

A Dehydrogenative Cross-Coupling Reaction Between Aromatic Aldehydes or Ketones with Dialkyl *H*-Phosphonates for Formyl or Acylphenylphosphonates

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300071, P. R. China

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Supporting Information

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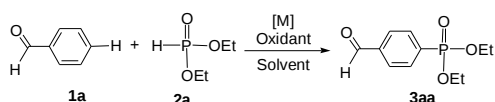
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1. General Information:

All aldehydes were distilled or purified via flash chromatography prior to use. Unless otherwise indicated, other reagents were purchased from commercial distributors and used without further purification. ^{13}P NMR, ^1H NMR and ^{13}C NMR were recorded at 162 MHz, 400 MHz and 100 MHz respectively, using tetramethylsilane as an internal standard. Mass spectra were obtained on an HRMS-EI instrument. Flash column chromatography was performed over silica gel 200-300 mesh.

2. Optimization of the Reaction Conditions

Table S1. Screening of reaction conditions.^a

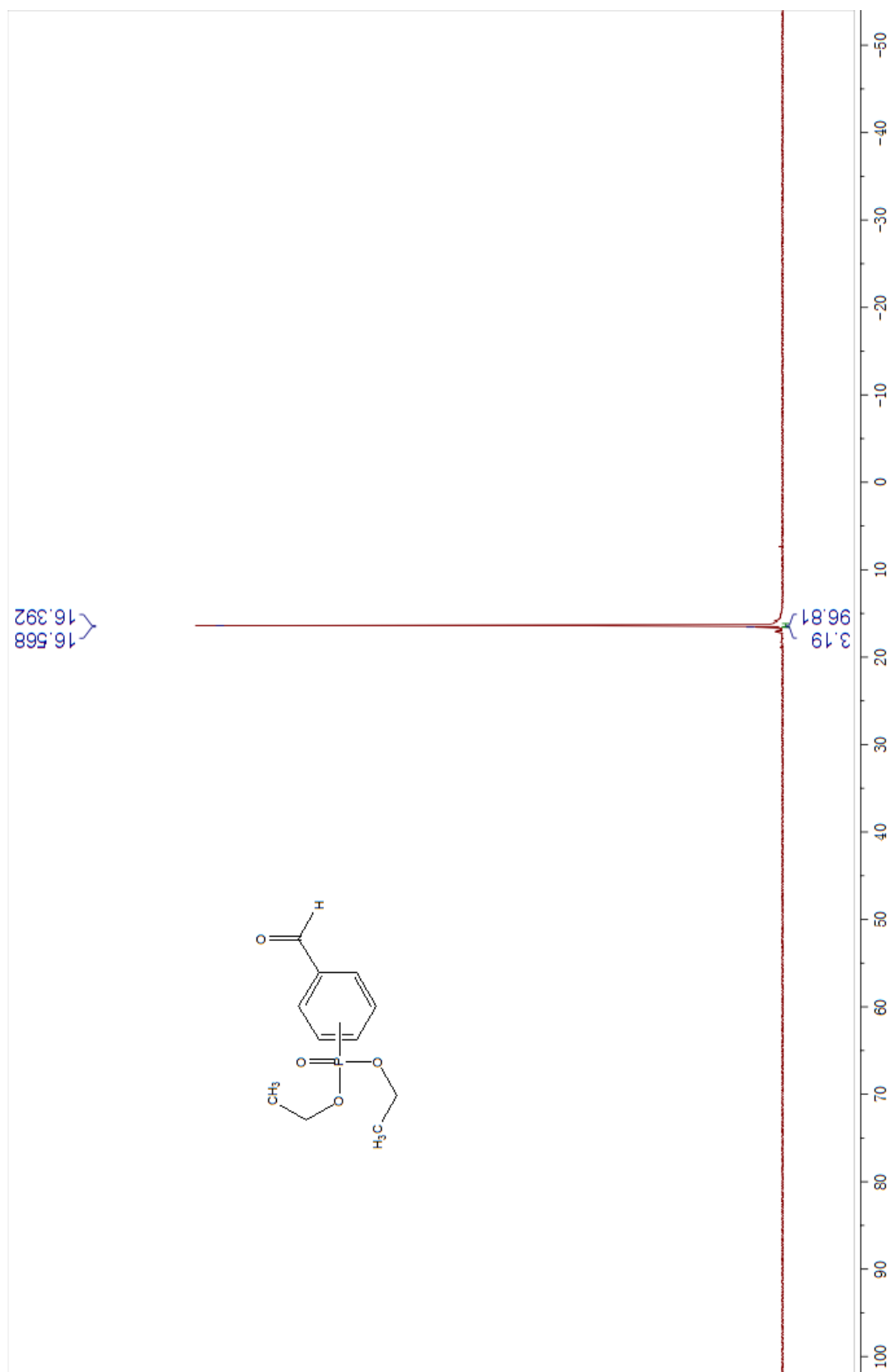


Entry	[M] (mol%)	[O] (equiv)	[S] (mL)	Yield (%) ^[b]
1	Cu(OTf) ₂ (10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN(3)	5
2	Cu(OAc) ₂ (10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN(3)	3
3	Pd(OAc) ₂ (10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN(3)	0
4	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN(3)	30
5	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	H ₂ O(3)	33
6	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN:H ₂ O(1.5:1.5)	53
7	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	Acetone:H ₂ O(1.5:1.5)	33
8	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	DCM:H ₂ O(1.5:1.5)	38
9	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	THF:H ₂ O(1.5:1.5)	40
10	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN:H ₂ O(0.5:0.5)	42
11	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN:H ₂ O(2.5:2.5)	68
12	Ag ₂ O(10)	K ₂ S ₂ O ₈ (3)	CH ₃ CN:H ₂ O(3:3)	63
13	Ag ₂ O(10)	K ₂ S ₂ O ₈ (2)	CH ₃ CN:H ₂ O(2.5:2.5)	73
14	Ag ₂ O(10)	K ₂ S ₂ O ₈ (1)	CH ₃ CN:H ₂ O(2.5:2.5)	58
15	Ag ₂ O(10)	DCP(1)	CH ₃ CN:H ₂ O(2.5:2.5)	0
16	Ag ₂ O(10)	NMO(2)	CH ₃ CN:H ₂ O(2.5:2.5)	0
17	Ag ₂ O(10)	TBHP(2)	CH ₃ CN:H ₂ O(2.5:2.5)	0
18	Ag ₂ O(10)	Na ₂ S ₂ O ₈ (3)	CH ₃ CN:H ₂ O(2.5:2.5)	65
19	Ag ₂ O(5)	K ₂ S ₂ O ₈ (2)	CH ₃ CN:H ₂ O(2.5:2.5)	73
20	Ag ₂ O(20)	K ₂ S ₂ O ₈ (2)	CH ₃ CN:H ₂ O(2.5:2.5)	63

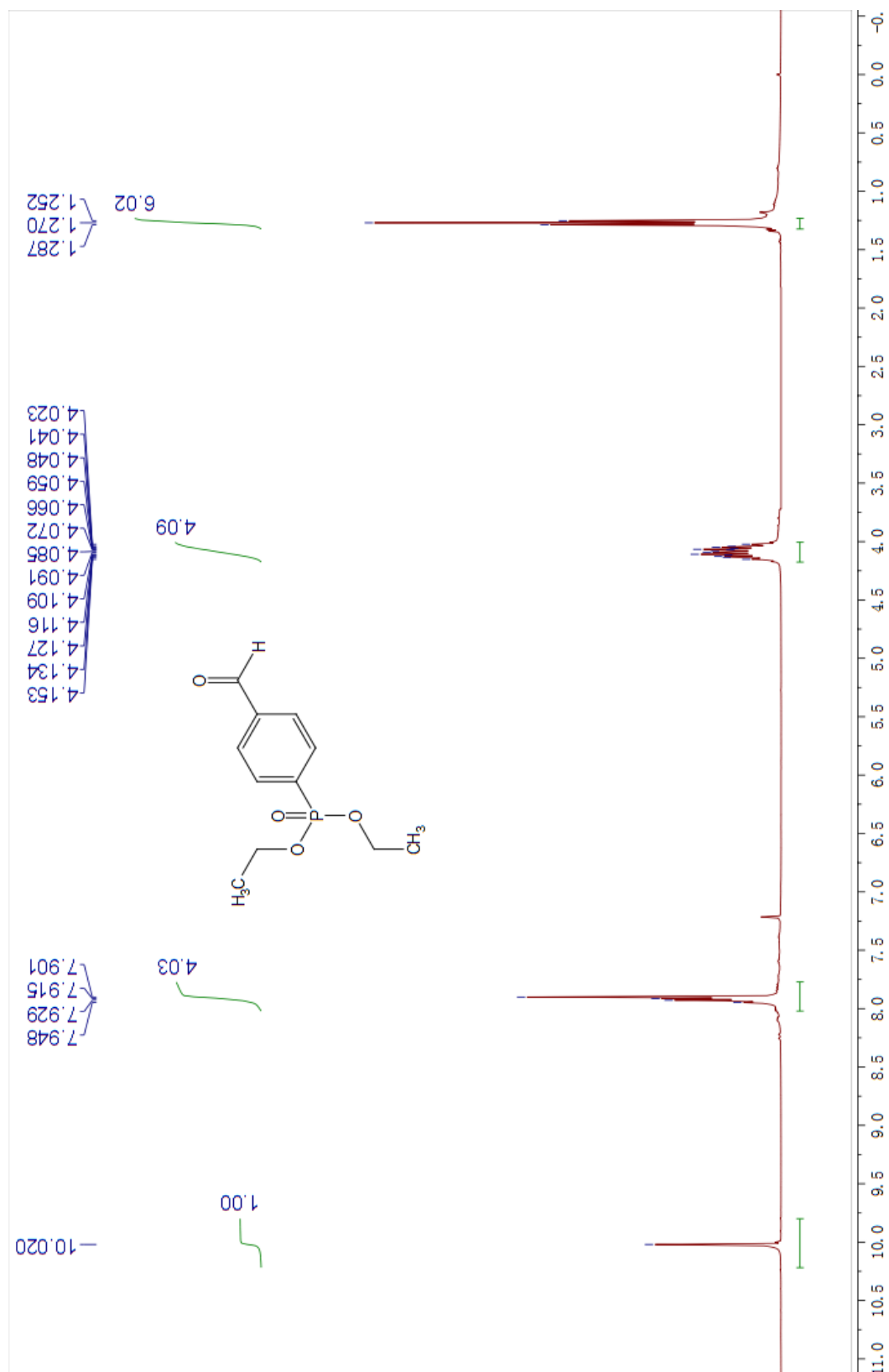
[a] Conditions: **1a** 0.5mmol, **2a** 1mmol, 100 °C, 1.5h; [b] Isolated yields.

3. ^{31}P NMR, ^1H NMR, ^{13}C NMR, and HR-MS Spectra of Products

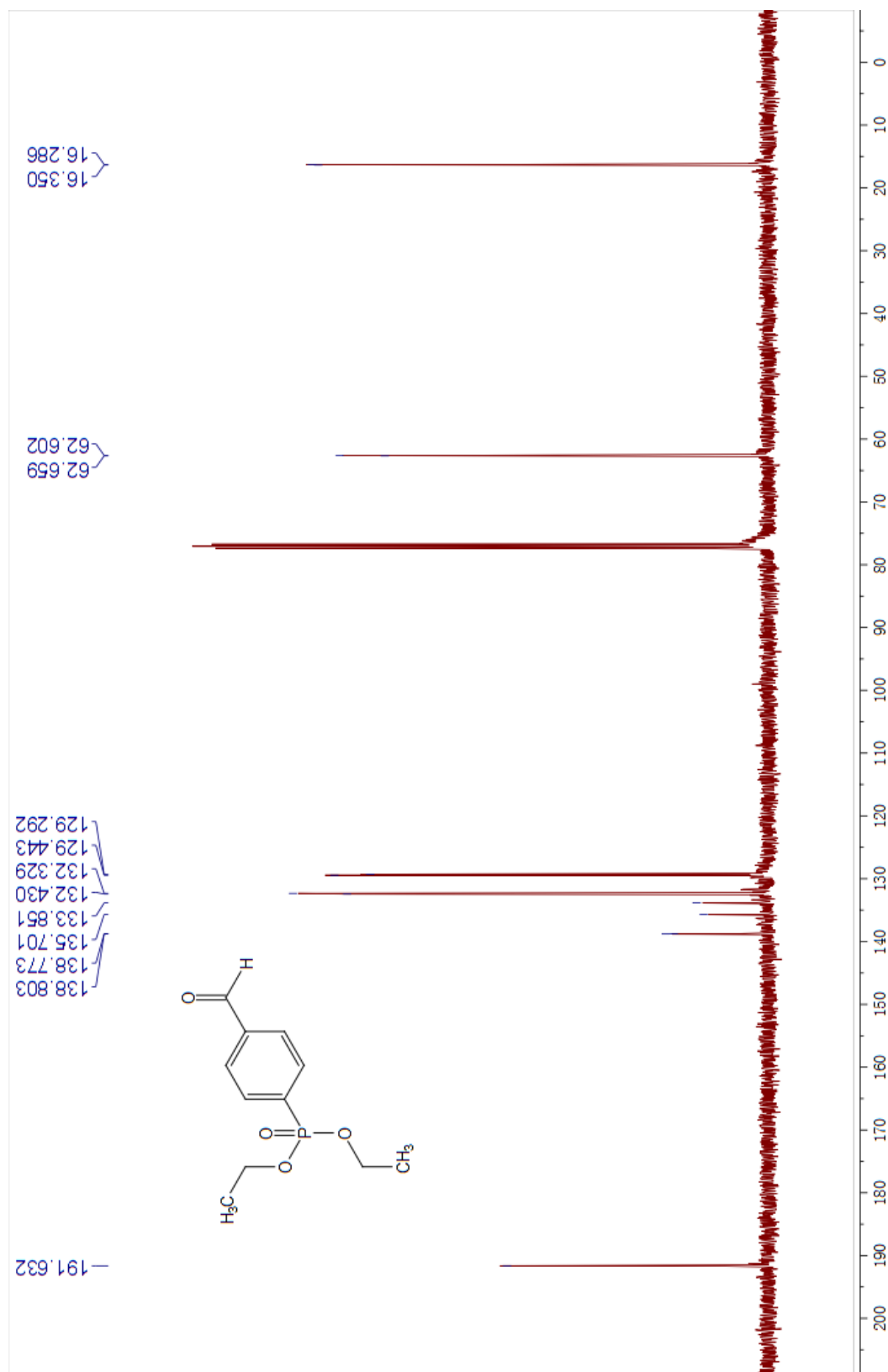
^{13}P NMR Spectrum of diethyl formylphenylphosphonate **3aa**



^1H NMR Spectrum of diethyl 4-formylphenylphosphonate **3aa**



¹³C NMR Spectrum of diethyl 4-formylphenylphosphonate **3aa**



HR-MS Spectrum of diethyl 4-formylphenylphosphonate **3aa**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

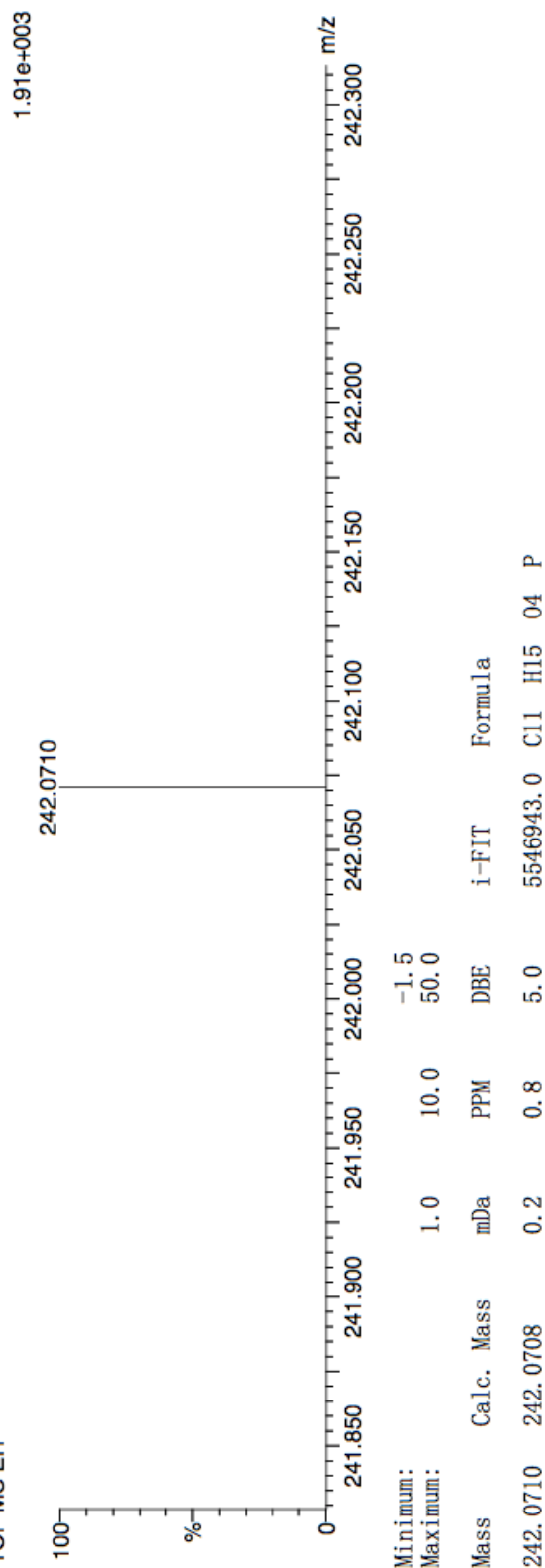
Monoisotopic Mass, Odd and Even Electron Ions
 45 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

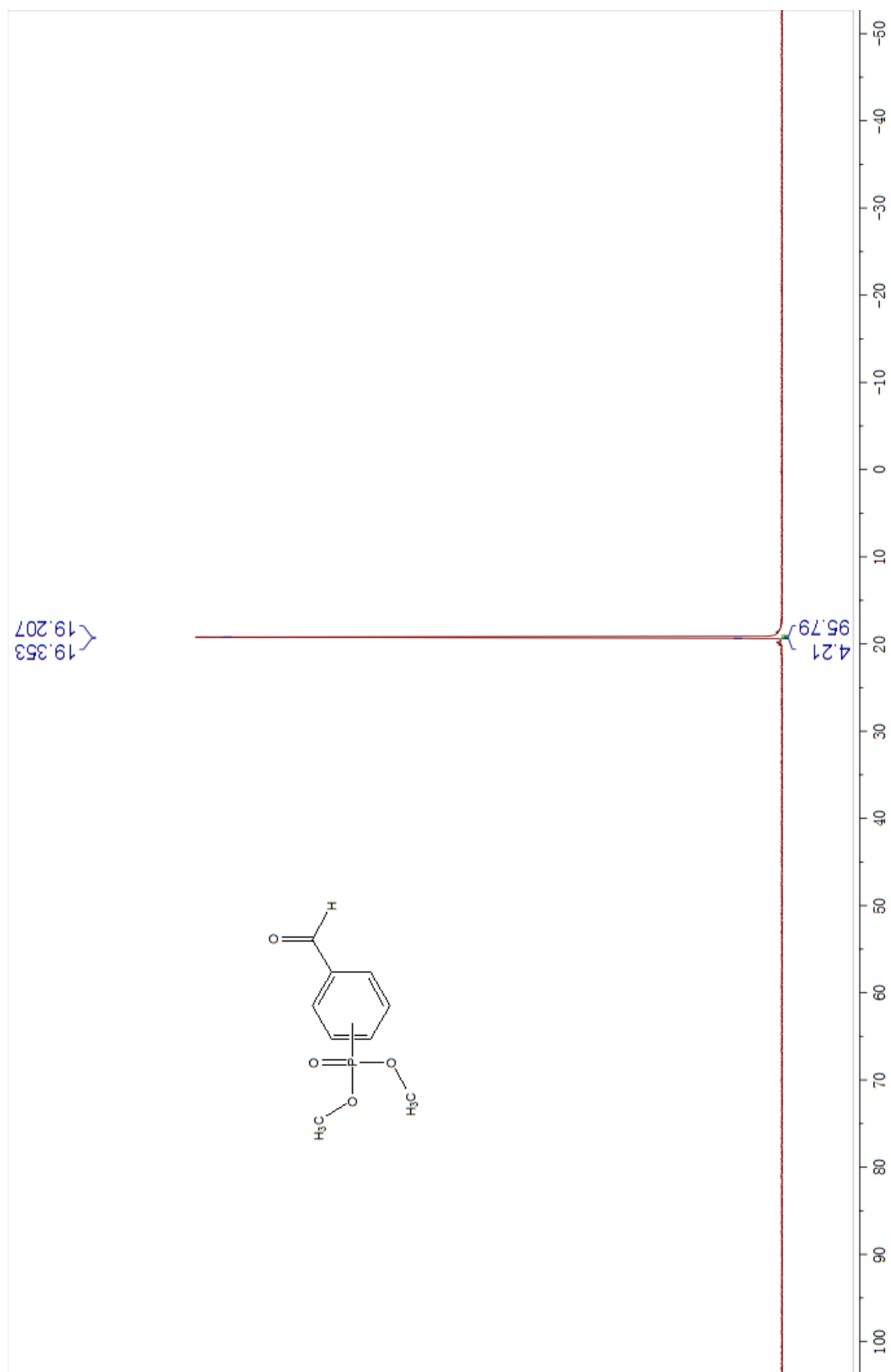
C: 0-50 H: 0-200 O: 0-6 P: 0-1

hxf-13 401 (2.474)

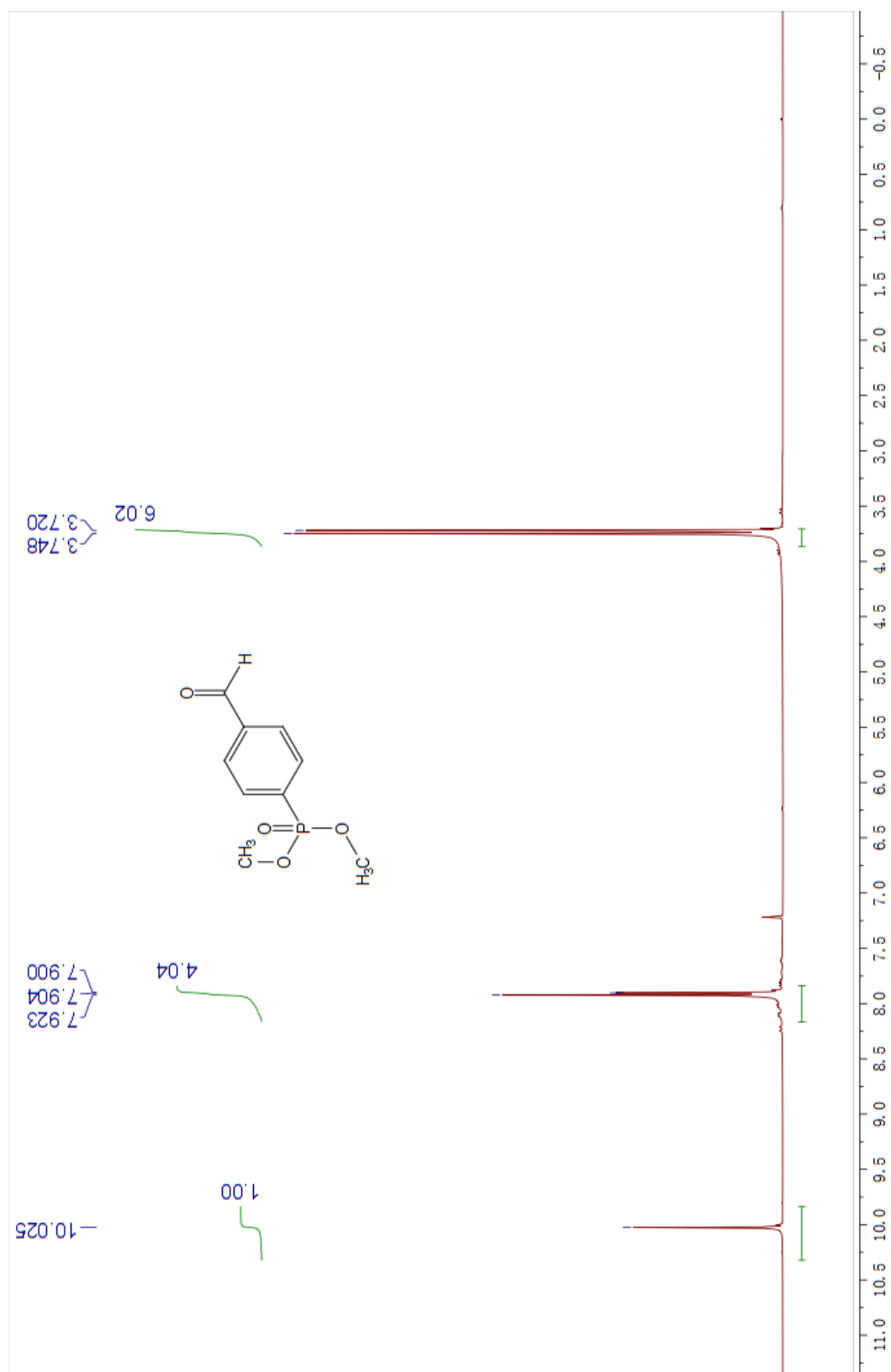
TOF MS EI+



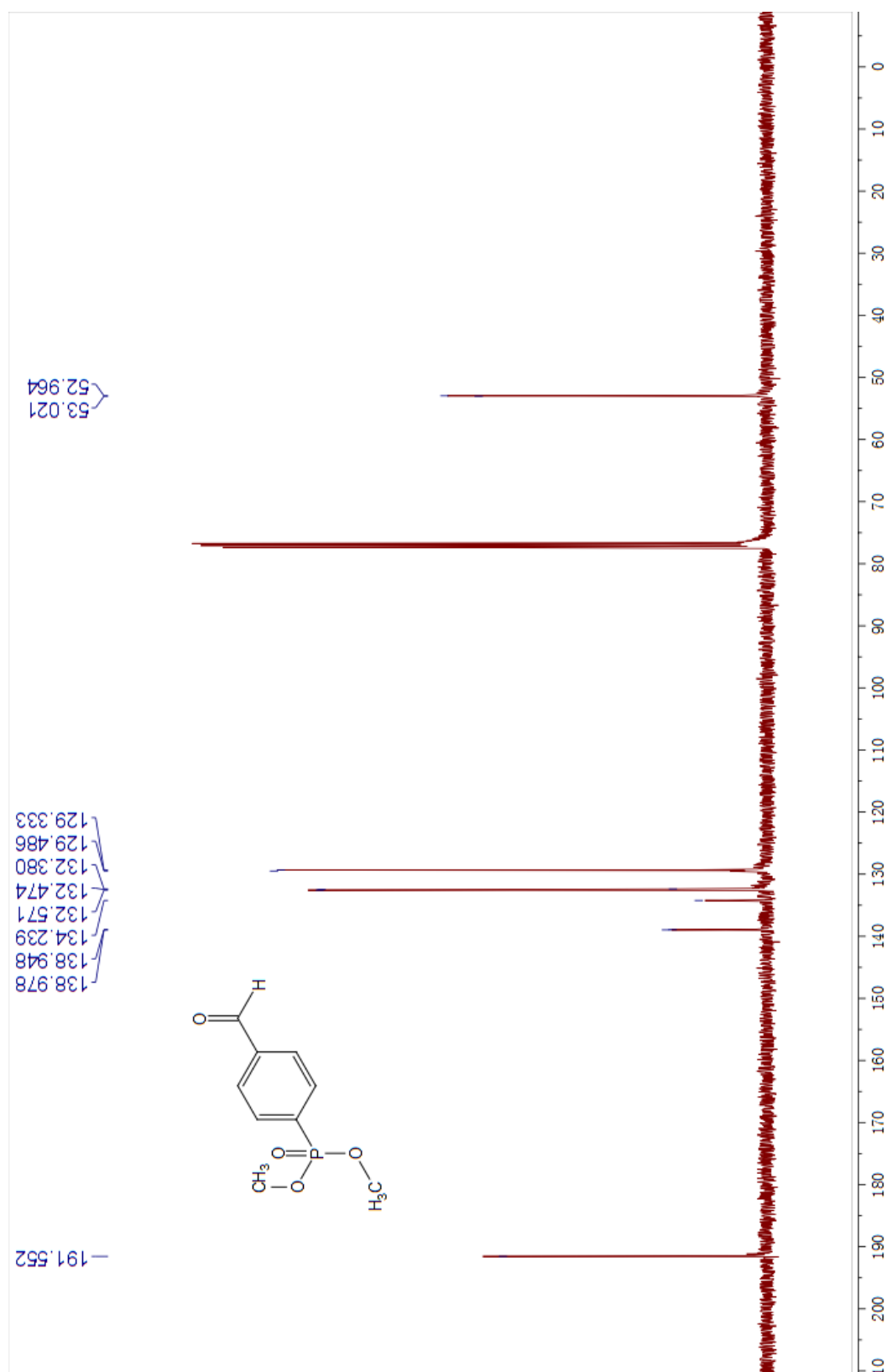
^{13}P NMR Spectrum of dimethyl formylphenylphosphonate **3ab**



^1H NMR Spectrum of dimethyl 4-formylphenylphosphonate **3ab**



^{13}C NMR Spectrum of dimethyl 4-formylphenylphosphonate **3ab**



HR-MS Spectrum of dimethyl 4-formylphenylphosphonate **3ab**

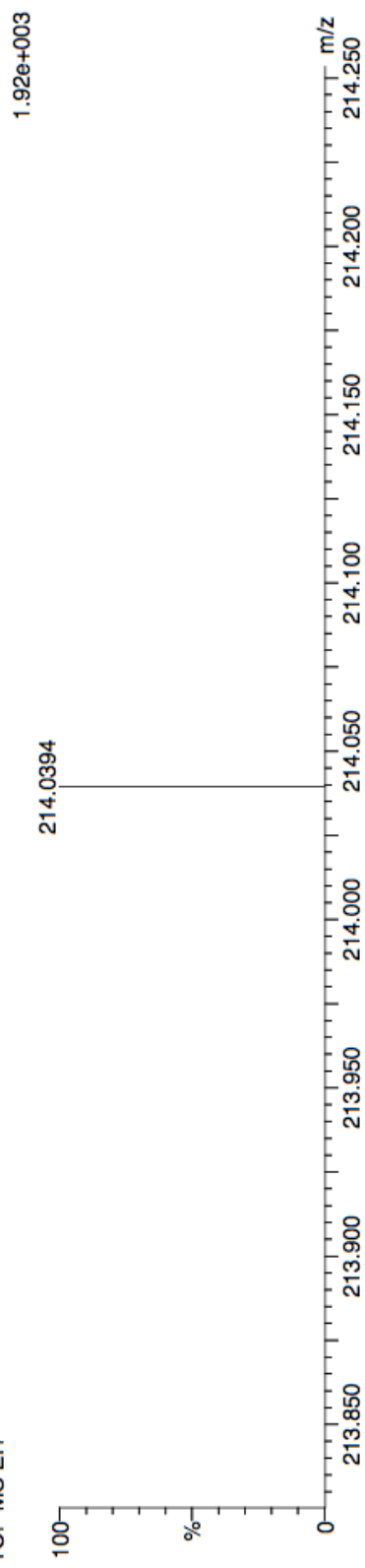
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 40 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:

C: 0-50 H: 0-200 O: 0-6 P: 0-1

hxf-14 403 (2.482)

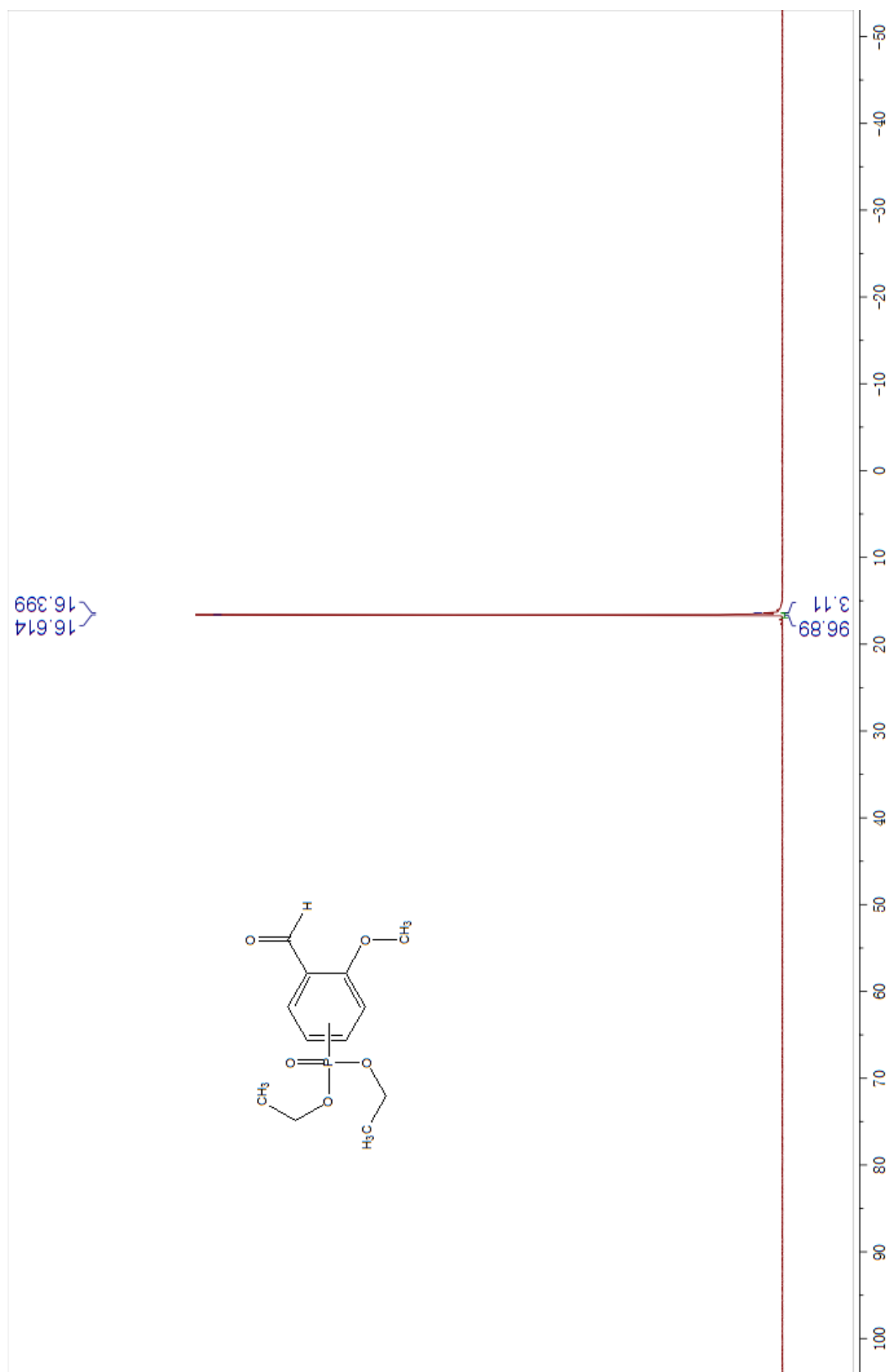
TOF MS EI+



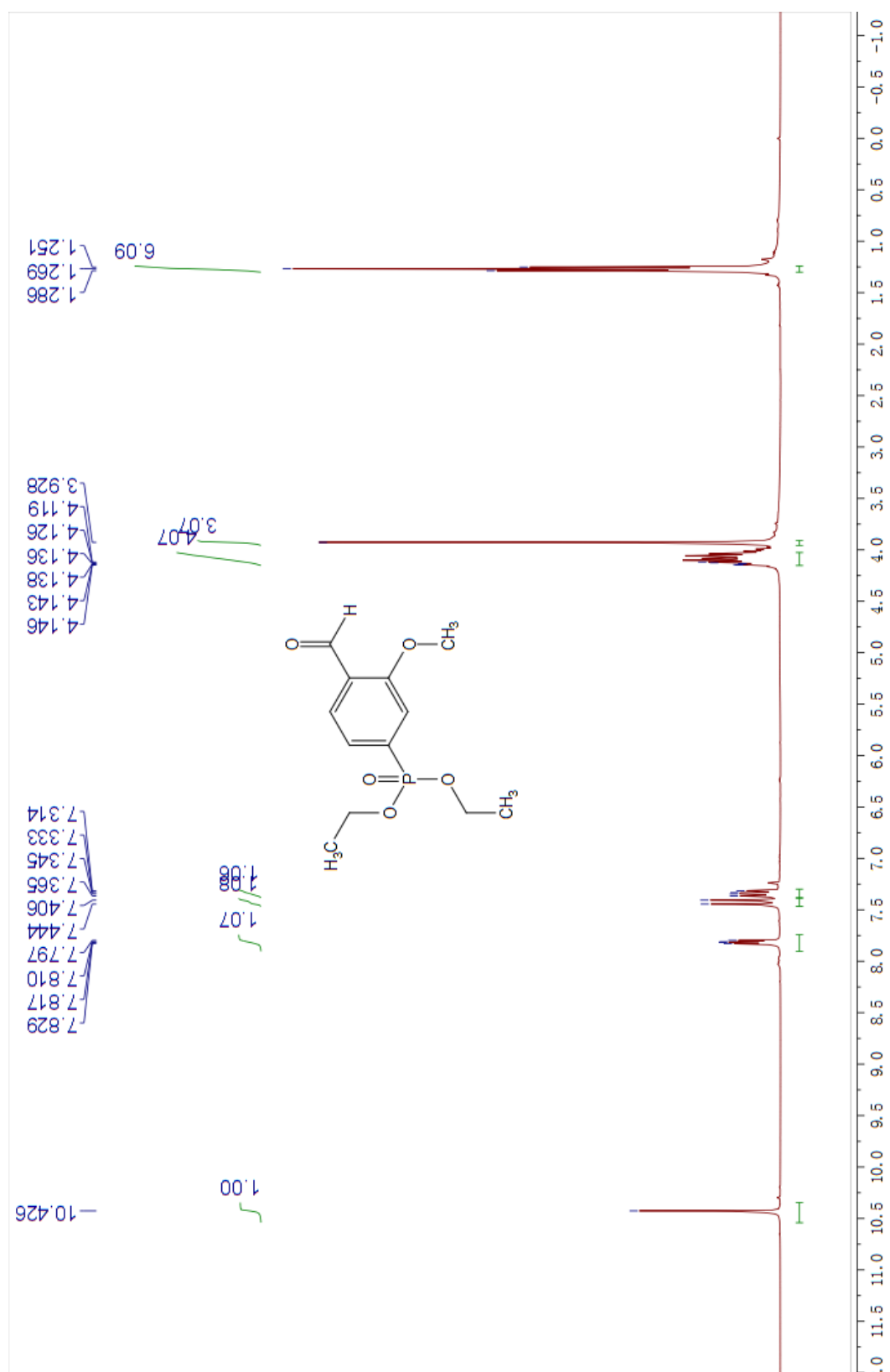
Minimum: -1.5
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
214.0394	214.0395	-0.1	-0.5	5.0	5546929.0	C9 H11 O4 P

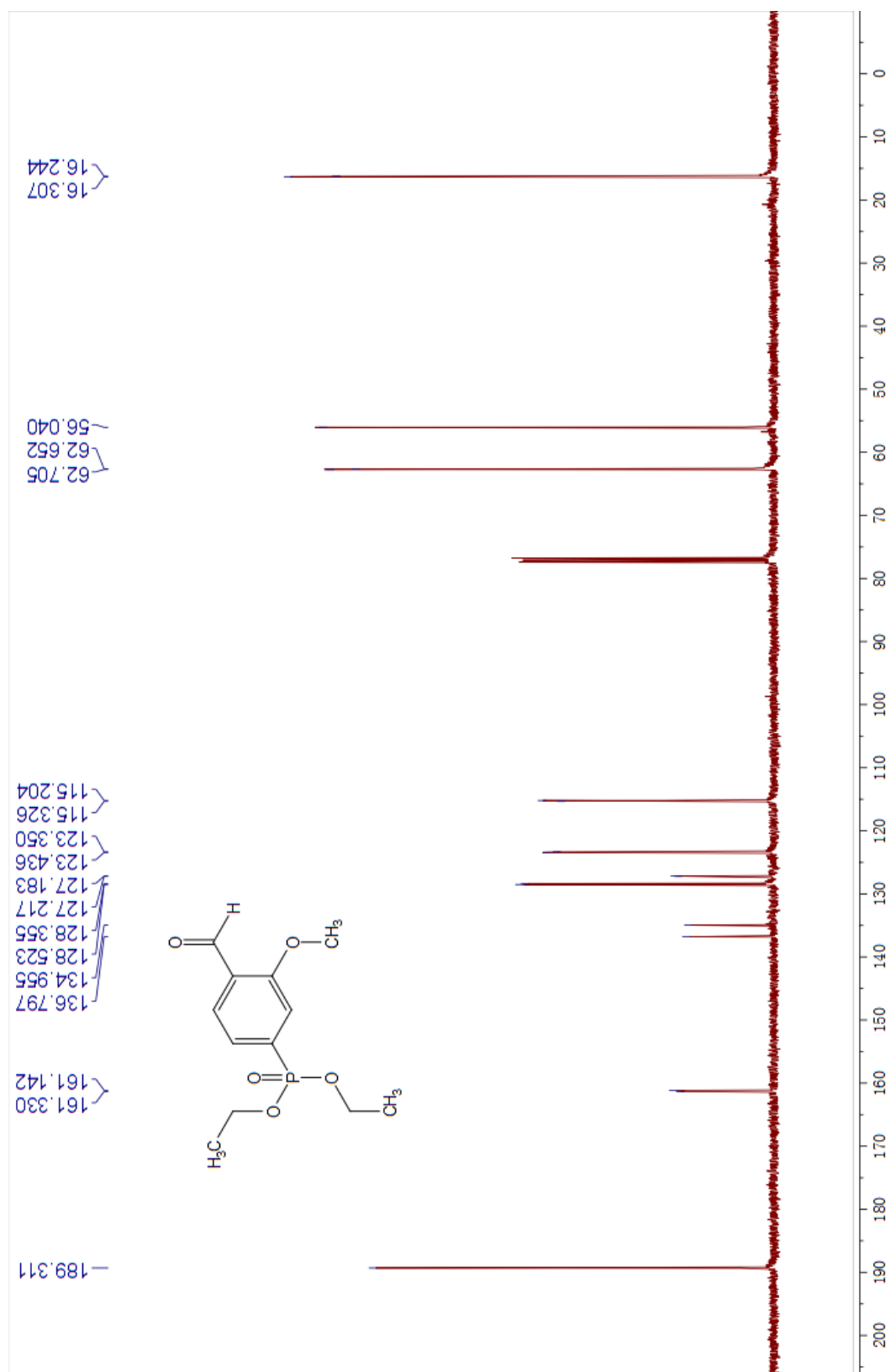
^{13}P NMR Spectrum of diethyl formyl-3-methoxyphenylphosphonate **3da**



^1H NMR Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate **3da**



^{13}C NMR Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate **3da**



HR-MS Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate **3da**

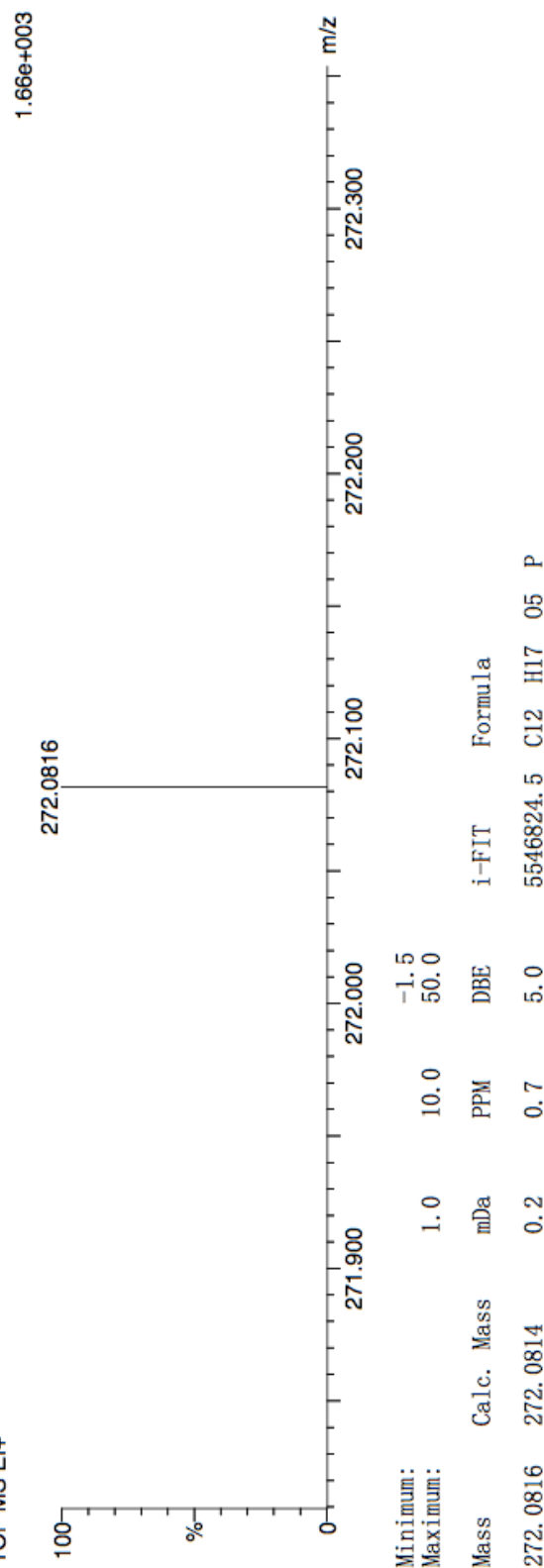
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
50 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

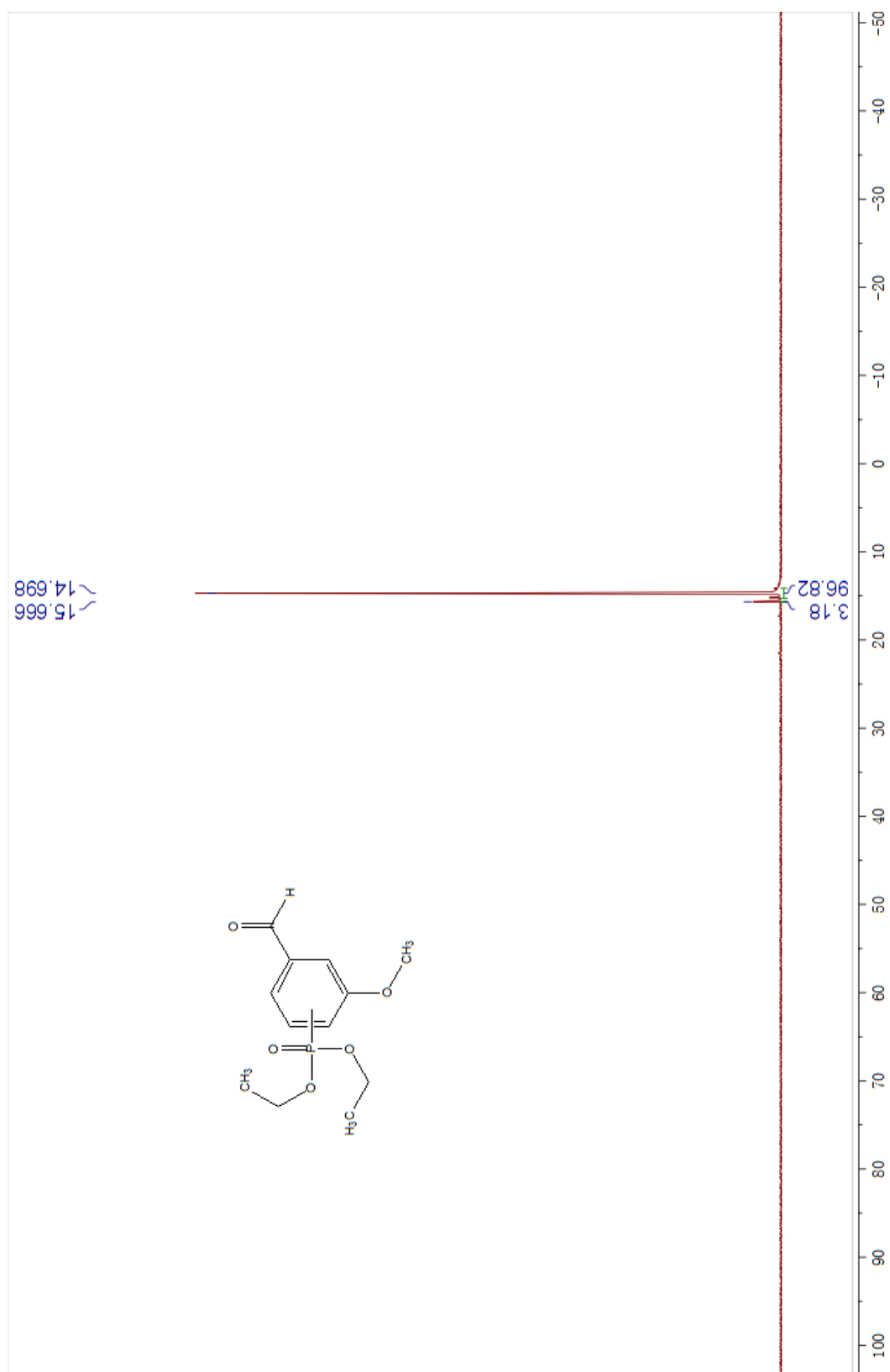
Elements Used:

C: 0-50 H: 0-200 O: 0-6 P: 0-1

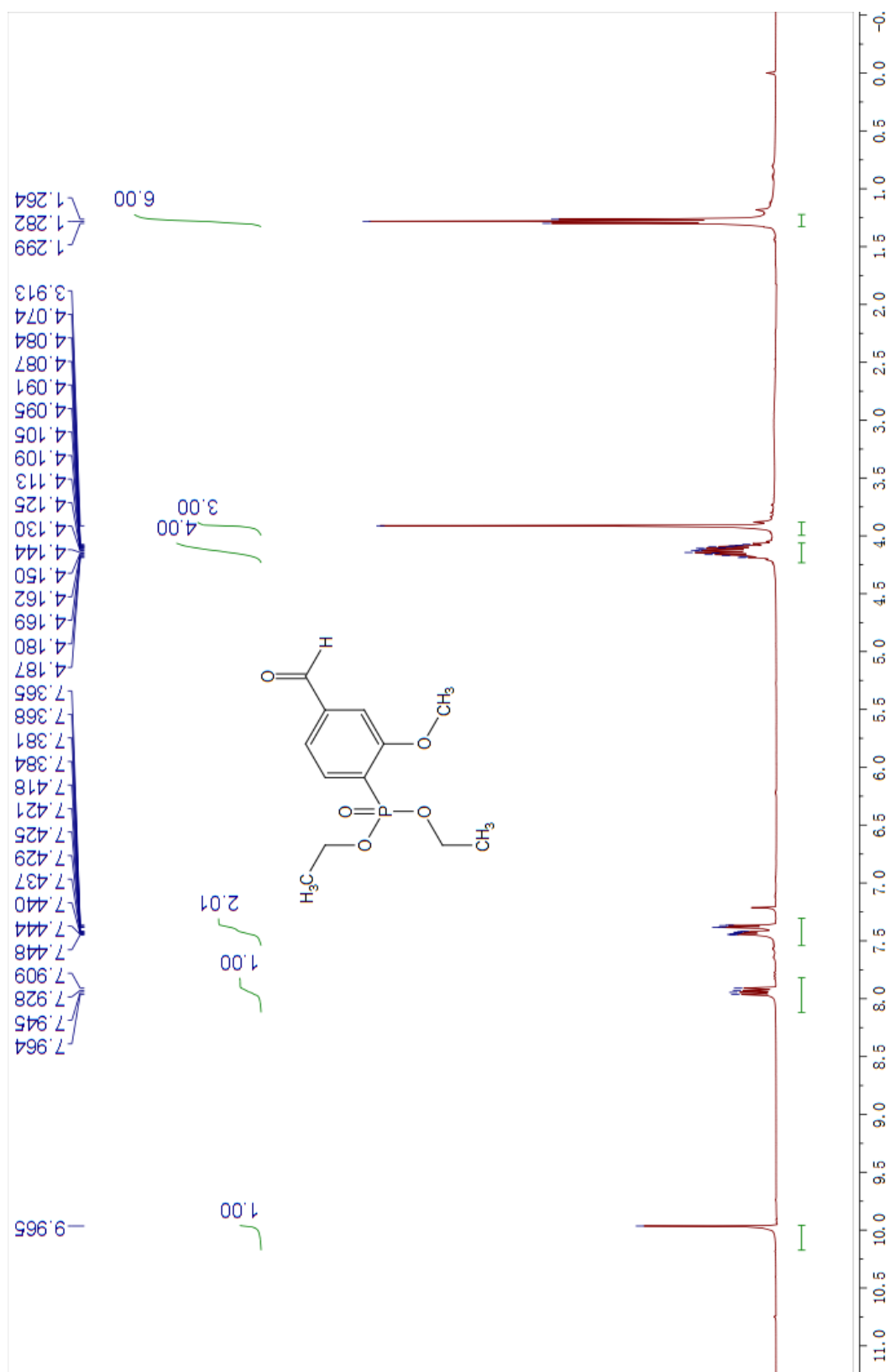
hxf-17 570 (3.094)
TOF MS EI+



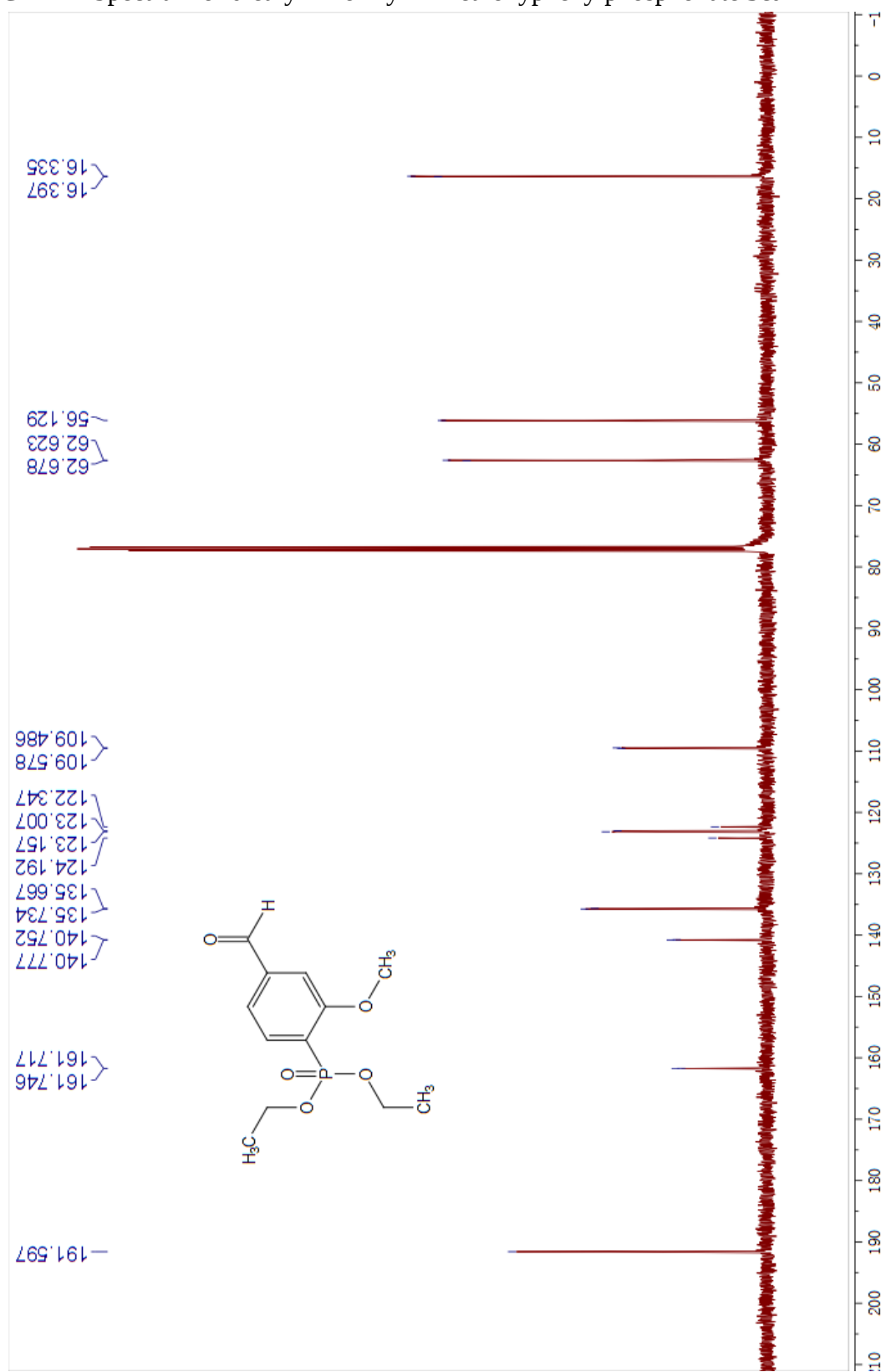
^{13}P NMR Spectrum of diethyl formyl-2-methoxyphenylphosphonate **3ea**



^1H NMR Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate **3ea**



¹³C NMR Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate **3ea**



HR-MS Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate **3ea**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

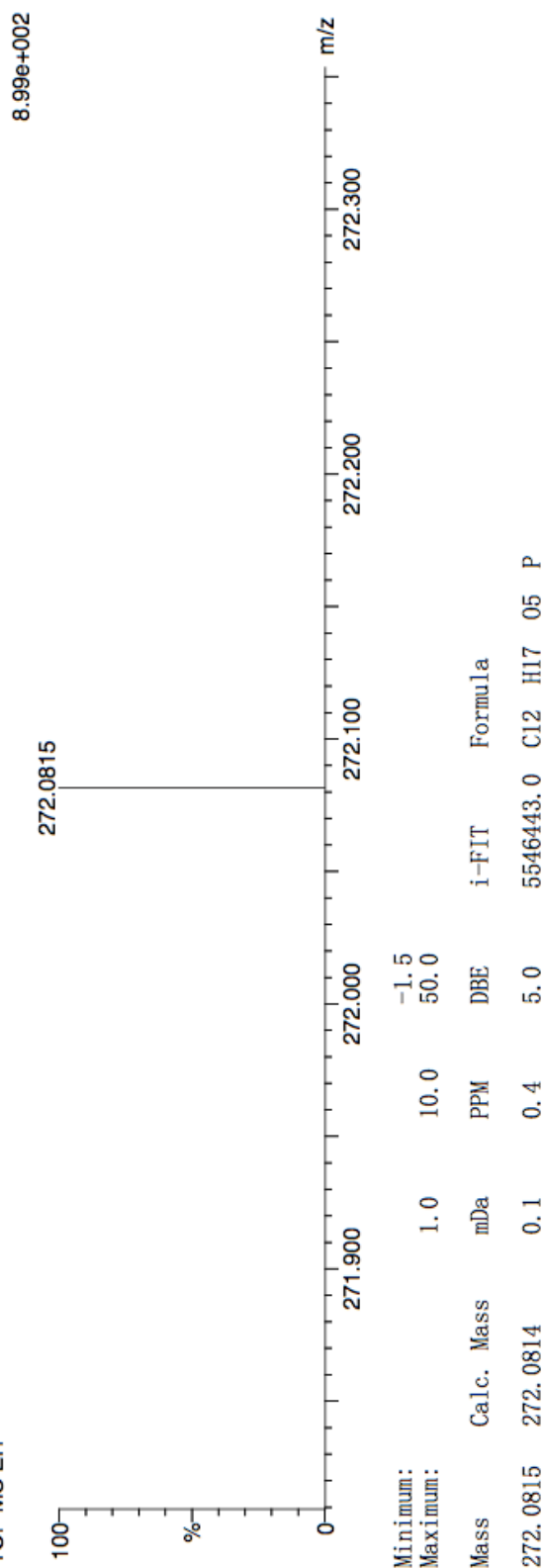
Monoisotopic Mass, Odd and Even Electron Ions
 50 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

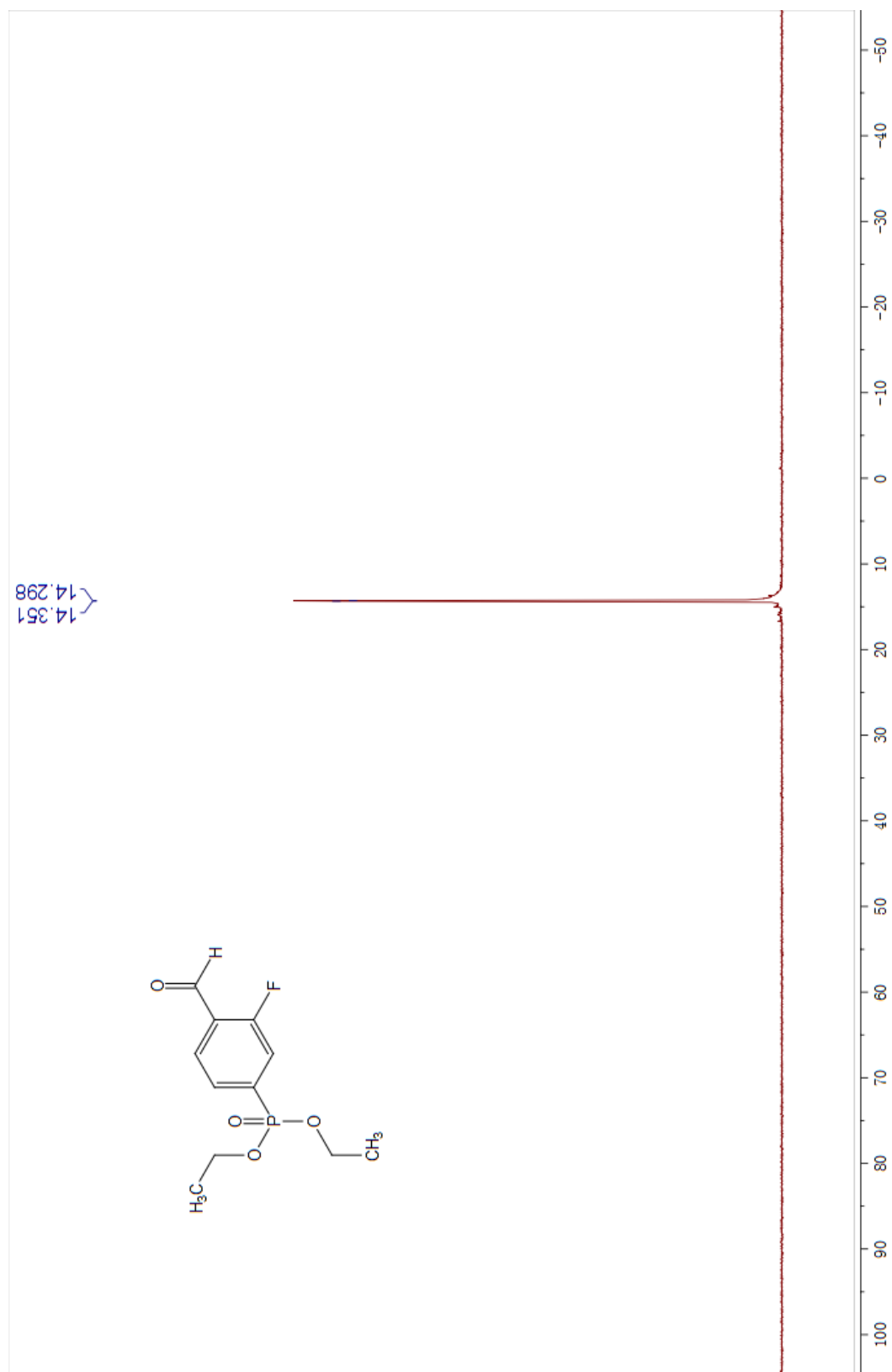
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hxf-18 570 (3.094)

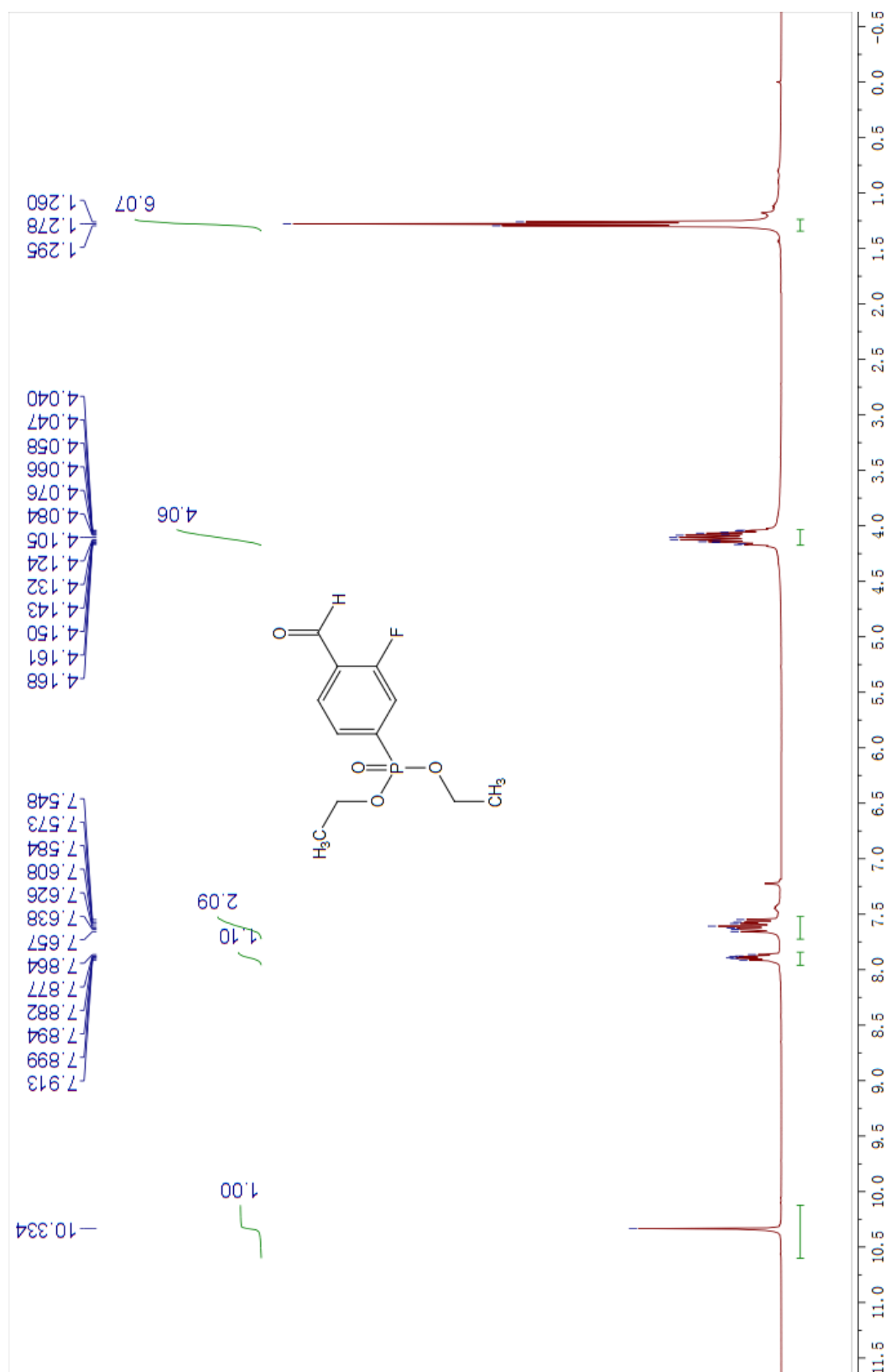
TOF MS EI+



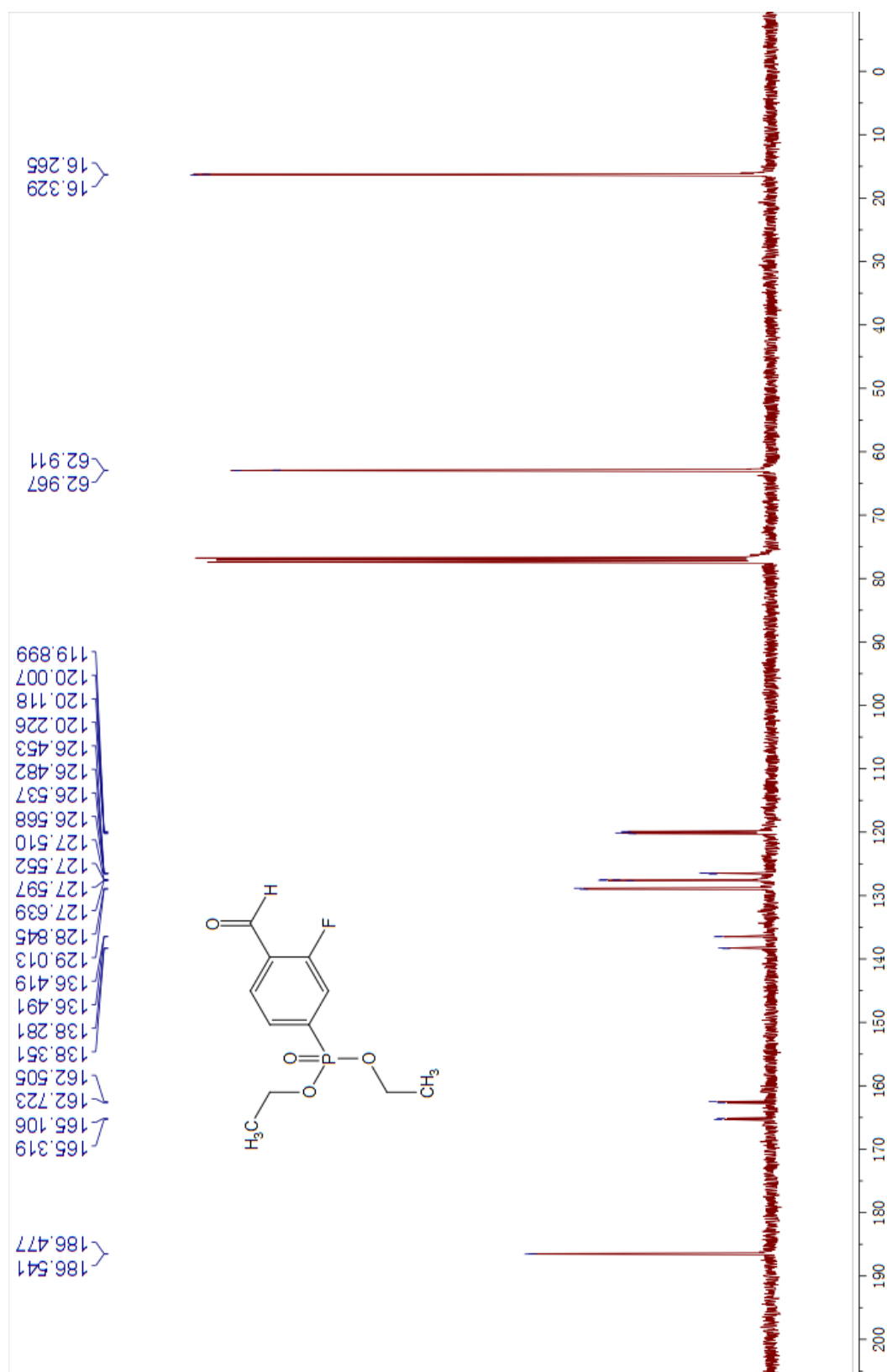
^{13}P NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**



^1H NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**



¹³C NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**

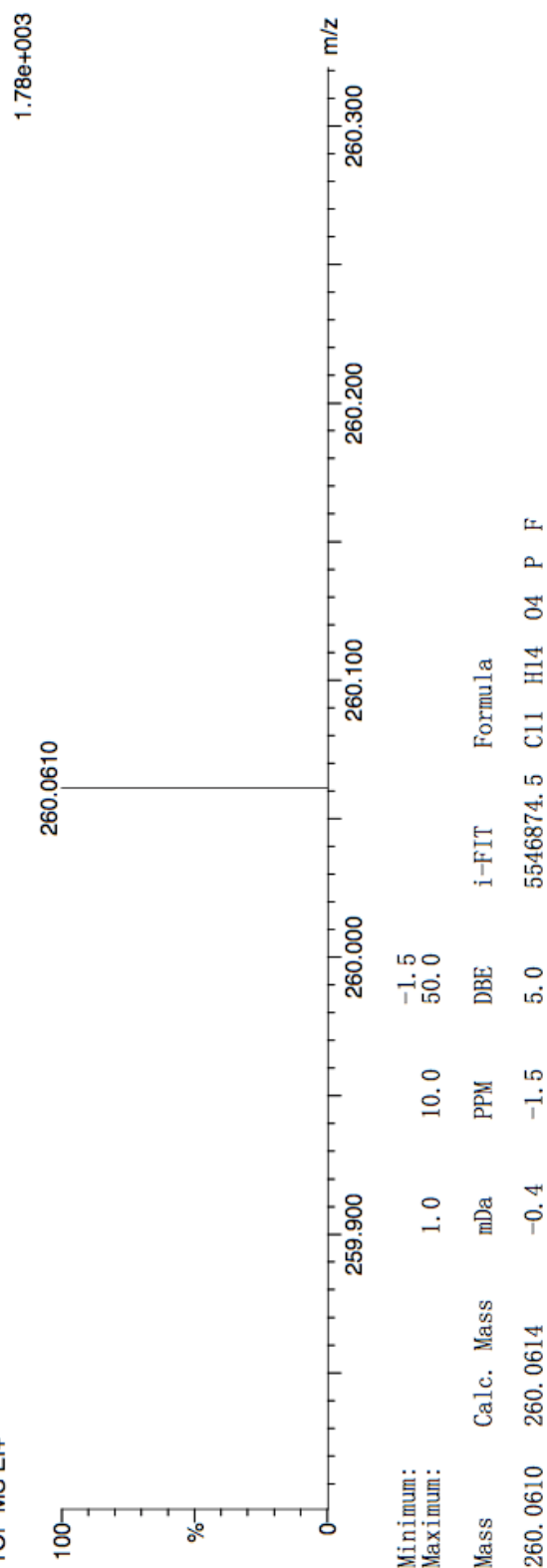


HR-MS Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**

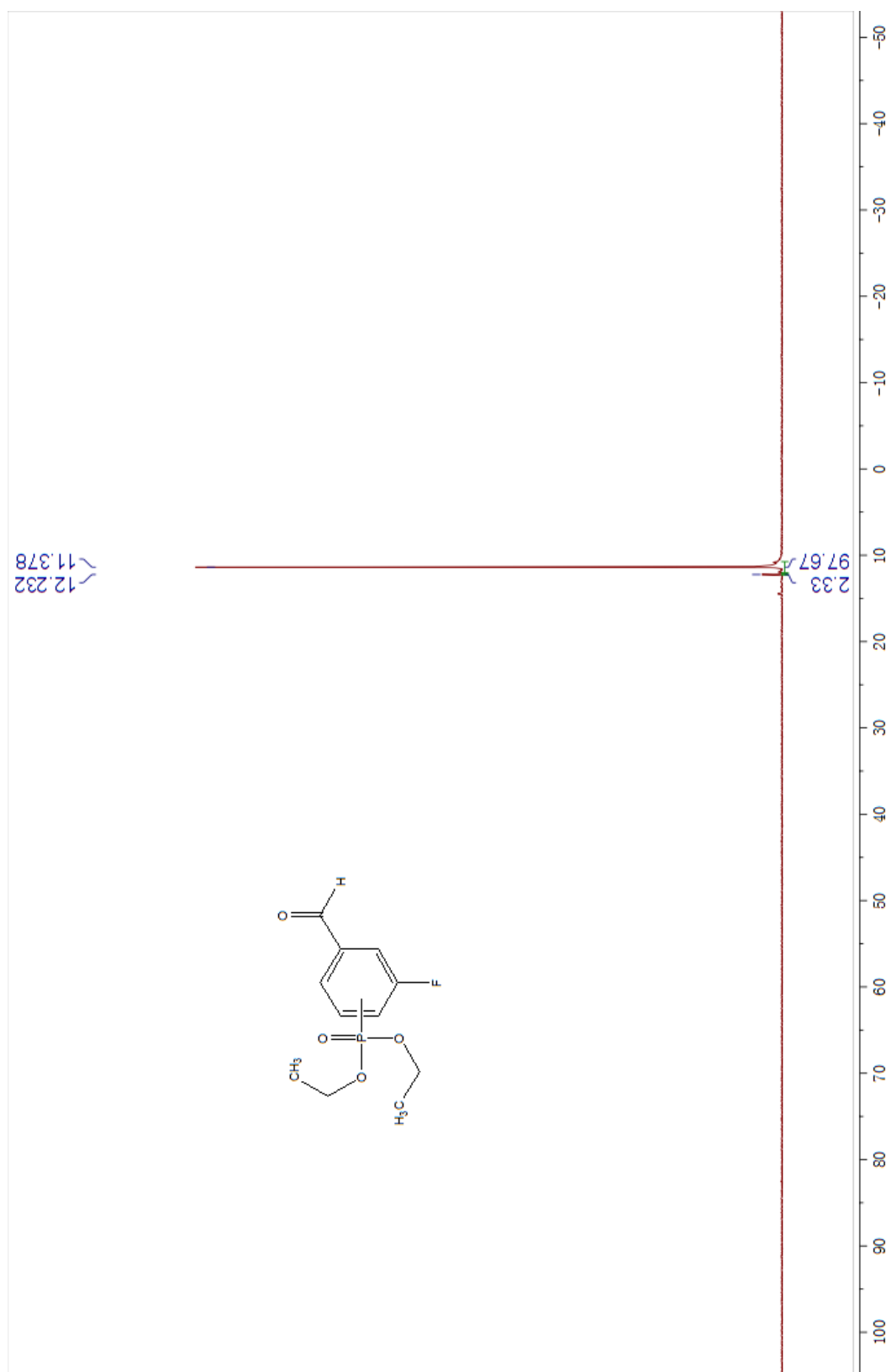
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 43 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 0-50 H: 0-200 O: 0-6 P: 0-1 F: 1-1

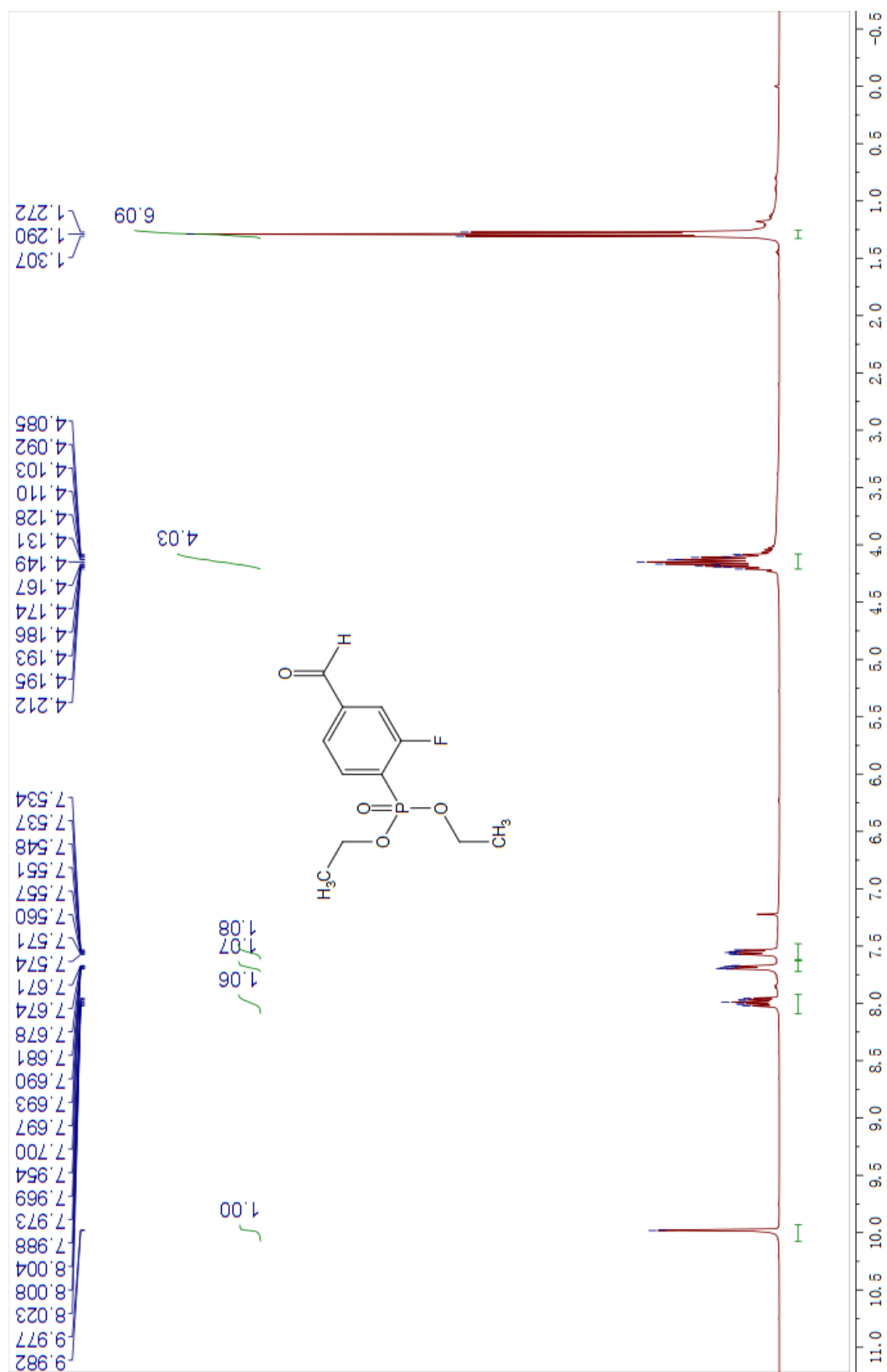
hxf-19 379 (2.394)
 TOF MS EI+



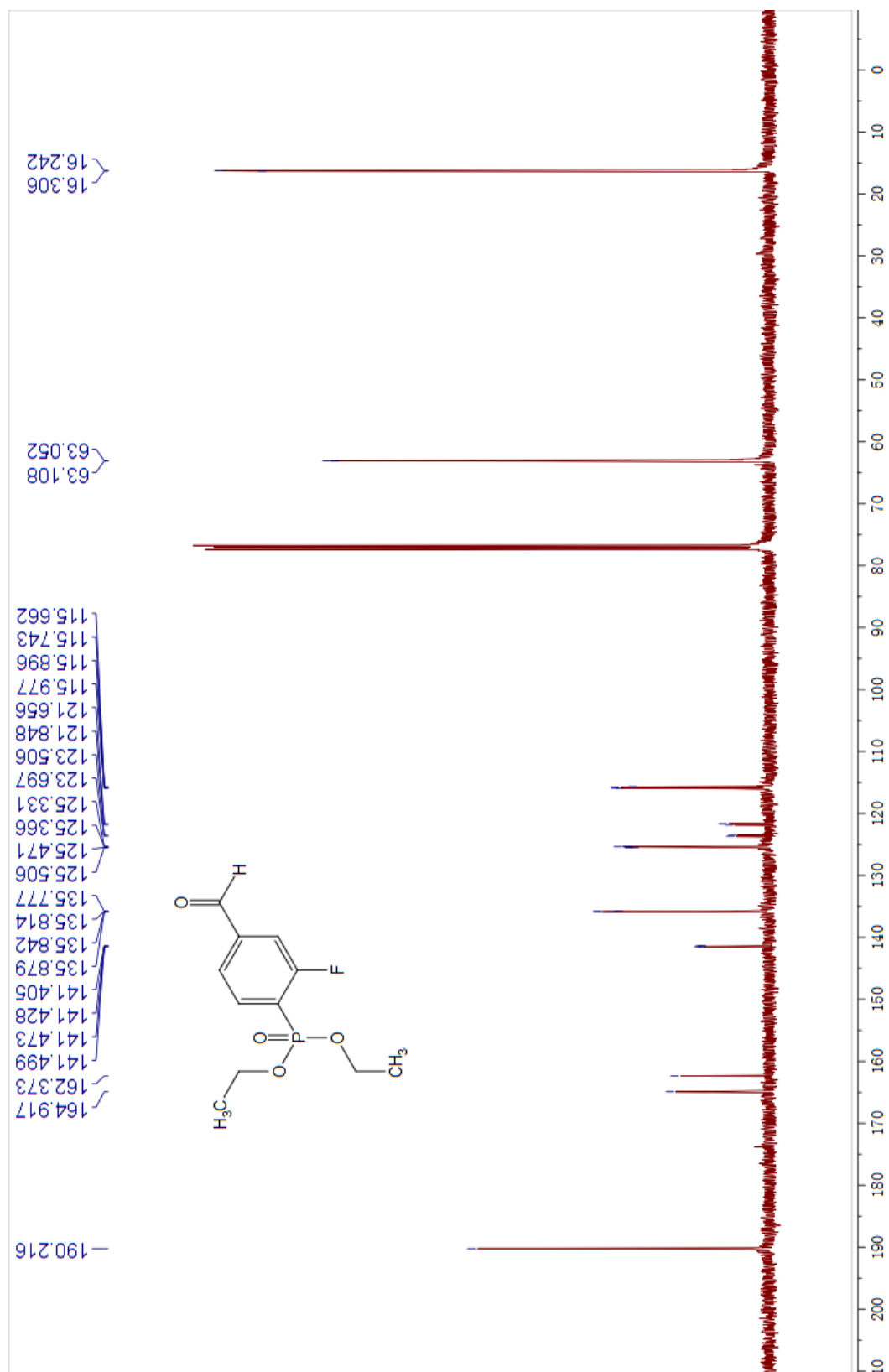
^{13}P NMR Spectrum of diethyl 2-fluoroformylphenylphosphonate **3ga**



¹H NMR Spectrum of (diethyl 2-fluoro-4-formylphenylphosphonate **3ga**



¹³C NMR Spectrum of diethyl 2-fluoro-4-formylphenylphosphonate **3ga**



HR-MS Spectrum of diethyl 2-fluoro-4-formylphenylphosphonate **3ga**

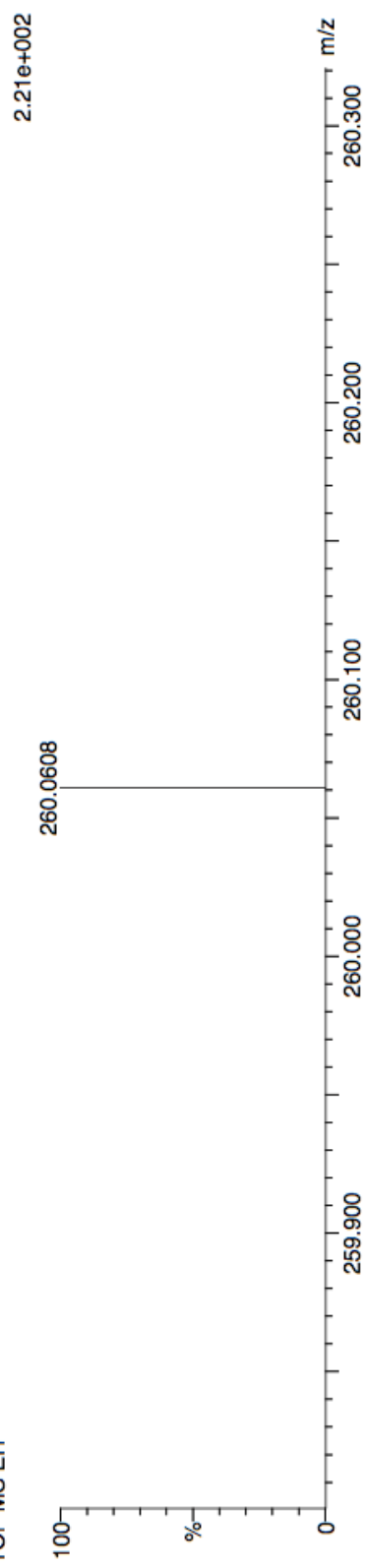
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
43 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:

C: 0-50 H: 0-200 O: 0-6 F: 1-1 P: 0-1

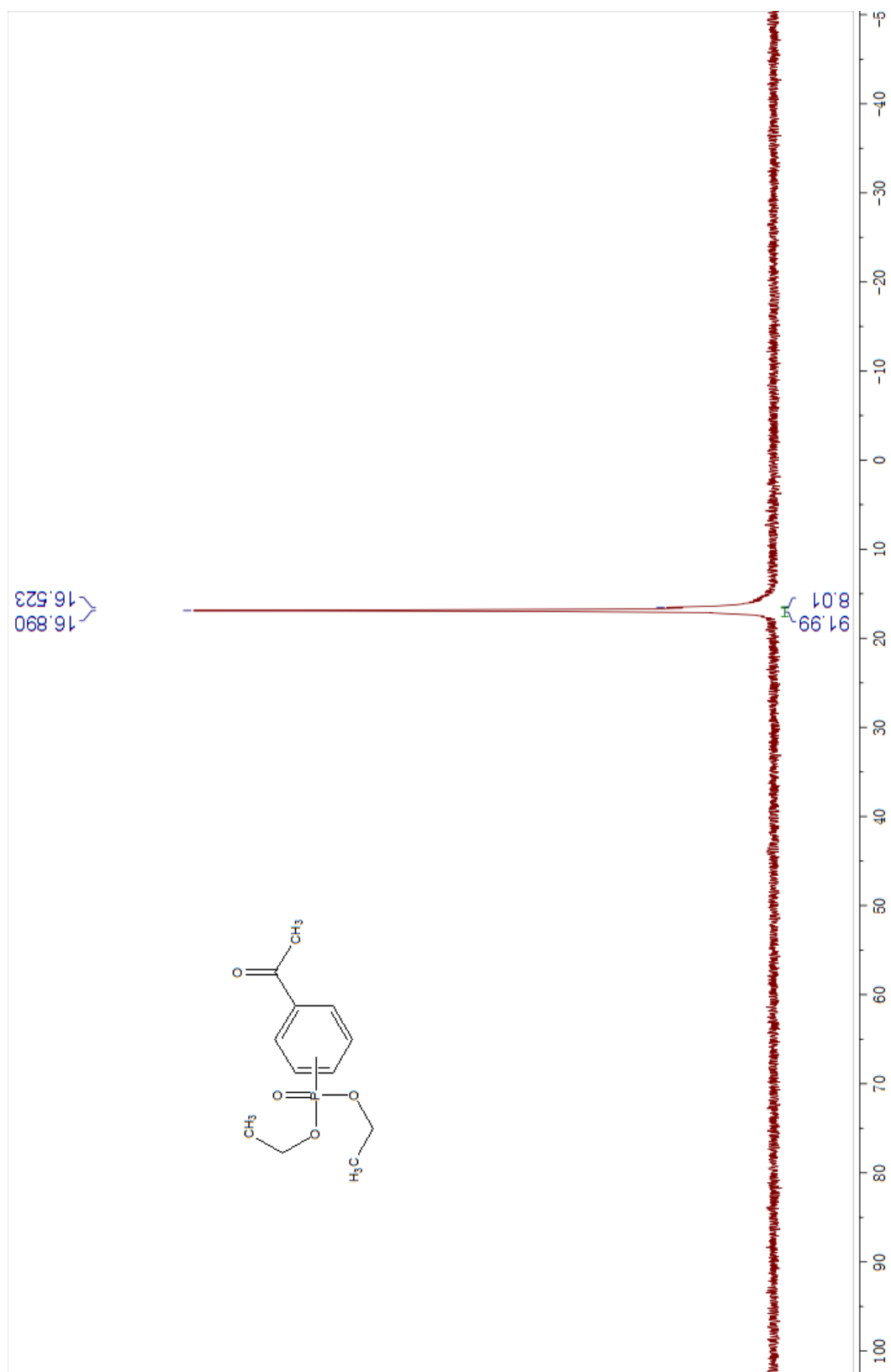
h₀-20 387 (2.423)

TOF MS EI+

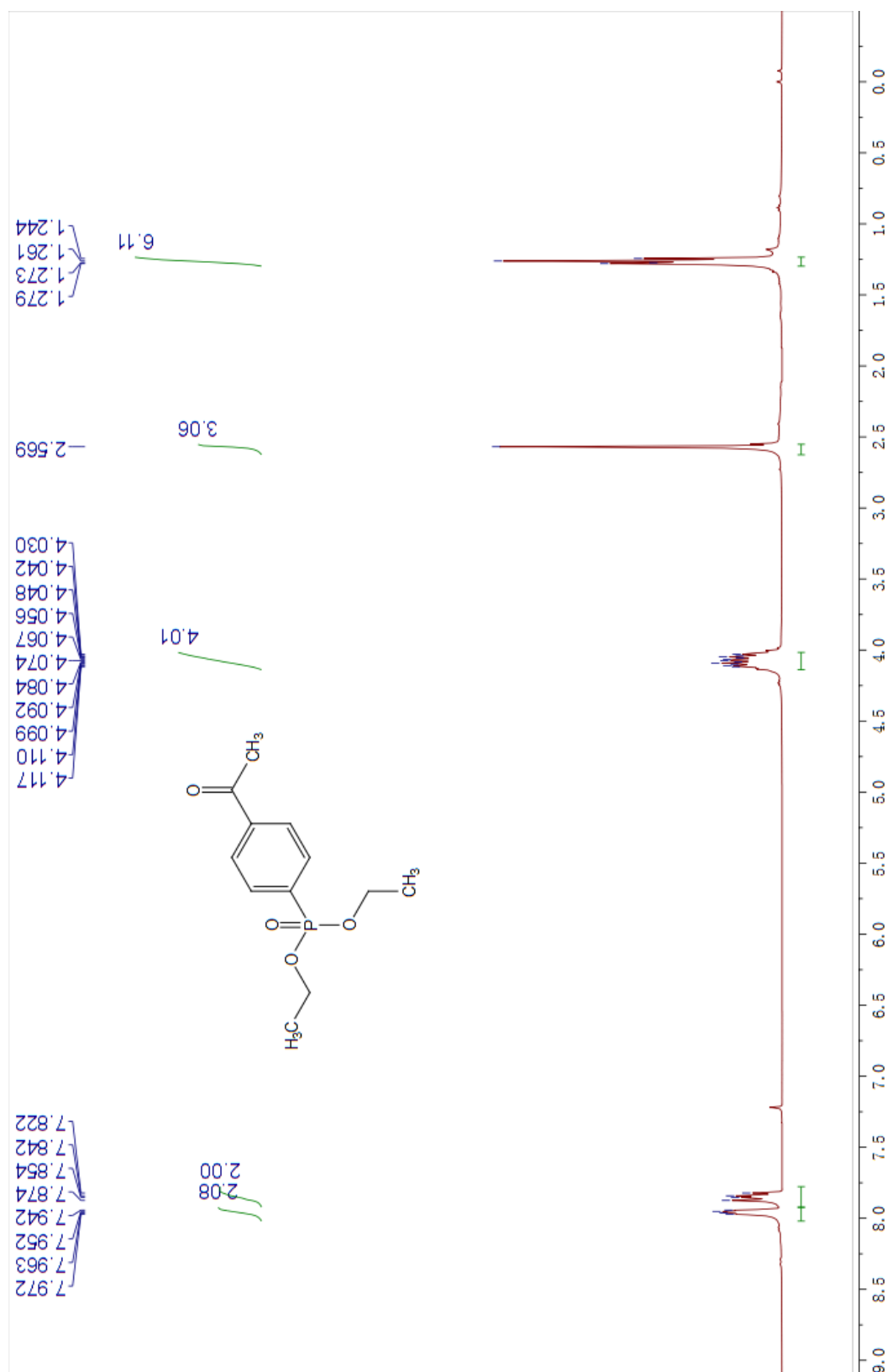


Minimum:						
Maximum:						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
260.0608	260.0614	-0.6	-2.3	5.0	5546105.0	C11 H14 O4 F P

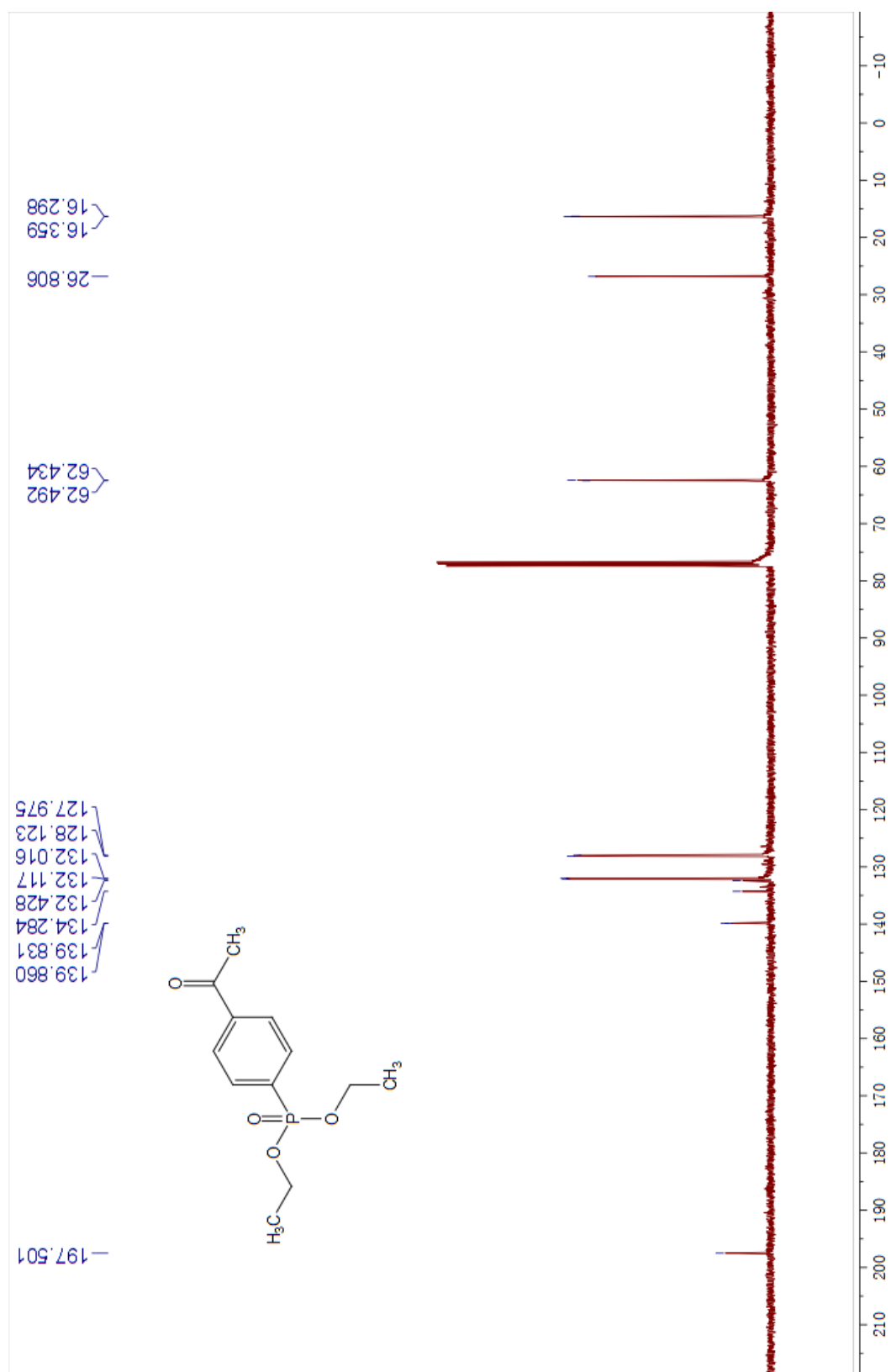
^{13}P NMR Spectrum of diethyl acetylphenylphosphonate **3ja**



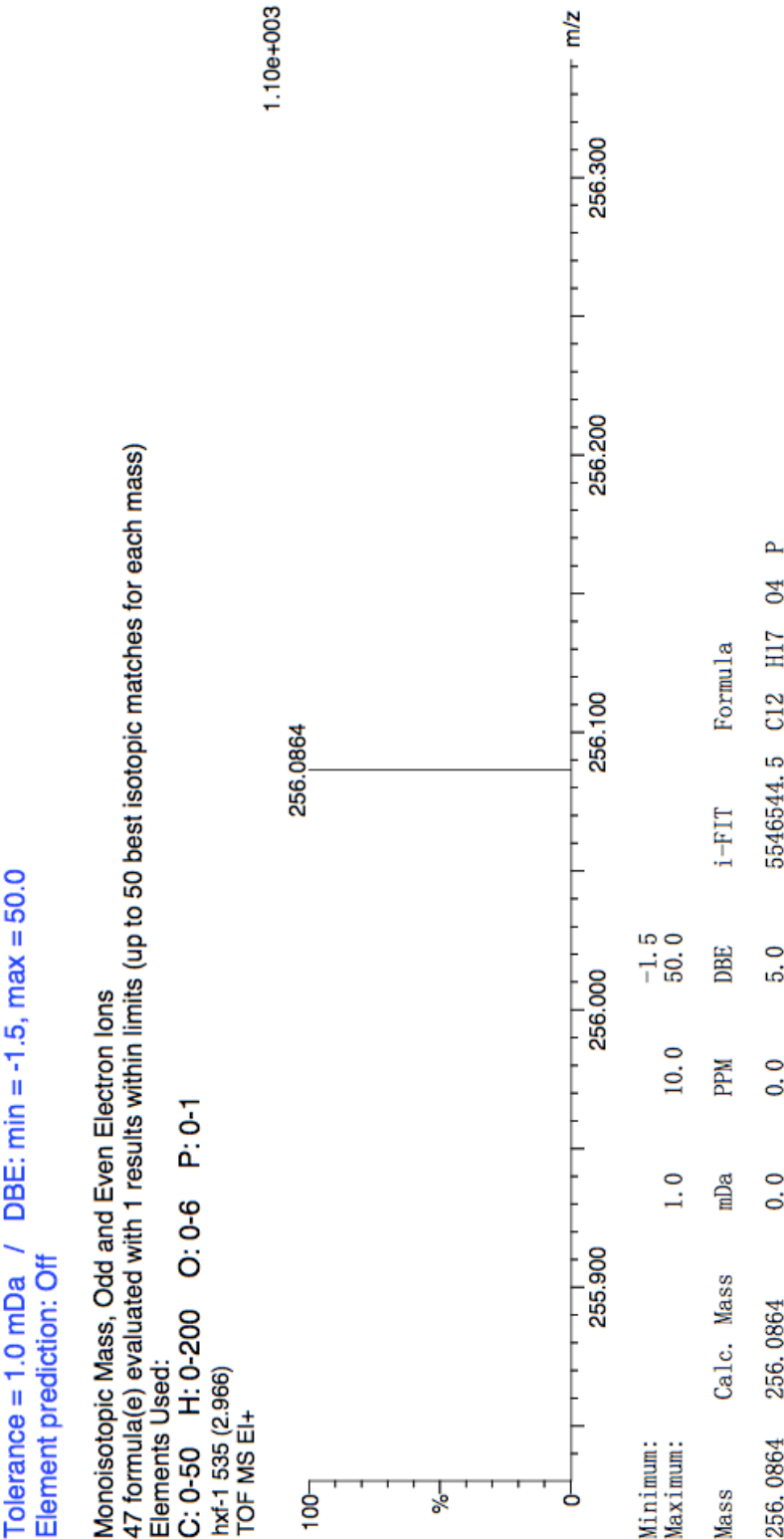
^1H NMR Spectrum of diethyl 4-acetylphenylphosphonate **3ja**



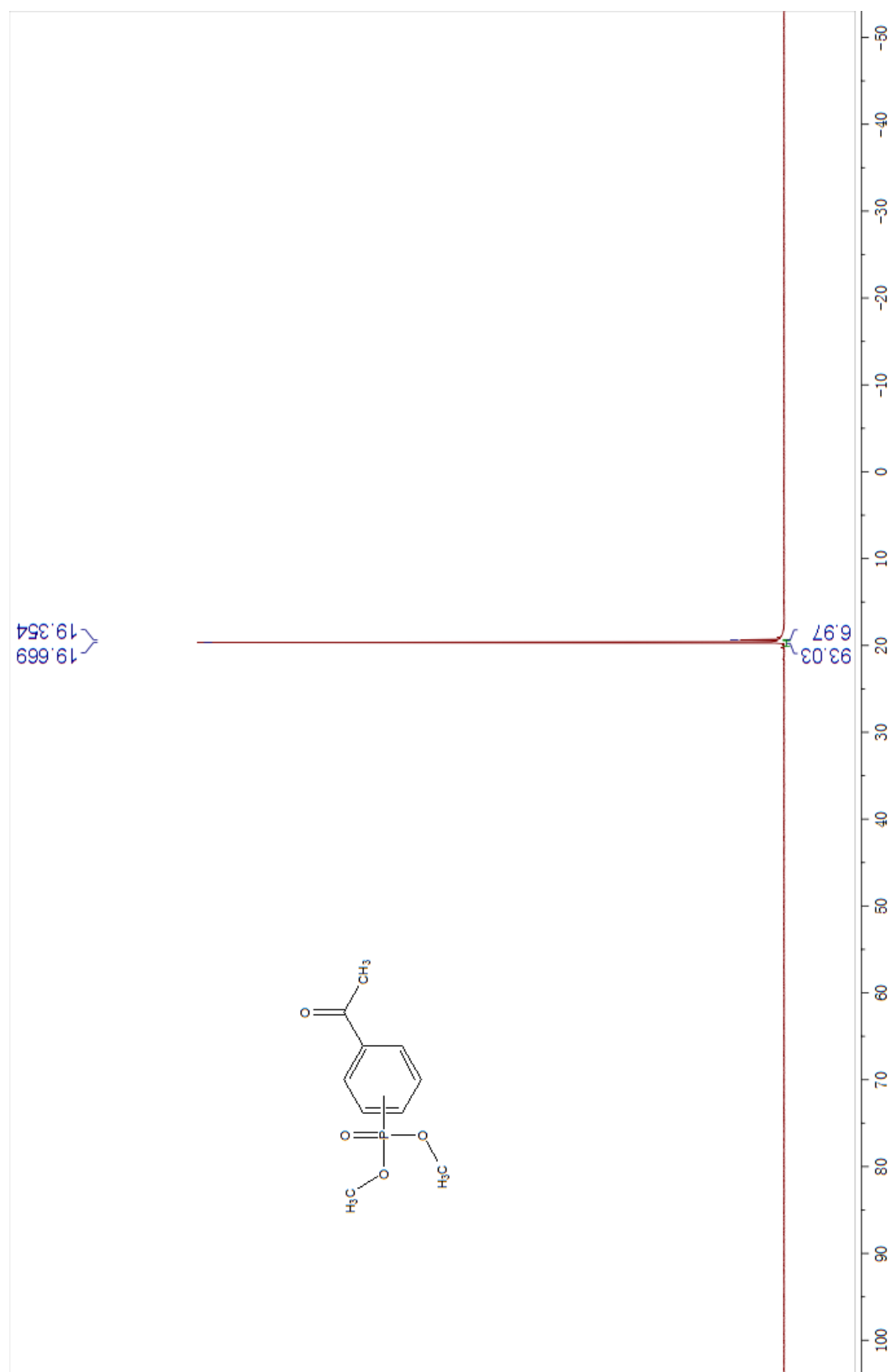
¹³C NMR Spectrum of diethyl 4-acetylphenylphosphonate **3ja**



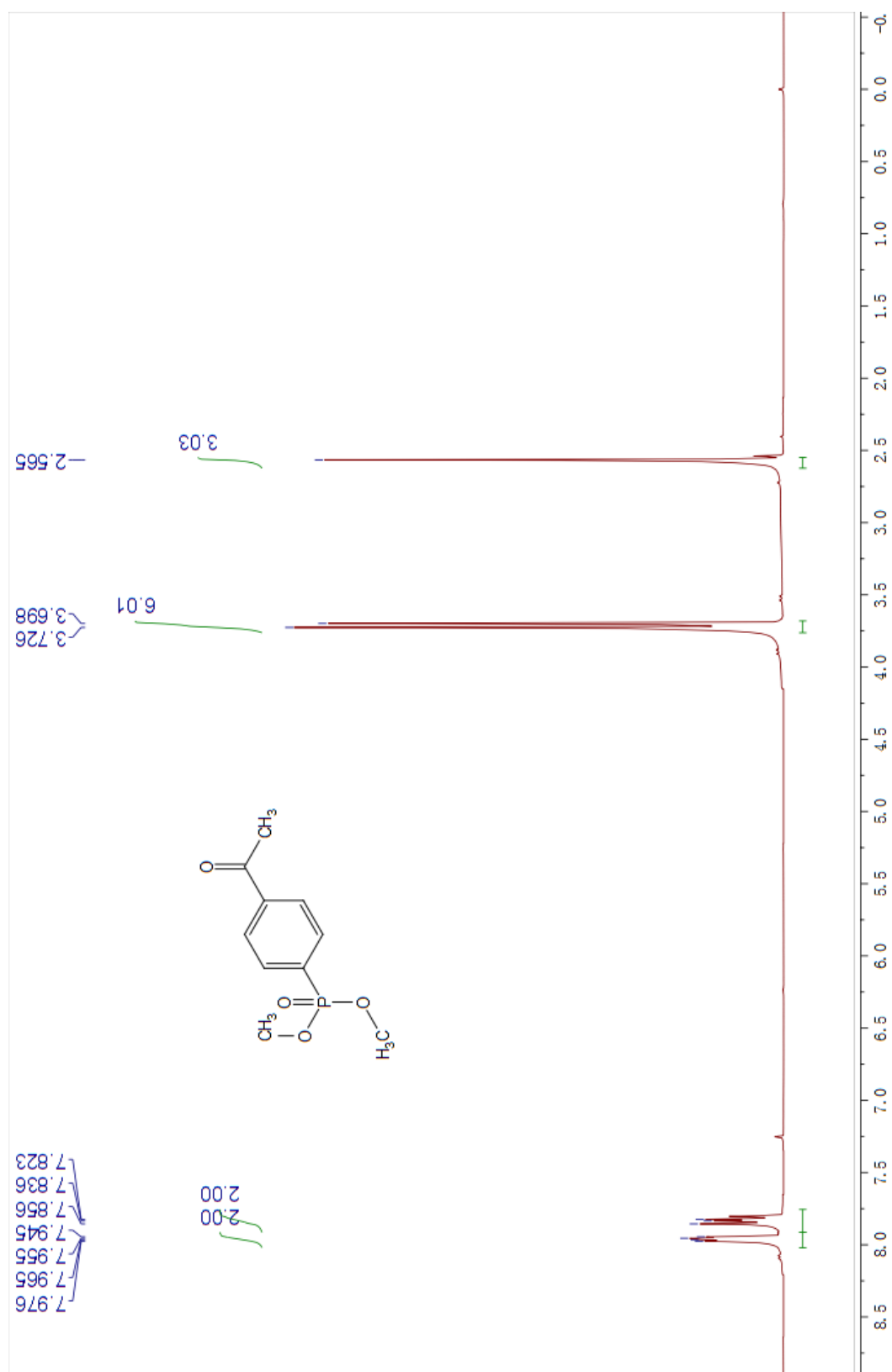
HR-MS Spectrum of diethyl 4-acetylphenylphosphonate **3ja**



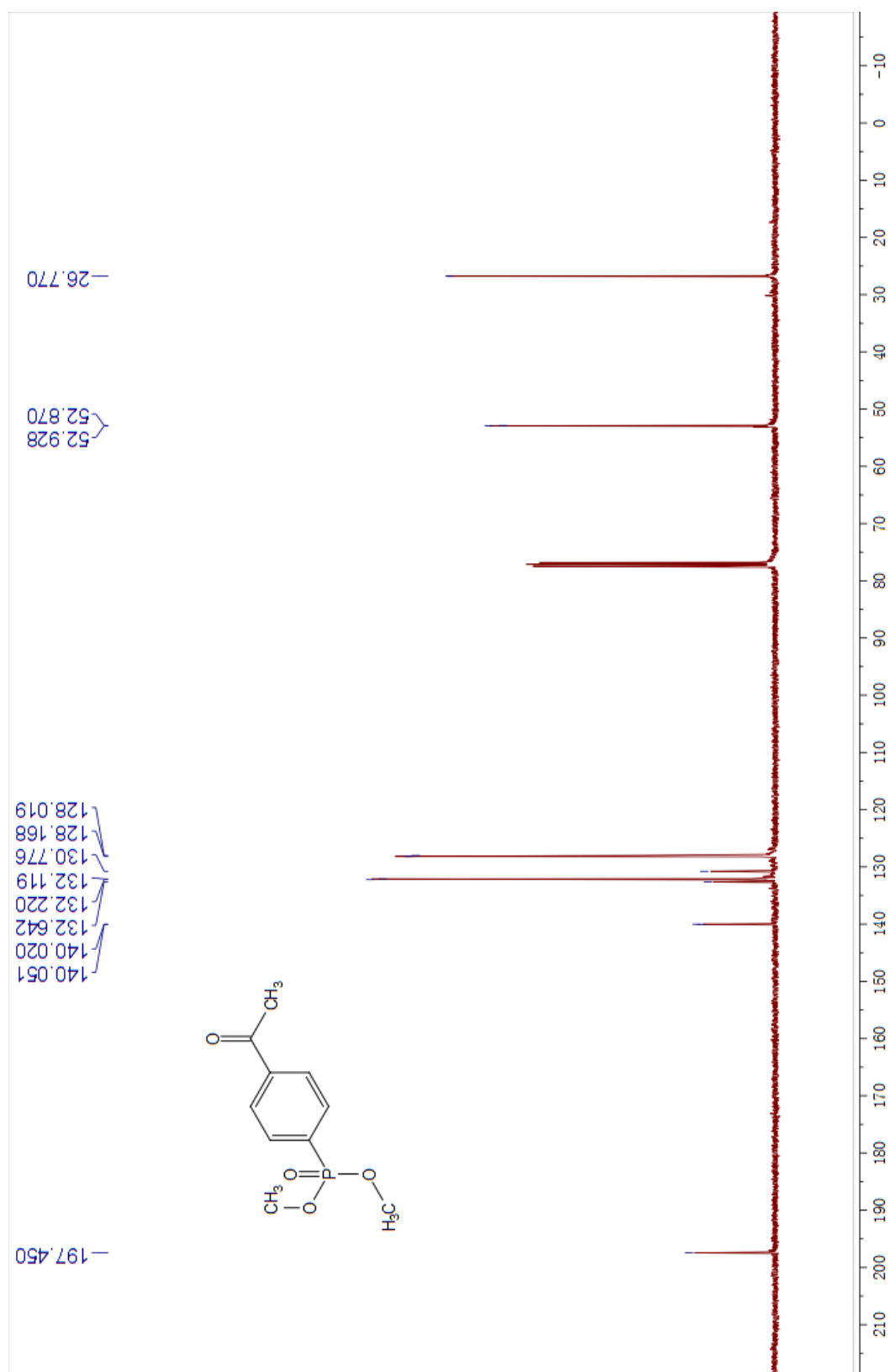
^{13}P NMR Spectrum of dimethyl acetylphenylphosphonate **3jb**



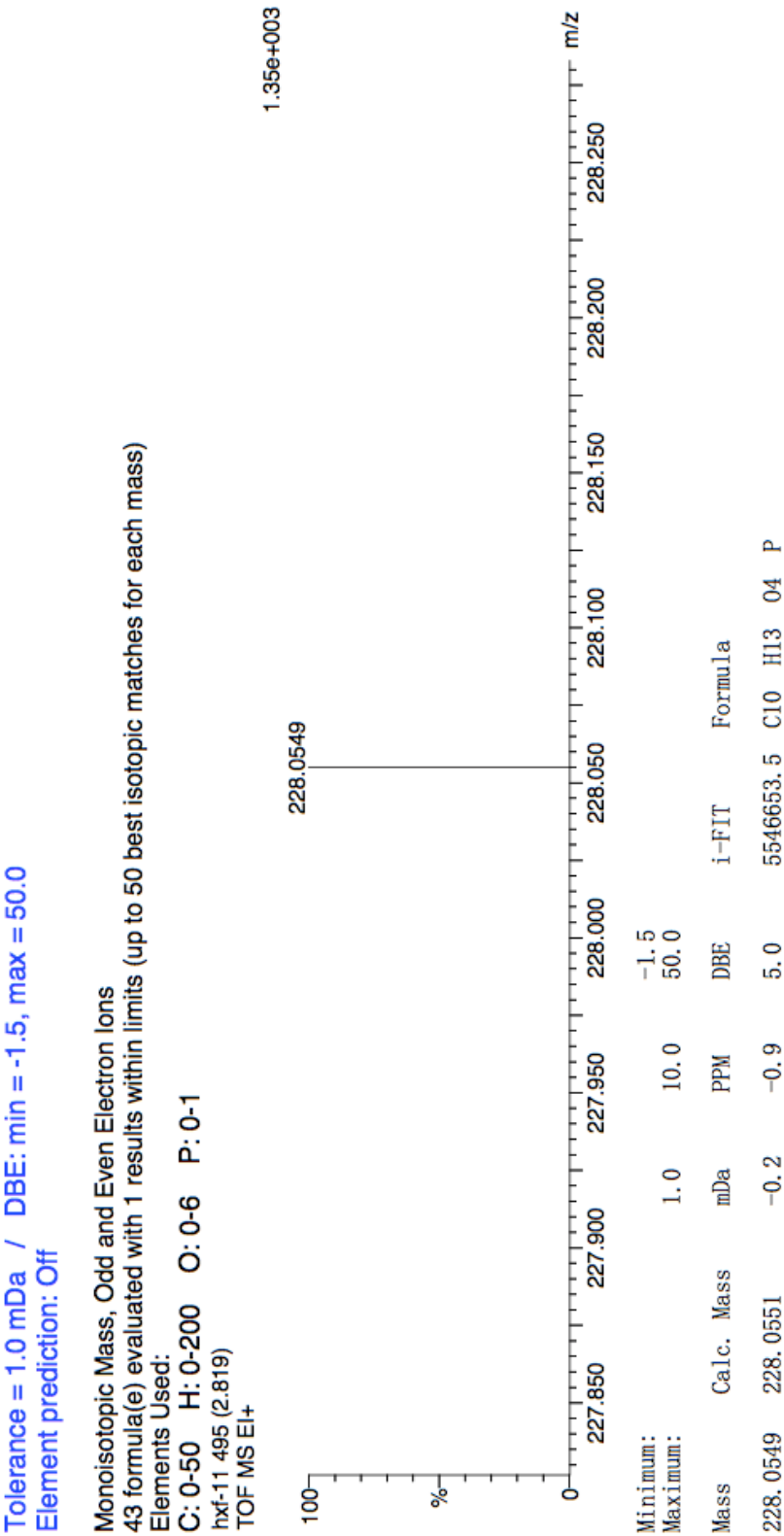
^1H NMR Spectrum of dimethyl 4-acetylphenylphosphonate **3jb**



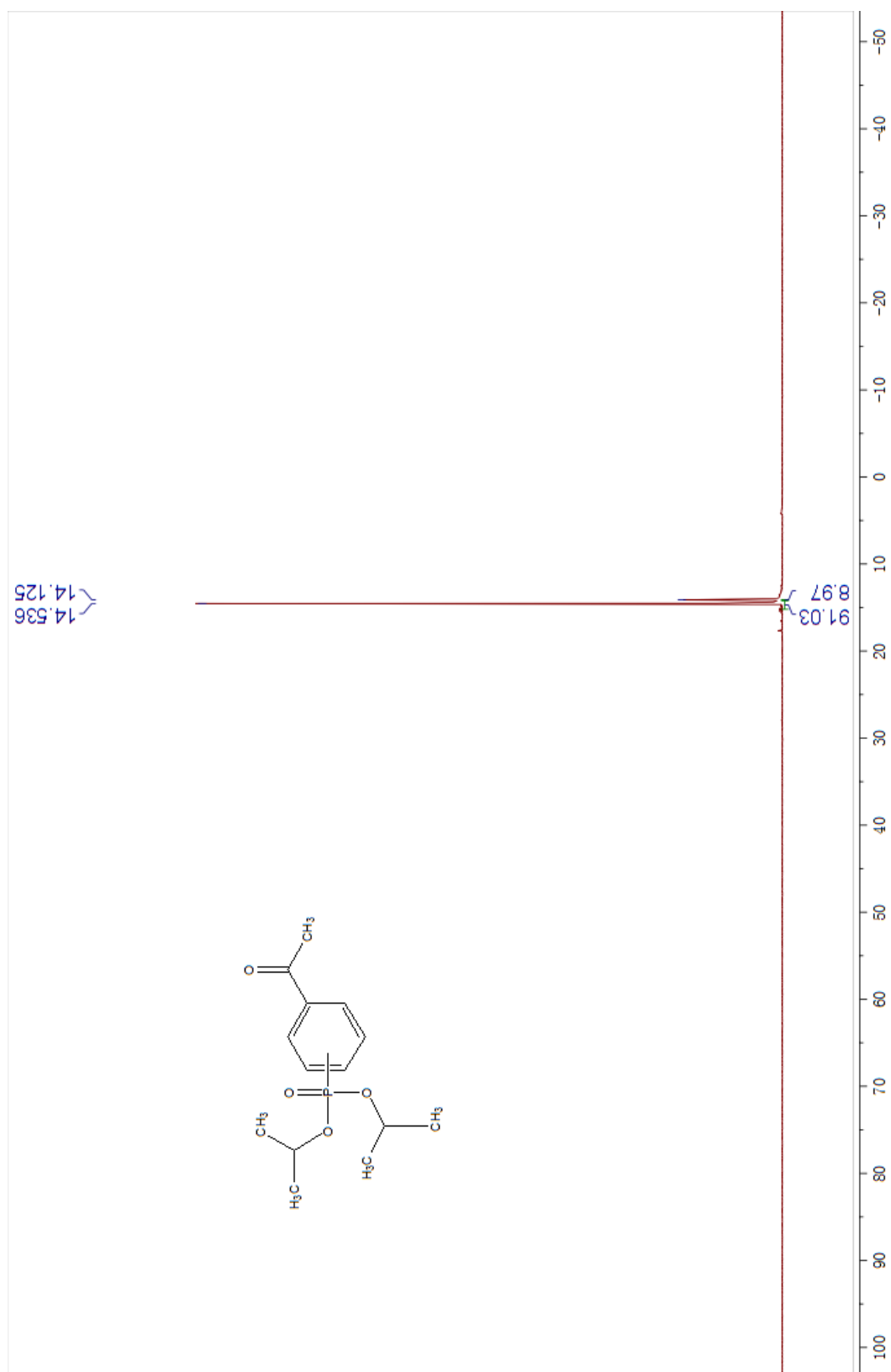
¹³C NMR Spectrum of dimethyl 4-acetylphenylphosphonate **3jb**



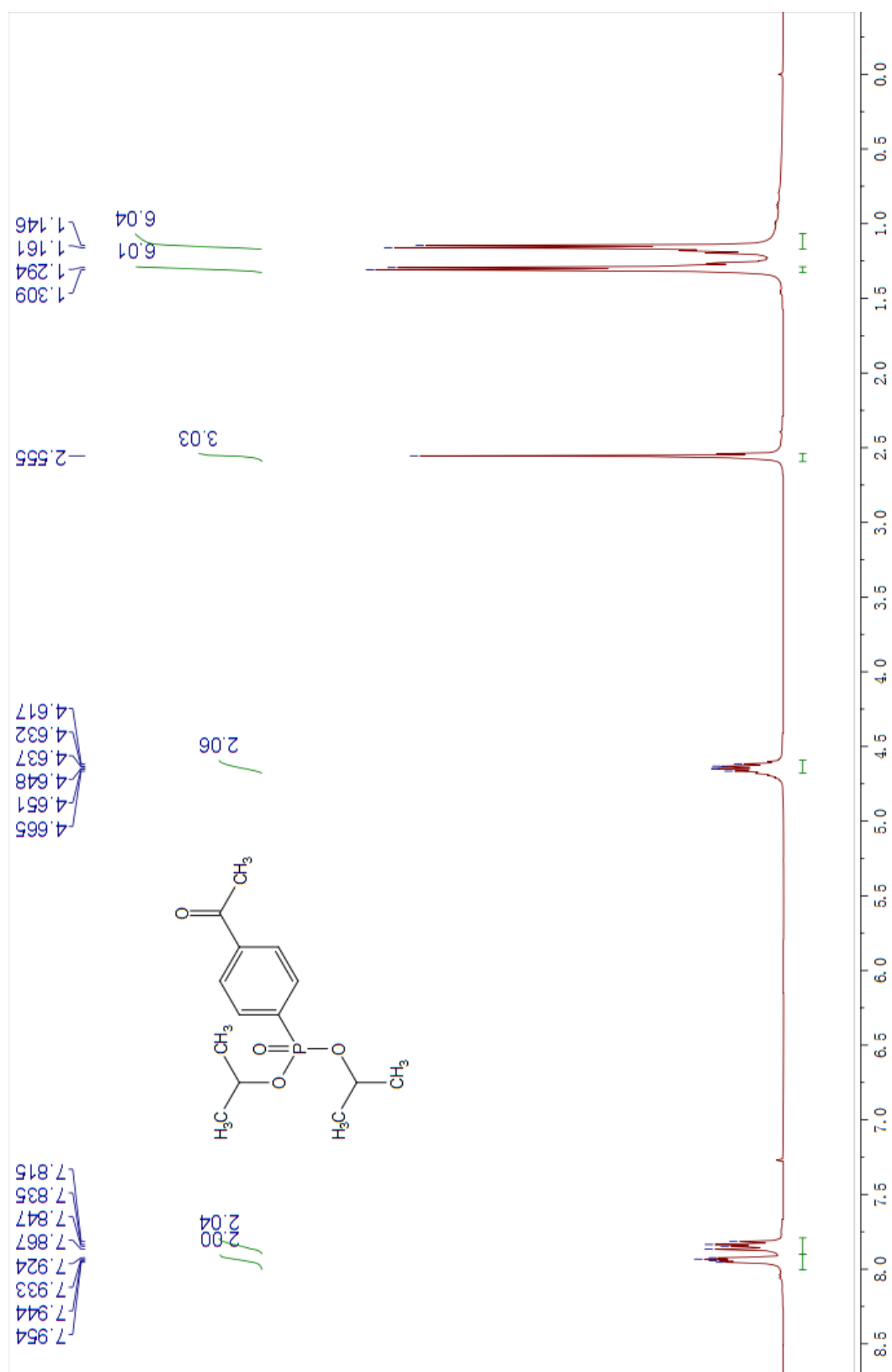
HR-MS Spectrum of dimethyl 4-acetylphenylphosphonate **3jb**



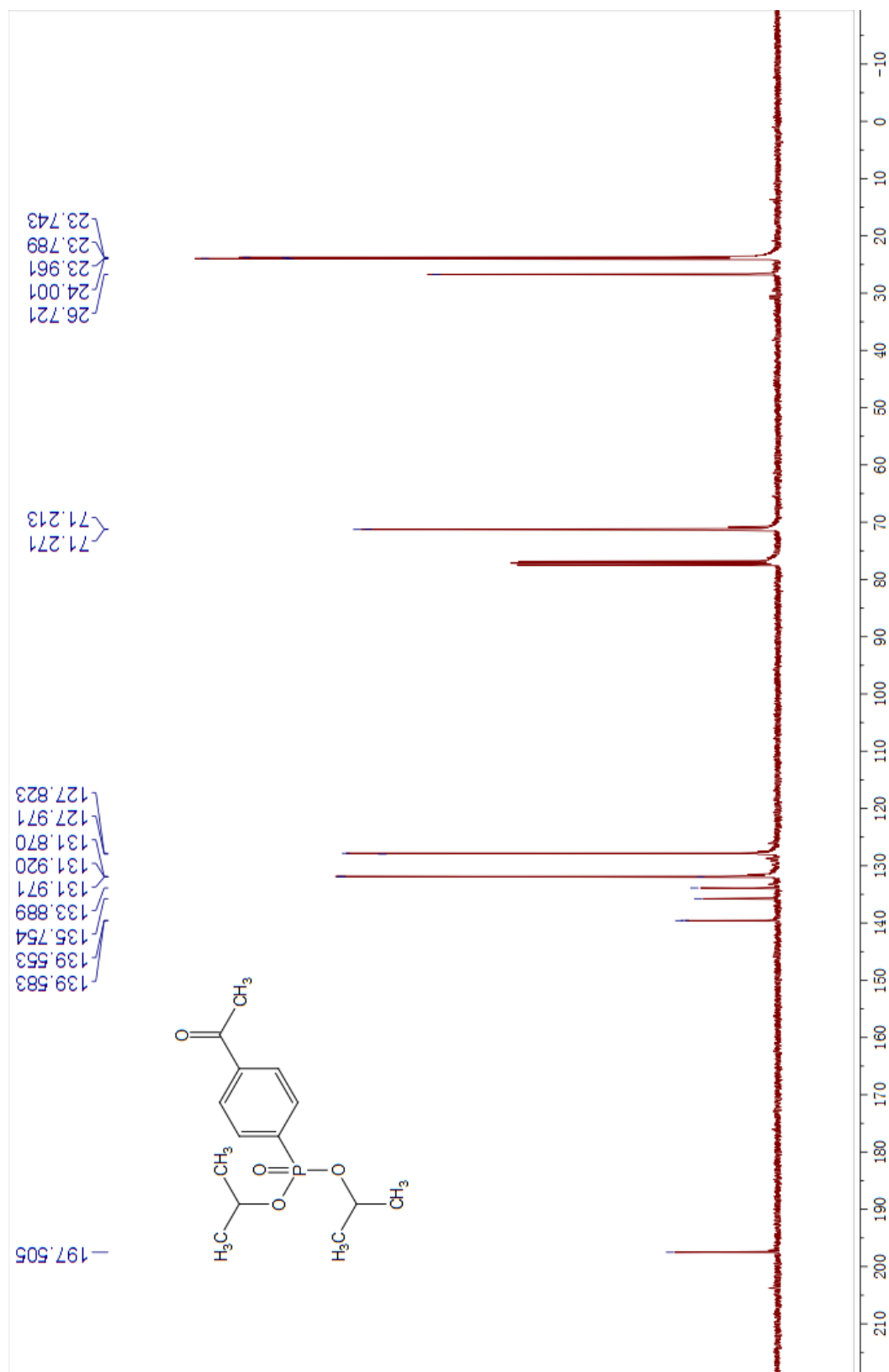
¹³P NMR Spectrum of diisopropyl acetylphenylphosphonate **3jc**



^1H NMR Spectrum of diisopropyl 4-acetylphenylphosphonate **3jc**



¹³C NMR Spectrum of diisopropyl 4-acetylphenylphosphonate **3jc**



HR-MS Spectrum of diisopropyl 4-acetylphenylphosphonate **3jc**

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 Element prediction: Off

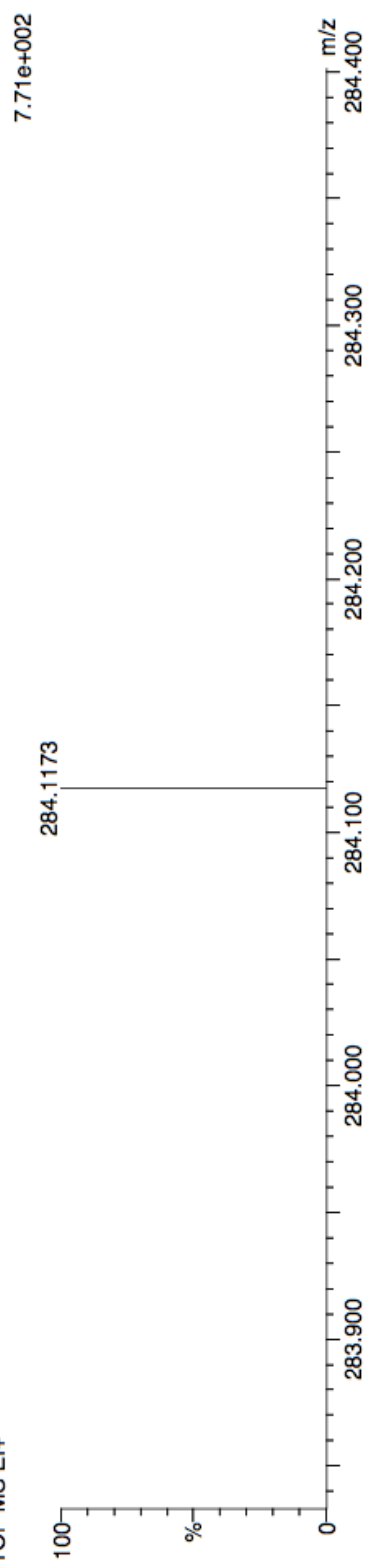
Monoisotopic Mass, Odd and Even Electron Ions
 52 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-50 H: 0-200 O: 0-6 P: 0-1

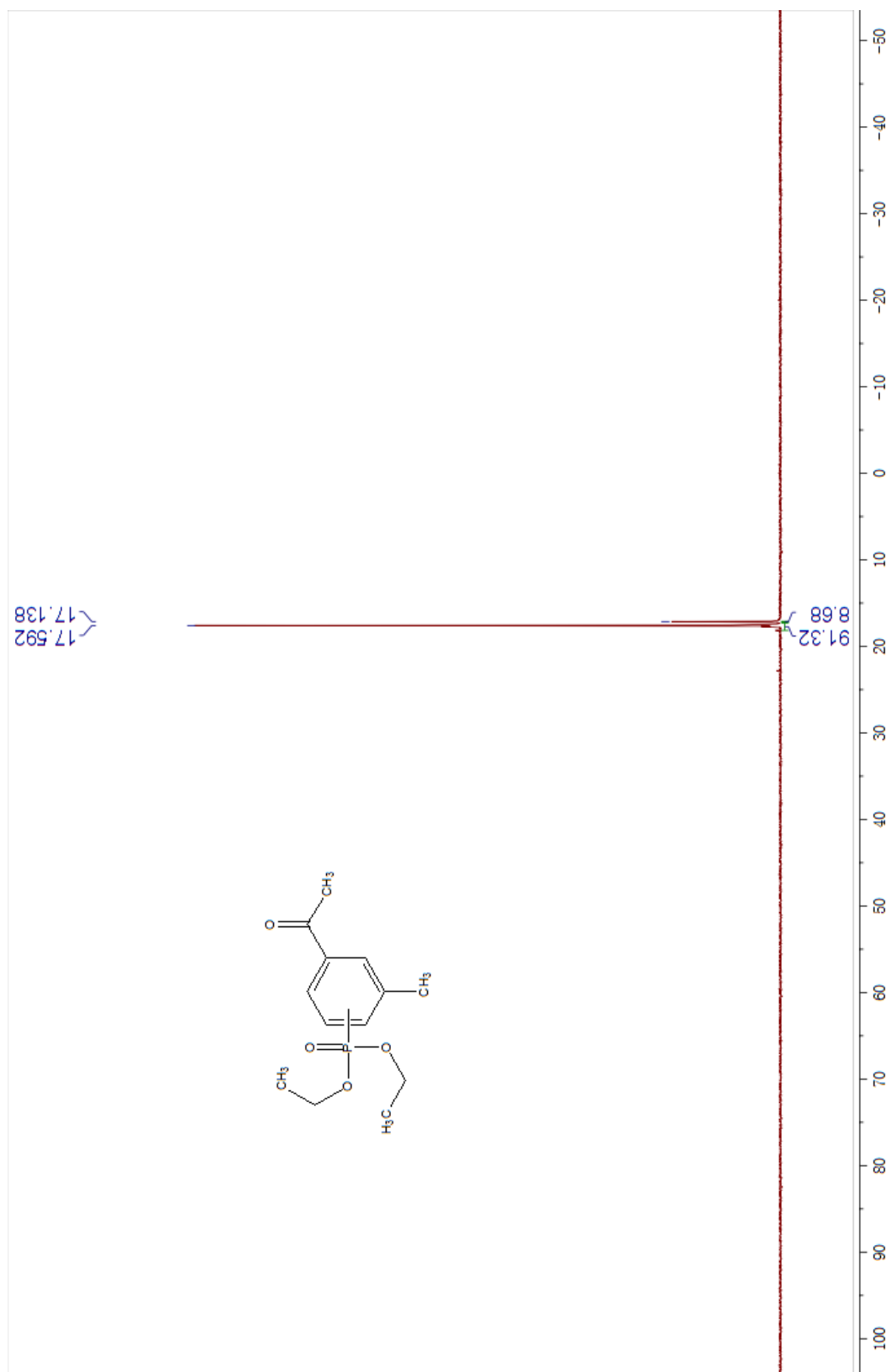
hxf-12 502 (2.845)

TOF MS EI+

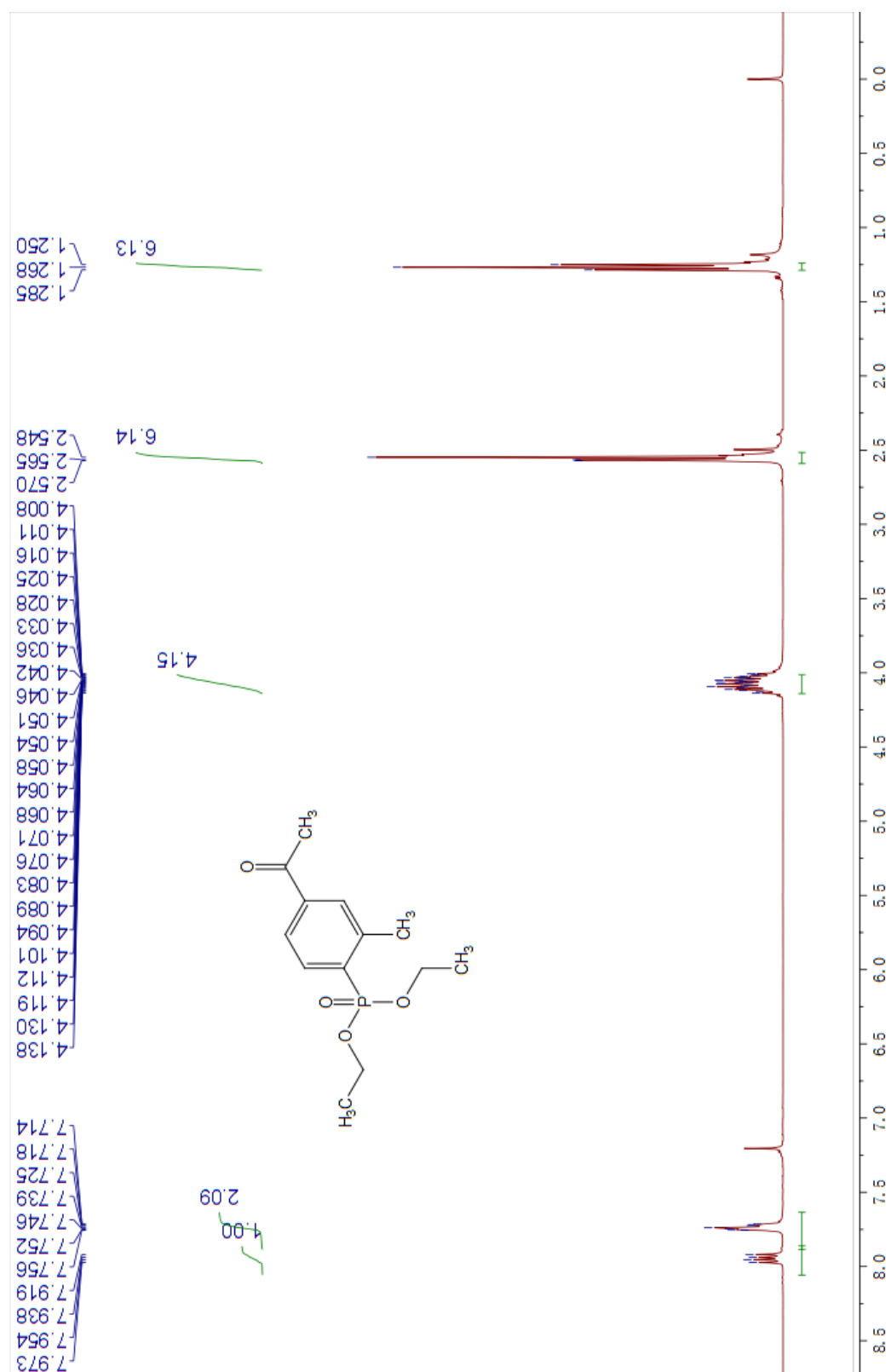


Minimum:				-1.5	
Maximum:				50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
284.1173	284.1177	-0.4	-1.4	5.0	5546386.0 C14 H21 O4 P

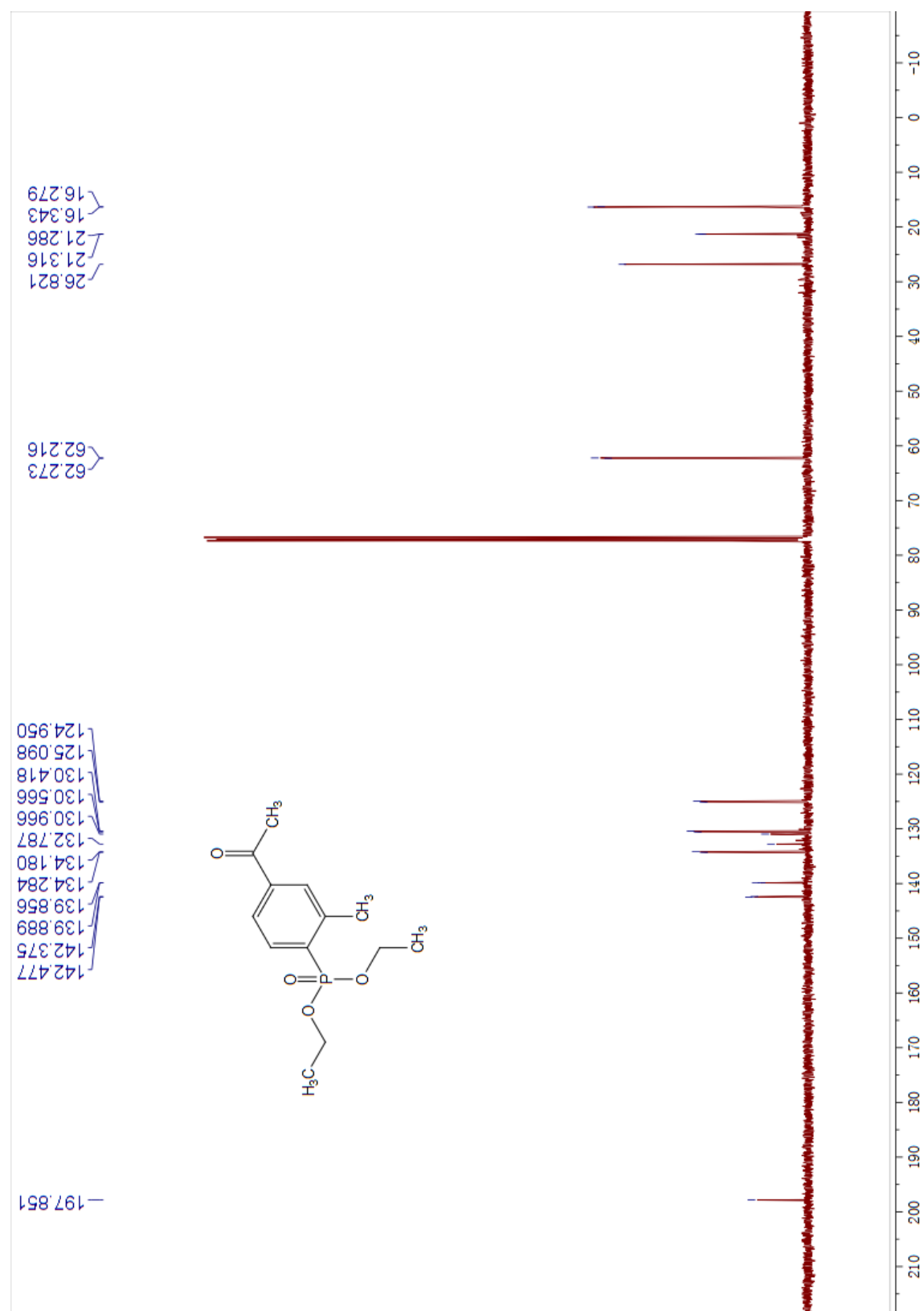
^{13}P NMR Spectrum of diethyl acetyl-2-methylphenylphosphonate **3ka**



^1H NMR Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate **3ka**



¹³C NMR Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate **3ka**



HR-MS Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate **3ka**

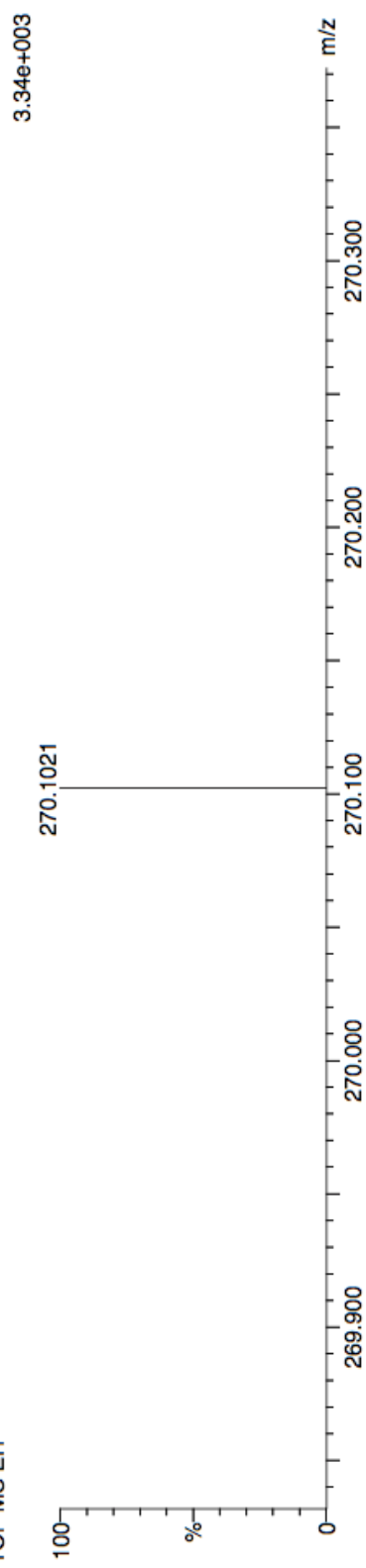
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 50 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:

C: 0-50 H: 0-200 O: 0-6 P: 0-1

hxf-3 494 (2.815)

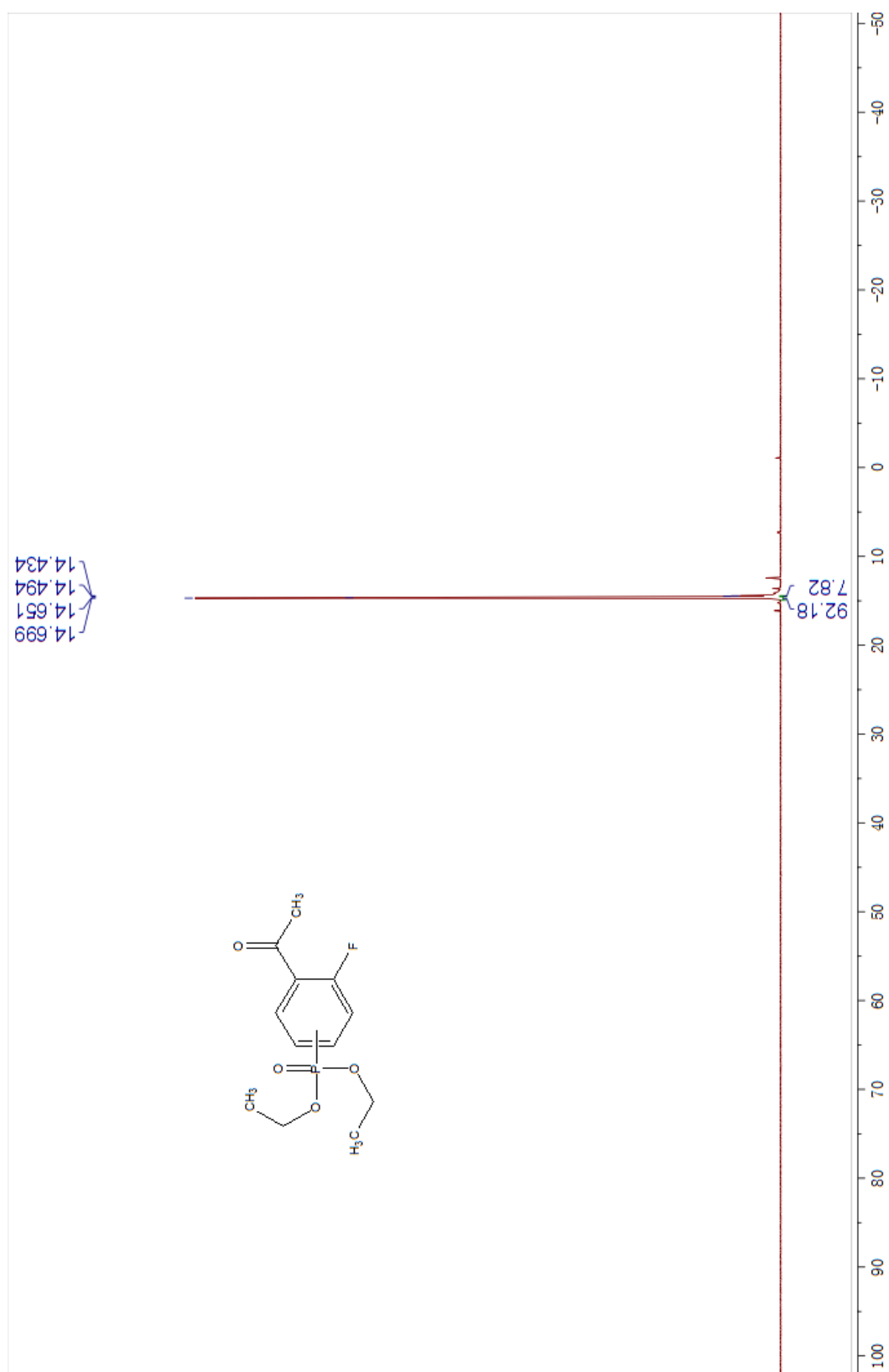
TOF MS EI+



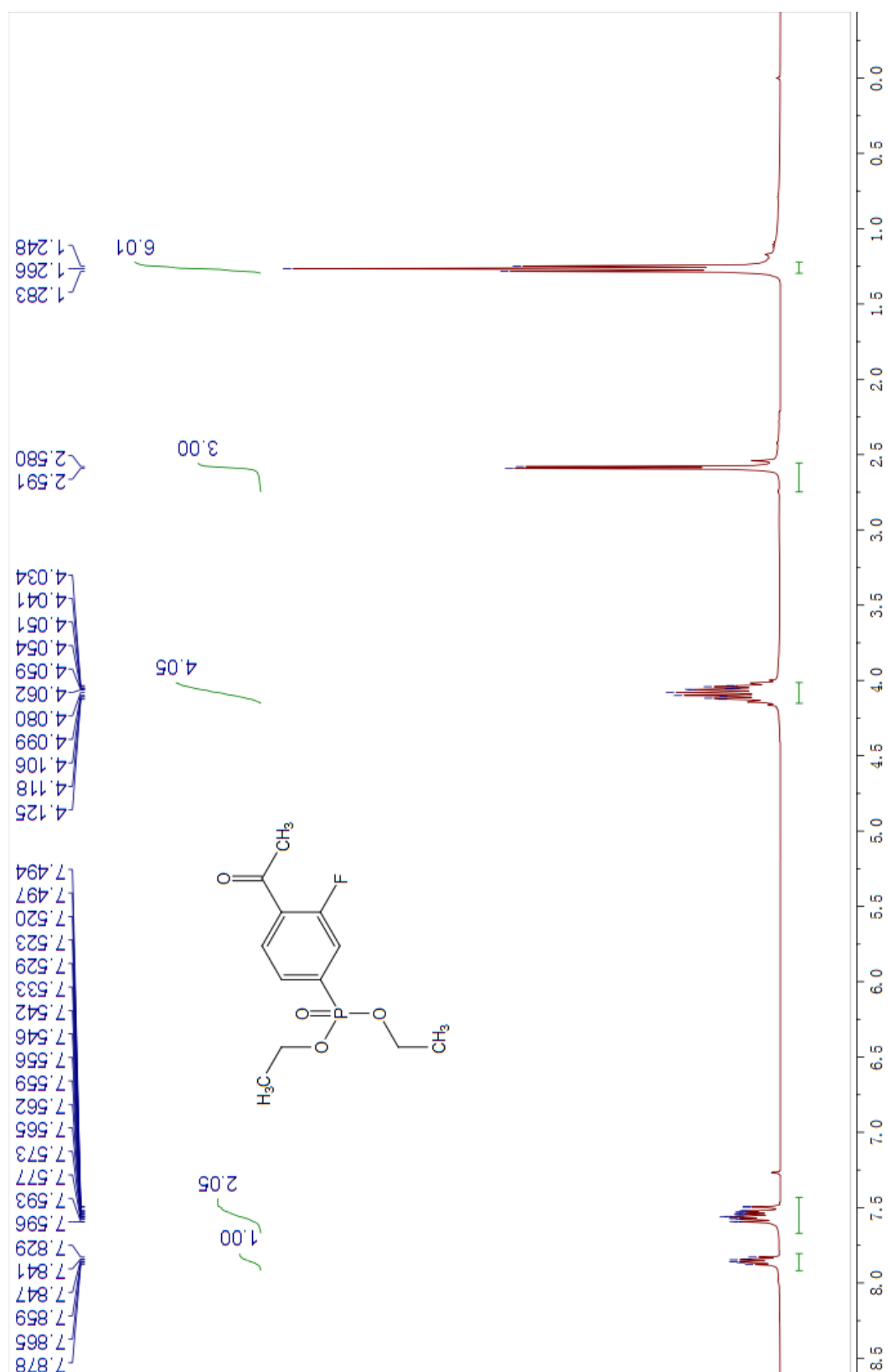
Minimum: -1.5
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
270.1021	270.1021	0.0	0.0	5.0	5547664.0	C13 H19 O4 P

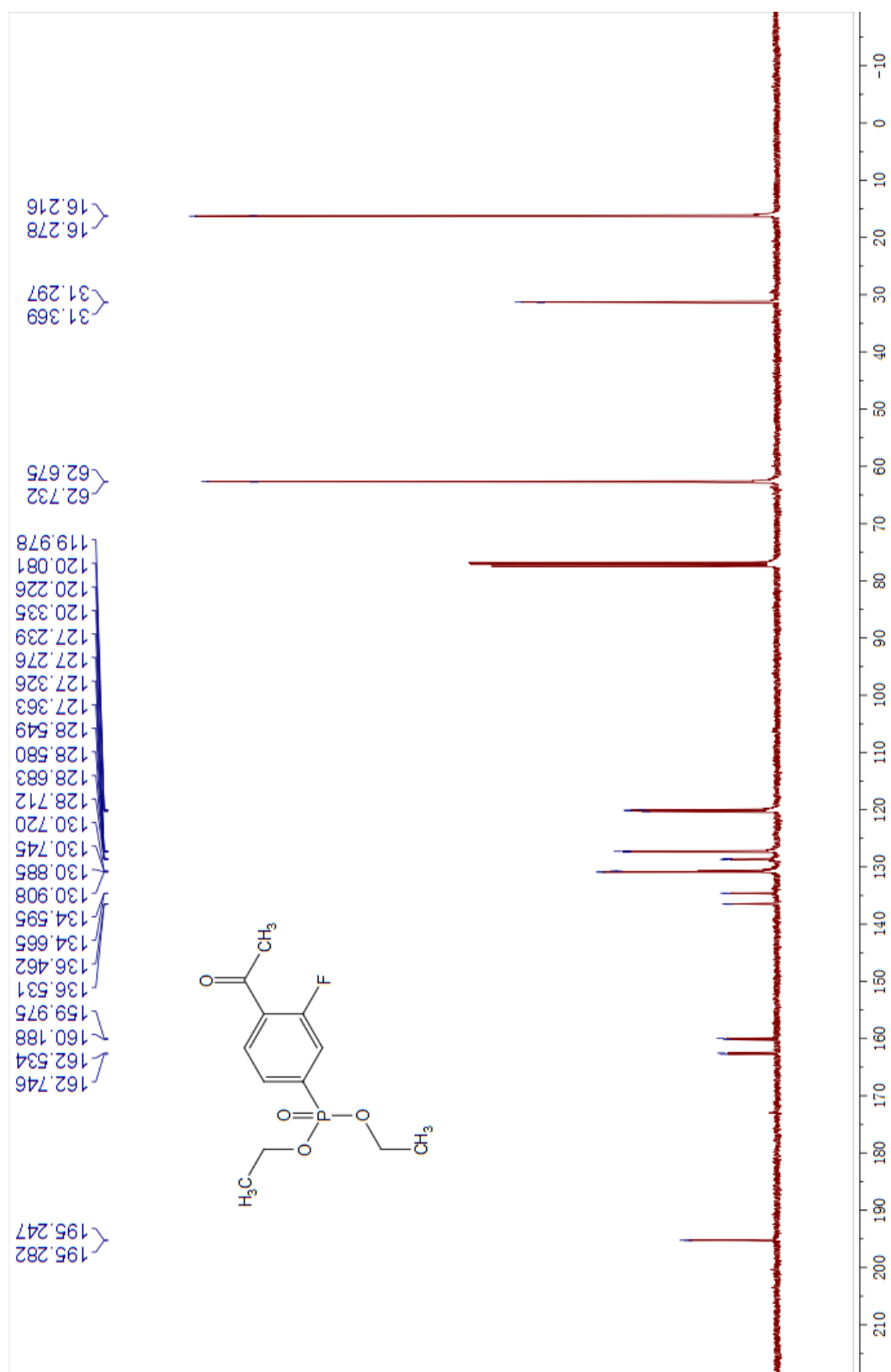
^{13}P NMR Spectrum of diethyl acetyl-3-fluorophenylphosphonate **3ma**



^1H NMR Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate **3ma**



¹³C NMR Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate **3ma**

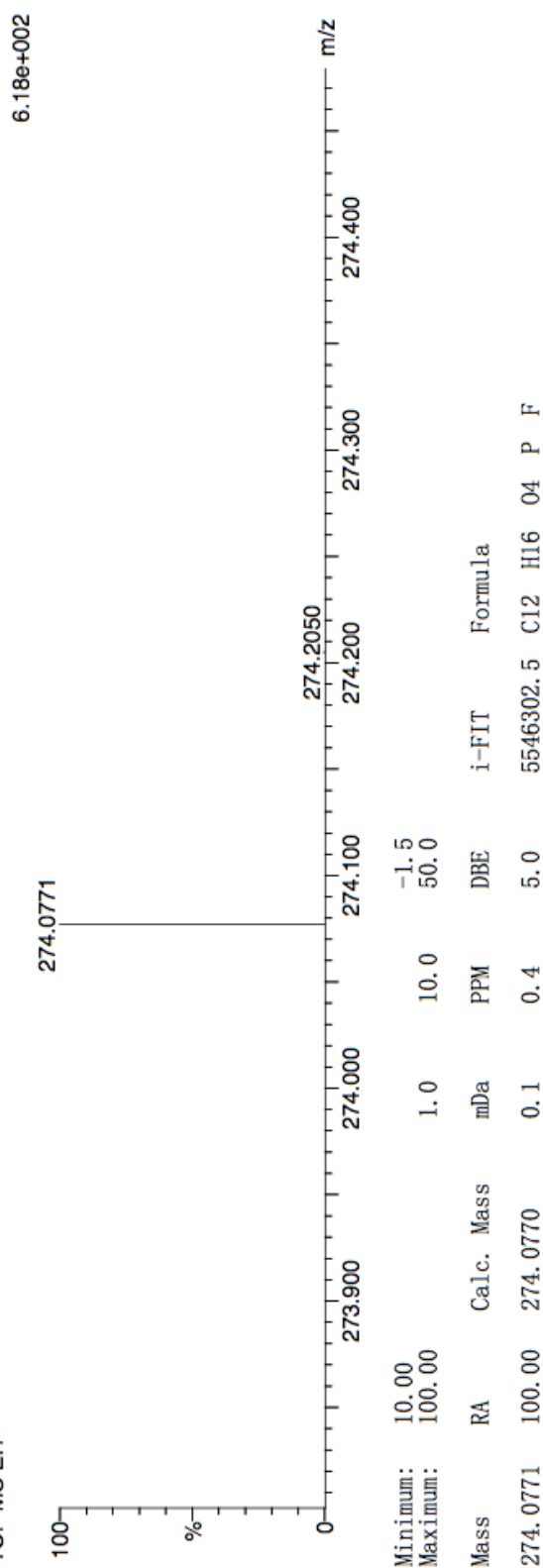


HR-MS Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate **3ma**

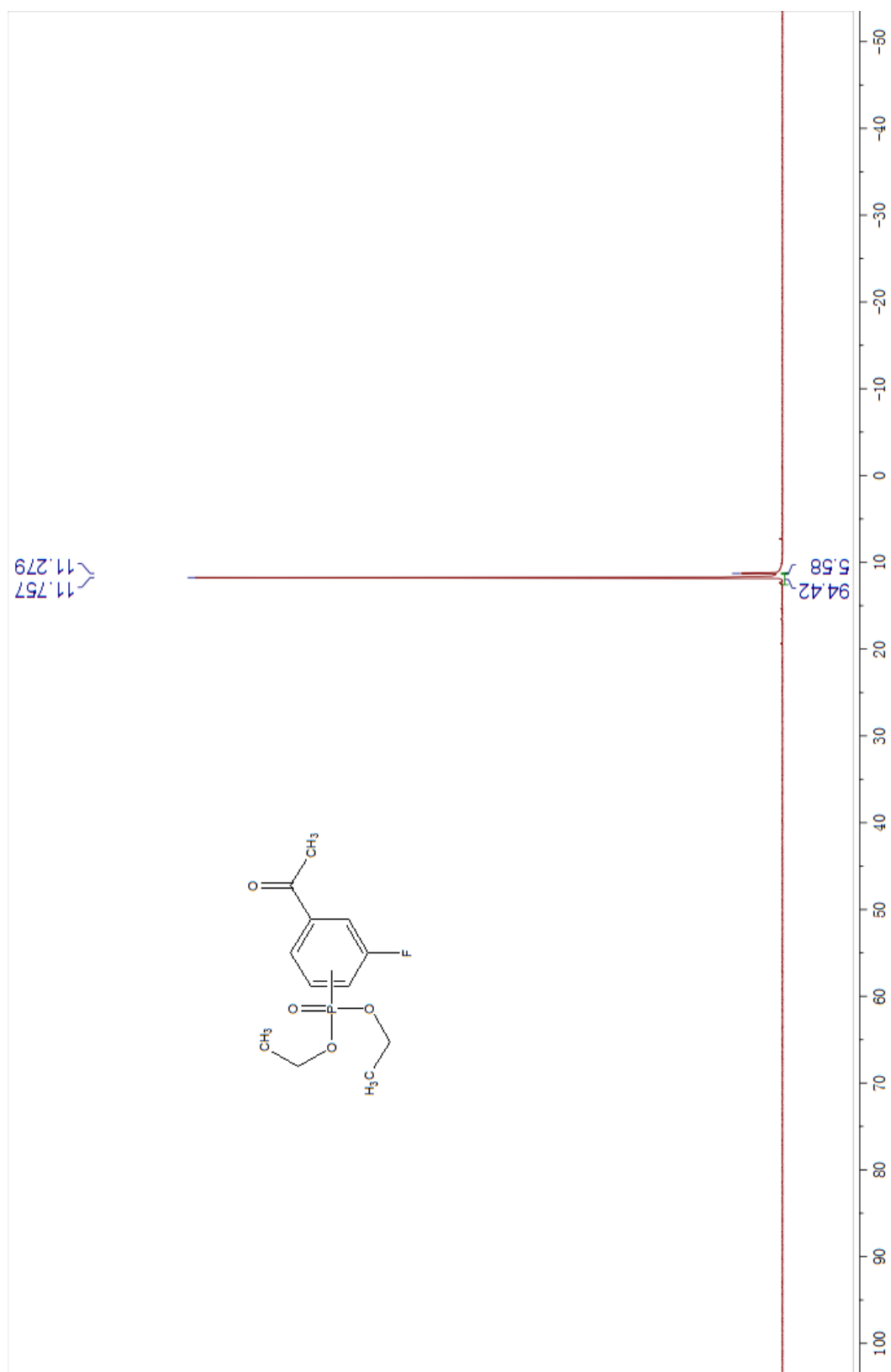
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 0-50 H: 0-200 O: 0-6 P: 0-1 F: 1-1

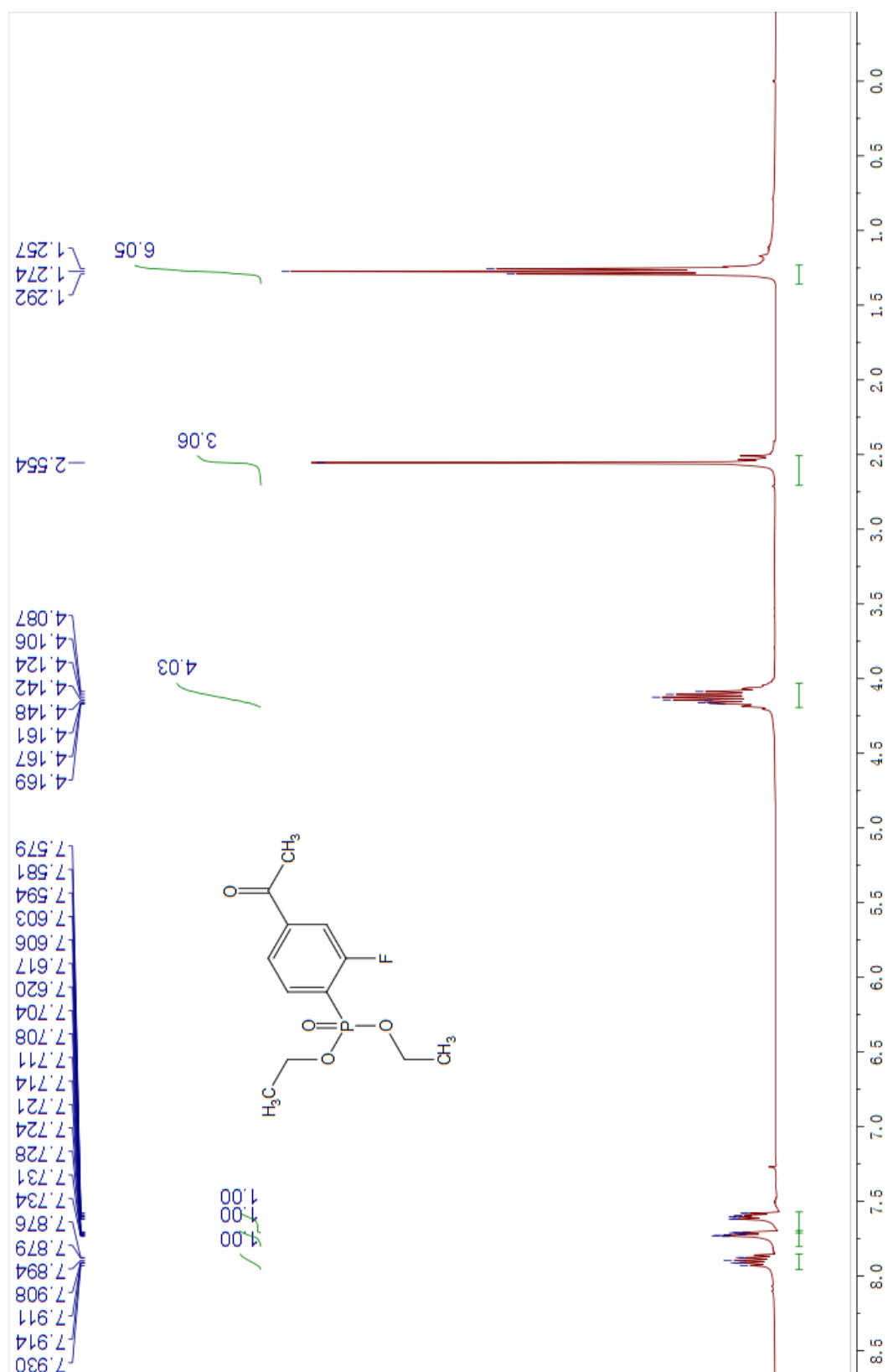
hxf-5 602 (3.212)
 TOF MS EI+



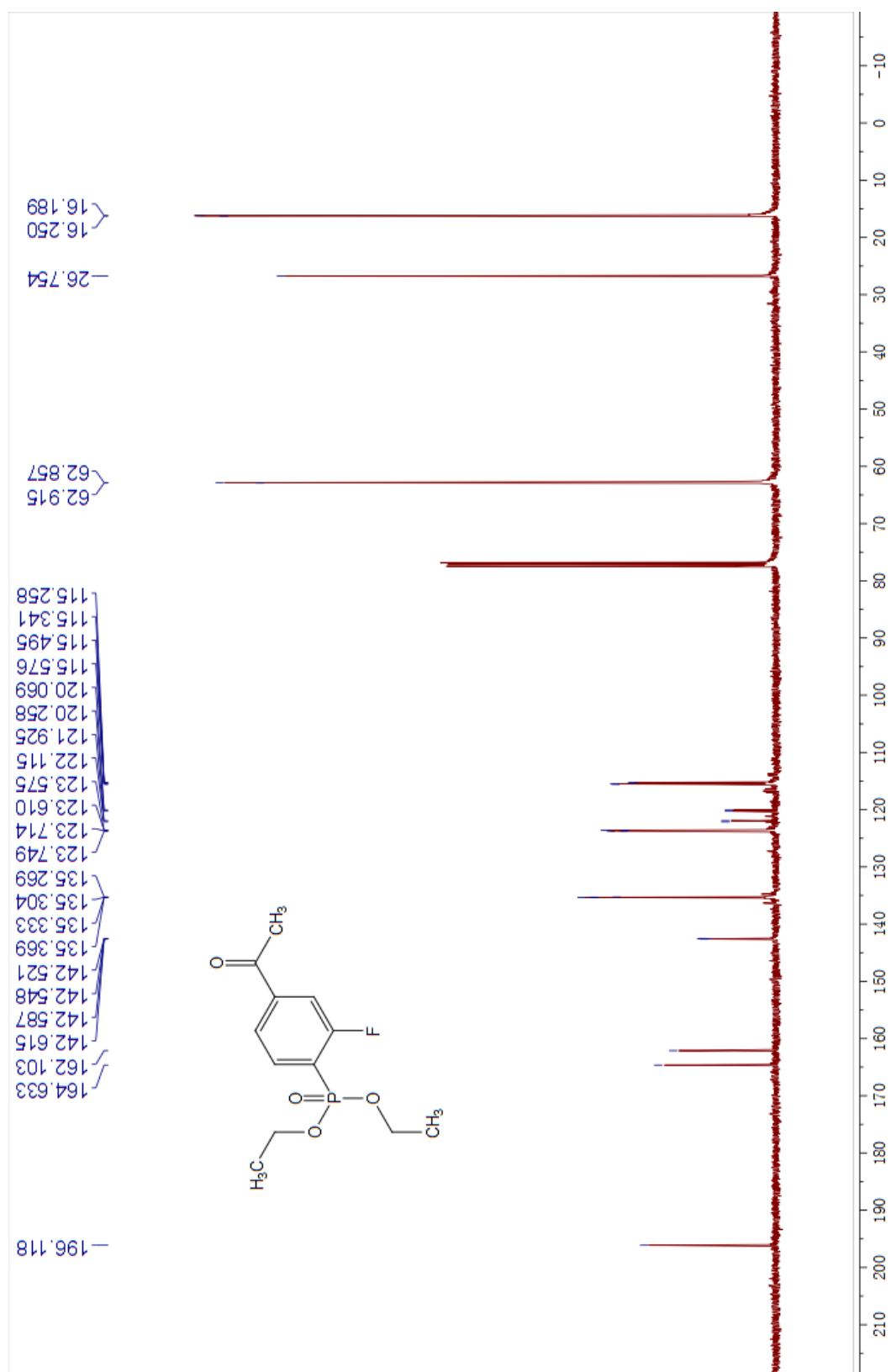
^{13}P NMR Spectrum of diethyl acetyl-2-fluorophenylphosphonate **3na**



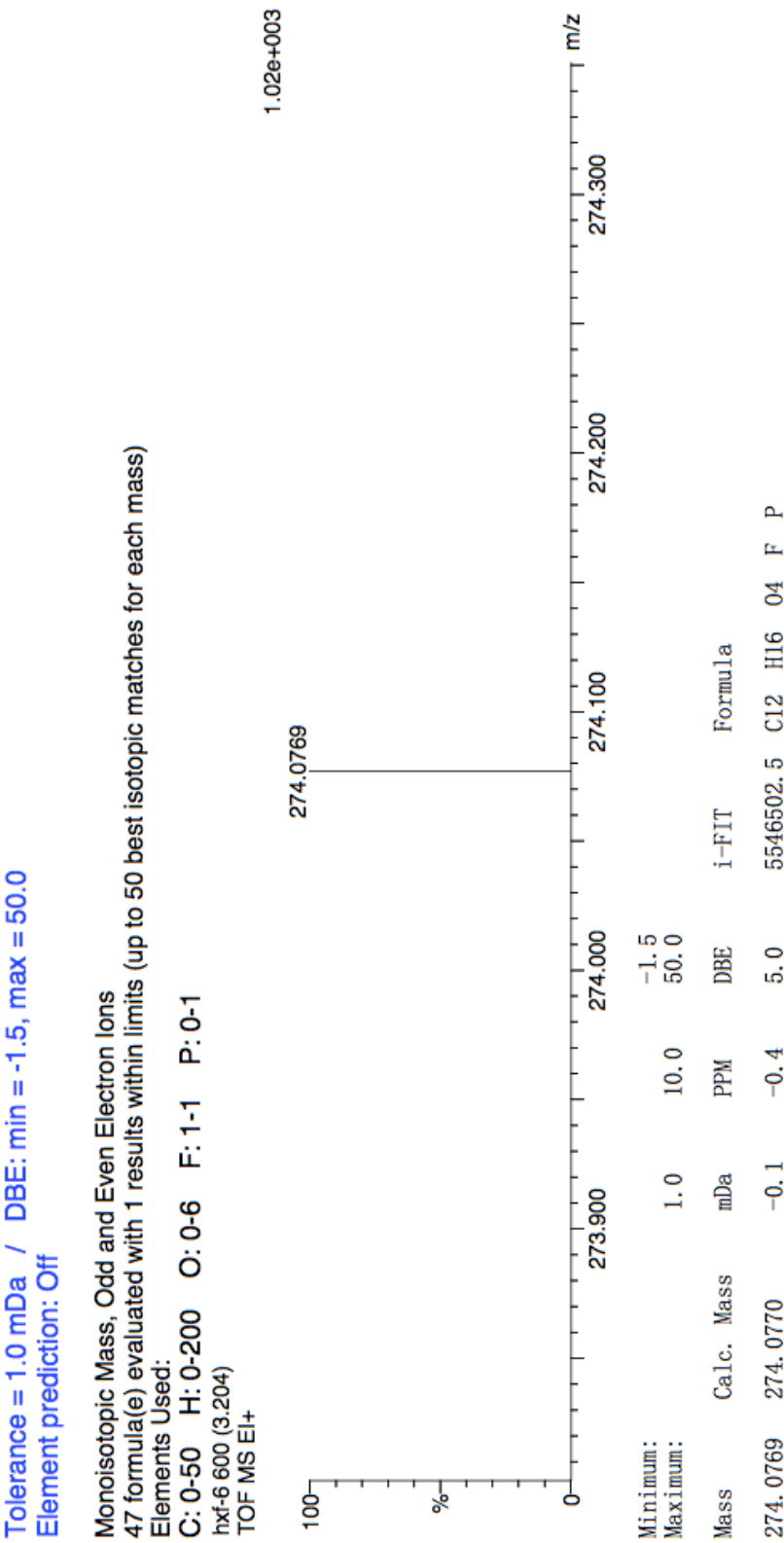
^1H NMR Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate **3na**



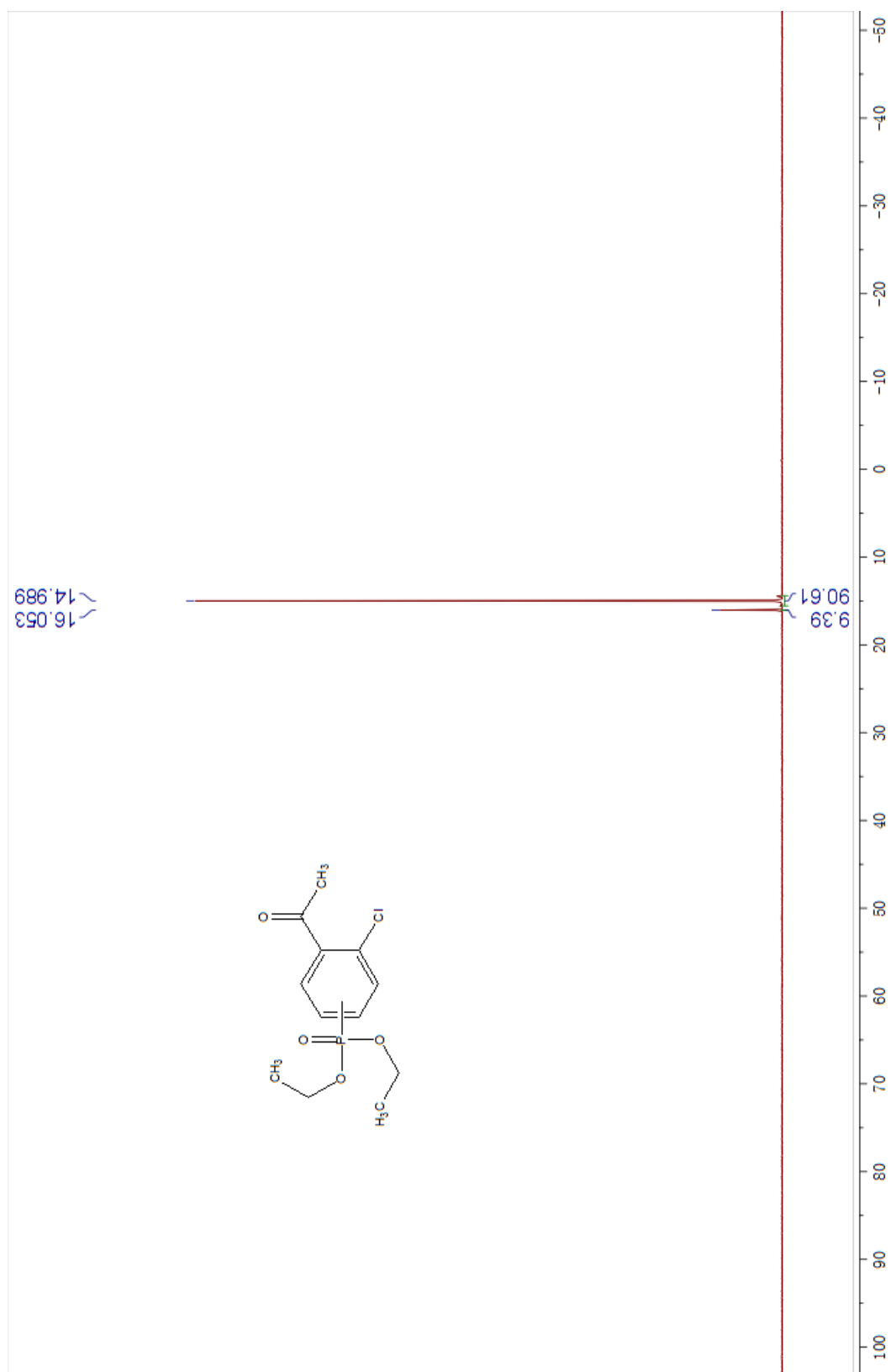
¹³C NMR Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate **3na**



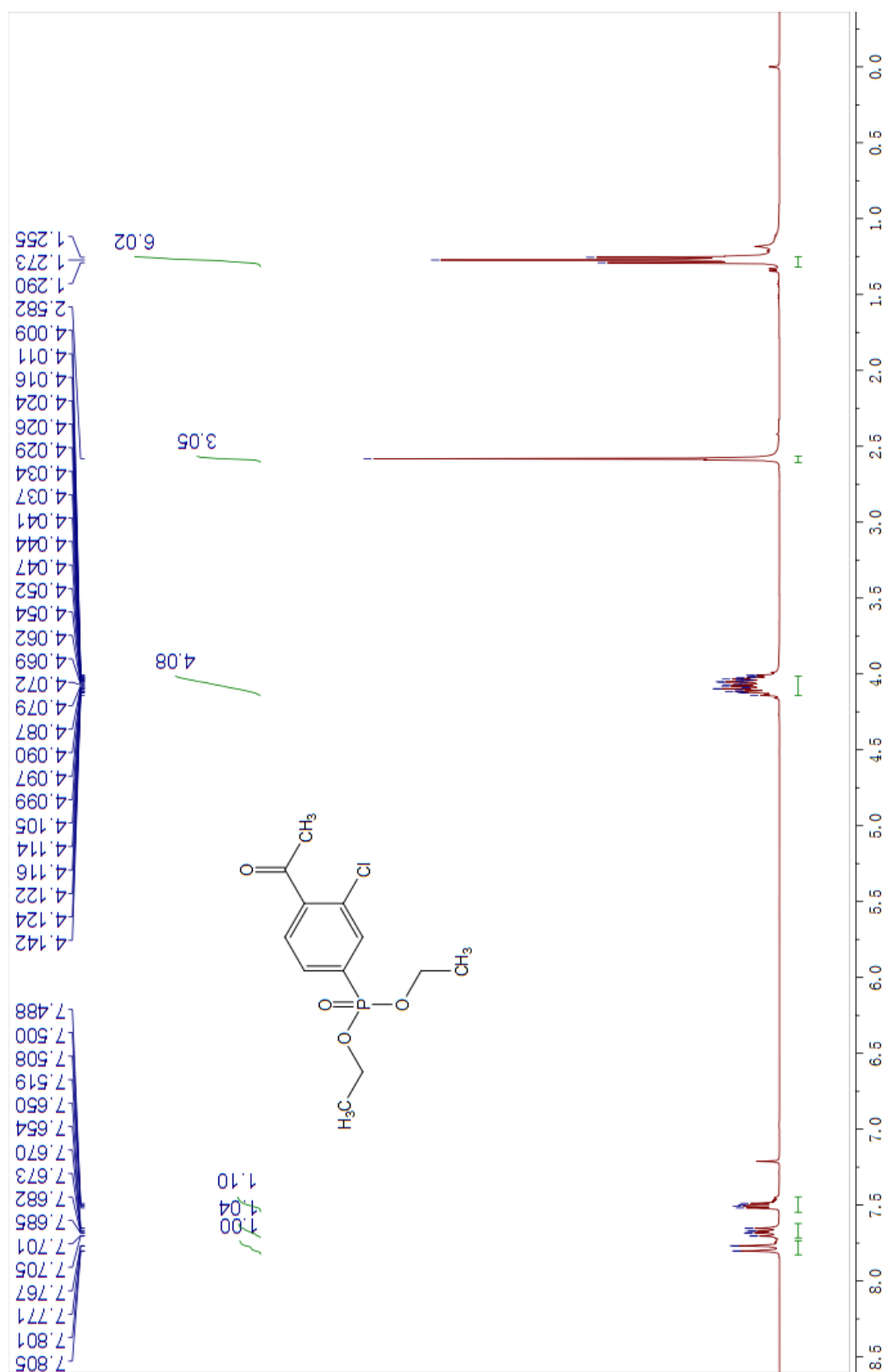
HR-MS Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate **3na**



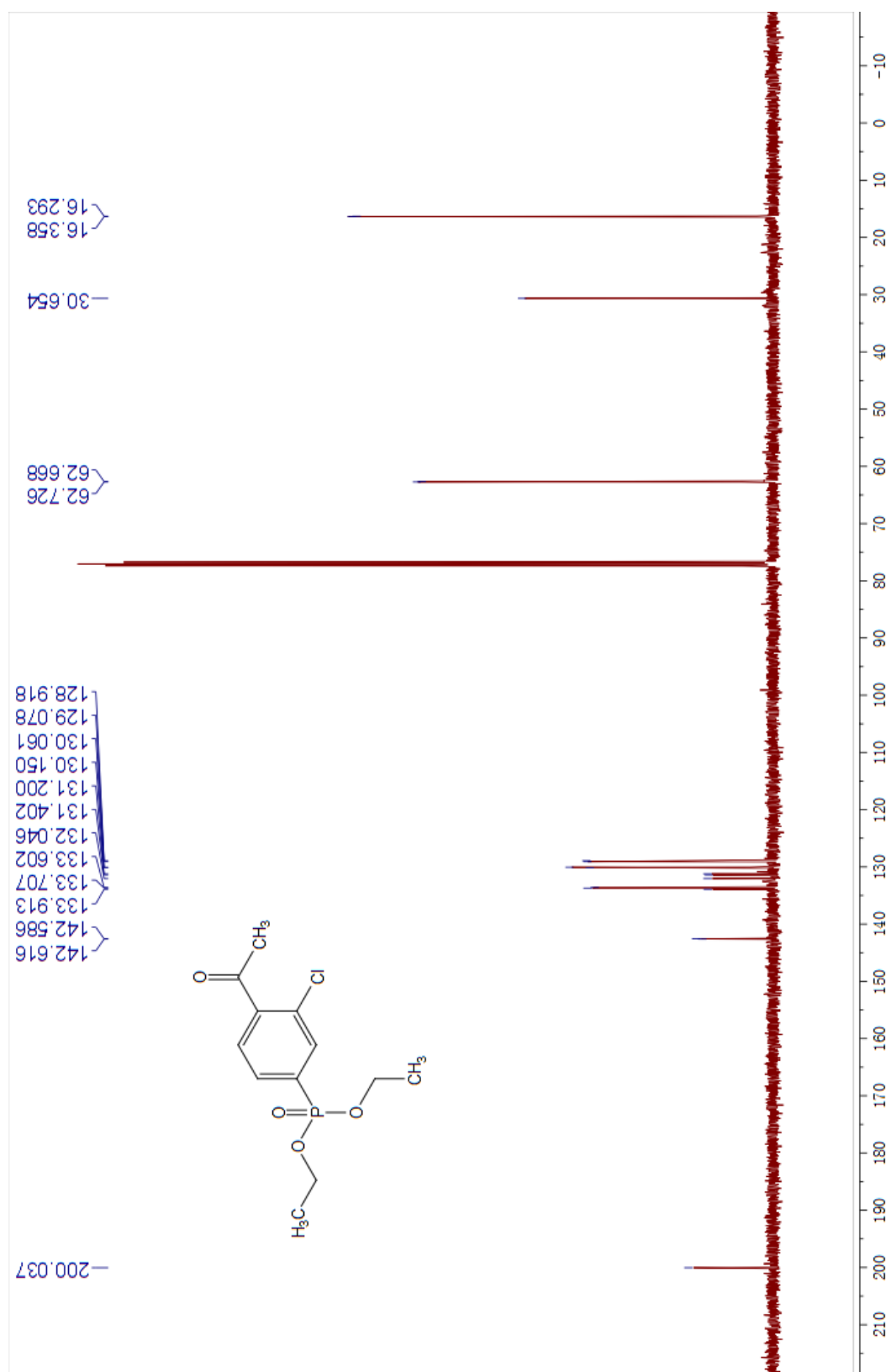
^{13}P NMR Spectrum of diethyl acetyl-3-chlorophenylphosphonate **30a**



^1H NMR Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **30a**



¹³C NMR Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **30a**



HR-MS Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **30a**

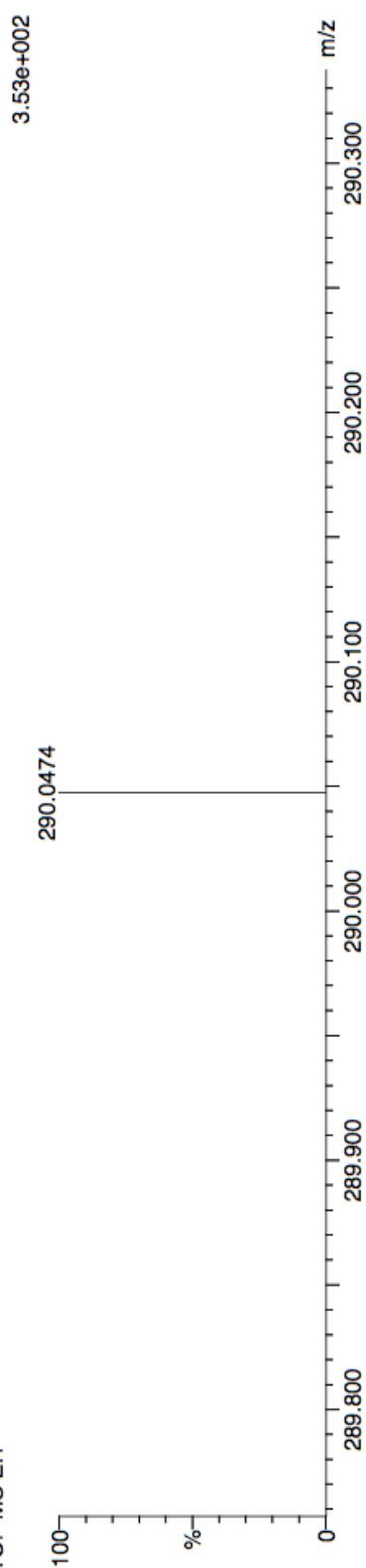
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
 47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:

C: 0-50 H: 0-200 O: 0-6 P: 0-1 Cl: 1-1

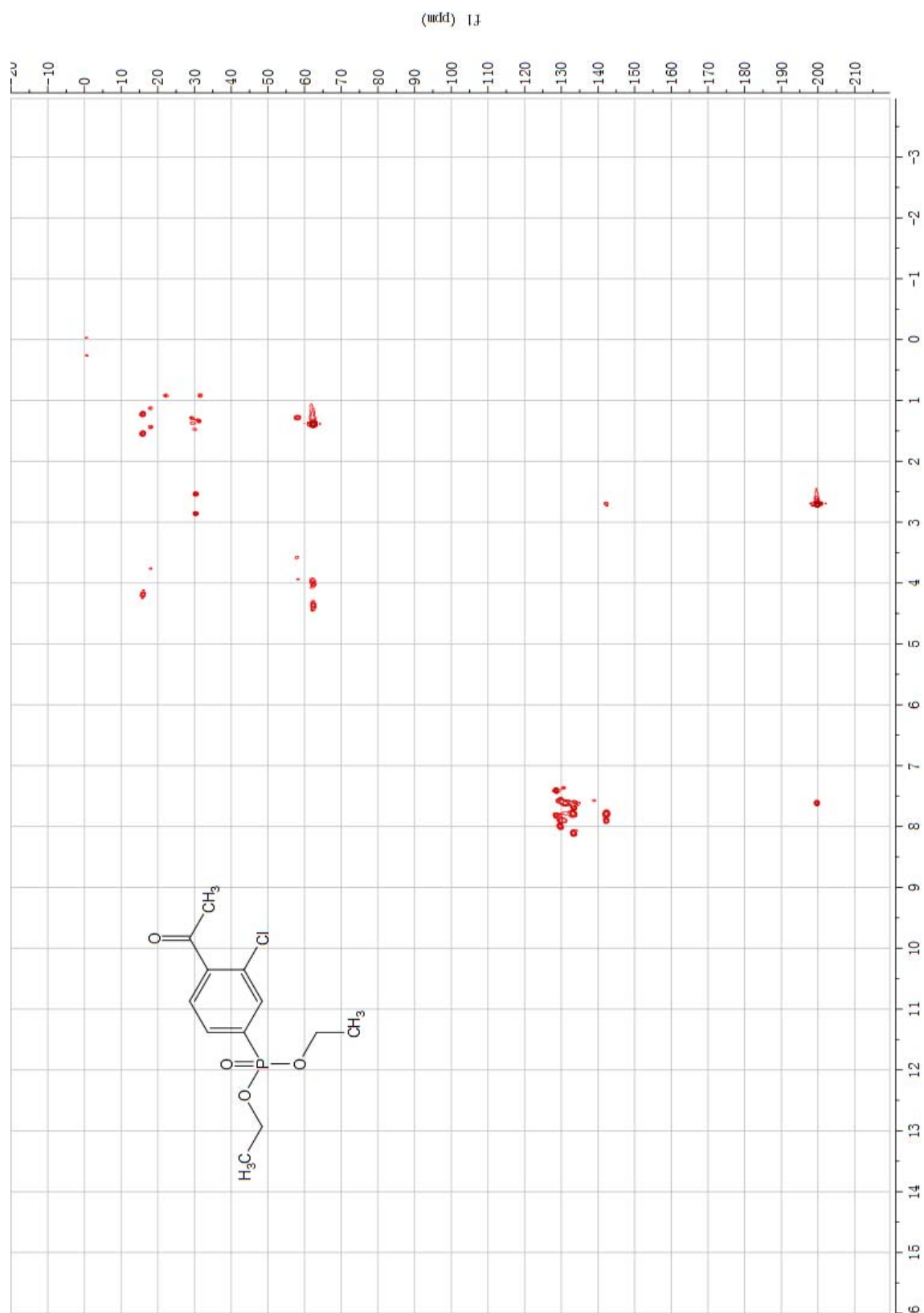
hxf-7 569 (3.091)

TOF MS EI+

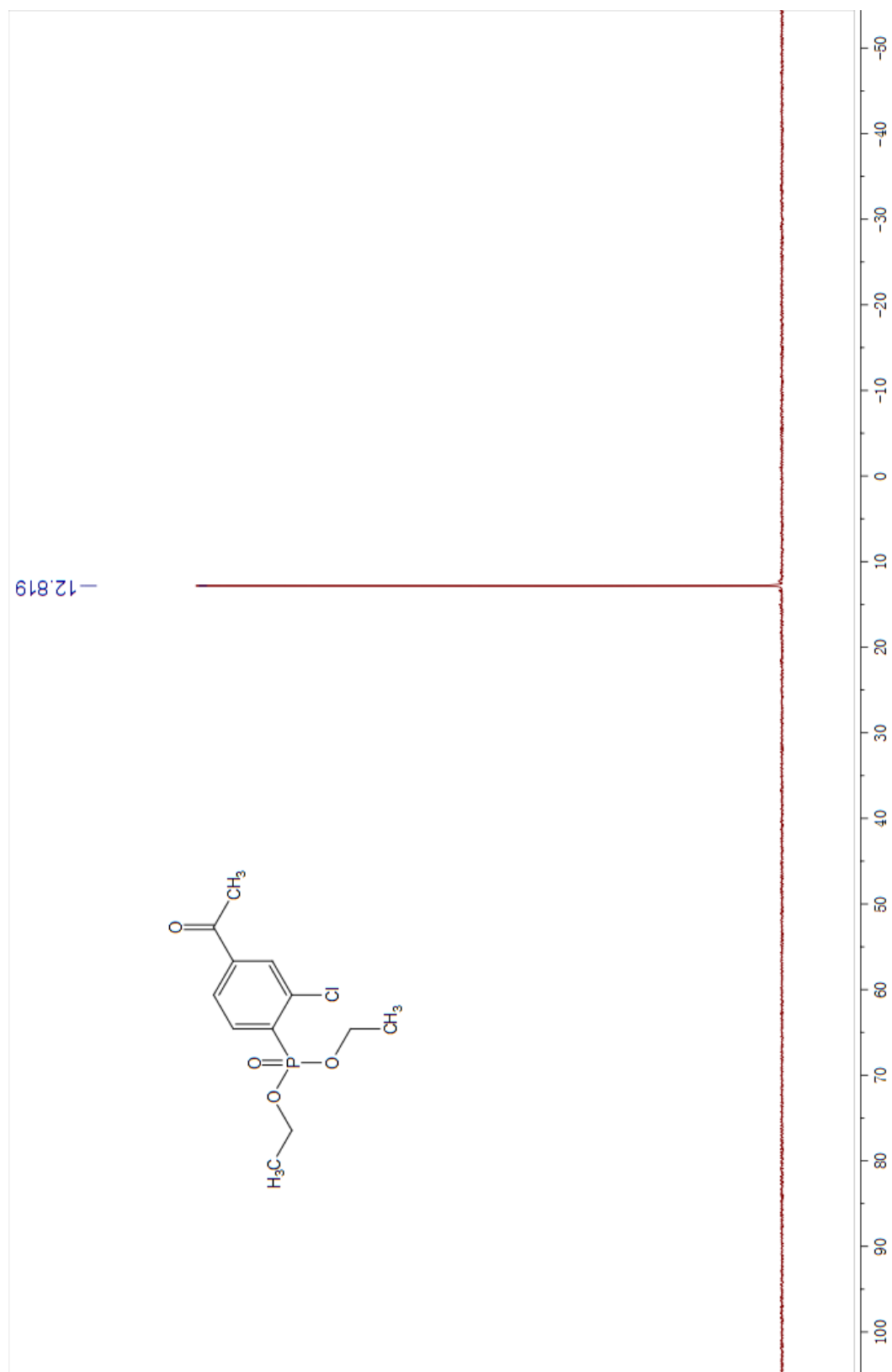


Minimum:				-1.5	
Maximum:				50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
290.0474	290.0475	-0.1	-0.3	5.0	5546194.5 C12 H16 O4 P Cl

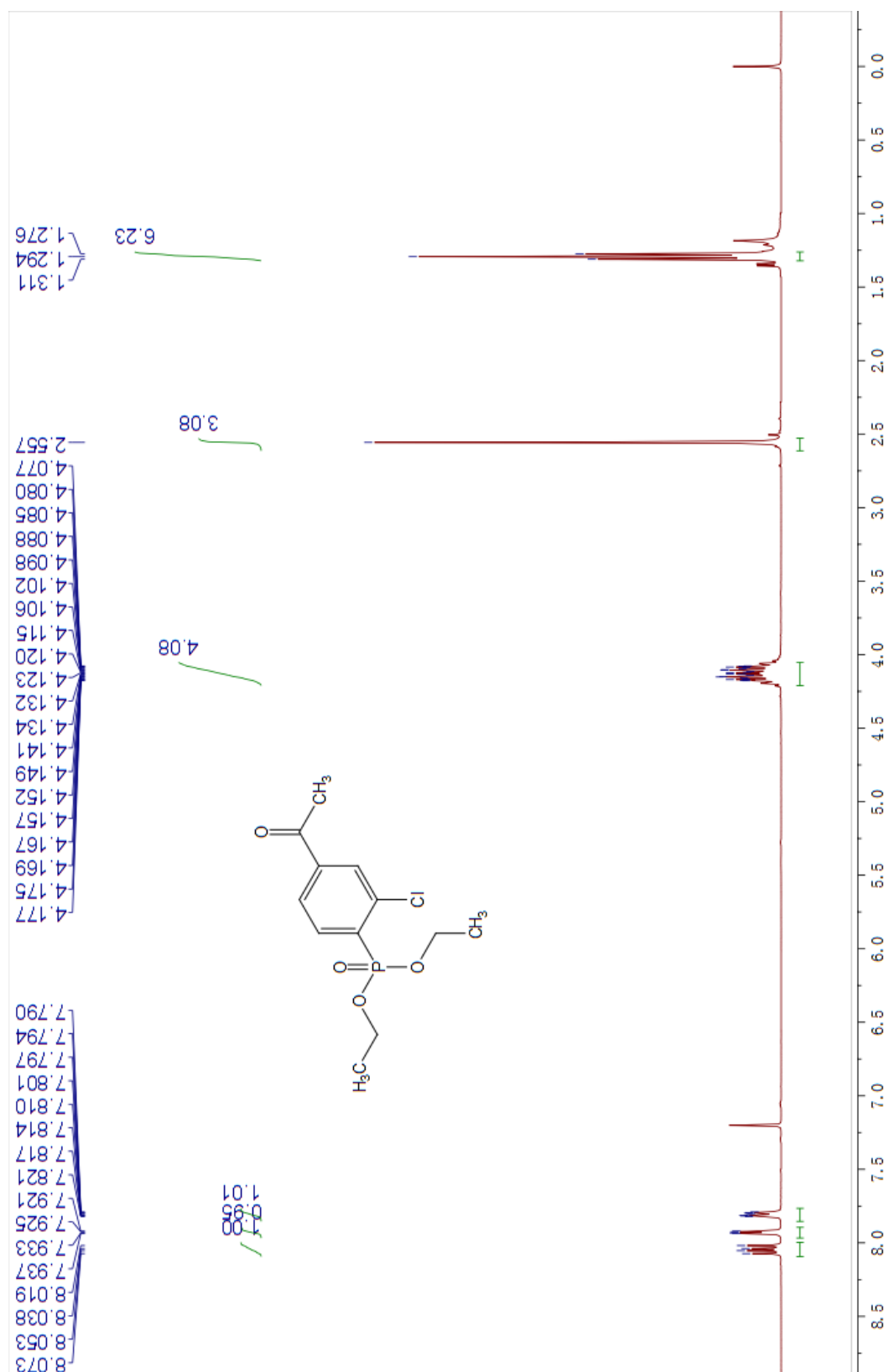
HMBC Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **30a**



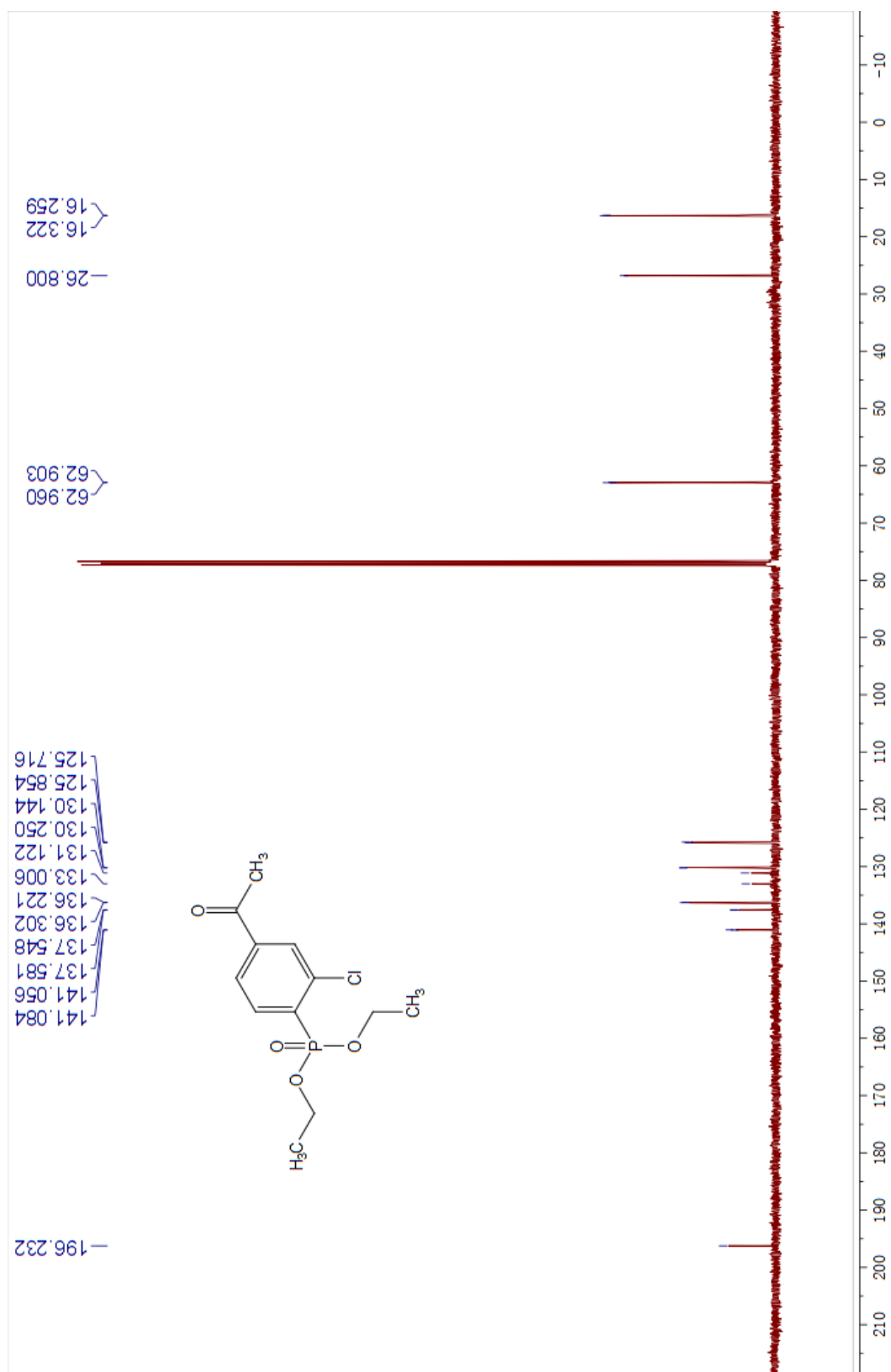
^{13}P NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



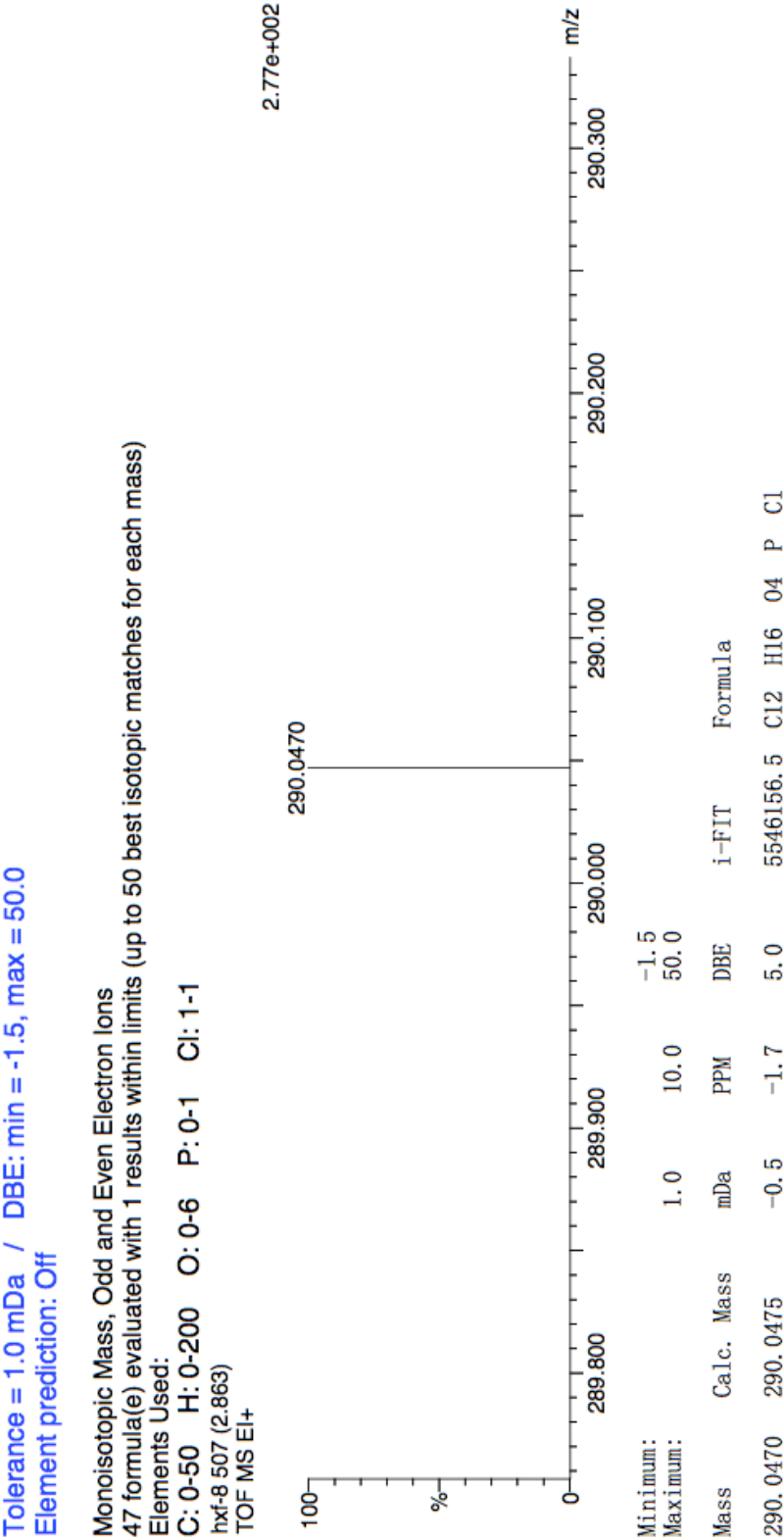
^1H NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



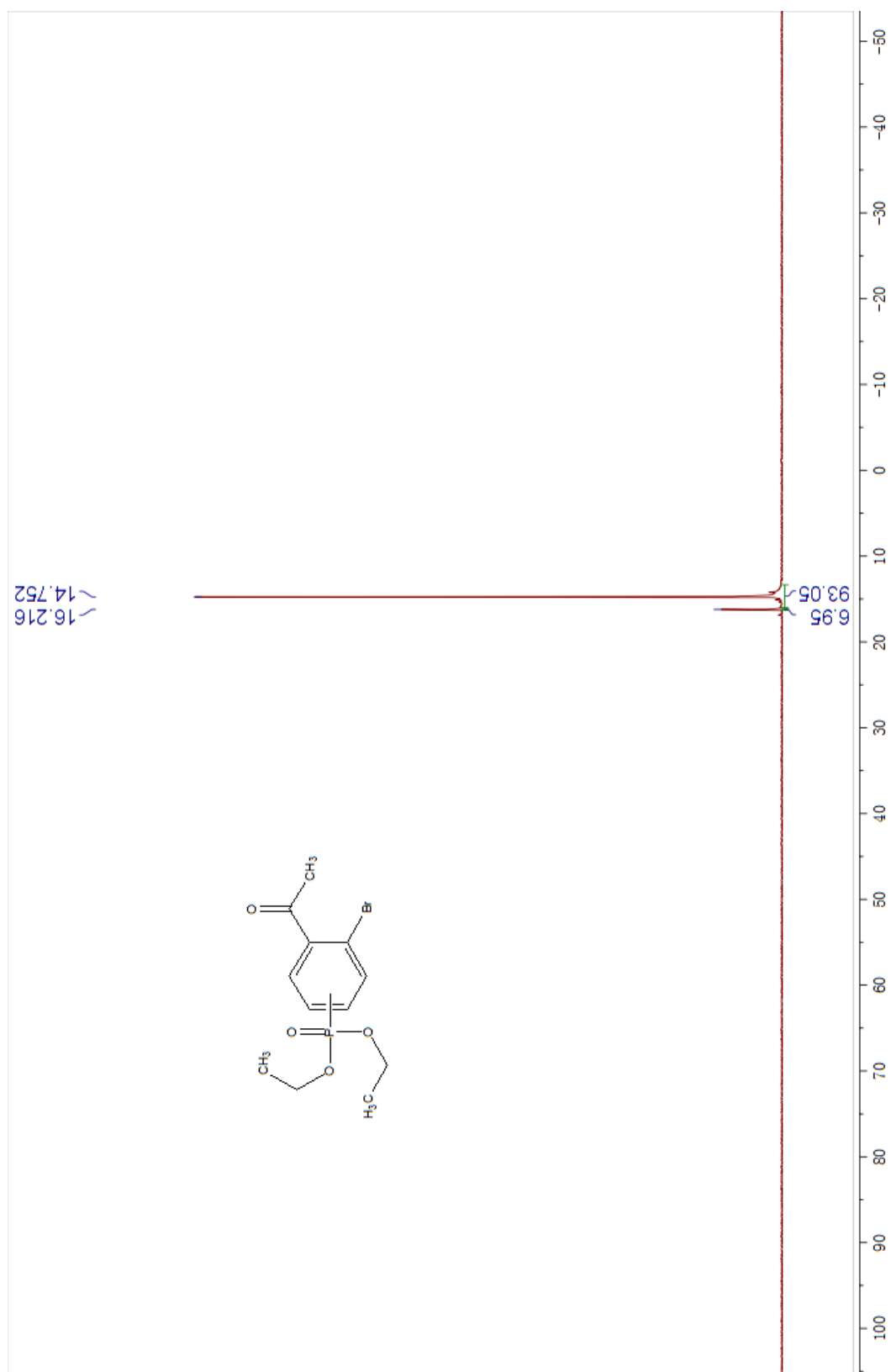
¹³C NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



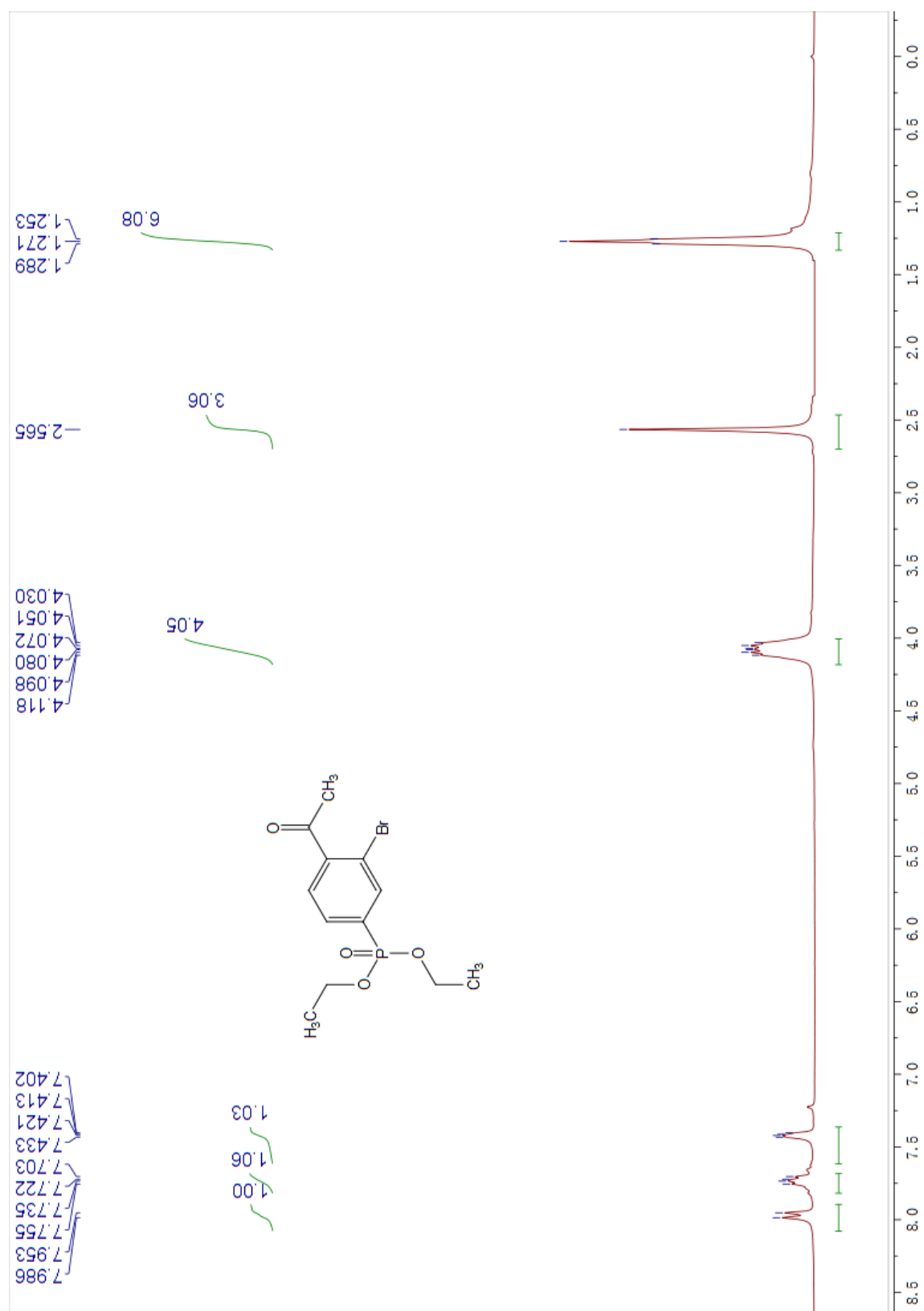
HR-MS Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



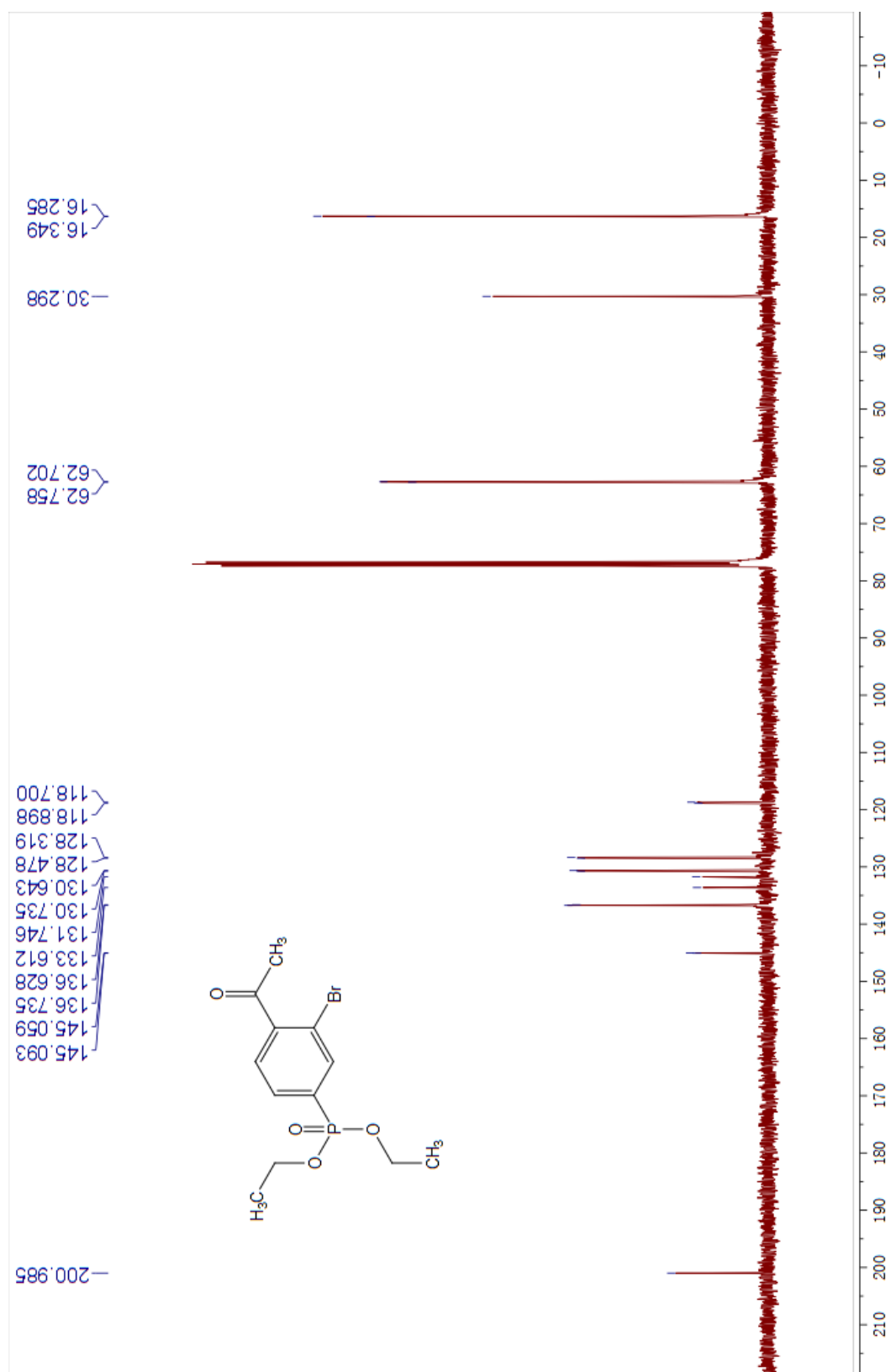
^{13}P NMR Spectrum of diethyl acetyl-3-bromophenylphosphonate **3qa**



^1H NMR Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate **3qa**



¹³C NMR Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate **3qa**

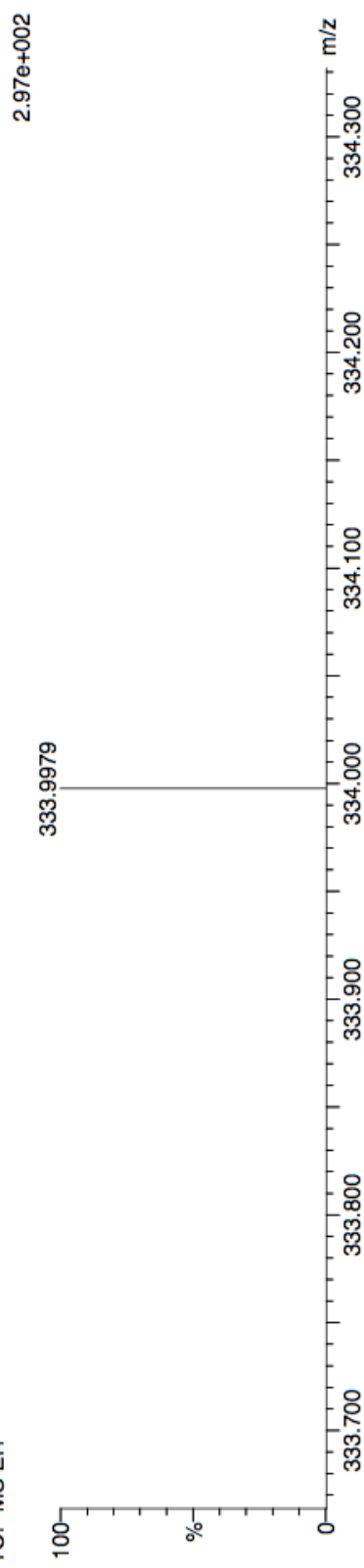


HR-MS Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate **3qa**

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

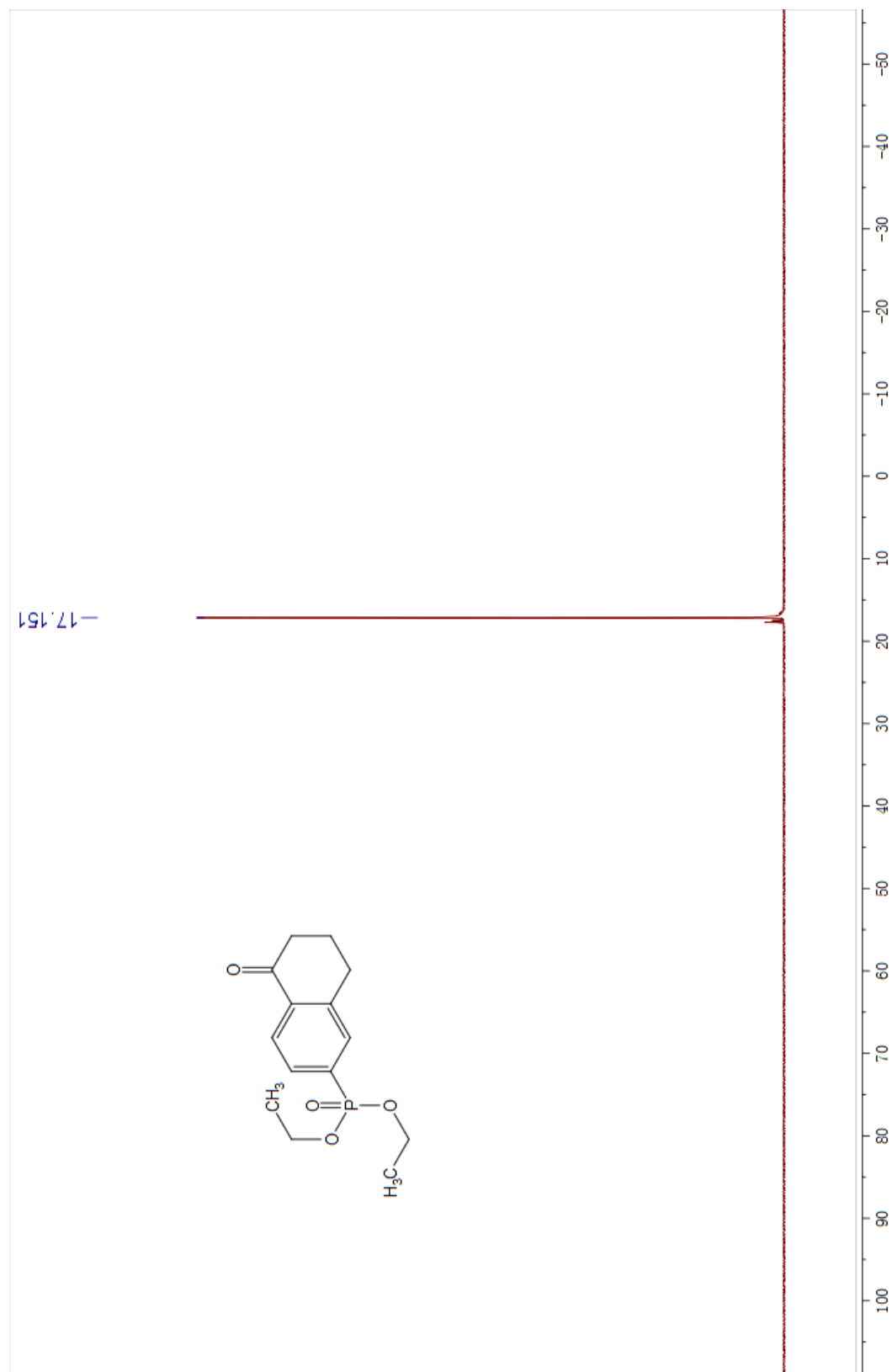
Monoisotopic Mass, Odd and Even Electron Ions
 77 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 0-50 H: 0-200 O: 0-6 P: 0-1 Br: 1-2

hxf-9 651 (3.391)
 TOF MS EI+

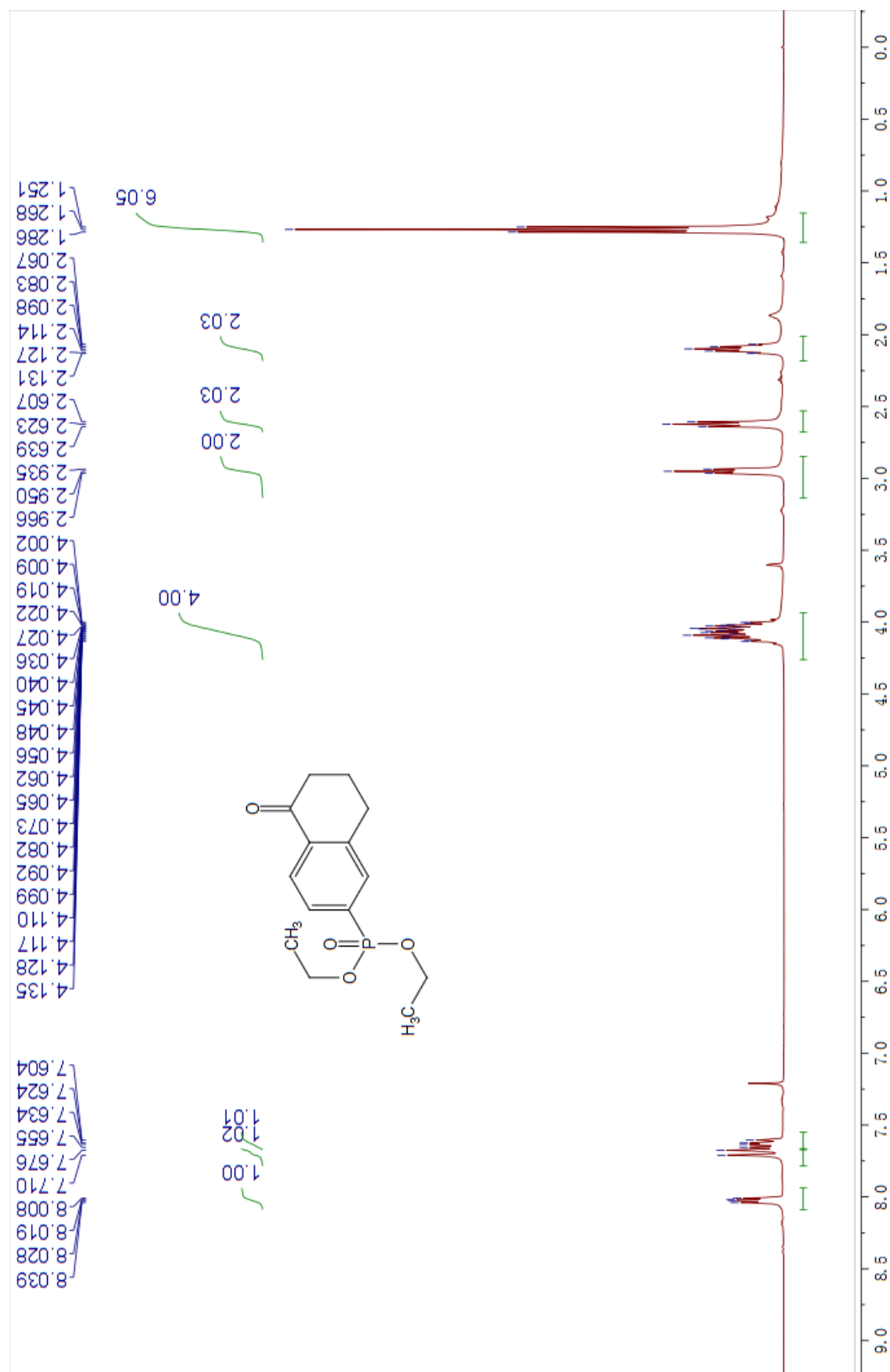


Minimum:					
Maximum:					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT Formula
333.9979	333.9970	0.9	2.7	5.0	5546172.0 C12 H16 O4 P Br

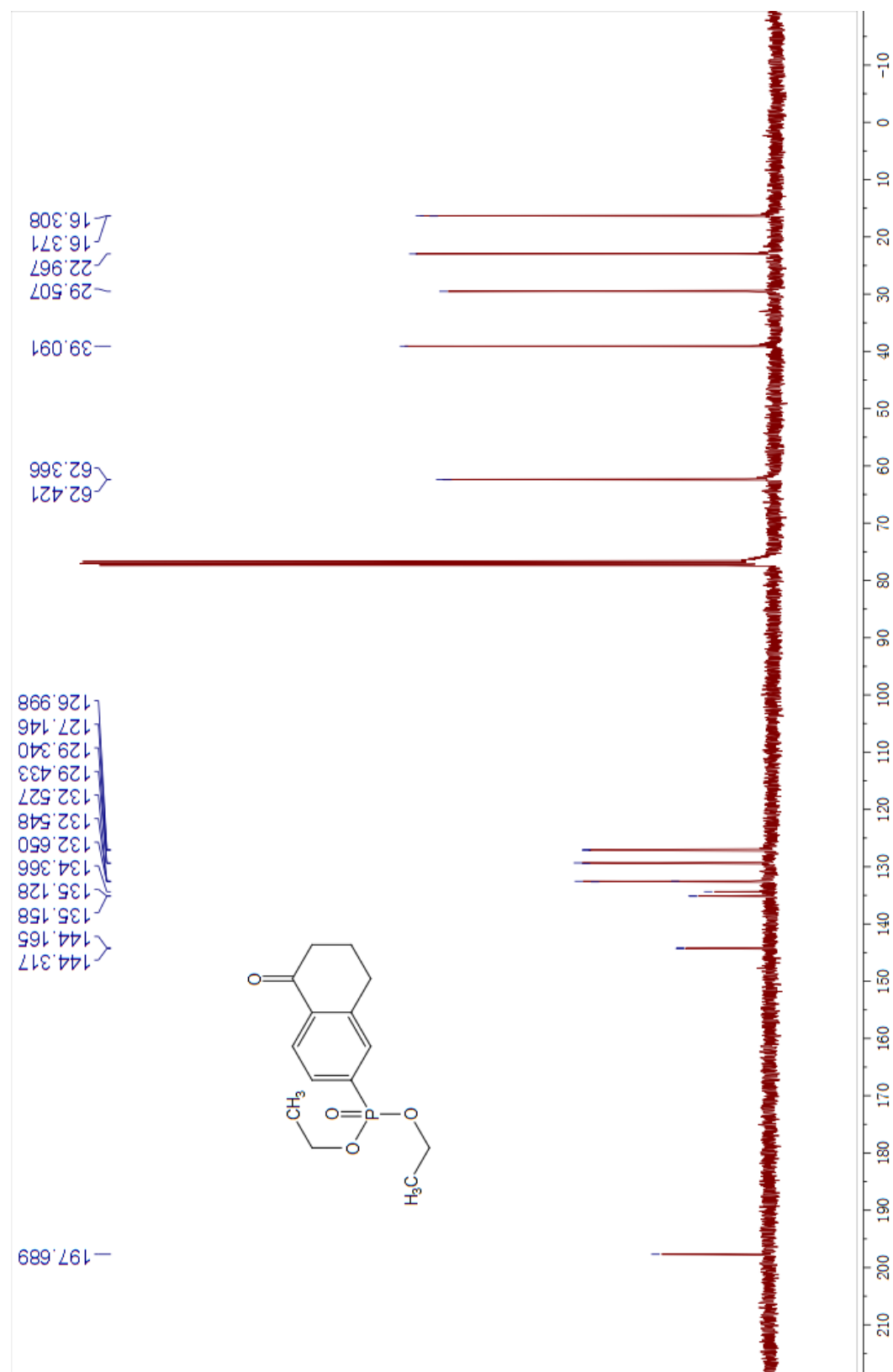
^{13}P NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate
3sa



^1H NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**



¹³C NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate
3sa



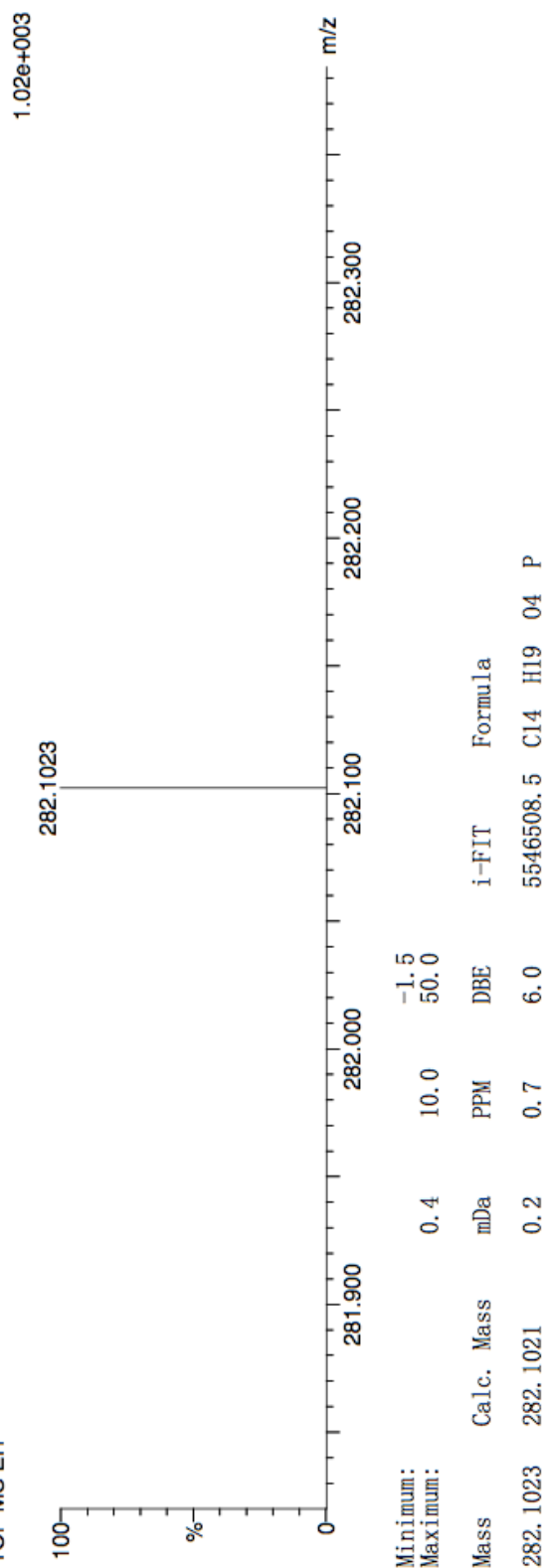
HR-MS Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**

Tolerance = 0.4 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

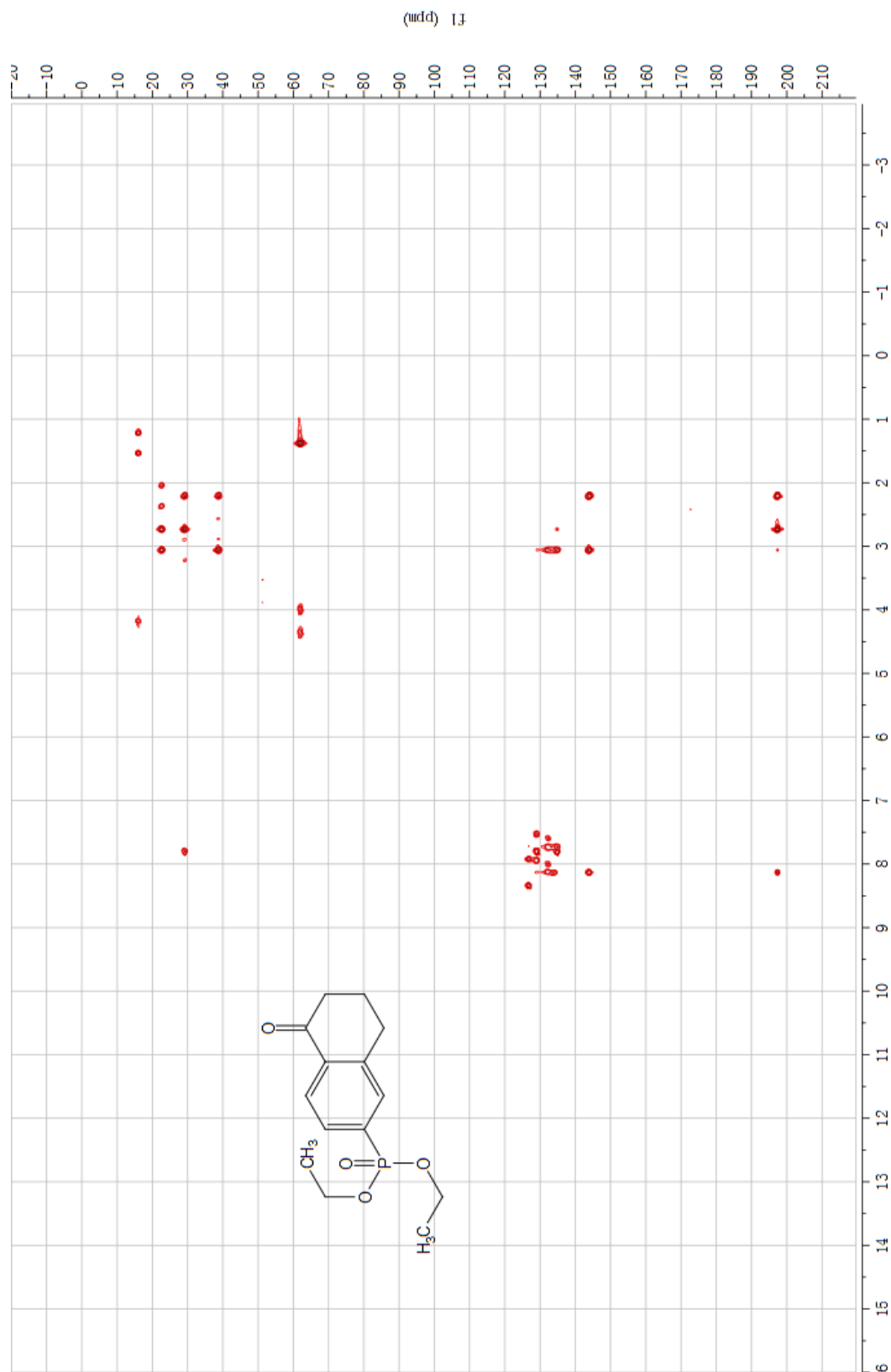
Monoisotopic Mass, Odd and Even Electron Ions
 46 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:

C: 0-50 H: 0-200 O: 0-5 P: 0-1

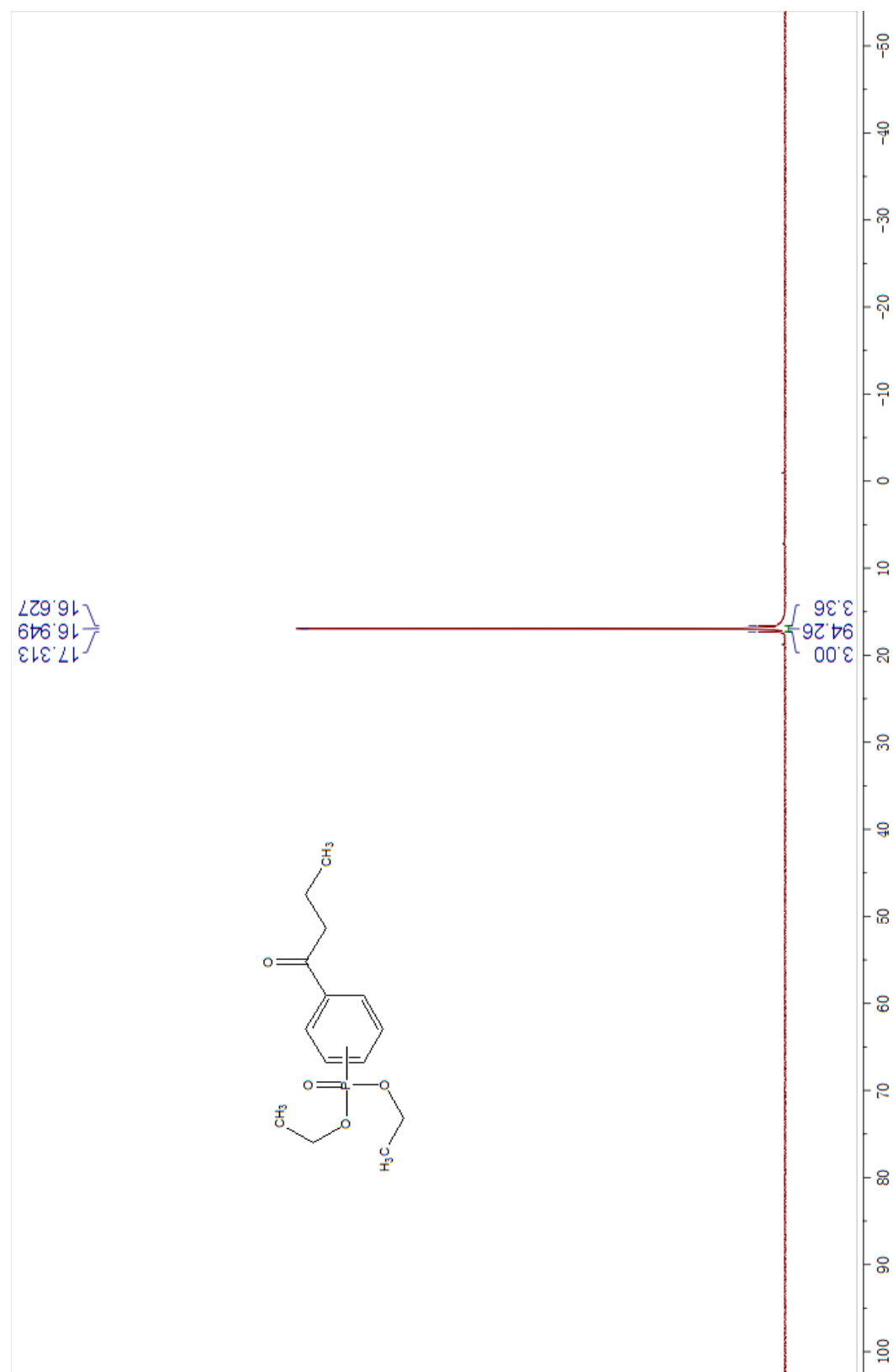
hxf141113-1 771 (3.850)
 TOF MS EI+



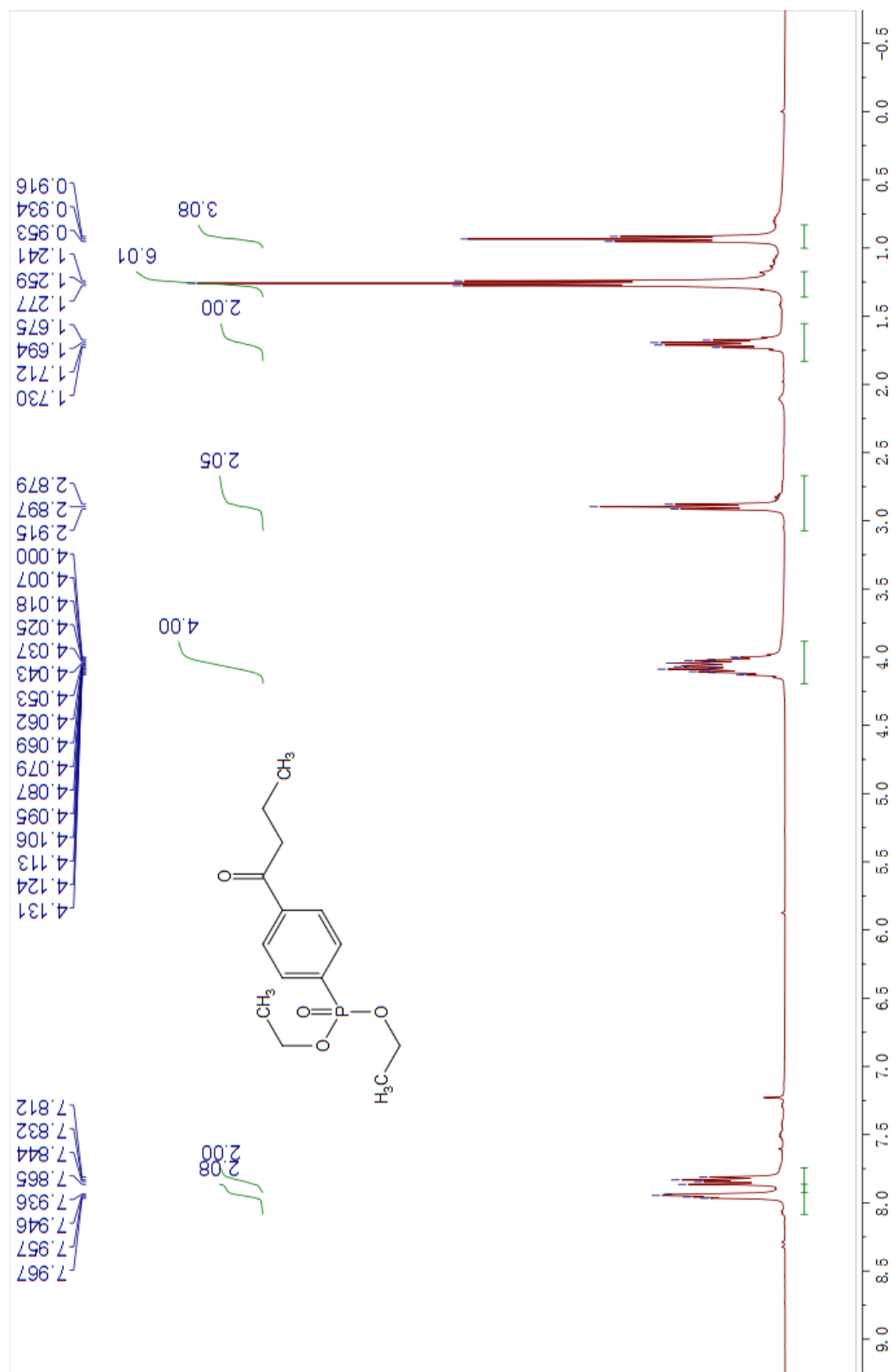
HMBC Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**



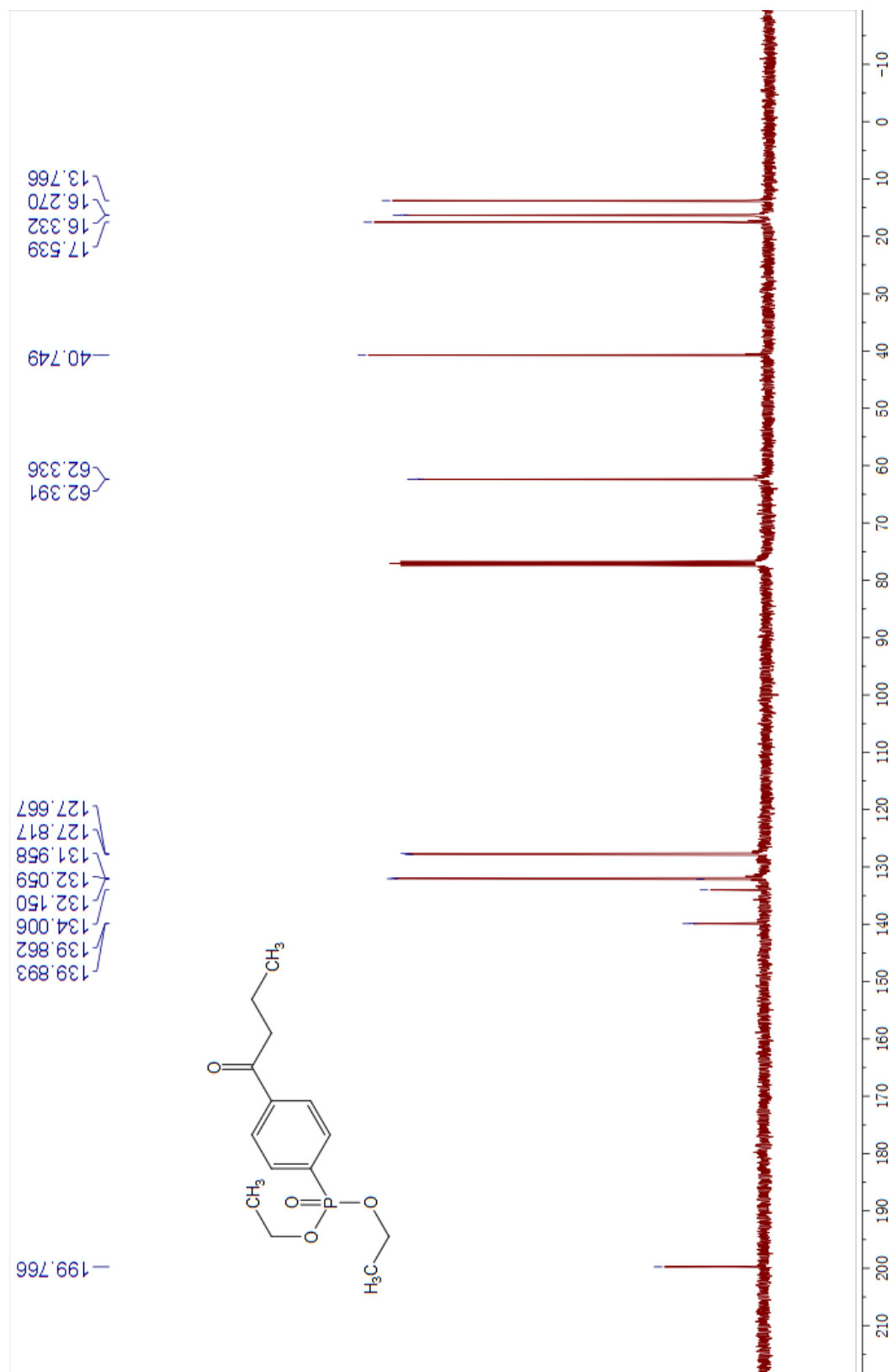
^{13}P NMR Spectrum of diethyl butanoylphenylphosphonate **3ua**



^1H NMR Spectrum of diethyl 4-butanoylphenylphosphonate **3ua**



¹³C NMR Spectrum of diethyl 4-butanoylphenylphosphonate **3ua**



HR-MS Spectrum of diethyl 4-butanoylphenylphosphonate **3ua**

Tolerance = 0.4 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off

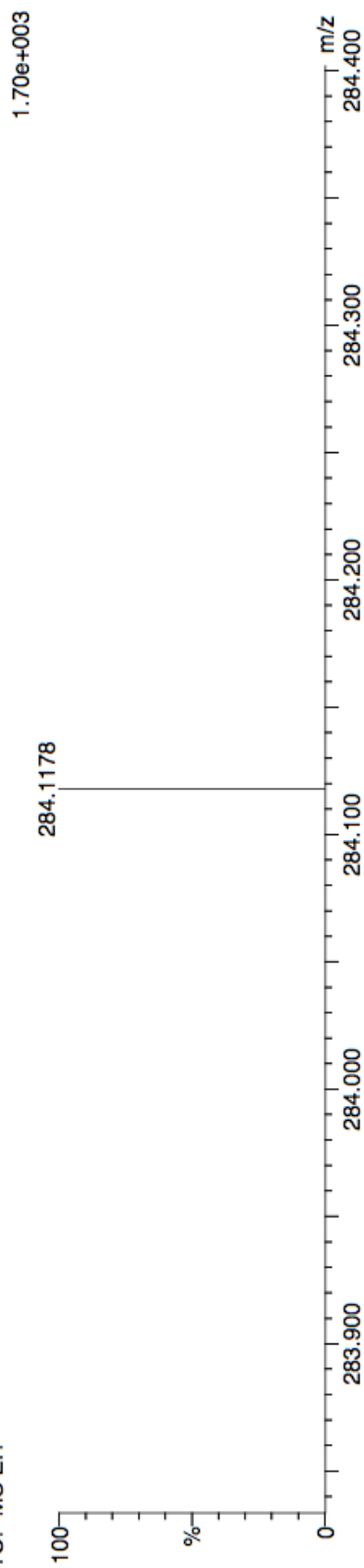
Monoisotopic Mass, Odd and Even Electron Ions
 46 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-50 H: 0-200 O: 0-5 P: 0-1

hxf141113-3 373 (2.390)

TOF MS EI+



Minimum: -1.5
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
284.1178	284.1177	0.1	0.4	5.0	5546849.0	C14 H21 O4 P