

# **Biomolecules**

## **Supporting Information for**

### **Late-stage Functionalisation of Polycyclic (*N*-hetero-)Aromatic Hydrocarbons by Detoxifying CYP5035S7 Monooxygenase of the White-Rot Fungus *Polyporus Arcularius***

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2 Institute of Chemistry, University of Graz, NAWI Graz, Graz, Austria

3 Field of Excellence BioHealth-University of Graz, Graz, Austria

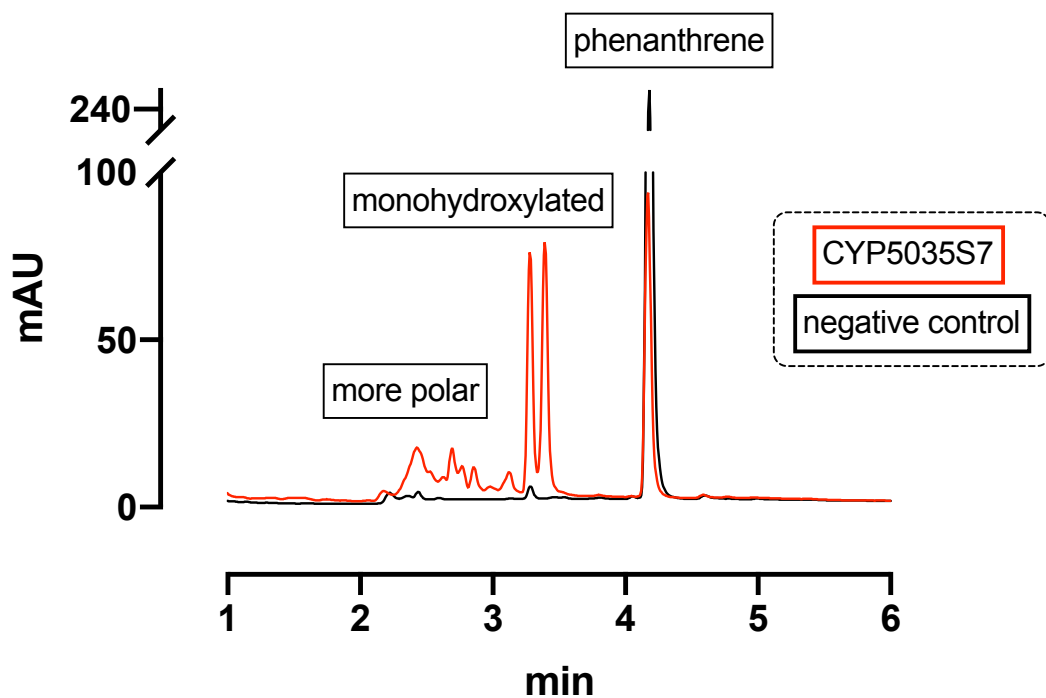
\* corresponding author: Nico D. Fessner

E-mail: nico.fessner11@alumni.imperial.ac.uk

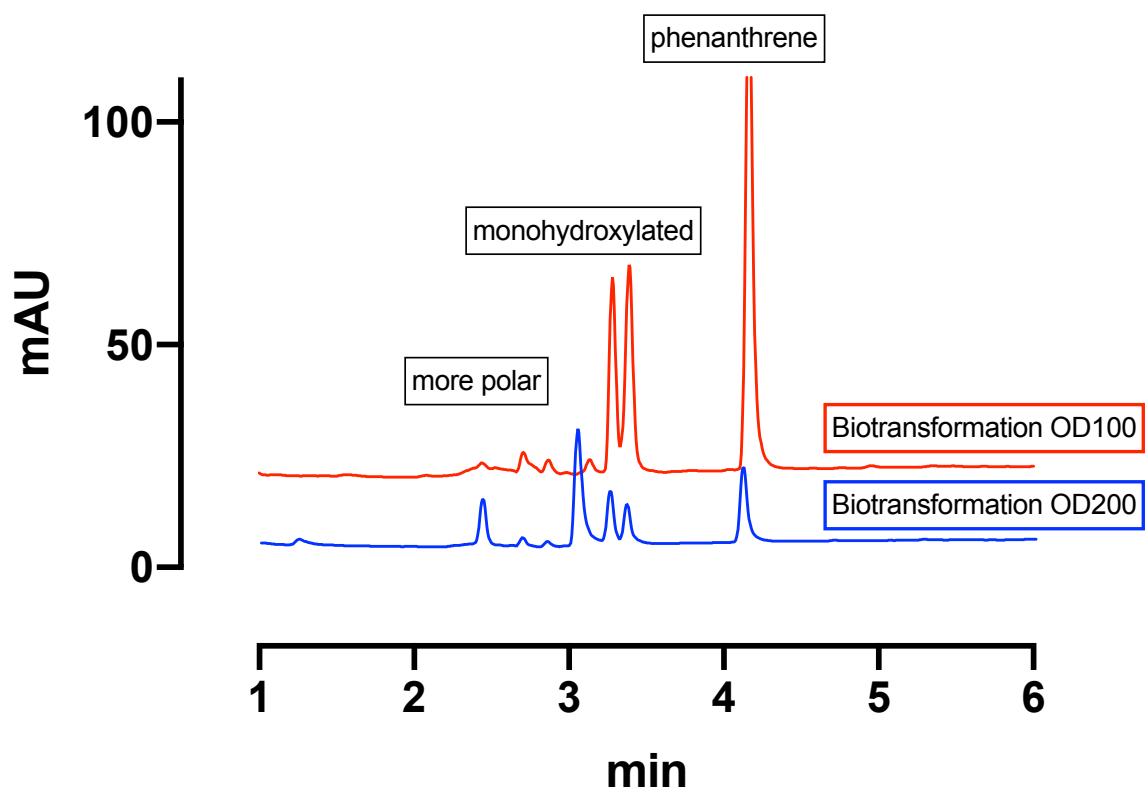
phone: (+43)-316-873-4074

Fax: (+43)-316-873-9302

# Phenanthrene

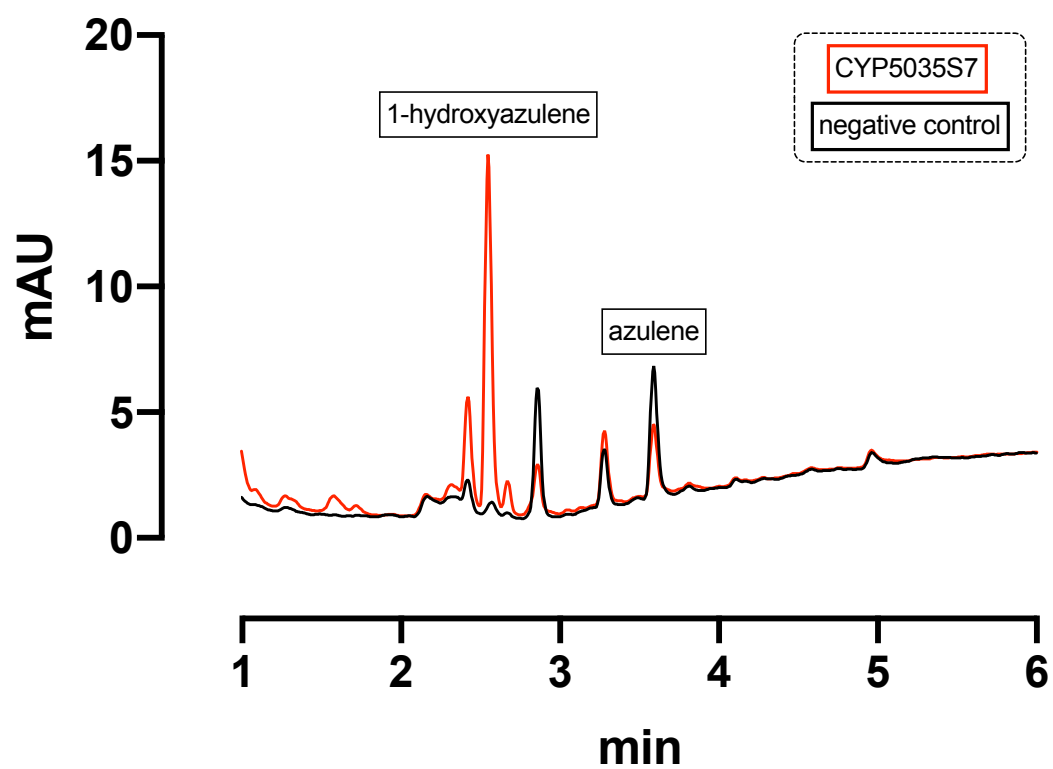


**Figure S1:** HPLC profile of phenanthrene conversion catalysed by CYP5035S7.

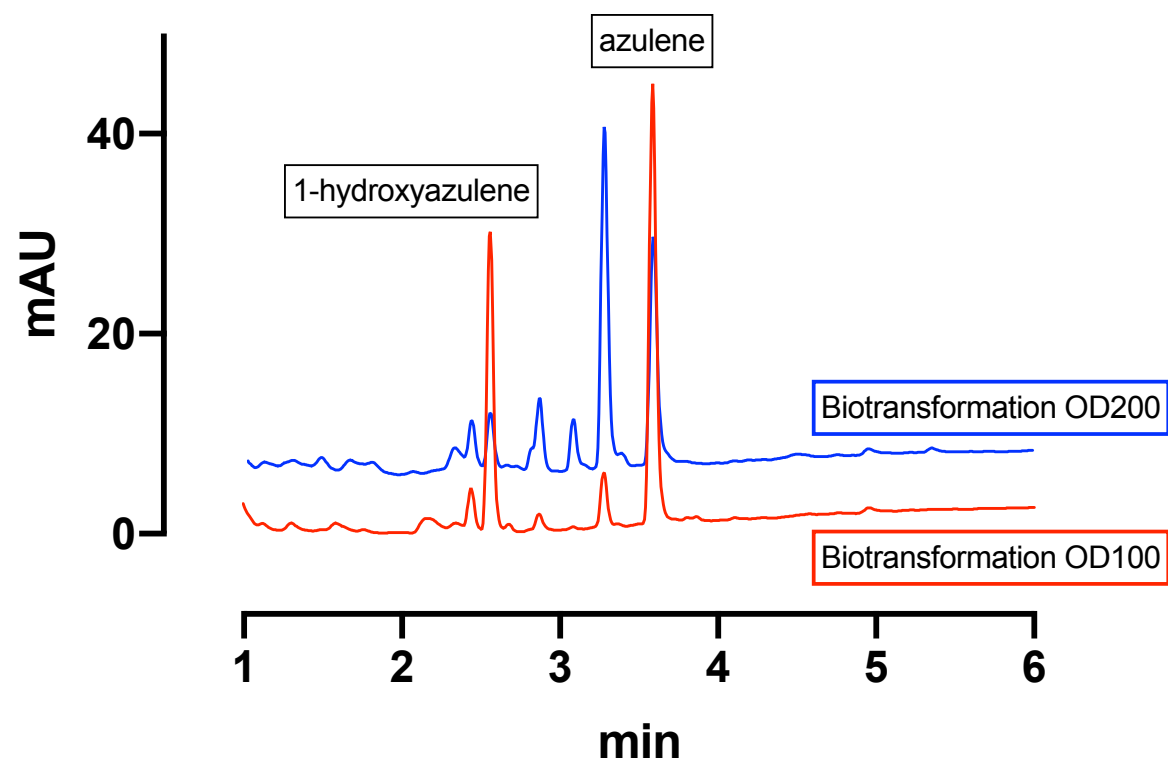


**Figure S2:** The difference between the HPLC profiles of the whole-cells biotransformation of phenanthrene catalysed by CYP5035S7 expressed in *P. pastoris* at different cell concentrations (OD).

# Azulene

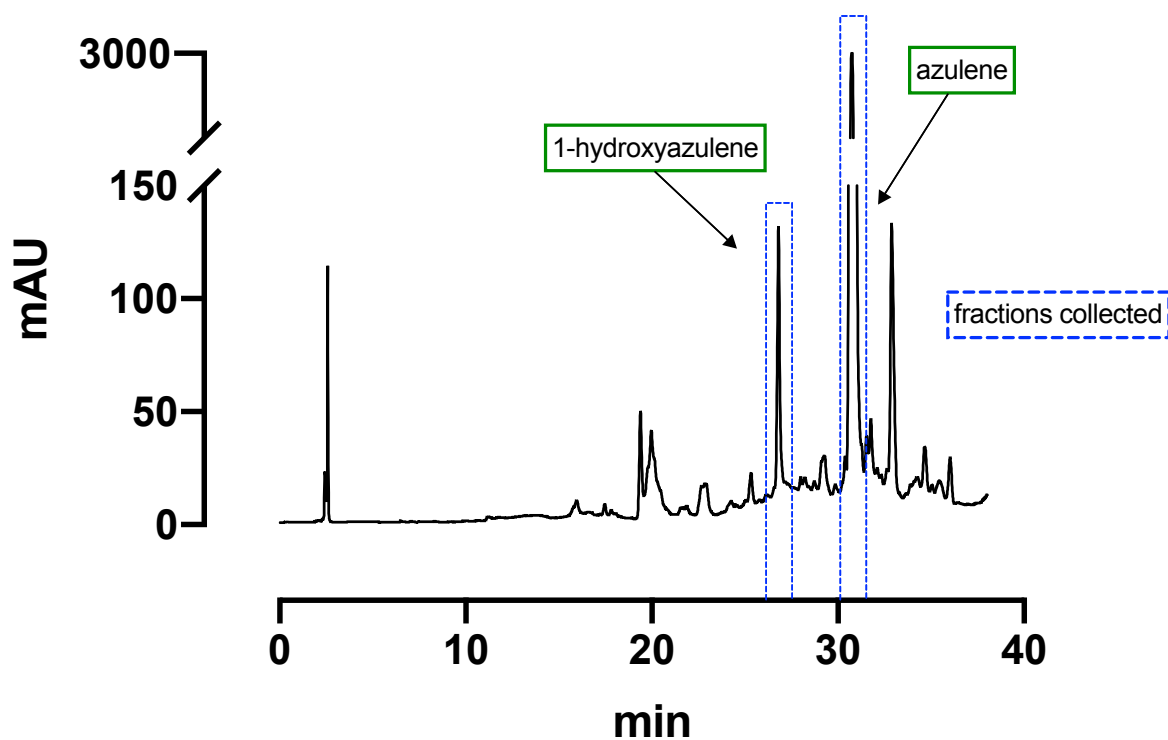


**Figure S3:** HPLC profile of azulene conversion catalysed by CYP5035S7.



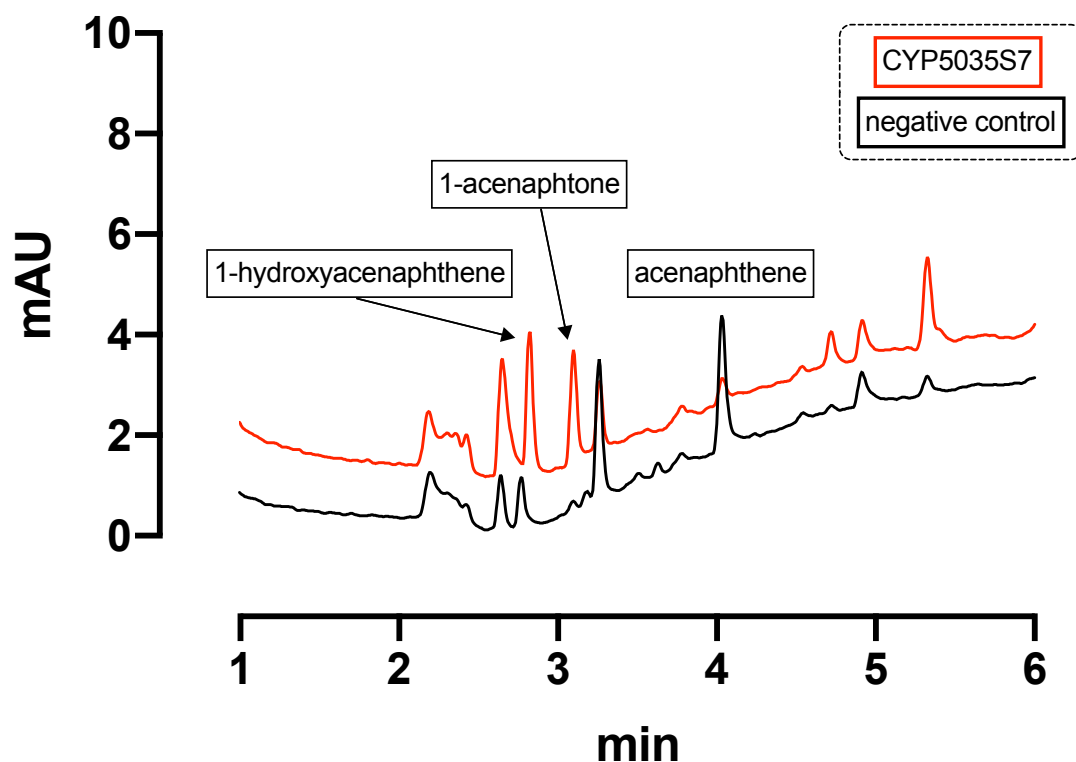
# Azulene

**Figure S4:** The difference between the HPLC profiles of the whole-cells biotransformation of azulene catalysed by CYP5035S7 expressed in *P. pastoris* at different cell concentrations (OD).

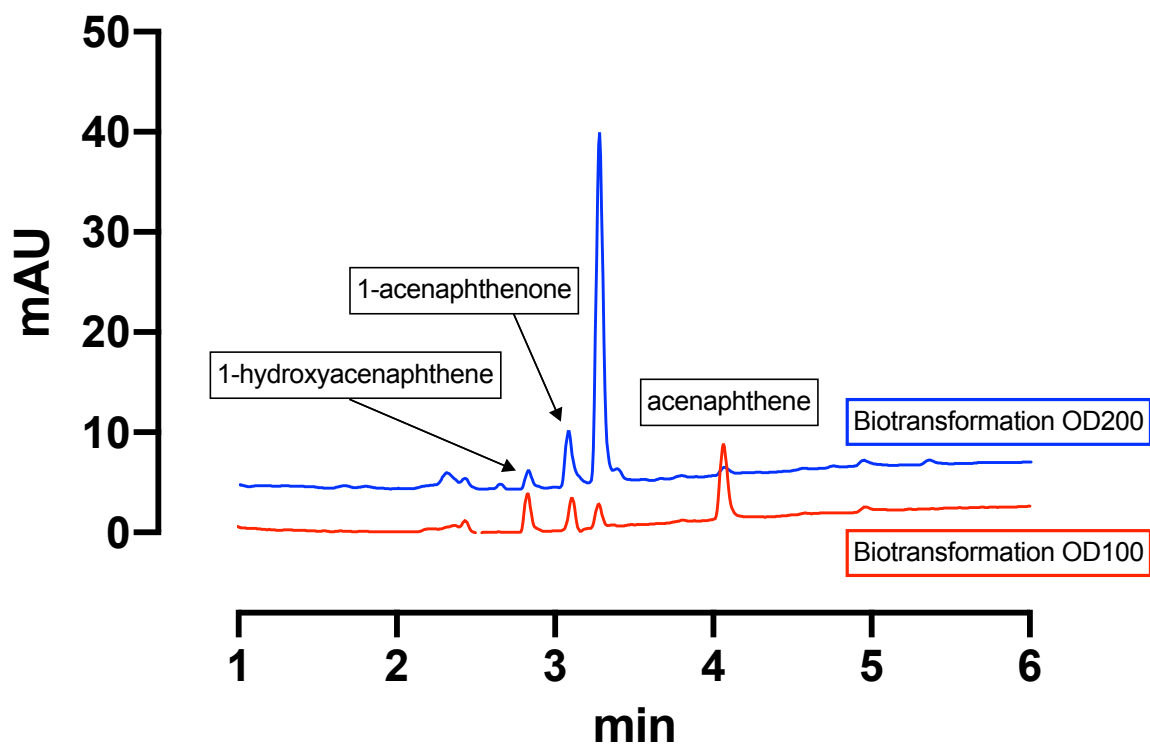


**Figure S5:** Preparative HPLC profile for product isolation of the scale-up azulene whole-cell biotransformation employing CYP5035S7. The blue dashed line indicates the fractions collected and the arrows indicate the corresponding products framed in green that were identified by NMR analysis.

# Acenaphthene

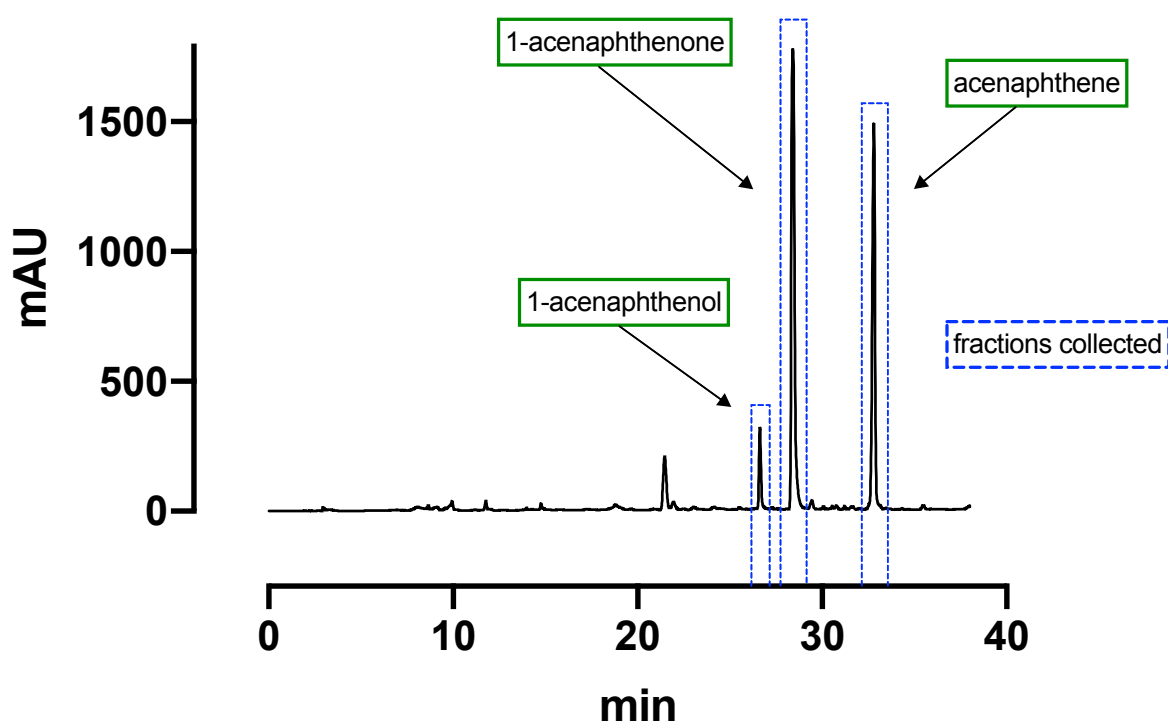


**Figure S6:** HPLC profile of acenaphthene conversion catalysed by CYP5035S7.



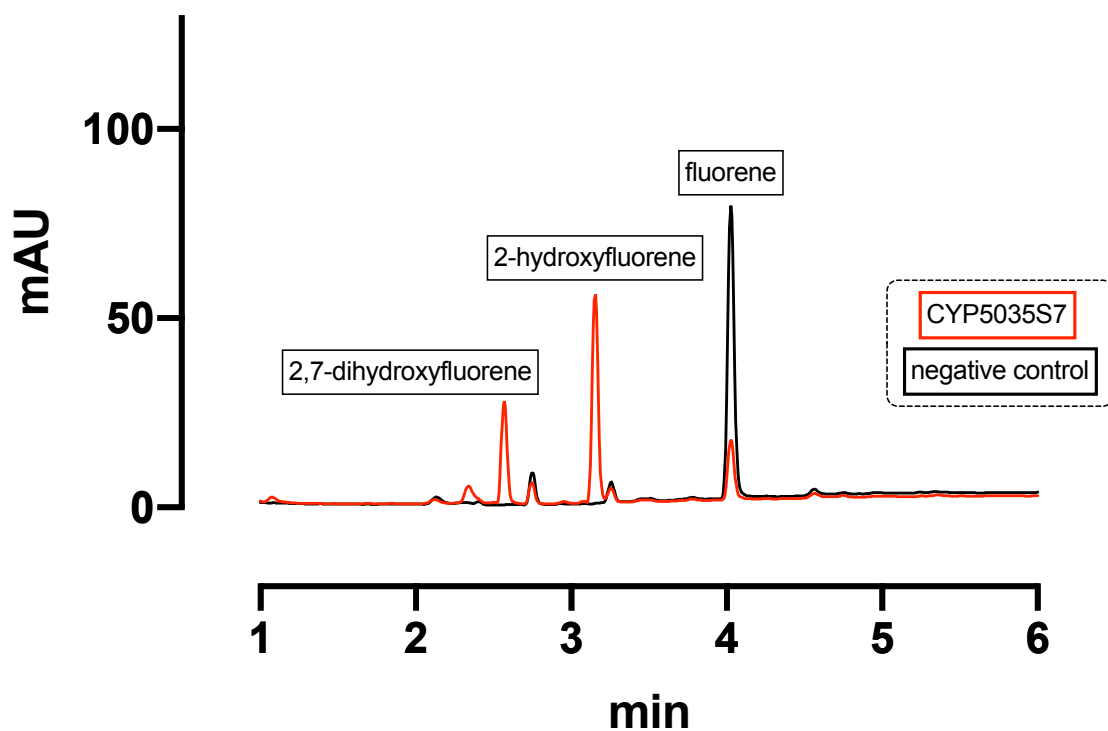
**Figure S7:** The difference between the HPLC profiles of the whole-cells biotransformation of acenaphthene catalysed by CYP5035S7 expressed in *P. pastoris* at different cell concentrations (OD).

# Acenaphthene

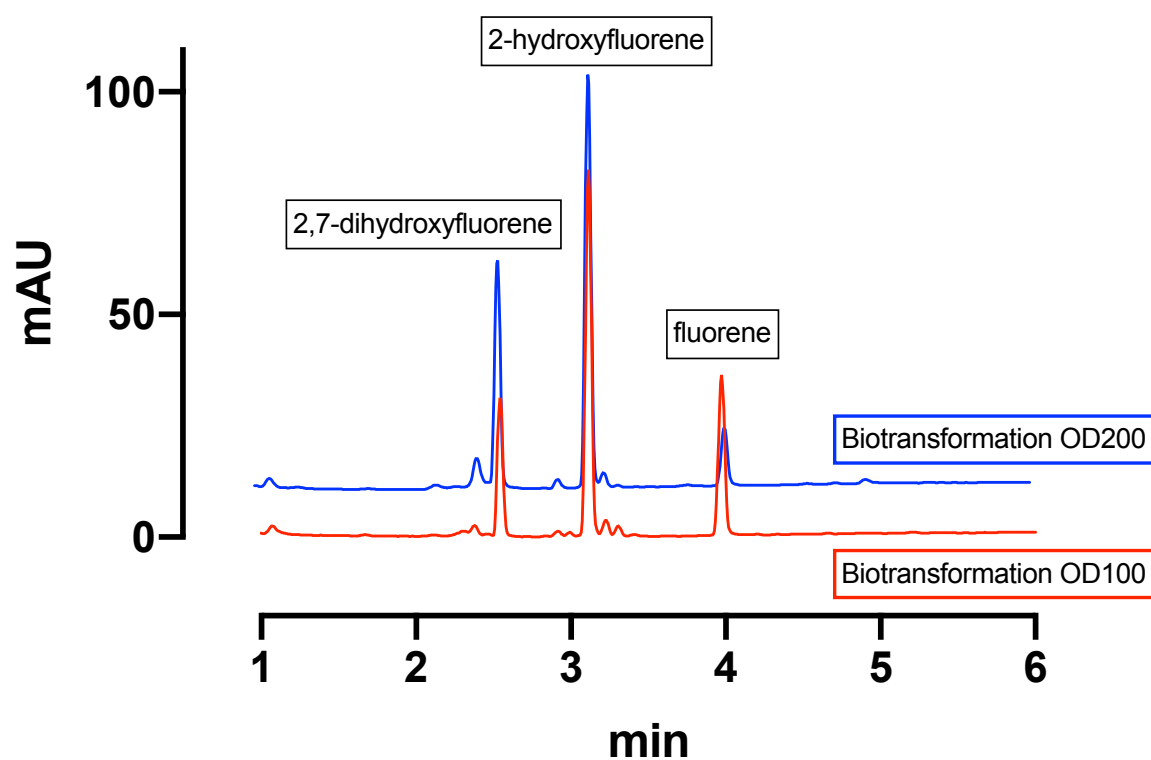


**Figure S8:** Preparative HPLC profile for product isolation of the scale-up anthracene whole-cell biotransformation employing CYP5035S7. The blue dashed line indicates the fractions collected and the arrows indicate the corresponding products framed in green that were identified by NMR analysis.

# Fluorene

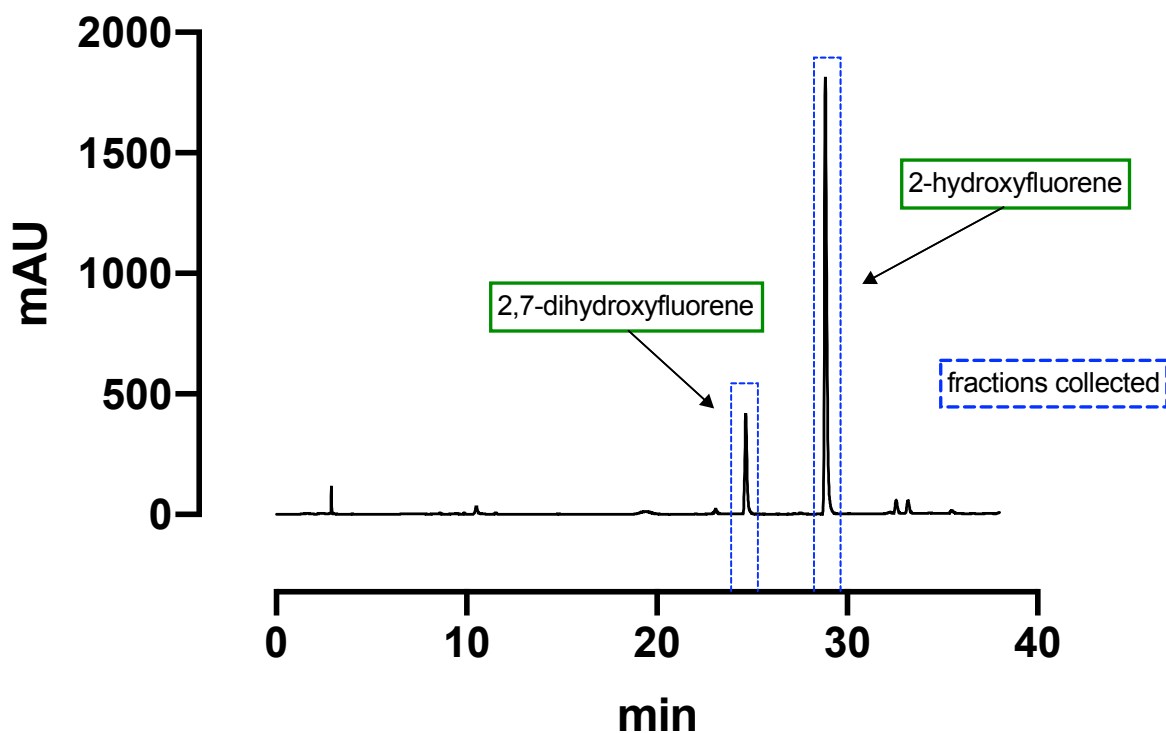


**Figure S9:** HPLC profile of fluorene conversion catalysed by CYP5035S7.



**Figure S10:** The difference between the HPLC profiles of the whole-cells biotransformation of fluorene catalysed by CYP5035S7 expressed in *P. pastoris* at different cell concentrations (OD).

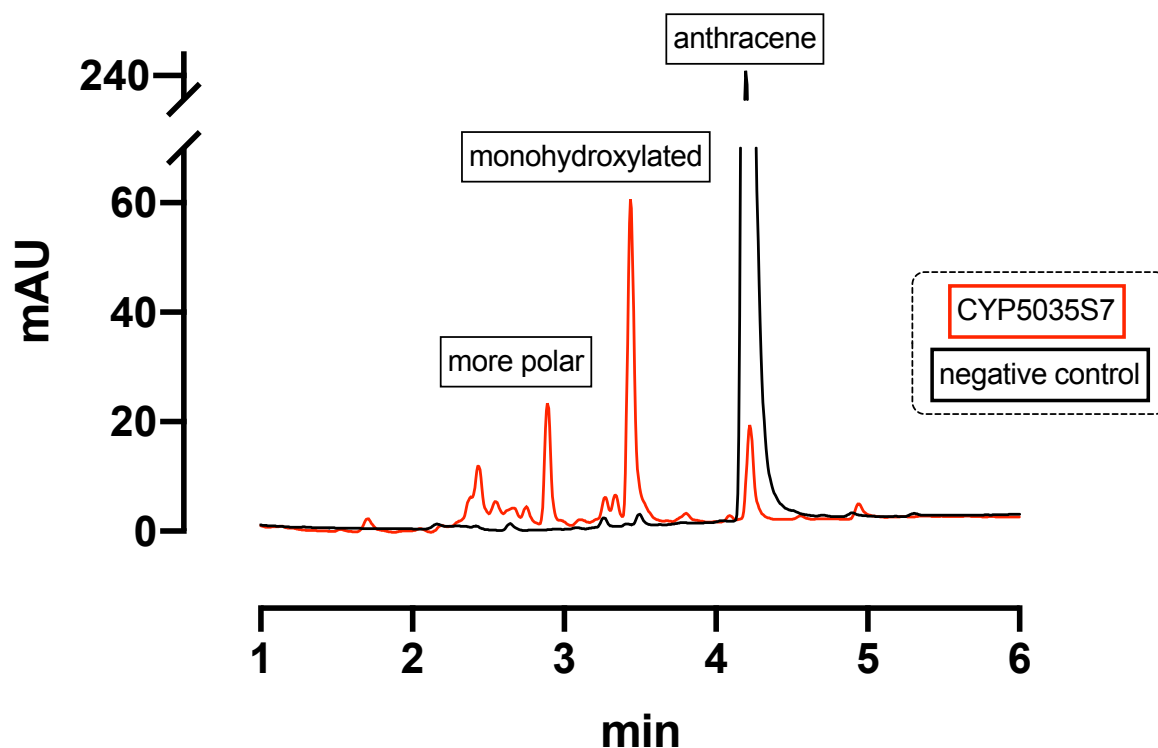
# Fluorene



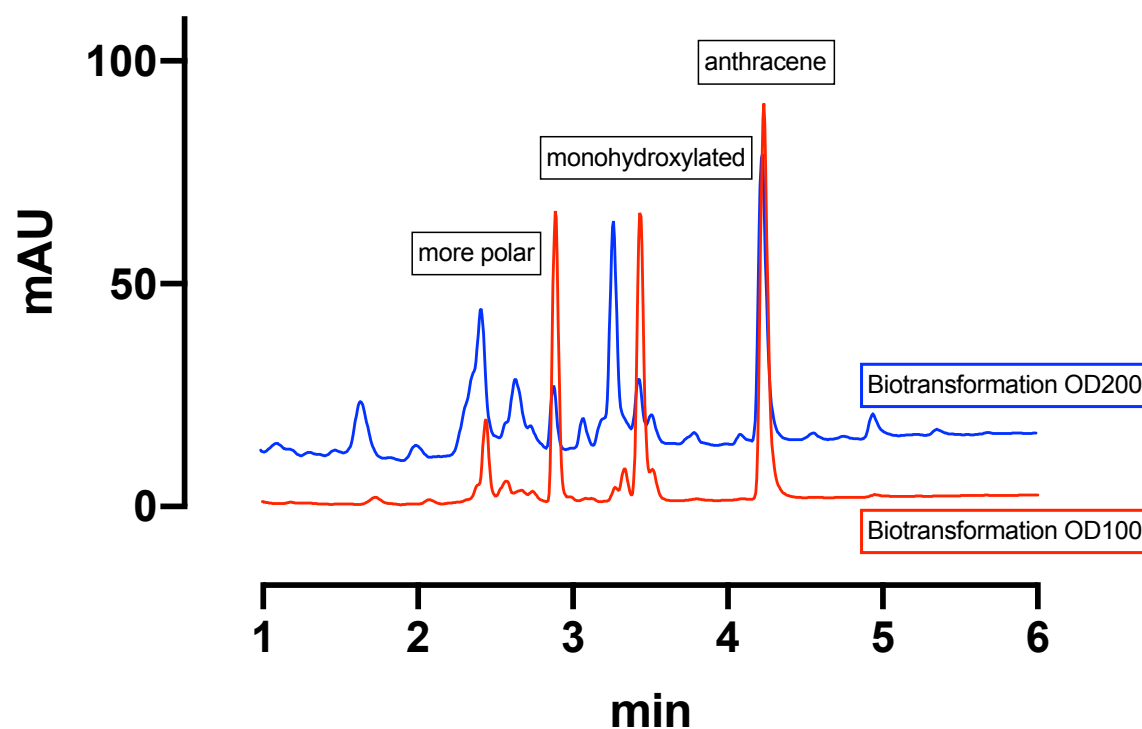
**Figure S11:** Preparative HPLC profile for product isolation of the scale-up fluorene whole-cell biotransformation employing CYP5035S7. The blue dashed line indicates the fractions collected and the arrows indicate the corresponding products framed in green that were identified by NMR analysis.



# Anthracene

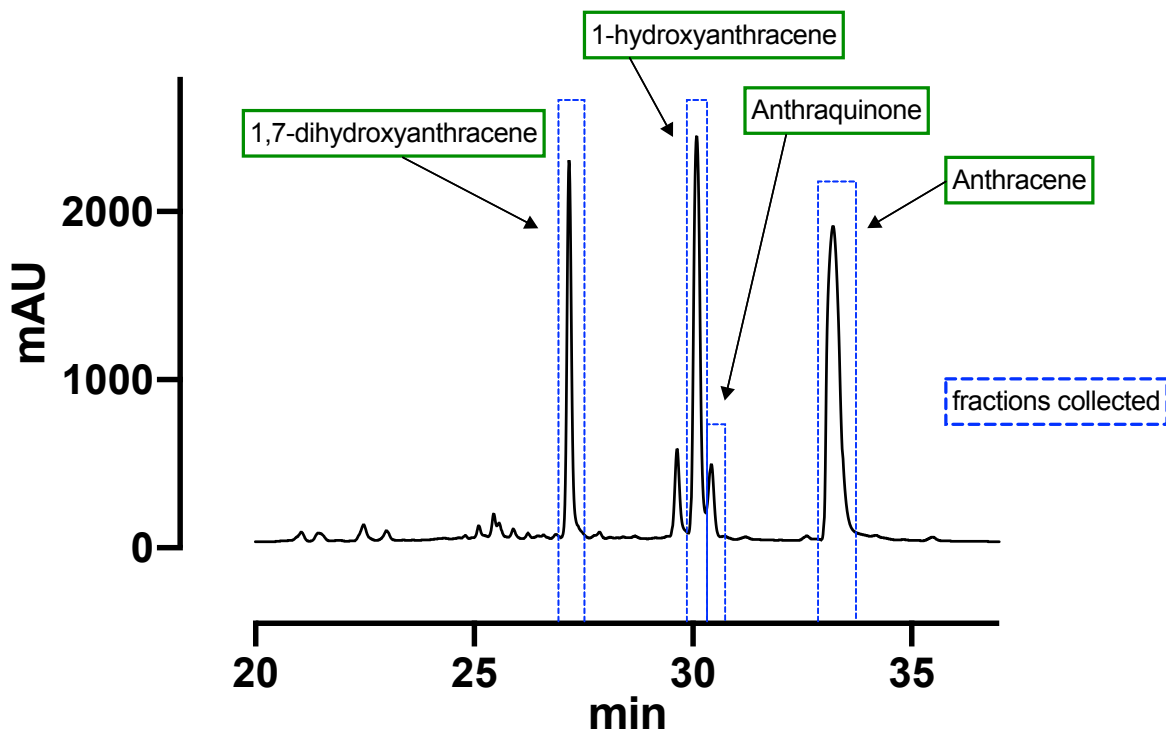


**Figure S12:** HPLC profile of anthracene conversion catalysed by CYP5035S7.

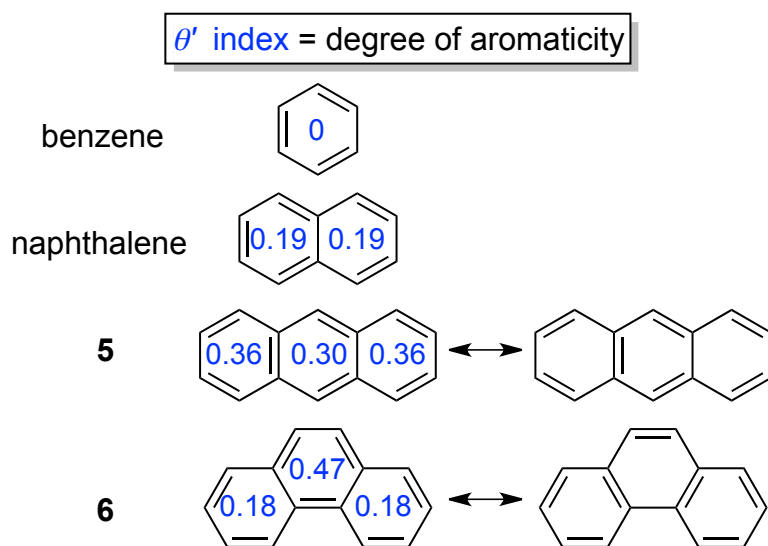


**Figure S13:** The difference between the HPLC profiles of the whole-cells biotransformation of anthracene catalysed by CYP5035S7 expressed in *P. pastoris* at different cell concentrations (OD).

# Anthracene



**Figure S14:** Preparative HPLC profile for product isolation of the scale-up anthracene whole-cell biotransformation employing CYP5035S7. The blue dashed line indicates the fractions collected and the arrows indicate the corresponding products framed in green that were identified by NMR analysis.



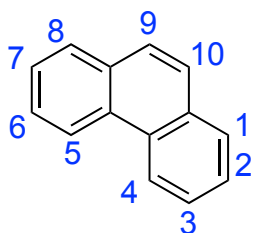
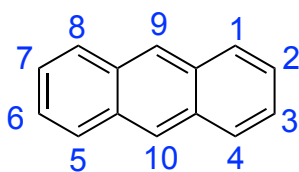
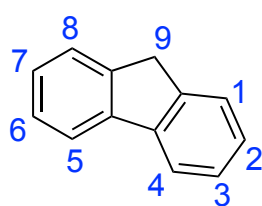
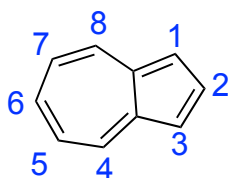
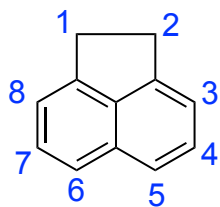
**Figure S15:** The degree of aromaticity according to the  $\theta'$  index<sup>[1]</sup> along with resonance structures of Clar's aromatic  $\pi$ -sextet approach of four PAH structures are shown.

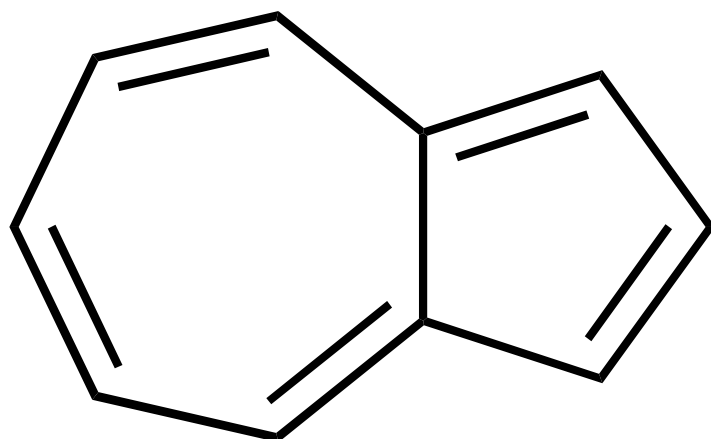
## References

- [1] M. Estévez-Fregoso, J. Hernández-Trujillo, *Phys. Chem. Chem. Phys.* **2016**, *18*, 11792–11799.

# NMR spectra

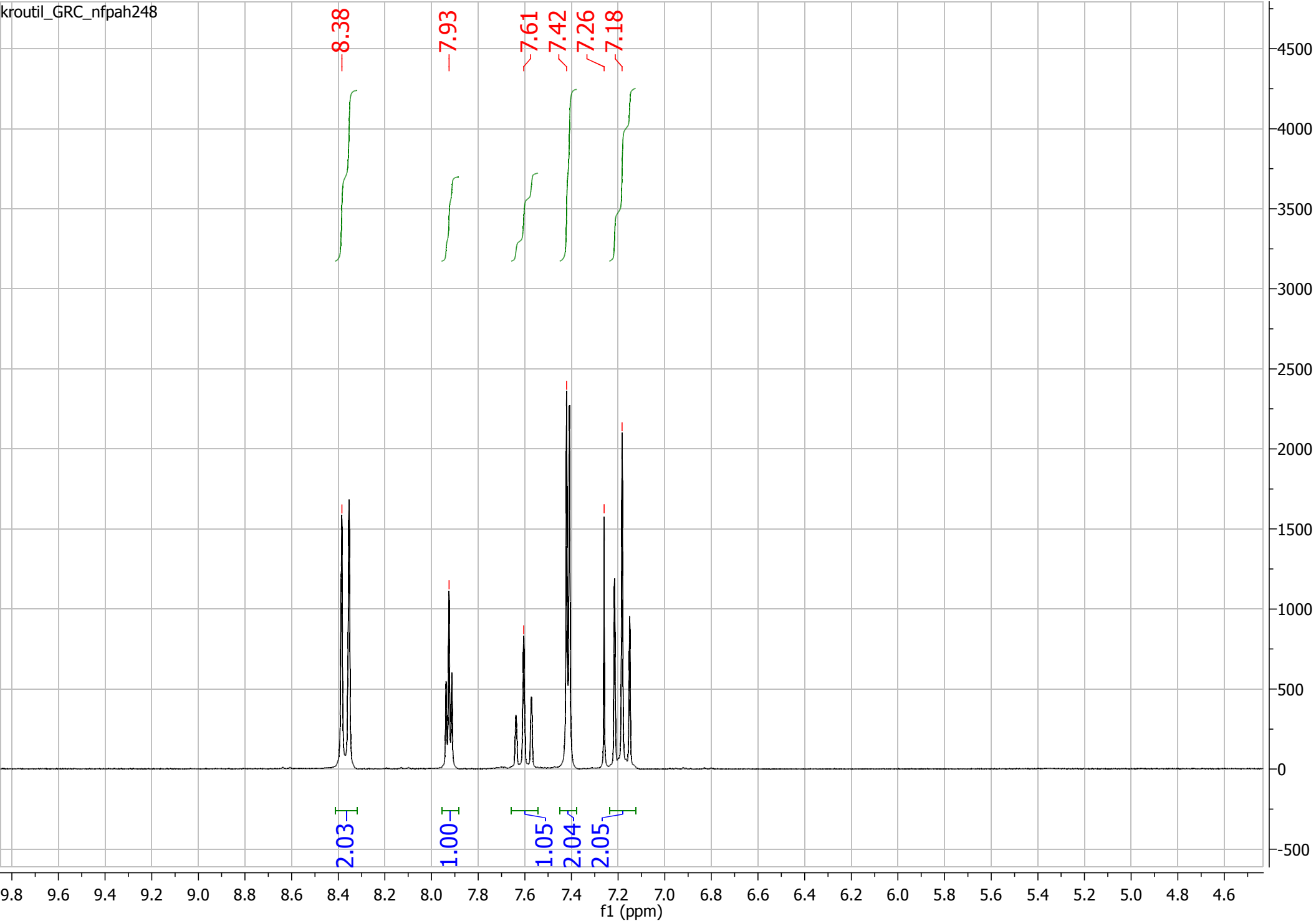
PAH numbering of the compounds converted by CYP5035S7 at semi-preparative-scale in this study:

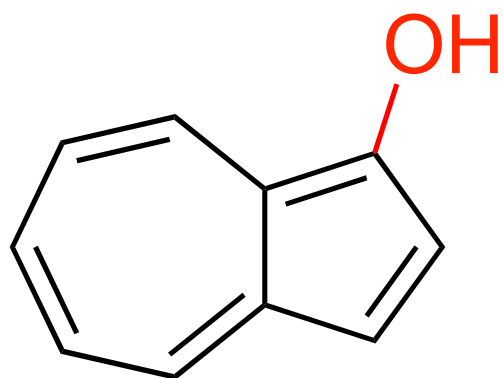




**2**

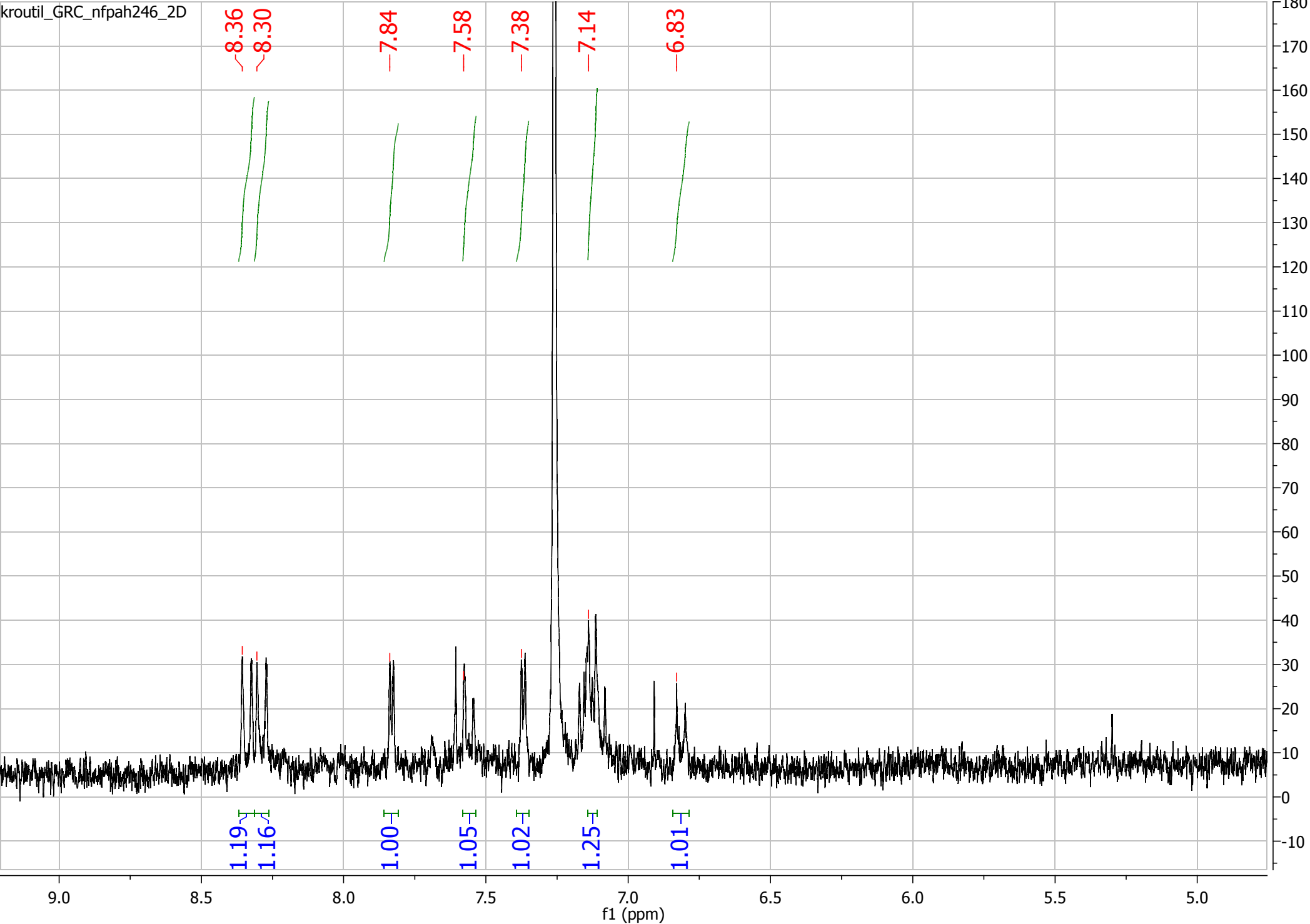
kroutil\_GRC\_nfpah248

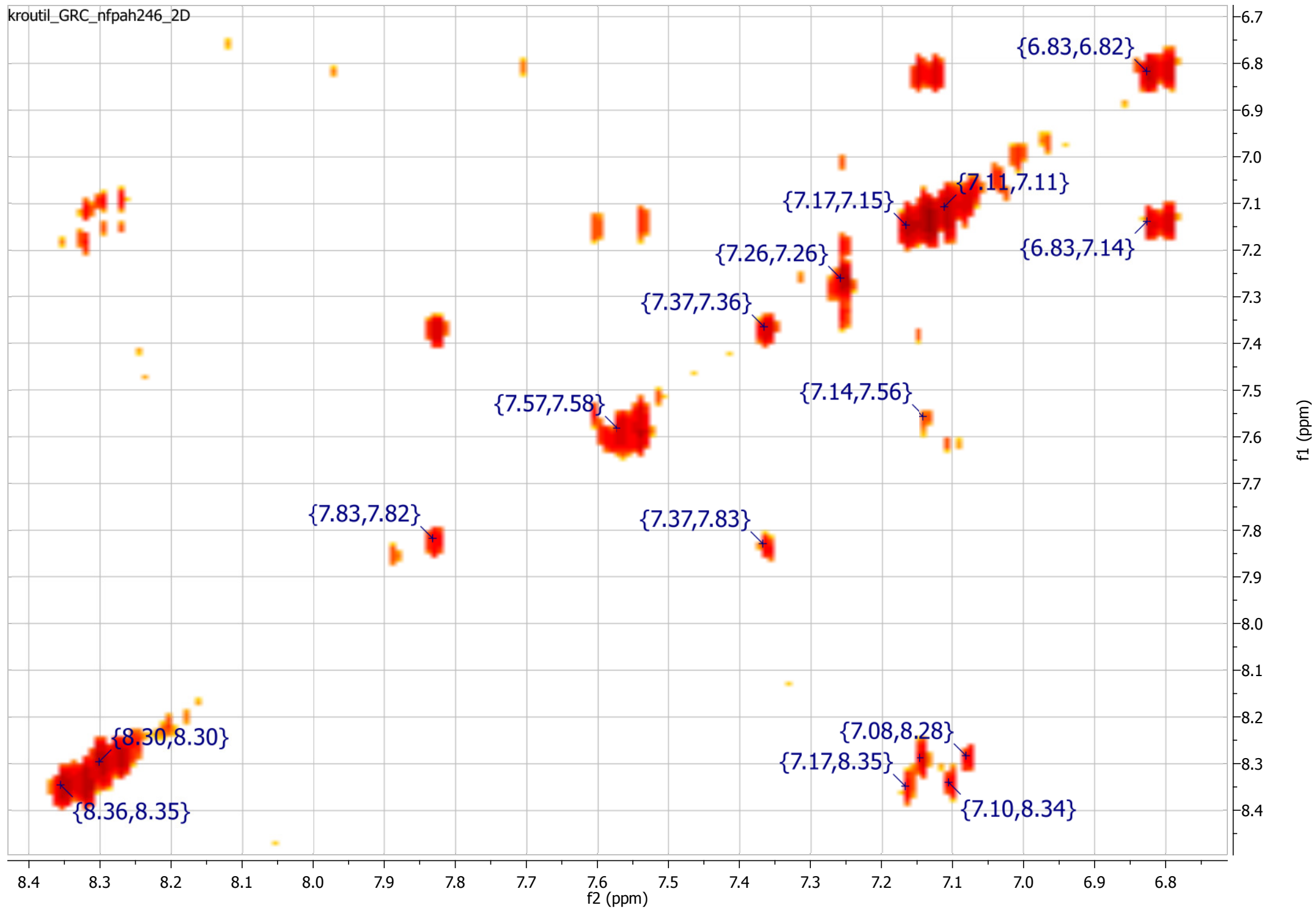




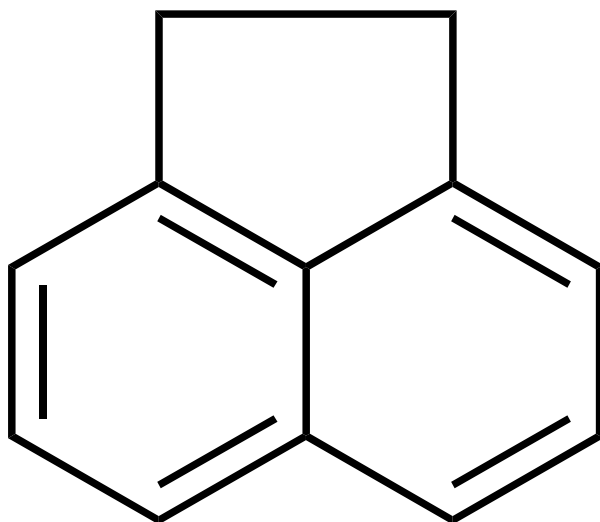
1-hydroxyazulene (**11**)

kroutil\_GRC\_nfpah246\_2D



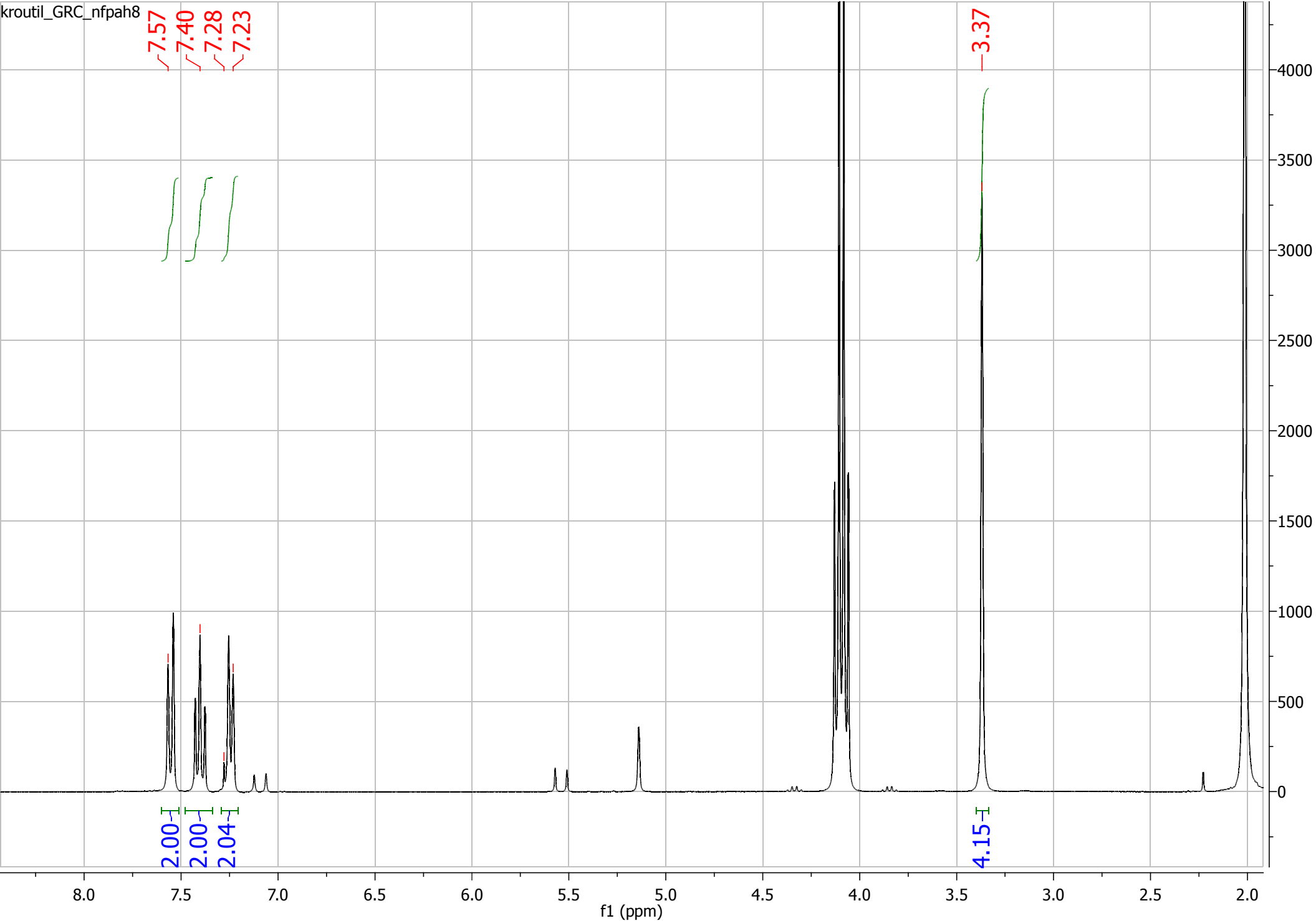


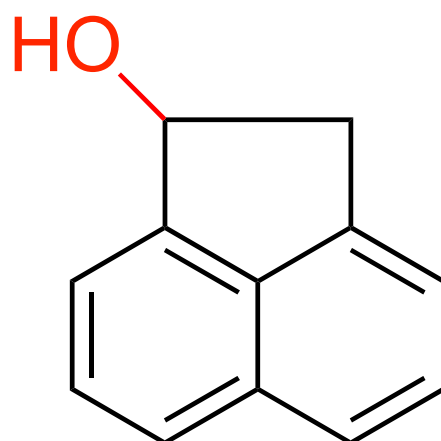




# 3

kroutil\_GRC\_nfpah8





1-hydroxyacenaphthene (**12**)

kroutil\_GRC\_nfpah5\_2D

7.77  
7.68  
7.57  
7.53  
7.33  
7.26

5.77

3.87

3.29

0.99  
1.00  
0.95  
0.82  
1.01  
0.98

1.02

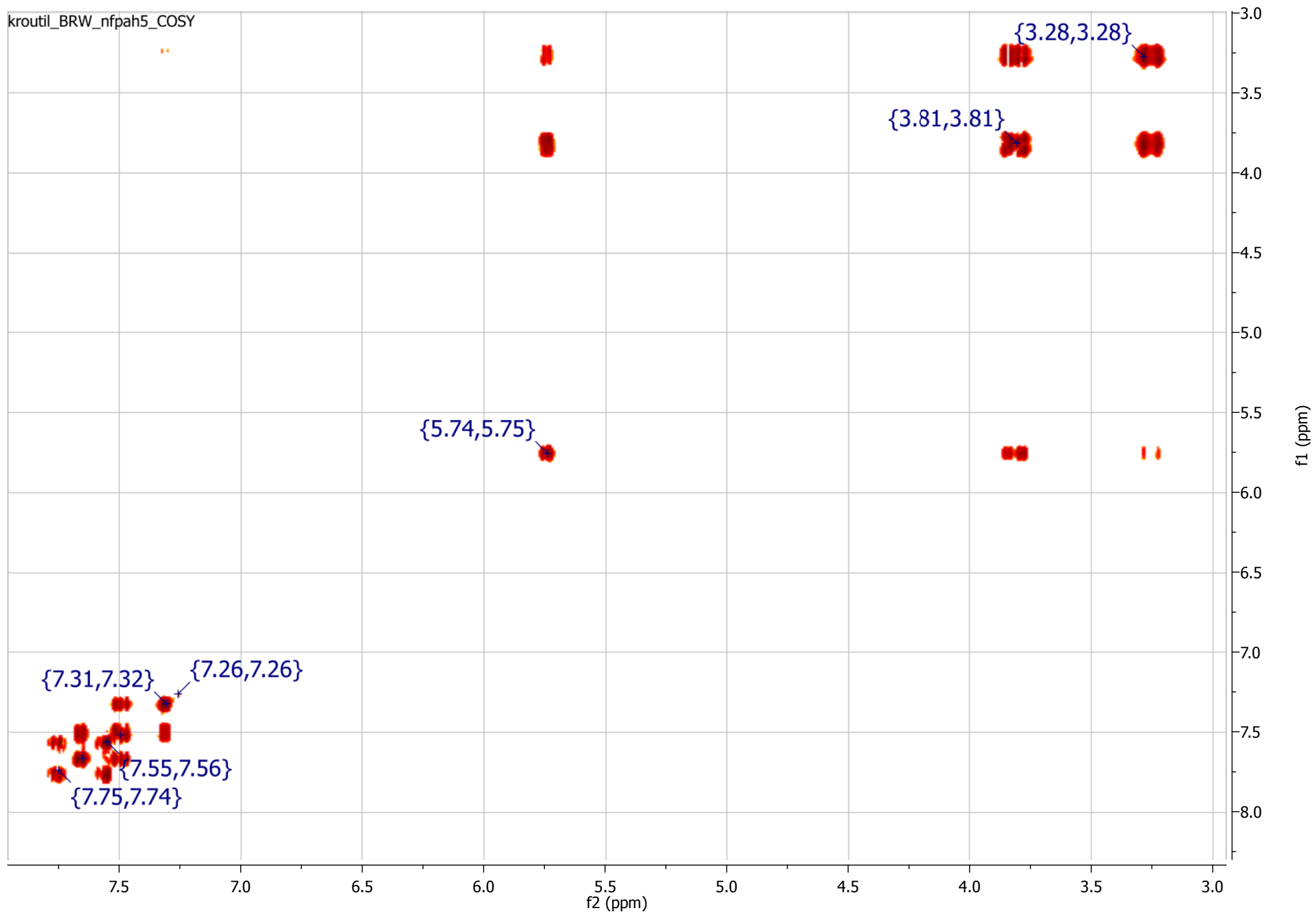
1.09

1.09

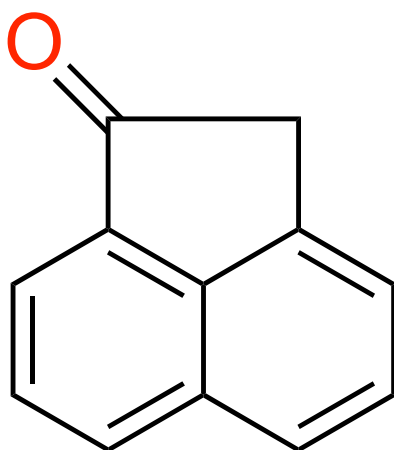
8.6 8.2 7.8 7.6 7.4 7.2 7.0 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8

f1 (ppm)

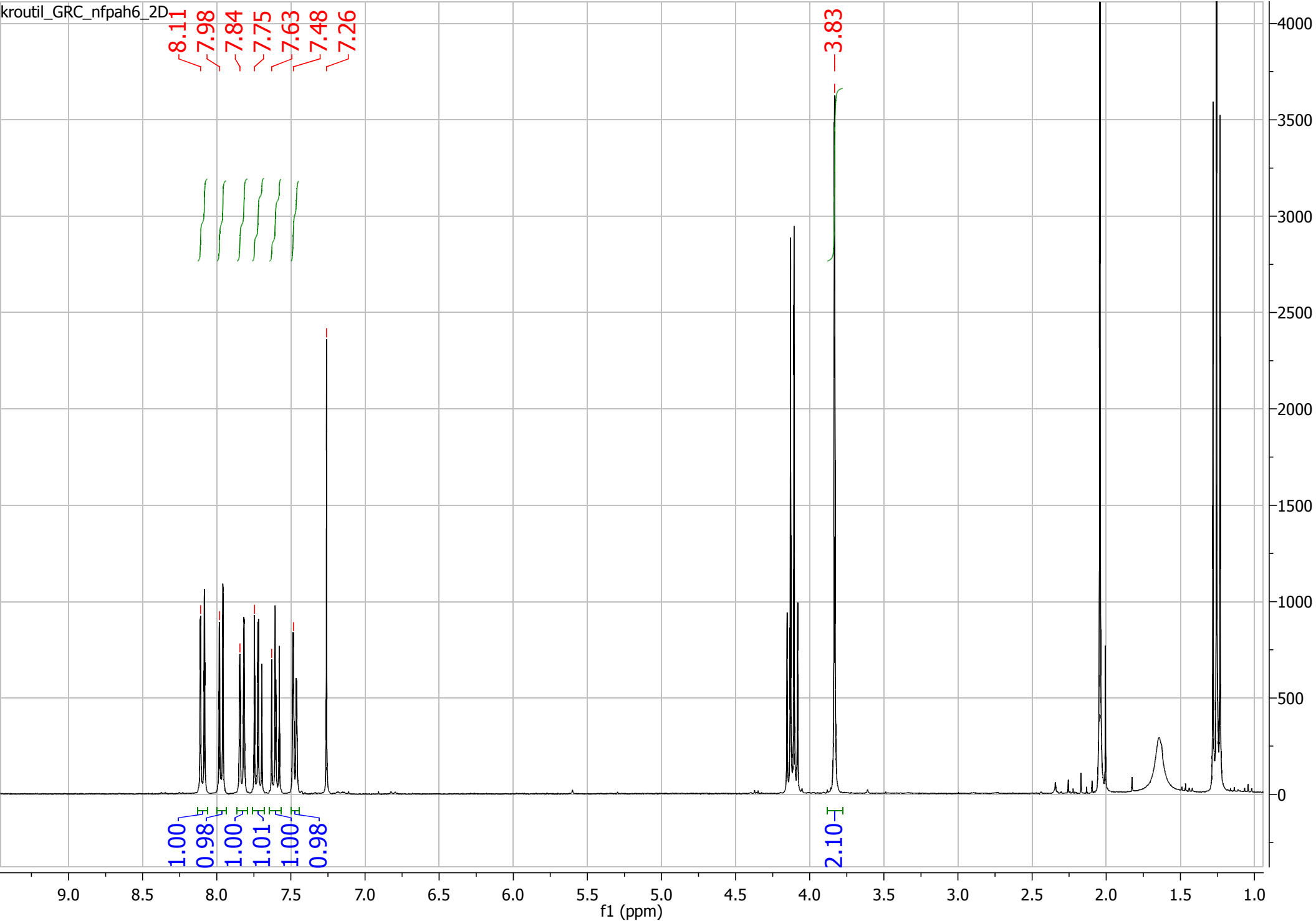
3400  
3200  
3000  
2800  
2600  
2400  
2200  
2000  
1800  
1600  
1400  
1200  
1000  
800  
600  
400  
200  
0  
-200





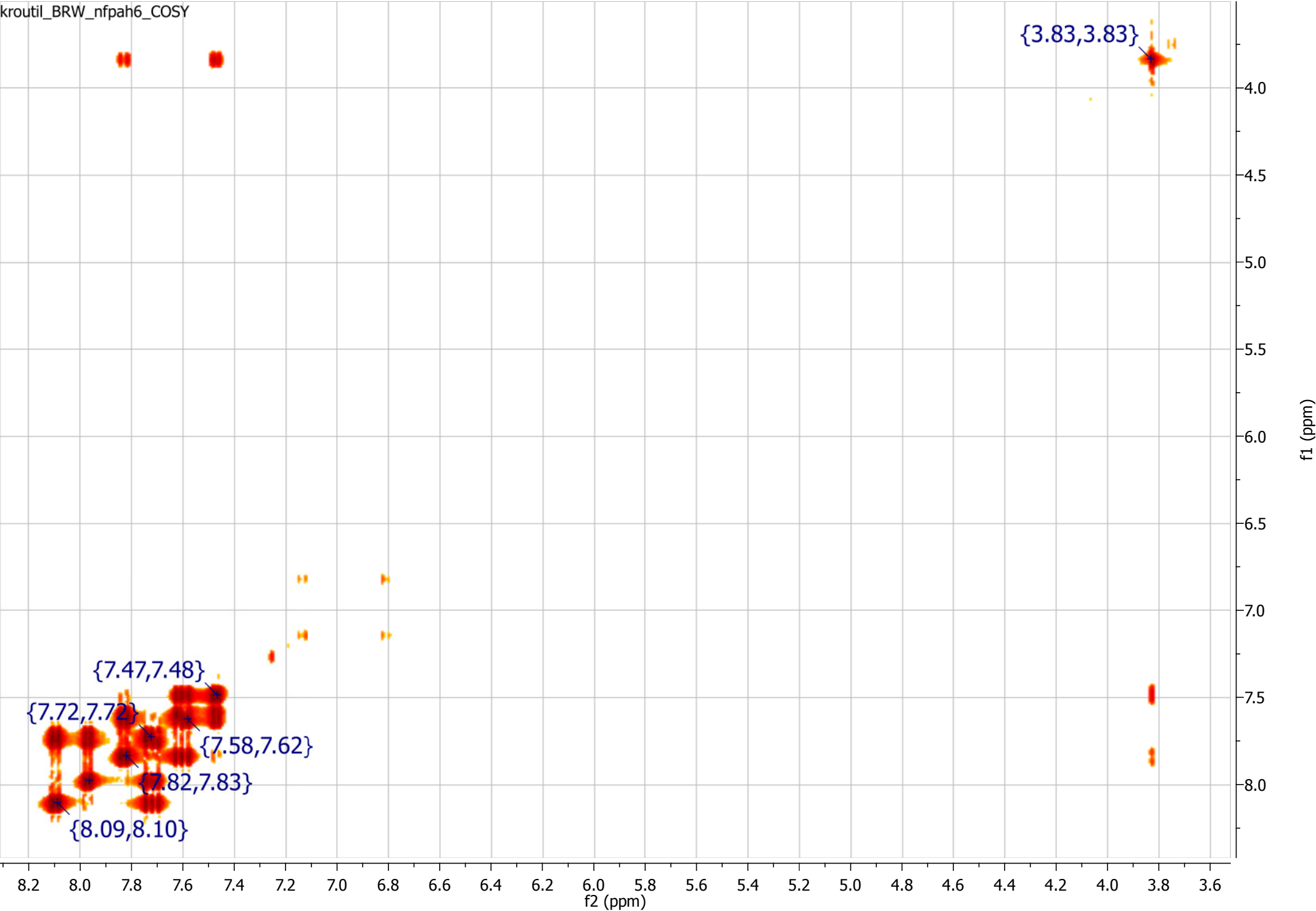


1-acenaphthenone (**13**)

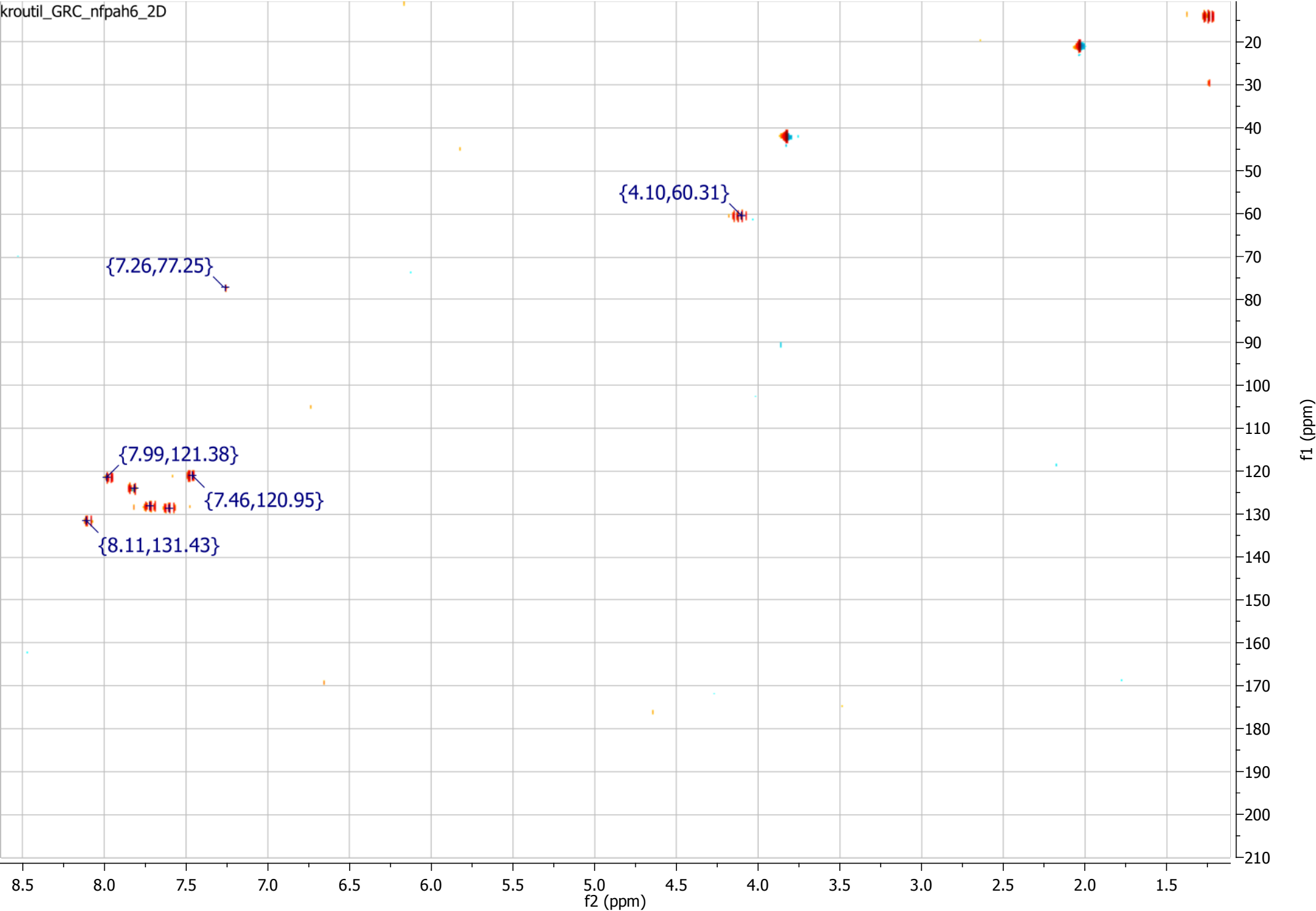


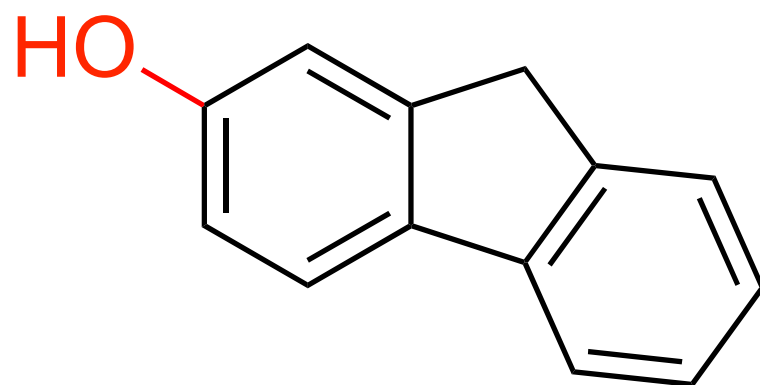


kroutil\_BRW\_nfpah6\_COSY



kroutil\_GRC\_nfpah6\_2D





2-hydroxyfluorene (**14**)

kroutil\_GRC\_nfpah234\_2D

7.69  
7.65  
7.51  
7.34  
7.26  
7.24  
7.03  
6.87

3.85

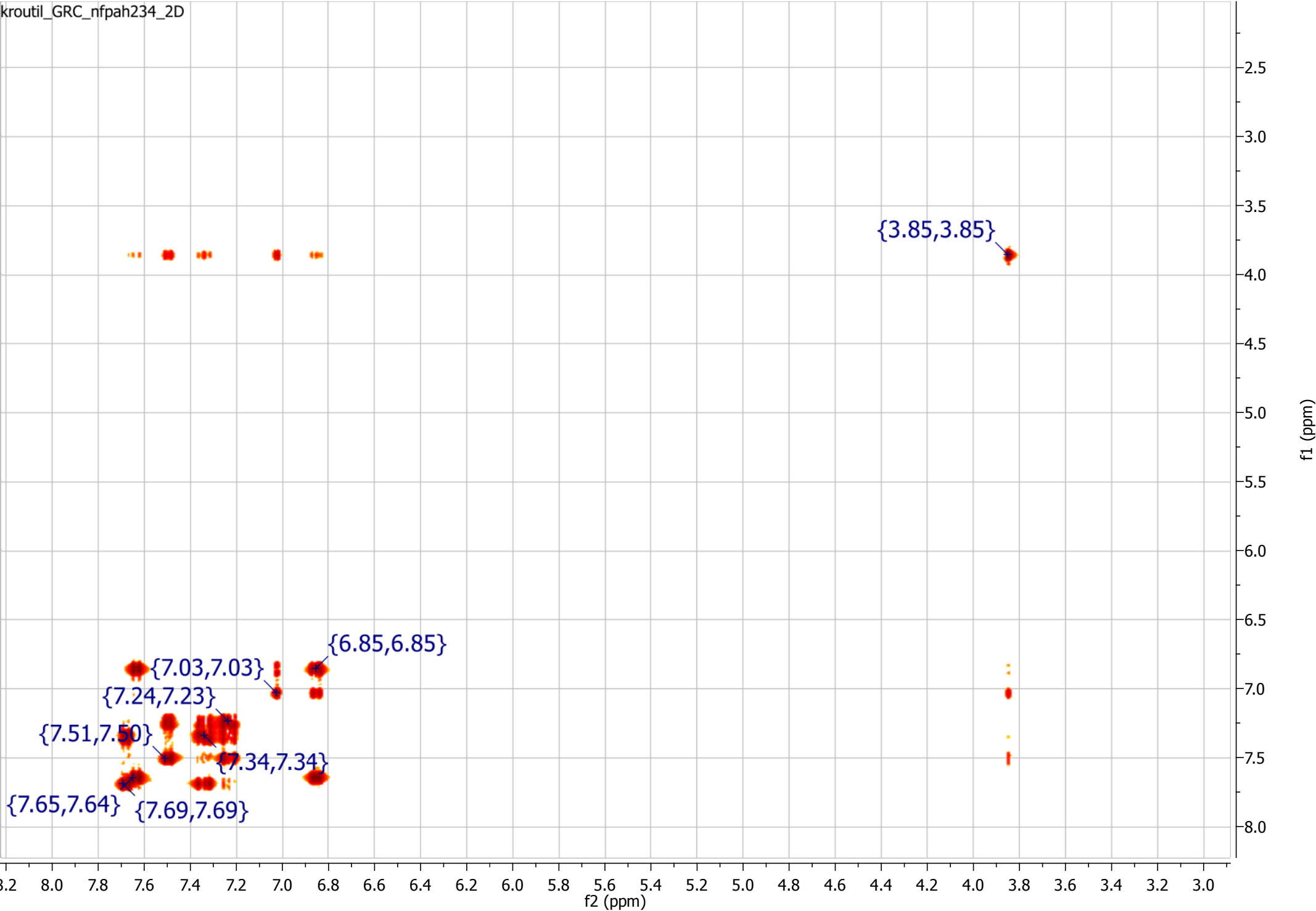
1.03  
0.99  
1.02  
1.04  
1.00  
1.00  
1.03

2.07

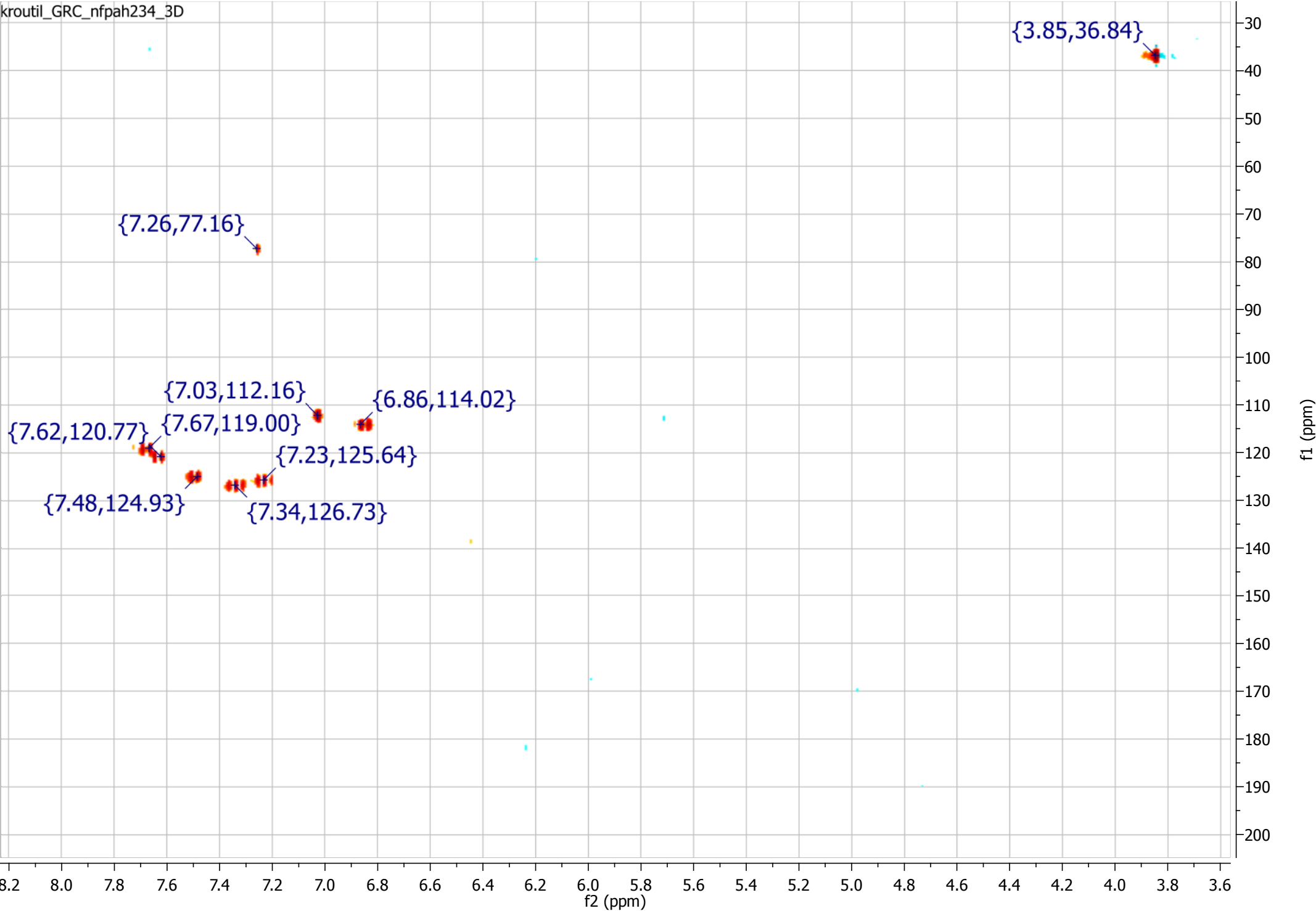
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0

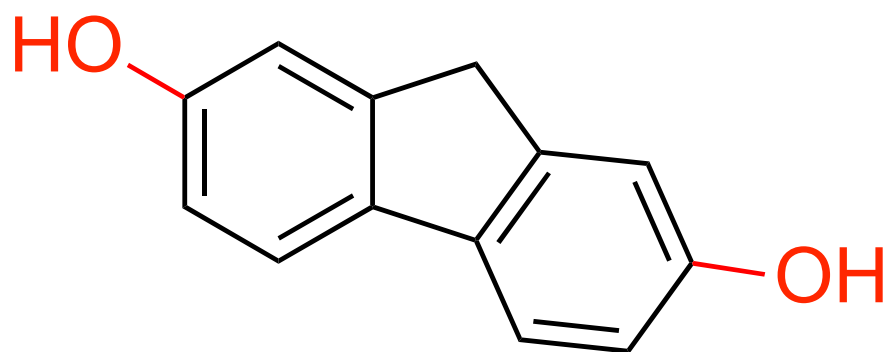
f1 (ppm)

kroutil\_GRC\_nfpah234\_2D

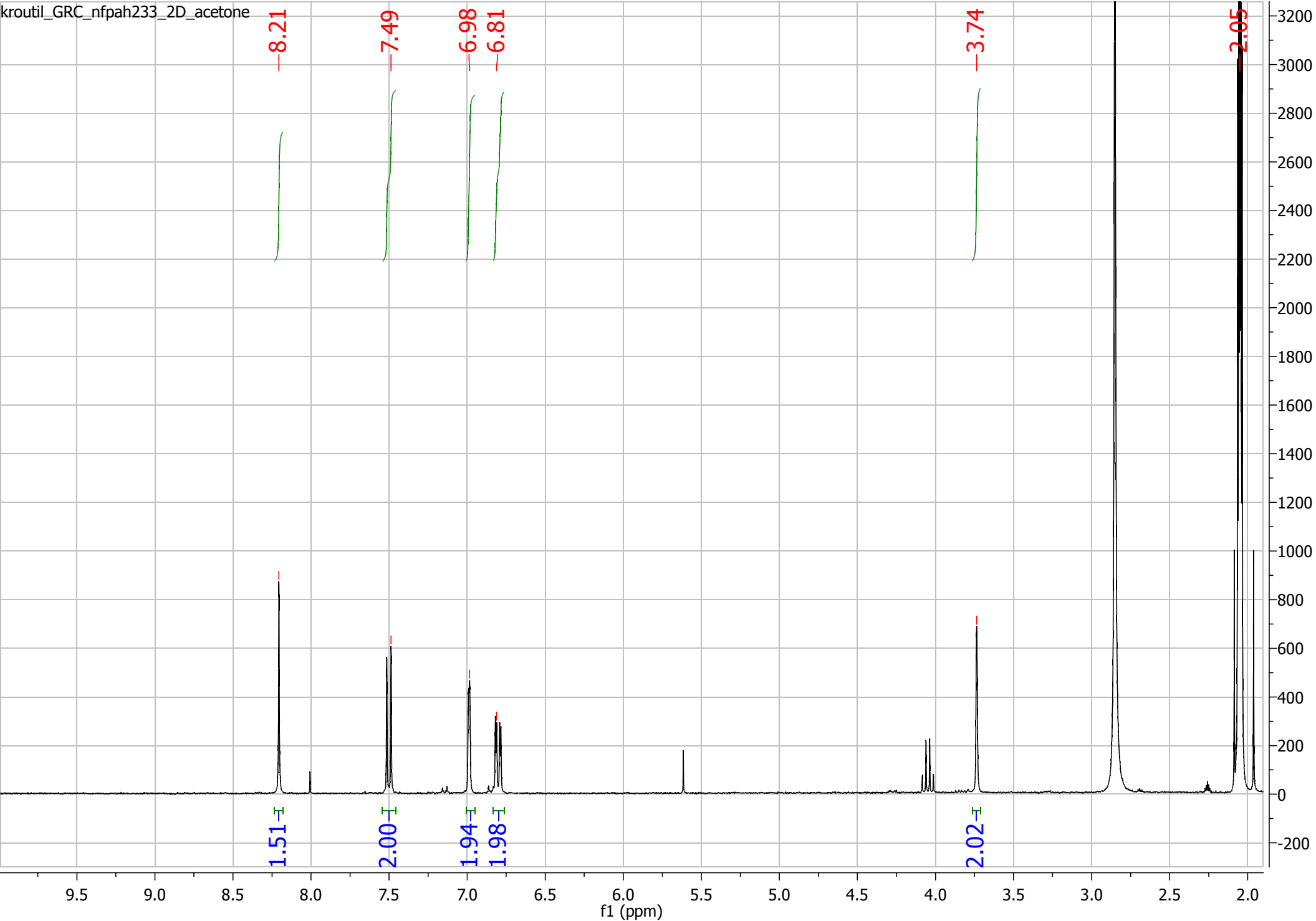


kroutil\_GRC\_nfpah234\_3D

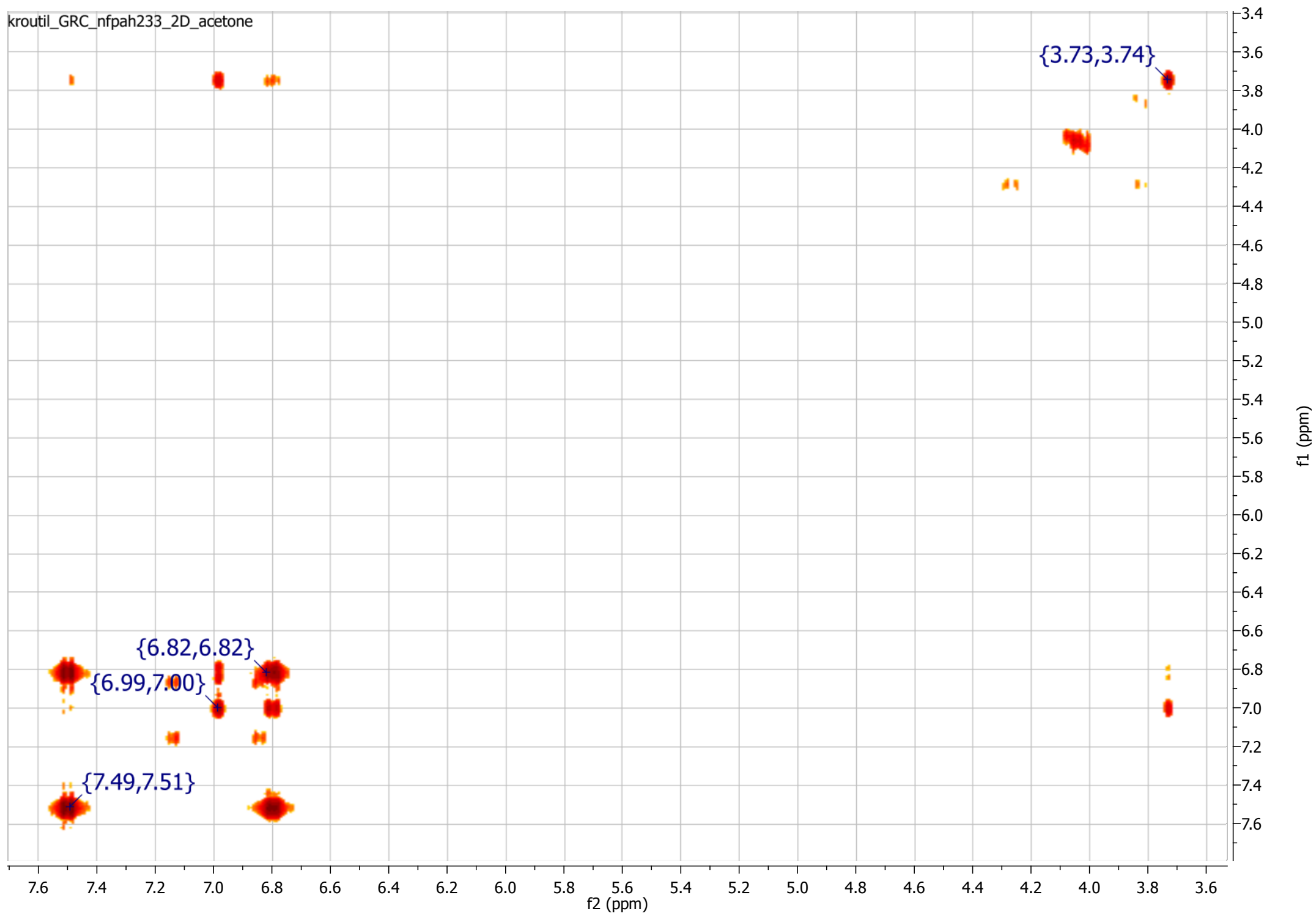


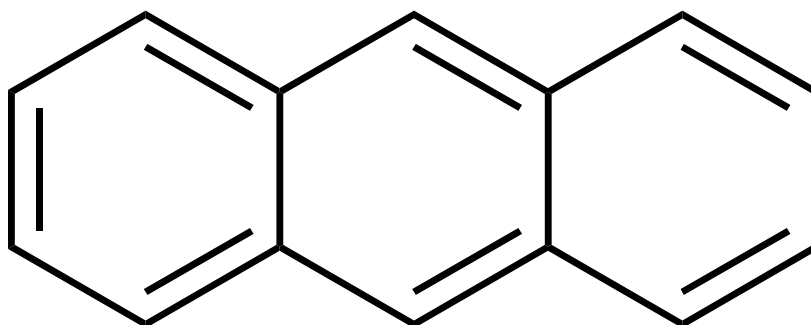


2,7-dihydroxyfluorene (**15**)

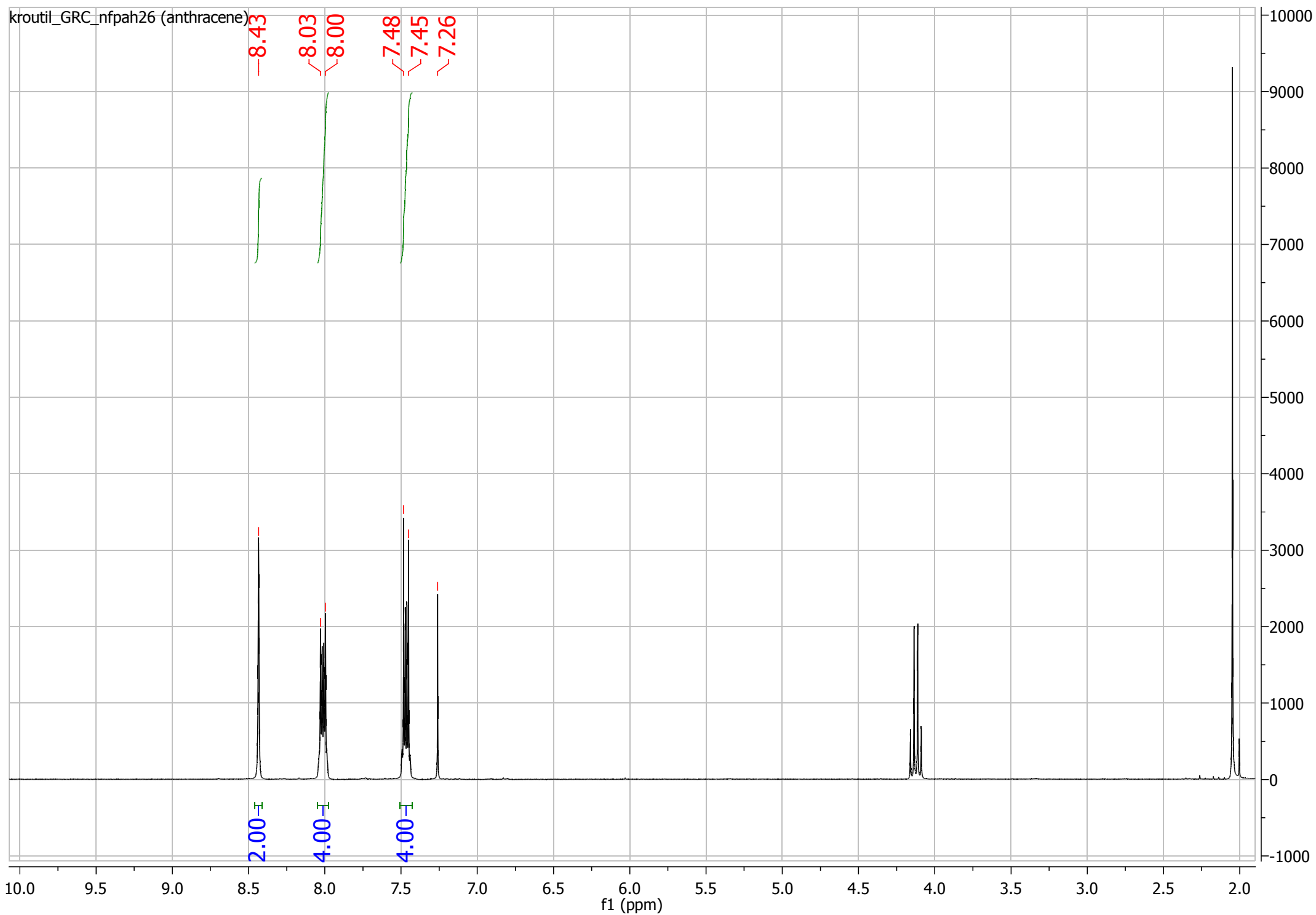


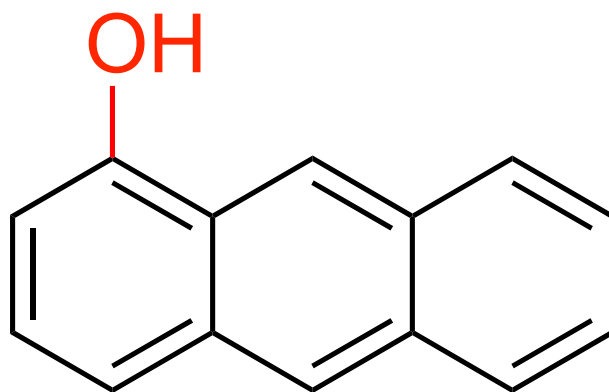






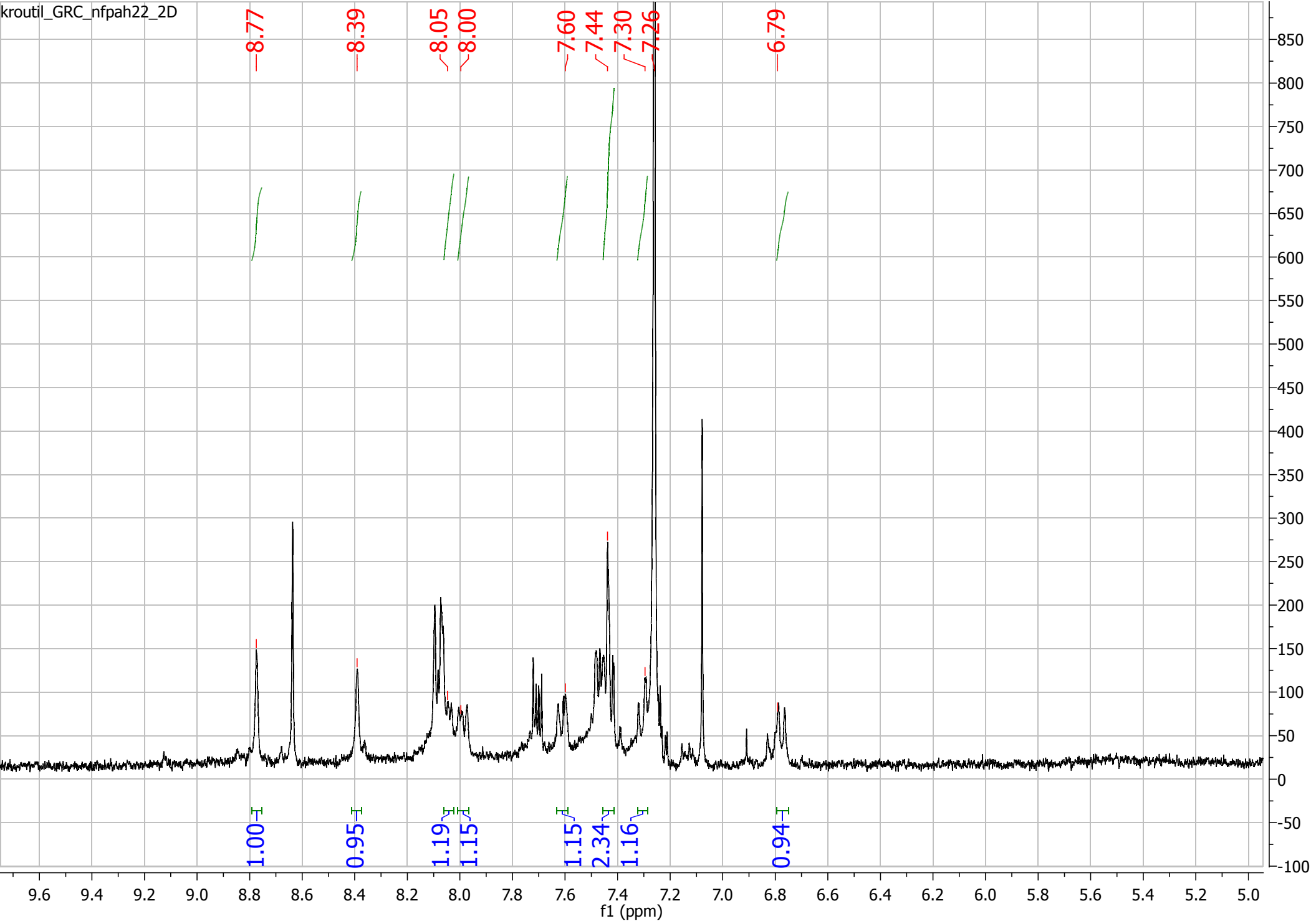
**5**



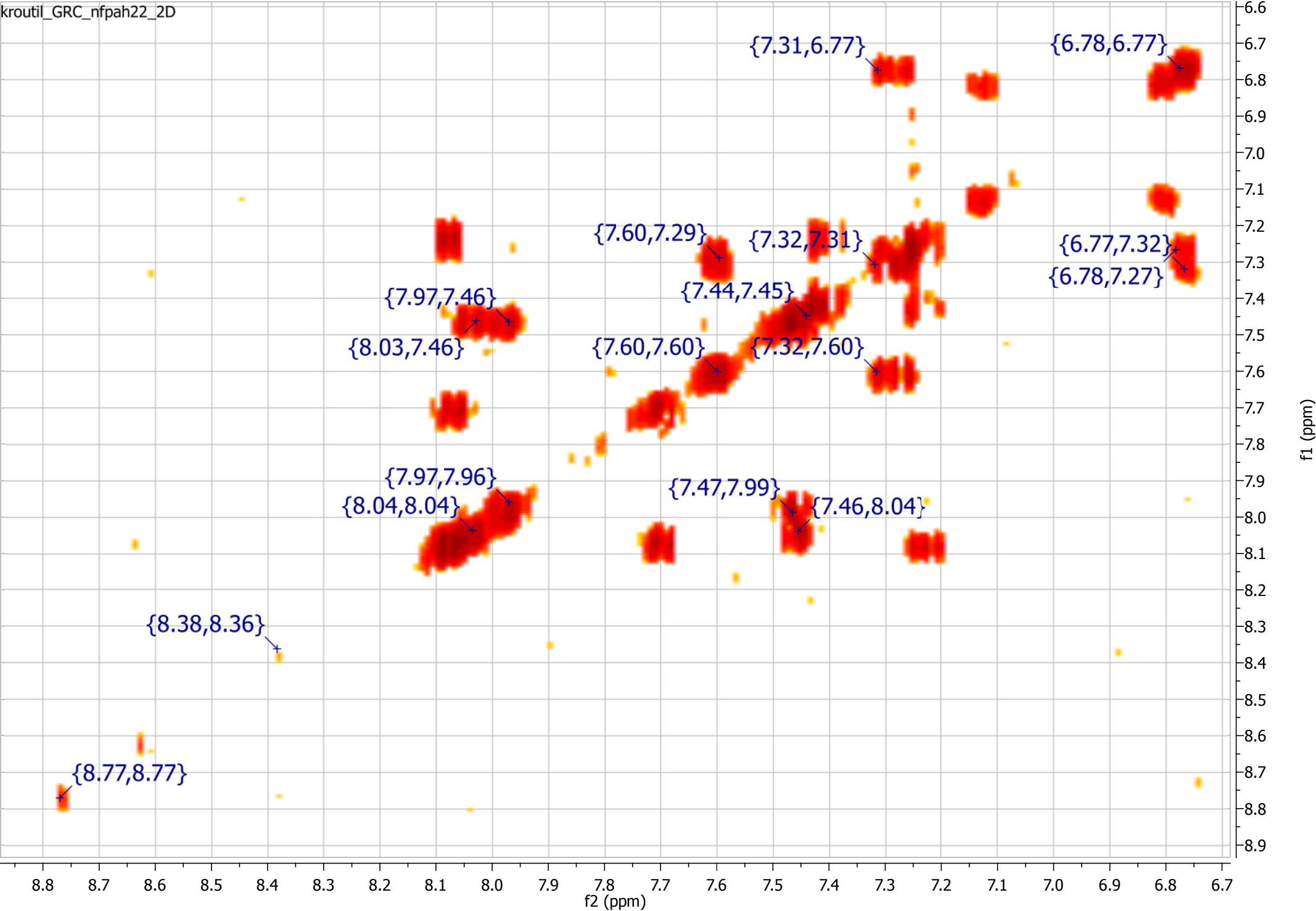


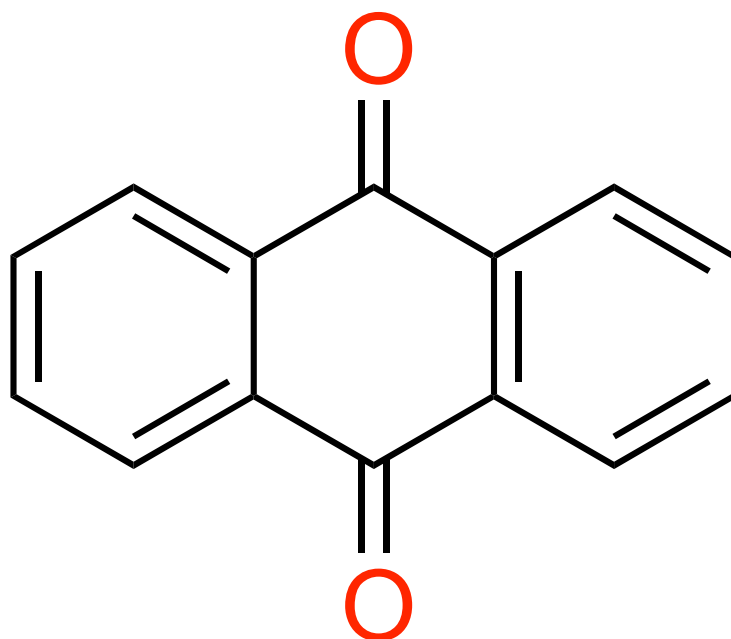
1-hydroxyanthracene (**16**)

kroutil\_GRC\_nfpah22\_2D



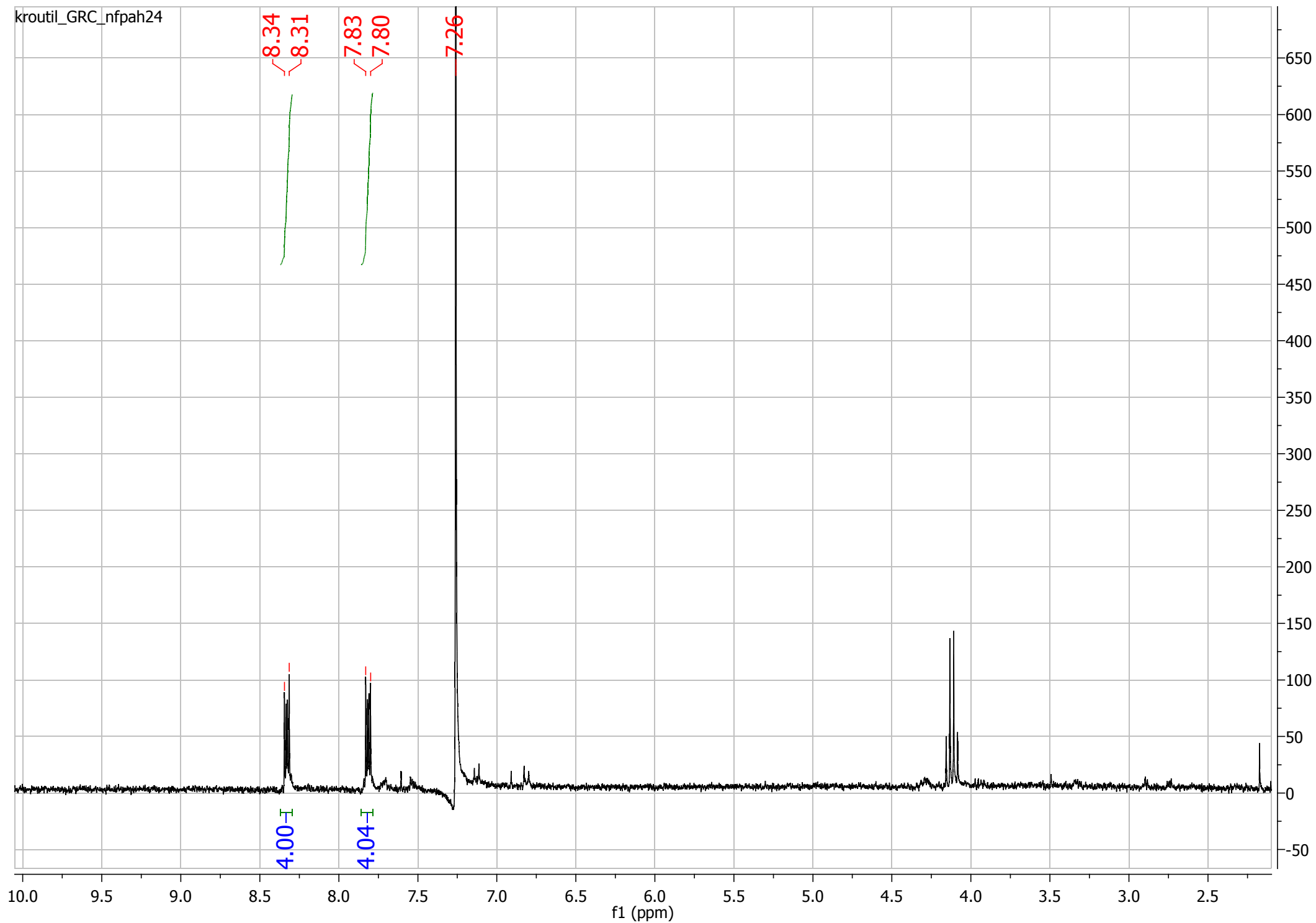
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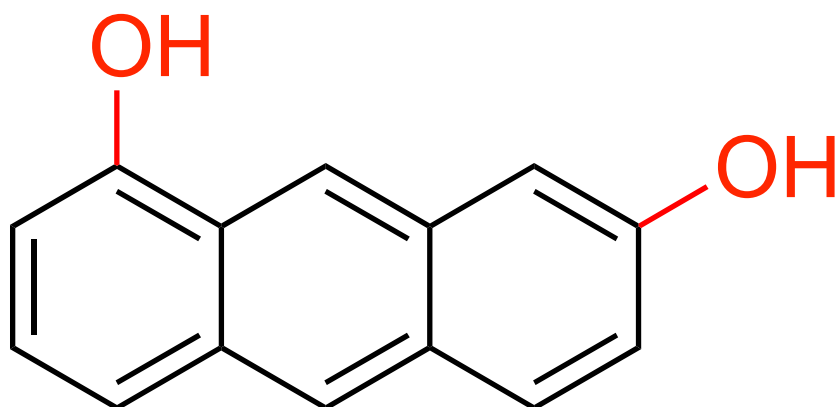


anthraquinone (**17**)

kroutil\_GRC\_nfpah24

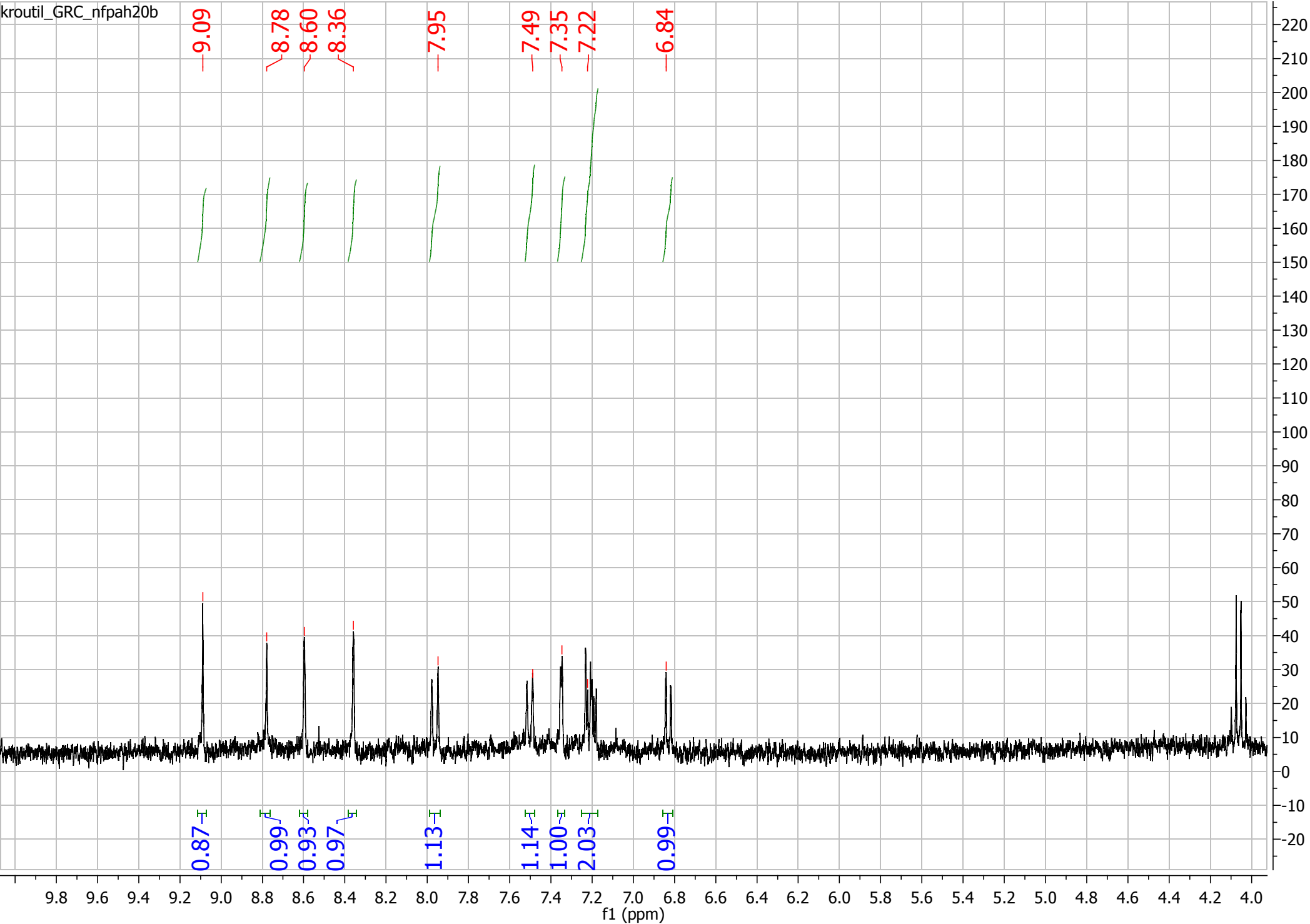


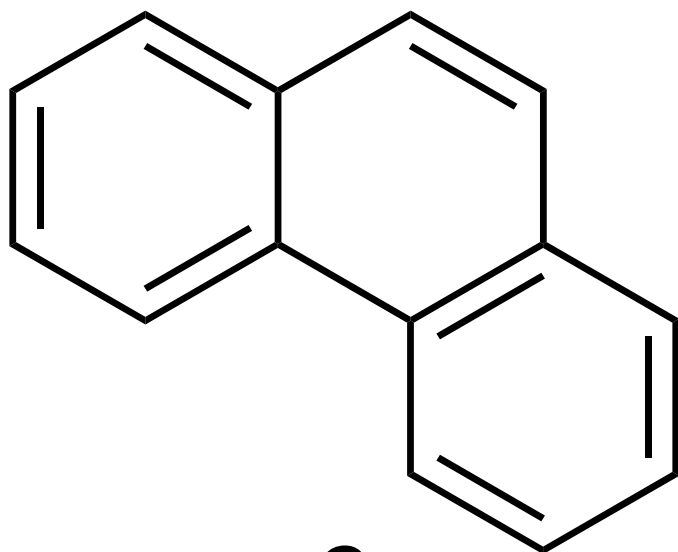




1,7-dihydroxyanthracene (**18**)

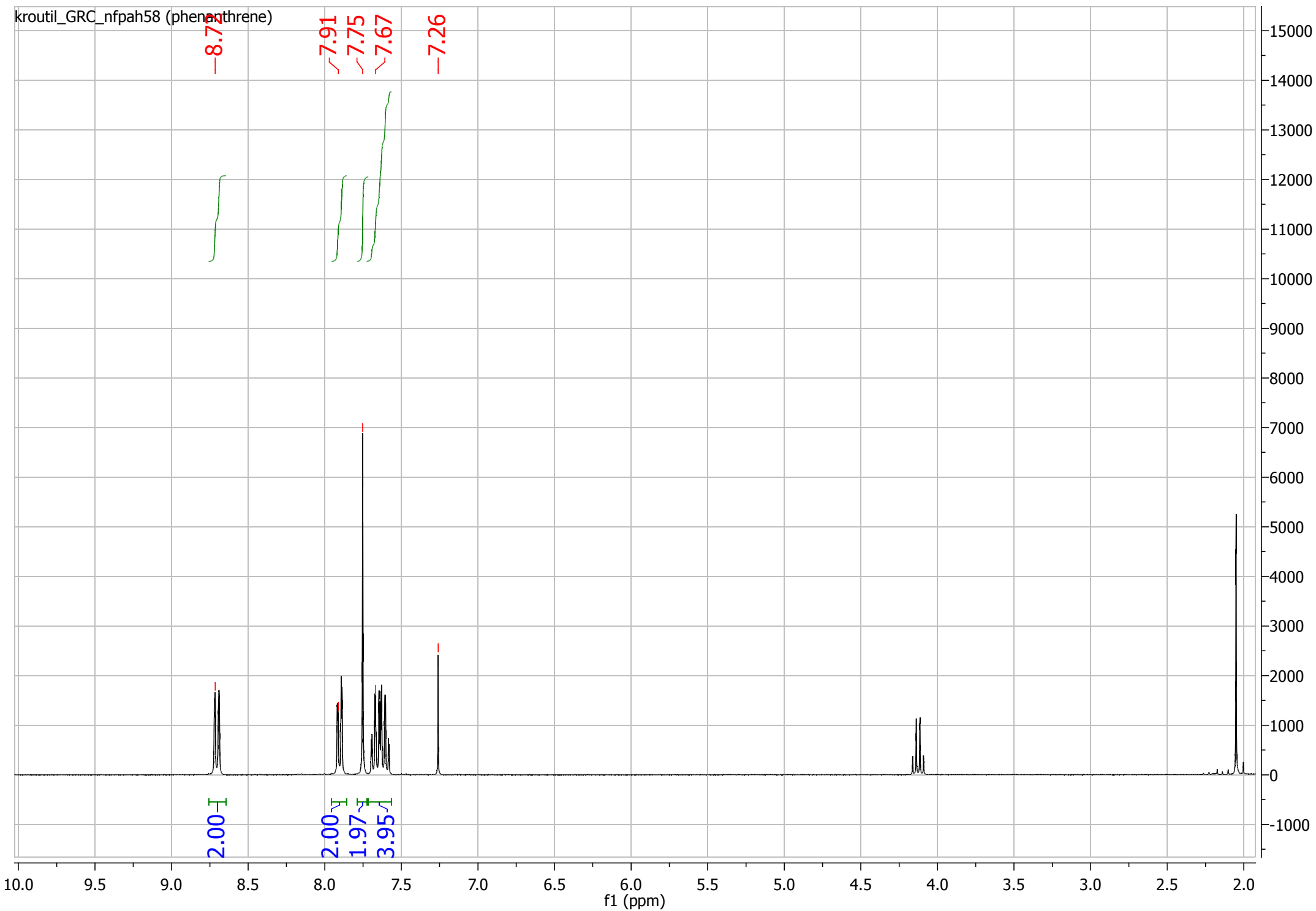
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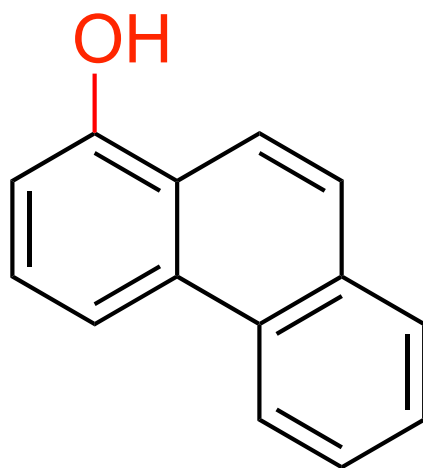




**6**

kroutil\_GRC\_nfpah58 (phenanthrene)

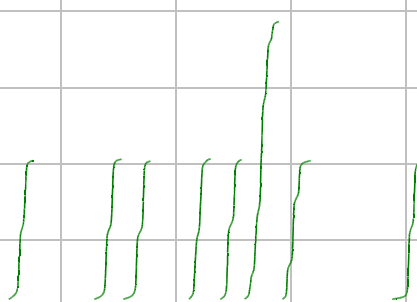




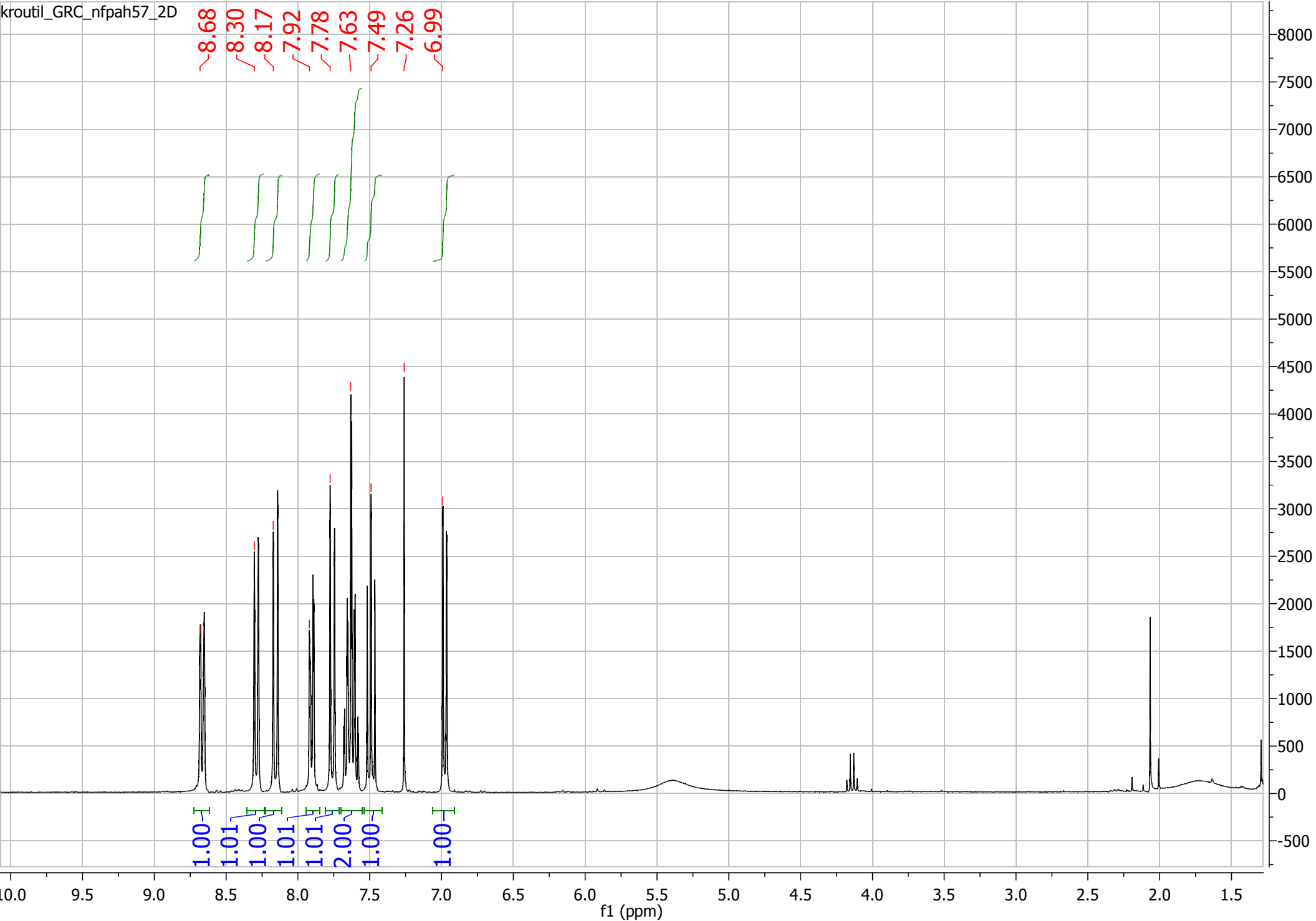
1-hydroxyphenanthrene (**19**)

kroutil\_GRC\_nfpah57\_2D

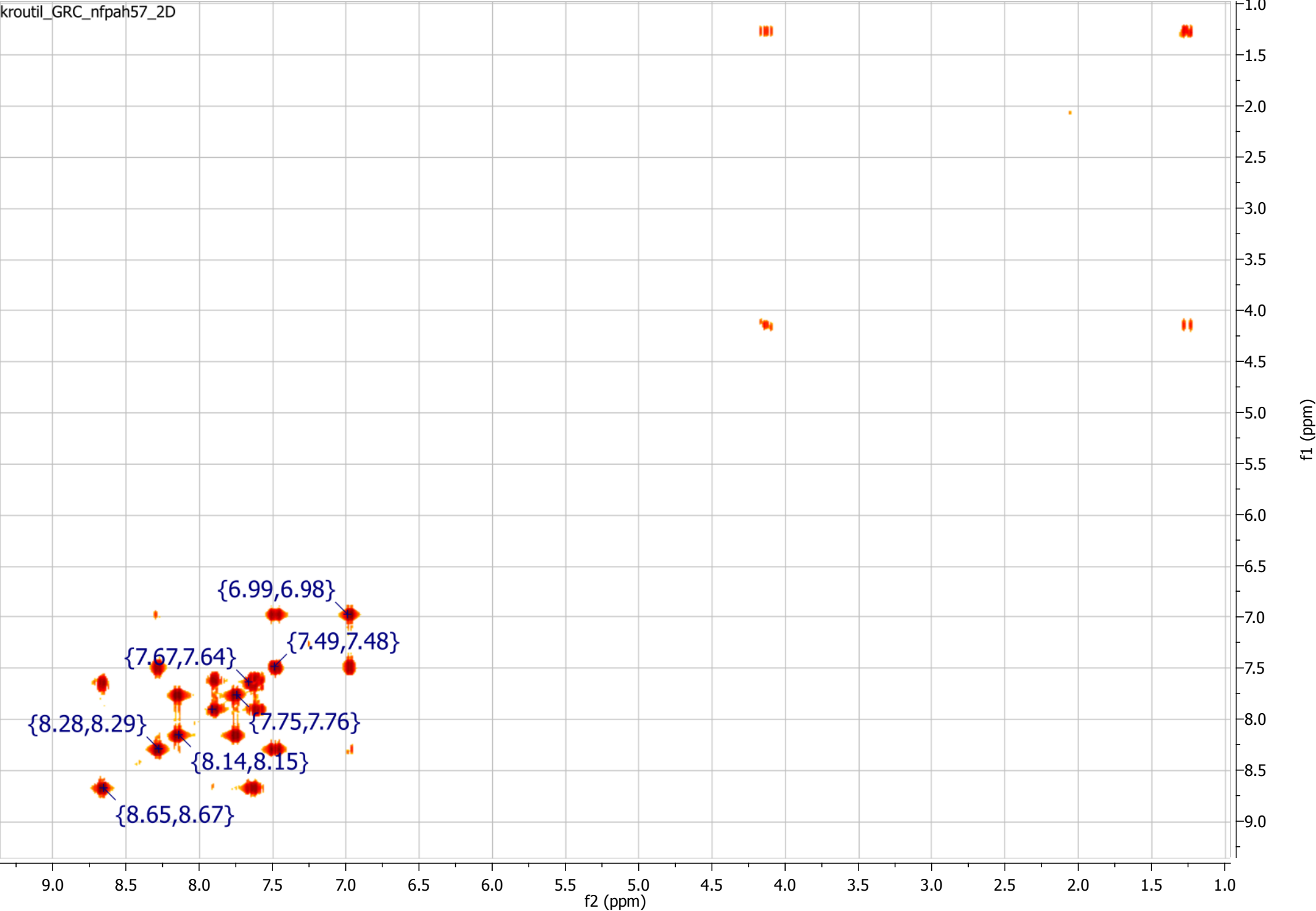
8.68  
8.30  
8.17  
7.92  
7.78  
7.63  
7.49  
7.26  
6.99



1.00  
1.01  
1.00  
1.01  
1.01  
2.00  
1.00  
1.00



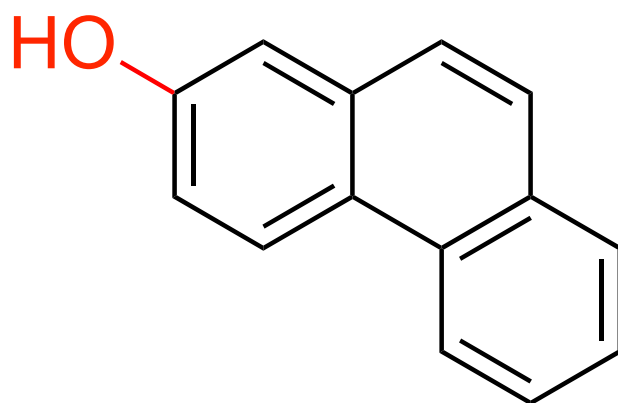
kroutil\_GRC\_nfpah57\_2D



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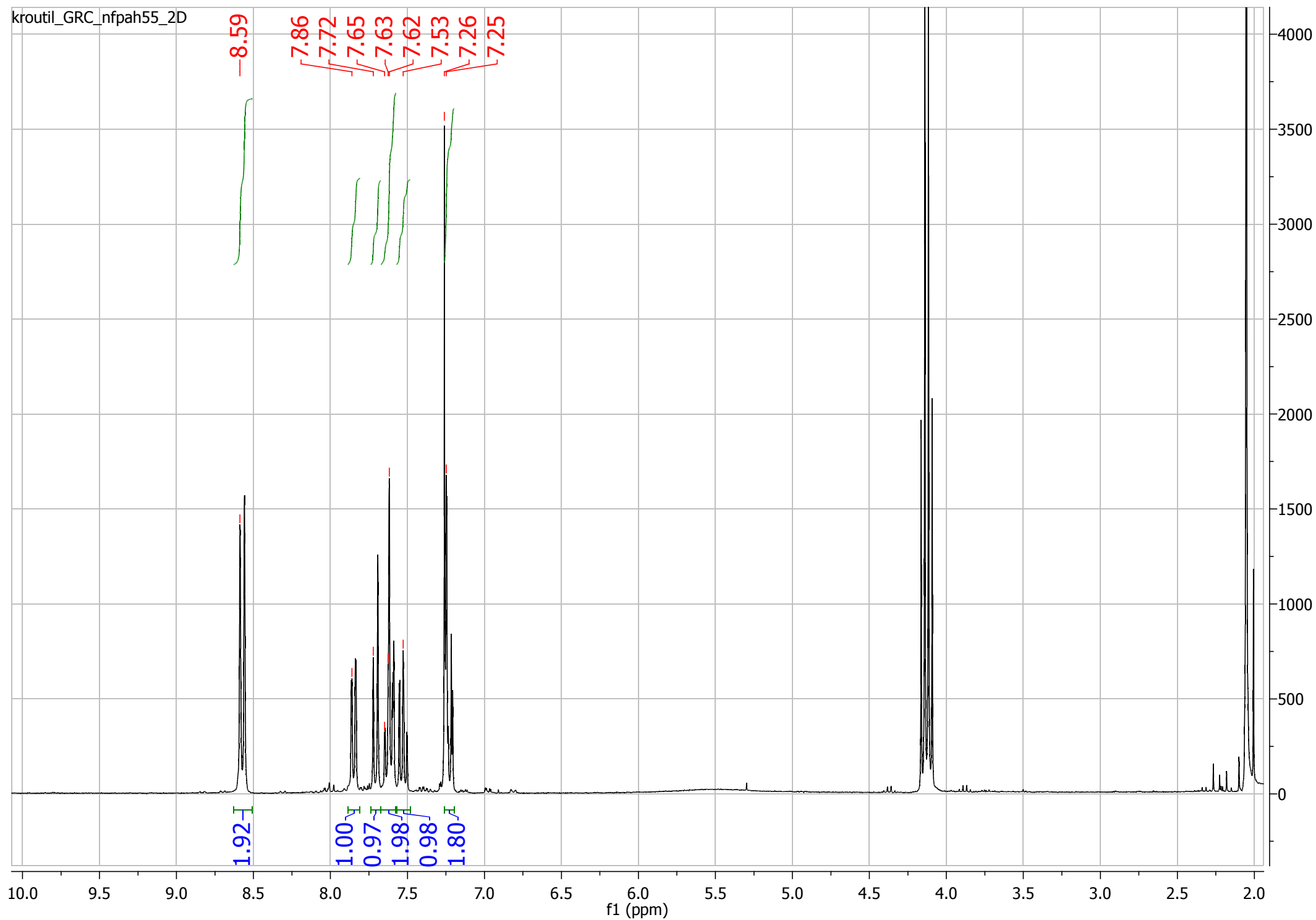




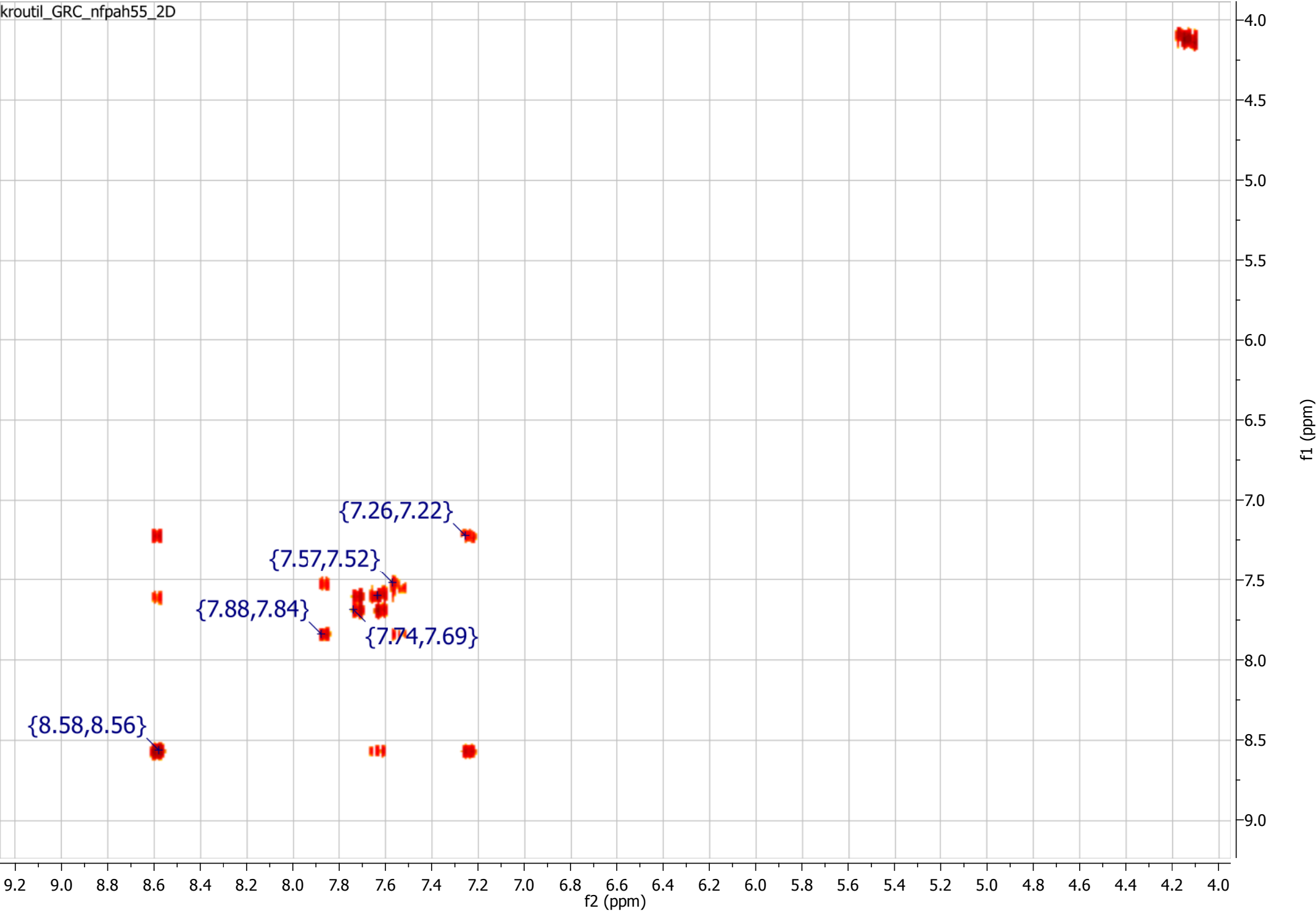


2-hydroxyphenanthrene (**20**)

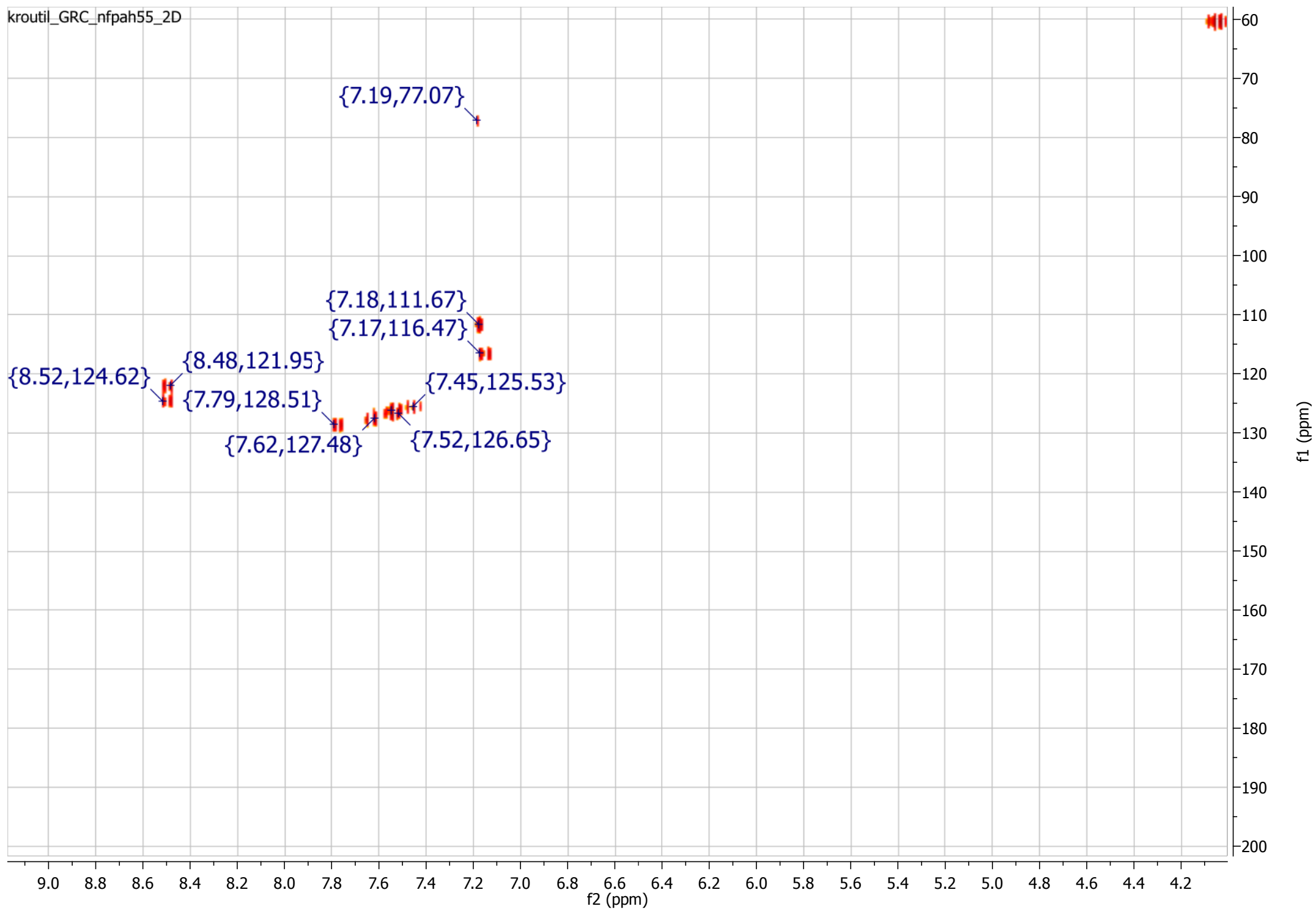
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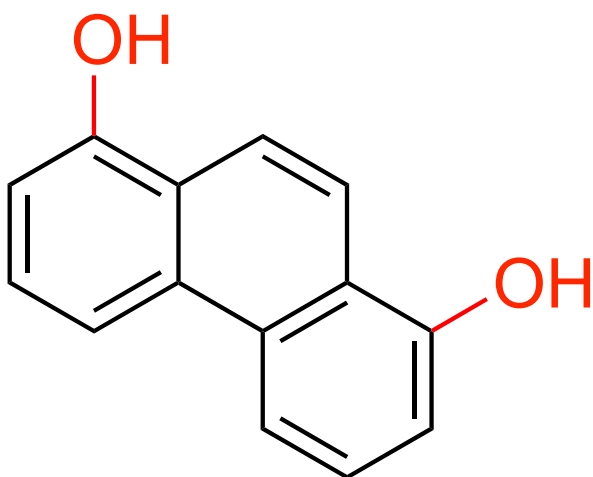


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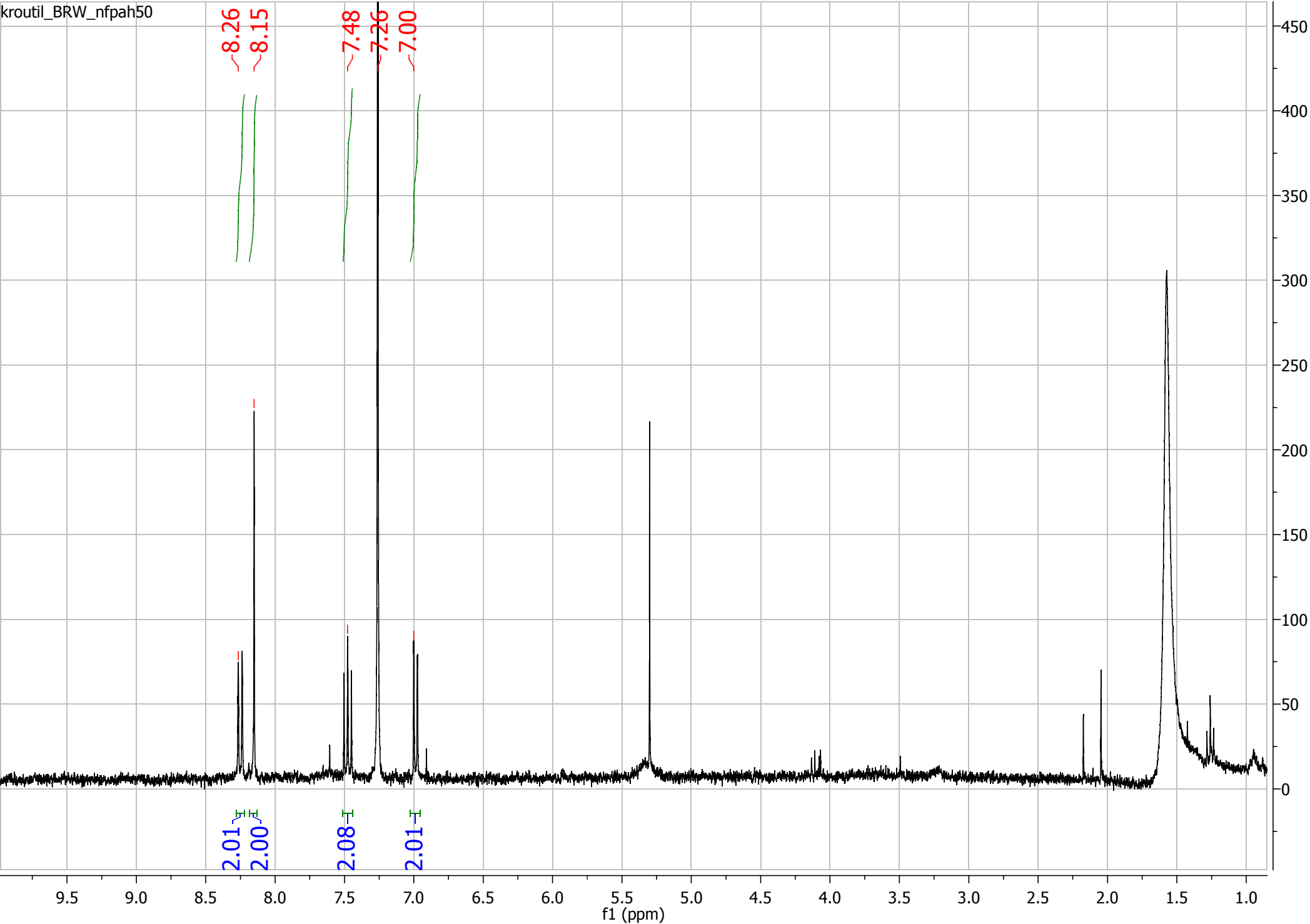
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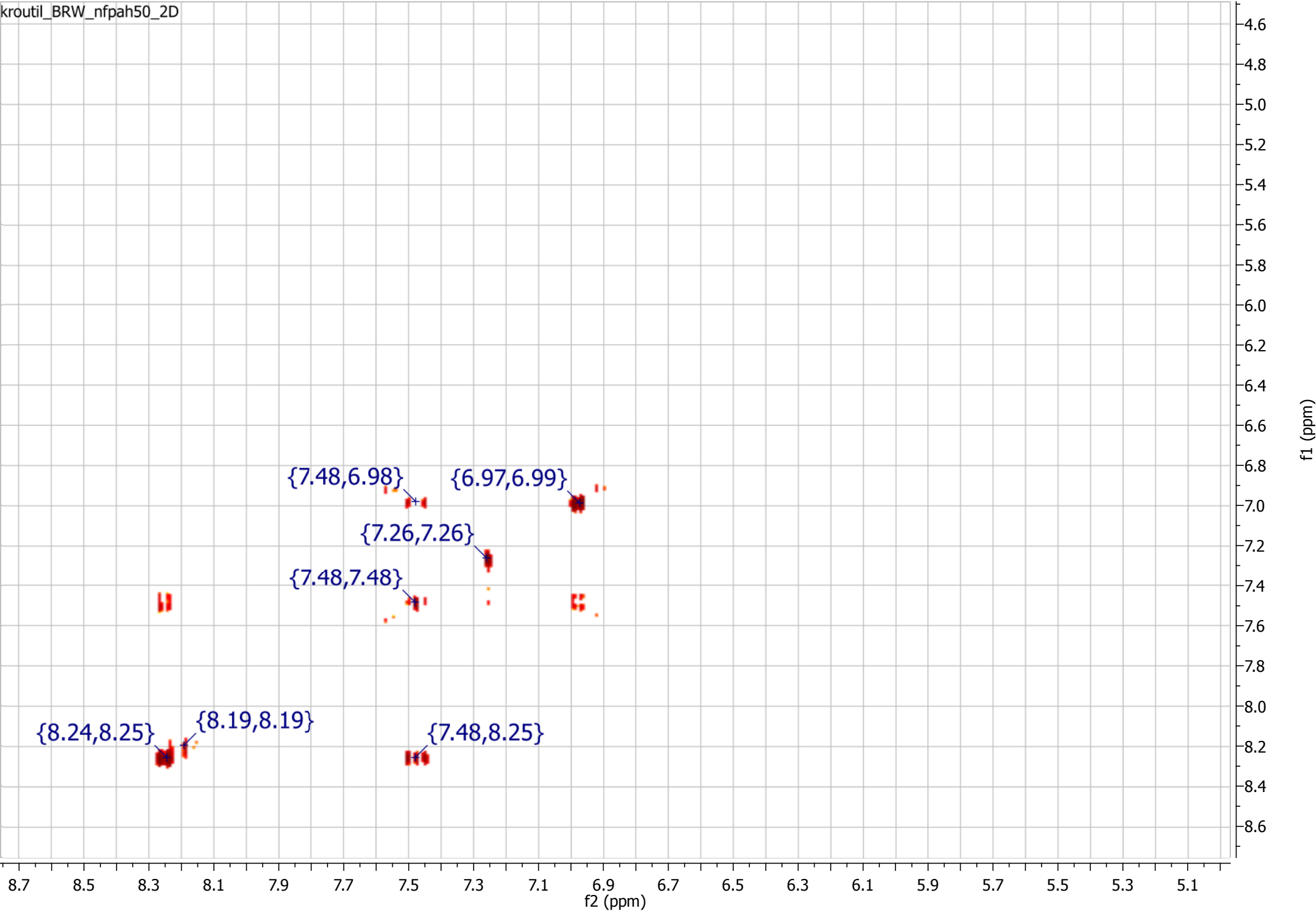


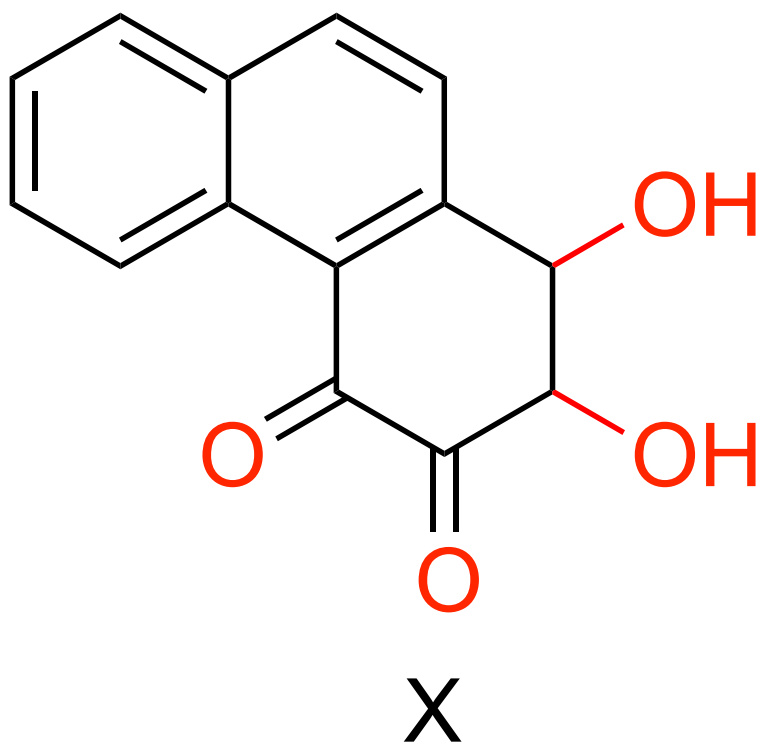
1,2-dihydroxyphenanthrene (**21**)

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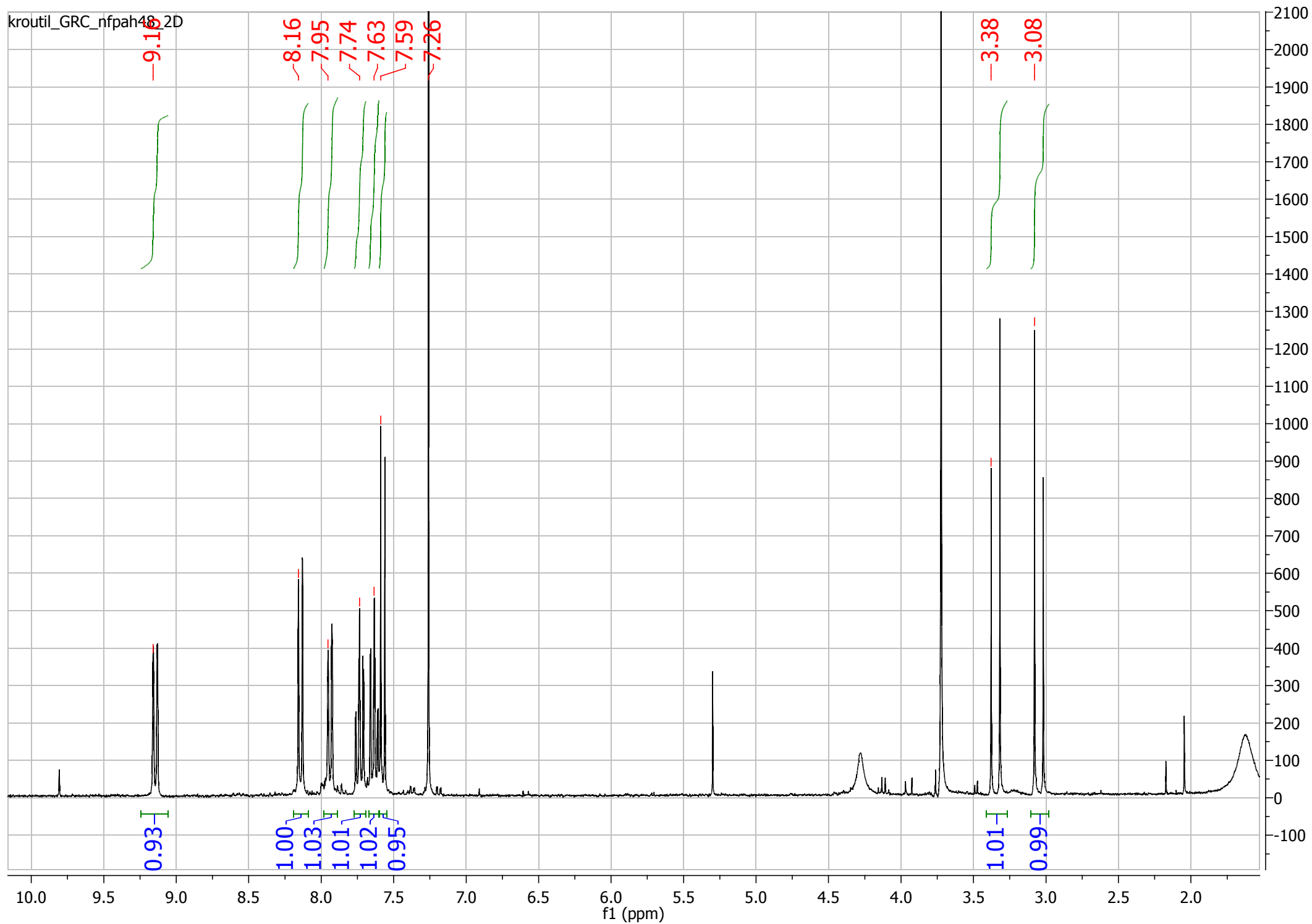


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kroutil\_GRC\_nfpah48\_2D

