Supplementary information for:

Ozonolysis of polycyclic aromatic hydrocarbons in participating solvents

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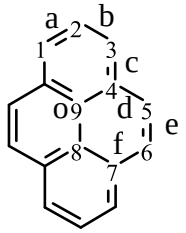
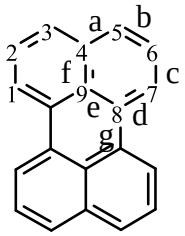
Local ionization energy surfaces

The structures was optimized using B3LYP/6-311G(d) with Guassian 09 rev C.01. Ionization energy surfaces was calculated at the same level using Spartan 10.

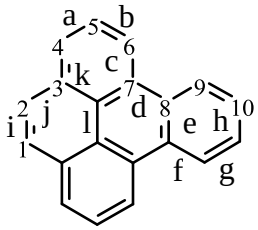
Table 1. All local IE values for bonds and atoms for PAHs pyrene **1** and perylene **2**. Highlighted are the lowest values.

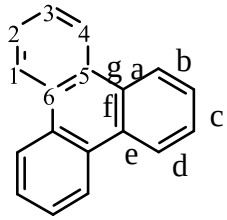




bond		atom		bond		atom	
a	9.30	1	9.16	a	9.89	1	9.21
b	9.32	2	9.61	b	9.13	2	9.40
c	9.46	3	9.16	c	9.61	3	9.16
d	10.22	4	10.04	d	9.46	4	10.05
e	8.99	5	9.41	e	10.13	5	9.17
f	10.22	6	9.42	f	10.17	6	9.38
o	10.20	7	10.05	g	10.68	7	9.20
p	10.30	8	10.01			8	9.92
		9	10.02			9	9.96

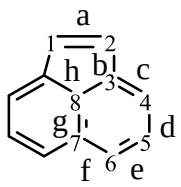
Table 2. All local IE values for bonds and atoms for PAHs B[e]P **4** and triphenylene **5**. Highlighted are the lowest values.





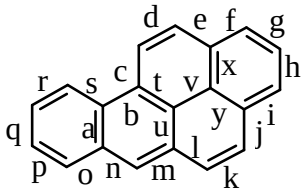
bond		atom		bond		atom	
a	9.32	1	9.25	a	9.64	1	9.22
b	9.38	2	9.24	b	9.20	2	9.32
c	9.57	3	10.08	c	9.53	3	9.30
d	10.58	4	9.20	d	9.22	4	9.22
e	9.92	5	9.37	e	9.66	5	9.90
f	9.79	6	9.18	f	9.92	6	9.90
g	9.21	7	9.91	g	10.49		
h	9.60	8	10.09				
i	9.00	9	9.26				
j	10.17	10	9.36				
k	10.18						
l	10.30						
x	9.75						

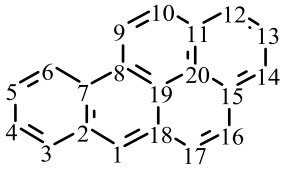
Table 3. All local IE values for bonds and atoms for PAH acenapthylene **6**. Highlighted are the lowest values.



bond		atom	
a	8.56	1	8.96
b	10.10	2	8.94
c	9.46	3	9.80
d	9.68	4	9.46
e	9.12	5	9.31
f	9.69	6	9.20
g	10.06	7	10.06
h	10.10	8	9.52

Table 4. All local IE values for bonds and atoms for PAH B[a]P **3**. Highlighted are the lowest values.





bond		atom	
a	10.14	1	9.11
b	10.15	2	10.06
c	10	3	9.41
d	9.04	4	9.28
e	10.15	5	9.31
f	9.73	6	9.35
g	9.28	7	9.94
h	9.41	8	9.96
i	9.64	9	9.31
j	10.25	10	9.35
k	8.97	11	10.03
l	10.33	12	9.15
m	9.34	13	9.45
n	9.89	14	9.18
o	9.82	15	10.06
p	9.12	16	9.35
q	9.65	17	9.38
r	9.12	18	10.02
s	9.88	19	9.96
t	10	20	9.96
u	10.4		
v	10.2		
x	10.17		
y	10.24		

Analysis of crude mixtures from ozonolysis of PAH 1-3

The scale was 3 mmol, total solvent volume 20.0 mL and each sample was treated with ozone for 90 s (5W, 0.25 bar, 0.5 L/min).

Vial 1 and 16 same. Vial 2-6 pyrene (DCM, pH1, pH 7, pH 14, MeOH) Vial 7-11 Perylene (DCM, pH1, pH 7, pH 14, MeOH) Vial 12-16 and 1 (DCM, pH 1, pH 7, pH 14, MeOH) Vial 17-19 solvent blanks (DCM, MeCN:MeOH, MeCN:H2O). For PAH and conditions see Table 5.
After ozonation, all solvent was gently removed *in vacu* (no heating) and the crude solid redissolved in Acetone-d_6:D_2O (0.6 mL:0.1 mL).

Table 5. Condition for ozonolysis of PAHs **2**, **1** and **3**.

Ozone conditions	Perylene	Pyrene	B[a]P
Dry DCM	2	7	12
H_2O pH 2	3	8	13
H_2O pH 7	4	9	14
H_2O pH 12	5	10	15
MeOH	6	11	1+16

MeOH: 5 mL DCM, 13 mL MeCN, 2 mL MeOH)
Dry DCM : 20 mL dry DCM
pH 1: 5 mL DCM, 14 mL MeCN, 1 mL 1M HCl (aq)
pH 7: 5 mL DCM, 14 mL MeCN, 1 mL H2O
pH 14: 5 mL DCM, 14 mL MecN, 1 mL 1M NaOH(aq)

Several color changes were observed and the samples 1-16 (and 17-20)was photographed before and after ozone was added. (Figure 1)

A small amount of samples ph 14 (5, 10 and 15) and pH 7 (4, 9 and 14) were removed and the pH values adjusted to pH 1 using conc. HCl (aq) to see if the differences in colors remained and were pH in depended. No color change by adjusting the pH values were observed. Since, samples 5, 10 and 15 (pH 14) had become a 2-phase system the solvent was removed and the product mixture re-dissolved in MeCN:DCM.

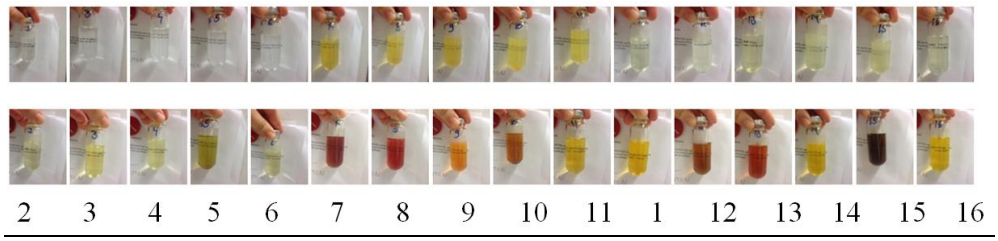
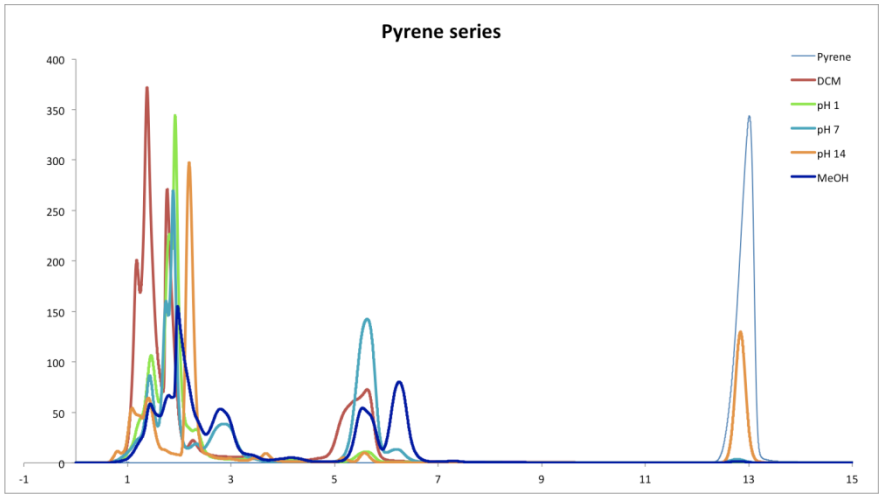
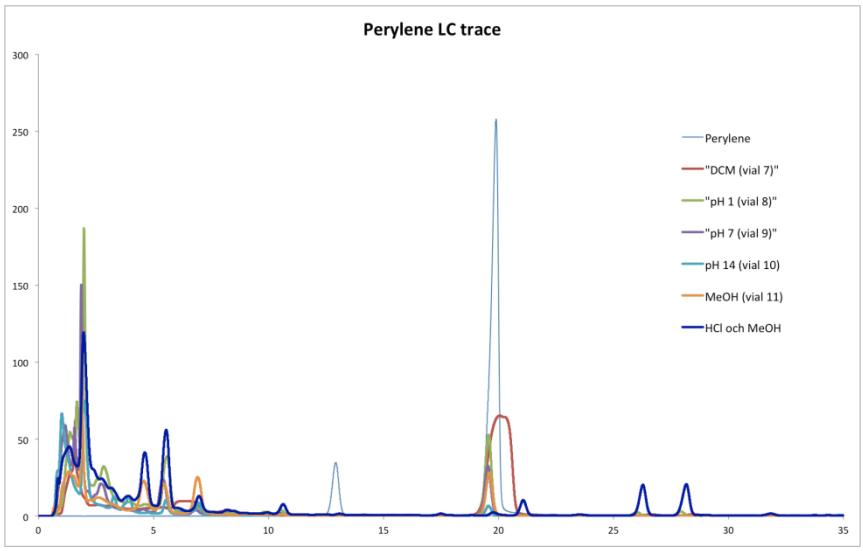


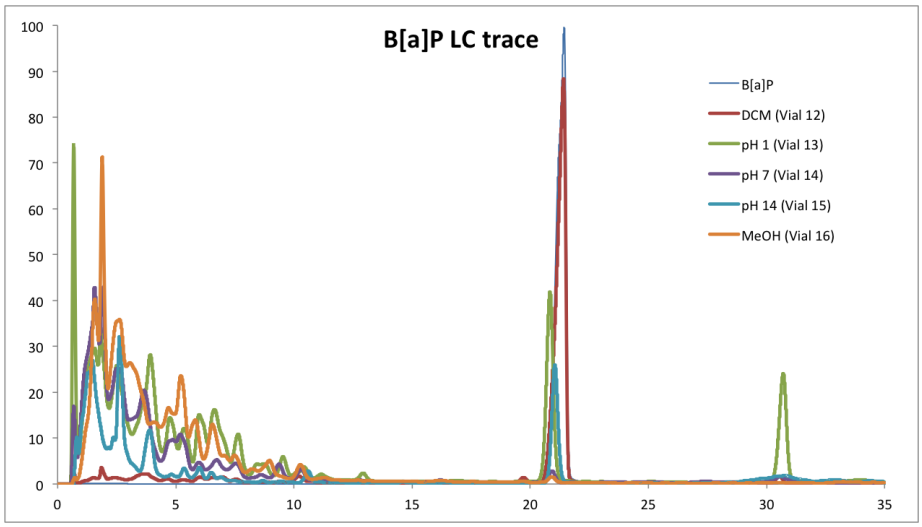
Figure 1. Samples 1-16 before and after ozonation. After adding the solvents and model compound the samples were sonicated for ca 30 s (prior to photographed and ozone). Pyrene 2-6, perylene 7-11 and BaP 1-16.

LC of ozone treated PAHs 1-3 crude reaction mixtures

Inj V: 20 uL (of 20 mL), gradient: 40:60 to 90:10 (acetonitrile:water with 0.01 % HCOOH) over 35 min. UV detector: 254 nm, column: ACE 3 C18, 50x2.1mm id, flow rate: 0.5 mL/min.







^{1}H NMR spectra of ozone treated PAHs 1-3 crude reaction mixtures

The solvent was removed from all samples and part of the solid reaction mixture re-dissolved in Aceton-d_6:D_2O (0.6:0.1) for ^{1}H NMR spectroscopy. (Figure 2-4)

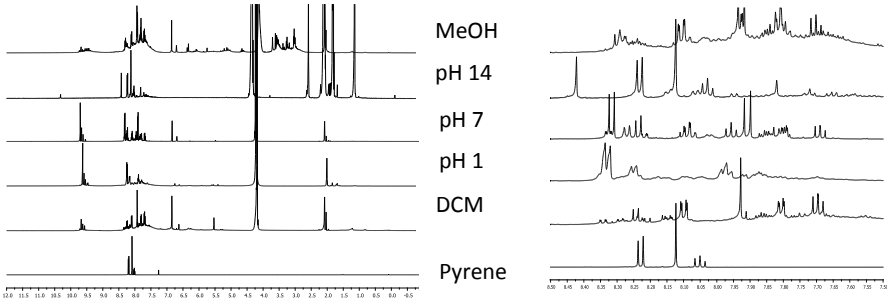


Figure 2. 1H NMR spectra of pyrene (**1**), treated (samples 2-6) and untreated with ozone during different conditions. From 0-12 ppm to the left and 7.5-8.5 ppm to the right.

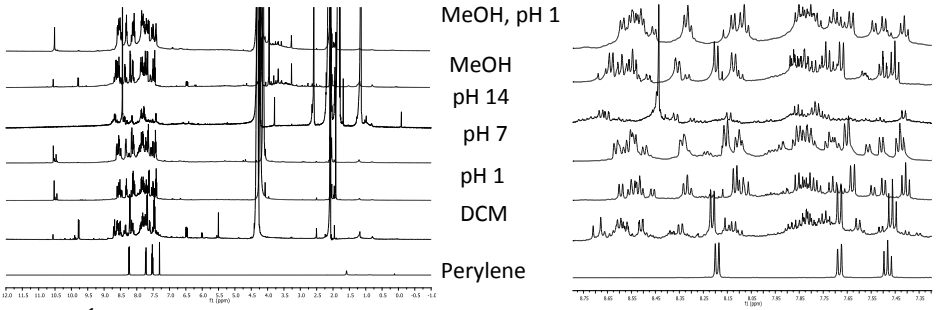


Figure 3. ^{1}H NMR spectra of perylene (**2**), treated (samples 7-11, 20) and untreated with ozone during different. From 0-12 ppm to the left and 7.3-8.8 ppm to the right.

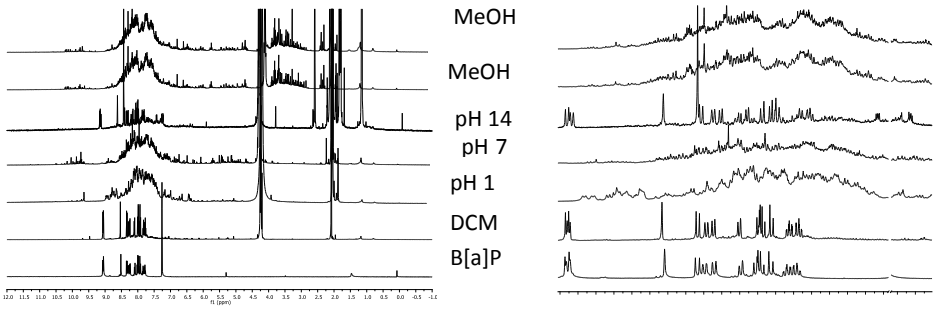


Figure 4. ^{1}H NMR spectra of B[a]P (**3**), treated (samples 12-16, 1) and untreated with ozone during different conditions. From 0-12 ppm to the left and 7.0-9.1 ppm to the right.

Prep HPLC traces

UV traces (264 nm) from ozonolysis in DCM:MeOH of pyrene **1**, perylene **2**, and triphenylene **5** are shown below. B[a]P **3** and acenapthylene **6** are not shown.

Perylene products **2a-d**

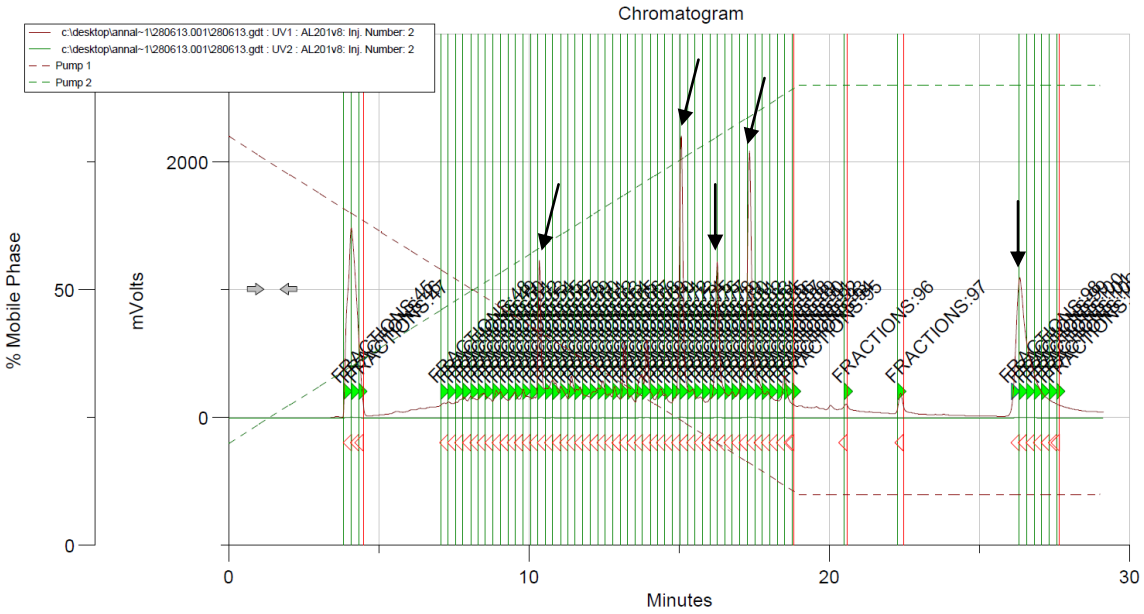


Figure 5. Isolation of 2a-d. Order f.l. : 2c, 2d, 2b, 2a and starting material 2.

Pyrene products **1a-e**

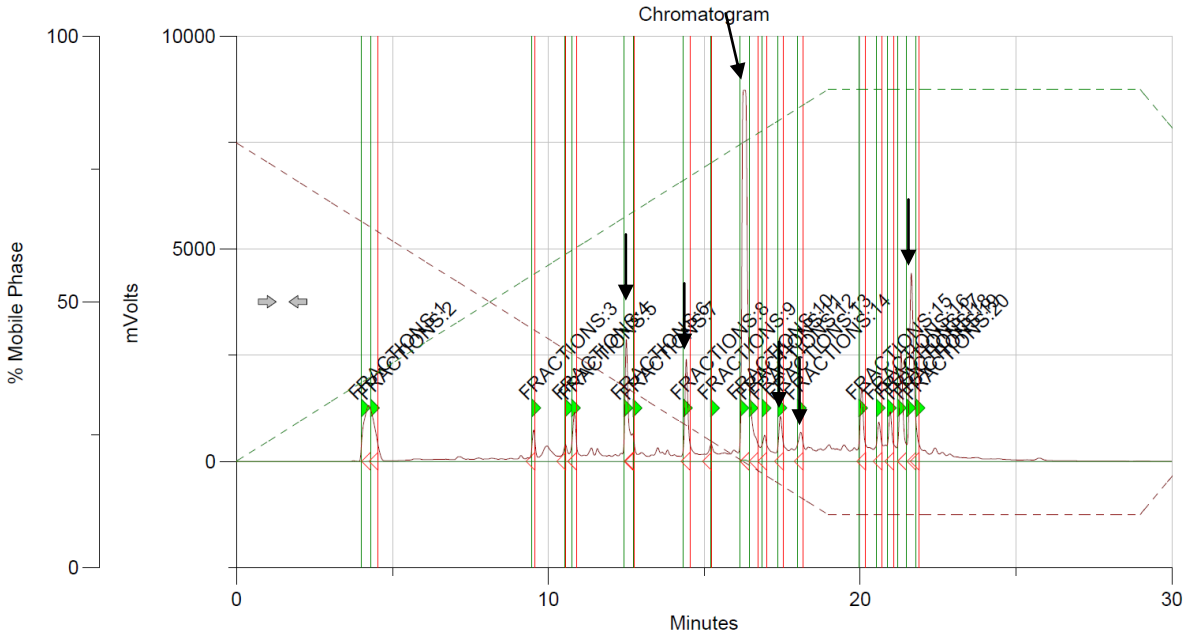


Figure 6. LC trace from ozonolysis of pyrene with MeOH. Collected: **1d**,**1e**,**1b**, **1a**, **1c** ,**1**

Triphenylene **5**

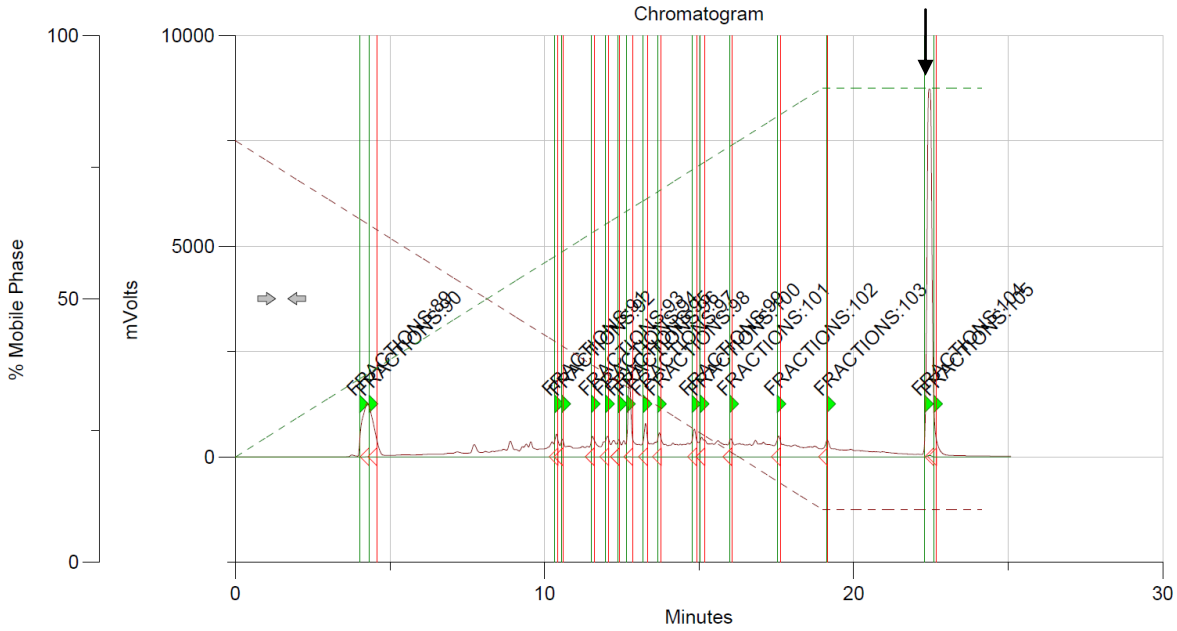


Figure 7. HPLC UV trace from triphenylene **5** ozonolyzed in MeOH. Arrow indicates triphenylene.

NMR spectra

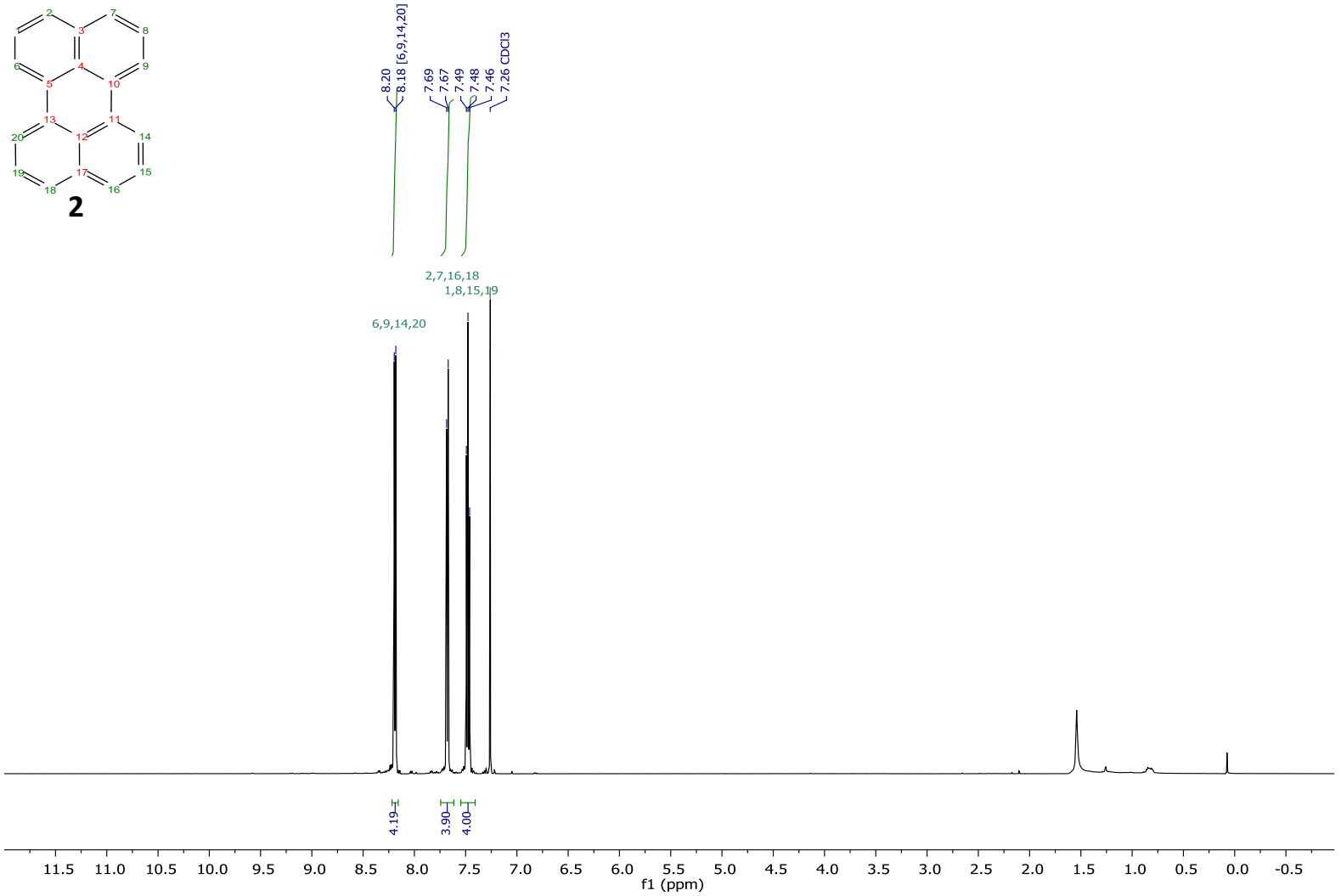


Figure 8. ^{1}H NMR spectrum of Perylene (**2**) in $CDCl_3$.

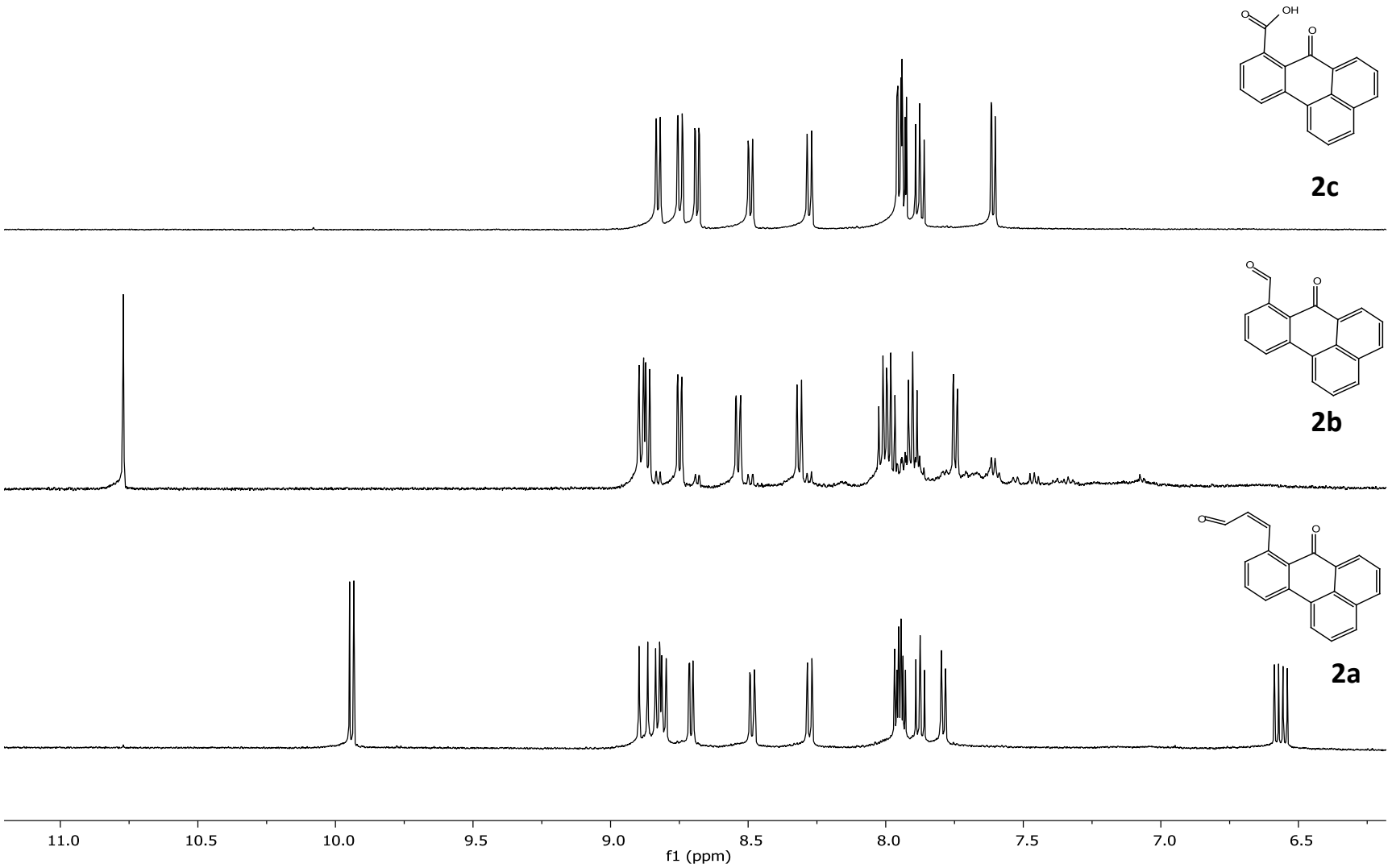


Figure 9. ^{1}H NMR spectra of Perylenes ozone products **2a-c** in Acetone-D_6.

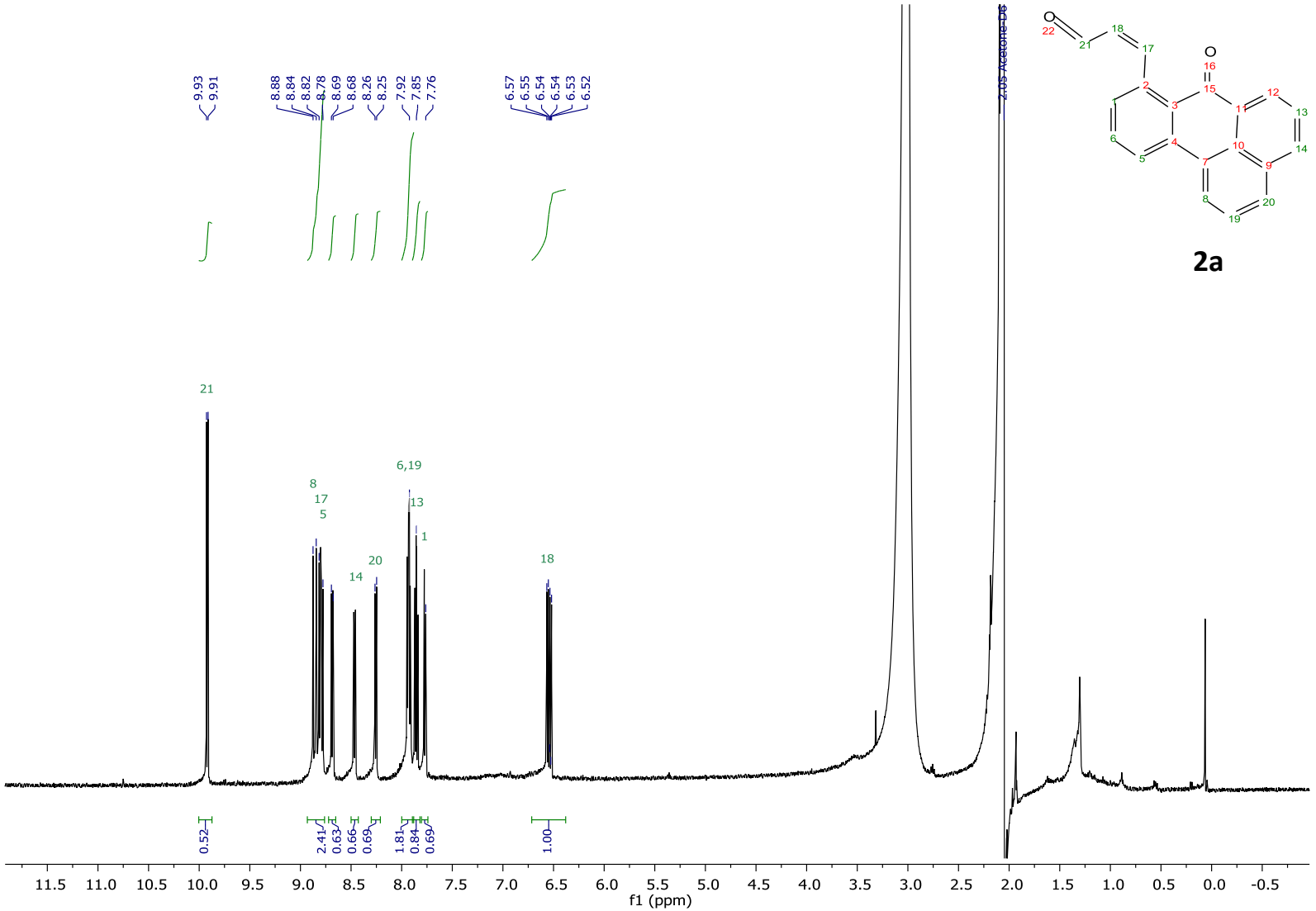


Figure 10. ^{1}H NMR spectrum of Perylene oxidation product **2a** in Acetone-D_6.

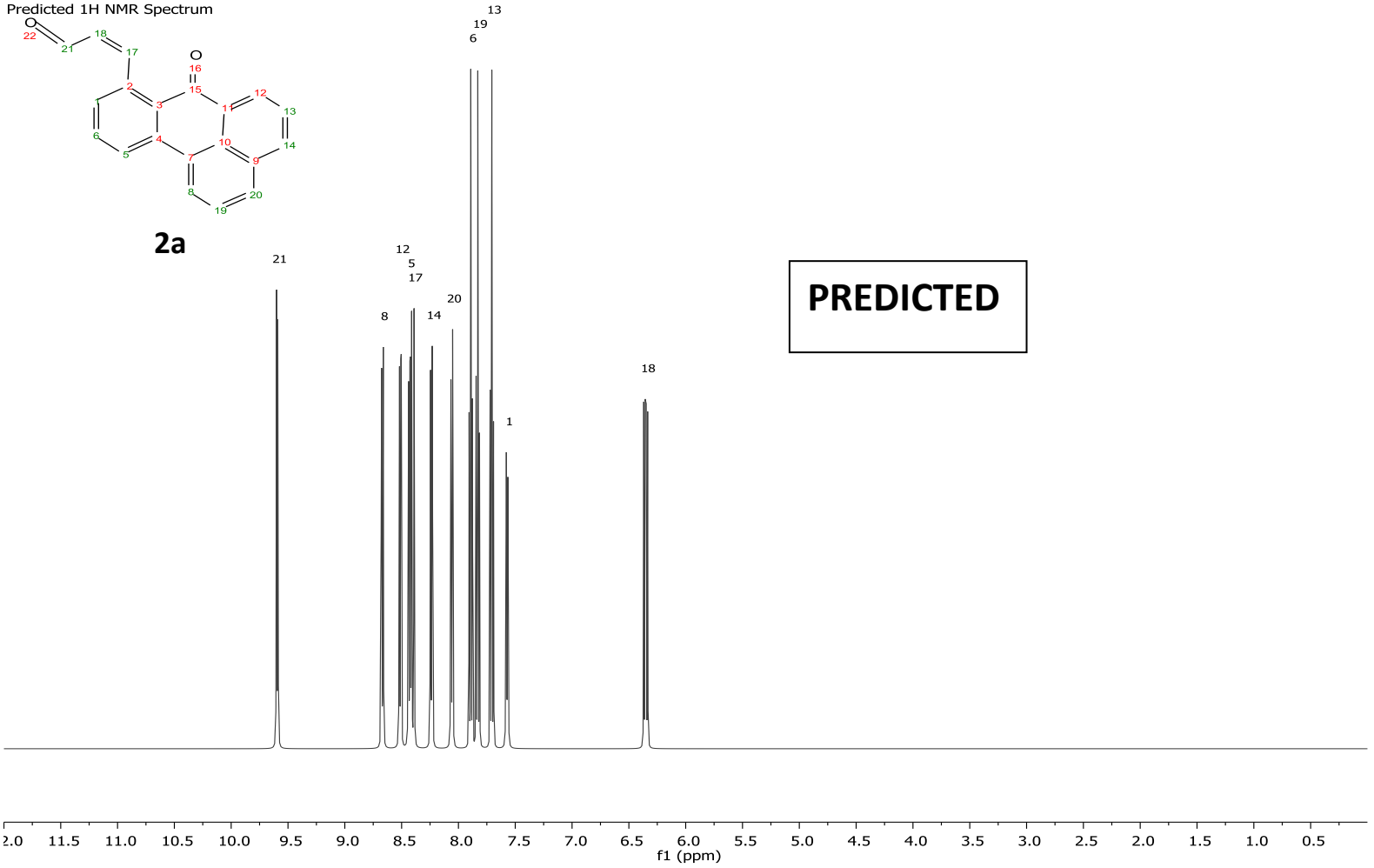


Figure 11. Predicted ^{1}H NMR spectrum of Perylene oxidation product **2a**.

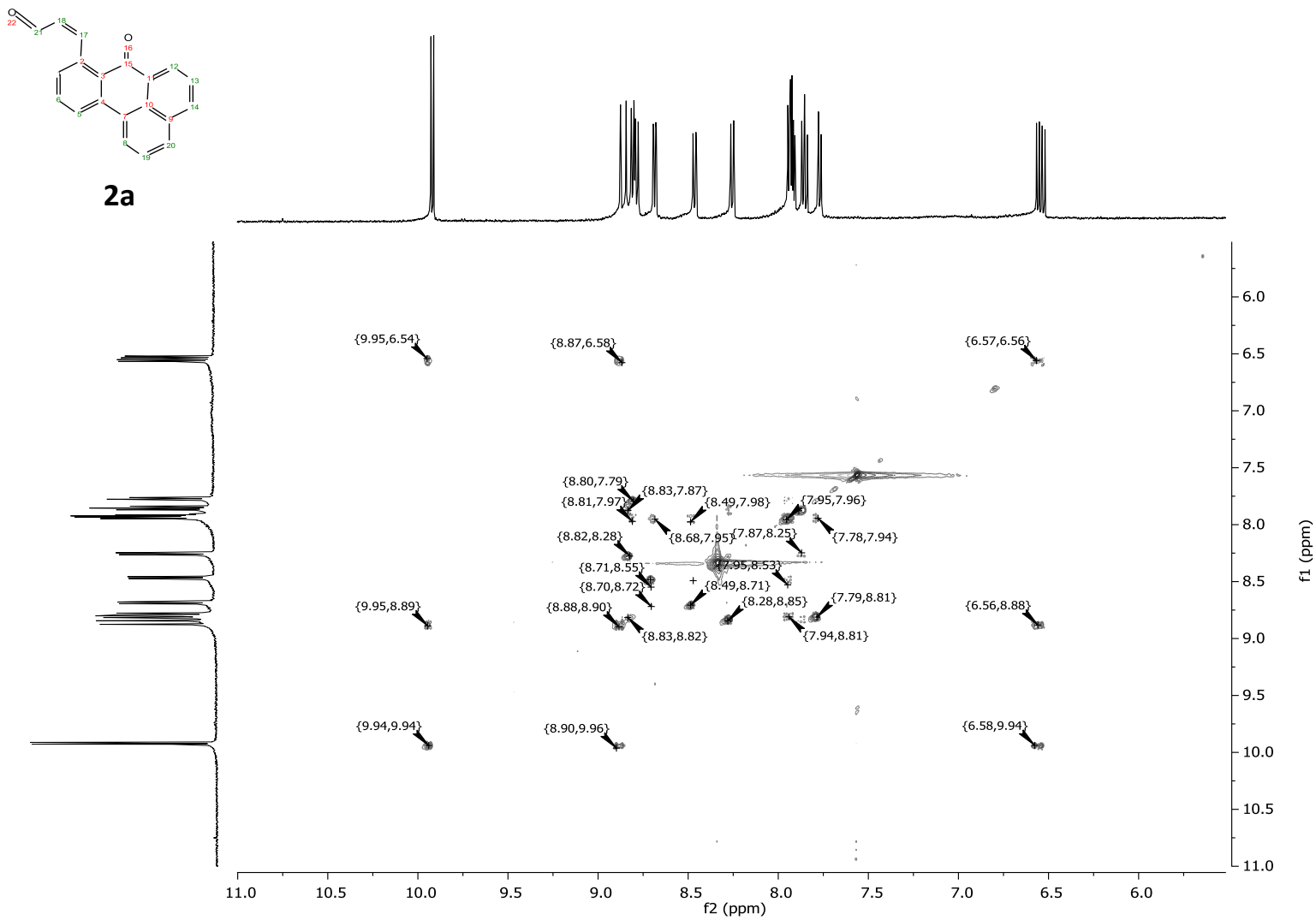


Figure 12. TOCSY spectrum of Perylene oxidation product **2a** in Acetone-D_6.

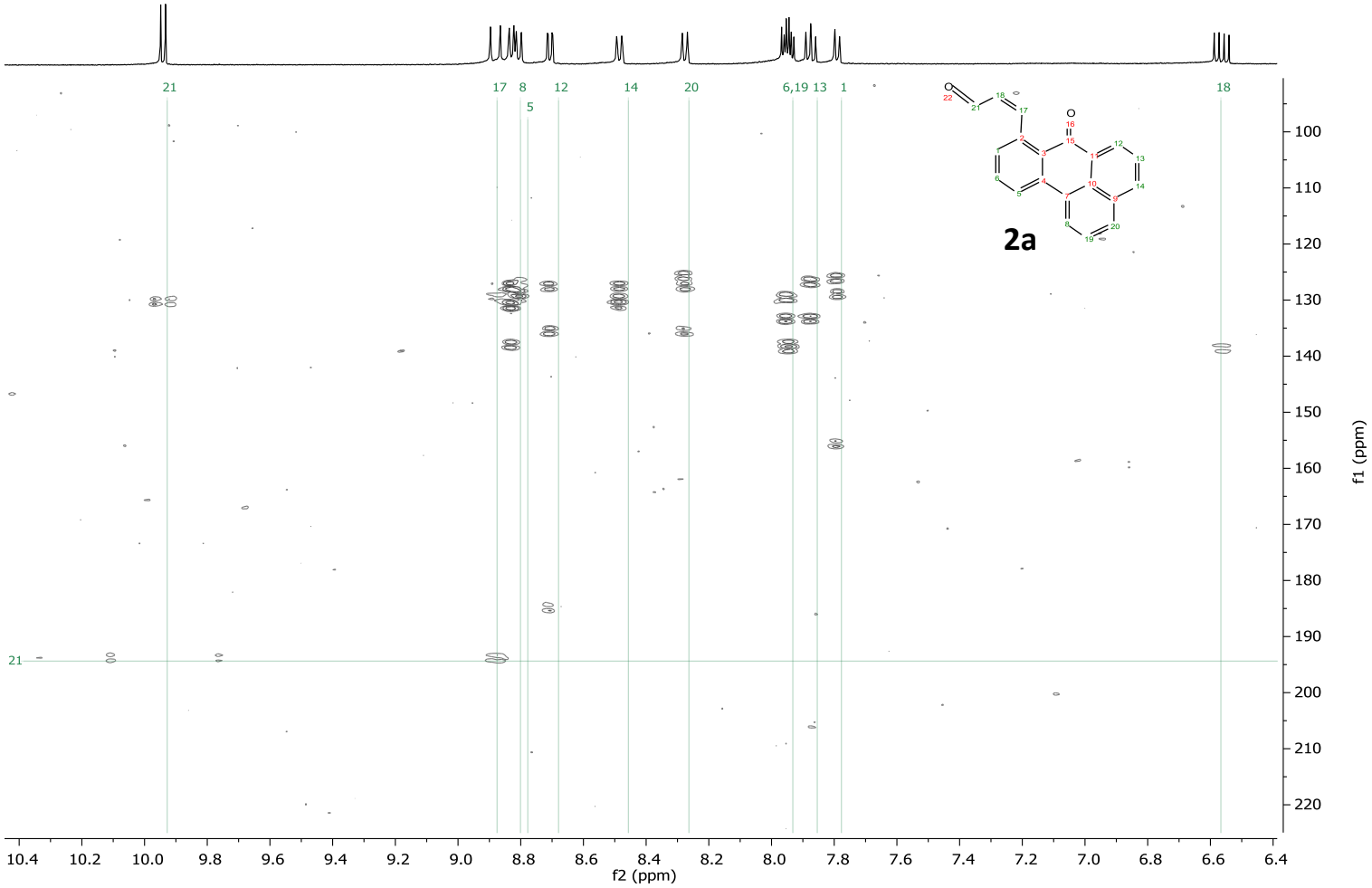


Figure 13. HMBC spectrum of Perylene oxidation product **2a** in Acetone-D_6.

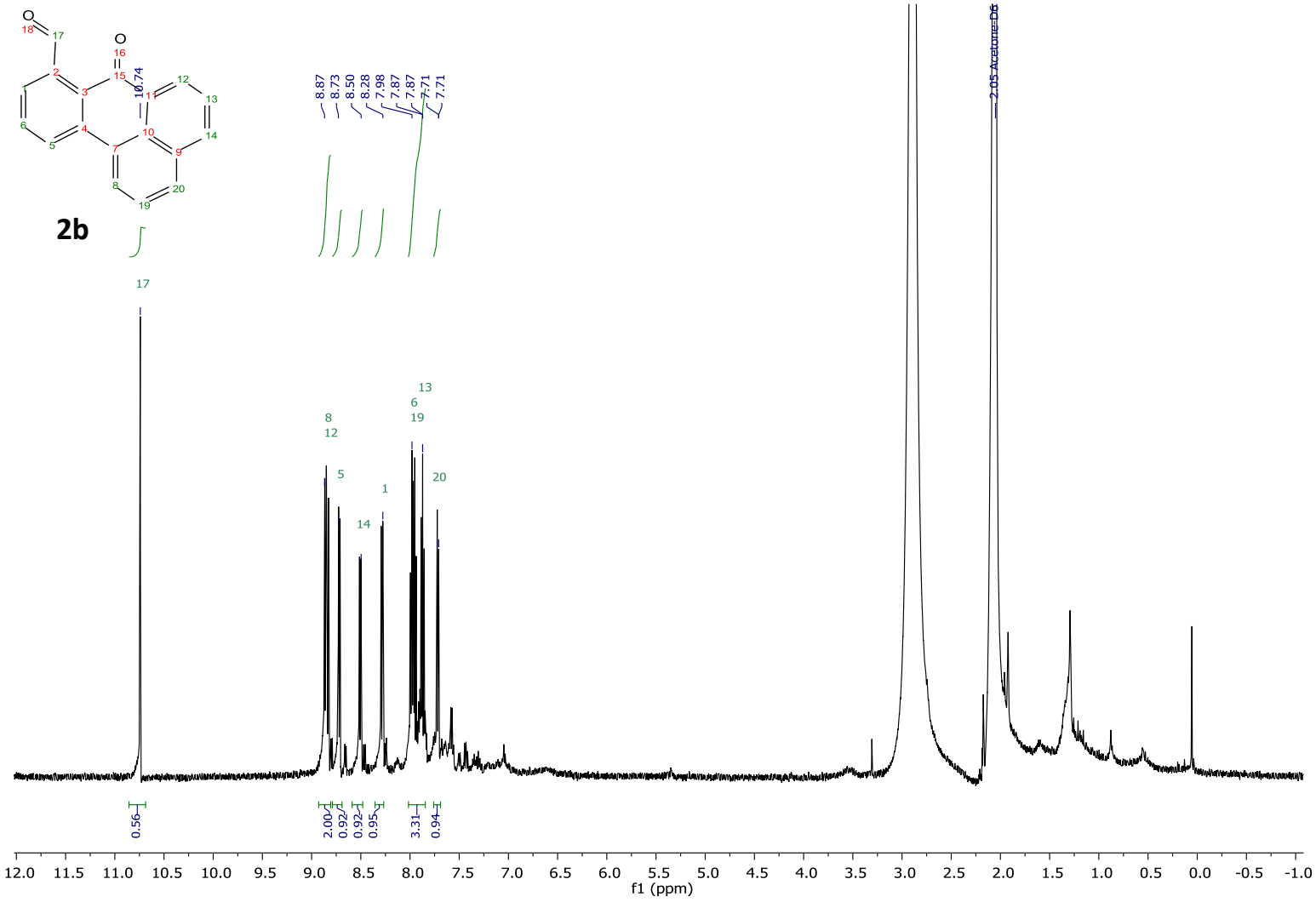


Figure 14. ^{1}H NMR spectrum of Perylene oxidation product **2b** in Acetone-D_6.

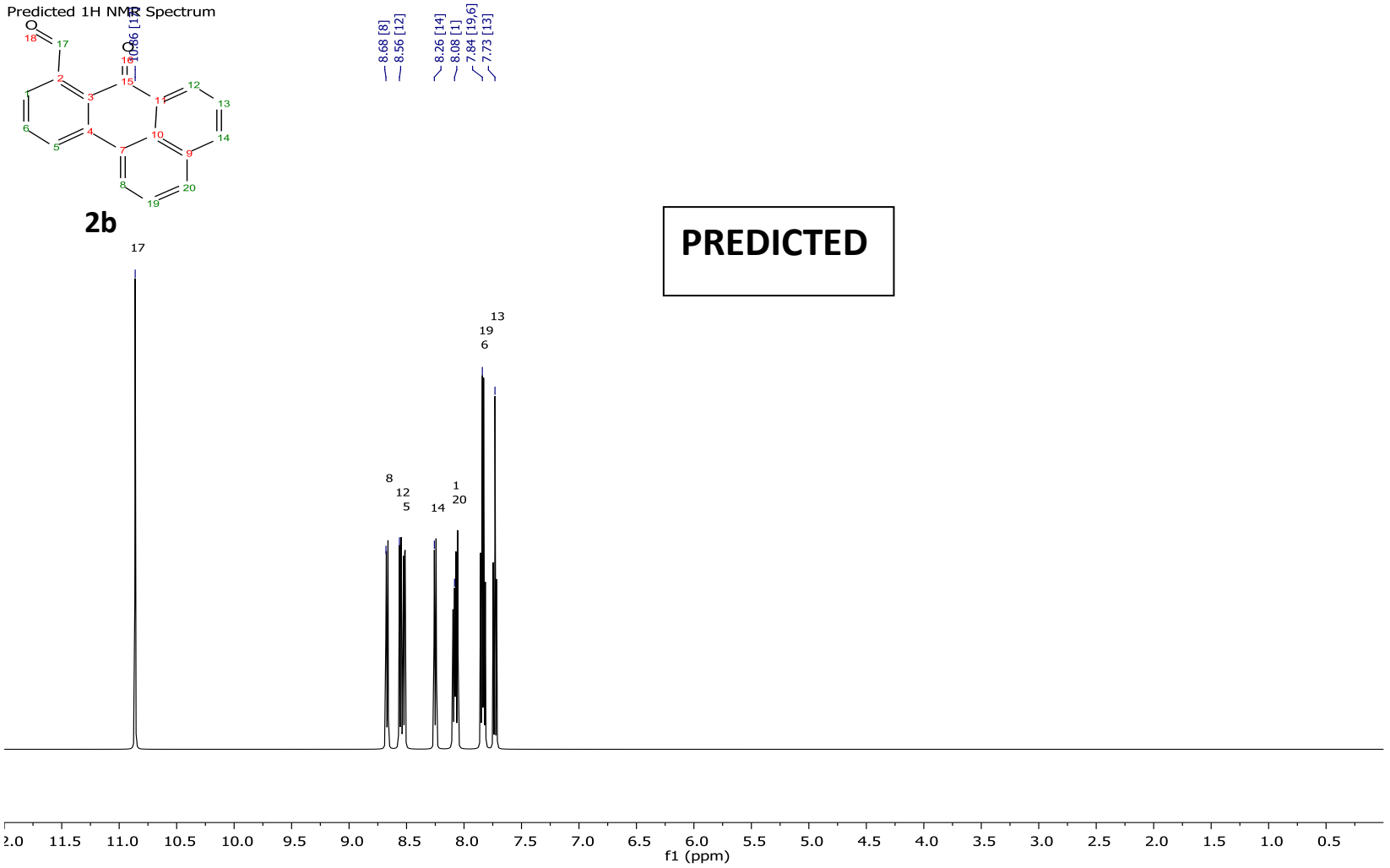


Figure 15. Predicted ^{1}H NMR spectrum of Perylene oxidation product **2b.**

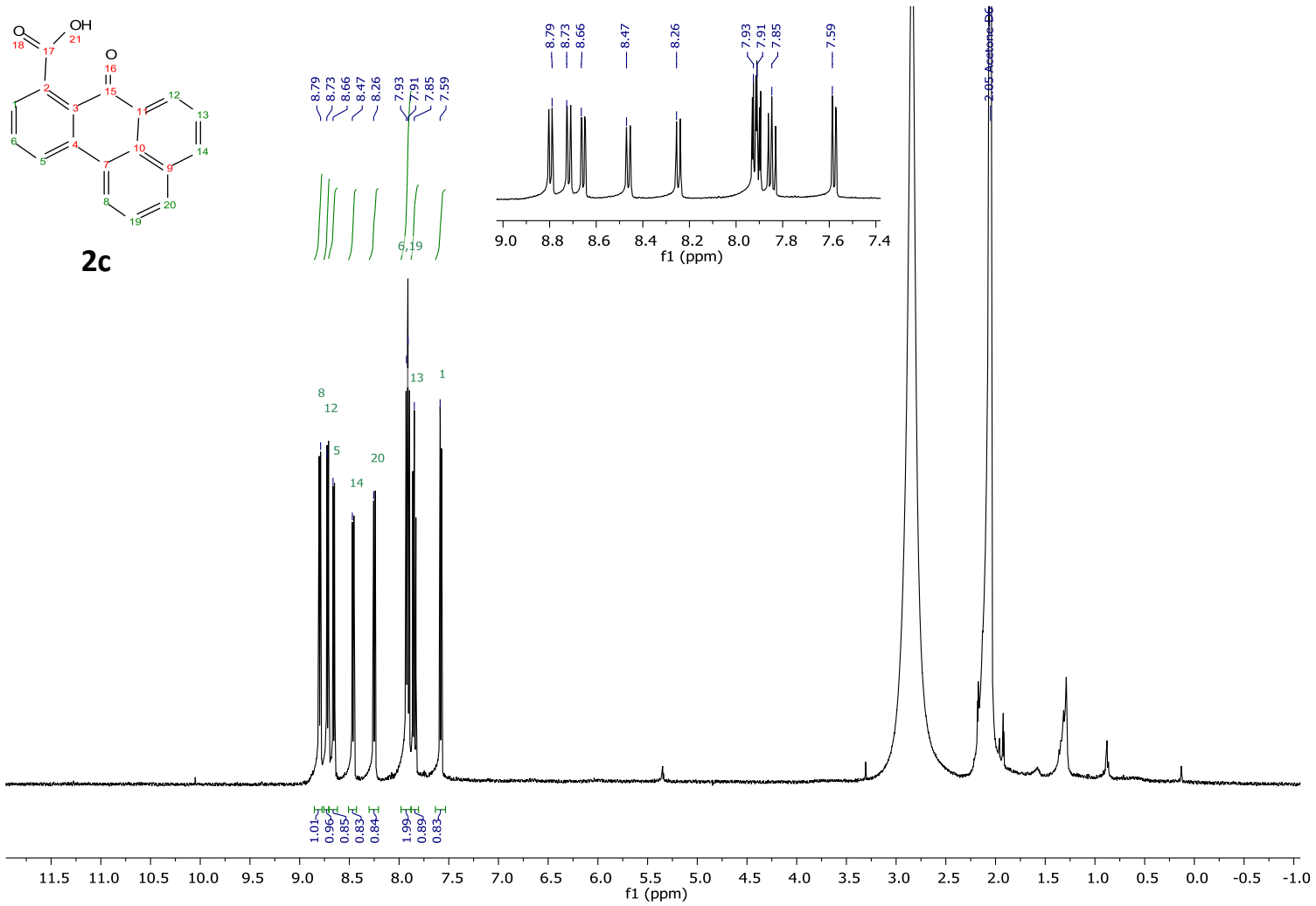


Figure 16. ^{1}H NMR spectrum of Perylene oxidation product **2c** in Acetone-D_6.

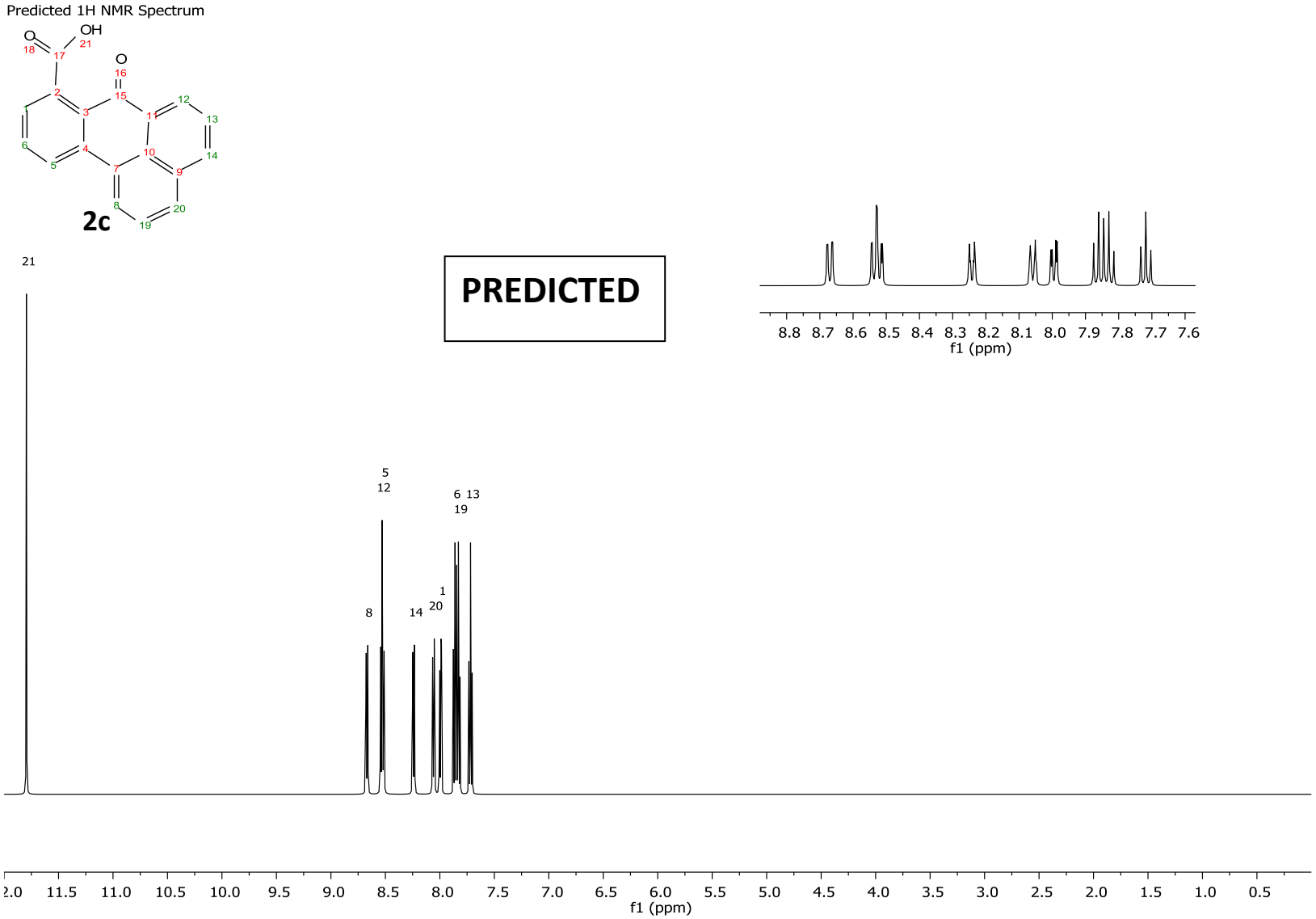


Figure 17. Predicted ^{1}H NMR spectrum of Perylene oxidation product **2c.**

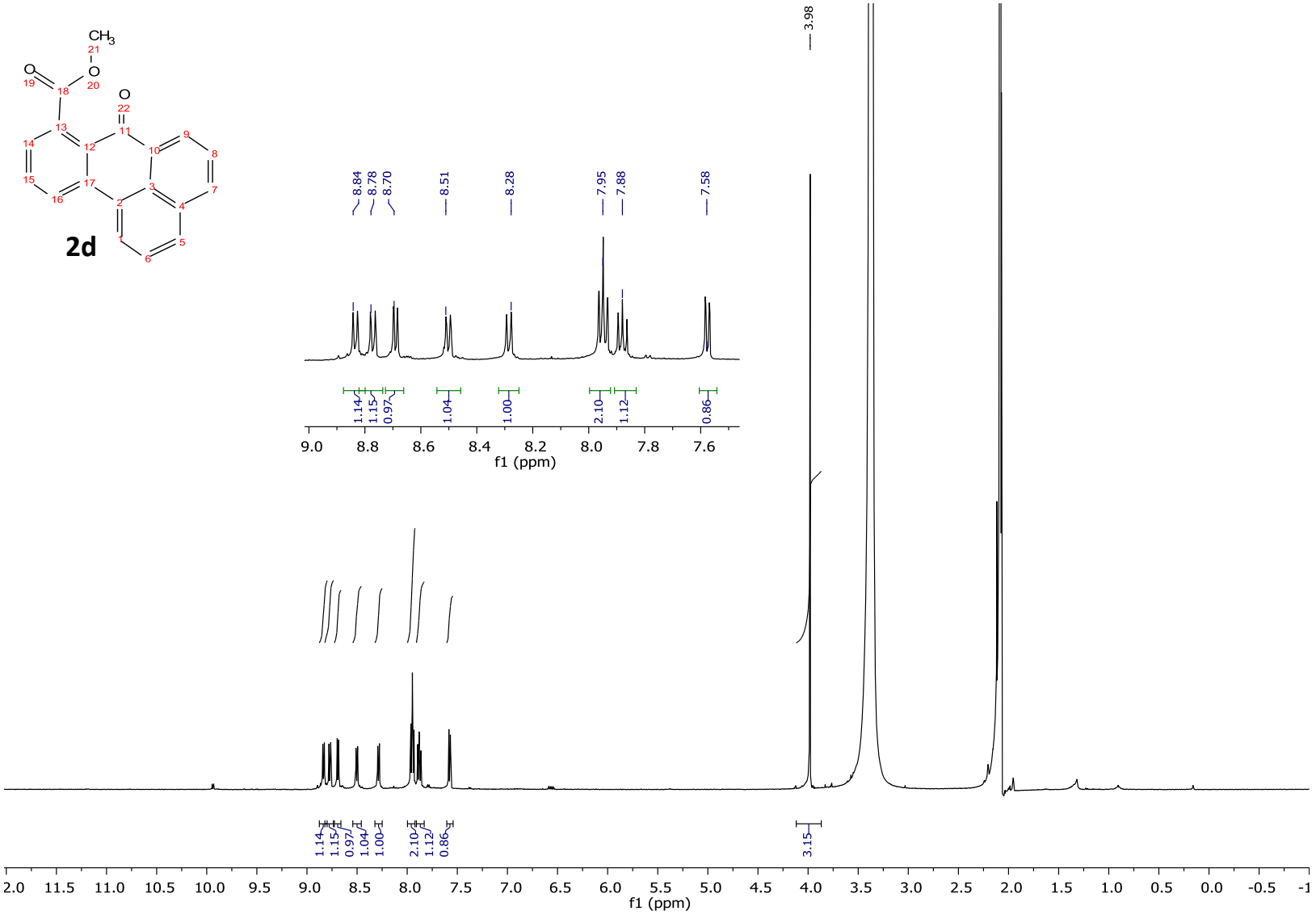


Figure 18. ^{1}H NMR spectrum of Perylene oxidation product **2d** in Acetone-D_6.

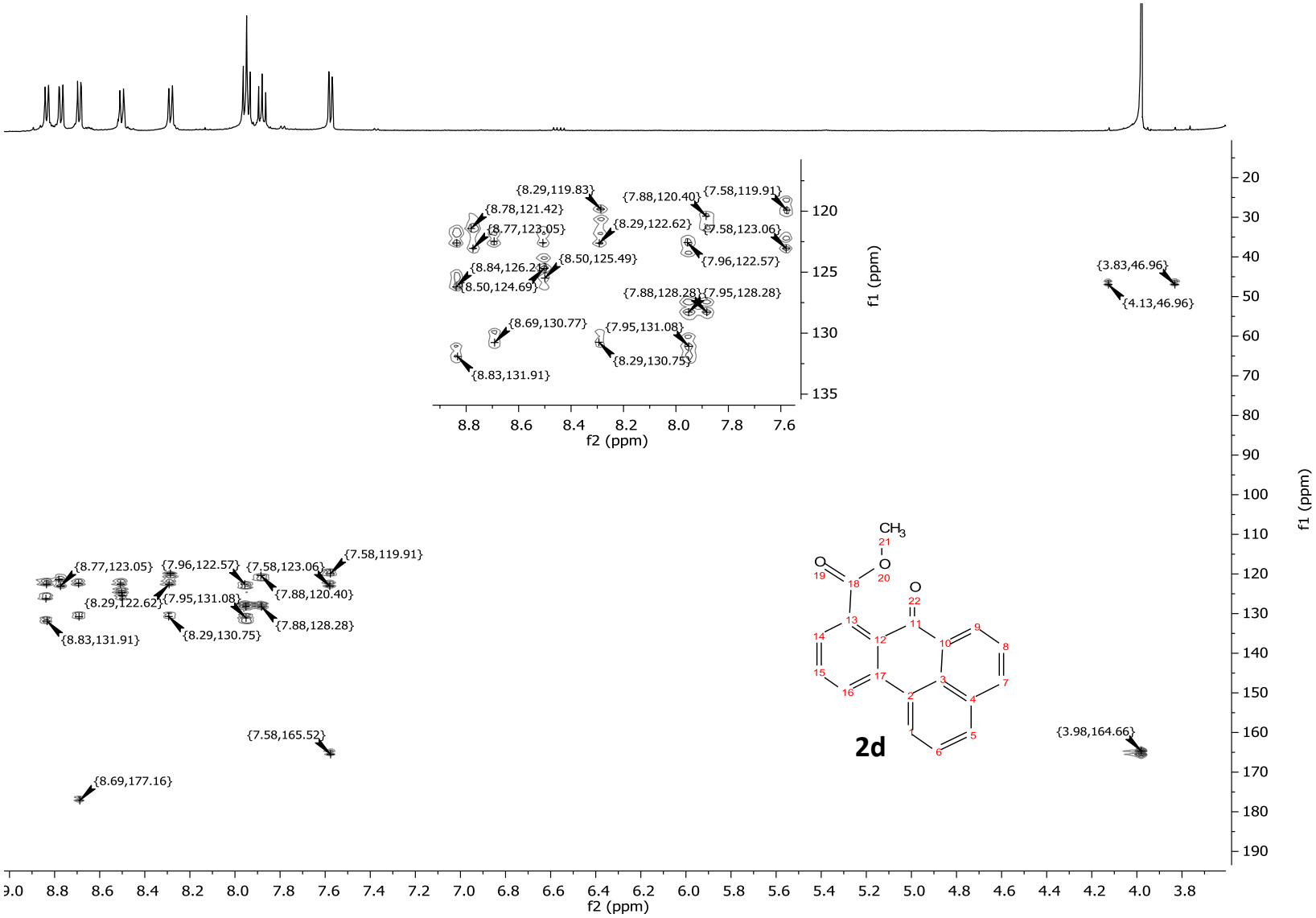


Figure 19. HMBC NMR spectrum of Perylene oxidation product **2d** in Acetone-D_6.

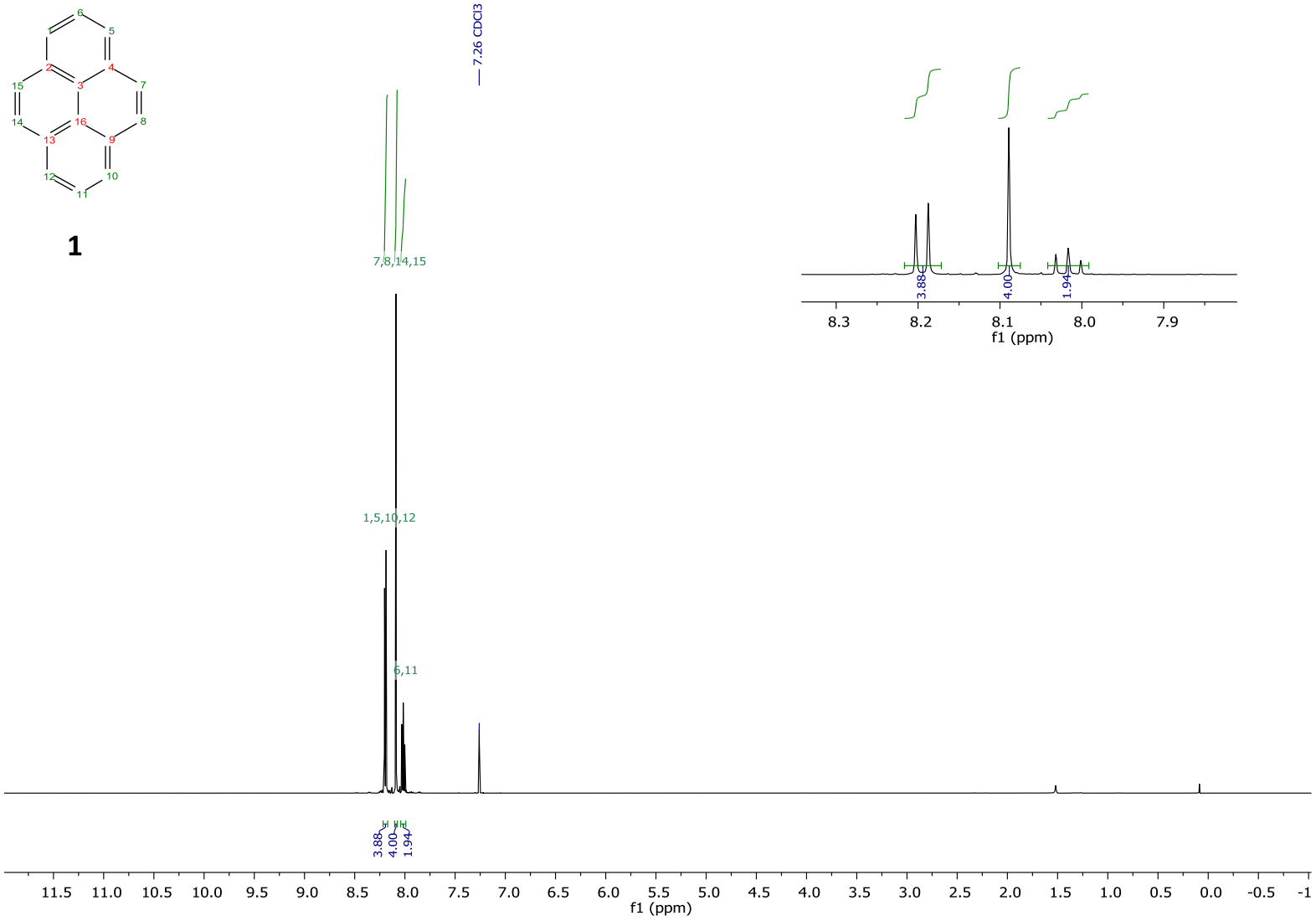


Figure 20. ^{1}H NMR spectrum of Pyrene **1** in $CDCl_3$.

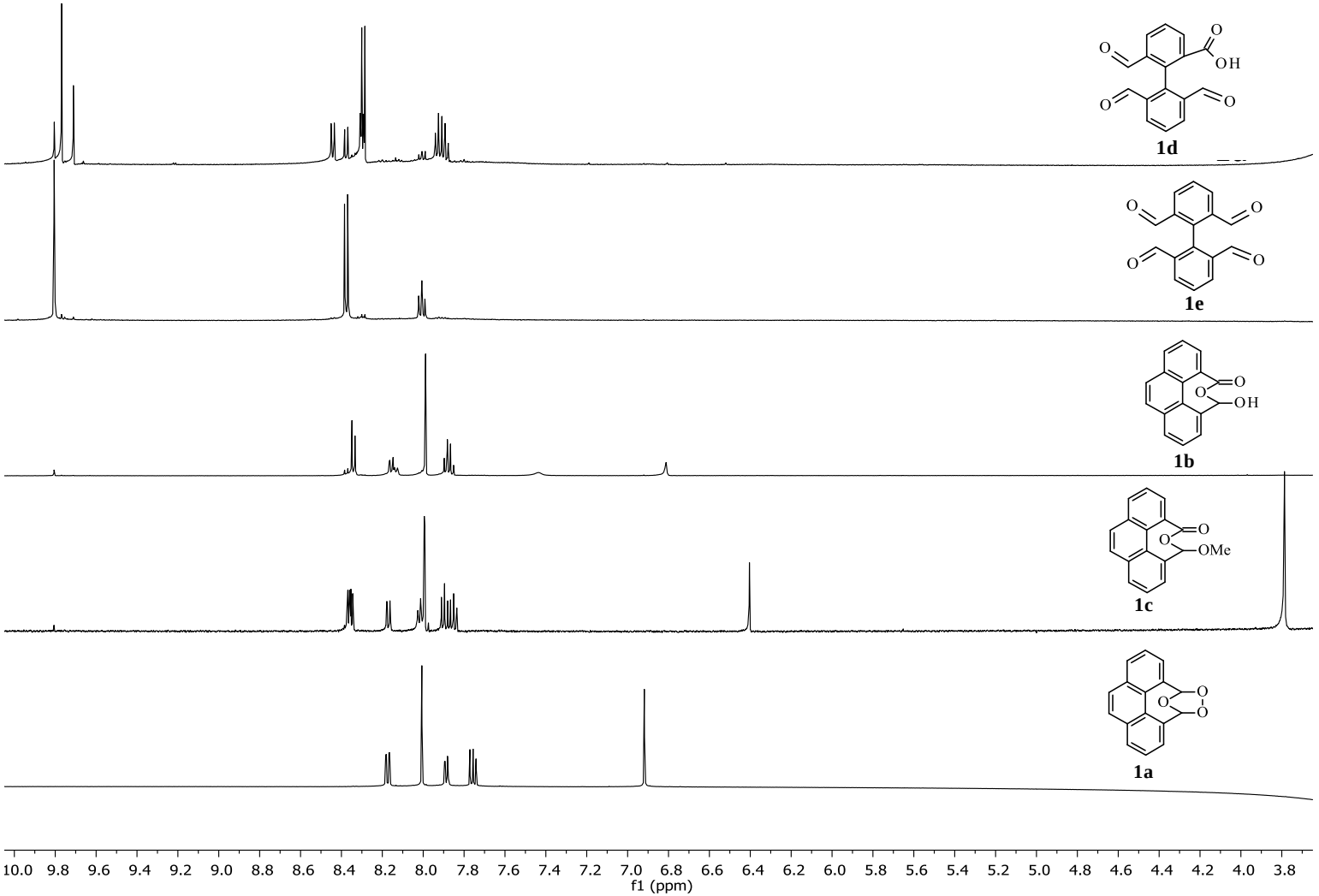


Figure 21. ^{1}H NMR spectra (3.8-10.0 ppm) of Pyrene oxidation products **1a-e** in Acetone-D_6.

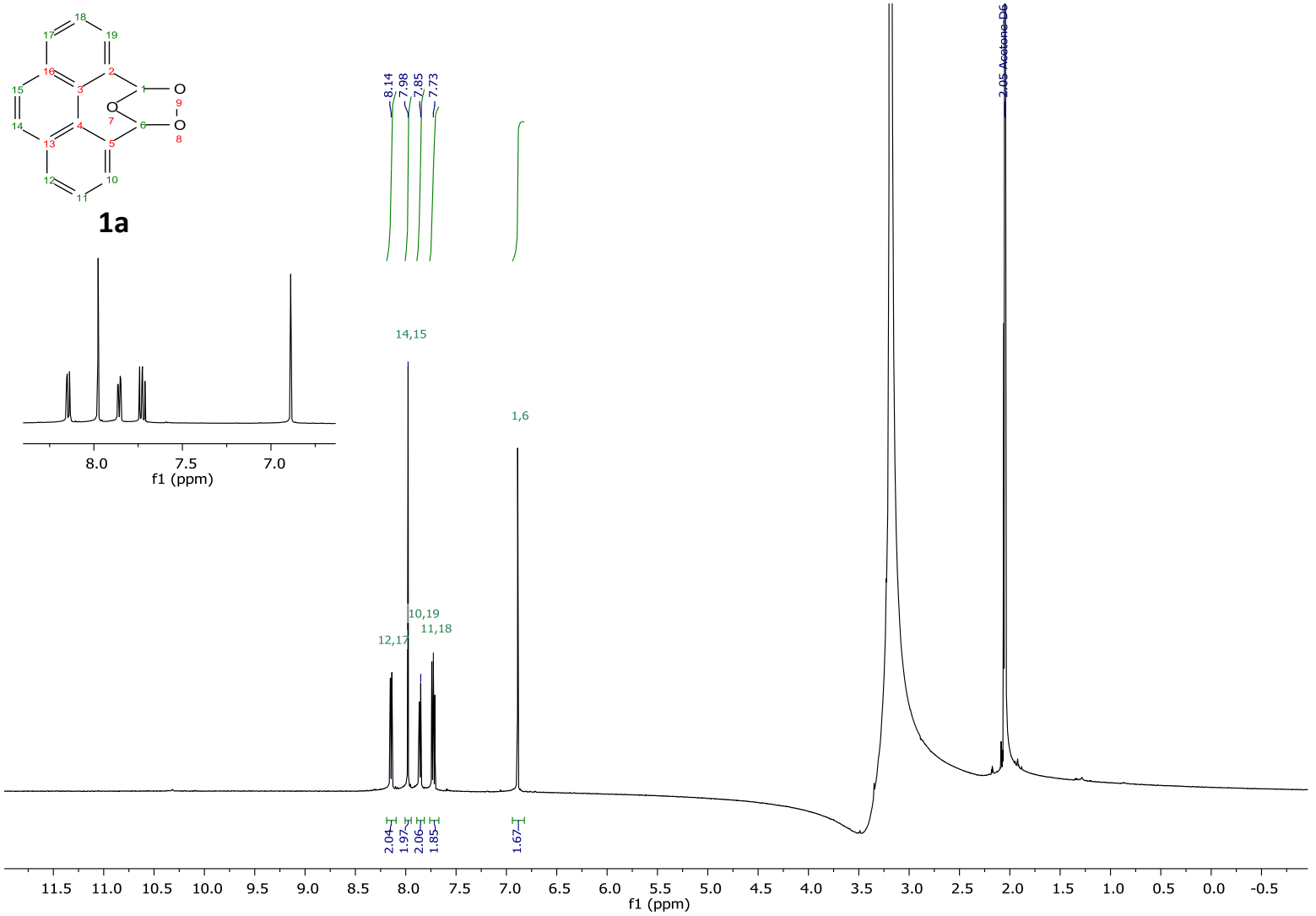


Figure 22. ^{1}H NMR spectrum of Pyrene oxidation product **1a** in Acetone-D_6.

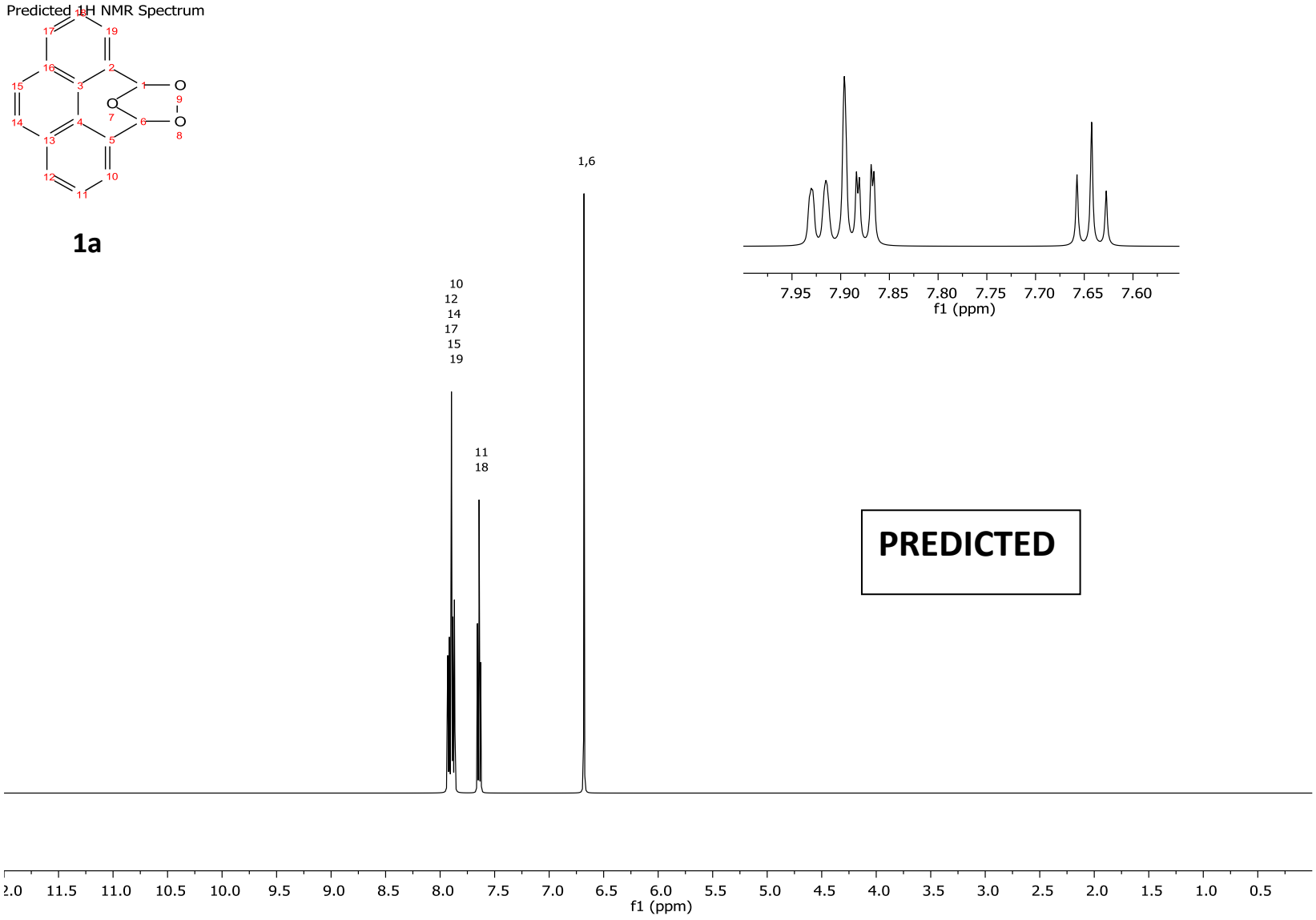


Figure 23. Predicted ^{1}H NMR spectrum of Pyrene oxidation product **1a.**

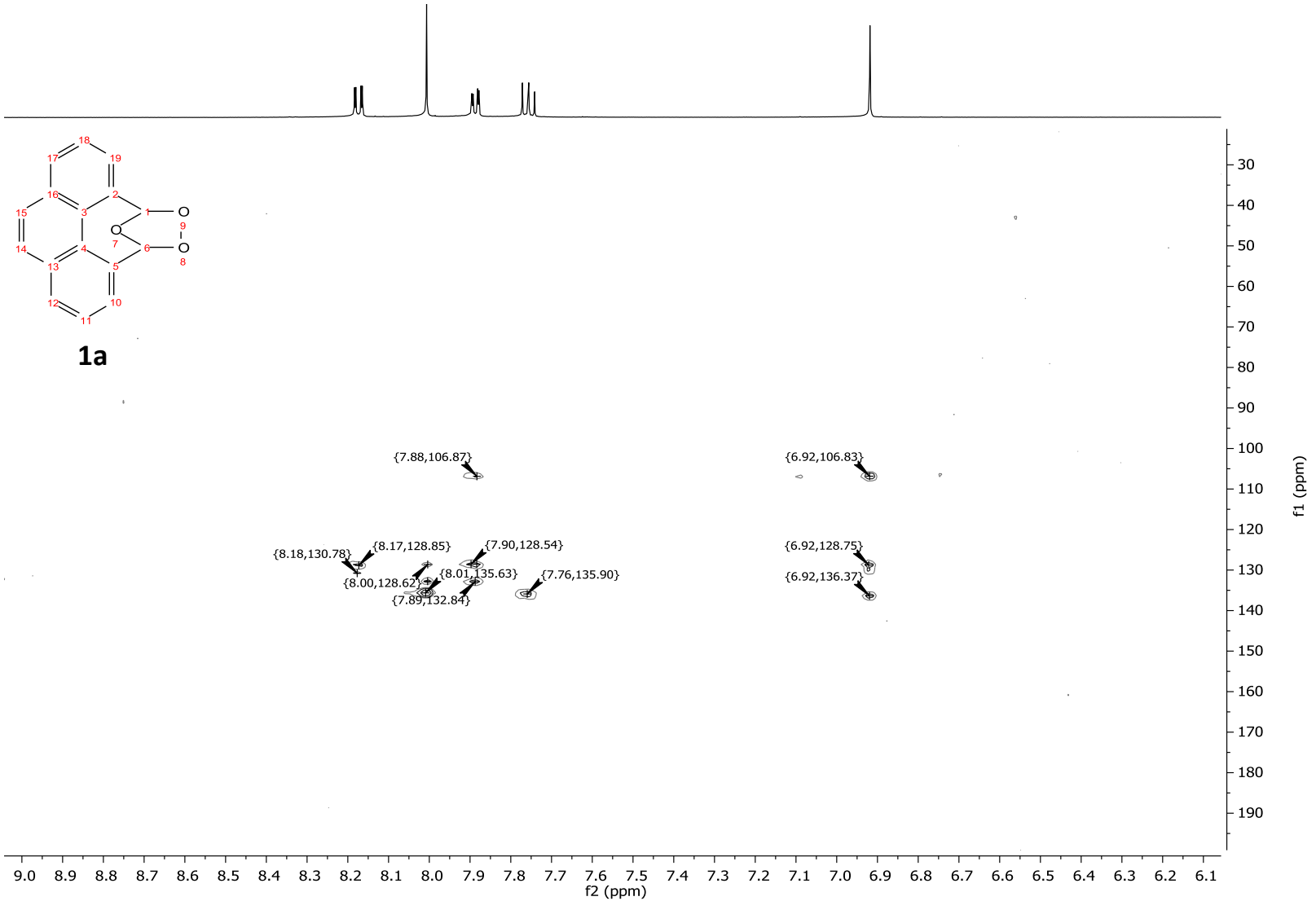


Figure 24. HMBC NMR spectrum of Pyrene oxidation product **1a** in Acetone-D_6.

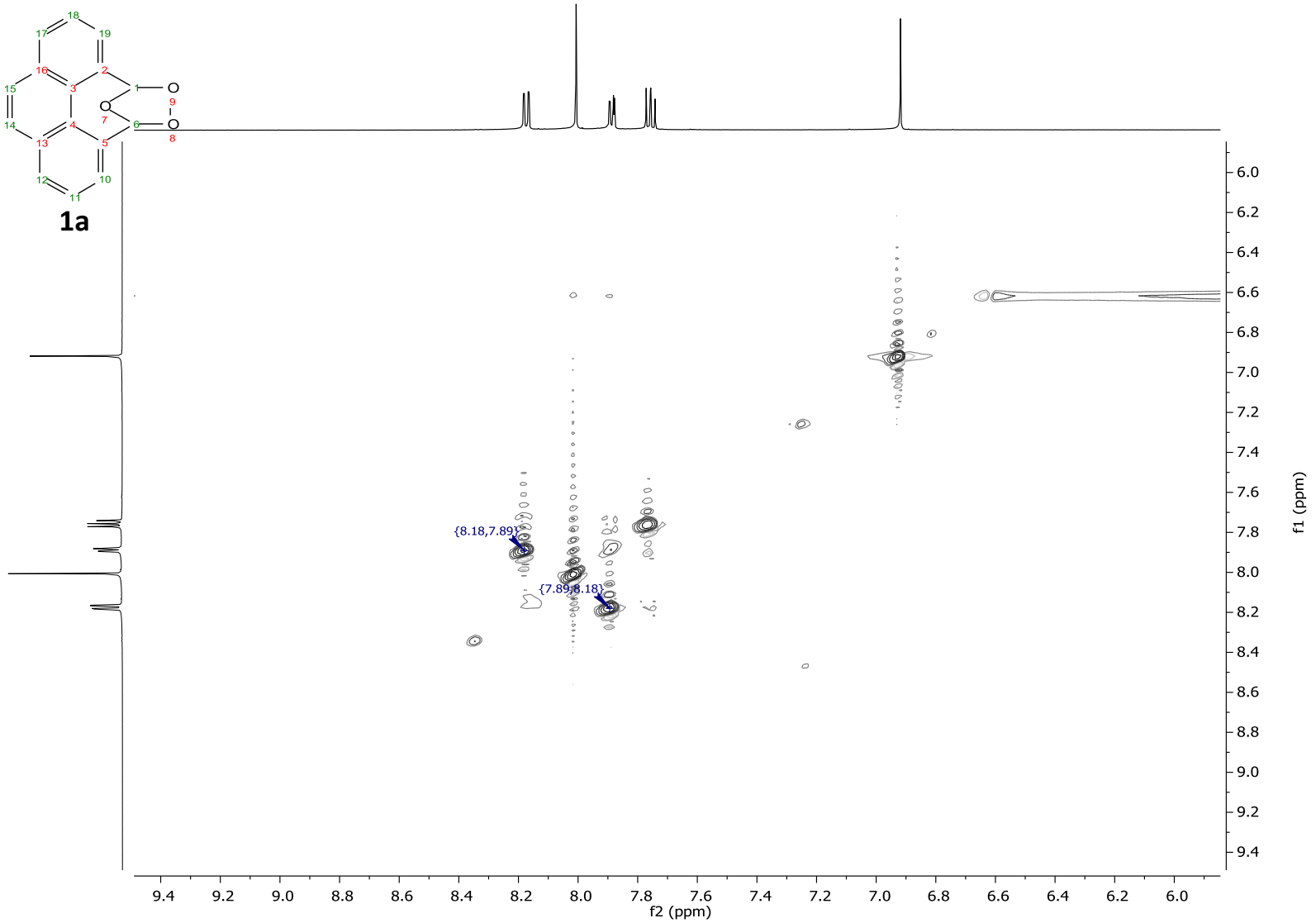


Figure 25. TOCSY NMR spectrum of Pyrene oxidation product **1a** in Acetone-D_6.

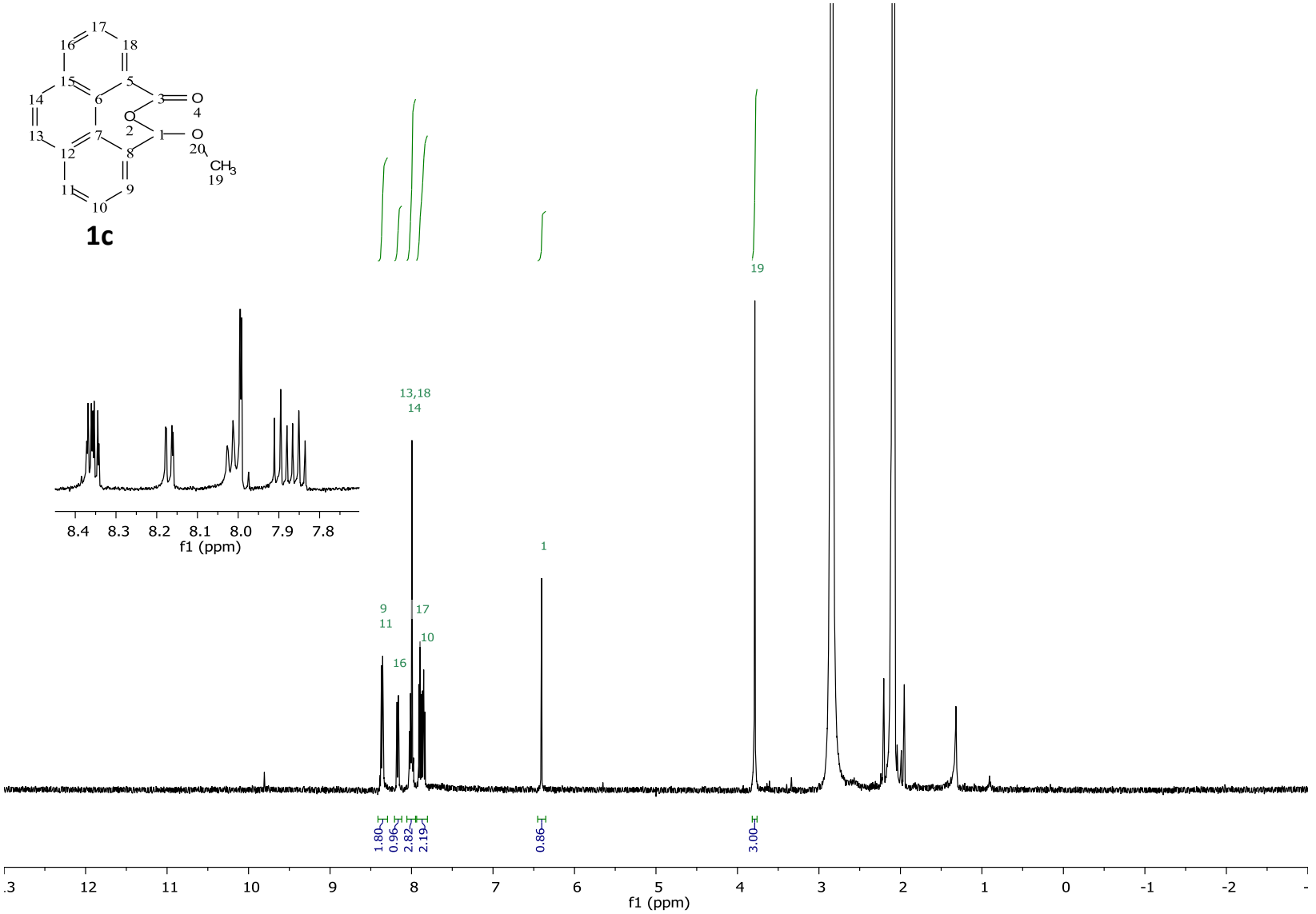


Figure 26. ^{1}H NMR spectrum of Pyrene oxidation product **1c** in Acetone-D_6.

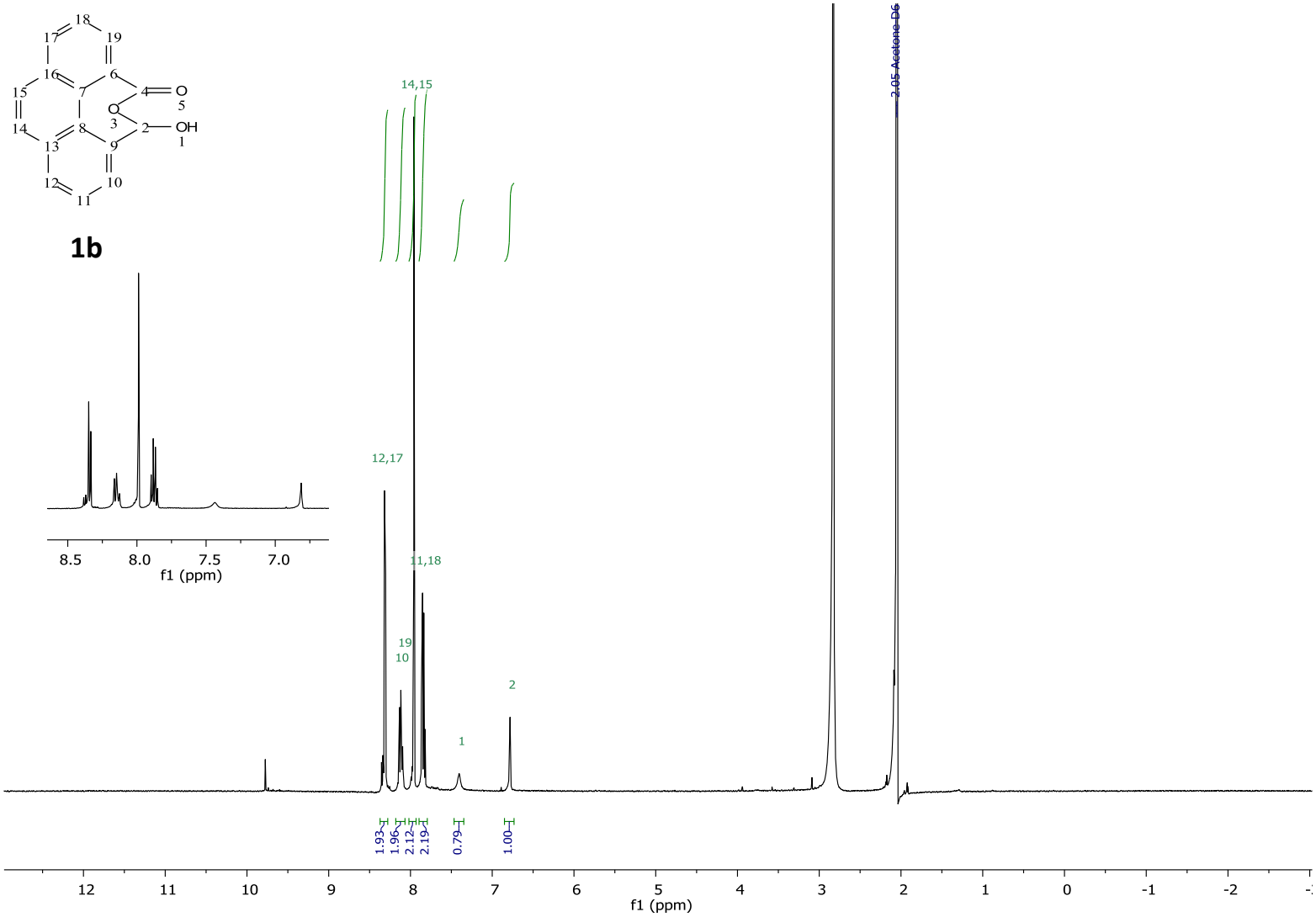


Figure 27. ^{1}H NMR spectrum of Pyrene oxidation product **1b** in Acetone-D_6.

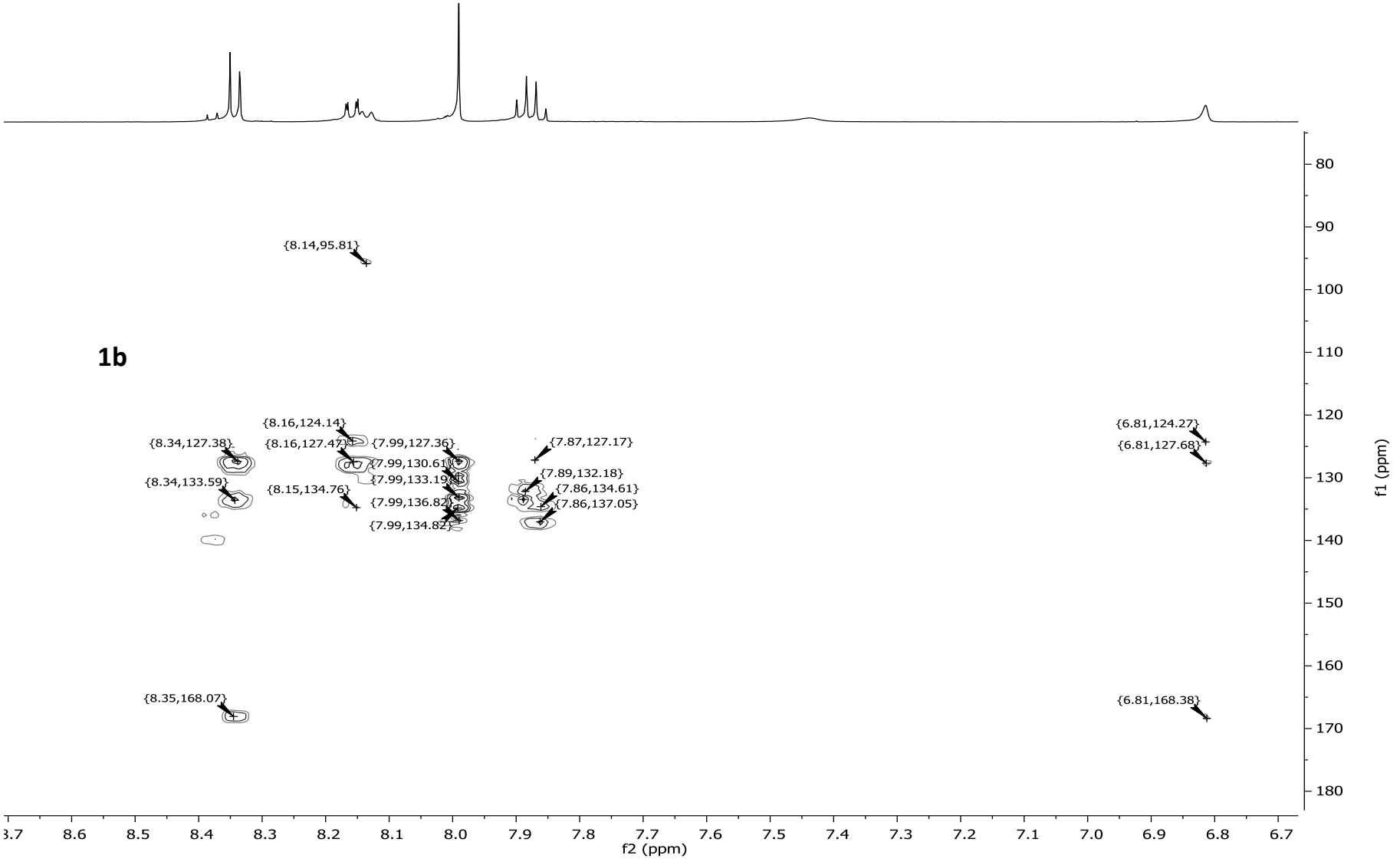


Figure 28. HMBC NMR spectrum of Pyrene oxidation product **1b** in Acetone-D_6.

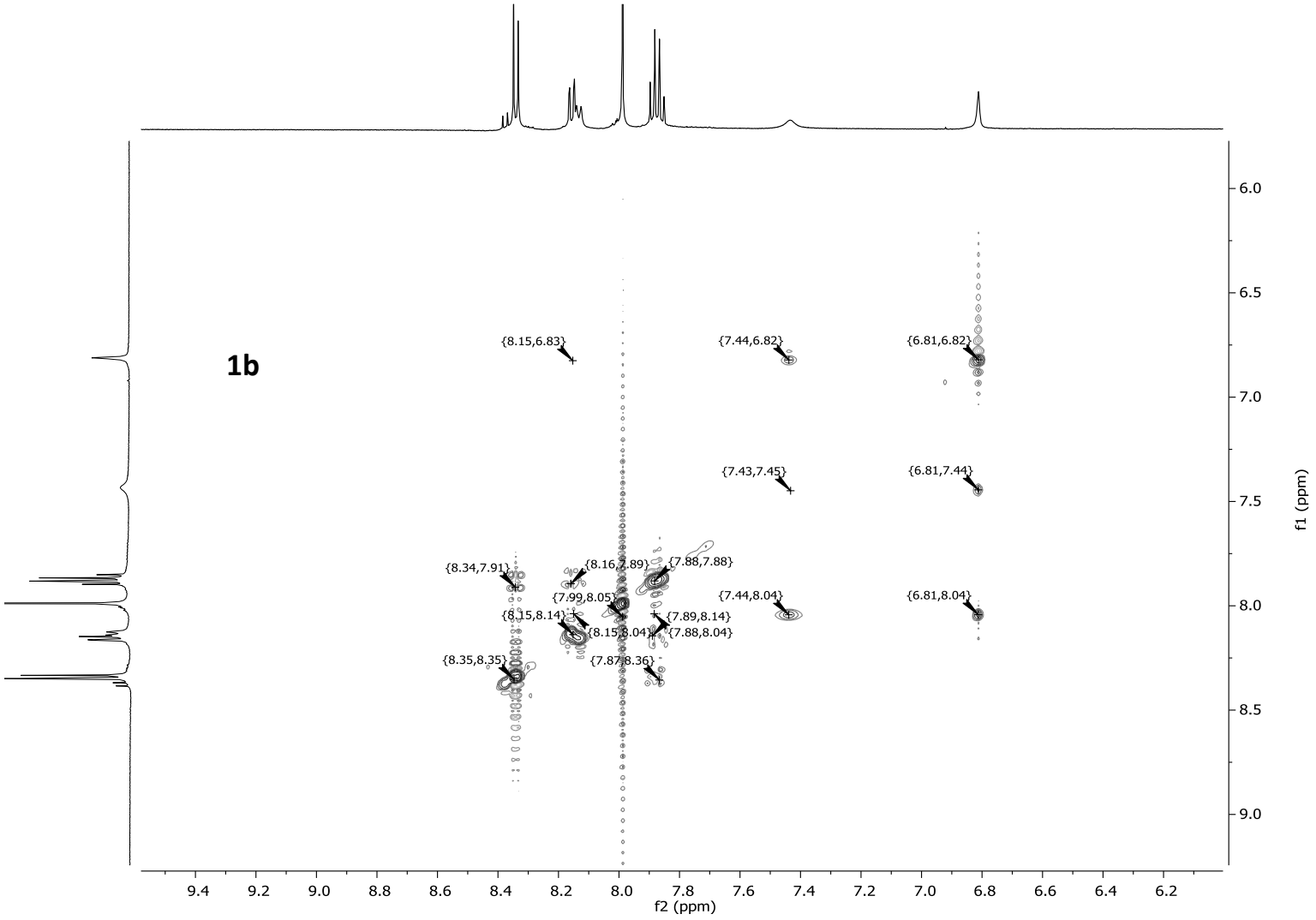


Figure 29. TOCSY NMR spectrum of Pyrene oxidation product **1b** in Acetone-D_6.

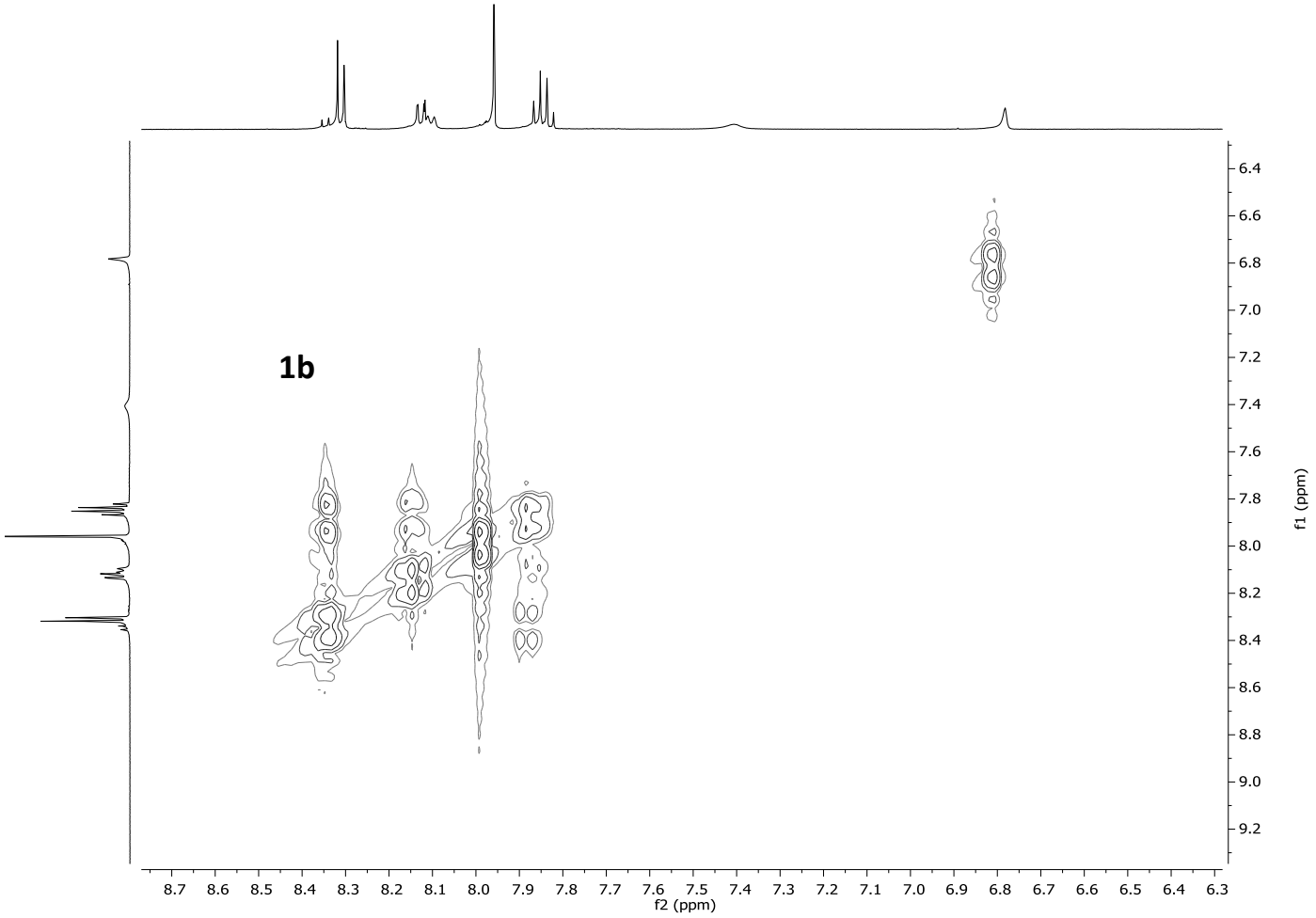


Figure 30. COSY NMR spectrum of Pyrene oxidation product **1b** in Acetone-D_6.

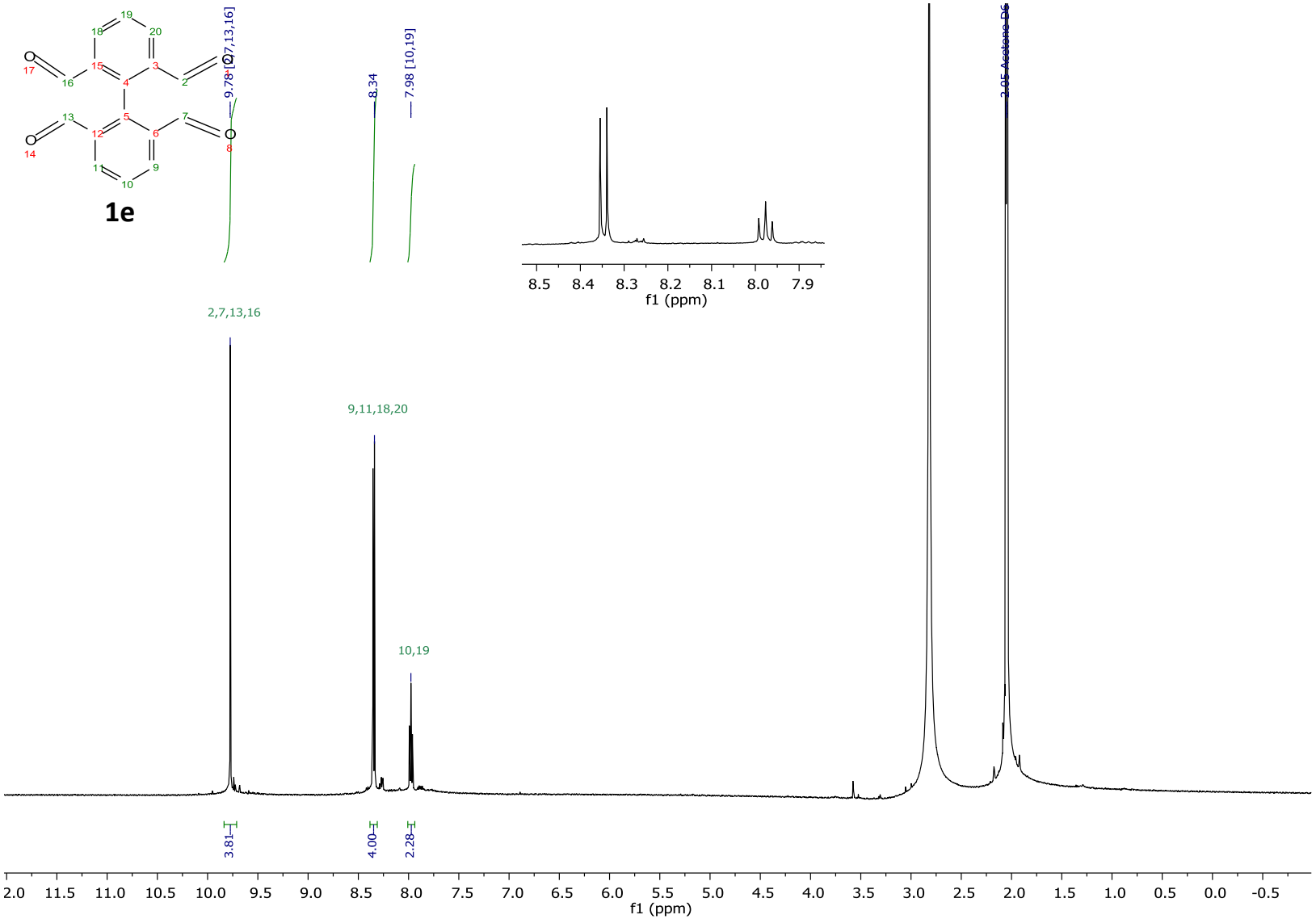


Figure 31. ^{1}H NMR spectrum of Pyrene oxidation product **1e** in Acetone-D_6.

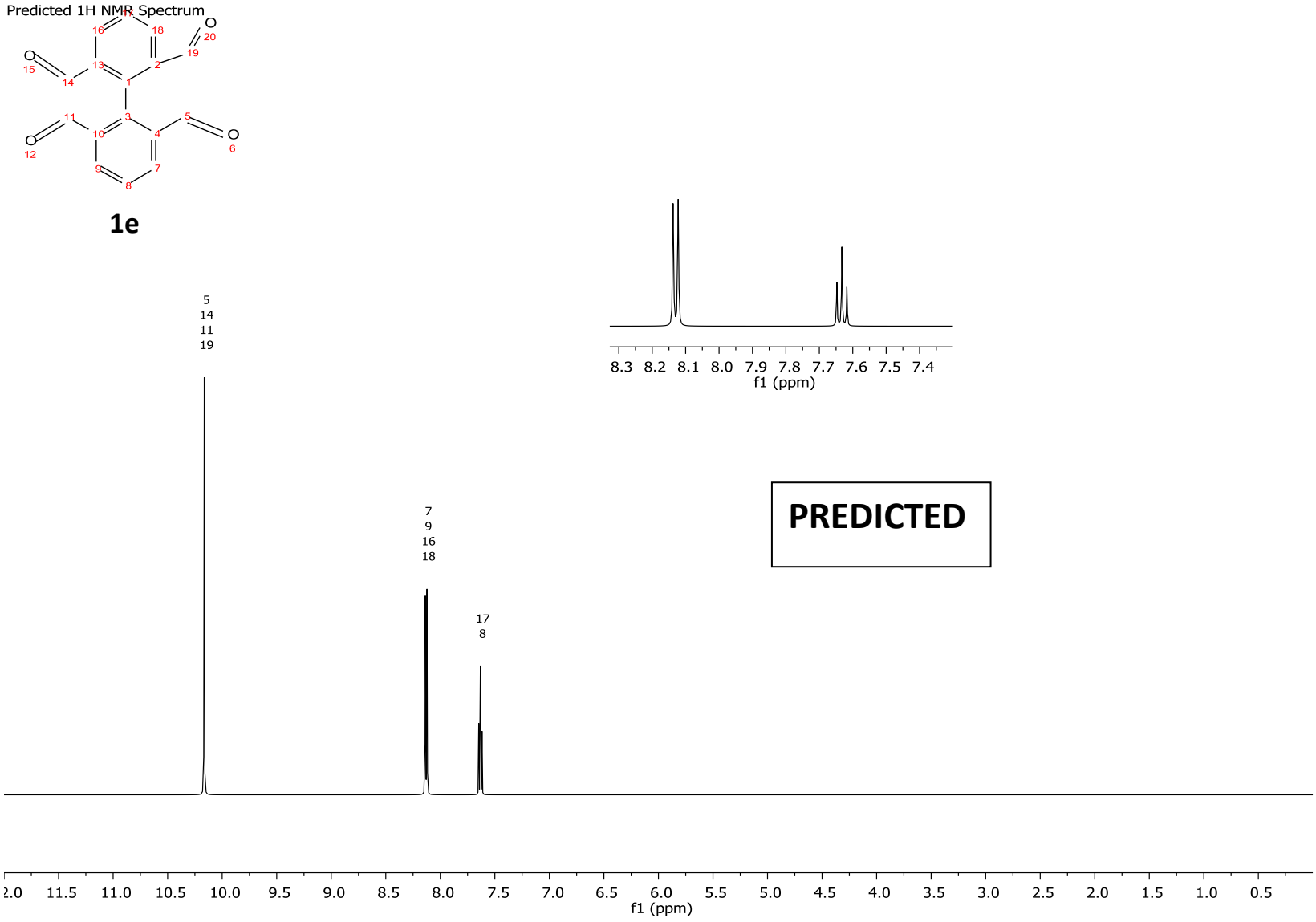


Figure 32. Predicted ^{1}H NMR spectrum of Pyrene oxidation product **1e.**

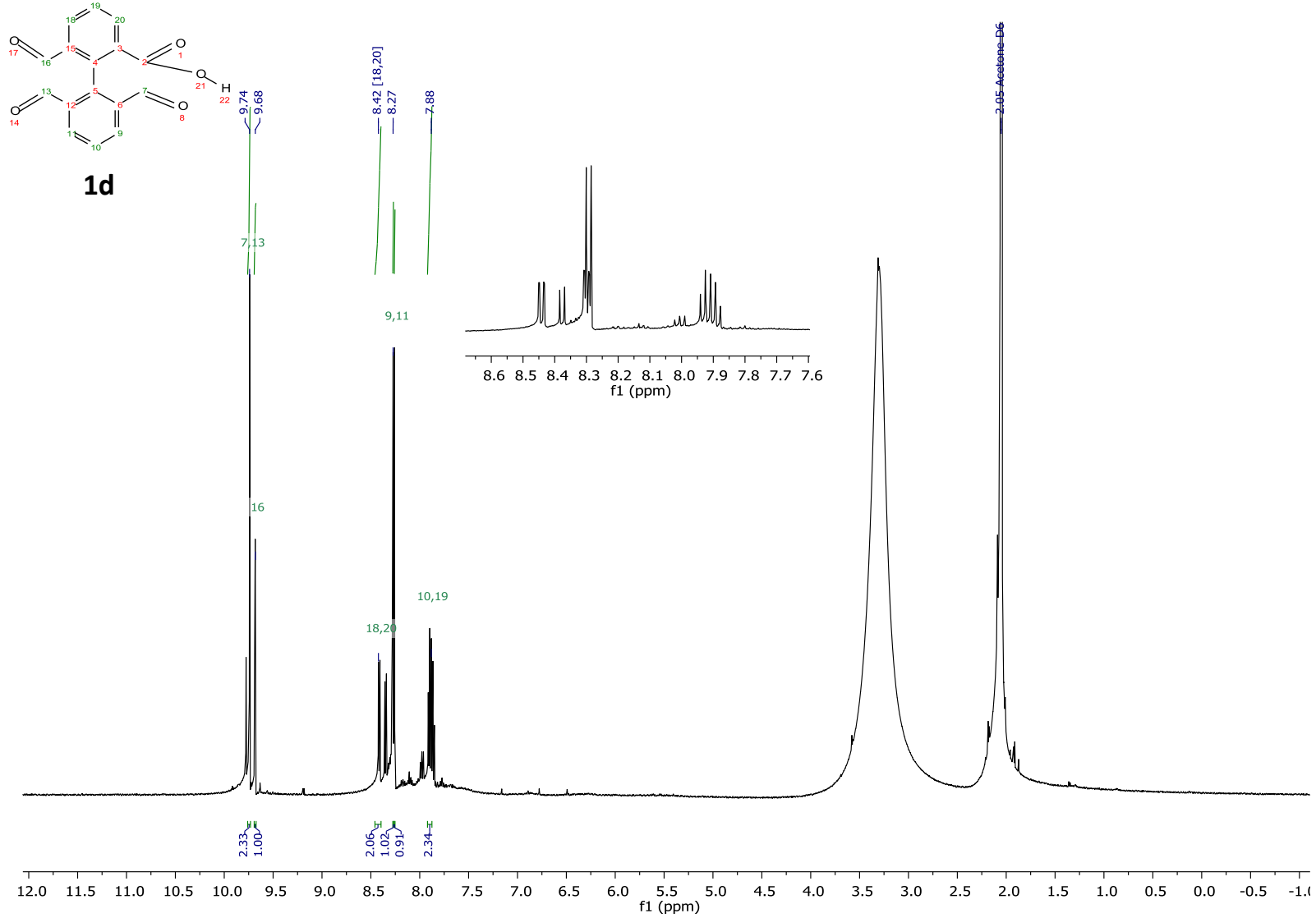


Figure 33. ^{1}H NMR spectrum of Pyrene oxidation product **1d** in Acetone-D_6.

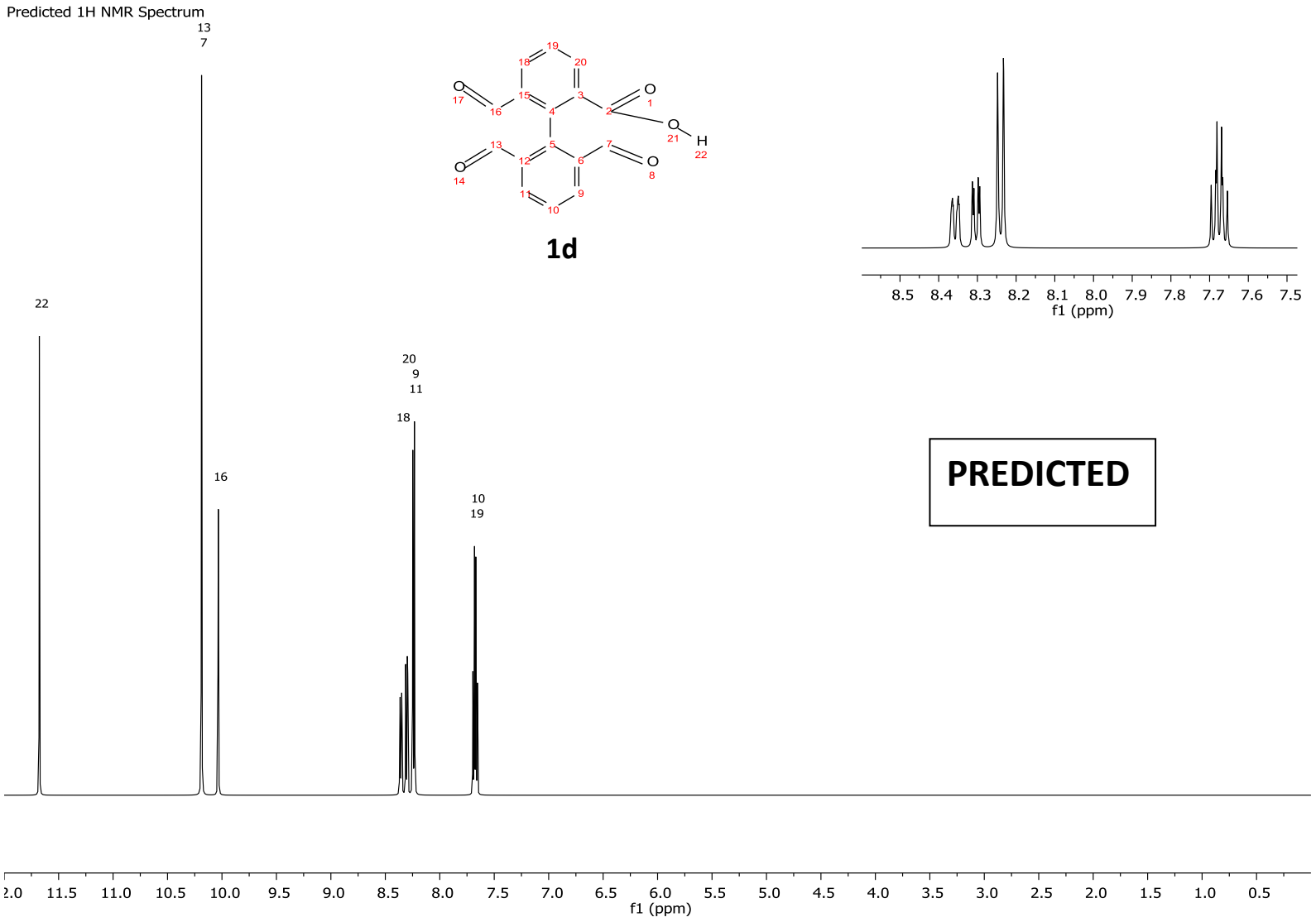


Figure 34. Predicted ^{1}H NMR spectrum of Pyrene oxidation product **1d.**

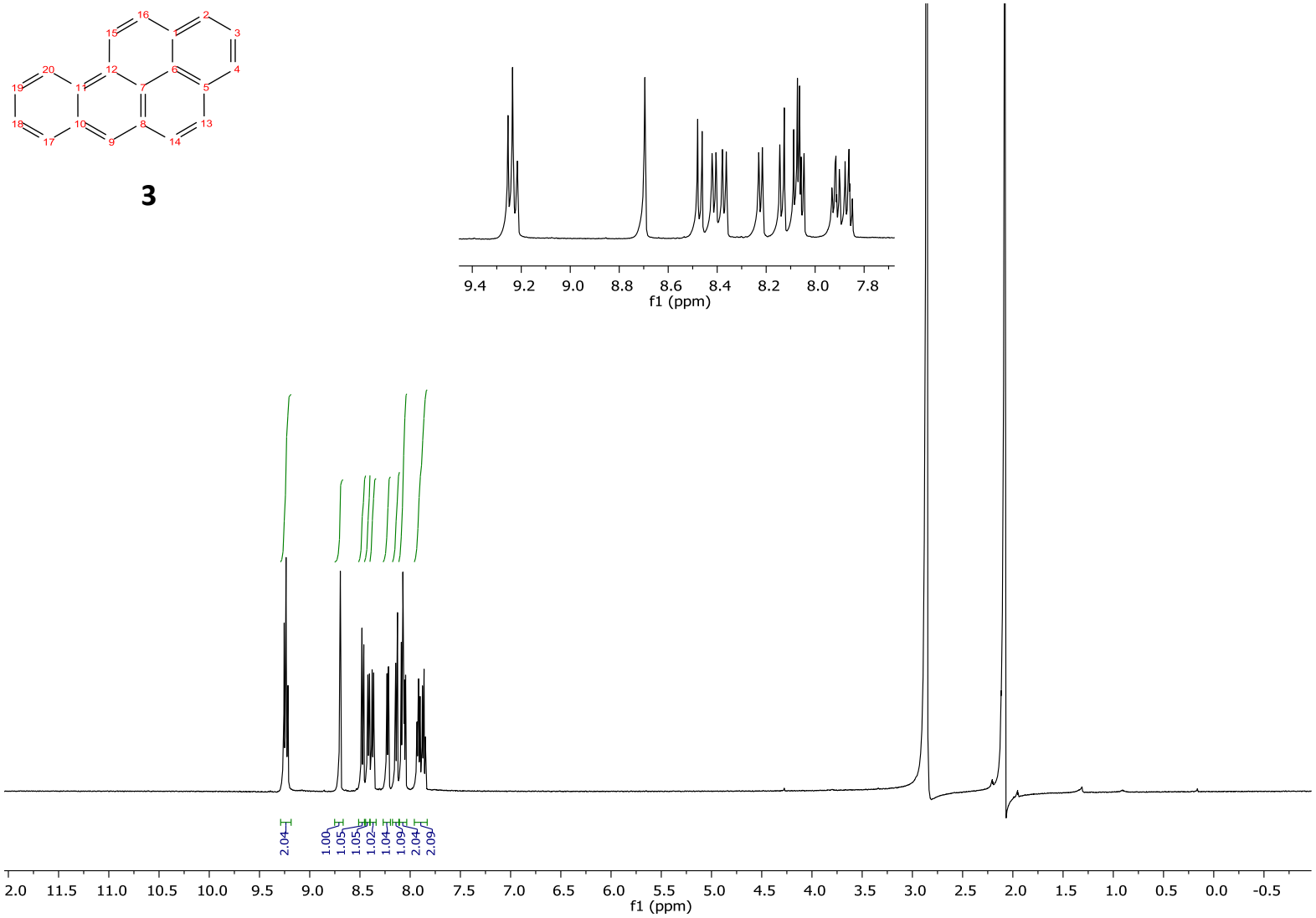


Figure 35. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **3** in Acetone-D_6.

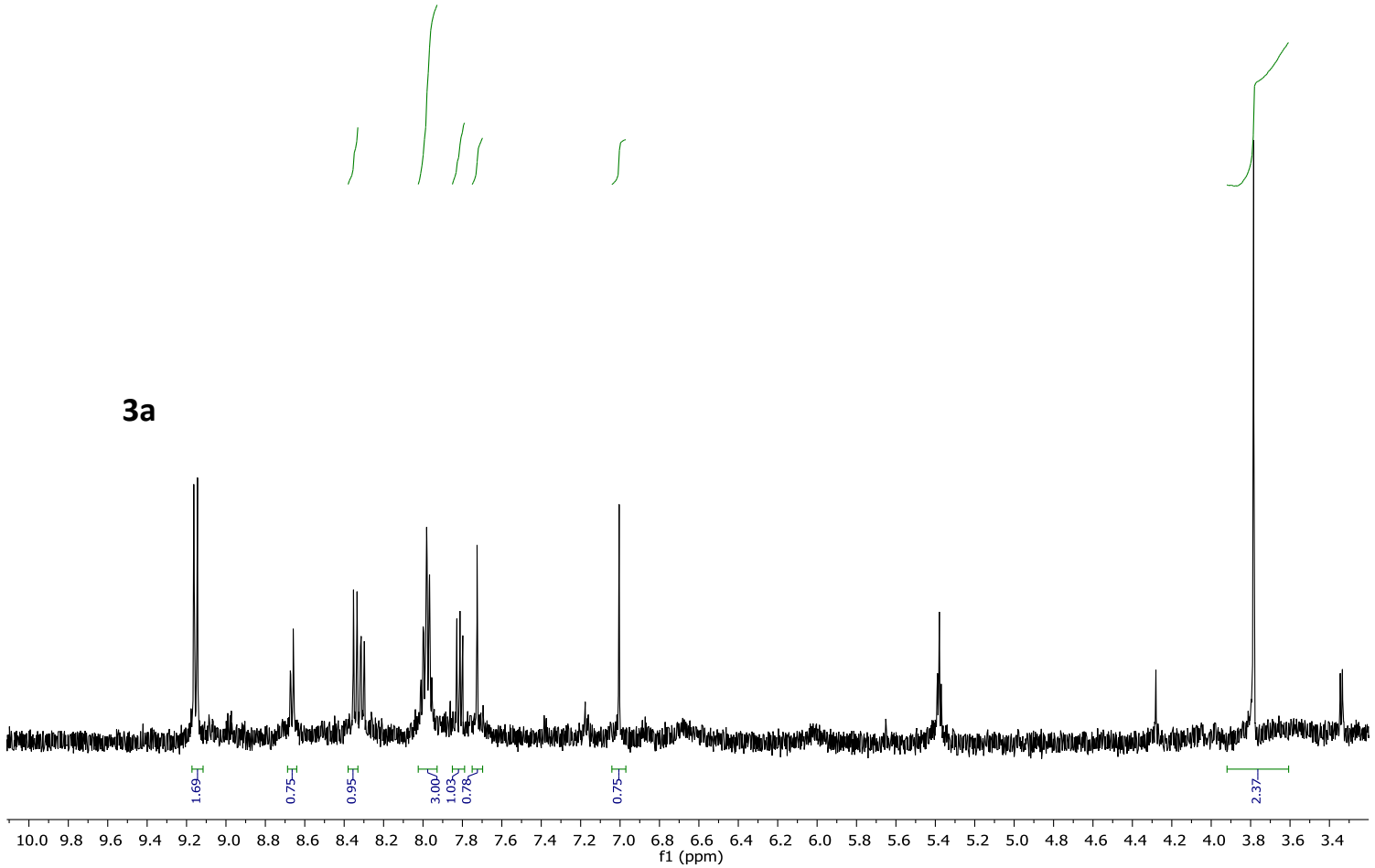


Figure 36. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3a** in Acetone-D_6.

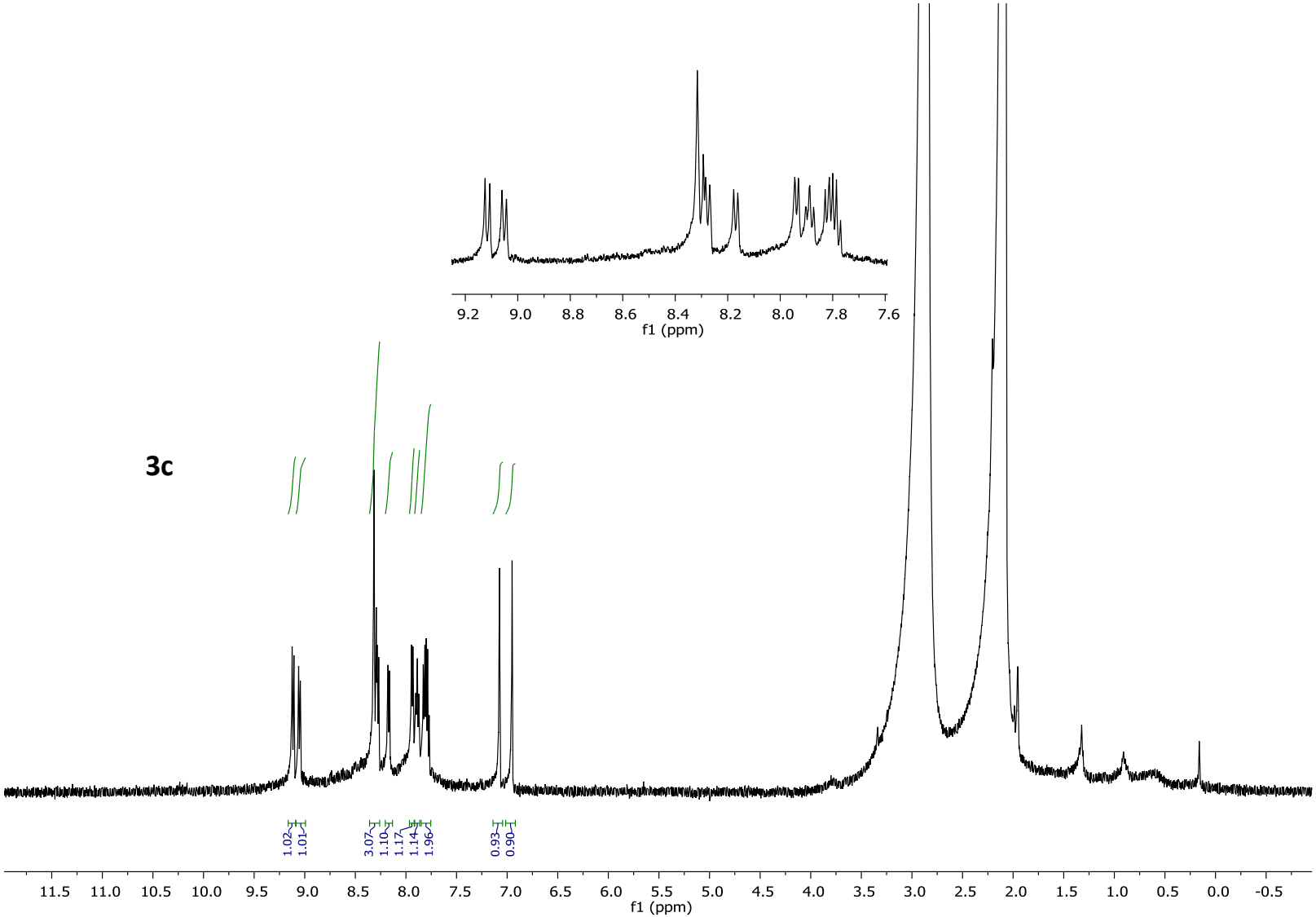


Figure 37. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3c** in Acetone-D_6.

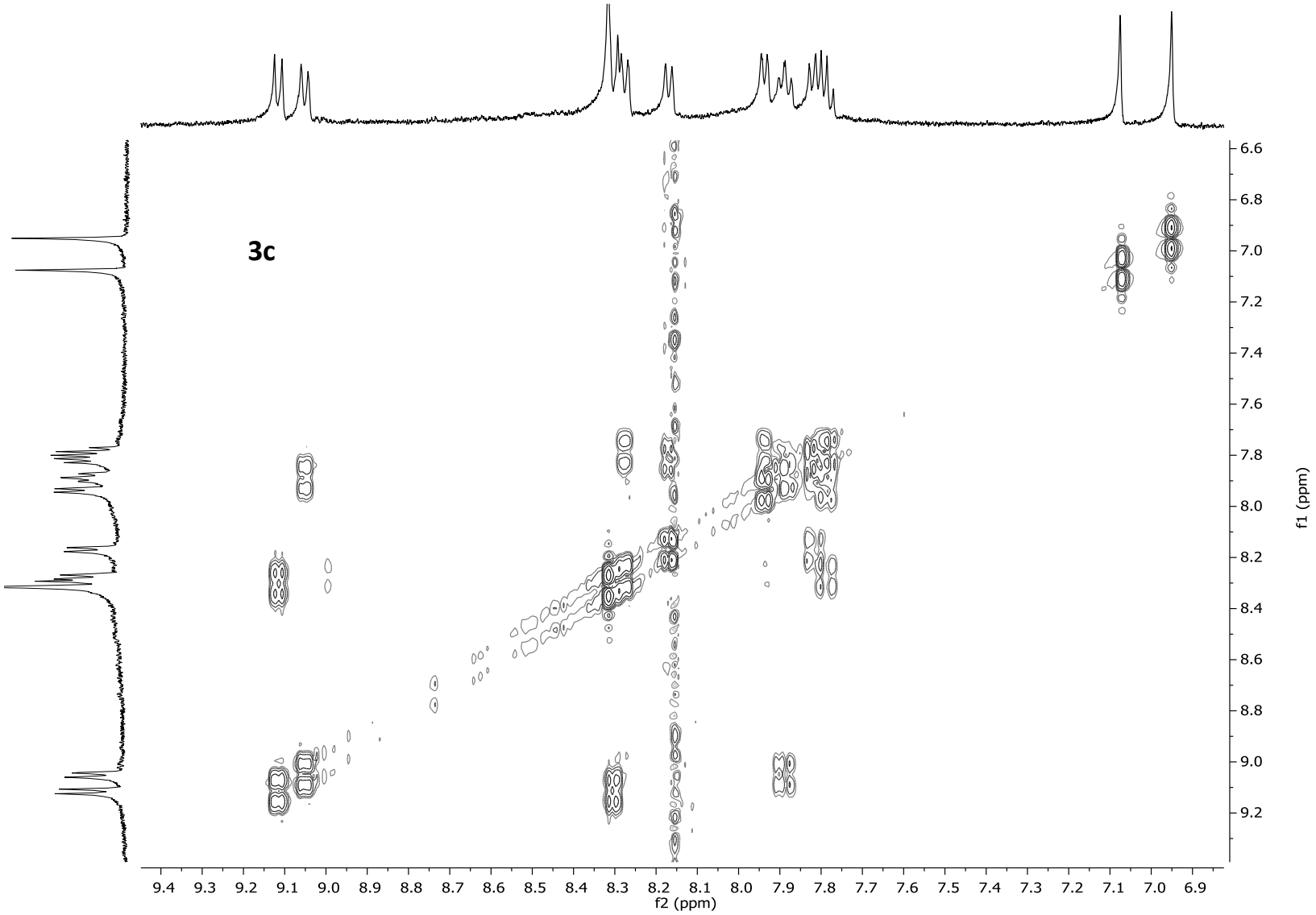


Figure 38. COSY NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3c** in Acetone-D_6.

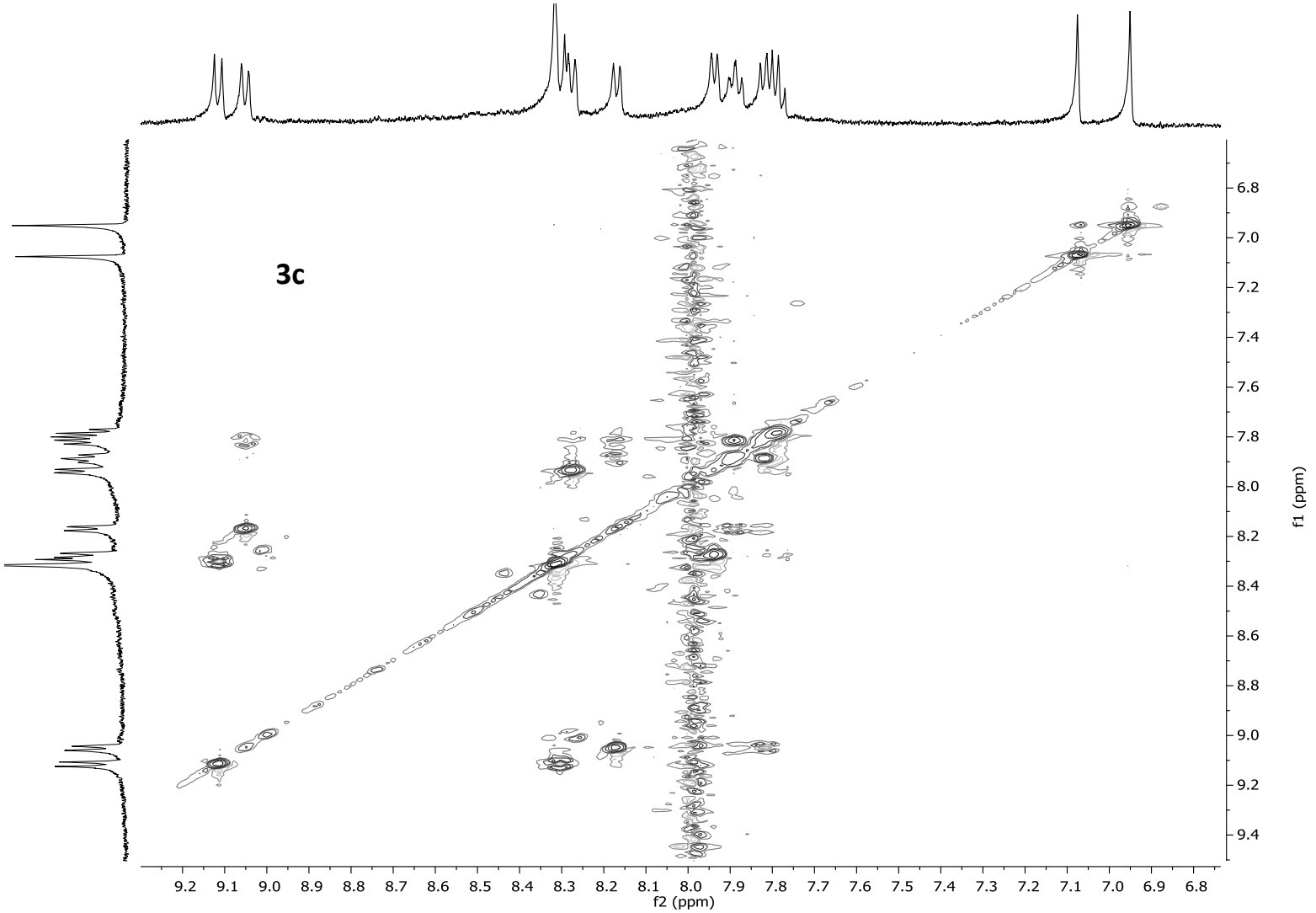


Figure 39. TOCSY NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3c** in Acetone-D_6.

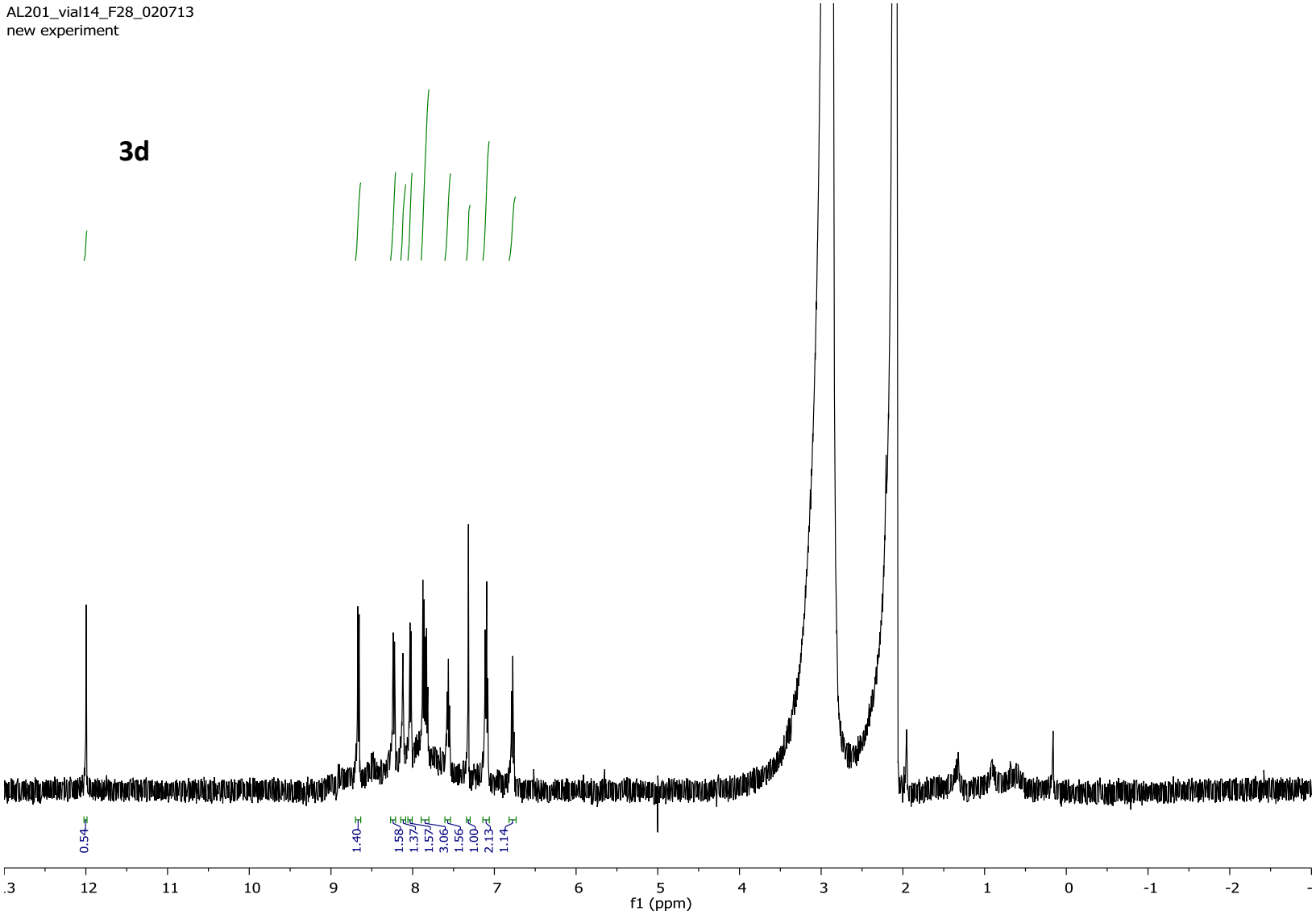


Figure 40. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3d** in Acetone-D_6.

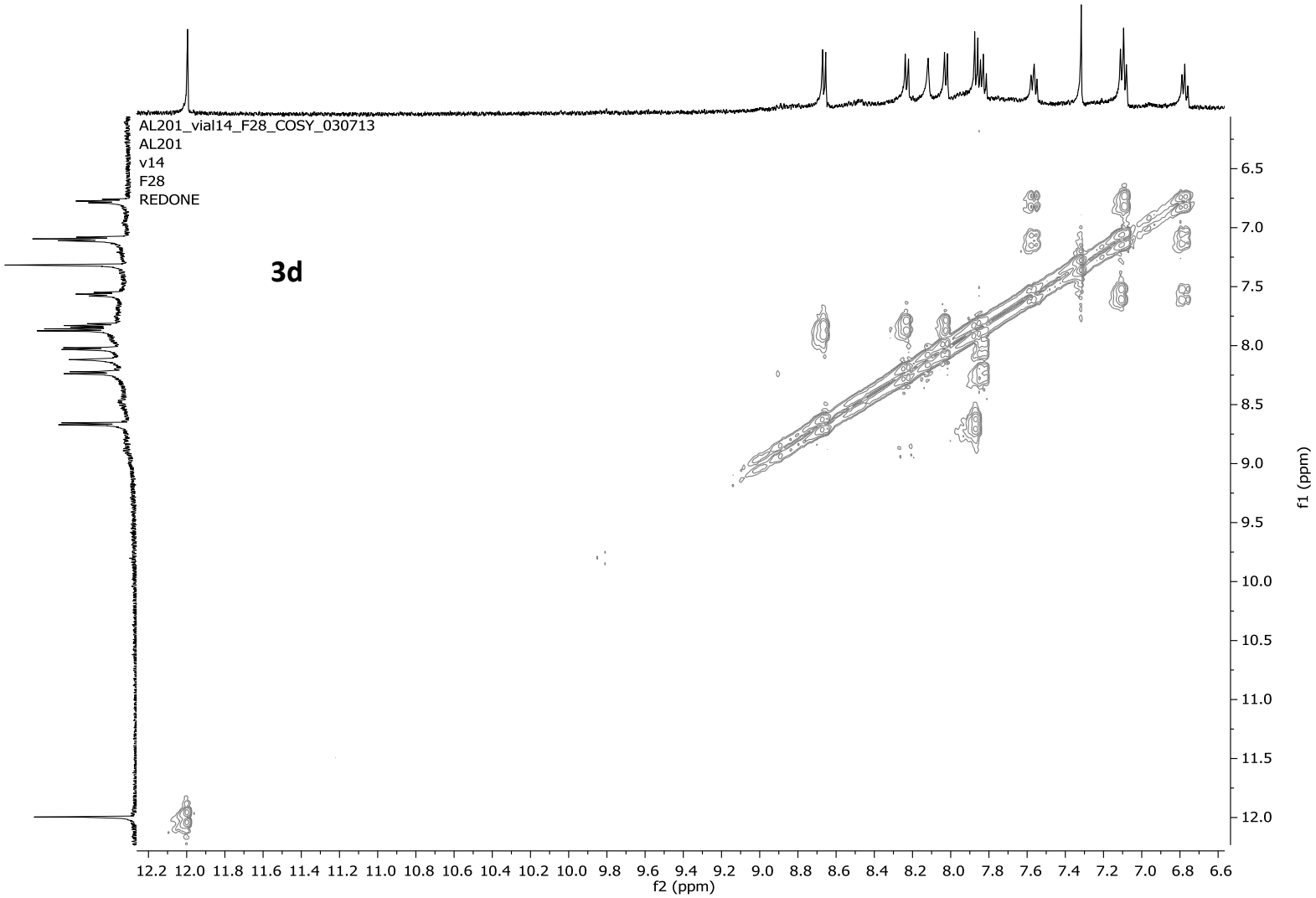


Figure 41. COSY spectrum of Benzo [a] Pyrene, B[a]P, unknown oxidation product **3d** in Acetone-D_6.

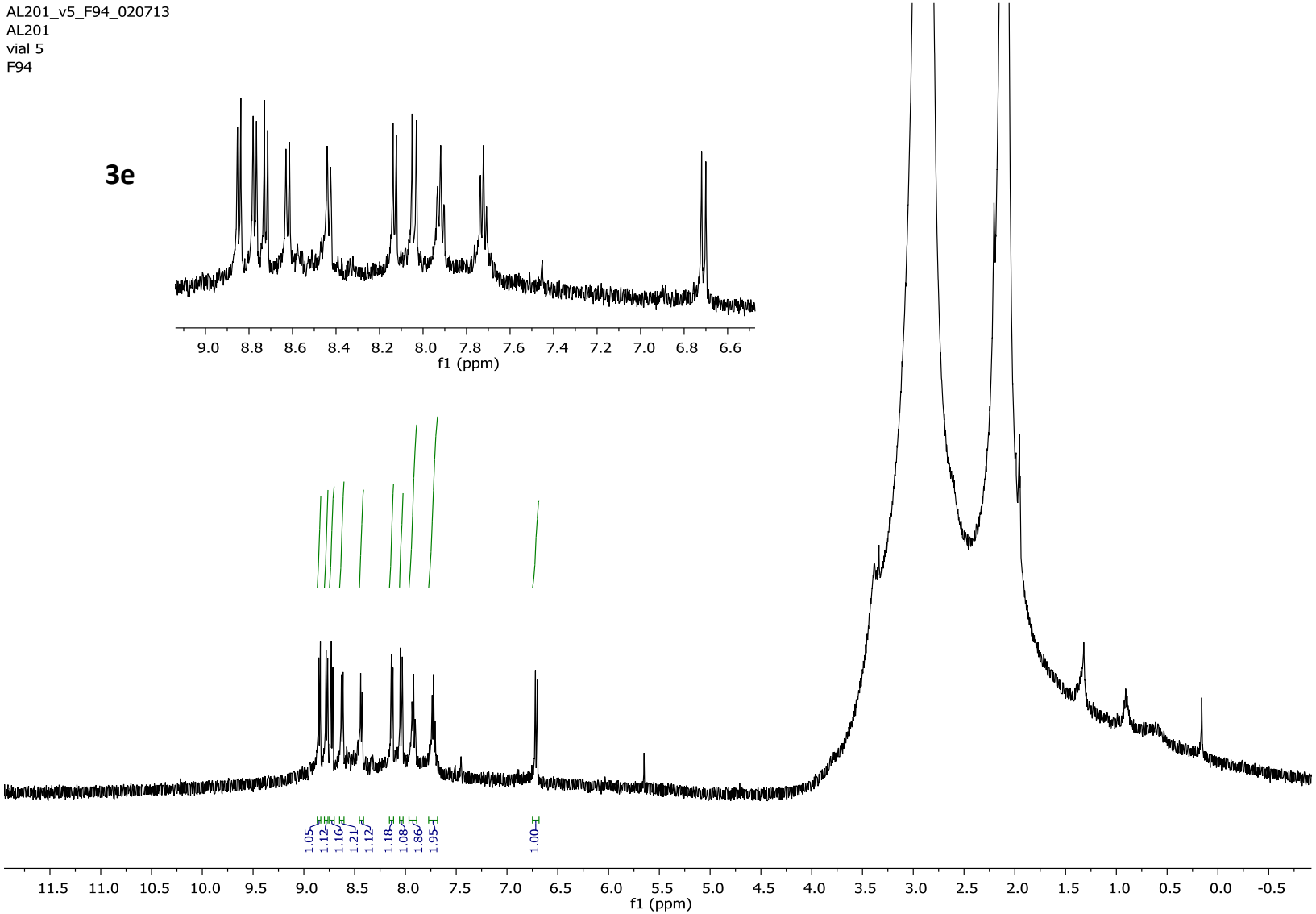


Figure 42. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3e** in Acetone-D_6.

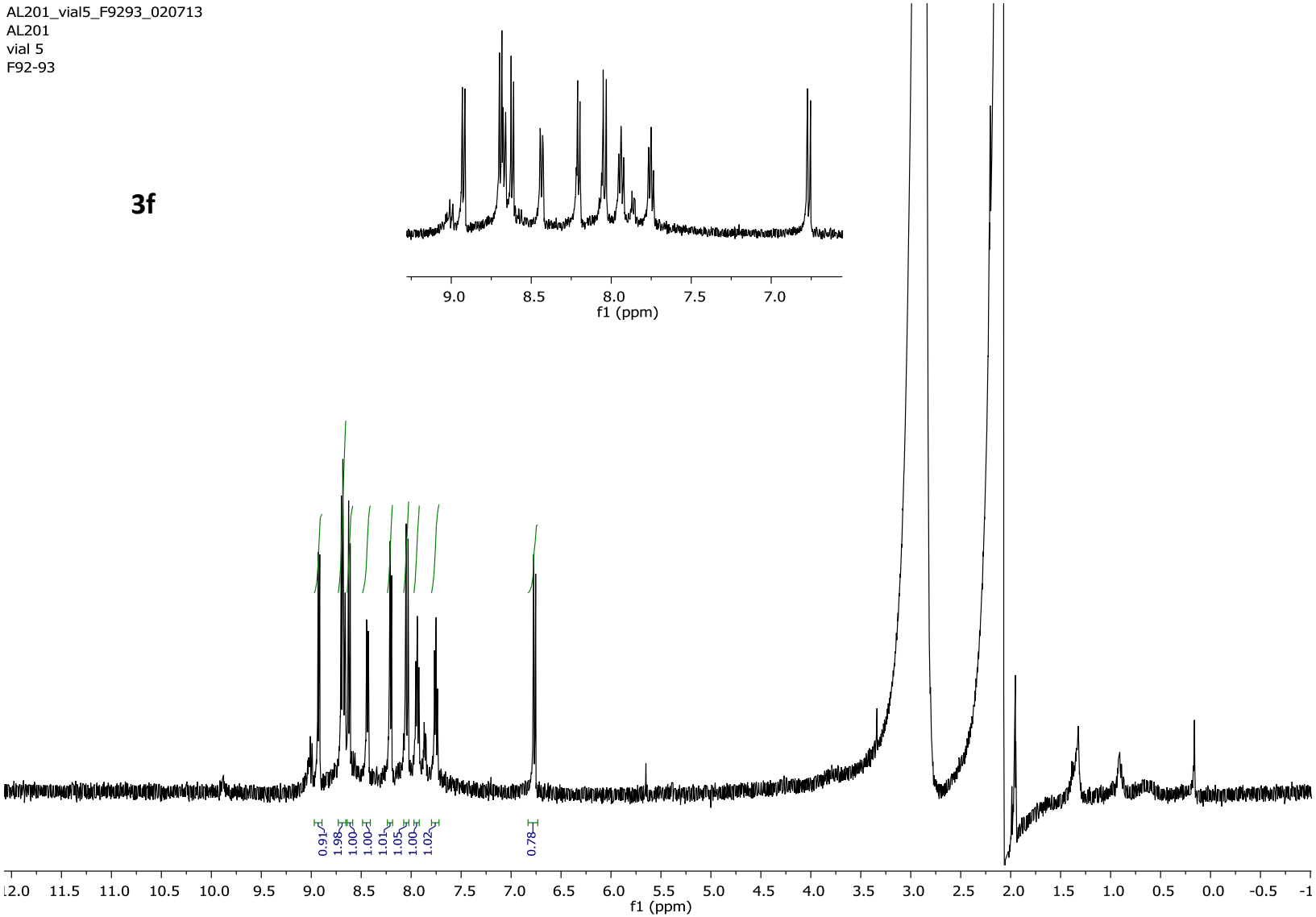


Figure 43. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3f** in Acetone-D_6.

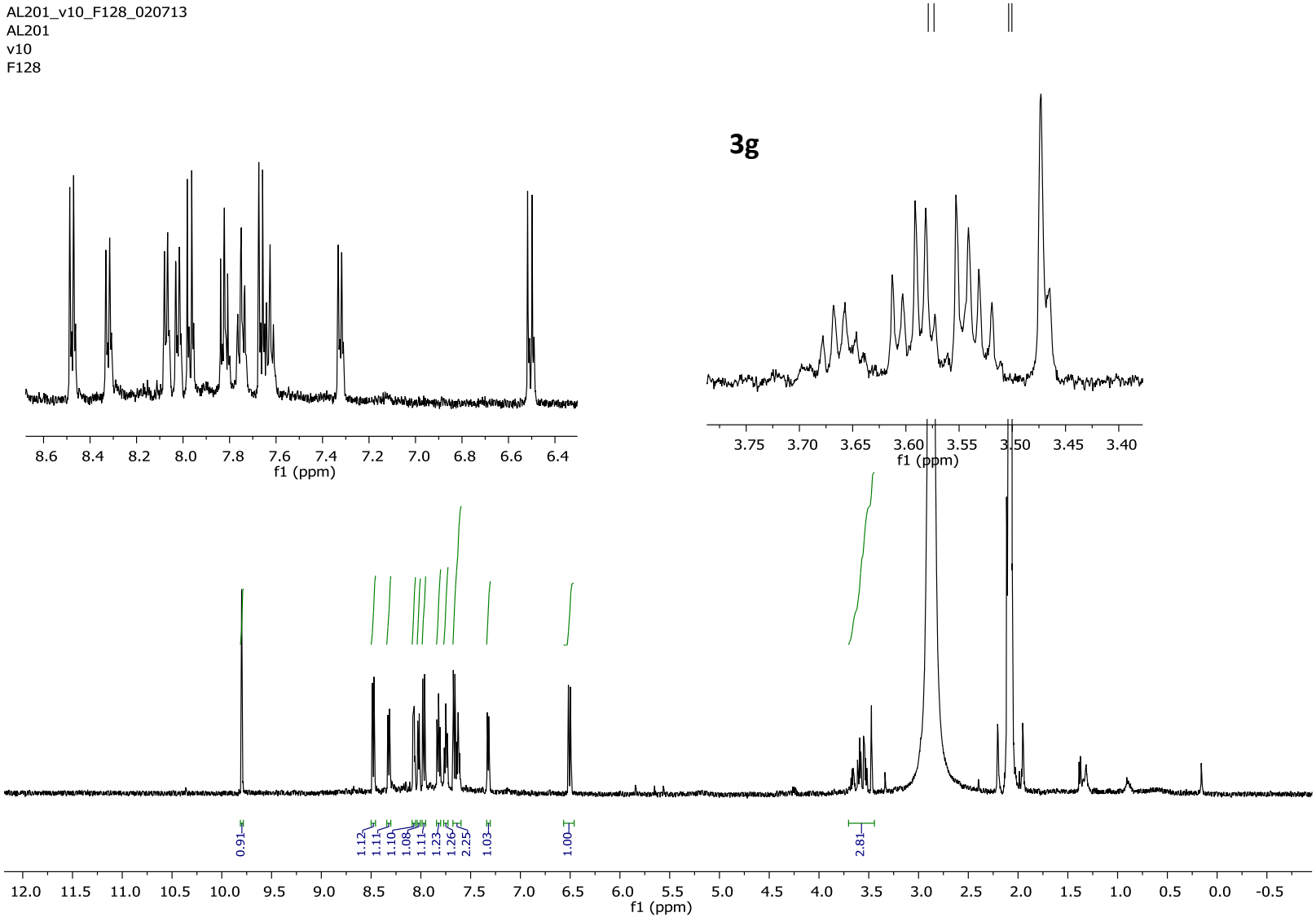


Figure 44. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3g** in Acetone-D_6.

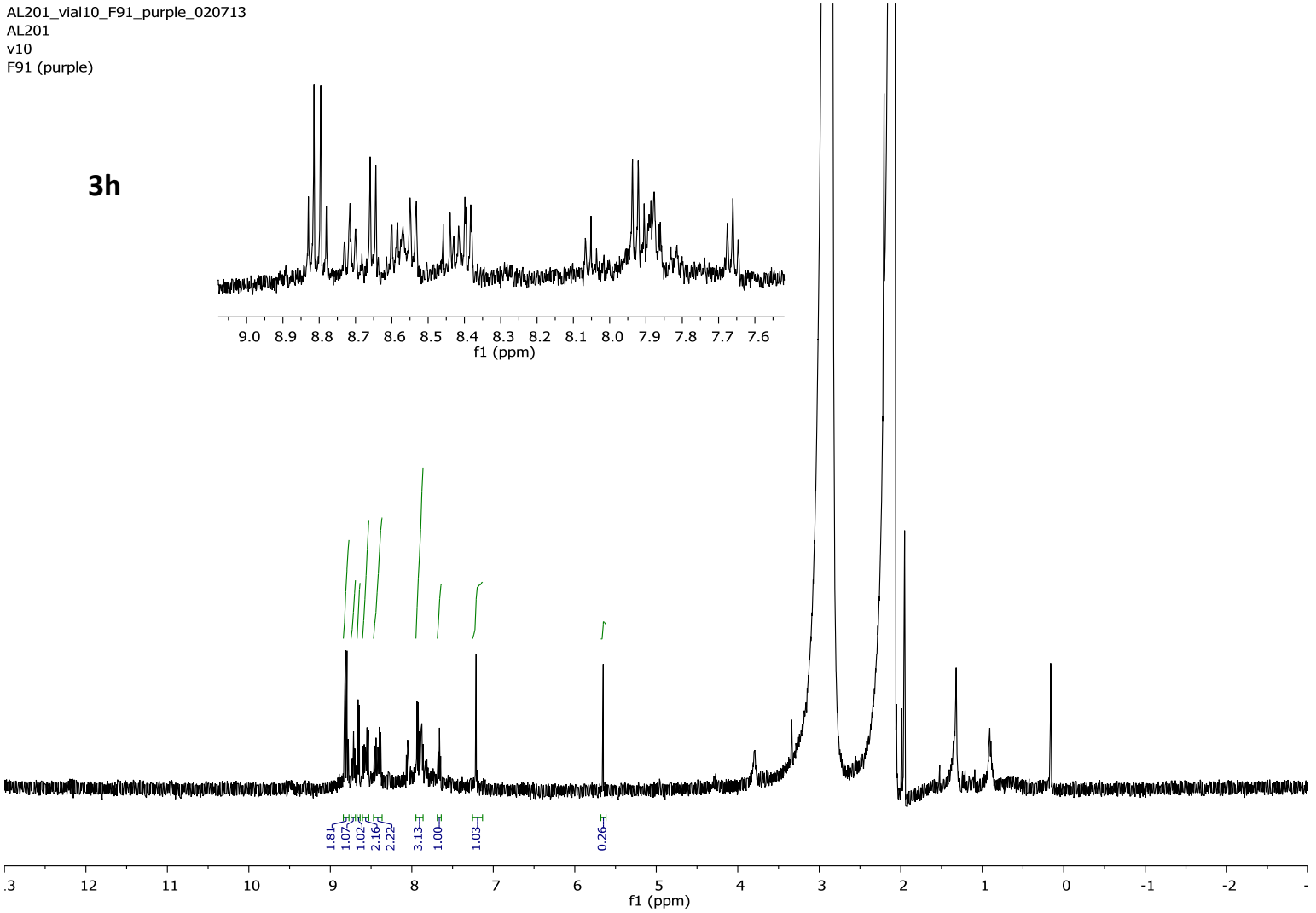


Figure 45. ^{1}H NMR spectrum of Benzo [a] Pyrene, B[a]P, **unknown** oxidation product **3h** in Acetone-D_6.

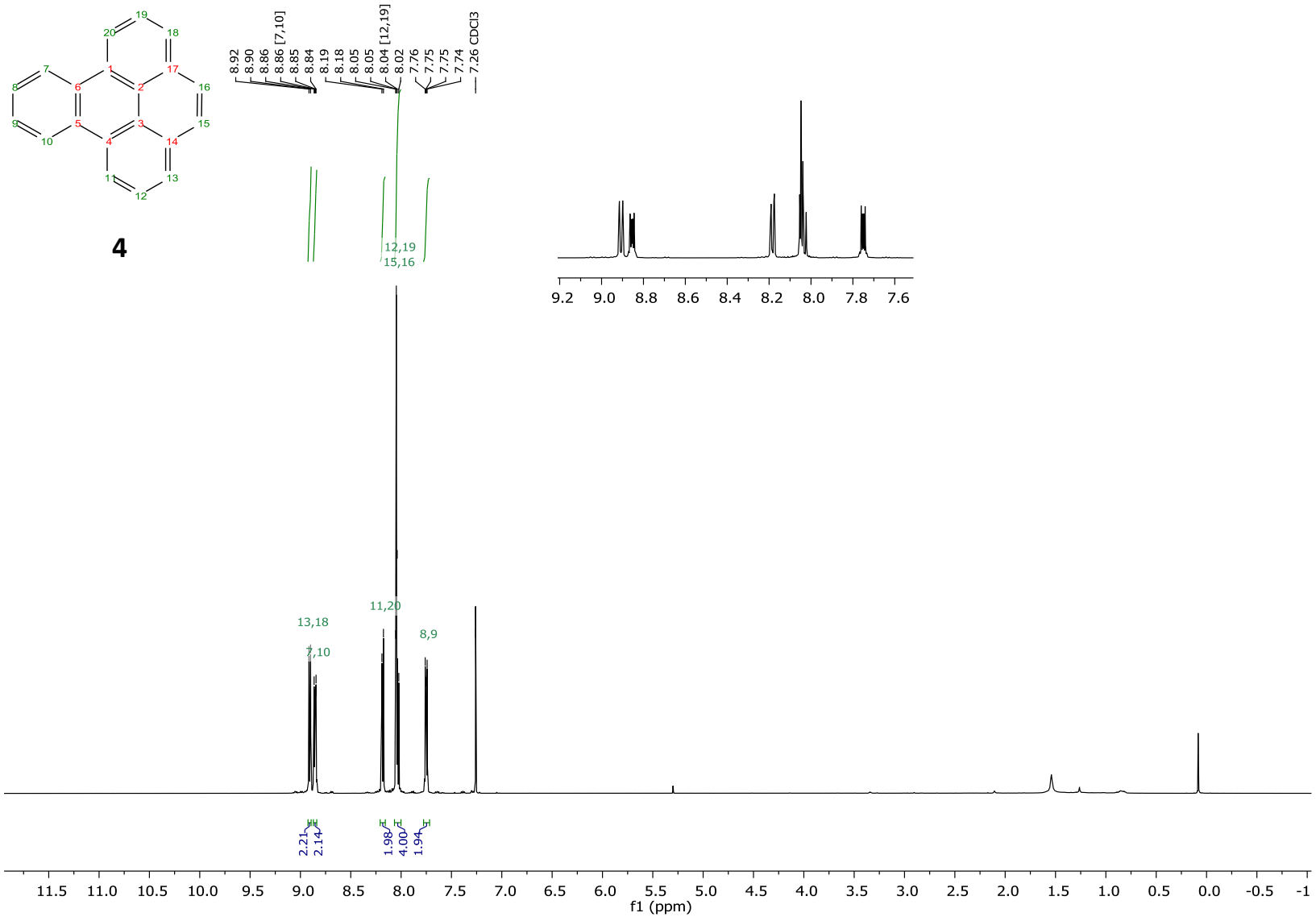


Figure 46. ^{1}H NMR spectrum of Benzo [e] Pyrene, B[e]P, **4** in Acetone-D_6.

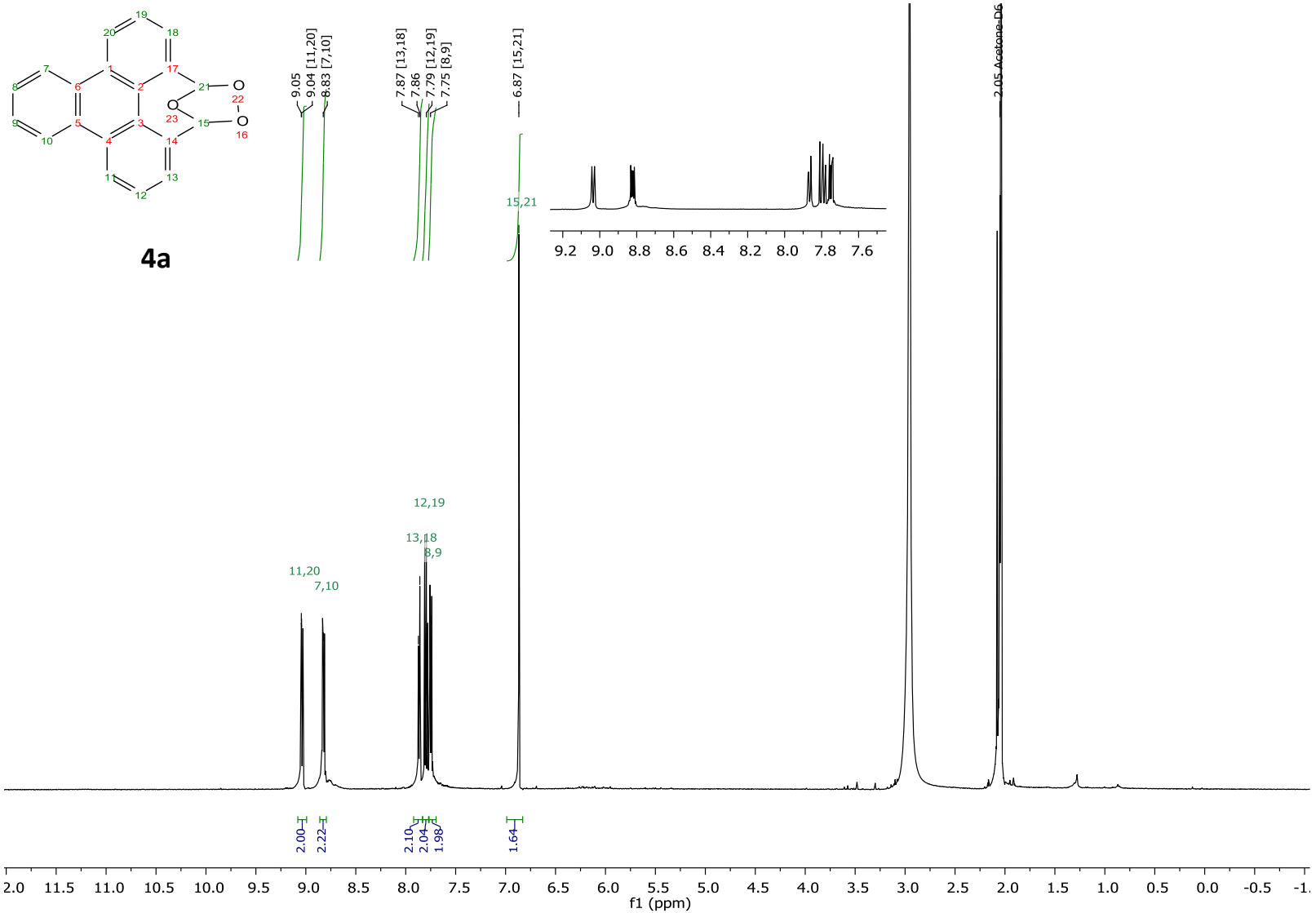


Figure 47. ^{1}H NMR spectrum of Benzo [e] Pyrene, B[e]P, oxidation product **4a** in Acetone-D_6.

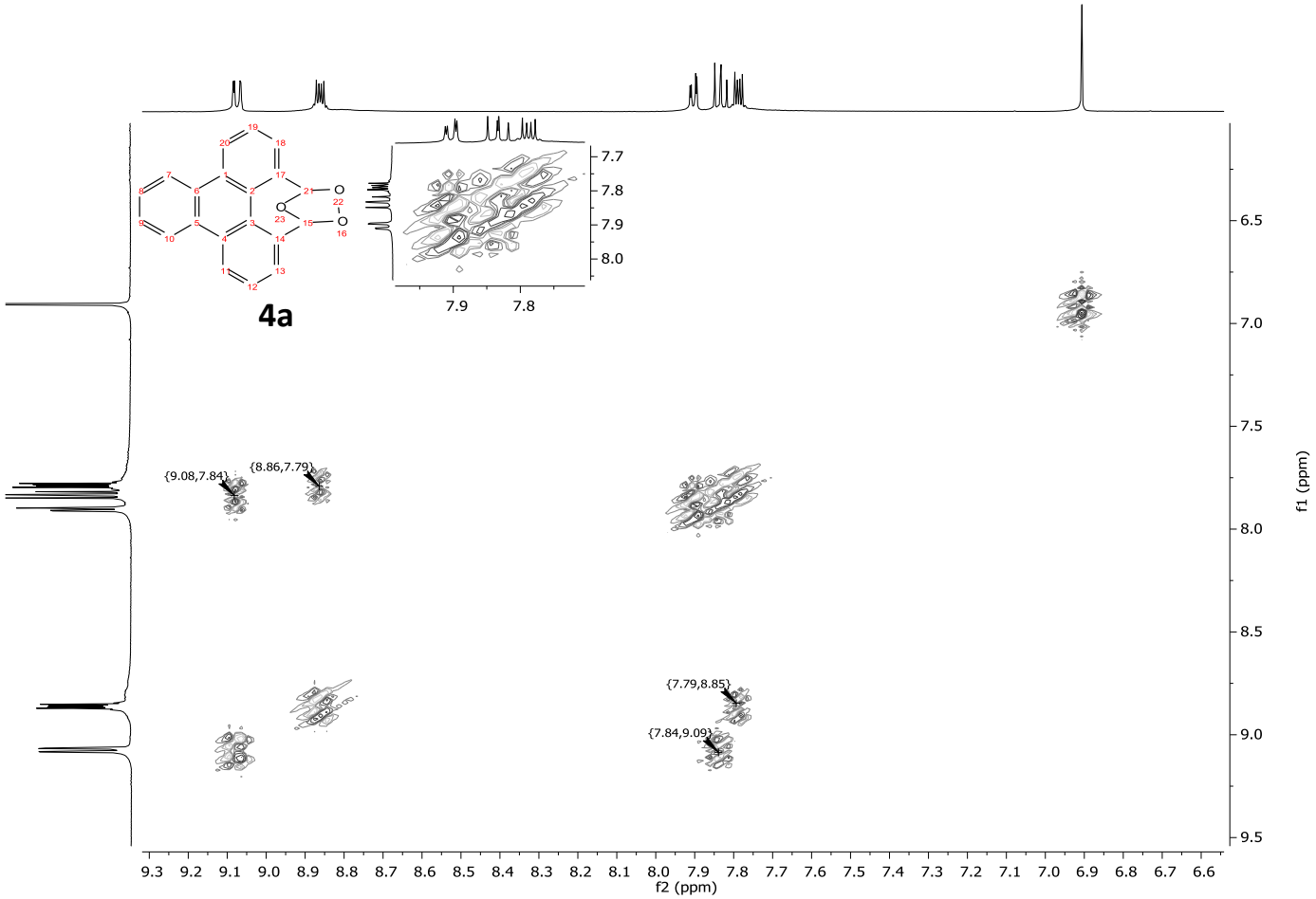


Figure 48. COSY NMR spectrum of Benzo [e] Pyrene, B[e]P, oxidation product **4a** in Acetone-D_6.

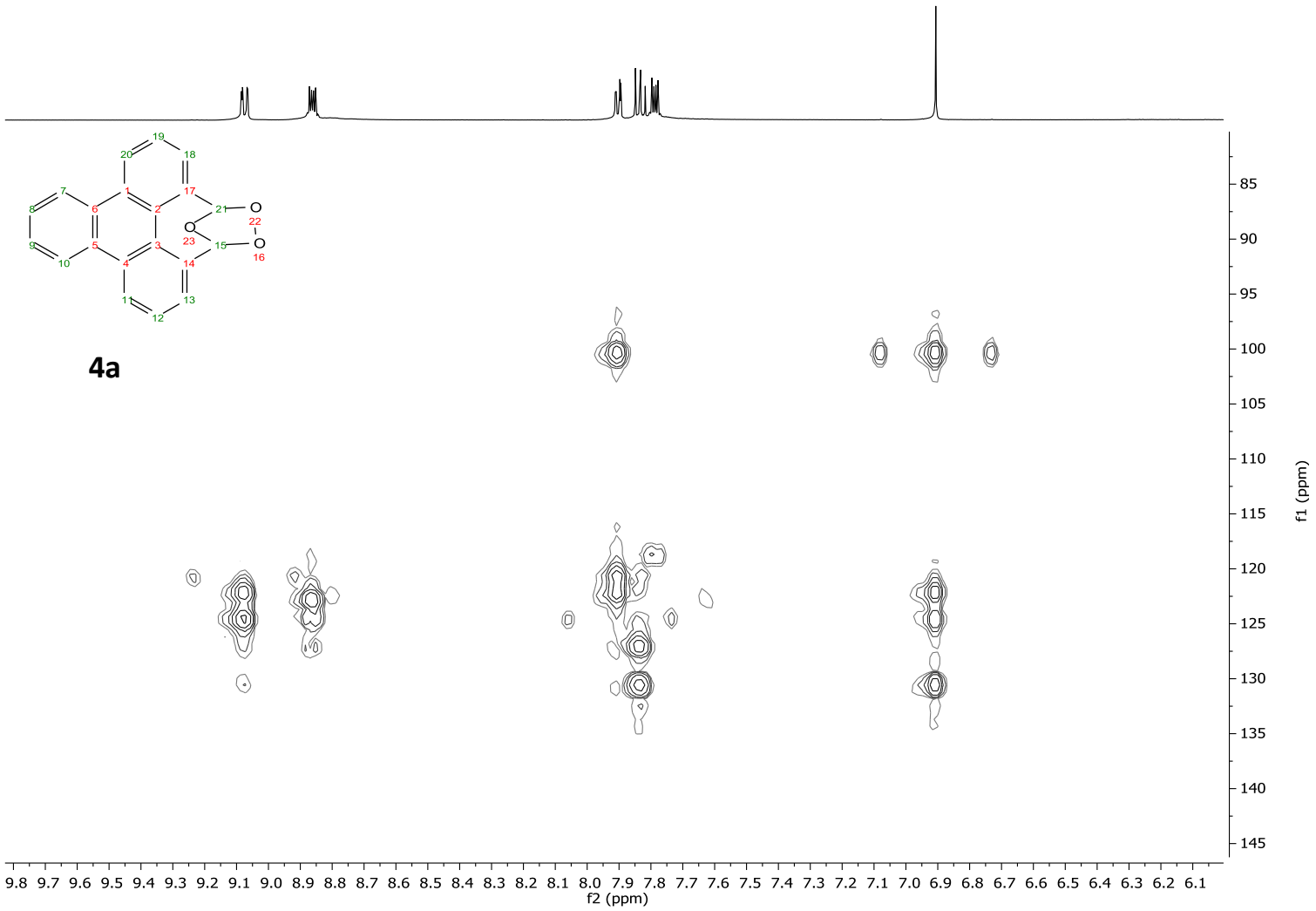


Figure 49. HMBC NMR spectrum of Benzo [e] Pyrene, B[e]P, oxidation product **4a** in Acetone-D_6.

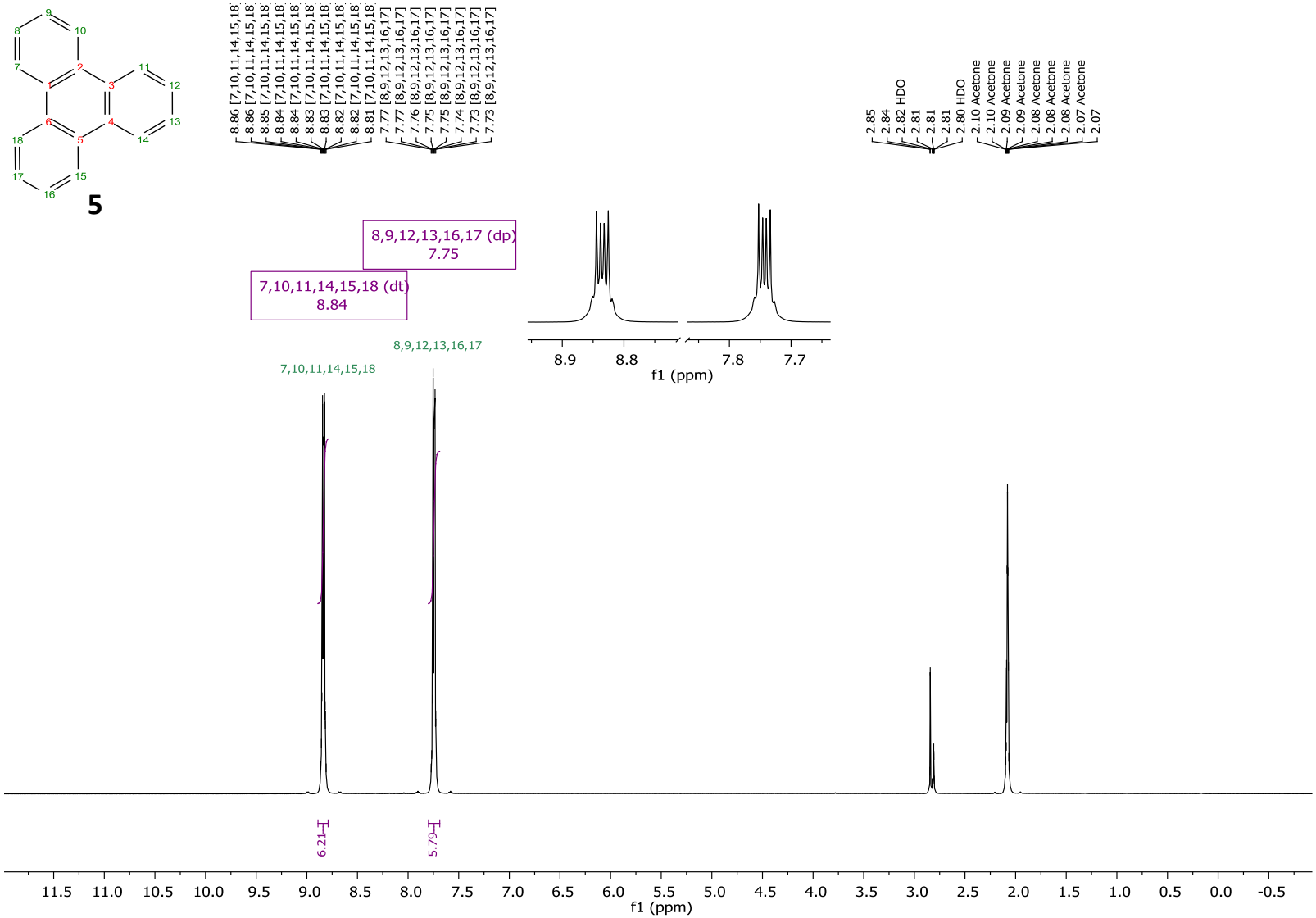


Figure 50. ^{1}H NMR spectrum of Triphenylene **5** in Acetone-D_6.

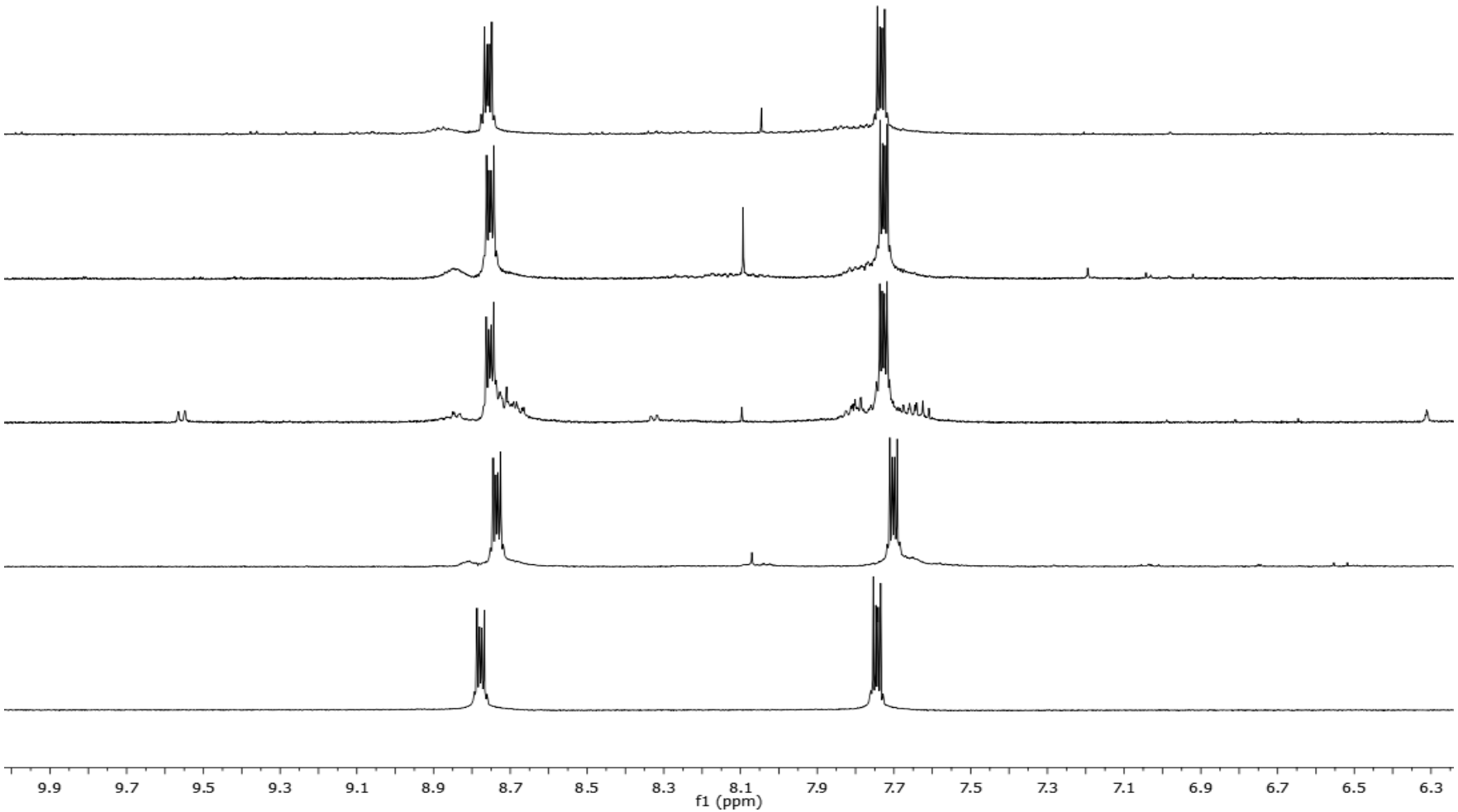


Figure 51. Bottom spectrum is untreated triphenylene **5**, then crude mixture from ozone treated **5** under dry conditions (300s or 500s) with water (300s) and top spectrum with MeOH (300s).

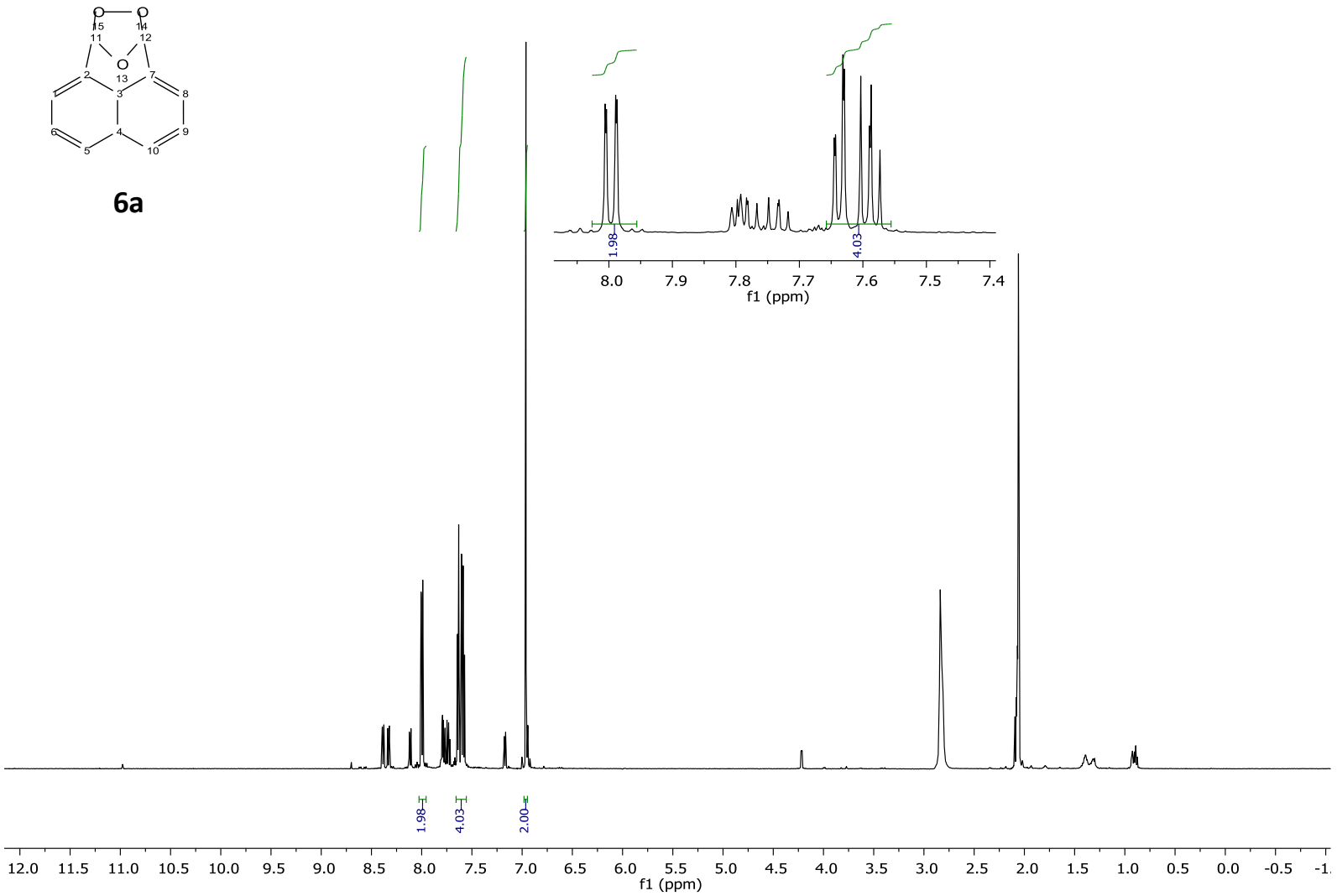


Figure 52. ^{1}H NMR spectrum of acenapthylene oxidation product **6a** in Acetone-D_6.

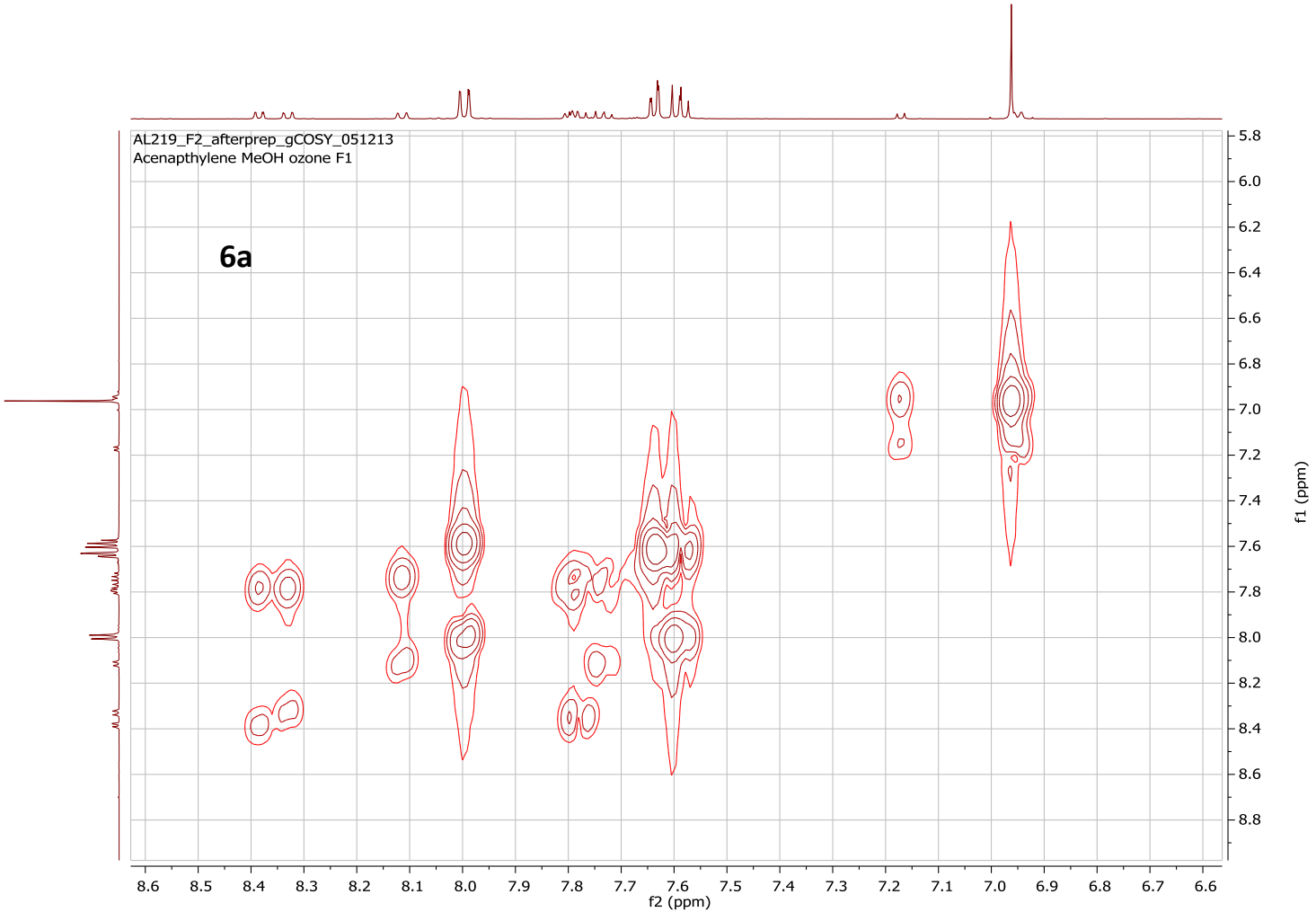


Figure 53. COSY NMR spectrum of acenapthylene **6** oxidation product **6a** in Acetone-D_6.

Cartesian coordinates and absolute energies

Pyrene

absolute energy
HF=-615.892818
Coordinates

C	1.427345	-1.234703	0.000000
C	2.829007	1.208717	0.000000
C	0.712555	0.000000	0.000000
C	2.829007	-1.208717	0.000000
C	3.518312	0.000000	0.000000
C	1.427345	1.234703	0.000000
H	3.377406	-2.146168	0.000000
H	4.603757	0.000000	0.000000
H	3.377406	2.146168	0.000000
C	-0.712555	0.000000	0.000000
C	-3.518312	0.000000	0.000000
C	-1.427345	-1.234703	0.000000
C	-1.427345	1.234703	0.000000
C	-2.829007	1.208717	0.000000
C	-2.829007	-1.208717	0.000000
H	-3.377406	2.146168	0.000000
H	-3.377406	-2.146168	0.000000
H	-4.603757	0.000000	0.000000
C	-0.679201	-2.460764	0.000000
H	-1.226157	-3.399138	0.000000
C	0.679201	-2.460764	0.000000
H	1.226157	-3.399138	0.000000
C	0.679201	2.460764	0.000000
H	1.226157	3.399138	0.000000
C	-0.679201	2.460764	0.000000
H	-1.226157	3.399138	0.000000

Acenaphthylene

absolute energy
HF=-462.179549
Coordinates

H	3.318592	0.000000	0.882057
C	2.386775	0.000000	0.324059
C	1.160491	0.000000	0.954032
C	1.280883	0.000000	-1.873629
C	0.000000	0.000000	0.144662
C	2.425626	0.000000	-1.099188
C	0.000000	0.000000	-1.249763
C	-1.160491	0.000000	0.954032
H	3.394053	0.000000	-1.589671
H	-1.359412	0.000000	-2.956844
H	1.359412	0.000000	-2.956844
C	-2.386775	0.000000	0.324059
H	-3.318592	0.000000	0.882057
C	-2.425626	0.000000	-1.099188
H	-3.394053	0.000000	-1.589671
C	-1.280883	0.000000	-1.873629
C	-0.680515	0.000000	2.345797
H	-1.315134	0.000000	3.223063
C	0.680515	0.000000	2.345797
H	1.315134	0.000000	3.223063

Anthracene

absolute energy
HF=-539.637523
Coordinates

H	4.600902	-1.245165	-0.000168
C	3.655435	-0.712228	-0.000068
H	2.477370	-2.490854	-0.000194
C	2.477022	-1.404634	-0.000099
C	2.477022	1.404634	0.000099
C	1.222135	-0.721413	-0.000017
C	3.655435	0.712228	0.000068
C	1.222135	0.721413	0.000017
C	0.000000	-1.401067	0.000000
H	4.600902	1.245165	0.000168
H	0.000000	2.488094	0.000000
H	2.477370	2.490854	0.000194
C	-1.222135	-0.721413	0.000017
H	0.000000	-2.488094	0.000000
C	-2.477022	-1.404634	0.000099
C	-1.222135	0.721413	-0.000017
H	-2.477370	2.490854	-0.000194
C	0.000000	1.401067	0.000000
C	-3.655435	-0.712228	0.000068
H	-2.477370	-2.490854	0.000194
H	-4.600902	-1.245165	0.000168
C	-3.655435	0.712228	-0.000068
H	-4.600902	1.245165	-0.000168
C	-2.477022	1.404634	-0.000099

Perylene

absolute energy
HF=-769.554191
Coordinates

H	3.435631	-3.346723	0.000000
C	2.896895	-2.404521	0.000000
H	4.666414	-1.198024	0.000000
C	3.580792	-1.214545	0.000000
C	0.747916	-1.242701	0.000000
C	2.876737	0.014115	0.000000
C	1.492672	-2.415094	0.000000
C	1.443429	0.008312	0.000000
C	3.571024	1.248442	0.000000
H	0.996399	-3.377319	0.000000
C	2.877827	2.432931	0.000000
H	4.656745	1.240620	0.000000
H	3.408947	3.379425	0.000000
C	1.473599	2.432094	0.000000
H	0.969549	3.390249	0.000000
C	0.738035	1.253642	0.000000
C	-0.737508	1.247637	0.000000
C	-0.727611	-1.248643	0.000000
C	-1.433101	-0.003318	0.000000
H	-0.958721	-3.385119	0.000000
C	-1.462797	-2.426987	0.000000
C	-2.867030	-2.427900	0.000000
C	-3.570226	1.219790	0.000000
H	-3.424836	3.351972	0.000000
C	-2.886226	2.409708	0.000000
H	-0.985676	3.382259	0.000000
C	-1.482031	2.420073	0.000000
H	-4.655846	1.203328	0.000000
H	-3.398016	-3.374446	0.000000
C	-2.866305	-0.009053	0.000000
C	-3.560428	-1.243453	0.000000
H	-4.646157	-1.235661	0.000000

Benzo [a] Pyrene

absolute energy
HF=-769.554191
Coordinates

C	-0.628855	-0.832910	0.000000
C	-1.488250	1.866967	0.000000
C	0.312118	0.226564	0.000000
C	-2.038386	-0.532047	0.000000
C	-2.455923	0.837920	0.000000
C	-0.133817	1.595998	0.000000
H	-1.826378	2.899962	0.000000
C	1.714162	-0.050032	0.000000
C	4.471654	-0.605350	0.000000
C	2.177508	-1.396473	0.000000
C	2.662612	1.018198	0.000000
C	4.026970	0.718728	0.000000
C	3.562559	-1.650078	0.000000
H	4.747801	1.531259	0.000000
H	3.911326	-2.678545	0.000000
H	5.536721	-0.814460	0.000000
C	1.207915	-2.443188	0.000000
H	1.553429	-3.473067	0.000000
C	-0.127799	-2.172835	0.000000
H	-0.823135	-3.002996	0.000000
C	0.851567	2.647334	0.000000
C	2.177493	2.374582	0.000000
H	2.904836	3.181231	0.000000
H	0.501011	3.675536	0.000000
C	-3.047202	-1.530041	0.000000
H	-2.771526	-2.577310	0.000000
C	-4.382897	-1.203289	0.000000
H	-5.129897	-1.990724	0.000000
C	-4.789316	0.149040	0.000000
H	-5.845859	0.397206	0.000000
C	-3.844038	1.142892	0.000000
H	-4.145483	2.186431	0.000000

Benzo [e] Pyrene

absolute energy
HF=-769.565296
Coordinates

C	1.420935	0.000000	2.111103
C	2.843319	0.000000	-0.296428
C	0.717545	0.000000	0.868036
C	2.823650	0.000000	2.113473
C	3.523603	0.000000	0.919420
C	1.444807	0.000000	-0.356188
H	3.352964	0.000000	3.061607
H	4.608947	0.000000	0.924303
H	3.430309	0.000000	-1.205737
C	-0.717545	0.000000	0.868036
C	-3.523603	0.000000	0.919420
C	-1.420935	0.000000	2.111103
C	-1.444807	0.000000	-0.356188
C	-2.843319	0.000000	-0.296428
C	-2.823650	0.000000	2.113473
H	-3.430309	0.000000	-1.205737
H	-3.352964	0.000000	3.061607
H	-4.608947	0.000000	0.924303
C	-0.677775	0.000000	3.337760
H	-1.228964	0.000000	4.273494
C	0.677775	0.000000	3.337760
H	1.228964	0.000000	4.273494
C	0.709732	0.000000	-1.625248
C	-0.709732	0.000000	-1.625248
C	1.381995	0.000000	-2.865837
H	2.464068	0.000000	-2.893580
C	0.699365	0.000000	-4.065819
H	1.248679	0.000000	-5.001721
C	-0.699365	0.000000	-4.065819
H	-1.248679	0.000000	-5.001721
C	-1.381995	0.000000	-2.865837
H	-2.464068	0.000000	-2.893580