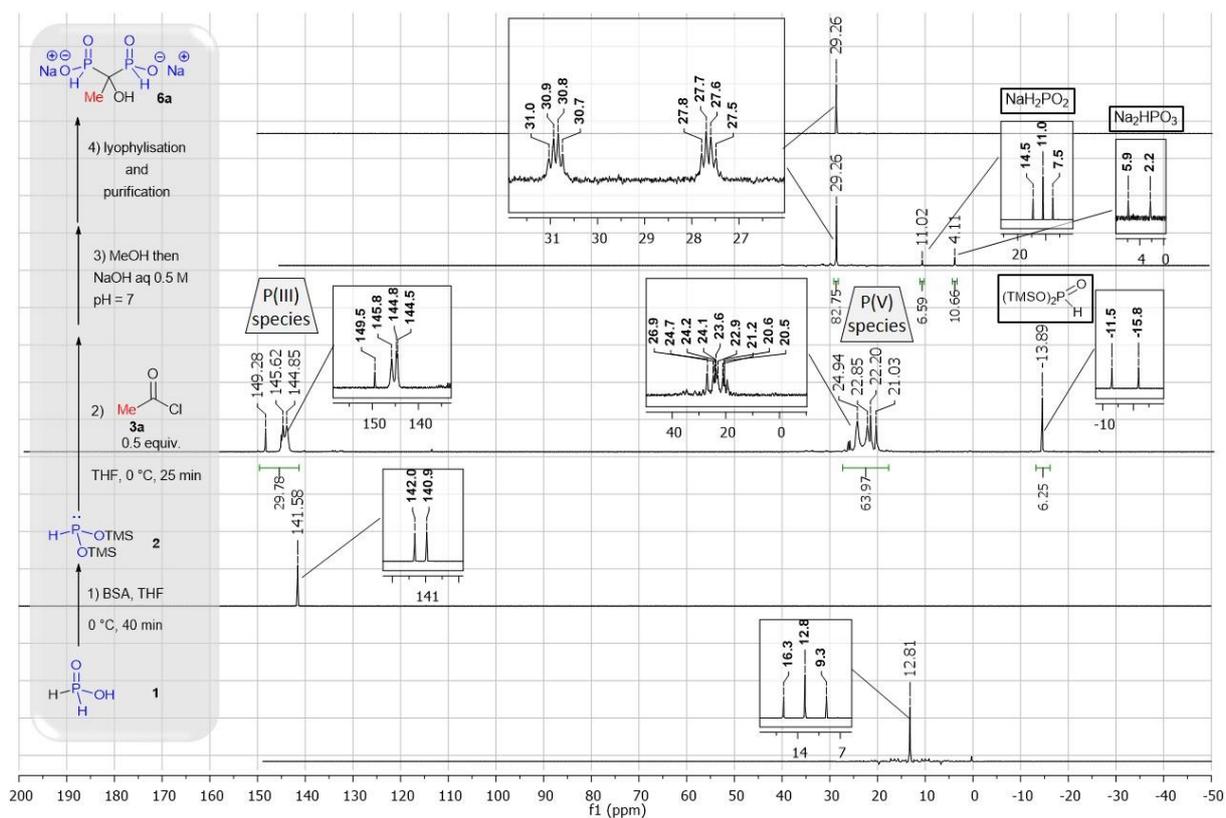


Supporting Information

Table of Contents:

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- II. Reaction parameter optimisations for benzoyl chloride substrate
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- IV. Titration of HMBPi **6c** and **6g**
- V. Spectral data

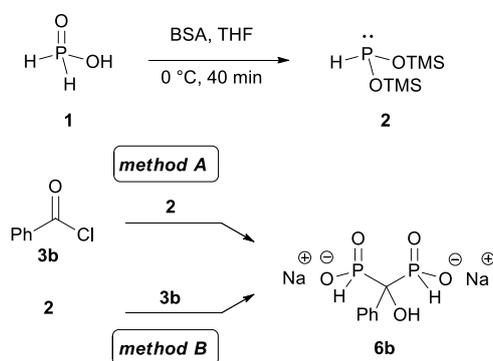
I. Reaction monitoring by ^{31}P NMR spectroscopy



Scheme 1 ^{31}P NMR monitoring of the reaction between hypophosphorous acid **1** and acetyl chloride **3a** in presence of *N,O*-bis(trimethylsilyl)acetamide (BSA). Spectra showed $^{31}\text{P}\{^1\text{H}\}$ NMR peaks whereas zooms indicated corresponding ^{31}P NMR spectra

II. Reaction parameter optimisations for benzoyl chloride substrate

Table 1 Reaction between benzoyl chloride **3b** and hypophosphorous acid **1** in presence of *N,O*-bis(trimethylsilyl)acetamide (BSA)^a



entry	method ^b	temp (°C)	[3a] (M)	[2] (M)	time ^c	Yield ^d (%)
1	A	-70	1.25	10	1.25 h	55
2	A	0	5	10	18 h	-
3	B	-70	5	1	25 min	44
4	B	0	5	10	25 min	51
5	B	0	5	1	15 min	34
6	B	0	1.25	10	25 min	57
7	B	0	5	5	20 min	87

^areaction conditions: **1** (10 mmol), BSA (20 mmol), **3b** (5 mmol), THF (3 mL), Ar, 0 °C. ^bFor details see experimental section. ^cReaction completion monitored by ³¹P{¹H} and ³¹P NMR; the indicated time includes the time of addition. ^dIsolated yield of *H*-HMBPi **6b**.

III. Identification of phosphino-phosphonate isomer (11)

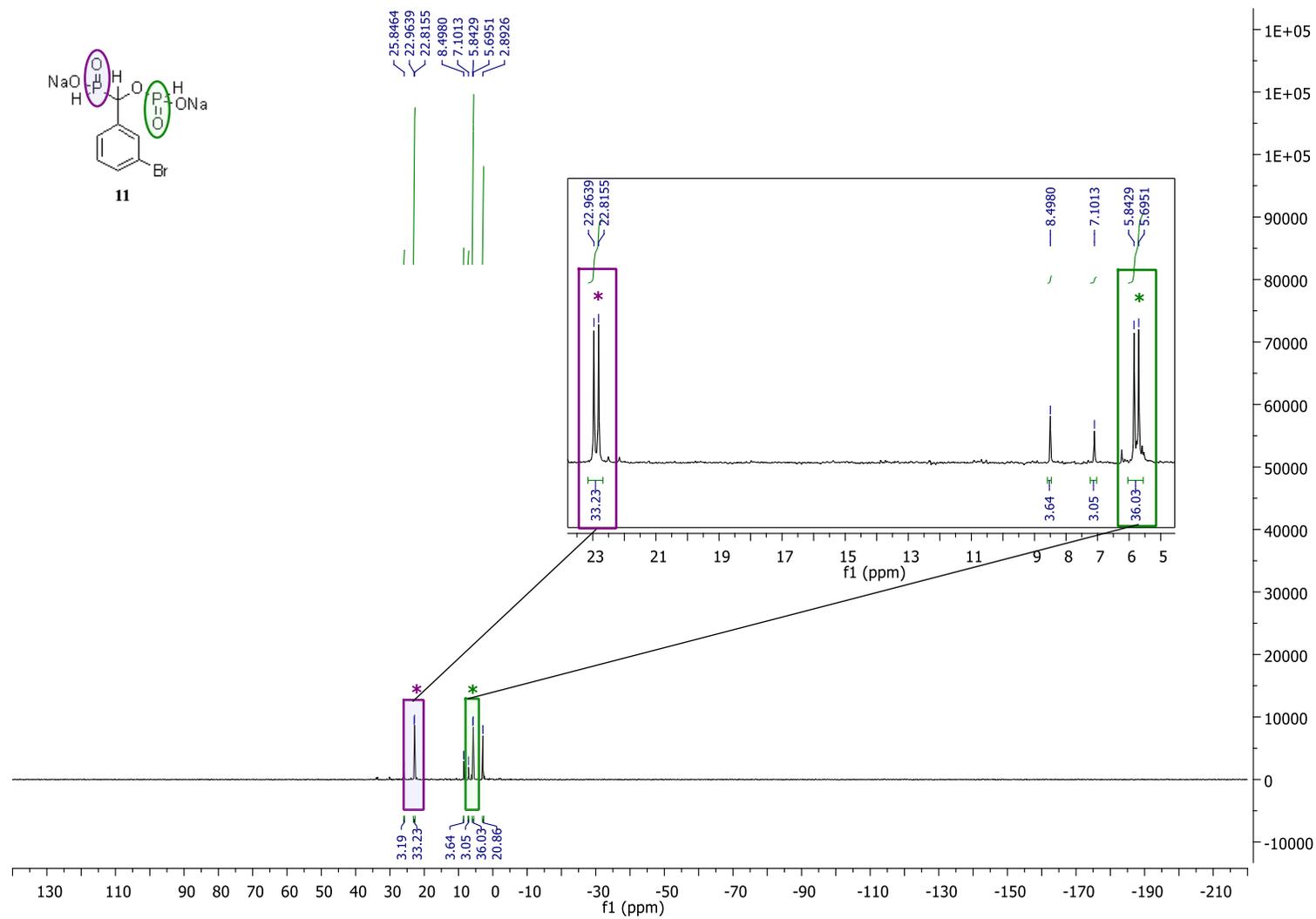


Figure 1a: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the phosphino-phosphonate isomer (11)

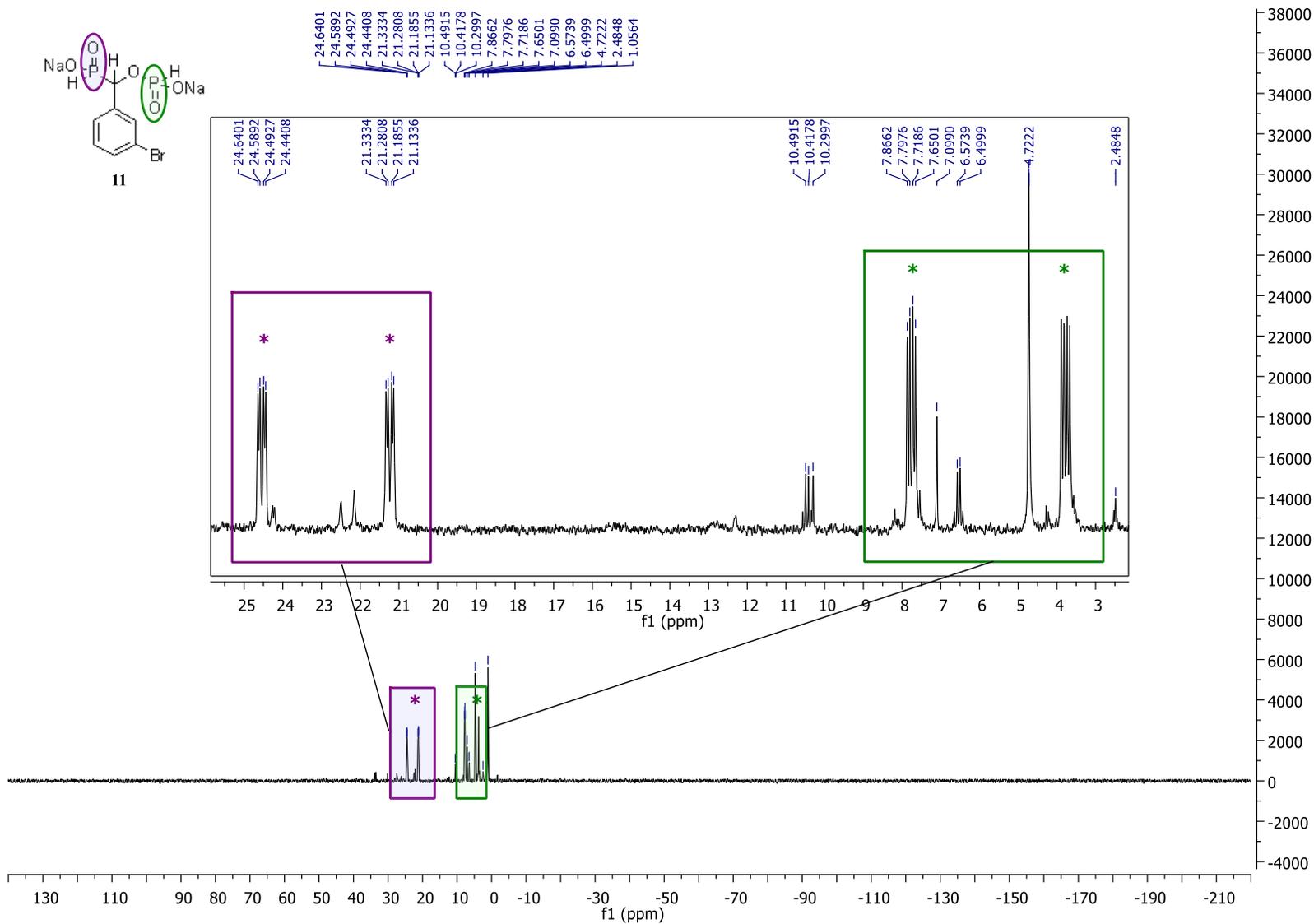


Figure 1b: ^{31}P NMR spectrum of the phosphino-phosphonate isomer (11)

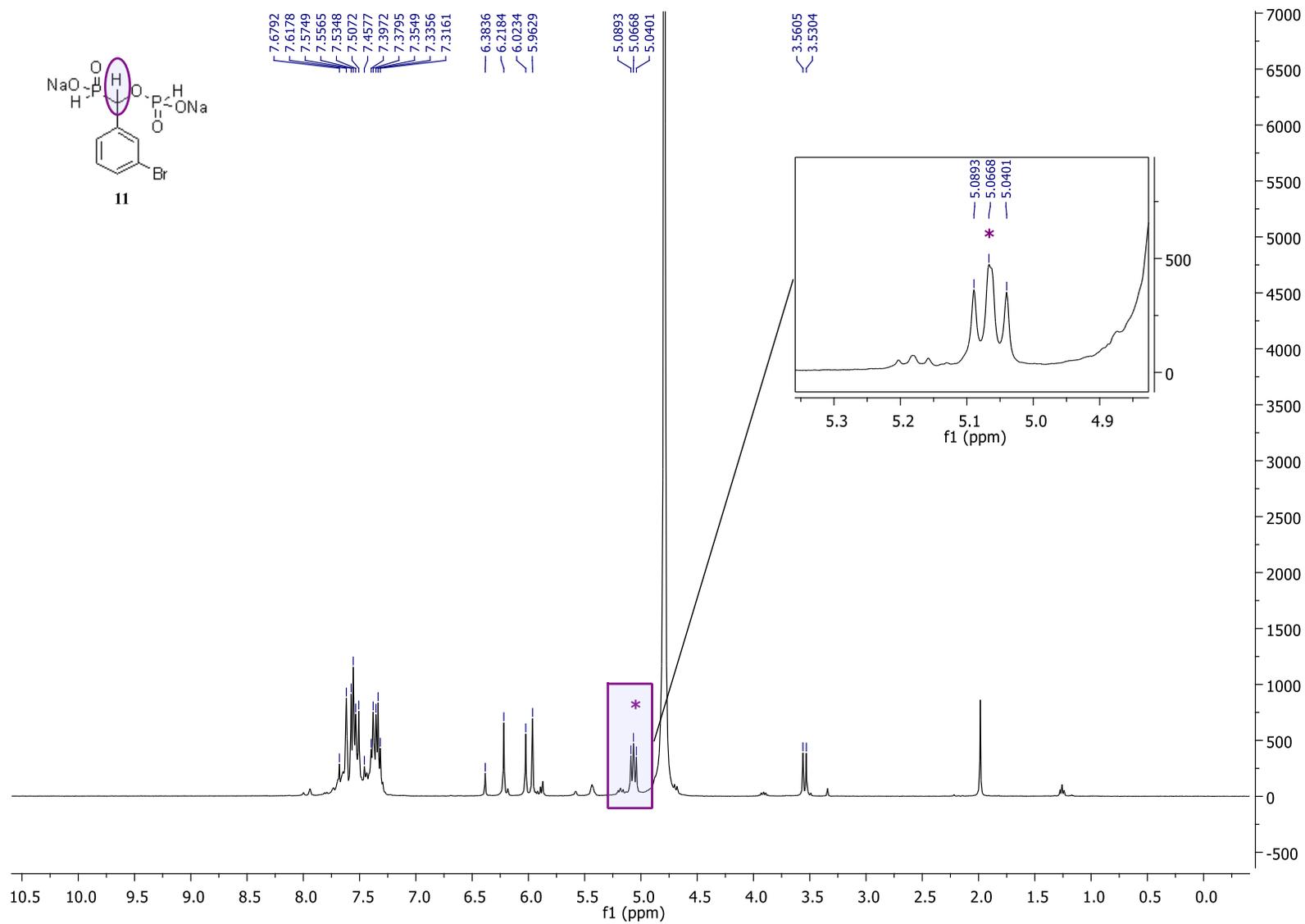


Figure 1c: ^1H NMR spectrum of the phosphino-phosphonate isomer (**11**)

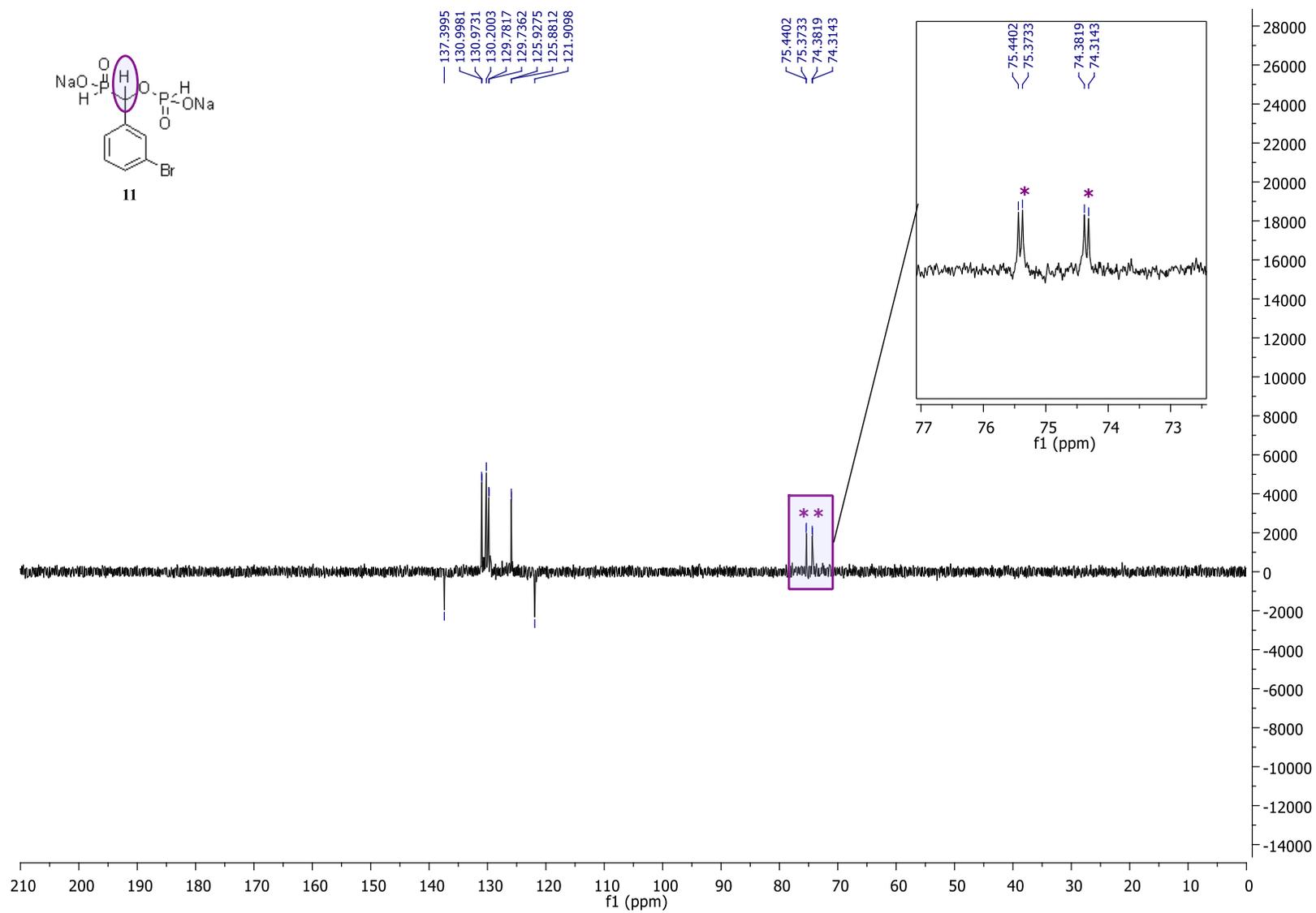


Figure 1d: ^{13}C Jmod NMR spectrum of the phosphino-phosphonate isomer (11)

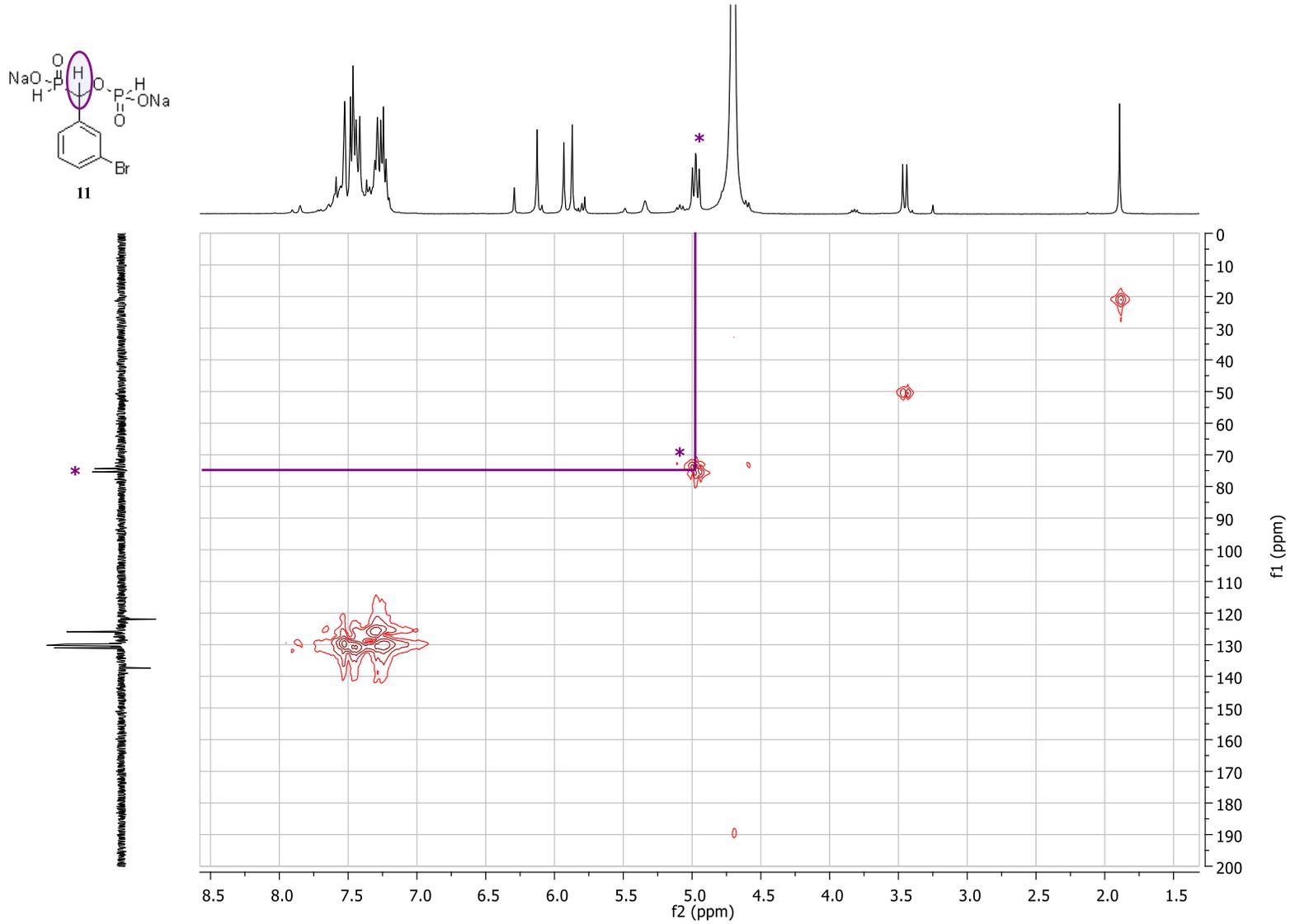


Figure 1e : HMQC spectrum of the phosphino-phosphonate isomer (11)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 500.0 PPM / DBE: min = -50.0, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions

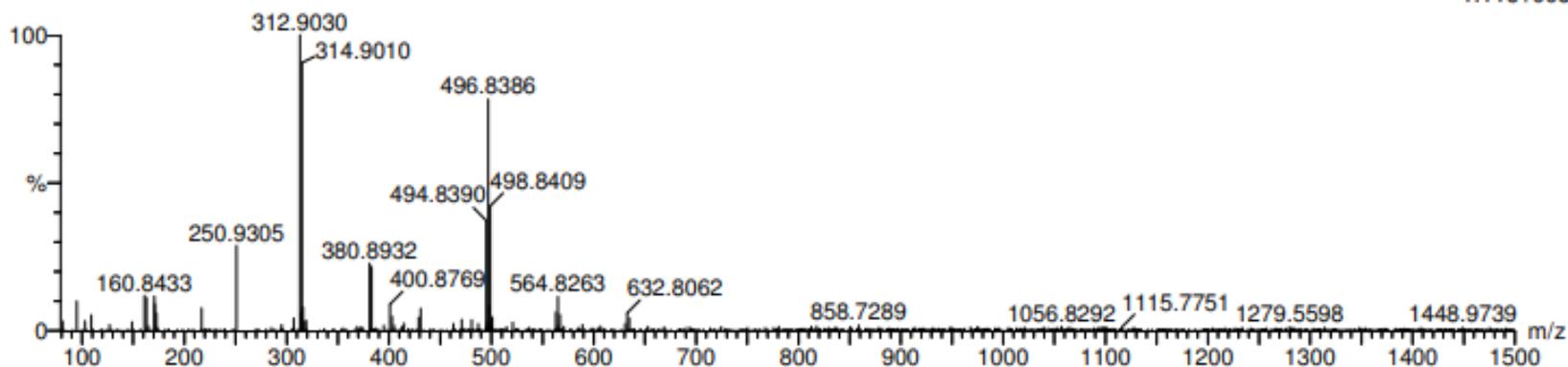
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 7-8 H: 8-9 O: 5-5 Na: 0-1 P: 2-2 Br: 1-1

VAUZEILLES_baron367-2 23 (0.615) Cm (19:23-38:63)

2: TOF MS ES-
1.11e+003



Minimum: -50.0
Maximum: 30.0 500.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
312.9030	312.9030	0.0	0.0	4.5	27.6	0.0	C7 H8 O5 P2 Br

Figure 1f: Mass Analysis Spectrum of the phosphino-phosphonate isomer (11)

IV. Titration of HMBPi 6c and 6g

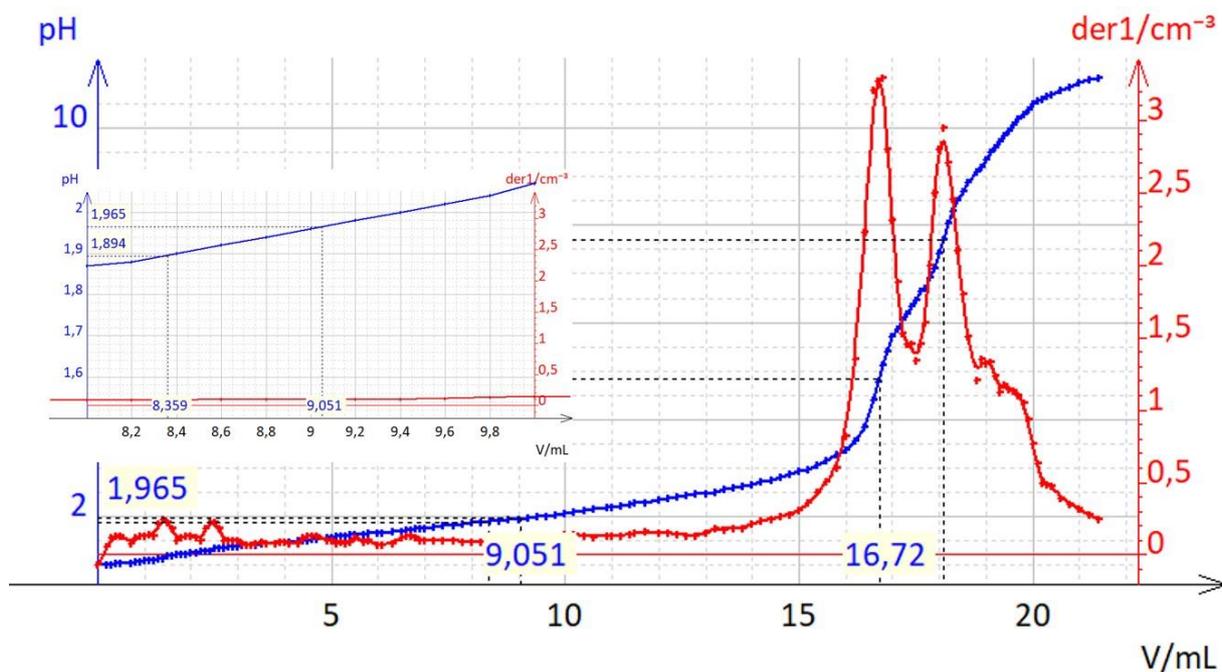


Figure 2a : Titration of HMBPi 6c by an aqueous solution of NaOH (0.04M)

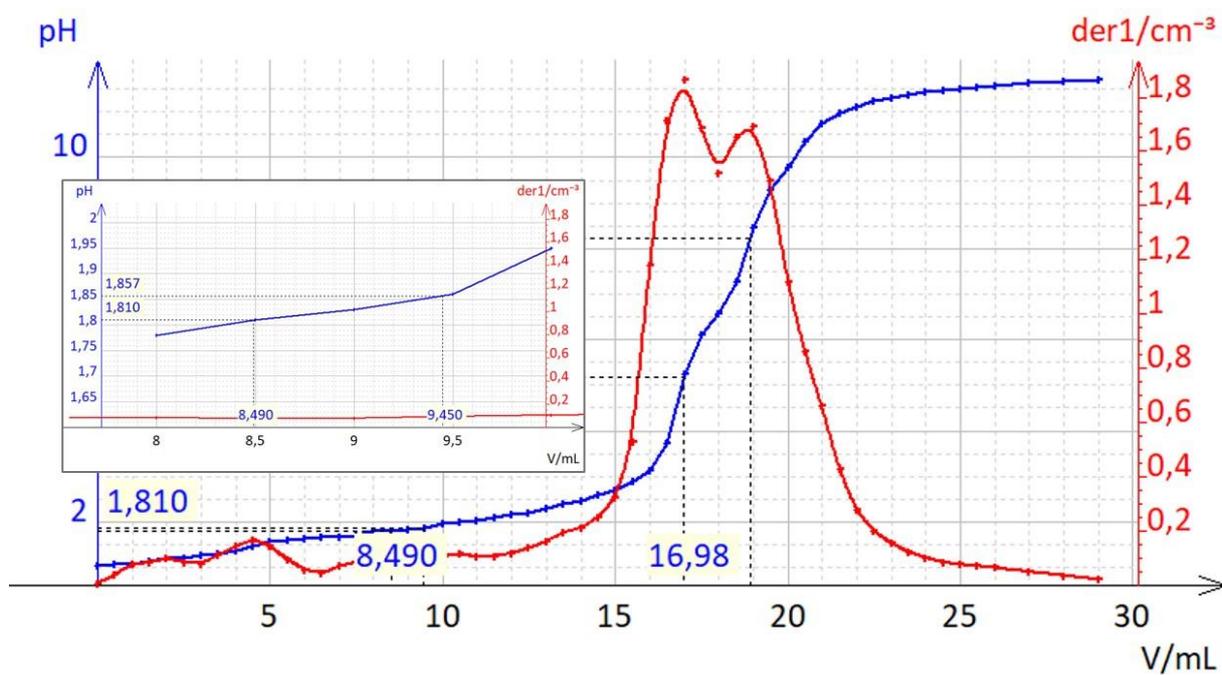


Figure 2b : Titration of HMBPi 6g by an aqueous solution of NaOH (0.04M)

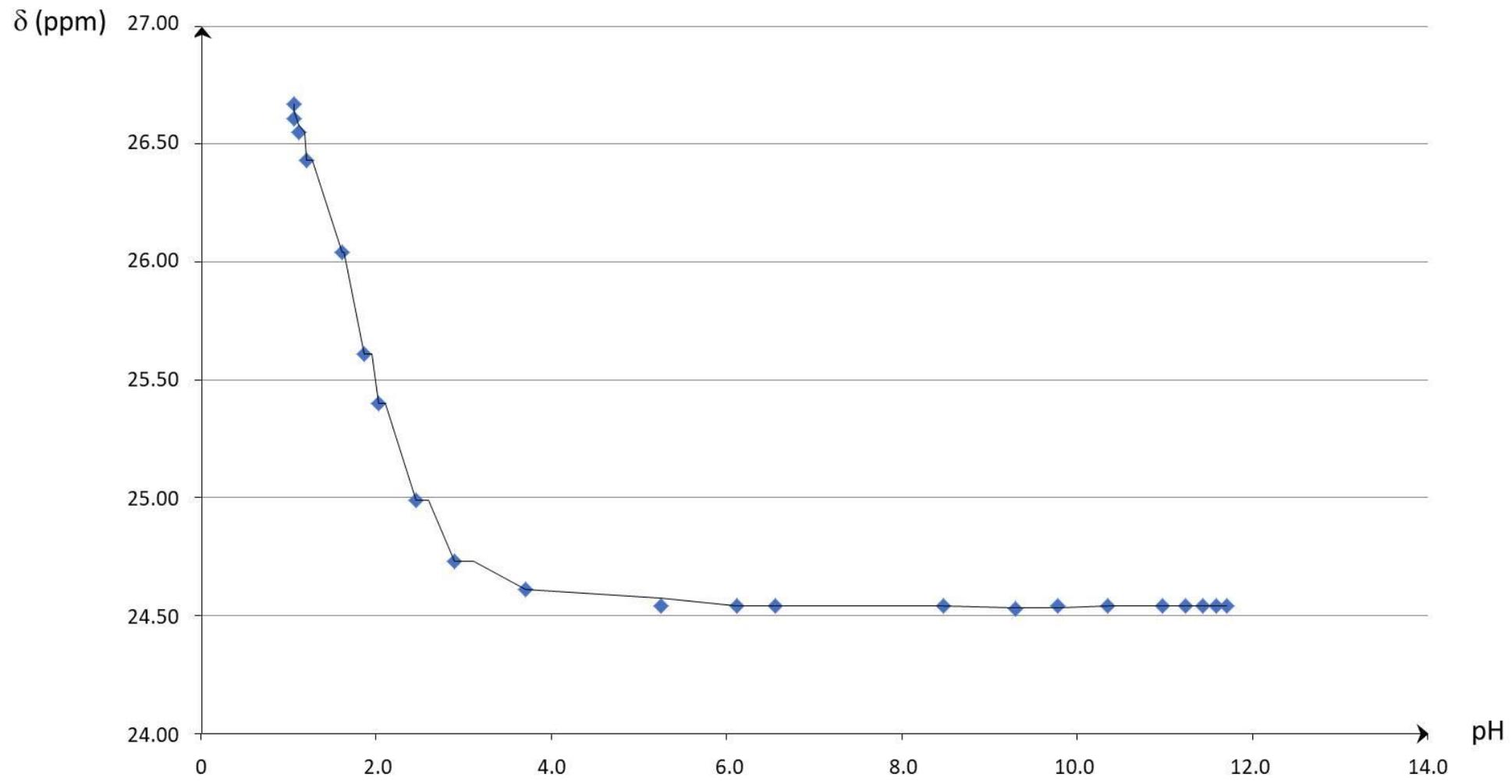


Figure 2c : NMR titration of HMBPi 6g by an aqueous solution of NaOH (0.04M)

V. Spectral data

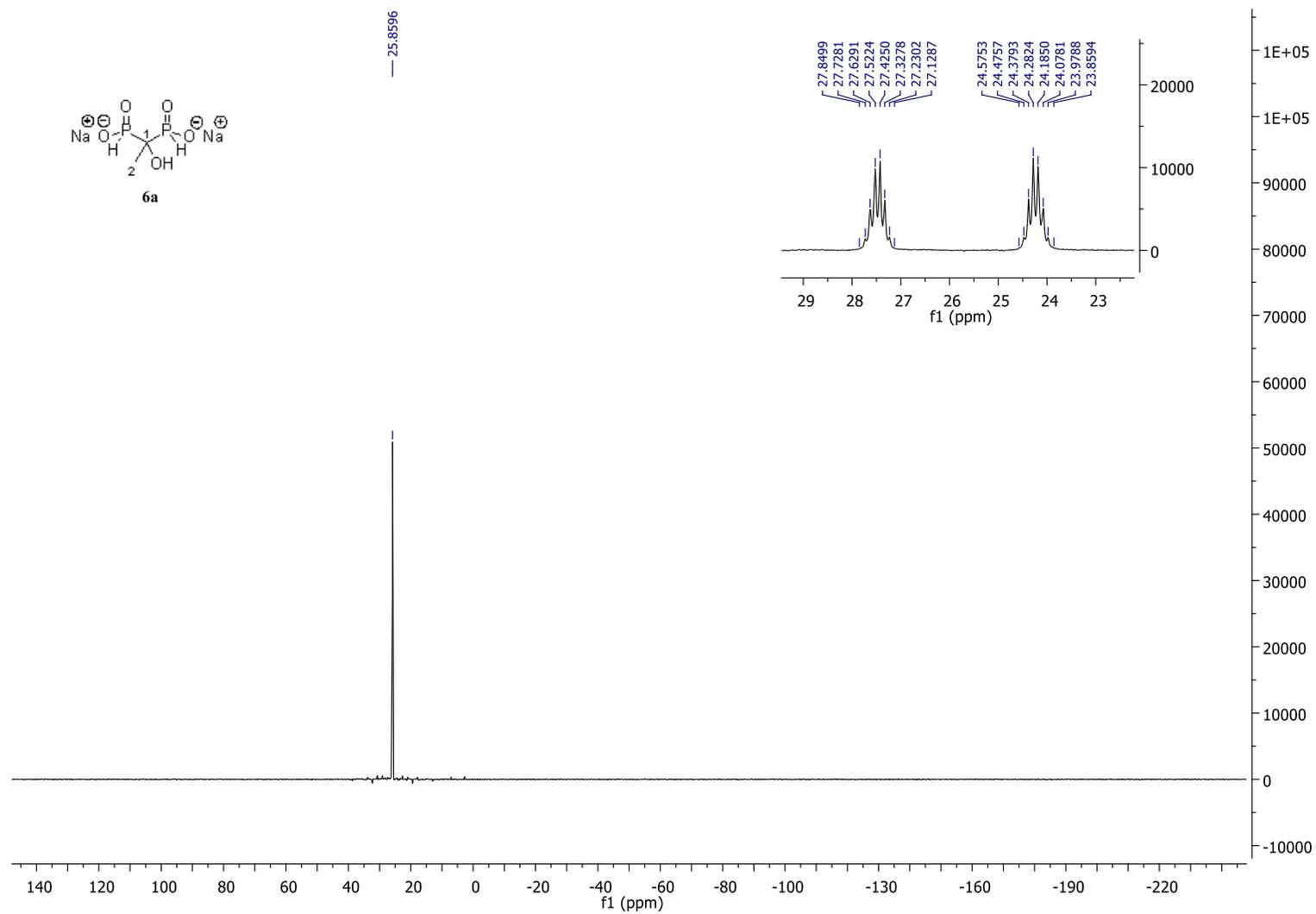


Figure 3: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxyethane-1,1-bis(*H*-phosphinate) disodium salt (6a)

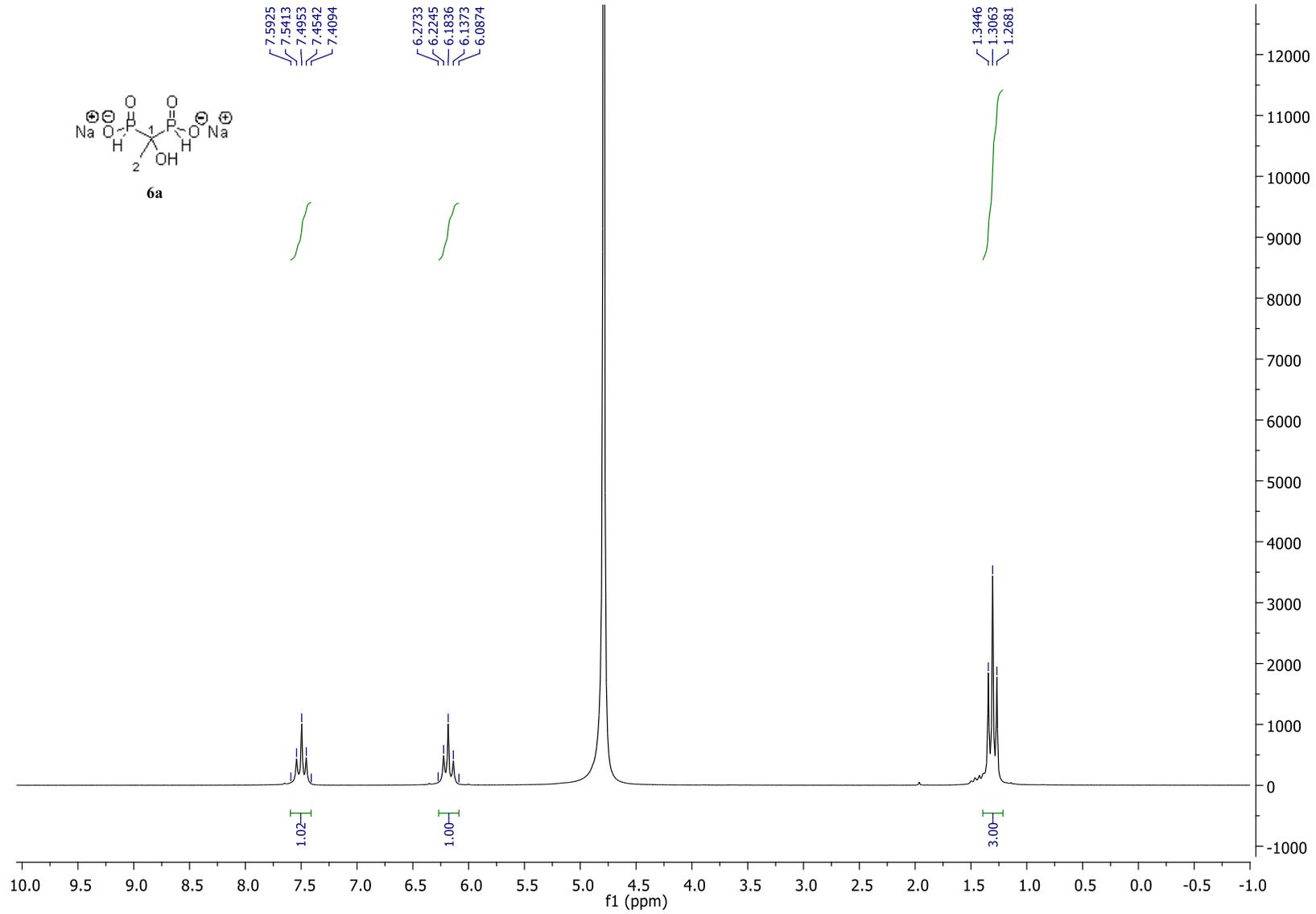


Figure 4: ^1H NMR spectrum of 1-hydroxyethane-1,1-bis(*H*-phosphinate) disodium salt (6a)

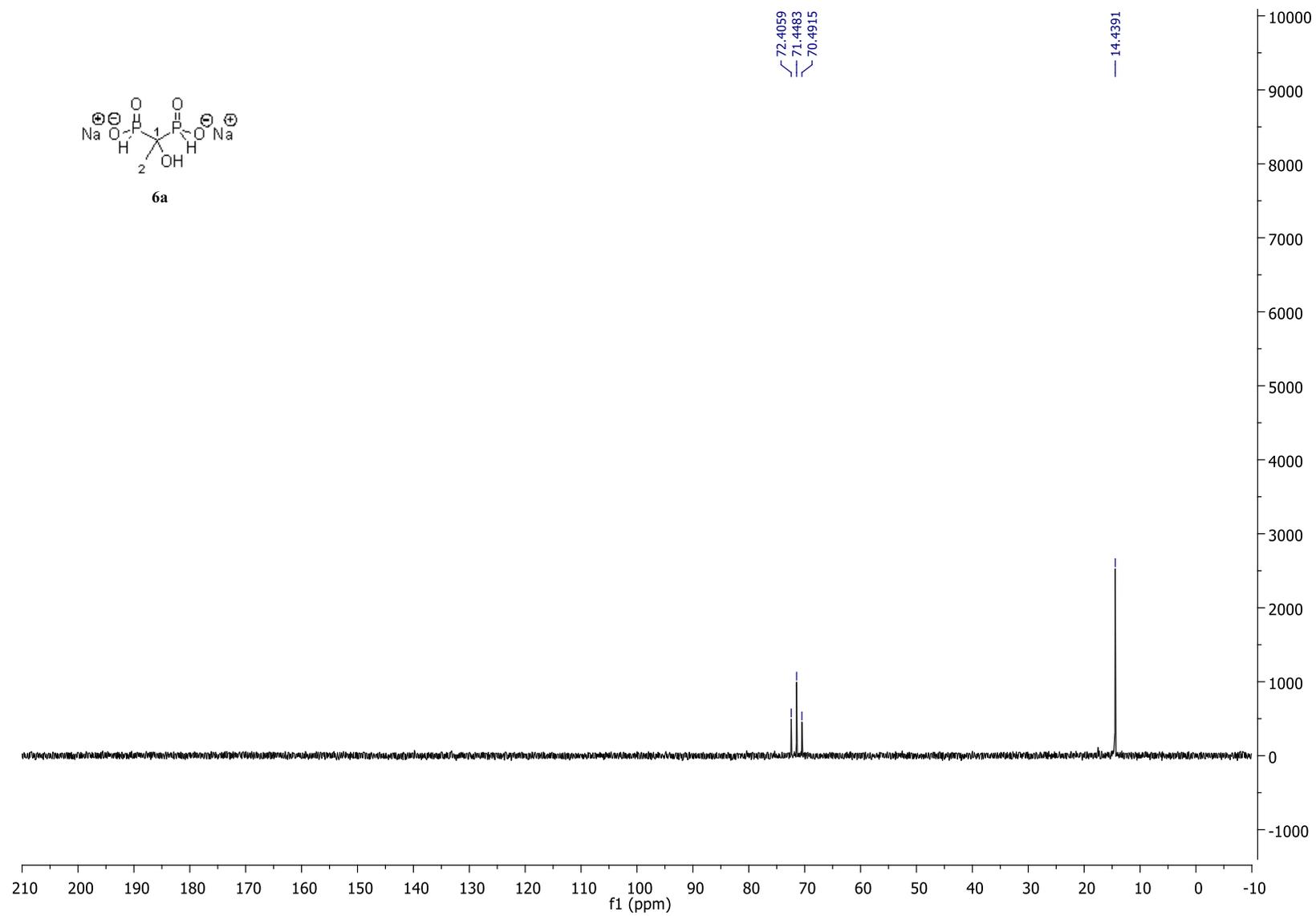


Figure 5: ¹³C NMR spectrum of 1-hydroxyethane-1,1-bis(*H*-phosphinate) disodium salt (6a)

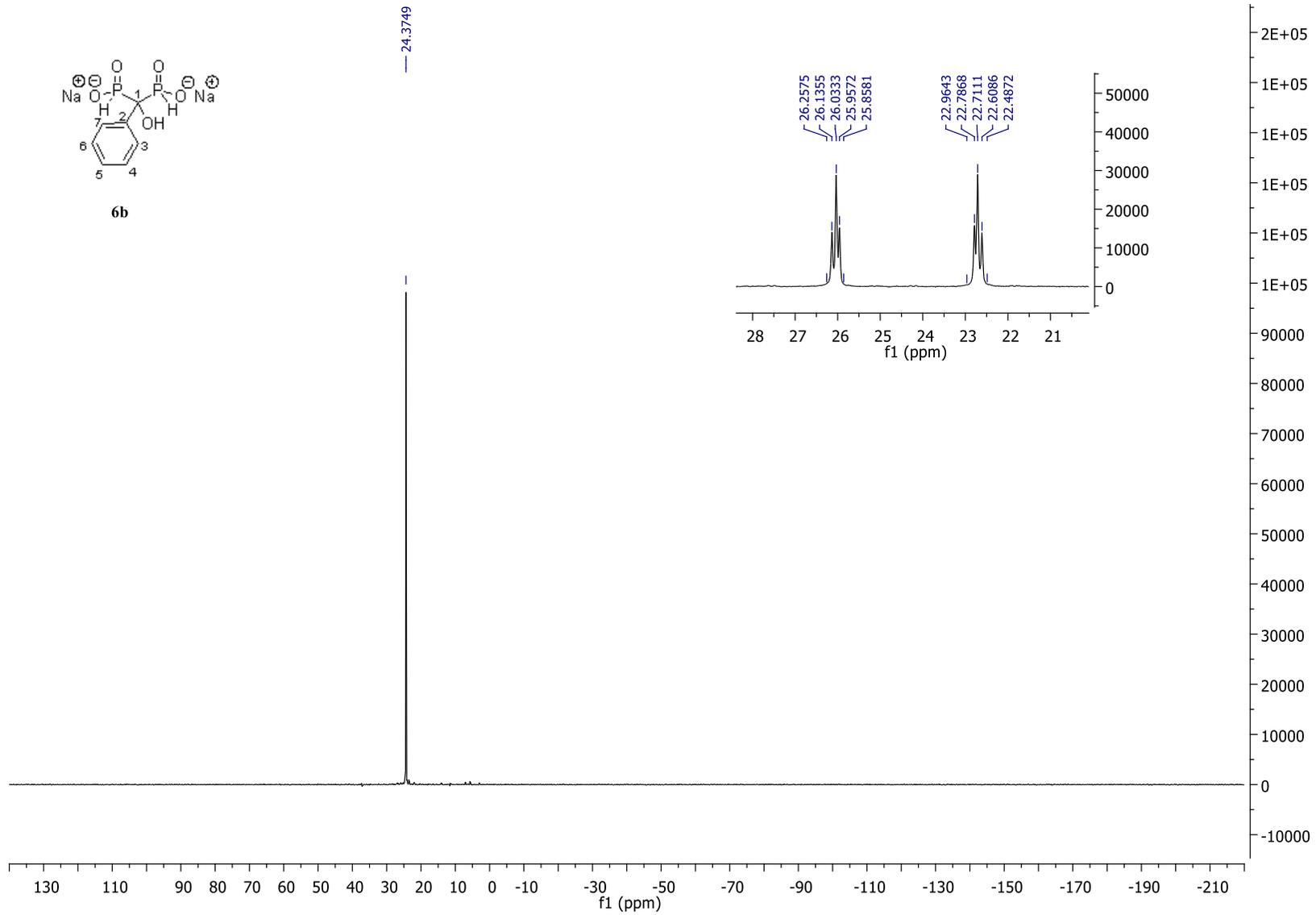


Figure 6: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-phenylmethane-1,1-bis(*H*-phosphinate) disodium salt (**6b**)

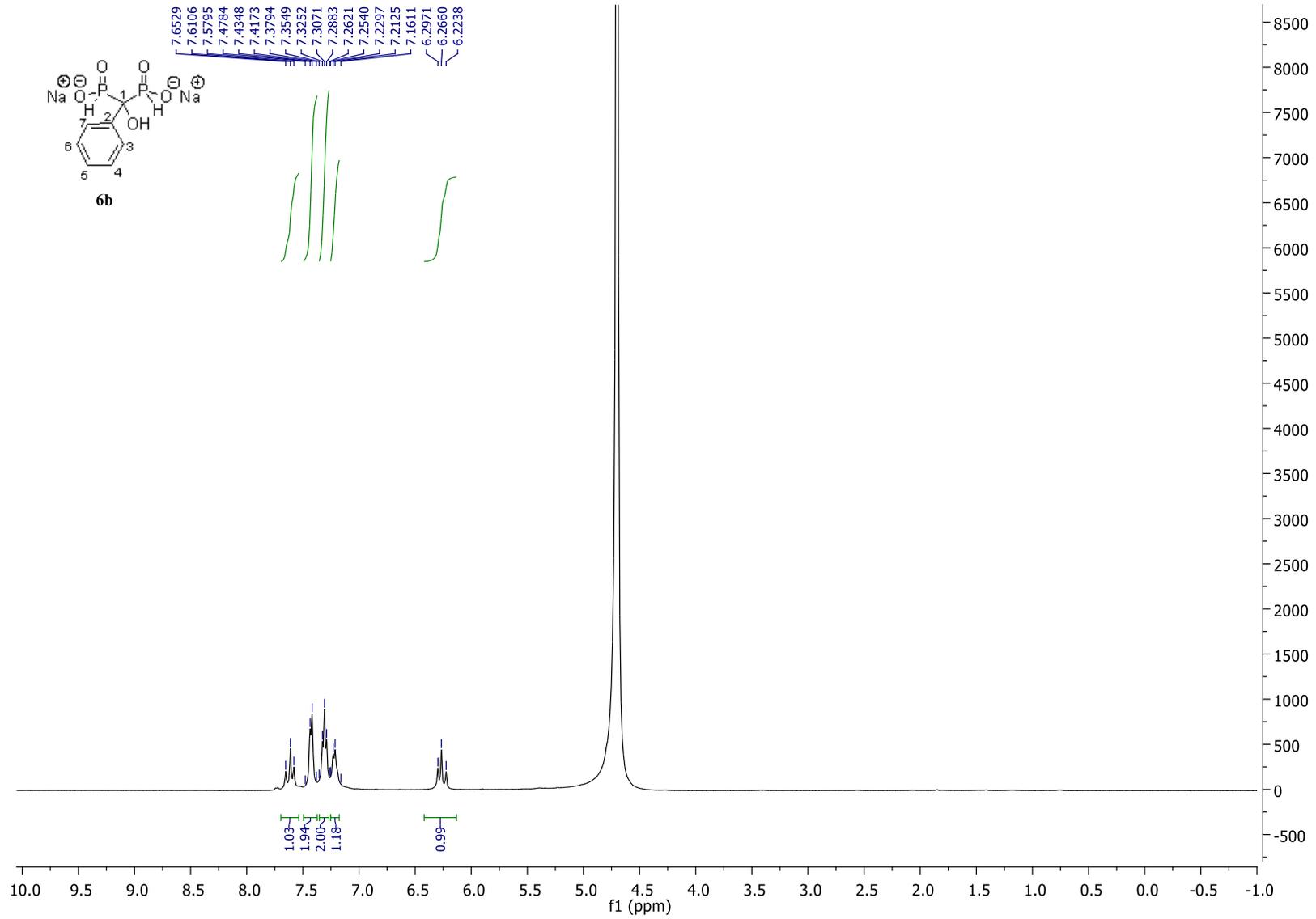


Figure 7: ^1H NMR spectrum of 1-hydroxy-1-phenylmethane-1,1-bis(*H*-phosphinate) disodium salt (6b)

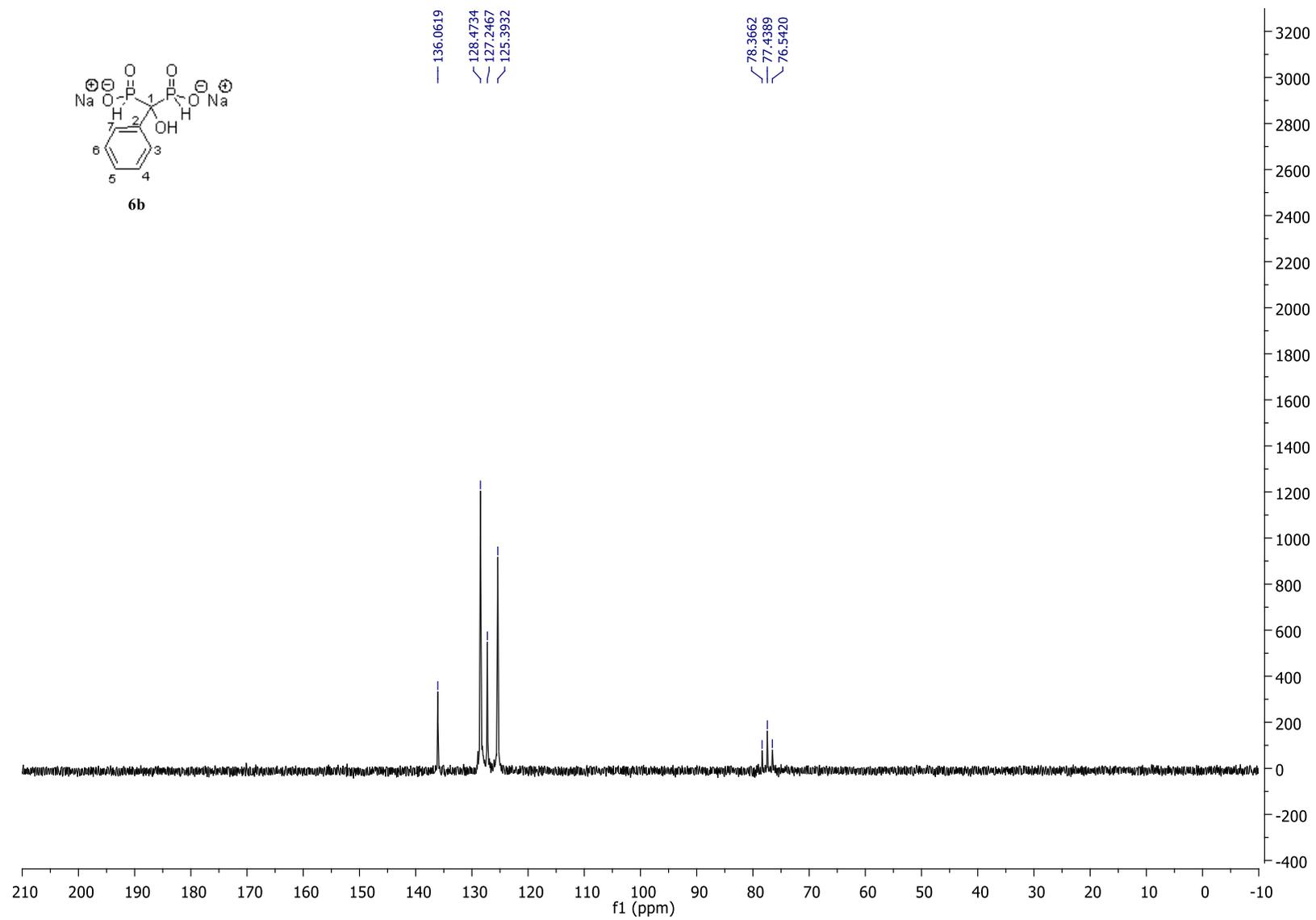


Figure 8: ¹³C NMR spectrum of 1-hydroxy-1-phenylmethane-1,1-bis(*H*-phosphinate) disodium salt (6b)

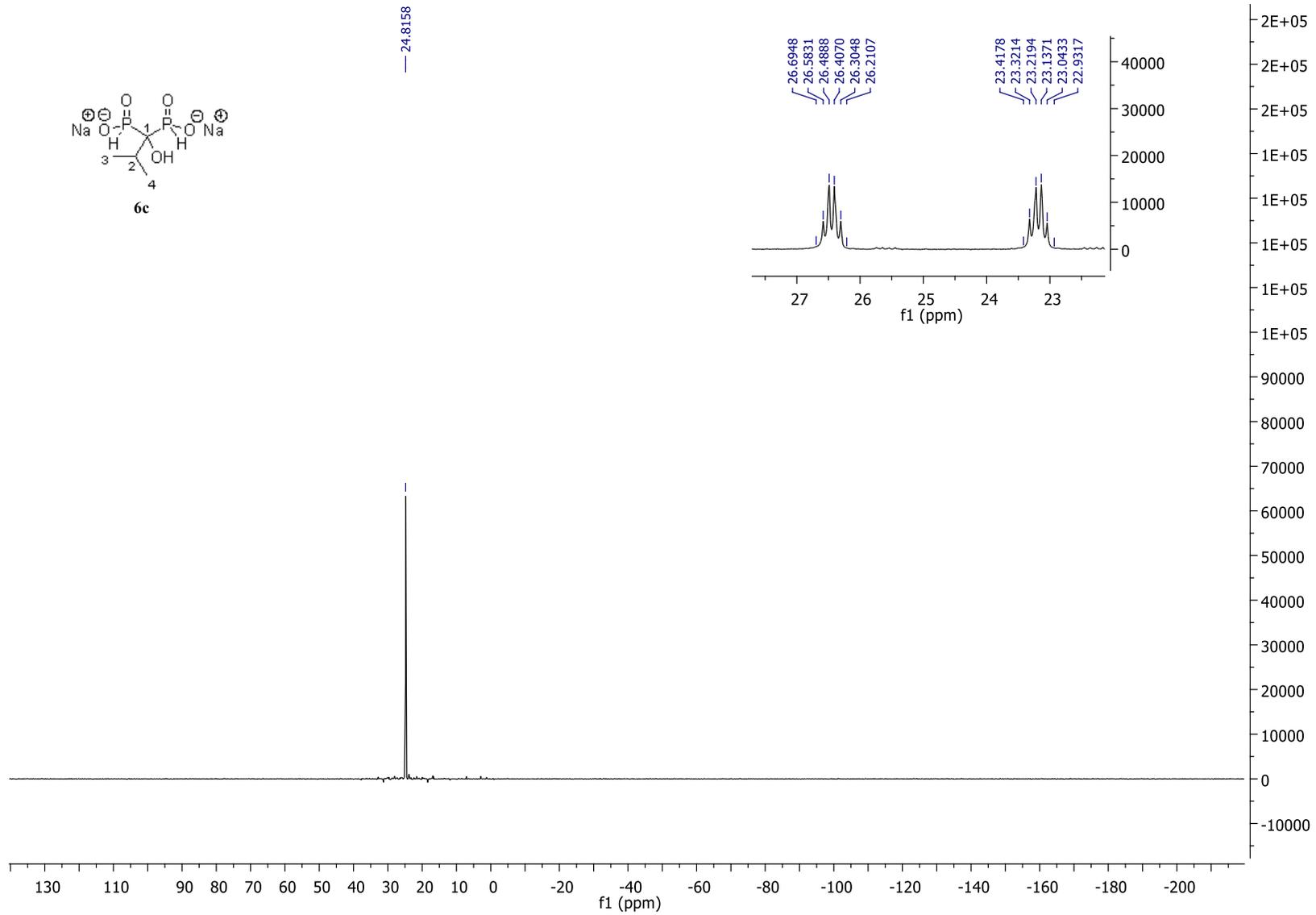


Figure 9: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-2-methylpropane-1,1-bis(*H*-phosphinate) disodium salt (**6c**)

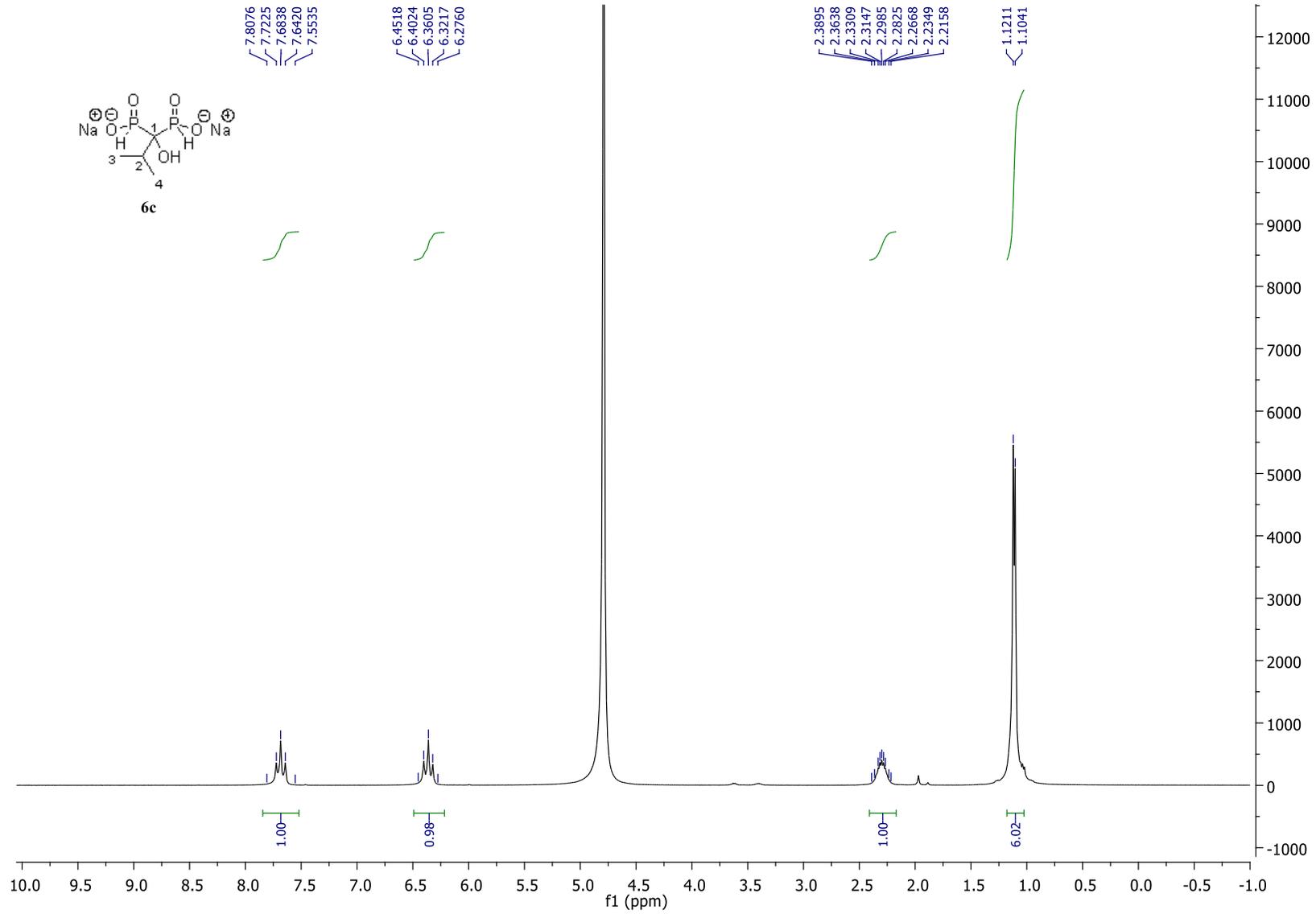


Figure 10: ^1H NMR spectrum of 1-hydroxy-2-methylpropane-1,1-bis(*H*-phosphinate) disodium salt (6c)

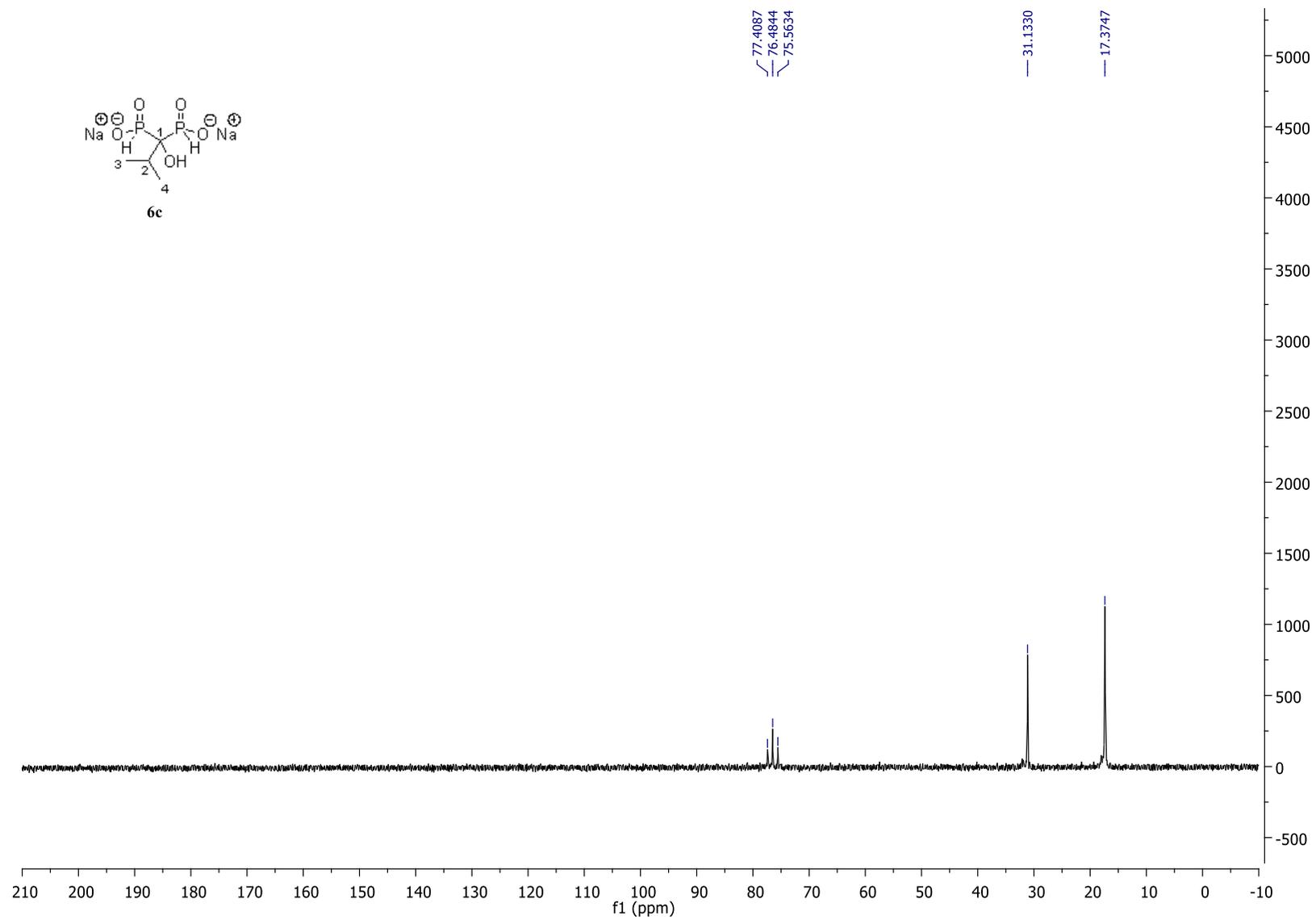


Figure 11: ^{13}C NMR spectrum of 1-hydroxy-2-methylpropane-1,1-bis(*H*-phosphinate) disodium salt (**6c**)

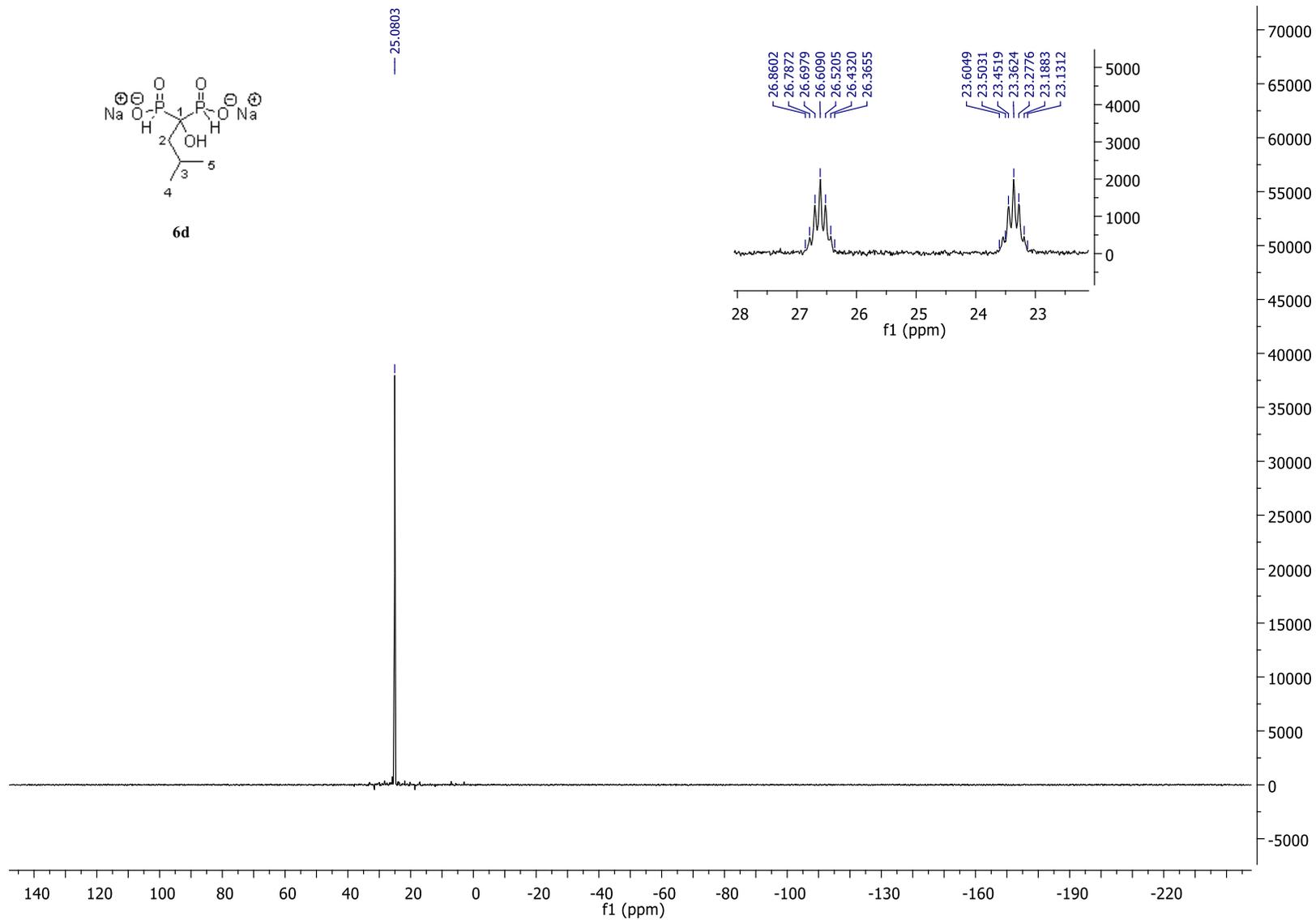


Figure 12: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-3-methylbutane-1,1-bis(*H*-phosphinate) disodium salt (6d)

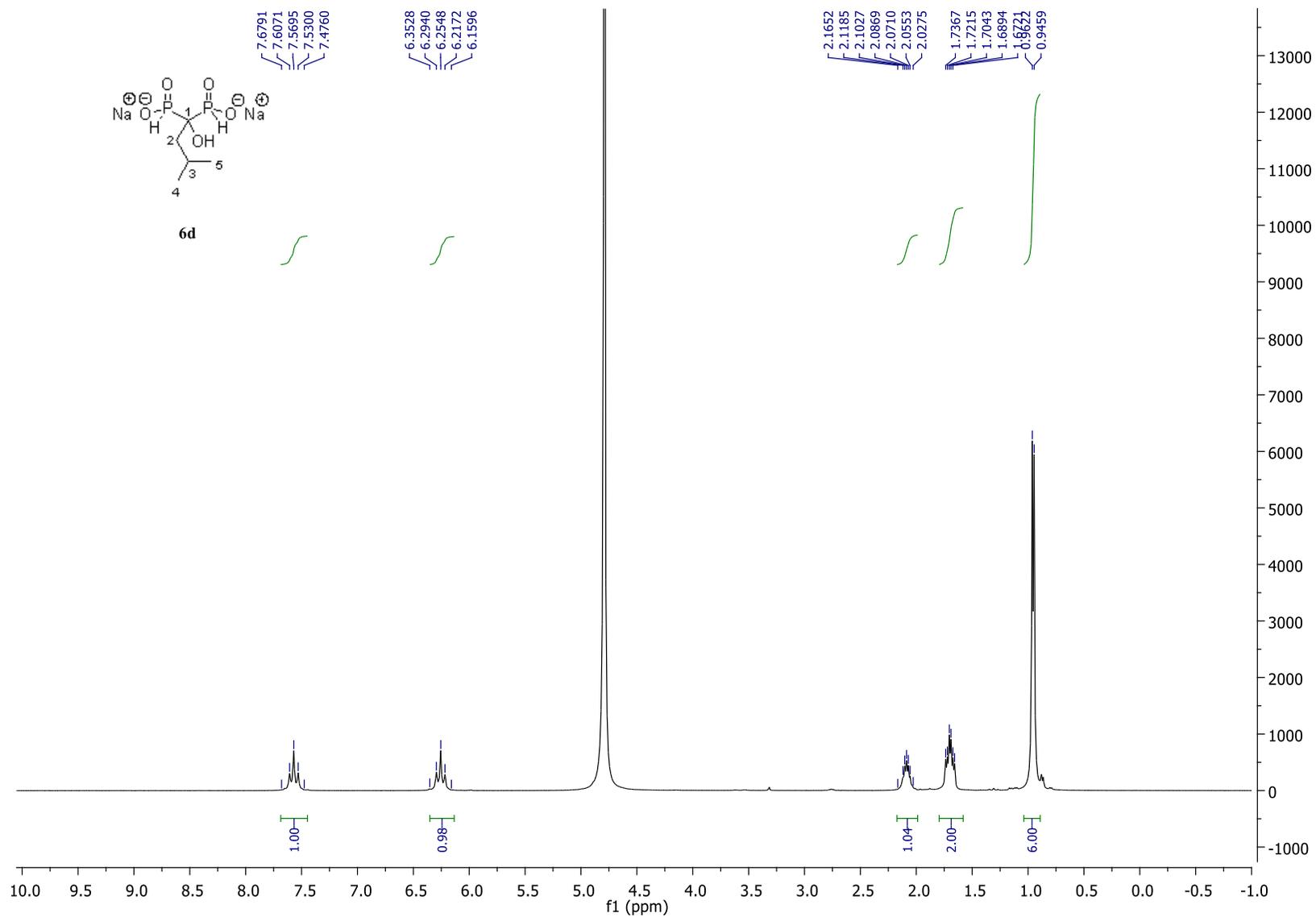


Figure 13: ¹H NMR spectrum of 1-hydroxy-3-methylbutane-1,1-bis(*H*-phosphinate) disodium salt (6d)

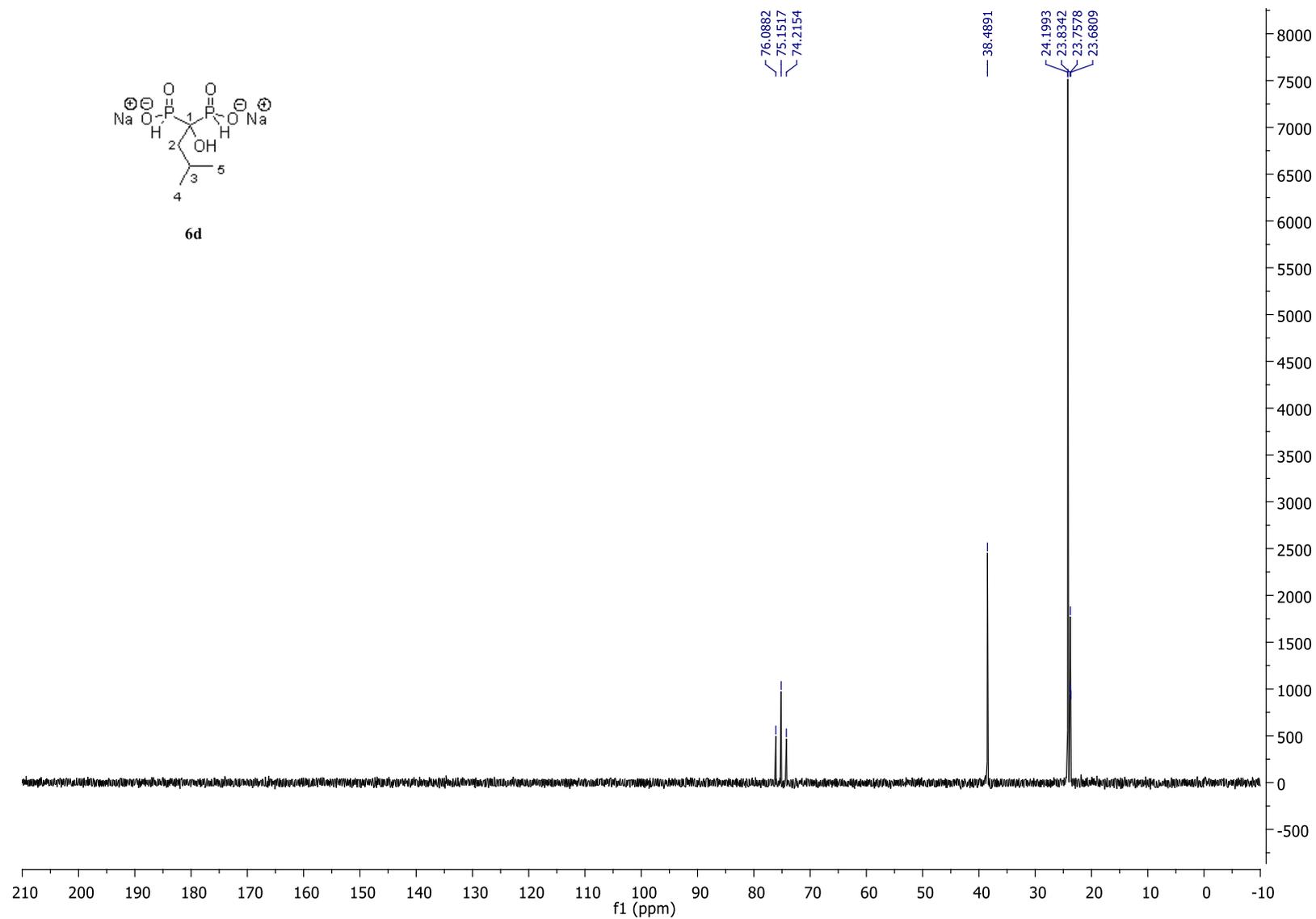


Figure 14: ¹³C NMR spectrum of 1-hydroxy-3-methylbutane-1,1-bis(*H*-phosphinate) disodium salt (6d)

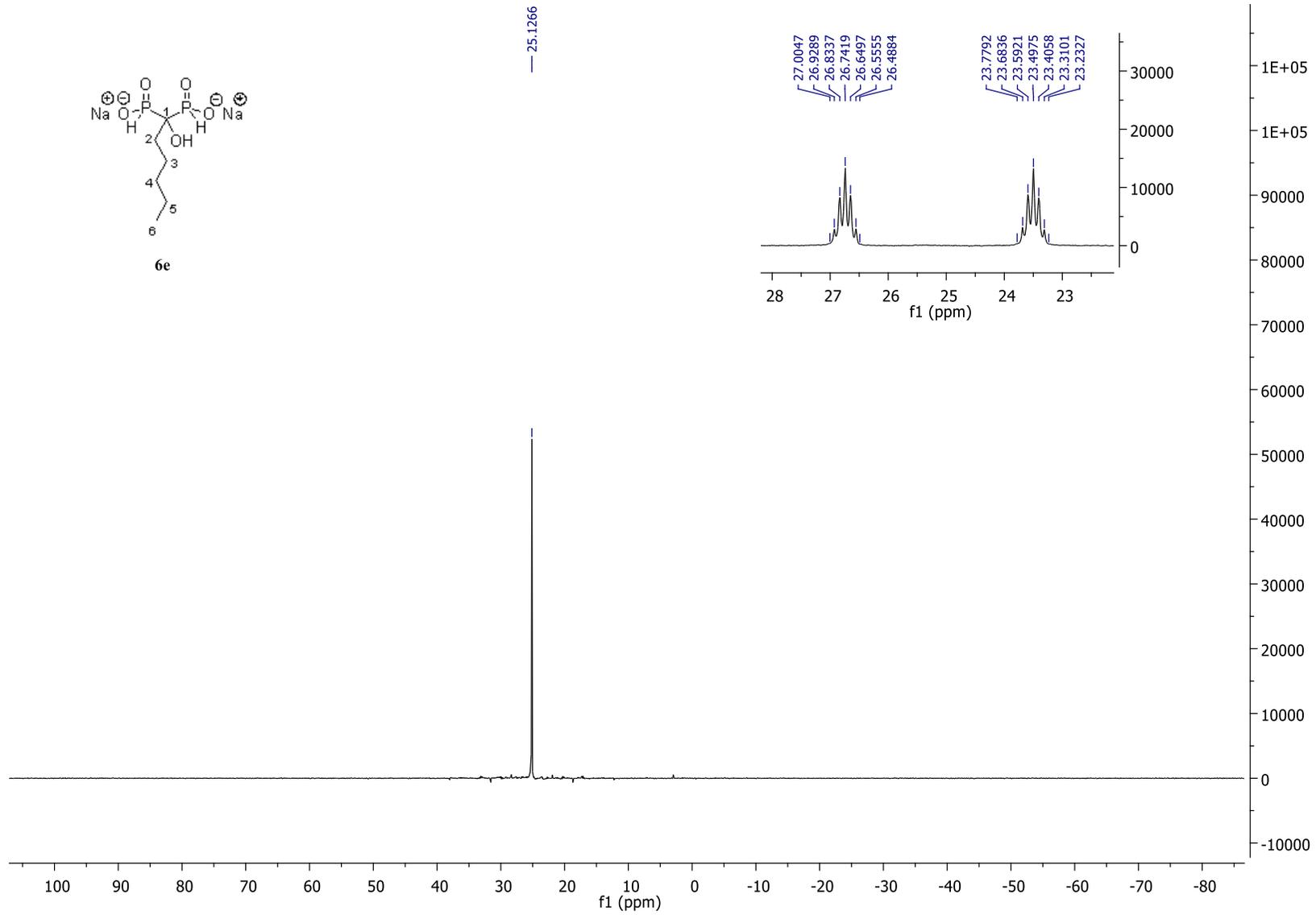


Figure 15: ³¹P{¹H} and ³¹P NMR spectra of 1-hydroxyhexane-1,1-bis(*H*-phosphinate) disodium salt (6e)

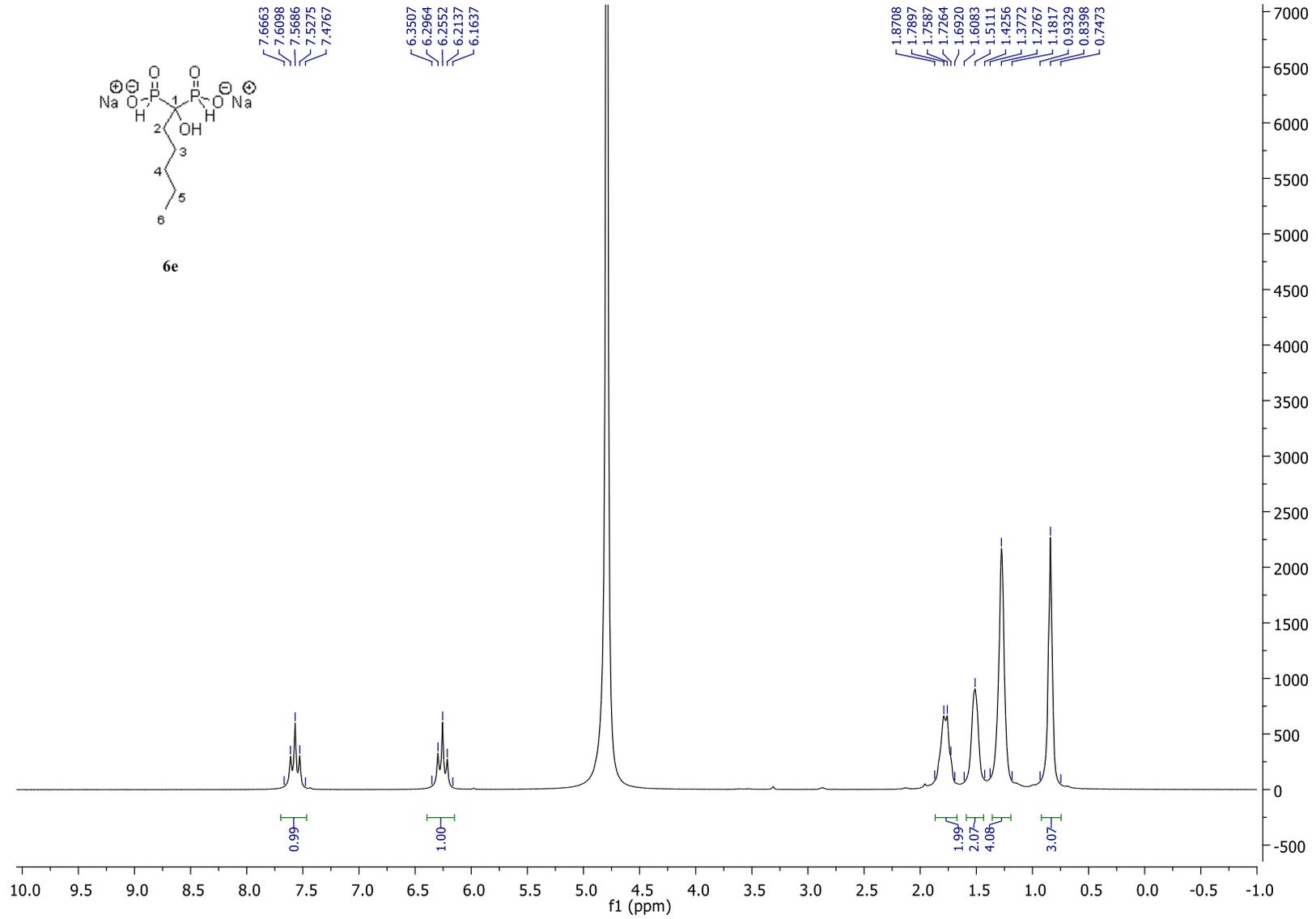


Figure 16: ^1H NMR spectrum of 1-hydroxyhexane-1,1-bis(*H*-phosphinate) disodium salt (6e)

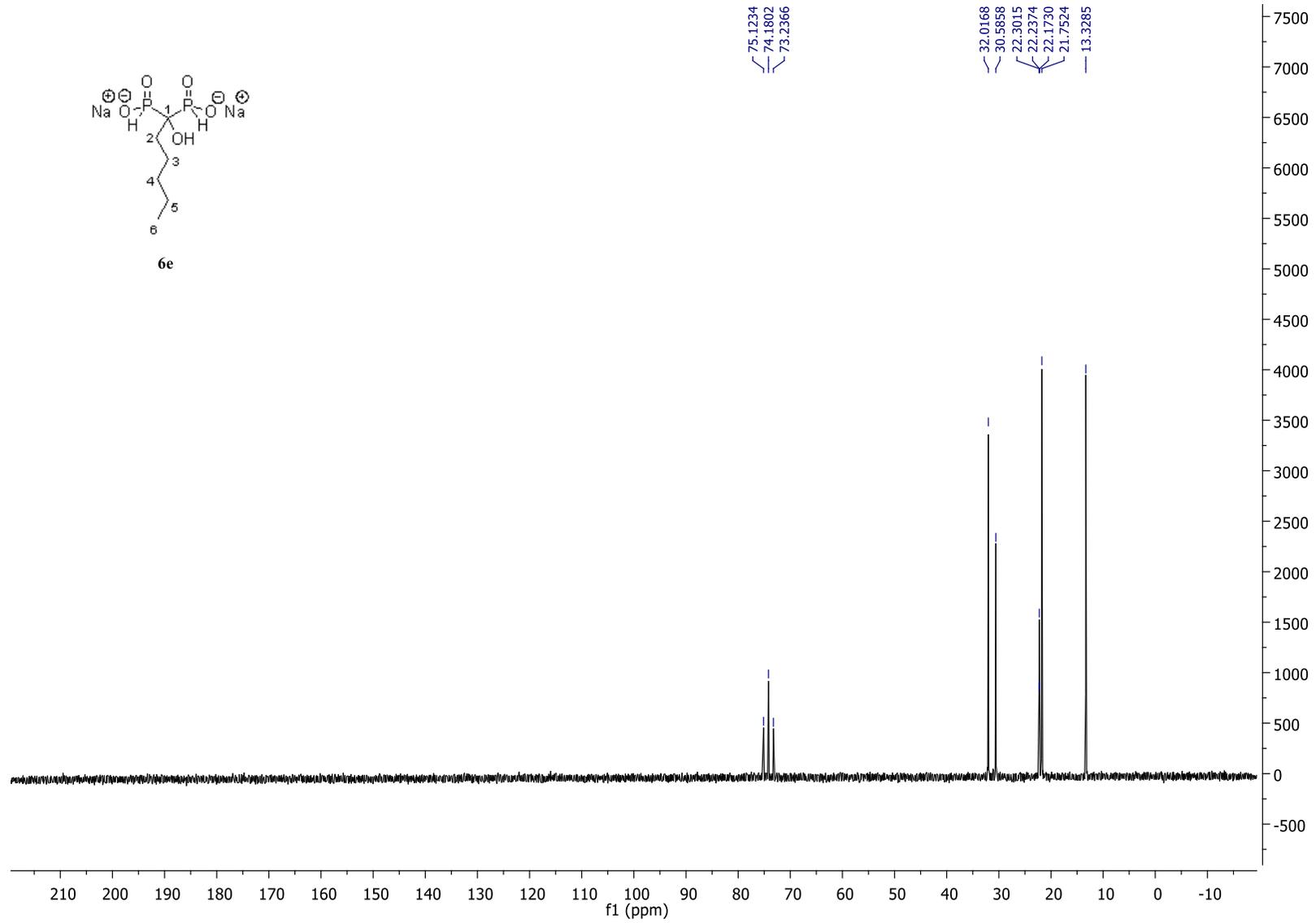


Figure 17: ¹³C NMR spectrum of 1-hydroxyhexane-1,1-bis(*H*-phosphinate) disodium salt (6e)

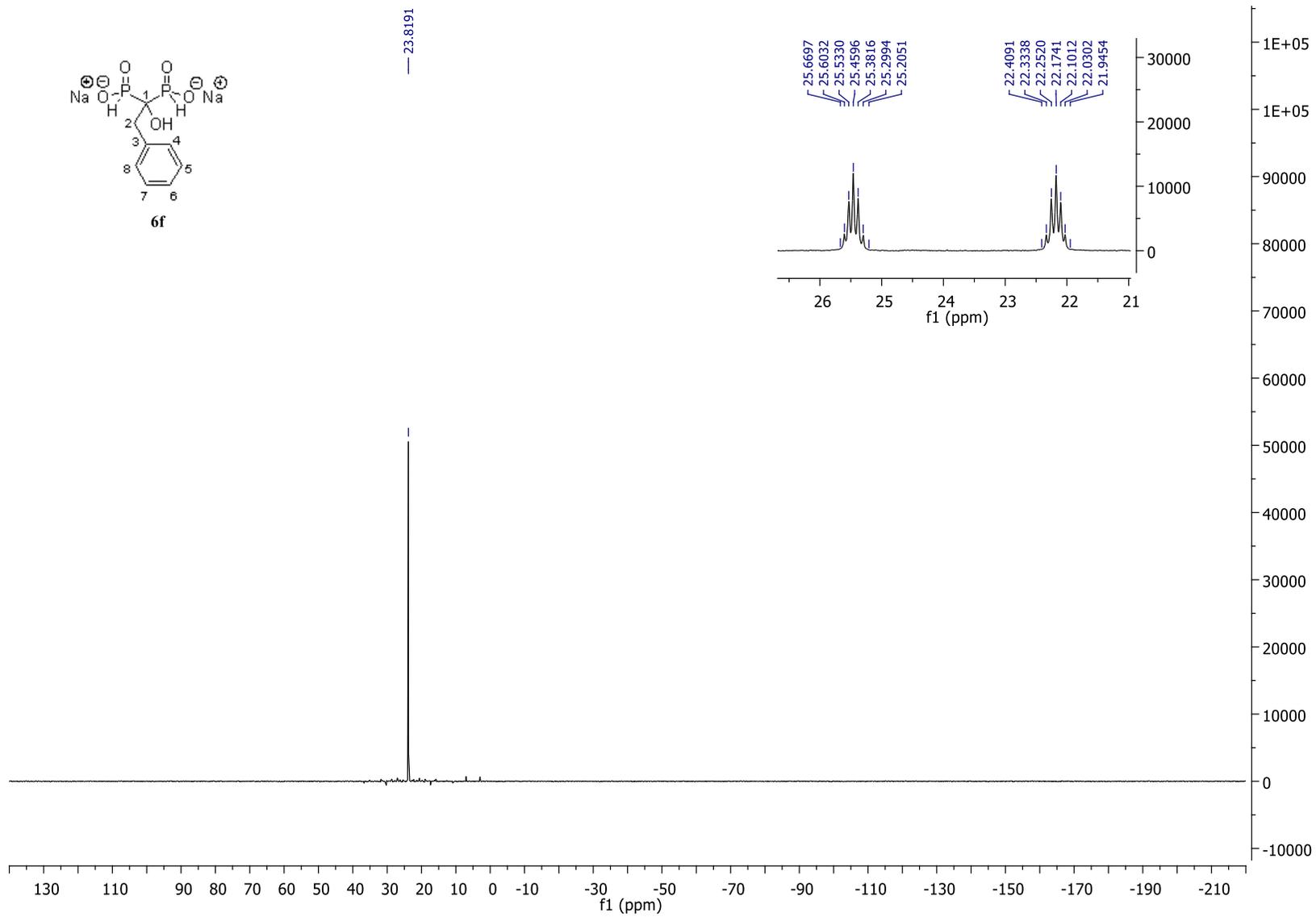


Figure 18: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-2-phenylethane-1,1-bis(*H*-phosphinate) disodium salt (6f)

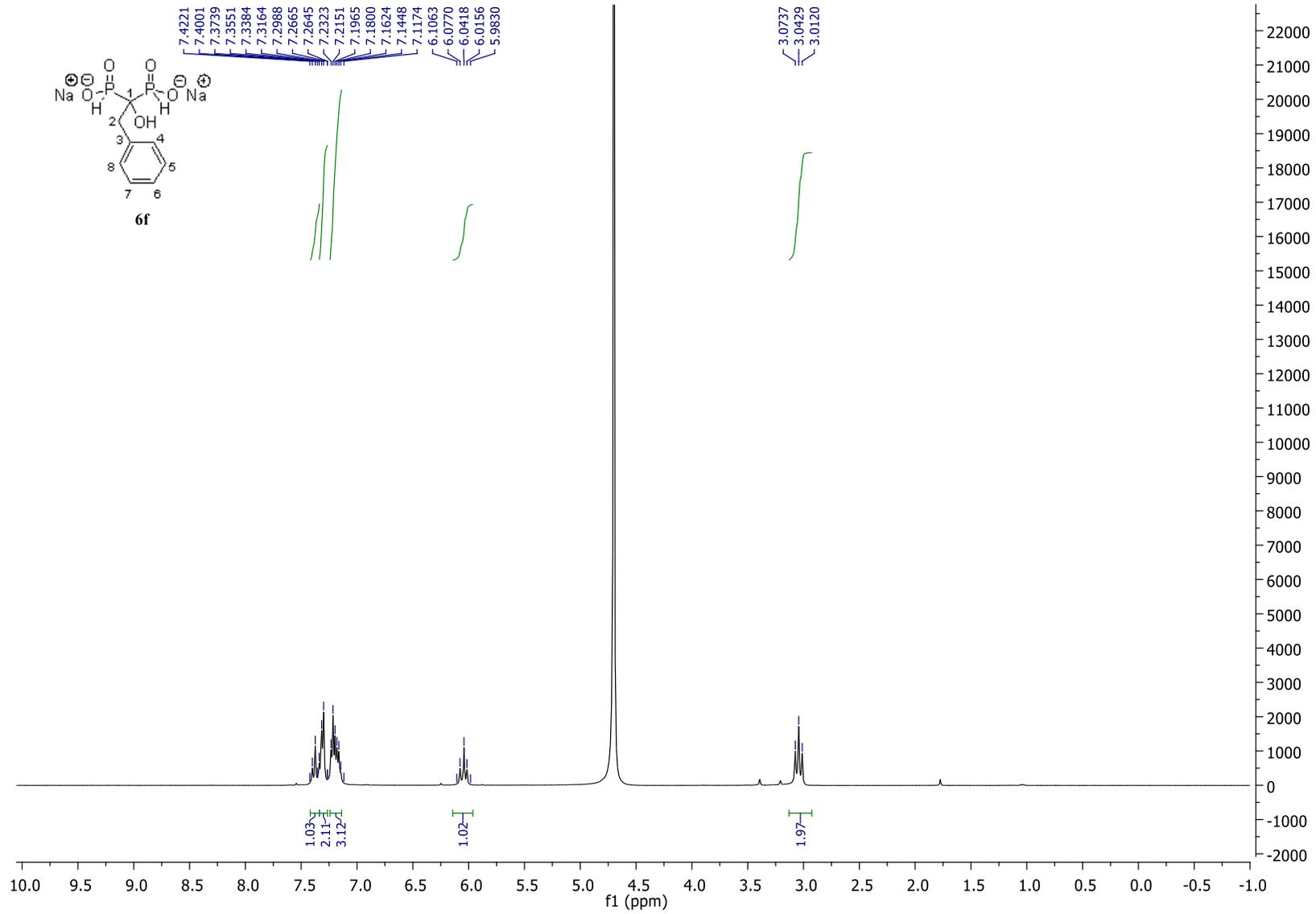


Figure 19: ¹H NMR spectrum of 1-hydroxy-2-phenylethane-1,1-bis(*H*-phosphinate) disodium salt (**6f**)

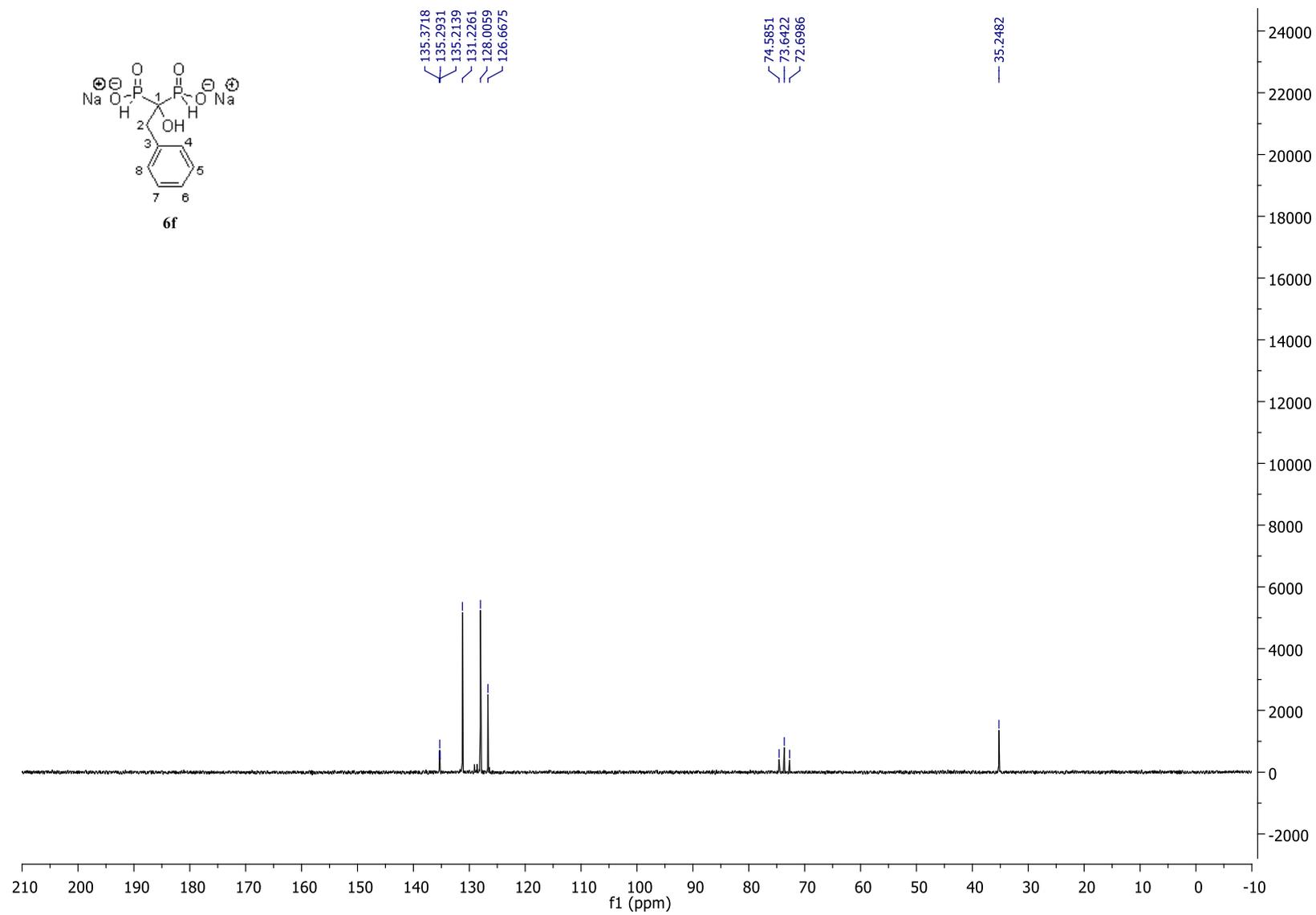


Figure 20: ¹³C NMR spectrum of (1-hydroxy-2-phenylethane-1,1-bis(*H*-phosphinate) disodium salt (6f))

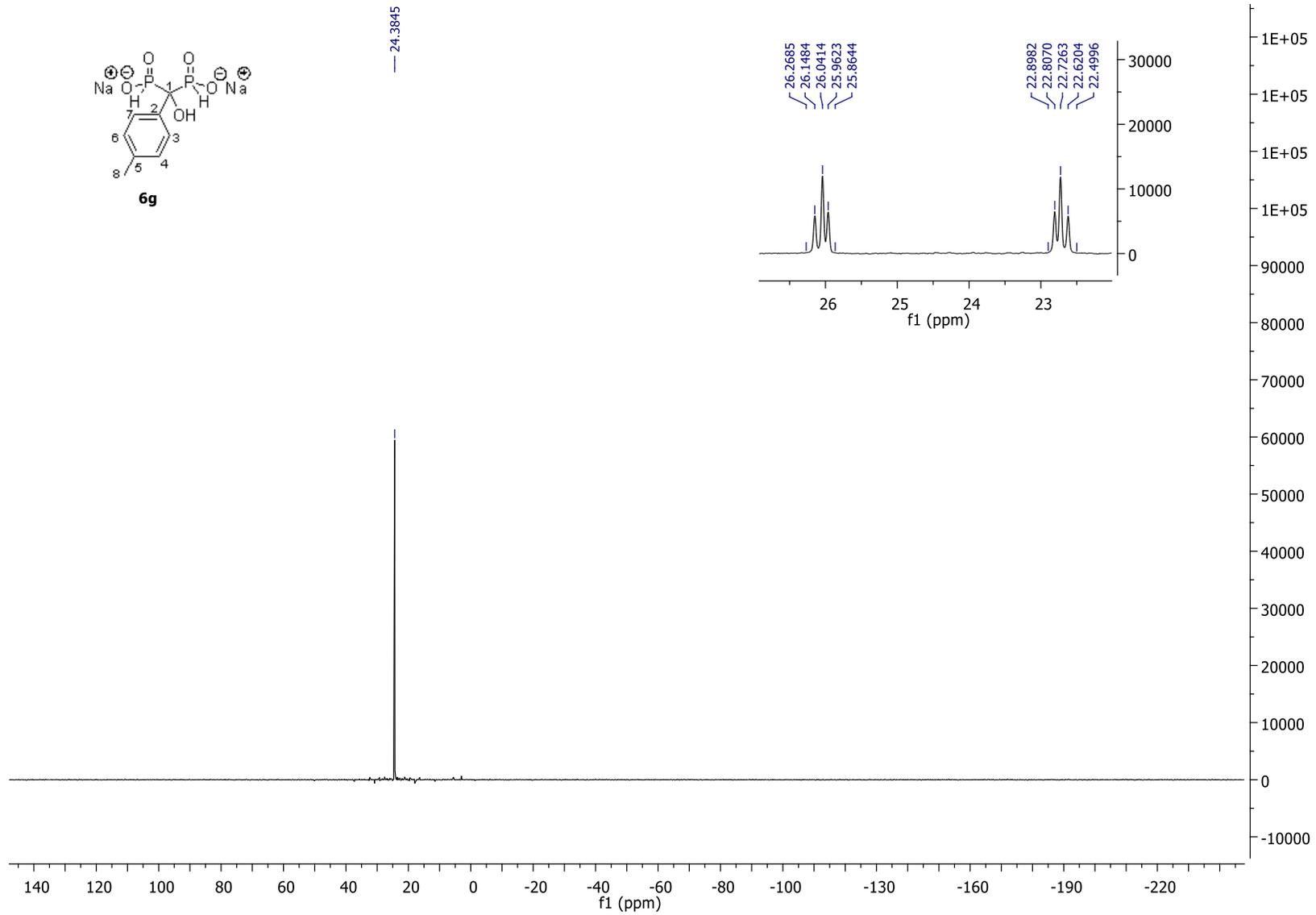


Figure 21: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(4-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6g)

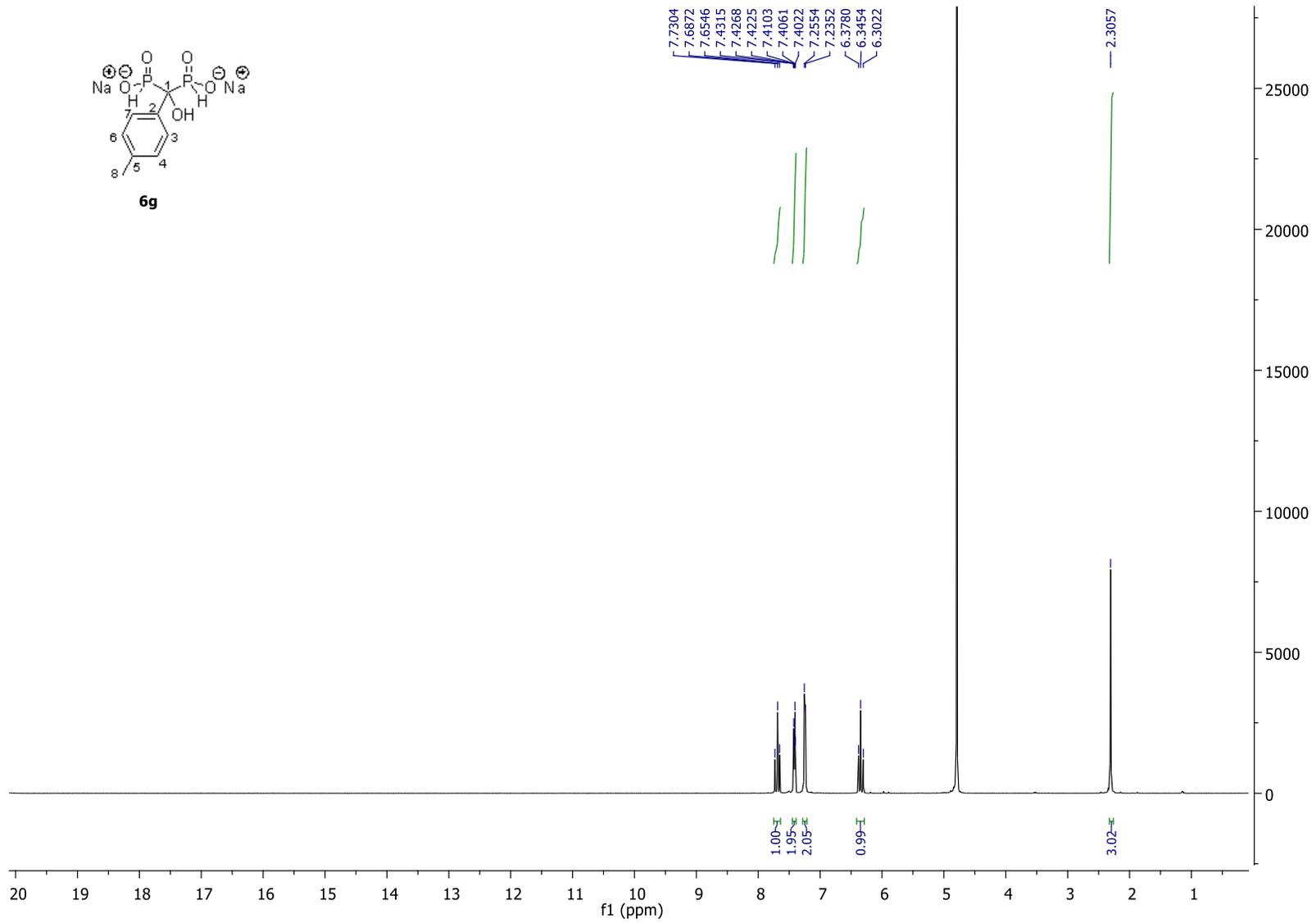


Figure 22: ¹H NMR spectrum of 1-hydroxy-1-(4-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6g**)

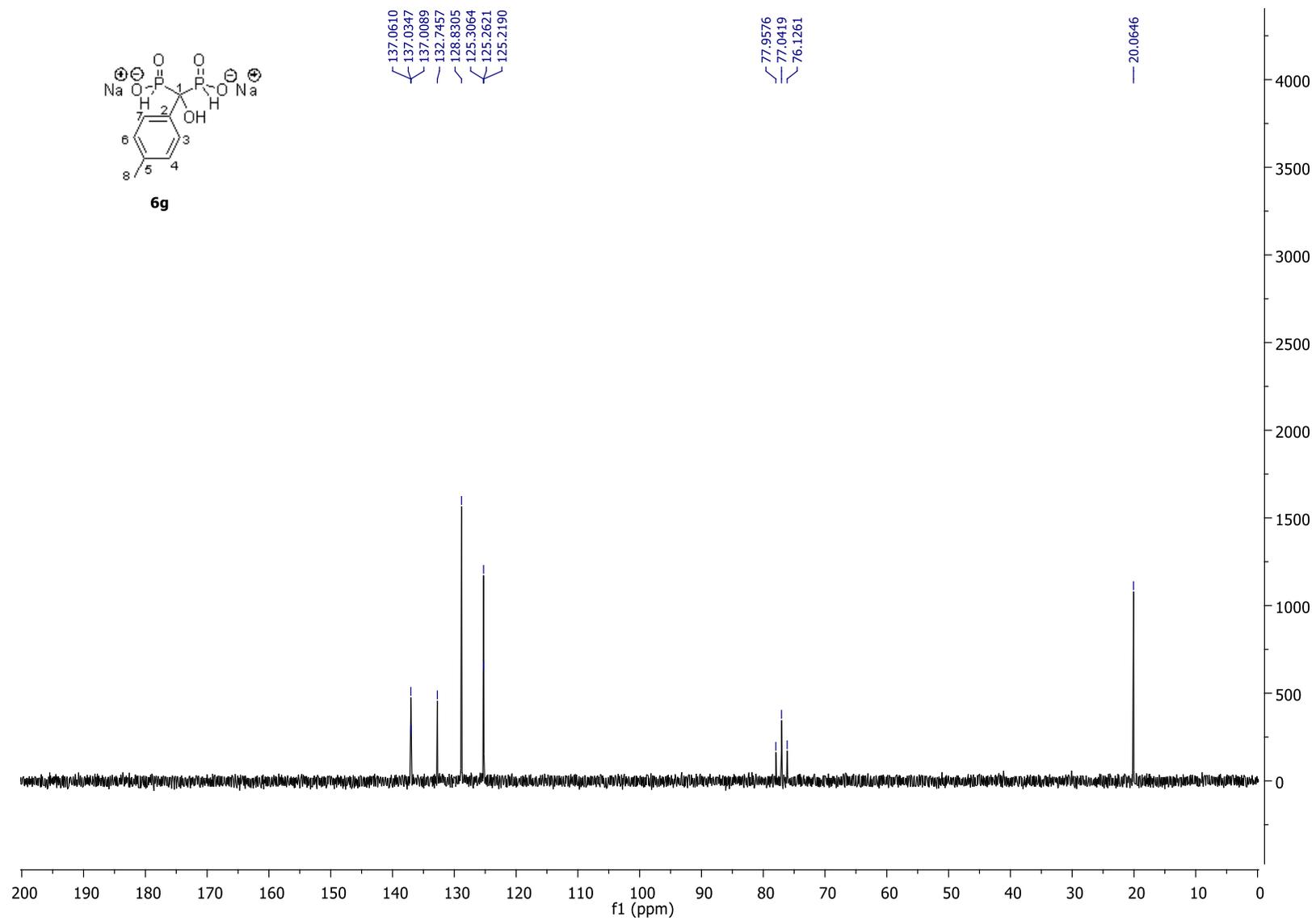


Figure 23: ¹³C NMR spectrum of 1-hydroxy-1-(4-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6g)

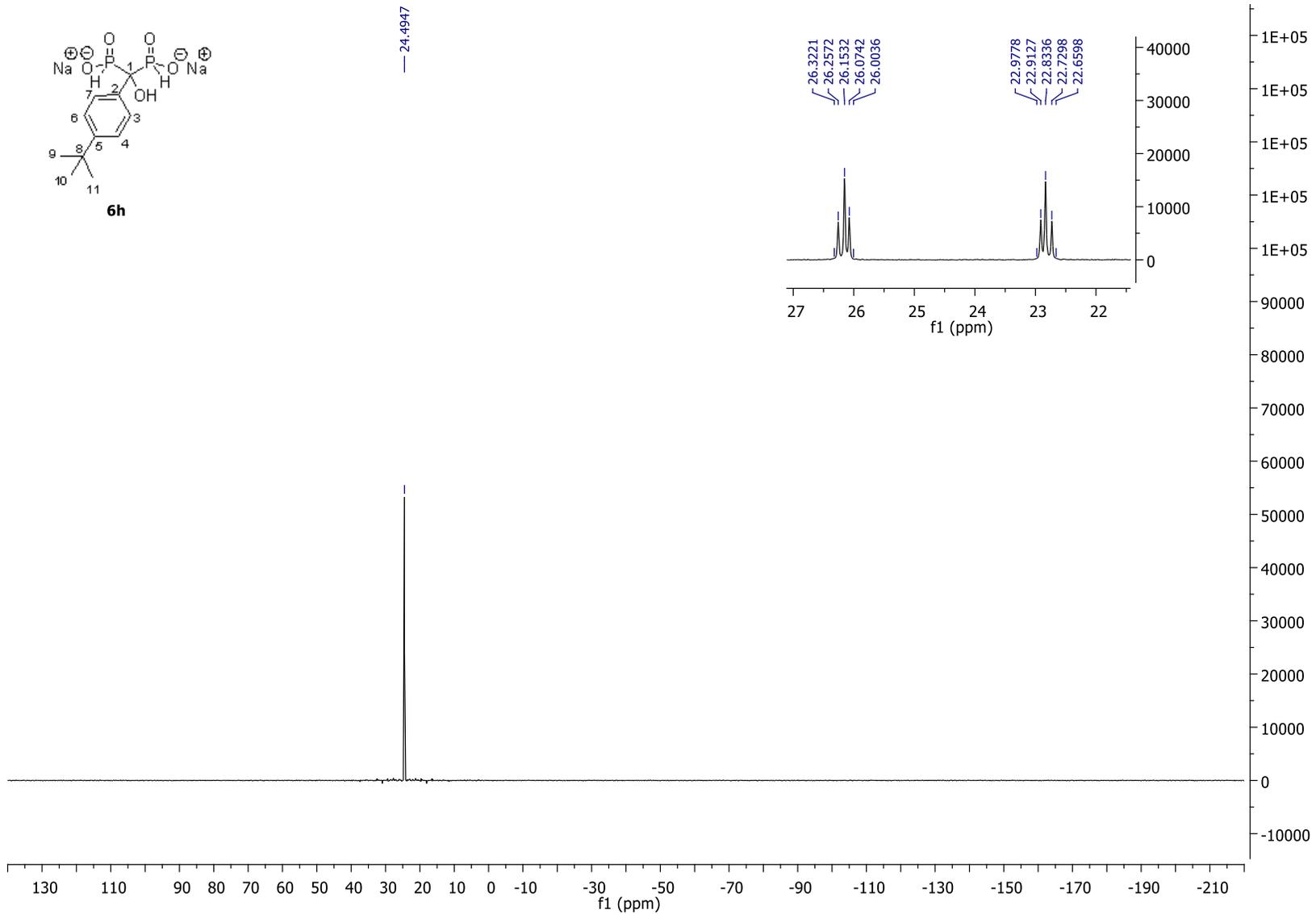


Figure 24: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(4-(*tert*-butyl)phenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6h)

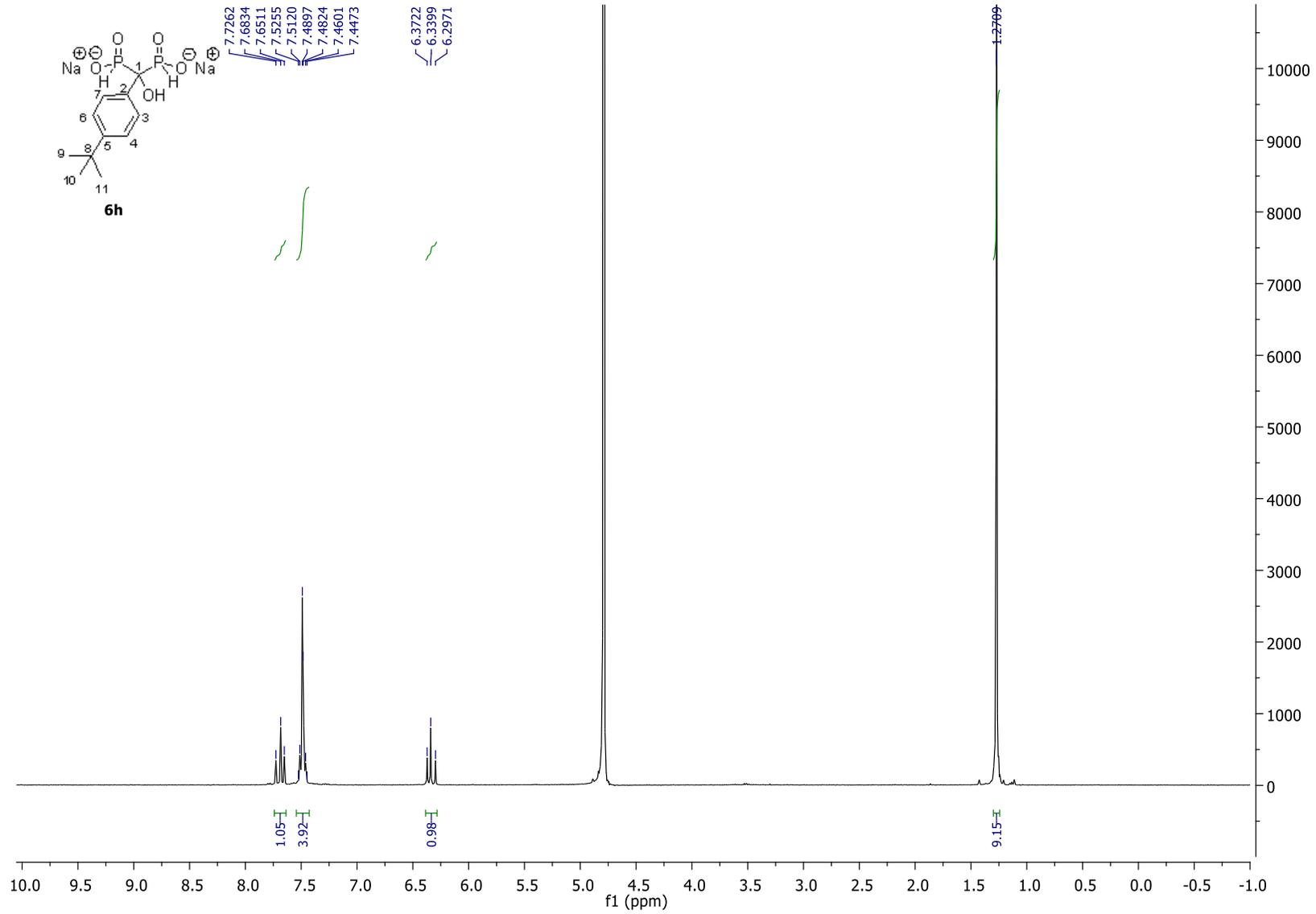


Figure 25: ¹H NMR spectrum of 1-hydroxy-1-(4-(*tert*-butyl)phenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6h)

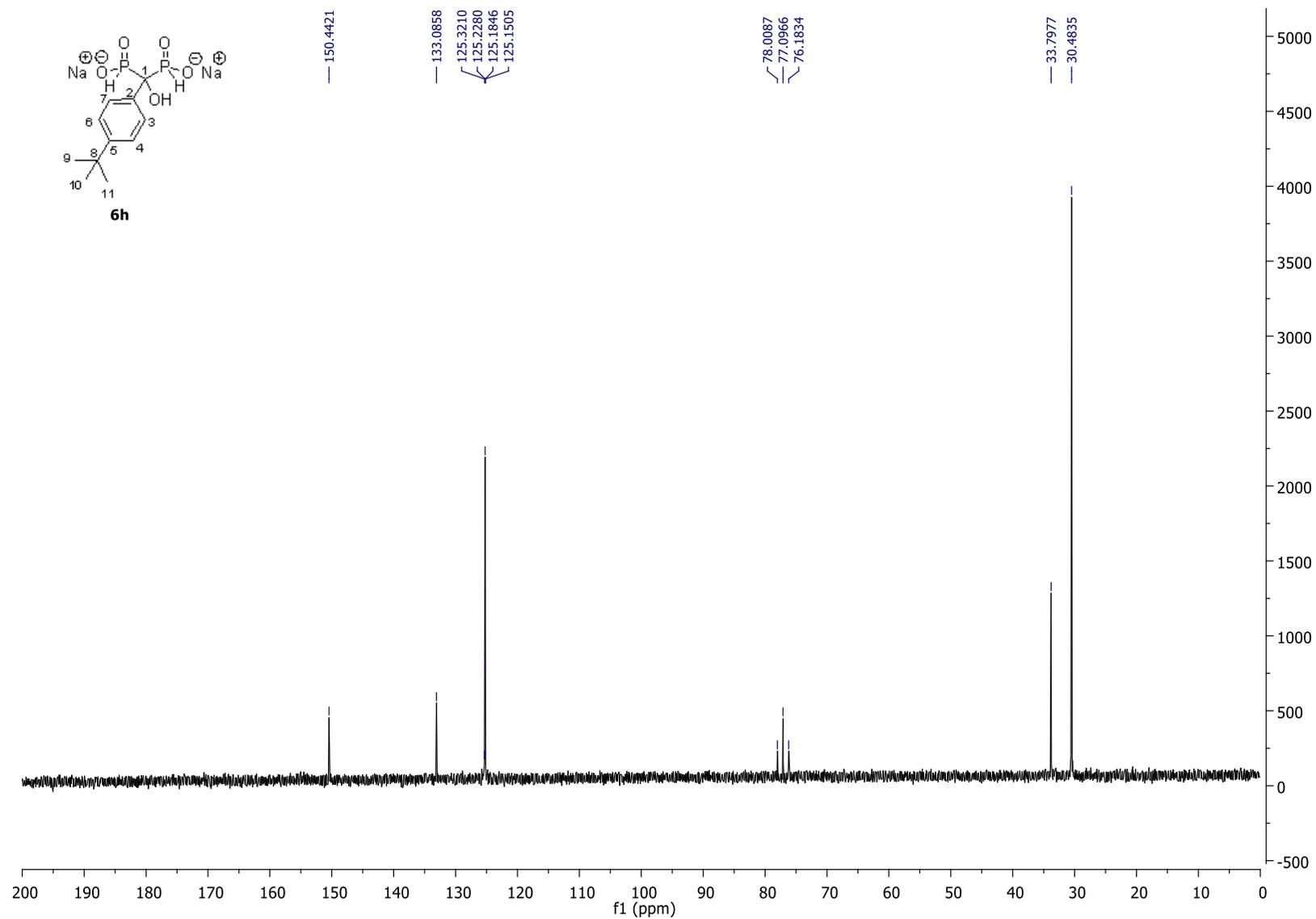


Figure 26: ¹³C NMR spectrum of 1-hydroxy-1-(4-(*tert*-butyl)phenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6h)

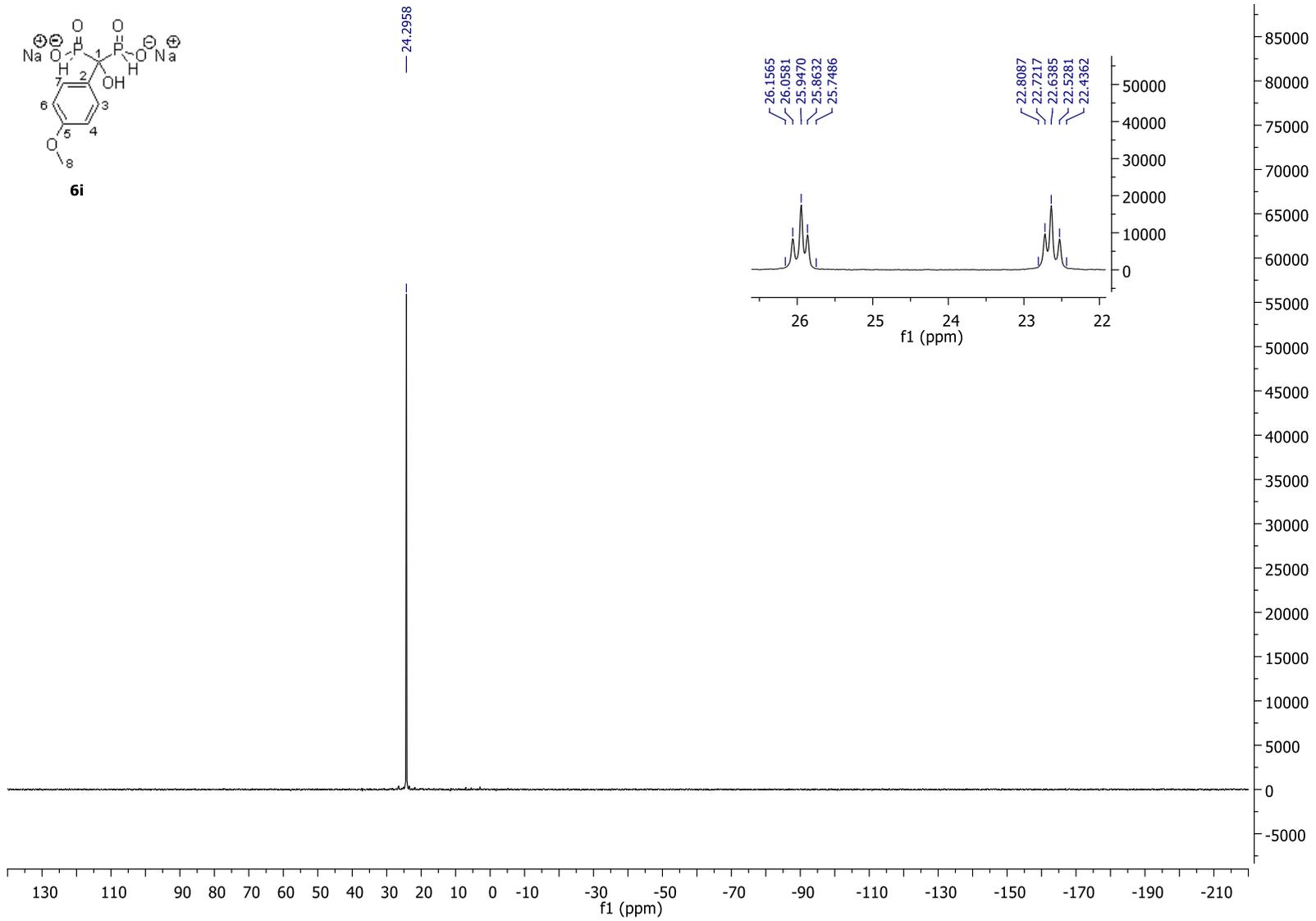


Figure 27: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(4-methoxyphenyl)methane-1,1-bis(*H*-phosphate) disodium salt (**6i**)

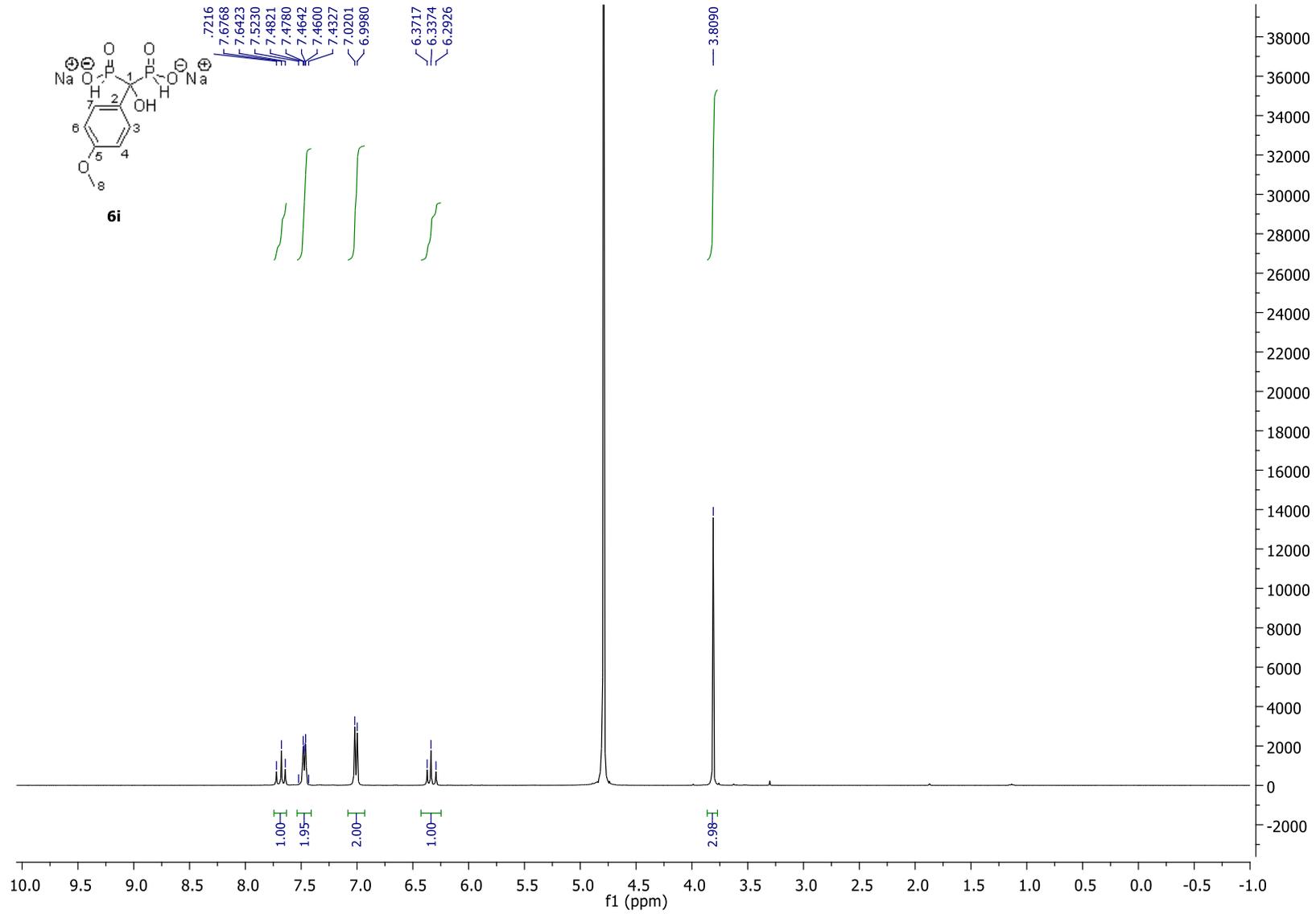


Figure 28: ¹H NMR spectrum of 1-hydroxy-1-(4-methoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6i**)

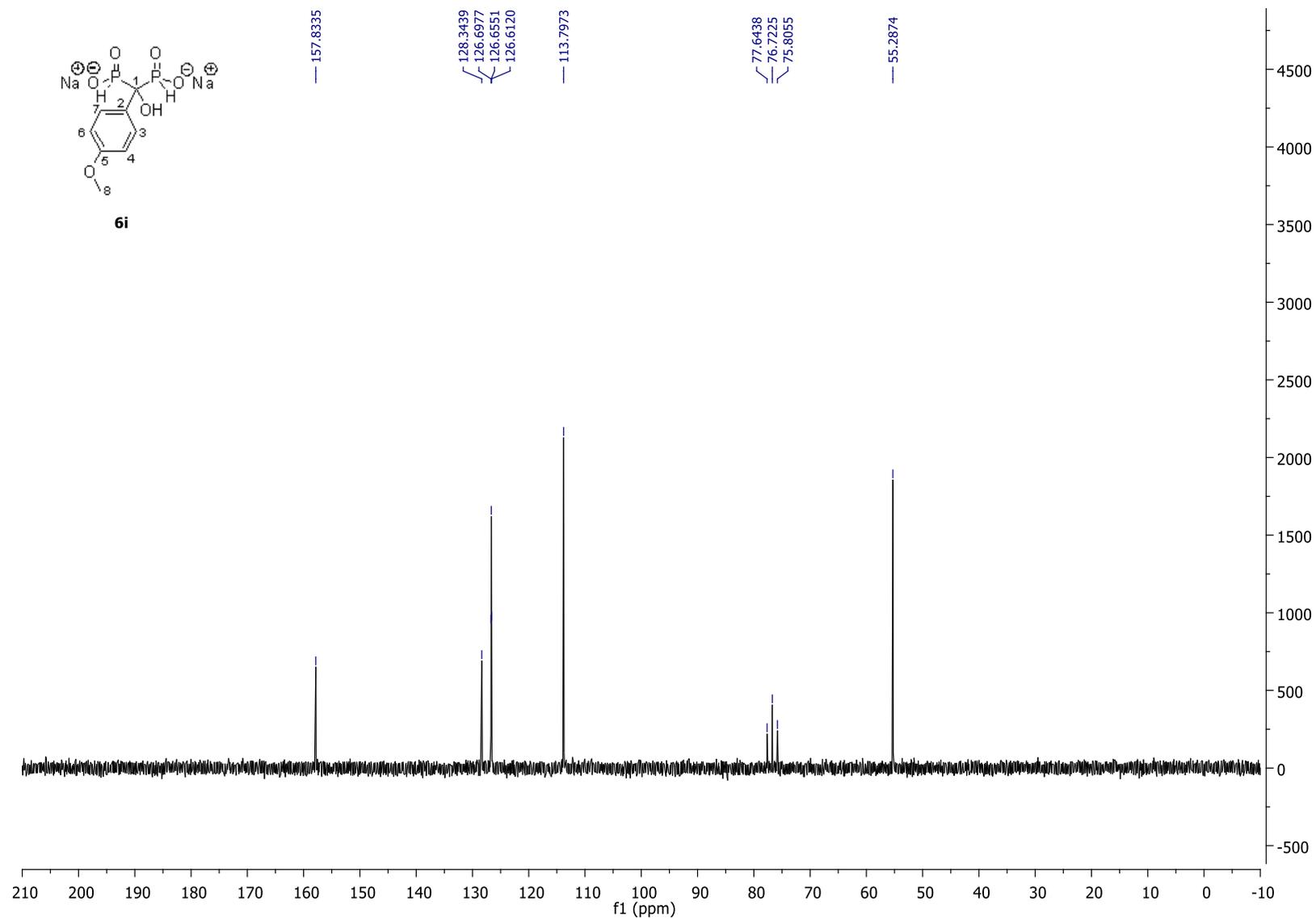


Figure 29: ¹³C NMR spectrum of 1-hydroxy-1-(4-methoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6i**)

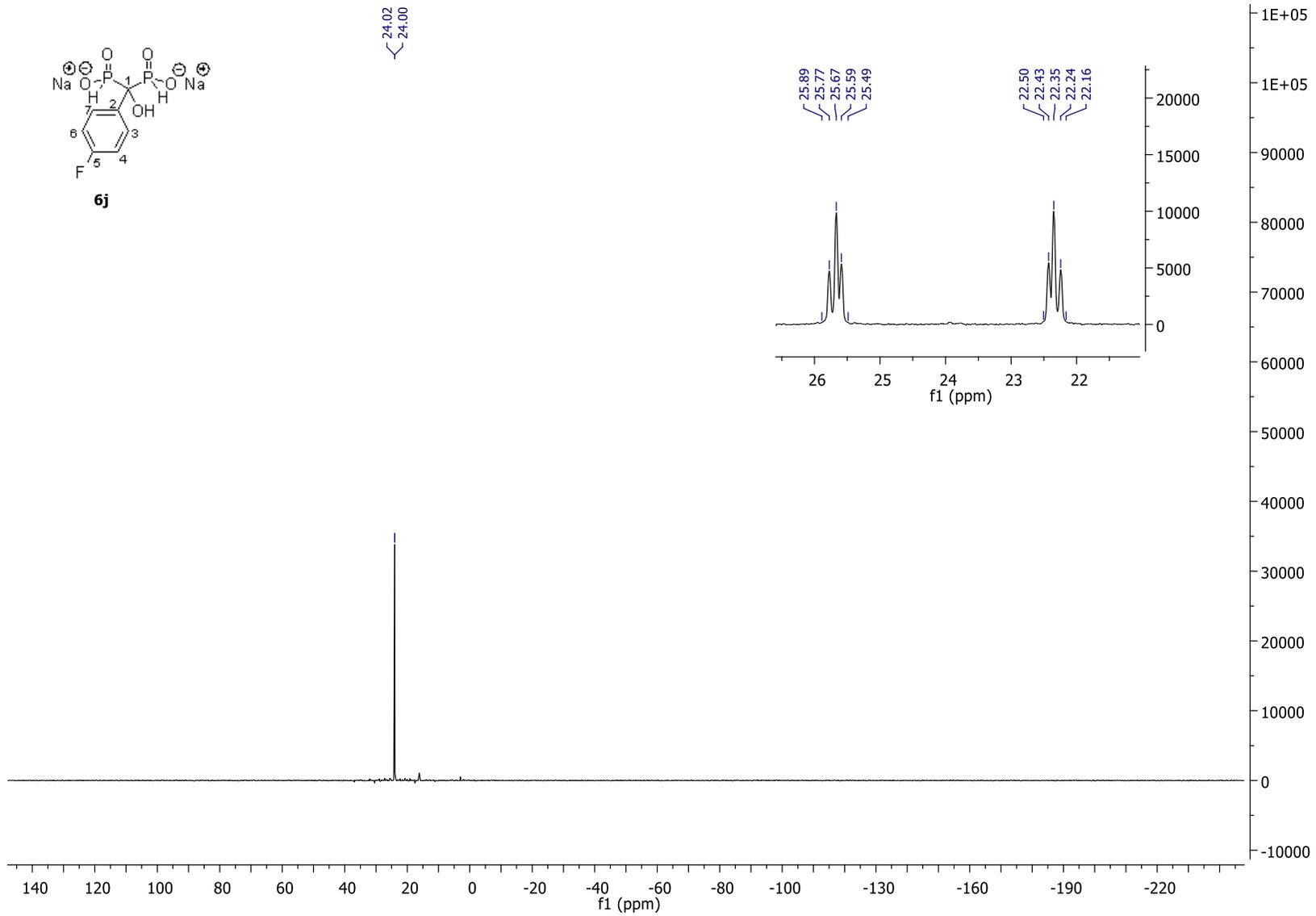


Figure 30: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(4-fluorophenyl)methane-1,1-bis(*H*-phosphate) disodium salt (**6j**)

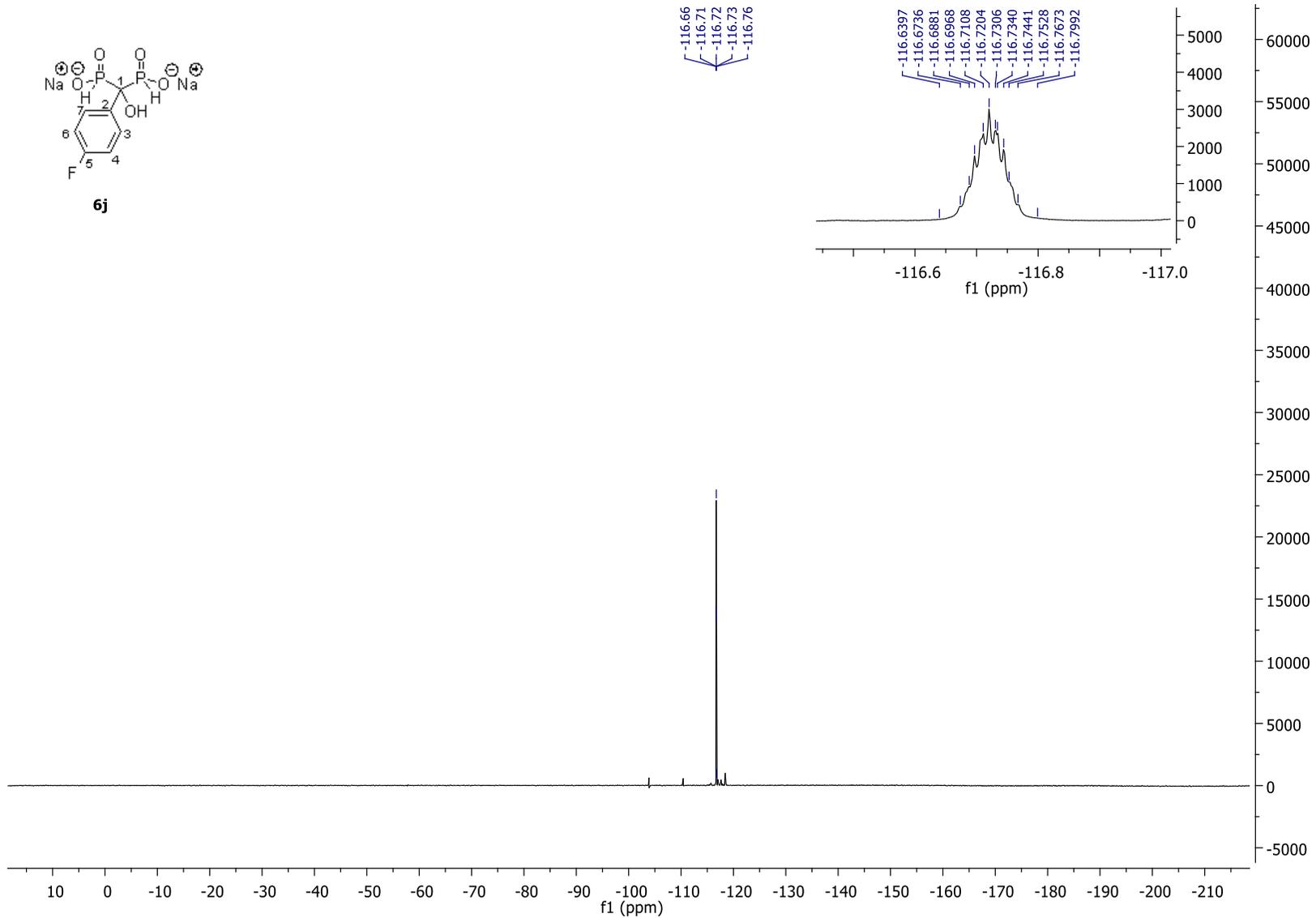


Figure 31: ^{19}F $\{^1\text{H}\}$ and ^{19}F NMR spectra of 1-hydroxy-1-(4-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6j)

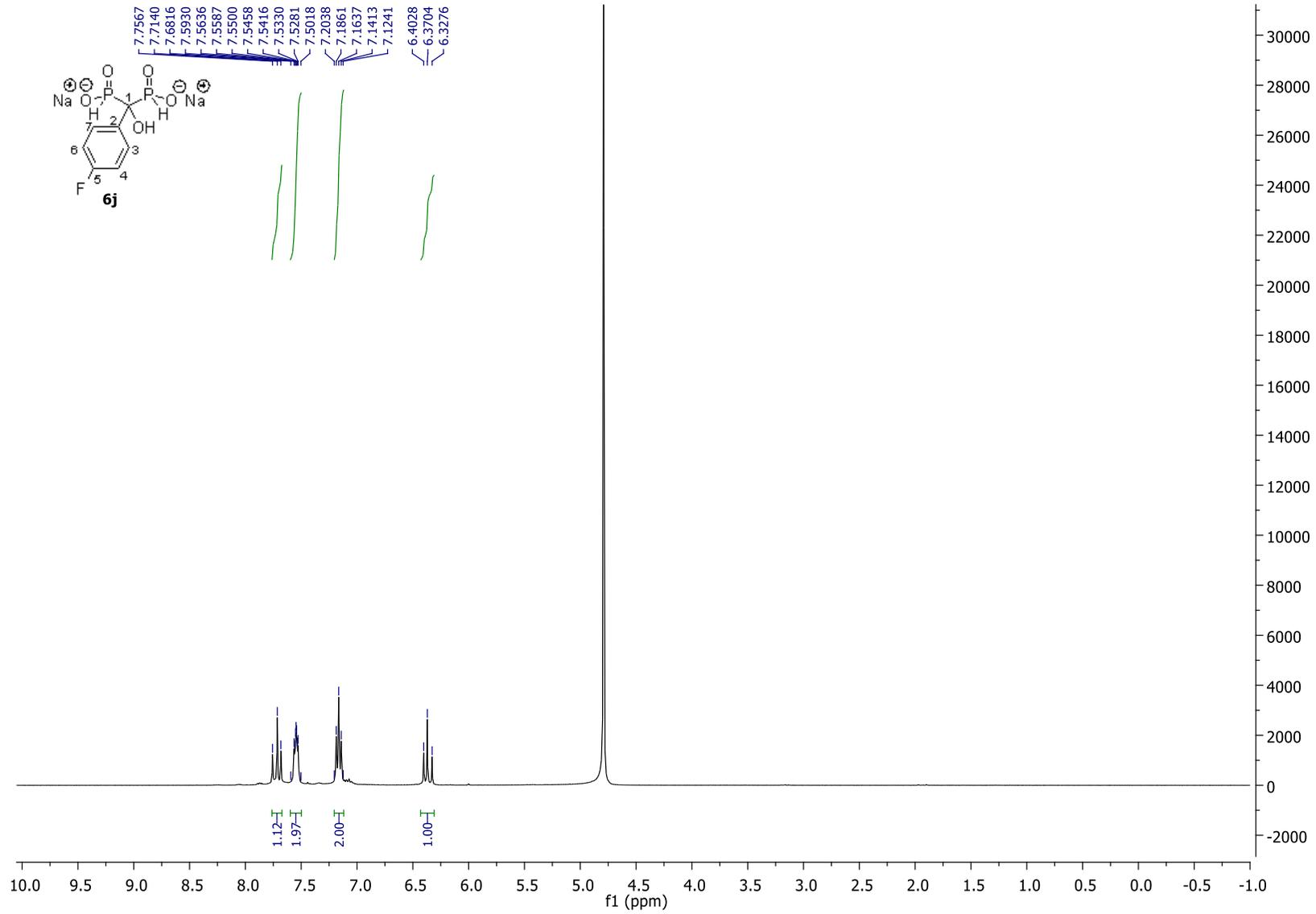


Figure 32: ¹H NMR spectrum of 1-hydroxy-1-(4-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6j)

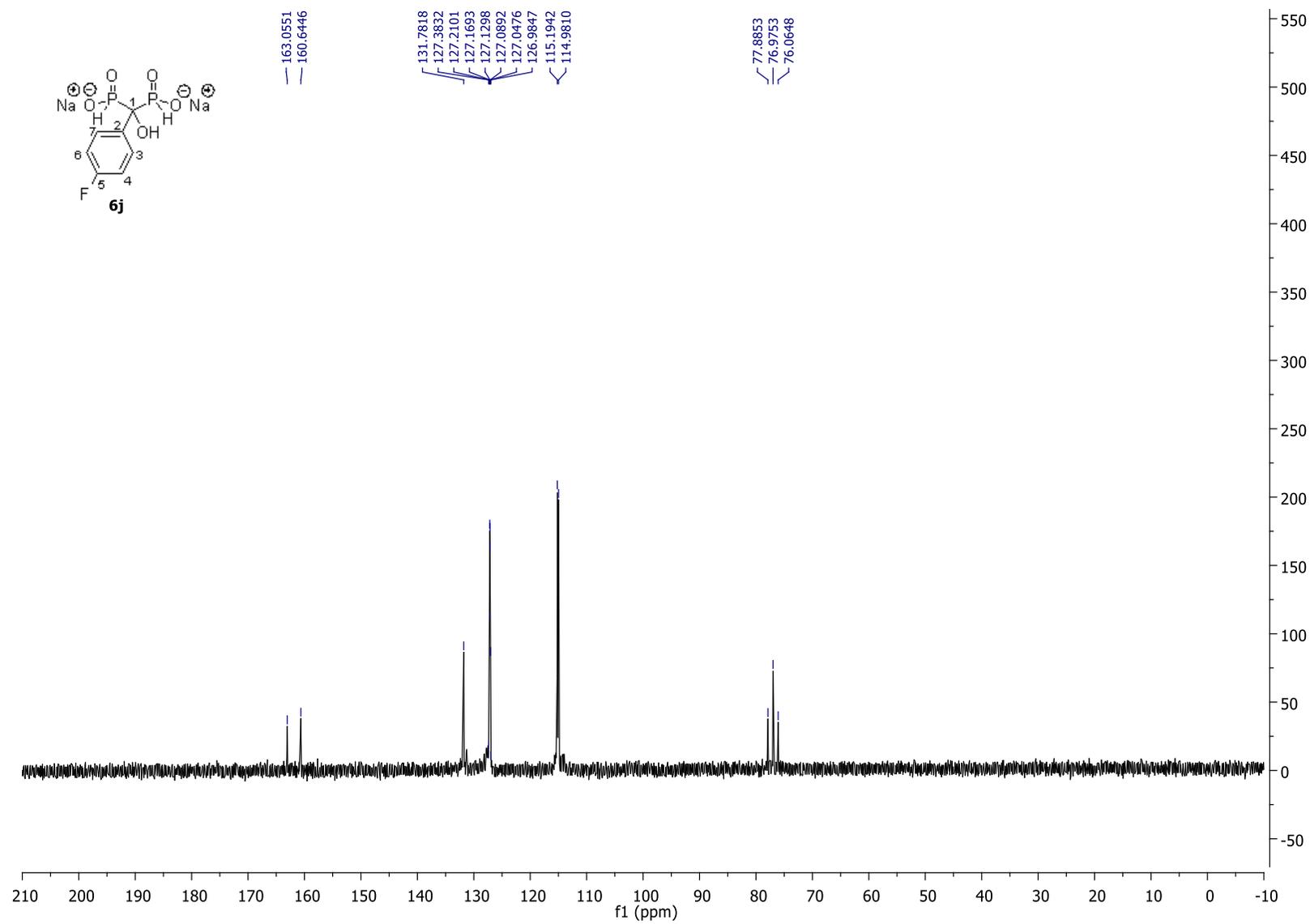


Figure 33: ¹³C NMR spectrum of 1-hydroxy-1-(4-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6j**)

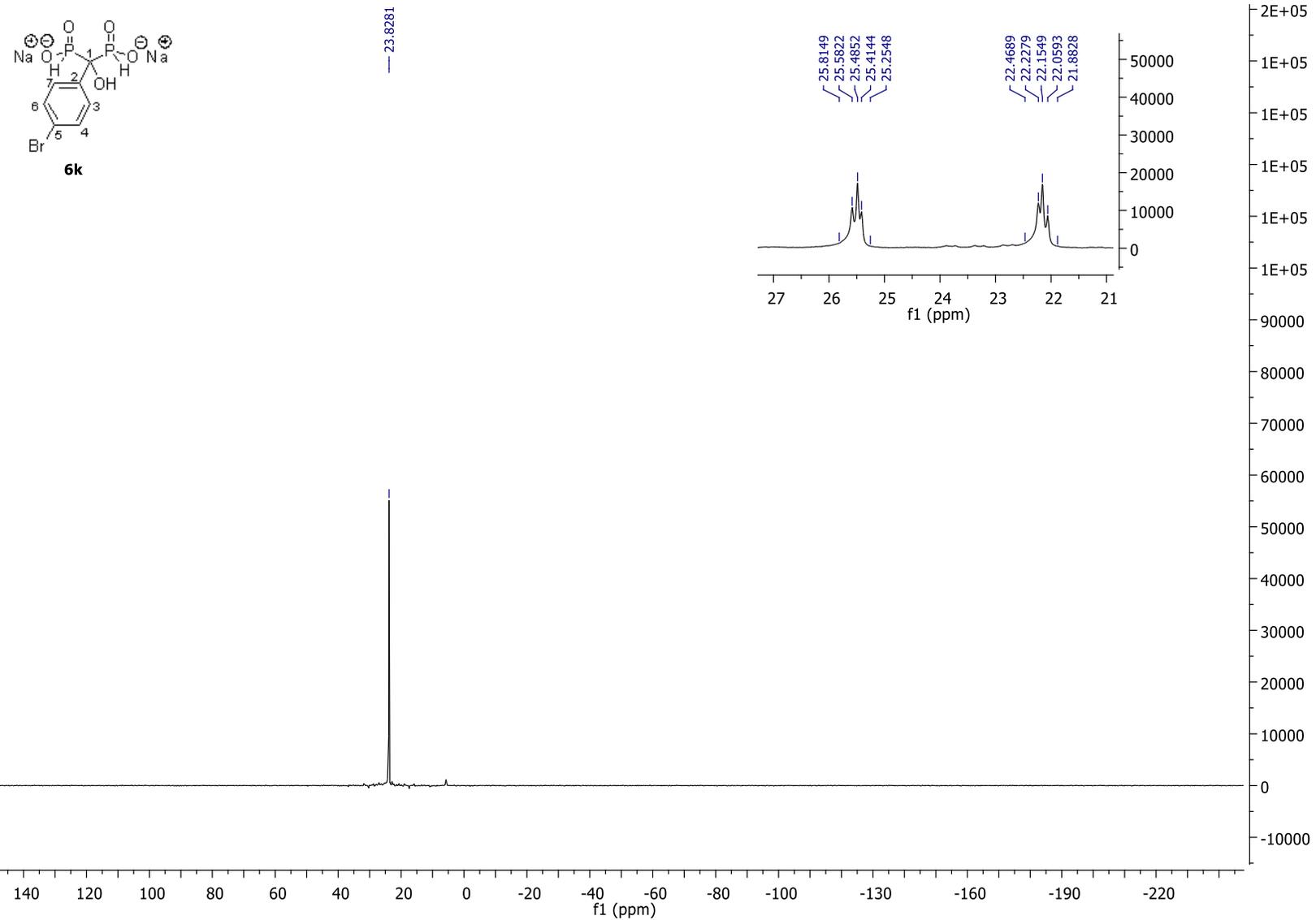


Figure 34: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(4-bromophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6k)

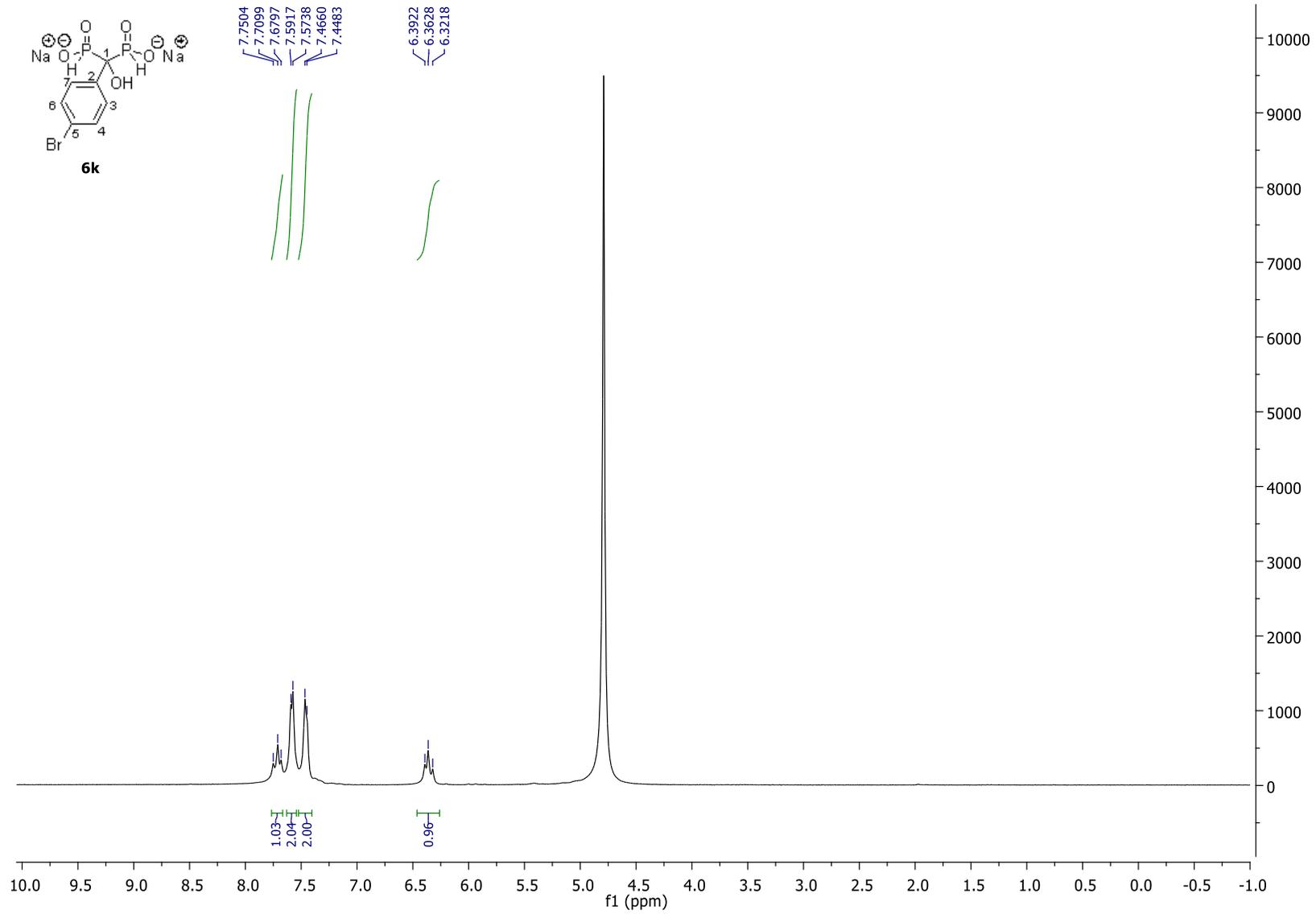


Figure 35: ¹H NMR spectrum of 1-hydroxy-1-(4-bromophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6k)

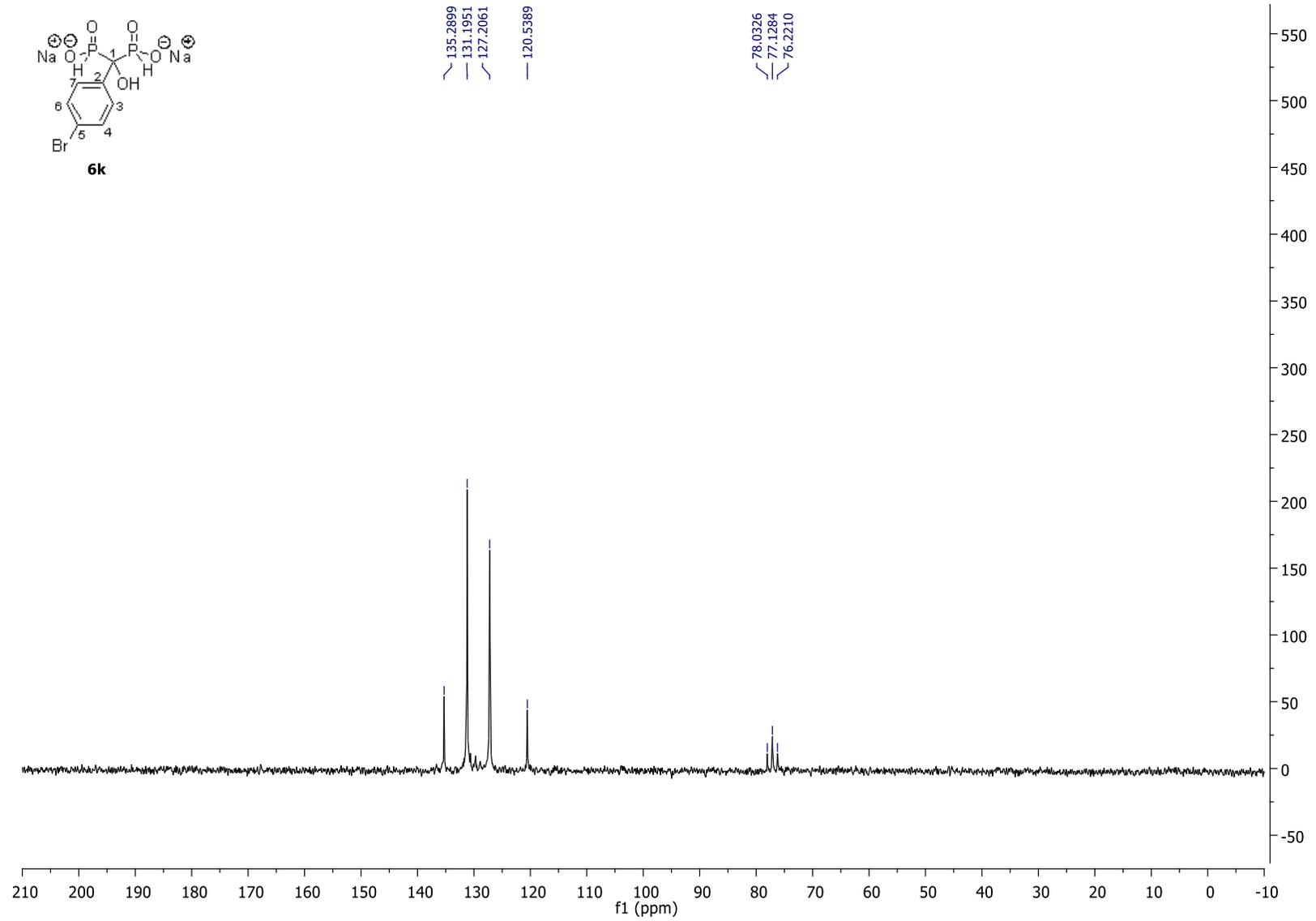


Figure 36: ¹³C NMR spectrum of 1-hydroxy-1-(4-bromophenyl)methane-1,1-bis(*H*-phosphate) disodium salt (**6k**)

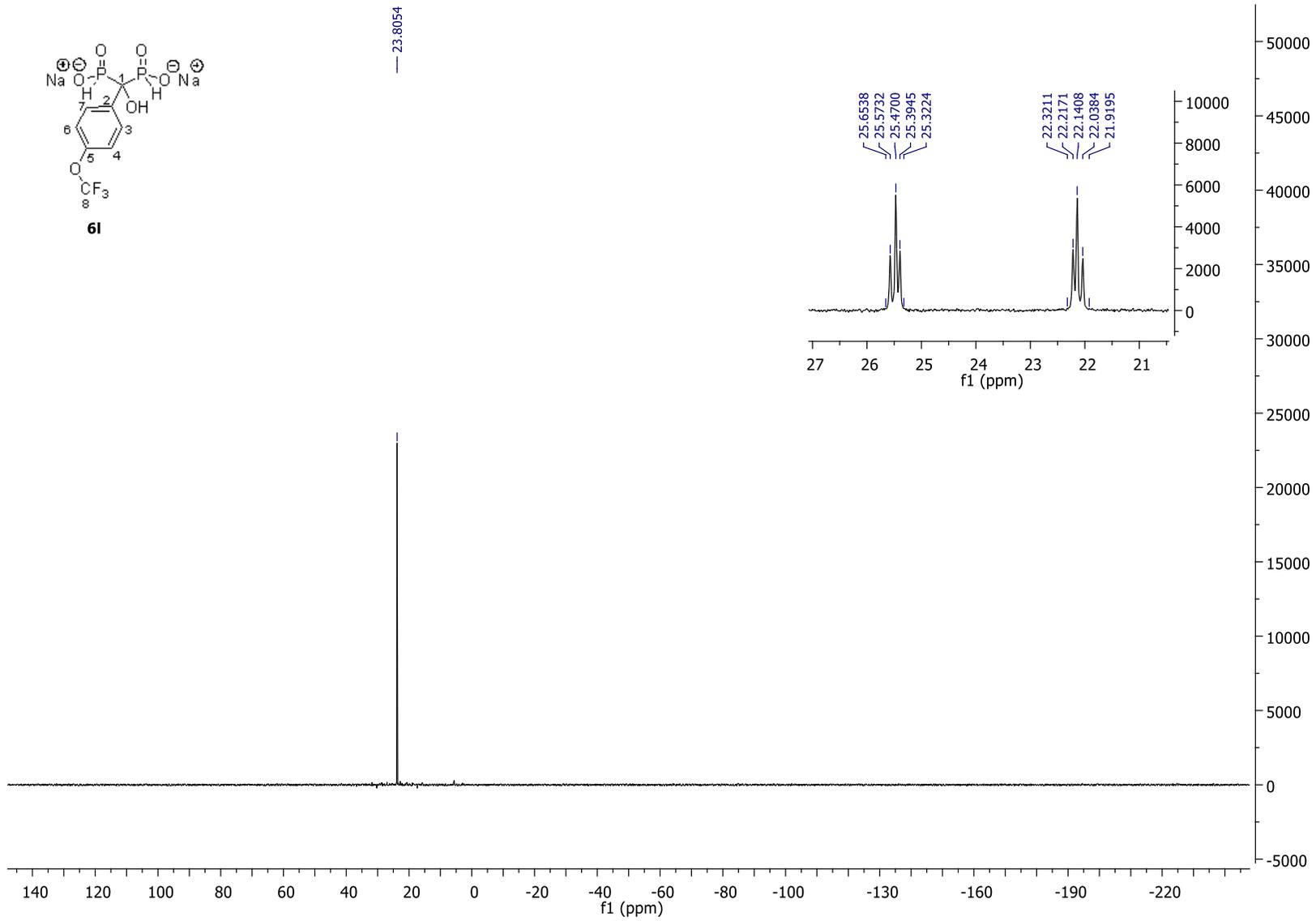


Figure 37: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(4-trifluoromethoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6I)

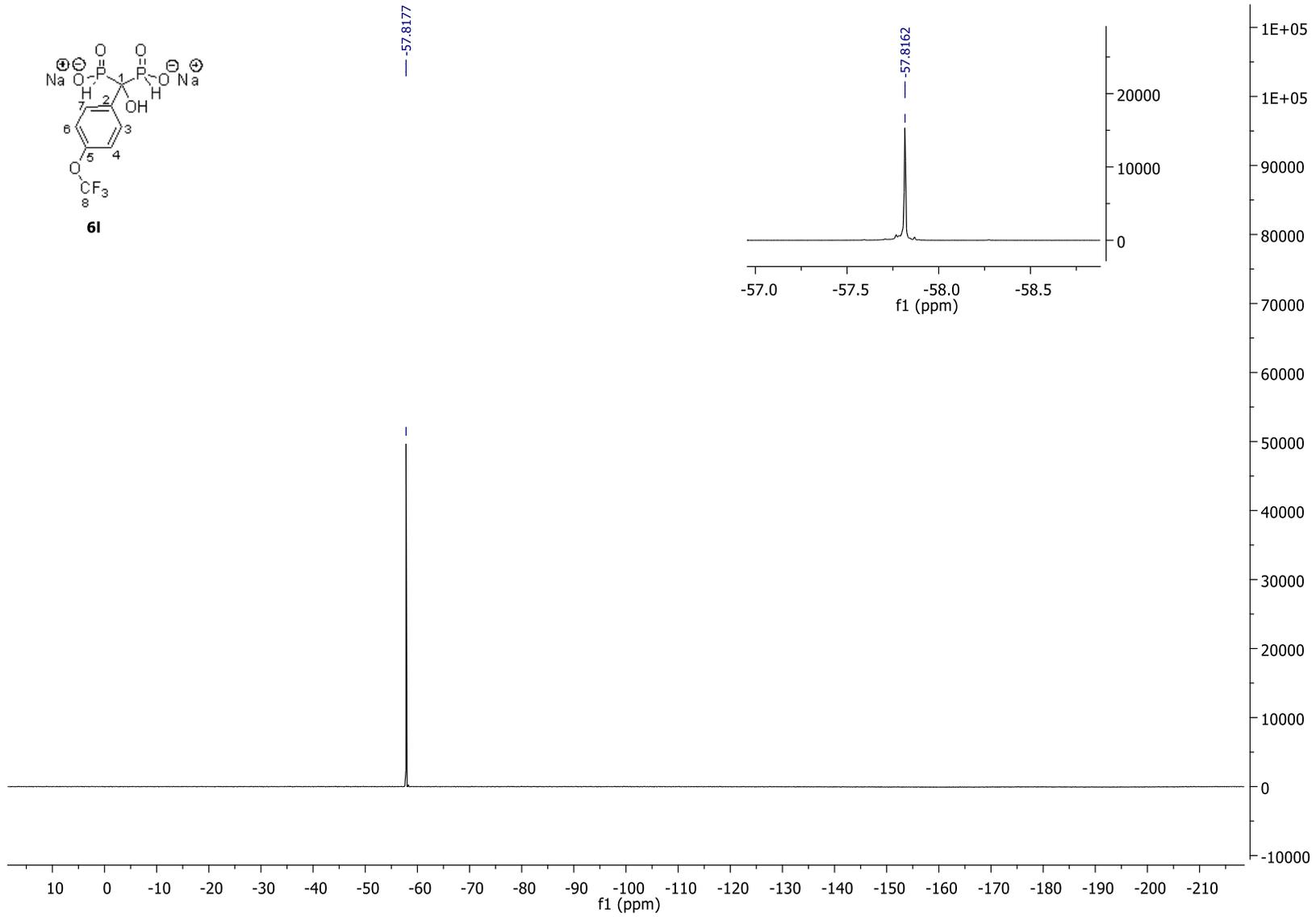


Figure 38: ^{19}F $\{^1\text{H}\}$ and ^{19}F NMR spectra of 1-hydroxy-1-(4-trifluoromethoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6l**)

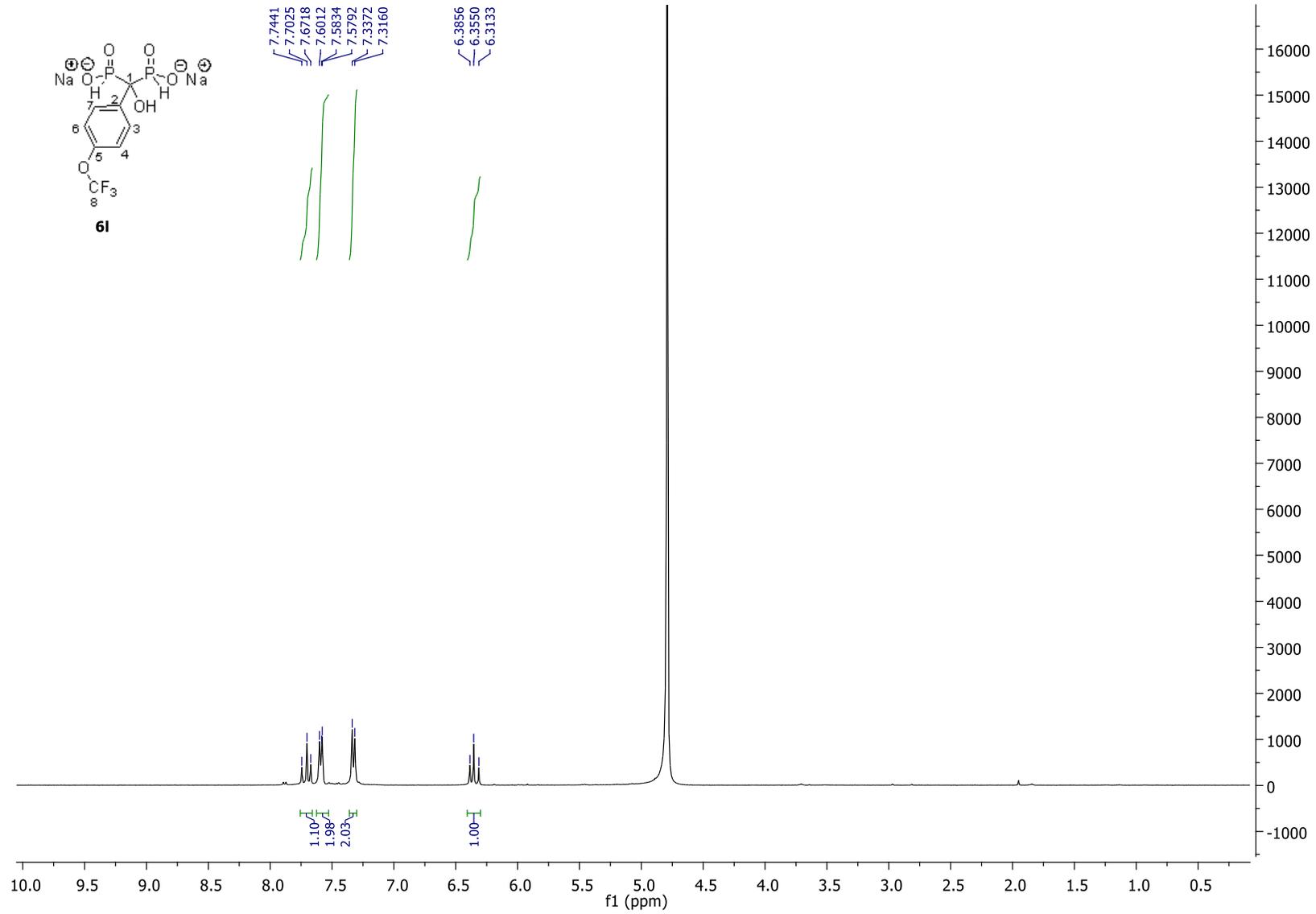


Figure 39: ¹H NMR spectrum of 1-hydroxy-1-(4-trifluoromethoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6I)

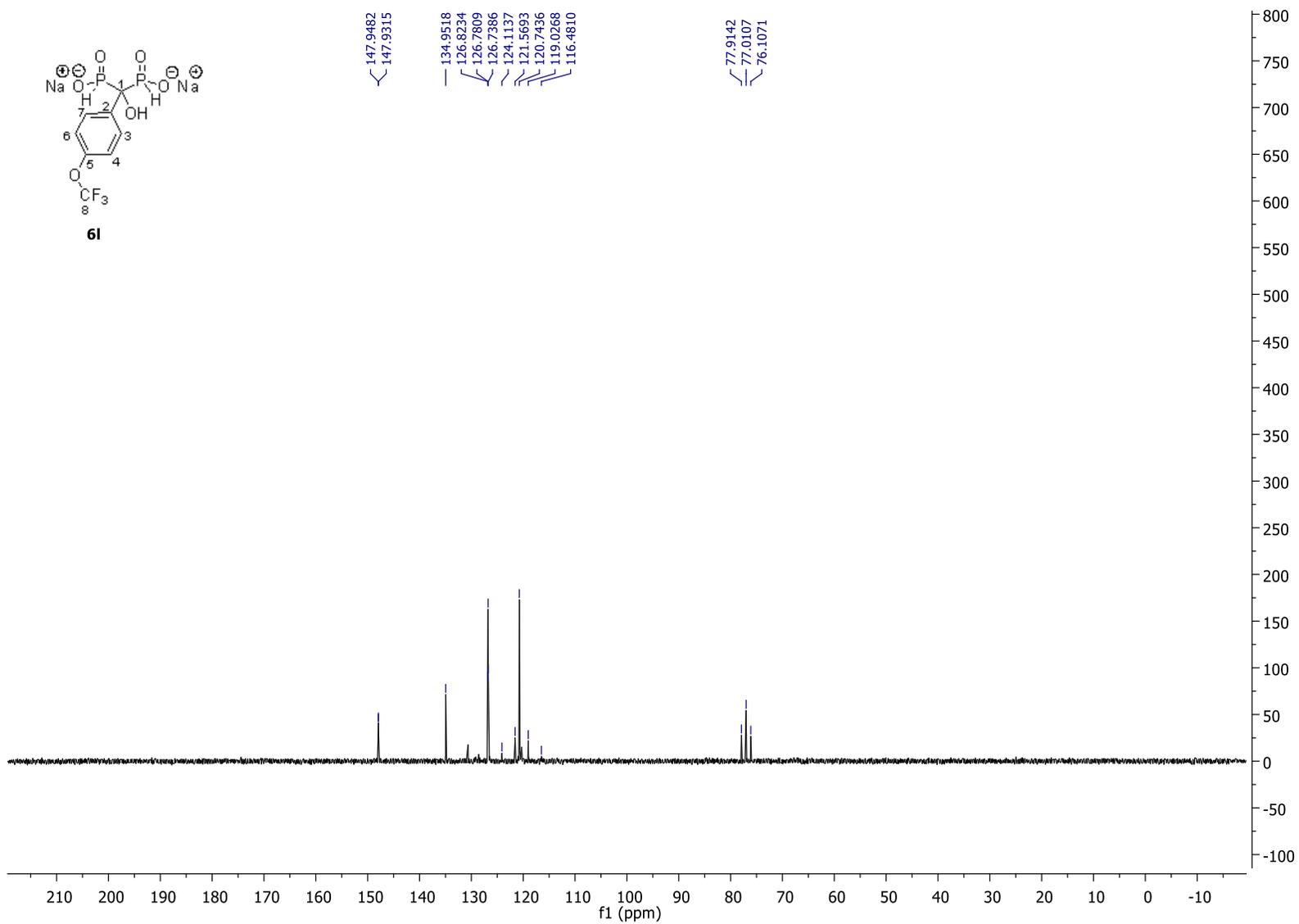


Figure 40: ¹³C NMR spectrum of 1-hydroxy-1-(4-trifluoromethoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6l)

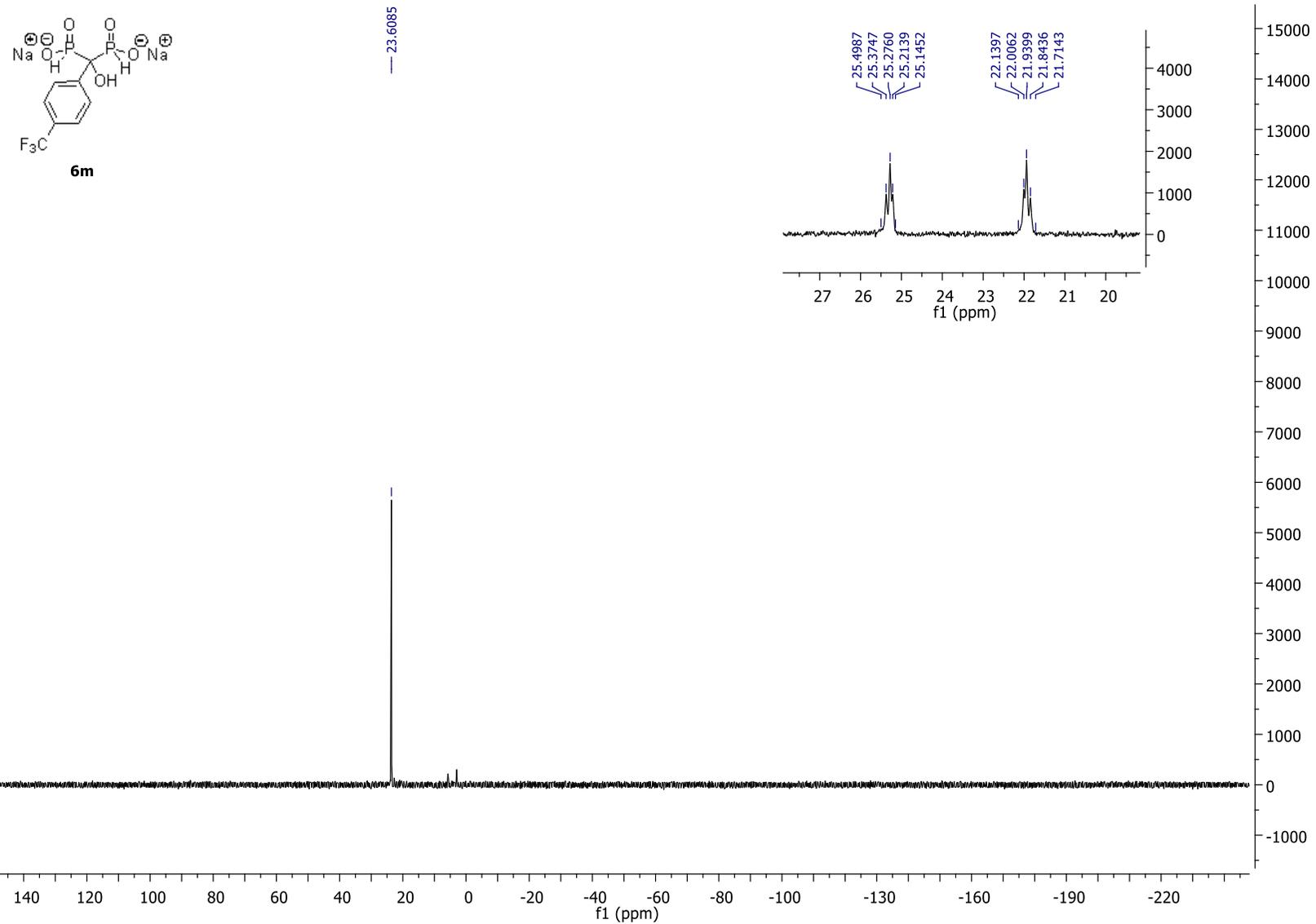


Figure 41: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(4-(trifluoromethyl)phenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6m)

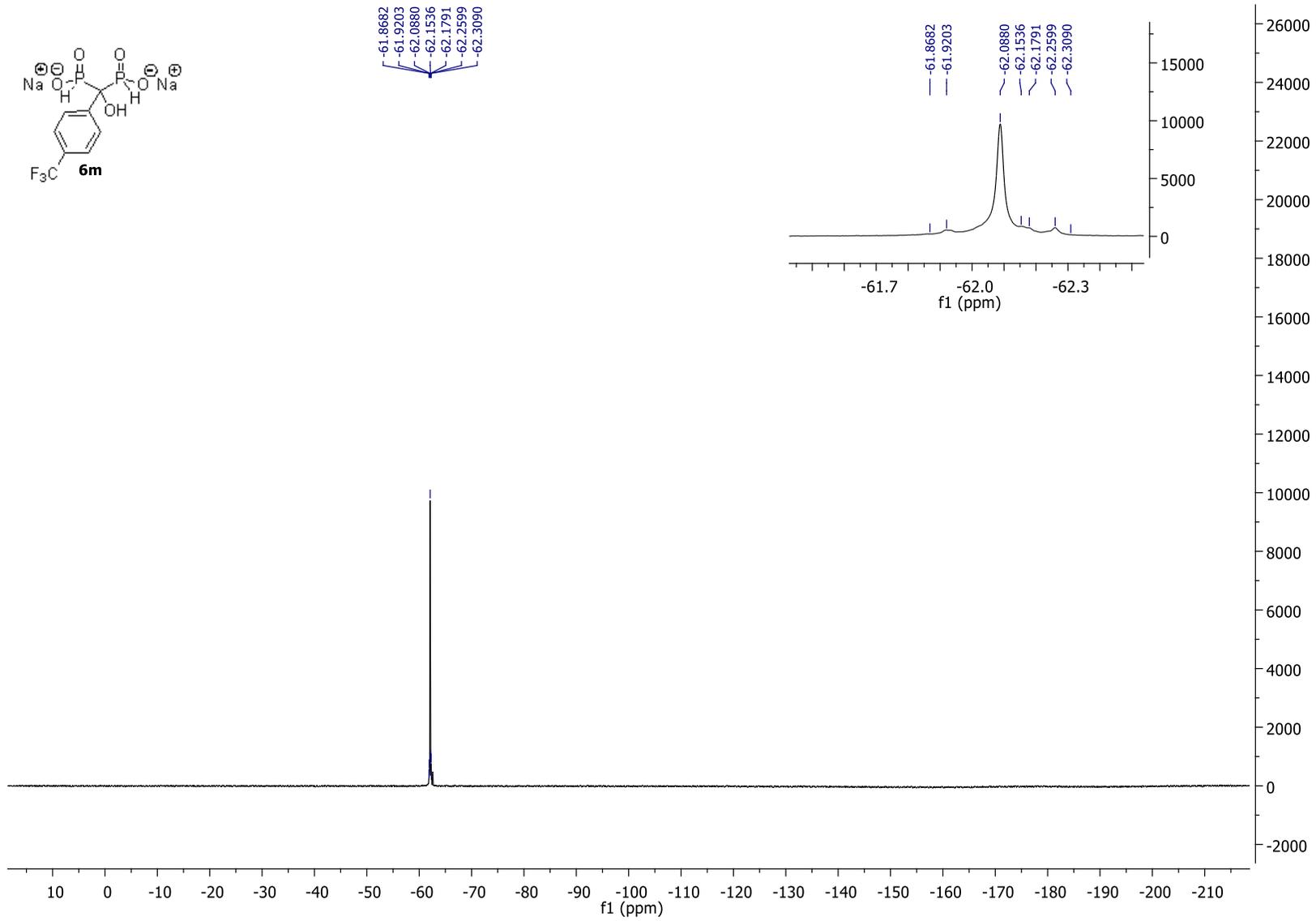


Figure 42: ^{19}F $\{^1\text{H}\}$ and ^{19}F NMR spectra of 1-hydroxy-1-(4-(trifluoromethyl)phenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6m)

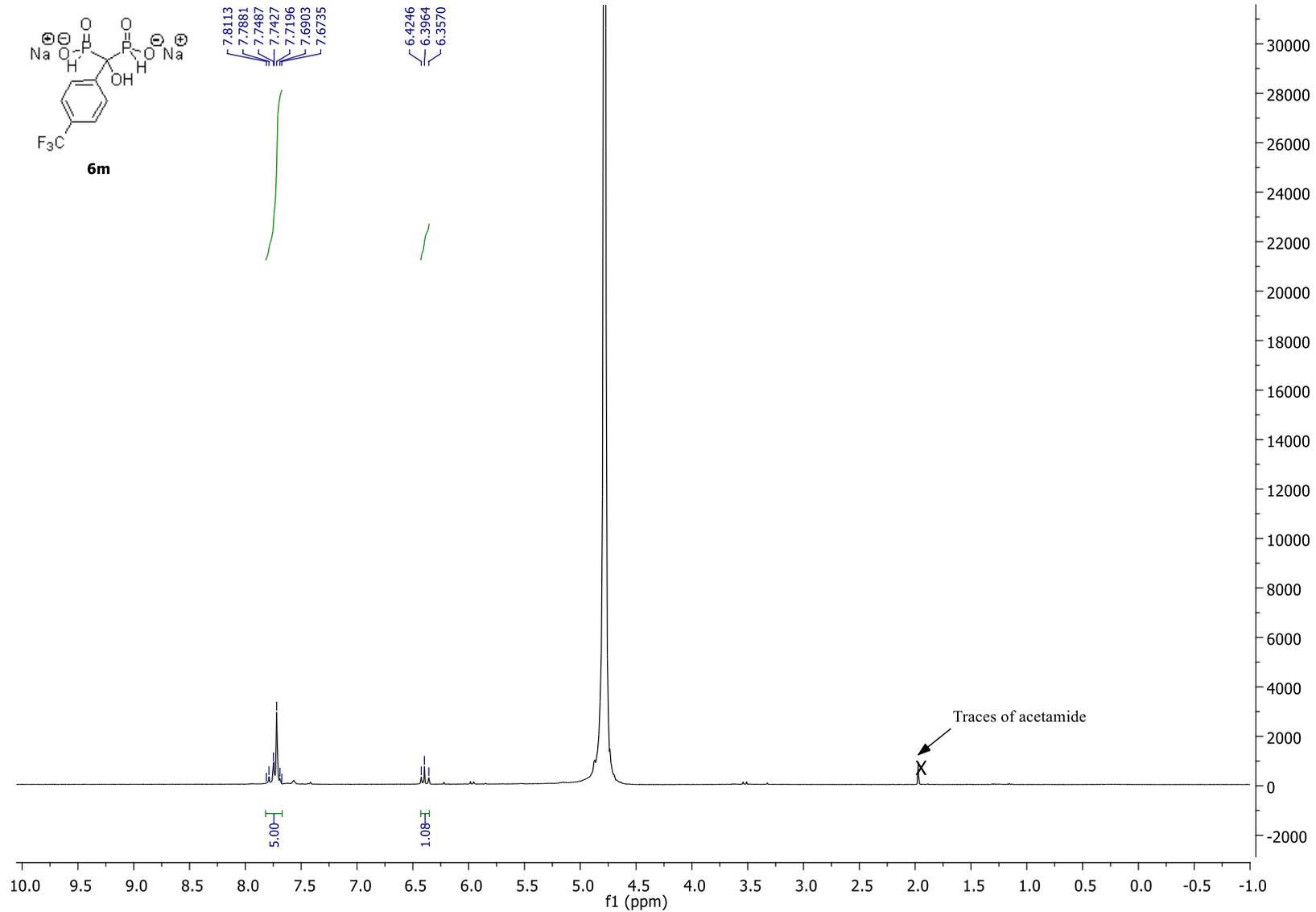


Figure 43 : ^1H NMR spectrum of 1-hydroxy-1-(4-(trifluoromethyl)phenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6m**)

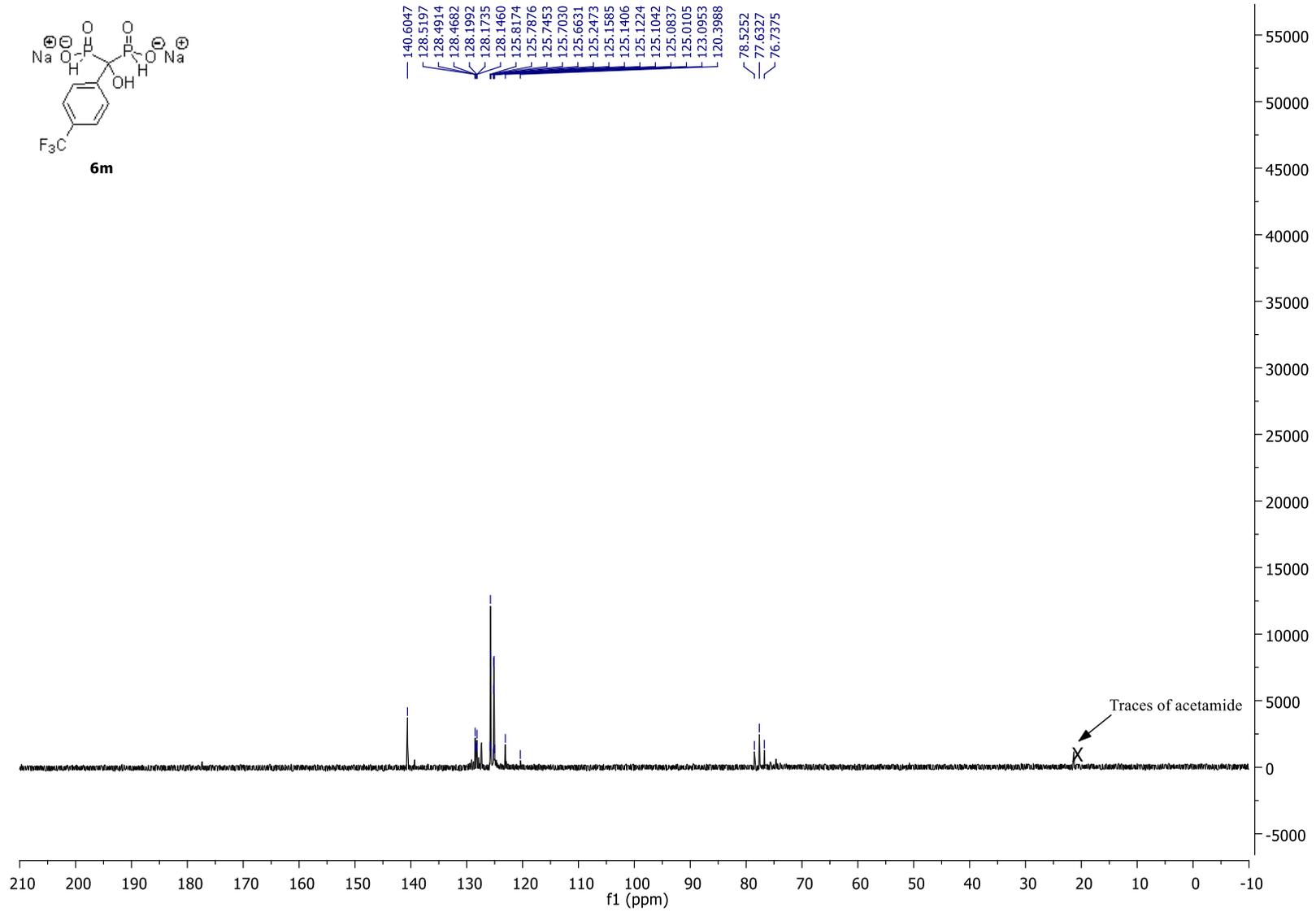


Figure 44: ¹³C NMR spectrum of 1-hydroxy-1-(4-(trifluoromethyl)phenyl)methane-1,1-bis(*H*-phosphate) disodium salt (6m)

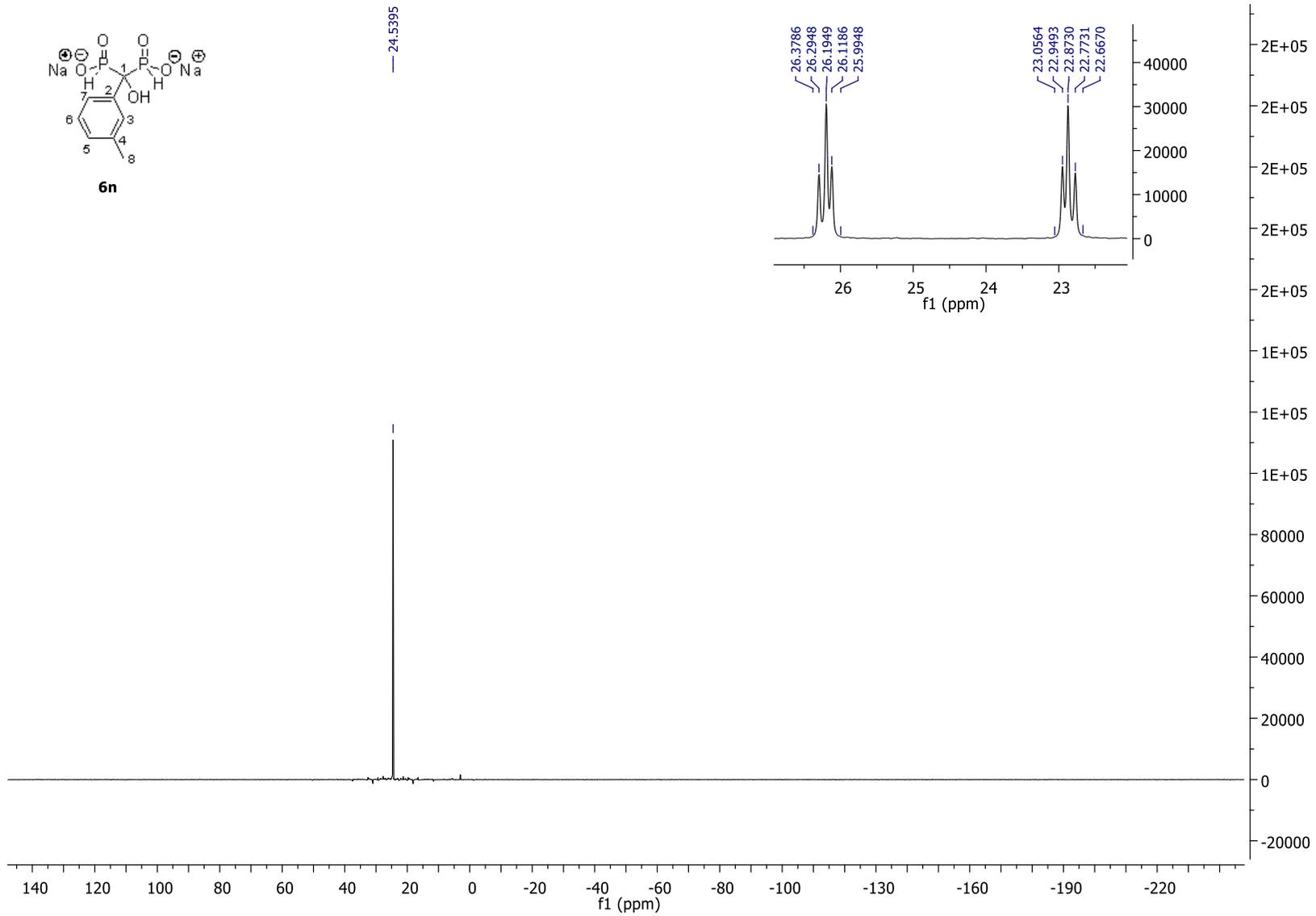


Figure 45: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(3-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6n)

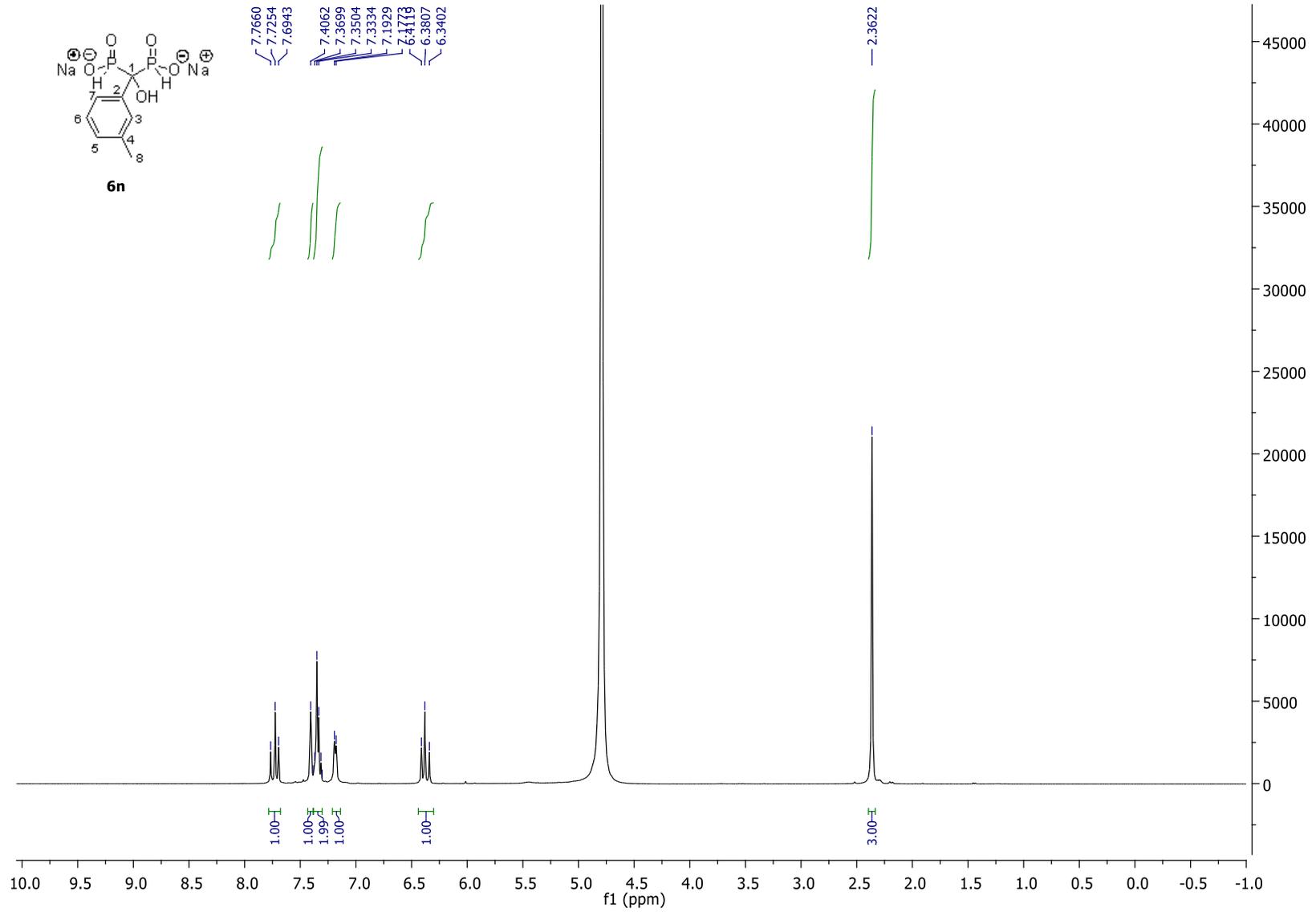


Figure 46: ¹H NMR spectrum of 1-hydroxy-1-(3-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6n)

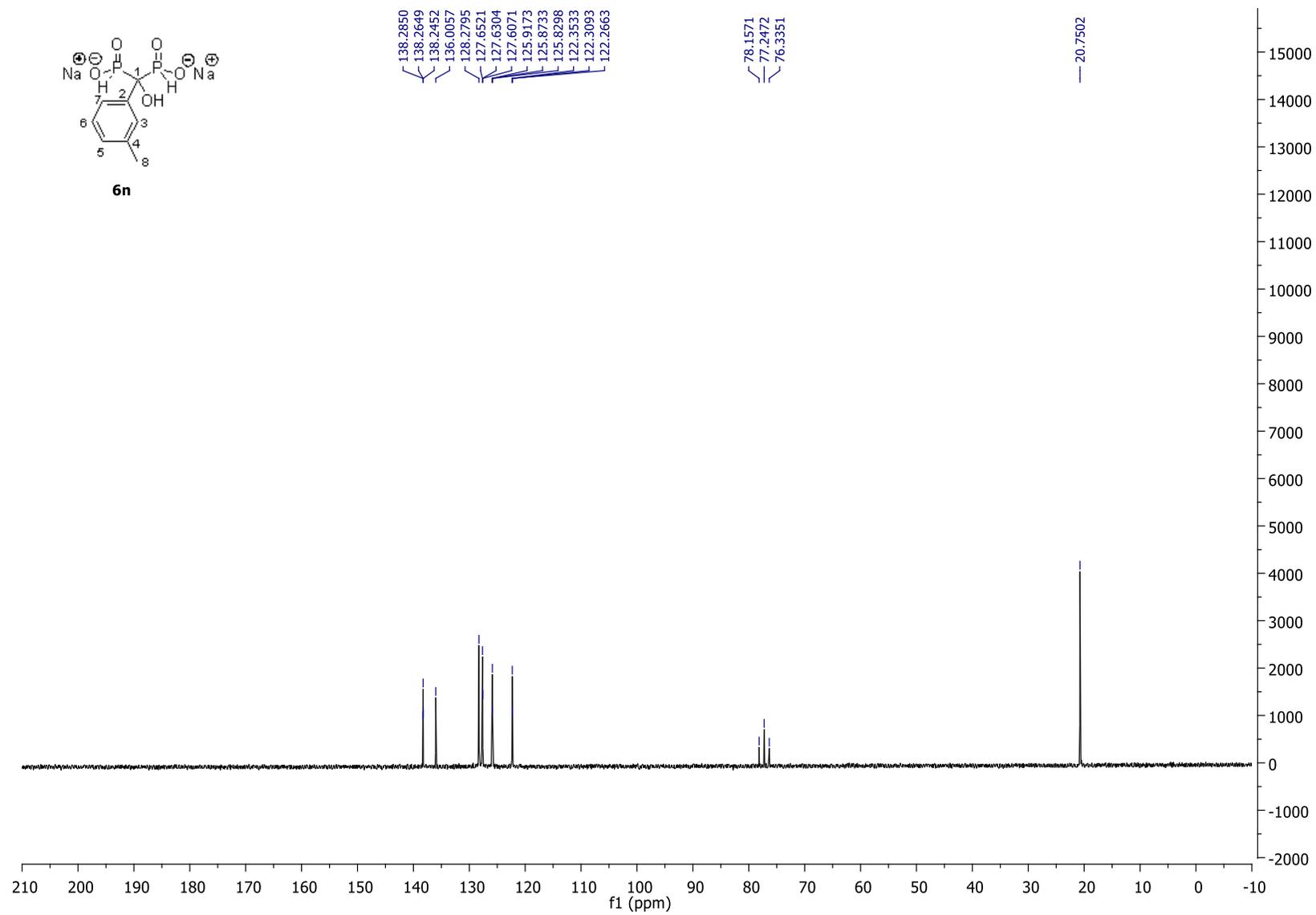


Figure 47: ^{13}C NMR spectrum of 1-hydroxy-1-(3-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6n**)

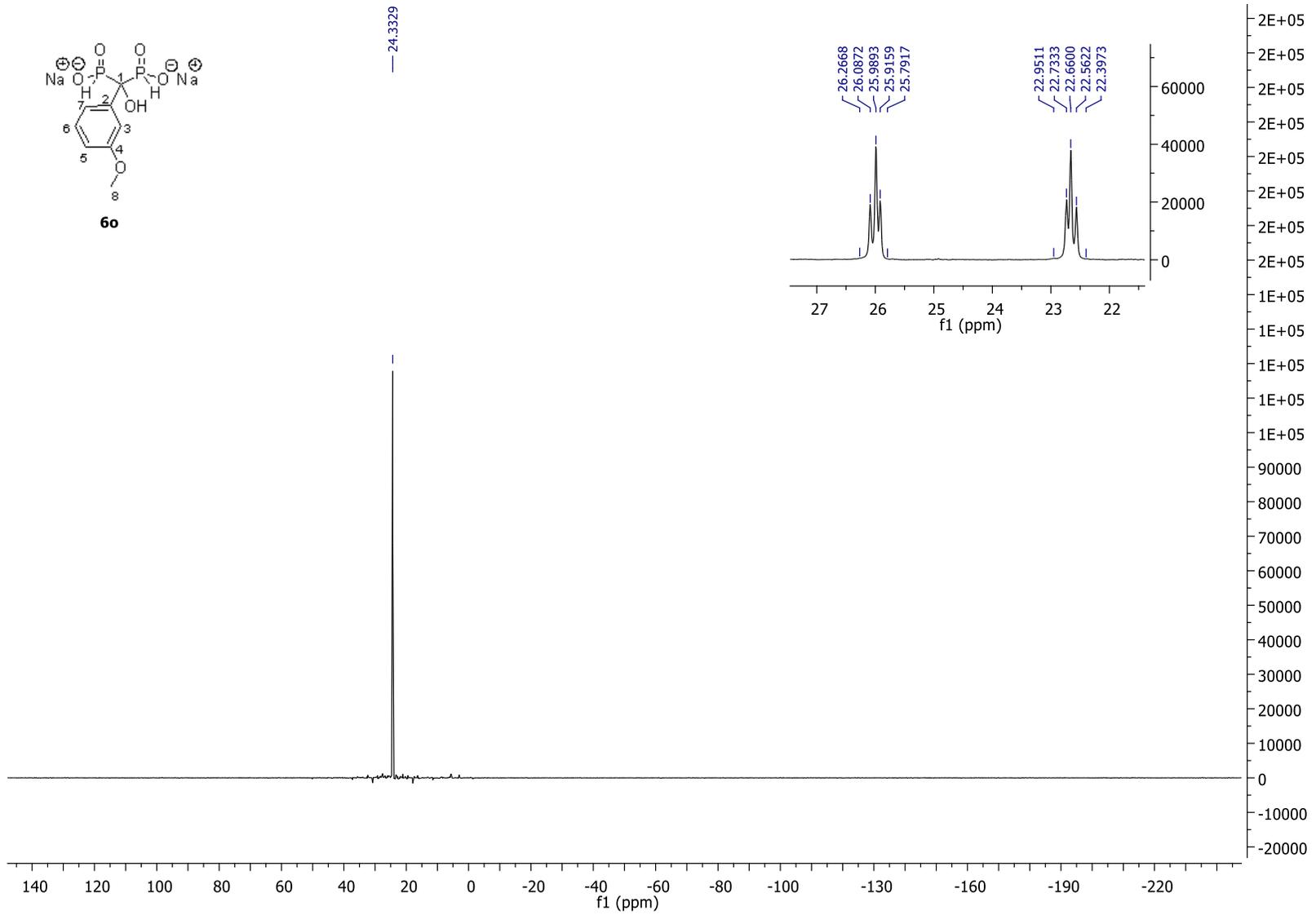


Figure 48: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(3-methoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6o**)

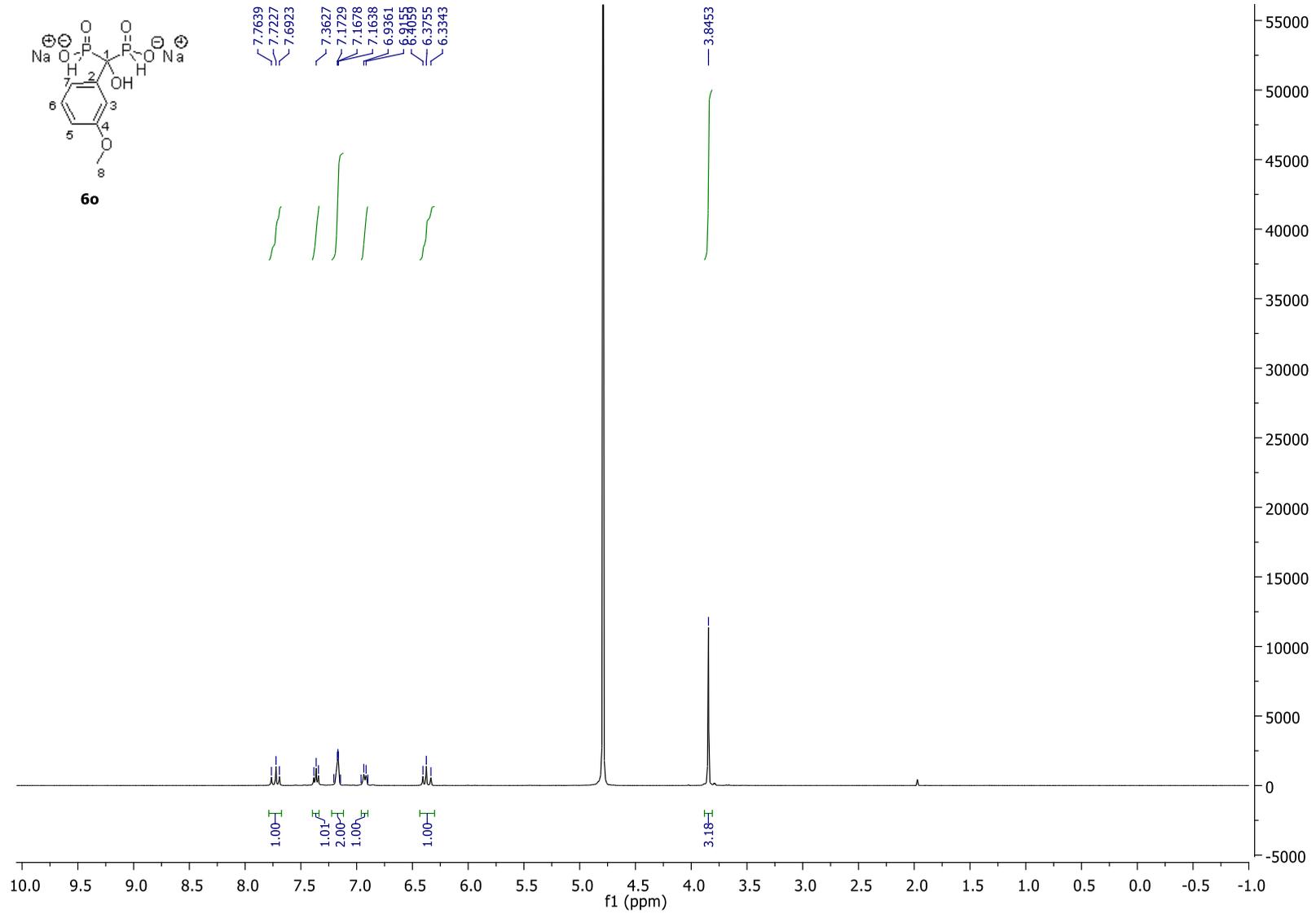


Figure 49: ¹H NMR spectrum of 1-hydroxy-1-(3-methoxyphenyl)methane-1,1-bis(*H*-phosphate) disodium salt (**60**)

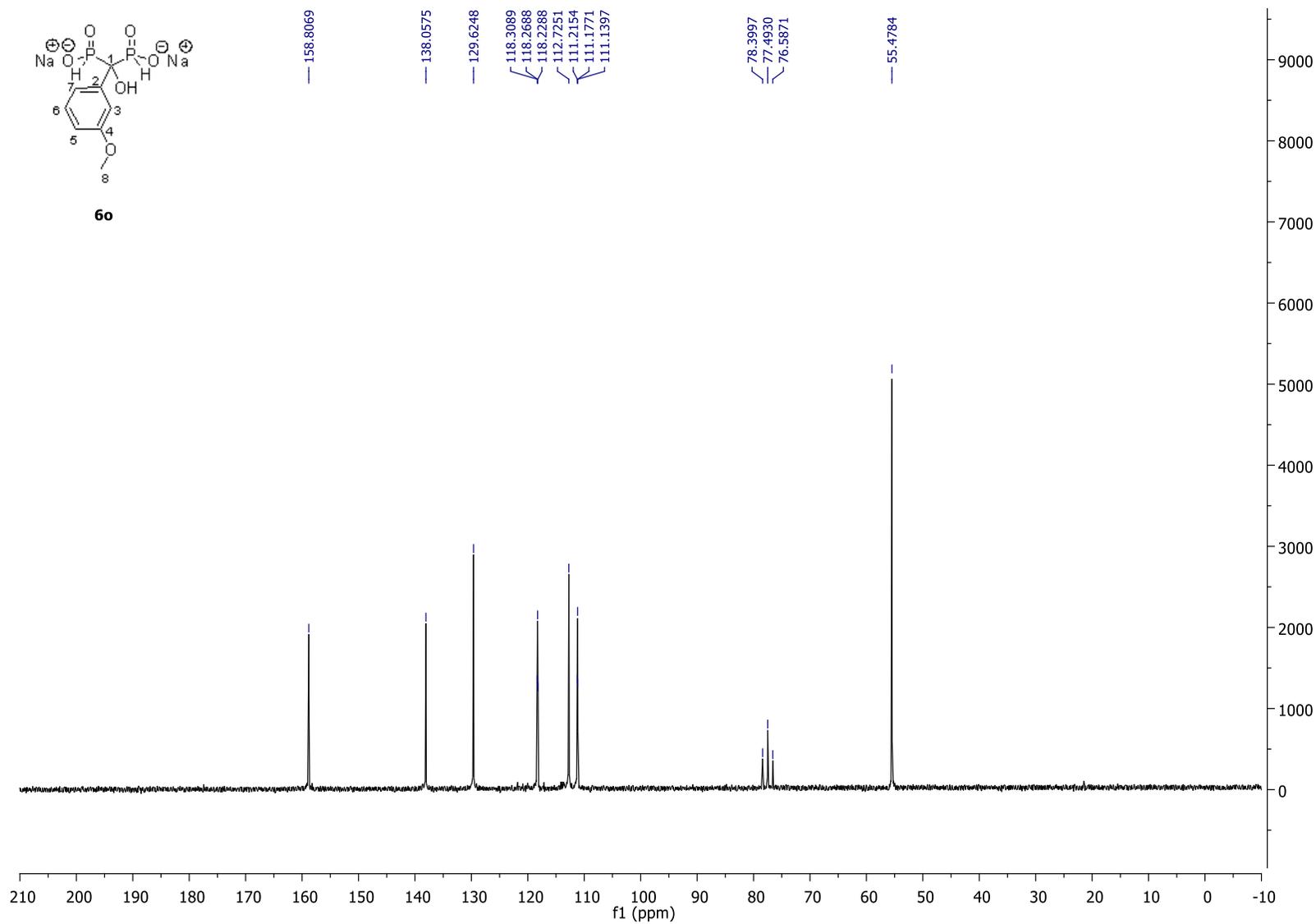


Figure 50: ¹³C NMR spectrum of 1-hydroxy-1-(3-methoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6o**)

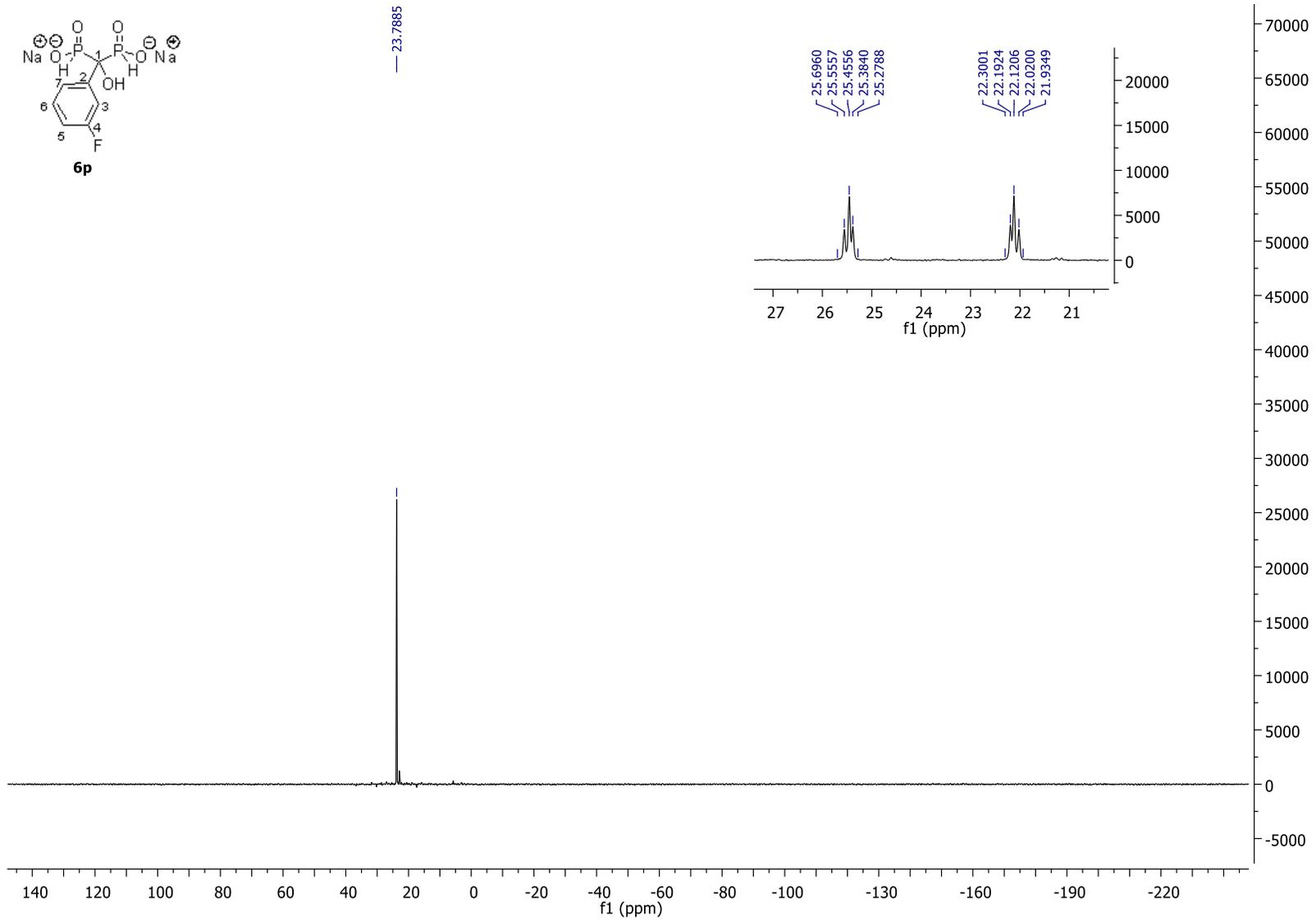


Figure 51: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(3-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6p)

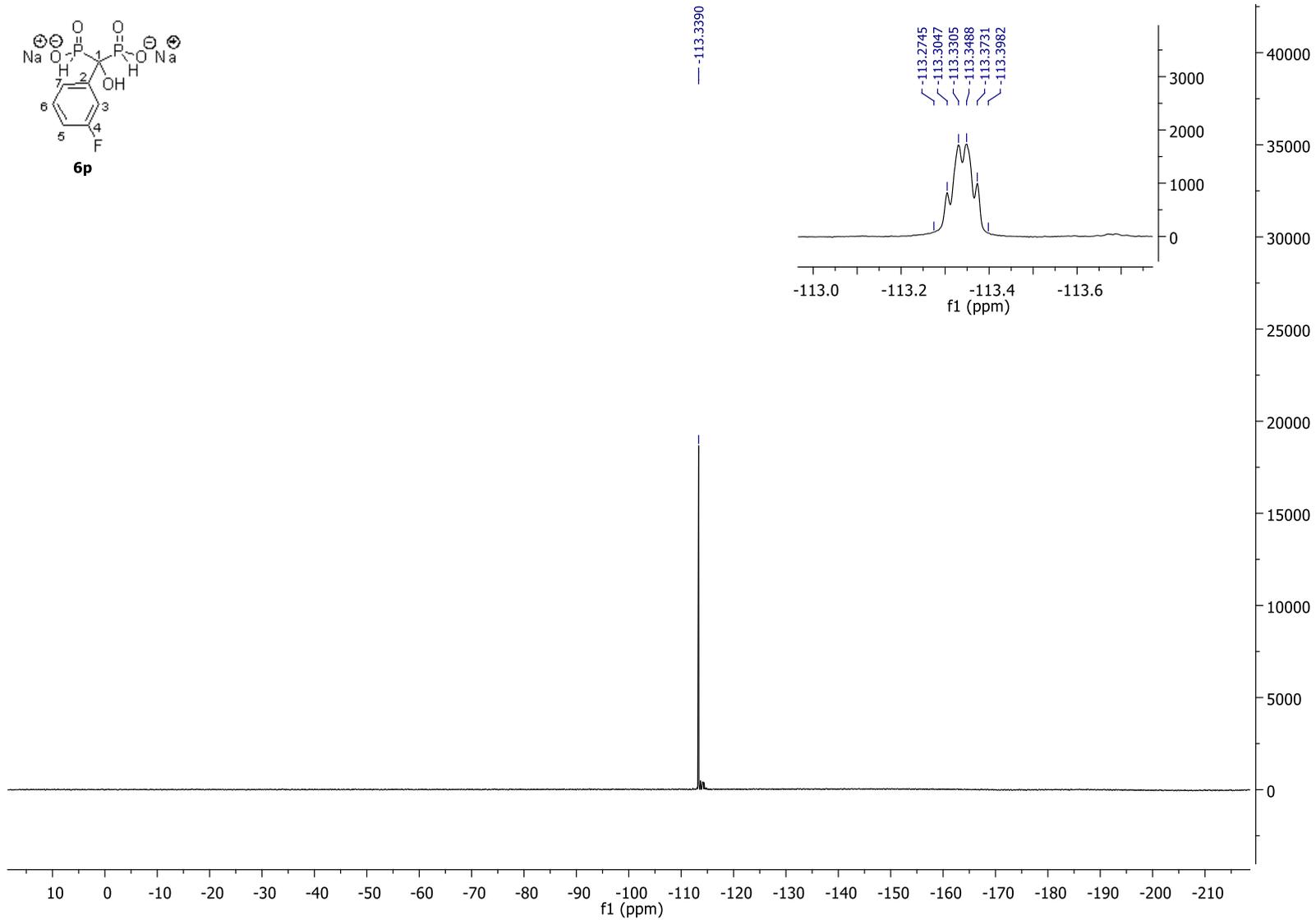


Figure 52: ^{19}F $\{^1\text{H}\}$ and ^{19}F NMR spectra of 1-hydroxy-1-(3-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6p**)

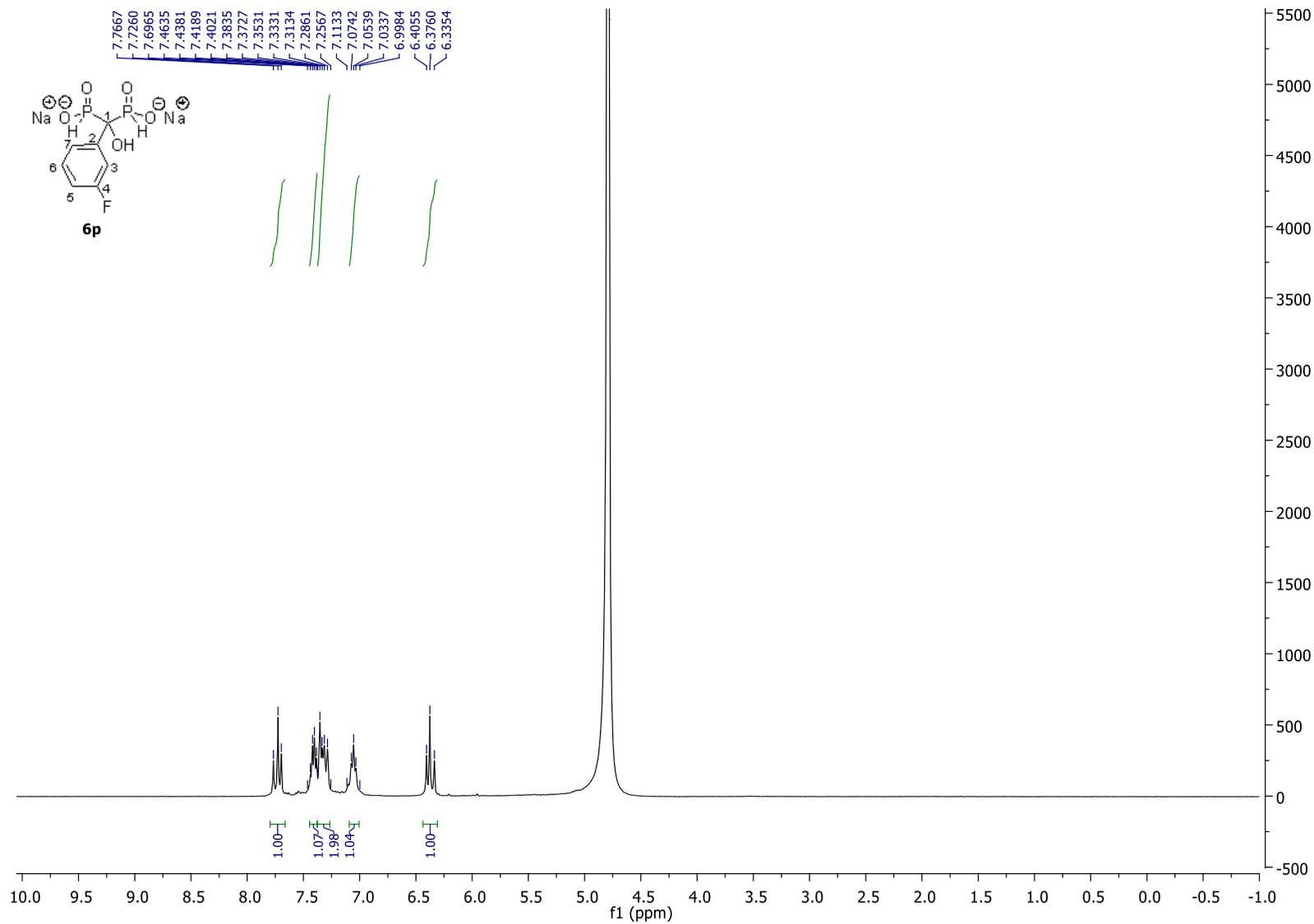


Figure 53: ¹H NMR spectrum of 1-hydroxy-1-(3-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6p)

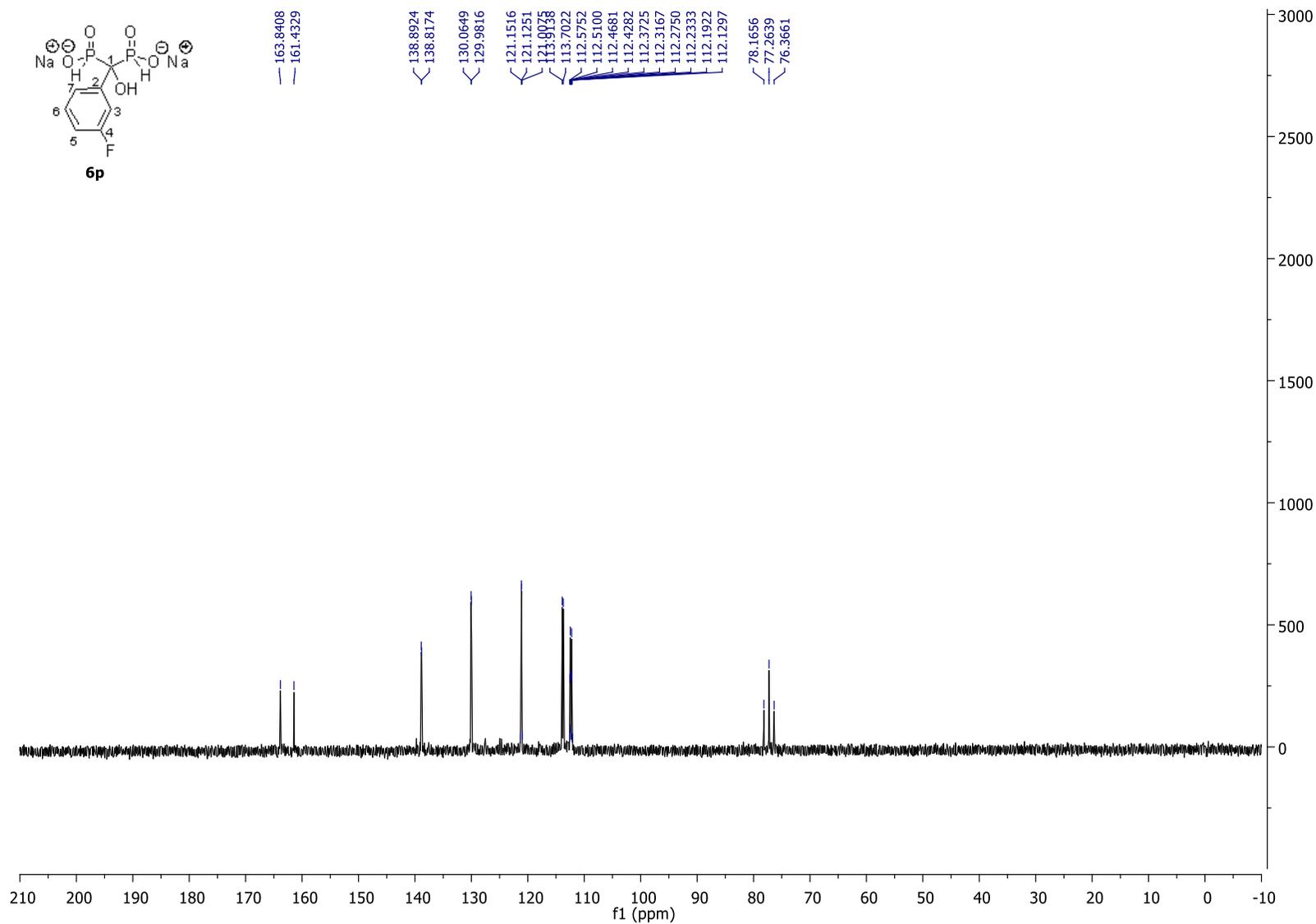


Figure 54: ^{13}C NMR spectrum of 1-hydroxy-1-(3-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6p)

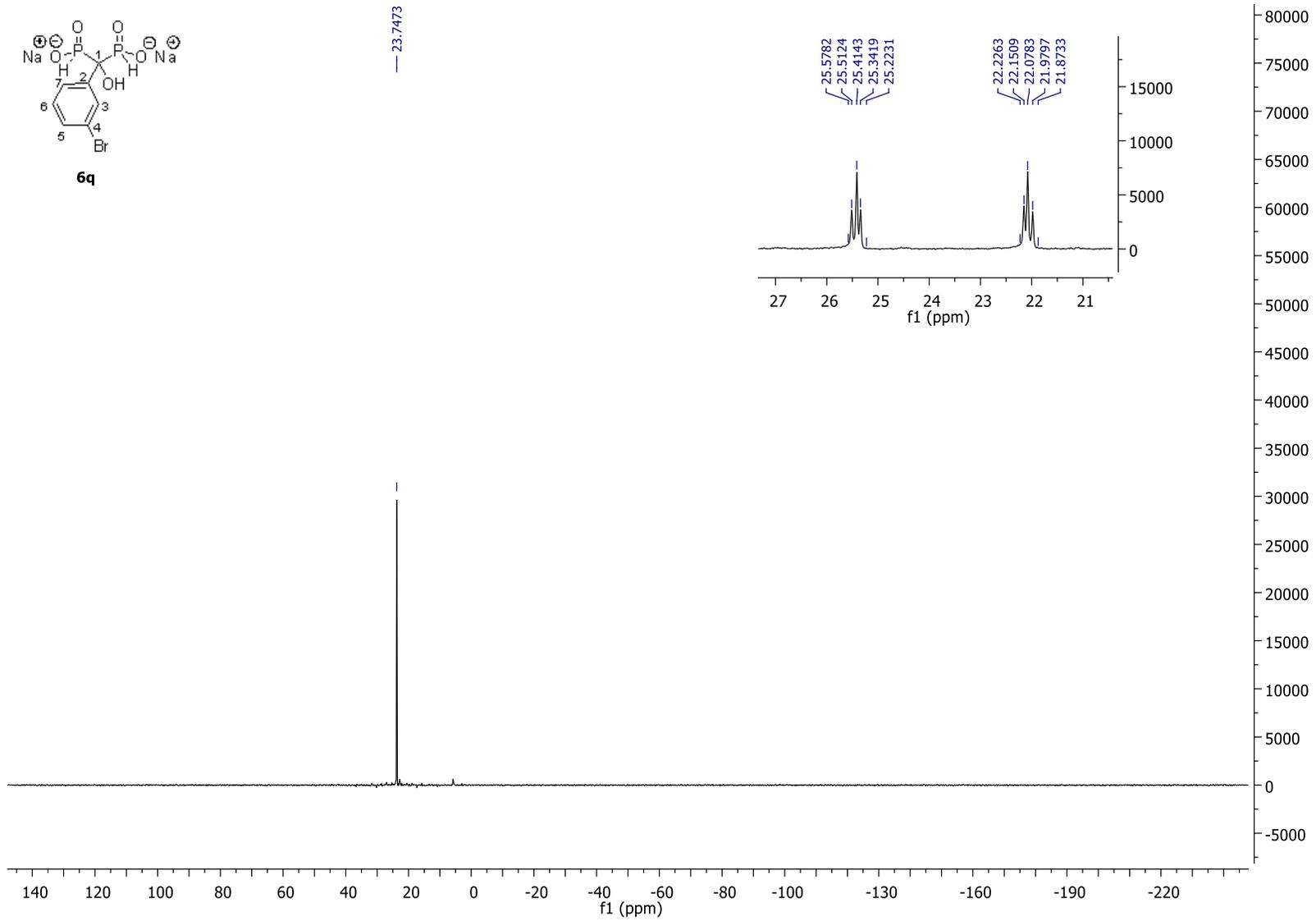


Figure 55: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(3-bromophenyl)methane-1,1-bis(*H*-phosphate) disodium salt (6q)

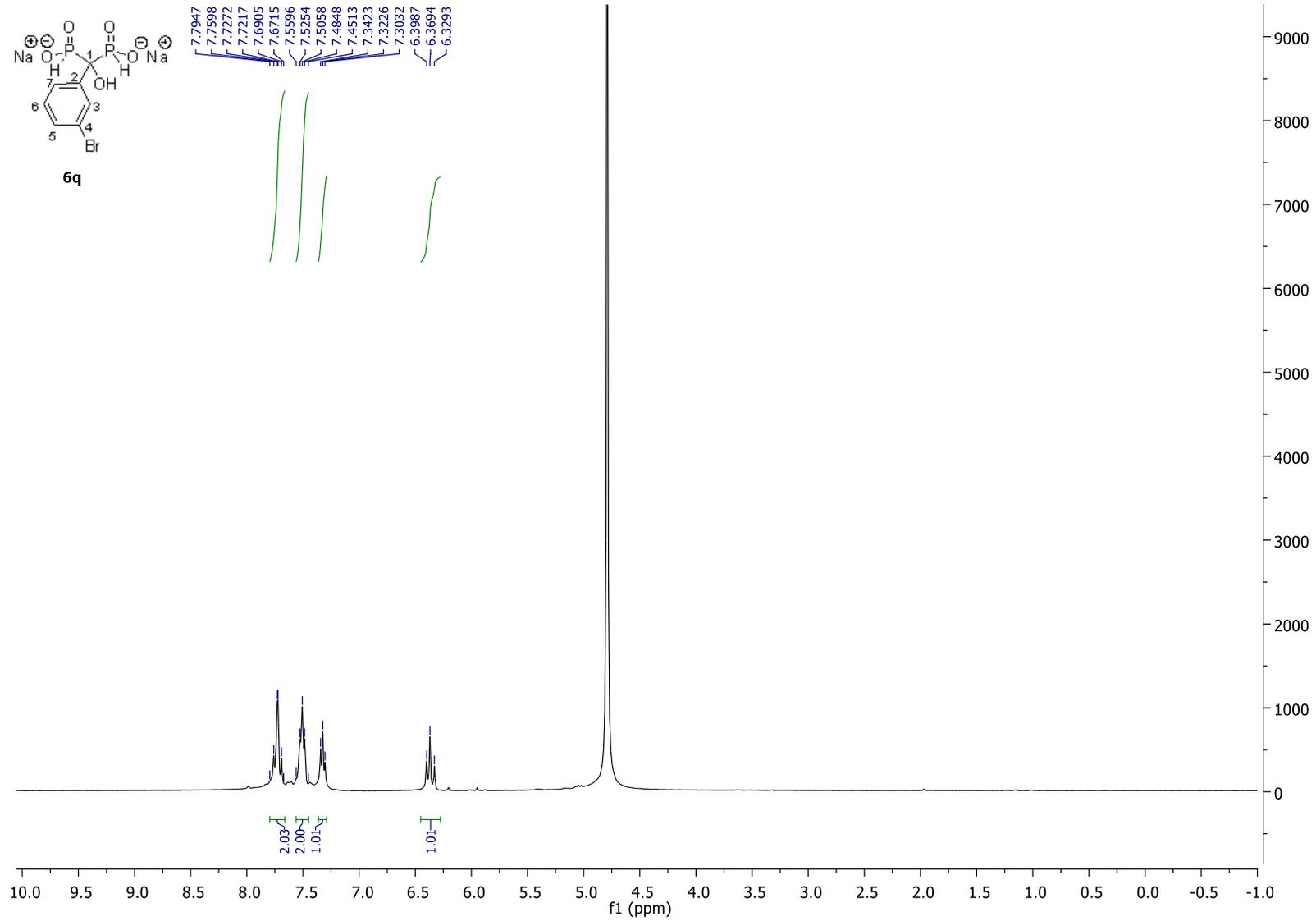


Figure S6: ^1H NMR spectrum of 1-hydroxy-1-(3-bromophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6q)

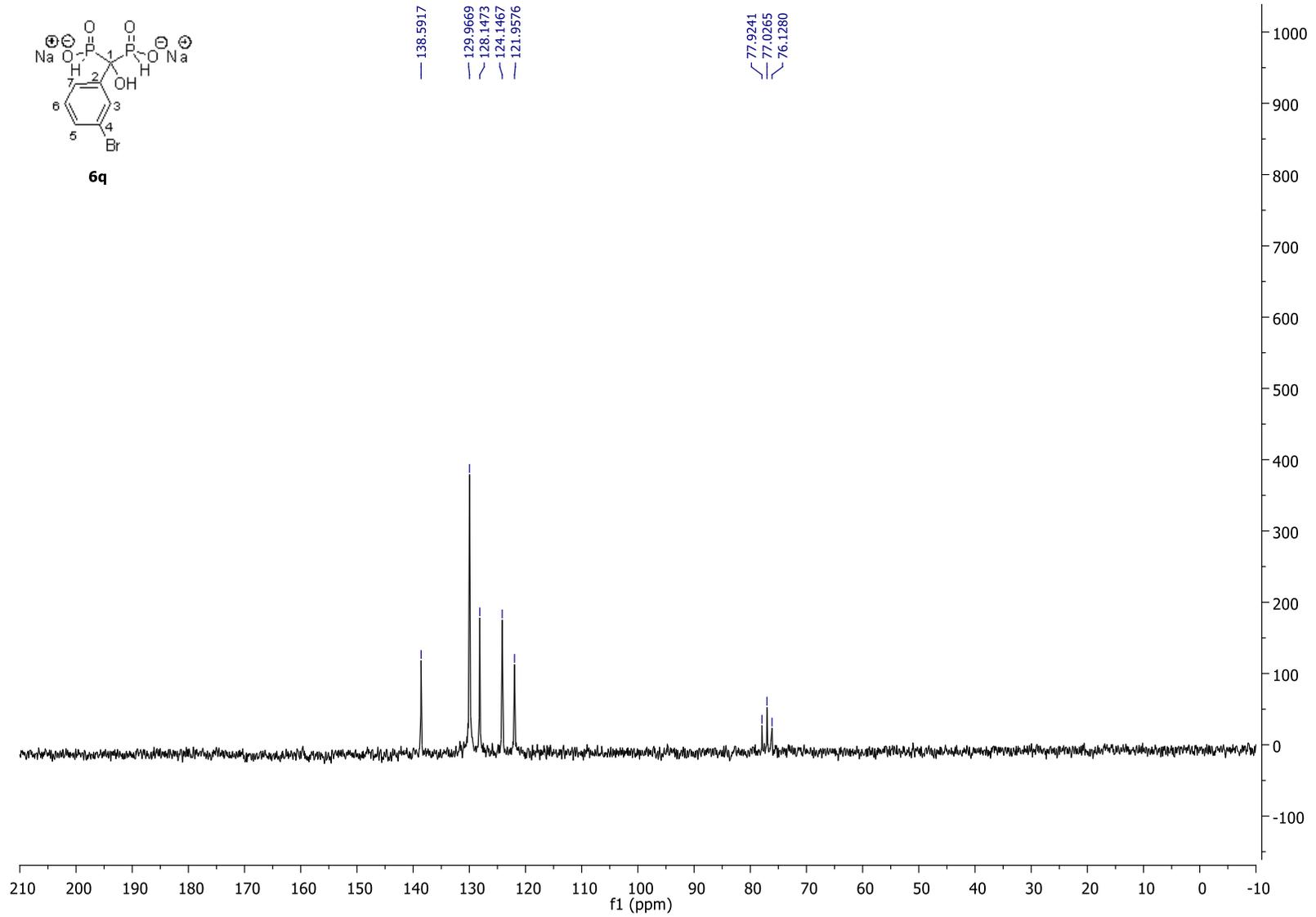


Figure 57: ¹³C NMR spectrum of 1-hydroxy-1-(3-bromophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6q)

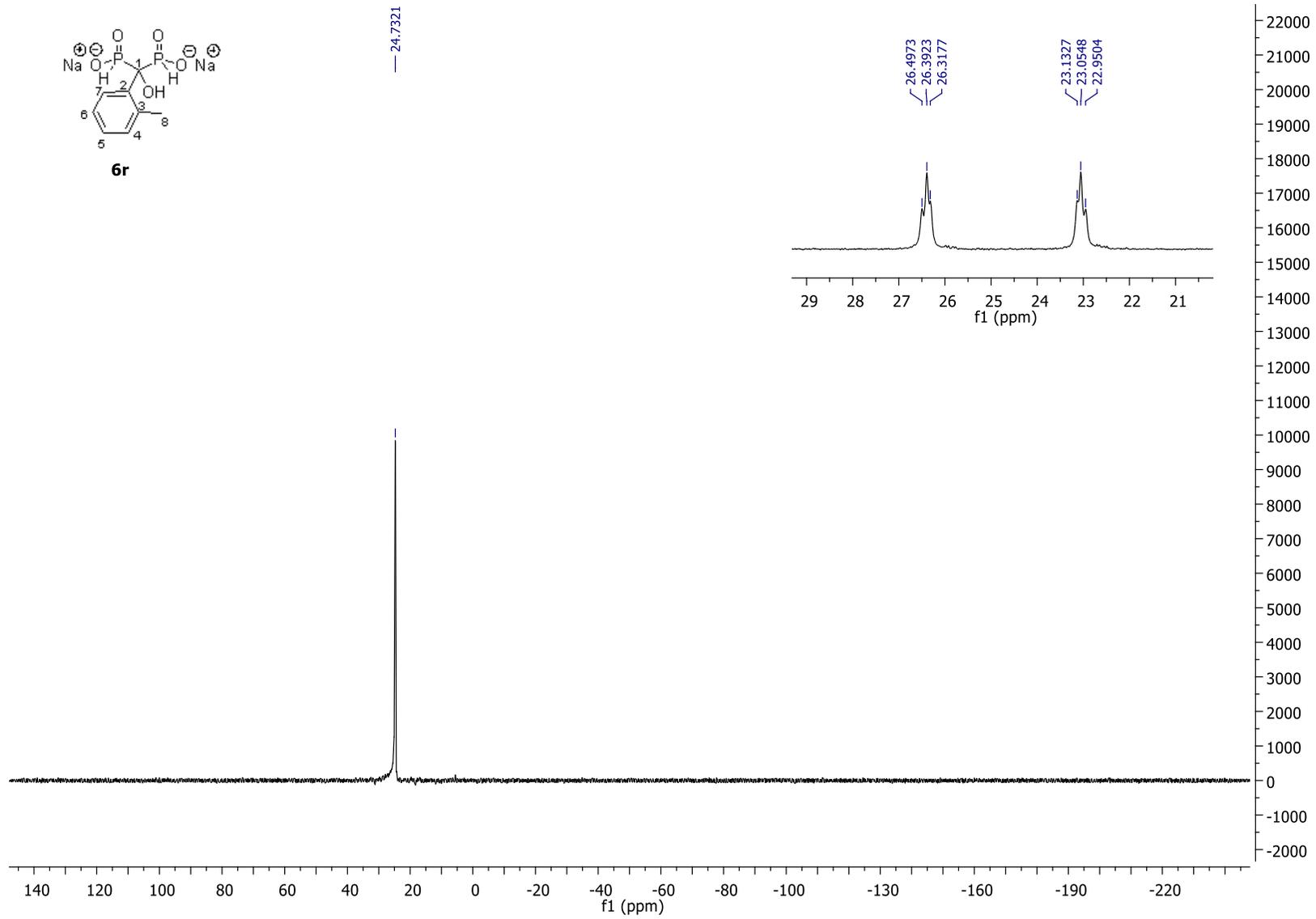


Figure 58: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(2-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6r**)

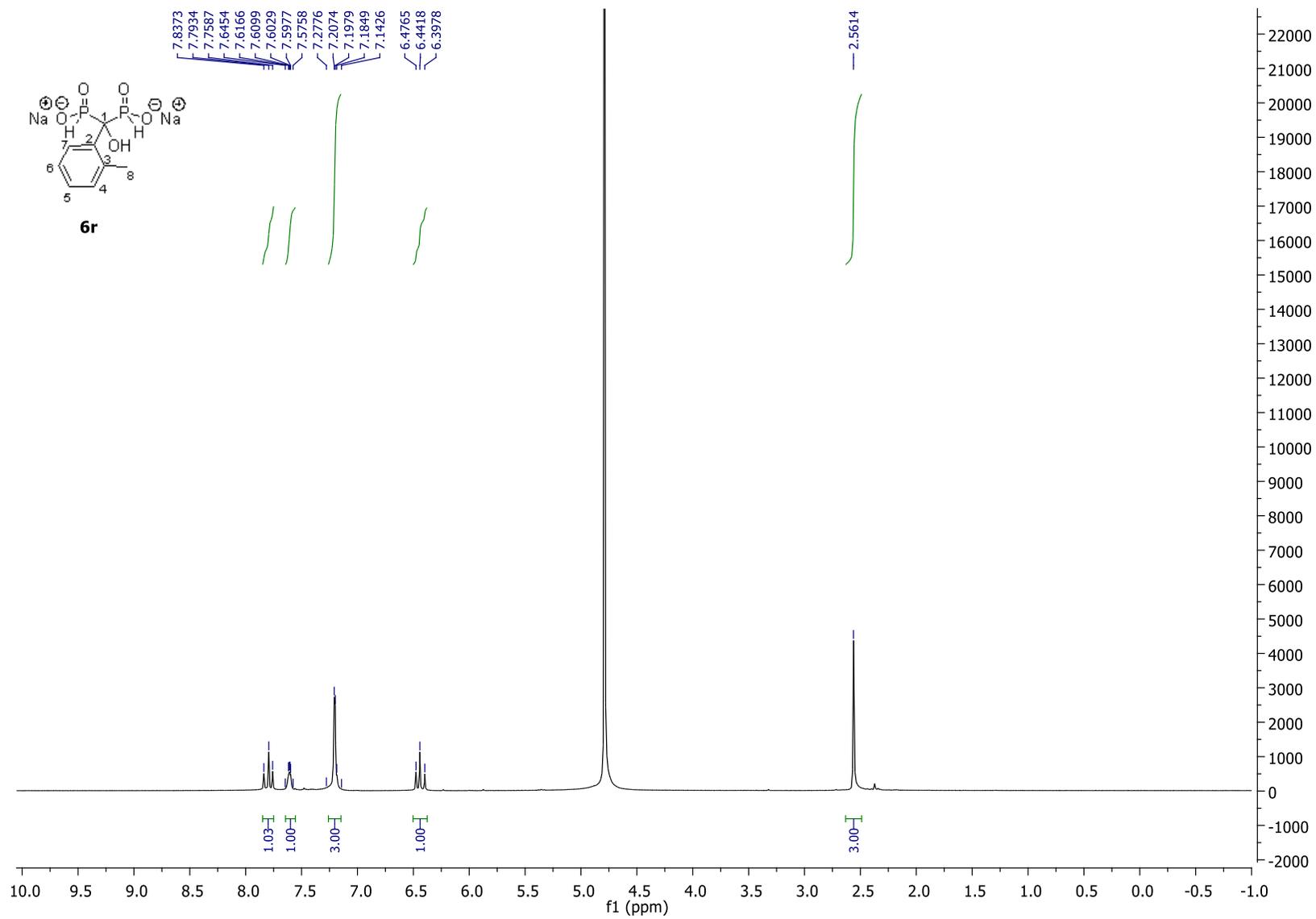


Figure S9: ¹H NMR spectrum of 1-hydroxy-1-(2-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6r**)

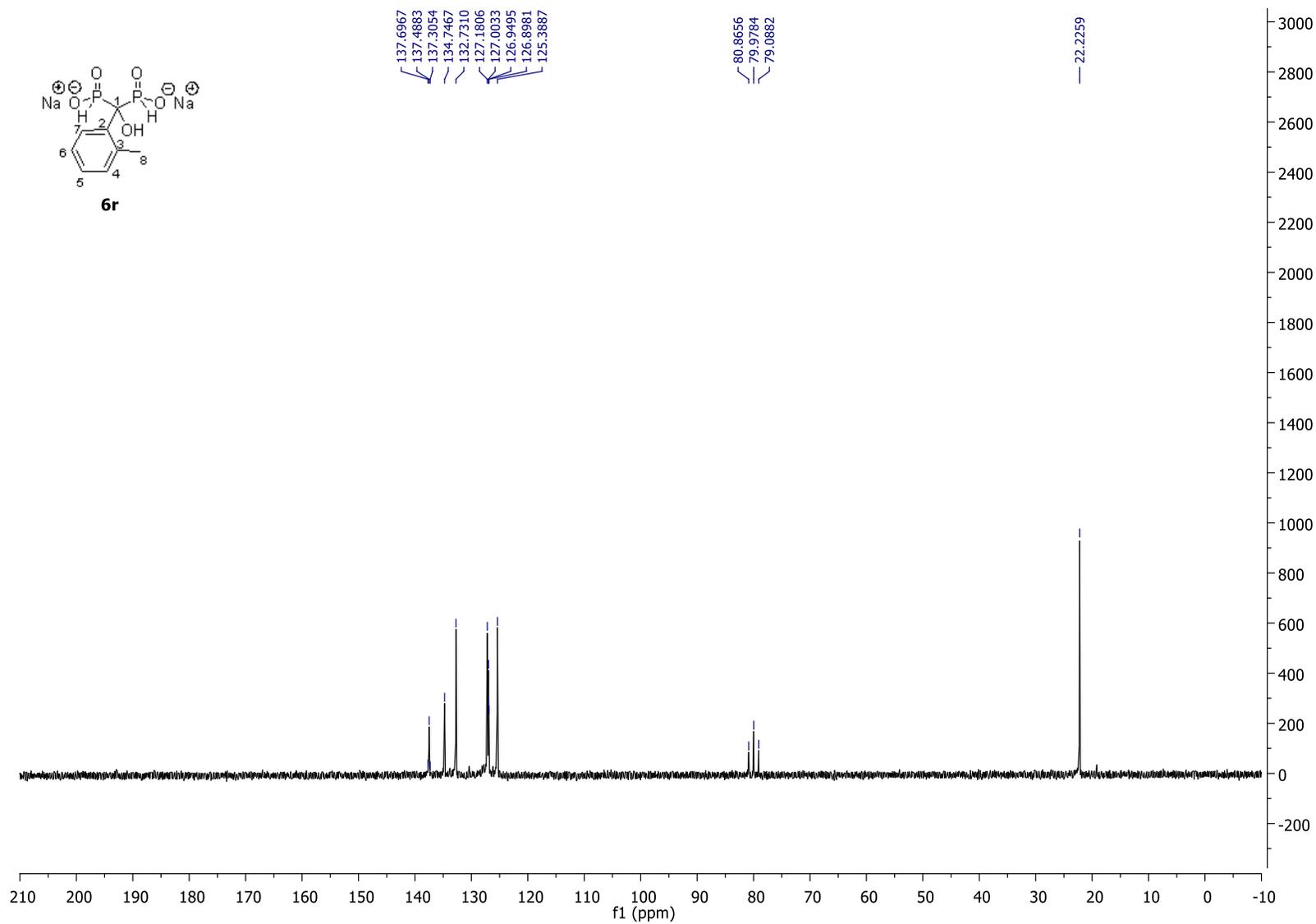


Figure 60: ¹³C NMR spectrum of 1-hydroxy-1-(2-tolyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6r)

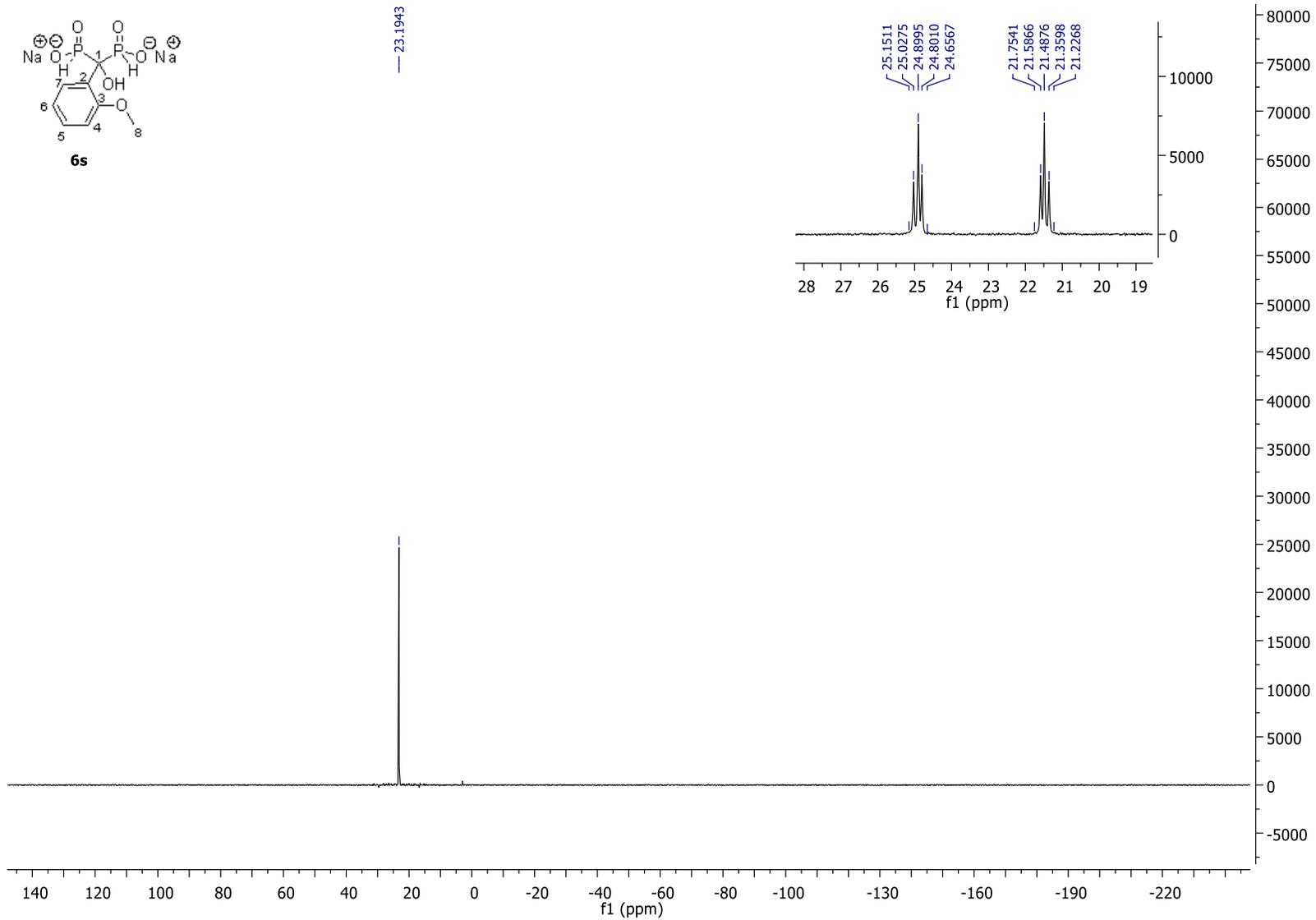


Figure 61: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(2-methoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6s)

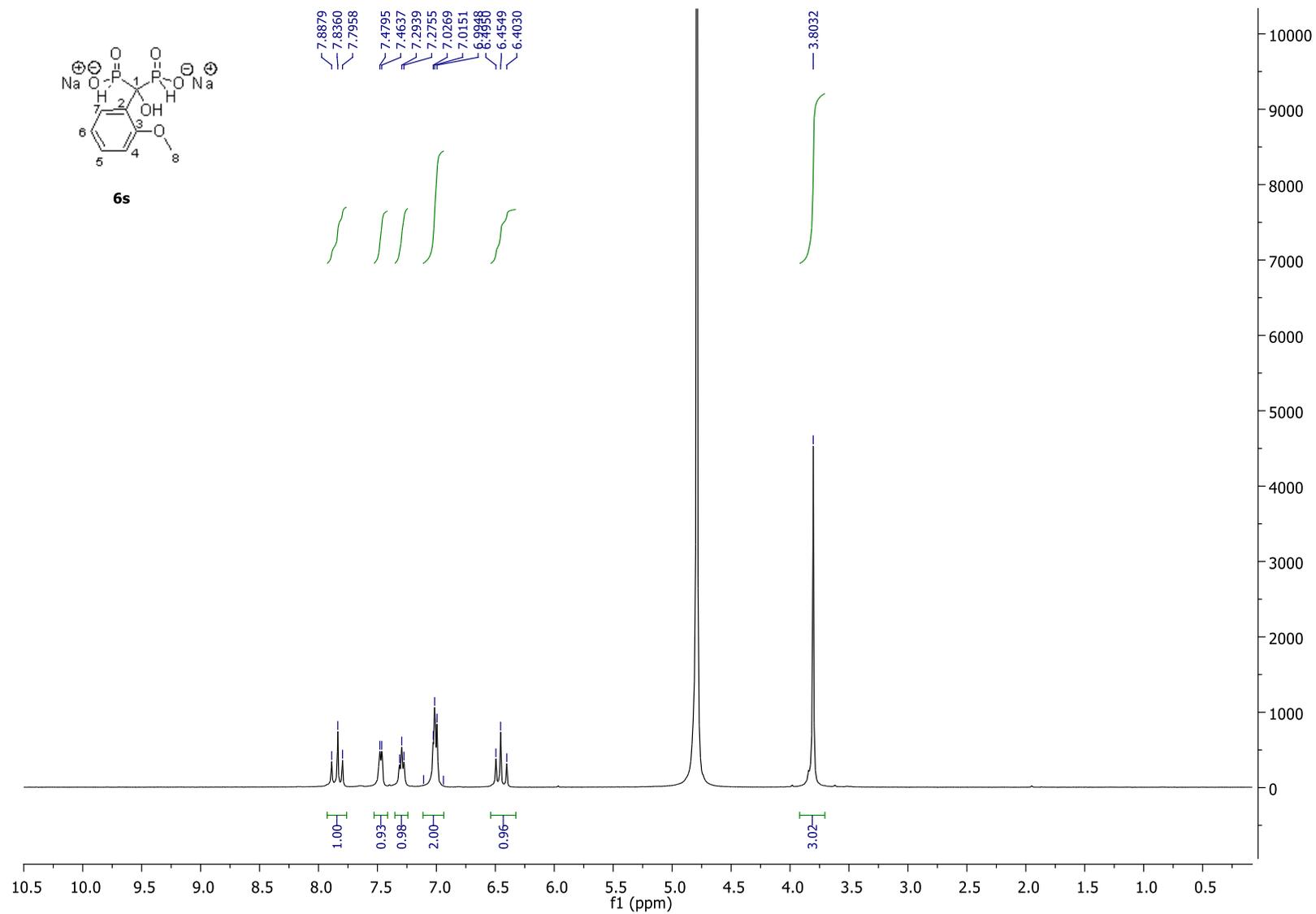


Figure 62: ¹H NMR spectrum of 1-hydroxy-1-(2-methoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6s)

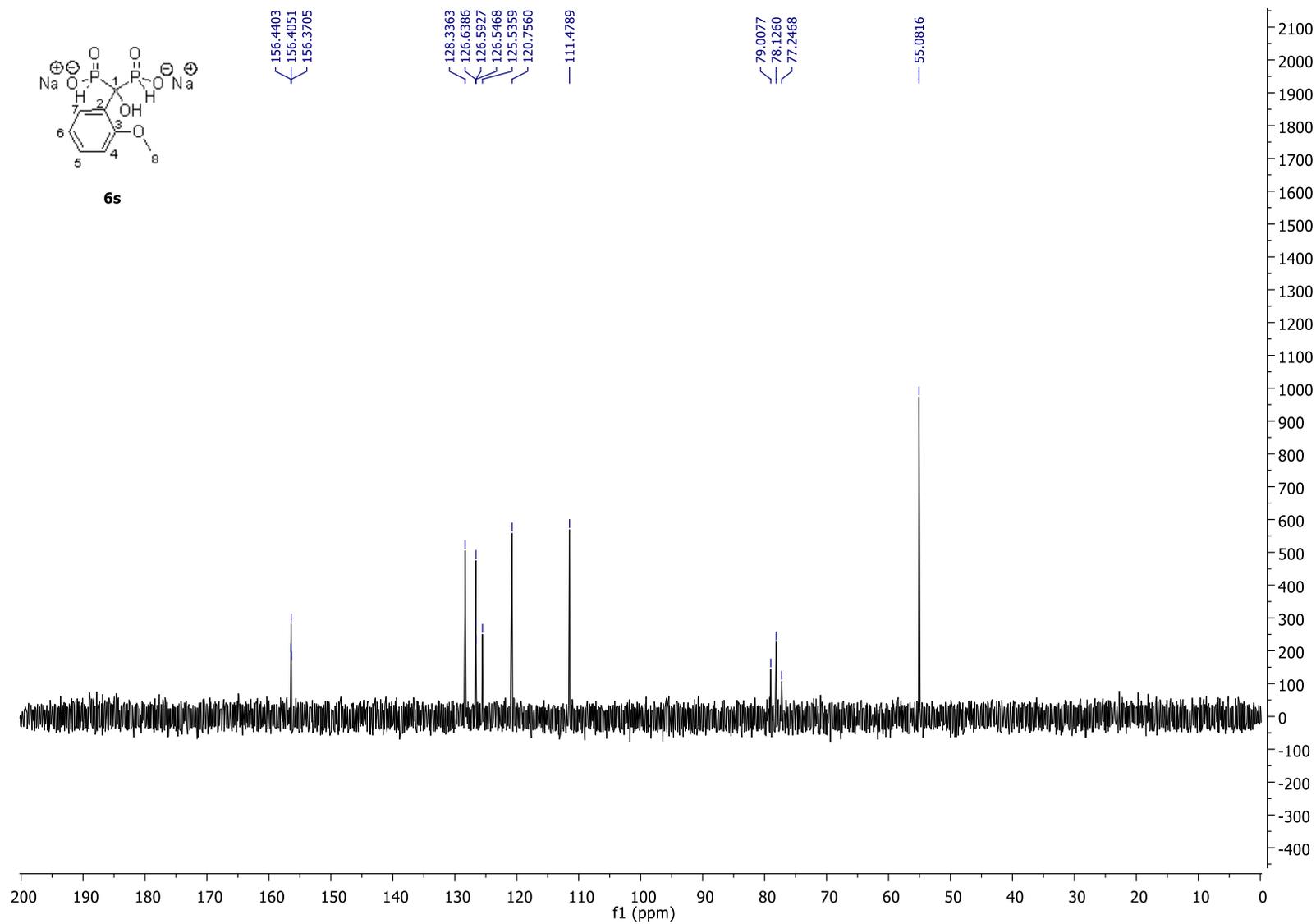


Figure 63: ^{13}C NMR spectrum of 1-hydroxy-1-(2-methoxyphenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6s)

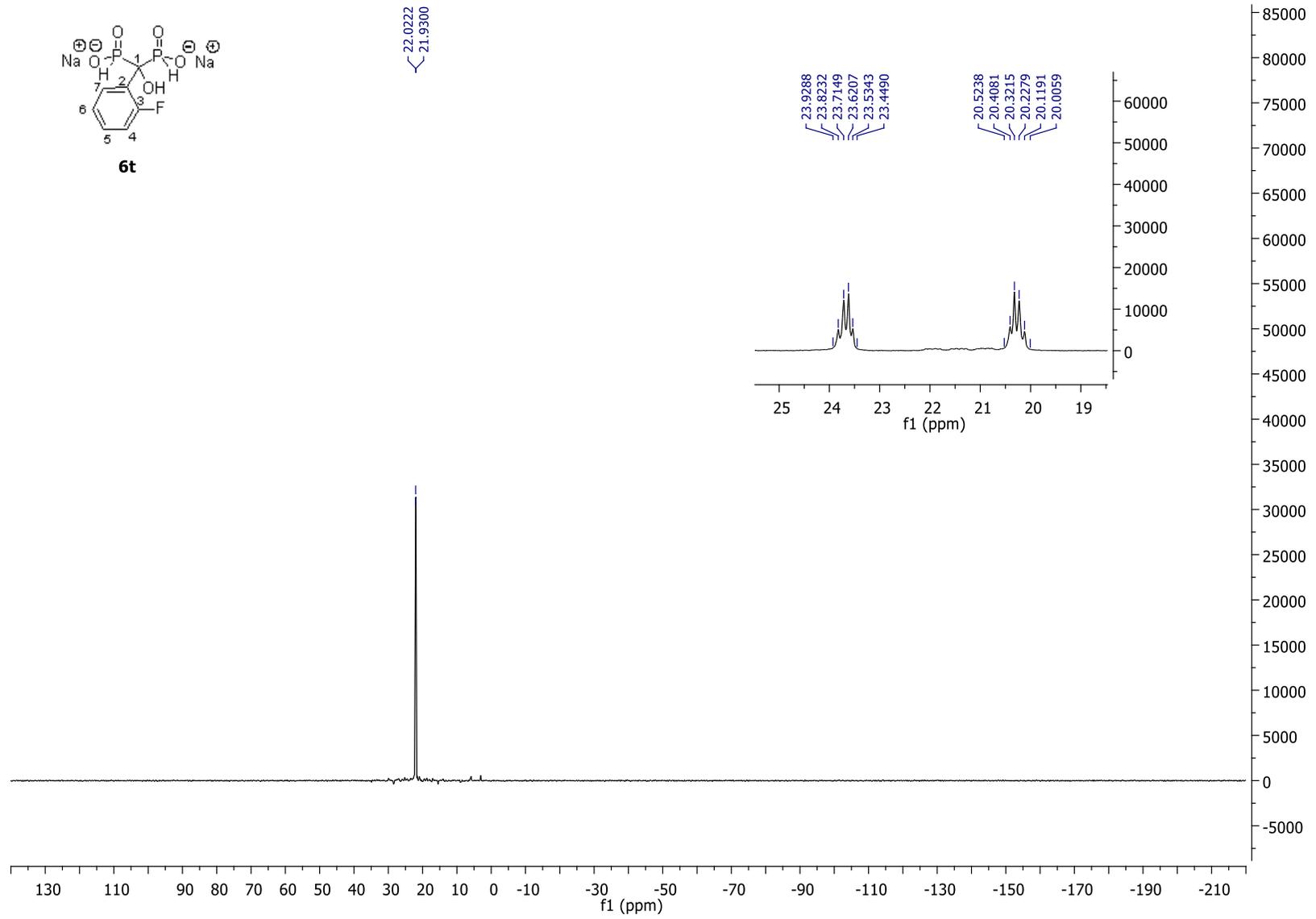


Figure 64: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(2-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6t)

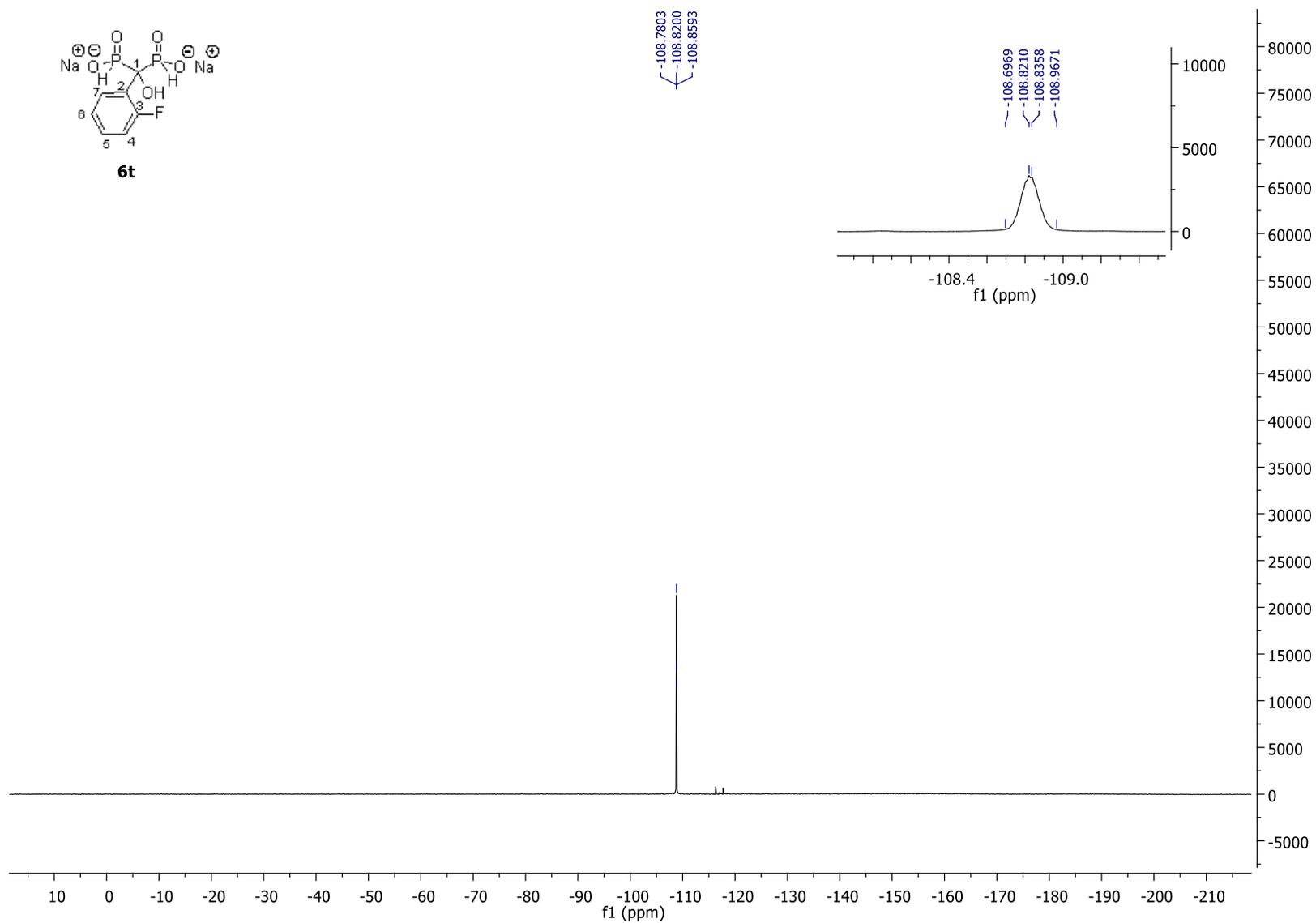


Figure 65: ^{19}F $\{^1\text{H}\}$ and ^{19}F NMR spectra of 1-hydroxy-1-(2-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6t)

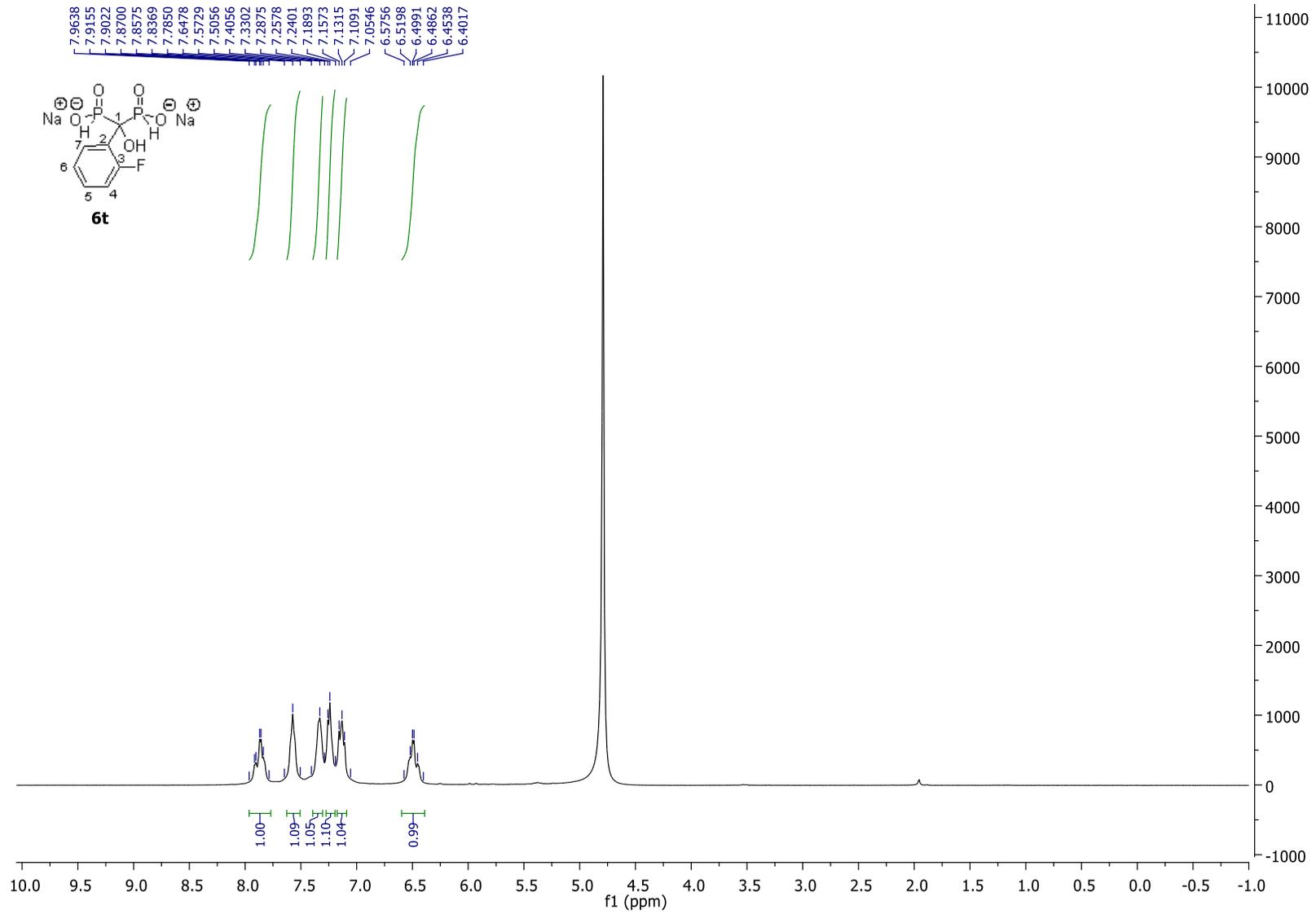
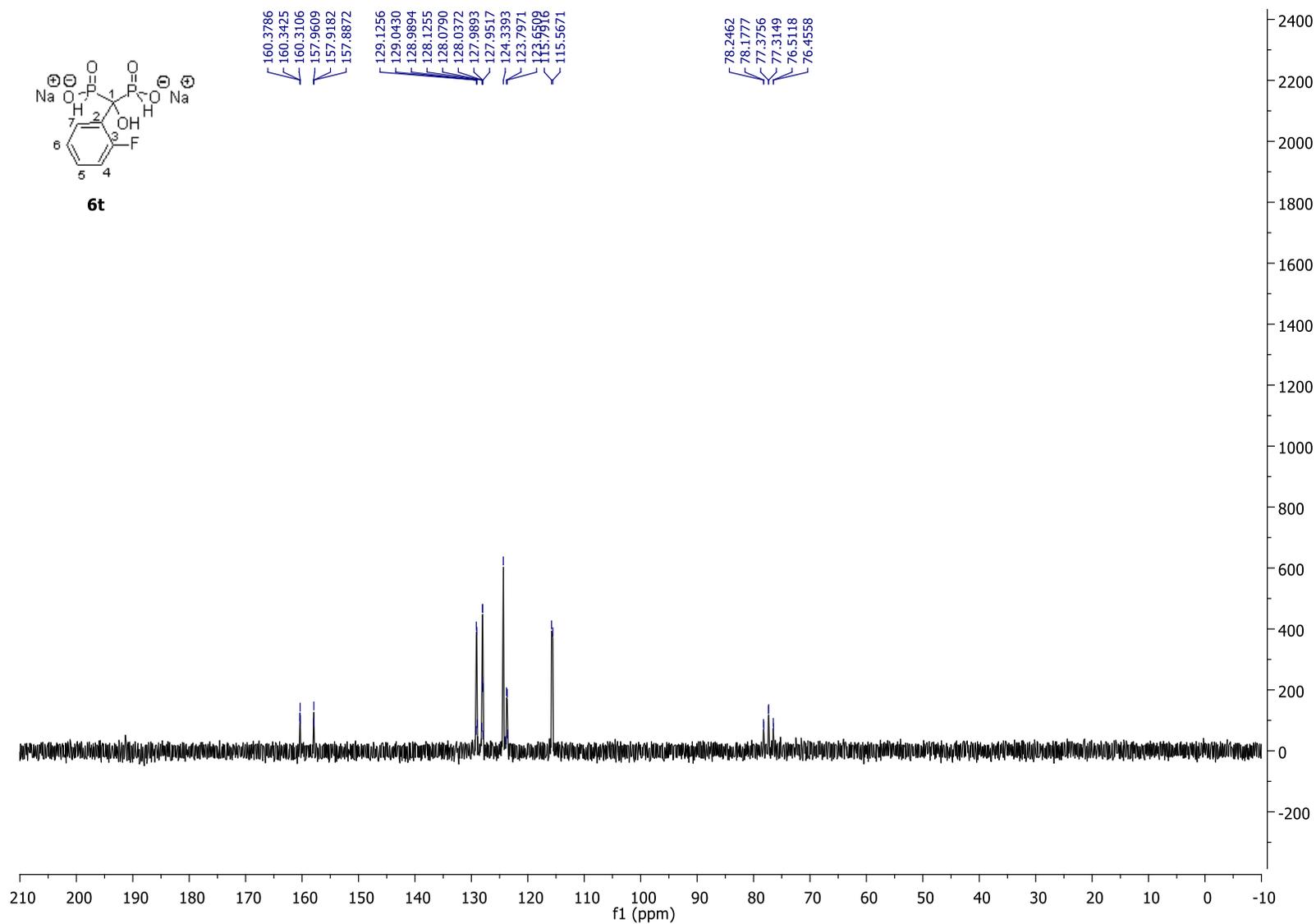


Figure 66: ¹H NMR spectrum of 1-hydroxy-1-(2-fluorophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6t**)



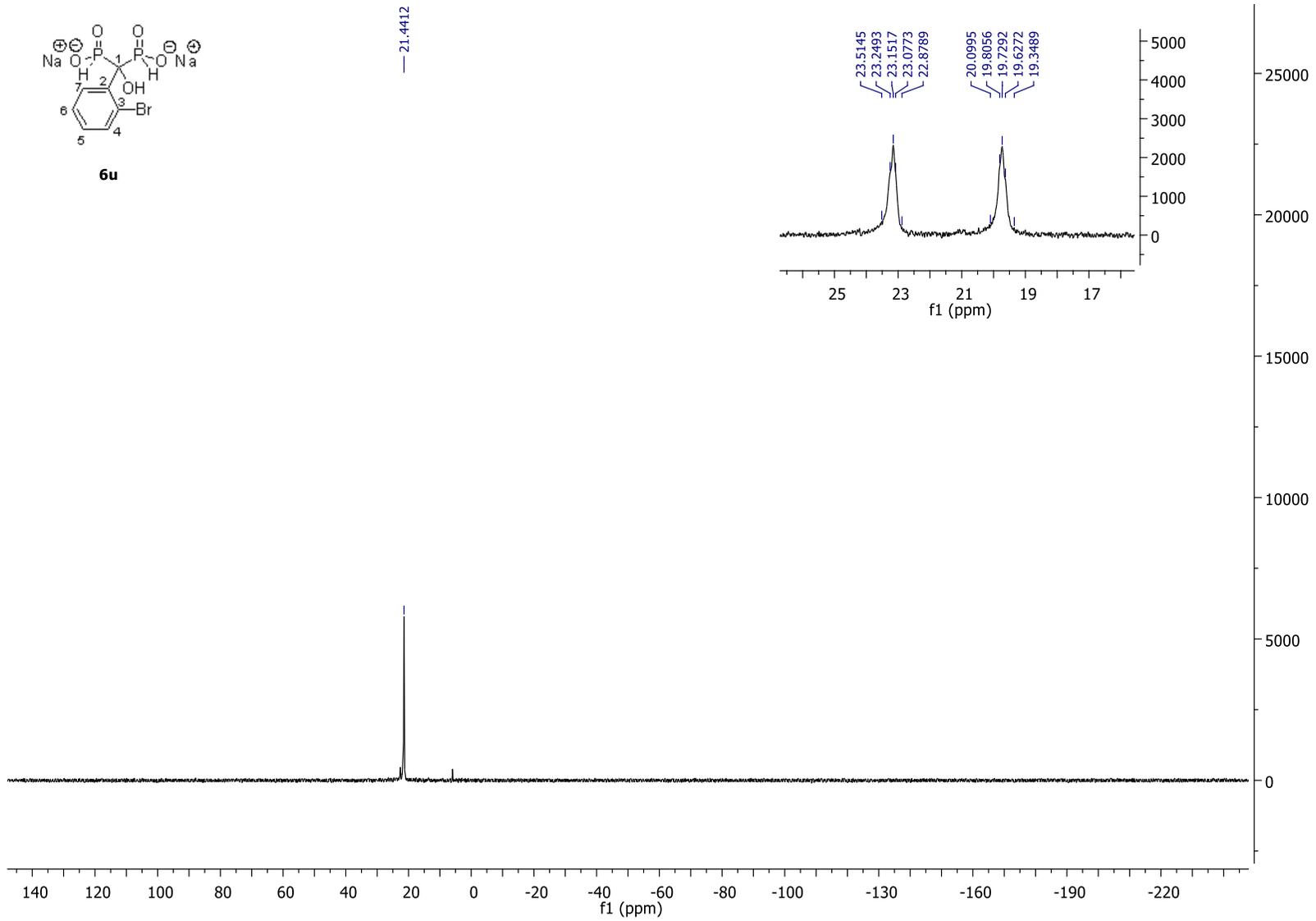


Figure 68: ³¹P{¹H} and ³¹P NMR spectra of 1-hydroxy-1-(2-bromophenyl)methane-1,1-bis(*H*-phosphate) disodium salt (**6u**)

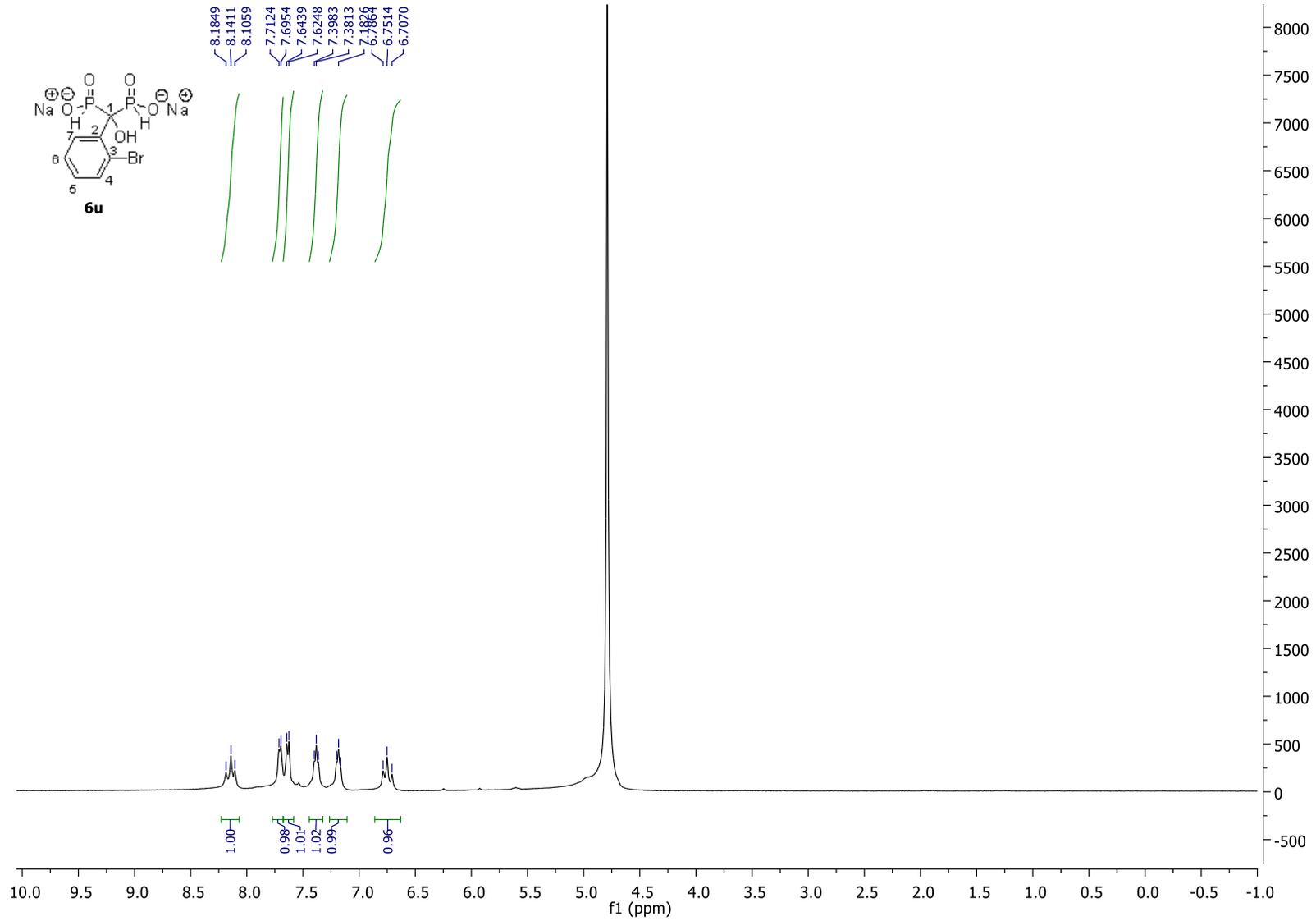


Figure 69: ¹H NMR spectrum of 1-hydroxy-1-(2-bromophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6u**)

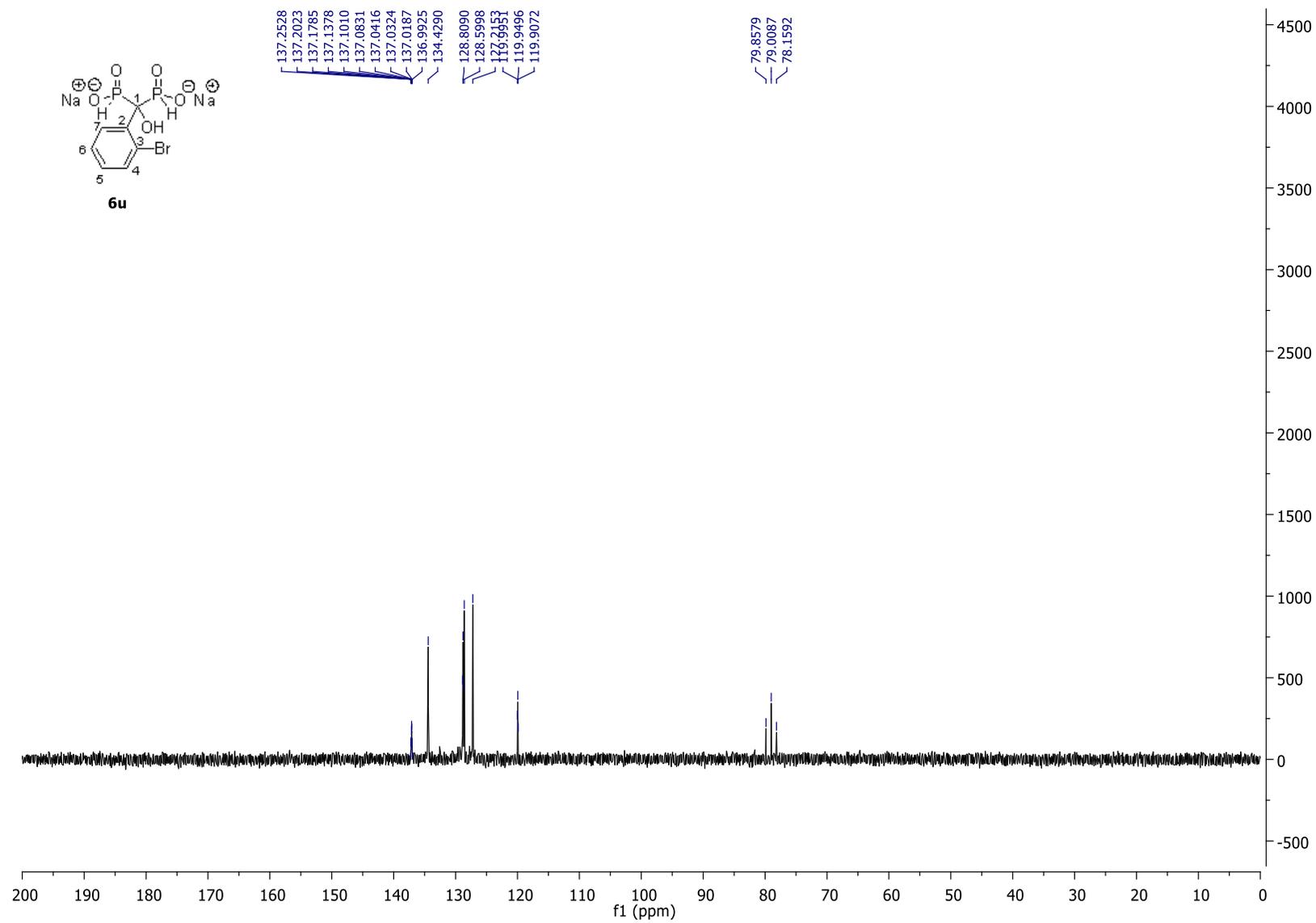


Figure 70: ^{13}C NMR spectrum of 1-hydroxy-1-(2-bromophenyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6u**)

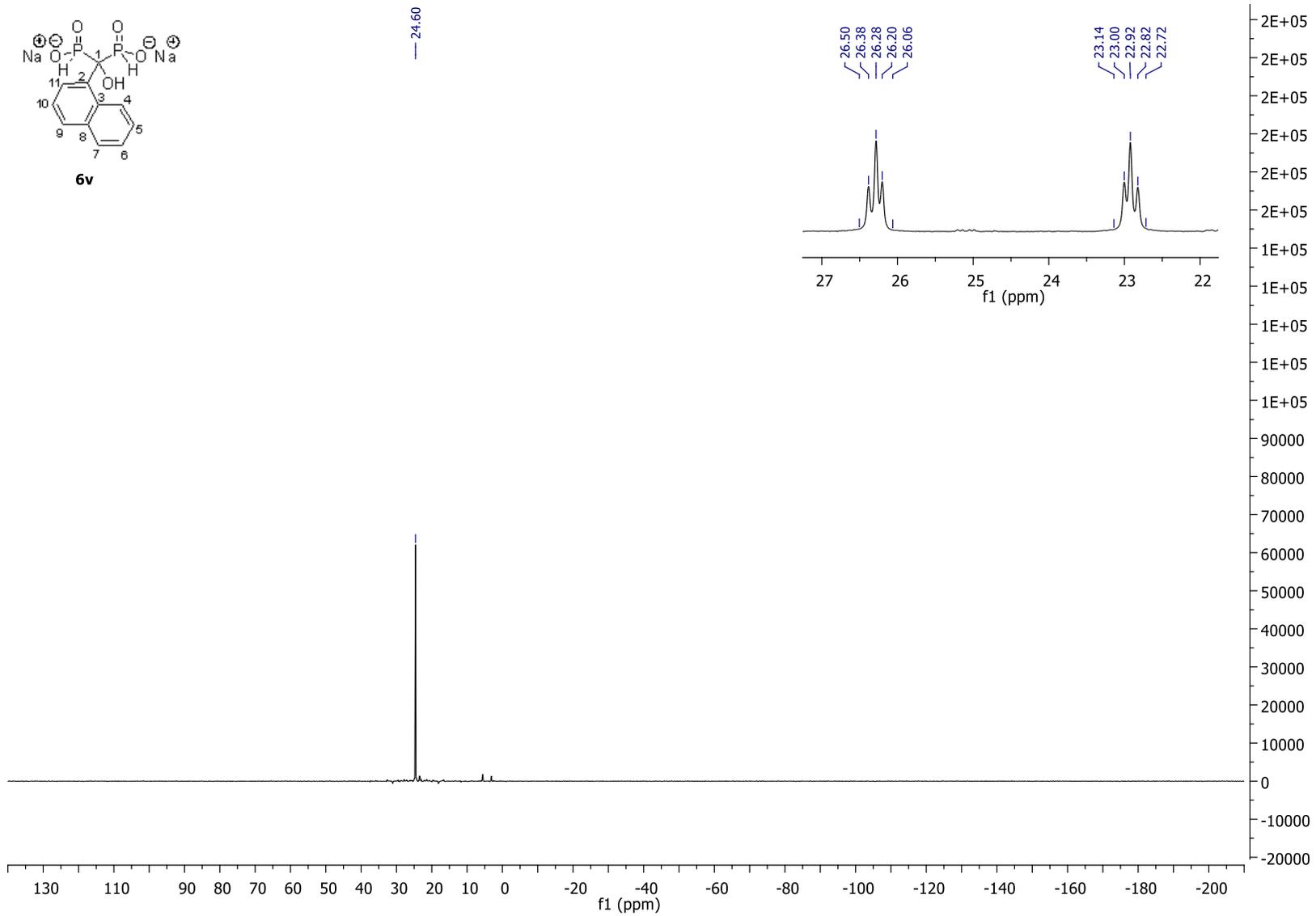
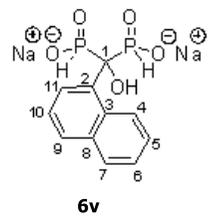


Figure 71: $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-naphthylmethane-1,1-bis(*H*-phosphinate) disodium salt (**6v**)

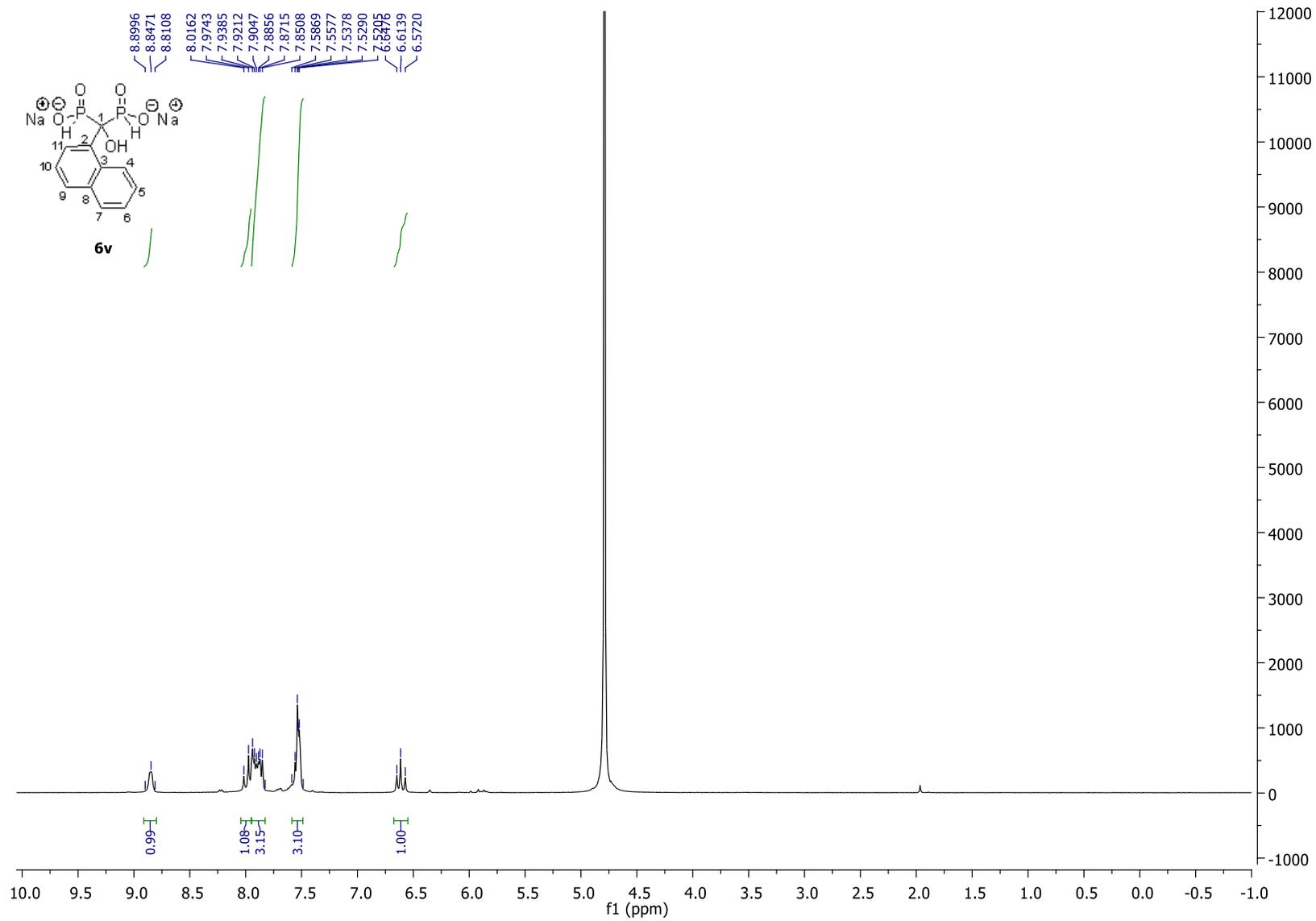


Figure 72: ^1H NMR spectrum of 1-hydroxy-1-naphthylmethane-1,1-bis(*H*-phosphinate) disodium salt (**6v**)

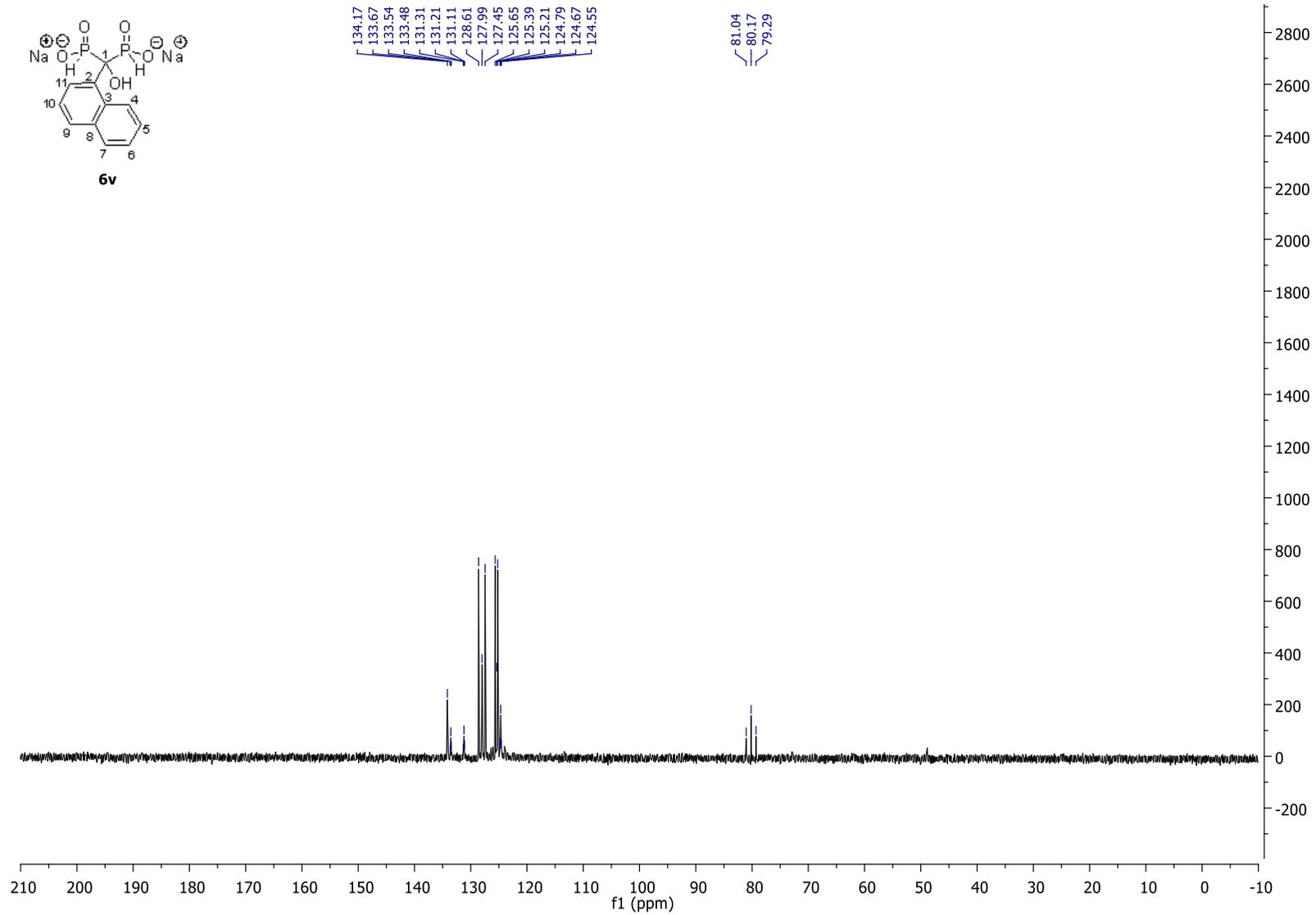


Figure 73: ^{13}C NMR spectrum of 1-hydroxy-1-naphthylmethane-1,1-bis(*H*-phosphinate) disodium salt (**6v**)

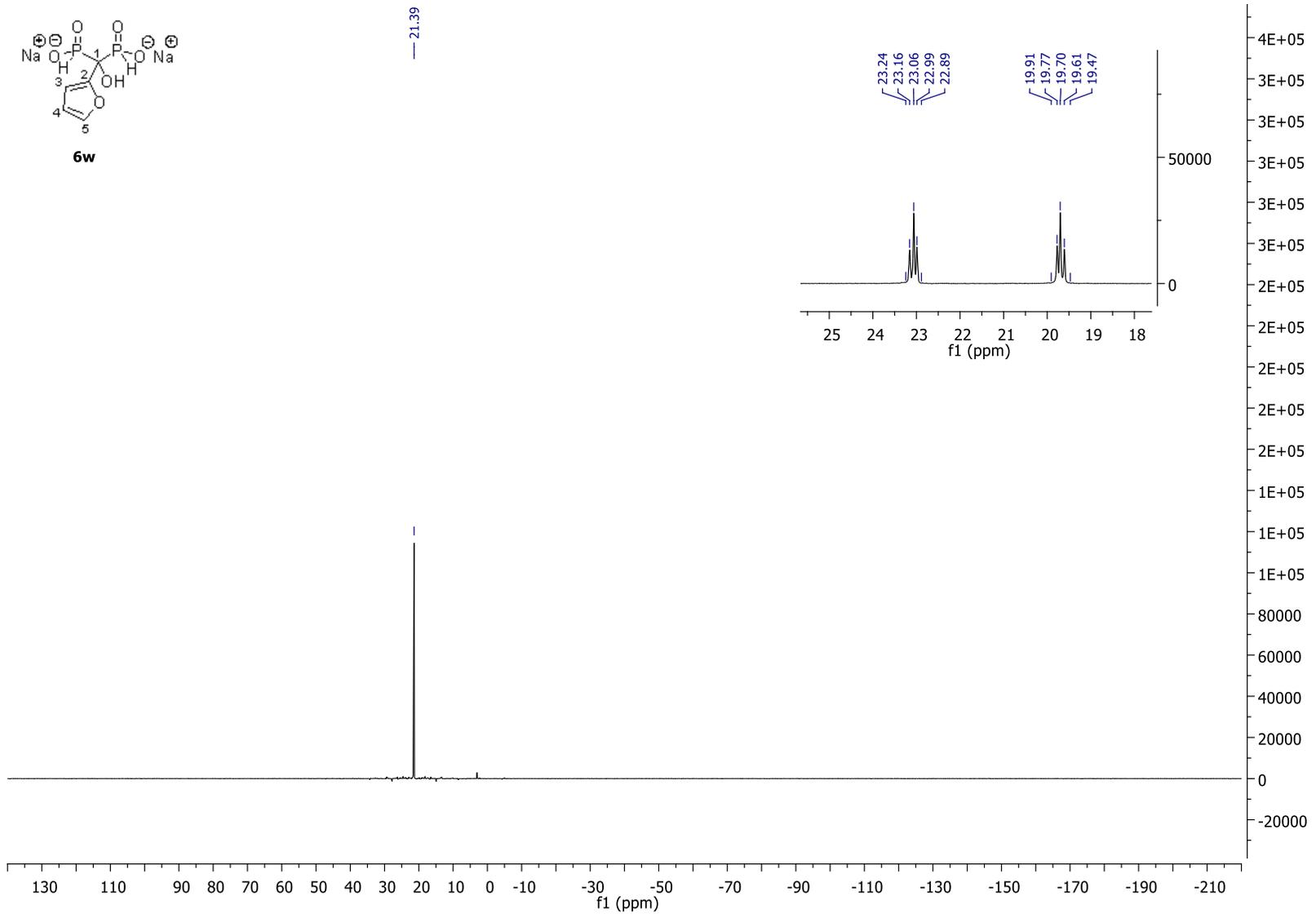


Figure 74: ³¹P{¹H} and ³¹P NMR spectra of 1-(fur-2-yl)-1-hydroxymethane-1,1-bis(*H*-phosphinate) disodium salt (**6w**)

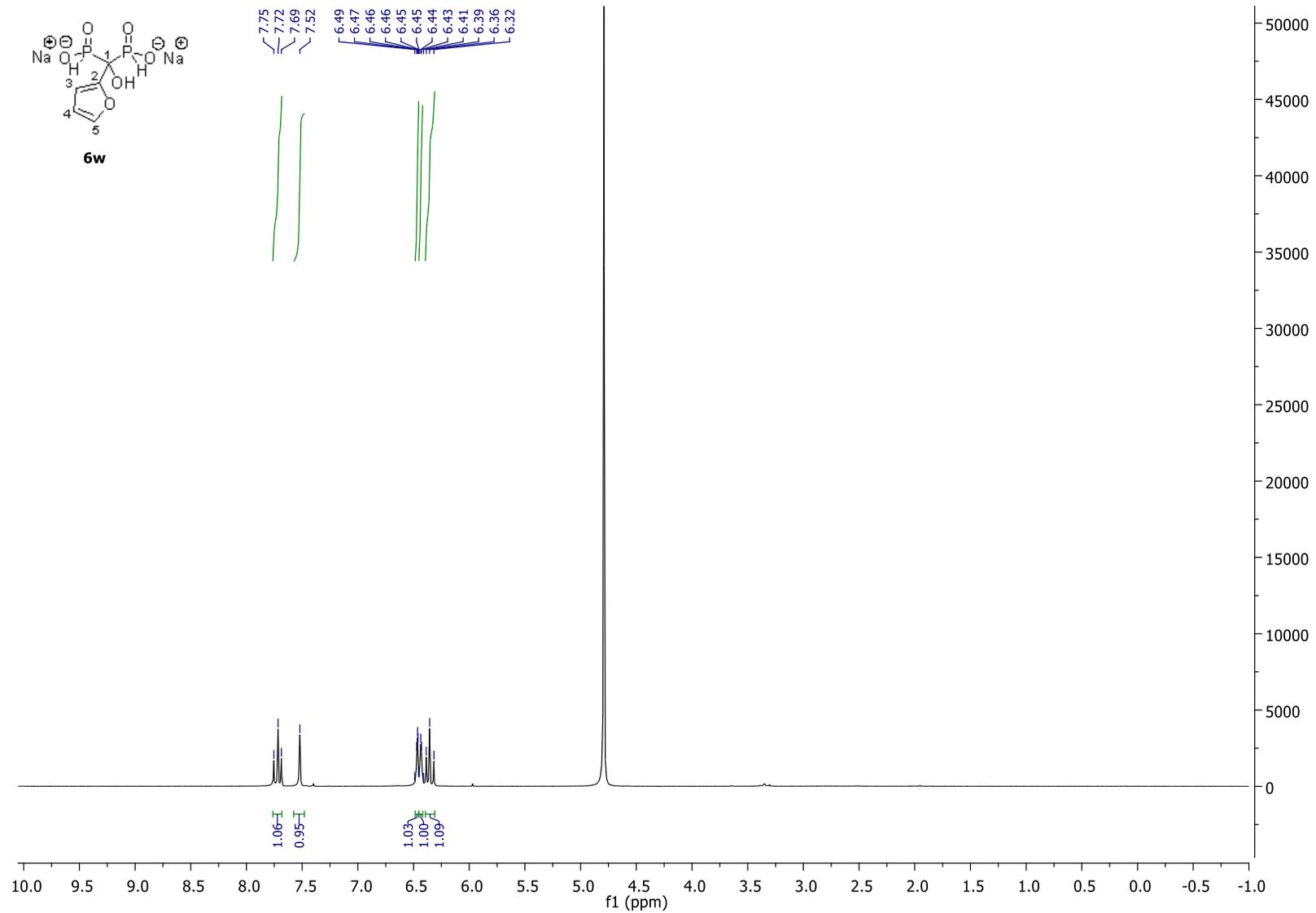


Figure 75: ¹H NMR spectrum of 1-(fur-2-yl)-1-hydroxymethane-1,1-bis(*H*-phosphinate) disodium salt (6w)

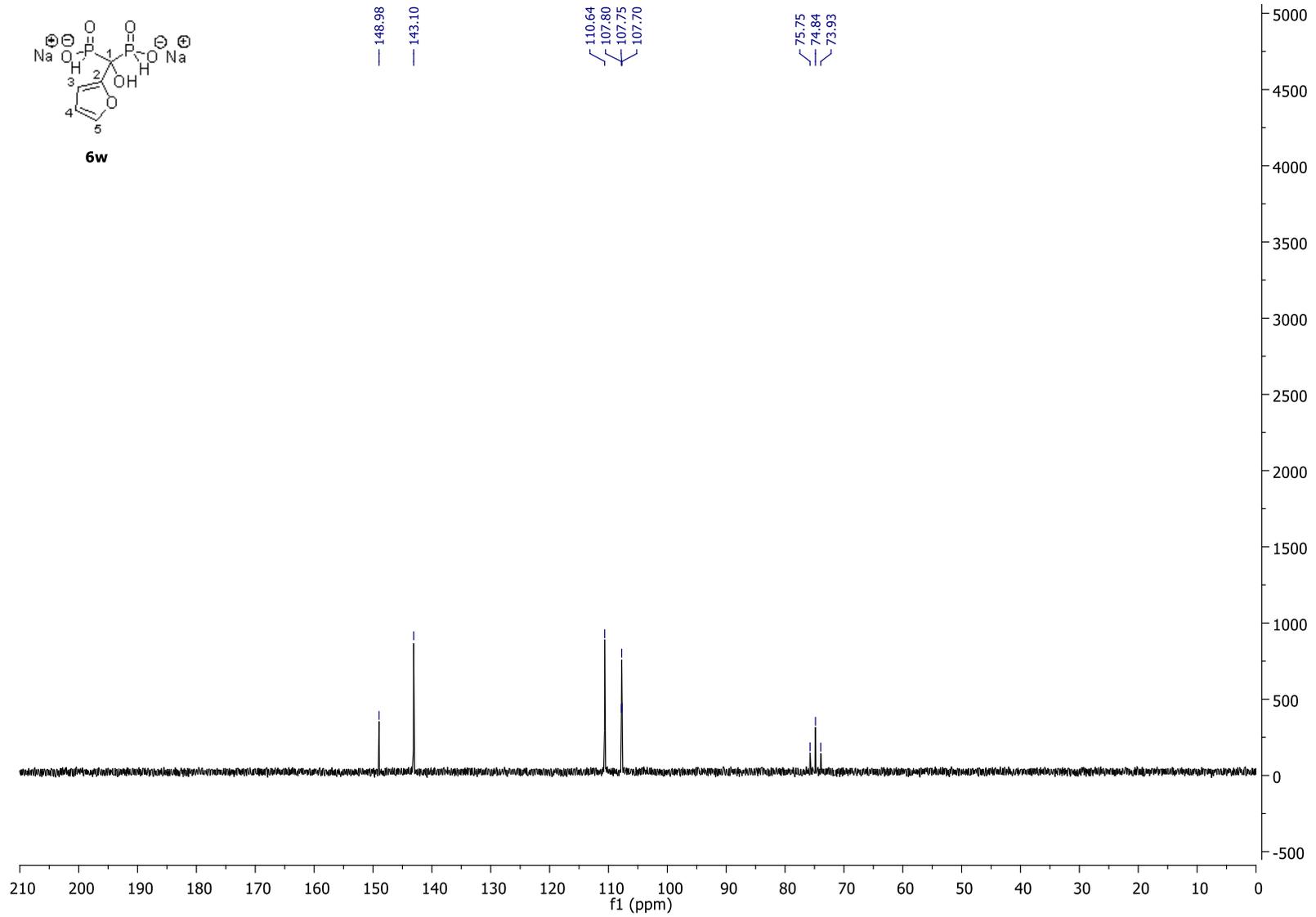


Figure 76: ¹³C NMR spectrum of 1-(fur-2-yl)-1-hydroxymethane-1,1-bis(*H*-phosphinate) disodium salt (6w)

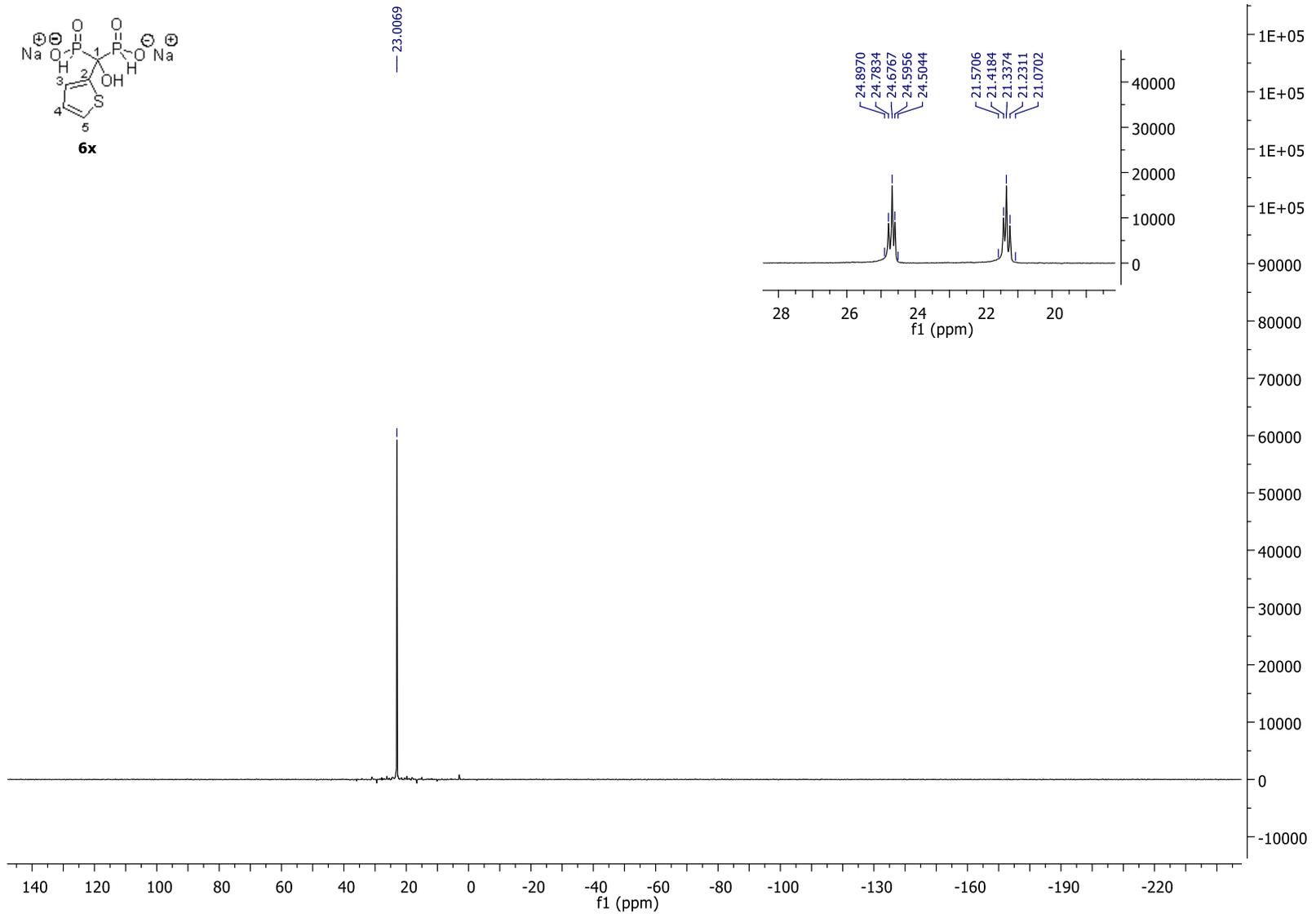


Figure 77 : ³¹P{¹H} and ³¹P NMR spectra of 1-hydroxy-1-(2-thienyl)methane-1,1-bis(*H*-phosphinate) disodium salt (**6x**)

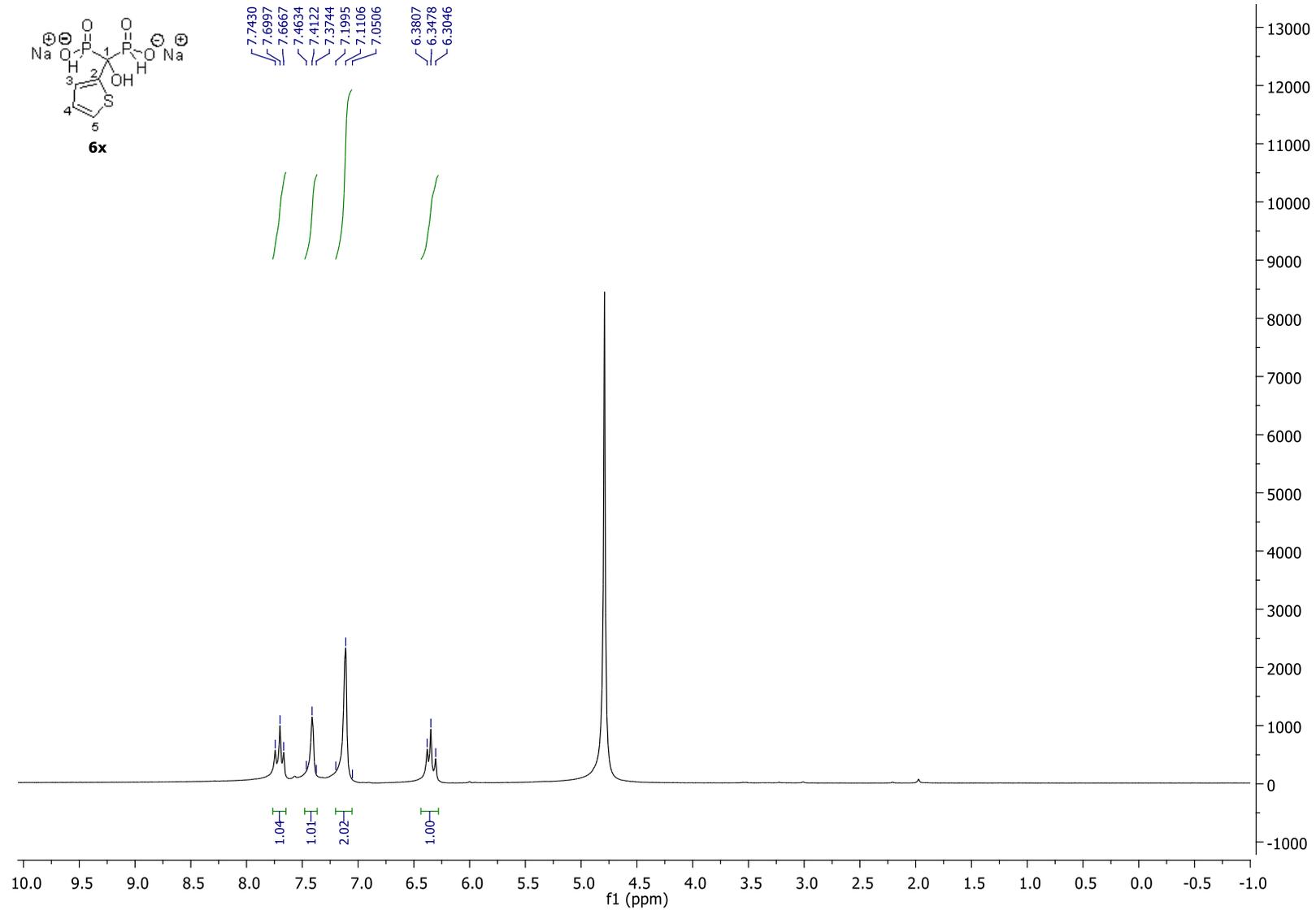


Figure 78 : ¹H NMR spectrum of 1-hydroxy-1-(2-thienyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6x)

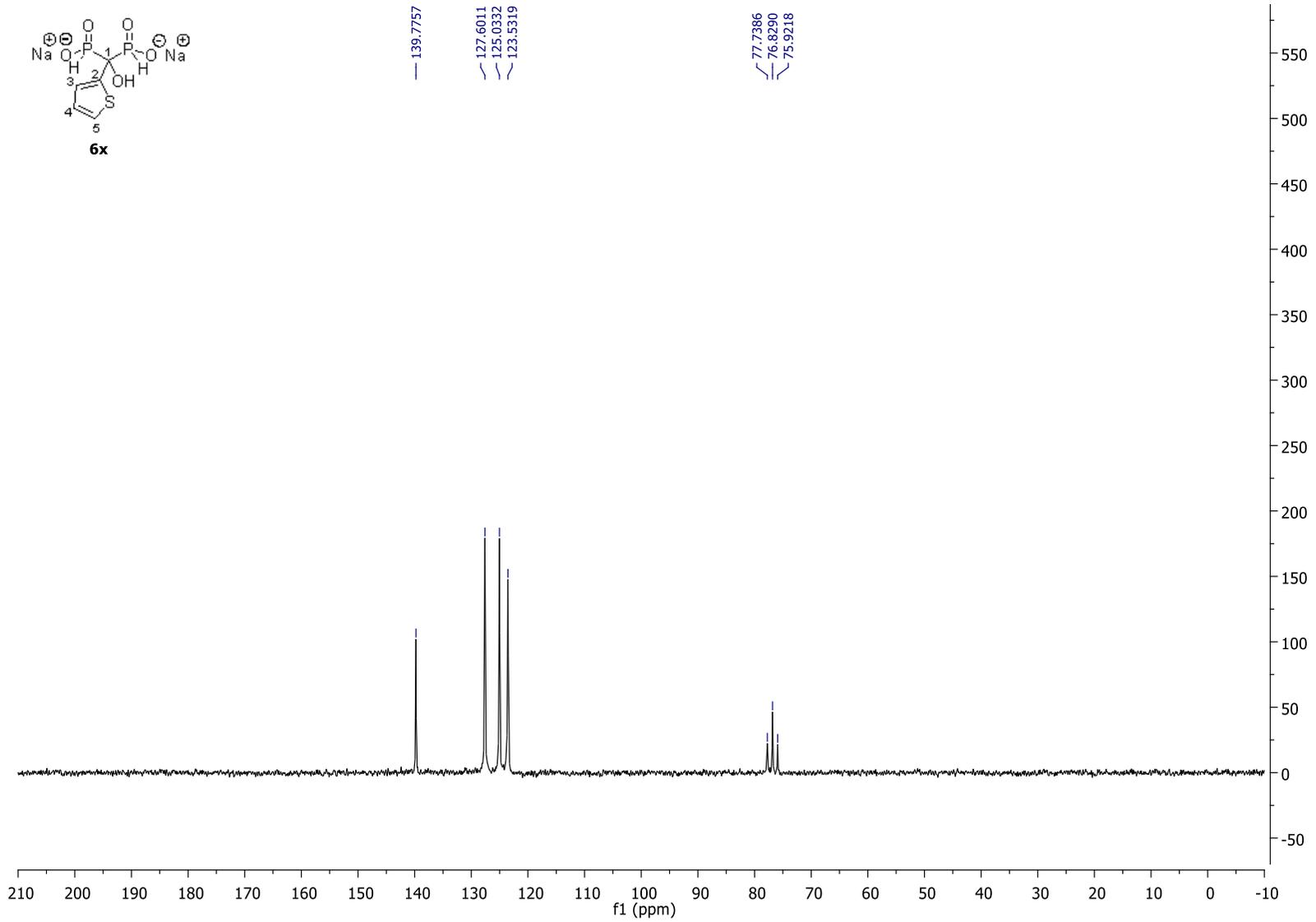


Figure 79 : ¹³C NMR spectrum of 1-hydroxy-1-(2-thienyl)methane-1,1-bis(*H*-phosphinate) disodium salt (6x)

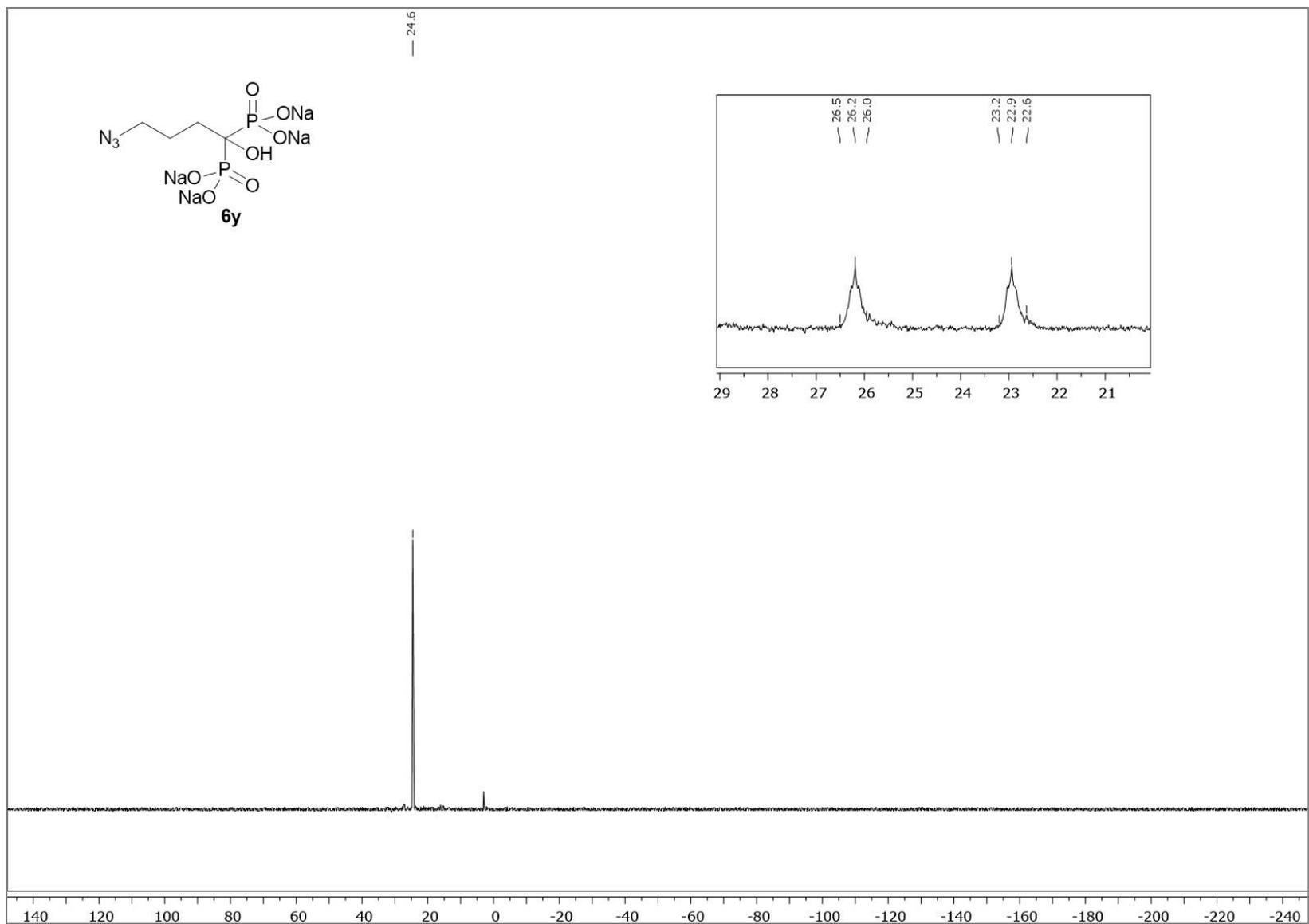


Figure 80 : $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(3-azidopropyl)methane-1,1-bis(H-phosphinate) disodium salt (**6y**)

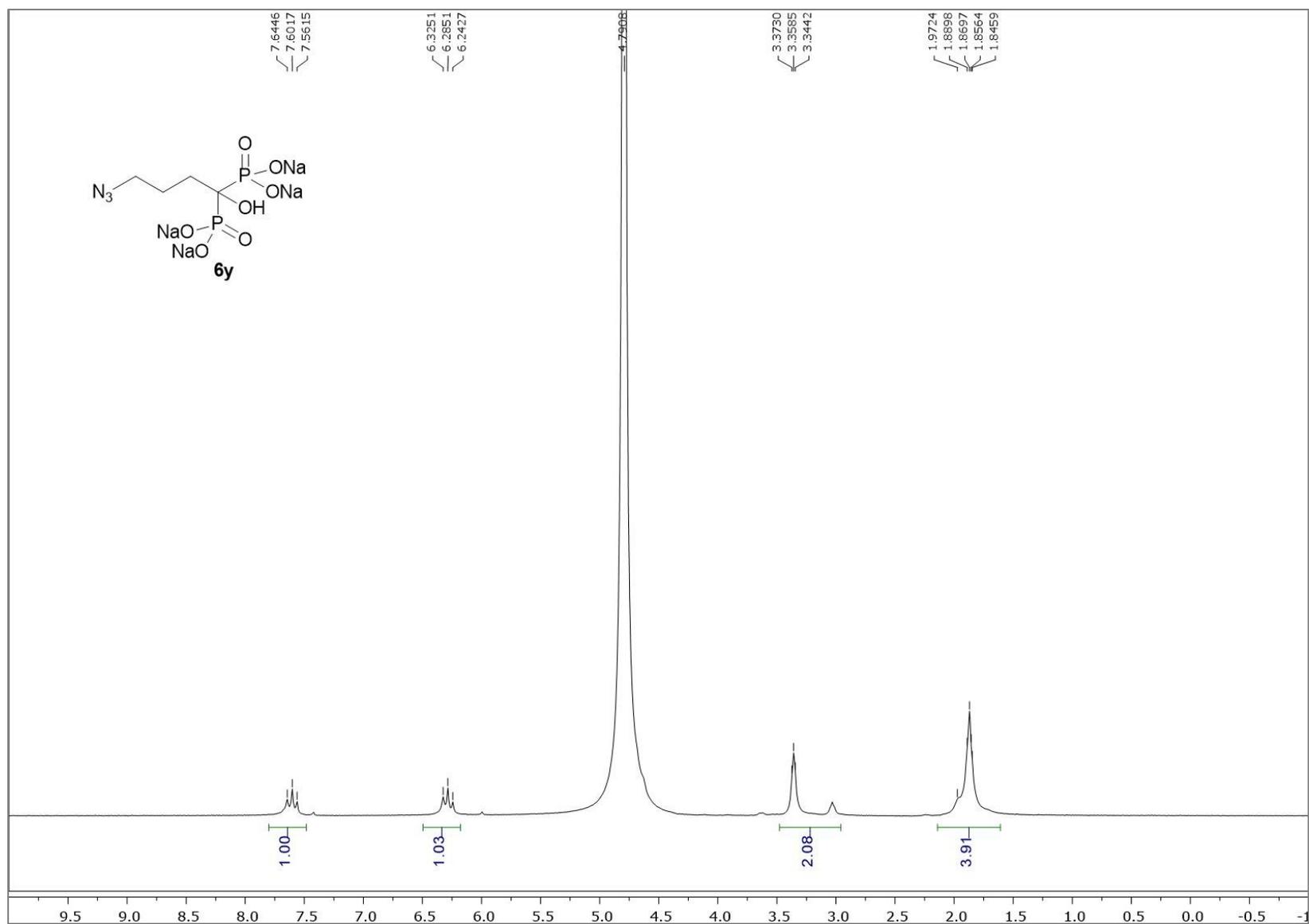


Figure 81 : ¹H NMR spectra of 1-hydroxy-1-(3-azidopropyl)methane-1,1-bis(H-phosphinate) disodium salt (6y)

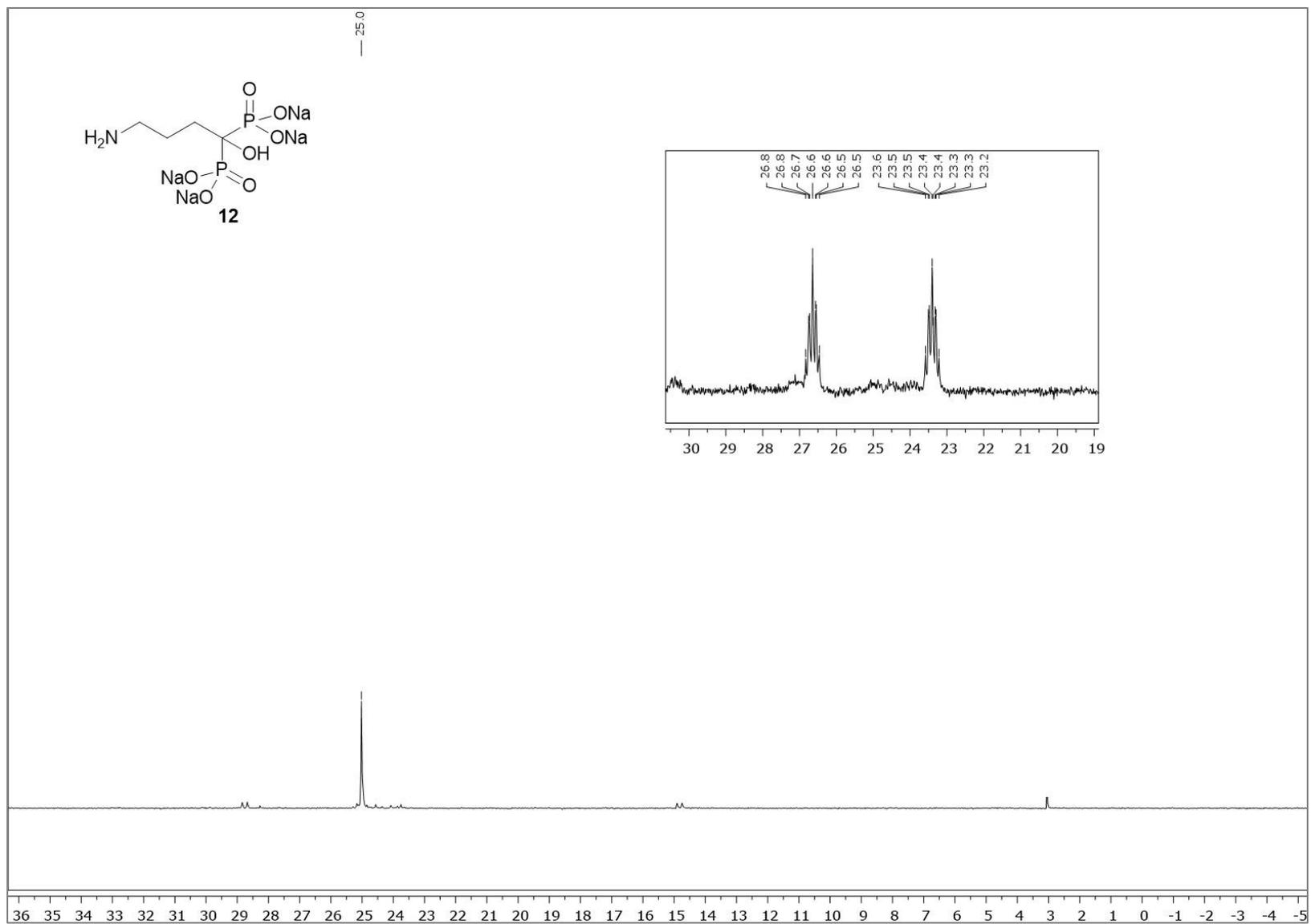


Figure 83 : $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of 1-hydroxy-1-(3-aminopropyl)methane-1,1-bis(*H*-phosphinate) disodium salt (12)

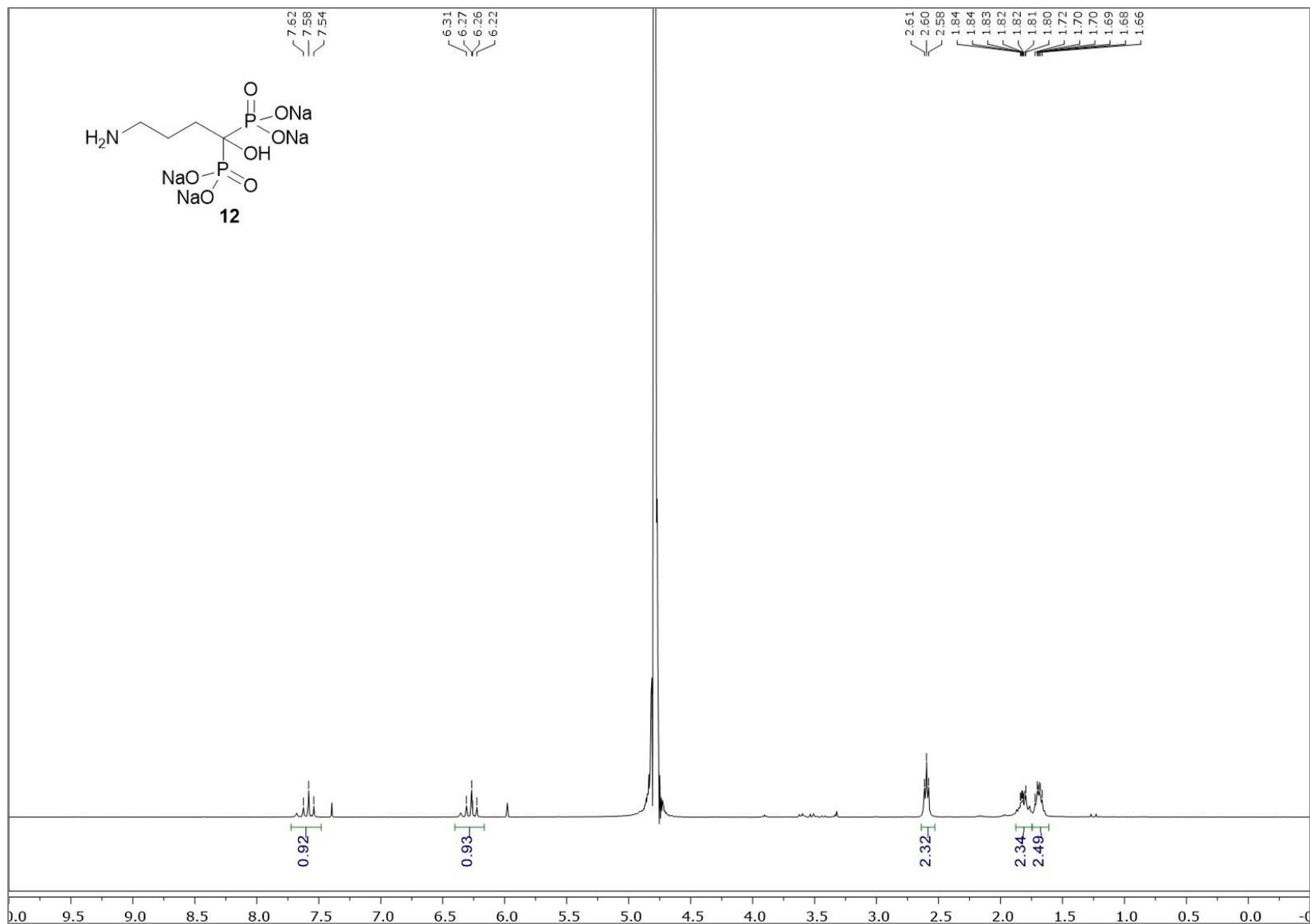


Figure 84 : ^1H NMR spectra of 1-hydroxy-1-(3-aminopropyl)methane-1,1-bis(*H*-phosphinate) disodium salt (12)

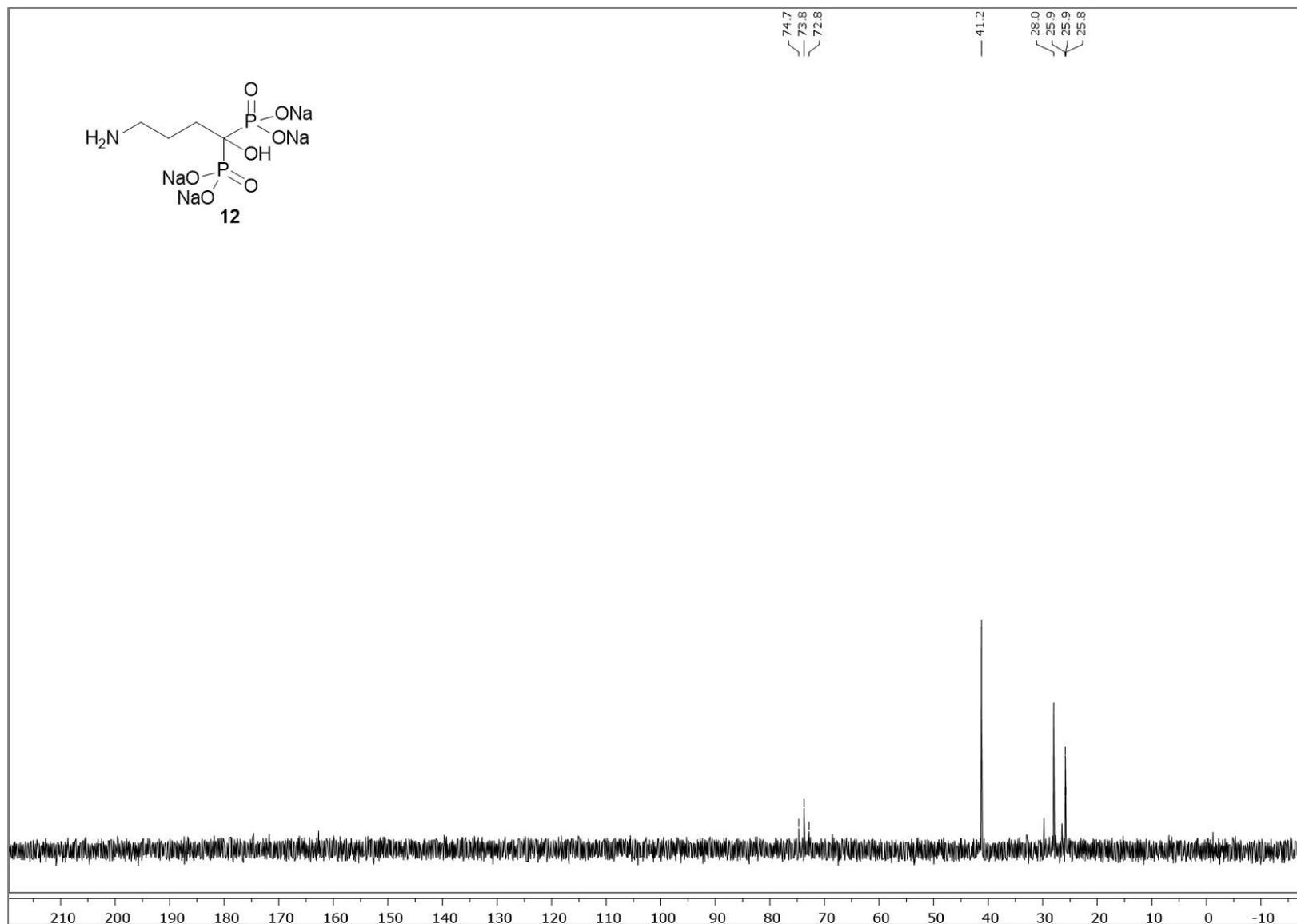


Figure 85 : ^{13}C NMR spectra of 1-hydroxy-1-(3-aminopropyl)methane-1,1-bis(*H*-phosphinate) disodium salt (12)