Electronic Supplementary Material (ESI) for Chemical Communications

Efficient asymmetric synthesis of trifluoromethylated β-aminophosphonates and their incorporation into dipeptides

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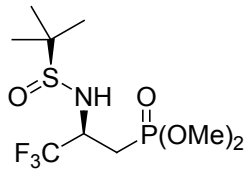
CONTENTS

General Information. NMR spectra were recorded on a Bruker DRX 500 or Varian Union Plus 400 spectrometers using TMS (^{1}H) and $CFCl_3$ (^{19}F) as an internal standards and H_3PO_4 (^{31}P) as an external standard. Chemical shifts (δ) are reported in ppm. J values are given in Hz. Analytical TLCs were performed with Merck Silica gel 60 F_{254} plates. Visualization was accomplished by spraying with solution of ceric ammonium molybdate followed by brief heating. Flash chromatography was carried out using Merck Silica gel 60 (0.040-0.063 mm). IR spectra were recorded on Bruker VERTEX 70 FT-IR spectrometer. Absorption bands are reported in cm^{-1}. Optical rotations were measured on Anton Paar MCP 300 Modular Circular Polarimeter with a 1.0 dm cell length, wavelength 589 nm, $[\alpha]_D$ values are given in deg.

Synthesis of (S_S,*R*)-dialkyl 2-(*tert*-butylsulfinylamino)-3,3,3-trifluoropropylphosphonates 4a-d; General Procedure.

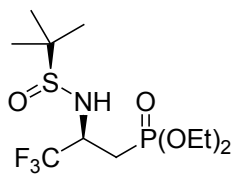
To a solution of appropriate dialkyl methylphosphonate (2.2 mmol) in THF (4 mL) *n*-BuLi (1.25 mL, 1.6 M in hexane, 2.0 mmol) was added dropwise via syringe at -78 °C and reaction mixture was stirred at this temperature for 1 h. Then pre-cooled to -78 °C solution of imine (*S*)-**1** (201 mg, 1.0 mmol) in THF (2 mL) was transferred *via* cannula into reaction mixture. After additional stirring for 0.5 h at -78 °C the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (6 mL) and warmed to room temperature. The solution was extracted with EtOAc (3 x 10 mL) and the combined organic phases were dried (Na_2SO_4) and concentrated. The residue was dried under a high vacuum pump (0.5 mm Hg) at 30-35 °C to remove excess of dialkyl methylphosphonate. The diastereoselectivity was determined by ^{19}F and ^{31}P NMR spectroscopy. Purification by flash chromatography afforded (S_S,*R*)-**4a-d** with 96-98% de.

***(S*$_S$,*R*)-Dimethyl 2-(*tert*-butylsulfinylamino)-3,3,3-trifluoropropylphosphonate (4a).**



Purification by flash chromatography on silica gel, eluent ethyl acetate-ethanol 10:0.4; yield 53%, mp 123-125 °C (from hexane); white needles; $[\alpha]_D^{20}$ +4.9 (c = 1.90, $CHCl_3$). IR (KBr): 3231, 2967, 2935, 2877, 1474, 1265, 1230, 1126, 1038 cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 1.22 (9 H, s), 2.17-2.24 (2 H, m), 3.73 (3 H, d, *J* = 3.3), 3.75 (3 H, d, *J* = 3.3), 4.01-4.12 (1 H, m), 4.56-4.60 (1 H, m); δ_C (100 MHz, $CDCl_3$, Me_4Si) 22.4 (s), 25.4 (d, $J_{C\text{-}P}$ = 147.5), 52.7 (d, $J_{C\text{-}P}$ = 6.6), 52.9 (d, $J_{C\text{-}P}$ = 6.6), 53.5 (qd, $J_{C\text{-}F}$ = 31.5, $J_{C\text{-}P}$ = 4.4), 57.4 (s), 124.6 (qd, $J_{C\text{-}F}$ = 283.2, $J_{C\text{-}P}$ = 16.1); δ_F (376 MHz, $CDCl_3$, $CFCl_3$) –76.0 (d, *J* = 6.0); δ_P (202 MHz, $CDCl_3$, H_3PO_4) 28.8 (s); MS(API-ES): m/z = 326.0 $[M + H]^+$; Found: C, 33.3; H, 6.0; N, 4.7; P, 9.4; S, 10.0. Calc. for $C_9H_{19}F_3NO_4PS$: C, 33.2; H, 5. 9; N, 4.3; P, 9.5; S, 9.9%.

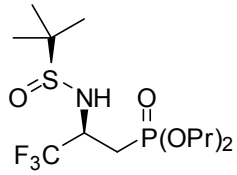
***(S*$_S$,*R*)-Diethyl 2-(*tert*-butylsulfinylamino)-3,3,3-trifluoropropylphosphonate (4b).**



Purification by flash chromatography on silica gel, eluent ethyl acetate-ethanol 10:0.2, followed by crystallisation from hexane-ethyl acetate, yield 55%; white needles; mp 123-124 °C (from hexane-ethylacetate); $[\alpha]_D^{20}$ +6.6 (c = 1.28, $CHCl_3$). IR (KBr) 3186, 2987, 2935, 2875, 1410,

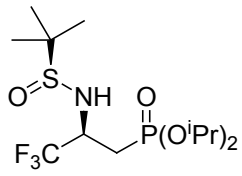
1264, 1229 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H (400 MHz, $CDCl_3$, Me_4Si) 1.21 (9 H, s), 1.29 (3 H, t, J = 7.0), 1.30 (3 H, t, J = 7.0), 2.15-2.22 (2 H, m), 3.04-4.13 (5 H, m), 4.48 (1 H, dm, J = 9.8); δ_C (100 MHz, $CDCl_3$, Me_4Si) 16.3 (d, J = 3.7), 16.4 (d, J = 3.7), 22.4 (s), 26.6 (d, J = 145.3), 54.1 (qd, J_{C-F} = 31.5, J_{C-P} = 5.1), 57.3 (s), 62.2 (d, J = 6.6), 62.4 (d, J = 6.6), 124.7 (qd, J_{C-F} = 283.2, J_{C-P} = 15.4); δ_F (376 MHz, $CDCl_3$, $CFCl_3$) –75.6 (d, J = 7.1); δ_P (202 MHz, $CDCl_3$, H_3PO_4) 26.0 (s); MS(API-ES): m/z = 354.2 $[M + H]^+$; Found: C, 37.2; H, 6.55; N, 4.1; P, 8.9; S, 9.4. Calc. for $C_{11}H_{23}F_3NO_4PS$: C, 37.4; H, 6.6; N, 4.0; P, 8.8; S, 9.1%.

(S_s,*R*)-Dipropyl 2-(*tert*-butylsulfinylamino)-3,3,3-trifluoropropylphosphonate (4c)



Purification by flash chromatography on silica gel, eluent ethyl acetate-ethanol 10:0.2; yield 68%, mp 73-75 °C (from hexane); white needles; $[\alpha]_D^{20}$ +2.8 (c = 1.12, $CHCl_3$). IR (KBr): 3483, 3177, 2970, 1474, 1062, 1002, 873, 505 cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.95 (6 H, br t, J = 7.0), 1.24 (9 H, s), 1.64-1.73 (4 H, m), 2.20-2.25 (2 H, m), 4.00 (4 H, br quint), 4.03-4.13 (1 H, m), 4.54 (1 H, d, J = 8.82); δ_C (100 MHz, $CDCl_3$, Me_4Si) 9.9 (s), 10.0 (s), 22.3 (s), 23.7 (d, J = 2.0), 23.8 (d, J = 2.0), 26.4 (d, J_{C-P} = 145.6), 54.0 (qd, J_{C-F} = 31.9, J_{C-P} = 5.0), 57.3 (s), 67.7 (d, J = 6.9), 67.9 (d, J = 6.9), 124.7 (qd, J_{C-F} = 283.2, J_{C-P} = 16.0); δ_F (376 MHz, $CDCl_3$, $CFCl_3$)–75.7 (d, J = 5.7); δ_P (202 MHz, $CDCl_3$, H_3PO_4) 26.0 (s); MS(API-ES): m/z = 383.2 $[M + H]^+$; Found: C, 40.85; H, 7.2; N, 3.7; P, 7.9; S, 8.7. Calc. for $C_{13}H_{27}F_3NO_4PS$: C, 40.9; H, 7.1; N, 3.7; P, 8.1; S, 8.4%.

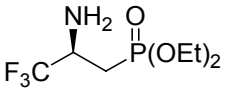
(S_s,*R*)- Diisopropyl 2-(*tert*-butylsulfinylamino)-3,3,3-trifluoropropylphosphonate (4d)



Purification by flash chromatography on silica gel, eluent ethyl acetate-ethanol 10:0.2; yield 75%, mp 64-65 °C (from hexane); white needles; $[\alpha]_D^{20}$ +1.2 (c = 1.67, $CHCl_3$). IR (KBr): 3443, 3116, 2988, 2932, 1265, 1219, 1059, 983 cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 1.20 (9 H, s), 1.26 (6 H, t, J = 2.4), 1.28 (6 H, t, J = 2.4), 2.09-2.16 (2 H, m), 3.94-4.07 (1 H, m), 4.55 (1 H, d, J = 9.4), 4.62–4.72 (2 H, m); δ_C (100 MHz, $CDCl_3$, Me_4Si) 22.5(s) , 23.9 (d, J = 4.4), 24.0 (d, J = 5.9), 24.1 (br s), 24.2 (d, J = 4.8), 28.0 (d, J = 146.7), 54.2 (qd, J = 31.6, J = 5.1), 57.3 (s), 71.2 (d, J = 6.6), 71.4 (d, J = 6.6), 124.8 (qd, J = 283.6, J = 15.4); δ_F (376 MHz, $CDCl_3$, $CFCl_3$) –

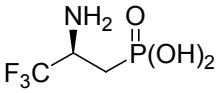
75.4 (d, J = 6.8); δ_P (202 MHz, $CDCl_3$, H_3PO_4) 23.9 (s); MS(API-ES): m/z = 382.2 $[M + H]^+$; Found: C, 41.0; H, 7.1; N, 3.4; P, 7.9; S, 8.55. Calc. for $C_{13}H_{27}F_3NO_4PS$: C, 40.9; H, 7.1; N, 3.7; P, 8.1; S, 8.4%.

(*R*)-Diethyl 2-amino-3,3,3-trifluoroethylphosphonate (5).



A solution of *N*-sulfinyl β-aminophosphonate (S_S,*R*)-**4b** (280 mg, 0.79 mmol) in alcohol (3.5 mL) and 4 N HCl (3.5mL) was stirred at room temperature for 18 h. The resulting solution was concentrated under reduced pressure, residue was dissolved in CH_2Cl_2 (4 mL) and neutralized to pH 7.5 with saturated $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layers were washed with water (5 mL), dried over Na_2SO_4 and concentrated to give 165 mg (83.5%) of **5** as white solid, mp 71-72°C (from hexane); $[\alpha]_D^{20}$ -21.2 (c = 1.71, $CHCl_3$). IR (KBr): 3386, 2989, 1254, 1232, 1168, 1116, 1031, 980, 523 cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 1.27 (3 H, t, J = 2.4), 1.28 (3 H, t, J = 2.4), 1.74 (2 H, s), 1.83 (1 H, ddd, J = 11.4, J_{H-H} = 15.4, J = 17.3), 2.08 (1 H, ddd, J = 20.7, J_{H-H} = 15.4, 2.2), 3.55-3.66 (1 H, m), 4.03-4.14 (4 H, m); δC (100 MHz, $CDCl_3$, Me_4Si) 16.4 (s), 16.5 (s), 27.1 (d, J = 146.7), 49.9 (qd, J_{C-F} = 30.8, J_{C-P} = 4.4), 62.1 (d, J = 6.6), 62.3 (d, J = 5.8), 125.8 (qd, J_{C-F} = 280.1, J_{C-P} = 23.2); δ_F (376 MHz, $CDCl_3$, $CFCl_3$) –80.4 (d, J = 6.0); δ_P (202 MHz, $CDCl_3$, H_3PO_4) 28.1 (s); MS(API-ES): m/z = 250.2 $[M + H]^+$; Found: C, 33.8; H, 6.2; N, 5.5; P, 12.6. Calc. for $C_7H_{15}F_3NO_3P$: C, 33.7; H, 6.1; N, 5.6; P, 12.4%.

(*R*)-2-Amino-3,3,3-trifluoropropylphosphonic acid (6)

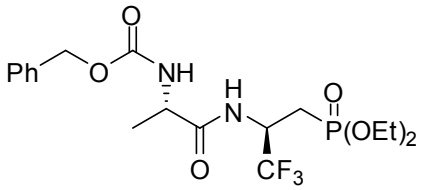


A solution of (*R*)-**5** (249 mg, 1 mmol) in 10 N HCl (6 mL) was refluxed for 6 h and then concentrated under reduce pressure to dryness. The resulting solid was treated with EtOH (3 mL) and propylene oxide (0.25 mL, 3.00 mmol) and the reaction mixture was stirred for 3 h. Precipitate was filtered off and washed with ether to provide product **6** (192 mg, 99%) as a white solid; mp 301-302 °C; $[\alpha]_D^{20}$ -14.7 (c = 1.10, H_2O); IR (KBr): 3005, 2819, 2567, 1287, 1219, 1172, 1113, 1012 cm^{-1}; δ_H (400 MHz, D_2O+CH_3CN) 1.85-1.96 (1 H, m), 2.08-2.18 (1 H, m), 4.10-4.21 (1 H, m); δ_C (100 MHz, D_2O+CH_3CN, Me_4Si) 24.7 (d, J = 131.3), 50.0 (qd, J_{C-F} = 33.7, J_{C-P} = 3.7), 123.9 (qd, J_{C-F} = 280.2, J_{C-P} = 19.0); δ_F (376 MHz, D_2O, $CFCl_3$) –74.2 (d, J = 6.8); δ_P (202 MHz, D_2O, H_3PO_4) 22.7 (s); MS(API-ES): m/z = 194.0 $[M + H]^+$; Found: C, 18.4; H, 3.9; N, 7.1; P, 15.9. Calc. for $C_3H_7F_3NO_3P$: C, 18.7; H, 3.65; N, 7.3; P, 16.1%.

General Procedure for Coupling of (*R*)-Diethyl 2-amino-3,3,3-trifluoroethylphosphonate (5).

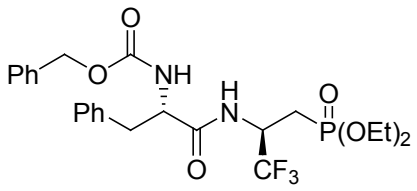
N-Methyl-morpholine (0.36 mmol) and isobutyl chloroformate (0.43 mmol) were added to a stirred solution of amino acid (0.36 mmol) in absolute ethyl acetate (16 mL) at -15 °C. After 30 min (*R*)-**5** (90 mg, 0.36 mmol) in dry ethyl acetate (10 mL) was added. The reaction mixture was stirred at -15 °C for 1 h and than at room temperature overnight. The reaction mixture was washed successively with H_2O, dilute citric acid, H_2O, saturated solution of $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Residue was treated with hexane and precipitate was filtered off.

(S,*R*)-Diethyl 2-(*N*-Cbz-alanylamino)-3,3,3-trifluoroethylphosphonate (7)



White solid; yield 55 %; mp 126–128°C (from hexane-ethyl acetate); $[\alpha]_D^{20}$ +4.3 (c 1.0, $CHCl_3$); δ_H NMR (400 MHz, $CDCl_3$, Me_4Si) 1.31 (3 H, t, J = 6.8), 1.32 (3 H, t, J = 6.8), 1.41 (3 H, d, J = 6.8), 2.03 – 2.24 (2 H, m), 4.04 – 4.13 (4 H, m), 4.38 (1 H, br s), 4.88-5.01 (1 H, m), 5.13 (2 H, s), 5.74 (1 H, br s), 7.01 (1 H, br s), 7.32-7.37 (5 H, m, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) 16.3 (s), 16.3(s), 18.5 (s), 24.9 (d, J = 148.6), 46.3 (qd, J = 32.0, J = 5.0), 50.6 (s), 62.3 (d, J = 6.0), 62.8 (d, J = 6.0), 67.0 (s), 124.5 (qd, $J_{C\text{-}F}$ = 282.2, $J_{C\text{-}P}$ = 20.4), 128.1, 128.2, 128.5, 136.3, 156.0, 172.5; δ_F (376 MHz, $CDCl_3$, $CFCl_3$) –76.2 (d, J = 6.9); δ_P (162 MHz, $CDCl_3$, H_3PO_4) 29.0 (s); MS(API-ES): m/z = 455.2 $[M + H]^+$; Found: C, 47.3; H, 5.9; N, 6.3; P, 6.6. Calc. for $C_{18}H_{26}F_3N_2O_6P$: C, 47.6; H, 5.8; N, 6.2; P, 6.8%.

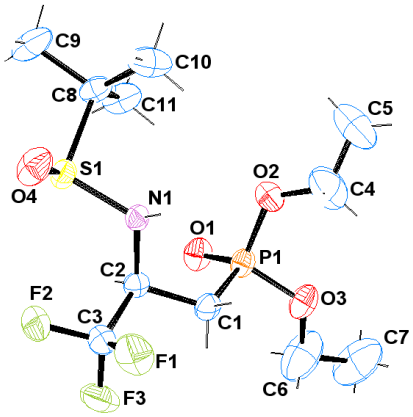
(S,*R*)-Diethyl 2-(*N*-Cbz-phenylalanylamino)-3,3,3-trifluoropropylphosphonate (8)



White solid; yield 60%; mp 144-146 °C (from hexane-ethyl acetate); $[\alpha]_D^{20}$ -4.0 (c 1.08 in $CHCl_3$); IR (KBr): 3325, 3280, 3069, 3038, 2975, 1692, 1670, 1538, 1269; cm^{-1}; δ_H (400 MHz, $CDCl_3$, Me_4Si) 1.28 (3 H, t, J = 6.9), 1.30 (3 H, t, J = 6.9), 1.94–2.21 (2 H, m), 2.96–3.06 (1 H, m), 3.20 (1 H, dd, J = 13.7, J = 6.2), 3.98–4.12 (4 H, m), 4.51 (1 H, m), 4.92 (1 H, m), 5.04 (2 H,

s), 5.54 (1 H, d, J = 8.1), 6.71 (1 H, m), 7.18 – 7.34 (10 H, m); δ_C (100 MHz, $CDCl_3$, Me_4Si) 16.3 (d, J = 2.9), 16.4 (d, J = 2.9), 24.9 (d, J = 146.0), 38.5 (s), 46.4 (qd, J = 32.3, J = 5.1), 56.2 (s), 62.4 (d, J = 6.6), 62.9 (d, J = 6.6), 66.9 (s), 126.9, 128.0, 128.1, 128.5, 128.6, 129.5, 136.3, 136.4, 156.0, 171.3; δ_F (376 MHz, $CDCl_3$, $CFCl_3$)–77.1 (br s); δ_P (202 MHz, $CDCl_3$, H_3PO_4) 26.2 (s); MS(API-ES): m/z = 531.2 $[M + H]^+$; Found: C, 54.38; H, 5.98; N, 5.4; P, 5.8. Calc. for $C_{24}H_{30}F_3N_2O_6P$: C, 54.3; H, 5.7; N, 5.3; P, 5.8%.

X-ray crystallography for 4b



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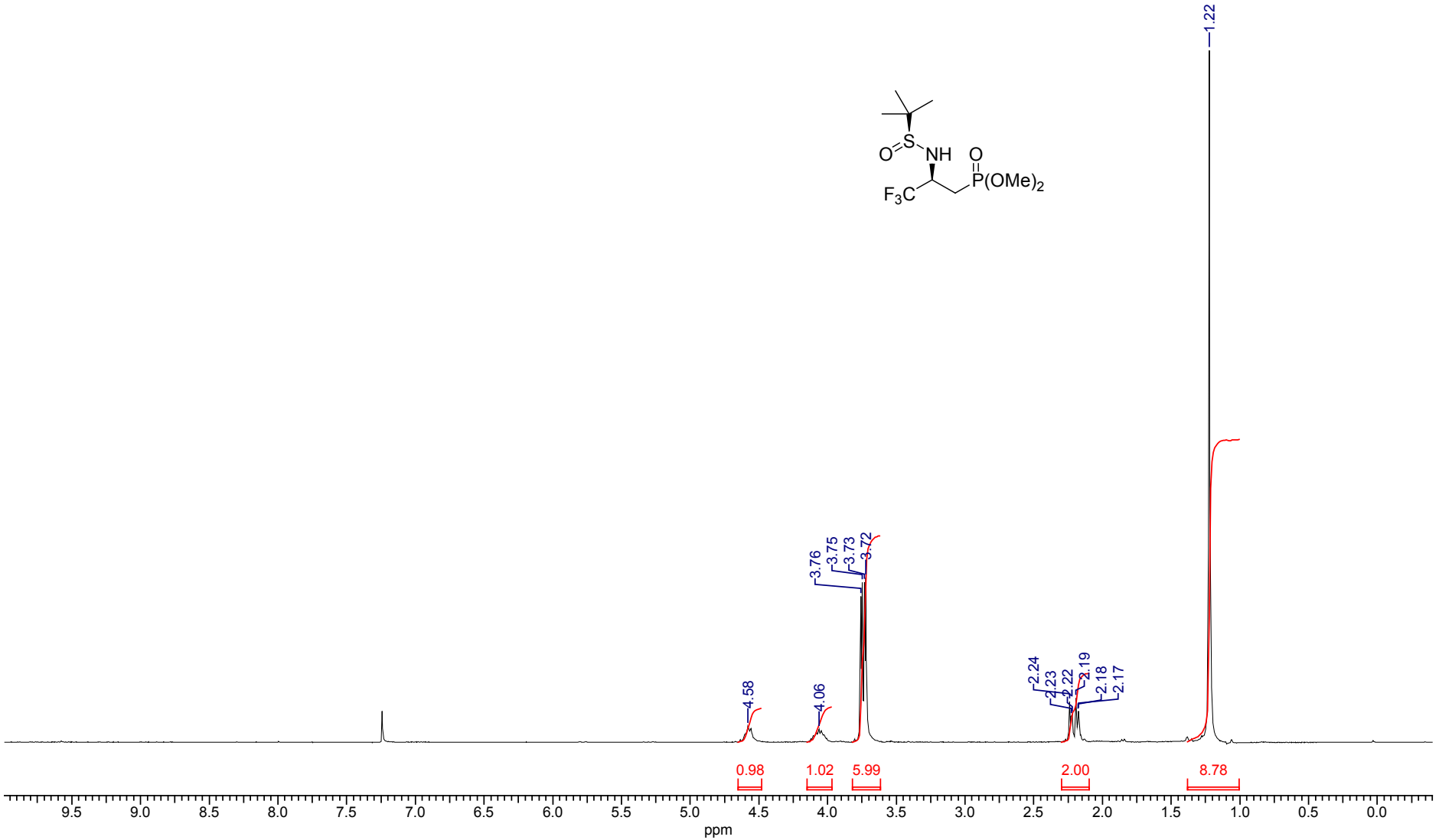

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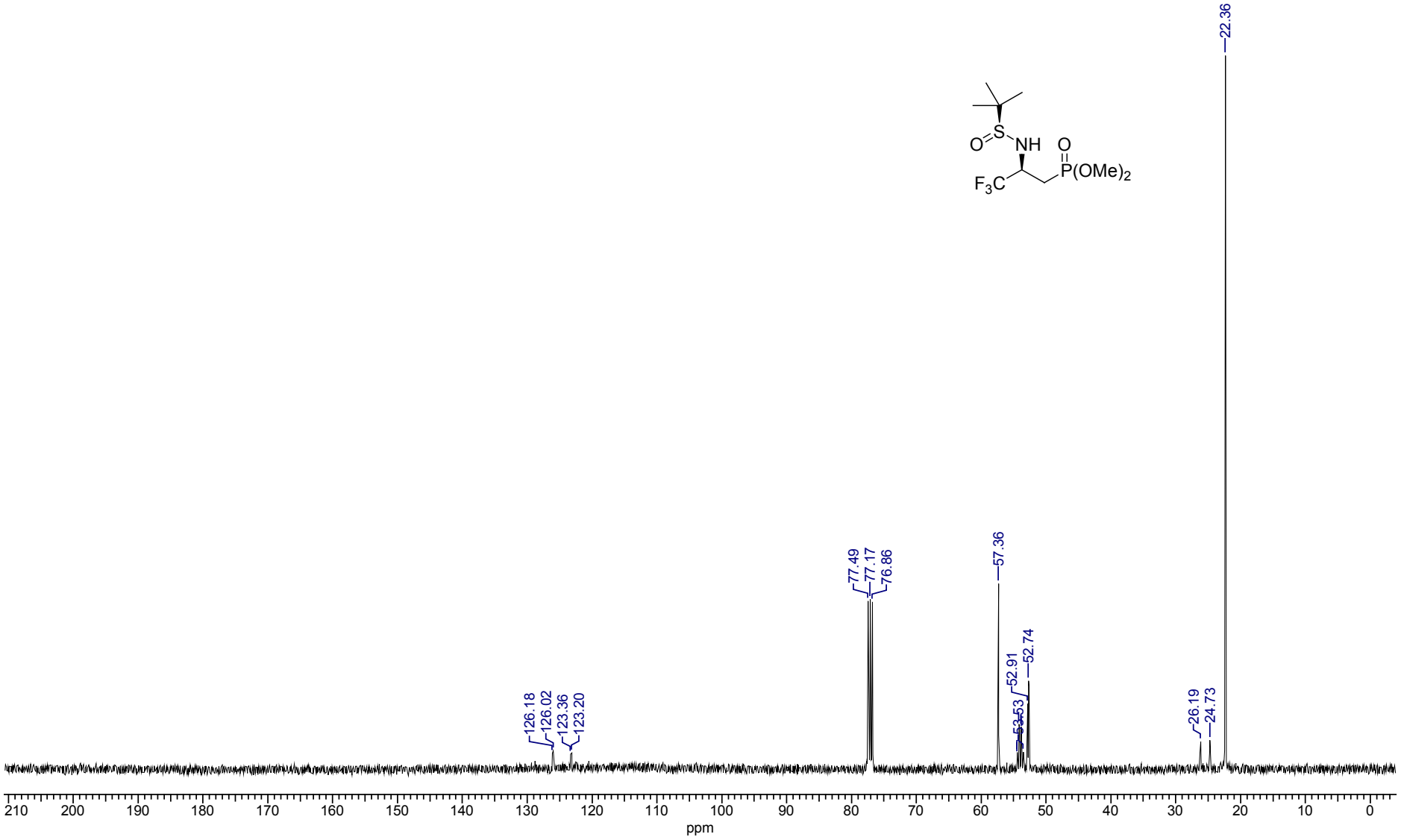

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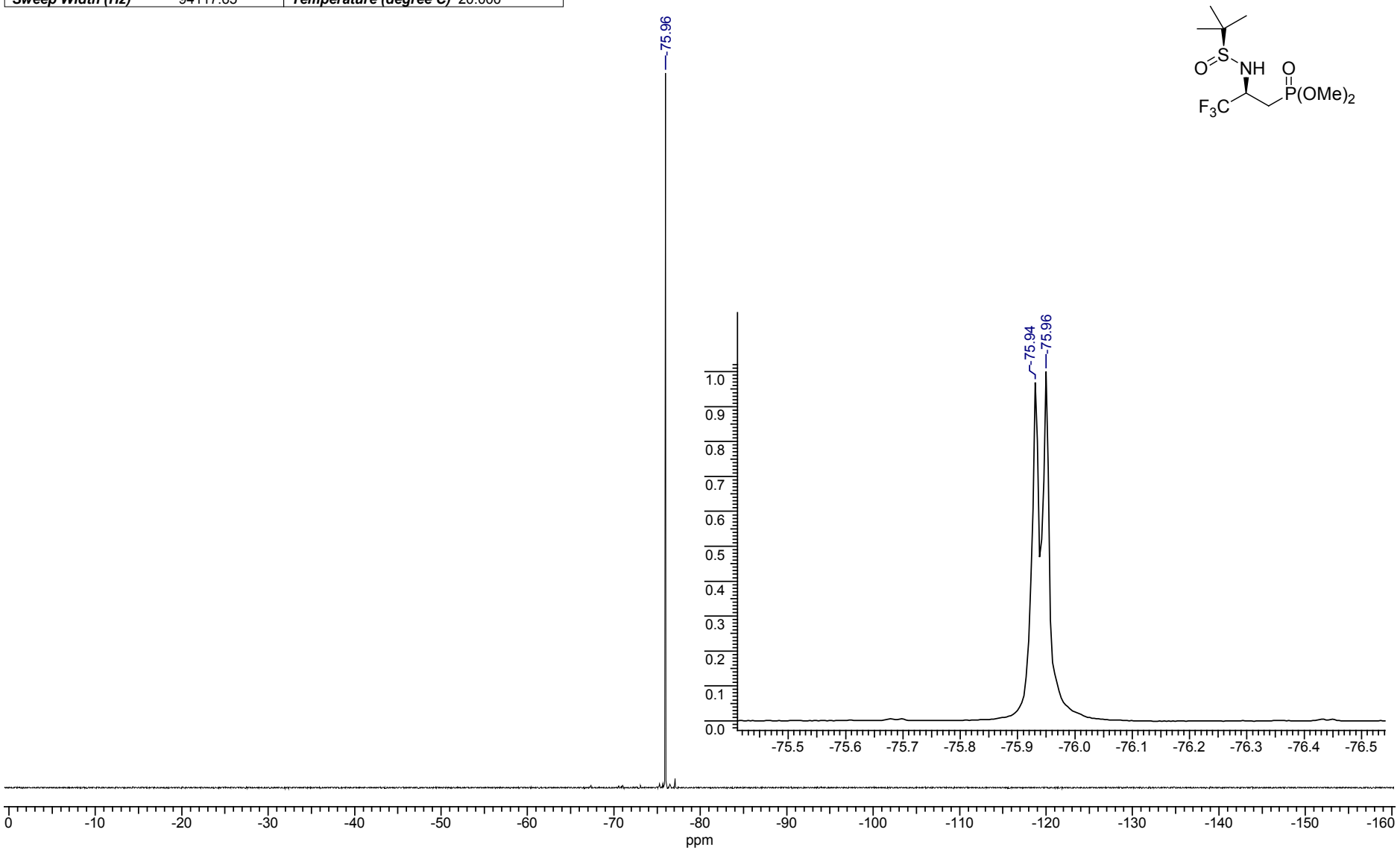

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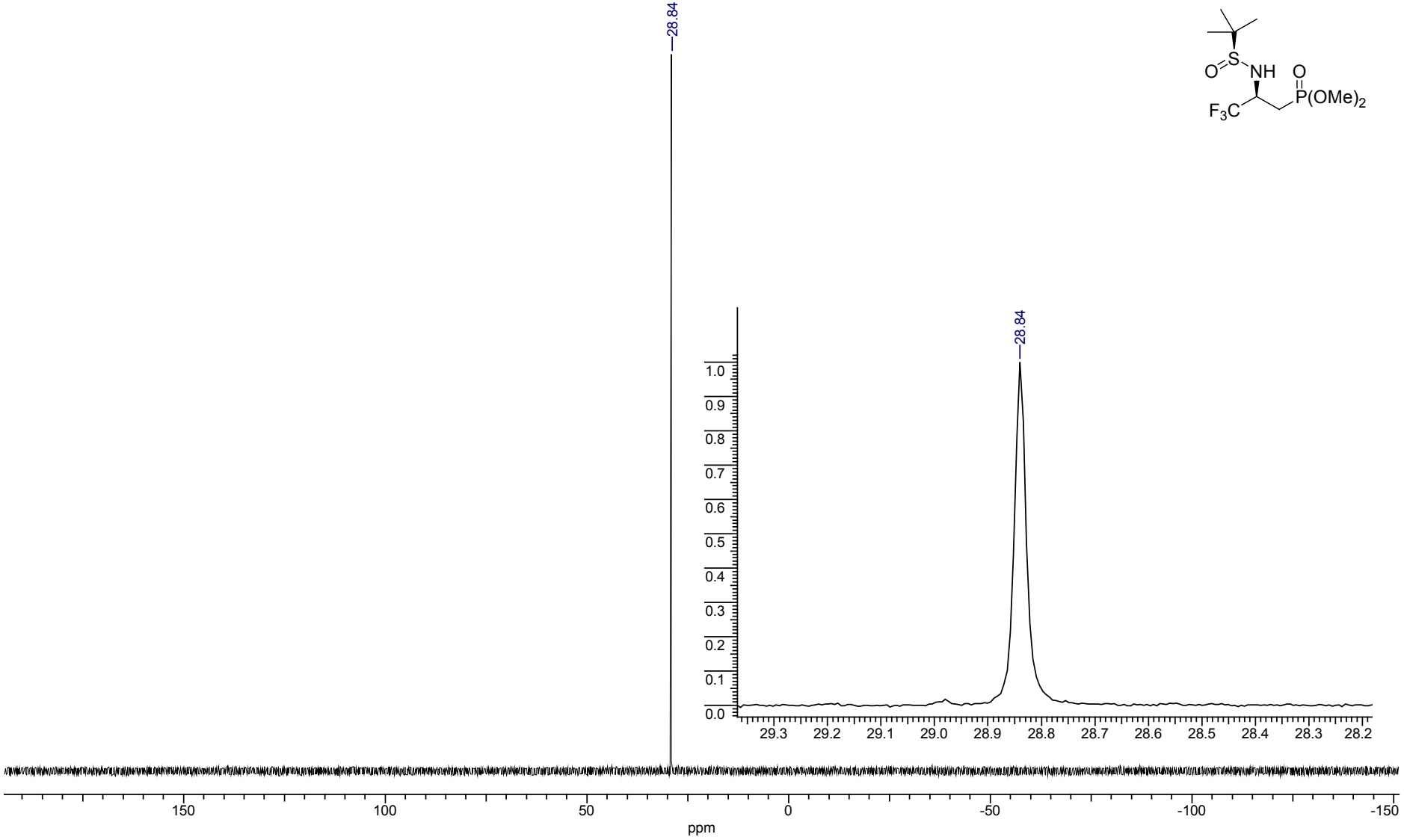

13 Jun 2012

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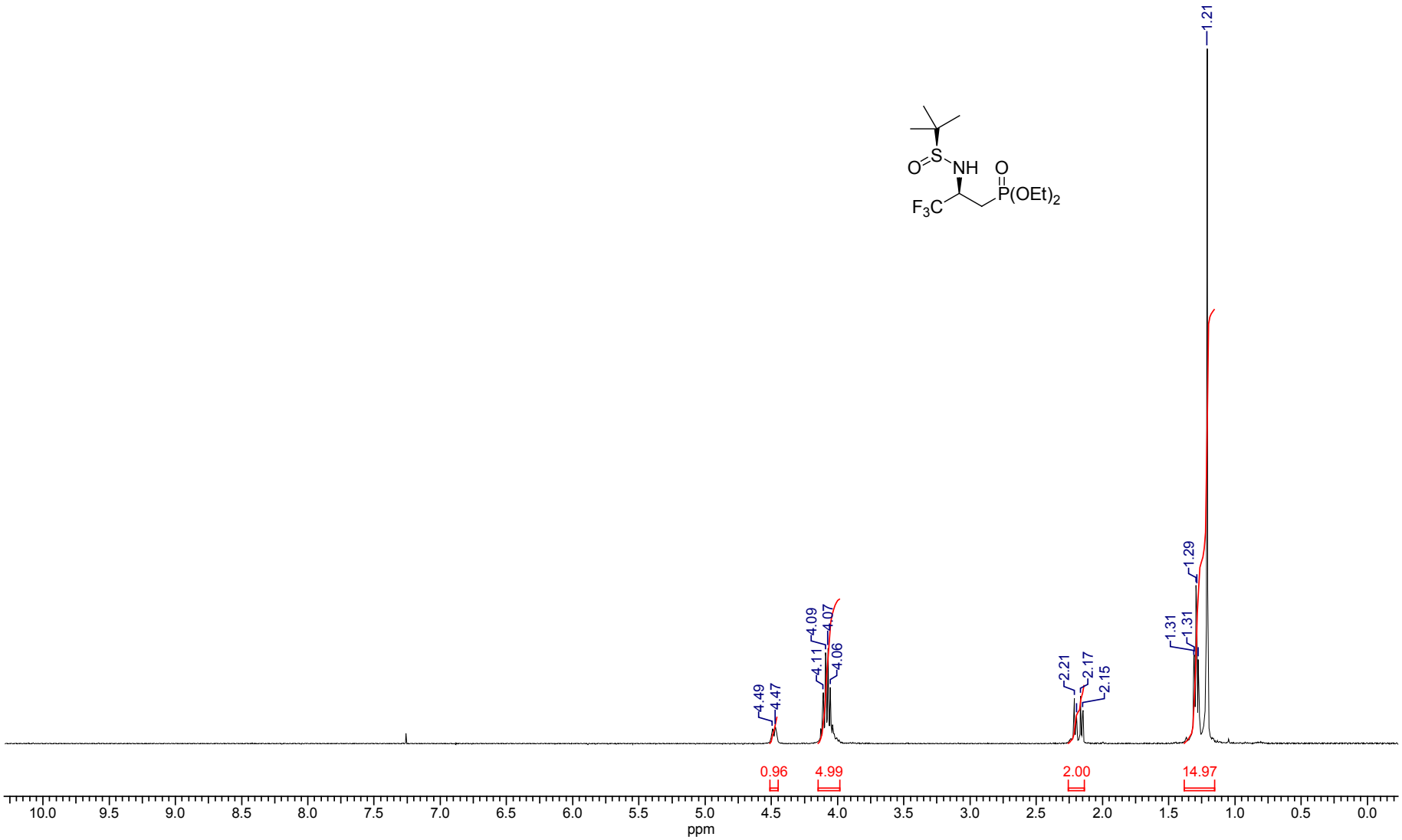
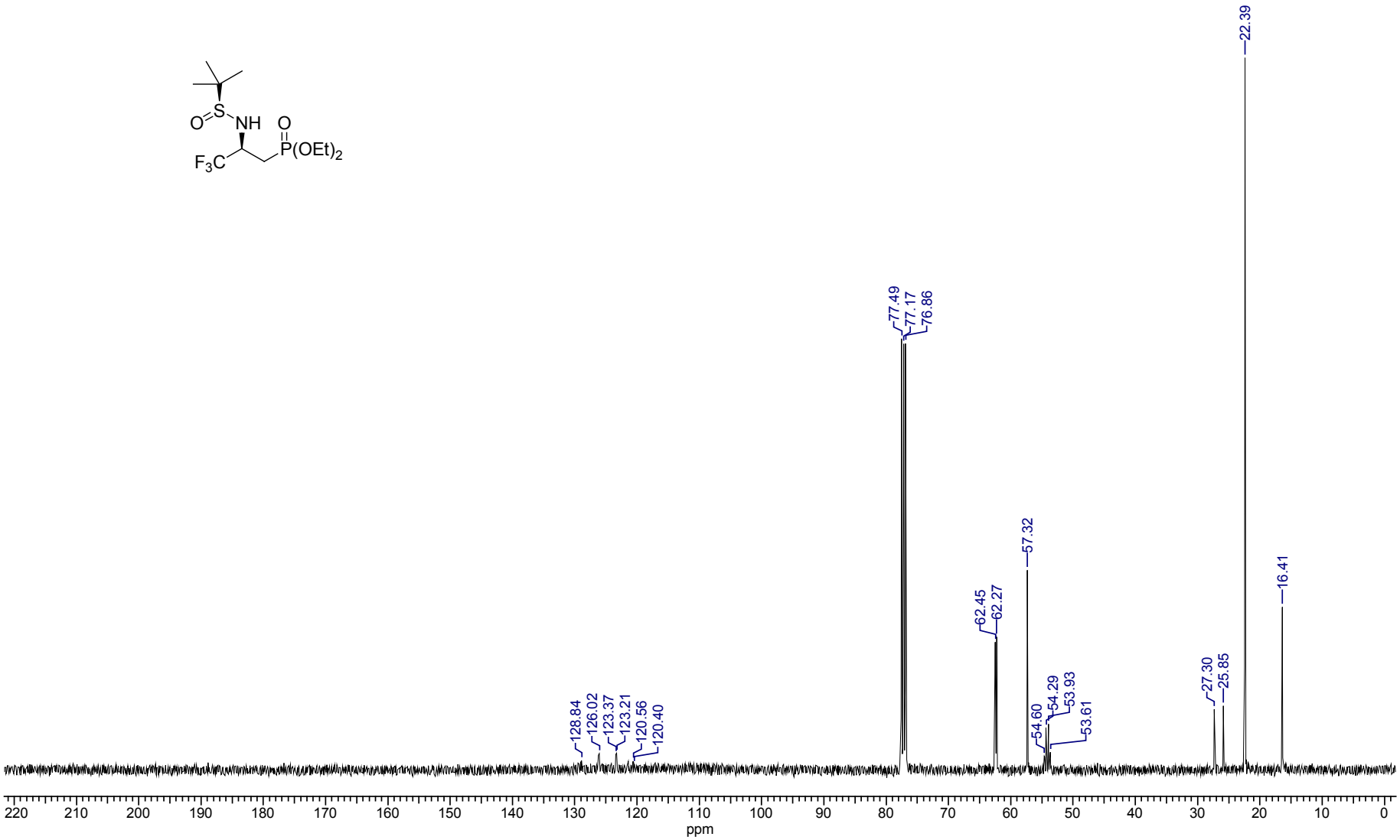


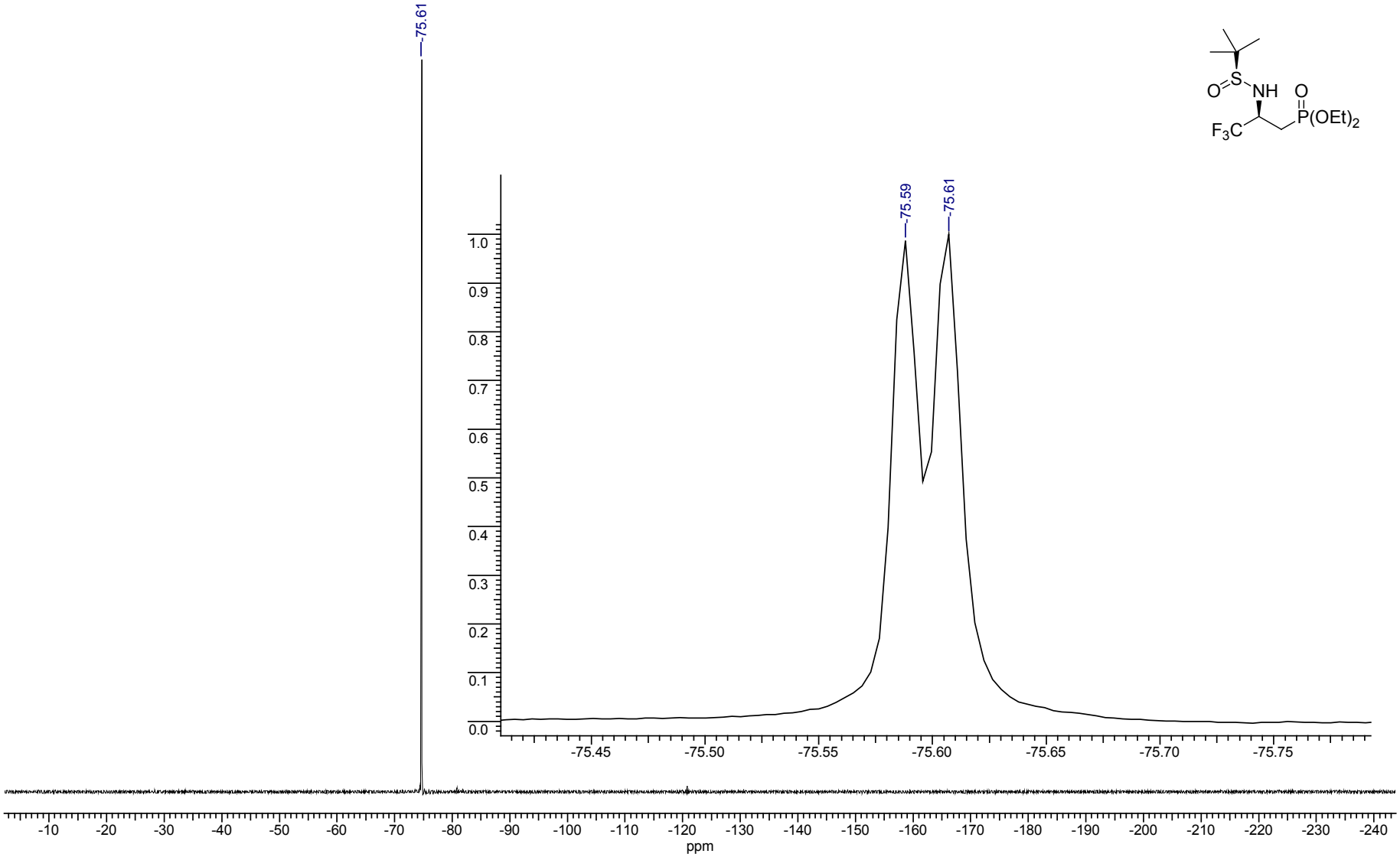
13 Jun 2012

Acquisition Time (sec)	0.6816	***Comment***	13C NMR Spectrum, CDCl3			***Date***	21 Mar 2012 12:56:32
File Name	D:\Nuts95\Data\AP\ap-4c\ap-4c_fid			***Frequency (MHz)***	100.62	***Nucleus***	13C ***Number of Transients*** 338
Original Points Count	32768	***Points Count***	32768	***Pulse Sequence***	zgpg30	***Solvent***	CHLOROFORM-D
Sweep Width (Hz)	24038.46						



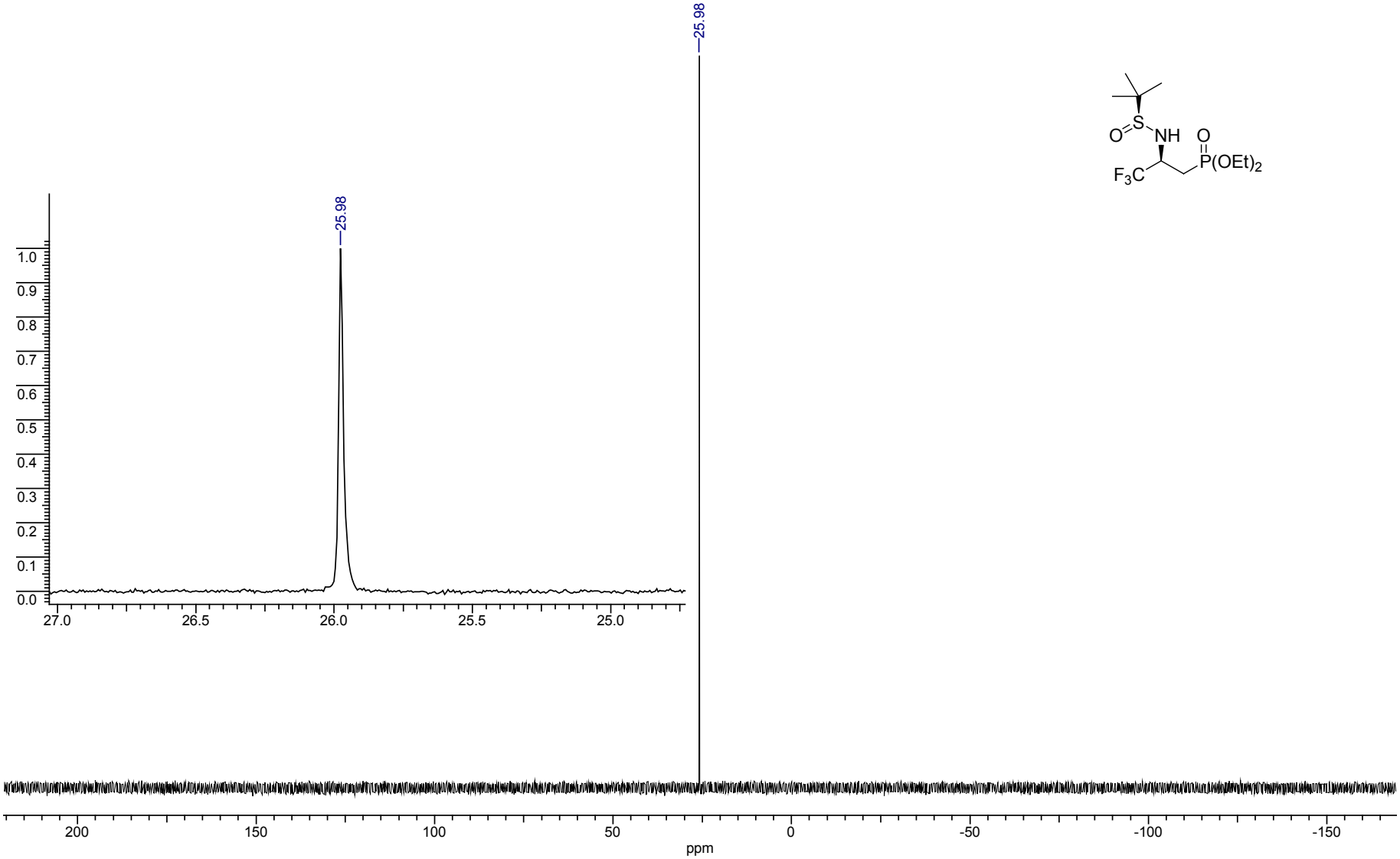
13 Jun 2012

Acquisition Time (sec)	0.3400	***Date***	Apr 10 2012	***File Name***	D:\Nuts95\Data\Spectra-Aminophoshonates\Diethyl methylphosphonate\P_53-F19				
Frequency (MHz)	376.29	***Nucleus***	19F	***Number of Transients***	4	***Original Points Count***	64000	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	94117.65	***Temperature (degree C)***	20.000

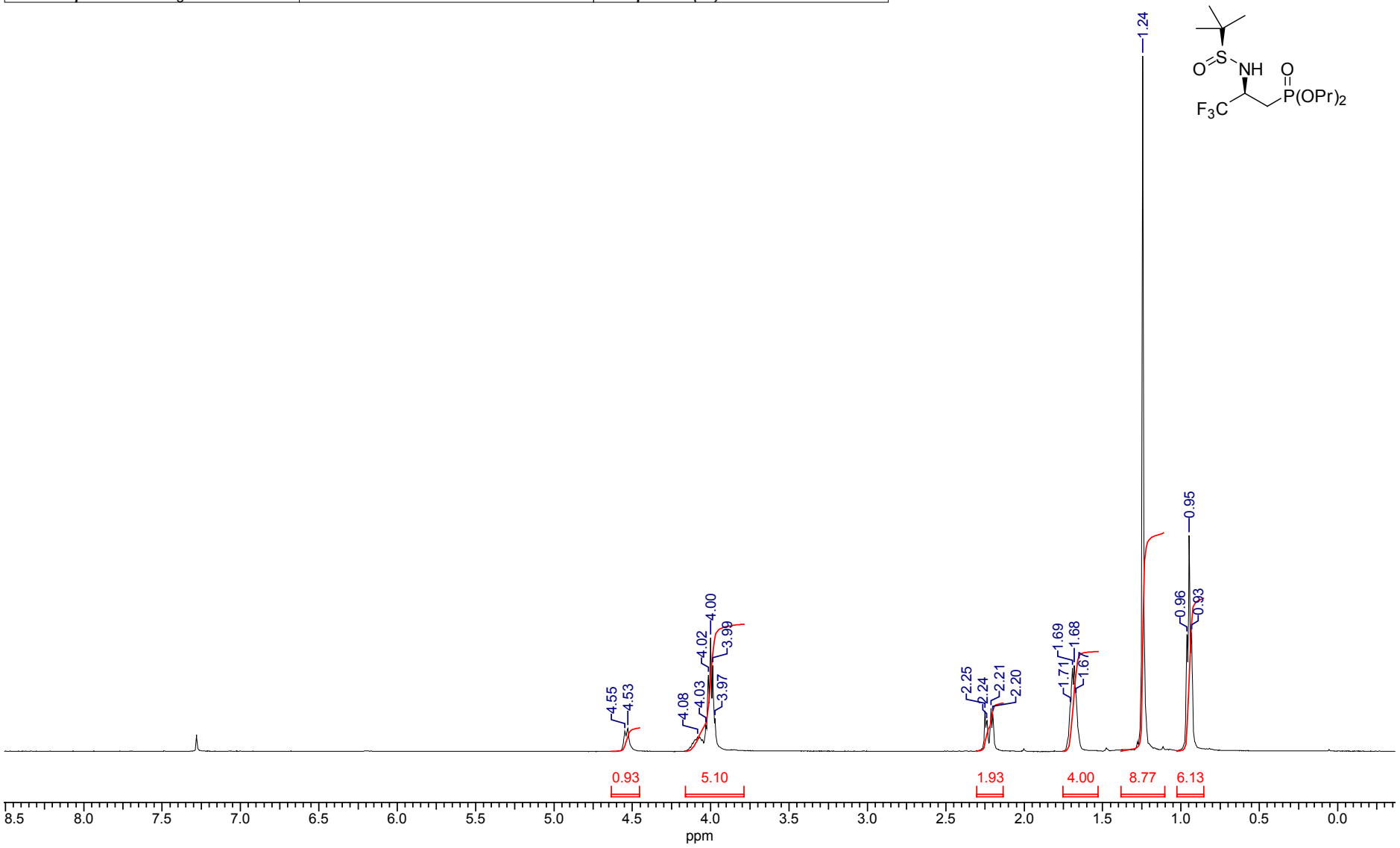


13 Jun 2012

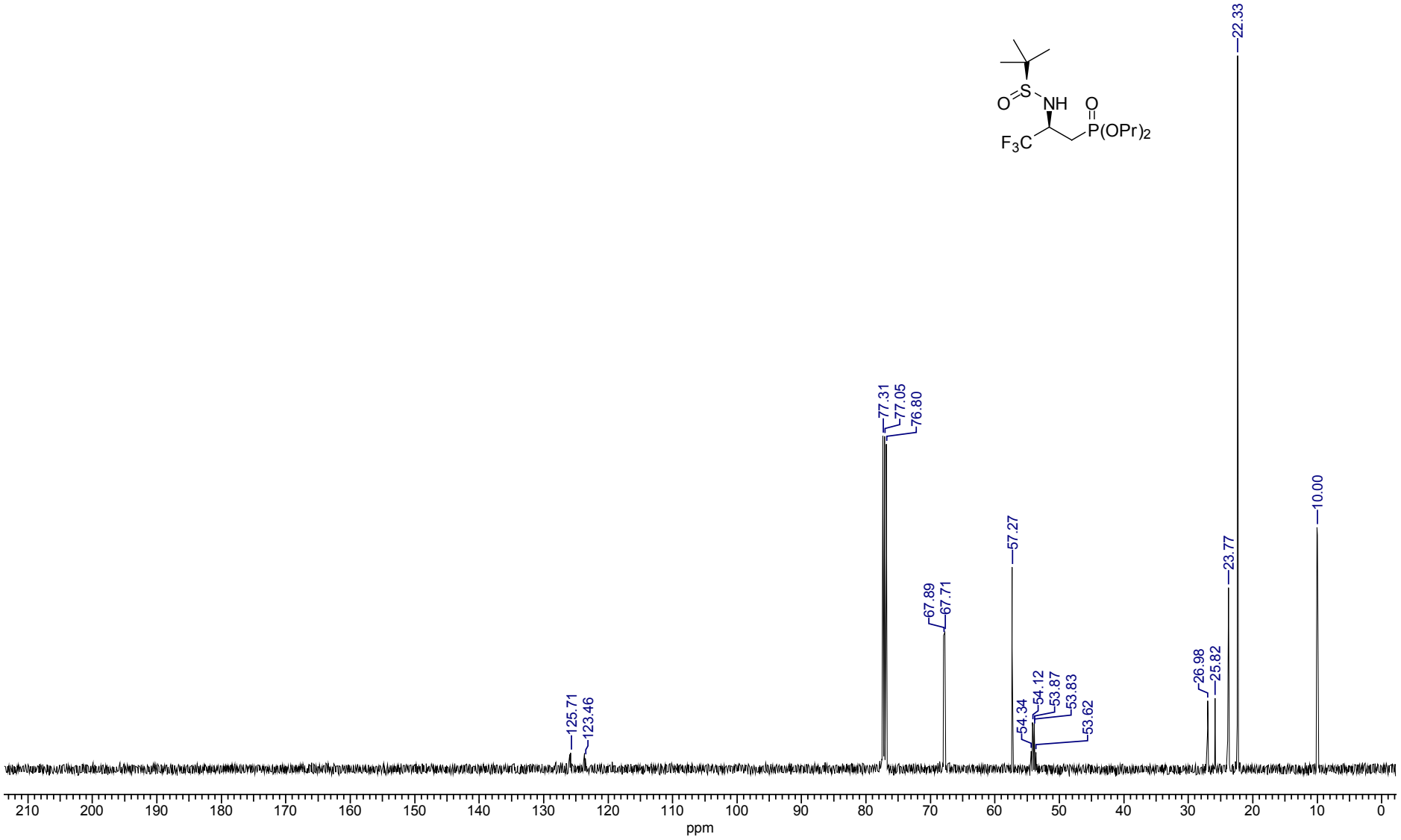
Acquisition Time (sec)	0.4063	***Date***	Tue Apr 03 08:12:47 2012		***File Name***	D:\Nuts95\Data\AP\ap-4p{H}.nmr	
Frequency (MHz)	202.44	***Nucleus***	31P	***Number of Transients*** 9	***Original Points Count***	65536	***Points Count*** 65536
Sweep Width (Hz)	80645.16	***Solvent***	CDCl3				



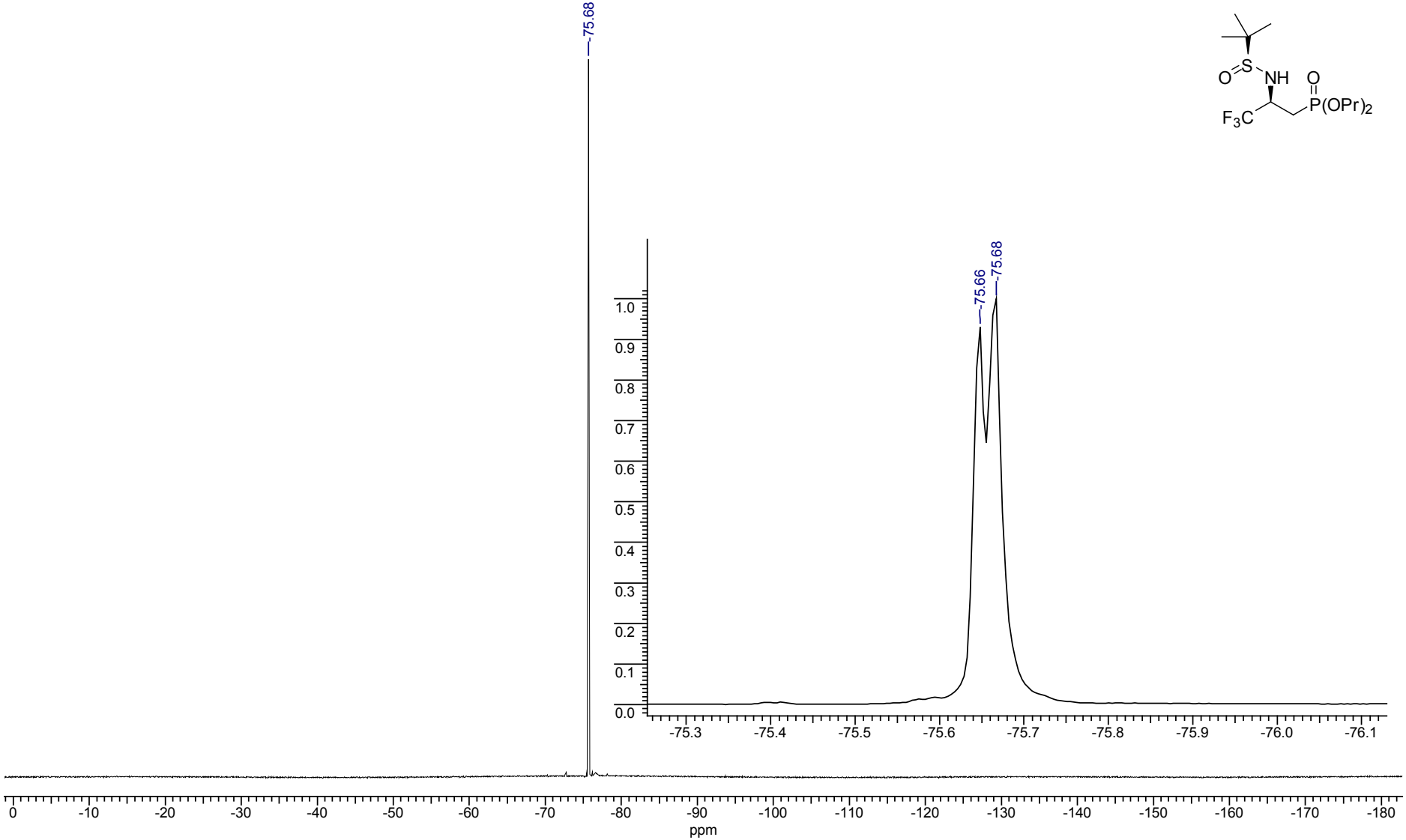
Acquisition Time (sec)	0.9634	***Comment***	Imported from UXNMR.			***Date***	08 Jun 2012 14:19:44
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Dipropylmethylphosphonate\P_85-1H\P_85-1H_001000fid					***Frequency (MHz)***	500.07
Nucleus	1H	***Number of Transients***	1	***Original Points Count***	16384	***Points Count***	16384
Pulse Sequence	zg	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	8503.40		



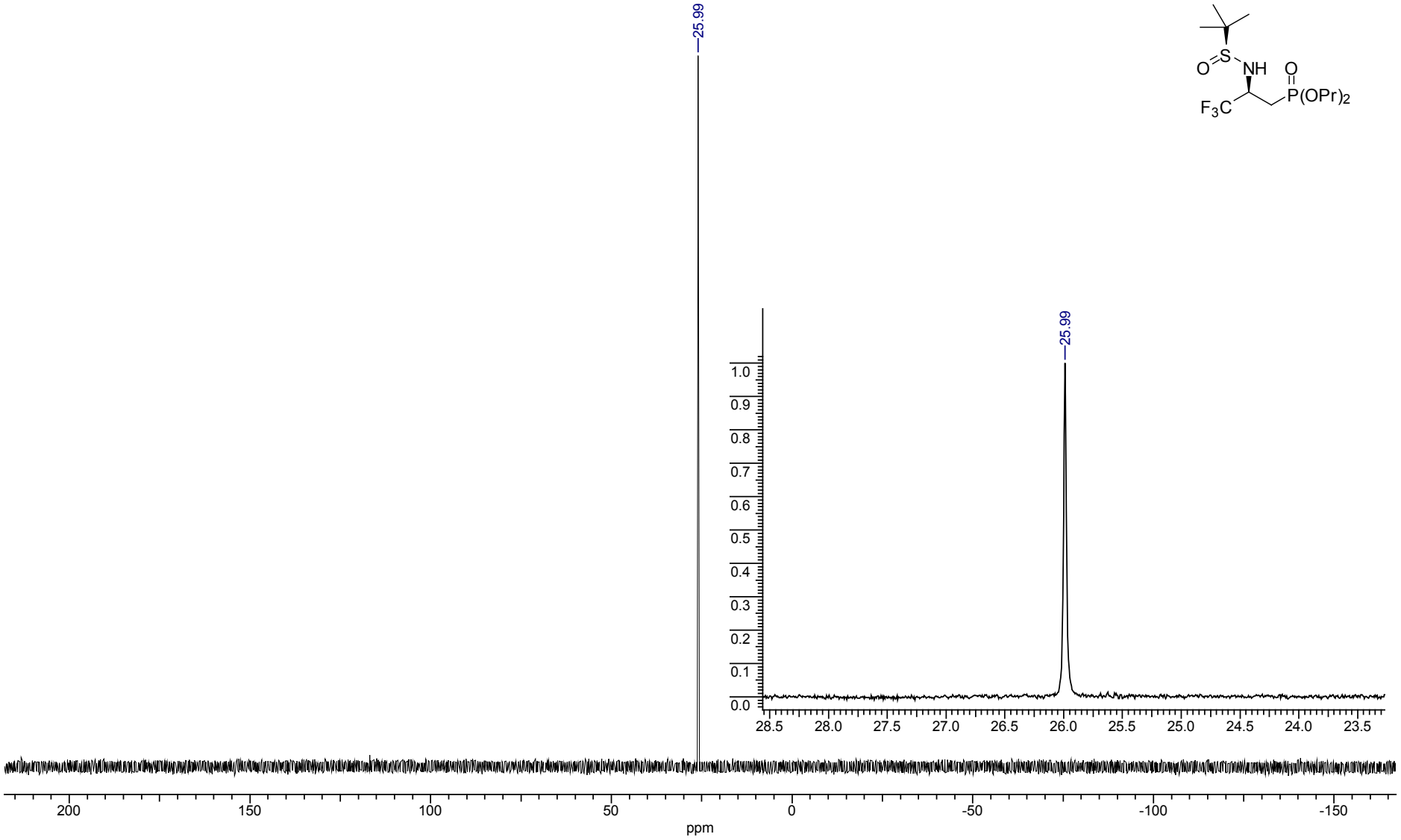
Acquisition Time (sec)	0.7834	***Comment***	Imported from UXNMR.			***Date***	08 Jun 2012 19:54:40
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Dipropylmethylphosphonate\P_85-C13\P_85-C13_001000fid					***Frequency (MHz)***	125.76
Nucleus	13C	***Number of Transients***	553	***Original Points Count***	51200	***Points Count***	65536
Pulse Sequence	zgpg	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	32679.74		



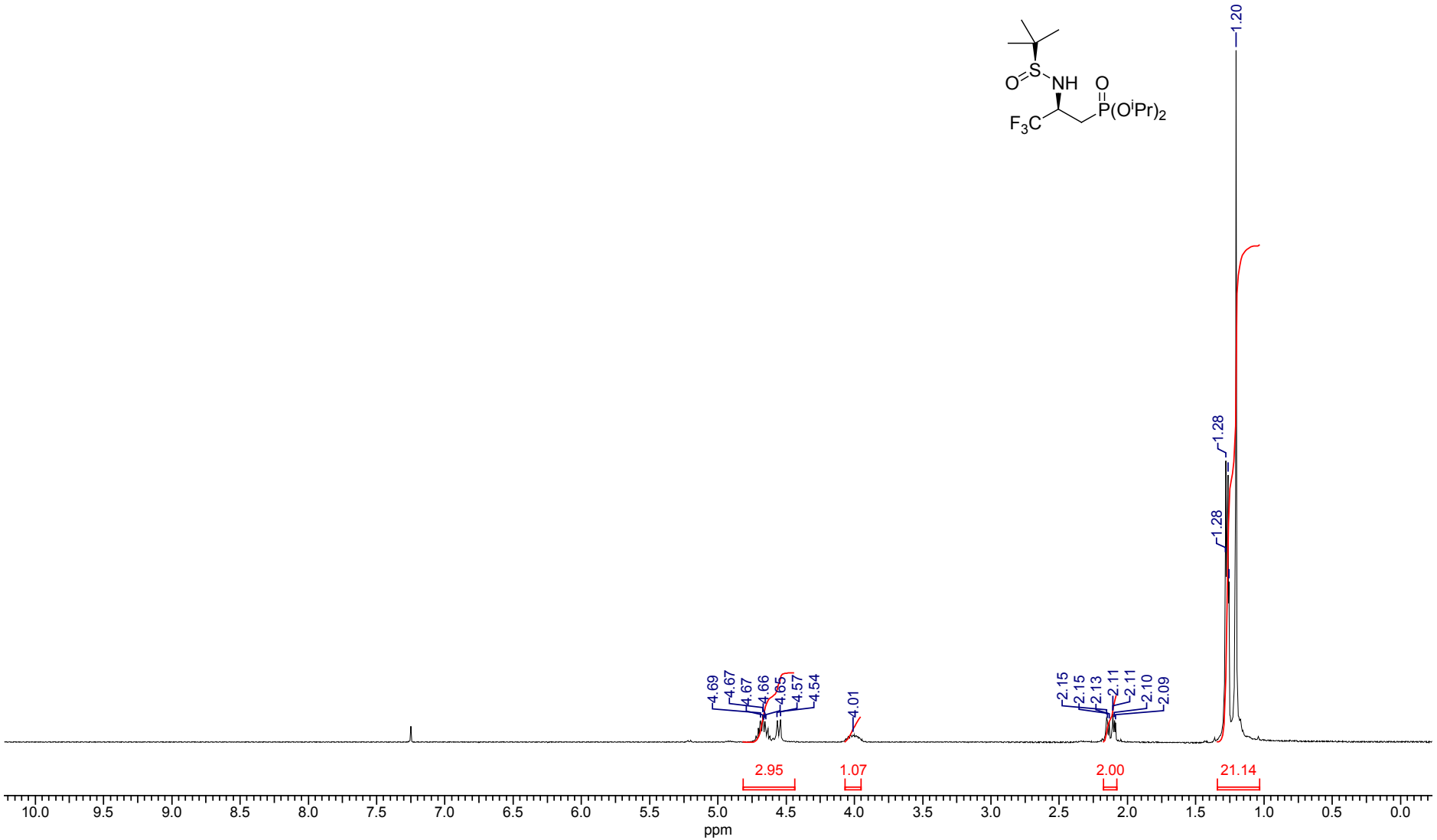
Acquisition Time (sec)	0.3400	***Date***	Jun 12 2012	***File Name***	D:\Nuts95\Data\Spectra-Aminophoshonates\Dipropylmethylphosphonate\P_85-F19		
Frequency (MHz)	376.29	***Nucleus***	19F	***Number of Transients***	4	***Original Points Count***	64000
Points Count	65536	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	94117.65	***Temperature (degree C)***	20.000				



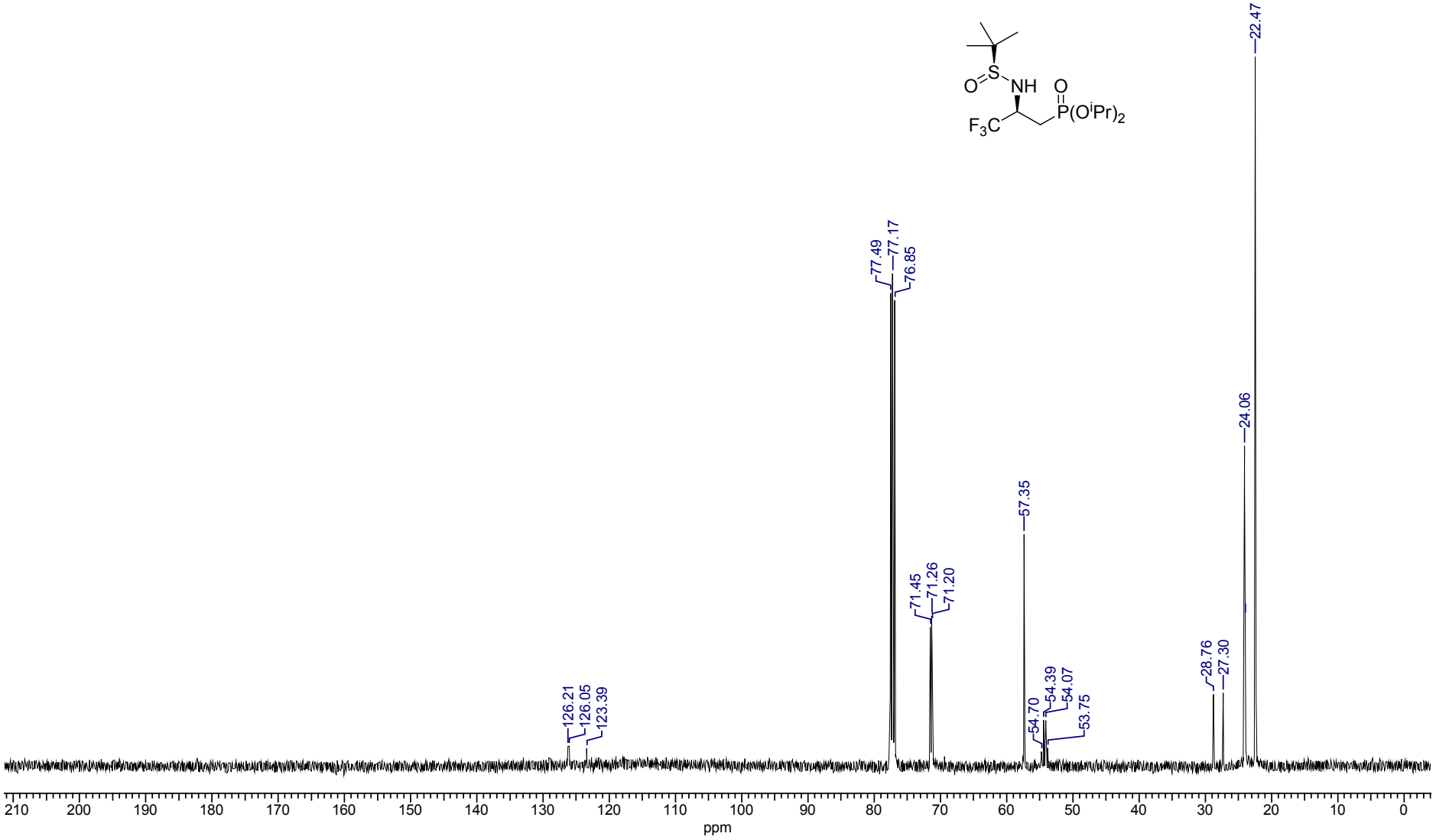
Acquisition Time (sec)	0.4063	***Comment***	Imported from UXNMR.			***Date***	23 Jul 2012 11:35:28
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Dipropylmethylphosphonate\IGp-101-P31\IGp-101-P31_001000fid					***Frequency (MHz)***	202.44
Nucleus	31P	***Number of Transients***	12	***Original Points Count***	65536	***Points Count***	65536
Pulse Sequence	zgpg	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	80645.16		



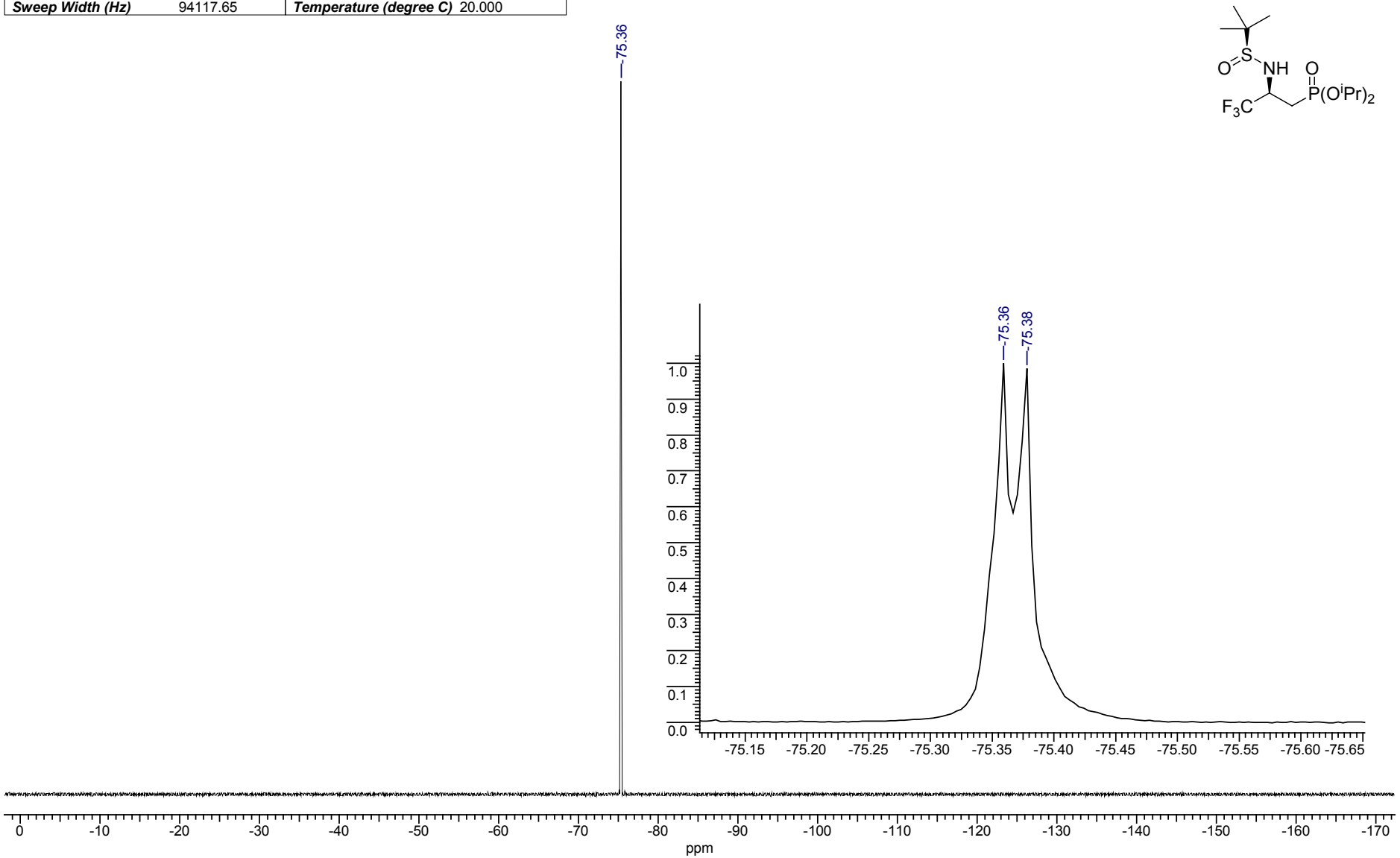
Acquisition Time (sec)	2.3962	***Comment***	Turchenyuk, N1	***Date***	11 Apr 2012 10:27:12		
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Diisopropyl methylphosphonate\1H\1H_fid					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	30720	***Points Count***	32768
Pulse Sequence	zg	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	6410.26
Temperature (degree C)	18.177						



Acquisition Time (sec)	0.6816	***Comment***	13C NMR Spectrum, CDCl3			***Date***	11 Apr 2012 11:14:08
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Diisopropyl methylphosphonate\13C\13C_fid					***Frequency (MHz)***	100.62
Nucleus	13C	***Number of Transients***	428	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	zgpg30	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	24038.46
Temperature (degree C)	18.412						

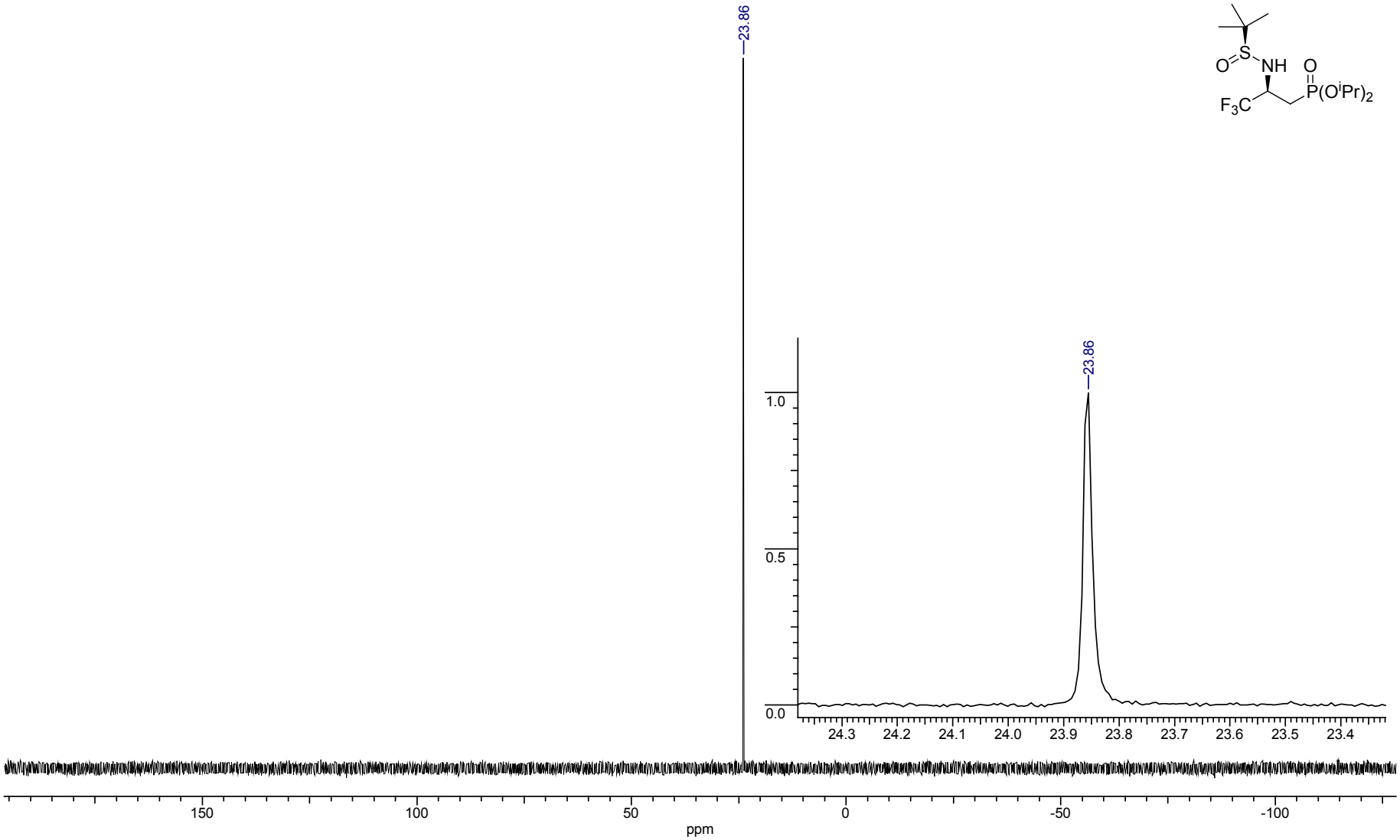


Acquisition Time (sec)	0.3400	***Date***	May 10 2012	***File Name***	D:\Nuts95\Data\Spectra-Aminophoshonates\Diisopropyl methylphosphonate\P_65-F19		
Frequency (MHz)	376.29	***Nucleus***	19F	***Number of Transients***	4	***Original Points Count***	64000
Points Count	65536	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	94117.65	***Temperature (degree C)***	20.000				

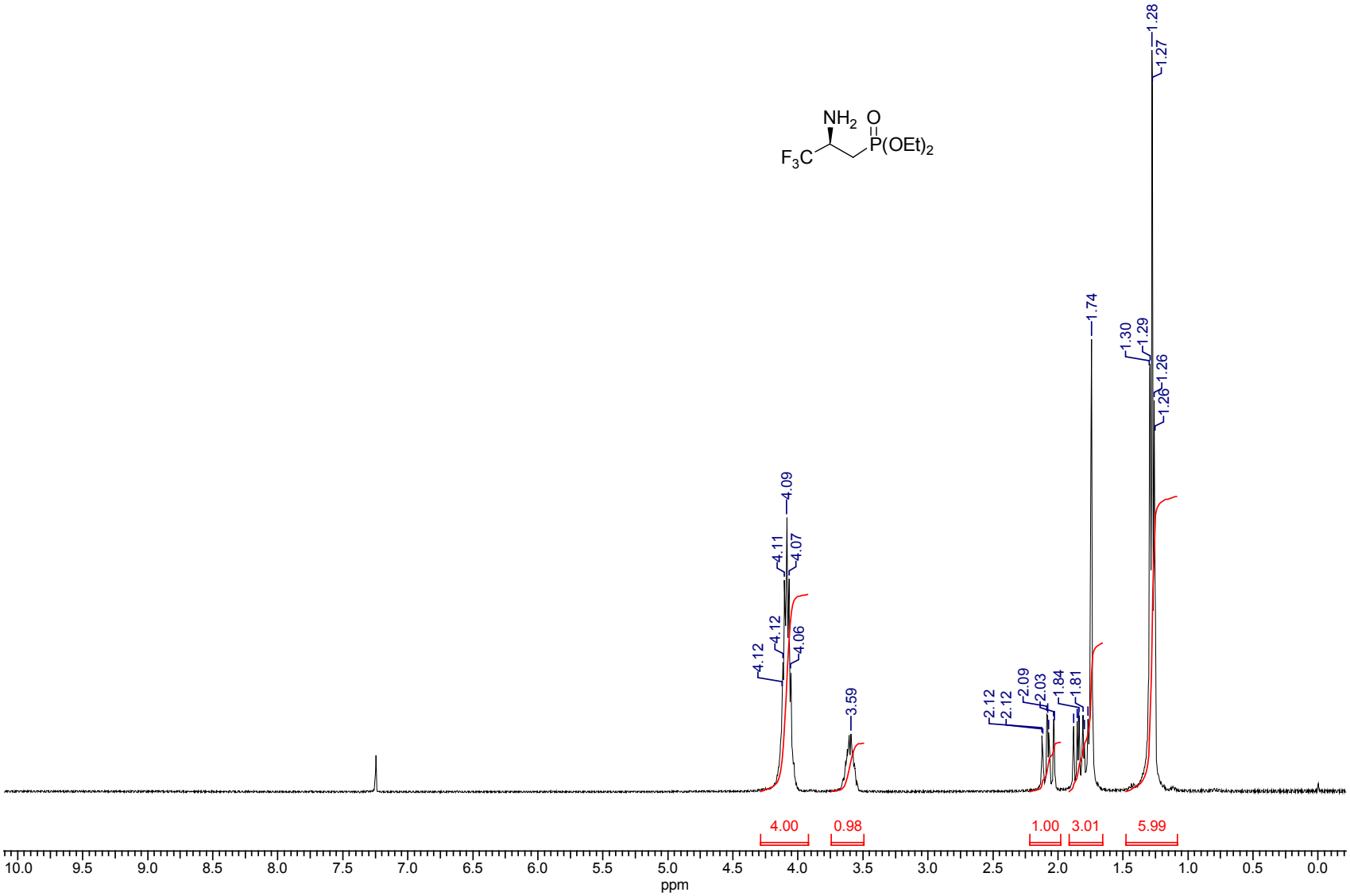


22 Jun 2012

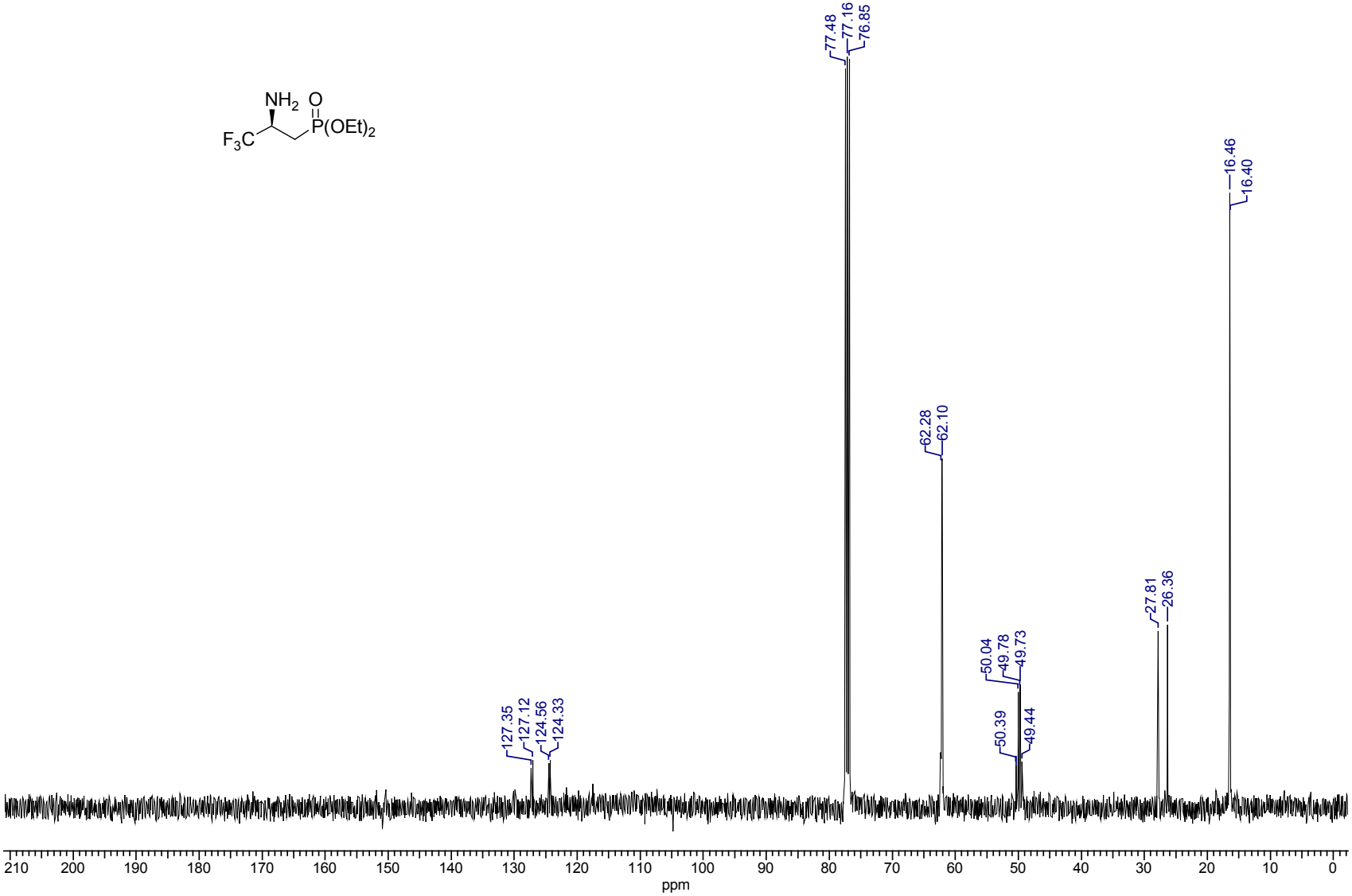
Acquisition Time (sec)	0.4063	***Comment***	Imported from UXNMR.			***Date***	08 May 2012 10:03:44
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Diisopropyl methylphosphonate\P_65-P31\P_65-P31_001000fid					***Frequency (MHz)***	202.44
Nucleus	31P	***Number of Transients***	14	***Original Points Count***	65536	***Points Count***	65536
Pulse Sequence	zgpg	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	80645.16		



Acquisition Time (sec)	2.3962	***Comment***	Turchenyuk, N1	***Date***	18 Apr 2012 10:42:08		
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Deprotected diethyl methylphosphonate\P_59-1H\P_59-1H_fid					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	30720	***Points Count***	32768
Pulse Sequence	zg	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	6410.26

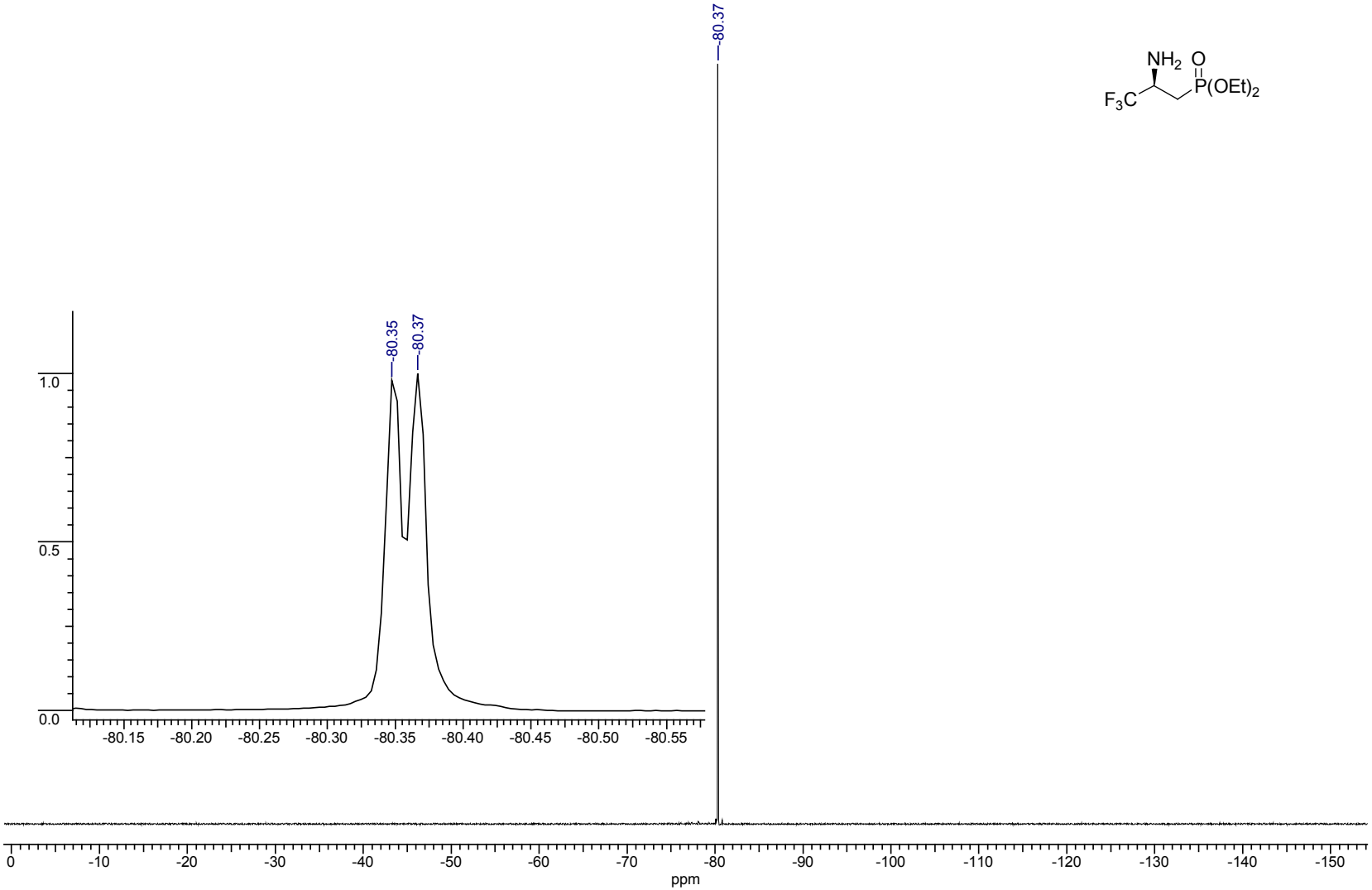


Acquisition Time (sec)	0.6816	***Comment***	13C NMR Spectrum, CDCl3			***Date***	18 Apr 2012 10:40:00
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Deprotected diethyl methylphosphonate\P_59-13C\P_59-13C_fid					***Frequency (MHz)***	100.62
Nucleus	13C	***Number of Transients***	199	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	zgpg30	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	24038.46		

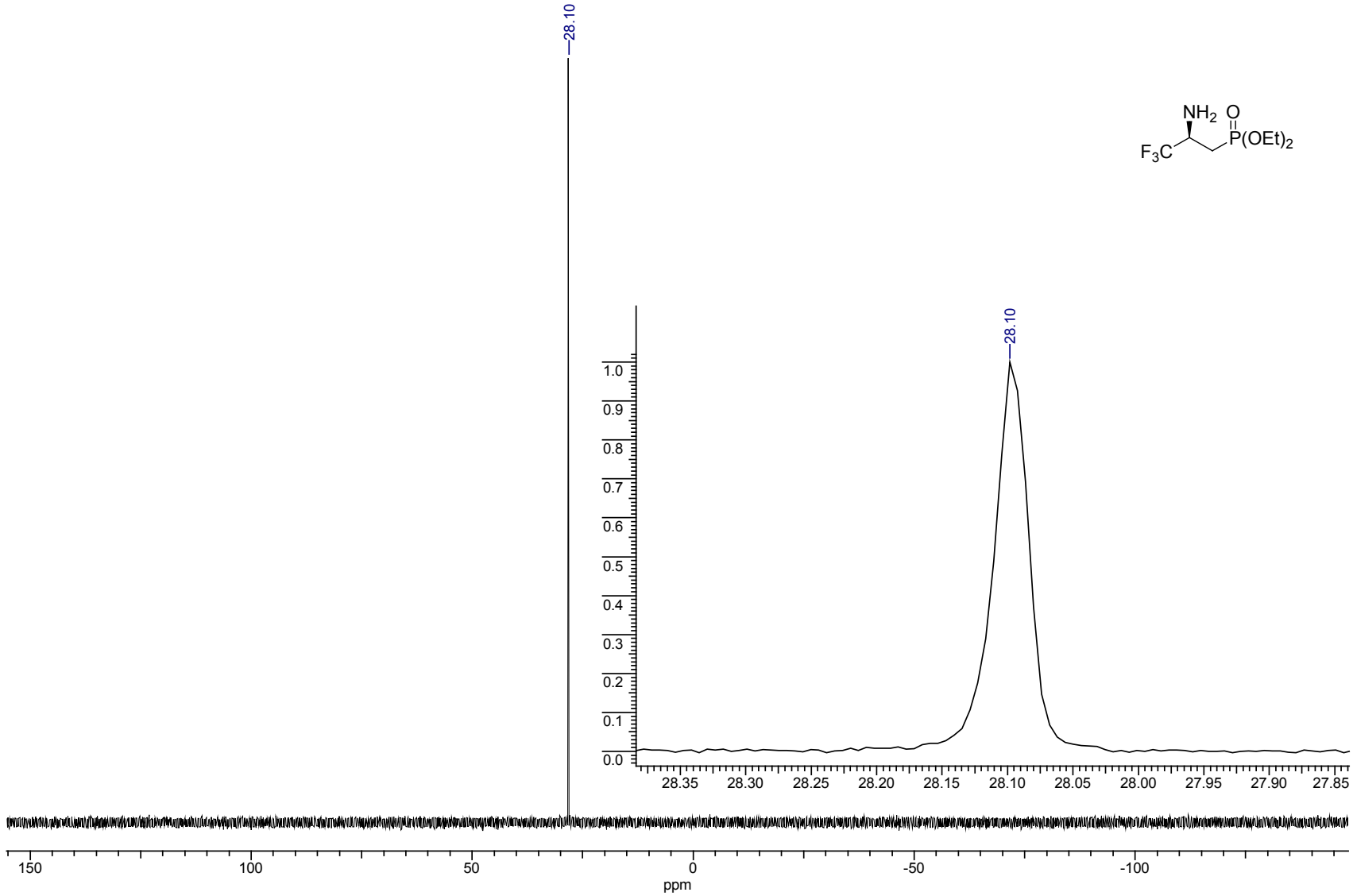


19 Jun 1997

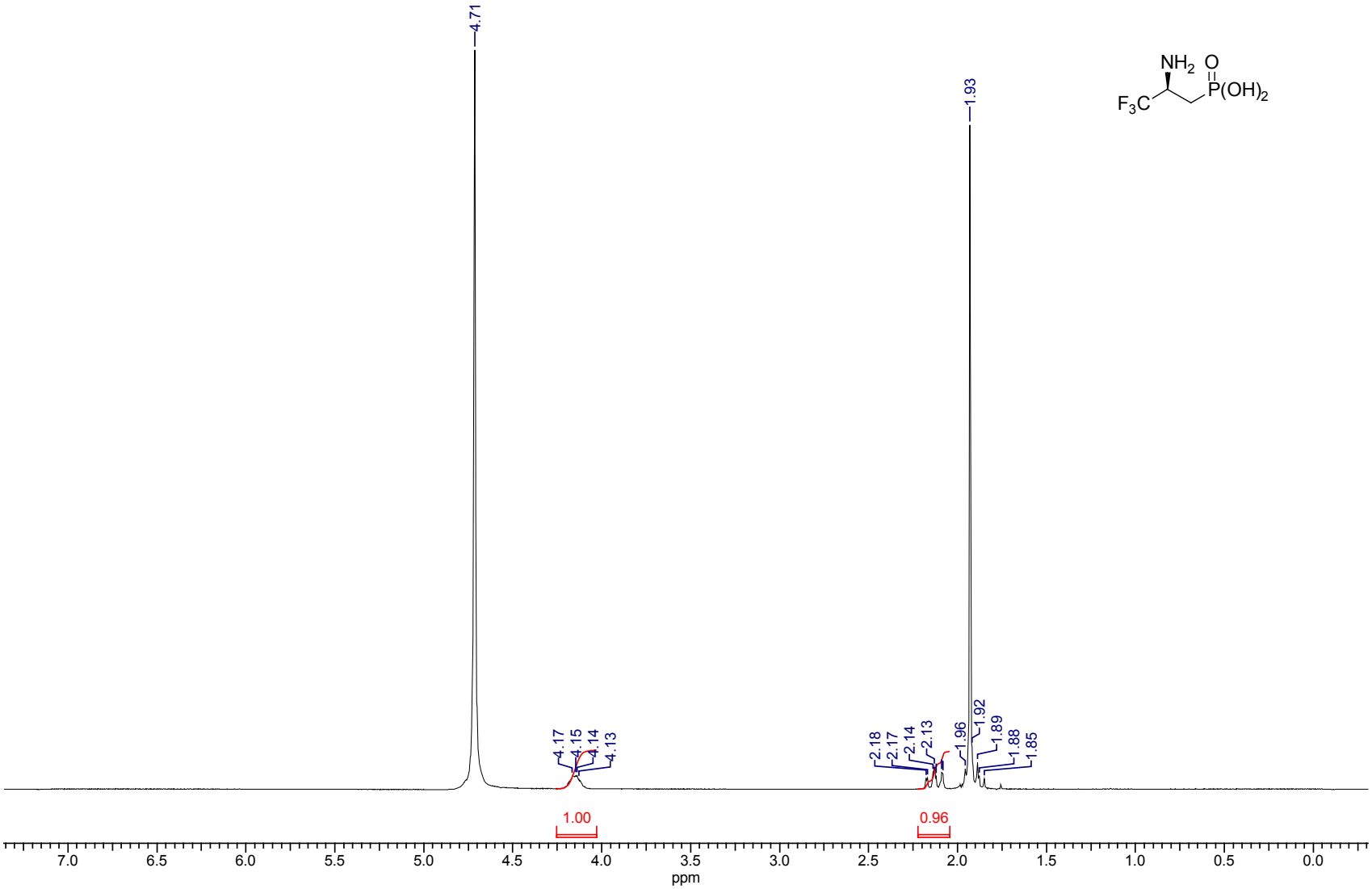
Acquisition Time (sec)	0.3400	***Date***	Apr 12 2012				
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Deprotected diethyl methylphosphonate\P_57-F19					***Frequency (MHz)***	376.29
Nucleus	19F	***Number of Transients***	4	***Original Points Count***	64000	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	94117.65
Temperature (degree C)	20.000						



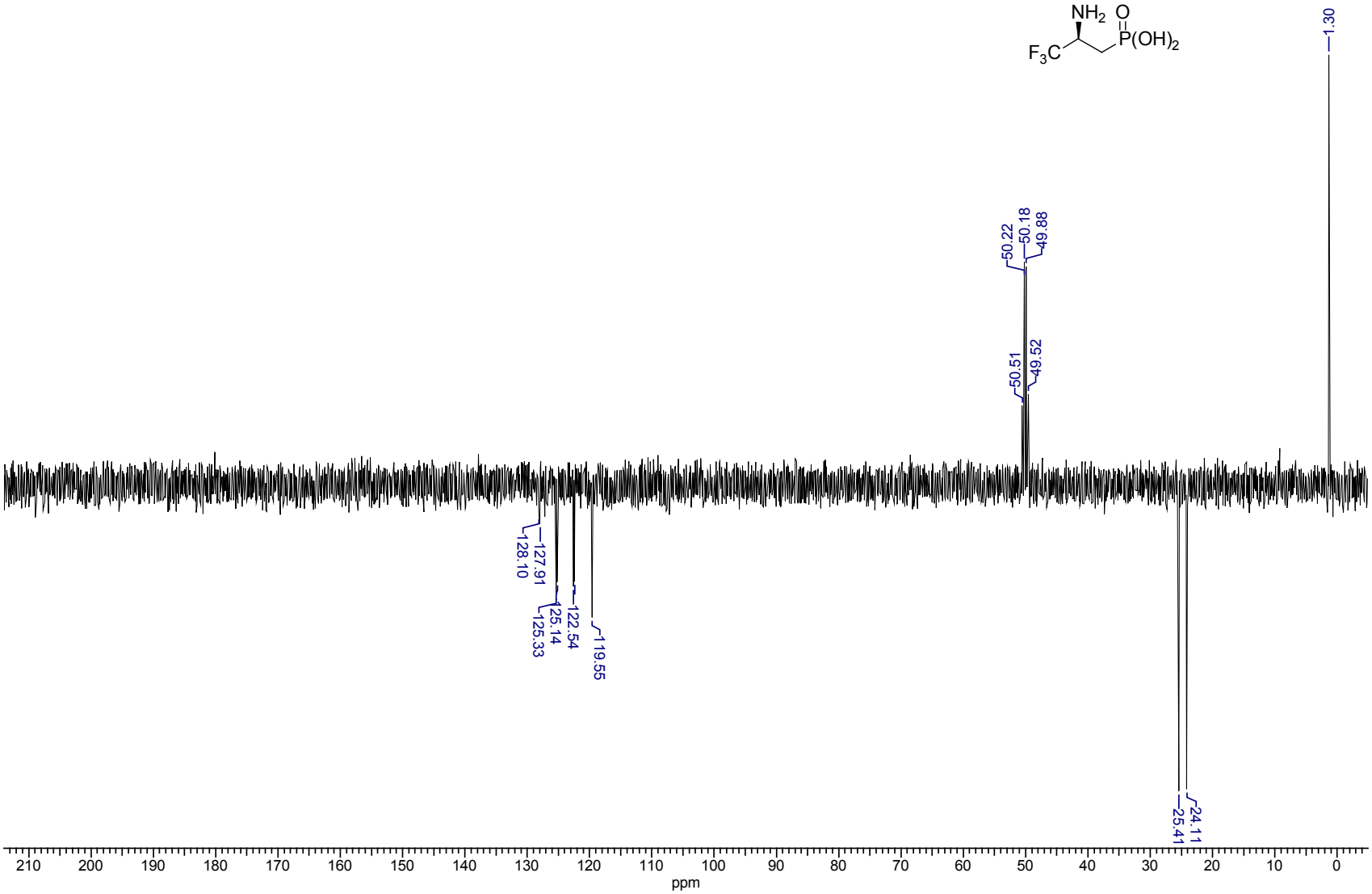
Acquisition Time (sec)	0.4063	***Comment***	Imported from UXNMR.			***Date***	28 Apr 2012 10:50:40
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Deprotected diethyl methylphosphonate\P_60-P31\P_60-P31_001000fid					***Frequency (MHz)***	202.44
Nucleus	31P	***Number of Transients***	10	***Original Points Count***	65536	***Points Count***	65536
Pulse Sequence	zgpg	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	80645.16		



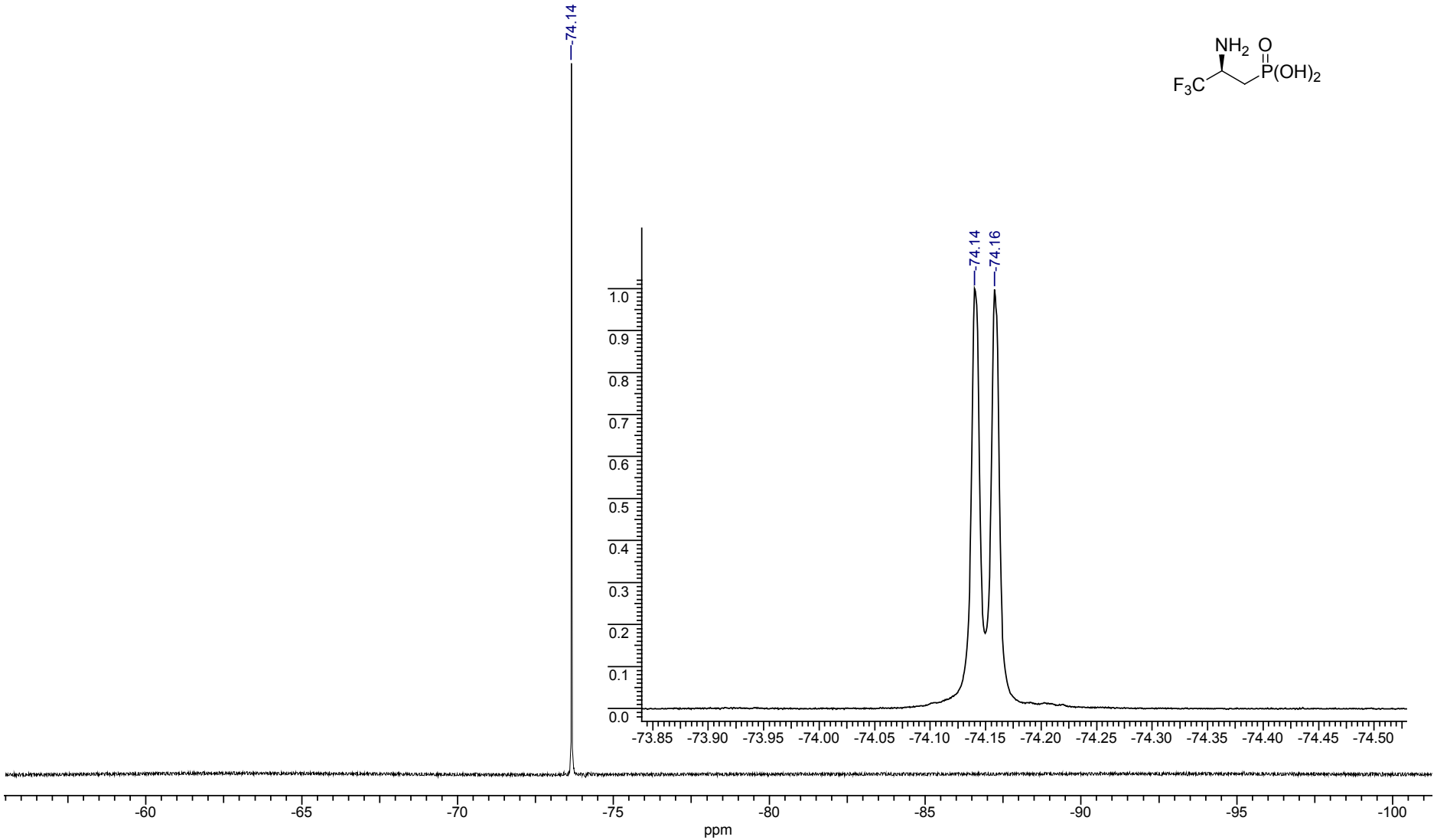
Acquisition Time (sec)	2.8049	***Comment***	1H NMR Spectrum, D2O			***Date***	23 May 2012 12:28:48
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Phosphonic acid\1H-D2O+CH3CN\1H-D2O+CH3CN_fid					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	16384	***Points Count***	16384
Pulse Sequence	zg	***Solvent***	D2O+CD3CN			***Sweep Width (Hz)***	2920.56
Temperature (degree C)	20.882						



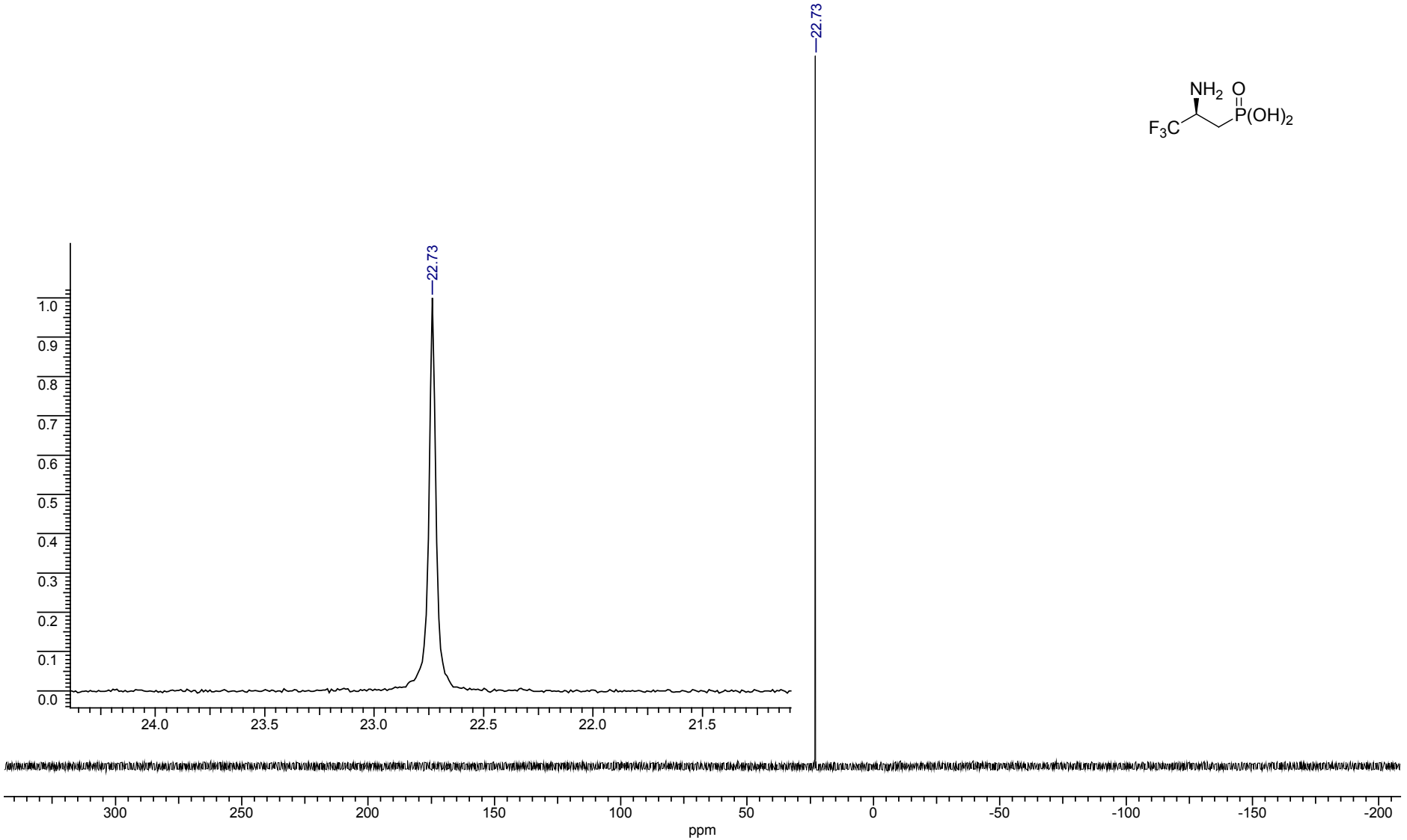
Acquisition Time (sec)	0.6816	***Comment***	13C APT NMR Spectrum, in D2O			***Date***	23 May 2012 12:30:56
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Phosphonic acid\13C-APT\13C-APT_fid					***Frequency (MHz)***	100.62
Nucleus	13C	***Number of Transients***	514	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	jmod	***Solvent***	DEUTERIUM OXIDE			***Sweep Width (Hz)***	24038.46
Temperature (degree C)	21.118						



Acquisition Time (sec)	1.2954	***Comment***	19F SENSITIVITY			***Date***	Jun 25 2012
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Phosphonic acid\p-91-f					***Frequency (MHz)***	376.41
Nucleus	19F	***Number of Transients***	256	***Original Points Count***	48000	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	D2O			***Sweep Width (Hz)***	18527.71
Temperature (degree C)	20.000						

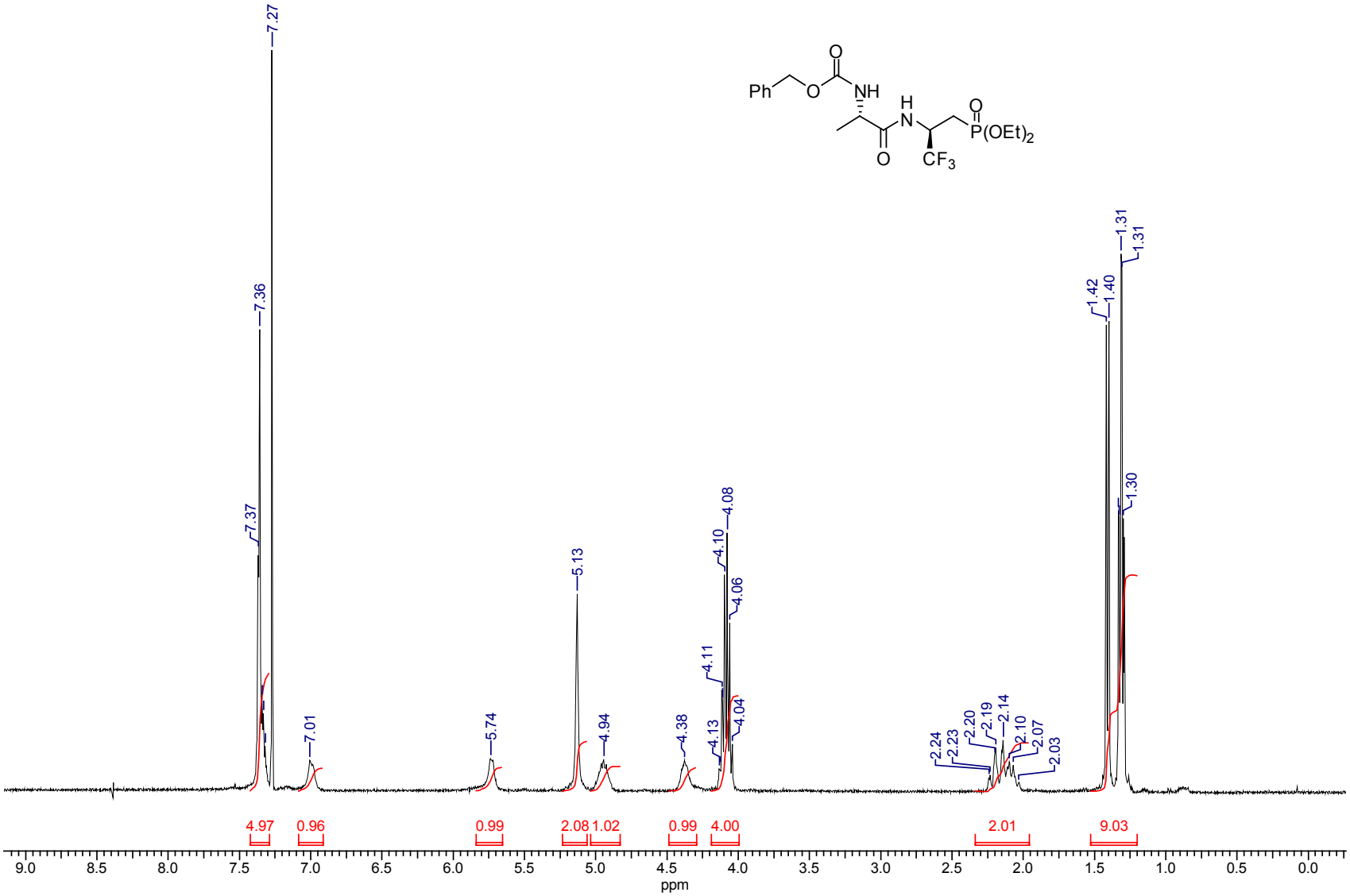


Acquisition Time (sec)	0.3200	***Comment***	DMSO 1203	***Date***	Jun 25 2012		
File Name	D:\Nuts95\Data\Spectra-Aminophoshonates\Phosphonic acid\p-91-p					***Frequency (MHz)***	161.96
Nucleus	31P	***Original Points Count***	64000	***Points Count***	65536	***Pulse Sequence***	s2pul
Solvent	D2O	***Sweep Width (Hz)***	100000.00	***Temperature (degree C)***	20.000		

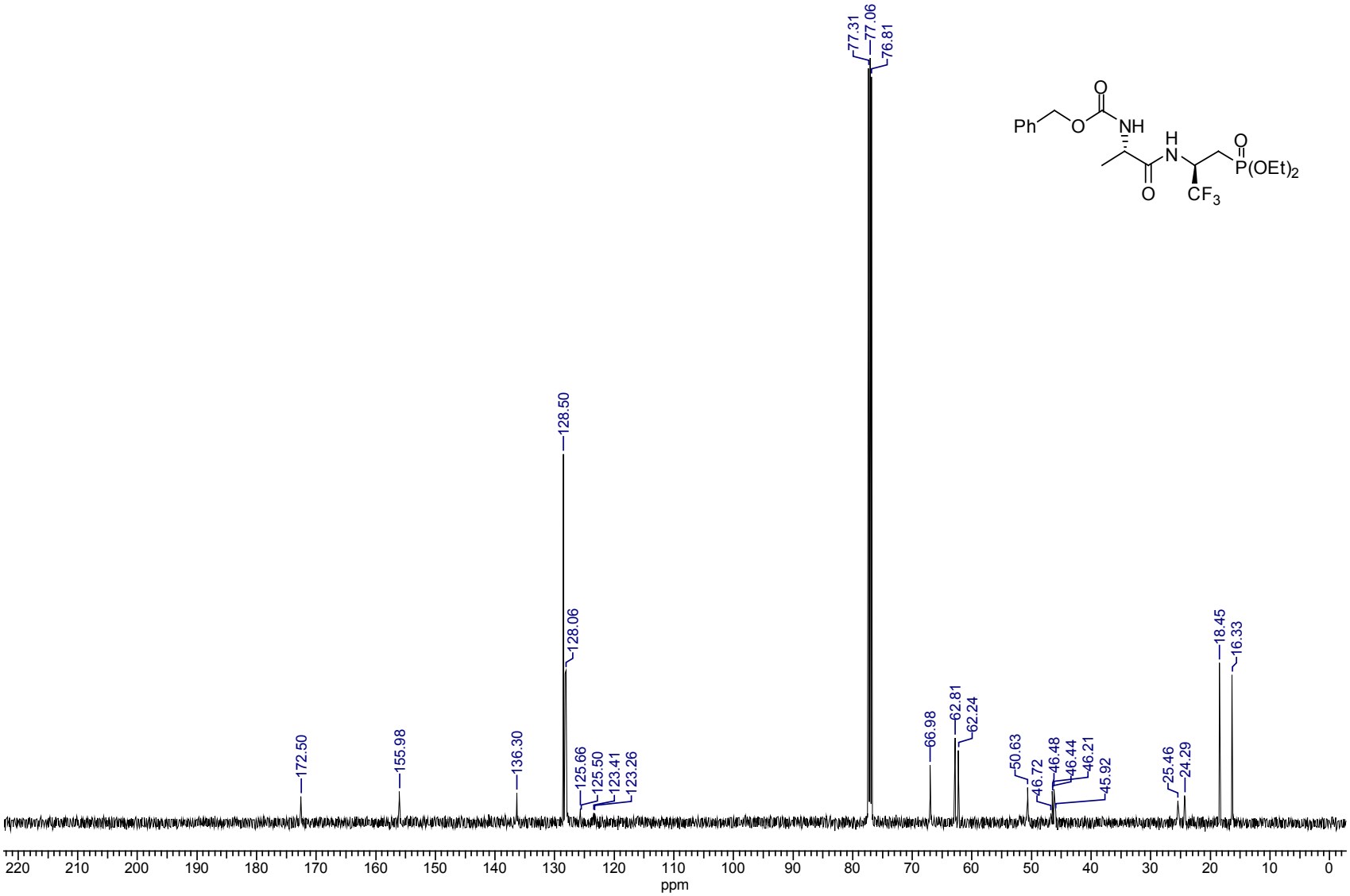


Acquisition Time (sec)	1.1250	***Comment***	CDCl3	***Date***	Jul 26 2012		
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide Ala\p-104					***Frequency (MHz)***	400.08
Number of Transients	8	***Original Points Count***	18000	***Points Count***	32768	***Pulse Sequence***	s2pul
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	20.000

Nucleus	1H

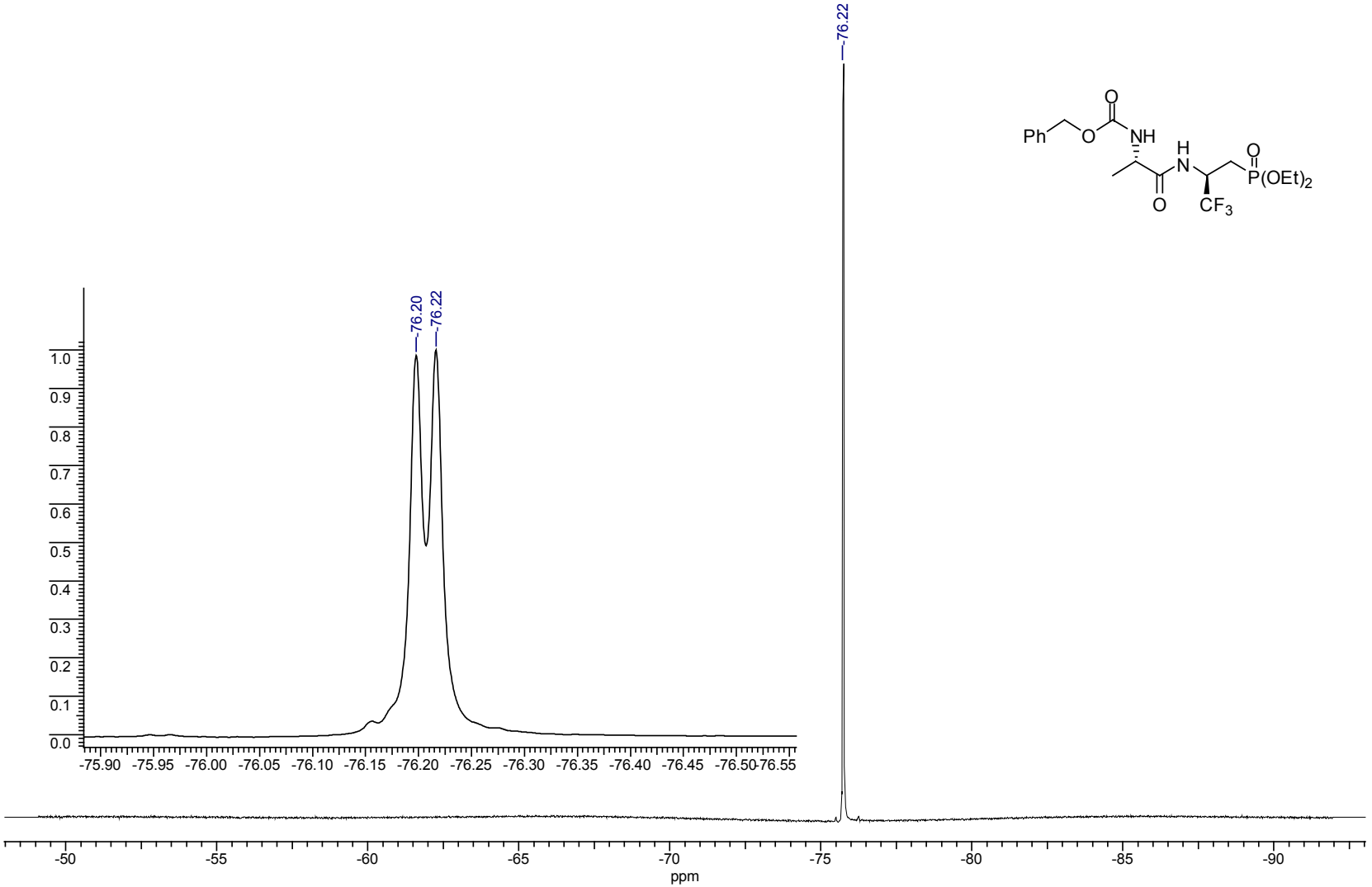


Acquisition Time (sec)	0.7834	***Comment***	Imported from UXNMR.			***Date***	23 Jul 2012 19:18:24
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide Ala\tyr-p103-C13\tyr-p103-C13_001000fid					***Frequency (MHz)***	125.76
Nucleus	13C	***Number of Transients***	583	***Original Points Count***	51200	***Points Count***	65536
Pulse Sequence	zgpg	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	32679.74		

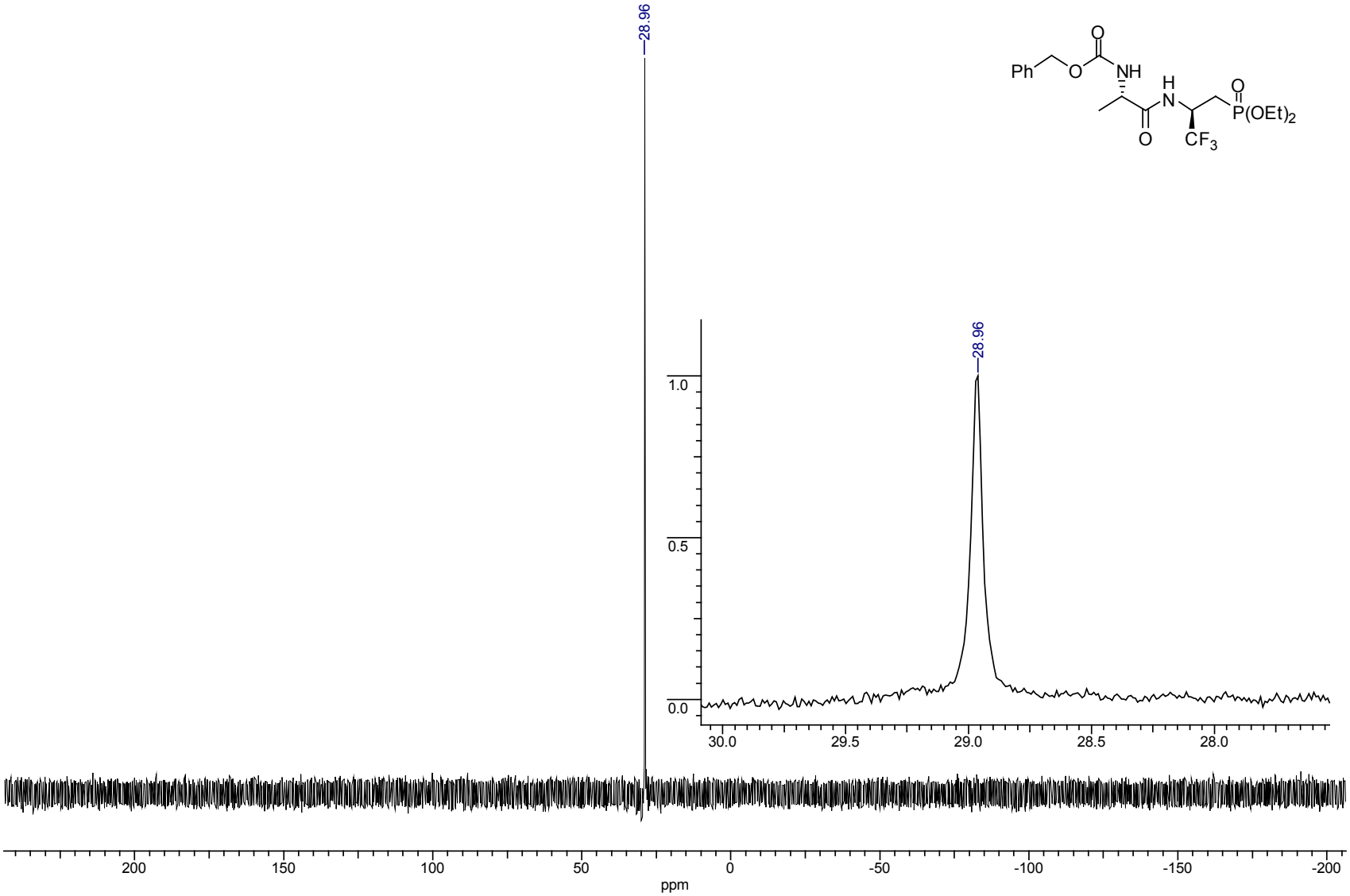


29 Jul 2012

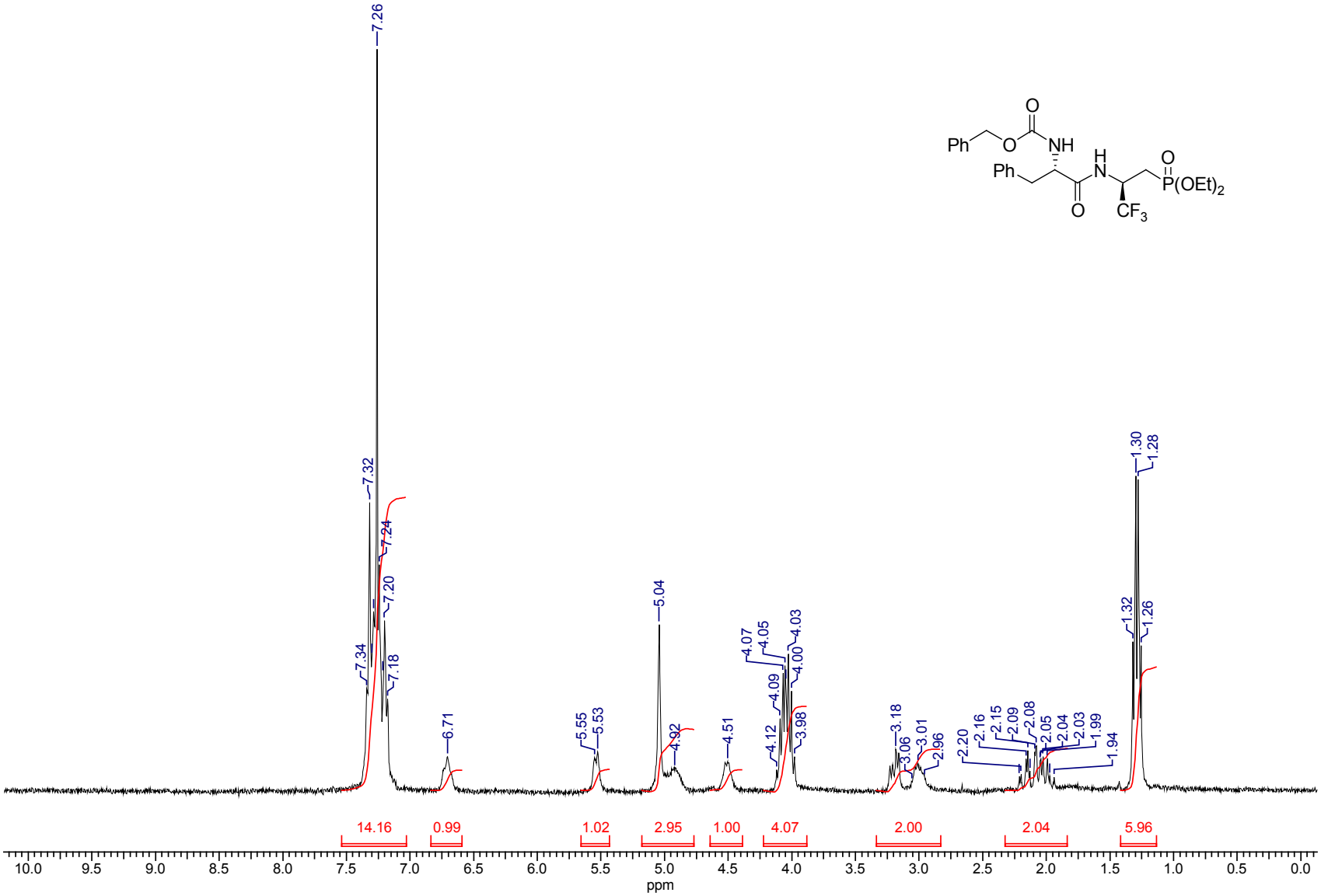
Acquisition Time (sec)	1.9816	***Comment***	19F SENSITIVITY			***Date***	Jul 26 2012
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide Ala\p-104-f					***Frequency (MHz)***	376.42
Nucleus	19F	***Number of Transients***	256	***Original Points Count***	64000	***Points Count***	65536
Pulse Sequence	s2pul	***Solvent***	TRIFLUOROACETIC ACID-D			***Sweep Width (Hz)***	16148.53
Temperature (degree C)	25.000						



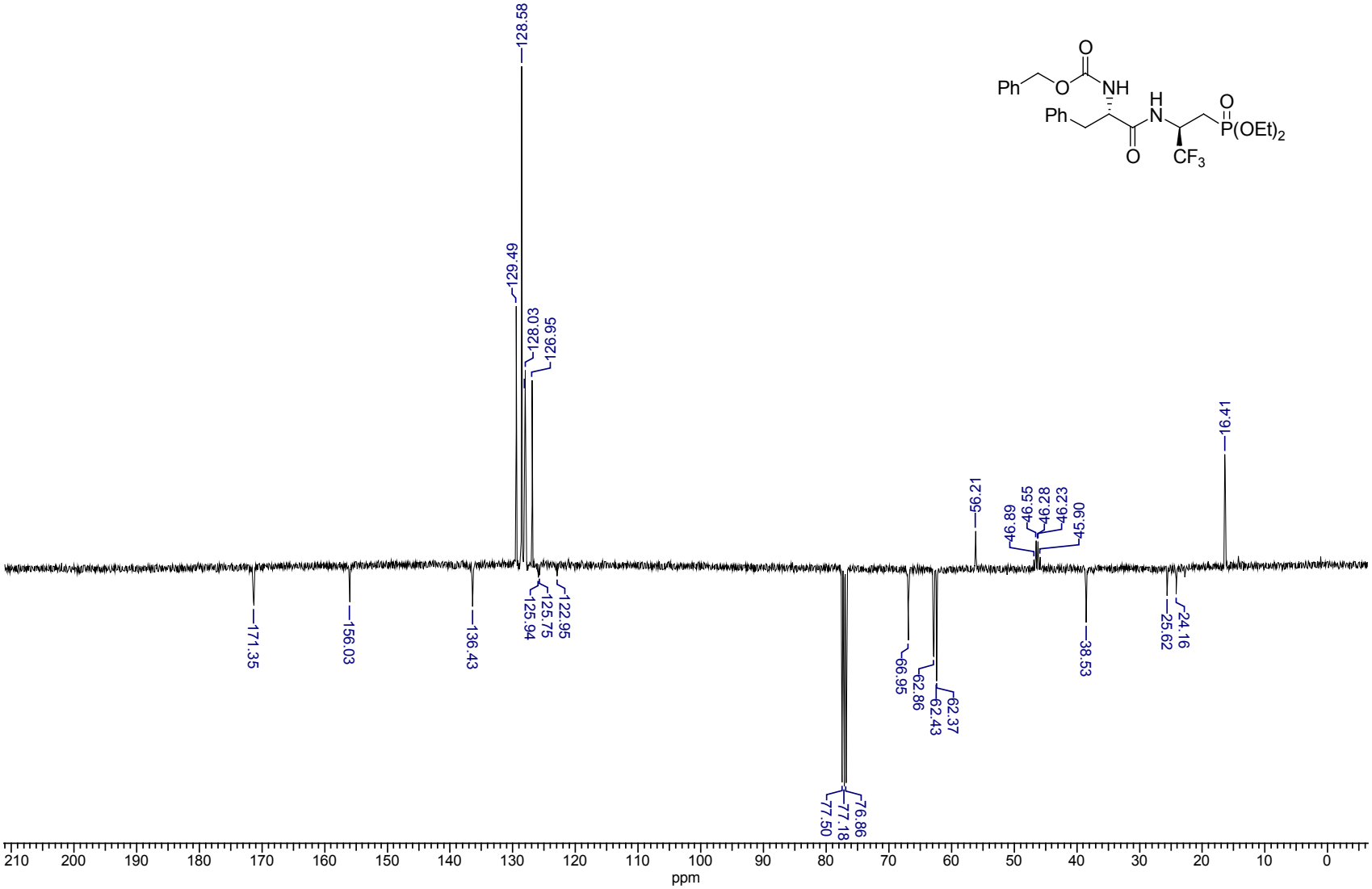
Acquisition Time (sec)	0.3200	***Comment***	DMSO 1203	***Date***	Jul 26 2012		
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide Ala\p-104-p					***Frequency (MHz)***	161.96
Nucleus	31P	***Original Points Count***	64000	***Points Count***	65536	***Pulse Sequence***	s2pul
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	100000.00	***Temperature (degree C)***	20.000



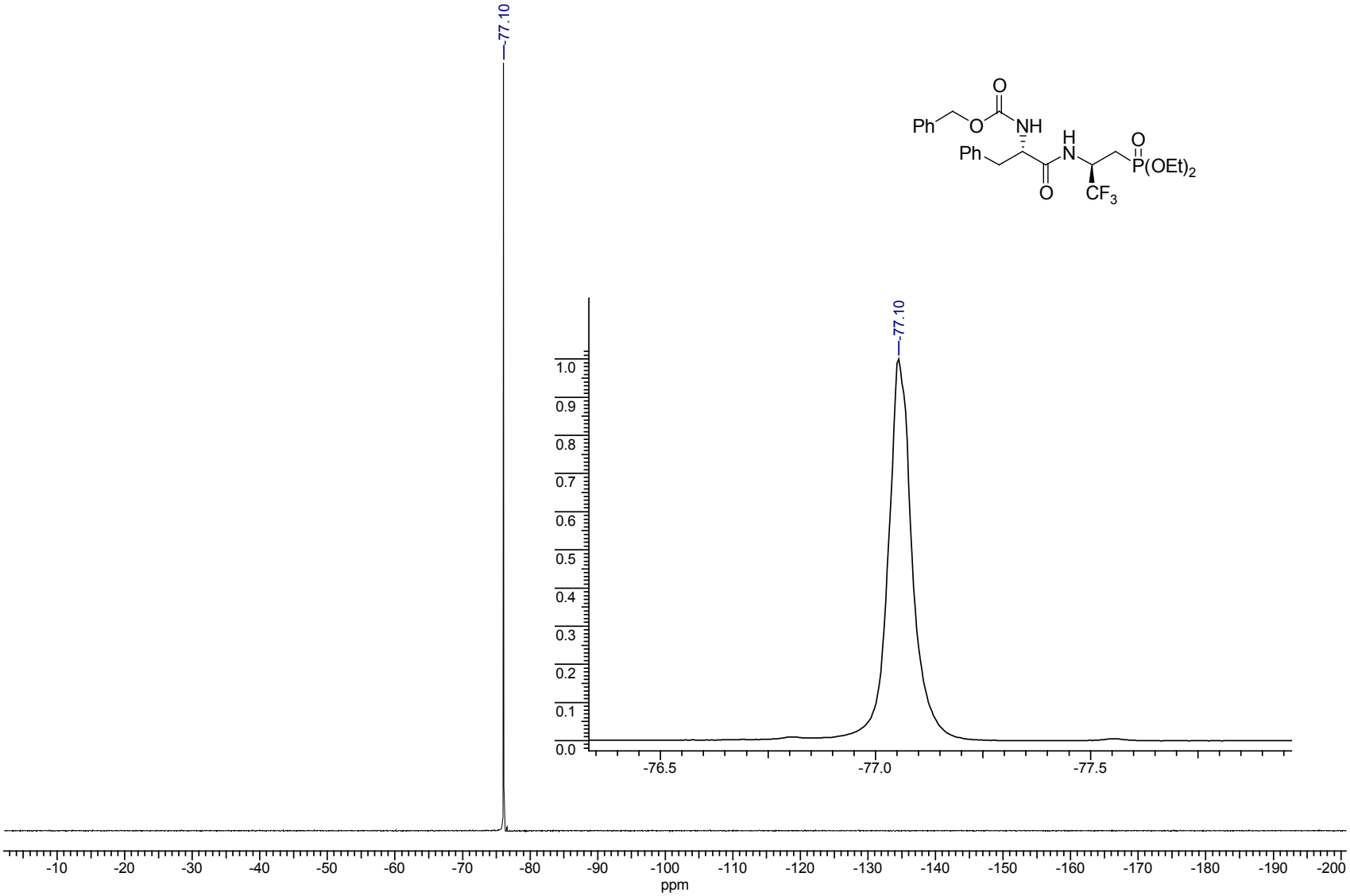
Acquisition Time (sec)	0.8566	***Comment***	LYBRICS Imported file	***Date***	08 Jun 2012 11:44:54
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide PhAla\1H	***Frequency (MHz)***	299.94	***Nucleus***	1H
Original Points Count	8736	***Points Count***	16384	***Sweep Width (Hz)***	5099.44	***Solvent***	CDCl3



Acquisition Time (sec)	0.6816	***Comment***	13C APT NMR Spectrum, in CDCl3			***Date***	27 Jun 2012 11:33:20
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide PhAla\13C-APT\13C-APT_fid					***Frequency (MHz)***	100.62
Nucleus	13C	***Number of Transients***	532	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	jmod	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	24038.46
Temperature (degree C)	21.706						



Acquisition Time (sec)	0.3400	***Date***	Jun 12 2012	***File Name***	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide PhAla\P_83-F19		
Frequency (MHz)	376.29	***Nucleus***	19F	***Number of Transients***	4	***Original Points Count***	64000
Points Count	65536	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	94117.65	***Temperature (degree C)***	20.000				



Acquisition Time (sec)	0.5000	***Comment***	Imported from UXNMR.	***Date***	08 Jun 2012 09:48:48
File Name	C:\Nuts\Data\Spectra-Aminophoshonates\Peptide PhAla\P_83-P31\P_83-P31_001000fid			***Frequency (MHz)***	202.44
Nucleus	31P	***Number of Transients***	24 ***Original Points Count*** 80641	***Points Count***	131072
Pulse Sequence	zg	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	80645.16