Supporting Information

α,*α*-Difluoro-*β*-iminophosphonates, an alternative toward the synthesis of *α*,*α*-difluoro-*β*-aminophosphonate derivatives

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I. General Considerations

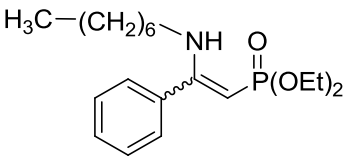
^{1}H NMR, ^{13}C NMR, ^{31}P NMR and **^{19}F NMR** spectra were recorded on a BRUKER DRX (400 MHz); BRUKER (400 MHz) AVANCE III HD NMR, Varian GEMINI 300 (300 MHz) and Varian 400 (400 MHz) spectrometers, unless otherwise noted. The chemical shifts are expressed in parts per million (ppm). For NMR spectroscopy as an internal standards the tetramethylsilane (TMS) (**^{1}H NMR** and **^{13}C NMR),** and trichloromonofluoromethane ($CFCl_3$) (**^{19}F NMR**) were used. For (**^{31}P NMR**) spectroscopy, 85% H_3PO_4 as external standard was used. Coupling constants are expressed in Hertz (Hz). The following abbreviations were used to express the multiplicities: s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), t (triplet), td (triplet of doublets), q (quartet), tq (triplet of quartets), m (multiplet), br d (broad doublet), br s (broad singlet), br t (broad triplet). Reactions monitored by ^{19}F, ^{31}P NMR during process were done with a DMSO-d_6 probe. ^{31}P NMR spectra and chosen of ^{19}F NMR were recorded with protons decoupled. ^{13}C NMR spectra were recorded as attached proton test experiment (APT). **Gas Chromatography - Mass spectra (GC-MS)** GC-MS spectra were performed on Varian GC-MS 4000 spectrometer (conditions: flow rate of 1 mL/min, injector temperature = 220 °C, column oven temperature 40 °C (3 min) → 15 °C/min → 280 °C (10 min), using chloroform as the solvent). **Mass spectra (MS)** High resolution spectra were performed by electrospray ionization (ESI): Laboratoire Mesures Physiques of University Montpellier II. Thin Layer Chromatography (TLC) was performed on commercially available Merck Kieselgel 60-F_{254} with ethyl acetate/hexane; ethyl acetate/heptane as developing systems. Visualization was performed with UV light then permanganate solution followed by heating. Permanganate solution ($KMnO_4$) was prepared in water (300 mL) with $KMnO_4$ (3 g), K_2CO_3 (20 g) and 5% NaOH water solution (5 mL). **Column chromatography** was performed in a glass column with silica gel (Merck Kieselgel 60 (230-400 mesh) using ethyl acetate (EtOAc) and *n*-hexane. Flash Column Chromatography was performed on Interchim puriFlash®430 compatible with 15 µm silica column using ethyl acetate (EtOAc) and *n*-heptane. ***Purification of solvents and reagents*** Solvents were purified by classical methodology: Toluene was distilled over calcium hydride (CaH_2) than stocked over 4Å MS. Acetonitrile, dichloromethane, ethanol were distilled over calcium hydride (CaH_2) prior to use. Tetrahydrofuran (THF) was distilled over sodium-benzophenone. Other reagents were supplied by Sigma-Aldrich and used without purification unless otherwise noted.

II. Spectra of compounds

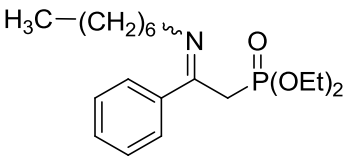
(*Z*/*E*)-diethyl (2-(heptylamino)-2-phenylvinyl)phosphonate 12a

(*E*/*Z*)-diethyl (2-(heptylimino)-2-phenylethyl)phosphonate 13a

Note: Ratio of enamines **12a** and imines **13a** after column chromatography equaled 92:8, respectively. Ratio of enamines (*Z*/*E*) **12a** equaled 85:15, respectively. Ratio of imines **13a** (*E*/*Z*) equaled 85:15, respectively.

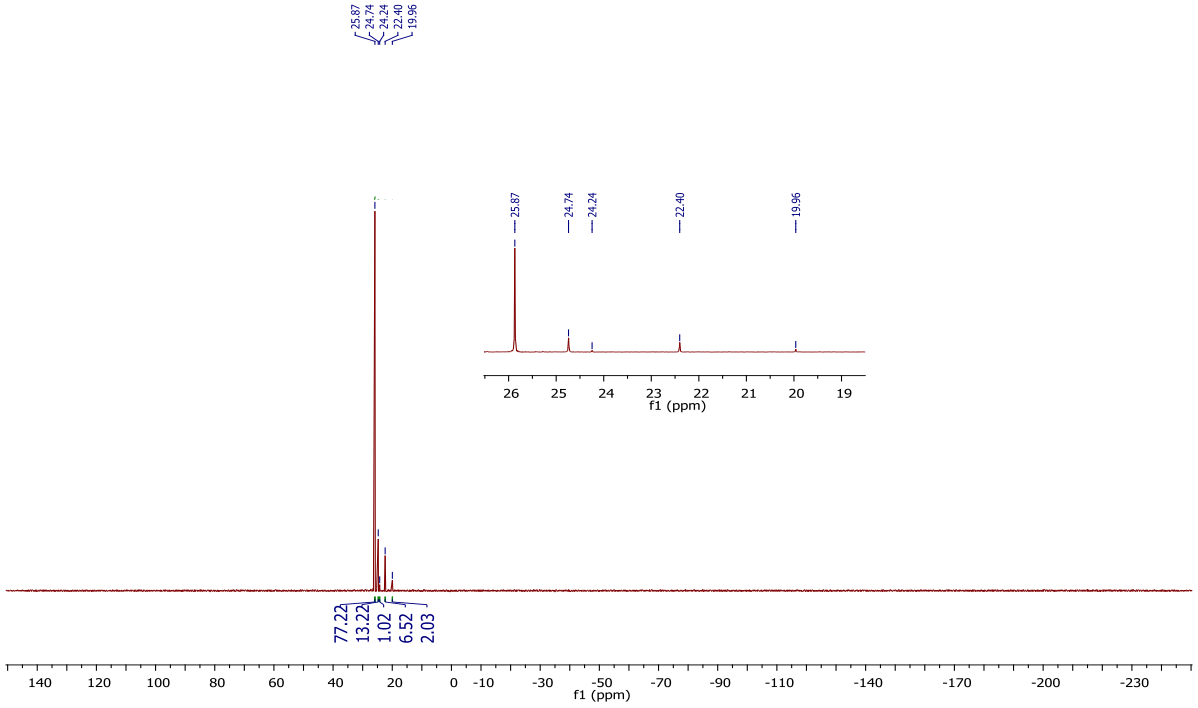


12a

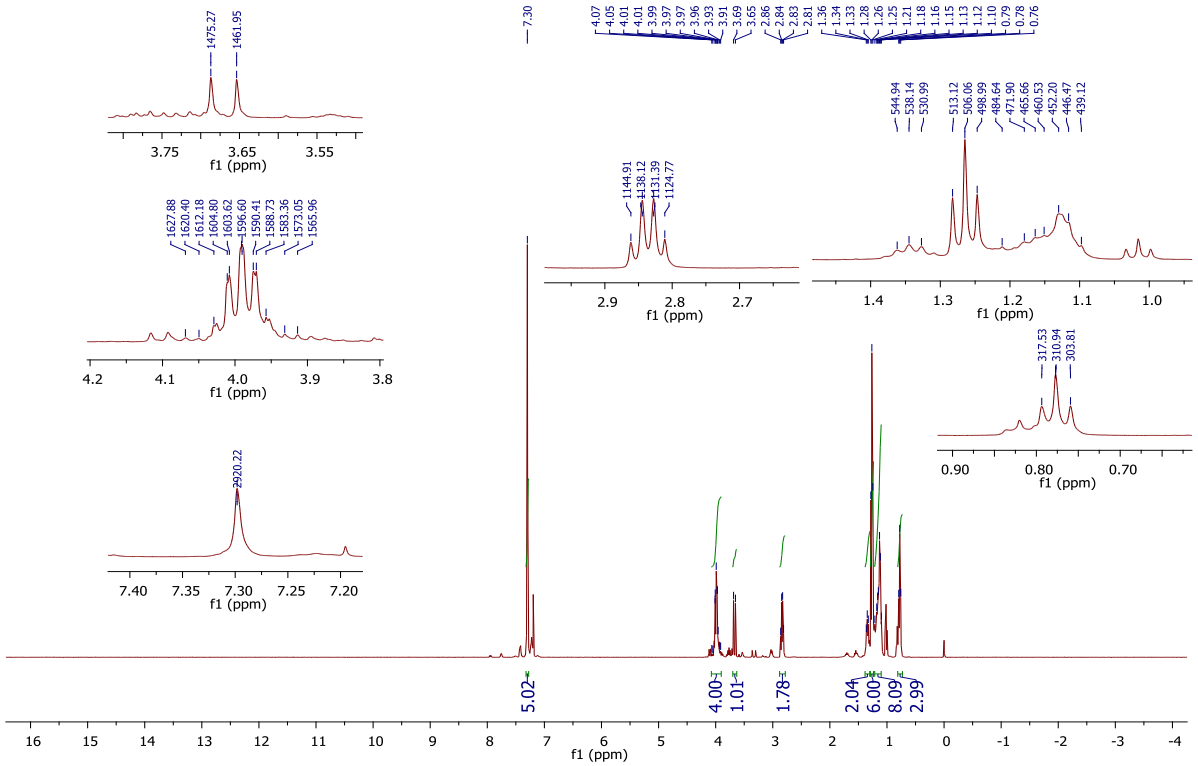


13a

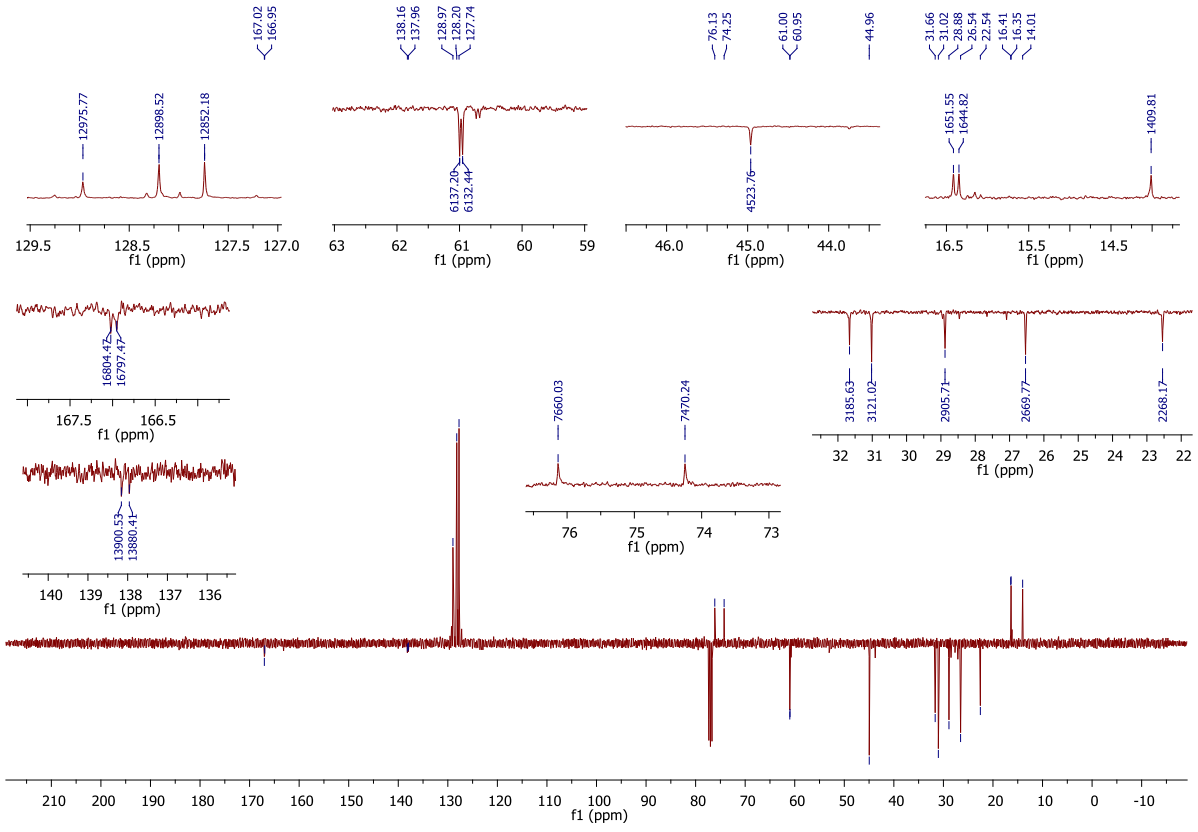
^{31}P NMR



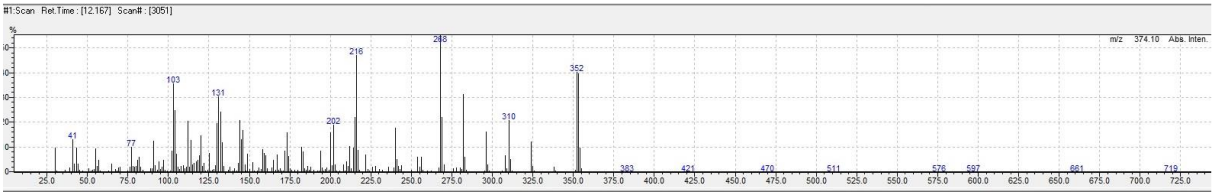
^{1}H NMR



^{13}C NMR



GC-MS



HRMS

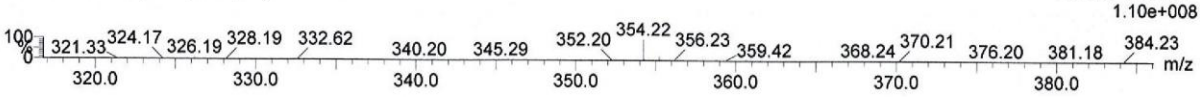
Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1643 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-110 N: 0-30 O: 0-30 P: 0-1

SYNAPT G2-S#UEB205
Y-JP15011201 4 (0.175) Cm (3:4)

MS292 f8-17

12-Jan-2015
1: TOF MS ES+
1.10e+008



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Maximum:		1.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
354.2199	354.2198	0.1	0.3	4.5	1381.9	n/a	n/a	C19 H33 N O3 P

SYNAPT G2-S#UEB205
Y-JP15011201 4 (0.175) Cm (3:4)

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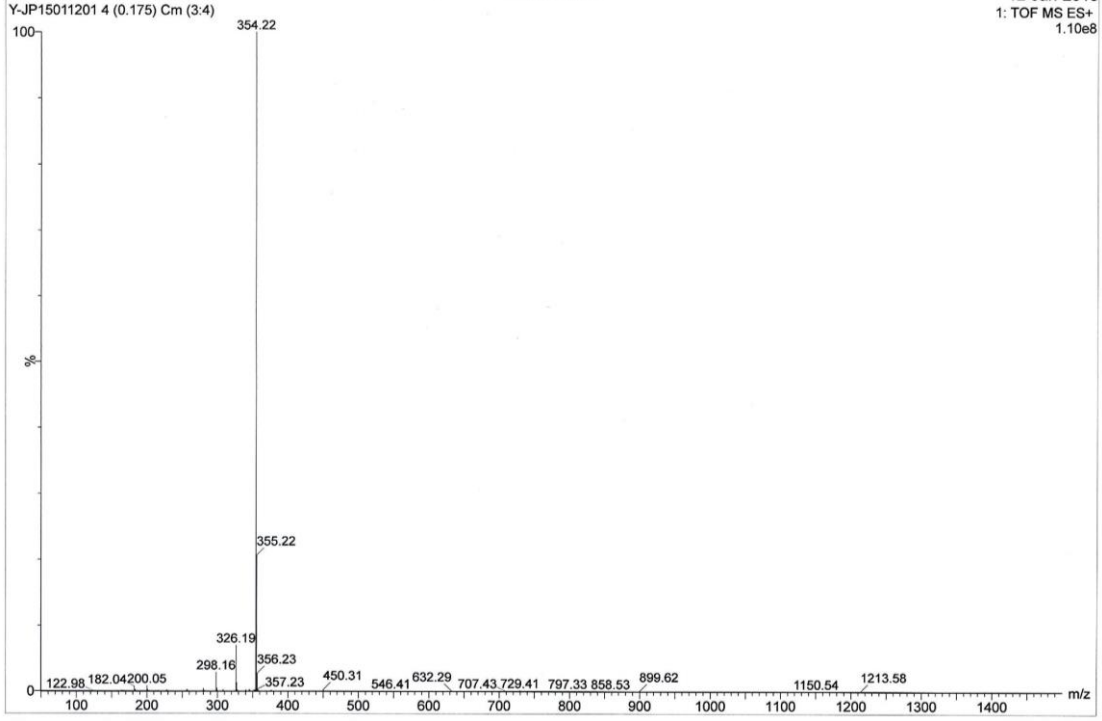
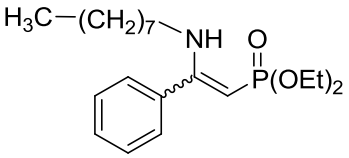
1.10e8



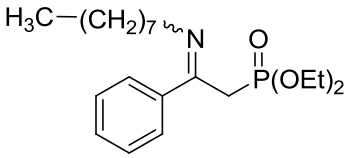
(*Z*/*E*)-diethyl (2-(octylamino)-2-phenylvinyl)phosphonate 12b

(*E*/*Z*)-diethyl (2-(octylimino)-2-phenylethyl)phosphonate 13b

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 93:7, respectively. Ratio of enamines (*Z*/*E*) **12b** equaled 87:13, respectively. Ratio of imines **13b** (*E*/*Z*) equaled 80:20, respectively.

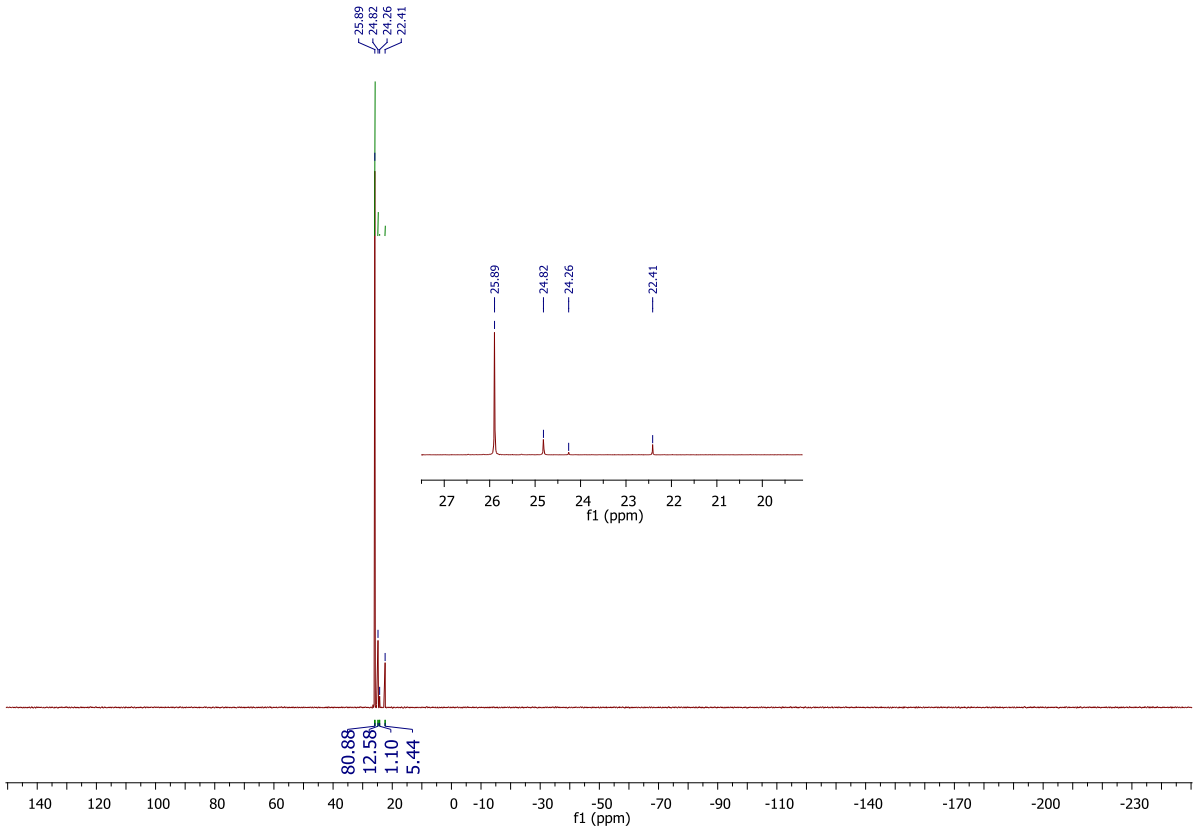


12b

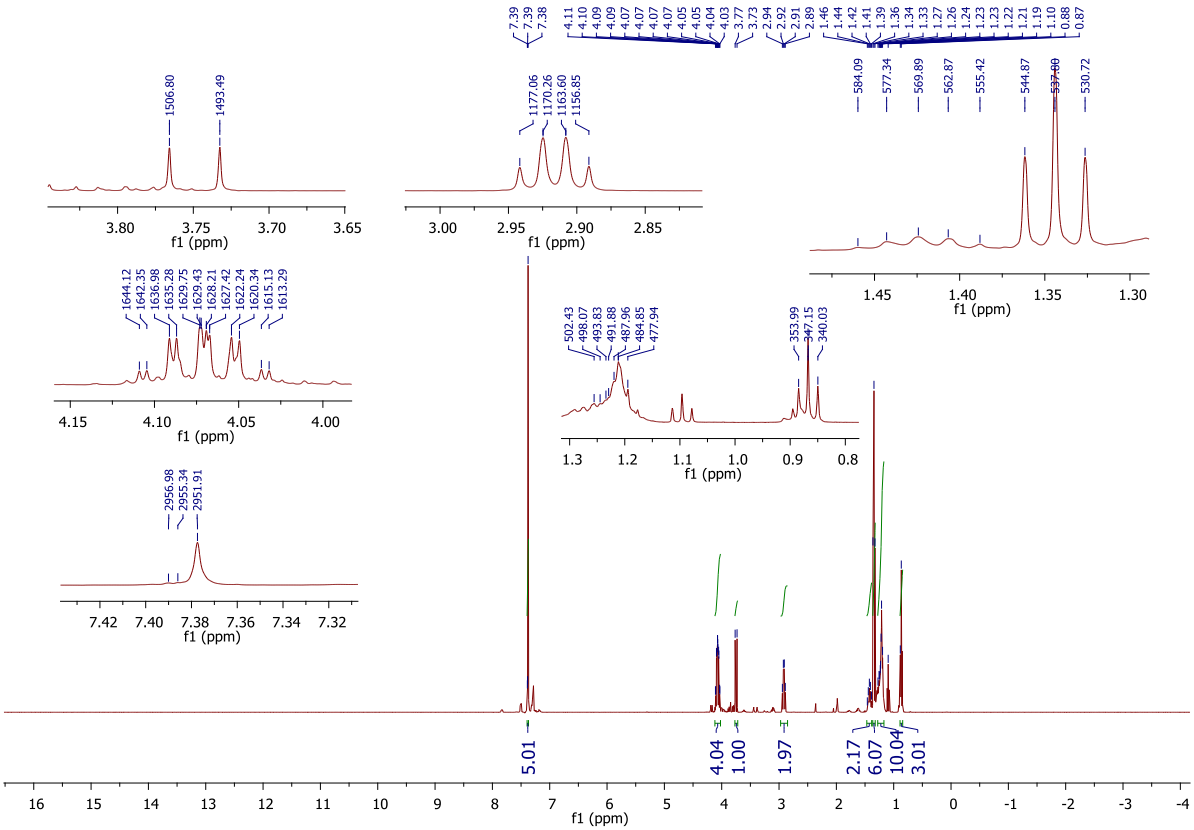


13b

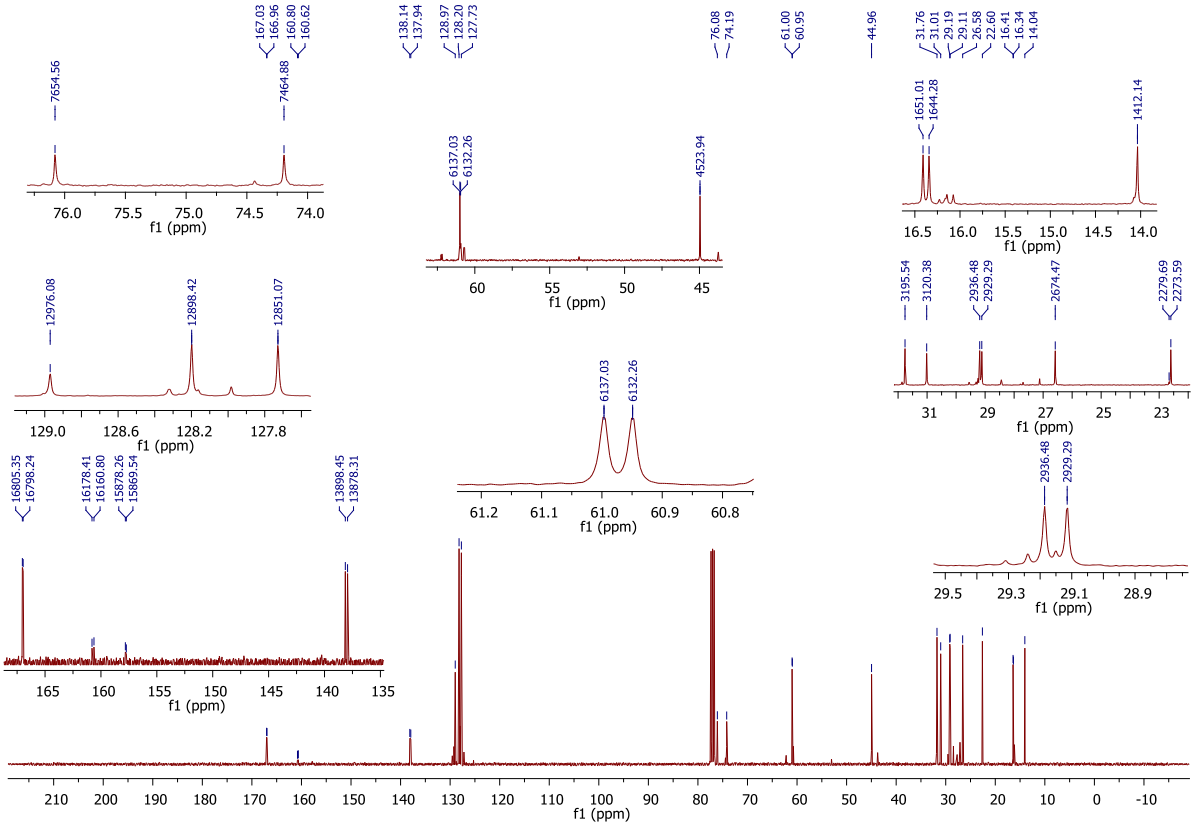
^{31}P NMR



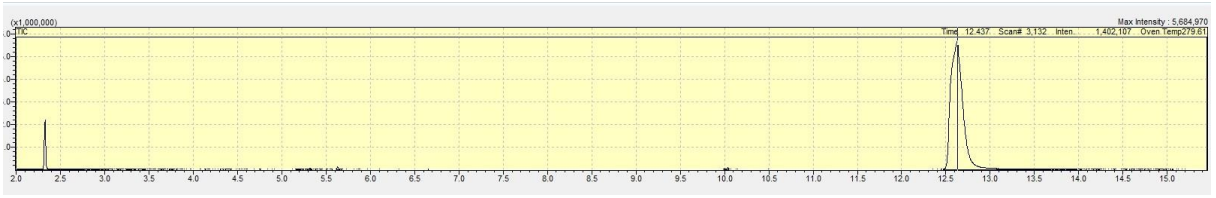
^{1}H NMR

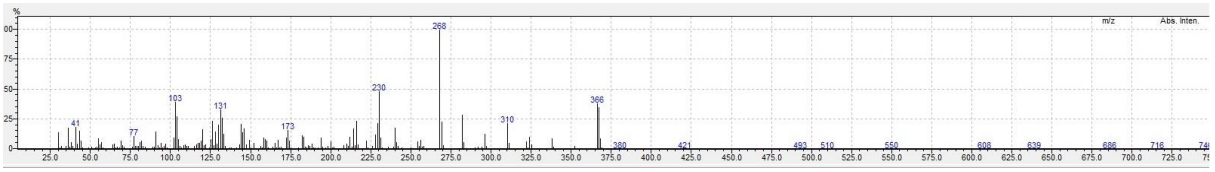


^{13}C NMR



GC-MS





HRMS

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 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
705 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 P: 1-1

SYNAPT G2-S#UEB205 MS300 06-Feb-2015
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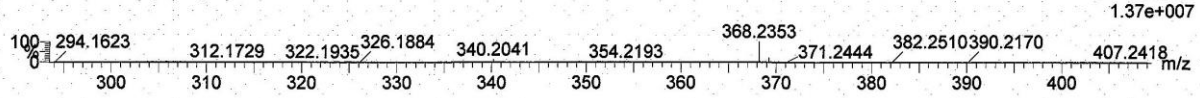
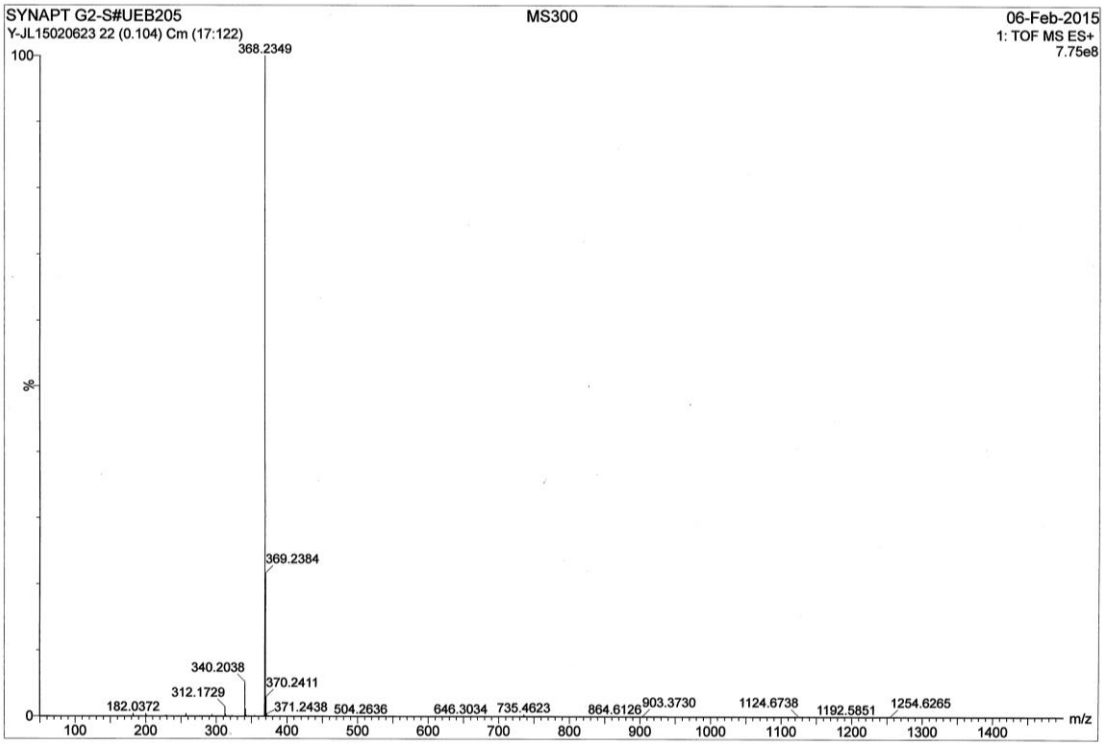
1.37e+007



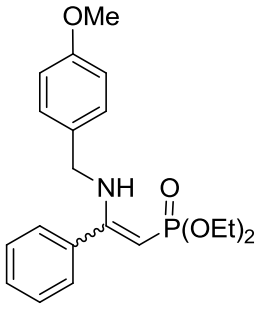
Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
368.2353	368.2355	-0.2	-0.5	4.5	1588.1	n/a	n/a	C20 H35 N O3 P



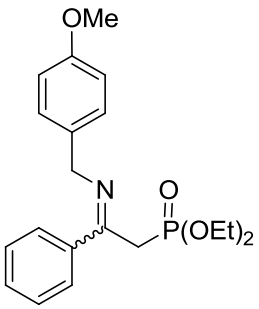
(*Z*/*E*)-diethyl (2-((4-methoxybenzyl)amino)-2-phenylvinyl)phosphonate 12c

(*E*/*Z*)-diethyl (2-((4-methoxybenzyl)imino)-2-phenylethyl)phosphonate 13c

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 91:9, respectively. Ratio of enamines (*Z*/*E*) **12c** equaled 83:17, respectively. Ratio of imines **13c** (*E*/*Z*) equaled 81:19, respectively.

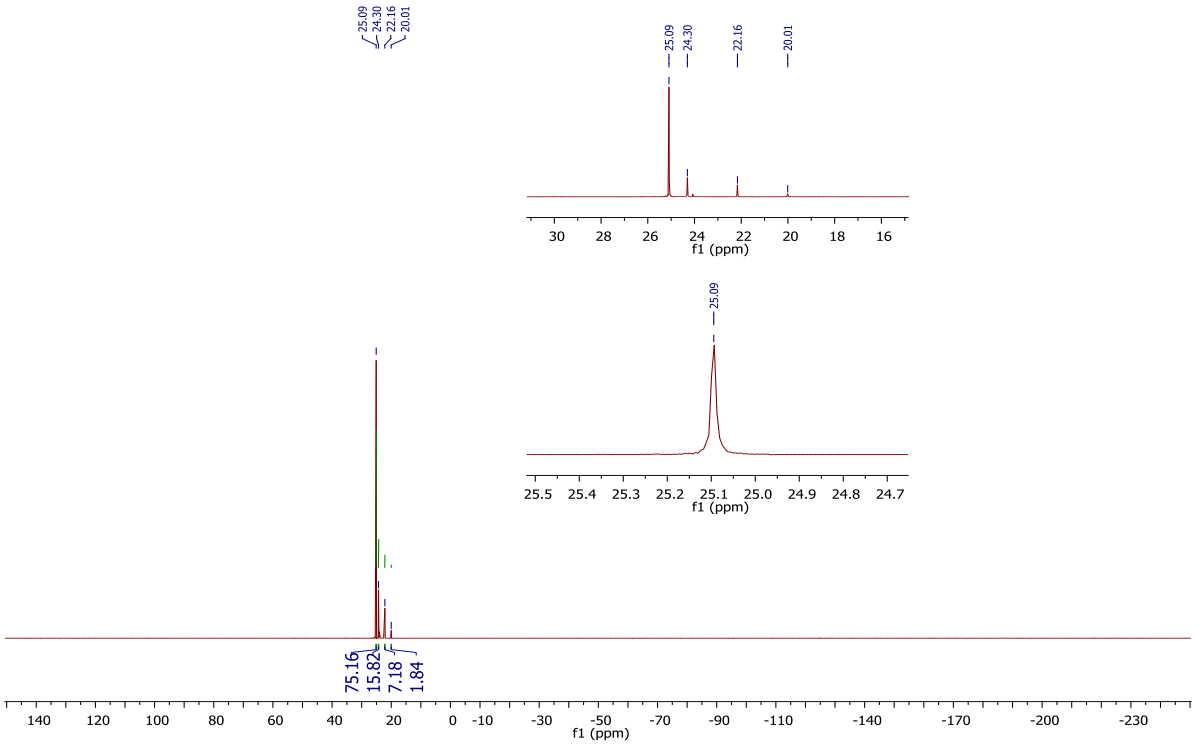


12c

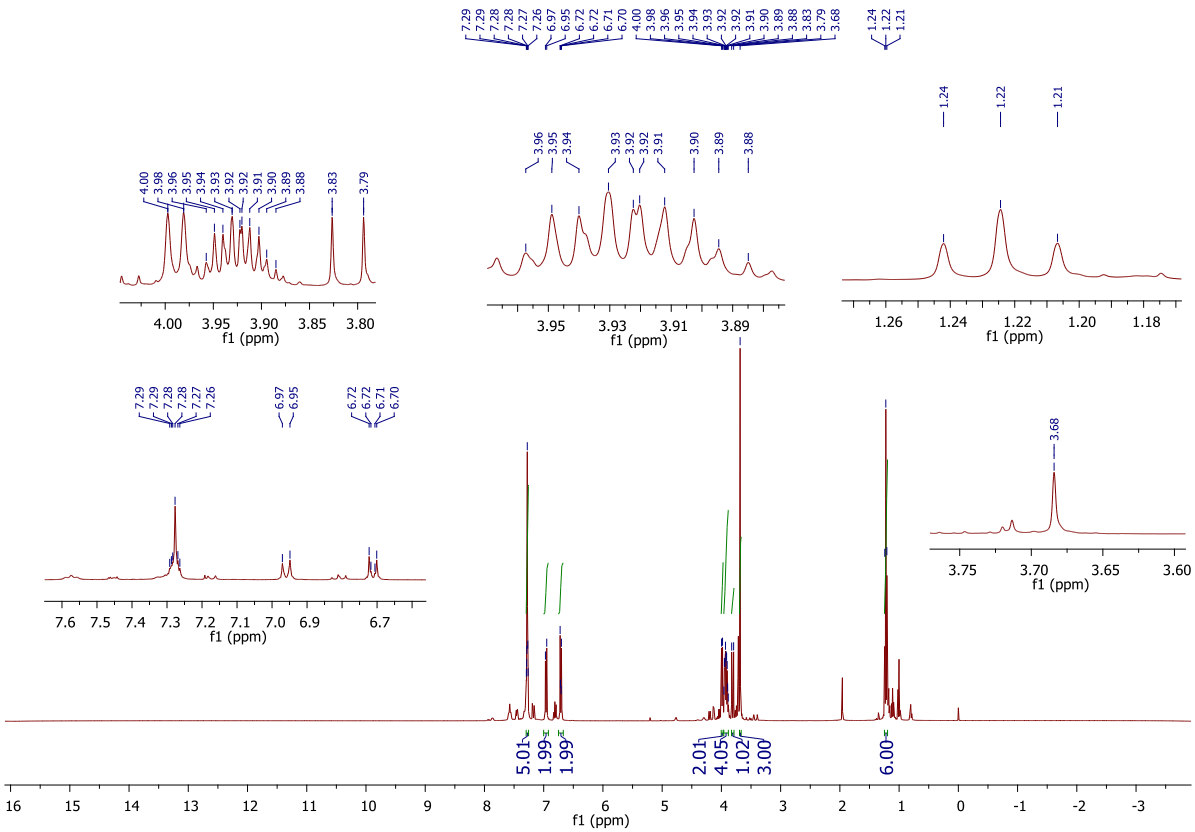


13c

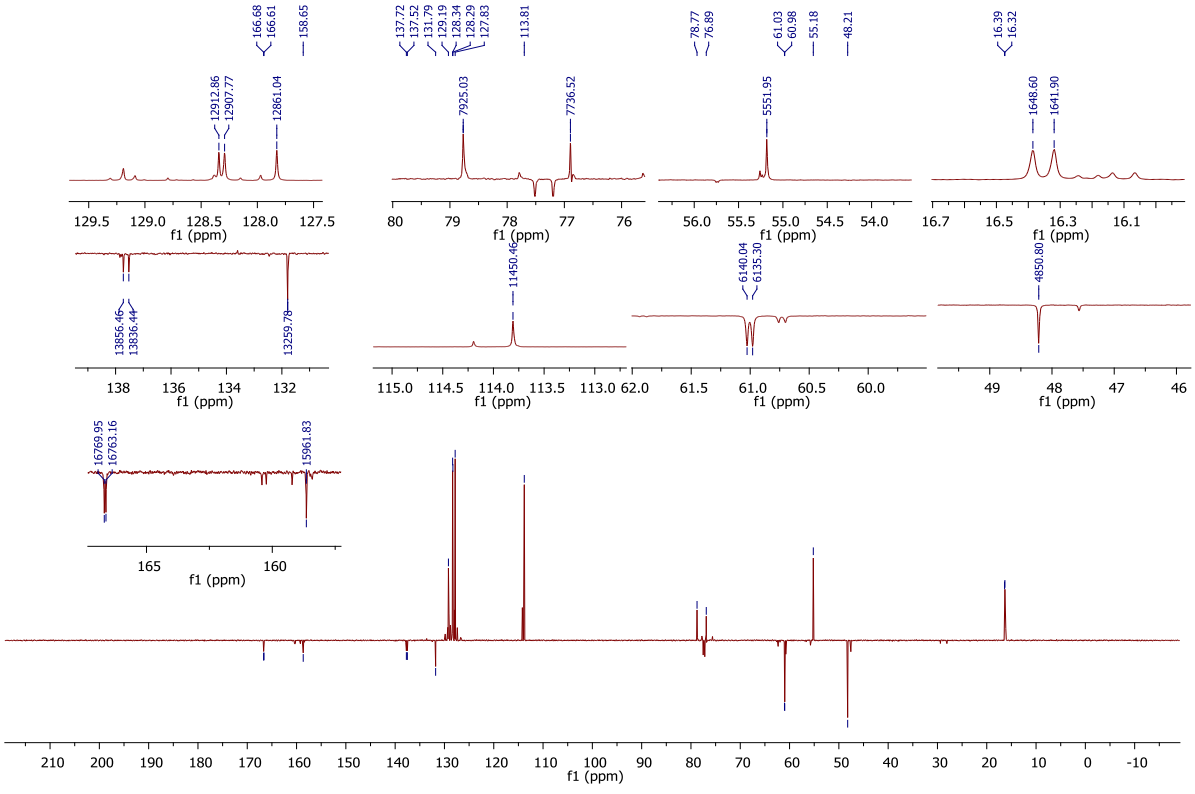
^{31}P NMR



^{1}H NMR



^{13}C NMR



HRMS

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 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
750 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 P: 1-1

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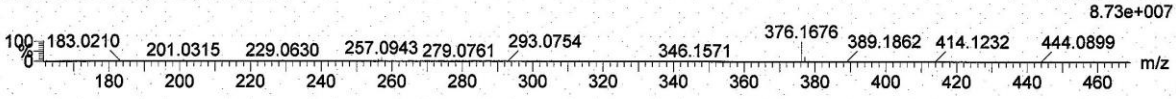
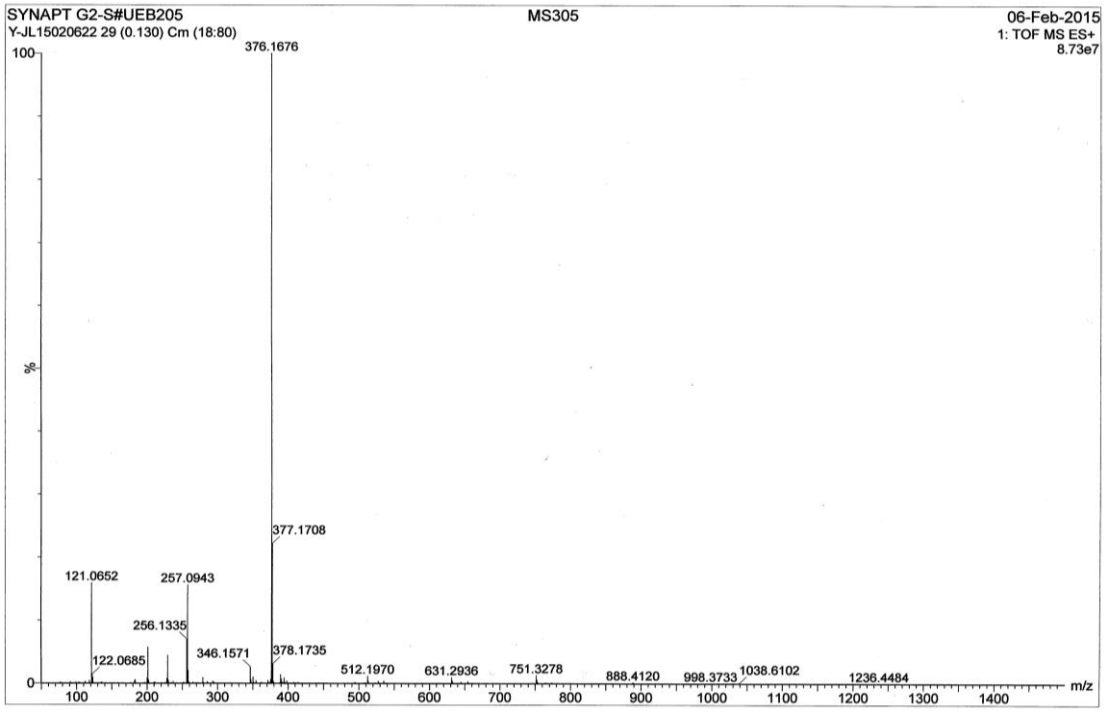
8.73e+007



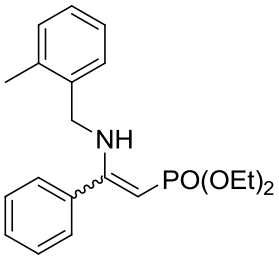
Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
376.1676	376.1678	-0.2	-0.5	8.5	3166.3	n/a	n/a	C20 H27 N O4 P



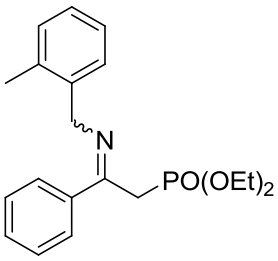
(Z/E)-diethyl (2-((2-methylbenzyl)amino)-2-phenylvinyl)phosphonate 12d

(*E/Z*)-diethyl (2-((2-methylbenzyl)imino)-2-phenylethyl)phosphonate 13d

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 91:9, respectively. Ratio of enamines (*Z*/*E*) **12d** equaled 84:16, respectively. Ratio of imines **13d** (*E/Z*) equaled 77:23, respectively.

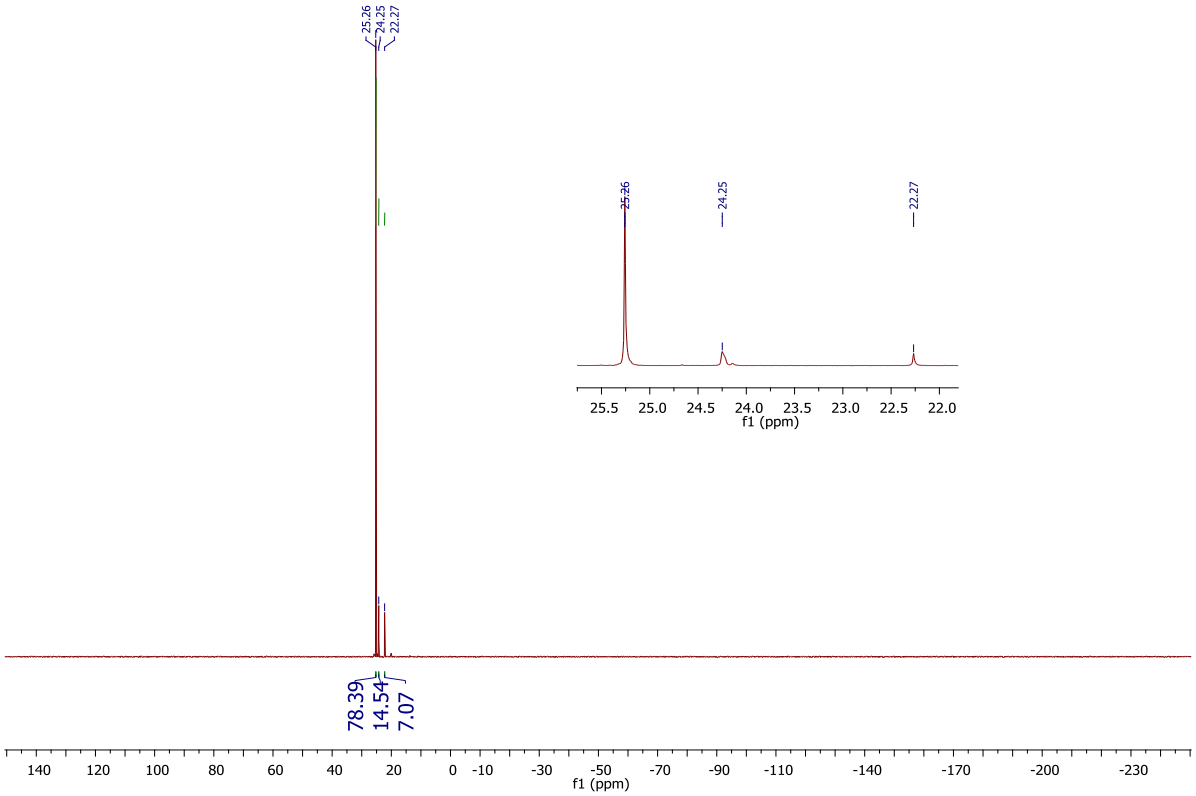


12d

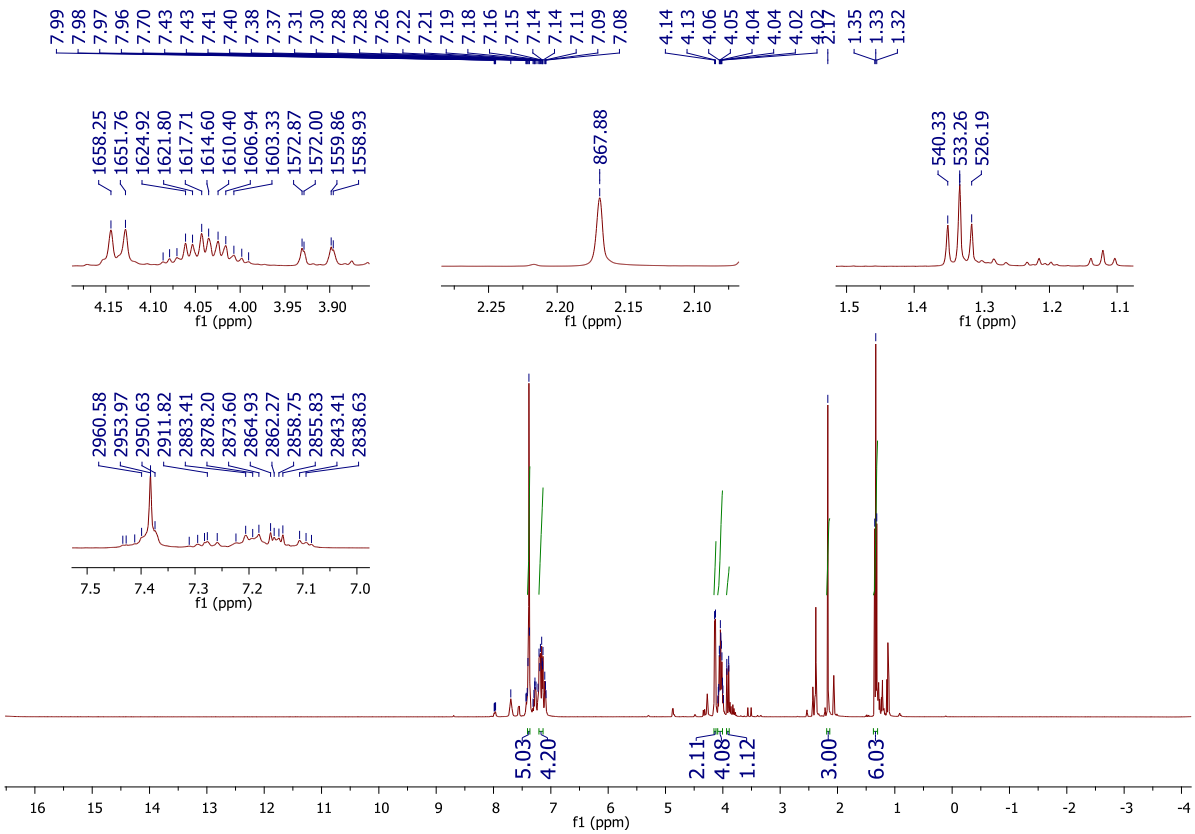


13d

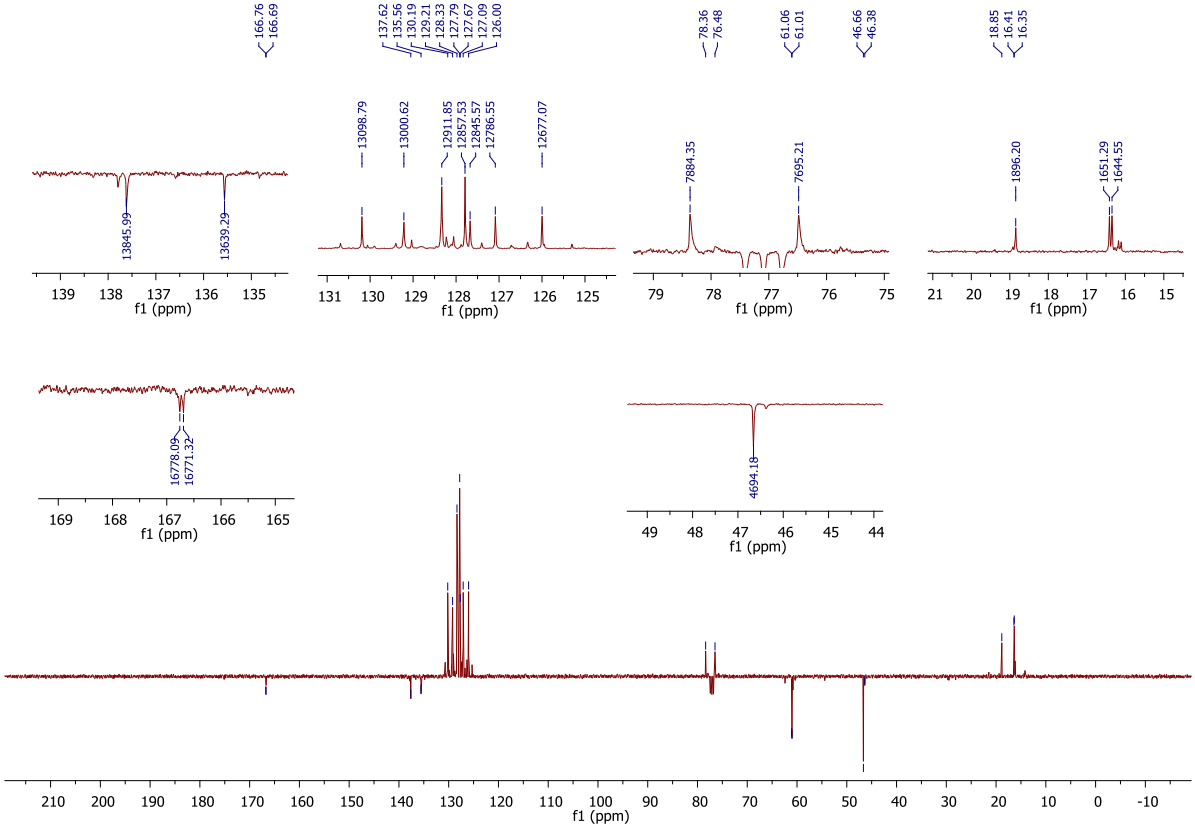
^{31}P NMR



^{1}H NMR



^{13}C NMR



HRMS

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 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
660 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 P: 1-1

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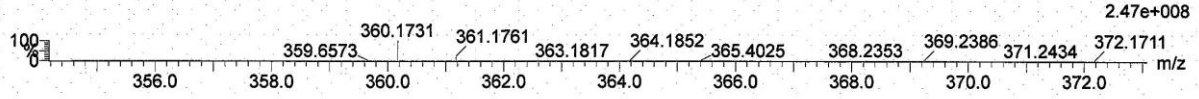
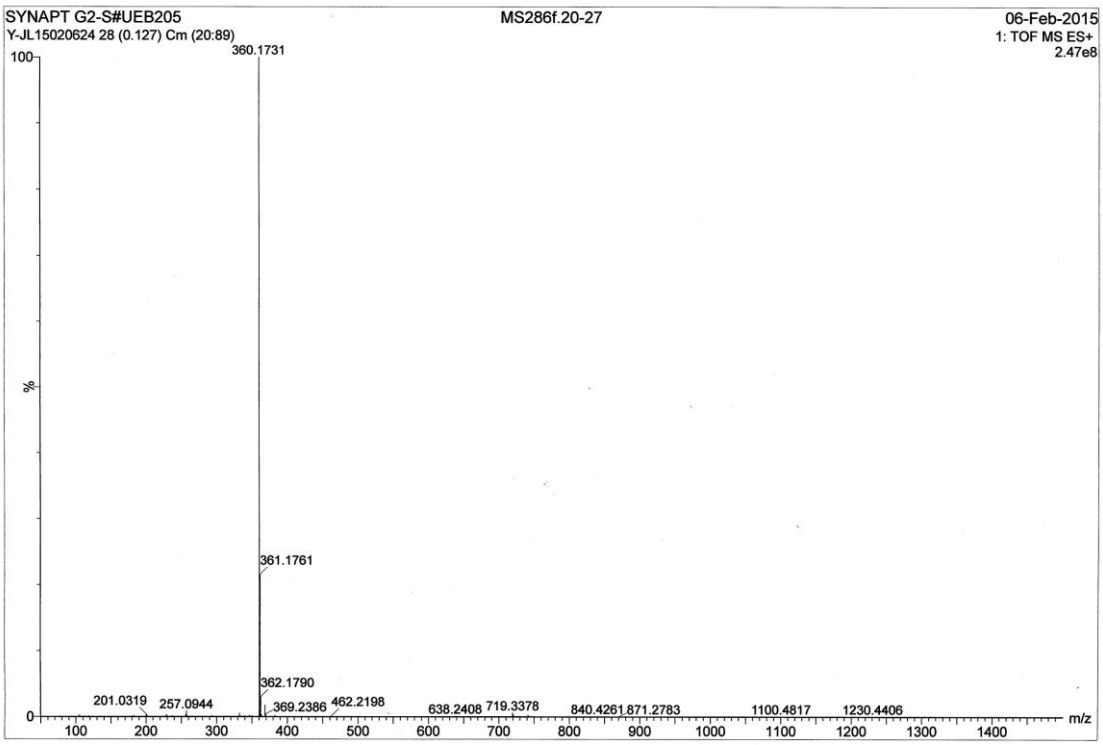
2.47e+008



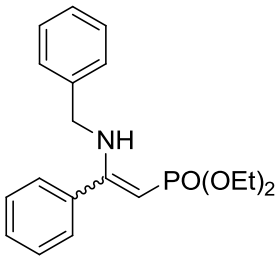
Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
360.1731	360.1729	0.2	0.6	8.5	3511.9	0.000	100.00	C20 H27 N O3 P
	360.1734	-0.3	-0.8	1.5	3529.5	17.627	0.00	C5 H23 N13 O4 P



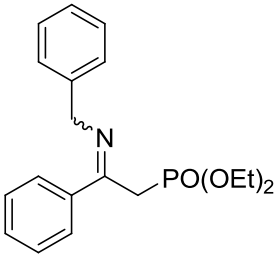
(*Z*/*E*)-diethyl (2-(benzylamino)-2-phenylvinyl)phosphonate 12e

(*E*/*Z*)-diethyl (2-(benzylimino)-2-phenylethyl)phosphonate 13e

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 91:9, respectively. Ratio of enamines (*Z*/E) **12e** equaled 84:16, respectively. Ratio of imines **13e** (*E*/*Z*) equaled 95:5, respectively.

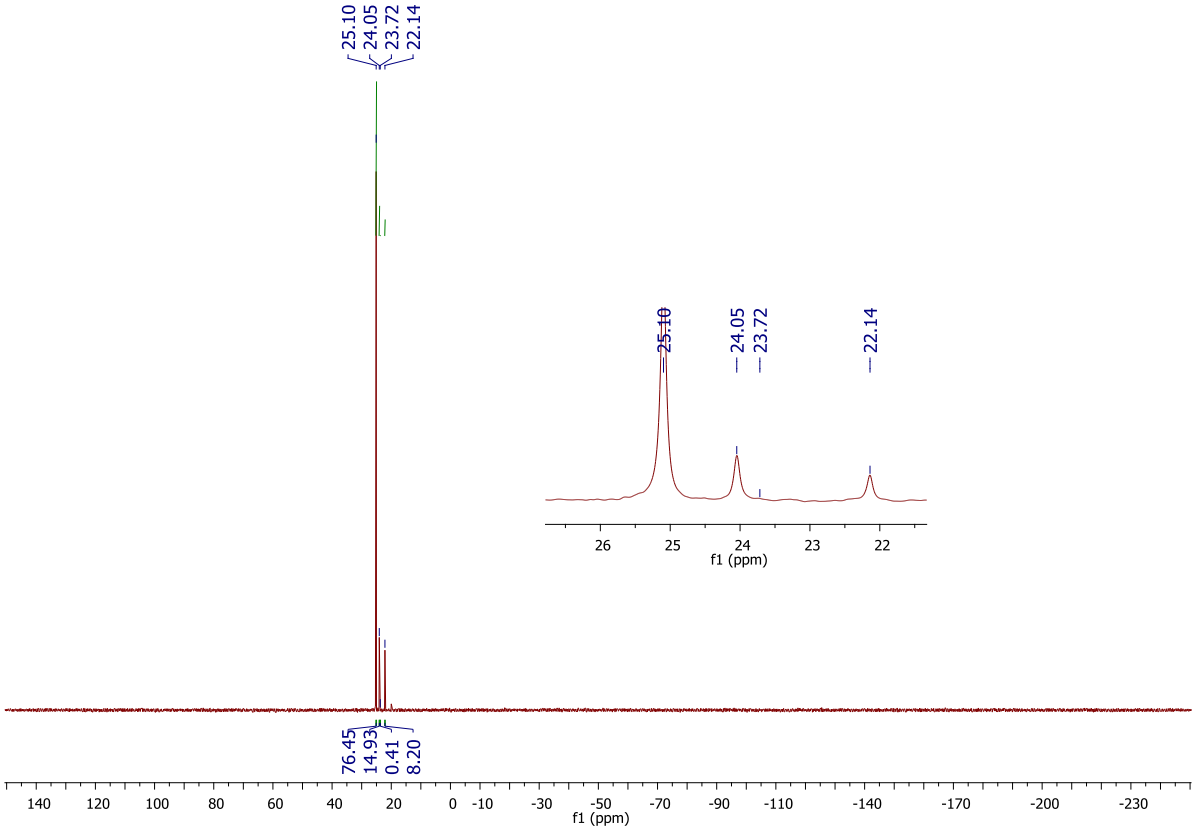


12e



13e

^{31}P NMR



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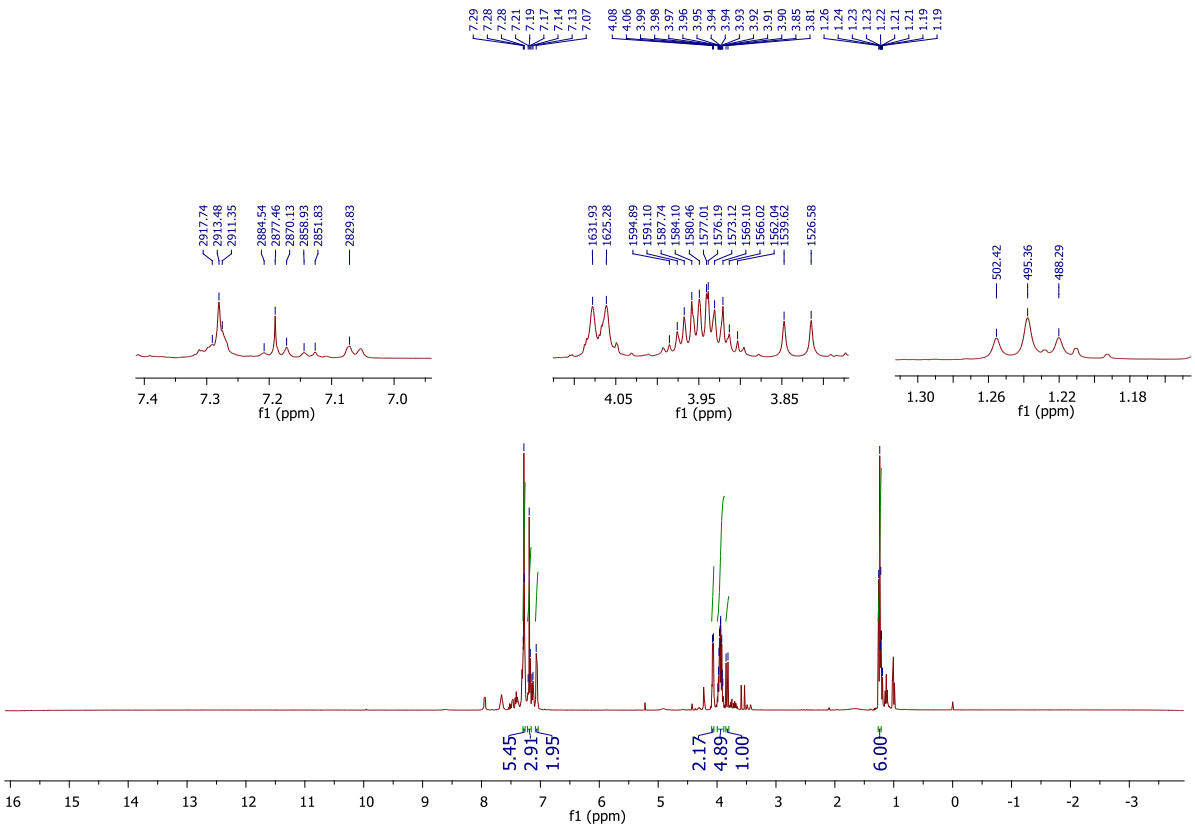
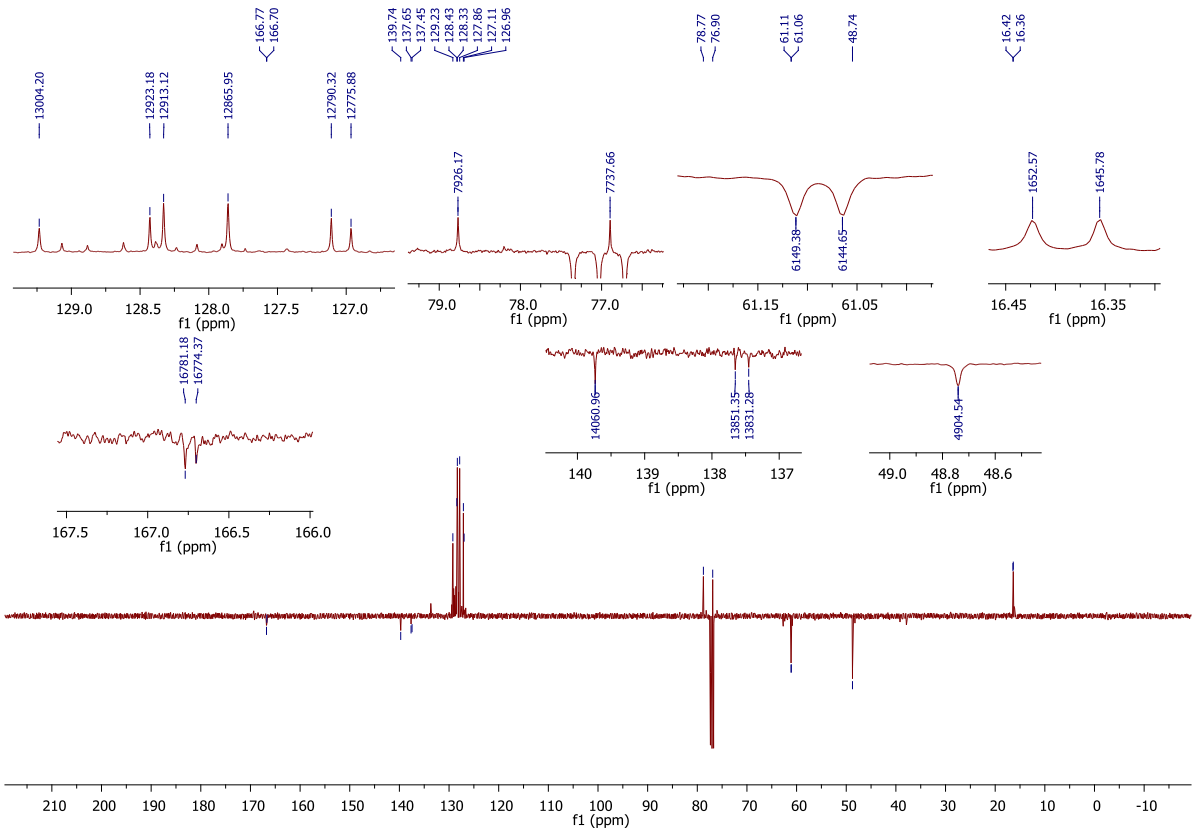


^{13}C NMR



GC-MS

Peak#	Ret.Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H
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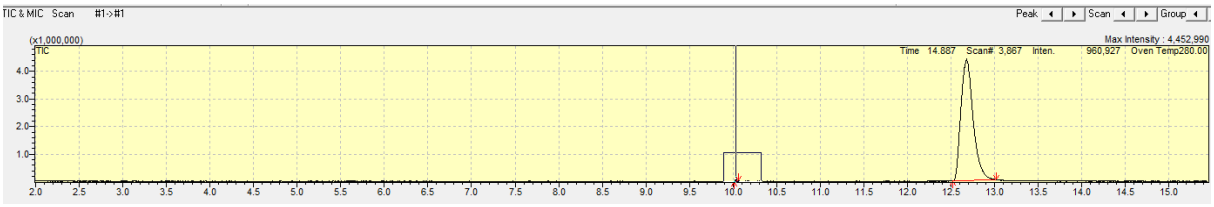
2	12.680	12.523	13.020	TIC	42836085	99.70	4383491	97.21	9.77

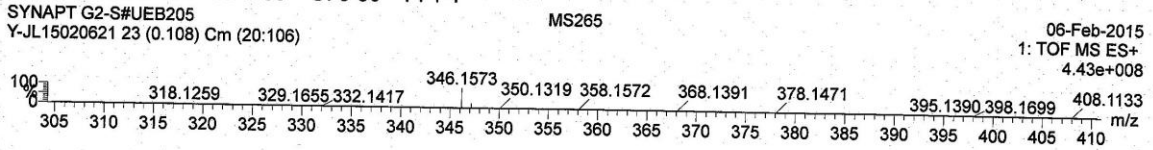


HRMS

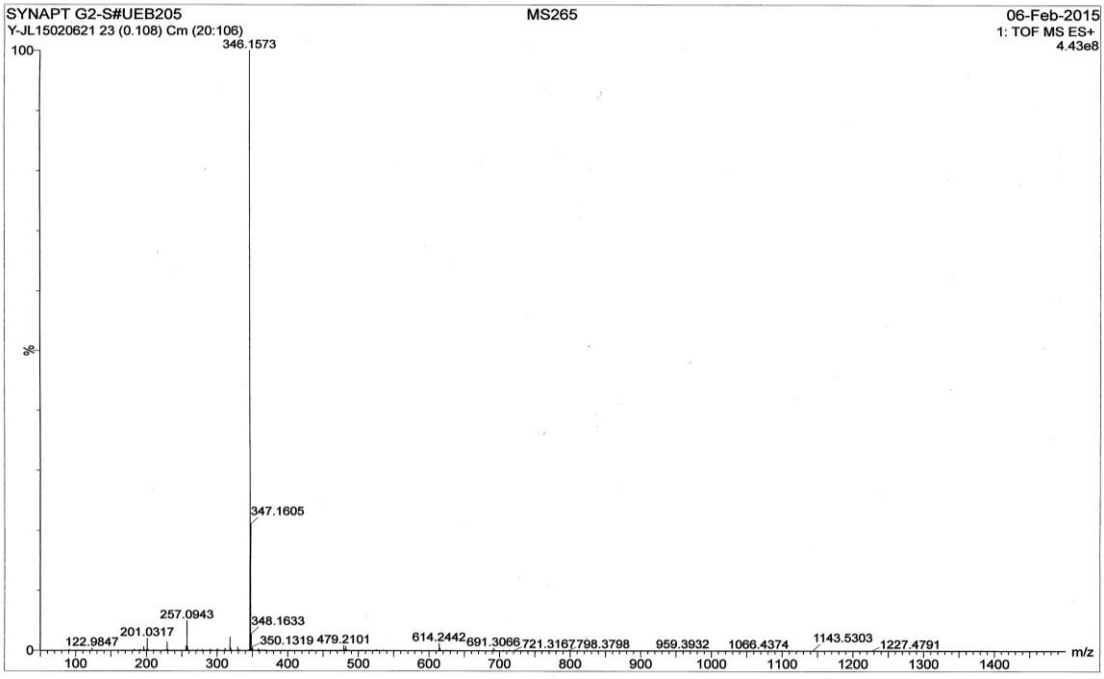
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 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
589 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 P: 1-1
SYNAPT G2-S#UEB205
Y-JL15020621 23 (0.108) Cm (20:106)



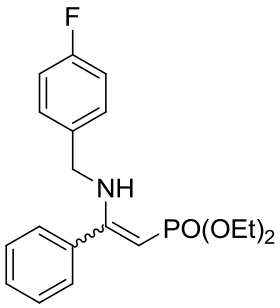
Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
346.1573	346.1572	0.1	0.3	8.5	3741.2	n/a	n/a	C19 H25 N O3 P



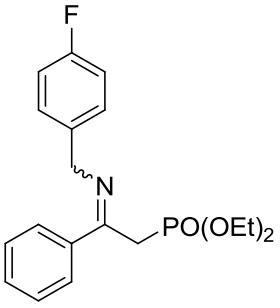
(*Z*/*E*)-diethyl (2-((4-fluorobenzyl)amino)-2-phenylvinyl)phosphonate 12f

(*E*/*Z*)-diethyl (2-((4-fluorobenzyl)imino)-2-phenylethyl)phosphonate 13f

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 90:10, respectively. Ratio of enamines (*Z*/*E*) **12f** equaled 86:14, respectively. Ratio of imines **13f** (*E*/*Z*) equaled 95:5, respectively.

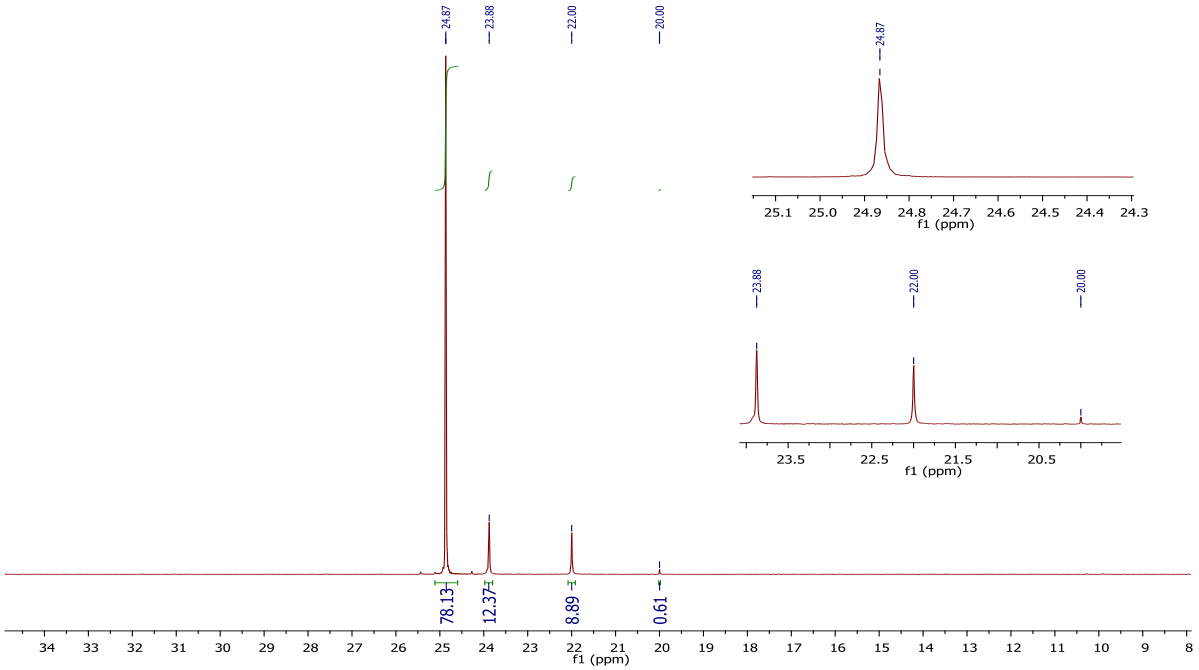


12f

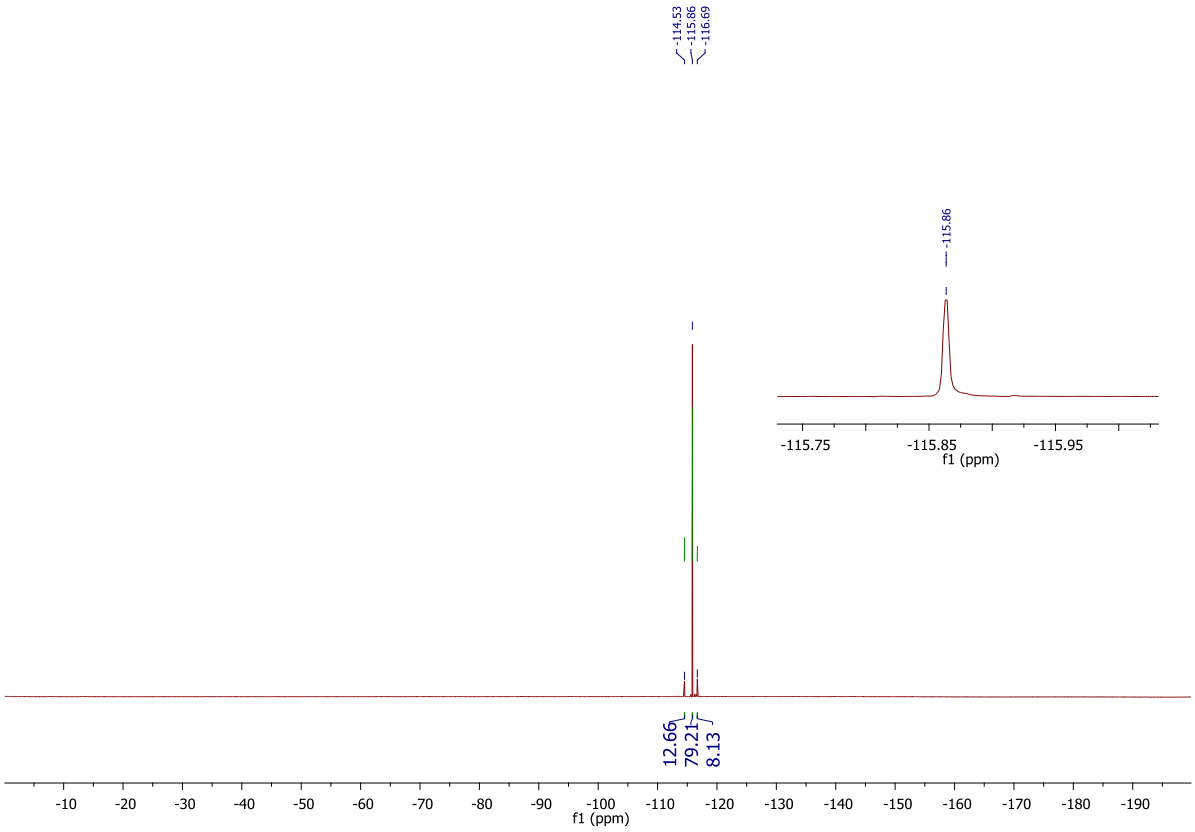


13f

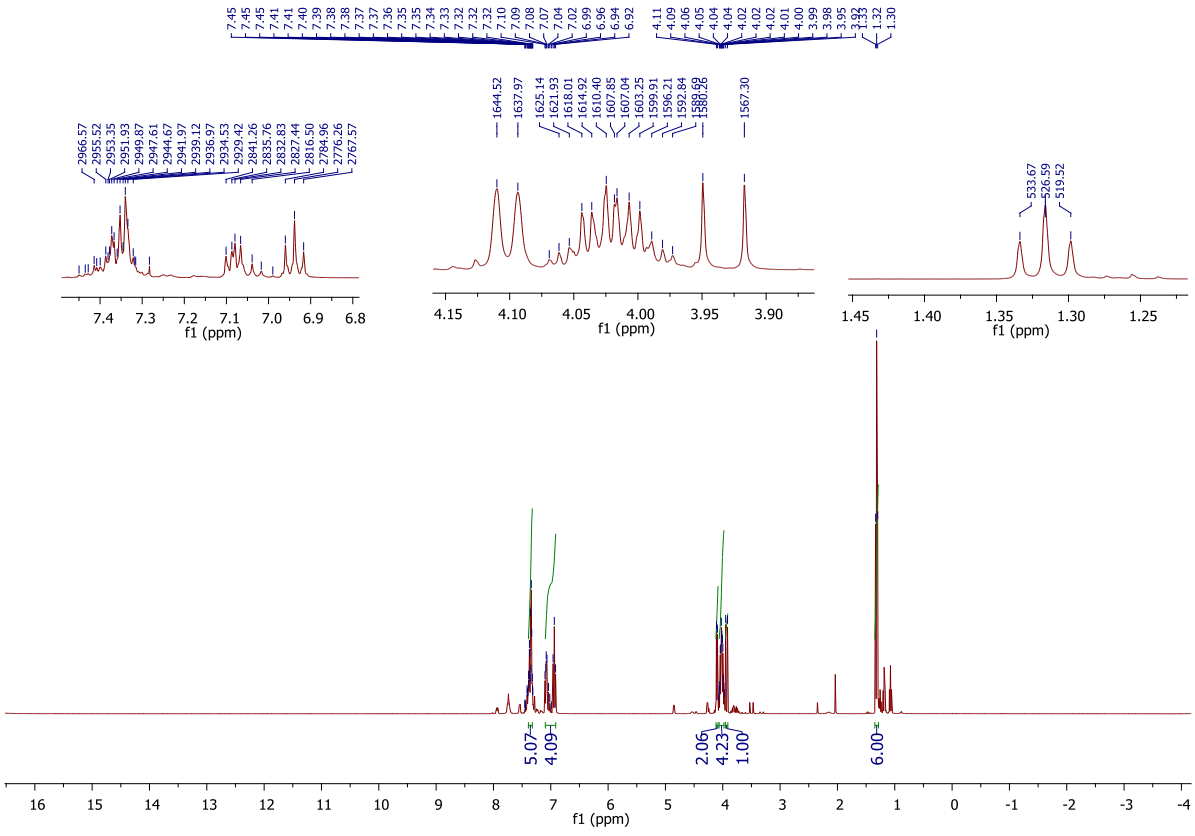
^{31}P NMR



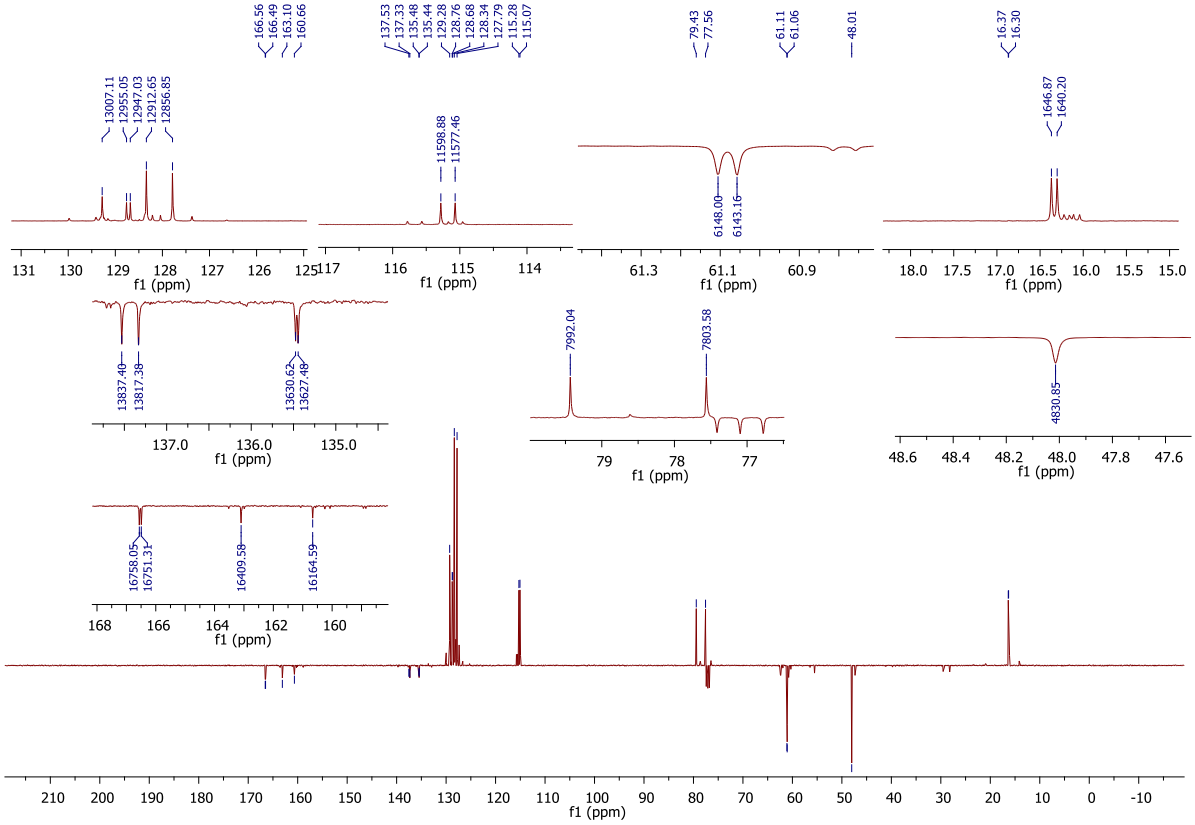
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR


166.56
166.49
163.10
160.66
137.53
137.33
135.48
135.44
129.28
128.76
128.68
128.34
127.79
115.28
115.07
79.43
77.56
61.11
61.06
48.01
16.37
16.30
13007.11
12955.05
12947.03
12912.65
12856.85
11598.88
11577.46
6148.00
6143.16
1646.87
1640.20
f1 (ppm)
13837.49
13817.38
13630.62
13627.48
7992.04
7803.58
4830.85
16758.05
16751.31
16409.58
16164.59

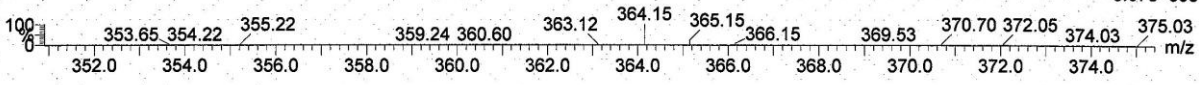
HRMS

Elemental Composition Report **Page 1**

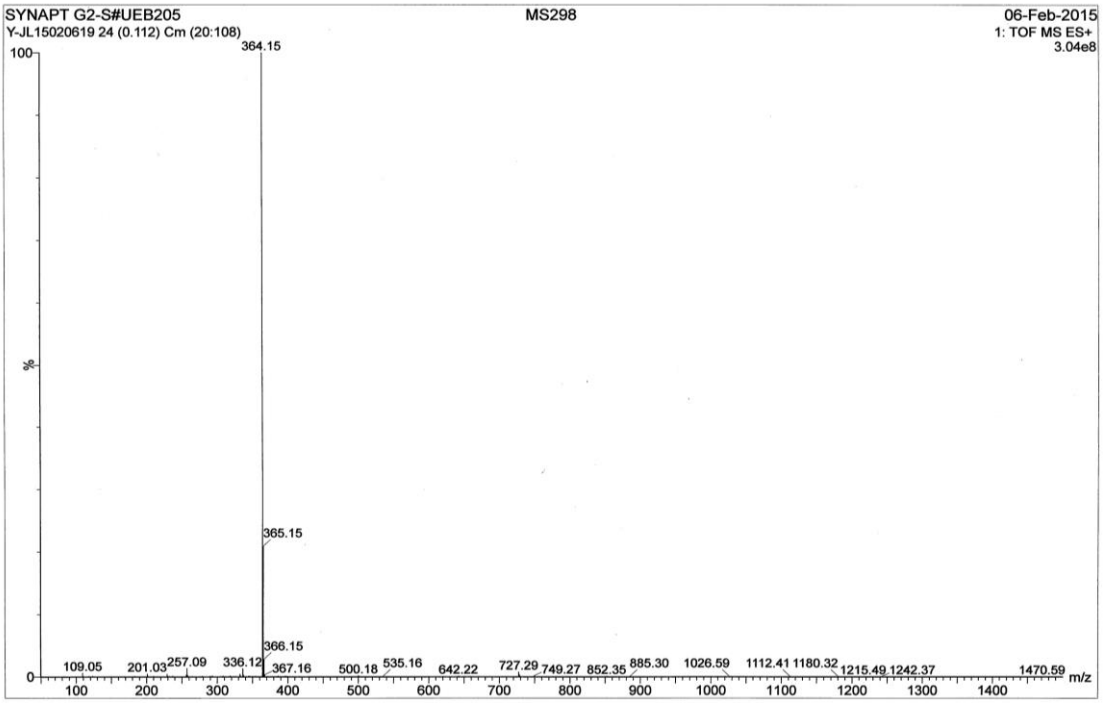
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1422 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

SYNAPT G2-S#UEB205
Y-JL15020619 52 (0.223)
MS298
06-Feb-2015
1: TOF MS ES+
3.37e+006



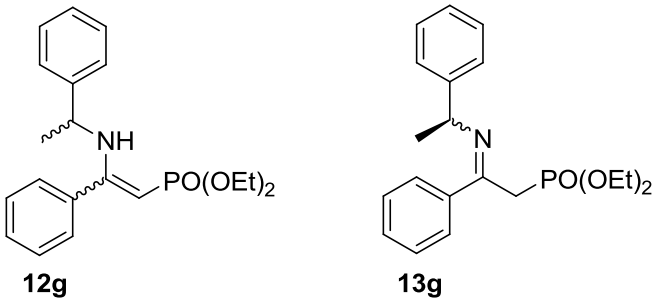
Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
364.1477	364.1478	-0.1	-0.3	8.5	1124.2	0.000	100.00	C19 H24 N O3 F P
	364.1474	0.3	0.8	1.5	1136.1	11.921	0.00	C9 H22 N7 O3 F3 P



(*Z*/*E*)-(*S*)-diethyl (2-phenyl-2-((1-phenylethyl)amino)vinyl)phosphonate 12g

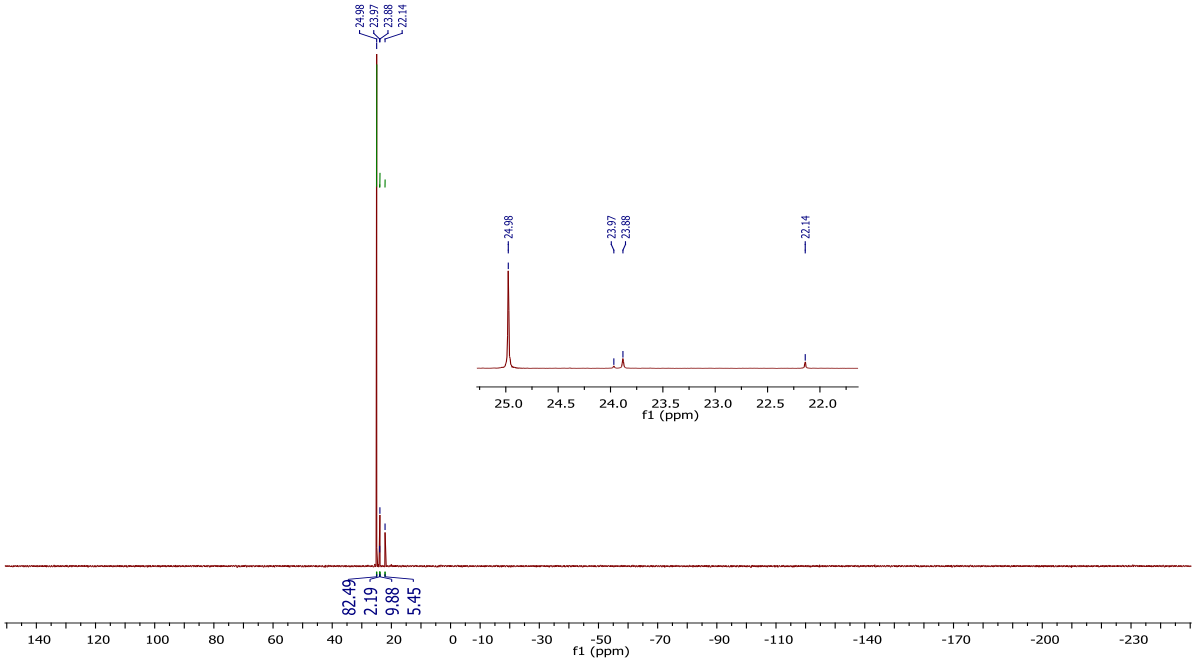
(*E*/*Z*)-(*S*)-diethyl (2-phenyl-2-((1-phenylethyl)imino)ethyl) phosphonate 13g

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 92:8, respectively. Ratio of enamines (*Z*/*E*) **12g** equaled 90:10, respectively. Ratio of imines **13g** (*E*/*Z*) equaled 70:30, respectively.

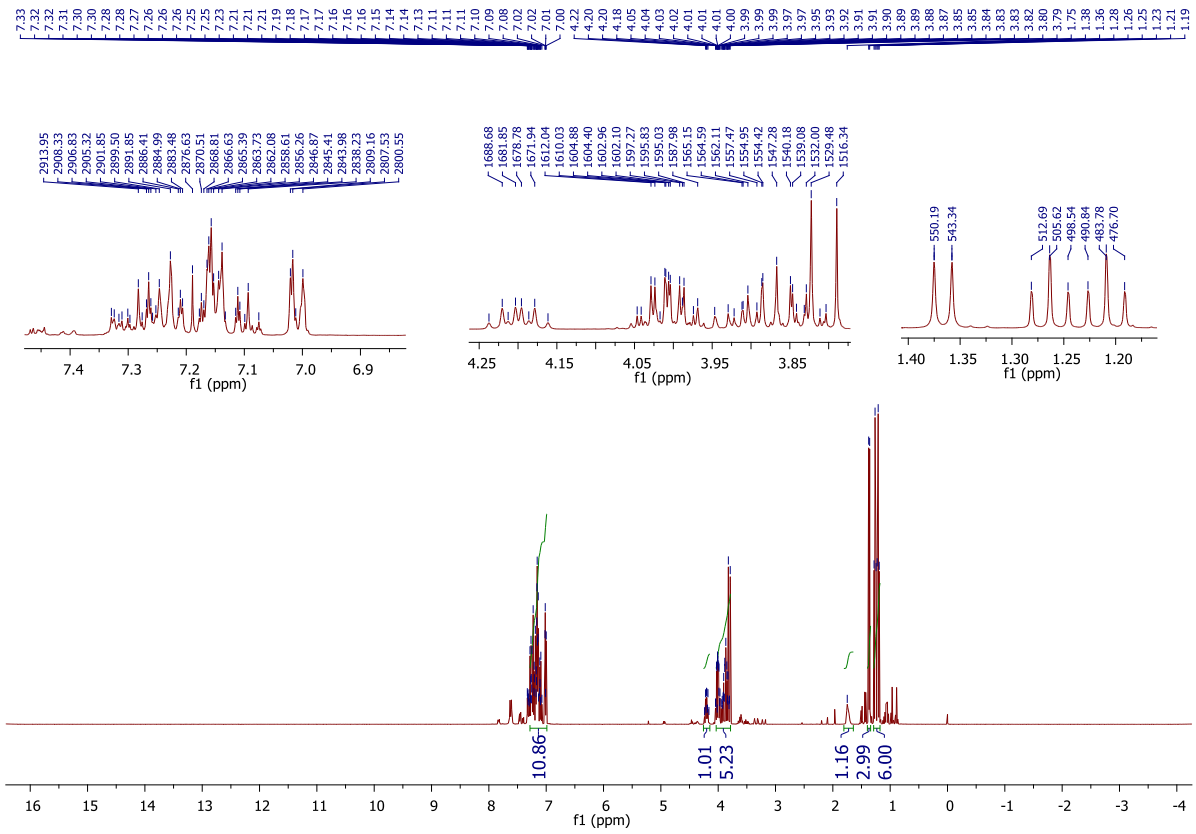


12g **13g**

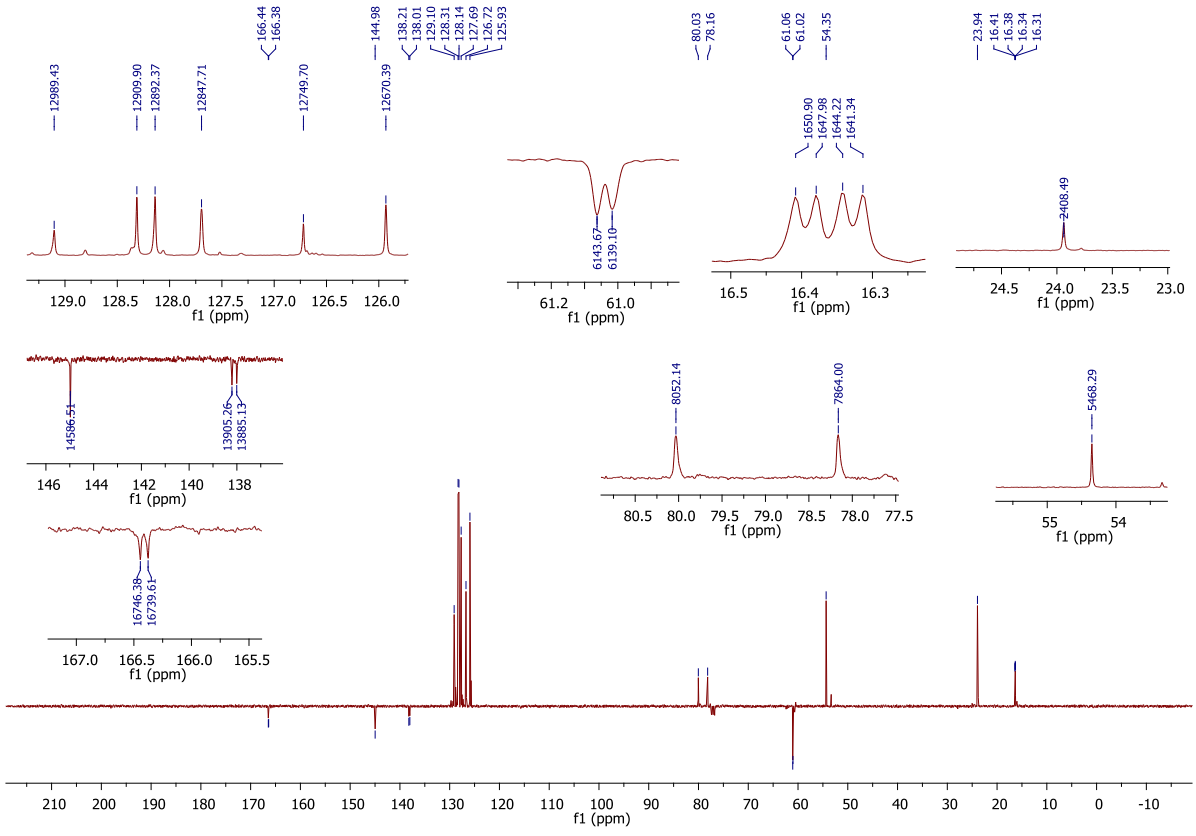
^{31}P NMR



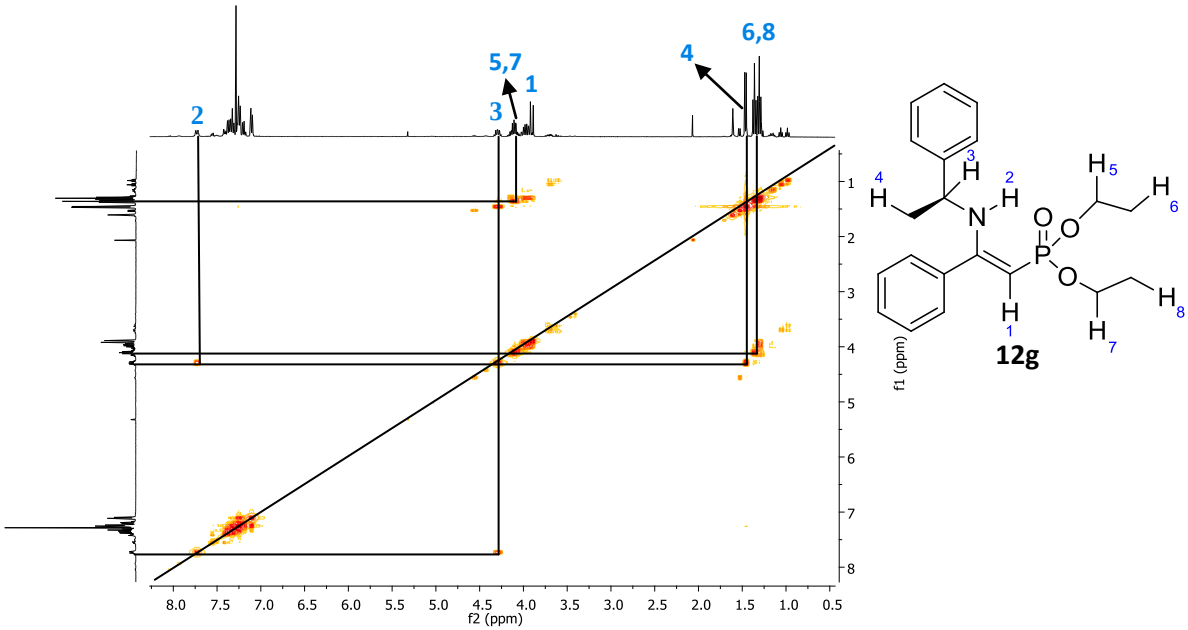
^{1}H NMR



^{13}C NMR



COSY ^{1}H-^{1}H



HRMS

Elemental Composition Report **Page 1**

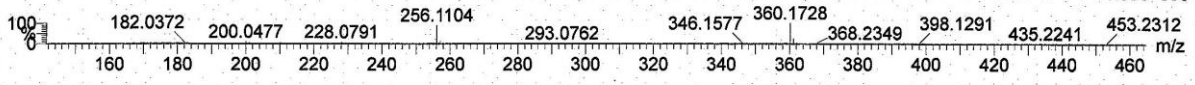
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
660 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 P: 1-1

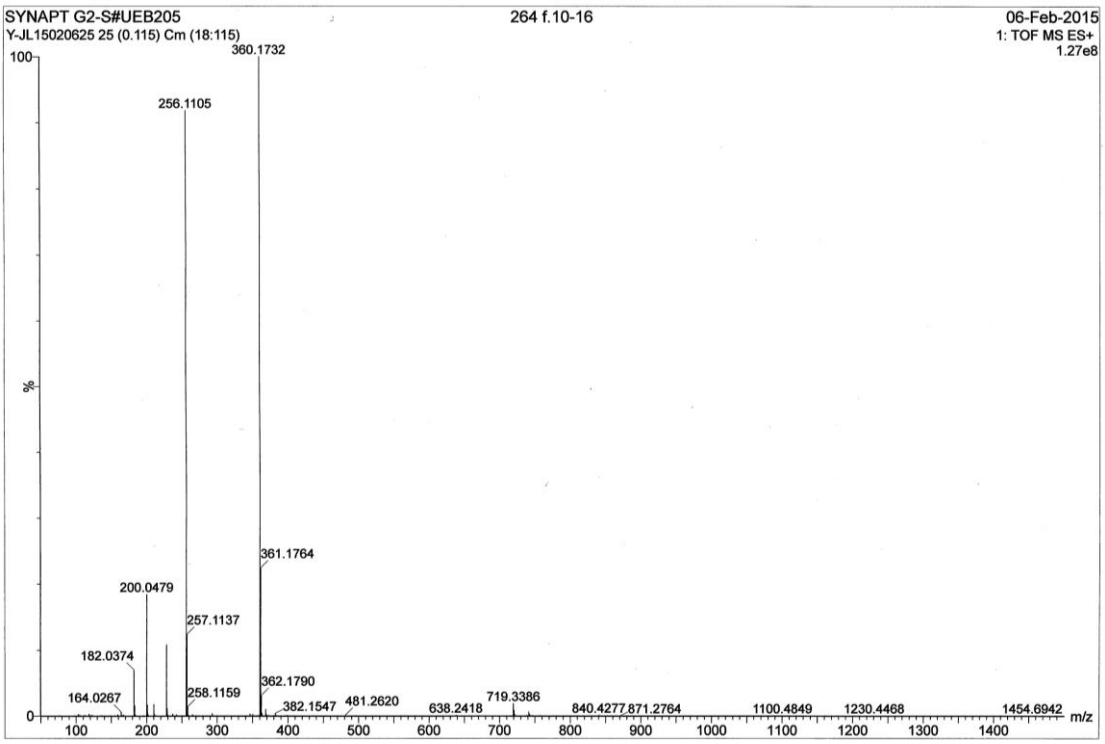
SYNAPT G2-S#UEB205
Y-JL15020625 48 (0.208)

264 f.10-16

06-Feb-2015
1: TOF MS ES+
1.59e+006



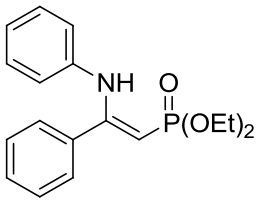
Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
360.1728	360.1729	-0.1	-0.3	8.5	915.0	n/a	n/a	C20 H27 N O3 P



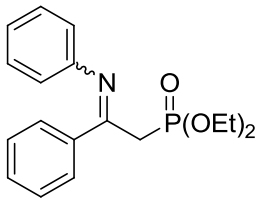
(*Z*)-diethyl (2-phenyl-2-(phenylamino)vinyl)phosphonate 12h

(*E/Z*)-diethyl (2-phenyl-2-(phenylimino)ethyl)phosphonate 13h

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 67:33 respectively. Only (*Z*)-enamine was formed. Ratio of imines **13h** (*E/Z*) equaled 91:9, respectively.

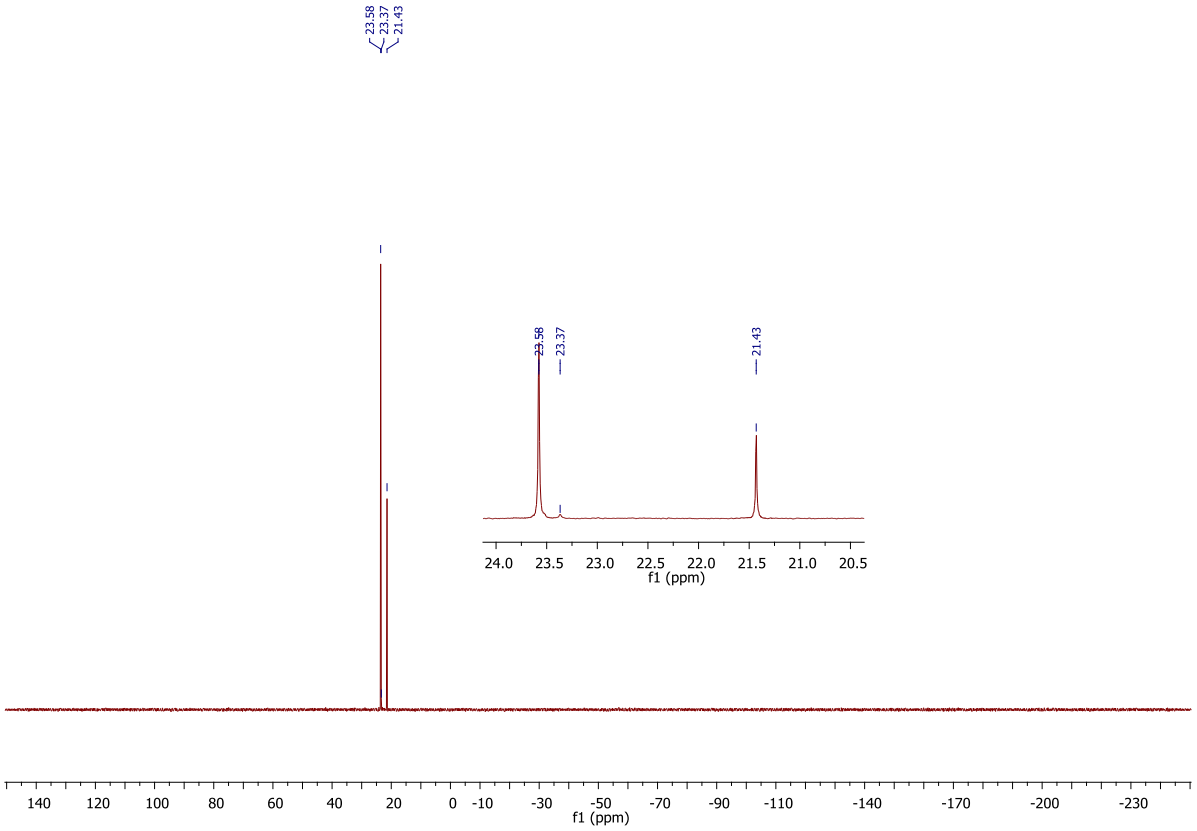


12h

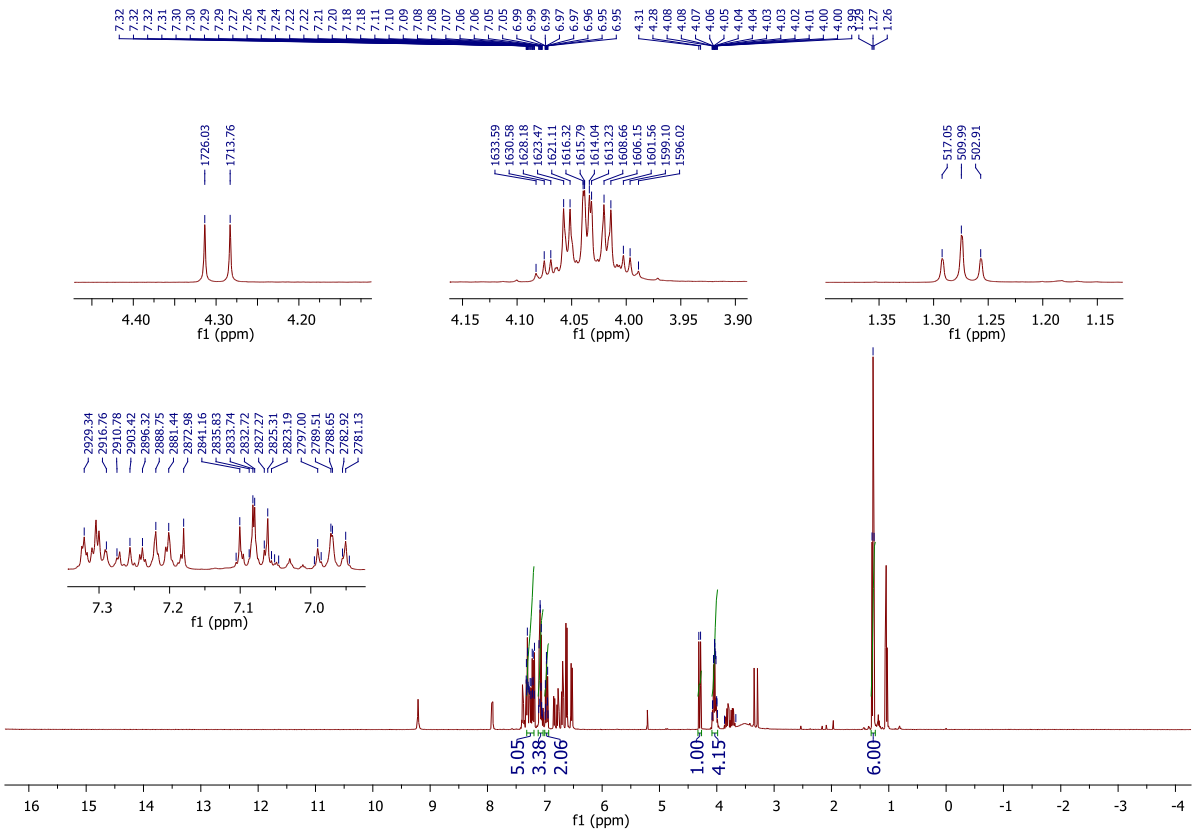


13h

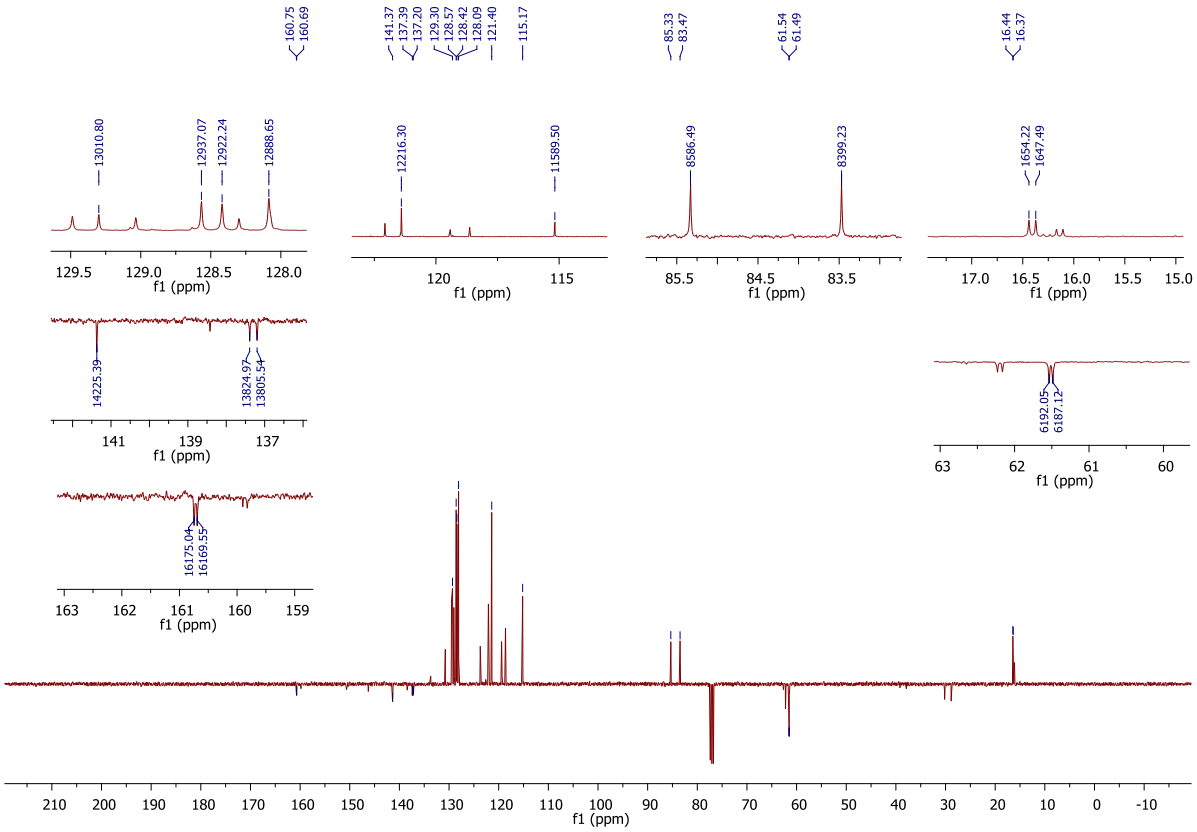
^{31}P NMR



^{1}H NMR



^{13}C NMR



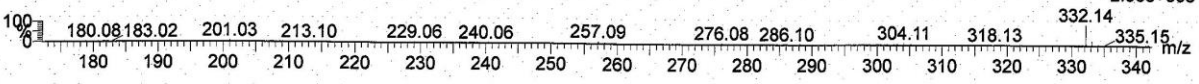
HRMS

Elemental Composition Report **Page 1**

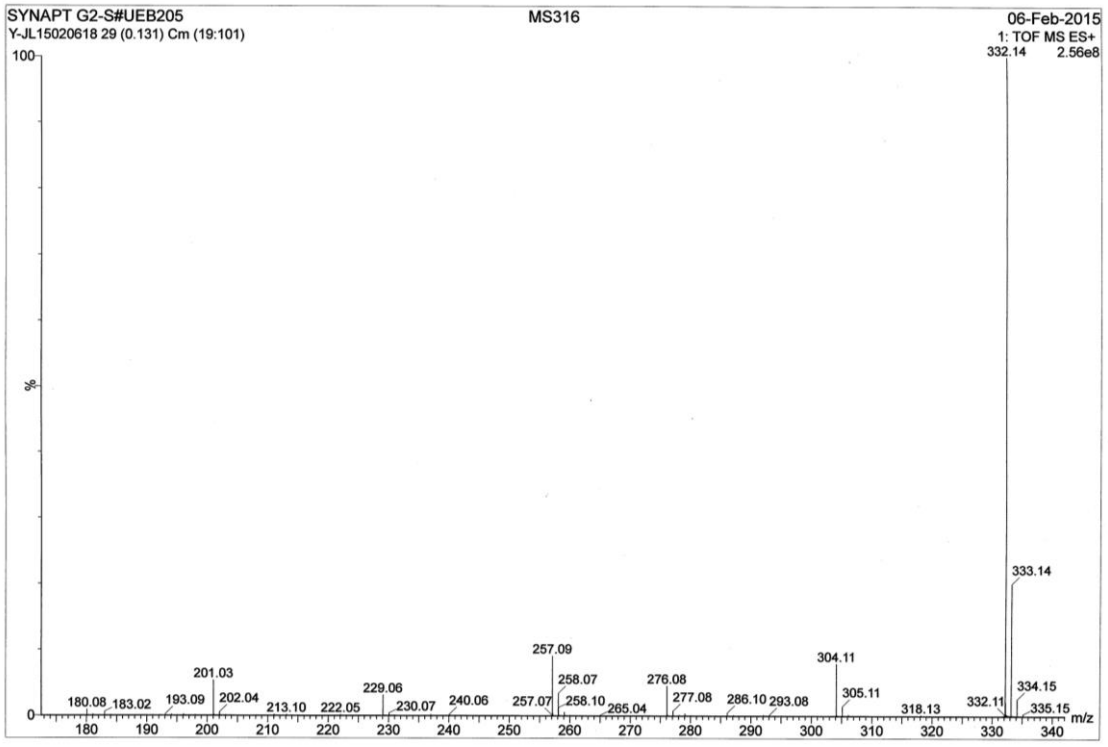
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
520 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 P: 1-1

SYNAPT G2-S#UEB205
Y-JL15020618 29 (0.131) Cm (19:101)
MS316
06-Feb-2015
1: TOF MS ES+
2.56e+008



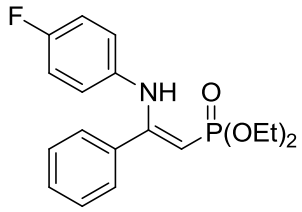
Minimum:		5.0	1.0	-1.5				
Maximum:				50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
332.1416	332.1416	0.0	0.0	8.5	3500.4	n/a	n/a	C18 H23 N O3 P



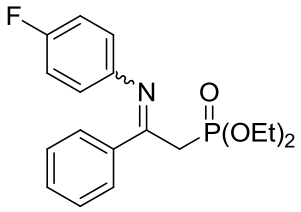
(*Z*/*E*)-diethyl (2-((4-fluorophenyl)amino)-2-phenylvinyl)phosphonate 12i

(*Z*/*E*)-diethyl (2-((4-fluorophenyl)imino)-2-phenylethyl)phosphonate 13i

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 63:37, respectively. Ratio of enamines (*Z*/*E*) **12i** equaled 99:1, respectively. Ratio of imines **13i** (*E*/*Z*) equaled 92:8, respectively.

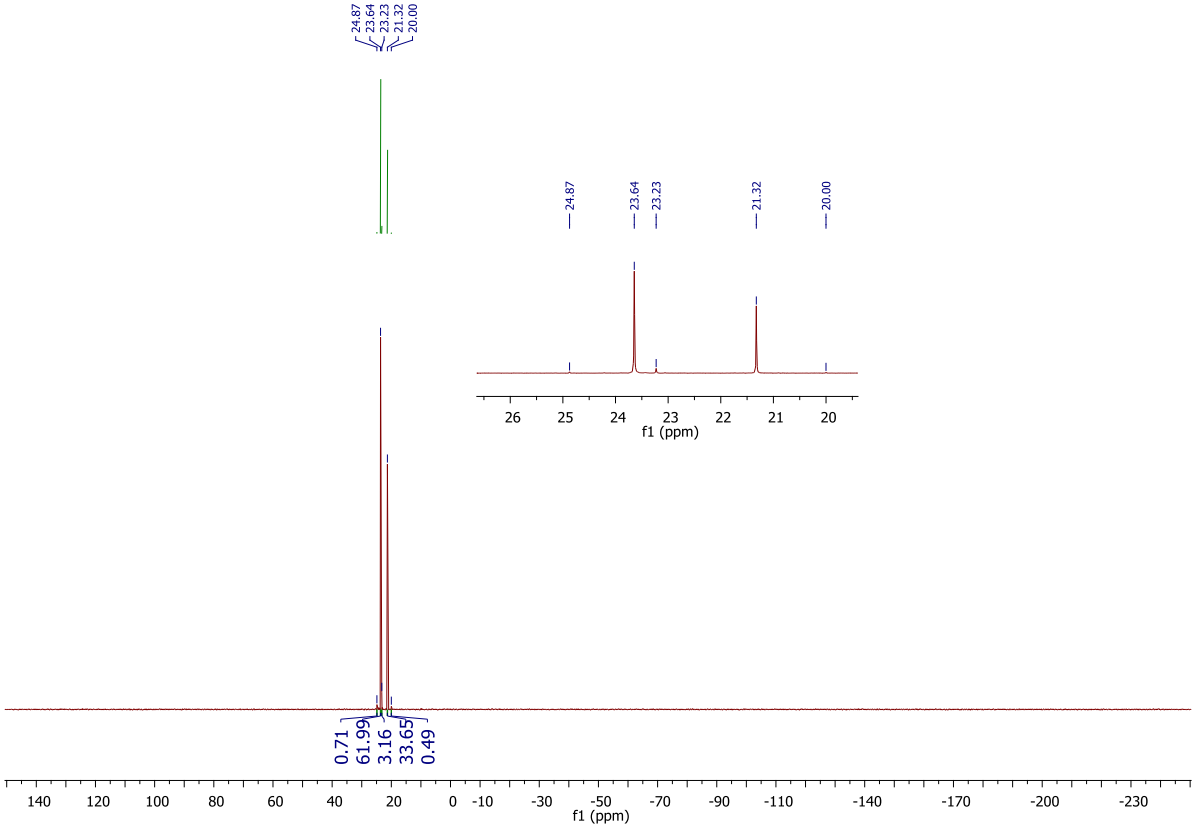


12i

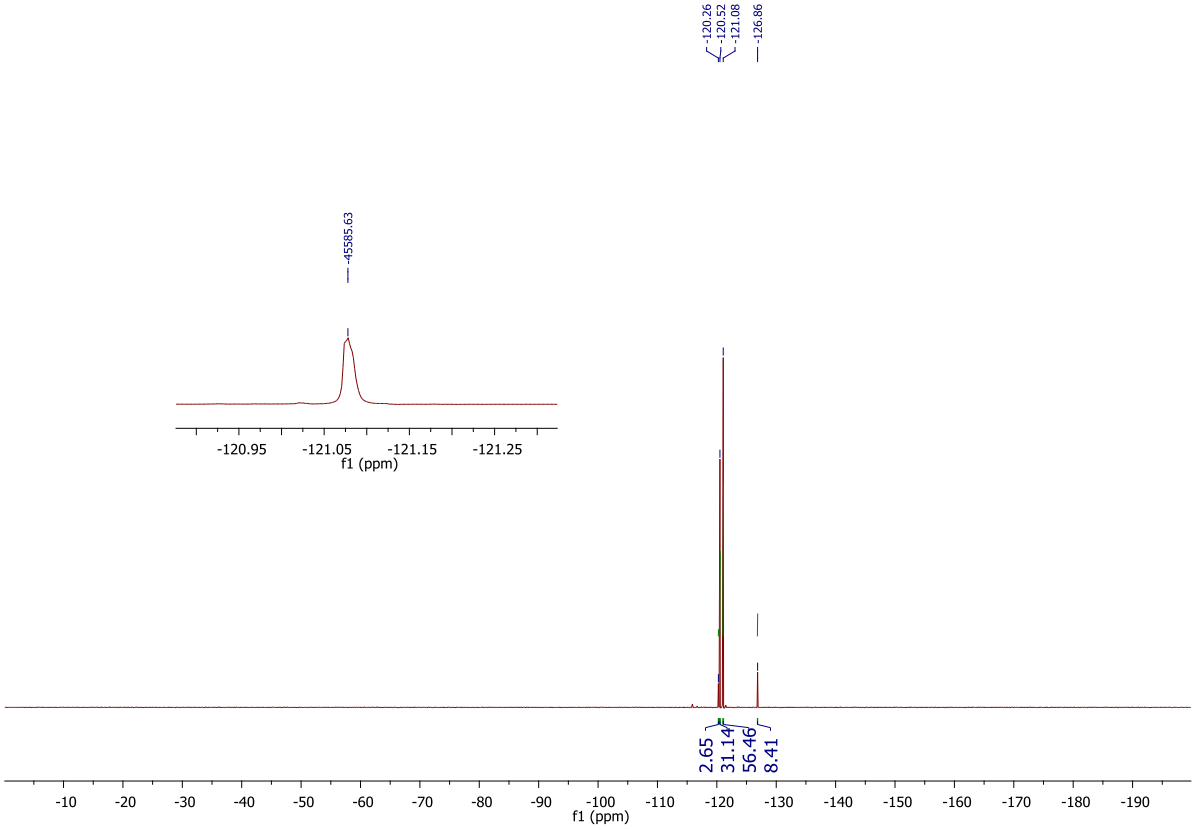


13i

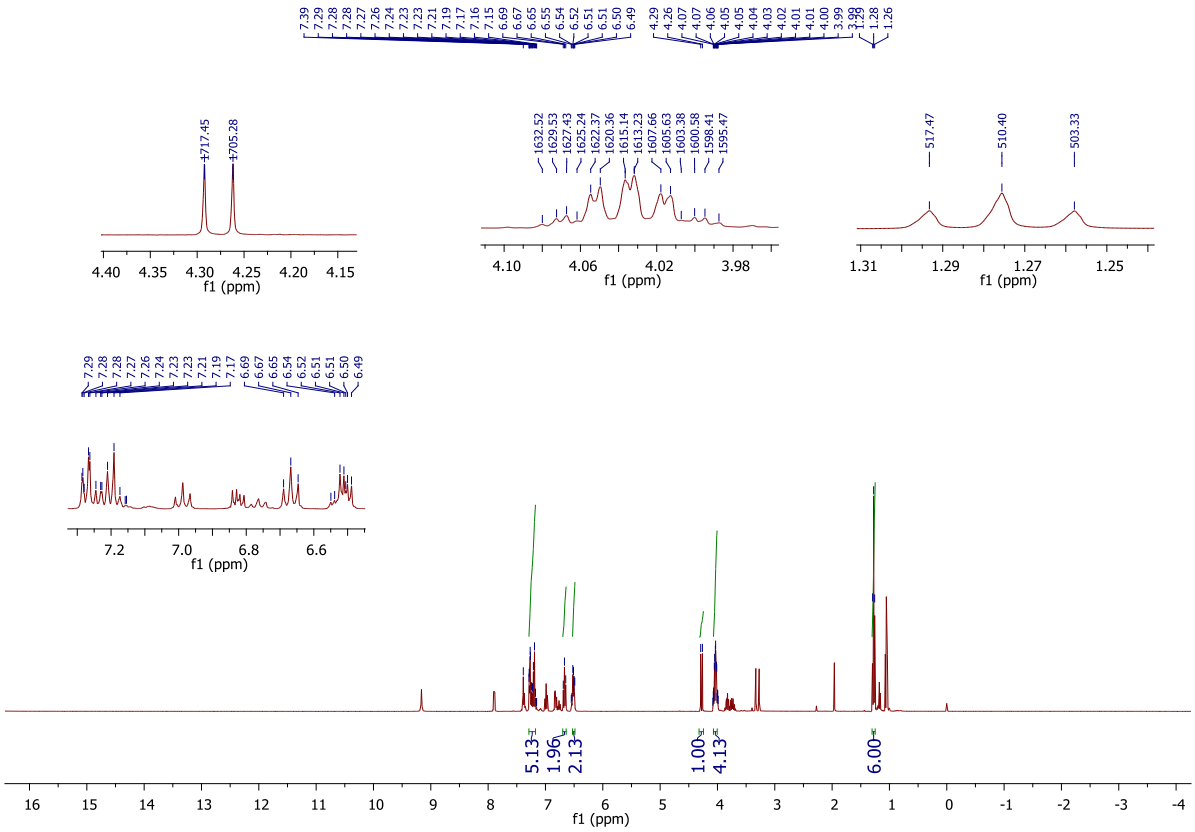
^{31}P NMR



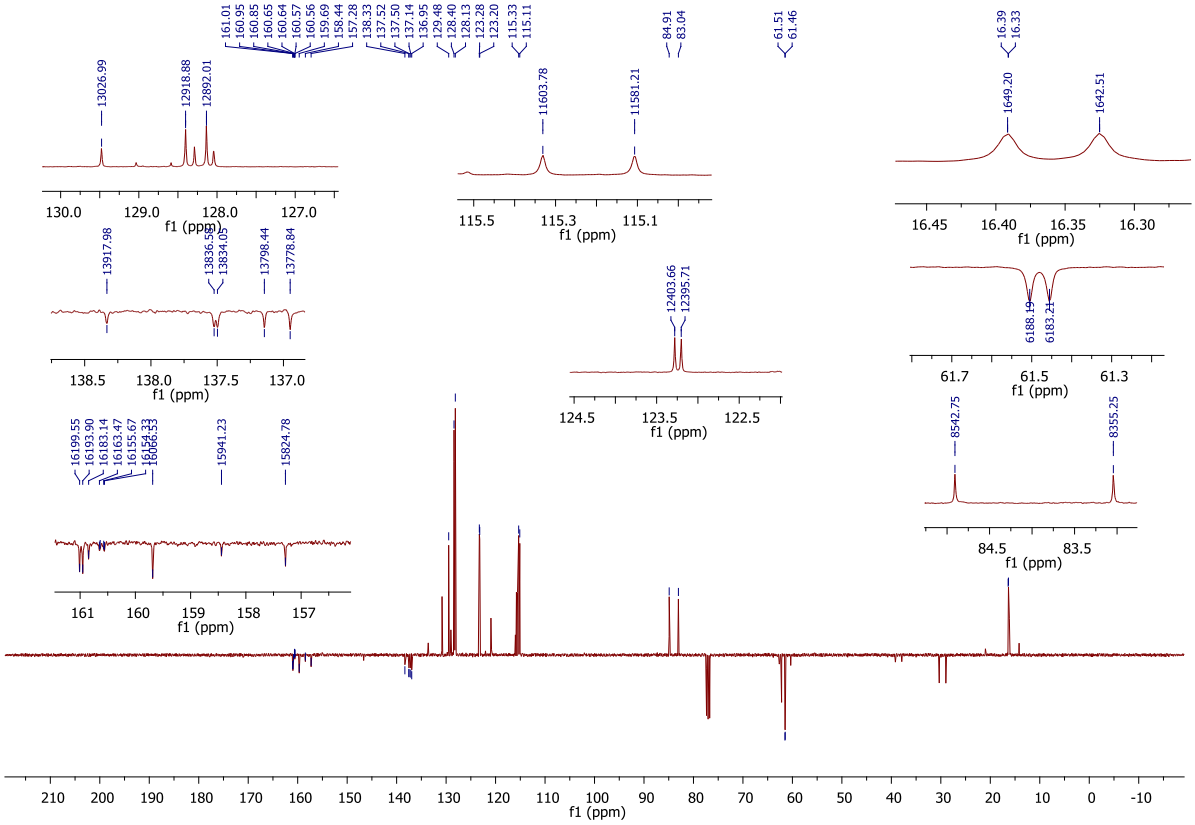
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR


161.01
160.95
160.85
160.65
160.64
160.57
160.56
159.69
158.44
157.28
138.33
137.52
137.50
137.14
136.95
129.48
128.40
128.13
123.28
123.20
115.33
115.11
84.91
83.04
61.51
61.46
16.39
16.33
13026.99
12918.88
12892.01
11603.78
11581.21
1649.20
1642.51
f1 (ppm)
13917.98
13836.58
13834.05
13798.44
13778.84
12403.66
12395.71
6188.19
6183.21
16199.55
16193.90
16183.14
16163.47
16155.67
16154.33
16068.33
15941.23
15824.78
8542.75
8355.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

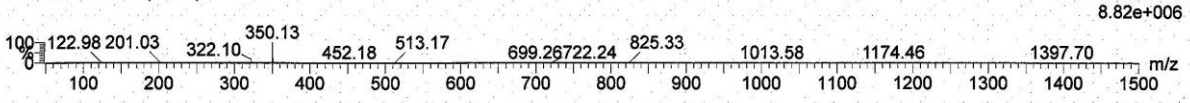
HRMS

Elemental Composition Report **Page 1**

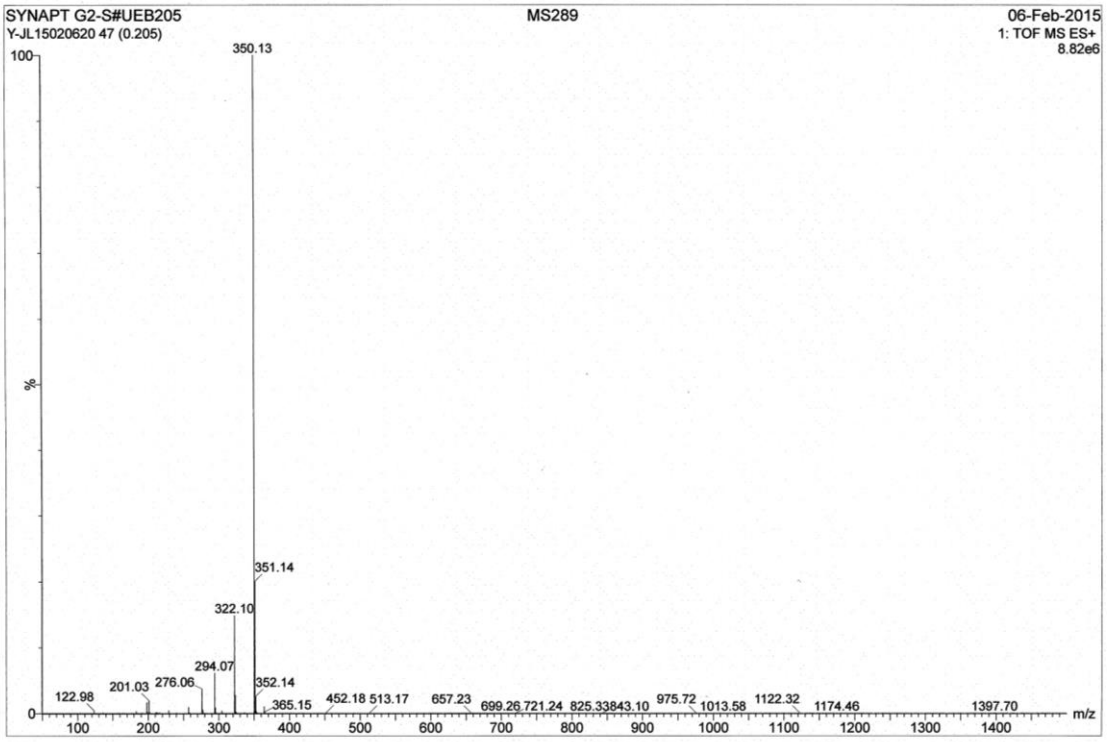
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
914 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 P: 1-1 F: 1-2

SYNAPT G2-S#UEB205 MS289 06-Feb-2015
Y-JL15020620 47 (0.205) 1: TOF MS ES+
8.82e+006



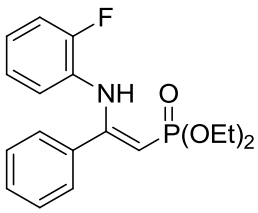
Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
350.1320	350.1321	-0.1	-0.3	8.5	1553.3	n/a	n/a	C18 H22 N O3 P F



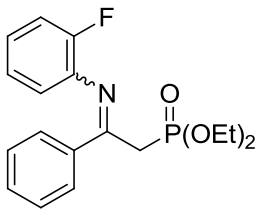
(*Z*)-diethyl (2-((2-fluorophenyl)amino)-2-phenylvinyl)phosphonate 12j

(*E*/*Z*)-diethyl (2-((2-fluorophenyl)imino)-2-phenylethyl)phosphonate 13j

Note: Ratio of enamines **12** and imines **13** after column chromatography equaled 61:39, respectively. Only (*Z*)-enamine was formed. Ratio of imines **13j** (*E*/*Z*) equaled 80:20, respectively.

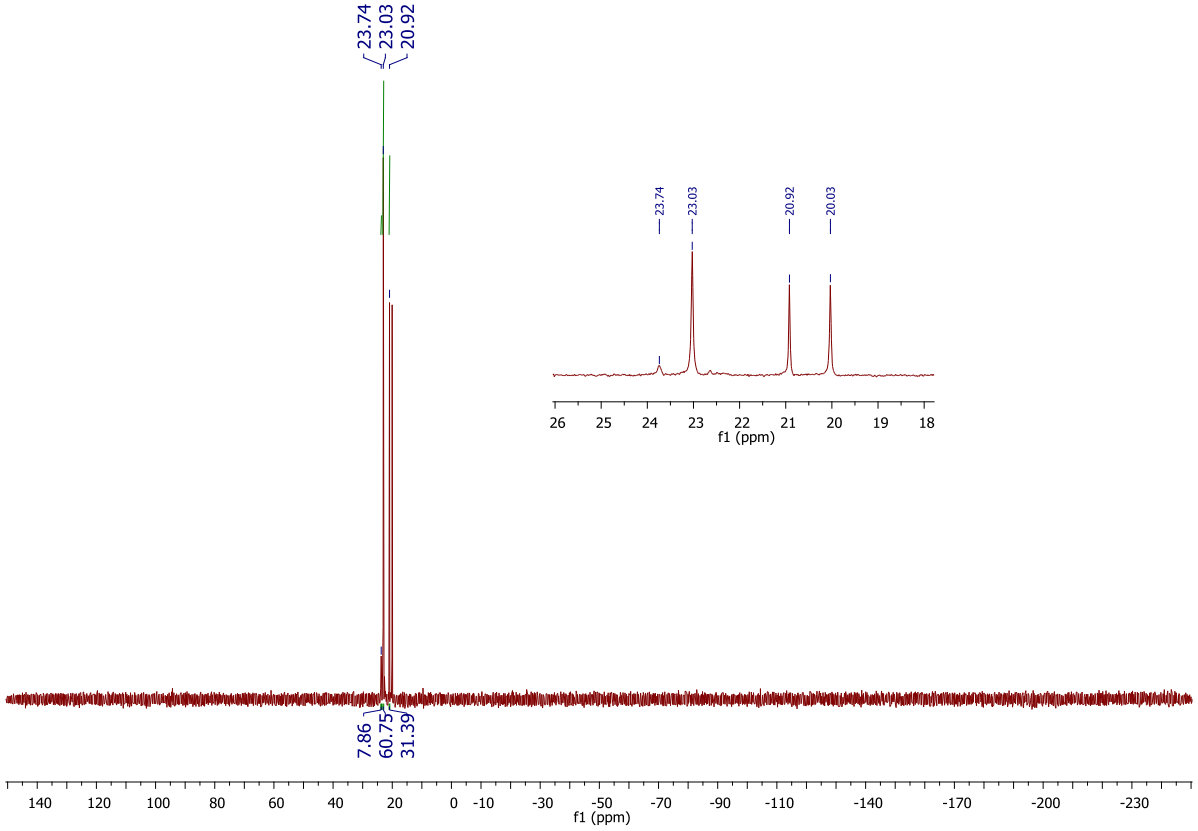


12j

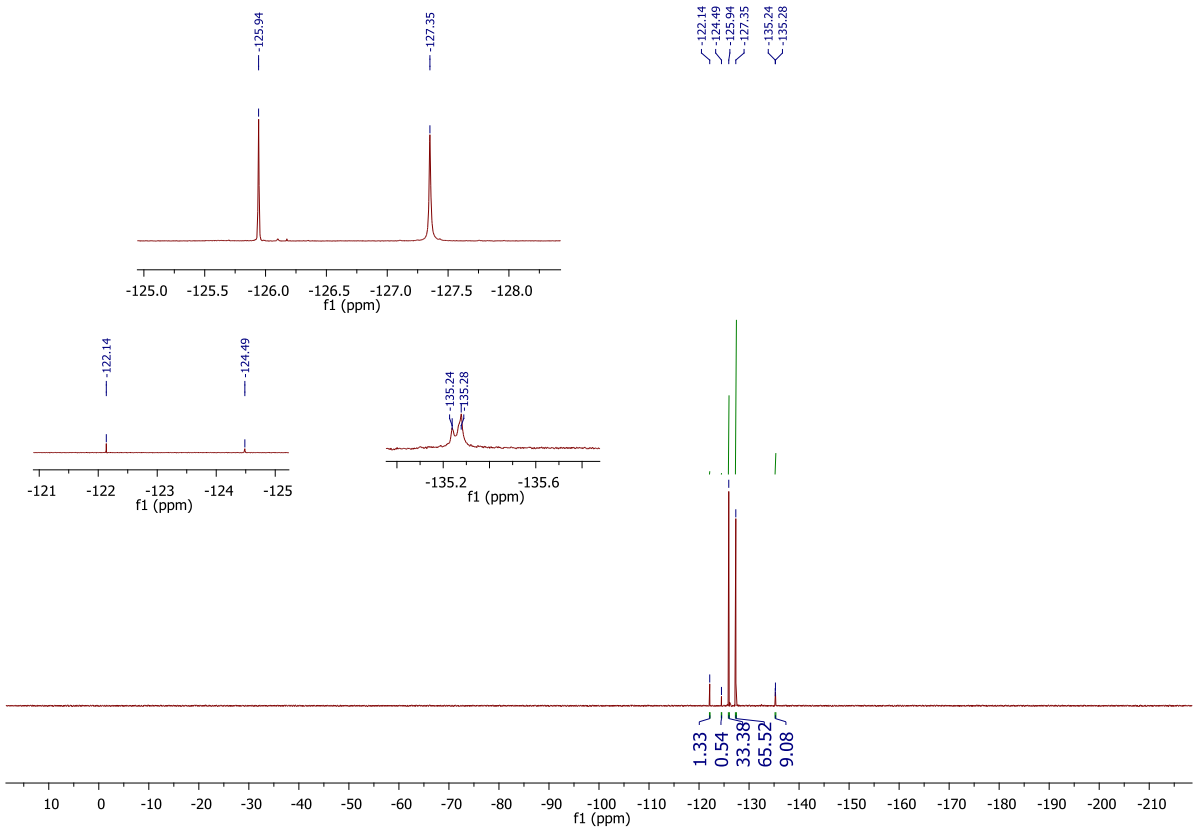


13j

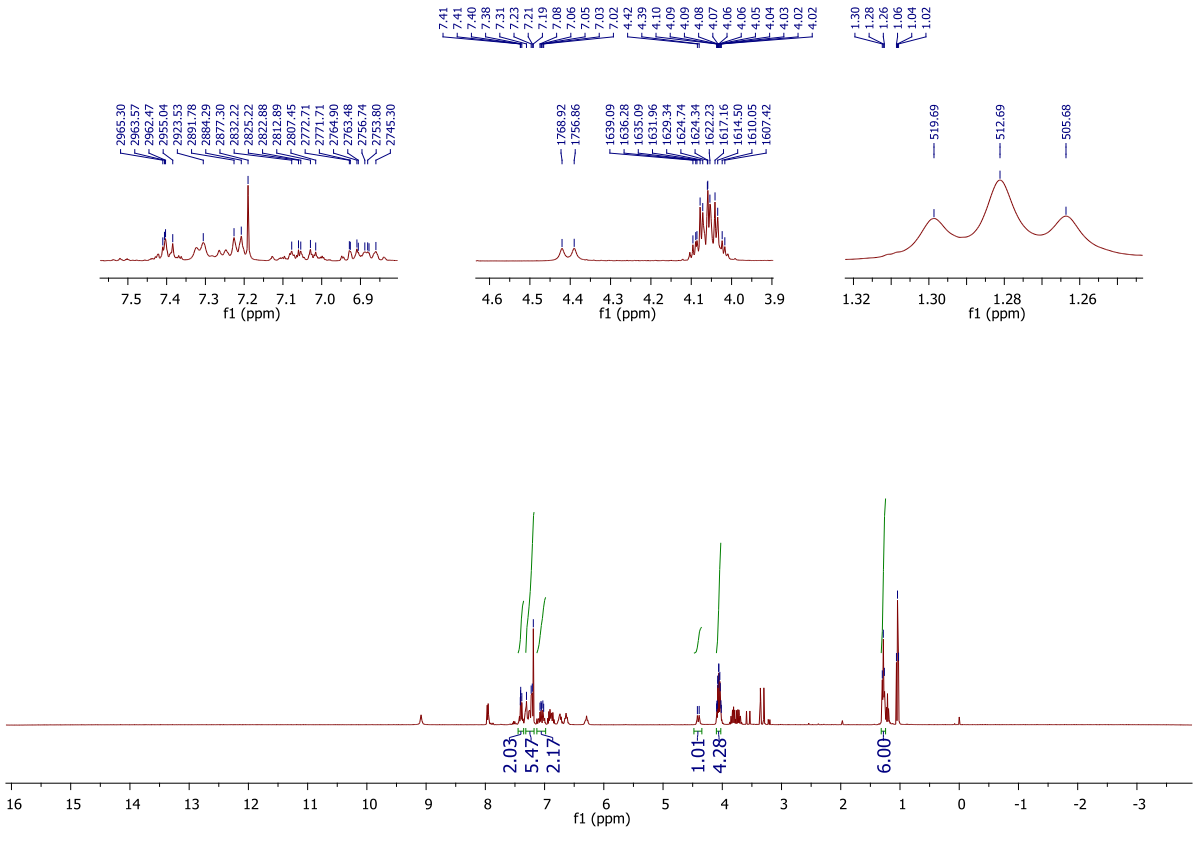
^{31}P NMR



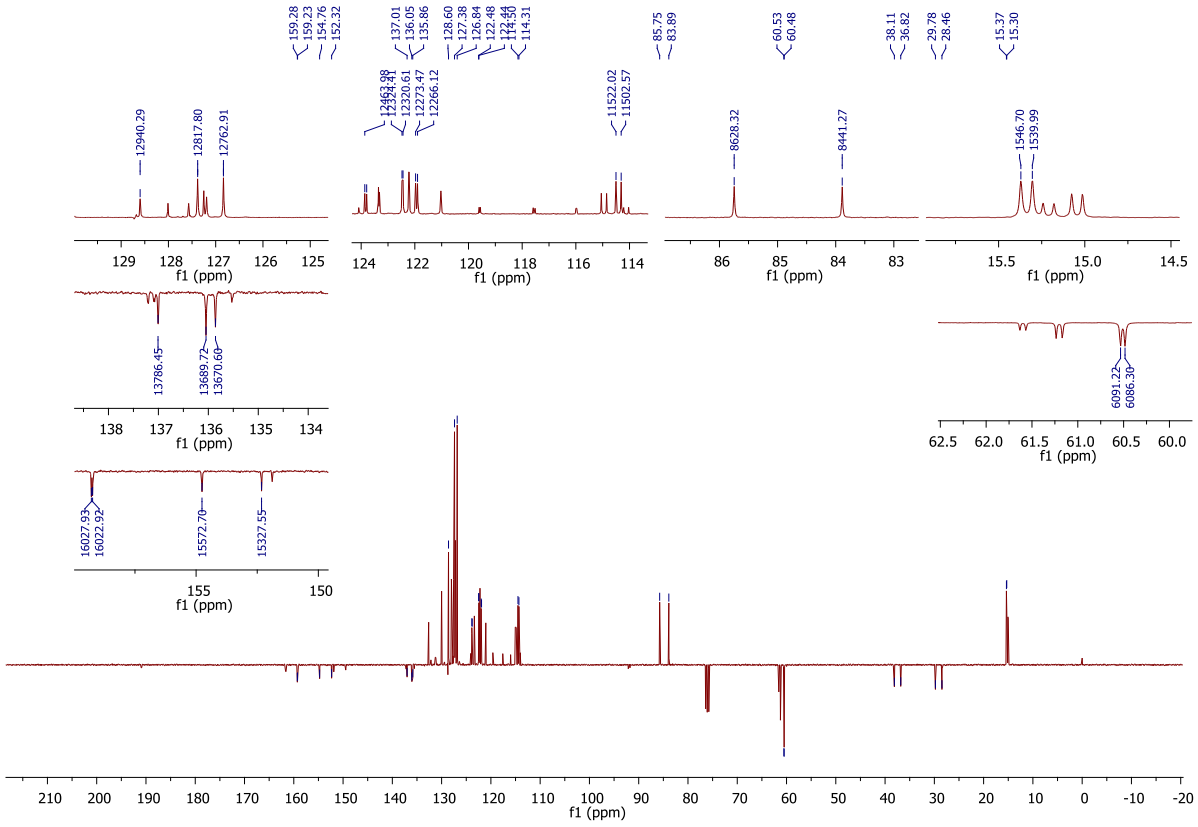
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



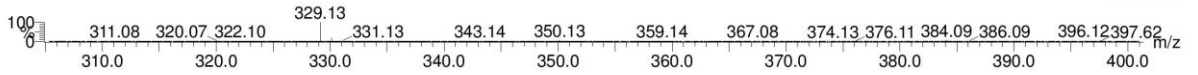
HRMS

Elemental Composition Report **Page 1**

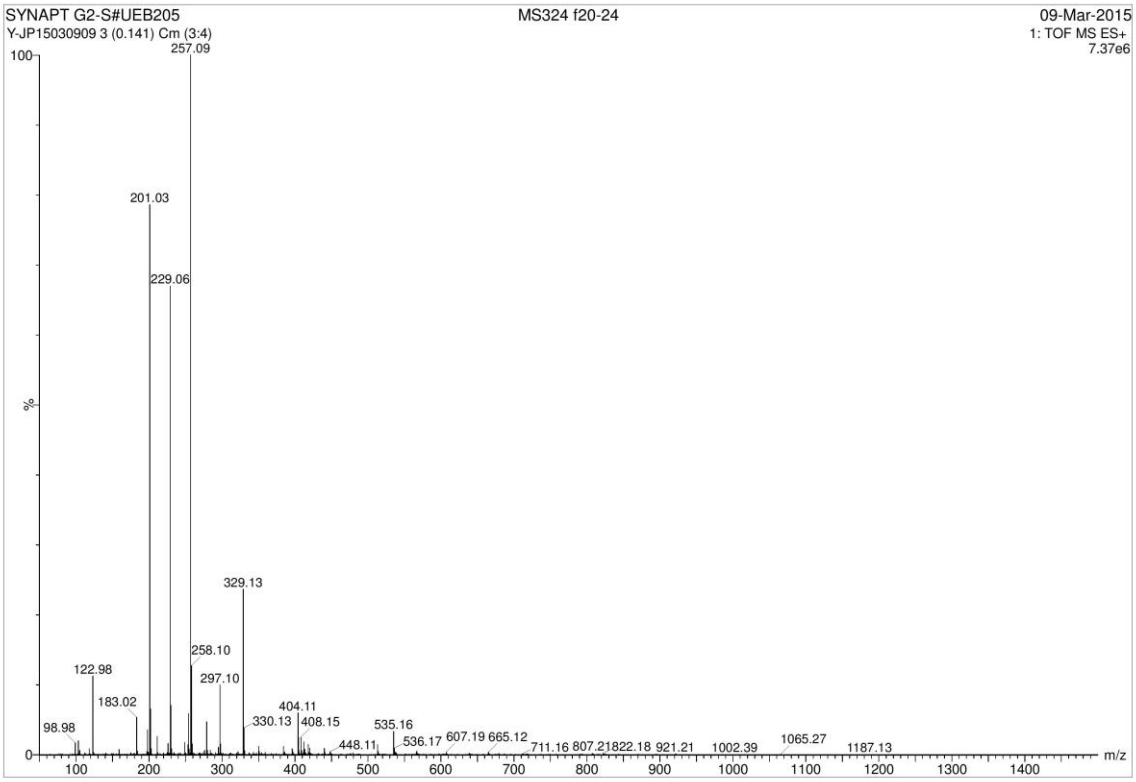
Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
527 formula(e) evaluated with 2 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 F: 1-1 P: 1-1

SYNAPT G2-S#UEB205 MS324 f20-24 09-Mar-2015
Y-JP15030909 3 (0.141) Cm (3:4) 1: TOF MS ES+
1.74e+006

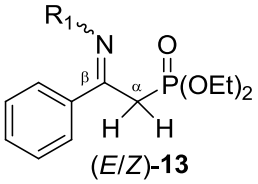


Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
350.1321	350.1321	0.0	0.0	8.5	1388.8	0.000	99.95	C18 H22 N O3 F P
	350.1326	-0.5	-1.4	1.5	1396.5	7.699	0.05	C3 H18 N13 O4 F P


SYNAPT G2-S#UEB205
MS324 f20-24
09-Mar-2015
Y-JP15030909 3 (0.141) Cm (3:4)
1: TOF MS ES+
7.37e6
100
%
0
257.09
201.03
229.06
329.13
258.10
122.98
297.10
183.02
404.11
330.13
408.15
98.98
535.16
448.11
536.17
607.19
665.12
711.16
807.21
822.18
921.21
1002.39
1065.27
1187.13
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400

Additional data for compounds 13 a-j

Table 1 ^{1}H NMR data for minor (*E*/*Z*)-forms of *β*-iminophosphonates 13a-j



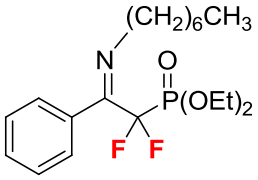
(*E*/*Z*)-**13**

R_1: **a**= $CH_3(CH_2)_6$, **b**= $CH_3(CH_2)_7$, **c**= 4-OCH_3Bn, **d**= 2-CH_3Bn, **e**= Bn, **f**= 4-FBn, **g**= (S)-(CH_3)CHPh, **h**= Ph, **i**= 4-FPh, **j**= 2-FPh

	δ [ppm]	**13a**	**13b**	**13c**	**13d**	**13e**
H *(E)*	(d)	3.38	3.41	3.40	3.53	3.53
	$^{2}J_{HP}$ [Hz]	23.4	23.4	23.4	23.4	23.4
H *(Z)*	(d)	3.15	3.23	3.21	3.37	3.35
	$^{2}J_{HP}$ [Hz]	21.5	21.9	22.0	22.1	22.1
	δ [ppm]	**13f**	**13g**	**13h**	**13i**	**13j**
H *(E)*	(d)	3.50	3.34 3.33	3.32	3.30	3.33
	$^{2}J_{HP}$ [Hz]	23.4	23.3[a]	23.3	23.3	23.4
H *(Z)*	(d)	3.32	3.20	3.39	3.37	3.26
	$^{2}J_{HP}$ [Hz]	22.1	22.1	22.5	22.5	22.9

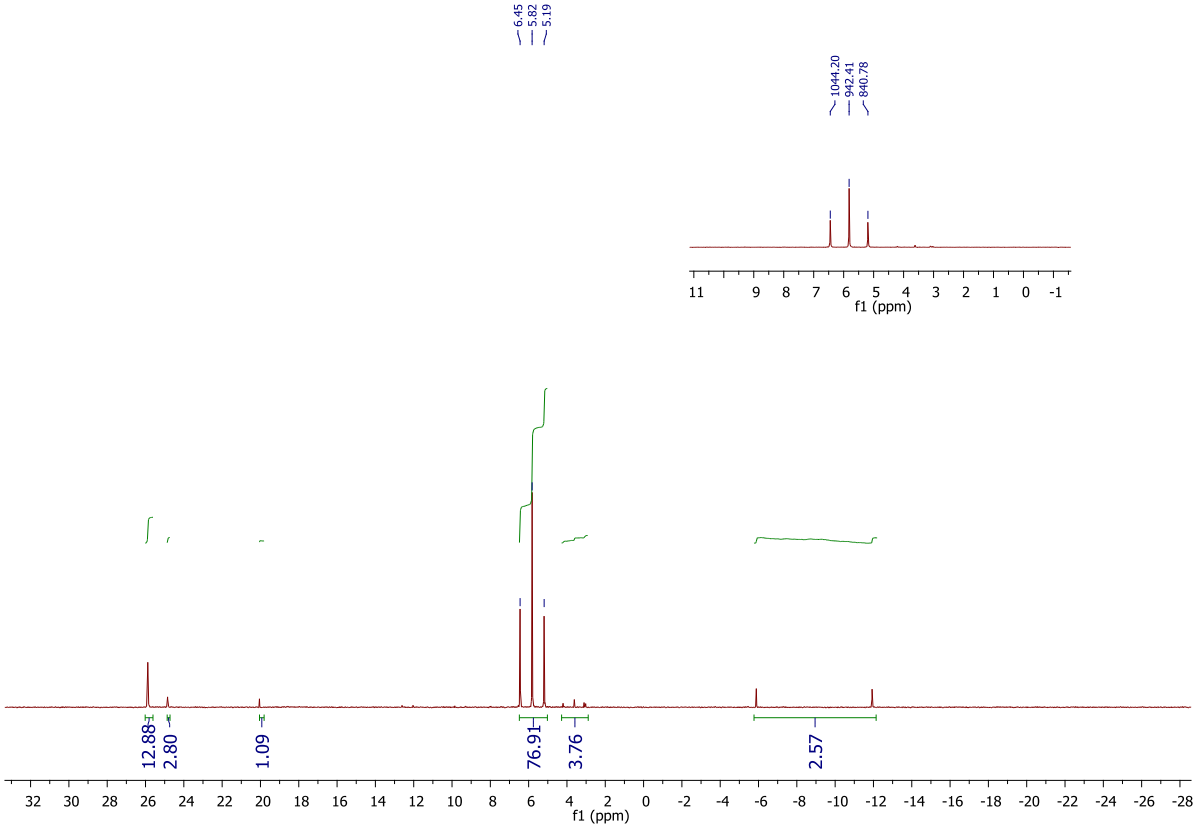
[a] signal derived from non chemically equivalent protons (diastereotopic) observed as two pair of doublets with the same coupling constant

(*Z*)-diethyl (1,1-difluoro-2-(heptylimino)-2-phenylethyl)phosphonate 14a

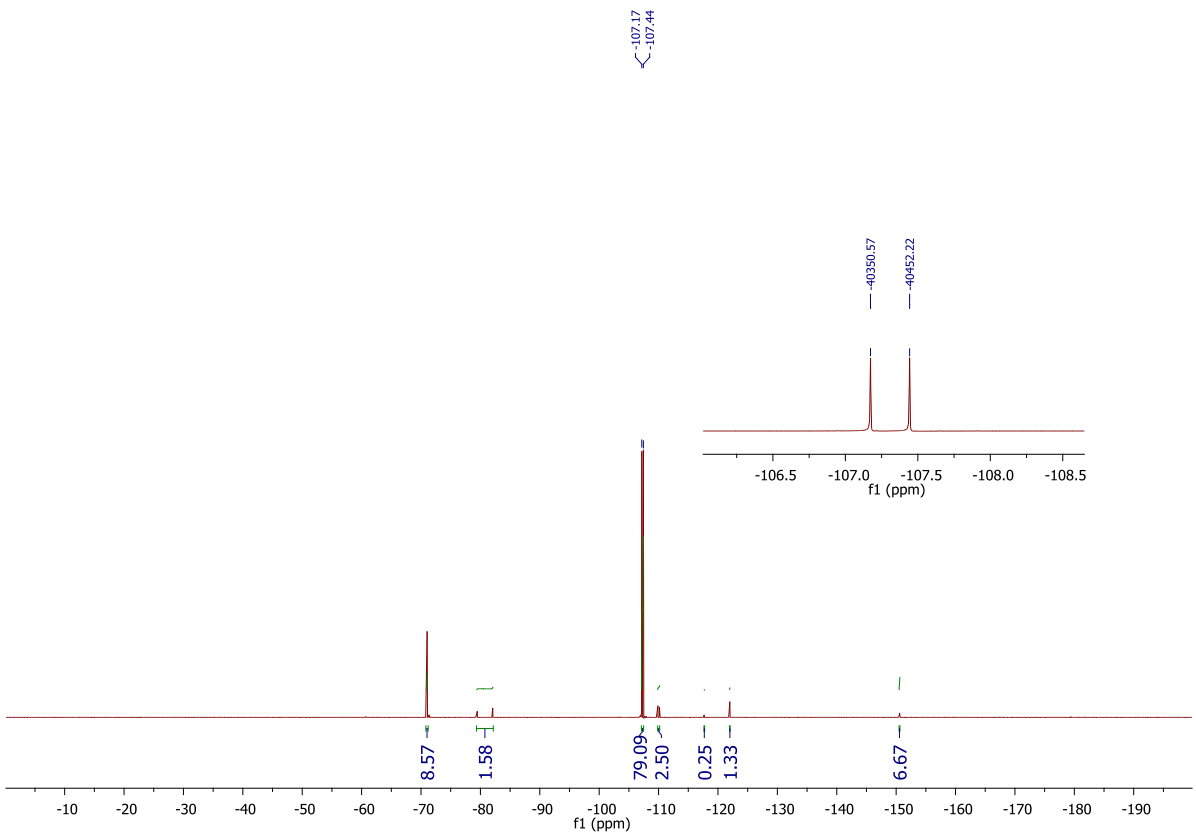


14a

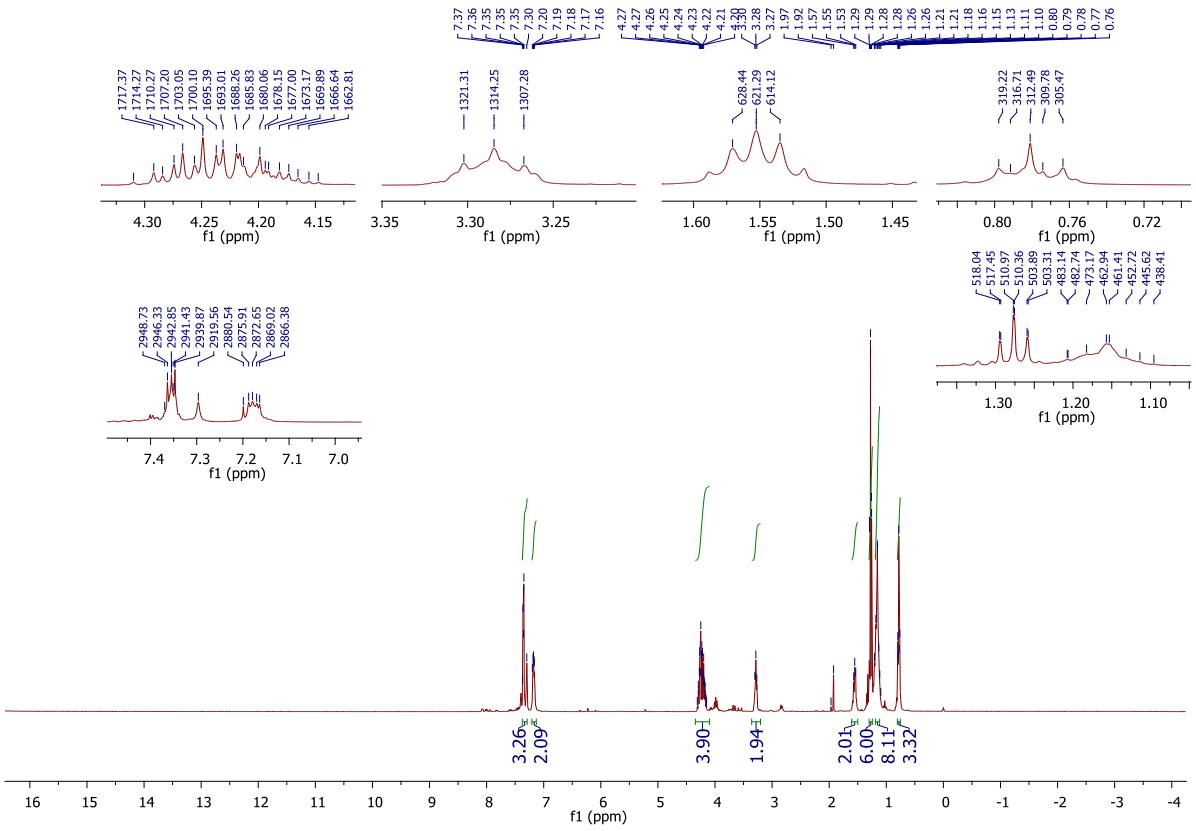
^{31}P NMR



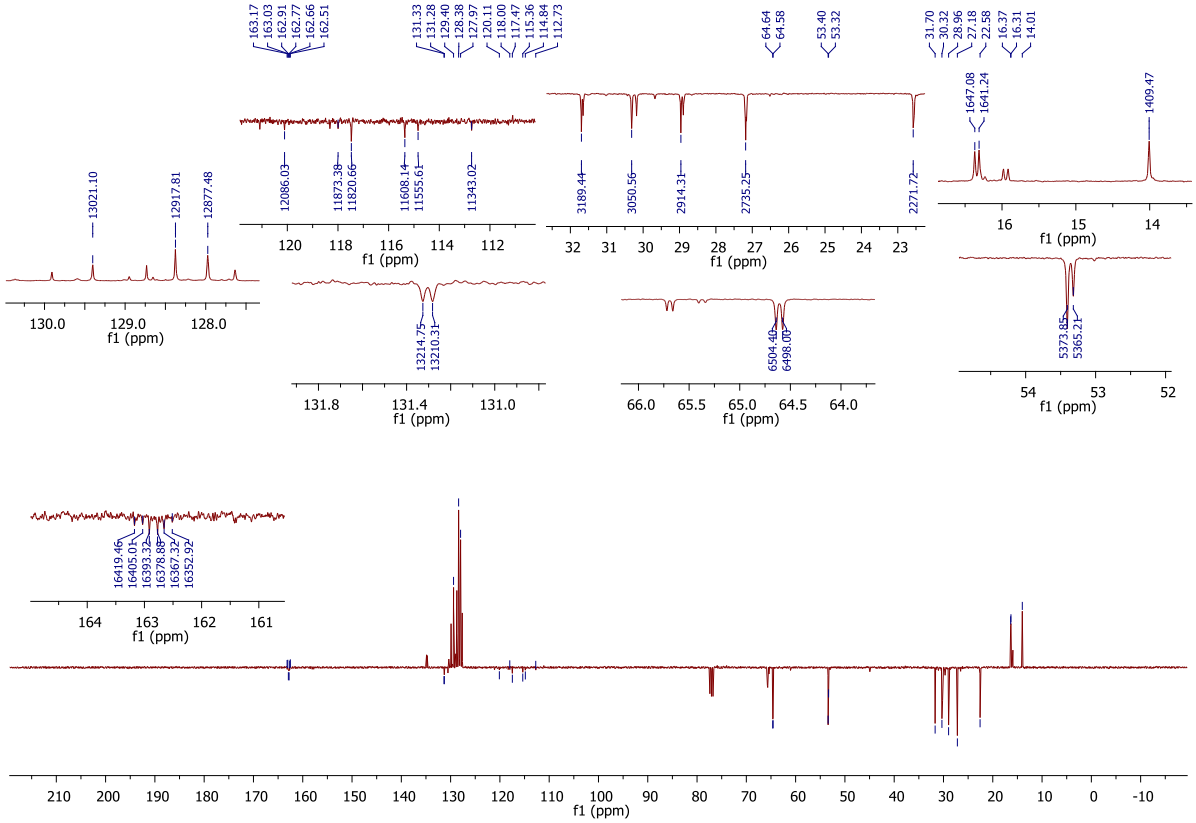
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



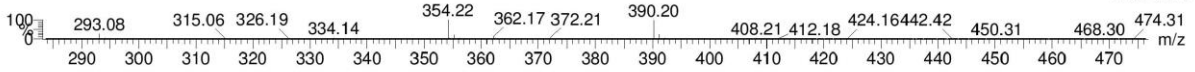
HRMS

Elemental Composition Report **Page 1**

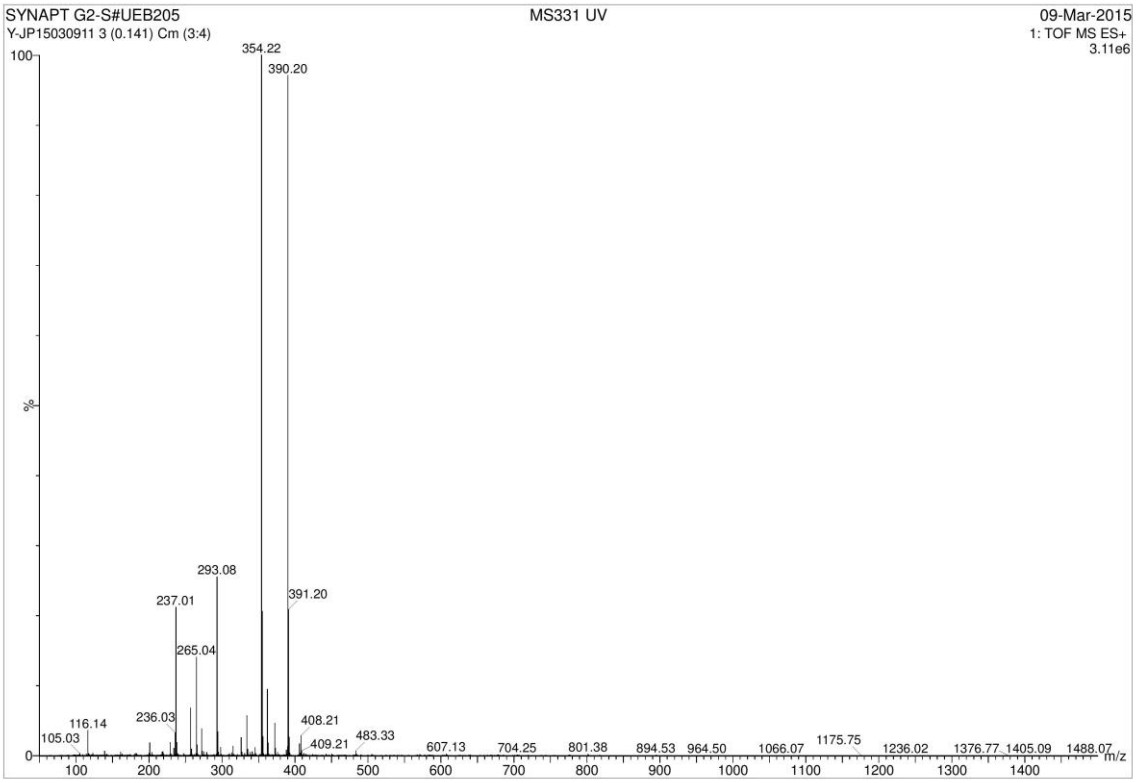
Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
638 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 F: 2-2 P: 1-1

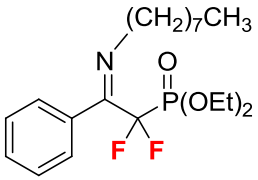
SYNAPT G2-S#UEB205 MS331 UV 09-Mar-2015
Y-JP15030911 3 (0.141) Cm (3:4) 1: TOF MS ES+
3.11e+006



Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
390.2008	390.2010	-0.2	-0.5	4.5	1722.1	n/a	n/a	C19 H31 N O3 F2 P

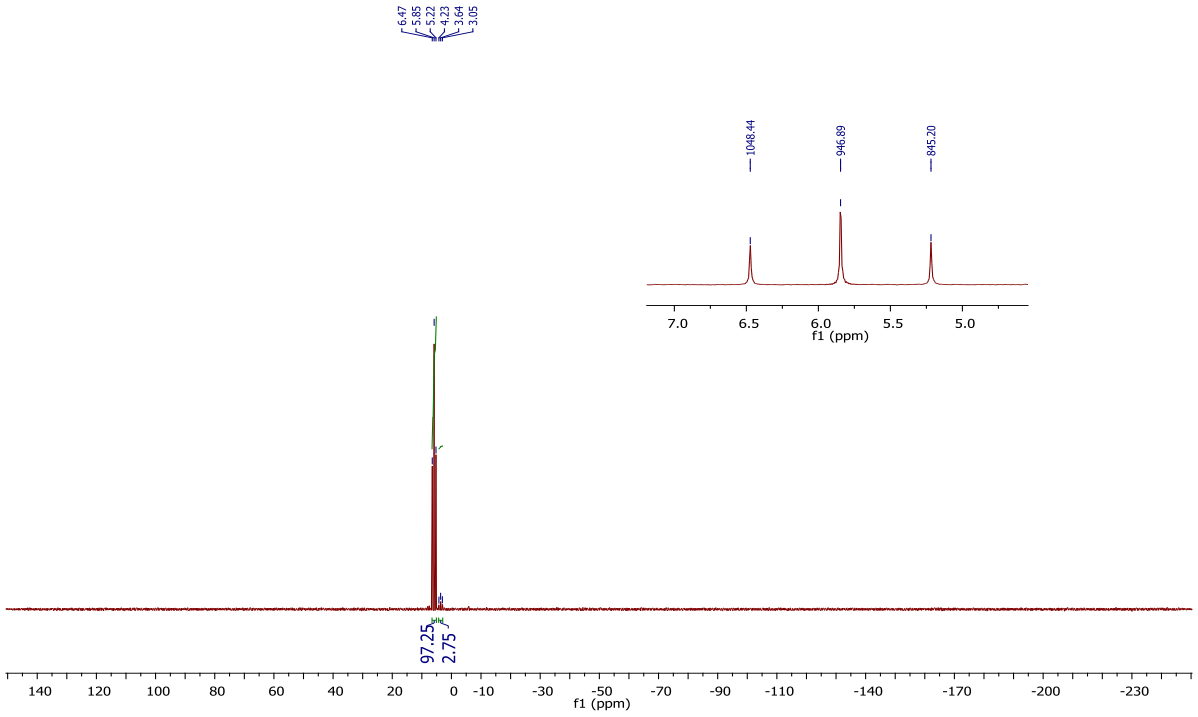

SYNAPT G2-S#UEB205
MS331 UV
09-Mar-2015
Y-JP15030911 3 (0.141) Cm (3:4)
1: TOF MS ES+
3.11e6
100
%
0
354.22
390.20
293.08
237.01
391.20
265.04
236.03
116.14
105.03
408.21
409.21
483.33
607.13
704.25
801.38
894.53
964.50
1066.07
1175.75
1236.02
1376.77
1405.09
1488.07
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z

(*Z*)-diethyl (1,1-difluoro-2-(octylimino)-2-phenylethyl) phosphonate 14b

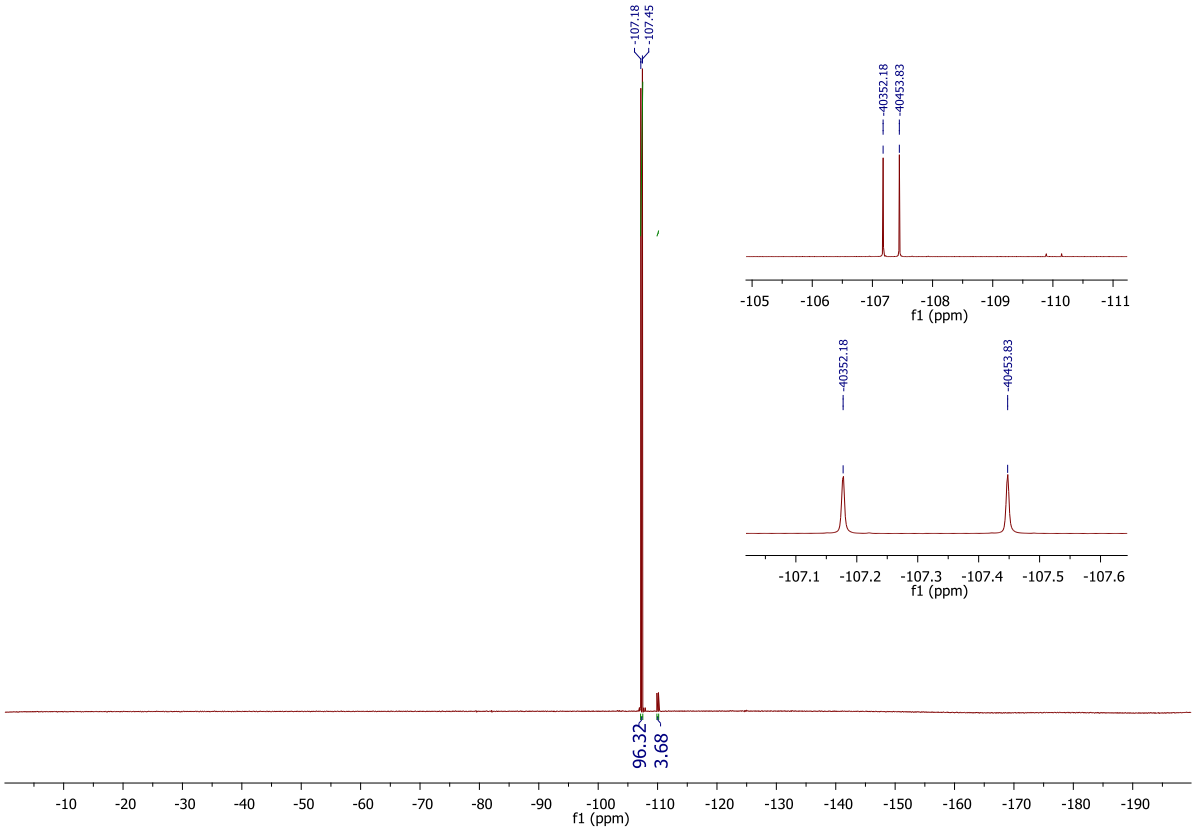


14b

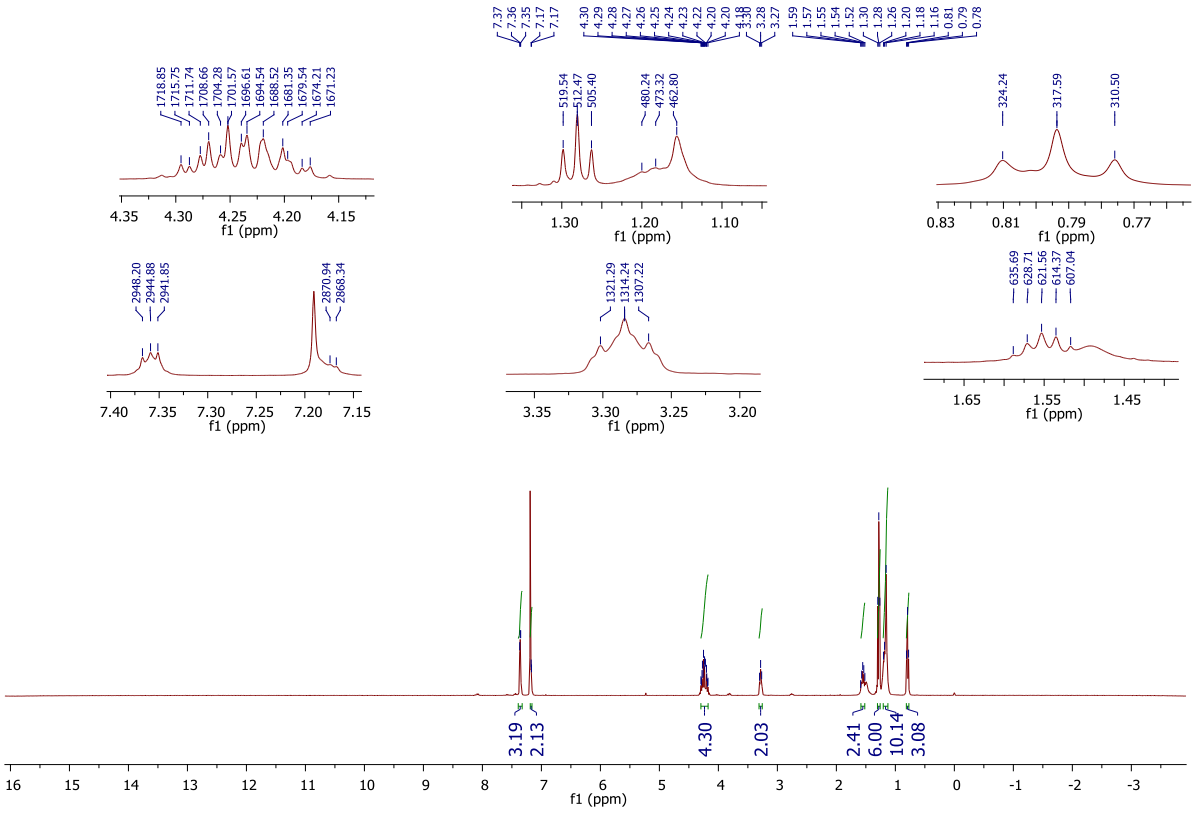
^{31}P NMR



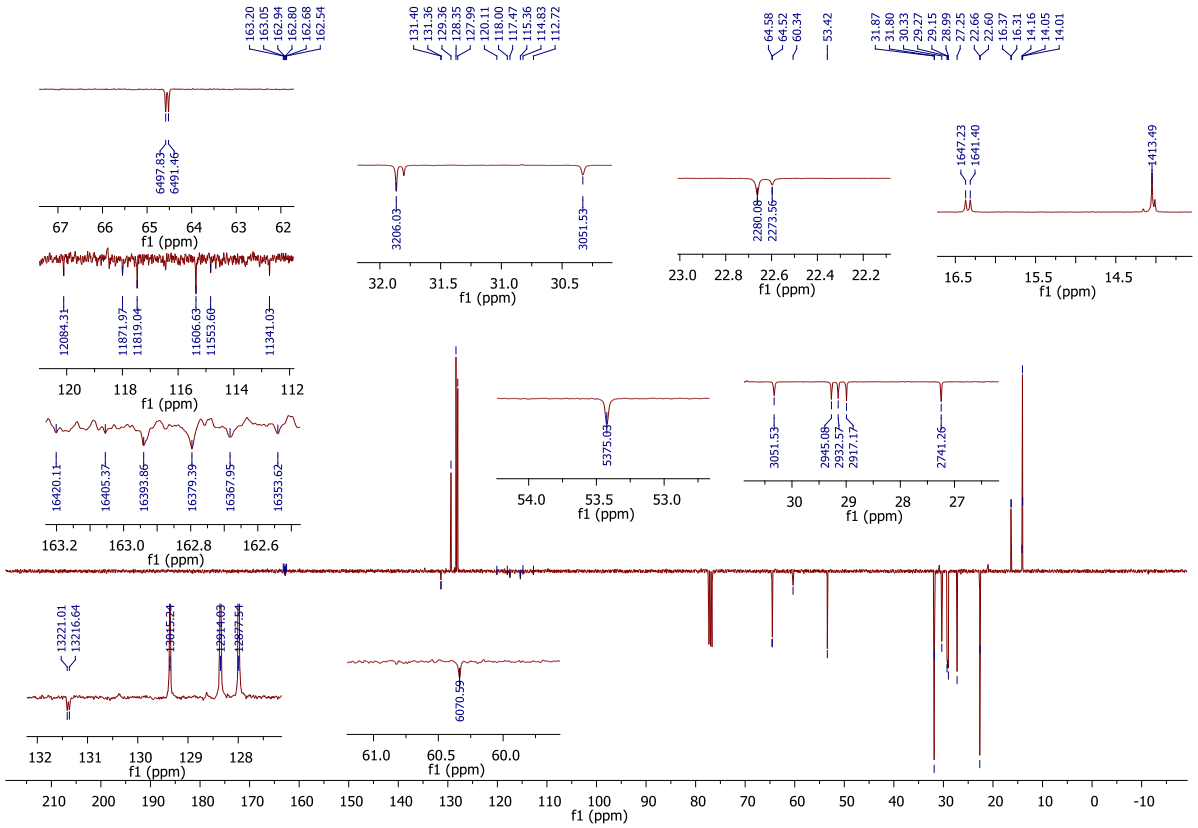
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



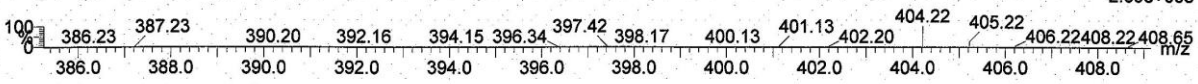
HRMS

Elemental Composition Report **Page 1**

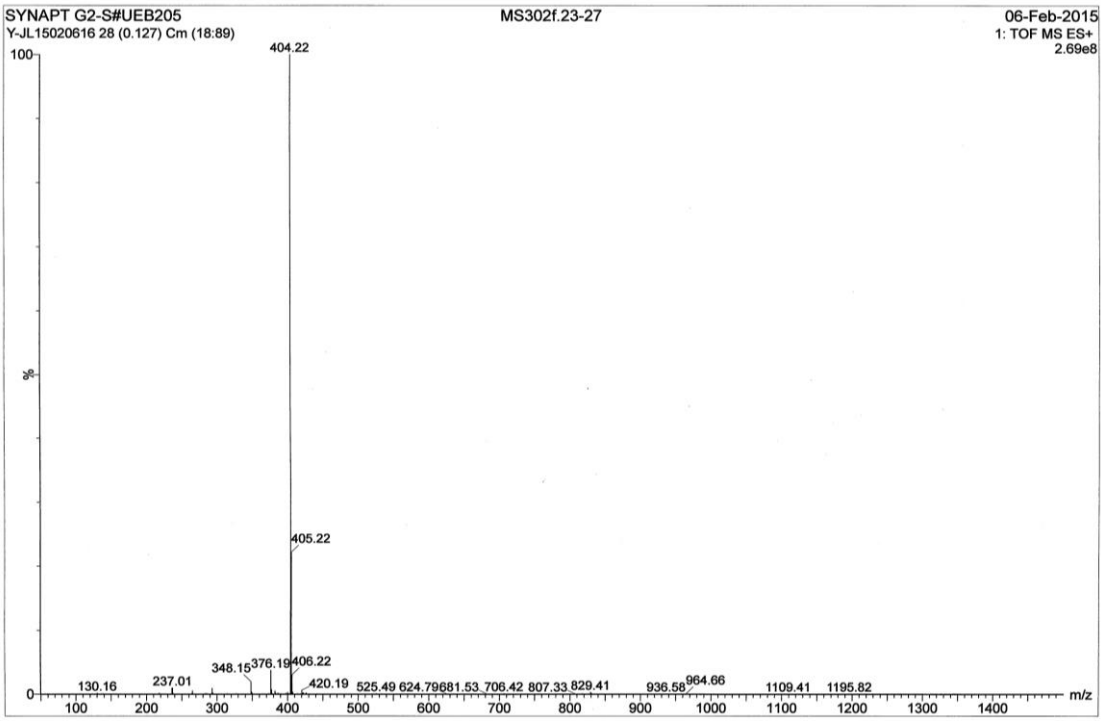
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1994 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

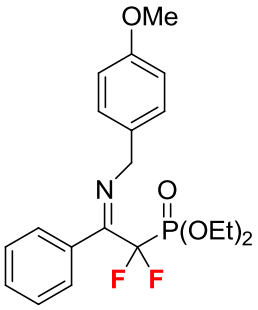
SYNAPT G2-S#UEB205 MS302f.23-27 06-Feb-2015
Y-JL15020616 28 (0.127) Cm (18:89) 1: TOF MS ES+
2.69e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
404.2163	404.2166	-0.3	-0.7	4.5	3444.9	0.000	100.00	C20 H33 N O3 F2 P
	404.2160	0.3	0.7	1.5	3463.7	18.817	0.00	C8 H28 N13 O3 F P

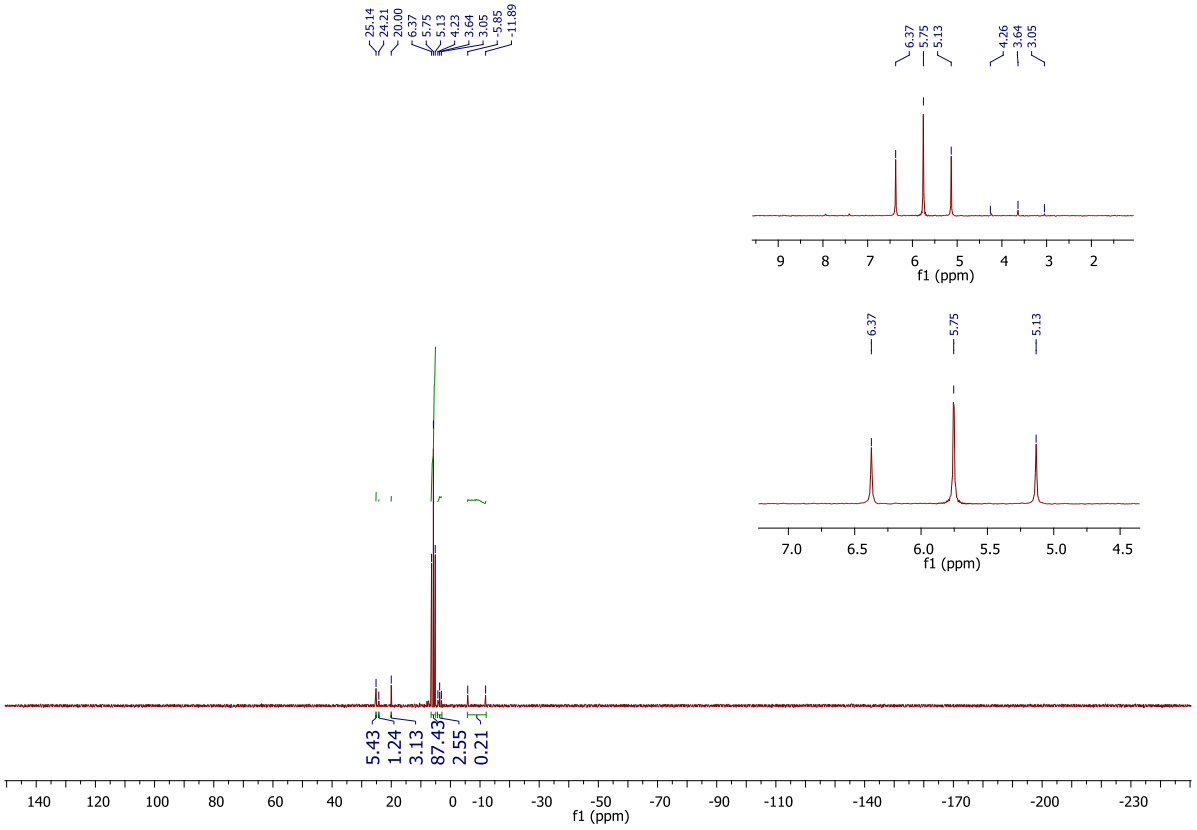

SYNAPT G2-S#UEB205
MS302f.23-27
06-Feb-2015
Y-JL15020616 28 (0.127) Cm (18:89)
1: TOF MS ES+
2.69e8
100
%
0
404.22
405.22
406.22
348.15
376.19
420.19
130.16
237.01
525.49
624.79
681.53
706.42
807.33
829.41
936.58
964.66
1109.41
1195.82
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z

(*Z*)-diethyl (1,1-difluoro-2-((4-methoxybenzyl)imino)-2-phenylethyl) phosphonate 14c

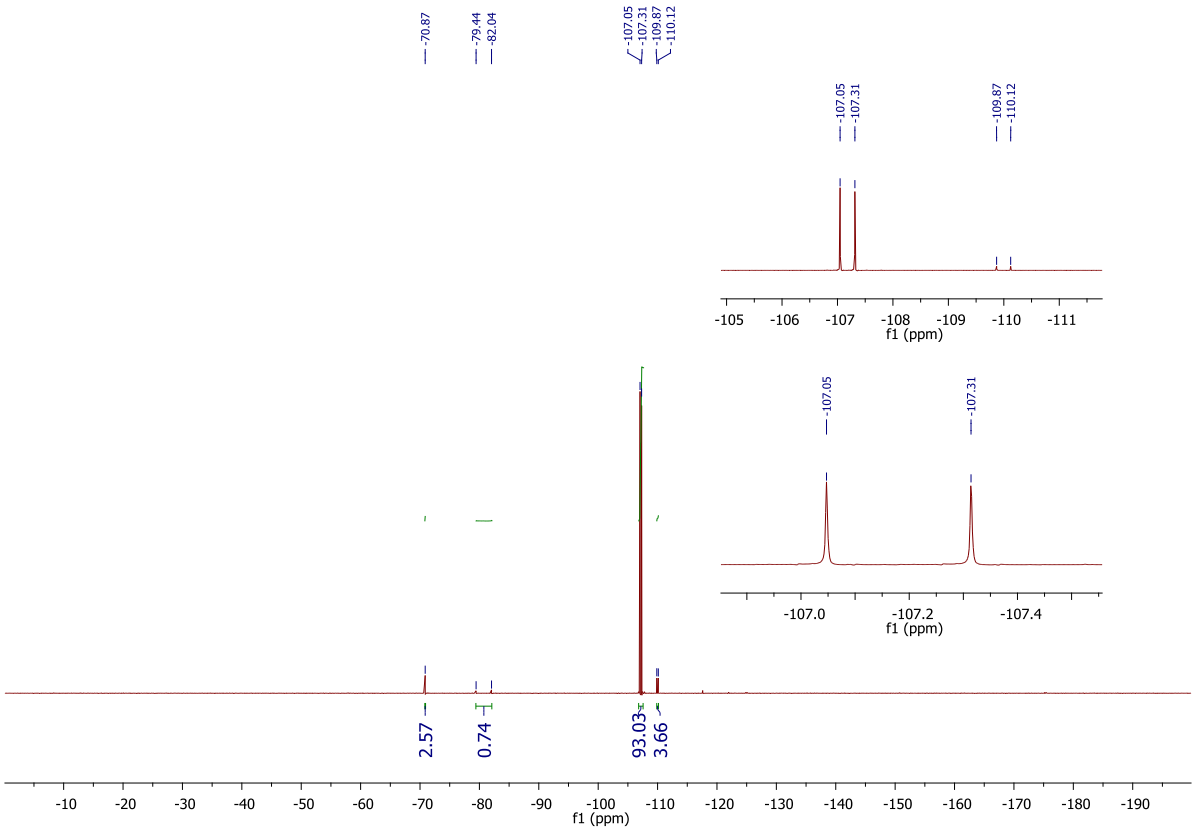


14c

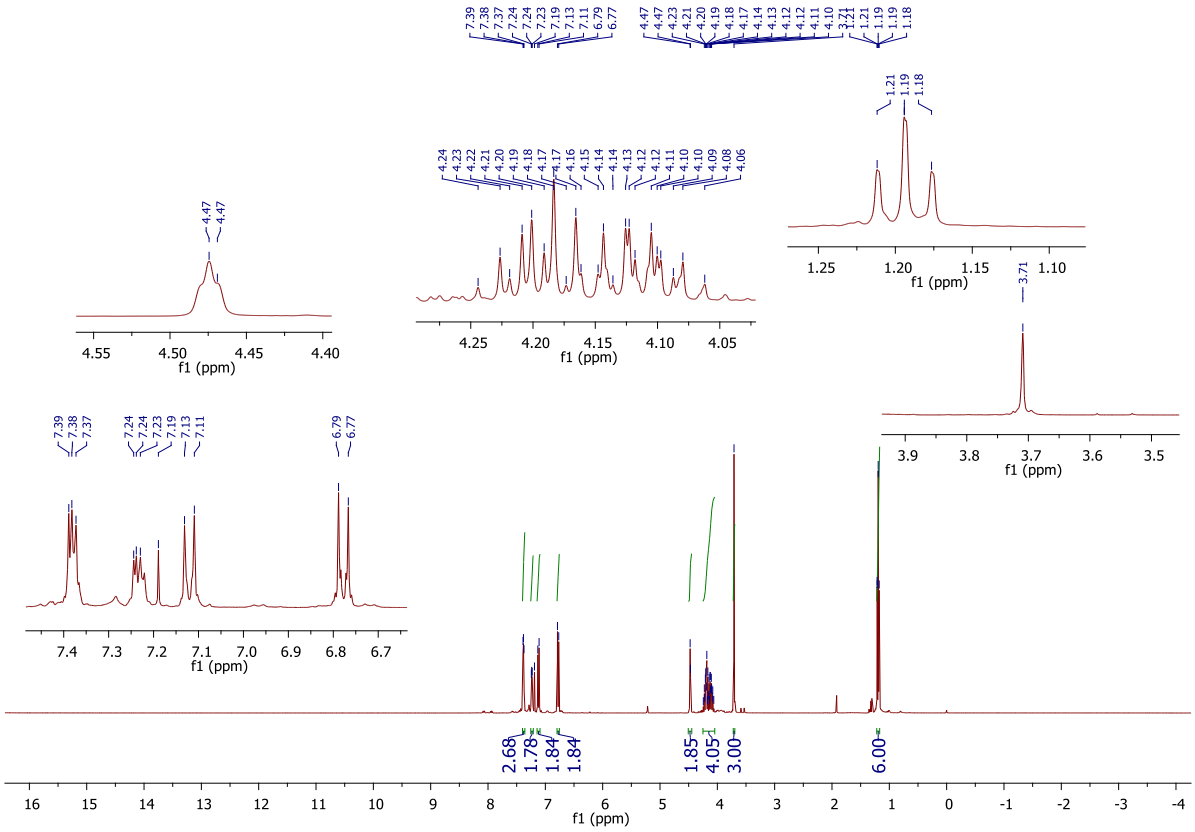
^{31}P NMR



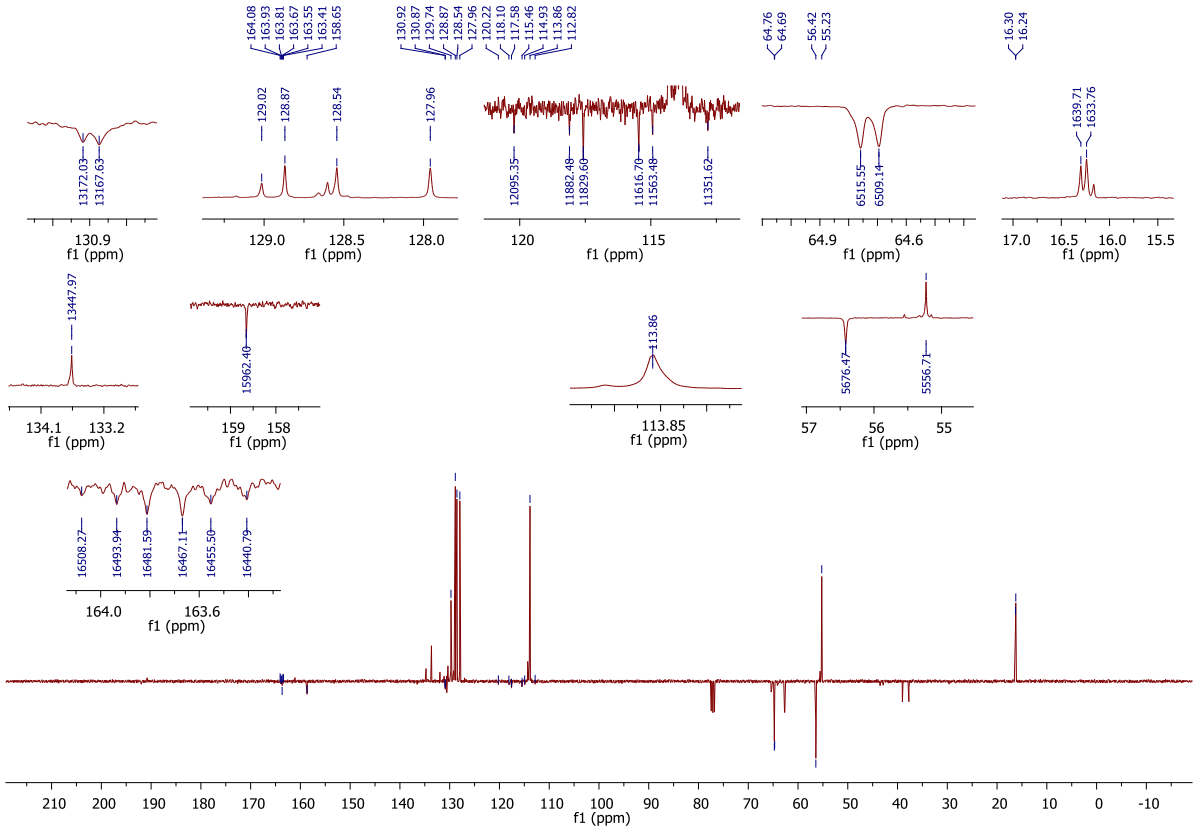
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



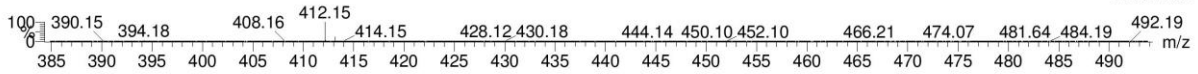
HRMS

Elemental Composition Report **Page 1**

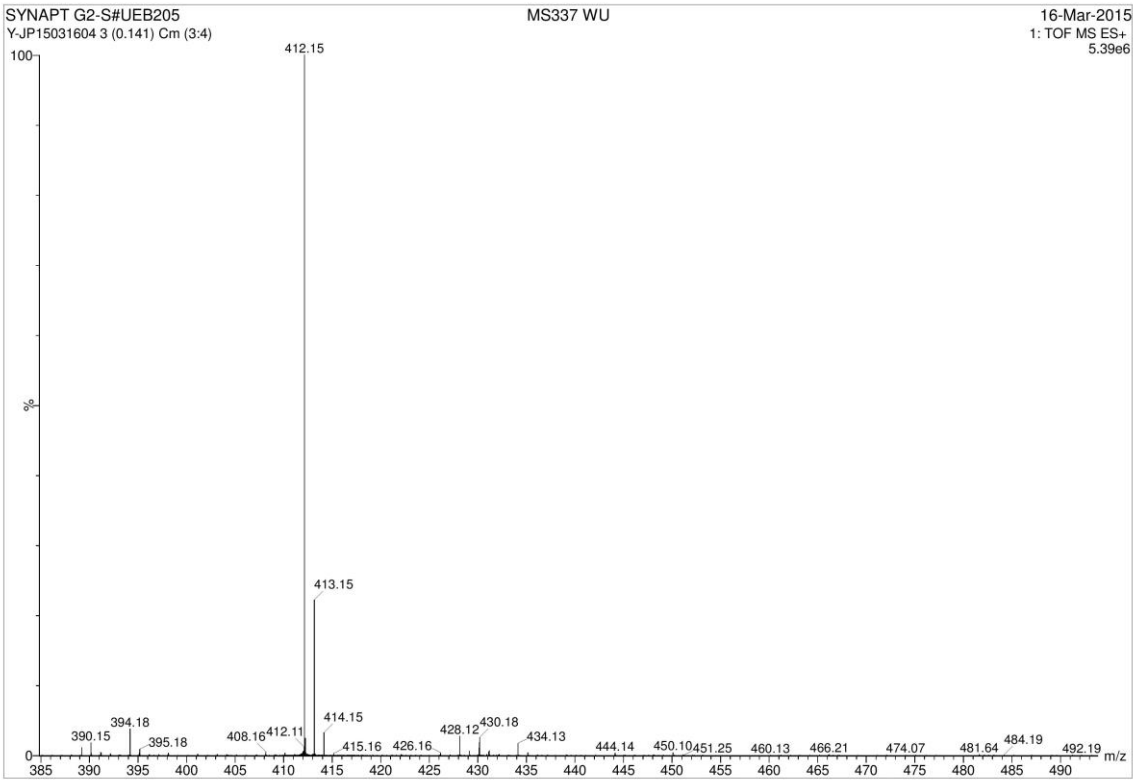
Single Mass Analysis
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
753 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 F: 2-2 P: 1-1

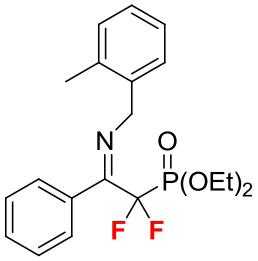
SYNAPT G2-S#UEB205 MS337 WU 16-Mar-2015
Y-JP15031604 3 (0.141) Cm (3:4) 1: TOF MS ES+
5.39e+006



Minimum:			-1.5				
Maximum:		1.0	2.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
412.1483	412.1489	-0.6	-1.5	8.5	1821.1	n/a	n/a	C20 H25 N O4 F2 P

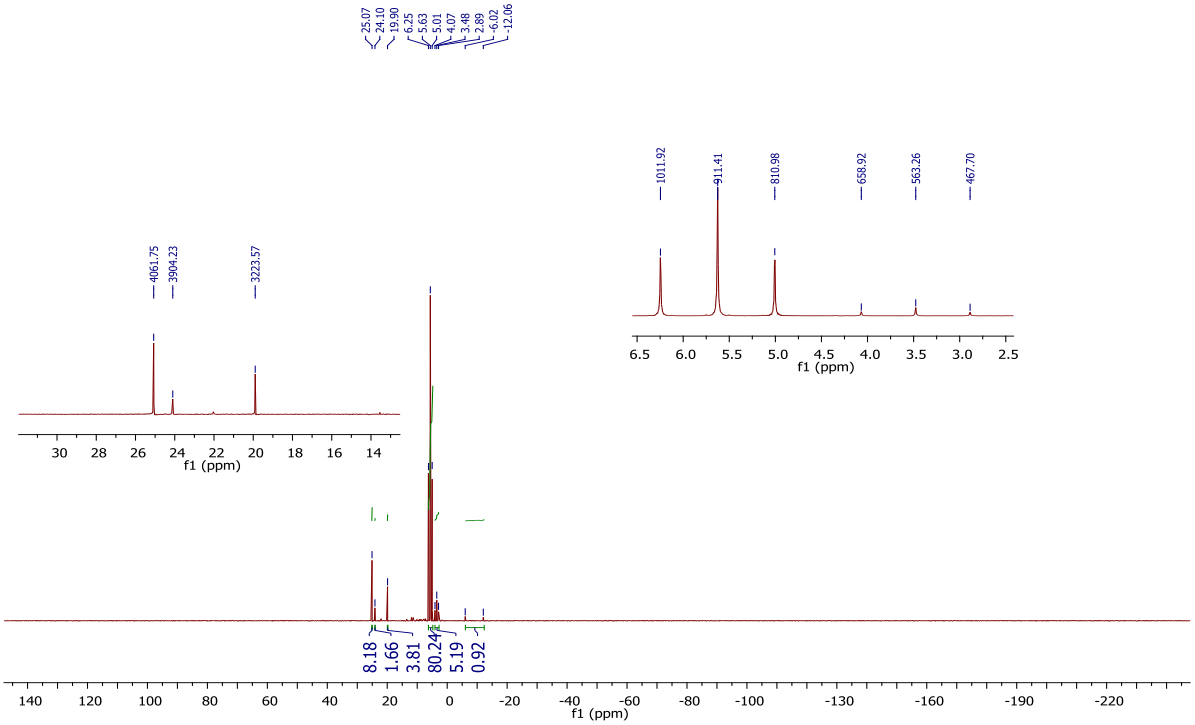

SYNAPT G2-S#UEB205
MS337 WU
16-Mar-2015
Y-JP15031604 3 (0.141) Cm (3:4)
1: TOF MS ES+
5.39e6
100
%
0
412.15
413.15
414.15
394.18
390.15
395.18
408.16
412.11
415.16
426.16
428.12
430.18
434.13
444.14
450.10
451.25
460.13
466.21
474.07
481.64
484.19
492.19
m/z
385
390
395
400
405
410
415
420
425
430
435
440
445
450
455
460
465
470
475
480
485
490

(*Z*)-diethyl (1,1-difluoro-2-((2-methylbenzyl)imino)-2-phenylethyl) phosphonate 14d

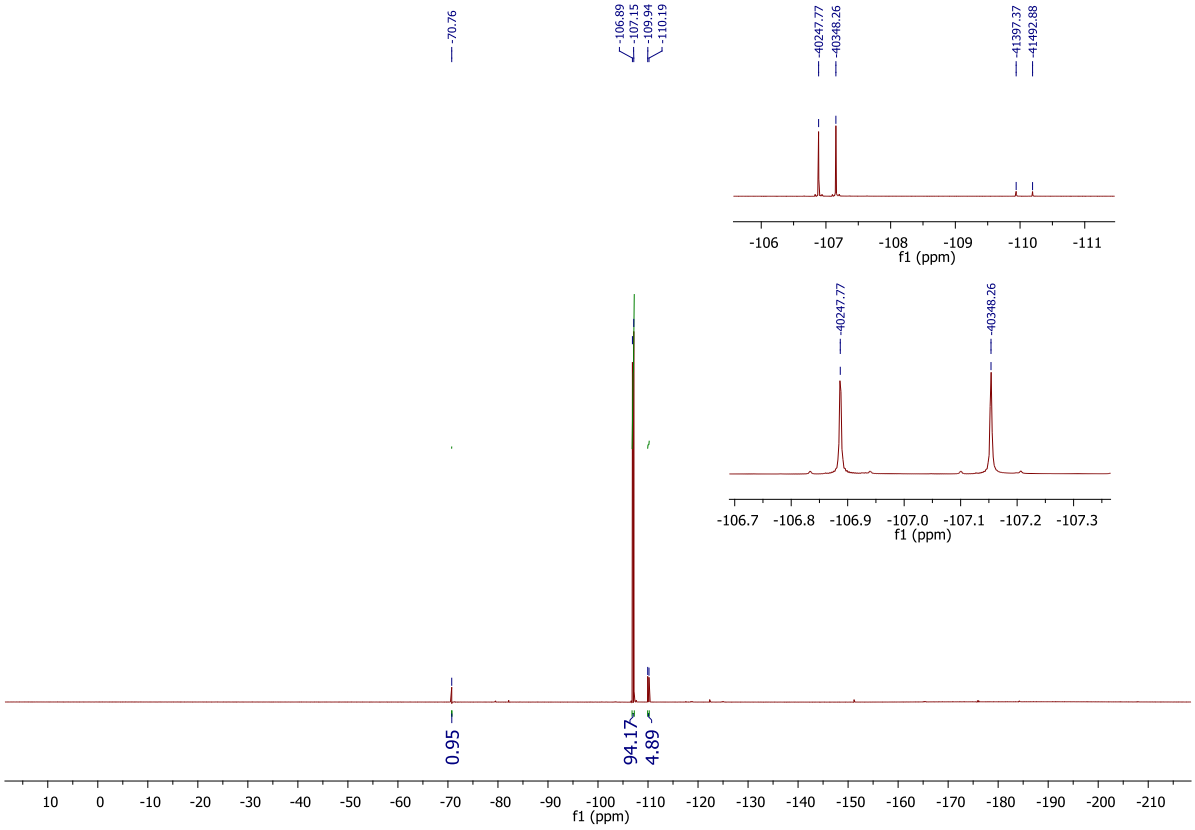


14d

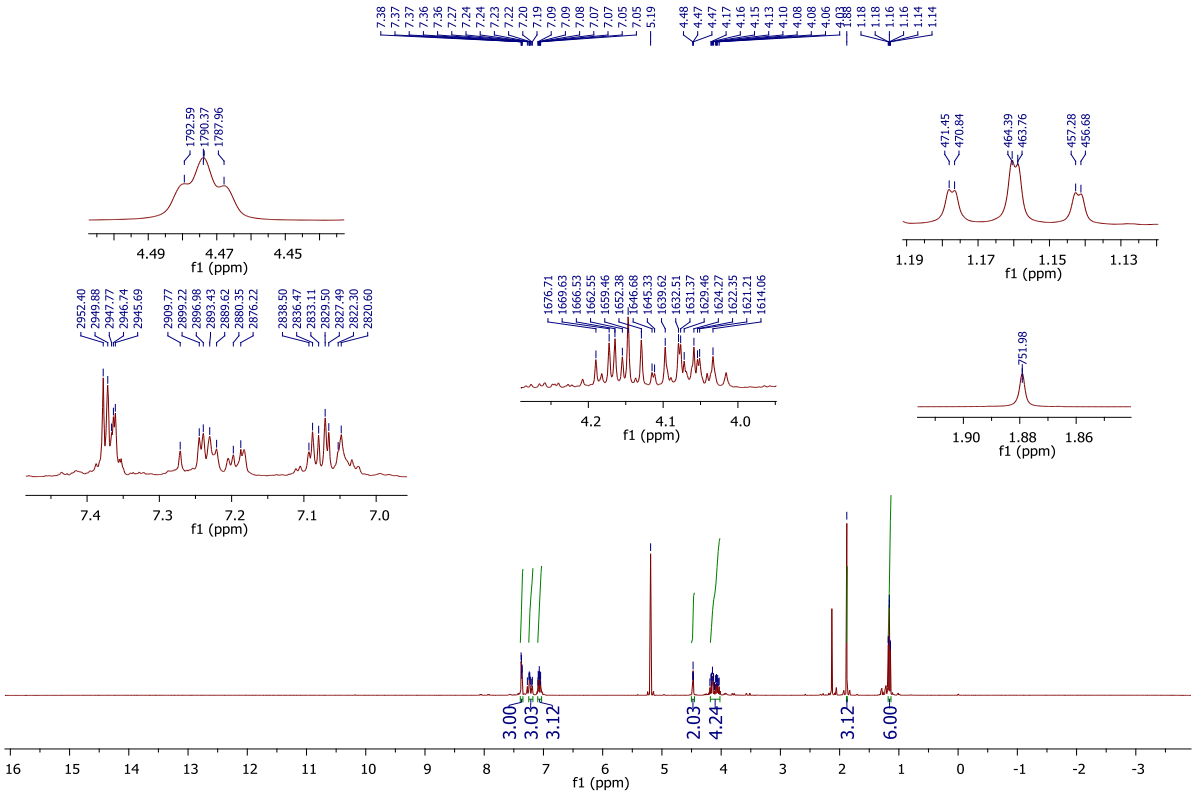
^{31}P NMR



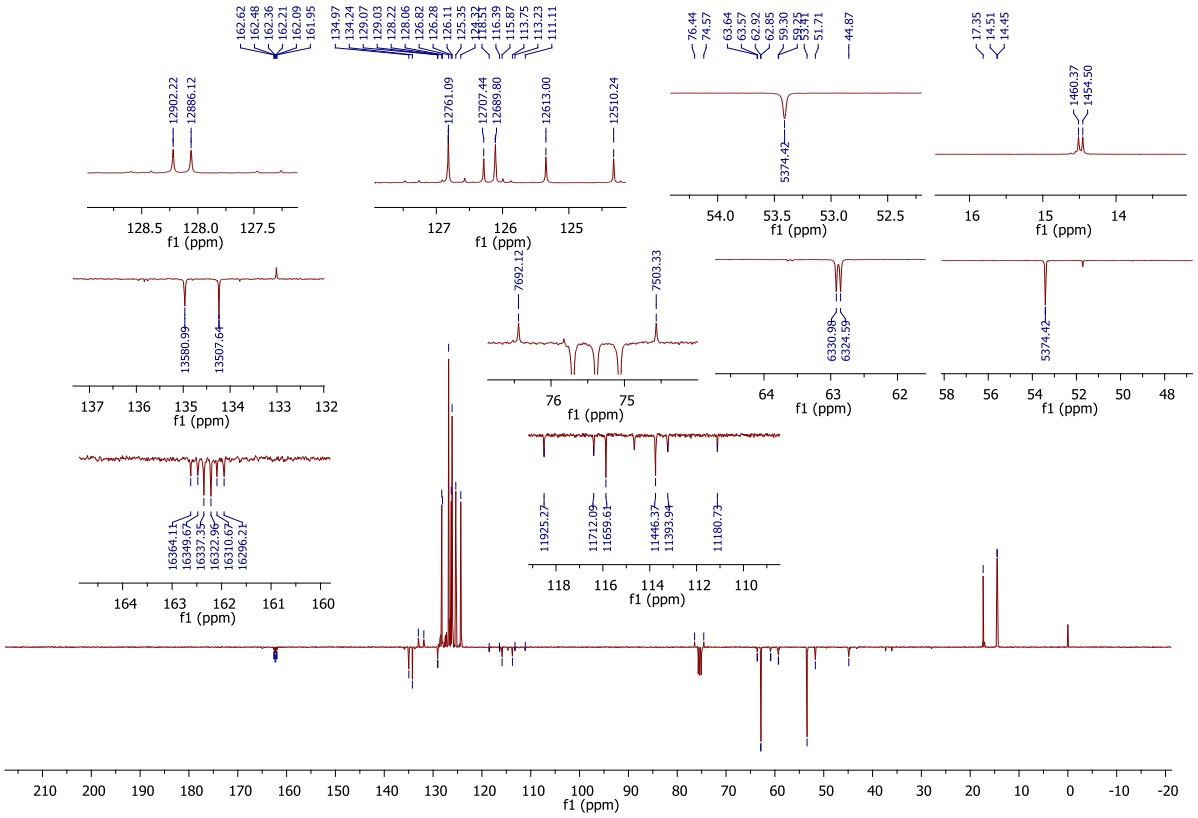
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR


162.62
162.48
162.36
162.21
162.09
161.95
134.97
134.24
129.07
129.03
128.22
128.06
126.82
126.28
126.11
125.35
124.32
116.39
115.87
113.75
113.23
111.11
76.44
74.57
63.64
63.57
62.92
62.85
59.30
59.25
53.41
51.71
44.87
17.35
14.51
14.45
12902.22
12886.12
12761.09
12707.44
12689.80
12613.00
12510.24
5374.42
1460.37
1454.50
13580.99
13507.64
7692.12
7503.33
6330.98
6324.59
5374.42
16364.11
16349.67
16337.35
16322.96
16310.67
16296.21
11925.27
11712.09
11659.61
11446.37
11393.94
11180.73
f1 (ppm)

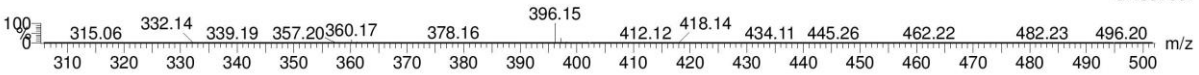
HRMS

Elemental Composition Report **Page 1**

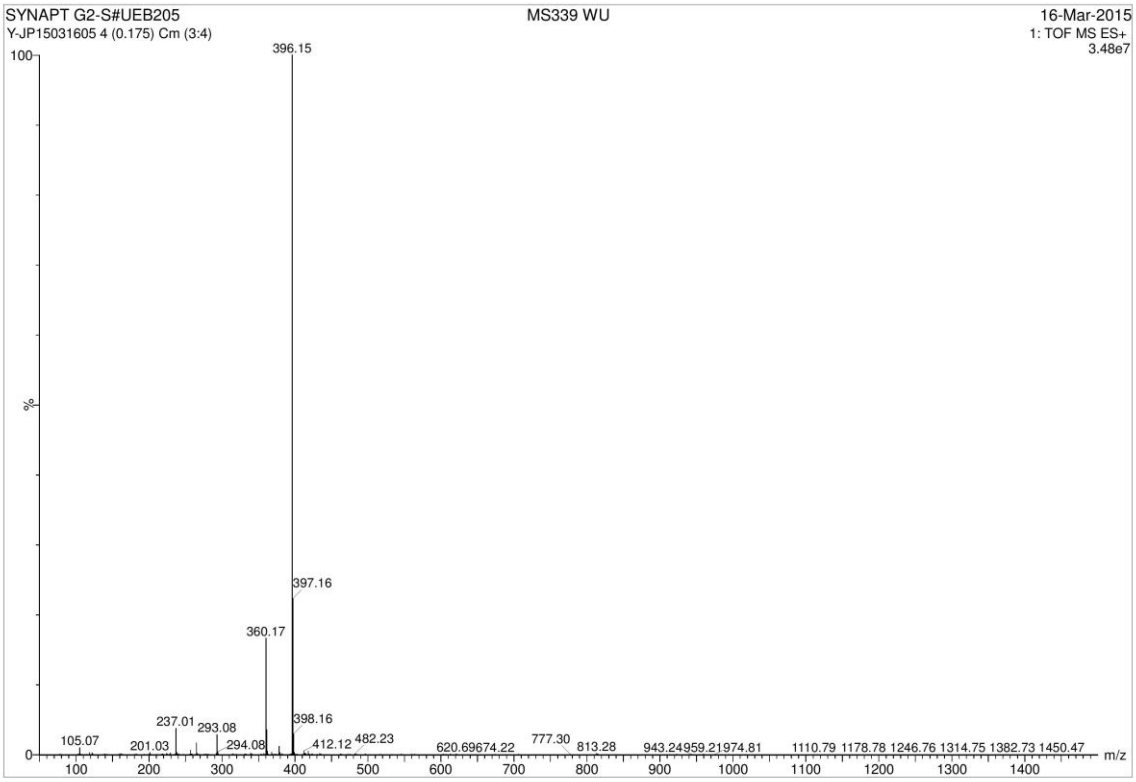
Single Mass Analysis
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
664 formula(e) evaluated with 2 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 F: 2-2 P: 1-1

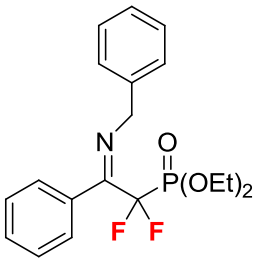
SYNAPT G2-S#UEB205 MS339 WU 16-Mar-2015
Y-JP15031605 4 (0.175) Cm (3:4) 1: TOF MS ES+
3.48e+007



Minimum:				-1.5				
Maximum:		1.0	2.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
396.1540	396.1540	0.0	0.0	8.5	1992.0	0.000	100.00	C20 H25 N O3 F2 P
	396.1545	-0.5	-1.3	1.5	2015.5	23.474	0.00	C5 H21 N13 O4 F2 P

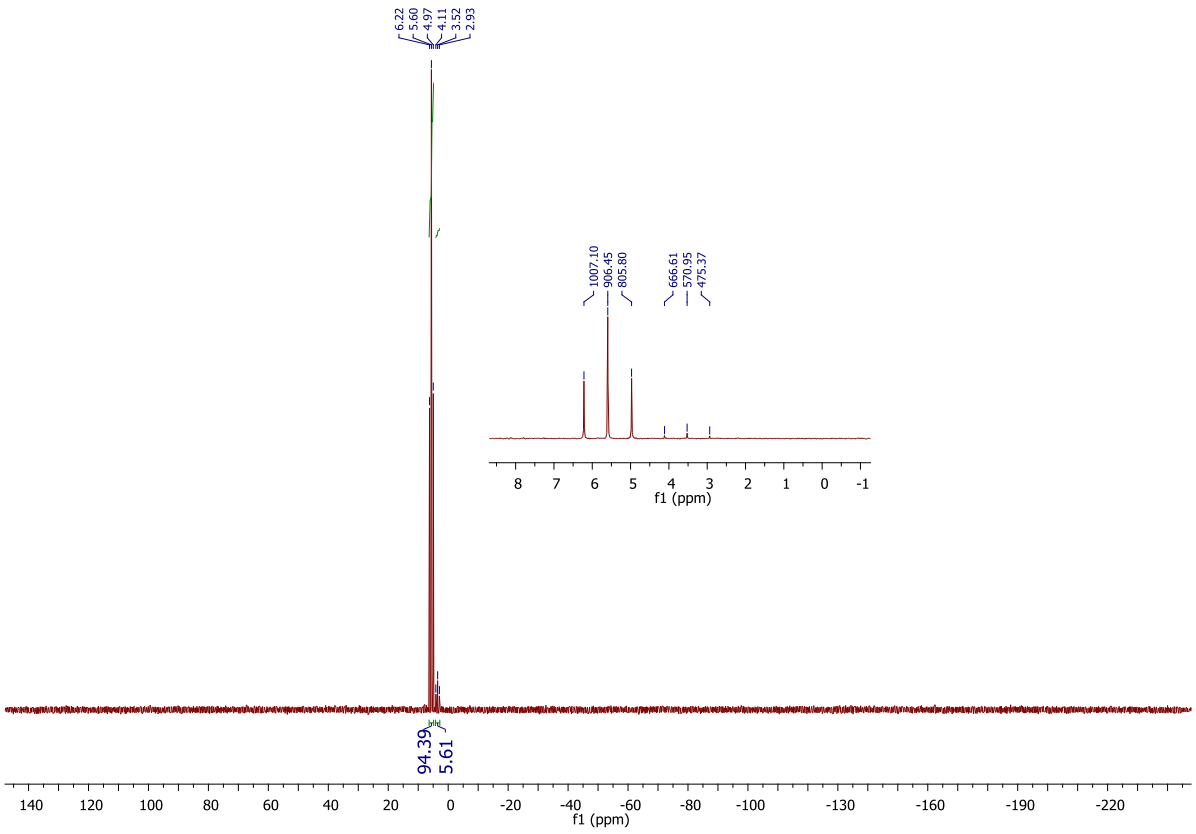


(*Z*)-diethyl (2-(benzylimino)-1,1-difluoro-2-phenylethyl)phosphonate 14e

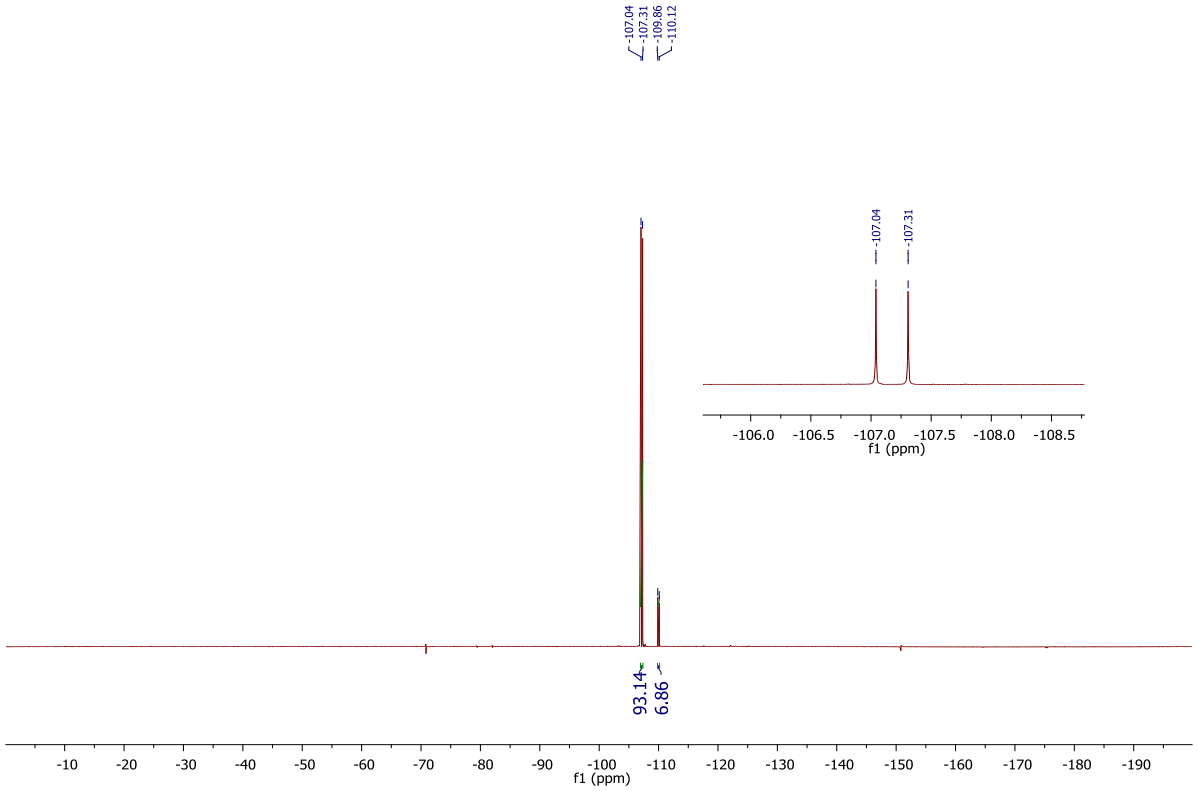


14e

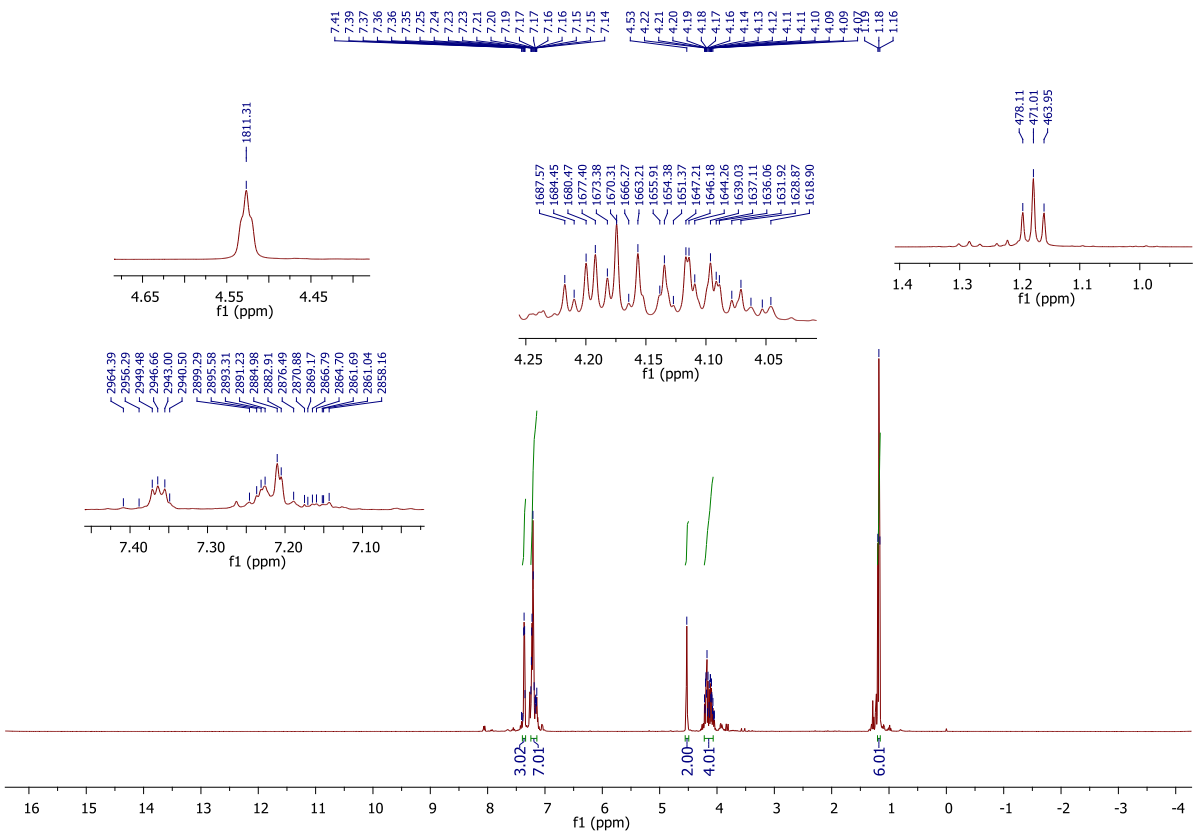
^{31}P NMR



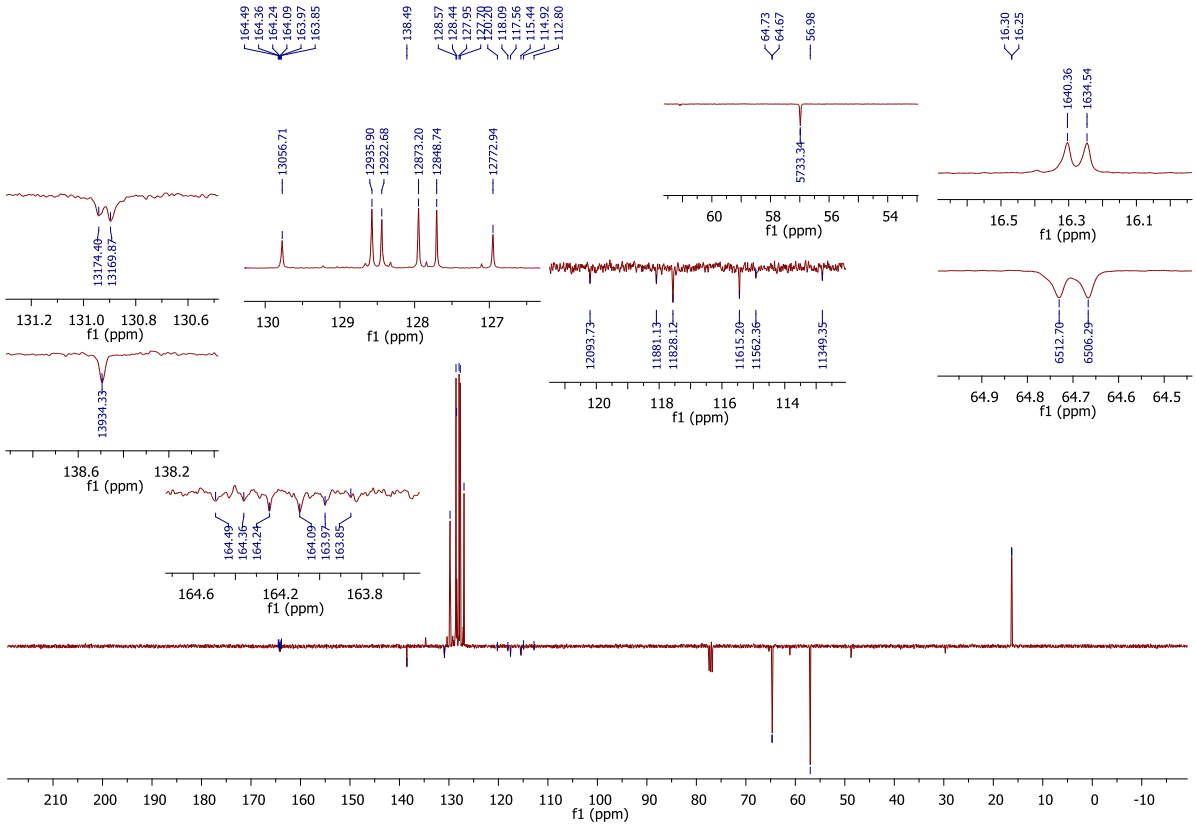
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



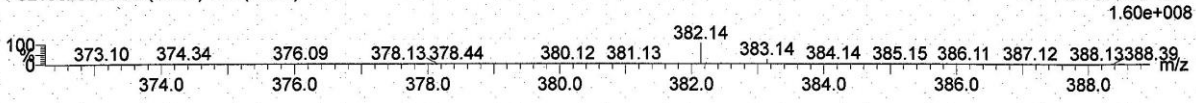
HRMS

Elemental Composition Report **Page 1**

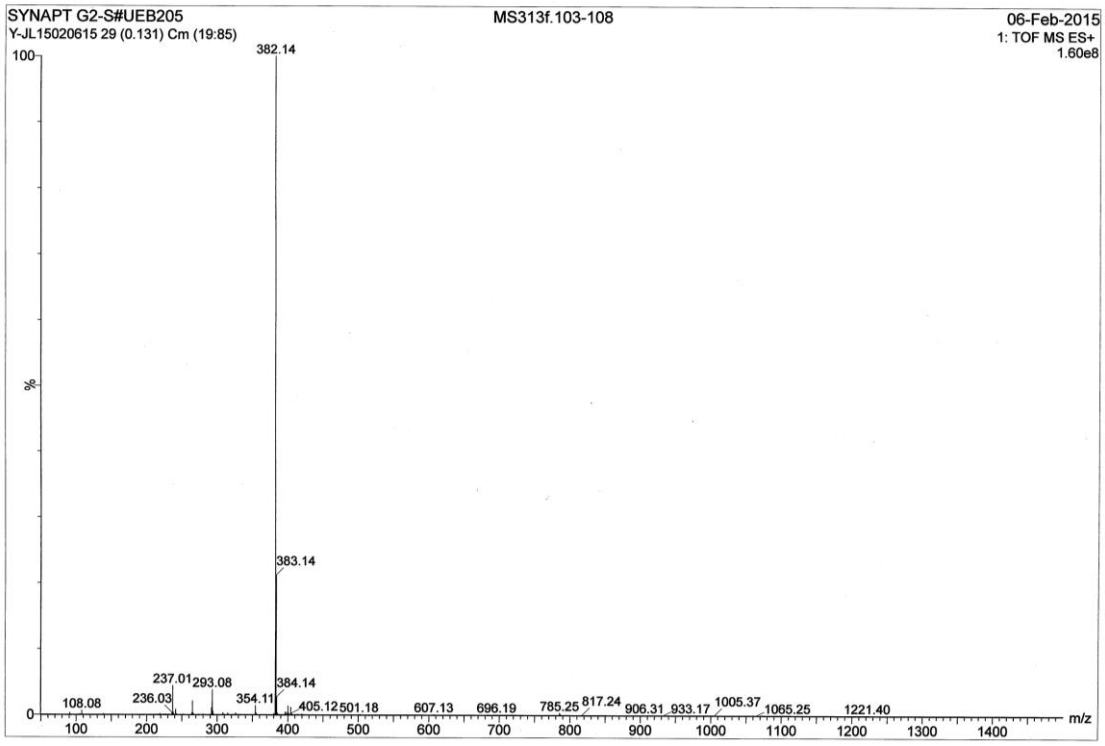
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1662 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

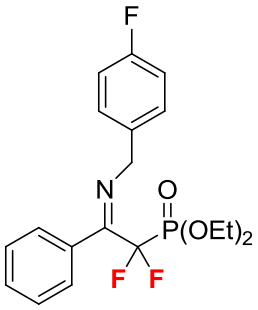
SYNAPT G2-S#UEB205 MS313f.103-108 06-Feb-2015
Y-JL15020615 29 (0.131) Cm (19:85) 1: TOF MS ES+
1.60e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
382.1384	382.1384	0.0	0.0	8.5	3297.8	n/a	n/a	C19 H23 N O3 F2 P

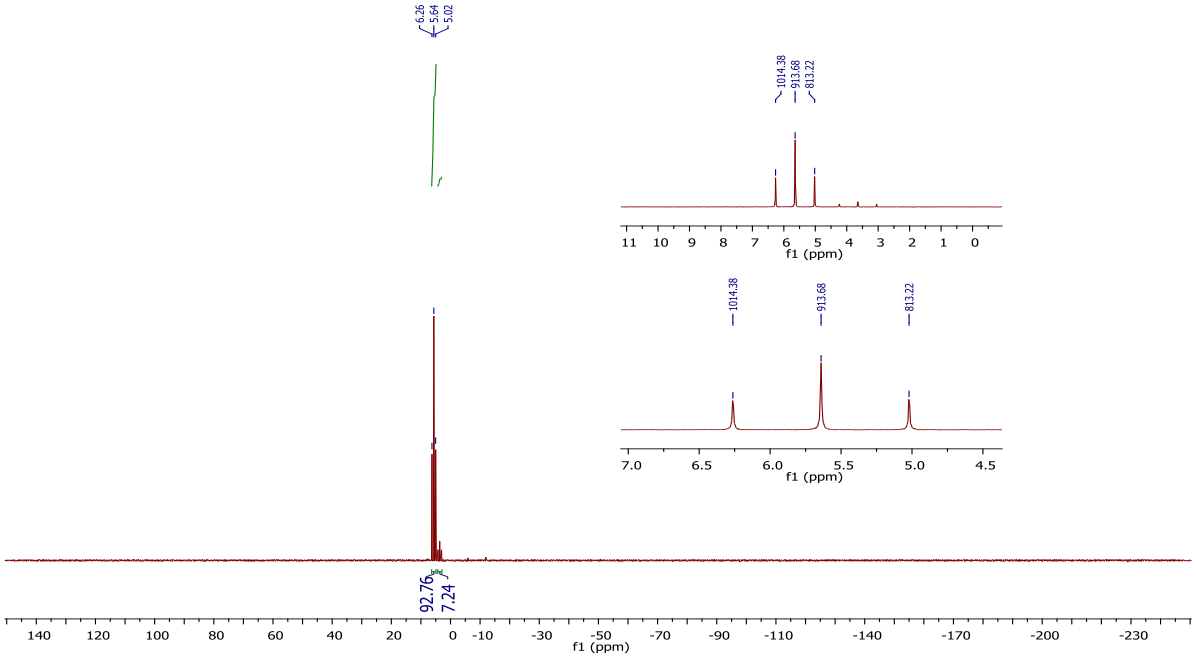

SYNAPT G2-S#UEB205
Y-JL15020615 29 (0.131) Cm (19:85)
MS313f.103-108
06-Feb-2015
1: TOF MS ES+
1.60e8
100
%
0
382.14
383.14
384.14
237.01
293.08
108.08
236.03
354.11
405.12
501.18
607.13
696.19
785.25
817.24
906.31
933.17
1005.37
1065.25
1221.40
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z

(*Z*)-diethyl (1,1-difluoro-2-((4-fluorobenzyl)imino)-2-phenylethyl) phosphonate 14f



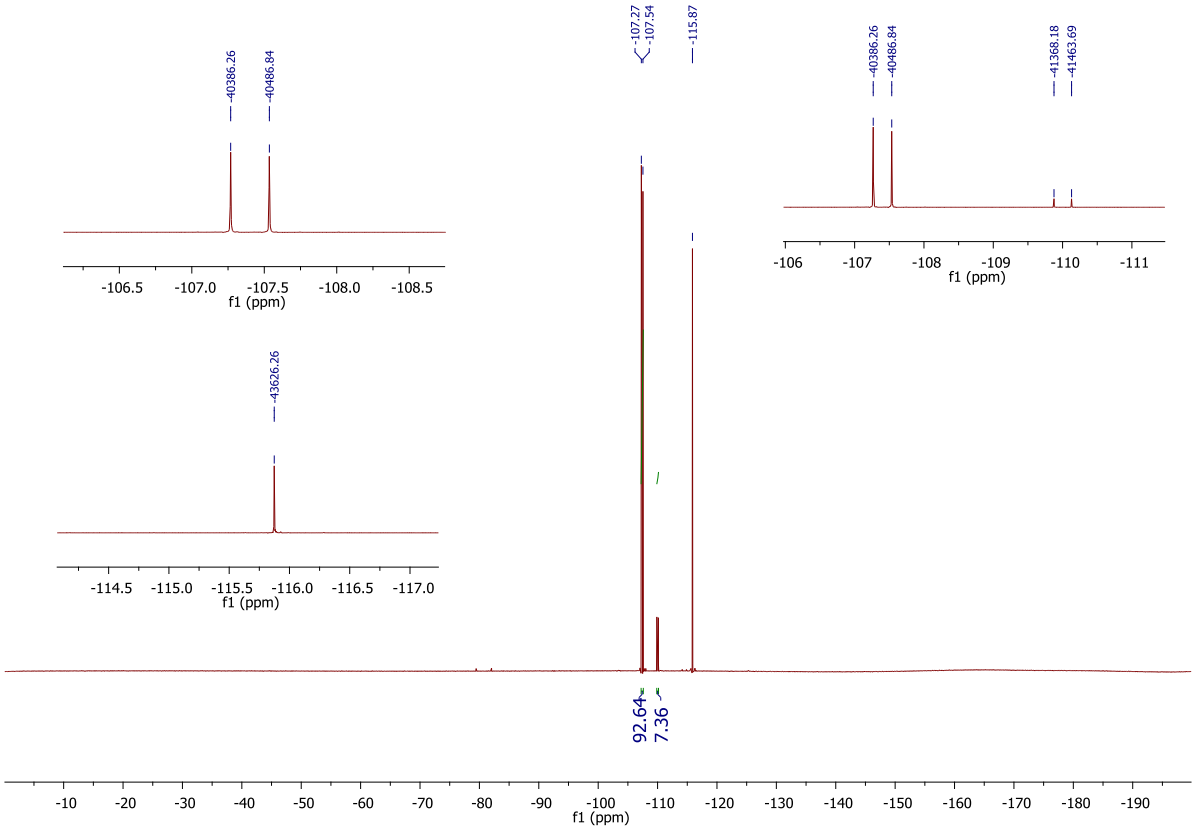
14f

^{31}P NMR

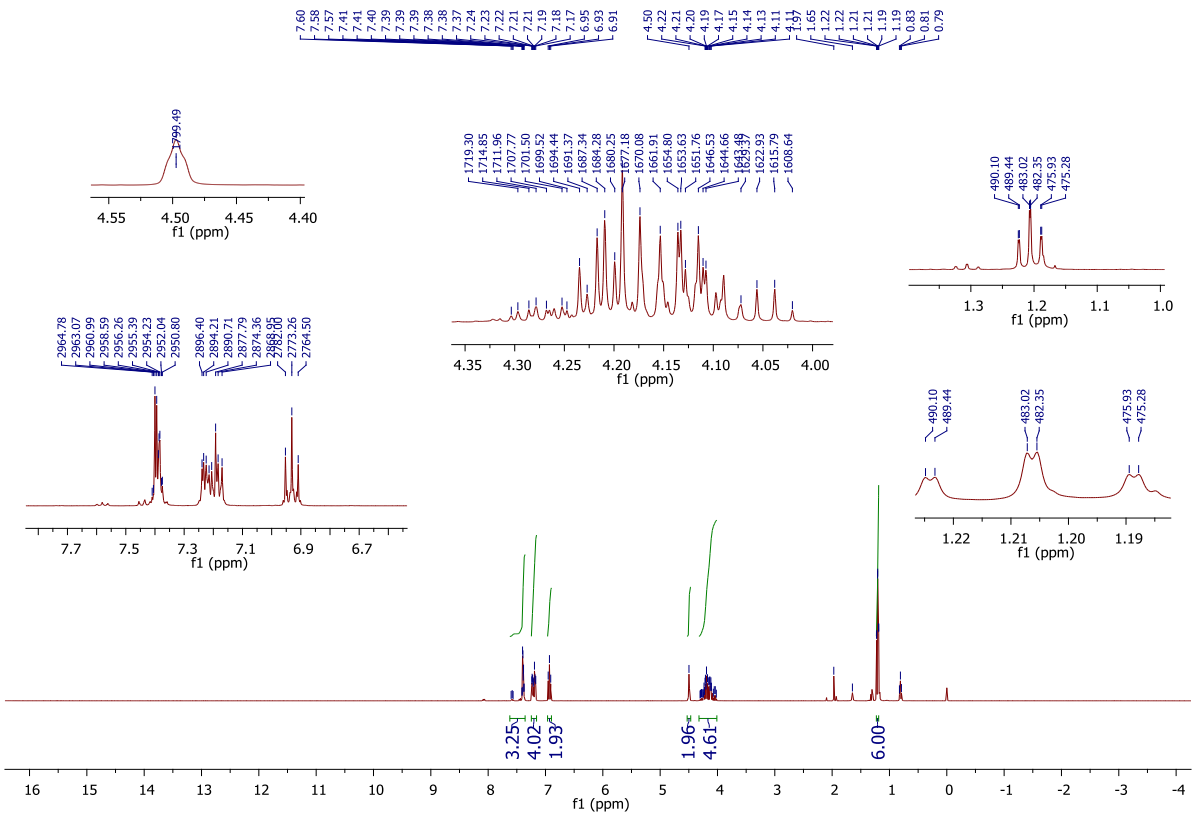


^{19}F NMR

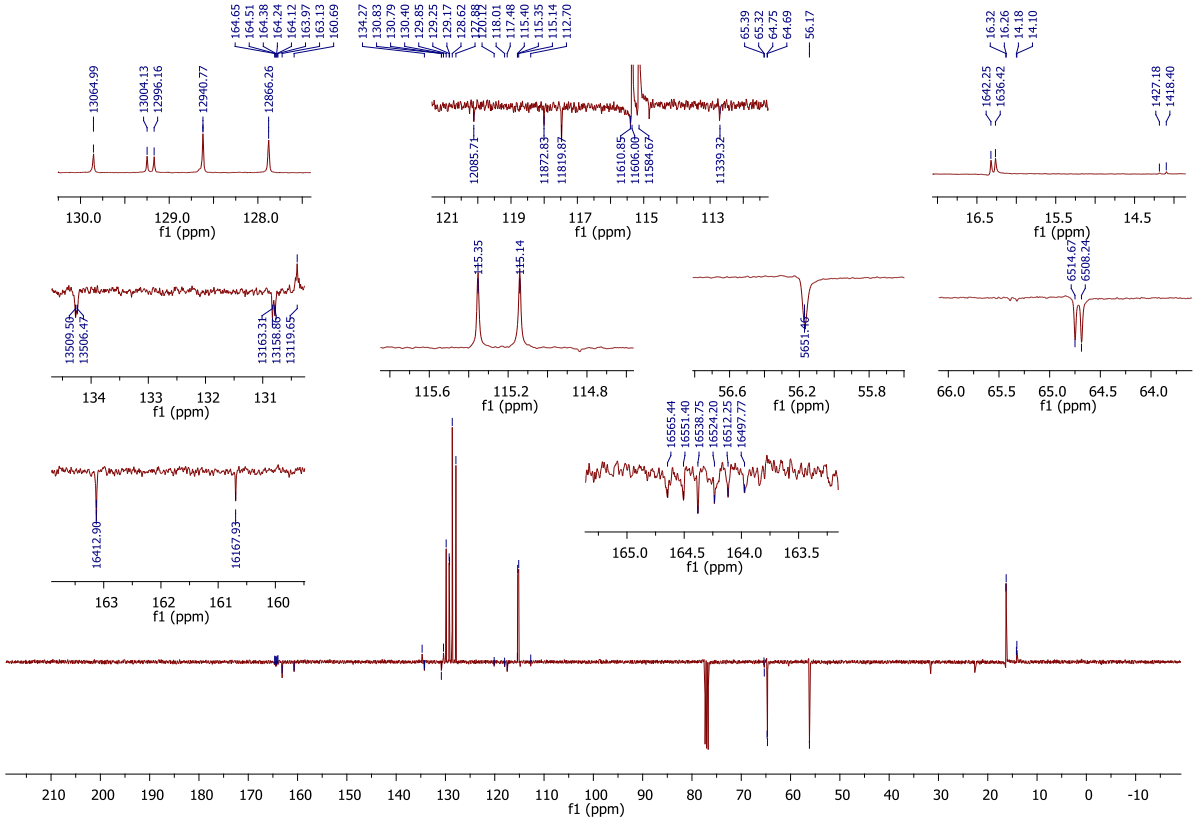
{H}



^{1}H NMR



^{13}C NMR


164.65
164.51
164.38
164.24
164.12
163.97
163.13
160.69
134.27
130.83
130.79
130.40
129.85
129.25
129.17
128.62
127.88
120.12
118.01
117.48
115.40
115.35
115.14
112.70
65.39
65.32
64.75
64.69
56.17
16.32
16.26
14.18
14.10
13064.99
13004.13
12996.16
12940.77
12866.26
12085.71
11872.83
11819.87
11610.85
11606.09
11584.67
11339.32
1642.25
1636.42
1427.18
1418.40
f1 (ppm)

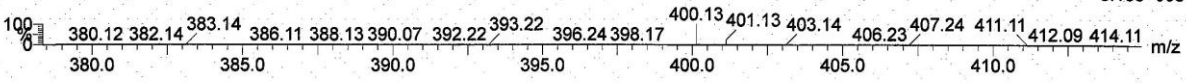
HRMS

Elemental Composition Report **Page 1**

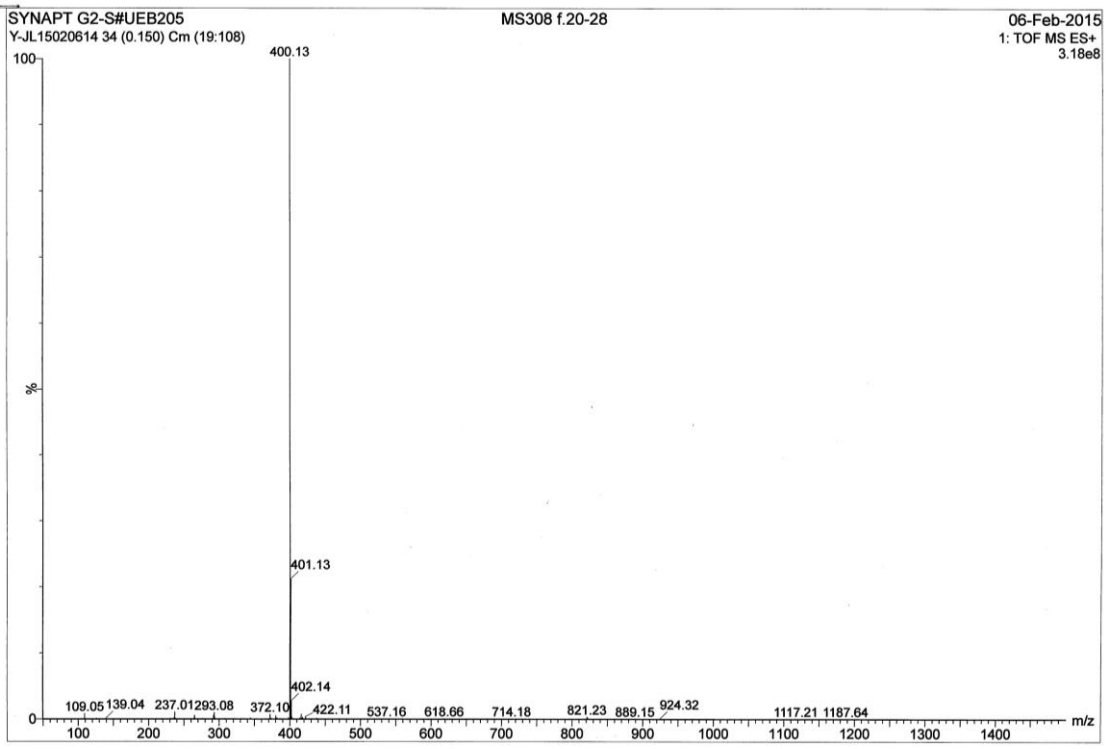
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1936 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

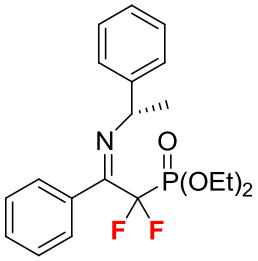
SYNAPT G2-S#UEB205 MS308 f.20-28 06-Feb-2015
Y-JL15020614 34 (0.150) Cm (19:108) 1: TOF MS ES+
3.18e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
400.1291	400.1289	0.2	0.5	8.5	3525.0	n/a	n/a	C19 H22 N O3 F3 P

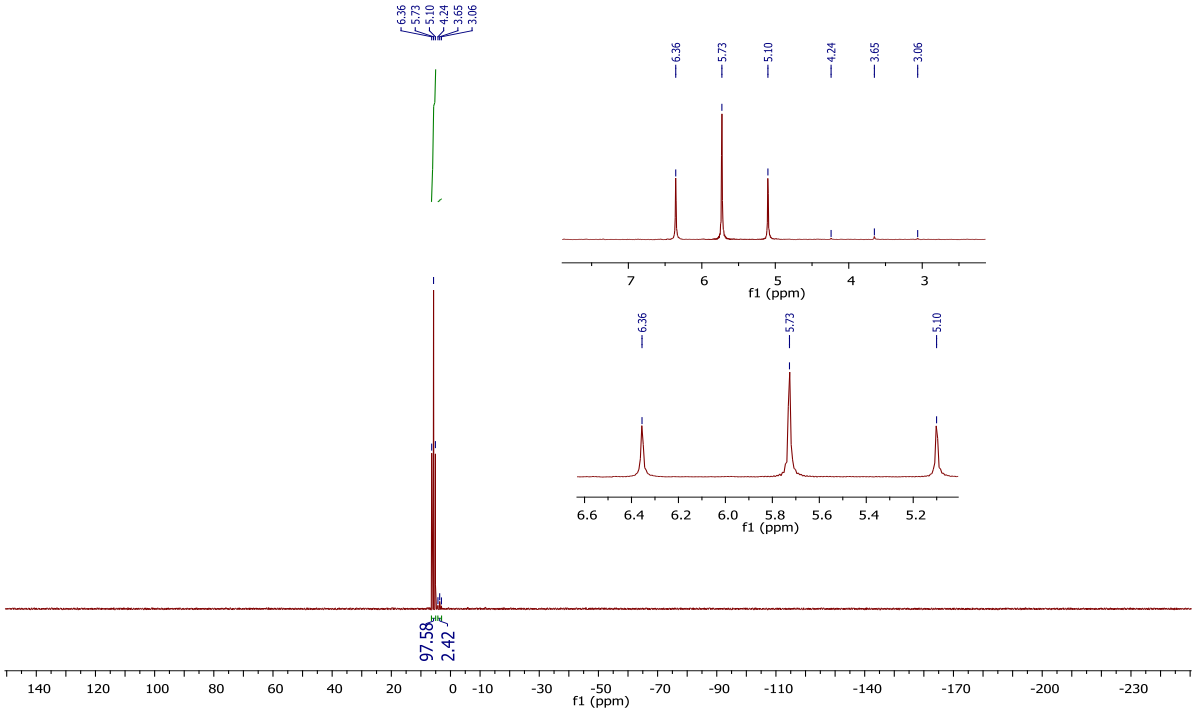


(*S,Z*)-diethyl (1,1-difluoro-2-phenyl-2-((1-phenylethyl)imino)ethyl) phosphonate 14g

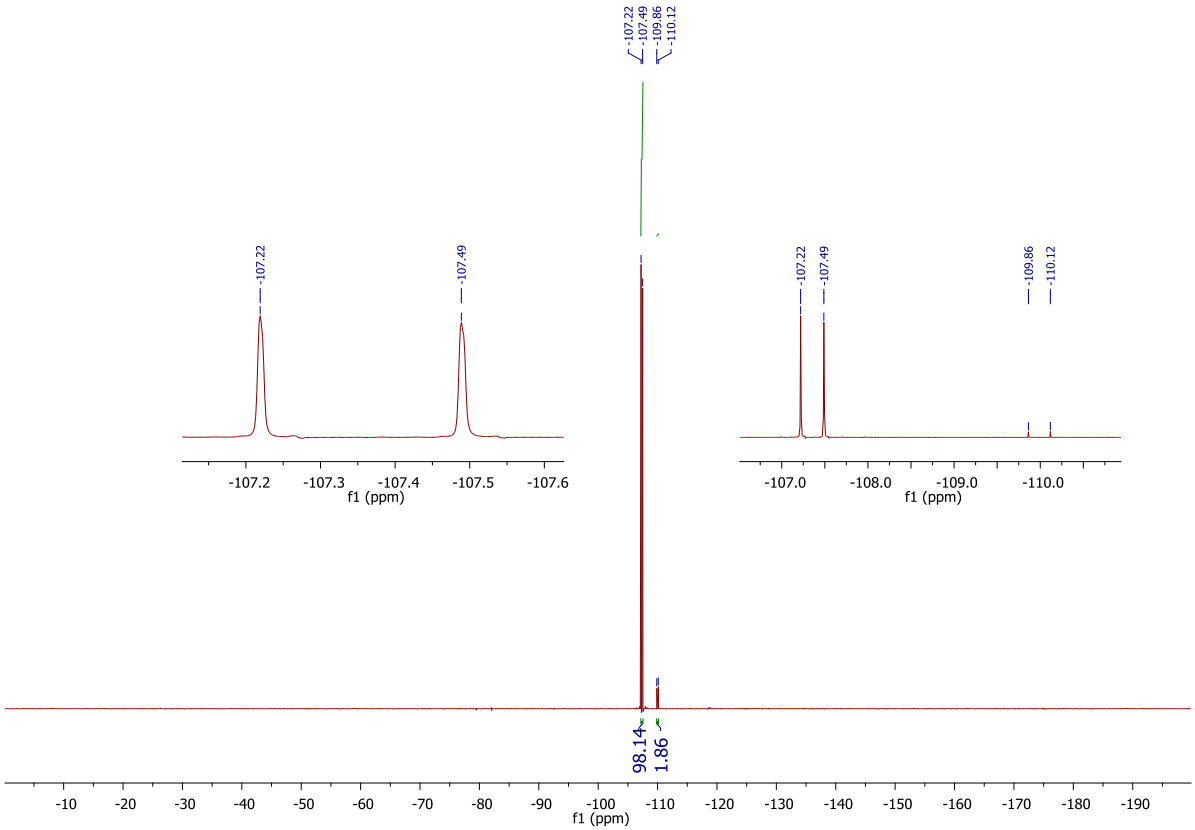


14g

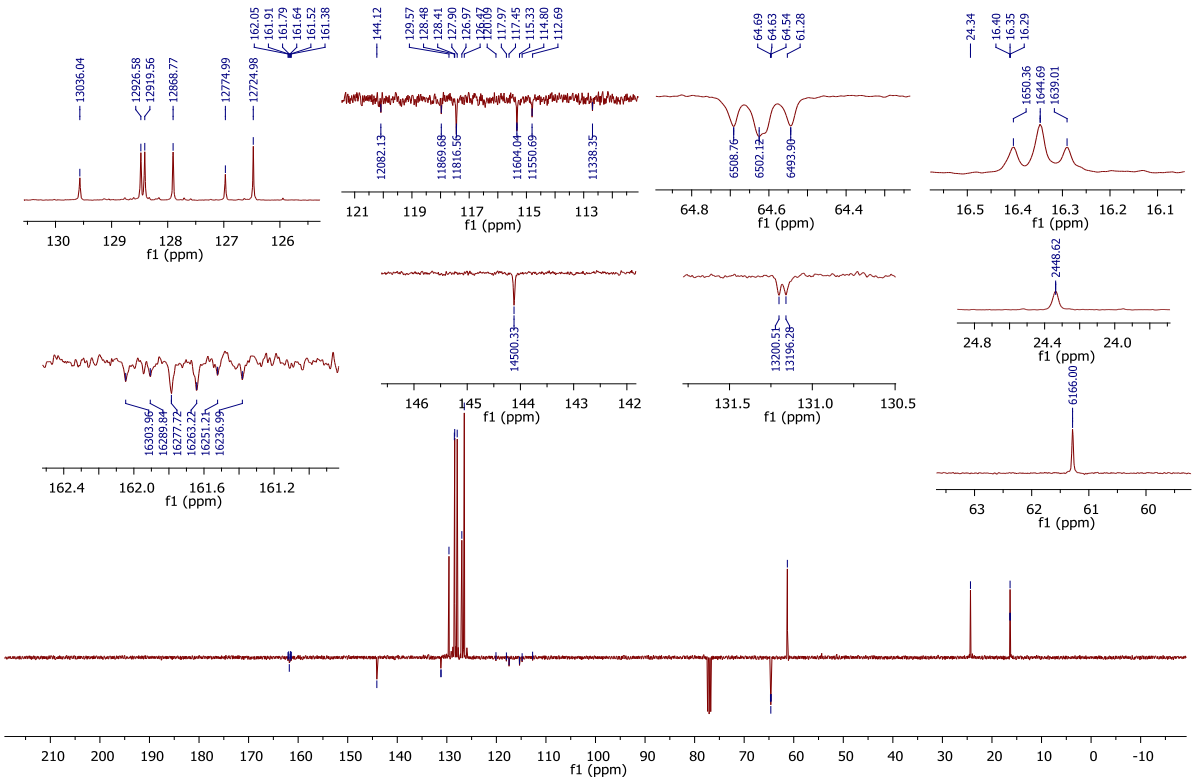
^{31}P NMR



^{19}F NMR {H}



^{1}H NMR



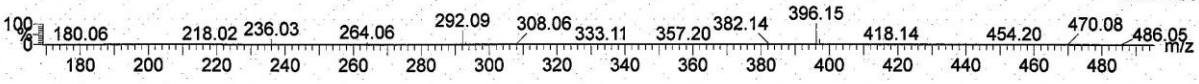
HRMS

Elemental Composition Report **Page 1**

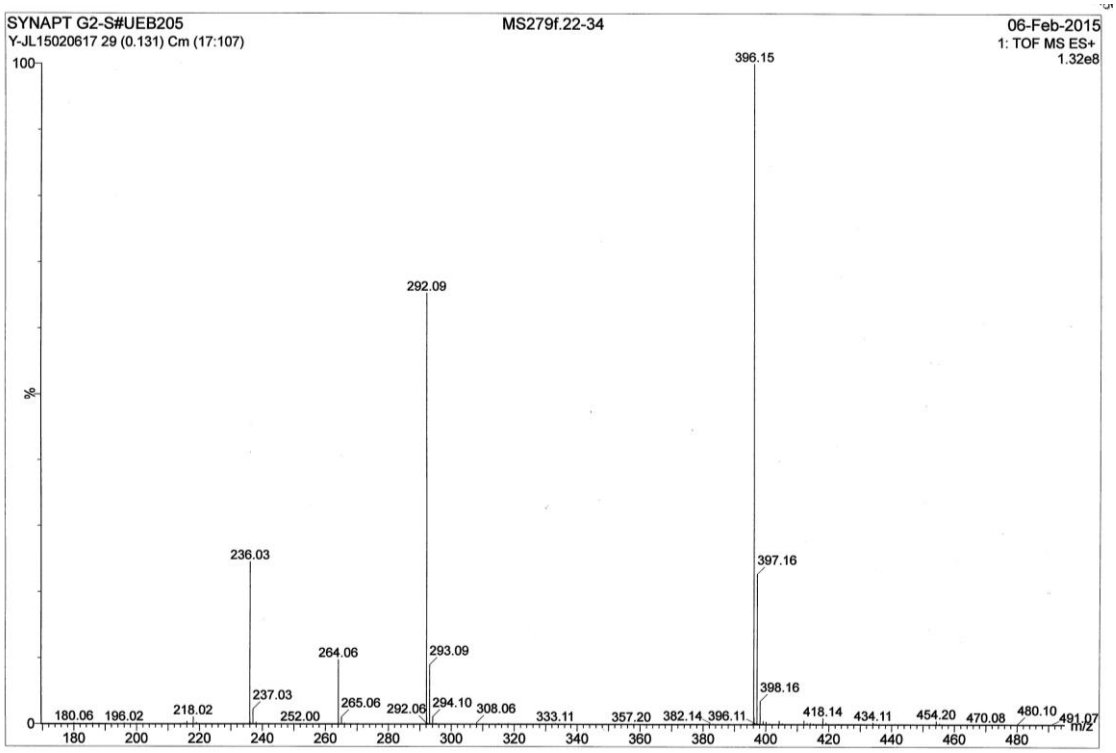
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1869 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

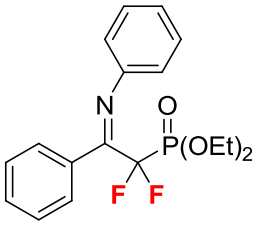
SYNAPT G2-S#UEB205 MS279f.22-34 06-Feb-2015
Y-JL15020617 29 (0.131) Cm (17:107) 1: TOF MS ES+
1.32e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
396.1537	396.1540	-0.3	-0.8	8.5	3253.3	0.000	100.00	C20 H25 N O3 F2 P
	396.1534	0.3	0.8	5.5	3267.9	14.548	0.00	C8 H20 N13 O3 F P

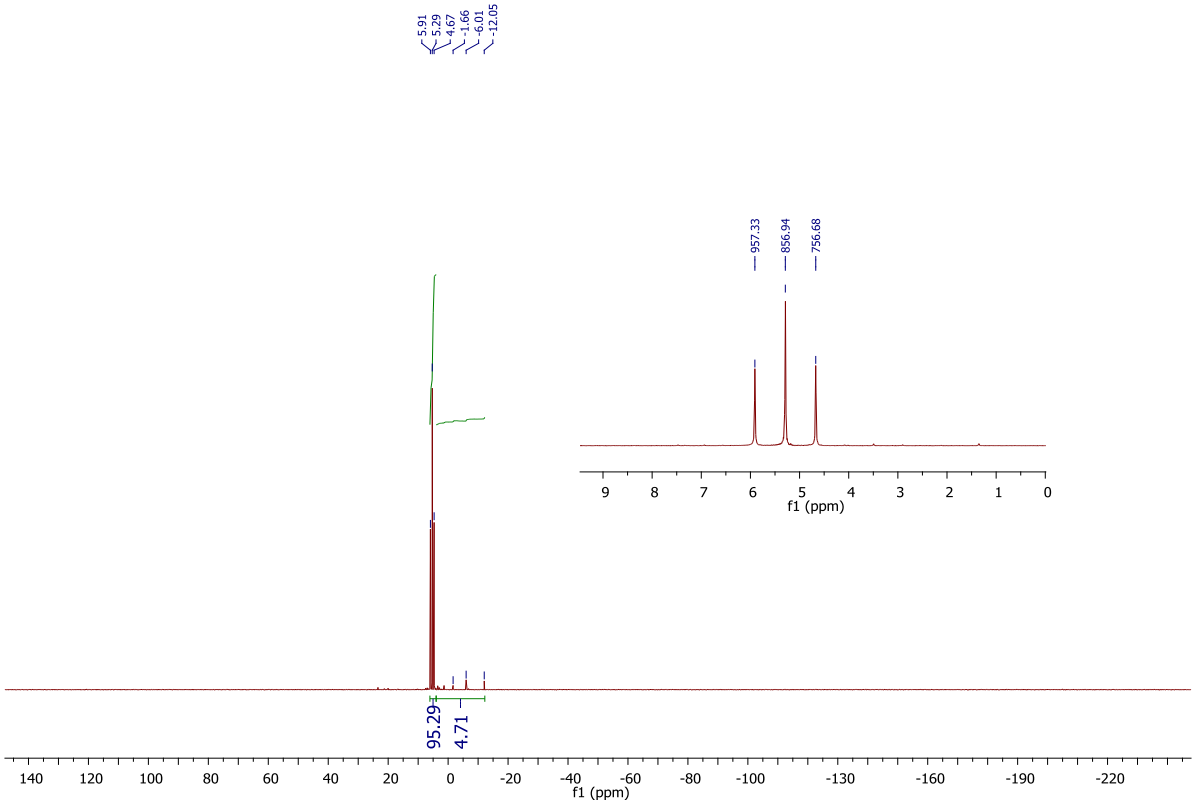


(*Z*)-diethyl (1,1-difluoro-2-phenyl-2-(phenylimino)ethyl)phosphonate 14h

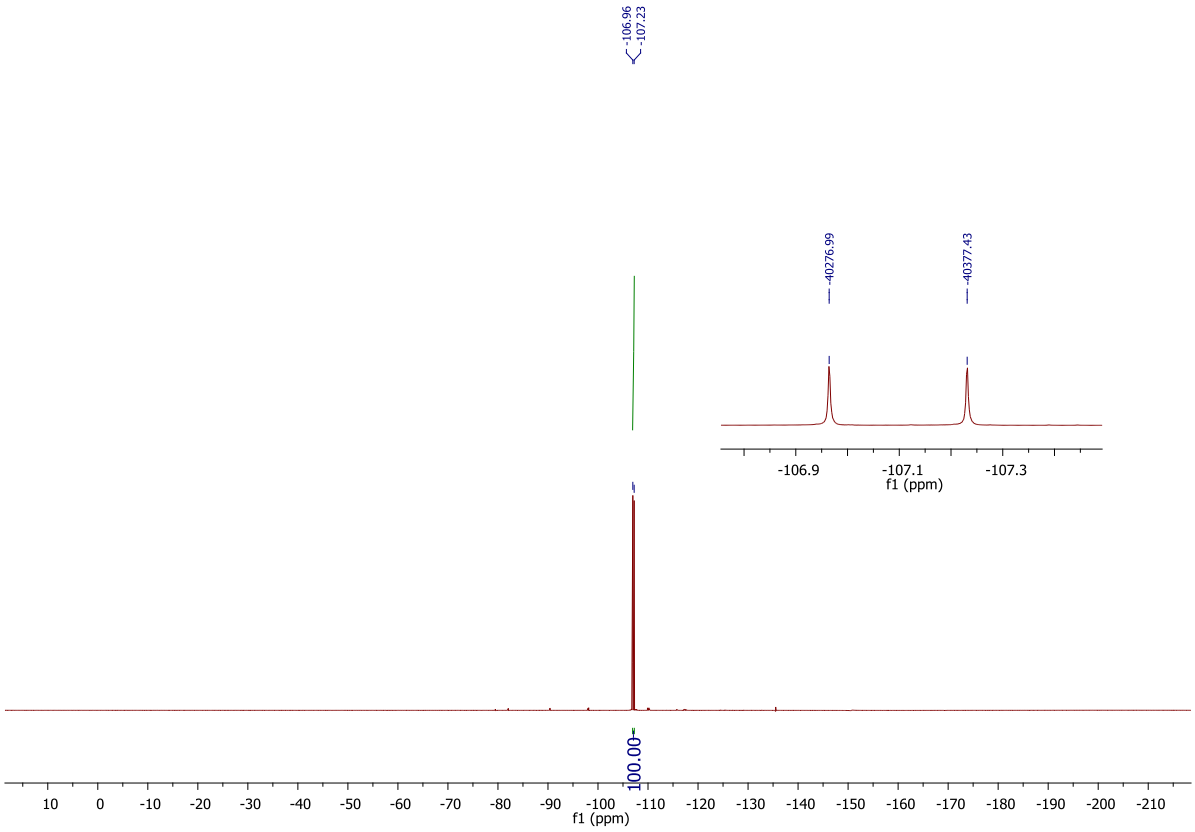


14h

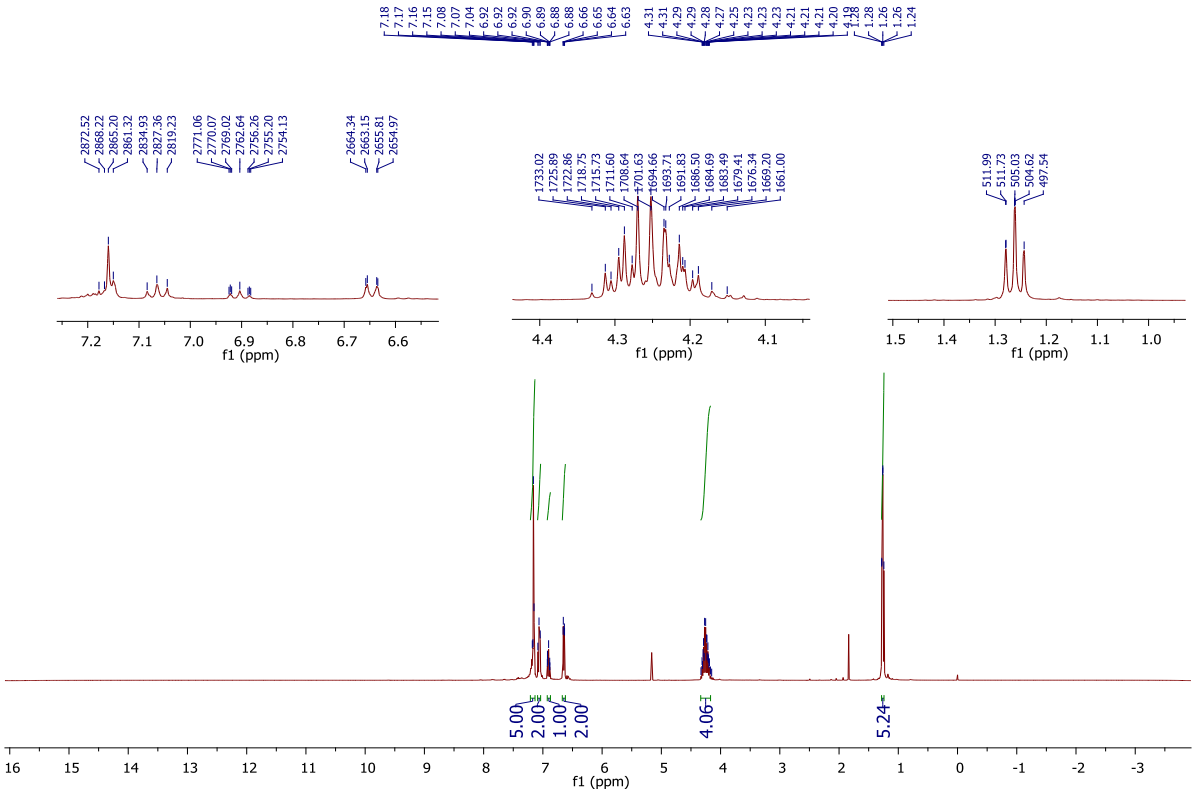
^{31}P NMR



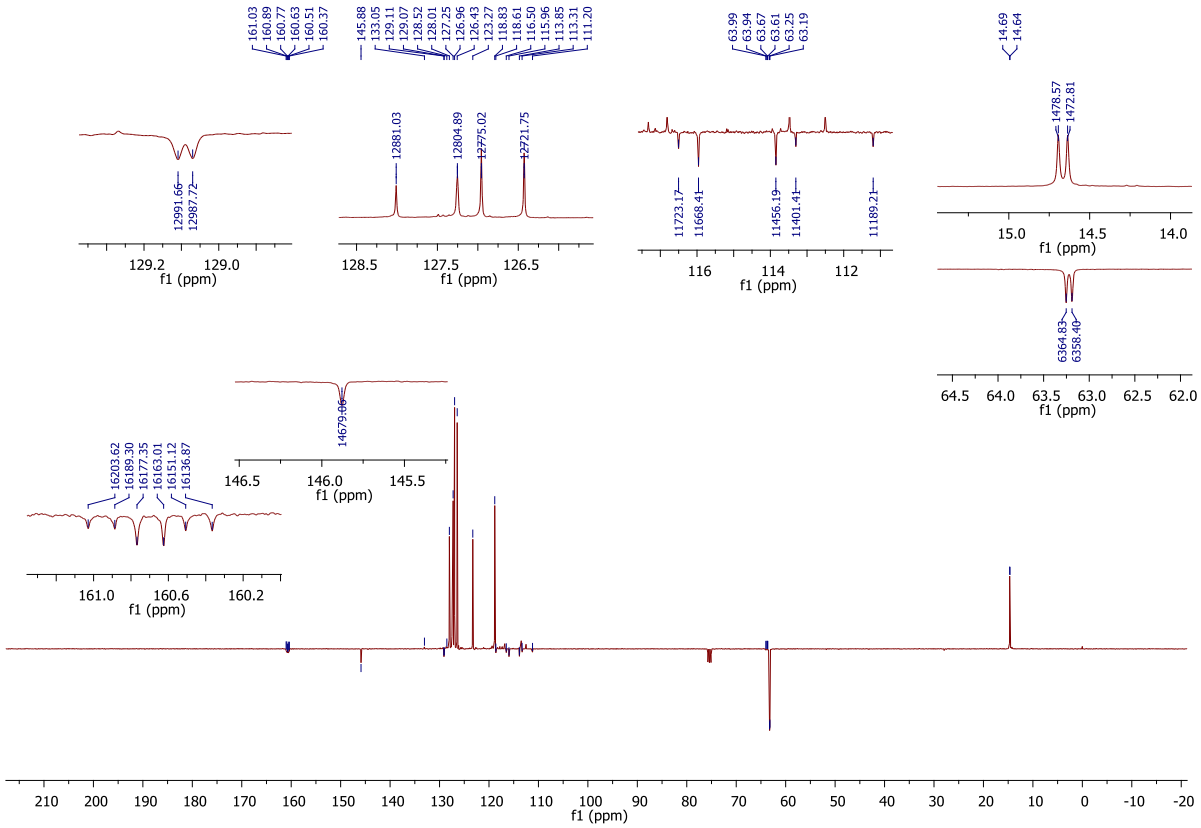
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



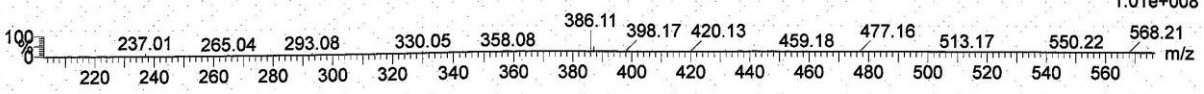
HRMS

Elemental Composition Report **Page 1**

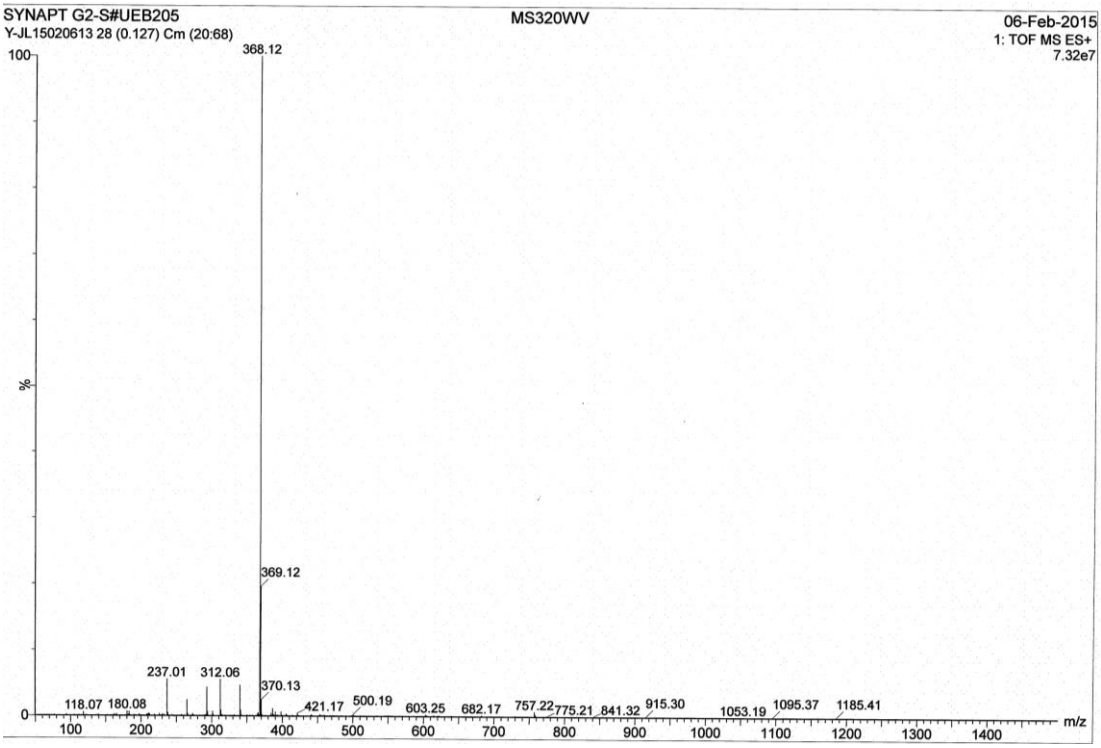
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1724 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

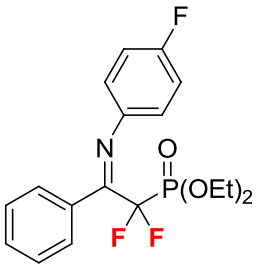
SYNAPT G2-S#UEB205 MS303 f.11-15 06-Feb-2015
Y-JL15020612 28 (0.127) Cm (19:64) 1: TOF MS ES+
1.01e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
386.1136	386.1133	0.3	0.8	8.5	3065.7	n/a	n/a	C18 H20 N O3 F3 P

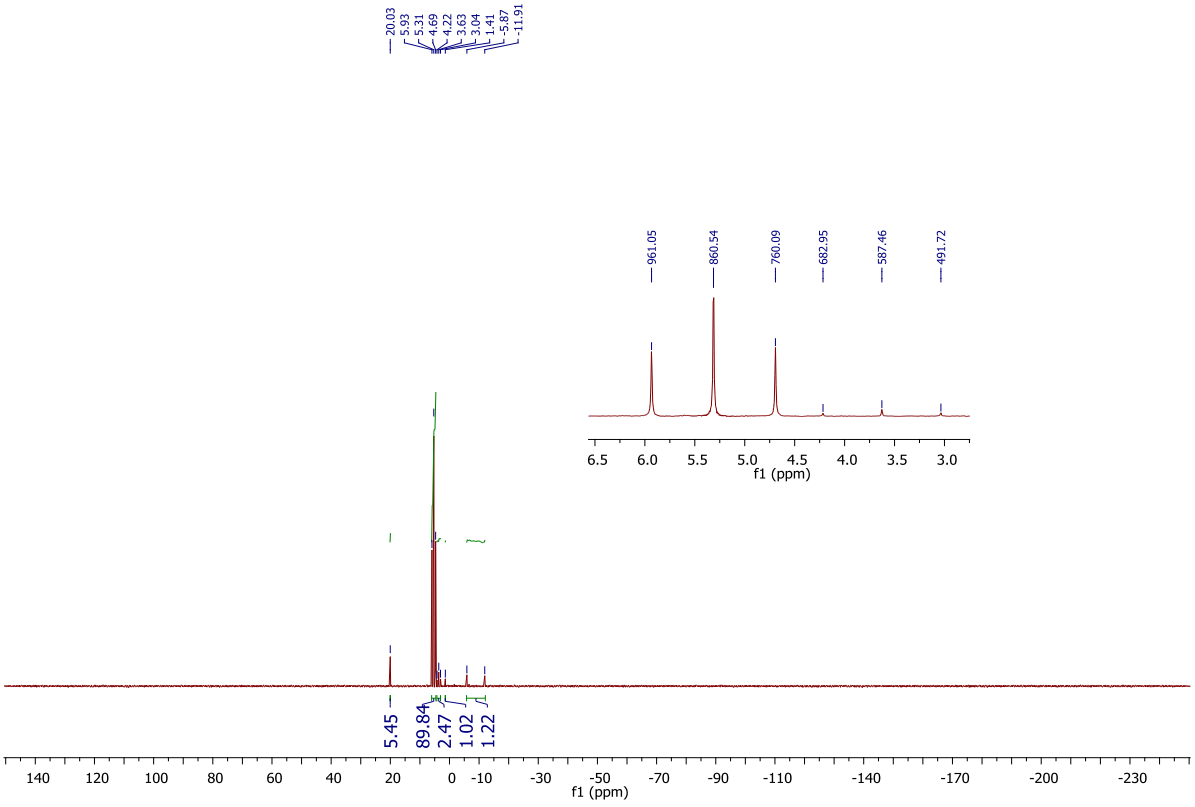

SYNAPT G2-S#UEB205
Y-JL15020613 28 (0.127) Cm (20:68)
MS320WV
06-Feb-2015
1: TOF MS ES+
7.32e7
100
%
0
368.12
369.12
237.01
312.06
370.13
118.07
180.08
421.17
500.19
603.25
682.17
757.22
775.21
841.32
915.30
1053.19
1095.37
1185.41
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z

(*Z*)-diethyl (1,1-difluoro-2-((4-fluorophenyl)imino)-2-phenylethyl) phosphonate 14i

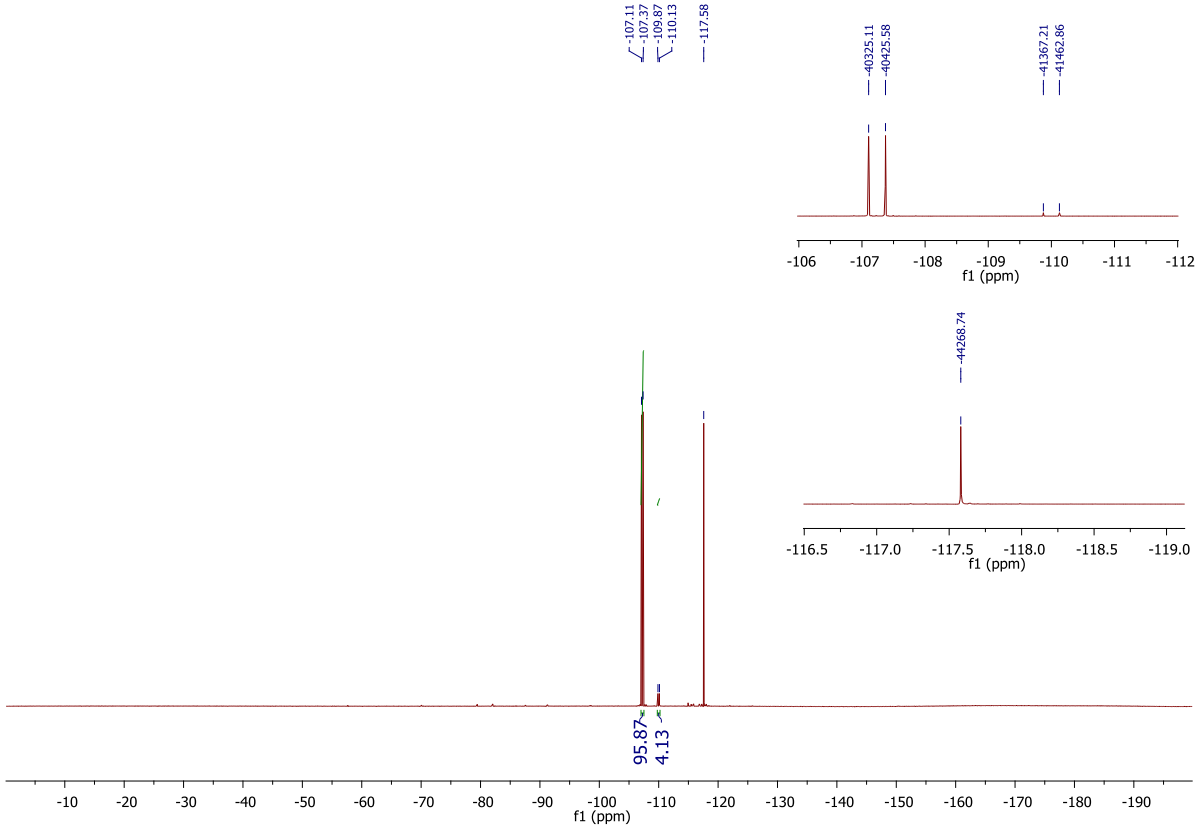


14i

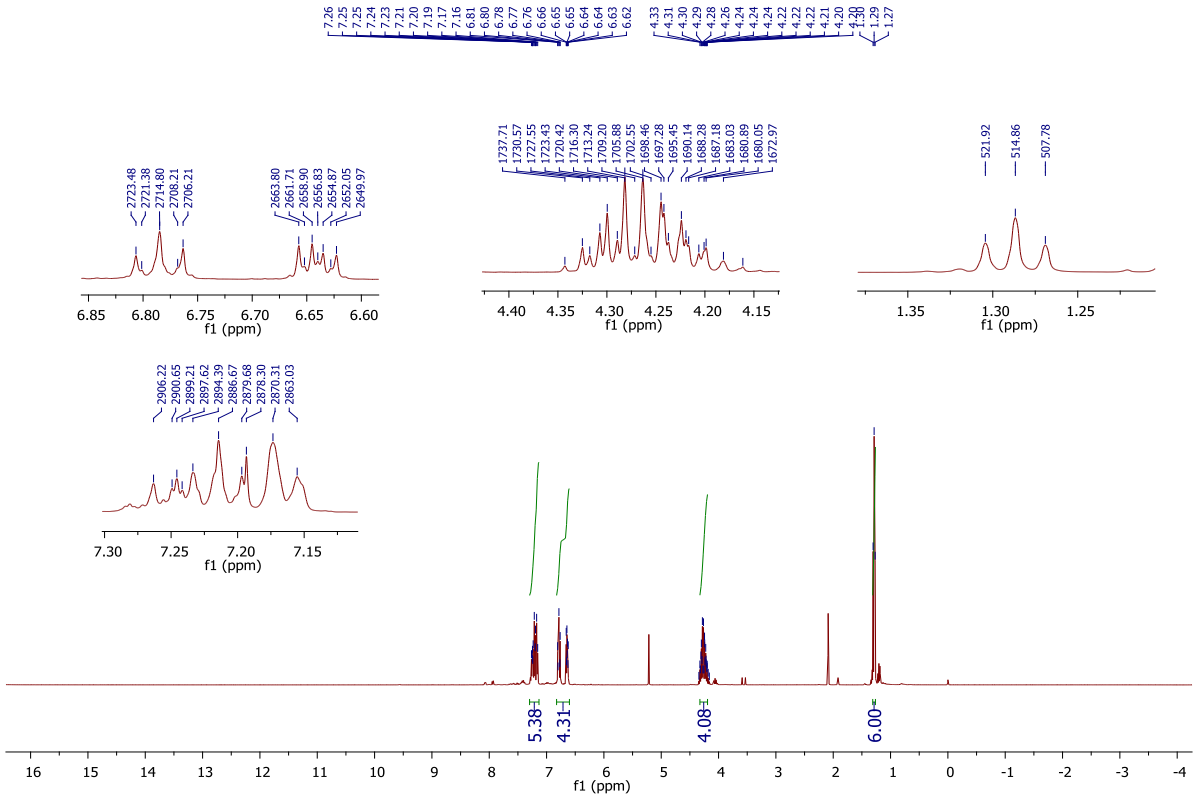
^{31}P NMR



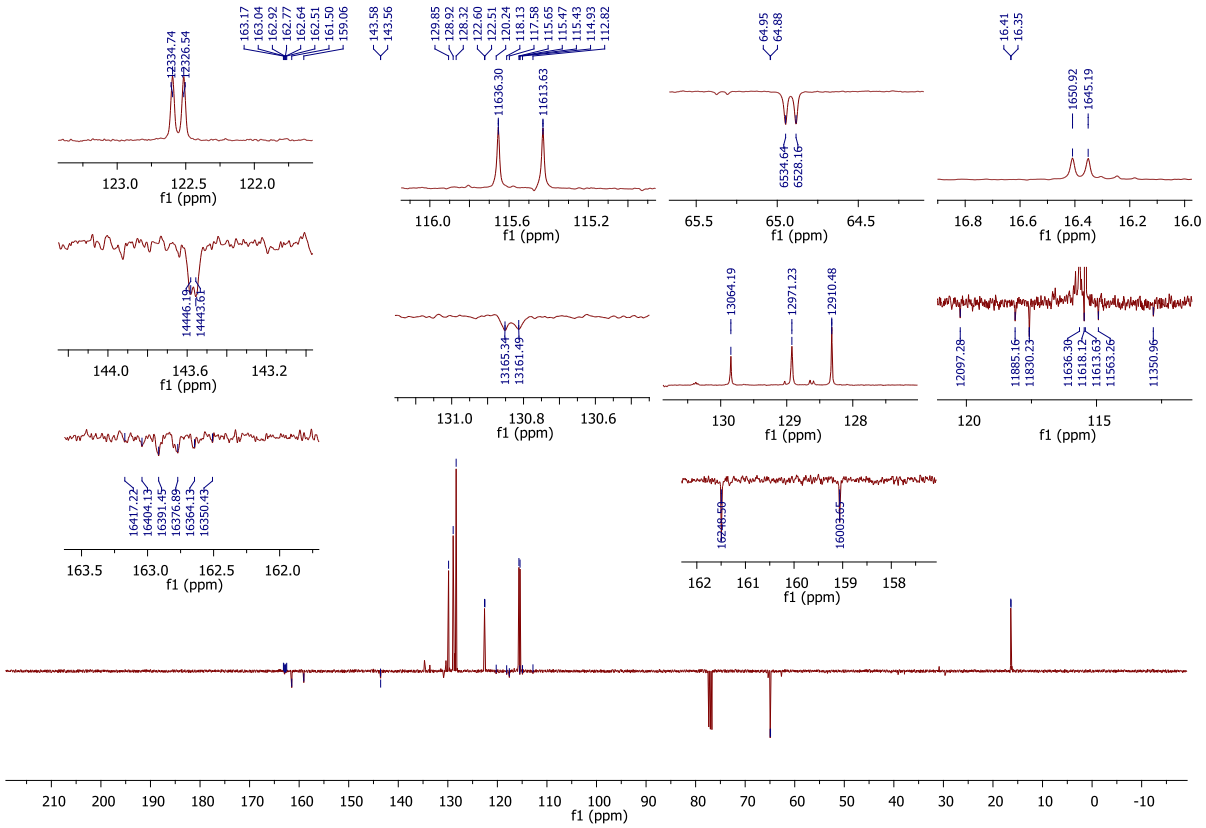
^{19}F NMR {H}



^{1}H NMR



^{31}C NMR



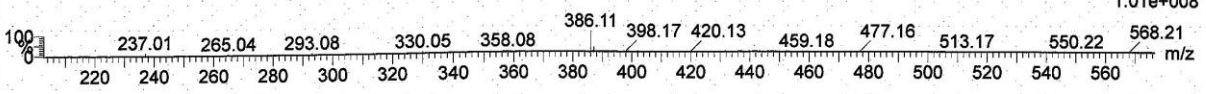
HRMS

Elemental Composition Report **Page 1**

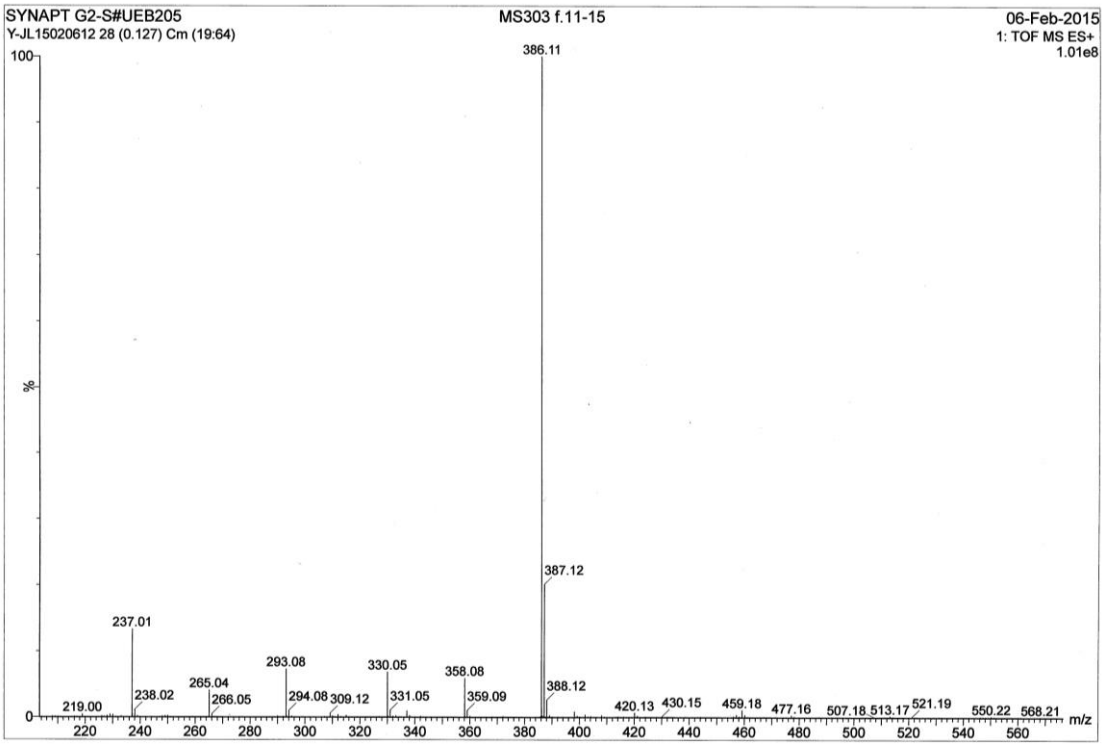
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1724 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

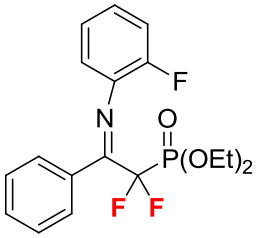
SYNAPT G2-S#UEB205 MS303 f.11-15 06-Feb-2015
Y-JL15020612 28 (0.127) Cm (19:64) 1: TOF MS ES+
1.01e+008



Minimum:		5.0	1.0	-1.5				
Maximum:				50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
386.1136	386.1133	0.3	0.8	8.5	3065.7	n/a	n/a	C18 H20 N O3 F3 P

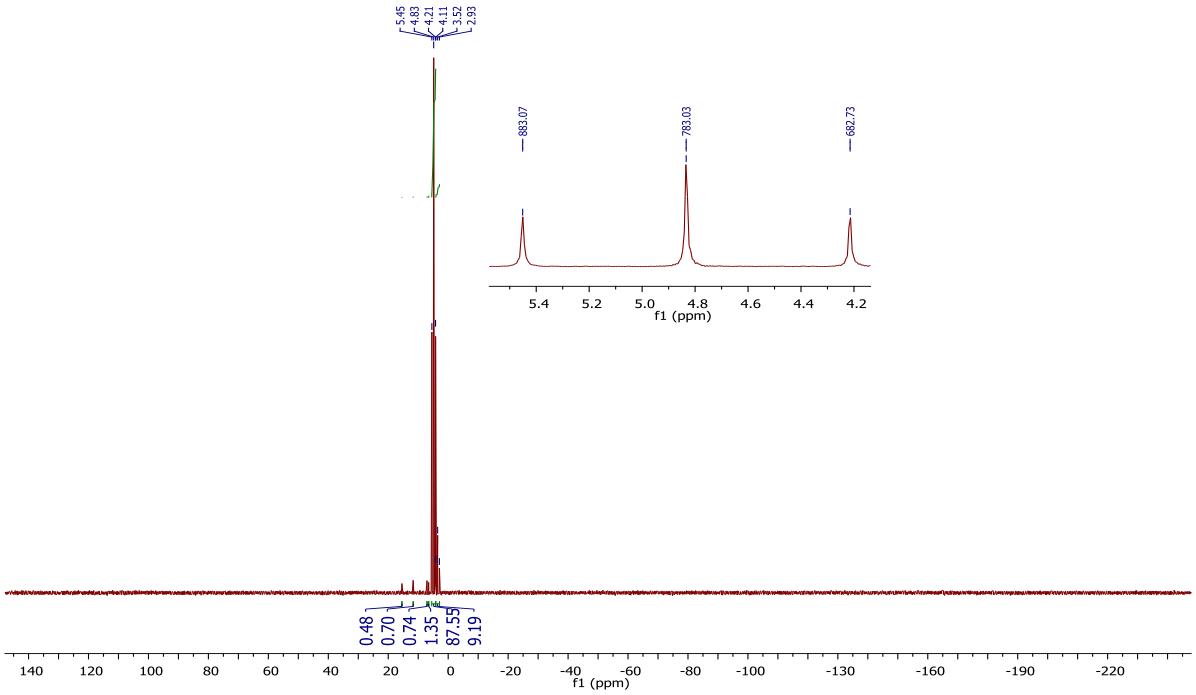

SYNAPT G2-S#UEB205
Y-JL15020612 28 (0.127) Cm (19:64)
MS303 f.11-15
06-Feb-2015
1: TOF MS ES+
1.01e8
100
%
0
386.11
387.12
237.01
293.08
330.05
358.08
265.04
388.12
238.02
266.05
294.08
309.12
331.05
359.09
219.00
420.13
430.15
459.18
477.16
507.18
513.17
521.19
550.22
568.21
m/z
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
560

(*Z*)-diethyl (1,1-difluoro-2-((2-fluorophenyl)imino)-2-phenylethyl) phosphonate 14i

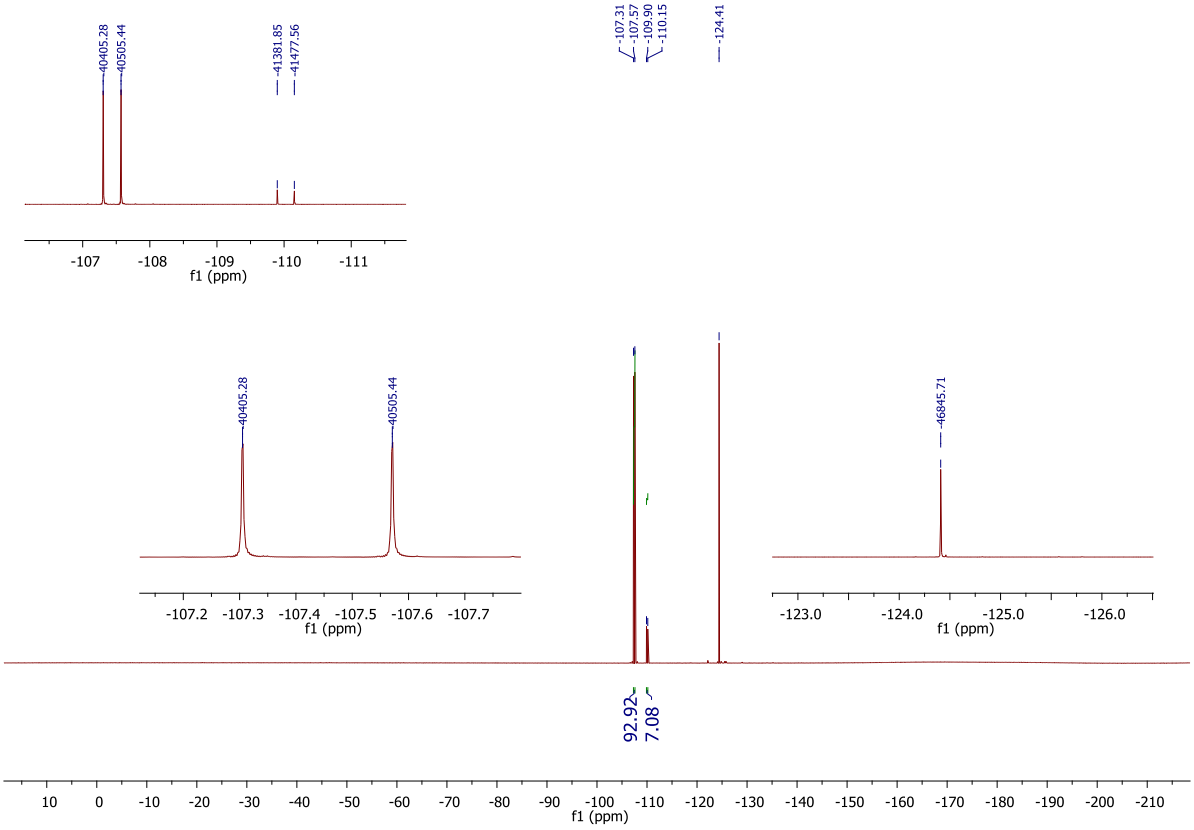


14i

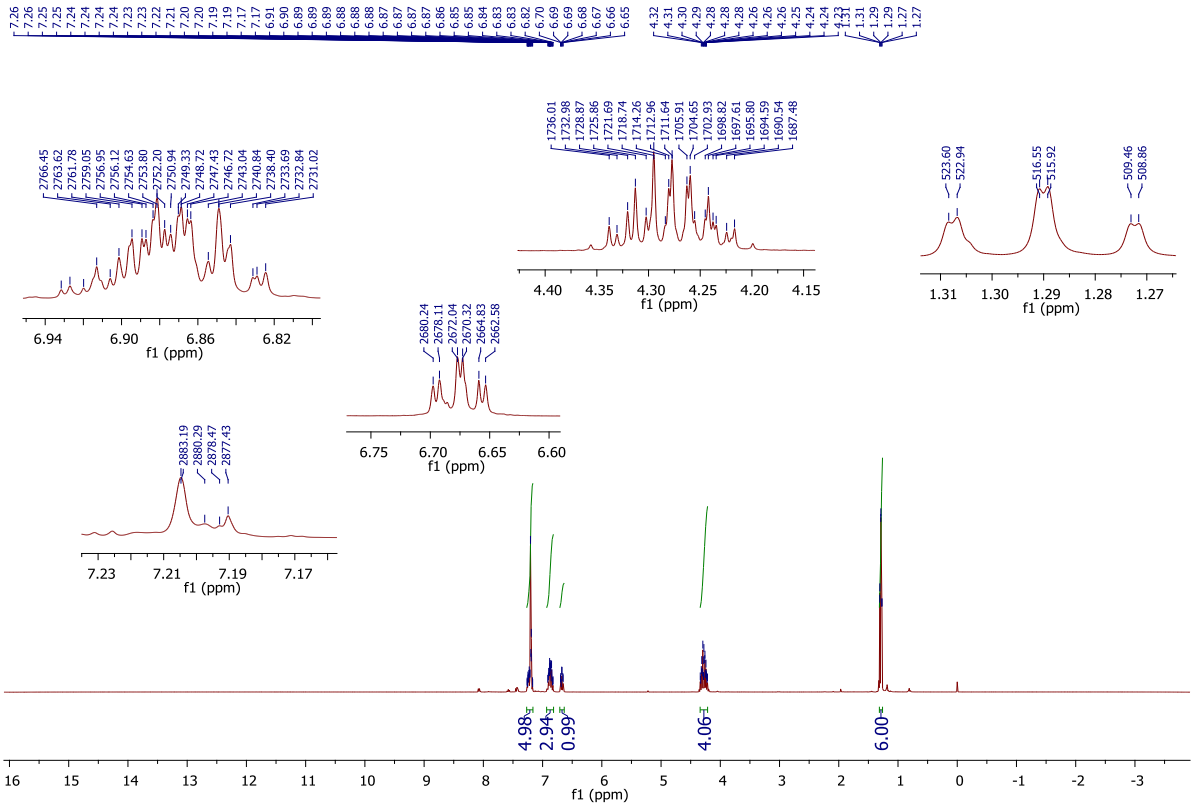
^{31}P NMR



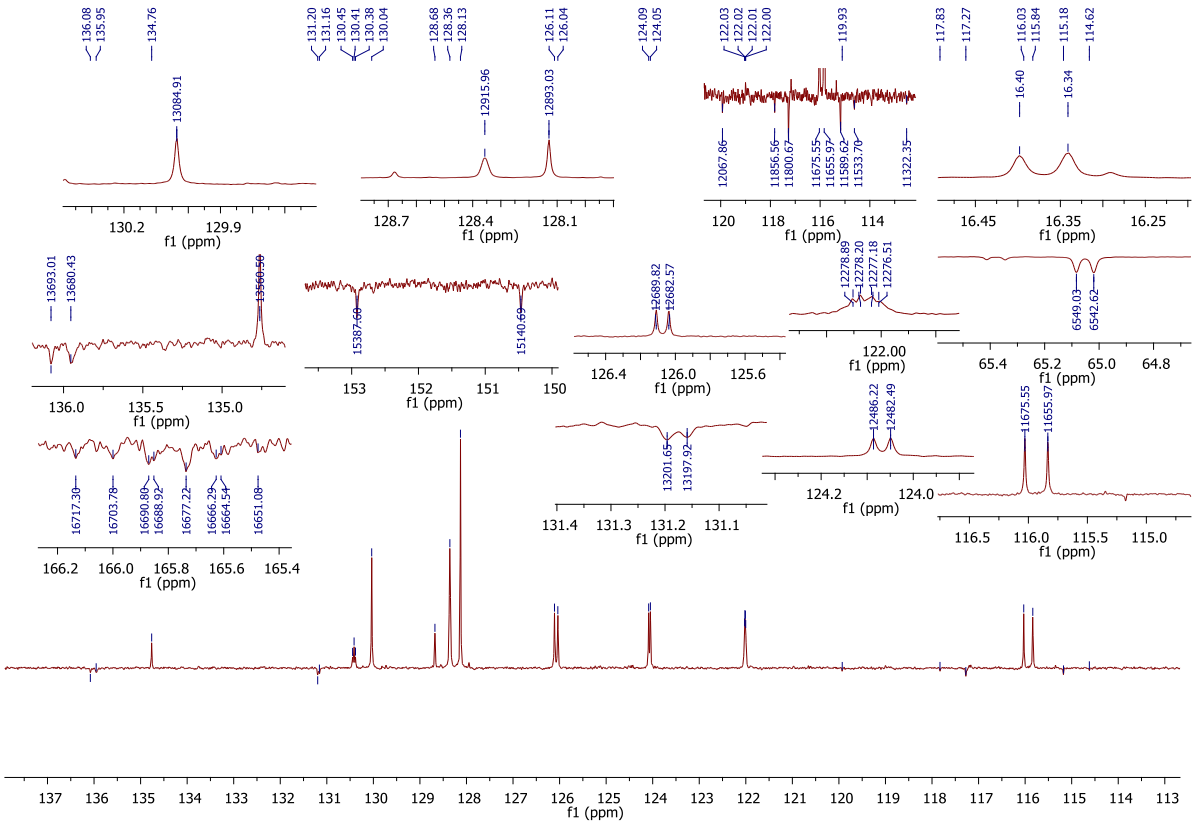
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



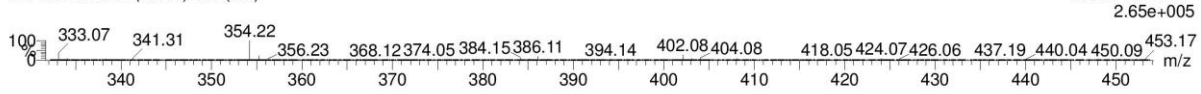
HRMS

Elemental Composition Report **Page 1**

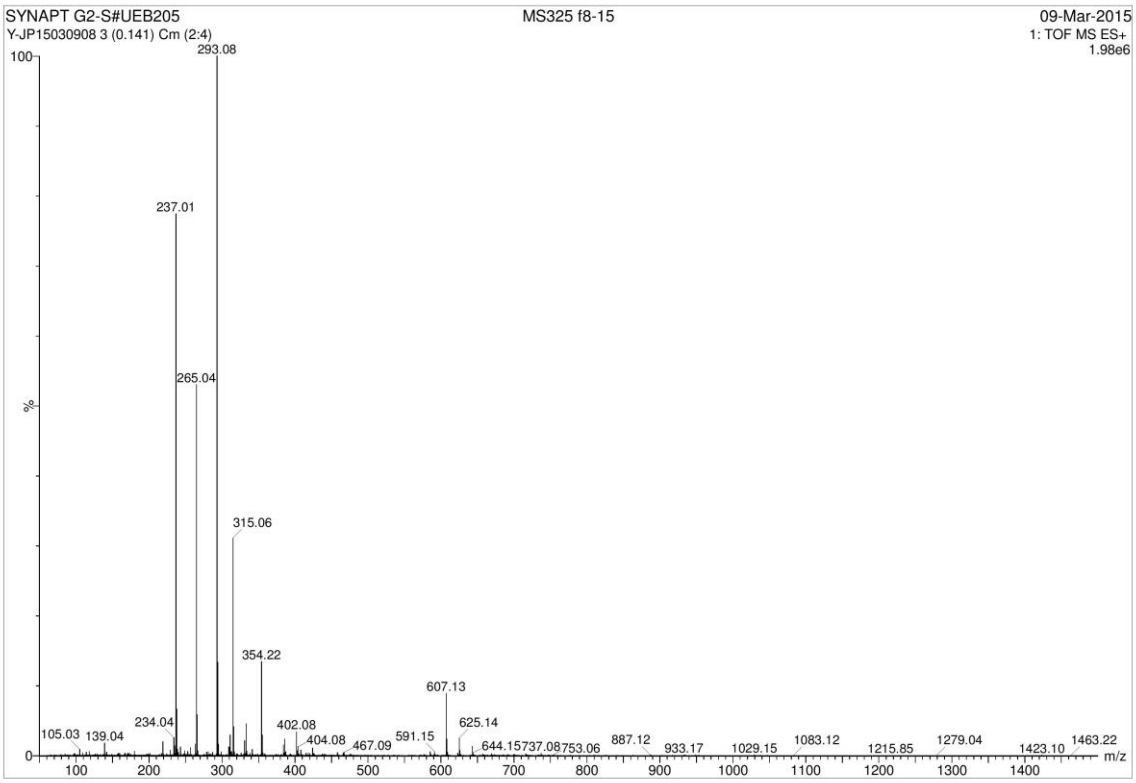
Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
494 formula(e) evaluated with 2 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 F: 3-3 P: 1-1

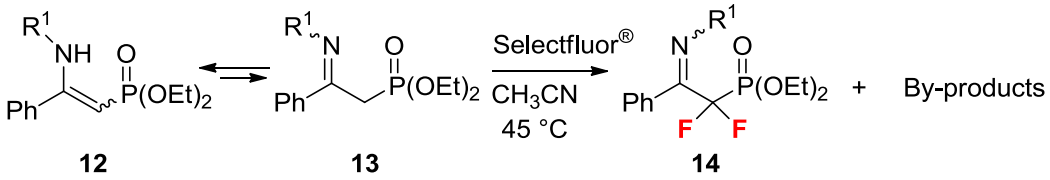
SYNAPT G2-S#UEB205 MS325 f8-15 09-Mar-2015
Y-JP15030908 3 (0.141) Cm (2:4) 1: TOF MS ES+
2.65e+005



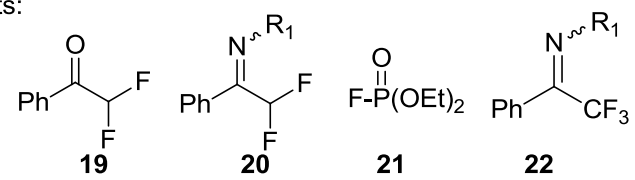
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
386.1137	386.1133	0.4	1.0	8.5	980.5	0.000	100.00	C18 H20 N O3 F3 P
	386.1138	-0.1	-0.3	1.5	993.3	12.840	0.00	C3 H16 N13 O4 F3 P



III. By-products of electrophilic fluorination - diagnostic data



By-products:



Diagnostic signals for 2,2-difluoro-1-phenylethanone 19

^{1}H NMR ($CDCl_3$): $\delta_{H\sim}$ 6.3 (t, $^{2}J_{HF}$ = 53.5 Hz, 1H), **^{19}F NMR ($CDCl_3$):** $\delta_{F\sim}$ -122.6 (d, $^{2}J_{FH}$ = 53.5 Hz, 2F)

Diagnostic signals for 20

^{1}H NMR ($CDCl_3$): δ= 6.2 (t, $^{2}J_{HF}$ = 55.4 Hz, 1H), **^{19}F NMR ($CDCl_3$):** δ= ~ -118.1 (d, $^{2}J_{FH}$ = 55.4 Hz, 2F)

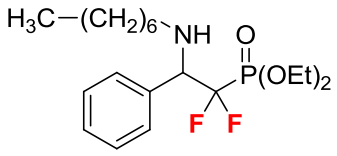
Diagnostic signals for 21

^{19}F NMR ($CDCl_3$): δ= -81.1 (d, $^2J_{FP}$ 966 Hz, 1F), **^{31}P NMR ($CDCl_3$):** δ= -9.2 (d, $^2J_{PF}$ 966 Hz, 1P), **GC-MS**: m/z = 156.1 [M^+]; retention time: 6 min

Diagnostic signals for 22

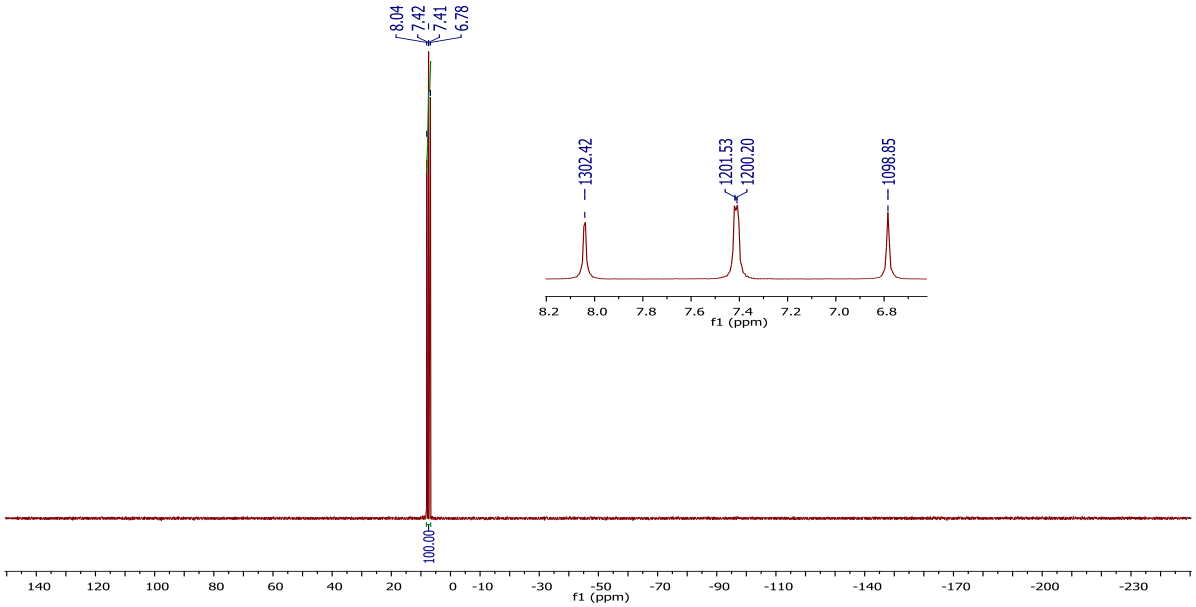
^{19}F NMR ($CDCl_3$): $\delta_{F\sim}$ -71.6 (s)

diethyl (1,1-difluoro-2-(heptylamino)-2-phenylethyl)phosphonate 15a

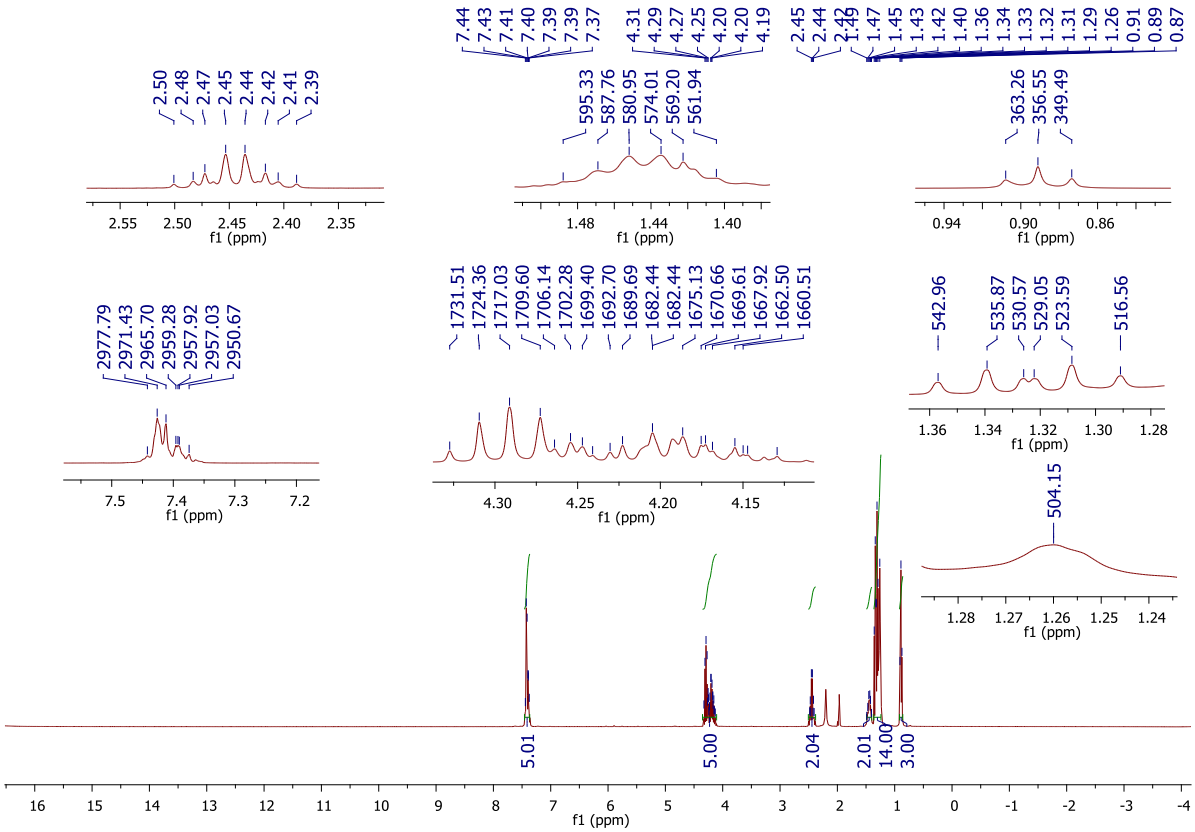


15a

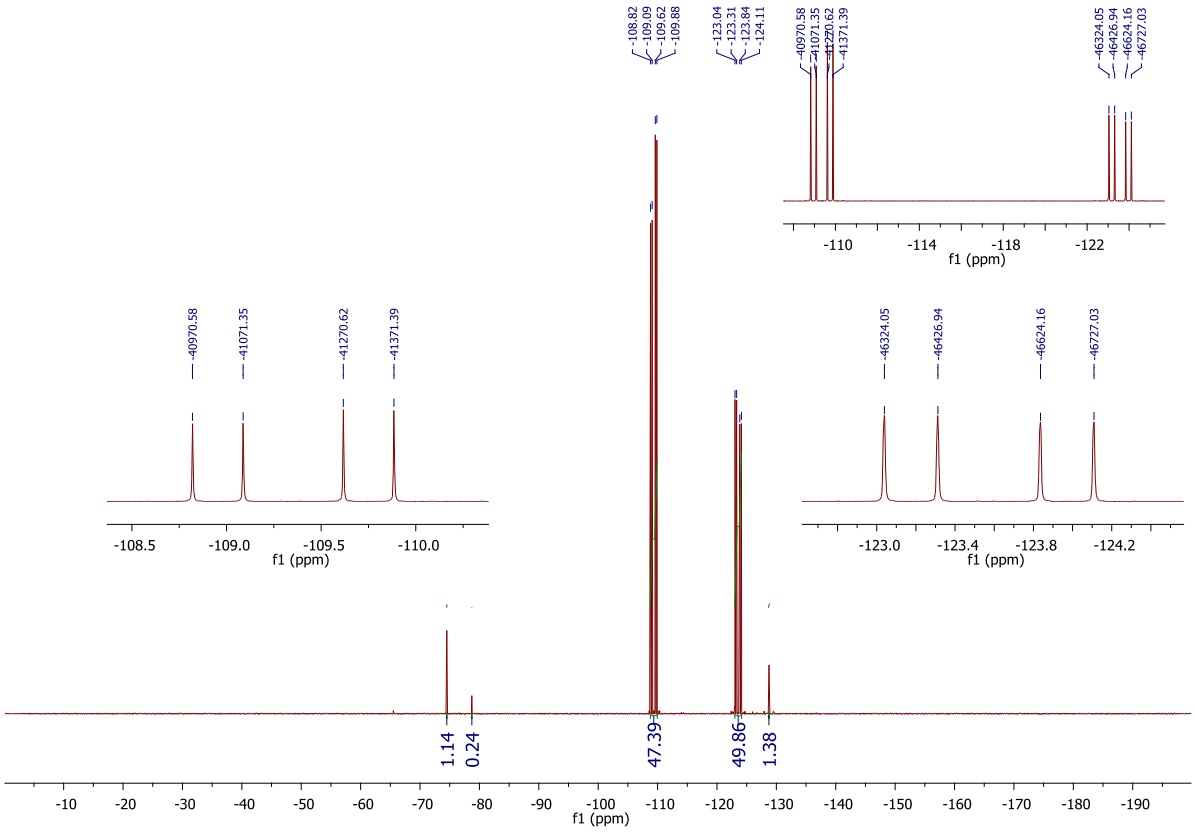
^{31}P NMR



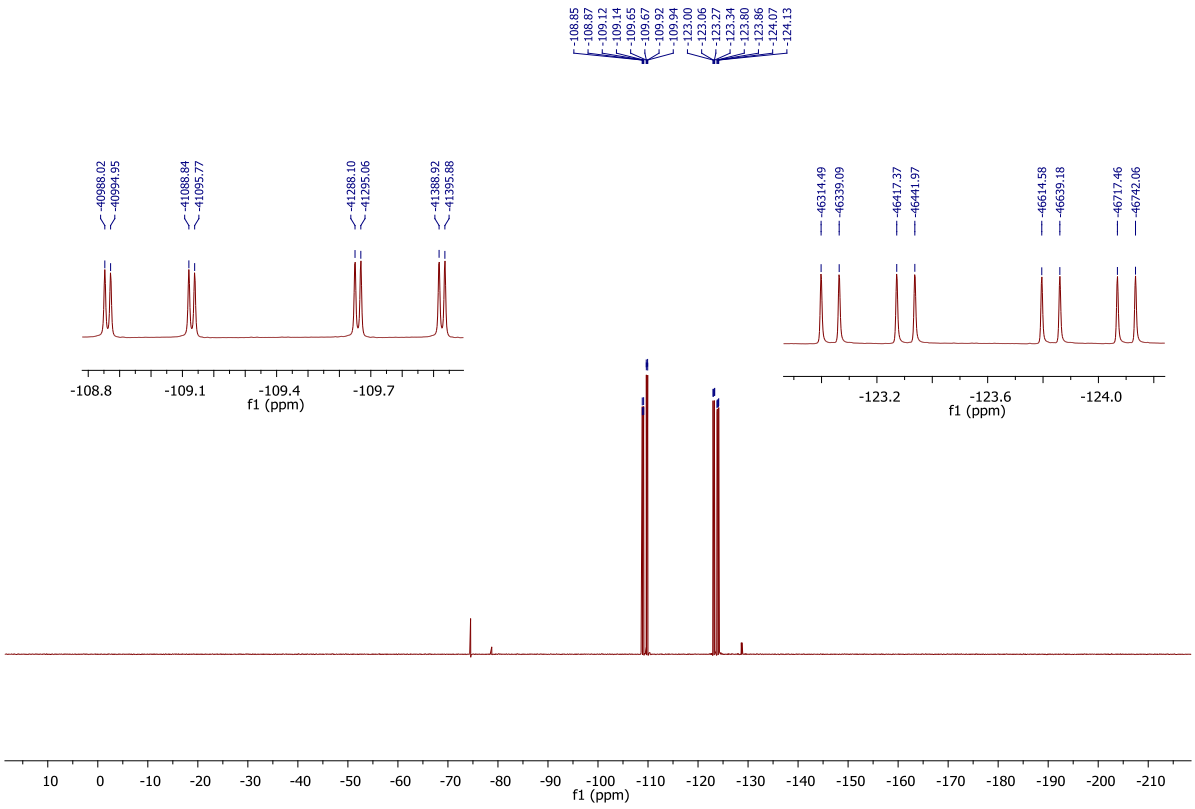
^{1}H NMR



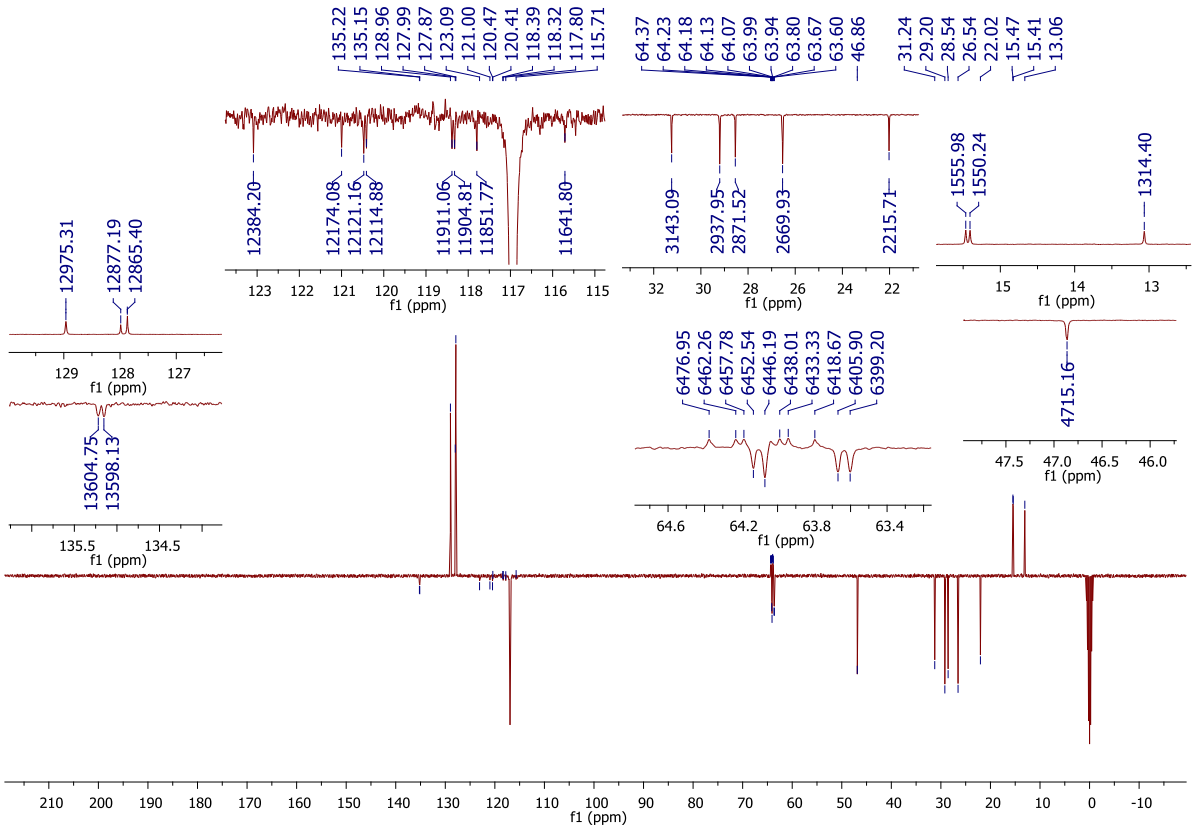
^{19}F NMR {H}



^{19}F NMR



^{13}C NMR



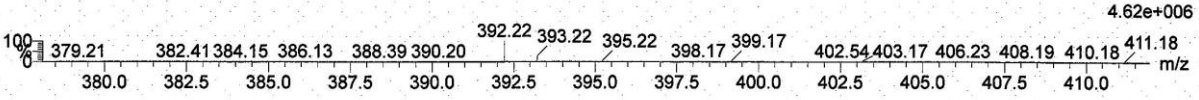
HRMS

Elemental Composition Report **Page 1**

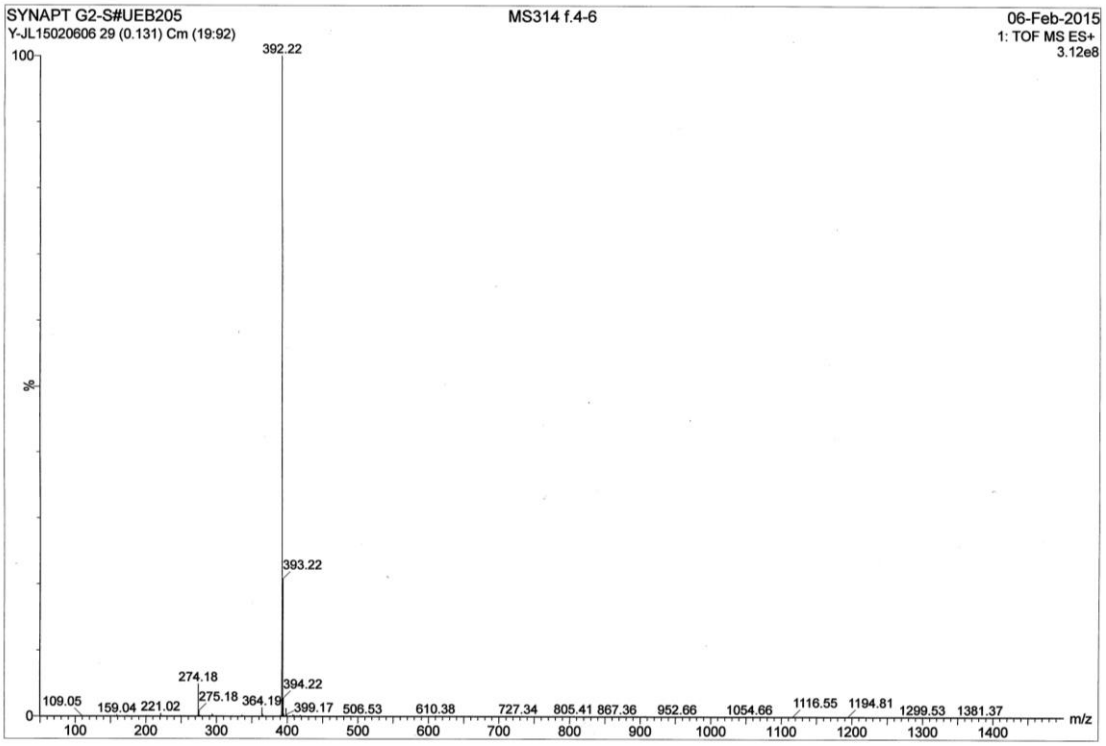
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2649 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 0-3 P: 1-1

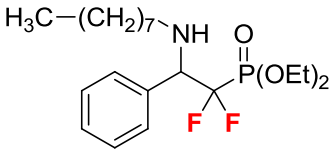
SYNAPT G2-S#UEB205 MS314 f.4-6 06-Feb-2015
Y-JL15020606 42 (0.180) 1: TOF MS ES+
4.62e+006



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
392.2166	392.2166	0.0	0.0	3.5	1206.3	n/a	n/a	C19 H33 N O3 F2 P

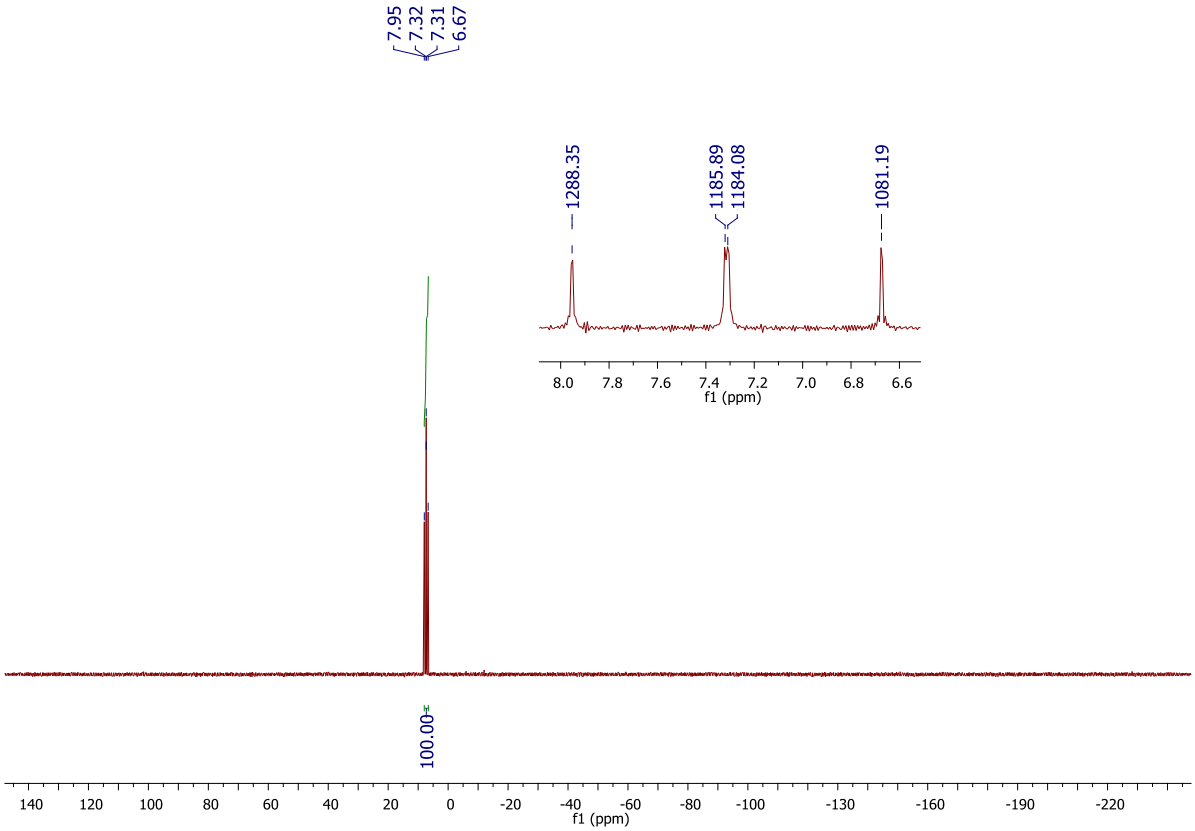


diethyl (1,1-difluoro-2-(octylamino)-2-phenylethyl)phosphonate 15b

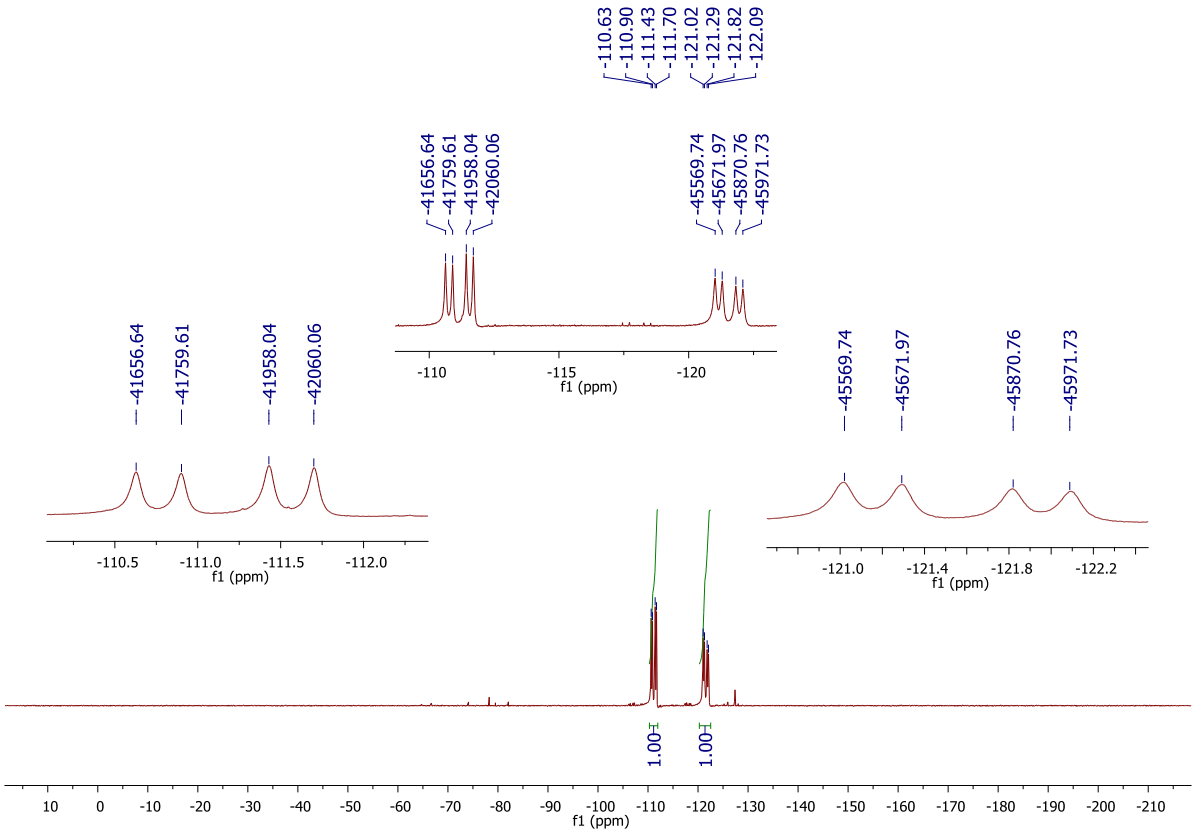


15b

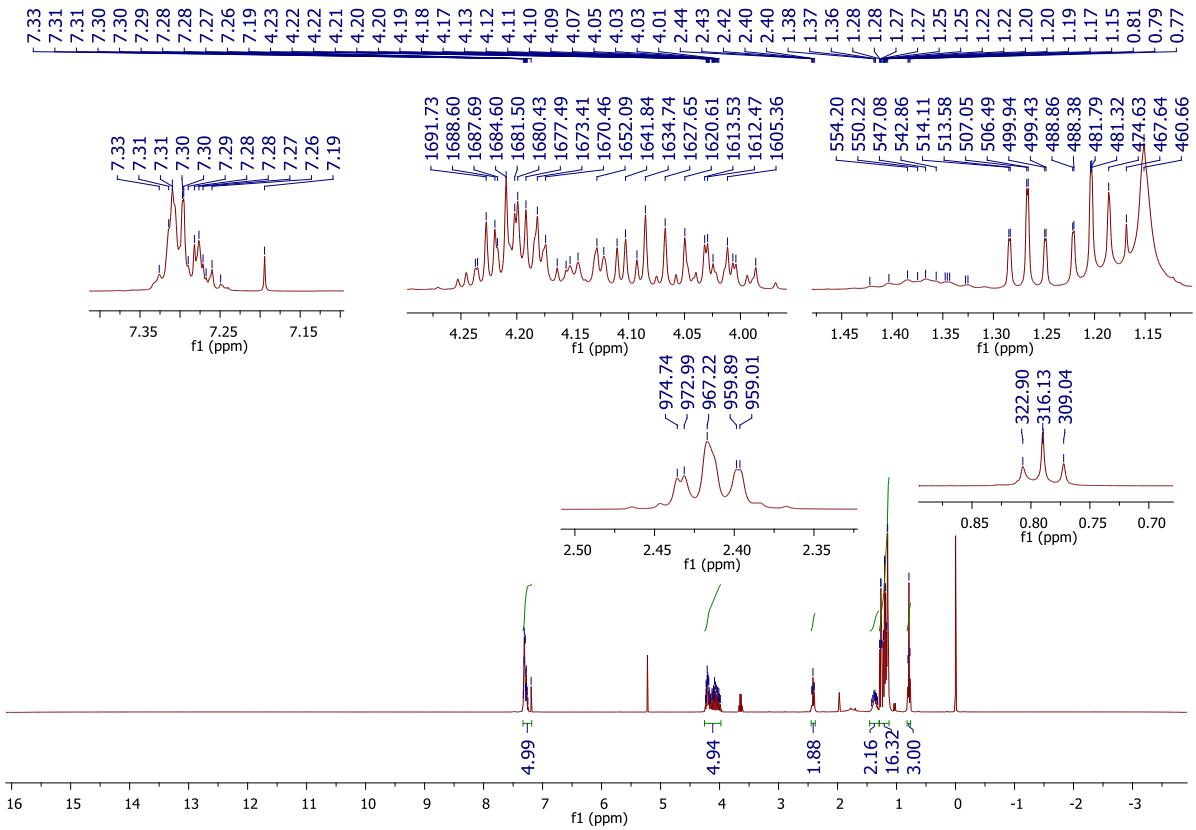
^{31}P NMR



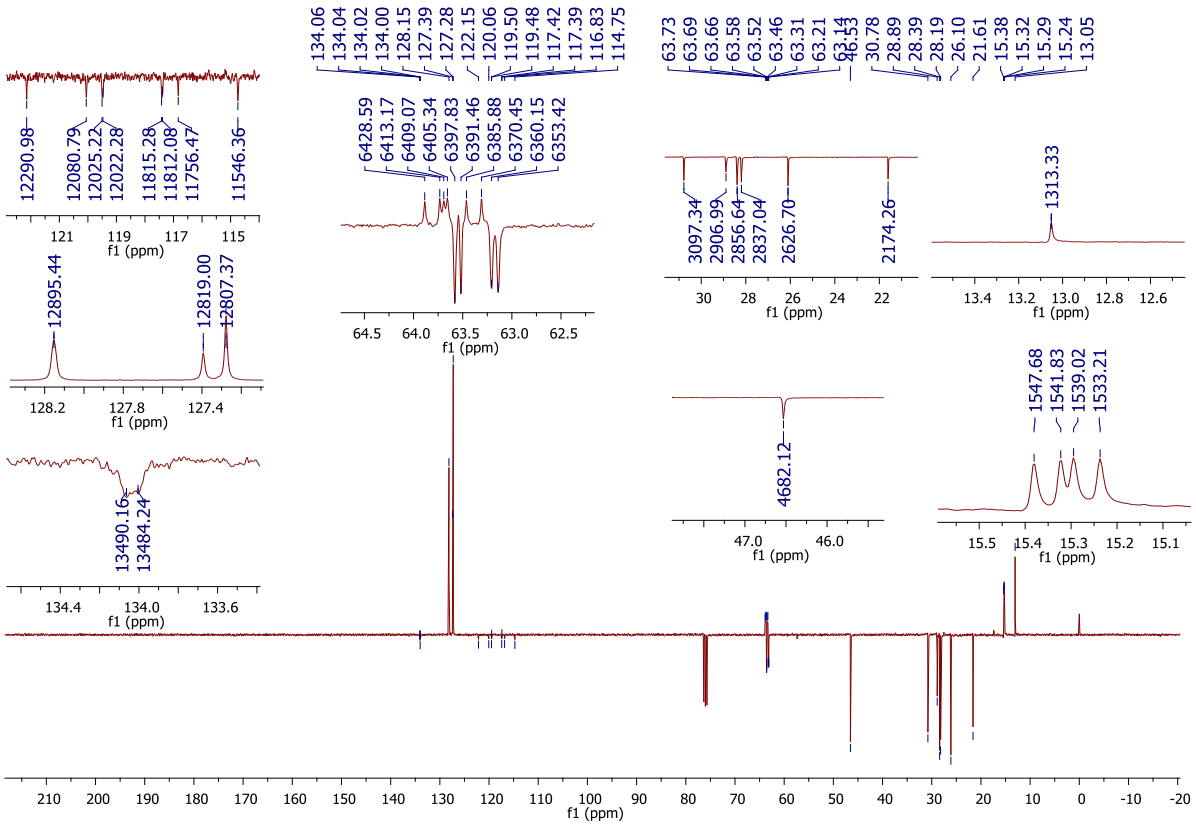
^{19}F NMR


-110.63
-110.90
-111.43
-111.70
-121.02
-121.29
-121.82
-122.09
-41656.64
-41759.61
-41958.04
-42060.06
-45569.74
-45671.97
-45870.76
-45971.73
f1 (ppm)
1.00
1.00

^{1}H NMR



^{13}C NMR



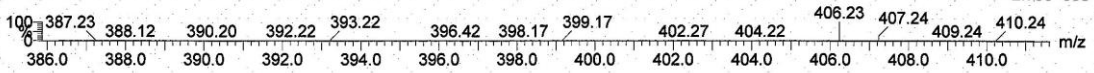
HRMS

Elemental Composition Report **Page 1**

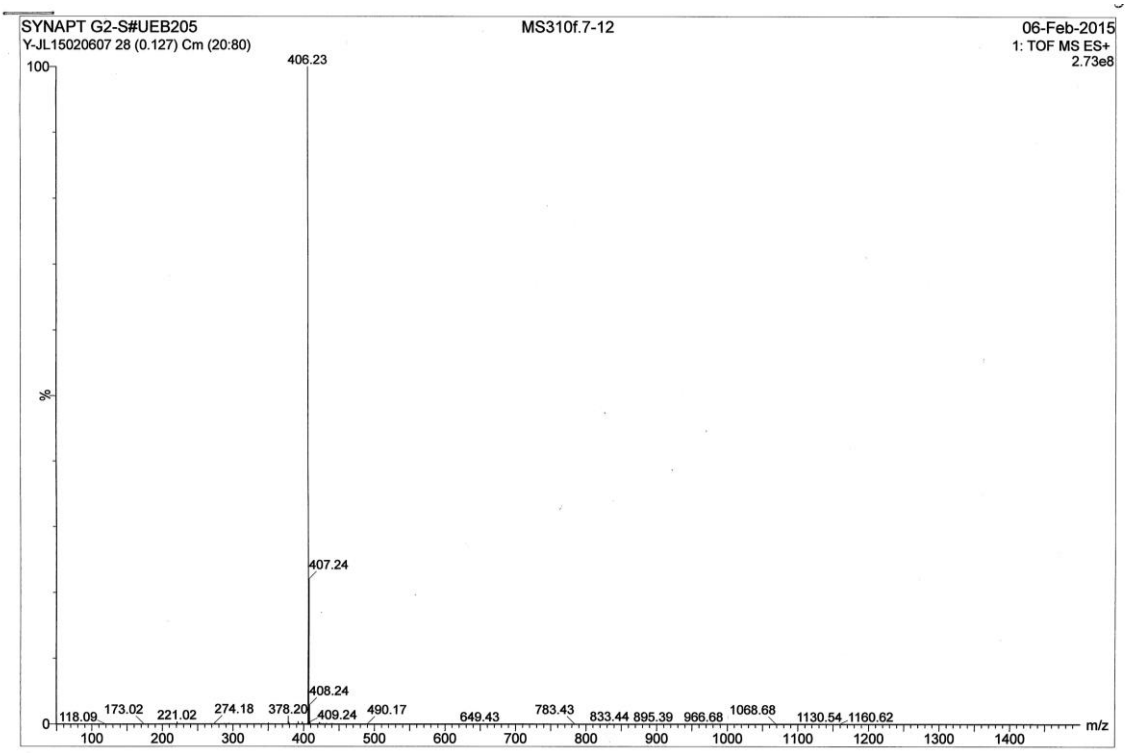
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2956 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 0-3 P: 1-1

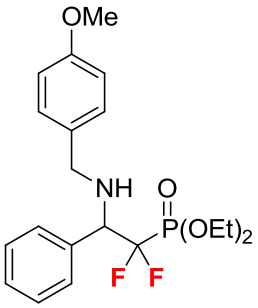
SYNAPT G2-S#UEB205 MS310f.7-12 06-Feb-2015
Y-JL15020607 28 (0.127) Cm (20:80) 1: TOF MS ES+
2.73e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
406.2325	406.2323	0.2	0.5	3.5	3499.1	n/a	n/a	C20 H35 N O3 F2 P

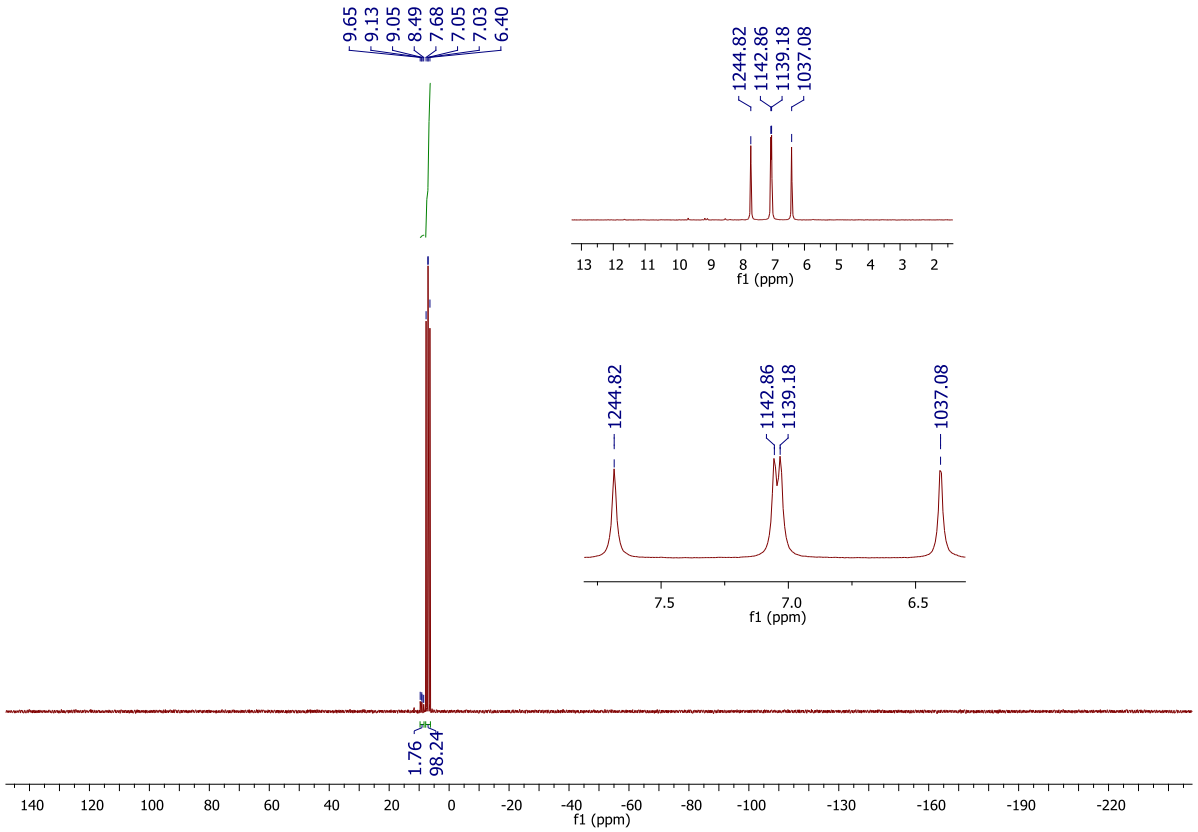


diethyl (1,1-difluoro-2-((4-methoxybenzyl)amino)-2-phenylethyl) phosphonate 15c

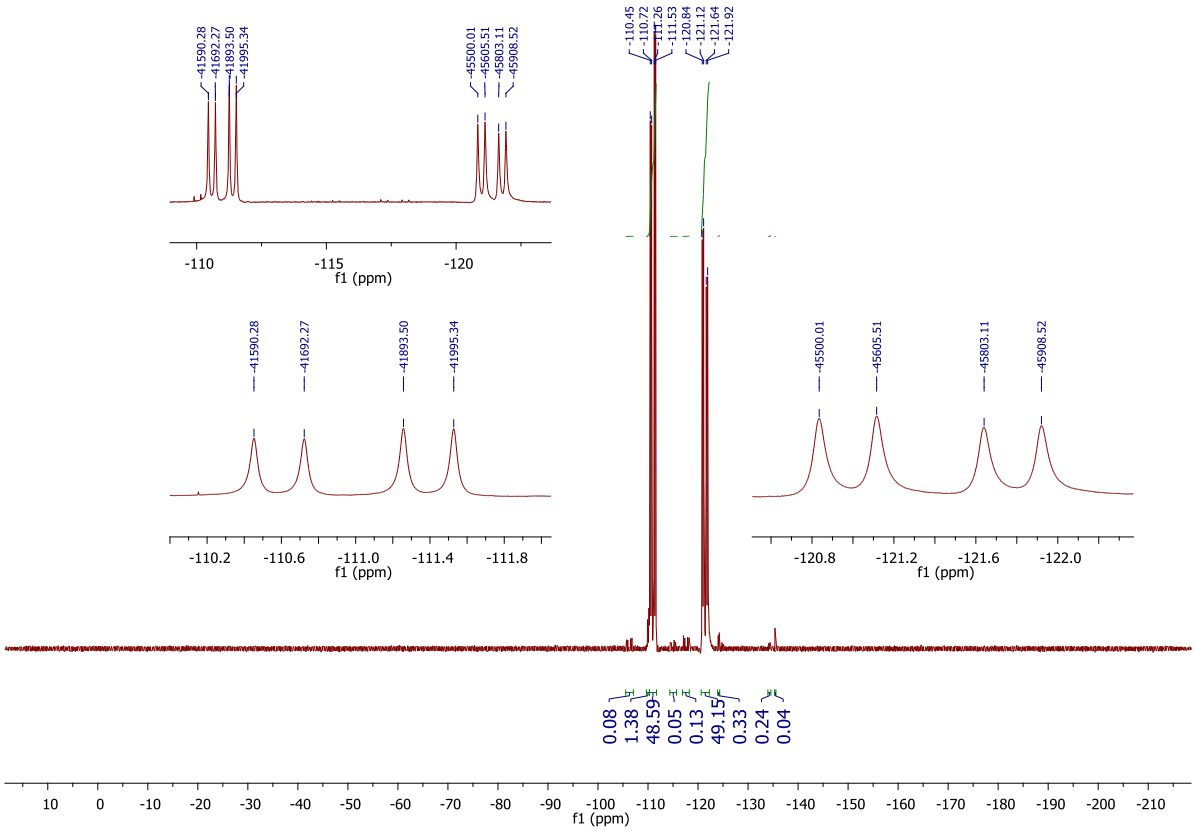


15c

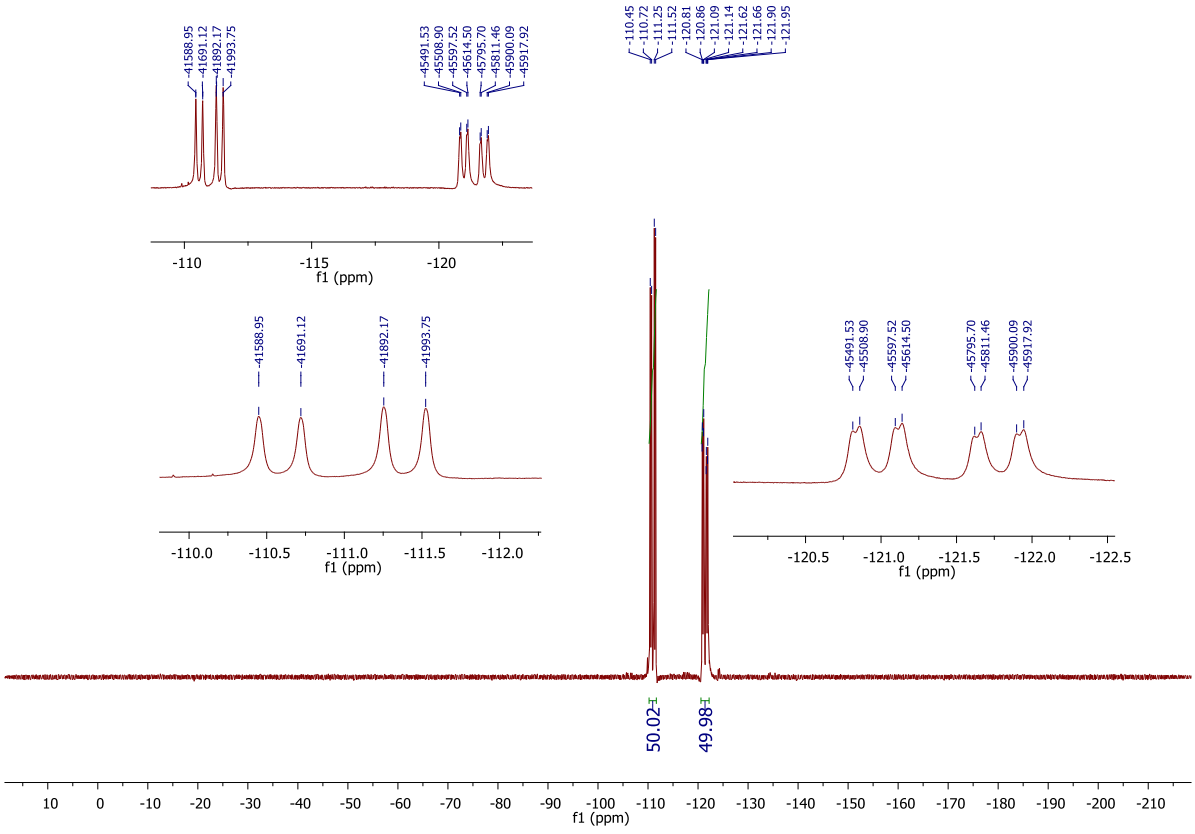
^{31}P NMR



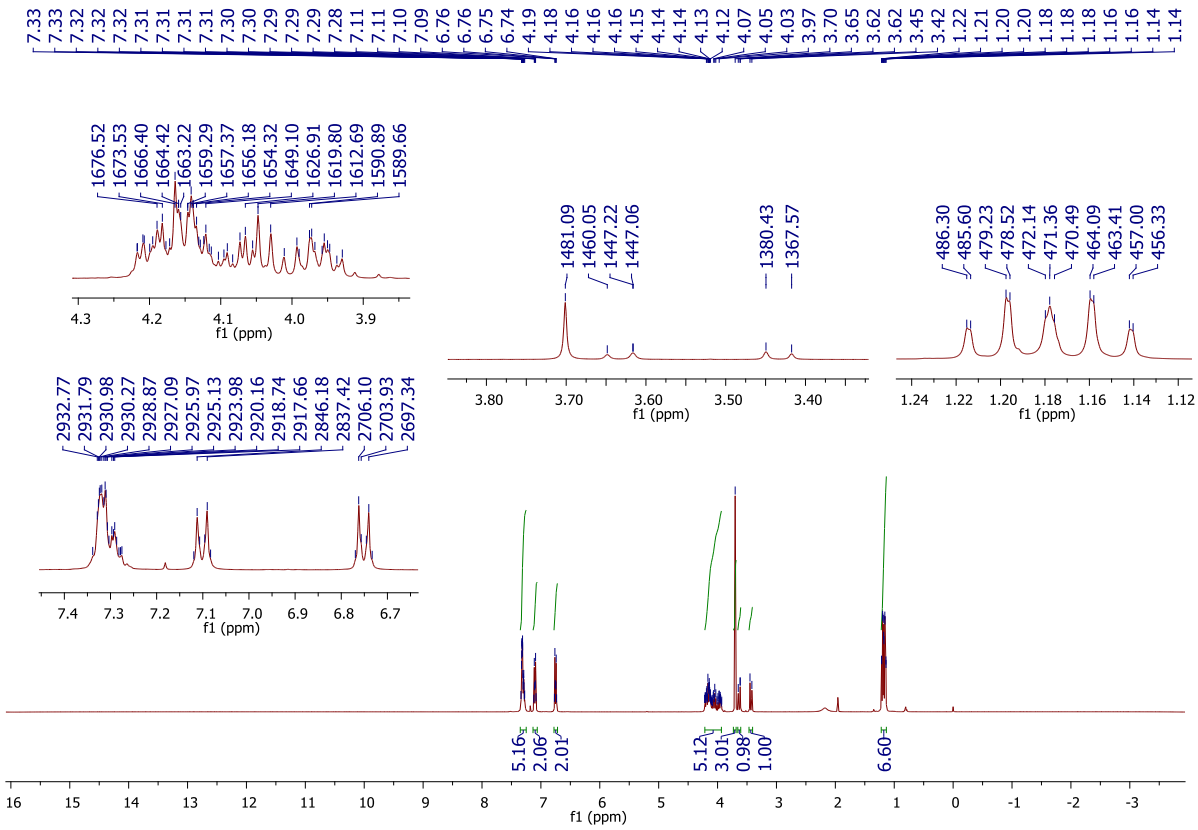
^{19}F NMR {H}



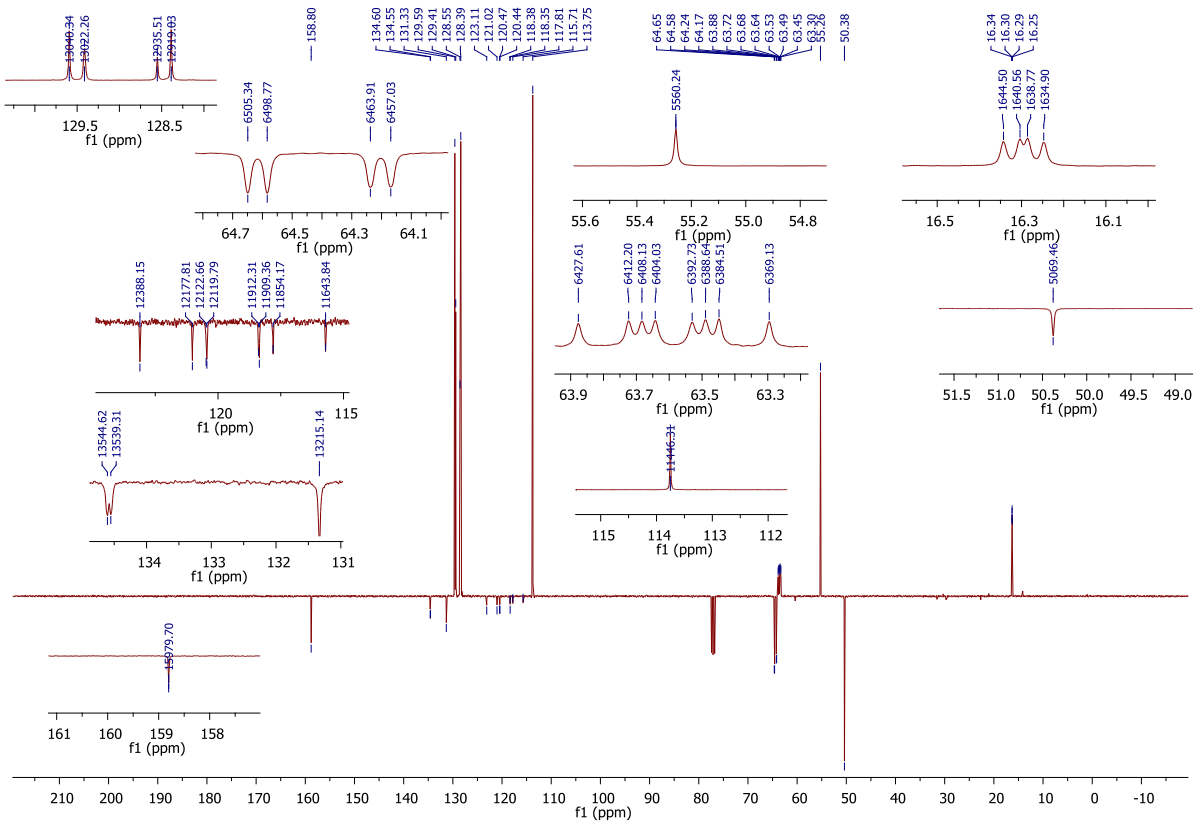
^{19}F NMR



^{1}H NMR



^{13}C NMR



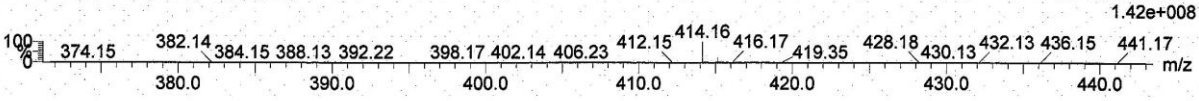
HRMS

Elemental Composition Report **Page 1**

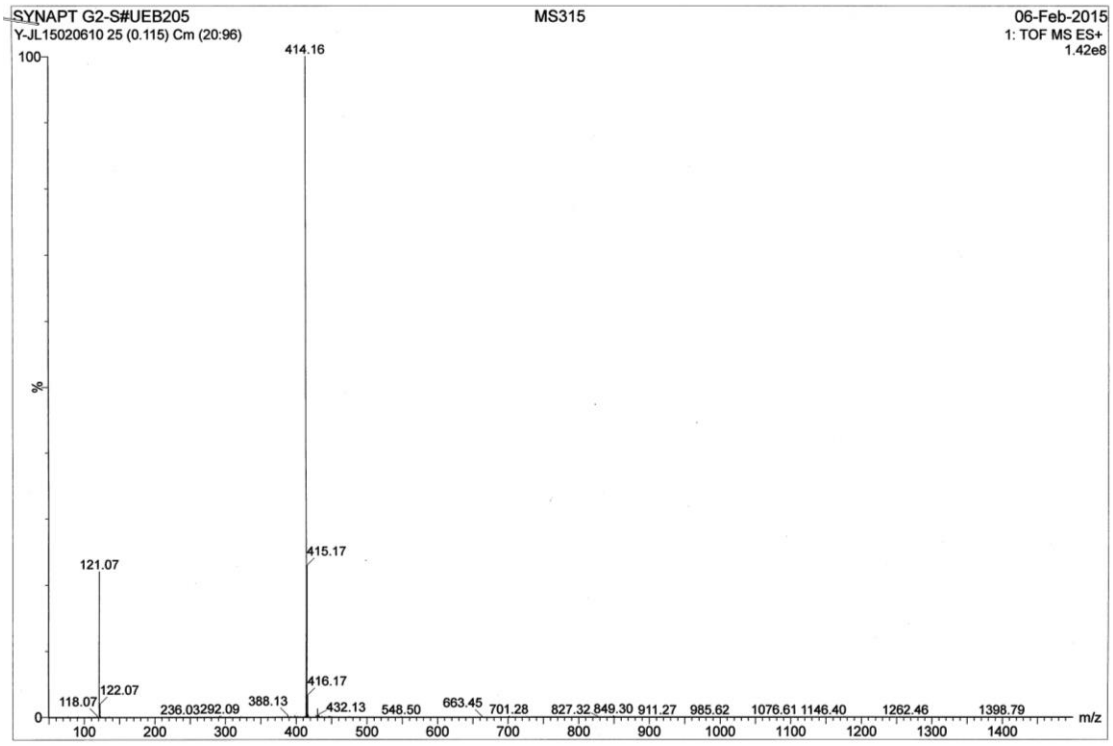
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2159 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

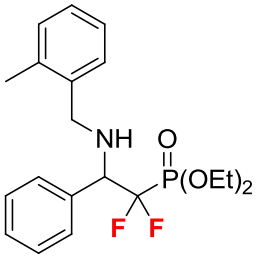
SYNAPT G2-S#UEB205 MS315 06-Feb-2015
Y-JL15020610 25 (0.115) Cm (20:96) 1: TOF MS ES+
1.42e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
414.1645	414.1646	-0.1	-0.2	7.5	3192.6	n/a	n/a	C20 H27 N O4 F2 P

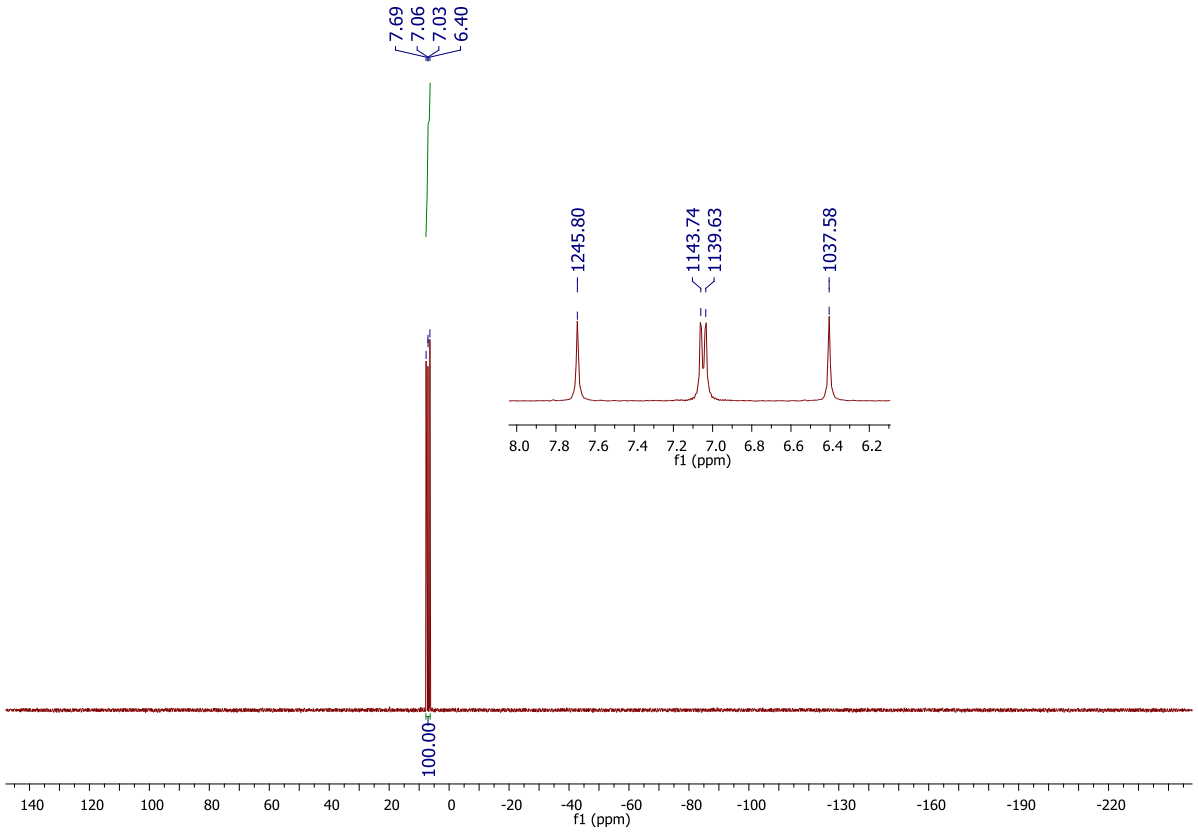


diethyl (1,1-difluoro-2-((2-methylbenzyl)amino)-2-phenylethyl) phosphonate 15d

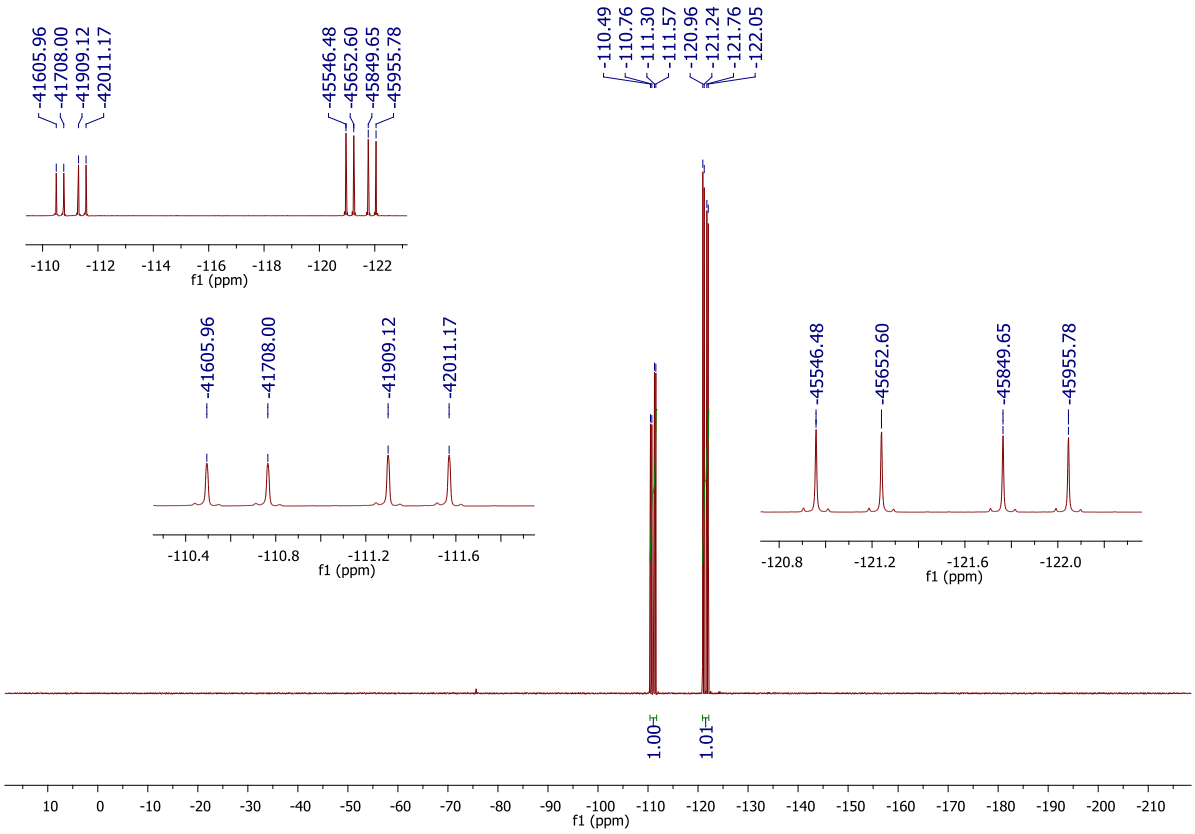


15d

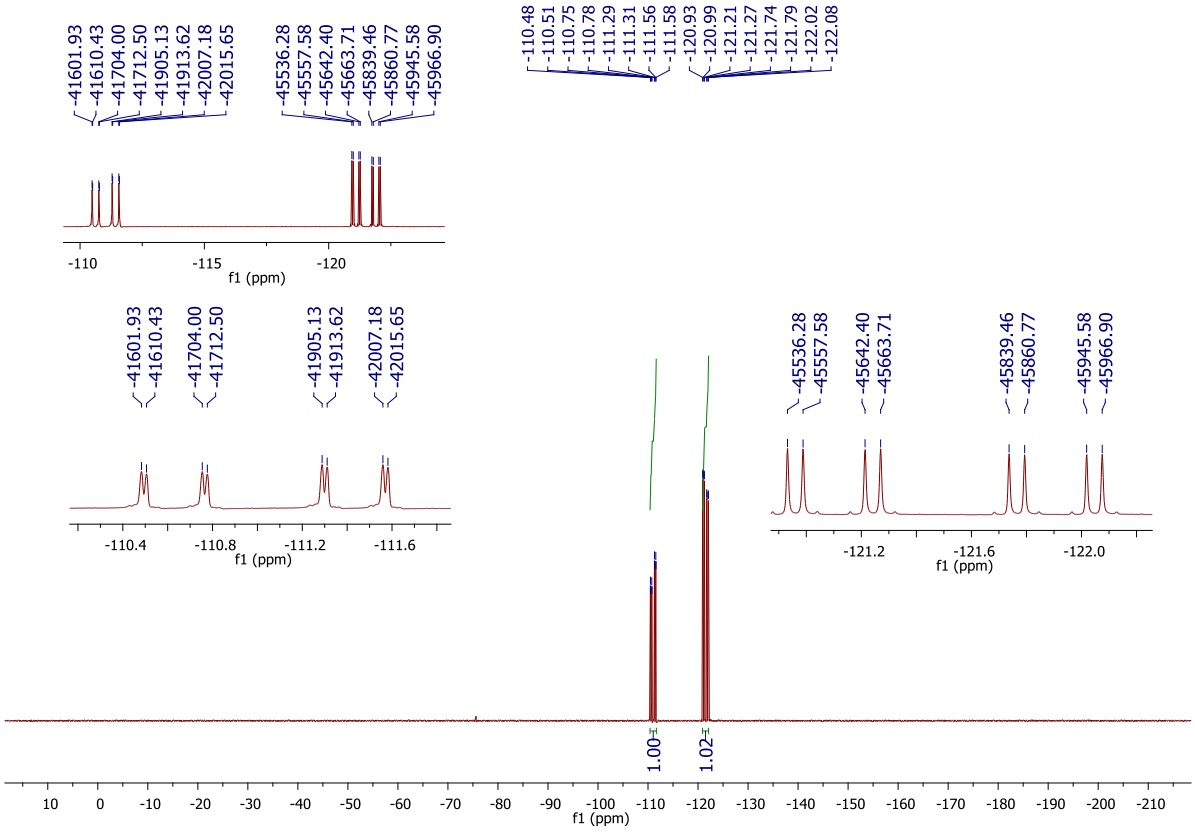
^{31}P NMR



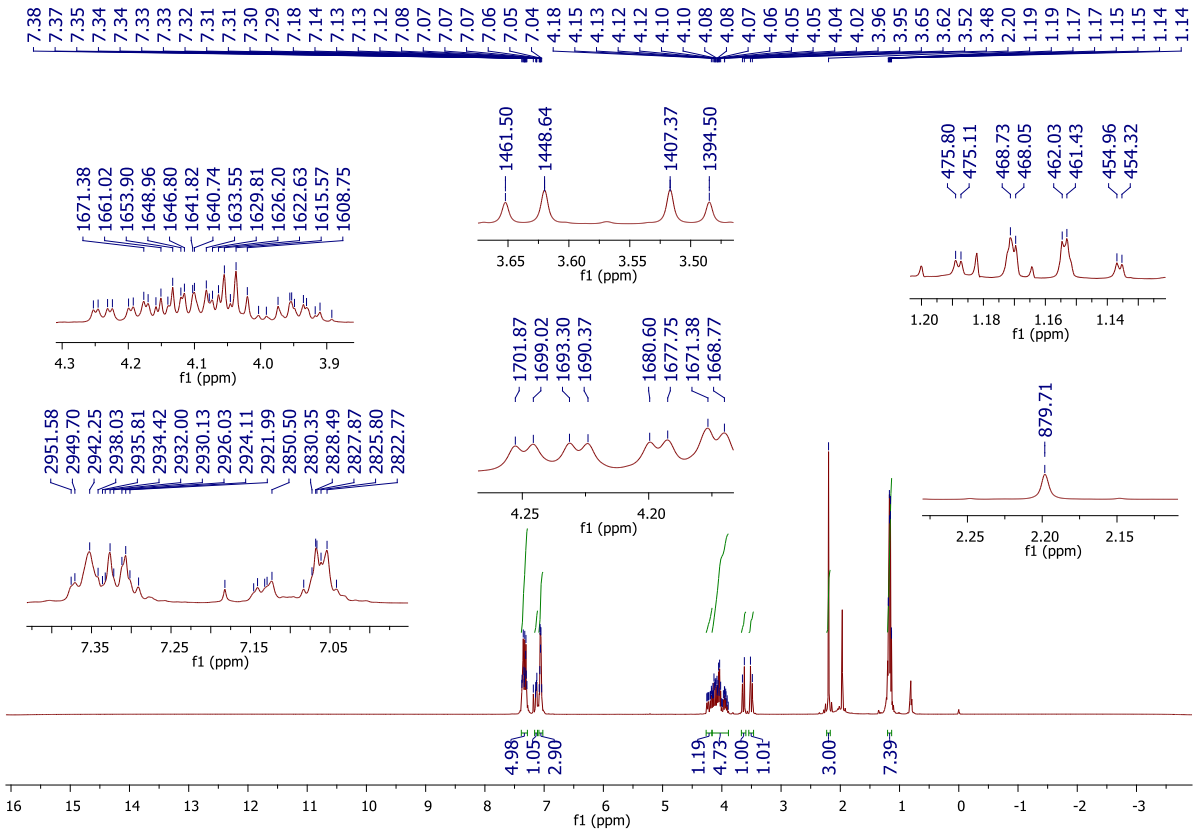
^{19}F NMR
{H}



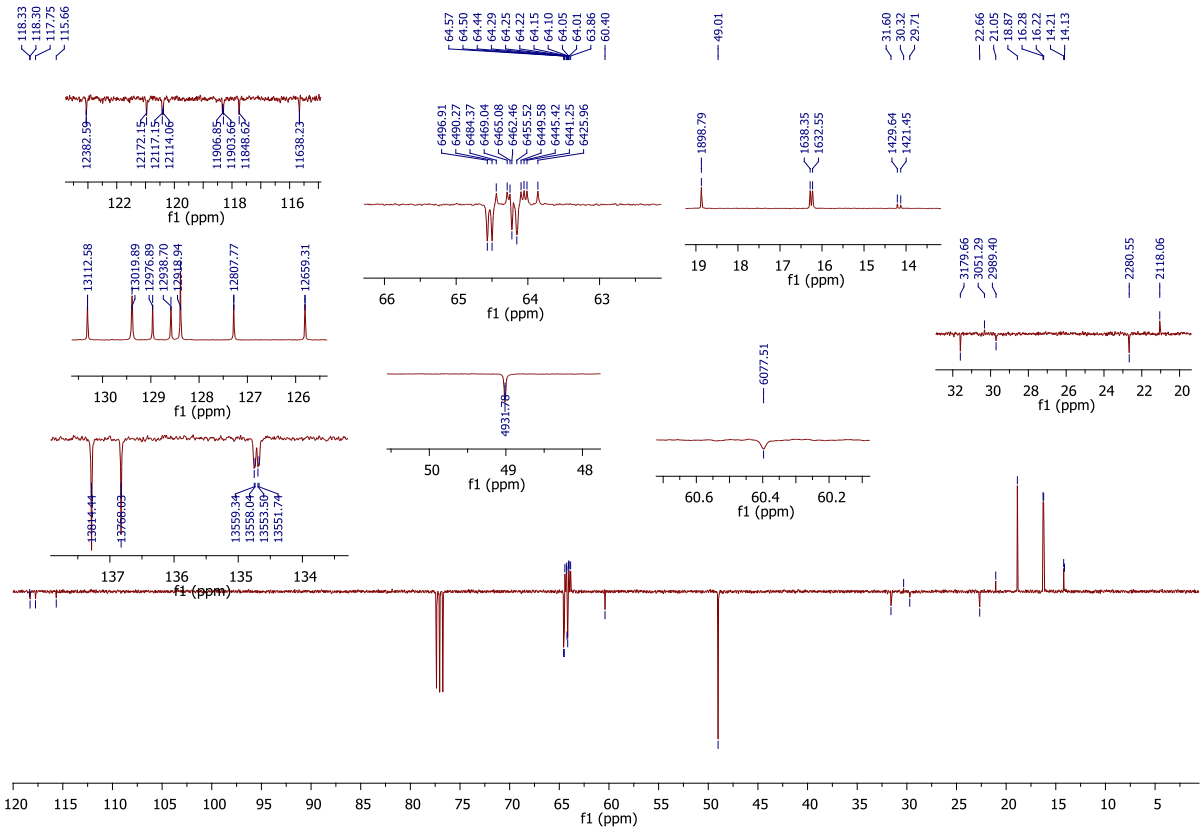
^{19}F NMR



^{1}H NMR



^{13}C NMR



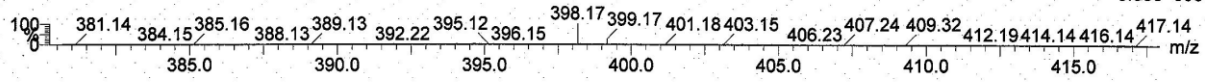
HRMS

Elemental Composition Report **Page 1**

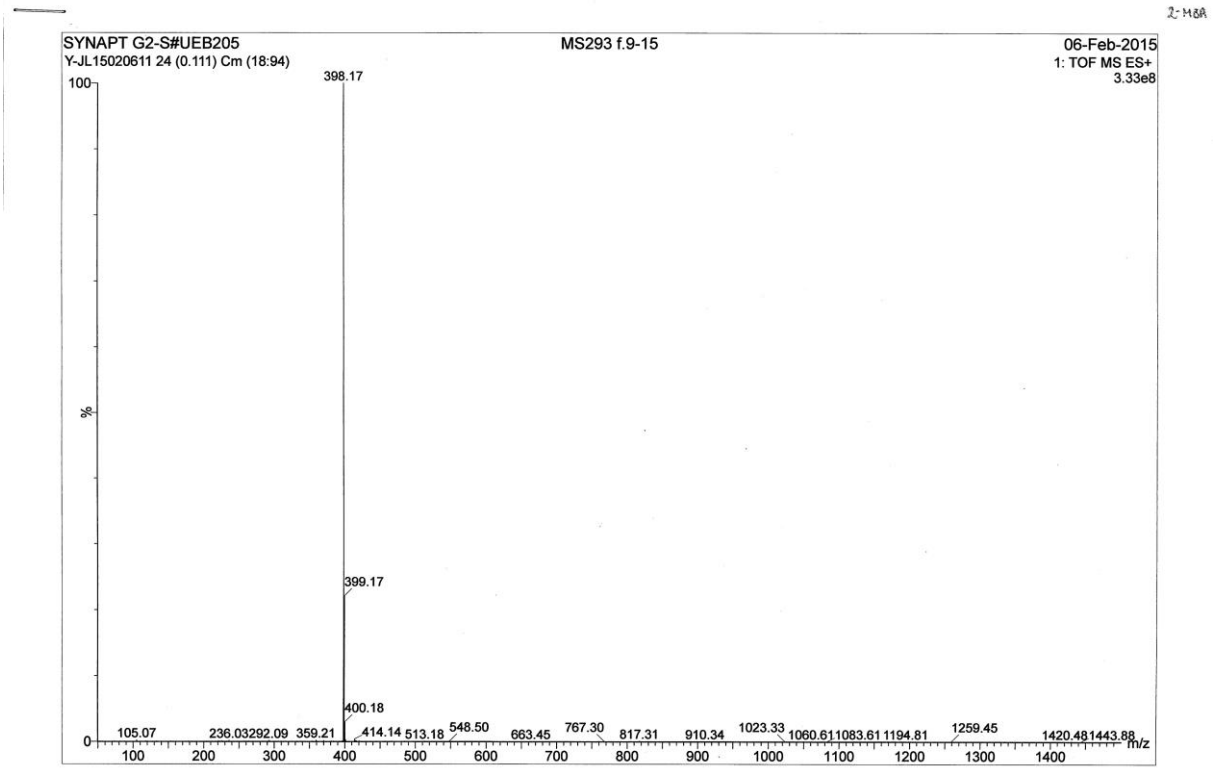
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1897 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

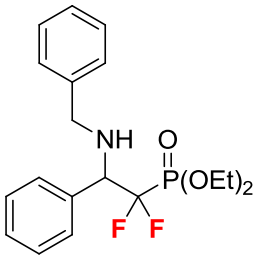
SYNAPT G2-S#UEB205 MS293 f.9-15 06-Feb-2015
Y-JL15020611 24 (0.111) Cm (18:94) 1: TOF MS ES+
3.33e+008



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
398.1693	398.1697	-0.4	-1.0	7.5	3546.2	0.000	100.00	C20 H27 N O3 F2 P
	398.1690	0.3	0.8	4.5	3564.9	18.688	0.00	C8 H22 N13 O3 F P



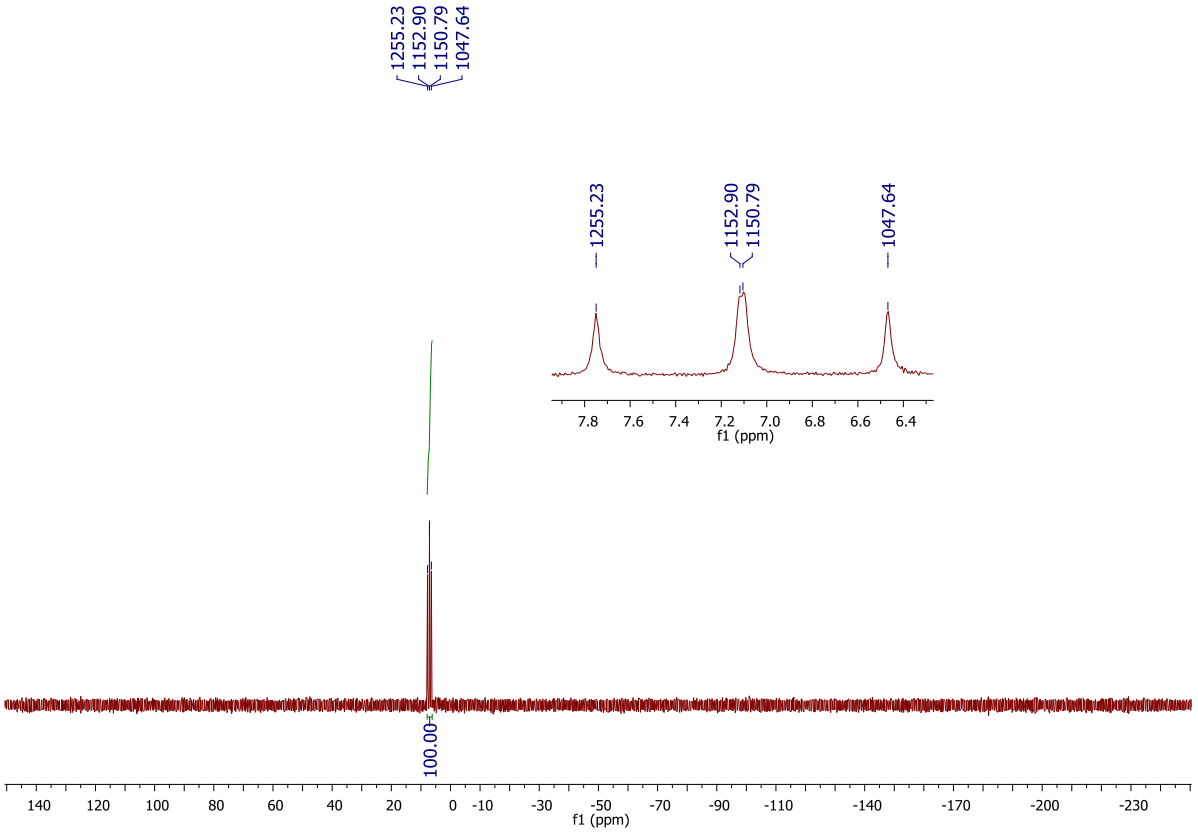
diethyl (2-(benzylamino)-1,1-difluoro-2-phenylethyl)phosphonate 15e



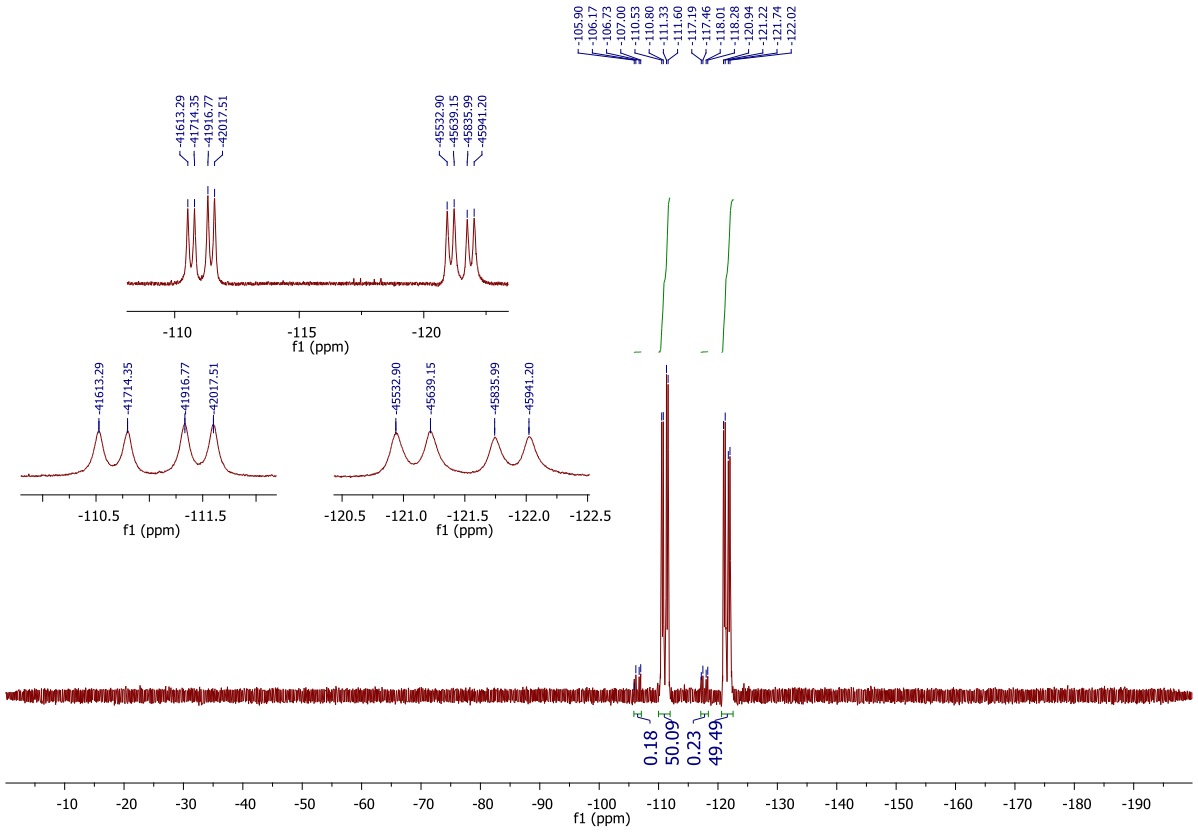
15e

.

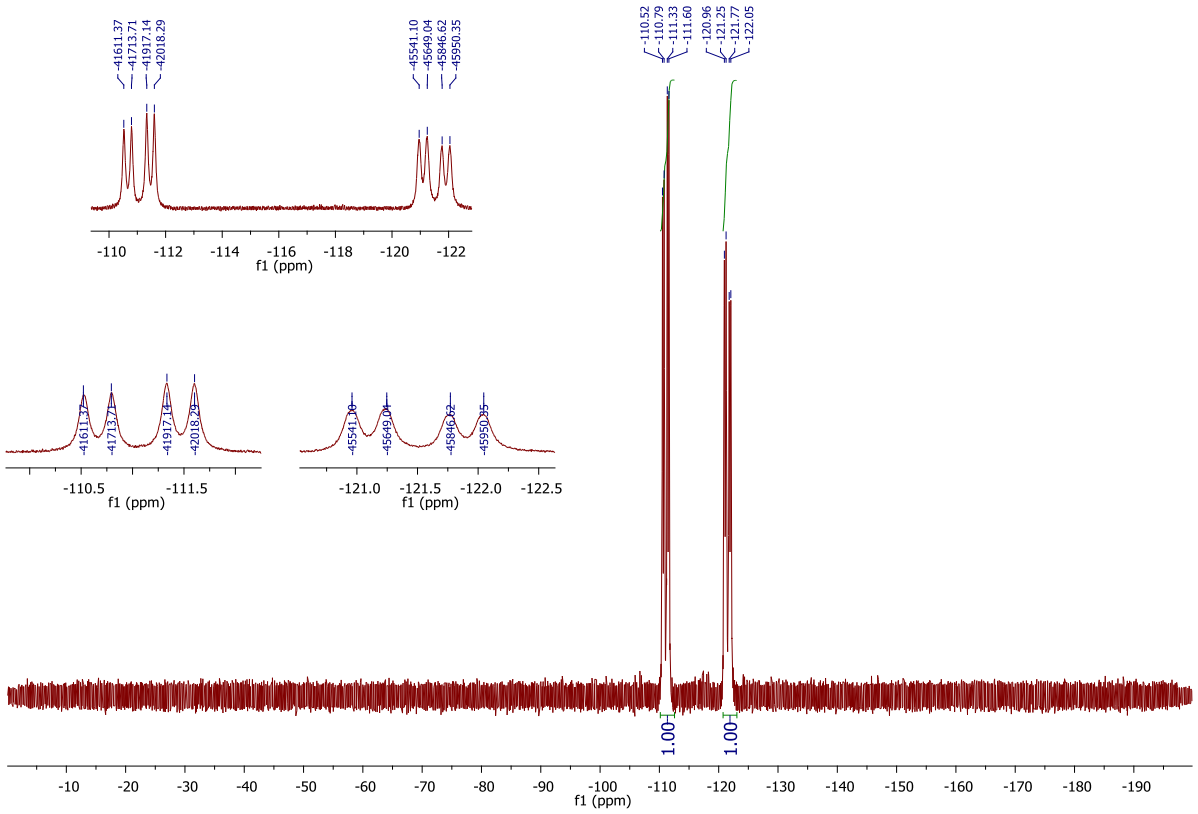
^{31}P NMR



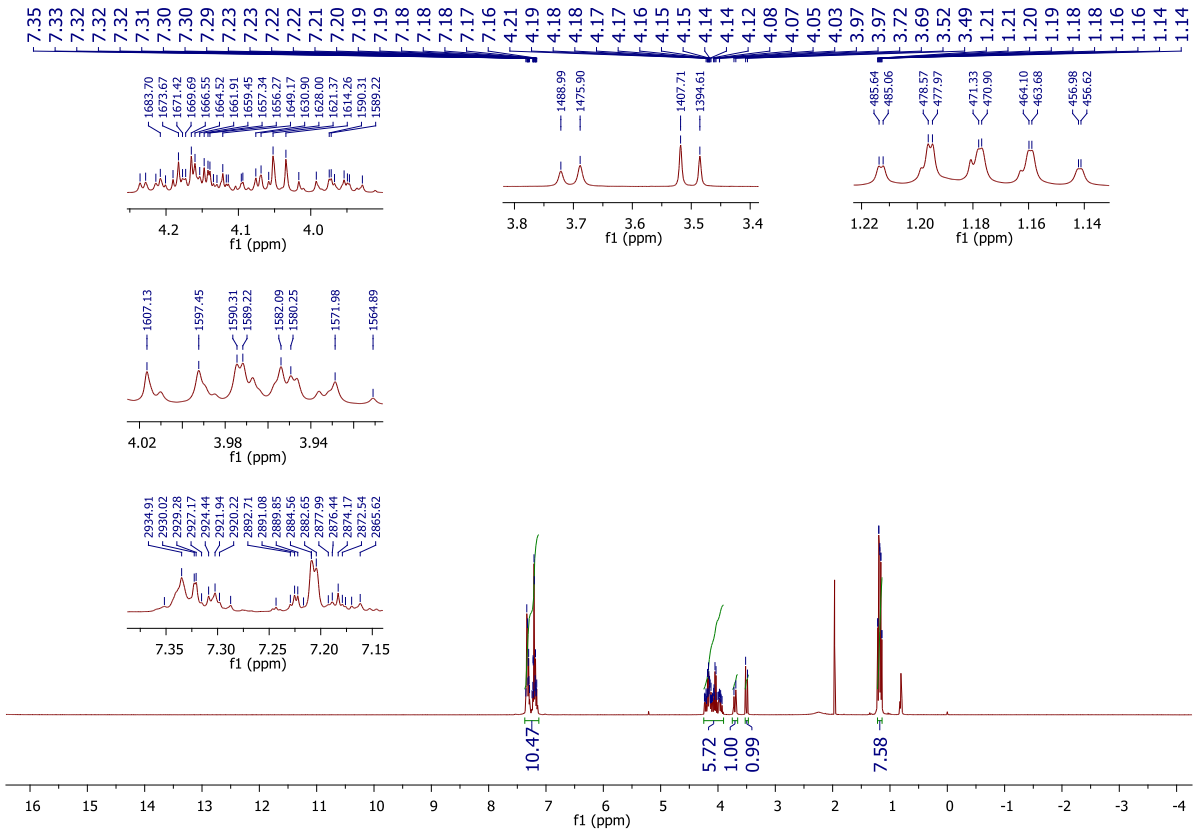
^{19}F NMR{H}



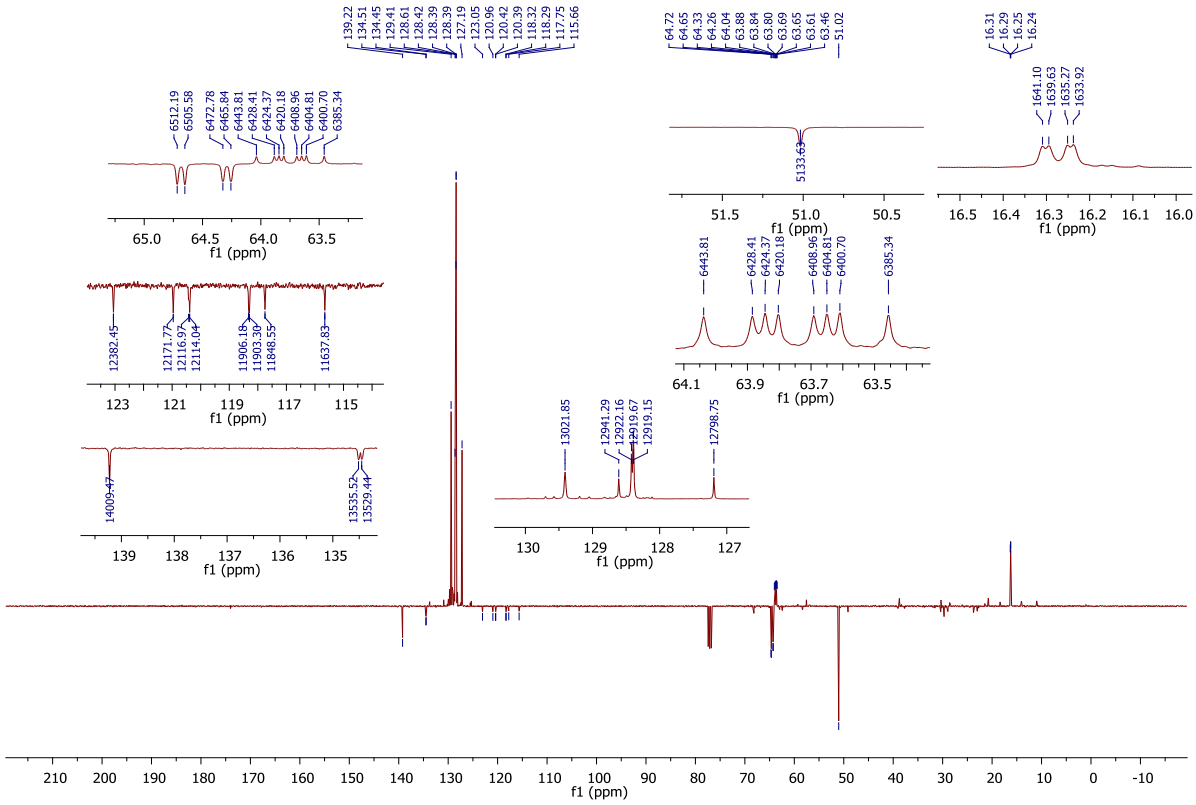
^{19}F NMR



^{1}H NMR



^{13}C NMR



HRMS

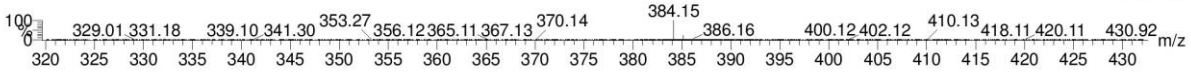
Elemental Composition Report

Single Mass Analysis

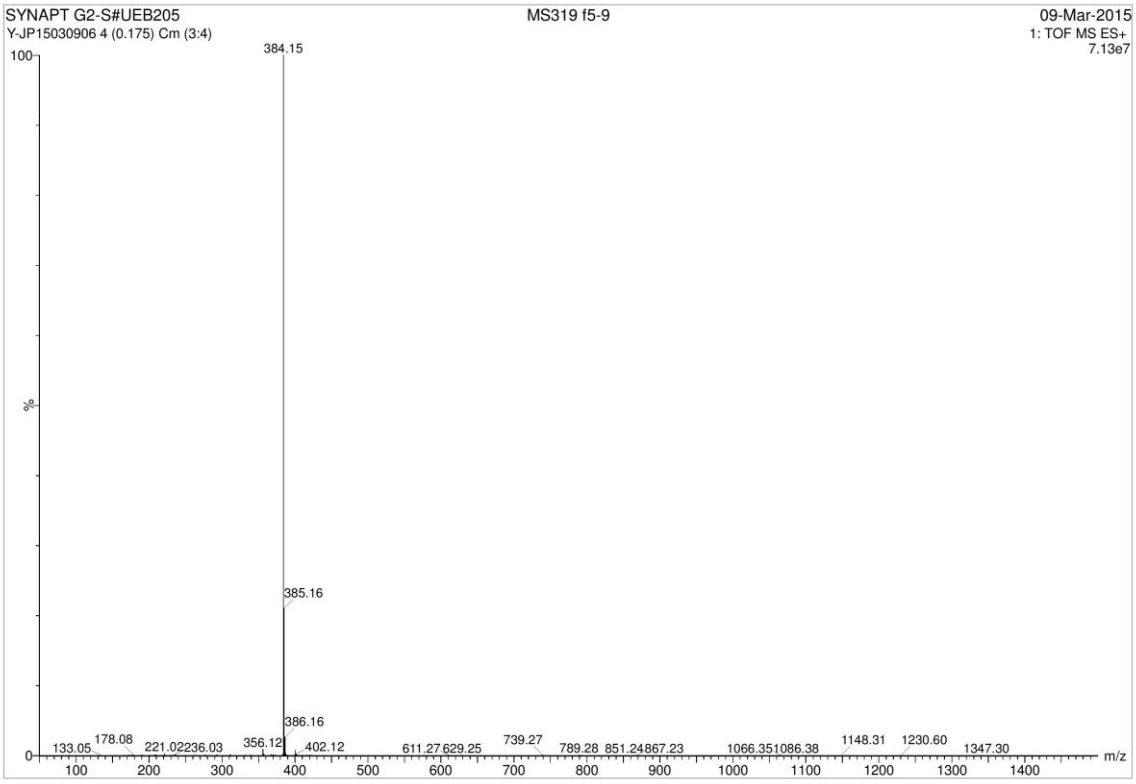
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
600 formula(e) evaluated with 2 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 F: 2-2 P: 1-1

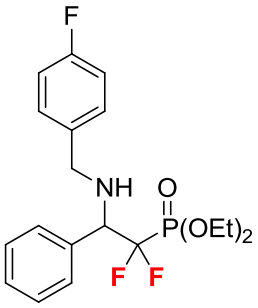
SYNAPT G2-S#UEB205 MS319 f5-9 09-Mar-2015
Y-JP15030906 10 (0.437) Cm (10:11) 1: TOF MS ES+
1.67e+006



Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
384.1541	384.1540	0.1	0.3	7.5	1651.5	0.000	100.00	C19 H25 N O3 F2 P
	384.1545	-0.4	-1.0	0.5	1675.0	23.522	0.00	C4 H21 N13 O4 F2 P

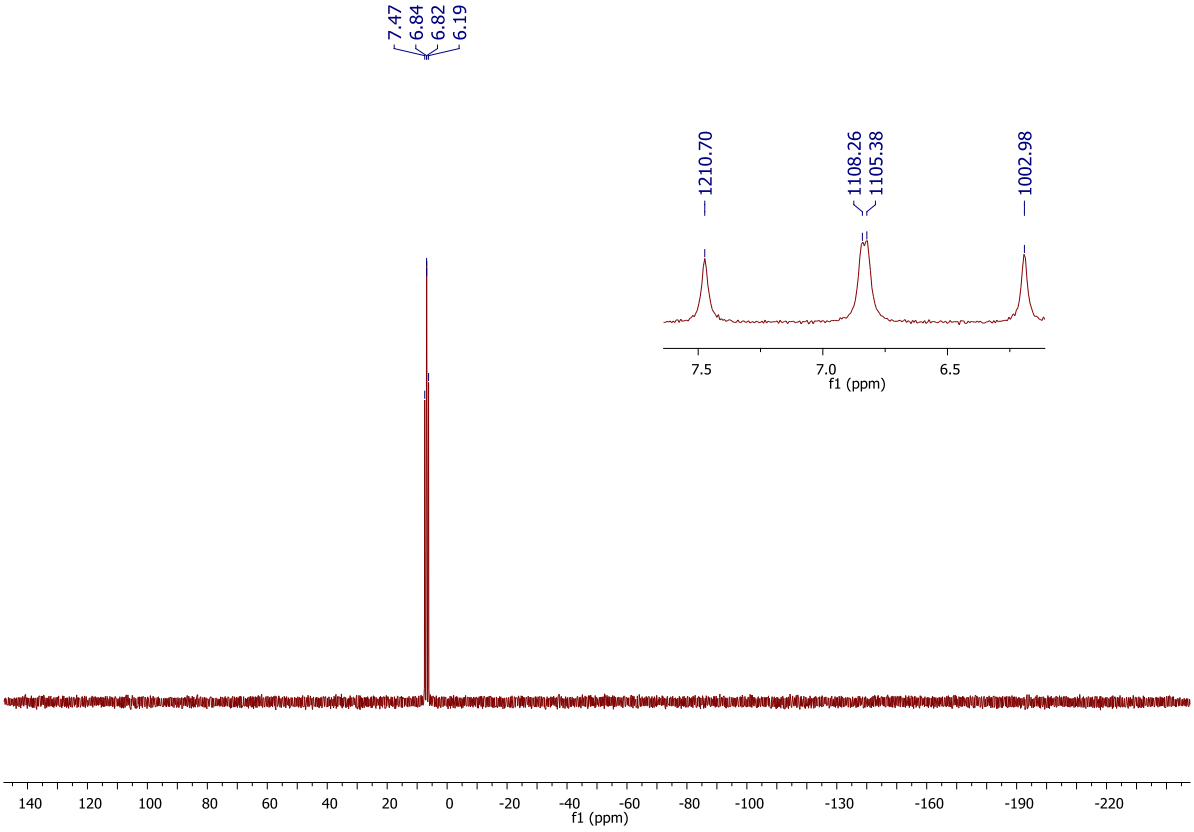


diethyl (1,1-difluoro-2-((4-fluorobenzyl)amino)-2-phenylethyl) phosphonate 15f

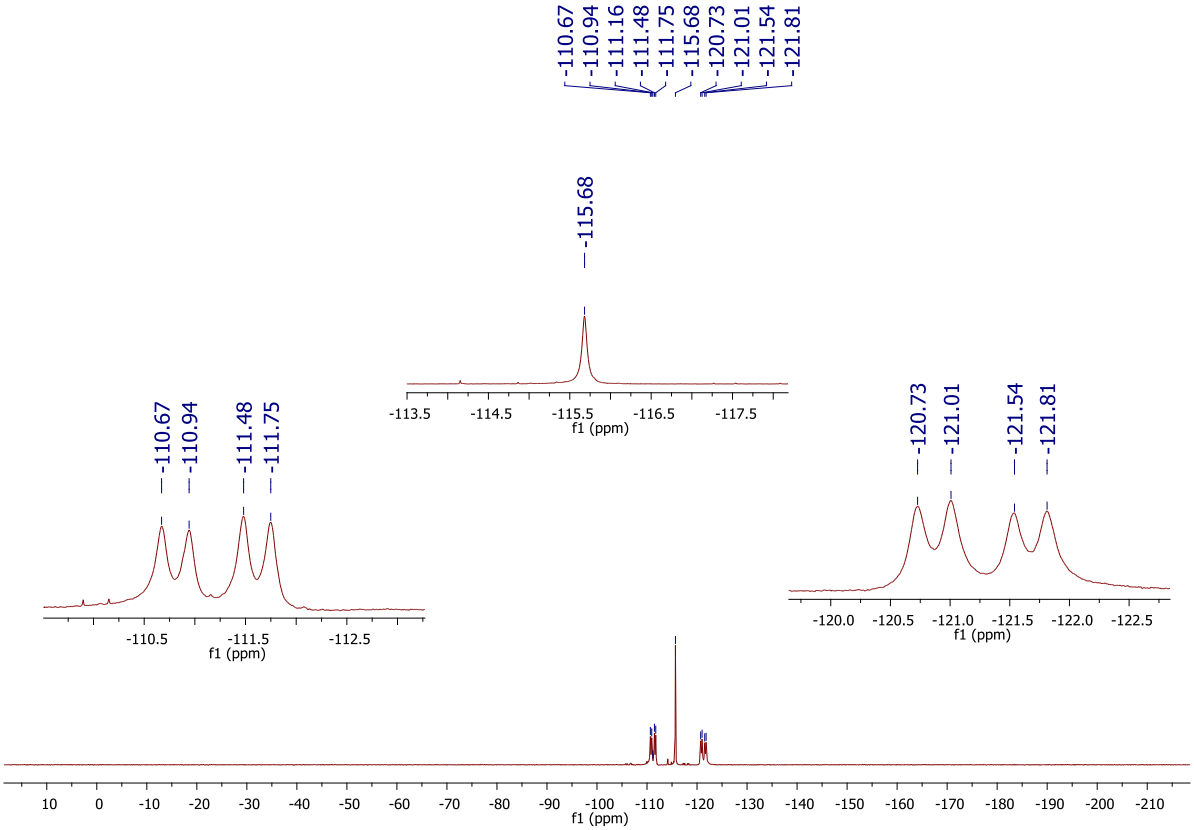


15f

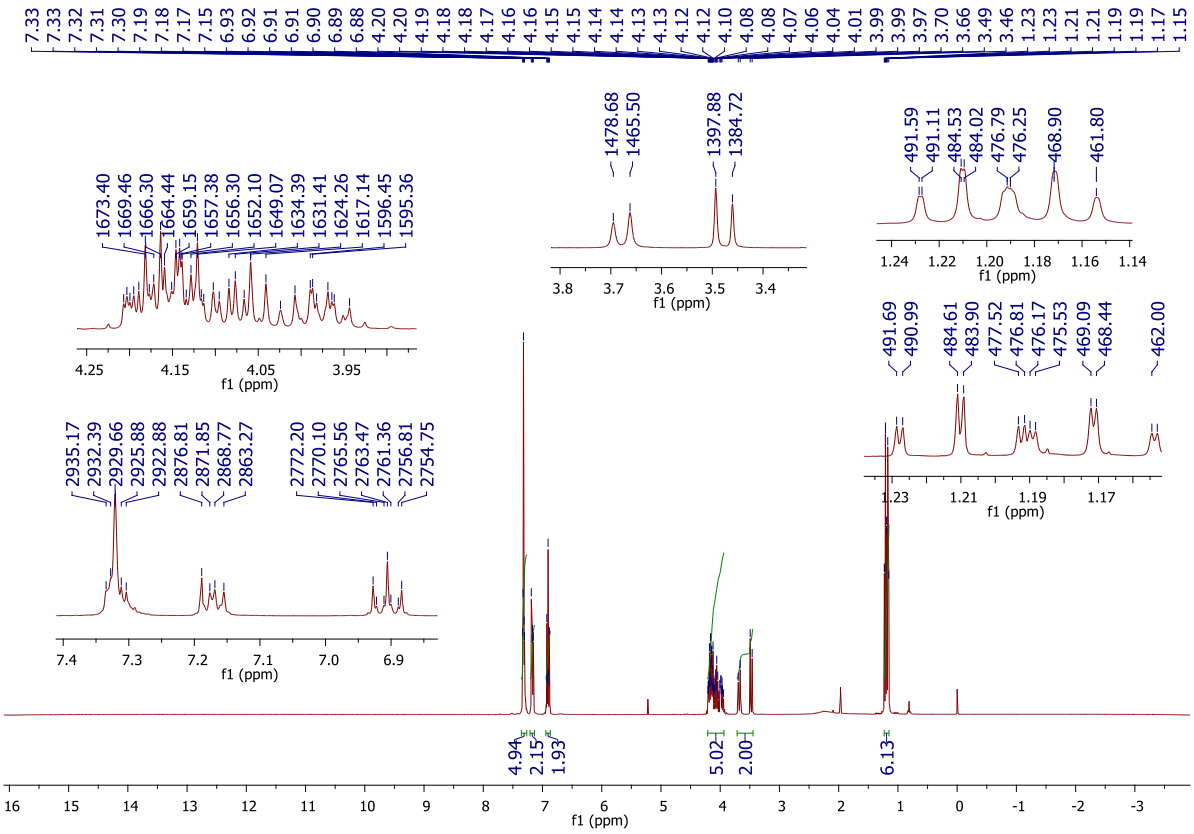
^{31}P NMR



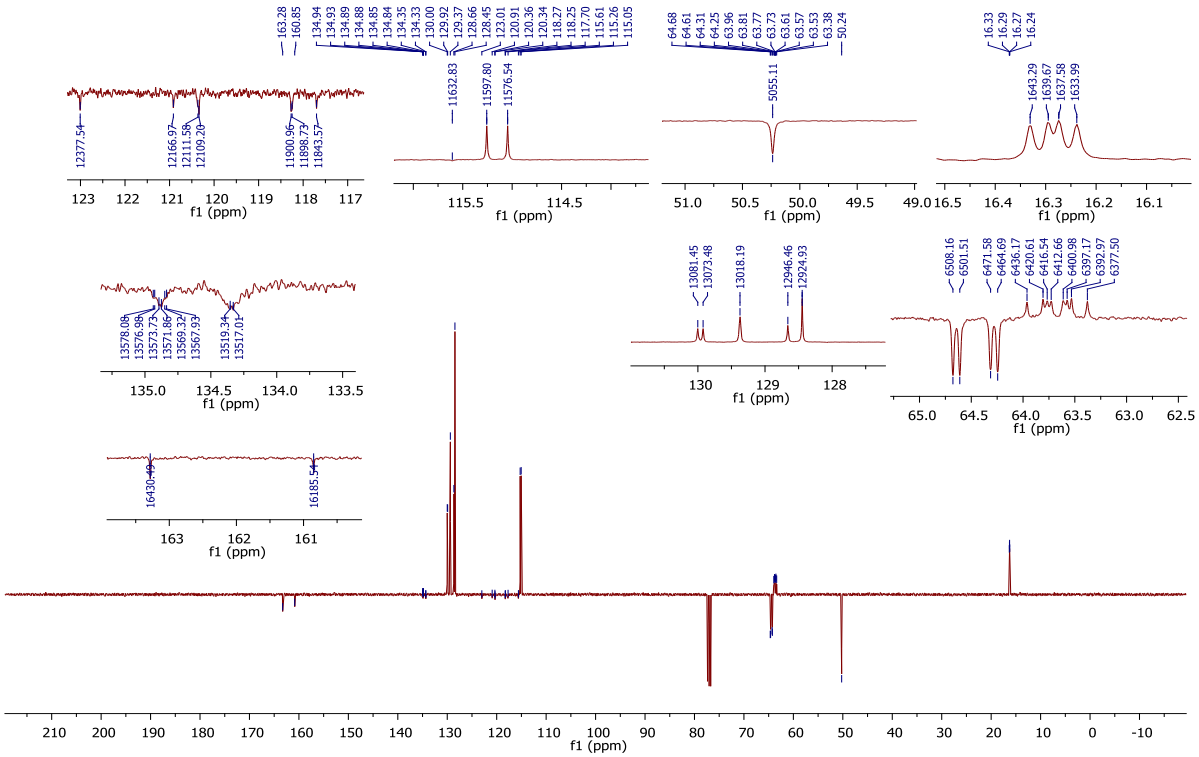
^{19}F NMR



^{1}H NMR



^{13}C NMR



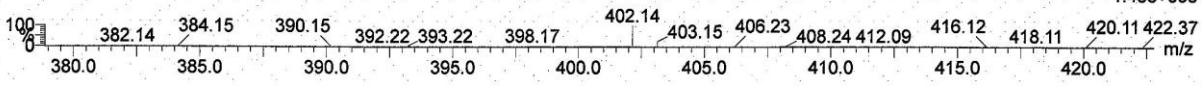
HRMS

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

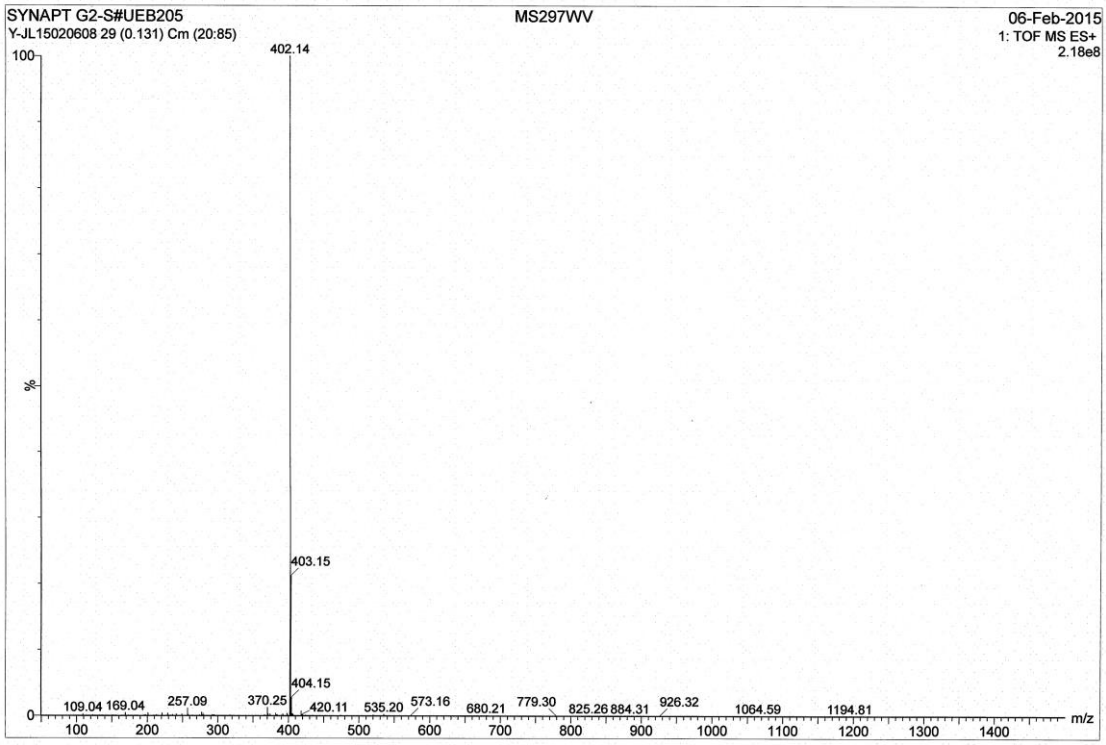
Monoisotopic Mass, Even Electron Ions
1969 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

SYNAPT G2-S#UEB205 MS297WV 06-Feb-2015
Y-JL15020608 52 (0.223) 1: TOF MS ES+
1.45e+006

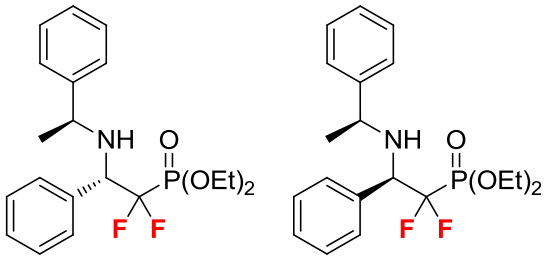


Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
402.1445	402.1446	-0.1	-0.2	7.5	735.4	0.004	99.58	C19 H24 N O3 F3 P
	402.1442	0.3	0.7	2.5	740.9	5.479	0.42	C13 H26 N3 O8 F P

4-FBn

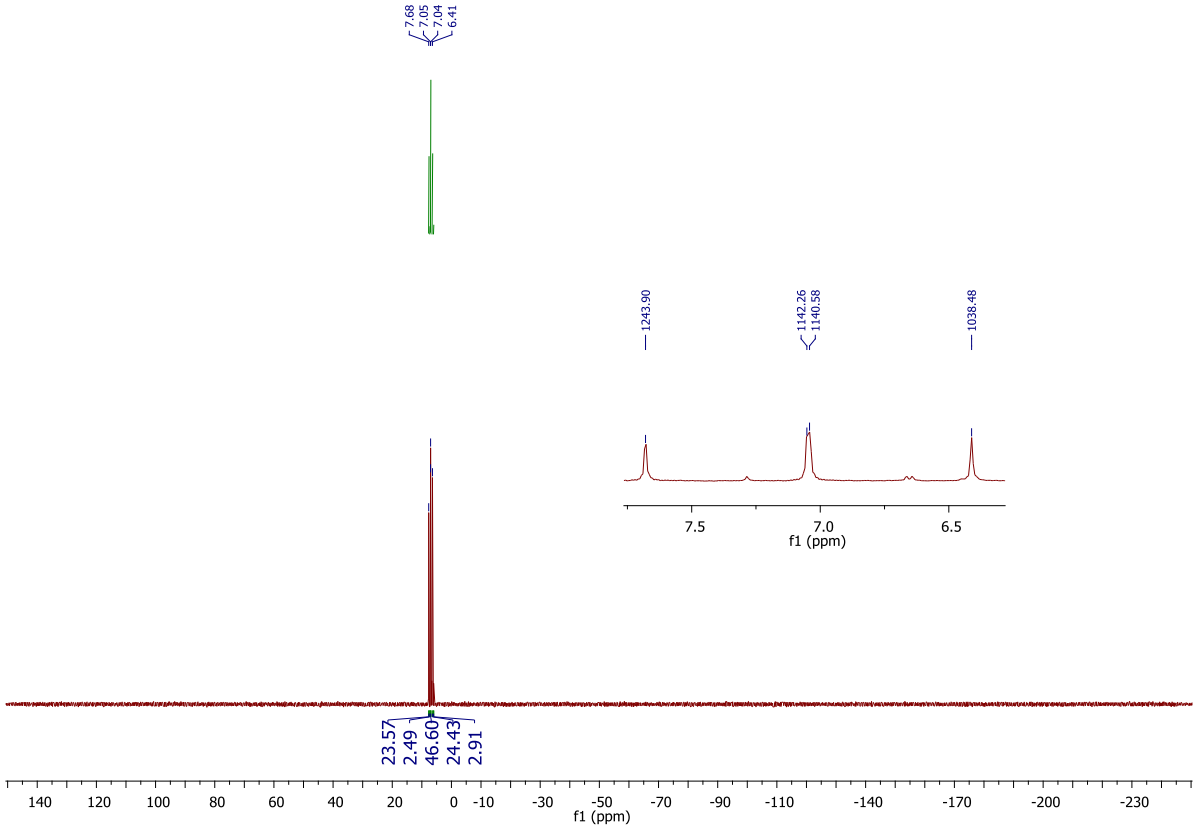

SYNAPT G2-S#UEB205
Y-JL15020608 29 (0.131) Cm (20:85)
MS297WV
06-Feb-2015
1: TOF MS ES+
2.18e8
100
%
0
402.14
403.15
404.15
109.04
169.04
257.09
370.25
420.11
535.20
573.16
680.21
779.30
825.26
884.31
926.32
1064.59
1194.81
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z

(*R*/*S*)-diethyl (1,1-difluoro-2-phenyl-2-(((*S*)-1-phenylethyl)amino) ethyl) phosphonate 15g

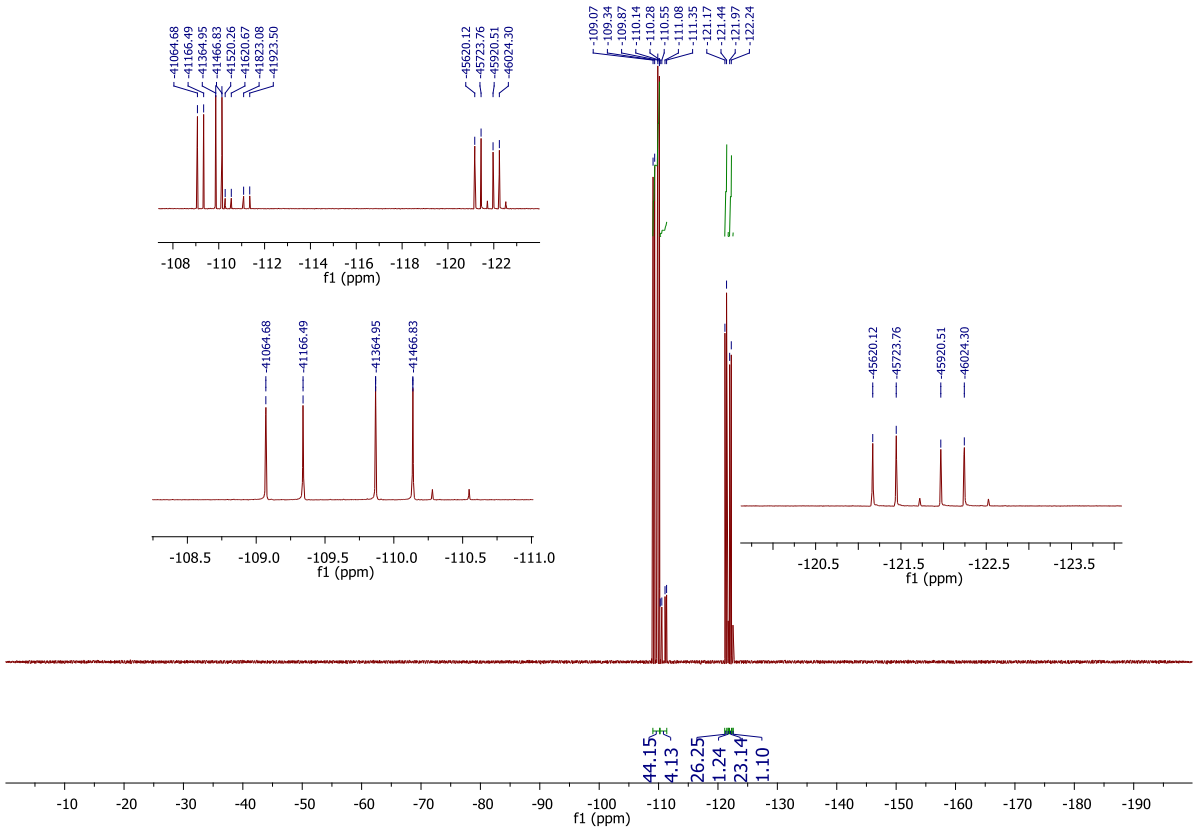


15g (91:9, dr, *S/R)*

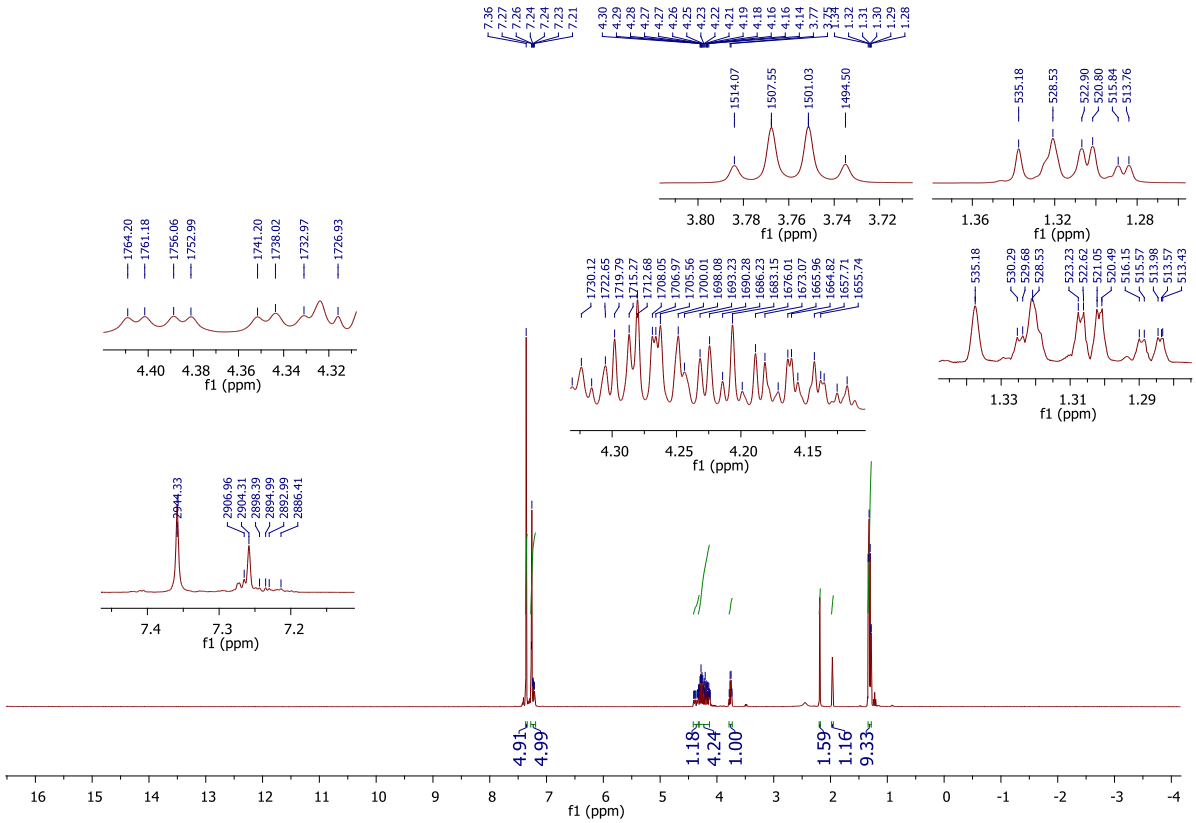
^{31}P NMR



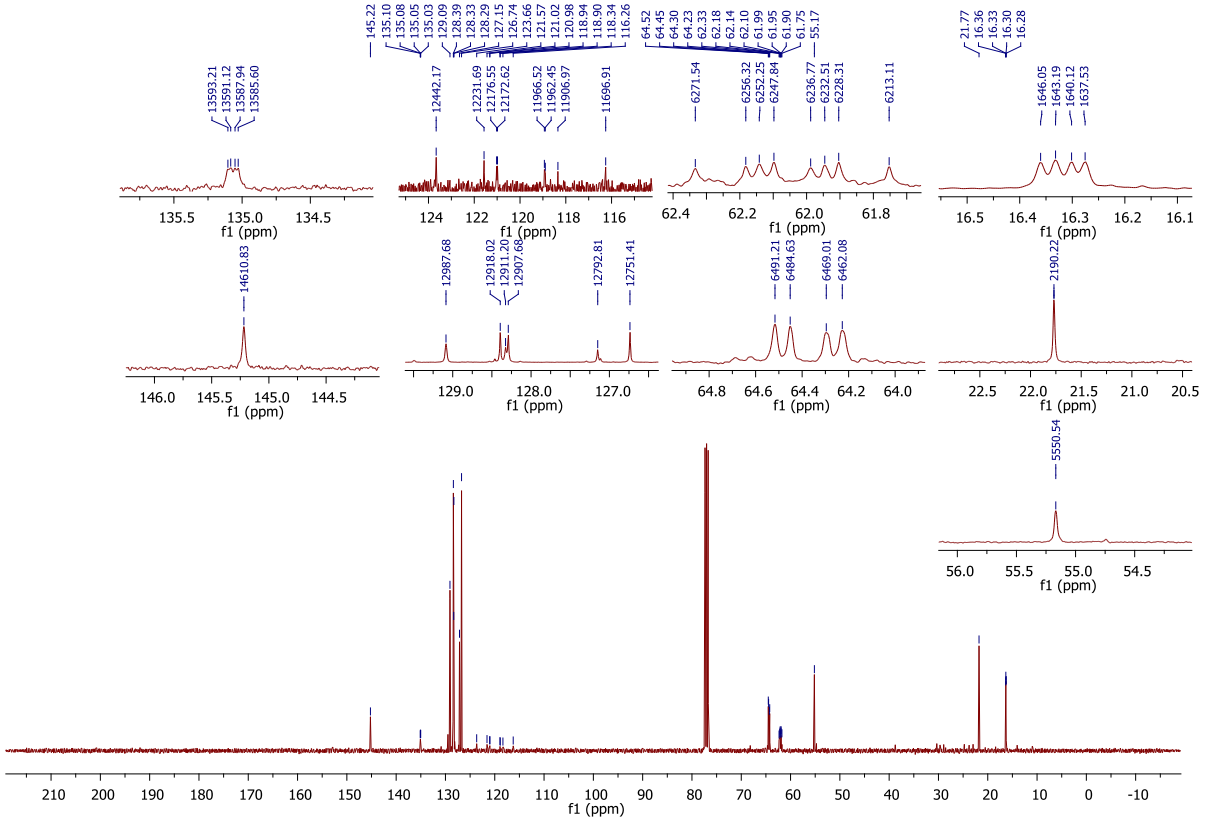
^{19}F NMR {H}



^{1}H NMR



^{13}C NMR



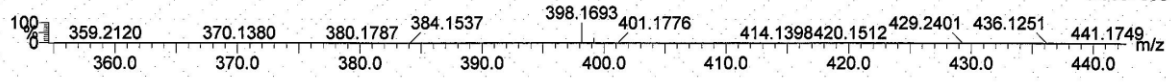
HRMS

Elemental Composition Report **Page 1**

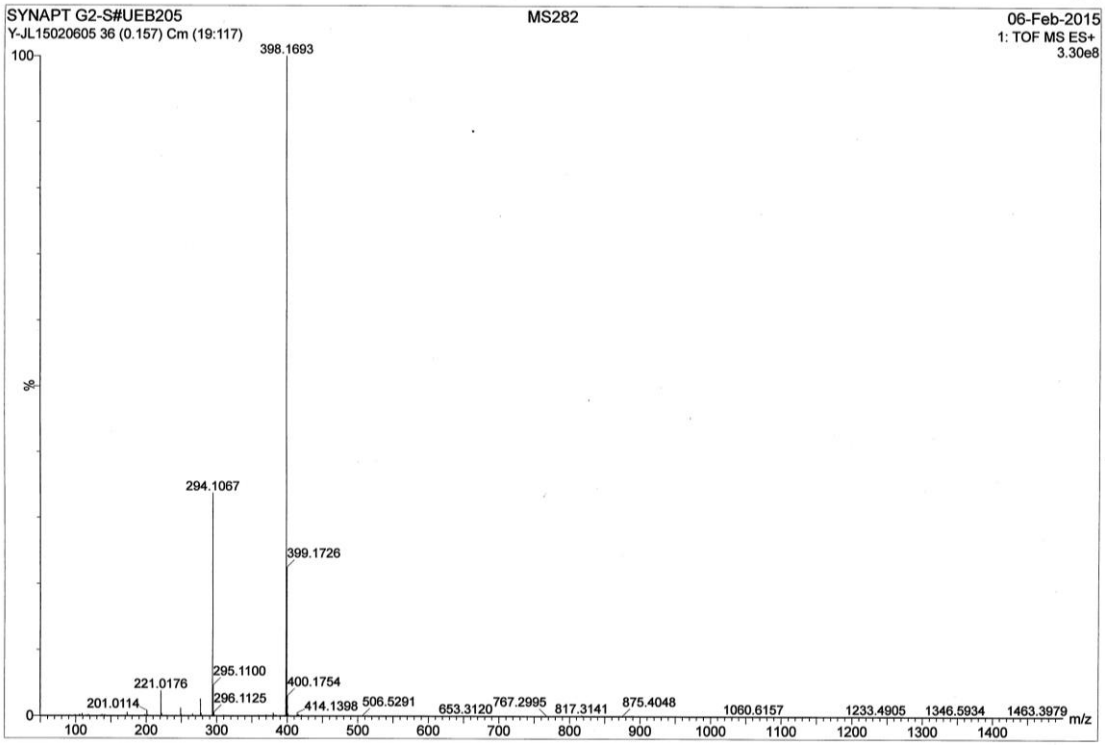
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

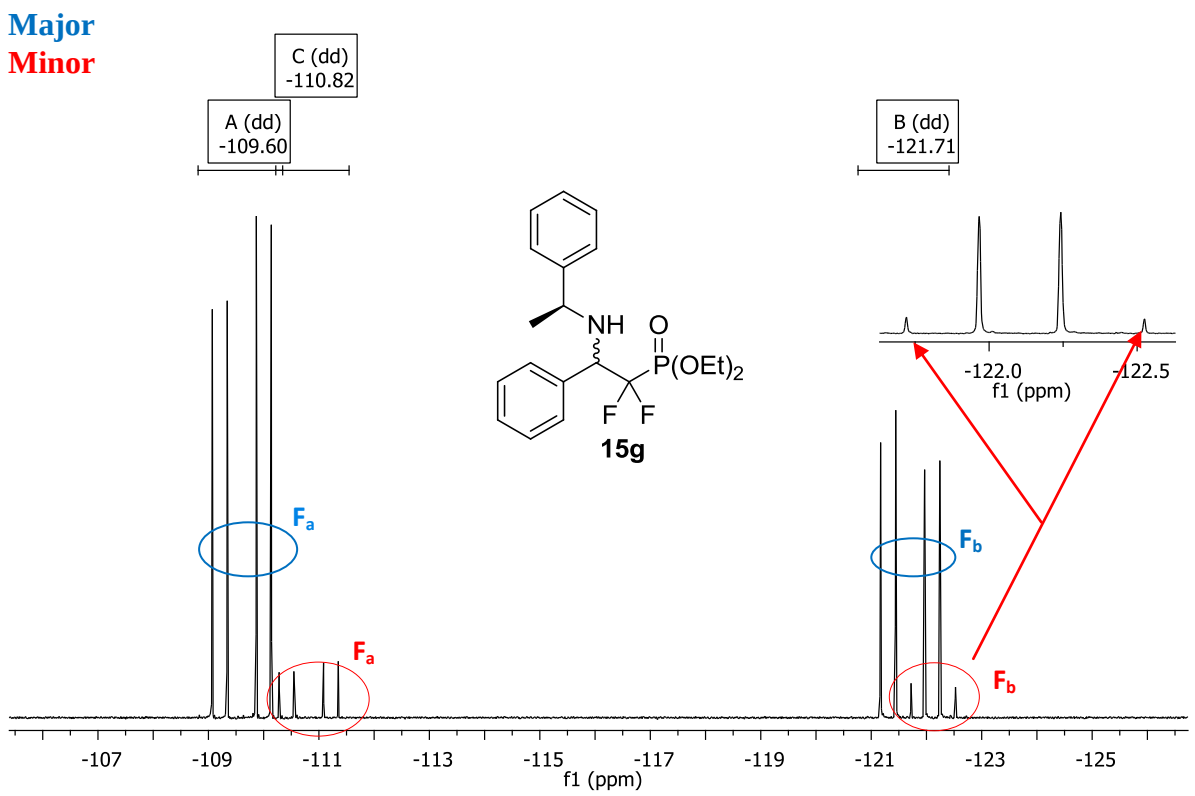
Monoisotopic Mass, Even Electron Ions
2789 formula(e) evaluated with 3 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 0-3 P: 1-1

SYNAPT G2-S#UEB205 MS282 06-Feb-2015
Y-JL15020605 36 (0.157) Cm (19:117) 1: TOF MS ES+
3.30e+008

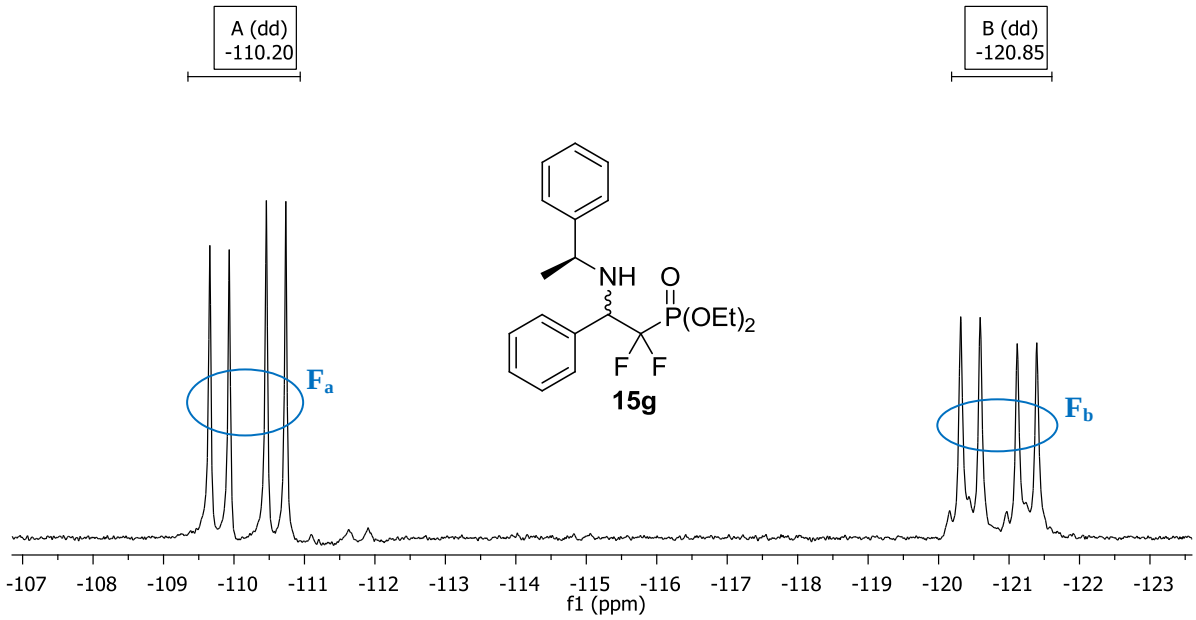


Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
398.1693	398.1697	-0.4	-1.0	7.5	3599.4	0.000	100.00	C20 H27 N O3 F2 P
	398.1692	0.1	0.3	2.5	3619.6	20.189	0.00	C14 H29 N3 O8 P
	398.1690	0.3	0.8	4.5	3626.2	26.811	0.00	C8 H22 N13 O3 F P


SYNAPT G2-S#UEB205
Y-JL15020605 36 (0.157) Cm (19:117)
MS282
06-Feb-2015
1: TOF MS ES+
3.30e8
100
%
0
398.1693
294.1067
399.1726
295.1100
221.0176
400.1754
296.1125
201.0114
414.1398
506.5291
653.3120
767.2995
817.3141
875.4048
1060.6157
1233.4905
1346.5934
1463.3979
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400

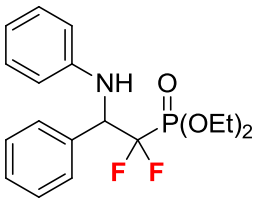


$^{19}F\{^{1}H\}$ NMR of 15g in acetonitrile (CD_3CN)



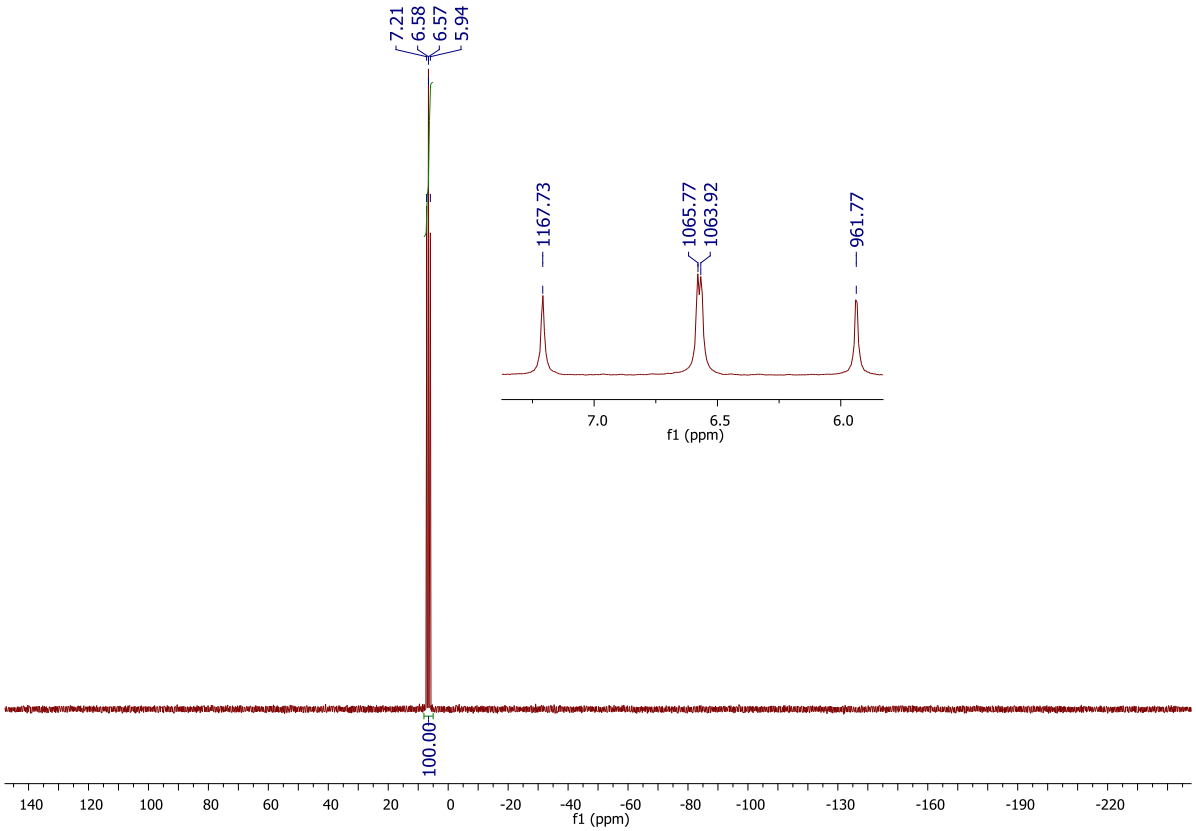
$^{19}F\{^{1}H\}$ NMR of 15g in chloroform ($CDCl_3$)

diethyl (1,1-difluoro-2-phenyl-2-(phenylamino)ethyl)phosphonate 15h

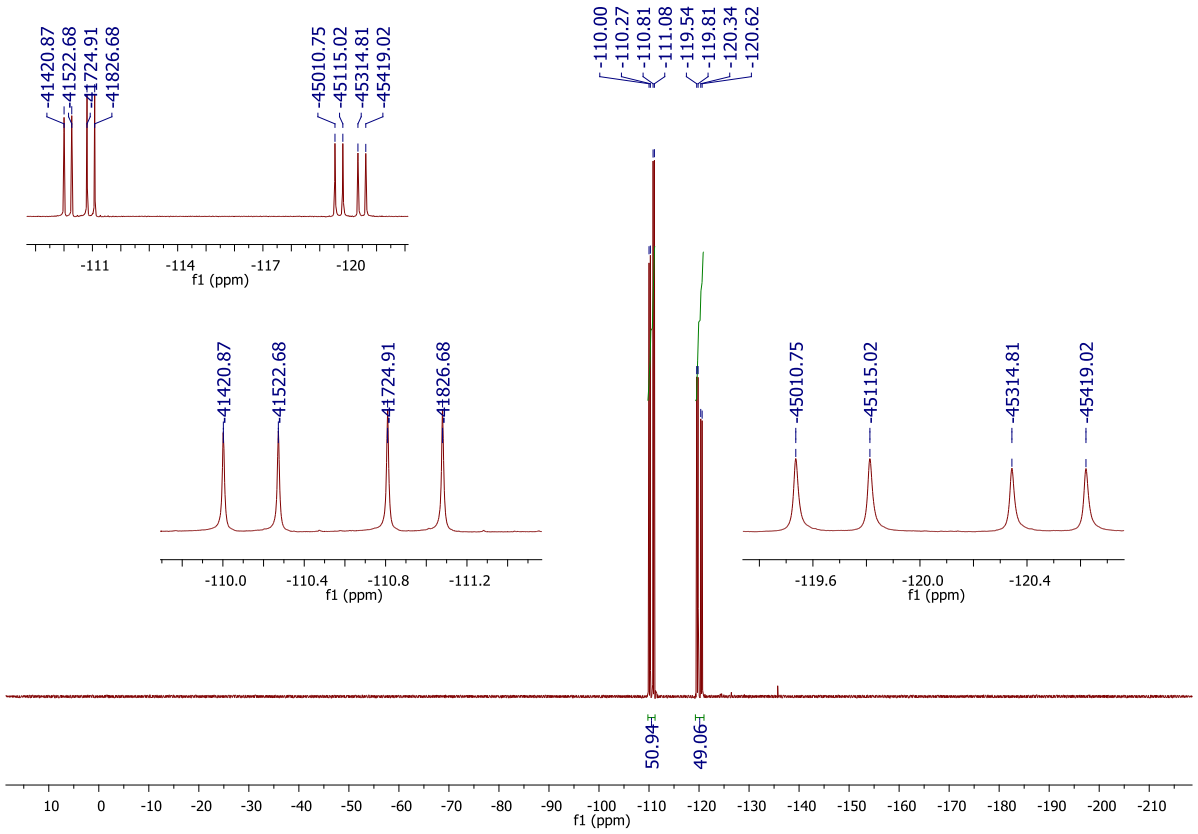


15h

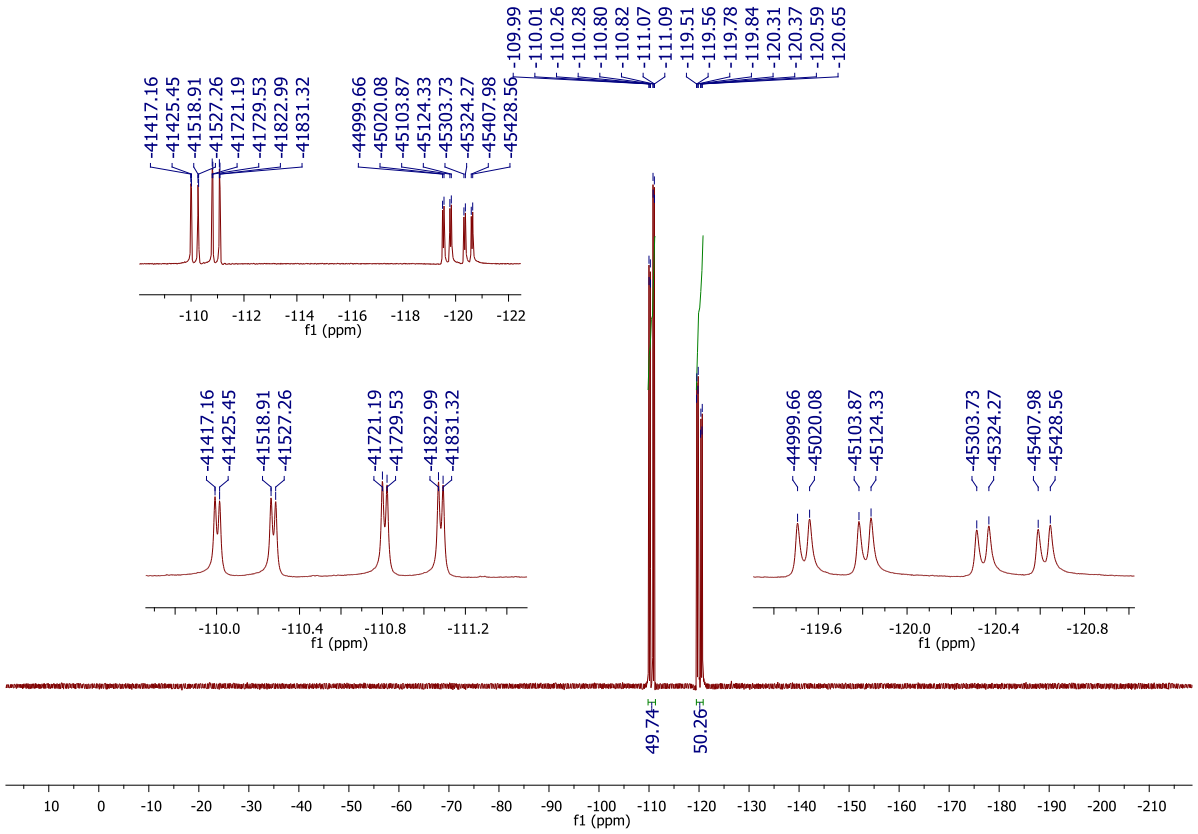
^{31}P NMR



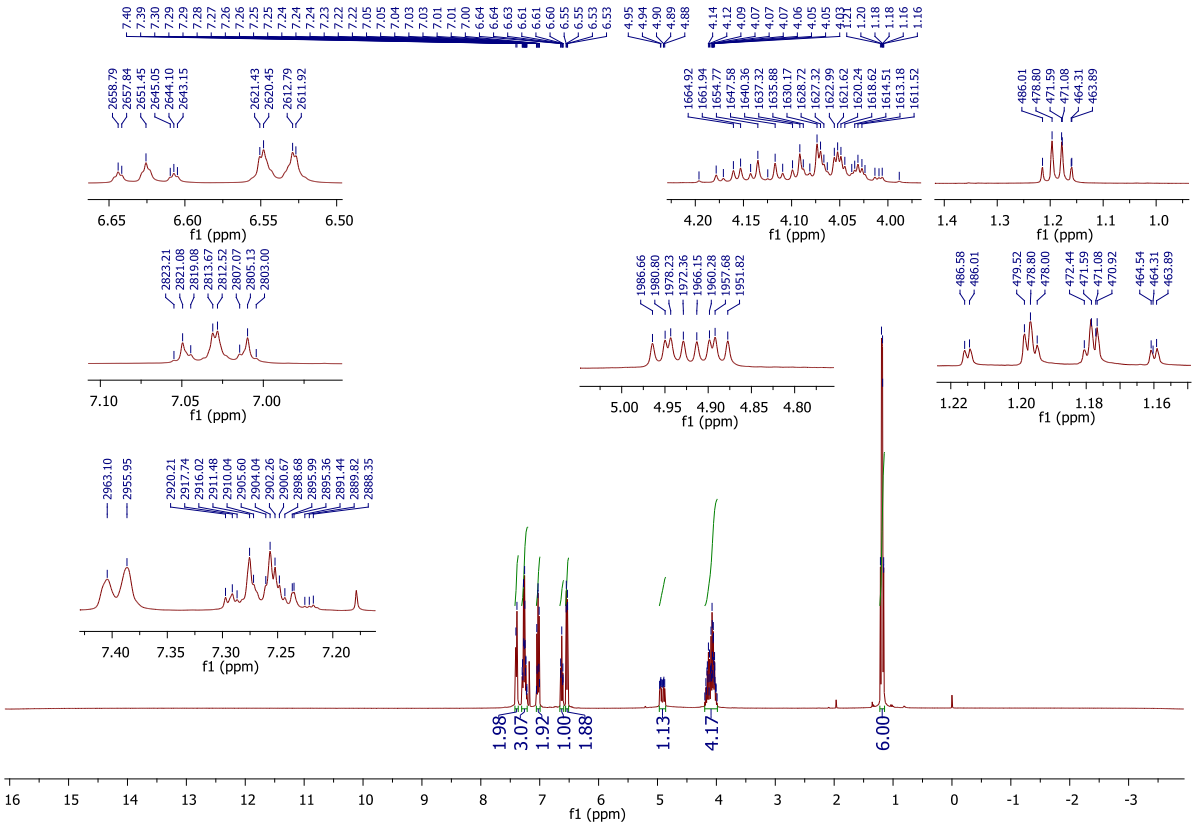
^{19}F NMR



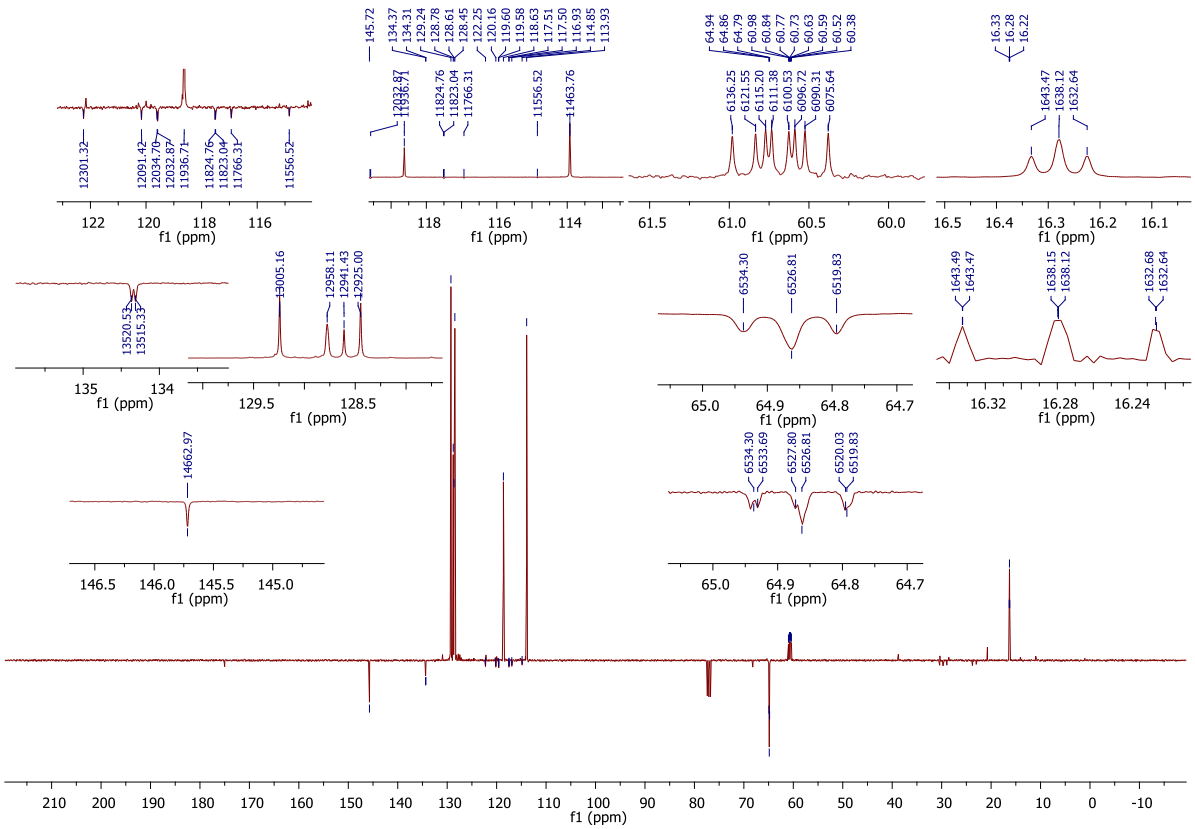
^{19}F NMR



^{1}H NMR



^{13}C NMR



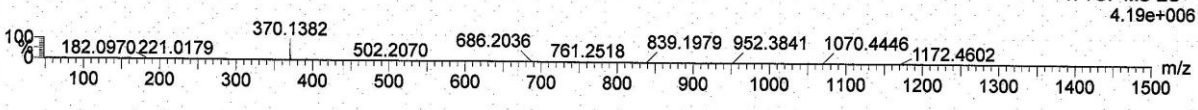
HRMS

Elemental Composition Report **Page 1**

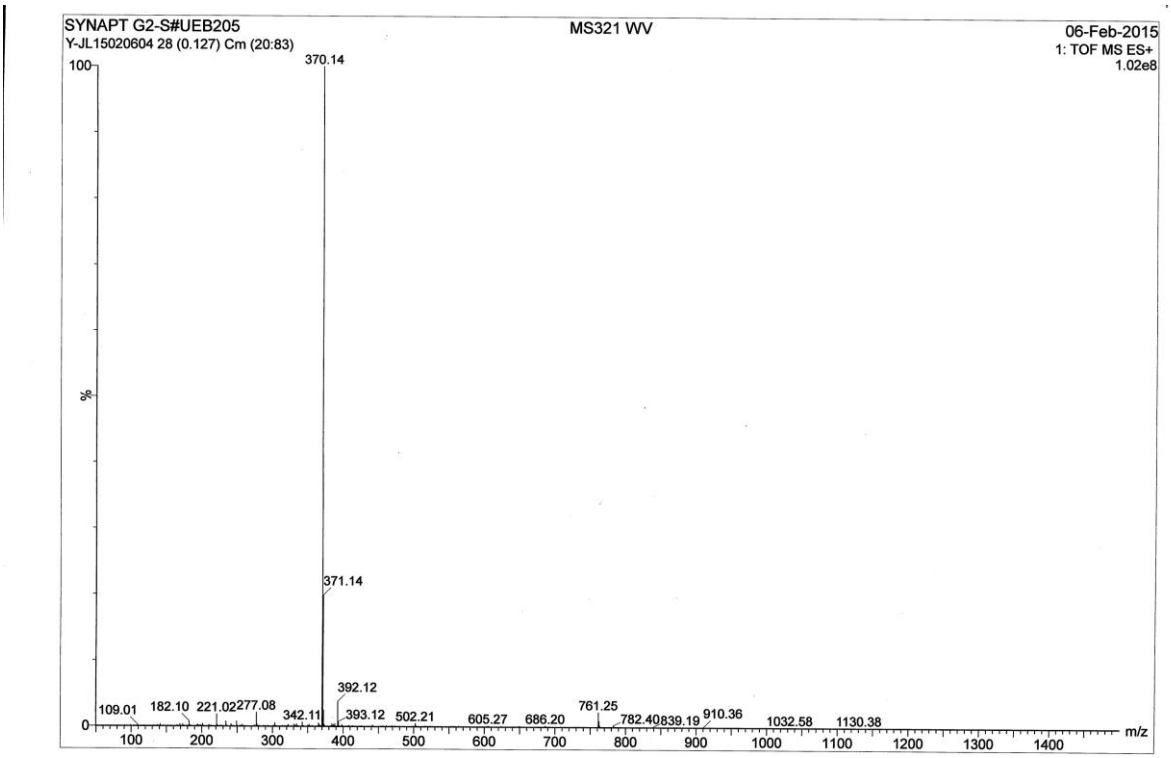
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2220 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 0-3 P: 1-1

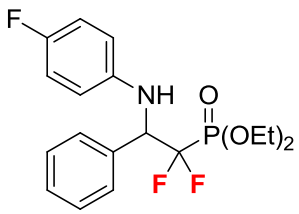
SYNAPT G2-S#UEB205
Y-JL15020604 31 (0.138)
MS321 WV
06-Feb-2015
1: TOF MS ES+
4.19e+006



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
370.1382	370.1384	-0.2	-0.5	7.5	1180.8	0.000	100.00	C18 H23 N O3 F2 P
	370.1379	0.3	0.8	2.5	1194.8	14.014	0.00	C12 H25 N3 O8 P

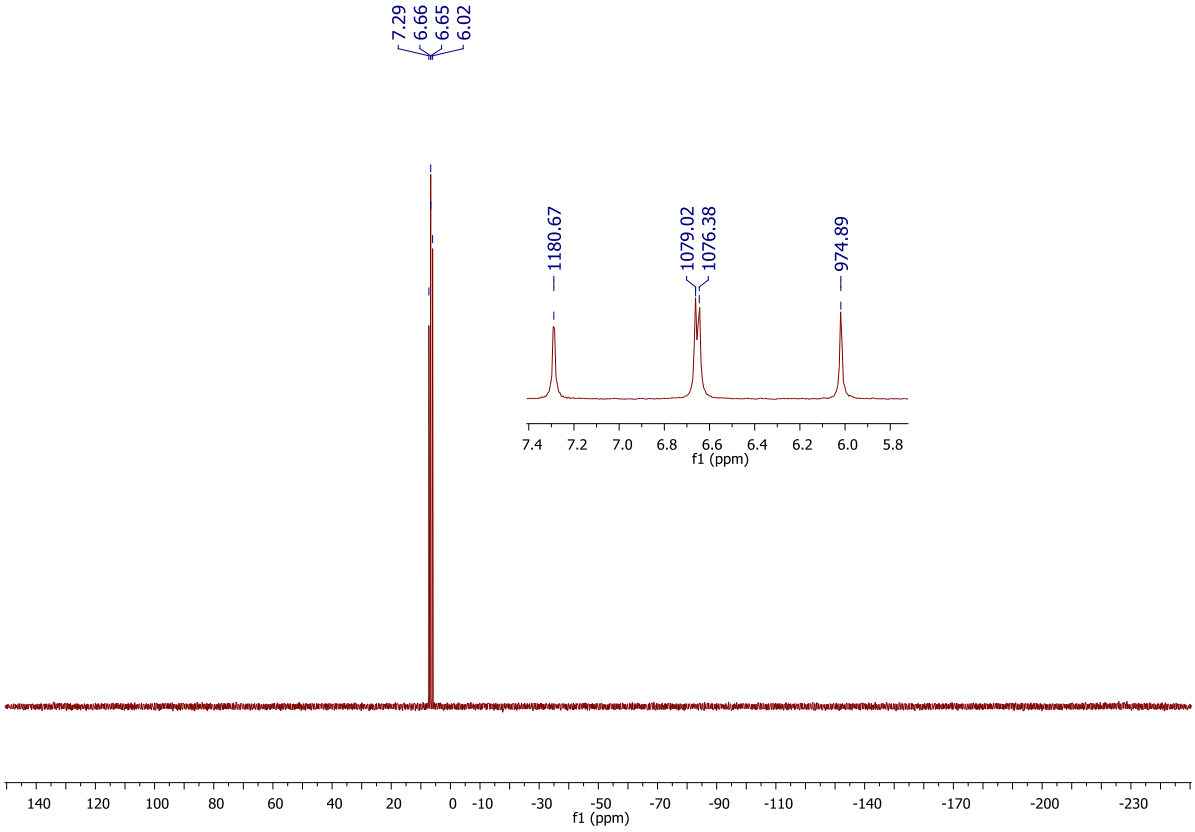


diethyl (1,1-difluoro-2-((4-fluorophenyl)amino)-2-phenylethyl) phosphonate 15i

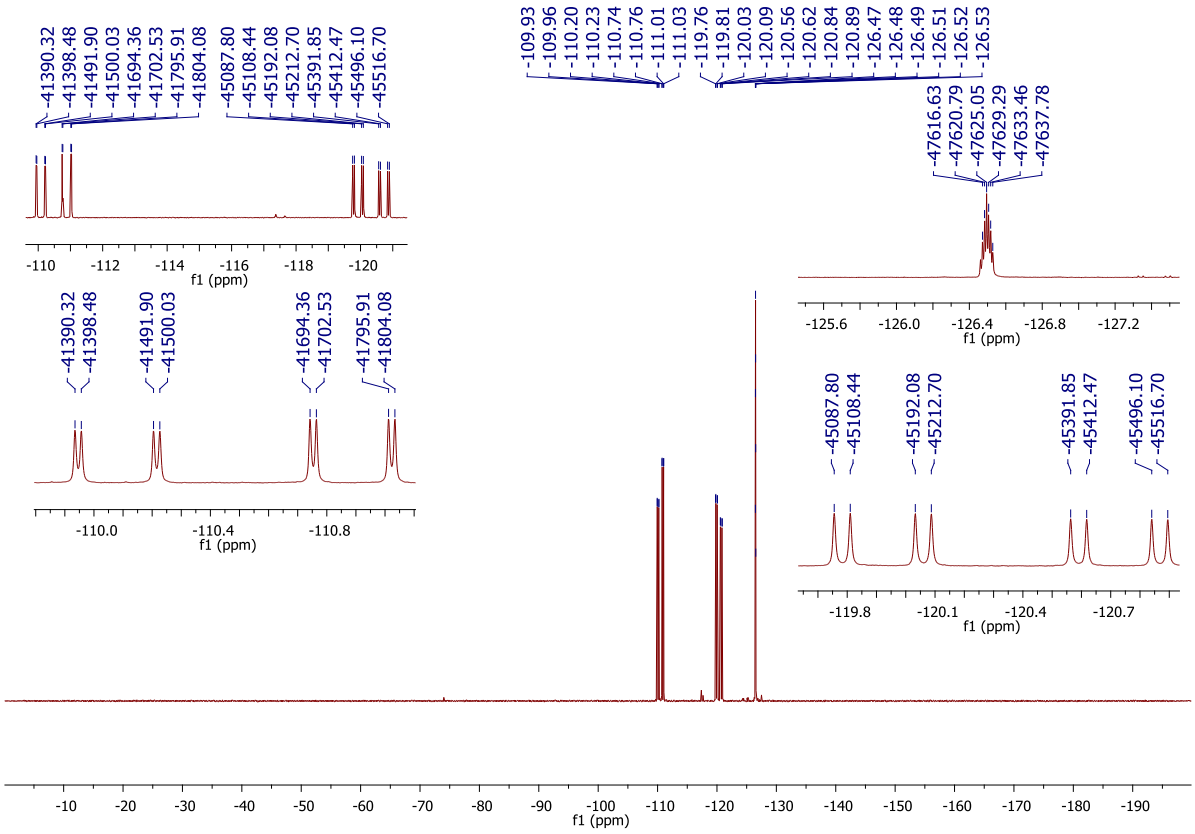


15i

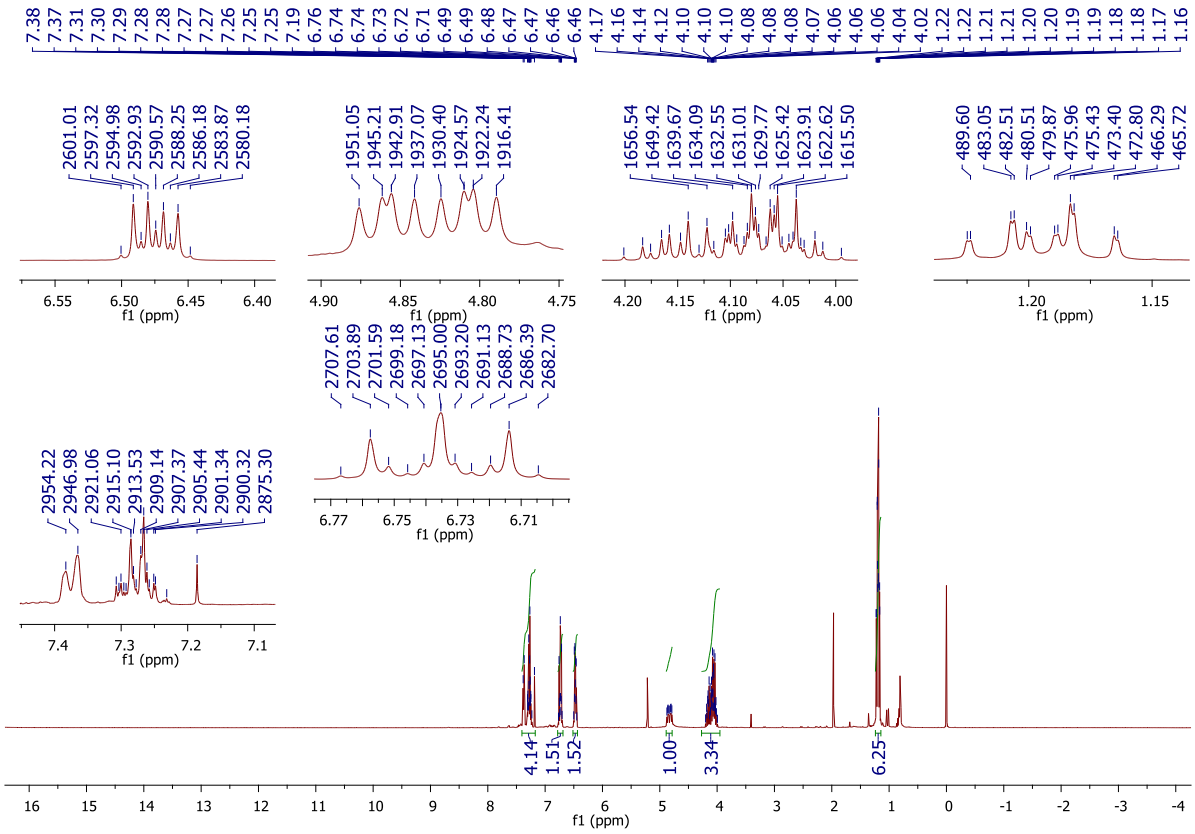
^{31}P NMR



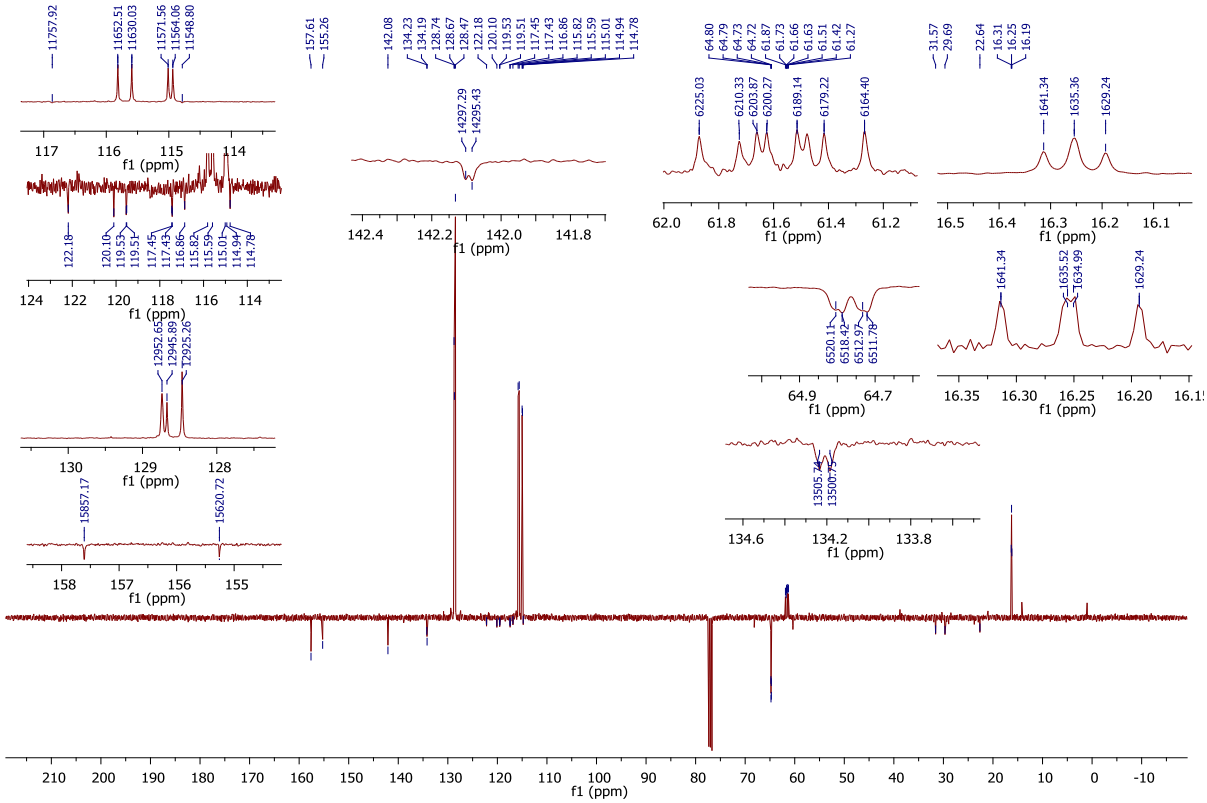
^{19}F NMR



^{1}H NMR



^{13}C NMR



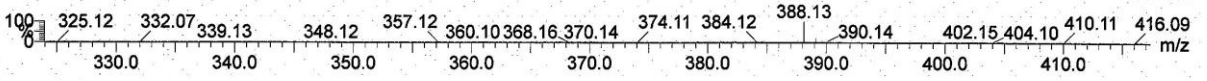
HRMS

Elemental Composition Report **Page 1**

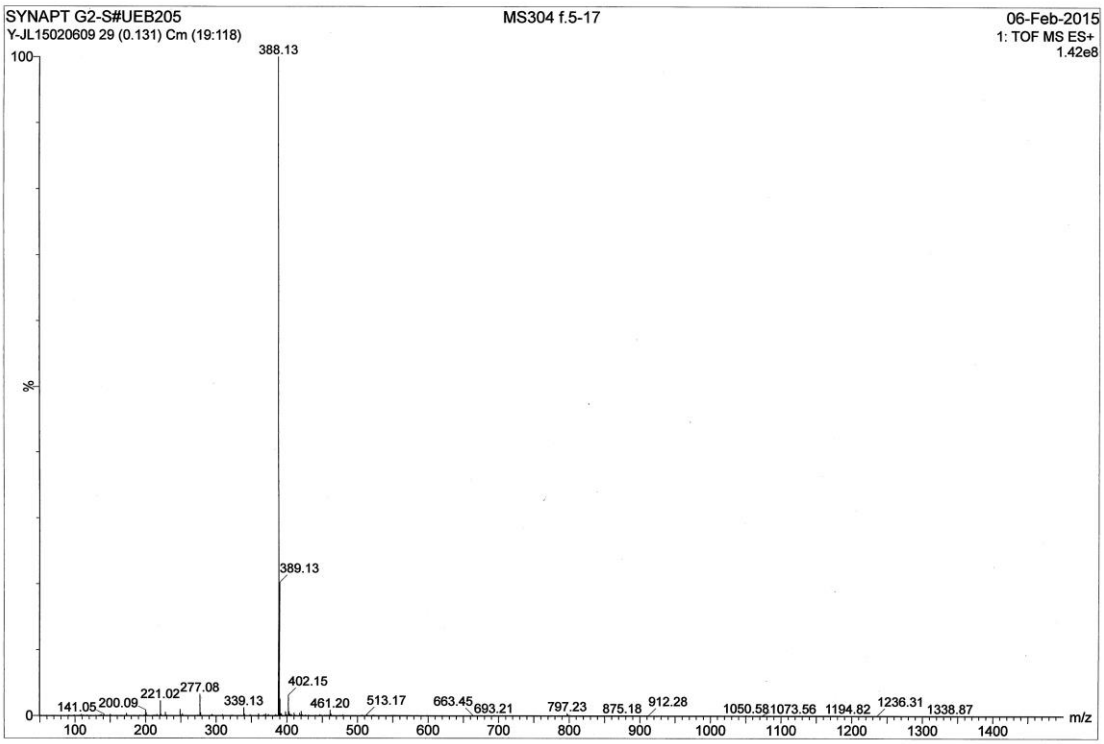
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1757 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 5-100 H: 0-100 N: 0-30 O: 0-30 F: 1-3 P: 1-1

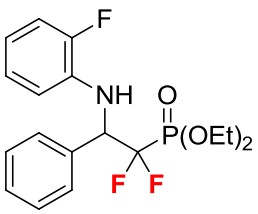
SYNAPT G2-S#UEB205 MS304 f.5-17 06-Feb-2015
Y-JL15020609 21 (0.100) 1: TOF MS ES+
2.59e+006



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
388.1289	388.1289	0.0	0.0	7.5	897.4	n/a	n/a	C18 H22 N O3 F3 P

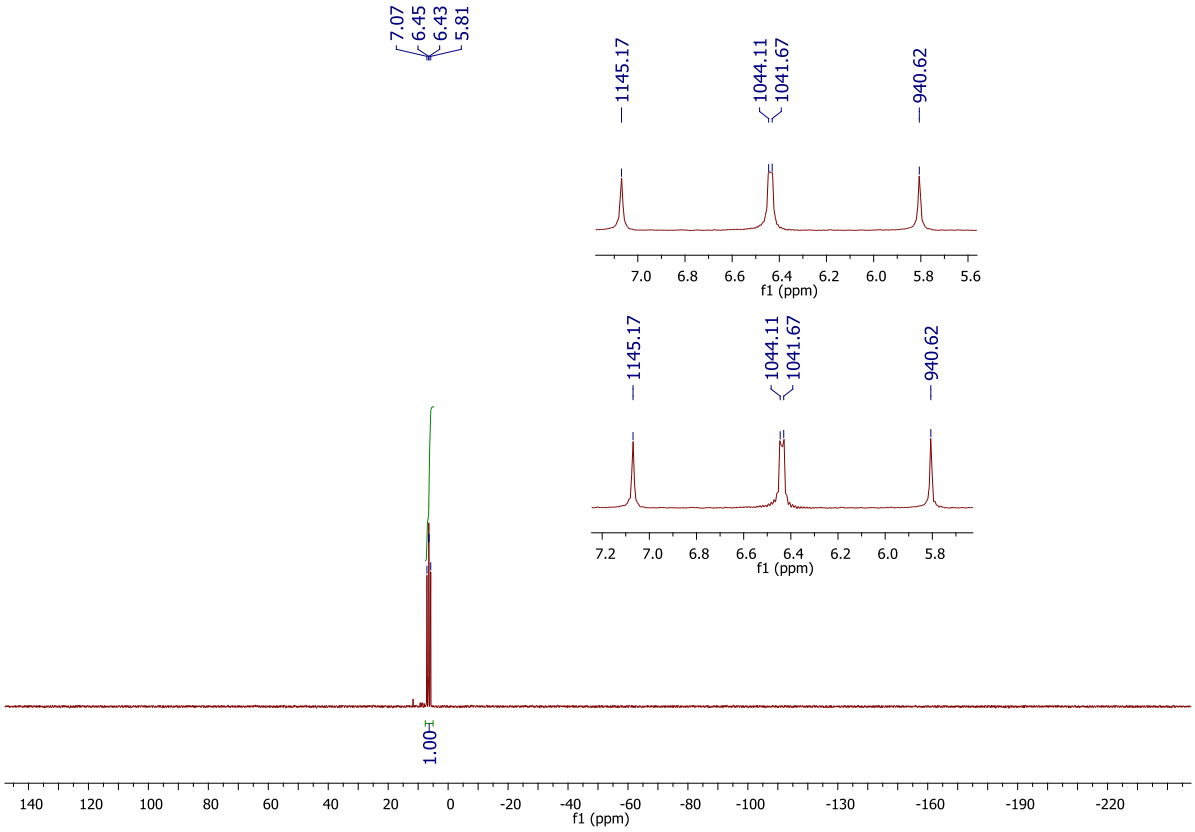

SYNAPT G2-S#UEB205
MS304 f.5-17
06-Feb-2015
Y-JL15020609 29 (0.131) Cm (19:118)
1: TOF MS ES+
1.42e8
100
%
0
388.13
389.13
402.15
141.05
200.09
221.02
277.08
339.13
461.20
513.17
663.45
693.21
797.23
875.18
912.28
1050.58
1073.56
1194.82
1236.31
1338.87
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z

diethyl (1,1-difluoro-2-((2-fluorophenyl)amino)-2-phenylethyl) phosphonate 15j



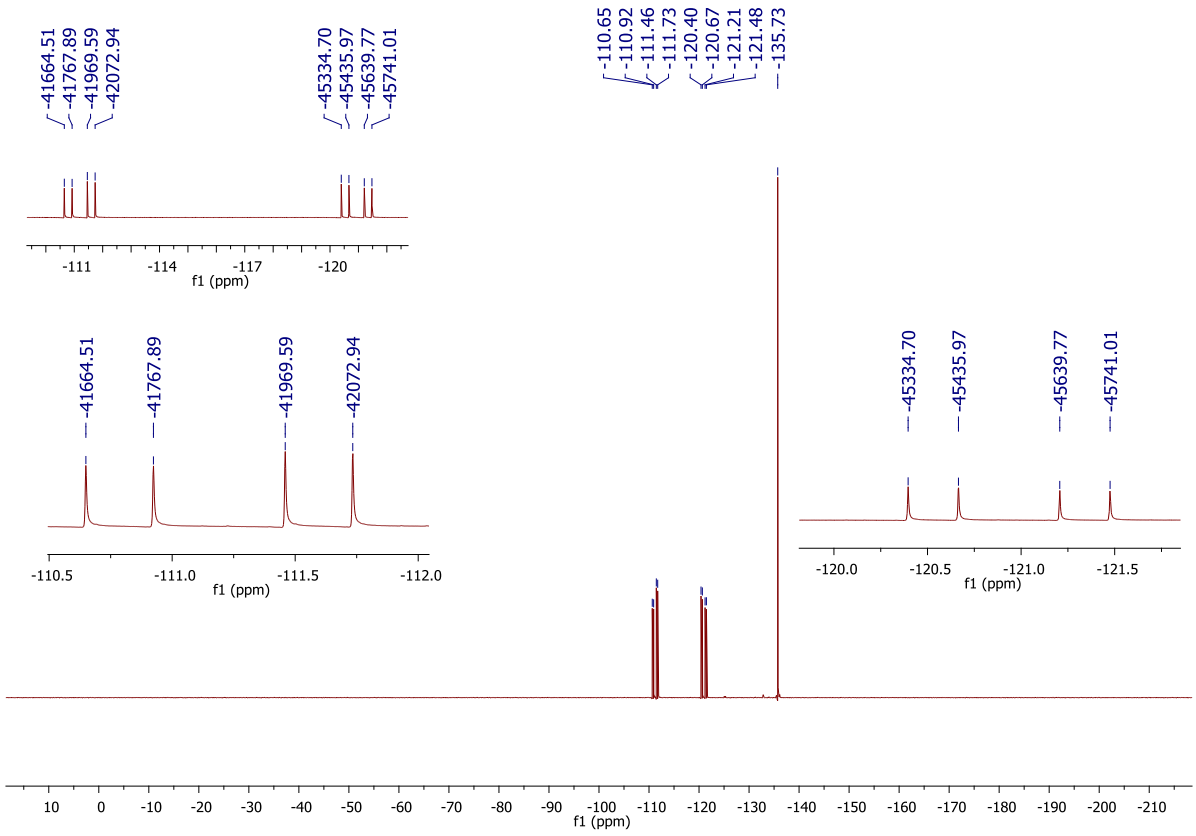
15j

^{31}P NMR

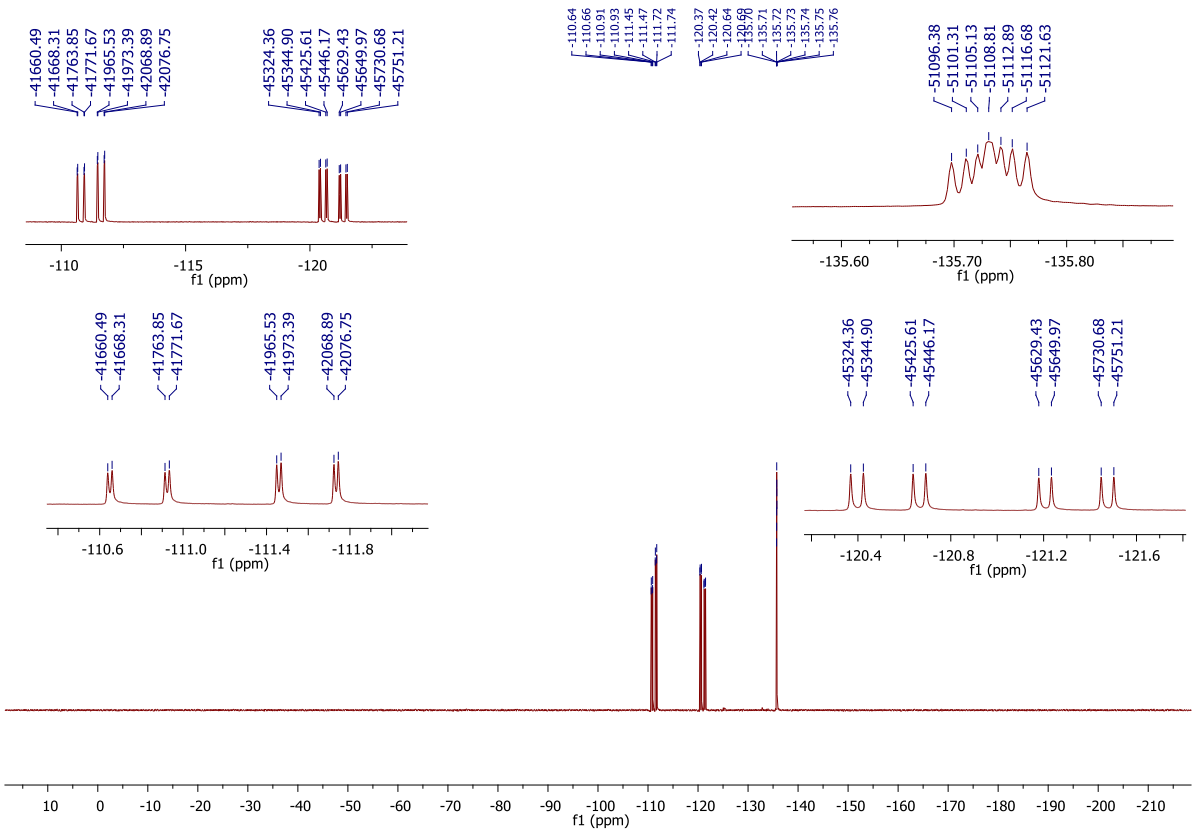


^{9}F NMR

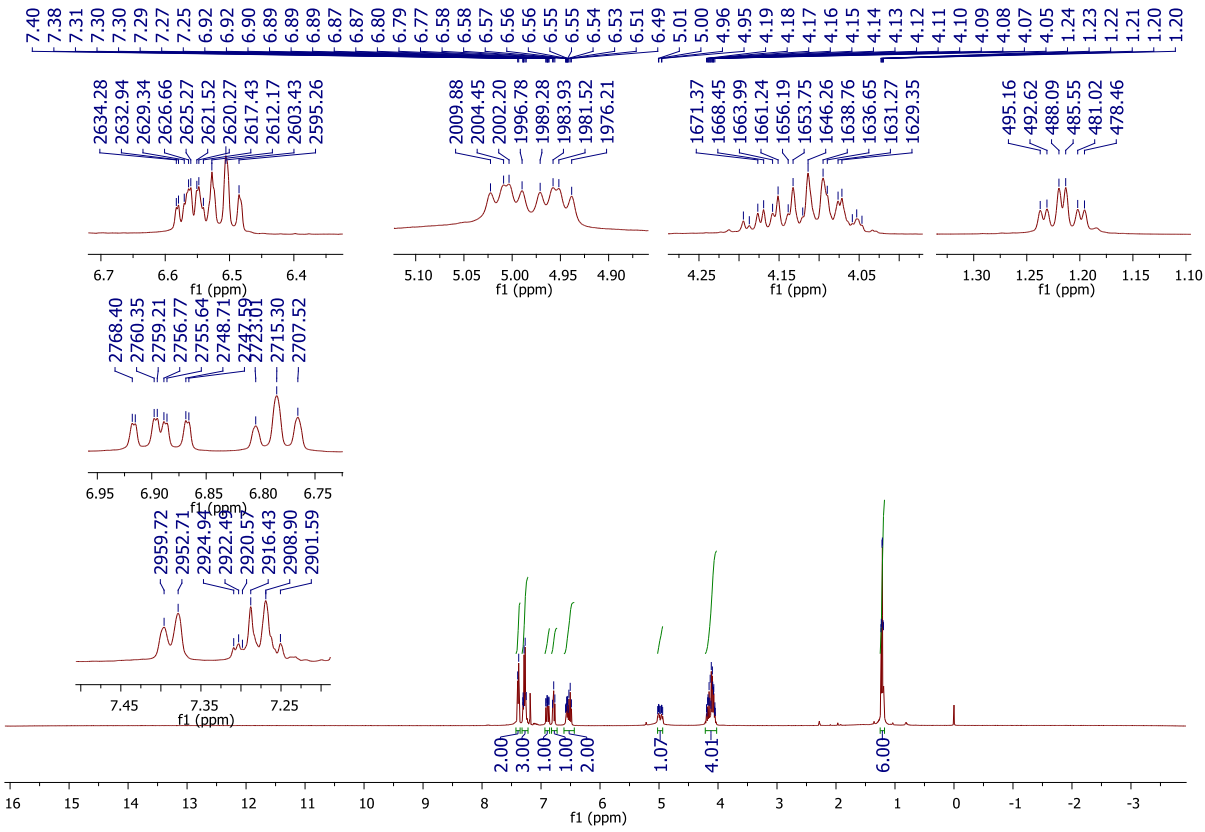
{H}


-41664.51
-41767.89
-41969.59
-42072.94
-45334.70
-45435.97
-45639.77
-45741.01
-110.65
-110.92
-111.46
-111.73
-120.40
-120.67
-121.21
-121.48
-135.73
f1 (ppm)

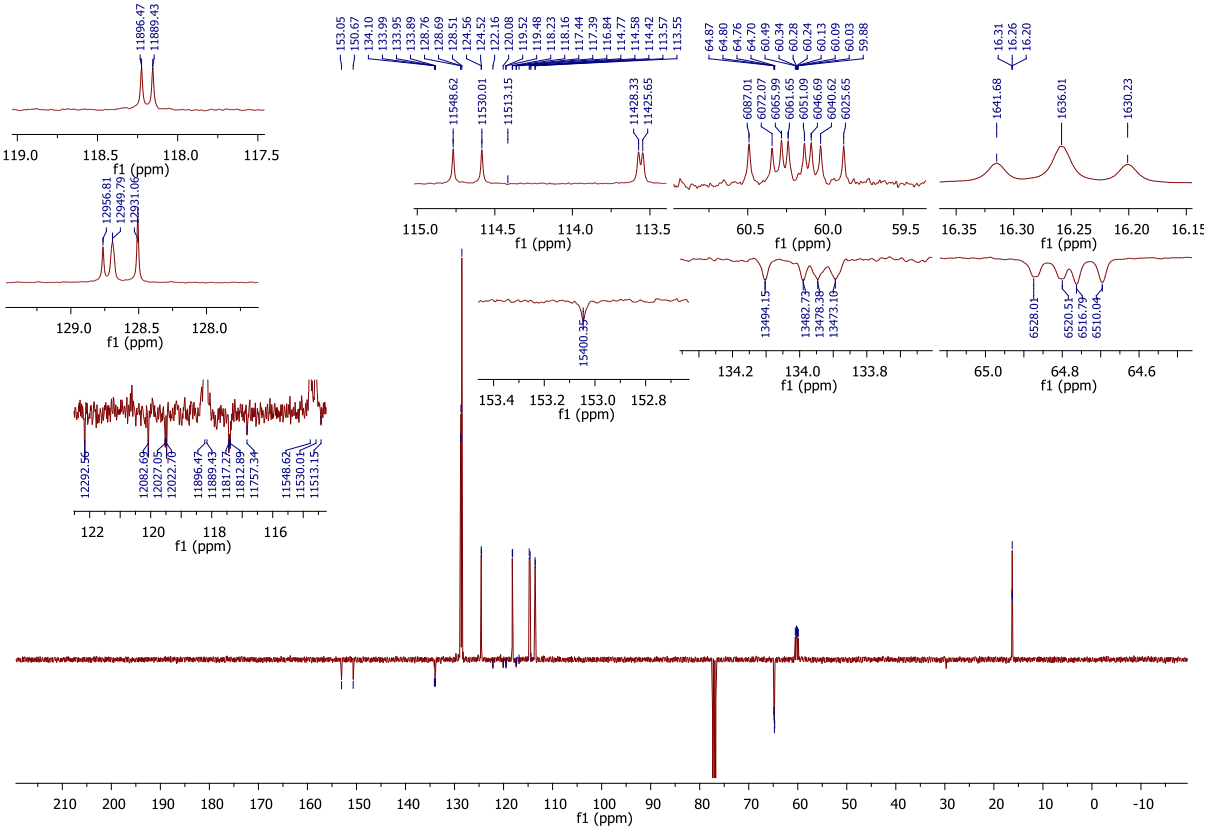
^{19}F NMR



^{1}H NMR



^{13}C NMR


11896.47
11889.43
119.0
118.5
118.0
117.5
f1 (ppm)
12956.81
12949.79
12931.06
129.0
128.5
128.0
f1 (ppm)
12292.56
12082.62
12027.05
12022.76
11896.47
11889.43
11817.27
11812.89
11757.34
11548.62
11530.01
11513.15
122
120
118
116
f1 (ppm)
153.05
150.67
134.10
133.99
133.95
133.89
128.76
128.69
128.51
124.56
124.52
122.16
120.08
119.52
119.48
118.23
118.16
117.44
117.39
116.84
114.77
114.58
114.42
113.57
113.55
11548.62
11530.01
11513.15
11428.33
11425.65
115.0
114.5
114.0
113.5
f1 (ppm)
15400.35
153.4
153.2
153.0
152.8
f1 (ppm)
64.87
64.80
64.76
64.70
60.49
60.34
60.28
60.24
60.13
60.09
60.03
59.88
6087.01
6072.07
6065.99
6061.65
6051.09
6046.69
6040.62
6025.65
60.5
60.0
59.5
f1 (ppm)
13494.15
13482.73
13478.38
13473.10
134.2
134.0
133.8
f1 (ppm)
16.31
16.26
16.20
1641.68
1636.01
1630.23
16.35
16.30
16.25
16.20
16.15
f1 (ppm)
6528.01
6520.51
6516.79
6510.04
65.0
64.8
64.6
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

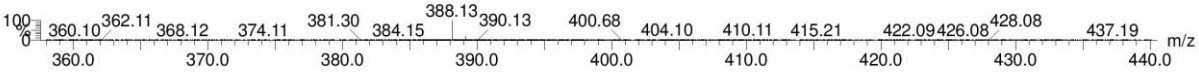
HRMS

Elemental Composition Report **Page 1**

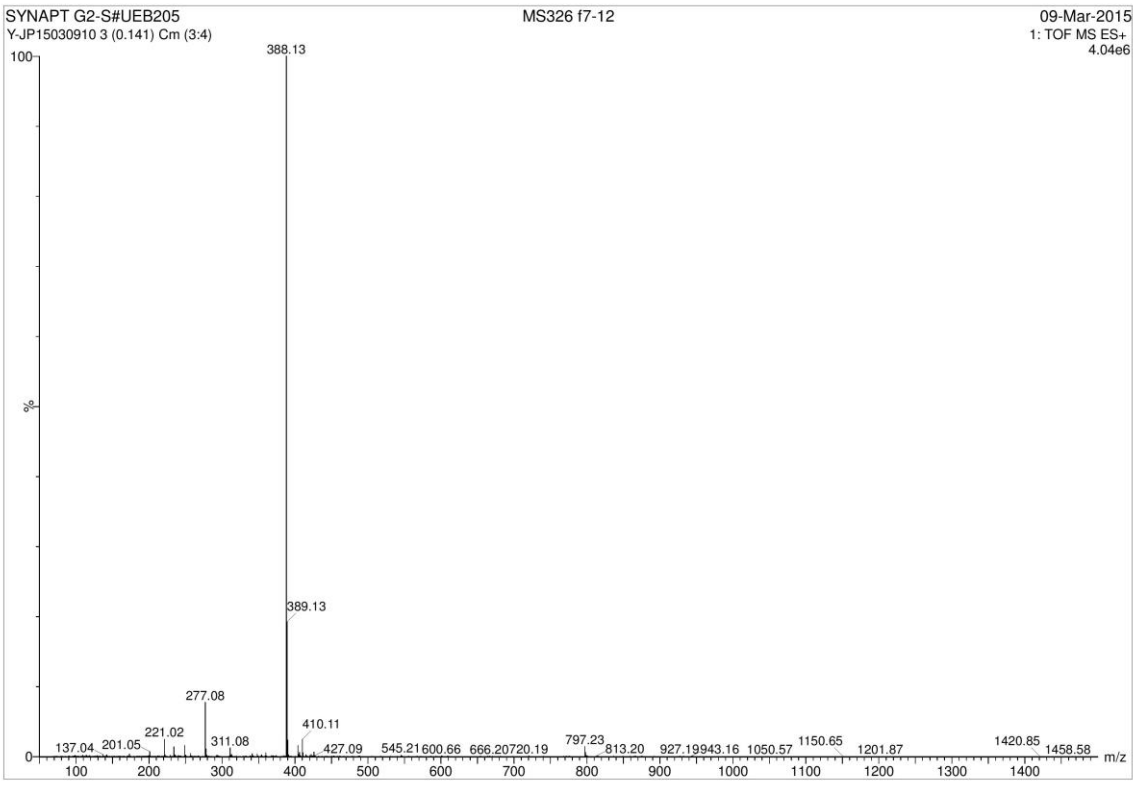
Single Mass Analysis
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
499 formula(e) evaluated with 2 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 F: 3-3 P: 1-1

SYNAPT G2-S#UEB205 MS326 f7-12 09-Mar-2015
Y-JP15030910 3 (0.141) Cm (3:4) 1: TOF MS ES+
4.04e+006



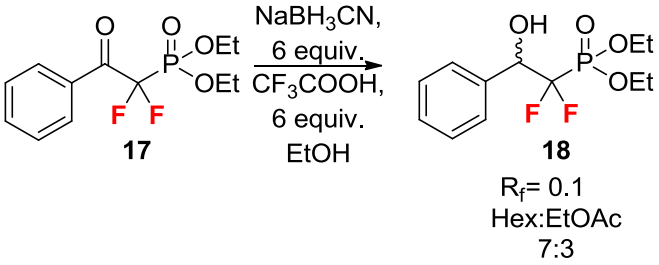
Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
388.1291	388.1289	0.2	0.5	7.5	1865.0	0.000	100.00	C18 H22 N O3 F3 P
	388.1294	-0.3	-0.8	0.5	1882.0	17.018	0.00	C3 H18 N13 O4 F3 P



IV. Additional information

Note: Due to the fact that some cases of **14** were contaminated by **17** the crude reaction mixture contained traces of diethyl (1,1-difluoro-2-hydroxy-2-phenylethyl)phosphonate **18 (scheme 1)**. Diagnostic signals for **18**: δ_F: -125.46 (ddd, $^2J_{FF}$ = 304.9 Hz, $^2J_{FP}$ = 105.5 Hz, $^3J_{FH}$ = 20.3 Hz, 1F), -115.18 (ddd, $^2J_{FF}$ = 304.9 Hz, $^2J_{FP}$ = 100.1 Hz, $^3J_{FH}$ = 6.3 Hz, 1F); δ_P: 6.82 (dd, $^2J_{PF}$ = 105.5 Hz, $^2J_{PF}$ = 100.1 Hz, 1P); R_f = 0.1. The separation of *α,α*-difluoromethylene-*β*-aminophosphonates **15** from **18** has been relatively easy to handle due to 0.35 difference in R_f (hexane:ethyl acetate 7:3).

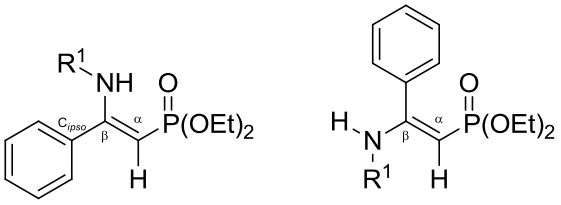
difluoro-2-hydroxy-2-phenylethyl)phosphonate 18



Scheme 1 **Reduction of *β*-ketophosphonate 17 with the use of $NaBH_3CN$ reagent**

V. Tables

Table 1 ^{31}P, ^{13}C, ^{1}H NMR δ for major (*Z*/*E*)-form of *β*-enaminophosphonates 12a-j.



(*Z*)-**12** (*E*)-**12**

	δ [ppm]	**12a**	**12b**	**12c**	**12d**	**12e**	**12f**	**12g**	**12h**	**12i**	**12j**
P	(s) *J* [Hz]	25.87	25.89	25.09	25.26	24.96	24.87	24.98	23.58	23.64	22.87
$C_{\alpha(Z)}$	(δ)	75.2	75.1	77.8	77.4	77.8	78.5	79.1	84.4	84.0	84.0
	$^{1}J_{CP}$ [Hz]	189.8	189.7	188.5	189.1	188.5	188.5	188.1	187.3	187.5	187.5
$C_{\alpha(E)}$	(δ)	75.4	75.5	76.7	76.8	77.1	77.5	78.7	-	-	-
	$^{1}J_{CP}$ [Hz]	218.3	218.4	217.4	217.6	217.4	217.3	217.7			
$C_{\beta(Z)}$	(δ)	167.0	167.0	166.6	166.7	166.7	166.5	166.4	160.7	159.3	161.0
	$^{2}J_{CP}$ [Hz]	7.0	7.1	6.8	6.8	6.8	6.7	6.8	5.5	5.0	5.8
$C_{\beta(E)}$	(δ)	160.7	160.7	160.3	-	-	137.4	138.1	137.3	136.0	137.1
	$^{2}J_{CP}$ [Hz]	17.7	17.6	17.5			20.0	20.1	19.4	19.1	19.6
$C_{ipso(Z)}$	(δ)	138.1	138.0	137.6	137.7	137.6	160.2	-	-	-	-
	$^{3}J_{CP}$ [Hz]	20.1	20.1	20.0	19.9	20.1	17.5				
$H_{(Z)}$	(δ)	3.67	3.75	3.80	3.91	3.83	3.93	3.81	4.30	4.41	4.28
	$^{2}J_{HP}$ [Hz]	13.3	13.3	13.1	13.0	13.0	13.0	13.1	12.3	12.1	12.2
$H_{(E)}$	(δ)	4.10	4.18	4.16	4.33	4.30	4.26	-	-	4.66	-
	$^{2}J_{HP}$ [Hz]	9.4	9.4	9.1	9.2	9.0	9.4			8.9	

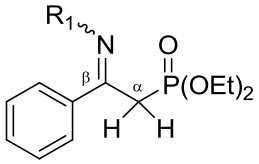
R^1: **a** = $CH_3(CH_2)_6$, **b** = $CH_3(CH_2)_7$, **c** = 4-$MeOC_6H_4CH_2$, **d** = 2-$MeC_6H_4CH_2$,**e** = Bn, **f** = 4-$FC_6H_4CH_2$, **g** = (*S*)-$Ph(CH_3)CH$, **h** = Ph, **i** = 4-FC_6H_4, **j** = 2-FC_6H_4

Table 2 ^{31}P NMR of compounds 12-(*Z*:*E*) and 13-(*E*:*Z*)

Entry	Compound	R^1	**12** enamine (Z:E) / **13** imine (E:Z)[a]	^{31}P NMR for *major* **12** (*Z*)-enamine / **13** (*E*)-imine	^{31}P NMR for *minor* **12** (*E*)-enamine / **13** (*Z*)-imine
1	**12-13a**	$CH_3(CH_2)_6$	92(85:15) / 8(85:15)	25.87 / 22.40	24.74 / 24.24
2	**12-13b**	$CH_3(CH_2)_7$	93(87:13) / 7(80:20)	25.89 / 22.41	24.82 / 24.26
3	**12-13c**	4-$MeOC_6H_4CH_2$	91(83:17) / 9(81:19)	25.09 / 22.16	24.30 / 24.07
4	**12-13d**	2-$MeC_6H_4CH_2$	91(84:16) / 9(77:23)	25.26/22.27	24.25 / 24.14
5	**12-13e**	Bn	91(84:16) / 9(95:5)	25.10 / 22.14	24.05 / 23.72
6	**12-13f**	4-$FC_6H_4CH_2$	90(86:14) / 10(95:5)	24.87 / 22.00	23.88 / 24.27
7	**12-13g**	(*S*)-$Ph(CH_3)CH$	92(90:10) / 8(70:30)	24.98 / 22.14	23.88 / 23.97
8	**12-13h**	Ph	67 / 33(91:9)	23.58 / 21.43	- / 23.37
9	**12-13i**	4-FC_6H_4	63(99:1) / 37(92:8)	23.64 / 21.32	24.87 / 23.23
10	**12-13j**	2-FC_6H_4	61 / 39(80:20)	23.03 / 20.92	- / 23.74

[a] Ratio has been assigned on the basis of ^{31}P NMR in $CDCl_3$ after column chromatography.

Table 3 ^{1}H NMR data for minor (*E*/*Z*)–forms of *β*–iminophosphonates 13a-j

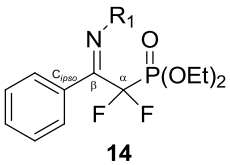


R_1: **a**= $CH_3(CH_2)_6$, **b**= $CH_3(CH_2)_7$, **c**= 4-$OMeC_6H_4CH_2$, **d**= 2-Me $C_6H_4CH_2$, **e**= Bn, **f**= 4-F $C_6H_4CH_2$, **g**= (*S*)-$Ph(CH_3)CH$, **h**= Ph, **i**= 4-F C_6H_4, **j**= 2-F C_6H_4

	δ [ppm]	**2.6a**	**2.6b**	**2.6c**	**2.6d**	**2.6e**
$H_{(E)}$	(d)	3.38	3.41	3.40	3.53	3.53
	$^2J_{HP}$ [Hz]	23.4	23.4	23.4	23.4	23.4
$H_{(Z)}$	(d)	3.15	3.23	3.21	3.37	3.35
	$^2J_{HP}$ [Hz]	21.5	21.9	22.0	22.1	22.1
	δ [ppm]	**2.6f**	**2.6g**	**2.6h**	**2.6i**	**2.6j**
$H_{(E)}$	(d)	3.50	3.34 3.33	3.32	3.30	3.33
	$^2J_{HP}$ [Hz]	23.4	23.3[a]	23.3	23.3	23.4
$H_{(Z)}$	(d)	3.32	3.20	3.39	3.37	3.26
	$^2J_{HP}$ [Hz]	22.1	22.1	22.5	22.5	22.9

[a] signal derived from non chemically equivalent protons (diastereotopic) observed as two pair of doublets with the same coupling constance

Table 4 ^{31}P, ^{13}C, ^{1}H NMR data for *α,α*-difluoromethylene-*β*-iminophosphonates 14



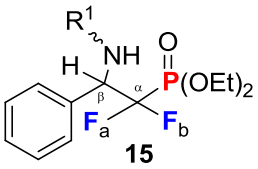
14

	14a	**14b**	**14c**	**14d**	**14d**	**14e**	**14f**	**14g**[b]	**14h**	**14i**	**14j**
	δ [ppm]										
P	(t)	5.82	5.85	5.75	5.63	5.60	5.64	5.73	5.29	5.31	4.83
	$^{2}J_{PF}$ [Hz]	101.7	101.6	100.8	100.5	100.7	100.6	101.6	100.3	100.5	100.2
F[a]	(d)	-107.31	-107.31	-107.7	-107.2	-107.17	-107.40	-107.9	-107.10	-107.24	-107.44
	$^{2}J_{FP}$ [Hz]	101.7	101.7	100.7	100.5	100.6	100.6	101.6	100.4	100.5	100.2
C_{α}	(td)	116.4	116.4	116.5	114.8	116.5	116.4	116.3	114.9	116.5	116.2
	$^{1}J_{CF}$ [Hz]	265.2	265.4	265.4	265.7	265.7	265.8	265.5	267.0	267.1	267.2
	$^{1}J_{CP}$ [Hz]	212.6	212.5	212.4	213.2	212.8	212.8	212.4	212.2	212.2	211.3
C_{β}	(td)	162.8	162.8	163.7	162.2	164.1	164.3	161.7	160.7	162.8	165.7[c]
	$^{2}J_{CF}$ [Hz]	26.0	26.0	26.6	26.8	24.8	26.6	26.4	26.2	26.1	26.1
	$^{2}J_{CP}$ [Hz]	14.4	14.5	14.7	14.4	12.6	14.5	14.2	14.3	13.4	20.9
											13.5

R_1: **a** = $CH_3(CH_2)_6$, **b** = $CH_3(CH_2)_7$, **c** = 4-$MeOC_6H_4CH_2$, **d** = 2-$MeC_6H_4CH_2$, **e** = Bn, **f** = 4-$FC_6H_4CH_2$, **g** = (*S*)-$Ph(CH_3)CH$, **h** = Ph, **i** = 4-FC_6H_4, **j** = 2-FC_6H_4.

[a] $^{19}F\{1H\}$ NMR. [b] Spectrum made in CD_3CN. [c] Signal appeared as (ddd).

Table 5 Spectroscopic data of *α*,*α*-difluoromethylene-*β*-aminophosphonates 15



15

δ [ppm]		**15a**	**15b**	**15c**	**15d**	**15e**
P	(dd)	7.41	7.31	7.04	7.05	7.10
	$^2J_{PF}$ [Hz]	102.5	104.5	105.7	106.6	103.8
		101.1	102.7	102.0	102.4	
F_a	(dd)	-109.35	-111.16	-110.99	-110.98	-111.06
	$^2J_{FP}$ [Hz]	300.0	300.9	303.2	303.4	303.3
		100.8	102.5	101.9	102.4	100.9
F_b	(dd)	-123.57	-121.56	-121.38	-121.33	-121.48
	$^2J_{FP}$ [Hz]	300.1	300.4	302.7	303.4	302.6
		102.9 Hz	101.6	105.8	106.7	105.7
H_β	(m)	4.26-3.96[c]	4.26-3.98[c]	4.24-3.92[c]	4.23-3.92[c]	4.34-4.12[c]
C_α	(ddd)	119.4	118.4	119.4	119.3	119.3
	$^1J_{CF}$ [Hz]	269.3	268.9	268.5	268.6	268.3
	$^1J_{CF}$ [Hz]	263.0	265.9	265.5	265.8	265.5
	$^1J_{CP}$ [Hz]	210.0	210.2	210.3	211.1	210.7
C_β	(ddd)	64.3-63.6[*]	63.6	63.5	64.1	63.7
	$^2J_{CF}$ [Hz]		24.3	23.6	23.6	23.6
	$^2J_{CP}$ [Hz]		19.4	19.5	19.4	19.5
			15.4	15.4	15.3	15.4
δ[ppm]		**15f**	**15g[ab]**	**15h**	**15i**	**15j**
P	(dd)	6.83	7.05	6.57	6.65	6.44
	$^2J_{PF}$ [Hz]	105.3	103.5	105.1	104.6	103.5
		102.4	102.0	102.2	101.7	101.1
F_a	(dd)	-111.21	-109.60	-110.30	-110.48	-111.19
	$^2J_{FP}$ [Hz]	303.8	300.5	304.1	304.1	305.1
		101.8	101.8	102.0	101.6	103.4
F_b	(dd)	-121.27	-121.71	-120.27	-120.33	-120.94
	$^2J_{FP}$ [Hz]	304.4	300.5	304.1	304.0	305.1
		104.1	103.7	105.2	104.3	101.3
H_β	(ddd)	4.21-3.93[c]	4.26-3.98[c]	4.92	4.83	4.98
	$^3J_{HF}$ [Hz]			20.5	20.7	20.5
	$^3J_{HF}$ [Hz]			8.4	8.2	8.0
	$^3J_{HP}$ [Hz]			5.9	5.8	5.2
C_α	(ddd)	119.3	119.9	118.5	118.4	122.3-113.8[c]
	$^1J_{CF}$ [Hz]	268.1	269.6	268.2	268.4	
	$^1J_{CF}$ [Hz]	265.9	265.6	266.6	266.5	
	$^1J_{CP}$ [Hz]	210.7	210.3	209.8	209.2	
C_β	(ddd)	63.6	62.0	60.6	61.5	60.1
	$^2J_{CF}$ [Hz]	23.5	23.7	24.9	24.7	25.4
	$^2J_{CF}$ [Hz]	19.6	19.3	21.1	21.1	21.0
	$^2J_{CP}$ [Hz]	15.5	15.2	14.7	14.8	14.9

R^1: **a** = $CH_3(CH_2)_6$, **b** = $CH_3(CH_2)_7$, **c** = 4-$MeOC_6H_4CH_2$, **d** = 2-$MeC_6H_4CH_2$, **e** = Bn, **f** = 4-$FC_6H_4CH_2$, **g** = (S)-Ph(CH_3)CH, **h** = Ph, **i** = 4-FC_6H_4, **j** = 2-FC_6H_4

[a] diastereomeric ratio of isolated product **15 g** (dr = 91:1) based on NMR.[b]Signals of major compound.[c] signal observed as multiplet