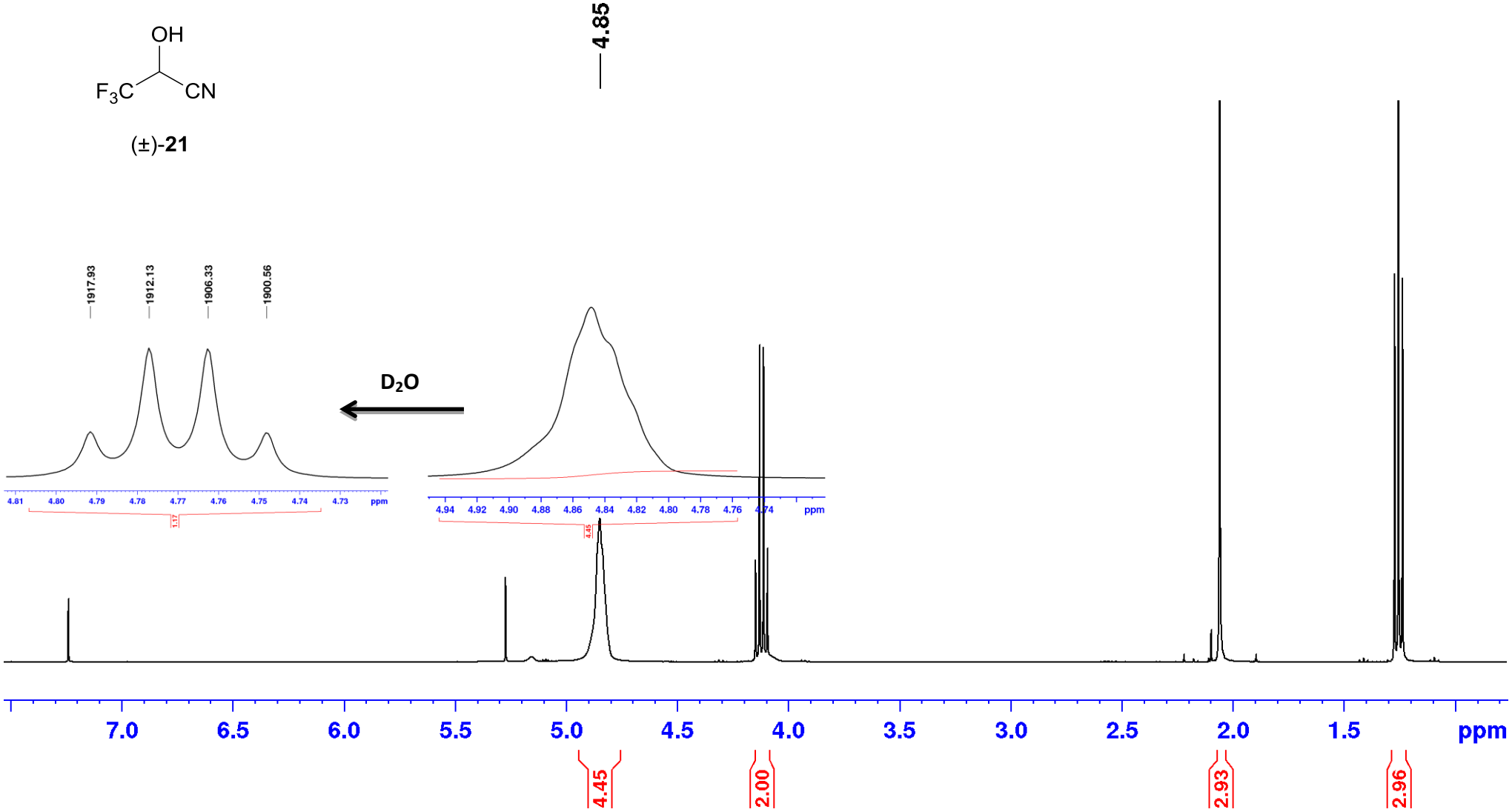
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

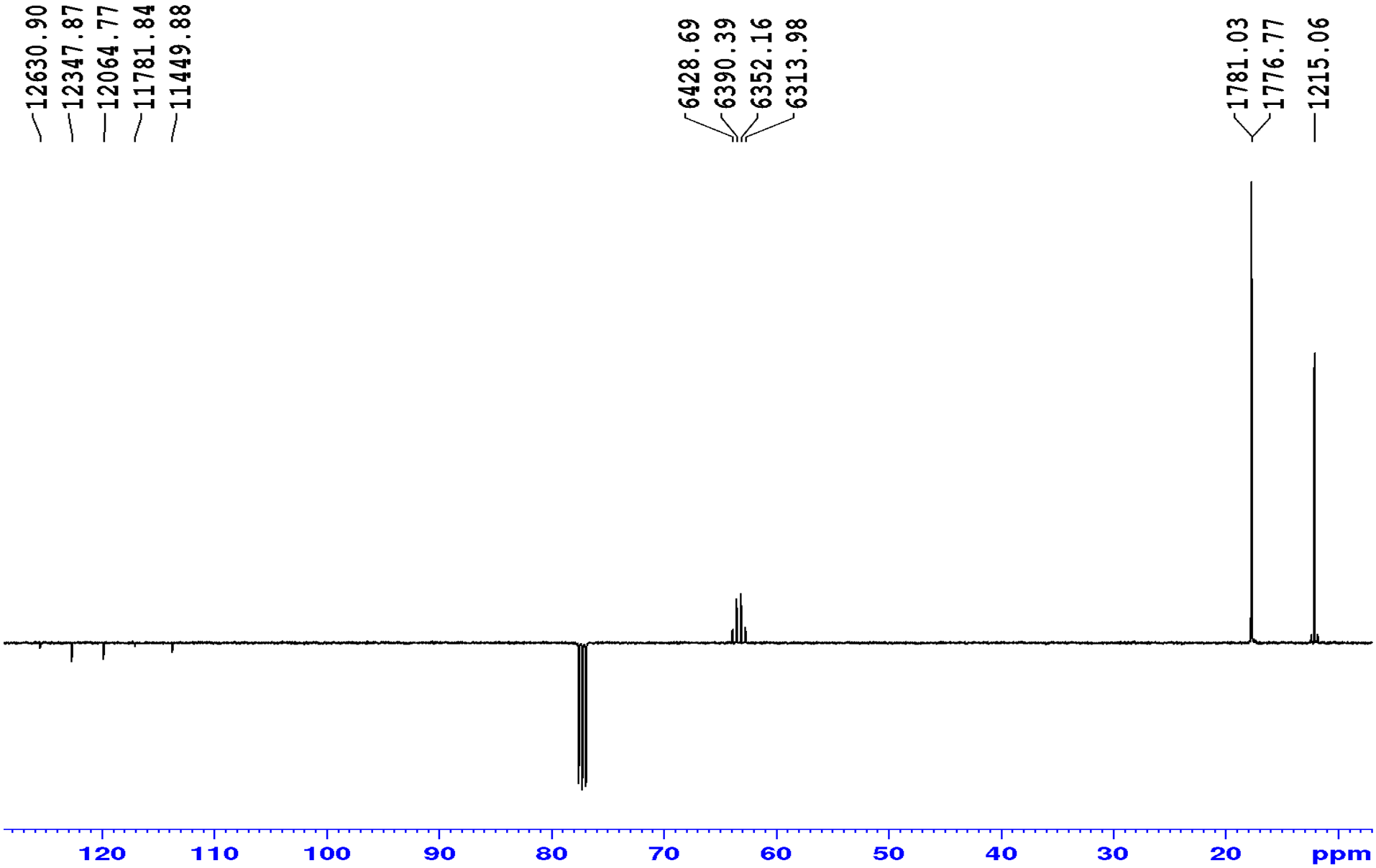
Supporting Information:

All assignments are given in the "Experimental part" of the publication. The first spectrum shown of each series is the full ^{1}H NMR spectrum. Expansions are depicted where they were regarded as necessary. Then the ^{13}C NMR spectrum is depicted in the same manner, followed by the ^{31}P NMR spectrum. 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 full ^{1}H NMRspectrum. Integrals are denoted below the x-axes where they are regarded as necessary and the integration range is marked. The numbering of the spectra is in accordance with the numbering of substances in the main text.

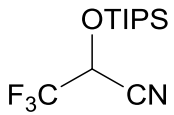
^{1}H NMR spectrum of (±)-3,3,3-Trifluoro-2-hydroxypropane nitrile [(±)-21] (400.27 MHz):



^{13}C NMR spectrumof (±)-21 (100.65 MHz):

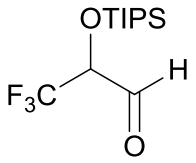


^{1}H NMR spectrum of (±)-3,3,3-Trifluoro-2-(triisopropylsiloxy)propane nitrile [(±)-22] (400.27 MHz):



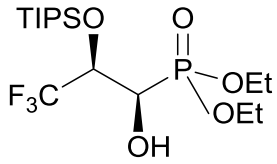
(±)-**22**

^{1}H NMR spectrum of(±)-3,3,3-Trifluoro-2-(triisopropylsiloxy)propanal [(±)-23] (400.27

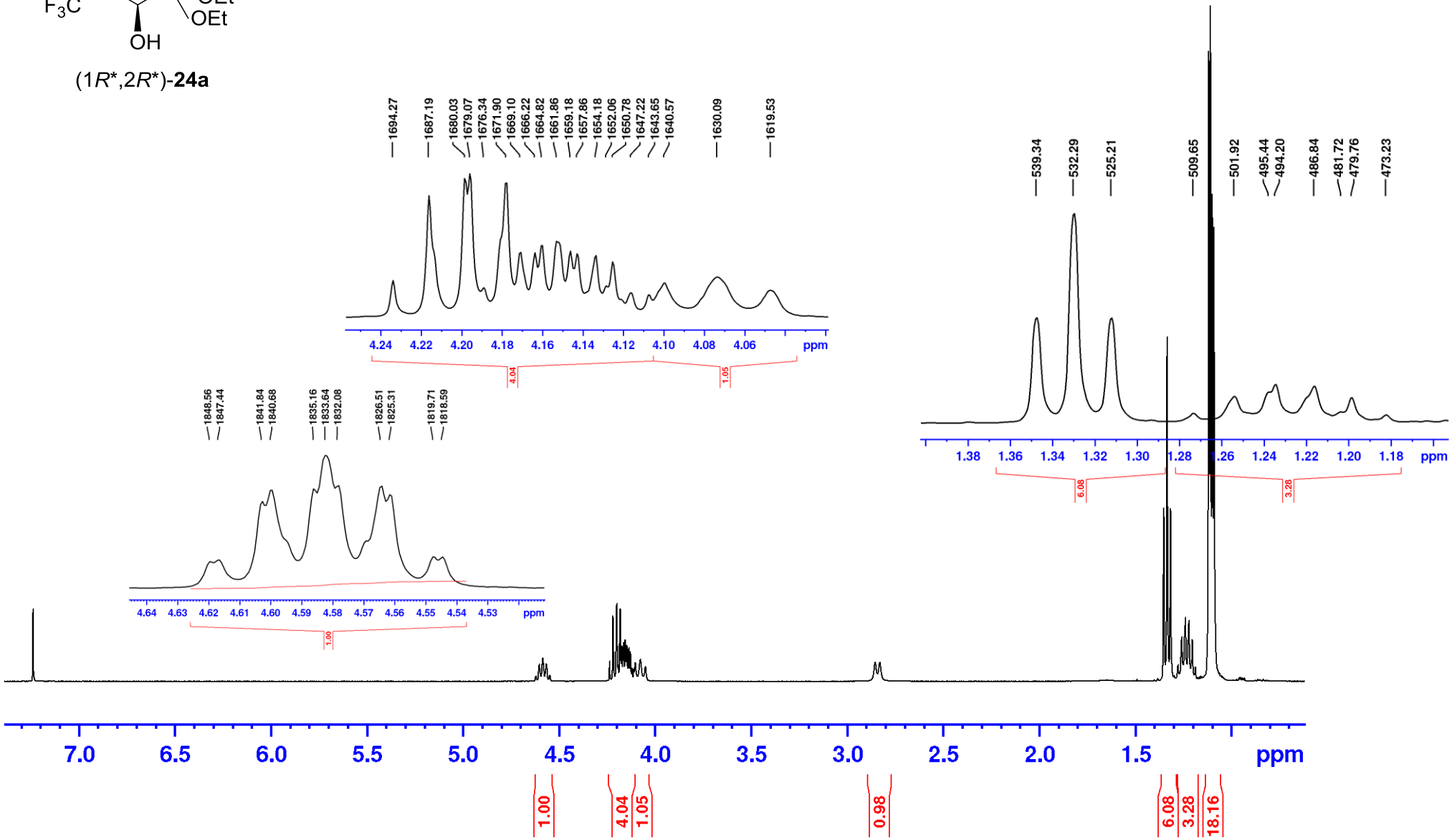


(±)-**23**

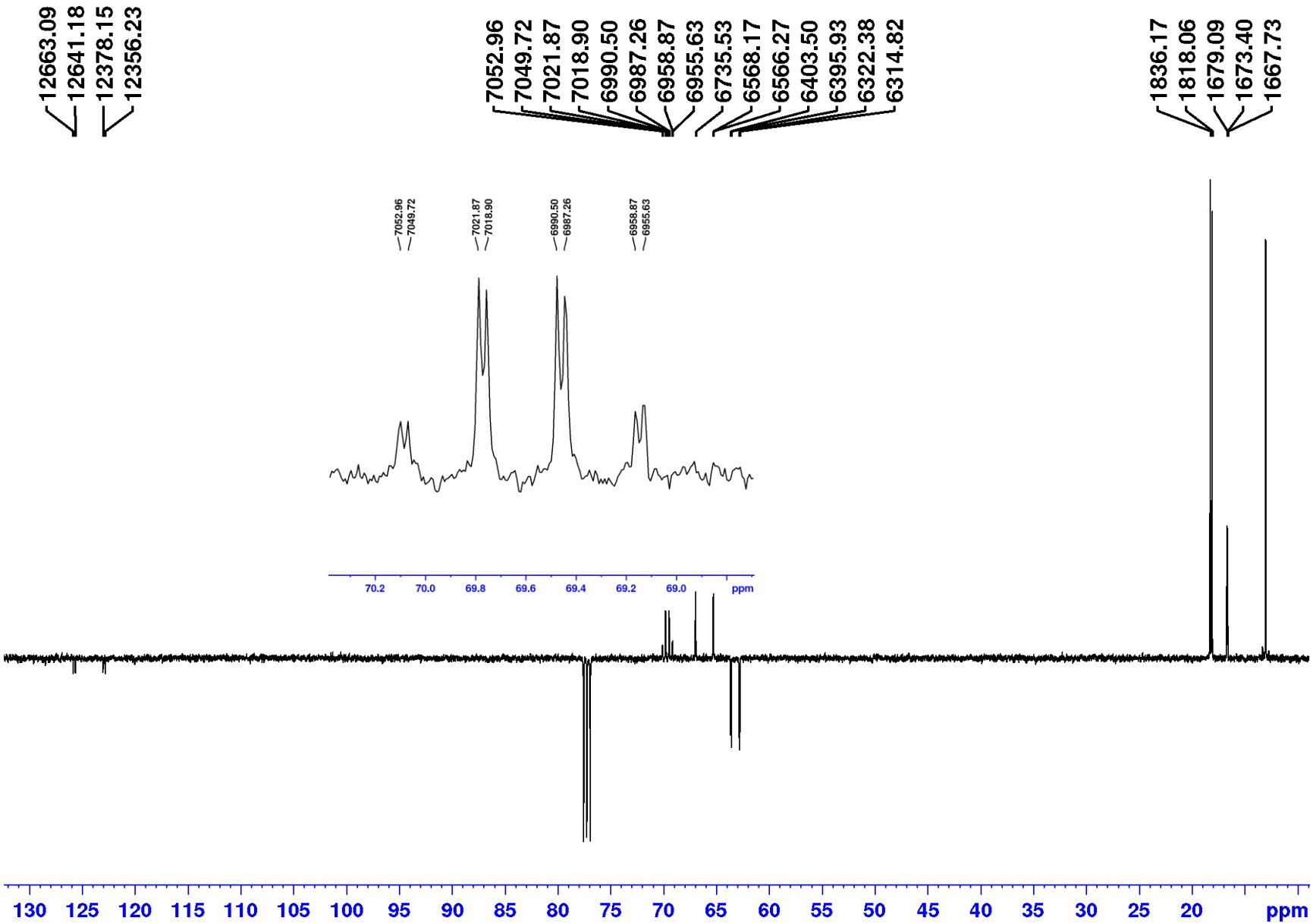
^{1}H NMR spectrumof (±)-(1*R,2*R**)-Diethyl 3,3,3-trifluoro-1-hydroxy-2-(triisopropylsilyloxy)-propylphosphonate [(±)-(1*R**,2*R**)-24a] (400.13 MHz):**



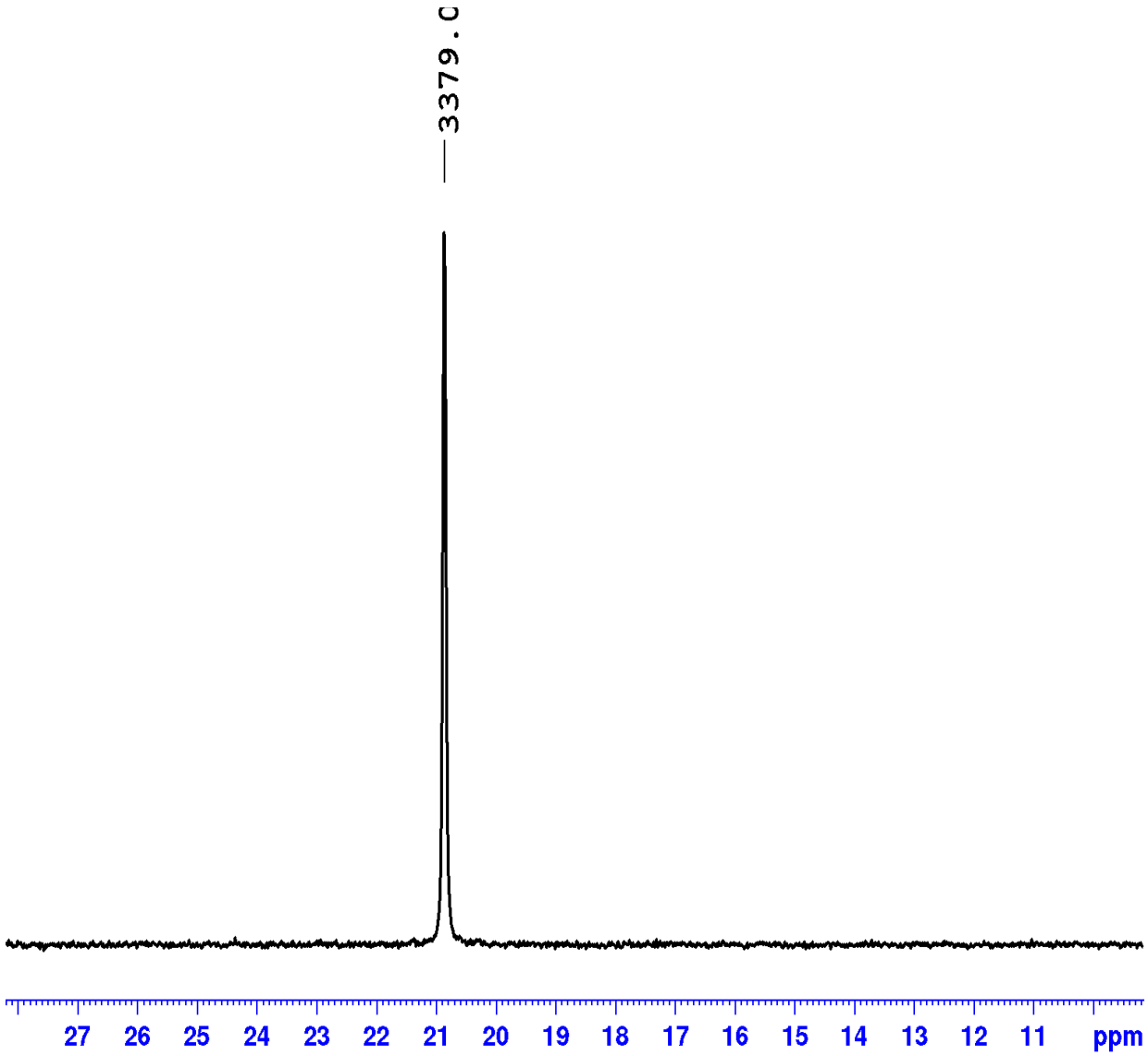
(1*R**,2*R**)-**24a**



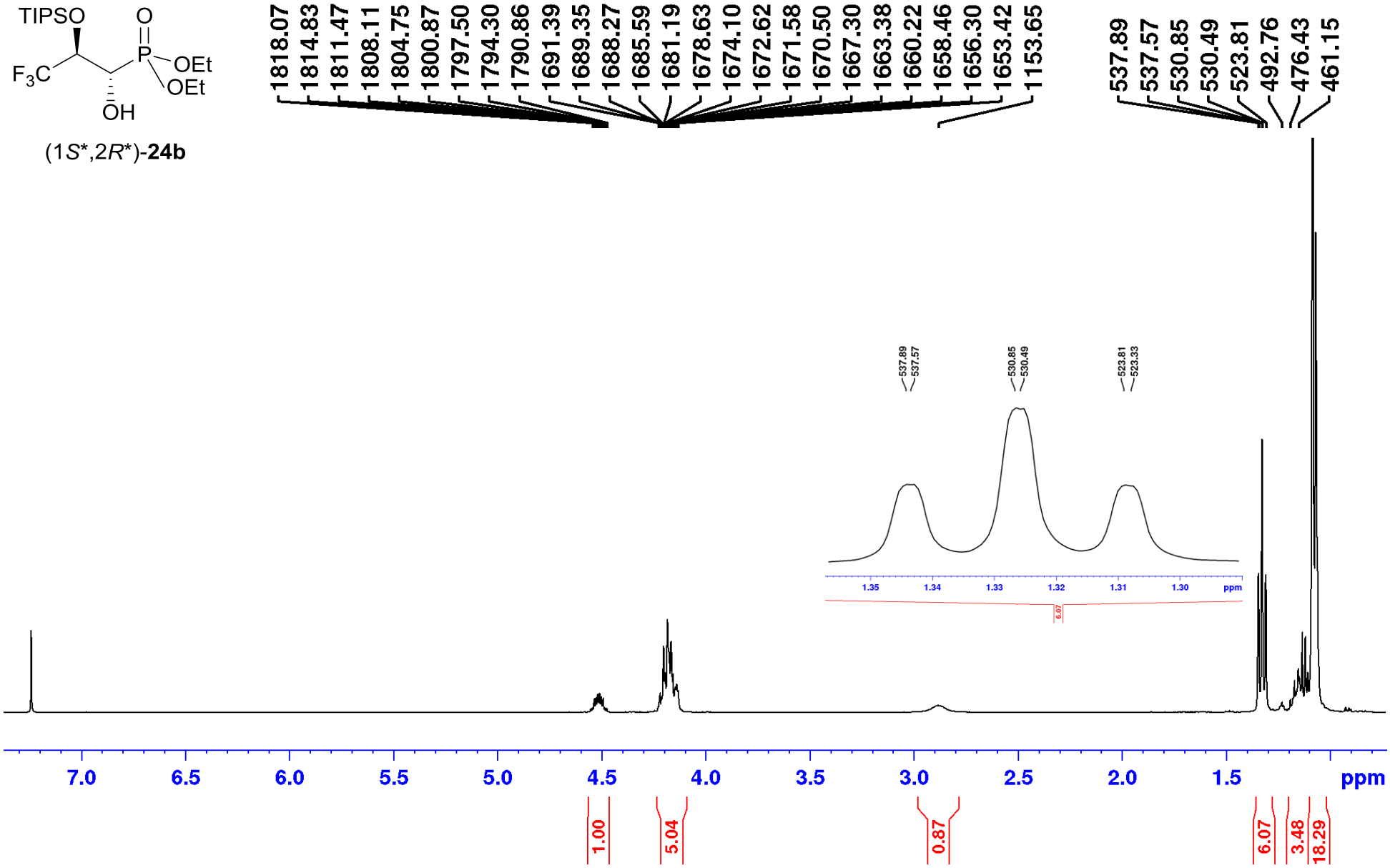
^{13}C NMR spectrum of (±)-(1*R,2*R**)-24a (100.61 MHz):**



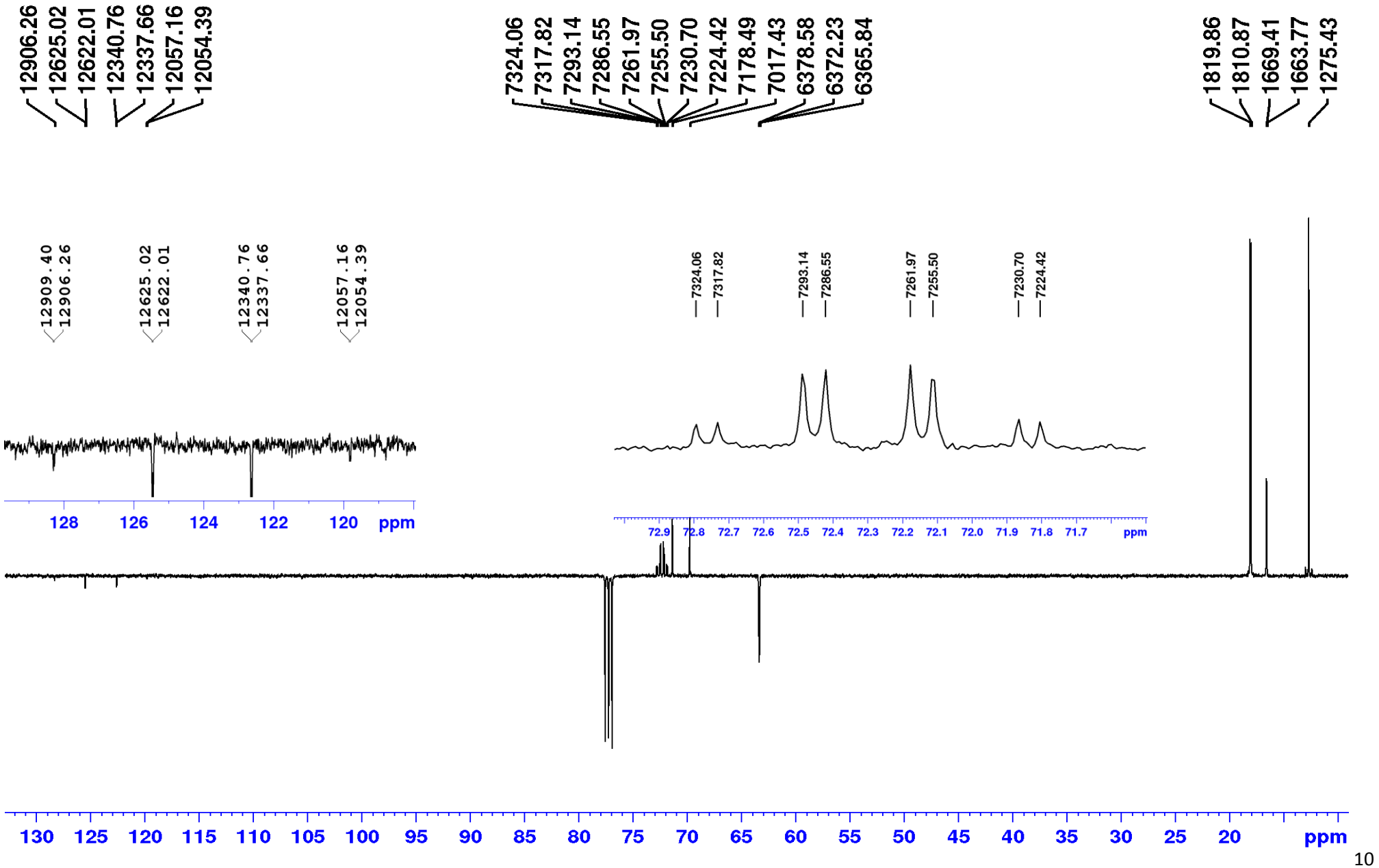
^{31}P NMR spectrum of (±)-(1*R,2*R**)-24 a (162.03 MHz):**



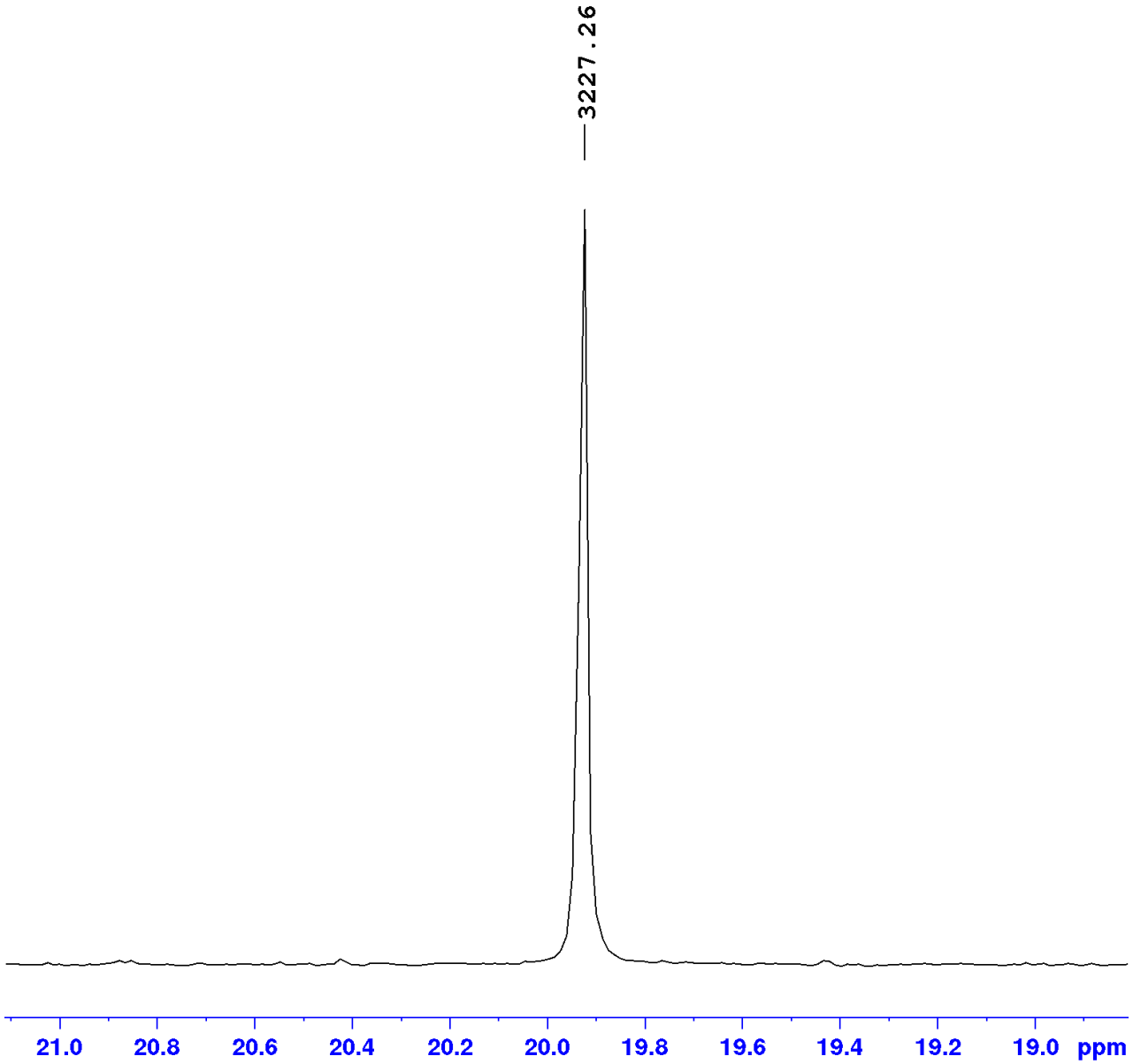
^{1}H NMR spectrum of (±)-(1*S,2*R**)-Diethyl 3,3,3-trifluoro-1-hydroxy-2-(triisopropylsilyloxy)-propylphosphonate [(±)-(1*S**,2*R**)-24b] (400.13 MHz):**



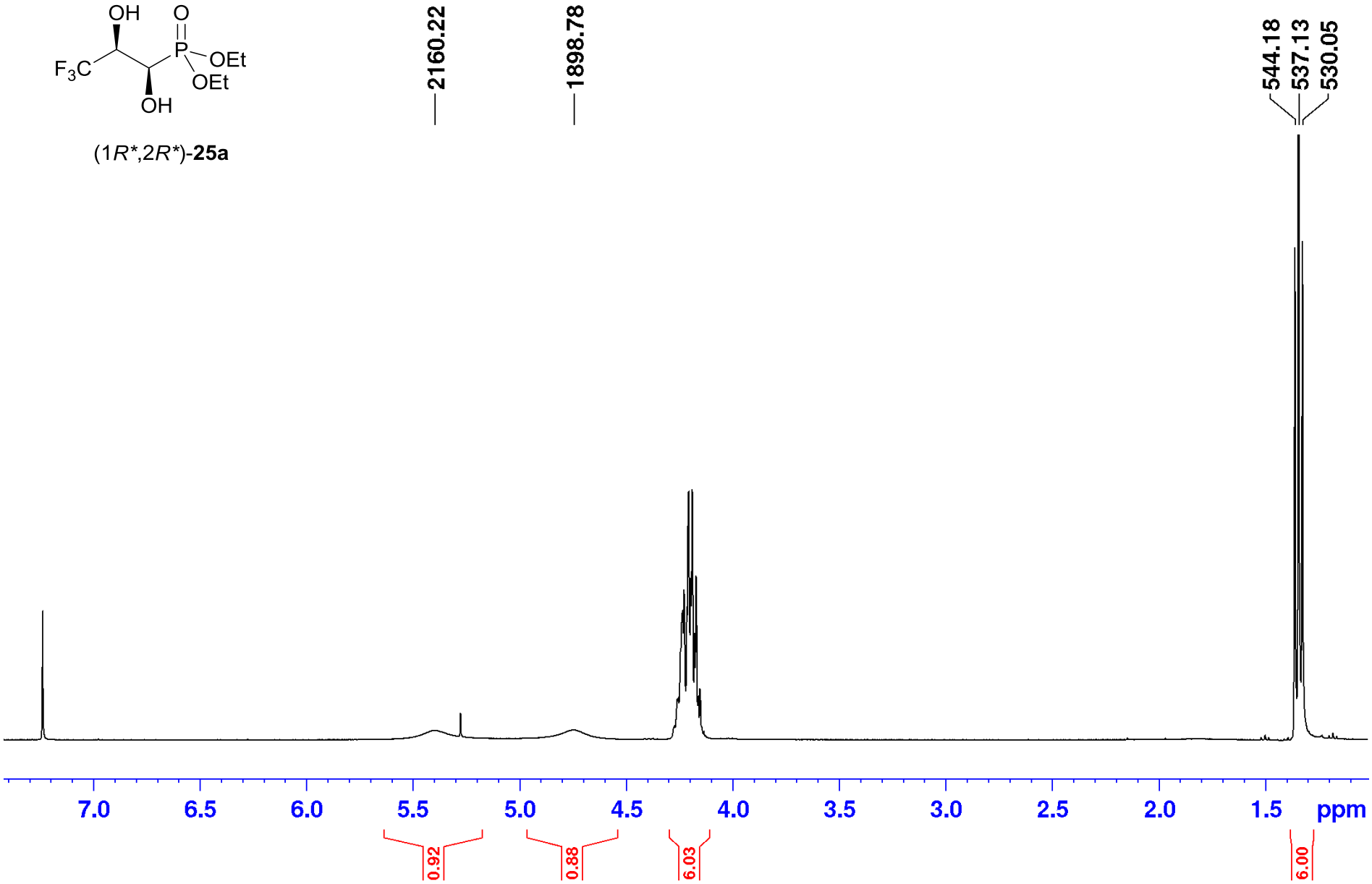
^{13}C NMR spectrum of (±)-(1*S,2*R**)-24b (100.61 MHz):**



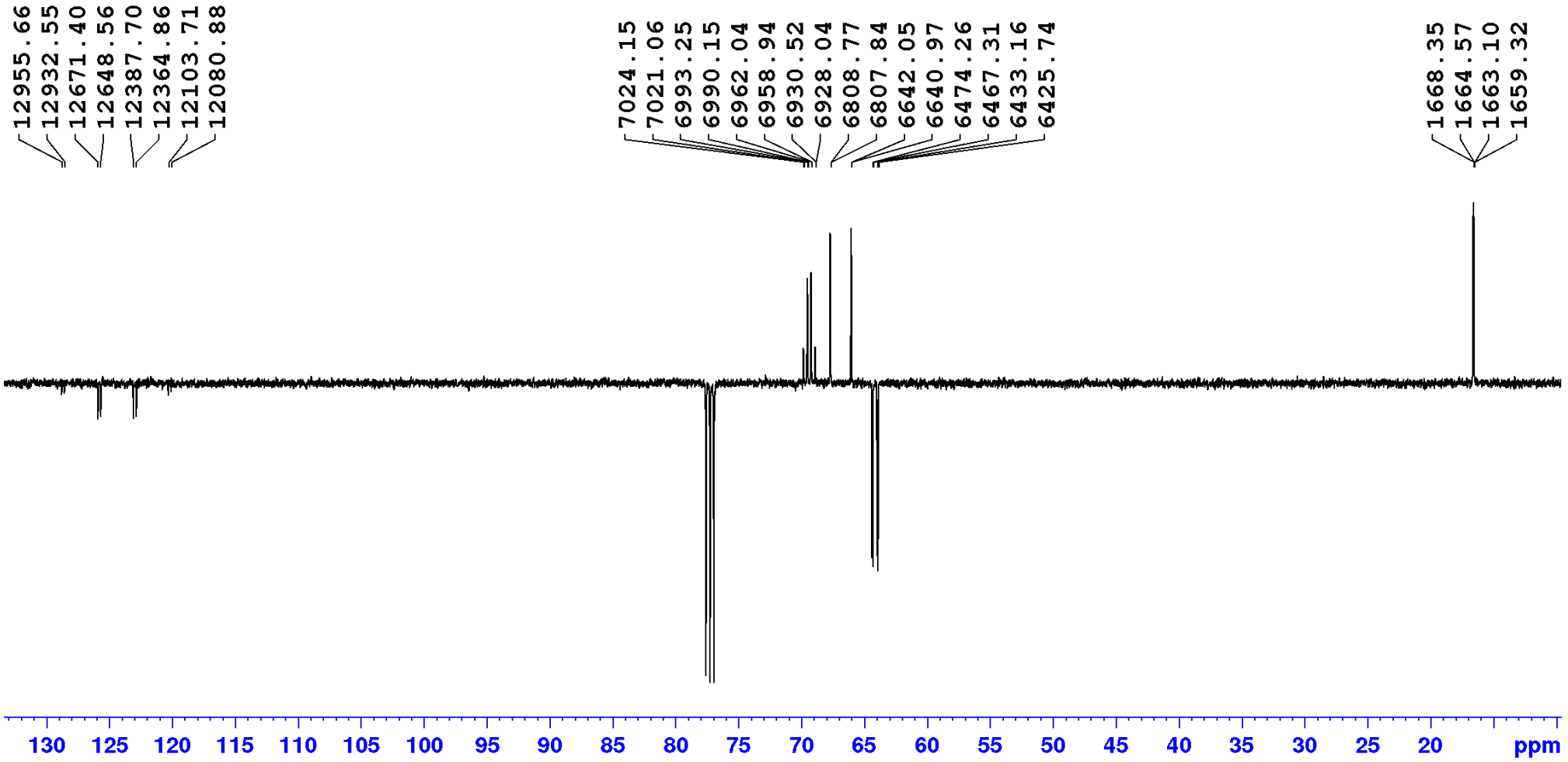
^{31}P NMR spectrum of (±)-(1*S,2*R**)-24b (162.03 MHz):**



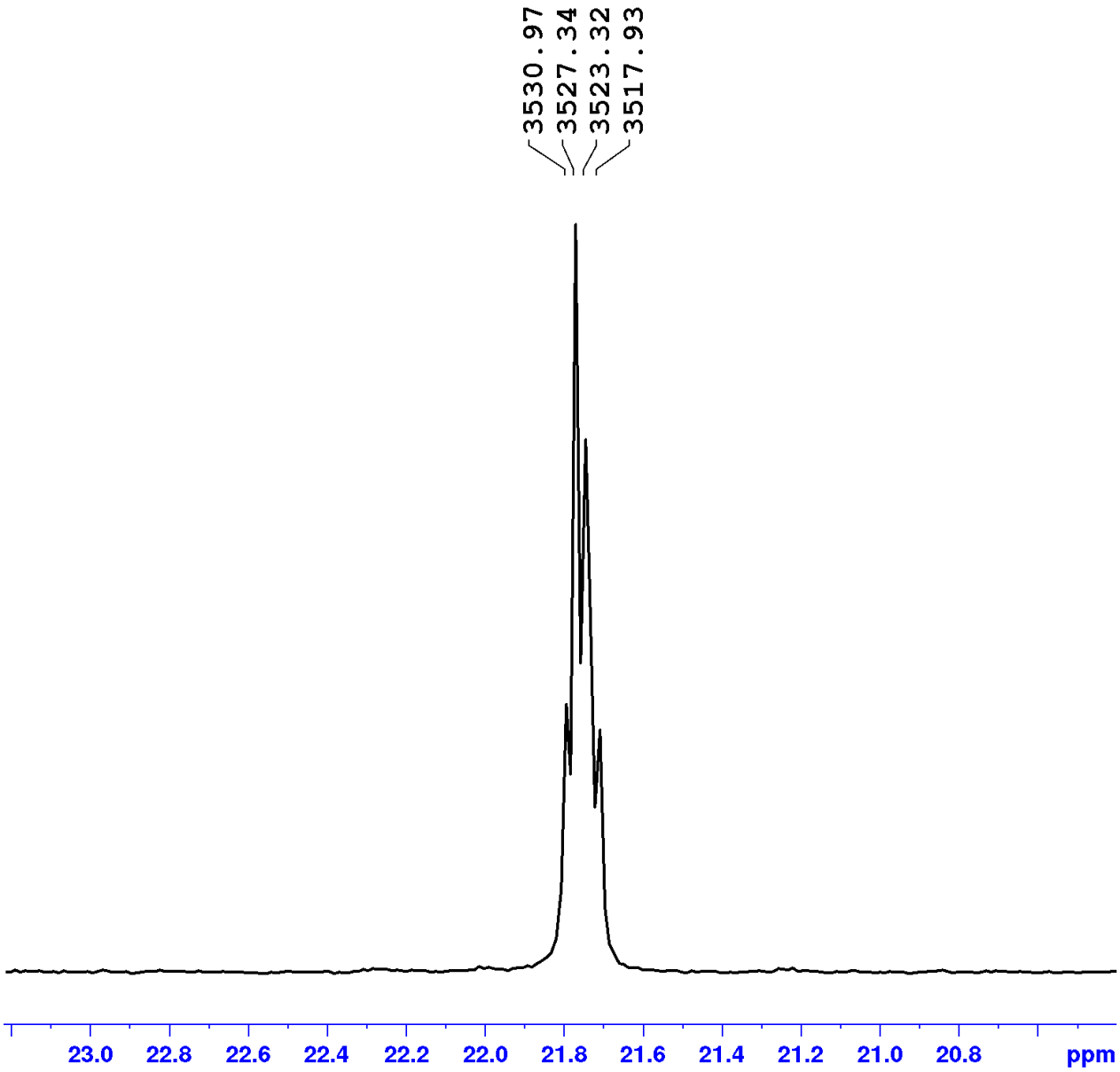
^{1}H NMR spectrum of (±)-(1*R,2*R**)-Diethyl 3,3,3-trifluoro-1,2-dihydroxypropylphosphonate [(±)-(1*R**,2*R**)-25a] (400.13 MHz):**



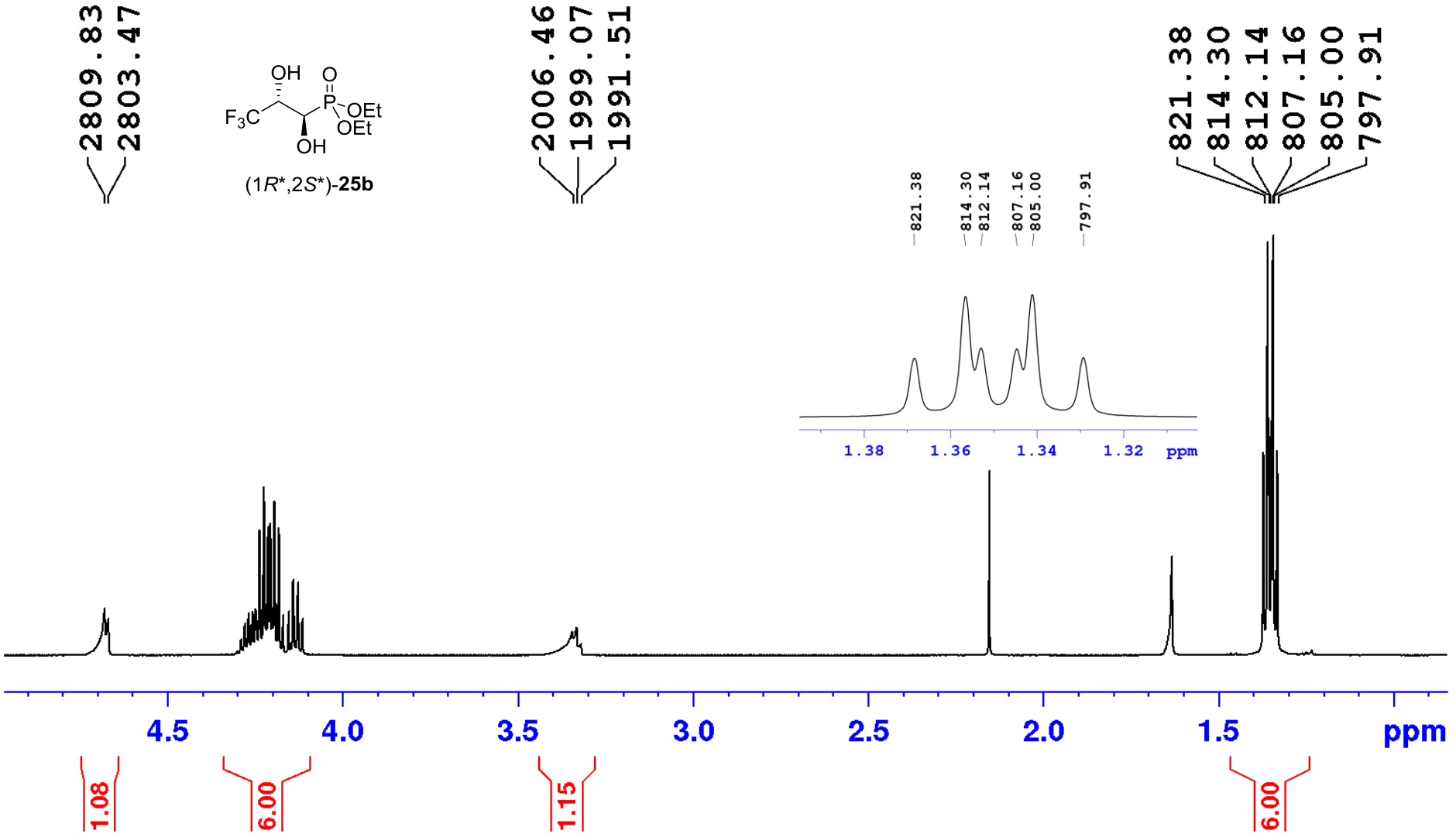
^{13}C NMR spectrum of (±)-(1*R,2*R**)-25a (100.61 MHz):**



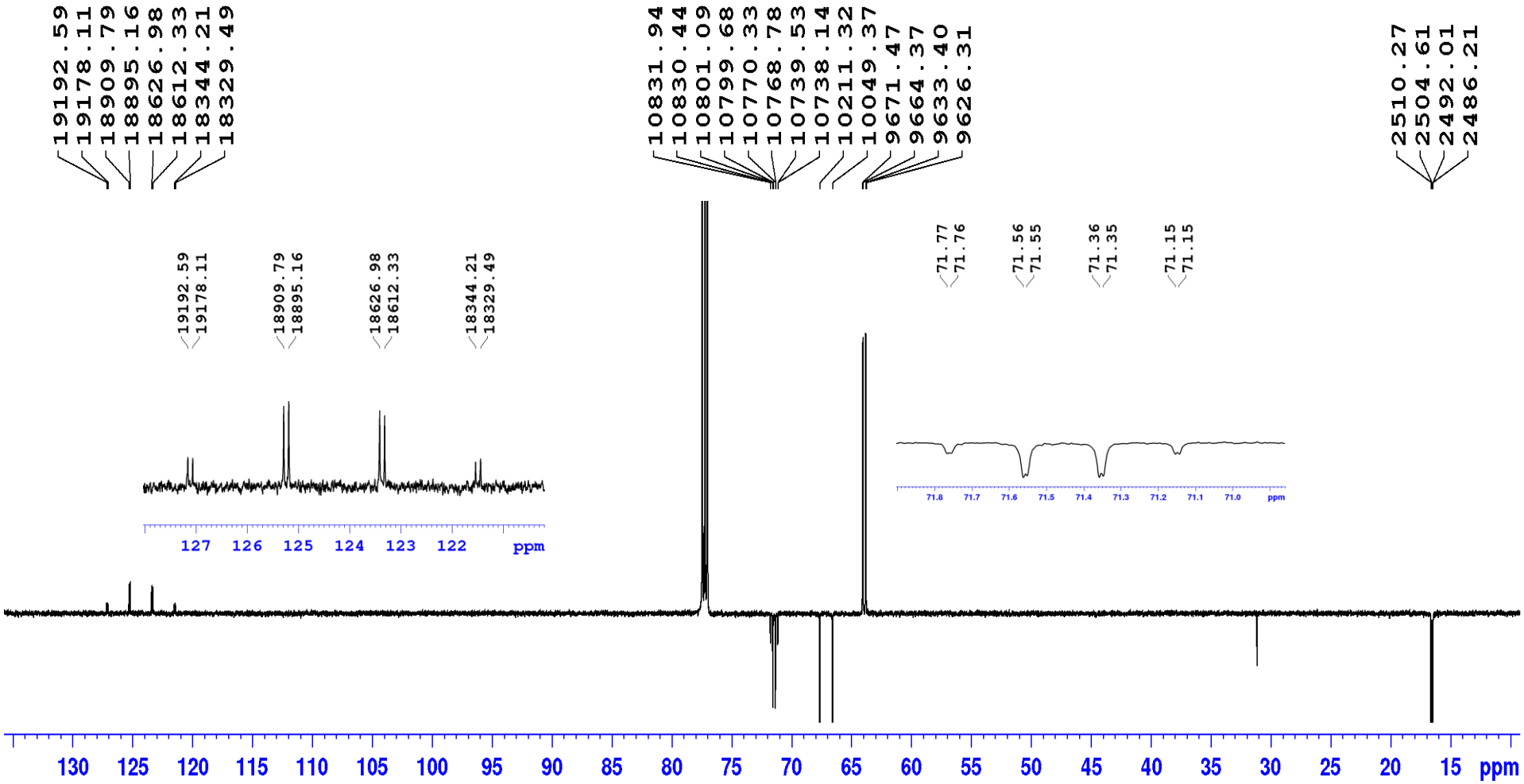
^{31}P NMR spectrum of (±)-(1*R,2*R**)-25a (161.98 MHz):**



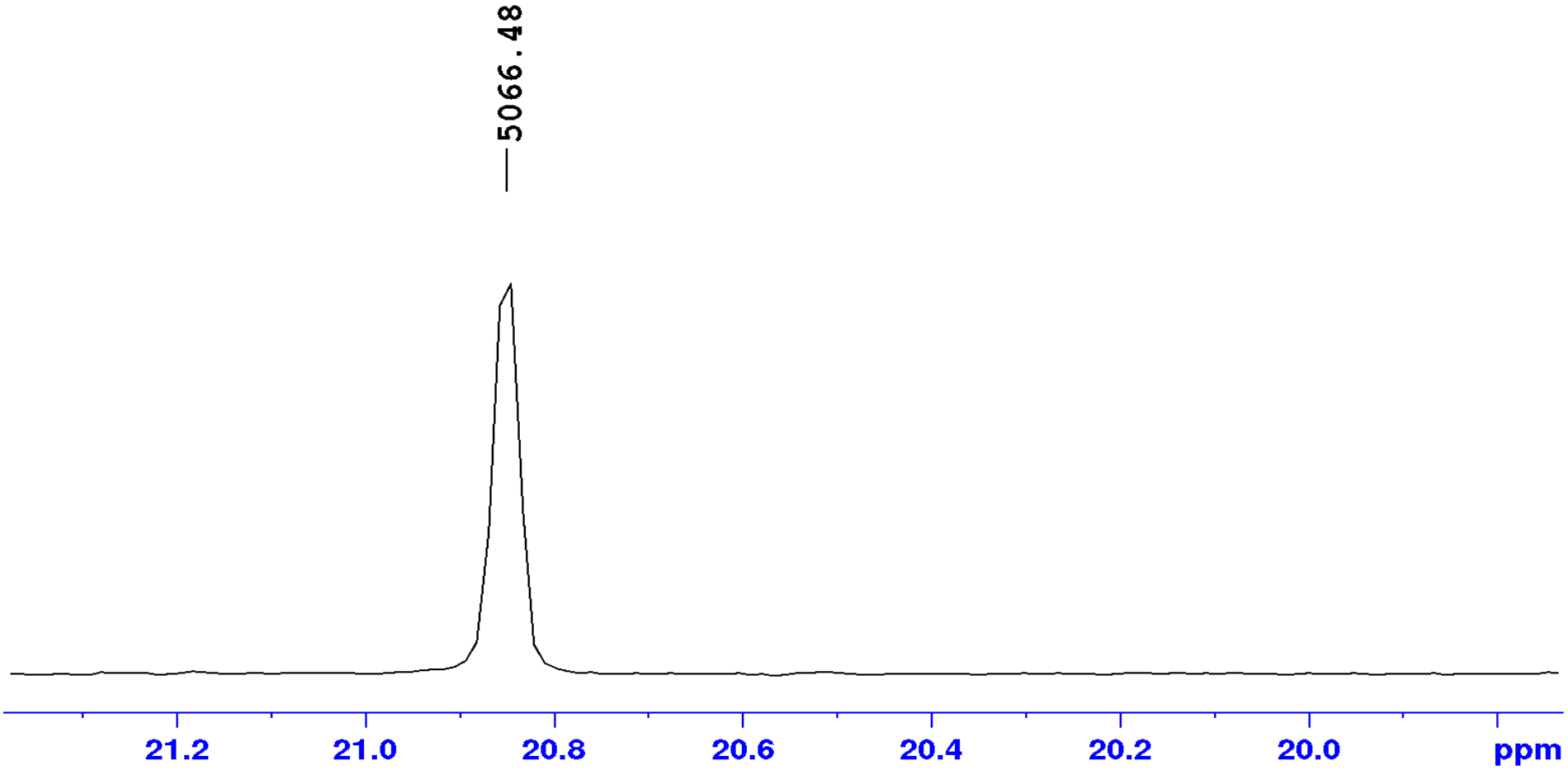
^{1}H NMR spectrum of (±)-(1*S,2*R**)-Diethyl 3,3,3-trifluoro-1,2-dihydroxypropylphosphonate [(±)-(1*R**,2*S**)-25b] (600.25 MHz):**



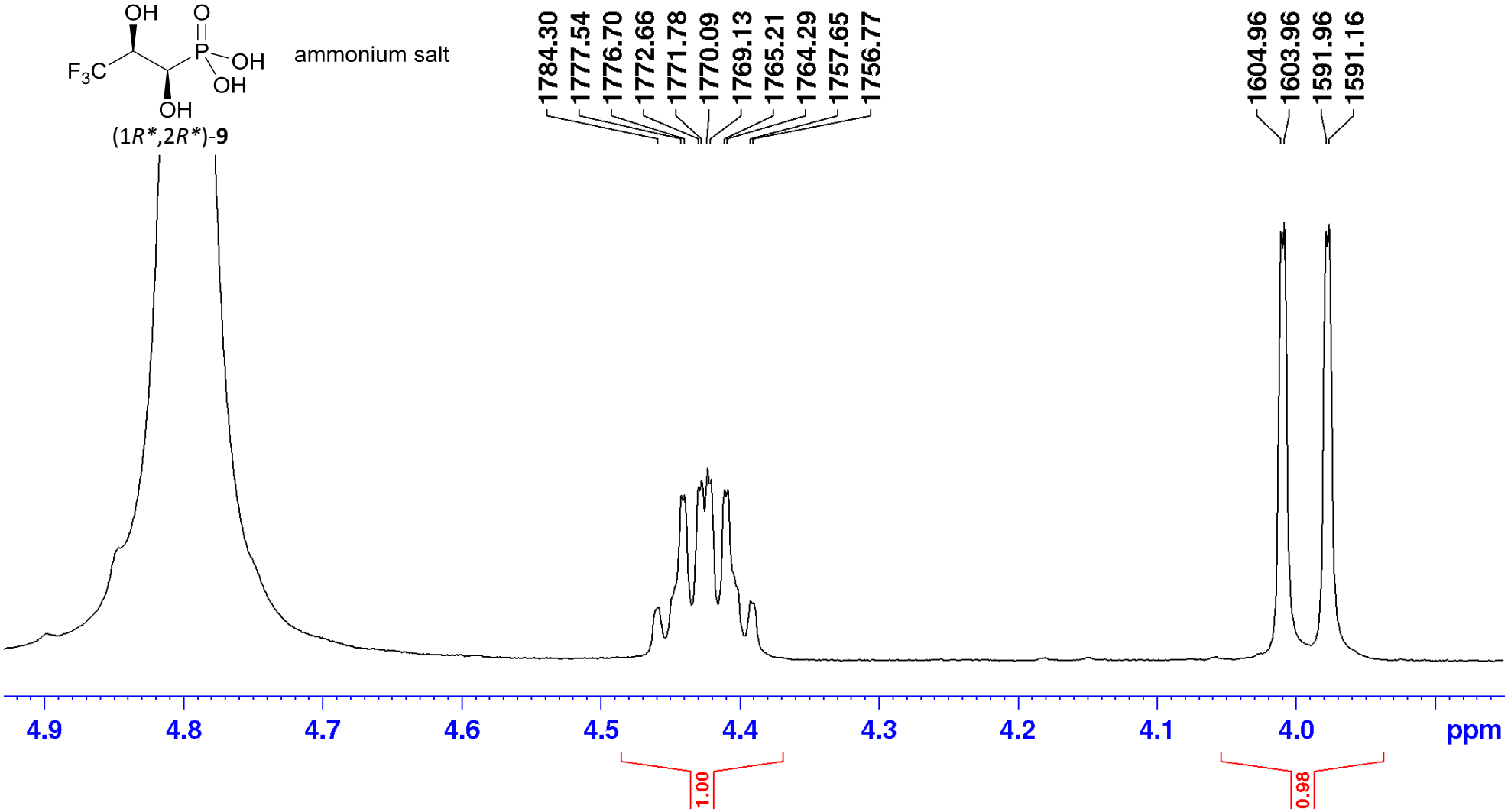
^{13}C NMR spectrum of (±)-(1*R,2*S**)-25b (150.95 MHz):**



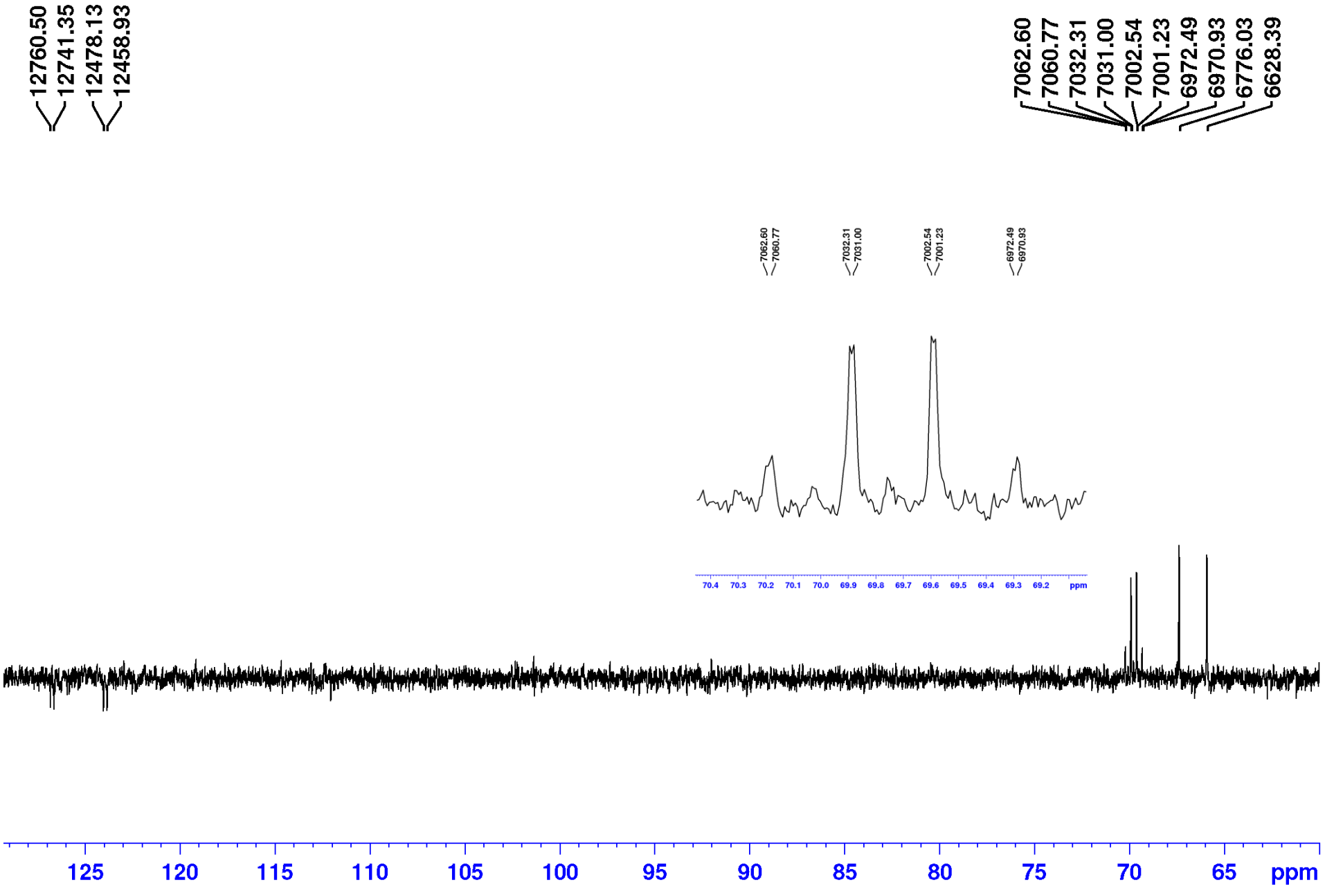
^{31}P NMR spectrum of (±)-(1*R,2*S**)-25b (242.97 MHz):**



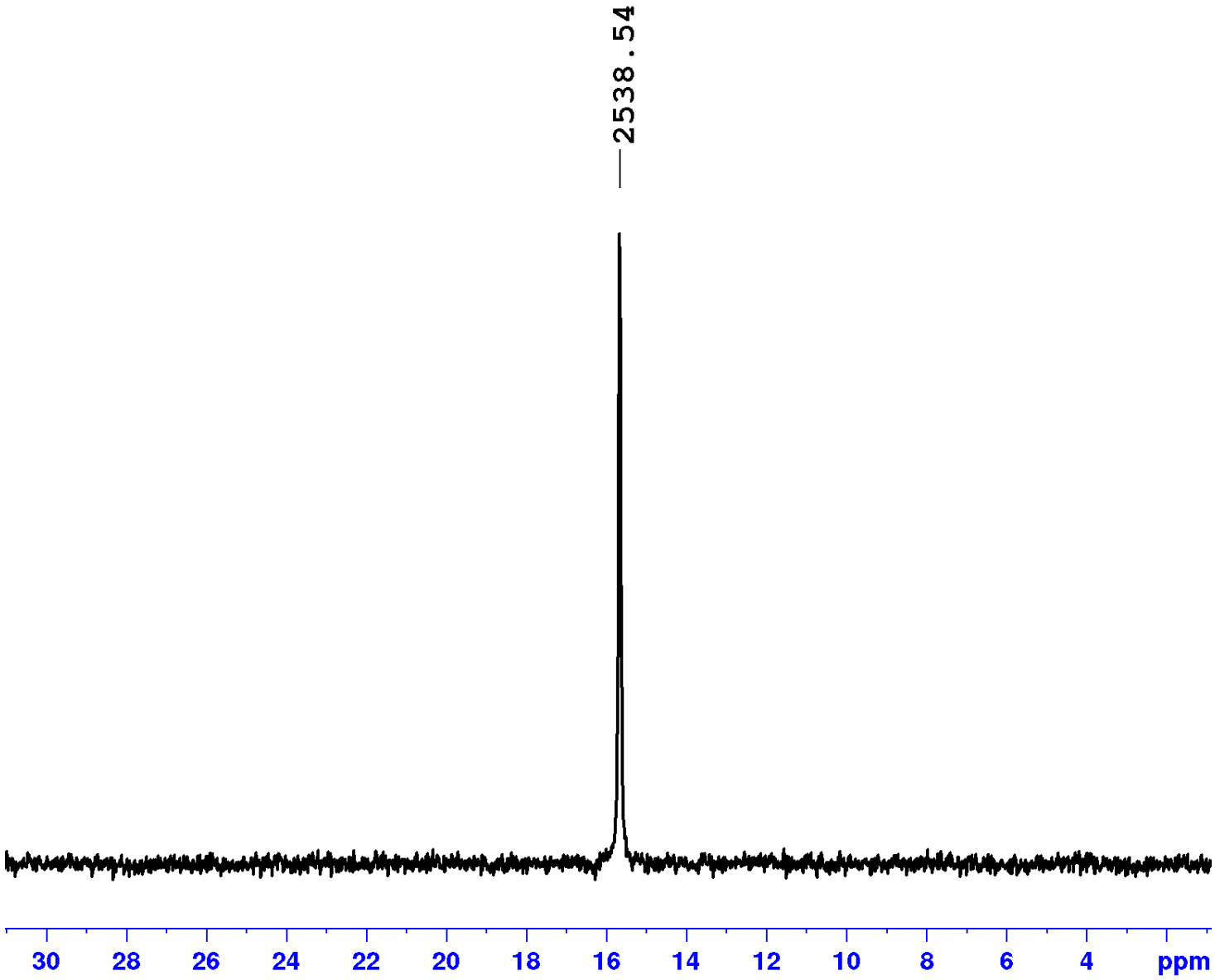
^{1}H NMR spectrum of (±)-(1*R,2*R**)-3,3,3-trifluoro-1,2-dihydroxypropylphosphonic acid ammonium salt [(±)-(1*R**,2*R**)-9] (400.13 MHz):**



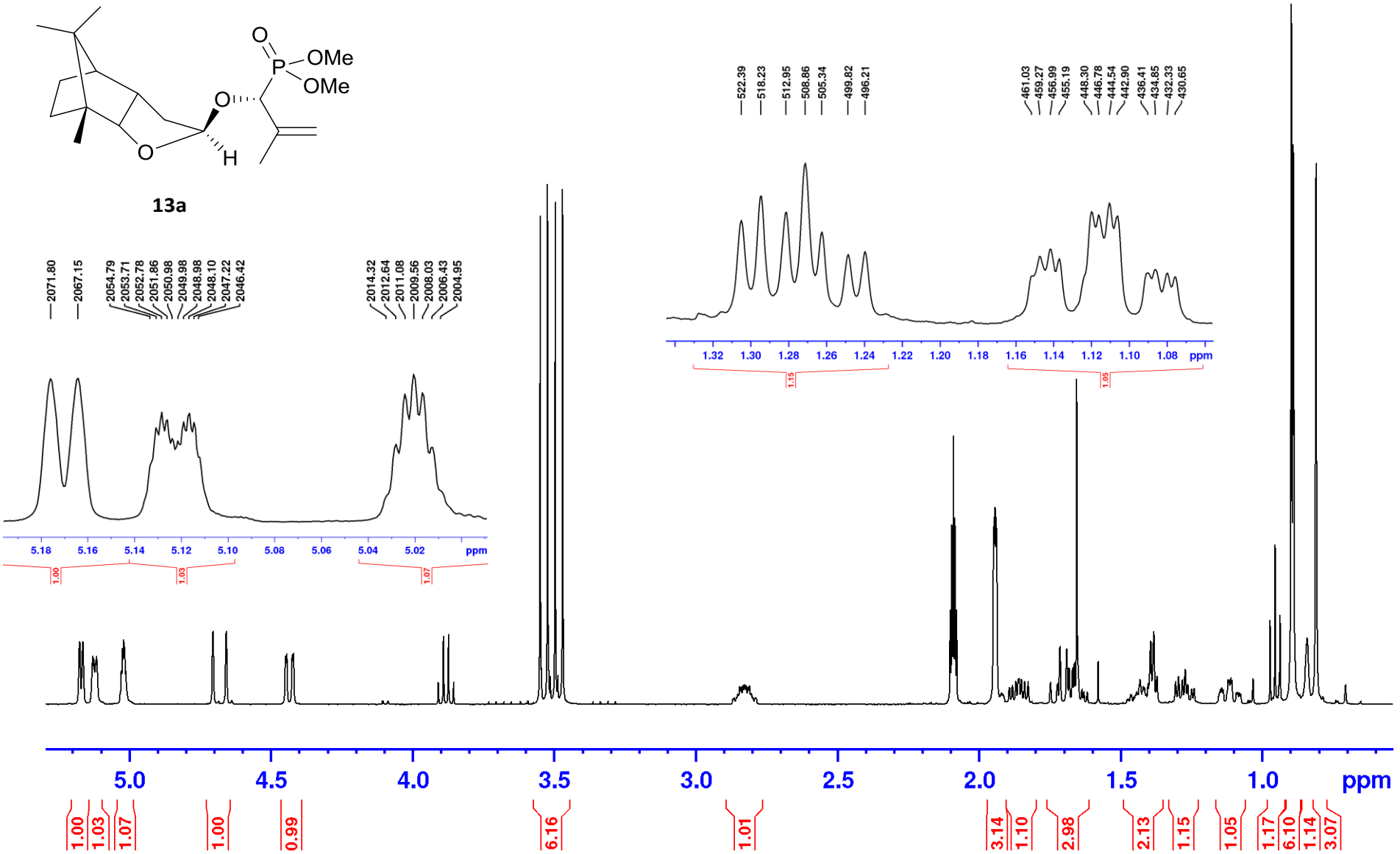
^{13}C NMR spectrum of (±)-(1*R,2*R**)-9 (100.61 MHz):**



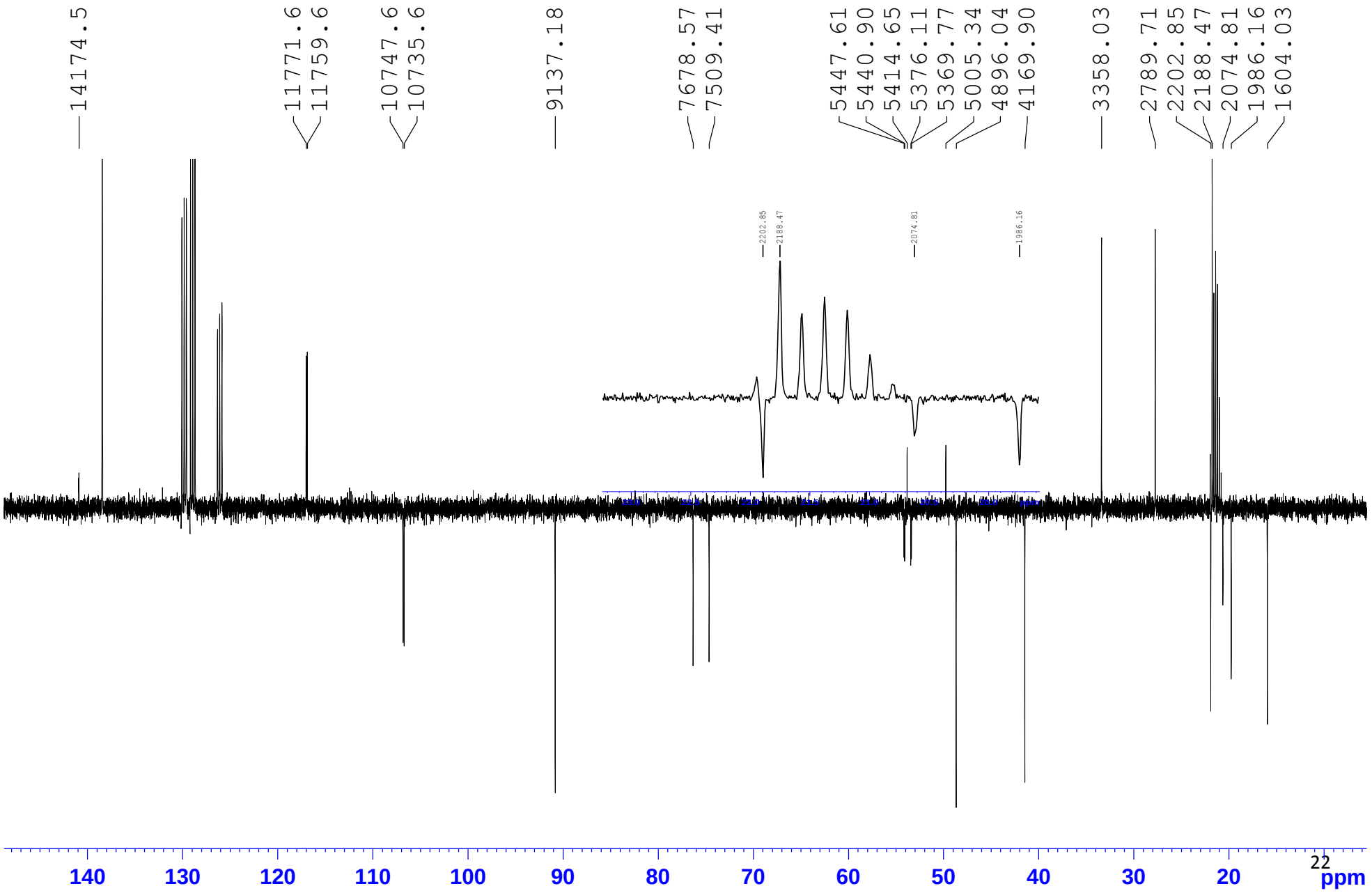
^{31}P NMR spectrum of [(±)-(1*R,2*R**)-9 (161.98 MHz):**



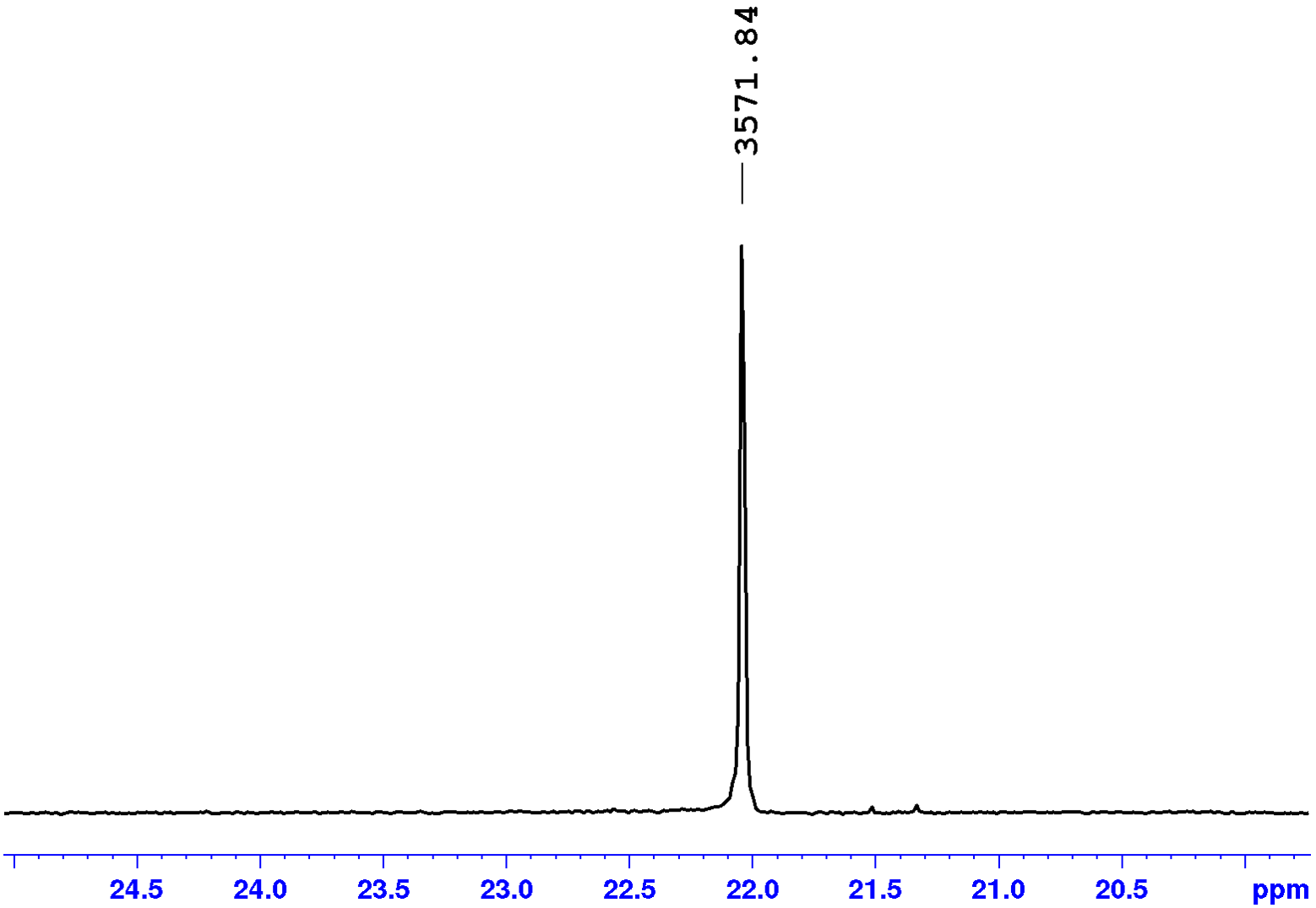
^{1}H NMR spectrum of the less polar acetal of dimethyl 1-hydroxy-2-methylallylphosphonate with Noe´s lactol [13a] (400.27 MHz):



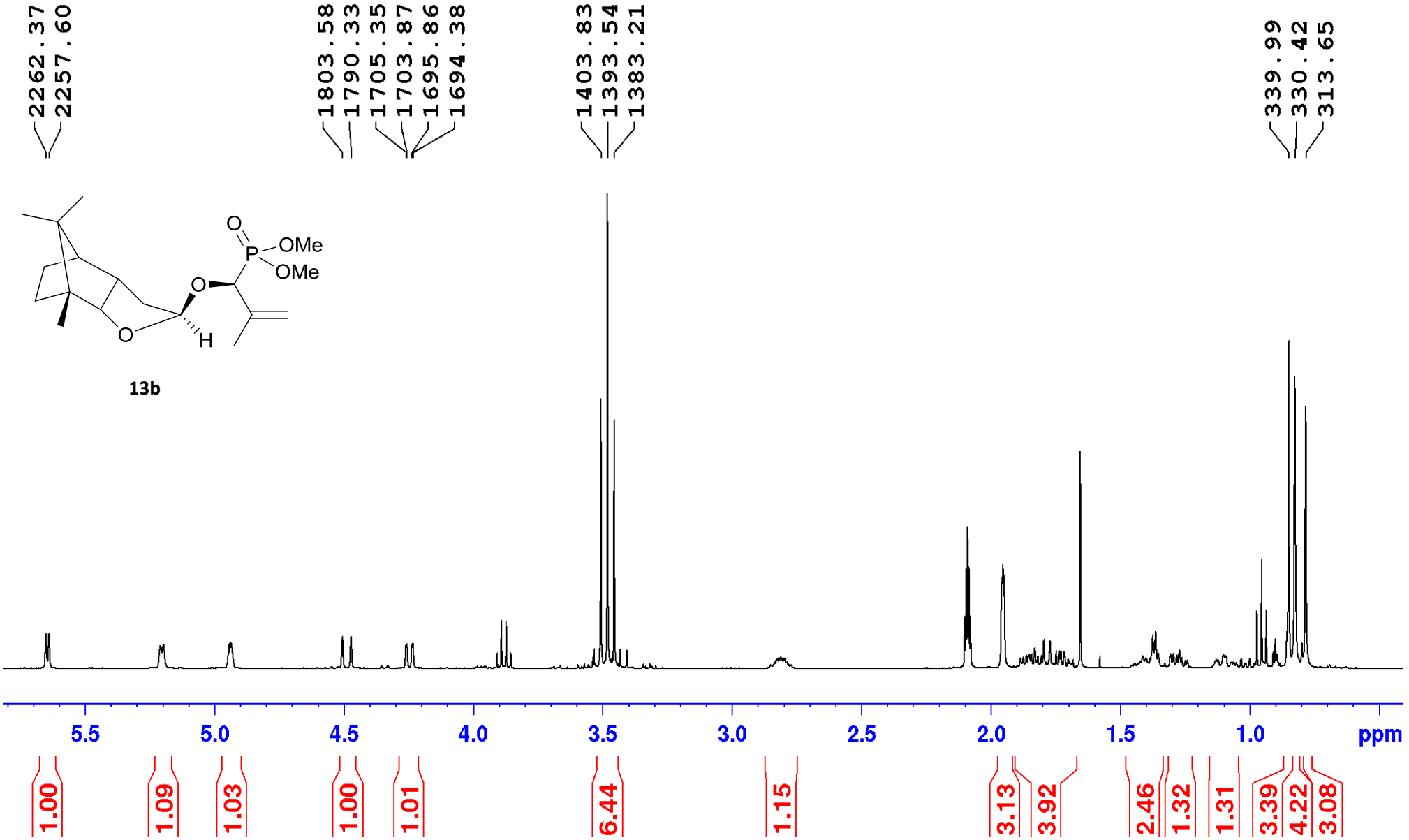
^{13}C NMR spectrum of 13a (100.61 MHz):



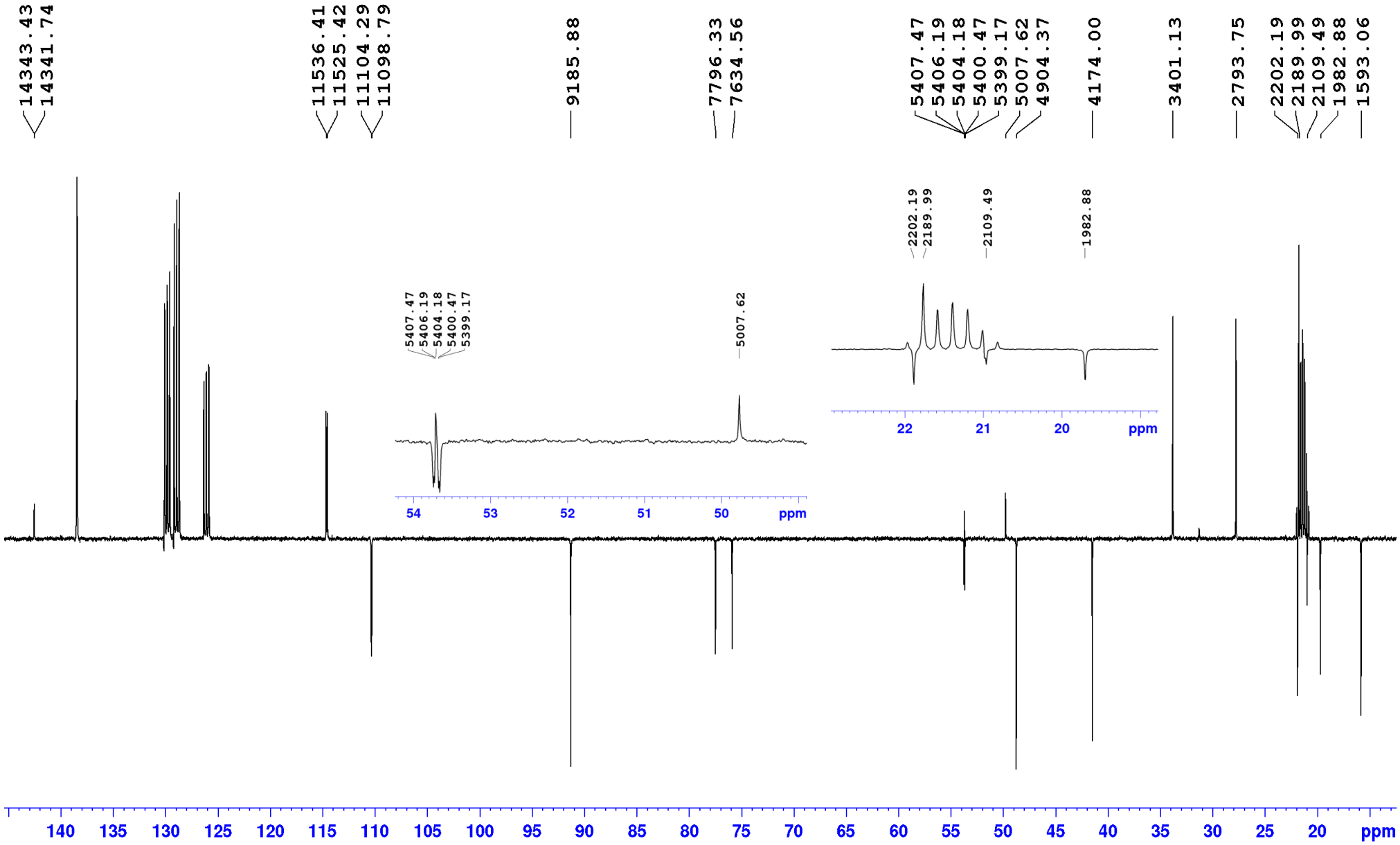
^{31}P NMR spectrum of 13a (162.03 MHz):



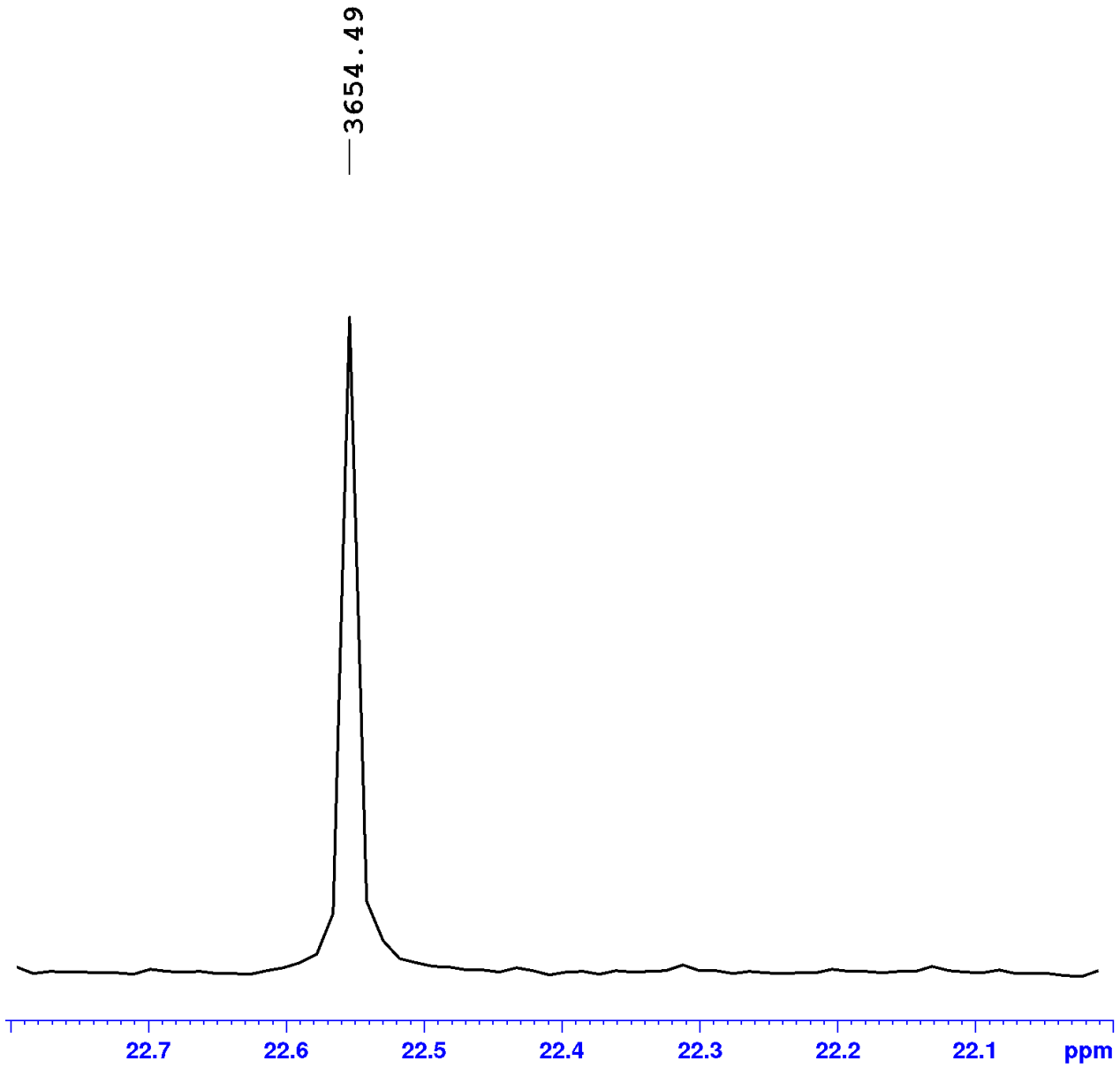
^{1}H NMR spectrum of the more polar acetal of dimethyl 1-hydroxy-2-methylallylphosphonate with Noe´s lactol [13b] (400.27 MHz):



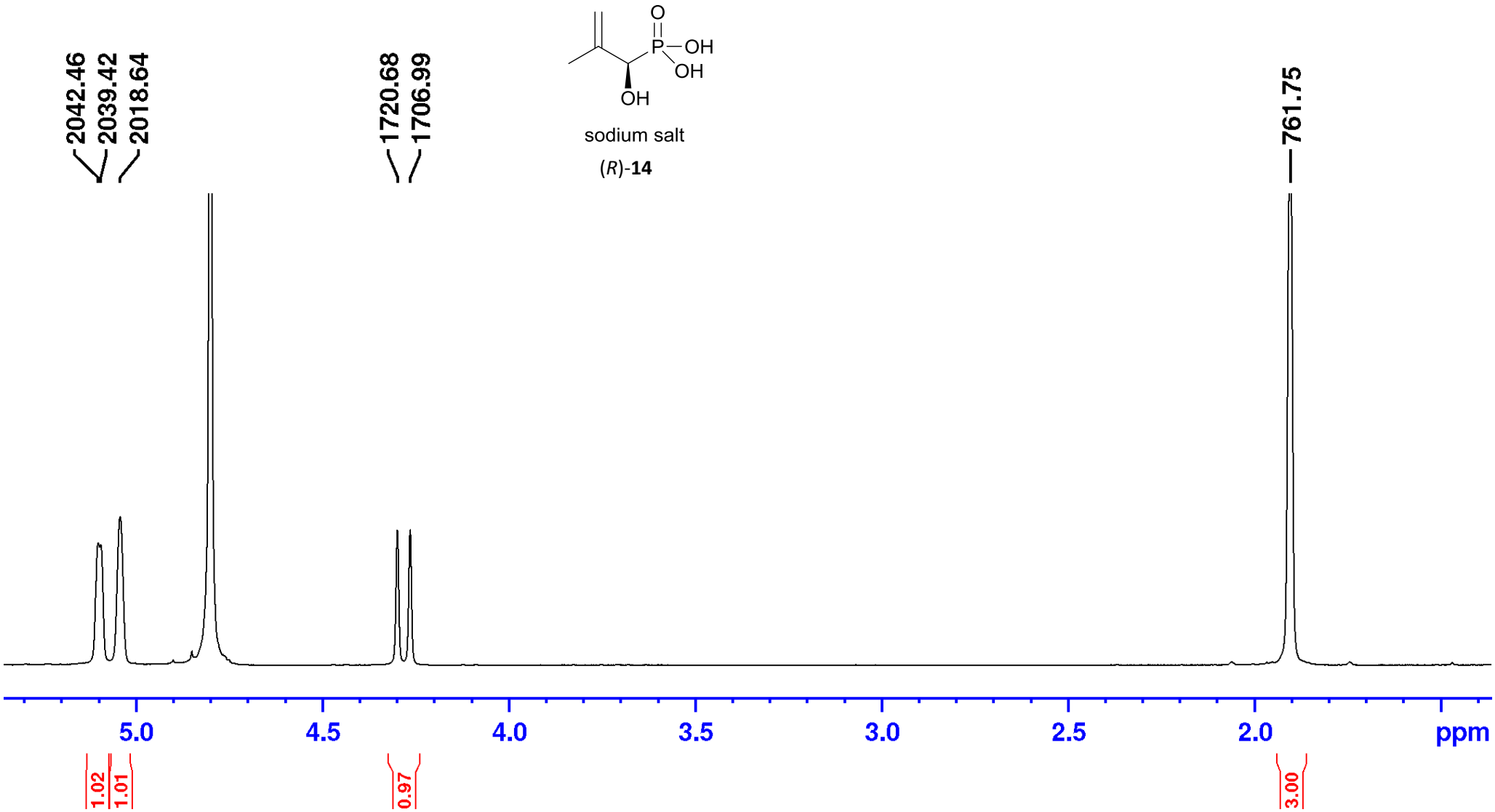
^{13}C NMR spectrum of 13b (100.61 MHz):



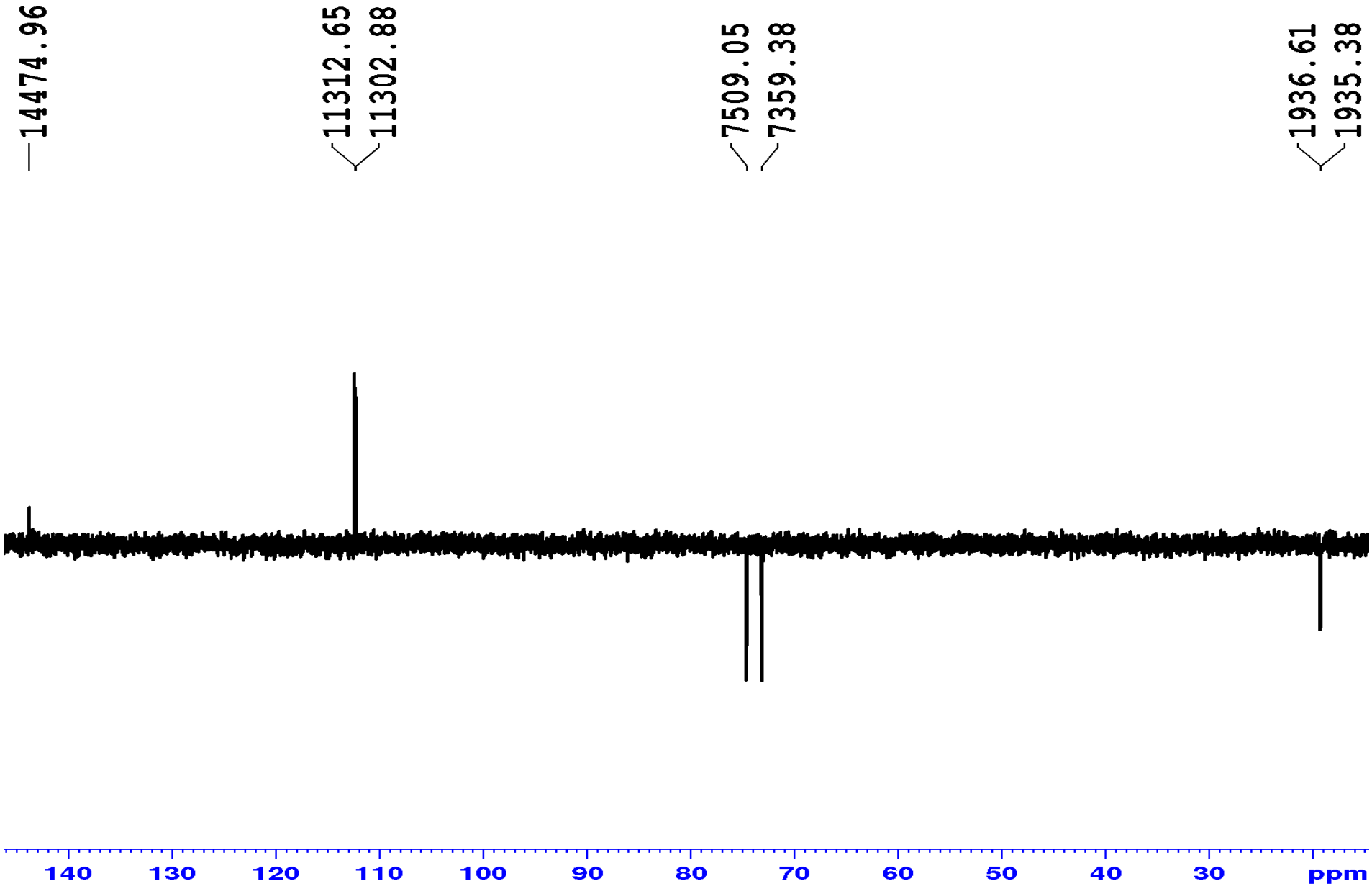
^{31}P NMR spectrum of 13b (162.03 MHz):



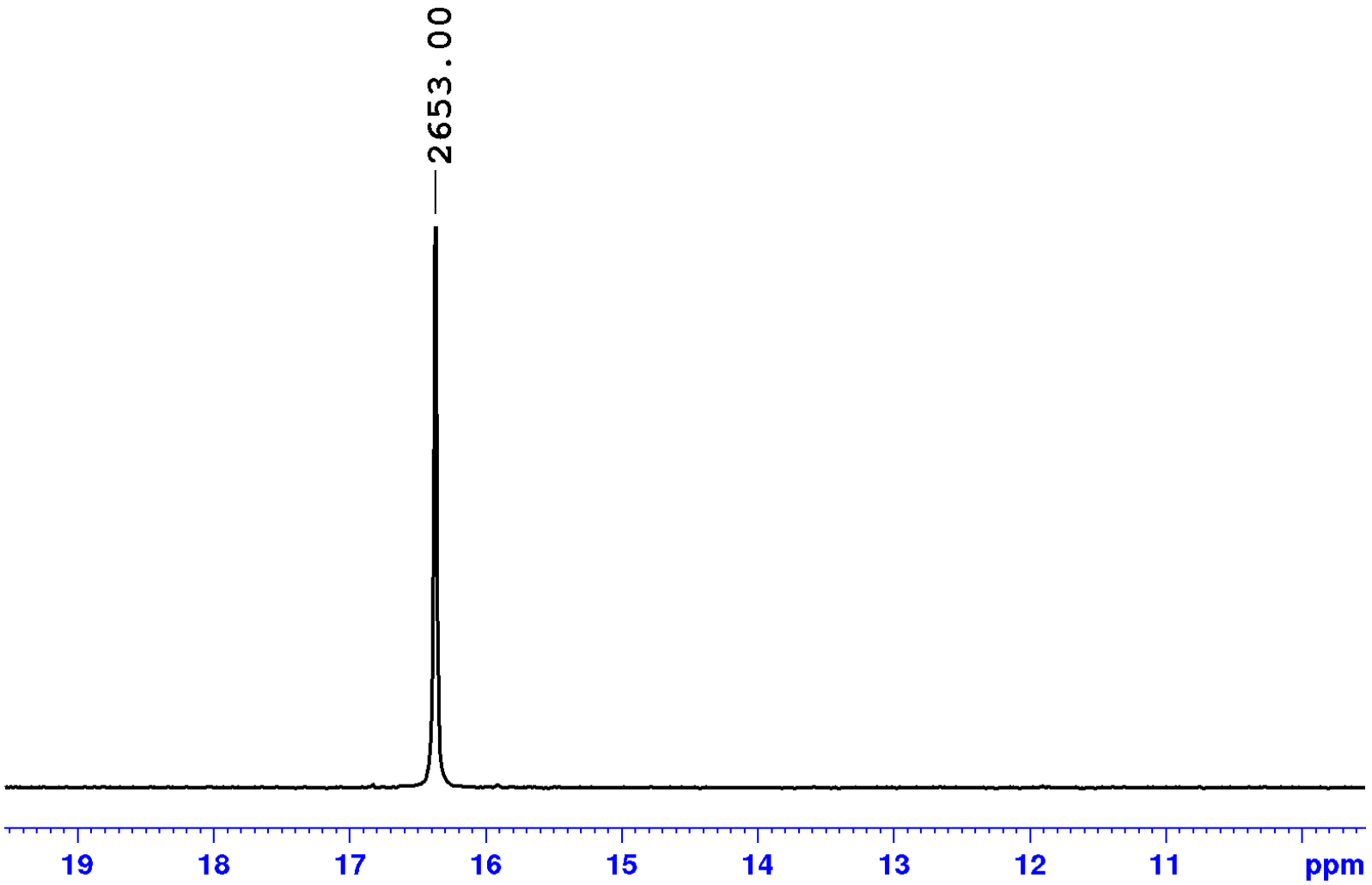
^{1}H NMR spectrum of the sodium salt of (*R*)-1-hydroxy-2-methylprop-2-enylphosphonic acid [(*R*)-14] (400.27 MHz):



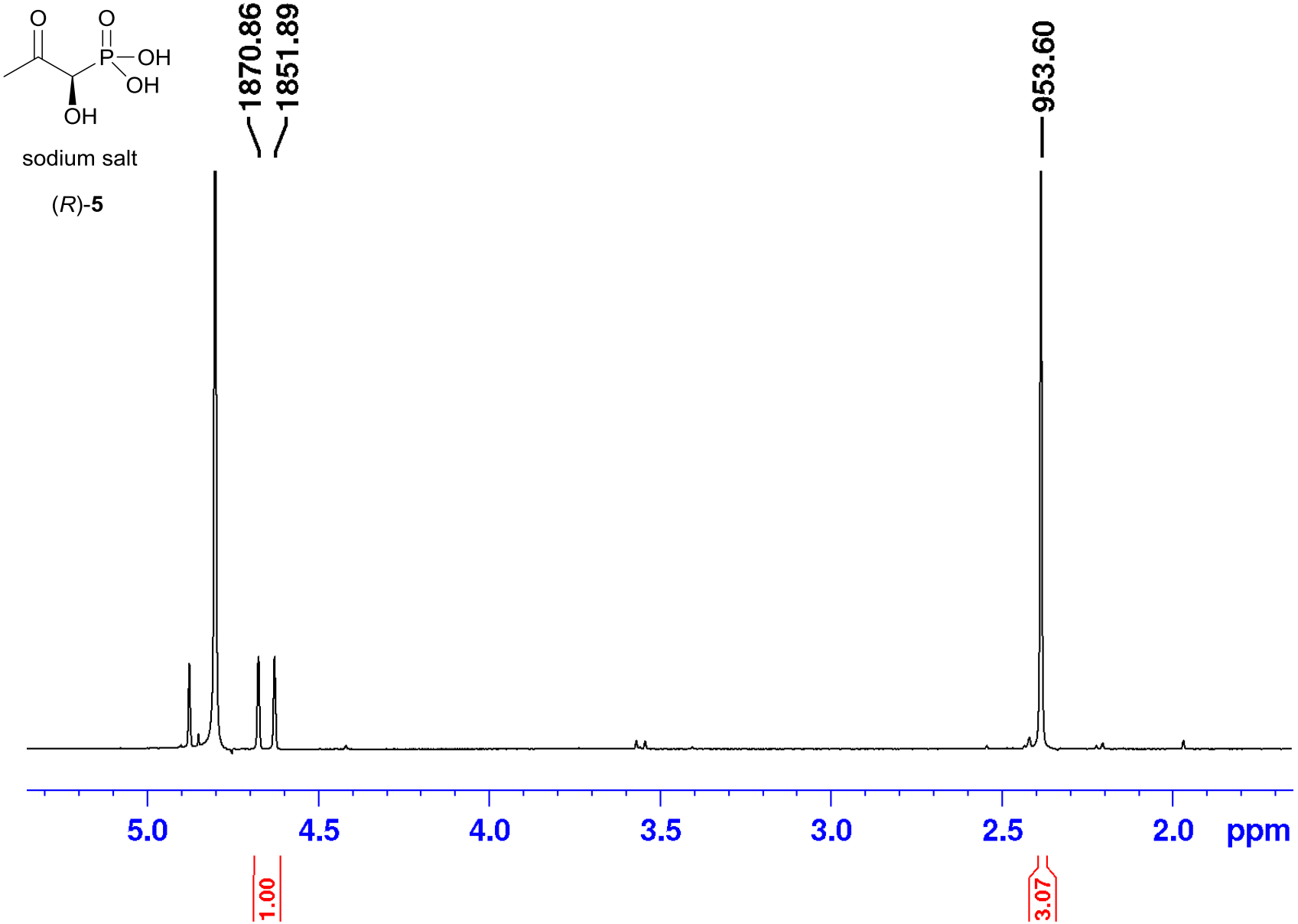
^{13}C NMR spectrum of (*R*)-14 (100.65 MHz):



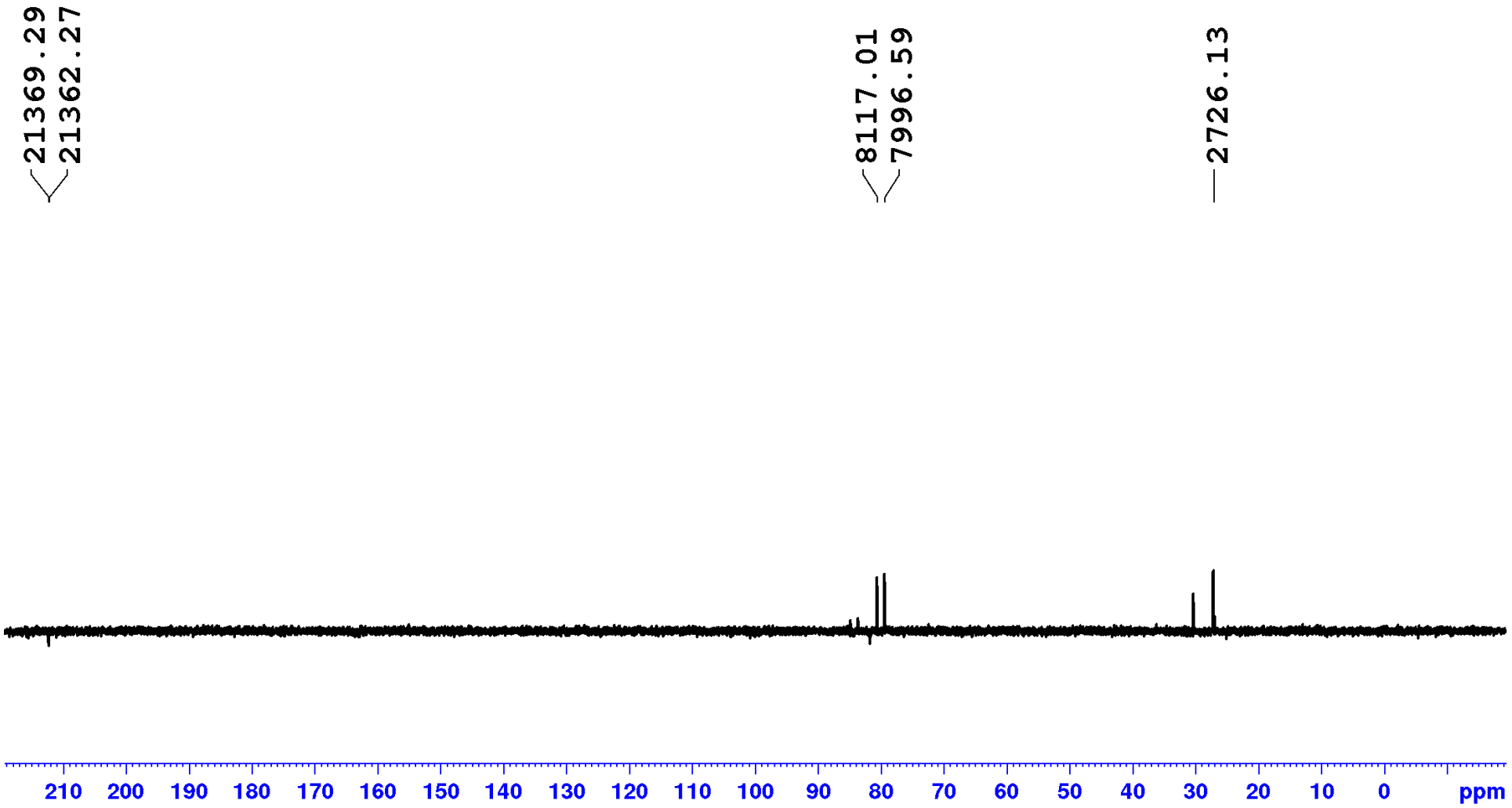
^{31}P NMR spectrum of (*R*)-14 (162.02 MHz):



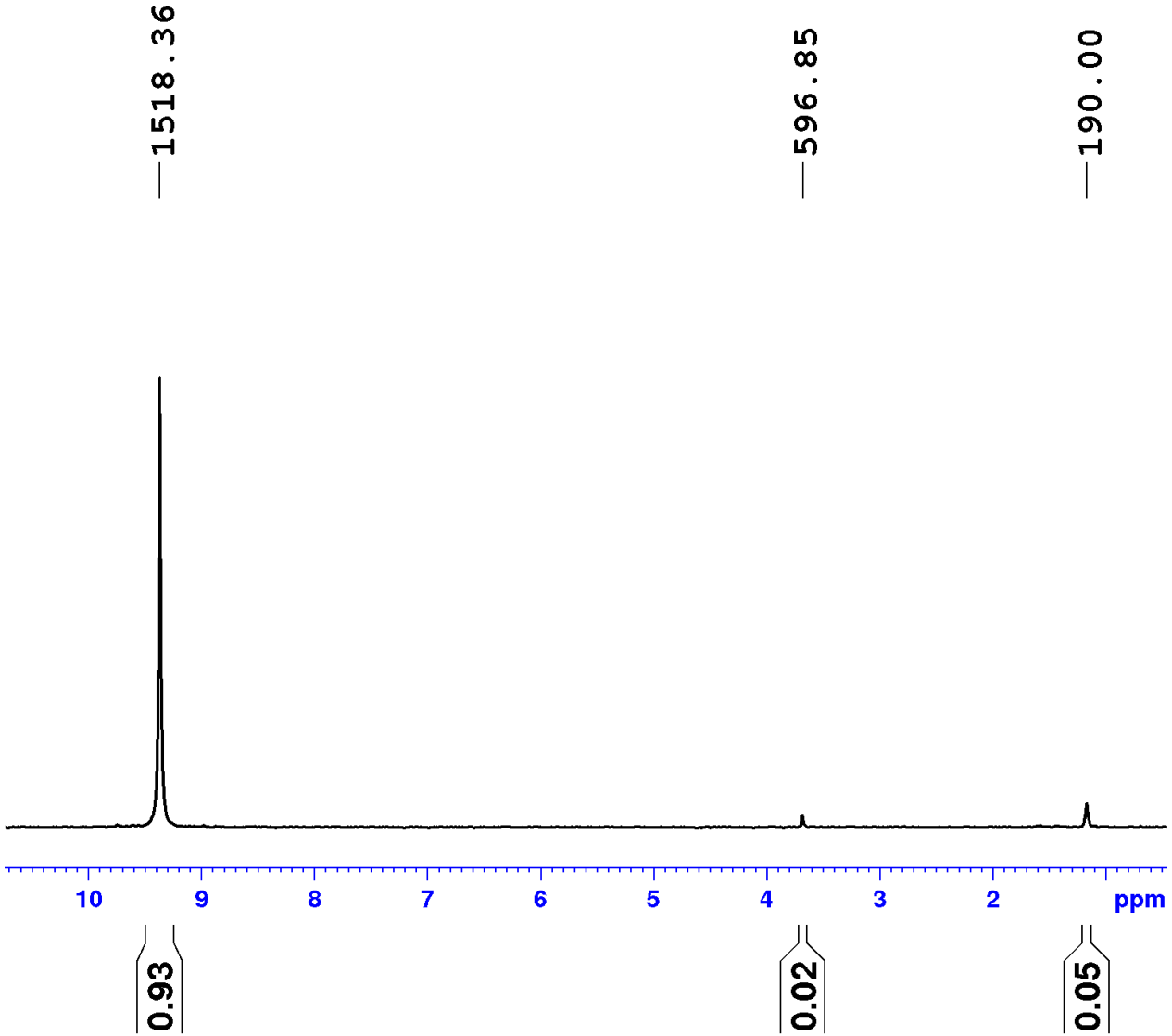
^{1}H NMR spectrum of the sodium salt of (*R*)-1-hydroxy-2-oxopropylphosphonic acid [(*R*)-5] (400.27 MHz):



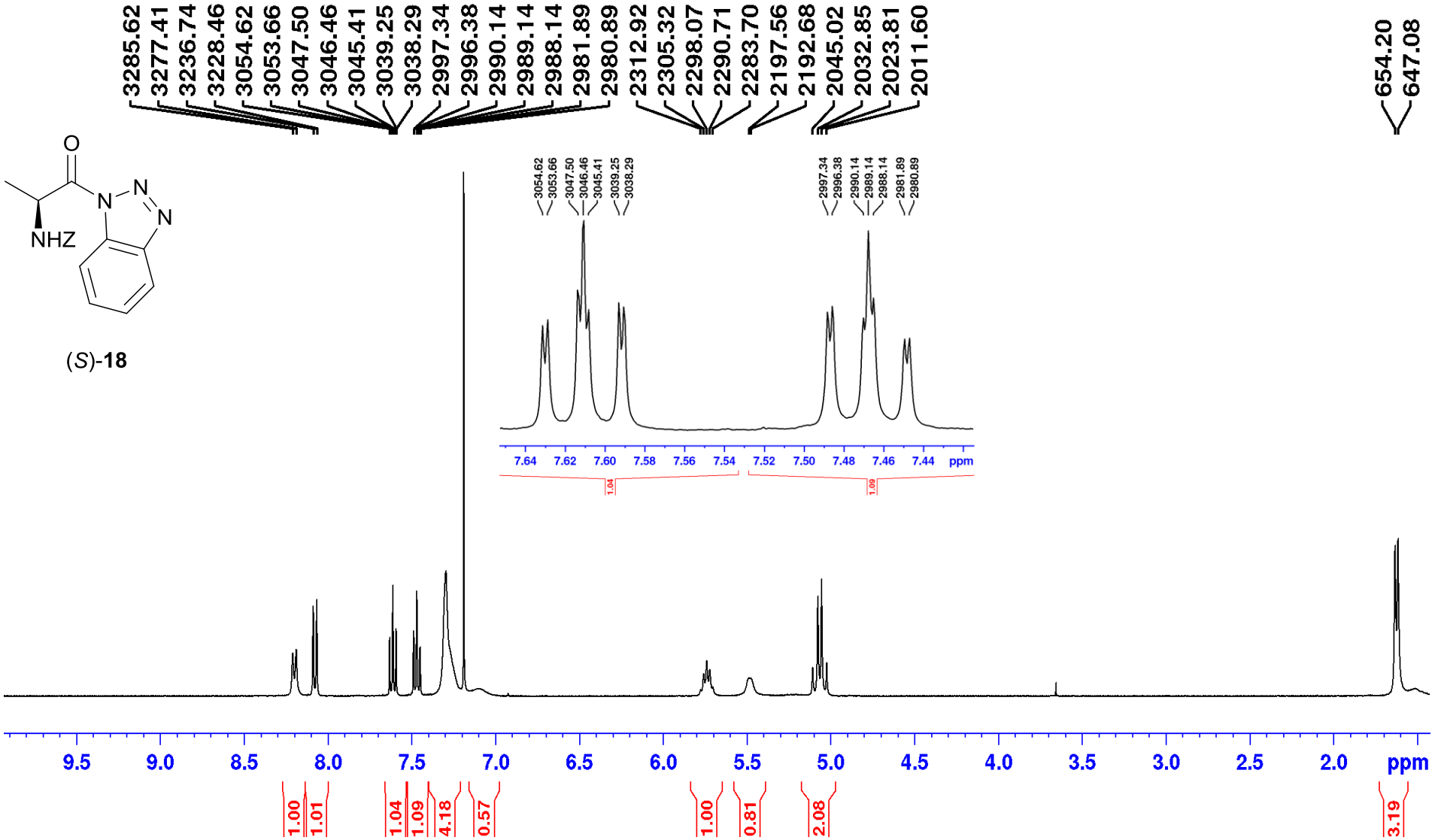
^{13}C NMR spectrum of (*R*)-5 (100.65 MHz):



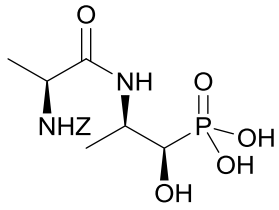
^{31}P NMR spectrum of (*R*)-5 (162.02 MHz):



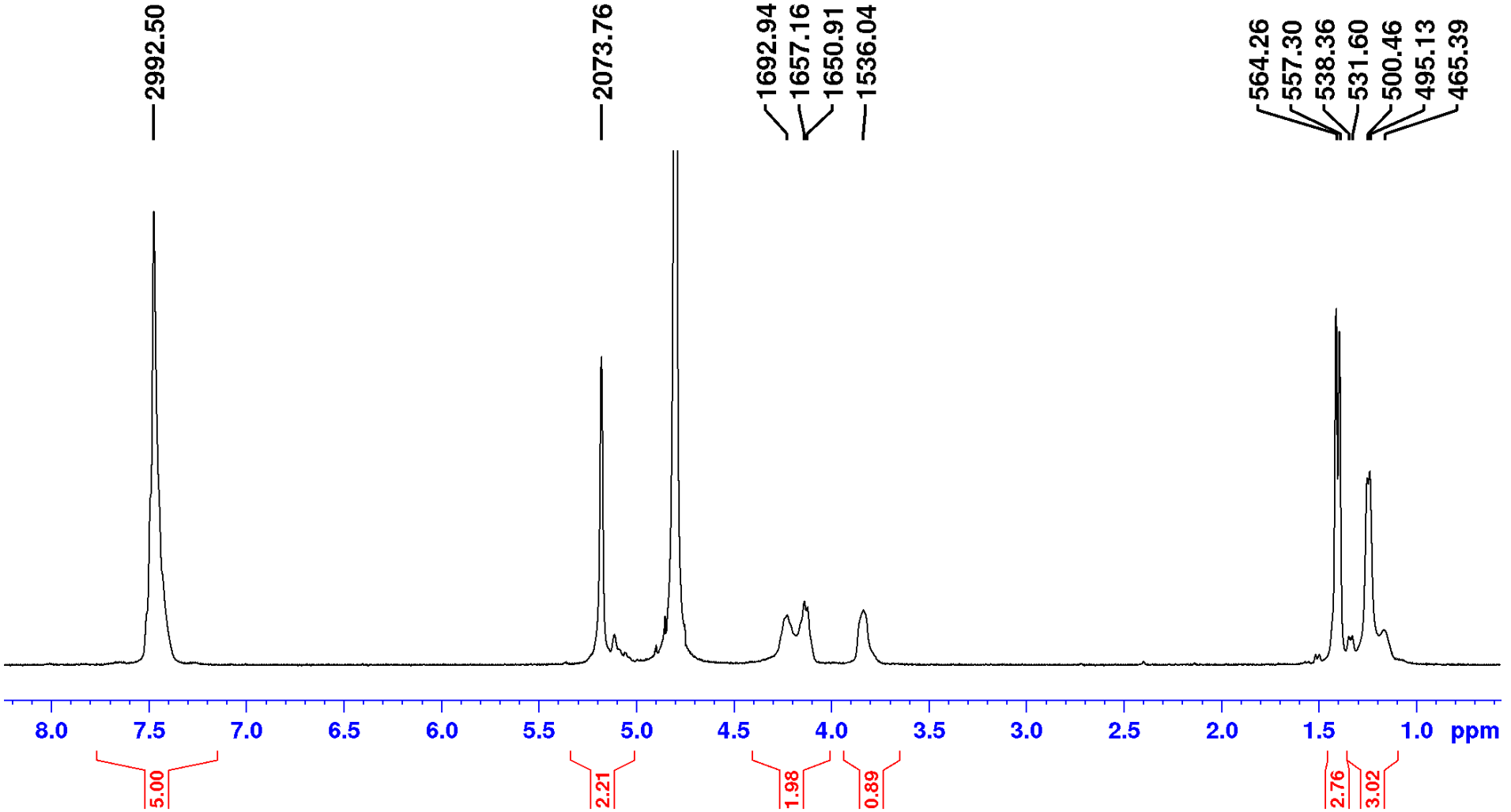
^{1}H NMR spectrum of benzotriazole-activated *Z*-L-alanine [(*S*)-18] (400.27 MHz):



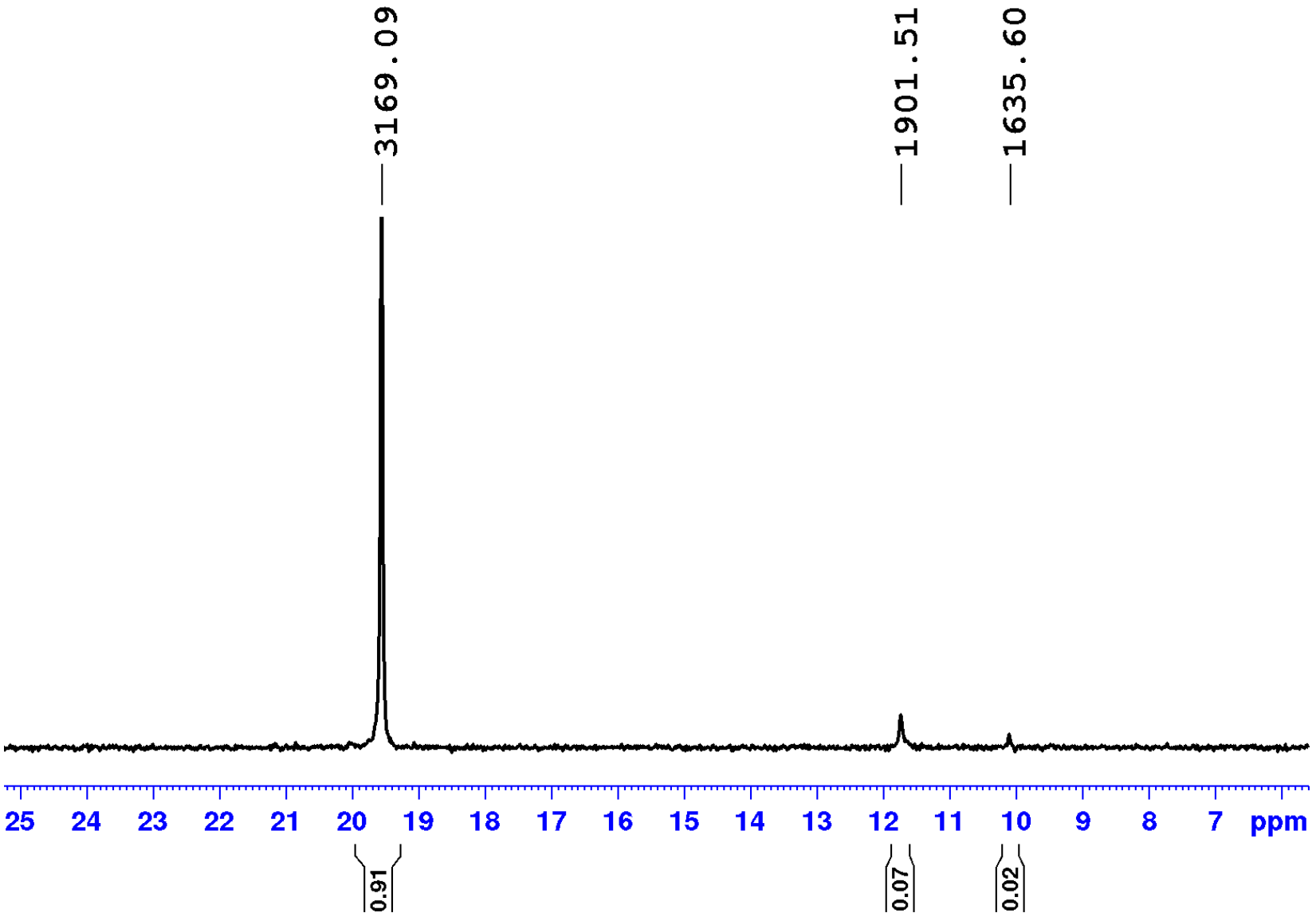
^{1}H NMR spectrum of *N*-(*Z*-L-alanyl)-(1*R*,2*R*,2'*S*)-2-amino-1-hydroxypropylphosphonic acid [(1*R*,2*R*, 2'*S*)-19] (400.27 MHz):



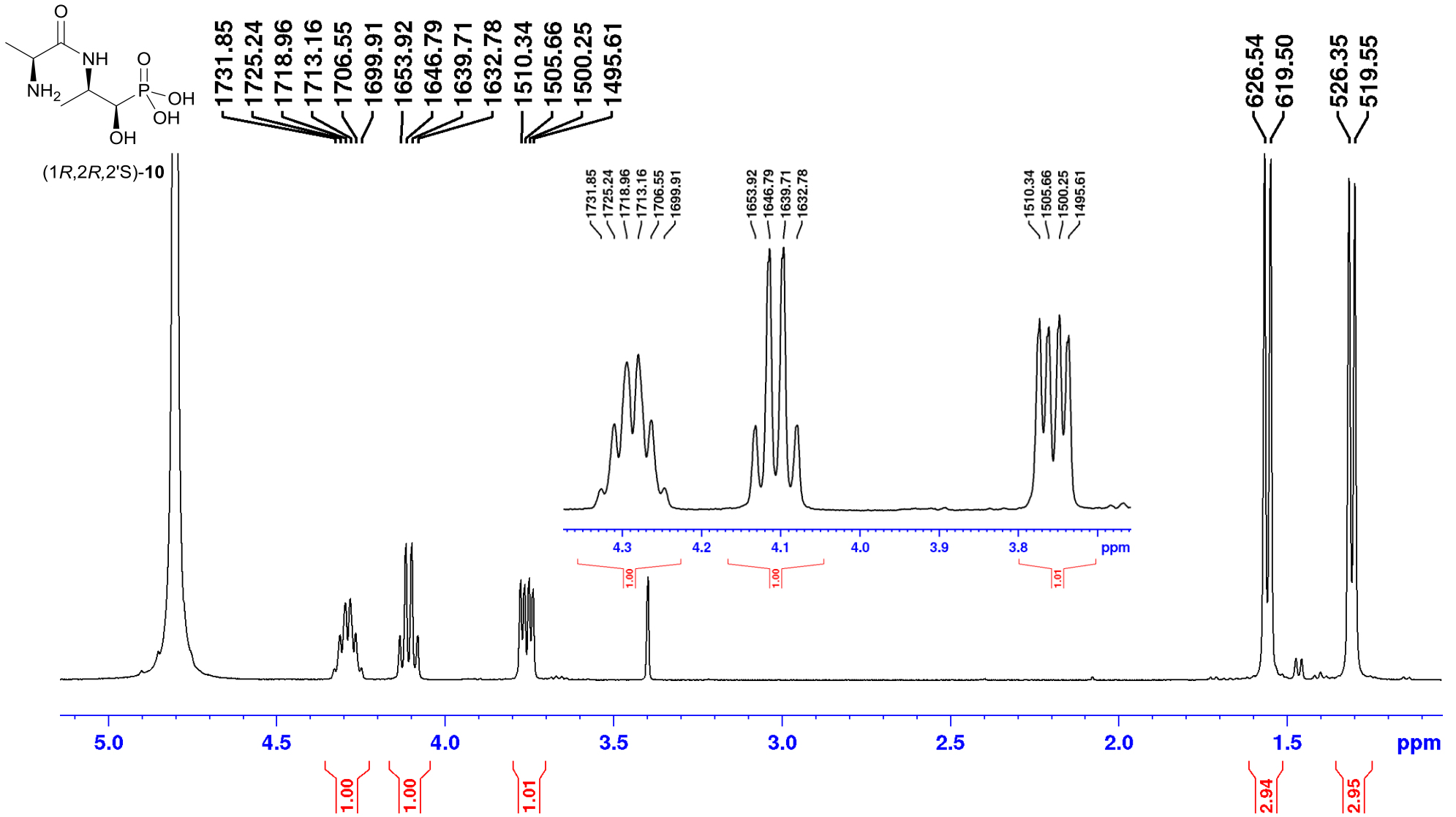
(1*R*,2*R*,2'*S*)-**19**



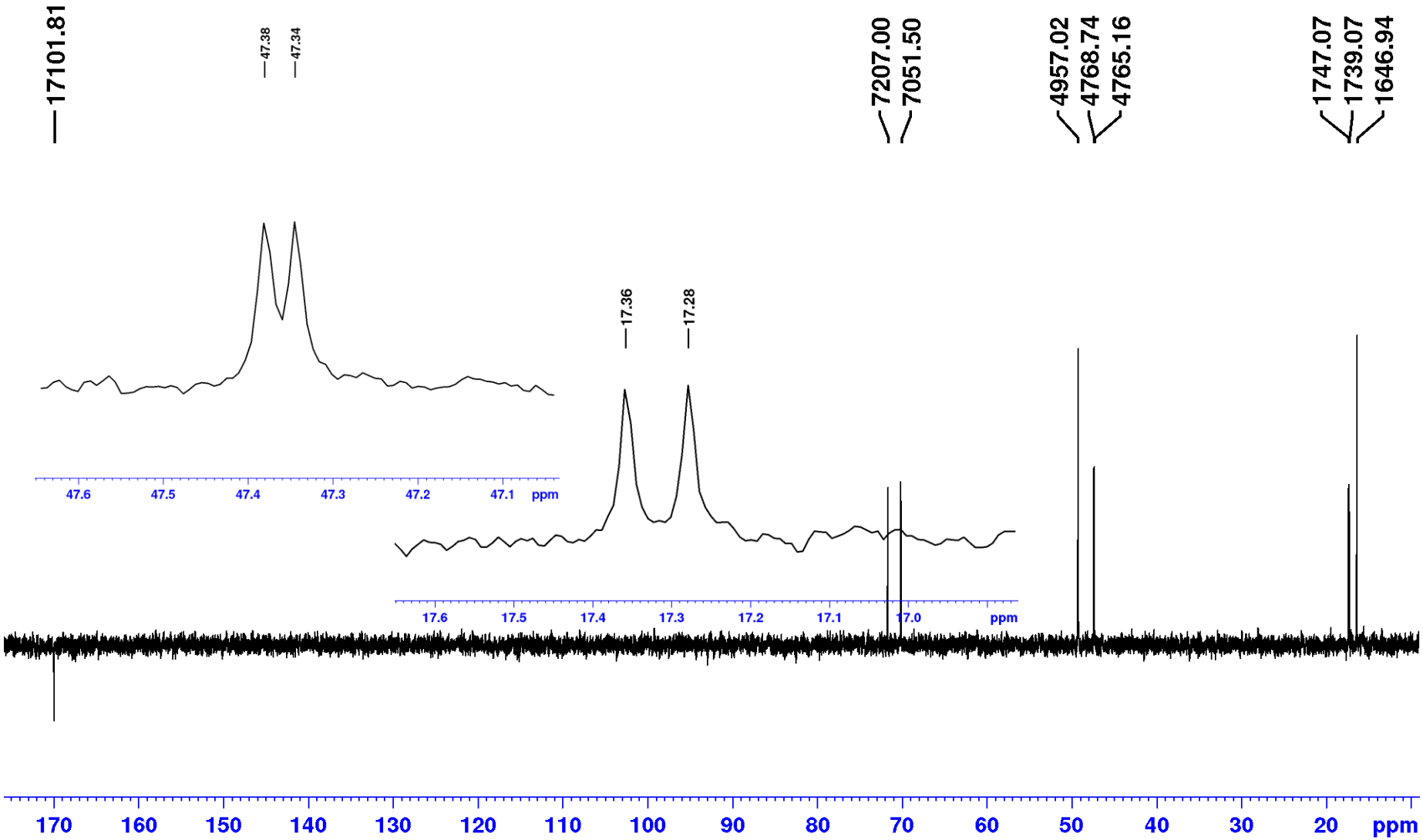
^{31}P NMR spectrum of (1*R*,2*R*,2'*S*)-19 (162.03 MHz):



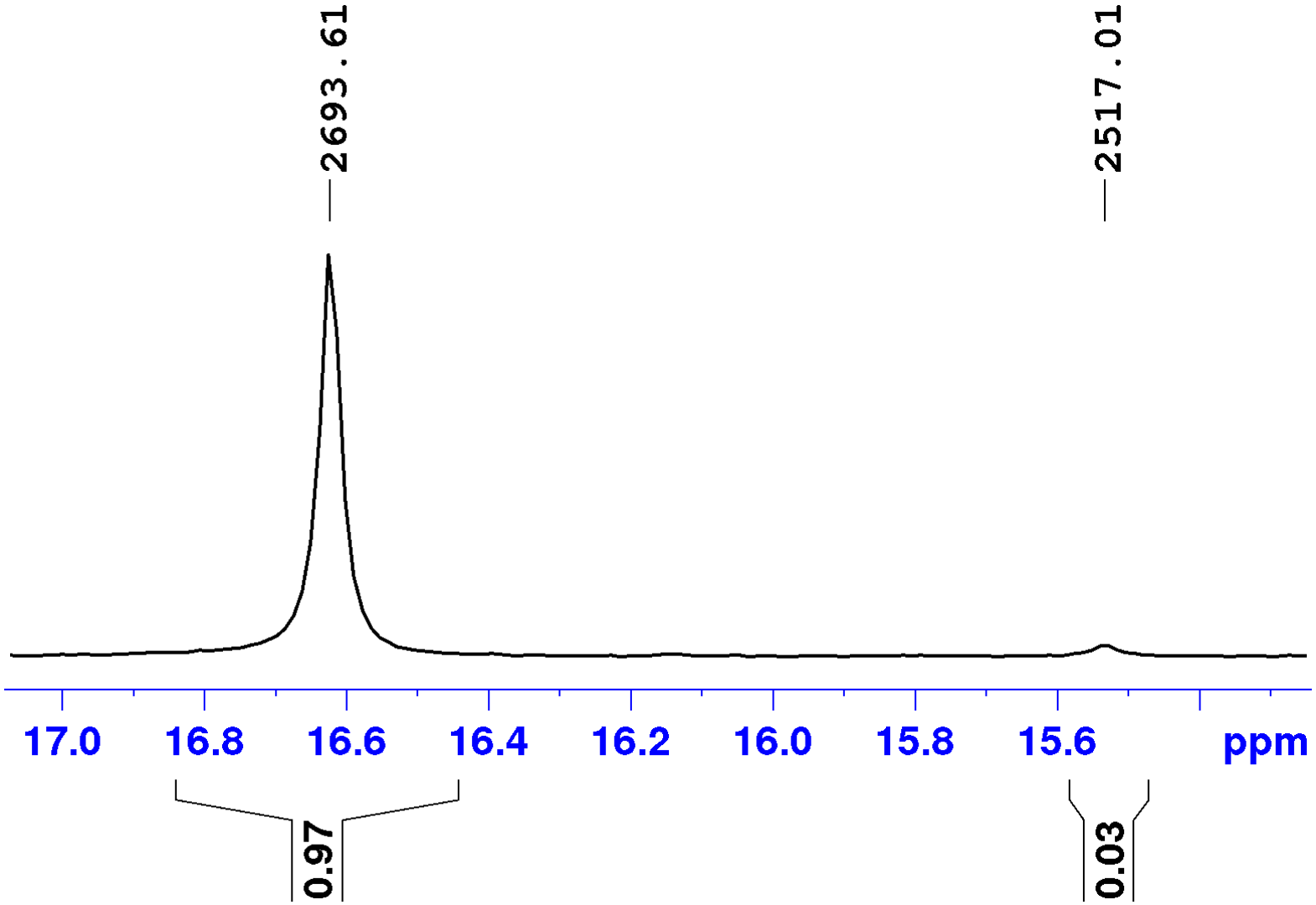
^{1}H NMR spectrumof (+)-*N*-(L-alanyl)-(1*R*,2*R*,2'*S*)-2-amino-1-hydroxypropylphosphonic acid [(1*R*,2*R*,2'*S*)-10] (400.27 MHz):



^{13}C NMR spectrum of (1*R*,2*R*,2'*S*)-10 (100.65 MHz):



^{31}P NMR spectrum of (1*R*,2*R*,2'*S*)-10 (162.03 MHz):



X-ray structure analysis

The X-ray intensity data was measured on Bruker D8 Venture diffractometer equipped with multilayer monochromators, Mo K/a INCOATEC micro focus sealed tube and Kryoflex II cooling device. 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 at calculated positions and refined with a riding model or as rotating groups. H1A is refined without any constraints or restraints. The following software was used: Frame integration, *Bruker SAINT software package*[1] using a narrow-frame algorithm, Absorption correction, *SADABS*[2] , structure solution, *SHELXL-2013*[3], refinement, *SHELXL-2013*[3], *OLEX2*[4], *SHELXLE*[5], molecular diagrams, *OLEX2*[4]. Experimental data and CCDC-code can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Tables 2 and 3. Table 4 shows a list of hydrogen bonds. Molecular structure in "Ortep View" is displayed in Figure 1.

Table 1 Experimental parameter and CCDC-Code.

Sample	Machine	Source	Temp.	Detector Distance	Time/ Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
25b	D8	Mo	100	40	20	647	0.8	1522706

(±)-(1*R**,2*S**)-Diethyl 3,3,3-trifluoro-1,2-dihydroxypropylphosphonate [(±)-(1*R**,2*S**)-25b].

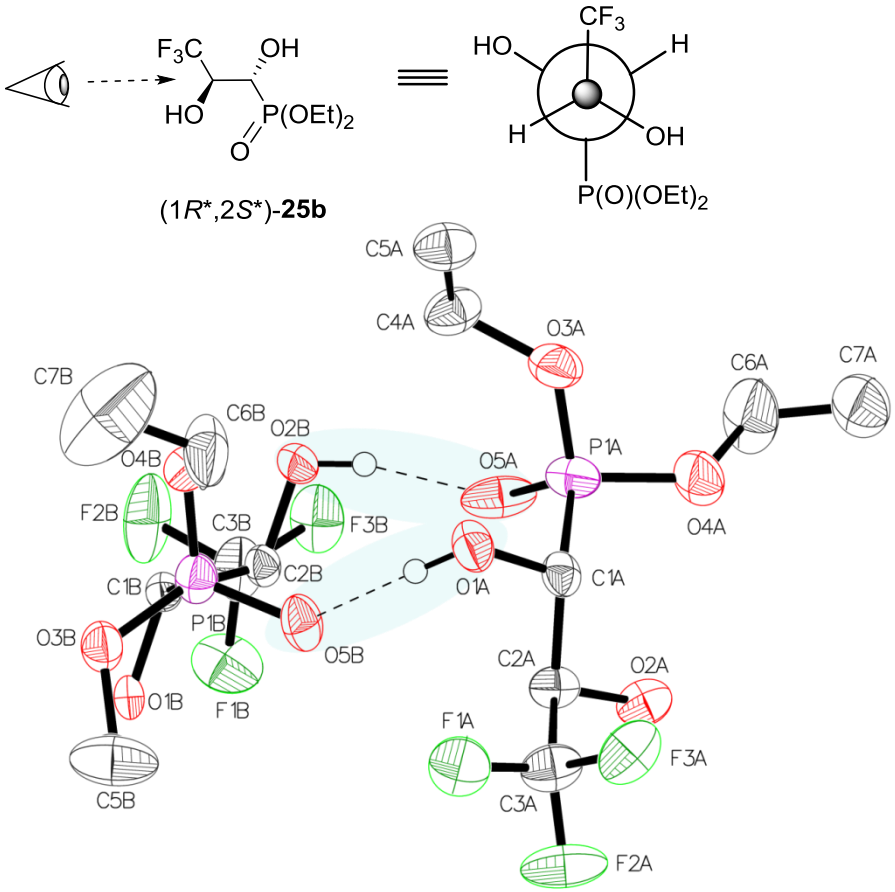


Figure 1 Asymmetric Unit of **25b**, drawn with 50% displacement ellipsoids. Disorder and hydrogen atoms omitted for clarity. O1 and O2 are located in anti position for both independent molecules. Two intermolecular hydrogen bonds (light blue shaded) in the asymmetric unit can be detected. Main residue disorder is 47 %. Bond precision: C-C = 0.0052 Å.

The above shown crystal structure shows the two hydroxyl groups of **25b** to be anti-orientated and **25b** thus to have (1*R**,2*S**)-configuration. [The assignment of the configurations at C1 and C2 is according to the CIP-rules attributing the following priorities to the respective substituents: **C1:** 1 = $P(O)(OEt)_2$, 2 = OH, 3 = $CH(OH)CF_3$, 4 = H; **C2:** 1 = OH, 2 = $CH(OH)P(O)(OEt)_2$, 3 = CF_3, 4 = H].

Table 2 Sample and crystal data of **25b**.

Chemical formula	C7H14O5F3P	**Crystal system**	monoclinic	
Formula weight [g/mol]	266.15	**Space group**	*P21/n*	
Temperature [K]	100	**Z**	8	
Measurement method	\Φ and \ω scans	**Volume [Å^3]**	2362.1(3)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	10.0601(8)	90
Crystal size / [mm^3]	0.436 × 0.392 × 0.28		15.2849(12)	90.477 (3)
Crystal habit	clear colourless block		15.3621 (11)	90

Density (calculated) / [g/cm^3]	1.497	**Absorption coefficient / [mm^{-1}]**	0.276
Abs. correction Tmin	0.746	**Abs. correction Tmax**	0.5087
Abs. correction type	multi-scan	**F(000) [e$^-$]**	1104

Table 3 Data collection and structure refinement of **25b**.

Index ranges	-11 ≤ h ≤ 12, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18	**Theta range for data collection [°]**	4.858 to 50.698	
Reflections number	34854	**Data / restraints / parameters**	4305/26/390	
Refinement method	Least squares	**Final R indices**	all data	R1 = 0.0725, wR2 = 0.1615
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$		I>2σ(I)	R1 = 0.0657, wR2 = 0.1566
Goodness-of-fit on F^2	1.084	**Weighting scheme**	$w=1/[\sigma^2(F_o^2)+(0.0548P)^2+5.3378P]$	
Largest diff. peak and hole [e Å^{-3}]	0.70/-0.6		where $P=(F_o^2+2F_c^2)/3$	

Table 4 Hydrogen Bonds in **25b**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
Intermolecular						
O2B	H2B	O5A	0.84	1.79	2.618(9)	166.8
O1D	H1D	O5C	0.84	2.01	2.81(2)	160.8
O1A	H1A	O5B	0.84	1.75	2.592(3)	177.5
O1B	H1B	O1A^2	0.84	1.74	2.56(3)	164.7
O2A	H2A	O5A^1	0.84	1.83	2.662(8)	169.5
O2A	H2A	O5C^1	0.84	1.99	2.80(3)	162.1
O2D	H2D	O1A^2	0.84	2.02	2.83(2)	163.0
^{1}-x+1, -y+1, -z; ^{2}-x+3/2, y-1/2, -z+1/2						

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