Supporting Information

Single-step in situ synthesis of bimetallic catalysts via gas-phase route: the case of PdZn-ZnO

Andrija Kokanović[a,b], Dunja Pupavac[c], Stephane Chenot[b], Stephane Guilet[b], Igor M. Opsenica[c*], Slavica Stankic[b*]

a Innovative center, Faculty of Chemistry, Belgrade, Ltd., Studentski trg 16, 11158 Belgrade, Serbia

b Sorbonne Université, CNRS UMR 7588, Institut des NanoSciences de Paris INSP, 4 place Jussieu 75252 Paris cedex 05, France

c University of Belgrade – Faculty of Chemistry, PO Box 51, Studentski trg 16, 11158 Belgrade, Serbia

Corresponding Authors:

Igor M. Opsenica, E-mail: igorop@chem.bg.ac.rs

Slavica Stankic, E-mail: slavica.stankic@insp.jussieu.fr

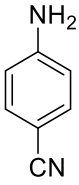
Experimental Procedure and Characterization Data for Products

Materials and Methods

General. Dry-flash chromatography was performed on SiO_2 (0.018–0.032 mm). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Ultrashield Avance III spectrometer (at 500 and 125 MHz, respectively) using $CDCl_3$ (unless stated otherwise) as the solvents. Chemical shifts are expressed in parts per million (ppm) on the (δ) scale. Chemical shifts were calibrated relative to those of the solvent. GC-MS spectra of the synthesized compounds were acquired on an Agilent Technologies 7890A apparatus equipped with a DB-5 MS column (30 m × 0.25 mm × 0.25 μm) or Agilent 19091N-113 column (30 m × 320 μm × 0.25 μm), a 5975C MSD and FID detector. The selected values are as follows: carrier gas was He (1.0 mL/min or 2.0 mL/min, depending on the column, respectively), temperature linearly increased from 40–315 °C (10 °C/min), injection volume: 1 μL, temperature: 250 °C, temperature (FID detector): 300 °C, and EI mass spectra range: m/z 40–550.

General procedure for the reduction of nitroarenes

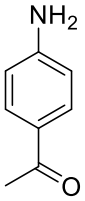
4-Aminobenzonitrile (2a)[1]



2a

To a round bottom cuvette equipped with a magnetic stirrer, 4-aminobenzonitrile **1a** (22.3 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) were added. Hydrogen was introduced into the reaction mixture through a rubber balloon (1 atm H_2) at room temperature, for 3 h. The reaction mixture was separated from the catalyst by filtering it through a thin layer of silica gel, and the layer was washed several times with methylene chloride. Solvents were removed under reduced pressure to obtain **2a** (17.7 mg, 99%) as a pale-yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.19 (s, 2H). **GC-MS**: m/z = 118.1 $[M]^+$.

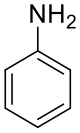
4-Aminoacetophenone (2b)[2]



2b

Following the general procedure for the reduction of nitroarenes, reaction was performed with 4-nitroacetophenone **1b** (24.8 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 8 h, to obtain **2b** (19.7 mg, 97%) as a pale-yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.79 (dd, *J* = 8.6, 1.5 Hz, 2H), 6.63 (dd, *J* = 8.7, 1.2 Hz, 2H), 4.20 (s, 2H), 2.49 (s, 3H). **GC-MS**: m/z = 135.1 $[M]^+$.

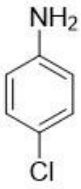
Aniline (2c)[3]



2c

Following the general procedure for the reduction of nitroarenes, reaction was performed with nitrobenzene **1c** (18.5 mg, 0.15 mmol) for 4 h, PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL), to obtain **2c** (13.7 mg, 98%) as an orange liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 7.6 Hz, 2H), 6.77 (td, *J* = 7.4, 0.9 Hz, 1H), 6.72 – 6.67 (m, 2H), 3.62 (s, 2H). **GC-MS**: m/z = 93.1 $[M]^+$.

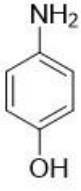
4-Chloroaniline (2d)[4]



2d

Following the general procedure for the reduction of nitroarenes, reaction was performed with 4-chloronitrobenzene **1d** (23.6 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 8 h, to obtain **2e** (18.9 mg, 99%) as an orange solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.10 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 3.63 (s, 2H). **GC-MS**: m/z = 127.1 $[M]^+$.

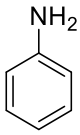
4-Aminophenol (2e)[5]



2e

Following the general procedure for the reduction of nitroarenes, reaction was performed with 4-nitrophenol **1e** (20.9 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 8 h, to obtain **2e** (15.5 mg, 95%) as a pale brown solid. **^{1}H NMR** (500 MHz, CD_3OD) δ = 6.66 – 6.62 (m, 2H), 6.62 – 6.58 (m, 2H). **GC-MS**: m/z = 109.1 $[M]^+$.

Aniline (2c)[3]

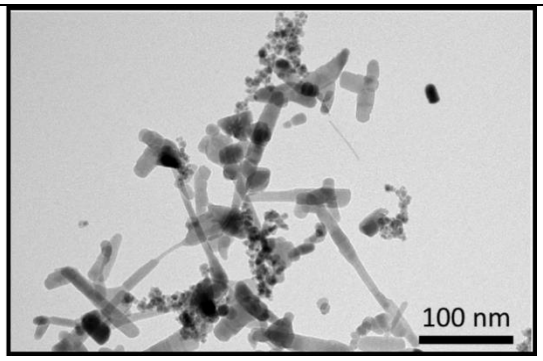
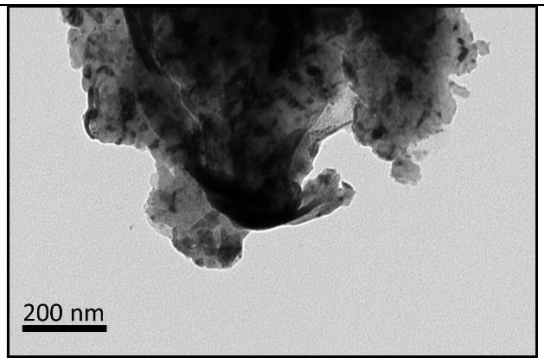


2c

Following the general procedure for the reduction of nitroarenes, reaction was performed with 4-bromonitrobenzene **1f** (30.3 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 8 h, to obtain **2c** (13.6 mg, 97 %) as an orange liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 7.6 Hz, 2H), 6.77 (td, *J* = 7.4, 0.9 Hz, 1H), 6.72 – 6.67 (m, 2H), 3.62 (s, 2H). **GC-MS**: m/z = 93.1 $[M]^+$.

Recycling of PdZn-ZnO catalyst for the hydrogenation of 4-nitrobenzonitrile (1a)

Reaction conditions were as follows: 4-nitrobenzonitrile **1a** (44.6 mg, 0.3 mmol), PdZn-ZnO (4.0 mg, 2.5 mol% Pd), MeOH (2.0 mL), room temperature, 3 h. Upon completion of the reaction cycle, the reaction mixture was centrifuged and decanted. Afterwards, the catalyst was washed with MeOH (2 × 1.0 mL) and dried under vacuum until completely dry. The catalyst was then used in the second and further reaction cycles, following the general procedure.

	
as-synthesized catalyst	catalyst after eight catalytic cycles

Hot filtration test

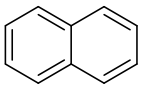
Reaction conditions were as follows: 4-nitrobenzonitrile **1a** (22.3 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd), MeOH (1.0 mL), room temperature, 3 h. Upon completion of the reaction cycle, the reaction mixture was heated at 50 °C and filtered through a hot funnel. **1a** (22.3 mg, 0.15 mmol) and MeOH (1 mL) were added into the obtained, clear filtrate, and the reaction proceeded for additional 3 h. Upon completion of the reaction cycle, column chromatography (Hex:EtOAc) was used to separate the starting compound from the product. 18.5 mg (83%) of **1a** was recovered from the reaction mixture.

Scale-up test

Following the general procedure for the reduction of nitroarenes, scale-up reaction was performed with 4-nitrobenzonitrile **1a** (148.1 mg, 1.0 mmol), PdZn-ZnO (13.3 mg, 2.5 mol% Pd) and MeOH (20.0 mL) for 3h, to obtain **2a** (114.6 mg, 97%) as a pale-yellow solid.

General procedure for the hydrodebromination of bromoarenes

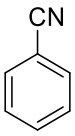
Naphthalene (4a)[6]



4a

To a round bottom cuvette equipped with a magnetic stirrer, 2-bromonaphtalene **3a** (31.1 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) were added. Hydrogen was introduced into the reaction mixture through a rubber balloon (1 atm H_2) at room temperature, for 24 h. The reaction mixture was separated from the catalyst by filtering it through a thin layer of silica gel, and the layer was washed several times with methylene chloride. Solvents were removed under reduced pressure to obtain to obtain **4a** (18.4 mg, 96%), as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.86 (dd, J = 6.2, 3.3 Hz, 4H), 7.50 (dd, J = 6.3, 3.2 Hz, 4H). **GC-MS**: m/z = 128.1 $[M]^+$.

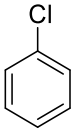
Benzonitrile (4b)



4b

Following the general procedure for the hydrodebromination of bromoarenes, reaction was performed with 4-bromobenzonitrile **3b** (27.3 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 4 h, to afford **4b. GC-MS** yield: 93%, based on naphthalene as an internal standard. GC-MS: m/z = 103.0 $[M]^+$.

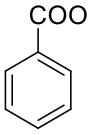
Chlorobenzene (4c)



4c

Following the general procedure for the hydrodebromination of bromoarenes, reaction was performed with 1-bromo-4-chlorobenzene **3c** (28.7 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 24 h, to afford **4c. GC-MS** yield: 95%, based on naphthalene as an internal standard. GC-MS: m/z = 112.0 $[M]^+$.

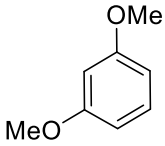
Benzoic acid (4d)[7]



4d

Following the general procedure for the hydrodebromination of bromoarenes, reaction was performed with 4-bromobenzoic acid **3d** (30.2 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 24 h, to afford **4d** (17.9 mg, 98%), as a. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H). **GC-MS**: m/z = 122.1 $[M]^+$.

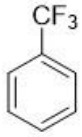
1,3-Dimethoxybenzene (4e)[8]



4e

Following the general procedure for the hydrodebromination of bromoarenes, reaction was performed with 1-bromo-3,5-dimethoxybenzene **3e** (32.6 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 3 h, to afford **4e** (20.7 mg, 99%), as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.19 (t, J = 8.2 Hz, 1H), 6.52 (dd, J = 8.2, 2.4 Hz, 2H), 6.48 (t, J = 2.3 Hz, 1H), 3.80 (s, 6H). **GC-MS**: m/z = 138.1 $[M]^+$.

(Trifluoromethyl)benzene (4f)

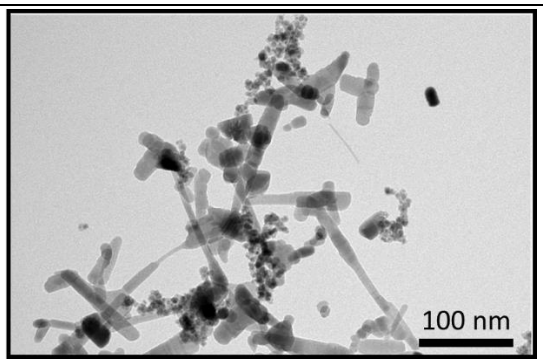
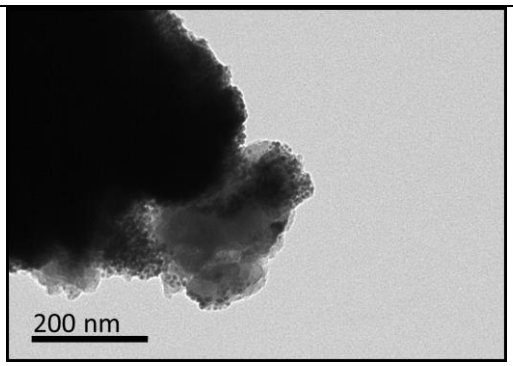


4f

Following the general procedure for the hydrodebromination of bromoarenes, reaction was performed with 1-bromo-3-(trifluoromethyl)benzene **3f** (33.8 mg, 0.15 mmol), PdZn-ZnO (2.0 mg, 2.5 mol% Pd) and methanol (2.0 mL) for 24 h, to afford **4f. GC-MS** yield: 99%, based on naphthalene as an internal standard. GC-MS: m/z = 146.0 $[M]^+$.

Recycling of PdZn-ZnO catalyst for the hydrodebromination of 1-bromo-3,5-dimethoxybenzene (3e)

Reaction conditions were as follows: 1-bromo-3,5-dimethoxybenzene **3e** (65.2 mg, 0.3 mmol), PdZn-ZnO (4.0 mg, 2.5 mol%), MeOH (2.0 mL), room temperature, 3 h. Upon completion of the reaction cycle, the reaction mixture was centrifuged and decanted. Afterwards, the catalyst was washed with MeOH (2 × 1.0 mL) and dried under vacuum until completely dry. The catalyst was then used in the second and further reaction cycles, following the general procedure.

	
as-synthesized catalyst	catalyst after three catalytic cycles

Figures

TEM

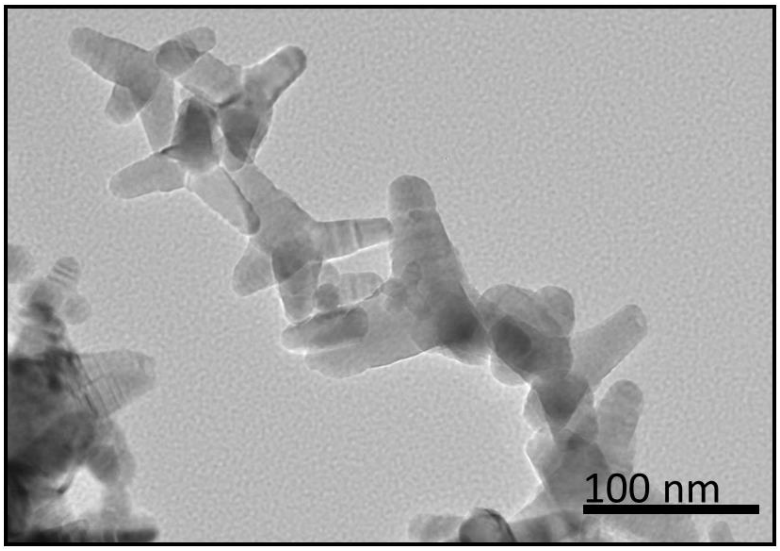


Figure S1. TEM image of CVS-ZnO.

XPS

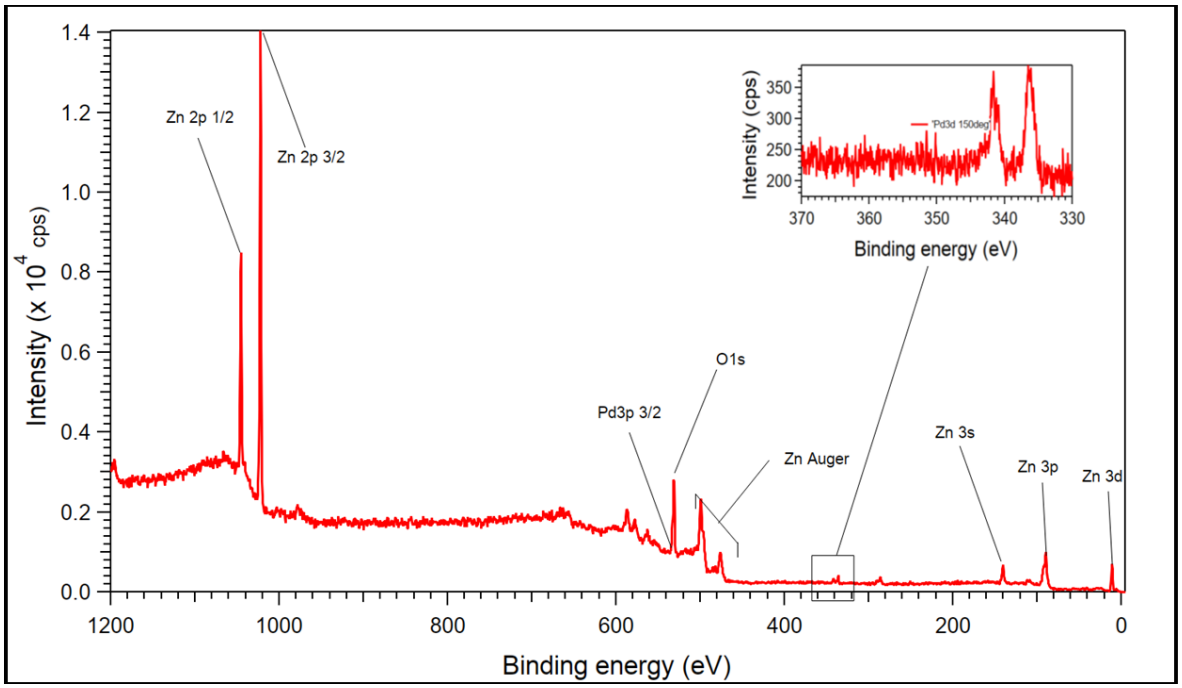


Figure S2. XPS wide scan.

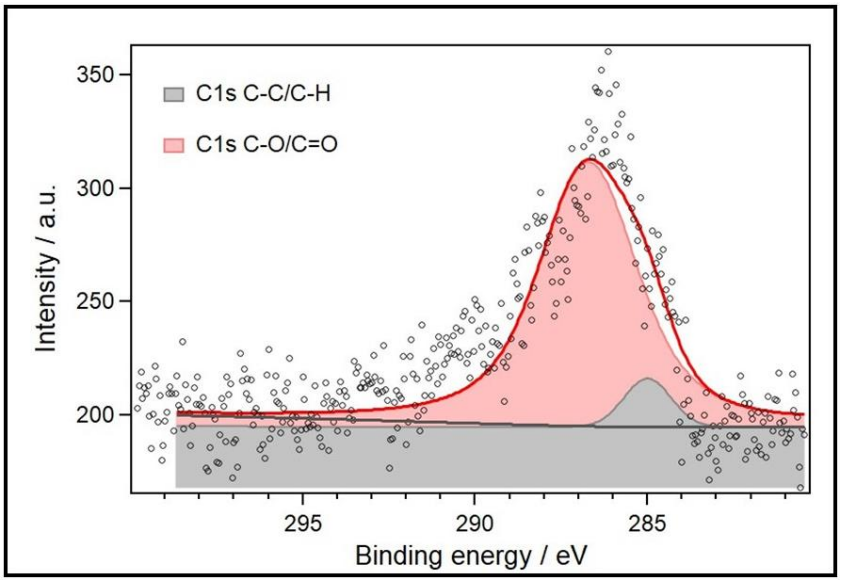


Figure S3. C1s region of XPS spectrum.

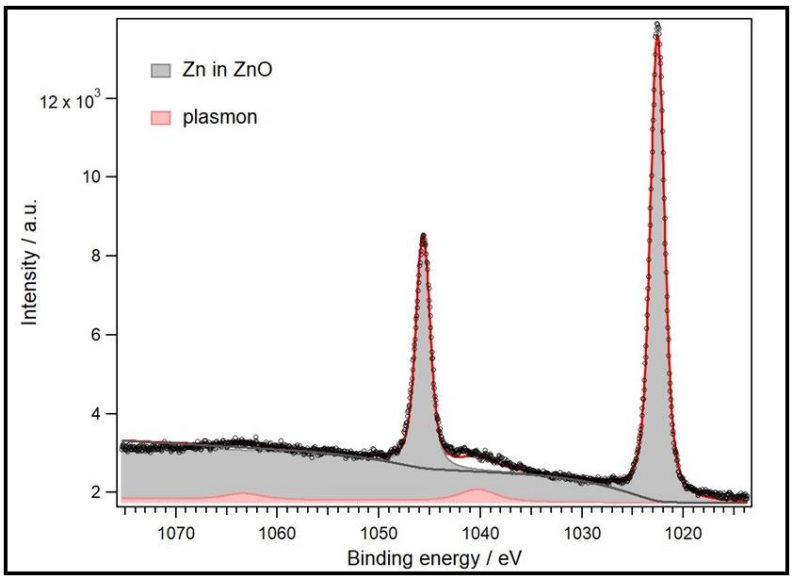


Figure S4. Zn2p region of XPS spectrum.

References

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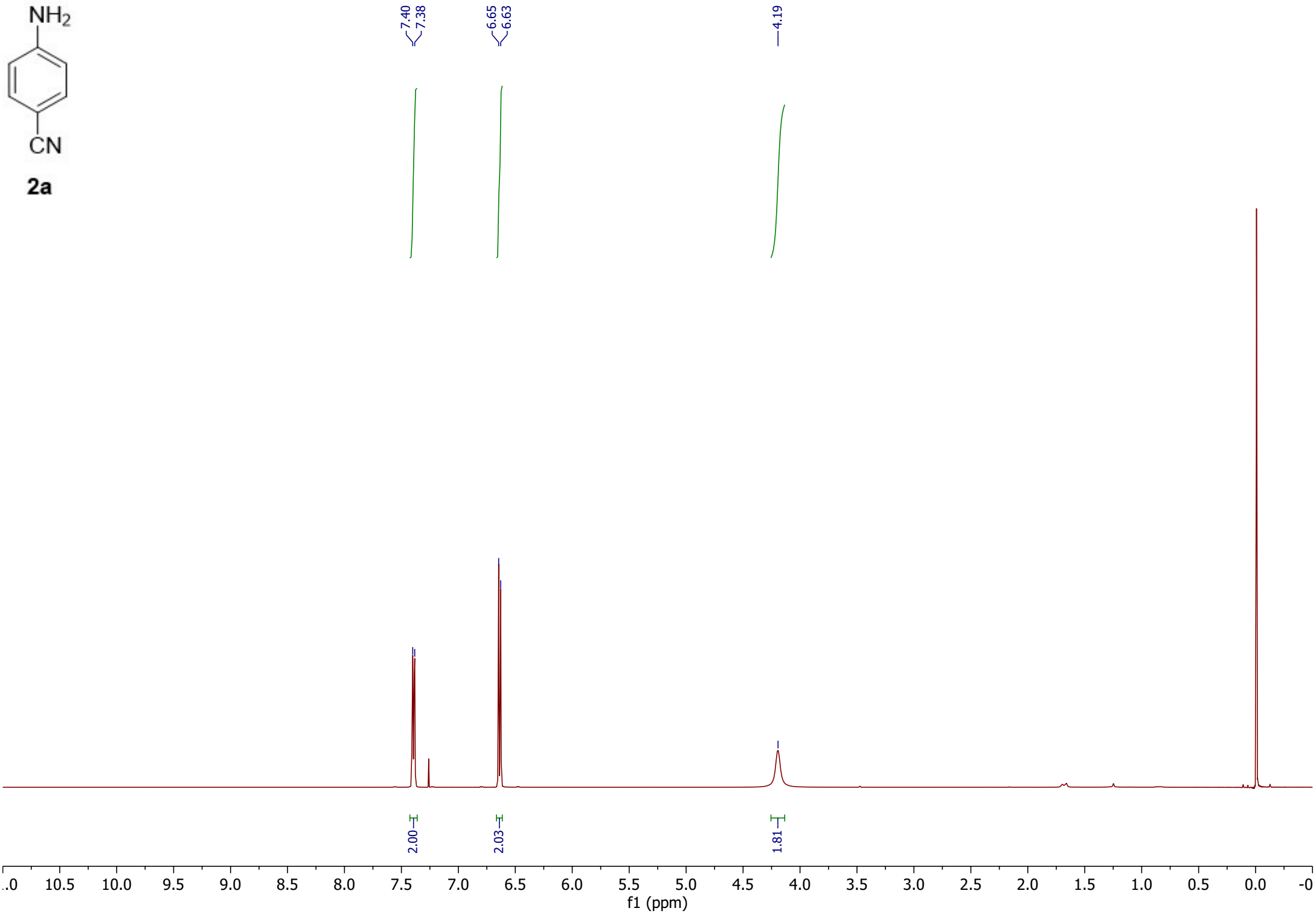
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CN
2a
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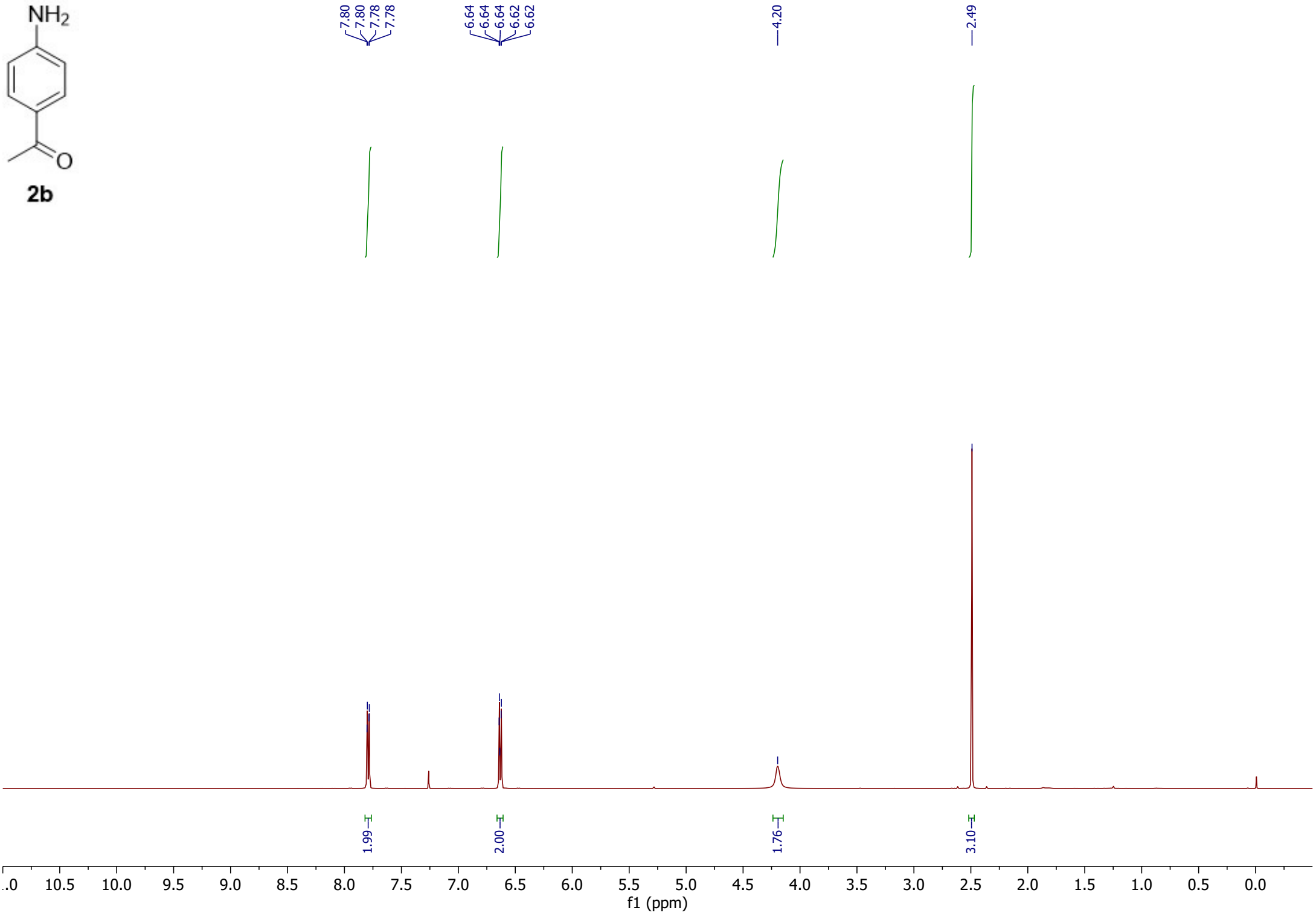
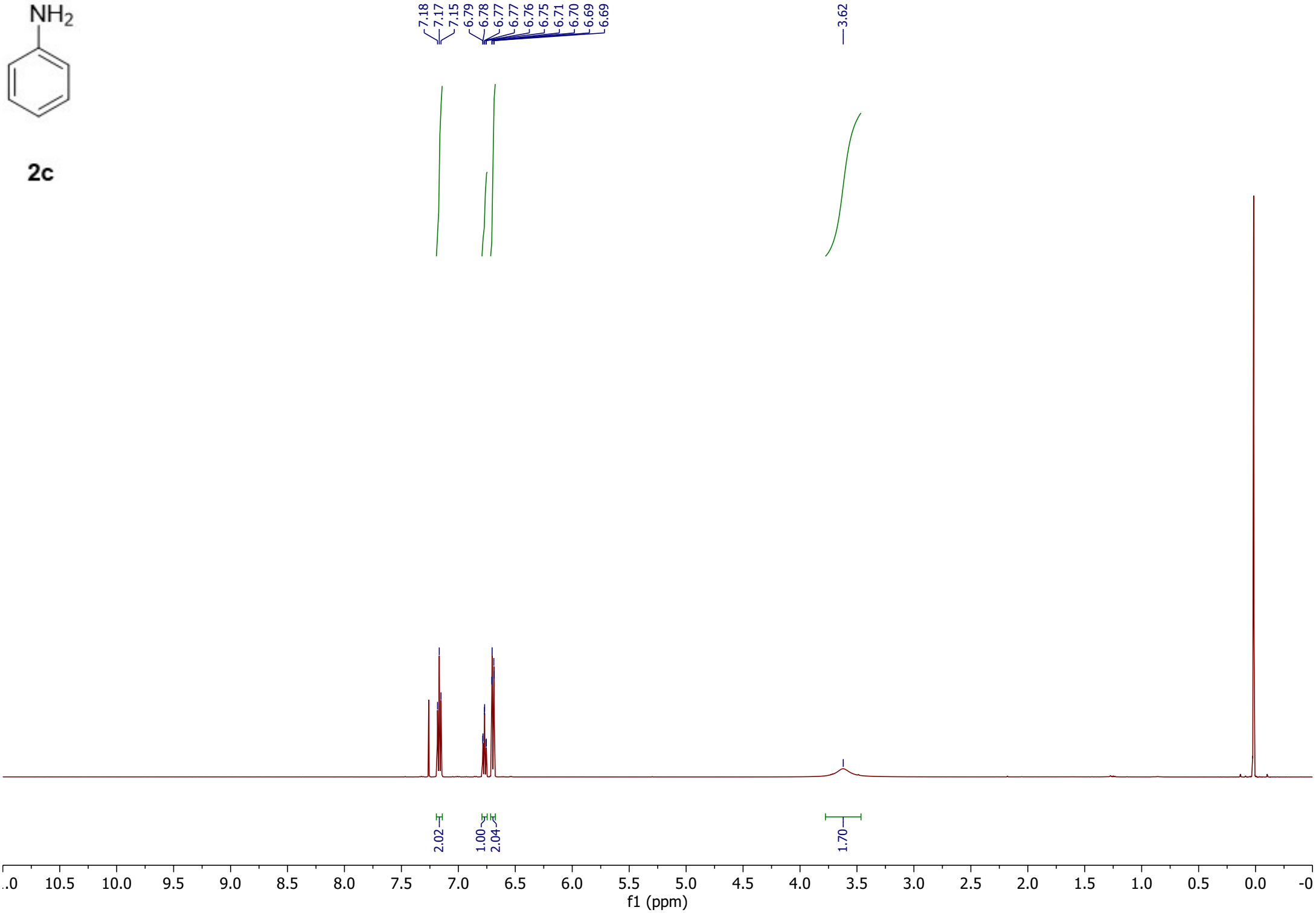
7.38
6.65
6.63
4.19
2.00
2.03
1.81
f1 (ppm)


NH2
O
2b
7.80
7.80
7.78
7.78
6.64
6.64
6.64
6.62
6.62
4.20
2.49
1.99
2.00
1.76
3.10
f1 (ppm)


NH2
2c
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7.15
6.79
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6.77
6.77
6.76
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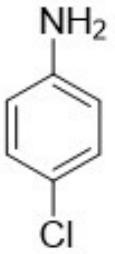
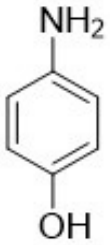
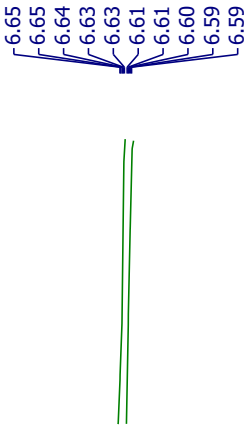
1.00
2.04
1.70
f1 (ppm)

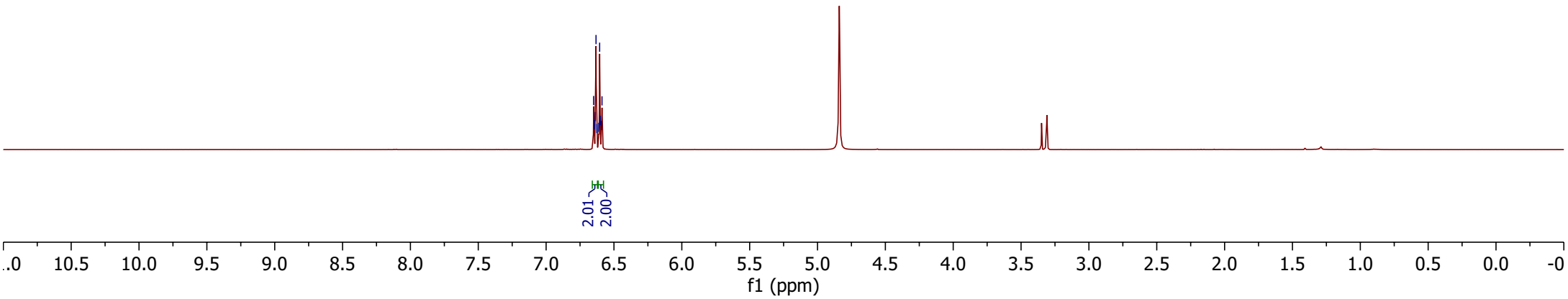


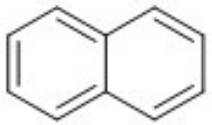
2d


NH2
OH

2e


6.65
6.65
6.64
6.63
6.63
6.61
6.61
6.60
6.59
6.59


2.01
2.00
10.5
10.0
9.5
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
1.5
1.0
0.5
0.0
f1 (ppm)

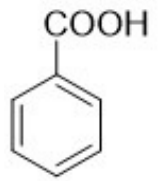


4a

7.87
7.87
7.86
7.86
7.51
7.50
7.50
7.49

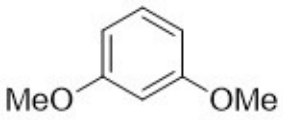
4.00
3.96

f1 (ppm)

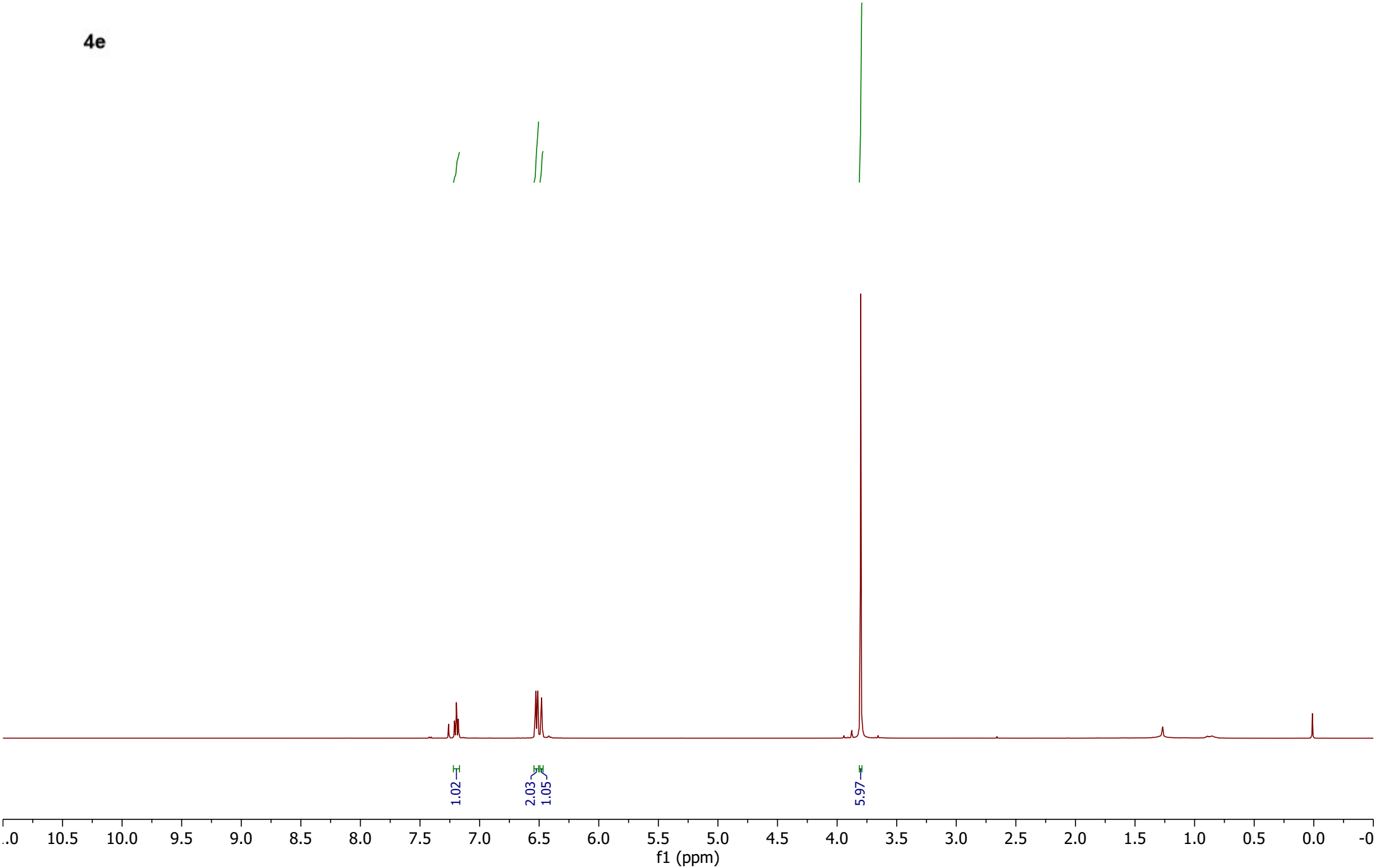

COOH

4d

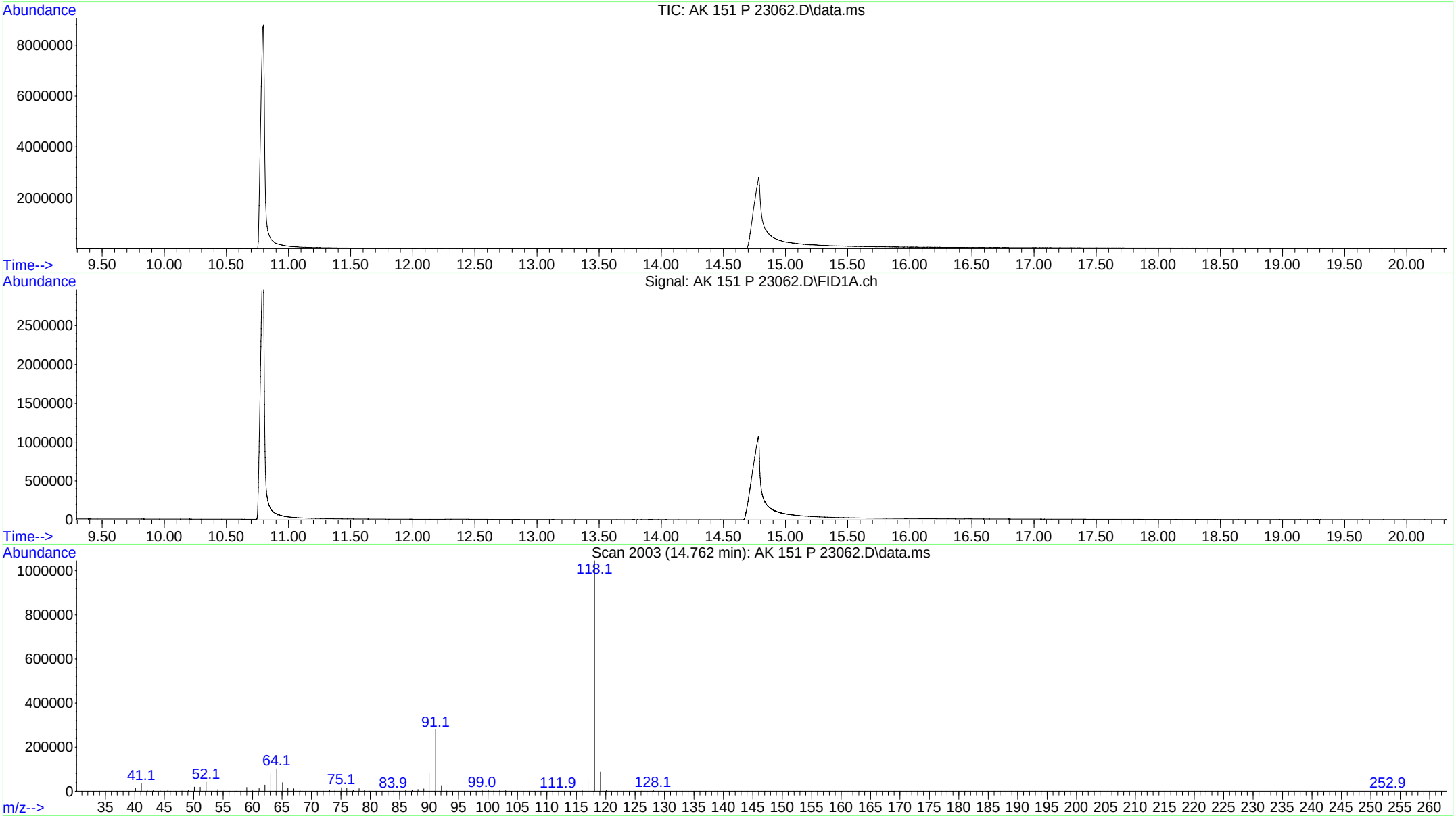
8.13
8.12
7.64
7.62
7.61
7.50
7.49
7.47
7.26 CDCl3
2.00
1.17
2.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


MeO
OMe

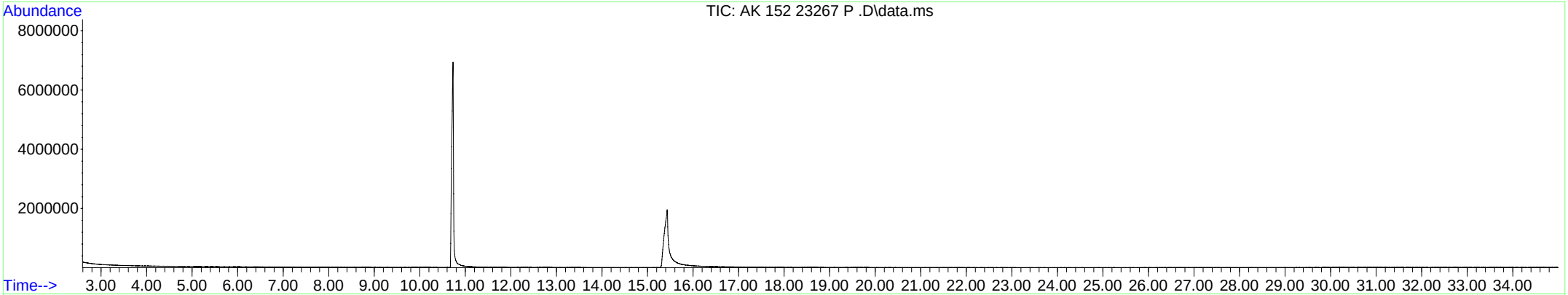
4e

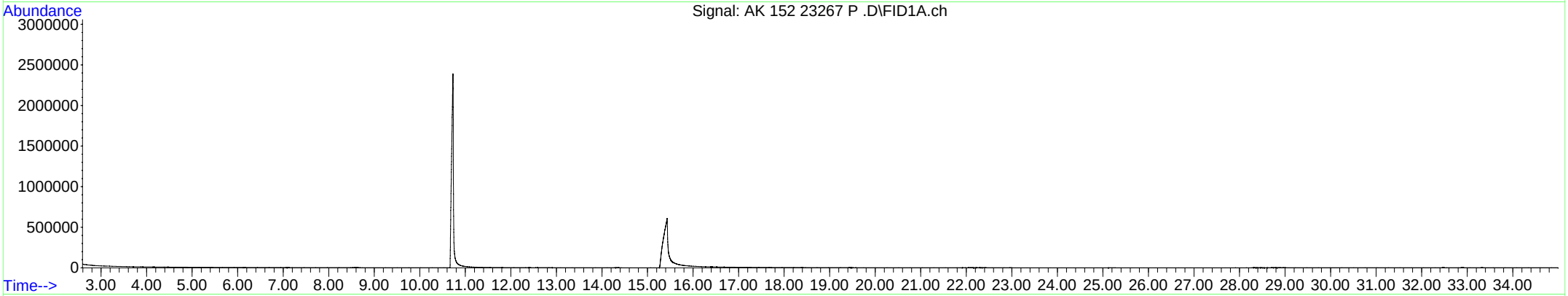

1.02
2.03
1.05
5.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

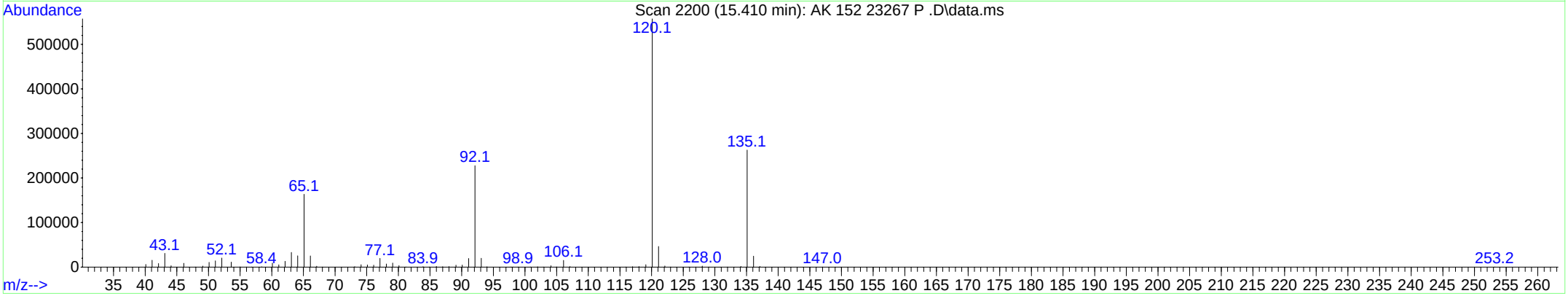
File :C:\MSD DATA\Sekvenca\20240212\AK 151 P 23062.D
Operator :
Acquired : 12 Feb 2024 23:18 using AcqMethod QC 5.M
Instrument : GCMS
Sample Name: **2a**
Misc Info :
Vial Number: 63



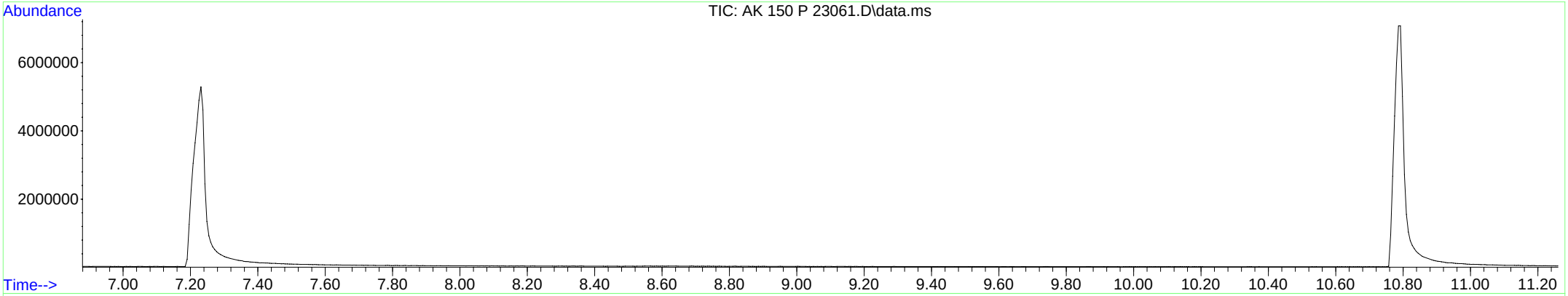
File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\AK 152 23
... 267 P .D
Operator :
Instrument : GCMS
Acquired : 27 Feb 2024 13:51 using AcqMethod QC 5 ak.M
Sample Name: **2b**
Misc Info :

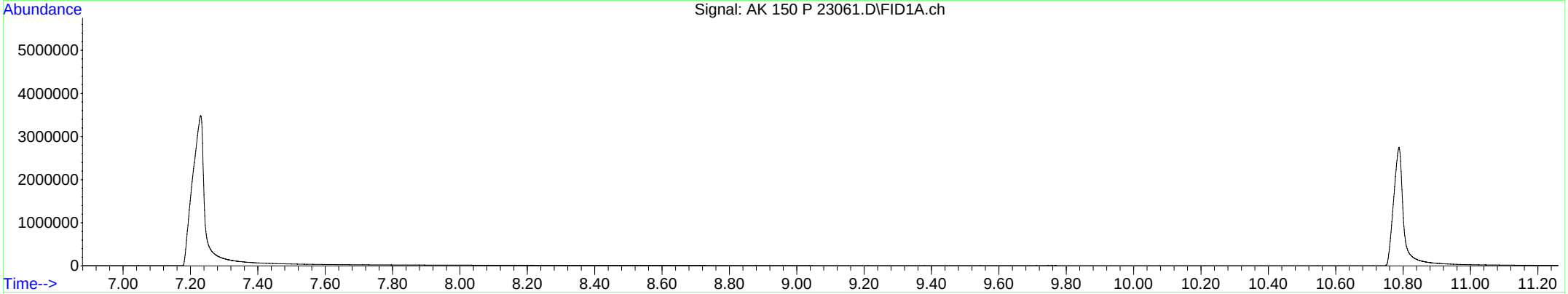


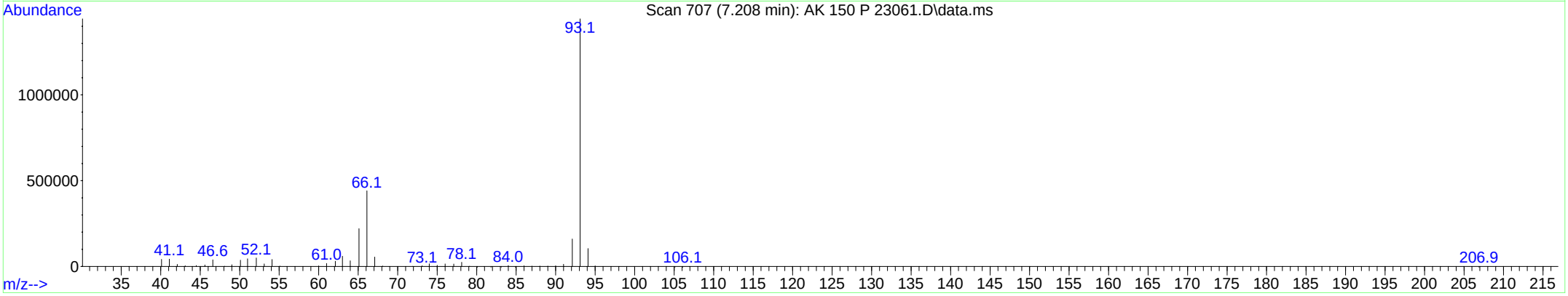




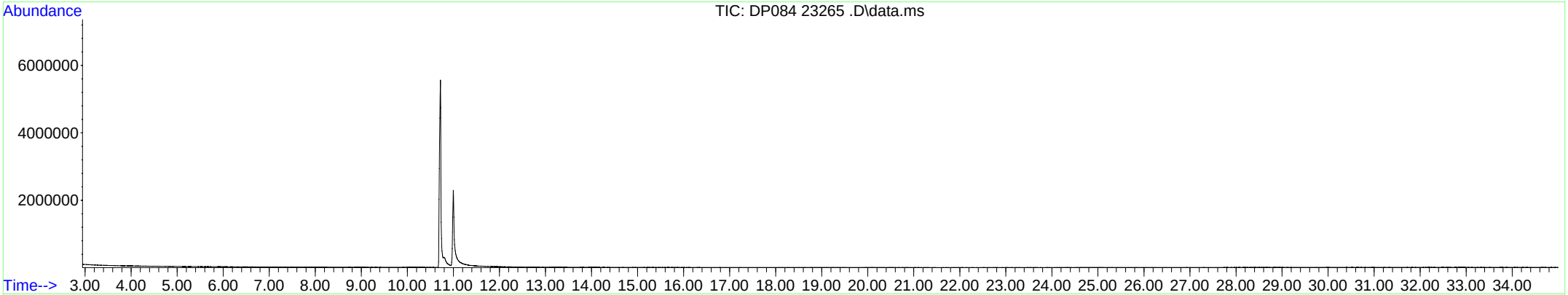
File :C:\MSD DATA\Sekvenca\20240212\AK 150 P 23061.D
Operator :
Acquired : 12 Feb 2024 20:25 using AcqMethod QC 5.M
Instrument : GCMS
Sample Name: **2c**
Misc Info :
Vial Number: 59

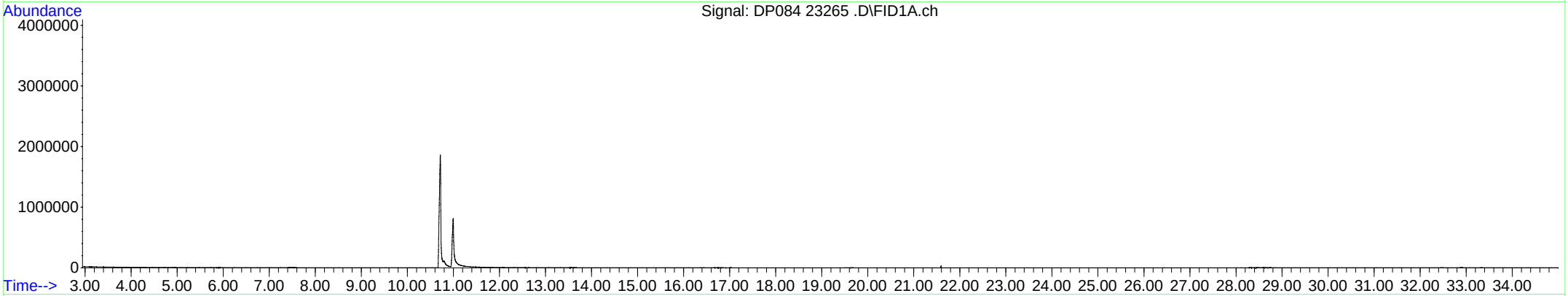


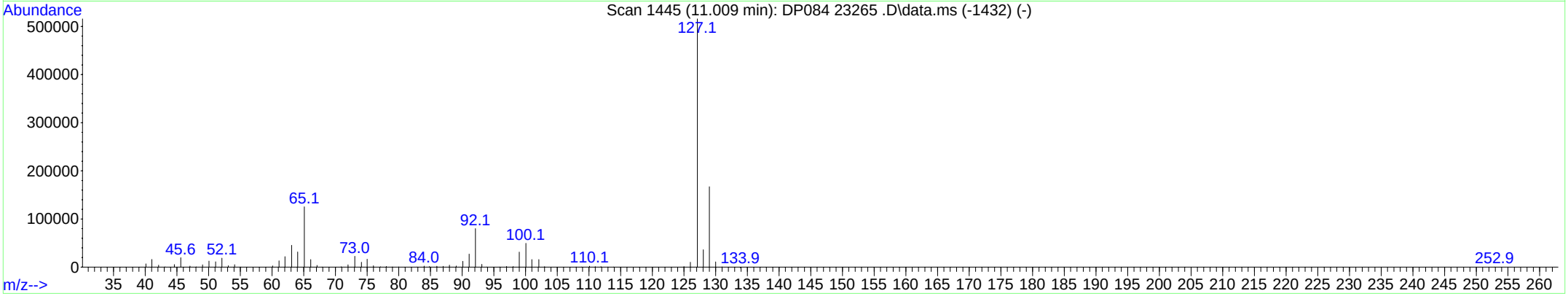




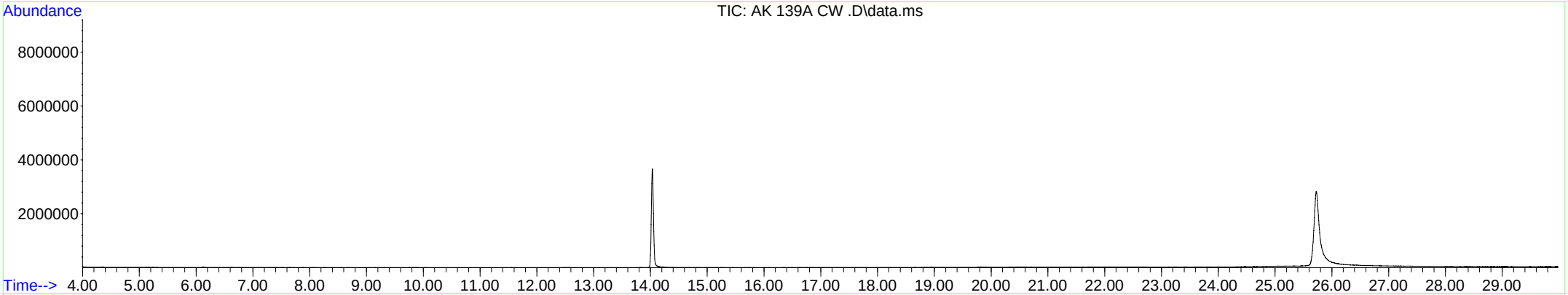
File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\DP084 232
... 65 .D
Operator :
Instrument : GCMS
Acquired : 27 Feb 2024 12:23 using AcqMethod QC 5 ak.M
Sample Name: **2d**
Misc Info :

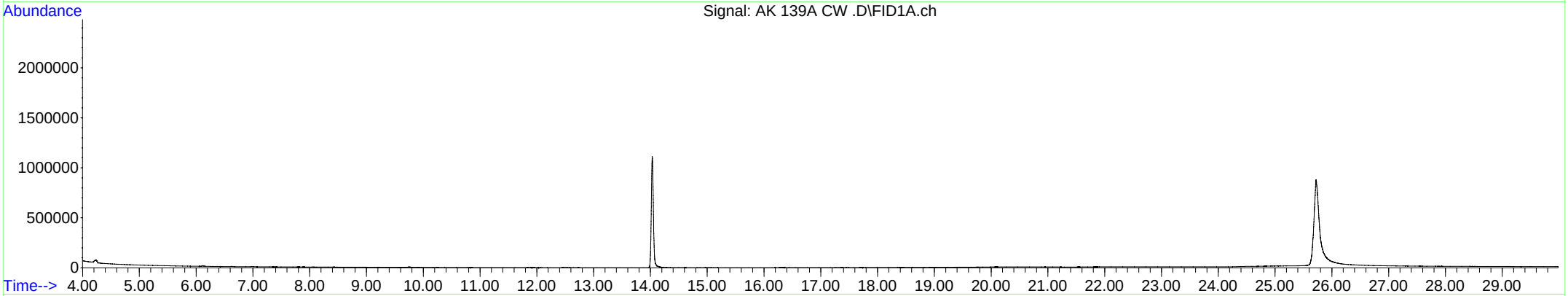


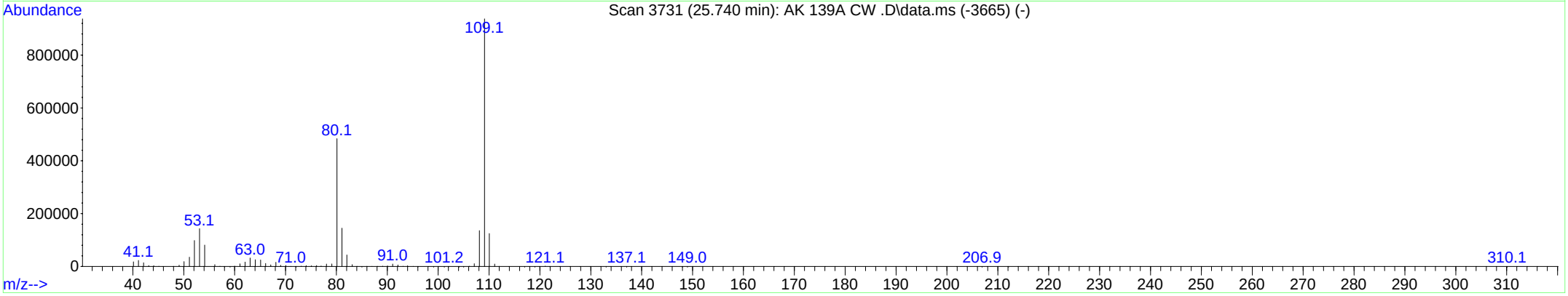




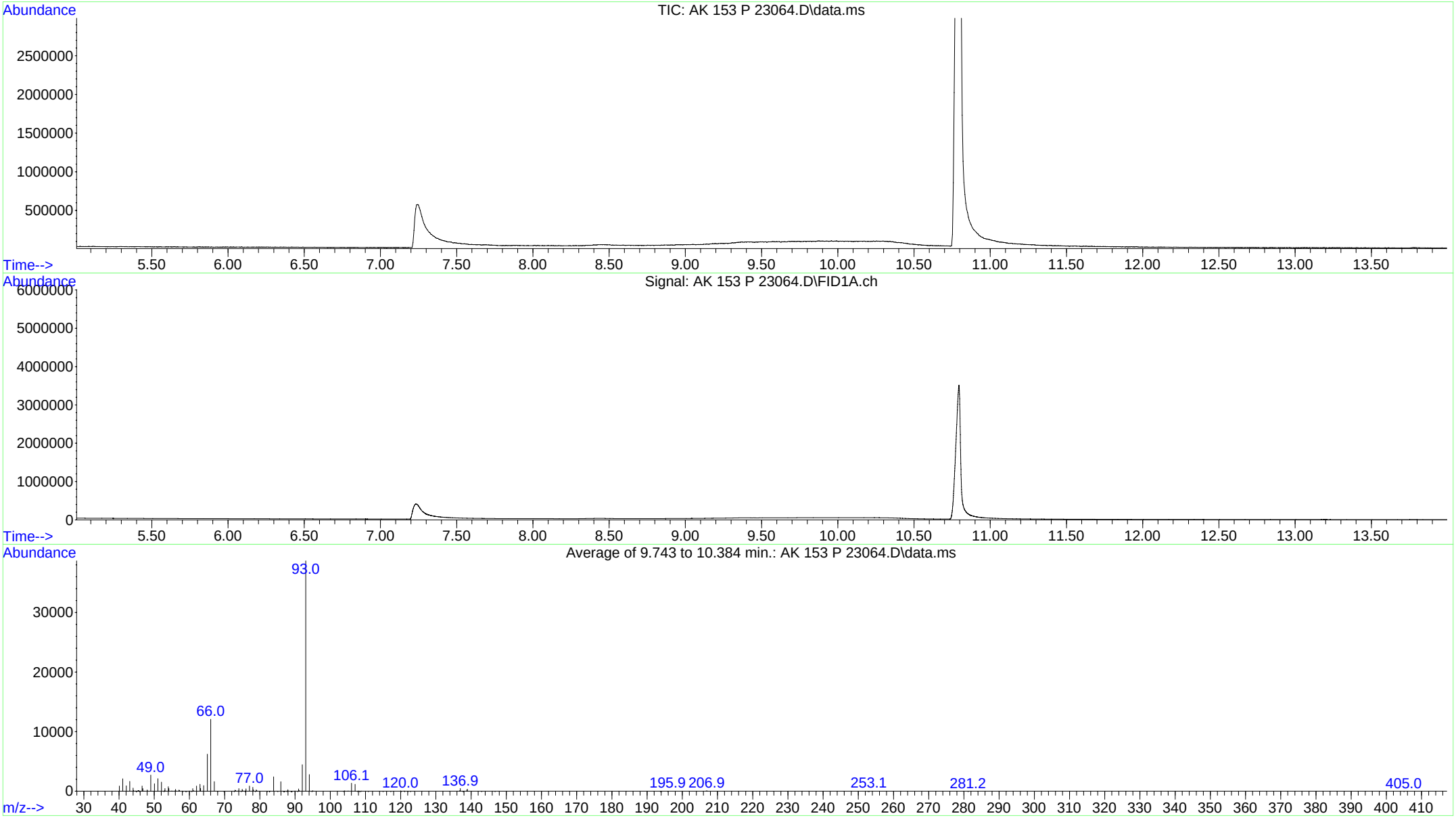
File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\AK 139A C
... W .D
Operator :
Instrument : GCMS
Acquired : 28 Feb 2024 12:48 using AcqMethod CW O 10.M
Sample Name: **2e**
Misc Info :



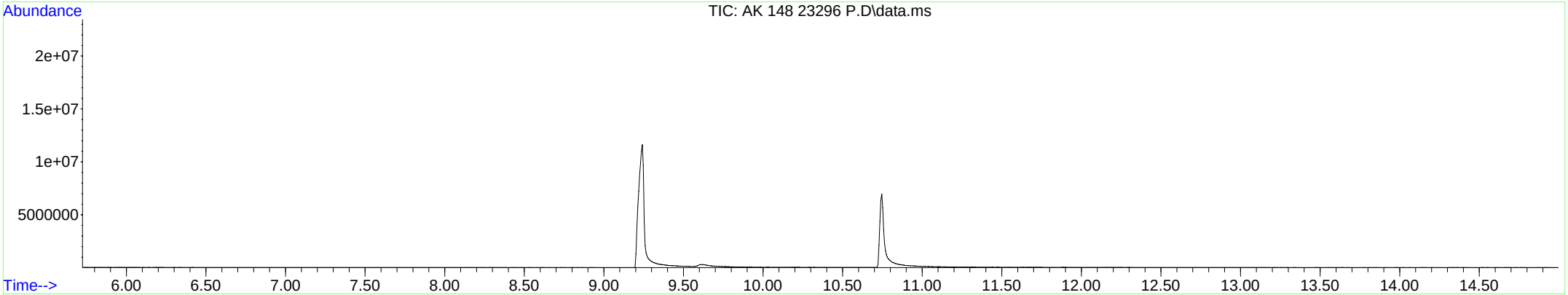


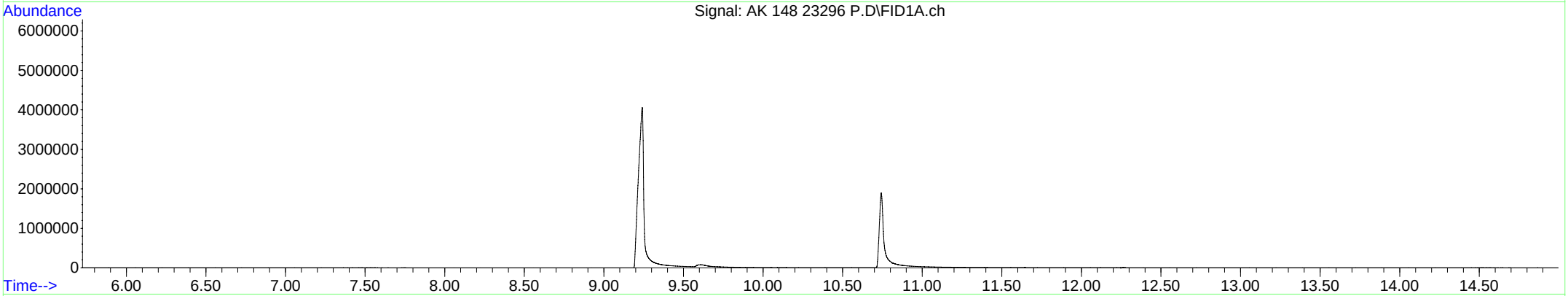


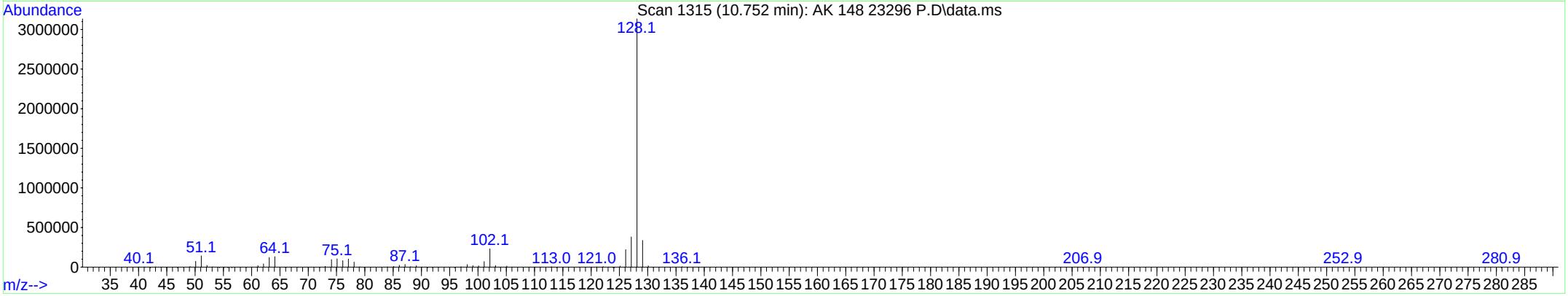
File :C:\MSD DATA\Sekvenca\20240212\AK 153 P 23064.D
Operator :
Acquired : 12 Feb 2024 21:08 using AcqMethod QC 5.M
Instrument : GCMS
Sample Name: **2c** from **1f**
Misc Info :
Vial Number: 60



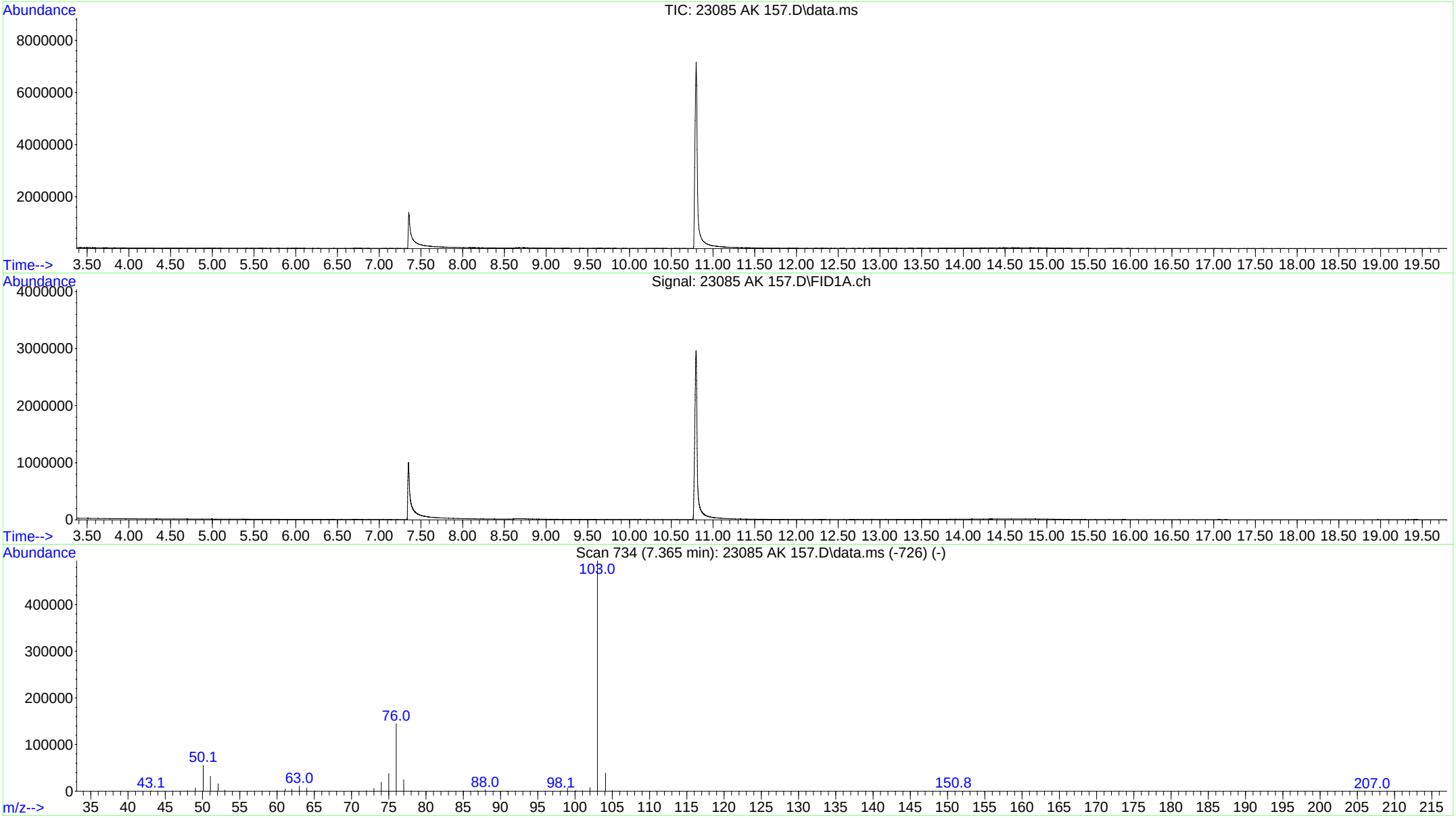
File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\AK 148 23
... 296 P.D
Operator :
Instrument : GCMS
Acquired : 29 Feb 2024 12:07 using AcqMethod QC 10.M
Sample Name: **4a**
Misc Info :



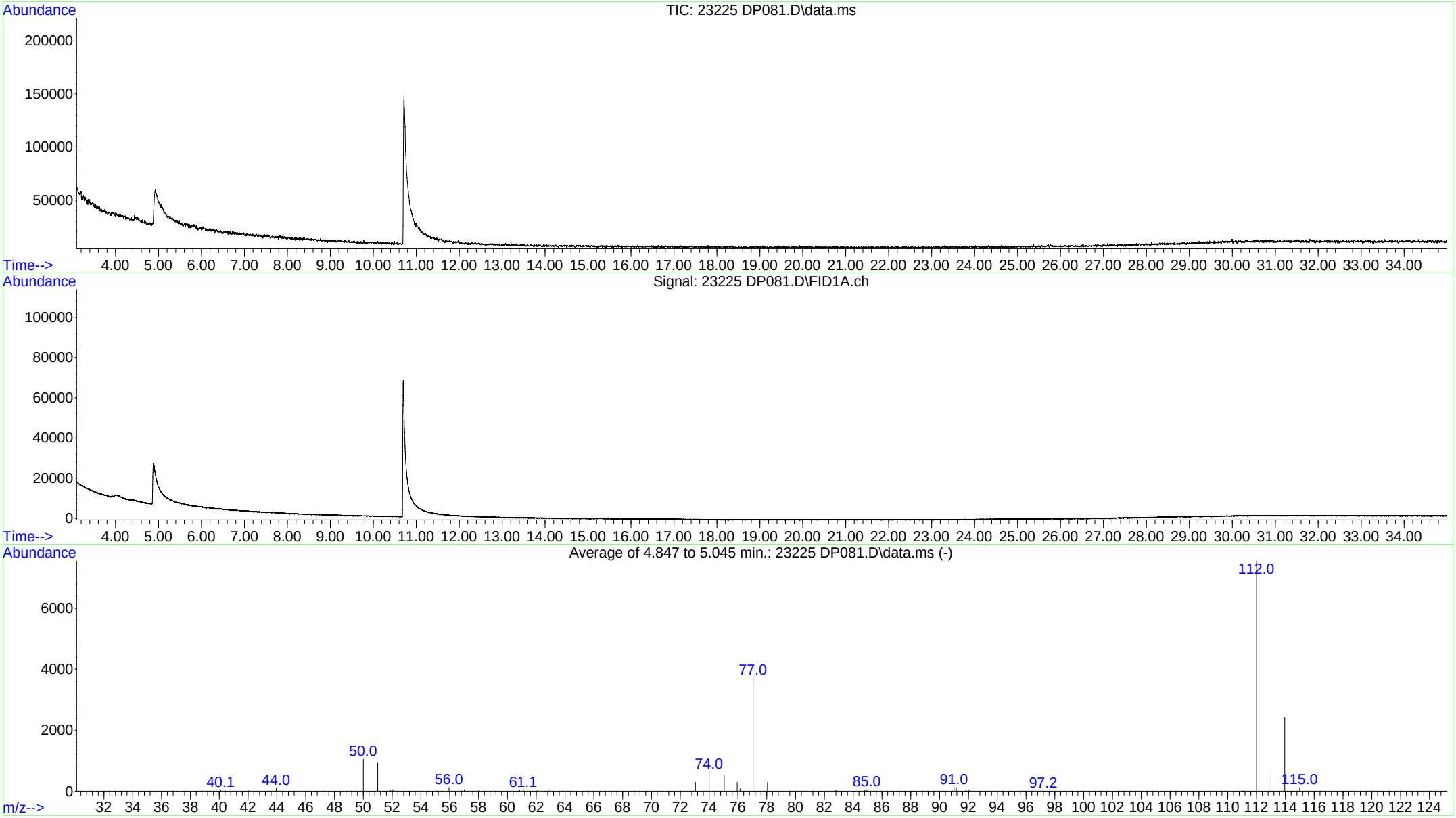




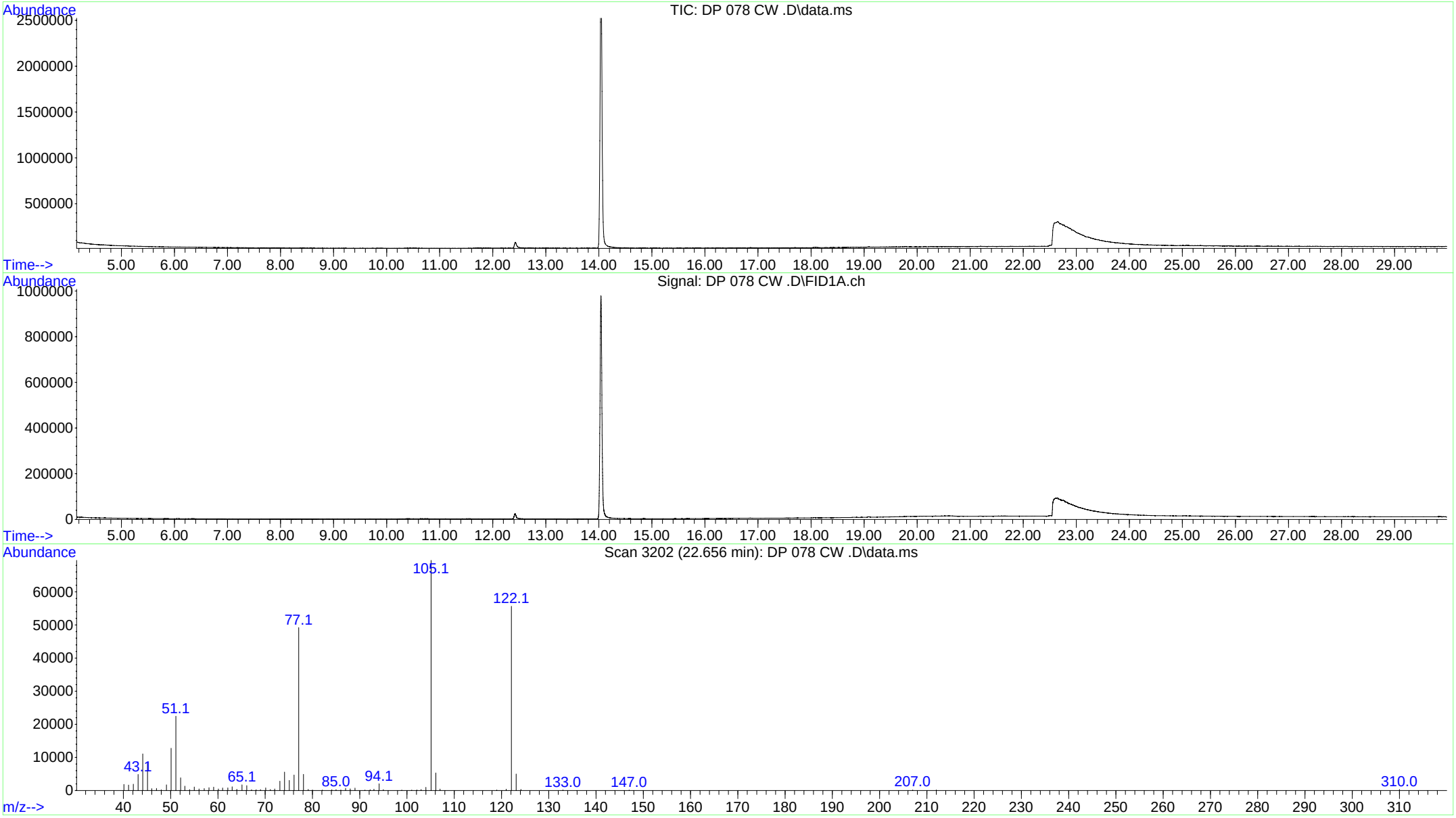
File :C:\MSD DATA\Sekvenca\20240213\23085 AK 157.D
Operator :
Acquired : 13 Feb 2024 17:30 using AcqMethod QC 10.M
Instrument : GCMS
Sample Name: **4b**
Misc Info :
Vial Number: 27



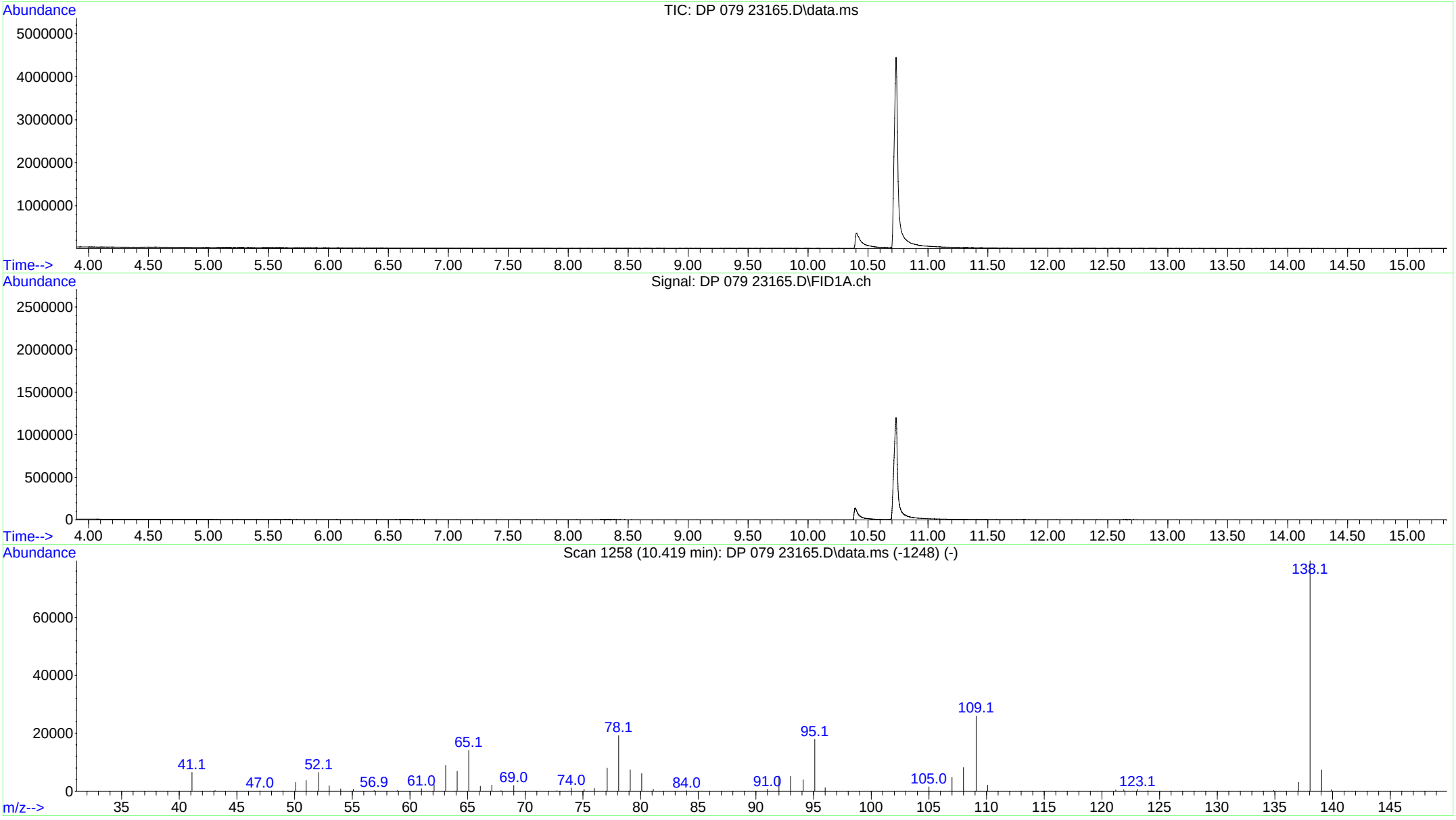
File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\23225 DP0
... 81.D
Operator :
Instrument : GCMS
Acquired : 23 Feb 2024 18:10 using AcqMethod QC 10.M
Sample Name: **4c**
Misc Info :



File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\DP 078 CW
... .D
Operator :
Instrument : GCMS
Acquired : 28 Feb 2024 12:10 using AcqMethod CW O 10.M
Sample Name: **4d**
Misc Info :



File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\DP 079 23
... 165.D
Operator :
Instrument : GCMS
Acquired : 21 Feb 2024 14:57 using AcqMethod QC 10.M
Sample Name: **4e**
Misc Info :



File :C:\MSD DATA\HEMIJA\IGOR OPSENICA\Kokanovic Andrija\23226 DP0
... 83 5SP.D
Operator :
Instrument : GCMS
Acquired : 27 Feb 2024 11:40 using AcqMethod QC 5 ak.M
Sample Name: **4f**
Misc Info :