

## Supplementary Information

### Regio-, chemo- and stereoselective deuterium labeling method of sugars based on ruthenium-catalyzed C-H bond activation

Yuta Fujiwra, Hiroki Iwata, Yoshinari Sawama, Yasunari Monguchi and Hironao Sajiki\*

*Laboratory of Organic Chemistry, Gifu Pharmaceutical University, Gifu 501-1196,  
Japan*

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## General

All the catalysts used in this study were obtained from the N.E. Chemcat Corporation. D<sub>2</sub>O (>99.9% D atom) was purchased from Spectra Gases, Inc. All other reagents were purchased from commercial sources and were used without purification. The <sup>1</sup>H and <sup>2</sup>H spectra were recorded by a JEOL AL-400, EX-400 (<sup>1</sup>H: 400 MHz, <sup>2</sup>H: 61 MHz) or ECA-500 spectrometer (<sup>1</sup>H: 500 MHz, <sup>2</sup>H: 61 MHz). Chemical shifts (δ) are expressed in ppm and are internally referenced to trimethylsilane or residual solvents (<sup>1</sup>H NMR: 0.00 ppm for TMS for CDCl<sub>3</sub>; <sup>2</sup>H NMR: 7.26 ppm for CHCl<sub>3</sub>). The FAB mass spectra were taken by a JEOL JMS-SX102A instrument at the Mass Spectrometry Laboratory of the Gifu Pharmaceutical University. Optical rotations were taken by a DIP-360 instrument. The heating reactions were carried out using a personal organic synthesizer, Chemist Plaza (Shibata Science Technology, Ltd.).

## Typical Procedure for the Ru/C-Catalyzed H-D Exchange of Sugars (Table 2).

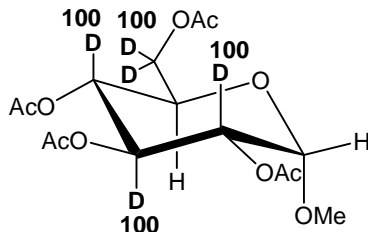
A suspension of the sugar (Entries 1–8 : 0.5 mmol; Entry 9: 0.25 mmol) and 10% Ru/C (Entries 1–7: 5 mol% of the substrate; Entries 8 and 9: 10 mol% of the sugar) in 2 cm<sup>3</sup> of D<sub>2</sub>O was stirred at 80 °C in a test tube under a hydrogen atmosphere (balloon). After the appropriate time, the mixture was cooled to room temperature and filtered using a membrane filter (Millipore, Millex<sup>®</sup>-LH, 0.45 μm) to remove the catalyst. The filtrate was then concentrated in vacuo. To the residue were added 2.5 mmol of acetic anhydride and 5.0 mmol of pyridine, and the mixture was stirred at room temperature for 24 h and concentrated in vacuo to give the deuterated *O*-acetylated glycoside.

## Evaluation of Deuterium Content

The deuterium content was determined by the <sup>1</sup>H NMR on the basis of the integration of the methyl protons of the methoxy group. For Entry 9, the integration of the proton at the 1 (anomeric) positions was employed instead of the methyl protons. The deuterium incorporation was also assigned by the <sup>2</sup>H NMR and FAB Mass spectra.

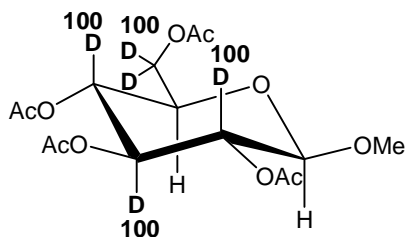
## Compound Data

### Methyl 2,3,4,6-tetraacetyl- $\alpha$ -D-glucopyranoside- $d_5$ (Table 2, Entry 1)



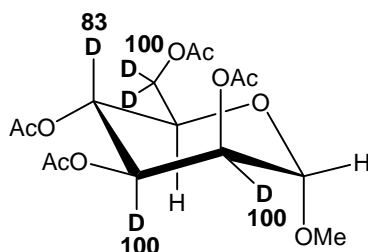
$[\alpha]_D^{20} = 107.4$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.95 (s, 1H), 3.98 (s, 1H), 3.42 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ):  $\delta$  5.36 (br s), 4.95 (br s), 4.8 (br s), 4.14 (br s), 3.99 (br s).

### Methyl 2,3,4,6-tetraacetyl- $\beta$ -D-glucopyranoside- $d_5$ (Table 2, Entry 2)



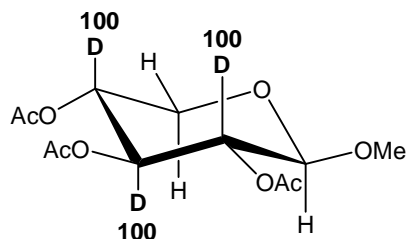
$[\alpha]_D^{21} = -16.5$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.43 (s, 1H), 3.69 (s, 1H), 3.51 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ):  $\delta$  5.16 (br s), 5.04 (br s), 4.93 (br s), 4.21 (br s), 4.01 (br s).

### Methyl 2,3,4,6-tetraacetyl- $\alpha$ -D-mannopyranoside- $d_5$ (Table 2, Entry 3)



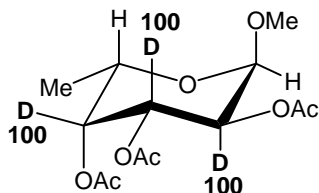
$[\alpha]_D^{22} = 44.4$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.29–5.27 (m, 0.17H), 4.71 (s, 1H), 3.96 (s, 1H), 3.41 (s, 3H), 2.16 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ):  $\delta$  5.16 (br s), 4.16 (br s), 4.01 (br s).

**Methyl 2,3,4-triacetyl- $\beta$ -D-xylopyranoside- $d_3$**  (Table 2, Entry 4)



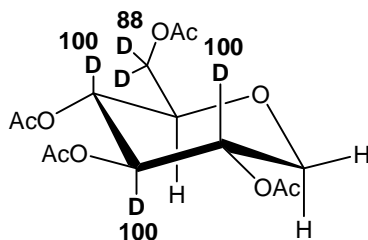
$[\alpha]_D^{20} = -65.2$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.40 (s, 1H), 4.14–4.11 (d,  $J = 11.7$  Hz, 1H), 3.47 (s, 3H), 3.39–3.36 (d,  $J = 11.7$  Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ):  $\delta$  5.06 (br s), 4.82 (br s).

**Methyl 2,3,4-triacetyl- $\alpha$ -L-fucopyranoside- $d_3$**  (Table 2, Entry 5)



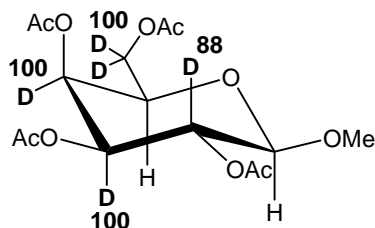
$[\alpha]_D^{21} = -127.0$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.94 (s, 1H), 4.15–4.10 (q,  $J = 6.59$  Hz, 1H), 3.40 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H), 1.16–1.15 (d,  $J = 6.59$  Hz, 3H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ):  $\delta$  5.22 (br s), 5.04 (br s).

**1-Deoxy-2,3,4,6-tetraacetyl-D-glucopyranoside- $d_5$**  (Table 2, Entry 6)



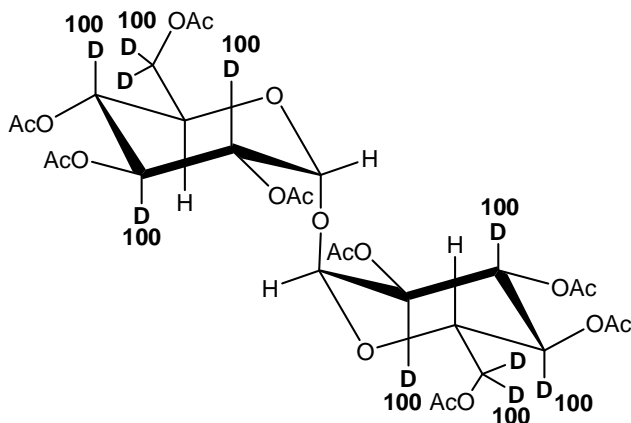
$[\alpha]_D^{21} = 29.6$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.40 (s, 1H), 4.19–4.12 (m, 1.25H), 3.59 (s, 1H), 3.32–3.30 (d,  $J = 8.7$  Hz, 1H), 2.10 (s, 3H), 2.04–2.03 (s, 9H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ): 5.19 (br s), 5.01 (br s), 4.18 (br s), 4.11 (br s).

**Methyl 2,3,4,6-tetraacetyl- $\beta$ -D-galactopyranoside- $d_5$**  (Table 2, Entry 8)



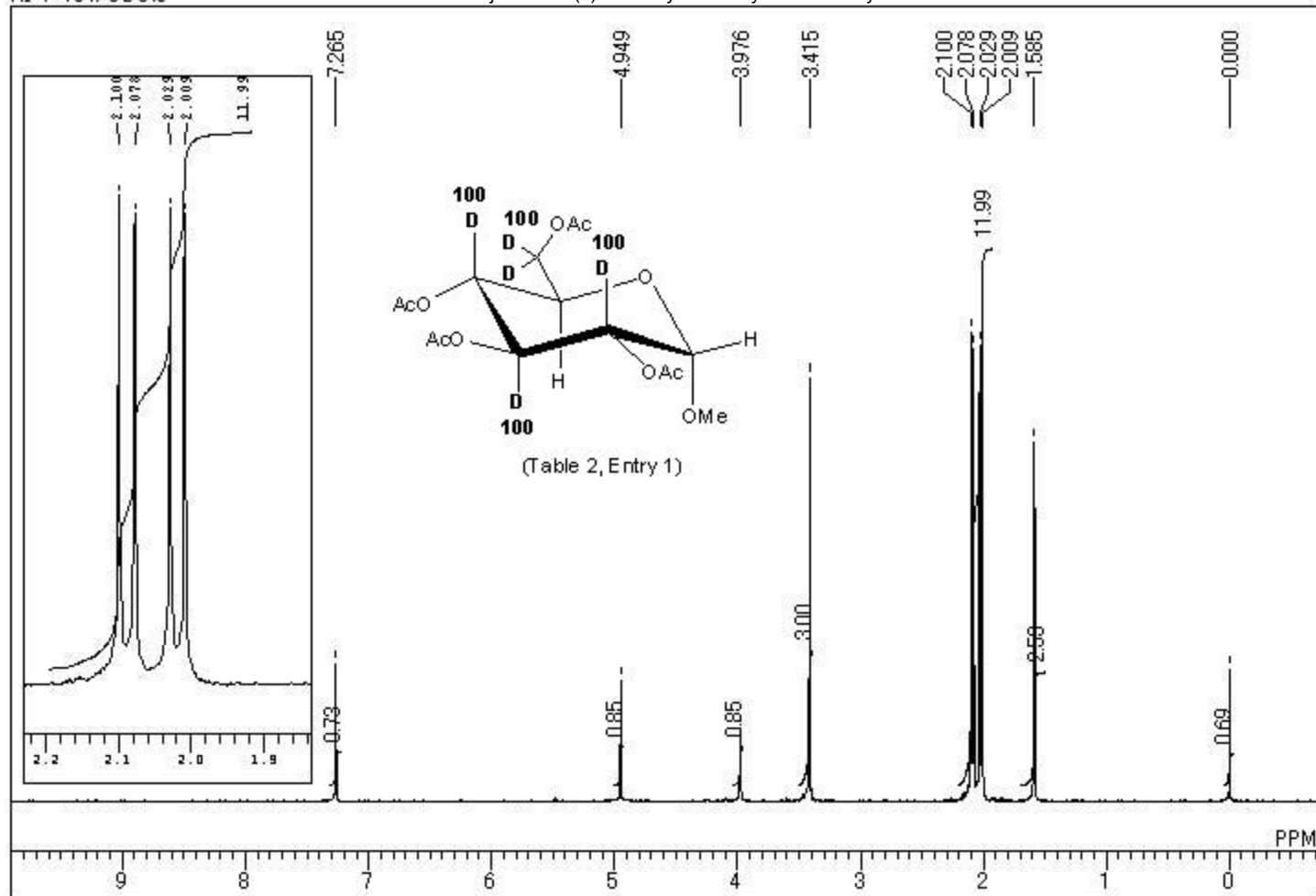
$[\alpha]_D^{21} = 103.5$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.19 (m, 0.12H), 4.40 (s, 1H), 3.90 (s, 1H), 3.52 (s, 3H), 2.15 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ):  $\delta$  5.30 (br s), 5.10 (br s), 4.95 (br s), 4.08 (br s).

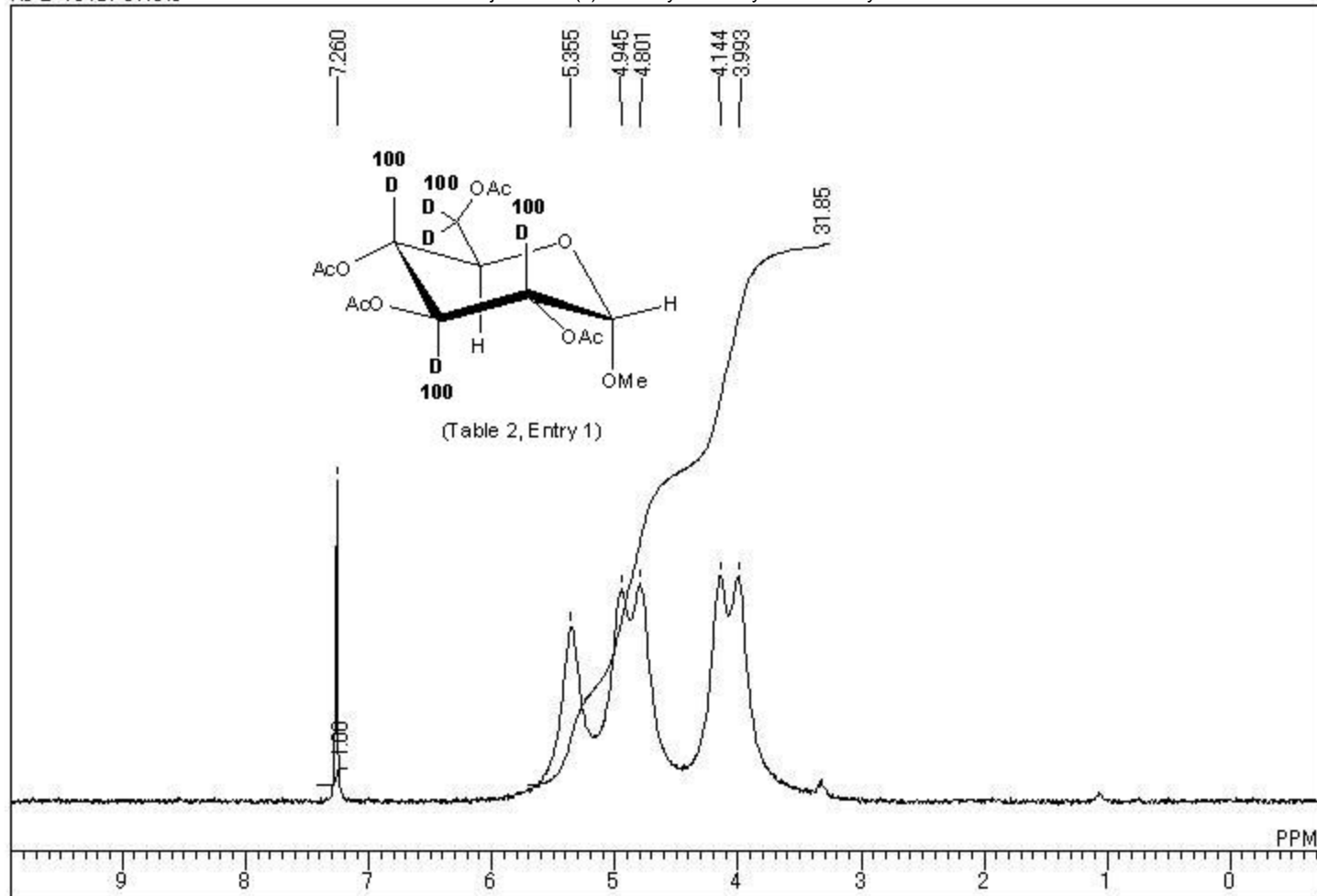
**2,2',3,3',4,4',6,6'-octaacetyl-treharose- $d_{10}$**  (Table 2, Entry 9)



$[\alpha]_D^{20} = 148.0$  ( $c = 0.1$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.28 (s, 1H), 4.04 (s, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H);  $^2\text{H NMR}$  ( $\text{CHCl}_3$ ):  $\delta$  5.44 (br s), 4.99 (br s), 4.16 (br s), 3.94 (br s).

HI-1-104/CDCI3





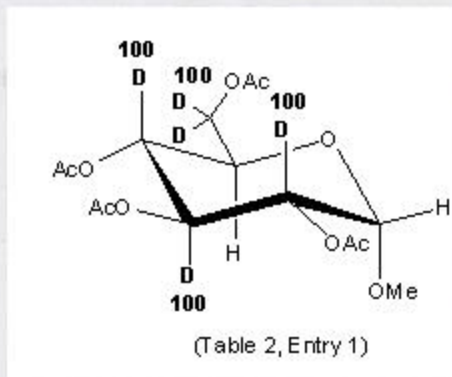
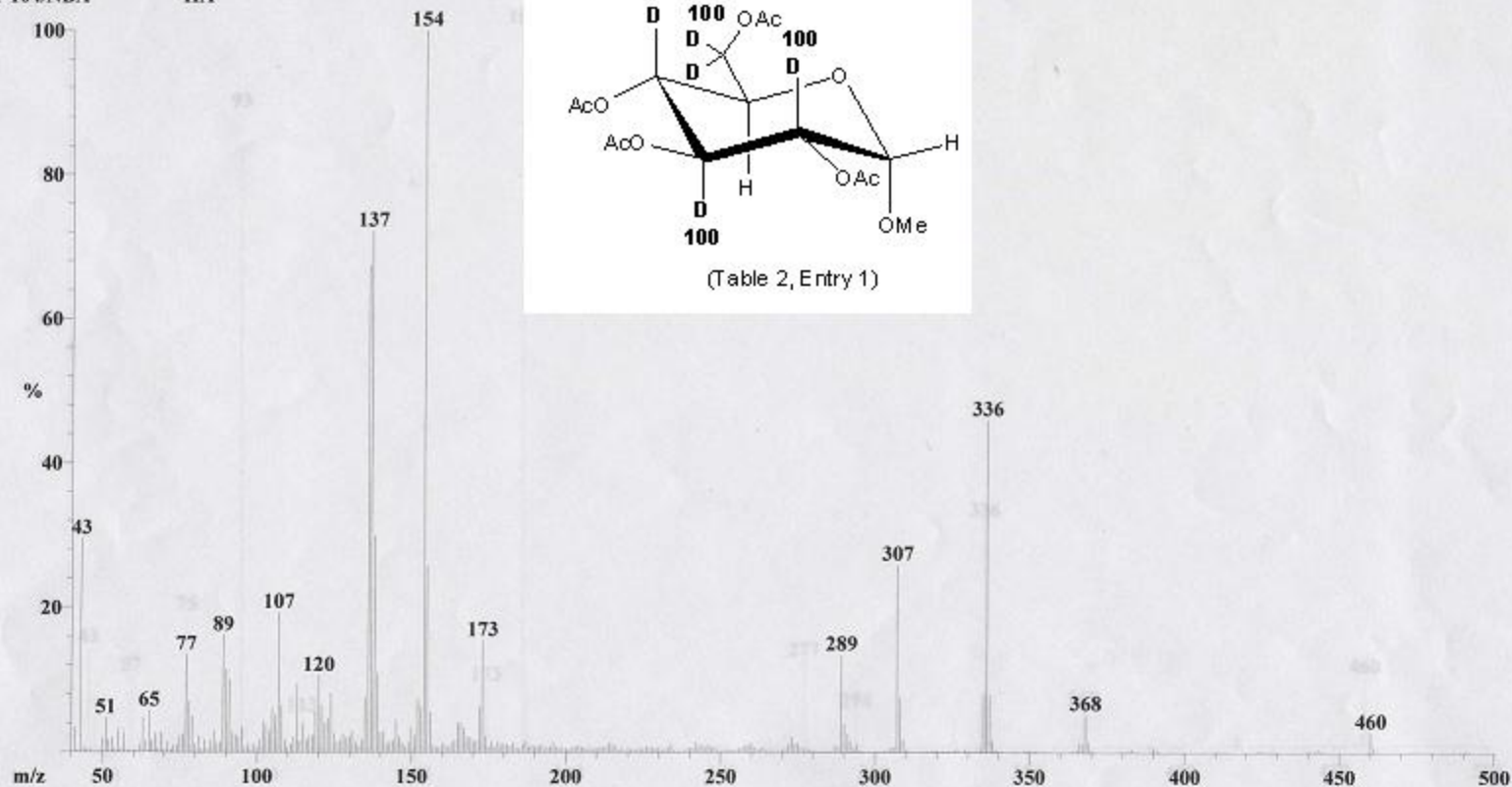
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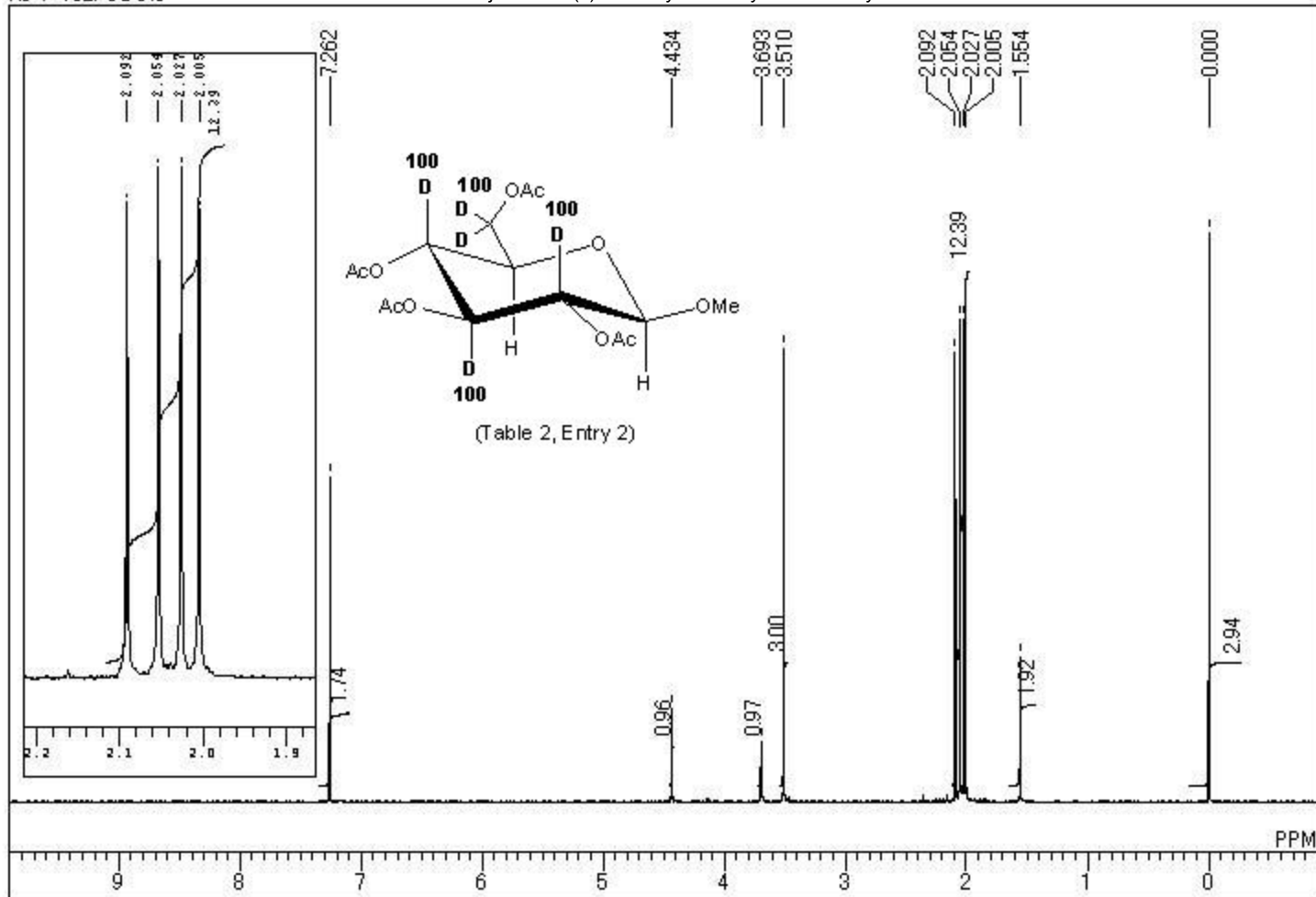
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HI-1-104/NBA HA

#Ions: 389

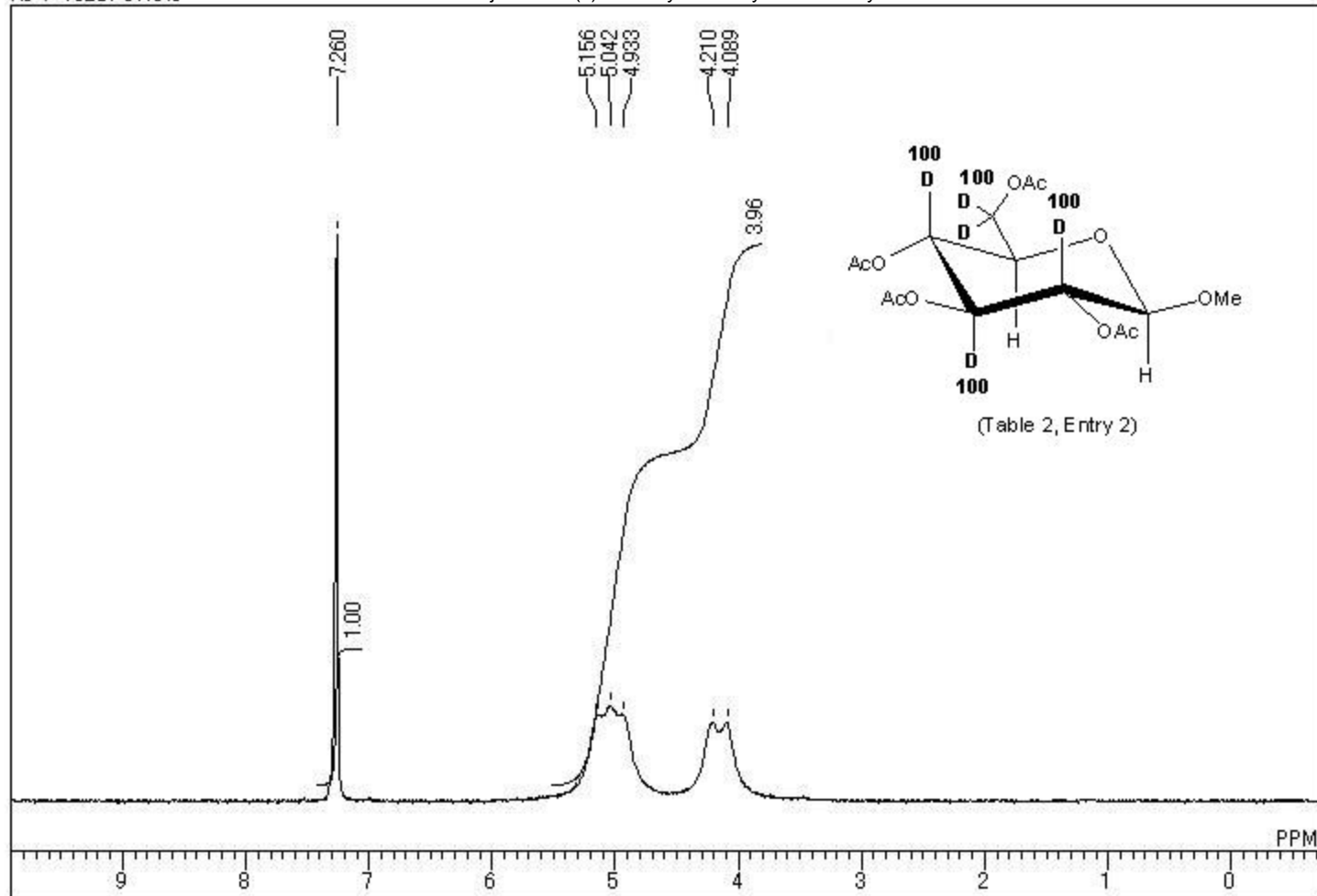




HI-1-152/CDCI3



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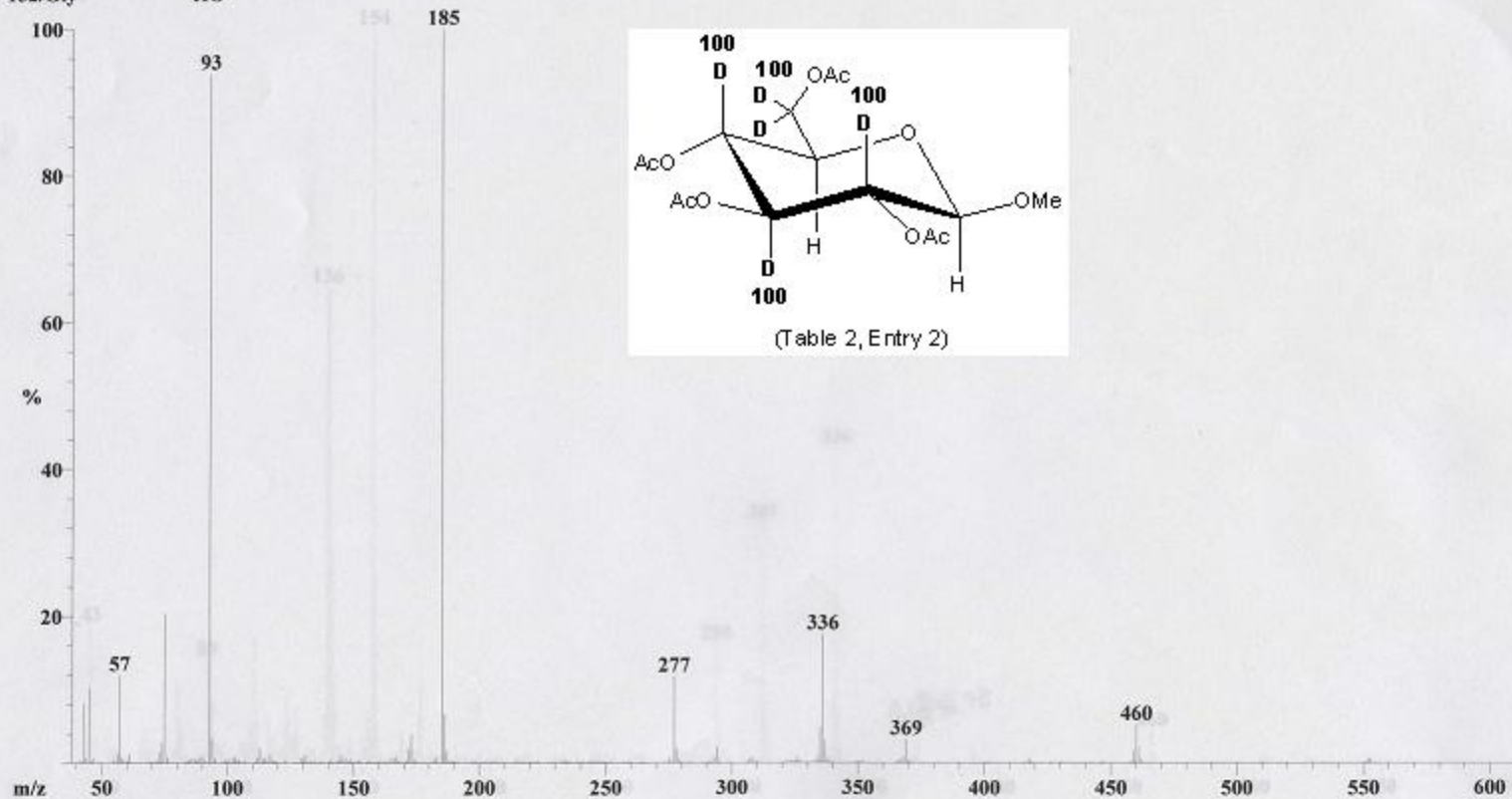
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Inlet: Direct

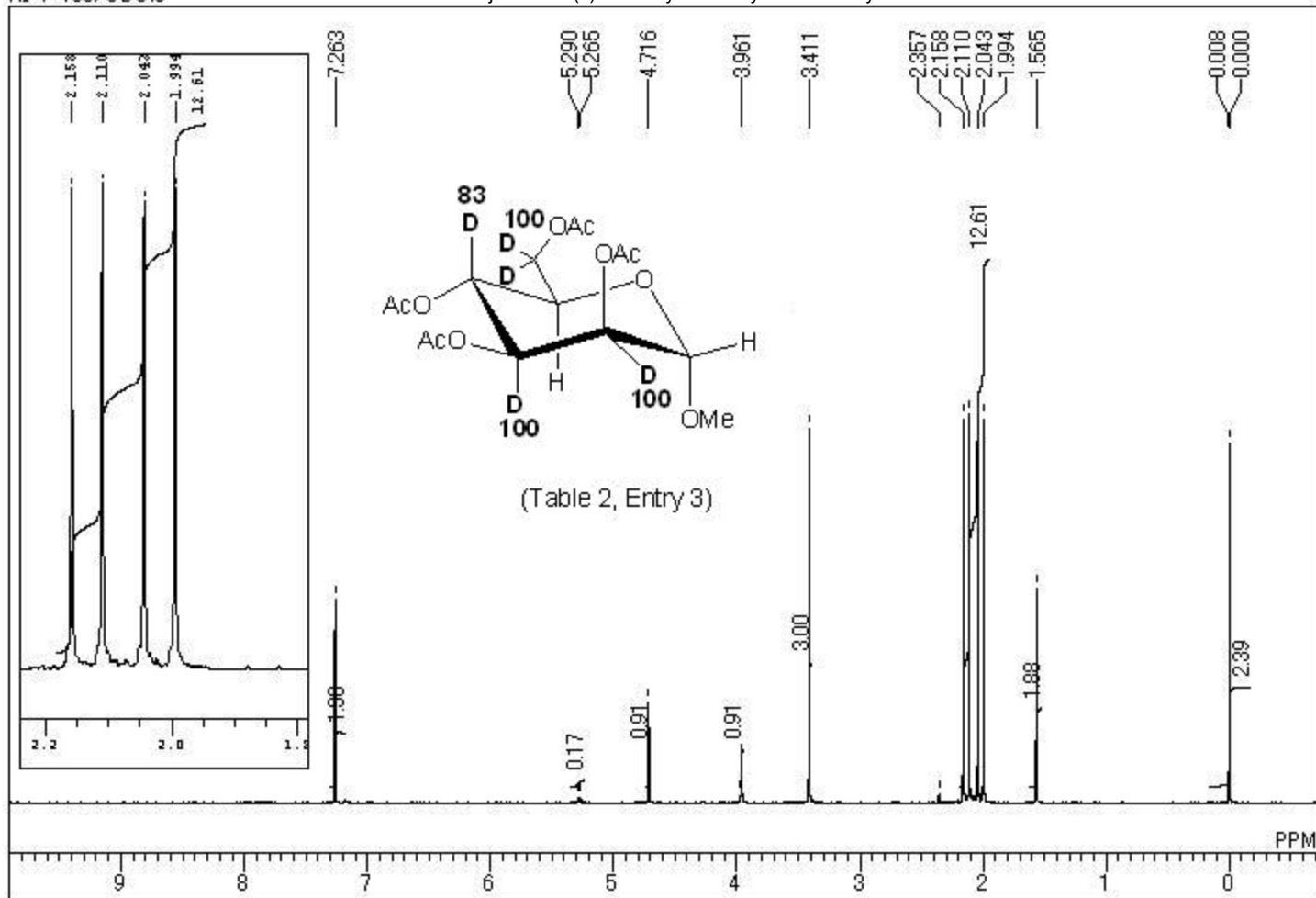
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Ionization mode: FAB+

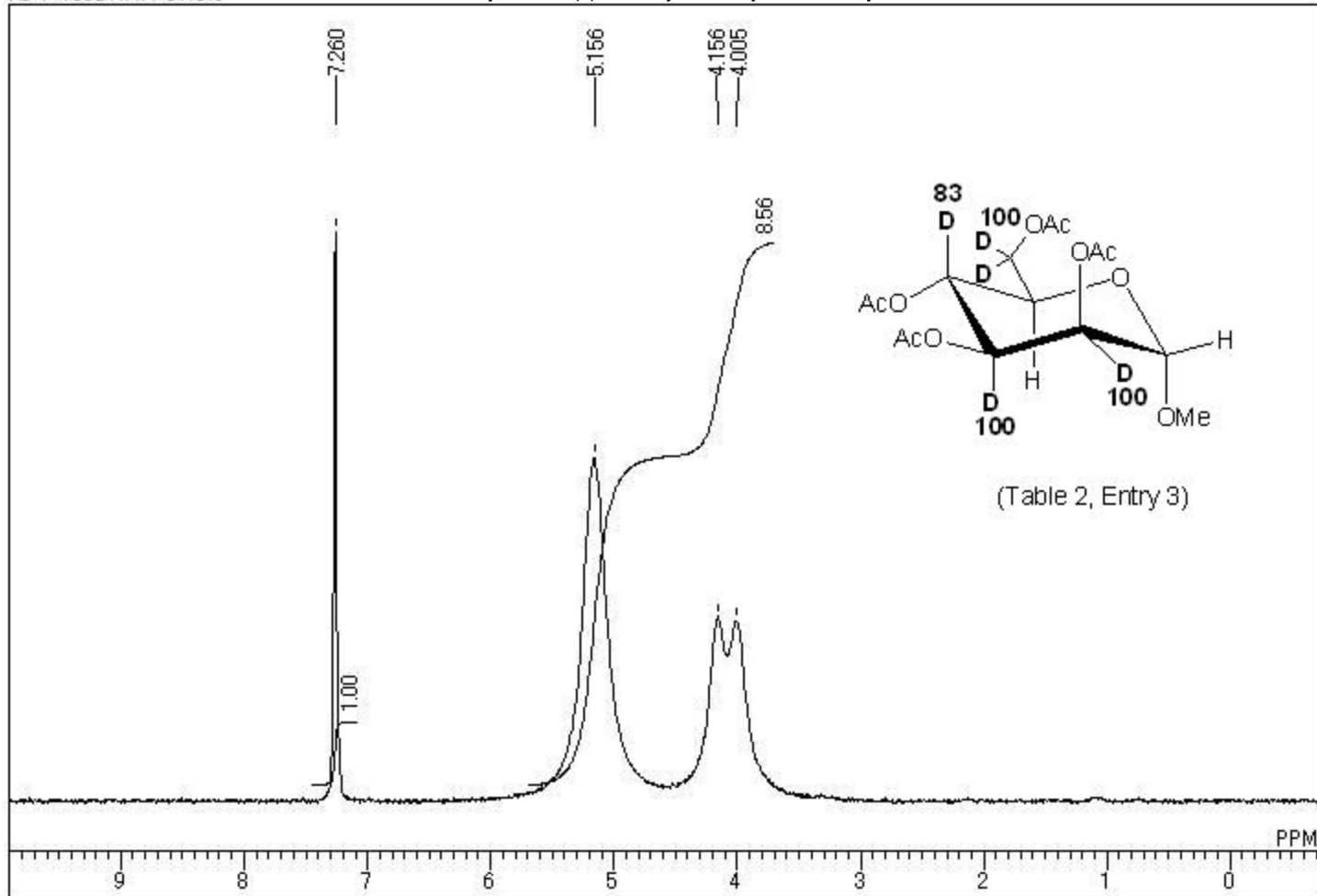
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Base: m/z 185; 80.5%FS TIC: 54664828  
HI-1-152/Gly HO

#Ions: 260



HI-1-155/CDCI3





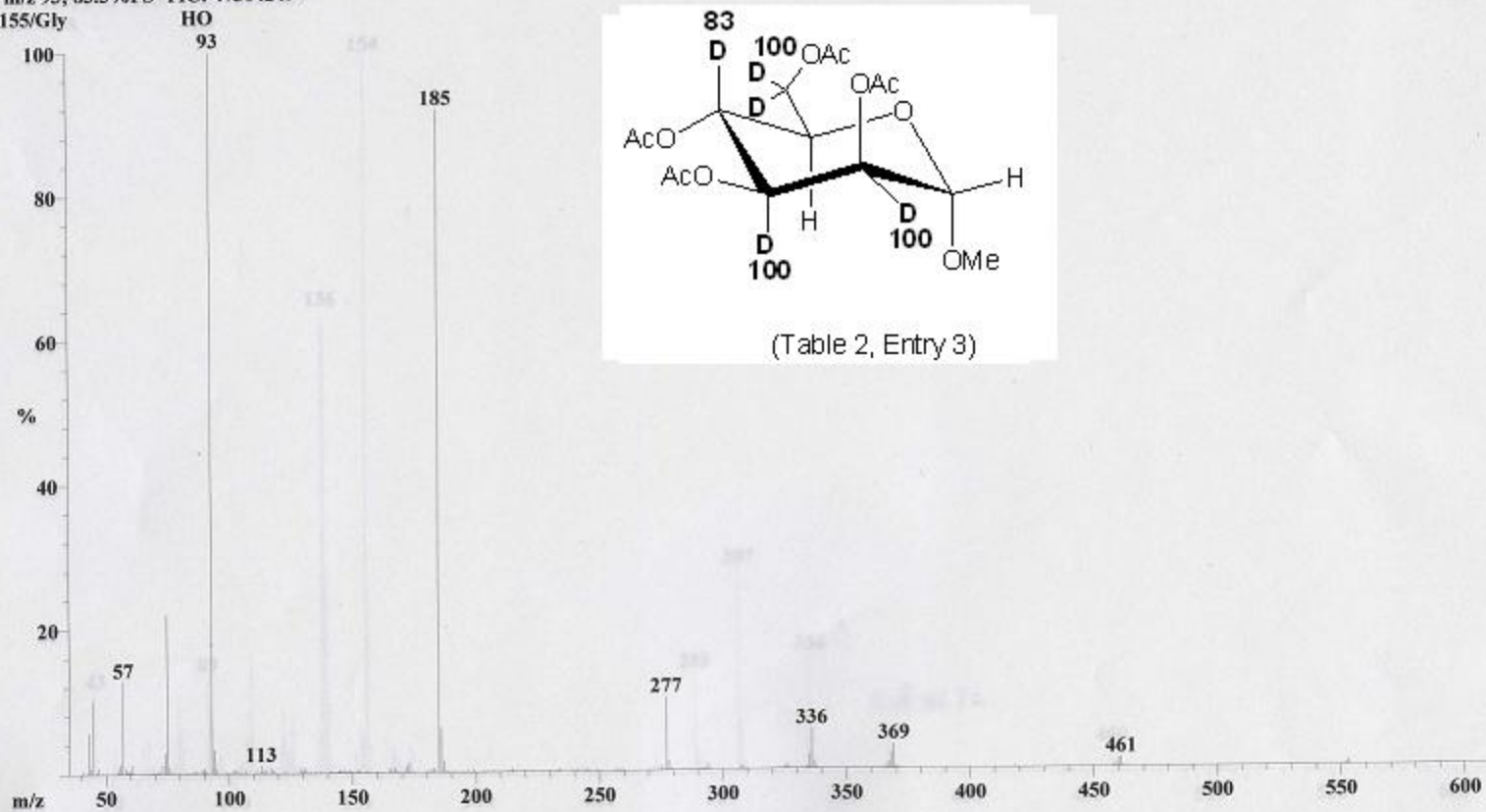
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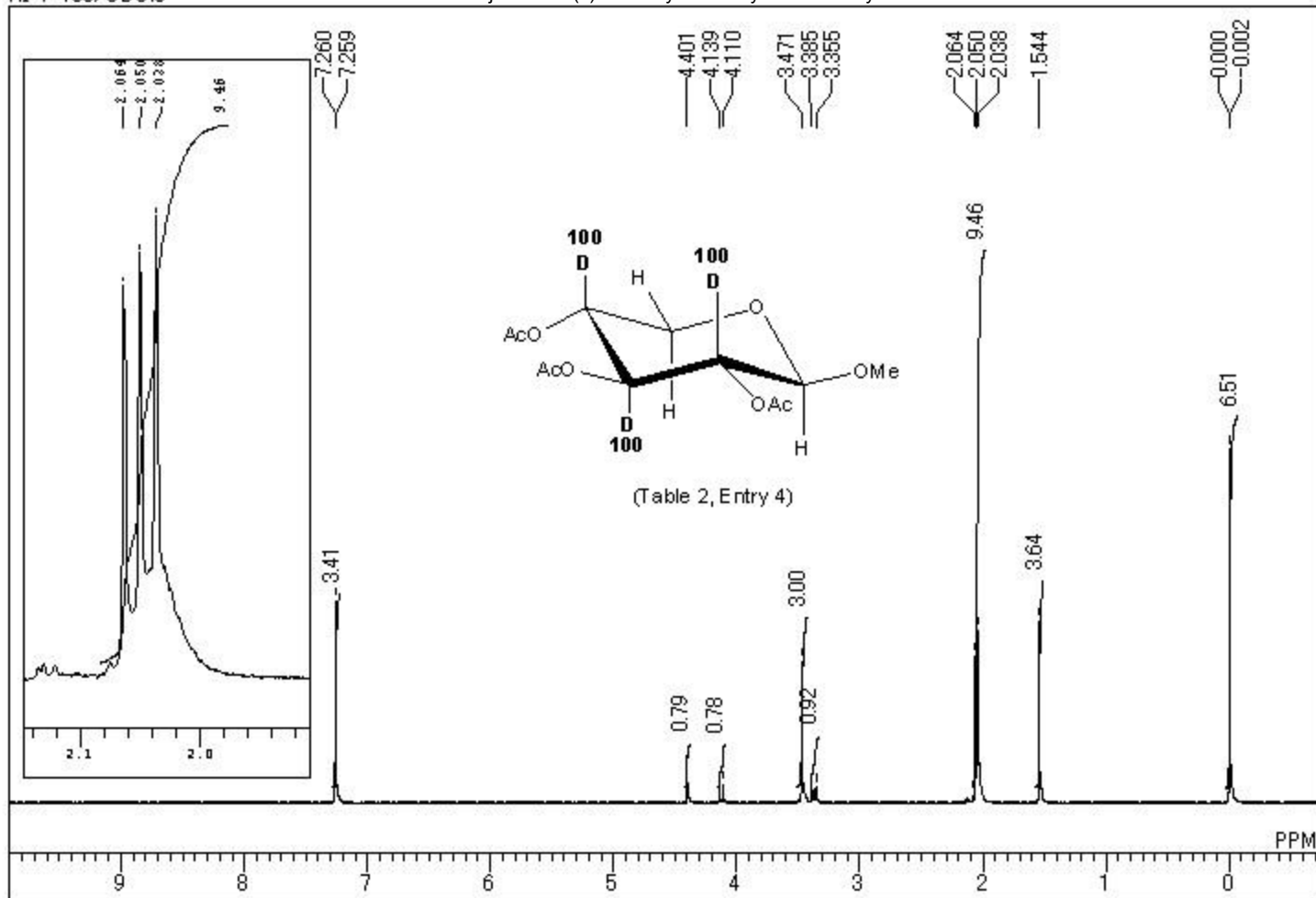
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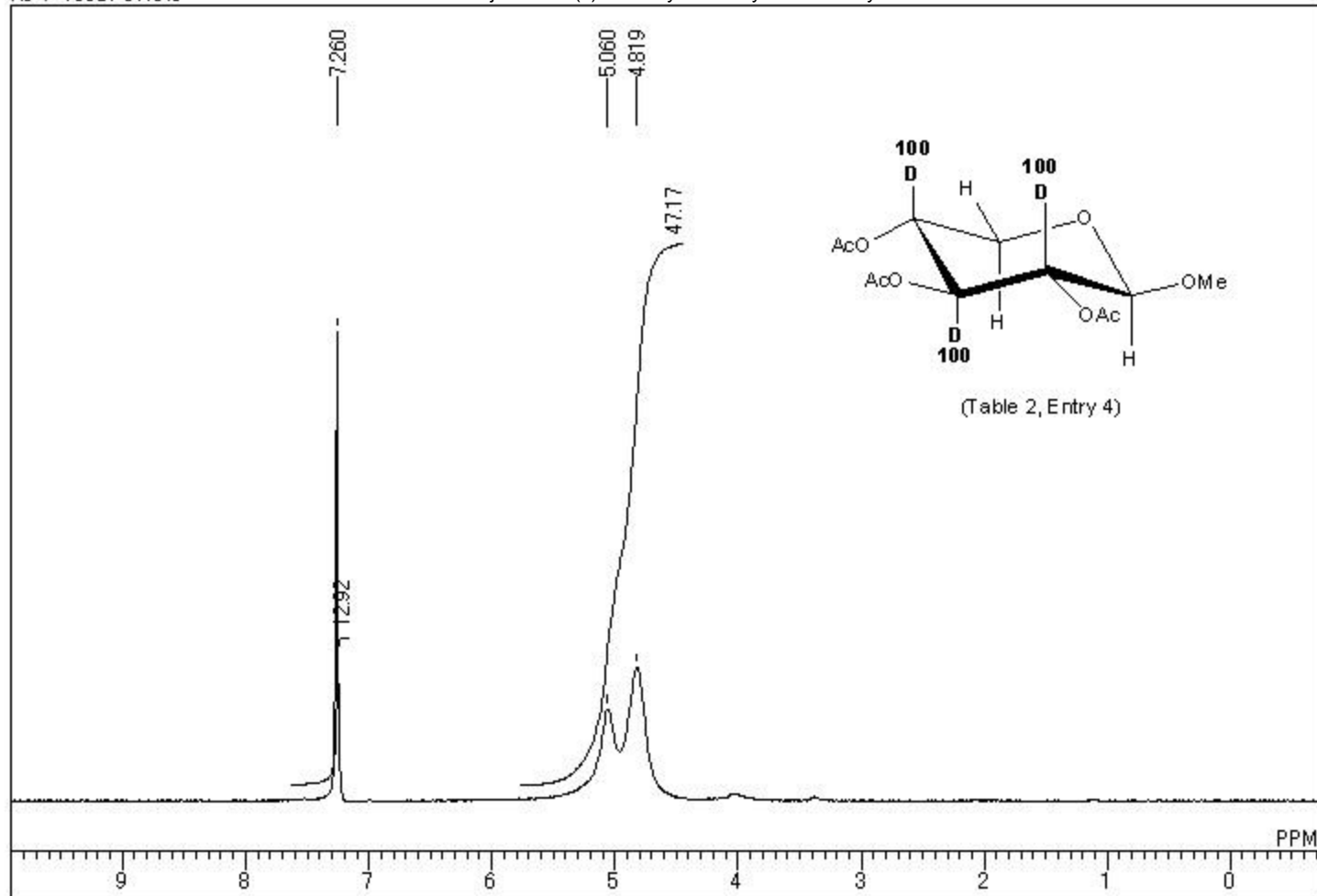
Scan: 2 R.T.: .15  
Base: m/z 93; 83.3%FS TIC: 47304249  
HI-1-155/Gly

#Ions: 167



HI-1-156/CDCI3





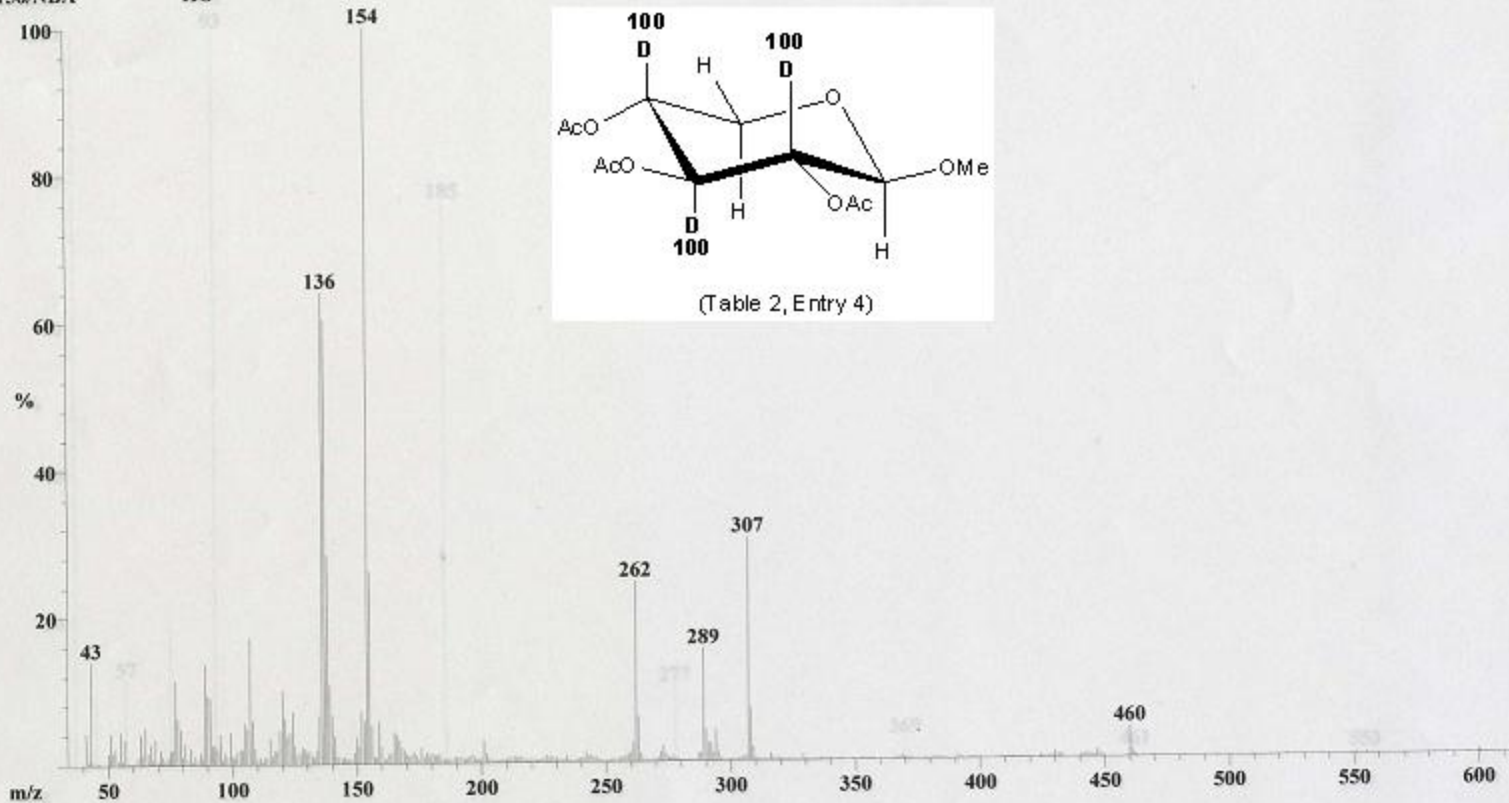


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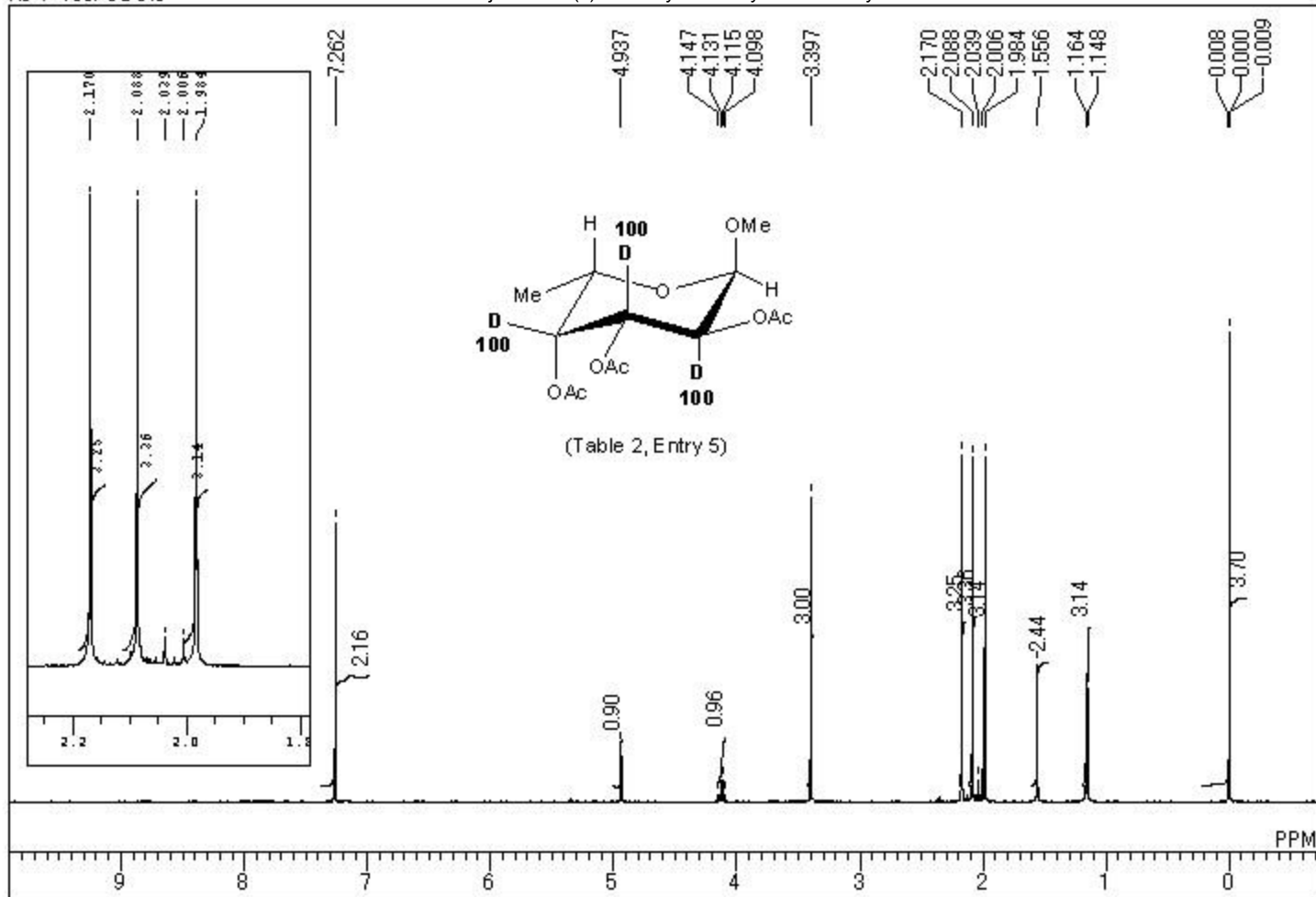
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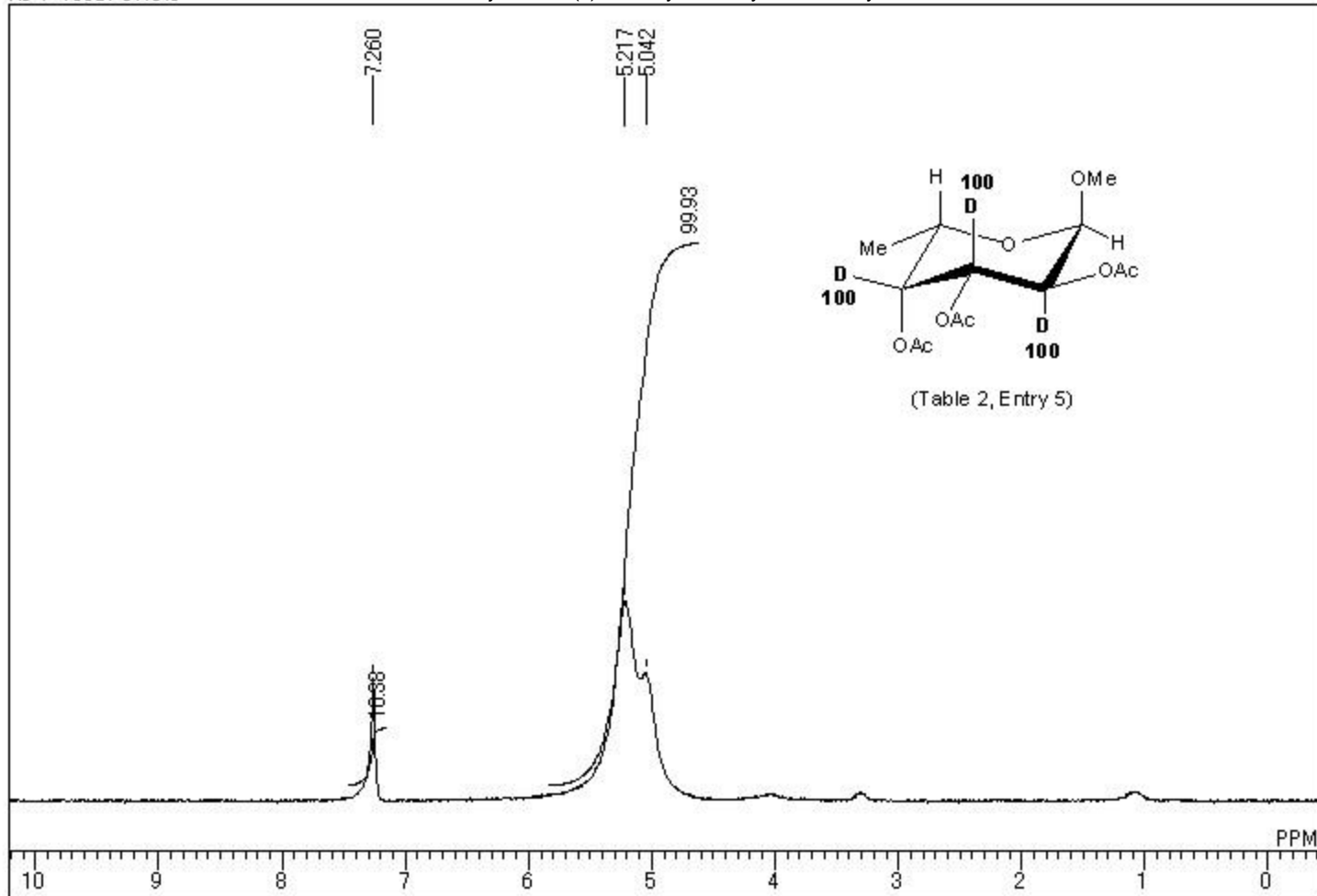
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HI-1-156/NBA HO

#Ions: 393



HI-1-158/CDCI3





DFILE  
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RGAIN

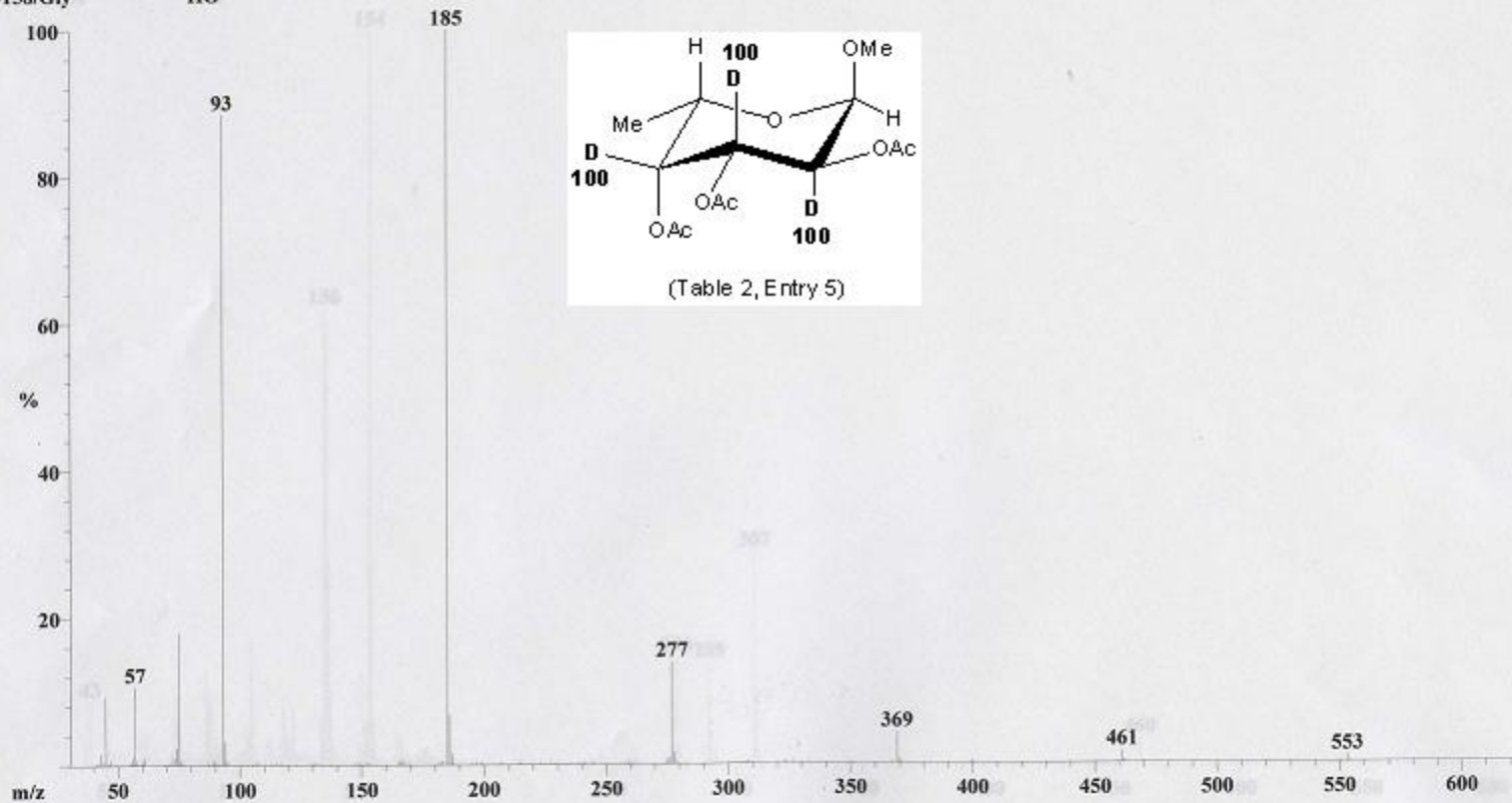
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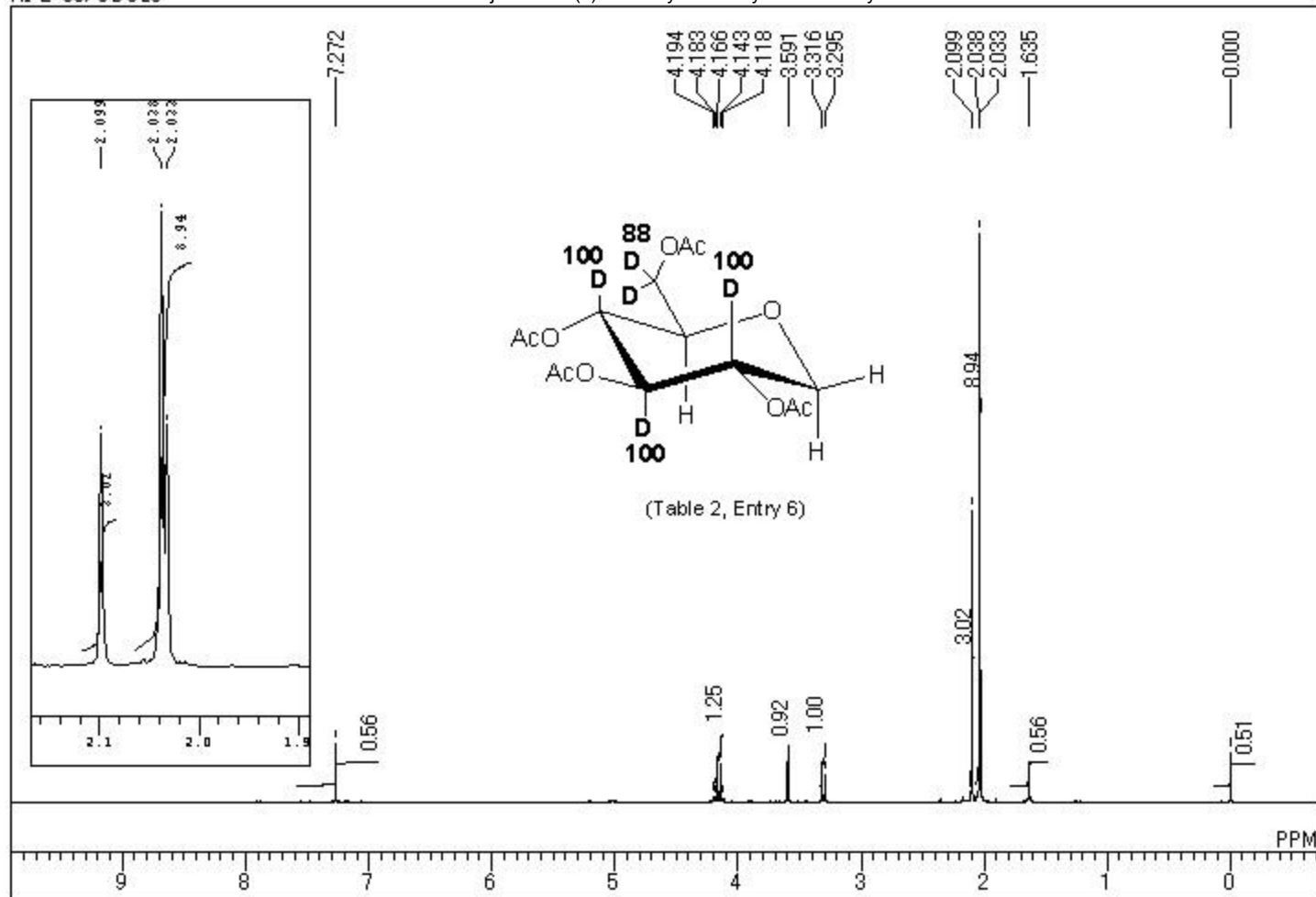
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HI-1-158/Gly HO

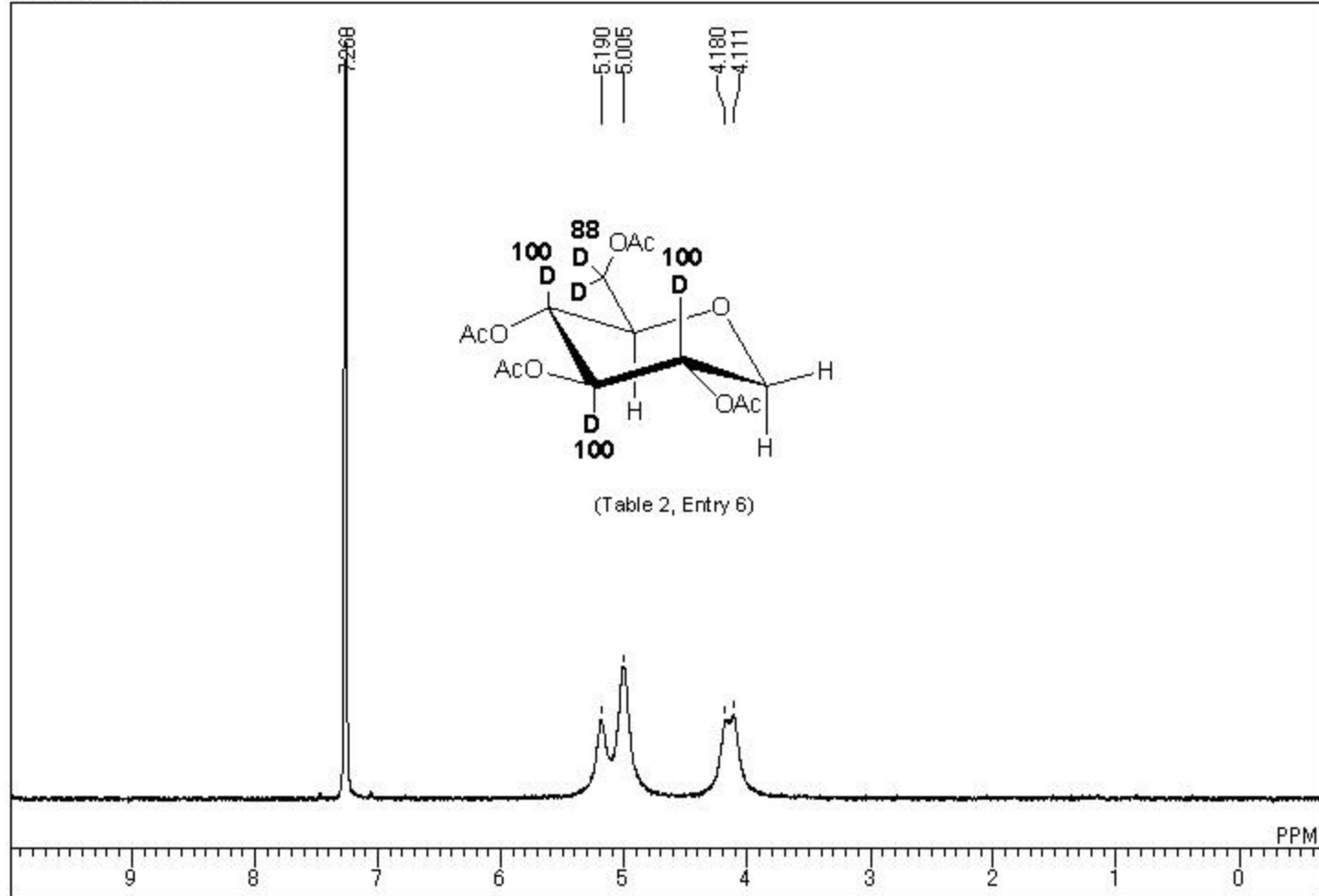
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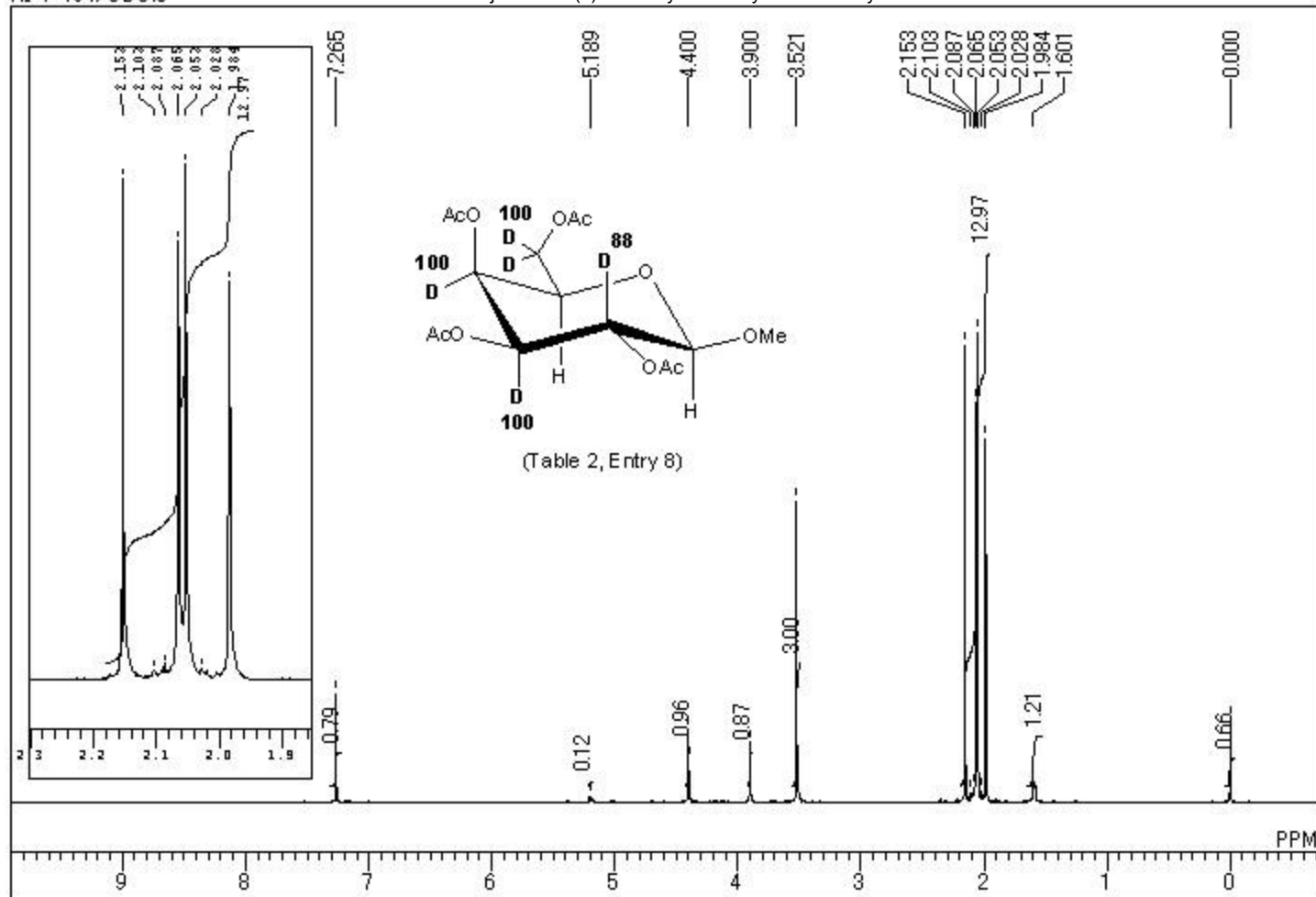


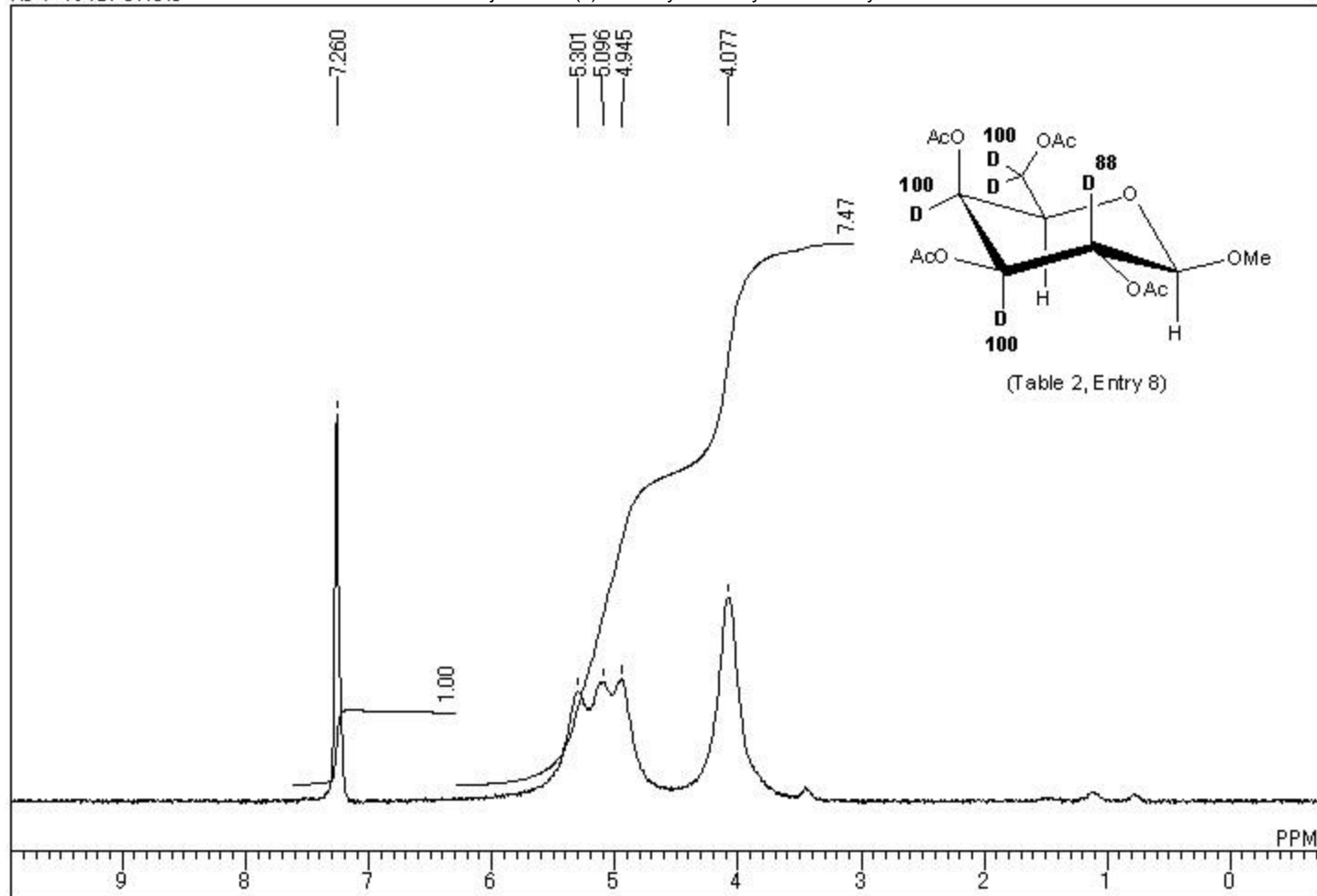


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 SLVNT  
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 RGAIN

(Table 2, Entry 6)









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Date Run: 12-7-2009 (Time Run: 18:11:38)  
Ionization mode: FAB+

403

Scan: 3 R.T.: .3  
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HI-1-194/NBA HA

#Ions: 413

