

**Supporting Information for**

**Diospentenols A and B, Two New Cyclopentapyrans Isolated from  
Abandoned Mine Bacterium *Streptomyces* sp. KMA-001**

**Jin-Soo Park,<sup>†,‡</sup> Jin Wook Cha,<sup>†</sup> Seong-Hwan Kim,<sup>§</sup> Dong-Chan Oh,<sup>§</sup> and Hak Cheol Kwon<sup>\*,†</sup>**

<sup>†</sup>*Natural Medicine Center, Korea Institute of Science and Technology (KIST), Gangneung 210-340, Republic of Korea;*

<sup>‡</sup>*Biotechnology Research Center, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8567, Japan;*

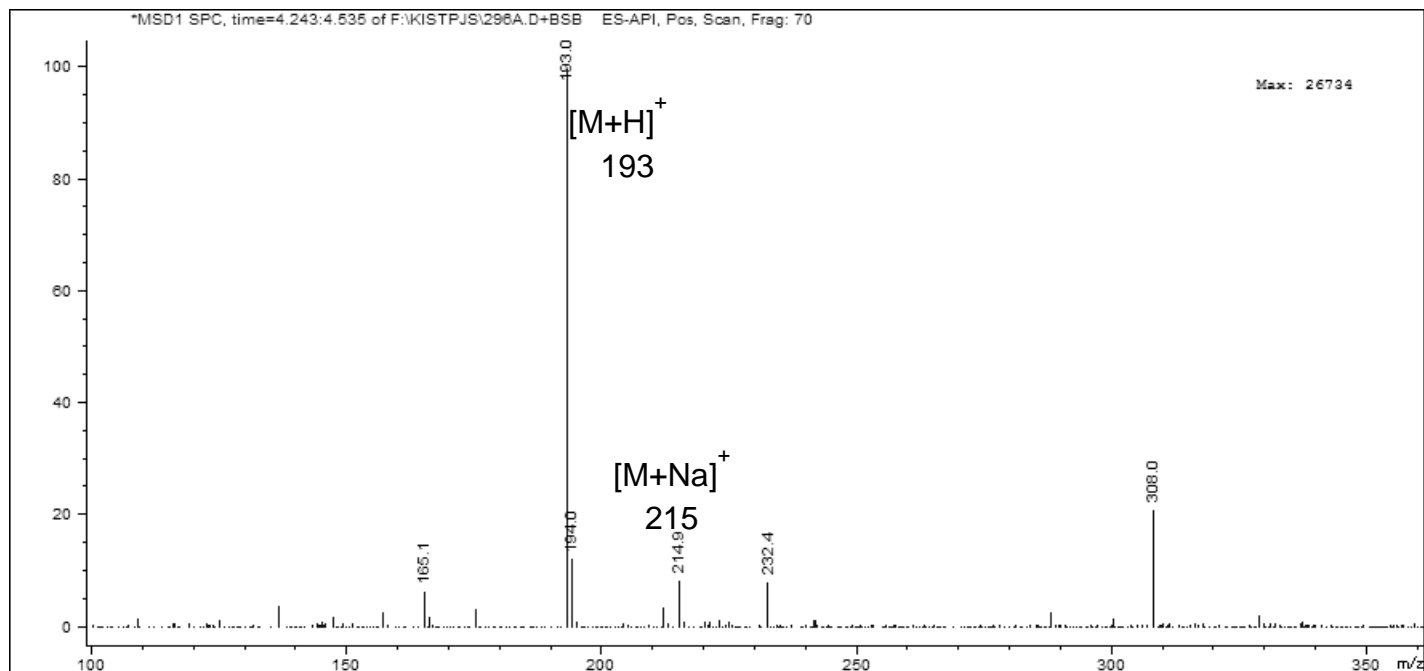
<sup>§</sup>*Natural Products Research Institute, College of Pharmacy, Seoul National University, Gwanak-gu, Seoul 151-742, Republic of Korea*

\*Corresponding author: [hkwon@kist.re.kr](mailto:hkwon@kist.re.kr)

## Table of Contents

<b>Figure S1.</b> LR ESI MS and HR EI MS data of diospenitenol A ( <b>1</b> ) .....	S04
<b>Figure S2.</b> <sup>1</sup> H NMR spectrum of diospenitenol A ( <b>1</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S05
<b>Figure S3.</b> <sup>13</sup> C NMR spectrum of diospenitenol A ( <b>1</b> ) (125 MHz, CD <sub>3</sub> OD) .....	S06
<b>Figure S4.</b> <sup>1</sup> H- <sup>1</sup> H gCOSY NMR spectrum of diospenitenol A ( <b>1</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S07
<b>Figure S5.</b> gHSQC NMR spectrum of diospenitenol A ( <b>1</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S08
<b>Figure S6.</b> gHMBC NMR spectrum of diospenitenol A ( <b>1</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S09
<b>Figure S7.</b> 1D NOE spectra of diospenitenol A ( <b>1</b> ), irradiation of H-7 and H-11 (500 MHz, CD <sub>3</sub> OD) .....	S10
<b>Figure S8.</b> LR ESI MS and HR EI MS data of diospenitenol B ( <b>2</b> ) .....	S11
<b>Figure S9.</b> <sup>1</sup> H NMR spectrum of diospenitenol B ( <b>2</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S12
<b>Figure S10.</b> <sup>13</sup> C NMR spectrum of diospenitenol B ( <b>2</b> ) (125 MHz, CD <sub>3</sub> OD) .....	S13
<b>Figure S11.</b> <sup>1</sup> H- <sup>1</sup> H gCOSY NMR spectrum of diospenitenol B ( <b>2</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S14
<b>Figure S12.</b> gHSQC NMR spectrum of diospenitenol B ( <b>2</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S15
<b>Figure S13.</b> gHMBC NMR spectrum of diospenitenol B ( <b>2</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S16
<b>Figure S14.</b> 1D NOE spectra of diospenitenol B ( <b>2</b> ), irradiation in H-7 and H-11 (500 MHz, CD <sub>3</sub> OD) .....	S17
<b>Figure S15.</b> <sup>1</sup> H NMR spectrum of 5- <i>O</i> -acetyldiospenitenol A ( <b>3</b> ) (500 MHz, CD <sub>3</sub> CN) .....	S18
<b>Figure S16.</b> <sup>1</sup> H NMR spectrum of 4,5-dihydro-6-hydroxydiospenitenol A ( <b>4</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S19
<b>Figure S17.</b> NOESY spectrum of 4,5-dihydro-6-hydroxydiospenitenol A ( <b>4</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S20
<b>Figure S18.</b> <sup>1</sup> H NMR spectrum of 5- <i>O</i> -methyldiospenitenol A ( <b>5</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S21
<b>Figure S19.</b> <sup>1</sup> H NMR spectrum of 5- <i>O</i> -methyl-6-hydroxydiospenitenol A ( <b>6</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S22
<b>Figure S20.</b> <sup>1</sup> H NMR spectrum of 5- <i>O</i> -methyl-6-hydroxydiospenitenol A ( <b>6</b> ) (500 MHz, pyridine- <i>d</i> <sub>5</sub> ) .....	S23

<b>Figure S21.</b> NOESY spectrum of 5- <i>O</i> -methyl-6-hydroxydiospentenol A ( <b>6</b> ) (500 MHz, pyridine- <i>d</i> <sub>5</sub> ) .....	S24
<b>Figure S22.</b> <sup>1</sup> H NMR spectrum of 4-deutro-5-hydro-6-hydroxydiospentenol B ( <b>7</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S25
<b>Figure S23.</b> NOESY spectrum of 4-deutro-5-hydro-6-hydroxydiospentenol B ( <b>7</b> ) (500 MHz, CD <sub>3</sub> OD) .....	S26
<b>Figure S24.</b> <sup>1</sup> H NMR spectrum of ( <i>S</i> )-MTPA ester of <b>6</b> (500 MHz, pyridine- <i>d</i> <sub>5</sub> ) .....	S27
<b>Figure S25.</b> CD spectra of diospentenols A ( <b>1</b> ) and B ( <b>2</b> ) .....	S28
<b>Figure S26.</b> HPLC results using reverse phase column (C8) and chiral column (Lux cellulose-1) .....	S29
<b>Figure S27.</b> <sup>1</sup> H NMR spectrum of diosphenol - containing fraction (500 MHz, CDCl <sub>3</sub> ) .....	S30



File: 3503  
 Sample: 296A  
 Instrument: JEOL JMS600  
 Inlet: Direct Probe

Date Run: 05-02-2008

Time Run: 15:17:27

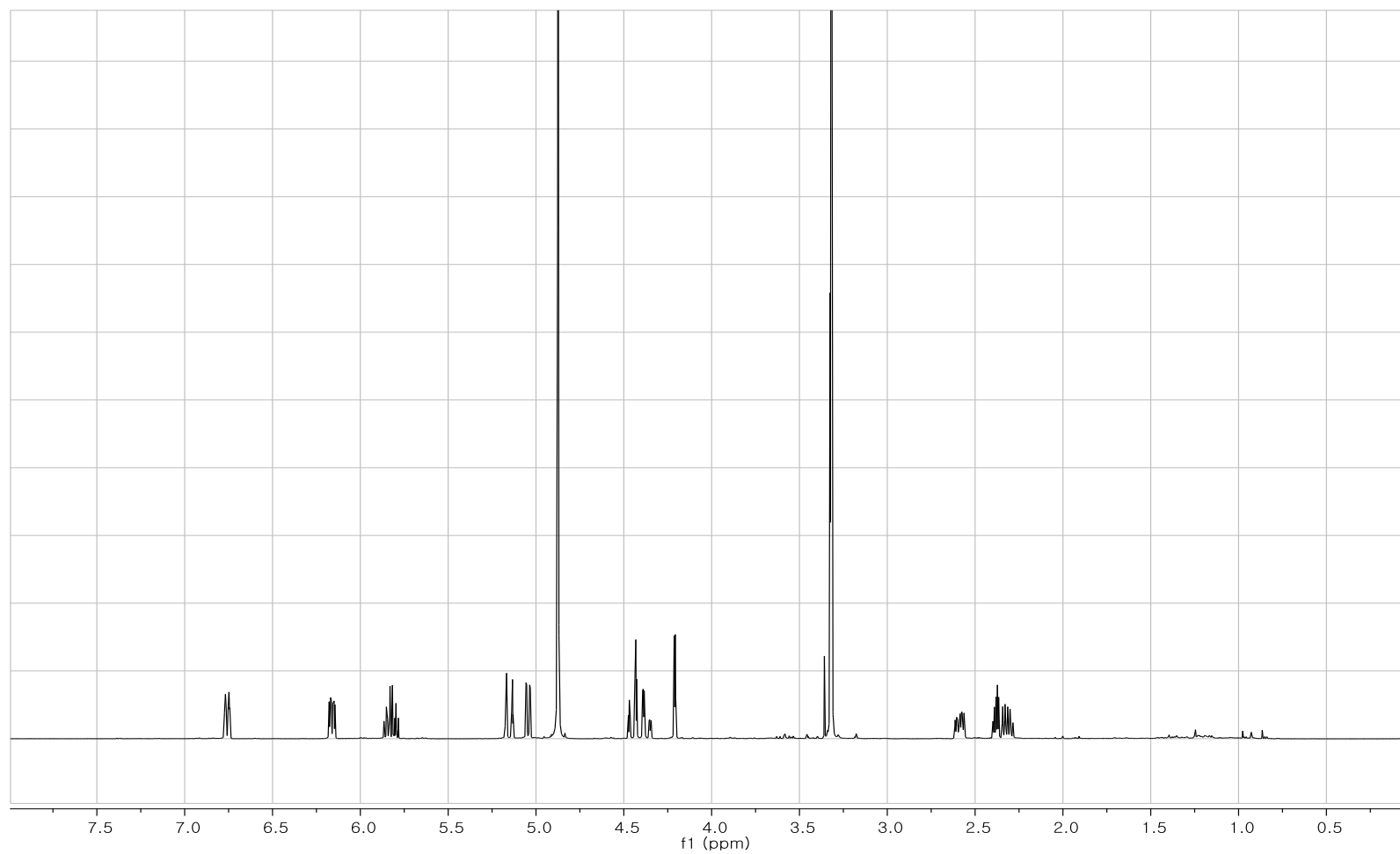
Ionization mode: EI+

Scan: 192  
 Base: m/z 192; 1.1%FS TIC: 1071131

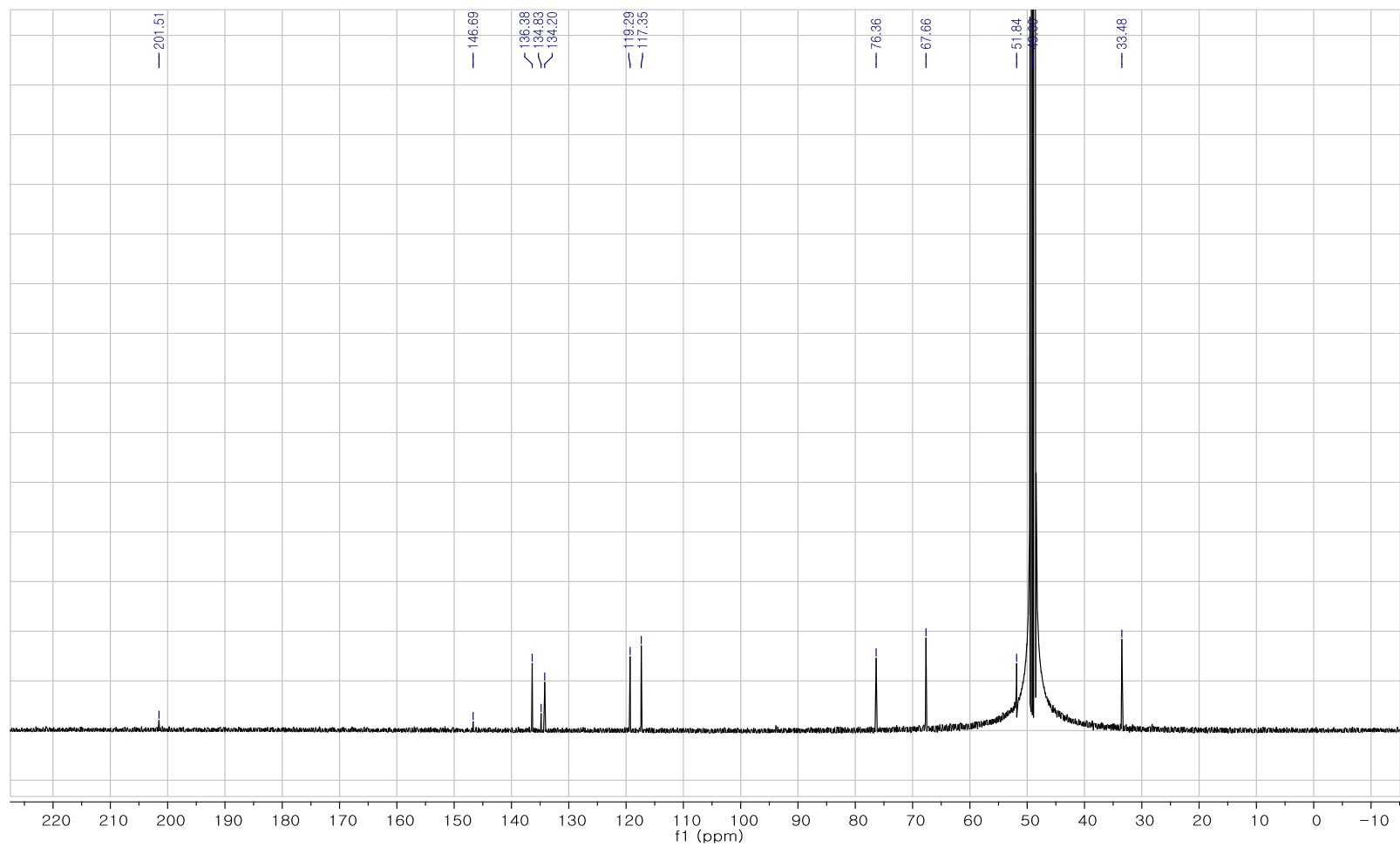
R.T.: 1:54.9

Selected Isotopes : C <sub>0-50</sub> H <sub>0-100</sub> O <sub>0-10</sub>			Error Limit : 20 ppm	
<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
192.0785	100.0%	C <sub>11</sub> H <sub>12</sub> O <sub>3</sub>	192.0786	0.7

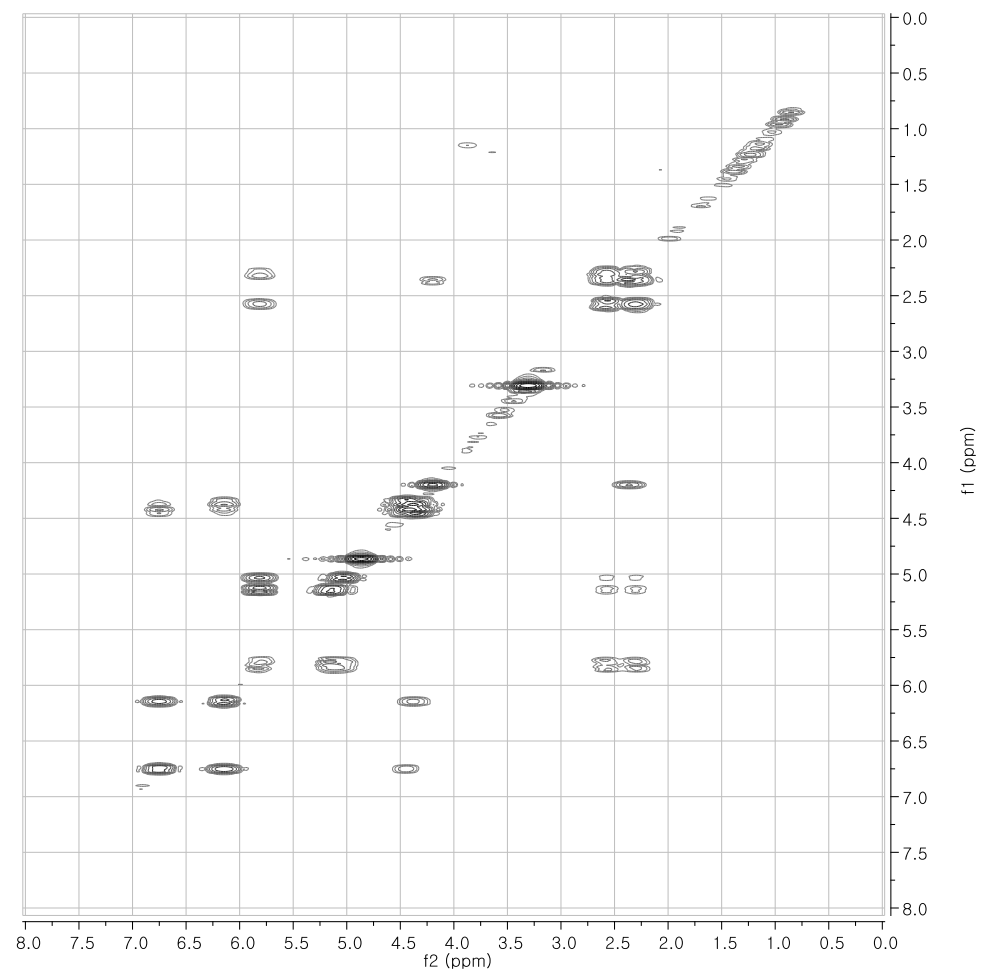
**Figure S1.** LR ESI MS (top) and HR EI MS (bottom) data of diospenenol A (**1**)



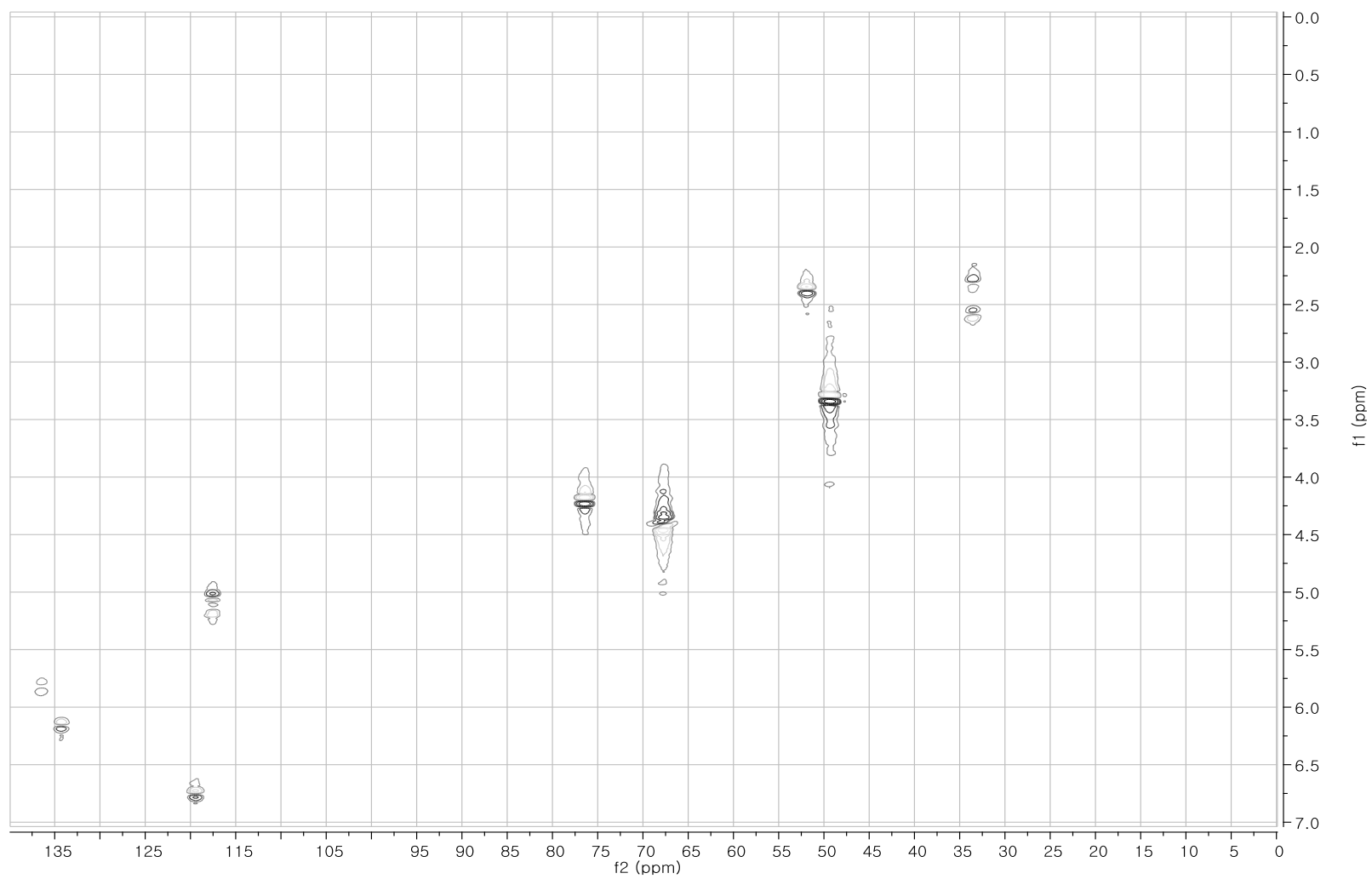
**Figure S2.**  $^1\text{H}$  NMR spectrum of diospenitenol A (1) (500 MHz,  $\text{CD}_3\text{OD}$ )



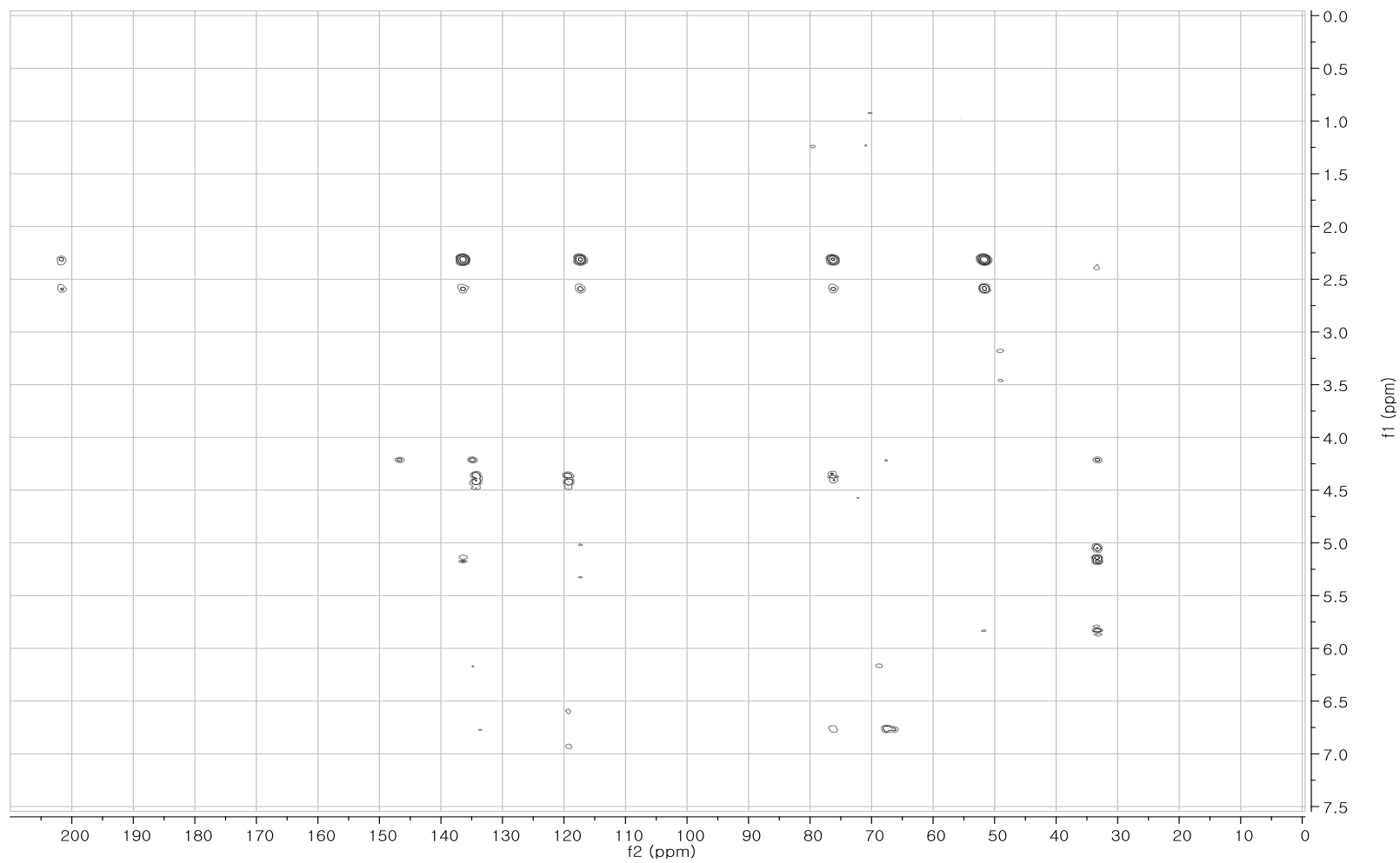
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of diospeninol A (1) (125 MHz,  $\text{CD}_3\text{OD}$ )



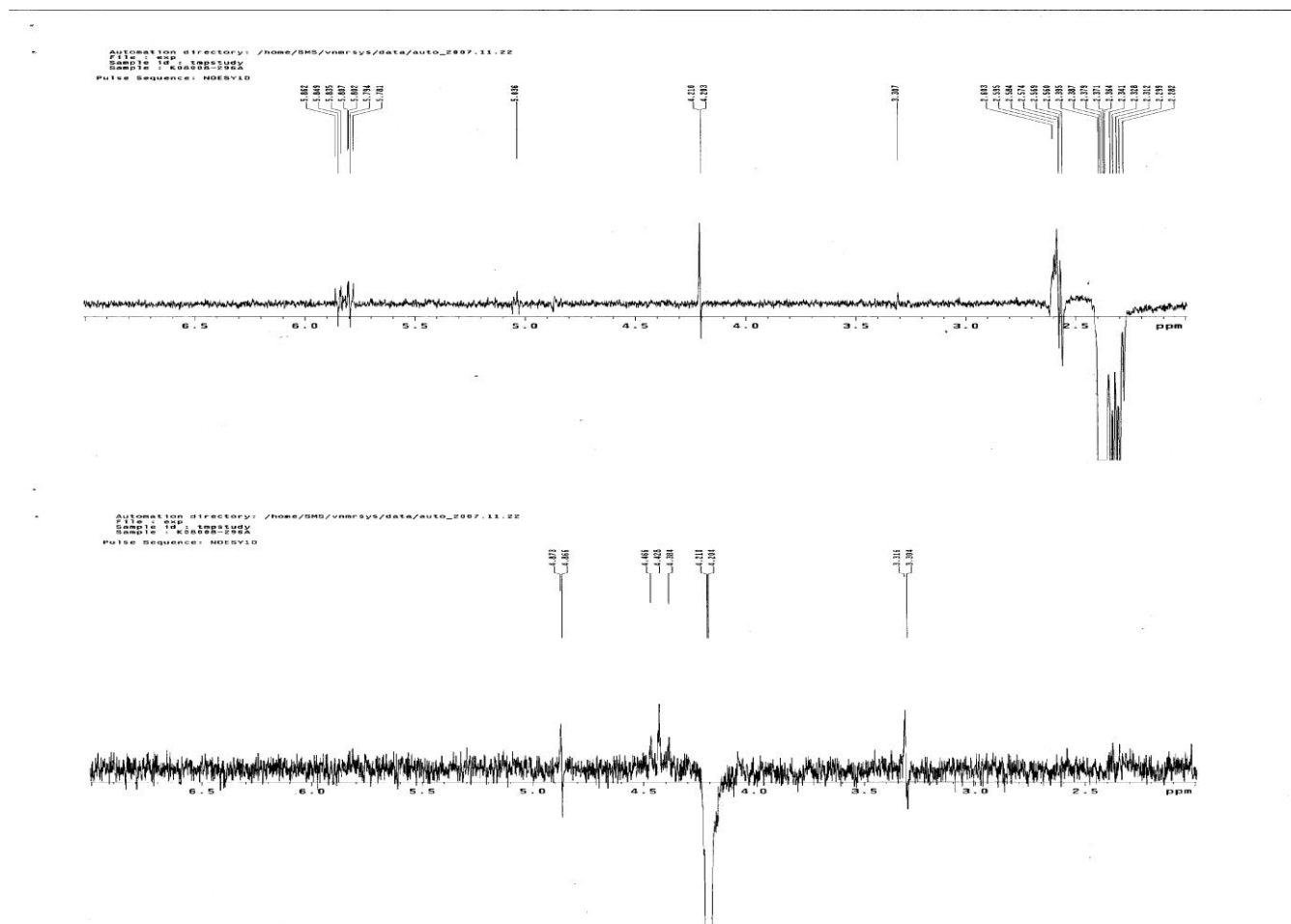
**Figure S4.**  $^1\text{H}$ - $^1\text{H}$  gCOSY NMR spectrum of diospenitenol A (**1**) (500 MHz,  $\text{CD}_3\text{OD}$ )



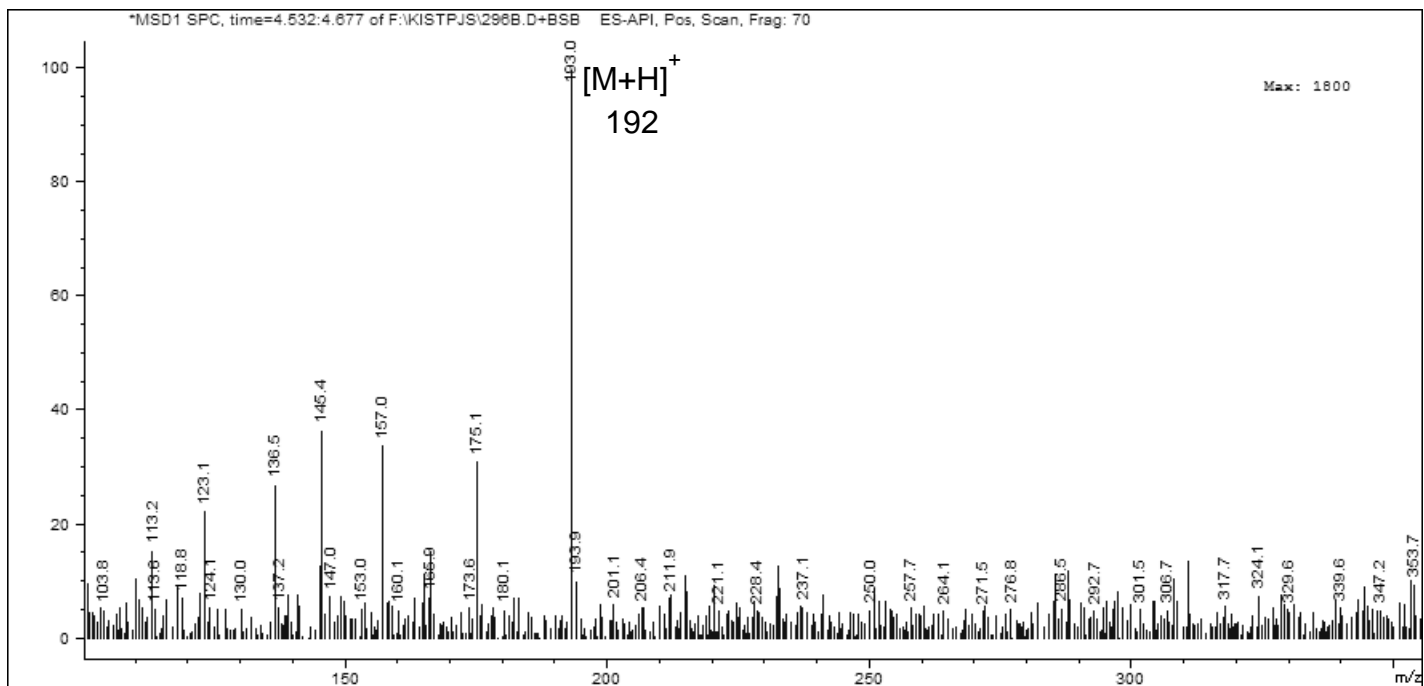
**Figure S5.** gHSQC NMR spectrum of diospeninol A (**1**) (500 MHz, CD<sub>3</sub>OD)



**Figure S6.** gHMBC NMR spectrum of diospenntenol A (**1**) (500 MHz, CD<sub>3</sub>OD)



**Figure S7.** 1D NOE spectra of diosphenol A (**1**), irradiation of H-7 (upper) and H-11 (bottom) (500 MHz, CD<sub>3</sub>OD)



File: 3504  
 Sample: 296B  
 Instrument: JEOL JMS600  
 Inlet: Direct Probe

Date Run: 05-02-2008

Time Run: 15:39:58

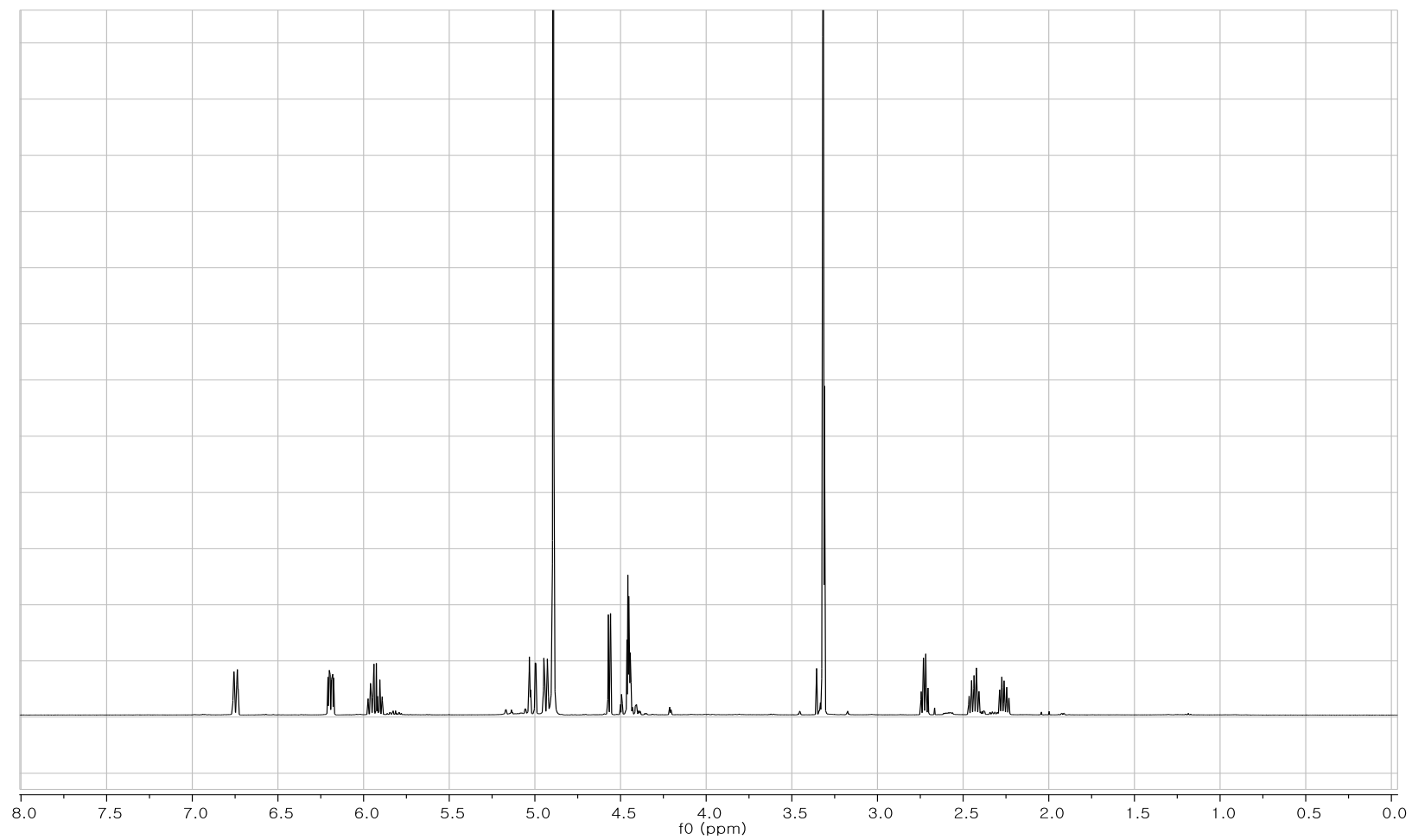
Scan: 87  
 Base: m/z 192, 9%FS TIC: 1074143

Ionization mode: EI+

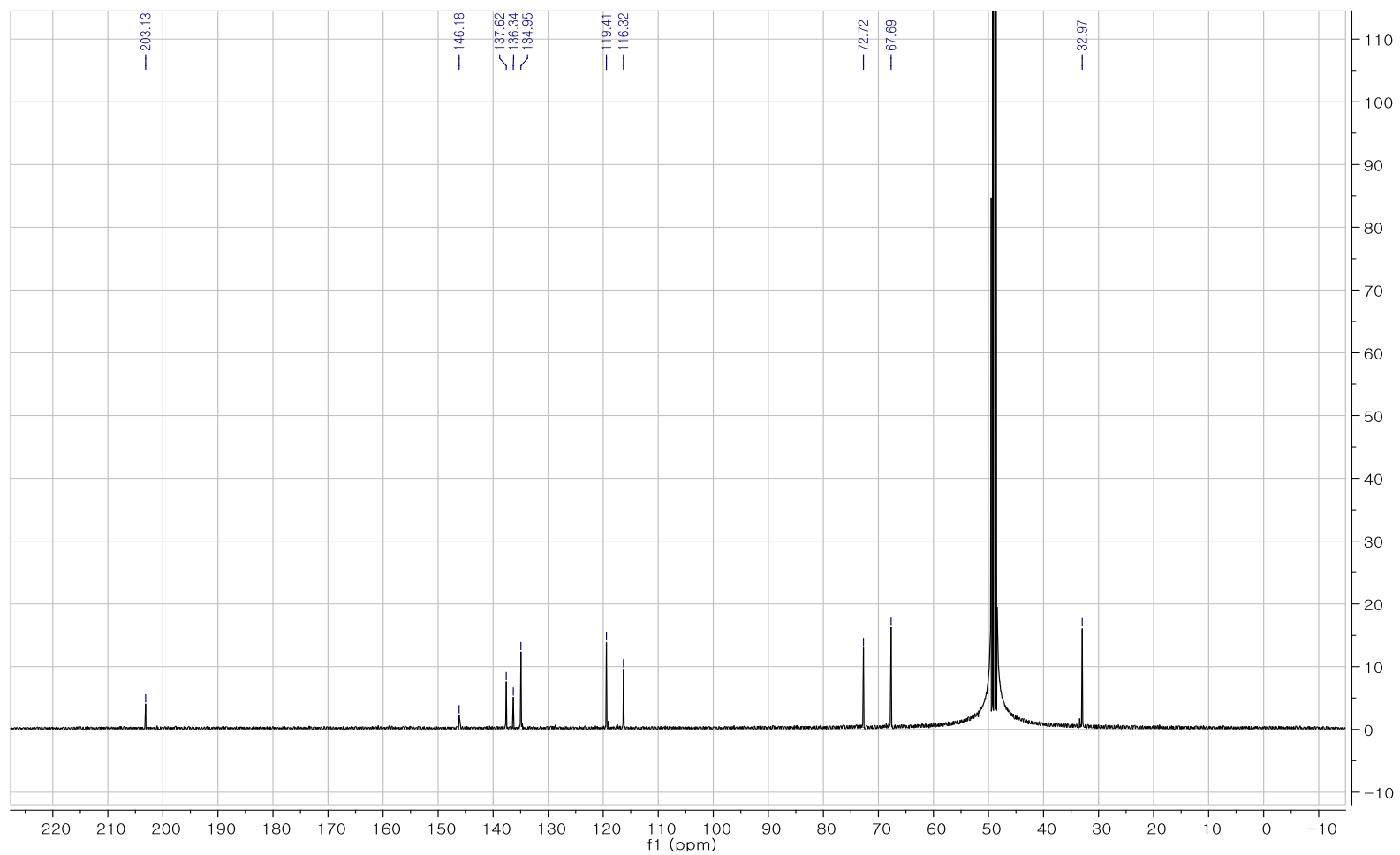
R.T.: 0:51.9

Selected Isotopes : C <sub>0.50</sub> H <sub>0.100</sub> O <sub>0.40</sub>		Error Limit : 20 ppm		
<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
192.0783	100.0%	C <sub>11</sub> H <sub>12</sub> O <sub>3</sub>	192.0786	1.7

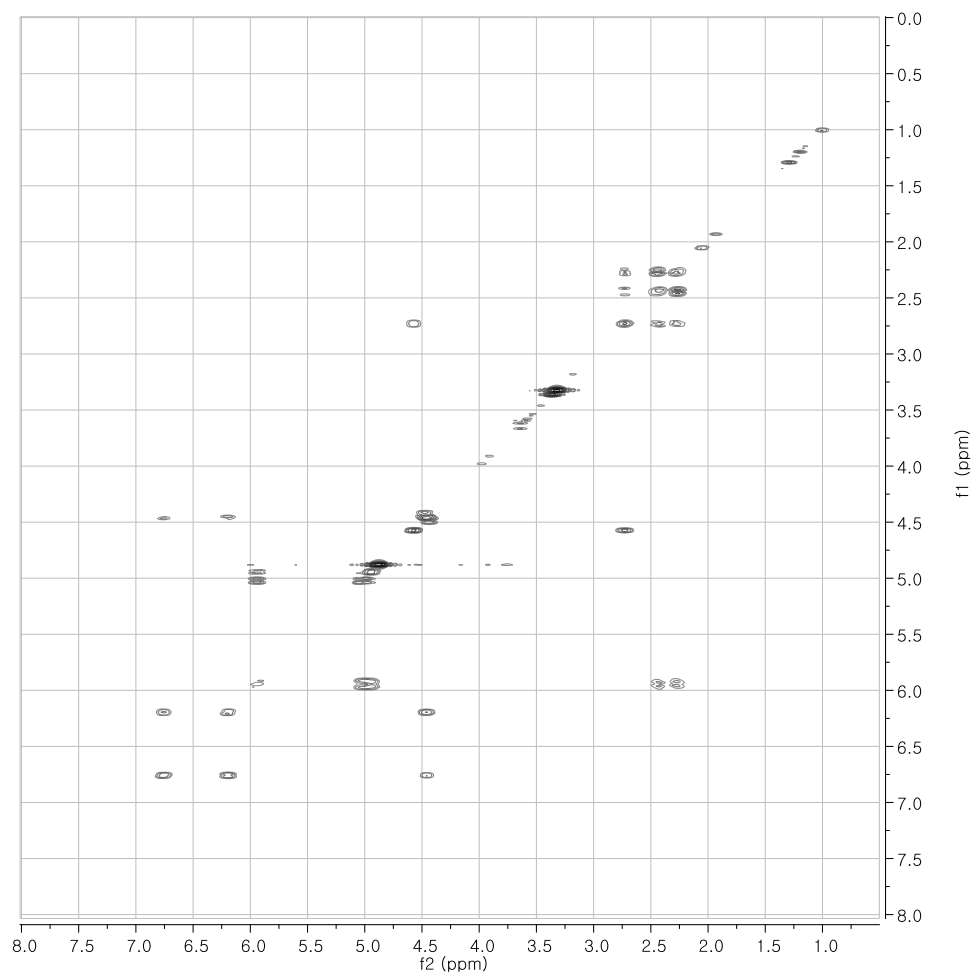
Figure S8. LR ESI MS (top) and HR EI MS (bottom) data of diospenatenol B (2)



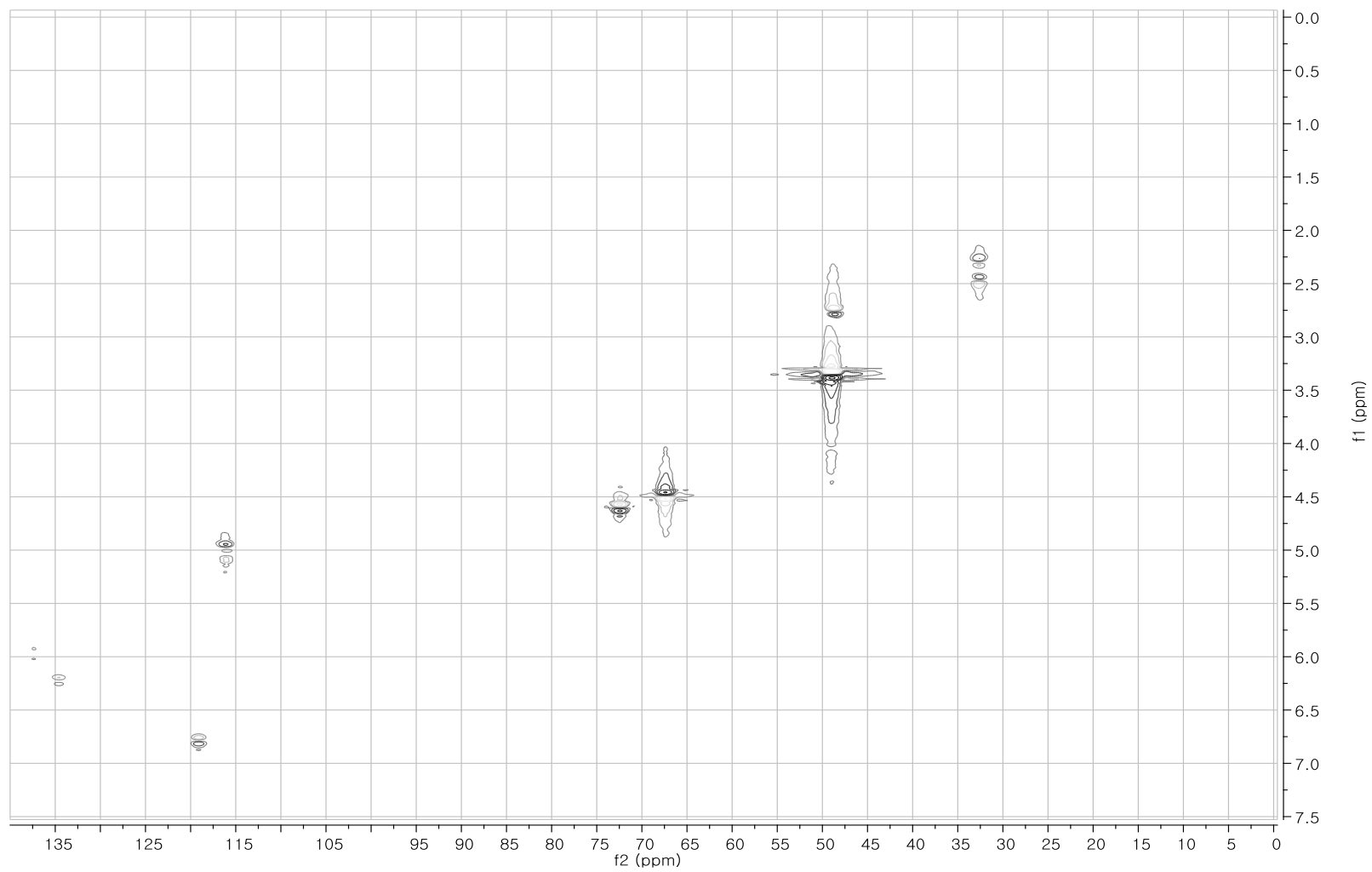
**Figure S9.**  $^1\text{H}$  NMR spectrum of diospeninol B (**2**) (500 MHz,  $\text{CD}_3\text{OD}$ )



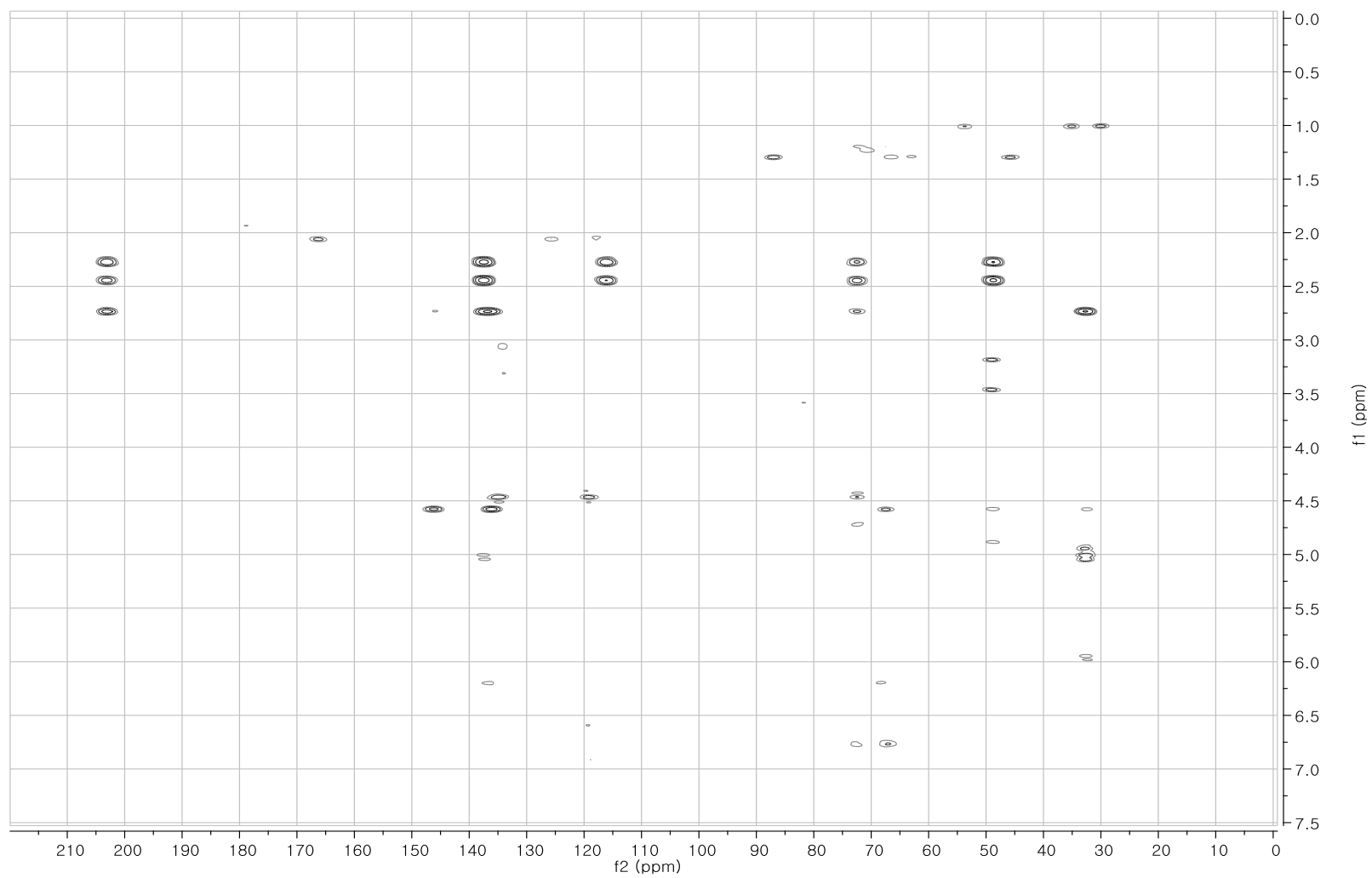
**Figure S10.**  $^{13}\text{C}$  NMR spectrum of diosipentol B (2) (125 MHz,  $\text{CD}_3\text{OD}$ )



**Figure S11.**  $^1\text{H}$ - $^1\text{H}$  gCOSY NMR spectrum of diosipentenol B (**2**) (500 MHz,  $\text{CD}_3\text{OD}$ )

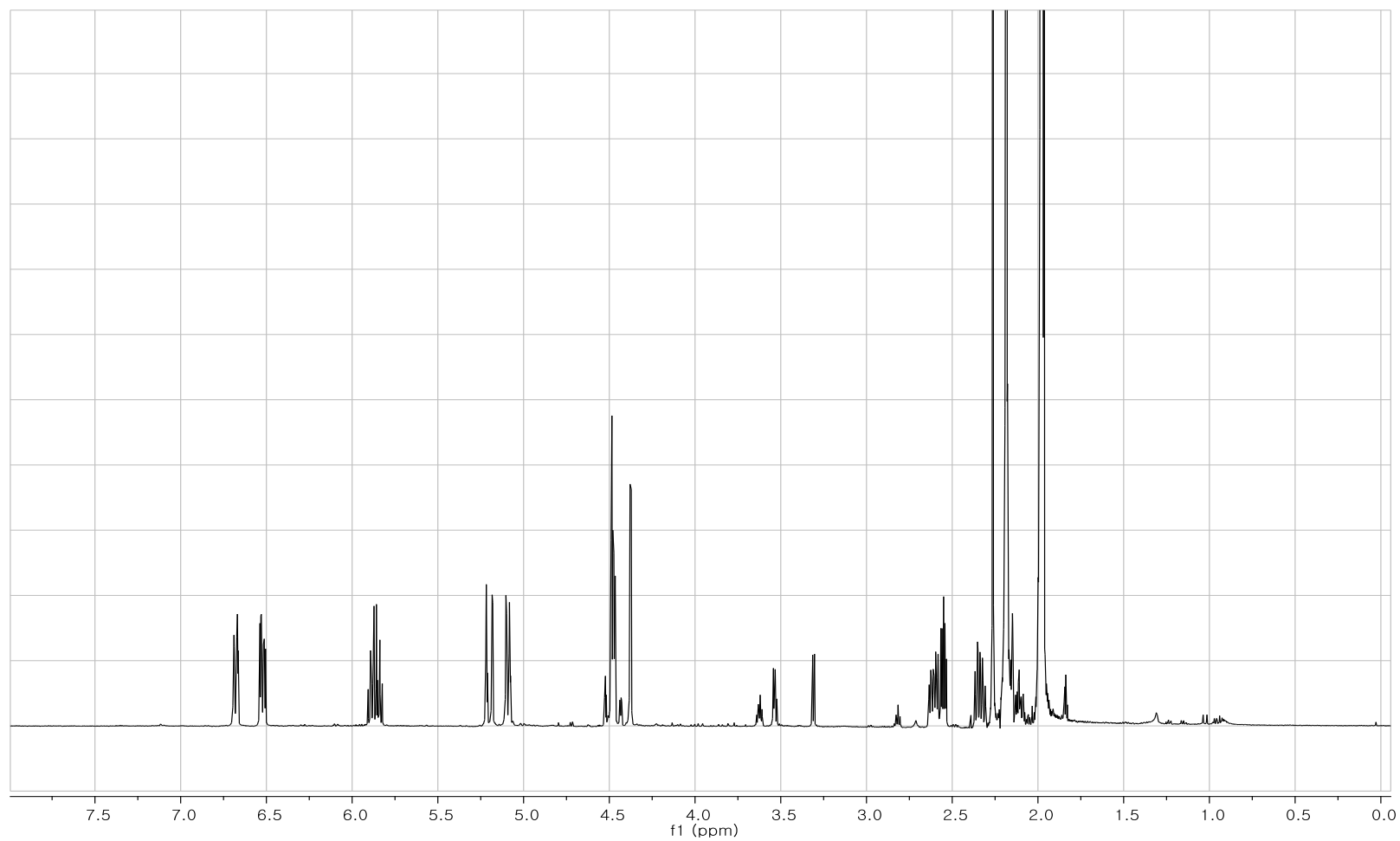


**Figure S12.** gHSQC NMR spectrum of diosphenol B (**2**) (500 MHz, CD<sub>3</sub>OD)

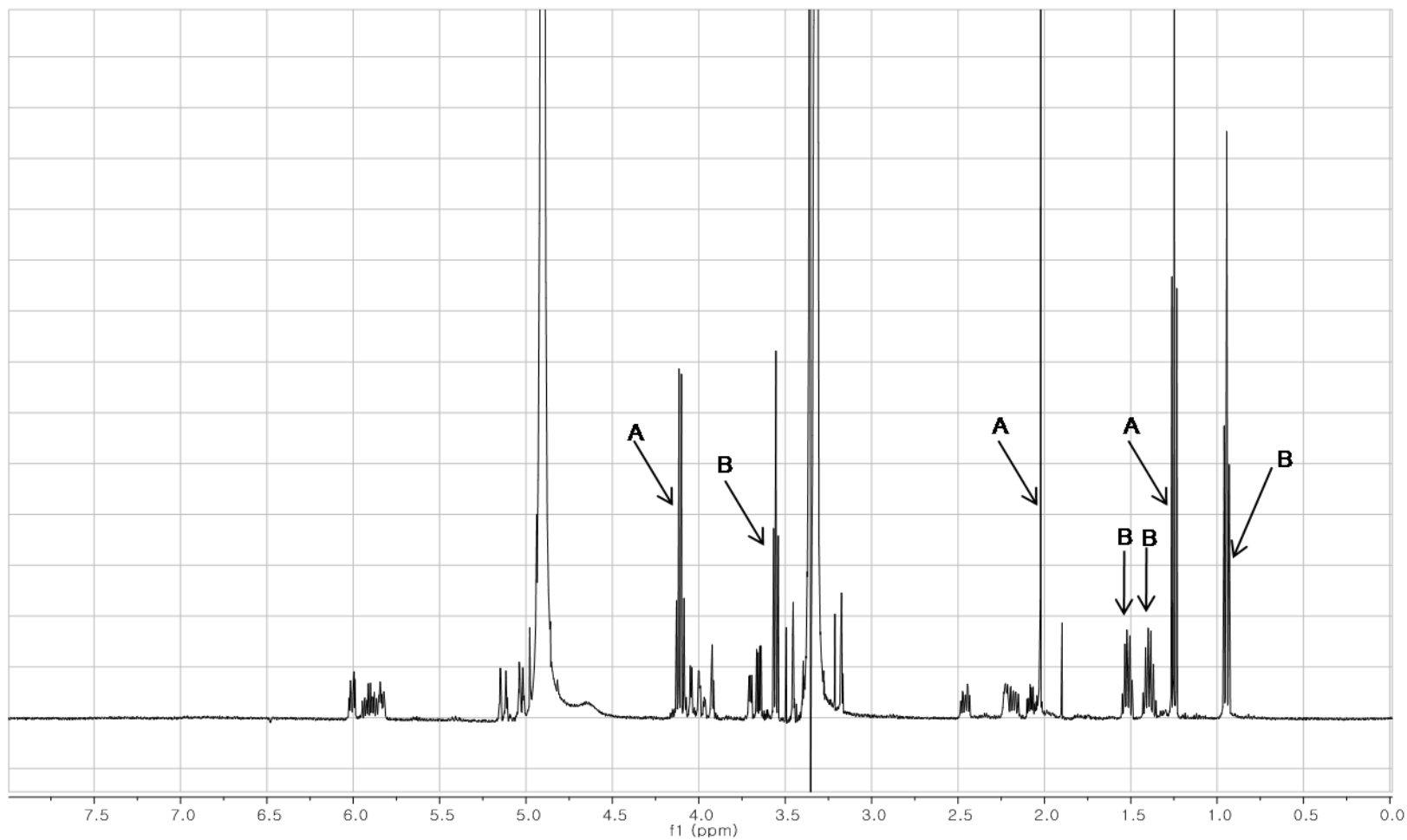


**Figure S13.** gHMBC NMR spectrum of diospeninol B (**2**) (500 MHz, CD<sub>3</sub>OD)





**Figure S15.** <sup>1</sup>H NMR spectrum of 5-O-acetyldiospenenol A (**3**) (500 MHz, CD<sub>3</sub>CN)



**Figure S16.**  $^1\text{H}$  NMR spectrum of 4,5-dihydro-6-hydroxydiospentenol A (**4**) (500 MHz,  $\text{CD}_3\text{OD}$ )  
(Arrows above the spectrum illustrate solvents mixed with **4**. A: ethyl acetate; B: butanol)

ac-296A-OH-3 (500 MHz, MeOD)  
Sample: 0616-ac-296A-OH-3  
Sample ID: s\_27\_0616-ac-296A-OH-3\_02  
File: /home/SMS/vnmrSYS/data/auto\_2008.06.12\_01/s\_27\_0616-ac-296A-OH-3\_02/data/0616-ac-296A-OH-3\_Noesy\_01.fid

Pulse Sequence: NOESY

Solvent: cd3od  
Temp: 22.0 C / 295.1 K  
Sample #27, Operator: SMS  
File: 0616-ac-296A-OH-3\_Noesy\_01  
VNMR5-500 "kist500"

Relax. delay 1.000 sec  
Mixing 0.400 sec  
Acq. time 0.128 sec  
Width 4006.4 Hz  
2D Width 4006.4 Hz  
8 repetitions  
2 x 256 increments  
OBSERVE H1, 499.8475939 MHz  
DATA PROCESSING  
Gauss apodization 0.059 sec  
F1 DATA PROCESSING  
Gauss apodization 0.118 sec  
FT size 4096 x 4096  
Total time 1 hr, 44 min, 31 sec

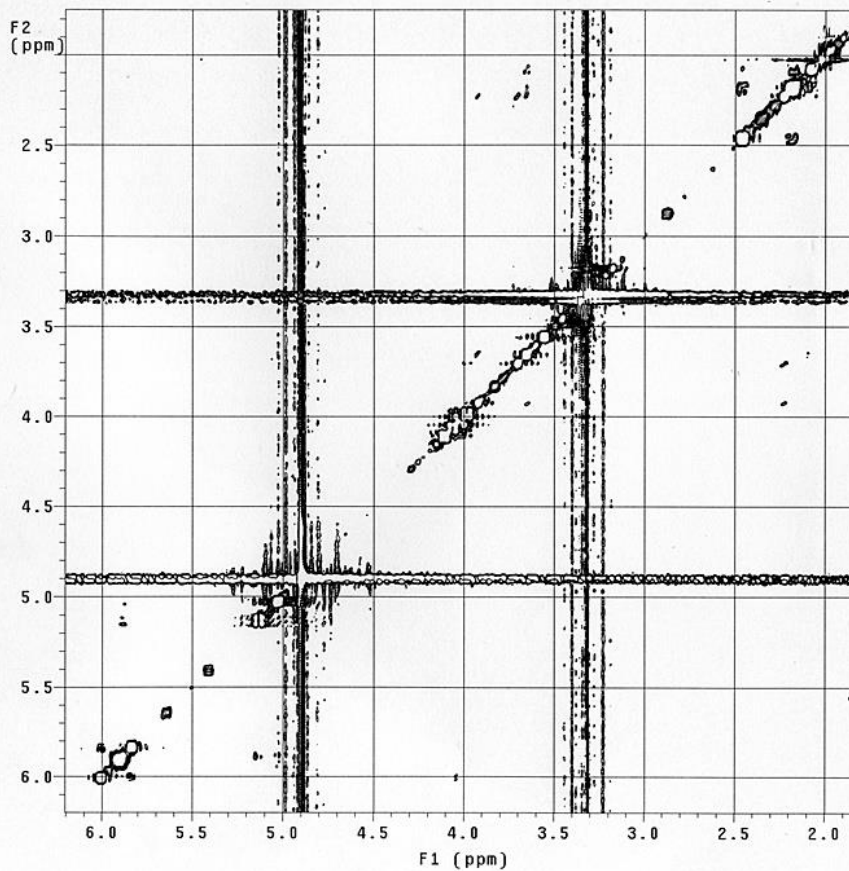
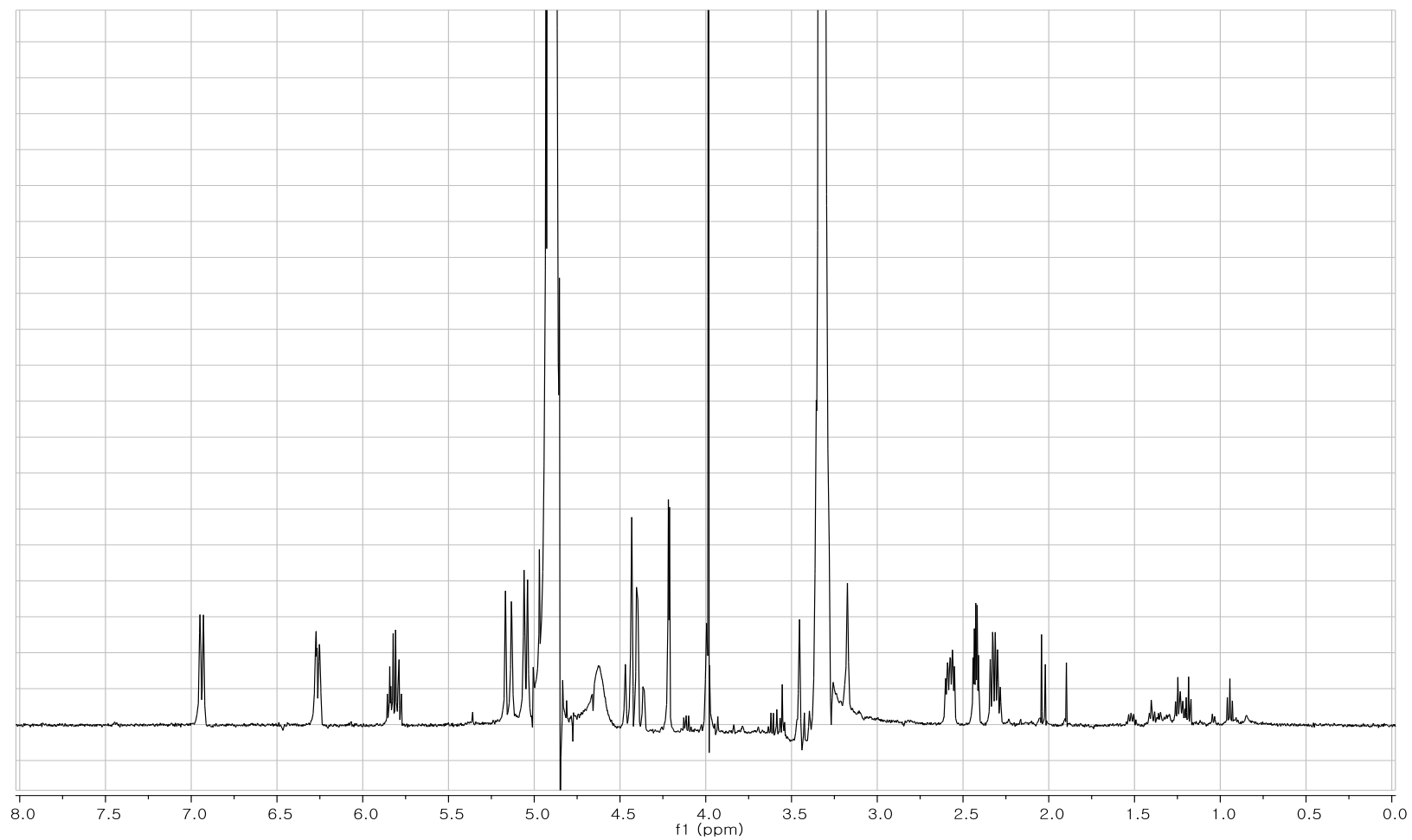
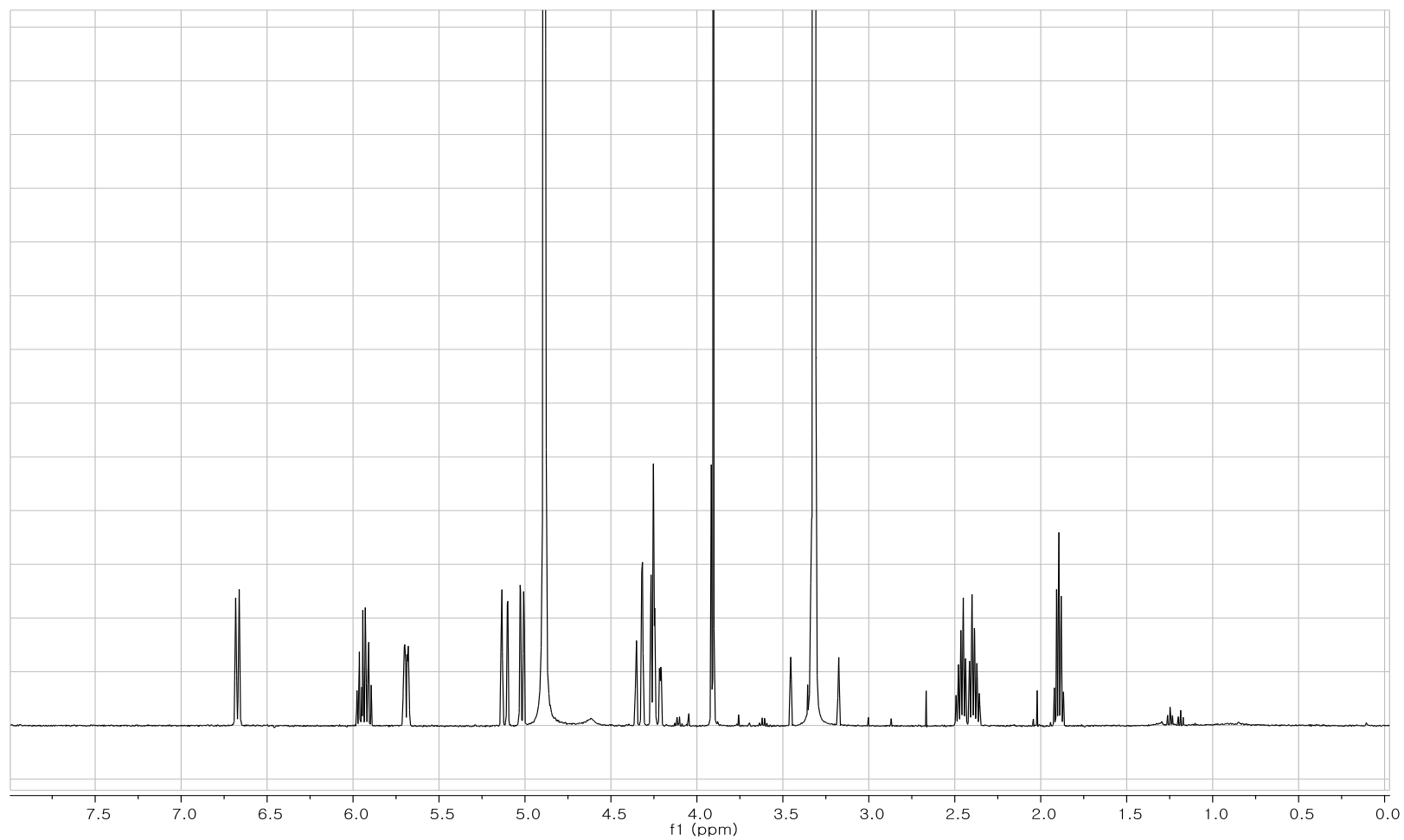


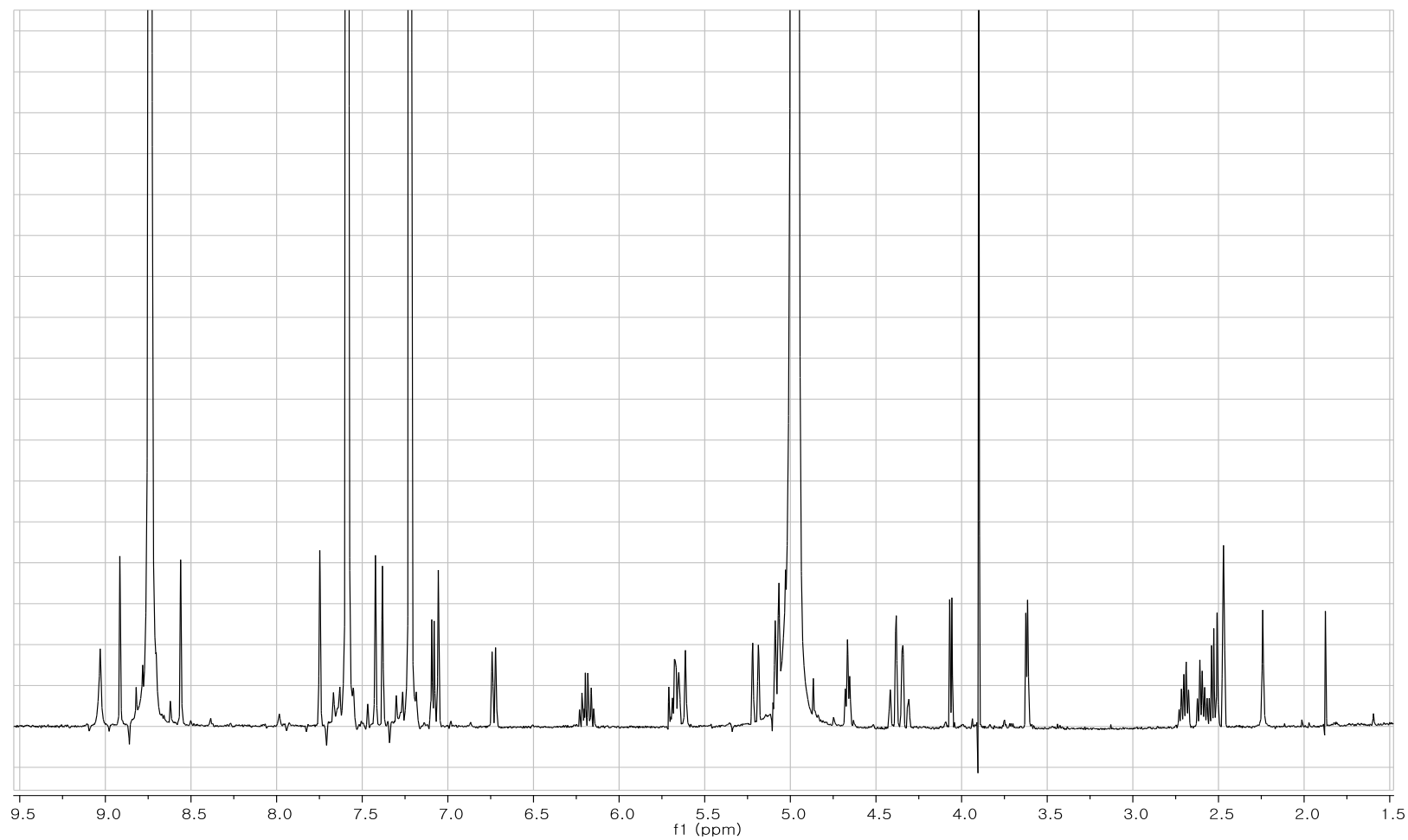
Figure S17. NOESY spectrum of 4,5-dihydro-6-hydroxydiospentenol A (**4**) (500 MHz, CD<sub>3</sub>OD)



**Figure S18.**  $^1\text{H}$  NMR spectrum of 5-*O*-methyldiospentenol A (**5**) (500 MHz,  $\text{CD}_3\text{OD}$ )



**Figure S19.**  $^1\text{H}$  NMR spectrum of 5-*O*-methyl-6-hydroxydiospentenol A (**6**) (500 MHz,  $\text{CD}_3\text{OD}$ )



**Figure S20.** <sup>1</sup>H NMR spectrum of 5-*O*-methyl-6-hydroxydiospenterol A (**6**) (500 MHz, pyridine-*d*<sub>5</sub>)

Me-296A-OH2-pyr (500 MHz, Pyridine) 090506

Sample: Me-296A-OH2-pyr  
Sample ID: s\_27\_Me-296A-OH2-pyr\_10  
File: home/SMS/vnmrSYS/data/auto\_2009.04.28/s\_27\_Me-296A-OH2-pyr\_10/data/Noesy\_01.fid

Pulse Sequence: NOESY

Solvent: pyridine  
Temp: 23.0 C / 296.1 K  
Sample #27, Operator: SMS  
File: Noesy\_01  
VNMR5-500 "kist500"

Relax. delay 2.000 sec  
Mixing 0.400 sec  
Acq. time 0.128 sec  
Width 5000.0 Hz  
2D Width 5000.0 Hz  
16 repetitions  
2 x 512 increments  
OBSERVE H1: 499.8456210 MHz  
DATA PROCESSING  
Gauss apodization 0.059 sec  
F1 DATA PROCESSING  
Gauss apodization 0.189 sec  
FT size 8192 x 8192  
Total time 11 hr, 35 min, 30 sec

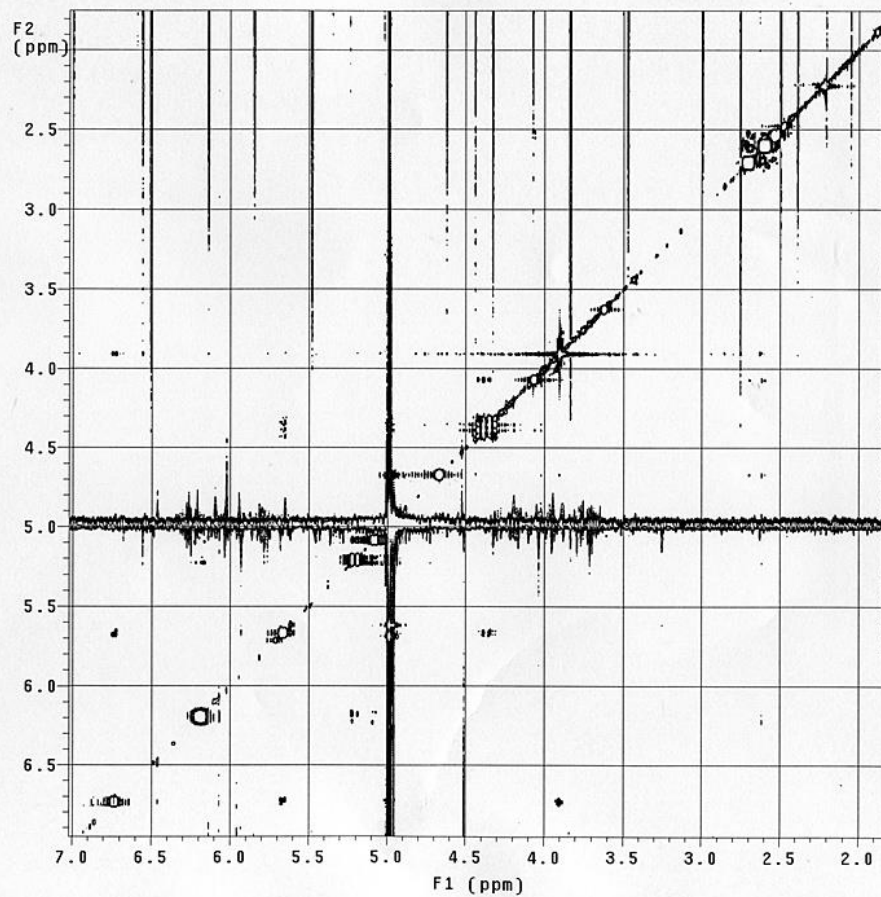
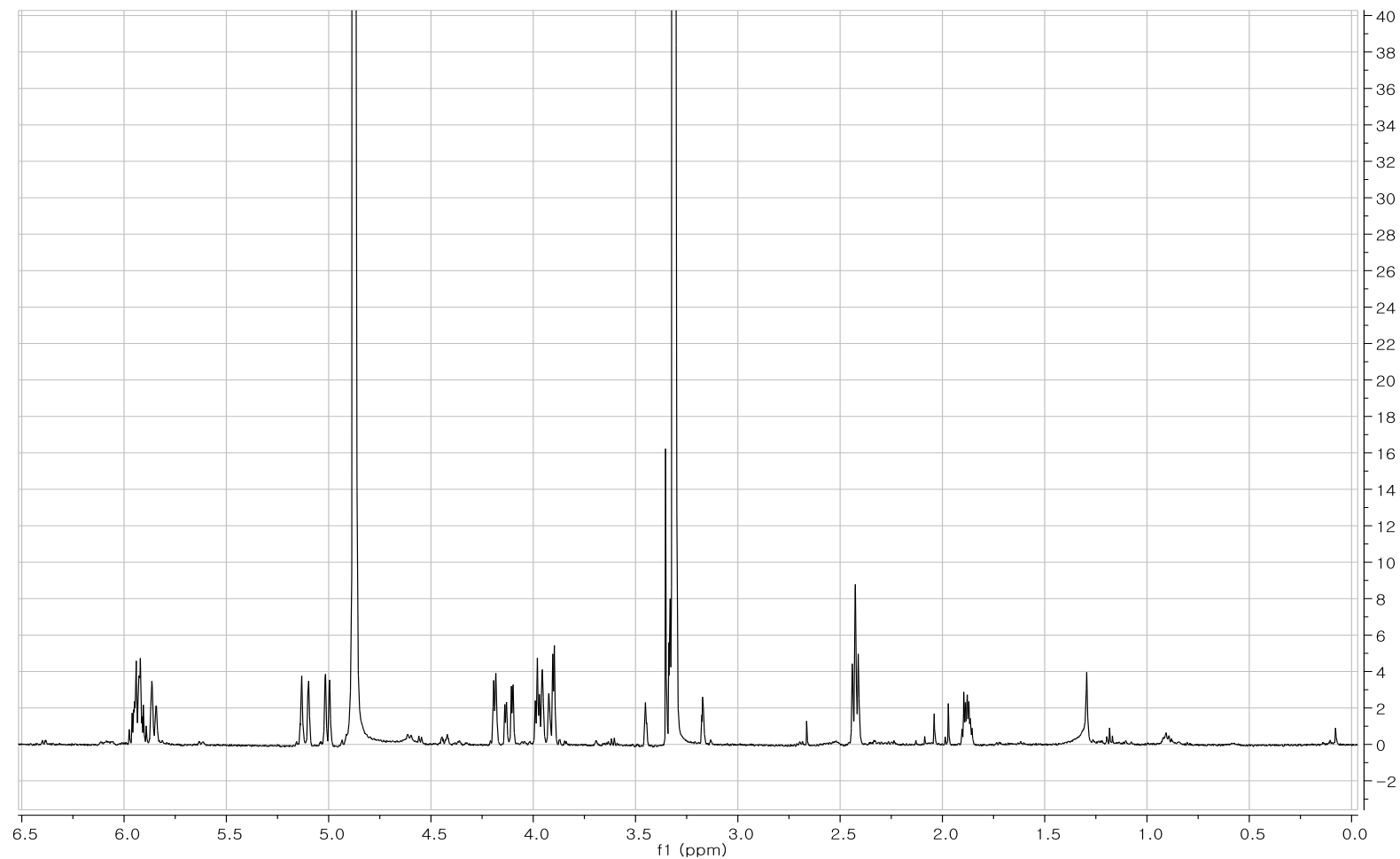


Figure S21. NOESY spectrum of 5-*O*-methyl-6-hydroxydiospentenol A (**6**) (500 MHz, pyridine-*d*<sub>5</sub>)



**Figure S22.** <sup>1</sup>H NMR spectrum of 4-deutero-5-hydro-6-hydroxydiospentenol B (7) (500 MHz, CD<sub>3</sub>OD)

296b-oh-jai-4 (500 MHz, methanol-d4)  
20090625

Sample: 296b-OH-jai-4  
Sample ID: s\_35\_296b-OH-jai-4\_01  
File: /home/SMS/vnmrSYS/data/auto\_2009.06.13/s\_35\_296b-OH-jai-4\_01/data/Noesy\_01.fid

Pulse Sequence: NOESY

Solvent: cd3od  
Temp: 22.0 C / 295.1 K  
Sample #35, Operator: SMS  
File: Noesy\_01  
VNMR5-500 "kist500"

Relax. delay 1.000 sec  
Mixing 0.400 sec  
Acq. time 0.128 sec  
Width 4006.4 Hz  
2D Width 4006.4 Hz  
32 repetitions  
2 x 256 increments  
OBSERVE H1, 499.8475939 MHz  
DATA PROCESSING  
Gauss apodization 0.059 sec  
F1 DATA PROCESSING  
Gauss apodization 0.118 sec  
FT size 4096 x 4096  
Total time 6 hr, 56 min, 54 sec

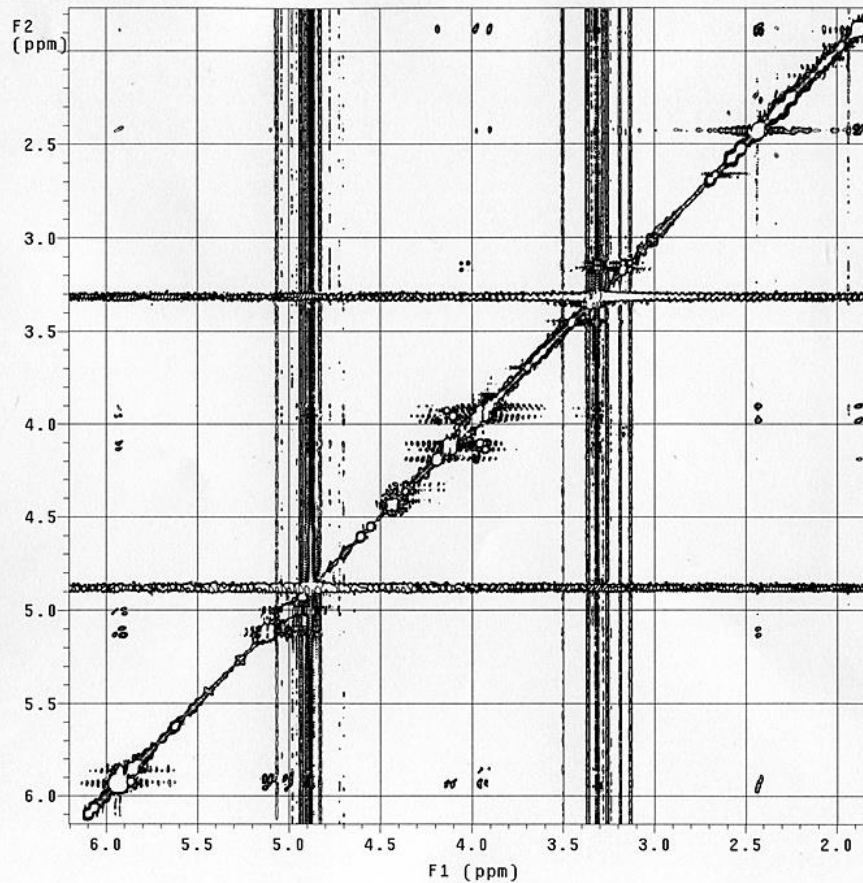
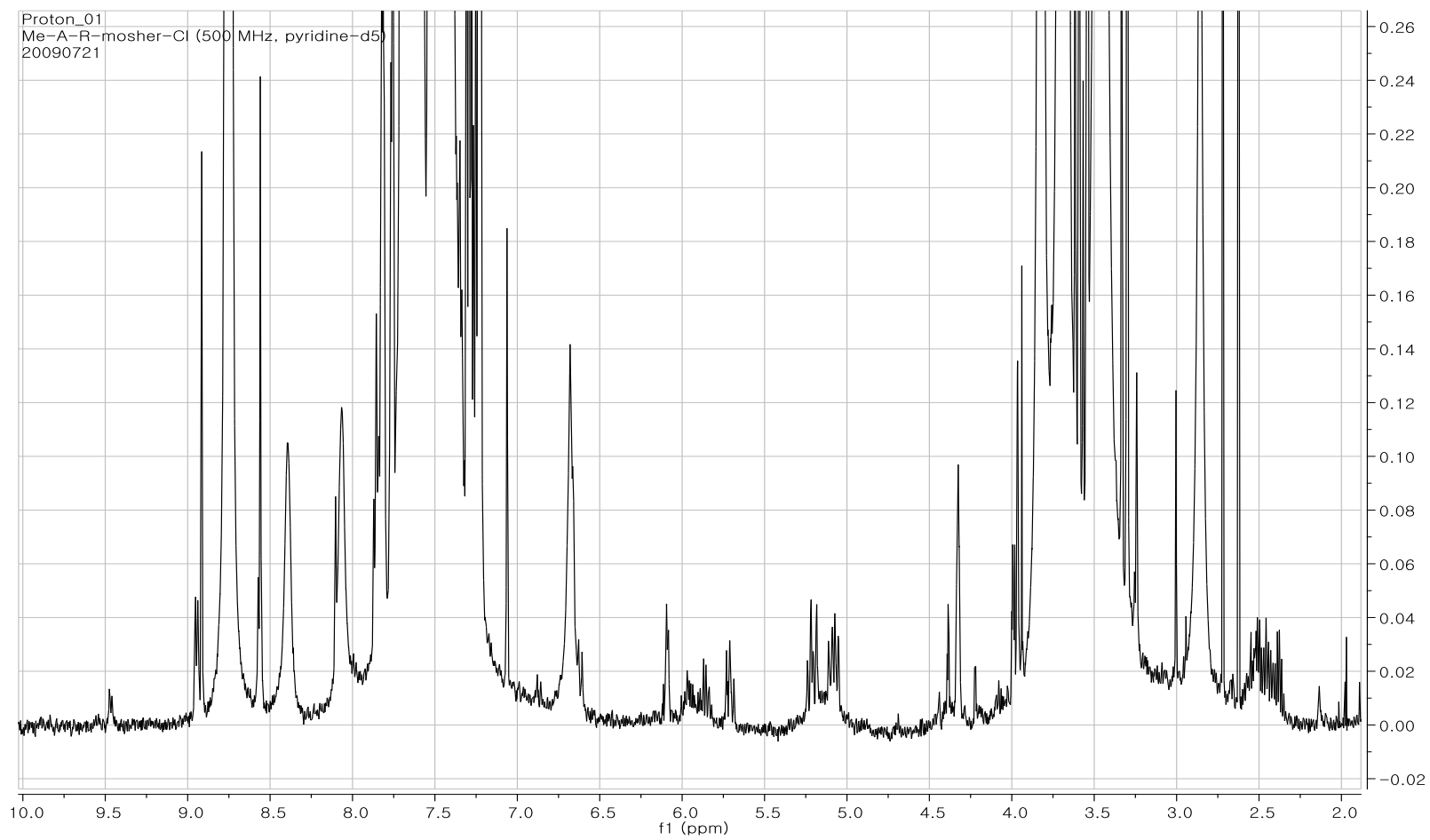
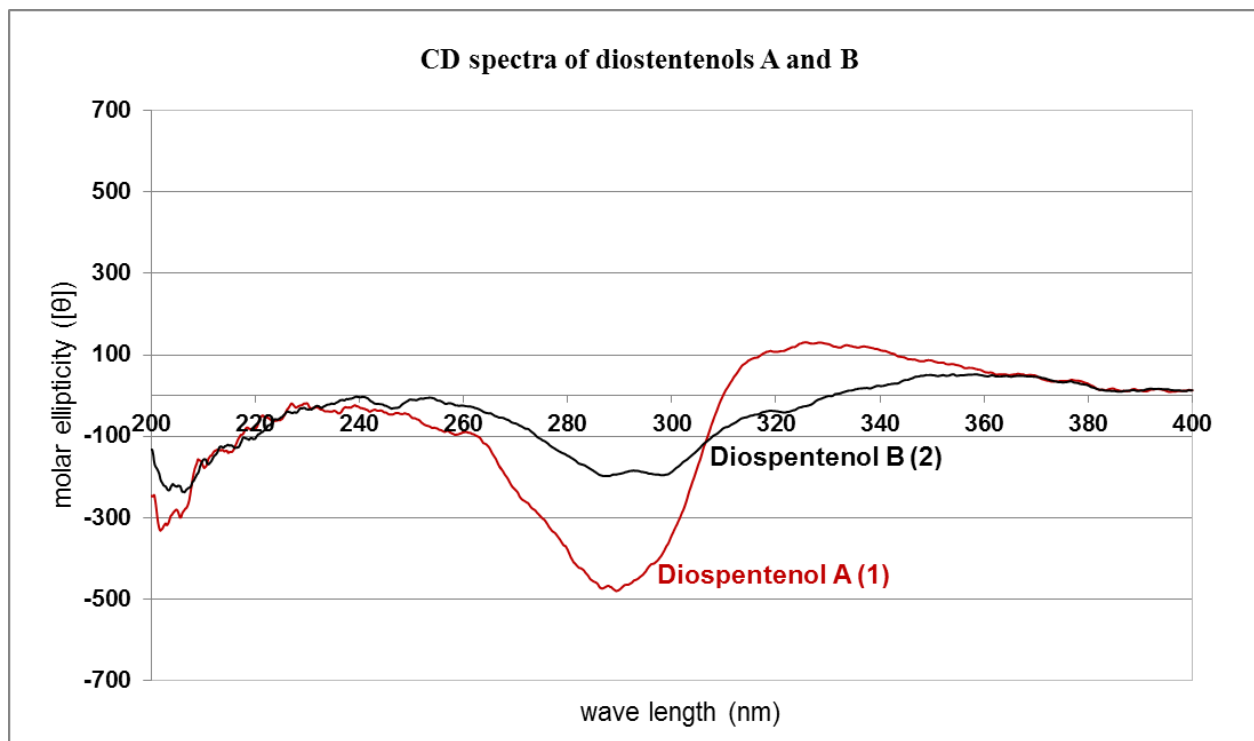


Figure S23. NOESY spectrum of 4-deutero-5-hydro-6-hydroxydiospentenol B (7) (500 MHz, CD<sub>3</sub>OD)

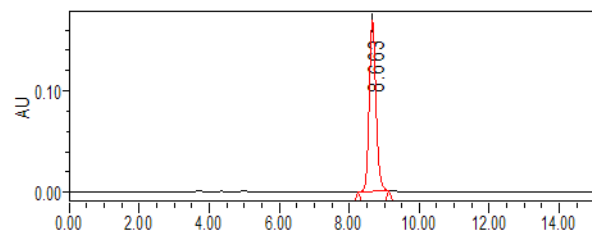


**Figure S24.**  $^1\text{H}$  NMR spectrum of (*S*)-MTPA ester of **6** (500 MHz, pyridine-*d*<sub>5</sub>)

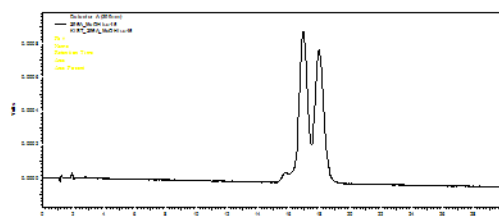


**Figure S25.** CD spectrum of diosptentenols A (1) and B (2)

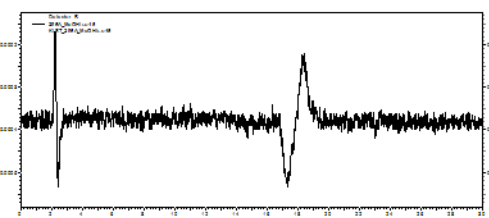
### Diospentenol A (1)



C8/UV

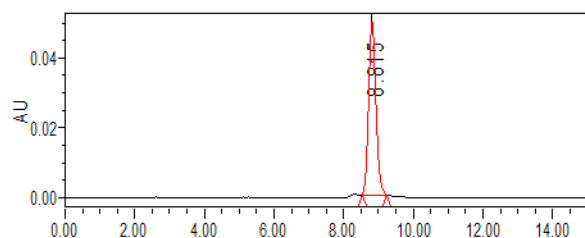


Lux cellulose-1/UV

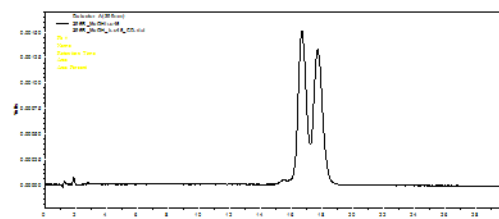


Lux cellulose-1/CD

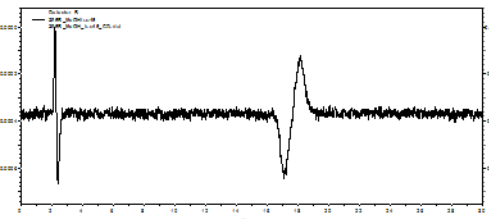
### Diospentenol B (2)



C8/UV

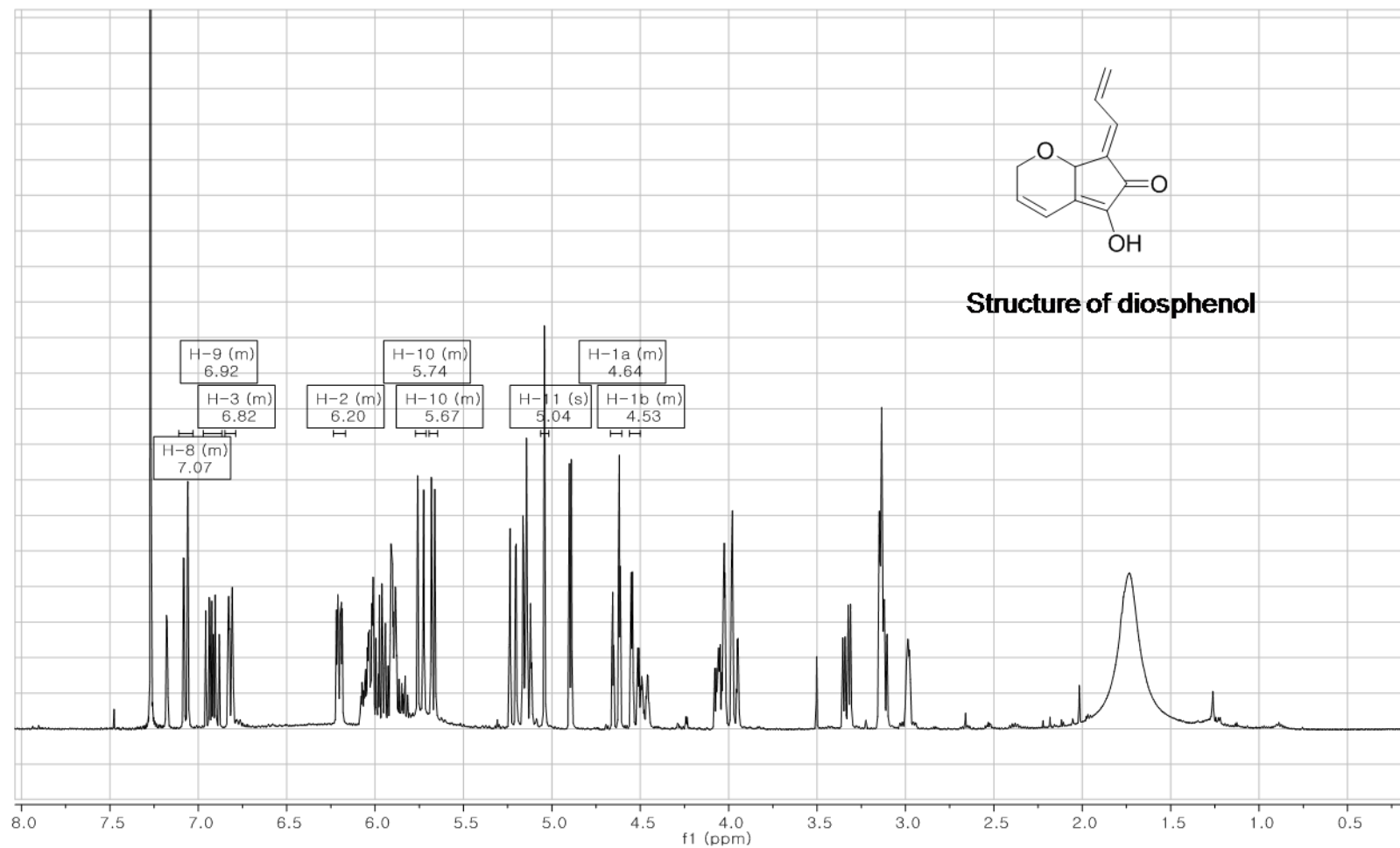


Lux cellulose-1/UV



Lux cellulose-1/CD

Figure S26. HPLC results using reverse phase column (C8) and chiral column (Lux cellulose-1) (300 nm)



**Figure S27.** <sup>1</sup>H NMR spectrum of diosphenol - containing fraction (500 MHz, CDCl<sub>3</sub>)