

Spectroscopic data

Compound 1 (Olea-12-ene 3-O- β -D-glucopyranoside): ^1H NMR (300 MHz, MeOD): δ H: 5.31 (1H, dd, $J=2.6, 0.2$ Hz, H-12), 4.22 (1H, d, $J=8.2$ Hz, H-1'), 3.41 (1H, d, $J=4.1$ Hz, H-3), 3.17 (1H, H-6'), 3.11 (1H, d, $J=9.2$ Hz, H-3'), 3.04 (1H, t), 2.89 (1H, t), 2.08 (1H, s, H-1), 1.86-2.02 (2H, m, H-2) 1.66 (1H, dd, $J=1.6, 6.8$ Hz, H-22), 1.60 (2H, dd, $J=$), 1.46-1.58 (2H, m, H-6) 1.23 (3H, s, H-5), 1.00 (3H, s, H-27) 0.98 (3H, s, H-29), 0.96 (3H, s, H-24), 0.90 (3H, H-25), 0.85 (3H, s,), 0.82 (3H, d, $J=1.9$ Hz, H-23), 0.81 (3H, s, H-30), 0.78 (3H, s, H-26), 0.65 (3H, s, H-28). ^{13}C NMR (75 MHz, DMSO- d_6): δ : 140.9 (C-13), 121.7 (C-12), 101.3 (C-1'), 77.3 (C-3), 77.3 (C-2'), 77.3 (C-4'), 73.9 (C-5'), 70.6 (C-3'), 61.6 (C-6'), 55.9 (C-5), 50.1 (C-18), 49.1 (C-17), 45.6 (C-9), 42.3 (C-14), 40.2 (C-4), 39.7 (C-8), 39.4 (C-20), 39.2 (C-19), 38.8 (C-1), 36.9 (C-10), 35.9 (C-22), 31.9 (C-7), 29.7 (C-21), 29.1 (C-15), 25.9 (C-23), 25.9 (C-2), 23.1 (C-16), 23.1 (C-27), 21.1 (C-30), 19.6 (C-28), 19.6 (C-6), 19.4 (C-29), 19.1 (C-26), 12.3 (C-24), 12.1 (C-25). TOF ES MS m/z 1176.1453 $[2\text{M}]^+$.

Compound 2 (isoquercitrin): ^1H NMR (300 MHz, MeOD): δ 7.73 (1H, d, $J=2.1$ Hz), 7.60 (1H, dd, $J=8.5, 2.1$ Hz), 6.88 (1H, d, $J=8.6$ Hz), 6.41 (1H, d, $J=2.1$ Hz), 6.22 (1H, d, $J=2.1$ Hz), 5.250 (d, 1H, $J=7.6$ Hz). ^{13}C NMR (75 MHz, MeOD): δ 179.5 (C-4), 166.0 (C-7), 163.0 (C-5), 159.0 (C-2), 158.5 (C-9), 149.9 (C-3'), 145.9 (C-4'), 135.6 (C-3), 123.2 (C-6'), 123.1 (C-1'), 117.6 (C-2'), 116.1 (C-5'), 105.7 (C-10), 104.3 (C-1''), 99.9 (C-6), 94.7 (C-8), 78.4 (C-5''), 78.1 (C-3''), 75.7 (C-2''), 71.1 (C-4''), 62.6 (C-6''). TOF ES HRMS m/z 463.0880 $[\text{M-H}]^+$.

Compound 3 (5,7,3',4'-tetrahydroxy-flavonol-3-O- $[\beta$ -D-glucopyranosyl-1 $\rightarrow$ 6)]- β -D-glucopyranoside (quercetin diglycoside): ^1H NMR (300 MHz, MeOD): δ H: 7.72 (1H, d, $J=2.0$), 7.68 (1H, dd, $J=8.4, 2.0$ Hz), 6.88 (1H, d, $J=8.2$ Hz), 6.42 (1H, d, $J=1.9$ Hz), 6.22 (1H, d, $J=1.8$ Hz), 5.25 (1H, d, $J=7.3$ Hz), 4.17 (1H, d, $J=7.6$ Hz). TOF ES HRMS m/z 649.1378 $[\text{M}+\text{Na}]^+$.

Table 1: Carbon 13 NMR data for Compound 1 (Olean-12-en-3-O- β -D-glucopyranoside) compared with literature*

SN	* β -Amyrin (125 MHz CDCl ₃)	Compound 1 (Olean-12-en-3-O- β -D-glucopyranoside) (75 MHz-DMSO _{d6})
1	38.8	38.7
2	27.4	27.8
3	79.2	76.9
4	39.0	39.0
5	55.4	55.4
6	18.6	18.9
7	32.9	31.4
8	40.2	40.1
9	47.4	48.6
10	37.2	36.8
11	23.8	22.6
12	121.9	121.2
13	145.4	140.5
14	41.9	41.8
15	26.4	25..4
16	27.1	28.7
17	32.7	31.3
18	47.8	48.6
19	47.0	45.1
20	31.3	30.7
21	37.4	36.8
22	34.9	35.5
23	15.7	11.7
24	28.3	28.7
25	15.8	11.8
26	17.0	18.6
27	26.2	25.4
28	28.6	29.3
29	33.7	35.5
30	23.9	22.6
1'		100.8
2'		76.8
3'		76.8
4'		73.5
5'		70.1
6'		61.1

* **Okoye *et al.* (2014). Pharm Biol. 52(11): 1478–1486 (Reference 21 in the manuscript):** Please note that the cited literature (Okoye et al., 2014) ^[21] acquired the carbon 13 data in deuterated chloroform at 125 MHz, while for compound 1 spectral data were acquired in deuterated dimethyl sulfoxide on 75 MHz spectrometer. These differences account for the occasional variations (our value vs. literature value), where such variations exist, in the chemical shift values for the carbon atoms.

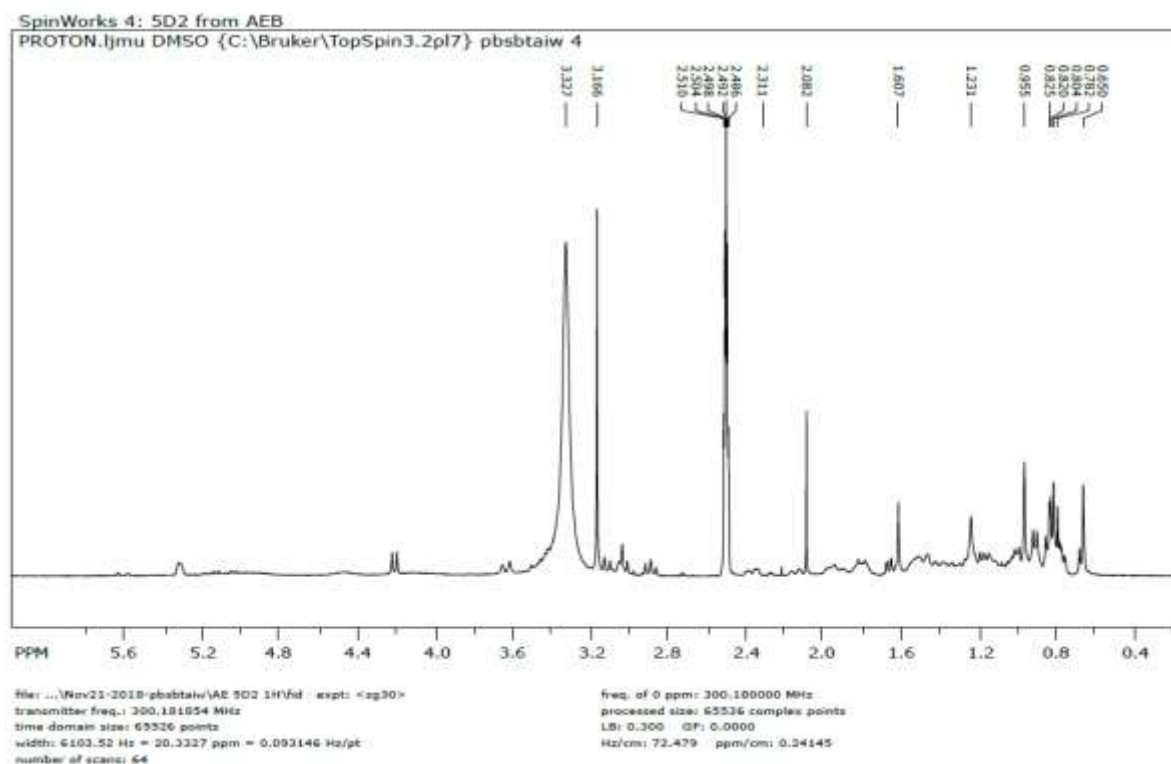
PLEASE NOTE:

Compound 1 (Olea-12-ene 3-O- β -D-glucopyranoside) is **AE 5D2**

Compound 2 (isoquercitrin) is **AE 5B2**

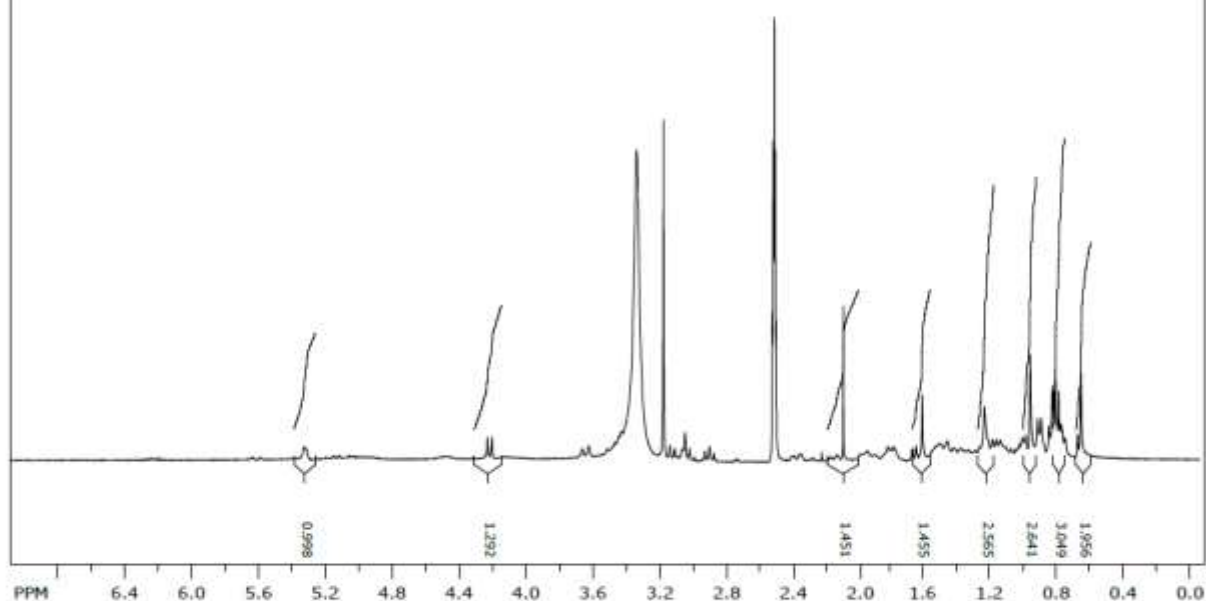
Compound 3 (5,7,3',4'-tetrahydroxy-flavonol-3-O-[β -D-glucopyranosyl-1 $\rightarrow$ 6])- β -D-glucopyranoside) is **AE Biii**

NMR for Compound 1



SpinWorks 4: 5D2 from AEB

PROTON.ljmu DMSO {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 4

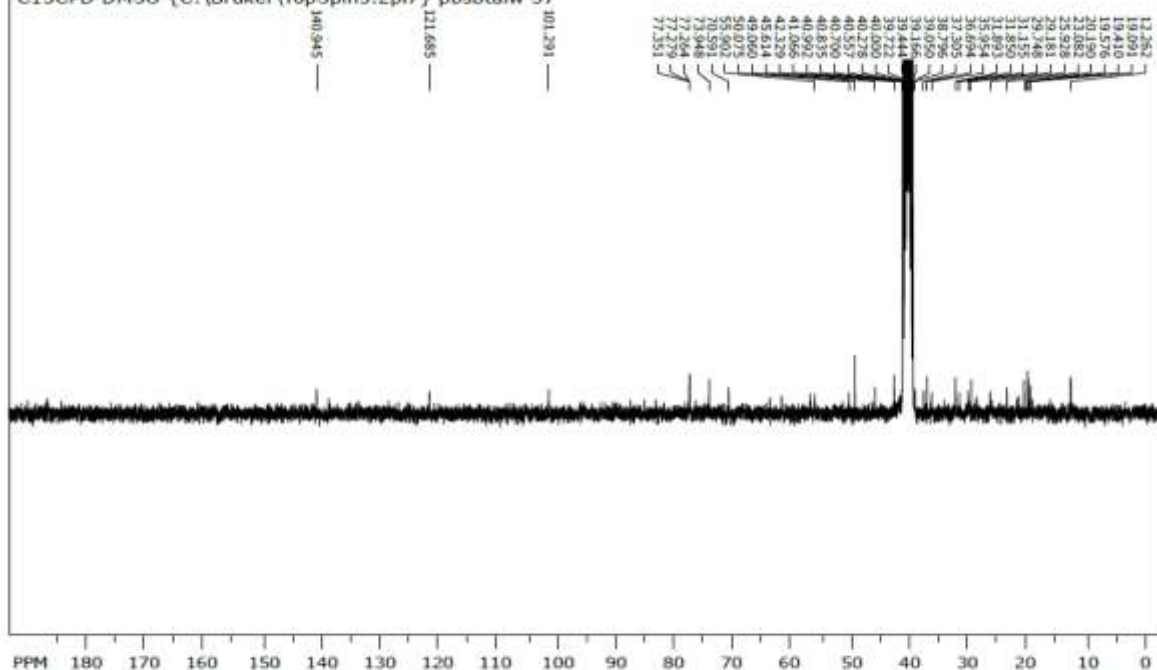


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width: 6103.52 Hz = 20.3327 ppm = 0.093146 Hz/pt
number of scans: 64

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Hz/cm: 86.103 ppm/cm: 0.28684

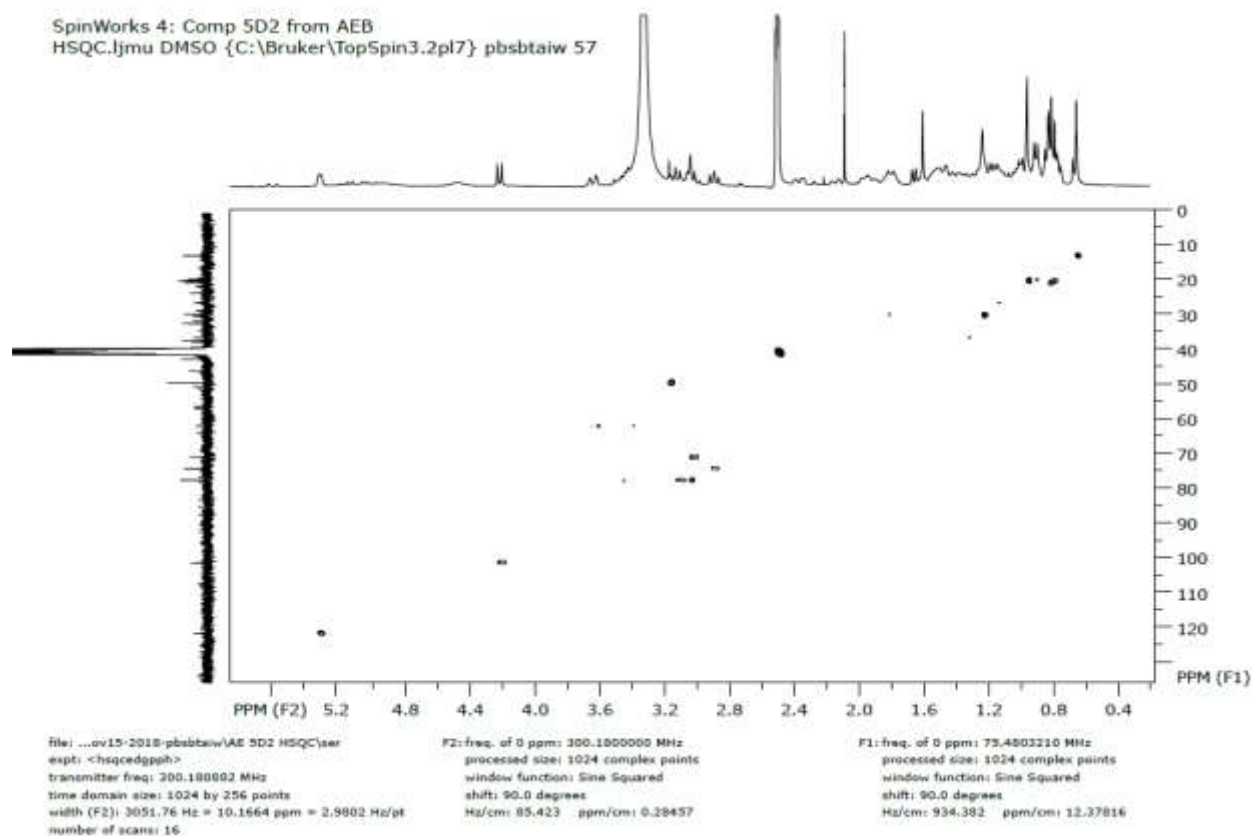
SpinWorks 4: Comp 5D2 from AEB

C13CPD DMSO {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 57

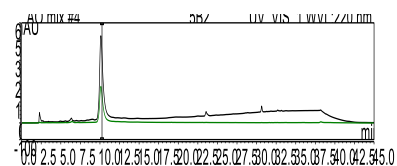


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number of scans: 15400

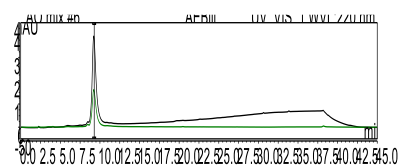
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Chromatogram for Compound 2

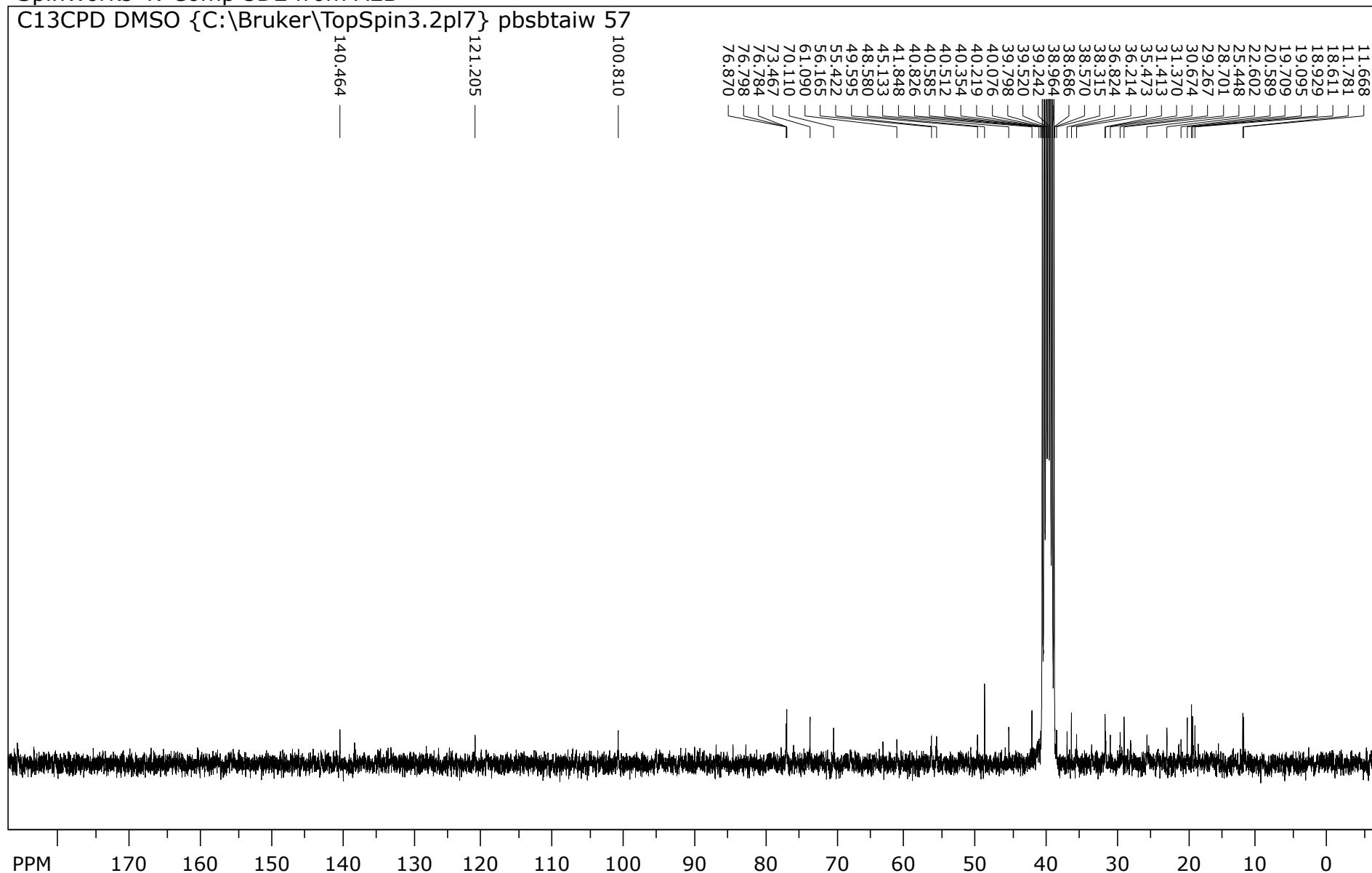


Chromatogram for Compound 3



SpinWorks 4: Comp 5D2 from AEB

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time domain size: 65532 points

width: 24414.06 Hz = 323.4170 ppm = 0.372552 Hz/pt

number of scans: 15400

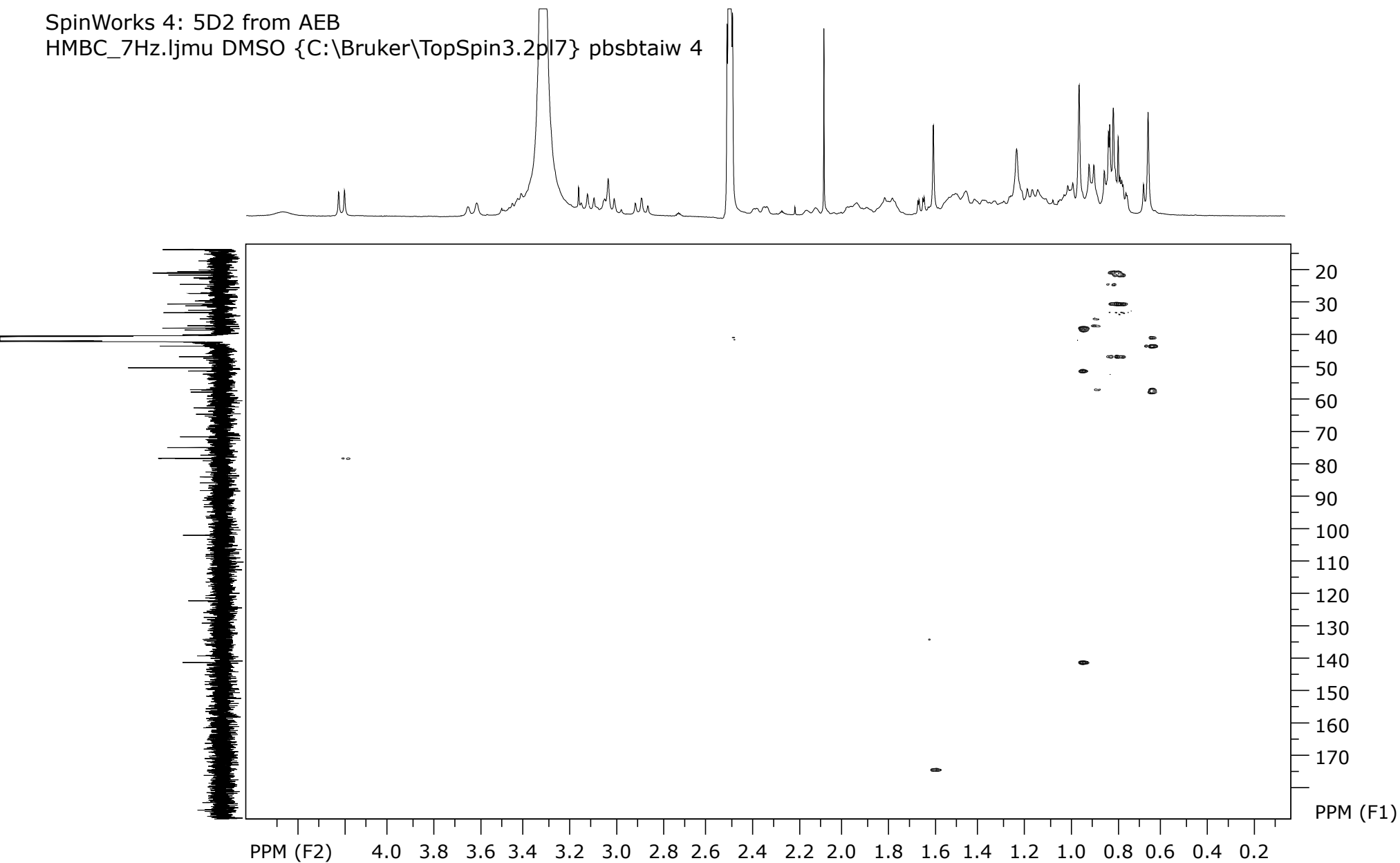
freq. of 0 ppm: 75.480356 MHz

processed size: 32768 complex points

LB: 1.000 GF: 0.0000

Hz/cm: 588.602 ppm/cm: 7.79731

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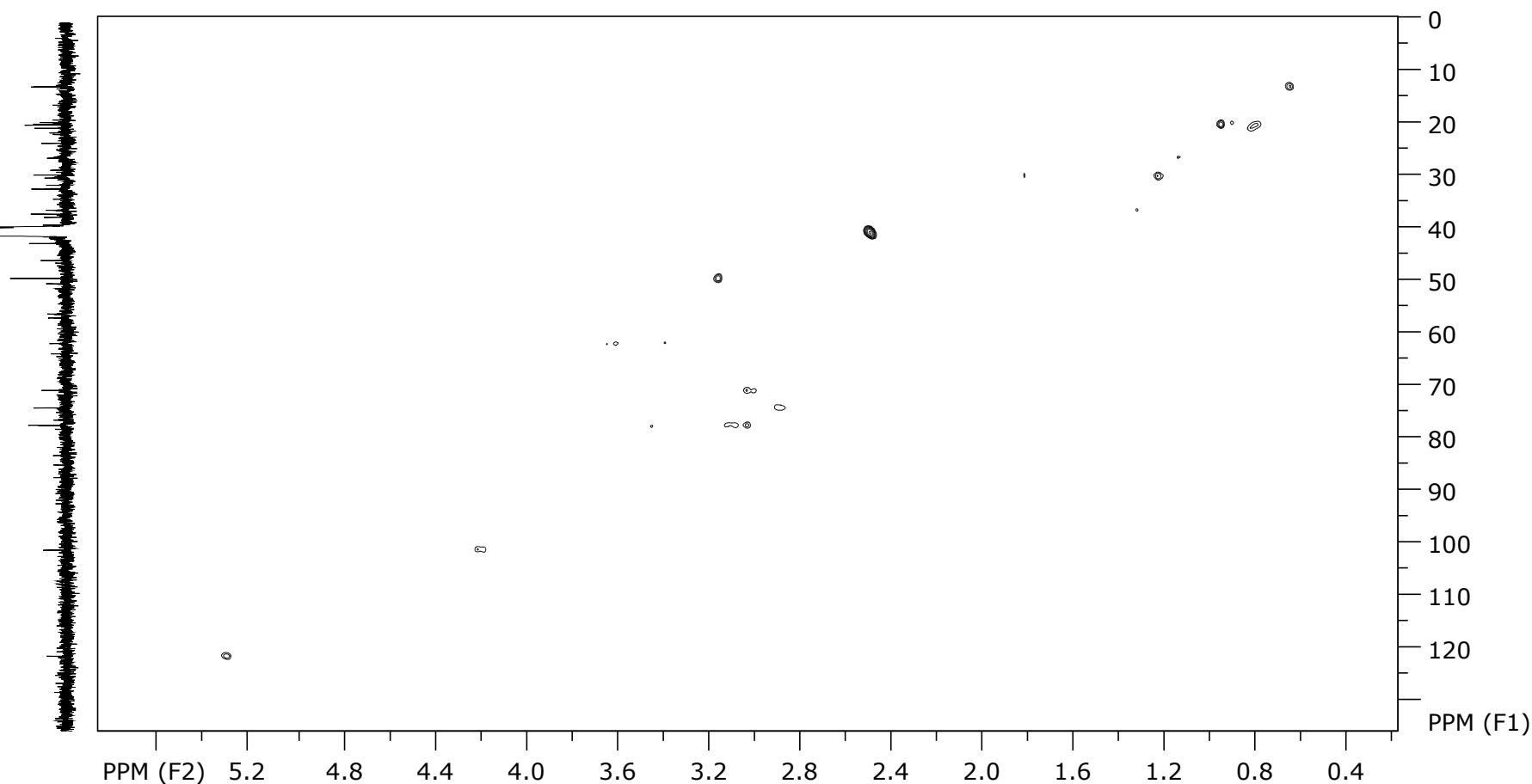
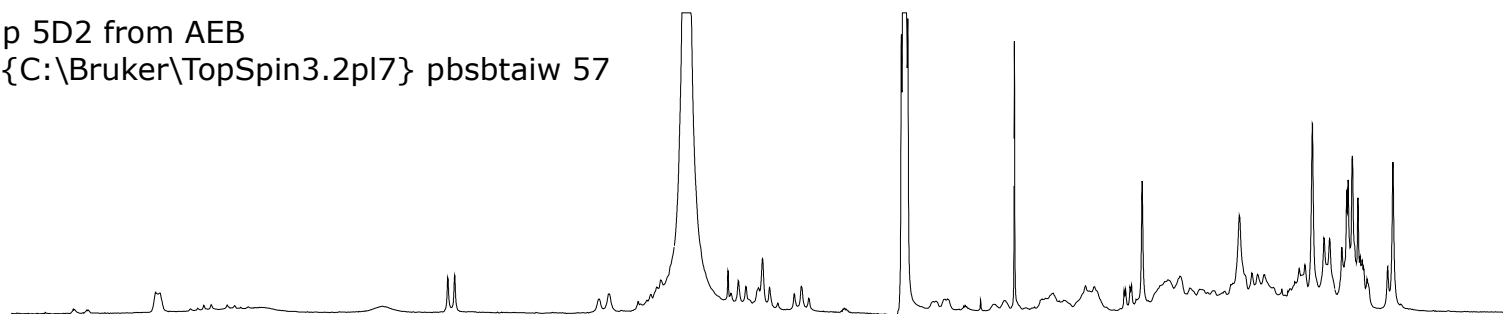


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number of scans: 32

F2: freq. of 0 ppm: 300.1800000 MHz
processed size: 2048 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 68.958 ppm/cm: 0.22972

F1: freq. of 0 ppm: 75.4803210 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 1218.528 ppm/cm: 16.14195

SpinWorks 4: Comp 5D2 from AEB
 HSQC.ljmu DMSO {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 57



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 time domain size: 1024 by 256 points
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F2: freq. of 0 ppm: 300.1800000 MHz
 processed size: 1024 complex points
 window function: Sine Squared
 shift: 90.0 degrees
 Hz/cm: 85.423 ppm/cm: 0.28457

F1: freq. of 0 ppm: 75.4803210 MHz
 processed size: 1024 complex points
 window function: Sine Squared
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LCT

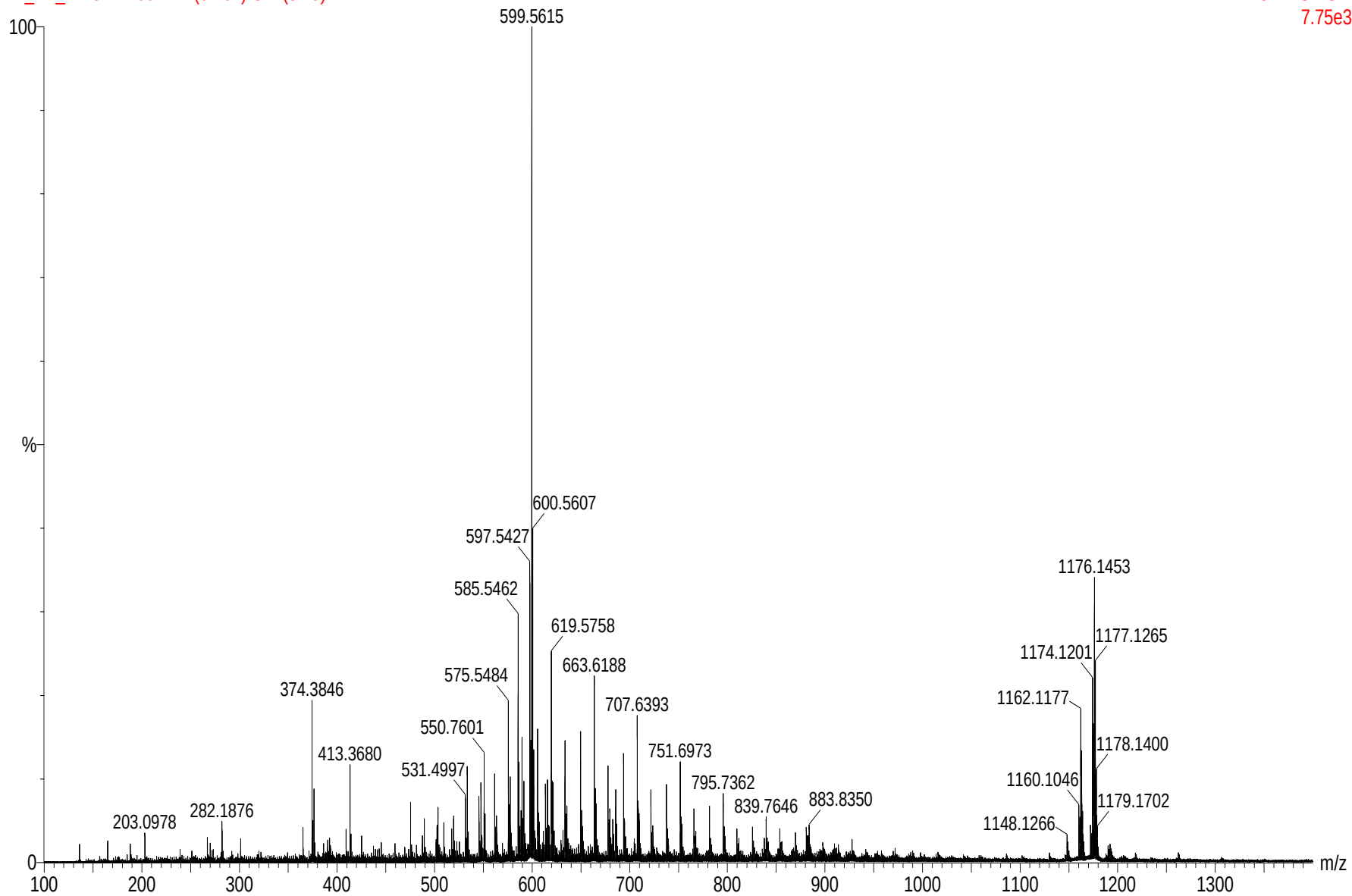
09-Jan-2019

15:24:42

1: TOF MS ES+

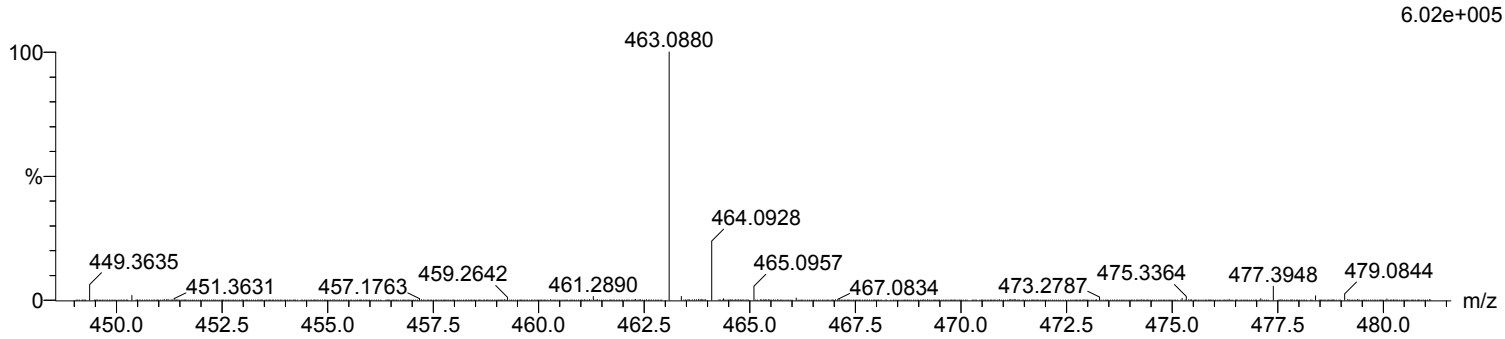
7.75e3

AF_TB_AE 5D2 100V 12 (0.202) Cm (3:29)



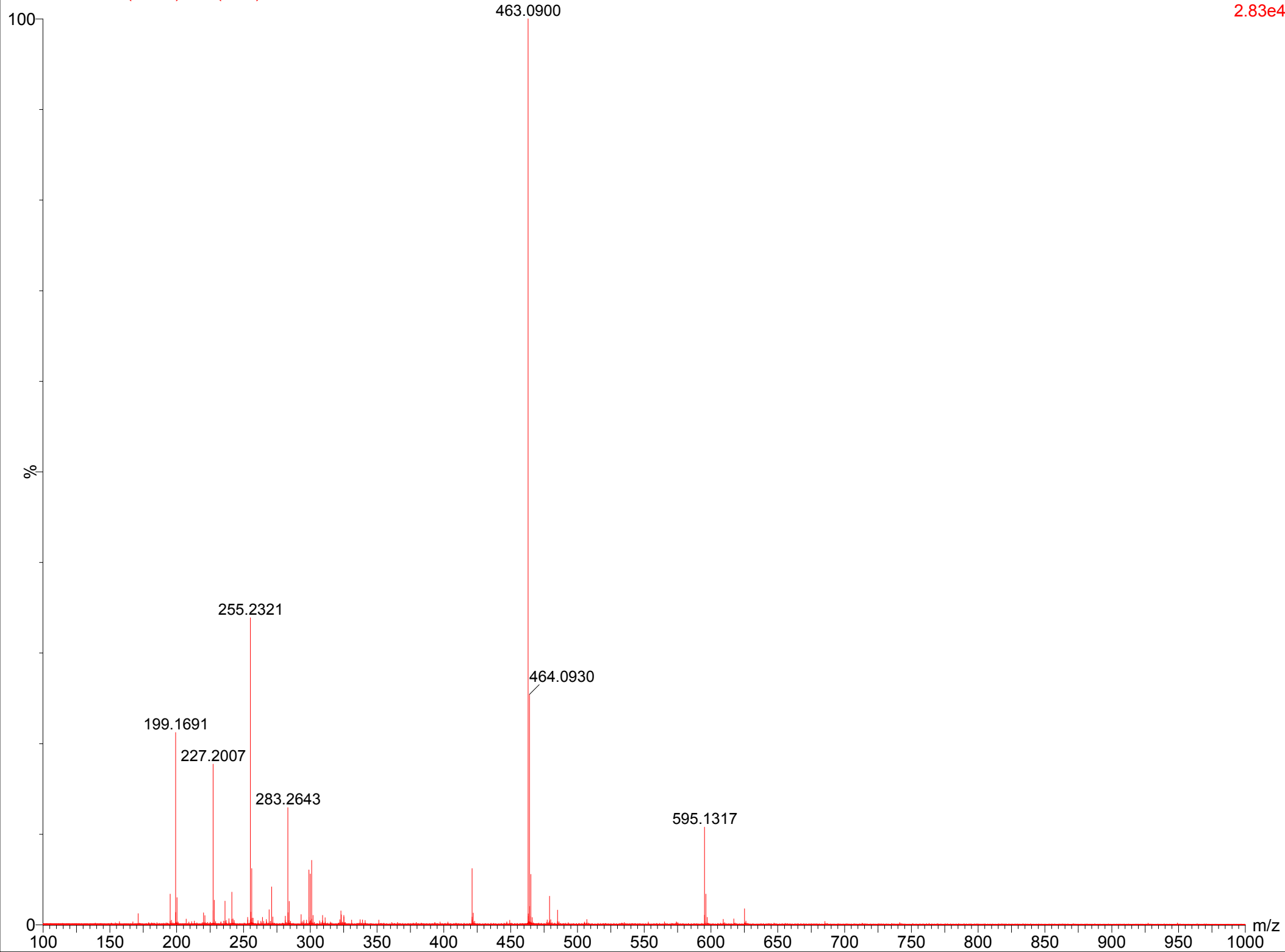
Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1860 formula(e) evaluated with 11 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-50 O: 0-50
AEB 2a 18 (0.574) Cm (1:61)
TOF MS ES-



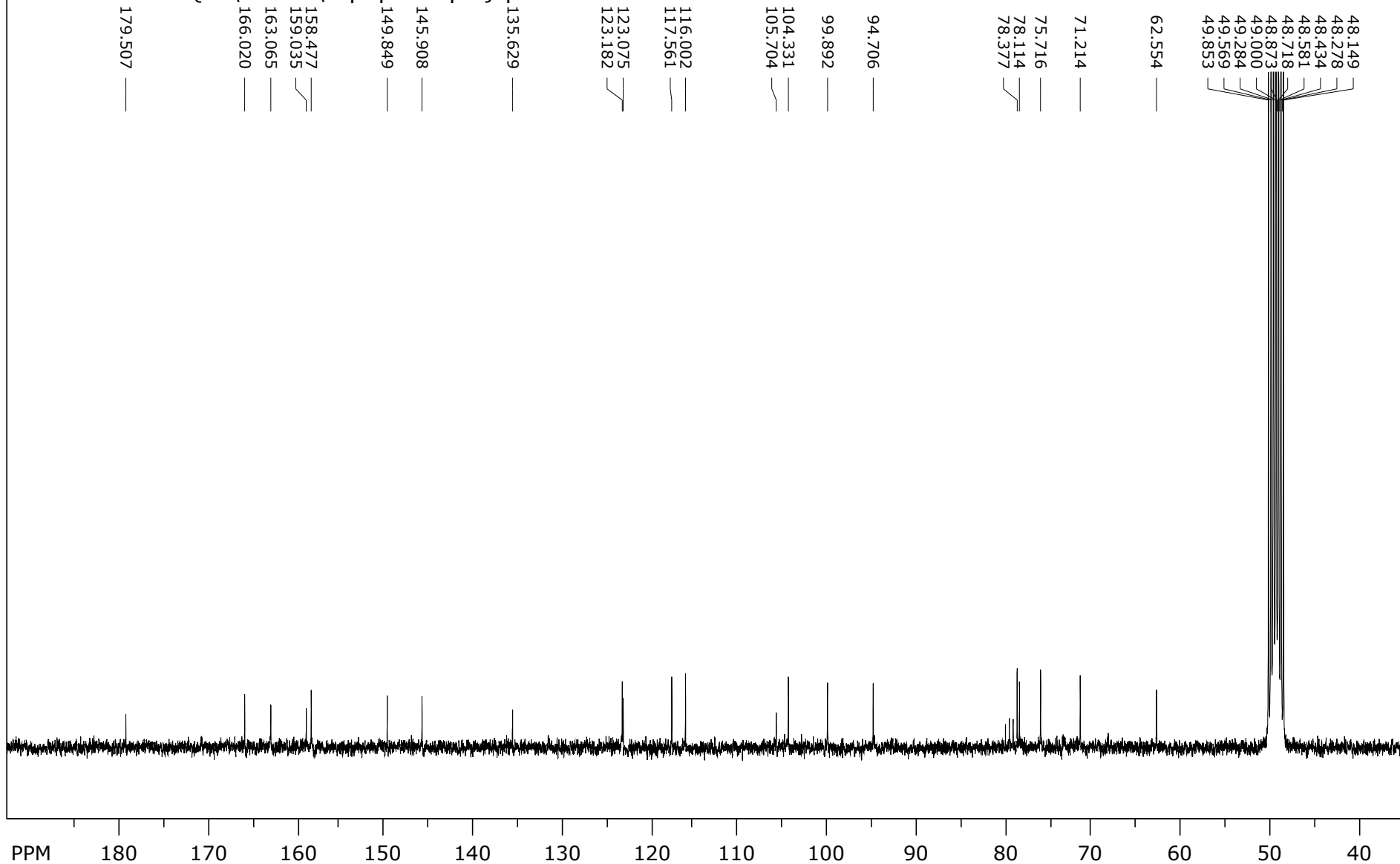
Minimum: -1.5
Maximum: 5.0 5.0 100.0

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	463.0882	-0.2	-0.4	5.5	572.7	14.0	C6 H15 N12 O13
	463.0877	0.3	0.6	12.5	558.7	0.0	C21 H19 O12
	463.0876	0.4	0.9	23.5	568.0	9.2	C19 H7 N14 O2
	463.0871	0.9	1.9	30.5	569.4	10.6	C34 H11 N2 O
	463.0890	-1.0	-2.2	17.5	564.0	5.2	C22 H15 N4 O8
	463.0868	1.2	2.6	0.5	573.3	14.6	C5 H19 N8 O17
	463.0868	1.2	2.6	11.5	574.9	16.1	C3 H7 N22 O7
	463.0895	-1.5	-3.2	-0.5	570.9	12.2	C9 H23 N2 O19
	463.0895	-1.5	-3.2	10.5	572.3	13.6	C7 H11 N16 O9
	463.0863	1.7	3.7	18.5	566.6	7.9	C18 H11 N10 O6



SpinWorks 4: AE 5B2

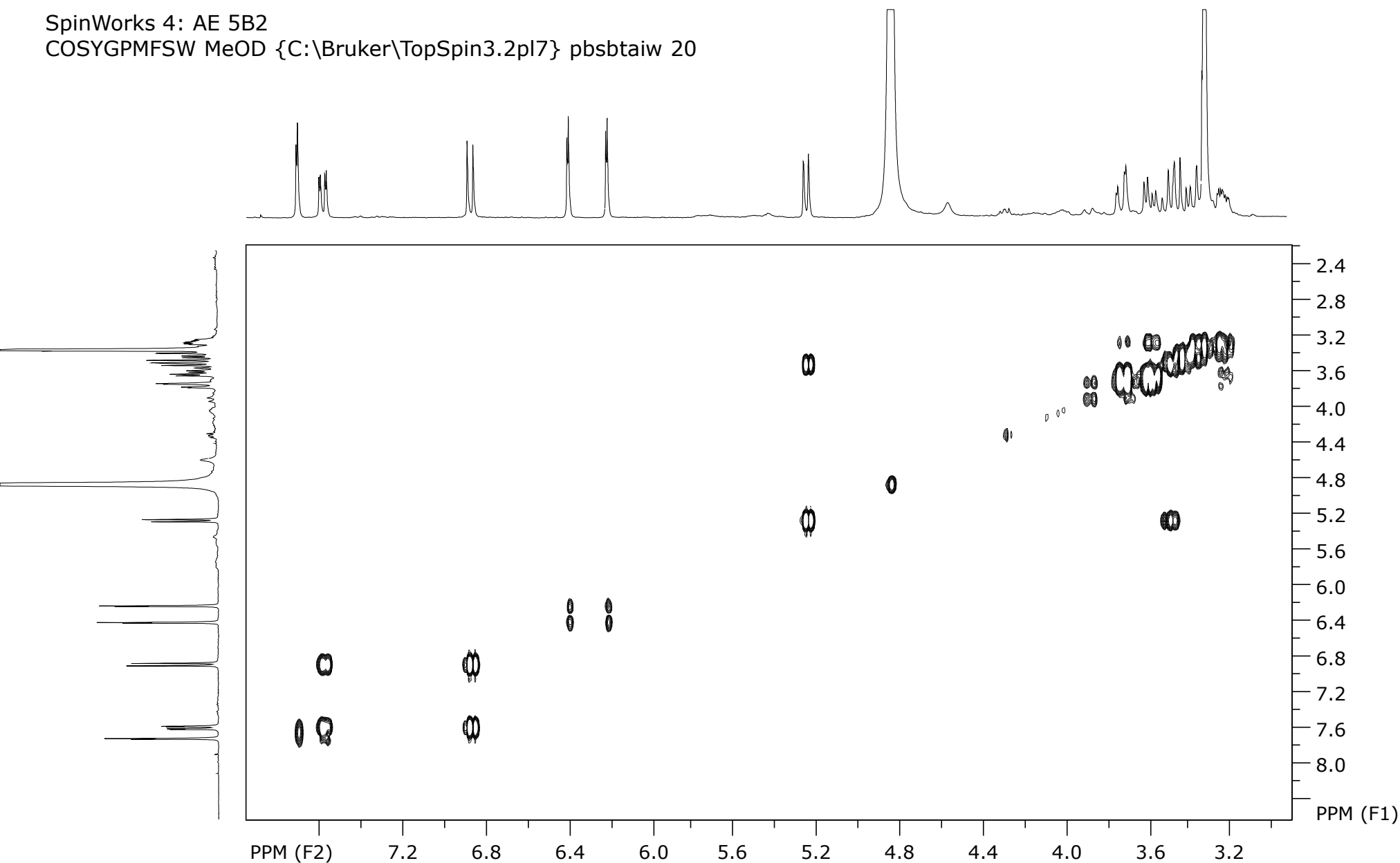
C13CPD MeOD {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 20



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 number of scans: 9216

freq. of 0 ppm: 75.480214 MHz
 processed size: 32768 complex points
 LB: 1.000 GF: 0.0000
 Hz/cm: 478.876 ppm/cm: 6.34375

SpinWorks 4: AE 5B2
 COSYGPMFSW MeOD {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 20

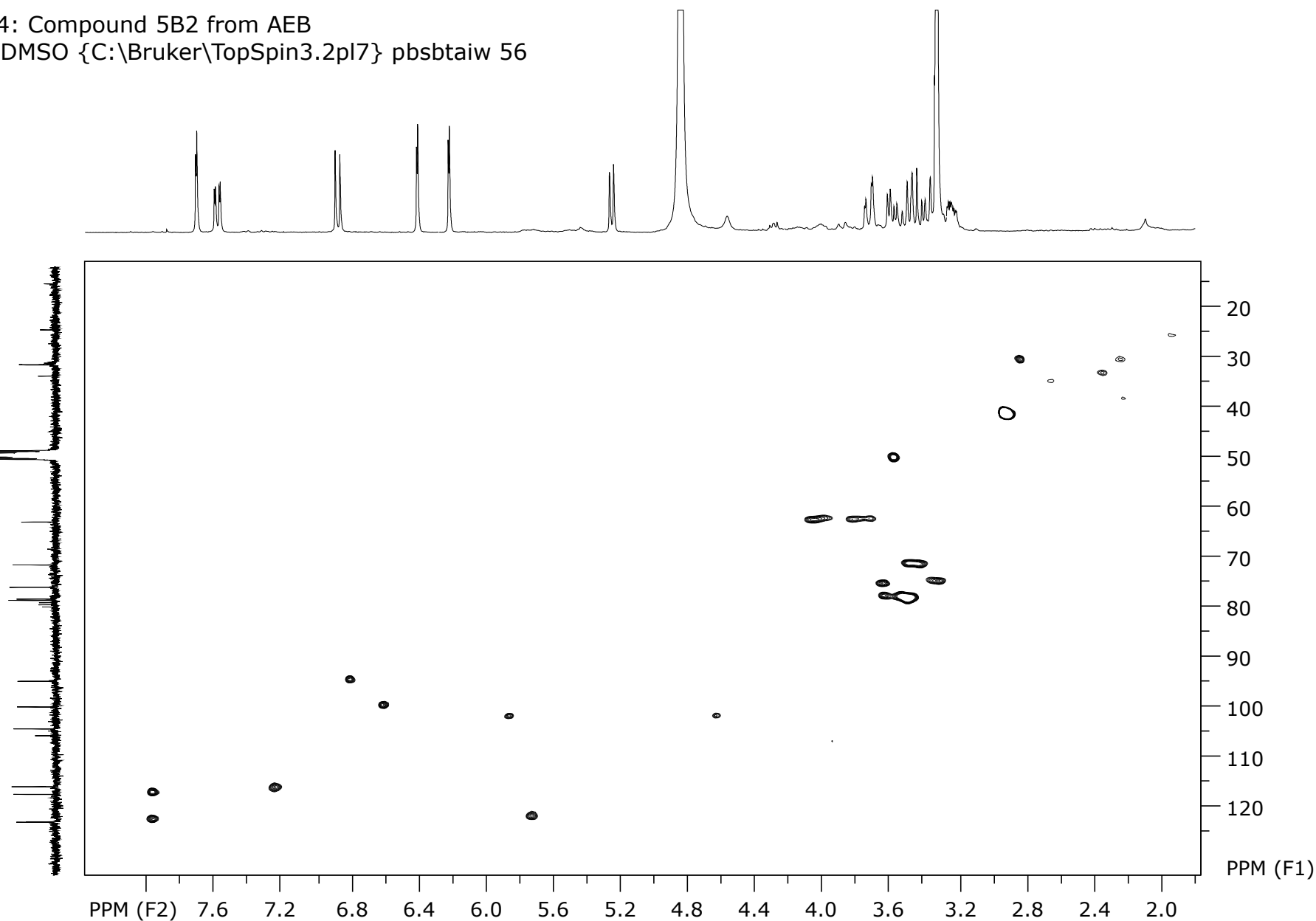


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 number of scans: 24

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 Hz/cm: 75.805 ppm/cm: 0.25253

F1: freq. of 0 ppm: 300.1800000 MHz
 processed size: 1024 complex points
 window function: Sine
 shift: 0.0 degrees
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SpinWorks 4: Compound 5B2 from AEB
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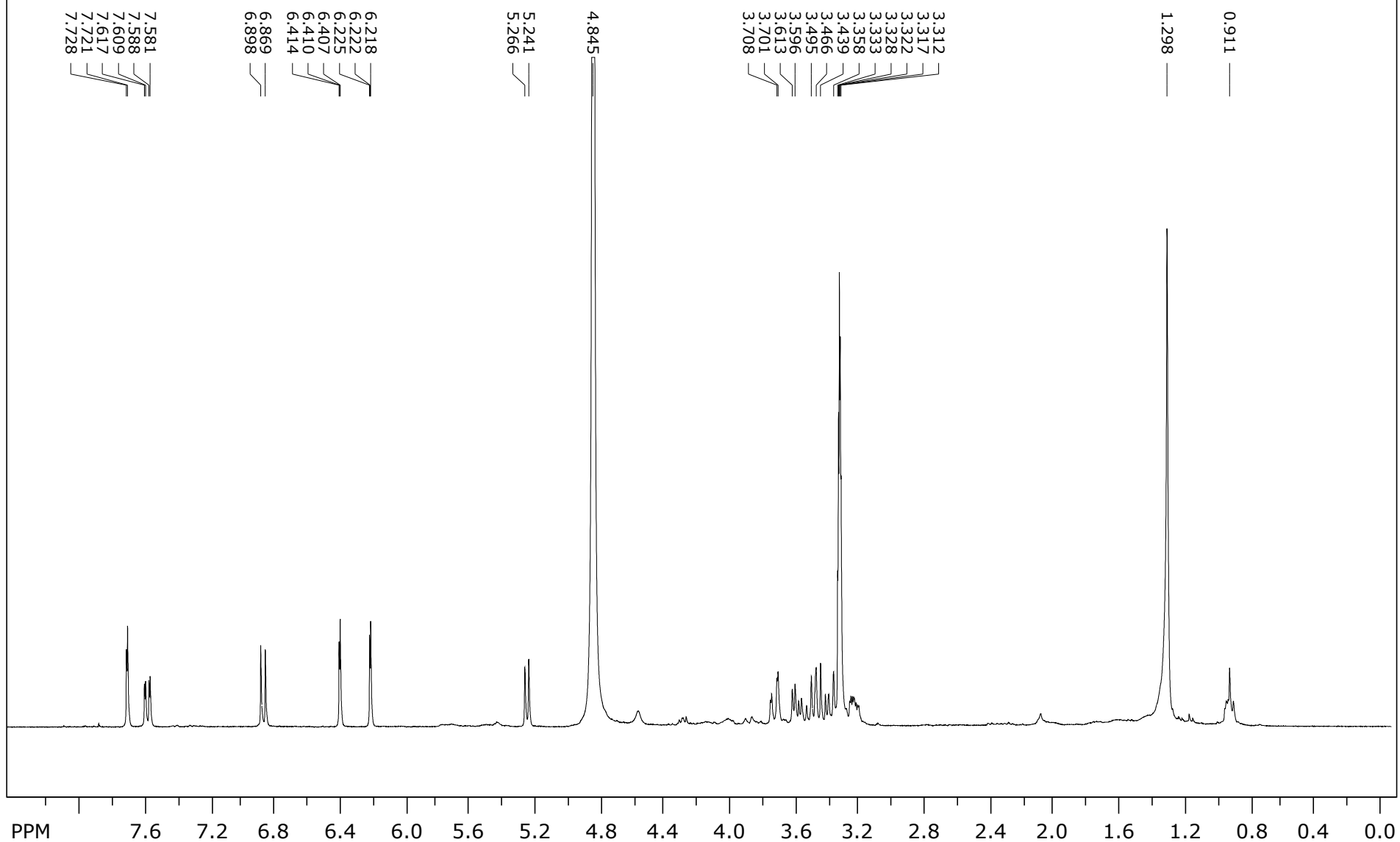
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 window function: Sine Squared
 shift: 90.0 degrees
 Hz/cm: 99.149 ppm/cm: 0.33029

F1: freq. of 0 ppm: 75.4803210 MHz
 processed size: 1024 complex points
 window function: Sine Squared
 shift: 90.0 degrees
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SpinWorks 4: AE 5B2

PROTON.ljmu MeOD {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 20

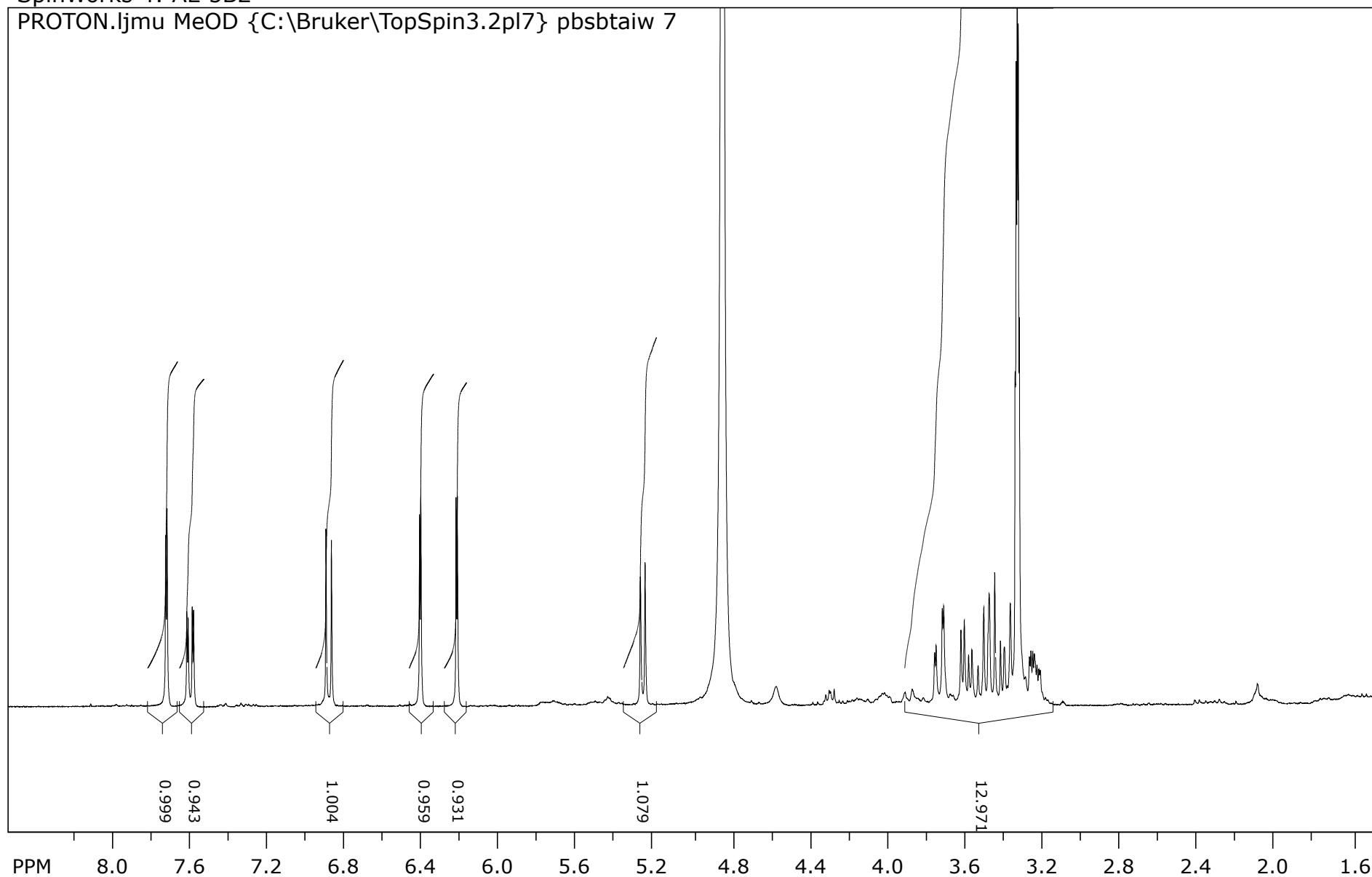


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 time domain size: 65526 points
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 number of scans: 128

freq. of 0 ppm: 300.180000 MHz
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SpinWorks 4: AE 5B2

PROTON.ljmu MeOD {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 7



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time domain size: 65526 points

width: 6103.52 Hz = 20.3327 ppm = 0.093146 Hz/pt

number of scans: 128

freq. of 0 ppm: 300.180000 MHz

processed size: 65536 complex points

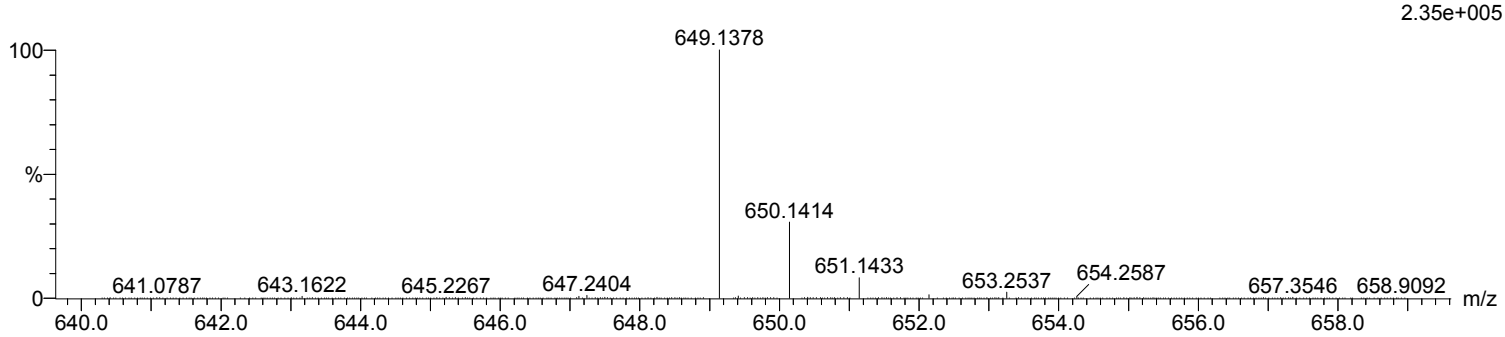
LB: 0.300 GF: 0.0000

Hz/cm: 85.038 ppm/cm: 0.28329

Single Mass Analysis

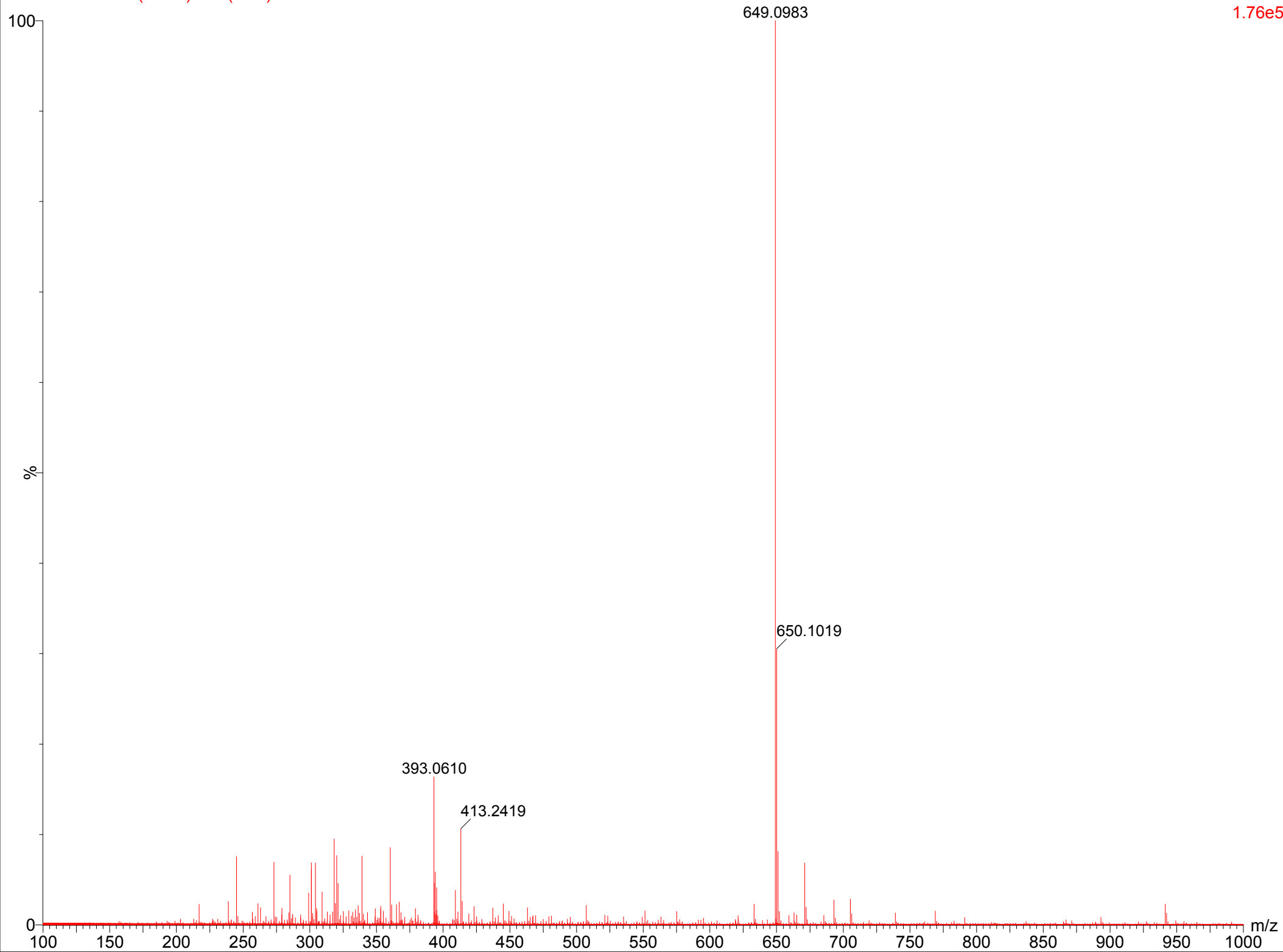
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
4038 formula(e) evaluated with 23 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-50 O: 0-50 Na: 1-1
AEB 3biii 40 (1.317) Cm (1:61)
TOF MS ES+



Minimum: -1.5
Maximum: 5.0 5.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula				
649.1378	649.1376	0.2	0.3	30.5	475.8	13.5	C40	H22	N2	O6	Na
	649.1381	-0.3	-0.5	12.5	462.3	0.0	C27	H30	O17		Na
	649.1381	-0.3	-0.5	23.5	471.1	8.8	C25	H18	N14	O7	Na
	649.1372	0.6	0.9	22.5	482.5	20.2	C7	H6	N36	O2	Na
	649.1372	0.6	0.9	11.5	479.9	17.7	C9	H18	N22	O12	Na
	649.1372	0.6	0.9	0.5	477.3	15.1	C11	H30	N8	O22	Na
	649.1386	-0.8	-1.2	5.5	476.8	14.5	C12	H26	N12	O18	Na
	649.1386	-0.8	-1.2	16.5	479.6	17.3	C10	H14	N26	O8	Na
	649.1367	1.1	1.7	18.5	469.9	7.6	C24	H22	N10	O11	Na
	649.1367	1.1	1.7	29.5	475.6	13.3	C22	H10	N24	O	Na
	649.1389	-1.1	-1.7	35.5	476.5	14.3	C41	H18	N6	O2	Na
	649.1394	-1.6	-2.5	17.5	469.7	7.4	C28	H26	N4	O13	Na
	649.1362	1.6	2.5	36.5	476.6	14.4	C37	H14	N12		Na
	649.1394	-1.6	-2.5	28.5	473.3	11.0	C26	H14	N18	O3	Na
	649.1359	1.9	2.9	6.5	480.7	18.4	C8	H22	N18	O16	Na
	649.1359	1.9	2.9	17.5	482.5	20.2	C6	H10	N32	O6	Na
	649.1399	-2.1	-3.2	21.5	479.7	17.4	C11	H10	N30	O4	Na
	649.1399	-2.1	-3.2	10.5	477.0	14.7	C13	H22	N16	O14	Na
	649.1399	-2.1	-3.2	-0.5	476.0	13.7	C15	H34	N2	O24	Na
	649.1354	2.4	3.7	24.5	475.3	13.1	C21	H14	N20	O5	Na

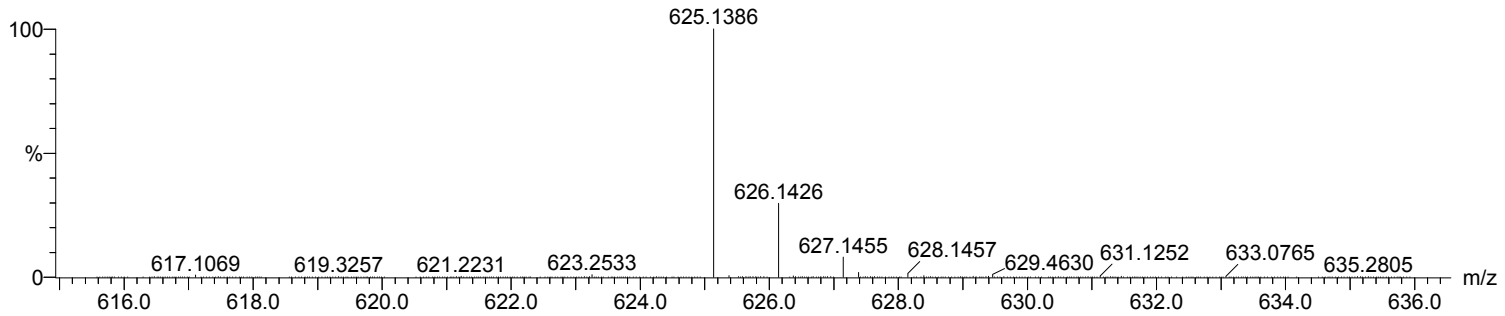


Single Mass Analysis

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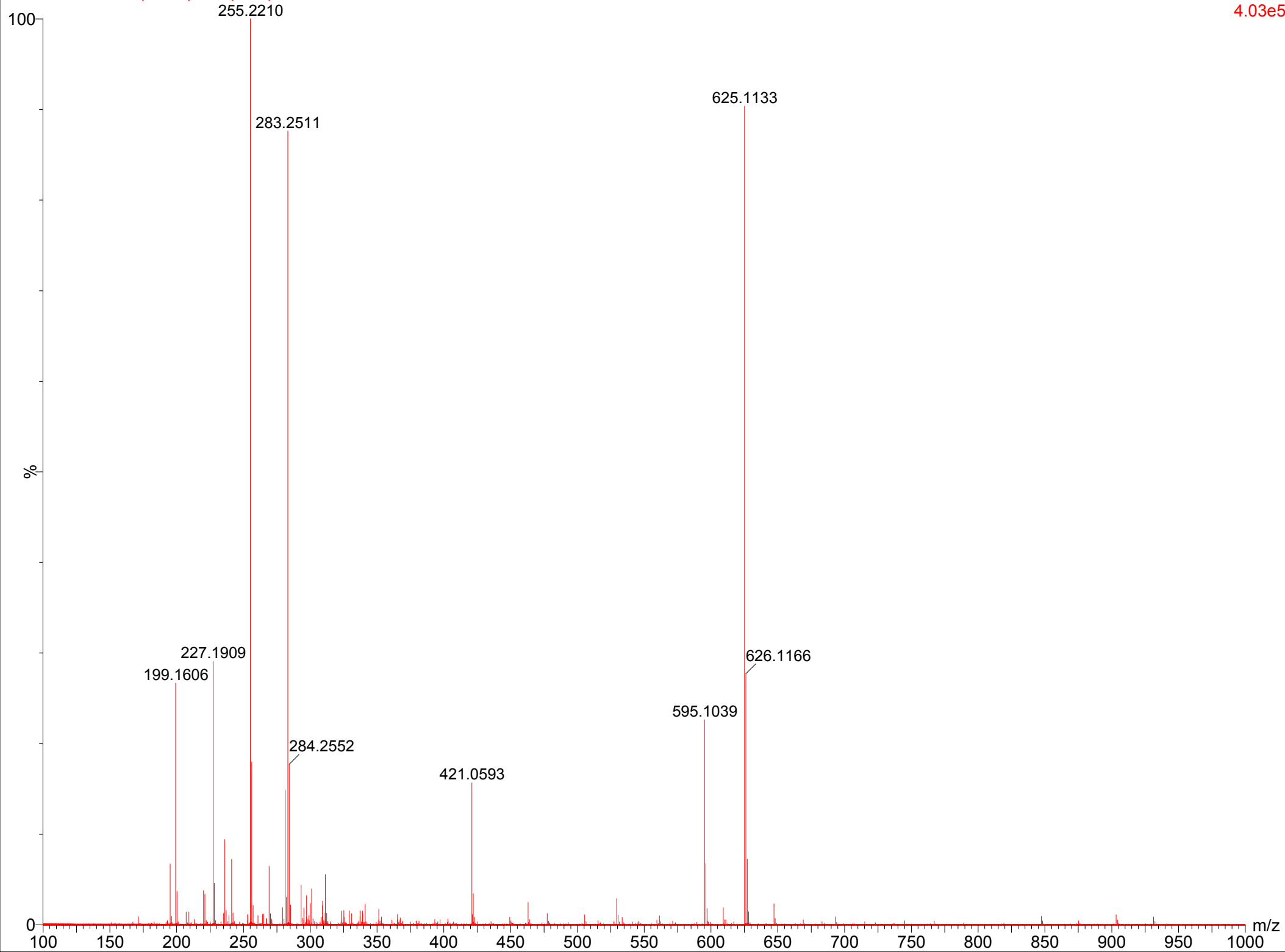
Monoisotopic Mass, Even Electron Ions
4157 formula(e) evaluated with 25 results within limits (up to 20 closest results for each mass)
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AEB 3biv 22 (0.708) Cm (1:61)
TOF MS ES-

5.02e+005



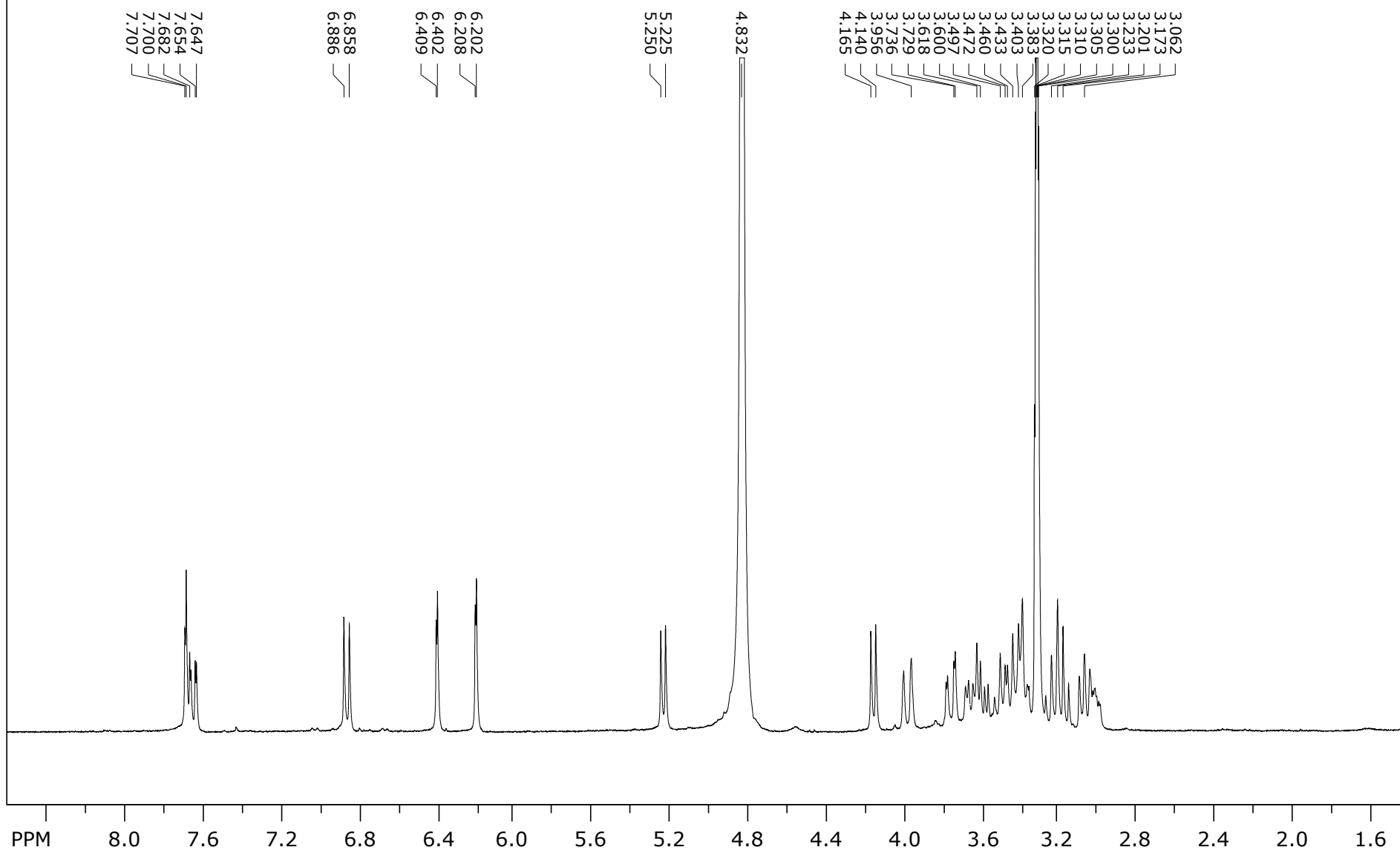
Minimum: -1.5
Maximum: 5.0 5.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
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	625.1383	0.3	0.5	18.5	483.5	15.7	C6 H9 N32 O6
	625.1383	0.3	0.5	7.5	481.6	13.8	C8 H21 N18 O16
	625.1391	-0.5	-0.8	19.5	471.9	4.1	C24 H21 N10 O11
	625.1391	-0.5	-0.8	30.5	477.5	9.7	C22 H9 N24 O
	625.1378	0.8	1.3	25.5	476.6	8.8	C21 H13 N20 O5
	625.1378	0.8	1.3	14.5	471.2	3.5	C23 H25 N6 O15
	625.1396	-1.0	-1.6	1.5	479.4	11.7	C11 H29 N8 O22
	625.1396	-1.0	-1.6	23.5	483.7	15.9	C7 H5 N36 O2
	625.1396	-1.0	-1.6	12.5	481.2	13.5	C9 H17 N22 O12
	625.1373	1.3	2.1	32.5	477.5	9.7	C36 H17 N8 O4
	625.1400	-1.4	-2.2	31.5	476.3	8.5	C40 H21 N2 O6
	625.1370	1.6	2.6	2.5	482.2	14.4	C7 H25 N14 O20
	625.1369	1.7	2.7	24.5	486.2	18.4	C3 H N42
	625.1369	1.7	2.7	13.5	483.6	15.9	C5 H13 N28 O10
	625.1405	-1.9	-3.0	24.5	474.3	6.5	C25 H17 N14 O7
	625.1405	-1.9	-3.0	13.5	467.8	0.1	C27 H29 O17
	625.1365	2.1	3.4	9.5	473.9	6.2	C22 H29 N2 O19
	625.1364	2.2	3.5	20.5	476.4	8.6	C20 H17 N16 O9
	625.1410	-2.4	-3.8	17.5	481.2	13.4	C10 H13 N26 O8



SpinWorks 4: AE Biii

PROTON.ljmu MeOD {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 45

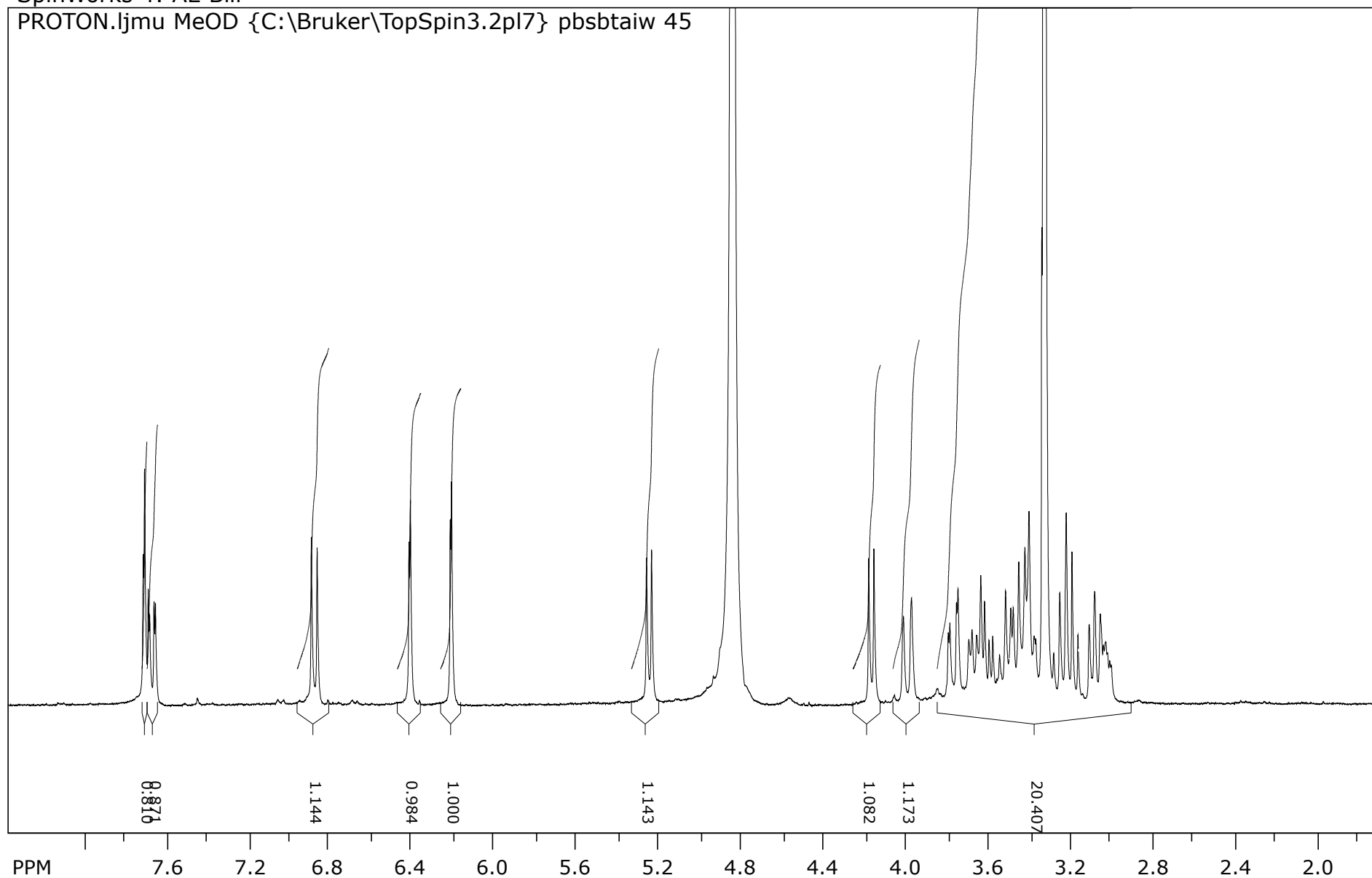


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 time domain size: 65526 points
 width: 6103.52 Hz = 20.3327 ppm = 0.093146 Hz/pt
 number of scans: 128

freq. of 0 ppm: 300.180004 MHz
 processed size: 65536 complex points
 LB: 0.300 GF: 0.0000
 Hz/cm: 86.648 ppm/cm: 0.28865

SpinWorks 4: AE Biii

PROTON.ljmu MeOD {C:\Bruker\TopSpin3.2pl7} pbsbtaiw 45



file: ...bsbtaiw\Jan17-2019-pbsbtaiw\20\fid expt: <zg30>
transmitter freq.: 300.181854 MHz
time domain size: 65526 points
width: 6103.52 Hz = 20.3327 ppm = 0.093146 Hz/pt
number of scans: 128

freq. of 0 ppm: 300.180000 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 80.335 ppm/cm: 0.26762