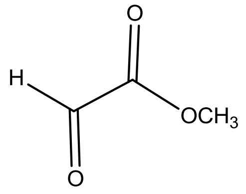
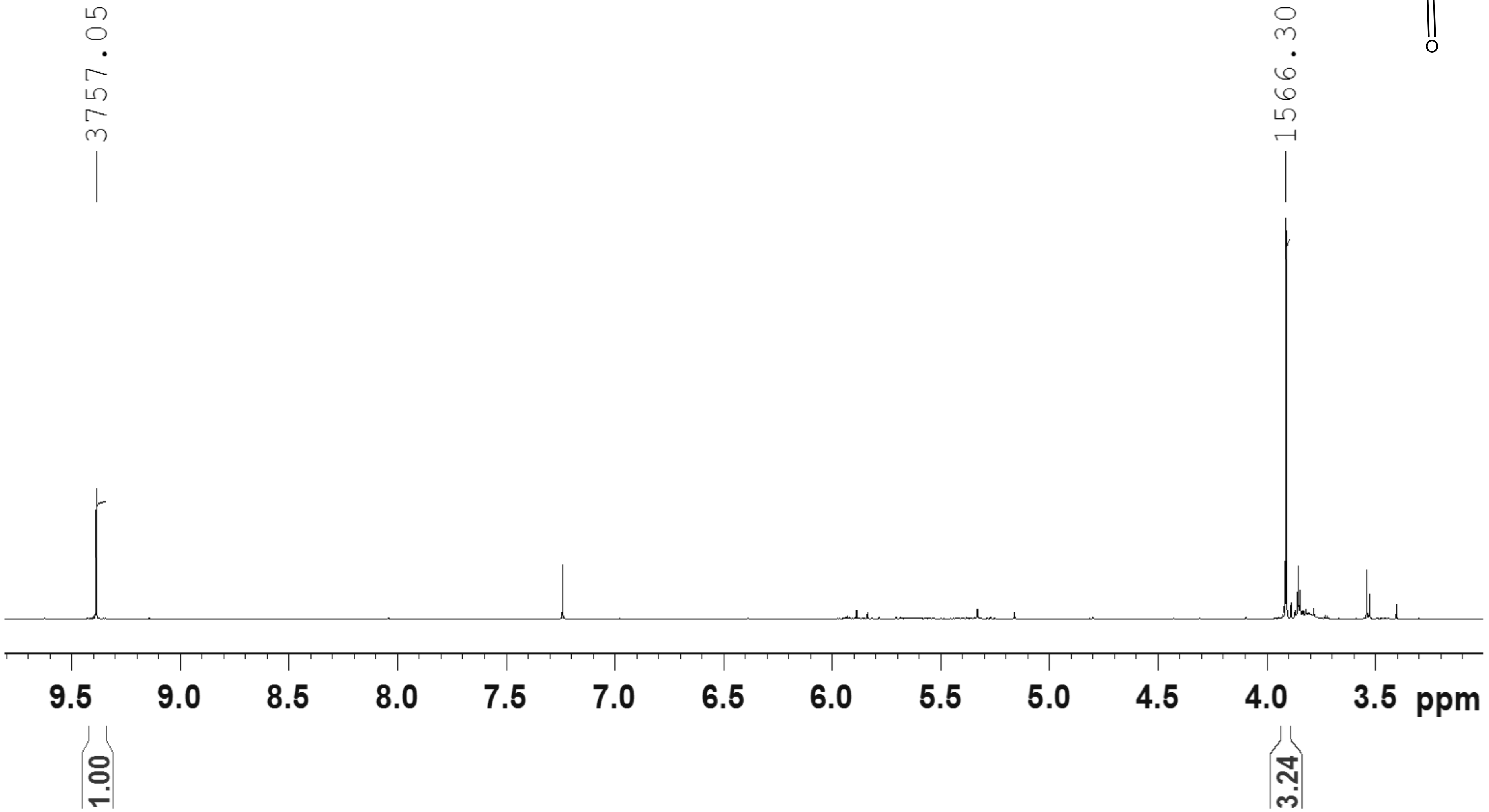
Supporting Information:

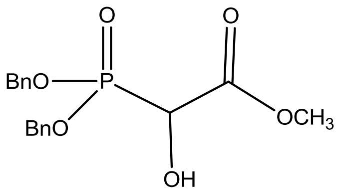
All assignments are given in the “Experimental part” of the publication. The first spectrum shown of each series is the full ^{1}H-spectrum. Expansions are depicted where they were regarded as necessary. Then the ^{13}C spectrum is depicted in the same manner. The x-axes is in ppm, while the peak labels are in Hz for all given spectra. Structures are always given on top of the ^{1}H full spectrum. Integrals are denoted below the x-axes and the integration range is marked. For 2D NMR experiments the ^{1}H NMR is dipicted above the spectrum and the ^{13}C NMR on the left hand side. The numbering of the spectra is in accordance with the numbering of substances in the main text.

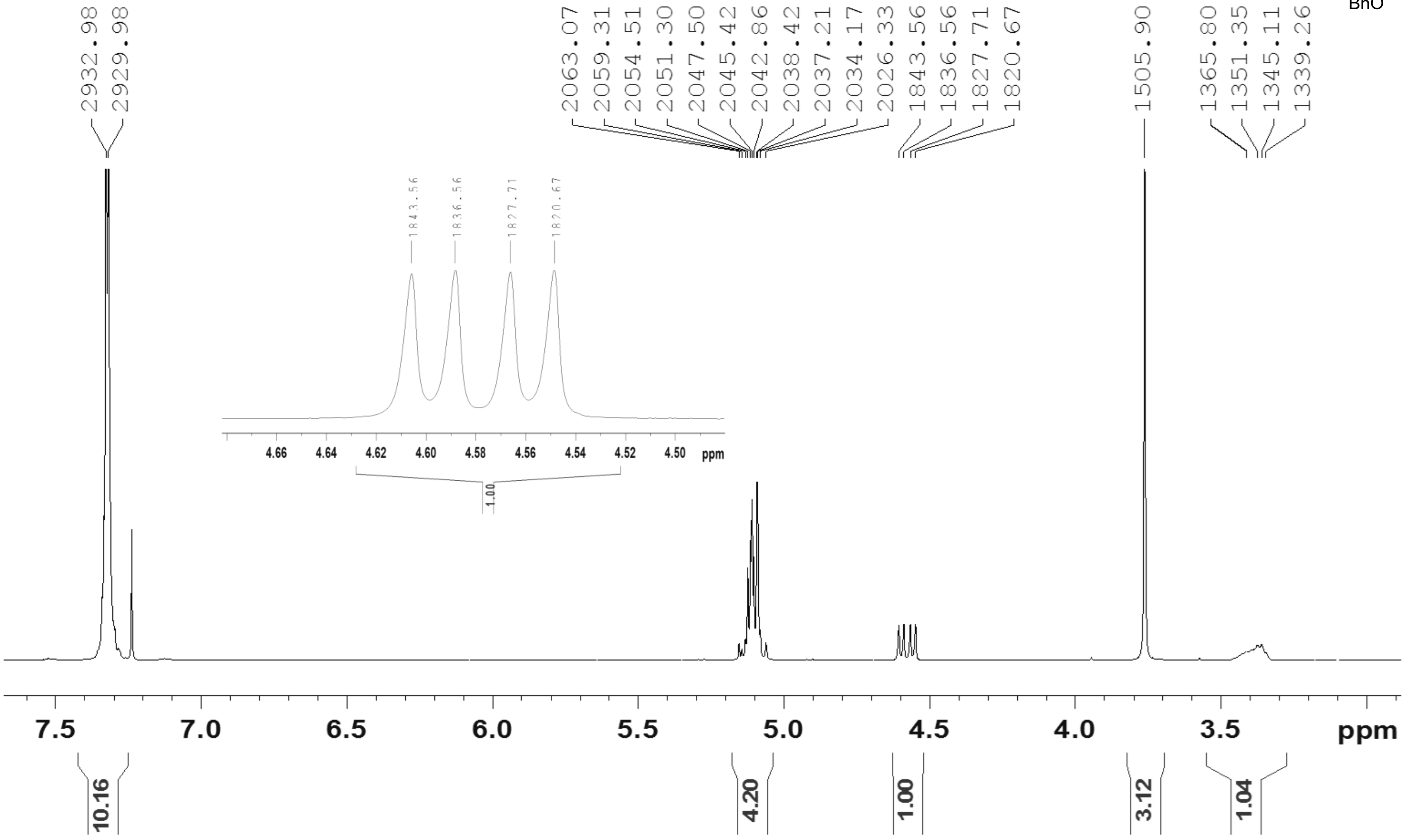
Methyl glyoxylate (7):

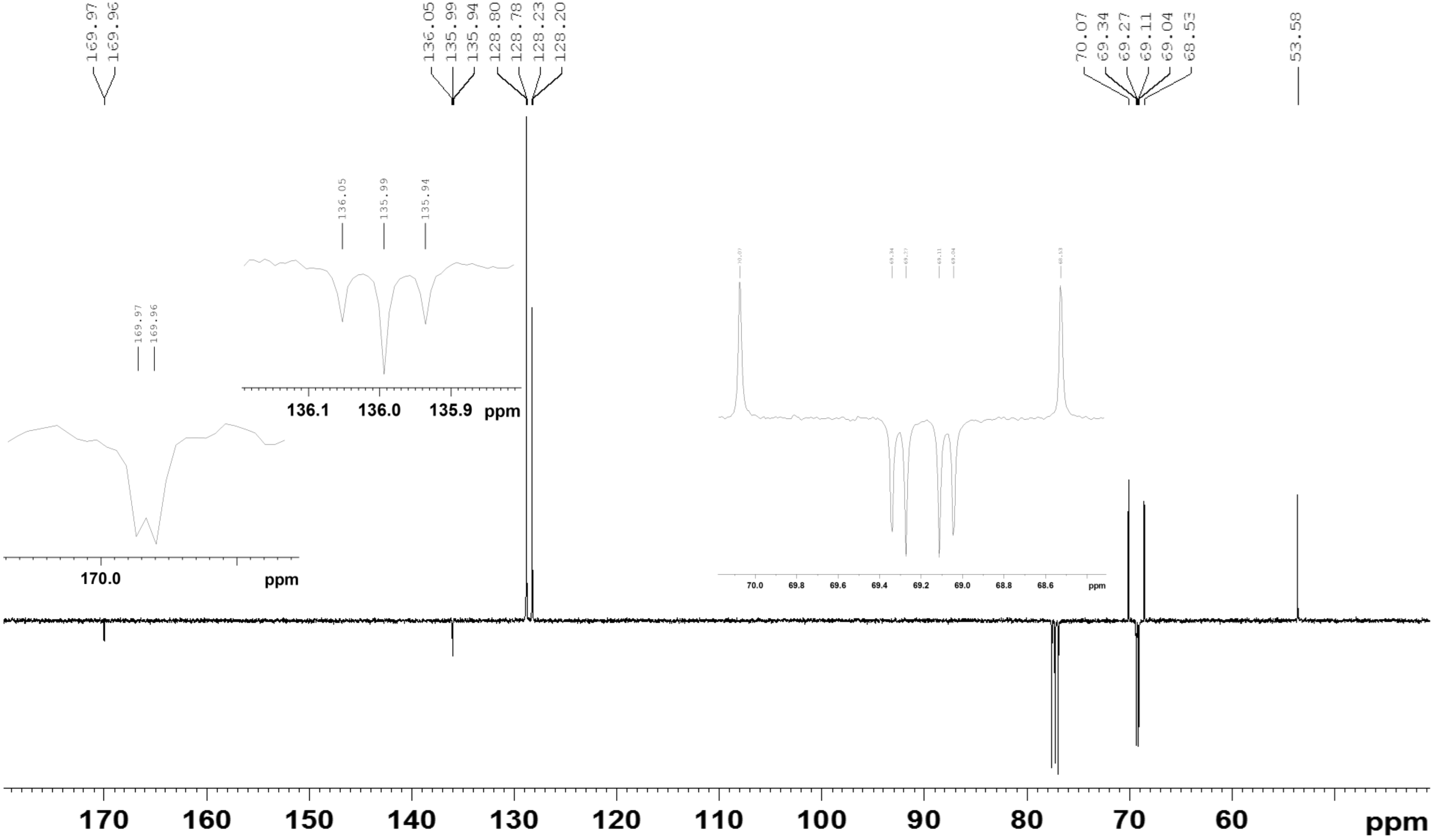




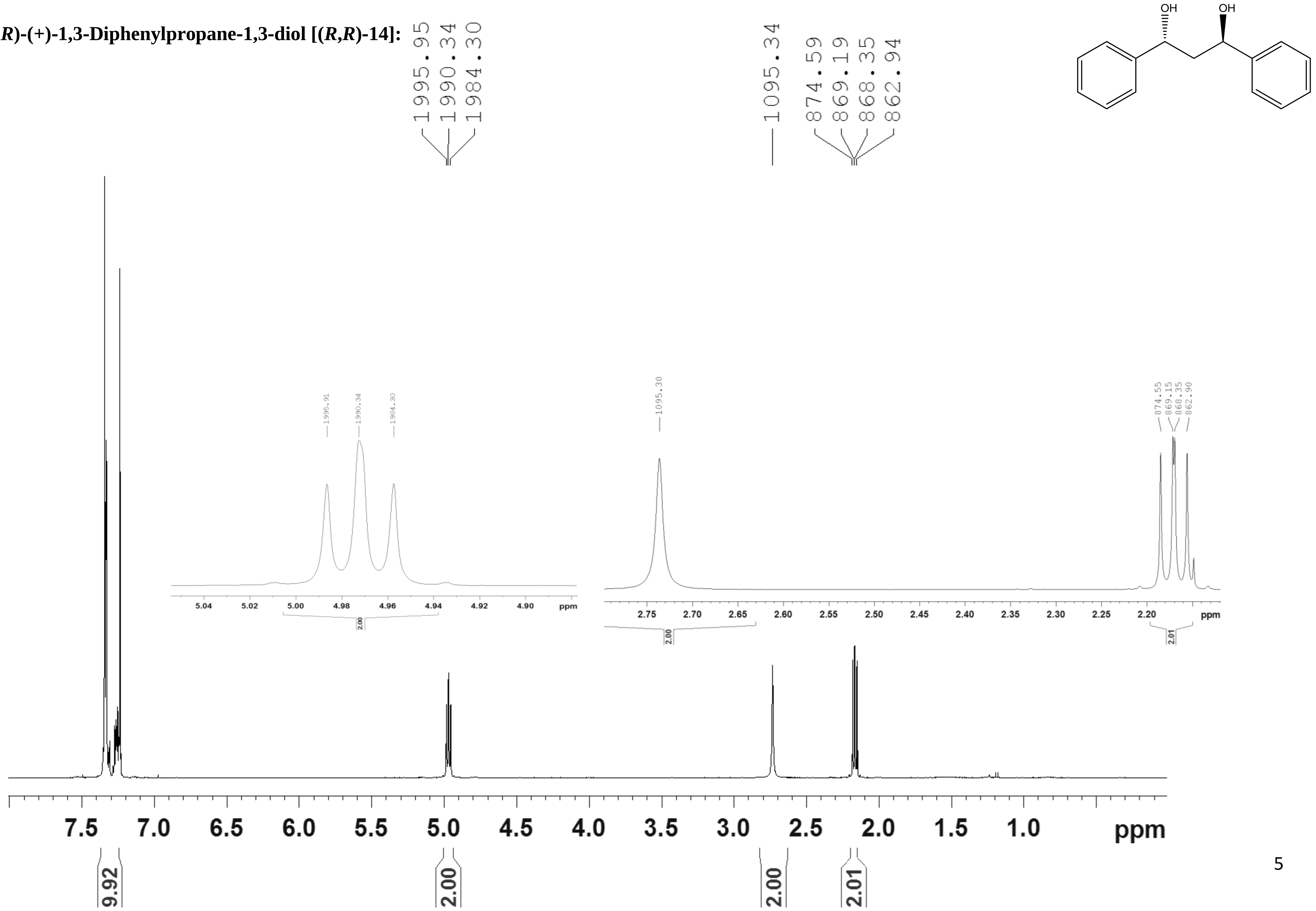
(±)-Methyl 2-(dibenzoxyphosphinyl)-2-hydroxyacetate [(±)-9]:

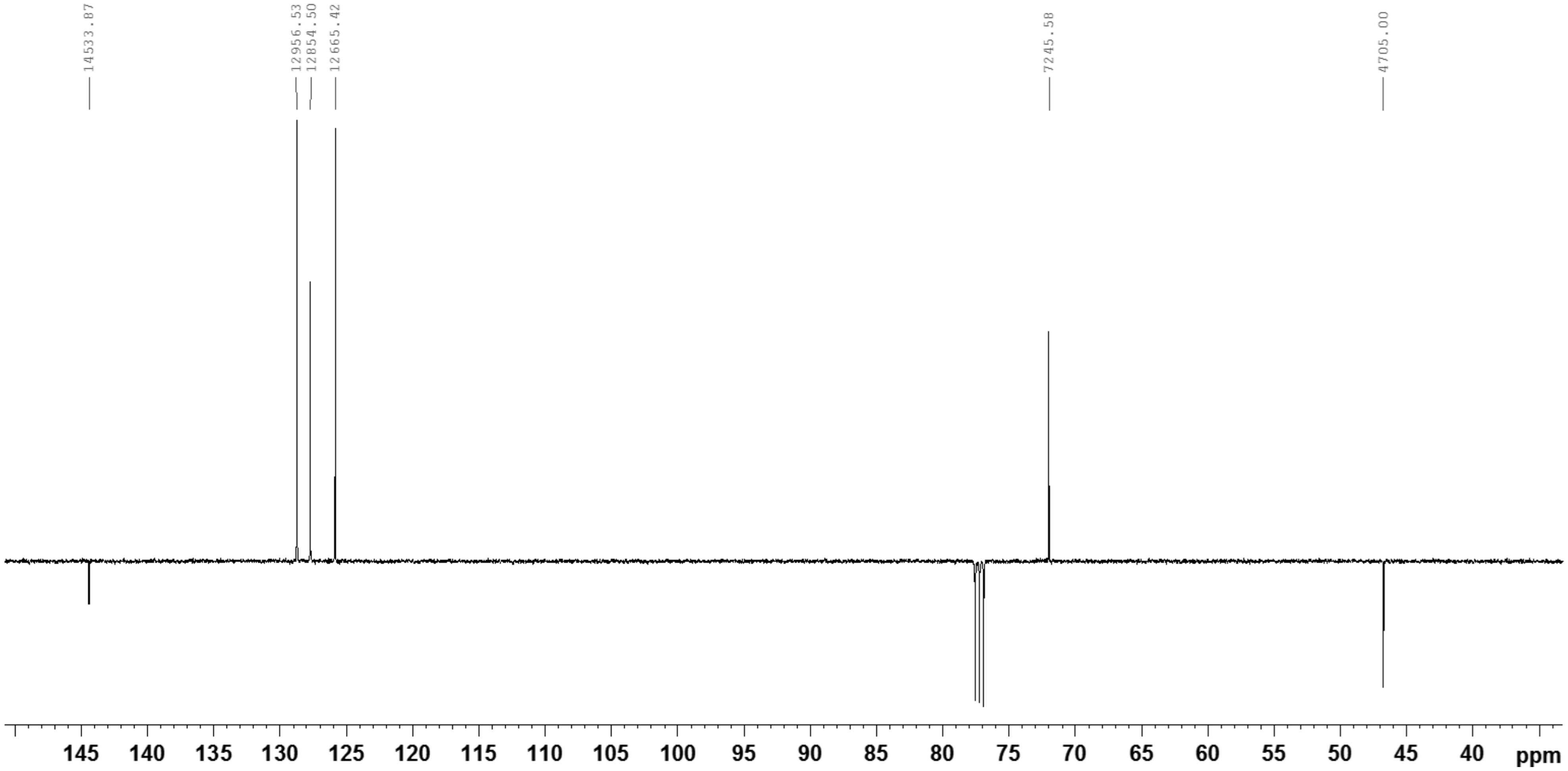


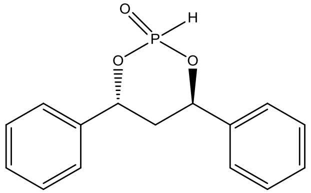



169.97
169.96
136.05
135.99
135.94
128.80
128.78
128.23
128.20
70.07
69.34
69.27
69.11
69.04
68.53
53.58
170.0
ppm
136.1
136.0
135.9
ppm
70.0
69.8
69.6
69.4
69.2
69.0
68.8
68.6
ppm
170
160
150
140
130
120
110
100
90
80
70
60
ppm

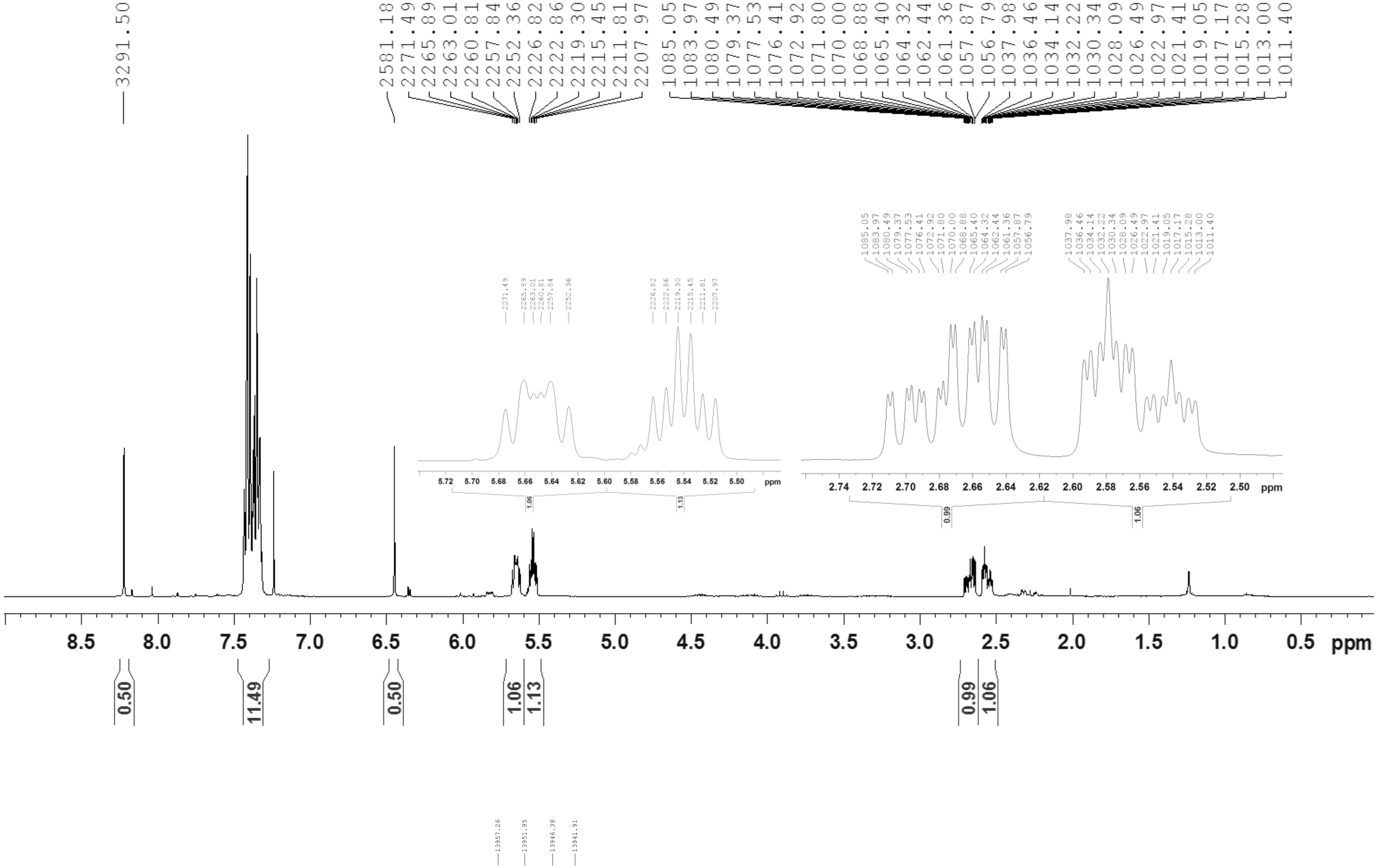
(*R*,*R*)-(+)-1,3-Diphenylpropane-1,3-diol [(*R*,*R*)-14]:

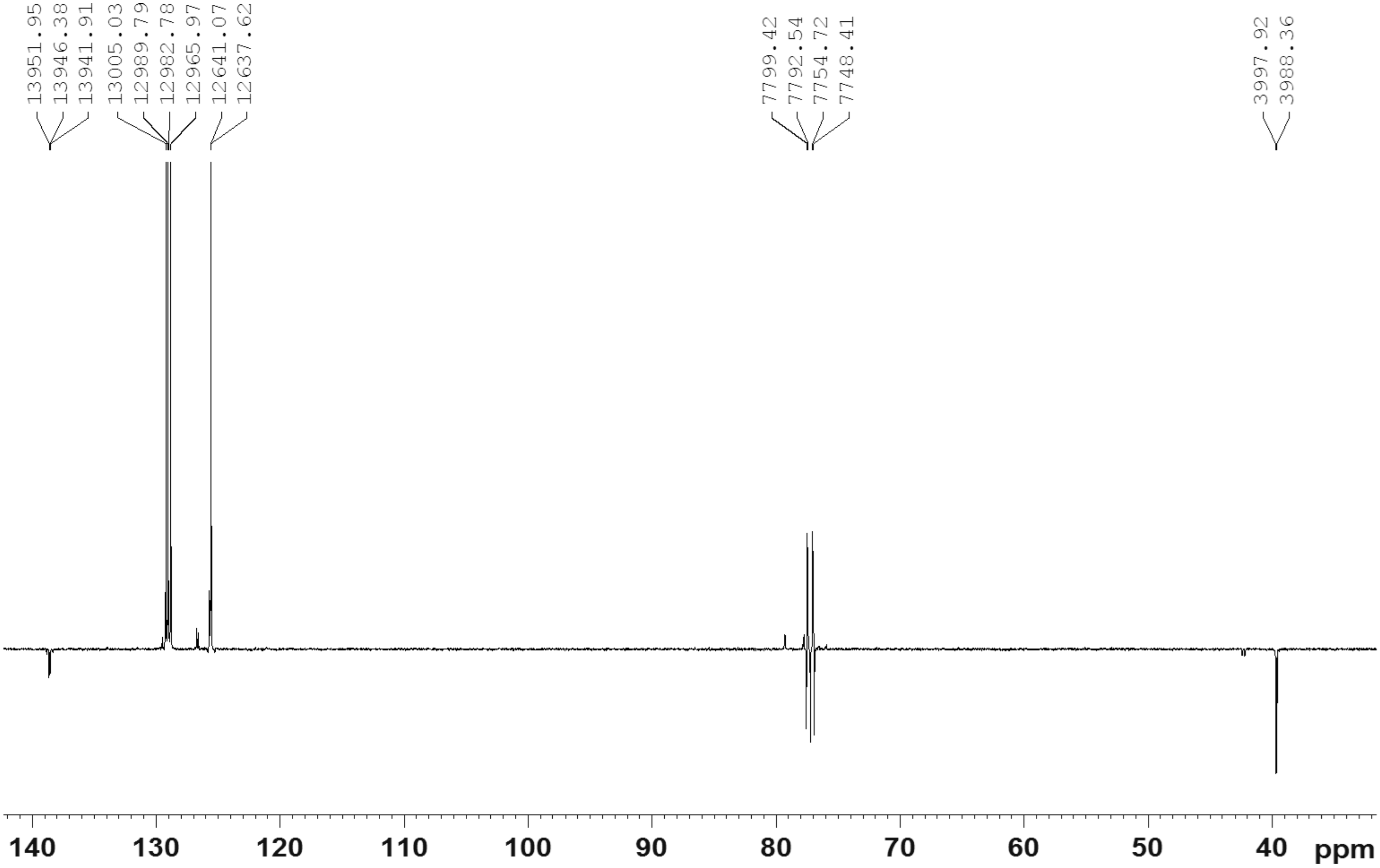


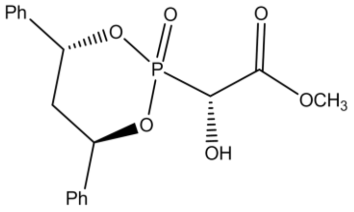

14533.87
12956.53
12854.50
12665.42
7245.58
4705.00
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
ppm



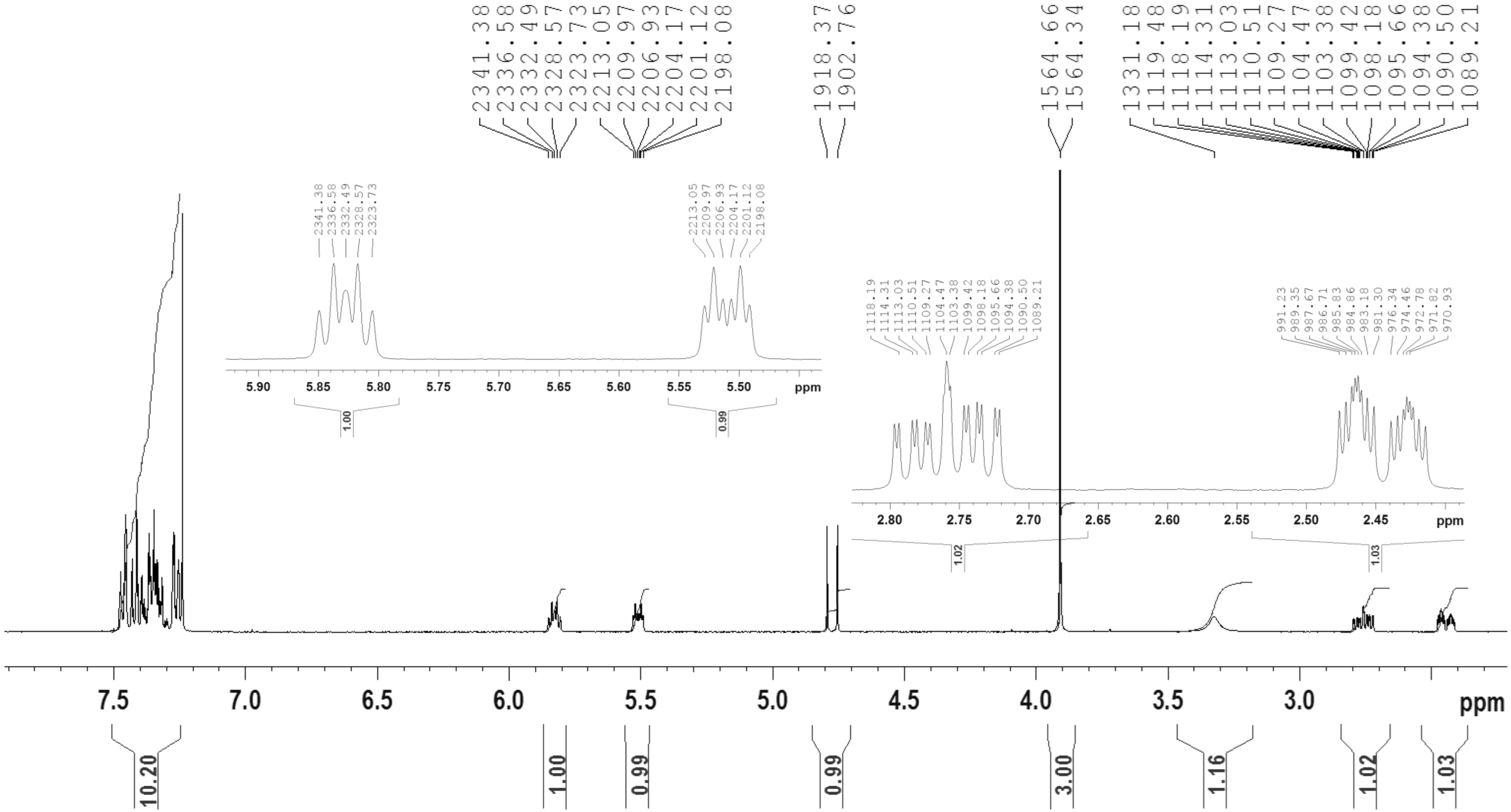
(4*R*,6*R*)-2-Hydro-2-oxo-4,6-diphenyl-1,3,2-dioxaphosphori-nane (15):

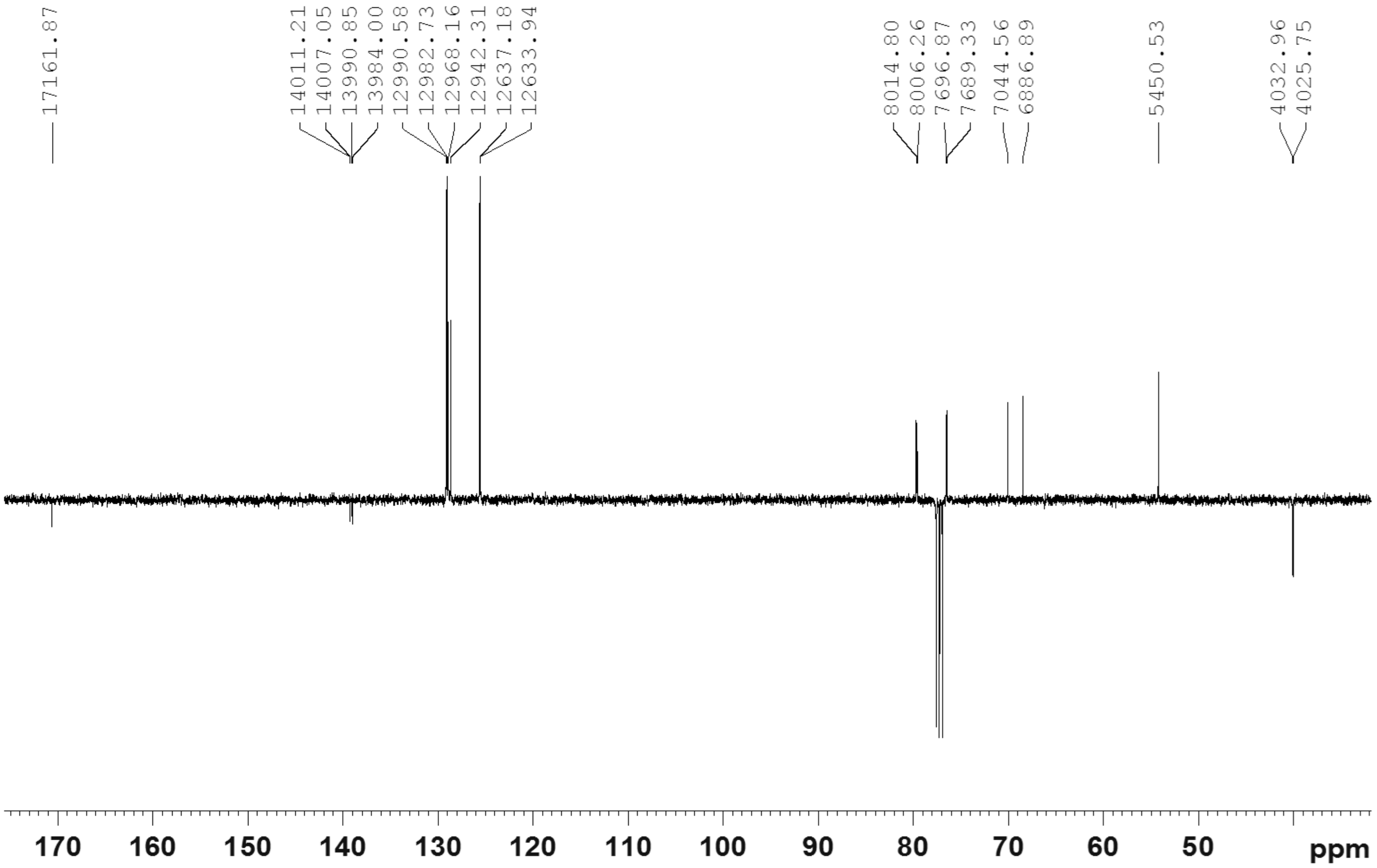



13951.95
13946.38
13941.91
13005.03
12989.79
12982.78
12965.97
12641.07
12637.62
7799.42
7792.54
7754.72
7748.41
3997.92
3988.36
140
130
120
110
100
90
80
70
60
50
40
ppm



Cyclic α-hydroxyphosphonate 16b:

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14007.05
13990.85
13984.00
12990.58
12982.73
12968.16
12942.31
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12633.94
8014.80
8006.26
7696.87
7689.33
7044.56
6886.89
5450.53
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4025.75
170
160
150
140
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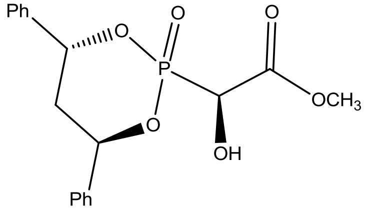
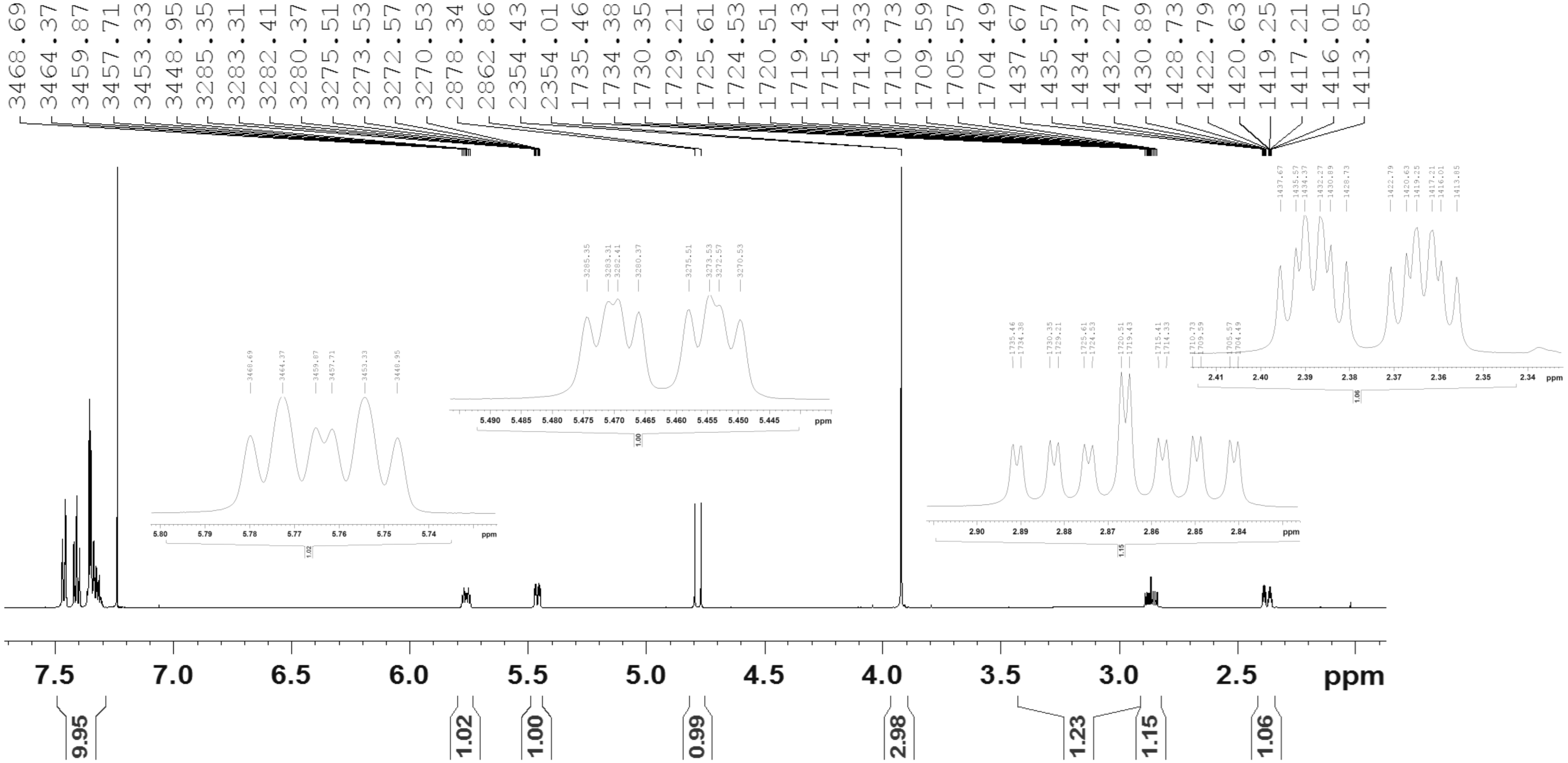
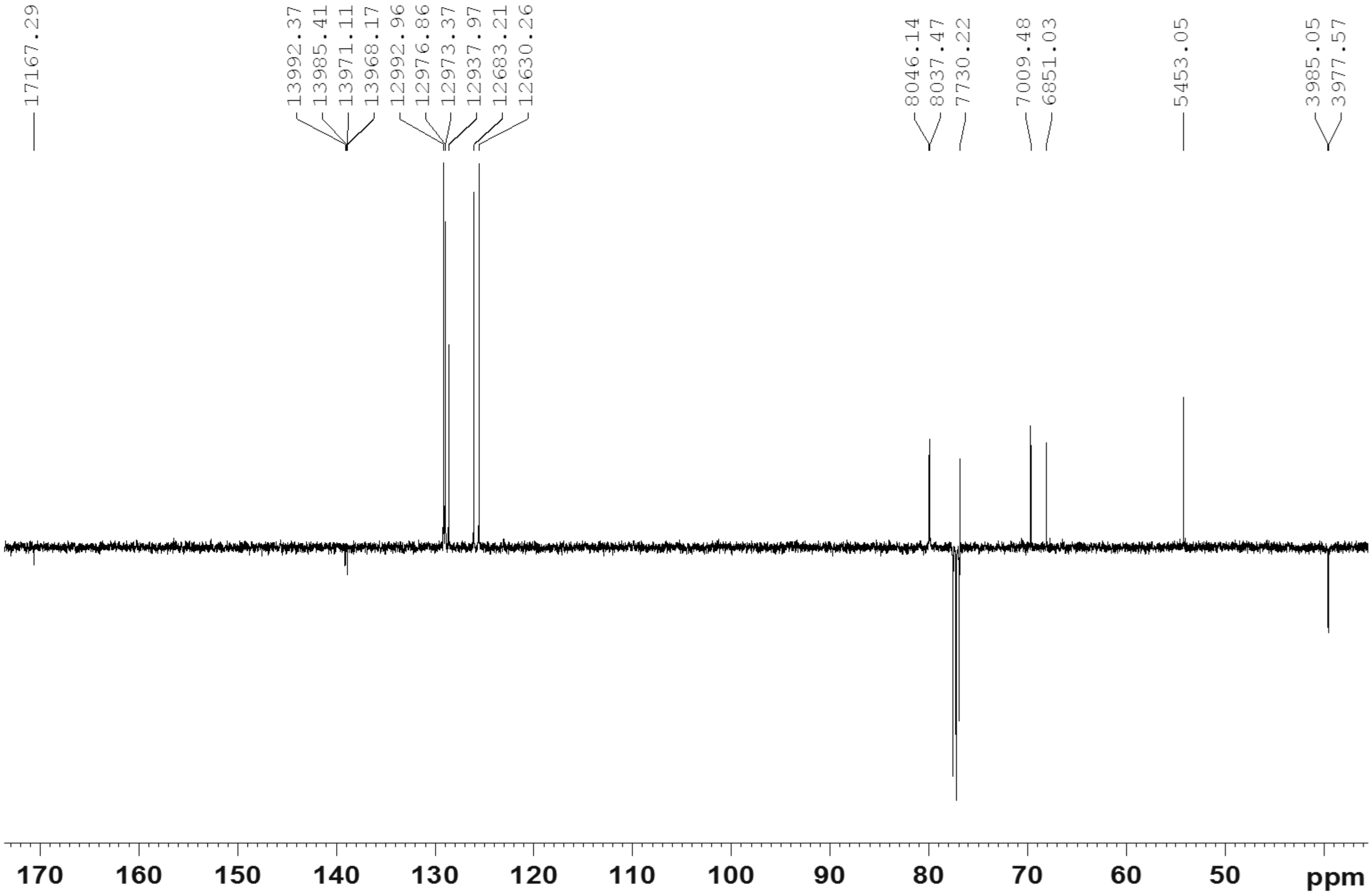
90
80
70
60
50
ppm



Cyclic α-hydroxyphosphonate 16a:




17167.29
13992.37
13985.41
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13968.17
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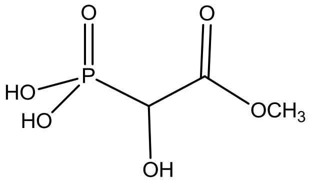
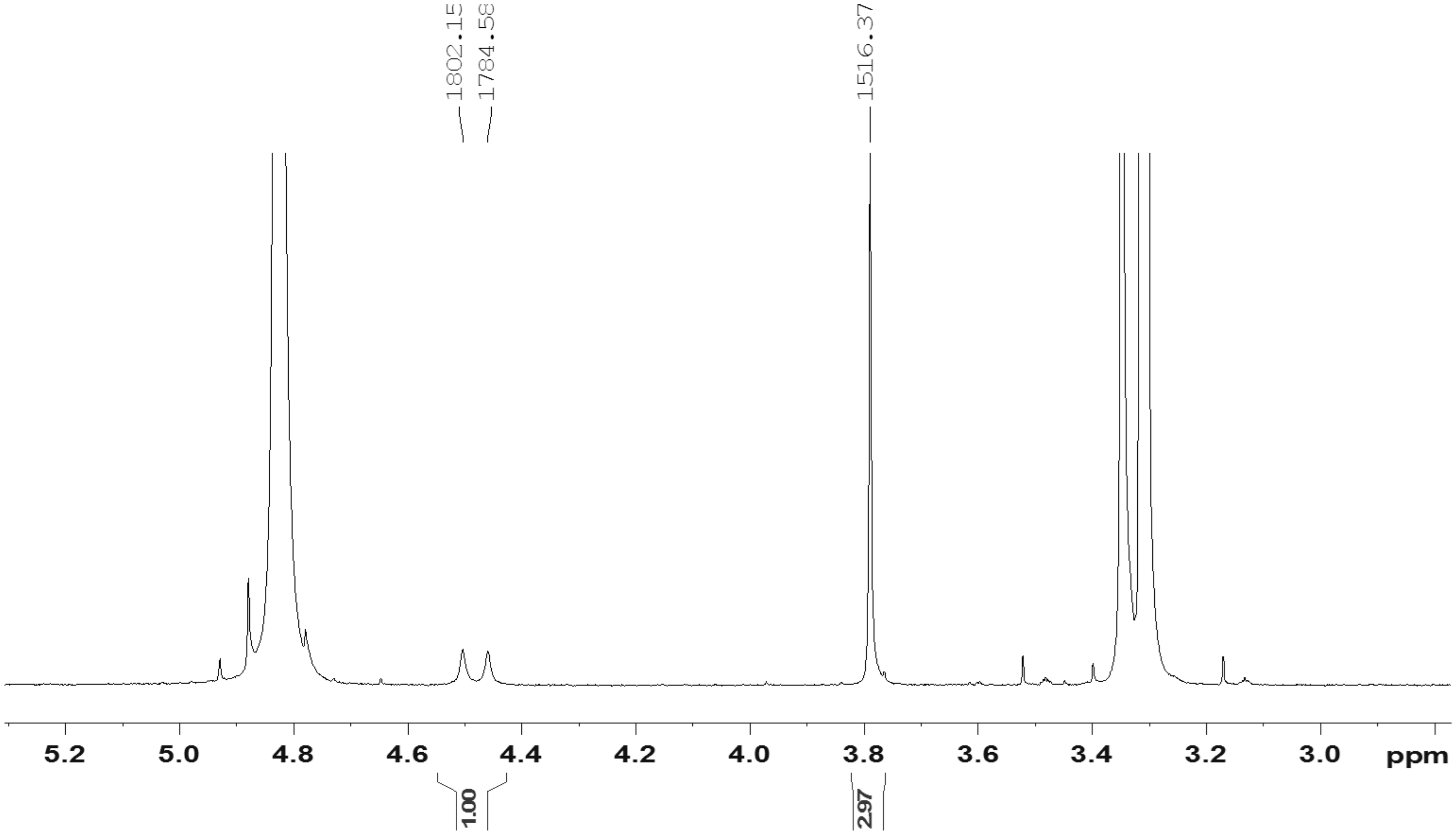
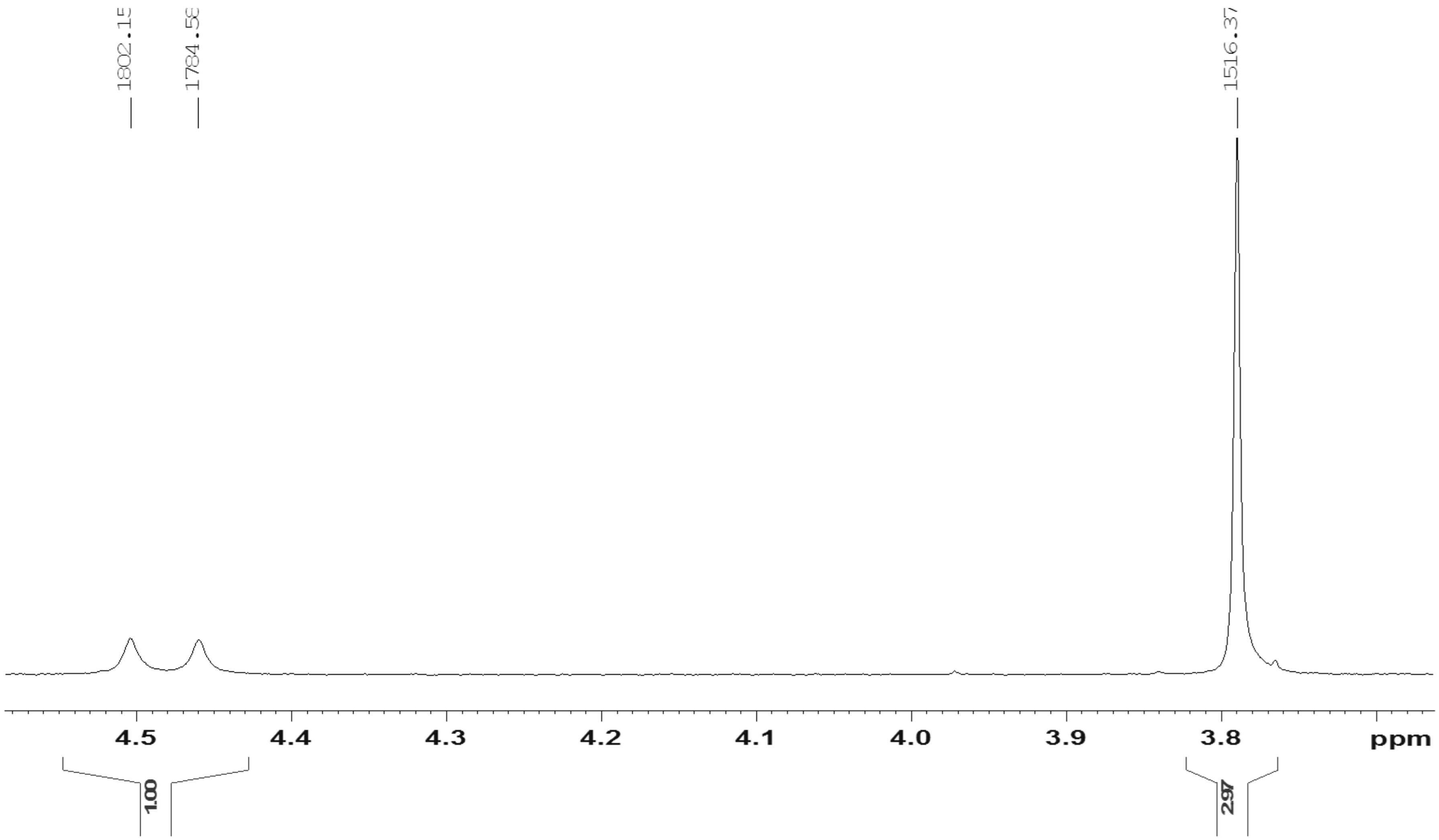
12973.37
12937.97
12683.21
12630.26
8046.14
8037.47
7730.22
7009.48
6851.03
5453.05
3985.05
3977.57
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm

(±)-1-Hydroxy-2-methoxy-2-oxoethylphosphonic acid (6):



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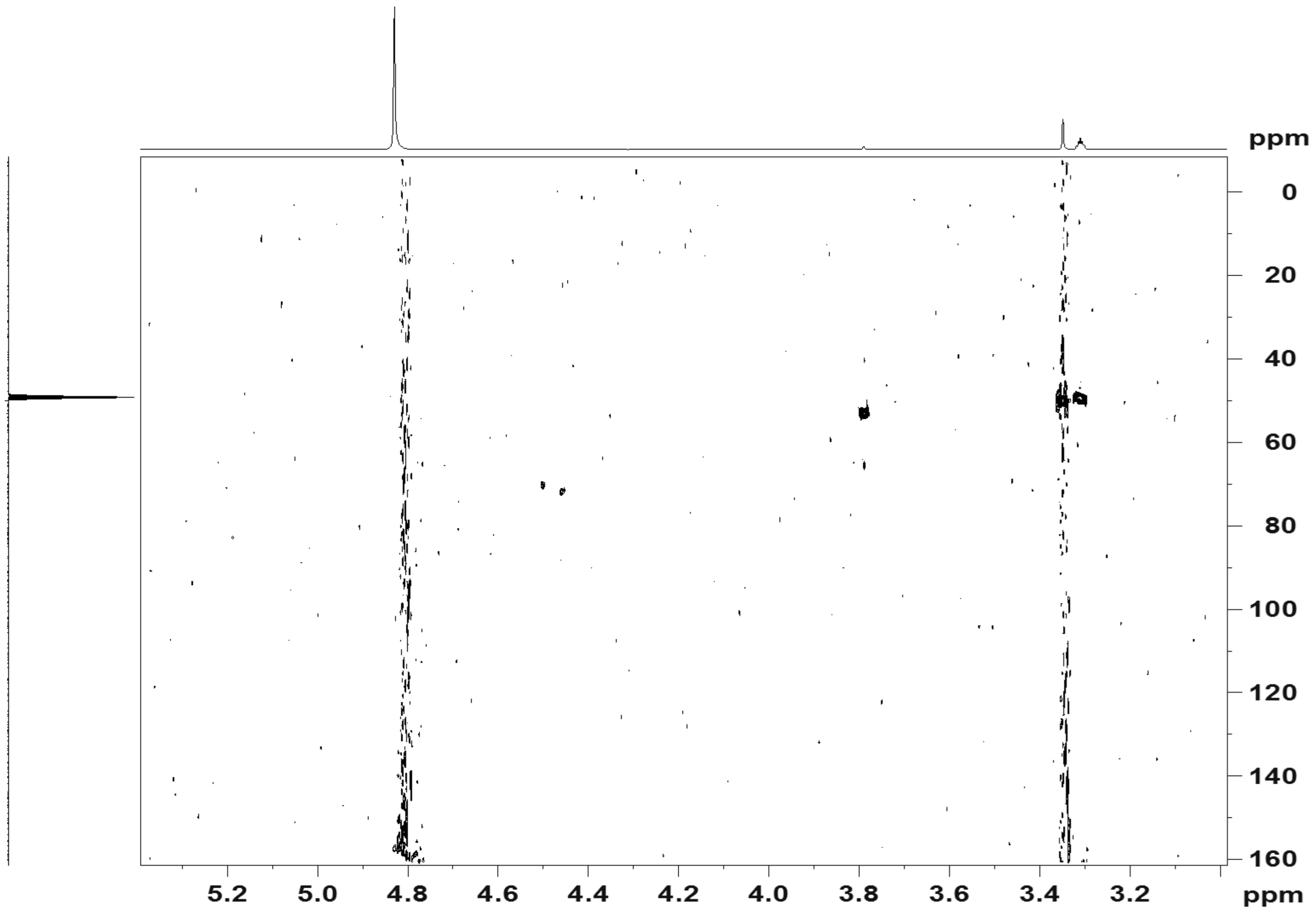
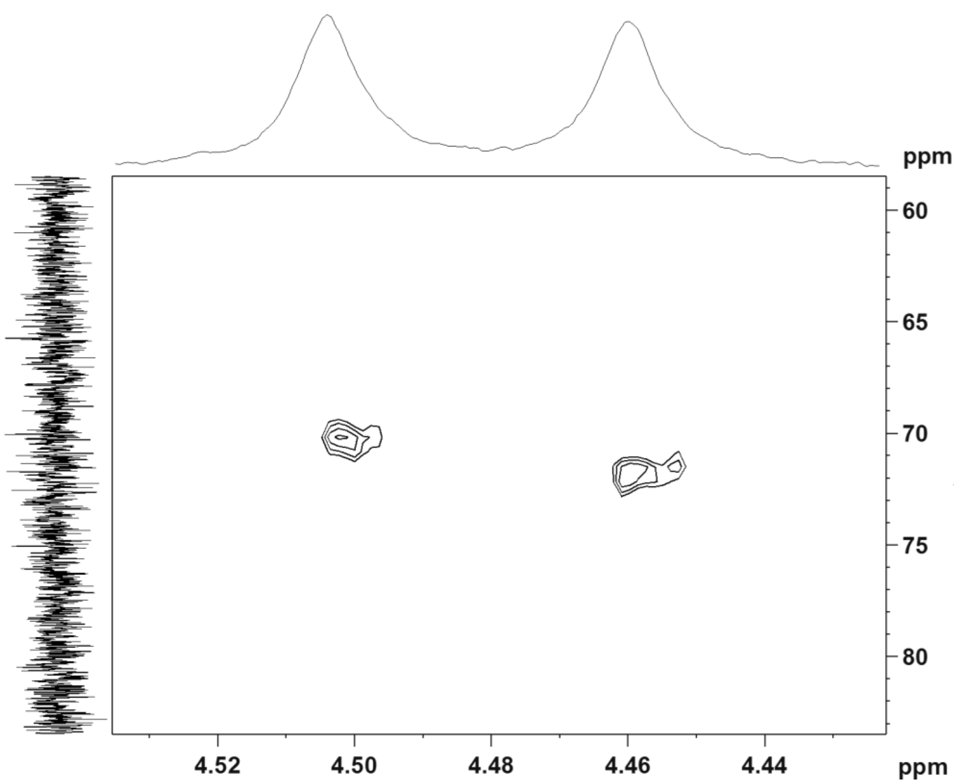
1784.58
1516.37
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
ppm
1.00
2.97

^{13}C NMR: (HSQC)

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65
70
75
80
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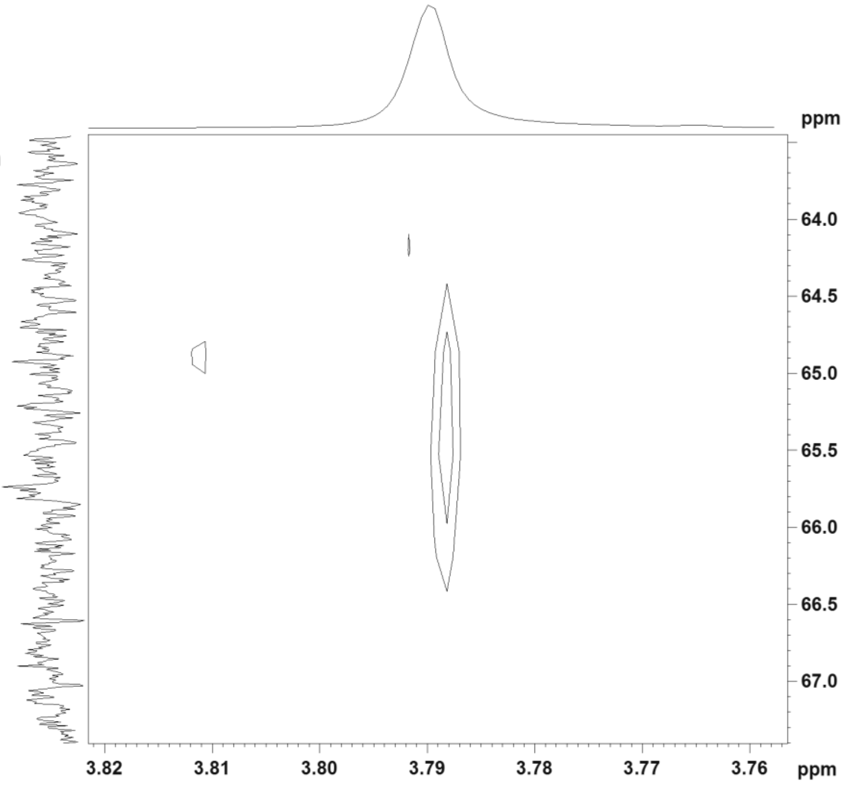
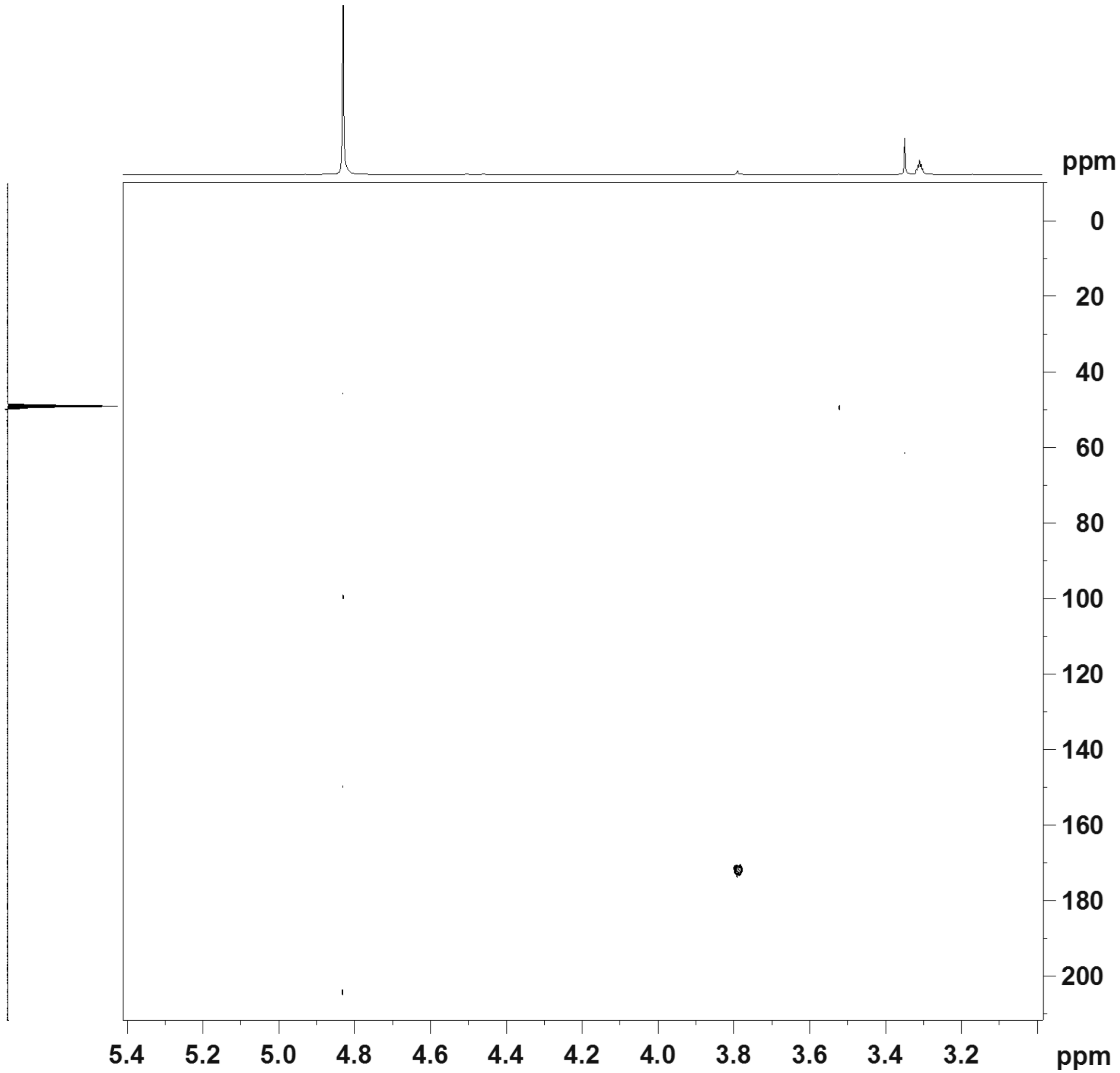
4.50
4.48
4.46
4.44
ppm


ppm
64.0
64.5
65.0
65.5
66.0
66.5
67.0
3.82
3.81
3.80
3.79
3.78
3.77
3.76
ppm

(HMBC)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20
40
60
80
100
120
140
160
180
200
5.4
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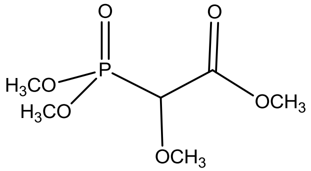
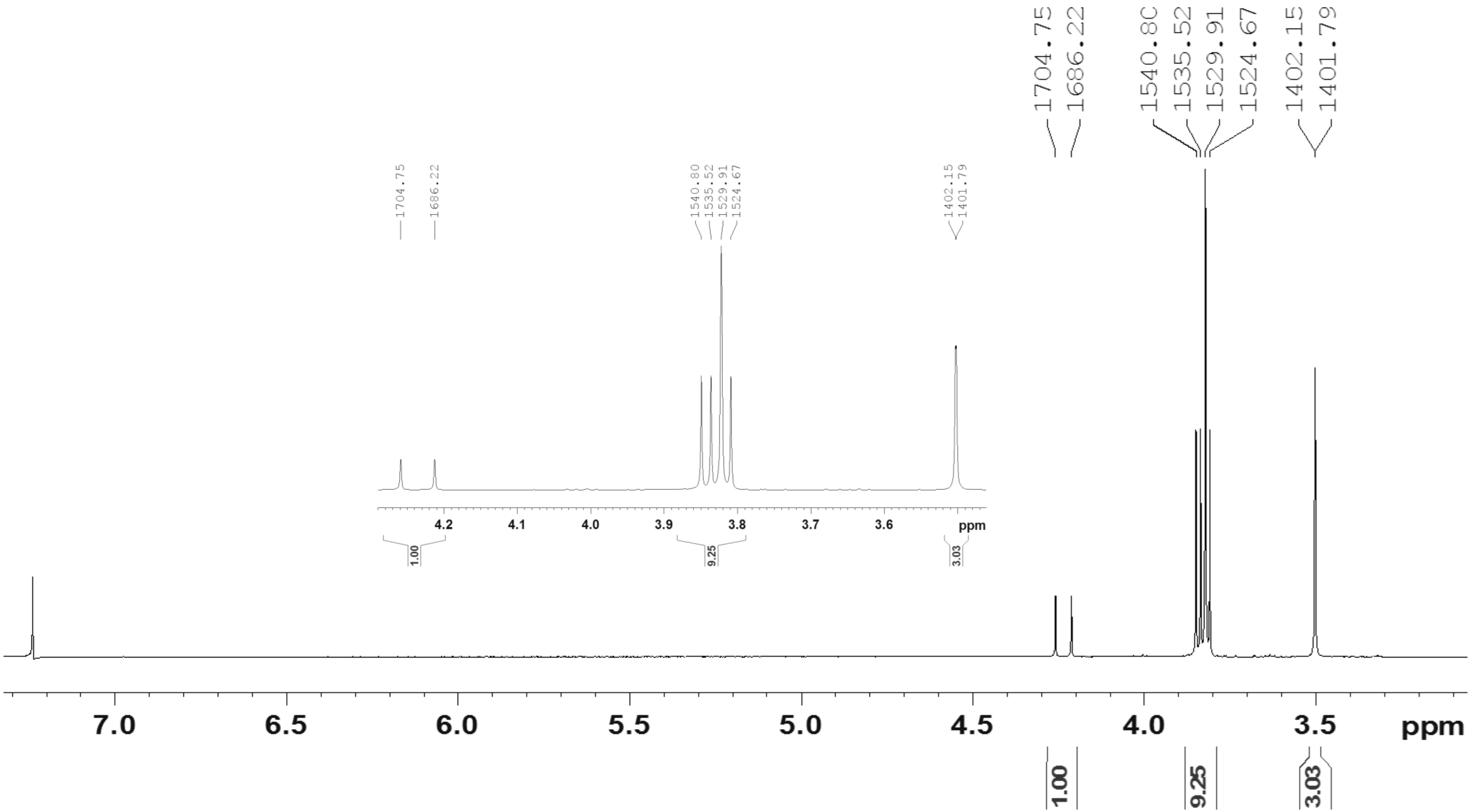
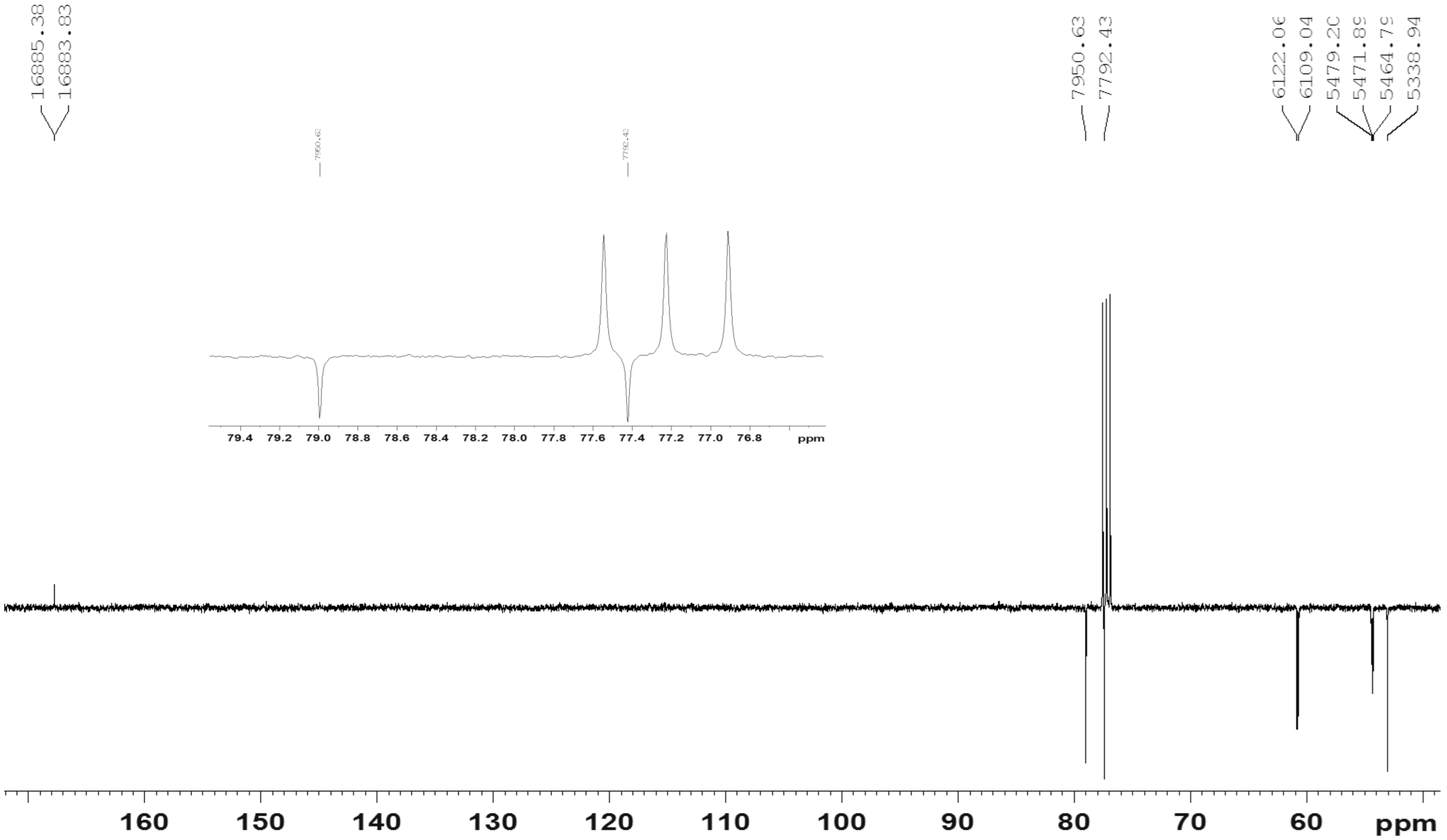
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm



(±)-Methyl 2-(dimethoxyphosphoryl)-2-methoxyacetate (20):




16885.38
16883.83
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6122.06
6109.04
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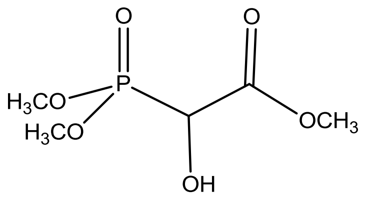
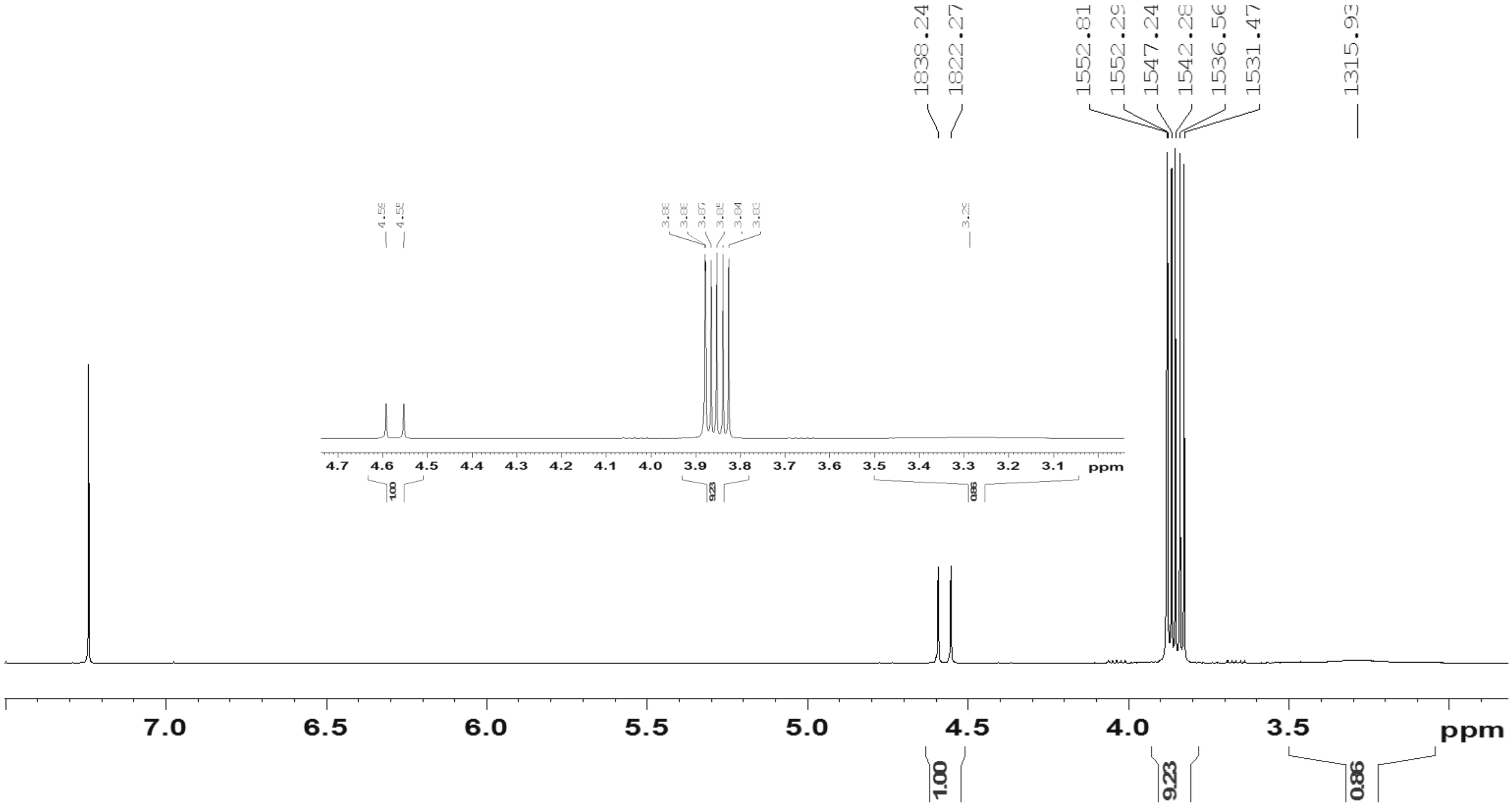
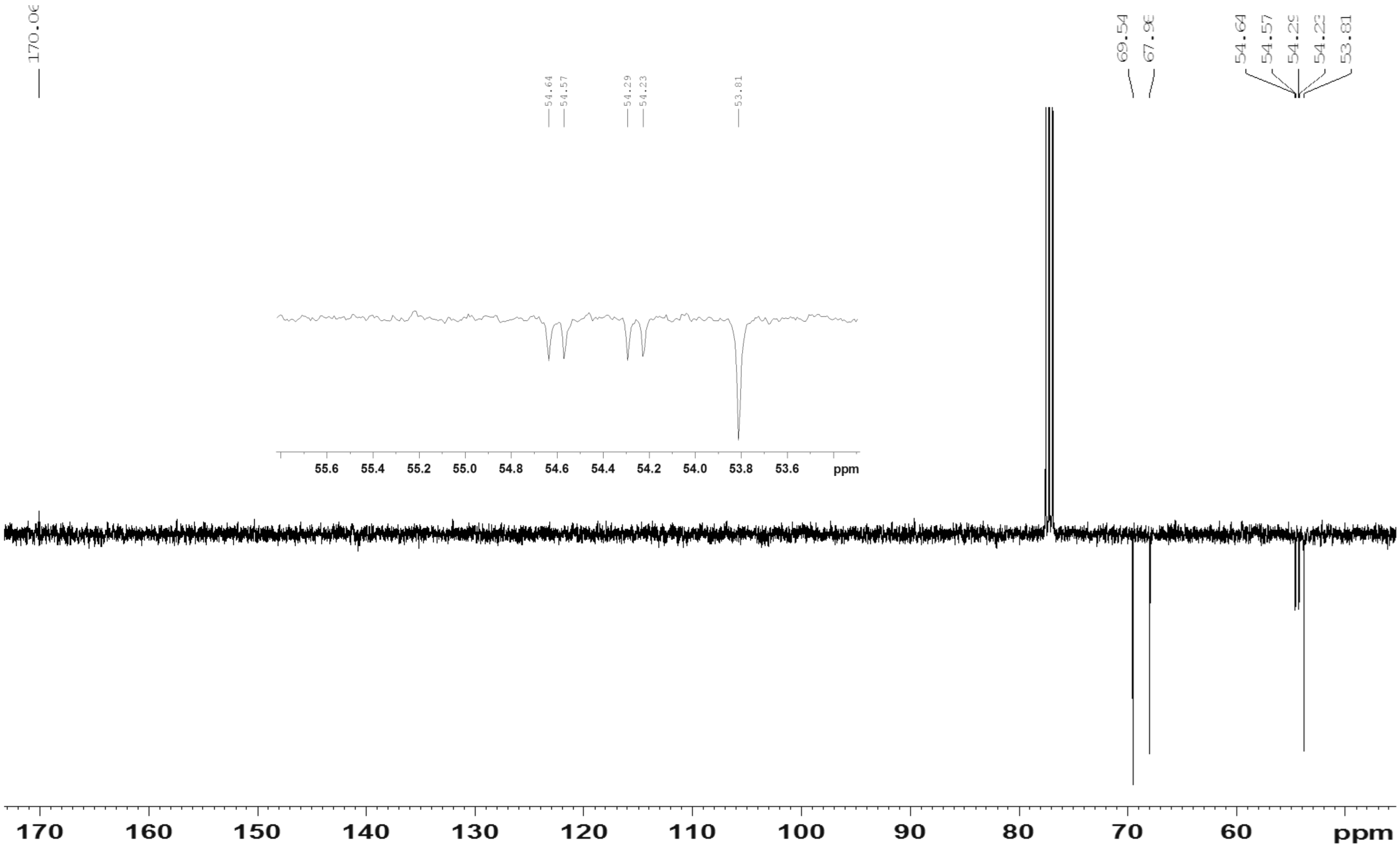
7950.63
7792.43
79.4
79.2
79.0
78.8
78.6
78.4
78.2
78.0
77.8
77.6
77.4
77.2
77.0
76.8
ppm
160
150
140
130
120
110
100
90
80
70
60
ppm

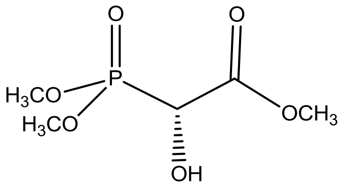
(±)-Methyl 2-(dimethoxyphosphoryl)-2-hydroxyacetate (19):

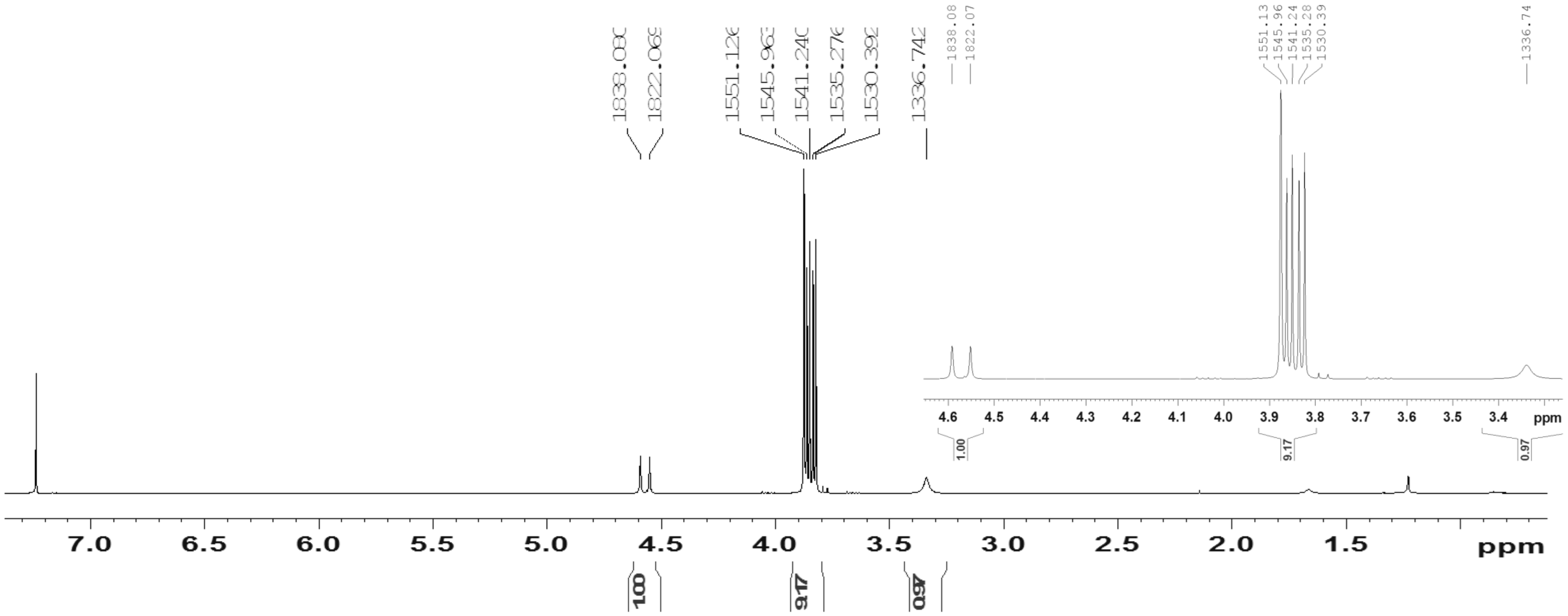





170.06
54.64
54.57
54.29
54.23
53.81
55.6
55.4
55.2
55.0
54.8
54.6
54.4
54.2
54.0
53.8
53.6
ppm
69.54
67.96
54.64
54.57
54.29
54.23
53.81
170
160
150
140
130
120
110
100
90
80
70
60
ppm

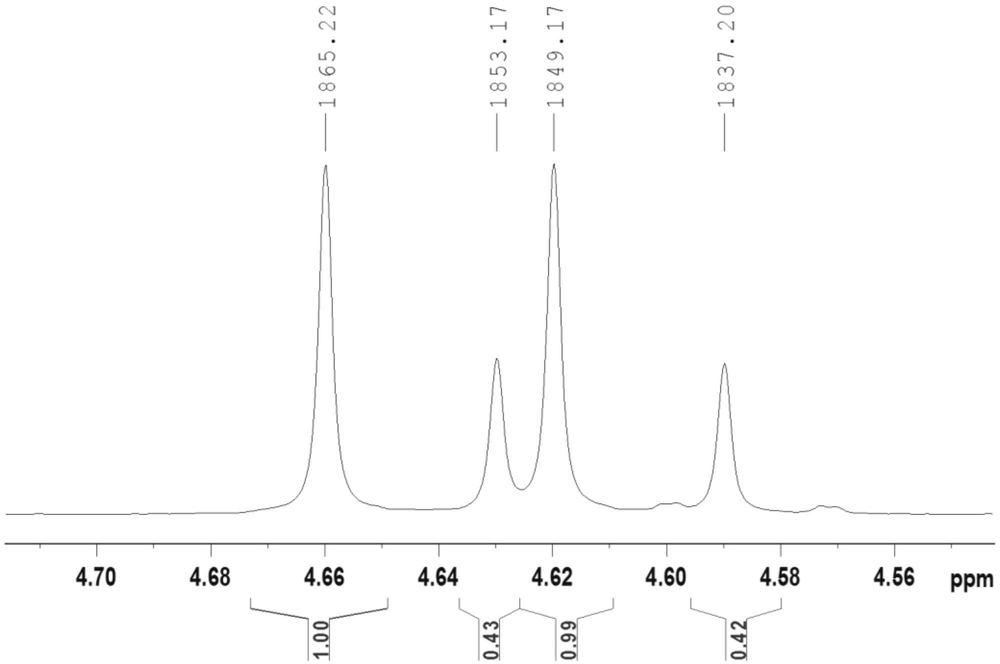
(*R*)-Methyl 2-(dimethoxyphosphinyl)-2-hydroxyacetate (19), obtained from 16b:



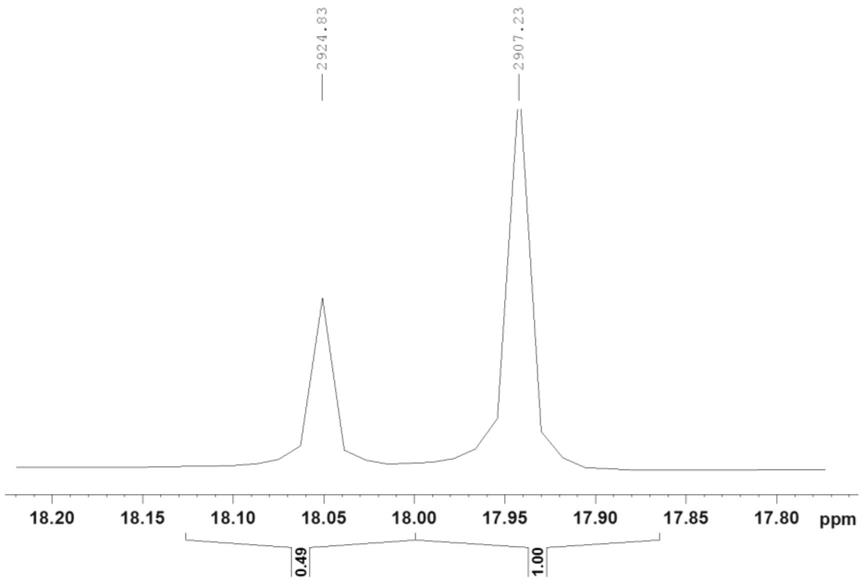


NMR of 19 obtained from 16b with chiral Shiftreagent ((*R*)-(+)-t-butyl(phenyl)monothiophosphinic acid):

^{1}**H NMR:** Expansion



^{31}**P NMR:**



X-ray crystallography.

X-ray diffraction measurements were performed on a Bruker X8 APEXII CCD diffractometer. Single crystals were positioned at 35 and 40 mm from the detector, and 7634 and 977 frames were measured, each for 3 and 10 s over 1° scan width for **16a** and **16b**, respectively. The data were processed using SAINT software.[1] Crystal data, data collection parameters, and structure refinement details are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in calculated positions and refined with a riding model. The following computer programs and hardware were used: structure solution, *SHELXS-97* and refinement, *SHELXL-97*;[2] molecular diagrams, ORTEP[3] computer, Intel CoreDuo.

Table 1. Crystal data and details of data collection for **16a** and **16b**.

Compound	**16a**	**16b**
empirical formula	$C_{18}H_{19}O_6P$	$2(C_{18}H_{19}O_6P)\cdot CH_2Cl_2$
fw	362.30	809.53
space group	$P2_12_12_1$	$P2_1$
a [Å]	9.7943(4)	10.9242(3)
b [Å]	10.0856(4)	9.4730(3)
c [Å]	17.1604(8)	18.5505(6)
β [°]		94.287(2)
V [Å^3]	1695.13(12)	1914.33(10)
Z	4	2
λ [Å]	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.420	1.404
crystal size [mm^3]	0.35 × 0.30 × 0.20	0.60 × 0.25 × 0.25
T [K]	150(2)	150(2)
μ [mm^{-1}]	0.194	0.315
2θ range	2.34 − 30.20	1.87 − 30.11
Limiting indices	$-13 \le h \le 13$ $-14 \le k \le 14$ $-24 \le l \le 24$	$-15 \le h \le 15$ $-13 \le k \le 13$ $-26 \le l \le 26$
Refl. collected	291851	36832
Reflections unique	5009	11113
Restraints/Parameters	0 / 227	1 / 480
GOF on F^2	1.018	1.022
R_1[a]	0.0295	0.0350

wR_2[b]	0.0837	0.0907
GOF[c]	1.018	1.022

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[c] $\mathrm{GOF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

References

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[1] *SAINT-Plus*, version 7.06a and APEX2; Bruker-Nonius AXS Inc.: Madison, WI, 2004.

[2] G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

[3] M. N. Burnett and G. K. Johnson, ORTEPIII. Report ORNL-6895. OAK Ridge National Laboratory; Tennessee, USA, 1996.