Lewis-Acid Catalyzed α -Functionalization of Ketals for the Regioselective Synthesis of α-Carbamoyl Ketals

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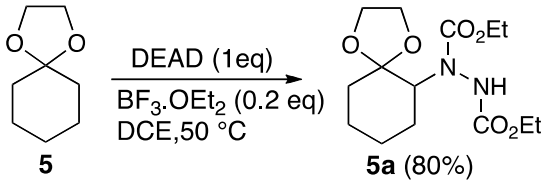
General Experimental

Melting points were measured on a Thomas-Hoover capillary tube apparatus and are uncorrected. Infrared spectra were recorded with a Nicolet FT-IR spectrophotometer as thin films on a NaCl disc unless otherwise noted. ^{1}H NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz as solutions in the indicated solvents and are reported in parts per million (ppm) relative to tetramethylsilane and referenced internally to residually protonated solvent. ^{13}C NMR spectra were recorded at 75 MHz on a General Electric QE-300 NMR spectrometer, and are referenced internally to the solvent indicated. Mass spectra were obtained on either a VG ZAB2E or a Finnegan TSQ70 spectrometer, using CI unless otherwise noted.

All reactions requiring anhydrous conditions were performed either in oven-dried (110 °C for greater than 5 hrs.) or flame-dried glassware under an atmosphere of dry argon. Anhydrous solvents were distilled under dry nitrogen or argon as follows: CH_2Cl_2 from CaH_2; THF and ethyl ether from sodium benzophenone ketyl; toluene and benzene from sodium wire; diglyme from CaH_2; acetone was dried over $CaSO_4$ and distilled. Reagents were purified in accordance with standard laboratory methods as given in Armarego and Chai.[1]

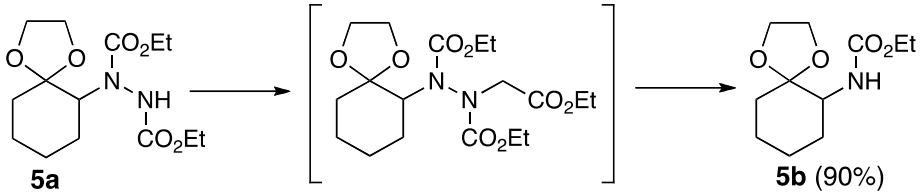
Reactions were monitored by thin layer chromatography using commercially available aluminum-backed plates coated with silica containing a fluorescent indicator (0.2 mm, Merck 60 F_{254}) and were visualized using standard techniques: UV fluorescence (254 or 365 nm); basic potassium permanganate solution; or 6 N aqueous H_2SO_4. Flash column chromatography was performed on silica gel (Kieselgel 60, 40-60 mm) using EtOAc/hexanes as eluent according to the method of Still *et al*.[2]

Carbamate resonance exhibited by the hydrazine adducts, even at 100 °C caused doubling of 1H NMR and 13C NMR signals.



5 **5a** (80%)

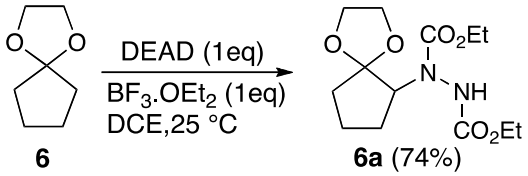
Cyclohexanone ethylene ketal **5** (40 mg, 0.282 mmol, 1 equiv) under argon was suspended in dry DCE (0.18 mL) at room temperature. To a stirring solution was added diethyl azodicarboxylate (0.05 ml, 0.282 mmol, 1 equiv) dropwise. This was followed by addition of distilled $BF_3.OEt_2$ (0.007 mL, 0.056 mmol, 0.2 equiv). The mixture was heated to 50 ˚C and stirred for 19 h at which point the starting material had been consumed, as indicated by tlc. The reaction was quenched with ethylene glycol (0.020 mL, 0.282 mmol, 1 equiv) followed 5 min later by addition of triethylamine (0.015 mL, 0.085 mmol, 0.3 equiv). The mixture was stirred for 5min then poured over stirring $NaHCO_3$ (20 mL) at 0 ˚C, and extracted with dichloromethane (3 x 5 mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **5a** (68 mg, 80%) as a white crystalline solid. Mp. 132-136 °C. IR (neat) 3307, 2980, 2940, 1750, 1716 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.45-6.90 (m, 1H), 3.64-4.50 (m, 9H), 0.78-2.02 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 110.7, 64.8, 63.9, 62.4, 61.6, 60.0, 58.4, 34.0, 26.7, 26.2, 24.3, 23.0, 21.0, 14.4. CI HRMS calcd. for $C_{14}H_{25}N_2O_6$ (M+H) 317.1713. Found 317.1713.



5a **5b** (90%)

Sodium hydride (76 mg 60% mineral oil dispersion, 1.905 mmol, 3 equiv) was added to a dry vial under argon and dissolved in dry diglyme (0.323 mL) at room temperature. In a separate vial **5a** (200 mg, 0.64 mmol, 1.0 equiv) was partially dissolved in diglyme (0.484 mL) with

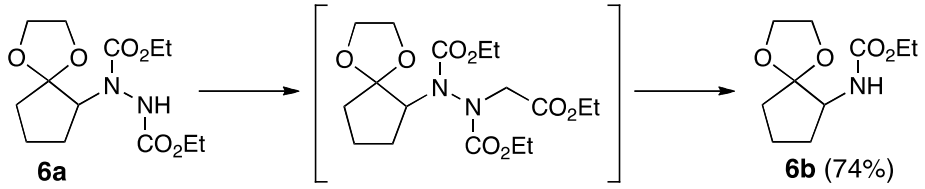
heating, and added to the original solution. Two subsequent rinses with diglyme (0.24 mL each) were used to transfer the remaining **5a** to the basic mixture. The mixture was stirred at room temperature for 30 min then it was placed in an ice bath. After 10 min at 0 °C, ethyl bromoacetate (156 mg, 0.953 mmol, 1.5 equiv) dissolved in diglyme (0.323 mL) was added dropwise. The temperature was held at 0 °C for 30 min then raised to room temperature for 2 h. The mixture was placed in an oil bath at 50 °C and stirred for 15 h, cooled to room temperature and poured over stirring NH_4Cl (20 mL) at 0 °C. The resulting solution was extracted with EtOAc (3 x 5 mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography yielded **5b** (131 mg, 90%) as a white crystalline solid. Mp. 50-53 °C.[3] IR (neat) 3320, 2935, 1700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.46-4.77 (m, 1H), 3.75-4.16 (m, 6H), 3.50-3.76 (m, 1H), 1.79-1.91 (m, 1H), 1.66-1.79 (m, 1H), 1.05-1.66 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 108.9, 65.3, 64.8, 60.6, 54.2, 34.1, 31.3, 23.9, 23.1, 14.6. ESI HRMS calcd. for $C_{11}H_{19}N_1O_4Na$ (M+Na) 252.1206. Found 252.1206.



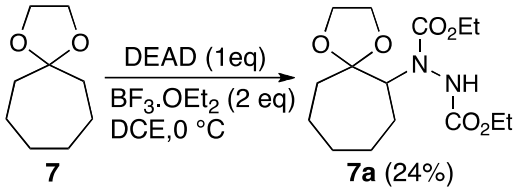
6 **6a** (74%)

Cyclopentanone ethylene ketal **6** (200 mg, 1.563 mmol, 1 equiv) under argon was suspended in dry DCE (0.782 mL) at room temperature. To this stirred solution was added diethyl azodicarboxylate (0.246 mL, 1.563 mmol, 1 equiv). This was followed by the addition of distilled $BF_3.OEt_2$ (0.039 mL, 0.313 mmol, 0.2 equiv) dropwise. The mixture was stirred at room temp for 5h at which point the starting material had been consumed, as indicated by tlc. The reaction was quenched with ethylene glycol (0.087 mL, 1.563mmol, 1 equiv) followed 5min later by triethylamine (0.065 mL, 0.469 mmol, 0.3 equiv). The mixture was stirred for another 5min, after which it was poured over stirring $NaHCO_3$ (20 mL) at 0 °C. The solution was extracted with dichloromethane (3 x 5 mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **6a** (329 mg, 74%) as a clear oil. IR (neat) 3297, 2980, 1751, 1714 cm^{-1}. ^1H NMR (300 MHz,

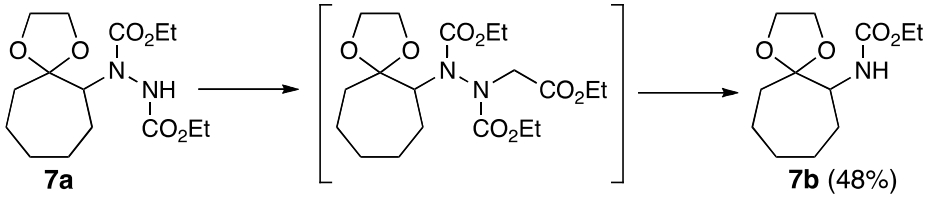
$CDCl_3$) δ 6.32-6.69 (m, 1H), 4.36-4.64 (m, 1H), 4.04-4.36 (m, 4H), 3.63-4.04 (m, 4H), 1.92-2.13 (m, 1H), 1.46-1.92 (m, 5H),1.14-1.38 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.7, 156.3, 116.4, 65.13, 64.1, 63.6, 62.5, 62.0, 36.0, 26.4, 20.6, 26.2, 14.5. CI HRMS calcd. for $C_{13}H_{23}N_2O_6$ (M+H) 303.1556. Found 303.1554.



Sodium hydride (40 mg 60% mineral oil dispersion, 0.997 mmol, 3 equiv) was added to a dry vial under argon and dissolved in dry diglyme (0.166 mL) at room temperature. In a separate vial **6a** (100 mg, 0.332 mmol, 1 equiv) was partially dissolved in diglyme (0.25 mL) with heating, and added to the original solution. Two subsequent rinses with diglyme (0.125 mL each) were used to transfer the remaining **6a** to the basic mixture. The mixture was stirred at room temperature for 30min and cooled in an ice bath. After 10min at 0 °C, ethyl bromoacetate (0.055 mL, 0.50 mmol, 1.5 equiv) in diglyme (0.166 mL) and added dropwise. The temperature was held at 0 °C for 30min then raised to room temperature for 2h. The mixture was placed in an oil bath at 50 °C and stirred for 15h, cooled to room temperature, and poured over stirring NH_4Cl (20 mL) at 0 °C. The solution was extracted with EtOAc (3 x 5 mL), and combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **6b** (53 mg, 74%) as a clear oil. IR (neat) 3342, 2976, 2891, 1715 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69-5.02 (m, 1H), 3.98-4.16 (q, 2H), 3.77-3.97 (m, 5H), 1.97-2.15 (m, 1H), 1.68-1.91 (m, 2H), 1.46-1.68 (m, 2H), 1.32-1.46 (m, 1H), 1.10-1.29 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 114.3, 64.0, 63.9, 59.7, 55.3, 33.1, 29.7, 17.9, 13.6. ESI HRMS calcd. for $C_{10}H_{18}NO_4$ (M+H) 216.1230. Found 216.1231.

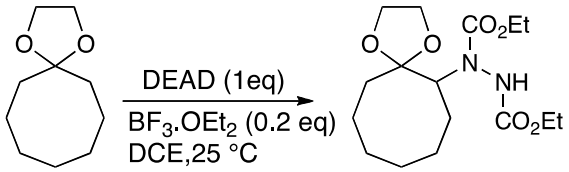


To a stirred solution of cycloheptanone ethylene ketal **7** (200 mg, 1.282 mol, 1 equiv) in dry DCE (0.321 mL) at room temperature was added diethyl azodicarboxylate (0.202 mL, 1.282 mmol, 1 equiv). This was followed by dropwise addition of distilled $BF_3.OEt_2$ (0.322 mL, 2.56 mmol, 2 equiv). The mixture was stirred at 0 °C for 66h at which point the starting material had been consumed, as indicated by tlc. The reaction was quenched with ethylene glycol (0.071 mL, 1.563 mmol, 1 equiv) followed after 5 min by triethylamine (0.532 mL, 3.845 mmol, 3 equiv). This mixture was stirred for another 5 min after which it was poured over stirring $NaHCO_3$ (20 mL) at 0 °C. The solution was extracted with DCM (3 x 5 mL), and the combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **7a** (97 mg, 24%) as a white crystalline solid. Mp. 56-57 °C. IR (neat) 3304, 2980, 2934, 1752, 1716 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.34-6.81 (m, 1H), 4.01-4.48 (m, 5H), 3.69-3.97 (m, 4H), 0.96-2.01 (m, 16H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.5, 156.0, 113.6, 113.3, 113.1, 64.5, 63.9, 62.7, 62.3, 61.8, 35.7, 35.5, 29.1, 27.5, 25.8, 25.4, 21.9, 14.4. CI HRMS calcd. for $C_{15}H_{27}N_2O_6$ (M+H) 331.1869. Found 331.1870.



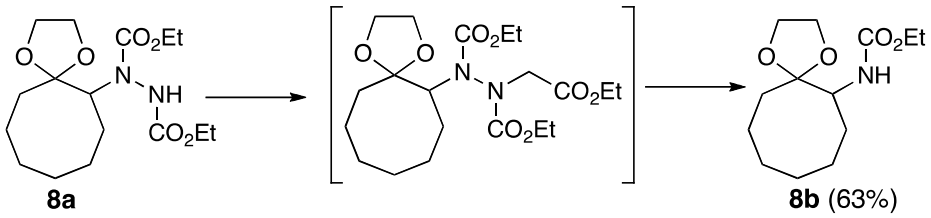
Sodium hydride (26mg 60% mineral oil dispersion, 3 equiv) was added to a dry vial under argon and dissolved in dry diglyme (0.107 mL) at room temperature. In a separate vial **7a** (71 mg, 0.215mmol, 1.0 equiv) was partially dissolved with diglyme (0.161 mL) and added to the above mixture. Two subsequent rinses with diglyme (0.080 mL each) were used to transfer the remaining **7a** to the basic mixture. The reaction was stirred at room temperature for 30 min then it was placed in an ice bath. After 10 min at 0 °C, ethyl bromoacetate (0.036 mL, 0.325

mmol, 1.5 equiv) was dissolved in diglyme (0.107 mL) and added dropwise. The temperature was held at 0 °C for 30 min, and raised to room temperature for 2h. The mixture was placed in an oil bath at 50 °C and stirred for 15 h. The mixture was then cooled to room temperature and poured over stirring NH_4Cl (20 mL) at 0 °C. The solution was extracted with EtOAc (3 x 5 mL), and the combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **7b** (5mg, 48%) as a clear oil. IR (neat) 3453, 3348, 2932, 1717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.75-5.05 (bd, 1H), 3.61-4.19 (m, 7H), 0.59-1.82 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 111.9, 65.4, 64.4, 60.6, 57.5, 35.5, 31.1, 28.1, 25.3, 21.0, 14.6. ESI HRMS calcd. for $C_{12}H_{22}NO_4$ (M+H) 244.1543. Found 244.1542.

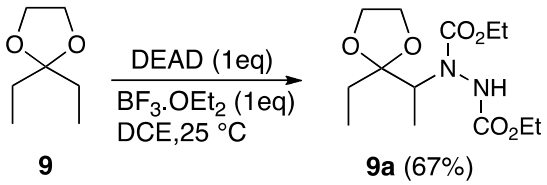


8 **8a** (86%)

To a stirred solution of cyclooctanone ethylene ketal **8** (50 mg, 0.294 mmol, 1 equiv) under argon in dry DCE (0.147 mL) at room temperature was added diethyl azodicarboxylate (0.046 ml, 0.294 mmol, 1 equiv) dropwise. This was followed by addition of distilled $BF_3.OEt_2$ (0.039 mL, 0.313 mmol, 0.2 equiv) dropwise. After 5h at room temperature the reaction was quenched with ethylene glycol (0.016 mL, 0.294 mmol, 1 equiv) followed 5min later by triethylamine (0.012 mL, 0.088 mmol, 0.3 equiv). The mixture was stirred for another 5min after which it was poured over stirring $NaHCO_3$ (20 mL) at 0 °C, and extracted with DCM (3 x 5 mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **8a** (83mg, 86%) as a white crystalline solid. Mp. 81-84 °C. IR (neat) 3308, 2980, 2929, 1750, 1717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.31-6.72 (m, 1H), 3.78-4.81 (m, 9H), 1.37-1.98 (m, 11H), 1.16-1.36 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 155.0, 113.2, 112.9, 63.4, 63.0, 61.4, 60.7, 58.6, 57.3, 31.2, 26.1, 25.7, 25.0, 24.8, 24.1, 20.7, 13.4. CI HRMS calcd. for $C_{16}H_{29}N_2O_6$ (M+H) 345.2026. Found 345.2023.

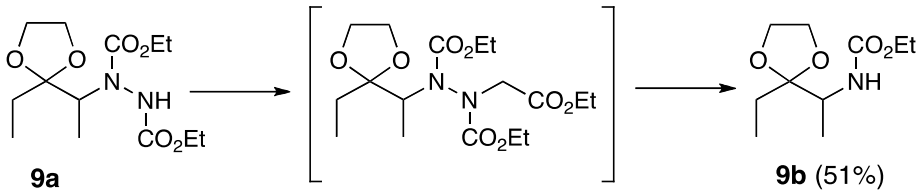


Sodium hydride (21 mg 60% mineral oil dispersion, 0.523mmol, 3 equiv) was added to a dry vial under argon and dissolved in dry diglyme (0.087 mL) at room temperature. In a separate vial **8a** (60 mg, 0.174mmol, 1 equiv) was partially dissolved with diglyme (0.131 mL) under gentle heating, and added to the original solution. Two subsequent rinses with diglyme (0.065 mL each) were used to transfer the remaining **8a** to the basic mixture. The mixture was stirred at room temperature for 30min then it was placed in an ice bath. After 10min at 0 °C, ethyl bromoacetate (0.029 mL, 0.262 mmol, 1.5 equiv) was dissolved in diglyme (0.087 mL) and added dropwise. The temperature was held at 0 °C for 30min then raised to room temperature for 2h. The mixture was placed in an oil bath at 50 °C and stirred for 15h. The mixture was cooled to room temperature, poured over stirring NH_4Cl (20 mL) at 0 °C, and extracted with EtOAc (3 x 5 mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **8b** (28 mg, 64%) as a clear oil. IR (neat) 3454, 3348, 2930, 1717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.69-4.98 (m, 1H), 3.82-4.19 (m, 7H), 1.38-1.85 (m, 12H), 1.06-1.28 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 112.3, 65.3, 64.9, 60.6, 54.2, 32.1, 32.0, 27.1, 26.7, 24.8, 21.7, 14.7. ESI HRMS calcd. for $C_{13}H_{24}NO_4$ (M+H) 258.1700. Found 258.1700.



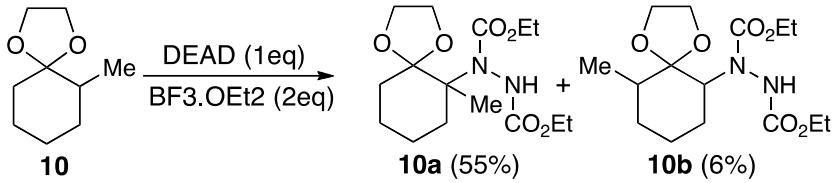
3-pentanone ethylene ketal **9** (200 mg, 1.538 mol, 1.0 equiv) under argon was suspended in dry DCE (0.385 mL) at room temperature. To a stirring solution was added diethyl azodicarboxylate (0.242 ml, 1.538 mmol, 1 equiv). This was followed by the dropwise addition

of distilled $BF_3.OEt_2$ (0.193 mL, 1.538 mmol, 1 equiv). The mixture was stirred at RT for 4.5h at which point the starting material had been consumed, as indicated by tlc. The reaction was quenched with ethylene glycol (0.085 mL, mmol, 1 equiv) followed 5min later by triethylamine (0.320 mL, 2.307 mmol, 1.5equiv). This mixture was stirred for another 5min after which it was poured over stirring $NaHCO_3$ (20 mL) at 0 °C, and extracted with DCM (3 x 5mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **9a** 296 mg, 67%) as a clear oil. IR (neat) 3302, 2981, 2941, 2886, 1750, 1711 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.08-6.68 (m, 1H), 3.80-4.68 (m, 9H), 0.91-1.85 (m, 11H), 0.73-0.90 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 156.0, 112.6, 66.0, 65.3, 62.5, 62.4, 61.8, 56.7, 55.4, 27.8, 14.4, 11.5, 10.9, 7.4. CI HRMS calcd. for $C_{13}H_{25}N_2O_6$ (M+H) 305.1713. Found 305.1714.



Sodium hydride (20 mg 60% mineral oil dispersion, 0.493 mmol, 3 equiv) was added to a dry vial under argon and dissolved with dry diglyme (0.082 mL) at room temperature. In a separate vial **9a** (50 mg, 0.164 mmol, 1 equiv) was partially dissolved in diglyme (0.123 mL) under heating, and added to the original solution. Two subsequent rinses with diglyme (0.062 mL each) were used to transfer the remaining **9a** to the basic mixture. The mixture was stirred at room temperature for 30 min then it was placed in an ice bath. After 10min at 0 °C, ethyl bromoacetate (0.028 mL, 0.246 mmol, 1.5 equiv) was dissolved in diglyme (0.082 mL) and added dropwise to the above mixture. The temperature was held at 0 °C for 30min, then raised to room temperature for 2h. The reaction was placed in an oil bath at 50 °C and stirred for 15h, cooled to room temperature and poured over stirring NH_4Cl (20 mL) at 0 °C. The solution was extracted with EtOAc (3 x 5mL), and the combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **9b** (18 mg, 51%) as a clear oil. IR (neat) 3340, 2974, 2879, 1699 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.45-4.79 (m, 1H), 3.76-4.26 (m, 7H), 1.47-1.69 (m, 2H), 1.09-1.27 (t, 3H), 0.98-1.09 (d, 3H), 0.76-

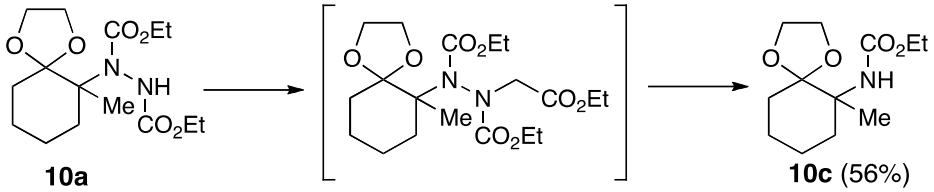
0.90 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 112.0, 65.9, 65.8, 60.7, 50.8, 27.7, 16.0, 14.6, 7.6. ESI HRMS calcd. for $C_{10}H_{20}NO_4$ (M+H) 218.1392. Found 218.1388.



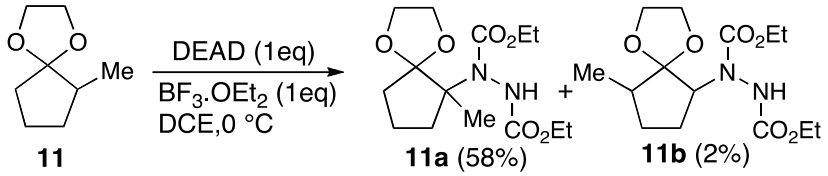
10 **10a** (55%) **10b** (6%)

2-methylcyclohexanone ethylene ketal **10** (200 mg, 1.282 mmol, 1 equiv) under argon was suspended in dry DCE (0.321 mL) at room temperature. To the stirred mixture was added diethyl azodicarboxylate (0.202 ml, 1.282 mmol, 1 equiv). This was followed by the dropwise addition of distilled $BF_3.OEt_2$ (0.322 mL, 2.564 mmol, 2 equiv). The mixture was stirred at 0 °C for 66h at which point the starting material had been consumed, as indicated by tlc. The reaction was quenched with ethylene glycol (0.071 mL, 1.563 mmol, 1 equiv) followed 5min later by triethylamine (0.532 mL, 3.845 mmol, 3 equiv). The mixture was stirred for another 5min after which it was poured over stirring $NaHCO_3$ (20 mL) at 0 °C. This solution was extracted with DCM (3 x 5 mL), and the combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **10a** (217mg, 55%) as a clear oil. IR (neat) 3297, 2983, 2940, 2872, 1750, 1715 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43-7.15 (m, 1H), 3.54-4.29 (m, 8H), 2.09-2.59 (m, 1H), 0.69-2.01 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 156.1, 113.6, 113.1, 68.0, 66.7, 64.8, 64.2, 62.0, 61.4, 36.0, 33.5, 31.5, 22.7, 21.4, 20.6, 14.3. CI HRMS calcd. for $C_{15}H_{26}N_2O_6$ (M+) 330.1791. Found 330.1790.

In the above reaction a by-product was isolated. Compound **10b** was only partially separable from its regioisomer **10a** through flash column chromatography. GCMS data was used to determine yield of **10b** (25 mg, 6%). Clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.44-7.07 (m, 1H), 3.47-4.36 (m, 9H), 0.76-2.54 (m, 16H). CI HRMS calcd. for $C_{15}H_{26}N_2O_6$ (M+) 330.1791. Found 330.1786.

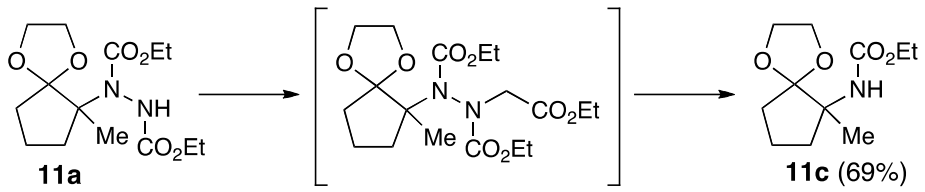


Sodium hydride (26 mg 60% mineral oil dispersion, 0.87 mmol, 3 equiv) was added to a dry vial under argon and dissolved with dry diglyme (0.145 mL) at room temperature. In a separate vial **10a** (9:1 major to minor hydrazine mixture, 96 mg, 0.290mmol, 1 equiv) was partially dissolved in diglyme (0.218 mL) under heating, and added to the original solution. Two subsequent rinses with diglyme (0.108 mL each) were used to transfer the remaining **10a** to the basic mixture. The mixture was stirred at room temperature for 30min then placed in an ice bath. After 10min at 0 °C, ethyl bromoacetate (0.048 mL, 0.436 mmol, 1.5 equiv) was dissolved in diglyme (0.145 mL) and added dropwise to the above mixture. The temperature was held at 0 °C for 30 min then raised to room temperature for 2h. The mixture was placed in an oil bath at 50 °C and stirred for 15h. The mixture was cooled to room temperature and poured over stirring NH_4Cl (20 mL) at 0 °C, and the solution extracted with EtOAc (3 x 5mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **10c** (29 mg, 56%) as a clear oil. IR (neat) 3429, 2980, 2936, 2889, 1728cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79-4.96 (s, 1H), 3.85-4.05 (m, 6H), 2.25-2.44 (m, 1H), 1.28-1.70 (m, 7H), 1.05-1.28 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 110.4, 65.4, 65.2, 60.0, 59.2, 33.3, 30.8, 23.2, 20.9, 19.7, 14.6. ESI HRMS calcd. for $C_{12}H_{22}NO_4$ (M+H) 244.1543. Found 244.1543.



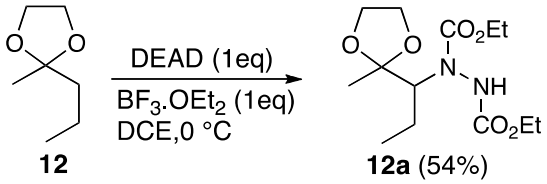
To a stirred solution of 2-methylcyclopentanone ethylene ketal **11** (200 mg, 1.408mol, 1.0 equiv) under argon in dry DCE (0.352 mL) at room temperature was treated with diethyl azodicarboxylate (0.222 ml, 1.408 mmol, 1 equiv). This was followed by the dropwise addition of distilled $BF_3.OEt_2$ (0.177 mL, 1.408 mmol, 1 equiv). The mixture was stirred at 0 °C for 5h at

which point the starting material had been consumed, as indicated by tlc. The reaction was quenched with ethylene glycol (0.078 mL, 1.408 mmol, 1 equiv) followed by triethylamine (0.292 mL, 2.816 mmol, 1.5 equiv), and poured over stirring $NaHCO_3$ (20 mL) at 0 °C. The solution was then extracted with DCM (3 x 5 mL), and combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **11a** (0.244 g, 58%) as a clear oil. IR (neat) 3316, 2980, 2900, 1751, 1718 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.18-6.55 (m, 1H), 3.70-4.33 (m, 9H), 0.93-2.40 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 156.5, 155.9, 118.5, 118.1, 71.1, 68.6, 64.8, 64.0, 62.0, 61.8, 61.6, 37.1, 36.5, 35.7, 33.1, 22.7, 20.5, 19.0, 17.5, 14.5, 14.4. CI HRMS calcd. for $C_{14}H_{25}N_2O_6$ (M+H) 317.1713. Found 317.1711. A by product with a mass relating to the minor isomer was identified in trace amounts by GCMS, corresponding to a **11b** (7 mg, 2%).



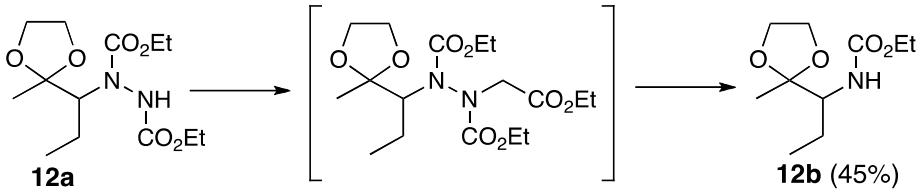
Sodium hydride (30 mg 60% mineral oil dispersion, 0.748 mmol, 3 equiv) was added to a dry vial under argon and dissolved with dry diglyme (0.126 mL) at room temperature. In a separate vial **11a** (80 mg, 0.253 mmol, 1 equiv) was partially dissolved in diglyme (0.190 mL) with heating, and added to the original solution. Two subsequent rinses with diglyme (0.095 mL each) were used to transfer the remaining **11a** to the basic mixture. The reaction was stirred at room temperature for 30min then it was placed in an ice bath. After 10min at 0 °C, ethyl bromoacetate (0.042 mL, 0.380 mmol, 1.5 equiv) was dissolved in diglyme (0.126 mL) and added dropwise. The temperature was held at 0 ˚C for 30min then raised to room temperature for 2h. The reaction was placed in an oil bath at 50 ˚C and stirred for 15 hrs. The reaction was then cooled to room temperature and poured over stirring NH_4Cl (20 mL) at 0 ˚C. This solution was extracted with EtOAc (3 x 5 mL), and the combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **11c** (40mg, 69%) as a clear oil. IR (neat) 3427, 2978, 2889, 1727 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 5.06-5.24 (s, 1H), 3.82-4.09 (m, 6H), 2.19-2.40 (m, 1H), 1.46-1.91 (m, 5H), 1.24-1.32

(s, 3H), 1.10-1.21 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 117.4, 65.1, 62.4, 60.1, 34.8, 33.3, 19.3, 18.1, 14.6. ESI HRMS calcd. for $C_{11}H_{20}NO_4$ (M+H) 230.1387. Found 230.1387.



12 **12a** (54%)

2-pentanone ethylene ketal **12** (200 mg, 1.538 mol, 1.0 equiv) under argon was suspended in dry DCE (0.385 mL) at room temperature. To this solution was added diethyl azodicarboxylate (0.242 ml, 1.538 mmol, 1 equiv). This was followed by the dropwise addition of distilled $BF_3.OEt_2$ (0.193 mL, 1.538 mmol, 1 equiv). The mixture was stirred at room temperature for 4.5h at which point the starting material had been consumed, as indicated by tlc. The reaction was quenched with ethylene glycol (0.085 mL, 1 equiv) followed by triethylamine (0.320 mL, 2.307 mmol, 1.5 equiv). The mixture was stirred for another 5min after which it was poured over stirring $NaHCO_3$ (20 mL) at 0 °C, and the solution was extracted with DCM (3 x 5 mL). The combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **12a** (239 mg, 54%) as a white crystalline solid. Mp. 73-76 °C. IR (neat) 3296, 2983, 2881, 1757, 1714 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96-6.38 (m, 1H), 3.77-4.30 (m, 9H), 0.63-1.75 (m, 14H). ^{13}C NMR (750 MHz, $CDCl_3$) δ 157.0, 156.8, 110.3, 67.7, 65.2, 64.4, 63.6, 62.5, 61.8, 53.4, 22.0, 18.8, 14.5, 14.1, 11.5. CI HRMS calcd. for $C_{13}H_{25}N_2O_6$ (M+H) 305.1713. Found 305.1712. A mass relating to the minor isomer was identified in trace amounts by GCMS, corresponding to a yield of less than 2%.



12a **12b** (45%)

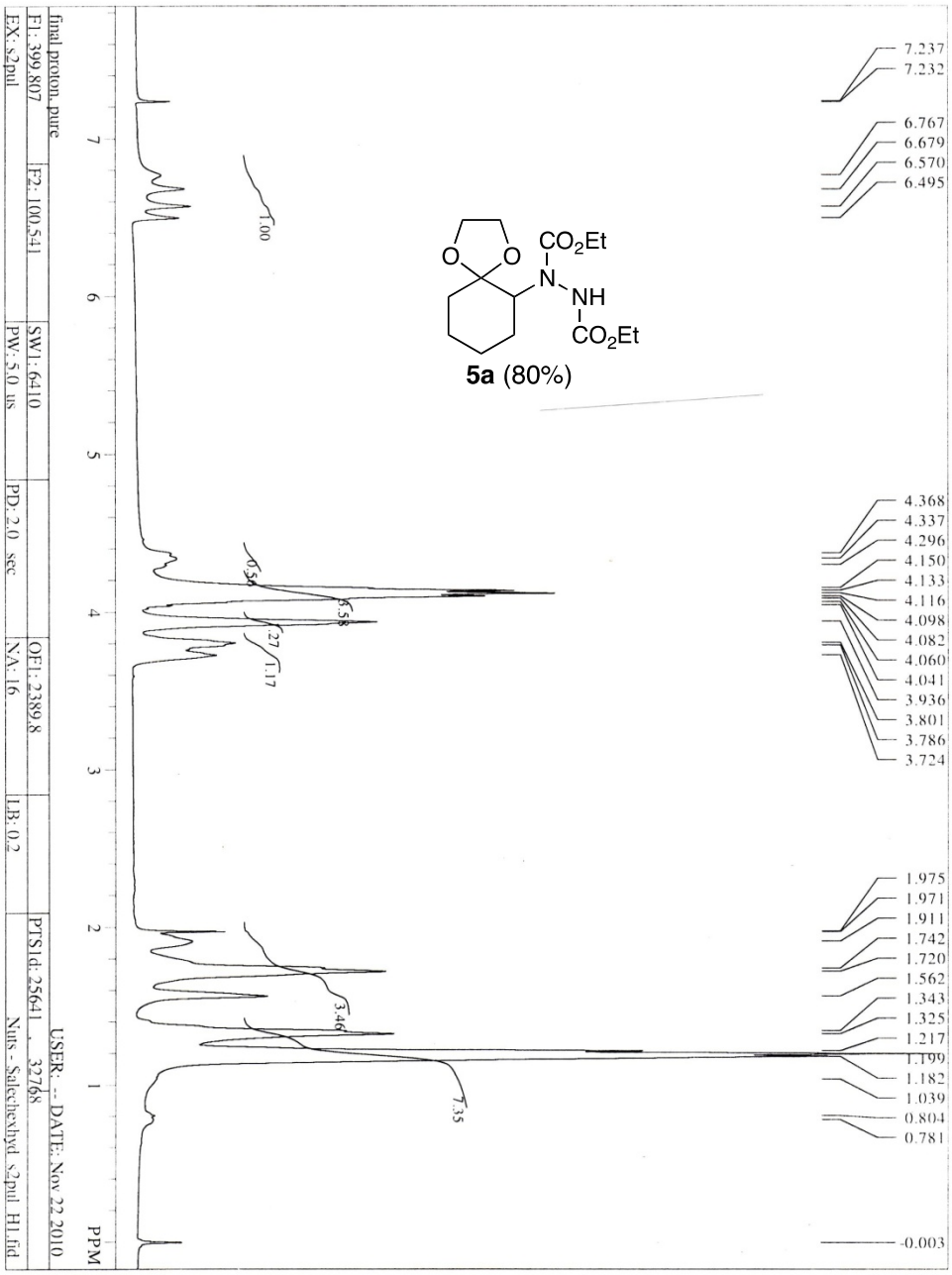
Sodium hydride (100 mg 60% mineral oil dispersion, 0.987 mmol, 3 equiv) was added to a dry vial under argon and dissolved with dry diglyme (0.165 mL) at room temperature. In a separate vial **12a** (100 mg, 0.329 mmol, 1 equiv) was partially dissolved in diglyme (0.247 mL) under heating, and added to the original solution. Two subsequent rinses with diglyme (0.123 mL each) were used to transfer the remaining **12a** to the basic mixture. The mixture was stirred at room temperature for 30min, then it was placed in an ice bath. After 10min at 0 °C, ethyl bromoacetate (0.055 mL, 0.494 mmol, 1.5 equiv) was dissolved in diglyme (0.165 mL) and added dropwise. The temperature was held at 0 °C for 30min then raised to room temperature for 2h. Next the mixture was placed in an oil bath at 50 °C and stirred for 15h. The mixture was cooled to room temperature and poured over stirring NH_4Cl (20 mL) at 0 °C, and the solution was extracted with EtOAc (3 x 5 mL), and the combined extracts were dried over Na_2SO_4, and solvent was evaporated *in vacuo*. Purification of the residue by column chromatography gave **12b** (32mg, 45%) as a clear oil. IR (neat) 3340, 2974, 2878, 1722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.30-4.63 (d, 1H), 3.98-4.14 (q, 2H), 3.79-3.98 (m, 4H), 3.49-3.71 (t, 1H), 1.57-1.77 (m, 1H), 1.09-1.28 (m, 7H), 0.82-0.93 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 110.3, 65.2, 65.1, 60.7, 58.4, 22.8, 21.5, 14.6, 10.6. ESI HRMS calcd. for $C_{10}H_{19}NO_4$(M+H) 218.1392. Found 218.1388.

References and Footnotes.

(1) Armarego, W. L. F.; Chai, C. L. L. Purification of Laboratory Chemicals. 5th ed., Elsevier: Oxford, **2003**.

(2) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem*. **1978**, *43*, 2923-2925.

(3) Tamejiro, H.; Shinsaki, F.; Hitosi, N. *Bull. Chem. Soc. Japan*. **1972**, *45*, 3500-3501.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4.098
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4.060
4.041
3.936
3.801
3.786
3.724
1.975
1.971
1.911
1.742
1.720
1.562
1.343
1.325
1.217
1.199
1.182
1.039
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0.781
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1.00
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0.58
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1.17
3.46
7.35
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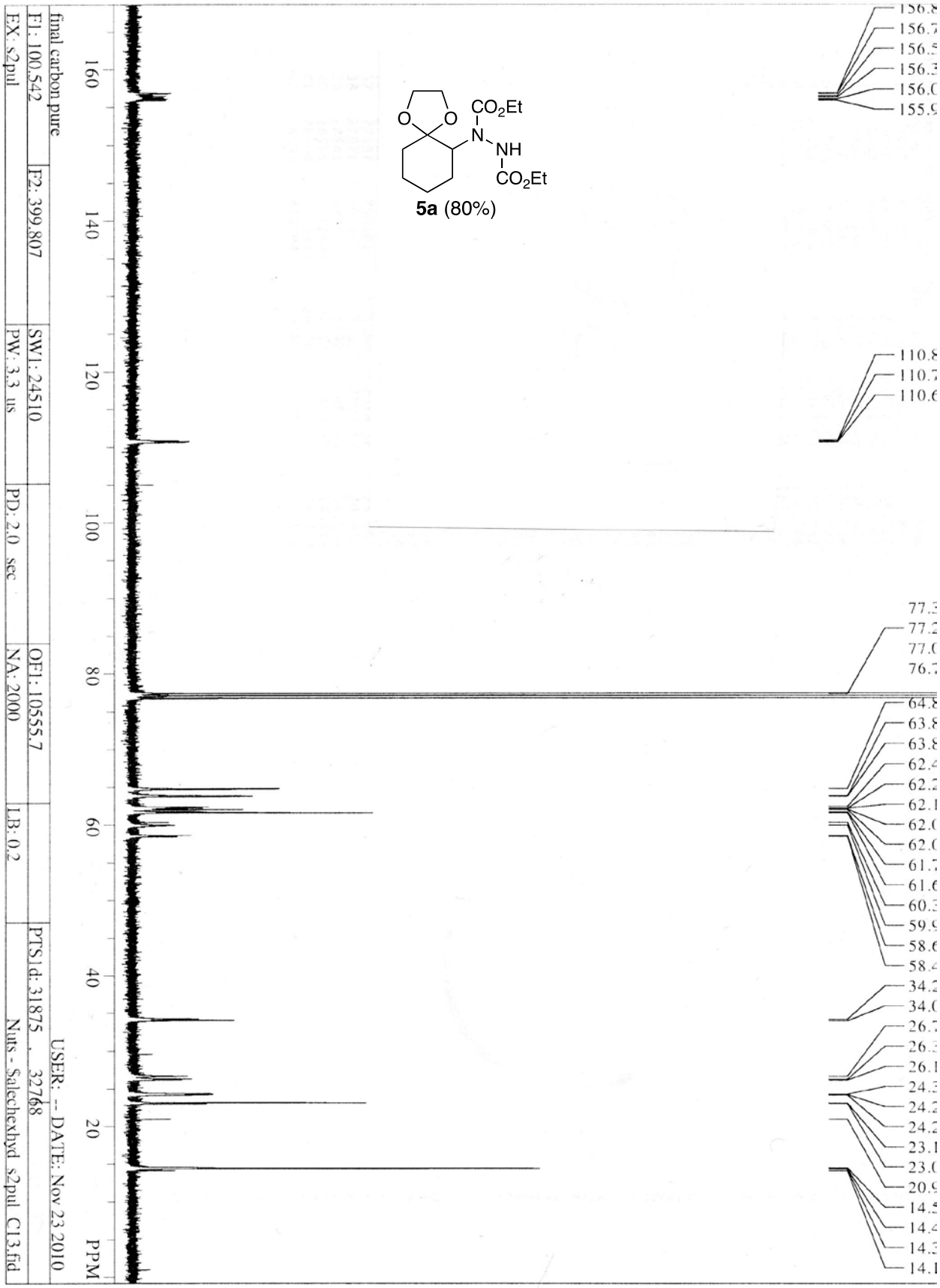
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59.9
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26.3
26.3
26.1
24.3
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23.1
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14.0
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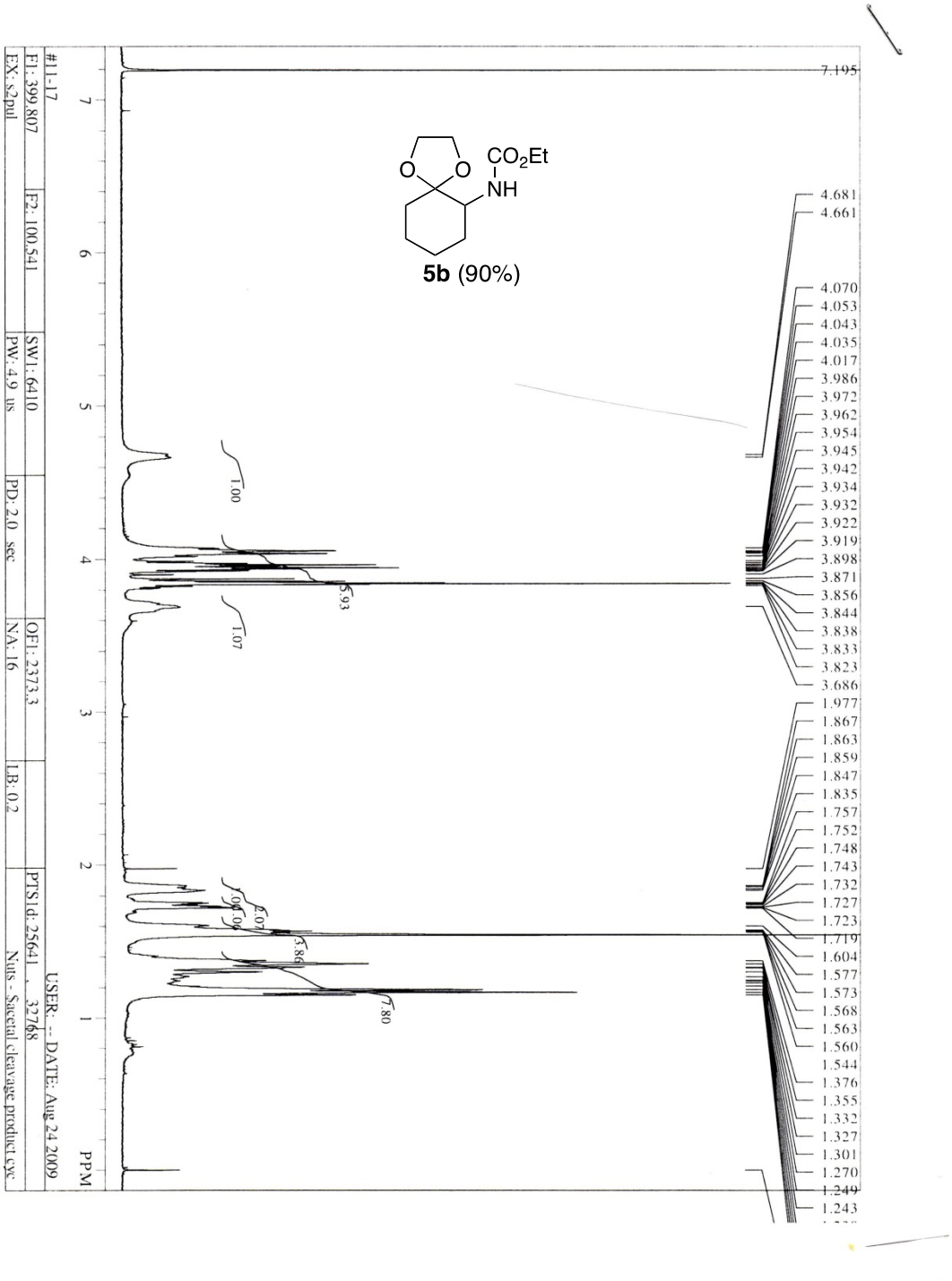
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NH
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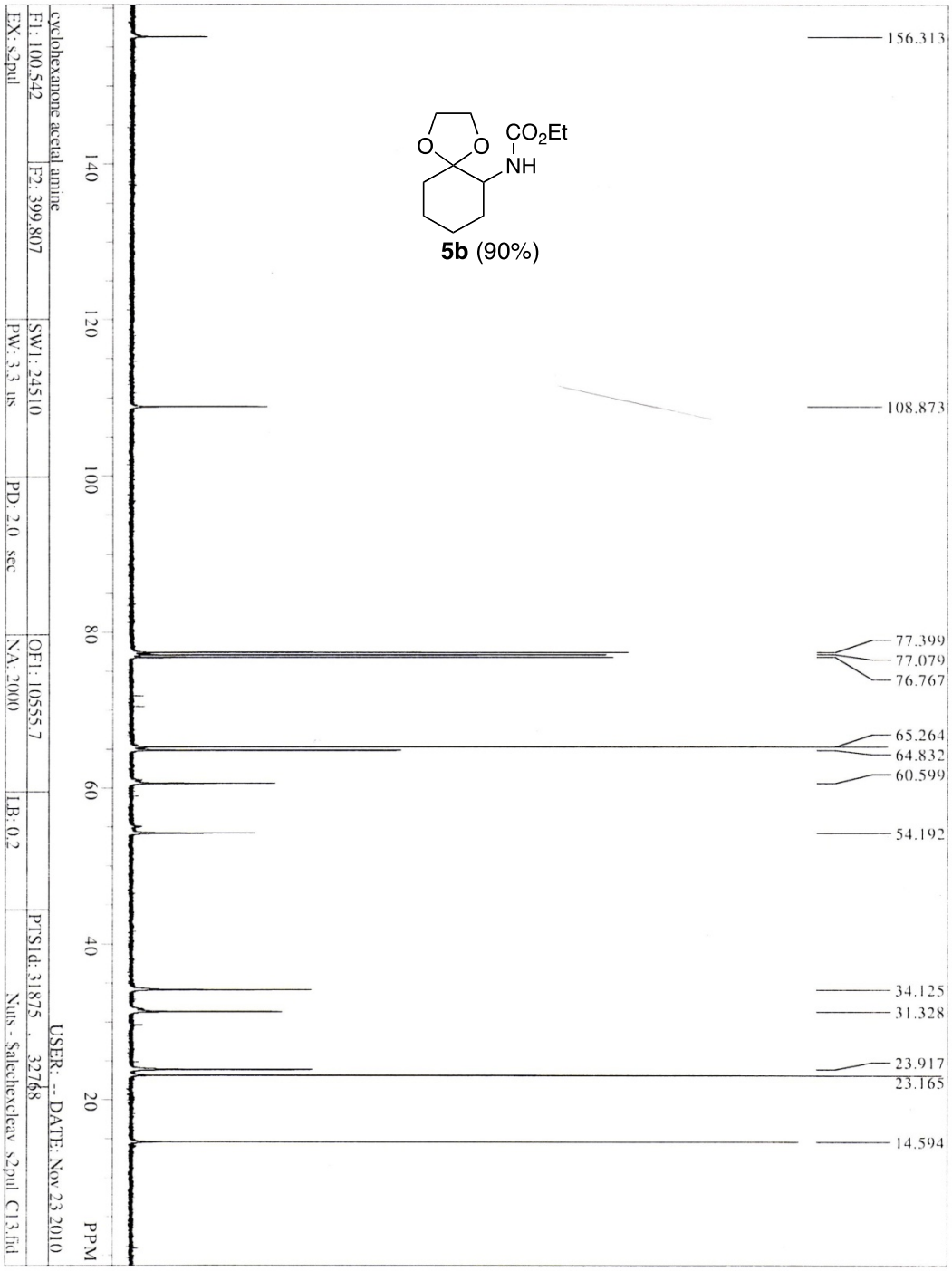
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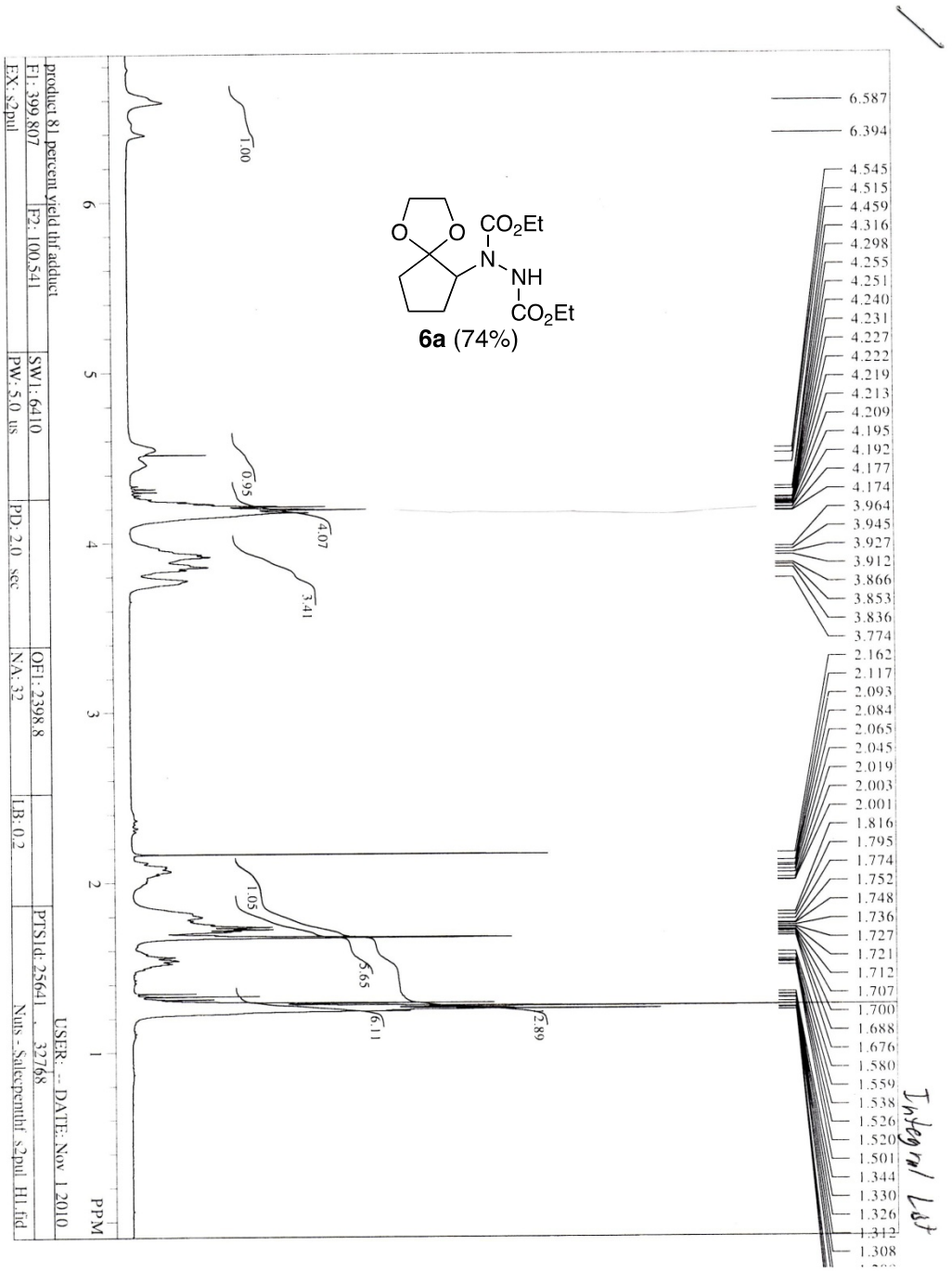
5b (90%)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32768
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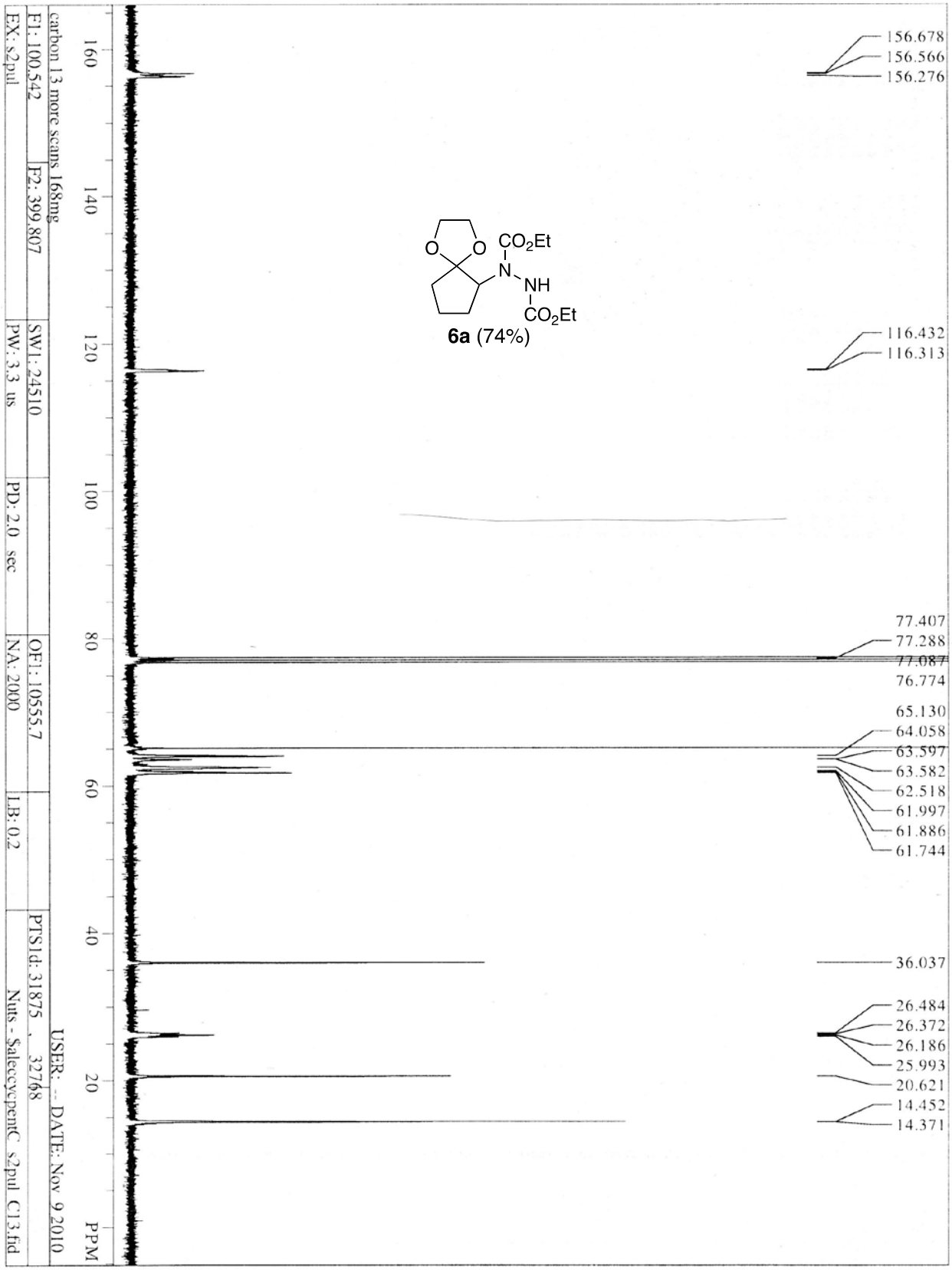
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O
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CO2Et
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120
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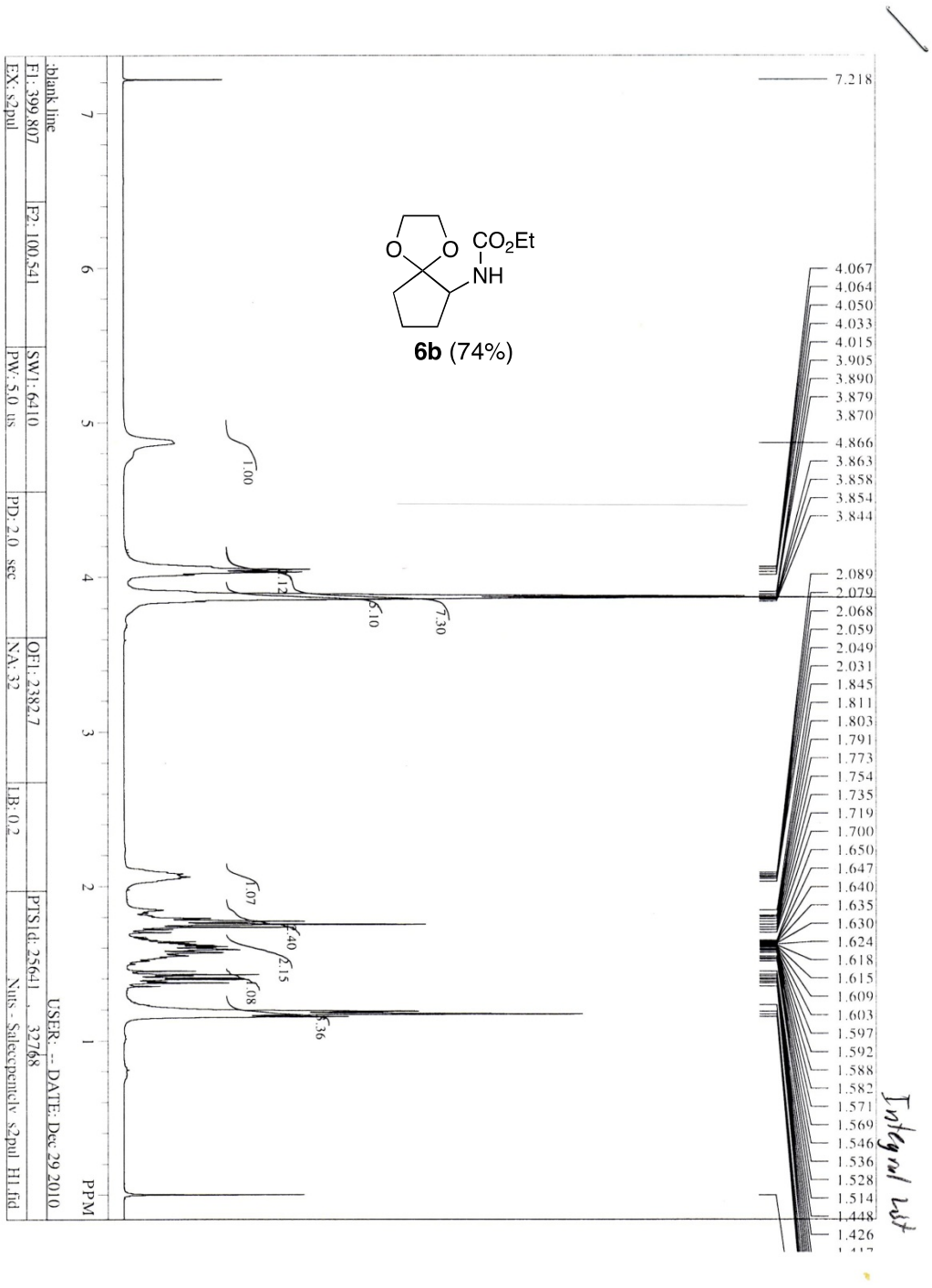
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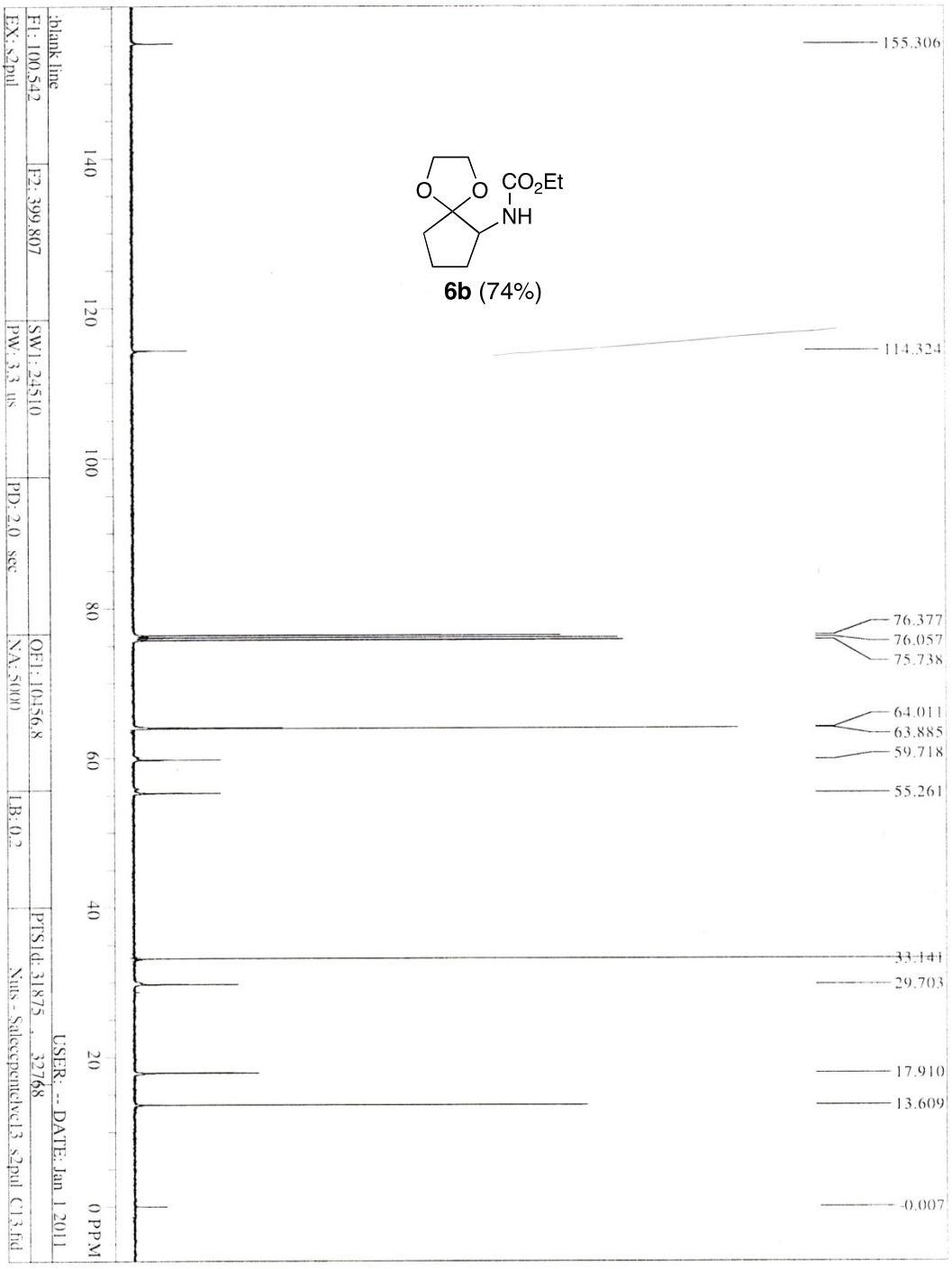
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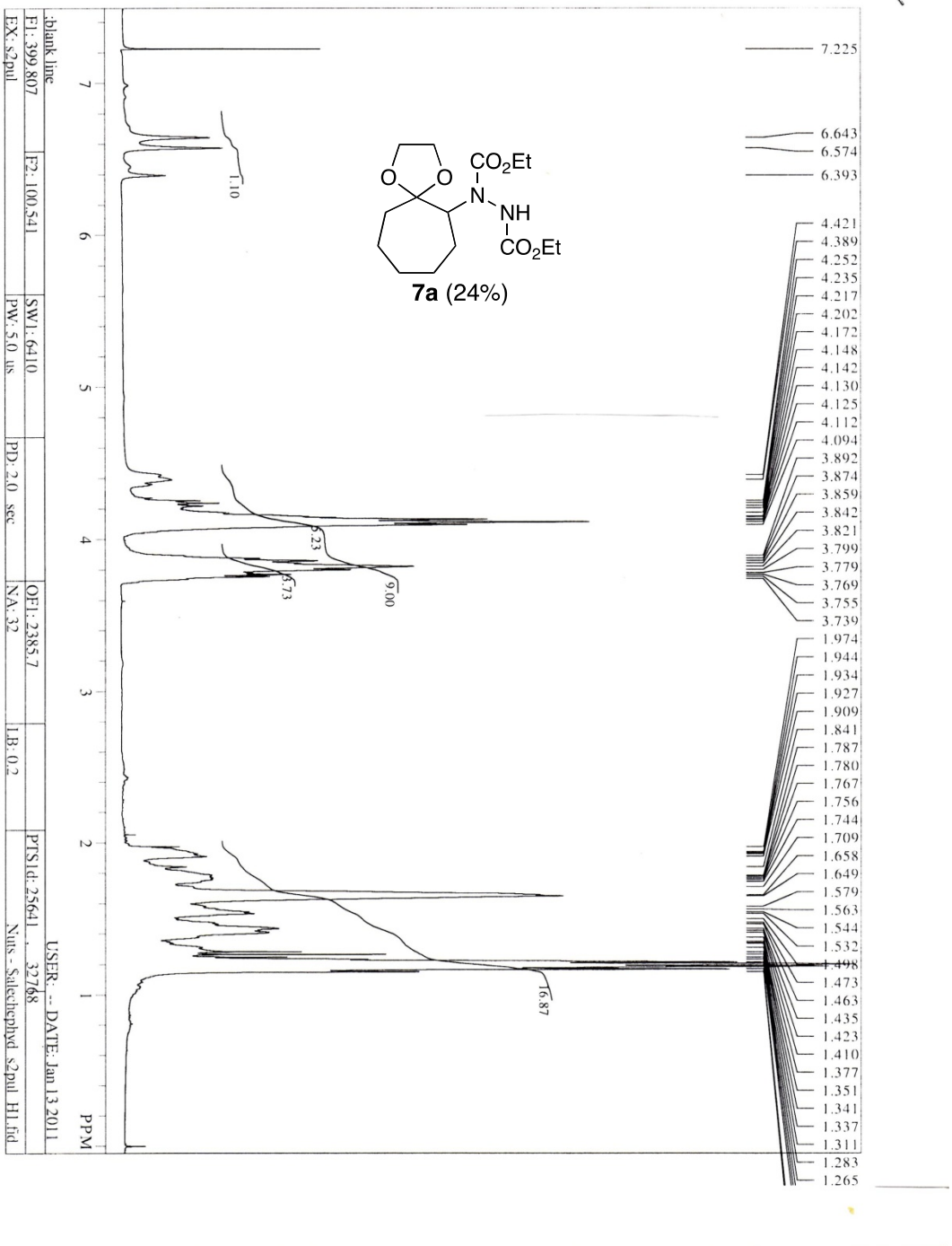
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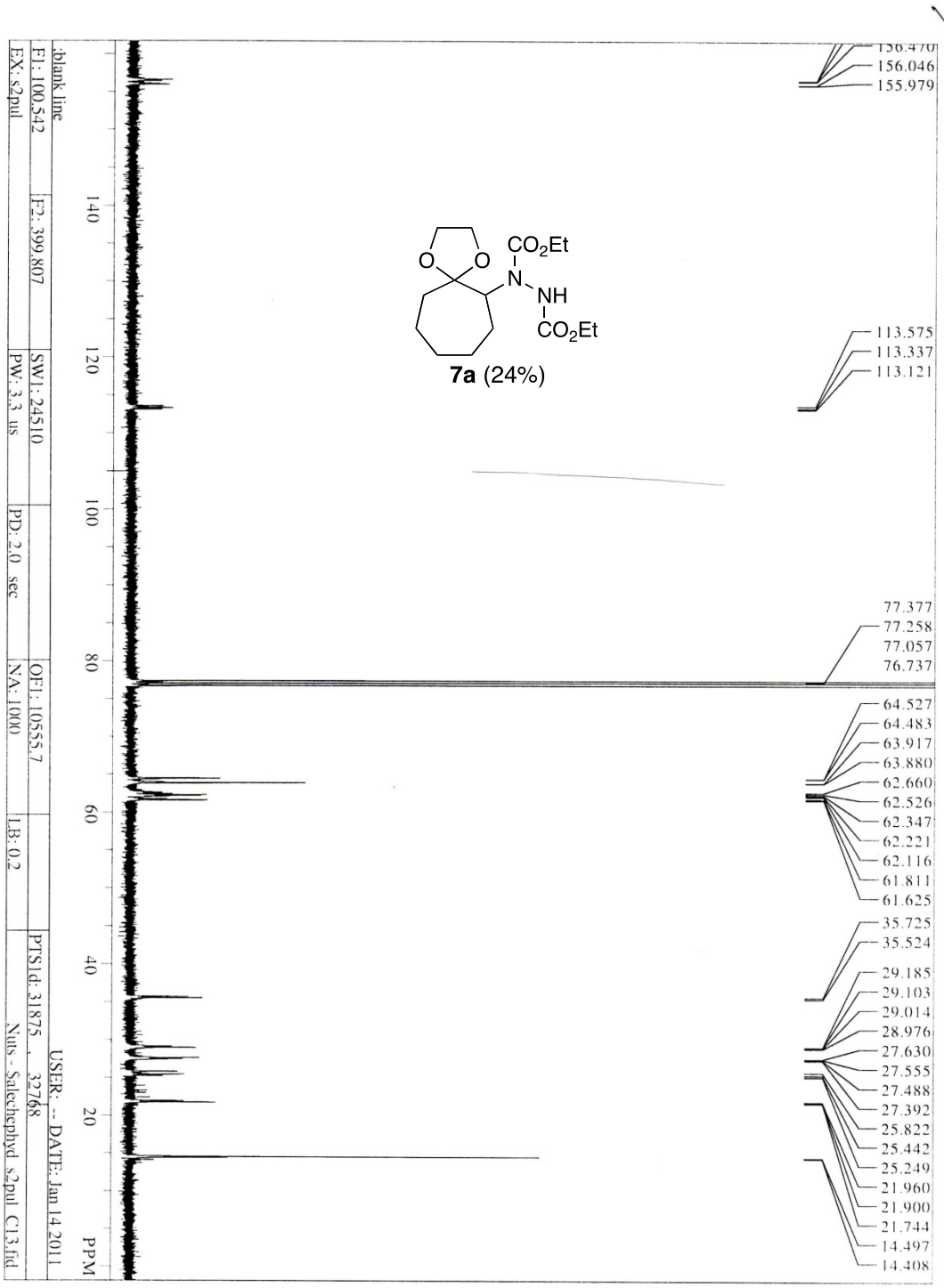
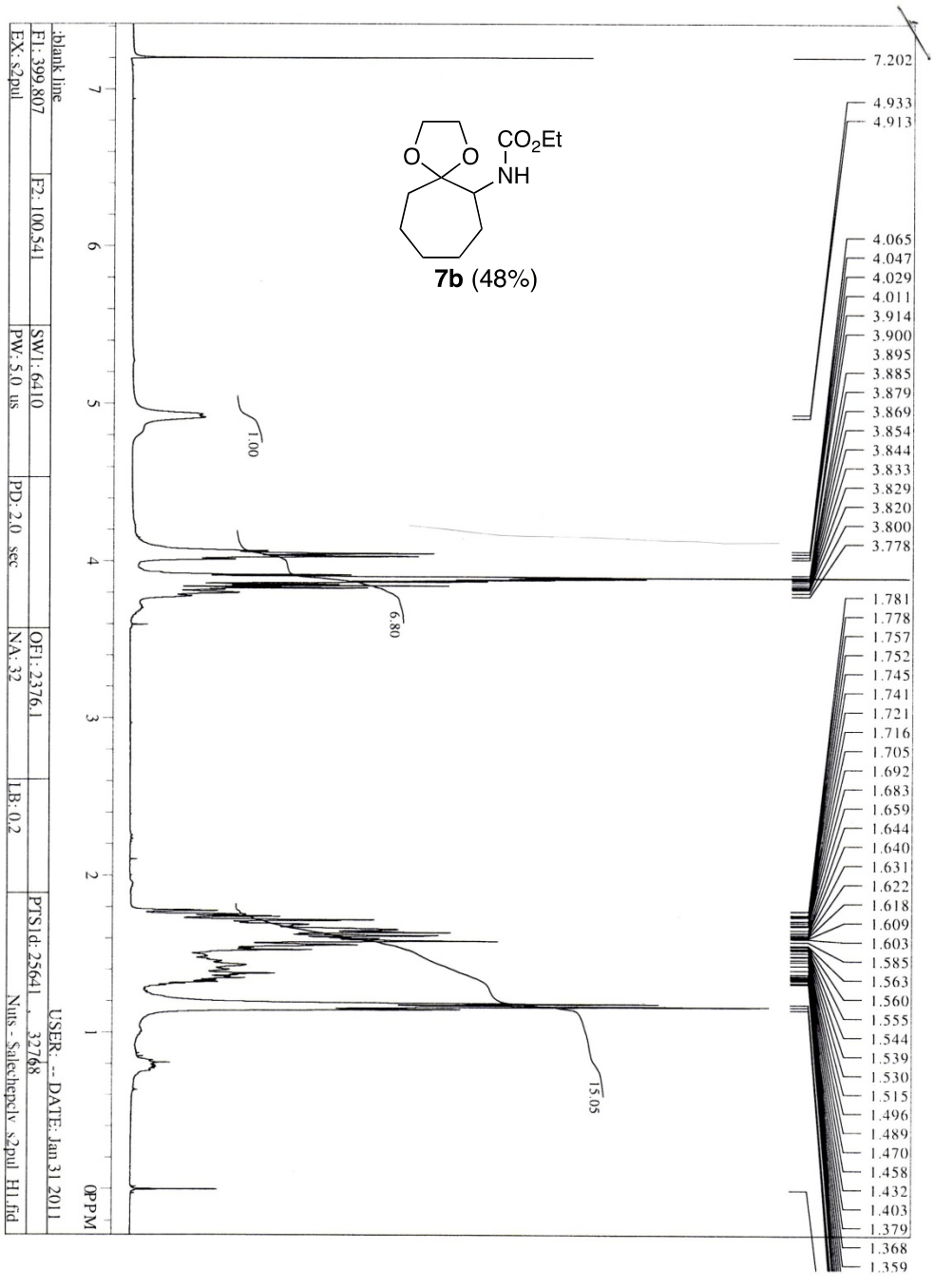
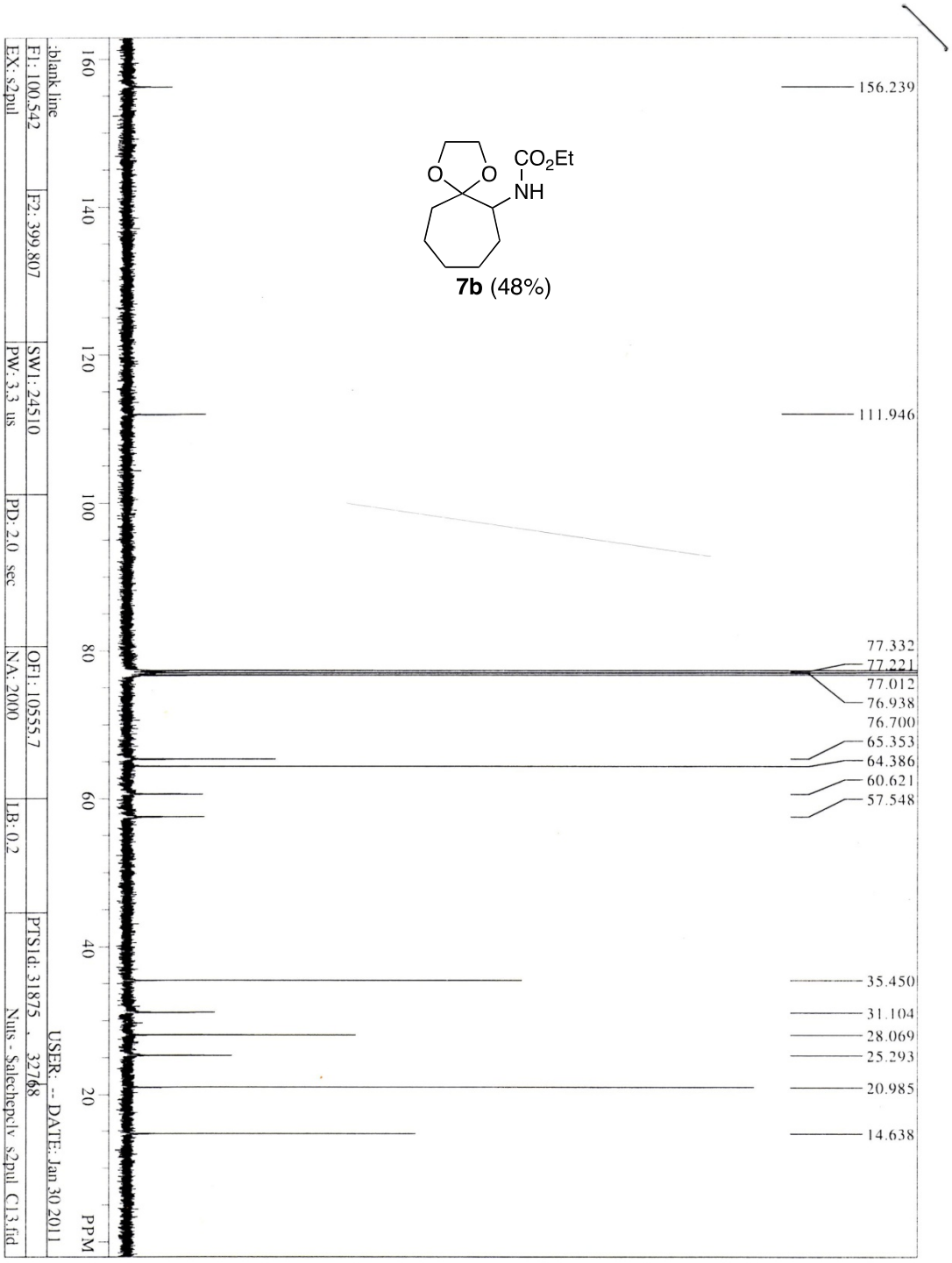
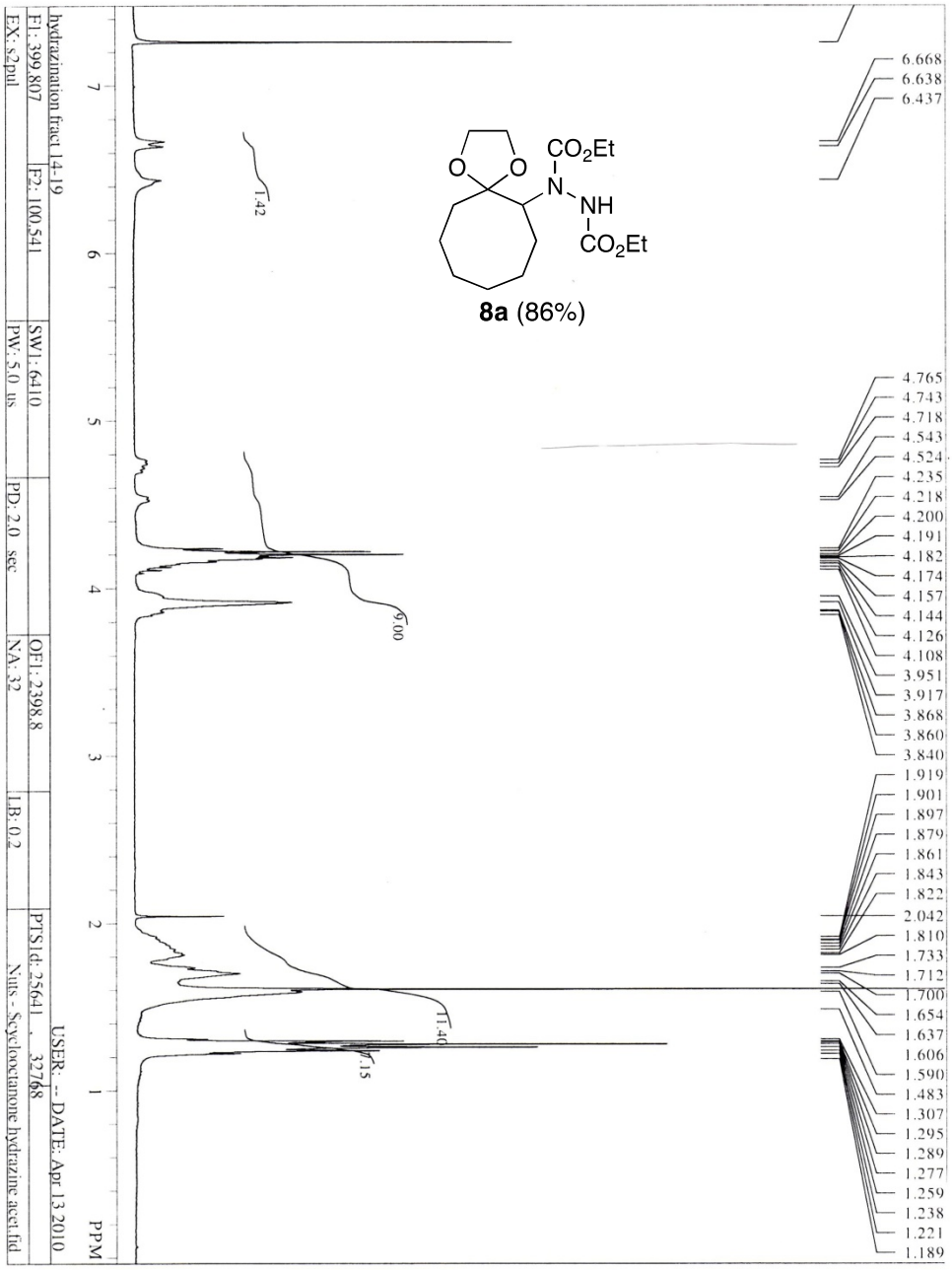
LB: 0.2
PTS1d: 25641 , 32768

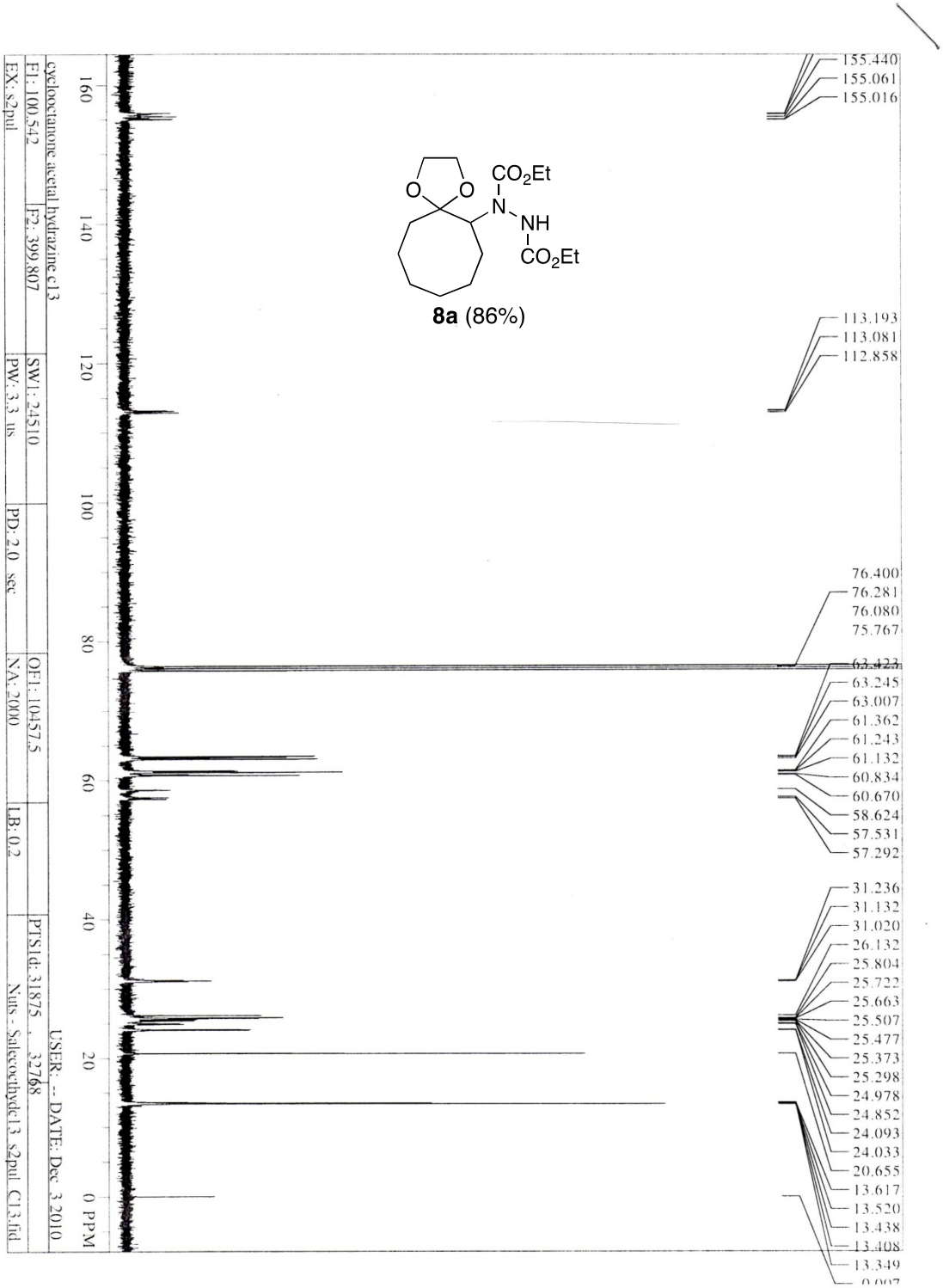

;blank line
F1: 100.542
F2: 399.807
EX: s2pul
SW1: 24510
PW: 3.3 us
PD: 2.0 sec
OF1: 10555.7
NA: 1000
LB: 0.2
PTS1d: 31875
32768
USER: -- DATE: Jan 14 2011
Nuts - Salechephyd s2pul C13.fid
140
120
100
80
60
40
20
PPM
O
O
CO2Et
N
NH
CO2Et
7a (24%)
156.470
156.046
155.979
113.575
113.337
113.121
77.377
77.258
77.057
76.737
64.527
64.483
63.917
63.880
62.660
62.526
62.347
62.221
62.116
61.811
61.625
35.725
35.524
29.185
29.103
29.014
28.976
27.630
27.555
27.488
27.392
25.822
25.442
25.249
21.960
21.900
21.744
14.497
14.408

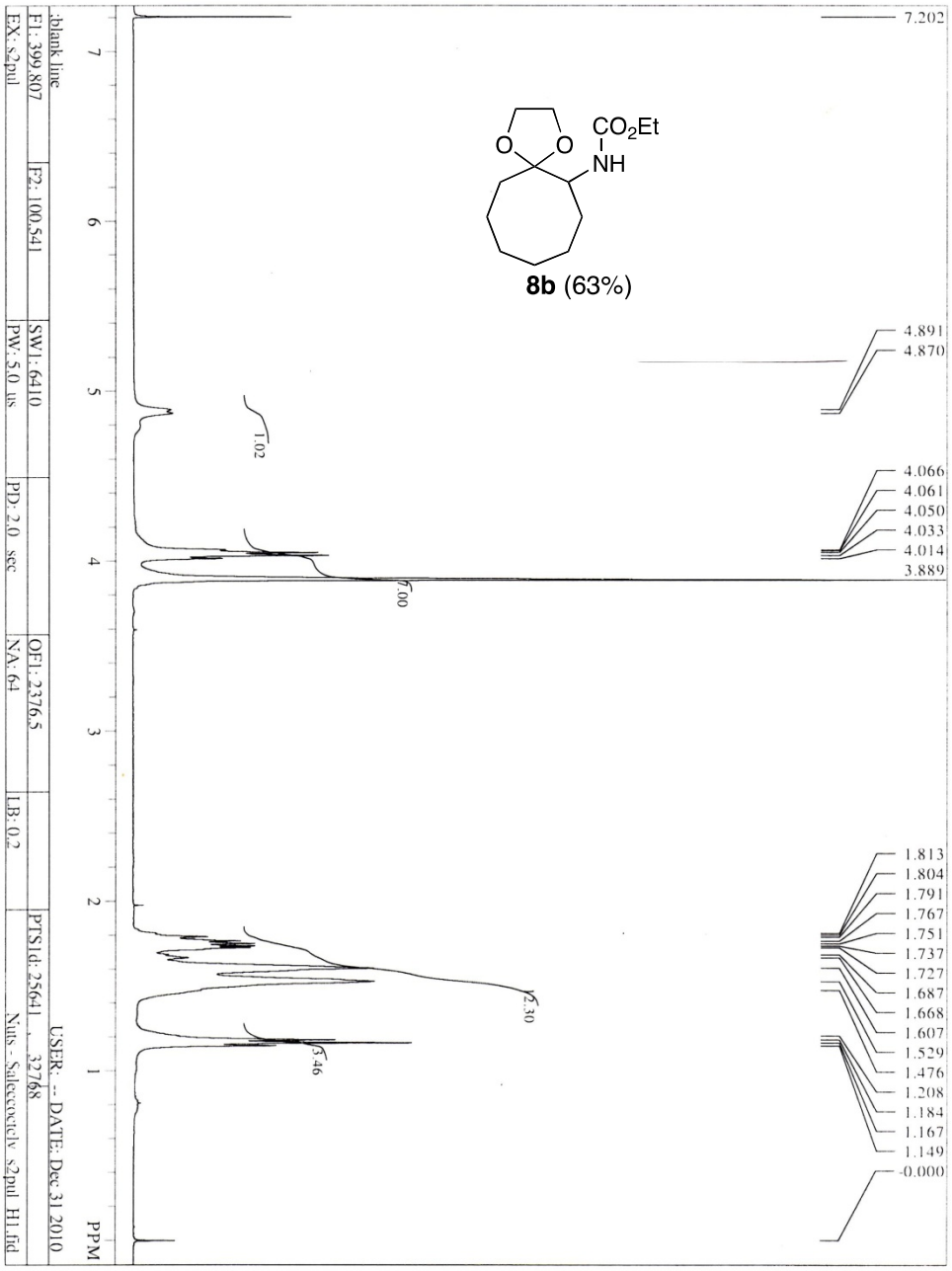

7b (48%)
7.202
4.933
4.913
4.065
4.047
4.029
4.011
3.914
3.900
3.895
3.885
3.879
3.869
3.854
3.844
3.833
3.829
3.820
3.800
3.778
1.781
1.778
1.757
1.752
1.745
1.741
1.721
1.716
1.705
1.692
1.683
1.659
1.644
1.640
1.631
1.622
1.618
1.609
1.603
1.585
1.563
1.560
1.555
1.544
1.539
1.530
1.515
1.496
1.489
1.470
1.458
1.432
1.403
1.379
1.368
1.359
1.00
6.80
15.05
(PPM
USER: -- DATE: Jan 31 2011
PTS1d: 25641 , 32768
Nuts - Salechepclv_s2pul H1.fid
;blank_line
F1: 399.807
F2: 100.541
EX: s2pul
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OF1: 2376.1
NA: 32
LB: 0.2

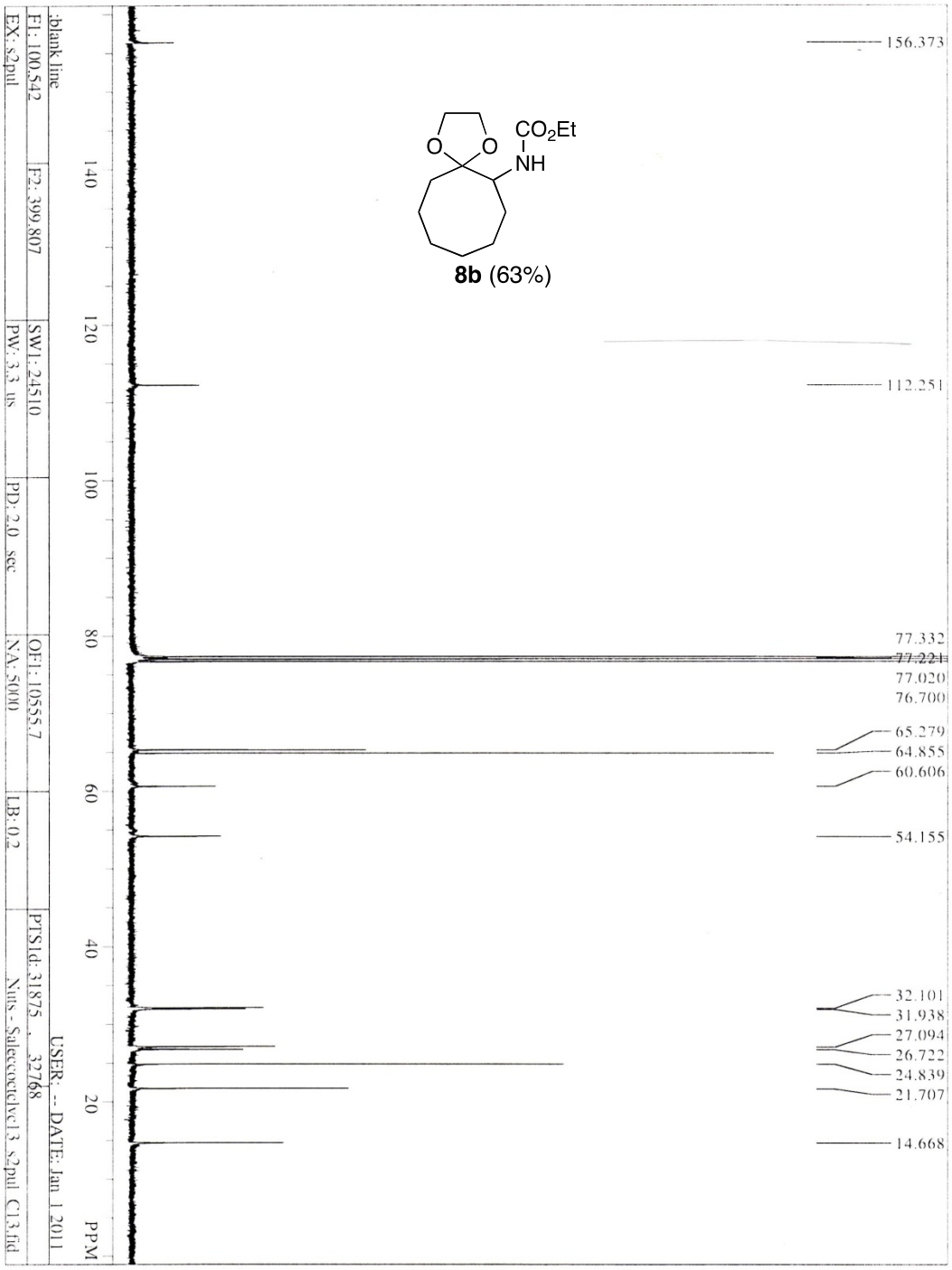

CO2Et
NH
O
O
7b (48%)
156.239
111.946
77.332
77.221
77.012
76.938
76.700
65.353
64.386
60.621
57.548
35.450
31.104
28.069
25.293
20.985
14.638
160
140
120
100
80
60
40
20
PPM
:blank line
F1: 100.542
F2: 399.807
SW1: 24510
PW: 3.3 us
PD: 2.0 sec
OF1: 10555.7
NA: 2000
LB: 0.2
PTS1d: 31875 . 32768
USER: -- DATE: Jan 30 2011
EX: s2pul
Nuts - Salechepclv_s2pul_C13.fid

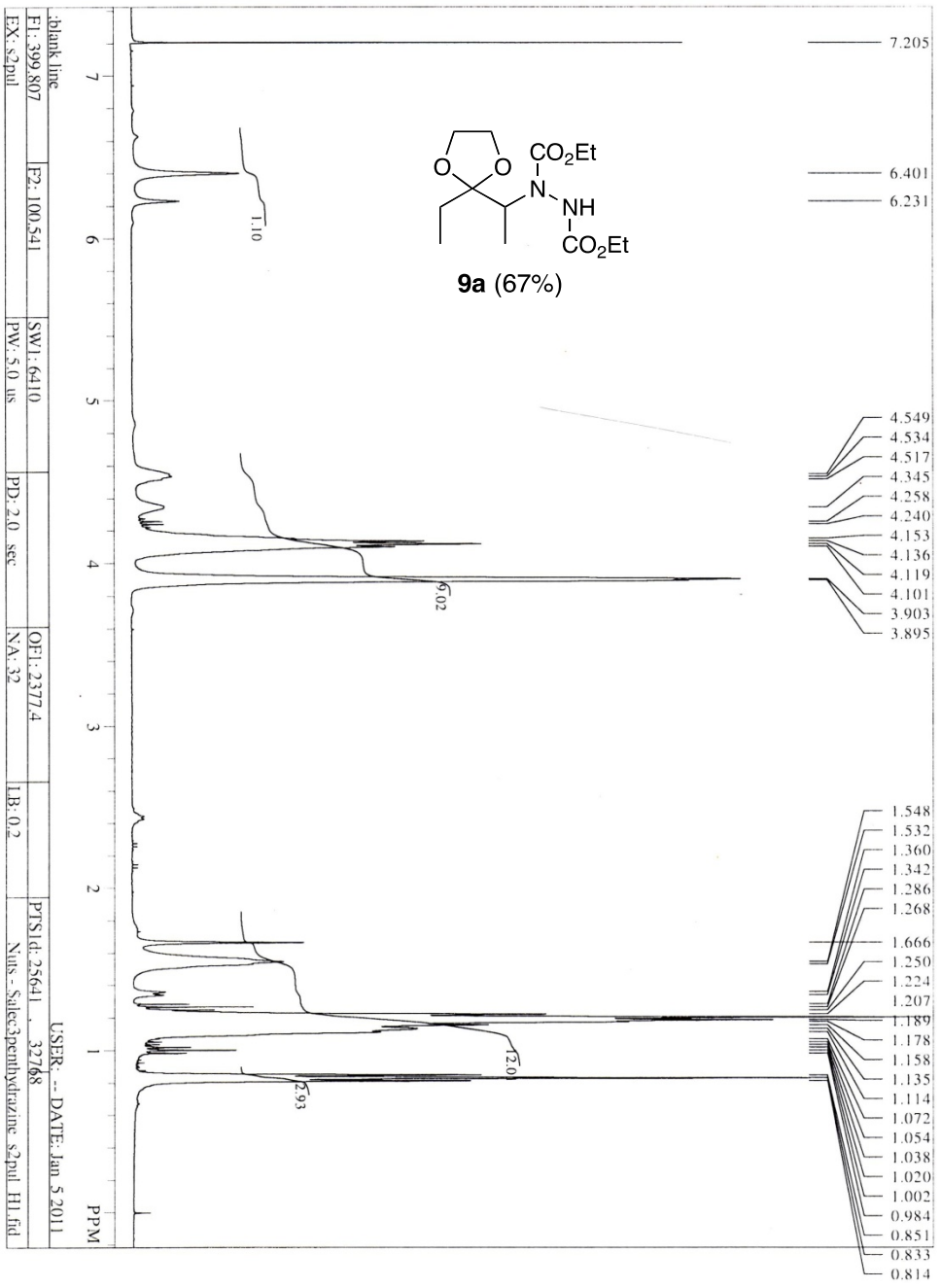

hydrazination fract 14-19
F1: 399.807
F2: 100.541
EX: s2pul
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OF1: 2398.8
NA: 32
LB: 0.2
PTS1d: 25641 , 32768
USER: -- DATE: Apr 13 2010
Nitts - Scycloctanone hydrazine acet.fid
PPM
1.42
9.00
11.40
3.15
6.668
6.638
6.437
4.765
4.743
4.718
4.543
4.524
4.235
4.218
4.200
4.191
4.182
4.174
4.157
4.144
4.126
4.108
3.951
3.917
3.868
3.860
3.840
1.919
1.901
1.897
1.879
1.861
1.843
1.822
2.042
1.810
1.733
1.712
1.700
1.654
1.637
1.606
1.590
1.483
1.307
1.295
1.289
1.277
1.259
1.238
1.221
1.189

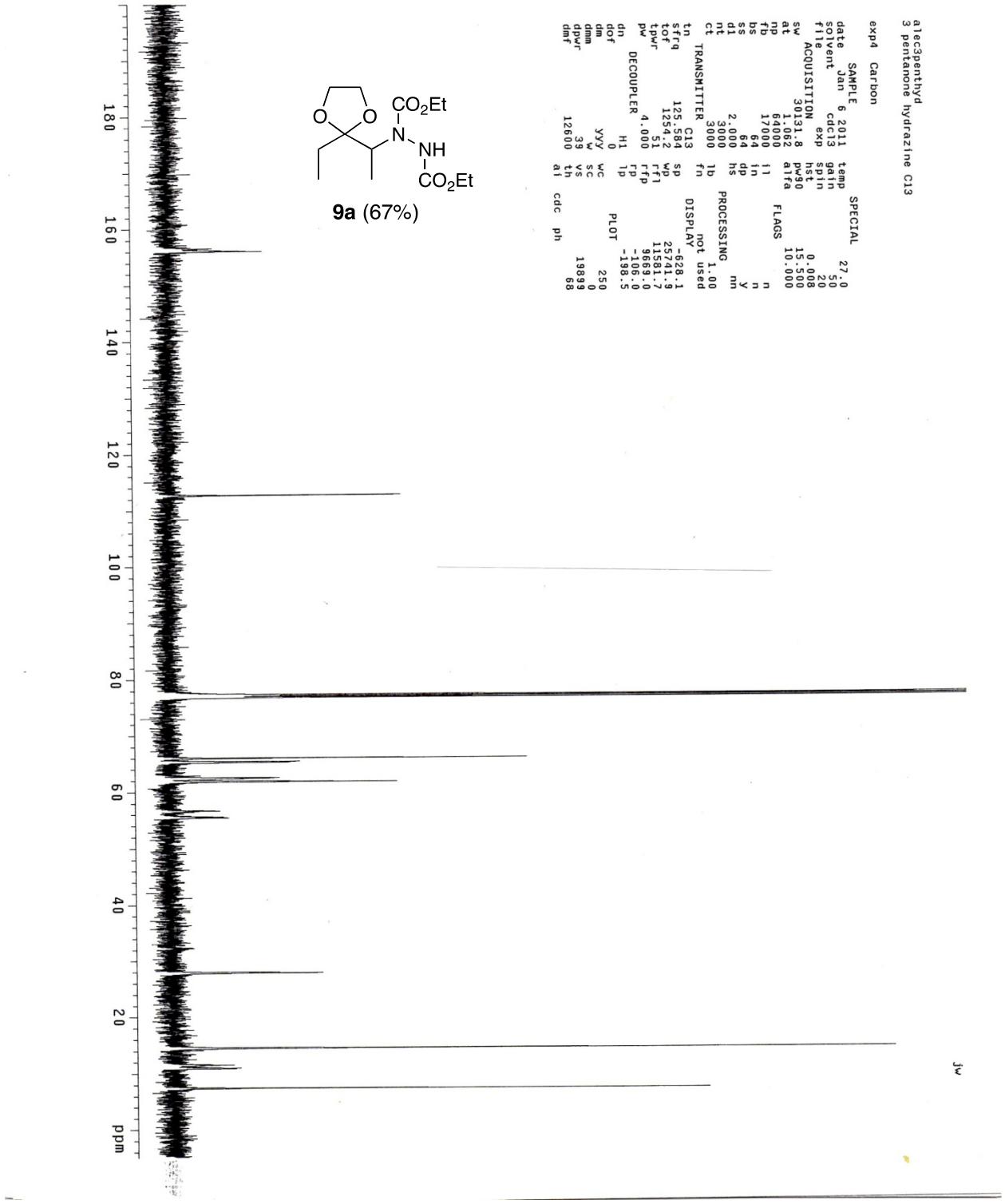
8a (86%)

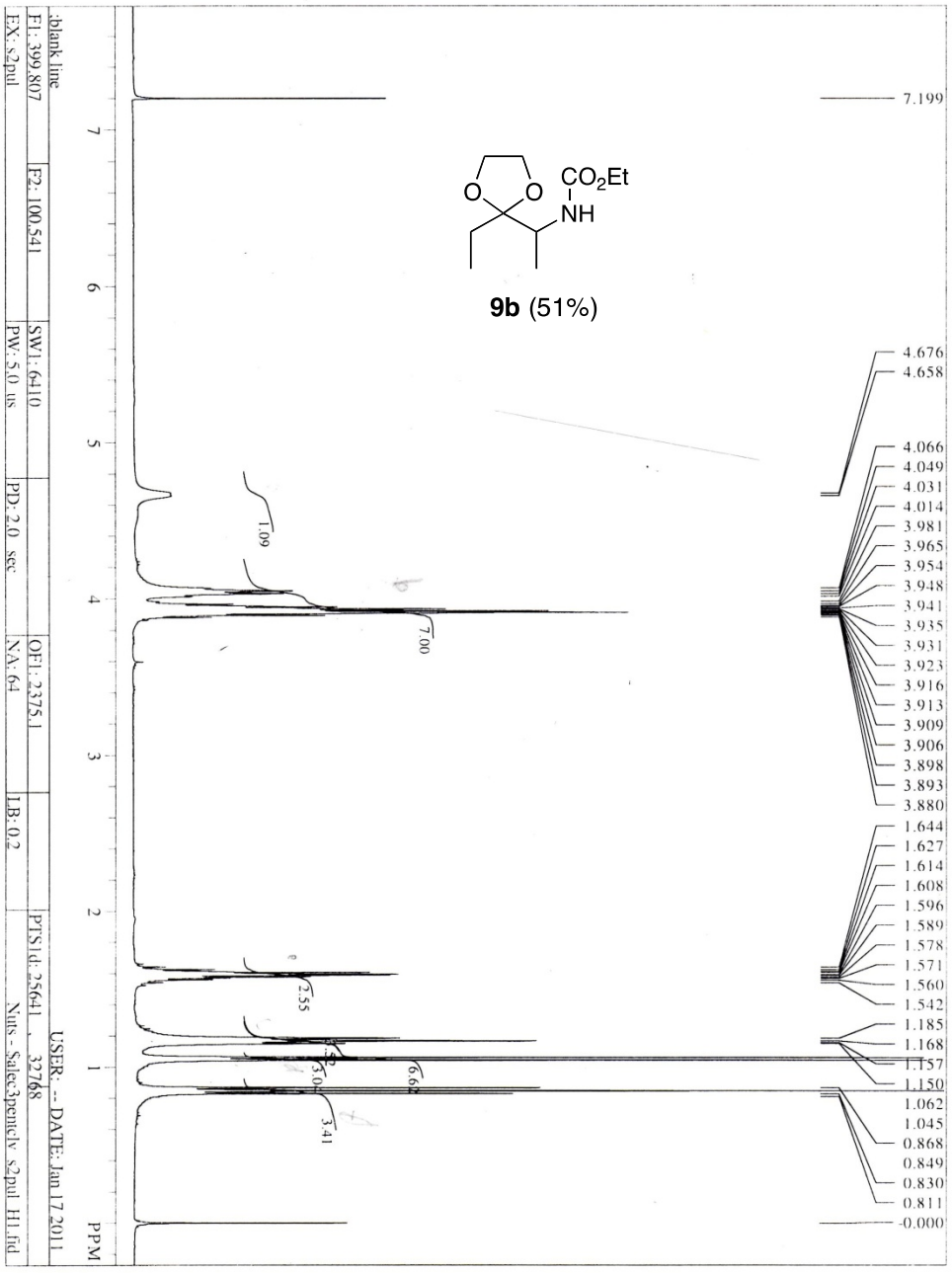

155.440
155.061
155.016
113.193
113.081
112.858
76.400
76.281
76.080
75.767
63.245
63.007
61.362
61.243
61.132
60.834
60.670
58.624
57.531
57.292
31.236
31.132
31.020
26.132
25.804
25.722
25.663
25.507
25.477
25.373
25.298
24.978
24.852
24.093
24.033
20.655
13.617
13.520
13.438
13.408
13.349
CO2Et
NH
CO2Et
8a (86%)
160
140
120
100
80
60
40
20
0 PPM
cyclooctanone acetal hydrazine c13
F1: 100.542
F2: 399.807
SW1: 24510
PW: 3.3 us
PD: 2.0 sec
OF1: 10457.5
NA: 2000
LB: 0.2
PTS1d: 31875 , 32768
EX: s2pul
USER: -- DATE: Dec 3 2010
Nuts - Salecoothyde13_s2pul_C13.fid

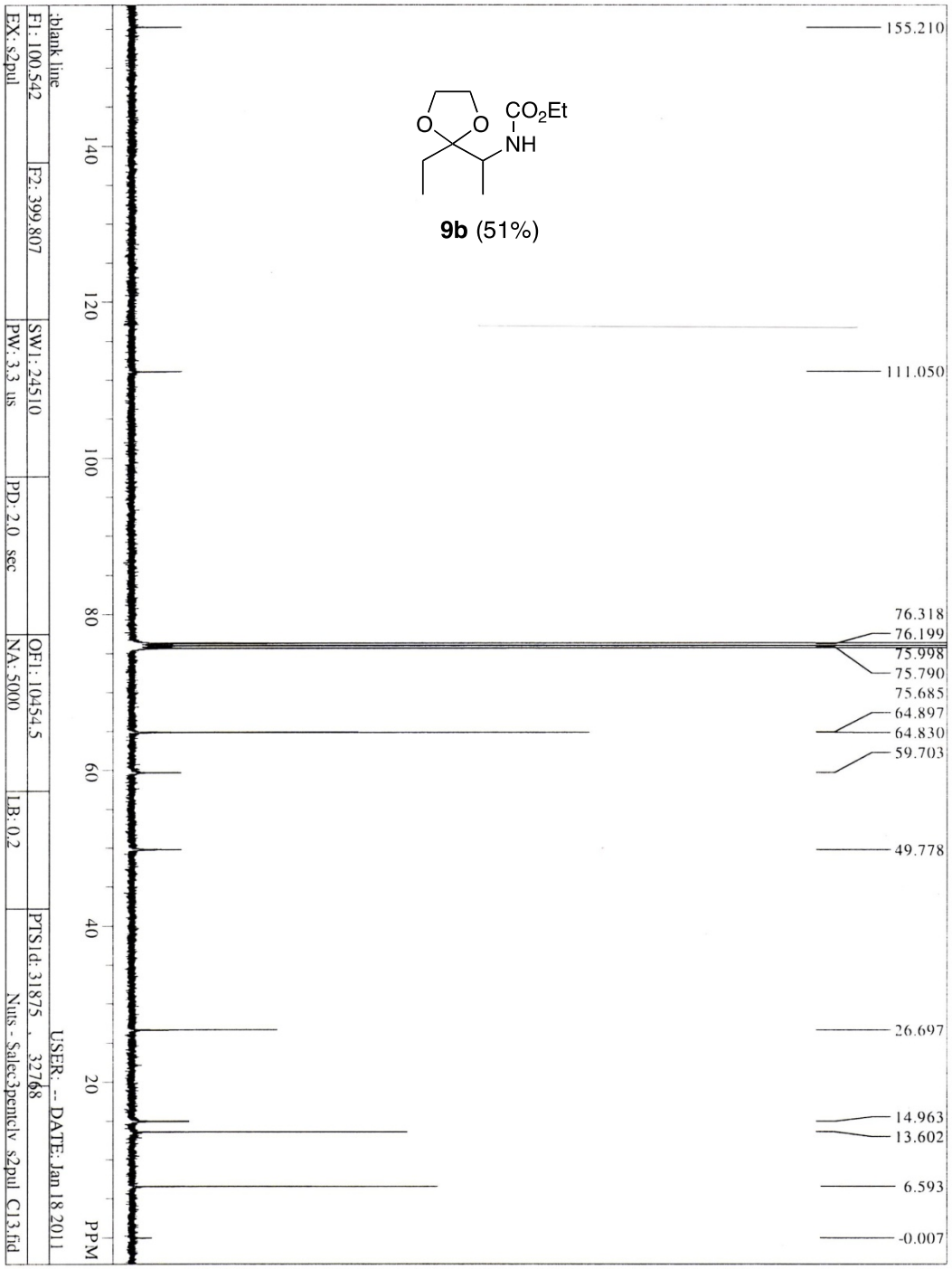

7.202
4.891
4.870
4.066
4.061
4.050
4.033
4.014
3.889
1.813
1.804
1.791
1.767
1.751
1.737
1.727
1.687
1.668
1.607
1.529
1.476
1.208
1.184
1.167
1.149
-0.000
1.02
7.00
2.30
5.46
PPM
CO2Et
NH
O
O
8b (63%)
;blank line
F1: 399.807
F2: 100.541
EX: s2pul
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OF1: 2376.5
NA: 64
LB: 0.2
PTS1d: 25641 32768
USER: -- DATE: Dec 31 2010
Nuts - Saleeenstein s2pul H1.fid

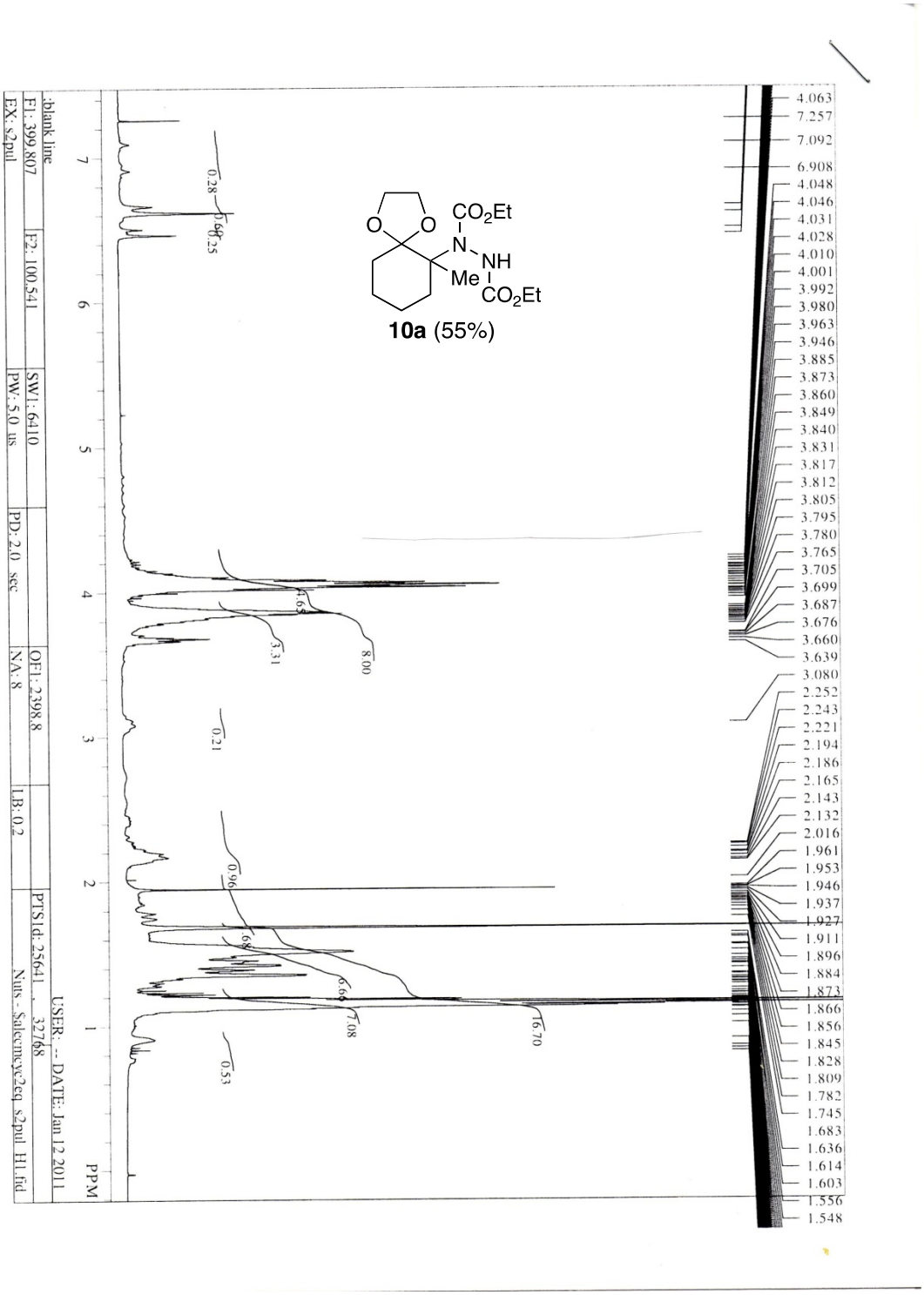

156.373
112.251
77.332
77.221
77.020
76.700
65.279
64.855
60.606
54.155
32.101
31.938
27.094
26.722
24.839
21.707
14.668
CO2Et
NH
O
O
8b (63%)
140
120
100
80
60
40
20
PPM
;blank line
F1: 100.542
F2: 399.807
SW1: 24510
OF1: 10555.7
PTS1d: 31875
32768
USER: -- DATE: Jan 1 2011
EX: s2pul
PW: 3.3 us
PD: 2.0 sec
NA: 5000
LB: 0.2
Nuts -- Salecocctclvc13_s2pul C13.fid

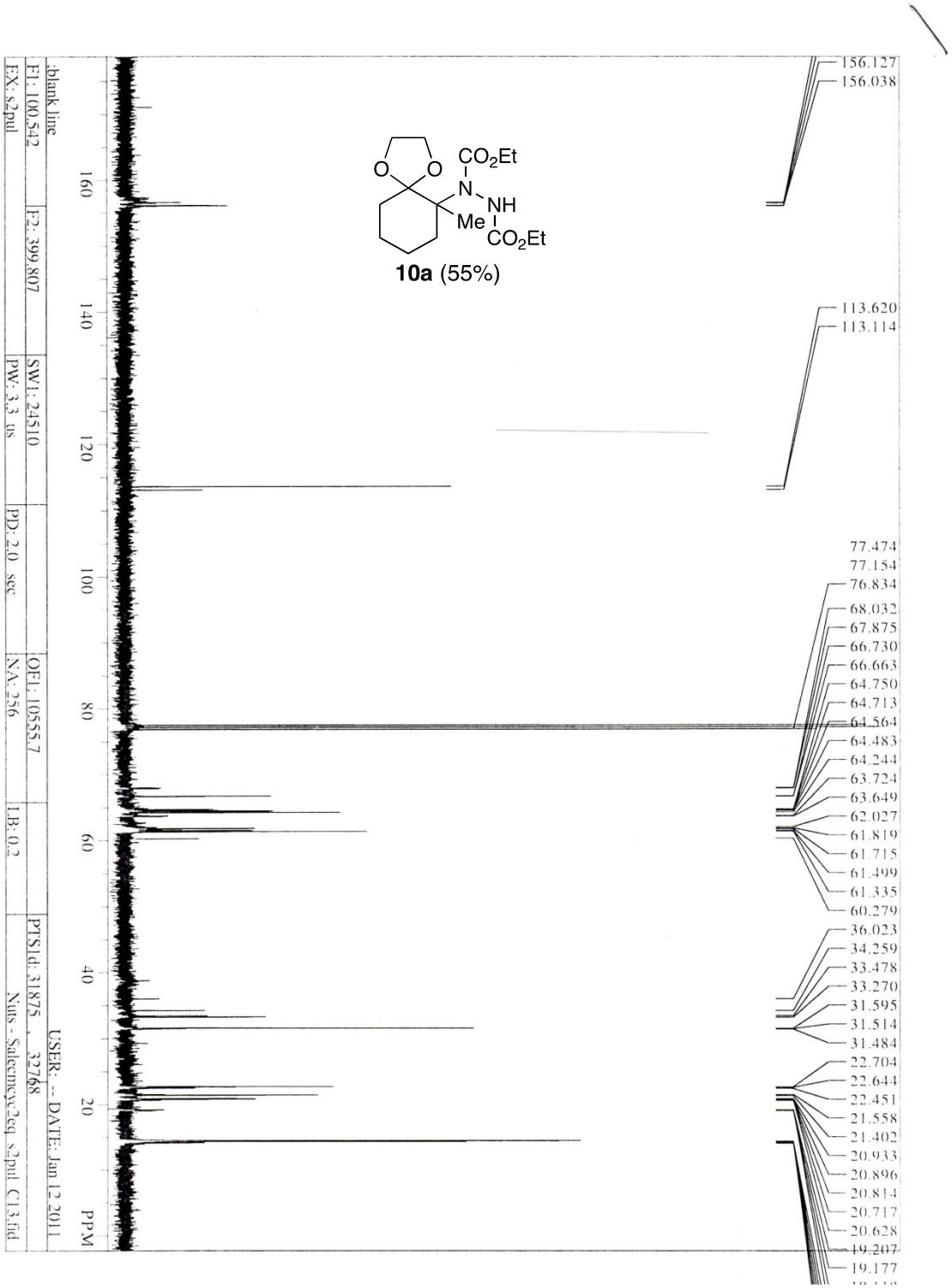

7.205
6.401
6.231
4.549
4.534
4.517
4.345
4.258
4.240
4.153
4.136
4.119
4.101
3.903
3.895
1.548
1.532
1.360
1.342
1.286
1.268
1.666
1.250
1.224
1.207
1.189
1.178
1.158
1.135
1.114
1.072
1.054
1.038
1.020
1.002
0.984
0.851
0.833
0.814
1.10
6.02
12.01
2.93
CO2Et
N
NH
CO2Et
9a (67%)
PPM
;blank line
F1: 399.807
F2: 100.541
EX: s2pul
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
QF1: 2377.4
NA: 32
LB: 0.2
PTS1d: 25641 , 32768
USER: -- DATE: Jan 5 2011
Nuts - Salec3pentbydrazine .s2pul H1.fid

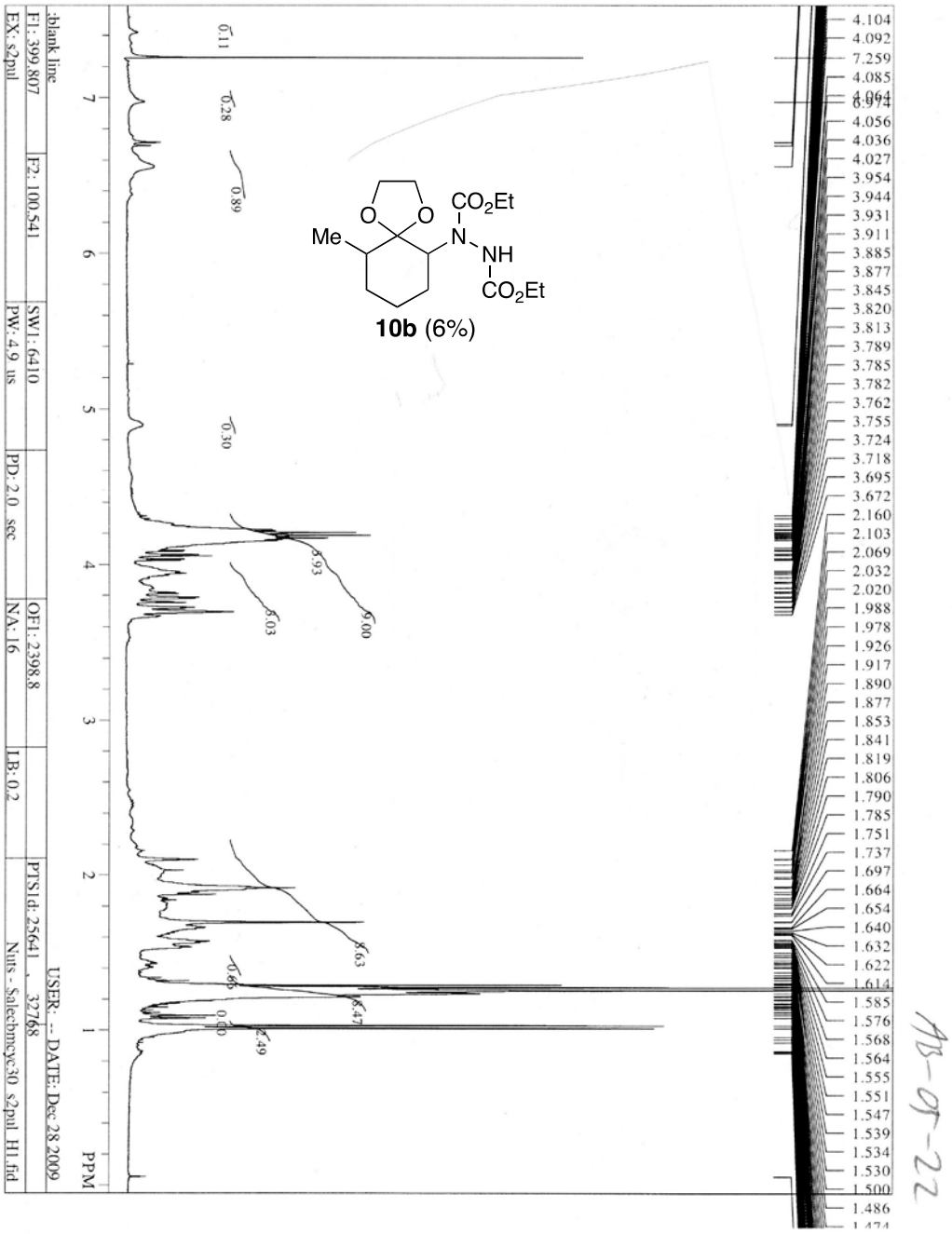

alec3penthyd
3 pentanone hydrazine C13
exp4 Carbon
SAMPLE
date Jan 6 2011
solvent cdcl3
file
ACQUISITION
sw 30131.8
at 1.0922
np 64000
fb 17000
bs 64
ss 2.000
d1 3000
nt 3000
ct
TRANSMITTER
tn C13
sfrq 125.584
tof 1254.2
tpwr 51
pw 4.000
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 39
dmf 12600
temp 27.0
gain
spin 50
hst 20
pw90 0.008
alfa 15.500
FLAGS 10.000
il
in n
dp n
hs y
PROCESSING nn
lb 1.00
fn not used
DISPLAY
sp -628.1
wp 25741.9
rfl 11581.7
rfp 9669.0
rp -106.0
lp -198.5
PLOT
wc 250
sc 0
vs 19899
th 68
ai cdc ph
CO2Et
N
NH
CO2Et
9a (67%)
180
160
140
120
100
80
60
40
20
ppm

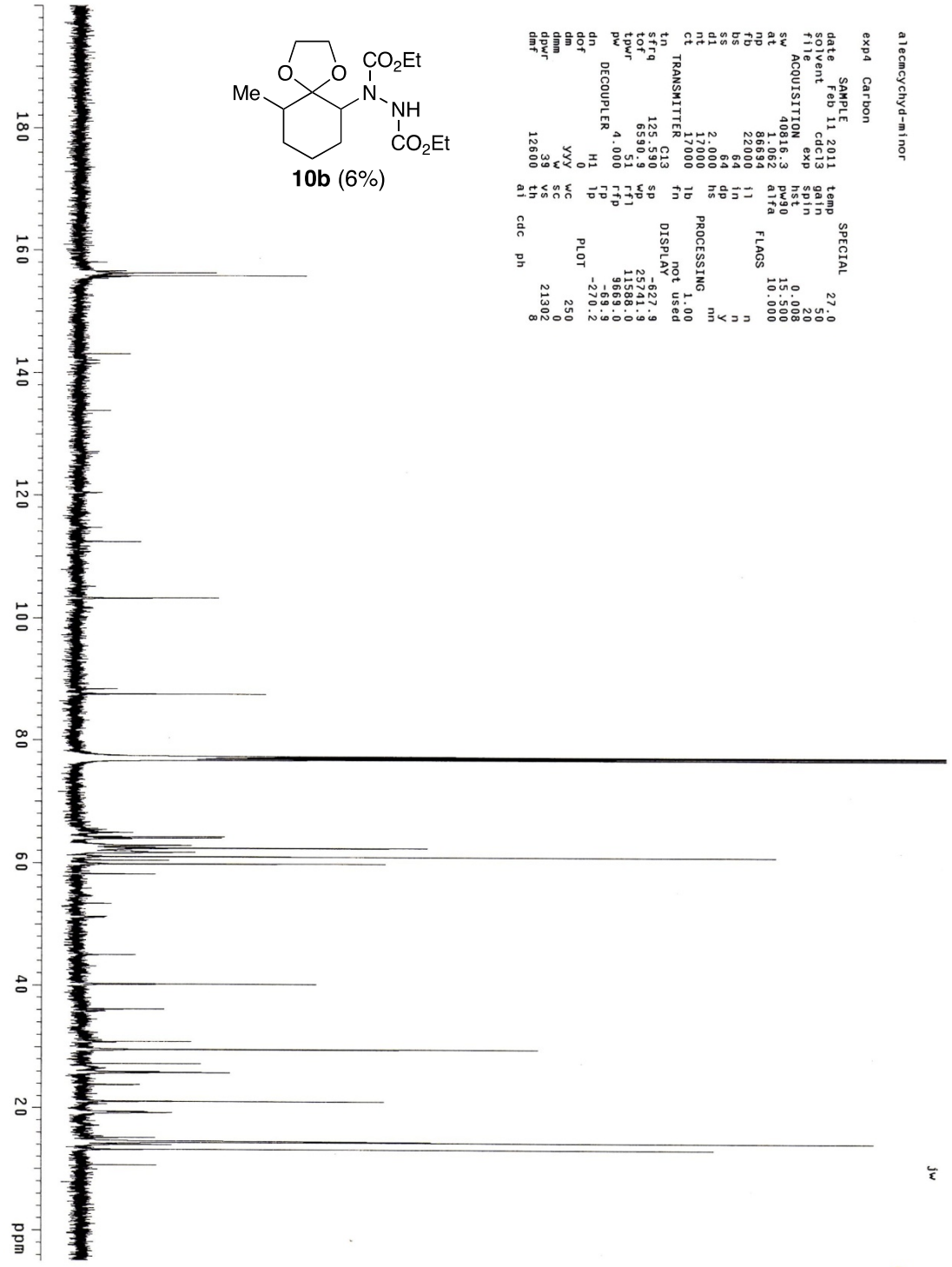

CO2Et
NH
9b (51%)
7.199
4.676
4.658
4.066
4.049
4.031
4.014
3.981
3.965
3.954
3.948
3.941
3.935
3.931
3.923
3.916
3.913
3.909
3.906
3.898
3.893
3.880
1.644
1.627
1.614
1.608
1.596
1.589
1.578
1.571
1.560
1.542
1.185
1.168
1.157
1.150
1.062
1.045
0.868
0.849
0.830
0.811
-0.000
1.09
7.00
2.55
3.0
6.62
3.41
PPM
USER: -- DATE: Jan 17 2011
PTS1d: 25641 32768
LB: 0.2
NA: 64
OE1: 2375.1
PD: 2.0 sec
PW: 5.0 us
SW1: 6410
F2: 100.541
F1: 399.807
EX: s2pul
blank line
Nuts - Salec3premclv s2pul H1.fid

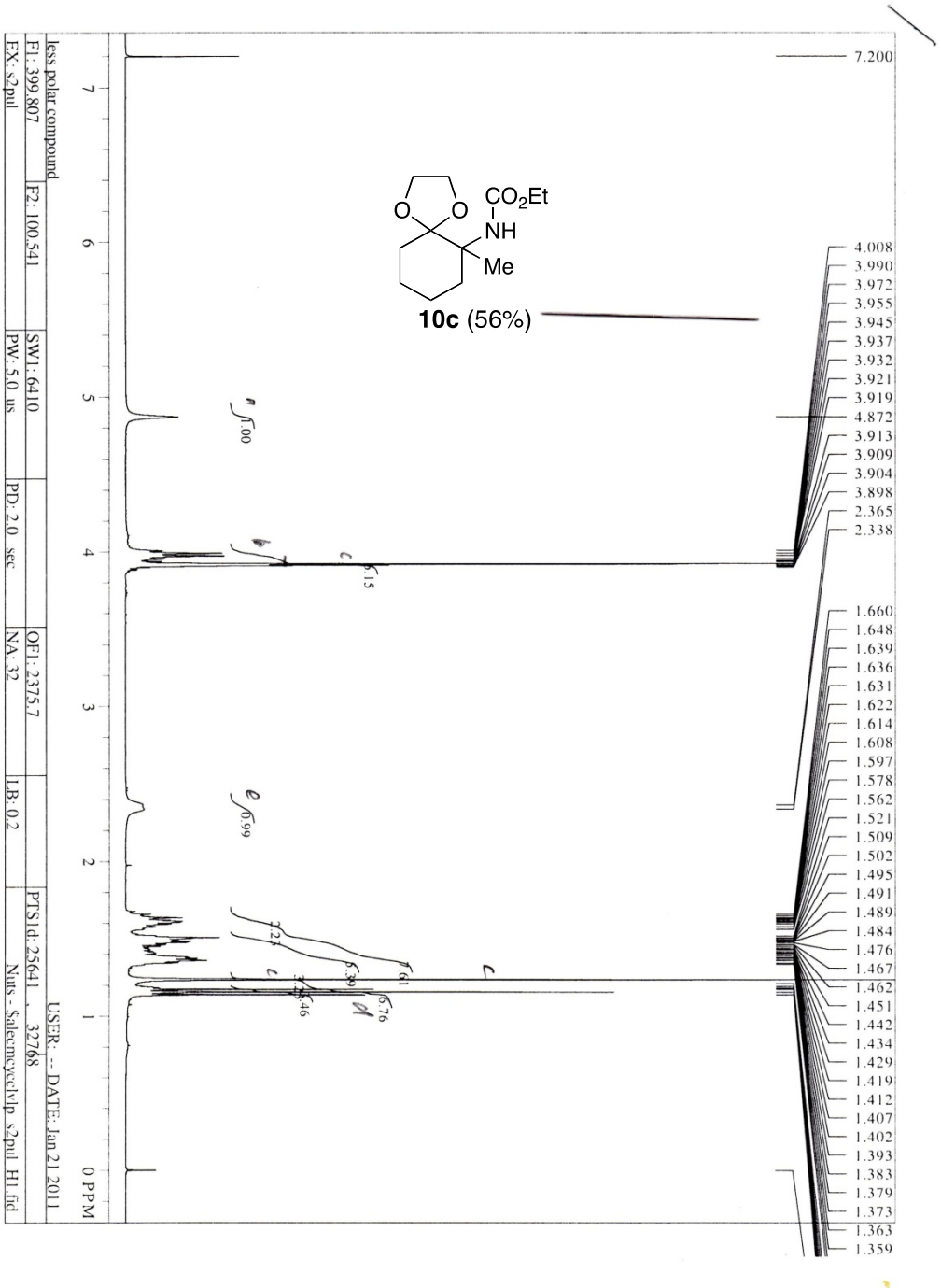

155.210
111.050
76.318
76.199
75.998
75.790
75.685
64.897
64.830
59.703
49.778
26.697
14.963
13.602
6.593
-0.007
PPM
140
120
100
80
60
40
20
O
O
CO2Et
NH
9b (51%)
;blank line
F1: 100.542
F2: 399.807
SW1: 24510
OF1: 10454.5
PTS1d: 31875 , 32768
PW: 3.3 us
PD: 2.0 sec
NA: 5000
LB: 0.2
EX: s2pul
USER: -- DATE: Jan 18 2011
Nuts - Salec3pentclv_s2pul C13.fid

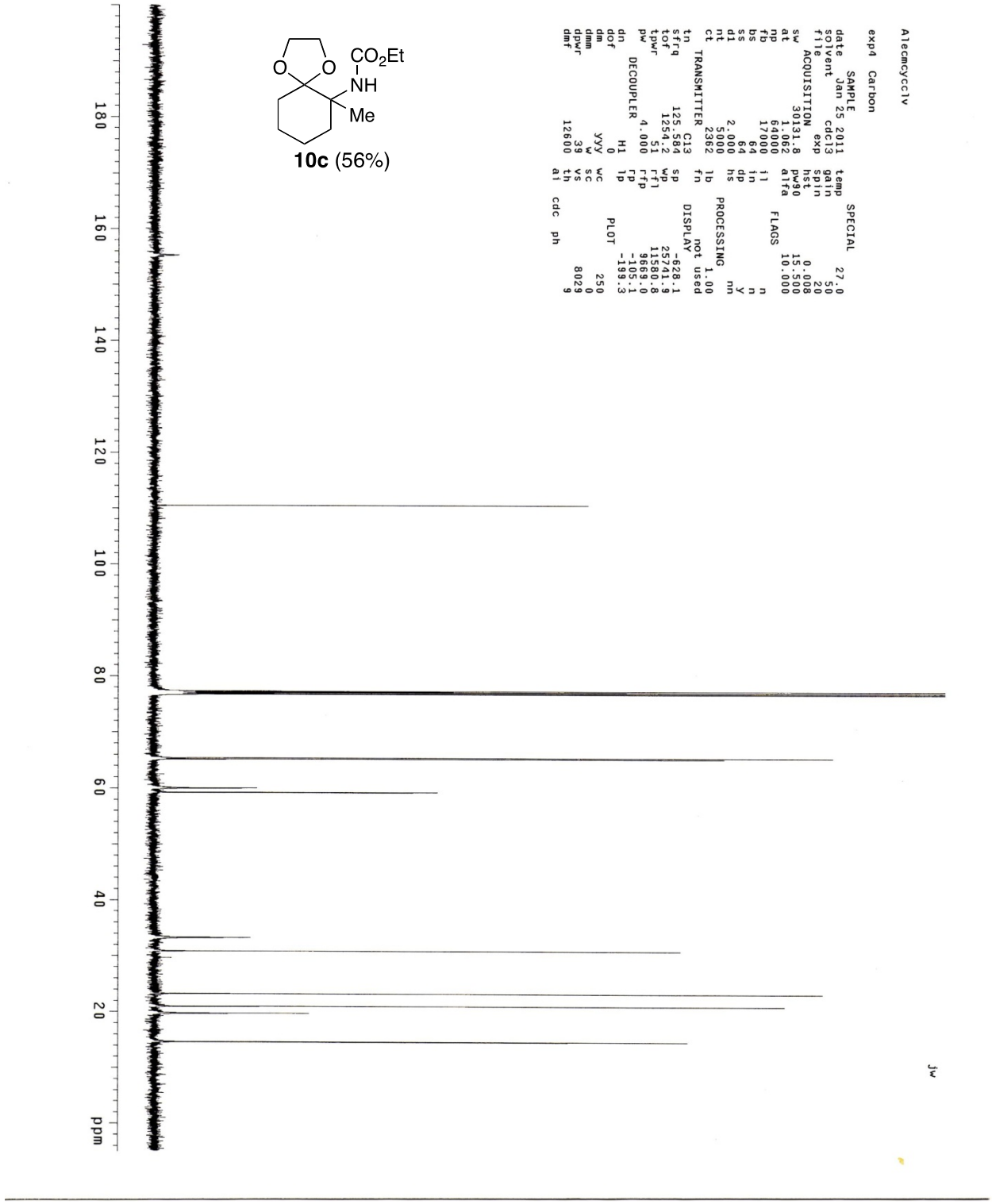

CO2Et
N
NH
Me
CO2Et
10a (55%)
4.063
7.257
7.092
6.908
4.048
4.046
4.031
4.028
4.010
4.001
3.992
3.980
3.963
3.946
3.885
3.873
3.860
3.849
3.840
3.831
3.817
3.812
3.805
3.795
3.780
3.765
3.705
3.699
3.687
3.676
3.660
3.639
3.080
2.252
2.243
2.221
2.194
2.186
2.165
2.143
2.132
2.016
1.961
1.953
1.946
1.937
1.927
1.911
1.896
1.884
1.873
1.866
1.856
1.845
1.828
1.809
1.782
1.745
1.683
1.636
1.614
1.603
1.556
1.548
0.28
0.25
1.63
3.31
8.00
0.21
0.96
6.68
6.66
7.08
16.70
0.53
PPM
USER: -- DATE: Jan 12 2011
PTS1d: 25641 32768
OF1: 2398.8
LB: 0.2
NA: 8
PD: 2.0 sec
SW1: 6410
PW: 5.0 us
F2: 100.541
F1: 399.807
EX: s2pul
;blank line
Nuts - Salecmcyc2eq_s2pul_H1.fid


156.127
156.038
113.620
113.114
77.474
77.154
76.834
68.032
67.875
66.730
66.663
64.750
64.713
64.564
64.483
64.244
63.724
63.649
62.027
61.819
61.715
61.499
61.335
60.279
36.023
34.259
33.478
33.270
31.595
31.514
31.484
22.704
22.644
22.451
21.558
21.402
20.933
20.896
20.814
20.717
20.628
19.207
19.177
CO2Et
N
NH
Me
CO2Et
10a (55%)
160
140
120
100
80
60
40
20
PPM
:blank line
F1: 100.542
F2: 399.807
SW1: 24510
PW: 3.3 us
PD: 2.0 sec
OF1: 10555.7
NA: 256
LB: 0.2
PTS1d: 31875 , 32768
USER: -- DATE: Jan 12 2011
EX: s2pul
Nuts - Salecmcyc2eq_s2pul C13.fid


CO2Et
O
O
N
Me
NH
CO2Et
10b (6%)
4.104
4.092
7.259
4.085
4.064
6.974
4.056
4.036
4.027
3.954
3.944
3.931
3.911
3.885
3.877
3.845
3.820
3.813
3.789
3.785
3.782
3.762
3.755
3.724
3.718
3.695
3.672
2.160
2.103
2.069
2.032
2.020
1.988
1.978
1.926
1.917
1.890
1.877
1.853
1.841
1.819
1.806
1.790
1.785
1.751
1.737
1.697
1.664
1.654
1.640
1.632
1.622
1.614
1.585
1.576
1.568
1.564
1.555
1.551
1.547
1.539
1.534
1.530
1.500
1.486
1.474
0.11
0.28
0.89
0.30
3.93
3.03
3.00
3.63
0.85
3.47
0.00
2.49
PPM
:blank line
F1: 399.807
F2: 100.541
SW1: 6410
PW: 4.9 us
PD: 2.0 sec
OF1: 2398.8
NA: 16
LB: 0.2
PTS1d: 25641 , 32768
USER: -- DATE: Dec 28 2009
EX: s2pul
Nuts - Salecbmcyc30 s2pul H1.fid
AB-08-22

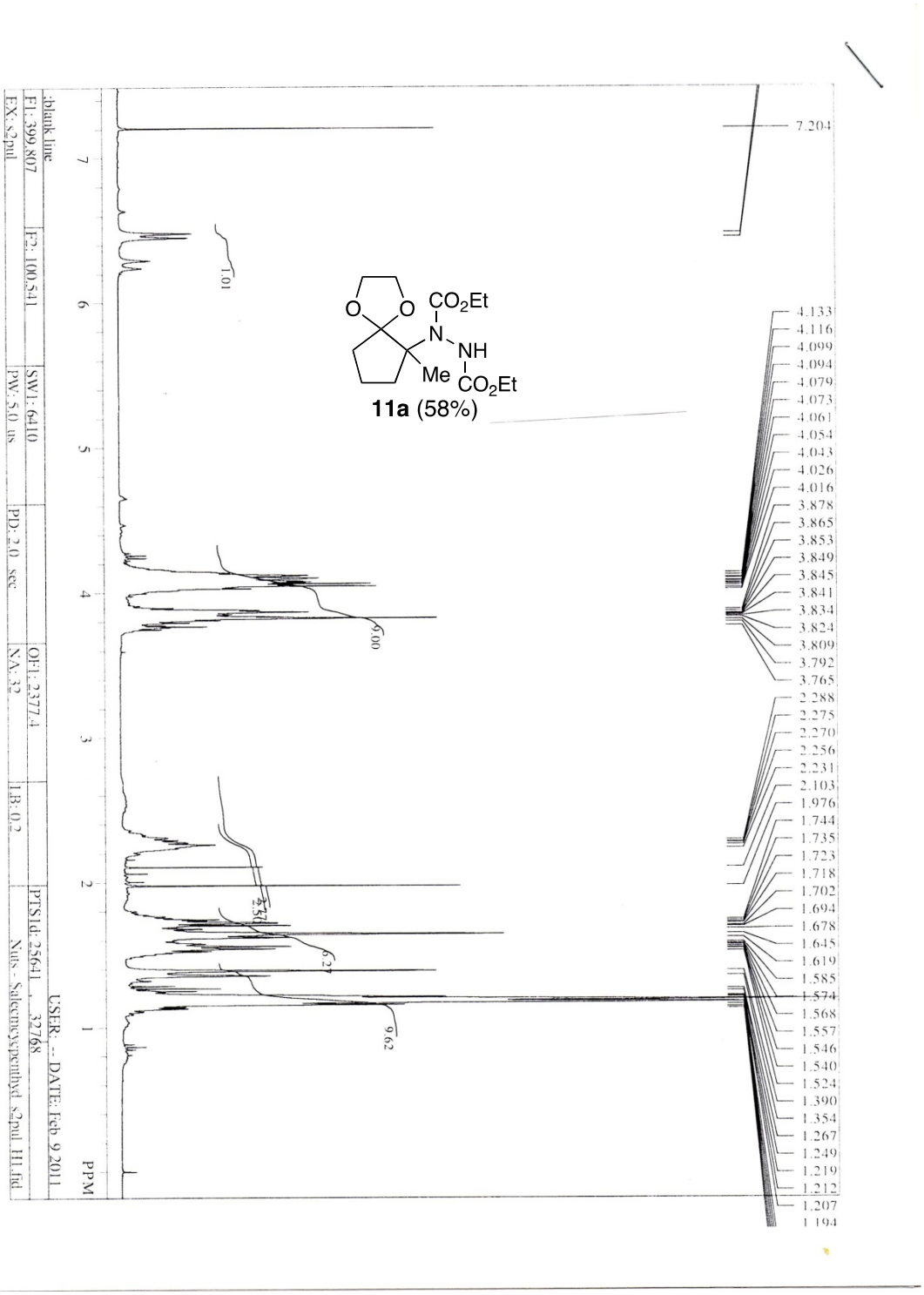

alecmcychyd-minor
exp4 Carbon
SAMPLE
date Feb 11 2011
solvent cdcl3
file spin
ACQUISITION
sw 40816.3
at 1.062
np 86694
fb 22000
bs 64
ss 64
d1 2.000
nt 17000
ct 17000
TRANSMITTER
tn C13
sfrq 125.590
tof 6590.9
tpwr 51
pw 4.000
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 39
dmf 12600
temp 27.0
gain 50
spin 20
hst 0.008
pw90 15.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -627.9
wp 25741.9
rf1 11588.0
rfp 9669.0
rp -69.9
lp -270.2
PLOT
wc 250
sc 0
vs 21302
th 8
ai cdc ph
CO2Et
NH
CO2Et
Me
10b (6%)
180
160
140
120
100
80
60
40
20
ppm
jw

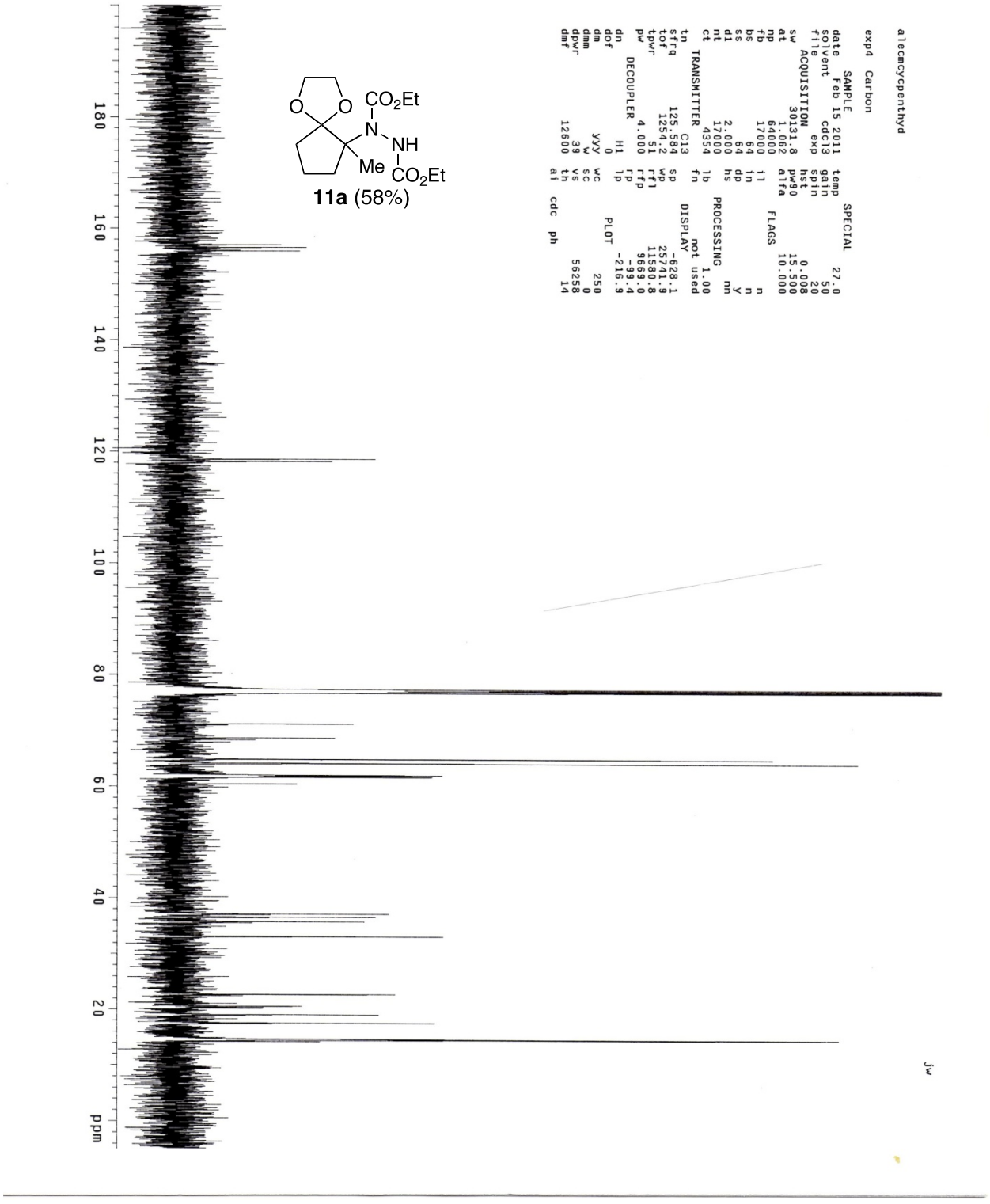

less polar compound
F1: 399.807
F2: 100.541
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OF1: 2375.7
NA: 32
LB: 0.2
PTS1d: 25641
USER: -- DATE: Jan 21 2011
32768
EX: s2pul
Nuts - Salecmcyccivlp s2pul H1.fid
CO2Et
NH
Me
10c (56%)
7.200
4.008
3.990
3.972
3.955
3.945
3.937
3.932
3.921
3.919
4.872
3.913
3.909
3.904
3.898
2.365
2.338
1.660
1.648
1.639
1.636
1.631
1.622
1.614
1.608
1.597
1.578
1.562
1.521
1.509
1.502
1.495
1.491
1.489
1.484
1.476
1.467
1.462
1.451
1.442
1.434
1.429
1.419
1.412
1.407
1.402
1.393
1.383
1.379
1.373
1.363
1.359
7
6
5
4
3
2
1
0 PPM

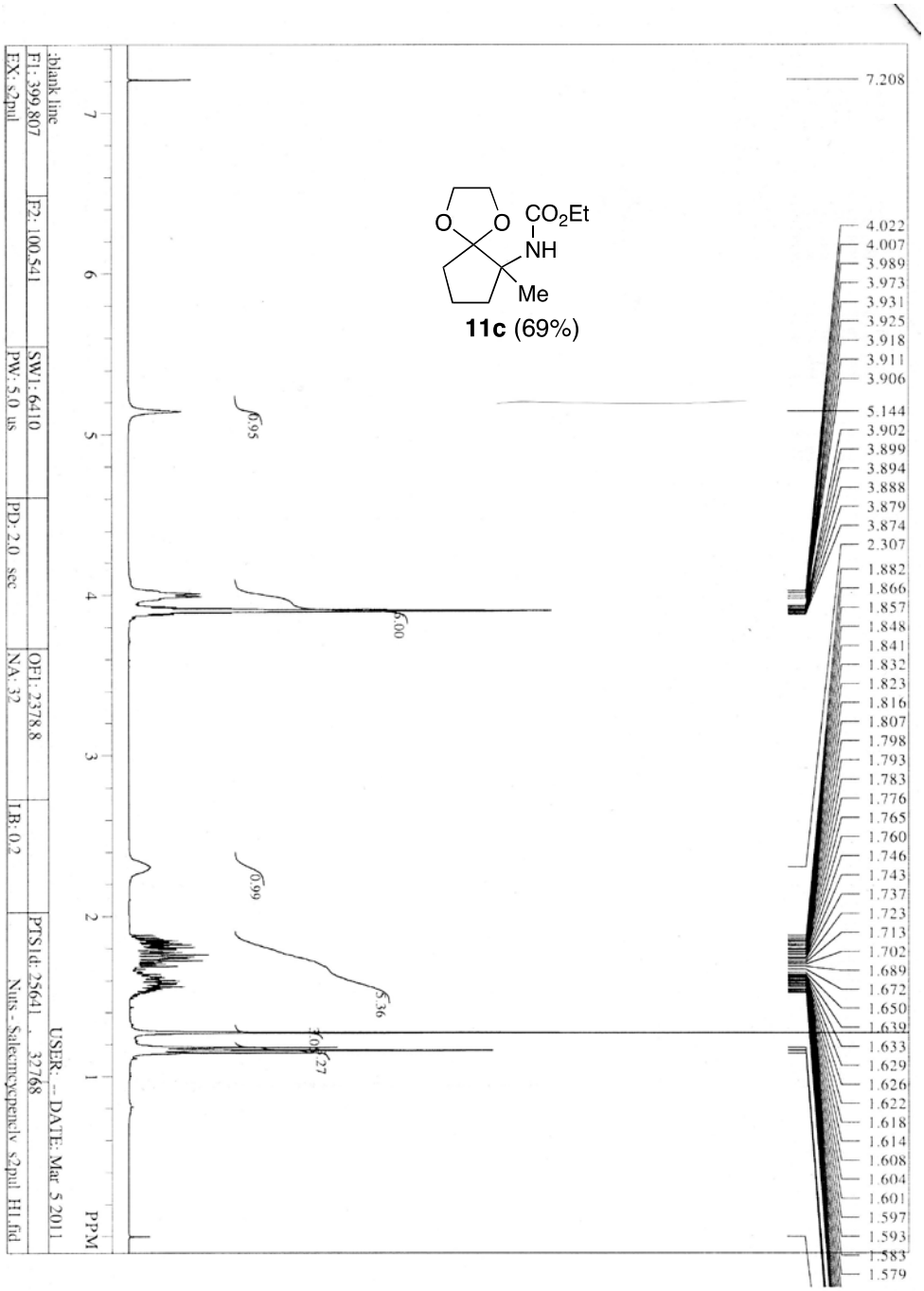

Alecmcycc1v
exp4 Carbon
SAMPLE
date Jan 25 2011
solvent cdcl3
file exp
ACQUISITION
sw 30131.8
at 1.062
np 64000
fb 17000
bs 64
ss 2.000
d1 5000
nt 2362
ct
TRANSMITTER
tn C13
sfrq 125.584
tof 1254.2
tpwr 51
pw 4.000
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 39
dmf 12600
temp
gain
spin
hst
pw90
alfa
FLAGS
il
in
dp
hs
PROCESSING
lb
fn
sp
wp
rfl
rfp
rp
lp
PLOT
wc
sc
vs
th
ai
cdc
SPECIAL
27.0
50
20
0.008
15.500
10.000
n
n
y
nn
1.00
not used
DISPLAY
-628.1
25741.9
11580.8
9669.0
-105.1
-199.3
250
0
8029
9
ph
jw
180
160
140
120
100
80
60
40
20
ppm

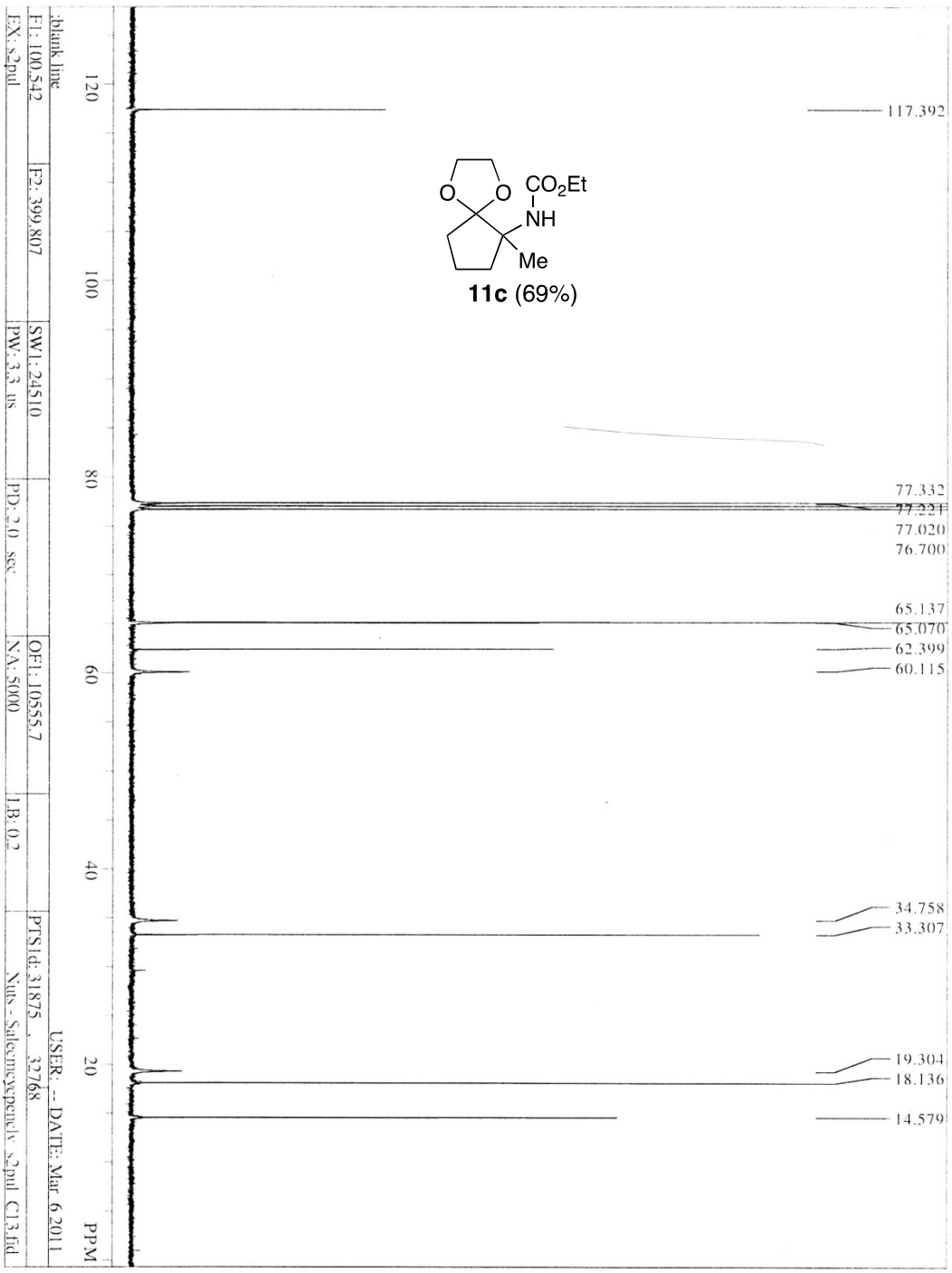
CO2Et
NH
Me

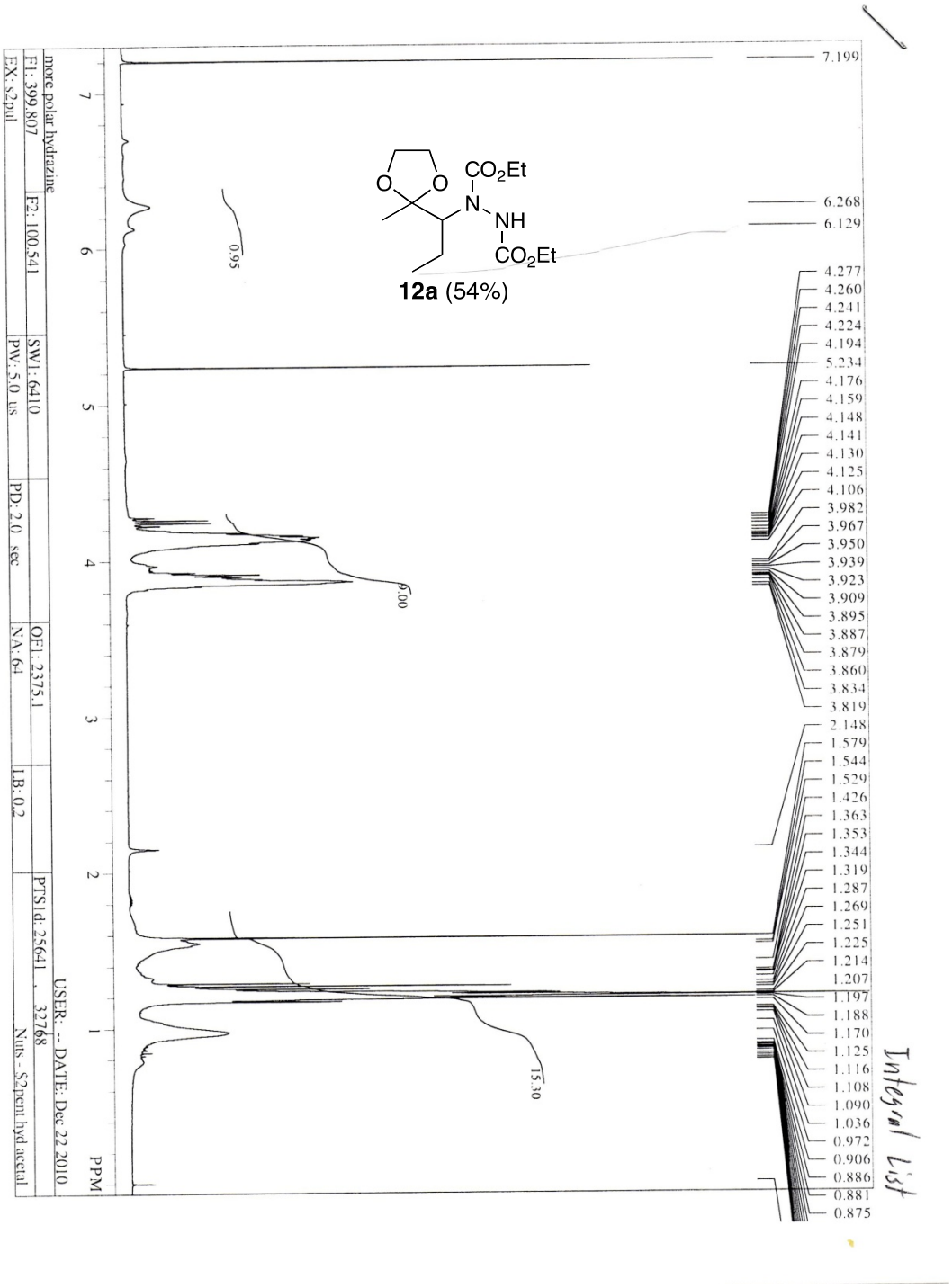
10c (56%)

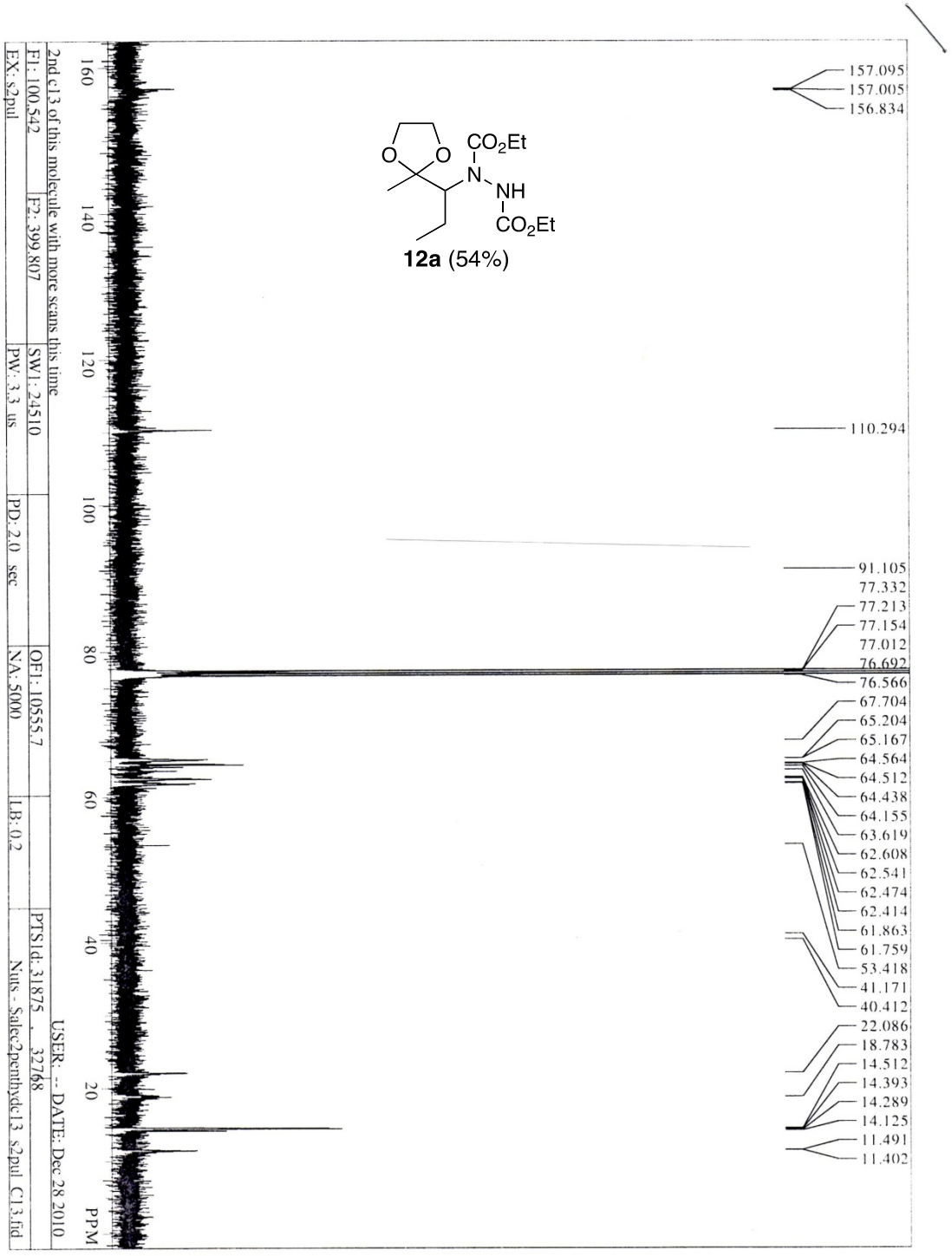

CO2Et
N
NH
Me
CO2Et
11a (58%)
7.204
4.133
4.116
4.099
4.094
4.079
4.073
4.061
4.054
4.043
4.026
4.016
3.878
3.865
3.853
3.849
3.845
3.841
3.834
3.824
3.809
3.792
3.765
2.288
2.275
2.270
2.256
2.231
2.103
1.976
1.744
1.735
1.723
1.718
1.702
1.694
1.678
1.645
1.619
1.585
1.574
1.568
1.557
1.546
1.540
1.524
1.390
1.354
1.267
1.249
1.219
1.212
1.207
1.194
1.01
9.00
2.51
6.24
9.62
7
6
5
4
3
2
1
PPM
blank line
F1: 399.807
F2: 100.541
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OH1: 2377.4
NA: 32
LB: 0.2
USER: -- DATE: Feb 9 2011
PTS1d: 25641 , 32768
EX: s2pul
Nuts - Salicenoxypentbyd .s2pul H1.fid

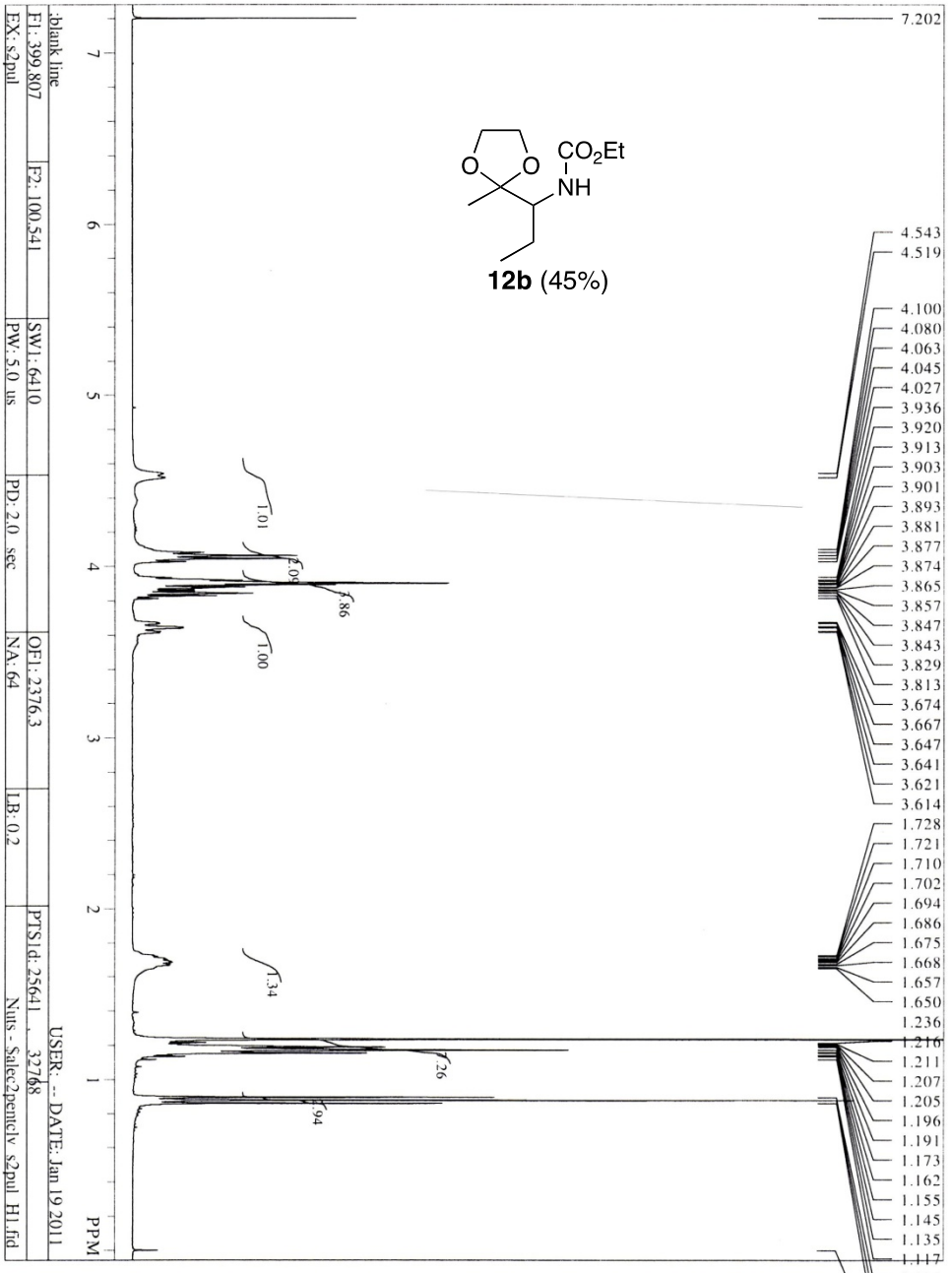

alecmcyclpenthyd
exp4 Carbon
SAMPLE
date Feb 15 2011
solvent cdcl3
file exp
ACQUISITION
sw 30131.8
at 1.062
np 64000
fb 17000
bs 64
ss 2.000
d1 17000
nt 4354
ct
TRANSMITTER
tn C13
sfrq 125.584
tof 1254.2
tpwr 51
pw 4.000
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 39
dmf 12600
temp 27.0
gain 50
spin 20
hst 0.008
pw90 15.500
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.1
wp 25741.9
rfl 11580.8
rfp 9669.0
rp -99.4
lp -216.9
PLOT
wc 250
sc 0
vs 56258
th 14
al cdc ph
CO2Et
N
NH
Me
CO2Et
11a (58%)
jw
180
160
140
120
100
80
60
40
20
ppm

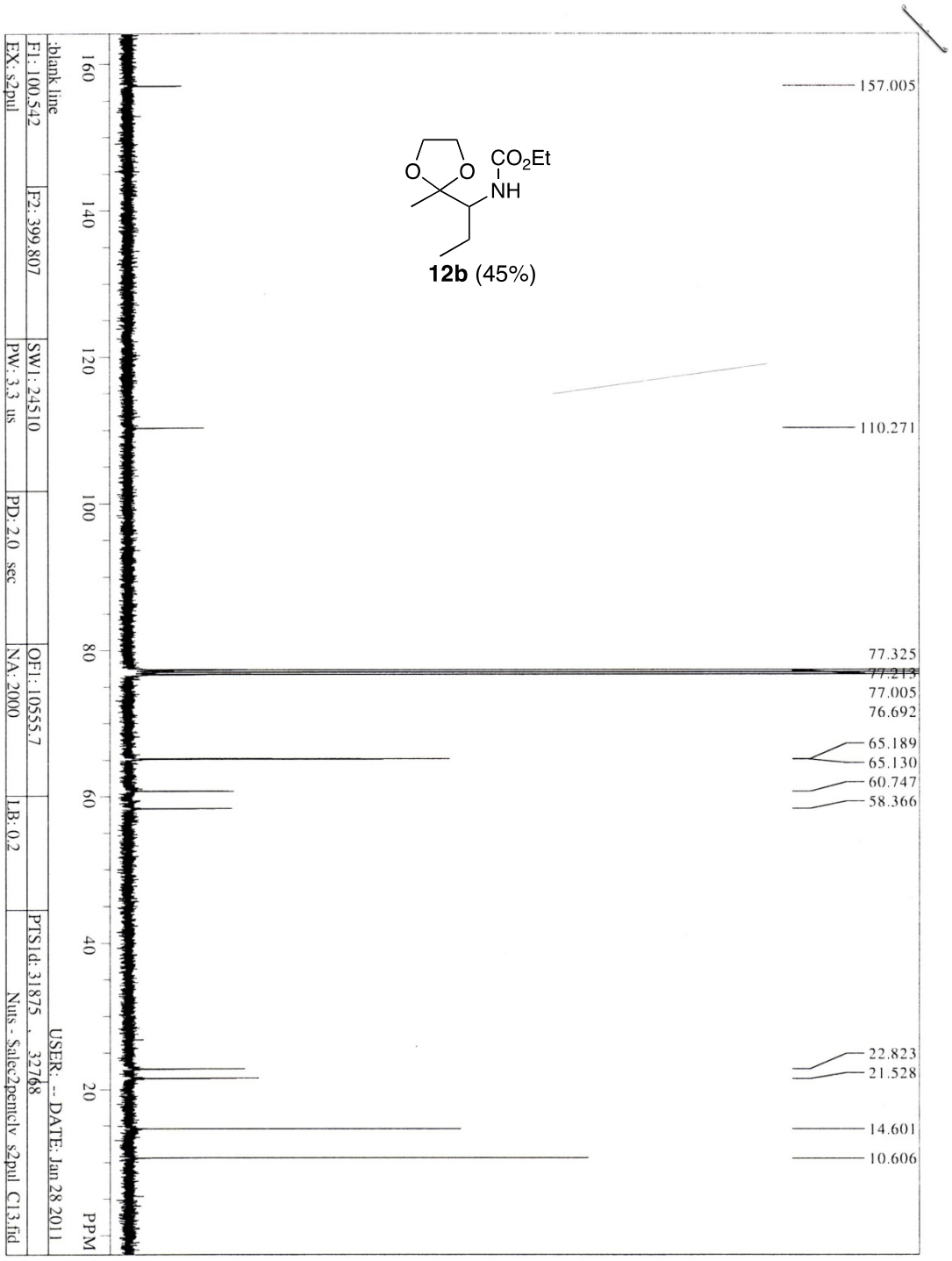

O
O
CO2Et
NH
Me
11c (69%)
7.208
4.022
4.007
3.989
3.973
3.931
3.925
3.918
3.911
3.906
5.144
3.902
3.899
3.894
3.888
3.879
3.874
2.307
1.882
1.866
1.857
1.848
1.841
1.832
1.823
1.816
1.807
1.798
1.793
1.783
1.776
1.765
1.760
1.746
1.743
1.737
1.723
1.713
1.702
1.689
1.672
1.650
1.639
1.633
1.629
1.626
1.622
1.618
1.614
1.608
1.604
1.601
1.597
1.593
1.583
1.579
6.95
6.00
5.99
5.36
1.05
1.27
PPM
USER: -- DATE: Mar 5 2011
Nuts - Salecmcyepencly s2pul H1.fid
;blank line
F1: 399.807
F2: 100.541
EX: s2pul
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OF1: 2378.8
NA: 32
LB: 0.2
PTS1d: 25641 - 32768


:blank line
F1: 100.542
F2: 399.807
SW1: 24510
PW: 3.3 us
PD: 2.0 sec
OF1: 10555.7
NA: 5000
LB: 0.2
PTS1d: 31875
32768
USER: -- DATE: Mar 6 2011
Nuts - Saleemcyperclv_2pul C13.fid
EX: s2pul
120
100
80
60
40
20
PPM
117.392
77.332
77.221
77.020
76.700
65.137
65.070
62.399
60.115
34.758
33.307
19.304
18.136
14.579
O
O
CO2Et
NH
Me
11c (69%)


more polar hydrazine
F1: 399.807
F2: 100.541
EX: s2pul
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OF1: 2375.1
NA: 64
LB: 0.2
PTS1d: 25641 . 32768
USER: -- DATE: Dec 22 2010
Nuts - S2pent hyd acetal
PPM
0.95
6.00
15.30
CO2Et
NH
CO2Et
12a (54%)
7.199
6.268
6.129
4.277
4.260
4.241
4.224
4.194
5.234
4.176
4.159
4.148
4.141
4.130
4.125
4.106
3.982
3.967
3.950
3.939
3.923
3.909
3.895
3.887
3.879
3.860
3.834
3.819
2.148
1.579
1.544
1.529
1.426
1.363
1.353
1.344
1.319
1.287
1.269
1.251
1.225
1.214
1.207
1.197
1.188
1.170
1.125
1.116
1.108
1.090
1.036
0.972
0.906
0.886
0.881
0.875
Integral List


CO2Et
N
NH
CO2Et
12a (54%)
157.095
157.005
156.834
110.294
91.105
77.332
77.213
77.154
77.012
76.692
76.566
67.704
65.204
65.167
64.564
64.512
64.438
64.155
63.619
62.608
62.541
62.474
62.414
61.863
61.759
53.418
41.171
40.412
22.086
18.783
14.512
14.393
14.289
14.125
11.491
11.402
160
140
120
100
80
60
40
20
PPM
2nd c13 of this molecule with more scans this time
F1: 100.542
F2: 399.807
SW1: 24510
OF1: 10555.7
PTS1d: 31875 . 32768
EX: s2pul
PW: 3.3 us
PD: 2.0 sec
NA: 5000
LB: 0.2
USER: -- DATE: Dec 28 2010
Nuts - Salec2penthycle13_s2pul_C13.fid


7.202
4.543
4.519
4.100
4.080
4.063
4.045
4.027
3.936
3.920
3.913
3.903
3.901
3.893
3.881
3.877
3.874
3.865
3.857
3.847
3.843
3.829
3.813
3.674
3.667
3.647
3.641
3.621
3.614
1.728
1.721
1.710
1.702
1.694
1.686
1.675
1.668
1.657
1.650
1.236
1.216
1.211
1.207
1.205
1.196
1.191
1.173
1.162
1.155
1.145
1.135
1.117
0.896
1.01
2.09
1.86
1.00
1.34
3.26
2.94
CO2Et
NH
O
O
12b (45%)
PPM
7
6
5
4
3
2
1
;blank line
F1: 399.807
F2: 100.541
EX: s2pul
SW1: 6410
PW: 5.0 us
PD: 2.0 sec
OF1: 2376.3
NA: 64
LB: 0.2
PTS1d: 25641 , 32768
USER: -- DATE: Jan 19 2011
Nuts - Salec2pemc1v s2pul H1.fid


157.005
110.271
77.325
77.213
77.005
76.692
65.189
65.130
60.747
58.366
22.823
21.528
14.601
10.606
CO2Et
NH
12b (45%)
160
140
120
100
80
60
40
20
PPM
:blank line
F1: 100.542
F2: 399.807
EX: s2pul
SW1: 24510
PW: 3.3 us
PD: 2.0 sec
OF1: 10555.7
NA: 2000
LB: 0.2
PTS1d: 31875 . 32768
USER: -- DATE: Jan 28 2011
Nuts - Salec2pentclv_s2pul C13.fid