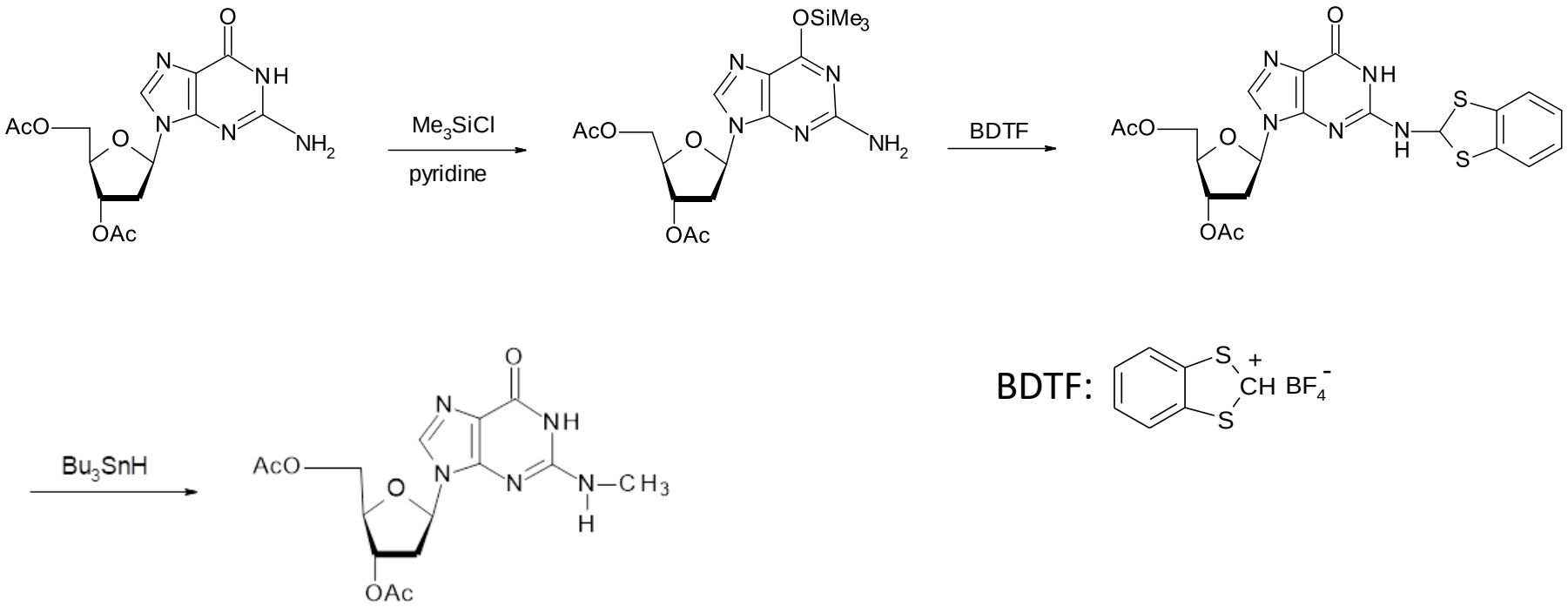
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information

Homopurine R_P-stereodefined phosphorothioate analogs of DNA with hampered Watson-Crick base pairings form Hoogsteen paired parallel duplexes with (2'-OMe)-RNA templates.

Anna Maciaszek*, Katarzyna Jastrzębska, Piotr Guga



Scheme 1S. Synthesis of an N^2-methylated derivative of 2'-deoxyguanosine

Figure 1S. Spectra for 5'-*O*-DMT-N^6-methyl-deoxyadenosine-3'-*O*-(2-thio-4,4-pentamethylene-1,3,2-oxathiaphospholane) – *fast* (**6f**)

A) HR MS

B) ^{31}P

C) ^{1}H NMR

D) ^{13}C NMR

Elemental Composition Report

Single Mass Analysis

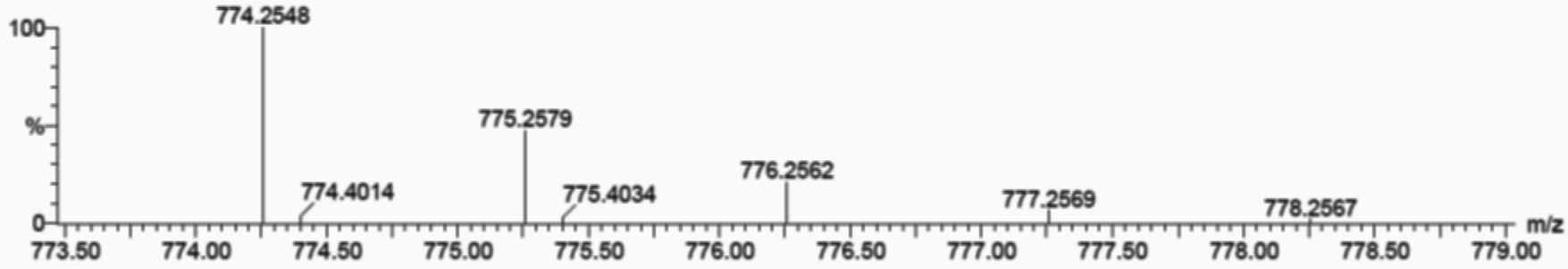
Tolerance = 2.5 PPM / DBE: min = -10.0, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5

A) HR MS

Monoisotopic Mass, Odd and Even Electron Ions
187 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-42 H: 0-50 N: 0-6 O: 2-7 P: 1-1 S: 0-3

180726_ADM_941 17 (0.197) Cm (14:21)
1: TOF MS ES+

4.13e+007



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Maximum:		15.0	2.5	60.0				
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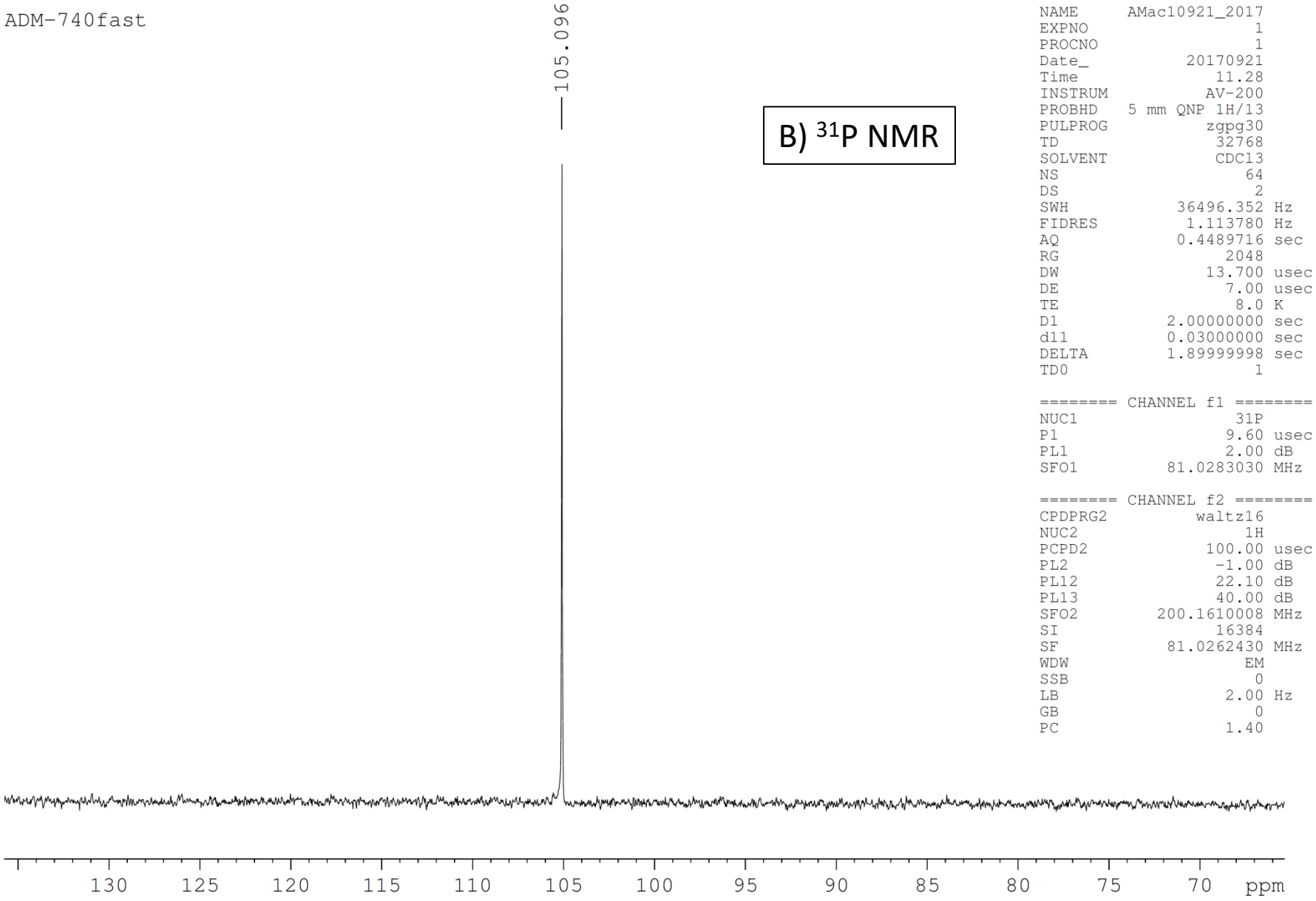
	774.2562	-1.4	-1.8	20.0	104.9	9.787	0.01	C41 H47 N2 O7 P S2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PROCNO 1
Date_ 20170921
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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SWH 36496.352 Hz
FIDRES 1.113780 Hz
AQ 0.4489716 sec
RG 2048
DW 13.700 usec
DE 7.00 usec
TE 8.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
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P1 9.60 usec
PL1 2.00 dB
SFO1 81.0283030 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.00 dB
PL12 22.10 dB
PL13 40.00 dB
SFO2 200.1610008 MHz
SI 16384
SF 81.0262430 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
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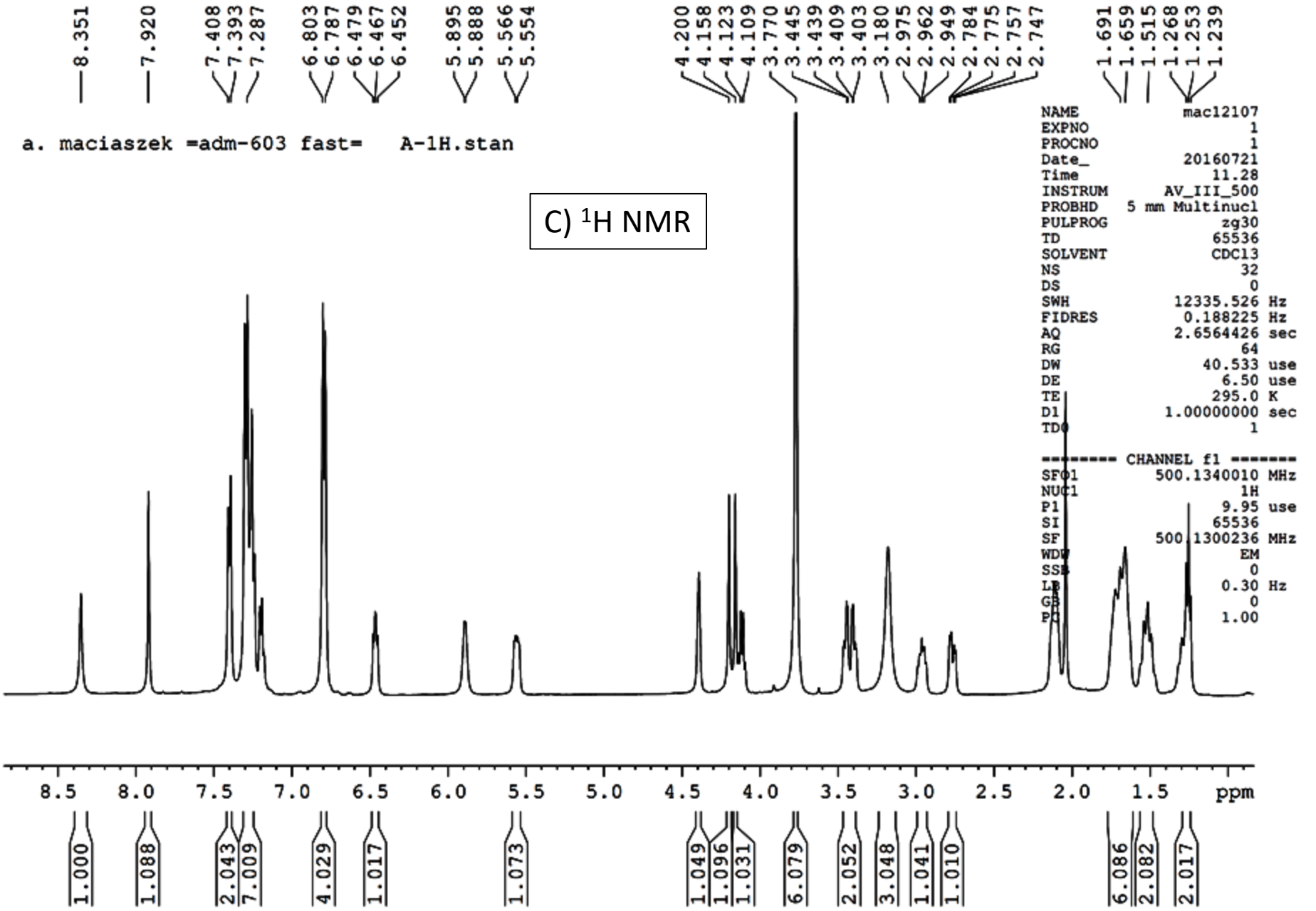
125
120
115
110
105
100
95
90
85
80
75
70
ppm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6.452
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5.888
5.566
5.554
4.200
4.158
4.123
4.109
3.770
3.445
3.439
3.409
3.403
3.180
2.975
2.962
2.949
2.784
2.775
2.757
2.747
1.691
1.659
1.515
1.268
1.253
1.239
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C) 1H NMR
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EXPNO 1
PROCNO 1
Date_ 20160721
Time 11.28
INSTRUM AV_III_500
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 64
DW 40.533 use
DE 6.50 use
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 =======
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NUC1 1H
P1 9.95 use
SI 65536
SF 500.1300236 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
ppm
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4.029
1.017
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1.041
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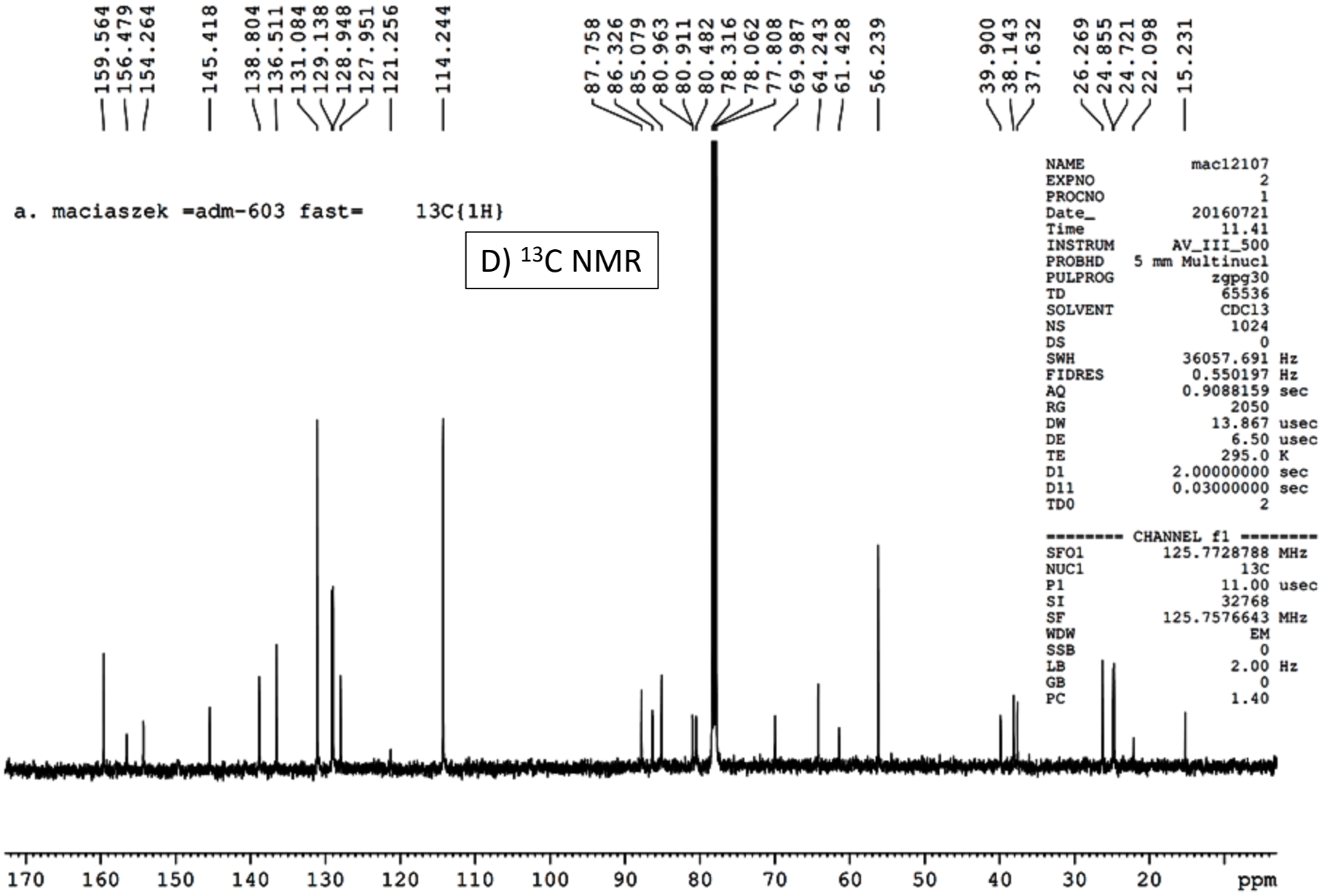
6.086
2.082
2.017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86.326
85.079
80.963
80.911
80.482
78.316
78.062
77.808
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64.243
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PROCNO 1
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TD 65536
SOLVENT CDCl3
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DS 0
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 2050
DW 13.867 usec
DE 6.50 usec
TE 295.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 2
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NUC1 13C
P1 11.00 usec
SI 32768
SF 125.7576643 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Figure 2S. Spectra for 5'-*O*-DMT-N^6-methyl-deoxyadenosine-3'-*O*-(2-thio-4,4-pentamethylene-1,3,2-oxathiaphospholane) – *slow* (**6s**)

A) HR MS

B) ^{31}P

C) ^{1}H NMR

D) ^{13}C NMR

Elemental Composition Report

A) HR MS

Single Mass Analysis
Tolerance = 2.5 PPM / DBE: min = -10.0, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Even Electron Ions
187 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-42 H: 0-50 N: 0-6 O: 2-7 P: 1-1 S: 0-3

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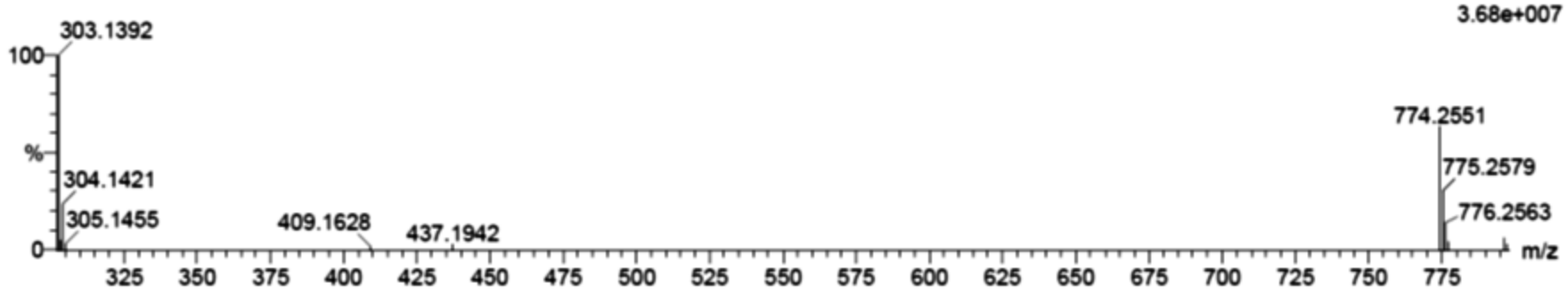
1: TOF MS ES+



Minimum:				-10.0				
Maximum:		15.0	2.5	60.0				
Mass	**Calc. Mass**	**mDa**	**PPM**	**DBE**	**i-FIT**	**Norm**	**Conf(%)**	**Formula**
774.2551	774.2549	0.2	0.3	20.5	125.3	n/a	n/a	C39 H45 N5 O6 P S2

ADM-741slow

105.233

B) ^{31}P NMR

NAME	AMac10921_2017	
EXPNO	2	
PROCNO	1	
Date_	20170921	
Time	11.35	
INSTRUM	AV-200	
PROBHD	5 mm QNP 1H/13	
PULPROG	zgpg30	
TD	32768	
SOLVENT	CDCl3	
NS	64	
DS	2	
SWH	36496.352	Hz
FIDRES	1.113780	Hz
AQ	0.4489716	sec
RG	2298.8	
DW	13.700	usec
DE	7.00	usec
TE	8.0	K
D1	2.00000000	sec
d11	0.03000000	sec
DELTA	1.89999998	sec
TD0	1	
========	CHANNEL f1	========
NUC1	31P	
P1	9.60	usec
PL1	2.00	dB
SFO1	81.0283030	MHz
========	CHANNEL f2	========
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	100.00	usec
PL2	-1.00	dB
PL12	22.10	dB
PL13	40.00	dB
SFO2	200.1610008	MHz
SI	16384	
SF	81.0262430	MHz
WDW	EM	
SSB	0	
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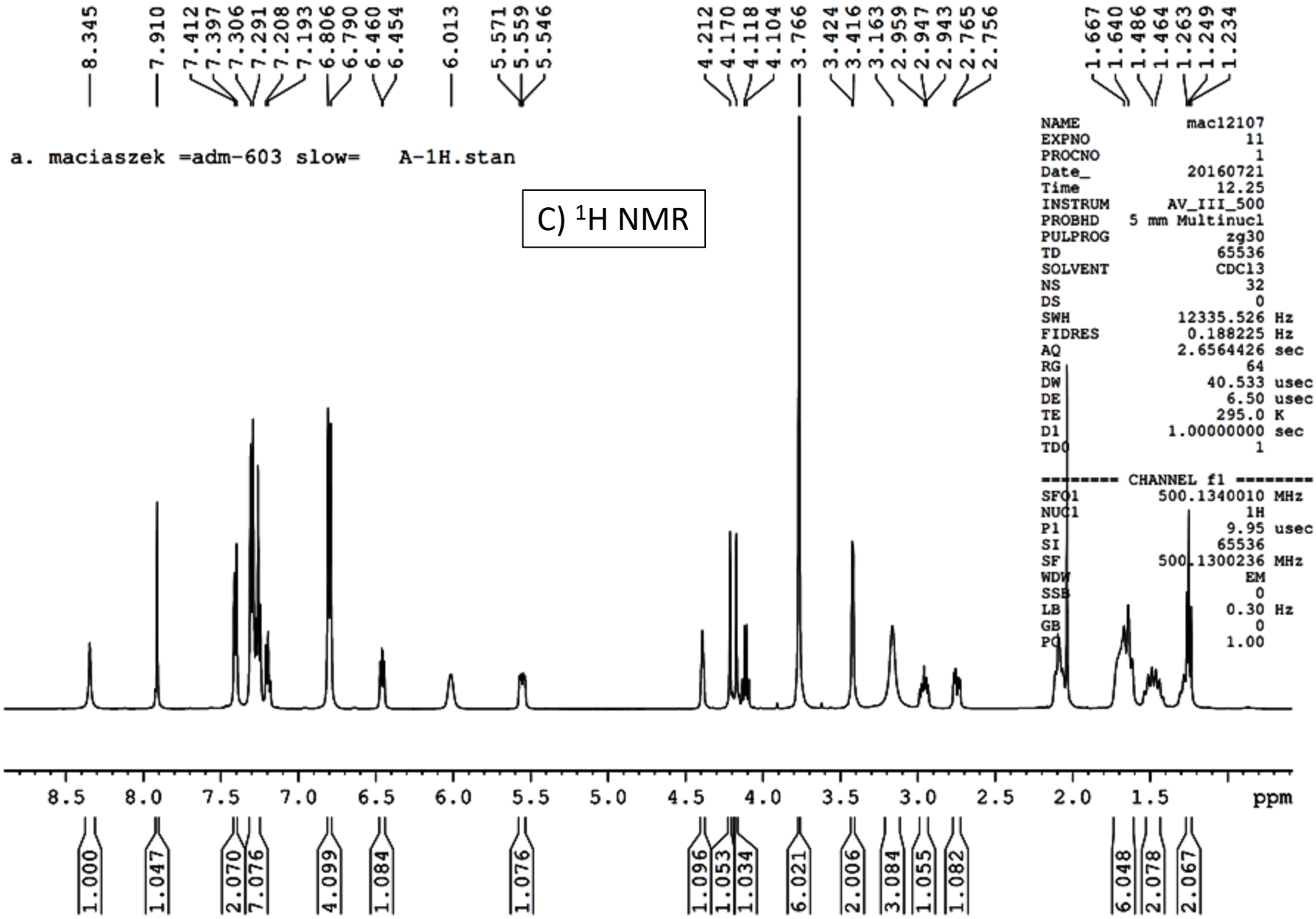
GB	0	
PC	1.40	

145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 ppm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6.013
5.571
5.559
5.546
4.212
4.170
4.118
4.104
3.766
3.424
3.416
3.163
2.959
2.947
2.943
2.765
2.756
1.667
1.640
1.486
1.464
1.263
1.249
1.234
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PROCNO 1
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 64
DW 40.533 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 500.1340010 MHz
NUC1 1H
P1 9.95 usec
SI 65536
SF 500.1300236 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
ppm
1.000
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7.076
4.099
1.084
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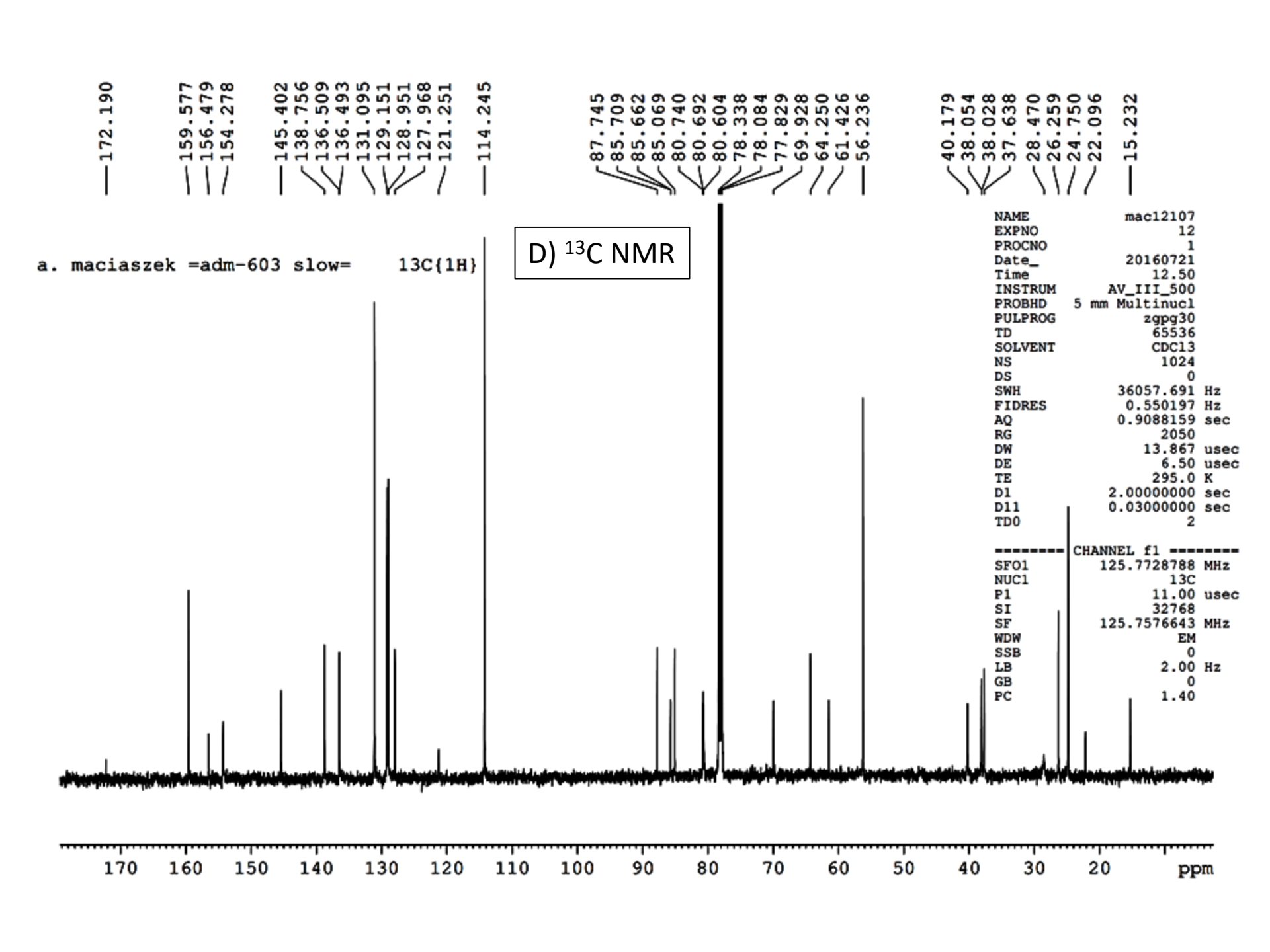
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114.245
87.745
85.709
85.662
85.069
80.740
80.692
80.604
78.338
78.084
77.829
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64.250
61.426
56.236
40.179
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37.638
28.470
26.259
24.750
22.096
15.232
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PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 0
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 2050
DW 13.867 usec
DE 6.50 usec
TE 295.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 2
CHANNEL f1
SFO1 125.7728788 MHz
NUC1 13C
P1 11.00 usec
SI 32768
SF 125.7576643 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Figure 3S. Spectra for 5'-*O*-DMT-N^2,N^2-dimethyl-O^6–DPC-deoxyguanosine-3'-*O*-(2-thio-4,4-pentamethylene-1,3,2-oxathiaphospholane) – *fast* (**7f**)

A) HR MS

B) ^{31}P

C) ^{1}H NMR

D) ^{13}C NMR

Elemental Composition Report

A) HR MS

Single Mass Analysis
Tolerance = 2.5 PPM / DBE: min = -10.0, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Even Electron Ions
171 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-55 H: 0-65 N: 0-7 O: 2-8 P: 1-1 S: 0-3

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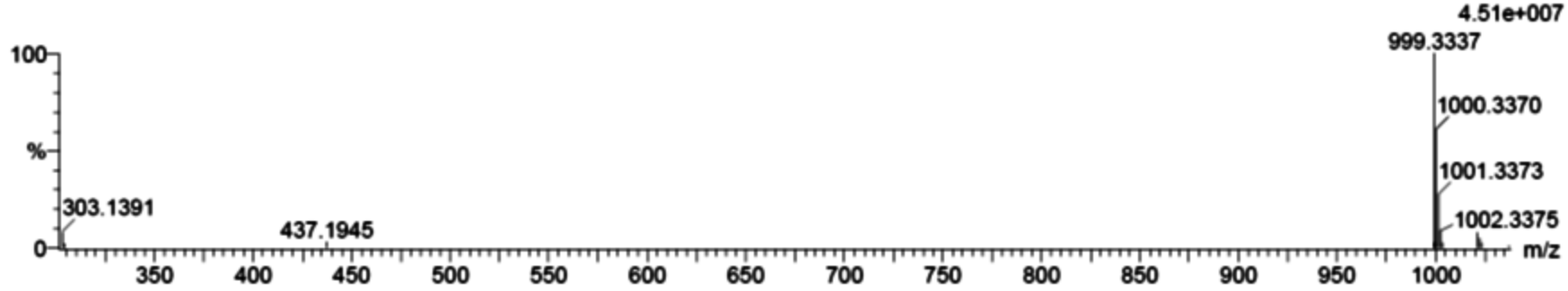
1: TOF MS ES+



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Maximum:		15.0	2.5	60.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
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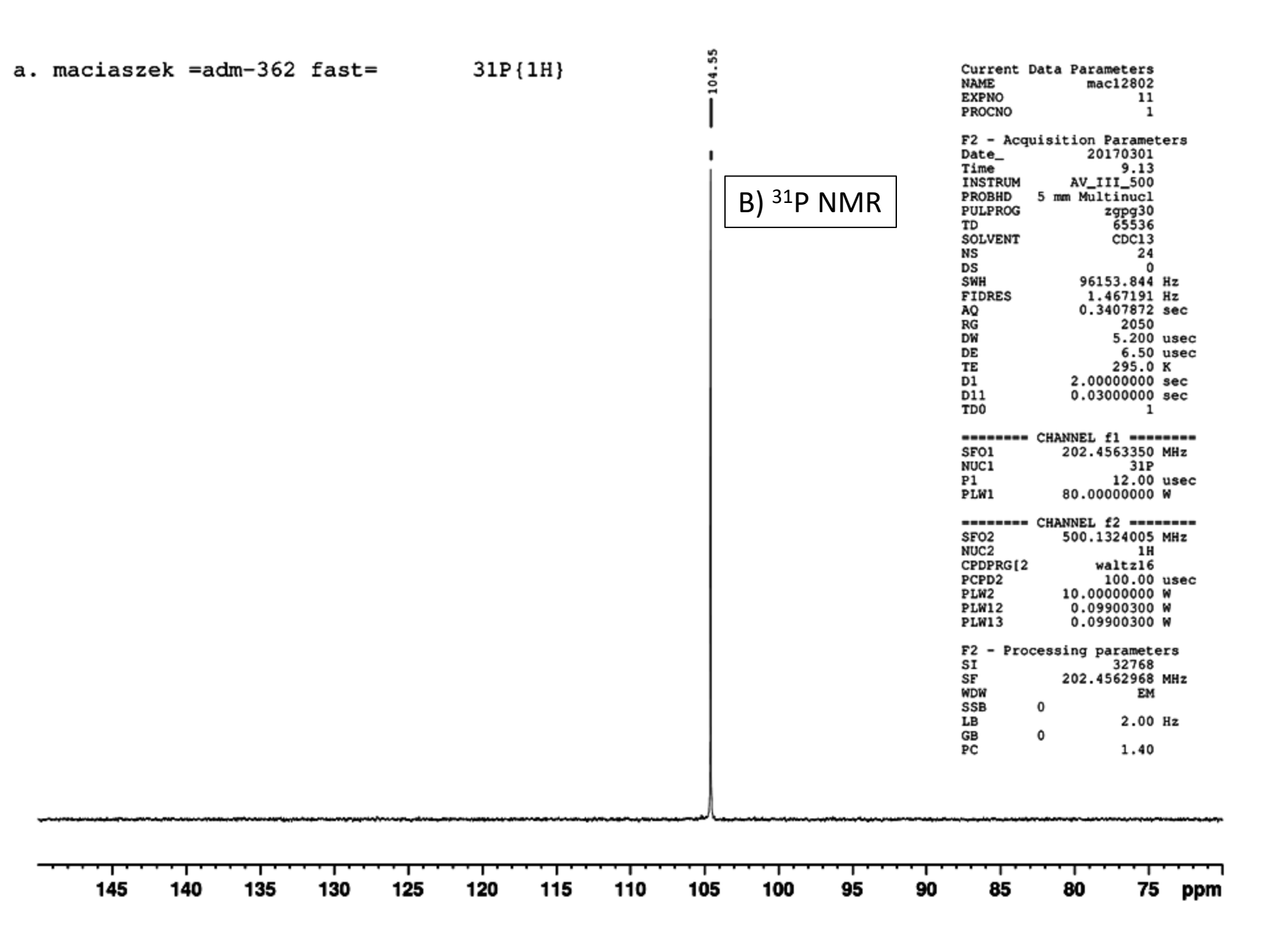
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
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DS 0
SWH 96153.844 Hz
FIDRES 1.467191 Hz
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RG 2050
DW 5.200 usec
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TE 295.0 K
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D11 0.03000000 sec
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NUC1 31P
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NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 10.00000000 W
PLW12 0.09900300 W
PLW13 0.09900300 W
F2 - Processing parameters
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SSB 0
LB 2.00 Hz
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PC 1.40
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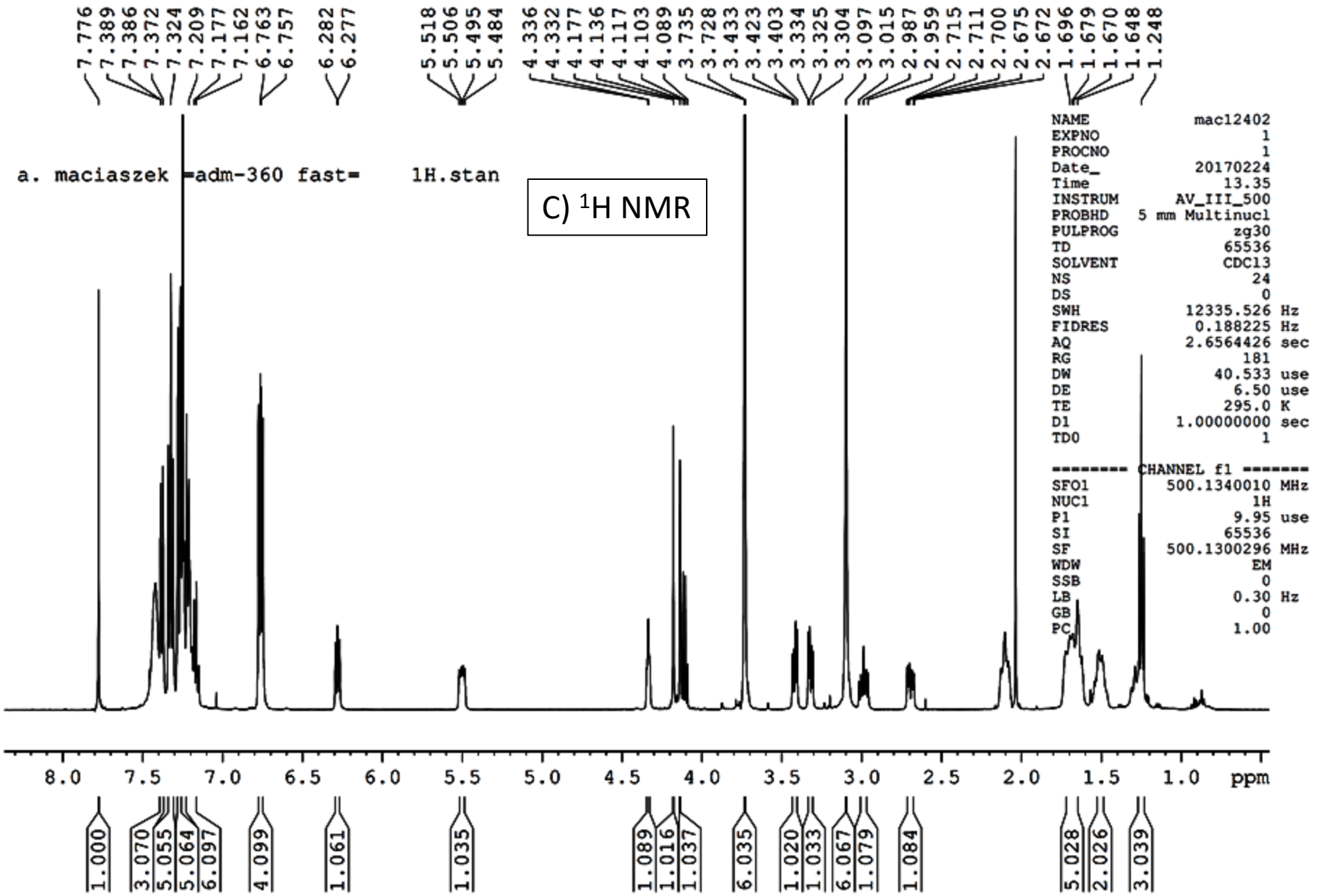
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PROCNO 1
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 24
DS 0
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 181
DW 40.533 use
DE 6.50 use
TE 295.0 K
D1 1.00000000 sec
TD0 1
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NUC1 1H
P1 9.95 use
SI 65536
SF 500.1300296 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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4.0
3.5
3.0
2.5
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1.5
1.0
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1.061
1.035
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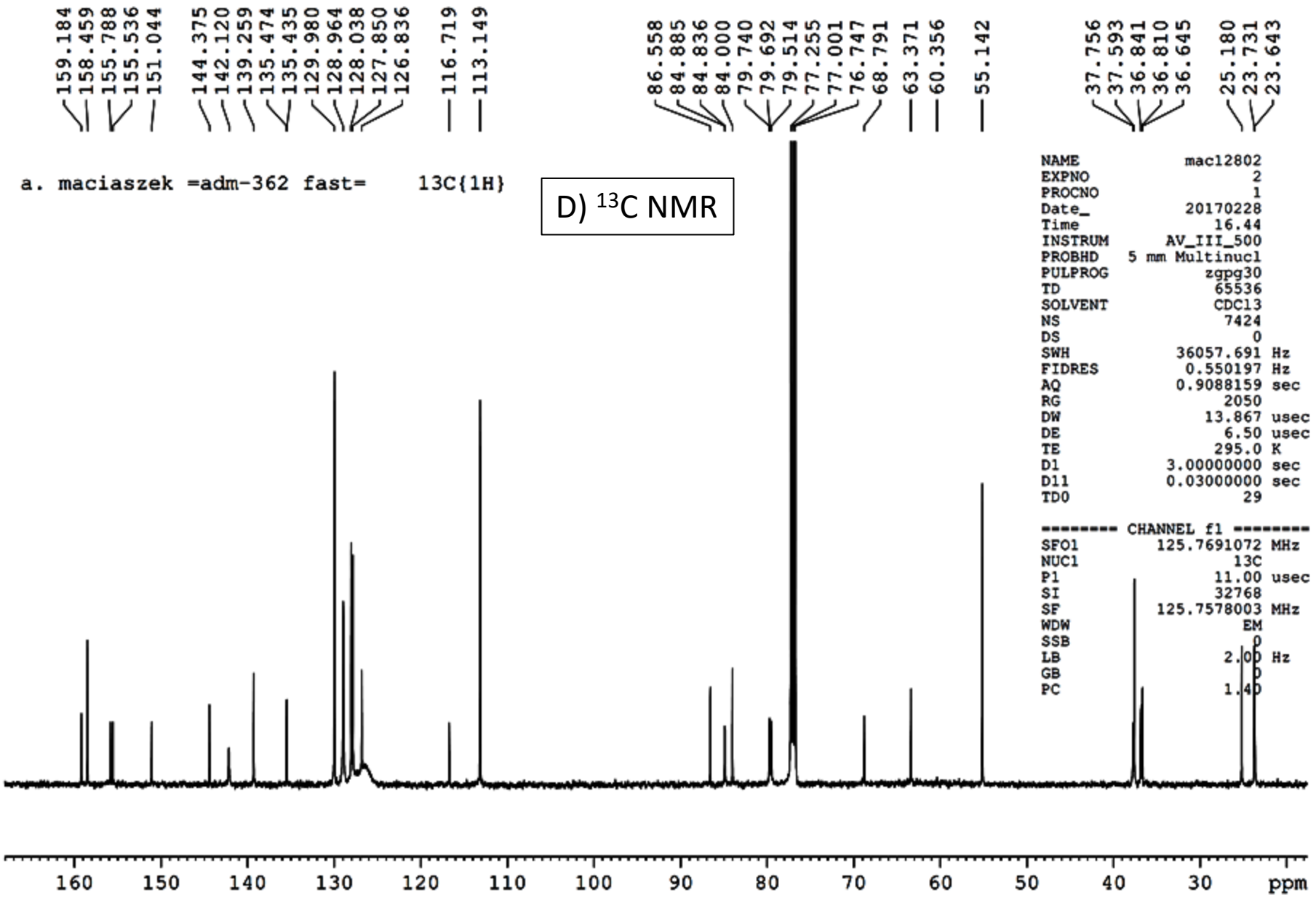
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77.001
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TD 65536
SOLVENT CDCl3
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FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 2050
DW 13.867 usec
DE 6.50 usec
TE 295.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 29
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NUC1 13C
P1 11.00 usec
SI 32768
SF 125.7578003 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

Figure 4S. Spectra for 5'-*O*-DMT-N^2,N^2-dimethyl-O^6–DPC-deoxyguanosine-3'-*O*-(2-thio-4,4-pentamethylene-1,3,2-oxathiaphospholane) – *fast* (**7s**)

A) HR MS

B) ^{31}P

C) ^{1}H NMR

D) ^{13}C NMR

Elemental Composition Report

A) HR MS

Single Mass Analysis
Tolerance = 2.5 PPM / DBE: min = -10.0, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 5

Monoisotopic Mass, Even Electron Ions
171 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-55 H: 0-65 N: 0-7 O: 2-8 P: 1-1 S: 0-3

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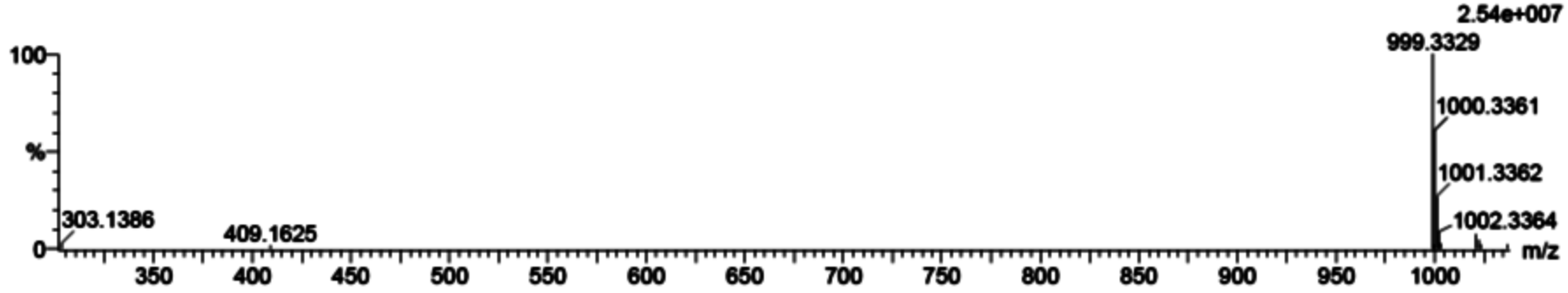
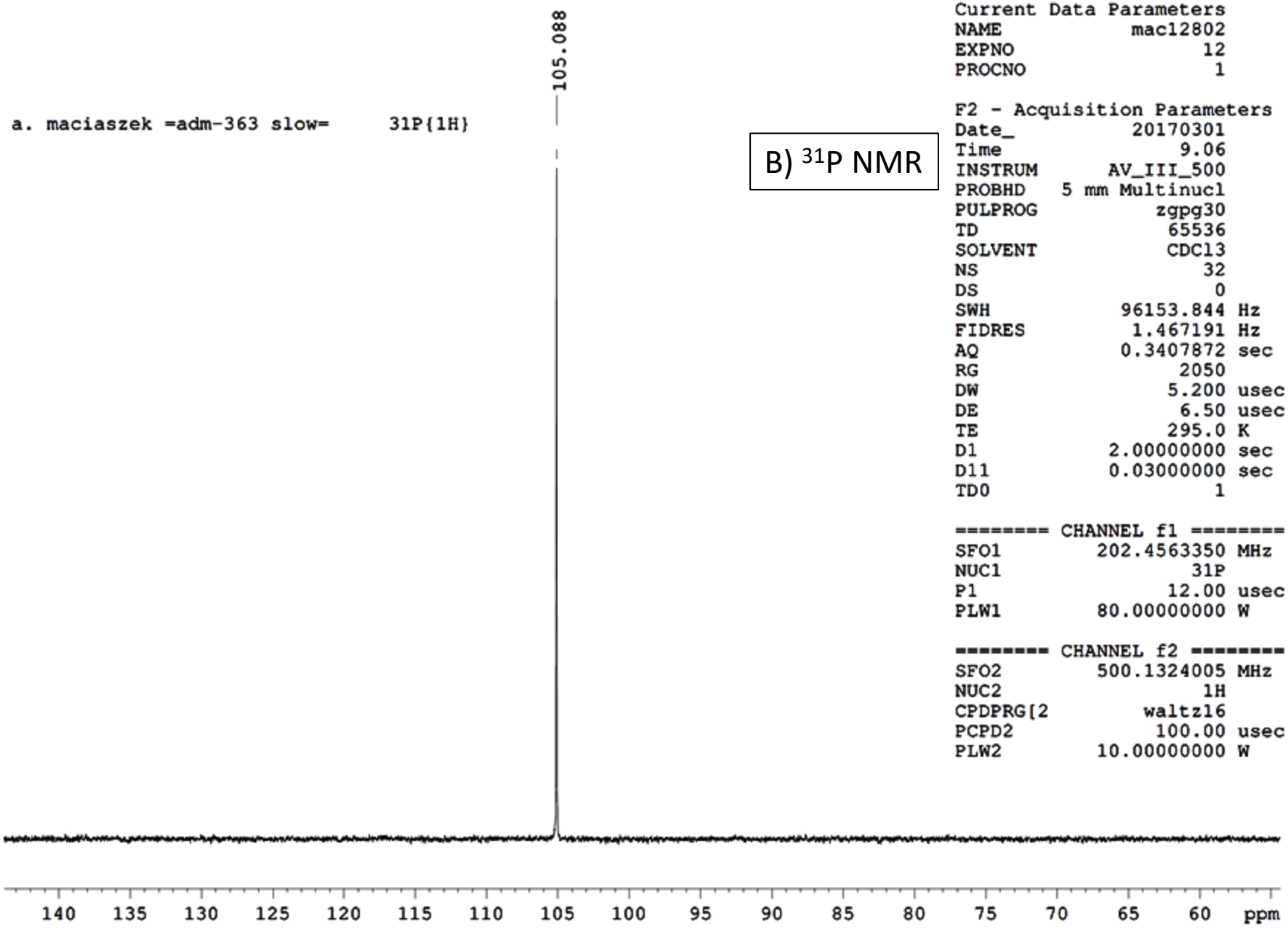
1: TOF MS ES+



Minimum:				-10.0				
Maximum:		15.0	2.5	60.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
999.3329	999.3339	-1.0	-1.0	29.5	79.2	n/a	n/a	C53 H56 N6 O8 P S2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B) 31P NMR
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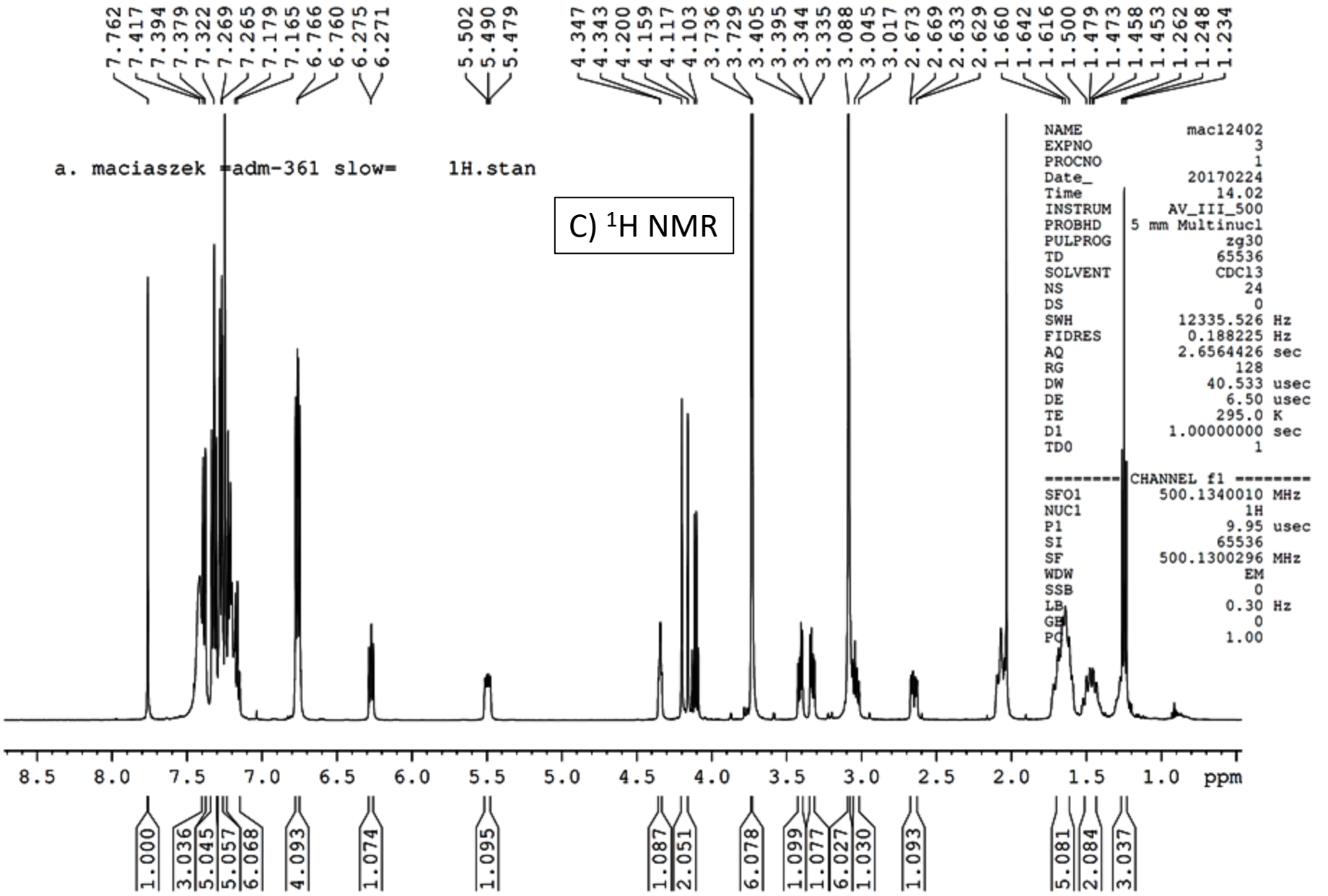
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170301
Time 9.06
INSTRUM AV_III_500
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 96153.844 Hz
FIDRES 1.467191 Hz
AQ 0.3407872 sec
RG 2050
DW 5.200 usec
DE 6.50 usec
TE 295.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 202.4563350 MHz
NUC1 31P
P1 12.00 usec
PLW1 80.00000000 W
======== CHANNEL f2 ========
SFO2 500.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 10.00000000 W
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 ppm


7.762
7.417
7.394
7.379
7.322
7.269
7.265
7.179
7.165
6.766
6.760
6.275
6.271
5.502
5.490
5.479
4.347
4.343
4.200
4.159
4.117
4.103
3.736
3.729
3.405
3.395
3.344
3.335
3.088
3.045
3.017
2.673
2.669
2.633
2.629
1.660
1.642
1.616
1.500
1.479
1.473
1.458
1.453
1.262
1.248
1.234
a. maciaszek +adm-361 slow= 1H.stan
C) 1H NMR
NAME mac12402
EXPNO 3
PROCNO 1
Date_ 20170224
Time 14.02
INSTRUM AV_III_500
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 24
DS 0
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6564426 sec
RG 128
DW 40.533 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 500.1340010 MHz
NUC1 1H
P1 9.95 usec
SI 65536
SF 500.1300296 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
1.000
3.036
5.045
5.057
6.068
4.093
1.074
1.095
1.087
2.051
6.078
1.099
1.077
6.027
1.030
1.093
5.081
2.084
3.037

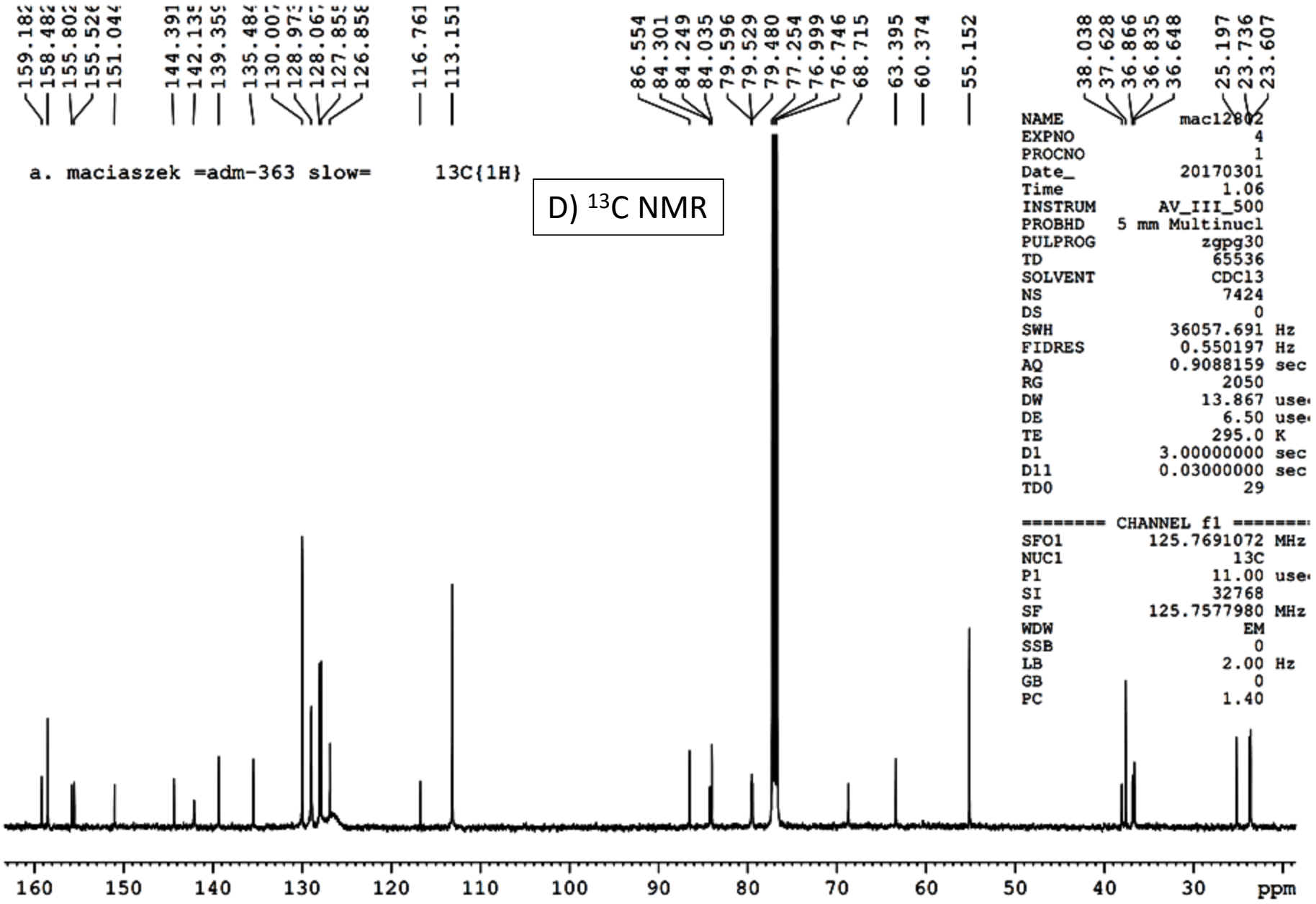
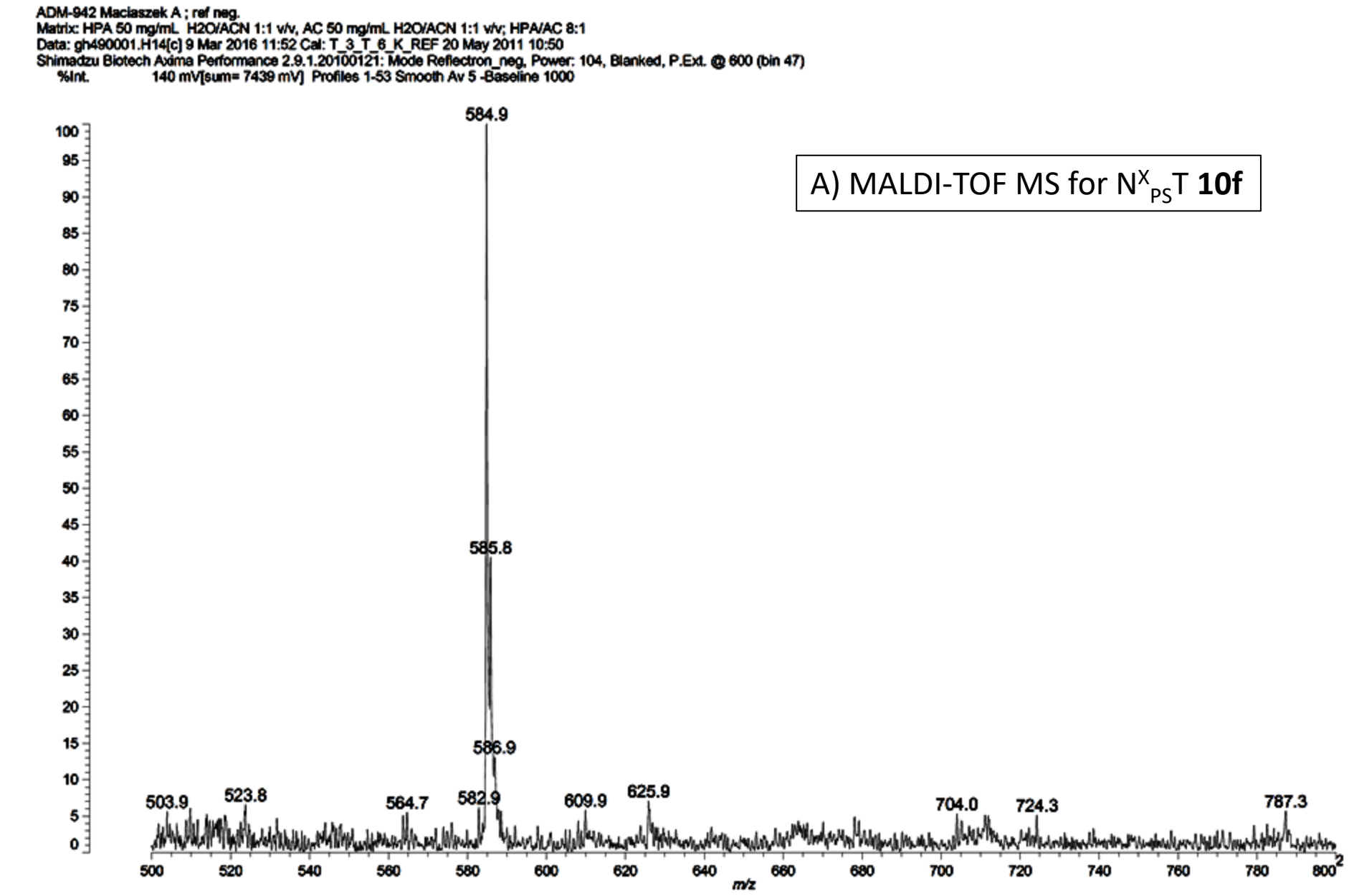
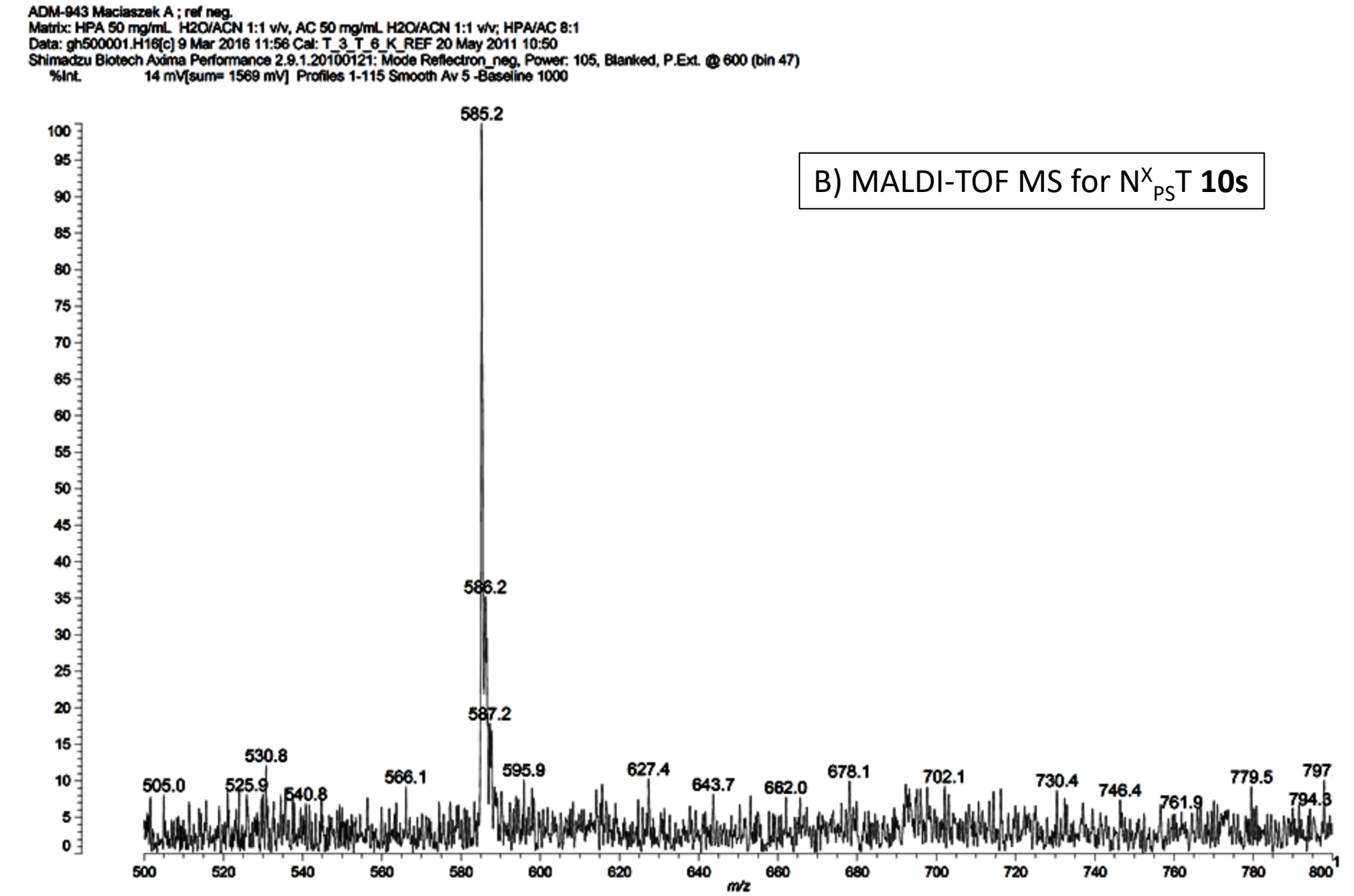
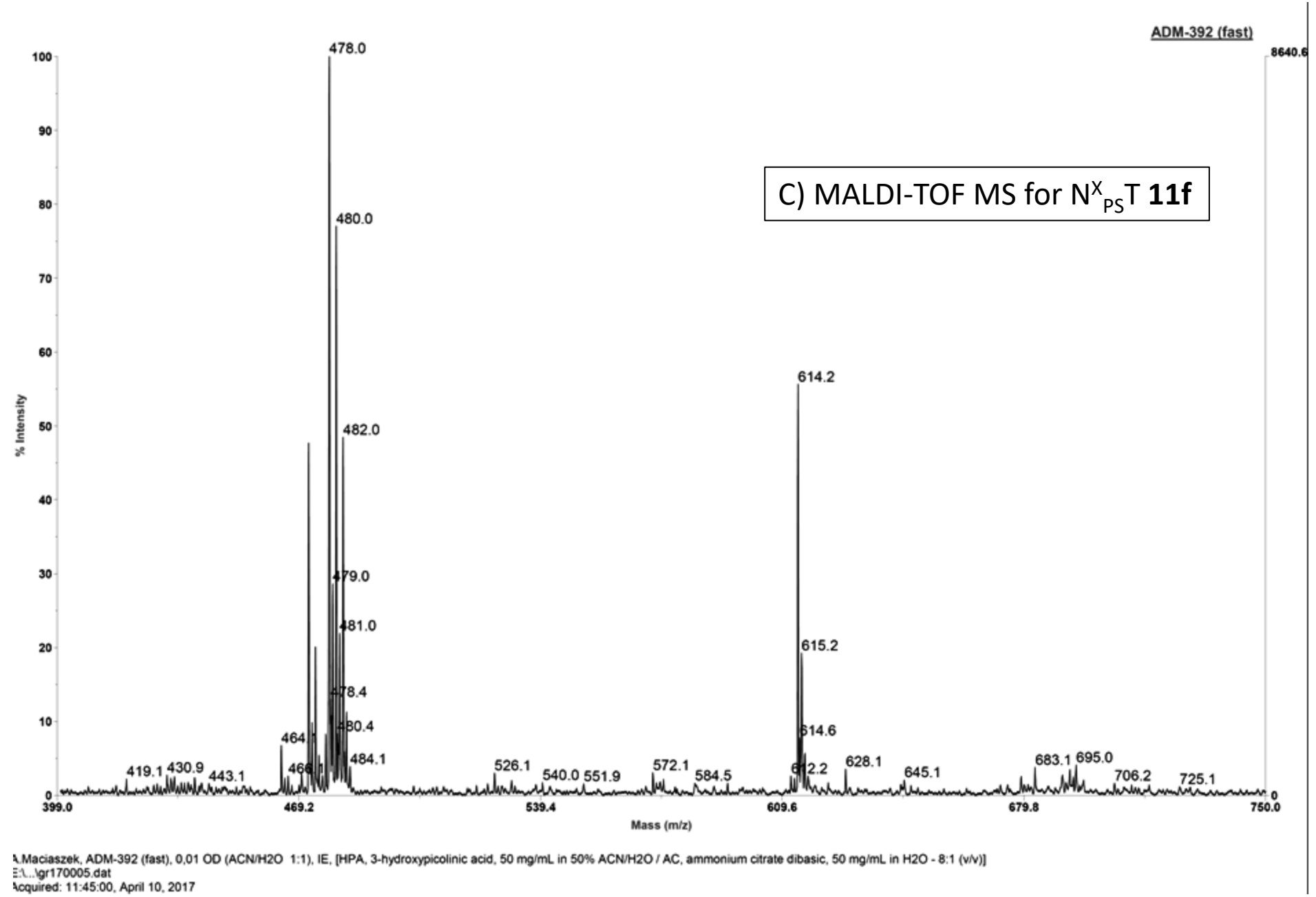

159.182
158.482
155.802
155.526
151.044
144.391
142.135
139.359
135.484
130.007
128.973
128.067
127.855
126.858
116.761
113.151
86.554
84.301
84.249
84.035
79.596
79.529
79.480
77.254
76.999
76.746
68.715
63.395
60.374
55.152
38.038
37.628
36.866
36.835
36.648
25.197
23.736
23.607
a. maciaszek =adm-363 slow= 13C{1H}
D) ^{13}C NMR
NAME mac12802
EXPNO 4
PROCNO 1
Date_ 20170301
Time 1.06
INSTRUM AV_III_500
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 7424
DS 0
SWH 36057.691 Hz
FIDRES 0.550197 Hz
AQ 0.9088159 sec
RG 2050
DW 13.867 use
DE 6.50 use
TE 295.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 29
======== CHANNEL f1 ========
SFO1 125.7691072 MHz
NUC1 13C
P1 11.00 use
SI 32768
SF 125.7577980 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

Figure 5S. MALDI-TOF mass spectra recorded for $N^{X}_{PS}T$ (**10f,s** and **11f,s**).

A) dinucleoside 3′,5′-phosphorothioate **10f**
B) dinucleoside 3′,5′-phosphorothioate **103**
C) dinucleoside 3′,5′-phosphorothioate **11f**
D) dinucleoside 3′,5′-phosphorothioate **11s**


ADM-942 Maciaszek A ; ref neg.
Matrix: HPA 50 mg/mL H2O/ACN 1:1 v/v, AC 50 mg/mL H2O/ACN 1:1 v/v; HPA/AC 8:1
Data: gh490001.H14[c] 9 Mar 2016 11:52 Cal: T_3_T_6_K_REF 20 May 2011 10:50
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Reflectron_neg, Power: 104, Blanked, P.Ext. @ 600 (bin 47)
%Int. 140 mV[sum= 7439 mV] Profiles 1-53 Smooth Av 5 -Baseline 1000
584.9
585.8
586.9
503.9
523.8
564.7
582.9
609.9
625.9
704.0
724.3
787.3
m/z
A) MALDI-TOF MS for $N^{X}_{PS}T$ **10f**


ADM-943 Maciaszek A ; ref neg.
Matrix: HPA 50 mg/mL H2O/ACN 1:1 v/v, AC 50 mg/mL H2O/ACN 1:1 v/v; HPA/AC 8:1
Data: gh500001.H16[c] 9 Mar 2016 11:56 Cal: T_3_T_6_K_REF 20 May 2011 10:50
Shimadzu Biotech Axima Performance 2.9.1.20100121: Mode Reflectron_neg, Power: 105, Blanked, P.Ext. @ 600 (bin 47)
%Int. 14 mV[sum= 1569 mV] Profiles 1-115 Smooth Av 5 -Baseline 1000
B) MALDI-TOF MS for N^X_PST 10s
585.2
586.2
587.2
530.8
505.0
525.9
540.8
566.1
595.9
627.4
643.7
662.0
678.1
702.1
730.4
746.4
761.9
779.5
794.3
797
m/z


ADM-392 (fast)
C) MALDI-TOF MS for $N^{X}_{PS}T$ **11f**
% Intensity
Mass (m/z)
478.0
480.0
482.0
479.0
481.0
478.4
480.4
484.1
464
466
419.1
430.9
443.1
526.1
540.0
551.9
572.1
584.5
614.2
615.2
614.6
612.2
628.1
645.1
683.1
695.0
706.2
725.1
8640.6
399.0
469.2
539.4
609.6
679.8
750.0
A.Maciaszek, ADM-392 (fast), 0,01 OD (ACN/H2O 1:1), IE, [HPA, 3-hydroxypicolinic acid, 50 mg/mL in 50% ACN/H2O / AC, ammonium citrate dibasic, 50 mg/mL in H2O - 8:1 (v/v)]
...\gr170005.dat
Acquired: 11:45:00, April 10, 2017

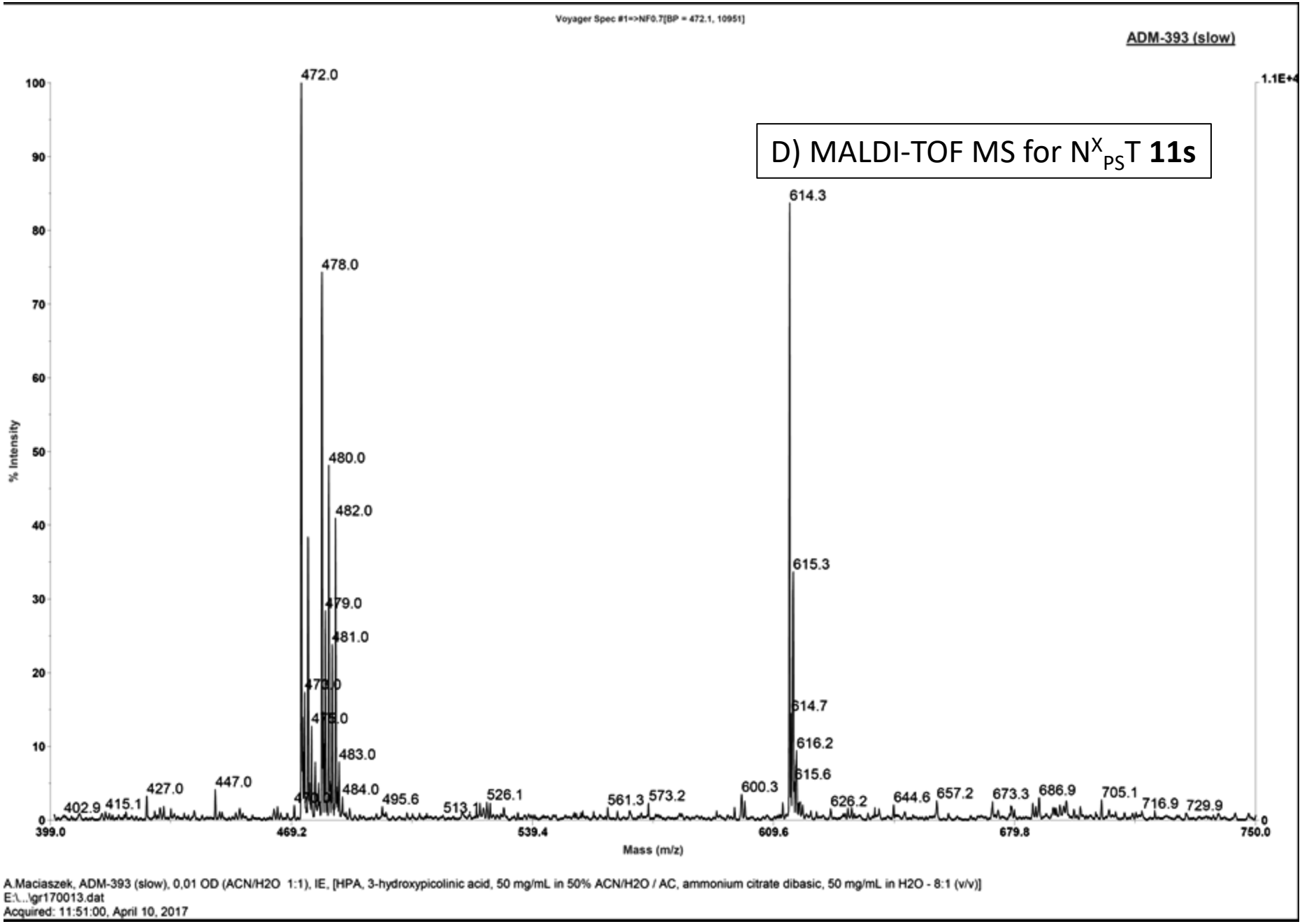
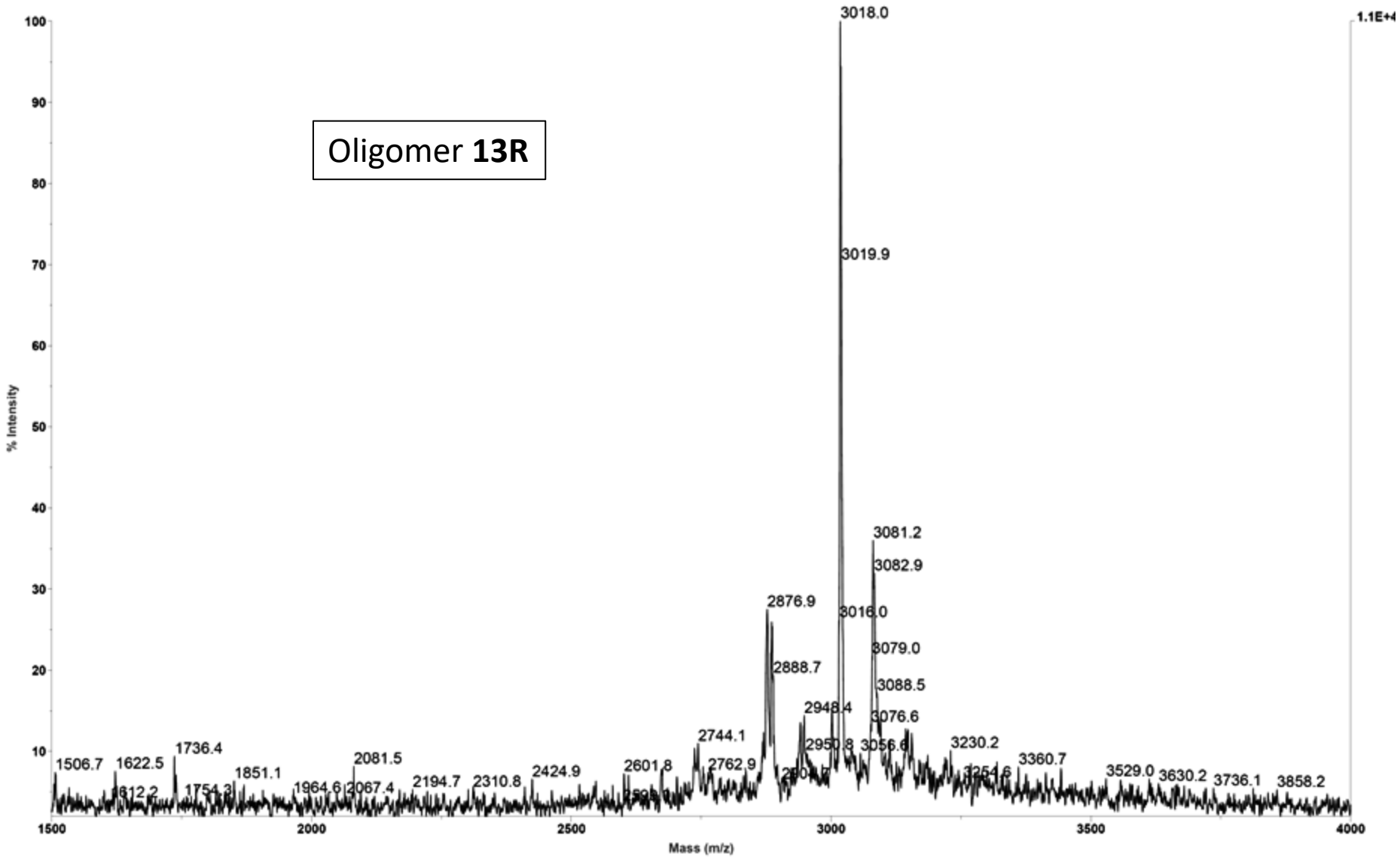

Voyager Spec #1=>NF0.7[BP = 472.1, 10951]
ADM-393 (slow)
D) MALDI-TOF MS for $N^{X}_{PS}T$ **11s**
% Intensity
Mass (m/z)
472.0
478.0
614.3
480.0
482.0
615.3
479.0
481.0
614.7
616.2
615.6
483.0
484.0
427.0
447.0
402.9
415.1
495.6
513.1
526.1
561.3
573.2
600.3
626.2
644.6
657.2
673.3
686.9
705.1
716.9
729.9
1.1E+4
399.0
469.2
539.4
609.6
679.8
750.0
A.Maciaszek, ADM-393 (slow), 0,01 OD (ACN/H2O 1:1), IE, [HPA, 3-hydroxypicolinic acid, 50 mg/mL in 50% ACN/H2O / AC, ammonium citrate dibasic, 50 mg/mL in H2O - 8:1 (v/v)]
E:\...\gr170013.dat
Acquired: 11:51:00, April 10, 2017

Figure 6S. MALDI-TOF mass spectra recorded for chimeric (R_P-PS)- and (S_P-PS)-DN(N^X)A oligomers

A) Oligomer **13R**
B) Oligomer **13S**
C) Oligomer **14R**
D) Oligomer **14S**
E) Oligomer **15R**

A.Maciaszek

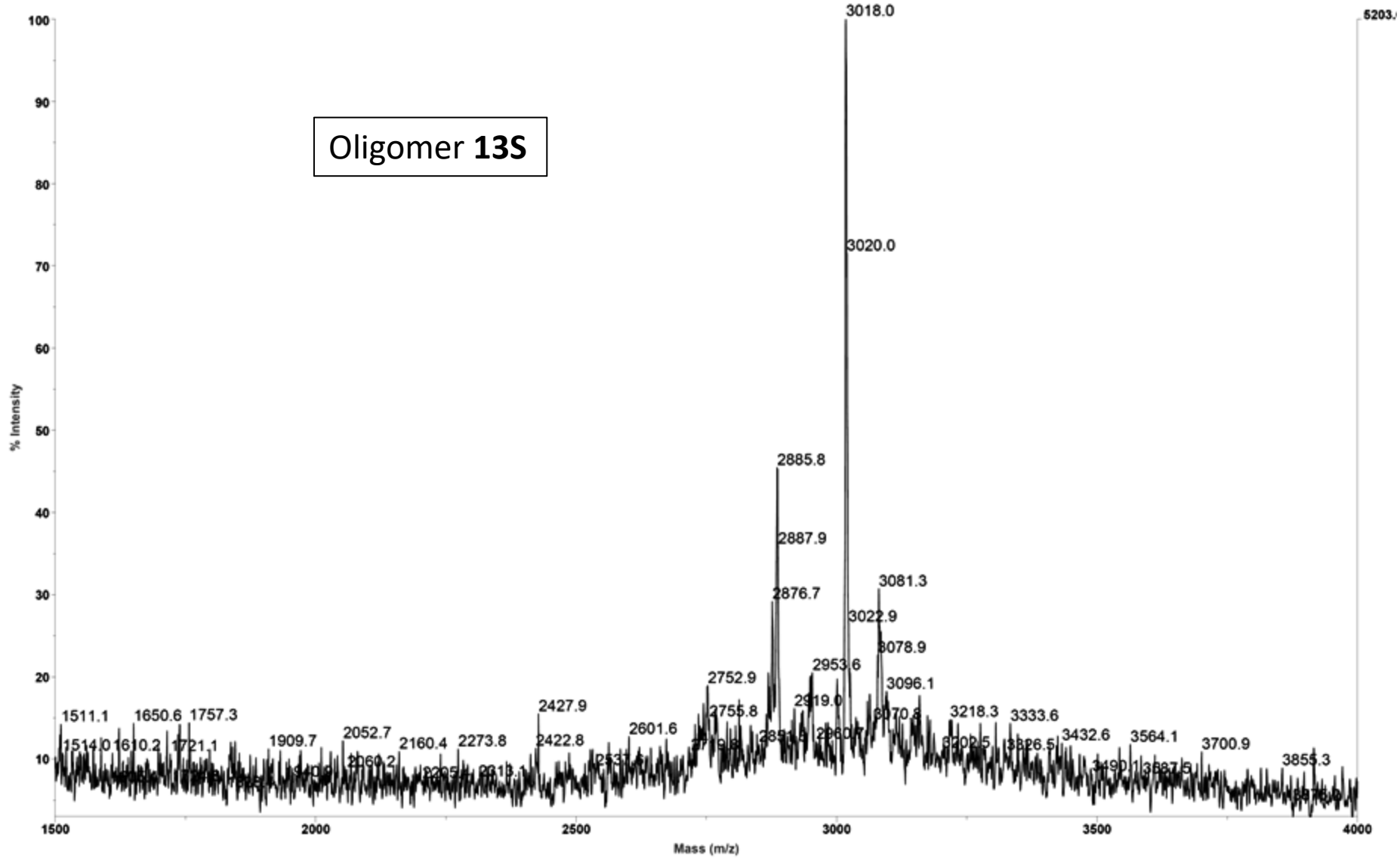
Oligomer **13R**



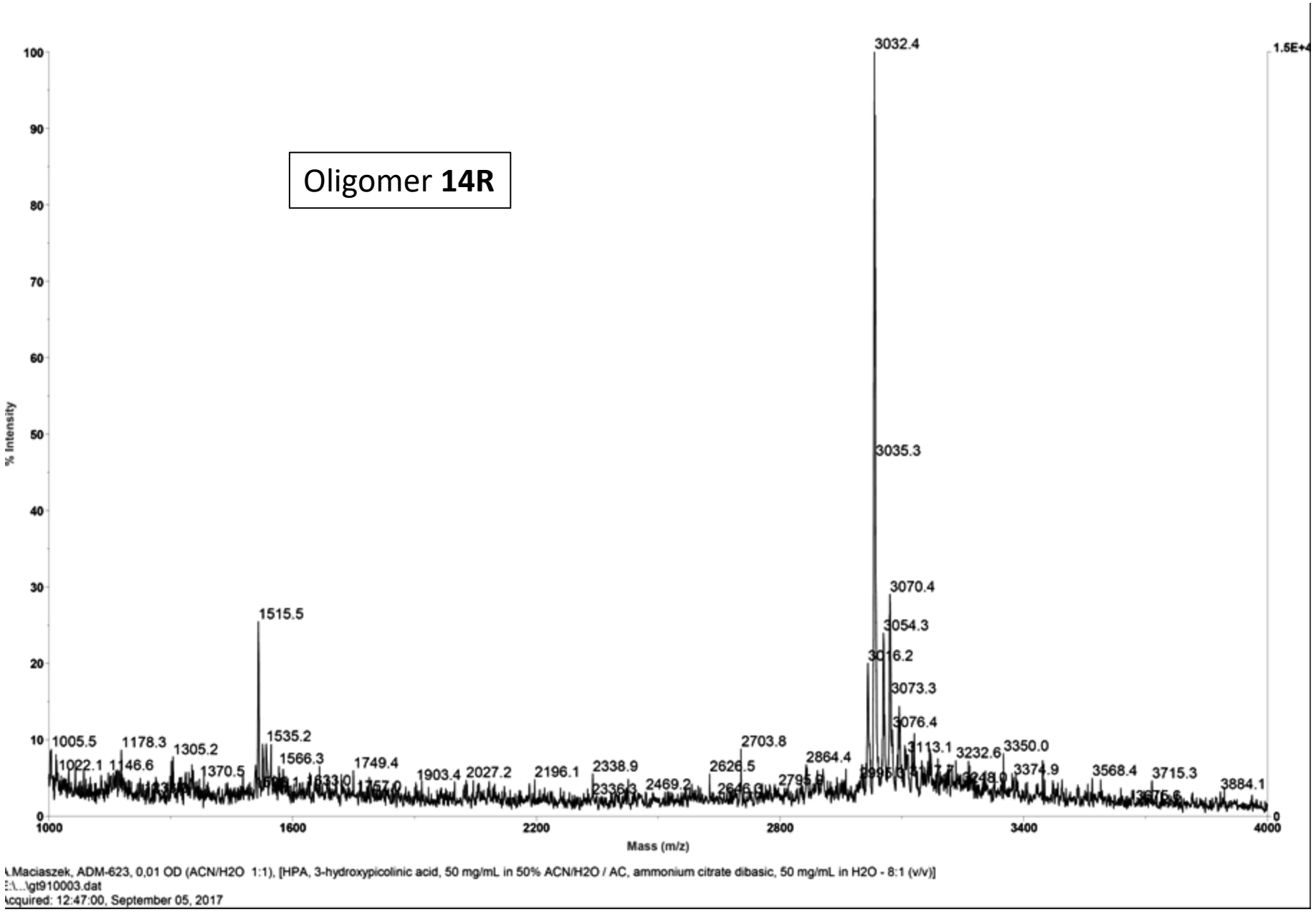
A.Maciaszek, N6-CH3-dA-9Rp, 0,01 OD (ACN/H2O 1:1), [HPA, 3-hydroxypicolinic acid, 50 mg/mL in 50% ACN/H2O / AC, ammonium citrate dibasic, 50 mg/mL in H2O - 8:1 (v/v)]
E:\...\gj280004.dat
Acquired: 15:12:00, June 06, 2016

A.Maciaszek

Oligomer **13S**



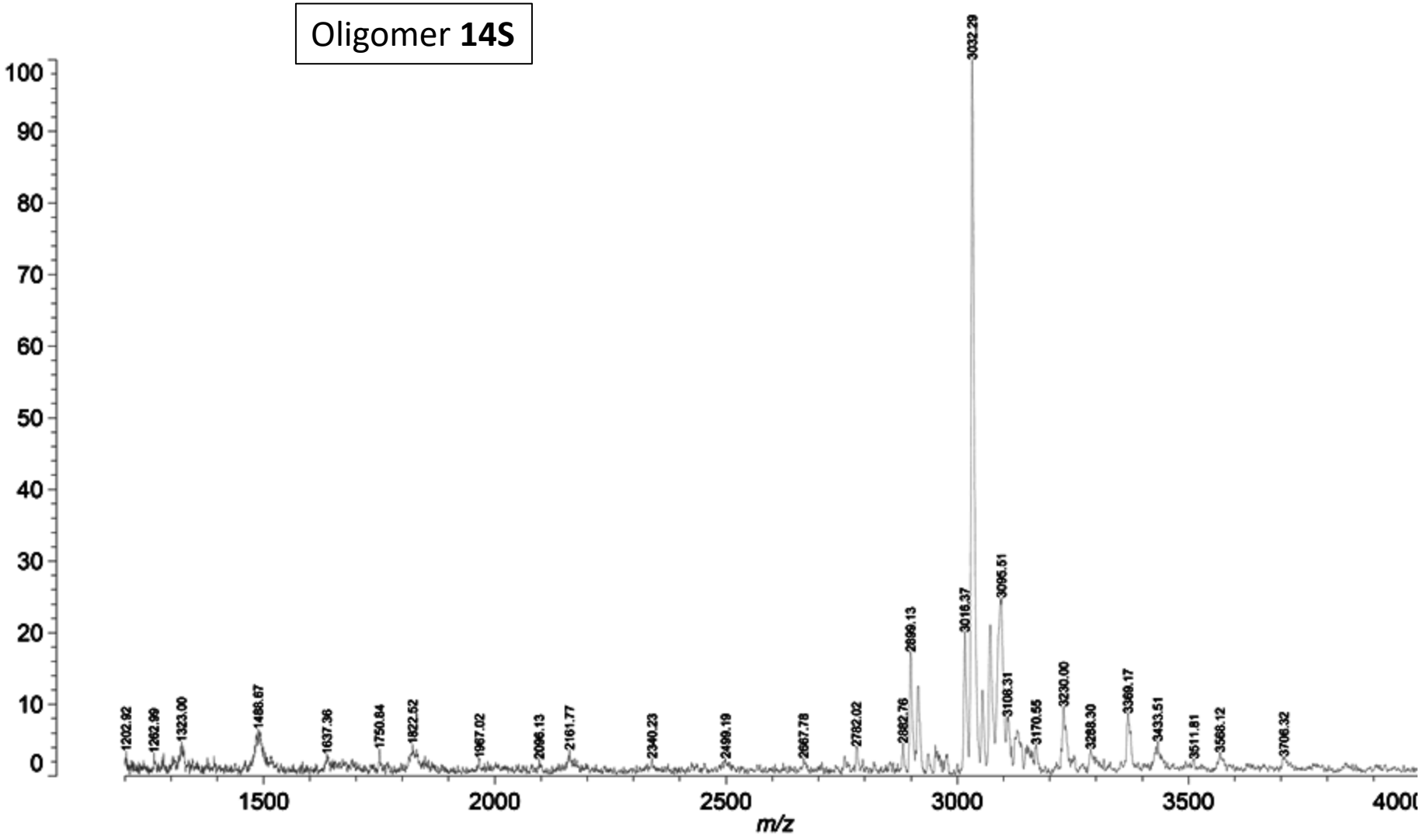
A.Maciaszek, N6-CH3-dA-9Sp, 0,01 OD (ACN/H2O 1:1), [HPA, 3-hydroxypicolinic acid, 50 mg/mL in 50% ACN/H2O / AC, ammonium citrate dibasic, 50 mg/mL in H2O - 8:1 (v/v)]
E:\...\gj290004.dat
Acquired: 15:15:00, June 06, 2016

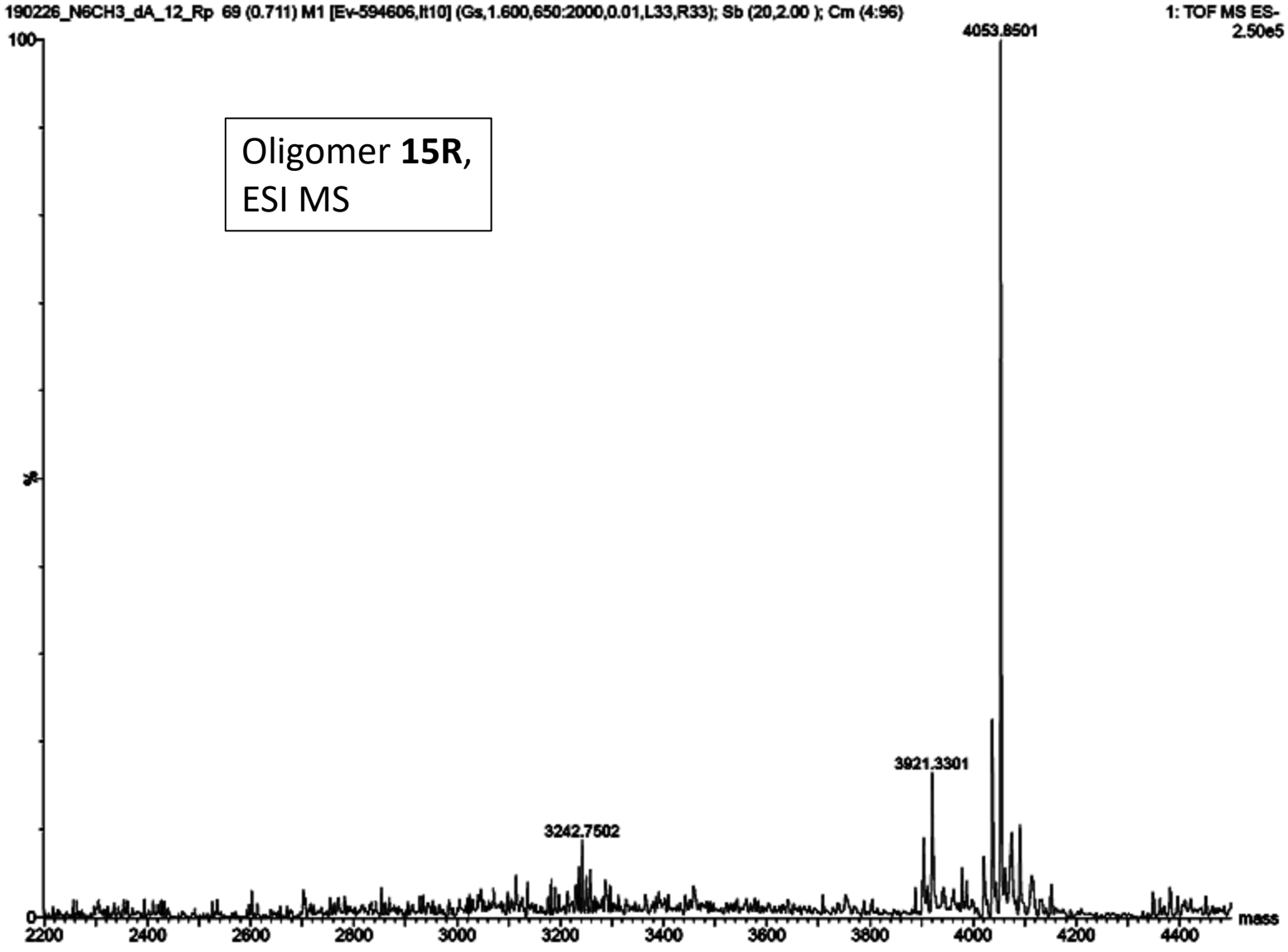


.Maciaszek, ADM-623, 0,01 OD (ACN/H2O 1:1), [HPA, 3-hydroxypicolinic acid, 50 mg/mL in 50% ACN/H2O / AC, ammonium citrate dibasic, 50 mg/mL in H2O - 8:1 (v/v)]
E:\...\gt910003.dat
Acquired: 12:47:00, September 05, 2017

ADM-641; A.Maciaszek; lin neg
Matrix: HPA 50 mg/mL H2O/ACN 1:1 v/v, AC 50 mg/mL H2O/ACN 1:1 v/v; HPA/AC 8:1
Data: g730001.L17[c] 27 Jul 2017 16:36 Cal: LIN_NEG 13 May 2010 11:44
%Int. 79 mV[sum= 3069 mV] Profiles 1-39 Smooth Av 15 -Baseline 1000

Oligomer **14S**





Oligomer **15R**,
ESI MS

Figure 7S. The melting curves recorded at pH 7.2 for **15R** mixed with **hR12** and/or **wR12**. No inflection point was detected.,

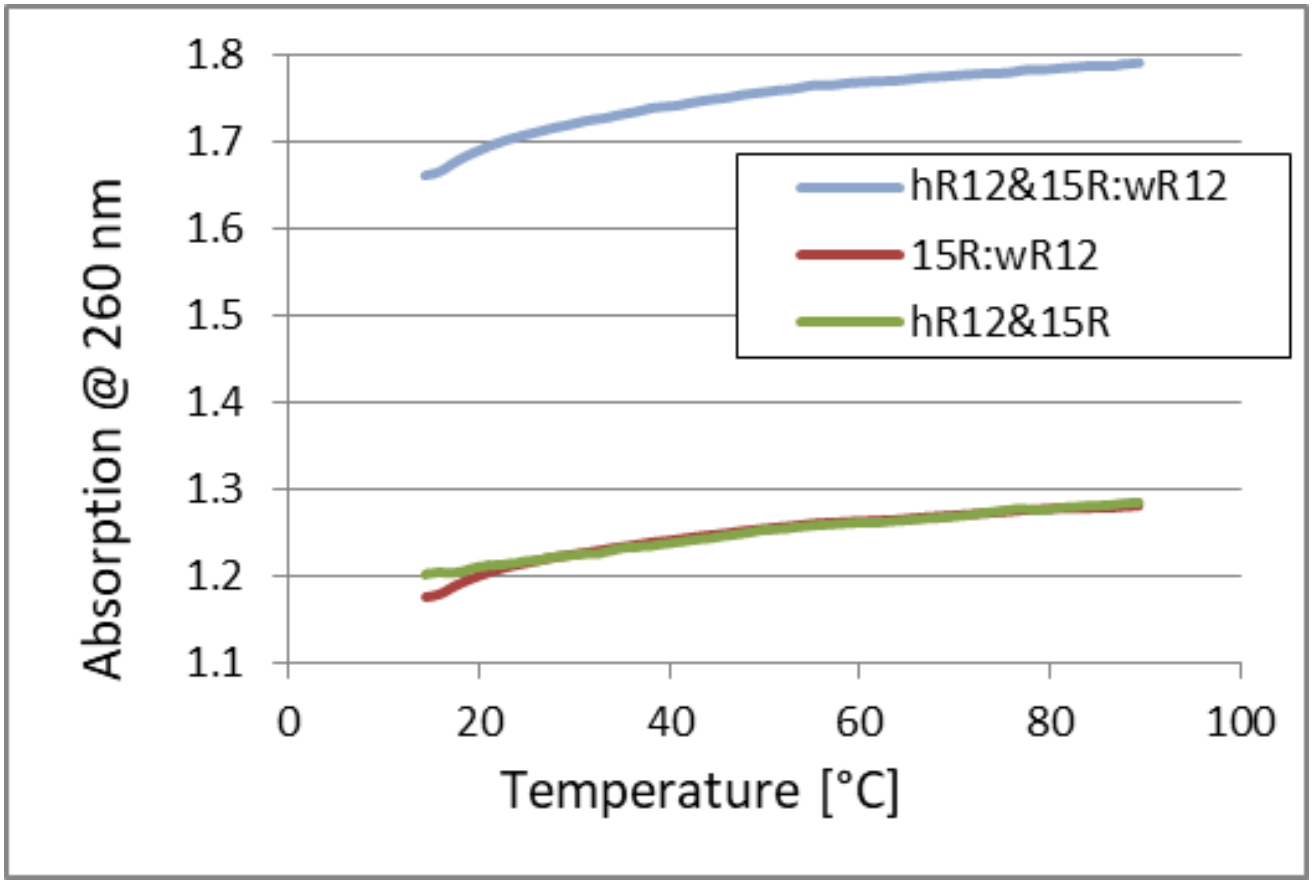


Figure 8S. The melting curves recorded at pH 5.4 for **15R** mixed with **hR12** and/or **wR12**. No inflection point was detected. Curves recorded for **15R** mixed with **wD12** and **16R** mixed with **hR12** are given as a reference.

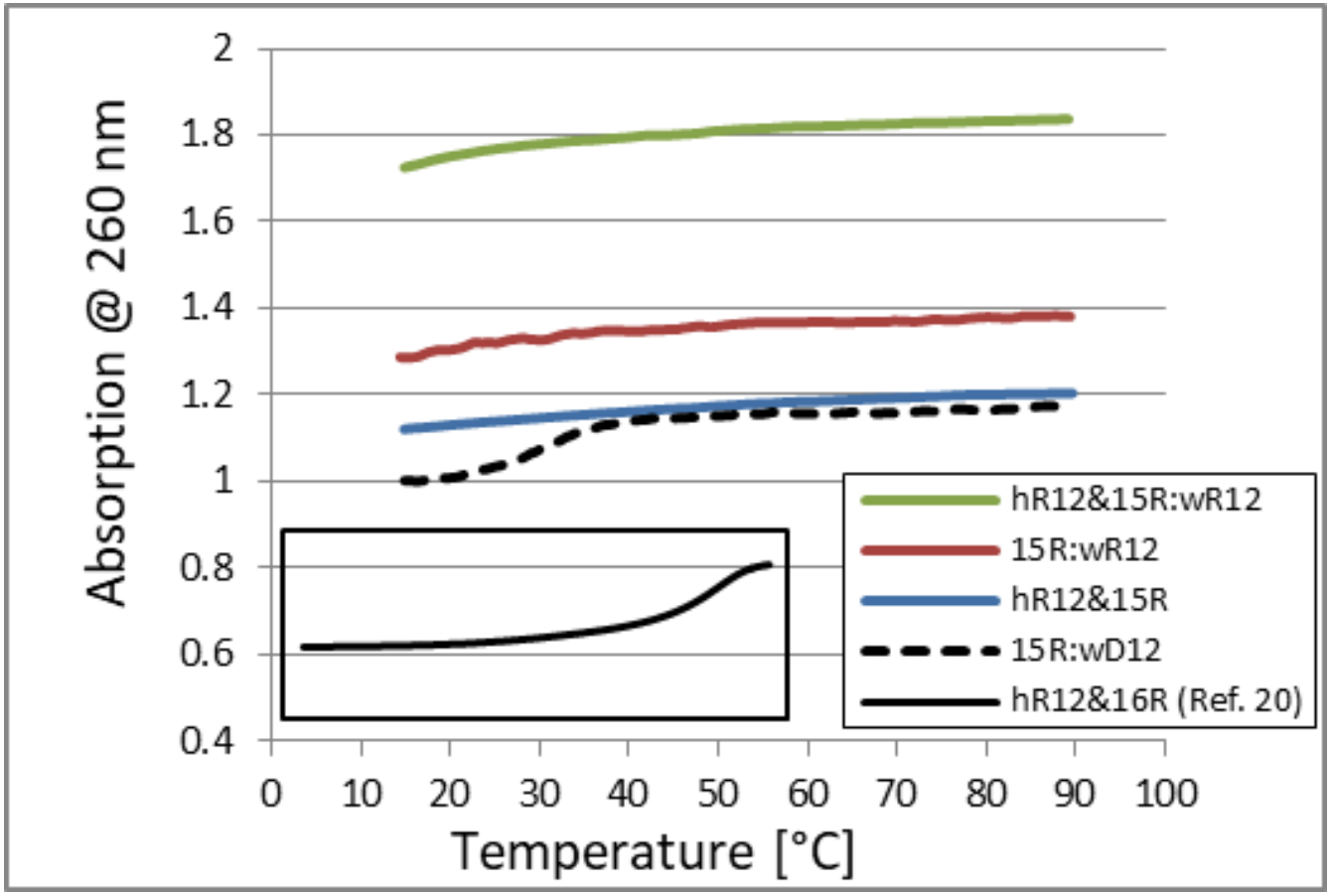
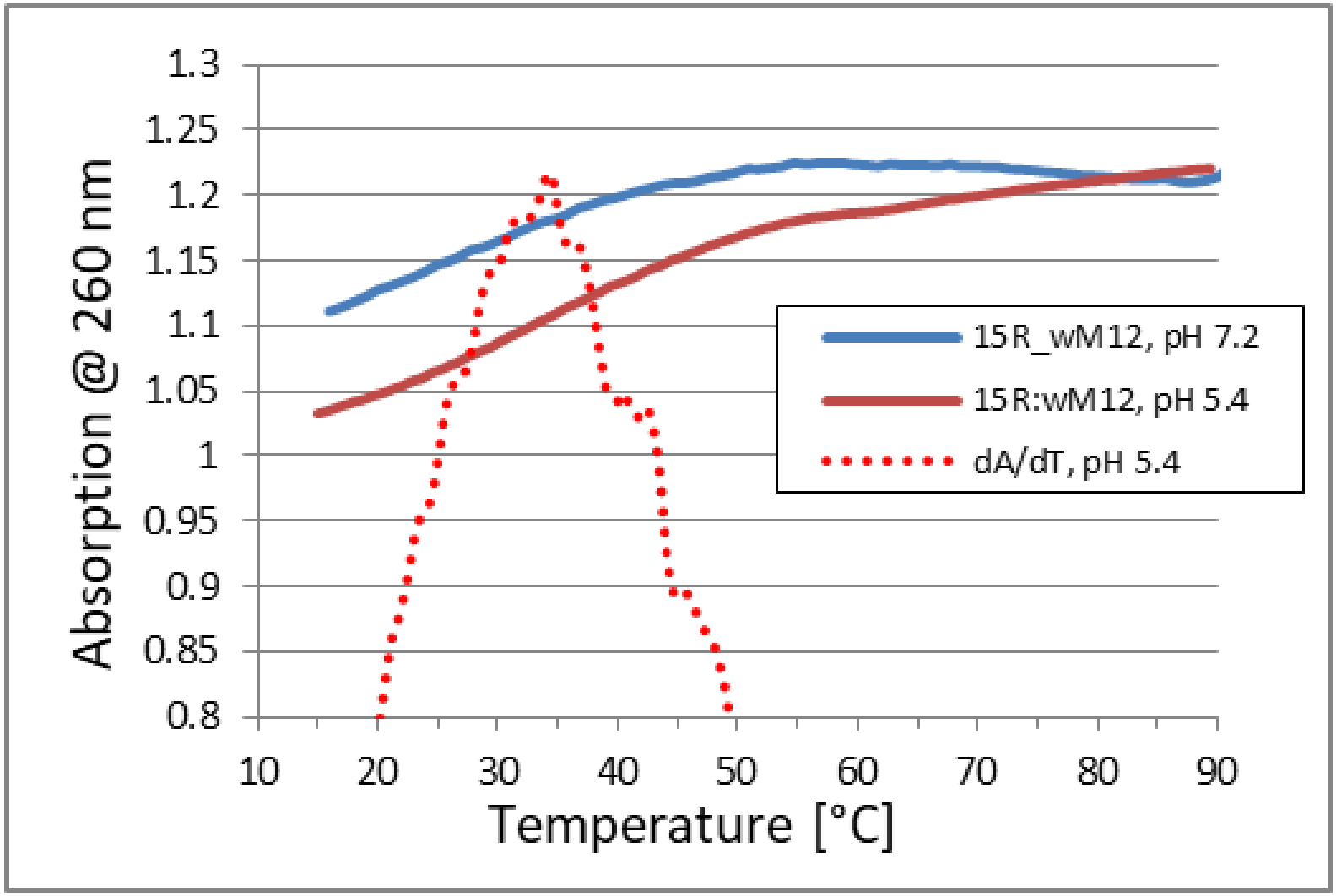


Figure 9S. The melting curves recorded at pH 7.2 or 5.4 for **15R** mixed with **wM12** and a plot of 1° derivative dA/dT for the pH 5.4 curve.



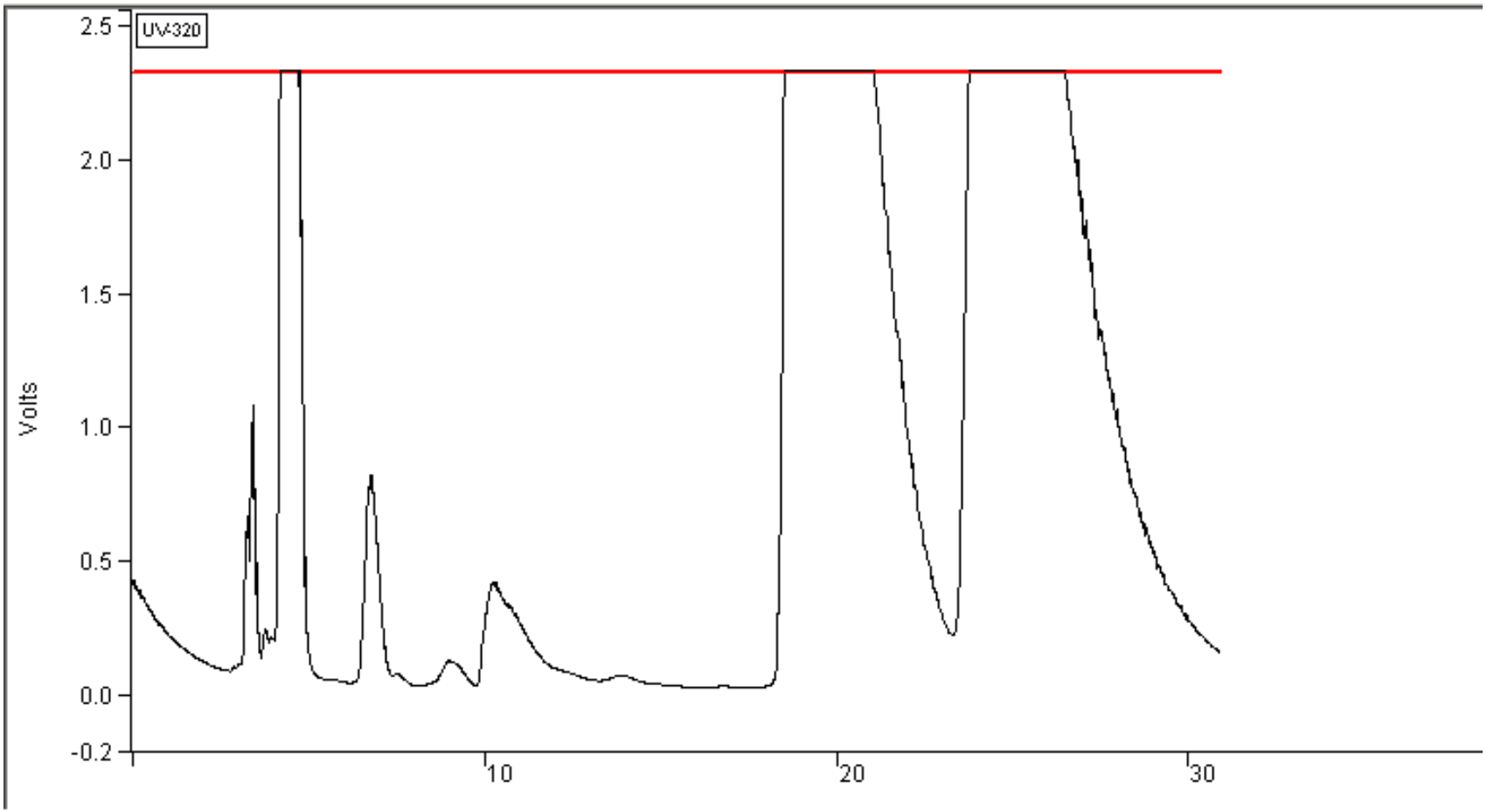


Figure 10S. A chromatogram recorded during search for the conditions suitable for separation of P-diastereomers. A silica gel column Phenomenex Luna 5u Silica column (100 Å; 250×10 mm) was loaded with ca. 70 mg of **6** and then eluted with ethyl acetate-hexane (7:3, v/v) at 5 ml min^{-1}. A detector set at 275 nm.

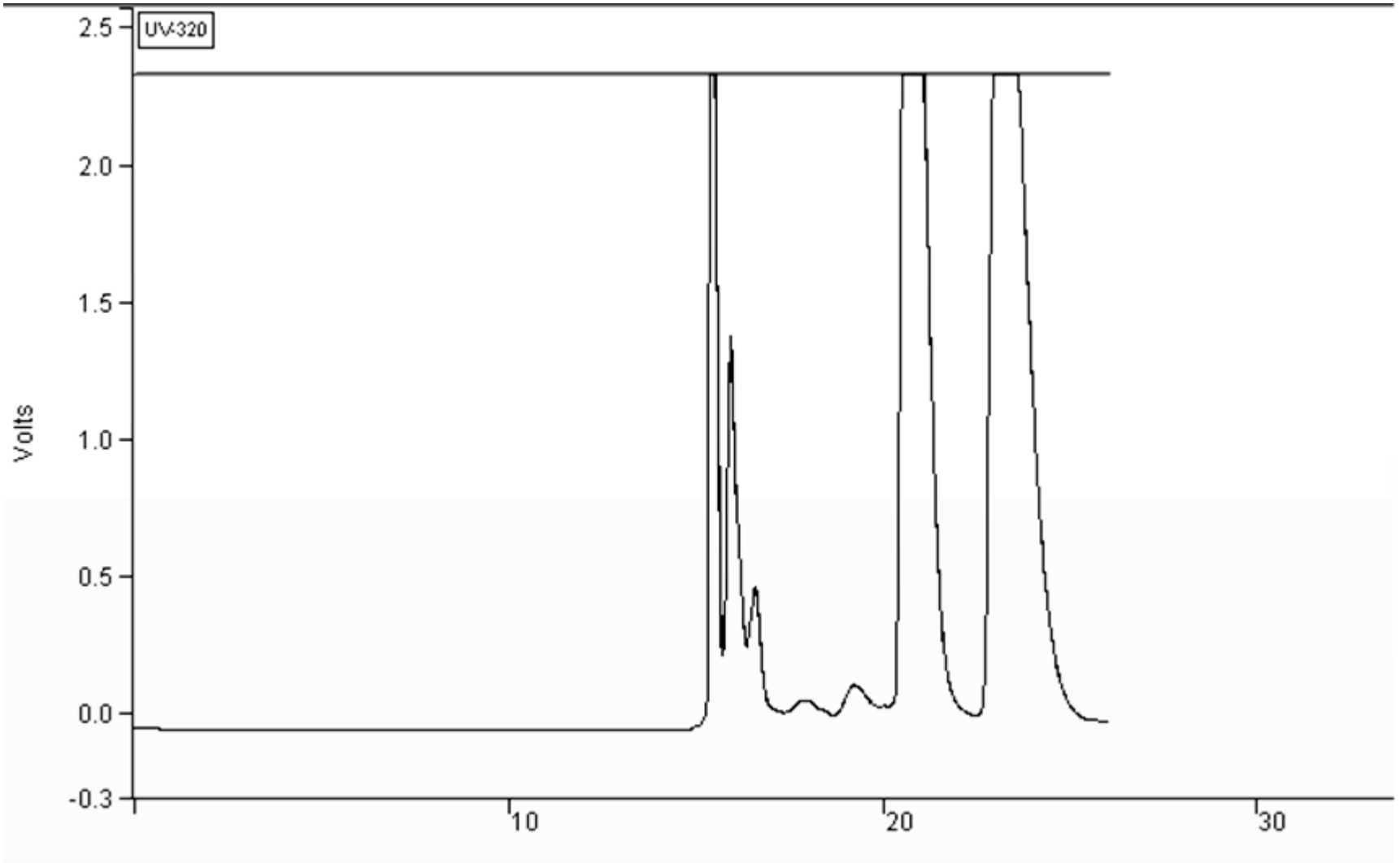


Figure 11S. A chromatogram recorded during search for the conditions suitable for separation of P-diastereomers of **7**. A silica gel column Phenomenex Luna 5u Silica column (100 Å; 250 × 10 mm) was loaded with ca. 30 mg of **7** and then eluted with ethyl acetate-hexane (1:1, v/v) at 5 ml min^{-1}. A detector set at 275 nm.