Supporting Information for

Carboxylation and Mitsunobu Reaction of Amines to Give Carbamates: Retention *vs* Inversion of Configuration is Substituent-Dependent

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General Experimental Information: Proton NMR spectra were recorded on Varian Unity or Varian Plus (500 or 400 MHz) spectrometers. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Low resolution electrospray mass spectra were recorded on a Micromass ZMD spectrometer using a Waters 2690 HPLC (2.1 x 100 mm C18 column, H_2O/MeCN w/0.05% TFA) for sample introduction. Samples provided for accurate mass measurement were taken up in acetonitrile:water:glacial acetic acid (50:50:0.1%v/v). The solutions were analyzed by use of electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) on either a Bruker Daltonics 3T or 7T Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. External calibration was accomplished with polypropylene glycol (425 or 750). Silica gel 60 (230-400) mesh from EM Science was used for flash column chromatography, and analytical thin layer chromatography was performed on EM Science Kieselgel 60 F254 plates. Solvents and reagents were obtained from commercial sources and used without further purification. The reported yields are the actual isolated yields of purified material and are not optimized.

2-[(2-Naphthylmethyl)amino]ethanol (4a): To a solution of ethanolamine (41.4 g, 678 mmol) in 600 mL of acetonitrile at room temperature was added dropwise a solution of 2-(bromomethyl)naphthalene (10.0 g, 45.2 mmol) in 125 mL of acetonitrile. After 2 hours, the solution was concentrated *in vacuo*, and the residue partitioned between dichloromethane and saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted three times with dichloromethane, and the combined organics were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude product was recrystallized from hot EtOAc-hexane to provide **4a** as a white crystalline solid (5.88g, 65% yield). Analytical LCMS: single peak (1.00 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >95% pure by UV (215 nm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.88 (m, 4H), 7.46-7.53 (m, 3H), 4.04 (s, 2H), 3.72 (t, *J* = 5.0 Hz, 2H), 2.89 (t, *J* = 5.0 Hz, 2H), 2.16 (br s, 2H); *m/z* (ES$^+$) = 202.3 (MH$^+$).

General procedure for carboxylation/Mitsunobu cyclization (Table 2):
3-(2-Naphthylmethyl)-1,3-oxazolidin-2-one (6a): To a solution of 2-[(2-naphthylmethyl)amino]ethanol (**4a**) (100 mg, 0.497 mmol, 1.0 equiv.) in 2.5 mL of anhydrous acetonitrile was added 1,8-diazabicyclo[5.4.0]undec-7-ene (7 µL, 0.05 mmol, 0.1 equiv.). The resulting heterogeneous solution was then stirred under an atmosphere of carbon dioxide gas *via* a balloon, during which the mixture turned homogeneous momentarily and then heterogeneous. After 45 minutes, the reaction was cooled to 0 °C. *n*-Bu_3P was added (0.260 mL, 1.04 mmol, 2.1 equiv.), followed by a solution of di-*tert*-butyl azodicarboxylate (240 mg, 1.04 mmol, 2.1 equiv.) in 1 ml of acetonitrile in a dropwise manner. Over a period of 20 minutes the system became homogeneous. Removal of the solvent *in vacuo* afforded a clear yellow residue which was purified by flash chromatography (30-50% EtOAc/hexanes) to give 1-(2-naphthylmethyl)-2-oxazolidinone **6a** (104 mg, 92%) as a white solid. Analytical LCMS: single peak (2.22 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >97% pure by UV (215 nm); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.81-7.86 (m, 3H), 7.73 (br s, 1H), 7.48-7.52 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 4.60 (s, 2H), 4.31 (t, *J* = 7.1 Hz, 2H) and 3.45 (t, *J* = 7.1 Hz, 2H) ppm; *m/z* (ES$^+$) = 228.2 (MH$^+$); HRMS (APCI) exact mass calcd for $C_{14}H_{14}NO_2$ (M+H$^+$): 228.1019; found 228.1032.

3-Phenyl-1,3-oxazolidin-2-one (6b):[1] Analytical LCMS: single peak (1.64 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >99% pure by UV (215 nm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (br d, *J* = 9 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.49 (t, *J* = 8 Hz, 2H), 4.07 (t, *J* = 8 Hz, 2H); *m/z* (ES$^+$) = 164.2 (MH$^+$); HRMS (APCI) exact mass calcd for $C_9H_{10}NO_2$ (M+H$^+$): 164.0706; found 164.0712.

(4*R*)-4-Benzyl-1,3-oxazolidin-2-one (6c):[2] Analytical HPLC: single peak (1.73 min, CH_3CN/7.4 mM aq NH_4OH, 5 min gradient) 95.8% pure by UV (254 nm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.1 Hz, 2H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.20 (br d, *J* = 7 Hz, 2H), 4.95 (br s, 1H), 4.51 (dd, *J* = 9 and 8 Hz, 1H), 4.18 (dd, *J* = 8.8 and 5.6 Hz, 1H), 4.10 (m, 1H), 2.91 (dd, *J* = 13.4 and 5.6 Hz, 1H), 2.86 (dd, *J* = 13.4 and 8.3 Hz, 1H); *m/z* (ES^+) = 178.0 (MH^+); HRMS (APCI) exact mass calcd for $C_{10}H_{12}NO_2$ ($M+H^+$): 178.0863; found 178.0869.

(4*S*)-4-Phenyl-1,3-oxazolidin-2-one (6d):[3] Analytical LCMS: single peak (1.07 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) 97.3% pure by UV (215 nm); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.42 (m, 5H), 5.97 (br s, 1H), 4.96 (br t, *J* = 8 Hz, 1H), 4.74 (t, *J* = 8.6 Hz, 1H), 4.19 (dd, *J* = 8.6 and 6.9 Hz, 1H); *m/z* (ES^+) = 164.3 (MH^+); HRMS (APCI) exact mass calcd for $C_9H_{10}NO_2$ ($M+H^+$): 164.0706; found 164.0712.

(5*R*)-5-Phenyl-1,3-oxazolidin-2-one (6e):[4] Analytical LCMS: single peak (1.10 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >95% pure by UV (215 nm); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.43 (m, 5H), 5.68 (br s, 1H), 5.63 (br t, *J* = 8.2 Hz, 1H), 3.98 (t, *J* = 8.6 Hz, 1H), 3.54 (t, *J* = 8 Hz, 1H); *m/z* (ES^+) = 164.2 (MH^+); HRMS (APCI) exact mass calcd for $C_9H_{10}NO_2$ ($M+H^+$): 164.0706; found 164.0709; $[\alpha]_D^{22}$ = -24.6° (*c* 0.045, EtOH); literature value for opposite enantiomer: $[\alpha]_D^{25}$ = +23° (*c* 4.3, EtOH).

(4*R*,5*R*)-4-(Methoxymethyl)-5-phenyl-1,3-oxazolidin-2-one (6f):[5] Analytical LCMS: single peak (1.29 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >95% pure by UV (215 nm); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.40 (m, 5H), 5.77 (br s, 1H), 5.24 (d, *J* = 5.6 Hz, 1H), 3.89 (br q, *J* = 6 Hz, 1H), 3.55 (dd, *J* = 9.5 and 4.6 Hz, 1H), 3.51 (dd, *J* = 9.5 and 6.9 Hz, 1H),3.41 (s, 3H); *m/z* (ES^+) = 208.3 (MH^+); HRMS (APCI) exact mass calcd for $C_{10}H_{14}NO$ ($M+H^+-CO_2$): 164.1075; found 164.1075. Proof of structure was provided by hydrolysis to give (1*R*,2*R*)-2-amino-3-methoxy-1-phenylpropan-1-ol (**4f**). To a solution of **6f** (87 mg, 0.42 mmol) in 1 mL of ethanol was added 0.5 mL of 20% aqueous KOH solution. The mixture was heated at 60 °C for 3 days, then cooled to room temperature. The solution was partitioned between $CHCl_3$ and water, and the aqueous layer was extracted three times with $CHCl_3$. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (7-10% $MeOH/CH_2Cl_2$) gave **4f** as a colorless oil (38.8 mg, 50% yield), which was spectroscopically identical (^1H NMR, Analytical LCMS) to commercial material, and had the correct sign of optical rotation: $[\alpha]_D^{22}$ = +19.2° (*c* 0.030, $CHCl_3$); literature value: $[\alpha]_D^{25}$ = +25° (*c* 10.6, $CHCl_3$).

(4*R*,5*S*)-4-Methyl-5-phenyl-1,3-oxazolidin-2-one (6g):[6] Analytical HPLC: single peak (1.92 min, CH_3CN/7.4 mM aq NH_4OH, 5 min gradient) >99% pure by UV (254 nm); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.43 (m, 3H), 7.32 (br d, *J* = 8 Hz, 1H), 5.74 (d, *J* = 7.8 Hz, 1H), 5.08 (br s, 1H), 4.22 (dq, *J* = 7 and 7 Hz, 1H), 0.83 (d, *J* = 7.8 Hz, 3H); *m/z* (ES^+) = 178.2 (MH^+); HRMS (APCI) exact mass calcd for $C_{10}H_{12}NO_2$ ($M+H^+$): 178.0863; found 178.0870.

(4*R*,5*R*)-3,4-Dimethyl-5-phenyl-1,3-oxazolidin-2-one (6h):[7] Analytical HPLC: single peak (2.14 min, CH_3CN/7.4 mM aq NH_4OH, 5 min gradient) >99% pure by UV (254 nm); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.43 (m, 5H), 4.92 (d, *J* = 7.8 Hz, 1H), 3.55 (dq, *J* = 7 and 7 Hz, 1H), 2.88 (s, 3H), 1.38 (d, *J* = 7.8 Hz, 3H); *m/z* (ES^+) = 192.0 (MH^+); HRMS (APCI) exact mass calcd for $C_{11}H_{14}NO_2$ ($M+H^+$): 192.1019; found 192.1024; $[\alpha]_D^{22}$ = -30° (*c* 0.040, $CHCl_3$).

(4*R*,5*S*)-4,5-Diphenyl-1,3-oxazolidin-2-one (6i):[8] Analytical LCMS: single peak (1.73 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >97% pure by UV (215 nm); ^1H NMR (400 MHz, $CDCl_3$) δ 7.01-7.07 (m, 6H), 6.87-6.92 (m, 4H), 5.89 (d, *J* = 8.3 Hz, 1H), 5.73 (br s, 1H), 5.13 (d, *J* = 8.3 Hz, 1H); *m/z* (ES^+) = 240.3 (MH^+); HRMS (APCI) exact mass calcd for $C_{15}H_{14}NO_2$ ($M+H^+$): 240.1019; found 240.1025; $[\alpha]_D^{22}$ = +80.8° (*c* 0.013, $CHCl_3$) (measured $[\alpha]_D^{22}$ = -80.4° (*c* 0.013, $CHCl_3$) for authentic commercially available opposite enantiomer).

(4*S*,5*S*)-3-Benzyl-4,5-diphenyl-1,3-oxazolidin-2-one (6j): Analytical LCMS: single peak (3.20 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) 94% pure by UV (215 nm); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.41 (m, 3H), 7.26-7.29 (m, 3H), 7.22-7.24 (m, 6H), 7.17 (m, 1H), 7.10 (m, 1H), 7.07 (m, 1H), 5.22 (d, *J* = 7.4 Hz, 1H), 4.90 (d, *J* = 14.9 Hz, 1H), 4.25 (d, *J* = 7.4 Hz, 1H), 3.67 (d, *J* = 14.9 Hz, 1H); *m/z* (ES^+) = 330.1 (MH^+); HRMS (APCI) exact mass calcd for $C_{22}H_{20}NO_2$ ($M+H^+$): 330.1489; found 330.1479.

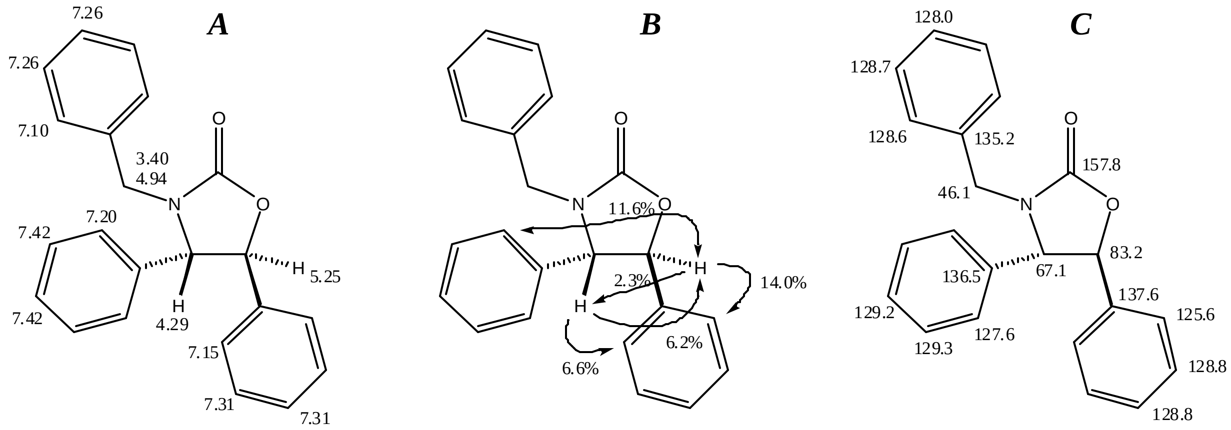

Figure 1. NMR spectral assignments for **6j** derived from ^{1}H NMR (600 MHz, $CDCl_3$), HMQC, qHMBC and difference NOE experiments. *A*: ^{1}H NMR assignments (ppm); **B**: NOE signal enhancements (%); *C*: ^{13}C NMR assignments (ppm).

Support for the structure assignment was provided by hydrolysis to give (1*S*,2*S*)-2-(benzylamino)-1,2-diphenylethanol. To a solution of **6j** (20 mg, 0.061 mmol) in 1 mL of ethanol was added 0.5 mL of 20% aqueous KOH solution. The mixture was heated to 60 °C for 24 hours, after which another portion of 20% aqueous KOH solution was added. After 1 hour the solution was cooled, then extracted three times with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give an oil (*m/z* (ES^+) = 304.2 (MH^+)), the ^{1}H NMR spectrum of which does not match commercially available (1*R*,2*S*)-2-(benzylamino)-1,2-diphenylethanol (**4j**).

(3a*R*,7a*S*)-3-Benzylhexahydro-1,3-benzoxazol-2(3*H*)-one (6k):[9] Analytical LCMS: single peak (2.31 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >97% pure by UV (215 nm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.38 (m, 5H), 4.80 (d, *J* = 15.1 Hz, 1H), 4.48 (q, *J* = 5 Hz, 1H), 4.06 (d, *J* = 15.1 Hz, 1H), 3.51 (q, *J* = 7 Hz, 1H), 1.95 (m, 1H), 1.77 (m, 2H), 1.58 (m, 2H), 1.50 (m, 1H), 1.44 (m, 1H), 1.24 (m, 1H); *m/z* (ES^+) = 232.1 (MH^+); HRMS (APCI) exact mass calcd for $C_{14}H_{18}NO_2$ ($M+H^+$): 232.1332; found 232.1341. Support for the structure assignment was provided by hydrolysis to give (1*S*,2*R*)-2-(benzylamino)cyclohexanol. To a solution of **6k** (20 mg, 0.086 mmol) in 1 mL of ethanol was added 0.5 mL of 20% aqueous KOH solution. The mixture was heated to 60 °C for 24 hours, after which another portion of 20% aqueous KOH solution was added. After 48 hours, the solution was cooled, then extracted three times with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give an oil (*m/z* (ES^+) = 206.3 (MH^+)), the ^{1}H NMR spectrum of which does not match commercially available (1*R*,2*R*)-2-(benzylamino)cyclohexanol (**4k**).

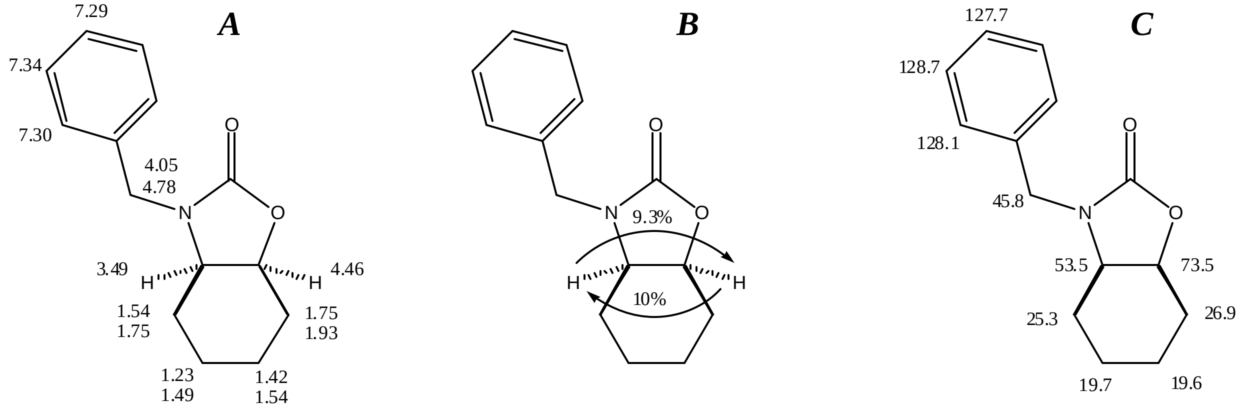

Figure 2. NMR spectral assignments for **6k** derived from ^{1}H NMR (600 MHz, $CDCl_3$), HMQC, GCOSY and difference NOE experiments. *A*: ^{1}H NMR assignments (ppm); *B*: NOE signal enhancements (%); *C*: ^{13}C NMR assignments (ppm).

(±)-4-Phenyl-1,3-oxazinan-2-one (9):[10] Analytical LCMS: single peak (1.04 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) >97% pure by UV (215 nm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (br t, *J* = 8 Hz, 2H), 7.31-7.35 (m, 3H), 5.55 (br s, 1H), 4.66 (t, *J* = 6.1 Hz, 1H), 4.28-4.34 (m, 2H), 2.26 (m, 1H), 1.98 (m, 1H); *m/z* (ES^+) = 178.3 (MH^+); HRMS (APCI) exact mass calcd for $C_{10}H_{12}NO_2$ ($M+H^+$): 178.0863; found 178.0870.

Intermolecular carboxylation/Mitsunobu reaction (eq 4):

Benzyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (23):[11] To a solution of 1,2,3,4-tetrahydroisoquinoline (**22**) (203 mg, 0.1.52 mmol, 1.0 equiv.) and benzyl alcohol (0.237 mL, 2.29 mmol, 1.5 equiv.) in 7 mL of anhydrous acetonitrile was added 1,8-diazabicyclo[5.4.0]undec-7-ene (23 µL, 0.15 mmol, 0.1 equiv.). The resulting solution was then stirred under an atmosphere of carbon dioxide gas *via* a balloon, during which the mixture remained homogeneous. After 45 minutes, the reaction was cooled to 0 °C. *n*-Bu_3P was added (0.799 mL, 3.20 mmol, 2.1 equiv.), followed by a solution of di-*tert*-butyl azodicarboxylate (737 mg, 3.20 mmol, 2.1 equiv.) in 2 ml of acetonitrile in a dropwise manner. After 20 minutes, removal of the solvent *in vacuo* afforded a clear yellow residue which was purified by flash chromatography (50-80% CH_2Cl_2/hexanes) to give benzyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate **23** (365 mg, 90%) as a colorless oil. Analytical LCMS: single peak (2.49 min, CH_3CN/H_2O/0.05% TFA, 4 min gradient) 97% pure by UV (215 nm); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.33-7.42 (m, 4H), 7.14-7.21 (m, 5H), 5.20 (s, 2H), 4.67 (s, 2H), 3.75 (br t, J = 5 Hz, 2H) and 2.87 (br s, 2H) ppm; *m/z* (ES^+) = 268.2 (MH^+); *m/z* (EI) = 176 ($C_{10}H_{10}NO_2$), 132 ($C_9H_{10}N$), 91 (C_7H_7).

Procedure for carboxylation/Mitsunobu cyclization using ^{18}O-labeled CO_2 (eq 2 and 3):

(Compounds 10 and 11): A mixture of aminoalcohol (either **4g** or **4h**, 0.33 mmol, 1.0 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (5 uL, 0.03 mmol, 0.1 equiv.) in 3 mL of anhydrous acetonitrile was degassed by bubbling argon through the solution for 20 minutes. The resulting solution was then stirred under an atmosphere of ^{18}O-labeled carbon dioxide gas (97 atom% ^{18}O; ISOTEC lot no. CR0916) *via* balloon, during which the mixture remained homogeneous. After 45 minutes, the reaction was cooled to 0 °C. *n*-Bu_3P was added (0.173 mL, 0.69 mmol, 2.1 equiv.), followed by a solution of di-*tert*-butyl azodicarboxylate (160 mg, 0.69 mmol, 2.1 equiv.) in 0.5 ml of degassed acetonitrile in a dropwise manner. After 20 minutes, LCMS analysis indicated the presence of a single product peak. Removal of the solvent *in vacuo* afforded a clear yellow residue which was analyzed directly by LCMS (ES), HRMS (APCI) and ^{1}H NMR spectroscopy. The ^{1}H NMR (500 MHz) spectrum of the crude reaction mixture containing **10** was identical to that for crude **6g**, and the corresponding spectrum of the crude reaction mixture containing **11** was identical to that for crude **6h**. Copies of the LCMS and HRMS spectra from these experiments are shown at the end of this document.

References:

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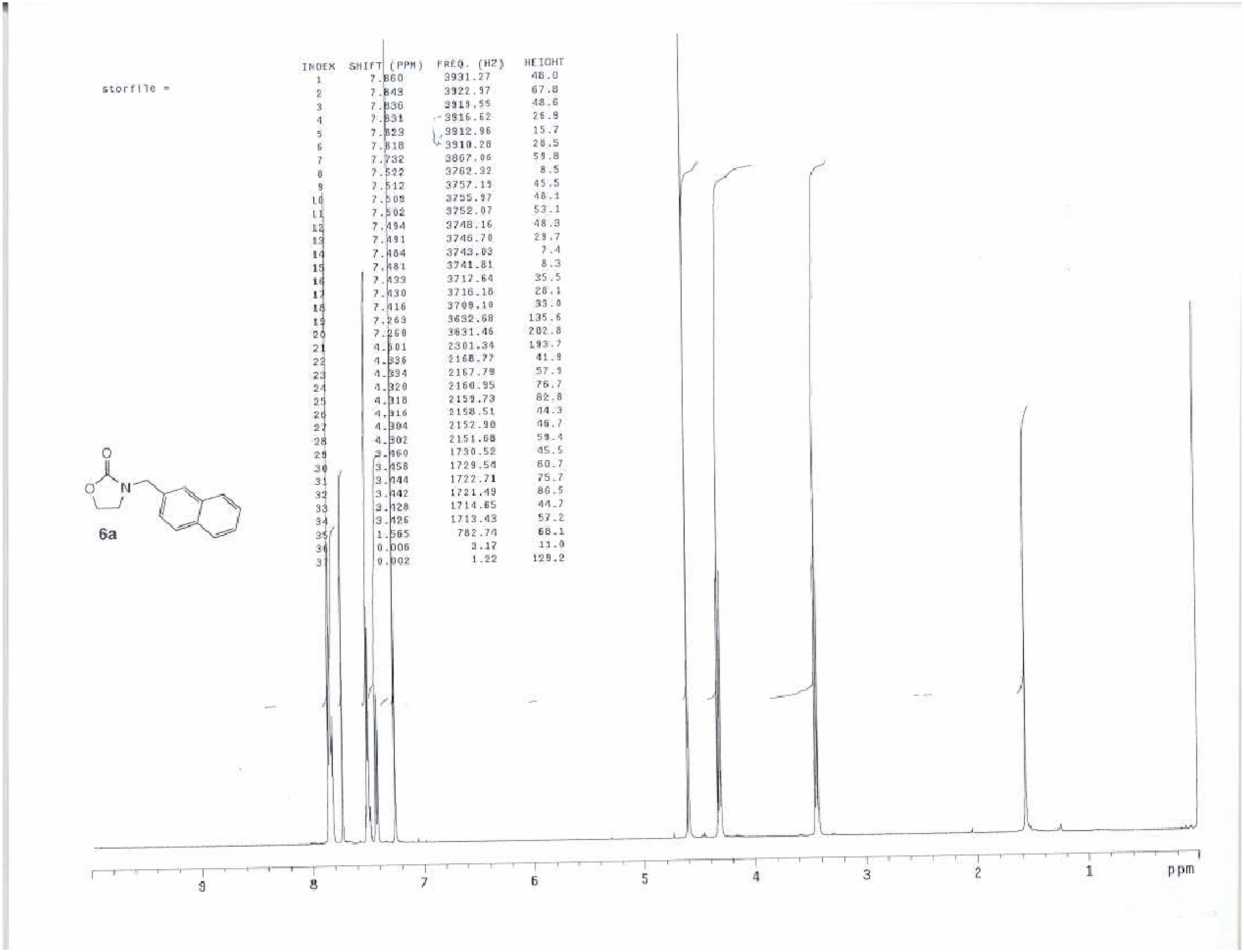
Following Pages:

Copies of the ^{1}H NMR spectra for compounds 6a-k, 9 and 23:



6a

storfile =

INDEX	SHIFT (PPM)	FREQ. (HZ)	HEIGHT
1	7.860	3931.27	48.0
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3	7.836	3919.55	48.6
4	7.831	3916.62	26.9
5	7.829	3912.96	15.7
6	7.818	3910.28	28.5
7	7.732	3867.06	59.8
8	7.522	3762.32	8.5
9	7.512	3757.19	45.5
10	7.509	3755.97	48.1
11	7.502	3752.07	53.1
12	7.494	3748.16	48.3
13	7.491	3746.70	29.7
14	7.484	3743.03	7.4
15	7.481	3741.81	8.3
16	7.433	3717.64	35.5
17	7.430	3716.18	28.1
18	7.416	3709.10	33.0
19	7.263	3632.68	135.6
20	7.260	3631.46	202.8
21	4.601	2301.34	193.7
22	4.336	2168.77	41.9
23	4.334	2167.79	57.9
24	4.320	2160.95	76.7
25	4.318	2159.73	82.8
26	4.316	2158.51	44.3
27	4.304	2152.90	46.7
28	4.302	2151.68	59.4
29	3.460	1730.52	45.5
30	3.458	1729.54	60.7
31	3.444	1722.71	75.7
32	3.442	1721.49	86.5
33	3.428	1714.65	44.7
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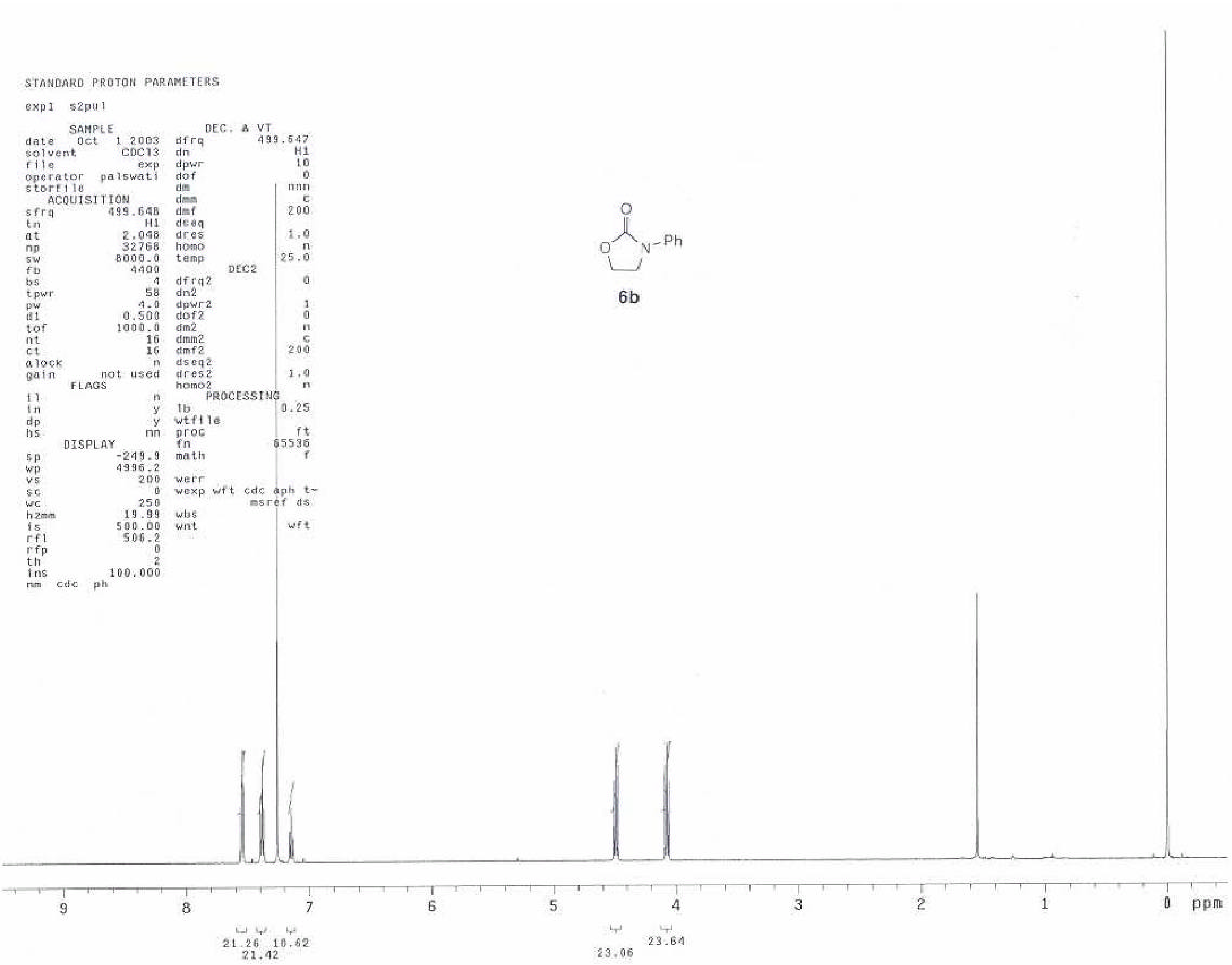

6b

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operator  palswati   dof               0
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tn               H1  dseq
at            2.048  dres            1.0
np            32768  homo              n
sw           8000.0  temp           25.0
fb             4400          DEC2
bs                4  dfrq2             0
tpwr             58  dn2
pw              4.0  dpwr2             1
d1            0.500  dof2              0
tof          1000.0  dm2               n
nt               16  dmm2              c
ct               16  dmf2            200
alock             n  dseq2
gain       not used  dres2           1.0
      FLAGS          homo2             n
il                n         PROCESSING
in                y  lb             0.25
dp                y  wtfile
hs               nn  proc             ft
     DISPLAY         fn            65536
sp           -249.9  math              f
wp           4996.2
vs              200  werr
sc                0  wexp wft cdc aph t-
wc              250             msref ds
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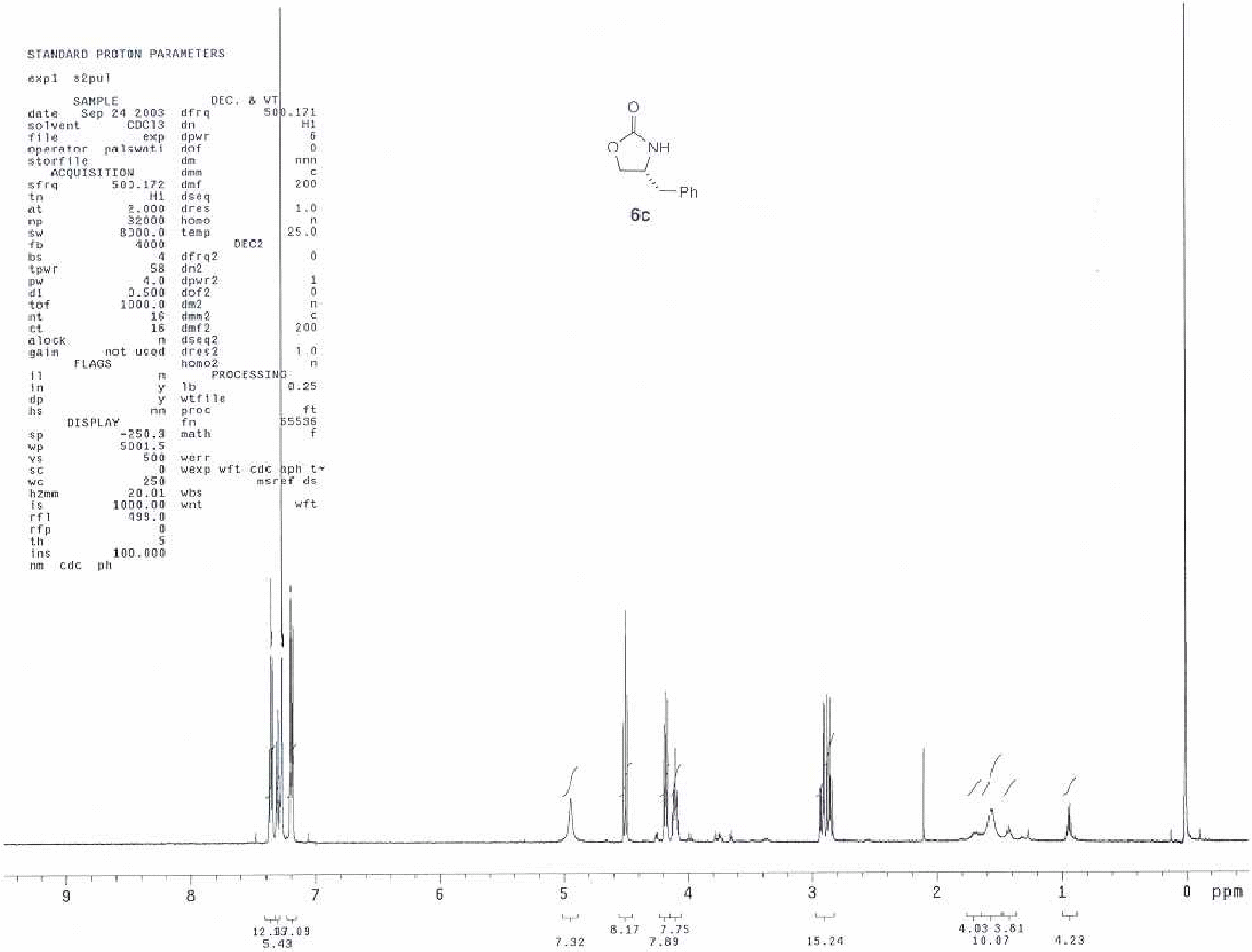

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STANDARD PROTON PARAMETERS

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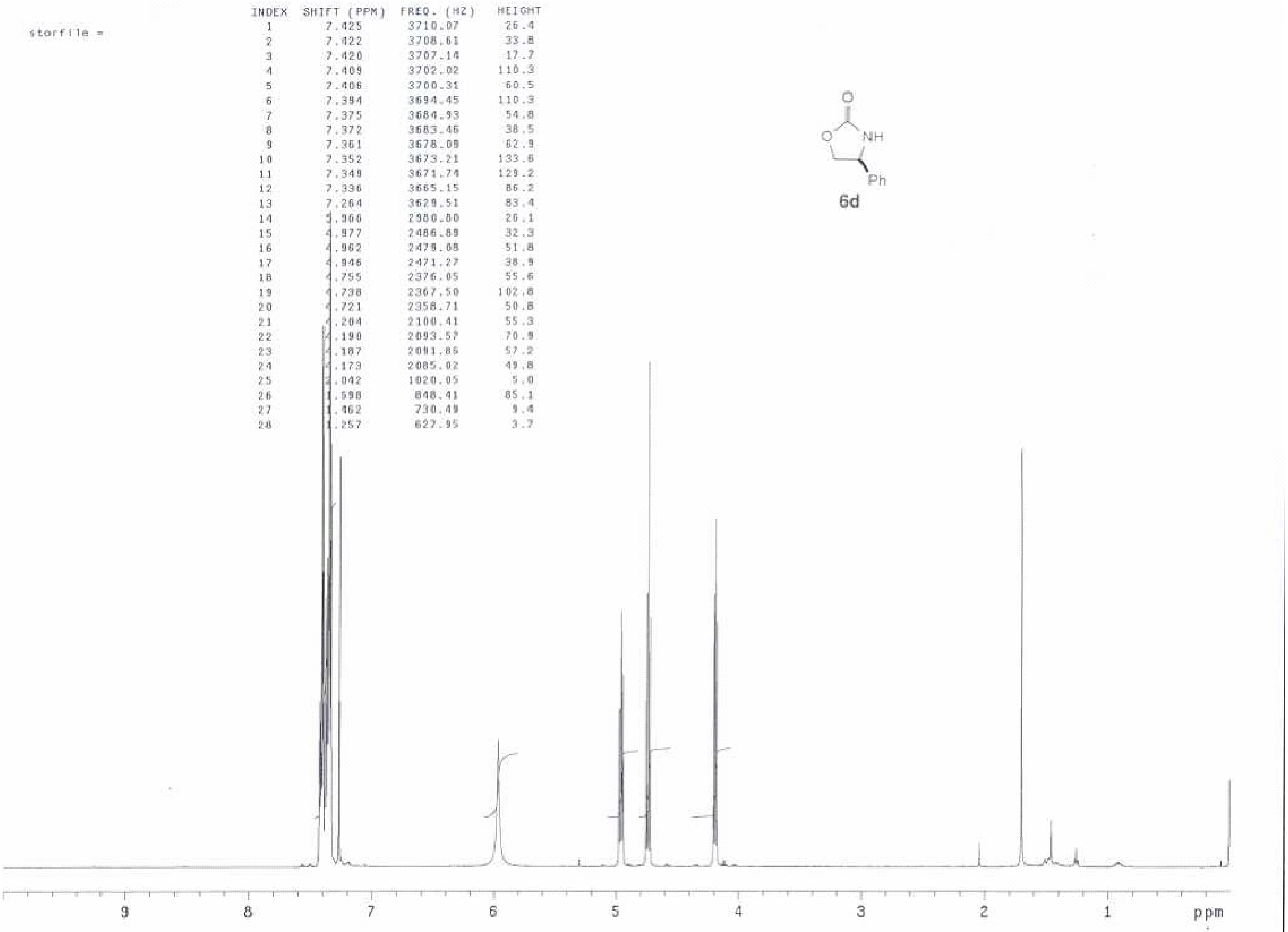
tn              H1  dseq
at           2.000  dres           1.0
np           32000  homo             n
sw          8000.0  temp          25.0
fb            4000          DEC2
bs               4  dfrq2            0
tpwr            58  dn2
pw             4.0  dpwr2            1
d1           0.500  dof2             0
tof         1000.0  dm2              n
nt              16  dmm2             c
ct              16  dmf2           200
alock            n  dseq2
gain      not used  dres2          1.0
      FLAGS         homo2            n
il               n        PROCESSING
in               y  lb            0.25
dp               y  wtfile
hs              nn  proc            ft
     DISPLAY        fn           65536
sp          -250.3  math             f
wp          5001.5
vs             500  werr
sc               0  wexp wft cdc aph t
wc             250          msref ds
hzmm         20.01  wbs
is         1000.00  wnt            wft
rfl          499.0
rfp              0
th               5
ins        100.000
nm  cdc  ph
```

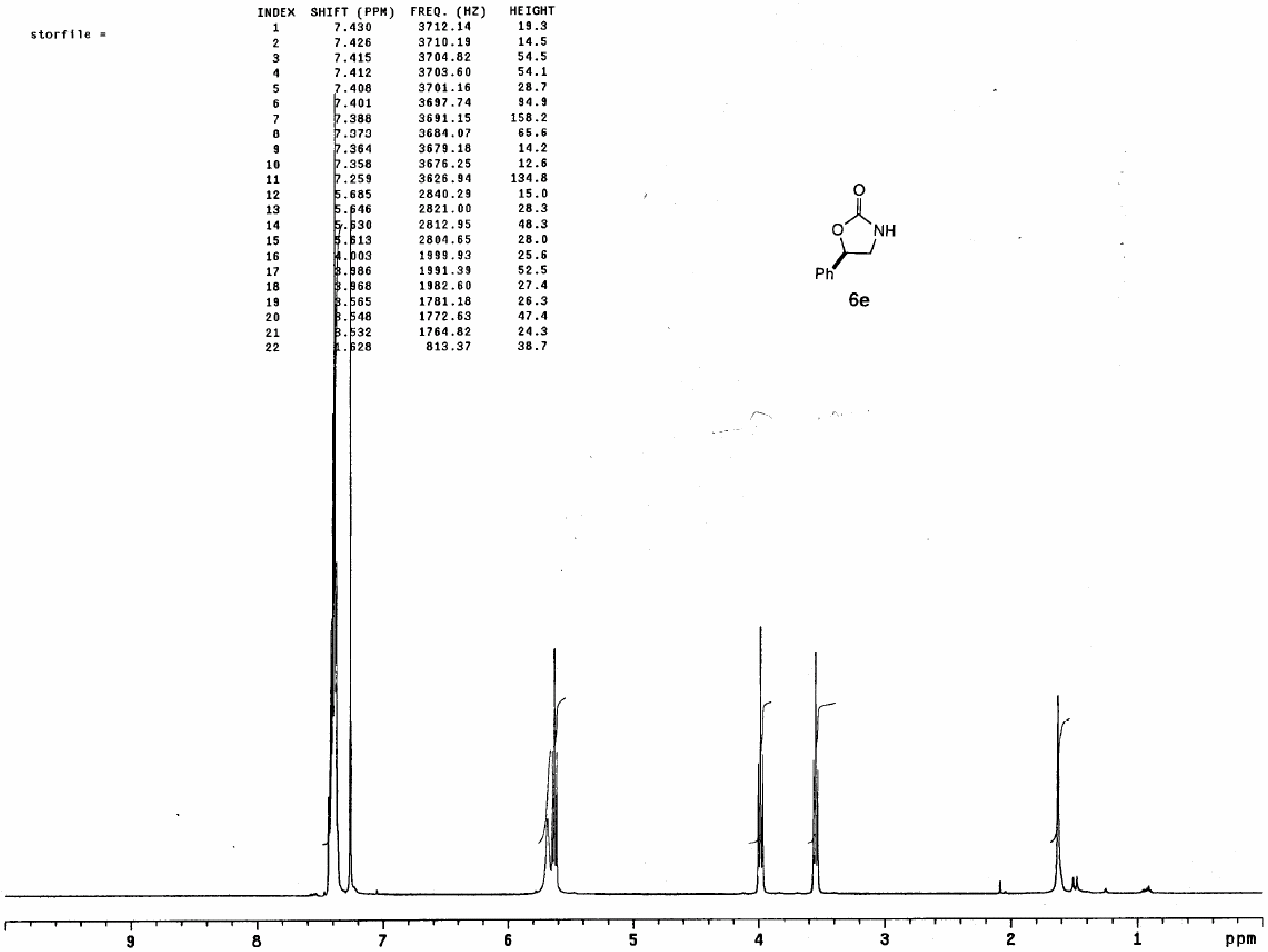
6c



6d

starfile =

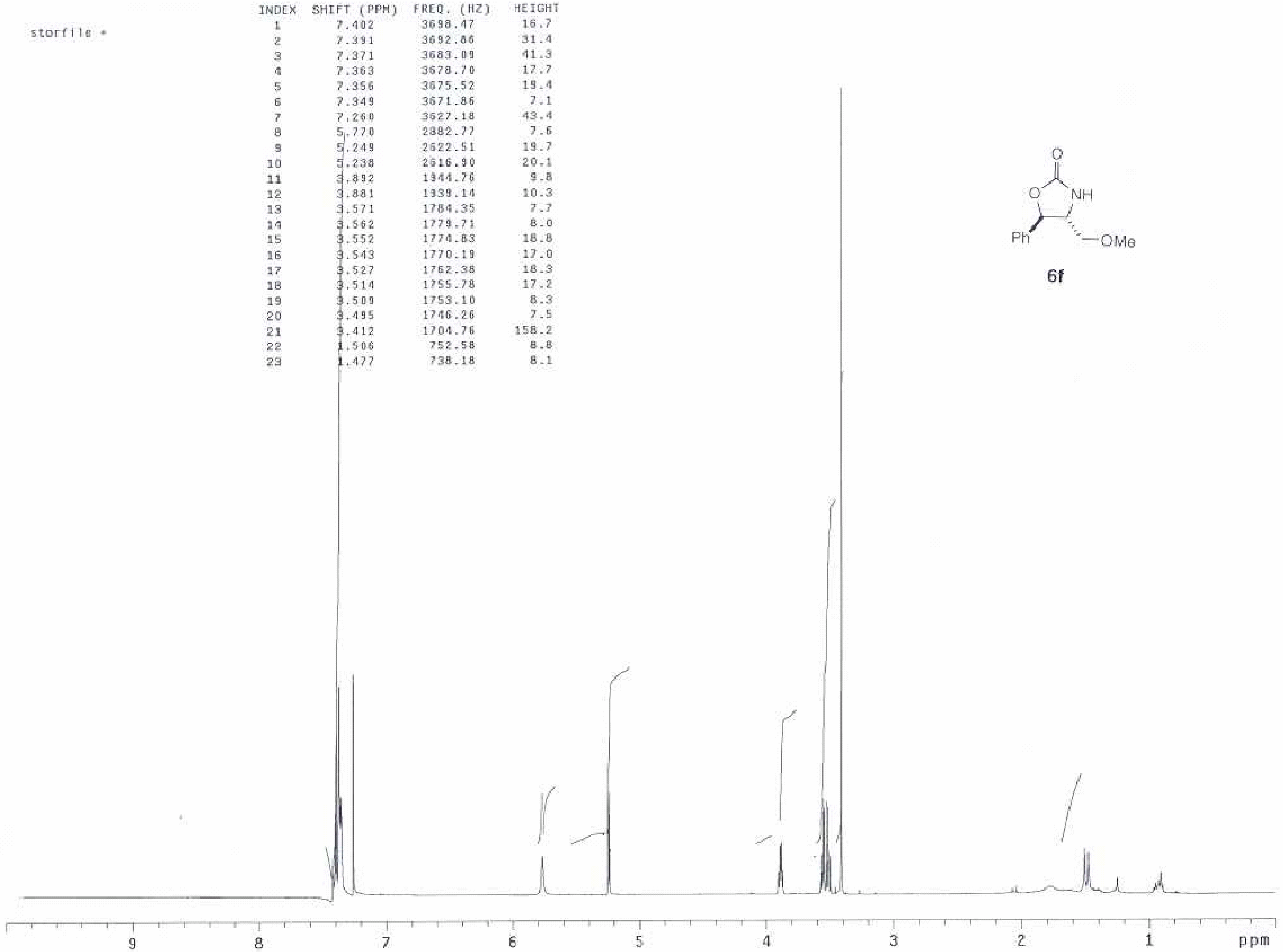
INDEX	SHIFT (PPM)	FREQ. (HZ)	HEIGHT
1	7.425	3710.07	26.4
2	7.422	3708.61	33.8
3	7.420	3707.14	17.7
4	7.409	3702.02	110.3
5	7.406	3700.31	60.5
6	7.394	3694.45	110.3
7	7.375	3684.93	54.8
8	7.372	3683.46	38.5
9	7.361	3678.09	62.9
10	7.352	3673.21	133.6
11	7.349	3671.74	129.2
12	7.336	3665.15	86.2
13	7.264	3629.51	83.4
14	5.966	2980.80	26.1
15	4.977	2486.89	32.3
16	4.962	2479.08	51.8
17	4.946	2471.27	38.9
18	4.755	2376.05	55.6
19	4.738	2367.50	102.8
20	4.721	2358.71	50.8
21	4.204	2100.41	55.3
22	4.190	2093.57	70.9
23	4.187	2091.86	57.2
24	4.173	2085.02	49.8
25	2.042	1020.05	5.0
26	1.698	848.41	85.1
27	1.462	730.49	9.4
28	1.257	627.95	3.7



6e

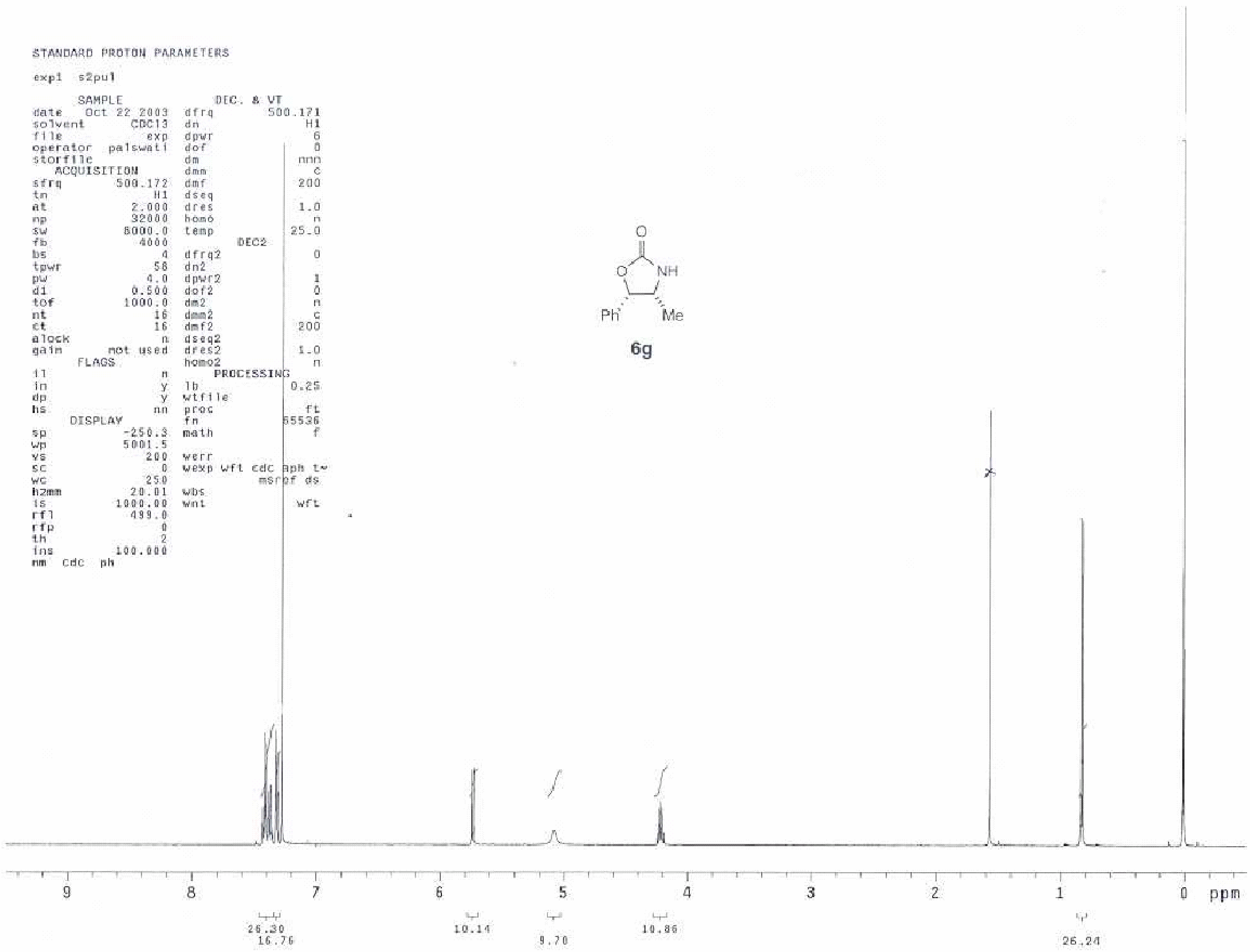
storfile =

INDEX	SHIFT (PPM)	FREQ. (HZ)	HEIGHT
1	7.430	3712.14	19.3
2	7.426	3710.19	14.5
3	7.415	3704.82	54.5
4	7.412	3703.60	54.1
5	7.408	3701.16	28.7
6	7.401	3697.74	94.9
7	7.388	3691.15	158.2
8	7.373	3684.07	65.6
9	7.364	3679.18	14.2
10	7.358	3676.25	12.6
11	7.259	3626.94	134.8
12	5.685	2840.29	15.0
13	5.646	2821.00	28.3
14	5.630	2812.95	48.3
15	5.613	2804.65	28.0
16	4.003	1999.93	25.6
17	3.986	1991.39	52.5
18	3.968	1982.60	27.4
19	3.565	1781.18	26.3
20	3.548	1772.63	47.4
21	3.532	1764.82	24.3
22	1.628	813.37	38.7



6f

INDEX	SHIFT (PPM)	FREQ. (HZ)	HEIGHT
1	7.402	3698.47	16.7
2	7.391	3692.86	31.4
3	7.371	3683.09	41.3
4	7.363	3678.70	17.7
5	7.356	3675.52	19.4
6	7.349	3671.86	7.1
7	7.260	3627.18	43.4
8	5.770	2882.77	7.6
9	5.249	2622.51	19.7
10	5.238	2616.90	20.1
11	3.892	1944.76	9.8
12	3.881	1939.14	10.3
13	3.571	1784.35	7.7
14	3.562	1779.71	8.0
15	3.552	1774.83	18.8
16	3.543	1770.19	17.0
17	3.527	1762.38	18.3
18	3.514	1755.78	17.2
19	3.509	1753.10	8.3
20	3.495	1746.26	7.5
21	3.412	1704.76	158.2
22	1.506	752.58	8.8
23	1.477	738.18	8.1

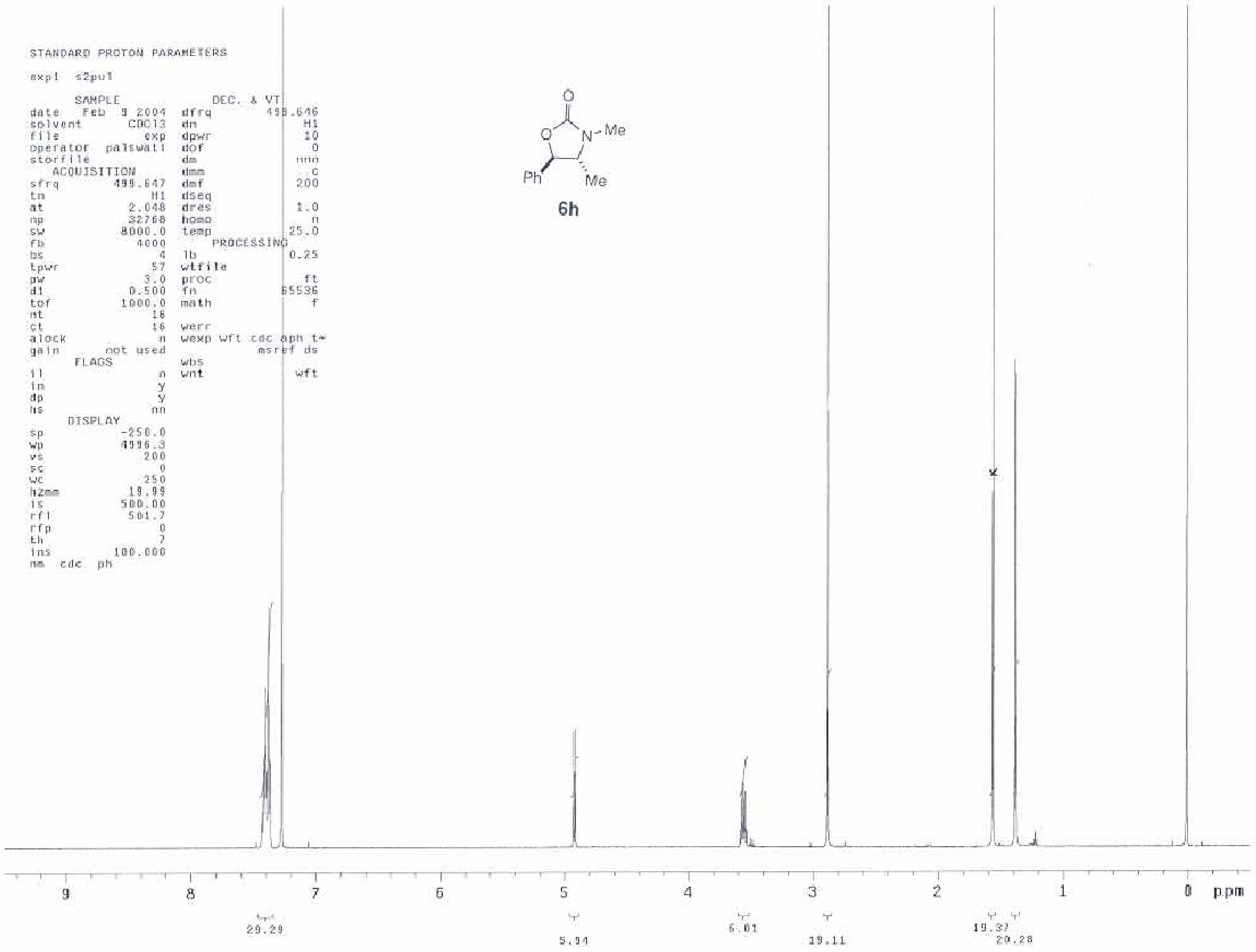


```
STANDARD PROTON PARAMETERS

exp1  s2pul

      SAMPLE             DEC. & VT
date   Oct 22 2003  dfrq       500.171
solvent      CDC13  dn              H1
file           exp  dpwr             6
operator  palswati  dof              0
storfile            dm             nnn
   ACQUISITION      dmm              c
sfrq       500.172  dmf            200
tn              H1  dseq
at           2.000  dres           1.0
np           32000  homo             n
sw          6000.0  temp          25.0
fb            4000          DEC2
bs               4  dfrq2            0
tpwr            58  dn2
pw             4.0  dpwr2            1
d1           0.500  dof2             0
tof         1000.0  dm2              n
nt              16  dmm2             c
ct              16  dmf2           200
alock            n  dseq2
gain      not used  dres2          1.0
      FLAGS         homo2            n
il               n       PROCESSING
in               y  lb            0.25
dp               y  wtfile
hs              nn  proc            ft
     DISPLAY        fn           65536
sp          -250.3  math             f
wp          5001.5
vs             200  werr
sc               0  wexp wft cdc aph t~
wc             250              msrof ds
hzmm         20.01  wbs
is         1000.00  wnt            wft
rfl          499.0
rfp              0
th               2
ins        100.000
mm  cdc  ph
```

6g

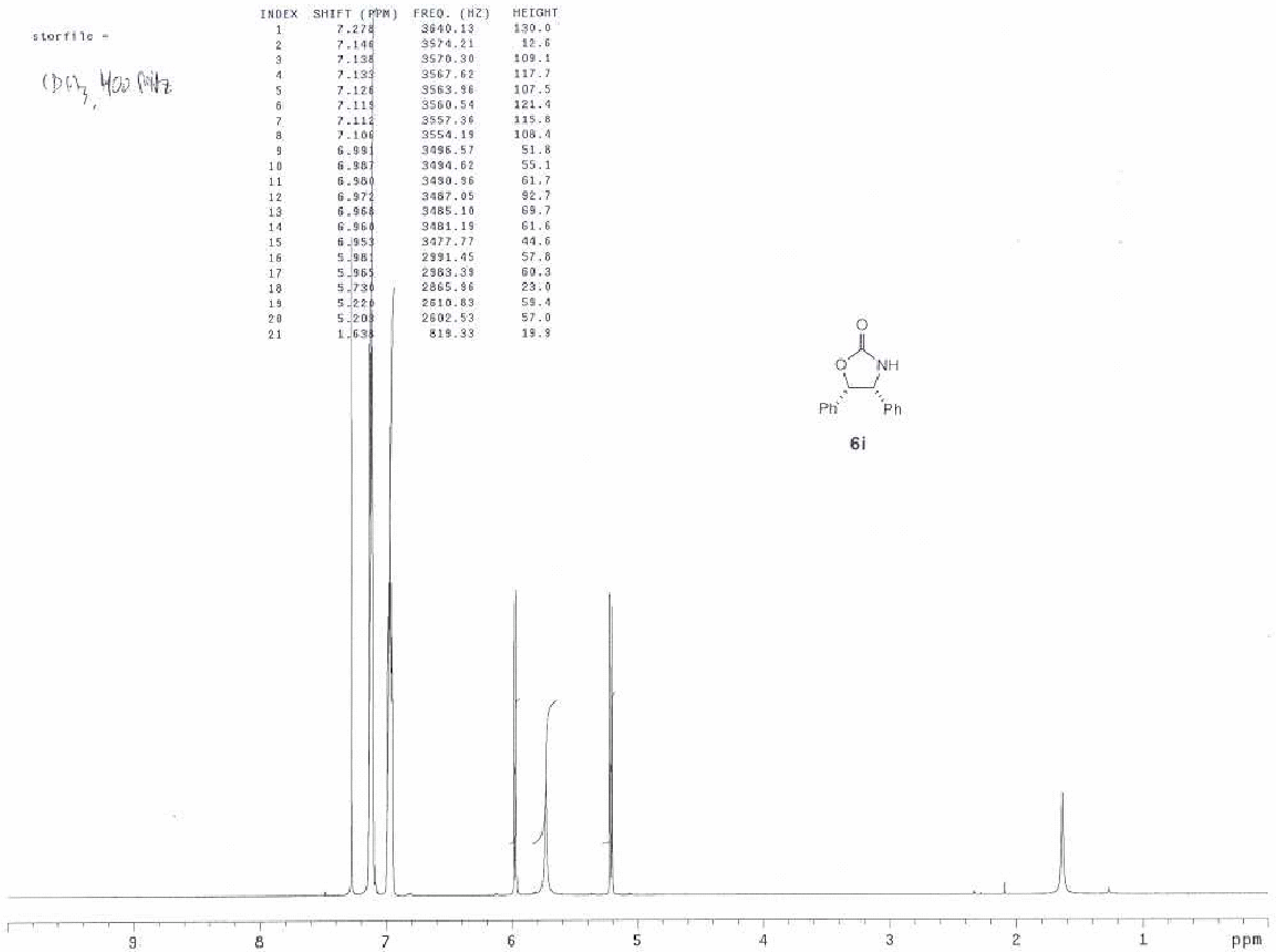


```
STANDARD PROTON PARAMETERS

expl  s2pul

      SAMPLE                 DEC. & VT
date    Feb  9 2004  dfrq        499.646
solvent       CDC13  dm               H1
file            exp  dpwr             10
operator  palswati1  dof               0
storfile             dm              nnn
   ACQUISITION       dmm               c
sfrq        499.647  dmf             200
tn               H1  dseq
at            2.048  dres            1.0
np            32768  homo              n
sw           8000.0  temp           25.0
fb             4000        PROCESSING
bs                4  lb             0.25
tpwr             57  wtfile
pw              3.0  proc             ft
d1            0.500  fn            65536
tof          1000.0  math              f
nt               16
ct               16  werr
alock             n  wexp wft cdc aph t*
gain       not used            msref ds
      FLAGS          wbs
il                n  wnt             wft
in                y
dp                y
hs               nn
     DISPLAY
sp           -250.0
wp           4996.3
vs              200
sc                0
wc              250
hzmm          19.99
is           500.00
rfl           501.7
rfp               0
th                7
ins         100.000
nm  cdc  ph
```

6h

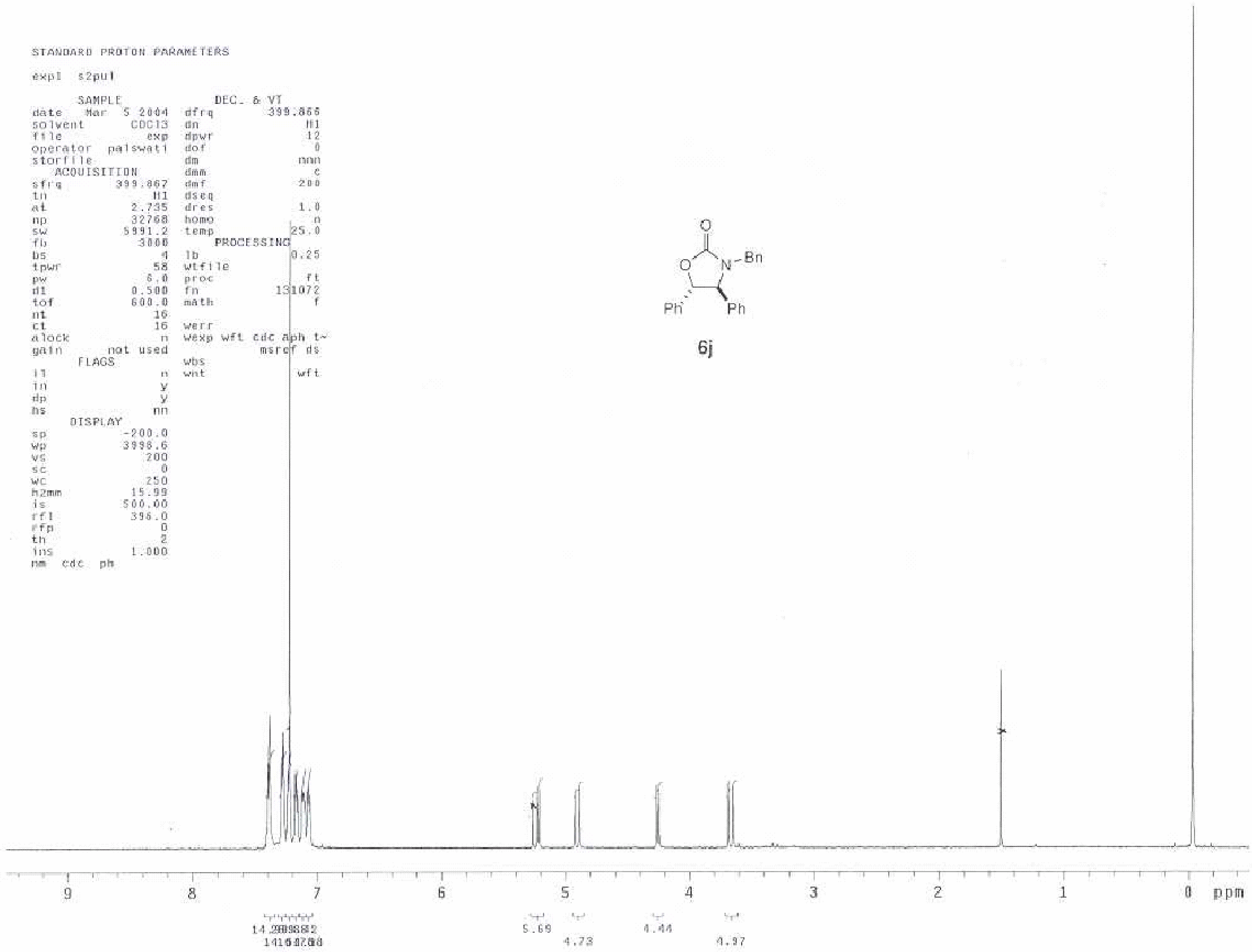


storfile =

$CDCl_3$, 400 MHz

INDEX	SHIFT (PPM)	FREQ. (HZ)	HEIGHT
1	7.278	3640.13	130.0
2	7.146	3574.21	12.6
3	7.138	3570.30	109.1
4	7.133	3567.62	117.7
5	7.126	3563.96	107.5
6	7.119	3560.54	121.4
7	7.112	3557.36	115.8
8	7.106	3554.19	108.4
9	6.991	3496.57	51.8
10	6.987	3494.62	55.1
11	6.980	3490.96	61.7
12	6.972	3487.05	92.7
13	6.968	3485.10	69.7
14	6.960	3481.19	61.6
15	6.953	3477.77	44.6
16	5.981	2991.45	57.8
17	5.965	2983.39	60.3
18	5.730	2865.96	23.0
19	5.220	2610.83	59.4
20	5.203	2602.53	57.0
21	1.638	819.33	19.9

6i

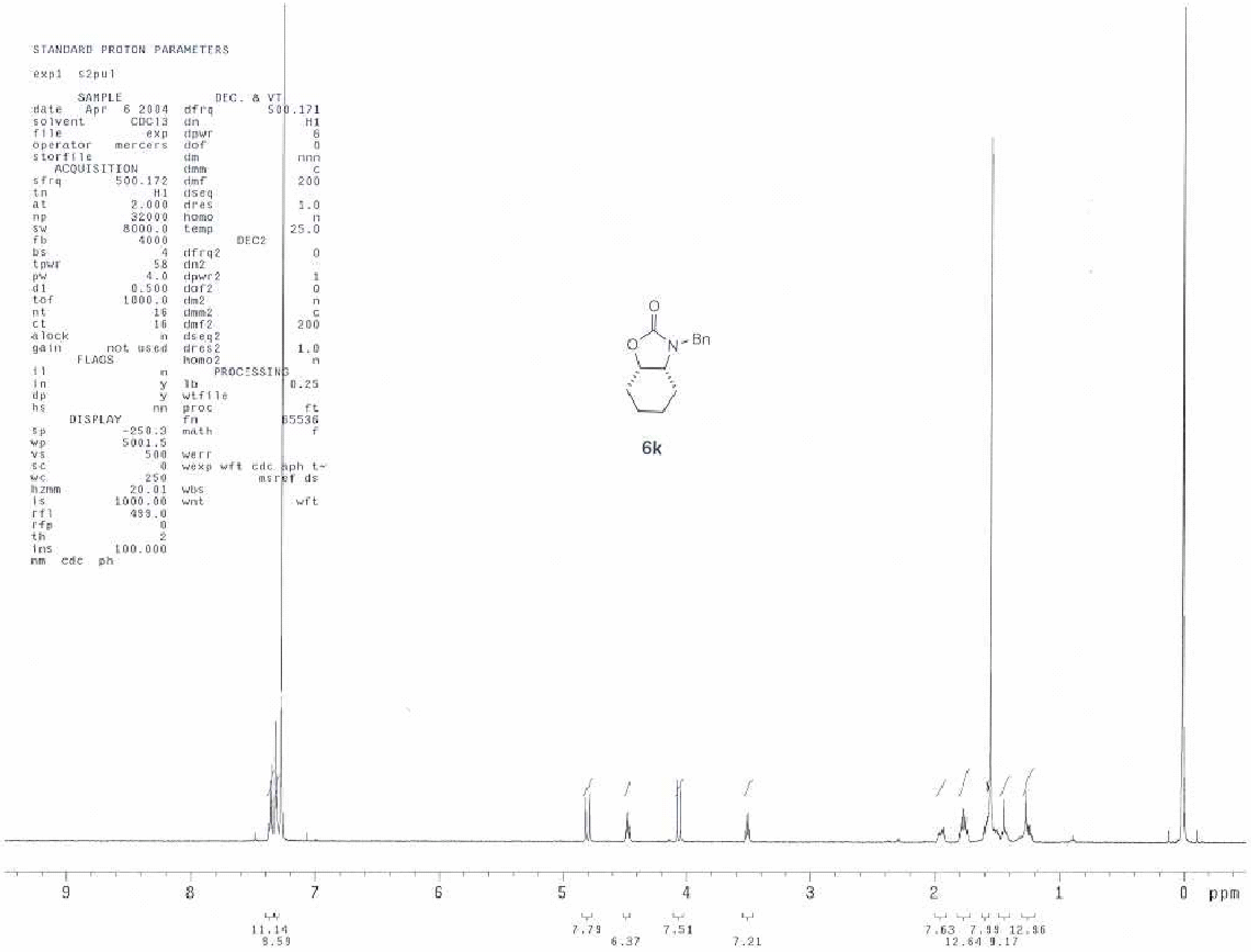


```
STANDARD PROTON PARAMETERS

expl  s2pul

      SAMPLE              DEC. & VT
date   Mar  5 2004   dfrq       399.866
solvent       CDC13   dn             H1
file            exp   dpwr           12
operator  palswati    dof             0
storfile              dm            nnn
   ACQUISITION        dmm             c
sfrq        399.867   dmf           200
tn               H1   dseq
at            2.735   dres          1.0
np            32768   homo            n
sw           5991.2   temp         25.0
fb             3000       PROCESSING
bs                4   lb           0.25
tpwr             58   wtfile
pw              6.0   proc           ft
d1            0.500   fn         131072
tof           600.0   math            f
nt               16
ct               16   werr
alock             n   wexp  wft cdc aph t~
gain       not used             msref ds
      FLAGS           wbs
il                n   wnt           wft
in                y
dp                y
hs               nn
     DISPLAY
sp           -200.0
wp           3998.6
vs              200
sc                0
wc              250
hzmm          15.99
is           500.00
rfl           396.0
rfp               0
th                2
ins           1.000
nm  cdc  ph
```

6j

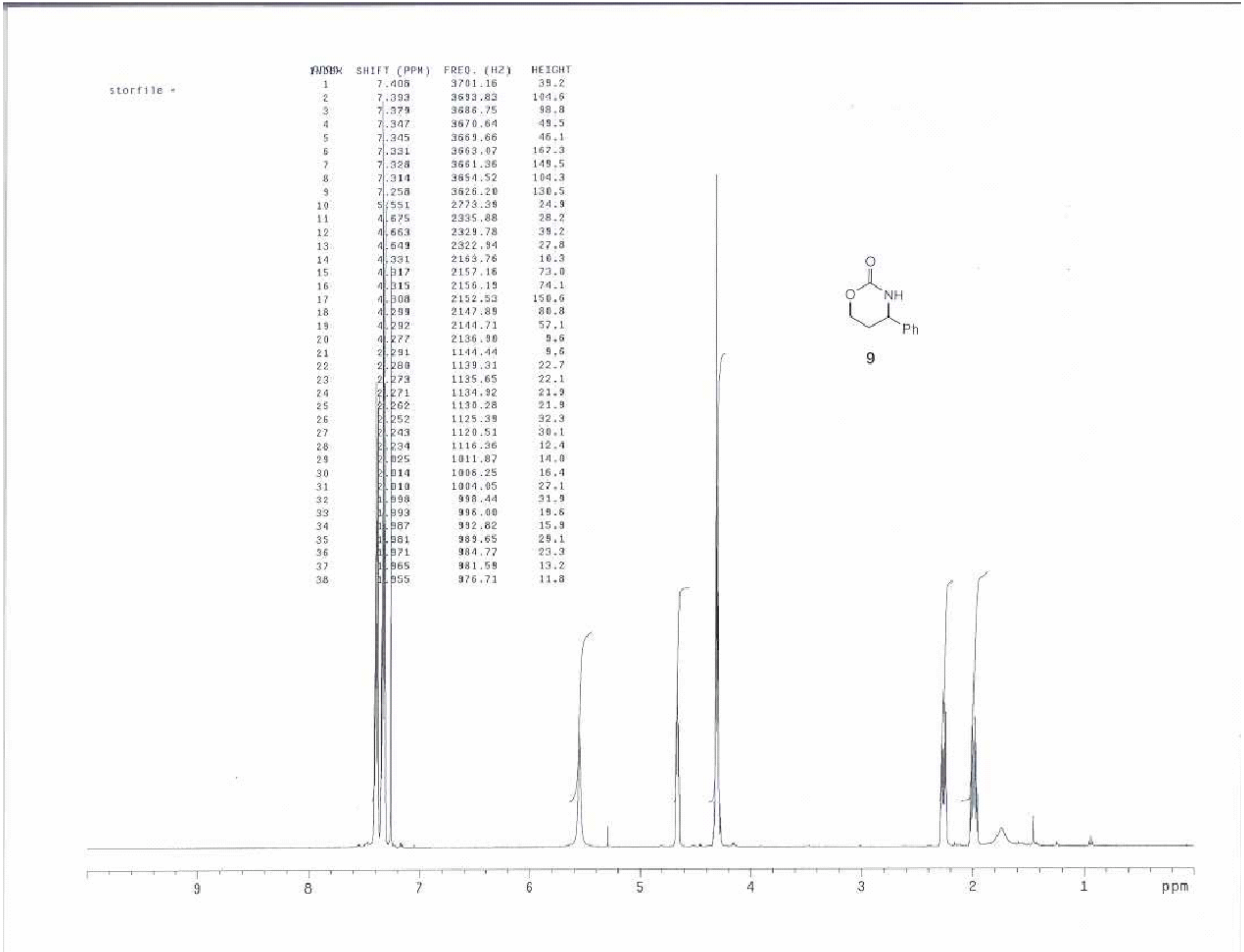


```
STANDARD PROTON PARAMETERS

exp1  s2pul

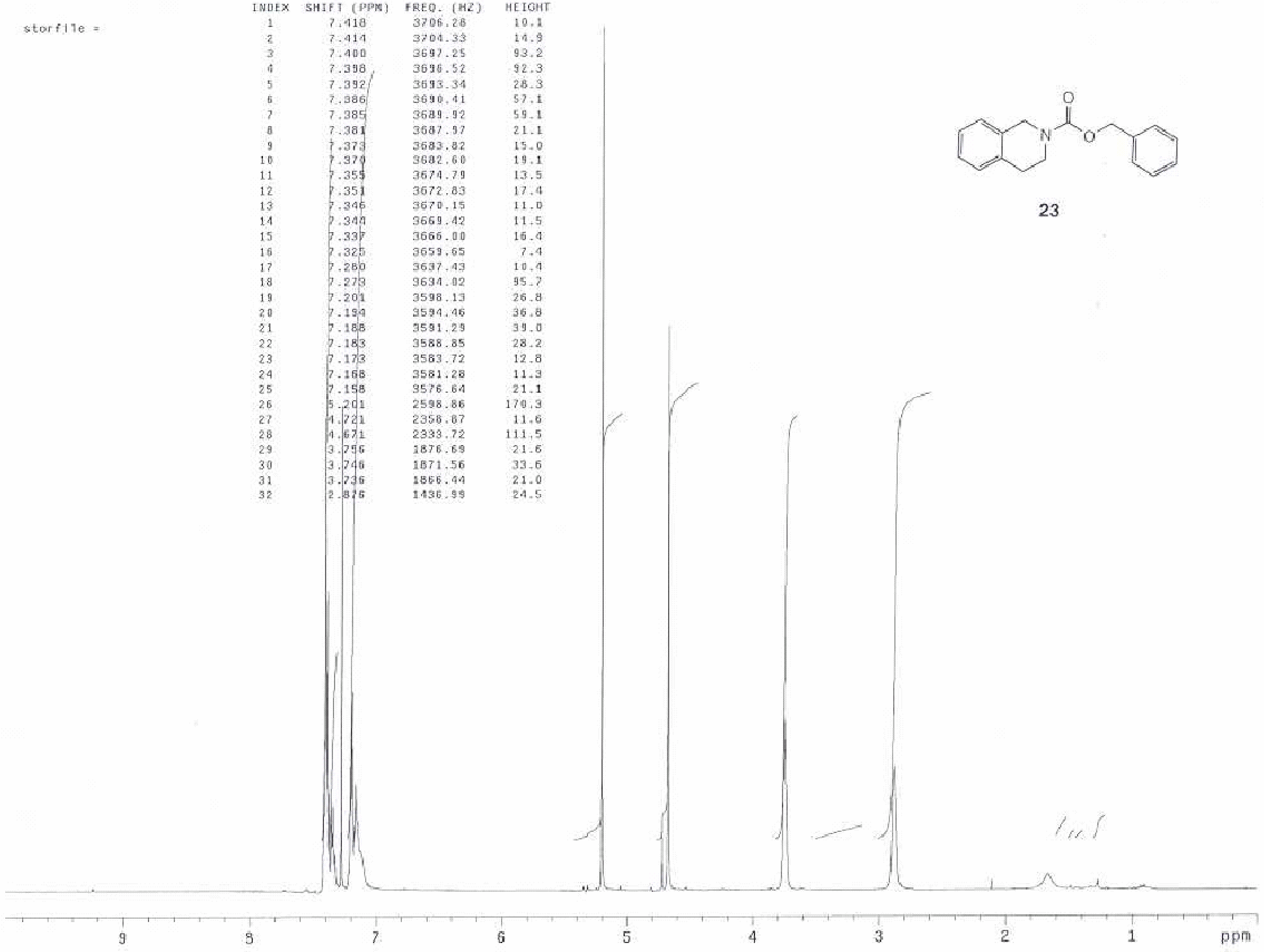
      SAMPLE                DEC. & VT
date    Apr  6 2004  dfrq       500.171
solvent       CDCl3  dn              H1
file            exp  dpwr             6
operator    mercers  dof              0
storfile             dm             nnn
   ACQUISITION       dmm              c
sfrq        500.172  dmf            200
tn               H1  dseq
at            2.000  dres           1.0
np            32000  homo             n
sw           8000.0  temp          25.0
fb             4000           DEC2
bs                4  dfrq2            0
tpwr             58  dn2
pw              4.0  dpwr2            1
d1            0.500  dof2             0
tof          1000.0  dm2              n
nt               16  dmm2             c
ct               16  dmf2           200
alock             n  dseq2
gain       not used  dres2          1.0
     FLAGS           homo2            n
il                n         PROCESSING
in                y  lb            0.25
dp                y  wtfile
hs               nn  proc            ft
     DISPLAY         fn           65536
sp           -250.3  math             f
wp           5001.5
vs              500  werr
sc                0  wexp wft cdc aph t-
wc              250             msref ds
hzmm          20.01  wbs
is          1000.00  wnt            wft
rfl           499.0
rfp               0
th                2
ins         100.000
nm  cdc  ph
```

6k



9

INDEX	SHIFT (PPM)	FREQ. (HZ)	HEIGHT
1	7.406	3701.16	39.2
2	7.393	3693.83	104.6
3	7.379	3686.75	98.8
4	7.347	3670.64	49.5
5	7.345	3669.66	46.1
6	7.331	3663.07	167.3
7	7.328	3661.36	149.5
8	7.314	3654.52	104.3
9	7.258	3626.20	130.5
10	5.551	2773.39	24.9
11	4.675	2335.88	28.2
12	4.663	2329.78	39.2
13	4.649	2322.94	27.8
14	4.331	2163.76	10.3
15	4.317	2157.16	73.0
16	4.315	2156.19	74.1
17	4.308	2152.53	150.6
18	4.299	2147.89	80.8
19	4.292	2144.71	57.1
20	4.277	2136.90	9.6
21	2.291	1144.44	9.6
22	2.280	1139.31	22.7
23	2.273	1135.65	22.1
24	2.271	1134.92	21.9
25	2.262	1130.28	21.9
26	2.252	1125.39	32.3
27	2.243	1120.51	30.1
28	2.234	1116.36	12.4
29	2.025	1011.87	14.0
30	2.014	1006.25	16.4
31	2.010	1004.05	27.1
32	1.998	998.44	31.9
33	1.993	996.00	19.6
34	1.987	992.82	15.9
35	1.981	989.65	29.1
36	1.971	984.77	23.3
37	1.965	981.59	13.2
38	1.955	976.71	11.8

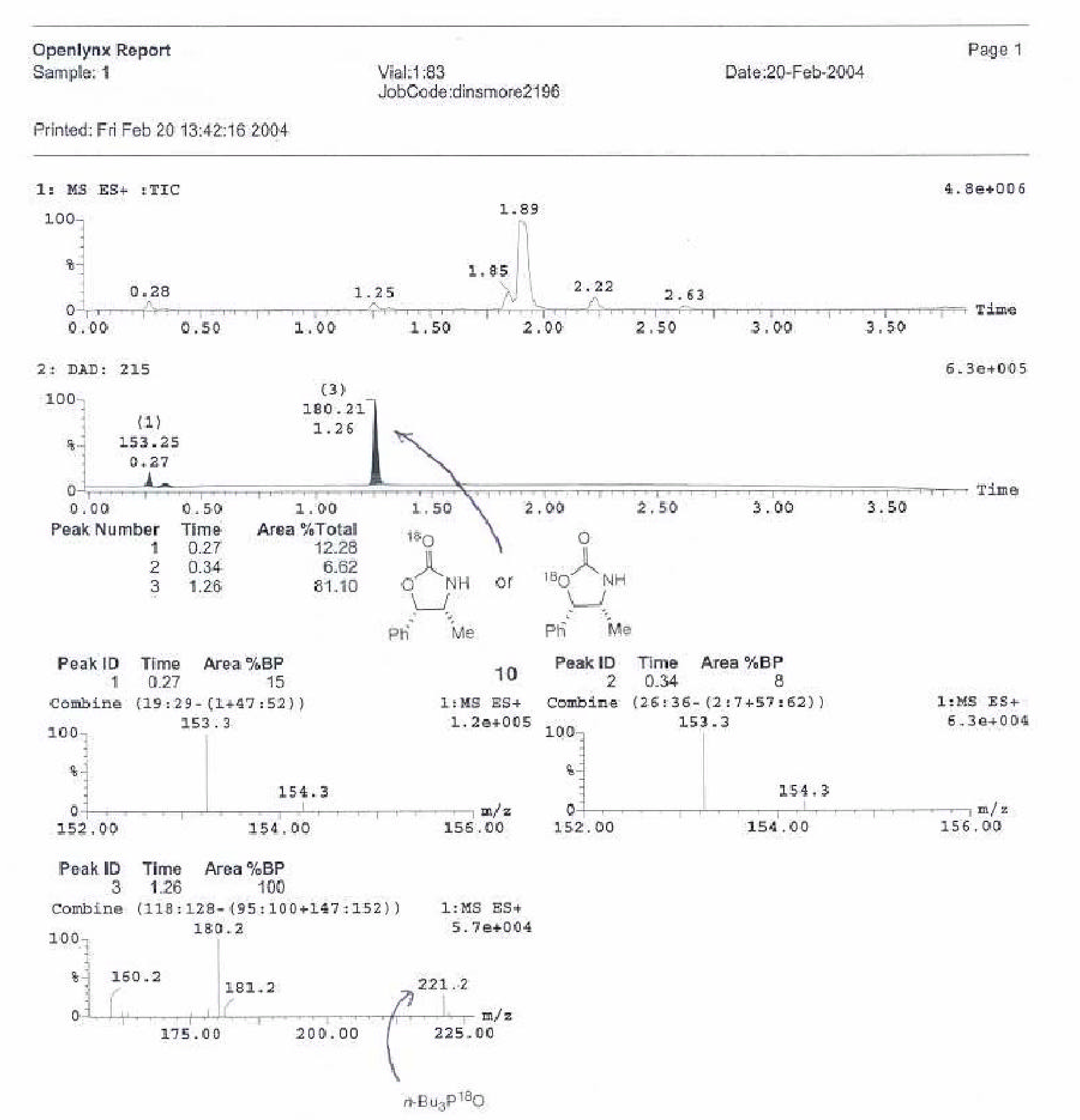


23

storfile =

INDEX	SHIFT (PPM)	FREQ. (HZ)	HEIGHT
1	7.418	3706.28	10.1
2	7.414	3704.33	14.9
3	7.400	3697.25	93.2
4	7.398	3696.52	92.3
5	7.392	3693.34	28.3
6	7.386	3690.41	57.1
7	7.385	3689.92	59.1
8	7.381	3687.97	21.1
9	7.373	3683.82	15.0
10	7.370	3682.60	19.1
11	7.355	3674.79	13.5
12	7.351	3672.83	17.4
13	7.346	3670.15	11.0
14	7.344	3669.42	11.5
15	7.337	3666.00	16.4
16	7.325	3659.65	7.4
17	7.280	3637.43	10.4
18	7.273	3634.02	95.7
19	7.201	3598.13	26.8
20	7.194	3594.46	36.8
21	7.188	3591.29	39.0
22	7.183	3588.85	28.2
23	7.173	3583.72	12.8
24	7.168	3581.28	11.3
25	7.158	3576.64	21.1
26	5.201	2598.86	170.3
27	4.721	2358.87	11.6
28	4.671	2333.72	111.5
29	3.756	1876.69	21.6
30	3.746	1871.56	33.6
31	3.736	1866.44	21.0
32	2.876	1436.99	24.5

Copies of the LCMS and HRMS spectra from the carboxylation/Mitsunobu cyclization reaction of 4g using ^{18}O-labeled CO$_2$ to give 10 (eq 2):



Openlynx Report
Sample: 1
Vial:1:83
JobCode:dinsmore2196
Date:20-Feb-2004
Page 1

Printed: Fri Feb 20 13:42:16 2004

Peak Number	Time	Area %Total
1	0.27	12.28
2	0.34	6.62
3	1.26	81.10

Peak ID	Time	Area %BP
1	0.27	15

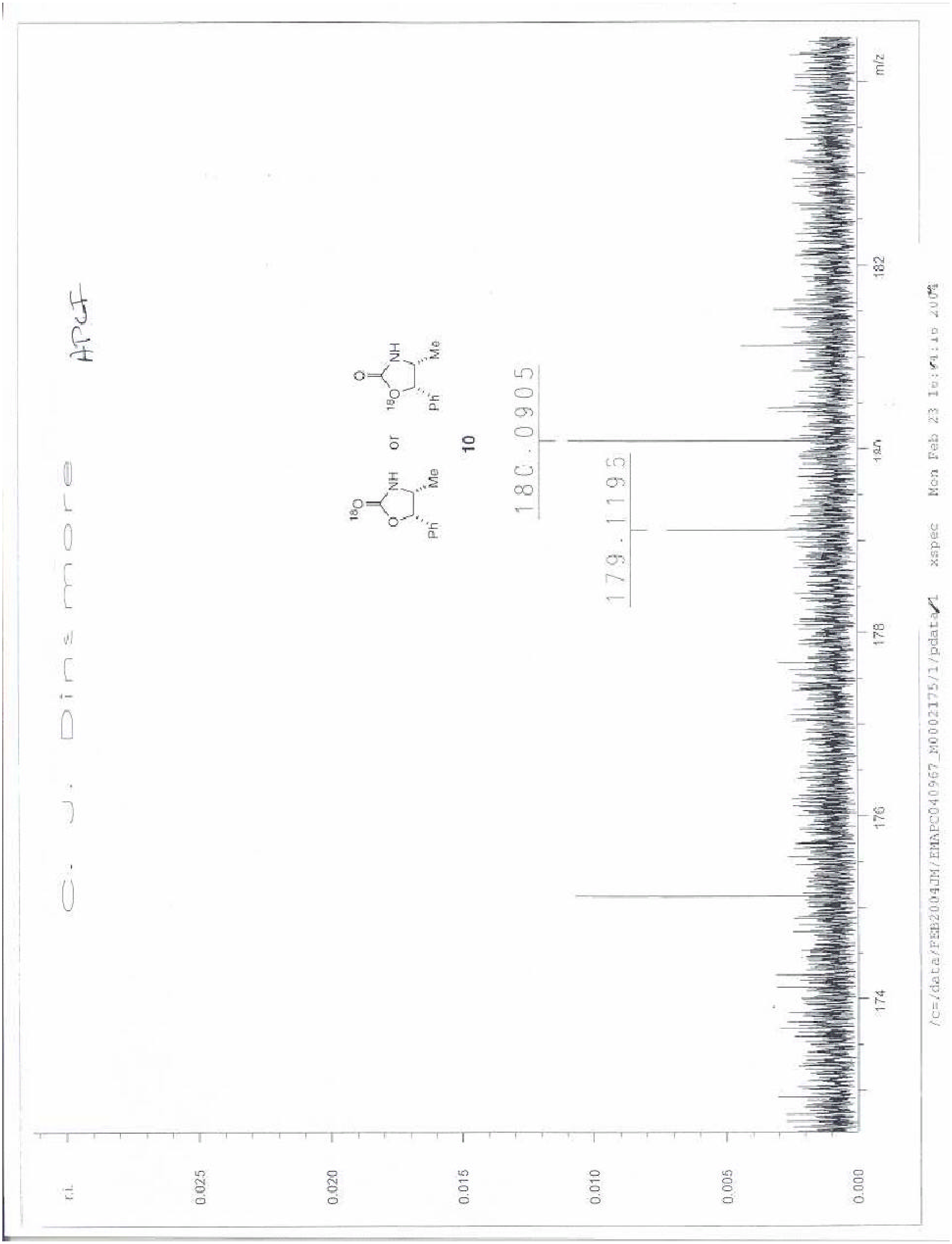
Combine (19:29-(1+47:52)) 1:MS ES+ 1.2e+005

Peak ID	Time	Area %BP
2	0.34	8

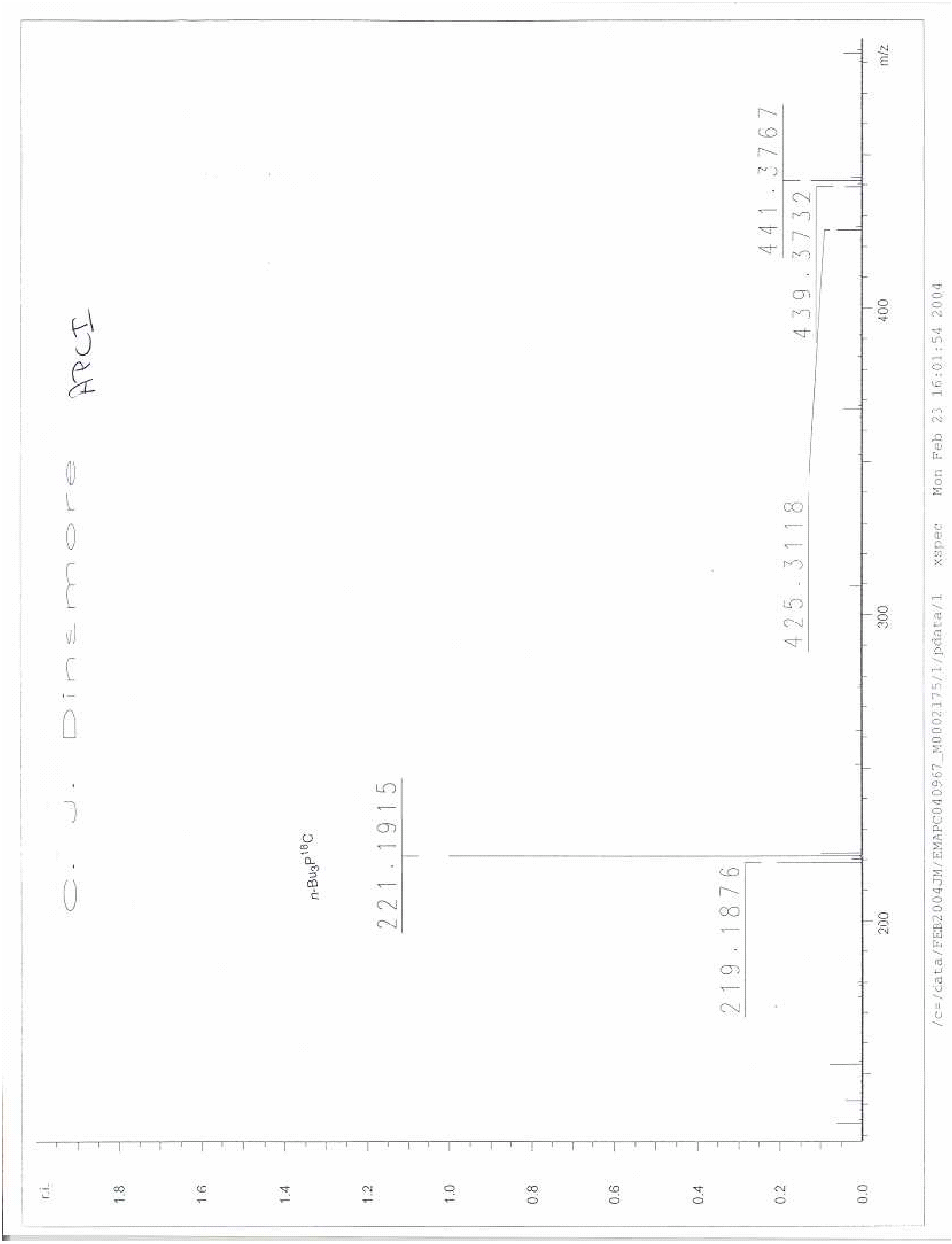
Combine (26:36-(2:7+57:62)) 1:MS ES+ 6.3e+004

Peak ID	Time	Area %BP
3	1.26	100

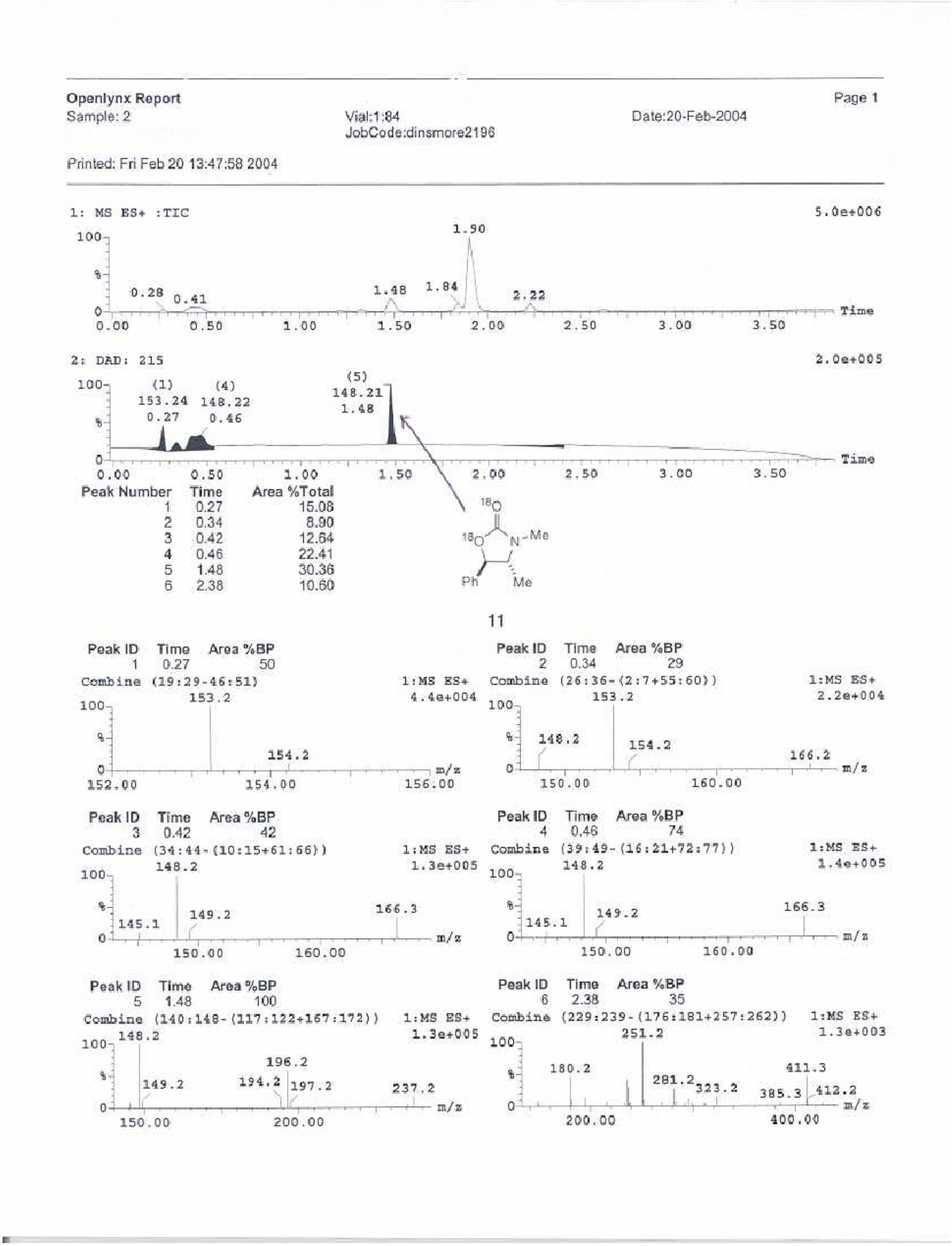
Combine (118:128-(95:100+147:152)) 1:MS ES+ 5.7e+004


C. J. Dinsmore
APCI
^{18}O
O
NH
Me
Ph
or
180.0905
179.1195
r.i.
0.000
0.005
0.010
0.015
0.020
0.025
m/z
174
176
178
180
182
/c=/data/FEB2004JM/EMAPC040967_M0002175/1/pdata/1 xspec Mon Feb 23 16:01:16 2004

10


C. J. Dinsmore
APCI
n-Bu$_3$P^{18}O
221.1915
219.1876
425.3118
439.3732
441.3767
r.i.
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
200
300
400
m/z
/c=/data/FEB2004JM/EMAPC040967_MD002175/1/pdata/1 xspec Mon Feb 23 16:01:54 2004

Copies of the LCMS and HRMS spectra from the carboxylation/Mitsunobu cyclization reaction of 4h using ^{18}O-labeled CO$_2$ to give 11 (eq 3):



Openlynx Report Page 1

Sample: 2 Vial:1:84 Date:20-Feb-2004

JobCode:dinsmore2196

Printed: Fri Feb 20 13:47:58 2004

Peak Number	Time	Area %Total
1	0.27	15.08
2	0.34	8.90
3	0.42	12.64
4	0.46	22.41
5	1.48	30.36
6	2.38	10.60

11

Peak ID	Time	Area %BP
1	0.27	50

Combine (19:29-46:51) 1:MS ES+ 4.4e+004

Peak ID	Time	Area %BP
2	0.34	29

Combine (26:36-(2:7+55:60)) 1:MS ES+ 2.2e+004

Peak ID	Time	Area %BP
3	0.42	42

Combine (34:44-(10:15+61:66)) 1:MS ES+ 1.3e+005

Peak ID	Time	Area %BP
4	0.46	74

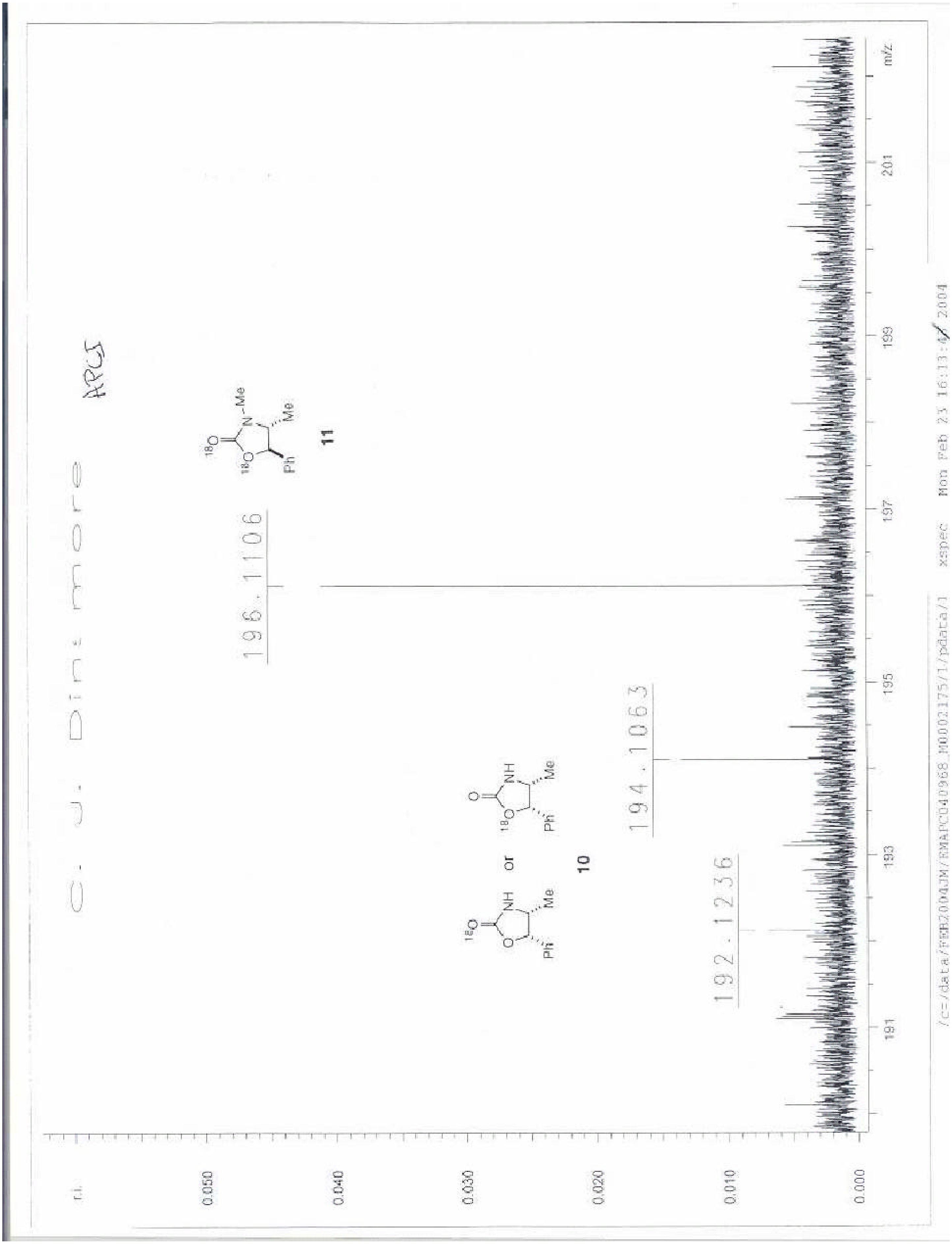
Combine (39:49-(16:21+72:77)) 1:MS ES+ 1.4e+005

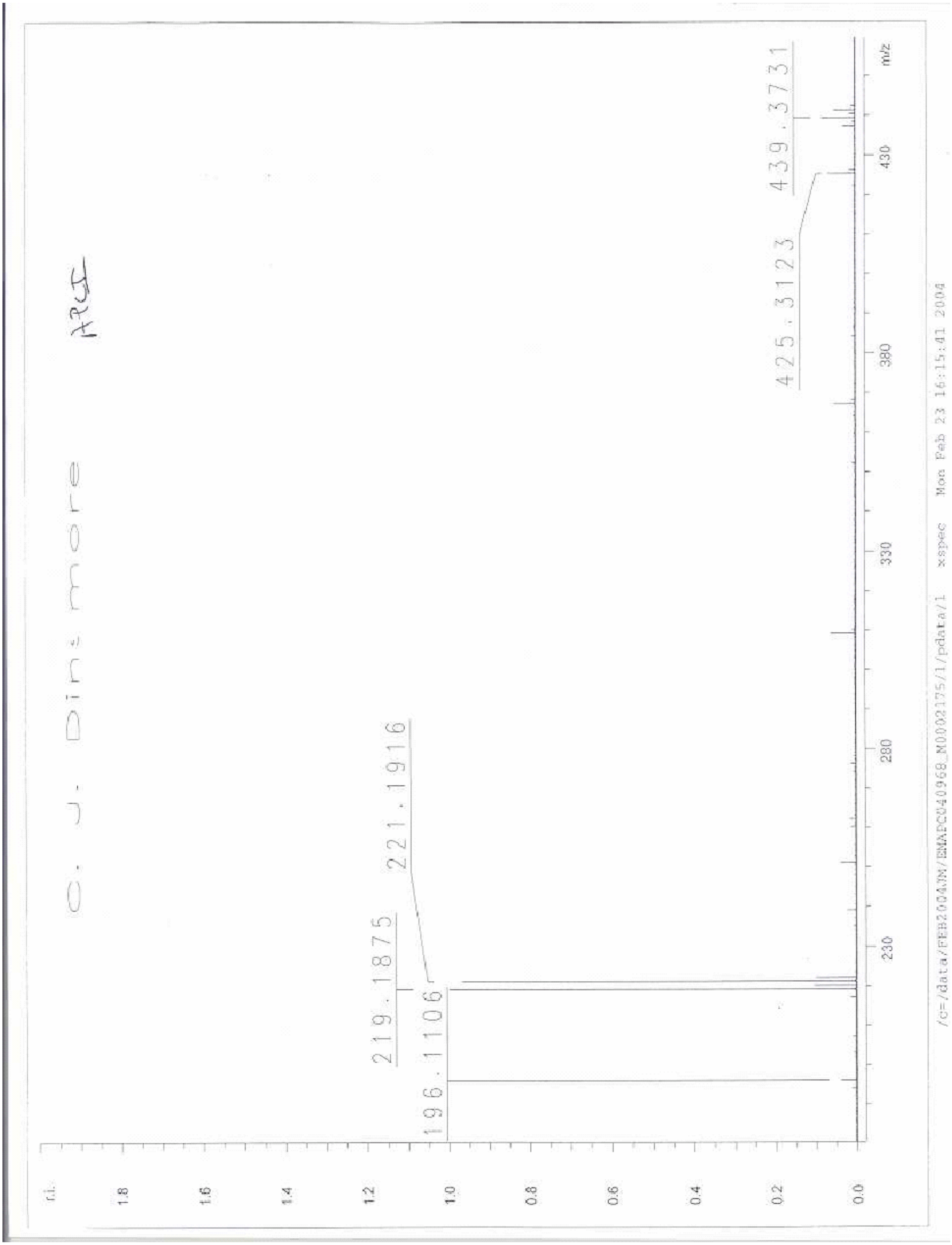
Peak ID	Time	Area %BP
5	1.48	100

Combine (140:148-(117:122+167:172)) 1:MS ES+ 1.3e+005

Peak ID	Time	Area %BP
6	2.38	35

Combine (229:239-(176:181+257:262)) 1:MS ES+ 1.3e+003


C. J. Dinsmore
APCI
196.1106
194.1063
192.1236
11
10
or
^{18}O
NH
N-Me
Me
Ph
r.i.
0.050
0.040
0.030
0.020
0.010
0.000
191
193
195
197
199
201
m/z
/c=/data/FEB2004JM/EMAPC040968_M0002175/1/pdata/1 xspec Mon Feb 23 16:13:4 2004


C. J. Dinsmore
APCI
196.1106
219.1875
221.1916
425.3123
439.3731
r.i.
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
230
280
330
380
430
m/z
/c=/data/FEB2004JM/EMAPC040968_M0002175/1/pdata/1 xspec Mon Feb 23 16:15:41 2004