Supplementary Material (ESI) for Chemical Communications

"Enantioselective Synthesis of α-Terpineol and Nephthenol by Intramolecular Acyl-oxazolidinone Enolate Alkylations."

Yinghua Jin and Robert M. Coates*

Department of Chemistry, University of Illinois, 600 South Mathews Ave, Urbana, IL 61801, USA

coates@scs.uiuc.edu

SUPPORTING INFORMATION

List of Contents

Materials and General Synthetic Methods

Materials were purchased from commercial suppliers and used without further purification, unless otherwise indicated. Ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone immediately prior to use. CH_3CN and DMF were distilled from P_2O_5 and stored over 3 Å molecular sieves. A commercial sample of methanesulfonyl chloride (Aldrich) was distilled from P_2O_5 before use.

All reactions, except those performed in aqueous solvent, were conducted under dry nitrogen in flame-dried glassware. Organic extracts from reaction workups were dried with anhydrous $MgSO_4$ or Na_2SO_4 and filtered before concentration. Unless otherwise specified, solvents were evaporated using a rotary evaporator after workup.

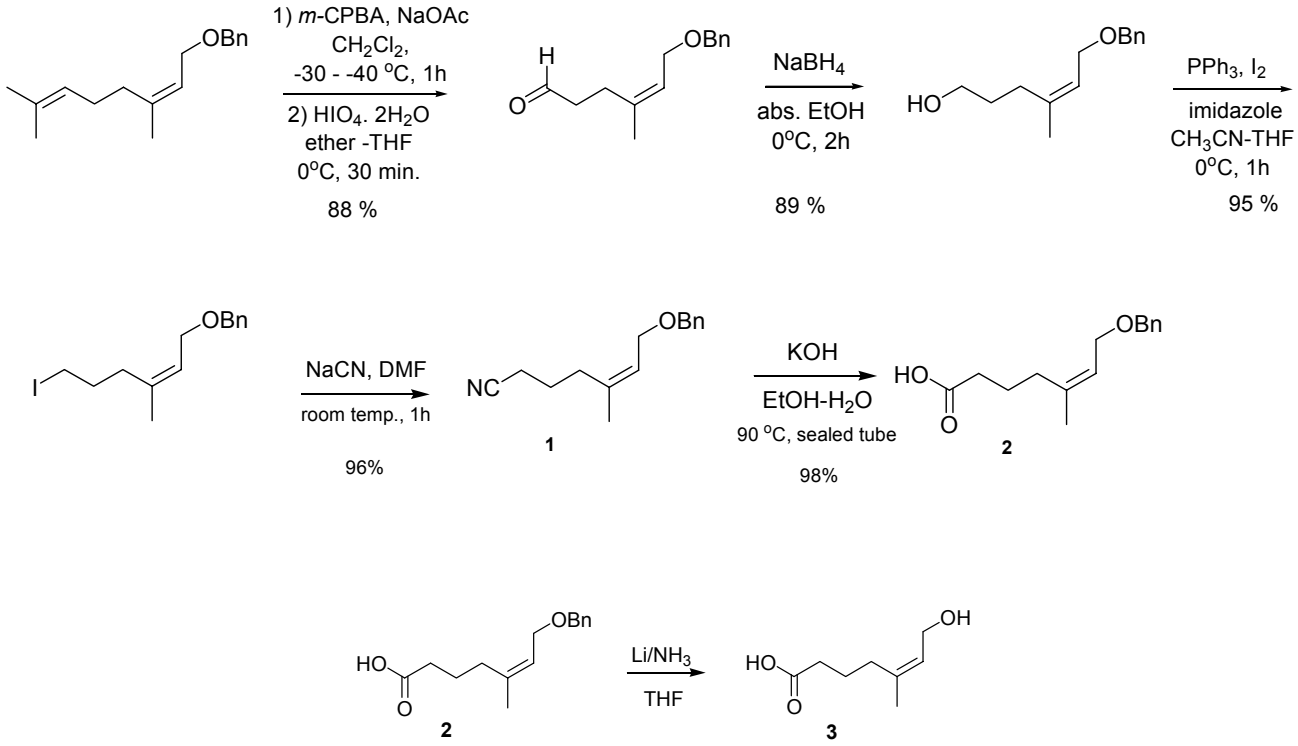
Flash column chromatography refers to the procedure of Still[1] and was performed by using a 100-150 times weight excess of silica gel 60 230-400 mesh ASTM from Merck. Fractions were analyzed by TLC using silica gel 60 F254 250 μm precoated-plates.

All GC analyses were performed on a Shimadzu GC-14A with 30-m Restek Rtx-5 column. IR spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer as neat liquids on NaCl plates. LR, HR ESI, EI and CI mass spectra were recorded on a Micromass ZAB-SE Spectrometer (Waters Corporation, Beverly, MA, USA) in the Mass Spectrometry Laboratory of the School of Chemical Sciences, University of Illinois, Urbana-Champaign. NMR spectra were taken on Unity 400, or Unity 500 spectrometers. $CHCl_3$ (7.26 ppm), C_6H_6 (7.15 ppm), toluene (7.09 ppm) were used as internal references. ^{1}H NMR data are reported in the order: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, coupling constants (*J*, Hz), assignments. Optical rotations were acquired on a JASCO DIP-370 Digital Polarimeter at 23 ^{o}C. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

[1] W. C. Still, M. Kahn, and A. Mitra., *J. Org. Chem*., 1978, **43**, 2923.

Unless otherwise specified, the purity of the compounds was estimated to be ≥ 95 % based on NMR spectral integration and/or GC analysis.

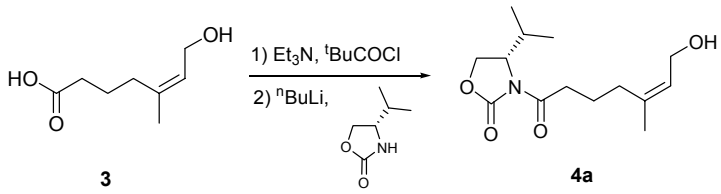
Synthesis of Benzyl Ether Acid 2 from Neryl Benzyl Ether



(*Z*)-7-Hydroxy-5-methylhept-5-enoic Acid (3). The procedure by Coates for a different compound was followed.[2] A solution of benzyloxy acid **2** (86 mg, 0.35 mmol) in THF (10 mL) was stirred and cooled at –78 °C, as ammonia gas was passed through the solution and liquid NH_3 (10 mL) was condensed. Lithium metal (block, 48 mg, 6.9 mmol) was cut into small slices (~0.5 mm thick) and added with stirring. The resulting dark blue mixture was stirred for 30 min at –78 °C. The reaction was quenched with MeOH (10 mL). The reaction mixture was slowly warmed to room temperature, as the liquid ammonia was blown off by a nitrogen stream. The solvent was evaporated in vacuo and water (20 mL) was added. The mixture was extracted with hexane (20 mL). The aqueous phase was acidified with 1N HCl until pH ~3 and extracted with Et_2O (3 x 20 mL). The combined ethereal extracts were washed with satd. NaCl (2 x 20

[2] R. M. Coates, D. A. Ley, and P. L. Cavender, *J. Org. Chem.*, 1978, **43**, 4915.

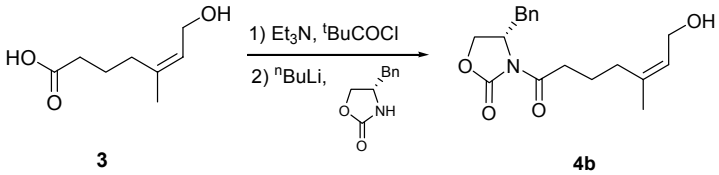
mL), dried over $MgSO_4$, and concentrated to give hydroxy acid **3** (46 mg, 84 %) as a yellow oil: TLC R_f 0.03 (10 % CH_3CN in EtOAc); IR (neat) ν_{max} 3318, 2936, 1708, 1409, 1247, 1048, 988 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.74 (s, 3H, C*H*$_3$), 1.76 (quintet, 2H, *J* = 7.2 Hz, C*H*$_2$), 2.16 (br t, 2H, *J* = 7.3 Hz, C*H*$_2$), 2.34 (t, 2H, *J* = 7.2 Hz, C*H*$_2$), 4.12 (d, 2H, *J* = 7.1 Hz, C*H*$_2$OH), 5.48 (t, 1H, *J* = 7.2 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.9, 23.2, 30.9, 33.4, 58.9, 125.2, 139.2, 179.1. HR-MS (CI): Calcd for $C_8H_{13}O_3$, 157.0865. Found, 157.0855.



(4*S*)-3-((*Z*)-7-Hydroxy-5-methylhept-5-enoyl)-4-isopropyl-2-oxazolidinone (4a). The *N*-acylation procedure reported by Joullié for a different compound was followed.[3] A solution of (*S*)-4-isopropyl-2-oxazolidinone (351 mg, 2.72 mmol) in THF (12 mL) was stirred and cooled at –78 °C, as *n*BuLi (1.6 M in hexane, 1.7 mL, 2.72 mmol) was added dropwise. The clear solution was stirred at –78 °C for 30 min. In a separate flask, a solution of acid **3** (430 mg, 2.72 mmol) in THF (15 mL) was stirred and cooled at 0 °C, as pivaloyl chloride (345 mg, 2.86 mmol) was added followed by Et_3N (289 mg, 2.86 mmol). The milky suspension was stirred at 0 °C for 10 min, and cooled to –78 °C. The solution of the lithio oxazolidinone was transferred by cannula into the above mixed anhydride at –78 °C. The resulting white suspension was stirred at –78 °C for 30 min. The reaction was quenched by the addition of water (30 mL). The mixture was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with satd. $NaHCO_3$ (100 mL), satd. NH_4Cl (100 mL), and satd. NaCl (100 mL); dried over $MgSO_4$; and concentrated. The residue was purified by flash column chromatography (30 % EtOAc in hexane) to give imide **4a** (579 mg, 79 %) as a yellow oil: IR (neat) ν_{max} 3406, 2964, 2976, 2855, 1780, 1702, 1387, 1207,

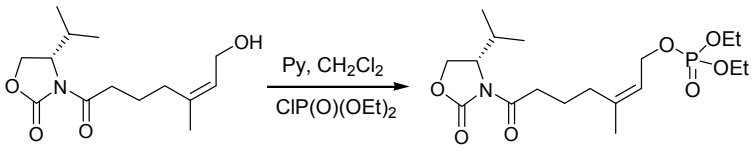
[3] V. Guerlavais, P. J. Carroll, and M. M. Joullié, *Tetrahedron: Asymmetry*, 2002, **13**, 675.

1018 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.88 (d, 3H, J = 7.0 Hz, CH_3), 0.92 (d, 3H, J = 6.8 Hz, CH_3), 1.65 (br s, 1H, -O*H*), 1.75 (q, 3H, J = 1.0 Hz, CH_3), 1.78 (quintet of d, 2H, J = 7.3, 2.0 Hz, CH_2), 2.16 (t, 2H, J = 7.5, CH_2), 2.37 (septet of d, 1H, J = 7.1, 3.9 Hz, CH(CH_3)$_2$), 2.83-2.98 (m, 2H, CH_2CO), 4.11 (dq, 2H, J = 7.2, 0.7 Hz, CH_2OH), 4.21 (ν_B of A<u>B</u>X, J_{BX} = 2.6 Hz, J_{AB} = 9.0 Hz, CH_2O), 4.27 (ν_A of <u>A</u>BX, J_{AX} = 8.7 Hz, J_{AB} = 9.0 Hz, CH_2O), 4.43 (ν_X of AB<u>X</u>, m, C*H*N); 5.50 (t of sextet, 1H, J = 7.2, 0.7 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 127 MHz) 14.8, 18.2, 22.6, 23.5, 28.6, 31.0, 35.1, 58.6, 59.1, 63.6, 125.5, 139.2, 154.4, 173.3; HR-MS (CI): Calcd for $C_{14}H_{22}NO_4$, 268.1545. Found, 268.1549.



3 **4b**

(4*S*)-3-((*Z*)-7-Hydroxy-5-methylhept-5-enoyl)-4-benzyl-2-oxazolidinone (4b). The *N*-acylation procedure described above was followed. Reaction of (4*S*)-benzyl-2-oxazolidinone (448 mg, 2.53 mmol) with mixed anhydride formed *in situ* from acid **3** (400 mg, 2.53 mmol) yielded imide **4b** (562 mg, 70 %) as a light yellow oil: IR (neat) ν_{max} 3406, 2932, 2360, 1780, 1699, 1454, 1388, 1352, 1212, 989, 703 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.68 (br s, 1H, -O*H*), 1.77 (d, 3H, J = 1.3 Hz, CH_3), 1.82 (quintet of d, 2H, J = 7.6, 1.4 Hz, CH_2), 2.19 (t, 2H, J = 7.5, CH_2), 2.76 (dd, 1H, J = 13.4, 9.7 Hz, CH_2Ph), 2.85-3.00 (m, 2H, CH_2CO), 3.31 (dd, 1H, J = 13.4, 3.4 Hz, CH_2Ph), 4.13 (dd, 2H, J = 7.3, 0.7 Hz, CH_2OH), 4.17 (ν_B of A<u>B</u>X, J_{BX} = 3.4 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.21 (ν_A of <u>A</u>BX, J_{AX} = 6.8 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.67 (ν_X of AB<u>X</u>, m, C*H*N); 5.51 (br t, 1H, J = 7.2, vinyl *H*), 7.20-7.37 (m, 5H, aromatic *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 22.4, 23.4, 31.0, 35.1, 38.1, 55.3, 59.1, 66.4, 125.6, 127.6, 129.2, 129.6, 135.4, 139.1, 153.7, 173.3; HR-MS (CI): Calcd for $C_{18}H_{24}NO_4$, 318.1705. Found, 318.1703.



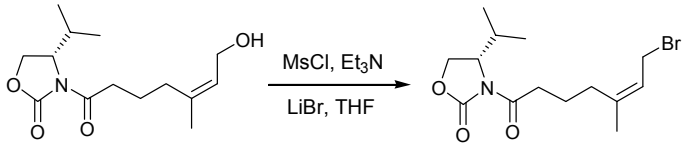
4a

(4*S*)-3-((*Z*)-7-Diethylphosphoryloxy-5-methylhept-5-enoyl)-4-isopropyl-2-oxazolidinone. The procedure reported by Coates was followed.[4] A solution of alcohol **4a** (50 mg, 0.19 mmol) and pyridine (18 mg, 0.22 mmol) in CH_2Cl_2 (1 mL) was stirred and cooled at 0 ^oC, as diethyl chlorophosphate (34 mg, 0.20 mmol) was added dropwise. The solution was stirred at 0 ^oC for 30 min, at which time TLC showed around 50 % conversion. Pyridine (18 mg, 0.22 mmol) was added followed by diethyl chlorophosphate (34 mg, 0.20 mmol). The solution was stirred for additional 10 min at 0 ^oC. TLC showed that all of the alcohol was consumed, and ether (10 mL) was added. The ethereal solution was washed with aq. HCl (1M, 3 x 10 mL), satd. $NaHCO_3$ (3 x 10 mL), and brine (10 mL); dried over anhydrous $MgSO_4$; and concentrated to give the phosphate (70 mg, ~93 %) as a colorless oil: TLC R_f 0.20 (50 % EtOAc in hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.82 (d, 3H, J = 6.8 Hz, CH_3), 0.86 (d, 3H, J = 7.2 Hz, CH_3), 1.28 (td, 6H, J = 7.0, 0.9 Hz, OCH_2CH_3), 1.69-1.72 (m, 2H, CH_2), 1.72 (br s, 3H, CH_3), 2.06-2.17 (m, 2H, CH_2), 2.31 (septet of d, 1H, J = 7.1, 3.9 Hz, C$H(CH_3)_2$), 2.77-2.92 (m, 2H, CH_2CO), 4.04 (quintet, 4 H, J = 7.5 Hz, OCH_2CH_3), 4.14-4.26 (m, 2H, CH_2O), 4.38 (m, 1H, C*H*N); 4.48 (t, 2H, J = 7.8 Hz, CH_2OP), 5.39 (t, 1H, J = 7.1 Hz, vinyl *H*). This compound was used in the enolate cyclization reactions without further purification.

[4] M. M. Ravn, Q. Jin, and R. M. Coates, *Eur. J. Org. Chem.*, 2000, 1401.

4a

(4*S*)-3-((*Z*)-7-Chloro-5-methylhept-5-enoyl)-4-benzyl-2-oxazolidinone. The chloride displacement procedure reported by Meyers was followed.[5] A suspension of LiCl (189 mg, 4.46 mmol), alcohol **4a** (120 mg, 0.45 mmol), and *s*-collidine (541 mg, 4.46 mmol) in DMF (2.5 mL) was stirred and cooled at 0 ^{o}C, as MsCl (154 mg, 1.34 mmol) was added. The suspension was stirred at 0 ^{o}C for 1h. Ice water (10 mL) was added, and the product was extracted with cold ether (3 x 15 mL). The combined organic extracts were washed with satd. $Cu(NO_3)_2$ (3 x 15 mL), satd. NaCl (20 mL), satd. $NaHCO_3$ (20 mL), and satd. NaCl (20 ml); dried over $MgSO_4$; concentrated to give the chloride (130 mg) containing Et_2O (15 % of weight) as a yellow oil: TLC R_f 0.43 (30 % EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (d, 3H, J = 7.0 Hz, CH_3), 0.90 (d, 3H, J = 7.1 Hz, CH_3), 1.76 (br s, 3H, CH_3), 1.73-1.81 (m, 2H, CH_2), 2.11-2.22 (m, 2H, CH_2), 2.35 (septet of d, 1H, J = 7.1, 3.9 Hz, CH(CH_3)$_2$), 2.82-2.99 (m, 2H, CH_2CO), 4.07 (br d, 2H, J = 8.1 Hz, CH_2Cl), 4.19 (ν_B of A<u>B</u>X, J_{BX} = 2.6 Hz, J_{AB} = 9.0 Hz, CH_2O), 4.25 (ν_A of <u>A</u>BX, J_{AX} = 8.2 Hz, J_{AB} = 9.0 Hz, CH_2O), 4.42 (ν_X of AB<u>X</u>, m, CHN); 5.46 (br t, 1H, J = 7.9 Hz, vinyl H). This compound was used in the enolate cyclization reactions without further purification.

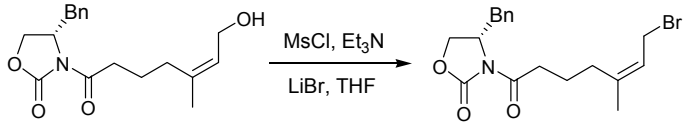


4a

(4*S*)-3-((*Z*)-7-Bromo-5-methylhept-5-enoyl)-4-isopropyl-2-oxazolidinone. The bromide displacement procedure reported by Corey was followed.[6] A solution of alcohol **4a** (69 mg, 0.26 mmol) in THF (1 mL) was stirred and cooled at –45 ^{o}C, as MsCl (44 mg, 0.38 mmol) was added followed by Et_3N (56 mg, 0.59 mmol). A white precipitate was formed immediately during the addition, and the resulting suspension was

[5] A. I. Meyers, and E. W. Collington, *J. Org. Chem*., 1971, **36**, 3044.
[6] E. J. Corey, G. Luo, and L. S. Lin, *J. Am. Chem. Soc.*, 1997, **119**, 9927.

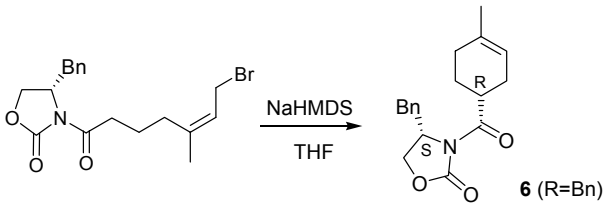
stirred at –45°C for 45 min. A solution of LiBr (102 mg, 1.17 mmol) in THF (1 mL) was added by cannula transfer. The suspension was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction mixture was poured into ice water (10 mL). The organic layer was separated and the aqueous layer was extracted with cold Et_2O (3 x 10 mL). The combined organic solution was washed with satd. $NaHCO_3$ (2 x 30 mL), and brine (30 mL); dried over anhydrous $MgSO_4$; and concentrated to give the bromide (78 mg) as a light yellow oil: TLC R_f 0.40 (30 % EtOAc in hexane); ^1H NMR (C_6D_6, 500 MHz) δ 0.44 (d, 3H, J = 7.0 Hz, CH_3), 0.55 (d, 3H, J = 7.0 Hz, CH_3), 1.49 (br s, 3H, CH_3), 1.66-1.76 (m, 2H, CH_2), 1.92-2.02 (m, 2H, CH_2), 2.15 (septet of d, 1H, J = 6.9, 3.9 Hz, CH(CH_3)$_2$), 2.75-2.96 (m, 2H, CH_2CO), 3.33-3.46 (m, 2H, CH_2O), 3.77-3.84 (m, 2H, CH_2Br), 3.95 (m, 1H, CHN), 5.35 (br t, 1H, J = 8.4 Hz, vinyl H); ^{13}C NMR (C_6D_6, 126 MHz) 14.5, 17.5, 22.6, 23.2, 28.5, 29.1, 30.8, 35.1, 58.2, 62.9, 122.6, 142.4, 154.0, 172.5. The bromide was used in the enolate cyclization reactions without purification.



4b

(4*S*)-3-((*Z*)-7-Bromo-5-methylhept-5-enoyl)-4-benzyl-2-oxazolidinone. The bromide displacement procedure reported by Corey was followed.[6] A solution of alcohol **4b** (150 mg) in THF (5 mL) was stirred and cooled at –45 °C, as MsCl (70 mg, 0.61 mmol) was added followed by Et_3N (90 mg, 0.95 mmol). A white precipitate was formed immediately during the addition (1-2 min), and the resulting suspension was stirred at –45°C for 45 min. A solution of LiBr (164 mg, 1.89 mmol) in THF (3 mL) was added by cannula transfer. The suspension was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction mixture was poured into ice water (5 mL). The organic layer was separated, and aqueous layer was extracted with cold Et_2O (3 x 10 mL). The combined organic solution was washed with satd. $NaHCO_3$ (2 x 30 mL), and brine (30 mL); dried over anhydrous $MgSO_4$; and concentrated to give the bromide (170

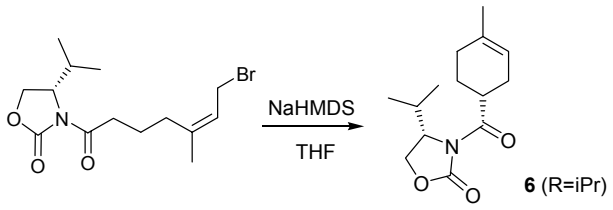
mg) as a light yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.80 (br s, 3H, C*H*$_3$), 1.85 (quintet, 2H, *J* = 8.3 Hz, C*H*$_2$), 2.18-2.30 (m, 2H, C*H*$_2$), 2.78 (dd, 1H, *J* = 13.3, 9.5 Hz, C*H*$_2$Ph), 2.87-3.03 (m, 2H, C*H*$_2$CO), 3.31 (dd, 1H, *J* = 13.3, 3.3 Hz, C*H*$_2$Ph), 4.03 (dd, 2H, *J* = 8.3, 2.0 Hz, C*H*$_2$OH), 4.16 (ν_B of A<u>B</u>X, J_{BX} = 3.6 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.20 (ν_A of <u>A</u>BX, J_{AX} = 7.0 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.68 (ν_X of AB<u>X</u>, m, C*H*N); 5.58 (br t, 1H, *J* = 8.5, vinyl *H*), 7.16-7.35 (m, 5H, aromatic *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) 22.3, 23.6, 29.5, 30.9, 35.2, 38.1, 55.4, 66.5, 122.4, 127.6, 129.2, 129.7, 135.5, 142.8, 153.7, 173.1. The bromide was used in the enolate cyclization reactions without purification.



6 (R=Bn)

(4*S*)-3-((4'*R*)-1'-Methylcyclohexene-4'-carbonyl)-4-benzyl-2-oxazolidinone (6). A solution of the bromide (170 mg, 0.89 mmol) in THF (4.5 mL) was stirred and cooled at –78 ^{o}C, as NaHMDS (1M solution in THF, 447 μL, 0.45 mmol) was added slowly over 15 min. The resulting yellowish solution was stirred at –78 ^{o}C for 1 h. Satd. NH_4Cl (5 mL) was added, and the mixture was warmed to room temperature. The product was extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (15 % EtOAc in hexane) to yield the imide **6** (R=Bn) as a white crystalline solid (89 mg, 67 %). Only one diastereomer was detected by GC analysis (R_t 15.38 min, Program: initial temperature 210 ^{o}C, hold for 5 min, 4 ^{o}C/min until 300 ^{o}C). Physical data for the imide **6**: TLC R_f 0.46 (30 % EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.67 (br s, 3H, C*H*$_3$), 1.73 (dtd, 1H, *J* = 12.6, 11.7, 5.6 Hz, C*H*$_2$), 1.91-1.97 (m, 2H, C*H*$_2$), 2.08-2.14 (m, 1H, C*H*$_2$); 2.21-2.32 (m, 2H, C*H*$_2$); 2.77 (dd, 1H, *J* = 13.3, 9.4 Hz, C*H*$_2$Ph), 3.26 (dd, 1H, *J* = 13.3, 3.3 Hz, C*H*$_2$Ph), 3.67 (dddd, 1H, *J* = 12.5, 10.1, 5.6, 2.8 Hz, C*H*CO); 4.17 (ν_B of A<u>B</u>X, J_{BX} = 3.2 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.18 (ν_A of <u>A</u>BX, J_{AX} = 7.8 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.68 (ν_X

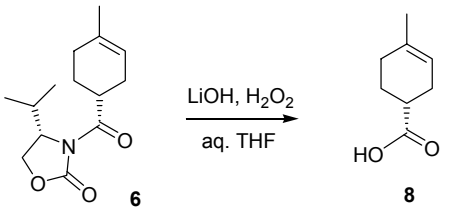
of ABX, m, C*H*N); 5.42 (br s, 1H, vinyl *H*), 7.19-7.34 (m, 5H, aromatic *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) 23.6, 25.9, 27.9, 29.6, 38.1, 38.6, 55.4, 66.2, 119.2, 127.5, 129.1, 129.6, 133.9, 135.5, 153.3, 176.7; $[\alpha]_D^{23}$ +106 ^{o} (*c* 1.25, $CHCl_3$) (lit.[7] $[\alpha]_{589}$ +113^o, *c* 1.63, CH_2Cl_2); m.p. 83-84 ^{o}C (lit. 85.7-86.6 ^{o}C); The S, R enantiomer ***ent*-6** (R=Bn) was also prepared from the enantiomeric oxazolidinone by the same procedure, yield 197 mg (74 %), $[\alpha]_D^{23}$ -113 ^{o} (*c* 1.6, CH_2Cl_2). The ^{1}H and ^{13}C NMR spectra were identical to those of the R, S enantiomer **6**. The physical data are in good agreement with the literature reported by Evans.[7]



6 (R=iPr)

(4*S*)-3-((4'*R*)-1'-Methylcyclohexene-4'-carbonyl)-4-isopropyl-2-oxazolidinone (6). The intramolecular alkylation procedure described above for compound **6** (R=Bn) was followed. Cyclization of the bromide (78 mg, 0.24 mmol) using NaHMDS (1M solution in THF, 258 μL, 0.26 mmol) at –78 ^{o}C for 1 h provided the cyclic product **6** (38 mg, 64 %) as a white crystalline solid: TLC R_f 0.41 (30 % EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (d, 3H, *J* = 7.0 Hz, C*H*$_3$), 0.91 (d, 3H, *J* = 7.0 Hz, C*H*$_3$), 1.65 (br s, 3H, C*H*$_3$), 1.71 (dtd, 1H, *J* = 12.7, 11.6, 5.6 Hz, C*H*$_2$), 1.86-2.00 (m, 2H, C*H*$_2$), 2.04-2.19 (m, 2H, C*H*$_2$); 2.19-2.38 (m, 2H, C*H*$_2$); 3.68 (dddd, 1H, *J* = 11.5, 10.2, 5.2, 2.7 Hz, C*H*CO); 4.19 (ν_B of ABX, J_{BX} = 3.3 Hz, J_{AB} = 9.0 Hz, C*H*$_2$O), 4.27 (ν_A of ABX, J_{AX} = 8.2 Hz, J_{AB} = 9.0 Hz, C*H*$_2$O), 4.45 (ν_X of ABX, m, C*H*N); 5.38 (br s, 1H, vinyl *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) 14.8, 18.1, 23.6, 25.5, 28.4, 28.6, 29.6, 38.7, 58.6, 63.4, 119.2, 134.1, 153.9, 176.7; m.p. 71.5-73.5 ^{o}C (lit.[7] 76.2-77.5 ^{o}C); $[\alpha]_D^{23}$ +118.8 ^{o} (*c* 6.2, $CHCl_3$); HR-MS (ESI): Calcd for $C_{14}H_{22}NO_3$, 252.1600. Found, 252.1600.

[7] D. A. Evans, K. T. Chapman, and J. Bisaha, *J. Am. Chem. Soc.*, 1988, **110**, 1238.
[8] D. A. Evans, T. C. Britton, and J. A. Ellman, *Tetrahedron Lett.*, 1987, **28**, 6141.

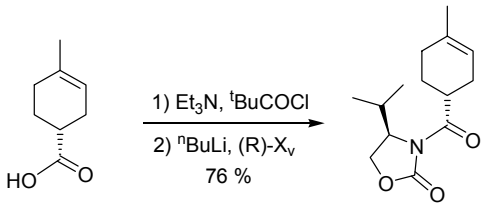


6 **8**

(*R*)-4-Methylcyclohex-3-enecarboxylic Acid (8). The procedure reported by Evans was followed.[8] A solution of imide **6** (62 mg, 0.25 mmol) in THF (3.75 mL) and H_2O (1.25 mL) was stirred and cooled at 0 ^oC, as hydrogen peroxide (30 % in H_2O, 168 μL, 1.48 mmol) was added, followed by LiOH (21 mg, 0.49 mmol). The mixture was allowed to warm to rt and stirred at rt for 18 h. An aqueous solution of Na_2SO_3 (10 %, 10 mL) was added. The solvent was evaporated, and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The aqueous solution was acidified with 3M HCl to pH ~3 and extracted with EtOAc (3 x 10 mL). The combined CH_2Cl_2 extracts were dried over $MgSO_4$ and concentrated to recover the oxazolidinone chiral auxiliary (64 mg, ~ 100 % recovery). The combined ethyl acetate extracts were dried over $MgSO_4$ and concentrated to give acid **8** (31 mg, 90 %) as a white solid: ^1H NMR ($CDCl_3$, 400 MHz) δ 1.66 (d, 3H, *J* = 1.0 Hz, C*H*$_3$), 1.68-1.77 (m, 1H, C*H*$_2$), 2.01-2.08 (m, 3H, C*H*$_2$), 2.23-2.28 (m, 2H, C*H*$_2$), 2.54 (dddd, 1H, *J* = 11.2, 9.0, 6.4, 2.7 Hz, C*H*CO), 5.39 (m, 1H, vinyl *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) 23.7, 25.4, 27.6, 29.3, 39.2, 119.2, 134.1, 182.9; m.p. 92-94 ^oC (lit.[9] 98-98.5 ^oC); $[\alpha]_D^{23}$ +67.9^o (*c* 1.4, $CHCl_3$) (lit.[10] $[\alpha]_D$ –68.6^o, *c* 0.5, $CHCl_3$). The data are in good agreement with the literature data reported by Oppolzer[10] and Wipf.[11]

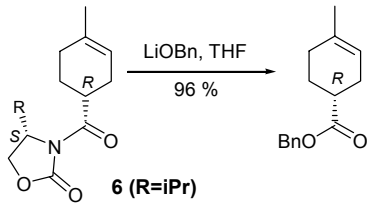
[9] L. Argenti, F. Bellina, A. Carpita, and R. Rossi, *Synth. Commun.*, 1995, **25**, 2909

[10] W. Oppolzer, M. Wills, M. J. Kelly, M. Signer, and J. Blagg, *Tetrahedron Lett.*, 1990, **31**, 5015.
[11] P. Wipf and W.-J. Xu, *Tetrahedron*, 1995, **51**, 4551.

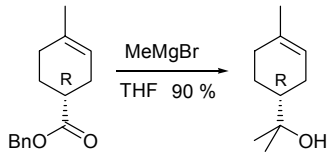


8 ***ent*-7**

(4*R*)-3-((4'*R*)-1'-Methylcyclohexene-4'-carbonyl)-4-isopropyl-2-oxazolidinone (*ent*-7). The *N*-acylation procedure described above for compound **3** was followed. N-Acylation of (4*R*)-4-isopropyl-2-oxazolidinone (18 mg, 0.14 mmol) with the mixed anhydride derived from acid **8** (20 mg, 0.14 mmol) provided (*R*, *R*)-imide ***ent*-7** (27 mg, 76 %) as a white solid: GC R_t 13.69 min for **6** (R=iPr), R_t 13.51 min for ***ent*-7**, Program: initial temperature 175 ^oC, hold for 5 min, 1 ^oC/min until 200 ^oC); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.88 (d, 3H, J = 6.8 Hz, CH_3), 0.91 (d, 3H, J = 7.1 Hz, CH_3), 1.66 (br s, 3H, CH_3), 1.66 (dtd, 1H, J = 12.3, 11.0, 5.2 Hz, CH_2), 1.93-2.21 (m, 4H, CH_2), 2.26-2.39 (m, 2H, CH_2); 3.68 (dddd, 1H, J = 11.0, 10.3, 5.1, 2.7 Hz, C*H*CO); 4.21 (ν_B of A<u>B</u>X, J_{BX} = 2.9 Hz, J_{AB} = 8.9 Hz, CH_2O), 4.27 (ν_A of <u>A</u>BX, J_{AX} = 8.3 Hz, J_{AB} = 8.9 Hz, CH_2O), 4.46 (ν_X of AB<u>X</u>, m, C*H*N); 5.39 (br s, 1H, vinyl *H*); ^1H NMR (C_7D_7, 500 MHz) δ 0.43 (d, 3H, J = 7.0 Hz, CH_3), 0.53 (d, 3H, J = 7.0 Hz, CH_3), 1.55 (br s, 3H, CH_3), 1.59-1.67 (m, 1H, CH_2), 1.76-1.80 (m, 2H, CH_2), 2.03-2.16 (m, 2H, CH_2); 2.50-2.58 (m, 1H, CH_2), 3.25 (ν_B of A<u>B</u>X, J_{BX} = 3.0 Hz, J_{AB} = 9.0 Hz, CH_2O), 3.38 (ν_A of <u>A</u>BX, J_{AX} = 8.7 Hz, J_{AB} = 9.0 Hz, CH_2O), 3.83 (tdd, 1H, J = 10.6, 4.8, 2.6 Hz, C*H*CO), 3.88 (ν_X of AB<u>X</u>, m, C*H*N); 5.36 (br s, 1H, vinyl *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 14.9, 18.1, 23.6, 26.9, 27.0, 28.6, 29.8, 38.6, 58.6, 63.4, 119.4, 133.8, 153.9, 176.6; ^{13}C NMR (C_7D_7, 126 MHz) 15.6, 18.6, 24.6, 28.3, 28.5, 29.6, 31.1, 39.9, 59.2, 63.7, 121.1, 134.5, 154.5, 176.8; $[\alpha]_D^{23}$ -68.4^o (*c* 2.2, $CHCl_3$); HR-MS (EI): Calcd for $C_{14}H_{21}NO_3$, 251.1521. Found, 251.1522.



(*R*)-Benzyl 4-Methylcyclohex-3-enecarboxylate. The procedure reported by Evans was followed.[7] A solution of benzyl alcohol (144 mg, 1.33 mmol) in THF (6 mL) was stirred and cooled at –78 ^{o}C, as ^{n}BuLi (623 μL, 1.00 mmol, 1.6 M in hexane) was added dropwise. The clear solution was stirred at –78 ^{o}C for 30 min. A solution of imide **6** (R=iPr) (167 mg, 0.66 mmol) in THF (1 ml) was added slowly at –78 ^{o}C, and the clear solution was allowed to warm to 0 ^{o}C. After stirring at 0 ^{o}C for 3 h, the reaction was quenched by the addition of satd. NH_4Cl (10 mL). The solvent was evaporated, and the aqueous solution was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated to give the crude product, which was purified by flash column chromatography (10 % EtOAc in hexane) to give the benzyl ester (147 mg, 96 %) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.66 (d, 3H, *J* = 1.3 Hz, C*H*$_3$), 1.71-1.79 (m, 1H, C*H*$_2$), 1.97-2.08 (m, 3H, C*H*$_2$), 2.26-2.29 (m, 2H, C*H*$_2$); 2.53-2.60 (m, 1H, C*H*CO); 5.15 (s, 2H, C*H*$_2$Ph), 5.39 (br s, 1H, vinyl *H*), 7.31-7.41 (m, 5H, aromatic *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) 23.7, 25.7, 27.8, 29.4, 39.4, 66.2, 119.4, 128.2, 128.3, 128.7, 133.9, 136.4, 176.0; $[\alpha]_D^{23}$ +60.7^{o} (*c* 2.5, CH_2Cl_2) (lit.[7] $[\alpha]_{589}$ +62.9^{o}, *c* 2.1, CH_2Cl_2); The S enantiomer was also prepared from the enantiomeric oxazolidinone ***ent*-6** (R=Bn) by the same procedure, yield 65 mg (94 %), $[\alpha]_D^{23}$ -59.7^{o} (*c* 6.0, CH_2Cl_2). The ^{1}H, and ^{13}C NMR spectra were identical to those of the R enantiomer. The data are in good agreement with the reported data by Evans.[7]

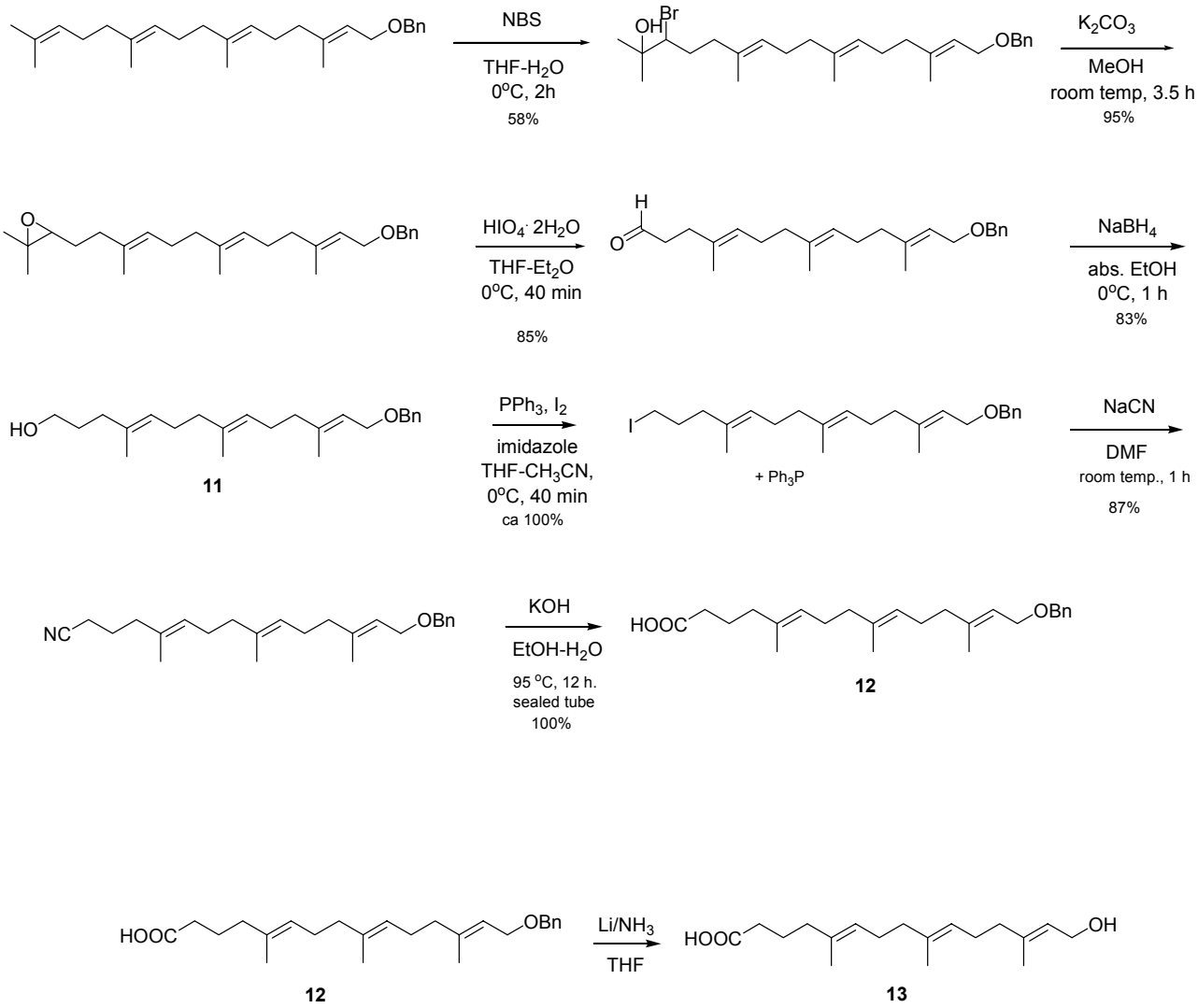


9

(+)-α-Terpineol (9). The procedure reported by Crimmins for a different compound was followed.[12] A solution of MeMgBr (3.0 M in THF, 1.74 mL, 5.21 mmol) in THF (3 mL) was stirred and cooled at 0 ^{o}C, as a solution of the benzyl ester (80 mg, 0.35 mmol) in THF (3 mL) was added slowly. The white suspension was stirred at 0 ^{o}C for 1 h and warmed to rt. The suspension turned to a colorless solution that was stirred at rt for 12 h. The reaction mixture was cooled to 0 ^{o}C, and satd. NH_4Cl (5mL) was added. The solvent was evaporated and the aqueous solution was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated. Purification of the residue by flash column chromatography (30 % EtOAc in hexane, 1 % Et_3N) yielded (+)-α-terpineol **9** (48 mg, 90 %) as a colorless oil: ^{1}H NMR (C_6D_6, 400 MHz) δ 1.01 (s, 3H, C*H*$_3$), 1.02 (s, 3H, C*H*$_3$), 1.17 (qd, 1H, *J* = 12.0, 5.6 Hz, C*H*$_2$), 1.38 (dddd, 1H, J = 12.4, 11.2, 4.9, 2.4 Hz, C*H*), 1.64 (br s, 3H, C*H*$_3$), 1.70-2.03 (m, 5H, C*H*$_2$), 5.41 (br s, 1H, vinyl *H*); ^{13}C NMR (C_6D_6, 100 MHz) 24.0, 24.6, 26.8, 27.6, 28.0, 31.7, 45.6, 72.2, 121.7, 133.9; $[\alpha]_D^{23}$ +93.3^{o} (c 2.2, $CHCl_3$) (lit.[7] $[\alpha]_{589}$ +94.1, neat; lit[13] $[\alpha]_D^{22}$ +101, *c* 0.1 $CHCl_3$). (-)-α-Terpineol (**ent-9**) was also prepared from the enantiomeric benzyl ester by the same procedure, yield 31 mg (86 %), $[\alpha]_D^{23}$ -96.4^{o} (c 3.1, $CHCl_3$). The ^{1}H, and ^{13}C NMR spectra were identical to those of (+)-α-terpineol. The data showed good agreement with the literature reports by Evans[7] and Piovetti.[13]

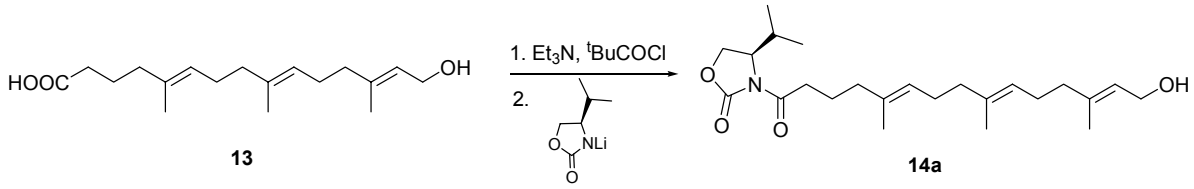
[12] M. T. Crimmins, and B. H. Brown, *J. Am. Chem. Soc.,* 2004, **126**, 10264.
[13] L. Piovetti, G. Combaut, and A. Diara, *Phytochemistry*, 1980, **19**, 2117.

Synthesis of Benzyl Ether Acid 12 from (*E*,*E*,*E*)-Geranylgeranyl Benzyl Ether



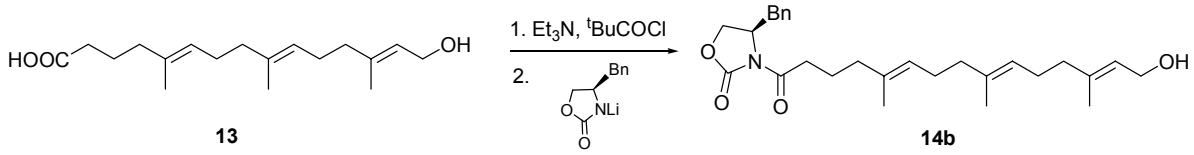
(5*E*,9*E*,13*E*)-15-Hydroxy-5,9,13-trimethylpentadeca-5,9,13-trienoic Acid (13). The procedure for the lithium-ammonia reduction described above for compound **2** was followed. A solution of benzyl ether **12** (2.82 g, 7.33 mmol) in THF (150 mL) was reduced with Li (509 mg, 73.3 mmol) in liquid NH_3 (150 mL) at –78 °C for 30 min to provide alcohol **13** (2.16 g, 100 %) as a light yellow oil: IR (neat) ν_{max} 3346, 2919, 2652, 1709, 1442, 1384, 1239, 993, 841 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.59 (s, 3H, C*H*$_3$), 1.60 (s, 3H, C*H*$_3$), 1.68 (br s, 3H, C*H*$_3$), 1.73 (quintet, 2H, *J* = 7.3 Hz, C*H*$_2$), 1.98-2.12 (m, 10H, C*H*$_2$), 2.30 (t, 2H, *J* = 7.6 Hz, C*H*$_2$COOH), 4.16 (d, 2H, *J* = 6.9 Hz, C*H*$_2$OH), 5.13 (br t, 2H, *J* = 7.0 Hz, vinyl *H*), 5.41 (t of sextet, 1H, *J* = 7.0, 1.0 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) 15.9, 16.1, 16.4, 22.9, 26.4, 26.6, 33.5,

39.0, 39.7, 59.5, 123.3, 124.2, 125.5, 133.9, 135.3, 140.0, 179.6; HR-MS (CI): Calcd for $C_{18}H_{29}O_3$, 293.2111. Found, 293.2116.



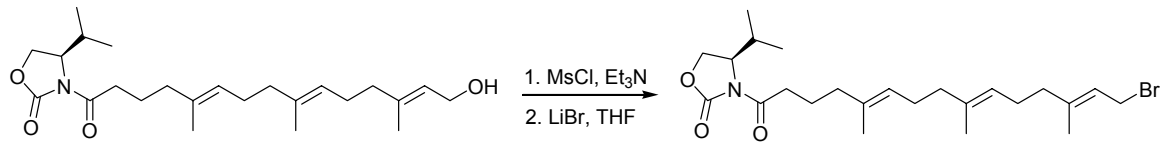
13 **14a**

(4*R*)-3-((5*E*,9*E*,13*E*)-15-Hydroxy-5,9,13-trimethylpentadeca-5,9,13-trienoyl)-4-isopropyl-2-oxazolidinone (14a). The N-acylation procedure described above for compound **3** was followed. A solution of (*R*)-4-isopropyl-2-oxazolidinone (132 mg, 1.02 mmol) in THF (4 mL) was stirred and cooled at –78 ^{o}C, as *n*BuLi (638 μL, 1.02 mmol, 1.6 M in hexane) was added dropwise. The clear solution was stirred at –78 ^{o}C for 30 min. In a separate flask, a solution of acid **13** (300 mg, 1.02 mmol) in THF (5 mL) was stirred and cooled at 0 ^{o}C, as pivaloyl chloride (129 mg, 1.07 mmol) was added followed by Et_3N (108 mg, 1.07 mmol). The milky suspension was stirred at 0 ^{o}C for 10 min, and cooled to –78 ^{o}C. The solution of the lithio oxazolidinone was transferred by cannula into the above mixed anhydride at –78 ^{o}C. The resulting white suspension was stirred at –78 ^{o}C for 30 min. After workup and purification as described previously, (*R*)-carboximide **14a** was obtained as a light yellow oil (316 mg, 77 %): IR (neat) ν_{max} 3406, 2963, 2927, 1784, 1703, 1386, 1206, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (d, 3H, *J* = 7.1 Hz, CH_3), 0.92 (d, 3H, *J* = 7.1 Hz, CH_3), 1.60 (br s, 6H, CH_3), 1.69 (br s, 3H, CH_3), 1.74-1.80 (m, 2H, CH_2), 1.97-2.13 (m, 10H, CH_2), 2.38 (septet of d, 1H, *J* = 7.0, 3.9 Hz, CH(CH_3)$_2$), 2.89 (m, 2H, AB system, CH_2CO), 4.16 (d, 2H, *J* = 6.8 Hz, CH_2OH), 4.21 (ν_B of A<u>B</u>X, J_{BX} = 3.2 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.27 (ν_A of <u>A</u>BX, J_{AX} = 8.2 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.43 (ν_X of AB<u>X</u>, m, CHN); 5.11 (t of sextet, 1H, *J* = 6.8, 1.0 Hz, vinyl *H*), 5.13 (t of sextet, 1H, *J* = 6.9, 1.0 Hz, vinyl *H*), 5.42 (t of sextet, 1H, *J* = 6.8, 1.2 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 14.9, 16.0, 16.2, 16.5, 18.2, 22.9, 26.5, 26.8, 28.6, 35.2, 39.1, 39.7, 39.8, 58.6, 59.6, 63.5, 123.6, 124.0, 125.3, 134.3, 135.5, 140.0, 154.3, 173.6; HR-MS (ESI): [M+H] Calcd for $C_{24}H_{40}NO_4$, 406.2957. Found, 406.2959.



13 14b

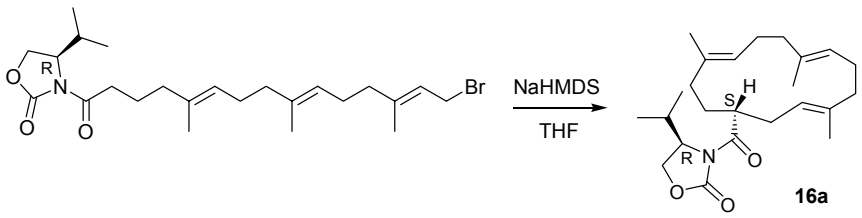
(4*R*)-3-((5*E*,9*E*,13*E*)-15-Hydroxy-5,9,13-trimethylpentadeca-5,9,13-trienoyl)-4-benzyl-2-oxazolidinone (14b). The N-acylation procedure described above for compound **3** was followed. The amounts and volumes were as follows: hydroxy acid **13** (300 mg, 1.02 mmol), pivaloyl chloride (129 mg, 1.07 mmol), Et_3N (108 mg, 1.07 mmol), THF (15 mL); (*R*)-4-benzyl-2-oxazolidinone (181 mg, 1.02 mmol), *n*BuLi (638 μL, 1.02 mmol), THF (10 mL). The reaction afforded 369 mg (80 %) of carboximide **14b** as a light yellow oil: TLC R_f 0.57 (50 % EtOAc in hexane); IR (neat) ν_{max} 3396, 2918, 2857, 1784, 1701, 1386, 1212, 999, 703 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.59 (br s, 3H, C*H*$_3$), 1.61 (br s, 3H, C*H*$_3$), 1.67 (br s, 3H, C*H*$_3$), 1.75-1.82 (m, 2H, C*H*$_2$), 1.97-2.13 (m, 10H, C*H*$_2$), 2.75 (dd, 1H, *J* = 13.1, 9.8 Hz, C*H*$_2$Ph), 2.89 (m, 2H, AB system, C*H*$_2$CO), 3.28 (dd, 1H, *J* = 13.1, 3.1 Hz, C*H*$_2$Ph), 4.13 (d, 2H, *J* = 6.7 Hz, C*H*$_2$OH), 4.14 (ν_B of A<u>B</u>X, J_{BX} = 3.2 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.18 (ν_A of <u>A</u>BX, J_{AX} = 7.6 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.66 (ν_X of AB<u>X</u>, m, C*H*N); 5.11 (t of sextet, 1H, *J* = 6.8, 1.2 Hz, vinyl *H*), 5.14 (t of sextet, 1H, *J* = 6.8, 1.2 Hz, vinyl *H*), 5.40 (t of sextet, 1H, *J* = 6.8, 1.2 Hz, vinyl *H*), 7.19-7.34 (m, 5H, aromatic *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 15.9, 16.1, 16.4, 22.6, 26.4, 26.7, 35.0, 38.0, 39.0, 39.6, 39.7, 55.2, 59.4, 66.3, 123.6, 124.0, 125.2, 127.5, 129.1, 129.6, 134.2, 135.36, 135.44, 139.6, 153.6, 173.6; HR-MS (EI): Calcd for $C_{28}H_{39}NO_4$, 453.2879. Found, 453.2880.



14a

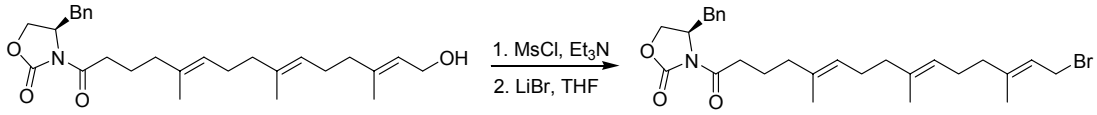
(4*R*)-3-((5*E*,9*E*,13*E*)-15-Bromo-5,9,13-trimethylpentadeca-5,9,13-trienoyl)-4-isopropyl-2-oxazolidinone. The procedure for the preparation of the allylic bromides described above on pp. 7-8 was followed. Reaction of alcohol **14a** (40 mg, 0.10 mmol) with MsCl (15 mg, 0.13 mmol) and Et_3N (19 mg, 0.20 mmol) in THF (2 mL), followed by displacement with LiBr (34 mg, 0.39 mmol) in THF (2 mL) gave

the bromide (47 mg). The bromide product was used directly in the following step without further purification. NMR data for the bromide follow: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85 (d, 3H, J = 7.1 Hz, CH_3), 0.89 (d, 3H, J = 7.1 Hz, CH_3), 1.57 (br s, 6H, CH_3), 1.70 (br s, 3H, CH_3), 1.66-1.76 (m, 2H, CH_2), 1.93-2.12 (m, 10H, CH_2), 2.35 (septet of d, 1H, J = 7.1, 3.9 Hz, CH(CH_3)$_2$), 2.85 (m, 2H, AB system, CH_2CO), 4.00 (d, 2H, J = 8.7 Hz, CH_2OH), 4.17 (ν_B of A<u>B</u>X, J_{BX} = 4.8 Hz, J_{AB} = 9.0 Hz, CH_2O), 4.24 (ν_A of <u>A</u>BX, J_{AX} = 9.9 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.41 (ν_X of AB<u>X</u>, m, CHN); 5.06 (t of sextet, 1H, J = 6.8, 1.2 Hz, vinyl H), 5.10 (t of sextet, 1H, J = 6.8, 1.2 Hz, vinyl H), 5.50 (t of sextet, 1H, J = 8.4, 1.3 Hz, vinyl H); ^{13}C NMR ($CDCl_3$, 126 MHz) 14.8, 15.9, 16.08, 16.16, 18.1, 22.8, 26.2, 26.7, 28.5, 29.9, 35.0, 39.0, 39.6, 39.7, 58.4, 63.4, 120.6, 123.5, 125.2, 134.2, 135.6, 143.7, 154.1, 173.4.

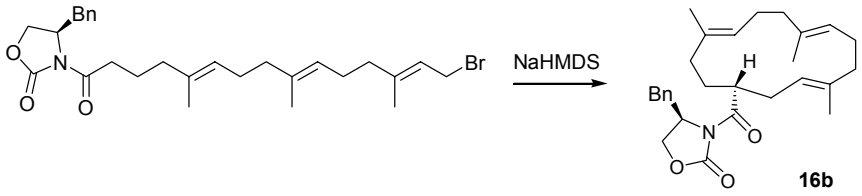


(4*R*)-3-((*S*,3*E*,7*E*,11*E*)- and (4*S*)-3-((*R*,3*E*,7*E*,11*E*)-4,8,12-Trimethylcyclotetradeca-3,7,11-trienecarbonyl)-4-isopropyl-2-oxazolidinones (16a and *ent*-16a). A solution of the preceding bromide (403 mg, 0.86 mmol) in THF (10 mL) was stirred and cooled at –78 ^{o}C as NaHMDS (1.0 M solution in THF, 559 μL) was added slowly over 10 min. The clear yellow solution was stirred at –78 ^{o}C for 30 min and was allowed to warm to rt. After stirring for 40 min at rt, the reaction was quenched by addition of satd. NH_4Cl (5 mL). The mixture was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated to give the crude product as a yellow oil (232 mg). The residue was purified by flash column chromatography (15 % EtOAc in hexane) to yield the cyclic product **16a** (106 mg, 49 %) as a colorless oil: TLC R_f 0.48 (30 % EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (d, 3H, J = 7.0 Hz, CH_3), 0.92 (d, 3H, J = 7.0 Hz, CH_3), 1.54 (br s, 3H, CH_3), 1.60 (br s, 6H, CH_3), 1.57-1.73 (m, 1H, CH_2), 1.88-2.39 (m, 14H, CH_2, CH(CH_3)$_2$), 3.70 (tt, 1H, J = 9.4, 3.2 Hz, CHCO), 4.20 (ν_B of A<u>B</u>X, J_{BX} = 3.2 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.26 (ν_A of <u>A</u>BX, J_{AX} = 8.3 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.47 (ν_X

of ABX, m, C*H*N); 4.99 (br t, 1H, *J* = 6.2 Hz, vinyl *H*), 5.07 (br t, 1H, *J* = 5.7 Hz, vinyl *H*), 5.19 (br t, 1H, *J* = 7.6 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 14.9, 15.4, 16.1, 18.1, 18.2, 23.8, 24.9, 26.6, 28.7, 31.3, 34.9, 39.0, 39.6, 42.9, 58.6, 63.3, 121.9, 122.4, 126.2, 133.6, 133.9, 136.7, 153.7, 176.7; $[\alpha]_D^{23}$ -57.8^o (*c* 2.6, $CHCl_3$); HR-MS (EI): Calcd for $C_{24}H_{37}NO_3$, 387.2773. Found, 387.2769; The R, S enantiomer ***ent*-16a** was also prepared from the enantiomeric oxazolidinone by the same procedure, yield 106 mg (49 %), $[\alpha]_D^{23}$ +53.7^o (*c* 4.0, $CHCl_3$). The ^{1}H and ^{13}C NMR spectra were identical to those of the S, R enantiomer.

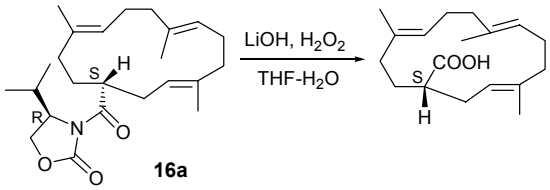


(4*R*)-3-((5*E*,9*E*,13*E*)-15-Bromo-5,9,13-trimethylpentadeca-5,9,13-trienoyl)-4-benzyl-2-oxazolidinone. The procedure for the preparation of allylic bromides described above on pp.7-8 was followed. Reaction of the alcohol (232 mg, 0.10 mmol) with MsCl (82 mg, 0.72 mmol) and Et_3N (105 mg, 1.10 mmol) in THF (10 mL), followed by displacement with LiBr (191 mg, 2.20 mmol) in THF (10 mL) gave the bromide (286 mg). The bromide product was used directly in the following step without purification.



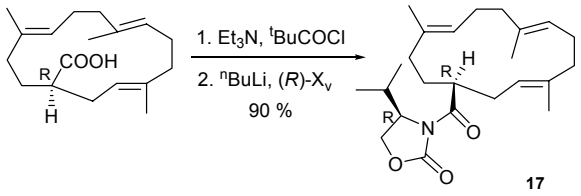
(4*R*)-3-((*S*,3*E*,7*E*,11*E*)-4,8,12-Trimethylcyclotetradeca-3,7,11-trienecarbonyl)-4-benzyl-2-oxazolidinone. A solution of the preceding bromide (166 mg, 0.32 mmol) in THF (3.2 mL) was stirred and cooled at –78 ^{o}C, as LiHMDS (1.0 M solution in THF, 321 μL) was added slowly over 10 min. The yellow solution was stirred at –78 ^{o}C for 20 min and was allowed to warm to rt. After stirring for 10 min at rt, the reaction was quenched by addition of satd. NH_4Cl (5 mL). The mixture was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated to give the

crude product as a yellow oil (153 mg). The residue was purified by flash column chromatography (15 % EtOAc in hexane) to yield the cyclic product **16b** (64 mg, 46 %) as a colorless oil: TLC R_f 0.48 (30 % EtOAc in hexane); IR (neat) ν_{max} 2924, 2855, 1784, 1699, 1385, 1210, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 01.56 (s, 3H, CH_3), 1.61 (br s, 3H, CH_3), 1.62 (br s, 6H, CH_3), 1.64-1.70 (m, 1H, CH_2), 1.73-1.79 (m, 1H, CH_2), 1.91-2.39 (m, 12H, CH_2), 2.78 (dd, 1H, J = 13.4, 9.5 Hz, CH_2Ph), 3.27 (dd, 1H, J = 13.4, 3.2 Hz, CH_2Ph), 3.68 (tt, 1H, J = 9.4, 3.4 Hz, C*H*CO), 4.18 (ν_B of A<u>B</u>X, J_{BX} = 2.8 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.21 (ν_A of <u>A</u>BX, J_{AX} = 7.3 Hz, J_{AB} = 9.1 Hz, CH_2O), 4.71 (ν_X of AB<u>X</u>, m, C*H*N); 5.00 (br t, 1H, J = 6.0 Hz, vinyl *H*), 5.08 (br t, 1H, J = 5.7 Hz, vinyl *H*), 5.21 (br t, 1H, J = 7.5 Hz, vinyl *H*), 7.22-7.36 (m, 5H, aromatic *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 15.4, 16.0, 18.2, 23.8, 25.0, 27.0, 30.7, 34.9, 38.2, 39.1, 39.6, 42.9, 55.6, 66.2, 121.9, 122.6, 126.2, 127.6, 129.2, 129.7, 133.6, 133.9, 135.6, 136.8, 153.1, 176.8; $[\alpha]_D^{23}$ -48.6° (*c* 0.7, $CHCl_3$); HR-MS (EI): Calcd for $C_{28}H_{37}NO_3$, 435.2773. Found, 435.2771.



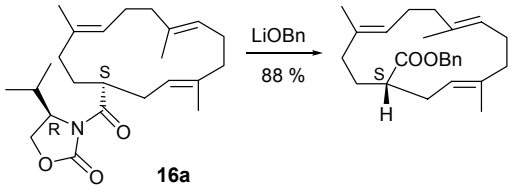
(*S*,3*E*,7*E*,11*E*)- and (*R*,3*E*,7*E*,11*E*)-4,8,12-Trimethylcyclotetradeca-3,7,11-trienecarboxylic Acids (Bisnor-cembrenoic Acids). The hydrolysis procedure described above for the preparation of compound **8** was followed. Hydrolysis of (*S*, *R*)-imide **16a** (82 mg, 0.21 mmol) with LiOH (18 mg, 0.42 mmol), 50 % aq. H_2O_2 (87 mg, 1.27 mmol) in THF (3.1 mL), and H_2O (1.0 mL) provided the acid (38 mg, 65 %) as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz); 1.60 (br s, 9H, 3CH_3), 1.68-2.42 (m, 15H), 4.96 (br t, 1H, J = 6.0 Hz, vinyl *H*), 5.03 (br t, 1H, J = 6.0 Hz, vinyl *H*), 5.15 (br t, 1H, J = 7.4 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 15.5, 15.8, 18.0, 23.9, 24.9, 27.7, 30.0, 34.7, 39.0, 39.5, 44.2, 122.2, 122.6, 126.1, 133.4, 133.7, 136.8, 183.5; The R enantiomer was also prepared from the enantiomeric oxazolidinone by

the same procedure, yield 42 mg (37 %), $[\alpha]_D^{23}$ +19.8° (*c* 4.2, $CHCl_3$); HR-MS (ESI): Calcd for $C_{18}H_{29}O_2$, 277.2168. Found, 277.2167. The ^1H and ^{13}C NMR spectra were identical to those of the S enantiomer.



17

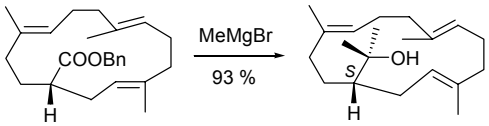
(4*R*)-3-((*R*,3*E*,7*E*,11*E*)-4,8,12-trimethylcyclotetradeca-3,7,11-trienecarbonyl)-4-benzyl-2-oxazolidinone (17). The N-acylation procedure described above for compound **3** was followed. The amounts and volumes of the reagents were as follows: the R acid (8 mg, 0.03 mmol), pivaloyl chloride (4 mg, 0.03 mmol), Et_3N (3 mg, 0.03 mmol), THF (1 mL); (*R*)-4-benzyl-2-oxazolidinone (4 mg, 0.03 mmol), *n*BuLi (18 μL, 0.03 mmol, 1.6 M solution in hexane), THF (1 mL). The reaction afforded 10 mg (90 %) of (*R*,*R*)-carboximide **17**: ^1H NMR ($CDCl_3$, 500 MHz) δ 0.89 (d, 3H, *J* = 6.9 Hz, C*H*$_3$), 0.93 (d, 3H, *J* = 6.9 Hz, C*H*$_3$), 1.56 (s, 3H, C*H*$_3$), 1.59 (s, 3H, C*H*$_3$), 1.60 (s, 3H, C*H*$_3$), 1.59-1.72 (m, 1H, C*H*$_2$), 1.77-1.83 (m, 1H, C*H*$_2$), 1.83-1.92 (m, 1H, C*H*$_2$), 2.02-2.30 (m, 11H, C*H*$_2$), 2.38 (septet of d, 1H, *J* = 7.0, 3.9 Hz, CH(CH$_3$)$_2$), 3.80 (tt, 1H, *J* = 8.6, 4.3 Hz, C*H*CO), 4.19 (ν_B of A<u>B</u>X, J_{BX} = 3.3 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.27 (ν_A of <u>A</u>BX, J_{AX} = 8.5 Hz, J_{AB} = 9.1 Hz, C*H*$_2$O), 4.49 (ν_X of AB<u>X</u>, m, C*H*N); 4.97 (br t, 1H, *J* = 5.8 Hz, vinyl *H*), 5.07 (br t, 1H, *J* = 6.1 Hz, vinyl *H*), 5.15 (br t, 1H, *J* = 7.5 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 14.8, 15.4, 15.9, 17.9, 18.2, 23.9, 25.0, 28.2, 28.5, 29.8, 34.8, 39.0, 39.7, 42.5, 58.7, 63.1, 122.2, 123.1, 126.2, 133.6, 133.8, 136.6, 153.8, 176.9; $[\alpha]_D^{23}$ -45.5° (*c* 0.8, $CHCl_3$).



16a

(*S*,3*E*,7*E*,11*E*)- and (*R*,3*E*,7*E*,11*E*)-Benzyl 4,8,12-Trimethylcyclotetradeca-3,7,11-trienecarboxylates. The transesterification procedure described above on p. 12 was followed. The amounts and volumes of the reagents were as follows: (*S*, *R*)-oxazolidinone **16a** (36 mg, 0.093 mmol), benzyl alcohol

(20 mg, 0.19 mmol), nBuLi (87 μL, 0.14 mmol, 1.6 M in hexane), and THF (1.5 mL). The yield was 30 mg (88 %) of the S benzyl ester: ^{1}H NMR ($CDCl_3$, 500 MHz) 1.56 (s, 3H, C*H*$_3$), 1.59 (s, 6H, C*H*$_3$), 1.74-1.79 (m, 3H, C*H*$_2$), 1.99-2.36 (m, 11H, C*H*$_2$), 2.40-2.45 (m, 1H, C*H*CO), 4.95 (br t, 1H, *J* = 5.9 Hz, vinyl *H*), 5.03 (br t, 1H, *J* = 6.0 Hz, vinyl *H*), 5.13 (br t, 1H, *J* = 6.8 Hz, vinyl *H*); 5.15 (d, 2H, *J* = 2.4 Hz, C*H*$_2$Ph), 7.31-7.39 (m, 5H, aromatic *H*); ^{13}C NMR ($CDCl_3$, 126 MHz) 15.5, 15.9, 18.1, 23.9, 24.9, 27.9, 30.2, 34.7, 39.0, 39.5, 44.4, 66.2, 122.3, 122.4, 126.1, 128.2, 128.3, 128.7, 133.5, 133.7, 136.5, 136.6, 176.6; LR-MS (EI): m/z 366.2; HR-MS (EI): Calcd for $C_{25}H_{34}O_2$, 366.2561. Found, 366.2559; $[\alpha]_D^{23}$ -21.1^o (*c* 1.05, $CHCl_3$); The R enantiomer was also prepared from the enantiomeric oxazolidinone by the same procedure, yield 20 mg (71 %), $[\alpha]_D^{23}$ +18.8^o (*c* 1.6, $CHCl_3$). The ^{1}H and ^{13}C NMR spectra were identical to those of the S enantiomer.

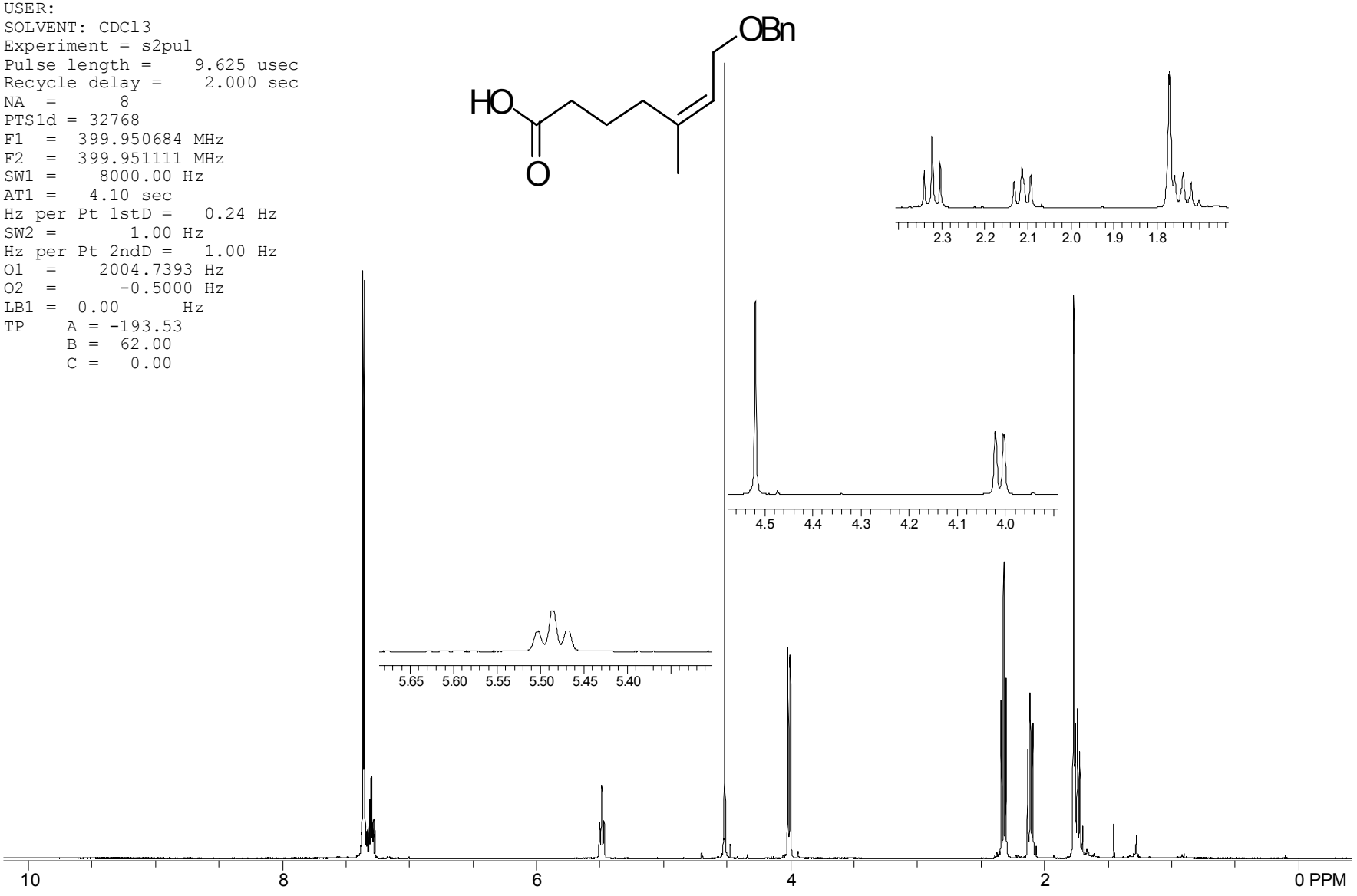


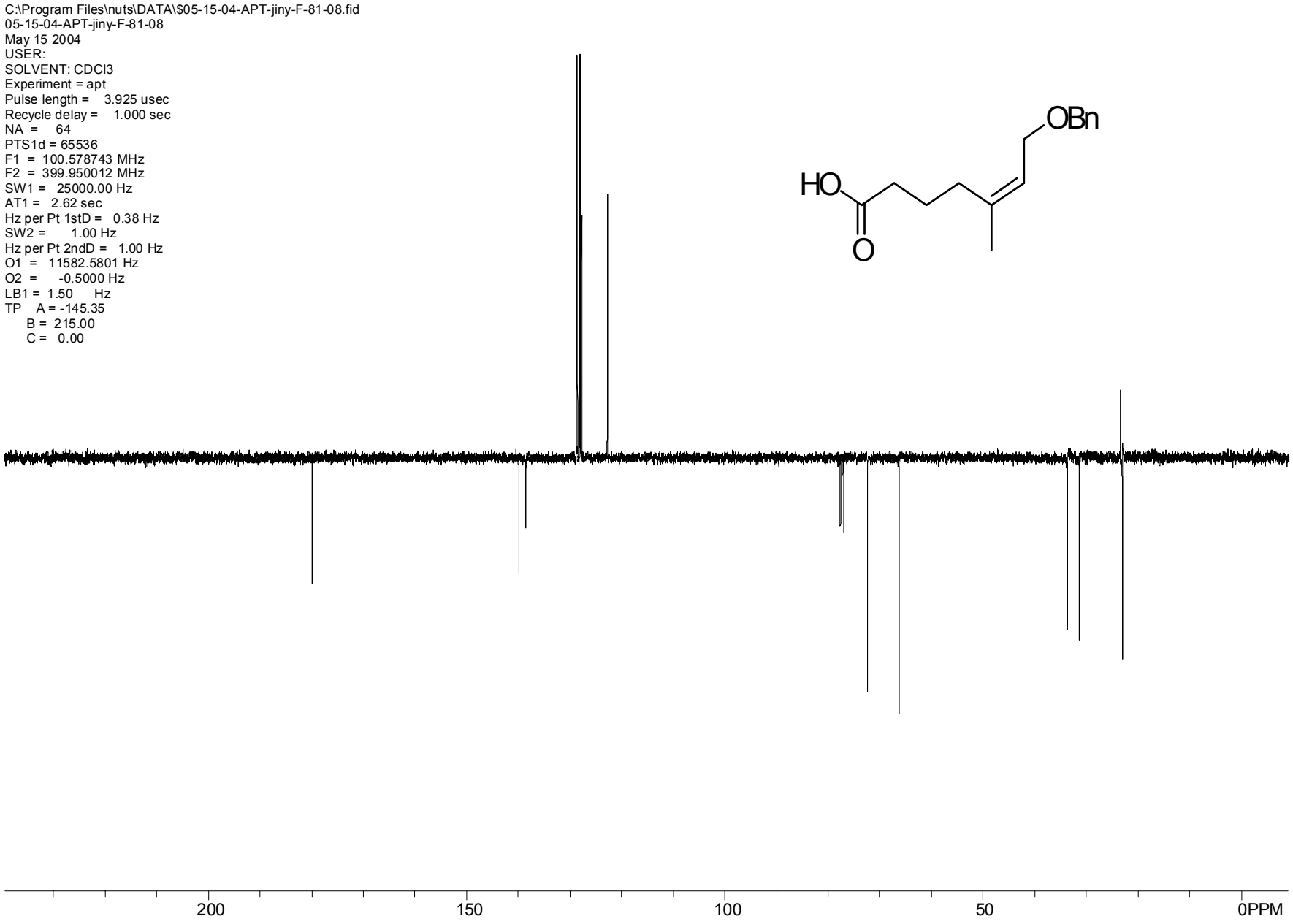
18

(+)- and (-)-Nephthenol (18 and ***ent*-18).** The procedure for addition of methylmagnesium bromide described above for the preparation of compound **9** was followed. Reaction of the S benzyl ester (18 mg, 0.049 mmol) with MeMgBr (3.0 M in THF, 245 μL) in THF (1 mL) provided (+)-nephthenol (**18**) (13 mg, 93 %) as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) 1.21 (s, 6H, C*H*$_3$), 1.23-1.36 (m, 3H, C*H*$_2$), 1.57 (s, 3H, C*H*$_3$), 1.58 (br s, 6H, C*H*$_3$), 1.62-1.70 (m, 1H, C*H*$_2$), 1.90 (ddd, 1H, J = 15.2, 8.1, 7.1 Hz), 1.99-2.23 (m, 11H, C*H*$_2$), 4.95 (br t, 1H, *J* = 5.8 Hz, vinyl *H*), 5.01 (br t, 1H, *J* = 6.8 Hz, vinyl *H*), 5.12 (br t, 1H, *J* = 7.1 Hz, vinyl *H*); ^{13}C NMR ($CDCl_3$, 100 MHz) 15.5, 15.8, 24.2, 24.9, 27.7, 27.9, 28.5, 28.6, 37.9, 39.0, 39.6, 48.6, 74.2, 125.2, 126.0, 126.2, 133.3, 133.6, 134.3; $[\alpha]_D^{23}$ +48^o (*c* 1.24, $CHCl_3$); for ***ent*-18**, lit.[14] $[\alpha]_{589}$ -43.0^o (*c* 0.72, $CHCl_3$); for **18,** lit.[15] $[\alpha]_{589}$ +25.3^o (*c* 2.1, $CHCl_3$). The NMR data agree with the literature report by Pfander.[14] The R enantiomer ***ent*-18** was also prepared from the enantiomeric benzyl

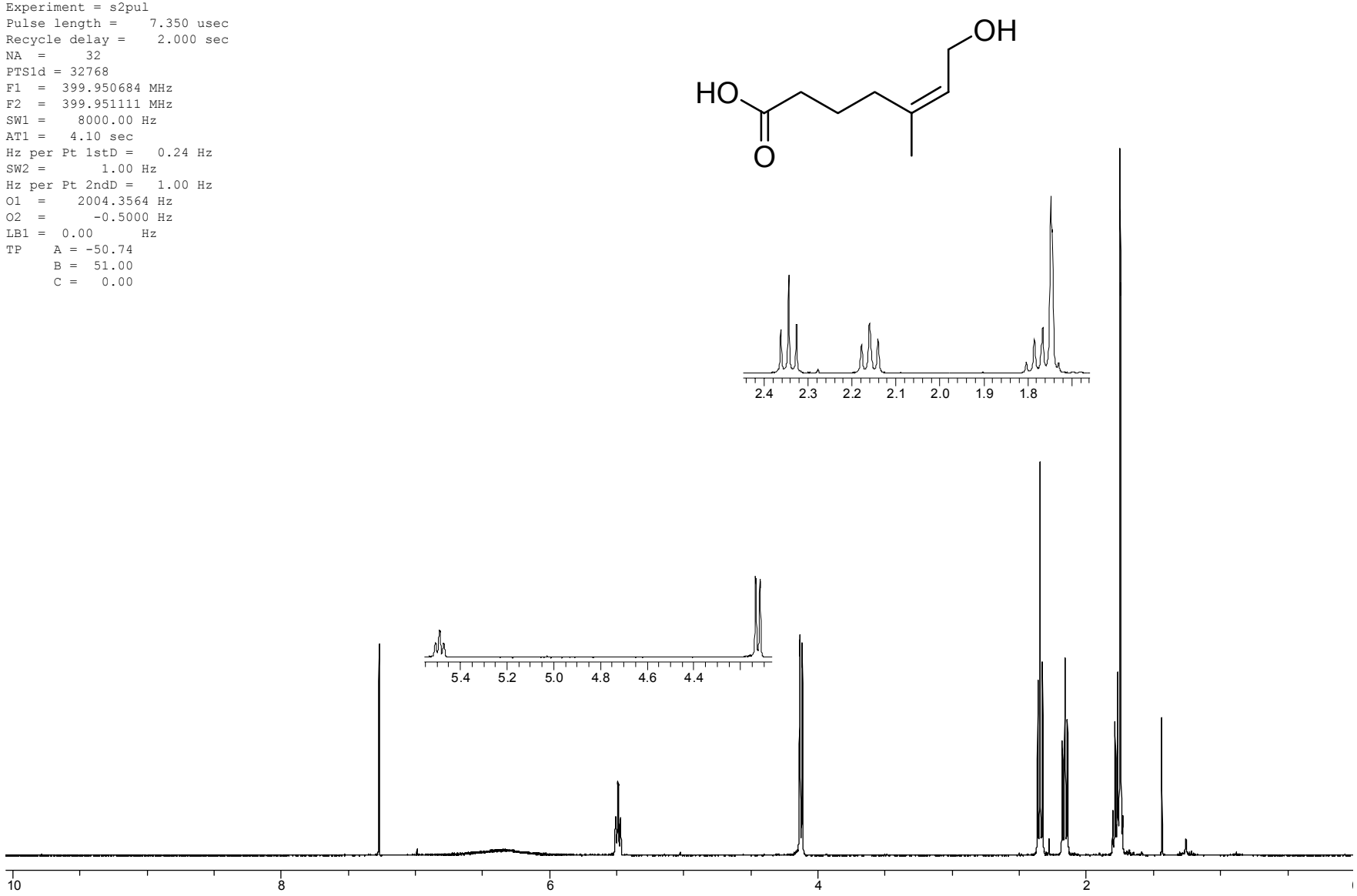
[14] I. Farkas, and H. Pfander, *Helv. Chem. Acta*, 1990, **73**, 1980.
[15] Y.-P. Shi, A. D. Rodríguez, and O. L. Padilla, *J. Nat. Prod.*, 2001, **64**, 1439.

ester by the same procedure, yield 12 mg (92 %), $[\alpha]_D^{23}$ -46.3^o (*c* 1.20, $CHCl_3$). The ^1H and ^{13}C NMR spectra were identical to those of the S enantiomer.

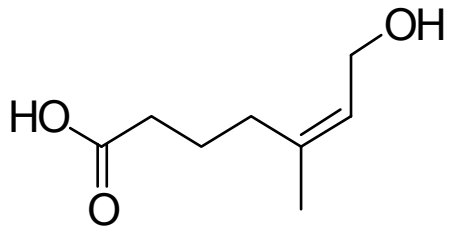


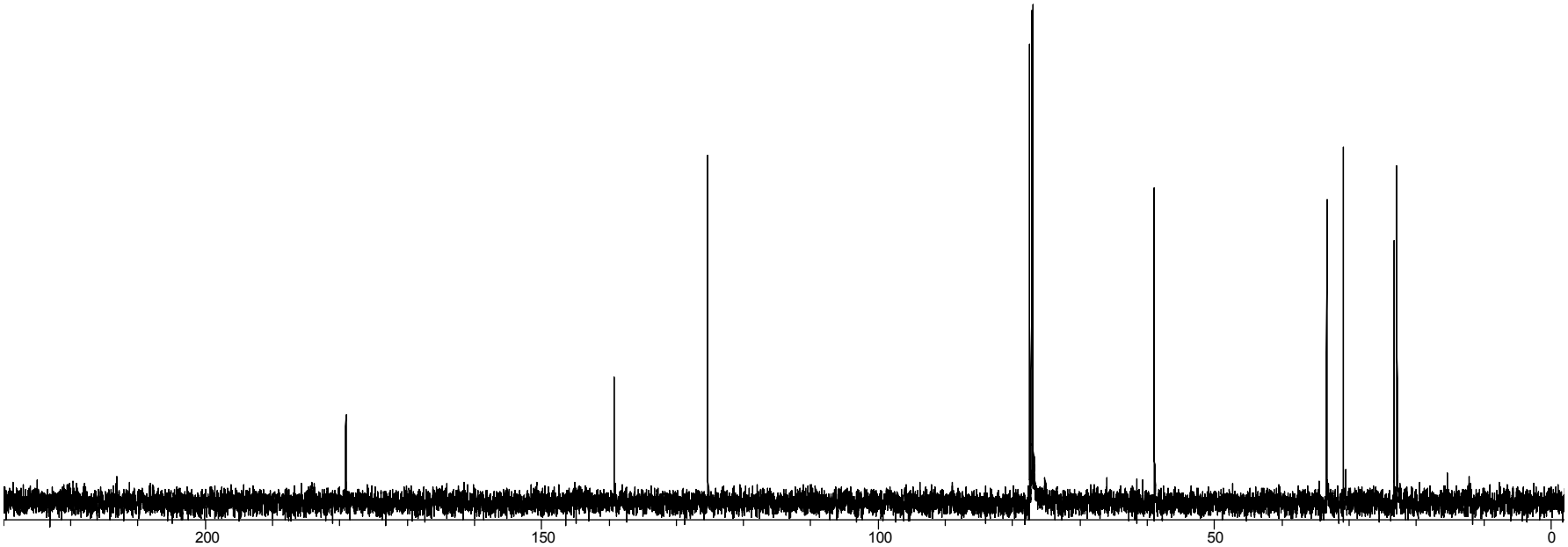


```
C:\Program Files\nuts\DATA\$10-28-05-jiny-F-82-09.fid
STANDARD 1H OBSERVE;blank line
Oct 27 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    7.350 usec
Recycle delay =    2.000 sec
NA  =     32
PTS1d = 32768
F1  =  399.950684 MHz
F2  =  399.951111 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2004.3564 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -50.74
      B =  51.00
      C =   0.00
```

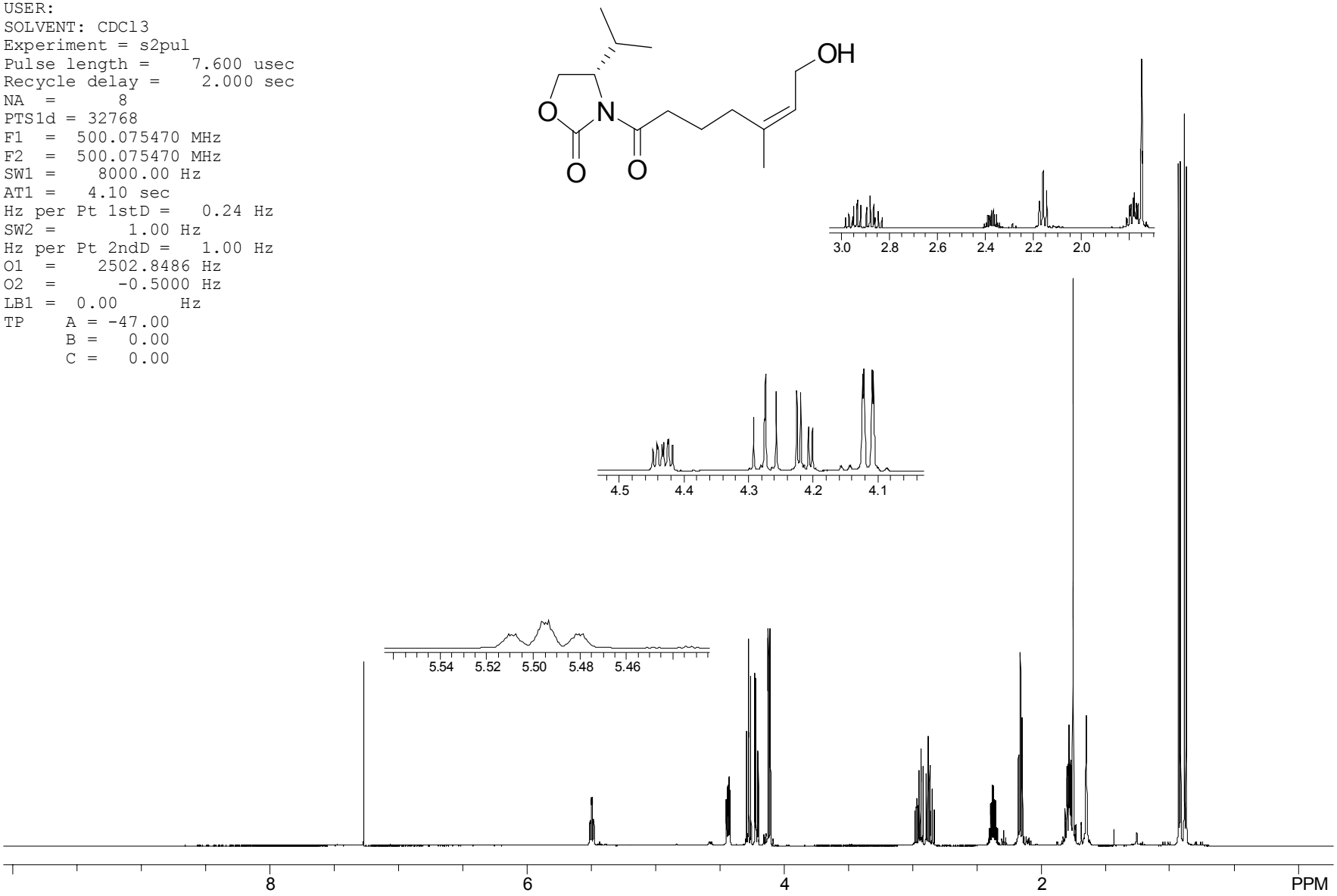


C:\Program Files\nuts\DATA\$10-26-05-jiny-13C-F-82-09.fid
10-26-05-jiny-13C-F-82-09
Oct 26 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length = 4.300 usec
Recycle delay = 1.000 sec
NA = 64
PTS1d = 65536
F1 = 125.662560 MHz
F2 = 499.698120 MHz
SW1 = 30165.91 Hz
AT1 = 2.17 sec
Hz per Pt 1stD = 0.46 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 13822.6582 Hz
O2 = -0.5000 Hz
LB1 = 1.50 Hz
TP A = -135.93
B = 103.00
C = 0.00

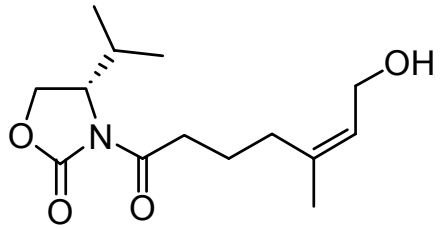


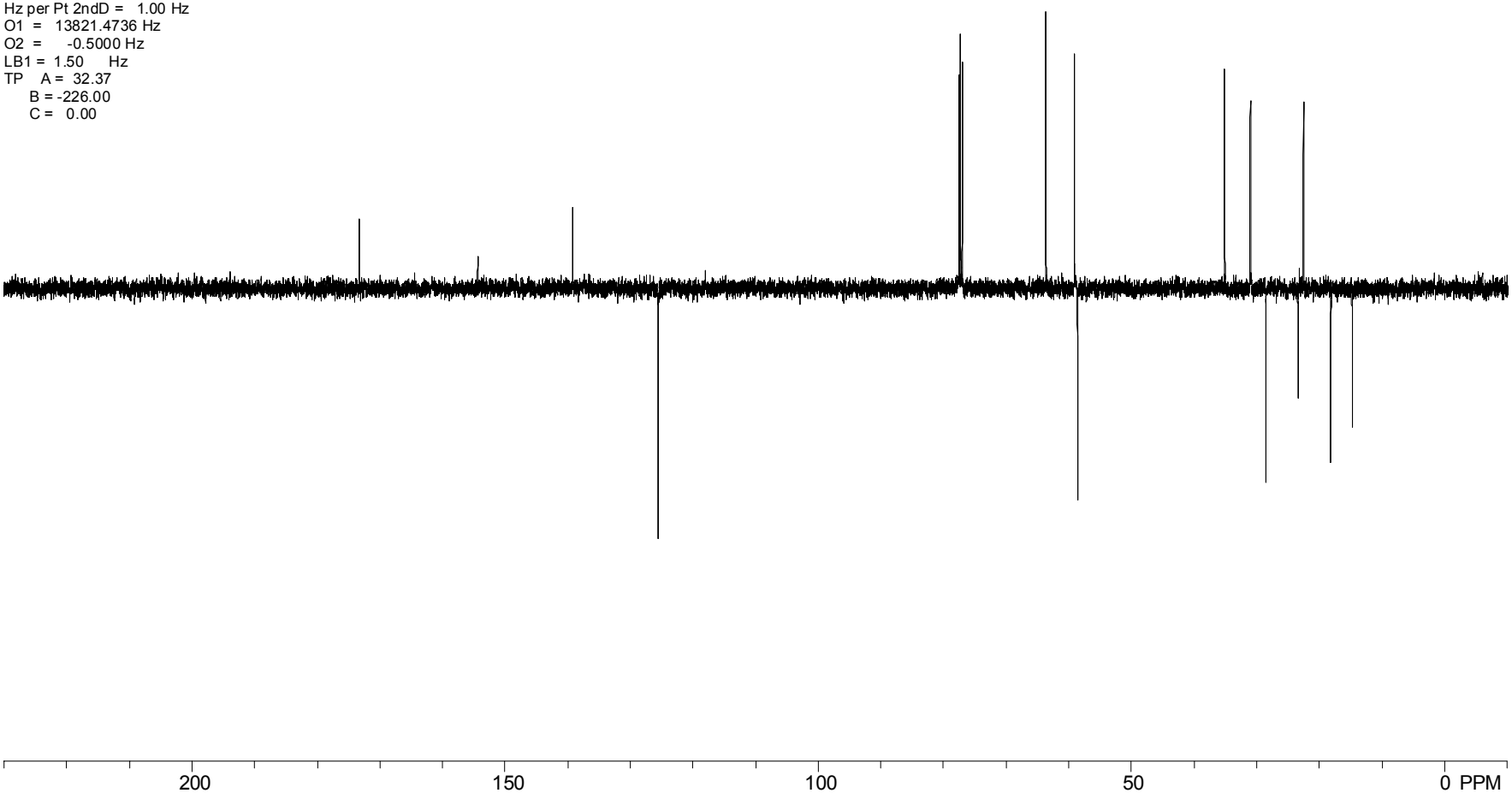


```
C:\Program Files\nuts\DATA\$09-16-05-jiny-H-87-14-I.fid
09-16-05-jiny-H-87-14-I
Sep 16 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    7.600 usec
Recycle delay =    2.000 sec
NA  =      8
PTS1d = 32768
F1  =  500.075470 MHz
F2  =  500.075470 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2502.8486 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -47.00
      B =   0.00
      C =   0.00
```

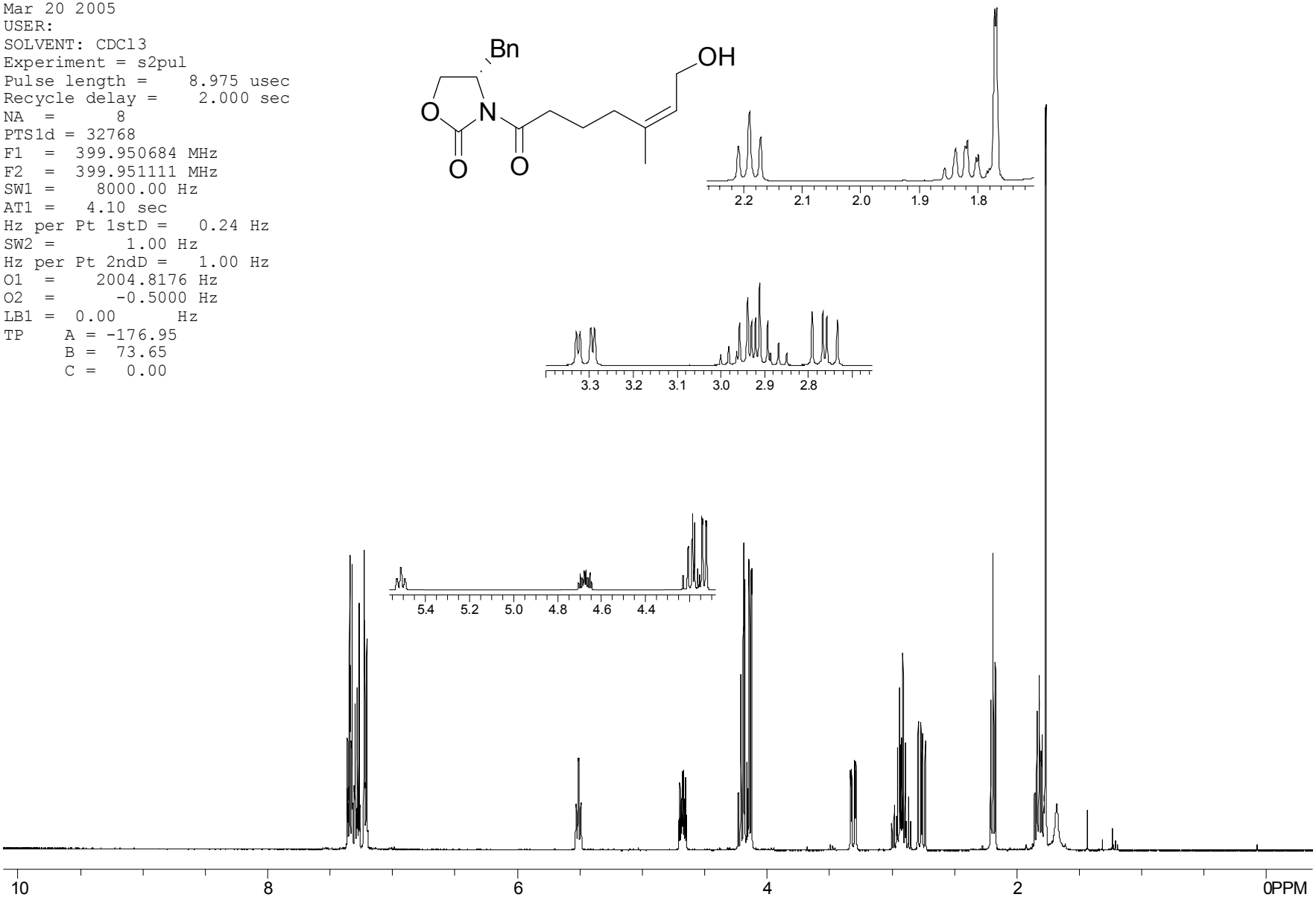


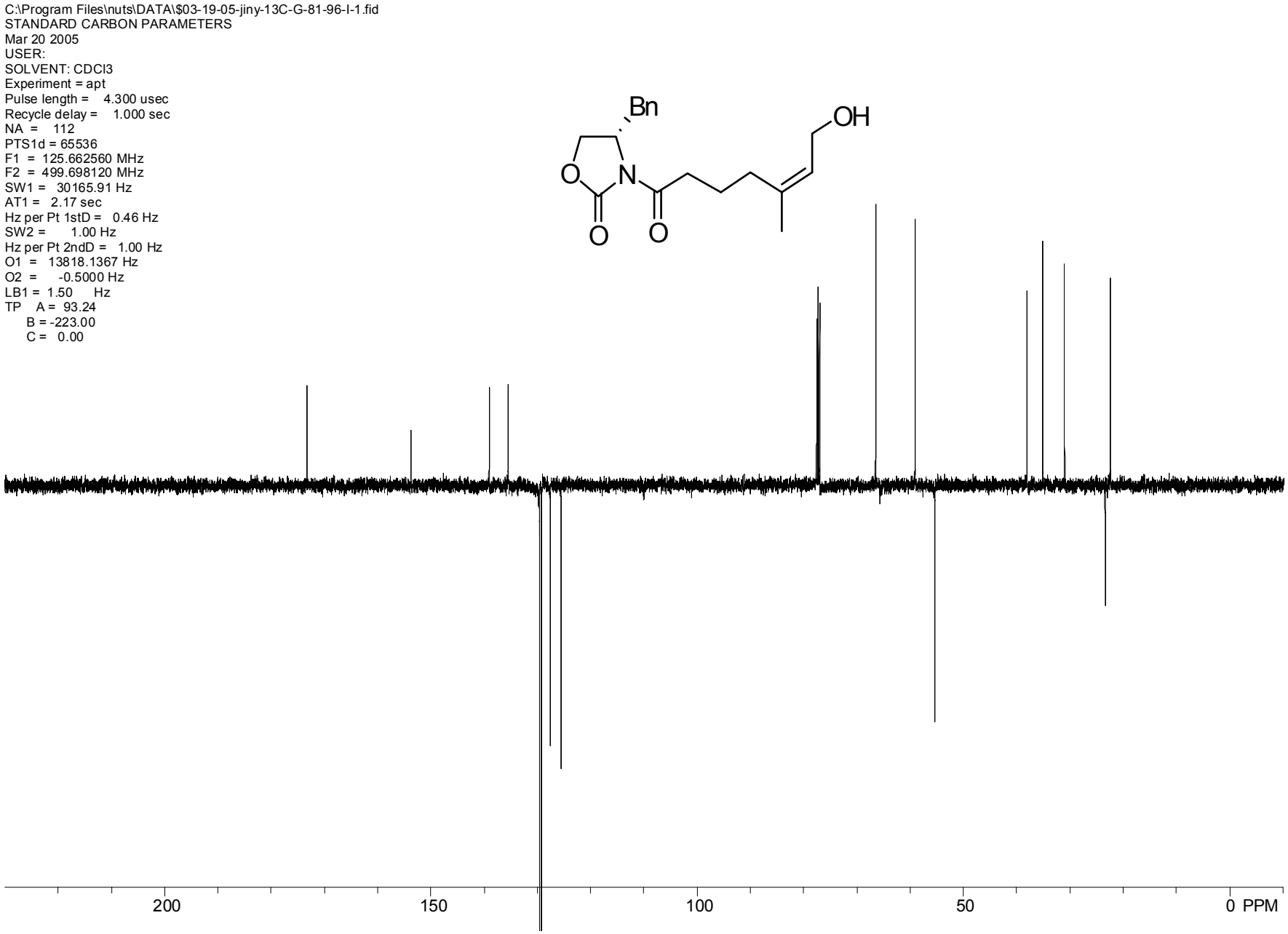
C:\Program Files\nuts\DATA\$10-29-05-jiny-APT-H-87-14-I.fid
10-29-05-jiny-13C-H-87-14-I
Oct 28 2005
USER:
SOLVENT: CDCl3
Experiment = apt
Pulse length = 4.300 usec
Recycle delay = 1.000 sec
NA = 208
PTS1d = 65536
F1 = 125.662560 MHz
F2 = 499.698120 MHz
SW1 = 30165.91 Hz
AT1 = 2.17 sec
Hz per Pt 1stD = 0.46 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 13821.4736 Hz
O2 = -0.5000 Hz
LB1 = 1.50 Hz
TP A = 32.37
B = -226.00
C = 0.00

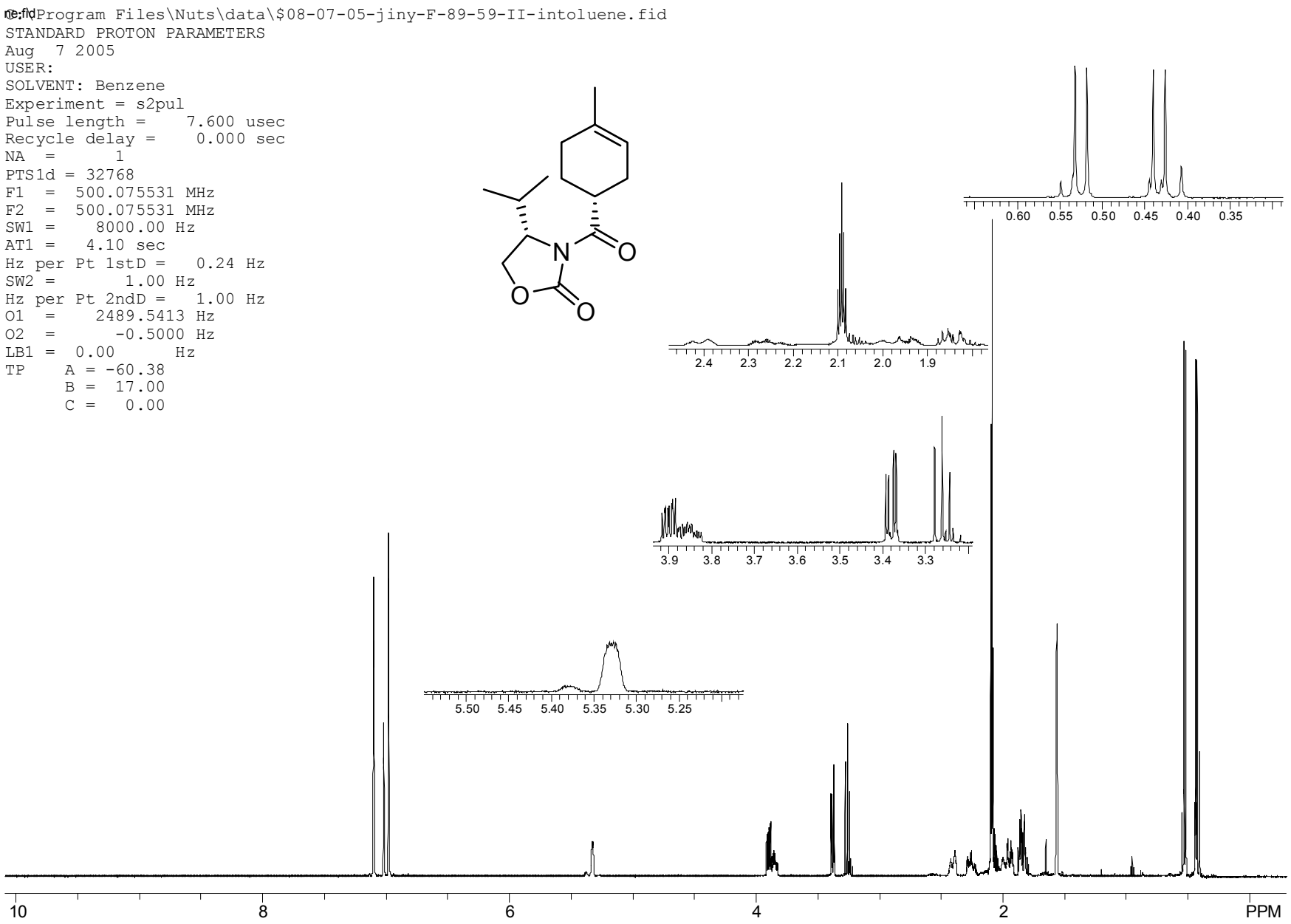


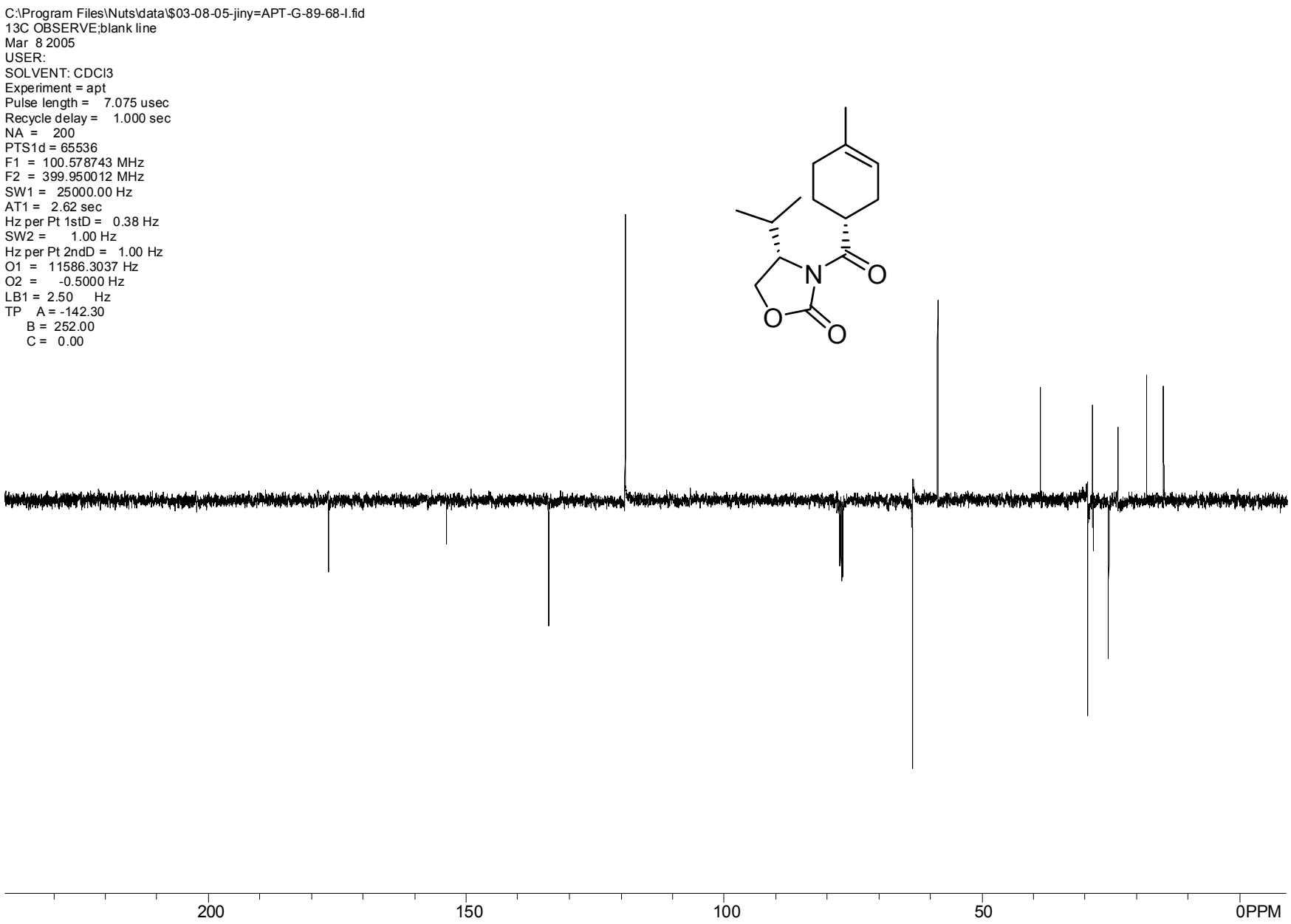


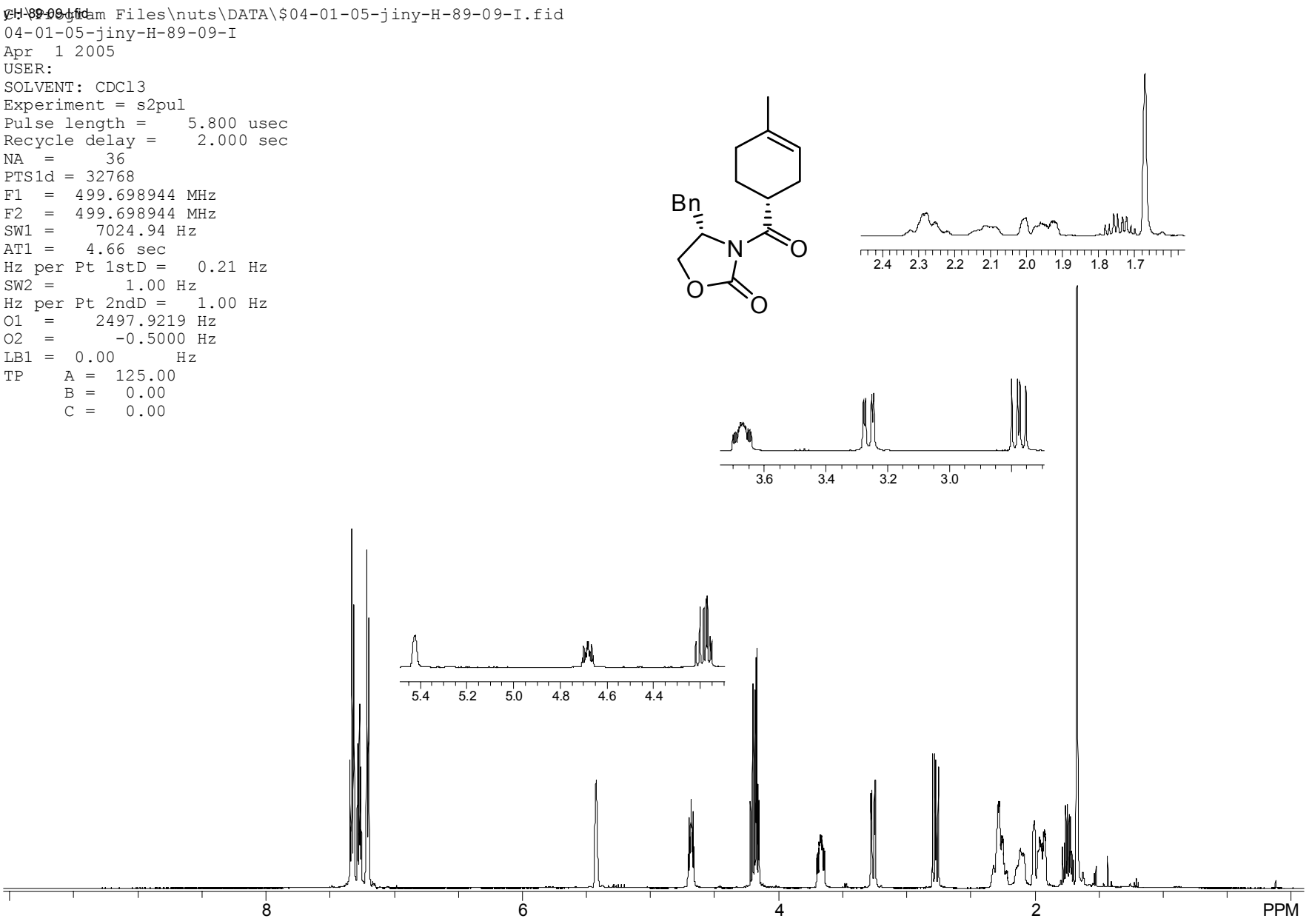
```
C:\Program Files\nuts\DATA\$03-19-05-jiny-G-81-96-I-1.fid
03-19-05-jiny-G-81-96-I-1
Mar 20 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    8.975 usec
Recycle delay =    2.000 sec
NA  =      8
PTS1d = 32768
F1  =  399.950684 MHz
F2  =  399.951111 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2004.8176 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -176.95
      B =  73.65
      C =   0.00
```



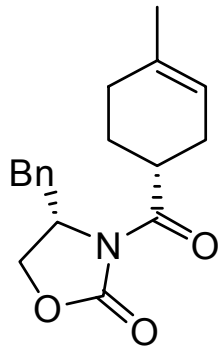


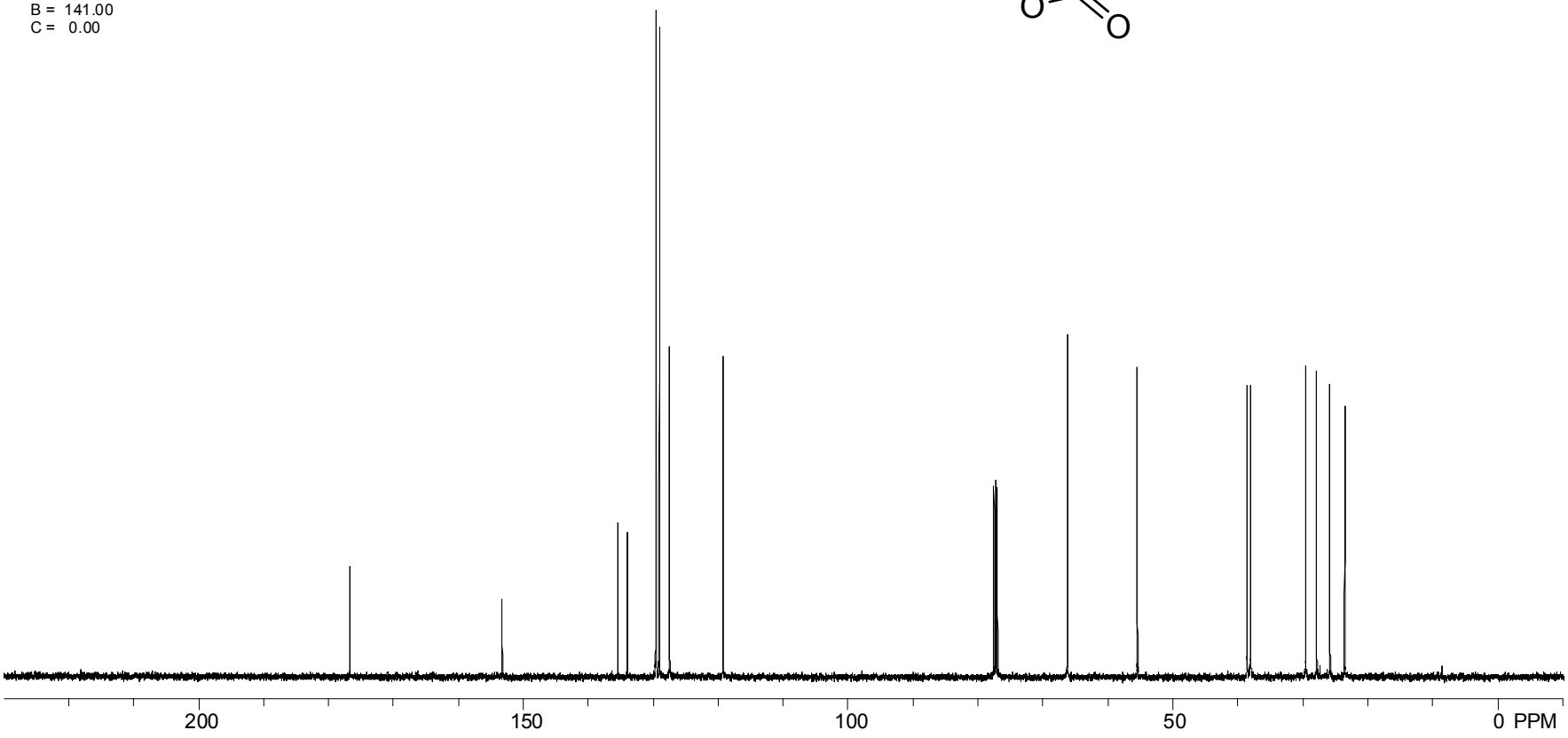

name Program Files\Nuts\data\$08-07-05-jiny-F-89-59-II-intoluene.fid
STANDARD PROTON PARAMETERS
Aug 7 2005
USER:
SOLVENT: Benzene
Experiment = s2pul
Pulse length = 7.600 usec
Recycle delay = 0.000 sec
NA = 1
PTS1d = 32768
F1 = 500.075531 MHz
F2 = 500.075531 MHz
SW1 = 8000.00 Hz
AT1 = 4.10 sec
Hz per Pt 1stD = 0.24 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2489.5413 Hz
O2 = -0.5000 Hz
LB1 = 0.00 Hz
TP A = -60.38
B = 17.00
C = 0.00
N
O
O
O
0.60 0.55 0.50 0.45 0.40 0.35
2.4 2.3 2.2 2.1 2.0 1.9
3.9 3.8 3.7 3.6 3.5 3.4 3.3
5.50 5.45 5.40 5.35 5.30 5.25
10 8 6 4 2 PPM

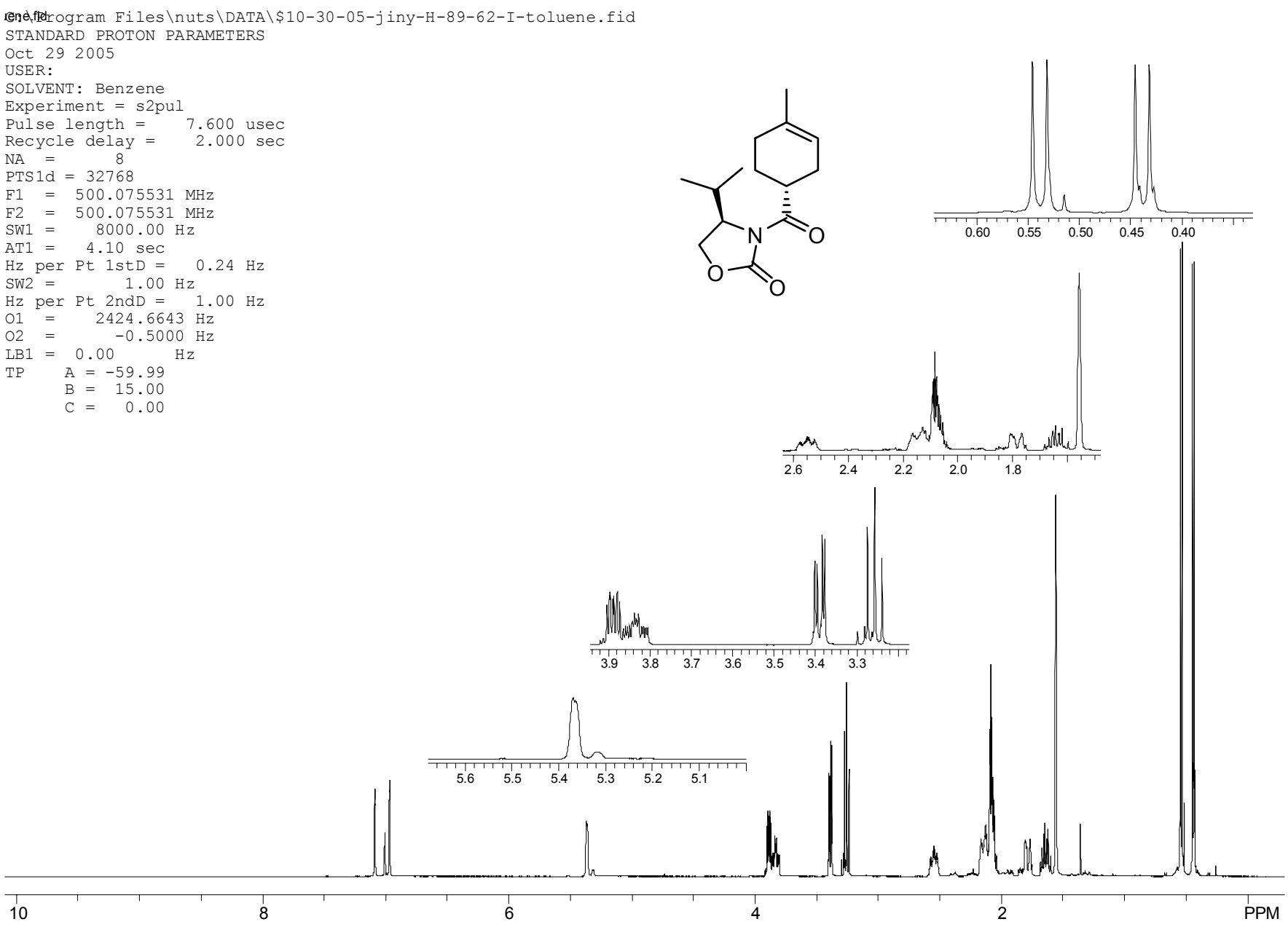

C:\Program Files\Nuts\data\$03-08-05-jiny=APT-G-89-68-I.fid
13C OBSERVE;blank line
Mar 8 2005
USER:
SOLVENT: CDCl3
Experiment = apt
Pulse length = 7.075 usec
Recycle delay = 1.000 sec
NA = 200
PTS1d = 65536
F1 = 100.578743 MHz
F2 = 399.950012 MHz
SW1 = 25000.00 Hz
AT1 = 2.62 sec
Hz per Pt 1stD = 0.38 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 11586.3037 Hz
O2 = -0.5000 Hz
LB1 = 2.50 Hz
TP A = -142.30
B = 252.00
C = 0.00
N
O
O
O
200
150
100
50
0PPM


C:\Program Files\nuts\DATA\$04-01-05-jiny-H-89-09-I.fid
04-01-05-jiny-H-89-09-I
Apr 1 2005
USER:
SOLVENT: CDC13
Experiment = s2pul
Pulse length = 5.800 usec
Recycle delay = 2.000 sec
NA = 36
PTS1d = 32768
F1 = 499.698944 MHz
F2 = 499.698944 MHz
SW1 = 7024.94 Hz
AT1 = 4.66 sec
Hz per Pt 1stD = 0.21 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2497.9219 Hz
O2 = -0.5000 Hz
LB1 = 0.00 Hz
TP A = 125.00
B = 0.00
C = 0.00
Bn
N
O
O
O
2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
3.6 3.4 3.2 3.0
5.4 5.2 5.0 4.8 4.6 4.4
8 6 4 2 PPM

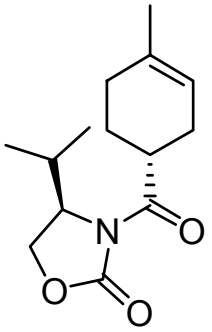
C:\Program Files\nuts\DATA\$04-01-05-jiny-13C-H-89-09-l.fid
STANDARD CARBON PARAMETERS
Apr 1 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length = 4.300 usec
Recycle delay = 1.000 sec
NA = 104
PTS1d = 65536
F1 = 125.662560 MHz
F2 = 499.698120 MHz
SW1 = 30165.91 Hz
AT1 = 2.17 sec
Hz per Pt 1stD = 0.46 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 13814.2998 Hz
O2 = -0.5000 Hz
LB1 = 1.50 Hz
TP A = -25.93
B = 141.00
C = 0.00

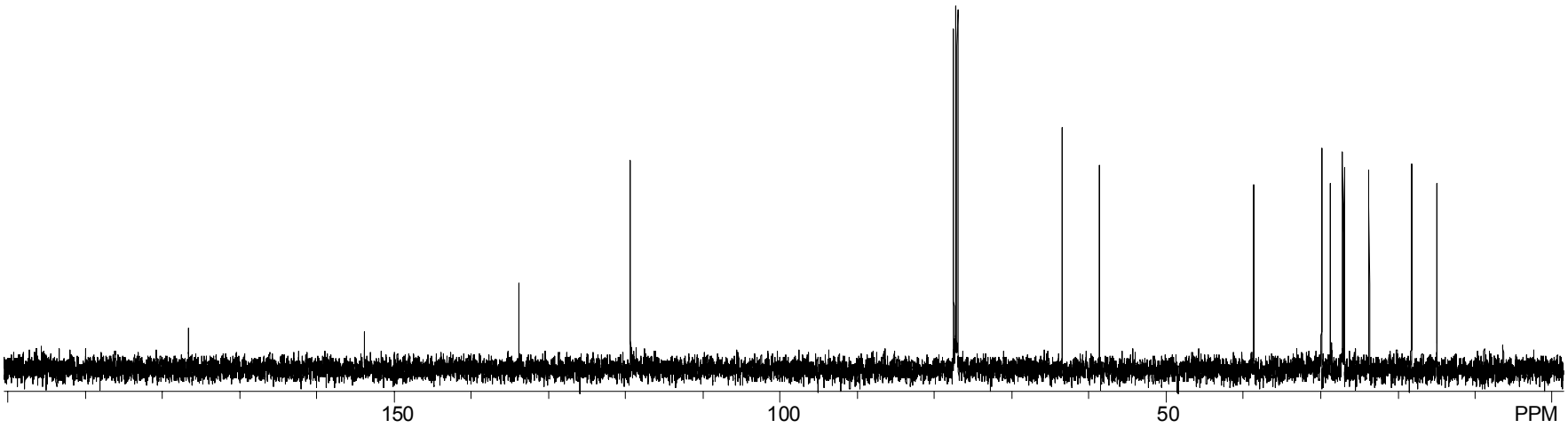




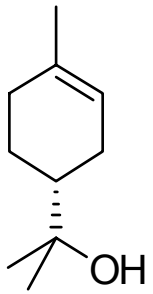


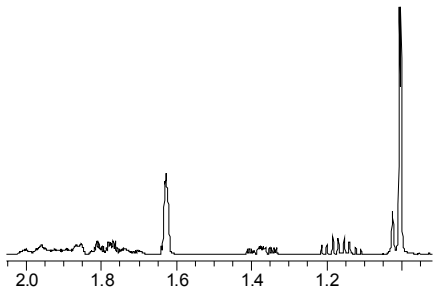
```
C:\Prijam Files\Data\06-20-05-jiny-13C-H-89-62-I-diastereomer\06-20-05-jiny-13C-H-89-62-I-diastereomer.fid
06-20-05-jiny-13C-H-89-62-I-diastereomer
Jun 20 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    4.300 usec
Recycle delay =    1.000 sec
NA  =     16
PTS1d = 65536
F1  =  125.662560 MHz
F2  =  499.698120 MHz
SW1 =   30165.91 Hz
AT1 =   2.17 sec
Hz per Pt 1stD =   0.46 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =   13820.5332 Hz
O2  =      -0.5000 Hz
LB1 =  1.50      Hz
TP    A = -215.51
      B =  242.00
      C =   0.00
```

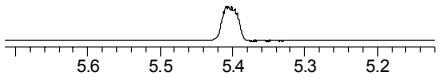




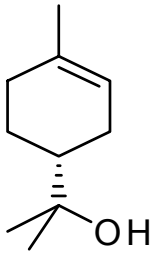
```
C:\Program Files\nuts\DATA\$05-20-05-jiny-H-131-40-I.fid
STANDARD 1H OBSERVE;blank line
May 20 2005
USER:
SOLVENT: Benzene
Experiment = s2pul
Pulse length =    8.975 usec
Recycle delay =    2.000 sec
NA  =      8
PTS1d = 32768
F1  =  399.950714 MHz
F2  =  399.951141 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2013.7126 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -121.89
      B =  53.00
      C =   0.00
```



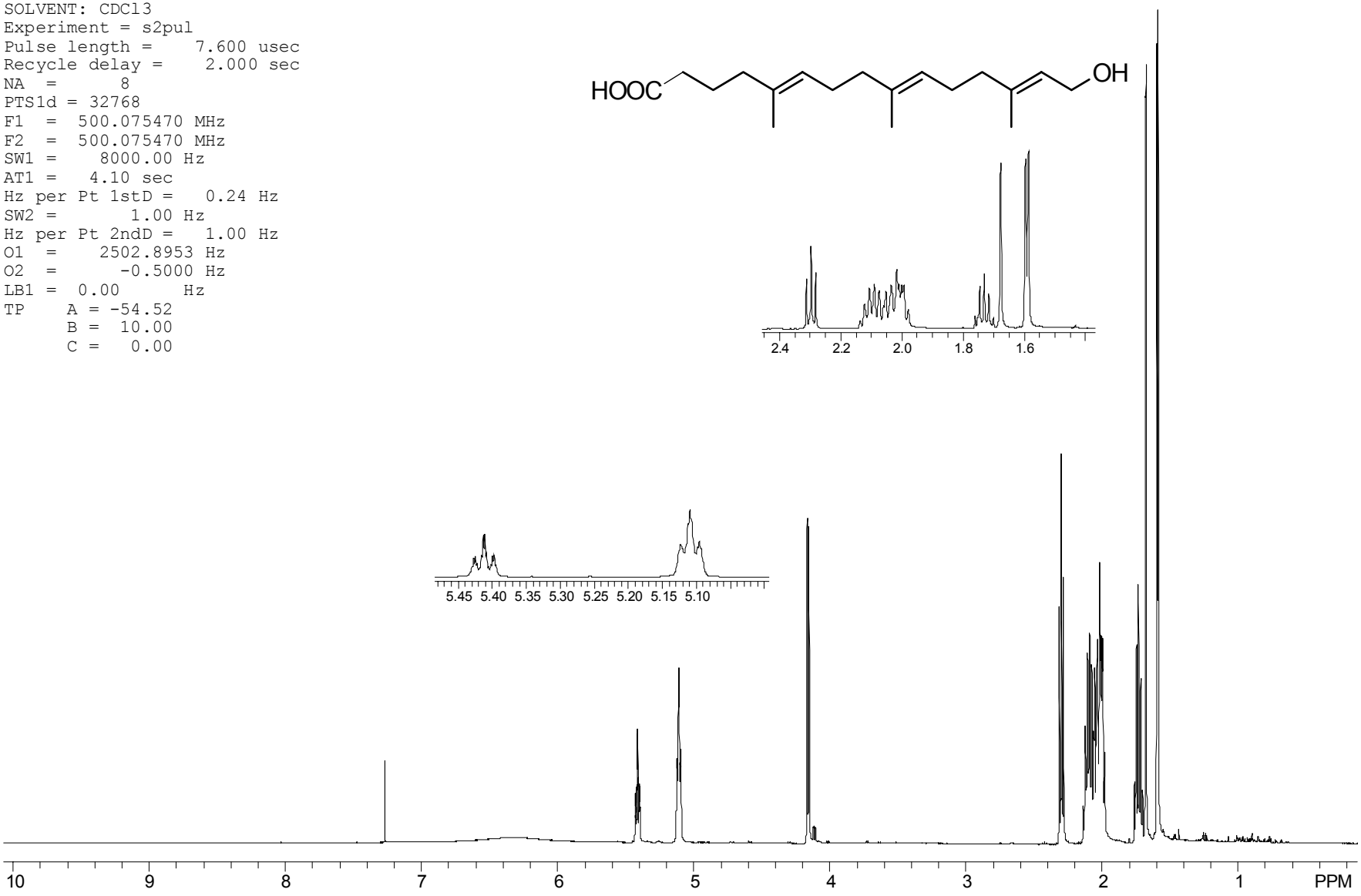




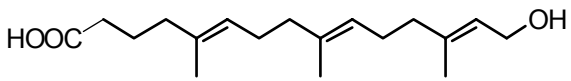
```
jiny\13C-H-131-40-I.fid
jiny\Program Files\nuts\DATA\$05-20-05-jiny-13C-H-131-40-I.fid
13C OBSERVE;blank line
May 20 2005
USER:
SOLVENT: Benzene
Experiment = s2pul
Pulse length =    7.075 usec
Recycle delay =    1.000 sec
NA  =    100
PTS1d = 65536
F1  =  100.578751 MHz
F2  =  399.950043 MHz
SW1 =   25000.00 Hz
AT1 =   2.62 sec
Hz per Pt 1stD =   0.38 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =   11602.0225 Hz
O2  =      -0.5000 Hz
LB1 =  1.50      Hz
TP    A = -215.42
      B =  212.00
      C =   0.00
```

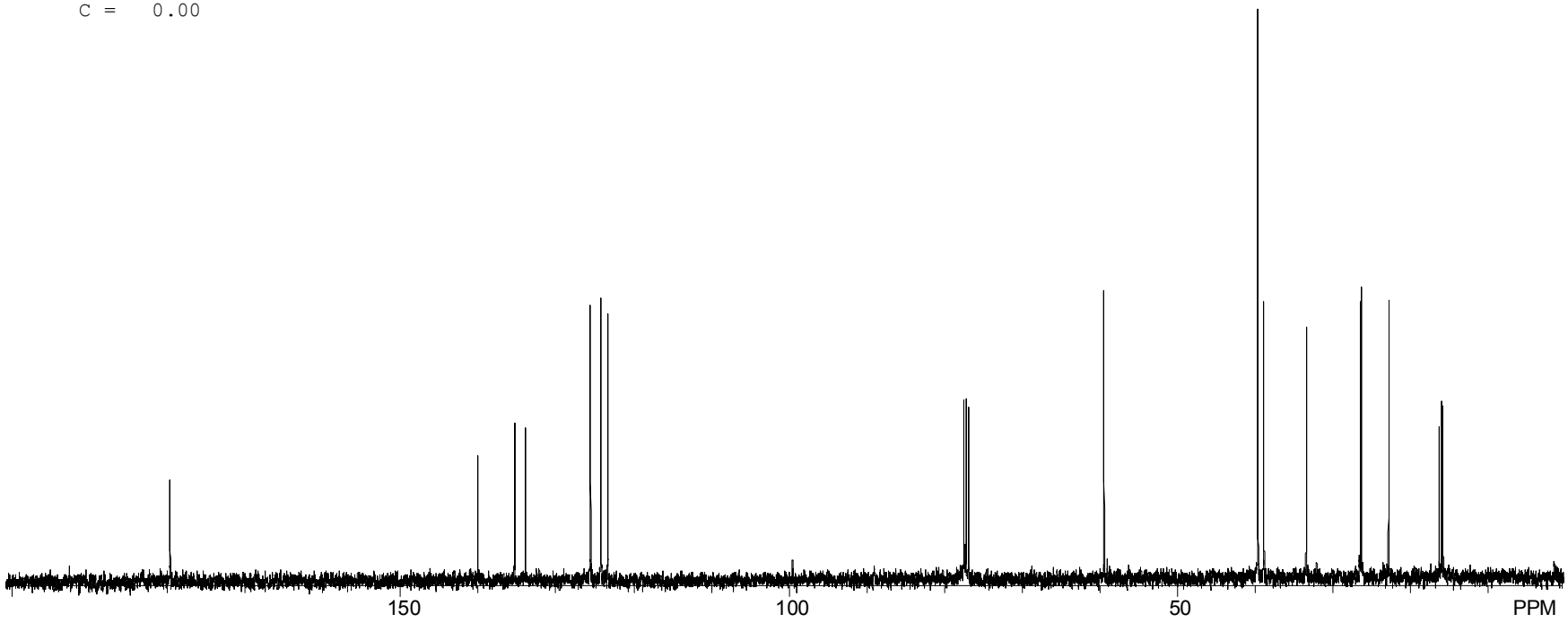


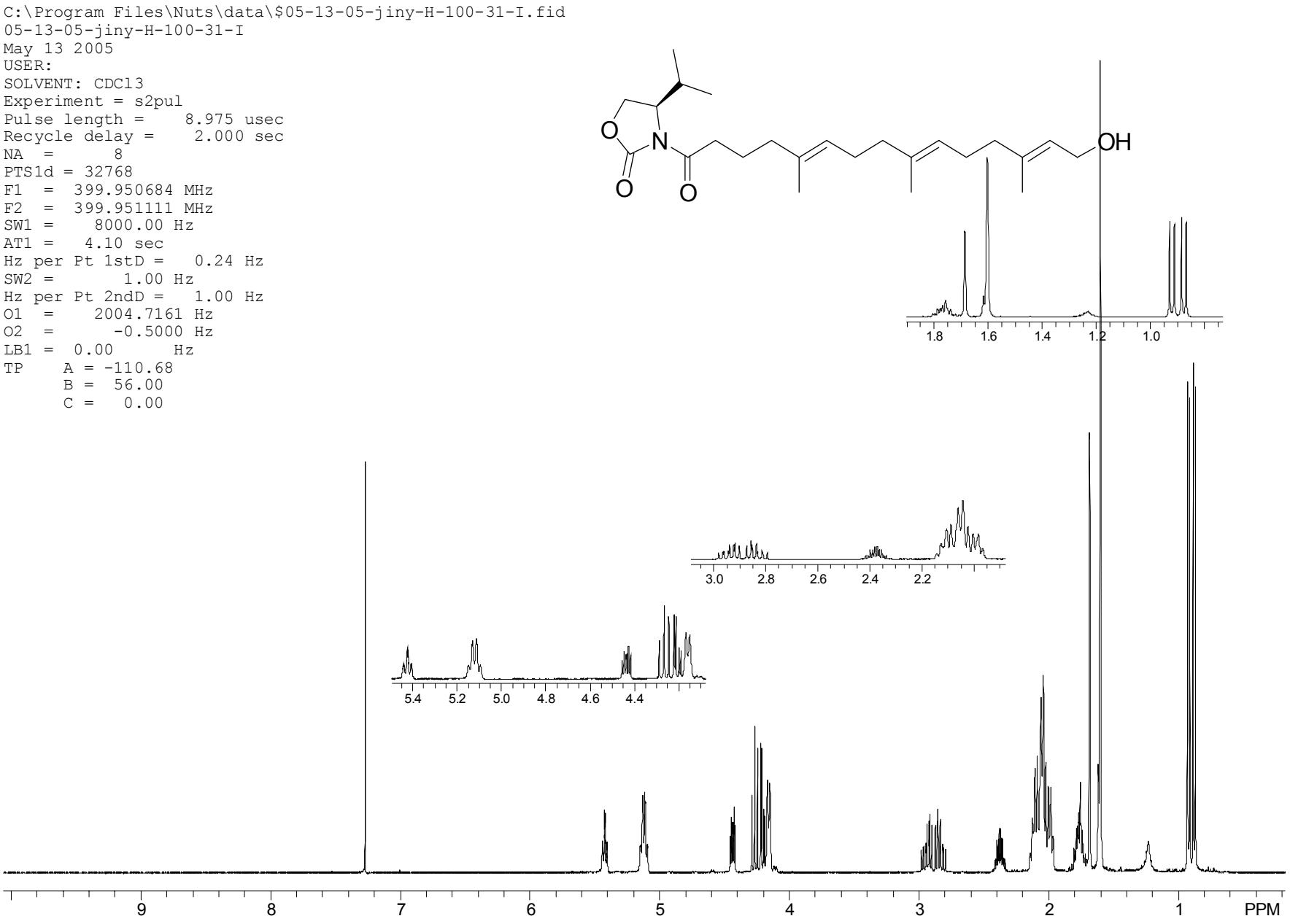
```
C:\Program Files\nuts\DATA\$05-27-05-jiny-H-99-30-I-2.fid
05-27-05-jiny-H-99-30-I-2
May 27 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    7.600 usec
Recycle delay =    2.000 sec
NA  =      8
PTS1d = 32768
F1  =  500.075470 MHz
F2  =  500.075470 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2502.8953 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -54.52
      B =  10.00
      C =   0.00
```

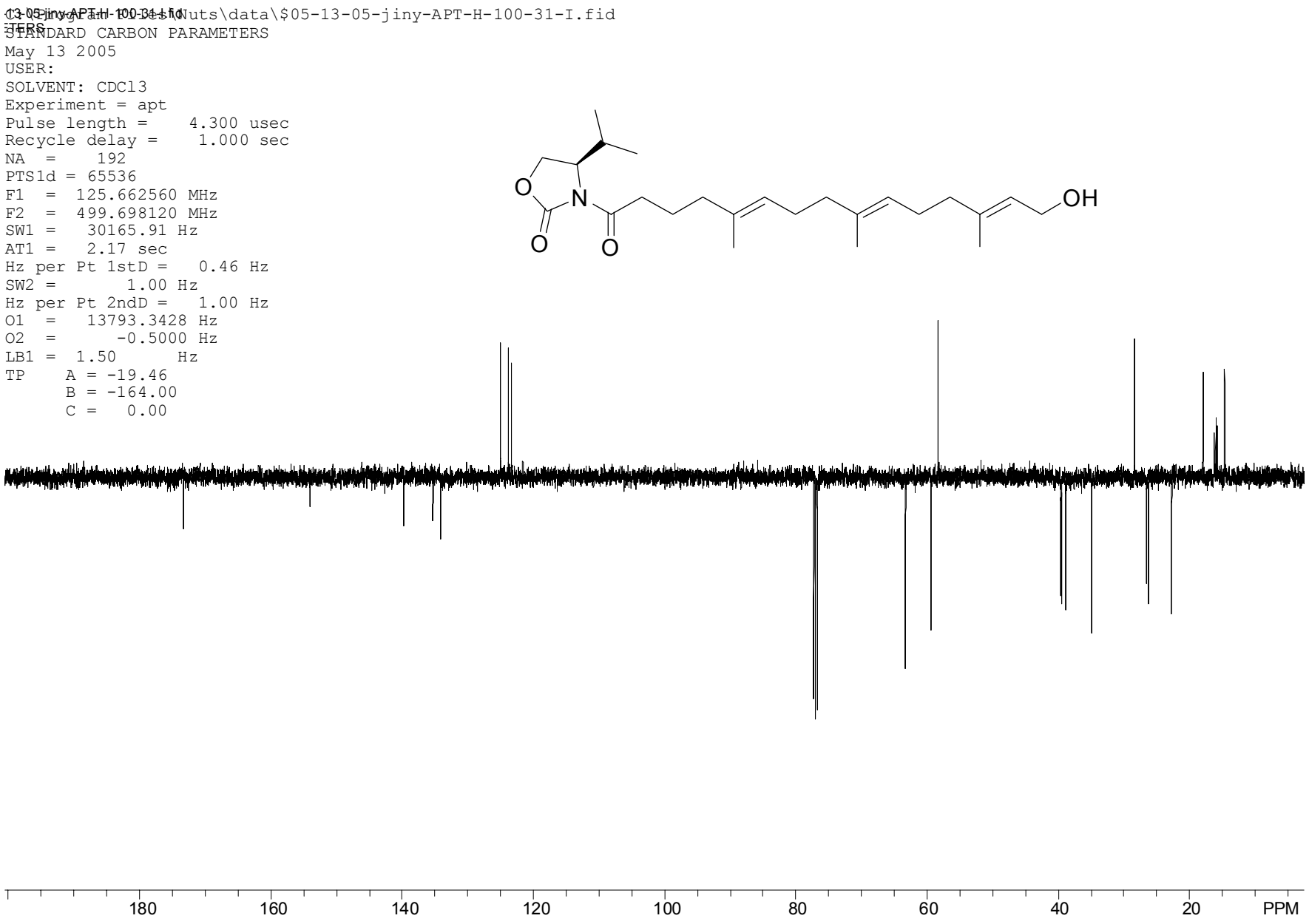


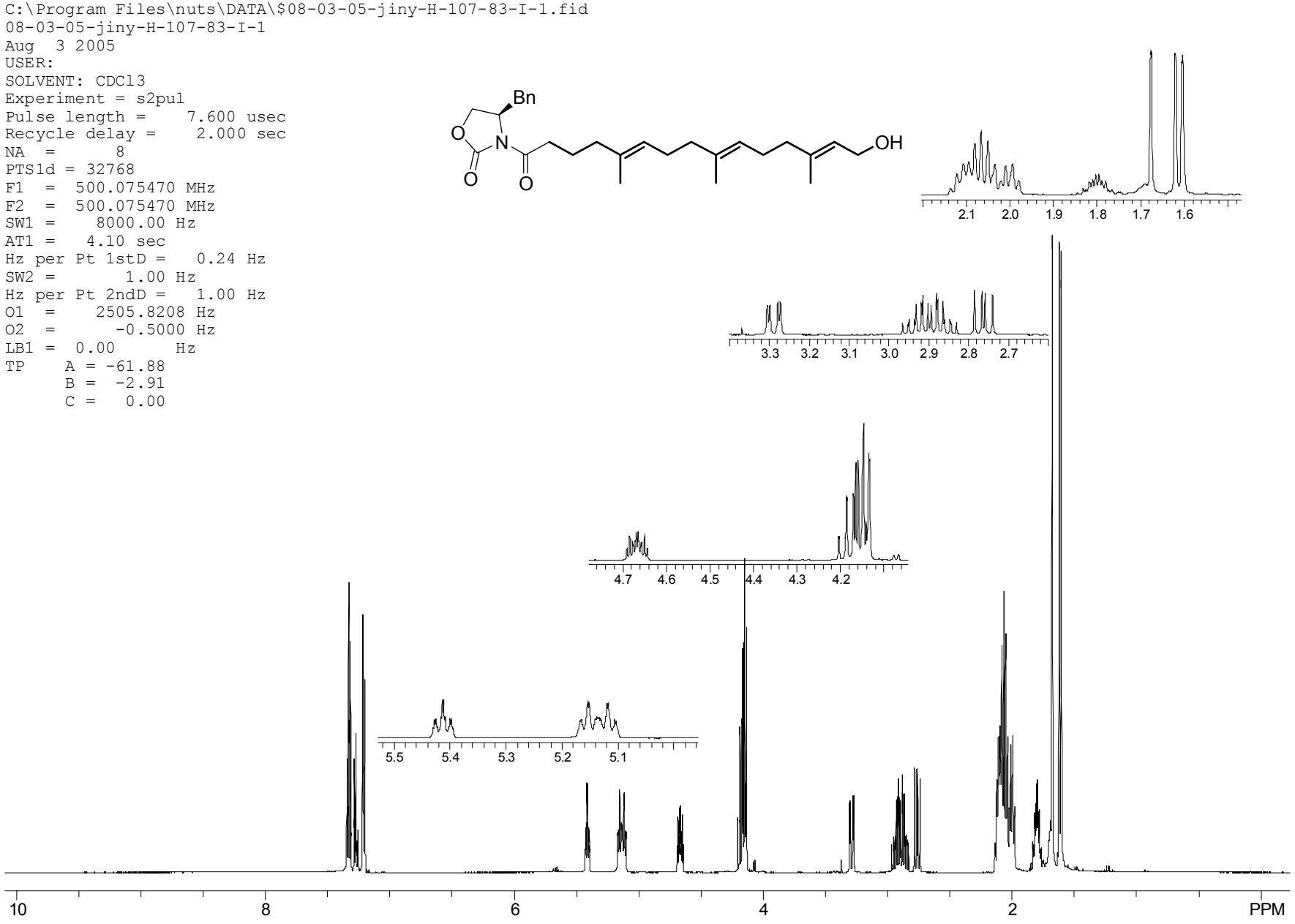
```
C:\CHEMPACK\Files\nuts\DATA\$05-27-05-jiny-13C-H-99-30-I-2.fid
13C OBSERVE;blank line
May 27 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    7.075 usec
Recycle delay =    1.000 sec
NA  =    144
PTS1d = 65536
F1  =  100.578743 MHz
F2  =  399.950012 MHz
SW1 =   25000.00 Hz
AT1 =   2.62 sec
Hz per Pt 1stD =   0.38 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =   11589.8672 Hz
O2  =      -0.5000 Hz
LB1 =  1.50      Hz
TP    A = -188.10
      B =  205.00
      C =   0.00
```



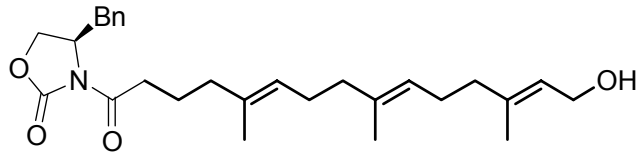


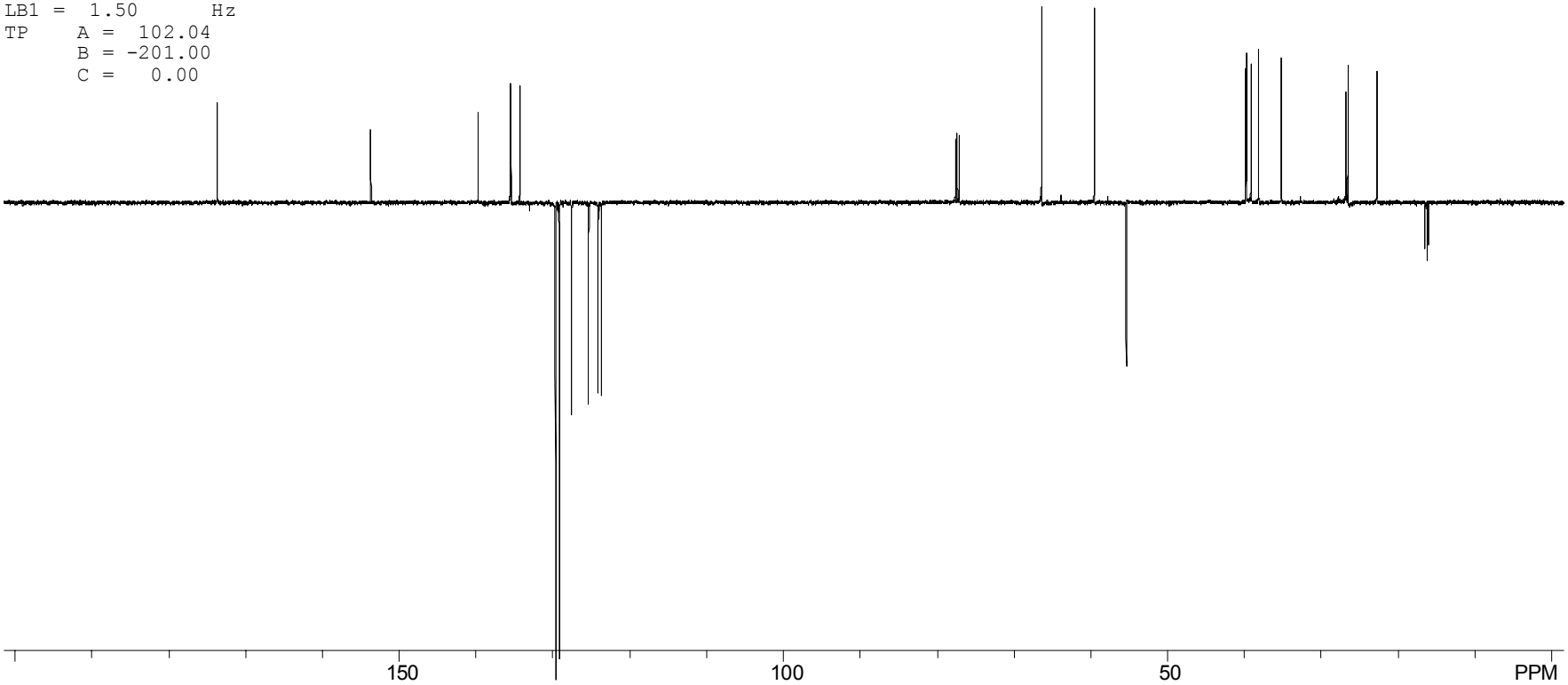

C:\Program Files\Nuts\data\$05-13-05-jiny-H-100-31-I.fid
05-13-05-jiny-H-100-31-I
May 13 2005
USER:
SOLVENT: CDC13
Experiment = s2pul
Pulse length = 8.975 usec
Recycle delay = 2.000 sec
NA = 8
PTS1d = 32768
F1 = 399.950684 MHz
F2 = 399.951111 MHz
SW1 = 8000.00 Hz
AT1 = 4.10 sec
Hz per Pt 1stD = 0.24 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2004.7161 Hz
O2 = -0.5000 Hz
LB1 = 0.00 Hz
TP A = -110.68
B = 56.00
C = 0.00
O
N
O
O
OH
1.8
1.6
1.4
1.2
1.0
3.0
2.8
2.6
2.4
2.2
5.4
5.2
5.0
4.8
4.6
4.4
9
8
7
6
5
4
3
2
1
PPM


13-05-jiny-APT-H-100-31-I
C:\Spinsolve 1.0 Test Nuts\data\$05-13-05-jiny-APT-H-100-31-I.fid
PARAMETERS
STANDARD CARBON PARAMETERS
May 13 2005
USER:
SOLVENT: CDCl3
Experiment = apt
Pulse length = 4.300 usec
Recycle delay = 1.000 sec
NA = 192
PTS1d = 65536
F1 = 125.662560 MHz
F2 = 499.698120 MHz
SW1 = 30165.91 Hz
AT1 = 2.17 sec
Hz per Pt 1stD = 0.46 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 13793.3428 Hz
O2 = -0.5000 Hz
LB1 = 1.50 Hz
TP A = -19.46
B = -164.00
C = 0.00
O
N
O
O
OH
180
160
140
120
100
80
60
40
20
PPM

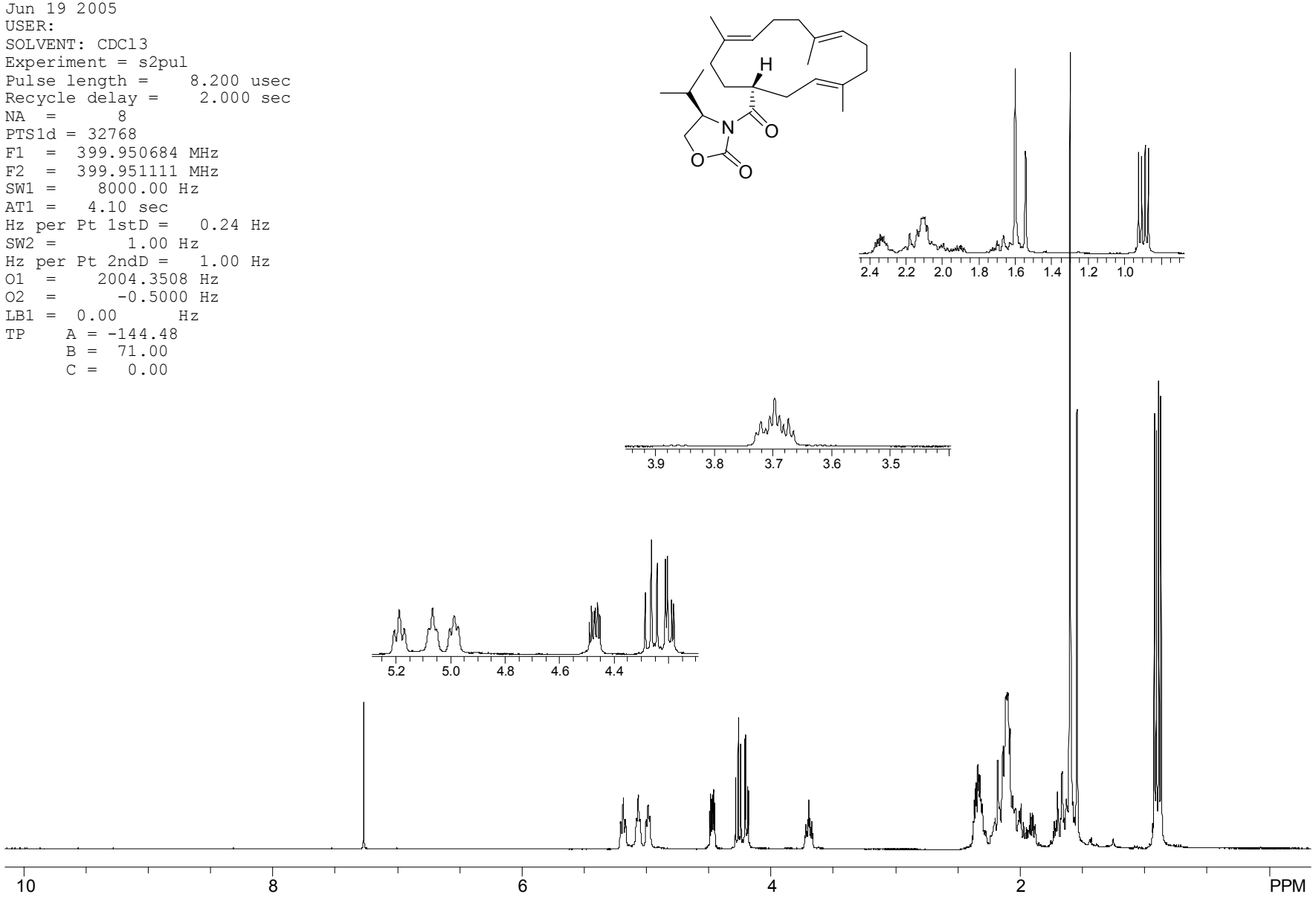

C:\Program Files\nuts\DATA\$08-03-05-jiny-H-107-83-I-1.fid
08-03-05-jiny-H-107-83-I-1
Aug 3 2005
USER:
SOLVENT: CDC13
Experiment = s2pul
Pulse length = 7.600 usec
Recycle delay = 2.000 sec
NA = 8
PTS1d = 32768
F1 = 500.075470 MHz
F2 = 500.075470 MHz
SW1 = 8000.00 Hz
AT1 = 4.10 sec
Hz per Pt 1stD = 0.24 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2505.8208 Hz
O2 = -0.5000 Hz
LB1 = 0.00 Hz
TP A = -61.88
B = -2.91
C = 0.00
Bn
O
N
O
O
OH
2.1 2.0 1.9 1.8 1.7 1.6
3.3 3.2 3.1 3.0 2.9 2.8 2.7
4.7 4.6 4.5 4.4 4.3 4.2
5.5 5.4 5.3 5.2 5.1
10 8 6 4 2 PPM

```
08-03-05-jiny-APT-H-107-83-I-1.fid
C:\Program Files\nmrs\DATA\$08-03-05-jiny-APT-H-107-83-I-1.fid
METERS
STANDARD CARBON PARAMETERS
Aug  3 2005
USER:
SOLVENT: CDCl3
Experiment = apt
Pulse length =    4.300 usec
Recycle delay =    1.000 sec
NA  =    176
PTS1d = 65536
F1  =  125.662560 MHz
F2  =  499.698120 MHz
SW1 =   30165.91 Hz
AT1 =   2.17 sec
Hz per Pt 1stD =   0.46 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =   13821.7402 Hz
O2  =      -0.5000 Hz
LB1 =  1.50      Hz
TP    A =  102.04
      B = -201.00
      C =   0.00
```

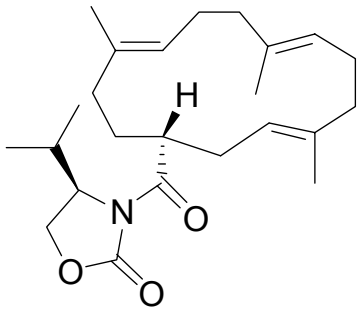


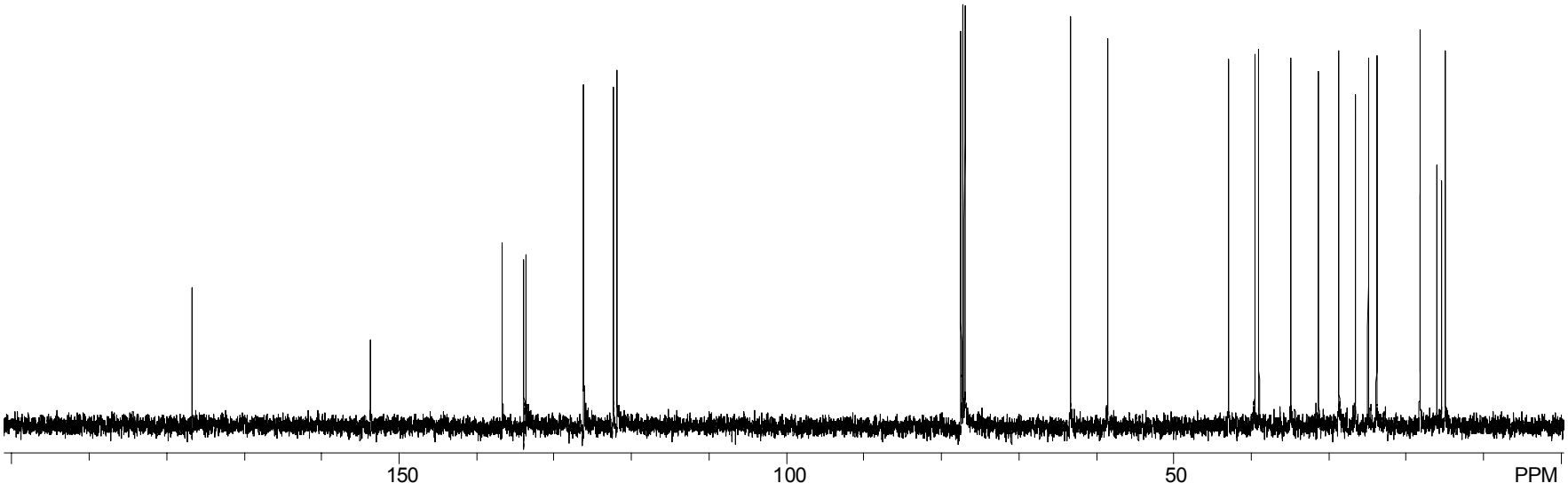


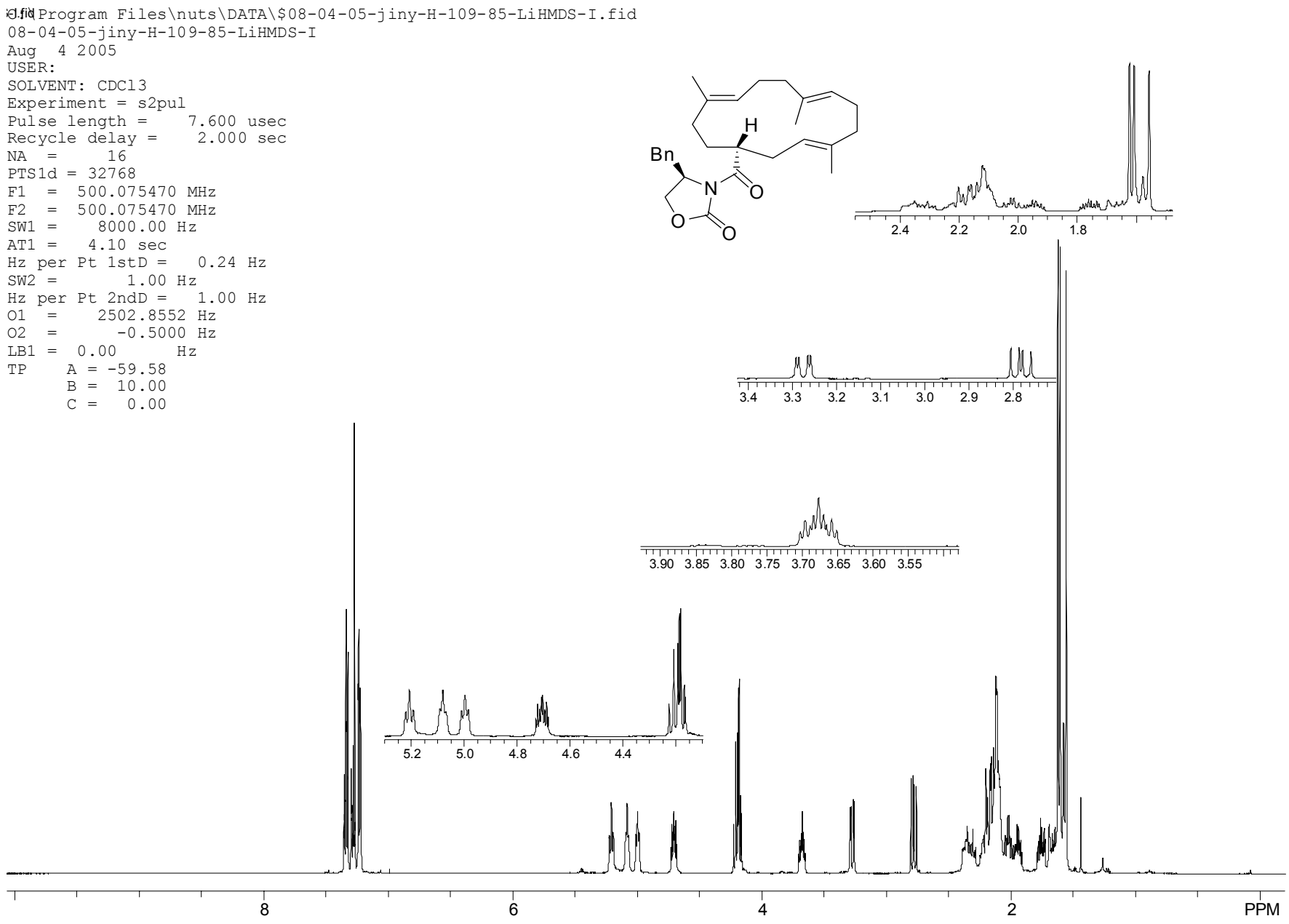
```
C:\Program Files\Nuts\data\$06-19-05-jiny-H-102-60-I.fid
06-19-05-jiny-H-102-60-I
Jun 19 2005
USER:
SOLVENT: CDC13
Experiment = s2pul
Pulse length =    8.200 usec
Recycle delay =    2.000 sec
NA  =      8
PTS1d = 32768
F1  =  399.950684 MHz
F2  =  399.951111 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2004.3508 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -144.48
      B =  71.00
      C =   0.00
```



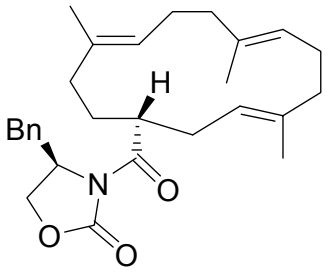
```
C:\Bruker\xau.1r\data\nuts\DATA\$06-12-05-jiny-13C-H-102-60-I.fid
STANDARD CARBON PARAMETERS
Jun 12 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    4.300 usec
Recycle delay =    1.000 sec
NA  =     80
PTS1d = 65536
F1  =  125.662560 MHz
F2  =  499.698120 MHz
SW1 =   30165.91 Hz
AT1 =   2.17 sec
Hz per Pt 1stD =   0.46 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =   13821.7402 Hz
O2  =      -0.5000 Hz
LB1 =  1.50      Hz
TP    A = -169.59
      B =  190.00
      C =   0.00
```

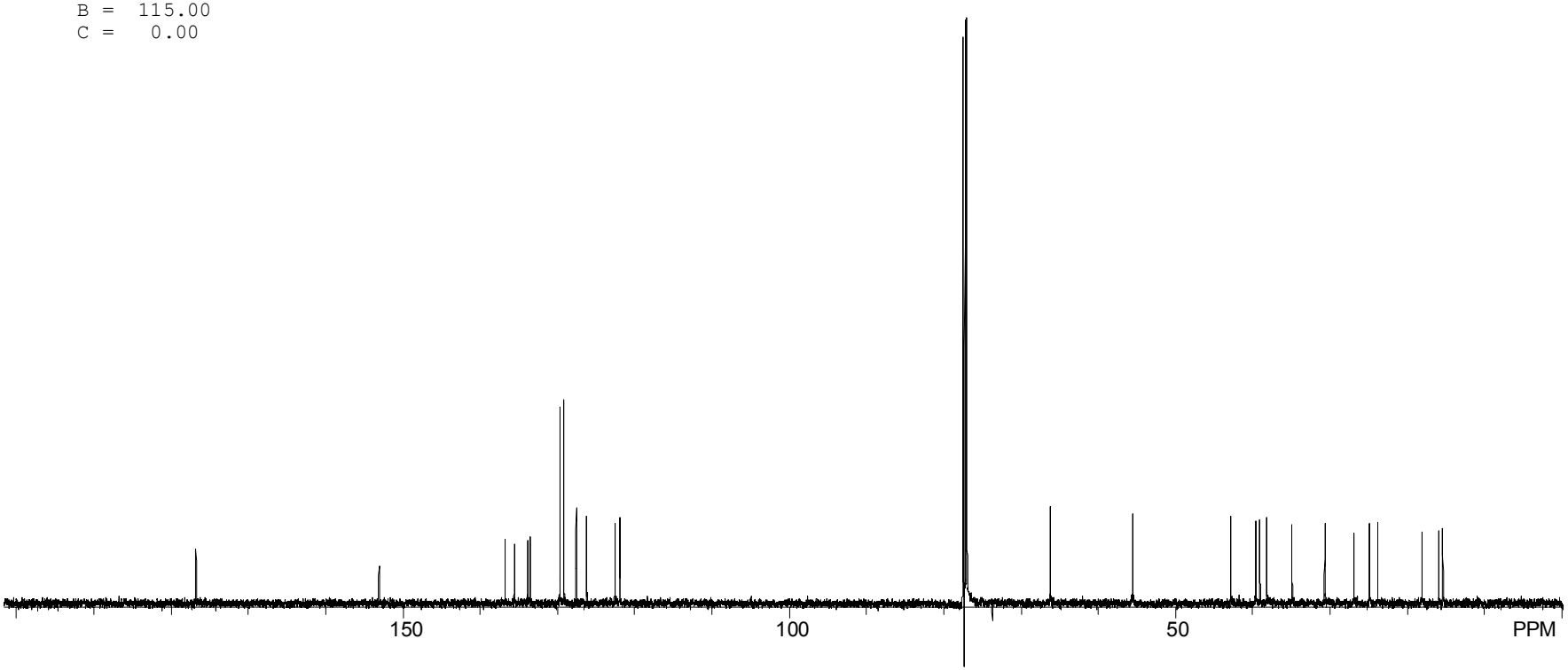


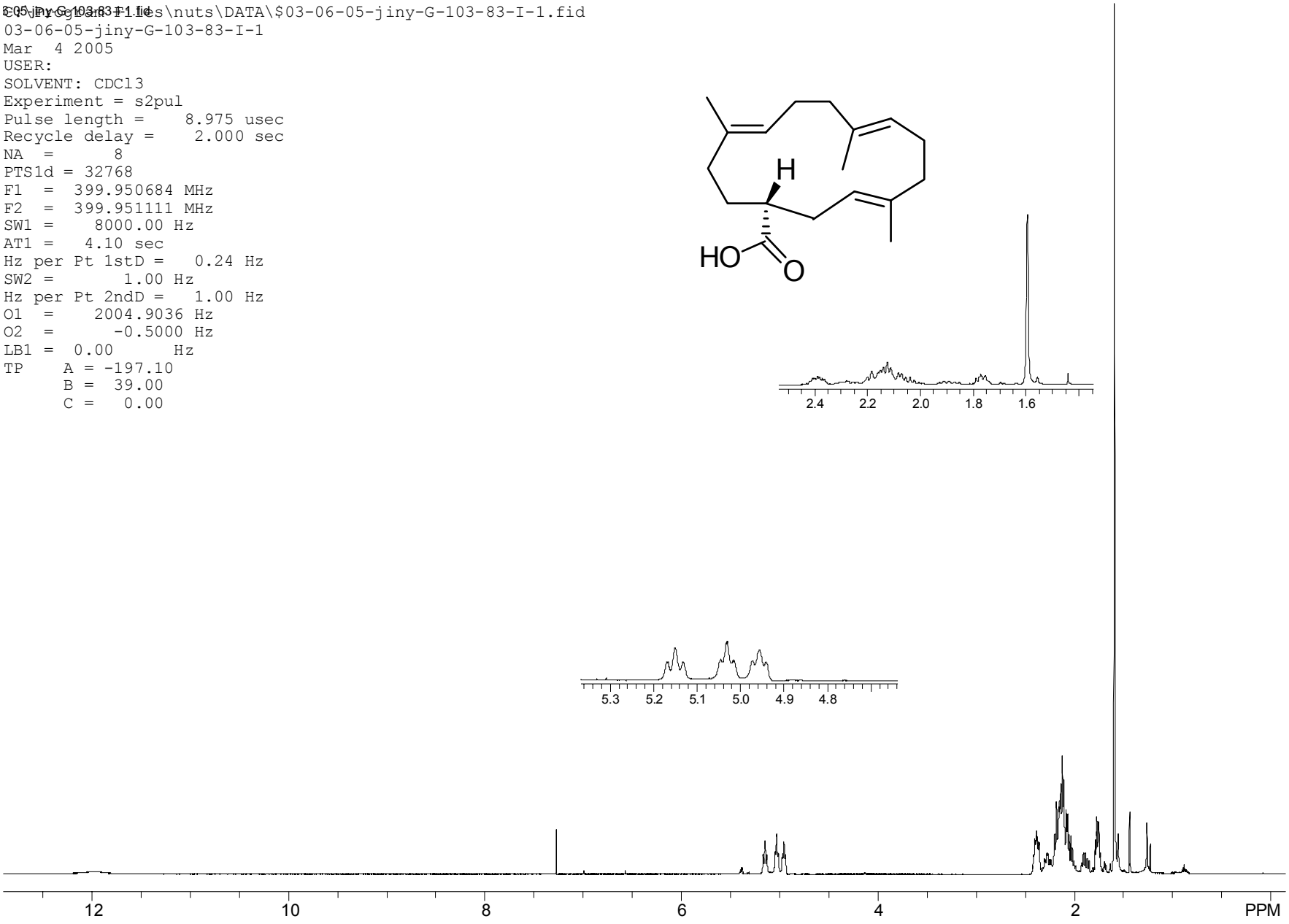


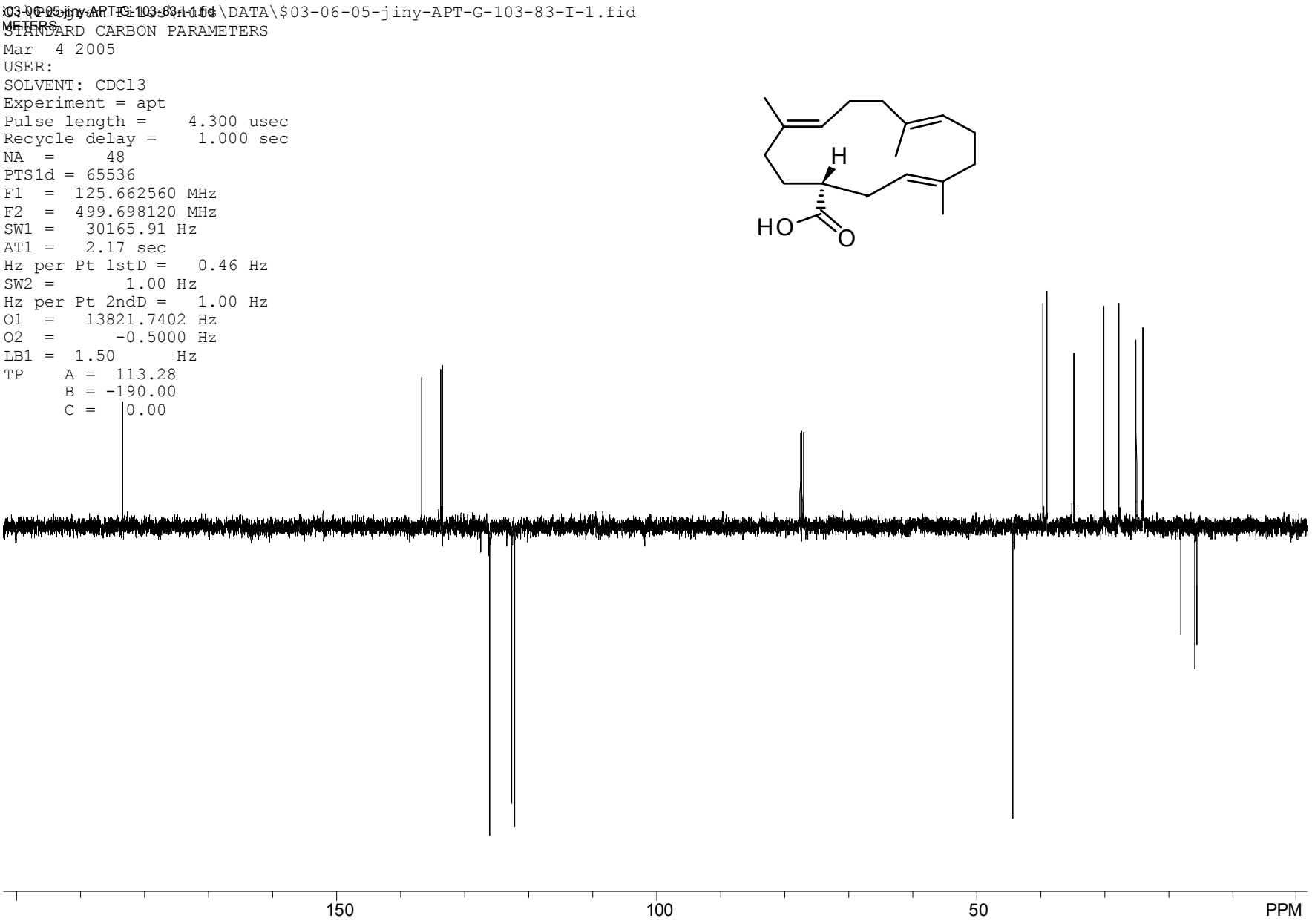

C:\Program Files\nuts\DATA\$08-04-05-jiny-H-109-85-LiHMDS-I.fid
08-04-05-jiny-H-109-85-LiHMDS-I
Aug 4 2005
USER:
SOLVENT: CDC13
Experiment = s2pul
Pulse length = 7.600 usec
Recycle delay = 2.000 sec
NA = 16
PTS1d = 32768
F1 = 500.075470 MHz
F2 = 500.075470 MHz
SW1 = 8000.00 Hz
AT1 = 4.10 sec
Hz per Pt 1stD = 0.24 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2502.8552 Hz
O2 = -0.5000 Hz
LB1 = 0.00 Hz
TP A = -59.58
B = 10.00
C = 0.00
H
Bn
N
O
O
O
2.4 2.2 2.0 1.8
3.4 3.3 3.2 3.1 3.0 2.9 2.8
3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55
5.2 5.0 4.8 4.6 4.4
8
6
4
2
PPM

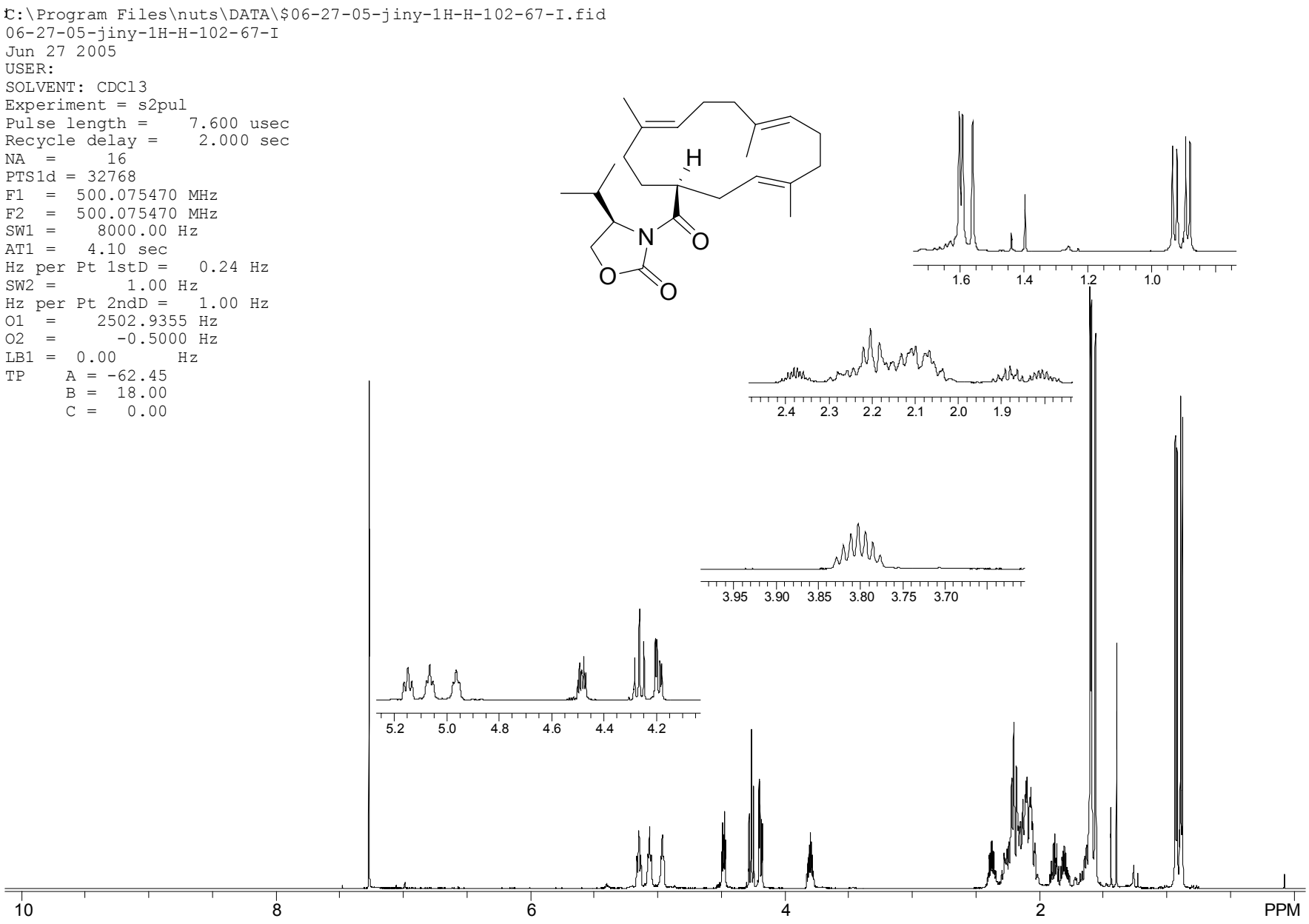
02-26-06-jiny-13C-H-109-85-I-LiHMDS.fid
02-26-06-jiny-13C-H-109-85-I-LiHMDS.10
02-26-06-jiny-13C-H-109-85-I-LiHMDS.20
02-26-06-jiny-13C-H-109-85-I-LiHMDS.30
02-26-06-jiny-13C-H-109-85-I-LiHMDS.40
C:\Varian\vnmr\data\JINY\DATA\$02-26-06-jiny-13C-H-109-85-I-LiHMDS.fid
PARAMETERS
STANDARD CARBON PARAMETERS
Feb 27 2006
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =   3.325 usec
Recycle delay =   1.000 sec
NA =   912
PTS1d = 65536
F1 = 125.662560 MHz
F2 = 499.698120 MHz
SW1 =   30165.91 Hz
AT1 =   2.17 sec
Hz per Pt 1stD =   0.46 Hz
SW2 =   1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1 =   13821.7402 Hz
O2 =   -0.5000 Hz
LB1 = 1.50   Hz
TP   A = -272.32
      B = 115.00
      C =   0.00

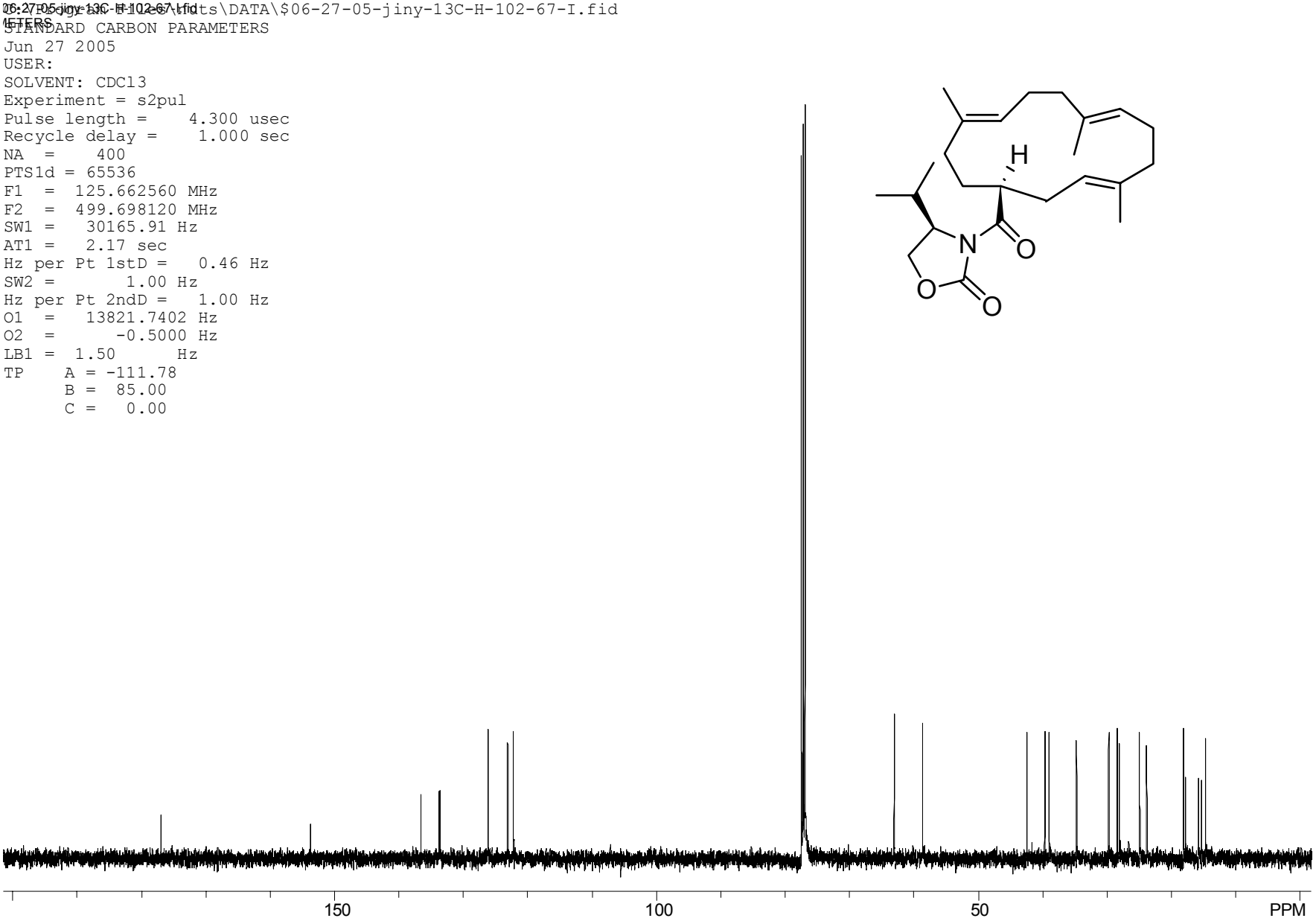




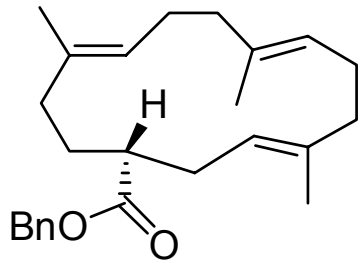

c:\jiny-g\data\nuts\DATA\$03-06-05-jiny-G-103-83-I-1.fid
03-06-05-jiny-G-103-83-I-1
Mar 4 2005
USER:
SOLVENT: CDC13
Experiment = s2pul
Pulse length = 8.975 usec
Recycle delay = 2.000 sec
NA = 8
PTS1d = 32768
F1 = 399.950684 MHz
F2 = 399.951111 MHz
SW1 = 8000.00 Hz
AT1 = 4.10 sec
Hz per Pt 1stD = 0.24 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2004.9036 Hz
O2 = -0.5000 Hz
LB1 = 0.00 Hz
TP A = -197.10
B = 39.00
C = 0.00
H
HO
O
2.4
2.2
2.0
1.8
1.6
5.3
5.2
5.1
5.0
4.9
4.8
12
10
8
6
4
2
PPM

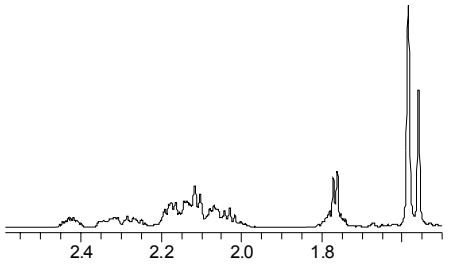

03-06-05-jiny-APT-G-103-83-I-1.fid
C:\Program Files\Varian\VNMR\DATA\$03-06-05-jiny-APT-G-103-83-I-1.fid
PARAMETERS
STANDARD CARBON PARAMETERS
Mar 4 2005
USER:
SOLVENT: CDCl3
Experiment = apt
Pulse length = 4.300 usec
Recycle delay = 1.000 sec
NA = 48
PTS1d = 65536
F1 = 125.662560 MHz
F2 = 499.698120 MHz
SW1 = 30165.91 Hz
AT1 = 2.17 sec
Hz per Pt 1stD = 0.46 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 13821.7402 Hz
O2 = -0.5000 Hz
LB1 = 1.50 Hz
TP A = 113.28
B = -190.00
C = 0.00
H
HO
O
150
100
50
PPM

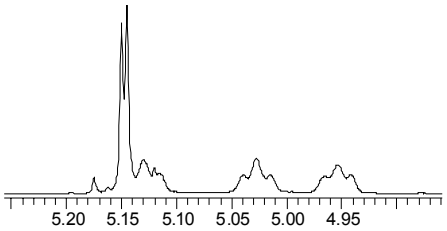

C:\Program Files\nuts\DATA\$06-27-05-jiny-1H-H-102-67-I.fid
06-27-05-jiny-1H-H-102-67-I
Jun 27 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length = 7.600 usec
Recycle delay = 2.000 sec
NA = 16
PTS1d = 32768
F1 = 500.075470 MHz
F2 = 500.075470 MHz
SW1 = 8000.00 Hz
AT1 = 4.10 sec
Hz per Pt 1stD = 0.24 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2502.9355 Hz
O2 = -0.5000 Hz
LB1 = 0.00 Hz
TP A = -62.45
B = 18.00
C = 0.00
H
N
O
O
O
1.6
1.4
1.2
1.0
2.4
2.3
2.2
2.1
2.0
1.9
3.95
3.90
3.85
3.80
3.75
3.70
5.2
5.0
4.8
4.6
4.4
4.2
10
8
6
4
2
PPM


06-27-05-jiny-13C-H-102-67.fid
C:\Program Files\Varian\vnmr\data\$06-27-05-jiny-13C-H-102-67-I.fid
STANDARD CARBON PARAMETERS
Jun 27 2005
USER:
SOLVENT: CDC13
Experiment = s2pul
Pulse length = 4.300 usec
Recycle delay = 1.000 sec
NA = 400
PTS1d = 65536
F1 = 125.662560 MHz
F2 = 499.698120 MHz
SW1 = 30165.91 Hz
AT1 = 2.17 sec
Hz per Pt 1stD = 0.46 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 13821.7402 Hz
O2 = -0.5000 Hz
LB1 = 1.50 Hz
TP A = -111.78
B = 85.00
C = 0.00
H
N
O
O
O
150
100
50
PPM

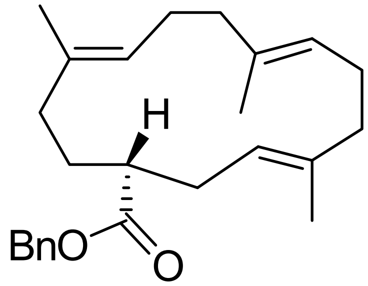
```
C:\Program Files\nuts\DATA\$05-27-05-jiny-H-135-43-I.fid
05-27-05-jiny-H-135-43-I
May 27 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    7.600 usec
Recycle delay =    2.000 sec
NA  =      8
PTS1d = 32768
F1  =  500.075470 MHz
F2  =  500.075470 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2503.2854 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -53.88
      B =  11.00
      C =   0.00
```

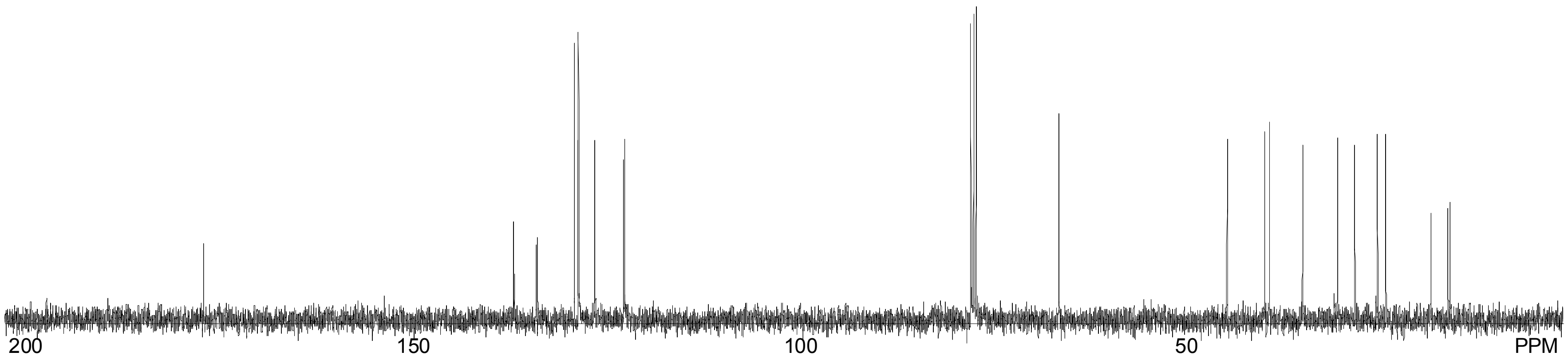




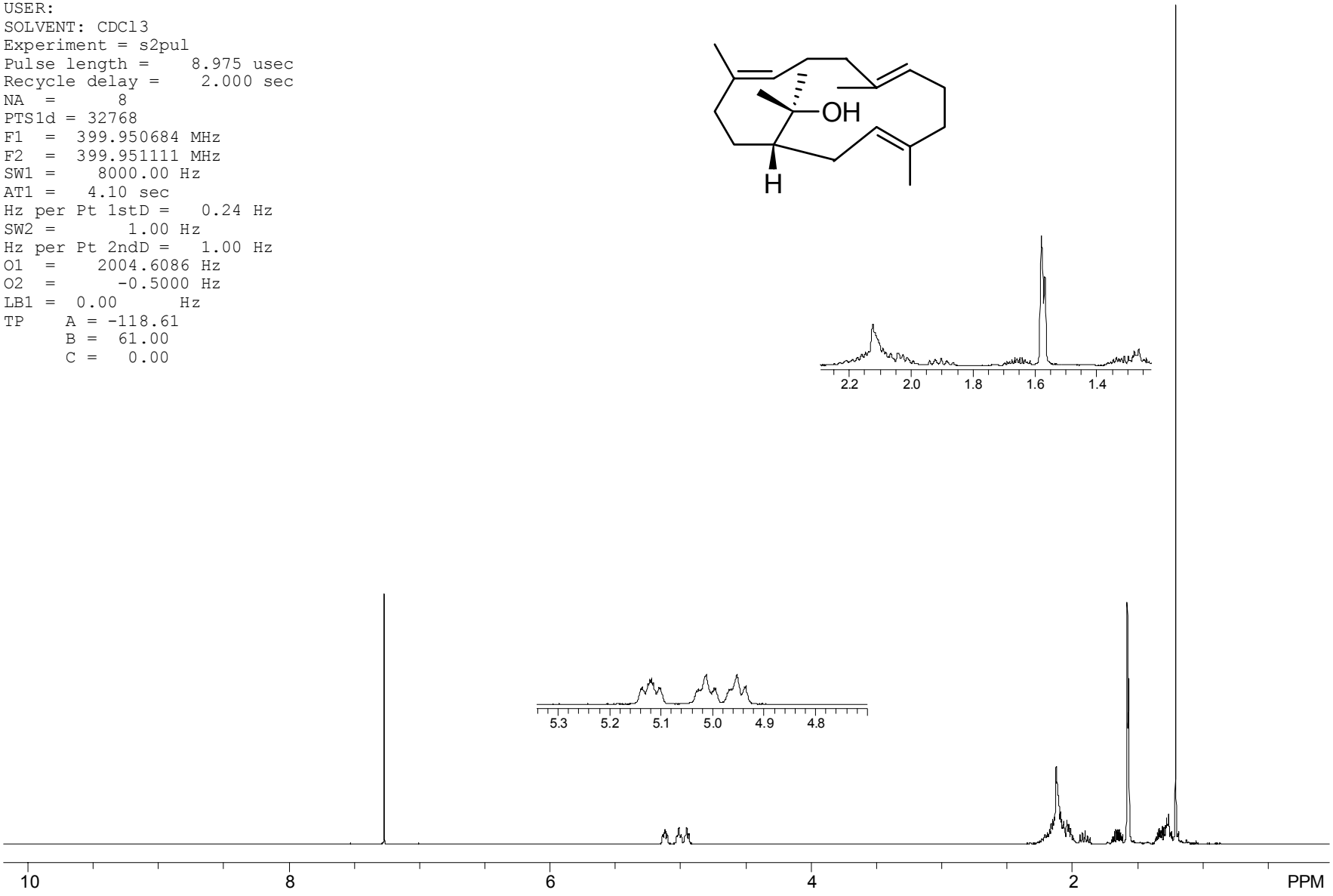


jiny-13C-H-135-43-I.fid
C:\Program Files\nuts\DATA\$05-26-05-jiny-13C-H-135-43-I.fid
13C OBSERVE;blank line
May 26 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length = 7.075 usec
Recycle delay = 1.000 sec
NA = 128
PTS1d = 65536
F1 = 100.578743 MHz
F2 = 399.950012 MHz
SW1 = 25000.00 Hz
AT1 = 2.62 sec
Hz per Pt 1stD = 0.38 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 11589.8672 Hz
O2 = -0.5000 Hz
LB1 = 1.50 Hz
TP A = -213.98
B = 230.00
C = 0.00





```
C:\Program Files\nuts\DATA\$05-30-05-jiny-H-136-44-I.fid
05-30-05-jiny-H-136-44-I
May 30 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    8.975 usec
Recycle delay =    2.000 sec
NA  =      8
PTS1d = 32768
F1  =  399.950684 MHz
F2  =  399.951111 MHz
SW1 =    8000.00 Hz
AT1 =   4.10 sec
Hz per Pt 1stD =   0.24 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    2004.6086 Hz
O2  =      -0.5000 Hz
LB1 =  0.00      Hz
TP    A = -118.61
      B =  61.00
      C =   0.00
```



```
jiny\13C-H-136-44-I.fid
C:\Program Files\nuts\DATA\$05-29-05-jiny-13C-H-136-44-I.fid
05/29/05,liux,C195C-237
May 29 2005
USER:
SOLVENT: CDCl3
Experiment = s2pul
Pulse length =    7.075 usec
Recycle delay =    1.000 sec
NA  =    352
PTS1d = 65536
F1  =  100.578743 MHz
F2  =  399.950012 MHz
SW1 =   25000.00 Hz
AT1 =   2.62 sec
Hz per Pt 1stD =   0.38 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =   11588.0996 Hz
O2  =      -0.5000 Hz
LB1 =  1.50      Hz
TP    A = -256.36
      B =  185.00
      C =   0.00
```