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

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Supporting Information

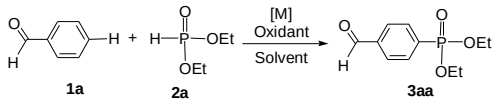
Contents

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, ^{1}H 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]

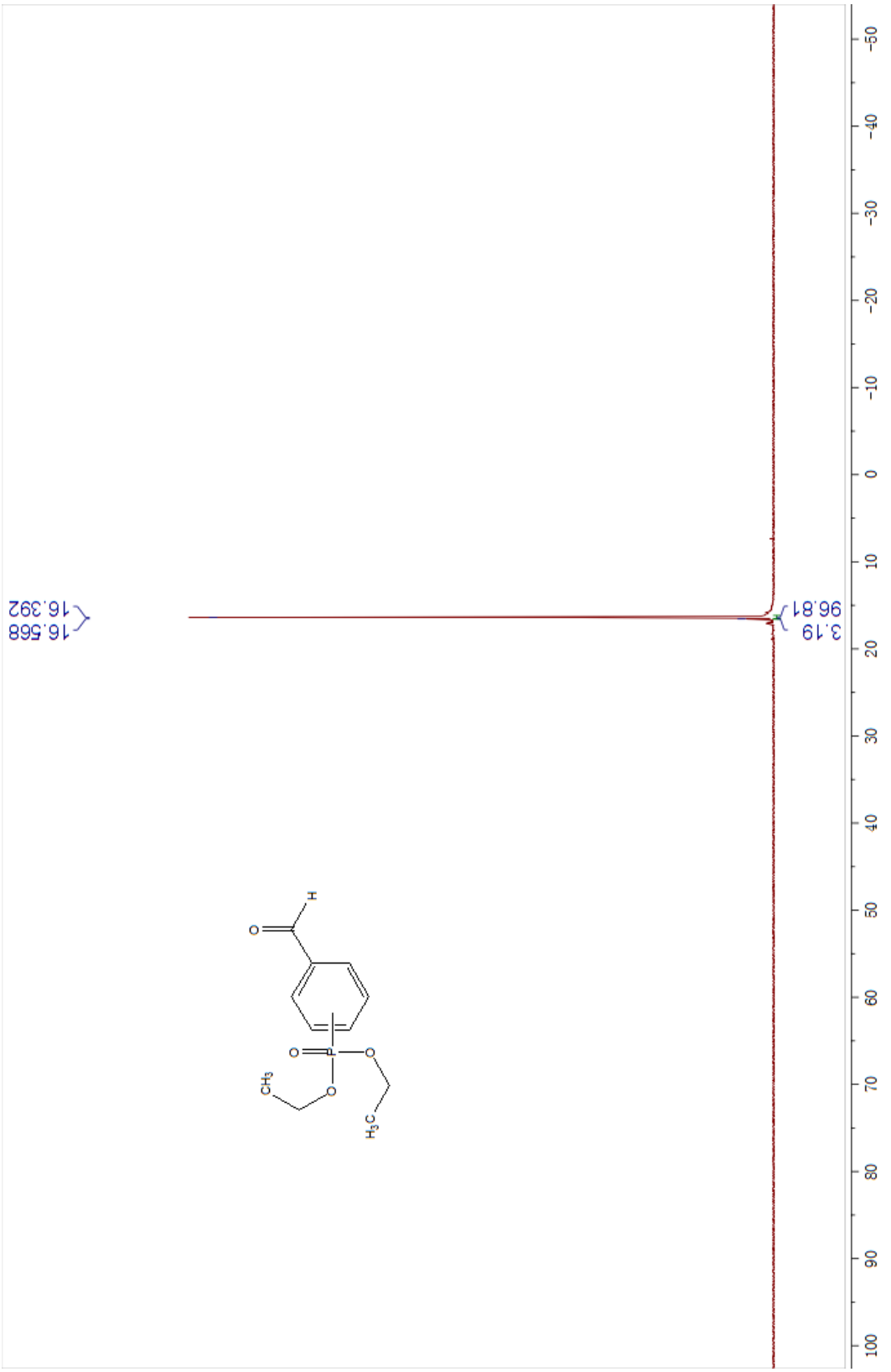


Entry	[M] (mol%)	[O] (equiv)	[S] (mL)	Yield (%)[b]
1	$Cu(OTf)_2$(10)	$K_2S_2O_8$(3)	CH_3CN(3)	5
2	$Cu(OAc)_2$(10)	$K_2S_2O_8$(3)	CH_3CN(3)	3
3	$Pd(OAC)_2$(10)	$K_2S_2O_8$(3)	CH_3CN(3)	0
4	Ag_2O(10)	$K_2S_2O_8$(3)	CH_3CN(3)	30
5	Ag_2O(10)	$K_2S_2O_8$(3)	H_2O(3)	33
6	Ag_2O(10)	$K_2S_2O_8$(3)	CH_3CN:H_2O(1.5:1.5)	53
7	Ag_2O(10)	$K_2S_2O_8$(3)	Acetone:H_2O(1.5:1.5)	33
8	Ag_2O(10)	$K_2S_2O_8$(3)	DCM:H_2O(1.5:1.5)	38
9	Ag_2O(10)	$K_2S_2O_8$(3)	THF:H_2O(1.5:1.5)	40
10	Ag_2O(10)	$K_2S_2O_8$(3)	CH_3CN:H_2O(0.5:0.5)	42
11	Ag_2O(10)	$K_2S_2O_8$(3)	CH_3CN:H_2O(2.5:2.5)	68
12	Ag_2O(10)	$K_2S_2O_8$(3)	CH_3CN:H_2O(3:3)	63
13	Ag_2O(10)	$K_2S_2O_8$(2)	CH_3CN:H_2O(2.5:2.5)	73
14	Ag_2O(10)	$K_2S_2O_8$(1)	CH_3CN:H_2O(2.5:2.5)	58
15	Ag_2O(10)	DCP(1)	CH_3CN:H_2O(2.5:2.5)	0
16	Ag_2O(10)	NMO(2)	CH_3CN:H_2O(2.5:2.5)	0
17	Ag_2O(10)	TBHP(2)	CH_3CN:H_2O(2.5:2.5)	0
18	Ag_2O(10)	$Na_2S_2O_8$(3)	CH_3CN:H_2O(2.5:2.5)	65
19	Ag_2O(5)	$K_2S_2O_8$(2)	CH_3CN:H_2O(2.5:2.5)	73
20	Ag_2O(20)	$K_2S_2O_8$(2)	CH_3CN:H_2O(2.5:2.5)	63

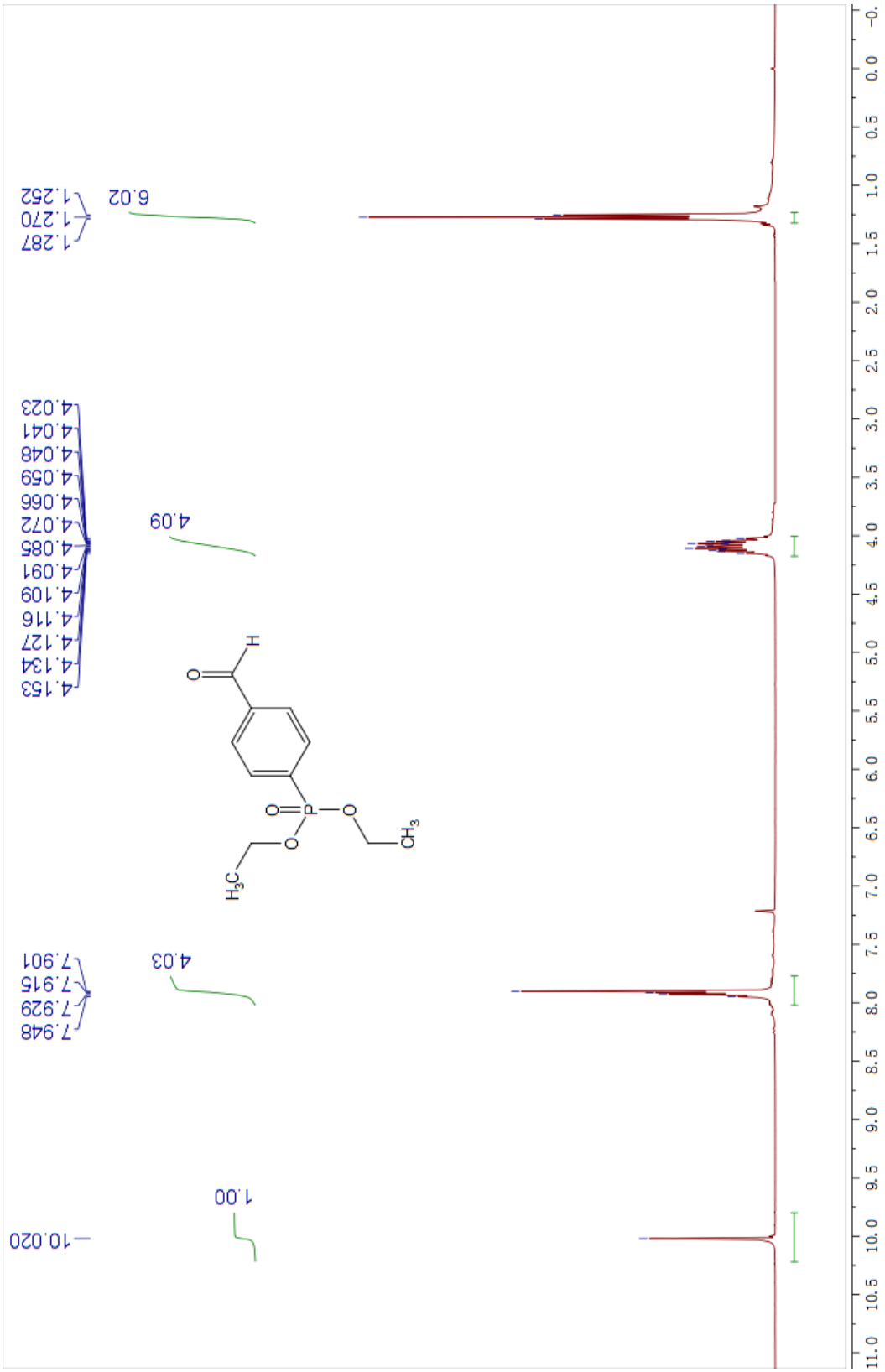
[a] Conditions: **1a** 0.5mmol, **2a** 1mmol, 100℃, 1.5h; [b] Isolated yields.

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

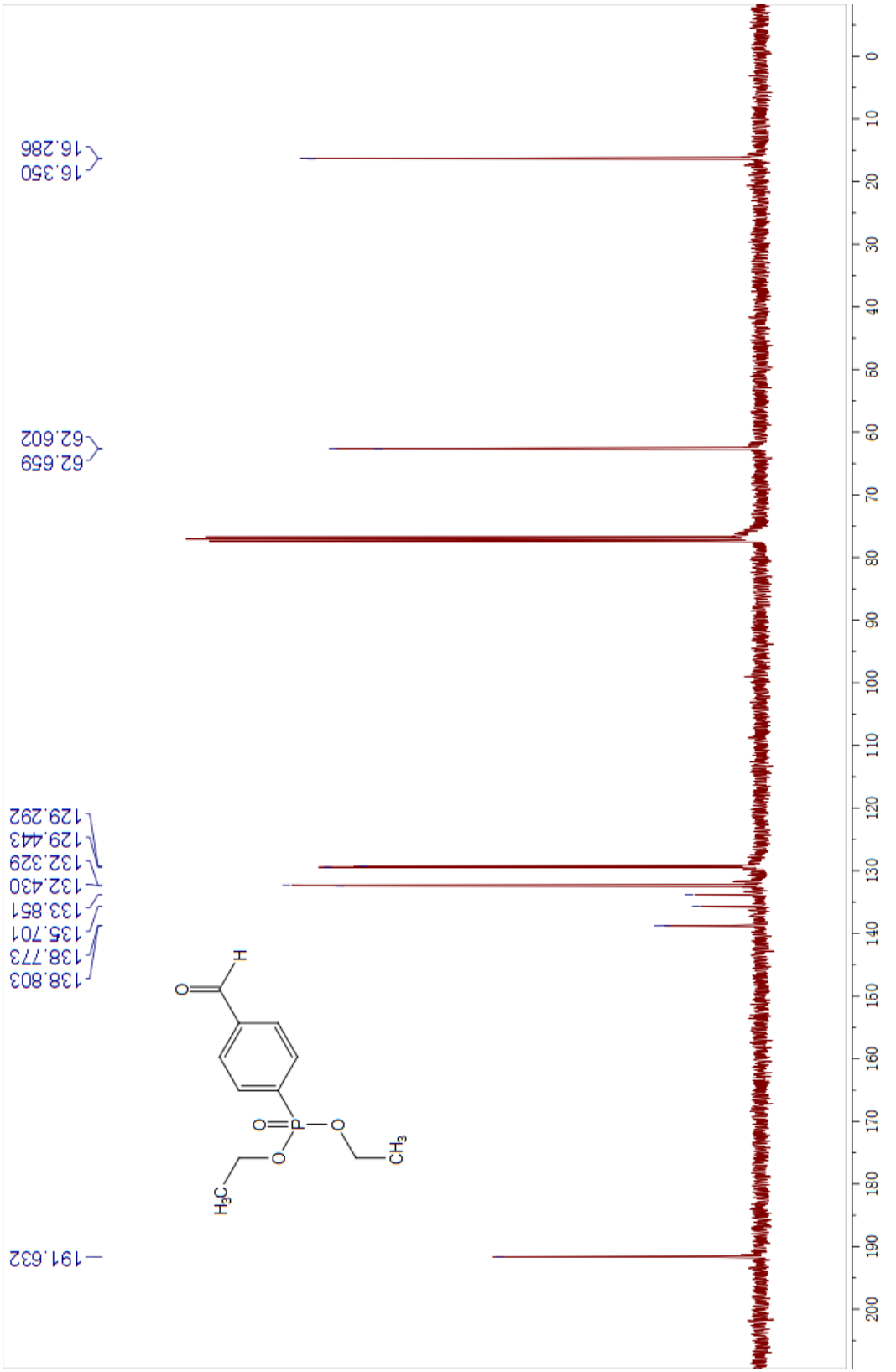
^{13}P NMR Spectrum of diethyl formylphenylphosphonate **3aa**



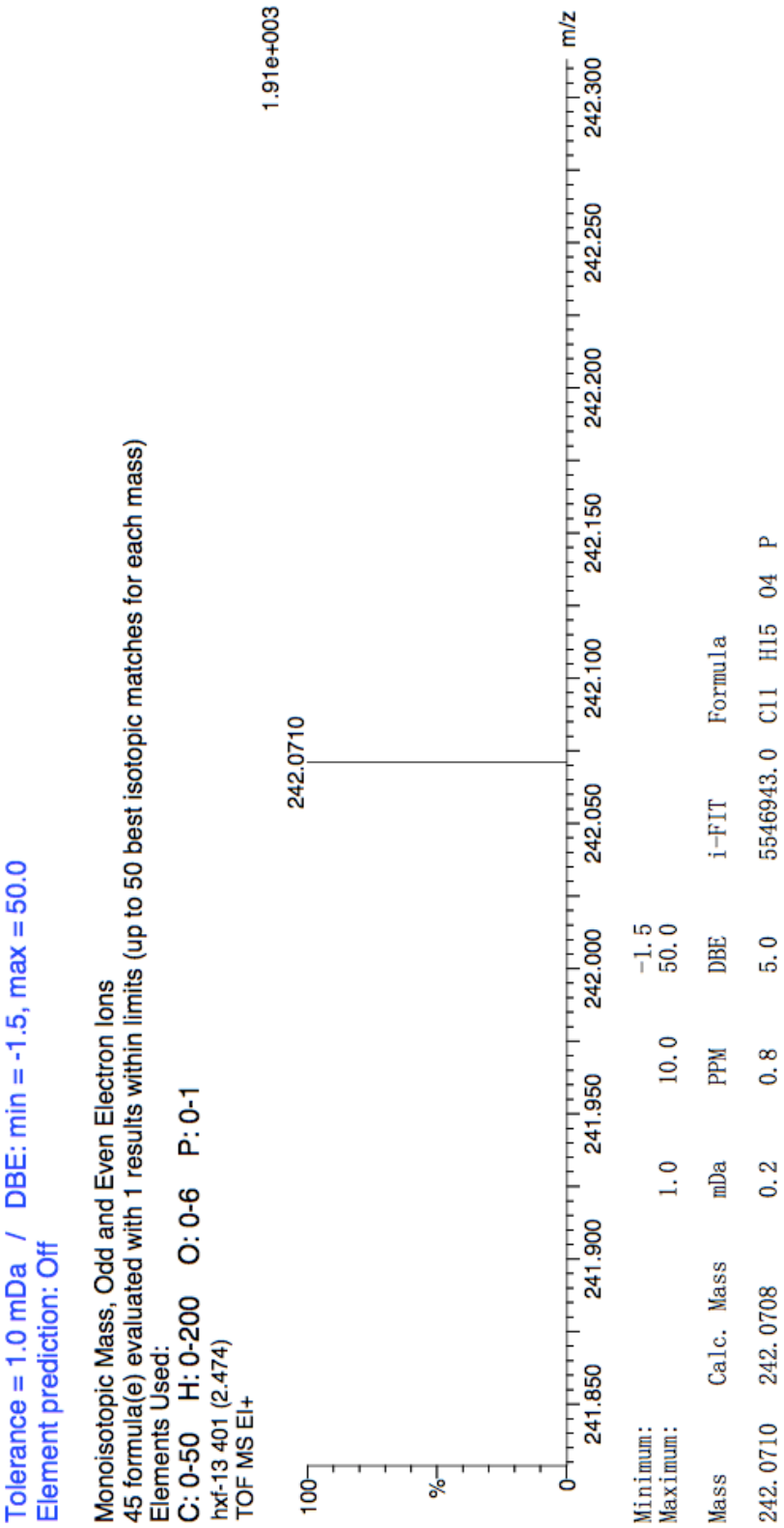
^{1}H NMR Spectrum of diethyl 4-formylphenylphosphonate **3aa**



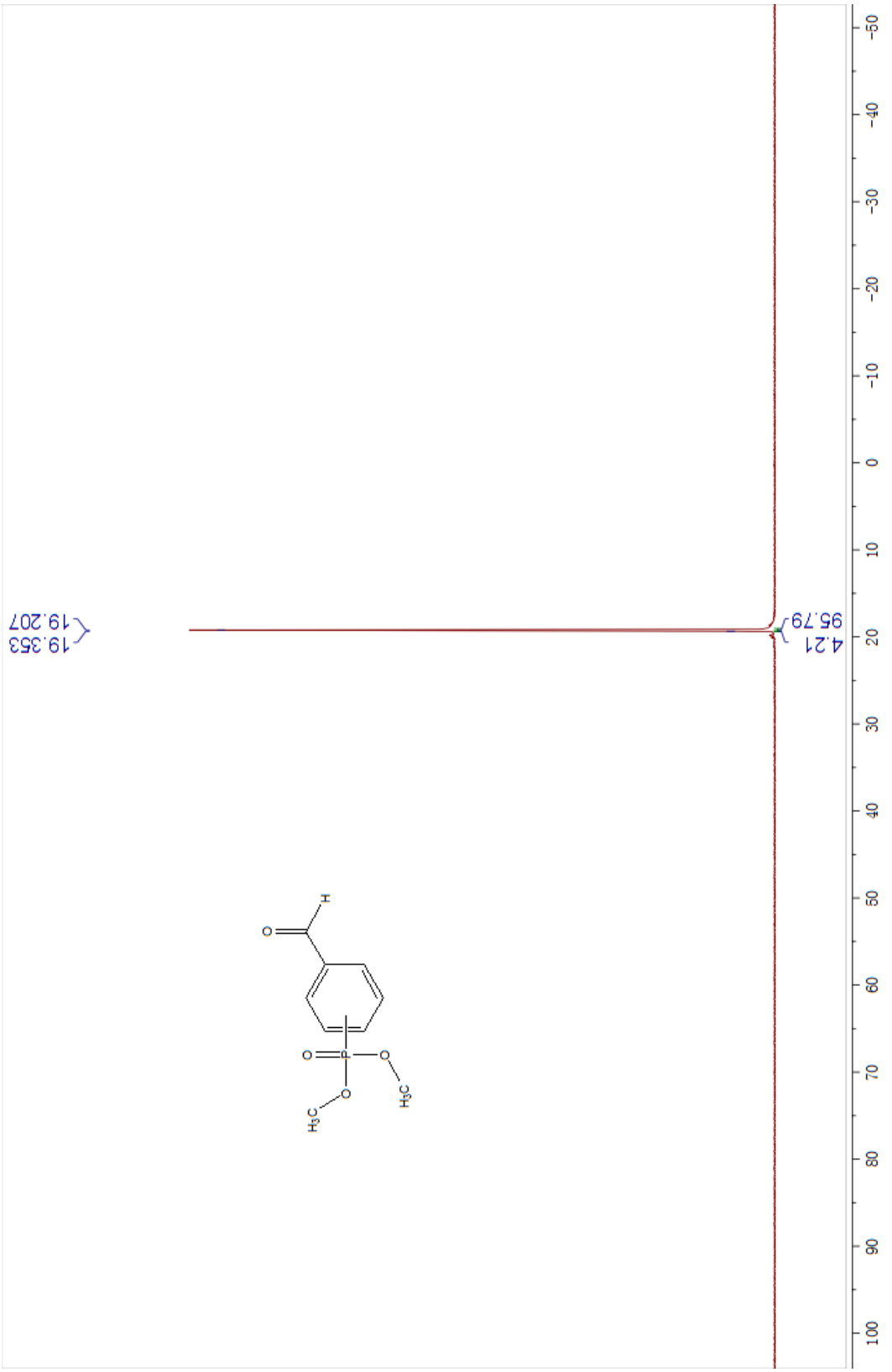
^{13}C NMR Spectrum of diethyl 4-formylphenylphosphonate **3aa**



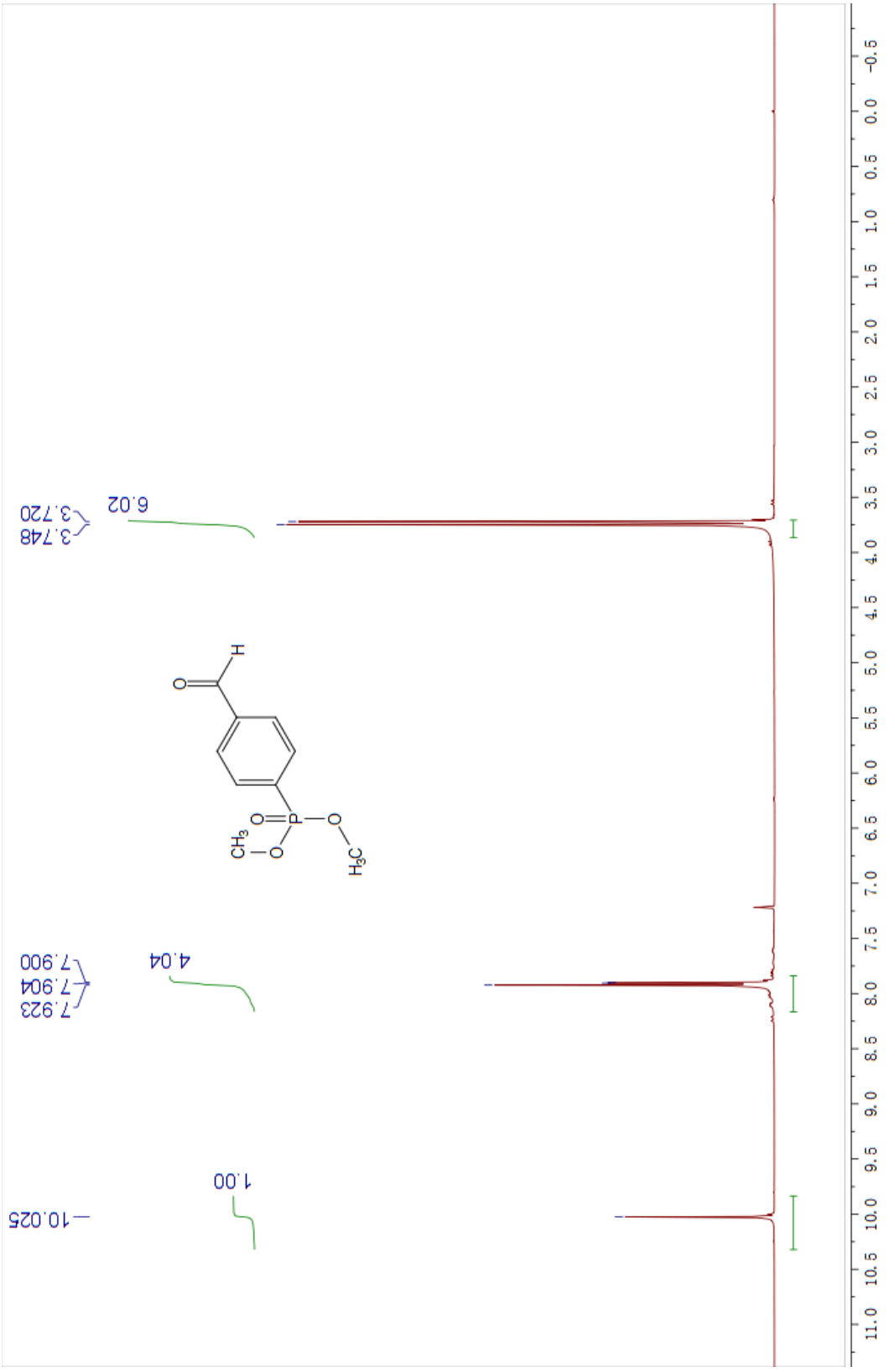
HR-MS Spectrum of diethyl 4-formylphenylphosphonate **3aa**



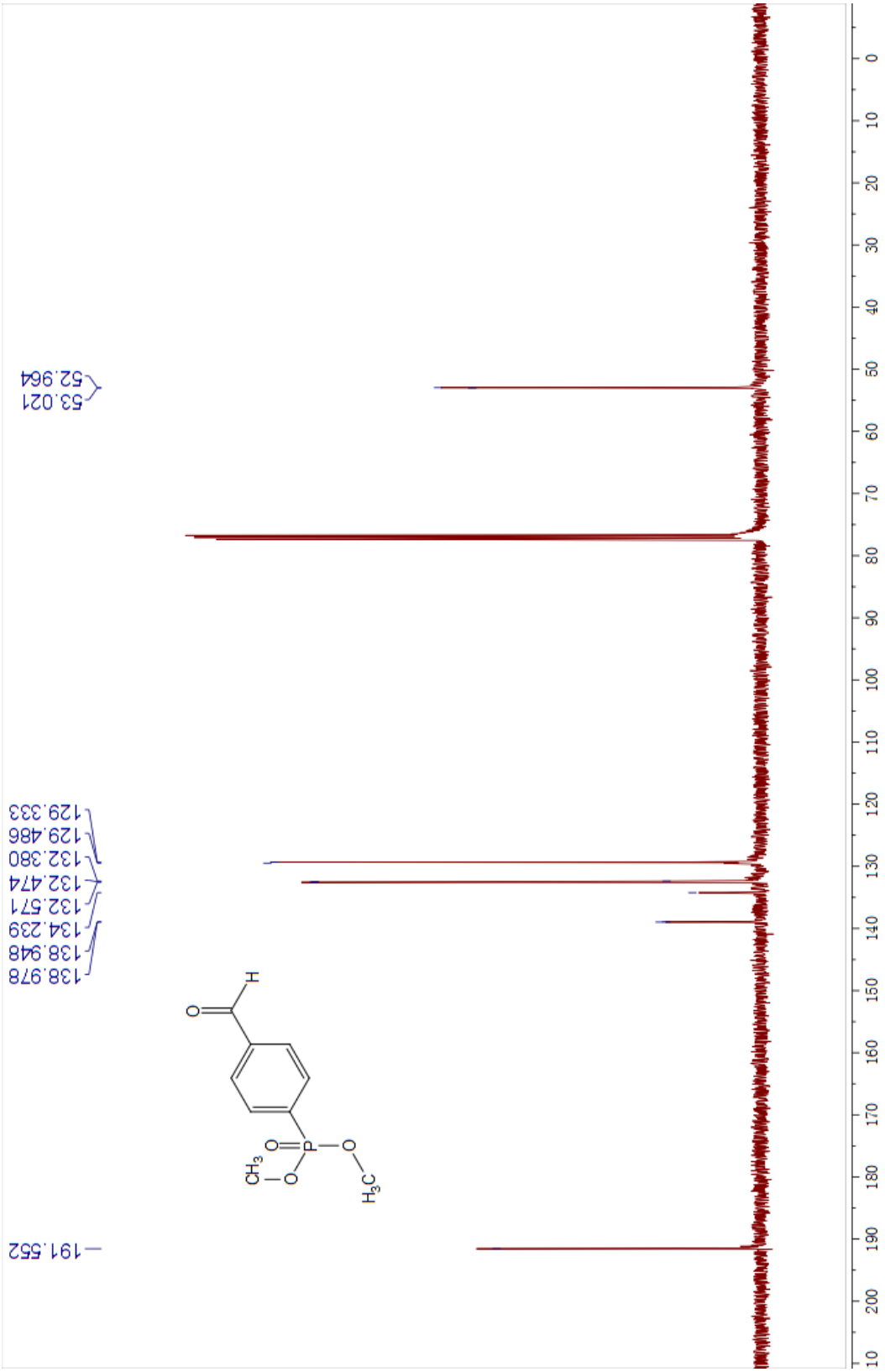
^{13}P NMR Spectrum of dimethyl formylphenylphosphonate **3ab**



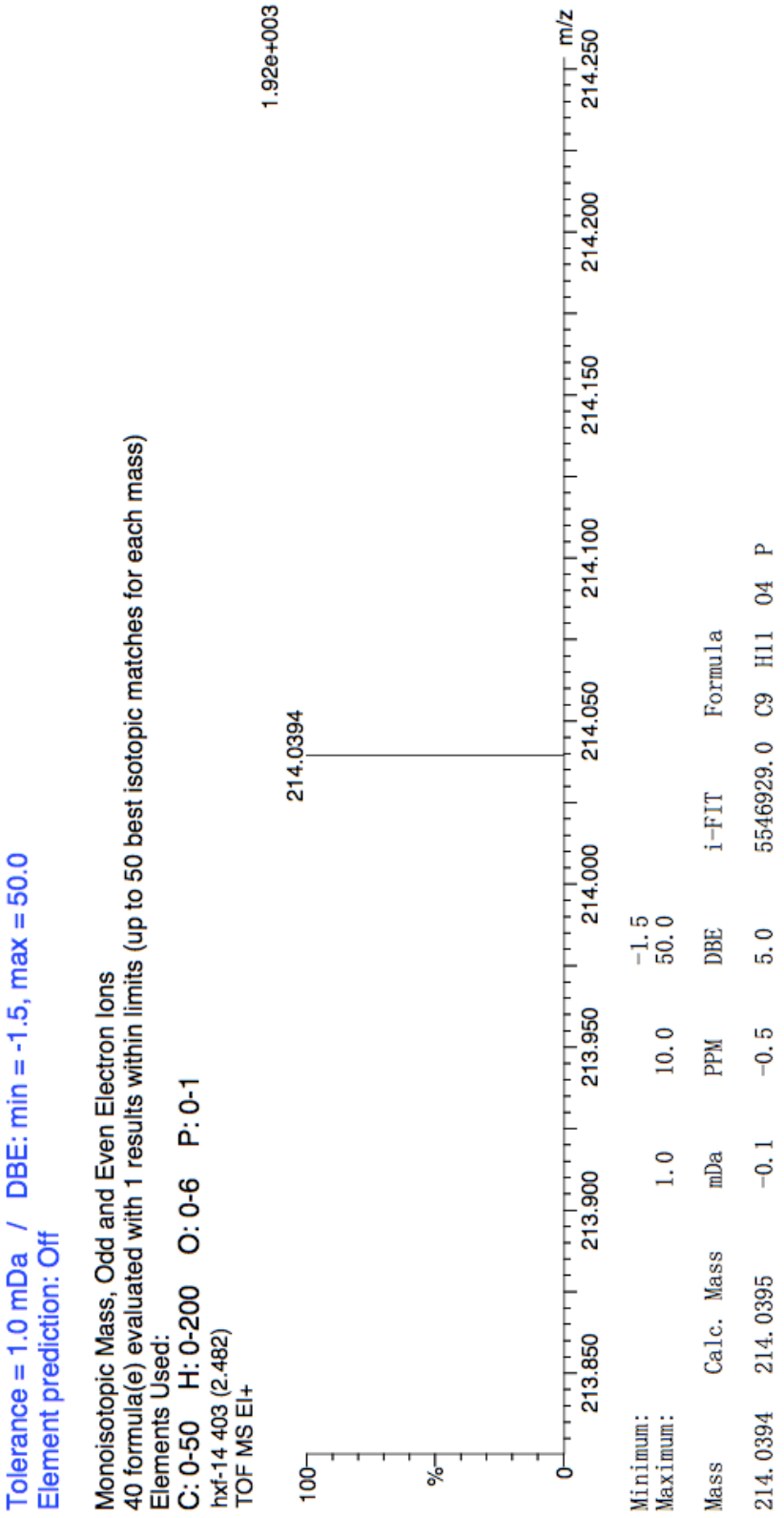
^{1}H NMR Spectrum of dimethyl 4-formylphenylphosphonate **3ab**



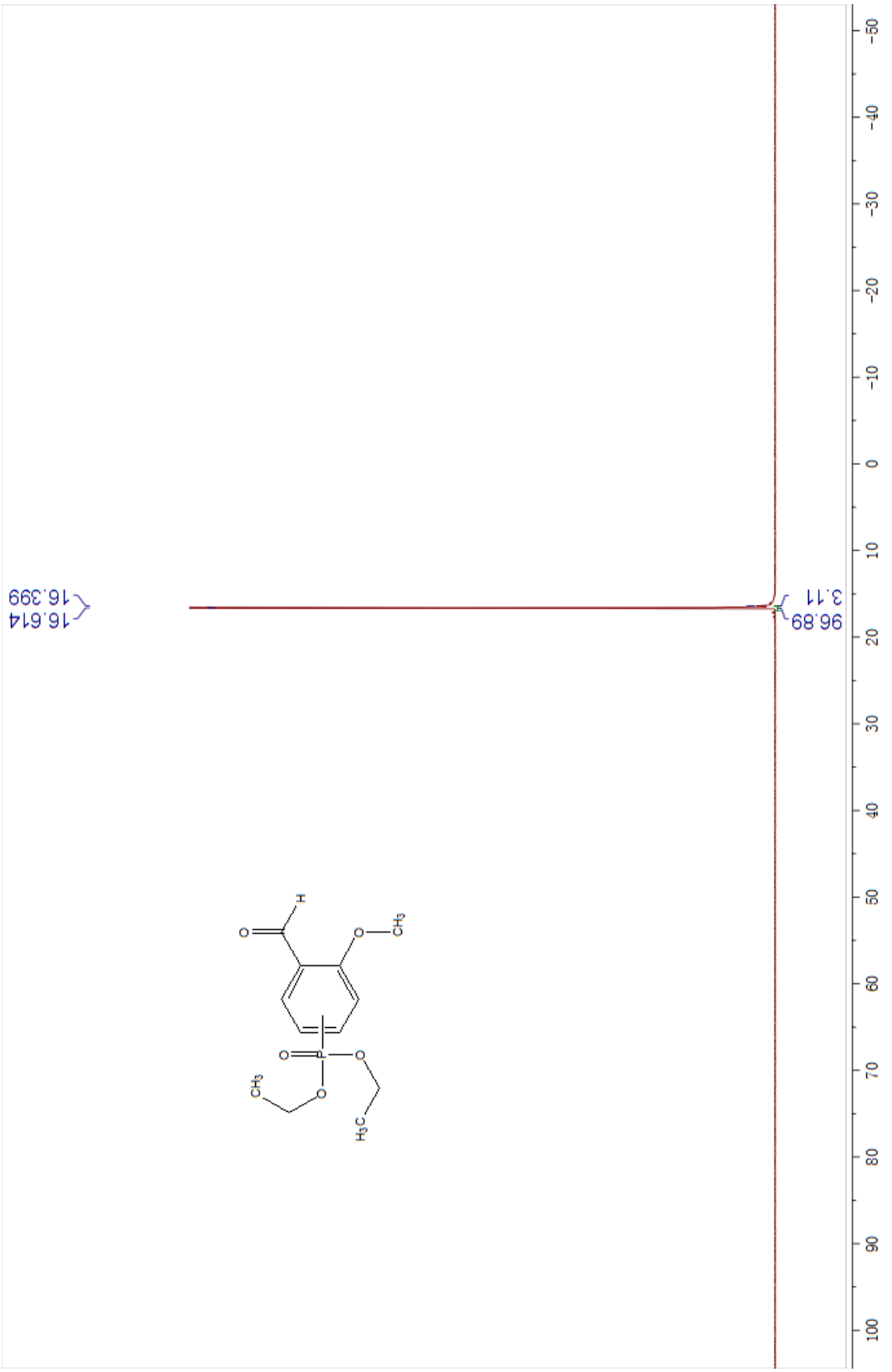
^{13}C NMR Spectrum of dimethyl 4-formylphenylphosphonate **3ab**



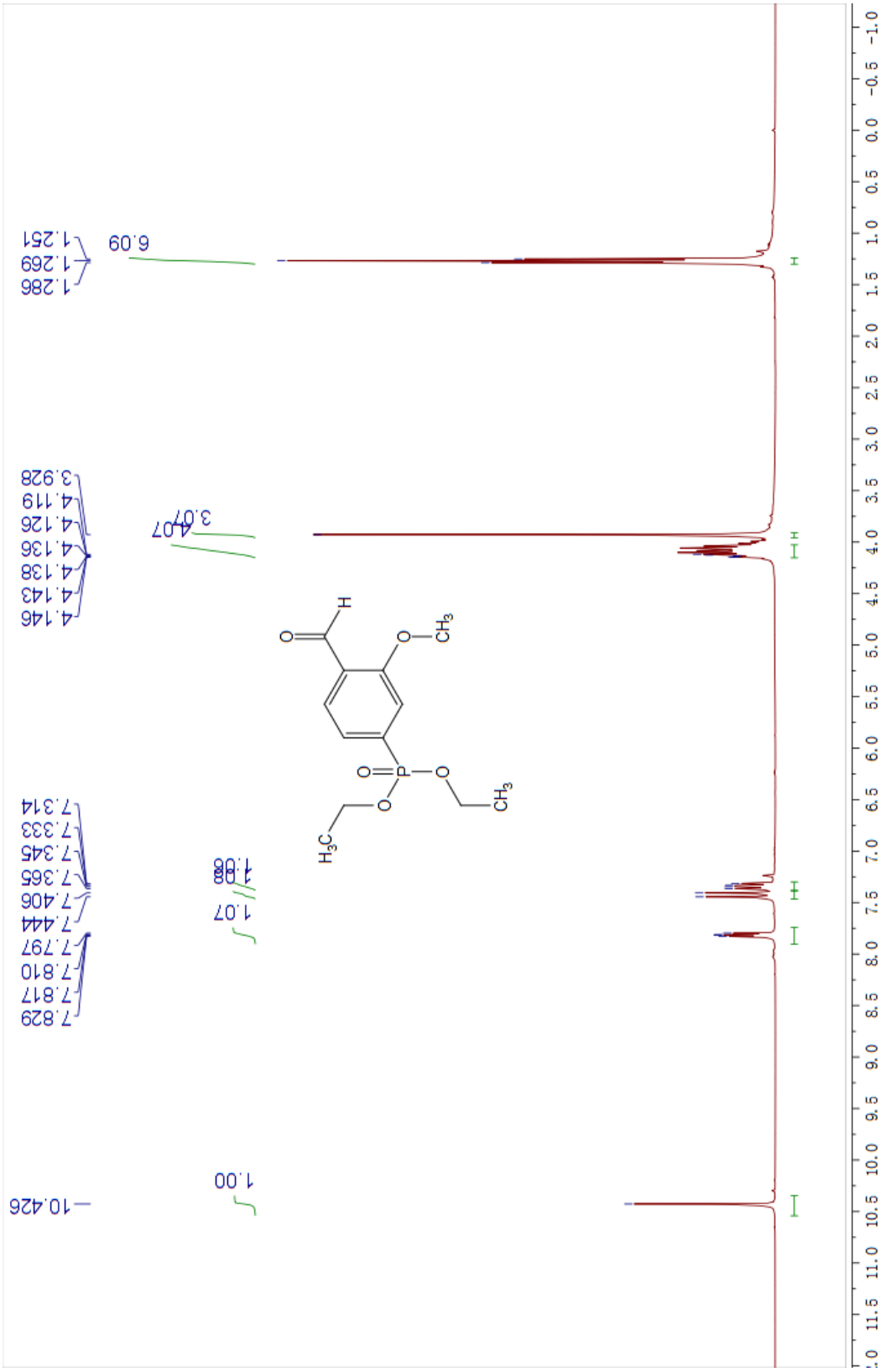
HR-MS Spectrum of dimethyl 4-formylphenylphosphonate **3ab**



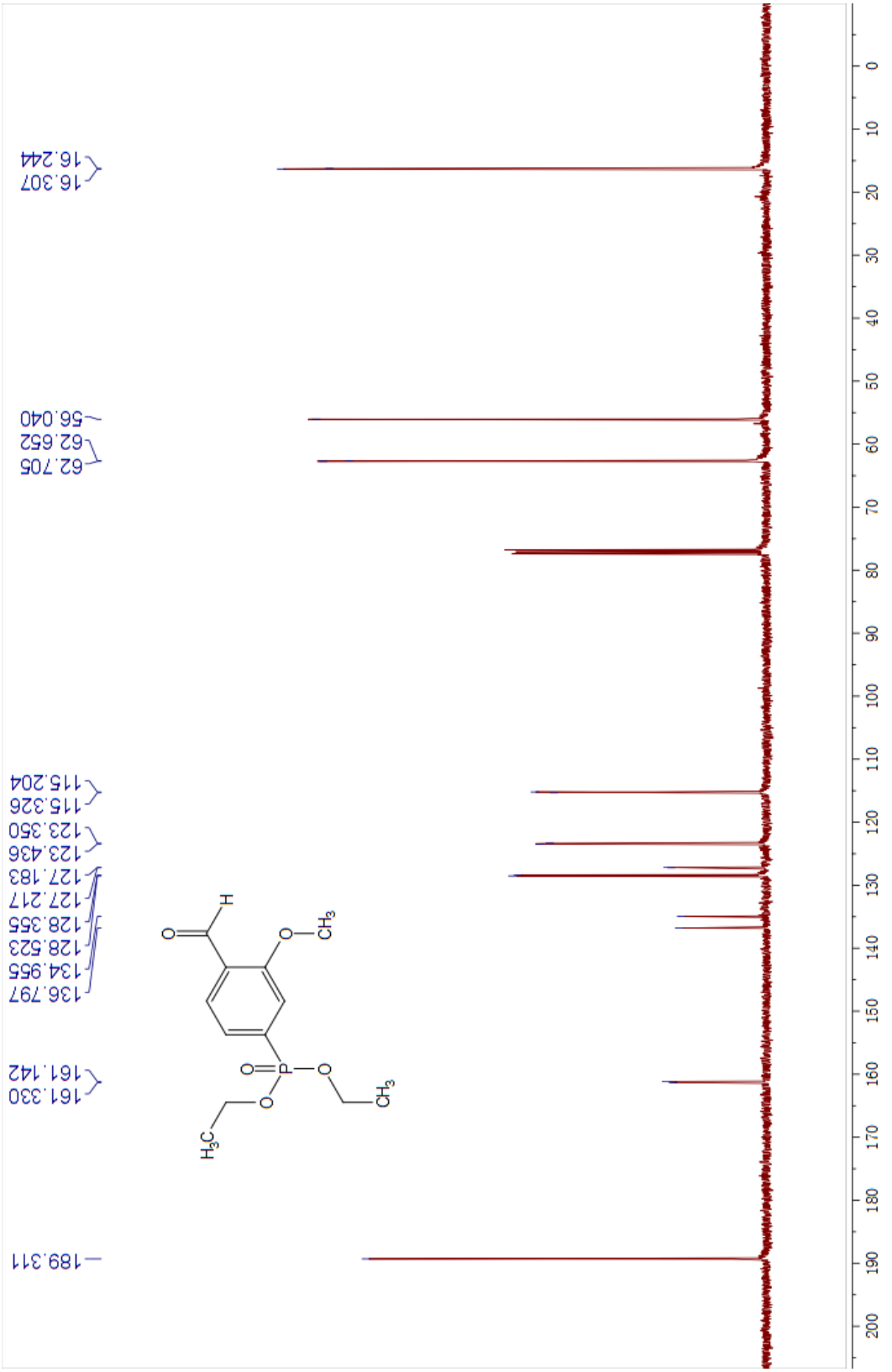
^{13}P NMR Spectrum of diethyl formyl-3-methoxyphenylphosphonate **3da**



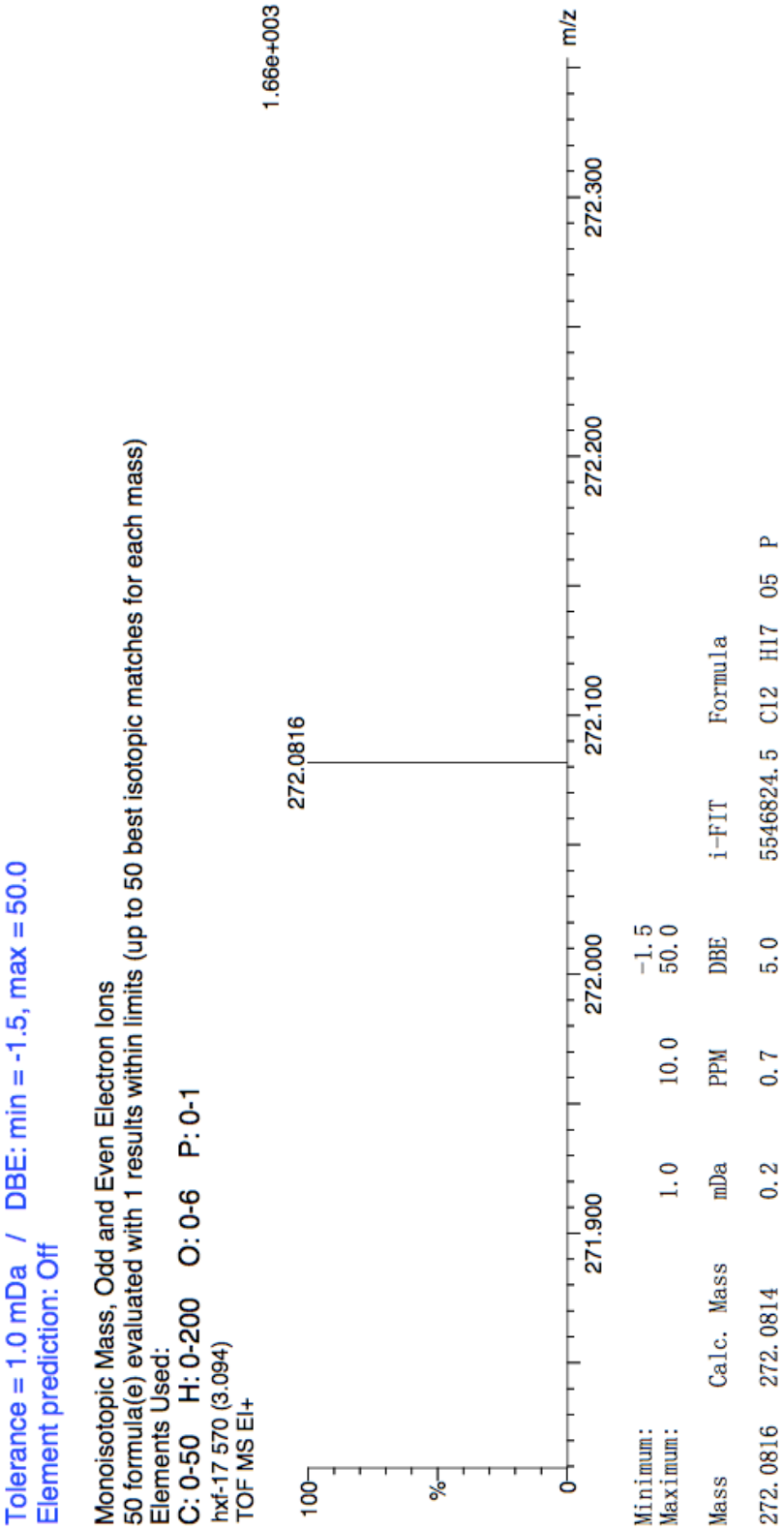
^{1}H NMR Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate **3da**



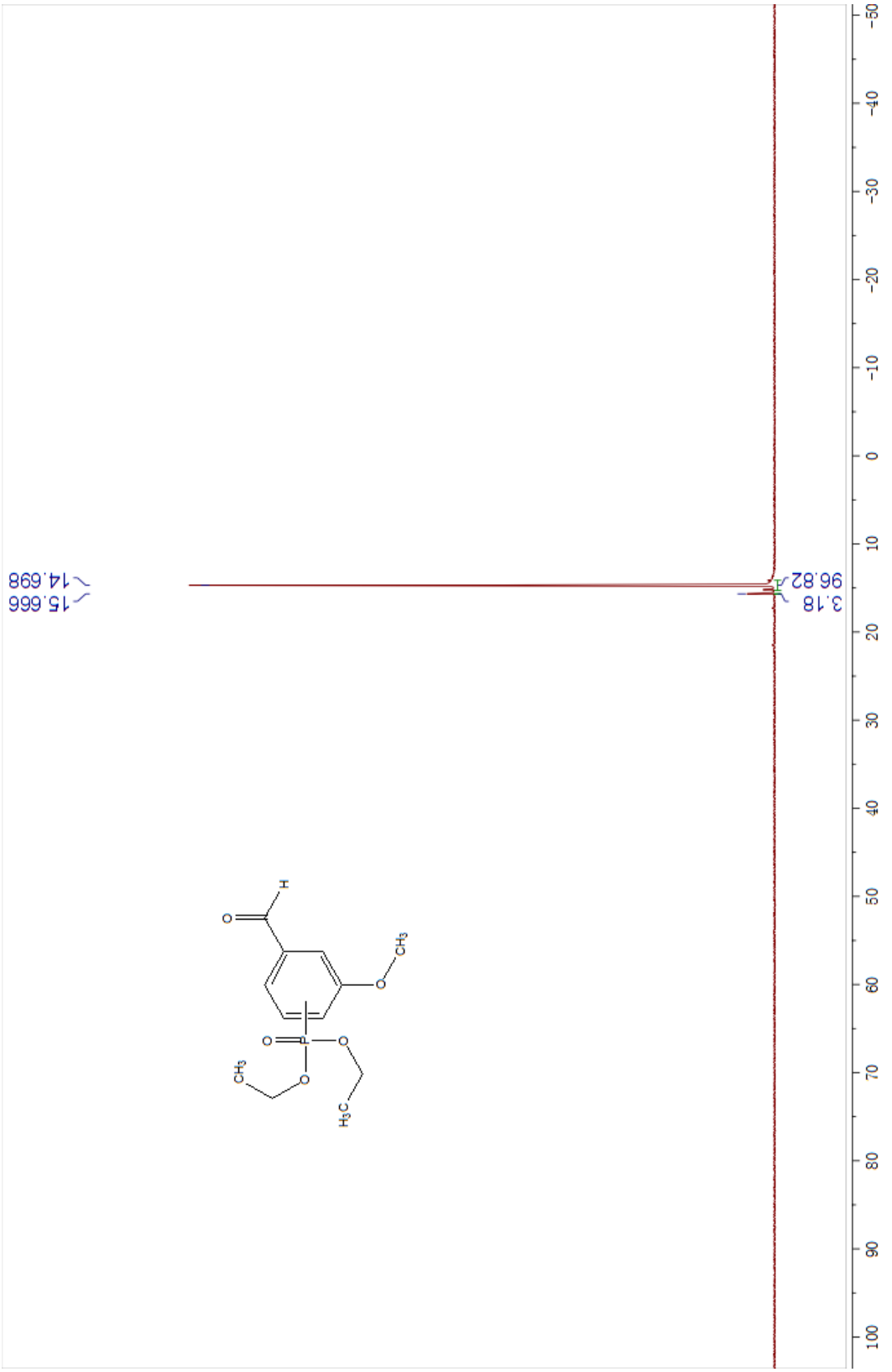
^{13}C NMR Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate **3da**



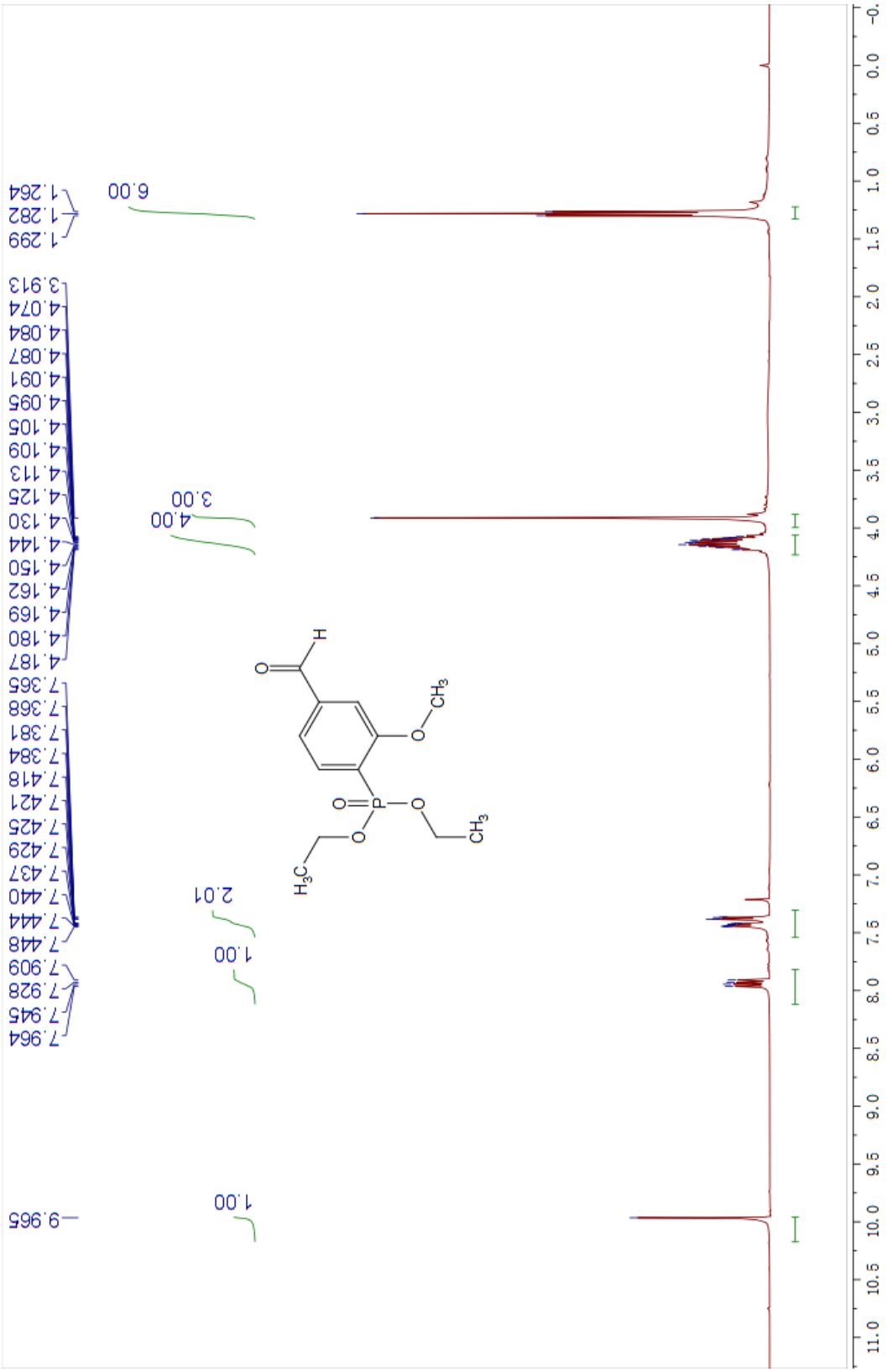
HR-MS Spectrum of diethyl 4-formyl-3-methoxyphenylphosphonate **3da**



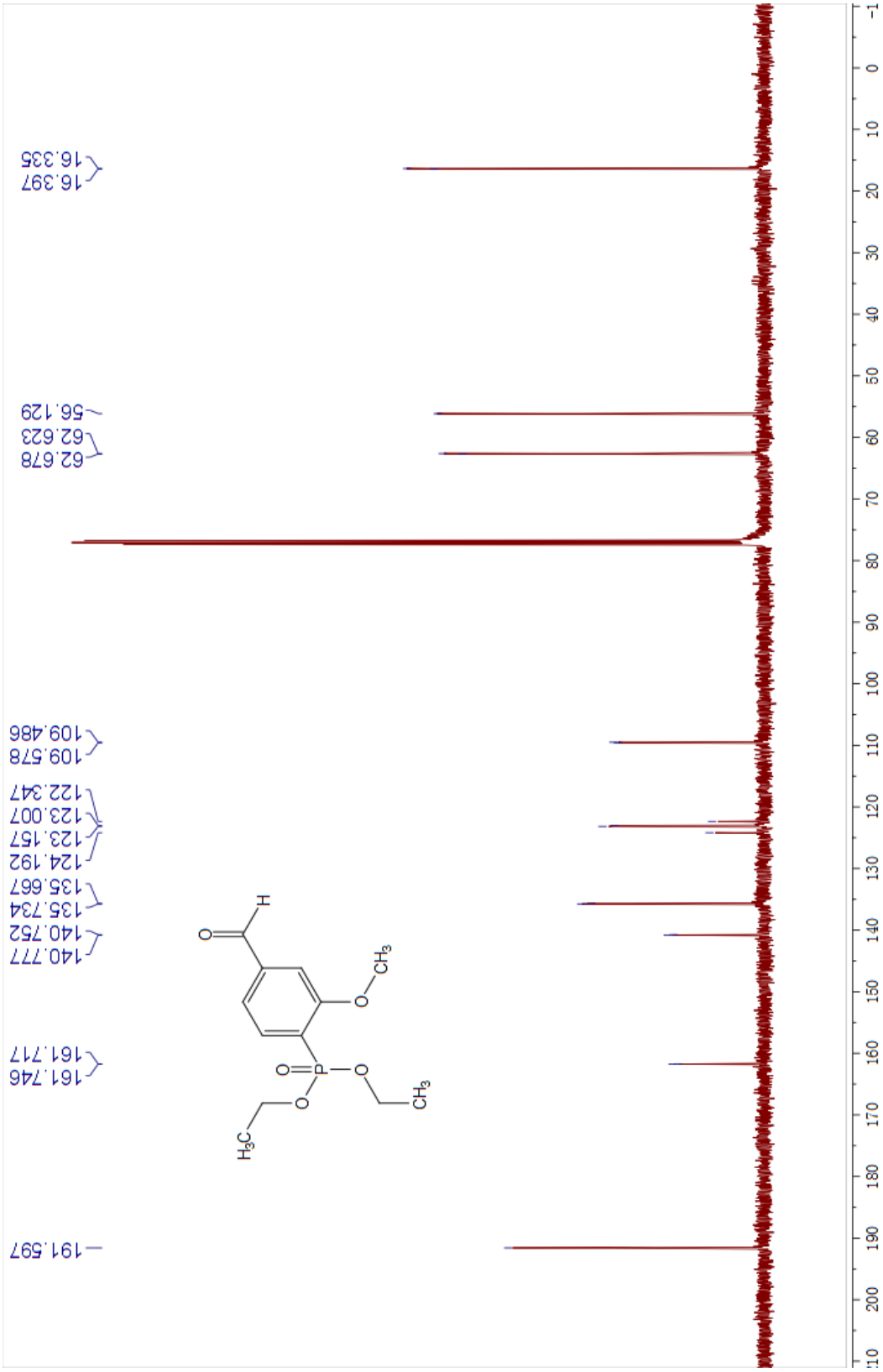
^{13}P NMR Spectrum of diethyl formyl-2-methoxyphenylphosphonate **3ea**



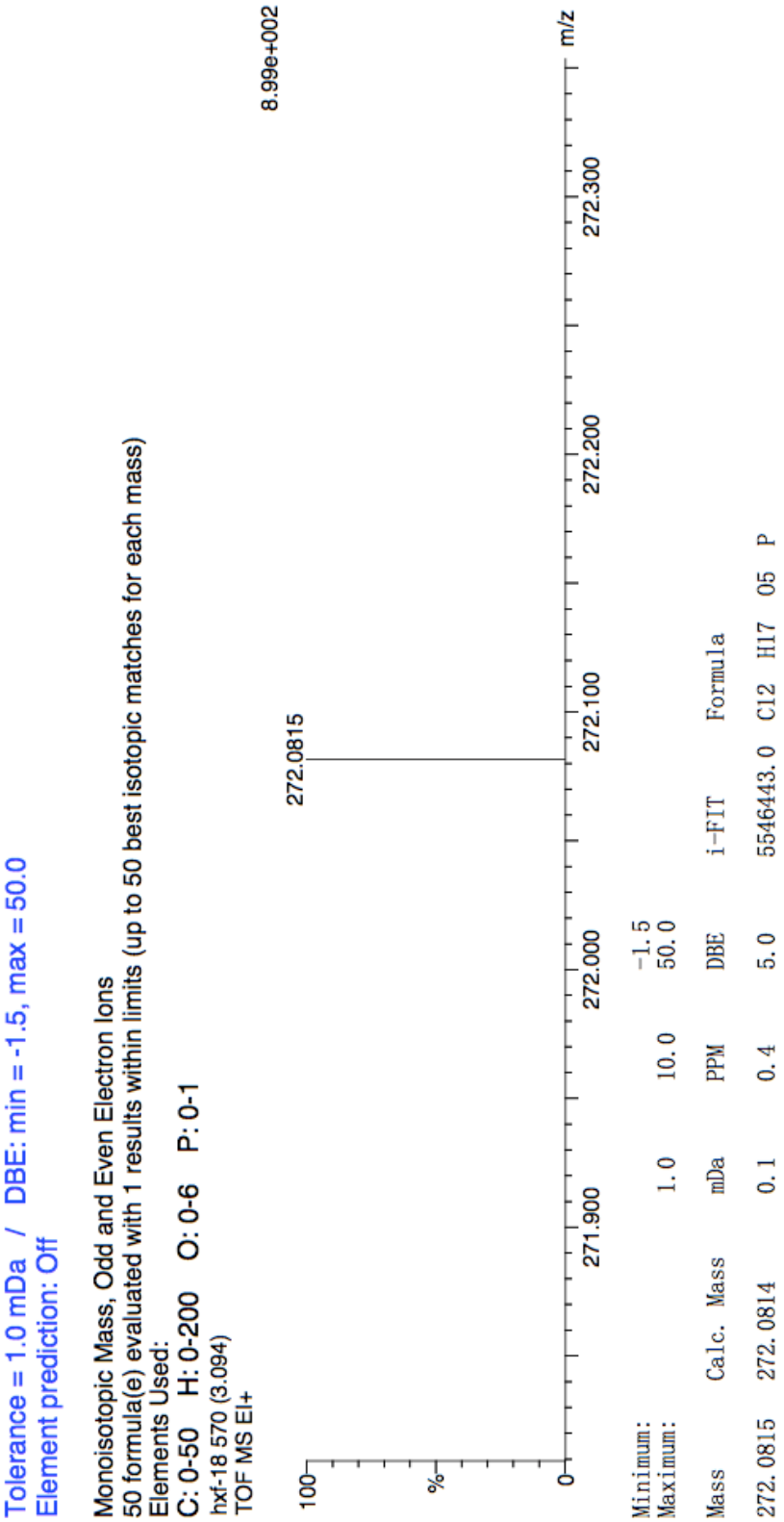
^{1}H NMR Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate **3ea**



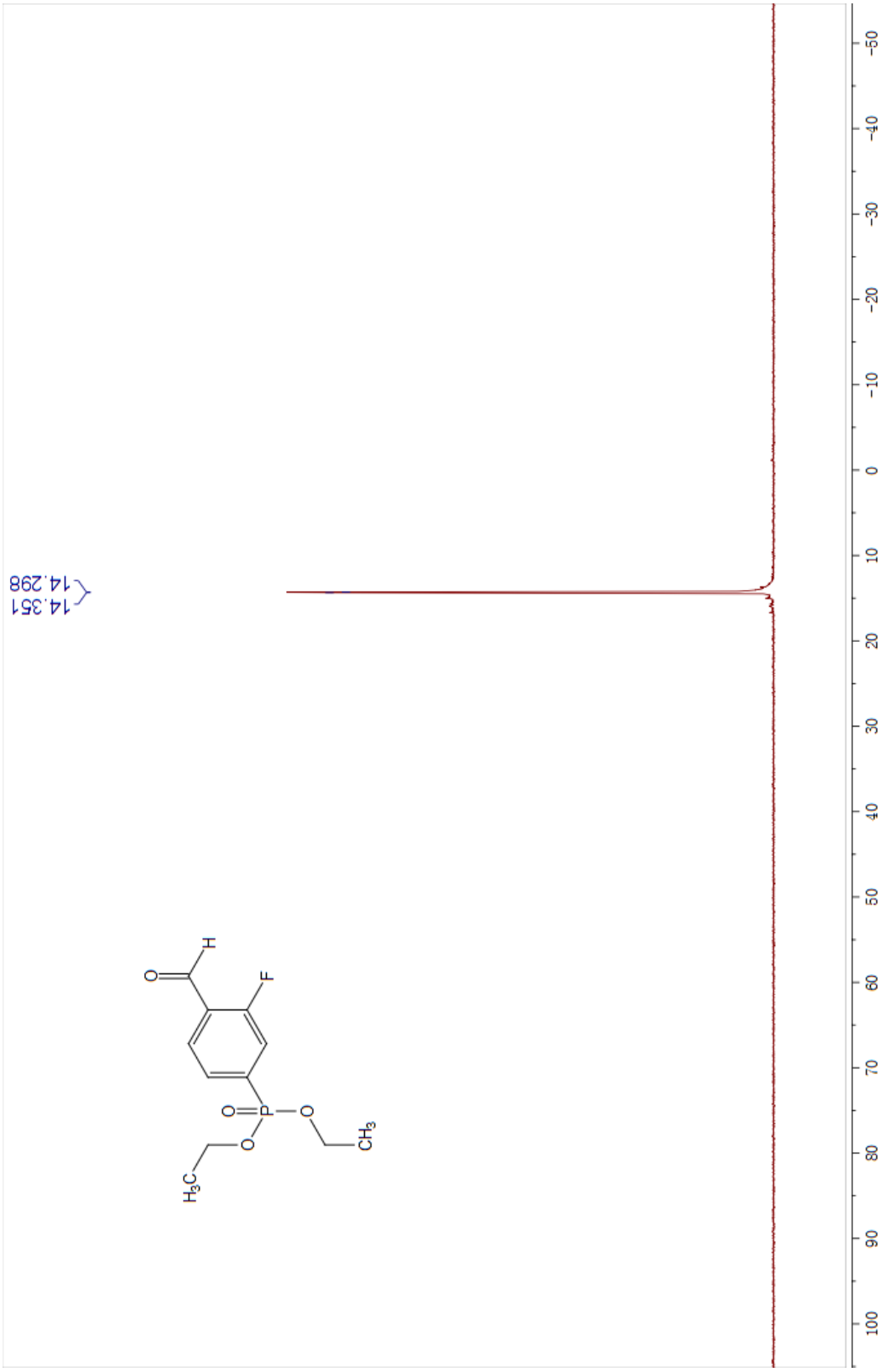
^{13}C NMR Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate **3ea**



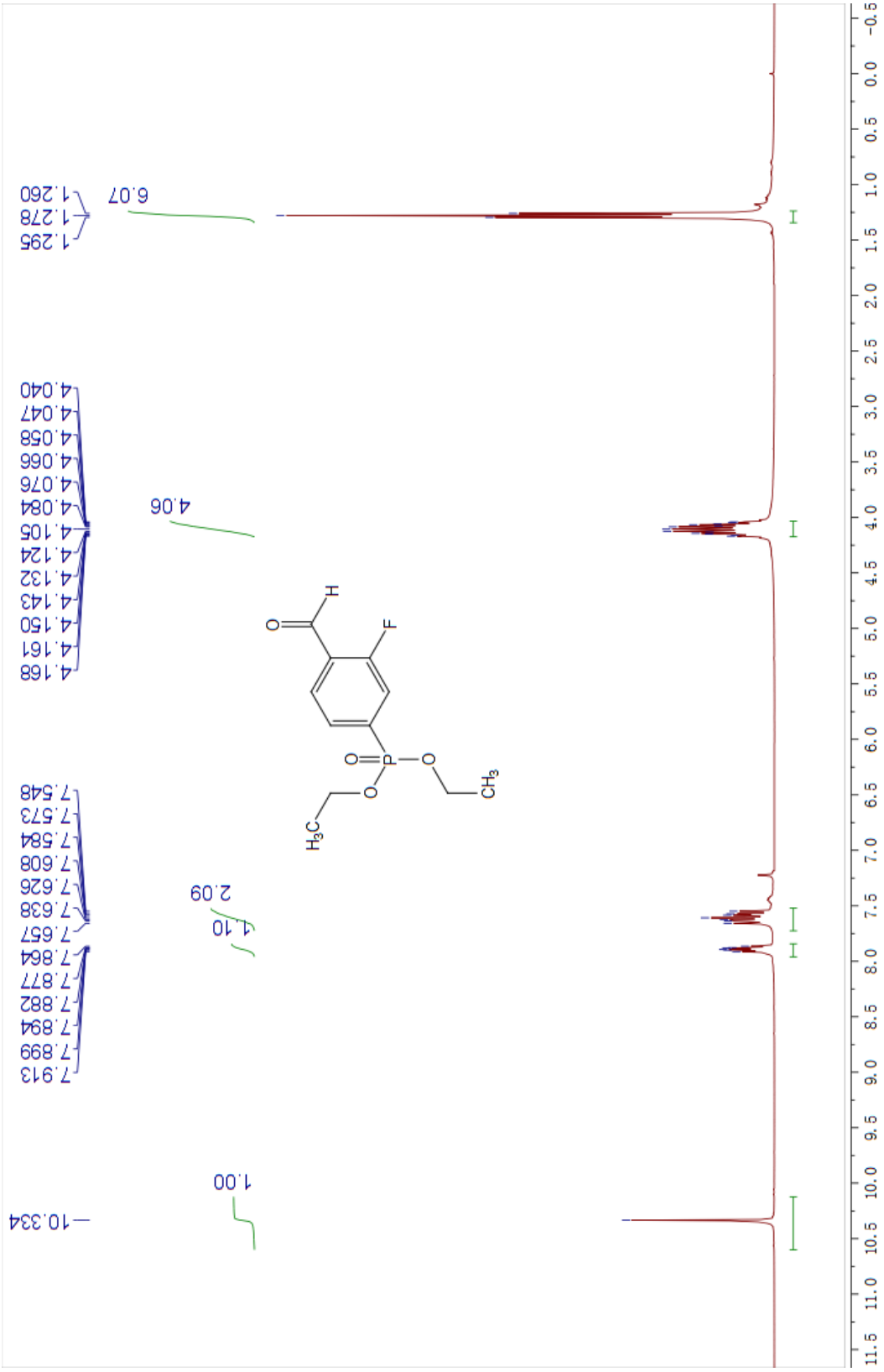
HR-MS Spectrum of diethyl 4-formyl-2-methoxyphenylphosphonate **3ea**



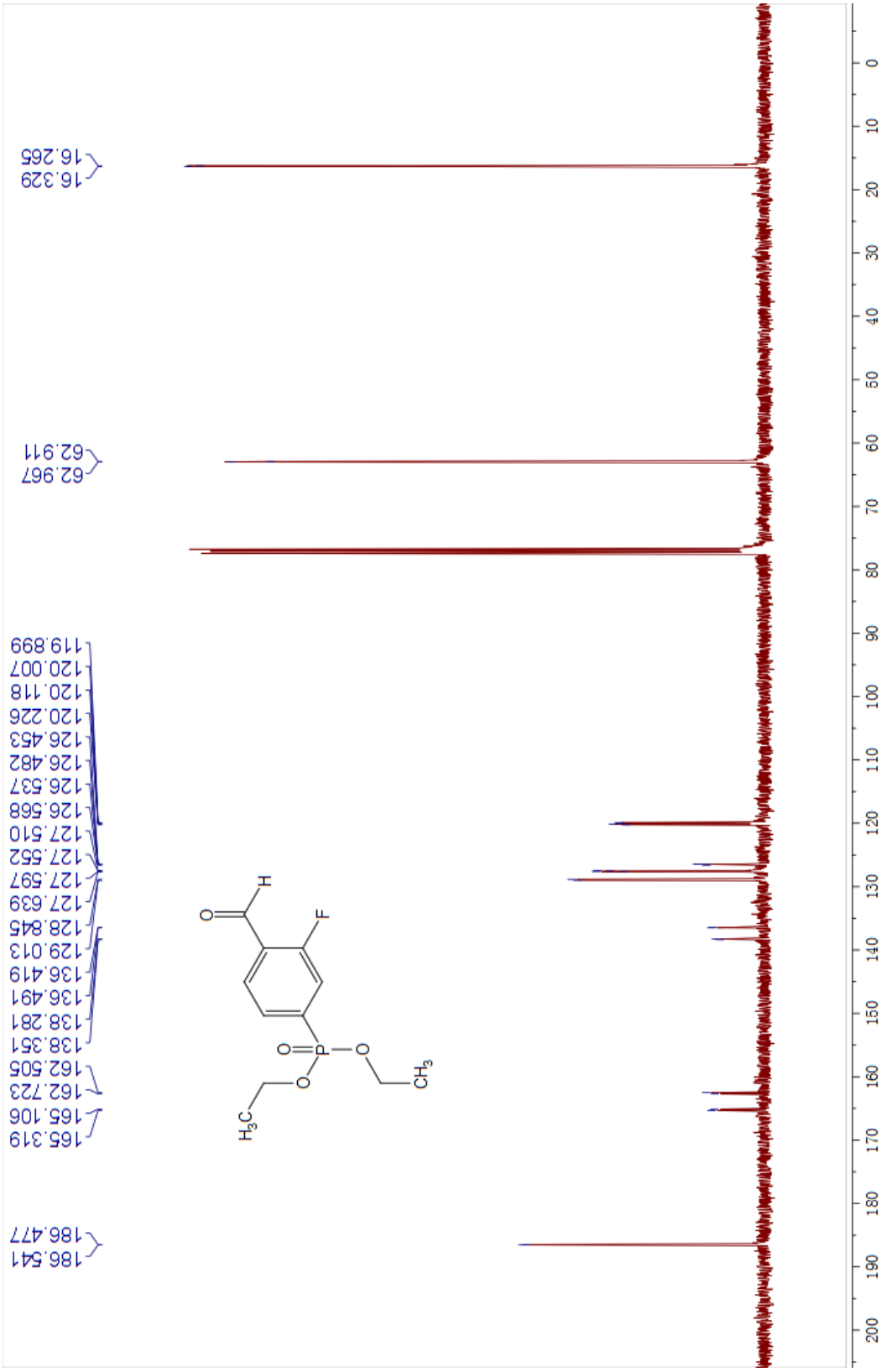
^{13}P NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**



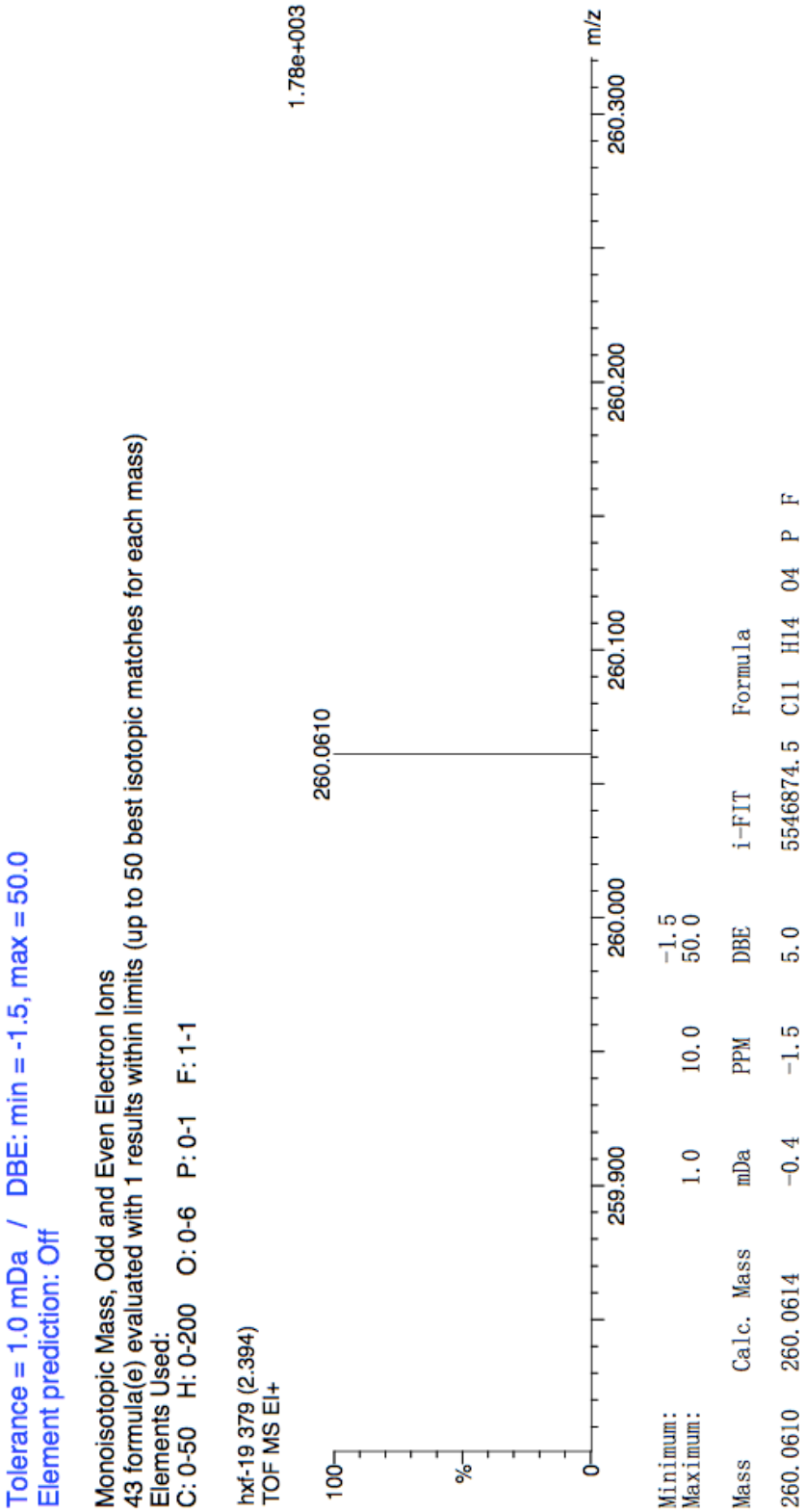
^{1}H NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**



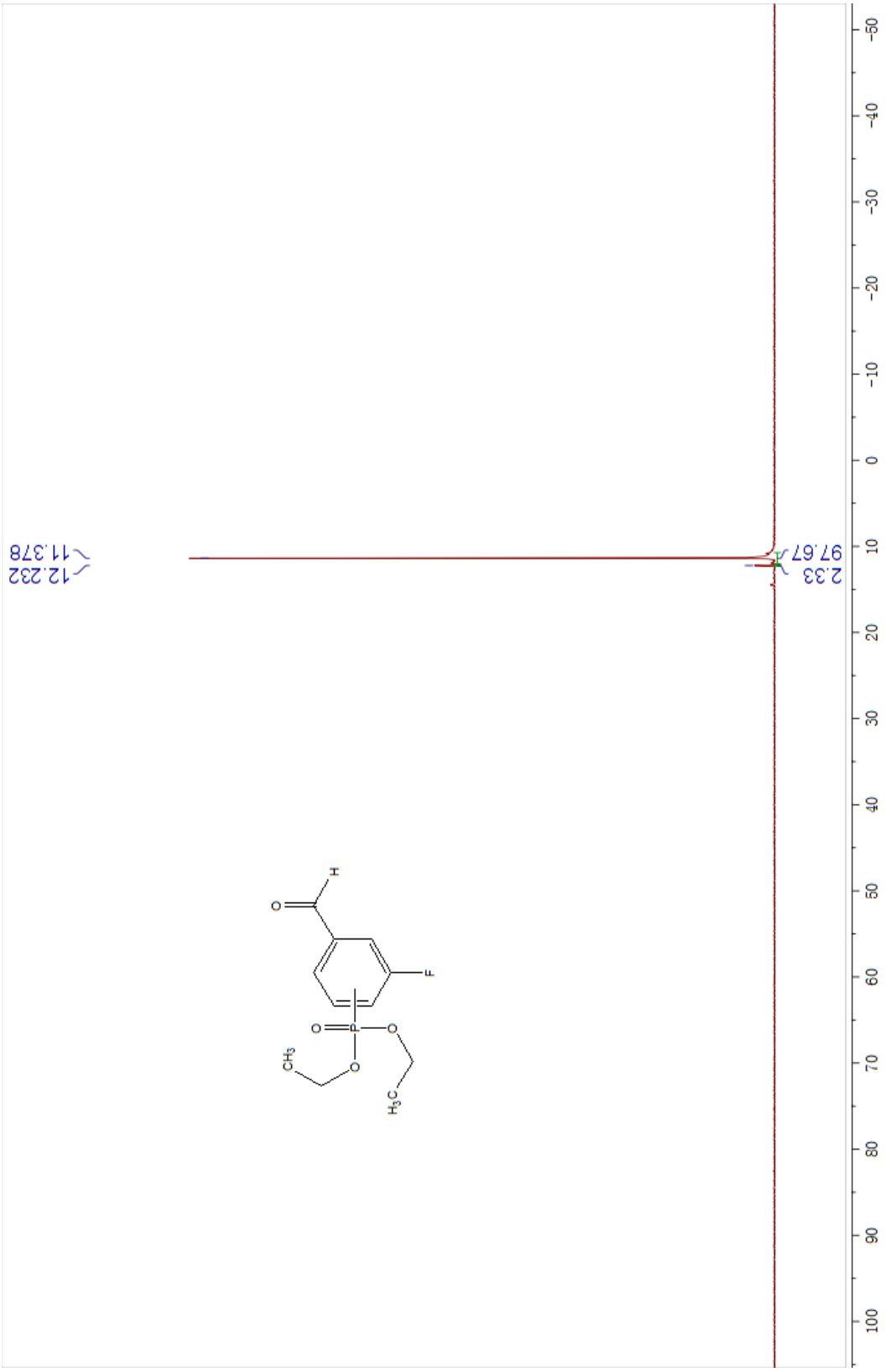
^{13}C NMR Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**



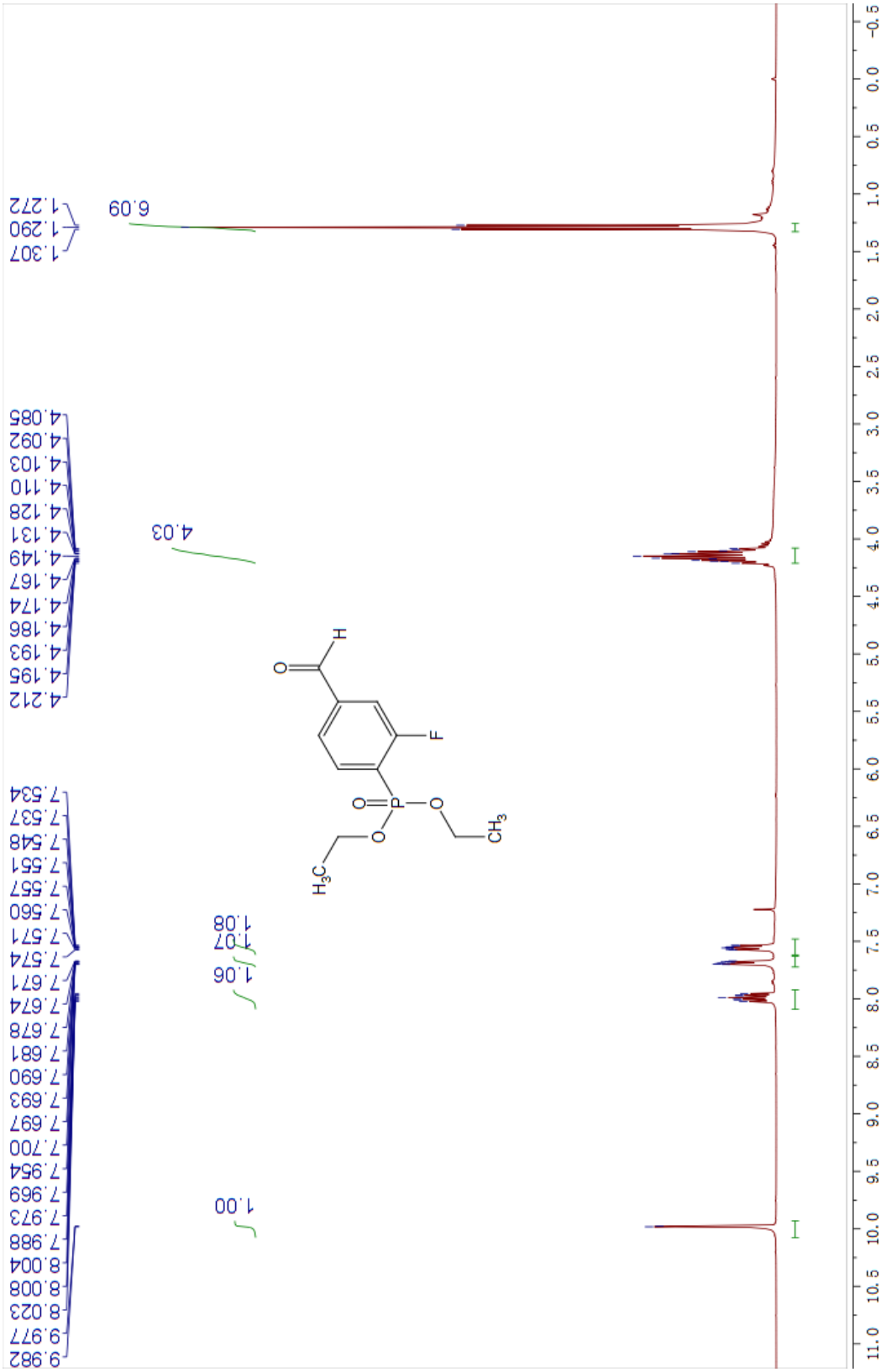
HR-MS Spectrum of diethyl 3-fluoro-4-formylphenylphosphonate **3fa**



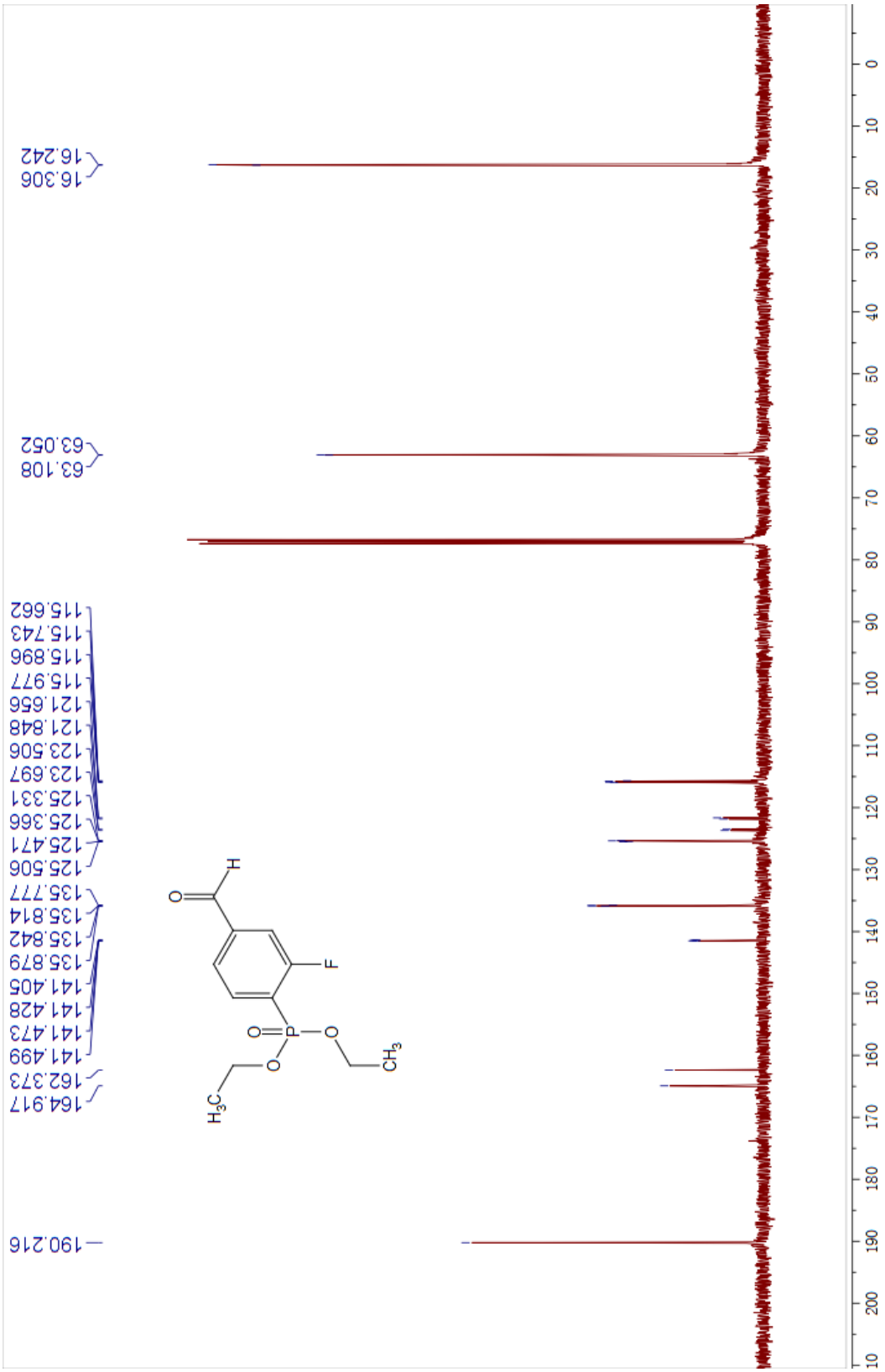
^{13}P NMR Spectrum of diethyl 2-fluoroformylphenylphosphonate **3ga**



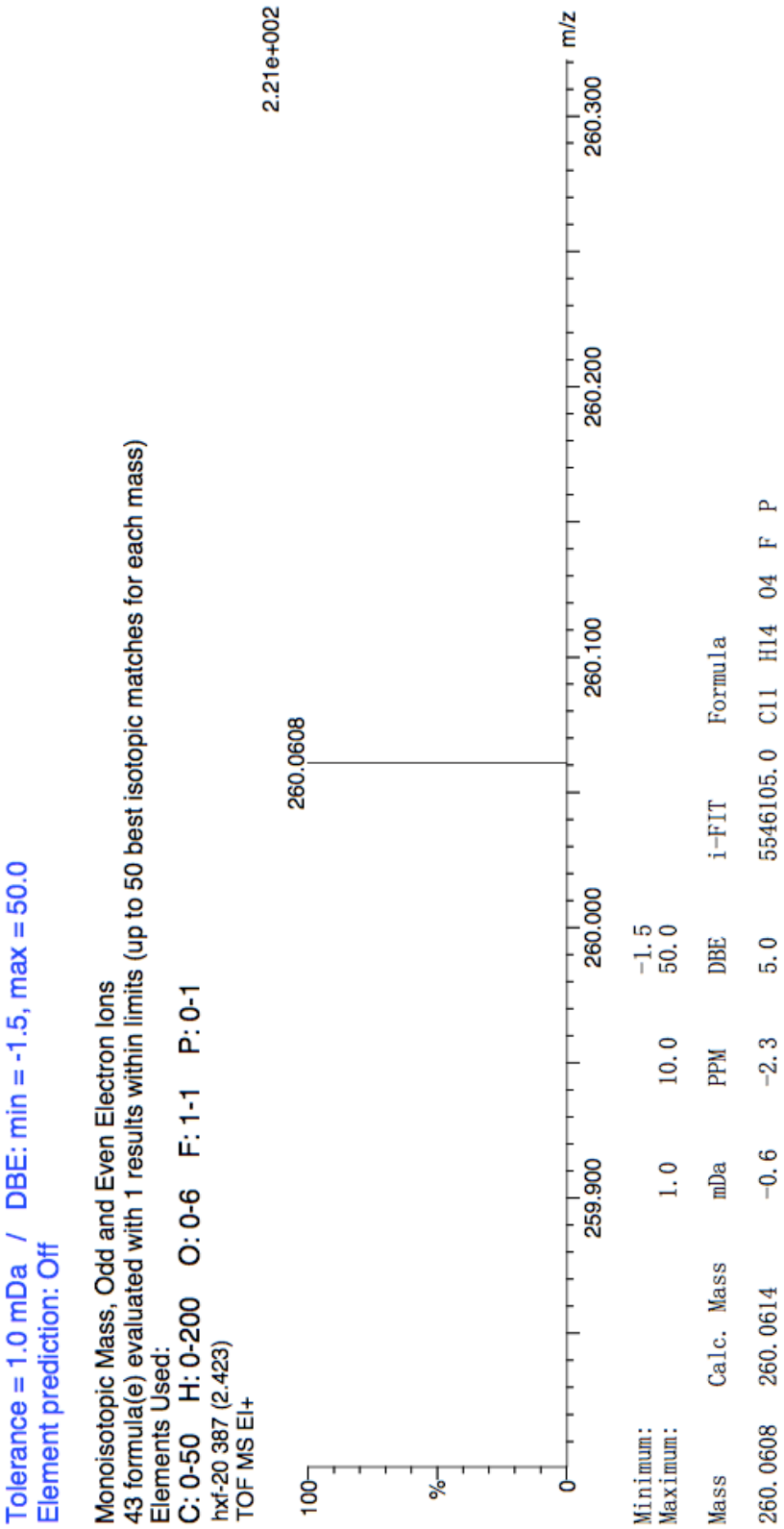
[1]H NMR Spectrum of (diethyl 2-fluoro-4-formylphenylphosphonate **3ga**



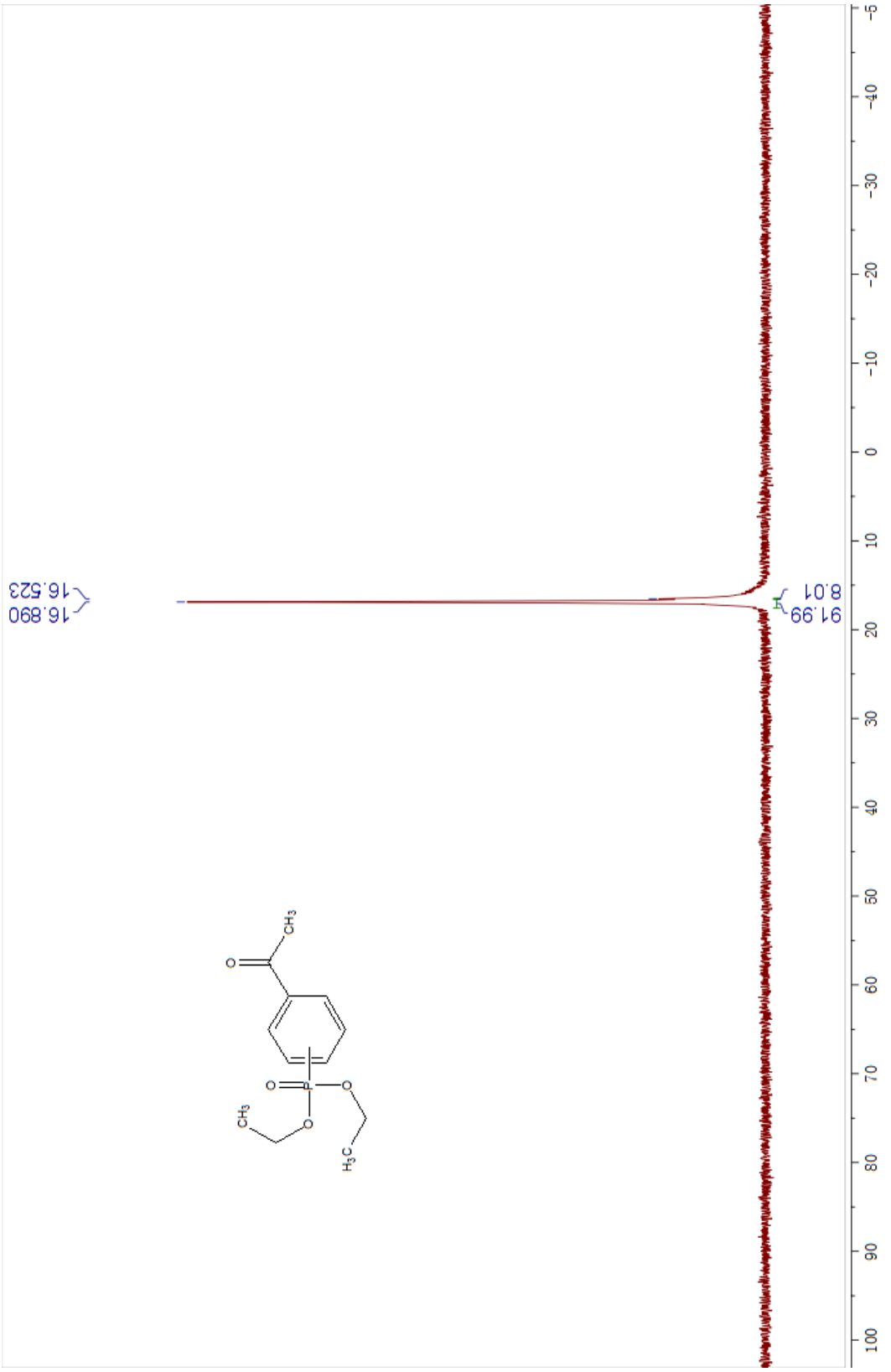
^{13}C NMR Spectrum of diethyl 2-fluoro-4-formylphenylphosphonate **3ga**



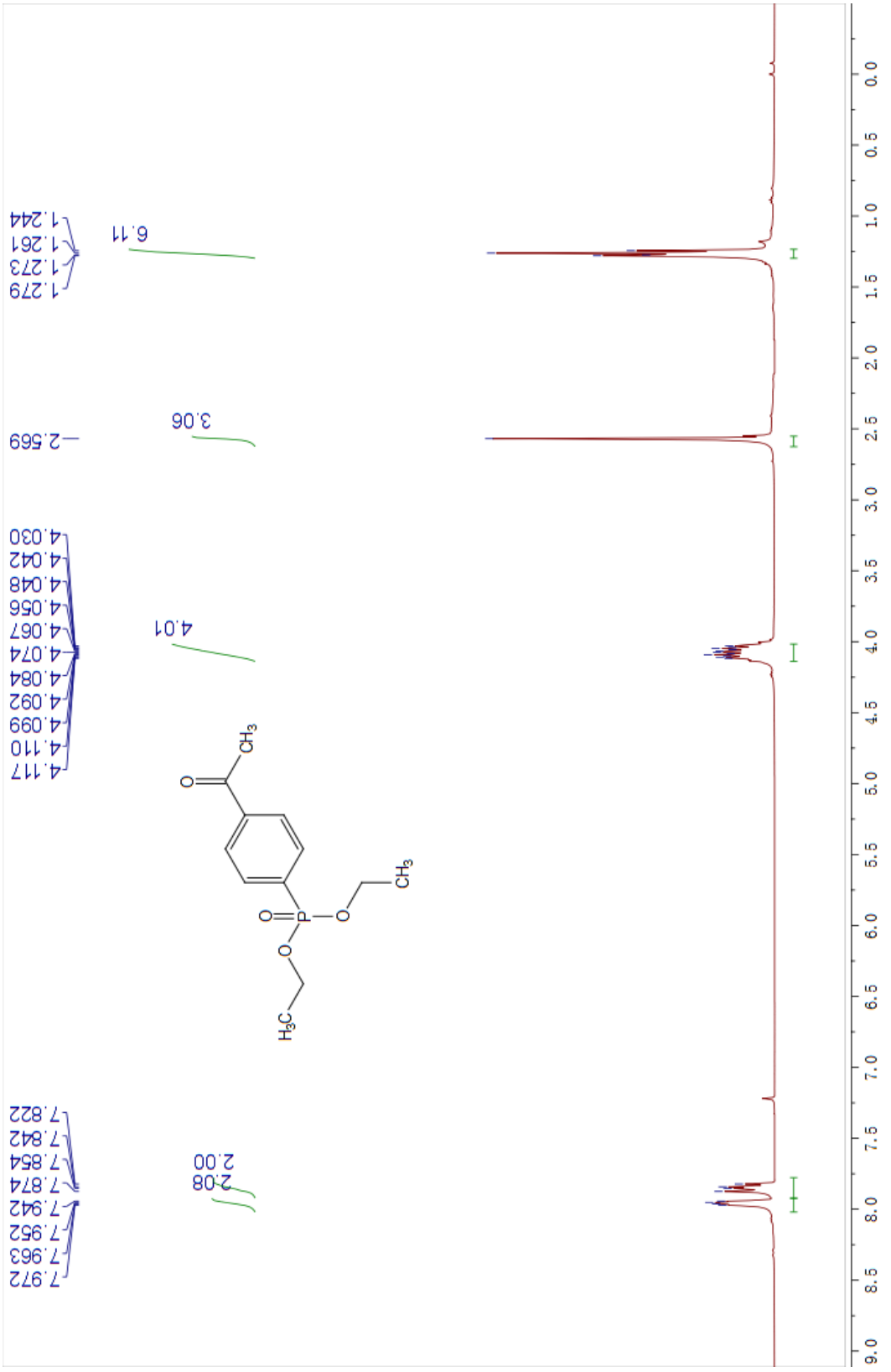
HR-MS Spectrum of diethyl 2-fluoro-4-formylphenylphosphonate **3ga**



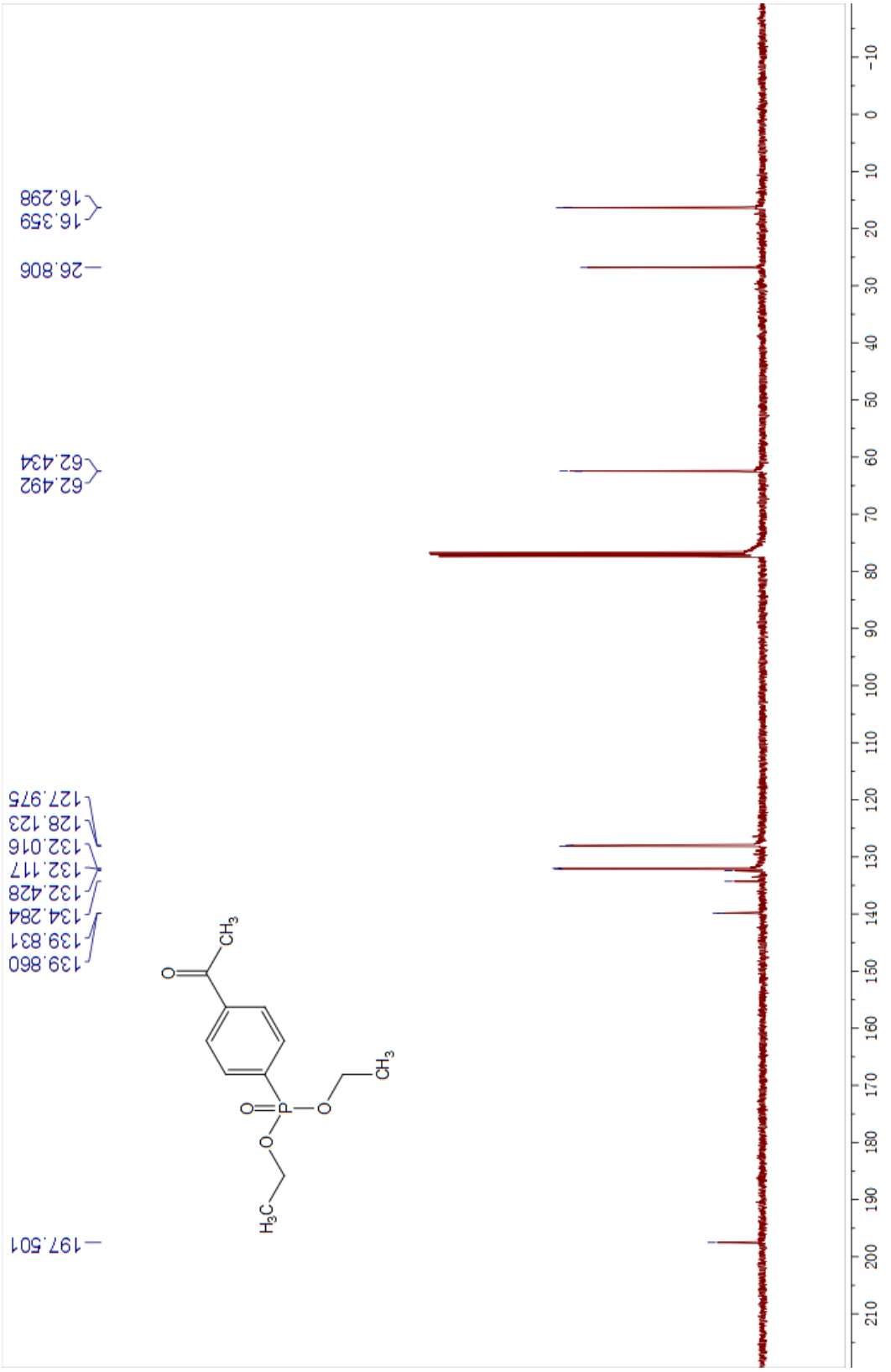
^{13}P NMR Spectrum of diethyl acetylphenylphosphonate **3ja**



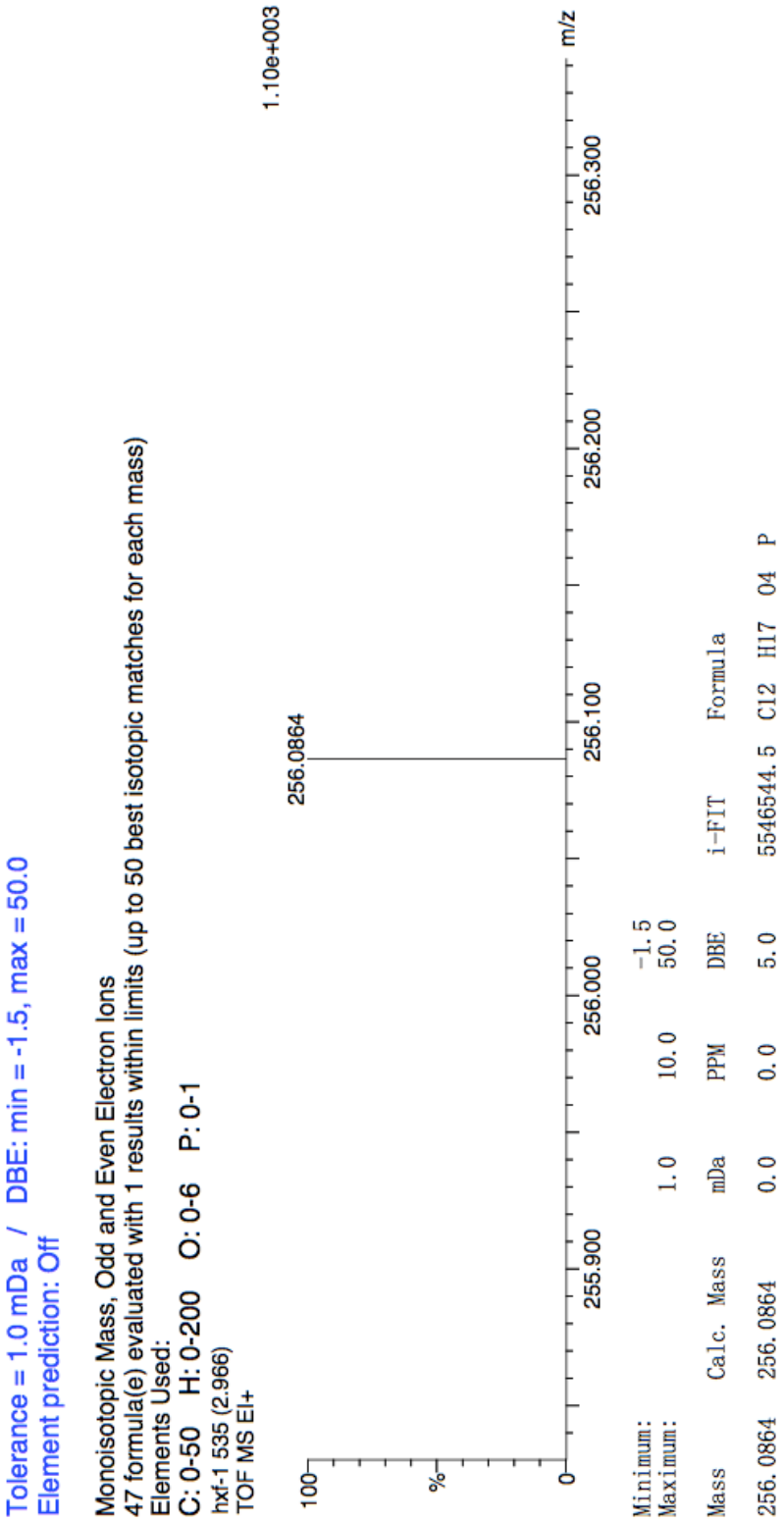
^{1}H NMR Spectrum of diethyl 4-acetylphenylphosphonate **3ja**



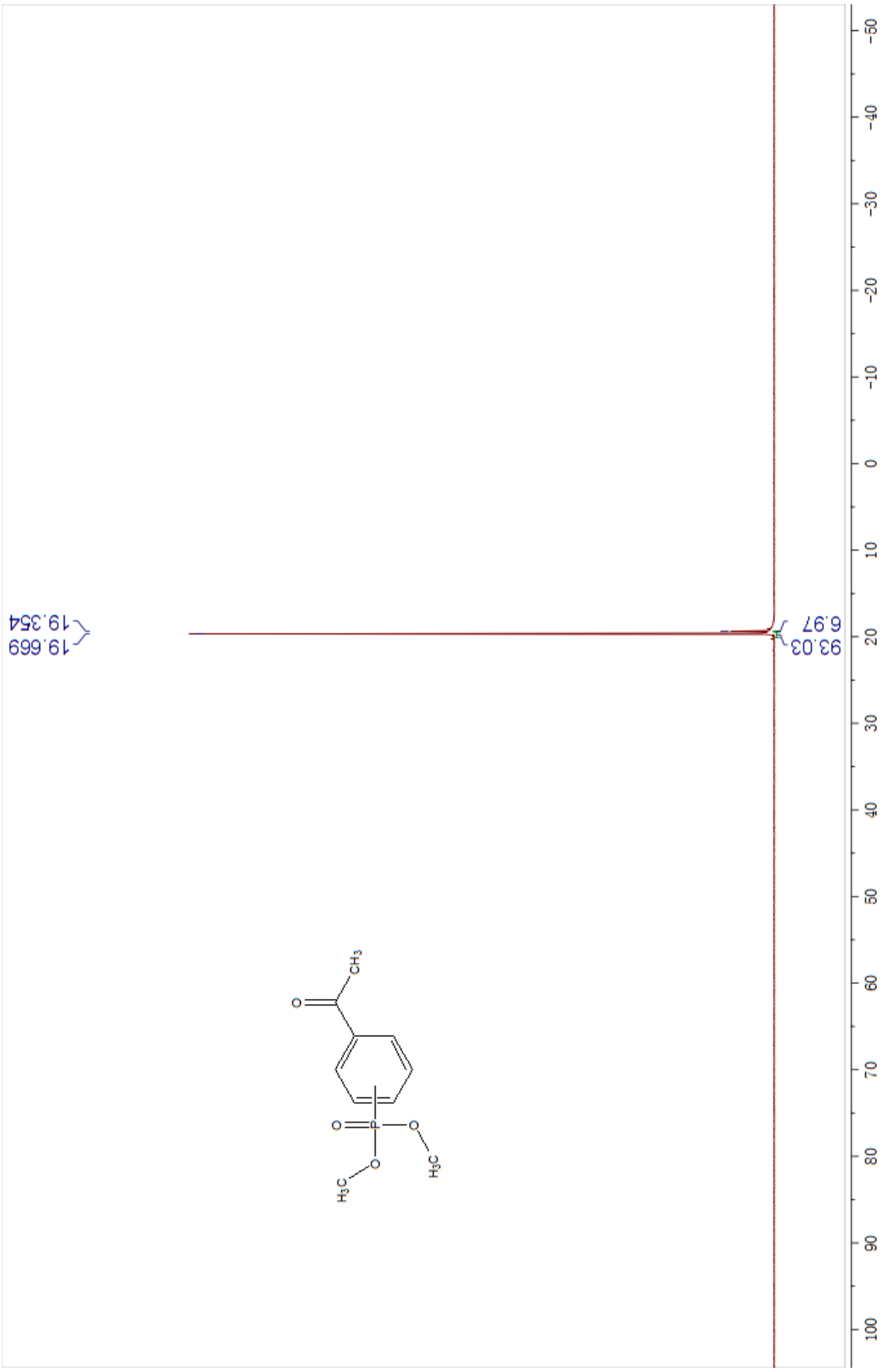
^{13}C NMR Spectrum of diethyl 4-acetylphenylphosphonate **3ja**



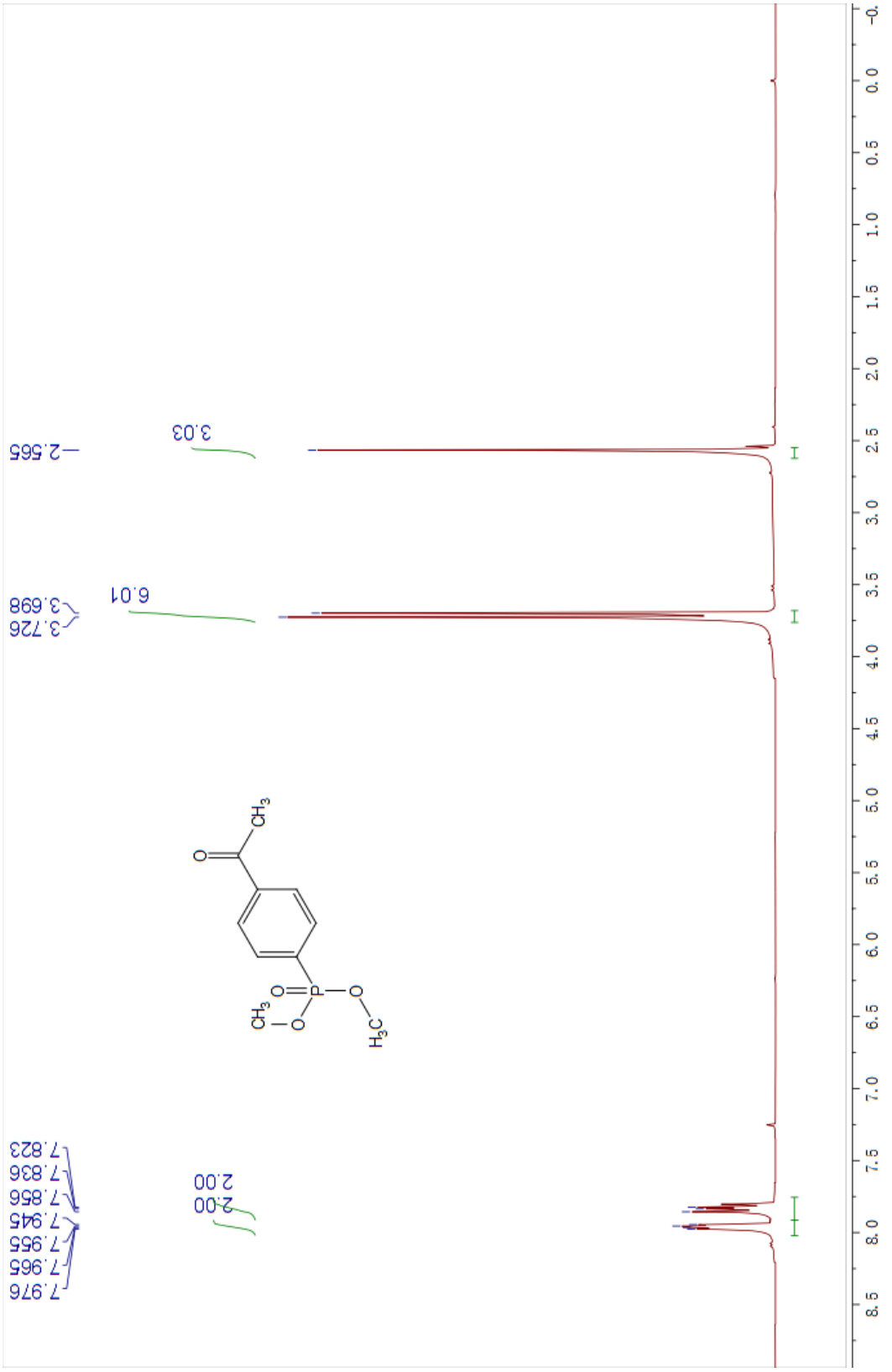
HR-MS Spectrum of diethyl 4-acetylphenylphosphonate **3ja**



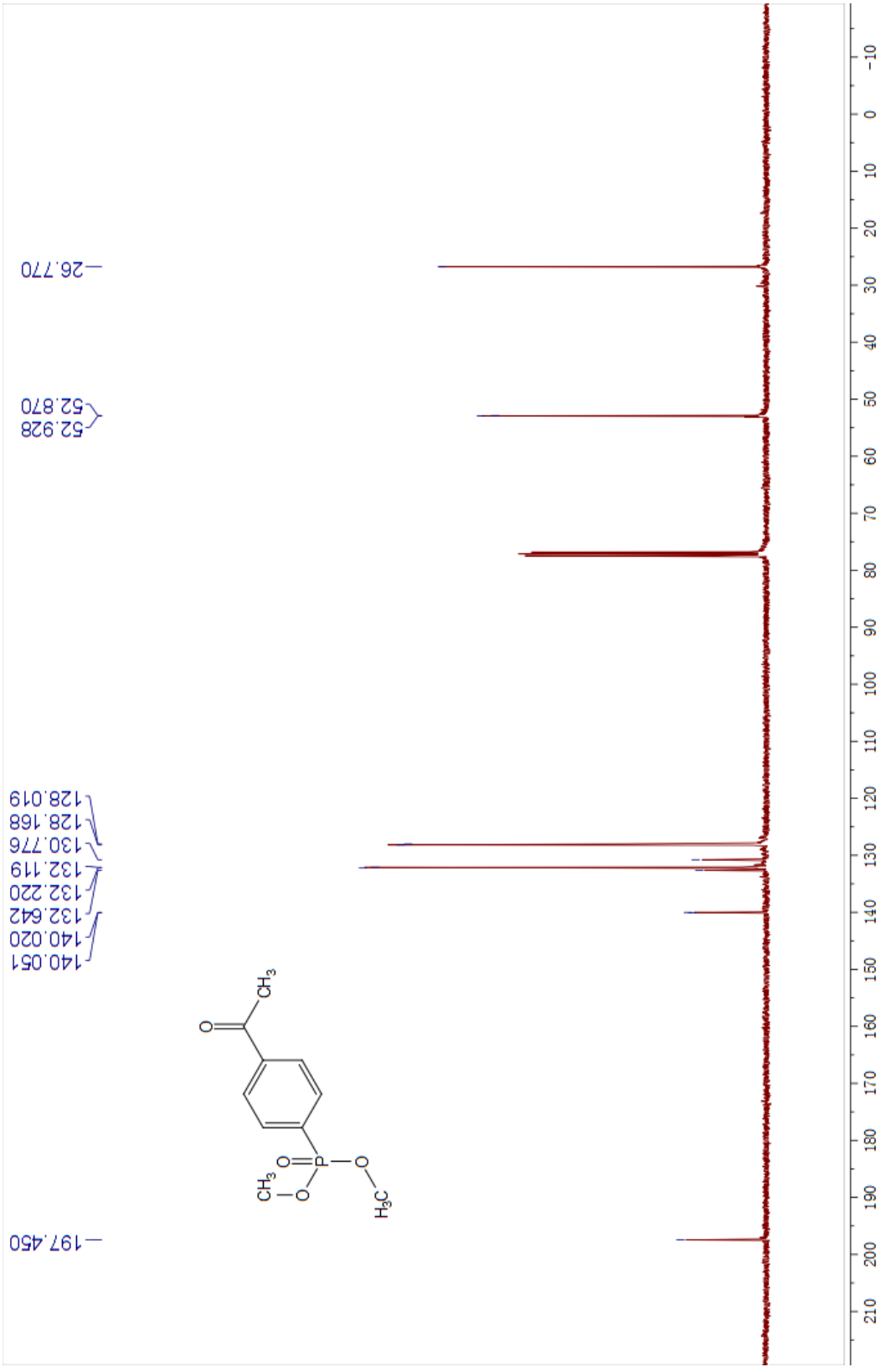
^{13}P NMR Spectrum of dimethyl acetylphenylphosphonate **3jb**



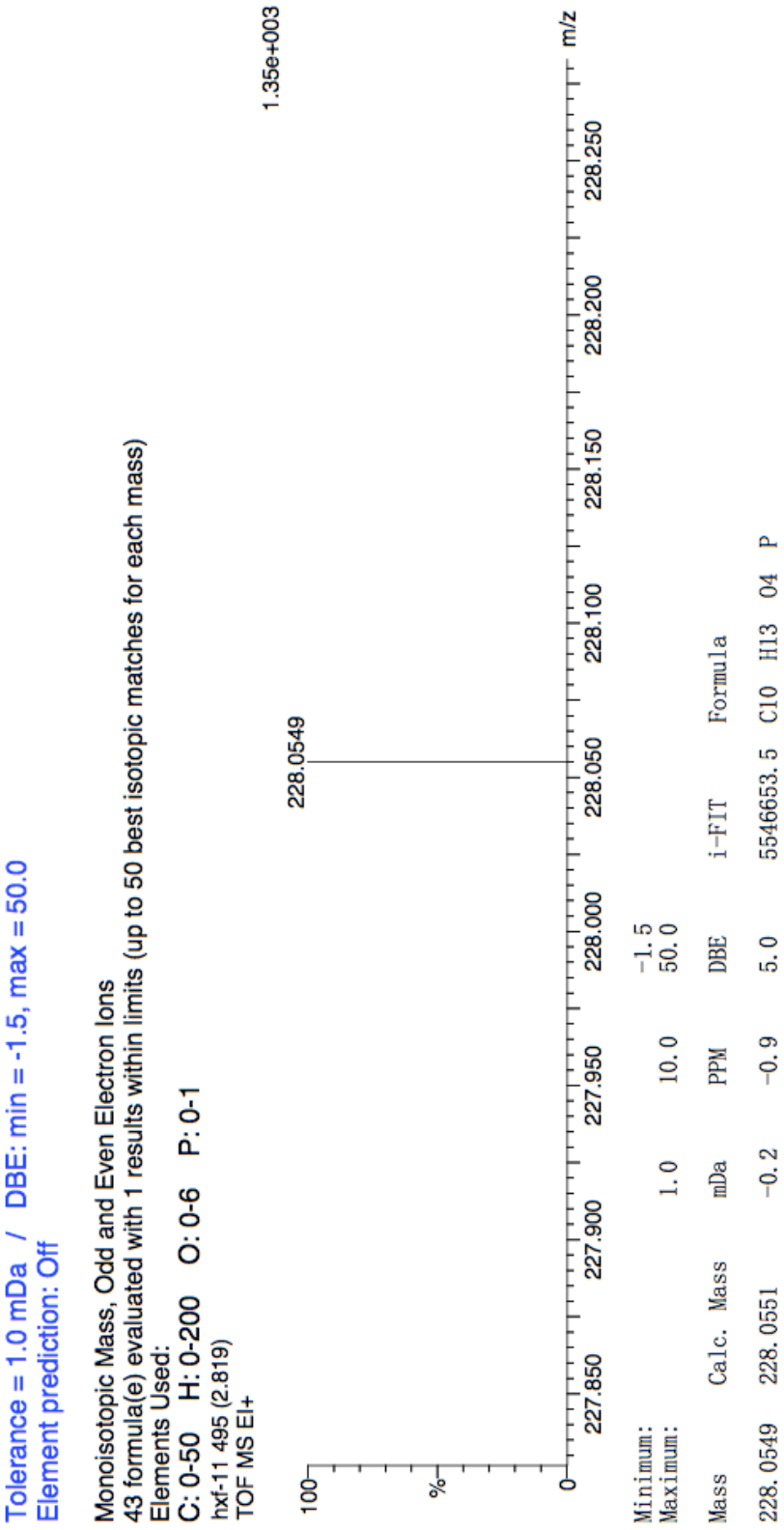
^{1}H NMR Spectrum of dimethyl 4-acetylphenylphosphonate **3jb**



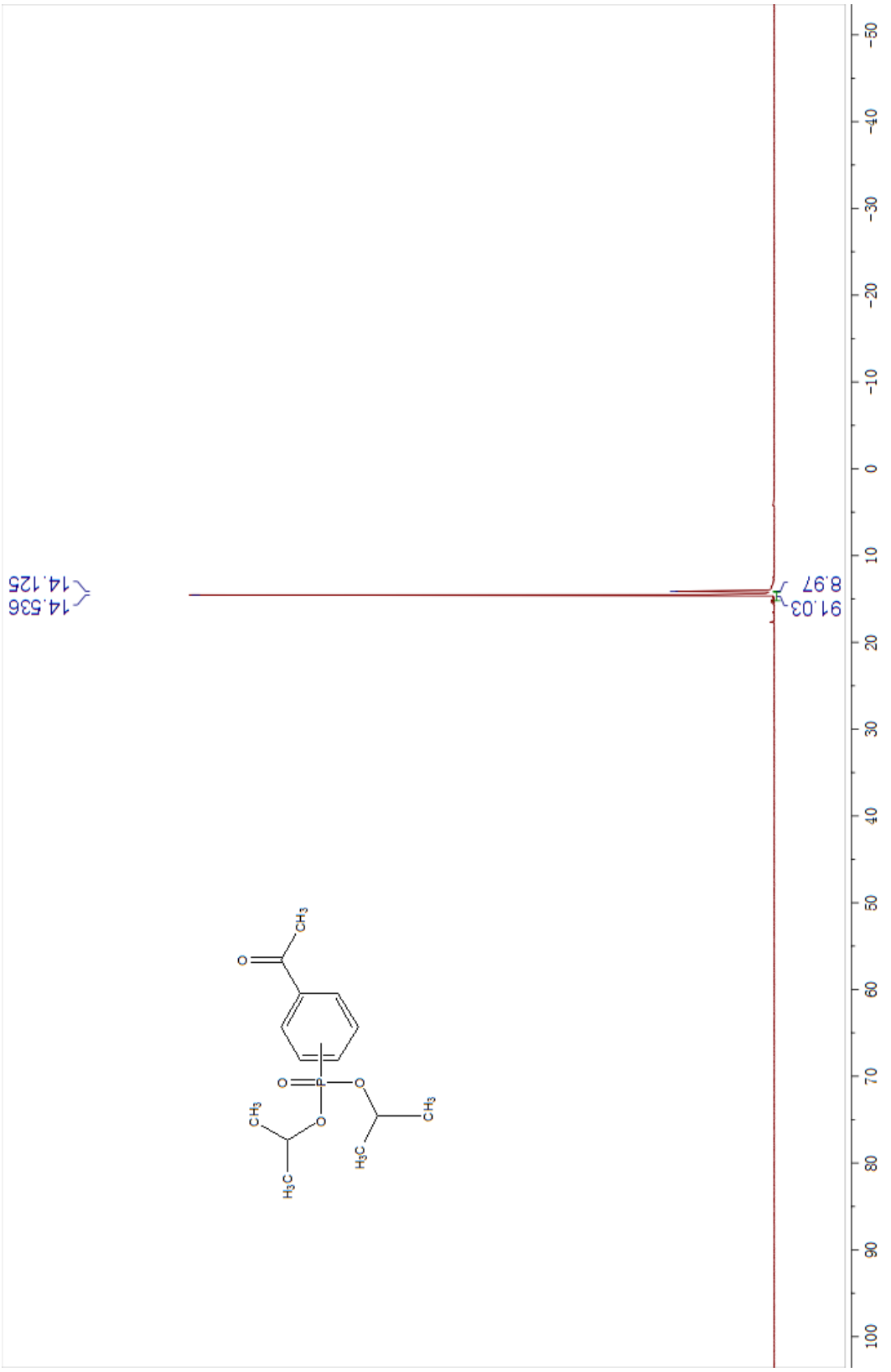
^{13}C NMR Spectrum of dimethyl 4-acetylphenylphosphonate **3jb**



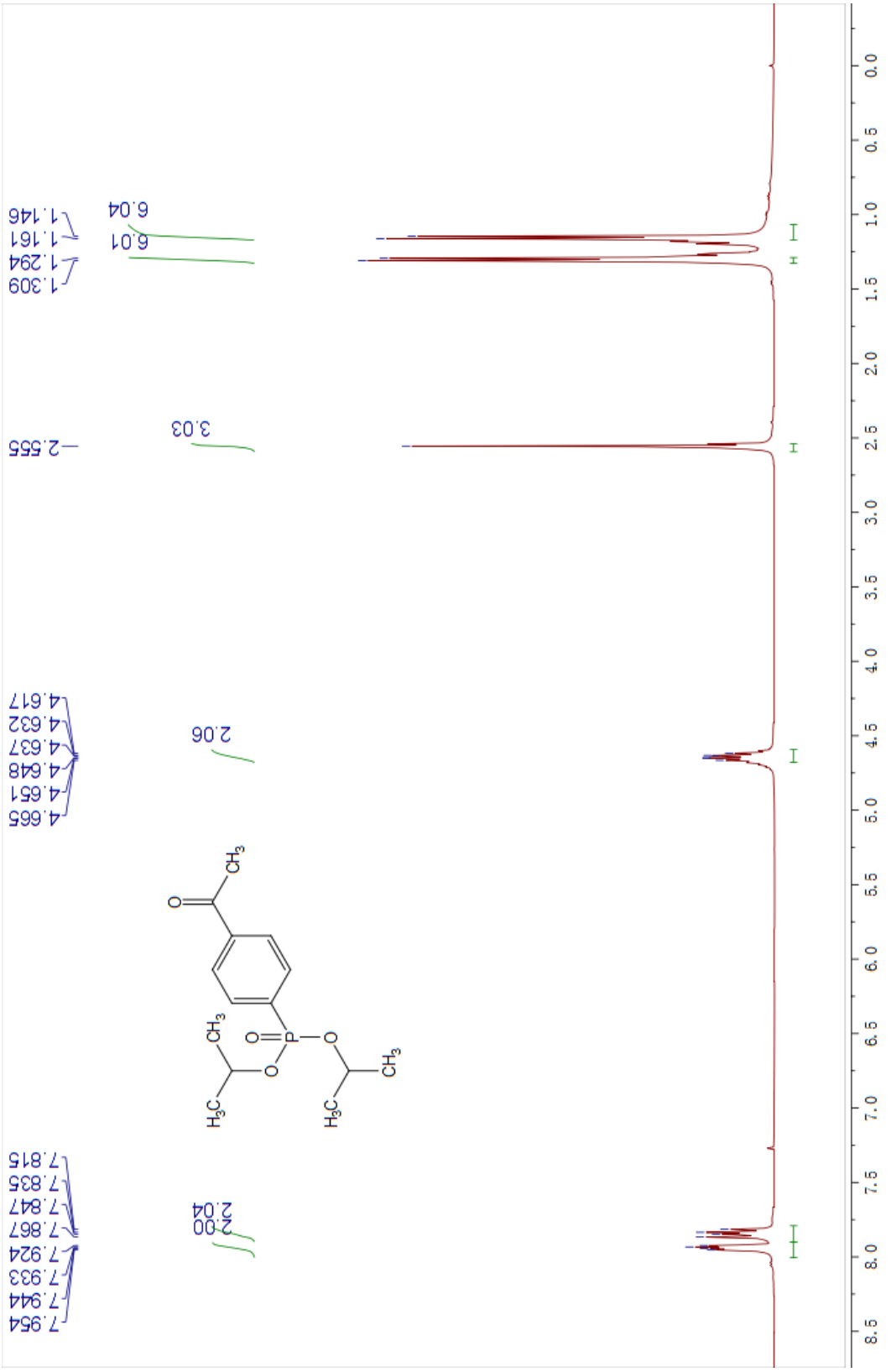
HR-MS Spectrum of dimethyl 4-acetylphenylphosphonate **3jb**



^{13}P NMR Spectrum of diisopropyl acetylphenylphosphonate **3jc**

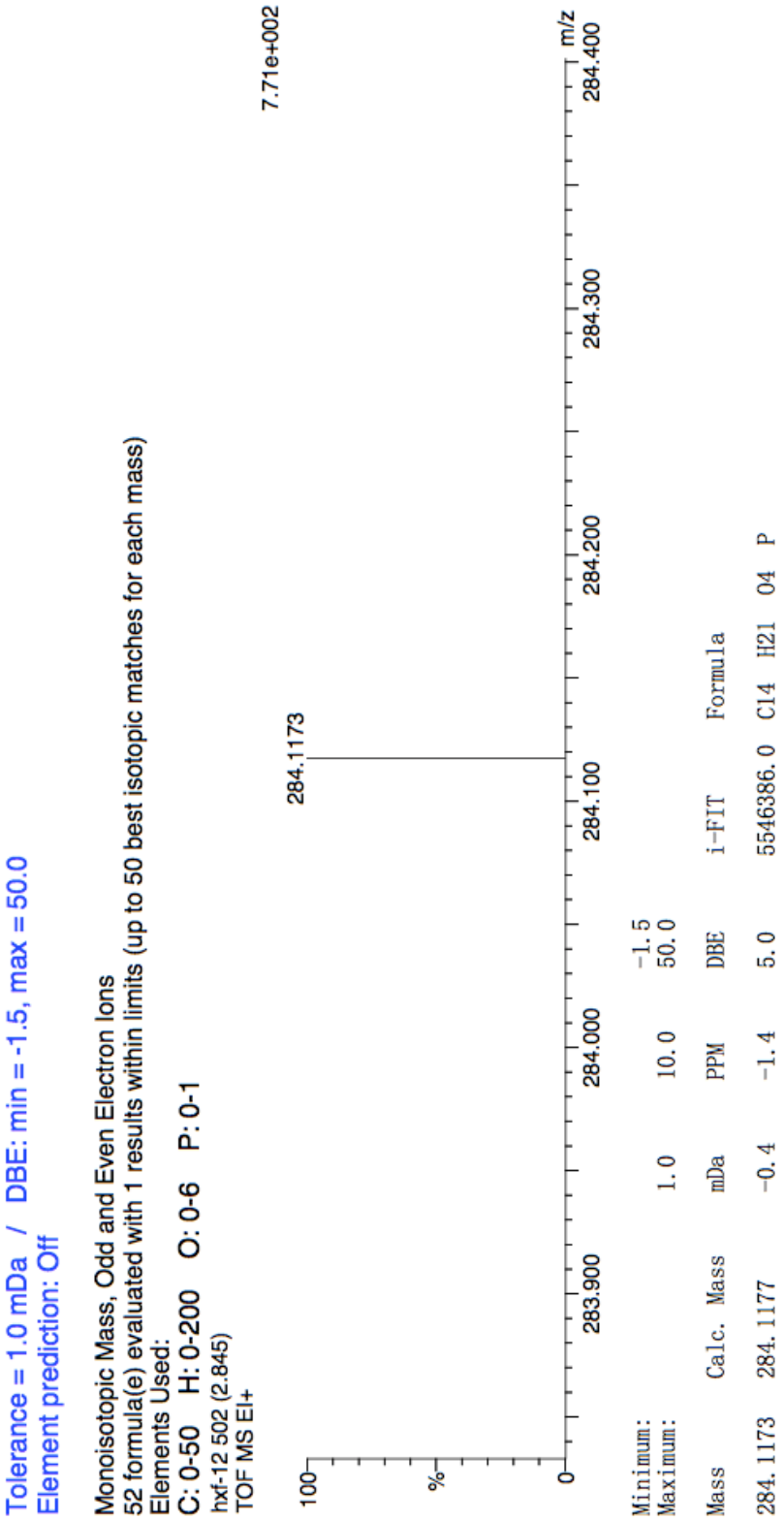


^{1}H NMR Spectrum of diisopropyl 4-acetylphenylphosphonate **3jc**

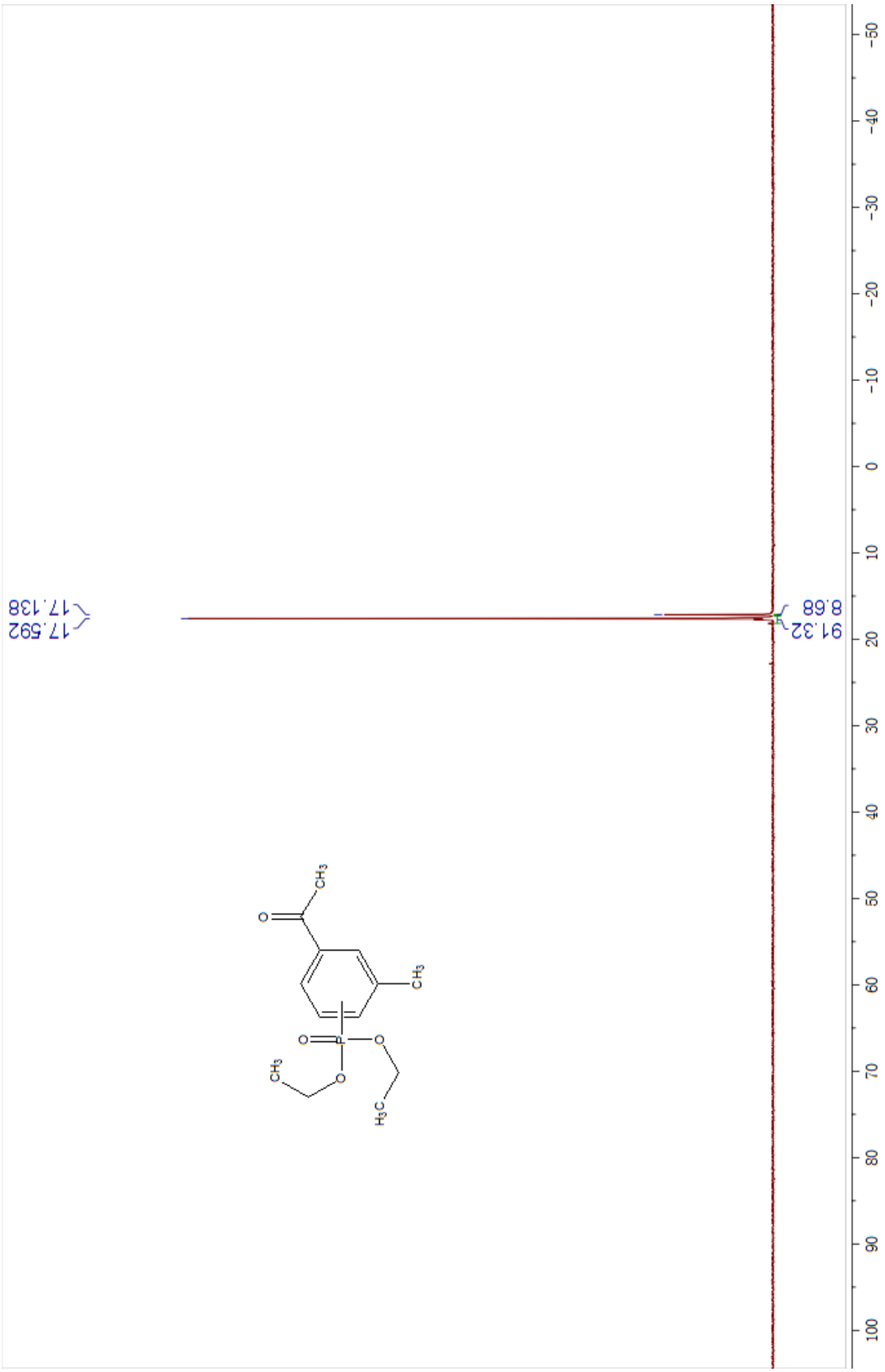


^{13}C NMR Spectrum of diisopropyl 4-acetylphenylphosphonate **3jc**

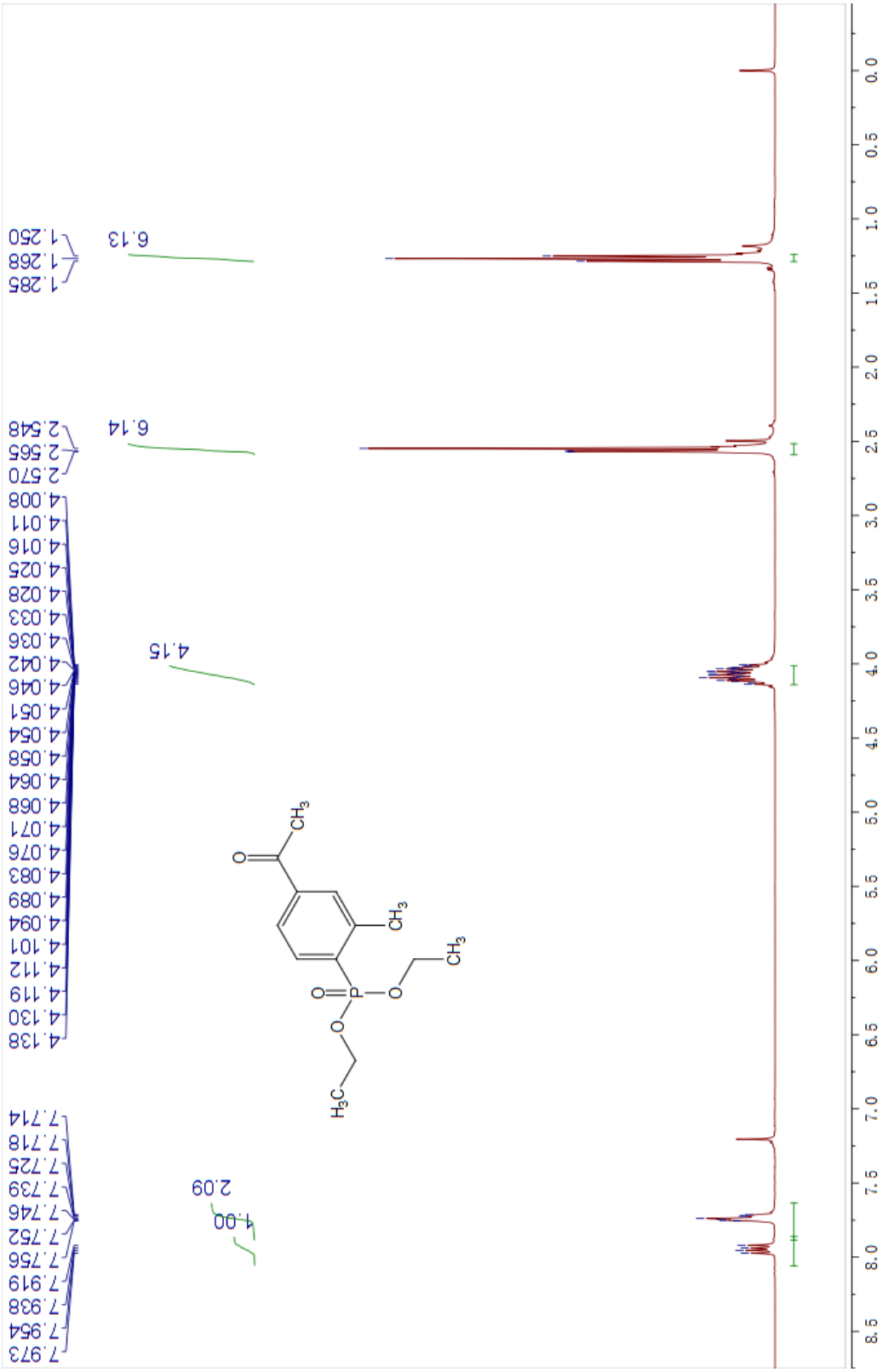
HR-MS Spectrum of diisopropyl 4-acetylphenylphosphonate **3jc**



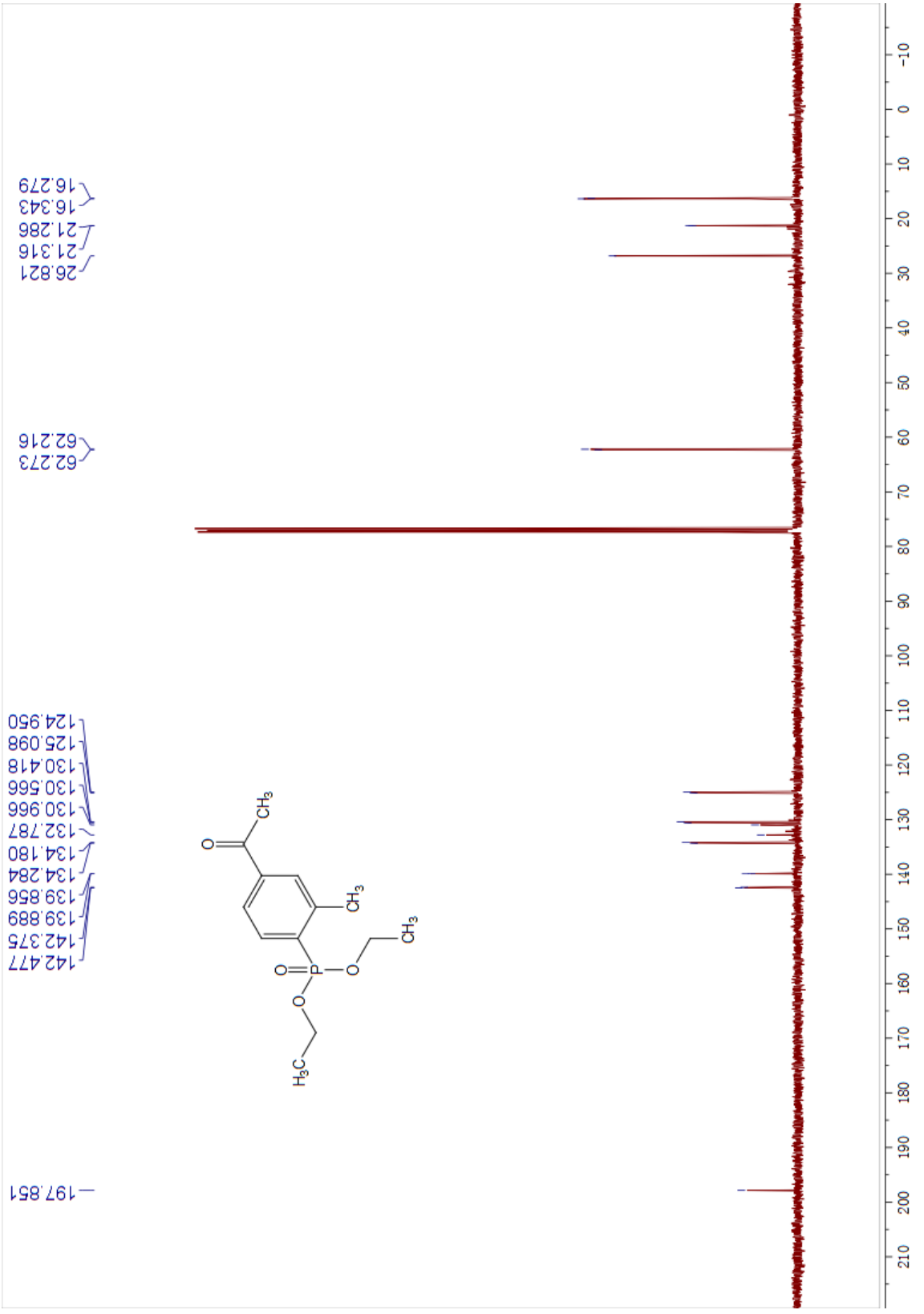
^{13}P NMR Spectrum of diethyl acetyl-2-methylphenylphosphonate **3ka**



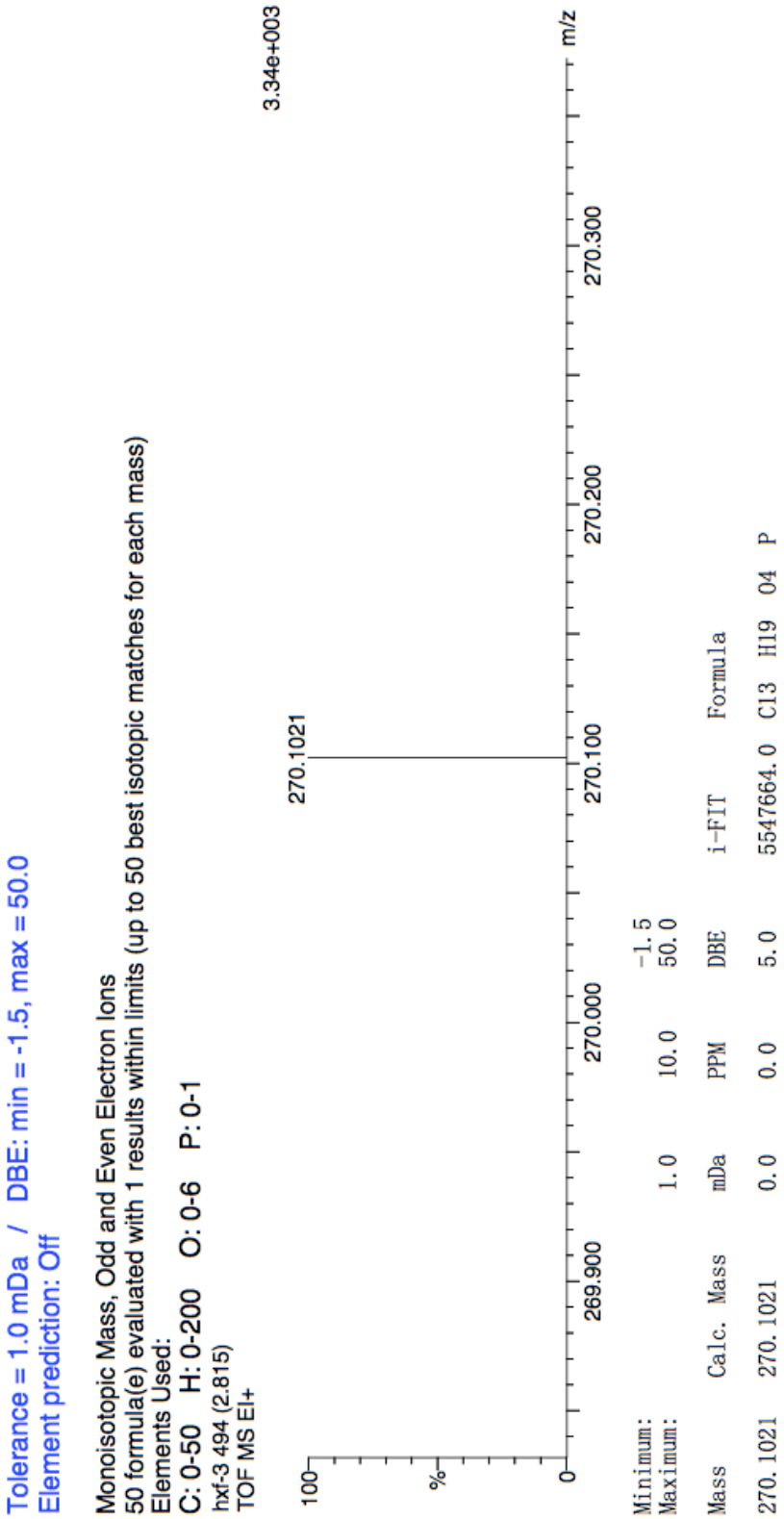
[1]H NMR Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate **3ka**



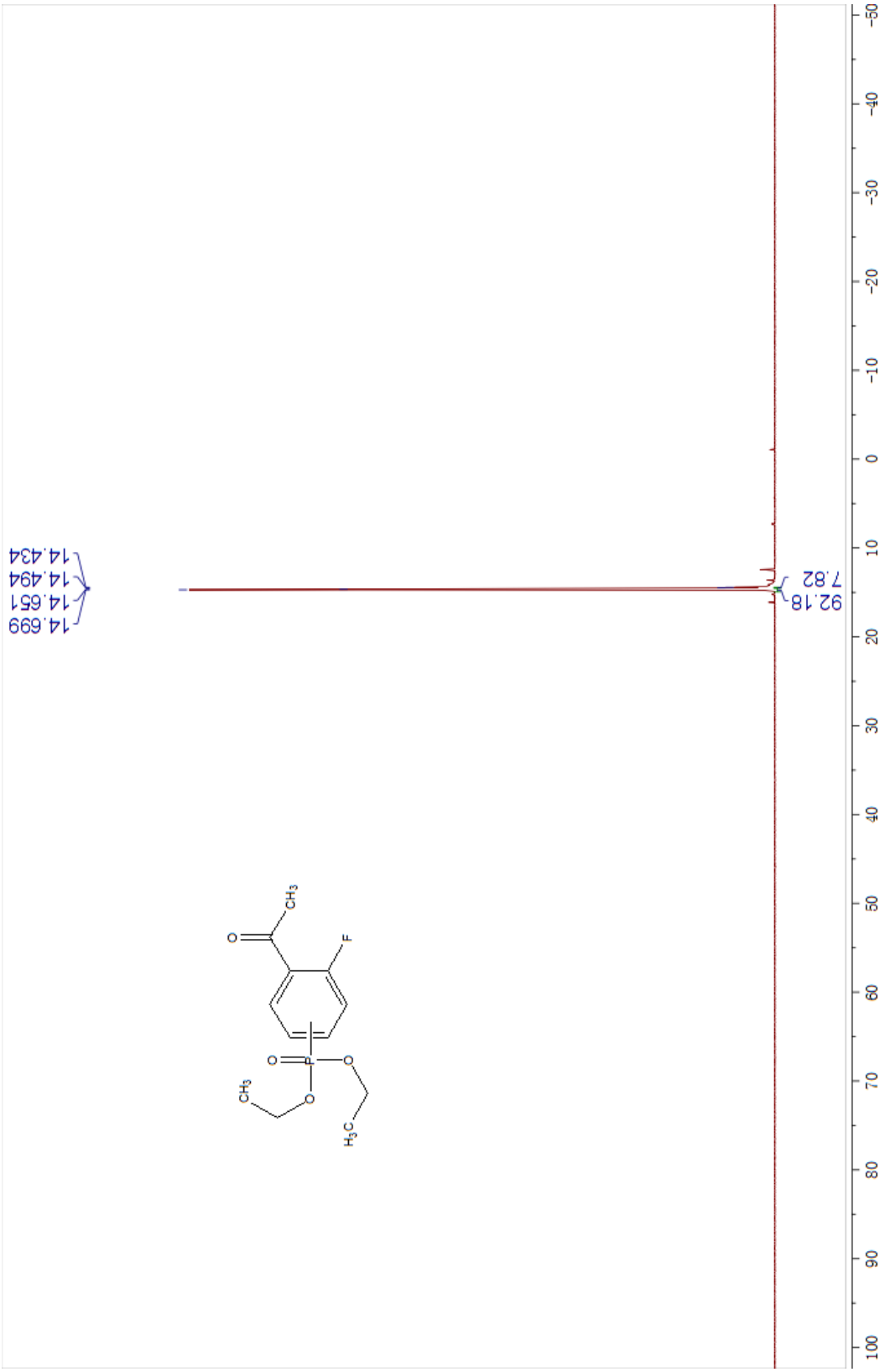
^{13}C NMR Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate **3ka**



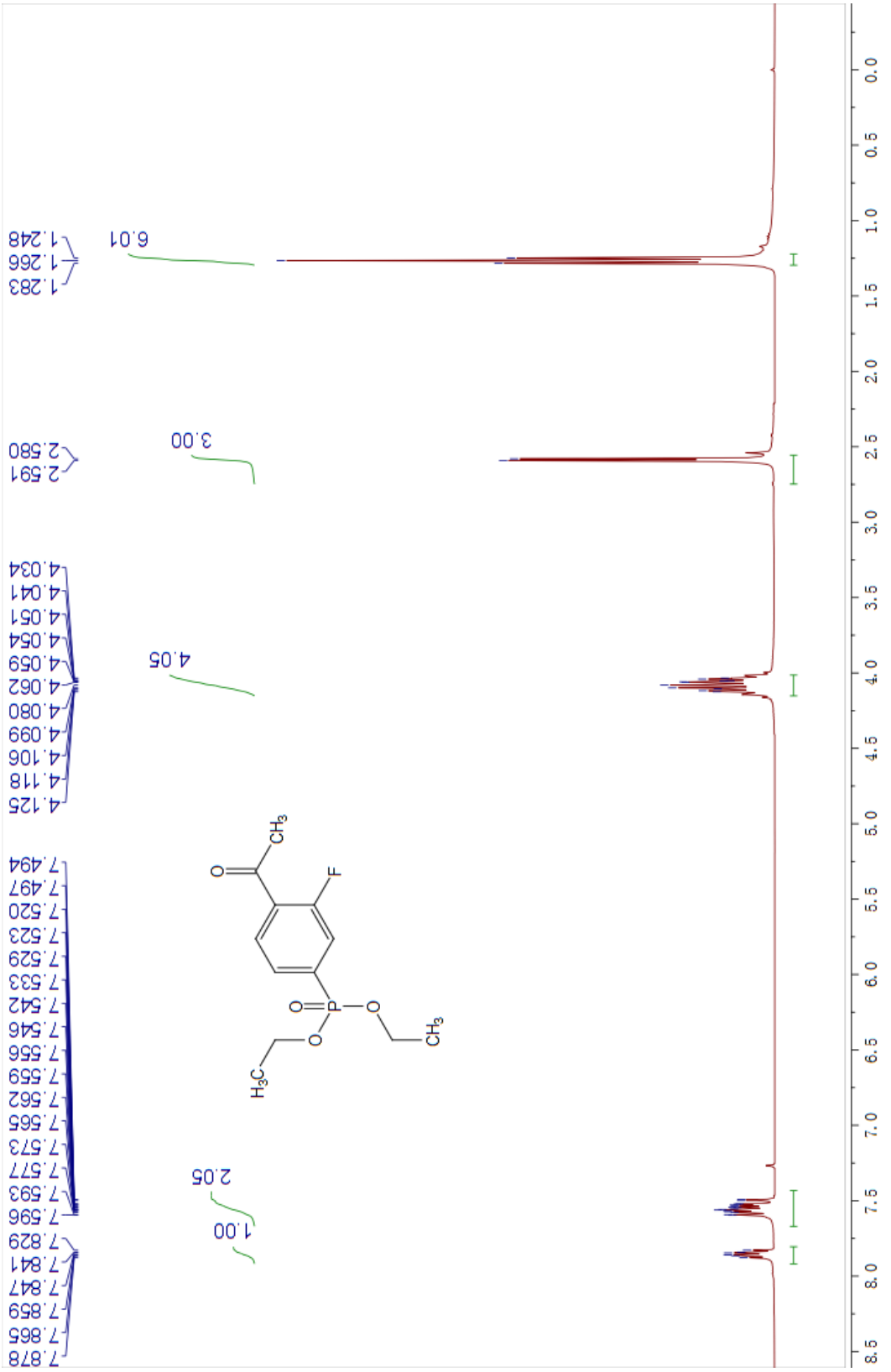
HR-MS Spectrum of diethyl 4-acetyl-2-methylphenylphosphonate **3ka**



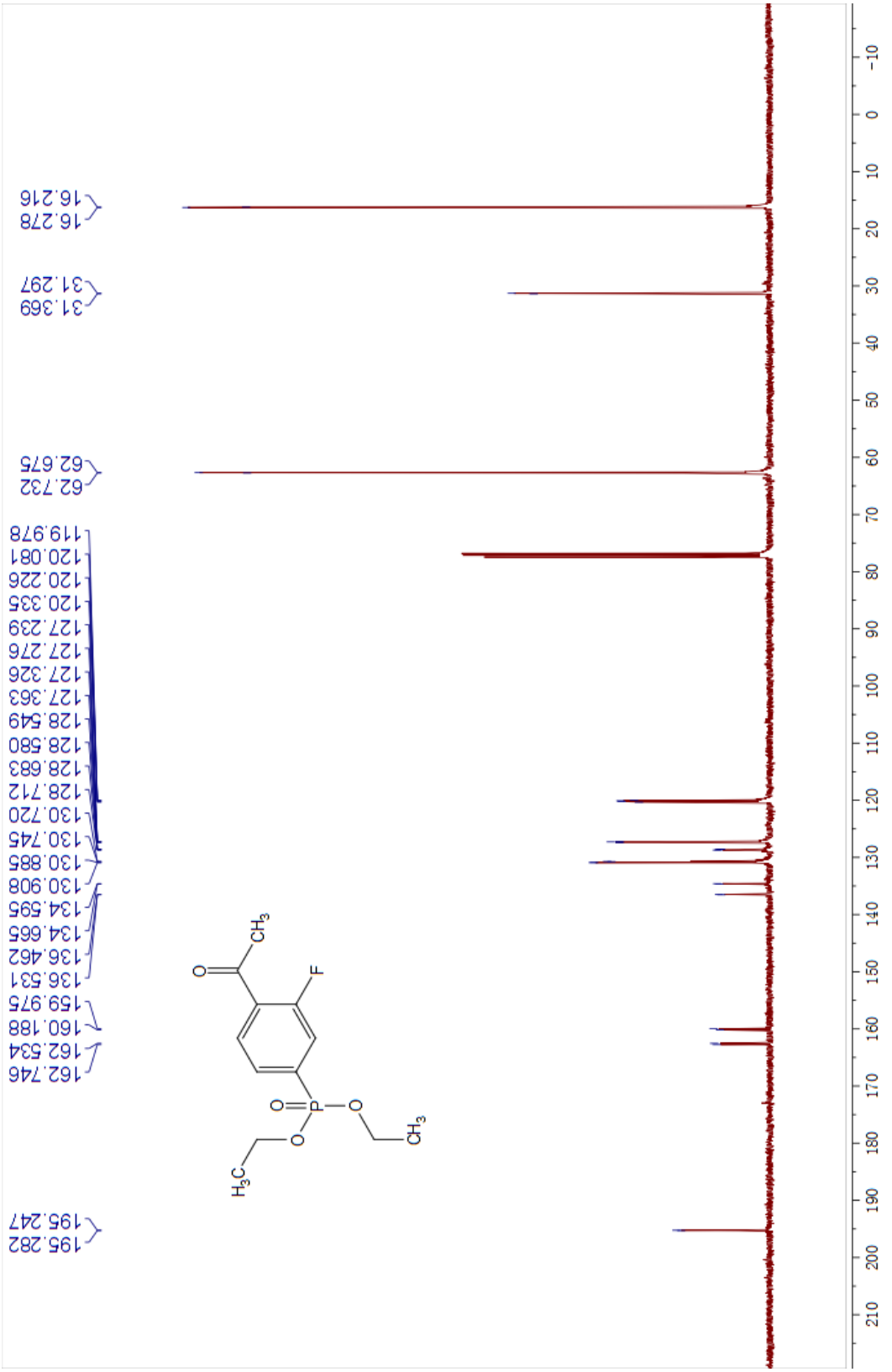
^{13}P NMR Spectrum of diethyl acetyl-3-fluorophenylphosphonate **3ma**



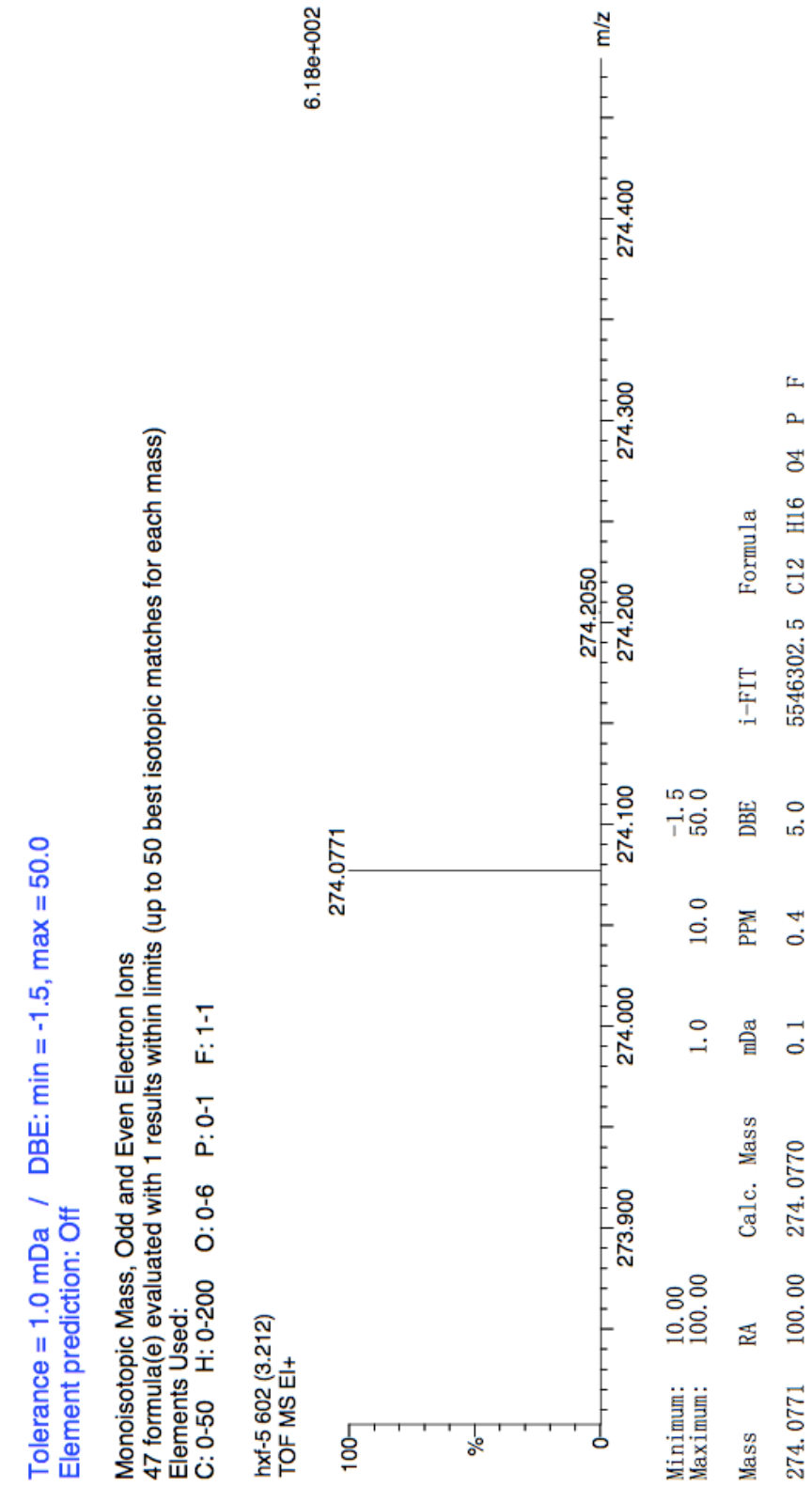
^{1}H NMR Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate **3ma**



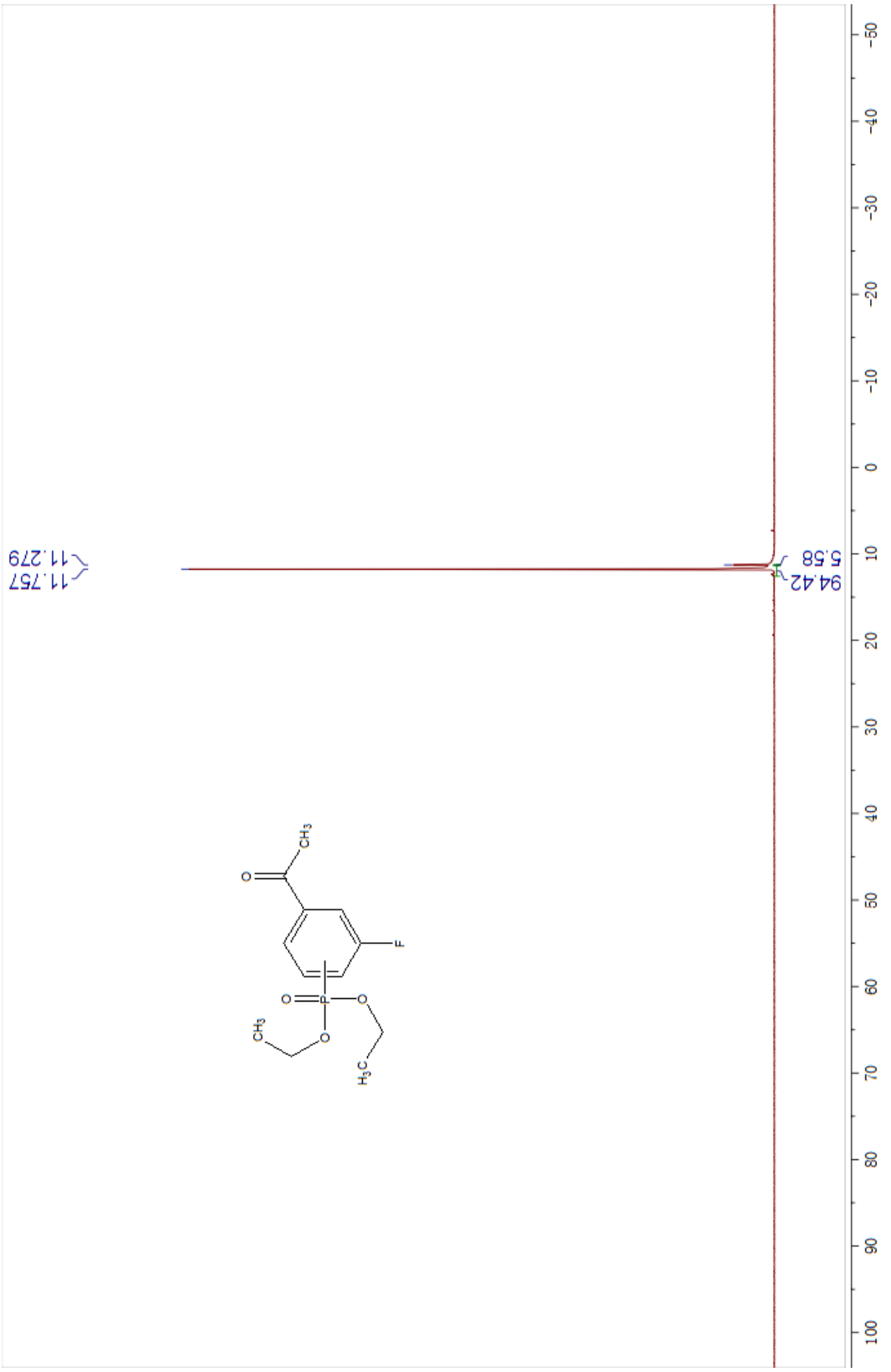
^{13}C NMR Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate **3ma**



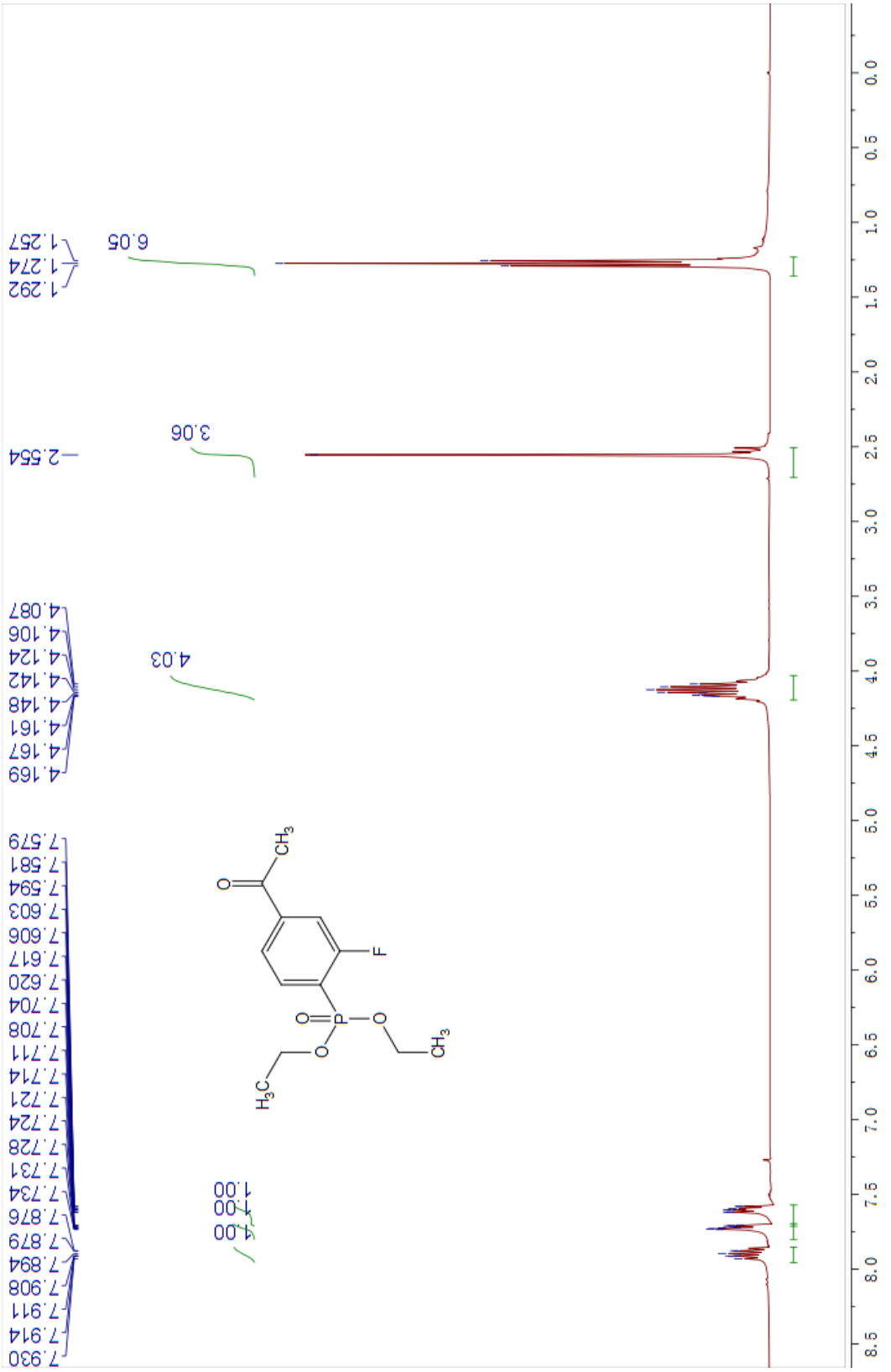
HR-MS Spectrum of diethyl 4-acetyl-3-fluorophenylphosphonate **3ma**



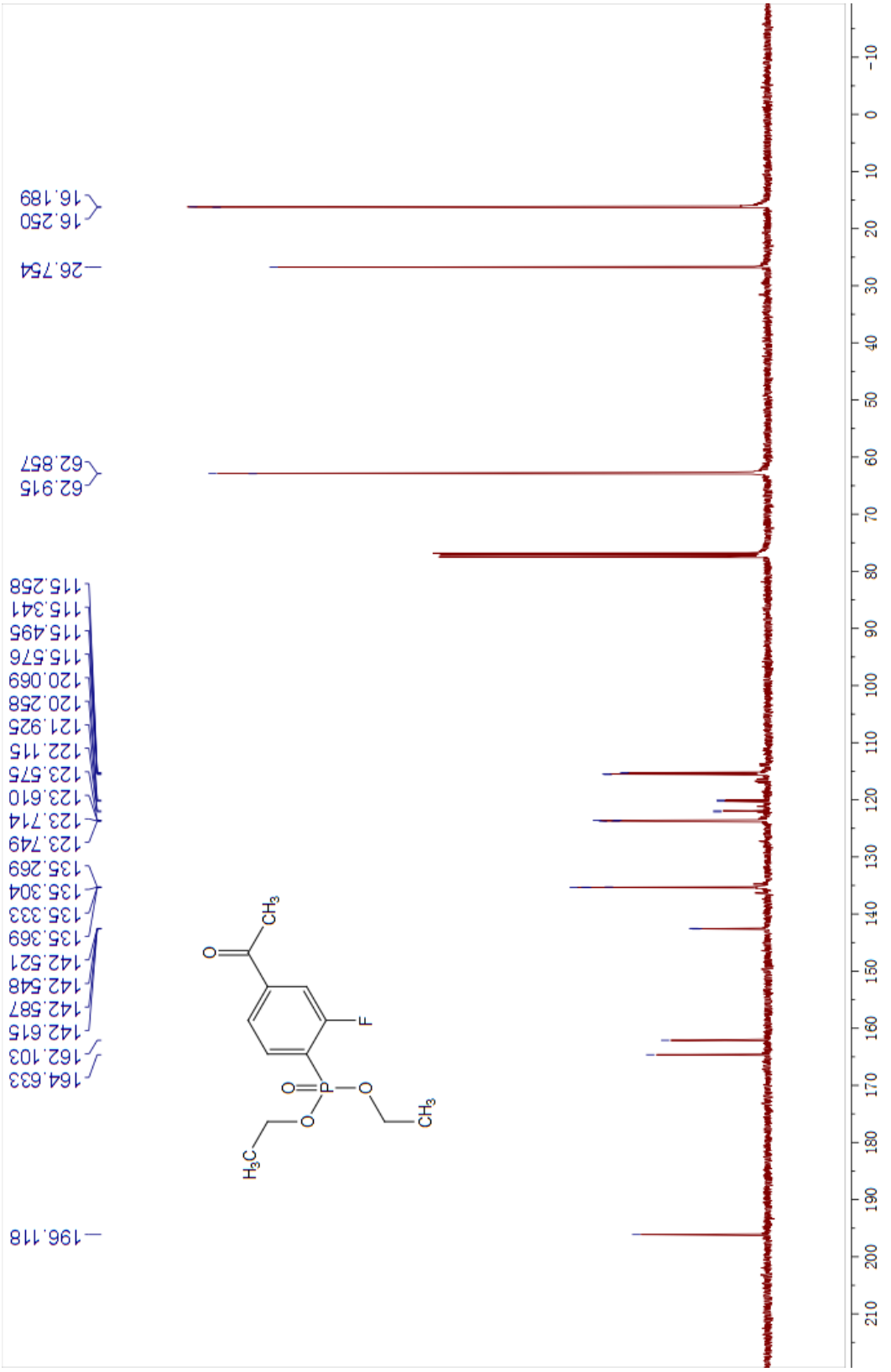
^{13}P NMR Spectrum of diethyl acetyl-2-fluorophenylphosphonate **3na**



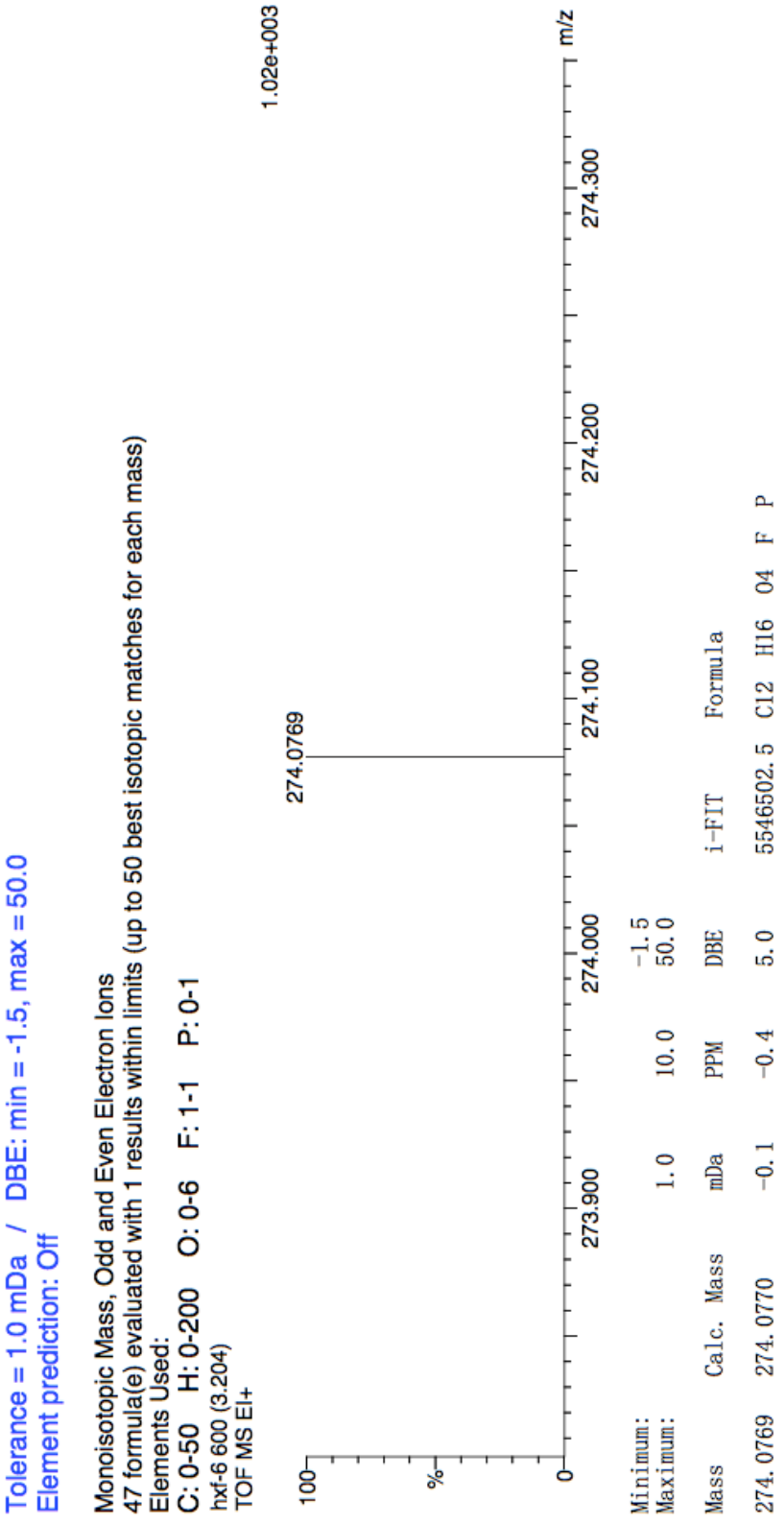
^{1}H NMR Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate **3na**



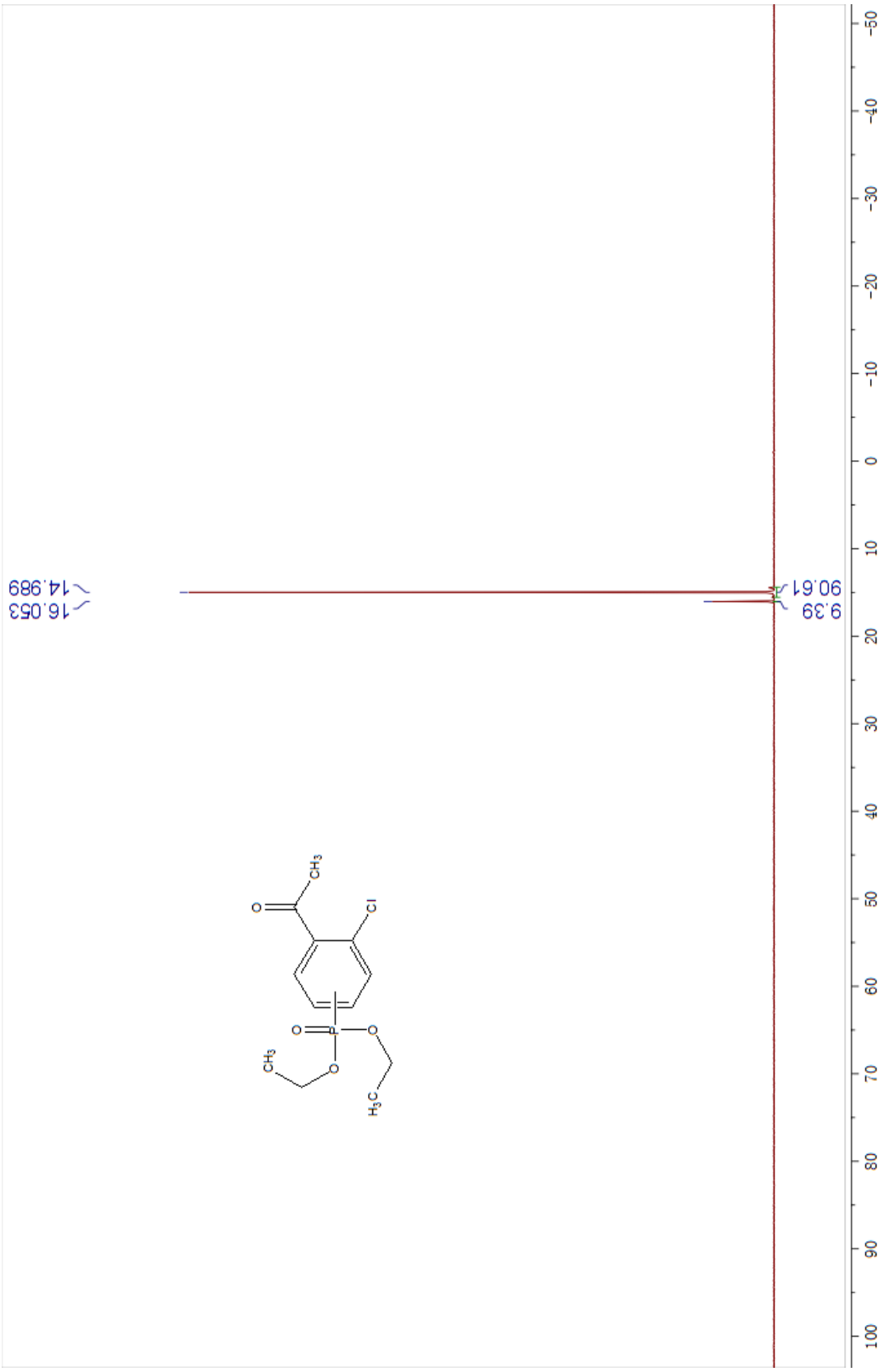
^{13}C NMR Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate **3na**



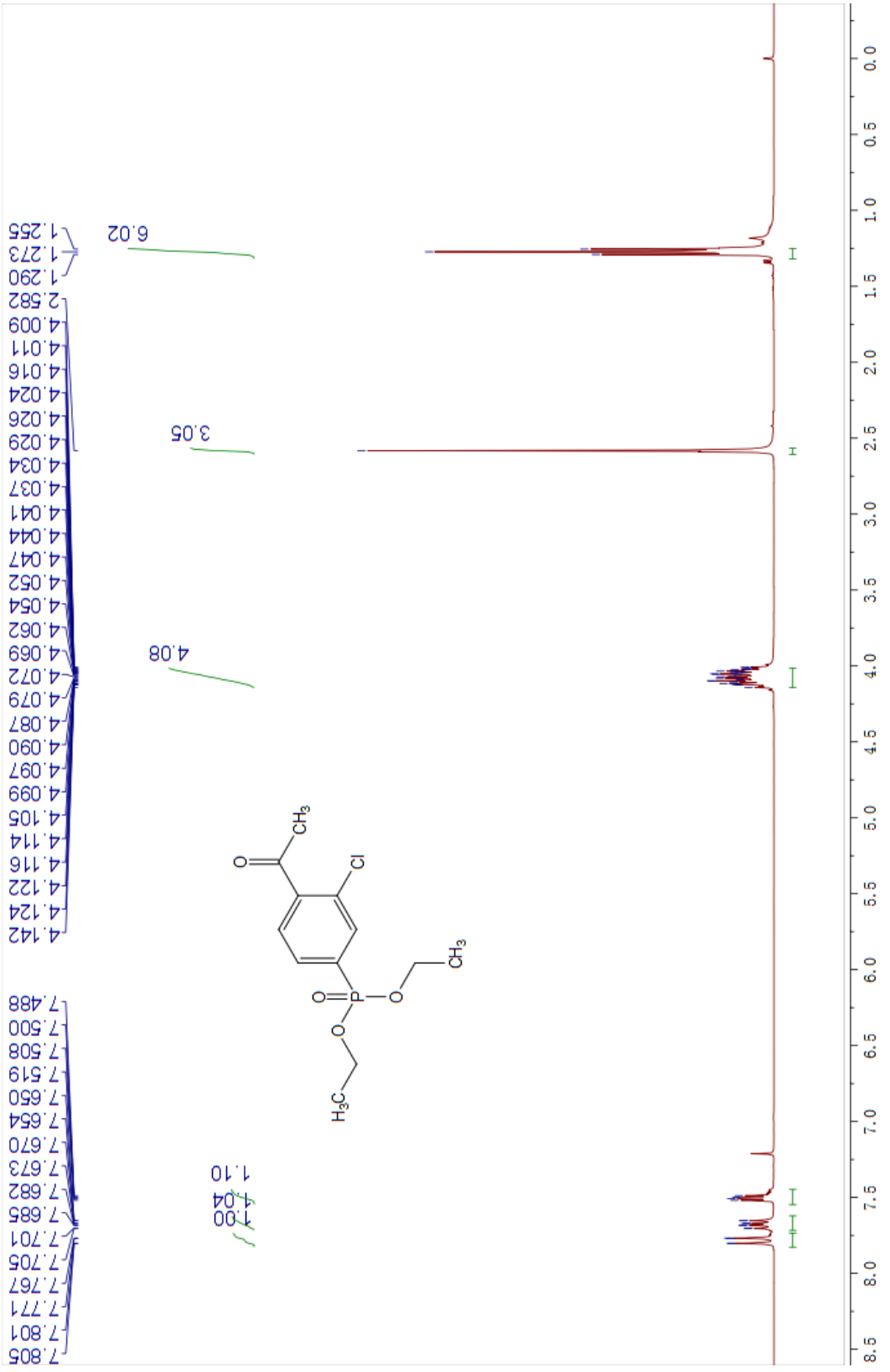
HR-MS Spectrum of diethyl 4-acetyl-2-fluorophenylphosphonate **3na**



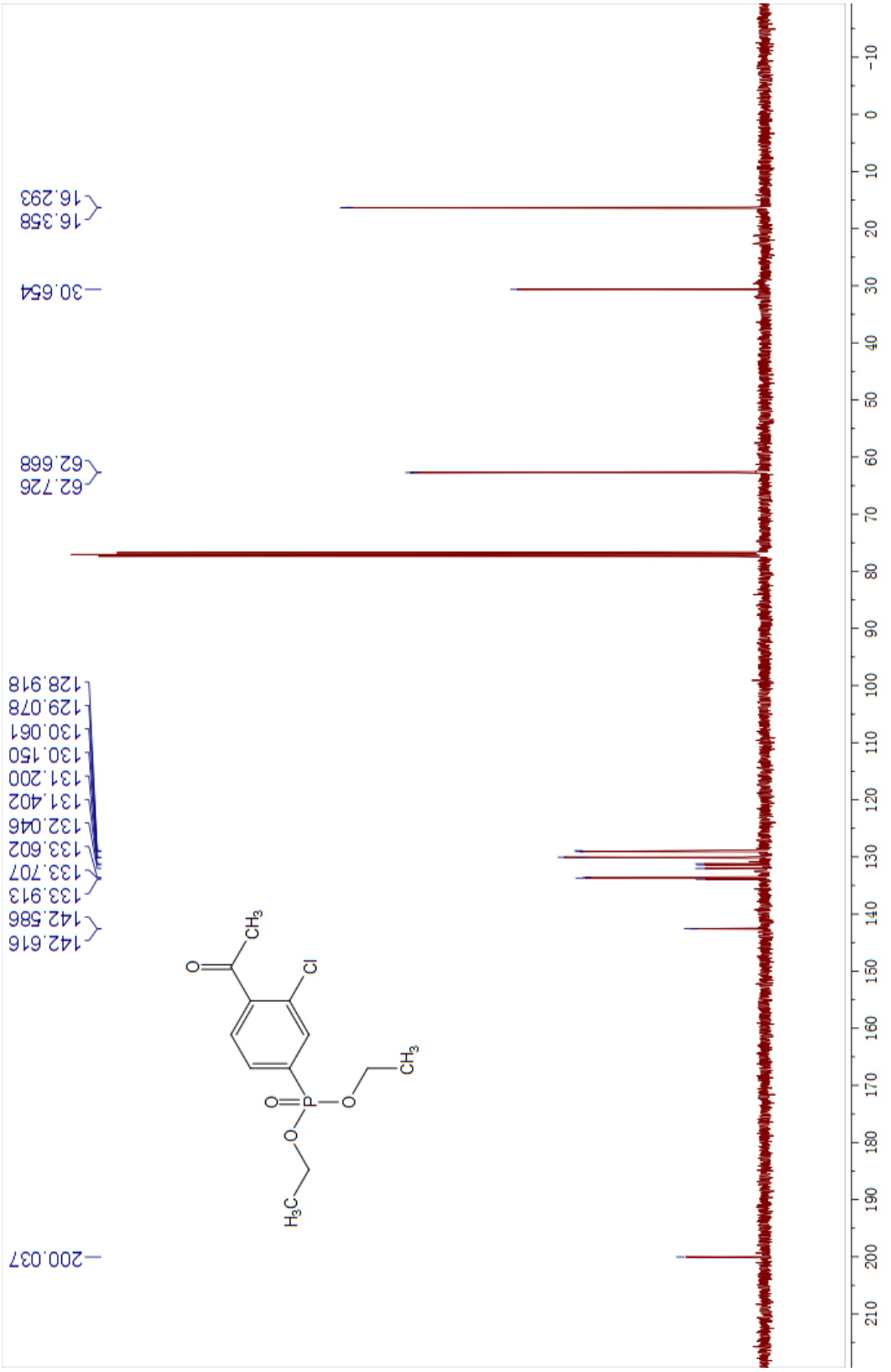
^{13}P NMR Spectrum of diethyl acetyl-3-chlorophenylphosphonate **3oa**



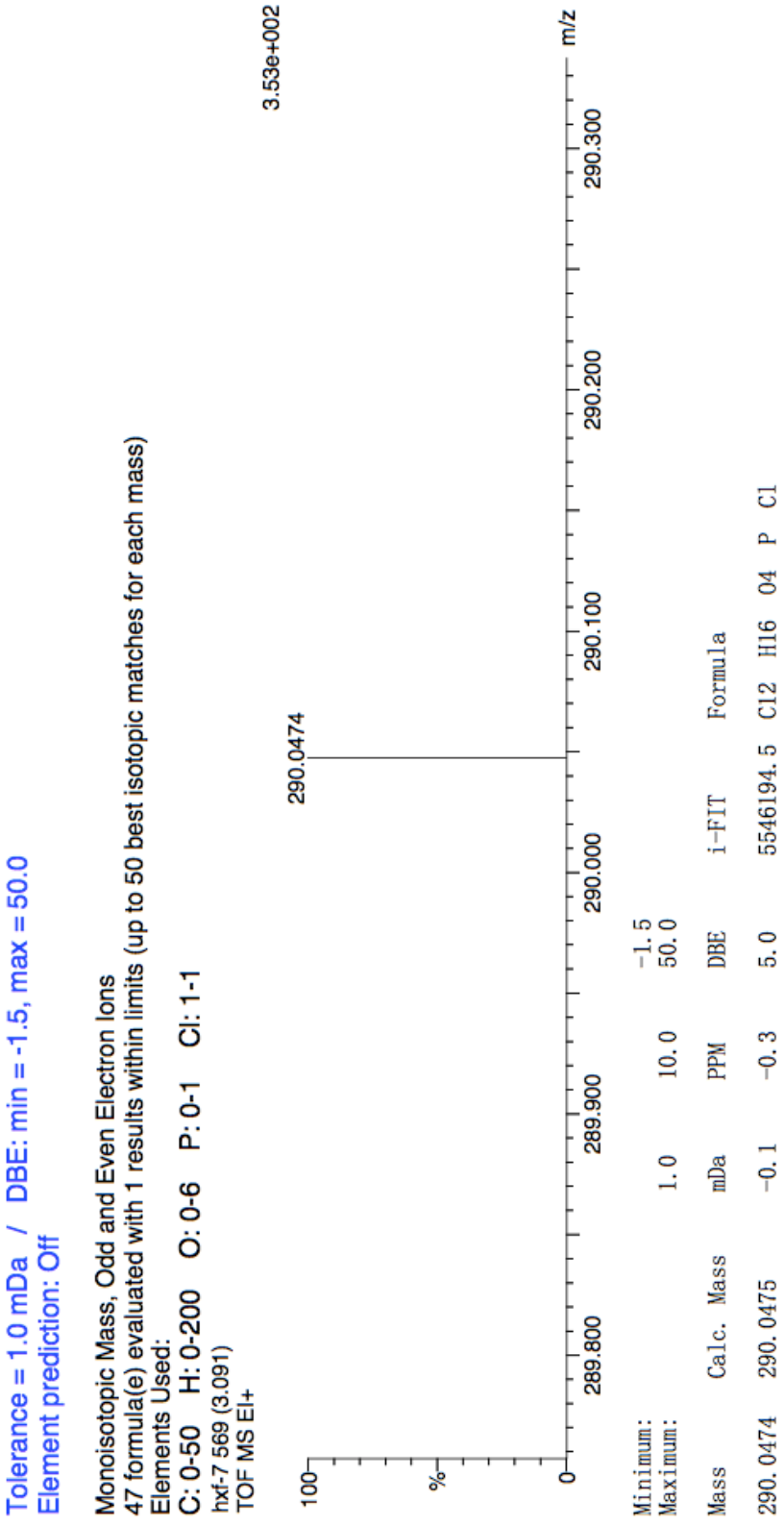
^{1}H NMR Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **3oa**



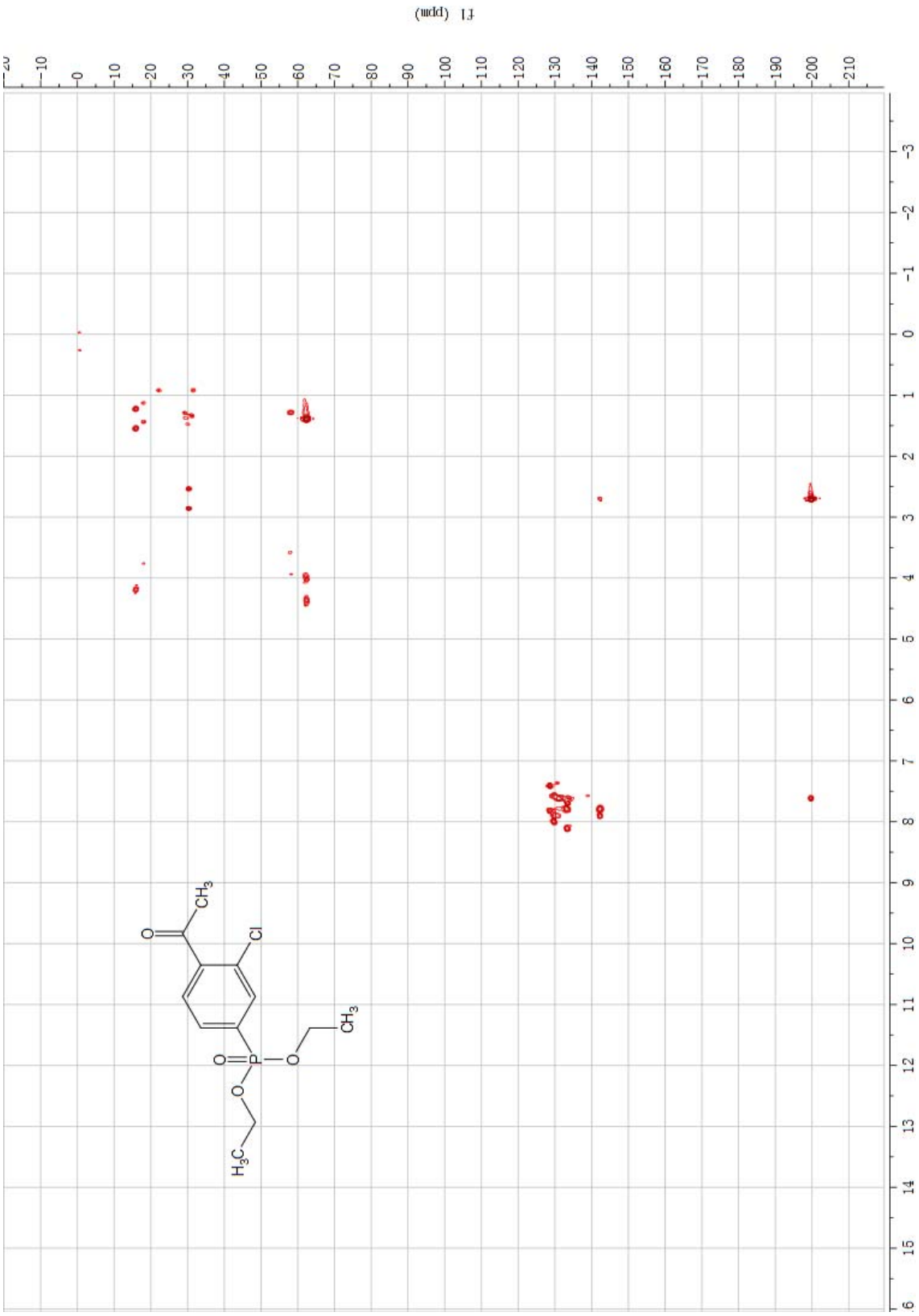
^{13}C NMR Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **3oa**



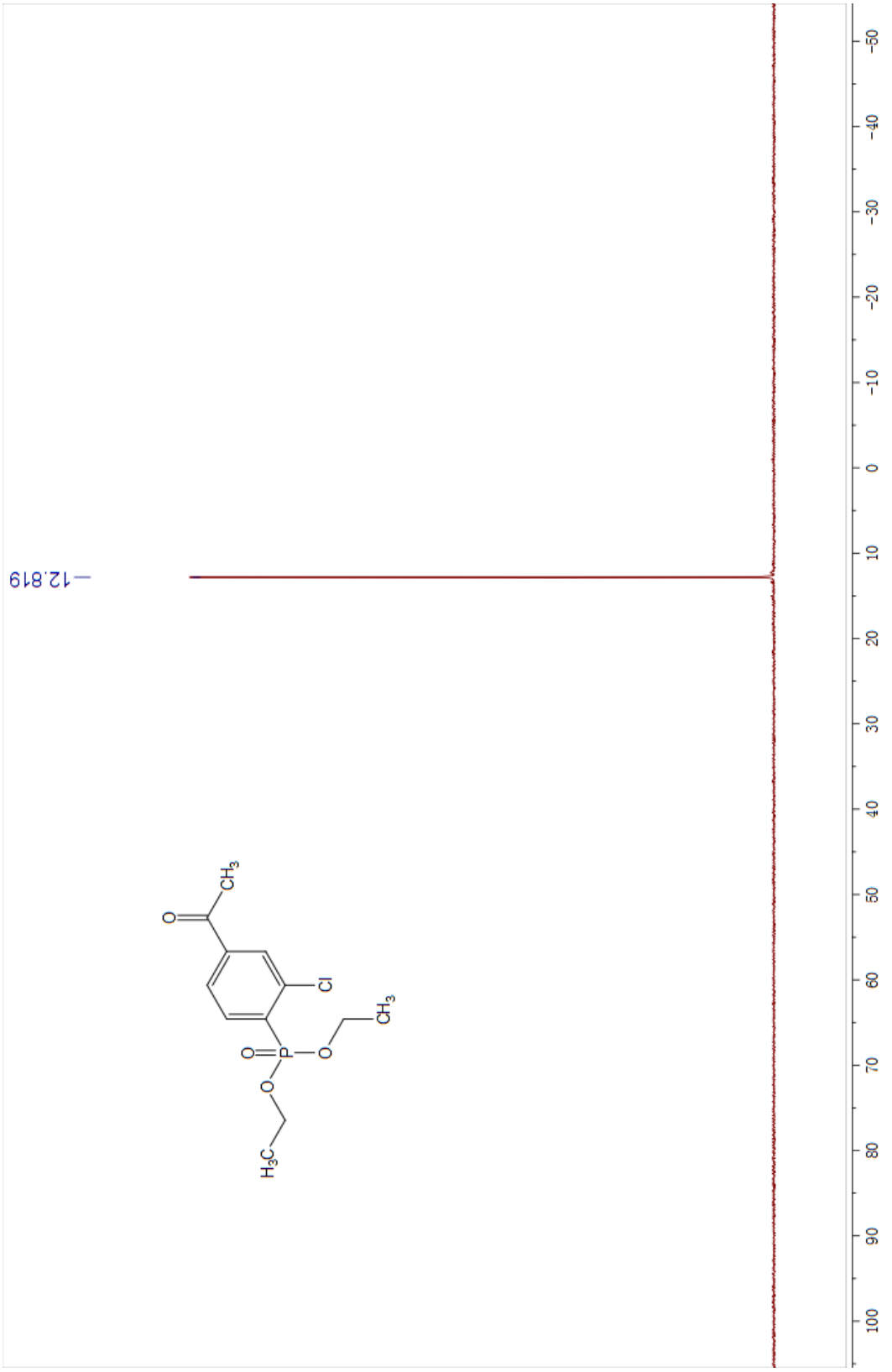
HR-MS Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **3oa**



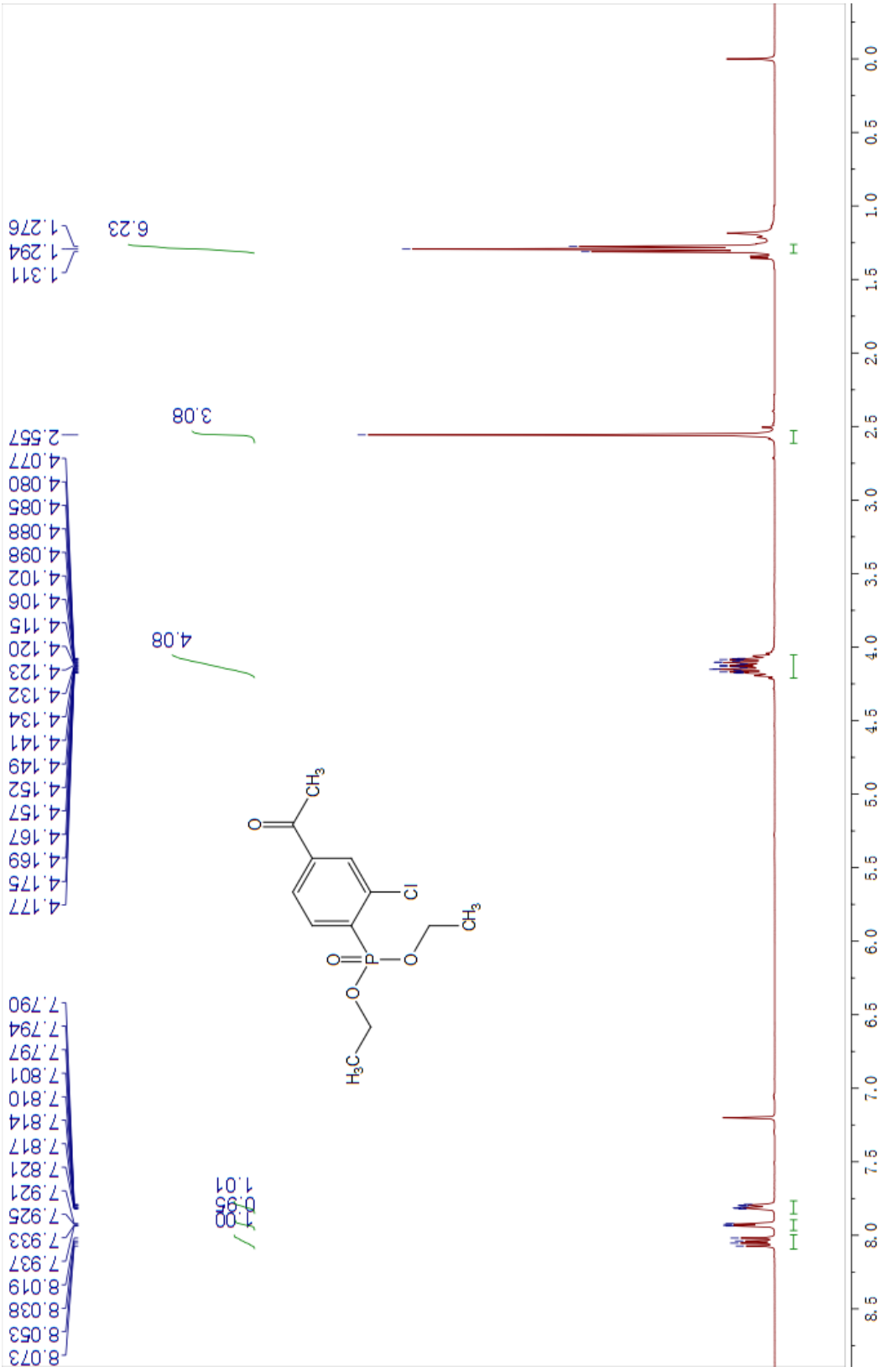
HMBC Spectrum of diethyl 4-acetyl-3-chlorophenylphosphonate **3oa**



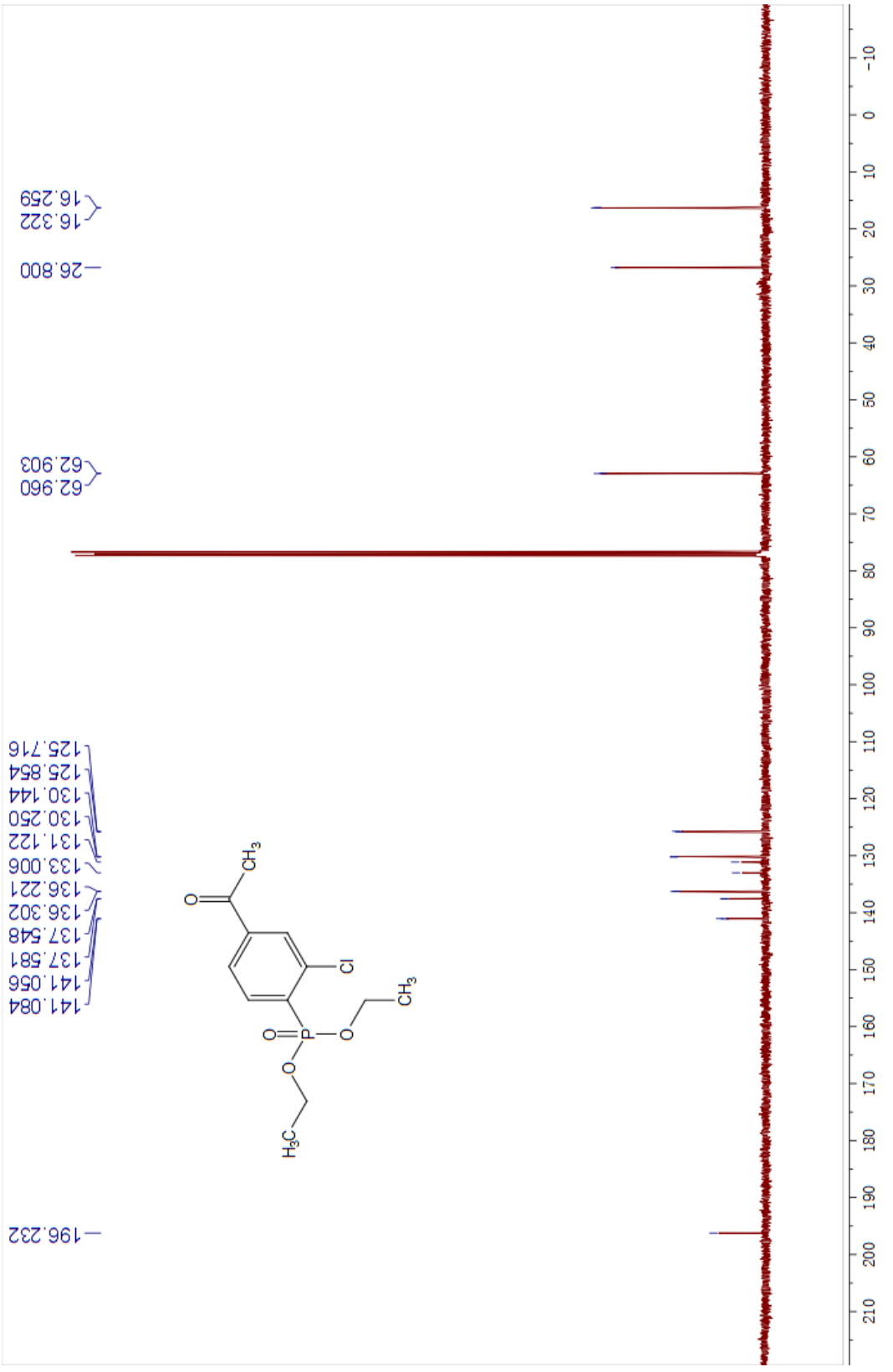
^{13}P NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



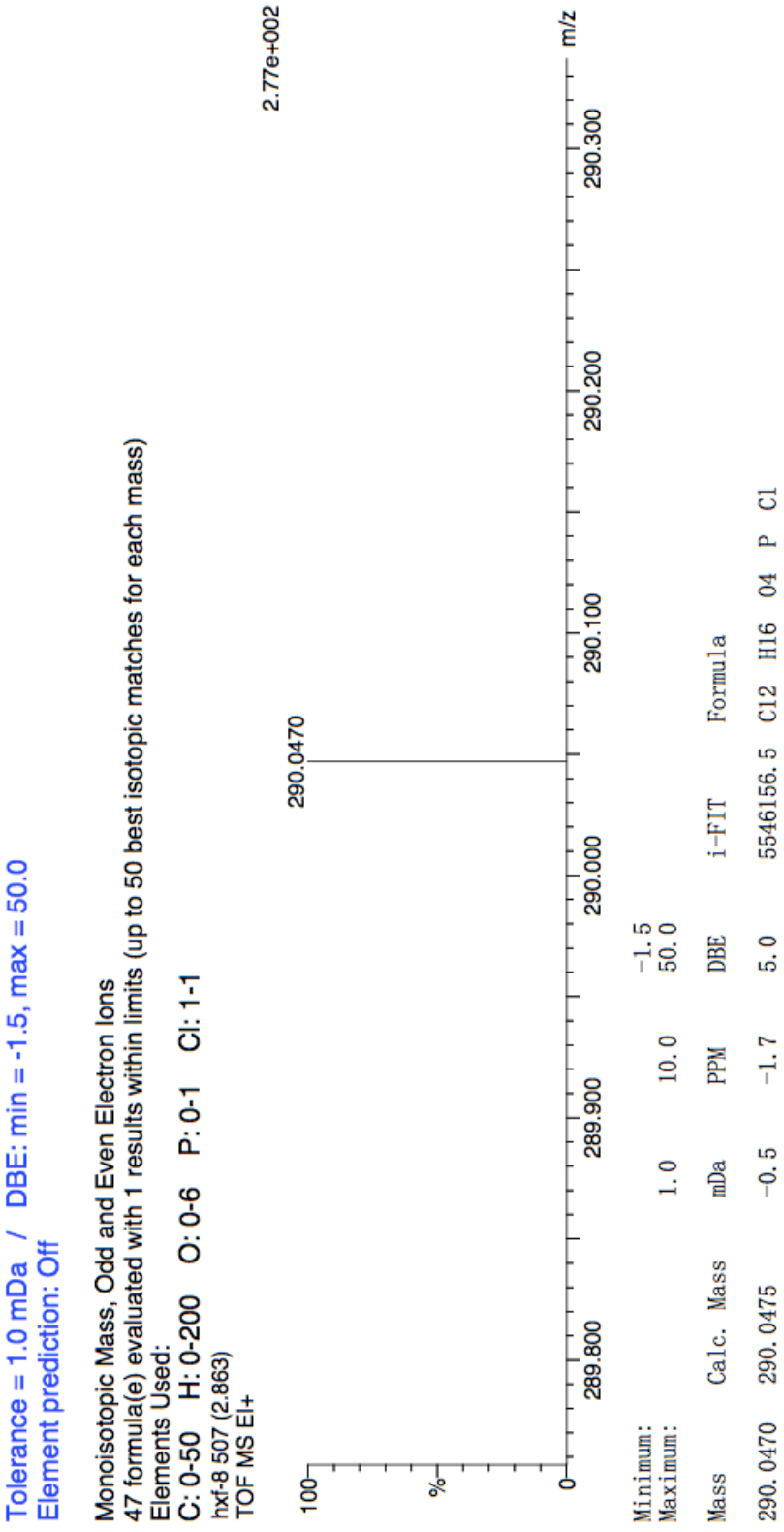
^{1}H NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



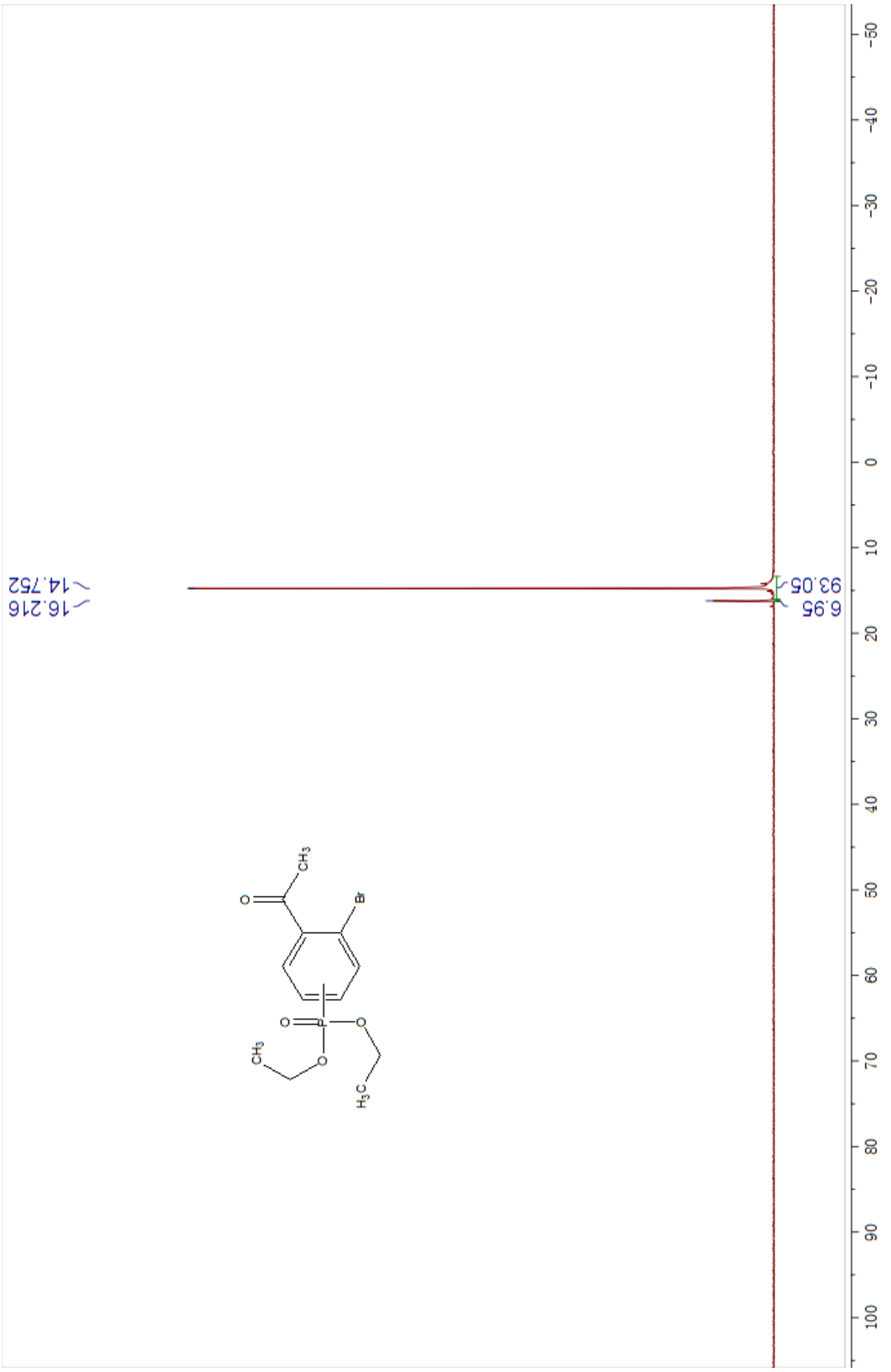
^{13}C NMR Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



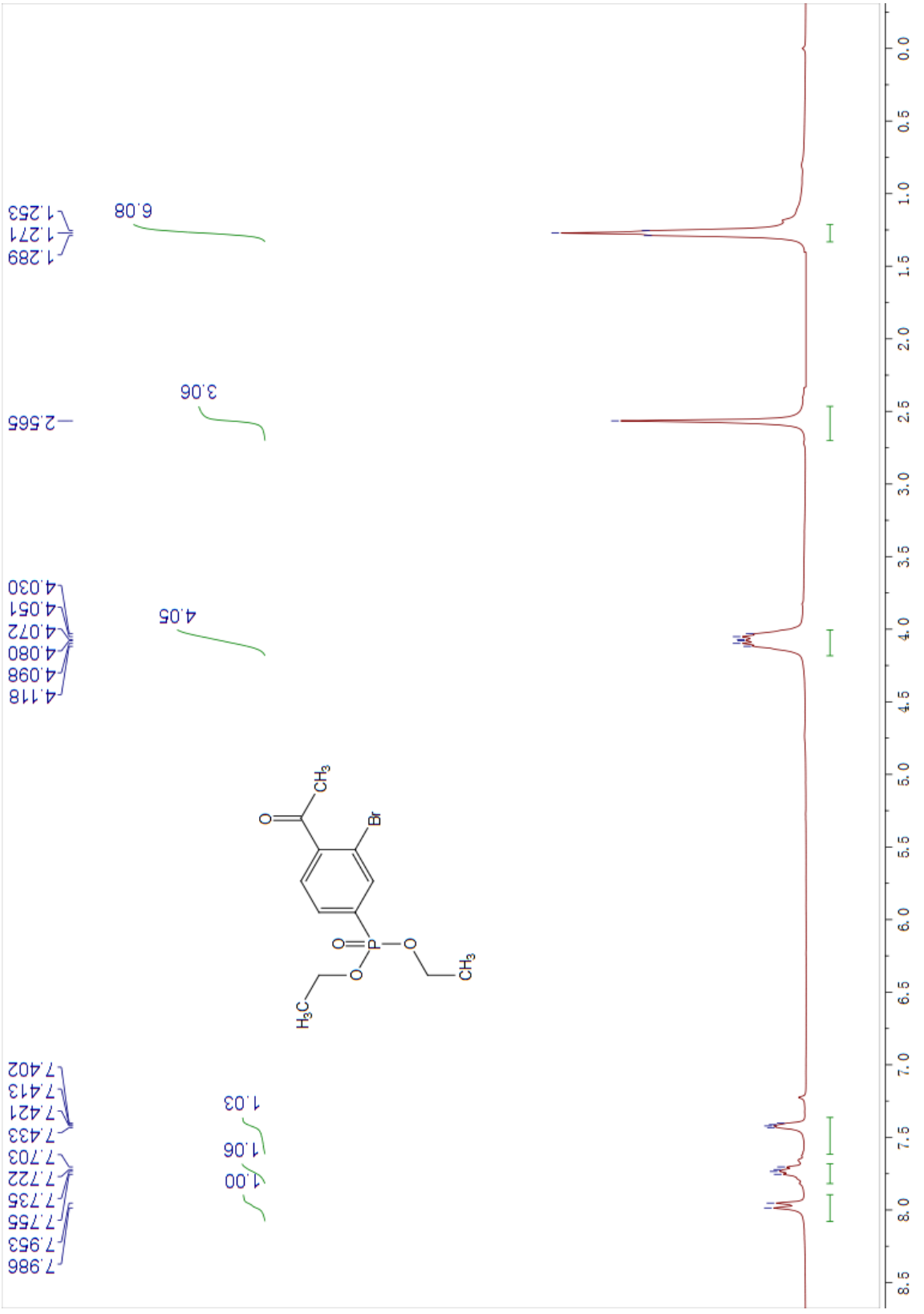
HR-MS Spectrum of diethyl 4-acetyl-2-chlorophenylphosphonate **3pa**



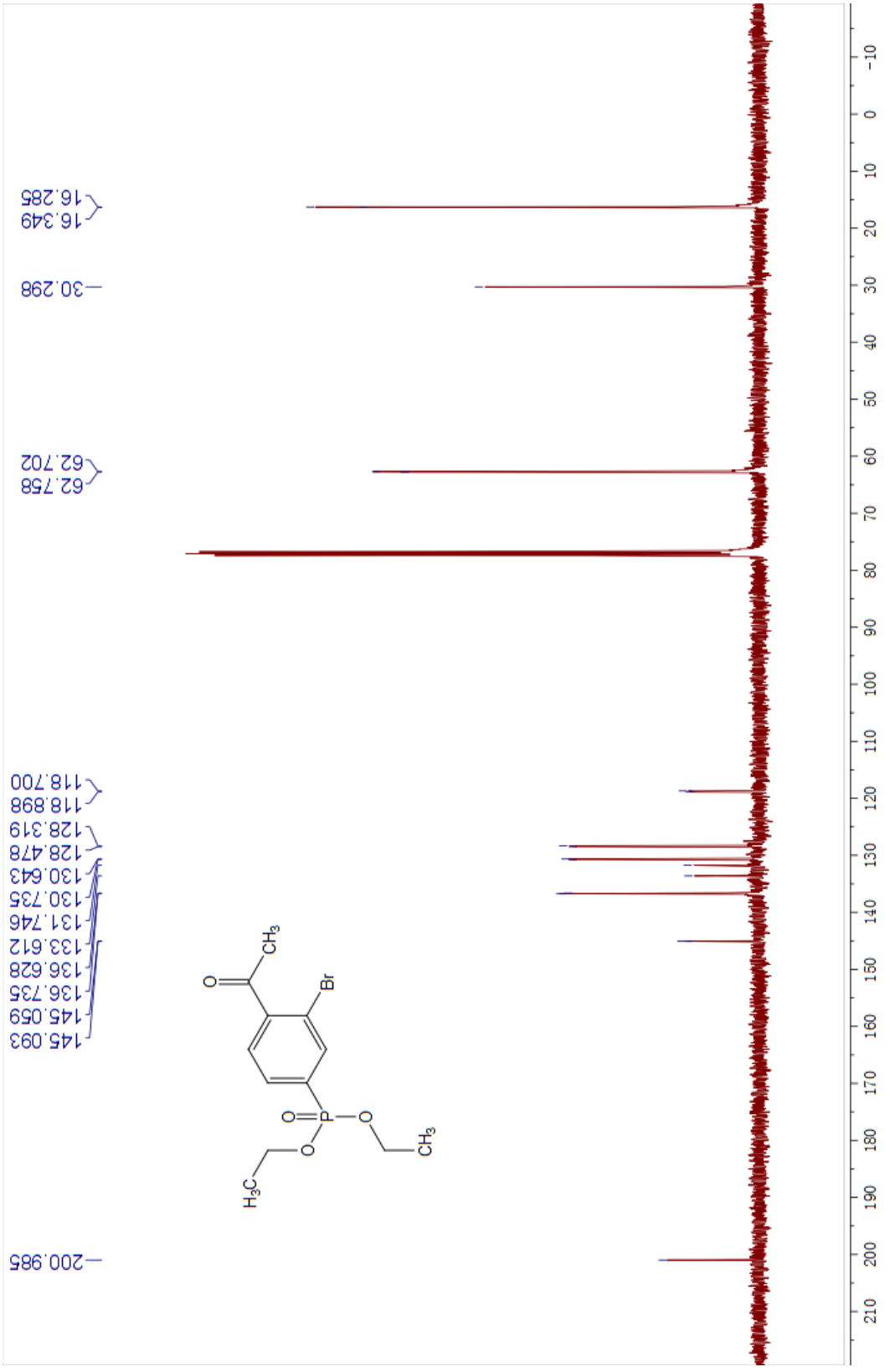
^{13}P NMR Spectrum of diethyl acetyl-3-bromophenylphosphonate **3qa**



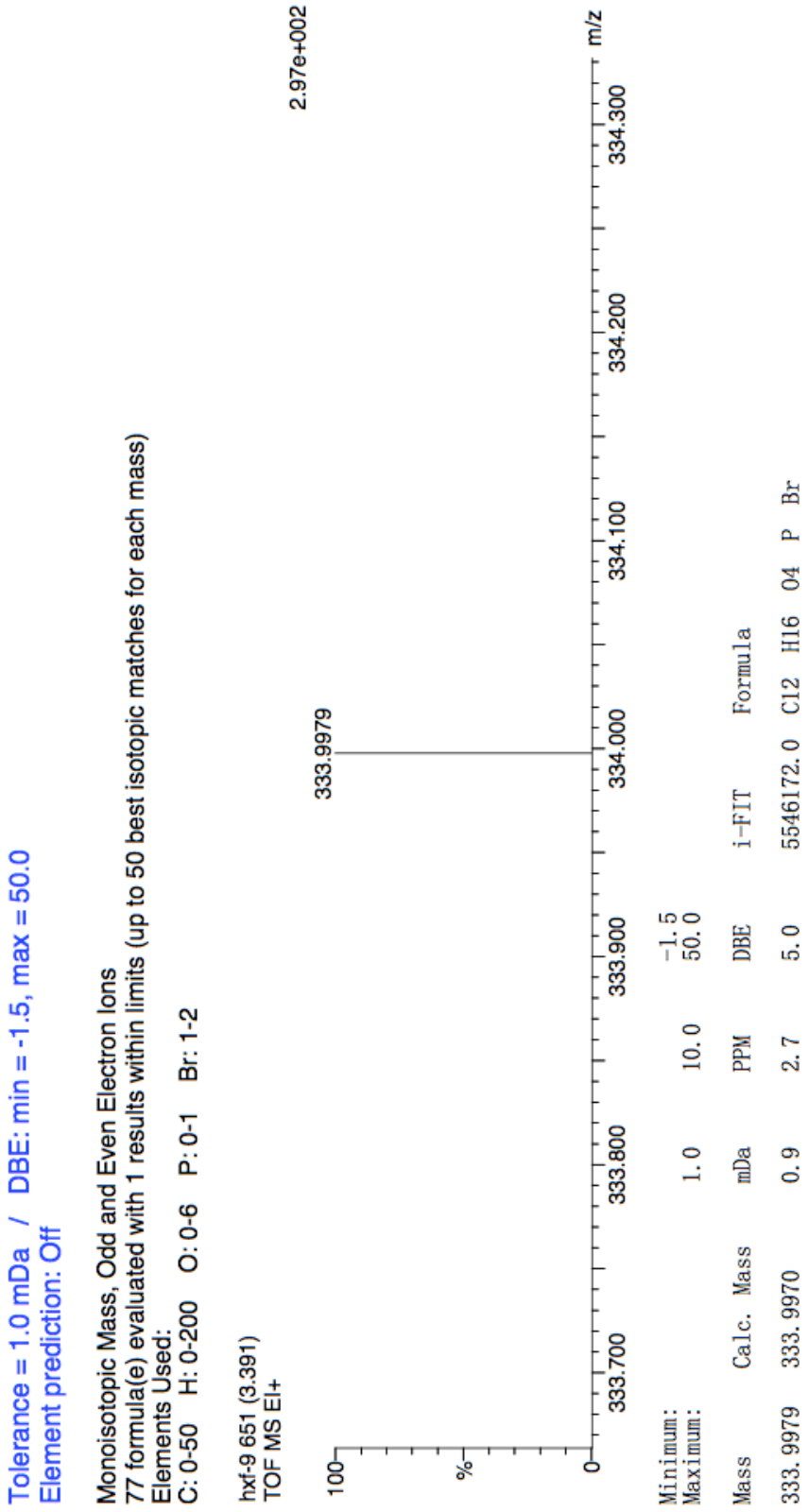
^{1}H NMR Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate **3qa**



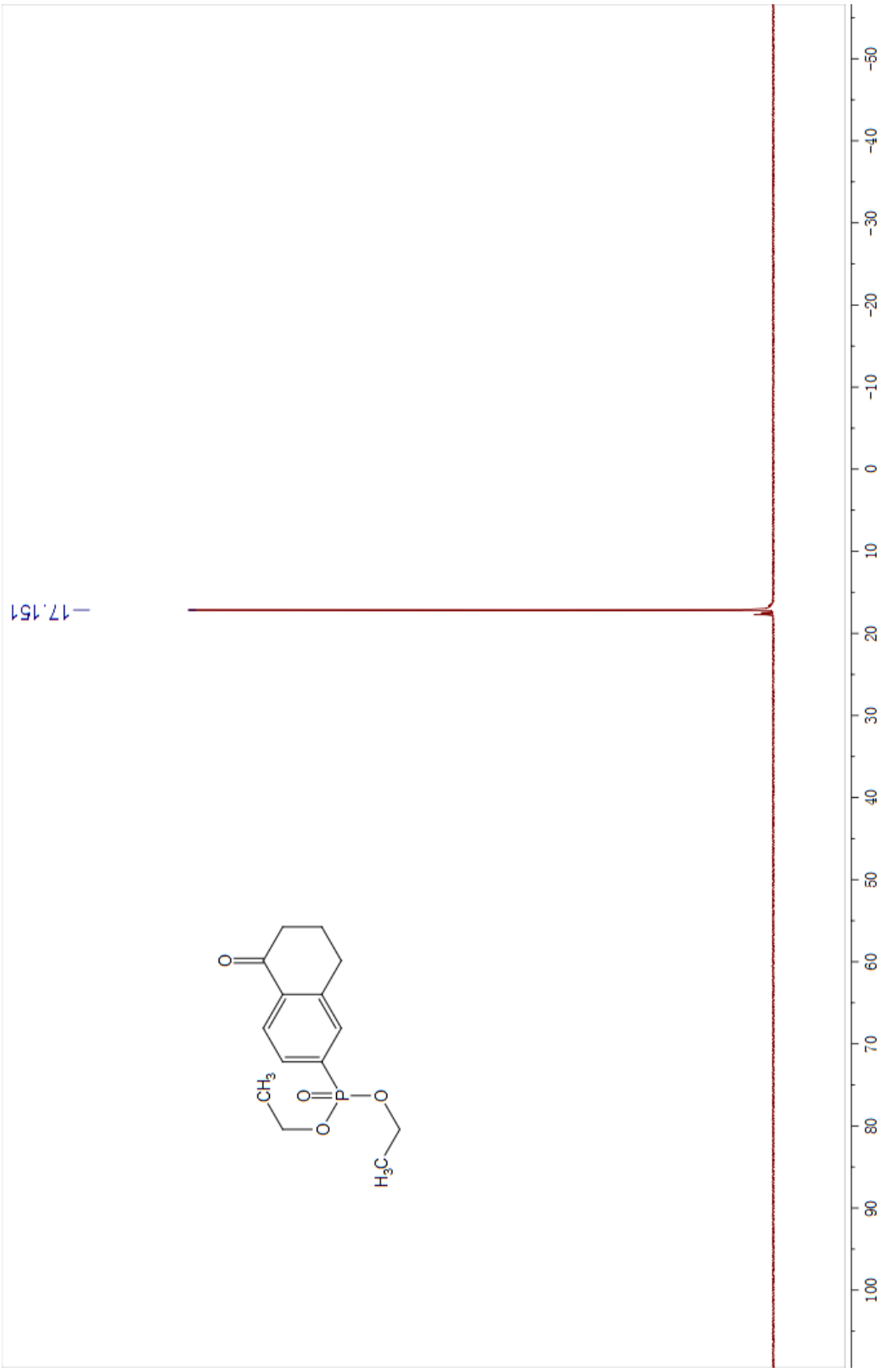
^{13}C NMR Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate **3qa**



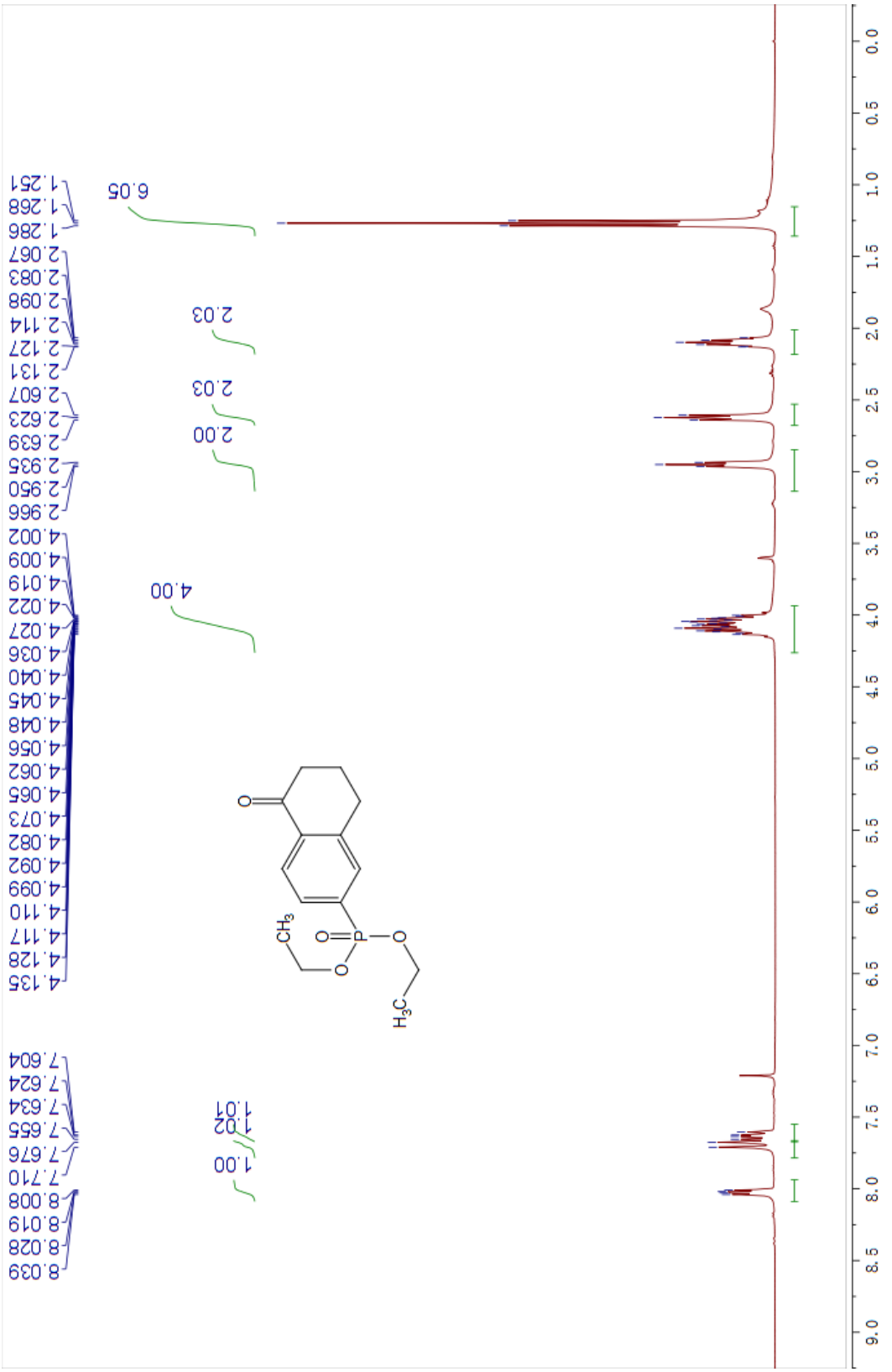
HR-MS Spectrum of diethyl 4-acetyl-3-bromophenylphosphonate **3qa**



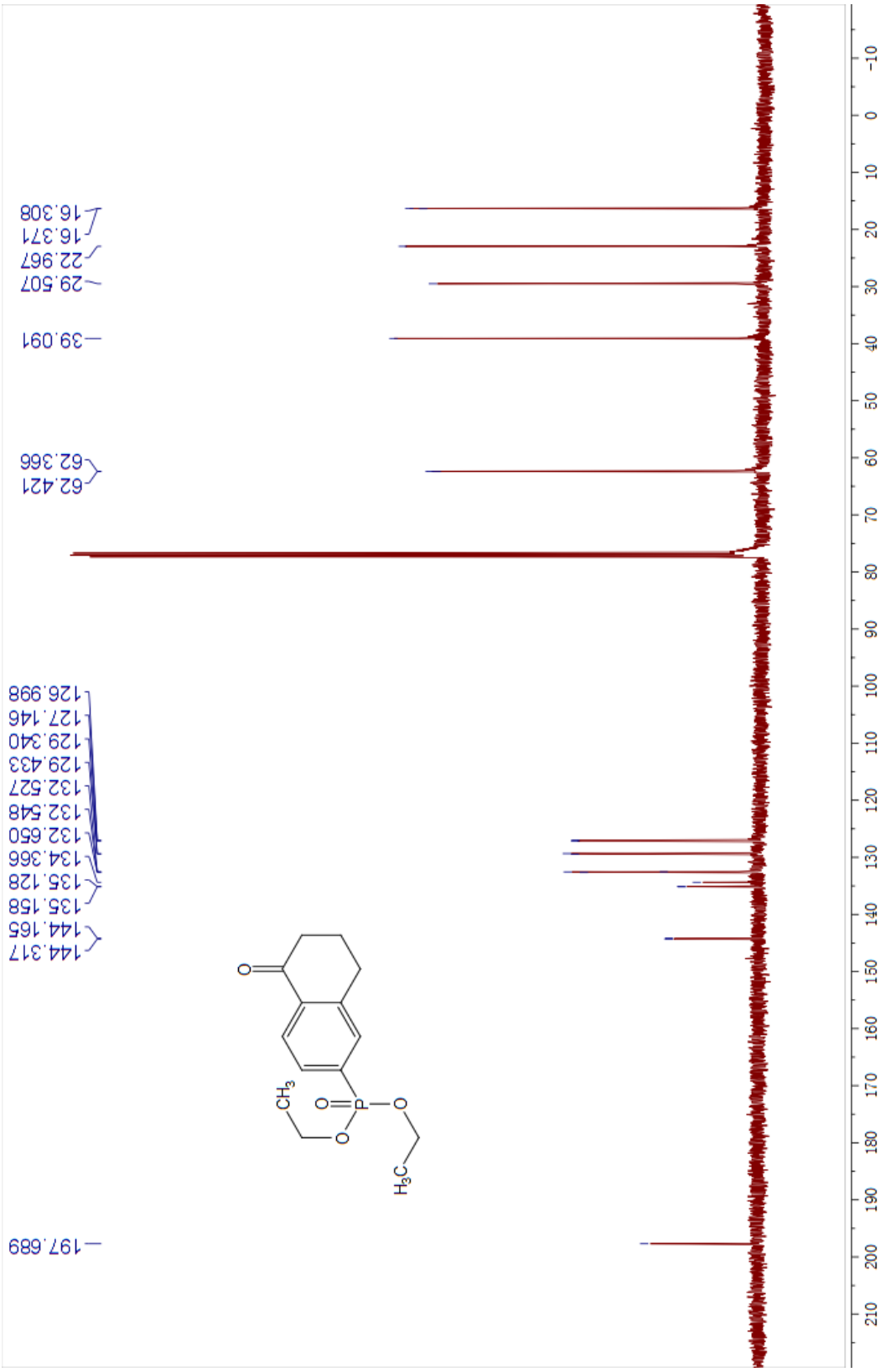
^{13}P NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**



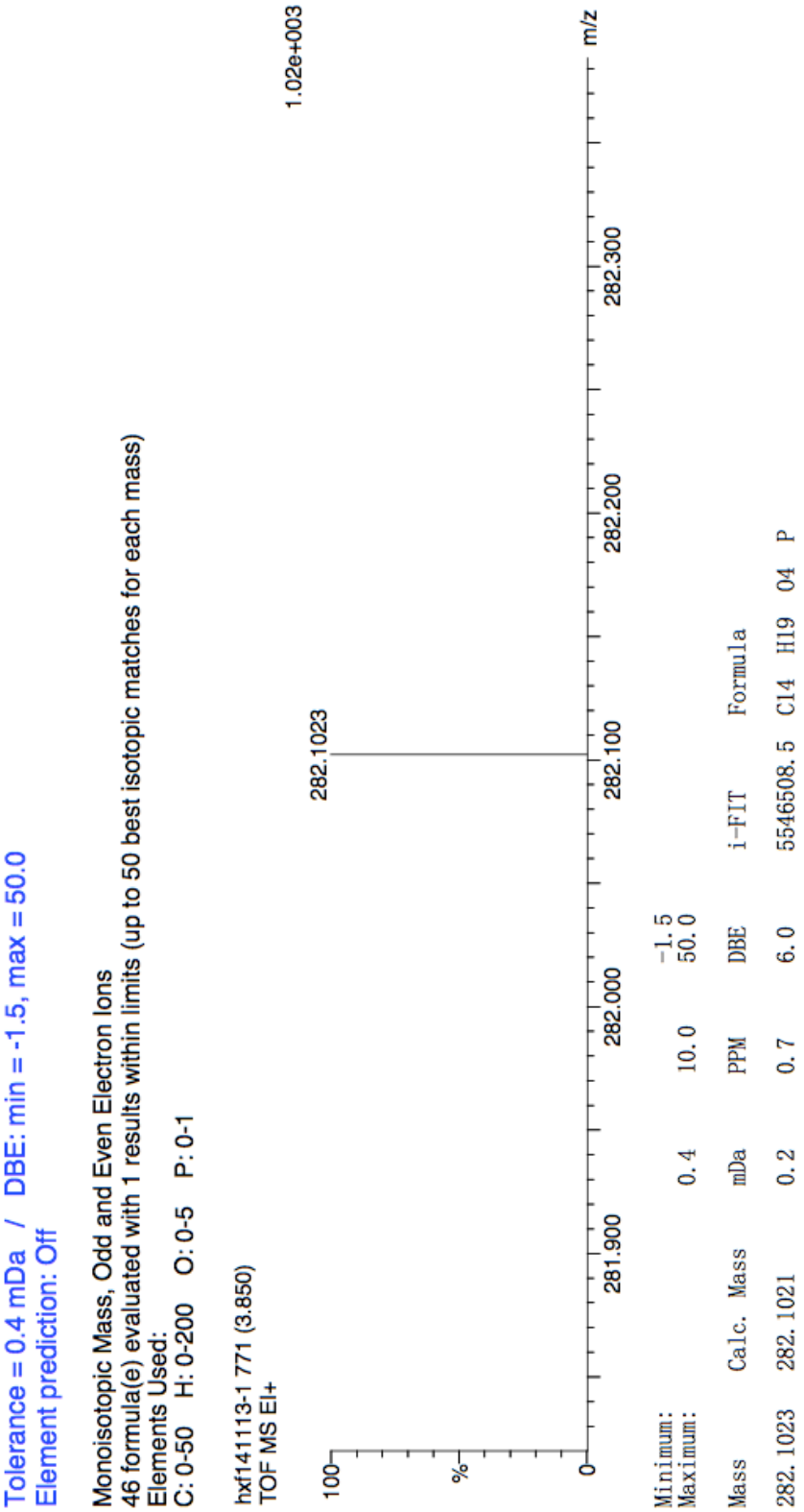
^{1}H NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**



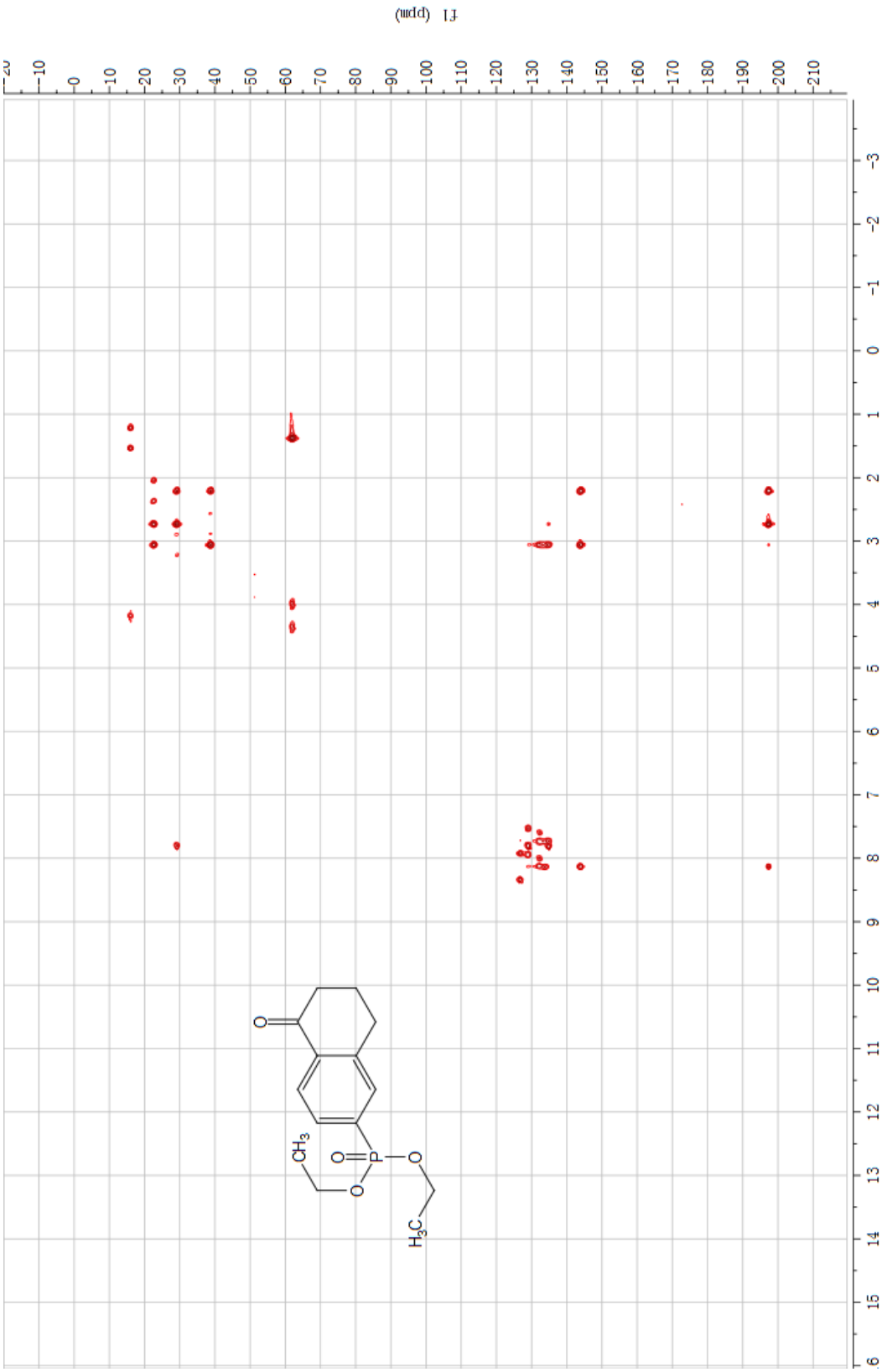
^{13}C NMR Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**



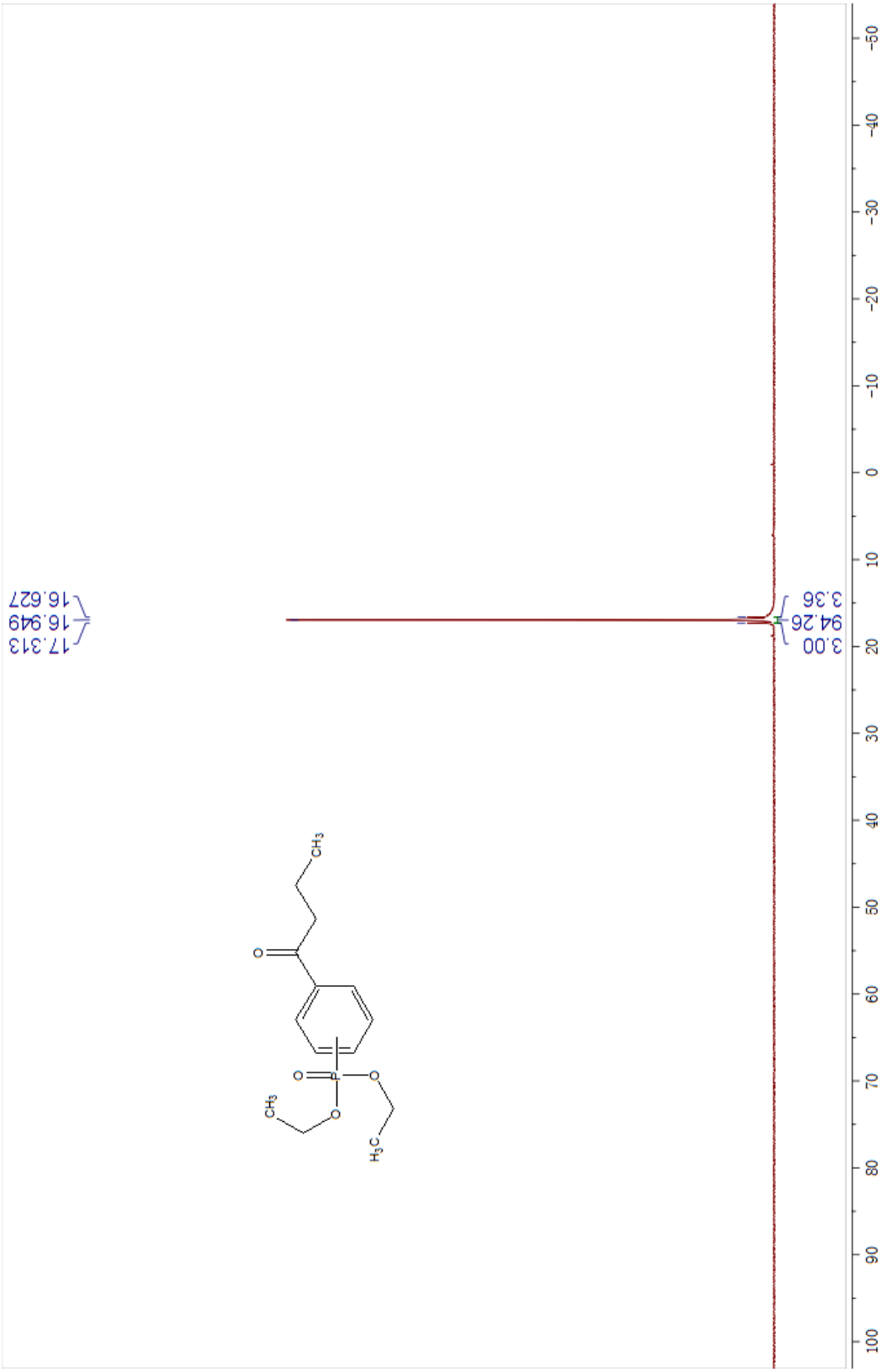
HR-MS Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**



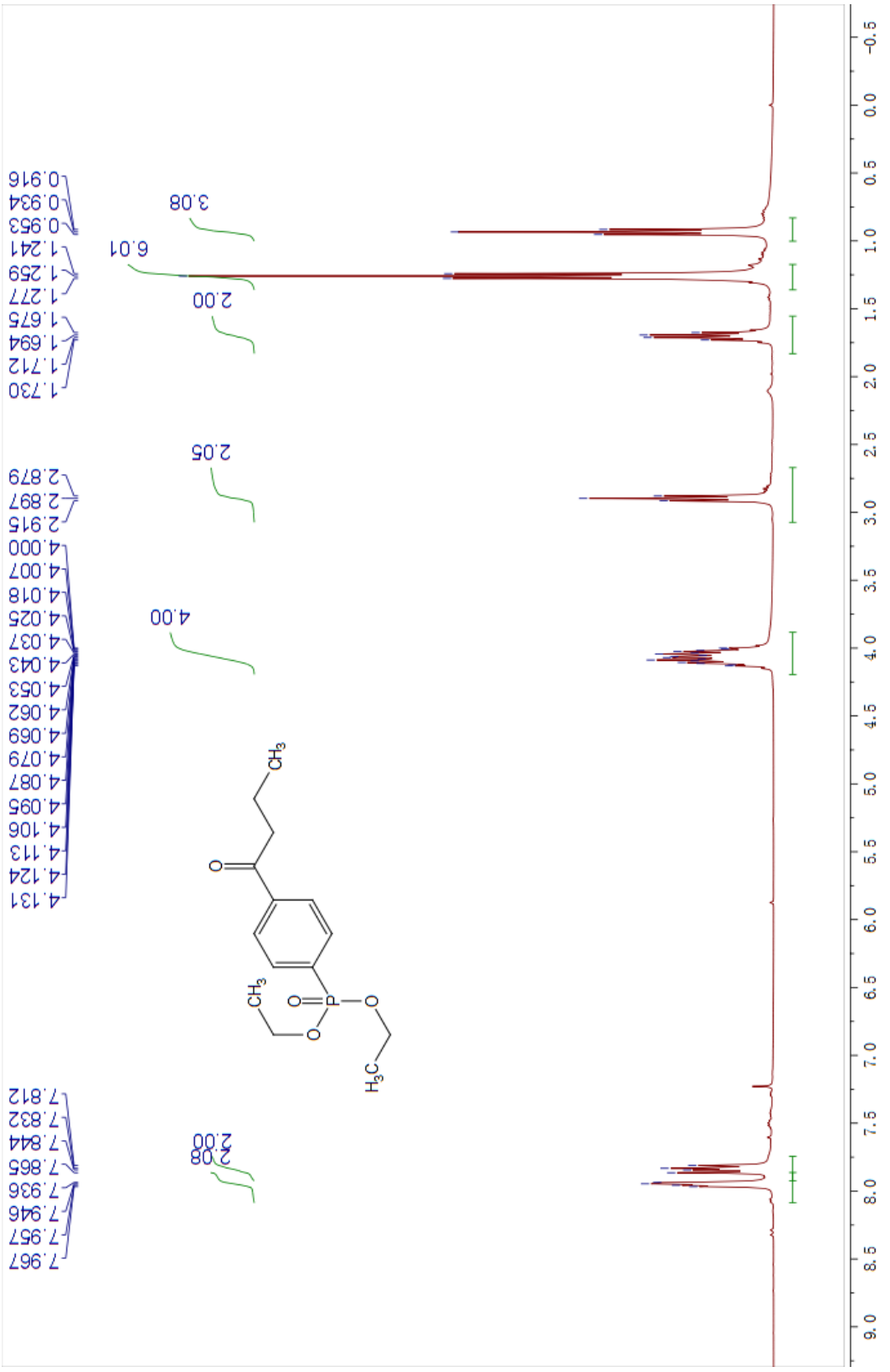
HMBC Spectrum of diethyl 5,6,7,8-tetrahydro5-oxo-2-naphthalenylphosphonate **3sa**



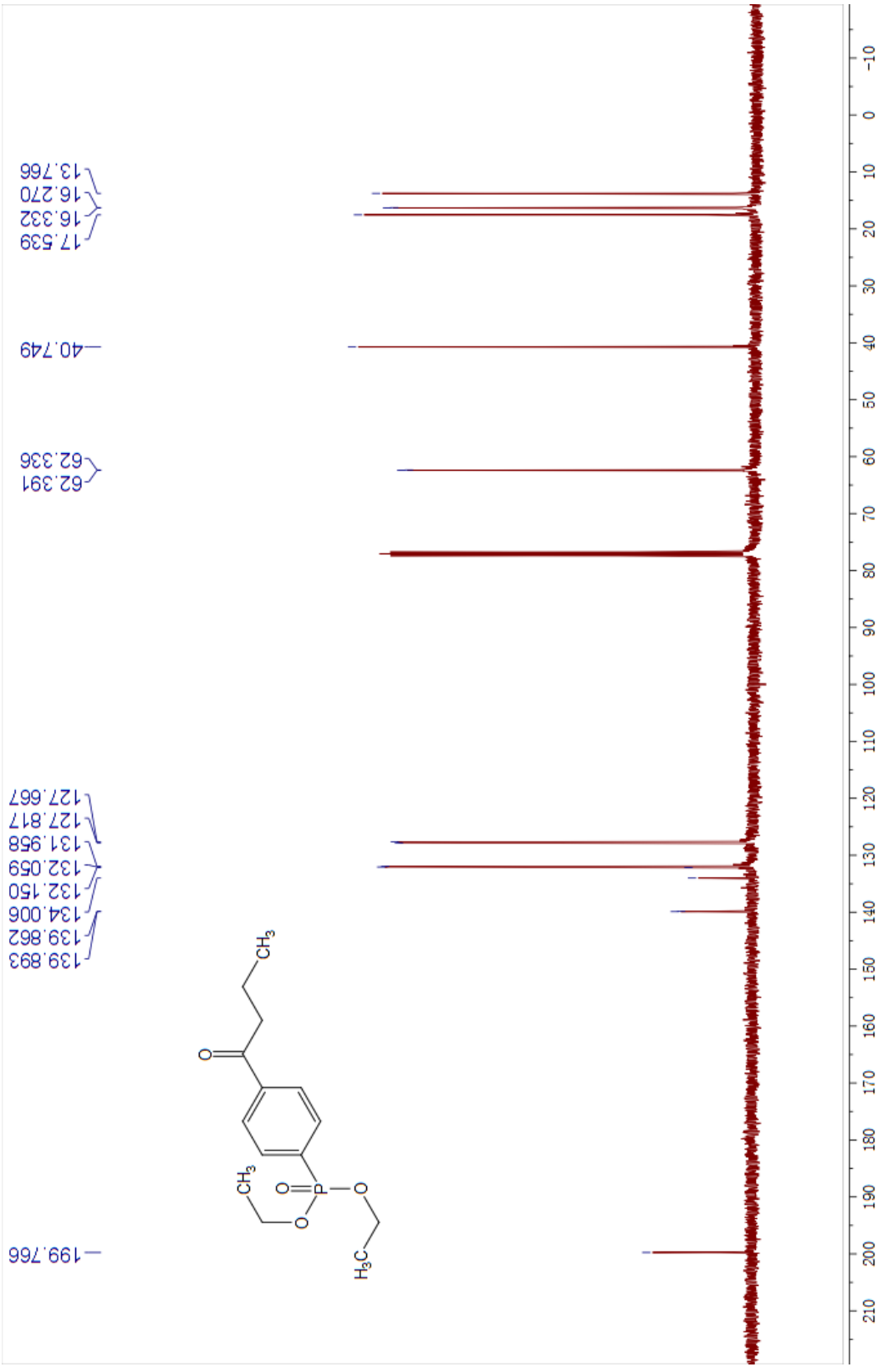
^{13}P NMR Spectrum of diethyl butanoylphenylphosphonate **3ua**



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



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



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