Chemo-enzymatic synthesis of renewable sterically-hindered phenolic antioxidants with tunable polarity from lignocellulose and vegetal oil components

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Electronic Supplementary Information

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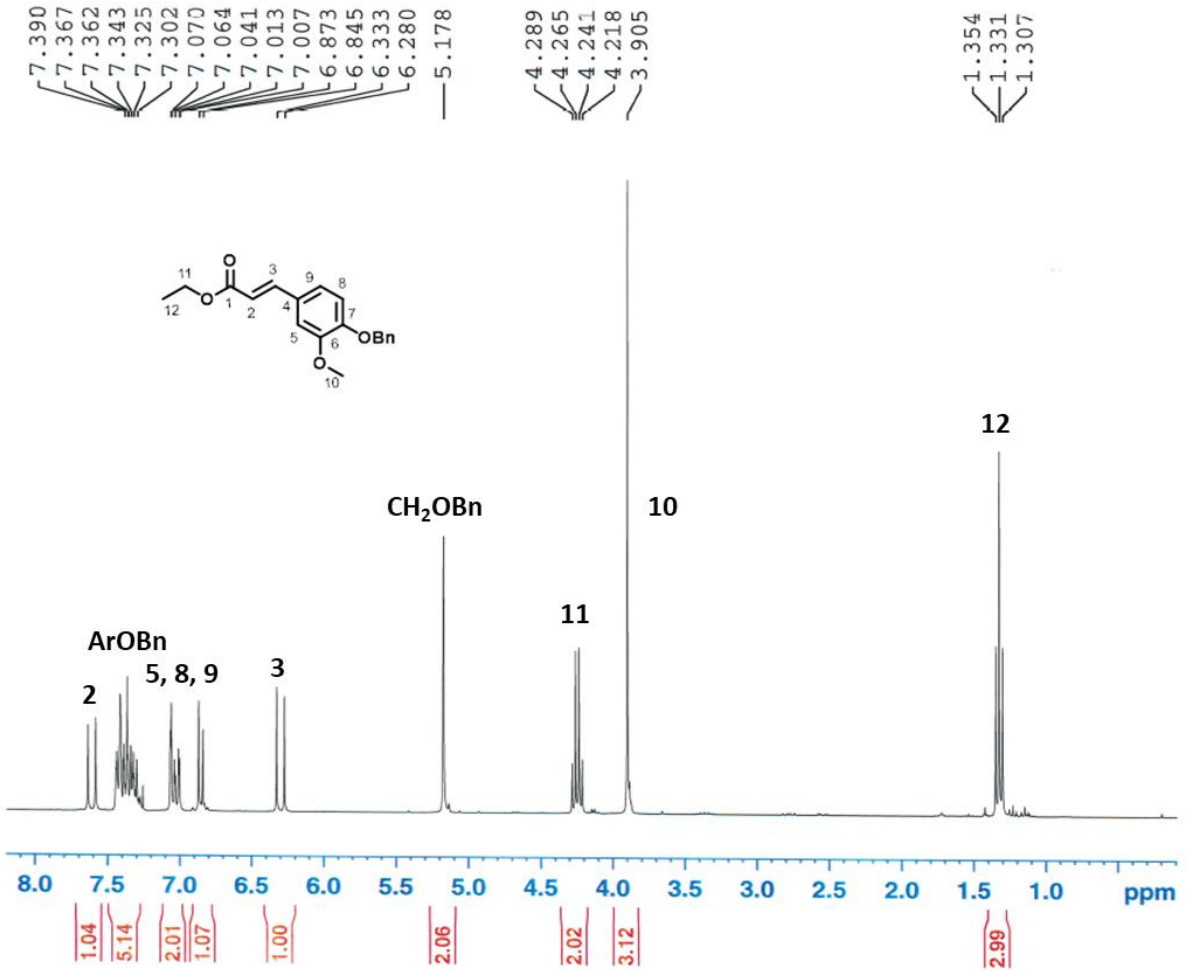
Molar constant for the calculation of Hansen solubility parameters.

Structural group	F_d ($J^{1/2}$ $cm^{-3/2}$ mol^{-1})	F_p^2 (J cm^{-3} mol^{-1})	E_h (J/mol)	V (cm^3 mol^{-1})
$-CH_3$	420	0	0	33.5
$-CH_2-$	270	0	0	16.1
-CH-	80	0	0	-1
>C<	-70	0	0	-19.2
Phenyl (trisubstituted)	1270	12100	0	33.4
-OH	210	250000	20000	10
-O-	100	160000	3000	3.8
-COO-	390	240100	7000	18
Plane of symmetry	/	Total x0.5 if 1 Total x0.25 if 2 Total x0 if 3 or more	Total x0 if 3 or more	/

F_d : dispersion contribution; F_p : polar contribution; E_h: hydrogen-bonding-energy contribution; V : molar volume

^{1}H NMR spectrum of benzylated ethyl ferulate ($CDCl_3$)

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EXPNO                   10
PROCNO                   1

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NS                   32
DS                    2
SWH            6103.516 Hz
FIDRES         0.093132 Hz
AQ             5.3687091 sec
RG               10.2315
DW               81.920 usec
DE                6.50 usec
TE                293.2 K
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TD0                   1

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NUC1                 1H
P1                8.70 usec
PLW1         23.00000000 W

F2 - Processing parameters
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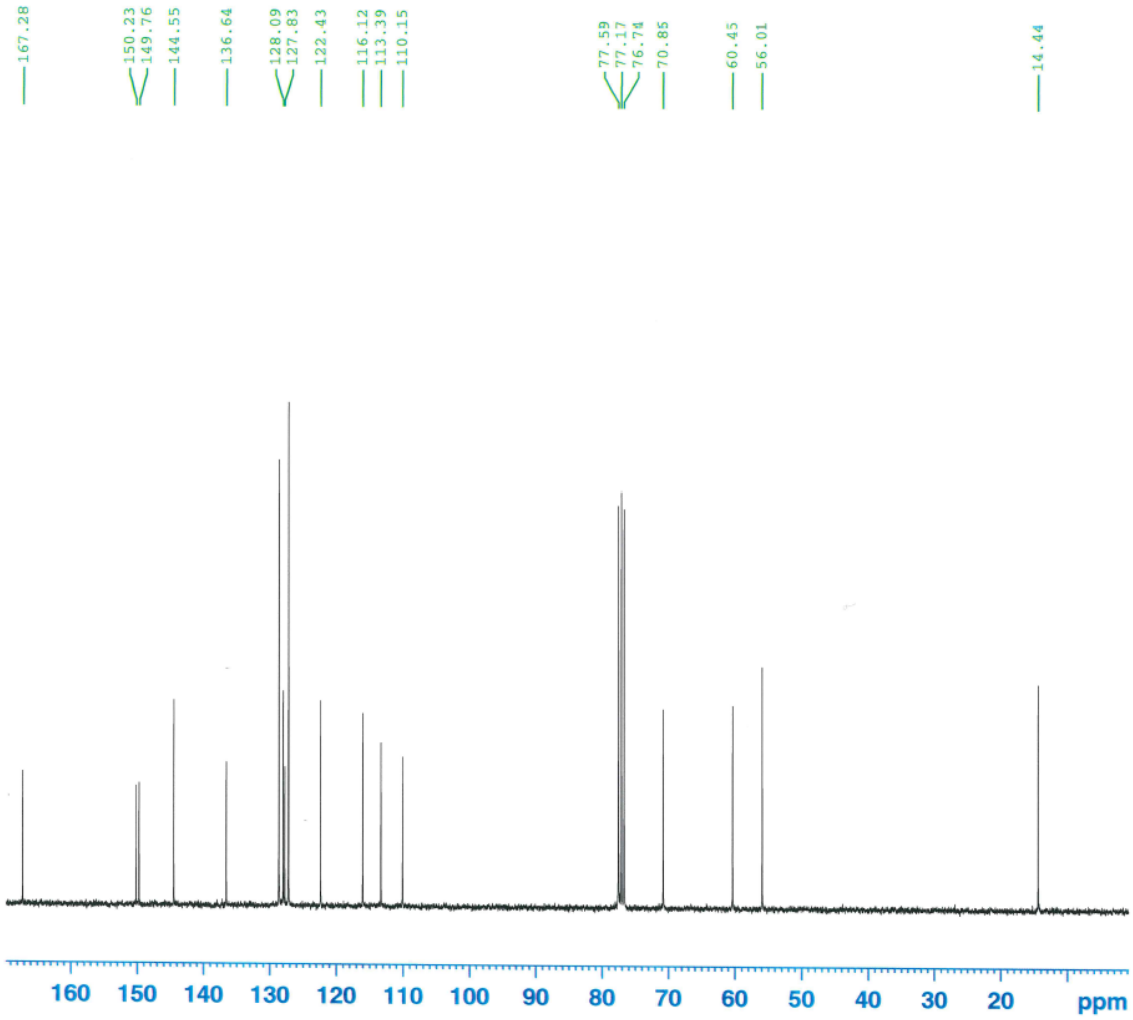
^{13}C NMR spectrum of benzylated ethyl ferulate ($CDCl_3$)

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EXPNO                   11
PROCNO                   1

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TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24414.063 Hz
FIDRES            0.372529 Hz
AQ                1.3421773 sec
RG                  501.187
DW                 20.480 usec
DE                  6.50 usec
TE                 293.2 K
D1            2.00000000 sec
D11           0.03000000 sec
D31           0.00001300 sec
D40           0.00439029 sec
L4                     37
L5                     53
P32                98.00 usec
TD0                     1

======== CHANNEL f1 ========
SFO1          75.4928982 MHz
NUC1                  13C
P1                 13.00 usec
PLW1         22.00000000 W

======== CHANNEL f2 ========
SFO2         300.2012008 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              98.00 usec
PLW2         23.00000000 W
PLW12         0.30000001 W
PLW13         0.23823000 W

F2 - Processing parameters
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SF            75.4853452 MHz
WDW                   EM
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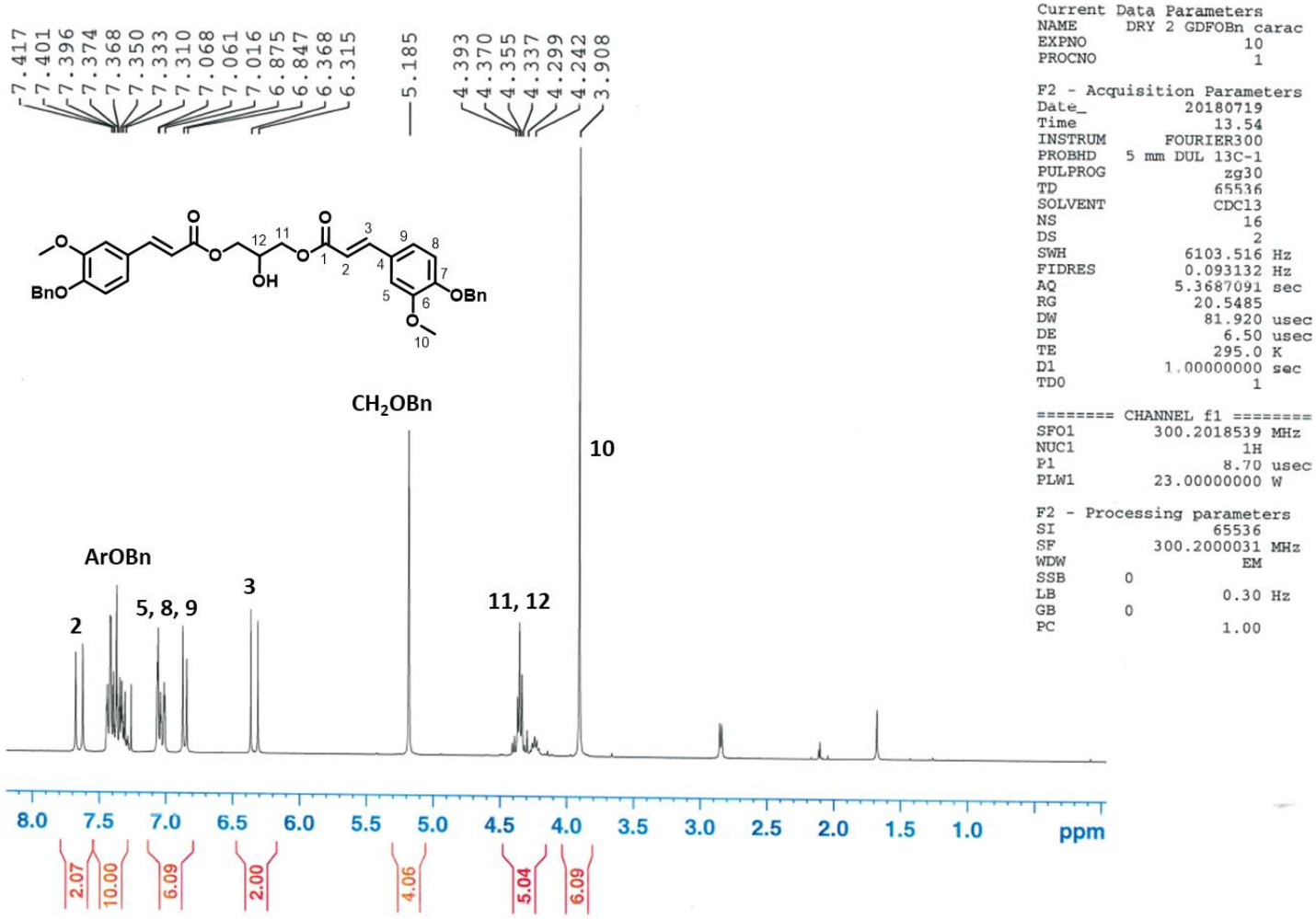
^{1}H NMR spectrum of GDFOBn from lipase catalysed transesterification ($CDCl_3$)

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NAME      DRY 2 GDFOBn carac
EXPNO                   10
PROCNO                   1

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Time                 13.54
INSTRUM         FOURIER300
PROBHD   5 mm DUL 13C-1
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6103.516 Hz
FIDRES           0.093132 Hz
AQ               5.3687091 sec
RG                 20.5485
DW                 81.920 usec
DE                  6.50 usec
TE                 295.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          300.2018539 MHz
NUC1                    1H
P1                   8.70 usec
PLW1         23.00000000 W

F2 - Processing parameters
SI                   65536
SF            300.2000031 MHz
WDW                     EM
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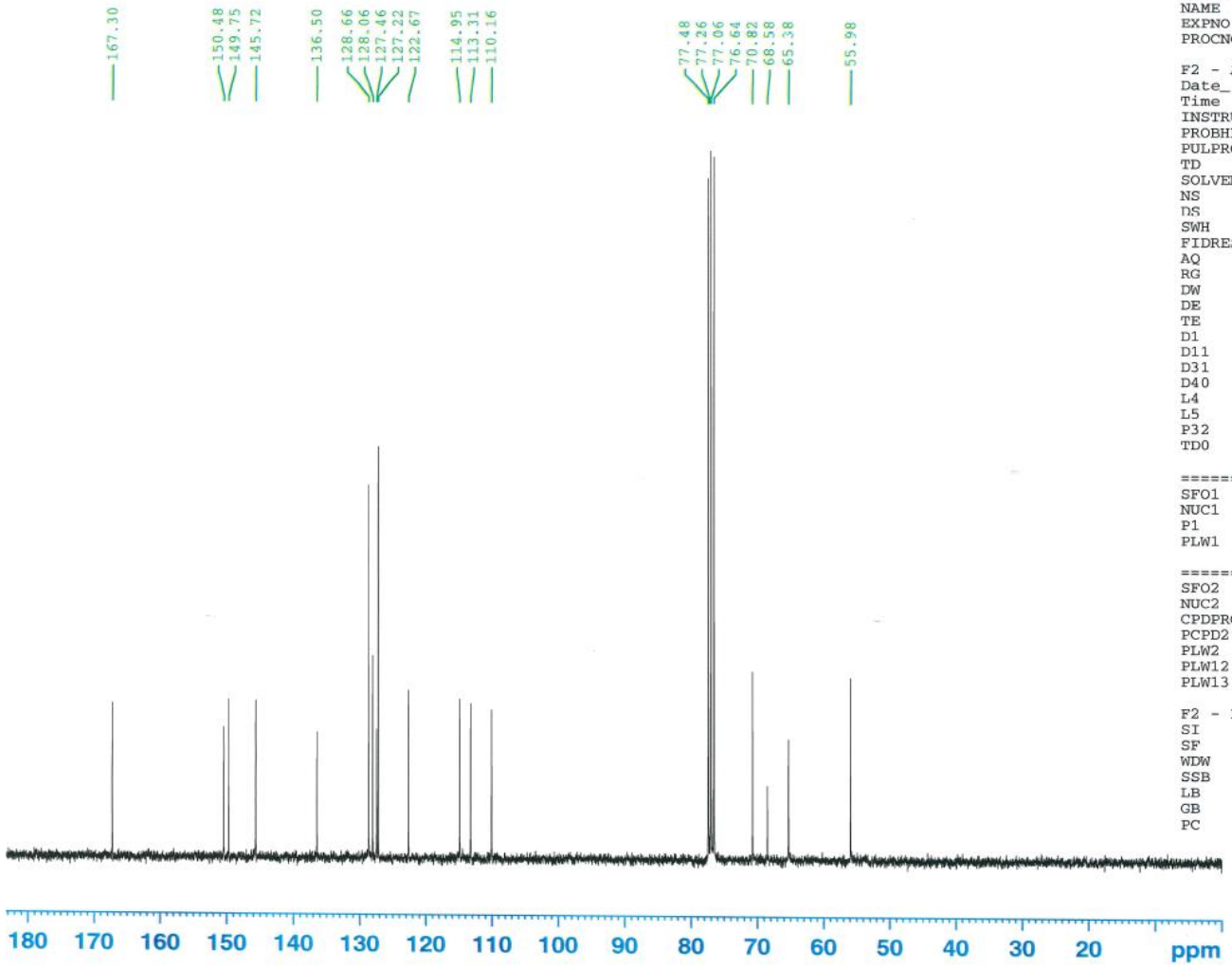
^{13}C NMR spectrum of GDFOBn from lipase catalysed transesterification ($CDCl_3$)

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EXPNO                 11
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TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24414.063 Hz
FIDRES         0.372529 Hz
AQ             1.3421773 sec
RG               501.187
DW              20.480 usec
DE               6.50 usec
TE              295.2 K
D1            2.00000000 sec
D11           0.03000000 sec
D31           0.00001300 sec
D40           0.00439029 sec
L4                    37
L5                    53
P32             98.00 usec
TD0                    1

======== CHANNEL f1 ========
SFO1         75.4928982 MHz
NUC1                 13C
P1                13.00 usec
PLW1        22.00000000 W

======== CHANNEL f2 ========
SFO2        300.2012008 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             98.00 usec
PLW2        23.00000000 W
PLW12        0.30000001 W
PLW13        0.23823000 W

F2 - Processing parameters
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LB                1.00 Hz
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PC                1.40
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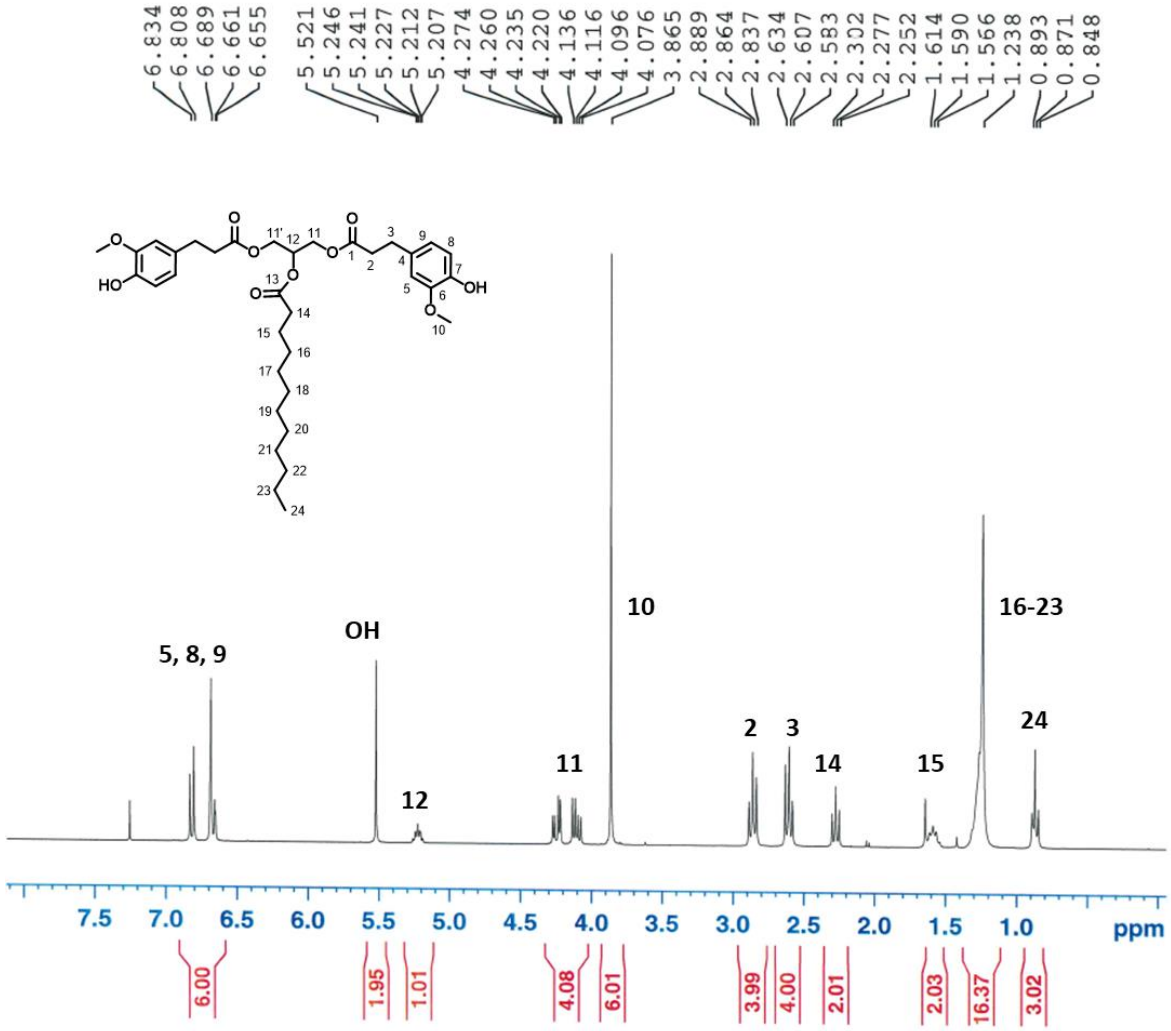
^{1}H NMR spectrum of GDF$_{10}$ (CDCl$_3$)

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EXPNO                   10
PROCNO                   1

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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6103.516 Hz
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RG                  14.0595
DW                  81.920 usec
DE                    6.50 usec
TE                   295.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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NUC1                    1H
P1                    8.70 usec
PLW1           23.00000000 W

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SI                    65536
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LB                    0.30 Hz
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PC                    1.00
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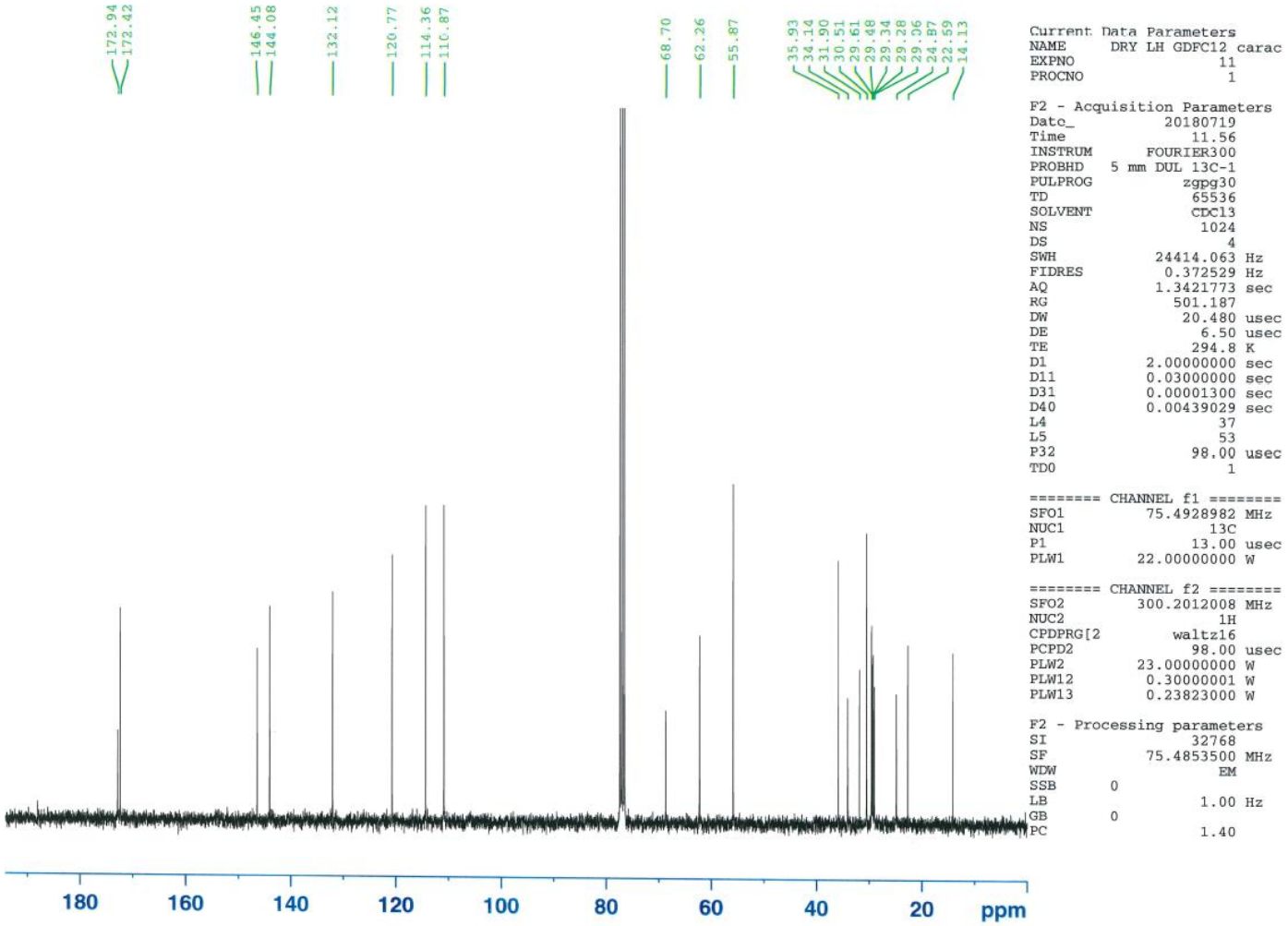
^{13}C NMR spectrum of GDF_{10} ($CDCl_3$)

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Current Data Parameters
NAME      DRY LH GDFC12 carac
EXPNO                   11
PROCNO                   1

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Time                 11.56
INSTRUM       FOURIER300
PROBHD   5 mm DUL 13C-1
PULPROG            zgpg30
TD                  65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24414.063 Hz
FIDRES               0.372529 Hz
AQ                   1.3421773 sec
RG                     501.187
DW                    20.480 usec
DE                     6.50 usec
TE                    294.8 K
D1                2.00000000 sec
D11               0.03000000 sec
D31               0.00001300 sec
D40               0.00439029 sec
L4                       37
L5                       53
P32                   98.00 usec
TD0                      1

======== CHANNEL f1 ========
SFO1             75.4928982 MHz
NUC1                    13C
P1                    13.00 usec
PLW1            22.00000000 W

======== CHANNEL f2 ========
SFO2            300.2012008 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 98.00 usec
PLW2            23.00000000 W
PLW12            0.30000001 W
PLW13            0.23823000 W

F2 - Processing parameters
SI                       32768
SF               75.4853500 MHz
WDW                        EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
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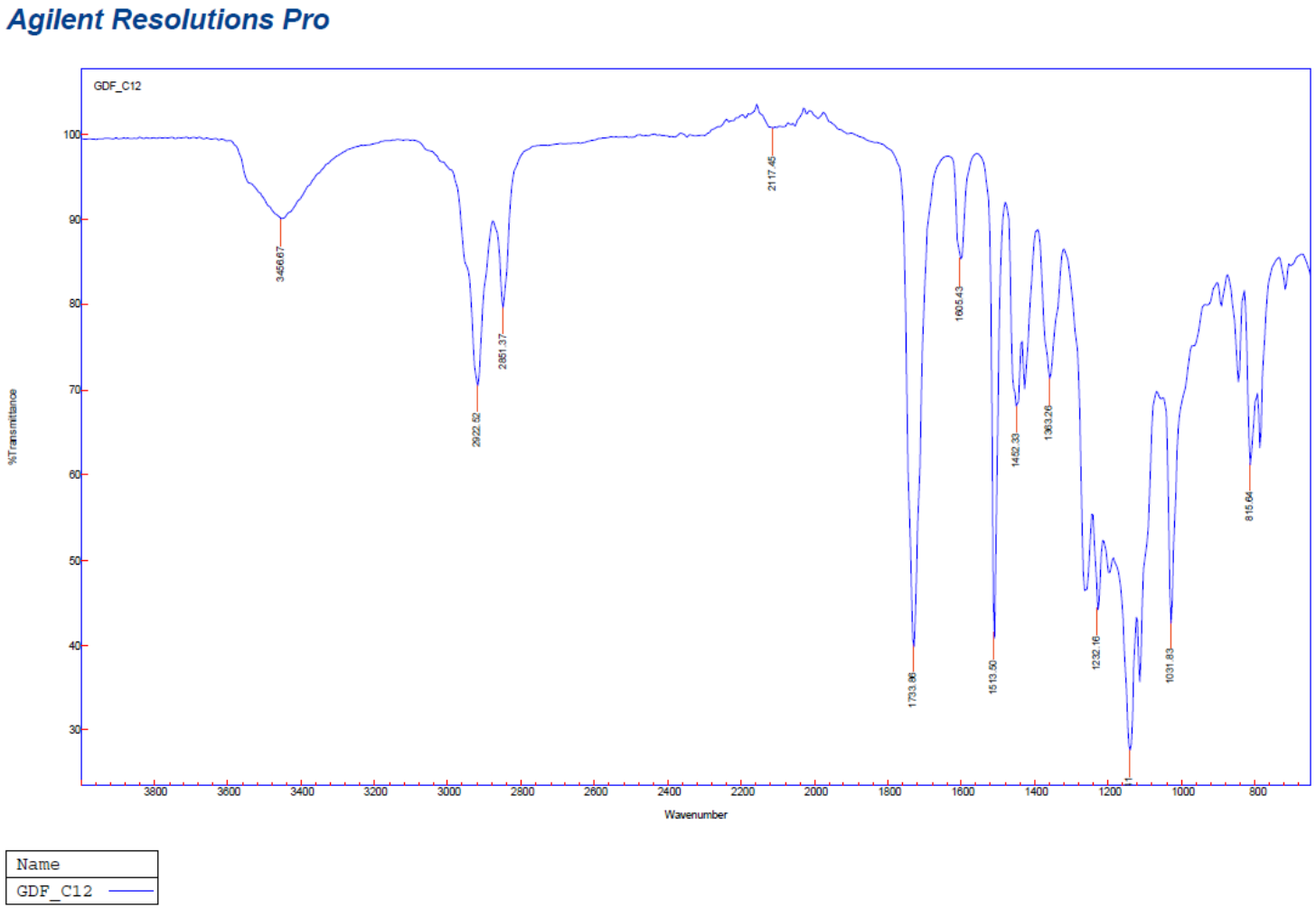
FT-IR spectra of GDF_{10}



HRMS analysis of GDF_{10}

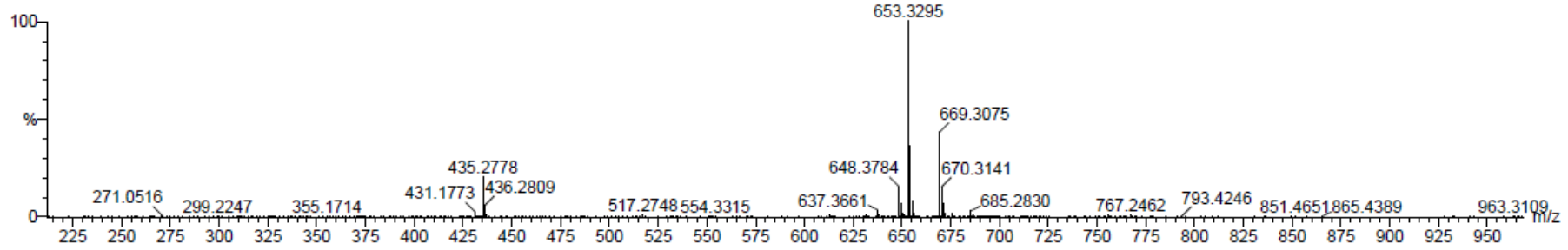
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
158 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-35 H: 0-200 O: 6-10 Na: 0-3 Al: 0-1 39K: 0-1 90Zr: 0-1

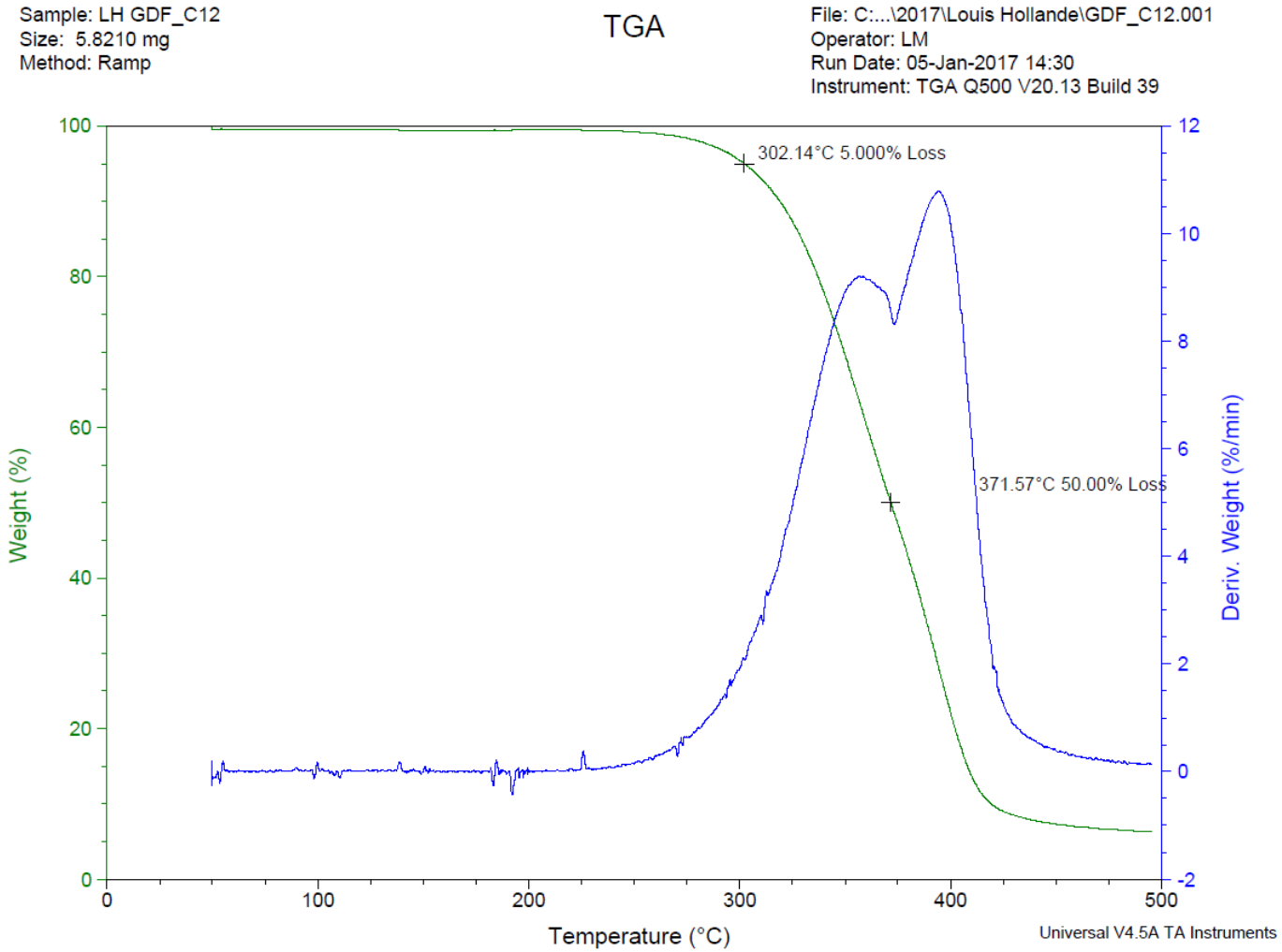
GDF_C12
17HR21 43 (1.409) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00); Cm (41:43)

1: TOF MS ES+
6.08e+003

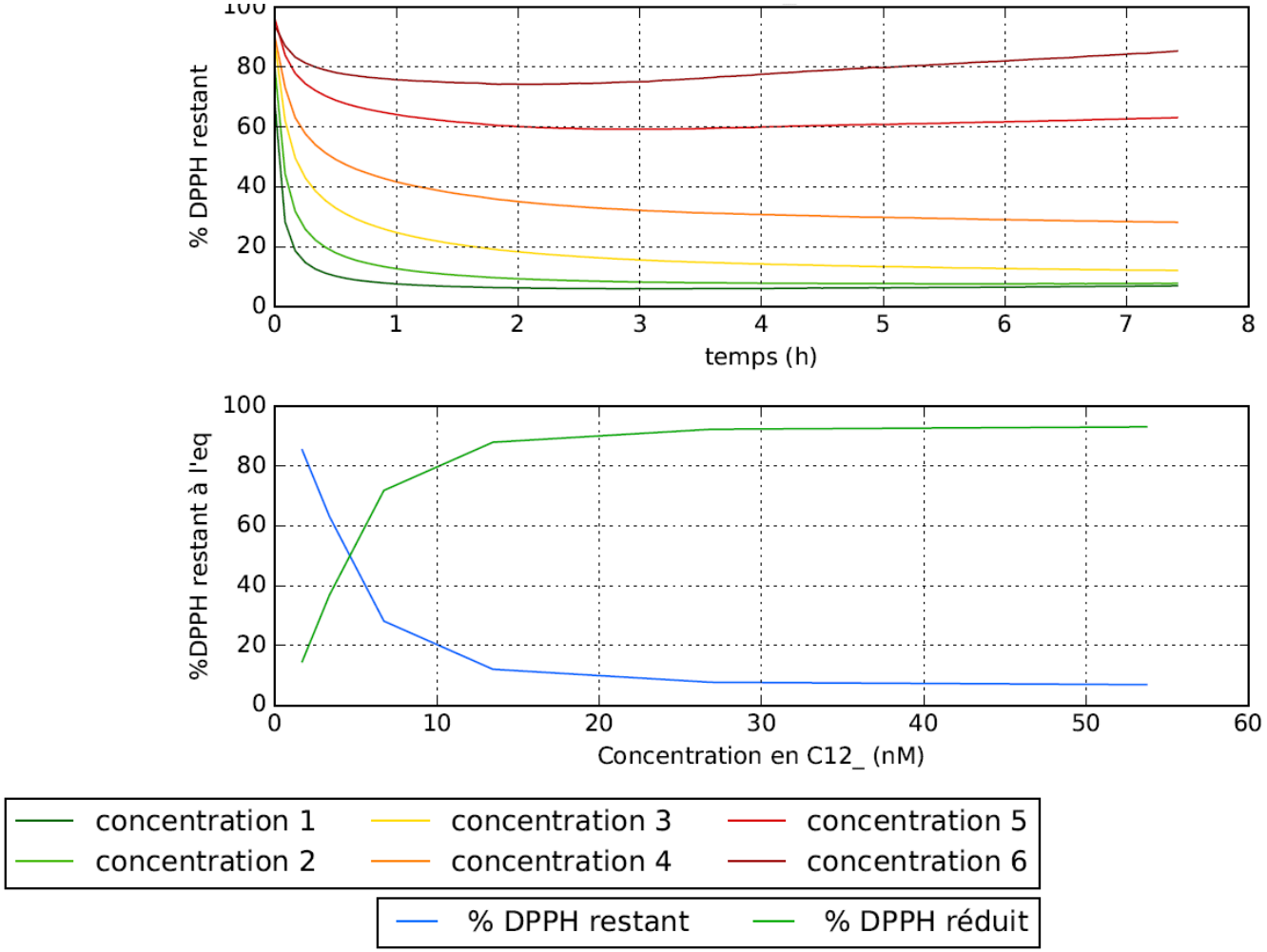


Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
653.3295	653.3302	-0.7	-1.1	10.5	19.4	C35 H50 O10 Na

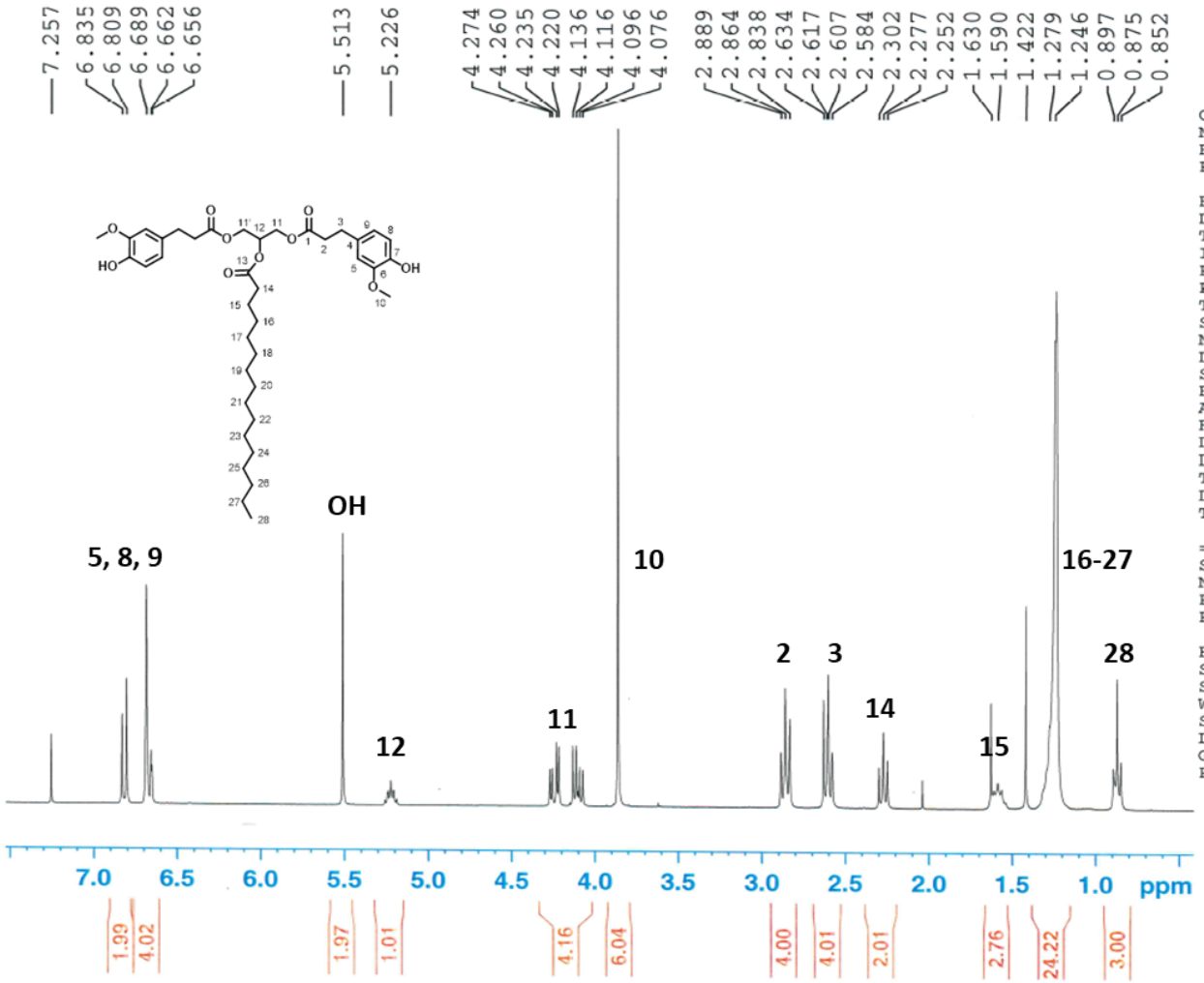
TGA analysis of GDF_{10}



DPPH analysis (EC_{50}) of GDF_{10}



^{1}H NMR spectrum of GDF_{14} ($CDCl_3$)

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PROCNO                   1

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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6103.516 Hz
FIDRES            0.093132 Hz
AQ                5.3687091 sec
RG                   14.1079
DW                  81.920 usec
DE                   6.50 usec
TE                  295.2 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           300.2018539 MHz
NUC1                    1H
P1                   8.70 usec
PLW1          23.00000000 W

F2 - Processing parameters
SI                   65536
SF             300.2000047 MHz
WDW                     EM
SSB          0
LB                   0.30 Hz
GB           0
PC                   1.00
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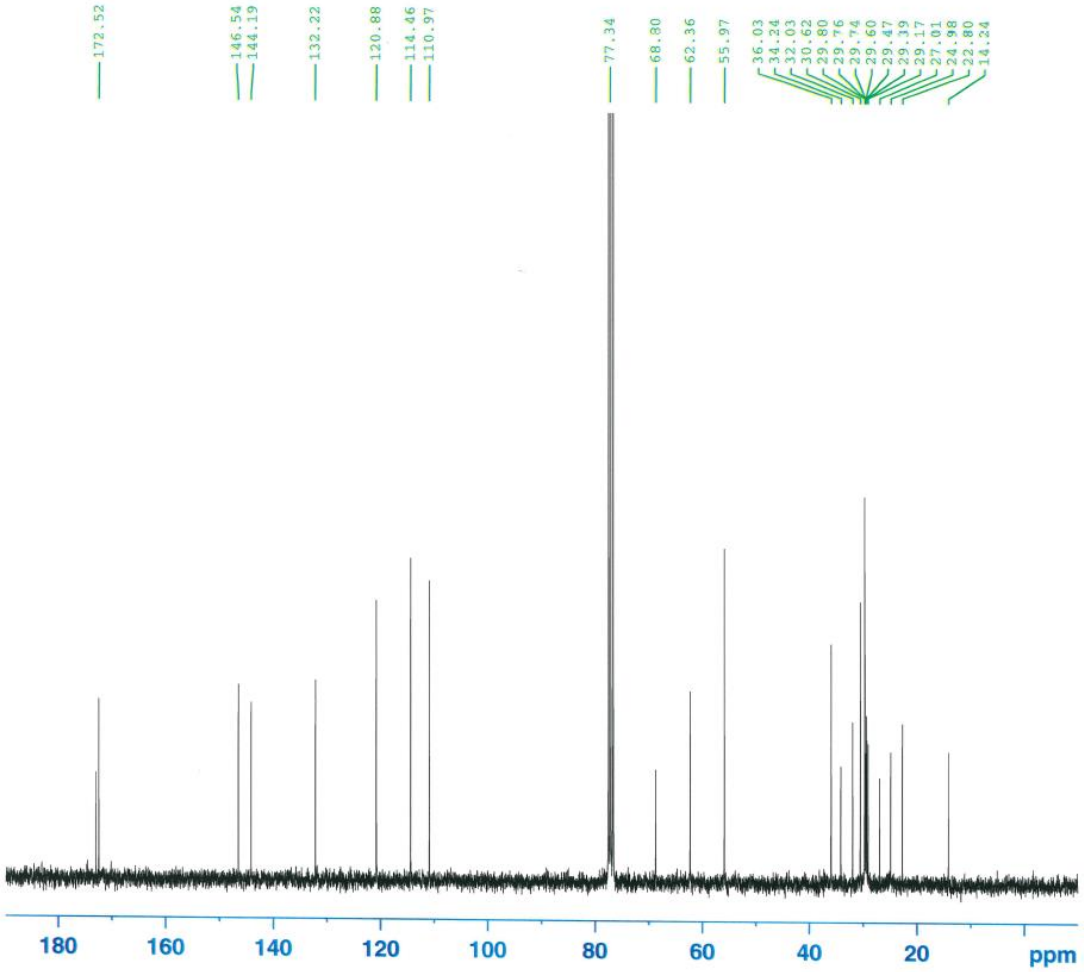
^{13}C NMR spectrum of GDF_{14} ($CDCl_3$)

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PROCNO                 1

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PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24414.063 Hz
FIDRES            0.372529 Hz
AQ                1.3421773 sec
RG                501.187
DW                20.480 usec
DE                 6.50 usec
TE                295.3 K
D1            2.00000000 sec
D11           0.03000000 sec
D31           0.00001300 sec
D40           0.00439029 sec
L4                    37
L5                    53
P32               98.00 usec
TD0                    1

======== CHANNEL f1 ========
SFO1          75.4928982 MHz
NUC1                  13C
P1                13.00 usec
PLW1         22.00000000 W

======== CHANNEL f2 ========
SFO2         300.2012008 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             98.00 usec
PLW2         23.00000000 W
PLW12         0.30000001 W
PLW13         0.23823000 W

F2 - Processing parameters
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SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
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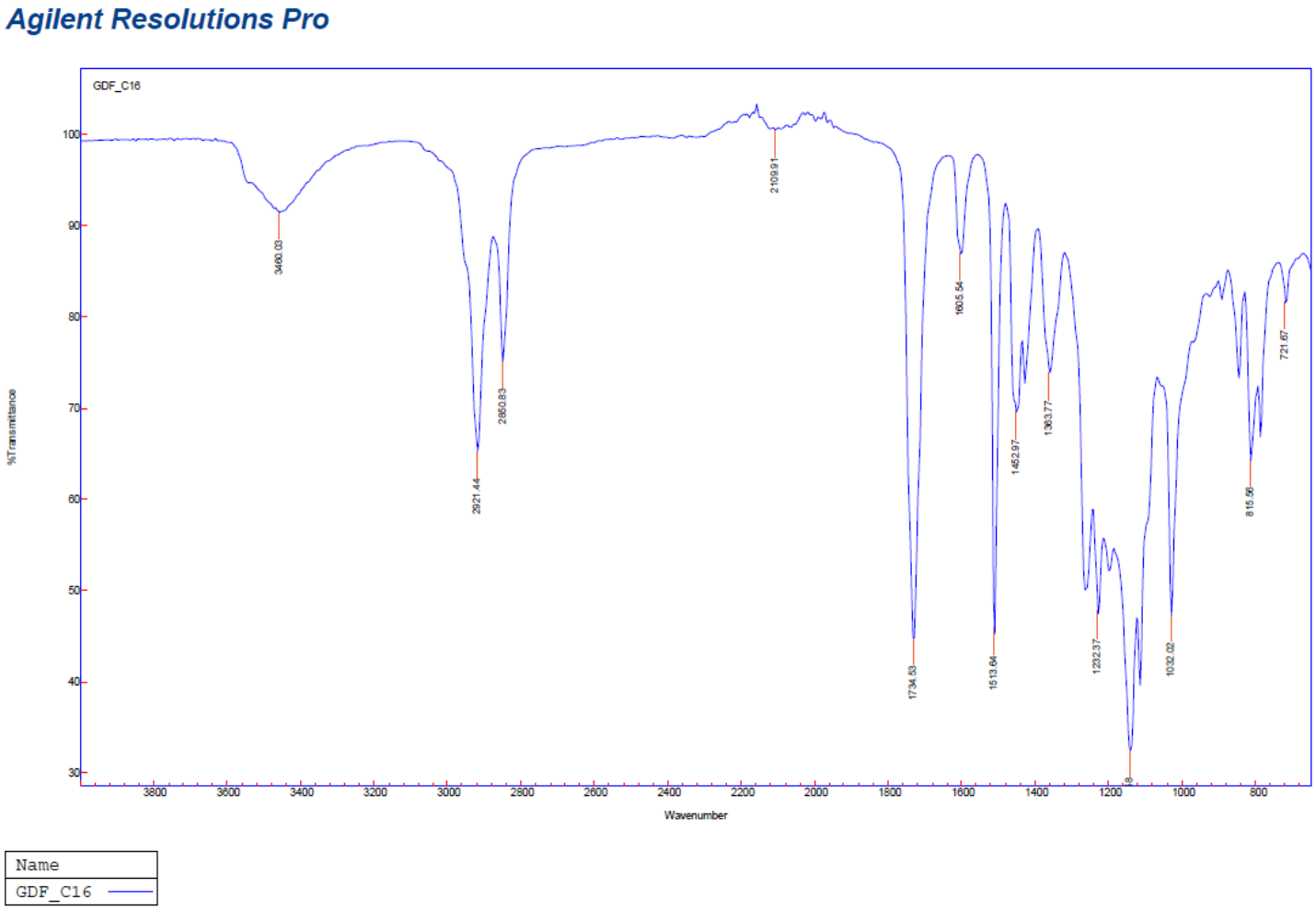
FT-IR spectra of GDF_{14}



HRMS analysis of GDF_{14}

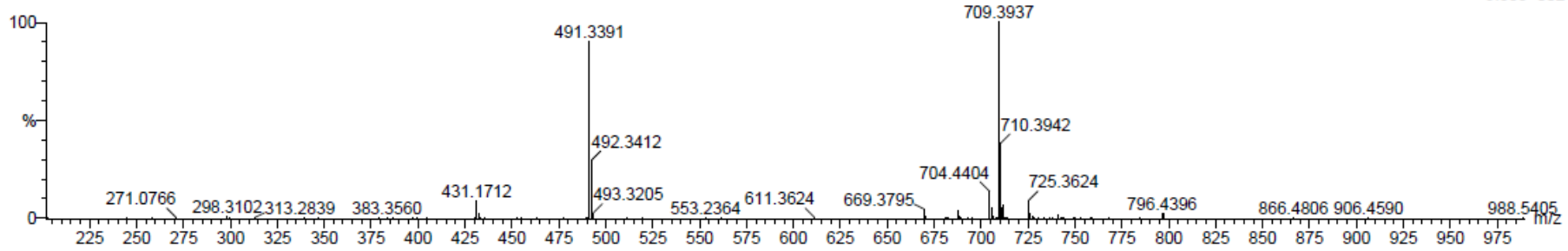
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
157 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 39-39 H: 0-200 O: 6-10 Na: 0-3 Al: 0-1 39K: 0-1 90Zr: 0-1

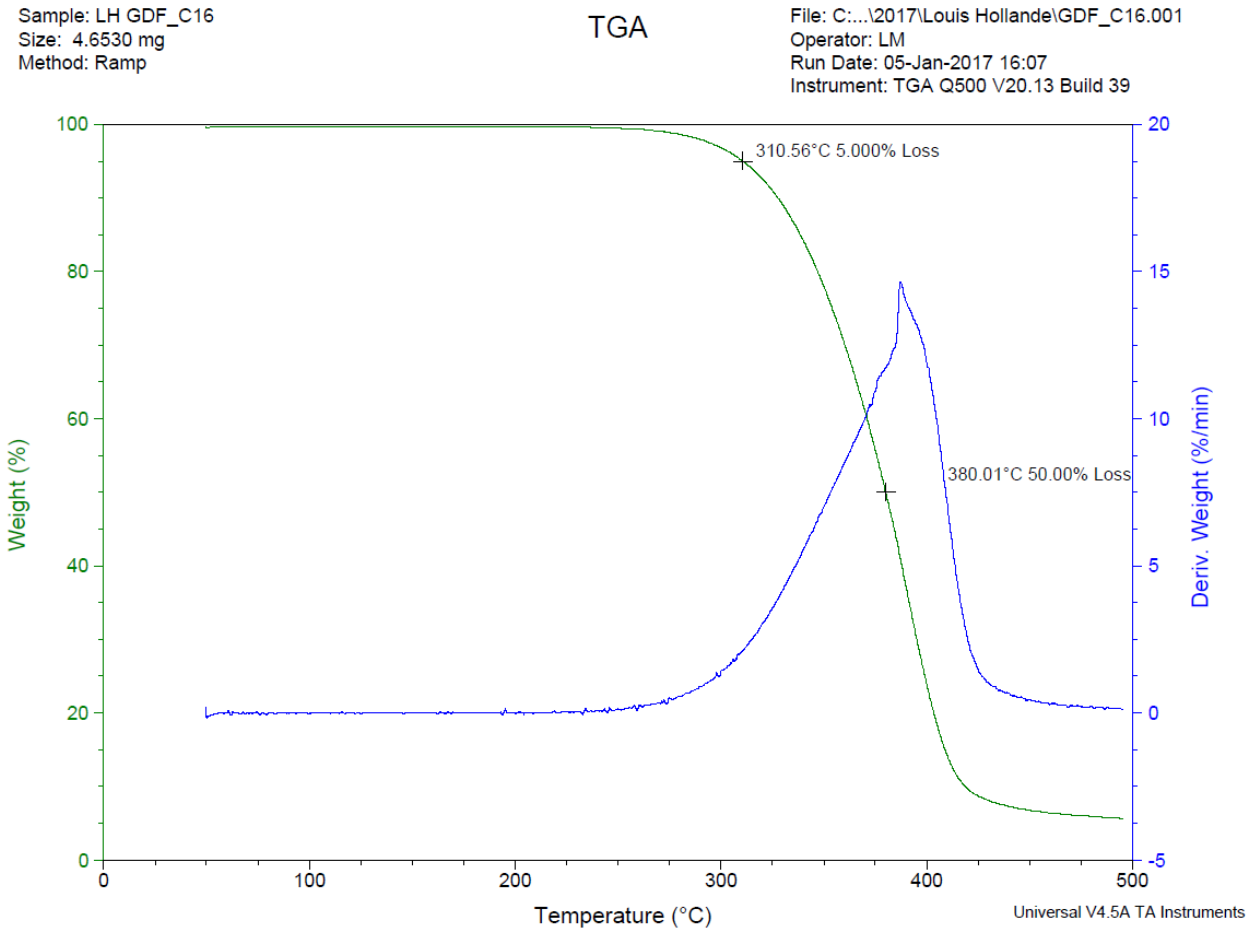
GDF_C16
17HR22 91 (2.965) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00); Cm (91:94)

1: TOF MS ES+
9.55e+002

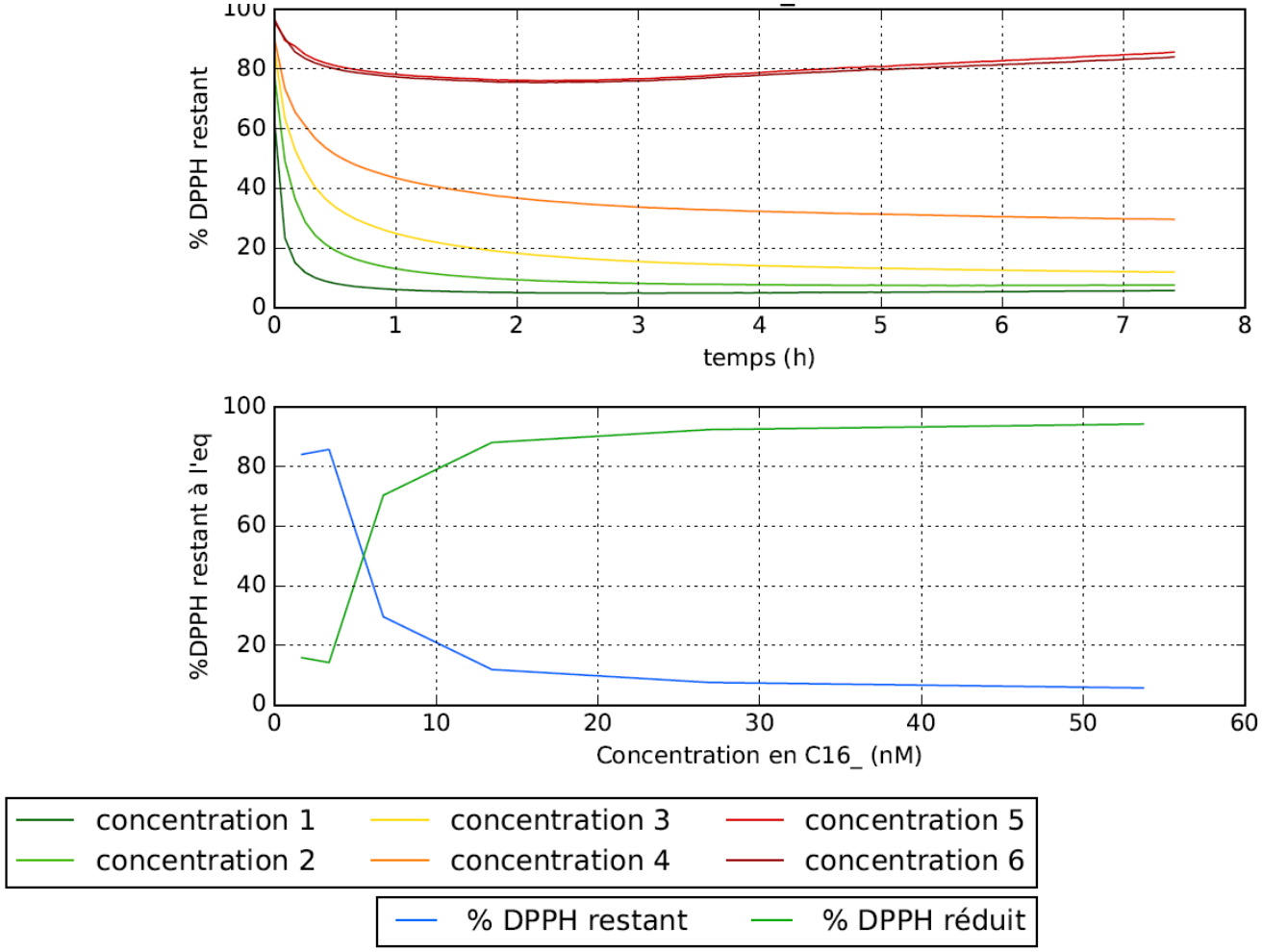


Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	**Calc. Mass**	**mDa**	**PPM**	**DBE**	**i-FIT**	**Formula**
709.3937	709.3928	0.9	1.3	10.5	27.7	C39 H58 O10 Na

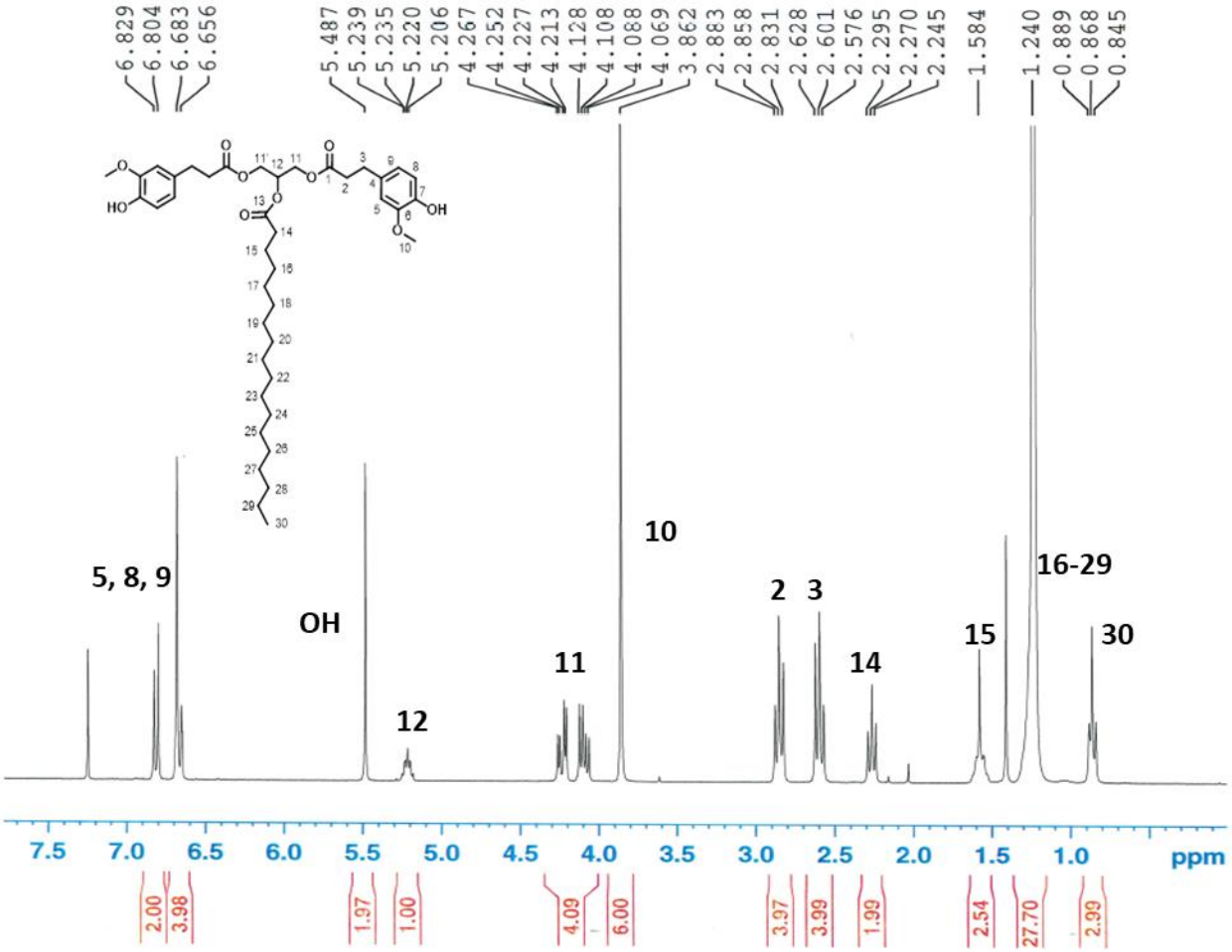
TGA analysis of GDF_{14}



DPPH analysis (EC_{50}) of GDF_{14}



^{1}H NMR spectrum of GDF_{16} ($CDCl_3$)

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EXPNO                 10
PROCNO                 1

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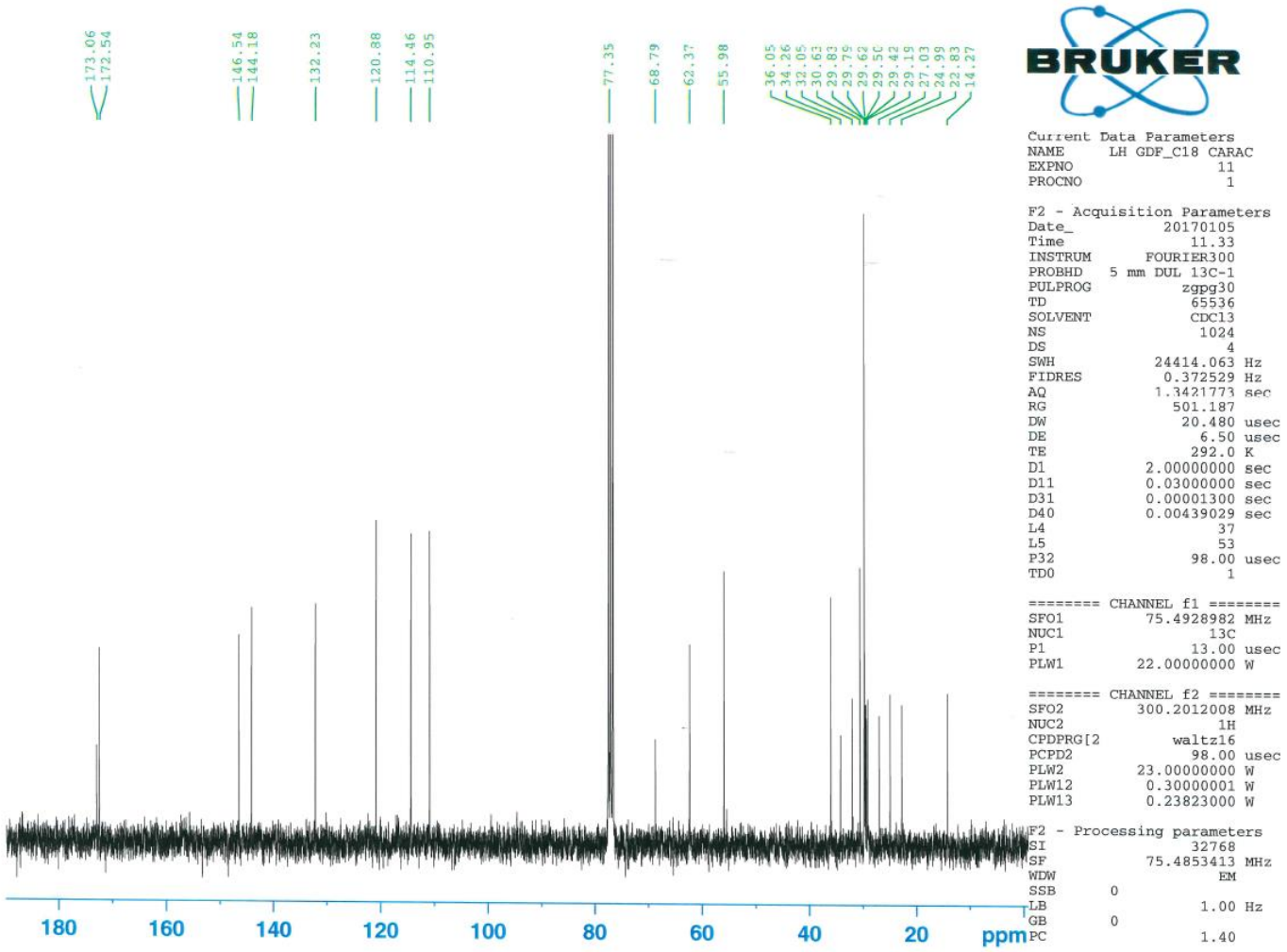
Time              11.29
INSTRUM       FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6103.516 Hz
FIDRES        0.093132 Hz
AQ            5.3687091 sec
RG               31.623
DW               81.920 usec
DE                6.50 usec
TE                291.9 K
D1           1.00000000 sec
TD0                   1

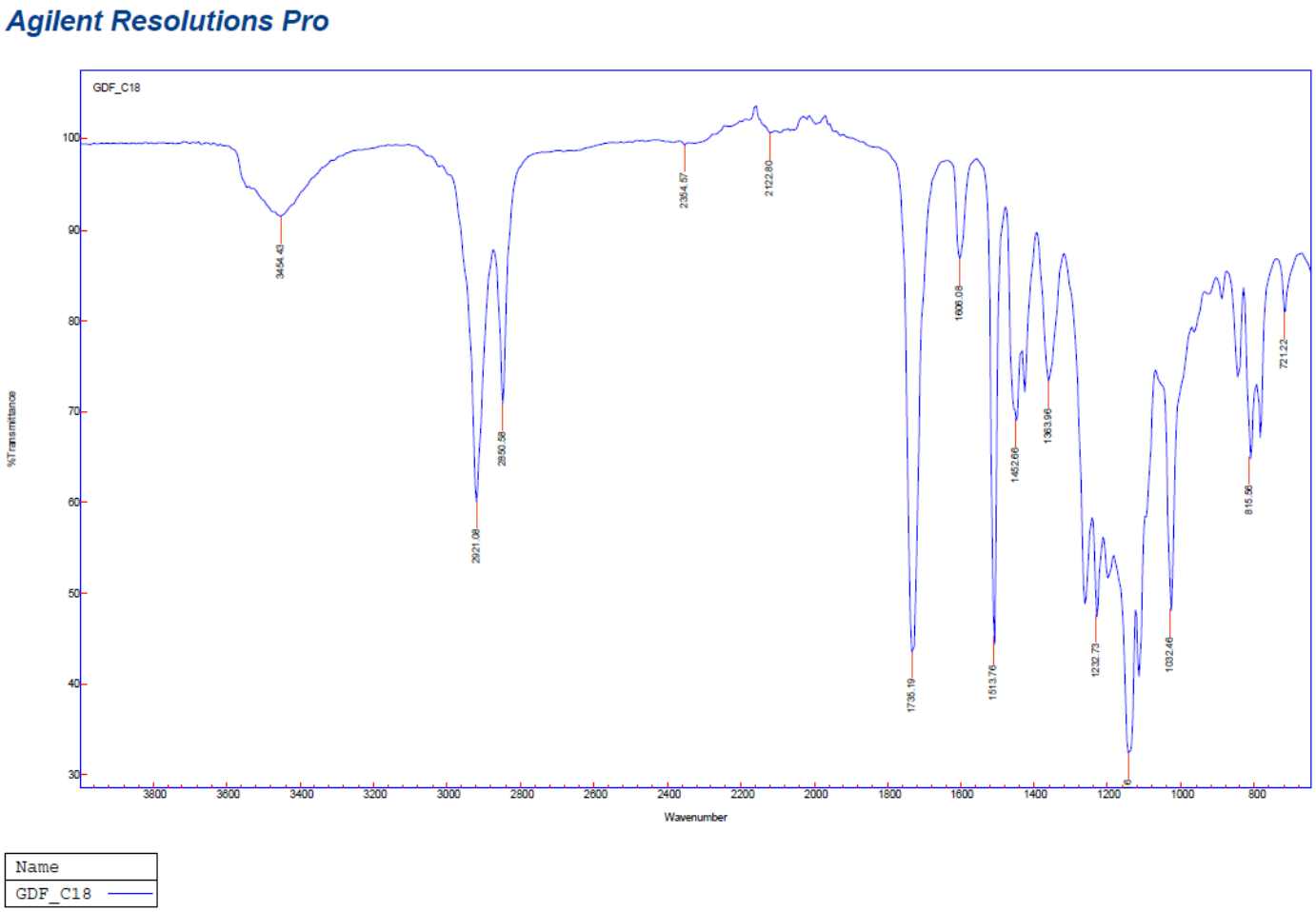
======== CHANNEL f1 ========
SFO1         300.2018539 MHz
NUC1                 1H
P1                 8.70 usec
PLW1        23.00000000 W

F2 - Processing parameters
SI                65536
SF           300.2000066 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C NMR spectrum of GDF_{16} ($CDCl_3$)



FT-IR spectra of GDF_{16}



HRMS analysis of GDF_{16}

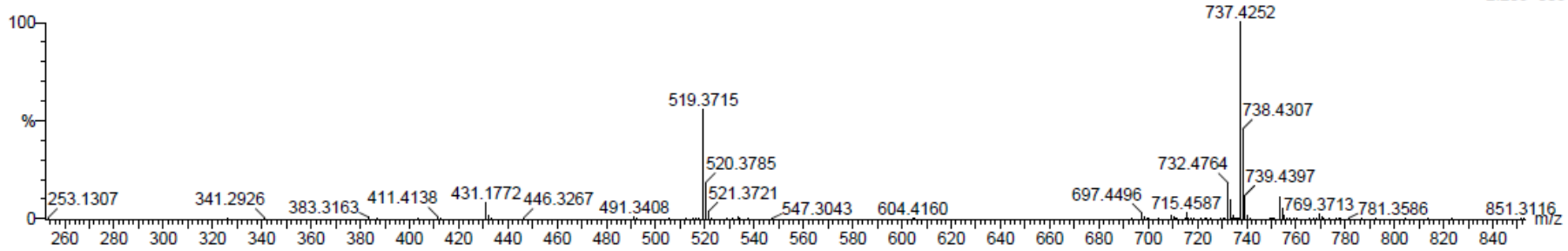
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
156 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 41-41 H: 0-200 O: 6-10 Na: 0-3 Al: 0-1 39K: 0-1 90Zr: 0-1

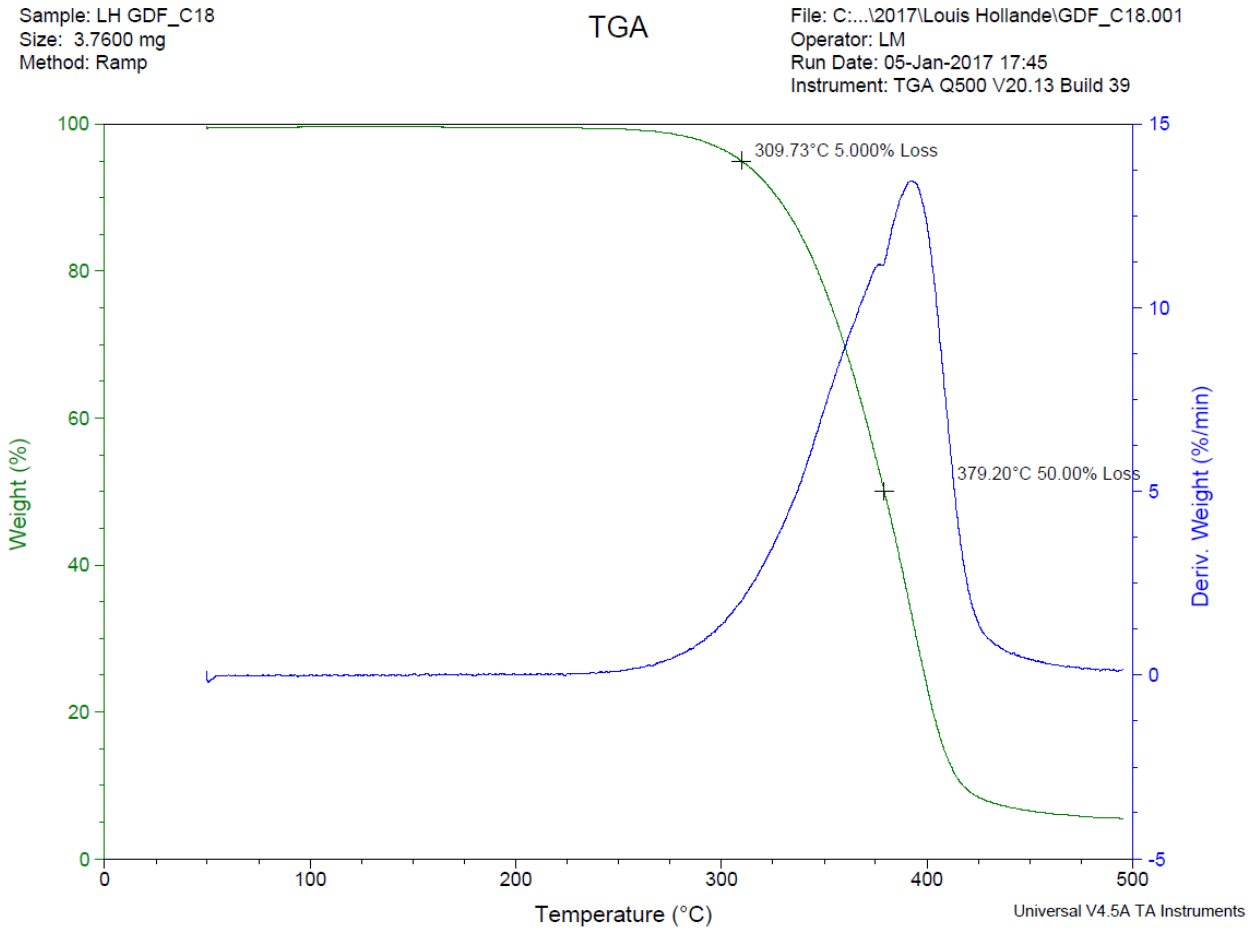
GDF_C18
17HR23 26 (0.839) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00); Cm (23:26)

1: TOF MS ES+
2.20e+003

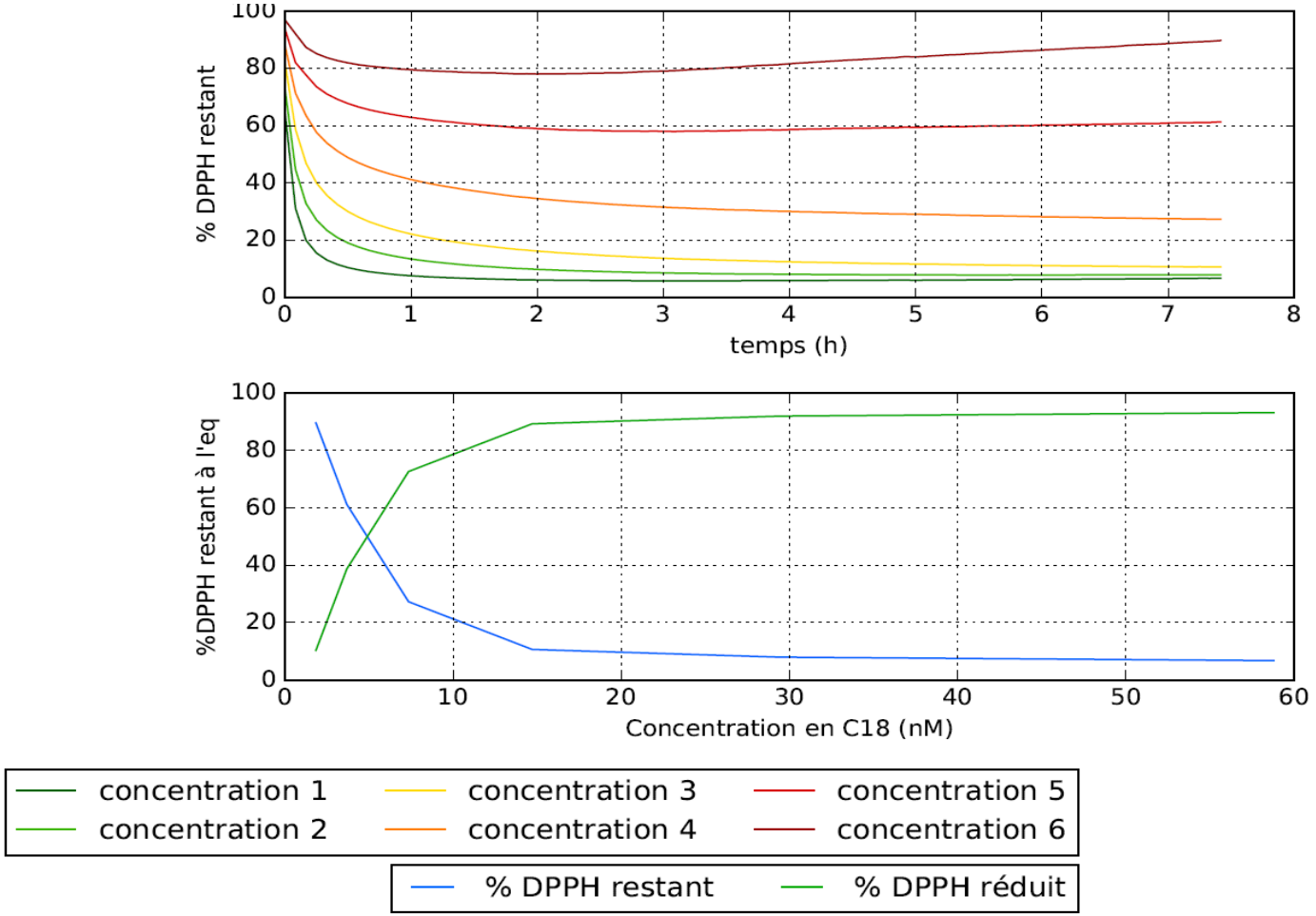


Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
737.4252	737.4241	1.1	1.5	10.5	0.9	C41 H62 O10 Na

TGA analysis of GDF_{16}



DPPH analysis (EC_{50}) of GDF_{16}



Kinetics behaviours at EC_{50} concentration for GDF_{10}, GDF_{14}, GDF_{16}, $Irganox_{1010}$, $Irganox_{1076}$