	62.40	62.0	62.0
C-7	68.03	67.7	67.7
C-5	75.92	75.5	75.4
C-3	125.77	125.3	125.4
C-3'	128.89	128.5	128.5
C-5'	128.89	128.5	128.5
C-1'	130.02	129.6	129.6
C-2'	130.09	129.6	129.7
C-6'	130.09	129.6	129.7
C-4'	133.68	133.2	133.3
C-4	140.10	139.7	139.7
C-2	161.54	161.0	161.1
8- $\text{O}\underline{\text{C}}\text{OPh}$	166.42	165.9	166.0
7- $\text{O}\underline{\text{C}}\text{OCH}_3$	170.03	169.4	169.5
5- $\text{O}\underline{\text{C}}\text{OCH}_3$	170.35	169.8	169.9