Supplementary material for review & publication online

Exploring synthetic pathways for nucleosidic derivatives of potent phosphoantigens

*Javier Alguacil[1], David Reyes[1], Yoann Aubin[1], Béatrice Roy[1], Christian Périgaud[1], Eric Champagne[2]
and Suzanne Peyrottes[1]**

[1] IBMM, UMR5247 CNRS- University of Montpellier-ENSCM, Campus Triolet, cc 1704, place E.
Bataillon, 34795 Montpellier, France
[2] Centre de Physiopathologie of Purpan, Toulouse, France
* Corresponding author: peyrottes@um2.fr

Table of Contents

Compound **1**   (2*E*)-2-Methyl-2-butene-1,4-diol
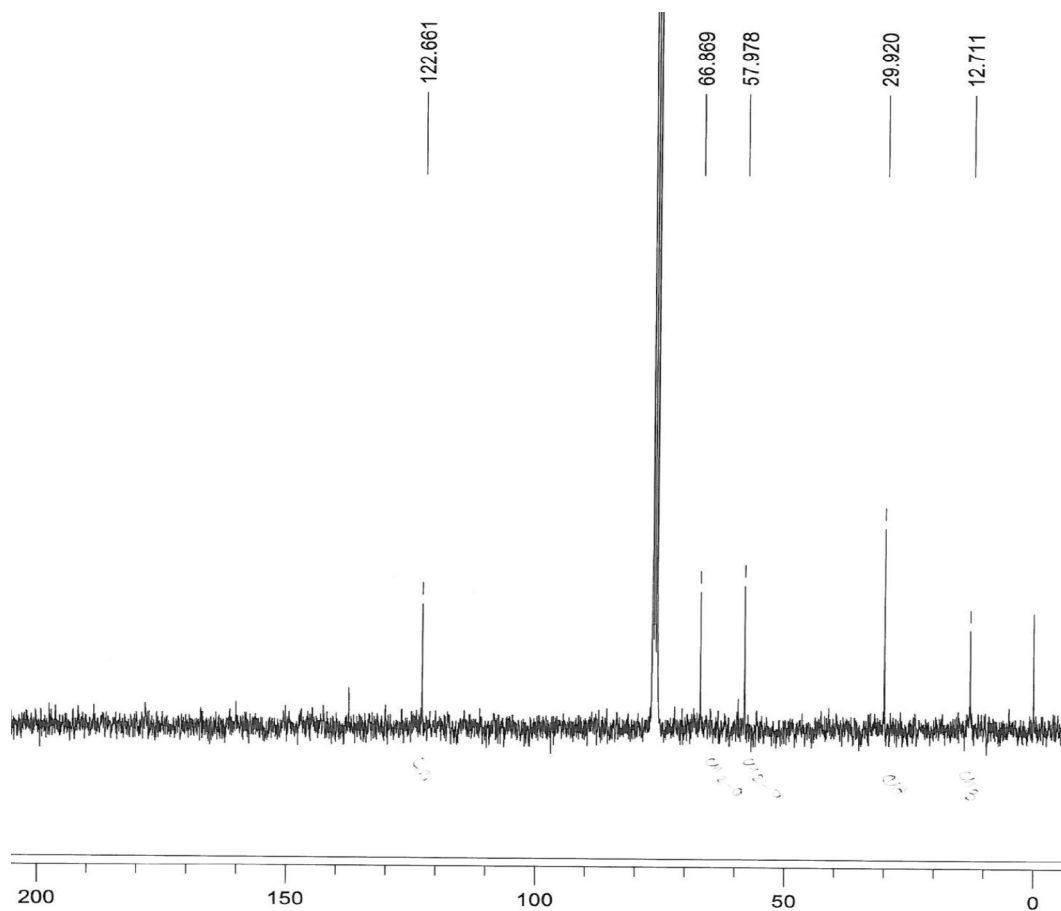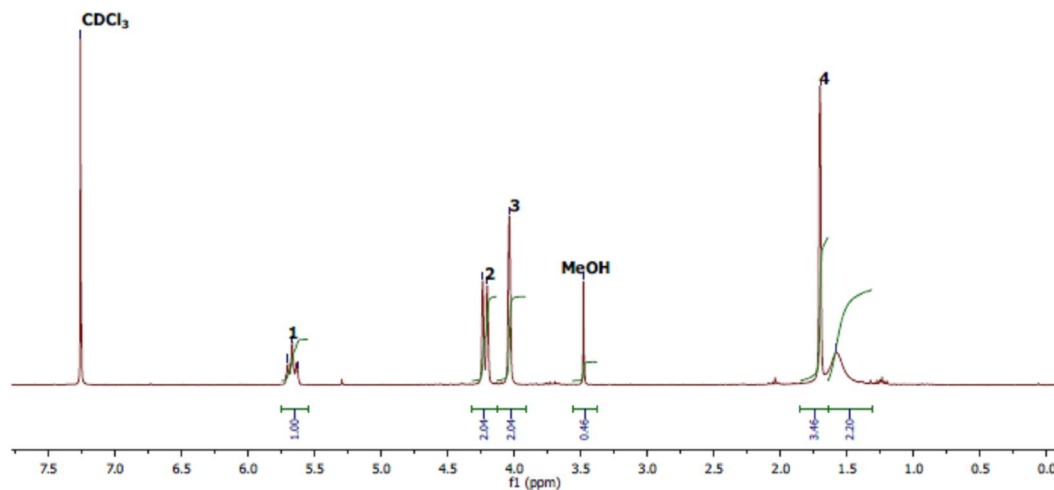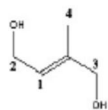
Compound **2**   **(2*E*)-4-Hydroxy-2-methyl-2-butenyl acetate**
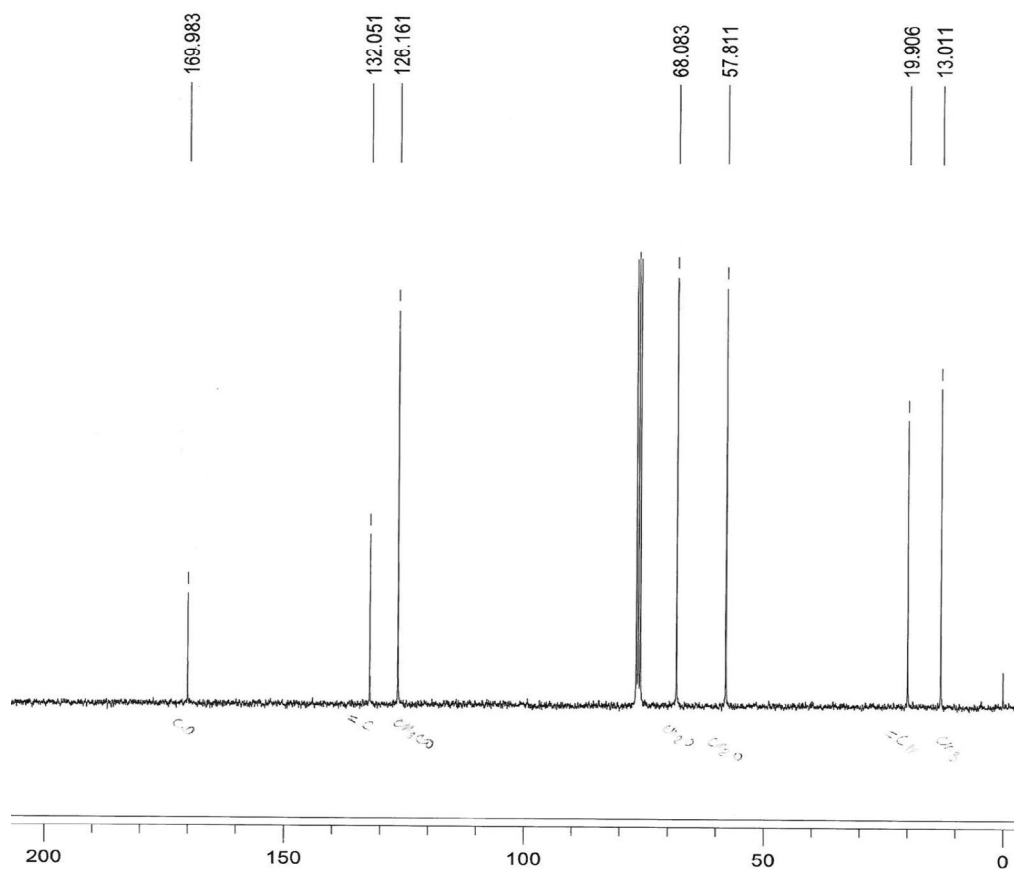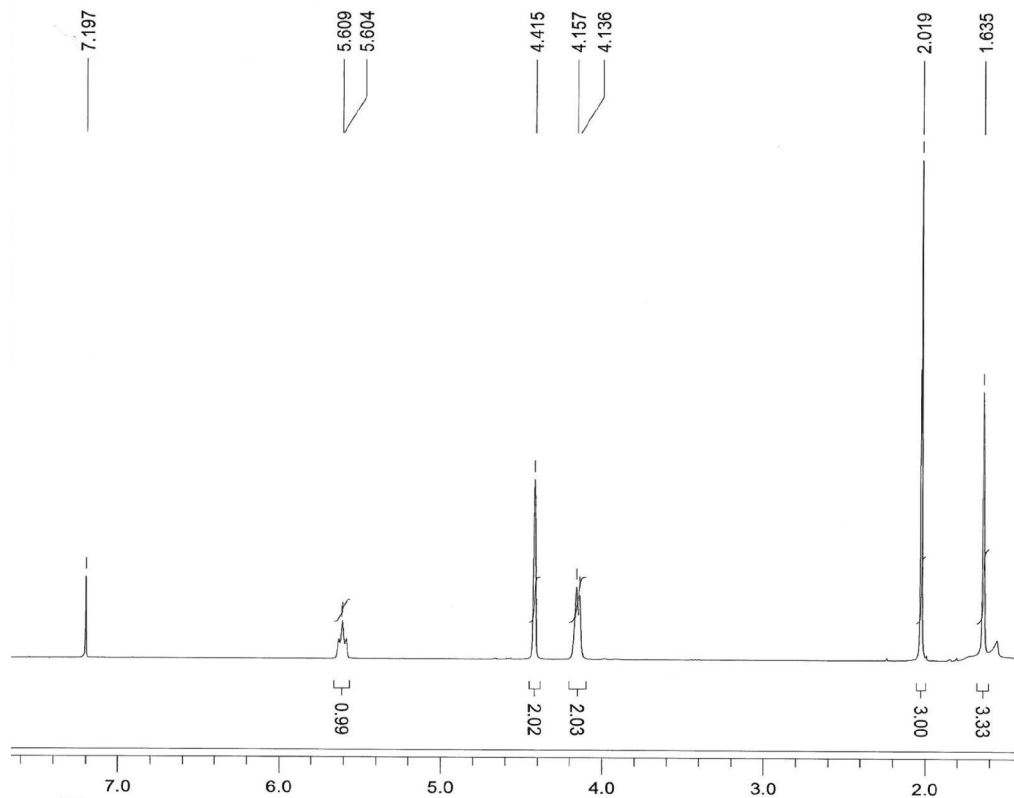
Regioisomer: **(2*E*)-4-Hydroxy-3-methyl-2-butenyl acetate**
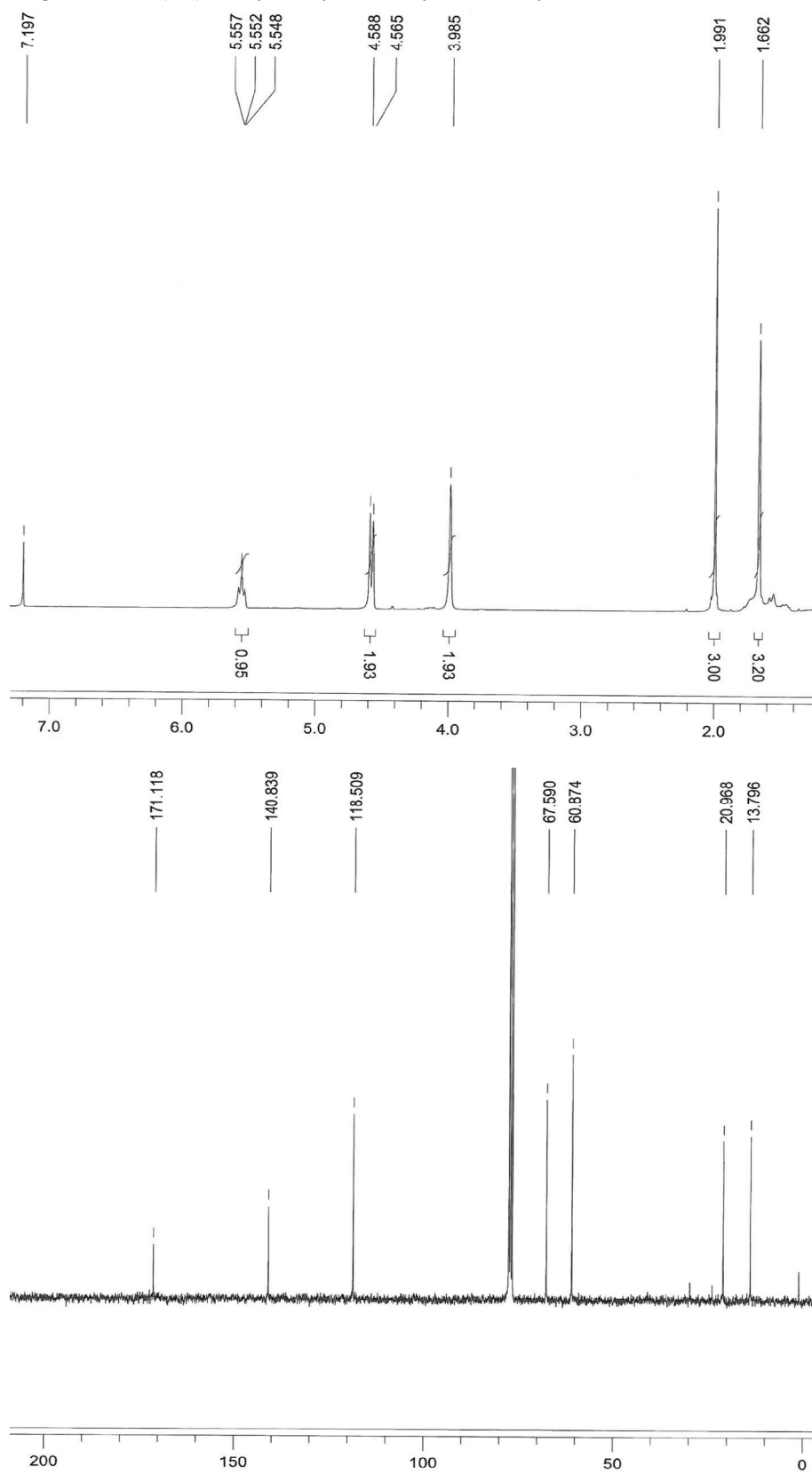
Compound **3** **Dimethyl-(2*E*)-2-methyl-2-butenodioate**
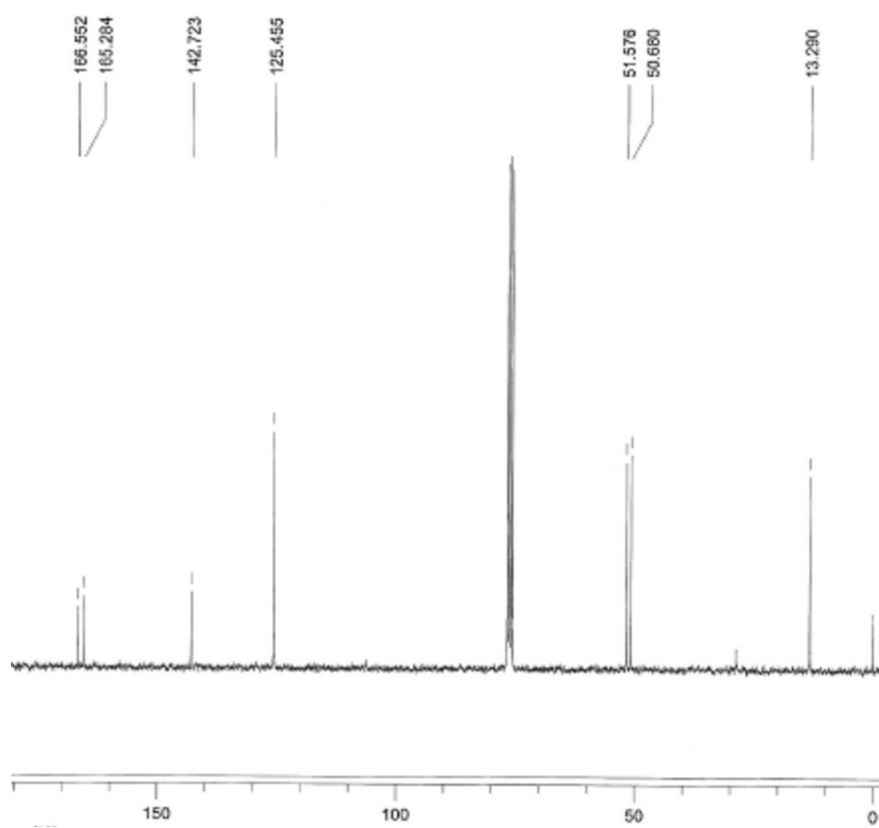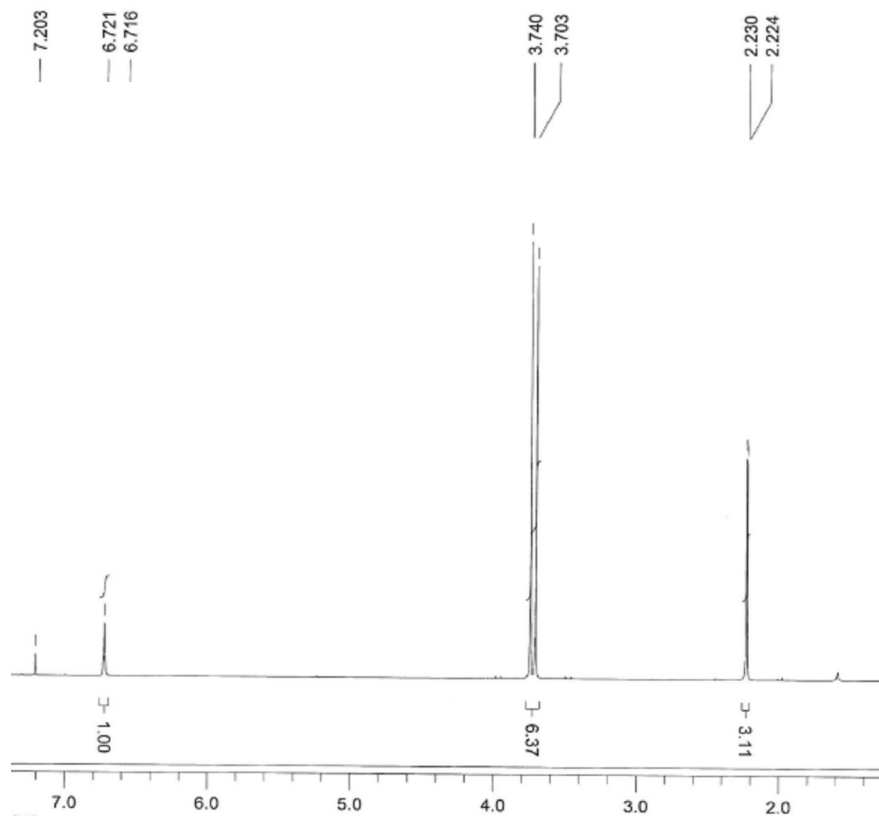
Compounds **4a** and **4b** isolated as a mixture
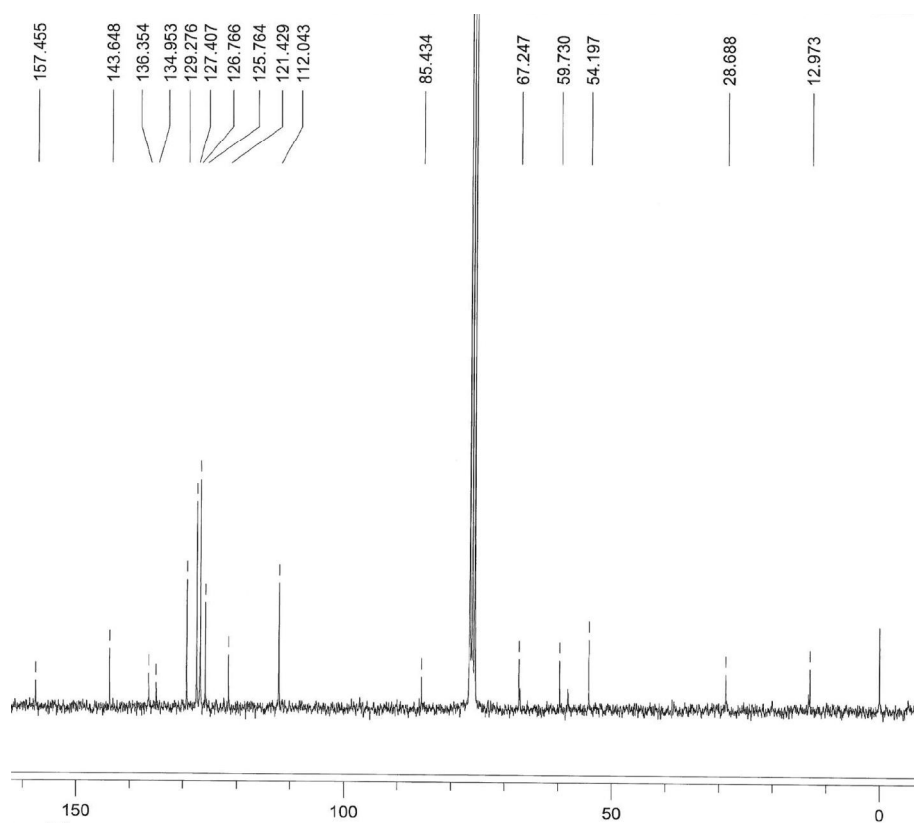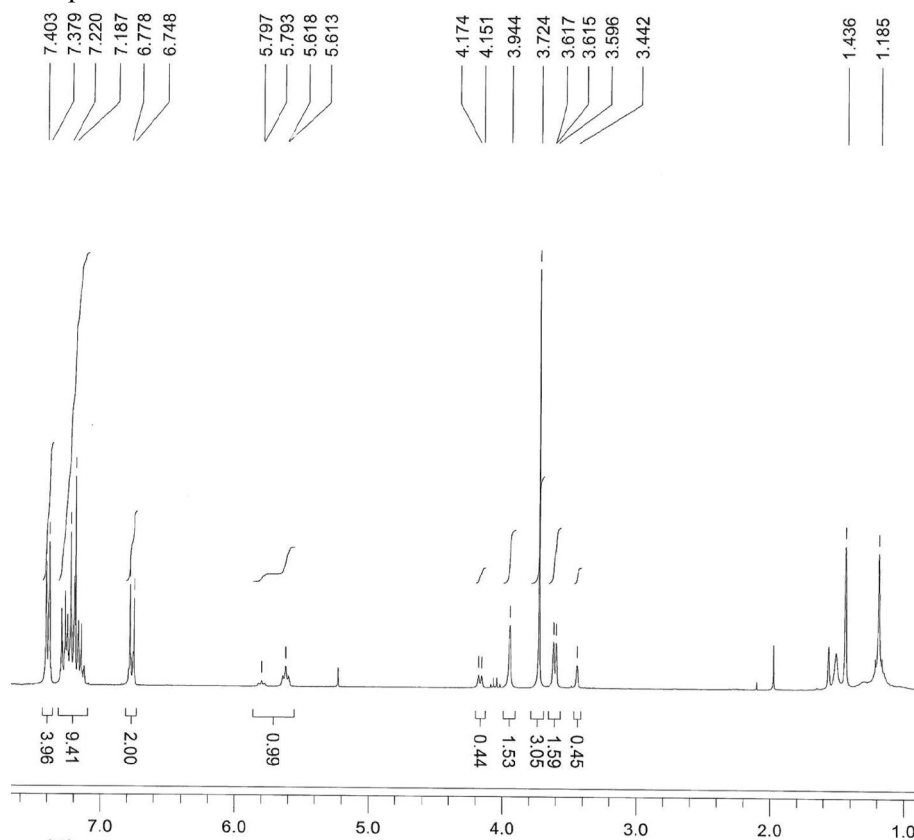
Compound **4a**
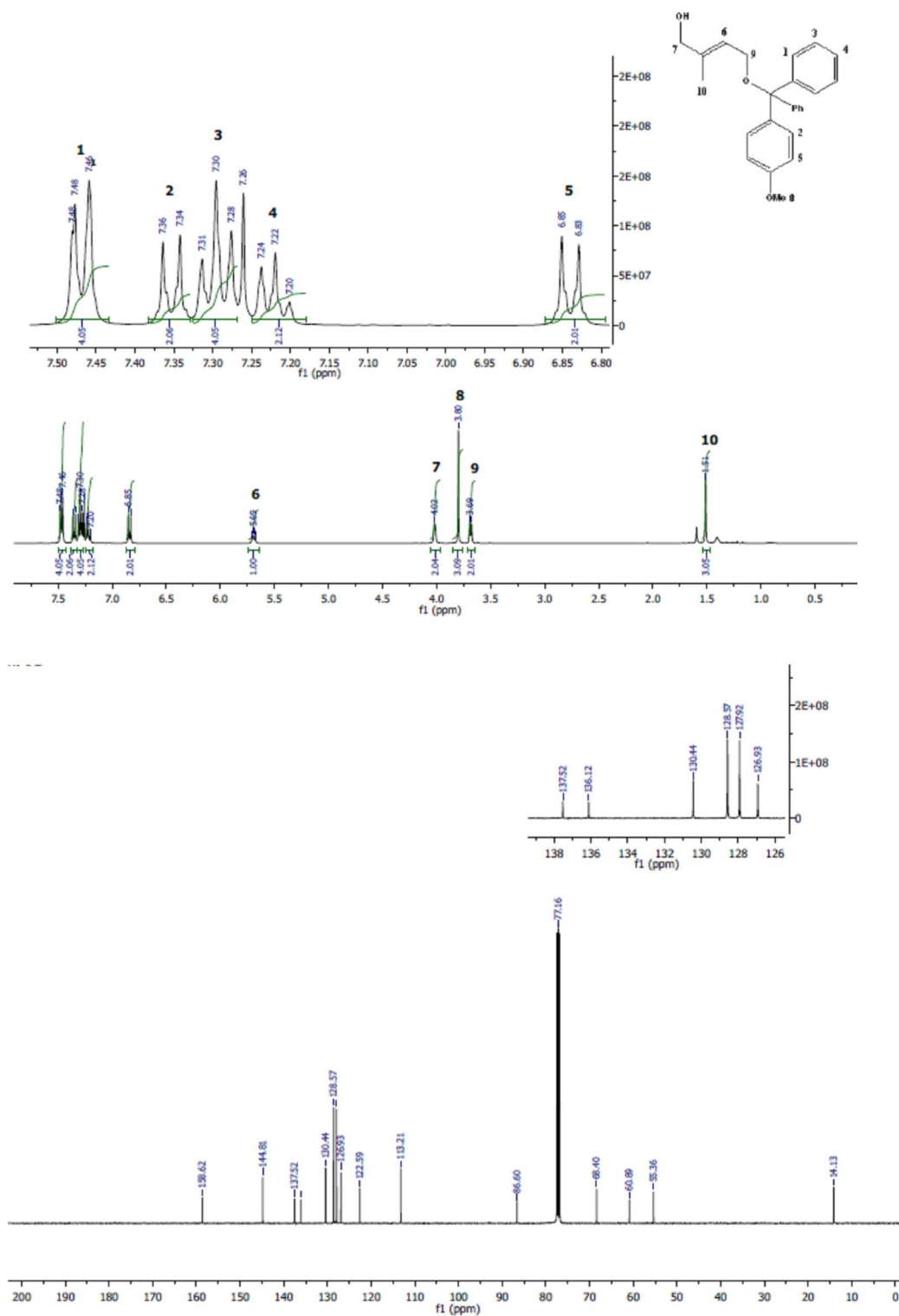
Compound **5**   **(2*E*)-4-Bromo-2-methyl-2-butenyl acetate**
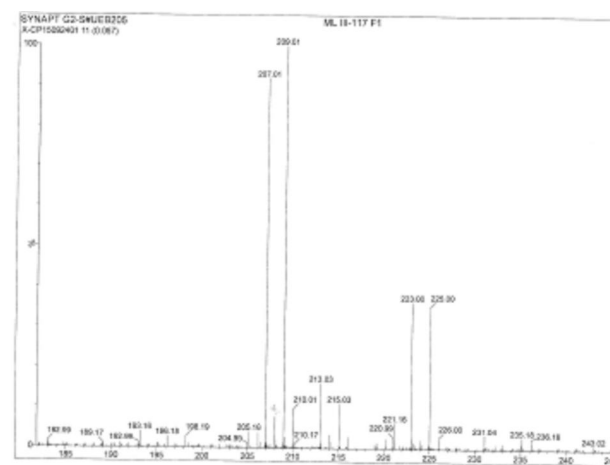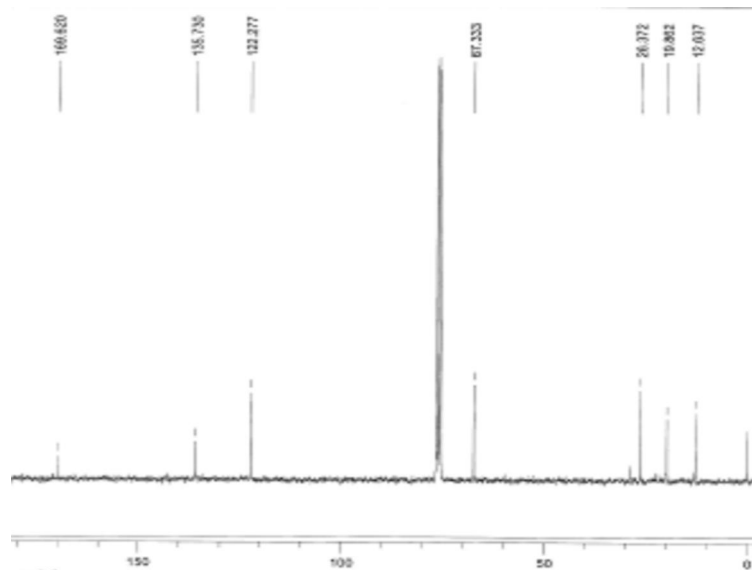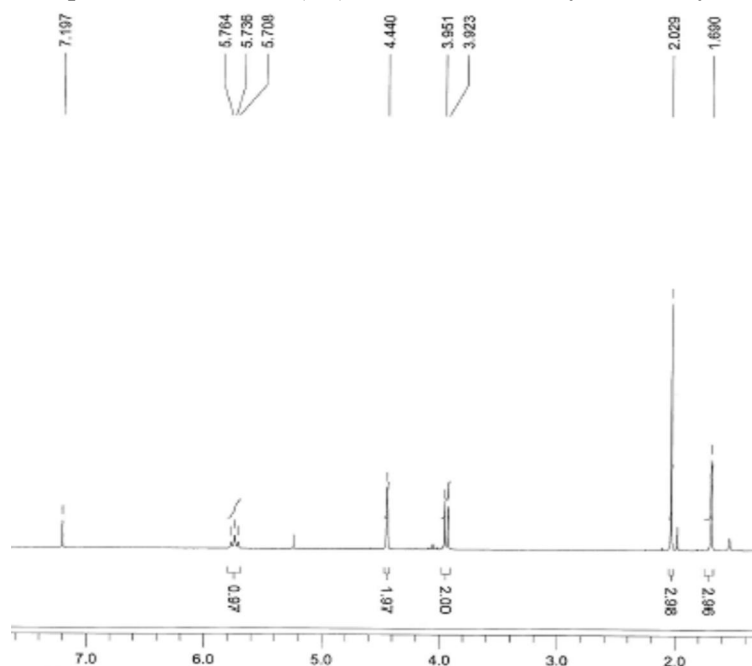
Compound 6 Isopentenyl-MonoP

JA 2.1568 F2
P31dec1H-SI CDCl3 /opt/topspin cp 9

SYNAPT G2-S#UEB205
X-CP15061201 3 (0.141) Cm (3:4)
JA 2.156B F2
12-Jun-2015
1: TOF MS ES-
3.21e6

245.00
165.03   166.04 : Dralc
353.05
96.97
331.07
313.06
433.02
226.99
519.09   541.07
158.92 166.04
354.06
512.99
599.06
685.13 707.11
787.03
873.15
953.12 1039.19
1141.14 1227.21 1307.18 1393.25
m/z

Compound **7 HDAM-MonoP**

SYNAPT G2-S#UEB205   JA 4.232 F2   12-Jun-2015
X-CP15061206 3 (0.141) Cm (3)   1: TOF MS ES-
     2.52e6
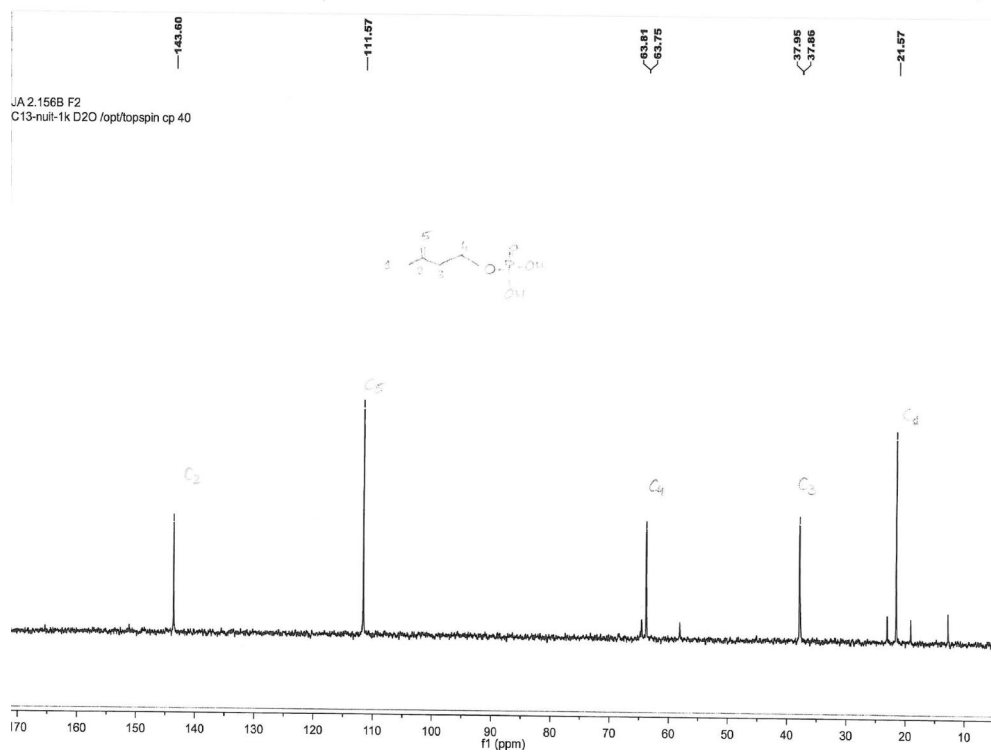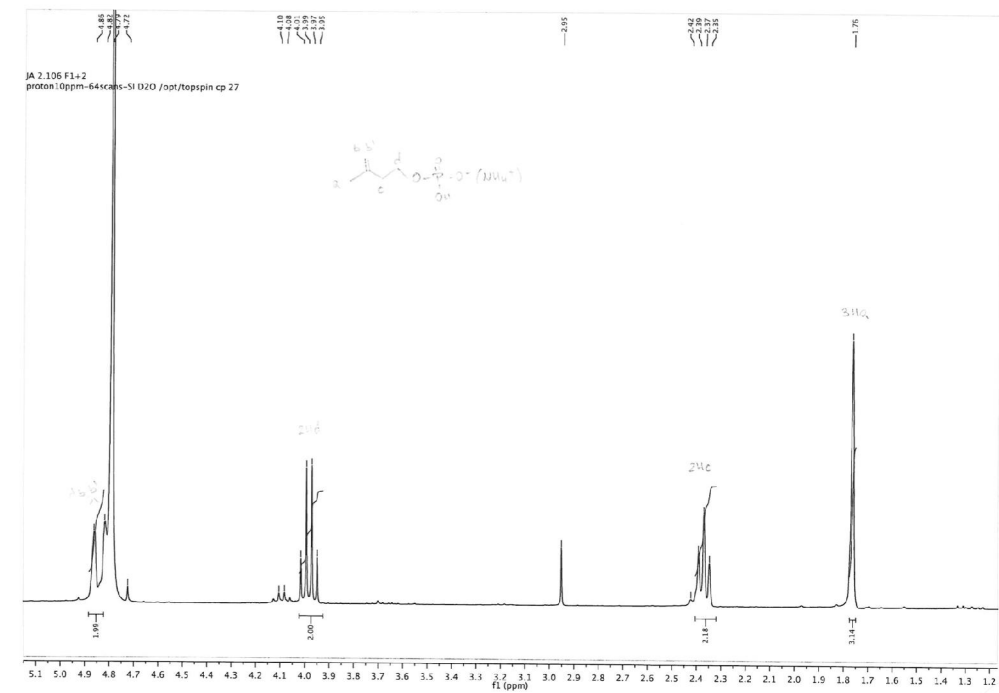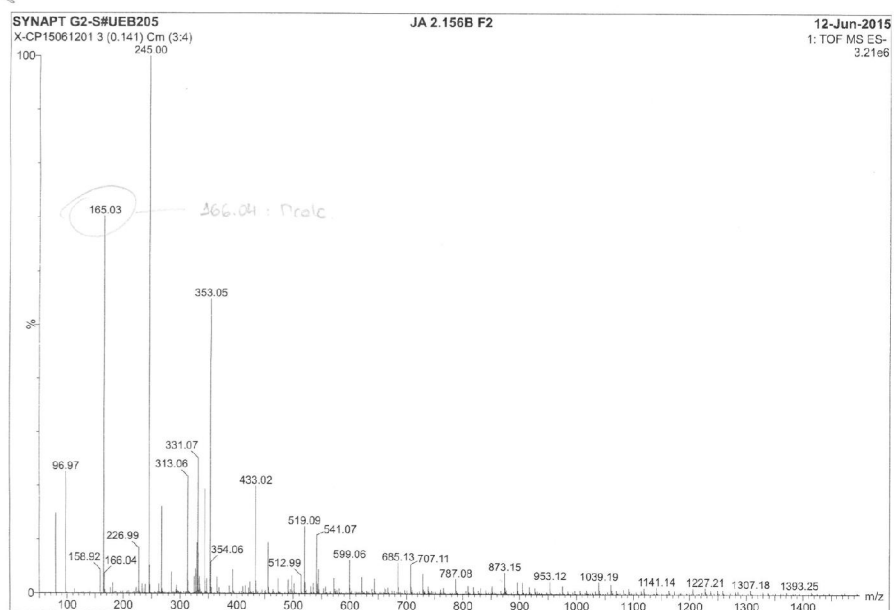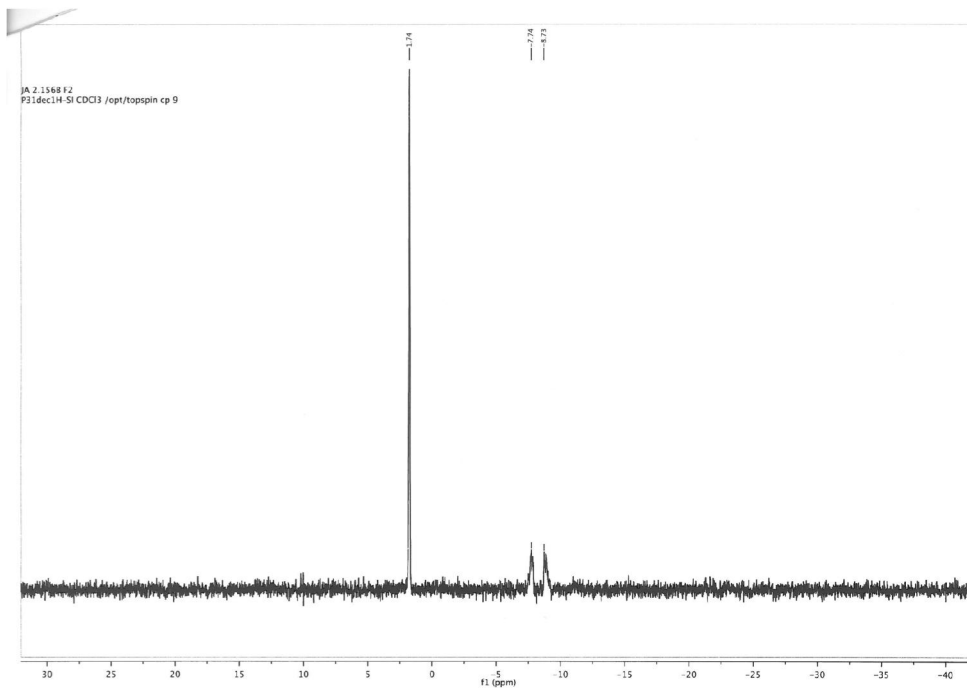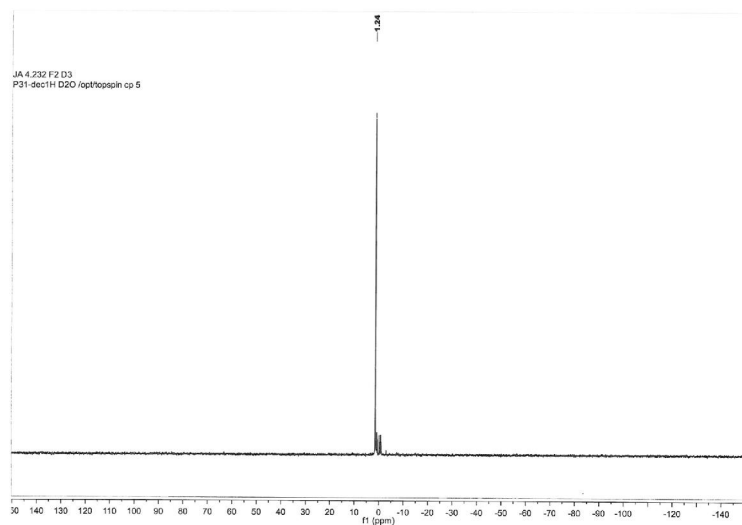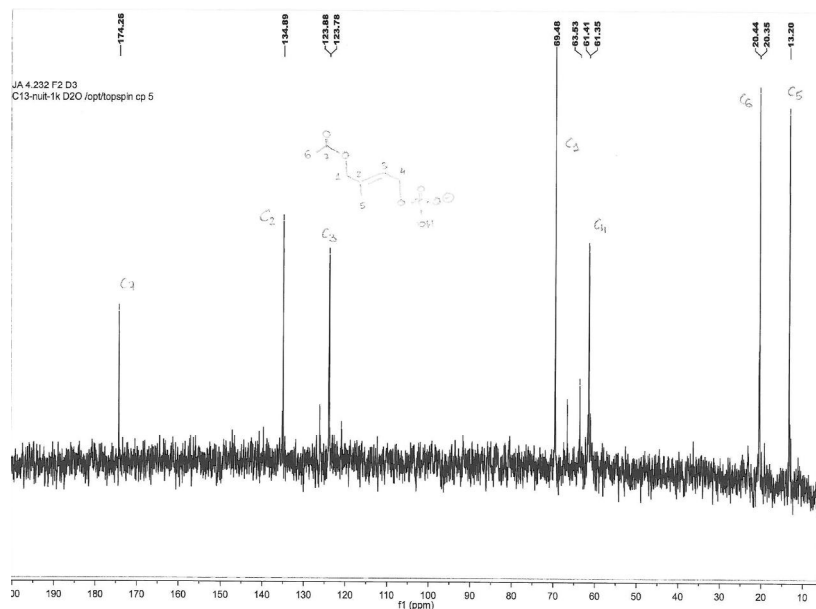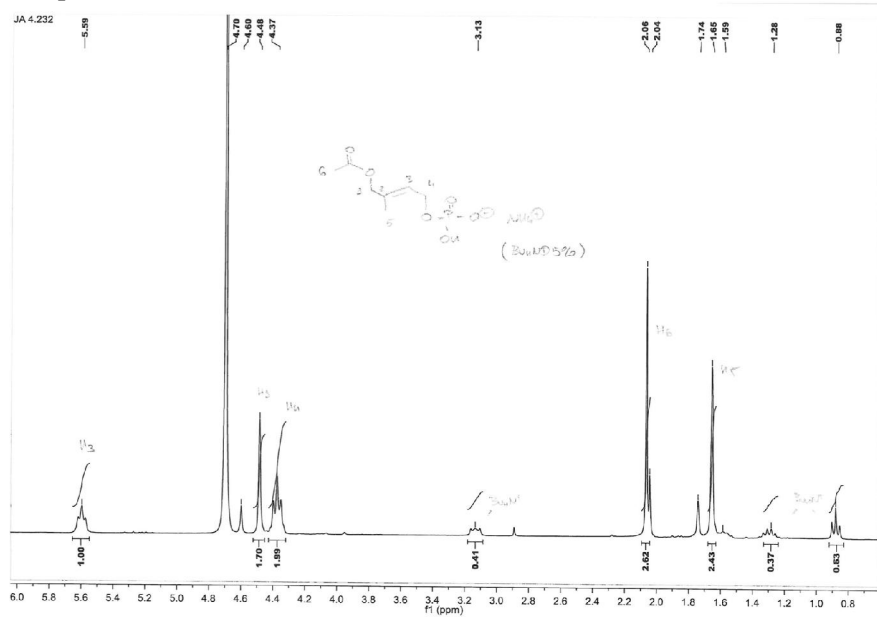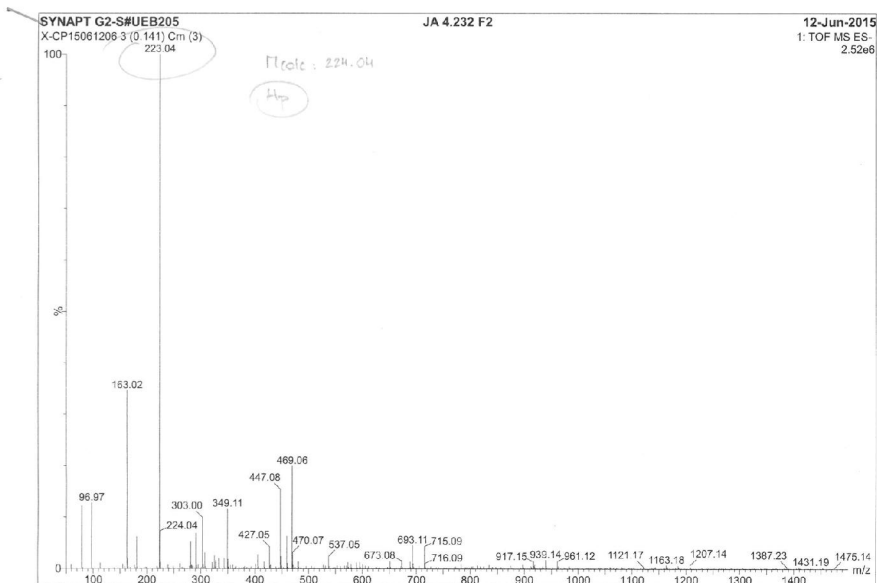
Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -50.0, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1178 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100   H: 0-100   N: 0-10   O: 0-20   P: 1-4

SYNAPT G2-S#UEB205
Z-CP15110607 4 (0.175) Cm (4)   JA 4.232 F2
     06-Nov-2015
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     1.57e+006
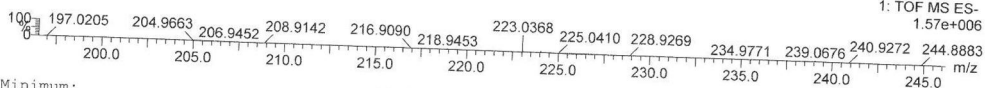
Minimum:				-50.0			
Maximum:		10.0	3.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
223.0368	223.0371	-0.3	-1.3	2.5	1545.6	0.000	99.99	C7 H12 O6 P
	223.0375	-0.7	-3.1	3.5	1554.7	9.038	0.01	C2 H9 N8 O P2
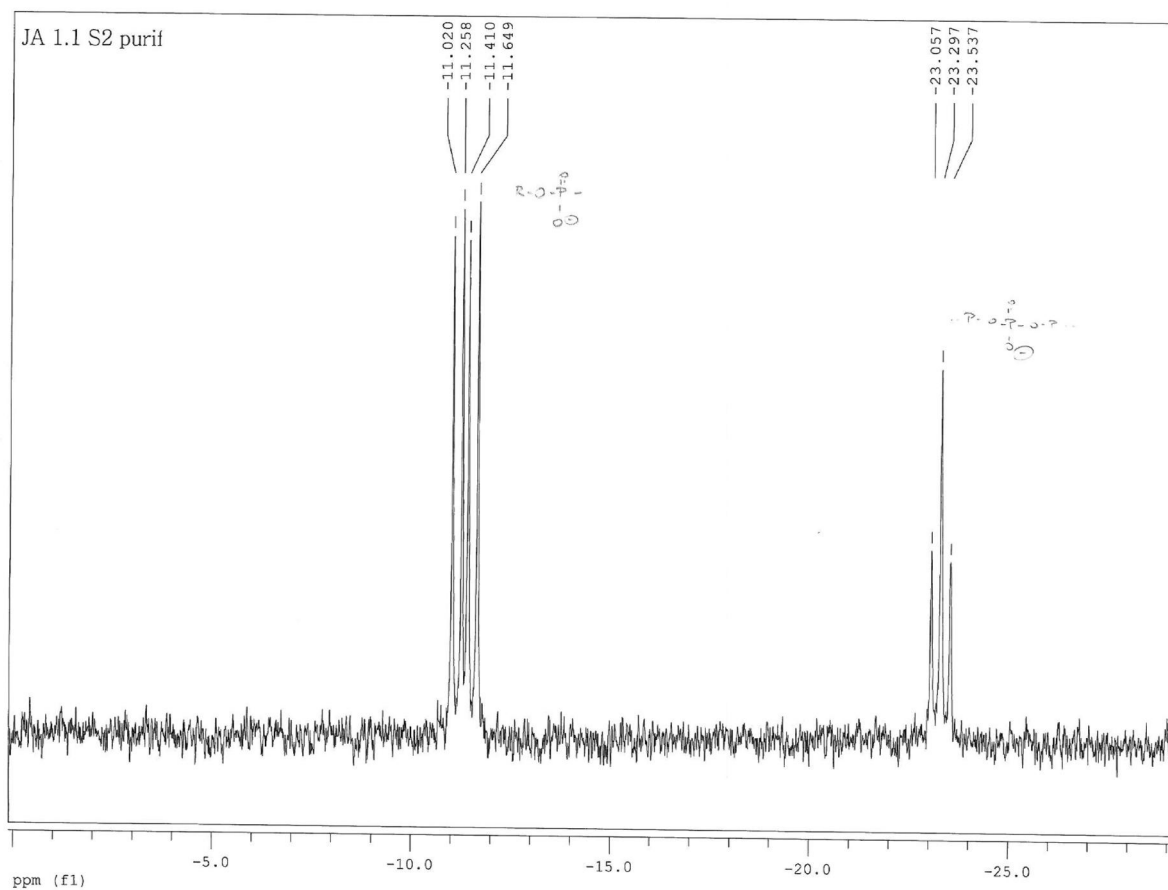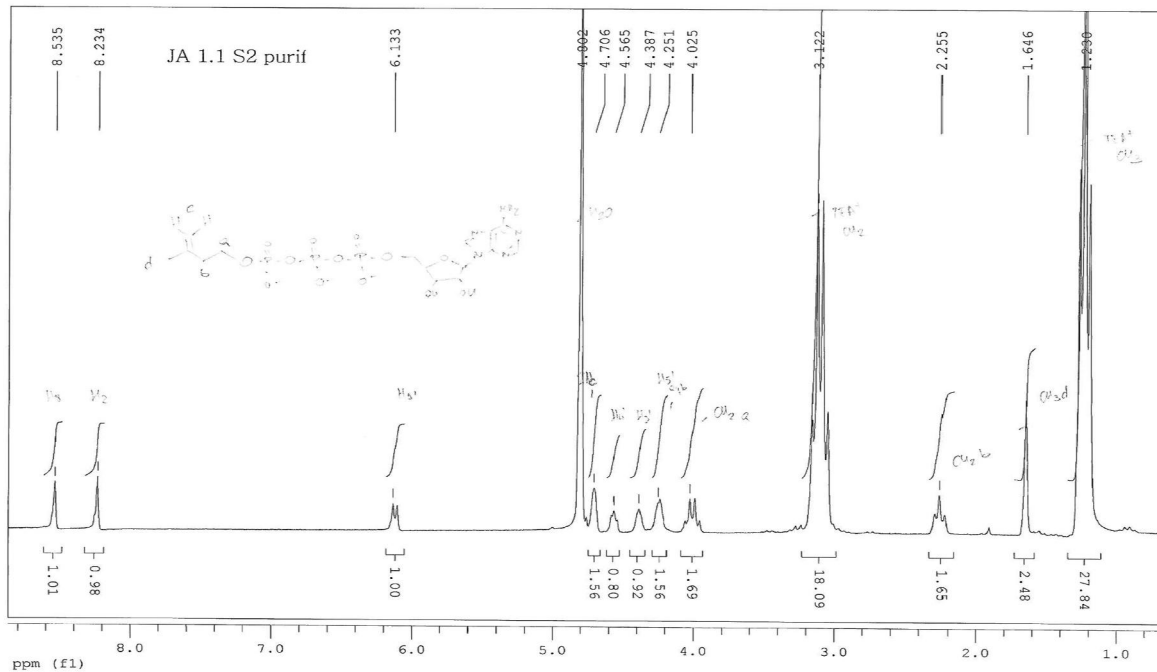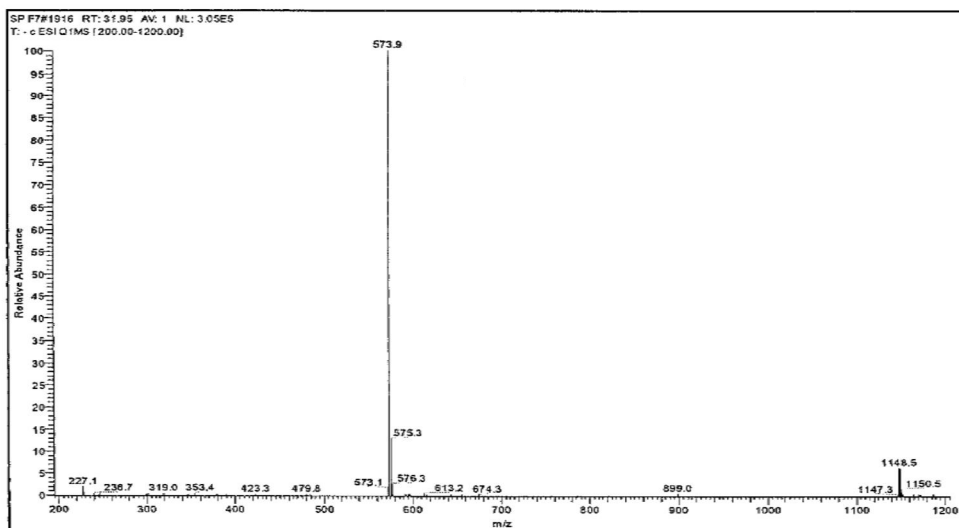
12

ApppI

JA 1.1 S2 purif

JA 1.1 S2 purif

SP F7#1916 RT: 31.95 AV: 1 NL: 3.05E5
T: - c ESI Q1MS [200.00-1200.00]

Empower
software

Javi

Reported by User: System   Project Name: AnalytiqueTPXBridge

S A M P L E   I N F O R M A T I O N

Sample Name:	Apppl	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	mardi 10 septembre 2013
Vial:	4	Acq. Method Set:	0_20A 30min
Injection #:	1	Date Processed:	mardi 10 septembre 2013
Injection Volume:	10,00 ul	Processing Method:	Default
Run Time:	30,0 Minutes	Channel Name:	Wvln Ch1
Sample Set Name:	analisis appph	Proc. Chnl. Descr.:	PDA 254,0 nm

Auto-Scaled Chromatogram
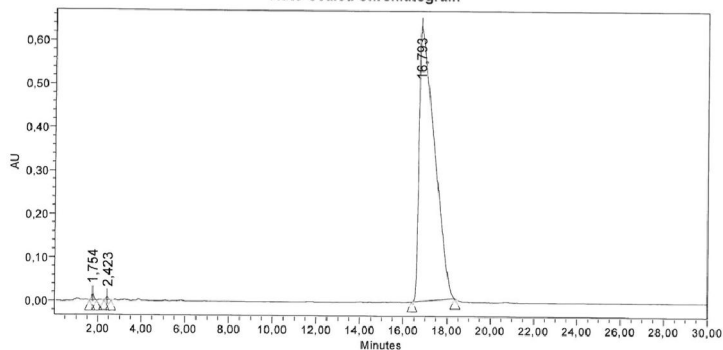
Peak Results

	Name	RT	Area	Height	% Area	Amount	Units
1		1,754	98340	15155	0,32		
2		2,423	58759	8019	0,19		
3		16,793	30371988	635300	99,49		
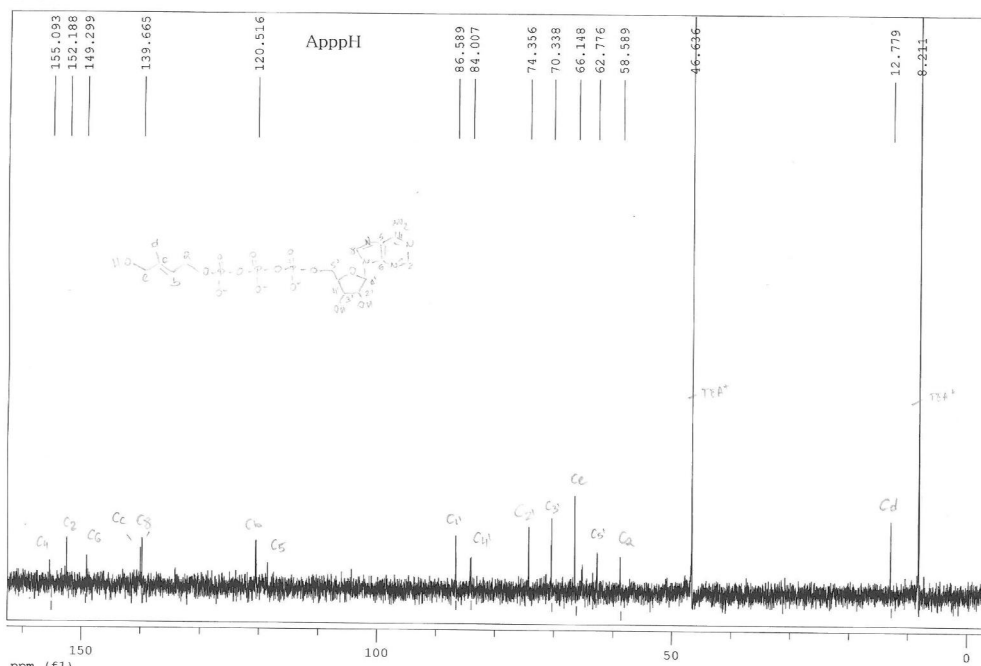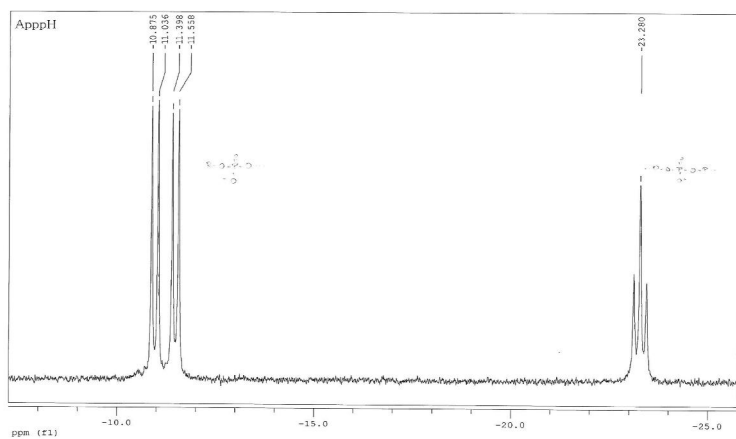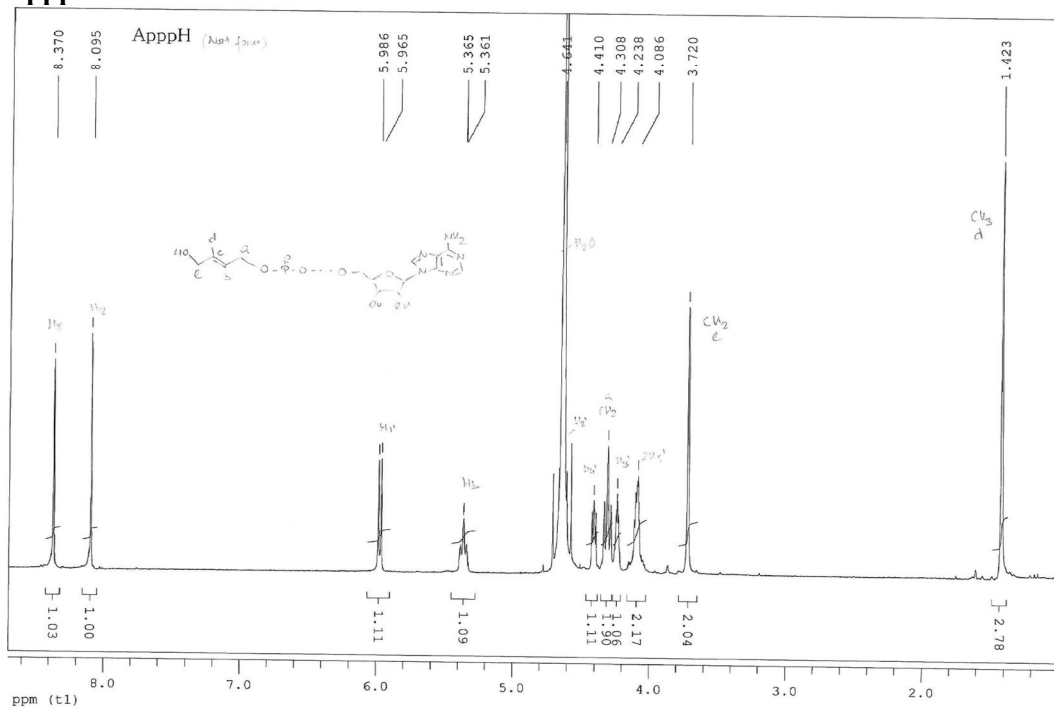
Report Method: Javi   Printed 14:10:05   mardi 10 septembre 2013   Page: 1 of 2

ApppH

Empower software

Javi

Reported by User: System   Project Name: AnalytiqueTPXBridge

S A M P L E   I N F O R M A T I O N

Sample Name:	ApppH
Sample Type:	Unknown
Vial:	2
Injection #:	1
Injection Volume:	10,00 ul
Run Time:	30,0 Minutes
Sample Set Name: analisis appph	

Acquired By:	System
Date Acquired:	mardi 10 septembre 2013
Acq. Method Set:	0_20A 30min
Date Processed:	mardi 10 septembre 2013
Processing Method:	Default
Channel Name:	WVln Ch1
Proc. Chnl. Descr.:	PDA 254,0 nm

Auto-Scaled Chromatogram

Peak Results
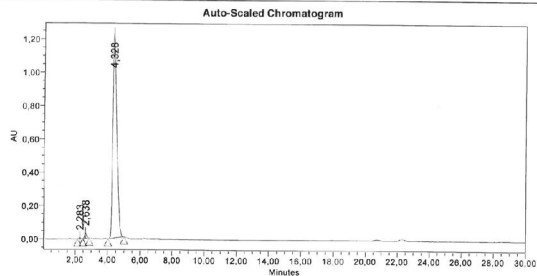
	Name	RT	Area	Height	% Area	Amount	Units
1		2,283	53168	7846	0,26		
2		2,638	257613	32850	1,24		
3		4,328	20445649	1243354	98,50		

Report Method: Javi   Printed 17:22:34   mardi 10 septembre 2013   Page: 1 of 2

SYNAPT G2-S#UEB205   ApppH   04-Sep-2013
Y-CP13090401 19 (0.398)   1: TOF MS ES-
                                                       3.74e6

calc. mass: 591.05
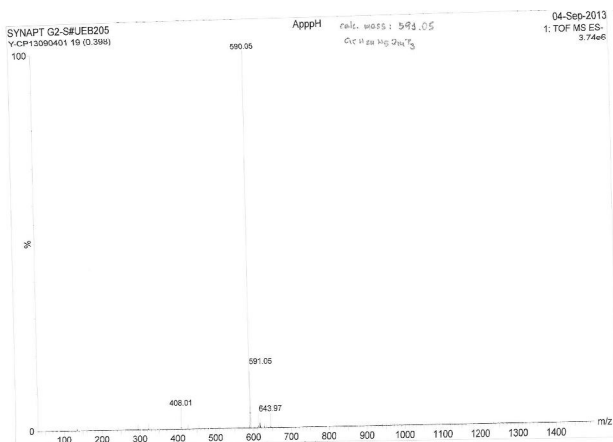
SYNAPT G2-S#UEB205   ApppH   04-Sep-2013
Y-CP13090401 19 (0.398)   1: TOF MS ES-
                                                                 6.94e+006
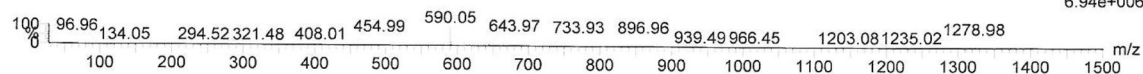
Minimum:			-10.0	
Maximum:	5.0	2.0	50.0	

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula	
590.0458	590.0454	0.4	0.7	8.5	891.6	0.249	77.96	C15 H23 N5 O14 P3	←
	590.0468	-1.0	-1.7	13.5	892.8	1.513	22.03	C16 H19 N9 O10 P3	
	590.0449	0.9	1.5	26.5	901.7	10.345	0.00	C28 H15 N7 O3 P3	

16

ApCppI

ApCppI-JA2.122 / D2O
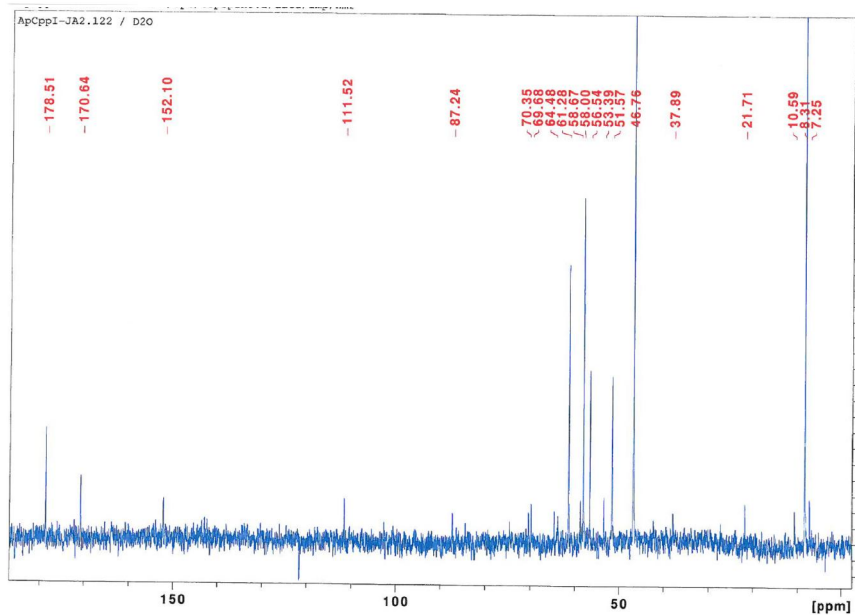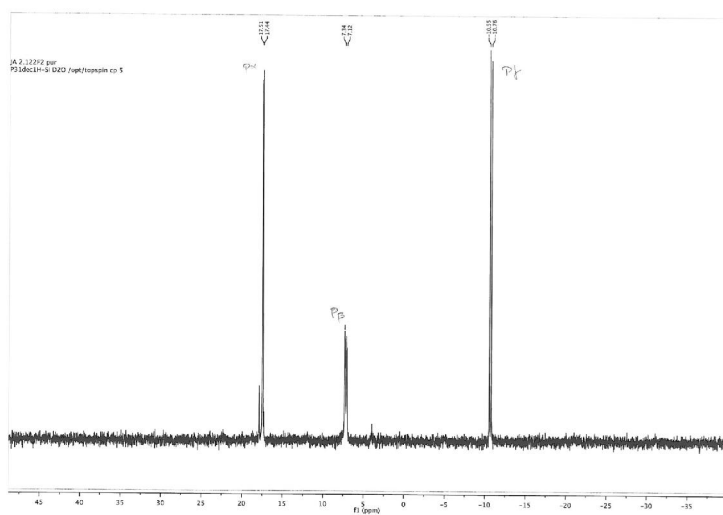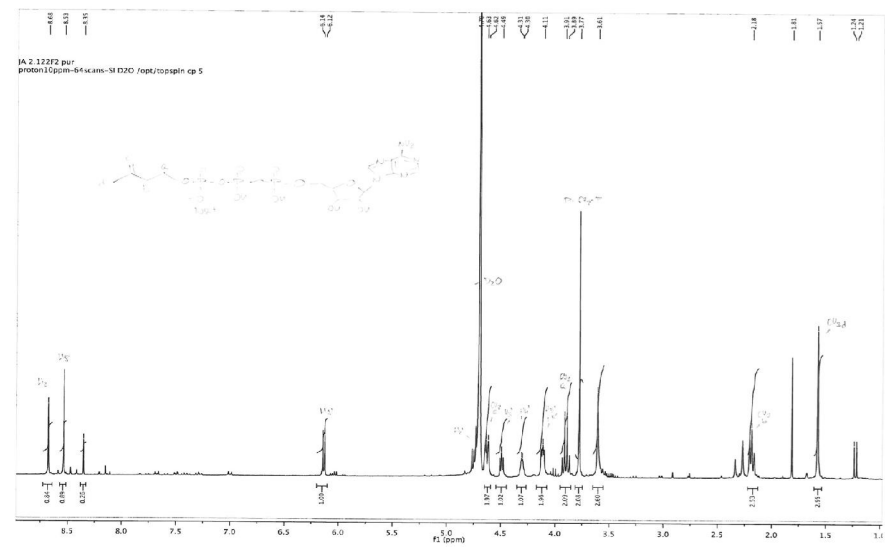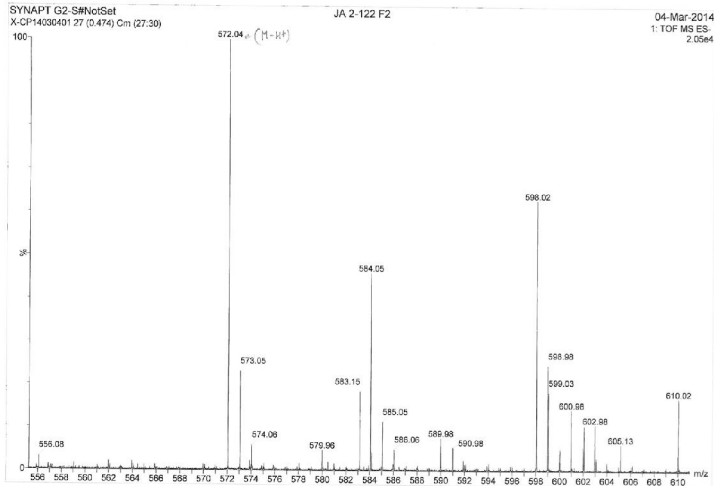
Single Mass Analysis

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

Monoisotopic Mass, Even Electron Ions
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Elements Used:
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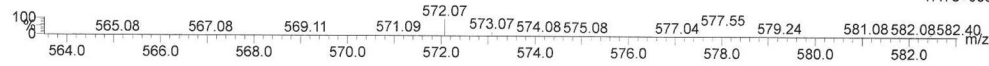
Minimum:				-1.5			
Maximum:		5.0	1.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
572.0715	572.0713	0.2	0.3	8.5	2835.2	0.003	99.73	C16 H25 N5 O12 P3
	572.0718	-0.3	-0.5	1.5	2848.8	13.619	0.00	C H21 N17 O13 P3
	572.0712	0.3	0.5	19.5	2841.1	5.930	0.27	C14 H13 N19 O2 P3

Javi Report

SAMPLE INFORMATION

Sample Name: JA 2.122F2 Na salt	Acquired By: Nucleotide
Sample Type: Unknown	Date Acquired: 26/03/14 16:46:22
Vial: 61	Acq. Method Set: Javi 0_100_30min
Injection #: 1	Date Processed: 26/03/14 17:18:42
Injection Volume: 100,00 ul	Processing Method: Javi
Run Time: 30,0 Minutes	Channel Name: 254
Sample Set Name: javi	Proc. Chnl. Descr.: PDA 260,0 nm
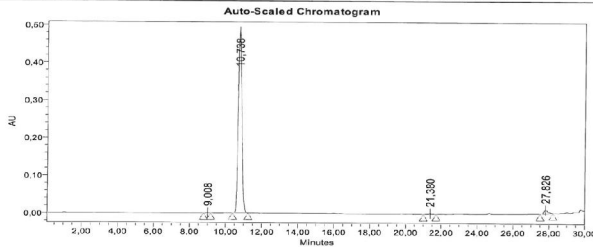
Auto-Scaled Chromatogram

Peak Results

	Name	RT	Area	% Area	Height
1		9,008	9935	0,14	1021
2		10,738	6706922	97,15	463821
3		21,380	31996	0,46	2011
4		27,826	154620	2,24	9744

Report Method: Javi   Printed 17:19:02 26/03/14   Page: 1 of 2

ApCppH

SYNAPT G2-S#NotSet
Y-CP14091610 3 (0.154)
JA3.179 F5-NH3
17-Sep-2014
1: TOF MS ES-
6.12e6
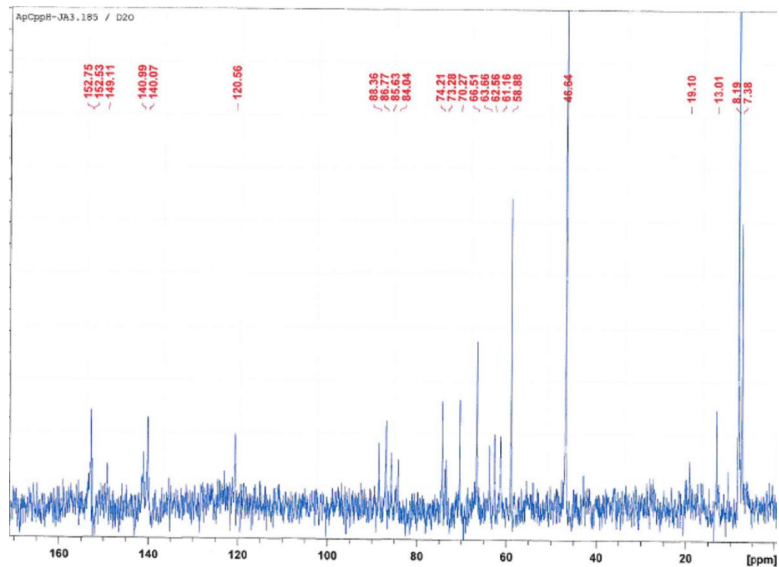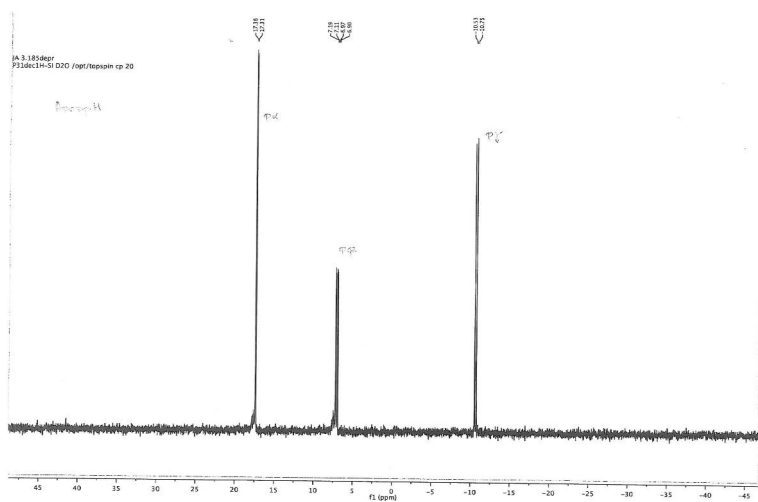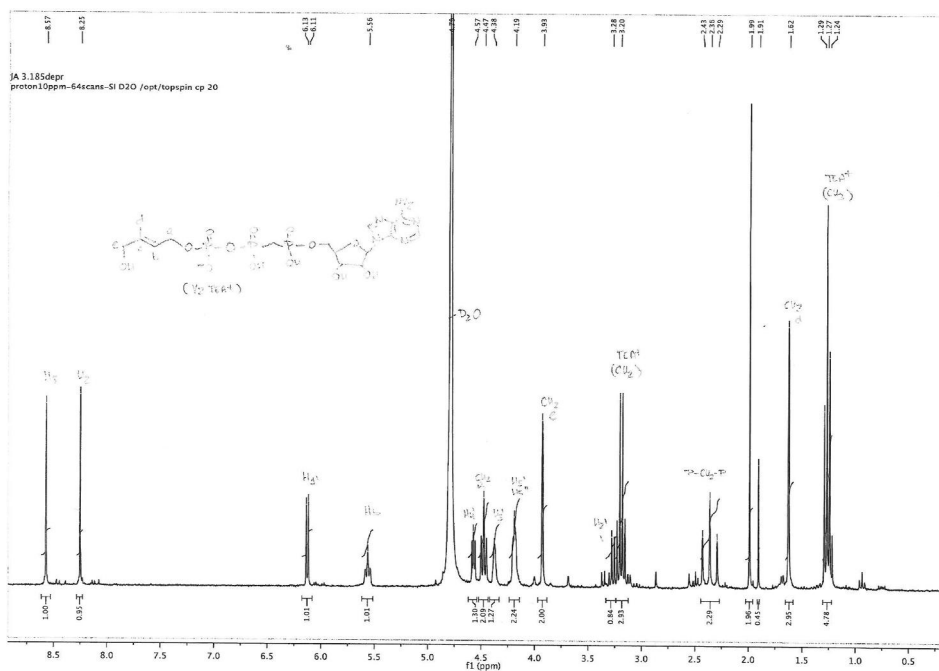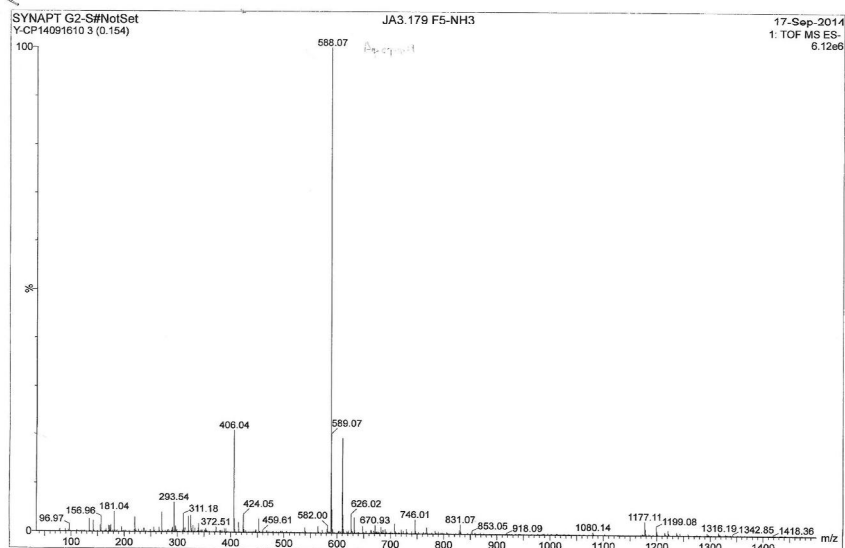
Single Mass Analysis
Tolerance = 1.0 PPM   /   DBE: min = -50.0, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9669 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100   H: 0-100   N: 0-10   O: 0-20   P: 1-5

SYNAPT G2-S#UEB205
Z-CP15110605 11 (0.491)
ApCpph JA3.185
06-Nov-2015
1: TOF MS ES-
5.70e+005
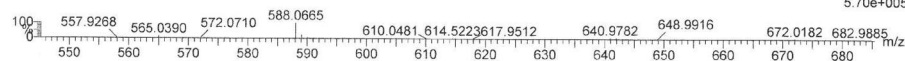
Minimum:				-50.0			
Maximum:		10.0	1.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
588.0665	588.0662	0.3	0.5	8.5	977.6	0.000	99.95	C16 H25 N5 O13 P3
	588.0663	0.2	0.3	17.5	985.6	8.023	0.03	C21 H23 N9 O2 P5
	588.0668	-0.3	-0.5	-0.5	987.3	9.747	0.01	C8 H31 N7 O13 P5
	588.0669	-0.4	-0.7	22.5	987.5	9.899	0.01	C25 H15 N7 O9 P
	588.0660	0.5	0.9	16.5	987.6	10.038	0.00	C26 H26 N O7 P4
	588.0664	0.1	0.2	0.5	989.7	12.148	0.00	C6 H24 N9 O19 P2
	588.0667	-0.2	-0.3	30.5	991.5	13.936	0.00	C35 H16 N3 O3 P2

Auto-Scaled Chromatogram
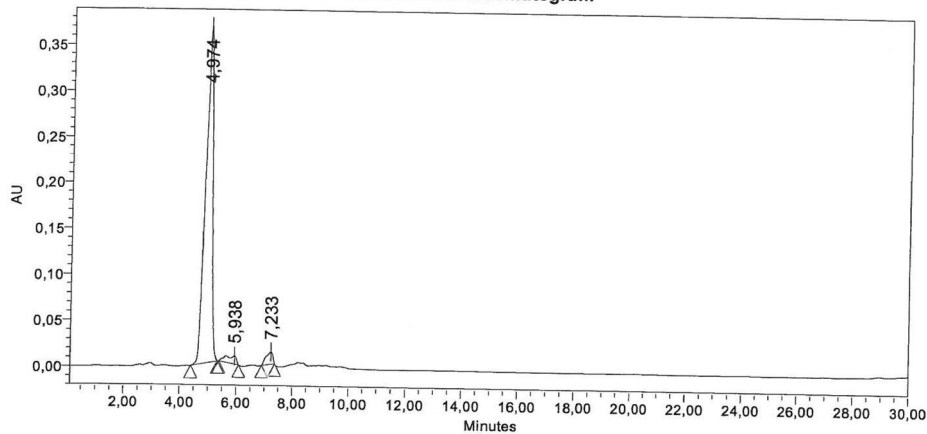
Peak Results

	Name	RT	Area	% Area	Height
1		4,974	6328874	93,56	367408
2		5,938	218423	3,23	8868
3		7,233	217391	3,21	13346

UpppH
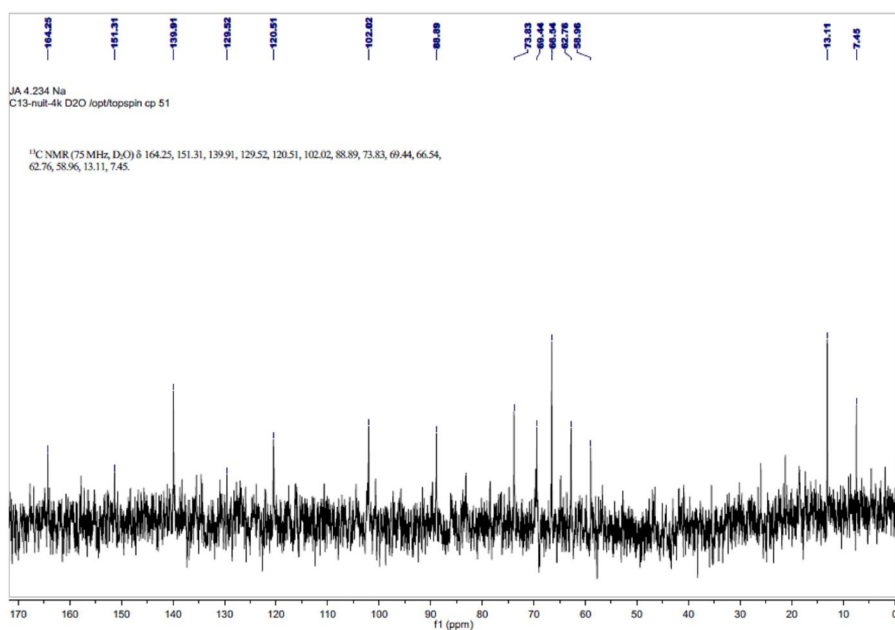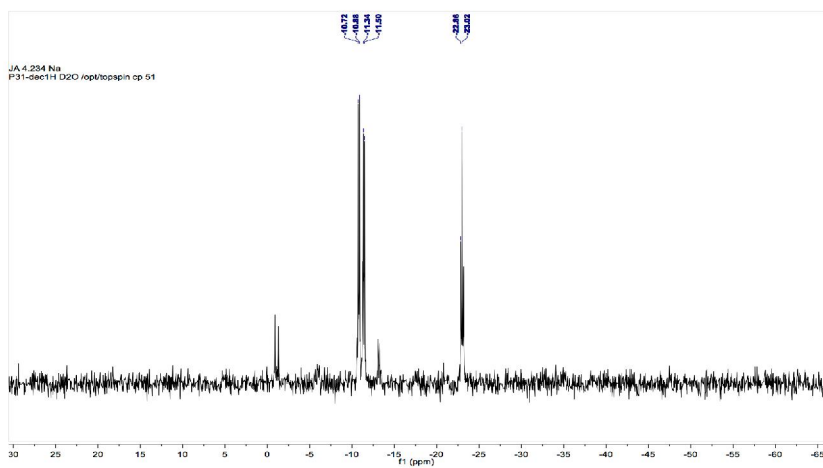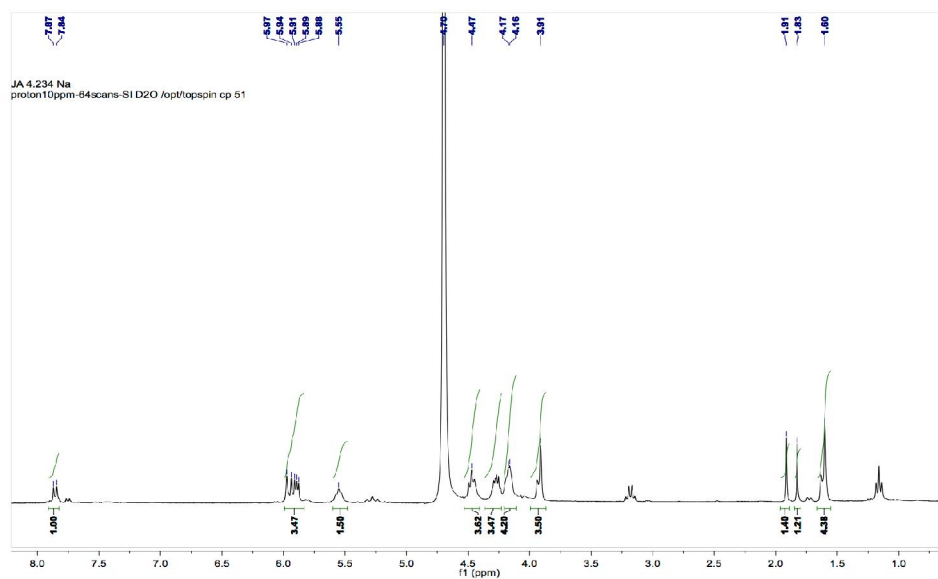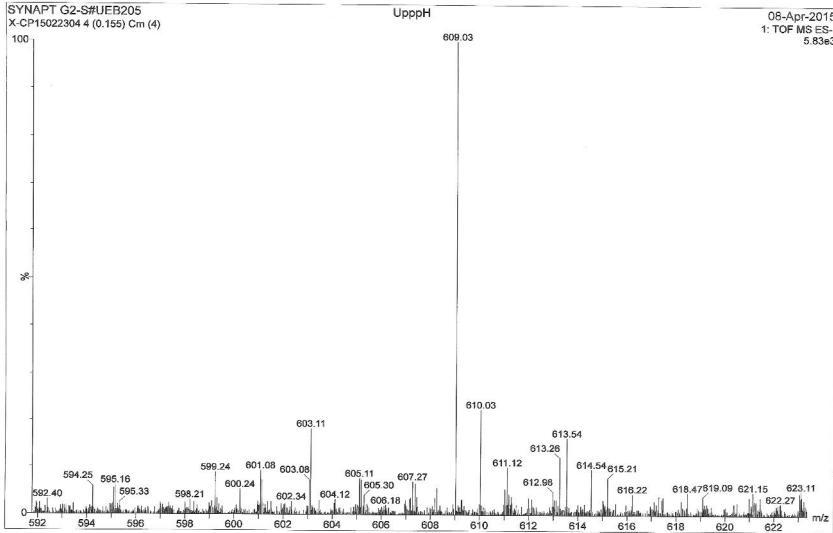
JA 4.234 Na
proton10ppm-64scans-SI D2O /opt/topspin cp 51

JA 4.234 Na
P31-dec1H D2O /opt/topspin cp 51

JA 4.234 Na
C13-nuit-4k D2O /opt/topspin cp 51

^{13}C NMR (75 MHz, D$_2$O) δ 164.25, 151.31, 139.91, 129.52, 120.51, 102.02, 88.89, 73.83, 69.44, 66.54, 62.76, 58.96, 13.11, 7.45.

Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -50.0, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
5764 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-10 O: 0-20 P: 2-4

SYNAPT G2-S#UEB205
Z-CP15110608 6 (0.262)

UpppH - JA 4.234

06-Nov-2015
1: TOF MS ES-
3.35e+005

Minimum:				-50.0				
Maximum:		10.0	1.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
567.0185	567.0182	0.3	0.5	6.5	1094.7	0.018	98.22	C14 H22 N2 O16 P3
	567.0190	-0.5	-0.9	29.5	1099.3	4.599	1.01	C28 H10 N8 O P3
	567.0185	0.0	0.0	7.5	1099.9	5.184	0.56	C9 H19 N10 O11 P4
	567.0187	-0.2	-0.4	28.5	1100.9	6.154	0.21	C33 H13 O6 P2

SAMPLE INFORMATION

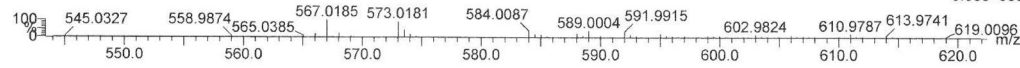|			
Sample Name:	UpppH pure	Acquired By:	Nucleotide
Sample Type:	Unknown	Date Acquired:	03/07/15 14:45:08
Vial:	53	Acq. Method Set:	Javi 0_100_30min
Injection #:	1	Date Processed:	03/07/15 16:08:09
Injection Volume:	50,00 ul	Processing Method	Javi
Run Time:	30,0 Minutes	Channel Name:	PDA Single 254,0 nm
Sample Set Name:	javi	Proc. Chnl. Descr.:	PDA 254,0 nm

Auto-Scaled Chromatogram
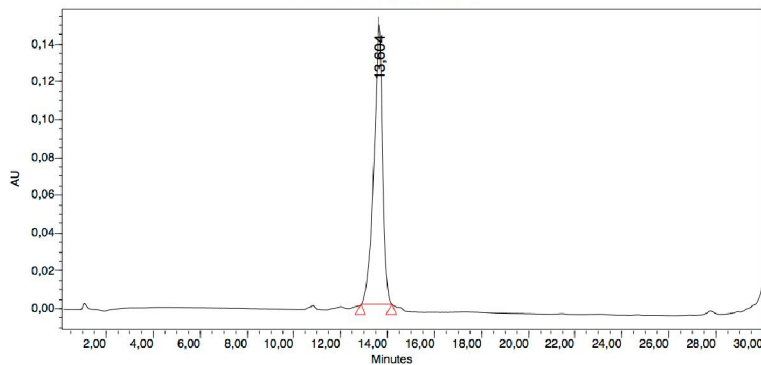
Peak Results

	Name	RT	Area	% Area	Height
1		13,604	3773946	100,00	148117

dTpppH

JA 4.233 Na
proton10ppm-64scans-SI D2O /opt/topspin cp 50

JA 4.233 Na
P31-dec1H D2O /opt/topspin cp 50

JA 4.233 Na
C13-nuit-4k D2O /opt/topspin cp 50

^{13}C NMR (75 MHz, D$_2$O) δ 167.95, 152.80, 139.87, 137.22, 120.45, 111.82, 84.87, 70.88, 66.56, 65.45, 62.79, 62.71, 38.55, 13.09, 11.83.

SYNAPT G2-S#UEB205
Z-CP15110606 10 (0.437) Cm (10)   dtPPPh - JA4.233   06-Nov-2015
                                                                  1: TOF MS ES-
                                                                        1.62e6

Single Mass Analysis
Tolerance = 1.0 PPM   /   DBE: min = -50.0, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
7717 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100   H: 0-100   N: 0-10   O: 0-20   P: 1-4

SYNAPT G2-S#UEB205
Z-CP15110606 10 (0.437) Cm (10)   dtPPPh - JA4.233   06-Nov-2015
                                                                  1: TOF MS ES-
                                                                      1.62e+006
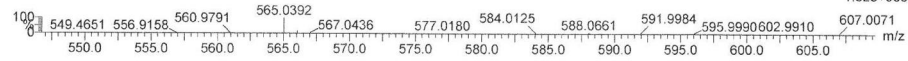
| Minimum: | | | -50.0 |
| Maximum: | 10.0 | 1.0 | 50.0 |

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
565.0392	565.0390	0.2	0.4	6.5	1242.3	0.140	86.96	C15 H24 N2 O15 P3
	565.0393	-0.1	-0.2	7.5	1244.2	2.058	12.78	C10 H21 N10 O10 P4
	565.0386	0.6	1.1	16.5	1248.2	5.998	0.25	C18 H15 N8 O10 P2
	565.0397	-0.5	-0.9	20.5	1251.1	8.879	0.01	C24 H14 N4 O11 P
	565.0392	0.0	0.0	38.5	1254.8	12.568	0.00	C37 H6 N6 P
	565.0395	-0.3	-0.5	28.5	1254.9	12.754	0.00	C34 H15 O5 P2

SAMPLE INFORMATION

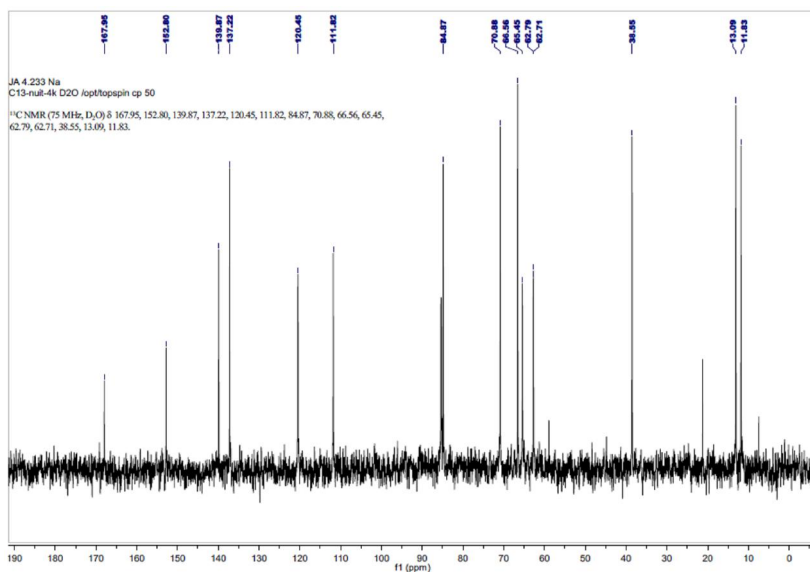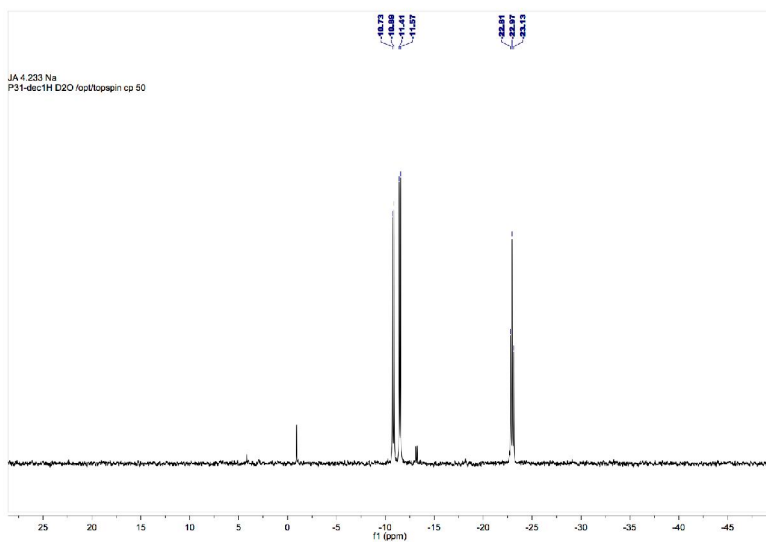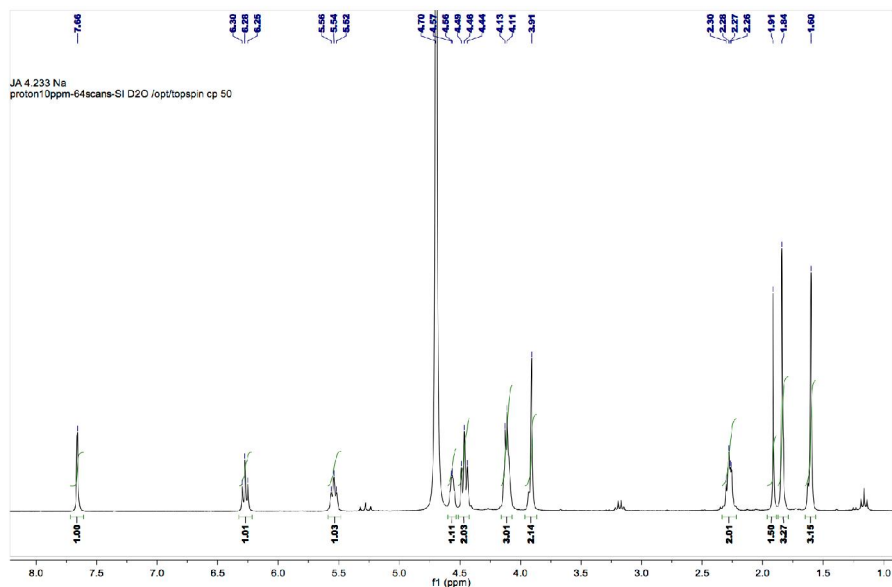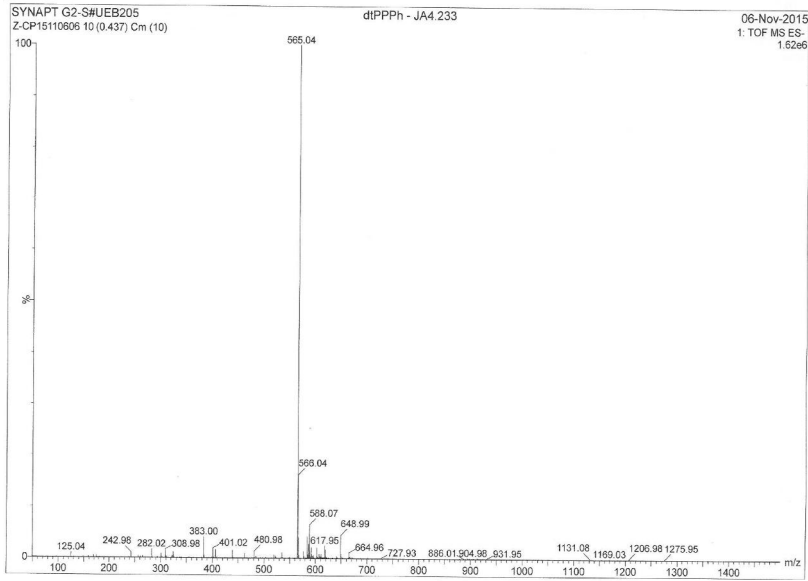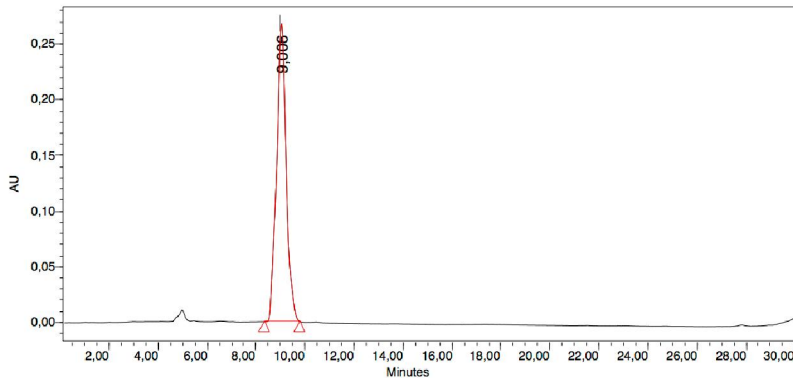|			
Sample Name:	dTpppH pure	Acquired By:	Nucleotide
Sample Type:	Unknown	Date Acquired:	03/07/15 16:48:57
Vial:	52	Acq. Method Set:	Javi 0_100_30min
Injection #:	1	Date Processed:	03/07/15 17:31:17
Injection Volume:	20,00 ul	Processing Method:	Javi
Run Time:	30,0 Minutes	Channel Name:	PDA Single 254,0 nm
Sample Set Name:	javi	Proc. Chnl. Descr.:	PDA 254,0 nm

Auto-Scaled Chromatogram

Peak Results

	Name	RT	Area	% Area	Height
1		9,006	7331789	100,00	268304