



## Iridoid glucosides in the genus *Veronica* (Plantaginaceae) from New Zealand

**Kroll-Møller, Phillip; Pedersen, Katja D; Gousiadou, Chrysoula; Kokubun, Tetsuo; Albach, Dirk; Taskova, Rilka; Garnock-Jones, Phil J.; Gotfredsen, Charlotte Held; Jensen, Søren Rosendal**

*Published in:*  
Phytochemistry

*Link to article, DOI:*  
[10.1016/j.phytochem.2017.04.025](https://doi.org/10.1016/j.phytochem.2017.04.025)

*Publication date:*  
2017

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Kroll-Møller, P., Pedersen, K. D., Gousiadou, C., Kokubun, T., Albach, D., Taskova, R., ... Jensen, S. R. (2017). Iridoid glucosides in the genus *Veronica* (Plantaginaceae) from New Zealand. *Phytochemistry*, 140, 174-180. <https://doi.org/10.1016/j.phytochem.2017.04.025>

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# Iridoid glucosides in the genus *Veronica* (Plantaginaceae) from New Zealand

Phillip Kroll-Møller<sup>a§</sup>, Katja D. Pedersen<sup>a§</sup>, Chrysoula Gousiadou<sup>a</sup>, Tetsuo Kokubun<sup>b</sup>, Dirk Albach<sup>c</sup>, Rilka Taskova<sup>d</sup>, Phil J. Garnock-Jones<sup>d</sup>, Charlotte H. Gotfredsen<sup>a</sup>, Søren Rosendal Jensen<sup>a\*</sup>

<sup>a</sup> Department of Chemistry, The Technical University of Denmark, Build. 207, DK-2800 Lyngby, Denmark

<sup>b</sup> Royal Botanic Gardens, Kew, Richmond, Surrey TW9 3AB, UK

<sup>c</sup> Institut für Biologie und Umweltwissenschaften, Carl von Ossietzky-Universität Oldenburg, 26111 Oldenburg, Germany

<sup>d</sup> School of Biological Sciences, Victoria University of Wellington, P.O. Box 600, Wellington 6140, New Zealand

## A B S T R A C T

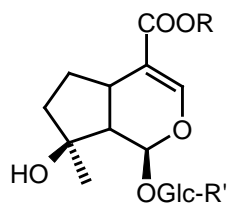
Four simple iridoid glucosides, three known esters of catalpol, seven esters of aucubin, and two phenylethanoids were isolated from *Veronica hookeri* (syn. *Hebe ciliolata*; Plantaginaceae). Of these, none of four aromatic (*p*-methoxybenzoyl, isovanilloyl, veratroyl, caffeoyl) 6-*O*-esters of aucubin and 6''-*O*-benzoyl mussaenosidic acid, had been reported from nature before. Similarly, three simple iridoid glucosides, two esters of 6-*O*-rhamnopyranosylcatalpol, and two phenylethanoid glucosides, as well as 1-*O*-benzoyl-3- $\alpha$ -glucuronosylglycerol, and 1-*O*- $\beta$ -benzoyl rutinose were isolated from *Veronica pinguifolia* (syn. *Hebe pinguifolia*). The compound 3''-*O*-benzoyl-2''-*O*-caffeoyl 6-*O*-rhamnopyranosylcatalpol had not been reported previously. The pattern of the structural features of the iridoid glucosides is overlaid onto the latest molecular phylogenetic framework of *Veronica* sects. *Hebe* and *Labiatooides*, and discussed in the context of evolutionary trends.

---

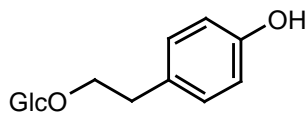
§ PK-M and KDP contributed equally to this work.

\* Corresponding author. Tel.: +45-20650984; fax: +45-45933968.

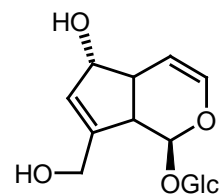
E-mail address: srj@kemi.dtu.dk (S.R. Jensen).



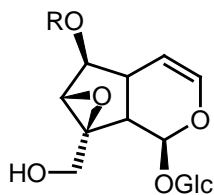
- 1;** R=R'=H  
**1a;** R=Me; R'=H  
**1b;** R=H; R'=6'-O-Benzoyl



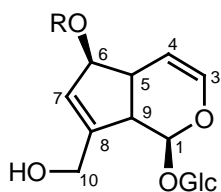
**2**



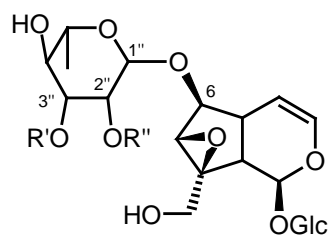
**3**



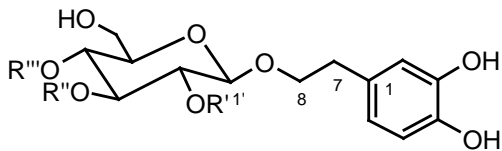
- 4;** R=H; Catalpol  
**4a;** R=Vanilloyl  
**4b;** R=Caffeoyl  
**4c;** R=isoFeruloyl



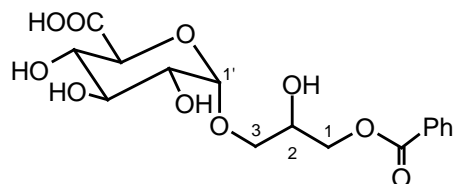
- 5;** R=H; Aucubin  
**5a;** R =Benzoyl  
**5b;** R=p-OH-Benzoyl  
**5c;** R=p-OMe-Benzoyl  
**5d;** R=3,4-diOH-Benzoyl  
**5e;** R=Vanilloyl  
**5f;** R=isoVanilloyl  
**5g;** R=3,4-diOMe-Benzoyl  
**5h;** R=Caffeoyl



- 6;** R'=R''=H  
**6a;** R'=Caffeoyl; R''=H  
**6b;** R'=Benzoyl; R''=Caffeoyl



- 7a;** R'=H; R''=Rha; R'''=Caffeoyl  
**7b;** R'=Ara; R''=Rha; R'''=Caffeoyl  
**7c;** R'=Xyl; R''=Rha; R'''=Caffeoyl



- 8;** 1-O-Benzoyl-3- $\alpha$ -glucuronosyl-glycerol

**List of Supporting Information**

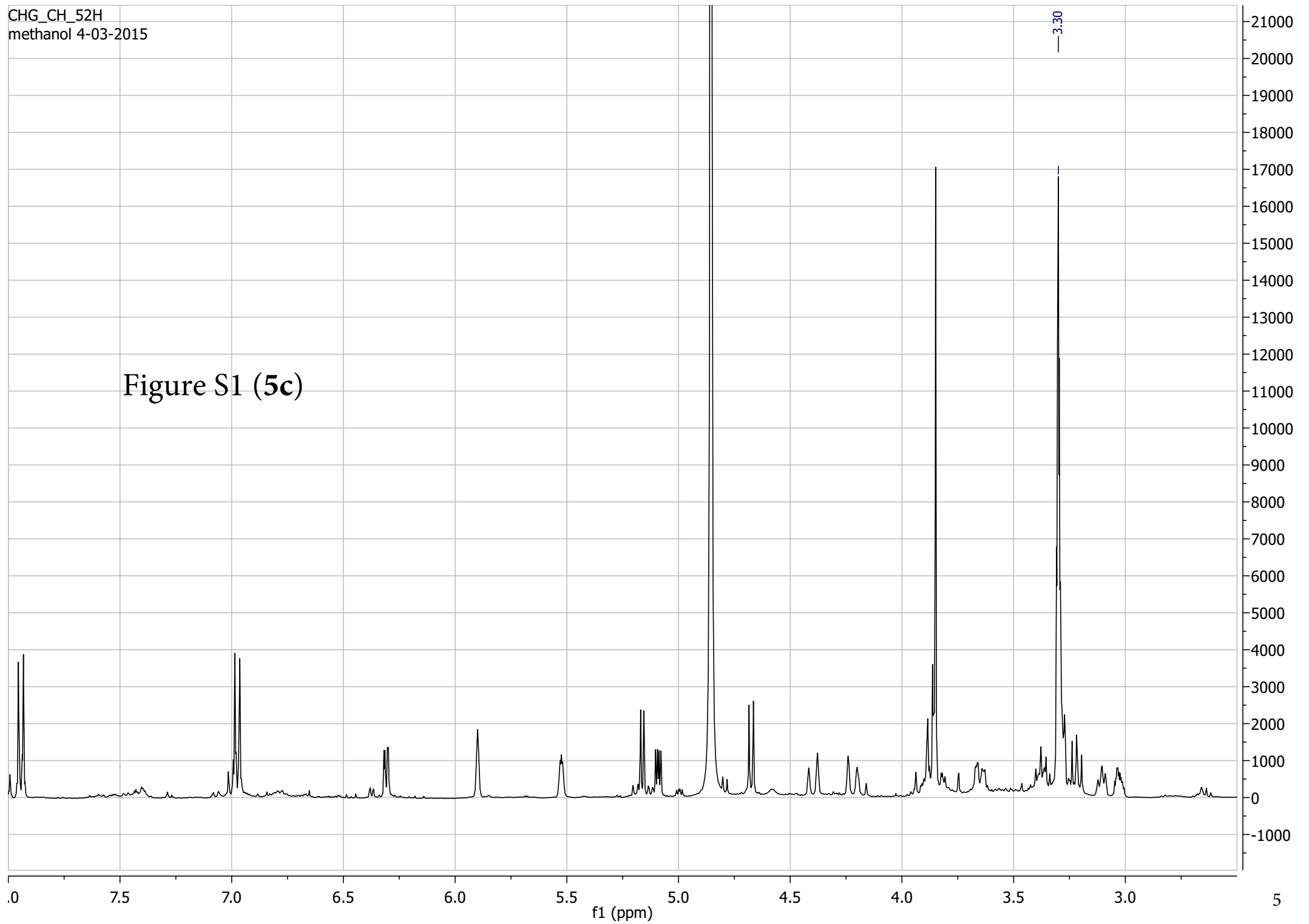
page

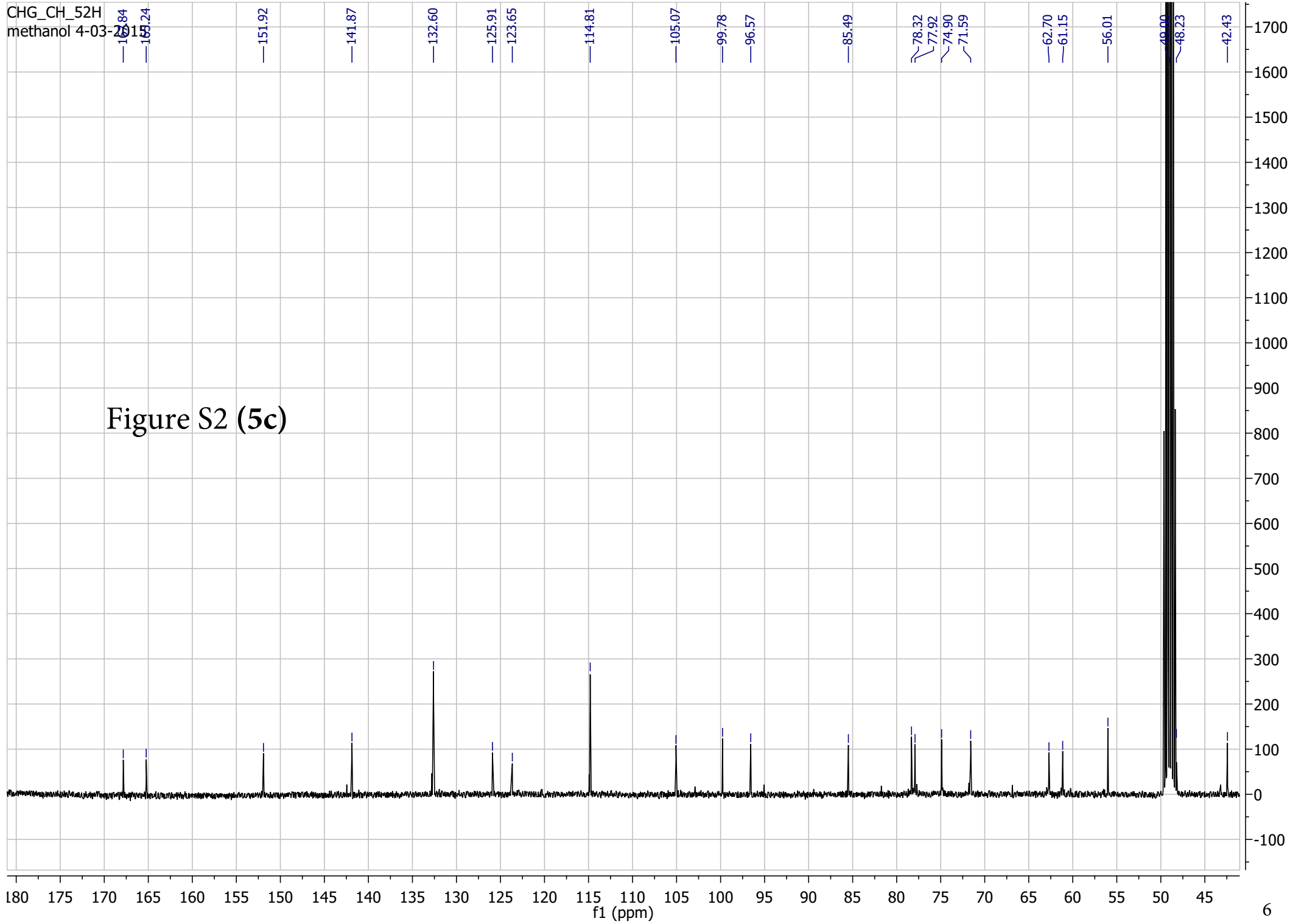
Table SI1	GenBank numbers of ITS-sequences used in the phylogenetic analysis	4
Figure S1	<sup>1</sup> H NMR (CD <sub>3</sub> OD, 400 MHz) of 6- <i>O-p</i> -Methoxybenzoylaucubin ( <b>5c</b> )	5
Figure S2	<sup>13</sup> C NMR (CD <sub>3</sub> OD, 100 MHz) of 6- <i>O-p</i> -Methoxybenzoylaucubin ( <b>5c</b> )	6
Figure S3	<sup>1</sup> H NMR (CD <sub>3</sub> OD, 400 MHz) of 6- <i>O</i> -Isovanilloylaucubin ( <b>5f</b> )	7
Figure S4	<sup>13</sup> C NMR (CD <sub>3</sub> OD, 100 MHz) of 6- <i>O</i> -Isovanilloylaucubin ( <b>5f</b> )	8
Figure S5	<sup>1</sup> H NMR (CD <sub>3</sub> OD, 400 MHz) of 6- <i>O</i> -Veratroylaucubin ( <b>5g</b> )	9
Figure S6	<sup>13</sup> C NMR (CD <sub>3</sub> OD, 100 MHz) of 6- <i>O</i> -Veratroylaucubin ( <b>5g</b> )	10
Figure S7	<sup>1</sup> H NMR (CD <sub>3</sub> OD, 400 MHz) of 6- <i>O</i> -( <i>E</i> )-Caffeoylaucubin ( <b>5h</b> )	11
Figure S8	<sup>13</sup> C NMR (CD <sub>3</sub> OD, 100 MHz) of 6- <i>O</i> -( <i>E</i> )-Caffeoylaucubin ( <b>5h</b> )	12
Figure S9	<sup>13</sup> C NMR (CD <sub>3</sub> OD, 100 MHz) of 3''- <i>O</i> -Benzoyl-2''- <i>O</i> -( <i>E</i> )-caffeoyl-6- <i>O</i> -rhamnopyranosylcatalpol ( <b>6b</b> )	13
Figure S10	<sup>1</sup> H NMR (CD <sub>3</sub> OD, 400 MHz) of 3''- <i>O</i> -Benzoyl-2''- <i>O</i> -( <i>E</i> )-caffeoyl-6- <i>O</i> -rhamnopyranosylcatalpol ( <b>6b</b> )	14
Figure S11	<sup>1</sup> H NMR (CD <sub>3</sub> OD, 400 MHz) of 6'- <i>O</i> -Benzoylmussaenosidic acid ( <b>1b</b> )	15
Figure S12	<sup>13</sup> C NMR (CD <sub>3</sub> OD, 100 MHz) of 6'- <i>O</i> -Benzoylmussaenosidic acid ( <b>1b</b> )	16

Table SII. GenBank numbers of ITS-sequences used in the phylogenetic analysis

Species	GenBank number
<i>V. brachysiphon</i> (Summerh.) Bean	KJ630628
<i>V. buchananii</i> Hook. f.	KJ630629
<i>V. catarractae</i> G. Forst.	AY034859
<i>V. cheesemanii</i> Benth.	AF229046
<i>V. ciliolata</i> (Hook. f.) Garn.-Jones	AF229037
<i>V. cupressoides</i> Hook. f.	AF037378
<i>V. derwentiana</i> Andrews	JX193655
<i>V. elliptica</i> G. Forst.	AF037392
<i>V. hookeriana</i> Walp.	AY34860
<i>V. hulkeana</i> F. Muell.	AF037379
<i>V. laudiana</i> Raoul	AF229043
<i>V. ligustrifolia</i> R. Cunn.	KJ630647
<i>V. odora</i> Hook. f.	AF037388
<i>V. pentasepala</i> (L. B. Moore) Garn.-Jones	FJ848076
<i>V. perfoliata</i> R. Br.	JX196844
<i>V. pulvinaris</i> Hook. f.	AF229038
<i>V. raoulii</i> Hook. f.	AF037380
<i>V. salicifolia</i> G. Forst.	AF037385
<i>V. speciosa</i> A. Cunn.	AY034864
<i>V. stenophylla</i> Steud.	KJ630661
<i>V. thomsonii</i> (Buchanan) Cheeseman	AF229039
<i>V. topiaria</i> (L. B. Moore) Garn.-Jones	KJ630666

Figure S1 (5c)





NMR400\_AEH\_CHGOU\_51UV5  
CHGOU 51UV5 i CD3OD  
1H  
29-02-16

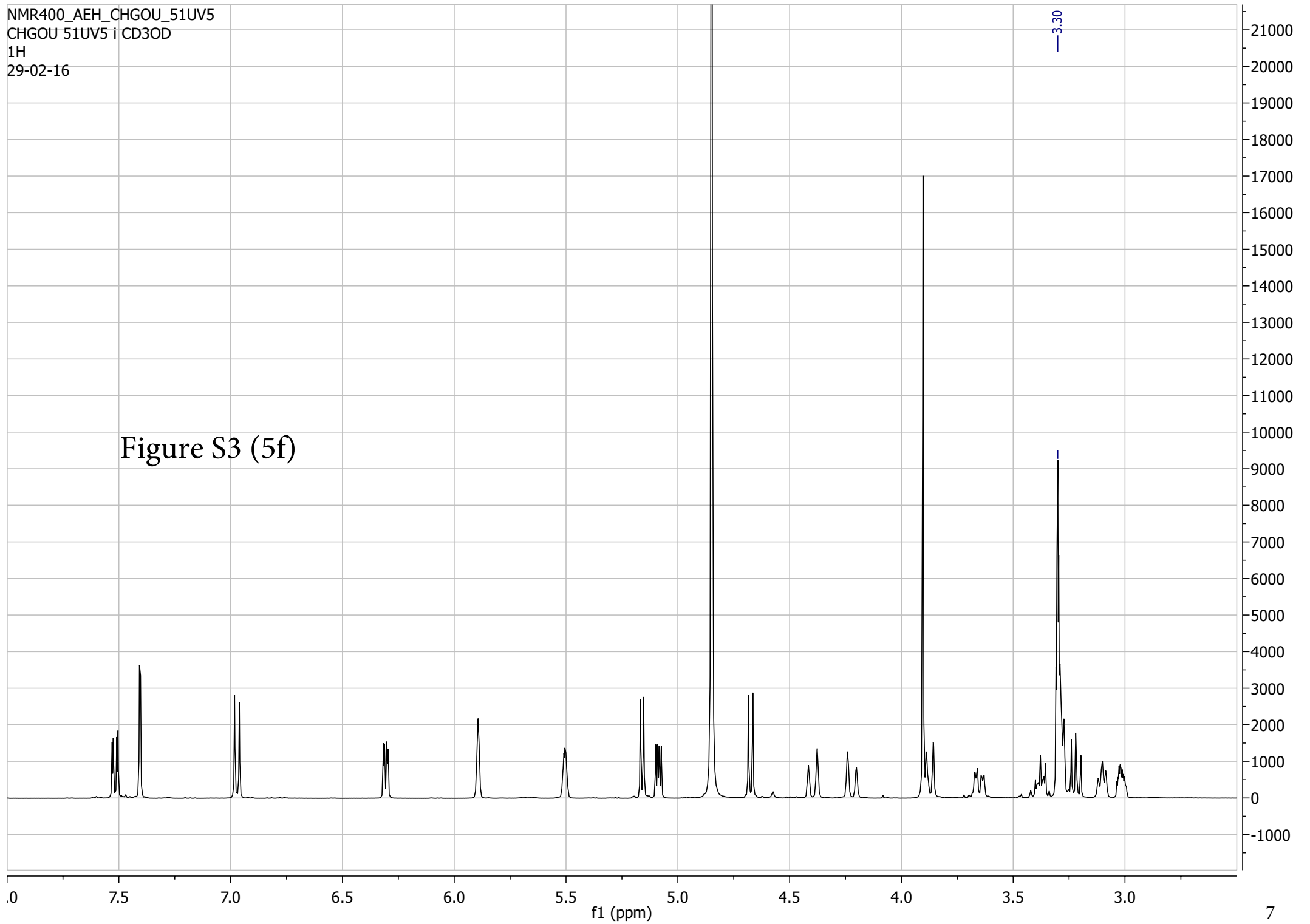


Figure S3 (5f)



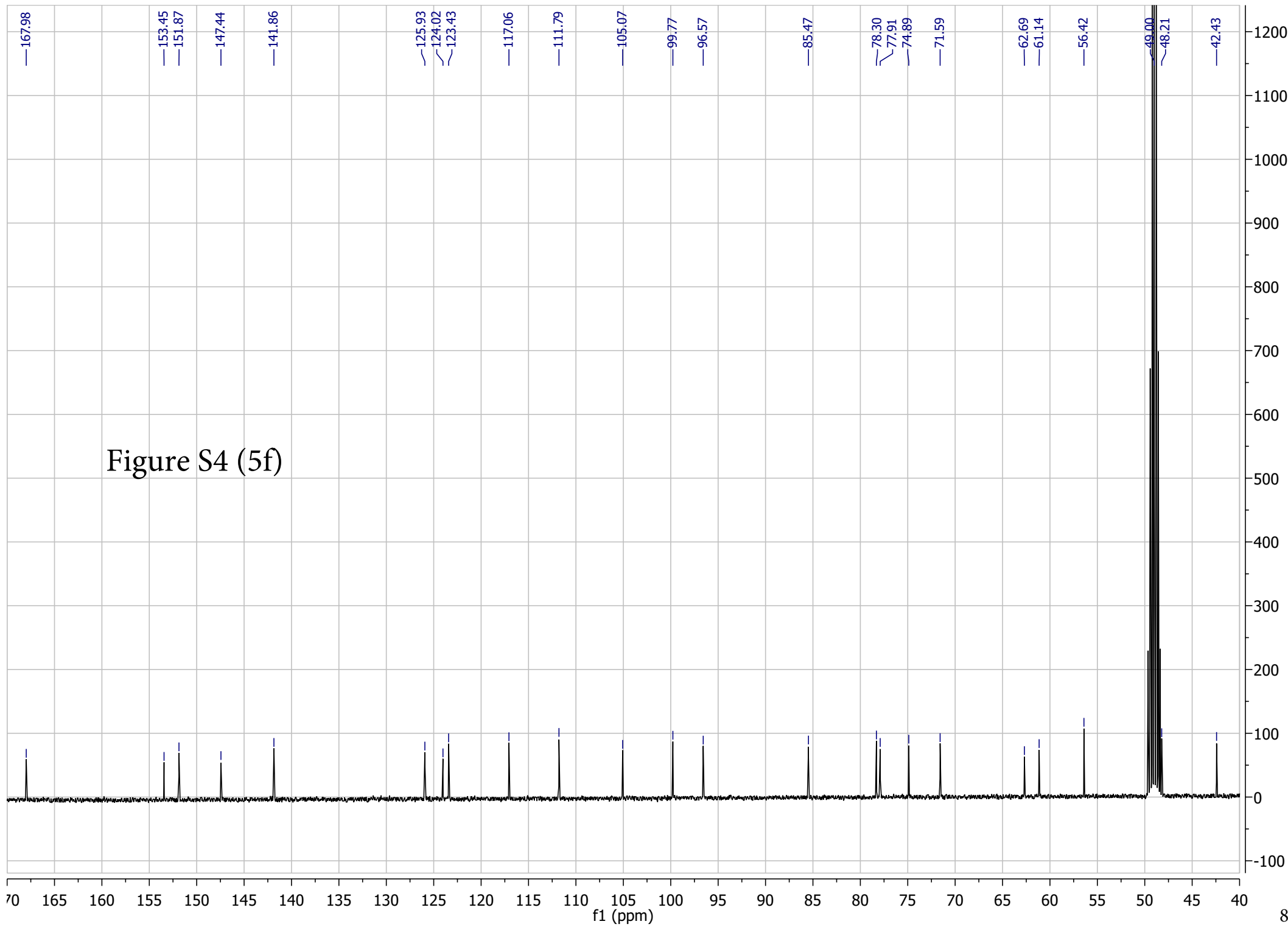
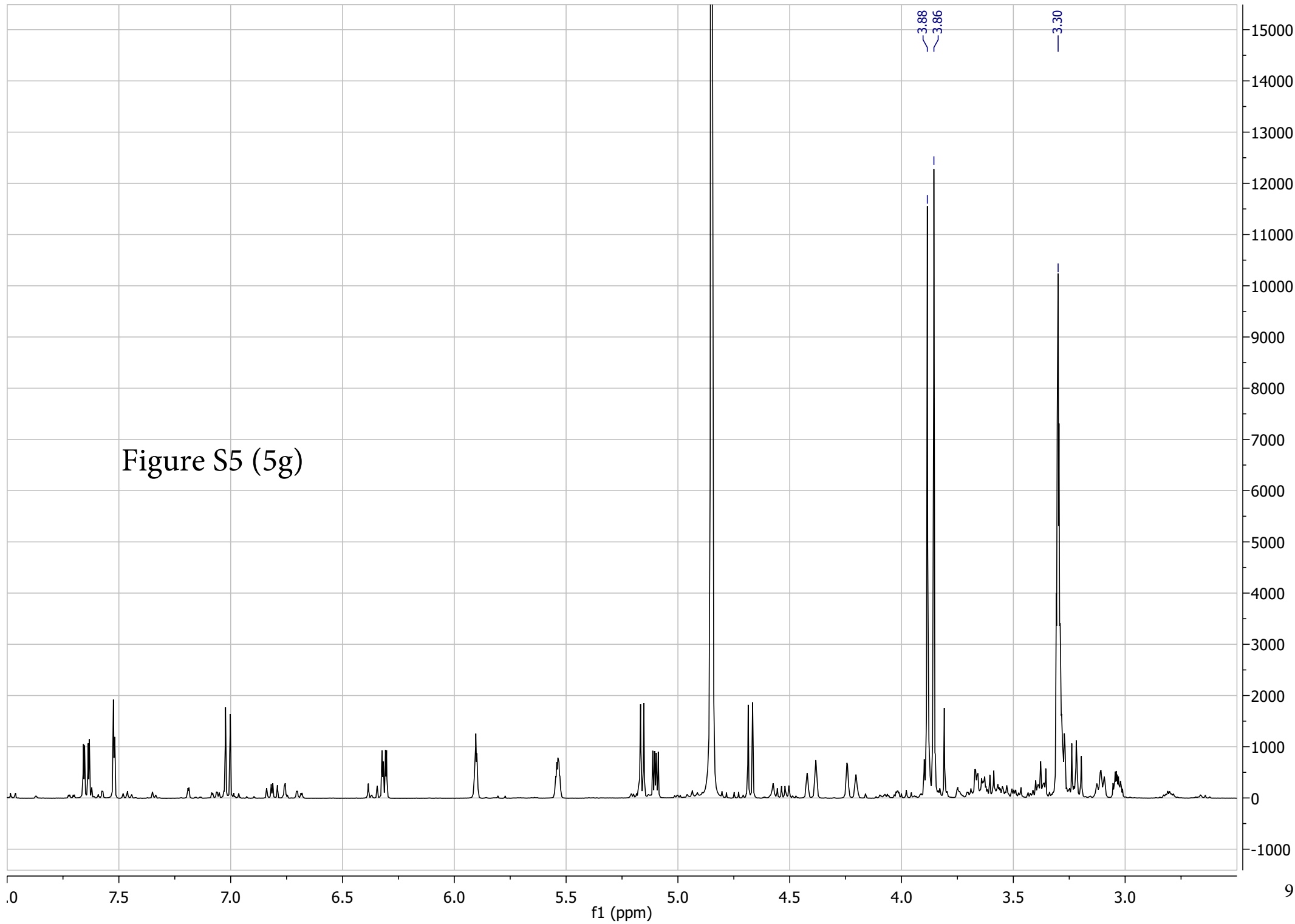
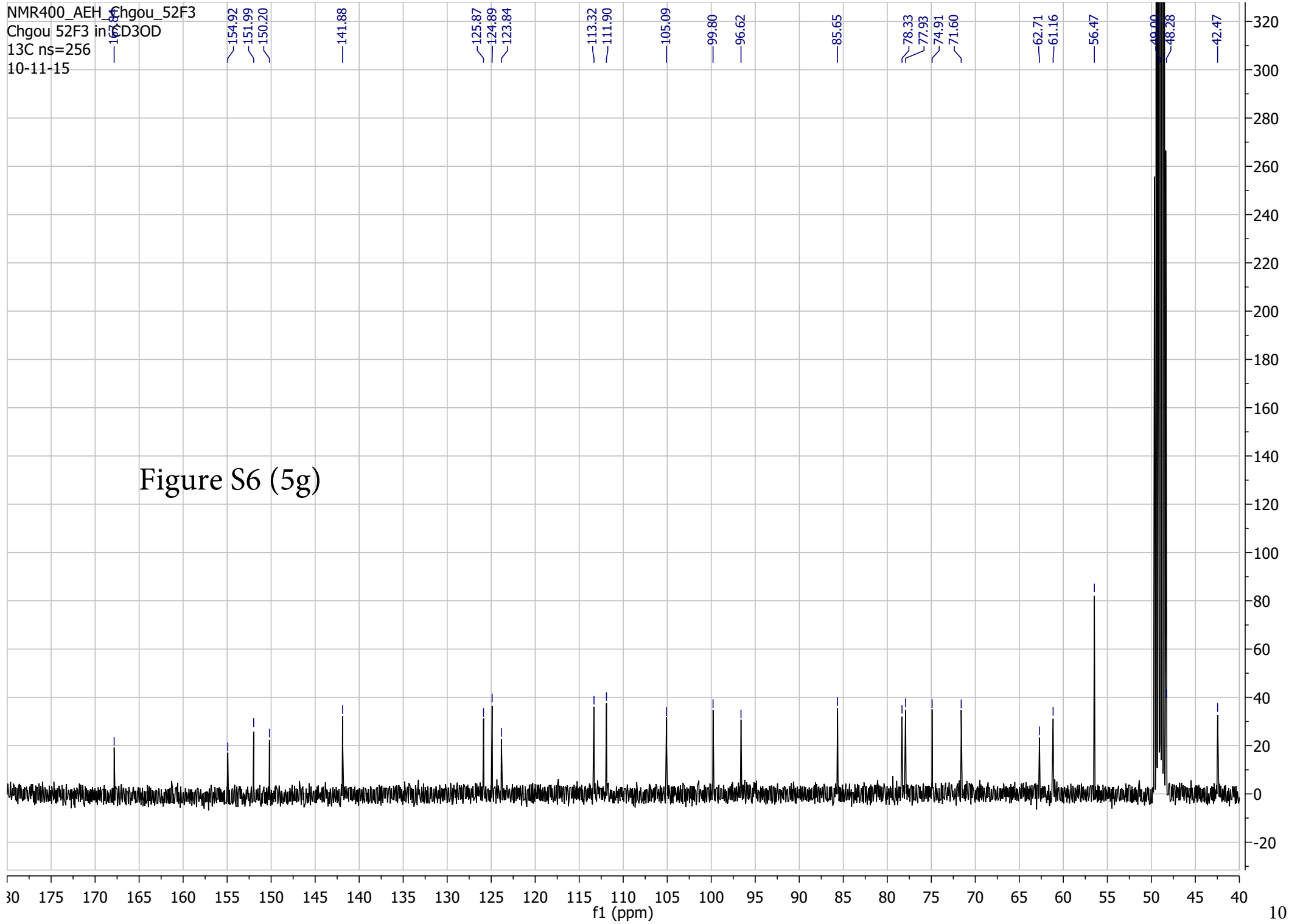


Figure S5 (5g)



NMR400\_AEH\_Chgou\_52F3  
Chgou 52F3 in CD3OD  
13C ns=256  
10-11-15



NMR400\_AEH\_Chgou\_51X1  
Chgou 51X1 in CD3OD  
1H  
11-11-15

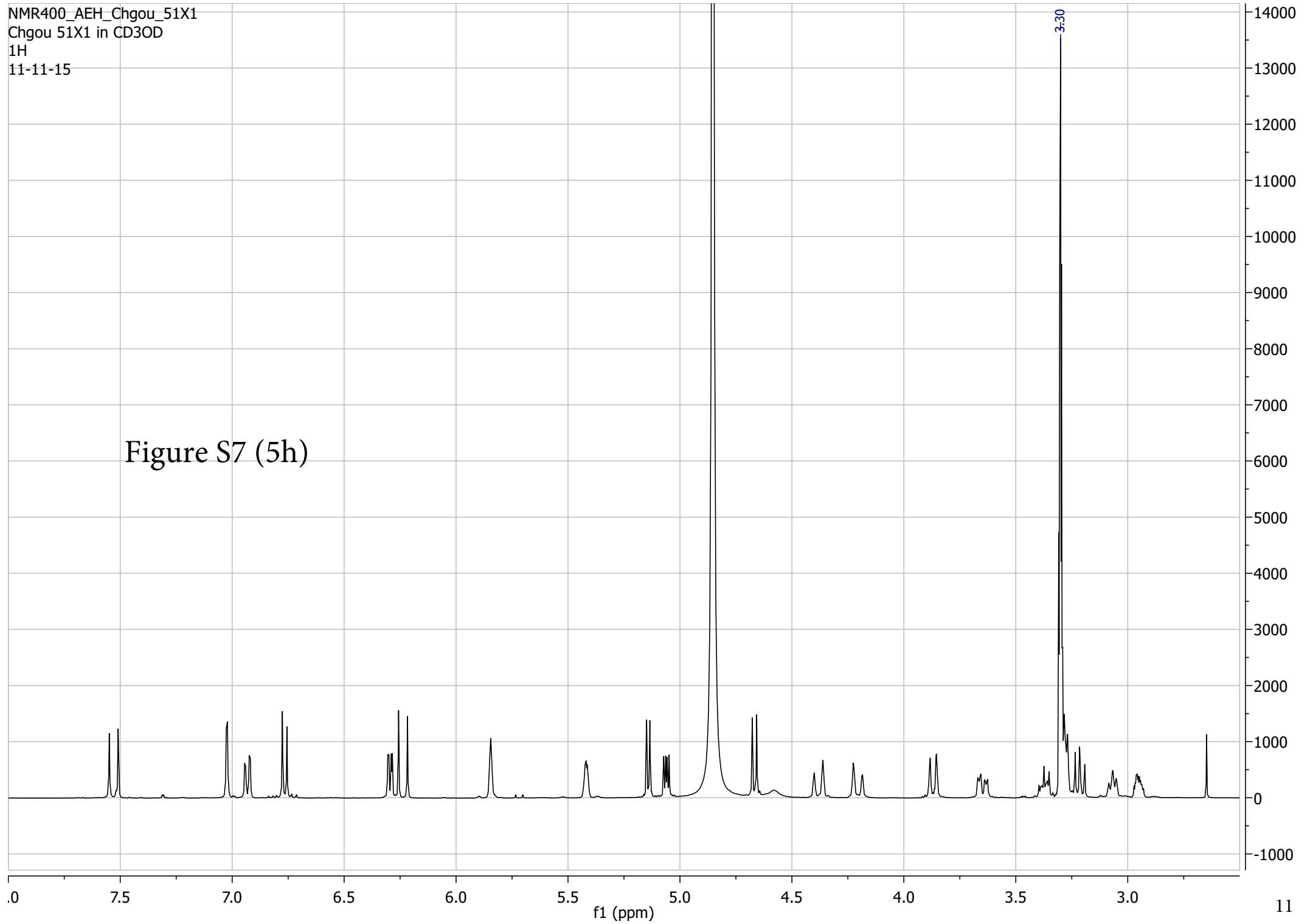
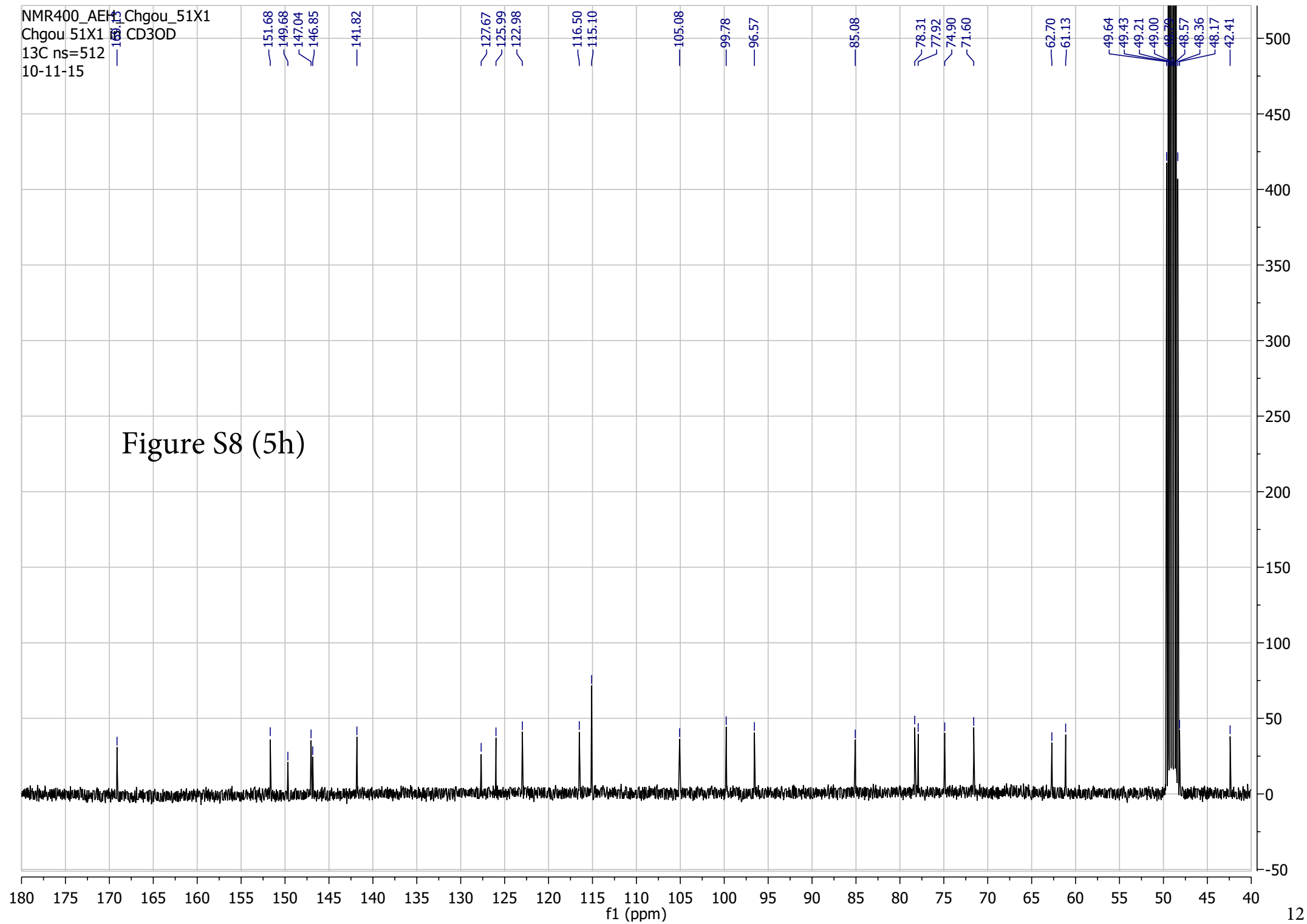
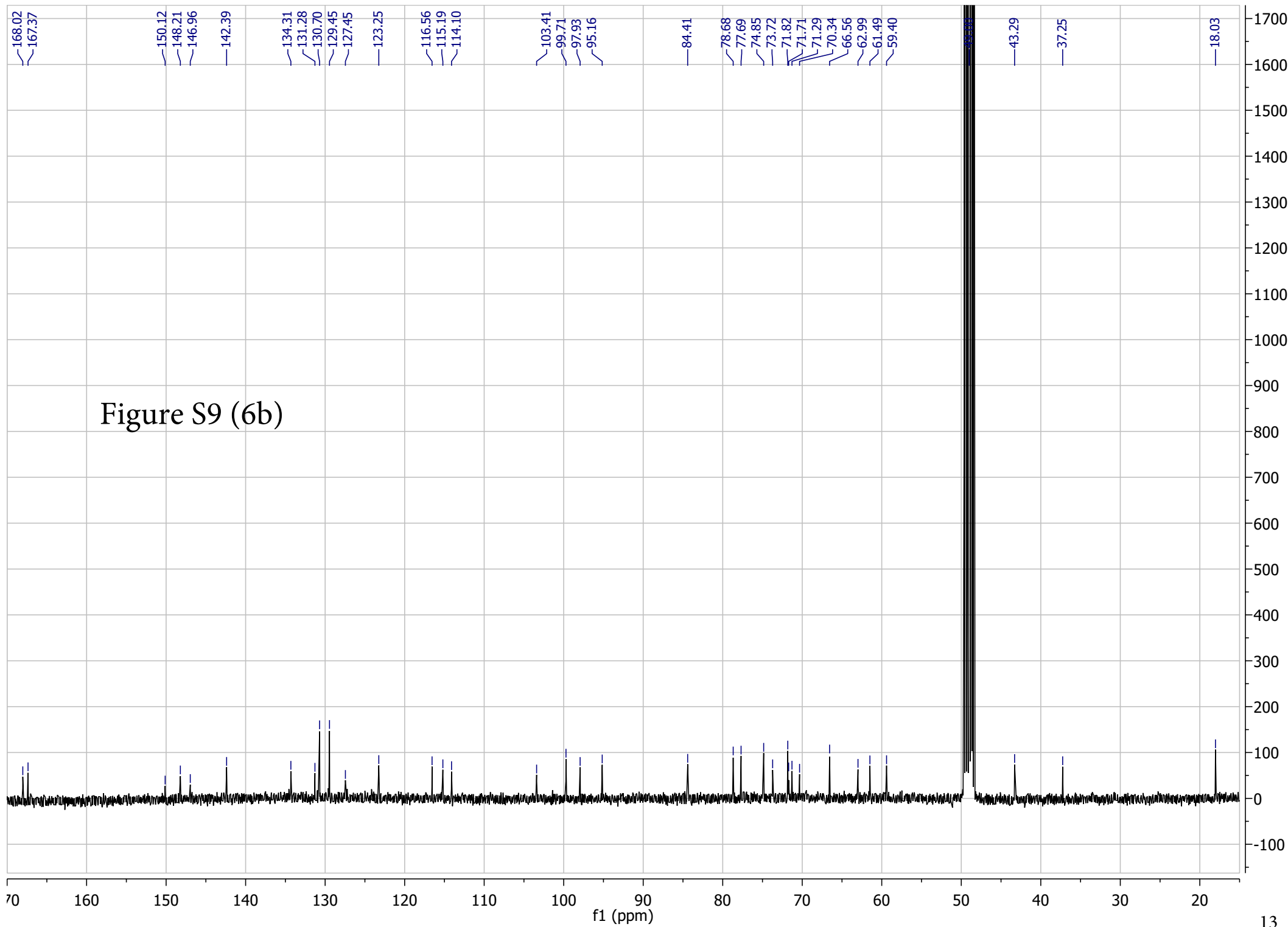


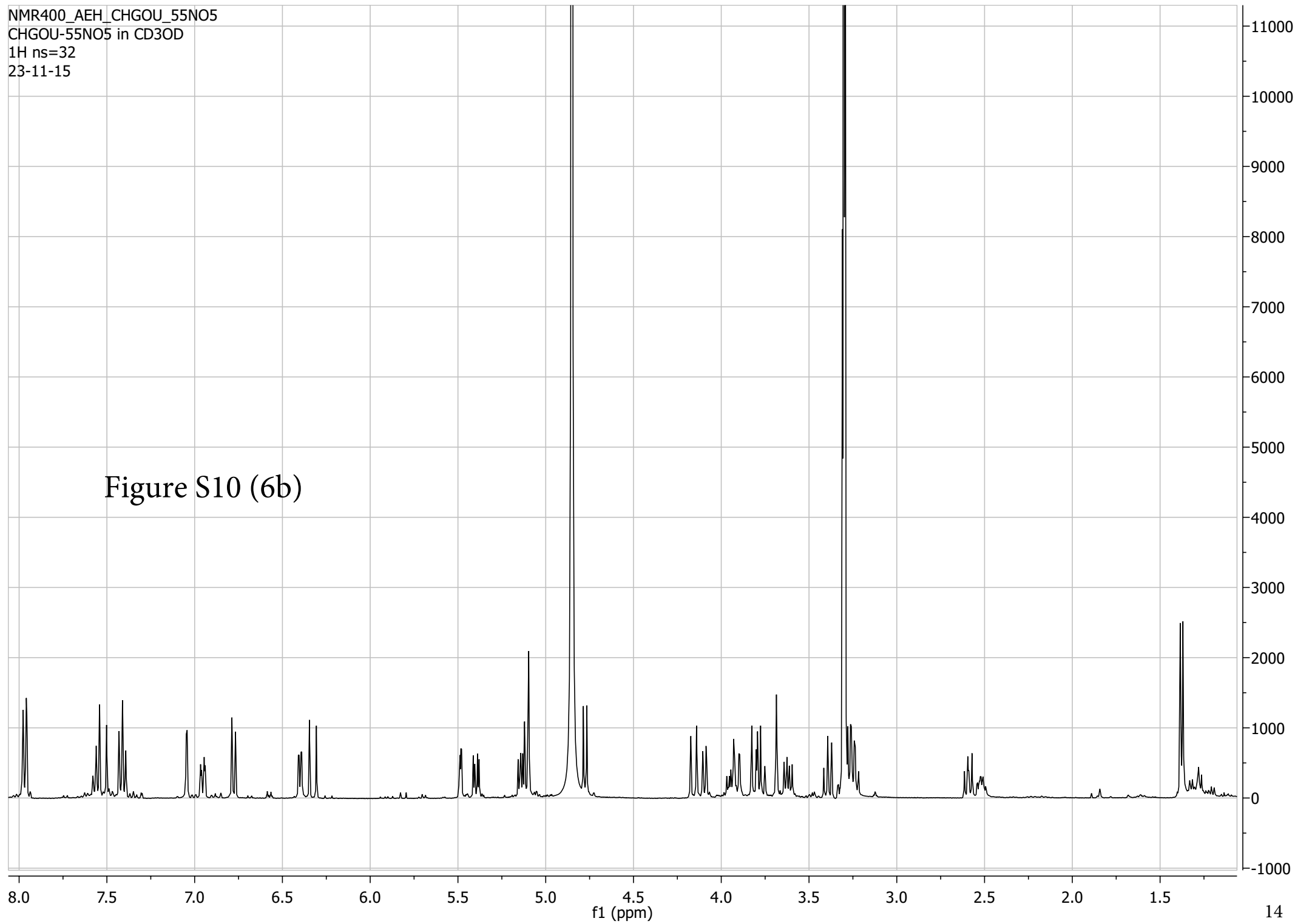
Figure S7 (5h)

NMR400\_AEH1 Chgou\_51X1  
Chgou 51X1 CD3OD  
13C ns=512  
10-11-15





NMR400\_AEH\_CHGOU\_55NO5  
CHGOU-55NO5 in CD3OD  
1H ns=32  
23-11-15



NMR400\_AEH\_GHGOU\_52F2  
CHGOU 52F2 in CD3OD  
1H  
09-11-15

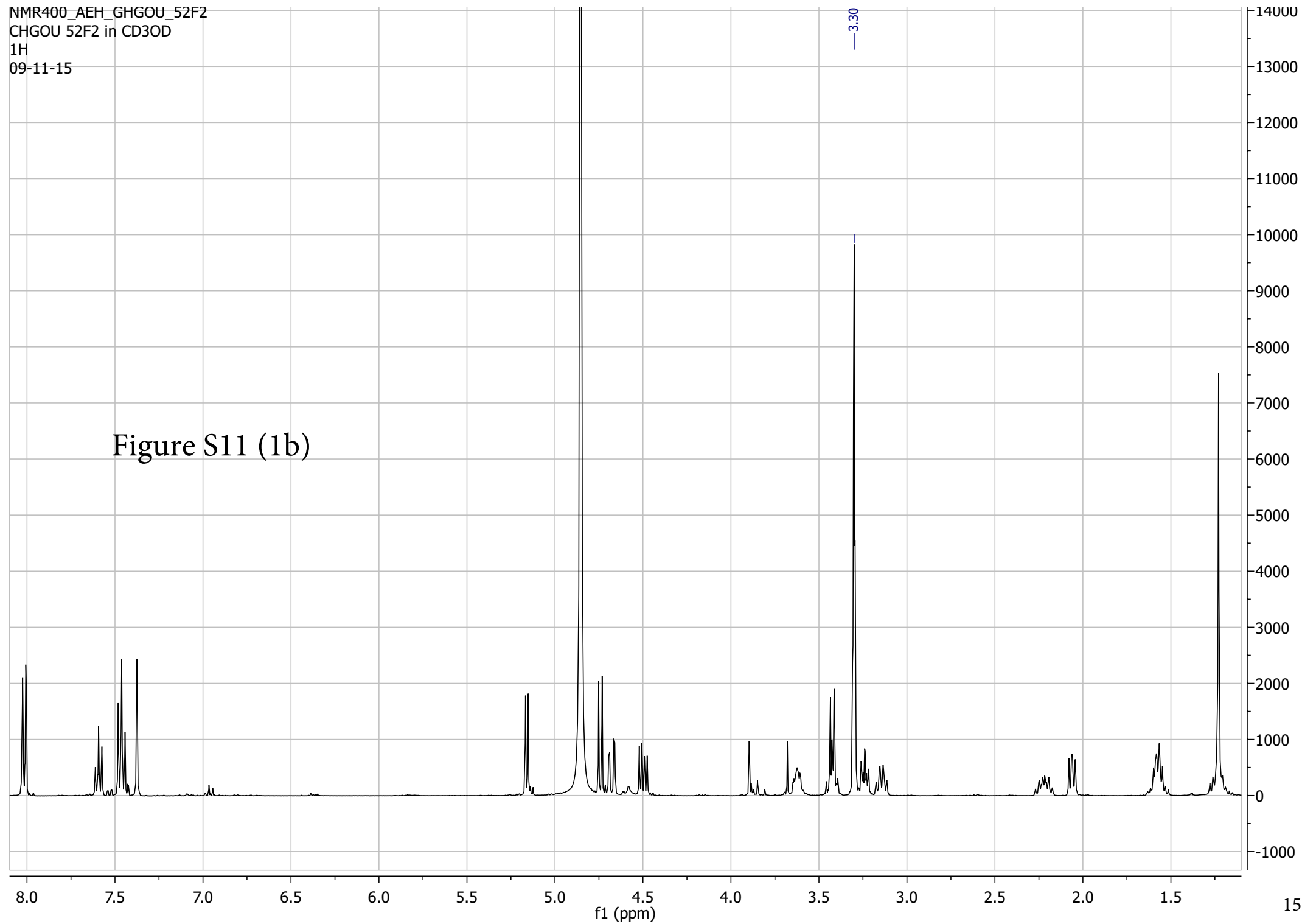




Figure S12 (1b)

