

Novel Route to Functionalized Tetraaryltetra[2,3]naphthaloporphyrins *via* Oxidative Aromatization

SUPPORTING INFORMATION

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Equipment and Measurements

The equipment used for analytical characterization of the compounds has been described elsewhere.¹ Solutions for phosphorescence measurements were deoxygenated by bubbling of Ar (Grade 6, BOC Gases, Inc.), after which the cuvettes were sealed. The absorbances of the samples at the wavelengths used for excitation were kept below 0.15 OD. The quantum yields were obtained by computing the integrals of the corrected emission spectra and referencing them to the fluorescence quantum yield of ZnTPP in deoxygenated benzene ($\phi_{\text{fluor}} = 0.033$).² The spectra were normalized by the optical density of the samples at the excitation wavelengths, relative photon intensity of the source and quantum efficiency of the detector throughout the emission range.

Materials and Synthesis

All solvents were purified according to the standard procedures. *Selecto* silica gel (Fisher) was used for column chromatography. All starting materials and reagents were purchased from Fisher Scientific, Inc. and Sigma-Aldrich, Inc. Ethyl isocyanoacetate was prepared from glycine ethyl ester hydrochloride according to the published method.³ 5,8,9,10-Tetrahydro-1,4-naphthoquinone **1** and 5,8-dimethoxy-1,4-dihydronaphthalene **8** were synthesized using another published method.⁴ Octalin **2** was obtained from **1** in 40% yield according to the published procedure.⁵ Sulfone **3** was prepared from **2** in 80% yield following the standard method.⁶ In the reported below UV-VIS absorption data, the numbers in parentheses are the absorbances of the samples, normalized by the absorbances of the maximal peaks in the spectra. These numbers are representative of the relative oscillator intensities for the given wavelengths.⁷

Pyrrole-ester (4): Synthesis of **4** followed the general protocol, described earlier.⁸ Ethyl isocyanoacetate (560 mg, 5.0 mmol) was added to a suspension of ^tBuOK (620 mg, 5.0 mmol) in 15 ml of freshly distilled THF (90%) at 0°C under Ar. A solution of sulfone **3** (1.1 g, 4.1 mmol) in 15 ml of THF was added to the mixture in one portion, and the mixture was left to react at r.t. under continuous stirring. After 4 h the volume of the mixture was reduced to about 10 ml by rotary evaporation. 100 ml of CH₂Cl₂ was added to the mixture, and the resulting solution was washed with water, then with brine and dried over Na₂SO₄. After evaporation of the solvent, the residue was dried in vacuum to remove isocyanacetate and purified on a silica gel column (eluent: CH₂Cl₂). Yield of pyrrole-ester **4**: 890 mg, 88%, colorless crystals. δ_H (CDCl₃): 8.74 (broad s, 1H), 6.60 (d, 1H, $J=3$ Hz), 4.29 (m, 2H), 3.05 (dd, 1H, $J_1=17$ Hz, $J_2=5$ Hz), 2.61 (dd, 1H, $J_1=15$ Hz, $J_2=4$ Hz), 2.23 (dd, 1H, $J_1=17$ Hz, $J_2=10$ Hz), 2.10 (dd, 1H, $J_1=16$ Hz, $J_2=11$ Hz), 1.85 (m, 2H), 1.75 (m, 2H), 1.28-1.35 (ovrlp. t+m, 3+4H), 1.08 (m, 2H); δ_C (CDCl₃): 161.52, 128.17, 122.13, 118.01, 117.3, 59.7, 38.9, 34.4, 34.3, 30.9, 29.7, 26.5, 14.6.

Porphyrin (6): Pyrrole-ester **4** (890 mg, 3.60 mmol) was refluxed under Ar with an excess of KOH (1.8 g, 27.3 mmol) in ethylene glycol (20 ml) for 20 min. The mixture was poured onto crushed ice, brine was added to reduce the emulsion and the product was extracted with CH₂Cl₂ (4×50 ml). The organic phase was thoroughly washed with water (200 ml), then with brine, dried over Na₂SO₄, and the solvent was removed in vacuum. The resulting material was purified on a short (ø2×10 cm) silica gel column (eluent: CH₂Cl₂). The solvent was removed in vacuum and the resulting oil was dissolved in 320

ml of CH_2Cl_2 . Methyl 4-formylbenzoate (530 mg, 3.25 mmol) was added to the mixture, and it was kept under continuous stirring in the dark under Ar for 10 min. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (102 mg, 0.72 mmol) was added in one portion, and the mixture was left to react at r.t. for 1.5 hrs. DDQ (900 mg, 4 mmol) was added, and the mixture was left to stir for an hour. The resulting green solution was washed with 10% aq. Na_2SO_3 (100 ml), then with 10% aq. Na_2CO_3 (100 ml) and finally with 5% aq. HCl, after which it was dried over Na_2SO_4 . The solvent was removed in vacuum, and the remaining material was twice purified on a silica gel column (eluent: CH_2Cl_2 , then CH_2Cl_2 -THF 10:1). A bright green band eluting with CH_2Cl_2 -THF was collected and the solvent was removed in vacuum. The remaining green solid was purified by repetitive precipitation from CH_2Cl_2 with hexane-ether mixture (4:1). Yield of **6**: 460 mg, 40%, green powder. δ_{H} (CDCl_3 -TFA): 8.4-8.6 (m, 16H), 4.20 (s, 12H), 2.6-0.2 (m, 56H); -1.3 (br s, 4H); MALDI-TOF: m/z 1280.2, calcd 1279.6; UV-VIS, λ_{max} nm (di-cation Cl_2^- , CH_2Cl_2): 467 (1.0), 615 (0.08), 671 (0.11).

Pd-porphyrin (Pd-6): An excess of PdCl_2 (20 mg, 0.11 mmol) was added to a solution of porphyrin **6** (100 mg, 0.078 mmol) in CH_3CN -THF (20 ml, 1:1), and the mixture was refluxed for 5 min. Et_3N (0.5 ml) was added, and the mixture was refluxed for additional 10 min. The conversion was monitored using UV-VIS spectroscopy (solvent CHCl_3 -AcOH). The reaction was stopped when the Soret absorption of the porphyrin-dication disappeared. The mixture was evaporated to dryness, and the remaining material was purified on a silica gel column (eluent: CH_2Cl_2) to give the product as a red amorphous solid. Yield of **Pd-6**: 93 mg, 97%. δ_{H} (CDCl_3): 8.5-7.9 (m, 16H), 4.09 (s, 12H), 2.4-0.6 (m, 56H); MALDI-TOF: m/z 1382.2, calcd 1384.0; UV-VIS, λ_{max} nm (CH_2Cl_2): 432 (1.0), 541 (0.11), 577 (0.09).

Cu-porphyrin (Cu-6): An excess of $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20 mg, 0.11 mmol) was added to a solution of porphyrin **6** (100 mg, 0.078 mmol) in CH_2Cl_2 -MeOH (20 ml, 10:1), and the mixture was refluxed for 15 min. The conversion was monitored using UV-VIS spectroscopy (solvent CHCl_3 -AcOH). The reaction was stopped when the Soret absorption of the porphyrin-dication disappeared. The mixture was evaporated to dryness, and the remaining material was purified on a silica gel column (eluent: CH_2Cl_2) to give the product as a red amorphous solid. Yield of Cu-porphyrin **Cu-6**: 100 mg, 99%. MALDI-TOF: m/z 1307.5, calcd 1307.3; UV-VIS, λ_{max} nm (CH_2Cl_2): 428 (1.0), 560 (0.091), 593 (0.05).

Cu-tetranaphthaloporphyrin (Cu-7a): Porphyrin **Cu-6** (30 mg, 0.023 mmol) was dissolved in 30 ml of freshly distilled dry toluene under Ar. DDQ (120 mg, 0.54 mmol) and $\text{Sc}(\text{OTf})_3$ (100 mg, 0.2 mmol) were added and the mixture was refluxed for 20 min. The color of the solution changed to from red to brown-green and a dark precipitate formed. The mixture was allowed to cool down and CH_2Cl_2 (50 ml) was added. The solution was washed with 10% aq. Na_2SO_3 solution (50 ml), then with water (100 ml), with brine (100 ml), and dried over Na_2SO_4 . The solvents were removed in vacuum, and the remaining solid was purified on a silica gel column (eluent: CH_2Cl_2 -THF, 30:1). The first green fraction contained mixture of porphyrins (see main text), which were poorly separated and eluted in the following order: **6**, partially oxidized **6**, **Cu-7a**. **Cu-7a** was collected, the solvent was evaporated in vacuum and the remaining solid was dried on a vacuum line. Yield of **Cu-7a**: 6 mg, 20%. MALDI-TOF: m/z 1308.9, calcd 1308.1;

UV-VIS, λ_{\max} nm (CH_2Cl_2): 446 (0.58), 478 (1.0), 665 (0.12), 731 (0.91).

Tetranaphthaloporphyryin (7a): Cu-7a (6 mg, 0.0045 mmol) was dissolved in 5 ml of polyphosphoric acid and stirred in a closed vessel for 4-5 h at 50°C, then at r.t. over night. MeOH (10 ml) and H_2SO_4 (2 ml) were added to the mixture and it was left to stir for 24 h. CH_2Cl_2 (50 ml) was added and the organic phase was washed with water, with 10% aq. NaHCO_3 solution, then with brine and dried over Na_2SO_4 . The solvent was removed in vacuum, and the remaining solid was purified on a silica gel column (eluent: CH_2Cl_2 -THF, 30:1). Green fraction was collected and the solvent was evaporated in vacuum. Yield of **7a**: 4 mg, 72%. MALDI-TOF: m/z 1274.6, calcd 1274.4. UV-VIS, λ_{\max} nm (free-base, CH_2Cl_2): 477 (0.63), 500 (1.0), 683 (0.13), 735 (0.40), 752 (0.33); UV-VIS, λ_{\max} nm (dication $(\text{CF}_3\text{CO}_2^-)_2$, CH_2Cl_2 -TFA): 531 (1.0), 726 (0.12), 802 (0.37).

Pd-tetranaphthaloporphyryin (Pd-7a): Pd-6 (93 mg, 0.067 mmol) was dissolved in 50 ml of dry toluene under Ar. DDQ (365 mg, 1.61 mmol) was added and the mixture was refluxed for 3-5 min. The color of the solution changed from red to brown and the product precipitated as a dark green powder. The mixture was allowed to cool down and the solvent was removed in vacuum. The resulting solid was dissolved in CH_2Cl_2 (several drops of EtOH were added to dissolve the remaining residue), washed with 10% aq. Na_2SO_3 solution, then with water, with brine, and dried over Na_2SO_4 . The solvent was removed in vacuum, and the solid was purified on a silica gel column (eluent: CH_2Cl_2 -THF, 30:1). The first green fraction was collected. The solvent was evaporated, and the remaining material was purified by precipitation from CH_2Cl_2 with hexane-ether mixture (5:1) to give the product as a dark green solid. Yield of **Pd-7a**: 42 mg, 46%. δ_H (CDCl_3 /pyridine- d_5): 8.16 (d, 8H, $J=8$ Hz), 7.93 (d, 8H, $J=8$ Hz), 7.10-7.13 (ovrlp. s+m, 8+8H), 6.87 (m, 8H), 3.57 (s, 12H); δ_C (CDCl_3 /pyridine- d_5): 165.7, 145.4, 136.8, 134.2 (ovrlp. w/solv.), 133.2, 129.8, 129.8, 129.7, 128.0, 125.0, 114.8, 51.3; MALDI-TOF: m/z 1351.9, calcd 1351.7; UV-VIS, λ_{\max} nm (CH_2Cl_2): 428 (0.42), 457 (0.83), 646 (0.12), 710 (0.75).

α -Chlorosulfone (9): Synthesis of compound **9** generally followed the published method.⁸ Solution of PhSCl (0.72 g, 5 mmol) in 10 ml of CH_2Cl_2 , prepared as described in ref. 8, was added dropwise to a stirred solution of **8** (950 mg, 5 mmol) in dry CH_2Cl_2 at -78°C under Ar. The mixture was allowed to warm up to r.t. and left under stirring and Ar overnight. The precipitated succinimide was filtered off, the solvent was evaporated and the resulting material was oxidized by MCPBA (3.0 g, 12.5 mmol). Yield of **9**: 1.78 g, 97%, colorless solid. δ_H (CDCl_3): 7.92-7.53 (m, 5H), 6.64 (s, 2H), 4.82 (m, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 3.32-3.37 (m, 1H), 3.17-3.21 (m, 4H).

Sulfones (10b) and (11): To a stirred solution of **9** (1.78 g, 4.85 mmol) in CH_2Cl_2 (5 ml) an excess of DBU (1.5 g, 10 mmol) was added in one portion, and the mixture was stirred at r.t. for 1 h. 10 ml of diethyl were added, and the solution was washed with 5% aq. HCl, then with brine, dried over Na_2SO_4 , and the solvent was removed in vacuum. During the chromatography of the remaining oil (silica gel, CH_2Cl_2) three fractions were collected. The first fraction crystallized upon removal of solvent to give light yellow crystals, identified as sulfone **11** (50 mg). TLC: R_f 0.8 (CH_2Cl_2), fluorescent blue spot in UV light. HR-MS: 351.0656 ($\text{M}^+ + \text{Na}$), calcd 351.0667; δ_H

(CDCl₃): 8.92 (s, 1H), 8.26 (d, 1H, *J*=9 Hz), 7.98+7.44-7.52 (m, 2+3H), 7.86 (d, 1H, *J*=9 Hz), 6.82 (d, 1H, *J*=8.5 Hz), 6.76 (d, 1H, *J*=8.5 Hz), 3.95 (s, 3H), 3.92 (s, 3H). The third fraction gave colorless solid (295 mg), identified as allylsulfone **10b**. TLC: *R_f*~0.5 (CH₂Cl₂), dark spot in UV light. HR-MS: 353.0830 (*M*⁺+Na), calcd 353.0824; δ_H (CDCl₃): 7.7-7.2 (m, 5H), 6.94 (d, 1H, *J*=10 Hz), 6.56 (d, 1H, *J*=8.5 Hz), 6.43 (d, 1H, *J*=8.5 Hz), 5.99 (dd, 1H, *J*₁=*J*₂=10 Hz), 3.91 (m, 1H), 3.75 (s, 3H), 3.65 (dd, 1H, *J*₁=18 Hz, *J*₂=4 Hz), 3.60 (s, 3H), 2.96 (dd, 1H, *J*₁=18 Hz, *J*₂=8 Hz). The intermediate fraction (890 mg) was identified by TLC and NMR as 1:1 mixture of **10b** and **11**.

Pyrrole-ester (12): Ester **12** was synthesized from allylsulfone (**10b**) (295 mg, 0.9 mmol) and ethyl isocyanoacetate (120 mg, 1.05 mmol) following the procedure described above for ester **4**. ^tBuOK, however, was taken in a large excess (300 mg, 2.2 mmol). TLC (CH₂Cl₂) of the reaction mixture revealed the presence of sulfone **11** (see above) along with the main product **12** (*R_f*~0.2, dark spot in UV light). The products were separated on a silica gel column (eluent: CH₂Cl₂). Yield of **12**: 90 mg, 33%, colorless solid. δ_H (CDCl₃): 8.92 (broad s, 1H), 7.24 (s, 1H), 6.80 (d, 1H, *J*=2 Hz), 6.69 (s, 2H), 3.36 (q, 2H, *J*=7 Hz), 4.06 (s, 2H), 3.82-3.83 (ovrl. s+d, 6H+2H), 1.49 (t, 3H, *J*=7 Hz); δ_C (CDCl₃): 161.4, 151.8, 151.5, 125.3, 124.8, 119.5, 118.2, 117.6, 107.1, 106.9, 59.9, 55.74, 55.70, 22.4, 20.9, 14.6.

Pyrrole (13): Pyrrole-ester **12** (60 mg, 0.2 mmol) was refluxed with KOH (130 mg, 2 mmol) under Ar in ethylene glycol for 30 min. The mixture was poured onto crushed ice, brine was added to reduce the emulsion and the product was extracted with CH₂Cl₂ (4×50 ml). The organic phase was thoroughly washed with water (200 ml), then with brine, dried over Na₂SO₄, and the solvent was removed in vacuum. The resulting material was purified on a short (ø2×10 cm) silica gel column (eluent: CH₂Cl₂). Yield of **13**: 35 mg, 77%. δ_H (CDCl₃): 8.06 (broad s, 1H), 6.70 (s, 2H), 6.66 (d, 2H, *J*=2.5 Hz), 3.88 (s, 4H), 3.84 (s, 6H); δ_C (CDCl₃): 151.6, 126.3, 117.3, 112.8, 106.9, 55.8, 21.1.

Tetranaphthaloporphyrin (7b): Pyrrole **13** (35 mg, 0.15 mmol) was dissolved in 15 ml of CH₂Cl₂, methyl 4-formylbenzoate (25 mg, 0.15 mmol) was added, and the mixture was kept under continuous stirring in the dark under Ar for 10 min. BF₃·Et₂O (4.2 mg, 0.03 mmol) was added in one portion, and the mixture was left to react at r.t. After 2 hrs DDQ (75 mg, 0.32 mmol) was added in one portion. After 10 min, the mixture was washed with 10% aq. Na₂SO₃ (2×30 ml), then with water. Organic phase, a fine suspension of green particles in CH₂Cl₂, was evaporated in vacuum. Remaining green solid, which is insoluble in most organic solvents, was repeatedly washed with water, EtOH, THF and CH₂Cl₂. Yield **7b**: 25 mg, 44%. **7b** is poorly soluble in pyridine and DMF, moderately soluble in hot benzonitrile and nitrobenzene. MALDI-TOF: *m/z* 1486.5, calcd 1487.5; UV-VIS, λ_{\max} nm (free-base, THF-PhCN, 10:1): 474 (0.48), 503 (1.0), 681 (0.13), 742 (0.52), 755 (0.48); UV-VIS, λ_{\max} nm (dication (CF₃CO₂)₂, THF-PhCN-TFA, 10:1:1): 528 (1.0), 742 (0.20), 808 (0.69).

Pd-tetranaphthaloporphyrin (Pd-7b): Porphyrin **7b** (10 mg, 0.006 mmol) was refluxed with PdCl₂ (5 mg, 0.03 mmol) in PhCN (3 ml) for 30 sec moment and a drop of pyridine was added. The warm mixture was filtered through Celite[®], the solution was diluted with THF, the precipitate was collected by centrifugation and repeatedly washed

with THF with subsequent centrifugation. The resulting green powder was dried in vacuum. Yield of **Pd-7b**: 8 mg, 80%. δ_H (PhNO₂-d₅/dmsO-d₆, 1:1, 80°C): 8.76 (d, 8H, $J=7$ Hz), 8.52 (d, 8H, $J=7$ Hz), 8.23 (s, 8H), 6.79 (s, 8H), 4.27 (s, 12H), 3.90 (s, 24H); MALDI-TOF: m/z 1590.7, calcd 1591.9; UV-VIS, λ_{\max} nm (THF-PhCN, 10:1): 430 (0.40), 461 (0.85), 648 (0.15), 717 (1.0).

Zn-tetranaphthaloporphyrin (Zn-7b): Porphyrin **7b** (10 mg, 0.006 mmol) was refluxed with ZnCl₂·2H₂O (5 mg, 0.03 mmol) in PhCN (3 ml) for a few seconds and a drop of pyridine was added. The warm mixture was filtered through Celite[®], the solution was diluted with THF, the precipitate was collected by centrifugation and repeatedly washed with THF-pyridine (10:1). The resulting green powder was dried in vacuum. Yield of **Zn-7b**: 7 mg, 70%. δ_H (PhNO₂-d₅): 8.95 (d, 8H, $J=7.5$ Hz), 8.65 (d, 8H, $J=8$ Hz), 8.62 (s, 8H), 6.77 (s, 8H), 4.22 (s, 12H), 3.89 (s, 24H); MALDI-TOF: m/z 1549.4, calcd 1550.9; UV-VIS, λ_{\max} nm (THF-PhCN, 10:1): 458 (0.27), 492 (1.0), 661 (0.09), 726 (0.63).

X-ray structure determination

Compound **Pd-7b**, PdC₈₆H₅₆N₄O₆Cl₄, crystallizes in the tetragonal space group I4₁/a (systematic absences $hk0$: $h=\text{odd}$, hkl : $h+k+l=\text{odd}$, and $00l$: $l \neq 4n$) with $a=17.628(3)\text{\AA}$, $c=23.372(5)\text{\AA}$, $V=7262(2)\text{\AA}^3$, $Z=4$ and $d_{\text{calc}}=1.392\text{ g/cm}^3$. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda=0.71069\text{ \AA}$) at a temperature of 143°K. Indexing was performed from a series of four 0.5° oscillation images with exposures of 30 sec per frame. A hemisphere of data was collected using 75 sec exposures and a crystal-to-detector distance of 35 mm. A total of 440 images were collected: one sweep was performed using ϕ -scans from -90° to +90° in 0.5° steps at $\omega = 0^\circ$ and $\chi = 0^\circ$ with a detector swing angle of -10°; a second sweep was done using ω -scans from -20° to +20° in 0.5° steps at $\chi = -90^\circ$ and $\phi = 0^\circ$ with a detector swing angle of -10°. Oscillation images were processed using CrystalClear,⁹ producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the teXsan¹⁰ program package for further processing and structure solution on a Silicon Graphics O₂ computer. A total of 24216 reflections were measured over the ranges $5.46 \leq 2\theta \leq 54.96^\circ$, $-22 \leq h \leq 16$, $-22 \leq k \leq 20$, $-29 \leq l \leq 22$ yielding 4046 unique reflections ($R_{\text{int}} = 0.0418$). The intensity data were corrected for Lorentz and polarization effects and for absorption, using REQAB^[11] (minimum and maximum transmission 0.664, 1.000).

The structure was solved by direct methods (SIR92).¹² During refinement, it became obvious that there was a region in the cell with severely disordered solvent; the data were corrected for the presence of disordered solvent by SQUEEZE.¹³ Refinement was by full-matrix least squares based on F^2 using SHELXL-93.¹⁴ All reflections were used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w=1/[\sigma^2(F_o^2) + 0.1741P^2 + 108.0003P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to $R_1=0.0817$ and $wR_2=0.2561$ for 3574 reflections for which $F > 4\sigma(F)$ and $R_1=0.0900$, $wR_2=0.2624$ and GOF = 0.884 for all 4046 unique, non-zero reflections and 219 variables.¹⁵ The maximum Δ/σ in the final

cycle of least squares was -0.002 and the two most prominent peaks in the final difference Fourier were +0.873 and -0.872 e/Å³.

Figure 1 is an ORTEP¹⁶ representation of the molecule with 30% probability thermal ellipsoids displayed.

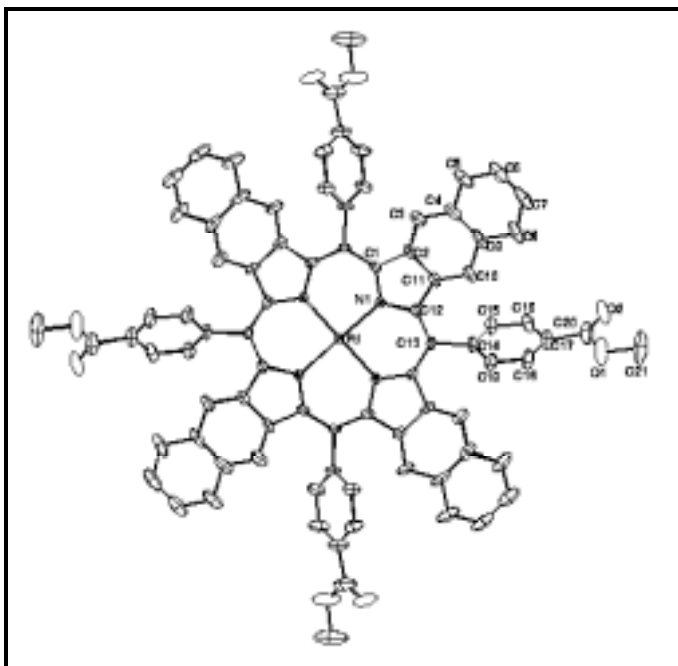


Figure 1. ORTEP drawing of **Pd-7a** with 30% probability thermal ellipsoids.

Normal-Coordinate Structural Decomposition (NSD) Analysis

NSD analyses of the X-ray crystal of **Pd-7a** structure were accomplished using a web-based NSD program.¹⁷ The results of the complete NSD decompositions are given in the tables below.

Pd-7b

NSD result generated from file PdTNP.pdb at Thu Mar 13 13:28:18 EST 2003

Summary of the NSD (in Å):

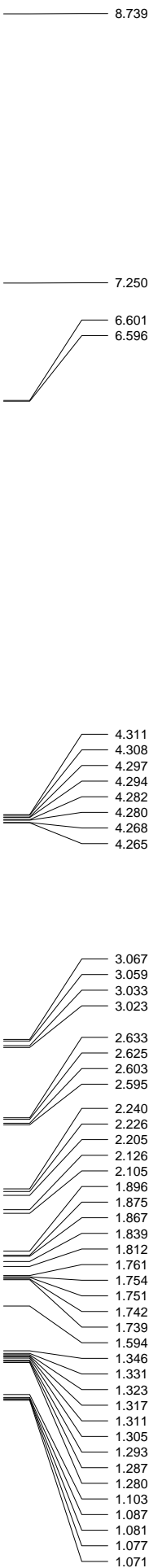
basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	Alg	A2g
min.	0.1931	0.0460	0.0002	-0.0005	-0.0000	0.0002	-0.1927	-0.0126
ext.	0.2259	0.0410	0.0002	-0.0005	-0.0000	0.0002	-0.1931	-0.0122
			-0.0000	-0.0001	0.0001	-0.0001	-0.1104	0.0389
comp.	0.3103	0.0000	0.0011	0.0010	0.0007	0.0008	0.3072	0.0431

basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	2.5666	0.0189	2.5477	0.3106	0.0000	0.0000	0.0000	0.0000
ext.	2.5698	0.0092	2.5454	0.3106	0.0000	0.0000	0.0000	0.0000
			-0.1237	-0.0321	-0.0000	-0.0000	-0.0000	-0.0000
comp.	2.5704	0.0000	2.5511	0.3141	0.0000	0.0000	0.0000	0.0000

References and Notes

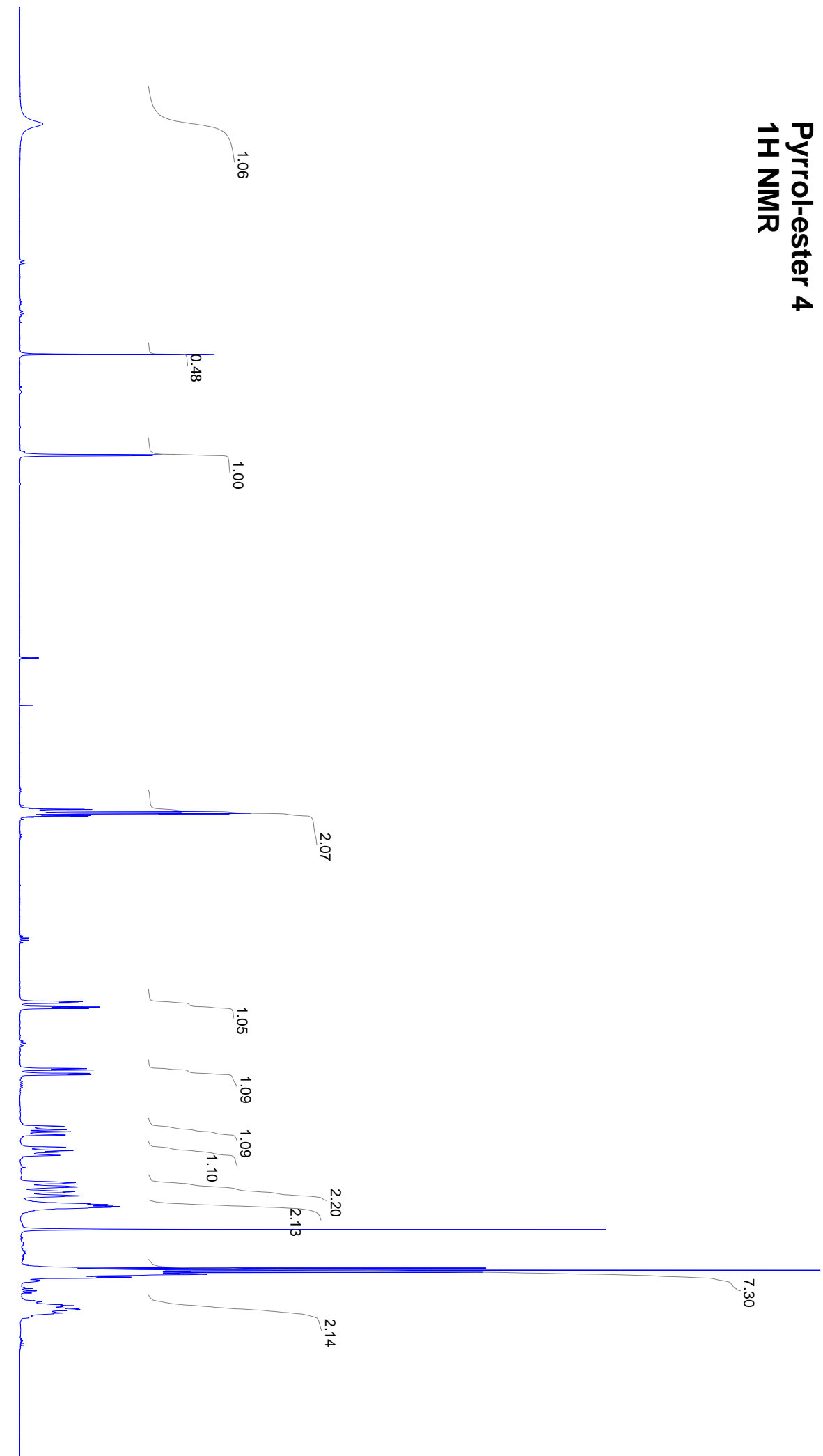
- (1) Rozhkov, V. V., Khajehpour, M., Vinogradov, S. A. *Inorg. Chem.*, **2003**, 42, 4253-4255.
- (2) D. J. Quimby, F. R. Longo, *J. Am. Chem. Soc.* **1975**, 97, 5111.
- (3) L. F. Tietze and T. Eicher, *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, Georg Thieme Verlag, New York, 1991.
- (4) A. V. Rama Rao, J. S. Yadav, K. Bal Reddy, A. R. Mehendale, *Tetrahedron*, 1984, **40**, 4643.
- (5) H. B. Henbest, M. Smith and A. Thomas, *J. Chem. Soc.*, 1958, 3293.
- (6) P. B. Hopkins, P.L. Fuchs, *J. Org. Chem.*, 1978, **43**, 1208.
- (7) The extinction coefficients of the Zn and Pd complexes reported in this work are very close to those reported recently for the basic Zn and Pd Ph₄TNP's (see ref. 1). The exact numbers will be reported elsewhere.
- (8) Y. Abel, E. Haake, G. Haake, W. Schmidt, D. Struve, A. Walter, F.-P. Montforts, *Helv. Chim. Acta*, 1998, **81**, 1978.
- (9) CrystalClear: Rigaku Corporation, 1999.
- (10) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).
- (11) REQAB4: R.A. Jacobsen, (1994). Private Communication.
- (12) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidoro, G. (1994). *J. Appl. Cryst.*, **27**, 435.
- (13) SQUEEZE: P. v.d. Sluis & A.L. Spek (1990). *Acta. Cryst.*, **A46**, 194.
- (14) SHELXL-93: Program for the Refinement of Crystal Structures, Sheldrick, G.M. (1993), University of Göttingen, Germany.
- (15) $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$
 $wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$
 $GOF = \{ \sum w (F_o^2 - F_c^2)^2 / (n - p) \}^{1/2}$
 where n = number of reflections and p = number of parameters refined.
- (16) "ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.
- (17) <http://jasheln.unm.edu/> NSD references: (a) W. Jentzen, X.-Z. Song, J. A. Shelnutt, *J. Phys.Chem. B* **1997**, 101, 1684-1699; (b) W. Jentzen, J. G. Ma, J. A. Shelnutt, *Biophys. J.* **1998**, 74, 753-763; For reviews see: (c) J. Shelnutt, *Molecular simulations and normal-coordinate structural analysis of porphyrins and heme proteins*, Ch. 50 in *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith, R. Guilard, Eds., Academic Press, 2000; (d) J. A. Shelnutt, *J. Porph. Phthal.* **2001**, 5, 300-311.

NMR spectra



Pyrrol-ester 4

¹H NMR

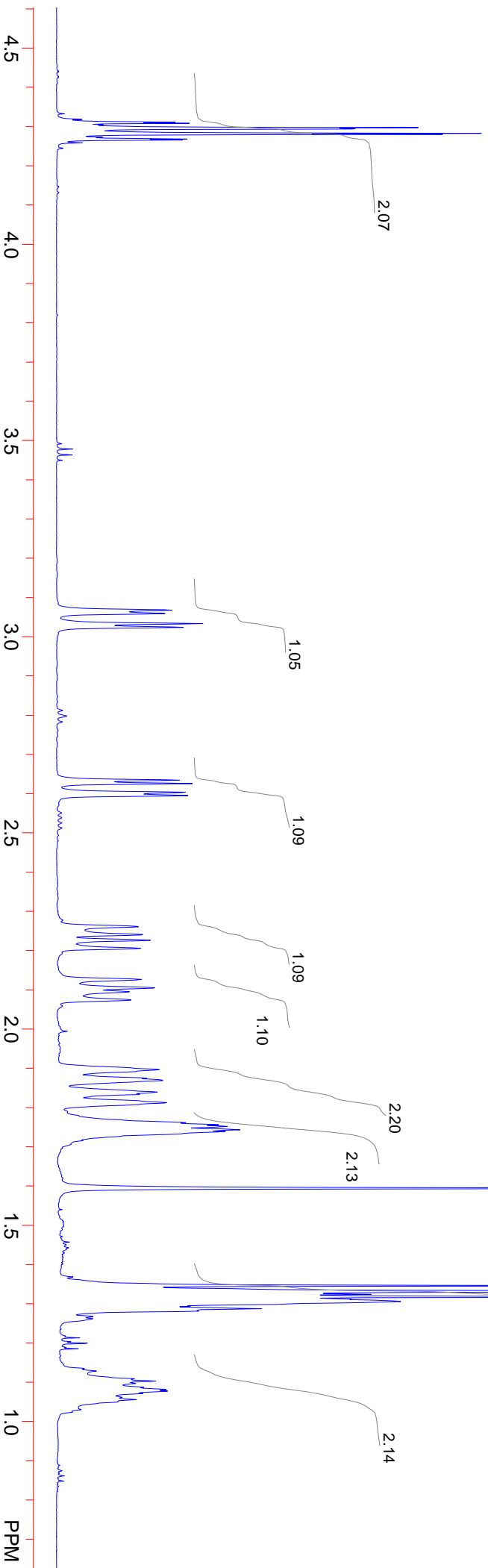
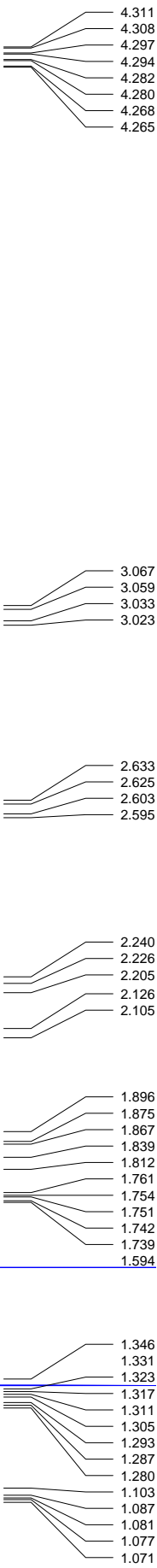


STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	PD: 0.0 sec	OF1: 2490.8	LB: 0.0	PTSLd: 32768
EX: s2pul		PW: 2.0 usec		NA: 50		

USER: -- DATE: Oct 5 2002

WinNuts - \$fb_ocypyr_1H.fid



STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	PD: 0.0 sec	OF1: 2490.8	LB: 0.0	PTSIId: 32768	USER: -- DATE: Oct 5 2002
EX: s2pul		PW: 2.0 usec		NA: 50			WinNuts - \$fb_ocpyr_1H.fid

pyrrol-ester 4
13C NMR

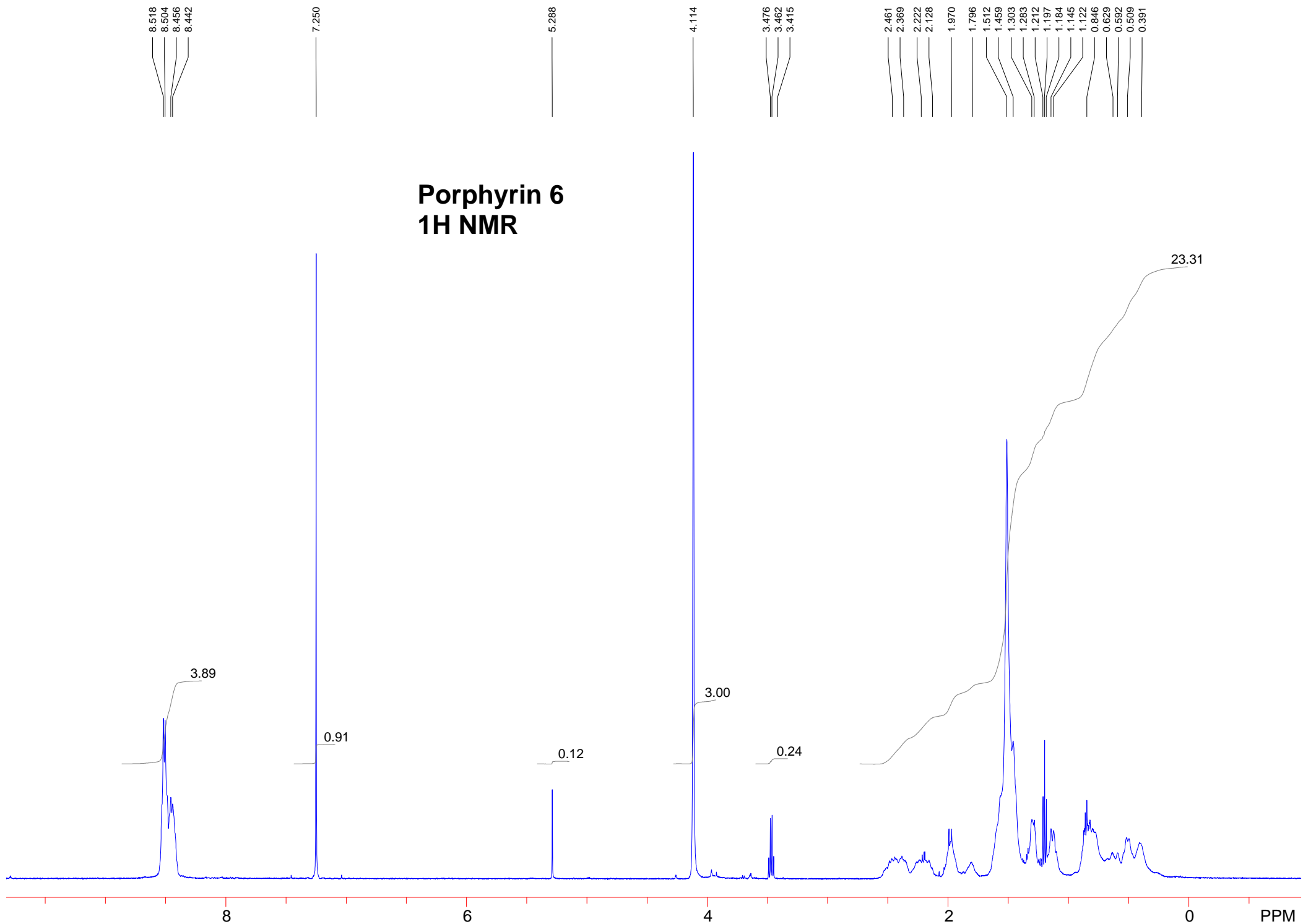


STANDARD CARBON PARAMETERS

F1: 125.700	F2: 499.855	SW1: 25000	PW: 13.0 usec	PD: 2.0 sec	OF1: 11922.2	NA: 15722	LB: 0.0	PTS: 8192	id: 8192	USER: -- DATE: Oct 5 2002
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EX: s2pul

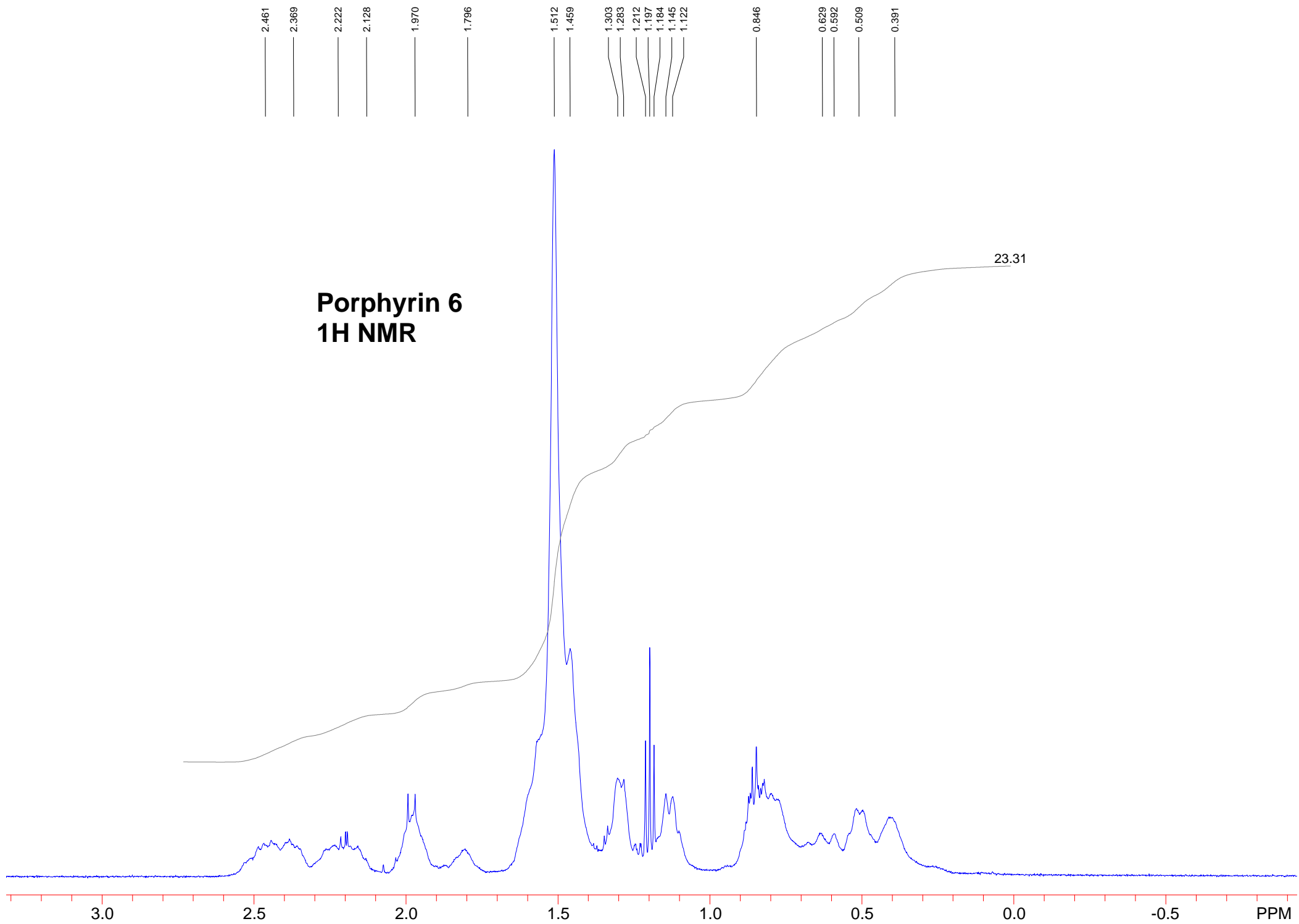
WinNus - \$fb_ocpyr_13C.fid



STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2490.9	PTS1d: 32768
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 8	LB: 0.0
WinNuts - \$fb_octdc.fid				

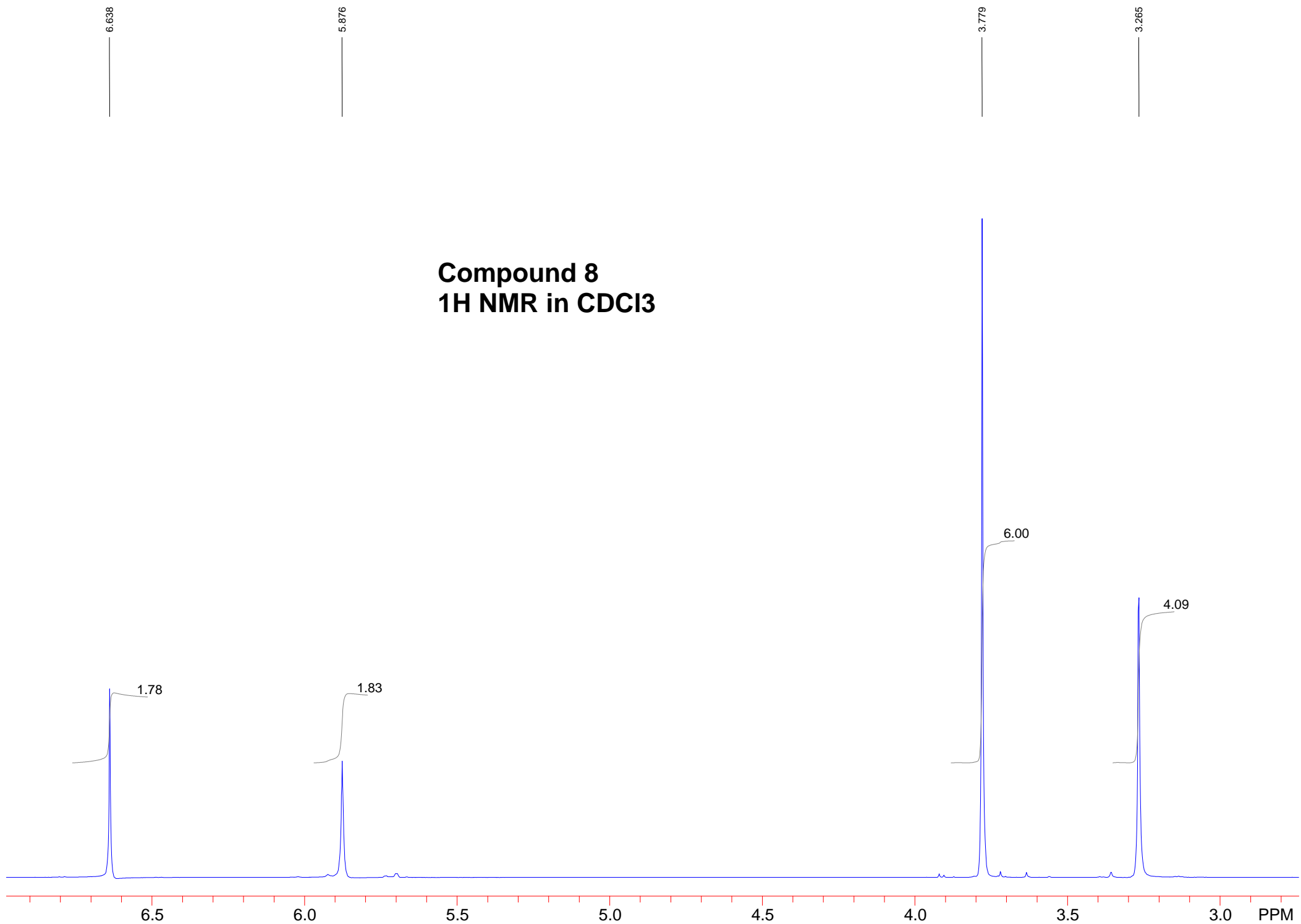
USER: -- DATE: Oct 5 2002



STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	PD: 0.0 sec	OF1: 2490.9	LB: 0.0	PTS1d: 32768	USER: -- DATE: Oct 5 2002
EX: s2pul	PW: 5.5 usec		NA: 8			WinNuts - \$fb_octdc.fid	

Compound 8
¹H NMR in CDCl₃

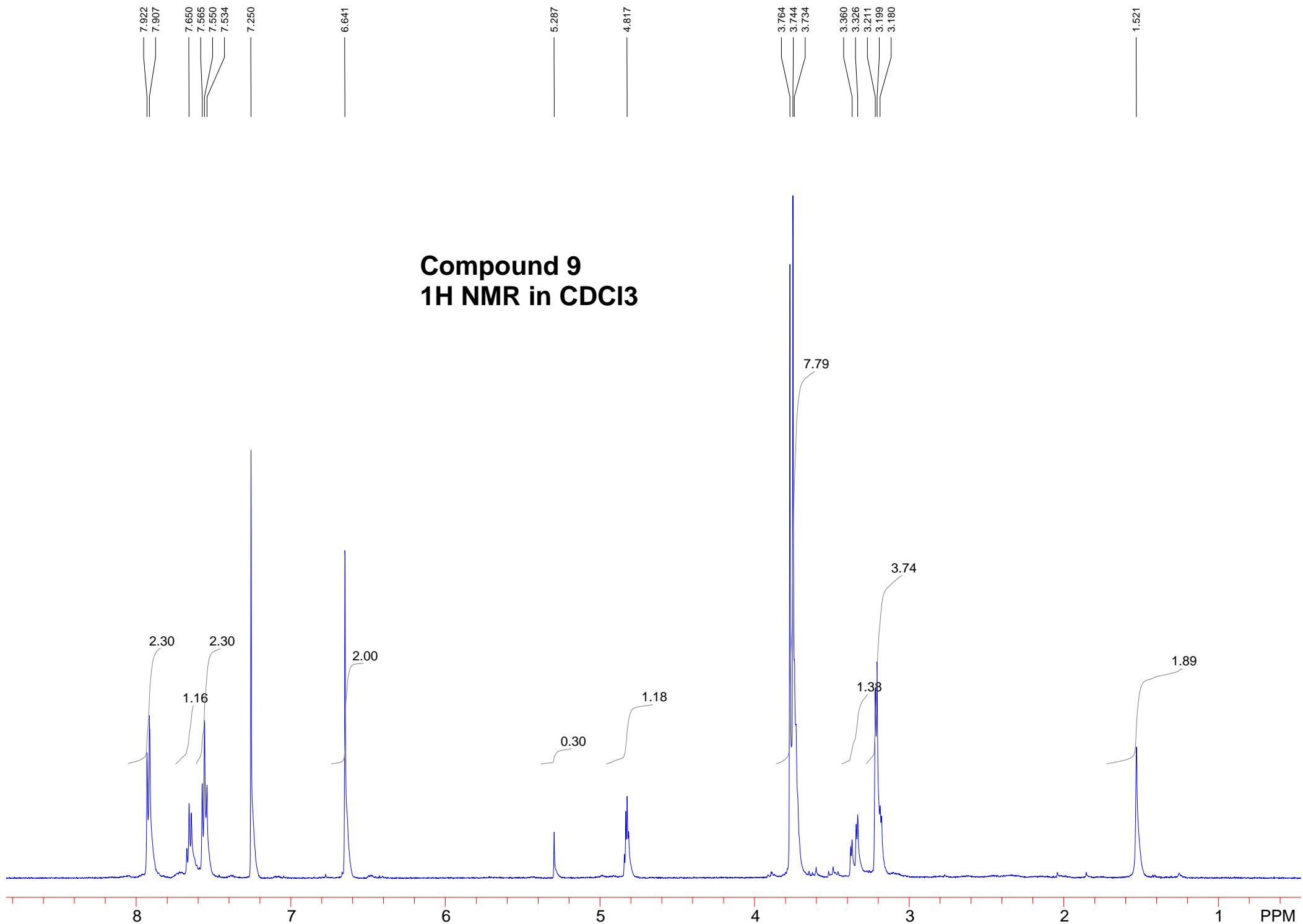


STANDARD PROTON PARAMETERS

USER: -- DATE: Nov 12 2002

F1: 499.855	F2: 499.855	SW1: 20000		OF1: 2491.0		PTS1d: 32768	
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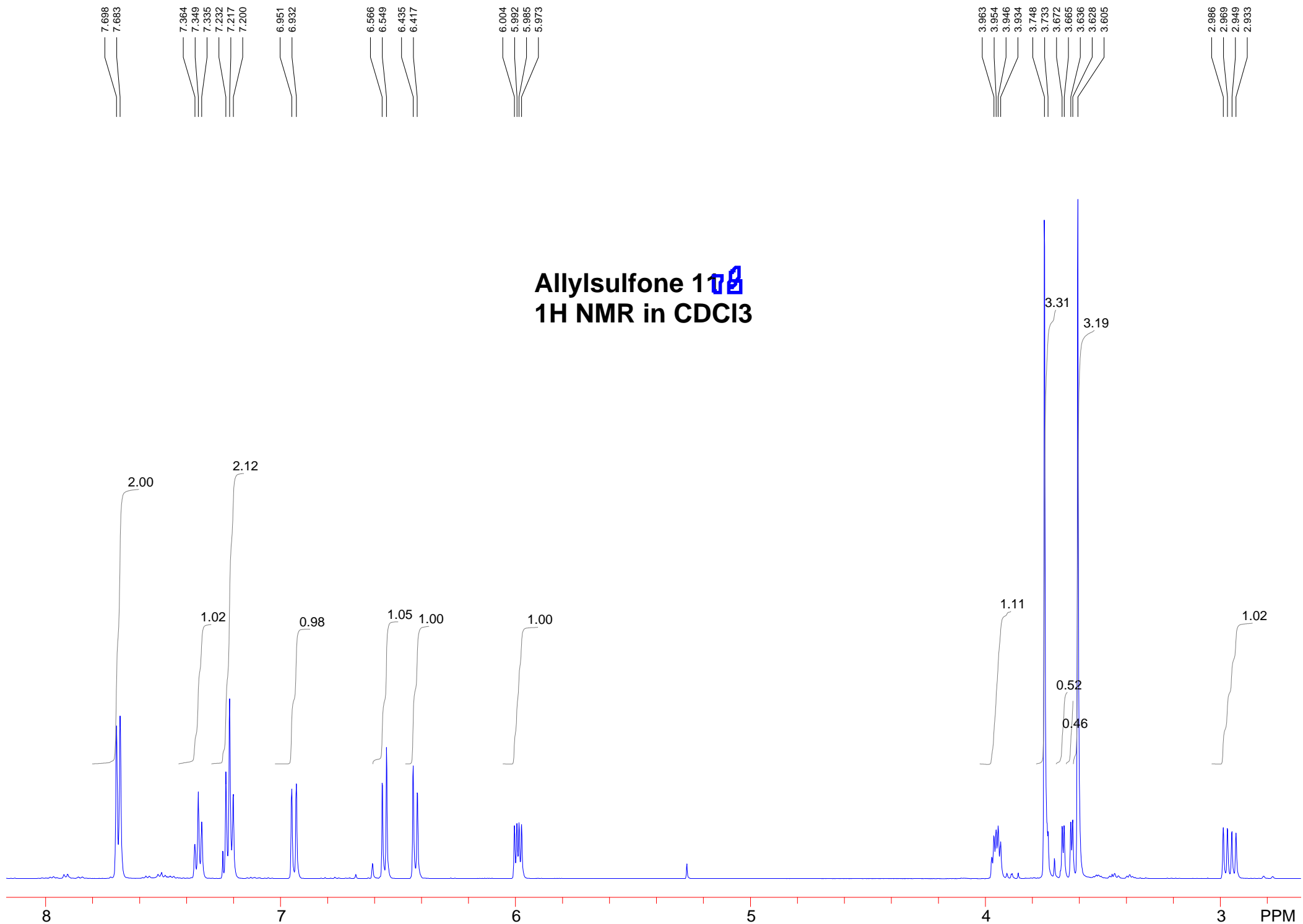
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 8	LB: 0.0	WinNuts - \$fb_dame.fid		
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STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2494.8	PTS1d: 32768
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 40	LB: 0.0
WinNuts - \$fb_meo_so2cl.fid				

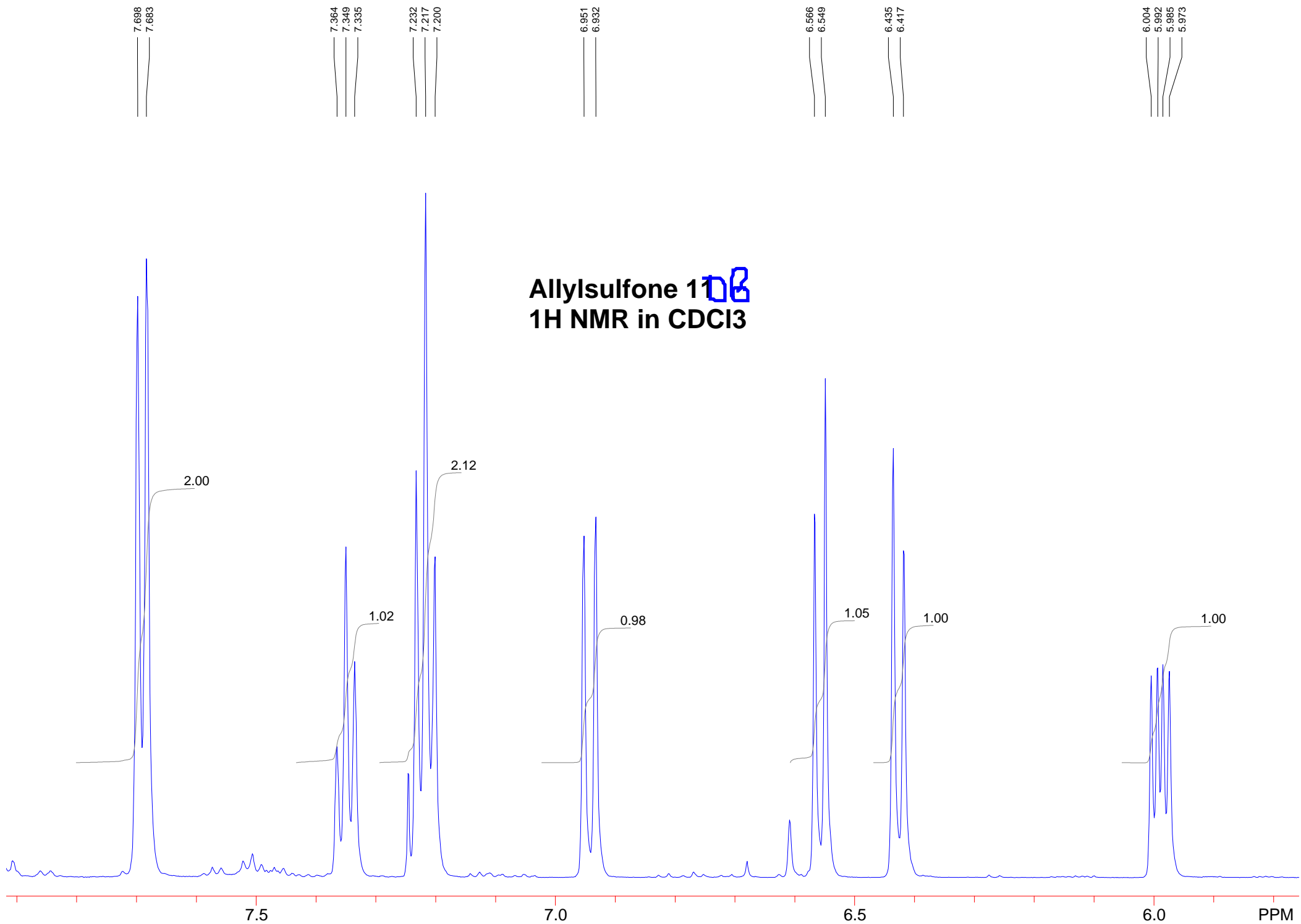
USER: -- DATE: Nov 20 2002



STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2490.8	PTS1d: 32768
EX: s2pul	PW: 3.0 usec	PD: 0.0 sec	NA: 8	LB: 0.0
WinNuts - \$fb_3black.fid				

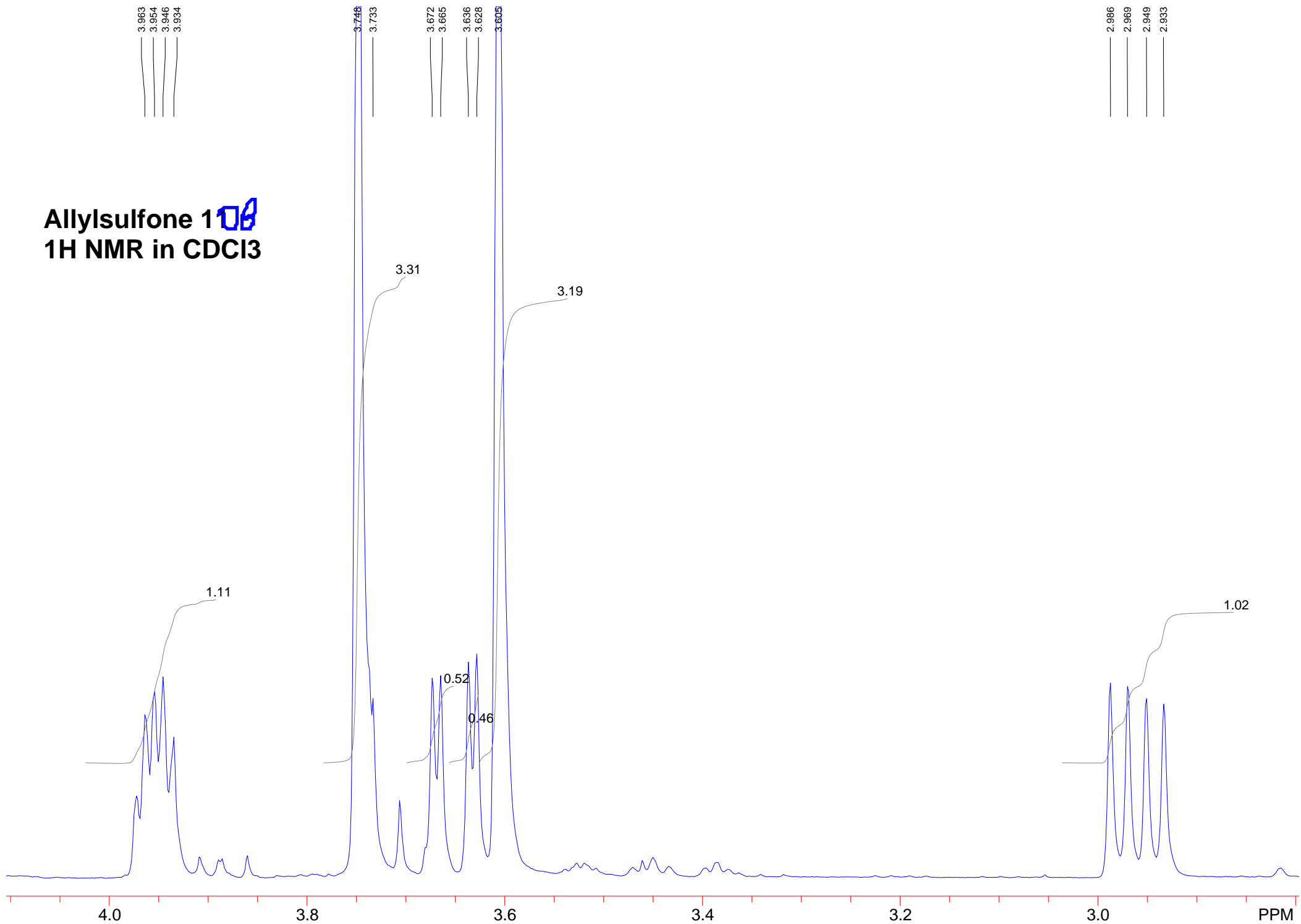
USER: -- DATE: Nov 22 2002



STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	PD: 0.0 sec	OF1: 2490.8	LB: 0.0	PTS1d: 32768	USER: -- DATE: Nov 22 2002
EX: s2pul	PW: 3.0 usec	NA: 8				WinNuts - \$fb_3black.fid	

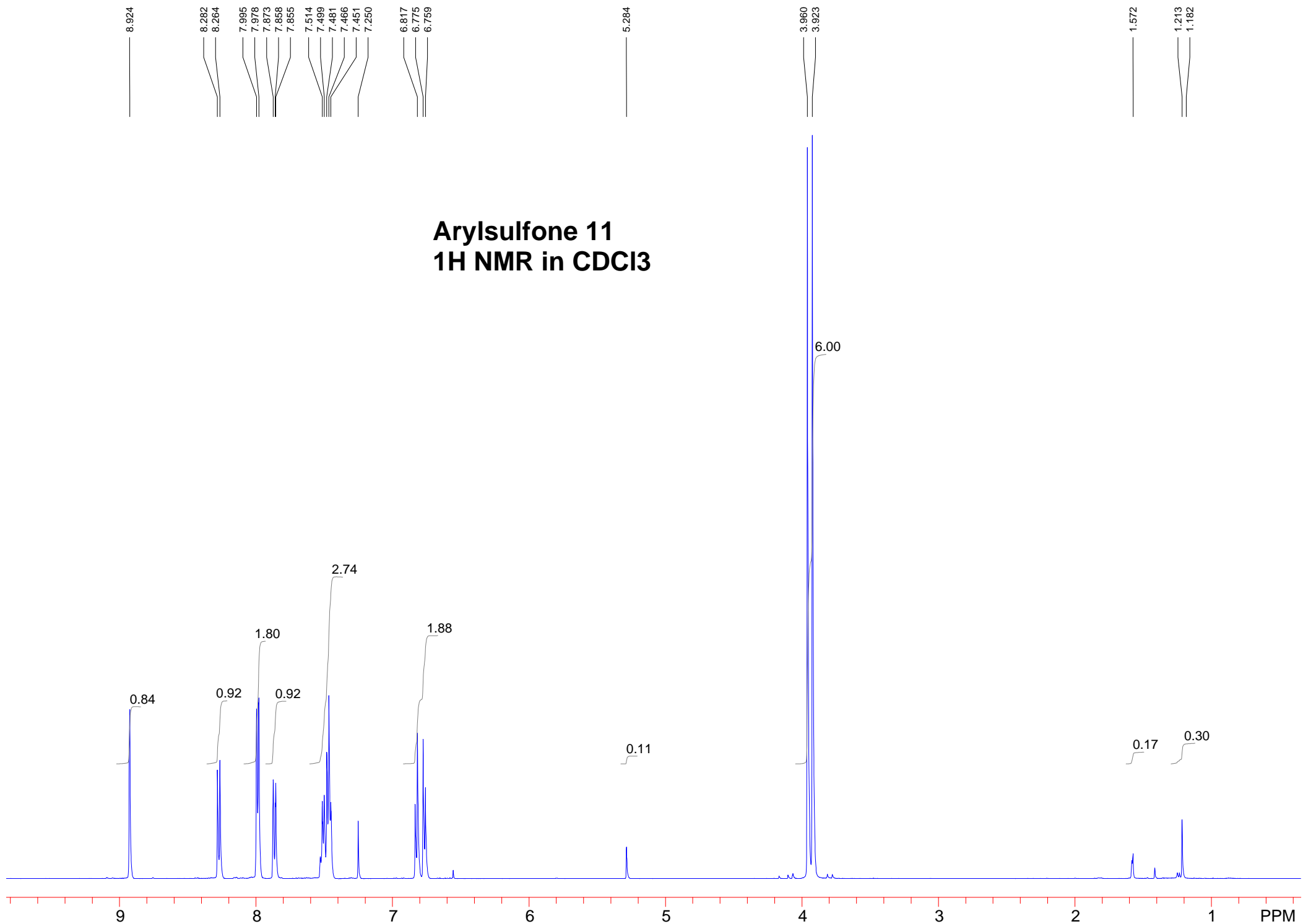
Allylsulfone 104
1H NMR in CDCl3



STANDARD PROTON PARAMETERS

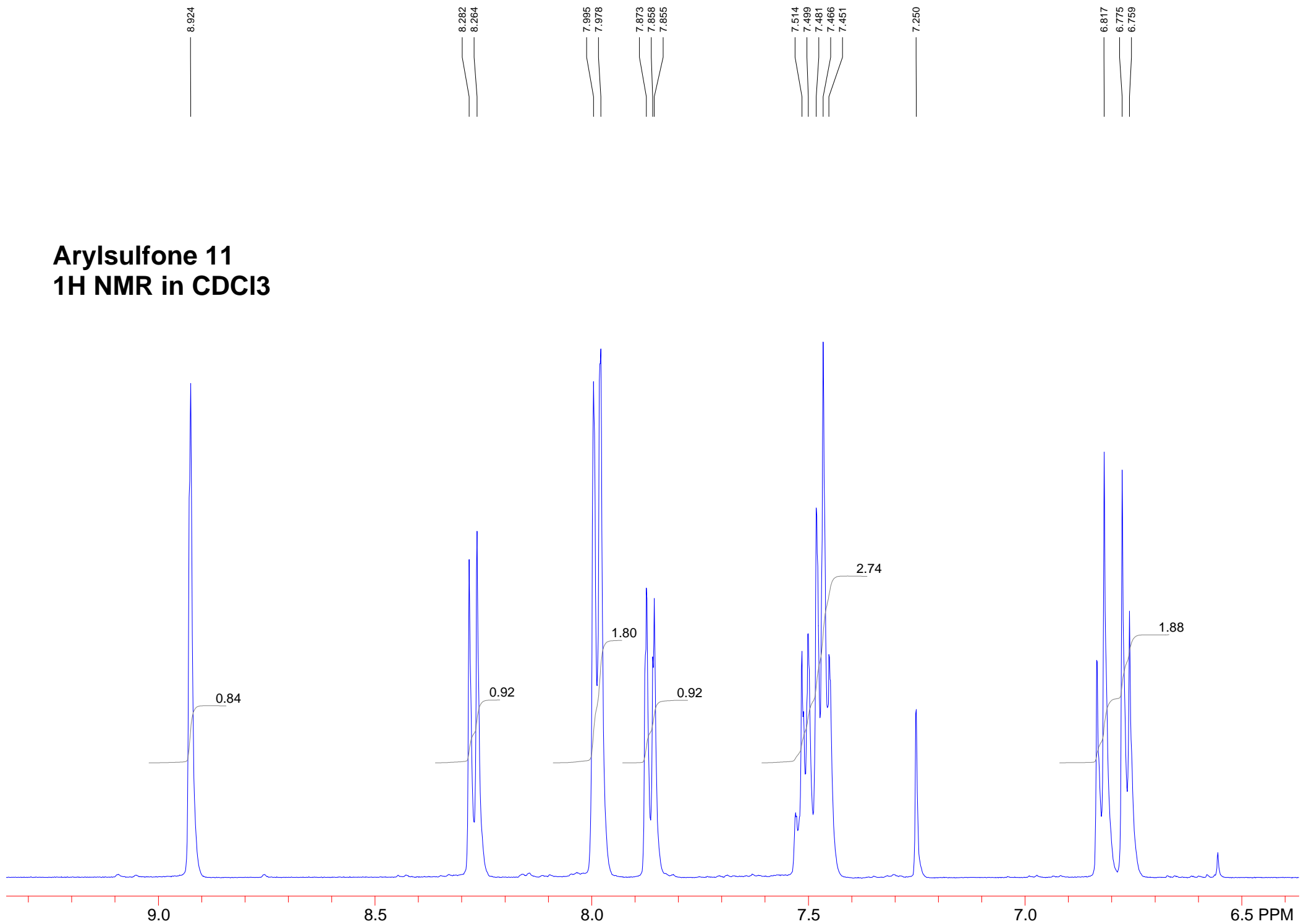
F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2490.8	PTS1d: 32768
EX: s2pul	PW: 3.0 usec	PD: 0.0 sec	NA: 8	LB: 0.0
WinNuts - \$fb_3black.fid				

USER: -- DATE: Nov 22 2002



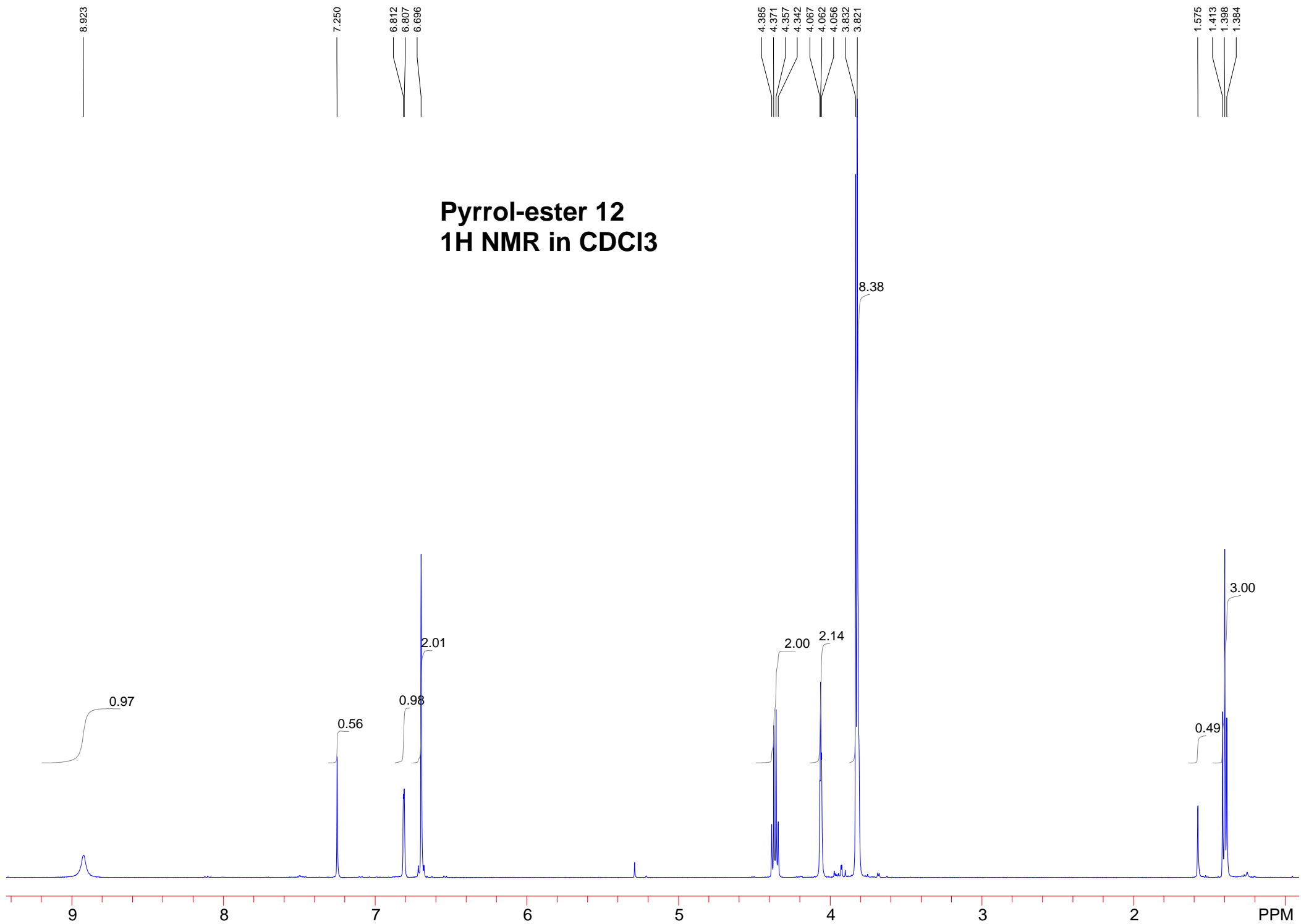
STANDARD PROTON PARAMETERS						USER: -- DATE: Nov 23 2002	
F1: 499.855	F2: 499.855	SW1: 20000		OF1: 2493.8		PTS1d: 32768	
EX: s2pul		PW: 5.5 usec	PD: 0.0 sec	NA: 8	LB: 0.0	WinNuts - \$fb_1blue1.fid	

Arylsulfone 11
¹H NMR in CDCl₃



STANDARD PROTON PARAMETERS

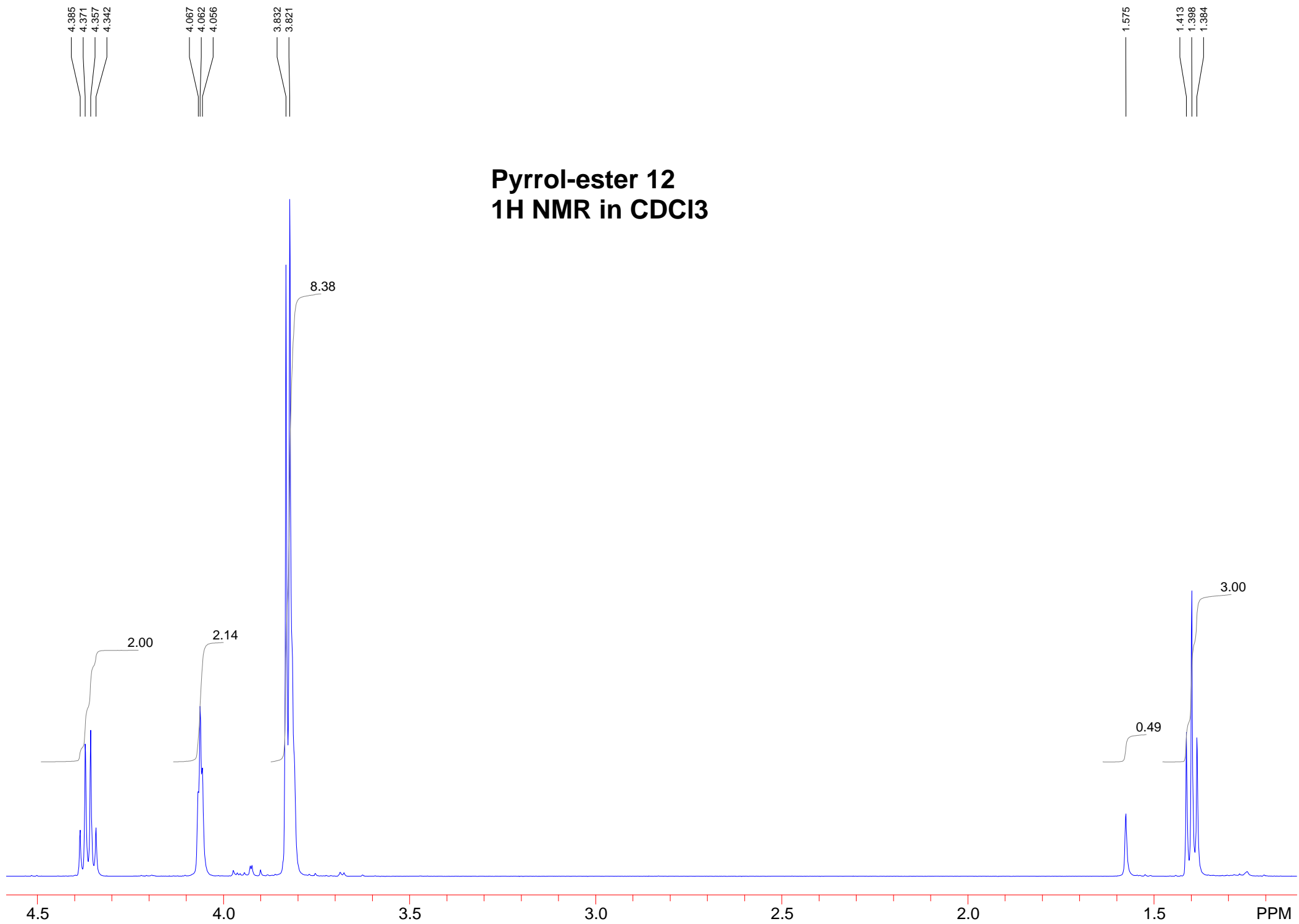
F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2493.8	PTS1d: 32768	USER: -- DATE: Nov 23 2002
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 8	LB: 0.0	WinNuts - \$fb_1blue1.fid



STANDARD PROTON PARAMETERS

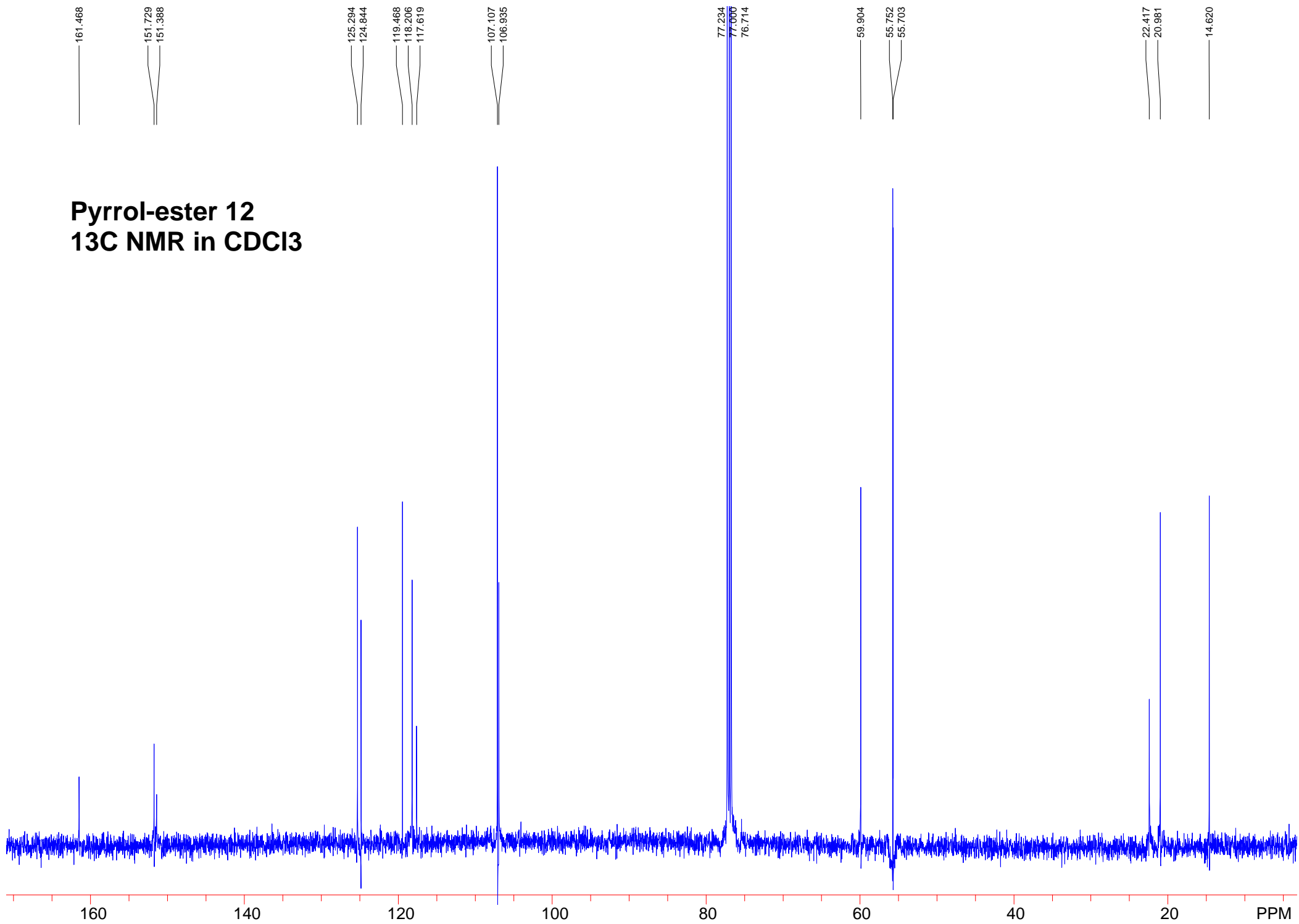
F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2493.2	PTS1d: 32768
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 8	LB: 0.0
WinNuts - \$12_1H				

USER: -- DATE: Nov 23 2002



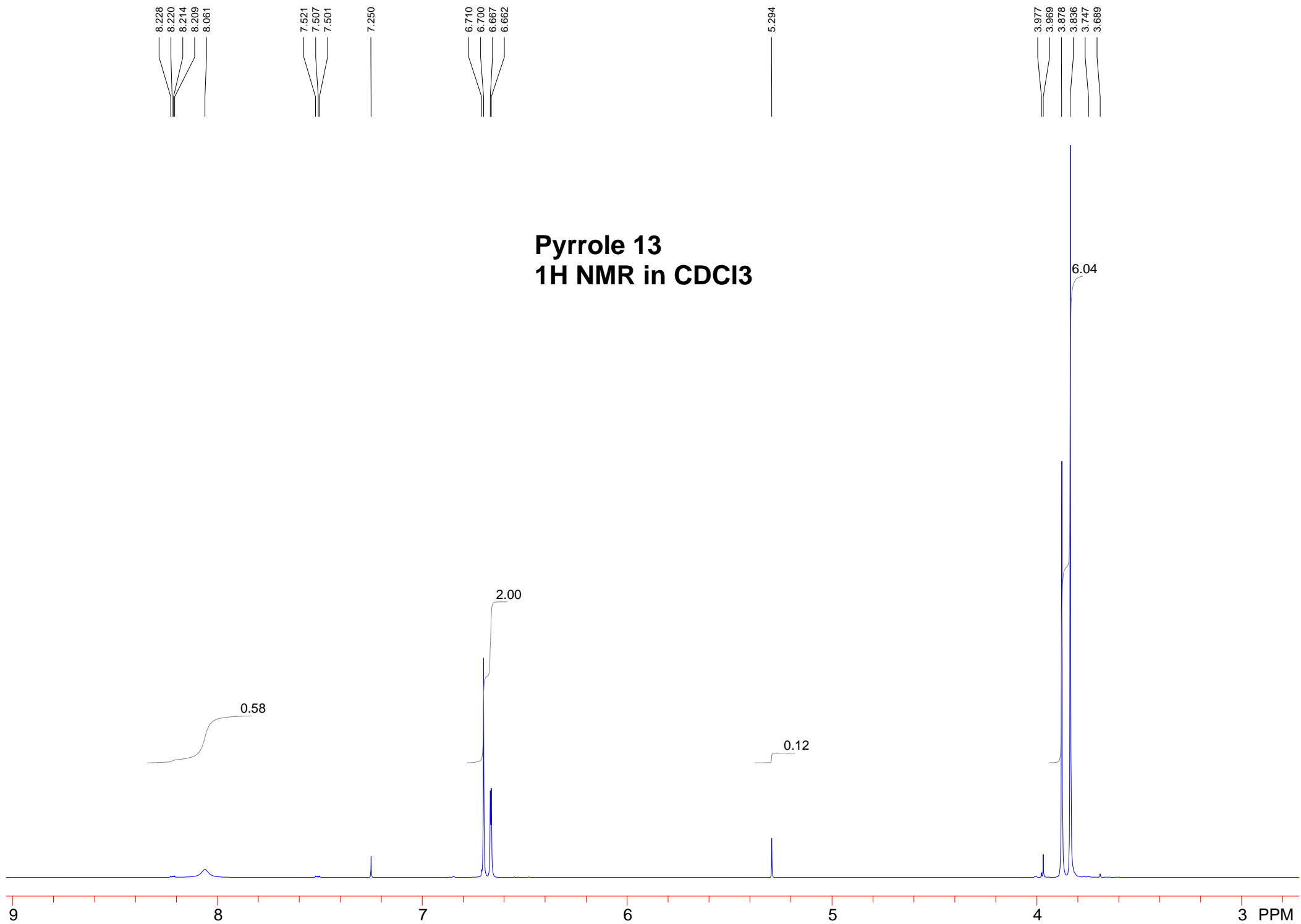
STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2493.2	PTS1d: 32768	USER: -- DATE: Nov 23 2002
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 8	LB: 0.0	WinNuts - \$12_1H



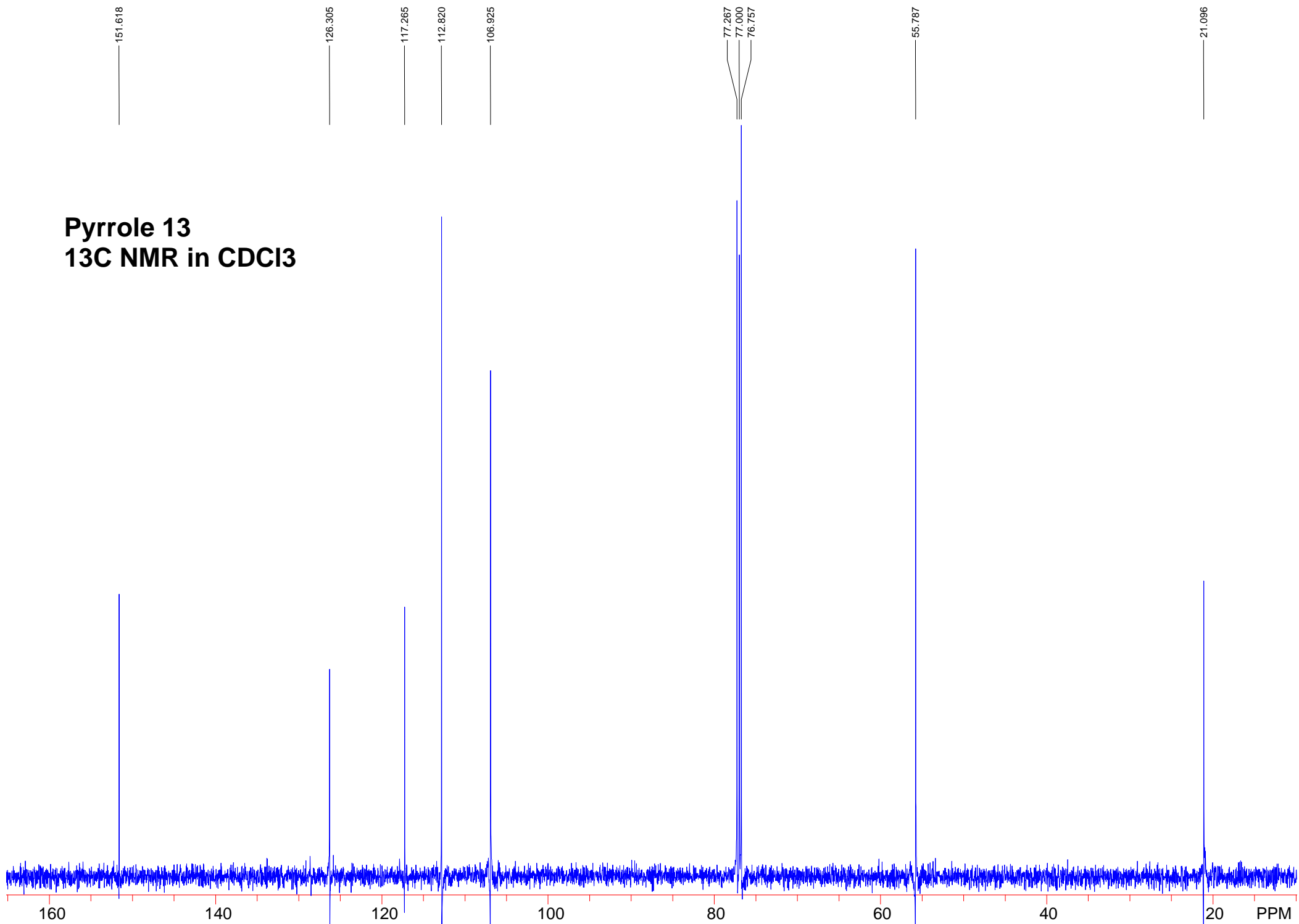
STANDARD CARBON PARAMETERS

F1: 125.700	F2: 499.855	SW1: 25000	OF1: 11914.8	PTS1d: 8192	USER: -- DATE: Nov 27 2002
EX: s2pul	PW: 13.0 usec	PD: 2.0 sec	NA: 16335	LB: 0.0	WinNuts - \$12_13C



STANDARD PROTON PARAMETERS						USER: -- DATE: Nov 30 2002	
F1: 499.855	F2: 499.855	SW1: 20000		OF1: 2490.8		PTS1d: 32768	
EX: s2pul		PW: 5.5 usec	PD: 0.0 sec	NA: 20	LB: 0.0	WinNuts - \$fb_meopyr_1H.fid	

Pyrrole 13
¹³C NMR in CDCl₃

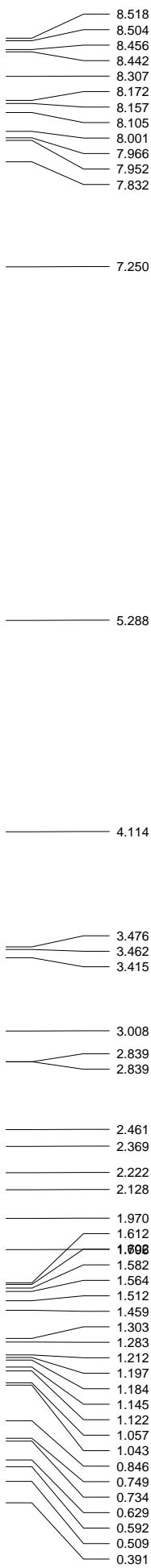


STANDARD CARBON PARAMETERS

USER: -- DATE: Nov 30 2002

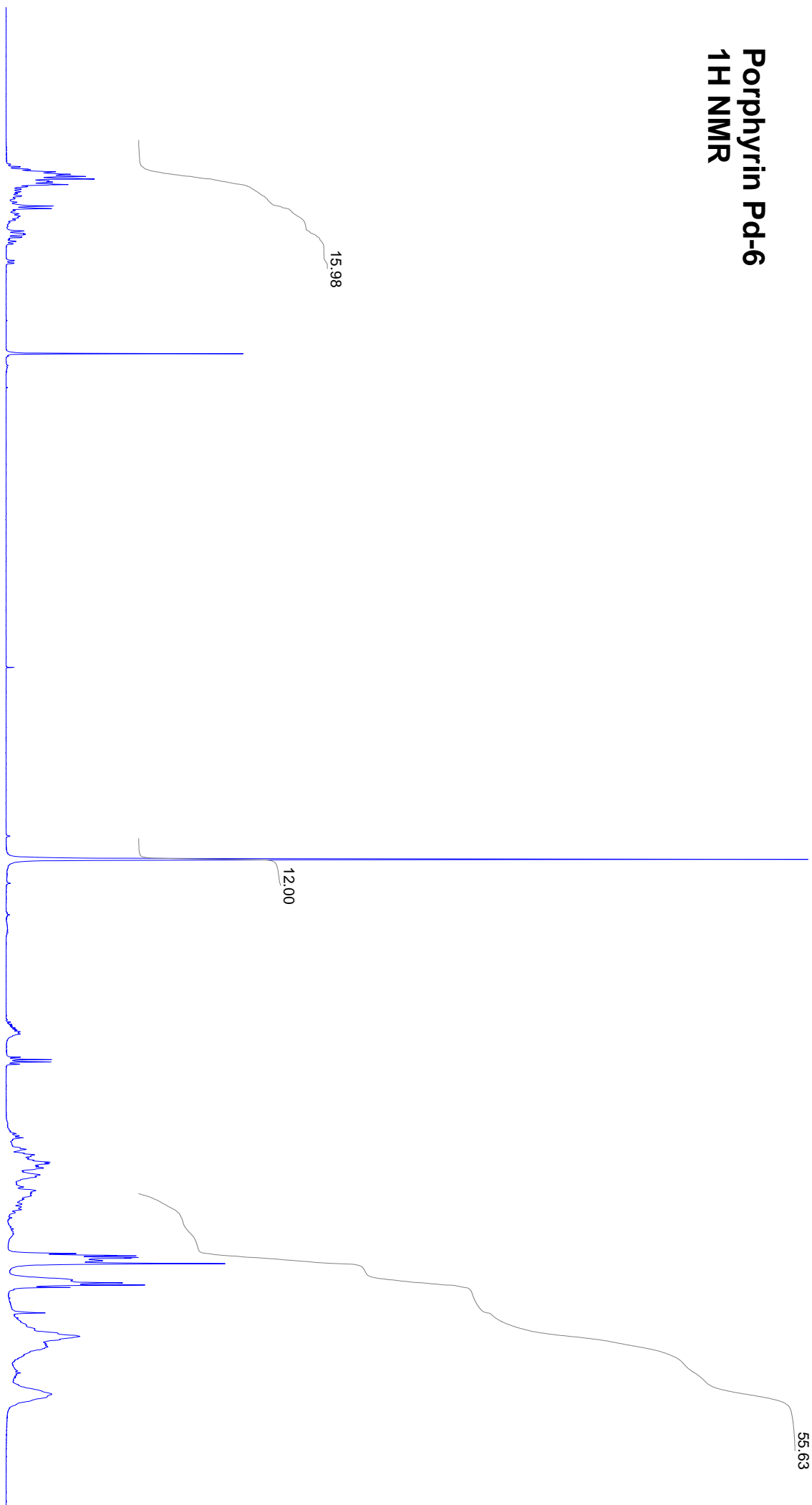
F1: 125.700	F2: 499.855	SW1: 25000	OF1: 11911.6	PTS1d: 8192
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EX: s2pul	PW: 13.0 usec	PD: 2.0 sec	NA: 661	LB: 0.0	WinNuts - \$13_13C
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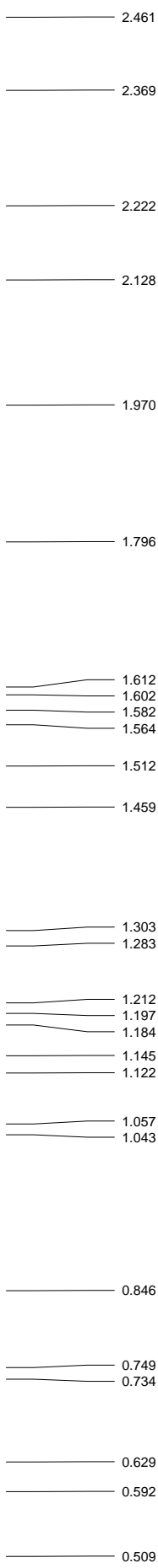
Porphyrin Pd-6

¹H NMR

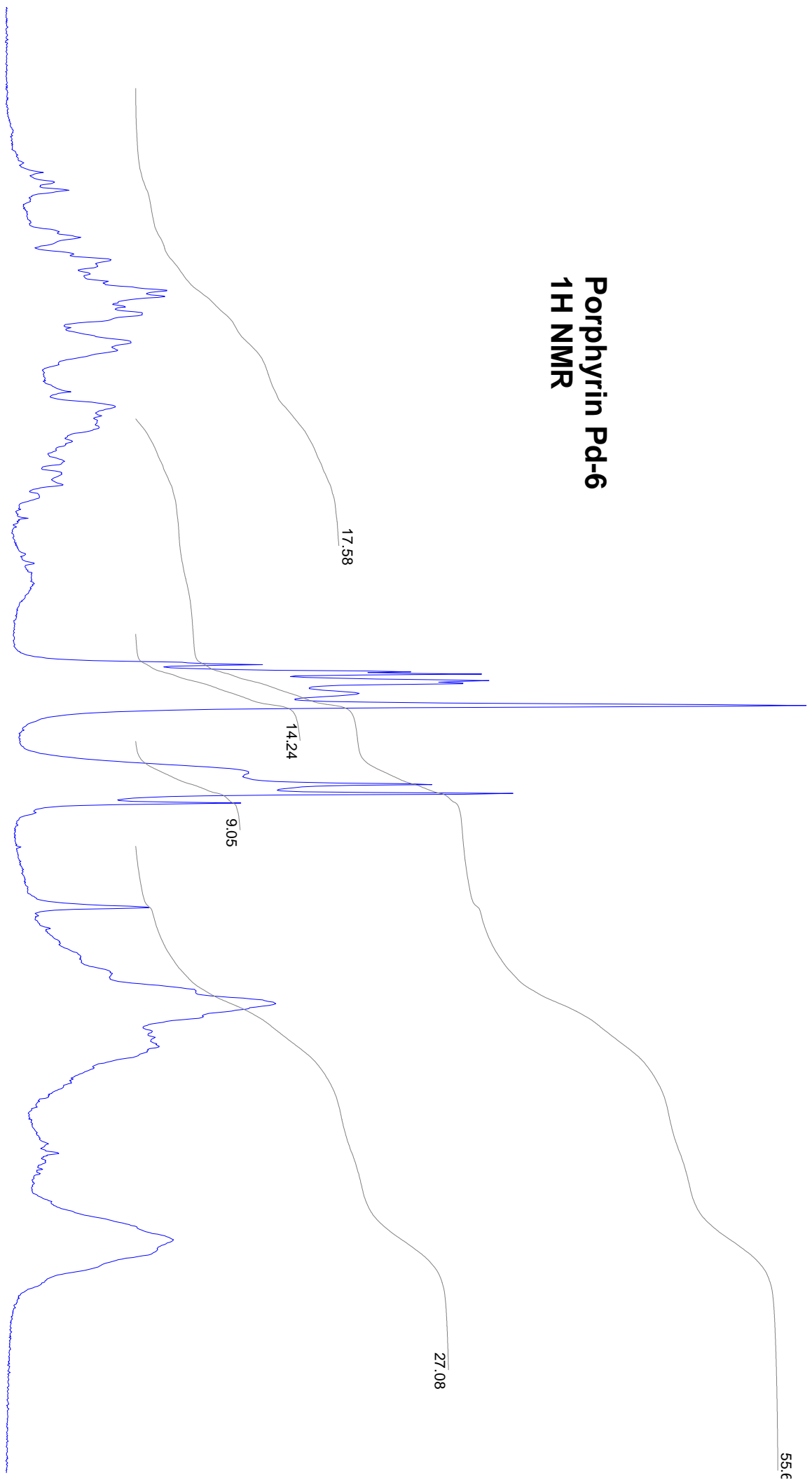


STANDARD PROTON PARAMETERS

F1: 499,855	F2: 499,855	SW1: 20000	OF1: 2490.8	PTSId: 32768
EX: s2pul		PW: 1.5 usec	PD: 0.0 sec	NA: 8
			LB: 0.0	
USER: -- DATE: Oct 8 2002				
WinNuts - \$fb_octTCHPpd.fid				

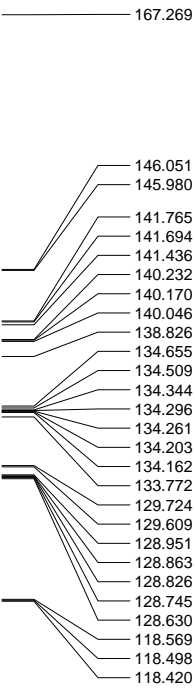


Porphyrin Pd-6 ¹H NMR

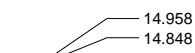
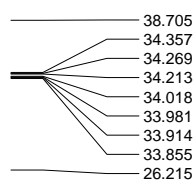
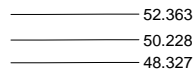


STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	PD: 0.0 sec	OF1: 2490.8	LB: 0.0	PTSId: 32768	USER: -- DATE: Oct 8 2002
EX: s2pul		PW: 1.5 usec		NA: 8			WinNuts - \$fb_octCHPpd.fid



Porphyrin Pd-6
13H NMR



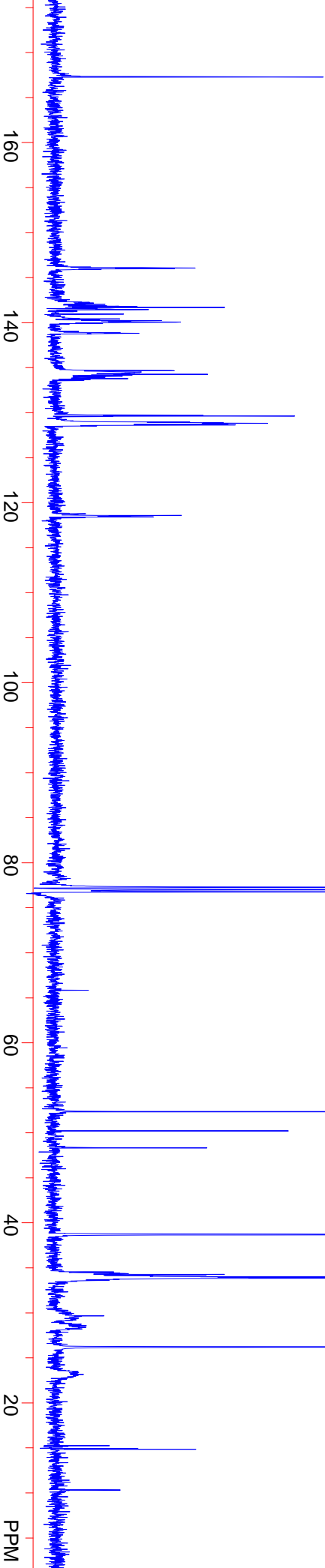
STANDARD CARBON PARAMETERS

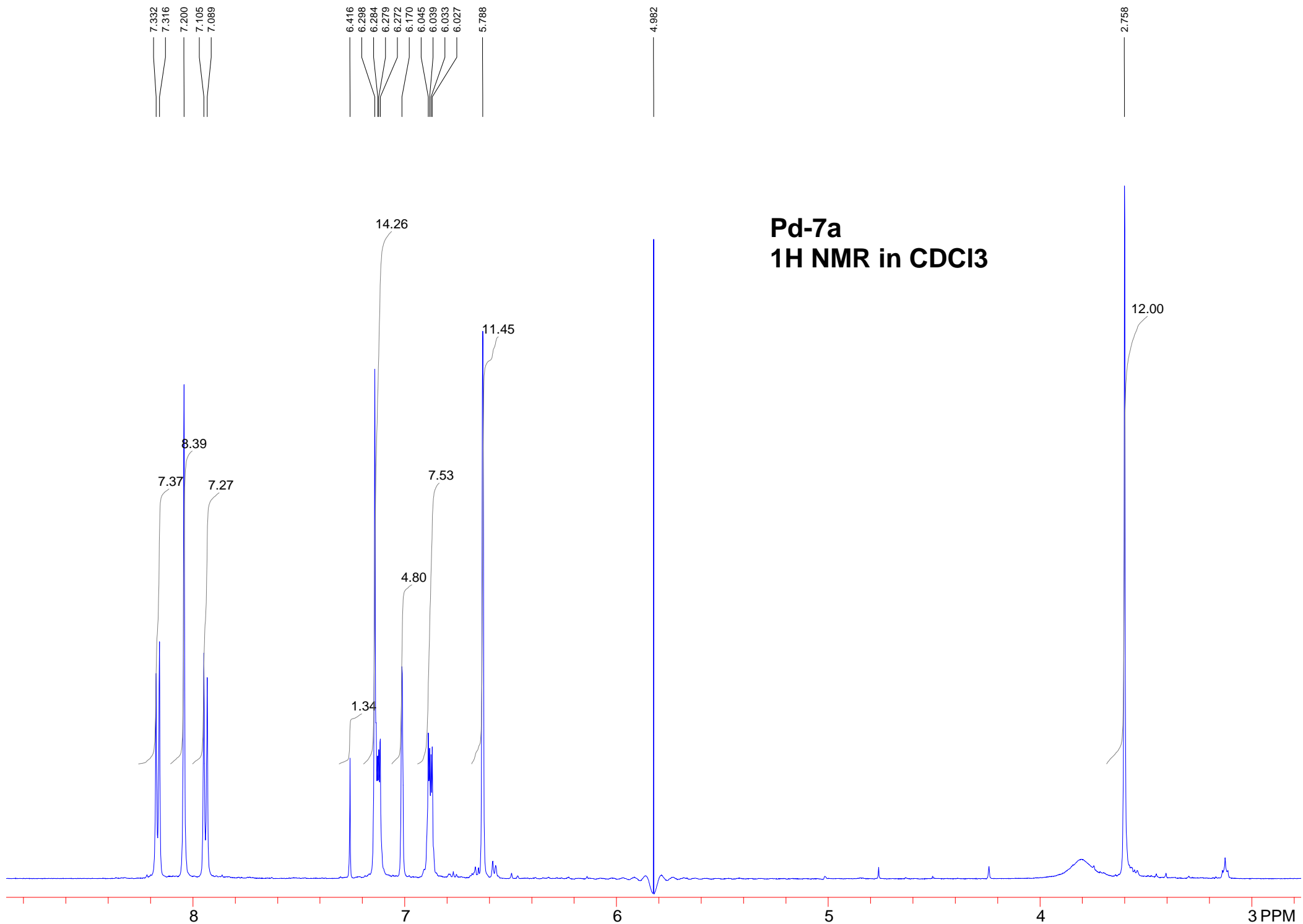
F1: 125.700	F2: 499.855	SW1: 25000	PD: 2.0 sec	OF1: 11909.8	LB: 0.0	PTSId: 8192
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EX: s2pul

USER: -- DATE: Dec 2 2002

WinNuts - \$fb_13C.fid

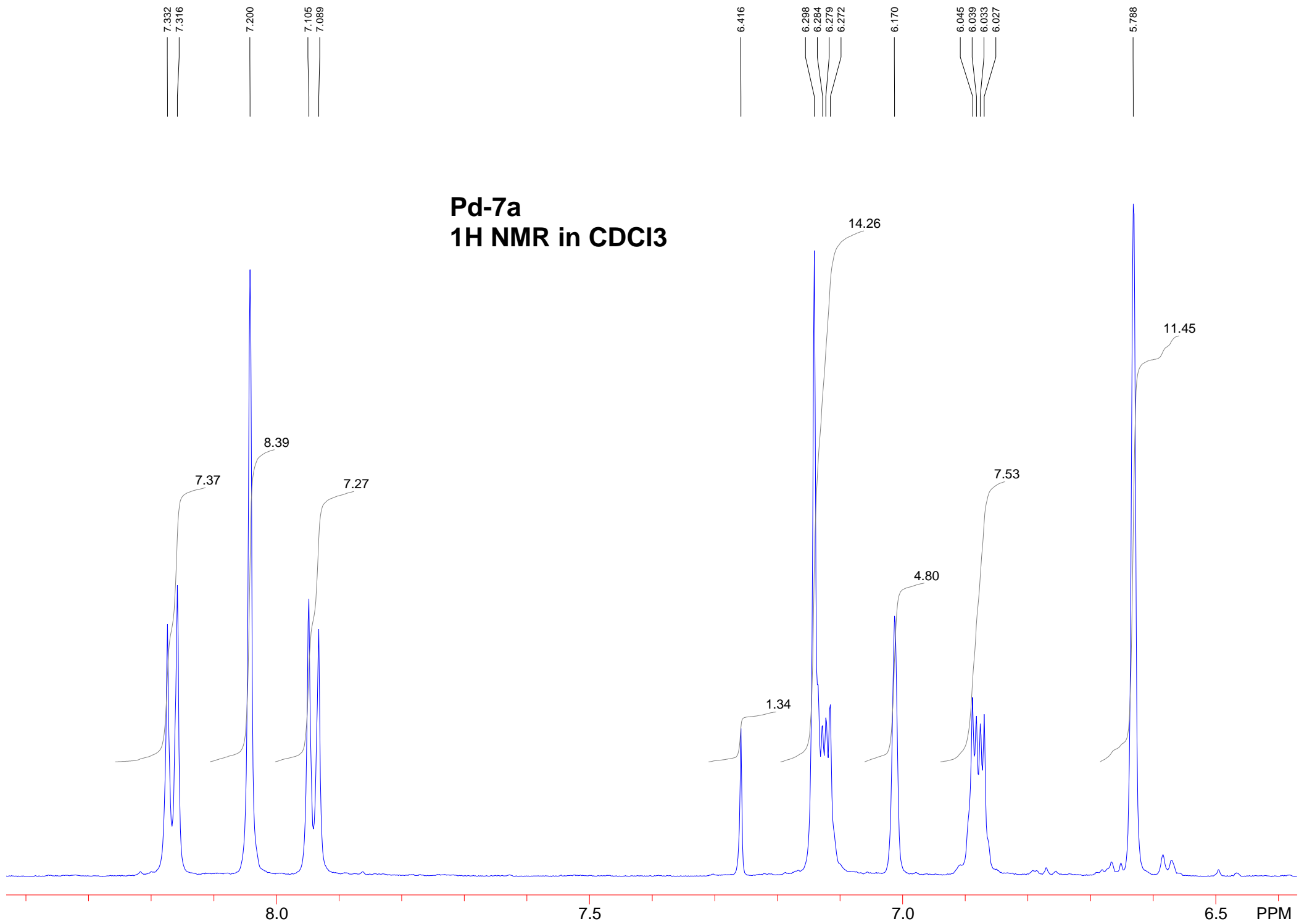




STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2911.8	PTS1d: 32768
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 1	LB: 0.0
WinNuts - \$fb_octpd_fin.fid				

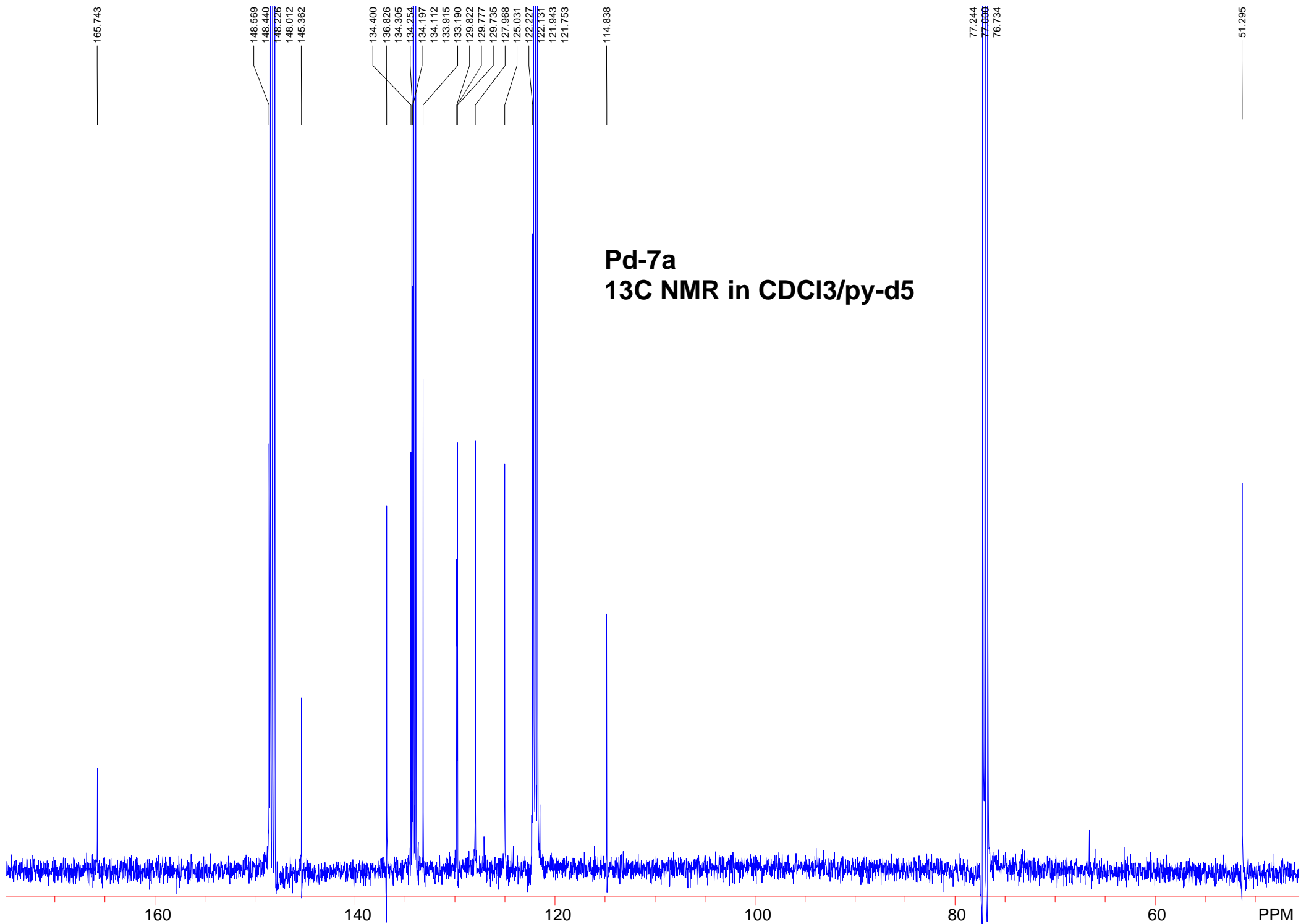
USER: -- DATE: Dec 15 2002



STANDARD PROTON PARAMETERS

F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2911.8	PTS1d: 32768
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 1	LB: 0.0
WinNuts - \$fb_octpd_fin.fid				

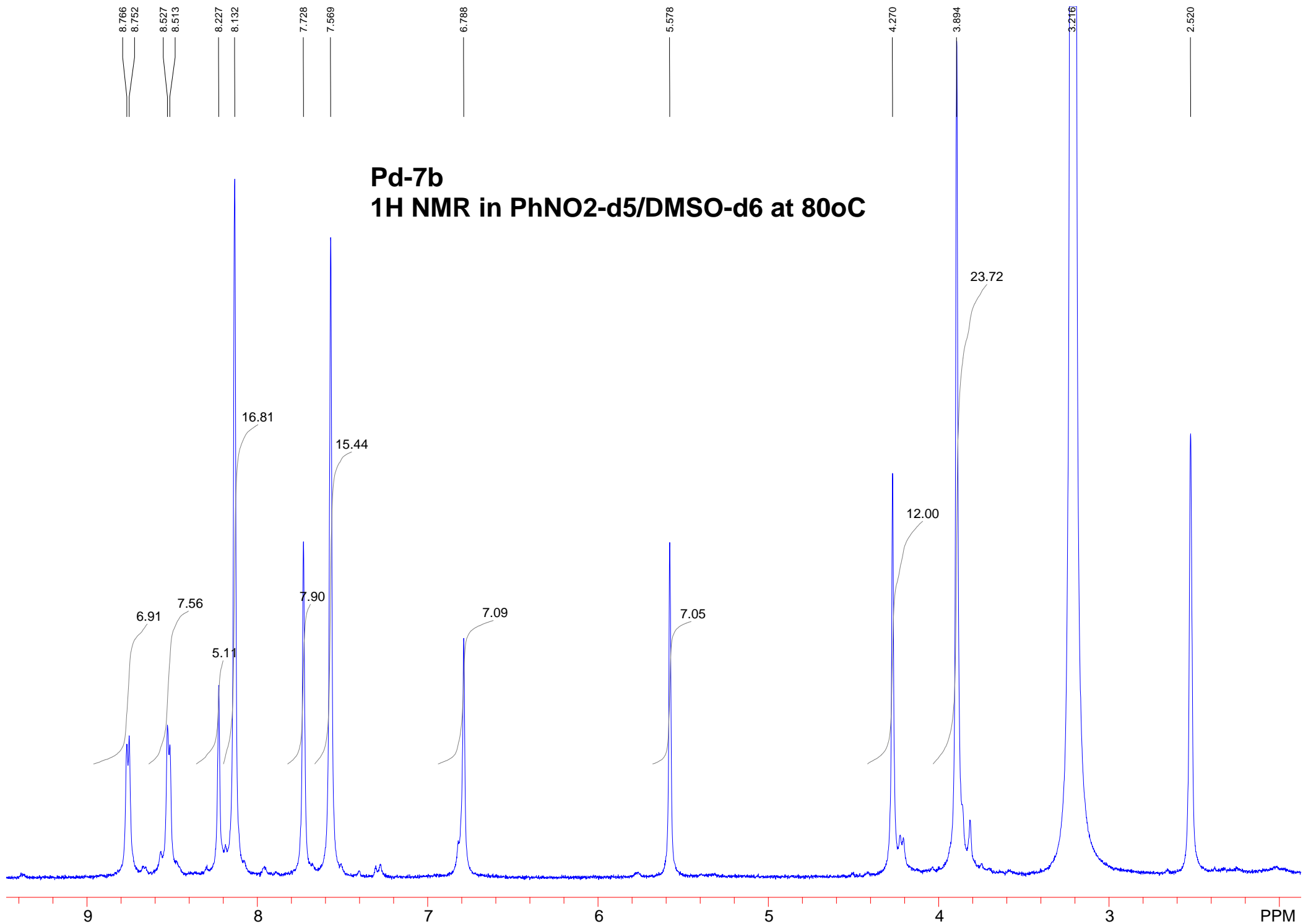
USER: -- DATE: Dec 15 2002



STANDARD CARBON PARAMETERS

F1: 125.700	F2: 499.855	SW1: 25000	OF1: 11936.4	PTS1d: 8192
EX: s2pul	PW: 13.0 usec	PD: 2.0 sec	NA: 14607	LB: 0.0
WinNuts - \$fb_octtnppd_13C				

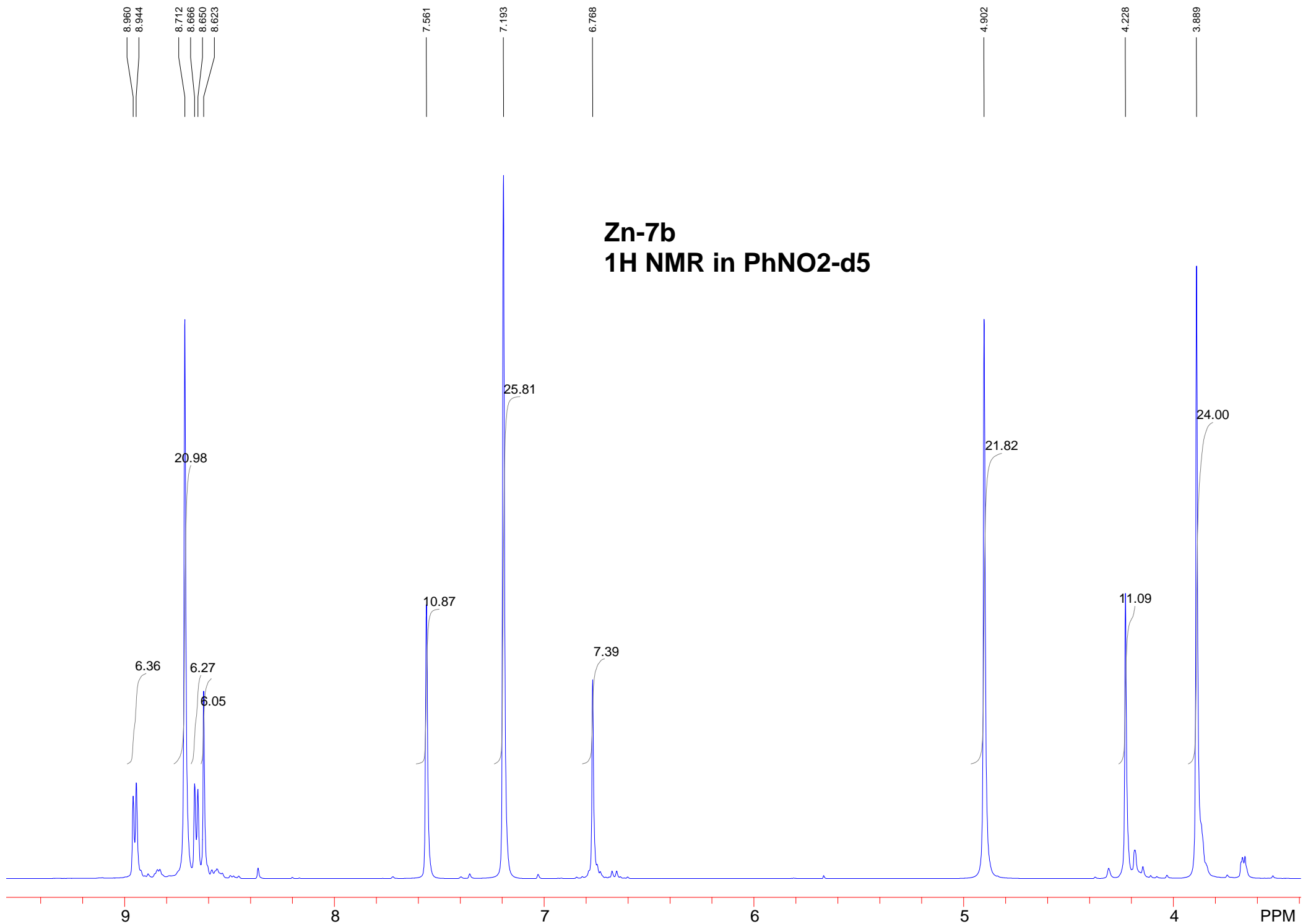
USER: -- DATE: Dec 15 2002



STANDARD PROTON PARAMETERS

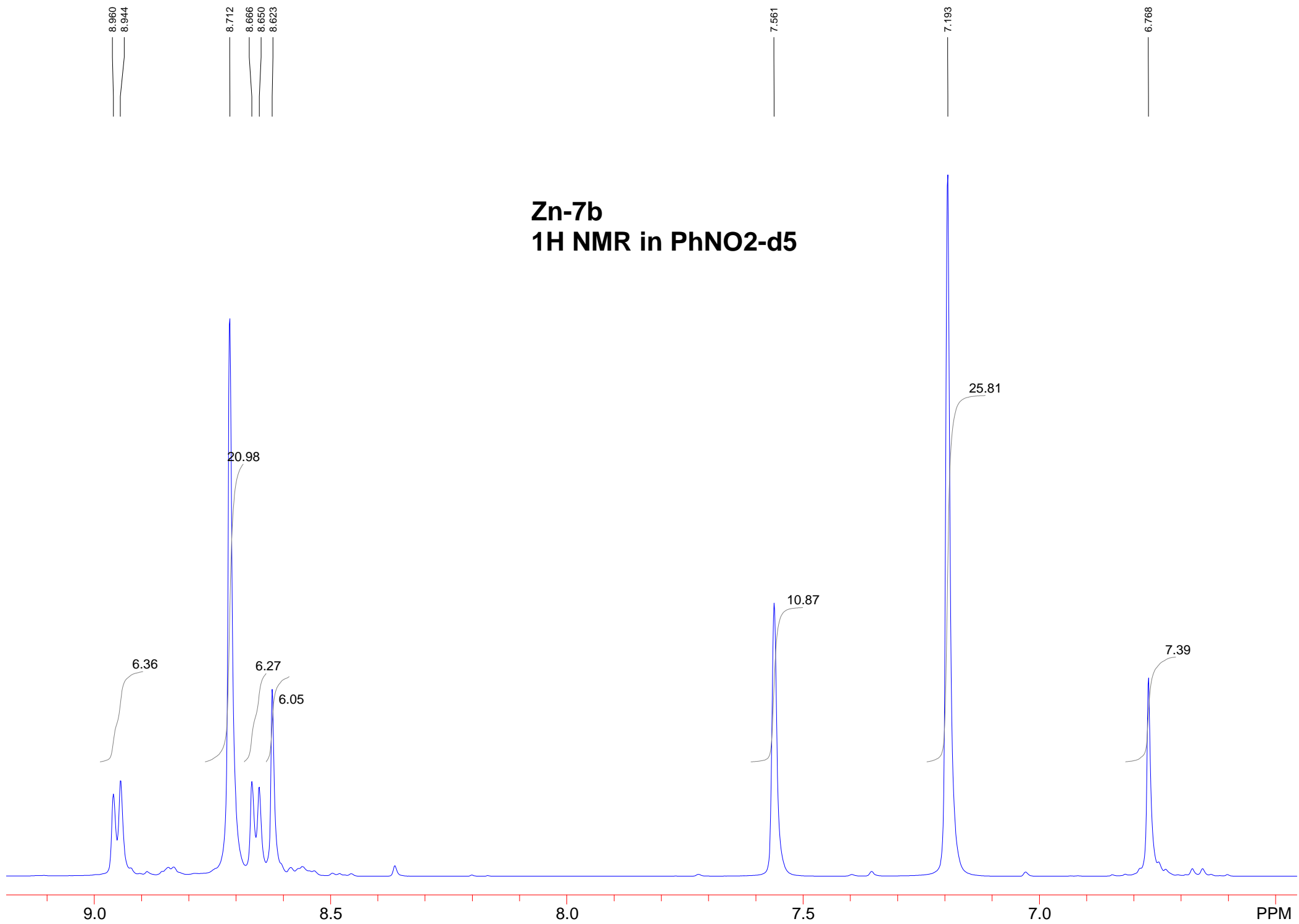
F1: 499.855	F2: 499.855	SW1: 20000	OF1: 2961.5	PTS1d: 32768
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 100	LB: 0.0
WinNuts - \$fb_meopd_dms03_80.fid				

USER: -- DATE: Dec 11 2002



STANDARD PROTON PARAMETERS						USER: -- DATE: Dec 10 2002	
F1: 499.855	F2: 499.855	SW1: 20000		OF1: 3249.5		PTS1d: 32768	
EX: s2pul		PW: 5.5 usec	PD: 0.0 sec	NA: 1000	LB: 0.0	WinNuts - \$Zn-7b	

Zn-7b
¹H NMR in PhNO₂-d₅



STANDARD PROTON PARAMETERS

USER: -- DATE: Dec 10 2002

F1: 499.855	F2: 499.855	SW1: 20000	OF1: 3249.5	PTS1d: 32768
EX: s2pul	PW: 5.5 usec	PD: 0.0 sec	NA: 1000	LB: 0.0
WinNuts - \$Zn-7b				