A General one step Synthesis of β-nitronitriles

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General experimental

Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen. All glassware was flame dried and allowed to cool under a stream of nitrogen before use. Cooling to 0 $^{\circ}$C was effected using an ice-water bath. Cooling to temperatures below 0 $^{\circ}$C was effected using dry ice-acetone mixtures. Reactions were monitored by thin layer chromatography (TLC) using Polygram® SIL G/UV_{254} 0.25 mm silica gel precoated plastic plates with fluorescent indicator. Sheets were visualised using ultra-violet light (254 nm) and/or anisaldehyde or $KMnO_4$ solutions, as appropriate. Flash column chromatography was performed using Fluorochem silica gel 60, 35-70 μ. The liquid phase was analytical grade 40-60 petroleum ether (petrol) and ethyl acetate (EtOAc) unless otherwise noted.

Purification of Solvents and Reagents:

Commercial solvents and reagents were used as supplied or purified in accordance with standard procedures, as described below.

Tetrahydrofuran (THF) was pre-dried over sodium wire and distilled under an atmosphere of dry nitrogen from sodium benzophenone ketal or obtained from a solvent tower, where degassed THF was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure.

Diethyl ether (Et_2O) was pre-dried over sodium wire and distilled under an atmosphere of dry nitrogen from sodium benzophenone ketal or obtained from a solvent tower, where degassed Et_2O was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure.

Toluene was obtained form a solvent tower, where degassed toluene was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure. Dichloromethane was distilled from calcium hydride powder or purchased as an analytical grade and stored over 4Å molecular sieves. Anhydrous MeCN was used as supplied.

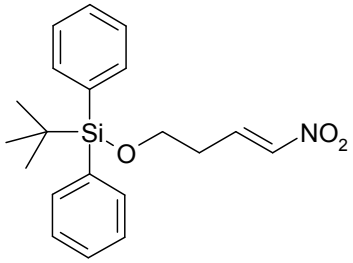
Characterisation:

Melting points are uncorrected and were recorded on a Reichert Melting Point Apparatus.

Optical rotations were recorded at 25 °C on a JASCO DIP-370 Digital Polarimeter and are reported in deg cm^2 g^{-1}. Infrared spectra are recorded on a Perkin-Elmer 1600 FTIR instrument as a thin film on sodium chloride discs or as dilute chloroform solutions. ^1H and ^{13}C NMR spectra were recorded on either a Bruker AV 400 or a Bruker DRX 500 as dilute solutions in deuterochloroform unless otherwise stated. All chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks. All chemical shifts are reported relative to chloroform (δ_H = 7.27 ppm, δ_c = 77.1 ppm). Coupling constants (*J*) are reported in Hertz and are recorded as observed in the spectrum without averaging. The multiplicity of an ^1H signal is designated by the following abbreviations: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet and quin = quintet, br = broad signal. ^{13}C multiplicities were assigned using a DEPT sequence. Where appropriate, HMQC and NOE experiments were carried out to aid assignment. Mass spectra were acquired on a VG micromass 70E, VG Autospec or Micromass LCTOF. Elemental analyses were performed on an Exeter Analytical Inc. CE440 Elemental Analyser.

Nitroalkenes 2 were prepared according to literature procedures[1] and their data was in accord with that published.[2]

***tert*-Butyl-((*E*)-4-nitro-but-3-enyloxy)-diphenyl-silane**

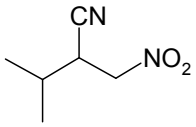


To a stirred solution of 3-(*tert*-Butyl-diphenyl-silanyloxy)-propionaldehyde[3] (789 mg, 2.52 mmol) in nitromethane (680 μL, 12.60 mmol) at rt was added triethylamine (35 μL, 0.25 mmol) dropwise over a 5 min period. The solution was stirred under N_2 for 16 h. Excess solvent was evaporated *in vaccuo* and the crude nitro-alcohol (670 mg, 1.79 mmol) dissolved in CH_2Cl_2 (6 mL), cooled to 0 ˚C and MsCl (278 μL, 3.59 mmol) followed by Ethyl-diisopropyl-amine (1.10 mL, 6.28 mmol) added. The solution was allowed to warm to rt and stirred under N_2 until TLC analysis indicated consumption of nitro-alcohol. Water and CH_2Cl_2 were added, and the organic phase separated, washed with 2 M HCl, brine, dried ($MgSO_4$) and concentrated to an orange oil, which was purified by flash chromatography (silica, 20-40 % CH_2Cl_2: petrol) to give the title compound as a yellow oil (341 mg, 53 %). Rf 0.37 (30 % DCM: petrol); IR ν_{max} ($CHCl_3$) 3106, 2932, 2859, 1651, 1353, 1095, 972 cm^{-1}; ^1H NMR δ 1.12 (9H, s, $(CH_3)_3C$), 2.48 (2H, dtd, *J* = 7.5, 6.0, 1.5, CH_2CH_2OSi), 3.83 (2H, t, *J* = 6.0,

CH_2OSi), 7.05 (1H, dt, *J* = 13.5, 1.5, CH=C*H*NO_2), 7.31 (1H, dt, *J* = 13.5, 7.5, C*H*=CHNO_2), 7.41 (4H, m, ArC*H*), 7.46 (2H, m, ArC*H*), 7.66 (4H, m, ArC*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.2 (*C*(CH_3)$_3$), 26.8 (C(*C*H_3)$_3$), 31.7 (*C*H_2CH_2OSi), 61.5 (*C*H_2OSi), 128.0 (Ar*C*H), 129.9 (Ar*C*H), 133.2 (Ar*C*), 135.5 (Ar*C*H), 139.8 (*C*=CHNO_2), 140.8 (*C*HNO_2); m/z (ESI$^+$) 378 (100 %, M+Na$^+$); HRMS $C_{20}H_{25}NNaO_3Si$ calcd. 378.14959, found 378.1493.

General method A for the synthesis of β-nitronitriles.

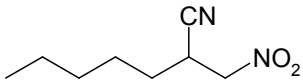
3-Methyl-2-nitromethylbutyronitrile



To a stirred solution of KCN (7.0 mg, 0.1 mmol) and 18-crown-6 (27.0 mg, 0.1 mmol) in MeCN (1.2 mL) was added (*E*)-3-methyl-1nitro-but-1-ene (120.0 mg, 1.0 mmol) and acetone cyanohydrin (114.0 μL), the mixture stirred at rt and monitored for consumption of nitro-alkene by TLC. The mixture was concentrated to an orange oil, which was purified by flash chromatography (silica, eluting with 50 % CH_2Cl_2: petrol) to afford the title compound (108.0 mg, 73 %) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.13 (3H, d, *J* = 6.8), 1.16 (3H, d, *J* = 6.8), 2.01 (1H, appt. oct, *J* = 4), 3.35 (1H, m), 4.52 (1H, dd, *J* = 14.0, 6.0), 4.63 (1H, dd, *J* = 14.0, 8.4). All data was in accord with the literature.[4]

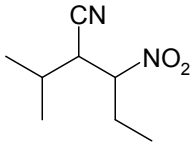
General method B for the synthesis of β-nitronitriles.

2-Nitromethyl-heptanenitrile



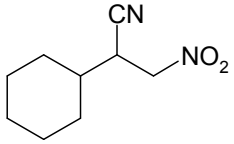
To a stirred solution of KCN (7.0 mg, 0.1 mmol), 18-crown-6 (27.0 mg, 0.1 mmol) and acetone cyanohydrin (109.8 μL, 1.2 mmol) in MeCN (1 mL) was added a solution of (*E*)-1-Nitro-hept-1-ene (143.0 mg, 1.0 mmol) in MeCN (5 mL) via syringe pump over a 5 h period. After complete addition a further portion of acetone cyanohydrin (109.8 μL, 1.2 mmol) was added and the solution stirred at rt and monitored for consumption of nitro-alkene by TLC. The mixture was concentrated to an orange oil and purified by flash chromatography (silica, eluting with 10 % acetone: petrol) to afford the title compound (116 mg, 68 %) as a colourless oil. Rf 0.17 (10 % acetone: petrol), IR ν_{max} (KBr disk) 2958, 2931, 2863, 2248, 1561, 1378 cm^{-1}. ^{1}H NMR δ 0.92 (3H, m), 1.35 (4H, m), 1.47-1.75 (4H, m), 3.40 (1H, m,), 4.51 (1H, ddd, *J* = 14.0, 7.6, 0.8), 4.64 (1H, ddd, *J* = 14.0, 7.6, 0.8). ^{13}C NMR δ 13.9 (*C*H_3), 22.3 (*C*H_2), 26.3 (*C*H_2), 29.4 (*C*H_2), 29.9 (*C*HCN), 30.9 (*C*H_2), 74.7 (*C*H_2NO_2), 118.0 (*C*N); m/z (EI$^+$) 193 (100%, M+Na$^+$). HRMS $C_8H_{14}N_2NaO_2$ calcd. 193.0947, found 193.0941. Anal. Calcd. for $C_8H_{14}N_2O_2$: C 56.45 %, H 8.29 %, N 16.46 %. Found C 56.17 %, H 8.25 %, N 16.16 %.

2-Isopropyl-3-nitro-pentanenitrile



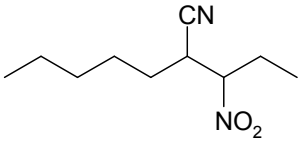
Synthesised using general procedure A. Isolated as a 1:1 mixture of diastereoisomers which were seperable by flash chromatography (silica, 40 % CH_2Cl_2: petrol) as a white solid (123 mg, 69 %), m.p. 41-42 ˚C. Rf 0.26 (40 % CH_2Cl_2: petrol); IR ν_{max} ($CHCl_3$) 2973, 2247, 1560, 1463, 1376 cm^{-1}. First eluted diastereoisomer: ^1H NMR δ 1.04 (3H, t, *J* = 7.6), 1.13 (6H, t, *J* = 6.8), 1.81 (1H m), 2.02-2.25 (2H, m), 3.21 (1H, dd, *J* = 10.4, 3.6), 4.60 (1H, td, *J* = 10.0, 3.2). ^{13}C NMR δ 9.9 (*C*H_3), 19.4 (*C*H_3), 21.0 (*C*H_3), 25.6 (*C*H_2), 27.8 (*C*H), 42.4 (*C*HCN), 87.2 (*C*HNO_2), 116.5 (*C*N). m/z (EI^+) 193 (100 %, M+Na^+). HRMS $C_8H_{14}N_2NaO_2$ calcd. 193.0938, found 193.09475.
Second eluted diastereomer ^1H NMR δ 1.04 (3H, t, *J* = 7.2), 1.12-1.17 (6H, m), 1.91-2.03 (2H, m), 2.11-2.23 (1H m), 2.85 (1H, appt t, *J* = 7.2), 4.58-4.65 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.9 (*C*H_3), 19.4 (*C*H_3), 20.9 (*C*H_3), 25.6 (*C*H_2), 27.8 (*C*H), 42.5 (*C*HCN), 87.2 (*C*HNO_2), 116.5 (*C*N).

2-Cyclohexyl-3-nitro-propionitrile



Synthesised using general procedure A. Isolated as a colourless oil (238 mg, 75 %). Rf 0.20 (50 % DCM: petrol); IR ν_{max} (KBr disk) 2930, 2856, 2245, 1558, 1450, 1430, 1377 cm^{-1}. ^1H NMR δ 1.19-1.29 (5H, m), 1.58-1.86 (6H, m), 3.34 (1H, m), 4.55 (1H, ddd, *J* = 13.6, 6.0, 1.6) 4.64 (1H, ddd, *J* = 13.6, 6.0, 1.6). ^{13}C NMR δ 25.2 (2 × *C*H_2), 25.7 (*C*H_2), 29.0 (*C*H_2), 31.0 (*C*H_2), 36.17 (*C*HCN), 37.5 (*C*H), 73.3 (*C*H_2NO_2), 117.2 (*C*N). m/z (EI^+) 205 (39 %, M+Na^+). HRMS $C_9H_{14}N_2NaO_2$ calcd. 205.0953, found 205.0930. Anal. calcd. for $C_9H_{14}N_2O_2$ C 59.32 %, H 7.74 %, N 15.37 %. Found C 59.45 %, H 7.84 %, N 15.34 %.

2-(1-Nitro-propyl)-heptanenitrile

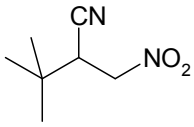


Synthesised using general procedure B, isolated as a colourless oil as a 1:1 mixture of diastereomers, seperable by flash chromatography (20 % ether: petrol). Rf 0.23 (20 % ether: petrol); IR ν_{max} ($CHCl_3$) 2931, 2864, 2248, 1561, 1459, 1374, 1354 cm^{-1}; ^1H NMR δ 0.9 (3H, m), 1.04 (3H, t, *J* = 7.2), 1.31-1.40 (4H, m), 1.42-1.66 (4H, m), 2.08-2.18 (2H, m), 3.22 (1H, td, *J* = 9.2, 4.0), 4.48 (1H, td, *J* = 9.6, 4.0); ^{13}C NMR δ 9.9 (*C*H_3), 13.8 (*C*H_3), 22.2 (*C*H_2), 26.0 (*C*H_2), 26.3 (*C*H_2), 29.5 (*C*H_2),

30.9 (*C*H_2), 35.7 (*C*HCN), 89.1 (*C*HNO_2), 117.6 (*C*N); m/z 221 (18 %, M+Na^+). HRMS $C_{10}H_{18}N_2NaO_2$ calcd. 221.12605, found 221.1258.

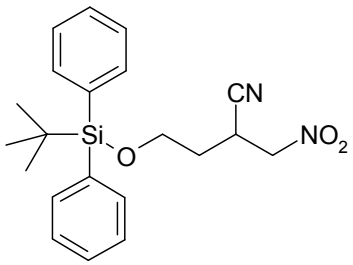
Second diastereomer NMR δ 0.88-0.96 (3H, m), 1.06 (3H, t, *J* = 7.2),1.37-1.47 (4H, m), 1.41-1.54 (1H, m), 1.54-1.69 (3H, m), 1.98 (1H, dqd, *J* = 14.4, 7.2, 4.8), 2.34 (1H, ddq, *J* = 14.8, 9.6, 7.4), 3.04 (1H, dt, *J* = 9.6, 5.6), 4.51 (1H, ddd, *J* = 10.0, 5.4, 5.2); ^{13}C NMR δ 10.1 (*C*H_3), 13.9 (*C*H_3), 22.3 (*C*H_2), 25.3 (*C*H_2), 26.7 (*C*H_2), 28.7 (*C*H_2), 31.0 (*C*H_2), 35.1 (*C*HCN), 88.4 (*C*HNO_2), 117.4 (*C*N).

3,3-Dimethyl-2-nitromethyl-butyronitrile



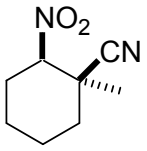
Synthesised using general procedure A, isolated as a white solid mp 45-47 ˚C (172 mg, 64 %). Rf 0.43 (40 % DCM: Petrol); IR ν_{max} ($CHCl_3$) 2971, 2248,1565, 13.74, 902 cm^{-1}; ^{1}H NMR δ 1.15 (9H, s), 3.27 (1H, dd, *J* = 7.8, 6.8), 4.57 (2H, dd, *J* = 7.8, 6.8); ^{13}C NMR δ 27.3 (*C*H_3), 33.4 (*C*), 41.5 (*C*HCN), 73.0 (*C*H_2NO_2), 117.7 (*C*N); m/z (EI$^+$) 179 (100 %, M+Na^+); HRMS $C_7H_{12}N_2NaO_2$ calcd. 179.0791. Found 179.0791.

4-(*tert*-Butyl-diphenyl-silanyloxy)-2-nitromethyl-butyronitrile



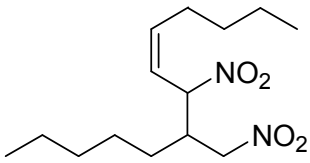
Synthesised by general procedure B, isolated as a yellow oil (143 mg, 76 %); Rf 0.08 (50 % DCM: petrol); IR ν_{max} ($CHCl_3$) 2932, 2860, 2306, 1565, 1375, 1266, 1112 cm^{-1}; ^{1}H NMR 1.08 (9H, s), 1.93 (2H, m), 3.77 (1H, m), 3.87 (2H, m), 4.60 (1H, dd, *J* = 8.8, 4.4), 4.67 (1H, dd, *J* = 8.8, 6.0), 7.44 (6H, m), 7. 66 (4H, m); ^{13}C NMR δ 19.2 (*C*), 26.9 (*C*H_3), 32.1 (*C*H_2), 60.0 (*C*H_2OSi), 74.5 (*C*H_2NO_2), 117.9 (*C*N), 127.9 (Ar*C*H), 129.9 (Ar*C*H), 132.6 (Ar*C*), 135.5 (Ar*C*H); m/z (ESI$^+$) 405 (100 %, M+Na^+), 383 (3 %, M+H^+); HRMS $C_{21}H_{26}N_2NaO_3Si$ calcd. 405.1605, found 405.1617, $C_{21}H_{27}N_2O_3Si$ calcd. 383.1785, found 383. 1790; Anal. Calcd for $C_{21}H_{26}N_2O_3Si$: C 65.94 %, H 6.85 %, N 7.32 %. Found C 65.67 %, H 6.81 %, N 7.14 %.

1-Methyl-2-nitro-cyclohexanecarbonitrile (6)



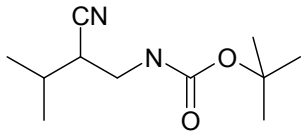
Synthesised using general procedure A, isolated as a white crystalline solid after crystallisation from ether/pentane mp 60.5 – 62.4 ˚C (31 mg, 84 %). Rf 0.48 (50% DCM: petrol); IR ν_{max} ($CHCl_3$) 2949, 2243, 1559, 1452, 1370 cm^{-1}; ^1H NMR δ 1.35-1.50 (2H, m), 1.49 (3H, s), 1.8 (2H, m), 2.02 (1H, m), 2.18 (1H, m), 2.24 (1H, dd, *J* = 10.0, 3.2), 2.28-2.33 (1H, m), 4.21 (1H, dd, *J* = 9.6, 3.2); ^{13}C δ 20.5 (CH_2), 23.9 (CH_2), 24.1 (CH_3), 29.0 (CH_2), 37.8 (CH_2), 38.4 (*C*), 90.5 ($CHNO_2$), 119.7 (*C*N); m/z (EI^+) 191 (100 %, $M+Na^+$); HRMS $C_8H_{12}N_2NaO_2$ calcd. 191.1868, found 191.0798; Anal Calcd. For $C_8H_{12}N_2O_2$ C 57.13 %, H 7.19 %, N 16.66 %. Found C 57.06 %, H 7.17 %, N 16.48 %.

(E)-7-Nitro-8-nitromethyl-tridec-5-ene (4)



Isolated as a by product during the synthesis of 2-Nitromethyl-heptanenitrile under the conditions described in Method A as a colourless oil (71 mg, 14 %): Rf 0.28 (40 % DCM: petrol); IR ν_{max} ($CHCl_3$) 3696, 2931, 2862, 1601, 1557, 1458, 1380, 908 cm^{-1}; ^1H NMR δ 0.89 (3H, t, *J* = 7.0), 0.92 (3H, t, *J* = 7.5), 1.20-1.50 (12H, m), 2.20 (2H, m), 2.83 (1H, m), 4.43 (1H, dd, *J* = 13.7, 5.2), 4.57 (1H, dd, *J* = 13.7, 5.6), 5.49 (1H, dd, *J* = 9.9, 8.8), 5.57 (1H, app tt, *J* = 10.4, 1.0), 5.96 (1H, dt, *J* = 10.4, 7.8); ^{13}C NMR δ 13.9 (2×CH_3), 22.3 (CH_2), 26.0 (CH_2), 27.7 (CH_2), 28.0 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 40.9 ($CHCH_2NO_2$), 74.5 (CH_2NO_2), 85.5 ($CHNO_2$), 120.8 (*C*H=CHCH$_2$), 141.6 (CH=*C*HCH$_2$); m/z (EI^+) 309 (100%, $M+Na^+$), 304 (3.4%, $M+NH_4^+$); HRMS $C_{14}H_{26}N_2NaO_4$ calcd. 309.1785. Found 309.1774. $C_{14}H30N_3O_4$ calcd. 304.2231. Found 304.2236.

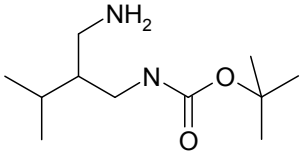
(2-Cyano-3-methyl-butyl)-carbamic acid *tert*-butyl ester (9)



To a stirred solution of 3-Methyl-2-nitromethylbutyronitrile **8** (0.30 g, 2.1 mmol) in EtOH (40 mL) was added Zinc powder (2.07 g, 31.7 mmol) and 6 M $HCl_{(aq)}$ (10 mL, and the reaction was stirred for 2 h. Excess zinc was removed by filtration, the EtOH removed *in vaccuo* and NaOH (15 %) added until pH 10. The aqueous layer was extracted into CH_2Cl_2, the combined organic layers washed with brine, dried ($MgSO_4$), and evaporated to dryness. The crude amino-nitrile (264 mg, 2.36 mmol)

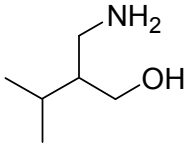
dissolved in CH_2Cl_2 (12 mL), Boc anhydride (566 mg, 2.59 mmol) added and the solution stirred at r.t. for 12 h. Excess solvent was removed *in vaccuo* and the resultant product purified by flash chromatography (silica, 20 % Et_2O: petrol) to yield the title compound (352 mg, 79 %) as a white solid (mp 54.3-55.3 ˚C). Rf 0.37 (30 % CH_2Cl_2: petrol); IR ν_{max} ($CHCl_3$) 3456, 2970, 2241, 1713, 1368 cm^{-1}; ^1H NMR δ 1.07 (3H, d, *J* = 6.8), 1.09 (3H, d, *J* = 6.8), 1.43 (9H, s), 1.90 (1H, appt. oct, *J* = 6.8), 2.78 (1H, ddd, *J* = 9.6, 5.2, 5.2), 3.18 (1H, ddd, *J* = 14.0, 9.6, 5.2), 3.47 (1H, ddd, *J* = 13.6, 5.2, 5.2), 5.05 (1H, brs); ^{13}C NMR δ 18.7 (*C*H_3), 20.9 (*C*H_3), 28.1 (*C*H), 28.7 (*C*H_3), 40.3 (*C*HCN), 41.7 (*C*H_2NH), 80.1 (*C*(CH_3)$_3$), 120.1 (*C*N), 155.7 (*C*=O); m/z (ESI) 235 ($M+Na^+$); HRMS $C_{11}H_{20}N_2NaO_2$ calcd. 235.1417. Found 235.1423. Anal. Calcd. For $C_{11}H_{20}N_2O_2$ C 62.24 %, H 9.50 %, N 13.20 %. Found C 62.27 %, H 9.62 %, N 13.16 %.

(2-Aminomethyl-3-methyl-butyl)-carbamic acid *tert*-butyl ester (10)



To a stirred solution of **9** (75.0 mg, 0.35 mmol) in Et_2O (2 mL) was added $LiAlH_4$ (50 mg, 1.41 mmol) and heated at reflux for 4 h. The reaction was allowed to cool to 0 °C, and water (0.5 mL), 20 % $NaOH_{(aq)}$ (0.5 mL) and water (1.5 mL) were added dropwise and sequentially. The granular precipitate was filtered through cotton wool, water and Et_2O added to the filtrate, the layers separated and the aqueous layer extracted twice with Et_2O. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated *in vaccuo* to yield the title compound as a yellow oil (68 mg, 89 %). Rf 0.12 (2 % MeOH: 1 % Net_3: CH_2Cl_2); IR ν_{max} ($CHCl_3$) 3455, 3387, 3310, 2875, 1713, 1391, 1366 cm^{-1}; ^1H NMR δ 0.89 (3H, d, *J* = 7.0), 0.91 (3H, d, *J* = 7.0), 1.28 (1H, m), 1.54 (2H, brs), 1.69 (1H, appt. oct, *J* = 6.8), 2.63 (1H, dd, *J* = 12.5, 7.5), 2.82 (1H, dd, *J* = 12.5, 4.0), 3.09 (1H, ddd, *J* = 13.0, 7.5, 5.5), 3.29 (1H, ddd, *J* = 13.0, 5.5, 5.5), 5.05 (1H, brs); ^{13}C NMR δ 19.7 (*C*H_3), 20.1 (*C*H_3), 27.8 (*C*H), 28.5 (*C*H_3), 41.3 (*C*H_2), 42.6 (*C*H_2), 47.1 (*C*H), 78.9 (*C*), 156.3 (*C*O). m/z 239 (16.6 %, $M+Na^+$); HRMS $C_{11}H_{24}N_2NaO_2$ calcd. 239.1730. Found 239.1724.

2-Aminomethyl-3-methyl-butan-1-ol (12)

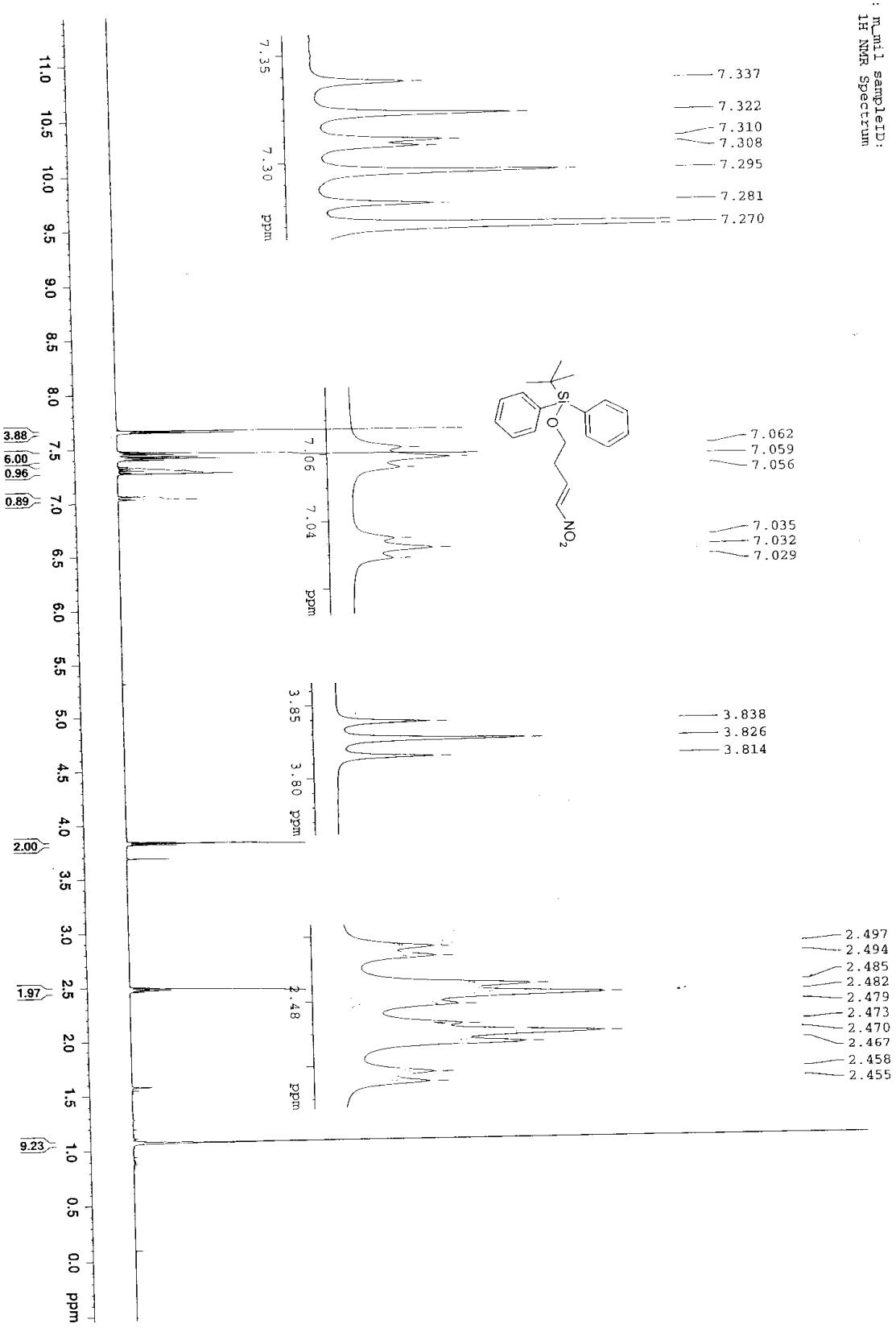


To a stirred solution of 3-Methyl-2-nitromethylbutyronitrile **(8)** (5.41g, 38.10 mmol) in THF (165 mL) at 0 °C was added a solution of $TiCl_3$ (20 % by weight in $HCl_{(aq)}$, 84.2 mL, 152.2 mmol). After 1 h the reaction was allowed to warm to rt and stirred until the purple colour disappeared (3-4 days). The reaction was extracted with ether (3 × 40 mL), and the combined extracts washed with brine,

dried ($MgSO_4$) and solvent removed *in vaccuo* to afford the crude and unstable α-cyano aldehyde **11** as a yellow oil (3.43 g). ^{1}H NMR δ 1.16 (3H, d, J=3.5), 1.24 (3H, d, J=3.5), 2.52 (1H, m), 3.41 (1H, dd, J=5.0, 0.8), 9.58 (1H, d, J=0.8); ^{13}C NMR δ 19.7 (*C*H_3), 21.3 (*C*H_3), 27.8 (*C*H), 51.9 (*C*H), 114.8 (*C*N), 191.9 (*C*O).

The yellow oil (3.43 g, 38.1 mmol) was immediately dissolved in Et_2O (200 mL), cooled to 0 °C and $LiAlH_4$ (8.68 g, 228.6 mmol) added portion-wise over 10 min. The mixture was heated at reflux for 4 h. The mixture was cooled to 0 °C and water (8.6 mL), 20 % $NaOH_{(aq)}$ (8.6 mL) and water (25.8 mL) were added dropwise and sequentially. After a granular precipitate had formed the solution was filtered through cotton wool, water and Et_2O added to the filtrate, the layers separated and the aqueous layer extracted twice with Et_2O. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated *in vaccuo.* The resulting oil was purified by ion exchange chromatography (SCX Strata^{TM}, 2M NH_3 in MeOH) to yield the title compound as a yellow oil (2.71 g, 77 %), which was further purified by bulb-to-bulb distillation to give a colourless oil (2.25 g, 64%). ^{1}H NMR δ 0.86 (3H, d, *J* = 1.4), 0.88 (3H, d, *J* = 1.4), 1.39 (1H, m), 1.63 (1H, appt oct, *J* = 6.5), 2.79 (1H, dd, *J* = 12.2, 9.2), 2.84 (2H, brs), 3.04 (1H, ddd, *J* = 12.1, 3.3, 1.6), 3.70 (1H, dd, *J* = 10.6, 8.3), 3.78 (1H, ddd, *J* = 10.6, 3.3, 1.5). All other data was in accord with the literature.[5]

1. a) Fieser, L. F.; Gates, M. *J. Am. Chem. Soc.* **1946**, *68*, 2249. b) Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138.
2. a) Kumaran, G.; Kulkarni, G.H. *Synthesis*, **1995**, 1545. b) Enders, D.; Wiedemann, J. *Synthesis*, **1996**, 1443.
3. Barry C.S.; Bushby, N.; Harding, J.R.; Willis, C.L., *Org. Lett*., **2005,** 7, 2683
4. Enders, D.; Syrig, R.; Raabe, G.; Fernández, R.; Gasch, C.; Lassaletta, J. *Synthesis*, **1996**, 48
5. Angle, S.R.; Belanger, D.S. *J. Org. Chem.,* **2004**, *69*, 4361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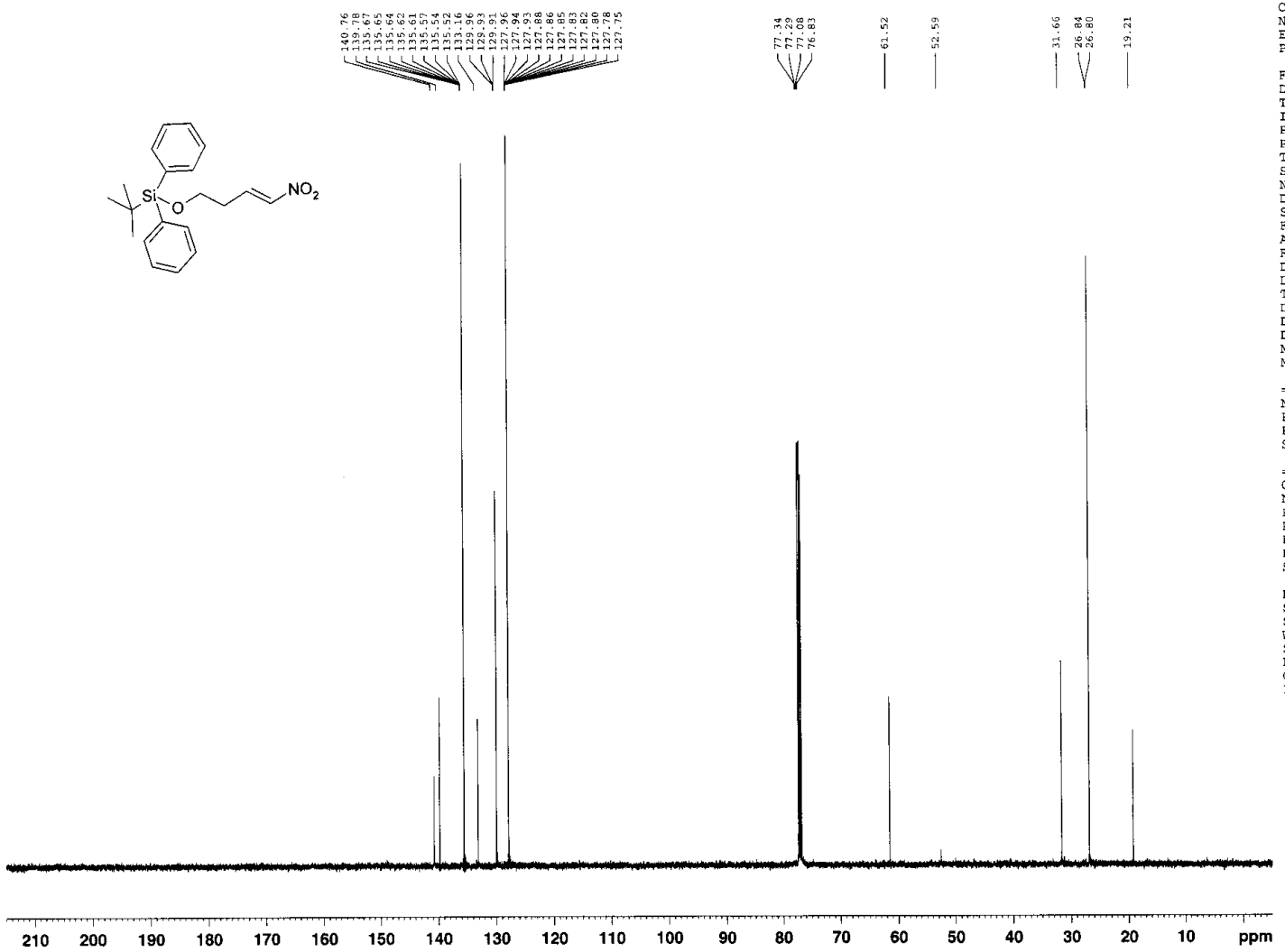
7.270
7.062
7.059
7.056
7.035
7.032
7.029
3.838
3.826
3.814
2.497
2.494
2.485
2.482
2.479
2.473
2.470
2.467
2.458
2.455
Si
O
NO2
3.88
6.00
0.96
0.89
2.00
1.97
9.23
ppm

userID: m_mil sampleID: mrm163
13C[CPD] Spectrum

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PROCNO                   1

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SOLVENT               CDCl3
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FIDRES            0.959672 Hz
AQ                0.5210612 sec
RG                   2896.3
DW                   15.900 use
DE                    6.00 use
TE                   300.0 K
D1              1.00000000 sec
D11             0.03000000 sec
DELTA           0.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

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NUC1                   13C
P1                    9.70 use
PL1                   4.00 dB
SFO1          125.7716219 MHz

======== CHANNEL f2 =======
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NUC2                   1H
PCPD2               100.00 use
PL2                  -3.00 dB
PL12                 16.00 dB
PL13                 18.00 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
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SF          125.7577890 MHz
WDW                     EM
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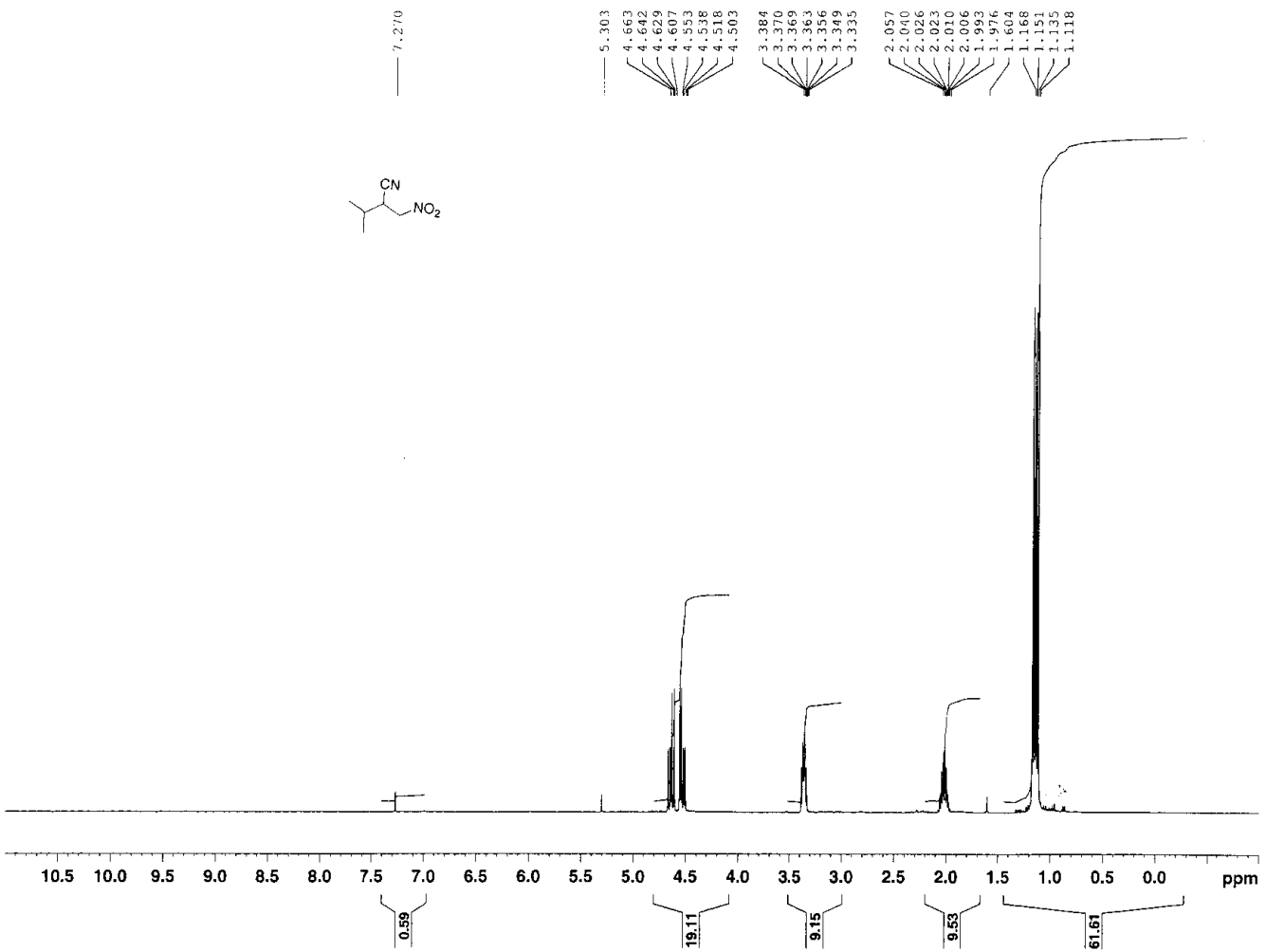
UserID m_mil SampleID mrm26 SupervisorID ander Lab Phone No. 1 Slot Number 42

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PROCNO                  1

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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                   50.8
DW                 60.800 usec
DE                  6.50 usec
TE                 295.9 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  7.00 usec
PL1                -0.90 dB
PL1W          11.52680206 W
SFO1          400.0724706 MHz

F2 - Processing parameters
SI                  65536
SF            400.0700042 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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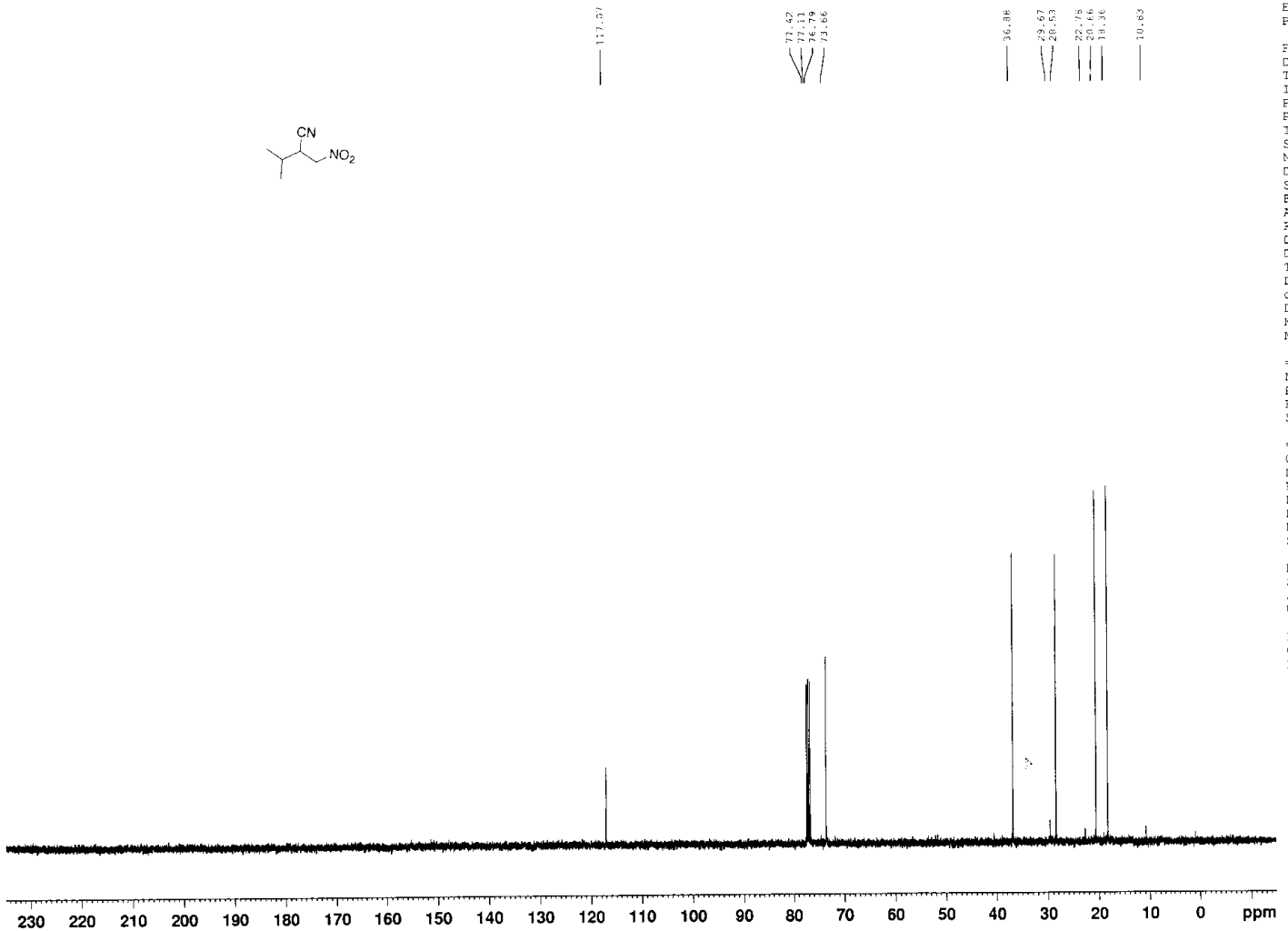
UserID m_mil SampleID mrm26 SupervisorID ander Lab Phone No. 13540 Slot Number 26

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Current Data Parameters
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PROCNO                         1

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Time                       13.48
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TD                          32768
SOLVENT                   CDCl3
NS                            128
DS                              2
SWH                   25125.629 Hz
FIDRES                0.766773 Hz
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RG                       18390.4
DW                        19.900 use
DE                         6.00 use
TE                       298.2 K
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d11                 0.03000000 sec
DELTA               0.89999998 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 =======
NUC1                         13C
P1                          7.55 use
PL1                         6.00 dB
SFO1               100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                      87.00 use
PL2                         0.00 dB
PL12                       21.00 dB
PL13                       26.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
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SF                 100.6127690 MHz
WDW                            EM
SSB                             0
LB                          1.00 Hz
GB                              0
PC                          1.40
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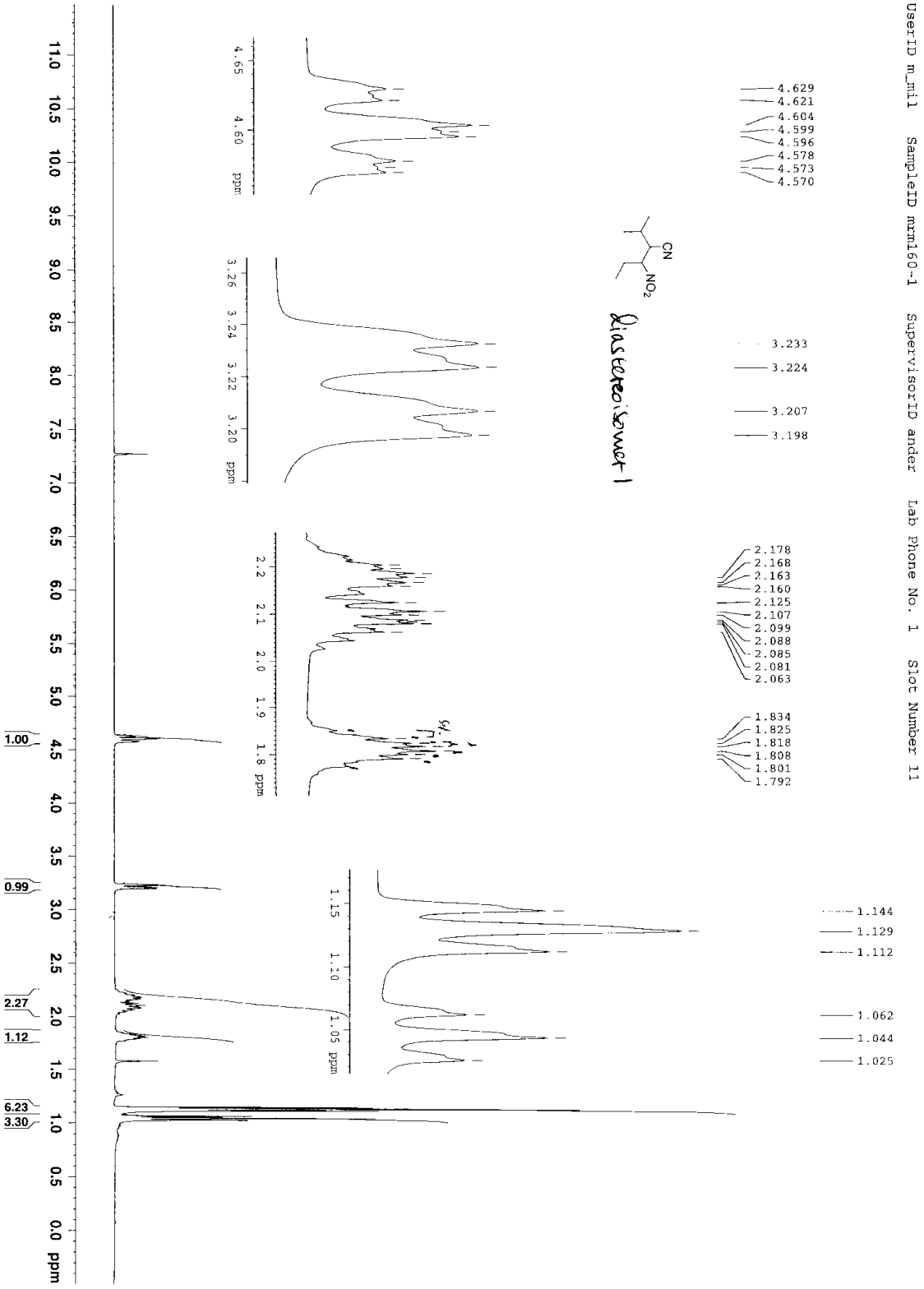
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3.207
3.198
2.178
2.168
2.163
2.160
2.125
2.107
2.099
2.088
2.085
2.081
2.063
1.834
1.825
1.818
1.808
1.801
1.792
1.144
1.129
1.112
1.062
1.044
1.025
CN
NO2
diastereoisomer 1
1.00
0.99
2.27
1.12
6.23
3.30
ppm

UserID m_mil SampleID mrm160-1 SupervisorID ander Lab Phone No. 1 Slot Number 11

diastereoisomer 1


```
Current Data Parameters
NAME        m_mil.mrm160
EXPNO                  6
PROCNO                 1

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Time               12.04
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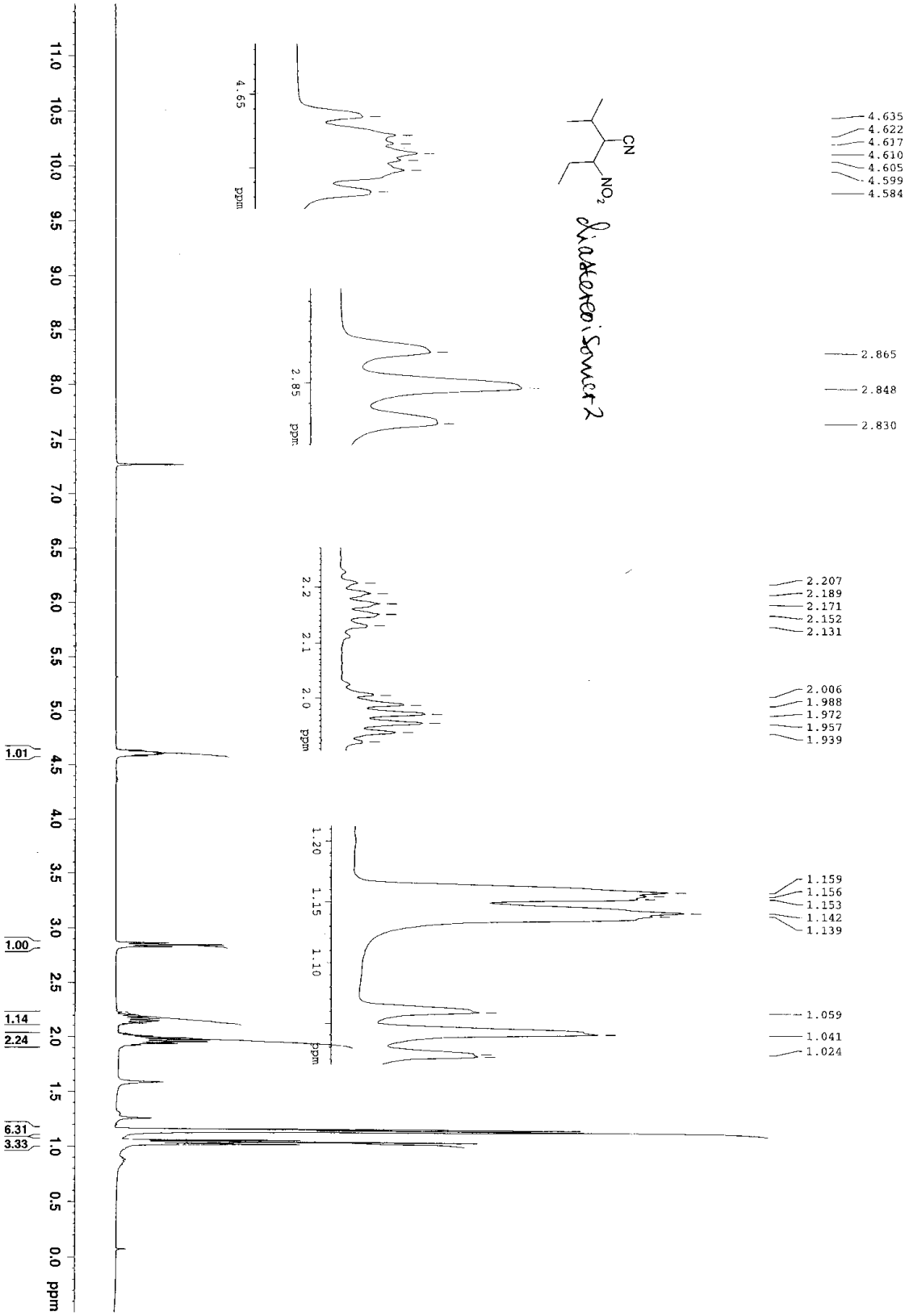
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   512
DS                     2
SWH            25125.629 Hz
FIDRES         0.766773 Hz
AQ             0.6521332 sec
RG                 32768
DW                19.900 use
DE                 6.00 use
TE                298.2 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 =======
NUC1                13C
P1                 7.55 use
PL1                6.00 dB
SFO1        100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2         waltz16
NUC2                1H
PCPD2             87.00 use
PL2                0.00 dB
PL12              21.00 dB
PL13              26.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```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2.189
2.171
2.152
2.131
2.006
1.988
1.972
1.957
1.939
1.159
1.156
1.153
1.142
1.139
1.059
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1.024
1.01
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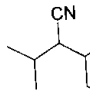
3.33
ppm

UserID m_mil SampleID mrm160-2 SupervisorID ander Lab Phone No. 1 Slot Number 12



diastereoisomer 2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Current Data Parameters
NAME                  m_mil.160
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
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Time                      12.28
INSTRUM                   av400
PROBHD    5 mm BBO BB-1H
PULPROG                zgpg30
TD                        32768
SOLVENT                   CDCl3
NS                          512
DS                            2
SWH                 25125.629 Hz
FIDRES                0.766773 Hz
AQ                    0.6521332 sec
RG                      23170.5
DW                       19.900 use
DE                        6.00 use
TE                       298.2 K
D1                  1.00000000 sec
d11                 0.03000000 sec
DELTA               0.89999998 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 =======
NUC1                        13C
P1                         7.55 use
PL1                        6.00 dB
SFO1               100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     87.00 use
PL2                        0.00 dB
PL12                      21.00 dB
PL13                      26.00 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127690 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
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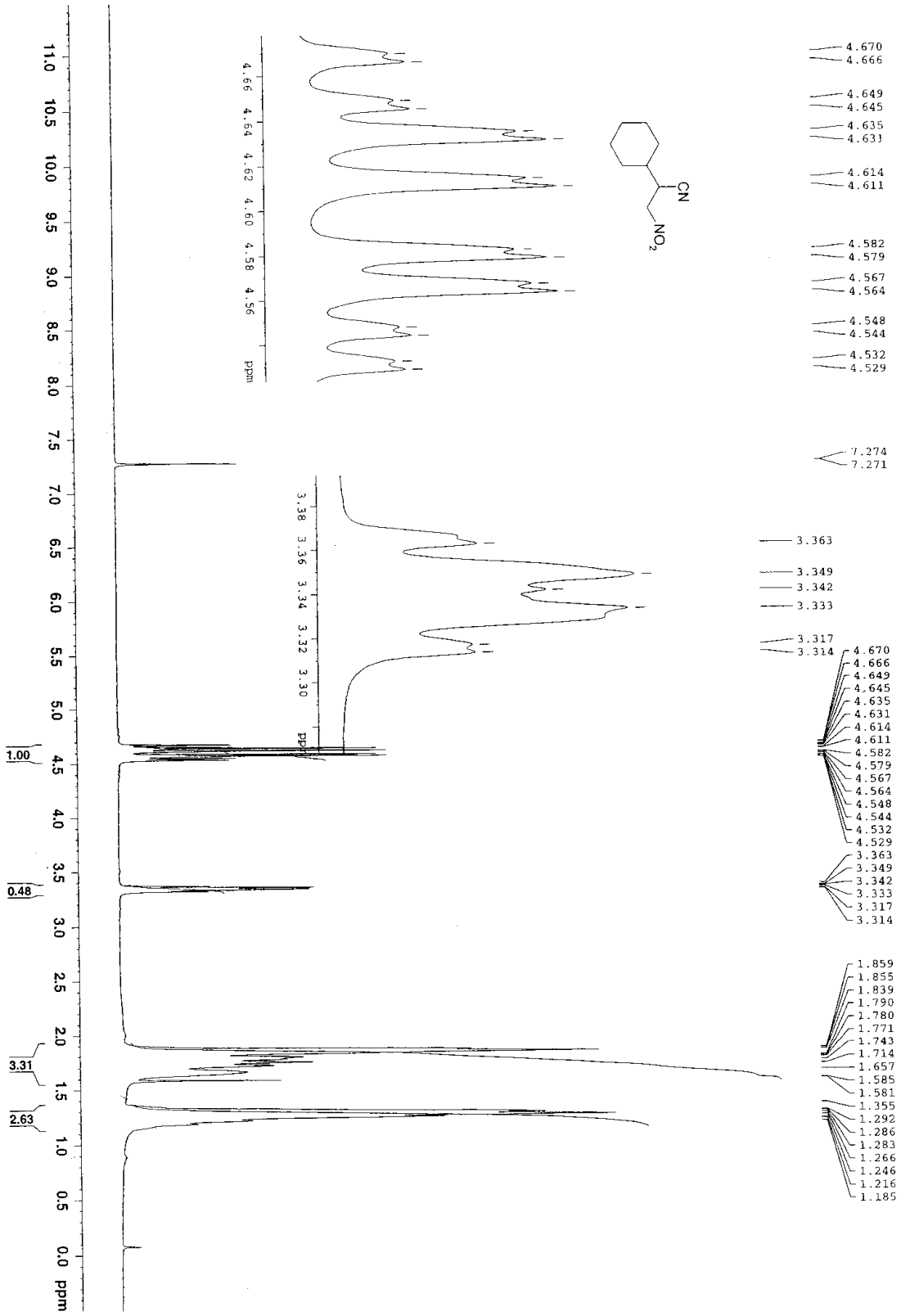
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4.548
4.544
4.532
4.529
7.274
7.271
3.363
3.349
3.342
3.333
3.317
3.314
1.859
1.855
1.839
1.790
1.780
1.771
1.743
1.714
1.657
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2.63
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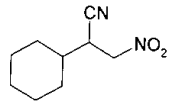
UserID m_mil SampleID mrm168 SupervisorID ander Lab Phone No. 12 Slot Number 38

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PROCNO                 1

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TD              32768
SOLVENT         CDCl3
NS               2048
DS                  2
SWH         25125.629 Hz
FIDRES       0.766773 Hz
AQ          0.6521332 sec
RG            23170.5
DW             19.900 use
DE              6.00 use
TE             298.2 K
D1          1.00000000 sec
d11         0.03000000 sec
DELTA       0.89999998 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 =======
NUC1               13C
P1                7.55 use
PL1               6.00 dB
SFO1       100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2        waltz16
NUC2               1H
PCPD2            87.00 use
PL2               0.00 dB
PL12             21.00 dB
PL13             26.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI              32768
SF         100.6127690 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
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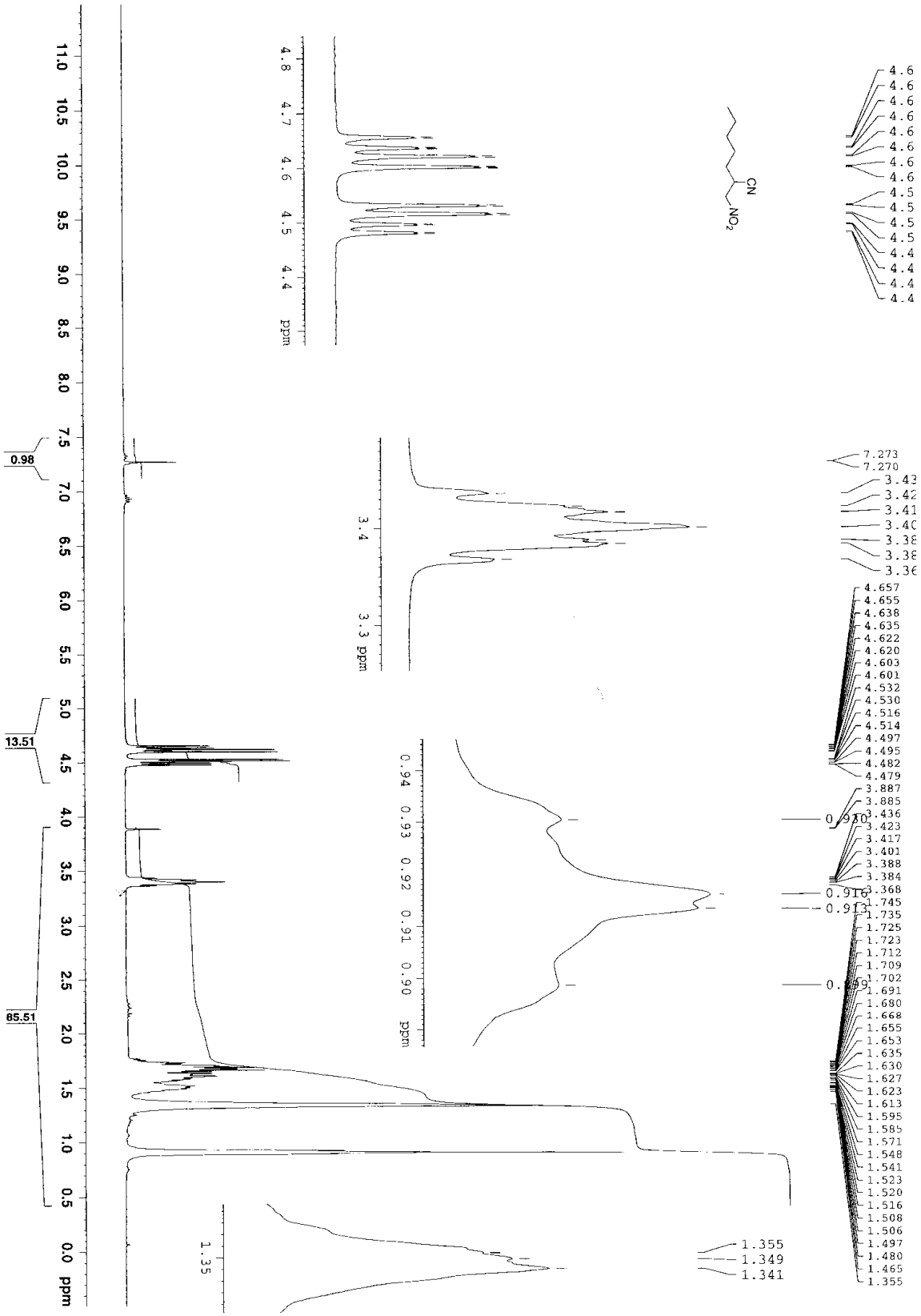
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4.8 4.7 4.6 4.5 4.4 ppm
3.4 3.3 ppm
0.94 0.93 0.92 0.91 0.90 ppm
1.35
4.6 4.6 4.6 4.6 4.6 4.6 4.6 4.6
4.5 4.5 4.5 4.5
4.4 4.4 4.4 4.4
7.273
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3.42
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3.40
3.38
3.38
3.36
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3.887 3.885 3.436 3.423 3.417 3.401 3.388 3.384 3.368
0.916
0.913
1.745 1.735 1.725 1.723 1.712 1.709 1.702 1.691 1.680 1.668 1.655 1.653 1.635 1.630 1.627 1.623 1.613 1.595 1.585 1.571 1.548 1.541 1.523 1.520 1.516 1.508 1.506 1.497 1.480 1.465 1.355
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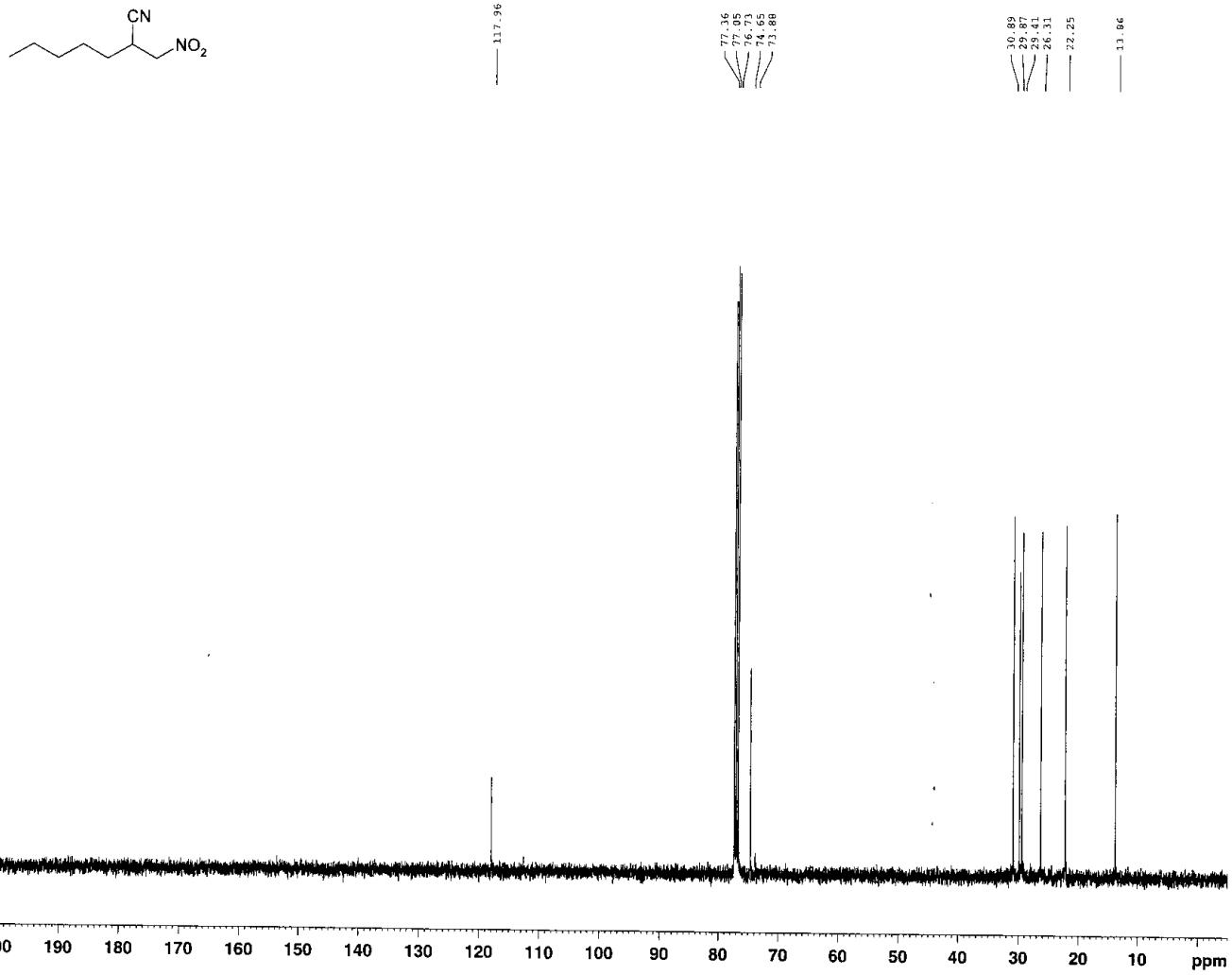
1.341

UserID m_mil SampleID mrm175 SupervisorID ander Lab Phone No. 1 Slot Number 7

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PROCNO                   1

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TD                  32768
SOLVENT             CDCl3
NS                    512
DS                      2
SWH           25125.629 Hz
FIDRES         0.766773 Hz
AQ             0.6521332 sec
RG                 7298.2
DW                19.900 use
DE                 6.00 use
TE                296.2 K
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d11           0.03000000 sec
DELTA         0.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 =======
NUC1                13C
P1                 8.25 use
PL1                6.00 dB
SFO1        100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                1H
PCPD2            105.00 use
PL2                0.00 dB
PL12              22.00 dB
PL13              26.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
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LB                 1.00 Hz
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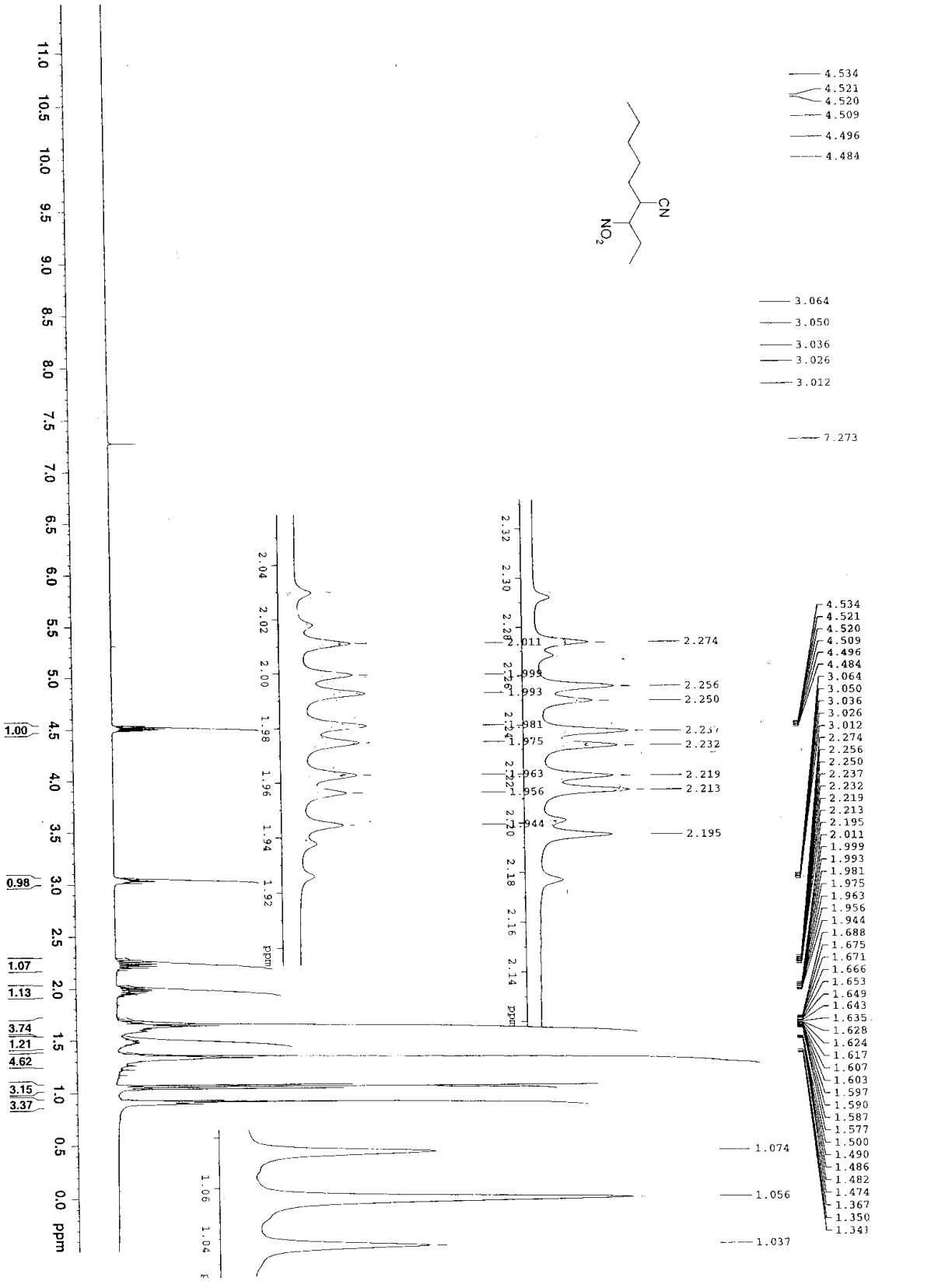
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2.256
2.250
2.237
2.232
2.219
2.213
2.195
1.074
1.056
1.037
1.00
0.98
1.07
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3.15
3.37
ppm

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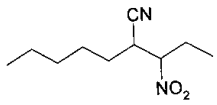


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PROCNO                 1

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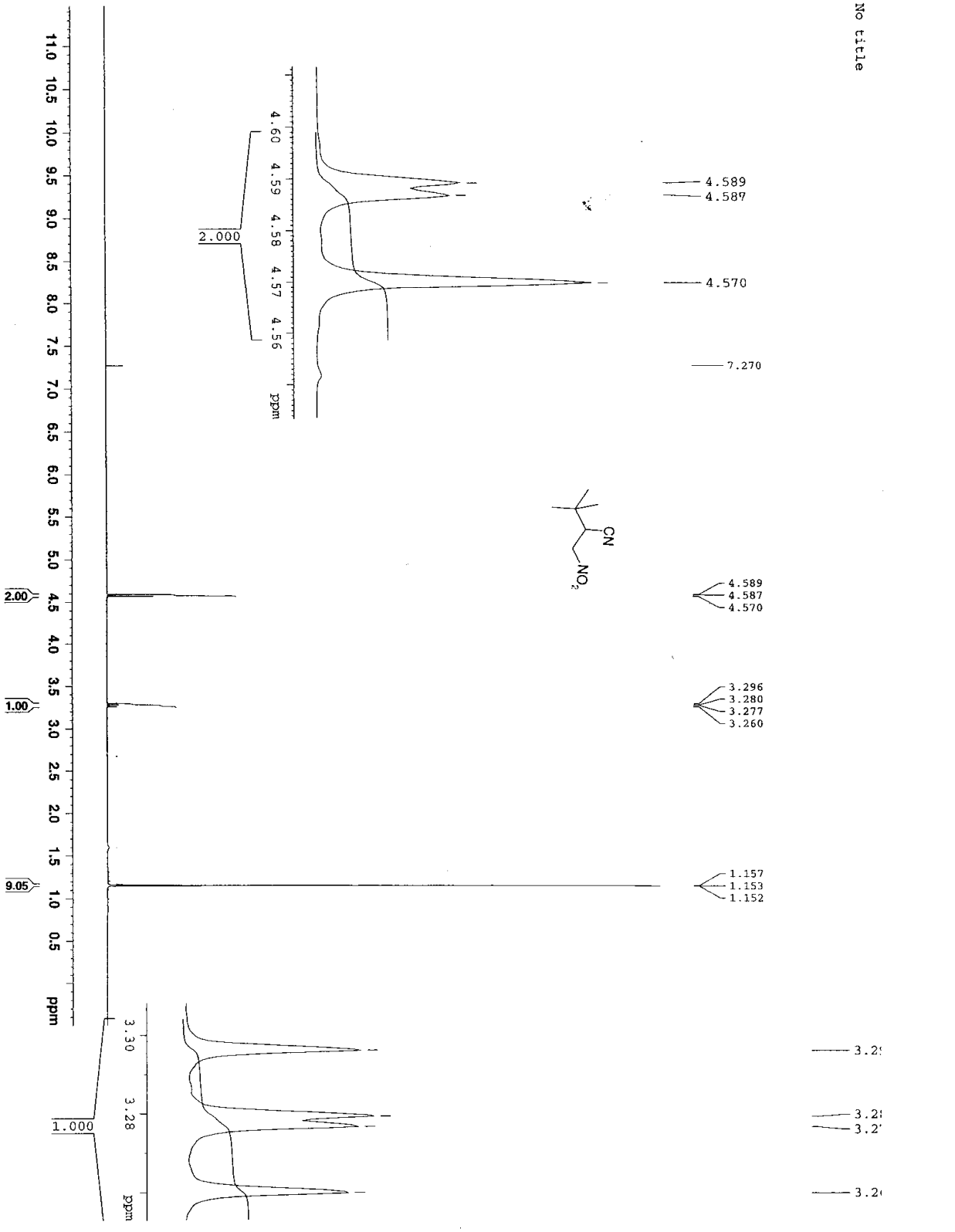
PULPROG         zgpg30
TD               32768
SOLVENT          CDCl3
NS                 128
DS                   2
SWH          25125.629 Hz
FIDRES        0.766773 Hz
AQ           0.6521332 sec
RG                8192
DW              19.900 use
DE               6.00 use
TE             298.2 K
D1          1.00000000 sec
d11         0.03000000 sec
DELTA       0.89999998 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

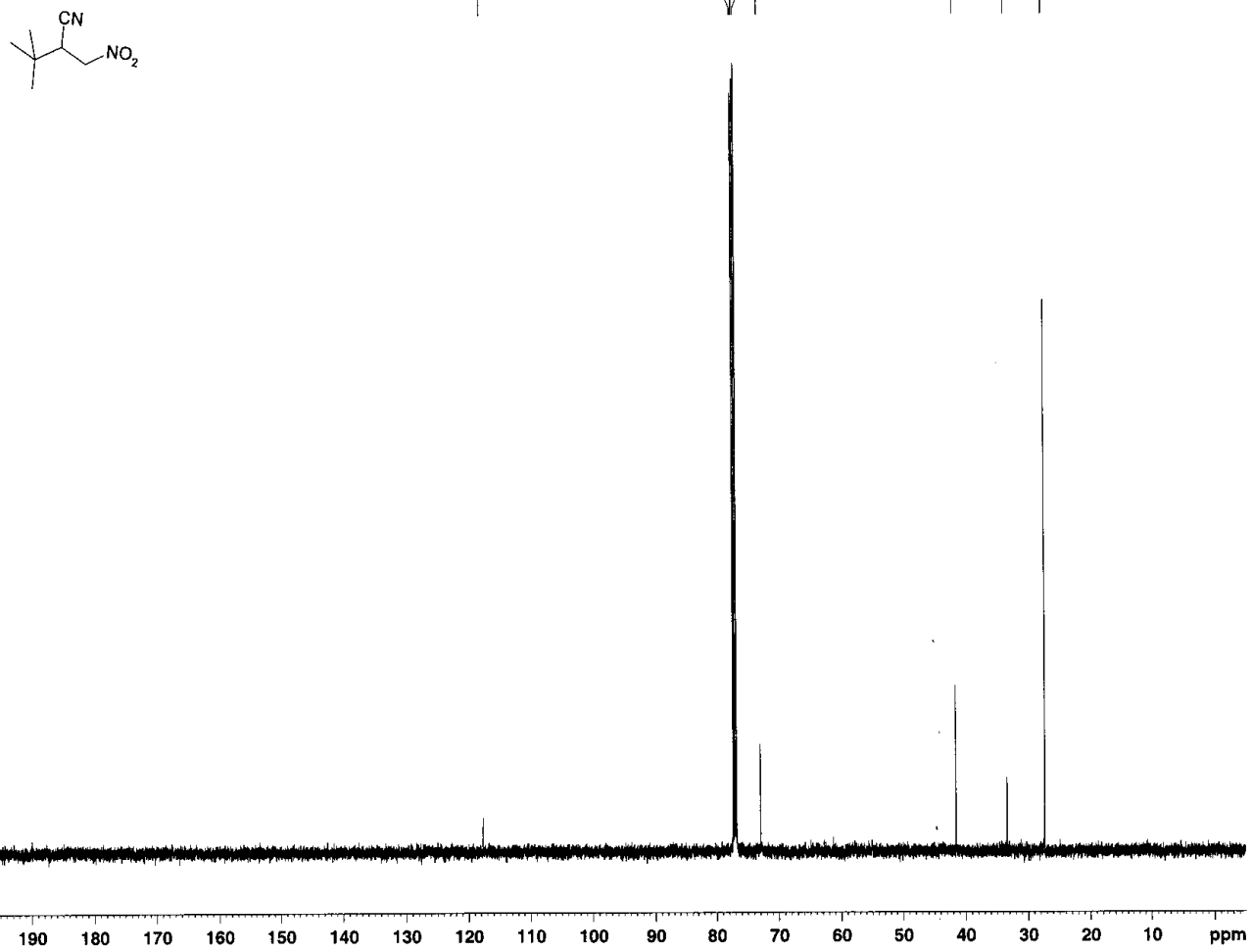
======== CHANNEL f1 =======
NUC1               13C
P1                8.25 use
PL1               6.00 dB
SFO1       100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2         waltz16
NUC2                1H
PCPD2          105.00 use
PL2              0.00 dB
PL12            22.00 dB
PL13            26.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI               32768
SF         100.6127690 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```


No title
4.589
4.587
4.570
7.270
4.589
4.587
4.570
3.296
3.280
3.277
3.260
1.157
1.153
1.152
CN
NO2
2.00
1.00
9.05
1.000
2.000
ppm

userID: m_mil sampleID: mrm131
13C[CPD] Spectrum



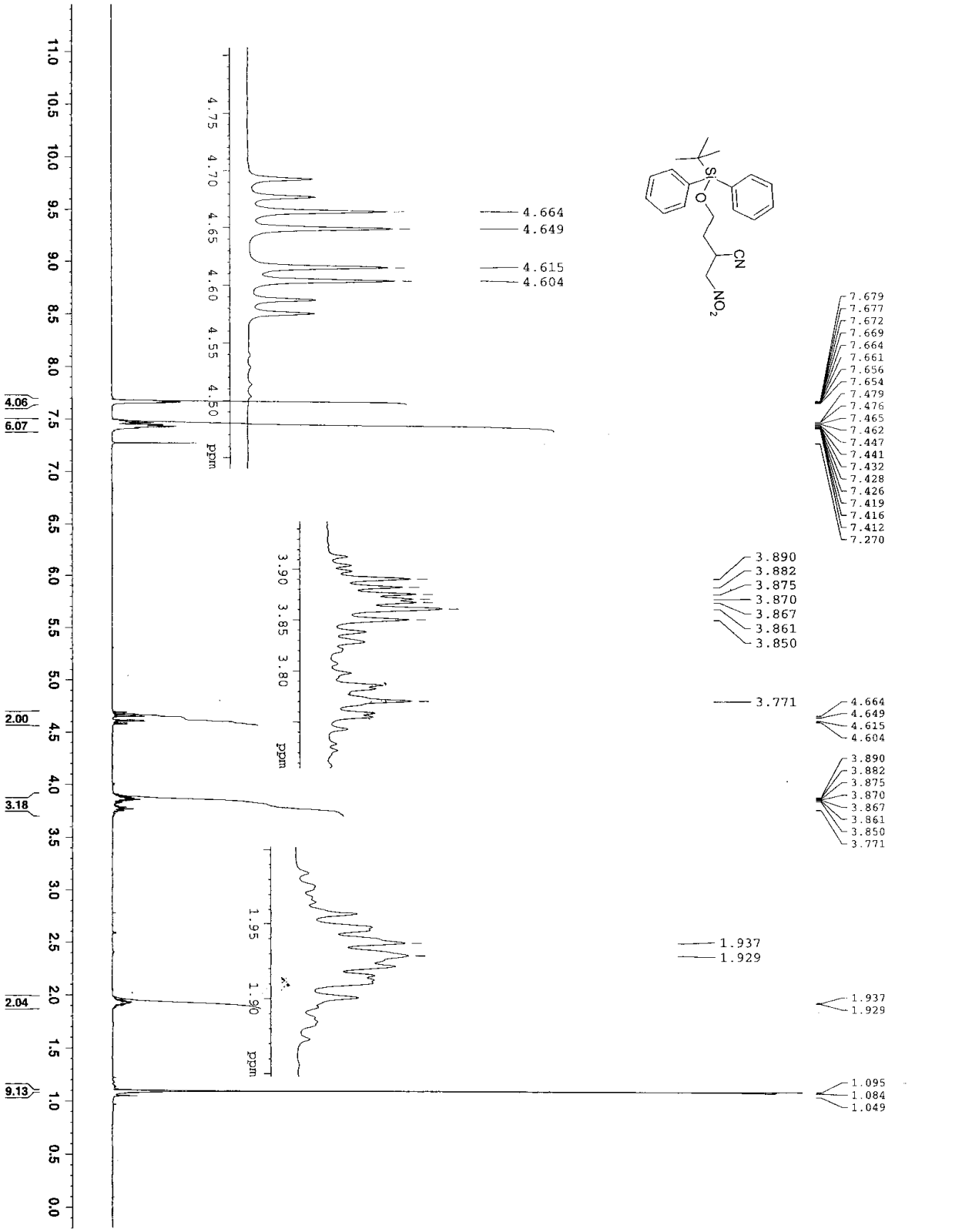

```
Current Data Parameters
NAME        m_mil.mrm131
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080121
Time               18.52
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  512
DS                    2
SWH           31446.541 Hz
FIDRES         0.959672 Hz
AQ            0.5210612 sec
RG                 3251
DW               15.900 use
DE                6.00 use
TE               300.0 K
D1           1.00000000 sec
D11          0.03000000 sec
DELTA        0.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

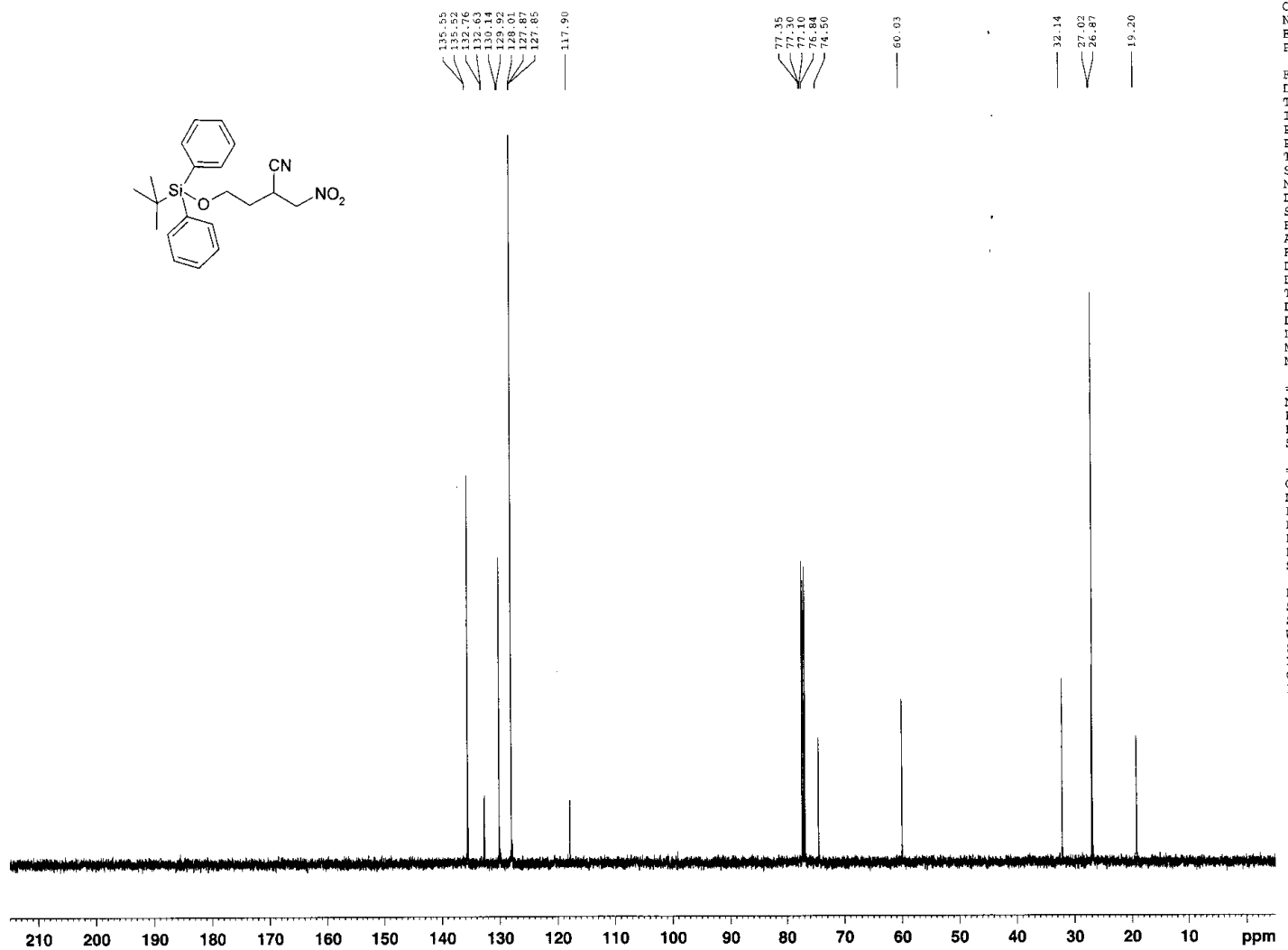
======== CHANNEL f1 =======
NUC1               13C
P1                9.70 use
PL1               4.00 dB
SFO1       125.7716219 MHz

======== CHANNEL f2 =======
CPDPRG2        waltz16
NUC2               1H
PCPD2           100.00 use
PL2              -3.00 dB
PL12             16.00 dB
PL13             18.00 dB
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF         125.7577890 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.00
```


4.664
4.649
4.615
4.604
7.679
7.677
7.672
7.669
7.664
7.661
7.656
7.654
7.479
7.476
7.465
7.462
7.447
7.441
7.432
7.428
7.426
7.419
7.416
7.412
7.270
3.890
3.882
3.875
3.870
3.867
3.861
3.850
3.771
1.937
1.929
1.095
1.084
1.049
CN
NO2
4.06
6.07
2.00
3.18
2.04
9.13
ppm

userID: m_mil sampleID: mrm272
13C[CPD] Spectrum




```
Current Data Parameters
NAME        m_mil.mrm272
EXPNO                  2
PROCNO                 1

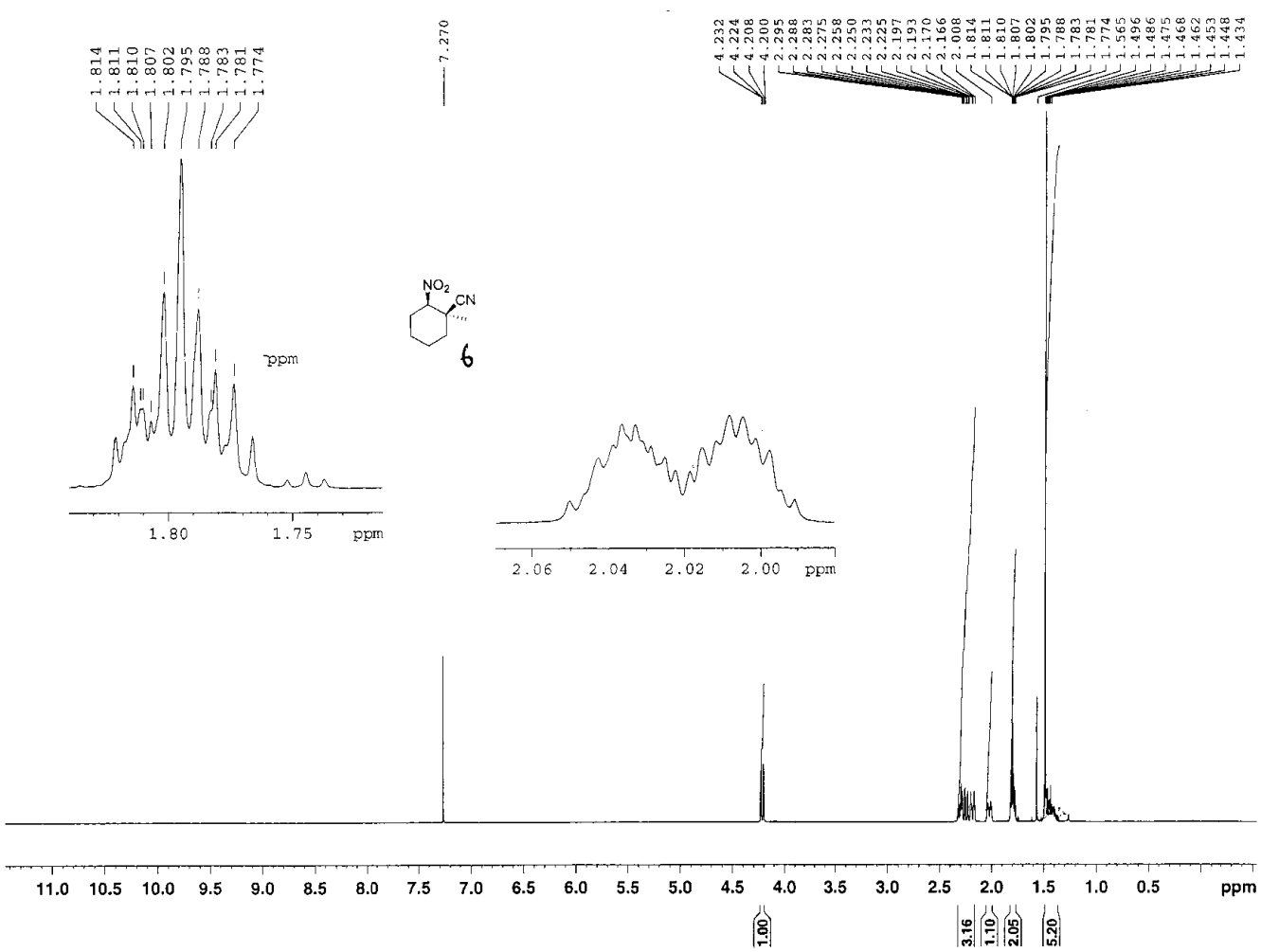
F2 - Acquisition Parameters
Date_           20071115
Time               18.06
INSTRUM           DRX500
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH           31446.541 Hz
FIDRES        0.959672 Hz
AQ            0.5210612 sec
RG                 8192
DW                15.900 use
DE                 6.00 use
TE                300.0 K
D1           1.00000000 sec
D11          0.03000000 sec
DELTA        0.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 =======
NUC1                13C
P1                 9.70 use
PL1                4.00 dB
SFO1       125.7716219 MHz

======== CHANNEL f2 =======
CPDPRG2         waltz16
NUC2                1H
PCPD2          100.00 use
PL2             -3.00 dB
PL12            16.00 dB
PL13            18.00 dB
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF         125.7577890 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.00
```

userID: m_mil sampleID: mrm215
1H NMR Spectrum



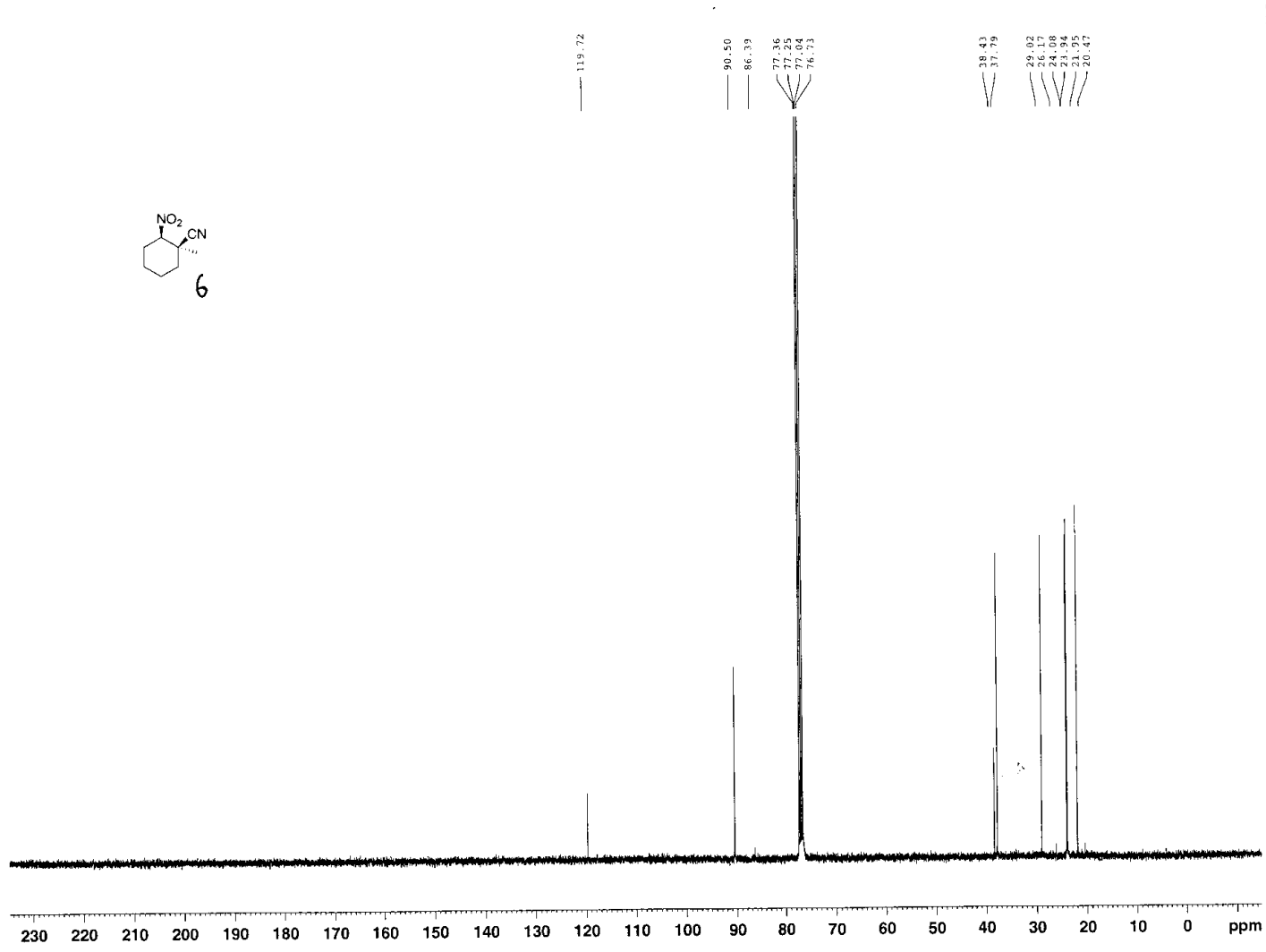

```
Current Data Parameters
NAME        m_mil.mrm215
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070920
Time               14.00
INSTRUM           DRX500
PROBHD   5 mm Multinucl
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                    16
DS                     2
SWH             5995.204 Hz
FIDRES          0.182959 Hz
AQ              2.7329011 sec
RG                 161.3
DW                83.400 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.93 usec
PL1                -3.00 dB
SFO1         500.1327507 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300243 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

UserID m_mil SampleID mrm215 SupervisorID ander Lab Phone No. 1 Slot Number 5



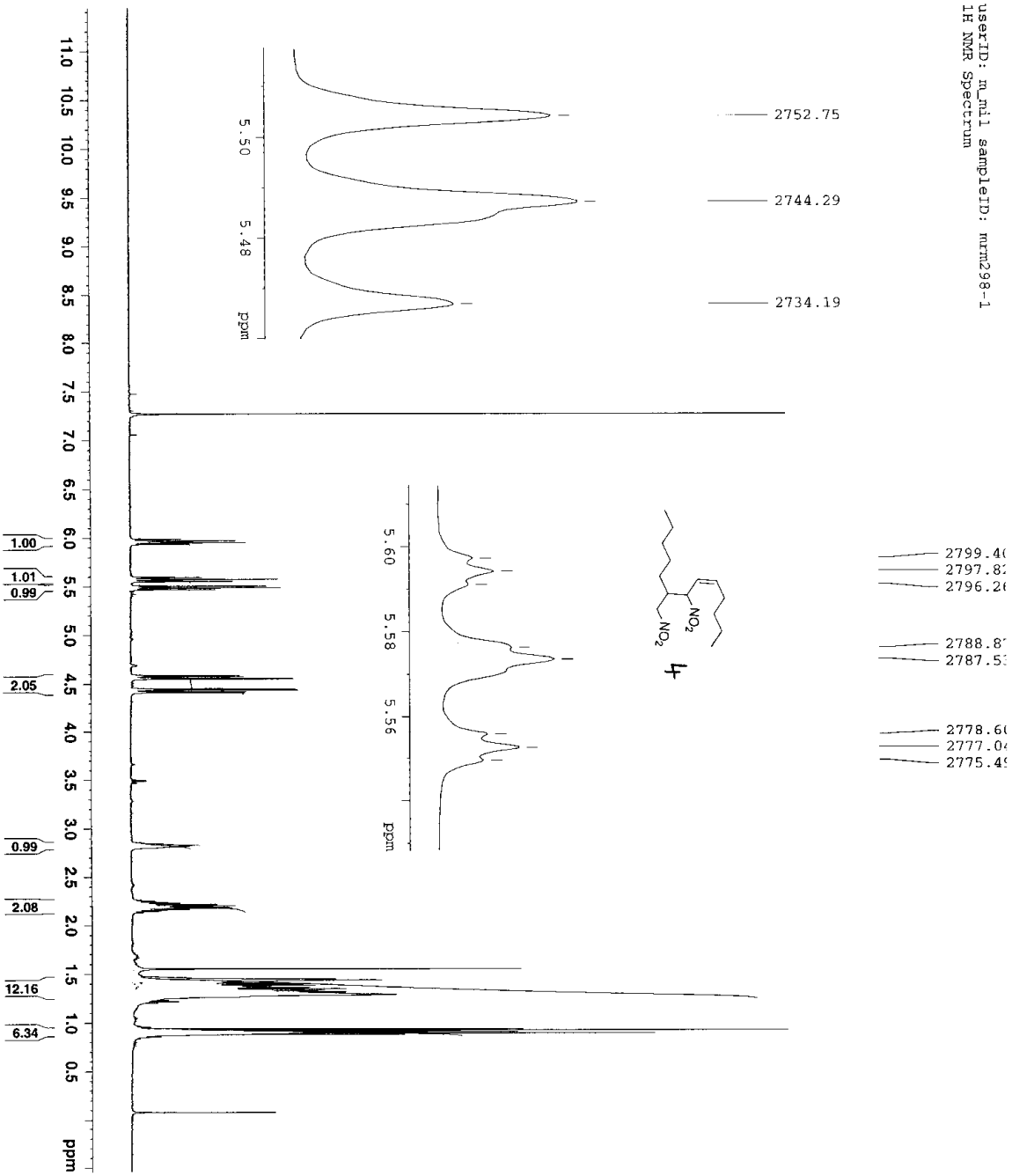

```
Current Data Parameters
NAME          m_mil.mrm215
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070911
Time                 22.48
INSTRUM              av400
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                    2048
DS                       2
SWH              25125.629 Hz
FIDRES           0.766773 Hz
AQ               0.6521332 sec
RG                  9195.2
DW                  19.900 use
DE                    6.00 use
TE                  296.2 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 =======
NUC1                   13C
P1                    8.25 use
PL1                   6.00 dB
SFO1          100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                   1H
PCPD2              105.00 use
PL2                 0.00 dB
PL12               22.00 dB
PL13               26.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



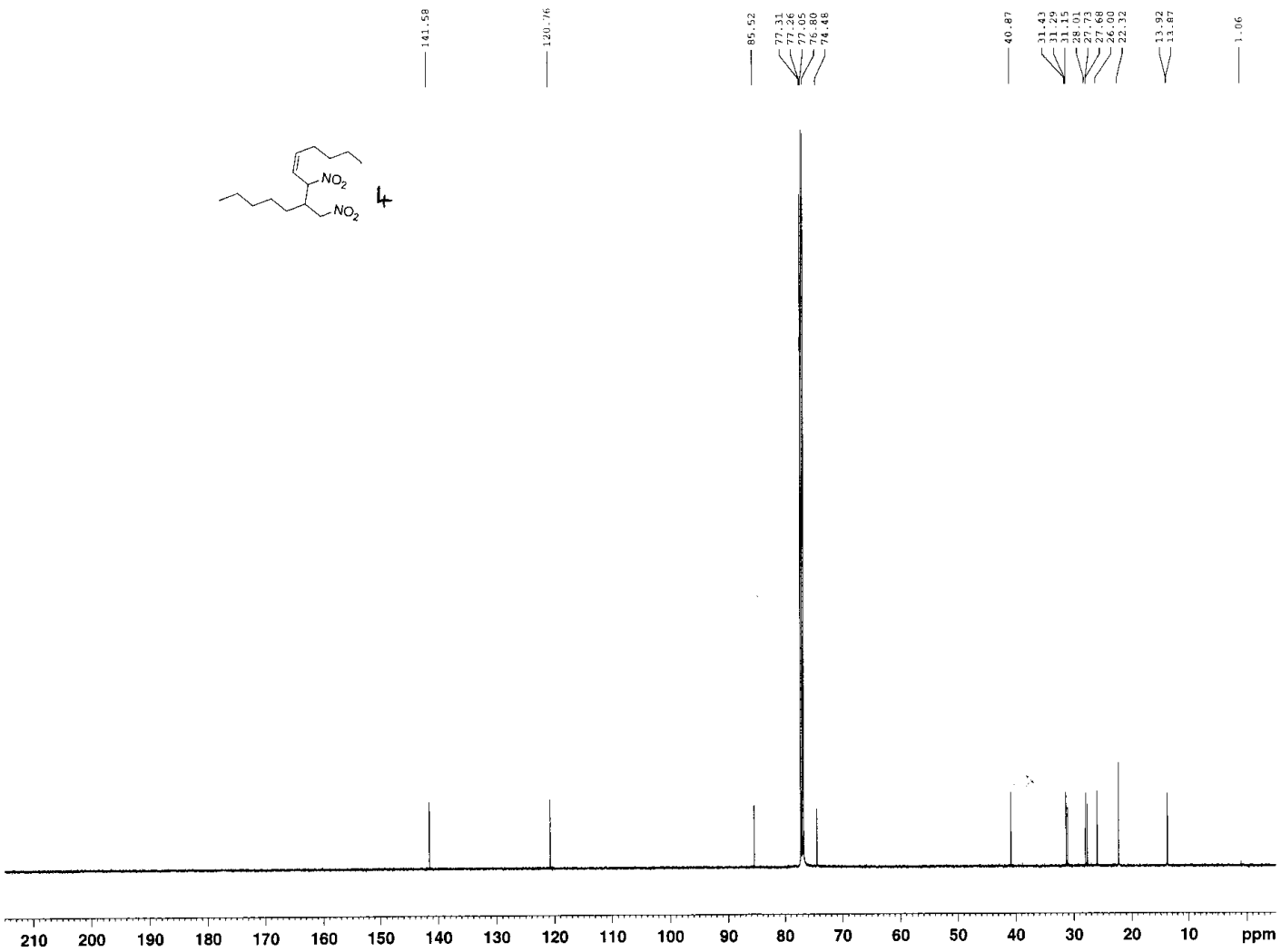

```
Current Data Parameters
NAME                  m_mil.mrm298-1
EXPNO                             4
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20080107
Time                         20.24
INSTRUM                     DRX500
PROBHD      5 mm Multinucl
PULPROG                   zg30
TD                           32768
SOLVENT                      CDCl3
NS                              16
DS                               2
SWH                       5995.204 Hz
FIDRES                    0.182959 Hz
AQ                        2.7329011 sec
RG                              114
DW                         83.400 usec
DE                          6.00 usec
TE                           300.0 K
D1                        1.00000000 sec
MCREST                    0.00000000 sec
MCWRK                     0.01500000 sec

======== CHANNEL f1 ========
NUC1                           1H
P1                          12.93 usec
PL1                         -3.00 dB
SFO1                  500.1327567 MHz

F2 - Processing parameters
SI                           32768
SF                    500.1300241 MHz
WDW                             EM
SSB                              0
LB                            0.30 Hz
GB                               0
PC                            1.00
```

userID: m_mil sampleID: mrm298-1
13C[CPD] Spectrum




```
Current Data Parameters
NAME      m_mil.mrm298-1
EXPNO                  5
PROCNO                 1

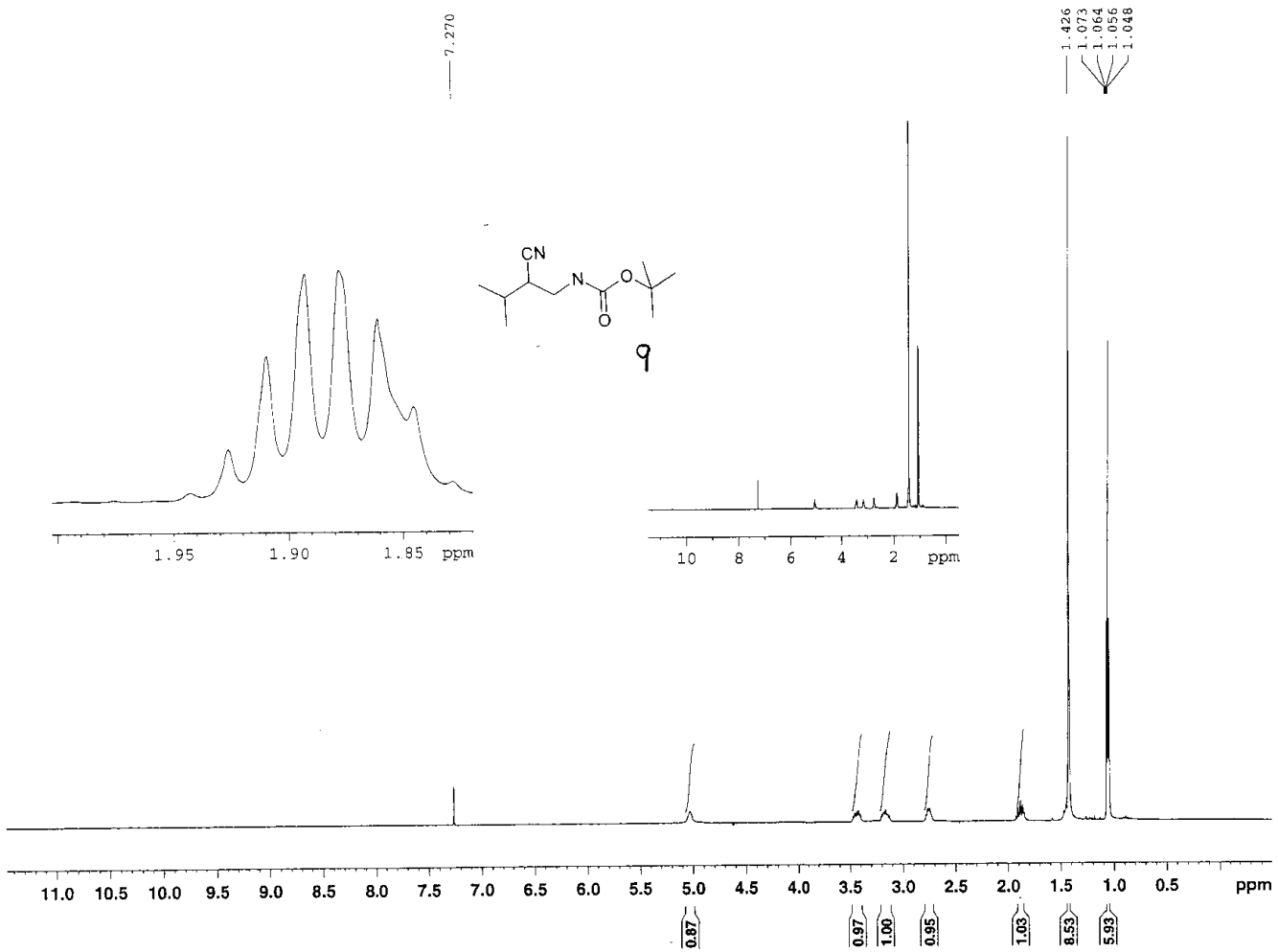
F2 - Acquisition Parameters
Date_           20080108
Time                1.42
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                12000
DS                    2
SWH           31446.541 Hz
FIDRES        0.959672 Hz
AQ            0.5210612 sec
RG                 4096
DW               15.900 use
DE                6.00 use
TE               300.0 K
D1           1.00000000 sec
D11          0.03000000 sec
DELTA        0.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 =======
NUC1                13C
P1                 9.70 use
PL1                4.00 dB
SFO1       125.7716219 MHz

======== CHANNEL f2 =======
CPDPRG2         waltz16
NUC2                1H
PCPD2           100.00 use
PL2              -3.00 dB
PL12             16.00 dB
PL13             18.00 dB
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF         125.7577890 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.00
```

UserID m_mil SampleID mrm239 SupervisorID ander Lab Phone No. 1 Slot Number 19



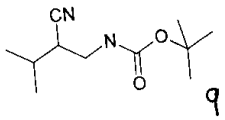

```
Current Data Parameters
NAME          m_mil.mrm239
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20071017
Time                  7.46
INSTRUM              av400
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               4789.272 Hz
FIDRES            0.146157 Hz
AQ                3.4210291 sec
RG                     45.3
DW                 104.400 usec
DE                   6.00 usec
TE                  298.2 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

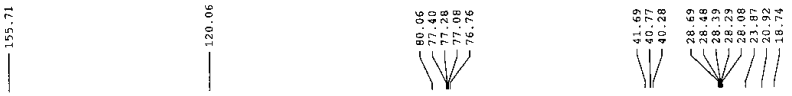
======== CHANNEL f1 ========
NUC1                    1H
P1                   7.55 usec
PL1                  0.00 dB
SFO1          400.1322007 MHz

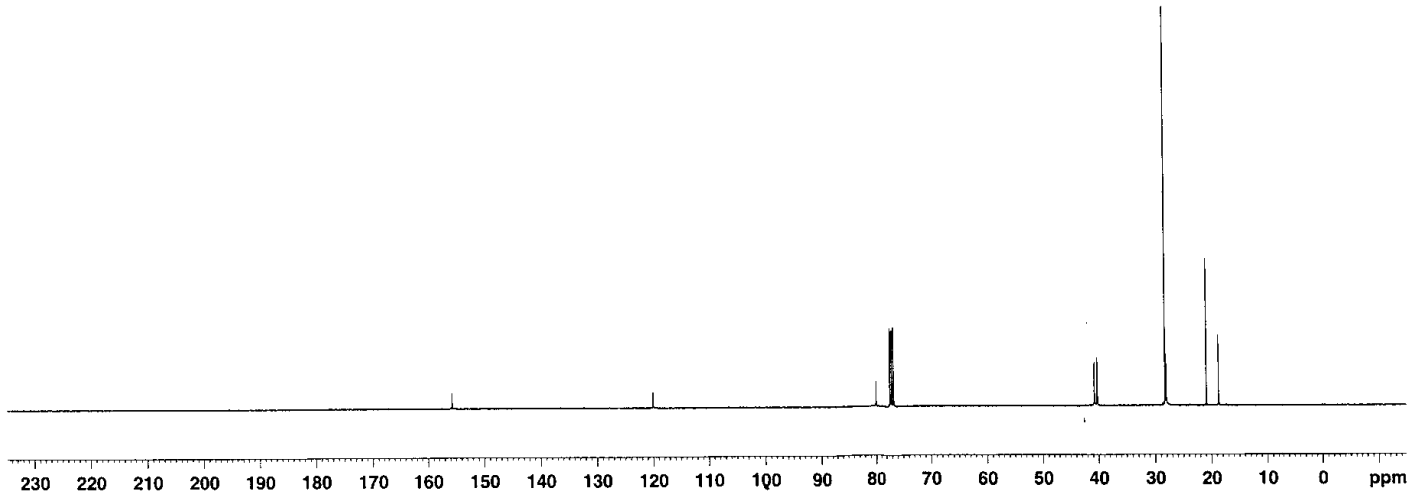
F2 - Processing parameters
SI                   32768
SF            400.1300053 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

UserID m_mil SampleID mrm239 SupervisorID ander Lab Phone No. 1 Slot Number 19



q





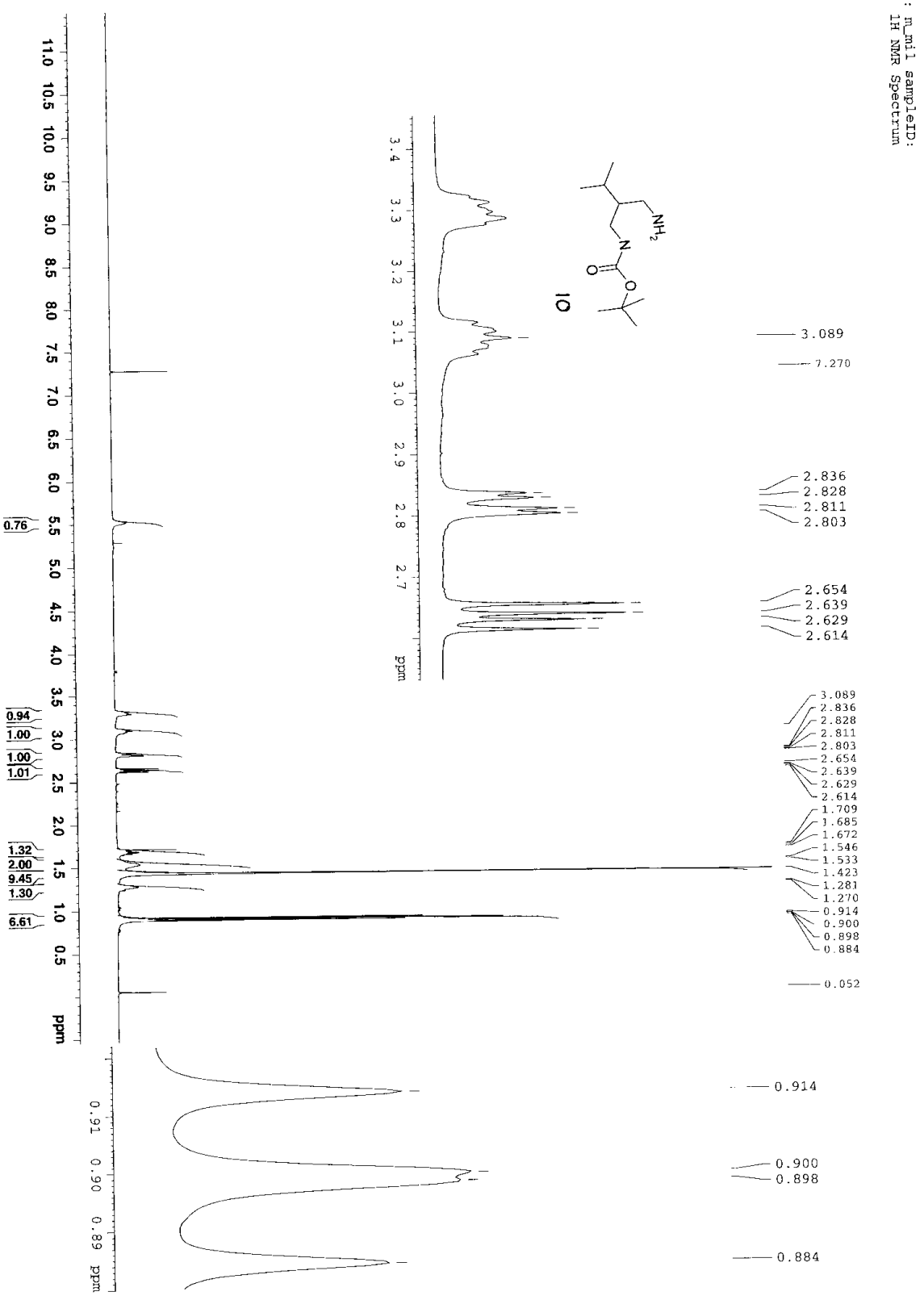

```
Current Data Parameters
NAME          m_mil.mrm239
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20071017
Time                 18.15
INSTRUM              av400
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                32768
SOLVENT           CDCl3
NS                 2048
DS                    2
SWH           25125.629 Hz
FIDRES         0.766773 Hz
AQ             0.6521332 sec
RG                 8192
DW                19.900 use
DE                 6.00 use
TE                298.2 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

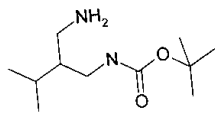
======== CHANNEL f1 =======
NUC1                13C
P1                 8.25 use
PL1                6.00 dB
SFO1       100.6238364 MHz

======== CHANNEL f2 =======
CPDPRG2         waltz16
NUC2                1H
PCPD2          105.00 use
PL2              0.00 dB
PL12            22.00 dB
PL13            26.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF         100.6127690 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```


: m_mi1 sampleID:
1H NMR Spectrum
NH2
N
O
O
10
3.089
7.270
2.836
2.828
2.811
2.803
2.654
2.639
2.629
2.614
1.709
1.685
1.672
1.546
1.533
1.423
1.281
1.270
0.914
0.900
0.898
0.884
0.052
0.76
0.94
1.00
1.00
1.01
1.32
2.00
9.45
1.30
6.61
ppm

userID: m_mil sampleID: mrm276
13C[CPD] Spectrum



10


```
Current Data Parameters
NAME          m_mil.mrm276
EXPNO                    2
PROCNO                   1

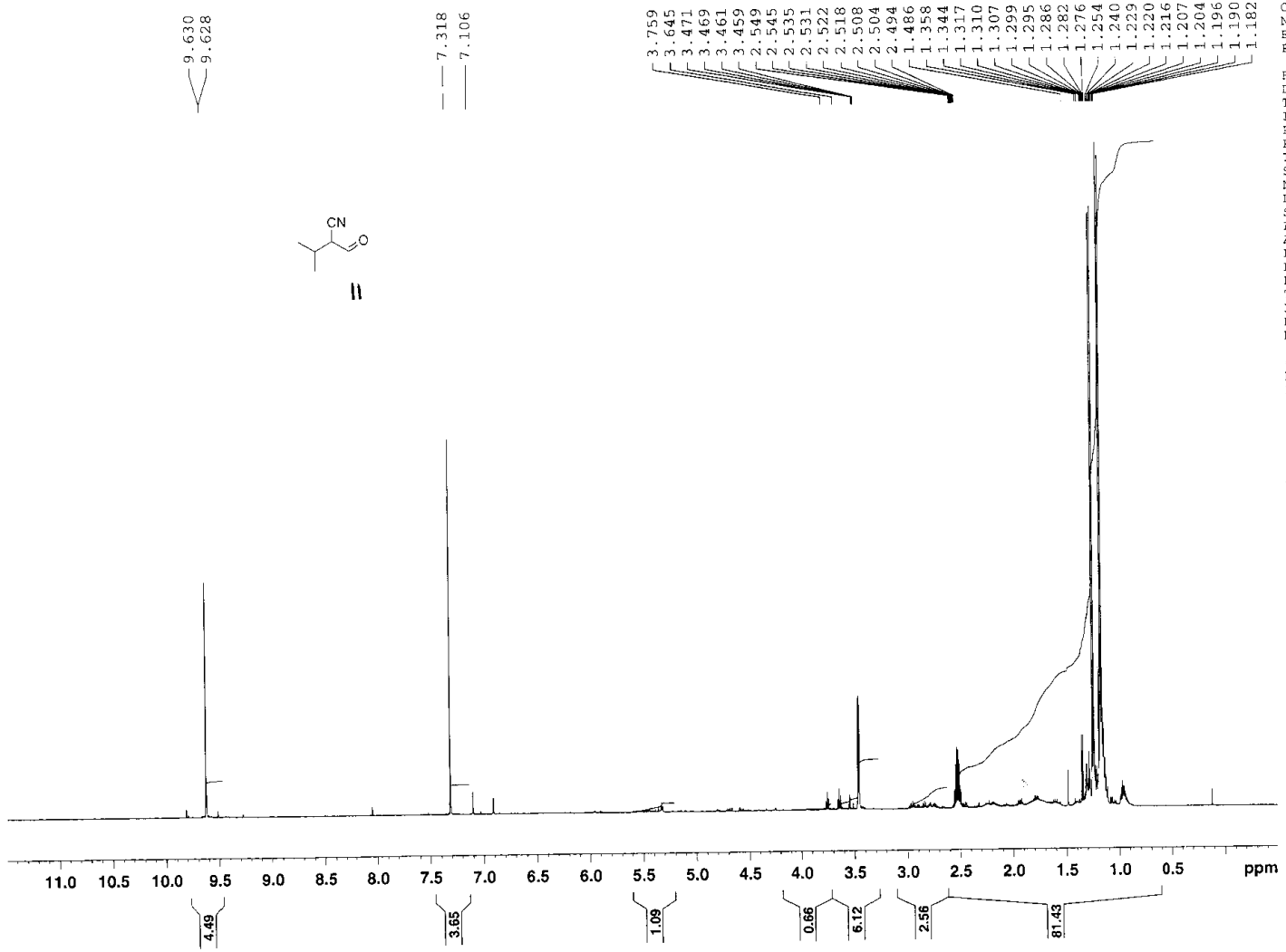
F2 - Acquisition Parameters
Date_             20071122
Time                 10.52
INSTRUM              DRX500
PROBHD   5 mm Multinucl
PULPROG              zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      512
DS                        2
SWH               31446.541 Hz
FIDRES            0.959672 Hz
AQ                0.5210612 sec
RG                   7298.2
DW                   15.900 use
DE                    6.00 use
TE                   300.0 K
D1              1.00000000 sec
D11             0.03000000 sec
DELTA           0.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 =======
NUC1                    13C
P1                    9.70 use
PL1                   4.00 dB
SFO1          125.7716219 MHz

======== CHANNEL f2 =======
CPDPRG2             waltz16
NUC2                    1H
PCPD2               100.00 use
PL2                  -3.00 dB
PL12                 16.00 dB
PL13                 18.00 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                    32768
SF            125.7577890 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.00
```

userID: m_mil sampleID: mrm294-2
1H NMR Spectrum



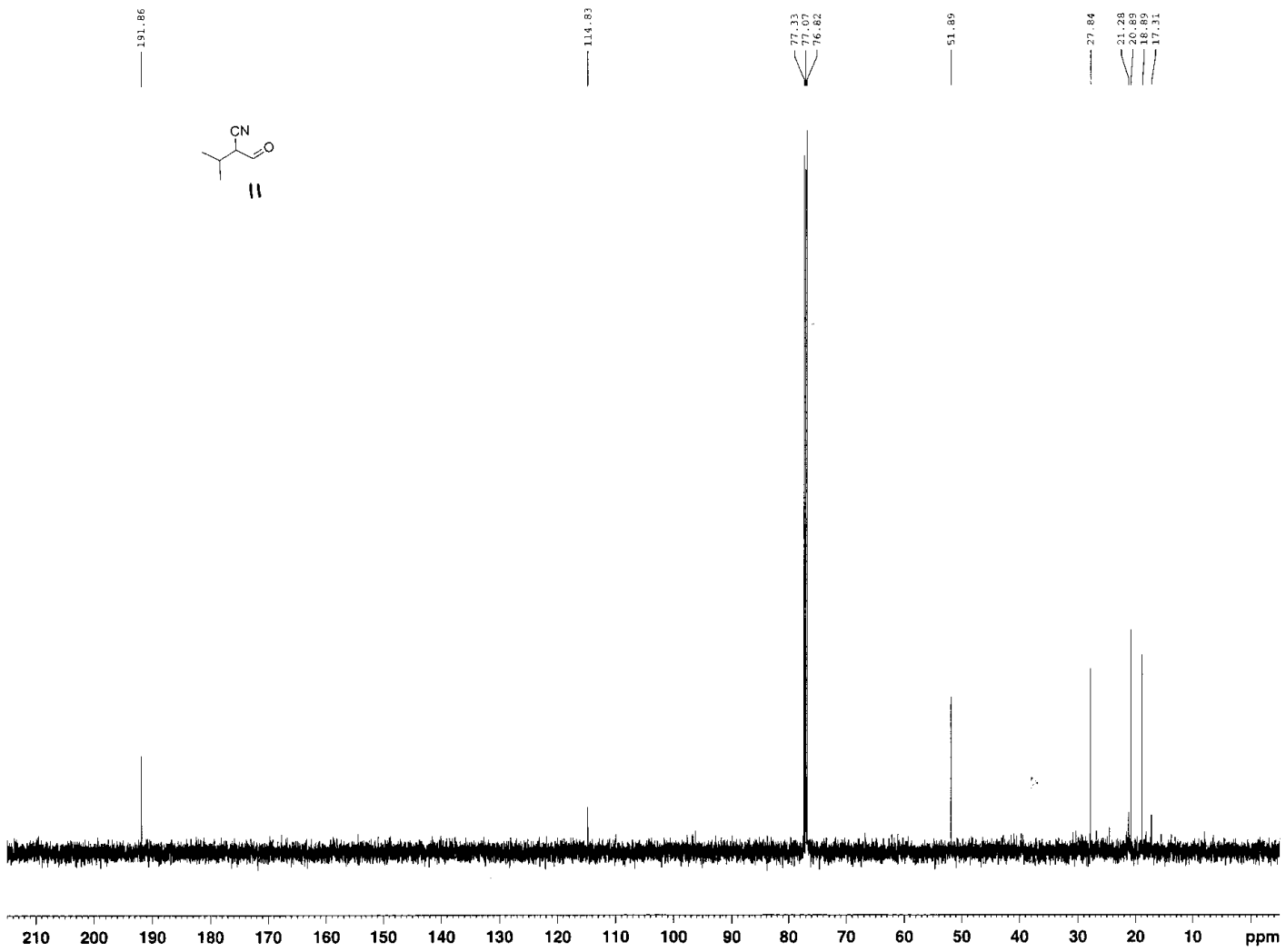

```
Current Data Parameters
NAME      m_mil.mrm294-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071218
Time               13.07
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           5995.204 Hz
FIDRES        0.182959 Hz
AQ            2.7329011 sec
RG                101.6
DW                83.400 use
DE                 6.00 use
TE                300.0 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 =======
NUC1                  1H
P1                12.93 use
PL1               -3.00 dB
SFO1        500.1327507 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                  1.00
```

userID: m_mil sampleID: mrm295
13C[CPD] Spectrum




```
Current Data Parameters
NAME        m_mil.mrm295
EXPNO                  3
PROCNO                 1

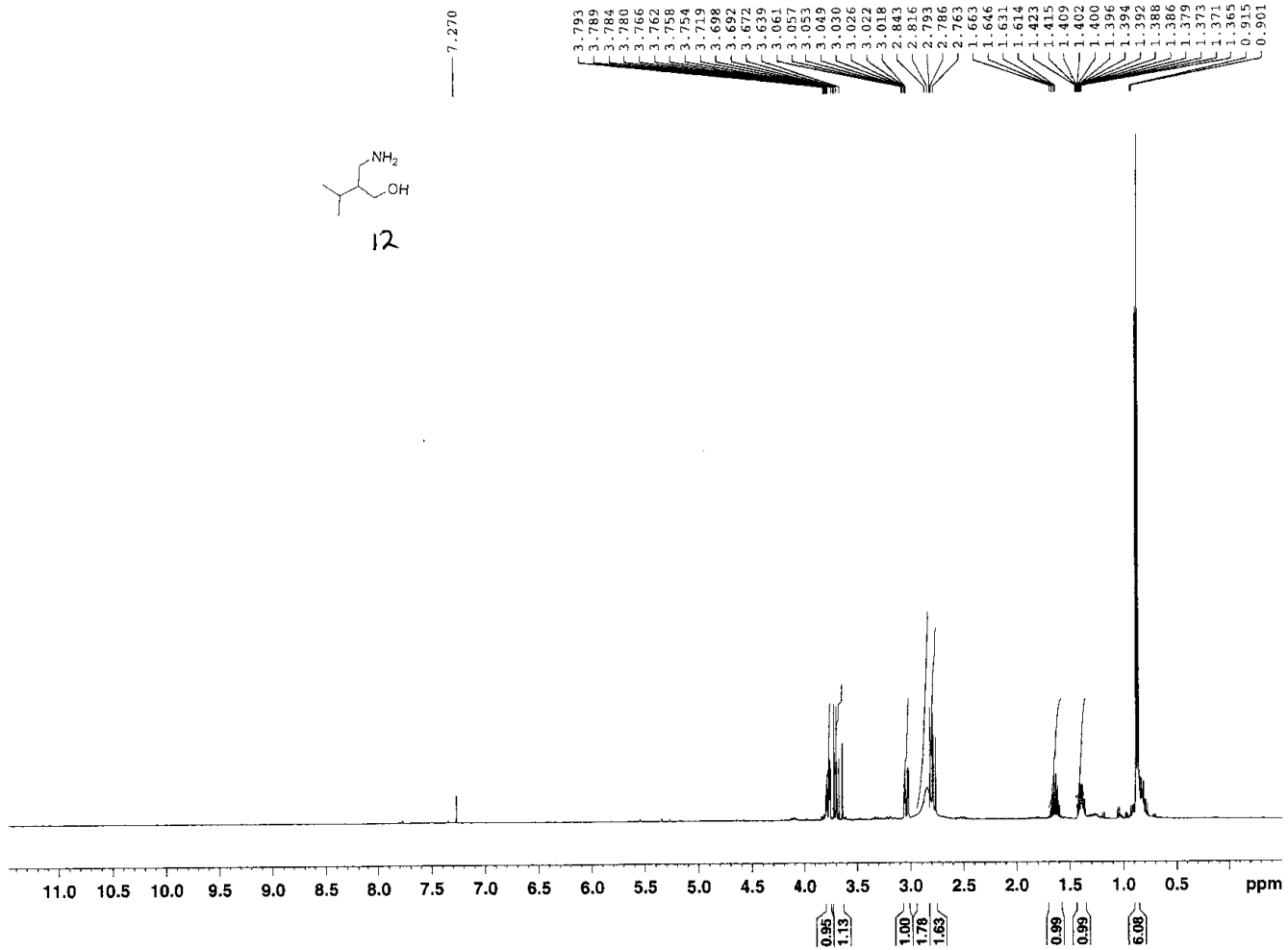
F2 - Acquisition Parameters
Date_           20080107
Time               16.00
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    2
SWH           31446.541 Hz
FIDRES         0.959672 Hz
AQ            0.5210612 sec
RG               2298.8
DW                15.900 use
DE                 6.00 use
TE                300.0 K
D1           1.00000000 sec
D11          0.03000000 sec
DELTA        0.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 =======
NUC1                13C
P1                 9.70 use
PL1                4.00 dB
SFO1        125.7716219 MHz

======== CHANNEL f2 =======
CPDPRG2         waltz16
NUC2                1H
PCPD2           100.00 use
PL2              -3.00 dB
PL12             16.00 dB
PL13             18.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

UserID m_mil SampleID mrm380-bulbtobulb SupervisorID ander Lab Phone No. 1 Slot Number 1



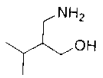

```
Current Data Parameters
NAME      m_mil.mrm380-bulbtobulb
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20080319
Time                        10.53
INSTRUM                      av400
PROBHD   5 mm BBO BB-1H
PULPROG                     zg30
TD                         32768
SOLVENT                    CDCl3
NS                            16
DS                             2
SWH                     4789.272 Hz
FIDRES                  0.146157 Hz
AQ                     3.4210291 sec
RG                          40.3
DW                       104.400 usec
DE                         6.00 usec
TE                       298.2 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                         9.10 usec
PL1                       -3.00 dB
PL1W                20.24796486 W
SFO1               400.1322007 MHz

F2 - Processing parameters
SI                         32768
SF                 400.1300053 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

UserID m_mil SampleID mrm380 SupervisorID ander Lab Phone No. 1 Slot Number 6



12

NAME	m_mil.mrm380
EXPNO	1
PROCNO	1
Date_	20080724
Time	12.26
INSTRUM	av400
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	512
DS	2
SWH	25125.629 Hz
FIDRES	0.766773 Hz
AQ	0.6521332 sec
RG	18390.4
DW	19.900 use
DE	10.00 use
TE	298.2 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 =======
NUC1	13C
P1	8.00 use
PL1	-2.20 dB
PL1W	57.11110687 W
SFO1	100.6238364 MHz
========	CHANNEL f2 =======
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 use
PL2	-2.10 dB
PL12	15.40 dB
PL13	16.40 dB
PL2W	16.45816231 W
PL12W	0.29267216 W
PL13W	0.23247775 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40