Synthetic studies on N-alkoxyamines: a mild and broadly applicable route starting from nitroxide radicals and aldehydes

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Supporting information

Content

General

NMR spectra were recorded at 300 or 400 MHz for ^{1}H-NMR and 75.5 or 100 MHz for ^{13}C-NMR. Chemical shifts were reported in the scale relative to the solvent used as an internal reference. MS measurements were collected on a ion trap mass spectrometer coupled with a gas chromatograph. The column was operated at a flow rate of 1 mL/min (Helium gas). The oven temperature was ramped between 60 and 360 °C at a rate of 30 °C/min. Alternatively, probes were directly inserted in the mass spectrometer source by a direct sample probe system in the direct exposure probe (DEP) mode. For structure confirmation, the system was operated in the PCI mode with isobutane as reagent gas. Masses were recorded as $[M+H]^{+}$. HRMS measurements were conducted on a LC-MS-MS system through flow injection. Molpeaks were determined in the positive mode. The mass calibration was conducted via external calibration.

In general, reactions were carried out in glassware under regular atmosphere. No precautions were taken to exclude moisture. Solvents and aldehydes were used as is without prior purification. Reagents and aldehydes were obtained from commercial sources unless otherwise noted.

Attention: it is crucial to ensure that no residual peroxide is contained in the samples before starting distillations or complete drying!

Experimental procedures for non-commercial aldehydes

Cyclobutyl carbaldehyde was prepared according to: Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.

5.48 ml (63.86 mmol) oxalyl chloride were dissolved in 40 ml dichloromethane and cooled in a dry ice bath to – 75 °C under protective gas atmosphere. Then 9.07 ml (127.71 mmol) DMSO were added drop wise. A solution of 5.0 g (58.05 mmol) cyclobutane methanol in 40 ml methylene chloride was added and the mixture was stirred at – 75 °C for 1 h. After the addition of 40.40 ml (290.26 mmol) triethylamine and warming to rt, the mixture was washed with brine and water. The organic layer was separated, dried with Na_2SO_4, filtered and the solvent removed in vacuo. 1.06 g (12.6 mmol, 22%) cyclobutane carbaldehyde were obtained as a foul smelling, light yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 2.82 (m, 1H), 2.22 (m, 2H), 2.06 (m, 2H), 1.91 (m, 2H); MS: m/z = 85 $[M+H]^+$.

Cyclooctane carbaldehyde was prepared according to: Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.

3.32 ml (38.67 mmol) oxalyl chloride were dissolved in 40 ml dichloromethane and cooled in a dry ice bath to – 75 °C under protective gas atmosphere. Then 5.50 ml (77.33 mmol) DMSO were added drop wise. A solution of 5.0 g (35.15 mmol) cyclobutane methanol in 40 ml methylene chloride was added and the mixture was stirred at – 75 °C for 1 h. After the addition of 24.50 ml (175.76 mmol) triethylamine and warming to rt, the mixture was washed with brine and water. The organic layer was separated, dried with Na_2SO_4, filtered and the solvent removed *in vacuo*. 4.23 g (30.16 mmol, 86%) cyclooctane carbaldehyde were obtained as a light yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 2.36 (m, 1H), 1.92 (m, 2H), 1.69 (m, 2H), 1.45-1.62 (m, 10H); MS: m/z = 141 $[M+H]^+$.

2-Methyl-2-nitro-5-oxopentanoic acid ethyl ester was prepared according to: (a) Ballini, R.; Petrini, M. *Synthesis* **1986**, 1024-1026. (b) Hauck, S. PhD thesis, TU Kaiserslautern, **2007**, 173.

16.47 g (111.94 mmol) 2-nitro-propionic acid ethyl ester were dissolved in 100 ml acetonitrile under protective gas atmosphere and cooled to 0 °C. 2 ml Triethylamine and 11.0 ml (167.91 mmol) acroleine were added. The solution was stirred at 10 °C for 6.5 h. Then the mixture was treated with water, neutralized with aqueous HCl and extracted with methylene chloride. The organic layer was separated, dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. 18.34 g (90.26 mmol, 81 %) 2-methyl-2-nitro-5-oxopentanoic acid ethyl ester were obtained as yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 4.25 (q, *J* = 6.99 Hz, 3H), 2.58 (m, 2H), 2.49 (m, 2H), 1.77 (s, 3H), 1.28 (t, *J* = 6.99 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.5, 167.3, 91.9, 63.4, 38.8, 29.1, 22.2, 14.2; MS: m/z = 204 $[M+H]^+$.

Experimental procedures for compounds S-1 – S-27

General procedure for the synthesis of N-alkoxyamines: 4-hydroxy TEMPO and the required aldehyde (1.3-3 eq.) were dissolved in an appropriate solvent and 1-3.0 mol% of CuCl were added. At rt, 1.3-1.5 eq. of hydrogen peroxide (30% aqueous solution) were added over a period of 30-120 min. The reaction mixture was stirred at a temperature usually not higher than 40°C until all nitroxide radical was consumed. If required, more H_2O_2 or aldehyde were added. Residual H_2O_2 was thoroughly removed during the work-up process, (if necessary, $NaHSO_3$ solution can be used) and the crude products were purified by (flash) column chromatography or crystallization.

Synthesis of compounds S-1 to S-27

1-Methoxy-2,2,6,6-tetramethylpiperidin-4-ol (**S-1**). To a solution of 5.0 g (29.0 mmol) 4-hydroxy-TEMPO in 20 ml water was added CuCl (57 mg, 2 mol %) and acetaldehyde (6.6 ml, 116 mmol). 8.9 ml (87 mmol) 30 % H_2O_2 was added over a period of 30 min while keeping the temperature at 65 - 70 °C. After 4 h stirring at this temperature, the mixture is slowly cooled down to rt while the product started to precipitate. The pH of the reaction mixture was adjusted to ~8 using 10 % K_2CO_3 solution and the mixture was cooled down to 5 °C. The product was collected by filtration. The filter cake was washed successively with cold 10 % ascorbic acid solution and water. The filtrate was extracted with toluene, and the organic phase was washed with brine. Upon drying over Na_2SO_4, the organic phase was removed *in vacuo* to yield a tan residue. The combined crude product fractions were purified by distillation (0.04 mbar, 120 °C oilbath temp, bp ~ 90 °C) to give **S-1** as a white solid (3.9 g, 20.8 mmol, 72%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.94 (m, 1H), 3.61 (s, 3H), 1.79 (dd, *J* = 12.0, 4.0 Hz, 2H), 1.64 (br s, 1H), 1.46 (ps t, *J* = 12.0 Hz, 2H), 1.21 (2s, 6H), 1.26 (2s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 65.4 (t), 63.2 (2q), 60.0 (p), 48.2 (2s), 33.1 (2p), 20.9 (2p); IR (neat): ν max 3265, 2960, 1450, 1358,

1173, 1026 cm^{-1}; MS: m/z = 188 $[M+H]^+$; Anal. calcd. for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48. Found: C, 63.94; H, 11.22; N, 7.45.

1-Propoxy-2,2,6,6-tetramethylpiperidin-4-ol (S-2). To a mixture of 150.0 g (870.8 mmol) 4-hydroxy-TEMPO in 620 ml 1-butanol/water (1:4) was added CuCl (861 mg, 1 mol%) and butanal (94.2 g, 1.31 mol). 120 ml (1.18 mol) 30% H_2O_2 was added over a period of 30 min while keeping the temperature between 30 and 35 °C. Stirring was continued at 35 °C for 8 h, whereupon another 12 ml (118.0 mmol) H_2O_2 was added. After 6 h the reaction mixture was extracted with MTBE. The combined organic phases were washed with 2 N NaOH, water, 5 % Na_2EDTA, 10 % ascorbic acid solution, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to provide an off-white solid. Pure **S-2** was obtained after column chromatography (silica gel, hexane/acetone 9:1); (157.5 g, 731.5 mmol, 84 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.95 (m, 1H), 3.70 (q, *J* = 9.2 Hz, 2H), 1.80 (dd, *J* = 14.4, 3.2 Hz, 2H), 1.70 (br s, 1H, OH), 1.53 (m, 2H), 1.50 (m, 4H), 1.24 (2s, 6H), 1.15 (2s, 6H), 0.95 (t, *J* = 10.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 78.4 (s), 63.3 (t), 60.0 (2q), 48.3 (2s), 33.2 (2p), 21.9 (s), 21.0 (2p), 10.9 (p); IR (neat): ν max 3264, 2965, 1451, 1363, 1173, 1040 cm^{-1}; MS: m/z = 216 $[M+H]^+$; Anal. calcd. for $C_{12}H_{25}NO_2$: C, 66.93; H, 11.70; N, 6.50. Found: C, 66.73; H, 11.49; N, 6.38.

1-Isopropoxy-2,2,6,6-tetramethylpiperidin-4-ol (S-3). To a solution of 2.5 g (14.5 mmol) 4-hydroxy-TEMPO in 10 ml 2-propanol/water (1:5) was added CuCl (28.7 mg, 2 mol%) and 2-methylpropanal (1.57 g, 21.8 mmol). 2.5 g (21.8 mmol) 30 % H_2O_2 was added over a period of 30 min while keeping the temperature under 30 °C. After 12 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over $MgSO_4$ the organic phase was concentrated *in vacuo* to leave a green solid. The crude product was recrystallized from water/ethanol (1:1) to yield **S-3** as white crystals (2.9 g, 13.3 mmol, 91%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.99 (m, 2H), 1.82 (dd, *J* = 12.0, 3.6 Hz, 2H), 1.48 (ps t, *J* = 12.0 Hz, 2H), 1.40 (br s, 1H, OH), 1.18 (m, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 75.2 (t), 63.5 (t), 59.9 (2q), 48.8 (2s), 34.5 (2p), 22.3 (2p), 21.2 (2p); IR (neat): ν max 3264, 2973, 1448, 1372, 1151, 1082 cm^{-1}; MS:

m/z = 216 $[M+H]^+$; Anal. calcd. for $C_{12}H_{25}NO_2$: C, 66.93; H, 11.70; N, 6.50. Found: C, 66.68; H, 11.07; N, 6.34.

1-(1-Ethyl-pentyloxy)-2,2,6,6-tetramethylpiperidin-4-ol (S-4). To a solution of 60.0 g (348.3 mmol) 4-hydroxy-TEMPO in 92 g (717.5 mmol) 2-methylheptanal was added 0.86 g (2.5 mol%) CuCl. 30 % H_2O_2 (60.0 g, 522.5 mmol) was added over a period of 4 h at rt. The reaction mixture was stirred at 30 °C for 12 h, while every 4 h a further 10 ml of H_2O_2 were added. The mixture was diluted with MTBE and subsequently washed with 10 % ascorbic acid solution, NaOH, water, brine. After drying over $MgSO_4$ the organic phase was concentrated *in vacuo* to afford 102 g of a yellow oil. The crude product was heated *in vacuo* (0.05 mbar) at 70 °C for 8 h to remove residual aldehyde. The resulting product was filtered over silica gel (500 g, hexane/acetone 10:1) to yield 71.1 g (261.9 mmol, 75%) of **S-4** as a pale yellow oil after removal of the solvent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.00 (m, 1H), 3.70 (m, 1H), 1.80 (m, 2H), 1.69 (m, 1H), 1.48 (m, 3H), 1.32 (m, 4H), 1.18 (2s, 6H), 1.17 (2s, 6H), 0.98 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 83.2, 63.5, 60.3, 60.1, 48.9, 34.4, 32.0, 28.0, 25.3, 23.1, 21.4, 14.2, 11.8, 9.9; IR (neat): ν max 3349, 2931, 1468, 1395, 1189, 1048 cm^{-1}; MS: m/z = 272 $[M+H]^+$; Anal. calcd. for $C_{16}H_{33}NO_2$: C, 70.80; H, 12.25; N, 5.16. Found: C, 70.76; H, 12.17; N, 5.14.

1-*tert*-Butyloxy-2,2,6,6-tetramethylpiperidin-4-ol (S-5). To a solution of 25.0 g (145.1 mmol) 4-hydroxy-TEMPO in 100 ml ethanol/water (1:1), 24.8 g 30 % H_2O_2 and CuCl (390 mg, 2 mol%) was added 15.6 g (181.4 mmol) pivaloylaldehyde (15.6 g, 181.4 mmol) over a period of 20 min while cooling applying a water bath. The emulsion was stirred at rt. After approximately 1 h, a white precipitate started forming. After 8 h, another 5.6 g (49.2 mmol) H_2O_2 and 50 ml ethanol/water (1:1) were added and stirring was continued for 8 h. The reaction mixture was cooled to 5 °C, whereupon the solid was separated by filtration. The filter cake was thoroughly washed with water and subsequently dried at 45 °C (125 mbar) to give **S-5** (28.3 g, 123.3 mmol, 85%) as white crystals. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.93 (m, 1H), 1.89 (br s, 1H), 1.81 (dd, *J* = 12.4, 1.6 Hz, 2H), 1.45 (ps t, *J* = 12.0 Hz, 2H), 1.28 (s, 9H), 1.64 (2s, 6H), 1.29 (2s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 78.0 (q), 63.1 (t), 59.6 (2q), 49.2 (2s), 34.8 (2p), 29.5 (3p), 21.4 (2p); IR (neat): ν max 3268, 2975, 1472, 1449, 1371, 1168, 1044 cm^{-1}; MS: m/z = 230 $[M+H]^+$; Anal. calcd. for $C_{13}H_{27}NO_2$: C, 68.08; H, 11.87; N, 6.11. Found: C, 67.83; H, 11.69; N, 6.03.

1-Octyloxy-2,2,6,6-tetramethylpiperidin-4-ol (S-6). To a solution of 10.0 g (58.1 mmol) 4-hydroxy-TEMPO in 30 ml *tert*-butanol/water (2:1) was added CuCl (140 mg, 2.5 mol%) and nonanal (28.9, 203.2 mmol). 10.2 g (151.0 mmol) 50 % H_2O_2 was added under thorough stirring over a period of 75 min while keeping the temperature at 30 °C. After 12 h another 2 g of 50 % H_2O_2 was added and stirring was continued for 4 h at 40 °C. The mixture was extracted with hexane and successively washed with 10 % ascorbic acid solution, 10 % $NaHSO_3$ solution, 1 N NaOH, water, and brine. After drying over $MgSO_4$ the organic phase was concentrated *in vacuo* to provide a yellow oil. The crude product was purified by flash column chromatography (100 g silica gel, hexane/acetone 8:1) to give **S-6** (11.8 g, 41.3 mmol, 71 %) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.96 (m, 1H), 3.72 (t, *J* = 6.6 Hz, 2H), 1.81 (dd, *J* = 12.4, 4.0 Hz, 2H), 1.60-1.39 (m, 4H), 1.39-1.20 (m, 22H), 0.88 (t, *J* = 10.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 77.2 (s), 63.4 (t), 60.0 (2q), 48.3 (2s), 33.2 (p), 31.9 (s), 29.7 (s), 29.3 (s), 28.7 (s), 26.4 (s), 22.7 (s), 21.1 (p), 14.2 (p); IR (neat): ν max 3346, 2925, 2855, 1692, 1467, 1399, 1194, 1046 cm^{-1}; MS: m/z = 286 $[M+H]^+$; Anal. calcd. for $C_{17}H_{35}NO_2$: C, 71.53; H, 12.36; N, 4.91. Found: C, 71.38; H, 12.19; N, 4.85.

Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate (**S-7**). To a suspension of 100 g bis-(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl) sebacate (196 mmol) in a mixture consisting of 225 g heptane and 55 g *tert*-butanol was added 146.6 g (979 mmol) nonanal, 315 mg (1 mmol) hexadecyltrimethylammonium chloride, and 500 mg (5 mmol) CuCl. 75 g (1096 mmol) 50 % H_2O_2 was added over a period of 2 h while keeping the internal temperature between 28 – 35 °C. The temperature was raised to 40 °C and stirring was continued for 12 h. After 6 h, another 16.5 g of H_2O_2 was added. After 12 h, another 15 g of H_2O_2 was added and stirring was continued at 55 °C for 2-3 h. The green emulsion obtained was diluted with hexane and washed successively with 10 % Na_2CO_3 solution, 10 % Na_2EDTA solution, sat. Na_2CO_3, water, and brine. The organic phase was dried over Na_2SO_4 and subsequently removed *in vacuo*. The obtained yellow oil was stirred *in vacuo* (0.03 mbar) at 65 °C for 6 h. Chromatography over silica gel (1000g) with hexane/acetone 49:1 provided 109.4 g (148 mmol, 75%) of **S-7** as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.00 (m, 2H), 3.72 (t, *J* = 6.4 Hz, 4H), 2.25 (t, *J* = 6.6 Hz, 4H), 1.80 (m, 4H), 1.60-1.47 (m, 12H), 1.39 -1.12 (m, 52H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.4 (q), 77.04 (s), 67.5 (t), 59.9 (q), 44.1 (s), 34.6 (s), 33.1 (p), 31.9 (s), 29.7 (s),

29.8 (s), 29.7 (s), 29.4 (s), 29.3 (s), 29.1 (s), 29.0 (s), 28.7 (s), 26.44 (s), 25.0 (s), 22.7 (s), 20.9 (p), 14.0 (p); IR (neat): ν max 2927, 2855, 1733, 1457, 1360, 1173, 1001 cm^{-1}; MS: m/z = 737 $[M+H]^+$; Anal. calcd. for $C_{44}H_{84}N_2O_6$: C, 71.69; H, 11.49; N, 3.80. Found: C, 71.39; H, 11.58; N, 3.60.

1-Cyclobutoxy-2,2,6,6-tetramethylpiperidin-4-ol (S-8). To a solution of 0.79 g (4.57 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (16 mg, 3.5 mol%) and cyclobutane carbaldehyde (0.50 g, 5.95 mmol). 0.59 g (8.7 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature under 30 °C. After 18 h of stirring at rt, the mixture was stirred at 40 °C for 4 h. The product was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave a bright green oil which was purified by column chromatography (80 g silica gel, hexane/ethyl acetate 1:1) to give **S-8** (0.24 g, 1.1 mmol, 24%) as a colorless oil which solidified upon standing into a white wax. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.13 (m, 1H), 3.93 (m, 1H), 2.28 (m, 2H), 1.92 (m, 2H), 1.81 (m, 2H), 1.54-1.35 (m, 4H), 1.21 (m, 1H), 1.11 (2s, 6H), 1.07 (2s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 81.2 (t), 63.4 (t), 58.9 (2q), 48.2 (2s), 33.4 (2p), 32.4 (2s), 21.0 (2p), 11.1 (s). IR (neat): ν max 3227, 3004, 2973, 2928, 1469, 1371, 1360, 1342, 1246, 1236, 1087, 1048 cm^{-1}; HRMS (+ESI) calcd. $[C_{13}H_{25}NO_2]^+$ $[M+H]^+$ MS: 228.1964 found 228.1966.

1-Cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-ol (S-9). To a solution of 6.8 g (39.5 mmol) 4-hydroxy-TEMPO in 25 ml *tert*-butanol/water (2:1) was added copper(II) chloride (39 mg, 1 mol%) and cyclohexane carbaldehyde (4.42 g, 39.5 mmol). 8.9 g (78.9 mmol) 30 % H_2O_2 was added over a period of 30 min while keeping the temperature under 30 °C. After 12 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to leave a bright green oil (6.9 g, 90 % purity (GC)). The crude product was purified by column chromatography (80 g silica gel, hexane/acetone 9:1) to give **S-9** (6.3 g, 24.5 mmol, 62%) as a light chartreuse oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.98 (m, 1H), 3.63 (m, 1H), 2.06 (m, 2H), 1.81 (m, 4H), 1.57-1.48 (m, 3H), 1.37-1.13 (m, 6H), 1.21 (2s, 6H),

1.17 (2s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 81.9 (t), 63.4 (t), 60.0 (2q), 48.8 (2s), 34.5 (2p), 32.8 (2s), 25.9 (2s), 25.0 (2s), 21.2 (2p); IR (neat): ν max 3301, 2935, 2855, 1446, 1359, 1178, 1041 cm^{-1}; MS: m/z = 256 $[M+H]^+$; Anal. calcd. for $C_{15}H_{29}NO_2$: C, 70.54; H, 11.45; N, 5.48. Found: C, 70.18; H, 11.37; N, 5.35.

1-Cyclooctyloxy-2,2,6,6-tetramethylpiperidin-4-ol (S-10). To a solution of 1.00 g (5.8 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (16 mg, 3.5 mol%) and cyclooctyl carbaldehyde (1.06 g, 7.5 mmol). 0.59 g (8.7 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature under 30 °C. After 18 h of stirring at rt, the mixture was heated to 40 °C for 24 h. The mixture was then extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave a yellow oil. This was purified by column chromatography (80 g silica gel, hexane/ethyl acetate 2:1) to give **S-10** (0.73 g, 2.6 mmol, 45 %) as a pale yellow oil. After a short time, the oil solidified into a yellowish wax. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.96 (ddd, *J* = 16.2, 6.7, 4.9 Hz, 1H), 3.86 (ddd, *J* = 12.0, 8.4, 3.7 Hz, 1H), 2.00 (ddt, *J* = 11.6, 11.6, 7.8, 3.6 Hz, 2H), 1.81 (m, 2H), 1.44-1.74 (multiple m, 15H), 1.19 (s, 6H), 1.16 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 83.4, 63.5, 60.1, 48.9, 34.5, 31.1, 27.5, 25.7, 23.6, 21.4; IR (neat): ν max 3264, 3006, 2969, 2917, 2850, 1446, 1467, 1358, 1337, 1372, 1244, 1162, 1213, 1193, 1177, 1031, 1042 cm^{-1}; HRMS (+ESI) calcd. $[C_{17}H_{33}NO_2]^+$ $[M+H]^+$ MS: 284.2590 found 284.2587.

1-(Cyclohex-3-enyloxy)-2,2,6,6-tetramethylpiperidin-4-ol (S-11). To a solution of 7.5 g (43.5 mmol) 4-hydroxy-TEMPO in 25 ml *tert*-butanol/water (2:1) was added CuCl (43 mg, 1 mol%) and 3-cyclohexene-1-carboxaldehyde (7.19 g, 65.3 mmol). 7.1 g (69.7 mmol) 30 % H_2O_2 was added over a period of 30 min while keeping the temperature under 30 °C. After 12 h of stirring at 30 °C, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to leave a bright green oil (6.9 g, 90 purity (GC). The crude product was purified by flash column chromatography (100 g silica gel, hexane/acetone 12:1) to give **S-11** (7.9 g, 31.3 mmol, 72%) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.59 (m, 2H),

3.94 (m, 2H), 2.39 (m, 1H), 2.25-2.02 (m, 4H), 1.83 (m, 3H), 1.51 (m, 3H), 1.21 (2s, 6H), 1.17 (2s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 126.7 (t), 125.0 (t), 78.7 (t), 63.1 (t), 60.1 (q), 60.4 (q), 48.7 (2s), 34.5 (2p), 31.8 (s), 28.7 (s), 25.0 (s), 21.2 (2p); IR (neat): ν max 3372, 3009, 2930, 1447, 1359, 1174, 1026 cm^{-1}; MS: m/z = 254 $[M+H]^+$; Anal. calcd. for $C_{15}H_{27}NO_2$: C, 71.10; H, 10.74; N, 5.53. Found: C, 71.33; H, 10.49; N, 5.38.

1-(Bicyclo[2.2.1]hept-5-en-2-yloxy)-2,2,6,6-tetramethylpiperidin-4-ol (S-12). To a solution of 1.00 g (5.8 mmol) 4-hydroxy-TEMPO in 4 ml ethanol was added CuCl (14 mg, 2.5 mol%) and bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (1.1 g, 8.71 mmol). 1.0 g (8.7 mmol) 30 % H_2O_2 was added over a period of 2 h and the reaction mixture was stirred at rt for 48 h. The product was extracted with ethyl acetate. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave a yellow oil. The crude product was was purified by flash column chromatography (15 g silica gel, hexane/acetone 19:1) to give **S-12** (1.14 g, 4.3 mmol, 74%) as a white solid consisting of two isomers in a 9:1 ratio (exo/endo). Sublimation of this material (0.01 mbar, 80 °C) did not lead to an increase in purity. ^{1}H-NMR (400 MHz, $CDCl_3$) (major isomer): δ 6.15 (dd, *J* = 5.4, 2.7 Hz, 1H), 5.91 (dd, *J* = 5.4, 3.3 Hz, 1H), 3.93 (m, 2H), 3.09 (s, 1H), 2.74 (s, 1H), 2.00-1.05 (m, ~30H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.7, 138.1, 133.8, 131.8, 91.0, 87.9, 87.0, 63.1, 30.4, 60.0, 59.4, 59.3, 48.4, 47.5, 47.2, 46.6, 46.0, 41.2, 39.8, 36.6, 35.7, 34.7, 34.3, 33.9, 33.8, 30.6, 30.2, 21.2, 14.4, 13.1, 11.3; IR (neat): ν max 3378, 2969, 2936, 1478, 1452, 1372, 1340, 1245, 1165, 1031 cm^{-1}; MS: m/z = 266 $[M+H]^+$. Anal. calcd. for $C_{16}H_{27}NO_2$: C, 70.80; H, 9.90; N, 5.00. Found: C, 71.50; H, 10.13; N, 4.99.

1-(1,1-Dimethyl-but-3-enyloxy)-2,2,6,6-tetramethylpiperidin-4-ol (S-13). To a solution of 1.00 g (5.8 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (16 mg, 3.5 mol%) and 2,2-dimethyl-4-pentenal (1.02 ml, 7.5 mmol). 0.590 g (8.7 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature below 30 °C. After 28 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave **S-13** as a light yellow oil which solidified into a

yellowish wax after a short time (1.25 g, 4.89 mmol, 84%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.86 (dddd, *J* = 14.5, 12.2, 9.0, 7.3 Hz, 1H), 4.99 (m, 1H), 4.95 (tdd, *J* = 6.5, 2.4, 1.3, 1.3 Hz, 1H), 3.87 (tt, *J* = 11.5, 11.5, 4.2, 4.2 Hz, 1H), 2.30 (d, *J* = 7.2 Hz, 2H), 1.75 (tdd, *J* = 12.9, 3.8, 2.1, 2.1 Hz, 2H), 1.38 (ps t, *J* = 11.8 Hz, 2H), 1.18 (s, 6H), 1.10 (s, 6H), 1.07 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 135.7, 116.8, 79.2, 63.1, 59.8, 49.2, 47.8, 26.7, 21.6; IR (neat): ν max 3281, 3007, 2972, 2931, 1447, 1471, 1435, 1374, 1358, 1251, 1206, 1163, 1192, 1079, 1031 cm^{-1}; HRMS (+ESI) calcd. $[C_{15}H_{29}NO_2]^+$ $[M+H]^+$ MS: 256.2277 found 256.2278.

1-[((Z)-Non-3-enyl)oxy]-2,2,6,6-tetramethylpiperidin-4-ol (S-14). To a solution of 1.00 g (5.8 mmol) 4-hydroxy-TEMPO in 4 ml toluene/*tert*-butanol (1:1) was added CuCl (16 mg, 3.5 mol%) and cis-4-decenal (4.11 ml, 22.5 mmol). 0.59 g (8.7 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature below 30 °C. After 18 h of stirring at rt, the mixture was heated to 40 °C for 20 h. The mixture was subsequently extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave a yellow oil which was purified by column chromatography (120 g silica gel, hexane/ethyl acetate 1:1) to give **S-14** (0.99 g, 3.52 mmol, 61%) as a light yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.41 (m, 2H), 3.94 (m, 1H), 3.73 (t, *J* = 7.0 Hz, 2H), 2.27 (m, 2H), 2.03 (m, 2H), 1.79 (dd, *J* = 11.5 Hz, 3.2 Hz, 2 H), 1.45 (ps t, *J* = 11.9 Hz, 2H), 1.26-1.40 (multiple m, 6H), 1.19 (s, 6H), 1.14 (s, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 131.7, 125.8, 76.4, 63.4, 60.0, 48.3, 33.2, 31.5, 29.3, 27.2, 26.8, 22.6, 21.0, 14.1; IR (neat): ν max. 3329, 3006, 2925, 2857, 1467, 1456, 1372, 1369, 1045, 1030 cm^{-1}; HRMS (+ESI) calcd. $[C_{18}H_{35}NO_2]^+$ $[M+H]^+$ MS: 298.2741 found 298.2736.

1-(1-Phenyl-ethoxy)-2,2,6,6-tetramethylpiperidin-4-ol (S-15). To a solution of 1.0 g (5.8 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol was added CuCl (20 mg, 3.5 mol%) and 2-phenylpropionaldehyde (1.6 g, 11.6 mmol). 1.3 g (11.6 mmol) 30 % H_2O_2 was added over a period of 30 min. After 12 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to give an off-

white solid. The crude product was dissolved in boiling hexane (10 ml), and upon cooling the product crystallized as a white solid. The crystals were separated by filtration to give pure **S-15** (1.15g, 4.15 mmol, 68%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.24 (m, 5H), 4.80 (q, *J* = 6.8 Hz, 1H), 3.81 (m, 1H), 1.86 (dd, *J* = 8.8, 3.8 Hz, 1H), 1.75 (m, 1H), 1.61-1.40 (m, 2H), 1.53 (s, 3H), 1.37 (s, 3H), 1.25 (s, 3H), 1.11 (s, 3H), 0.70 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.5 (q), 128.1 (2t), 127.0 (t), 126.7 (2t), 83.2 (t), 63.3 (t), 60.2 (q), 60.0 (q), 48.9 (s), 48.8 (s), 34.5 (p), 34.2 (p), 23.5 (p), 21.3 (p); IR (neat): ν max 3274, 3004, 2924, 1449, 1374, 1212, 1043 cm^{-1}; MS: m/z = 278 $[M+H]^+$; Anal. calcd. for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.25; H, 9.09; N, 4.95.

2,2,6,6-Tetramethyl-1-(2-phenyl-propoxy)-piperidin-4-ol (S-16). To a solution of 10.0 g (58.1 mmol) 4-hydroxy-TEMPO in 30 ml water was added acetic acid (300 mg), CuCl (20 mg, 3.5 mol%) and 3-phenylbutyraldehyde (11.18 g, 75.47 mmol). 5.9 g (87.0 mmol) 50 % H_2O_2 was added over a period of 30 min. After 12 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to give an off-white solid. The crude product was dissolved in boiling hexane (10 ml), and upon cooling the product crystallized as a white solid. The crystals were separated by filtration to give pure **S-16** (1.15g, 4.15 mmol, 68%). Alternatively, the product can be purified by Kugelrohr® distillation (1.2×10^{-1} mbar, 110-130 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.27 (m, 5H), 3.94 (m, 1H), 3.84 (m, 2H), 3.01 (sext., *J* = 6.90, 6.90, 6.89, 6.89, 6.89 Hz, 1H), 1.78 (m, 2H), 1.44 (dt, *J* = 12.13, 12.10, 6.19 Hz, 2H), 1.35 (d, *J* = 7.03 Hz, 3H), 1.24 (m, 1H), 1.16 (s, 3H), 1.15 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.6, 128.1, 127.5, 126.2, 82.0, 63.3, 60.2, 48.3, 39.5, 33.1, 33.0, 21.1, 21.0, 18.2; IR (neat): ν max 3263, 2966, 2923, 2871, 1495, 1452, 1371, 1360, 1049, 1033 cm^{-1}; MS: m/z = 292 $[M+H]^+$; Anal. calcd. for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.01; H, 9.97; N, 4.83.

2-(4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy)-propionic acid ethyl ester (S-17). To a solution of 0.50 g (2.9 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (8 mg, 3.5 mol%) and 2-formyl propionic acid ethyl ester (0.49 g, 3.75 mmol). 0.30 g (4.35 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature below 30

°C. After 26 h of stirring at 30 °C, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave a yellow oil which was purified by column chromatography (80 g silica gel, hexane/ethyl acetate 2:1) to give **S-17** (0.50 g, 1.83 mmol, 63 %) as a light yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.30 (q, *J* = 7.0 Hz, 1H), 4.16 (ddd, *J* = 14.2, 7.1, 1.5 Hz, 2H), 3.95 (m, 1H), 1.79 (m, 2H), 1.45 (m, 2H), 1.40 (d, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 3H), 1.17 (2s, 6H), 1.07 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 174.1, 81.8, 63.0, 60.5, 59.9, 48.7, 48.4, 33.7, 33,0, 21.1, 21.0, 18.3, 14.1. IR (neat): ν max 3451, 2977, 2936, 1733, 1457, 1362, 1374, 1263, 1184, 1126, 1078, 1047, 1030 cm^{-1}; MS: m/z = 274 $[M+H]^+$. Anal. calcd. for $C_{14}H_{27}NO_4$: C, 61.51; H, 9.96; N, 5.12. Found: C, 61.79; H, 9.85; N, 5.01.

4-(4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy)-2-methyl-2-nitro-butyric acid ethyl ester (S-18). To a solution of 1.0 g (5.8 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (5 mg, 5 mol%) and 2-methyl-2-nitro-5-oxopentanoic acid ethyl ester (1.54 g, 7.5 mmol). 0.590 g (8.7 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature below 30 °C. After 22 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo*. The crude product was purified by flash column chromatography (50 g silica gel, hexan/acetone 10:1) to afford **S-18** as a pale yellow oil (1.28 g, 3.7 mmol, 64%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.27 (q, *J* = 7.1 Hz, 2H), 3.90 (m, 1H), 3.87 (m, 2H), 2.62 (m, 1H), 2.47 (m, 1H), 1.86 (s, 3H), 1.79 (dd, *J* = 12.3, 4.1 Hz, 2H), 1.43 (ps t, *J* = 12.5 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.10-1.28 (multiple s, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.3, 91.4, 71.6, 63.1, 62.9, 60.1, 48.1, 35.5, 33.1, 31.2, 21.1, 21.0, 13.8; IR (neat): ν max 3357, 2974, 2939, 1748, 1455, 1374, 1361, 1299, 1252, 1193, 1111, 1140, 1046, 1029 cm^{-1}; HRMS (+ESI) calcd. $[C_{16}H_{30}N_2O_6]^+$ $[M+H]^+$ MS: 347.2182 found 347.2174.

4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yl carbonic acid methyl ester (S-19). To a solution of 2.5 g (14.5 mmol) 4-hydroxy-TEMPO in 8 g (90.8 mmol) methyl glyoxylate was added CuCl

(28.7 mg, 2 mol%). 2.0 g (19.6 mmol) 30 % H_2O_2 was added over a period of 60 min. After 12 h of stirring at rt, the mixture was diluted with MTBE. The organic phase was washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to leave a white solid. The crude product was filtered over silica gel (20 g) using hexane/acetone (2:1) to yield **S-19** as a white solid (2.55g, 11.0 mmol, 76%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.01 (m, 1H), 3.82 (s, 3H), 1.89 (dd, *J* = 11.2, 4.2 Hz, 2H), 1.82 (br s, 1H), 1.67 (ps t, *J* = 11.2 Hz, 2H), 1.21 (2s, 6H), 1.15 (2s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.6 (q), 63.1 (t), 61.1 (2q), 55.5 (p), 48.1 (2s), 32.0 (2p), 21.6 (2p); IR (neat): ν max 3234, 2966, 1773, 1440, 1365, 1225, 1183, 1047 cm^{-1}; MS: m/z = 232 $[M+H]^+$; Anal. calcd. for $C_{11}H_{21}NO_4$: C, 57.12; H, 9.15; N, 6.06. Found: C, 57.34; H, 8.97; N, 5.83.

1-(2,2-Dimethoxy-ethoxy)-2,2,6,6-tetramethylpiperidin-4-ol (S-20). To a solution of 2.5 g (14.5 mmol) 4-hydroxy-TEMPO in 7.5 g (63.5 mmol) 3,3-dimethoxy propanal was added CuCl (28.7 mg, 2 mol%). 2.0 g (19.6 mmol) 30 % H_2O_2 was added over a period of 60 min. After 9 h of stirring at rt, the mixture was diluted with MTBE. The organic phase was successively washed with water, 1 N NaOH, 10% Na_2EDTA solution, water, and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to leave a white solid. The crude product was recrystallized from hexane/acetone (95:5) to yield **S-20** as a white solid (2.5g, 9.58 mmol, 66%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.49 (t, *J* = 5.2 Hz, 1H), 3.94 (m, 1H), 3.84 (2d, *J* = 5.2 Hz, 2H), 3.40 (2s, 6H), 2.72 (s, 1H), 1.81 (dd, *J* = 12.4, 4.0 Hz, 2H), 1.52 (br s, 1H), 1.48 (ps t, *J* = 11.6 Hz, 2H), 1.22 (2s, 6H), 1.16 (2s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 102.4 (t), 77.3 (s), 63.2 (t), 60.2 (2q), 53.9 (2p), 48.3 (2s), 33.1 (2p), 21.0 (2p); IR (neat): ν max 3401, 2974, 1718, 1469, 1374, 1193, 1077 cm^{-1}; MS: m/z = 262 $[M+H]^+$; Anal. calcd. for $C_{13}H_{27}NO_4$: C, 59.74; H, 10.41; N, 5.36. Found: C, 59.69; H, 10.32; N, 5.38.

Acetic acid 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxymethyl ester (S-21). To a solution of 1.0 g (5.8 mmol) 4-hydroxy-TEMPO in 5 ml toluene and 1.19 g (11.6 mmol) acetoxyacetaldehyd was added CuCl (11.4 mg, 2 mol%). 1.3 g (11.6 mmol) 30 % H_2O_2 was added over a period of 120 min. After 12 h of stirring at rt, the mixture was diluted with toluene. The organic phase was washed with 5 % ascorbic acid solution, 0.1 M Na_2CO_3 solution, water,

and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to leave a pale chartreuse oil. The crude product was heated to 35 °C for 4 h while applying a vacuum of 0.05 mbar to afford 0.97 g (4.0 mmol, 68 %) of pure **S-21** as an oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.45 (s, 2H), 3.99 (m, 1H), 2.10 (s, 3H), 1.86 (dd, *J* = 12.8, 6.4 Hz, 2H), 1.48 (ps t, *J* = 12.0 Hz, 2H), 1.21 (2s, 6H), 1.17 (2s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.3 (q), 93.4 (s), 63.0 (t), 60.2 (2q), 48.1 (2s), 33.3 (2p), 21.1 (3p); IR (neat): ν max 3378, 2975, 2938, 1735, 1458, 1364, 1220, 1008 cm^{-1}; HRMS (+ESI) calcd. $[C_{12}H_{23}NO_4]^+$ $[M+H]^+$ MS: 246.1670 found 246.1666.

4-(4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxymethyl)-piperidine-1-carboxylic acid *tert*-butyl ester (S-22). To a solution of 0.29 g (1.7 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (5 mg, 5 mol%) and N-Boc-piperidinyl-4-acetaldehyde (0.500 g, 2.2 mmol). 0.173 g (2.55 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature under 30 °C. After 21 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave **S-22** (0.252 g, 0.68 mmol, 40%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.07 (m, 2H), 3.92 (m, 1H), 3.59 (m, 2H), 2.68 (m, 2H), 1.76 (dd, *J* = 12.3, 4.0 Hz, 2H), 1.69 (m, 2H), 1.40-1.48 (m, 5H), 1.43 (s, 9H), 1.15 (s, 6H), 1.11 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.8, 80.9, 79.3, 62.3, 60.2, 48.2, 36.1, 33.2, 29.2, 28.5, 21.1; IR (neat): ν max 2974, 2927, 2868, 1669, 1468, 1364, 1423, 1273, 1243, 1168, 1145, 1045 cm^{-1}; HRMS (+ESI) calcd. $[C_{20}H_{38}N_2O_4]^+$ $[M+H]^+$ MS: 371.2904 found 371.2900.

4-Ethyl-4-(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy)-hexanenitrile (S-23). To a solution of 1.00 g (5.8 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (10 mg, 3.5 mol%) and 4-ethyl-4-formylhexanenitrile (1.21 ml, 7.5 mmol). 0.59 g (8.7 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature below 30 °C. After 5 h of stirring at rt, the mixture was heated to 40 °C and stirred for an additional 38 h. The mixture was then extracted with MTBE. The combined organic layers were washed with 10 % ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave a yellow oil which rapidly solidified into a light yellow

wax. Recrystallization of the wax in ethyl acetate and hexane yielded pure **S-23** (1.05 g, 3.5 mmol, 61%) as yellowish crystals. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.96 (tt, *J* = 11.5, 11.5, 4.3, 4.3 Hz, 1H), 2.63-2.55 (m, 2H), 2.15-2.07 (m, 2H), 1.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 1.83 (dd, *J* = 4.1, 1.8 Hz, 1H), 1.77 (dq, *J* = 7.6, 7.4, 7.4, 2.6 Hz, 4H), 1.46 (ps t, *J* = 11.9 Hz, 2H), 1.17 (s, 6H), 1.16 (s, 6H), 0.95 (t, *J* = 11.8, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 120.6, 81.6, 62.9, 60.2, 49.4, 34.6, 30.6, 21.9, 12.7, 9.5. IR (neat): ν max 3280, 2975, 2934, 2878, 2245, 1457, 1373, 1361, 1199, 1182, 1163, 1048, 1035 cm^{-1}; HRMS (+ESI) calcd. $[C_{17}H_{32}N_2O_2]^+$ $[M+H]^+$ MS: 297.2542 found 297.2557.

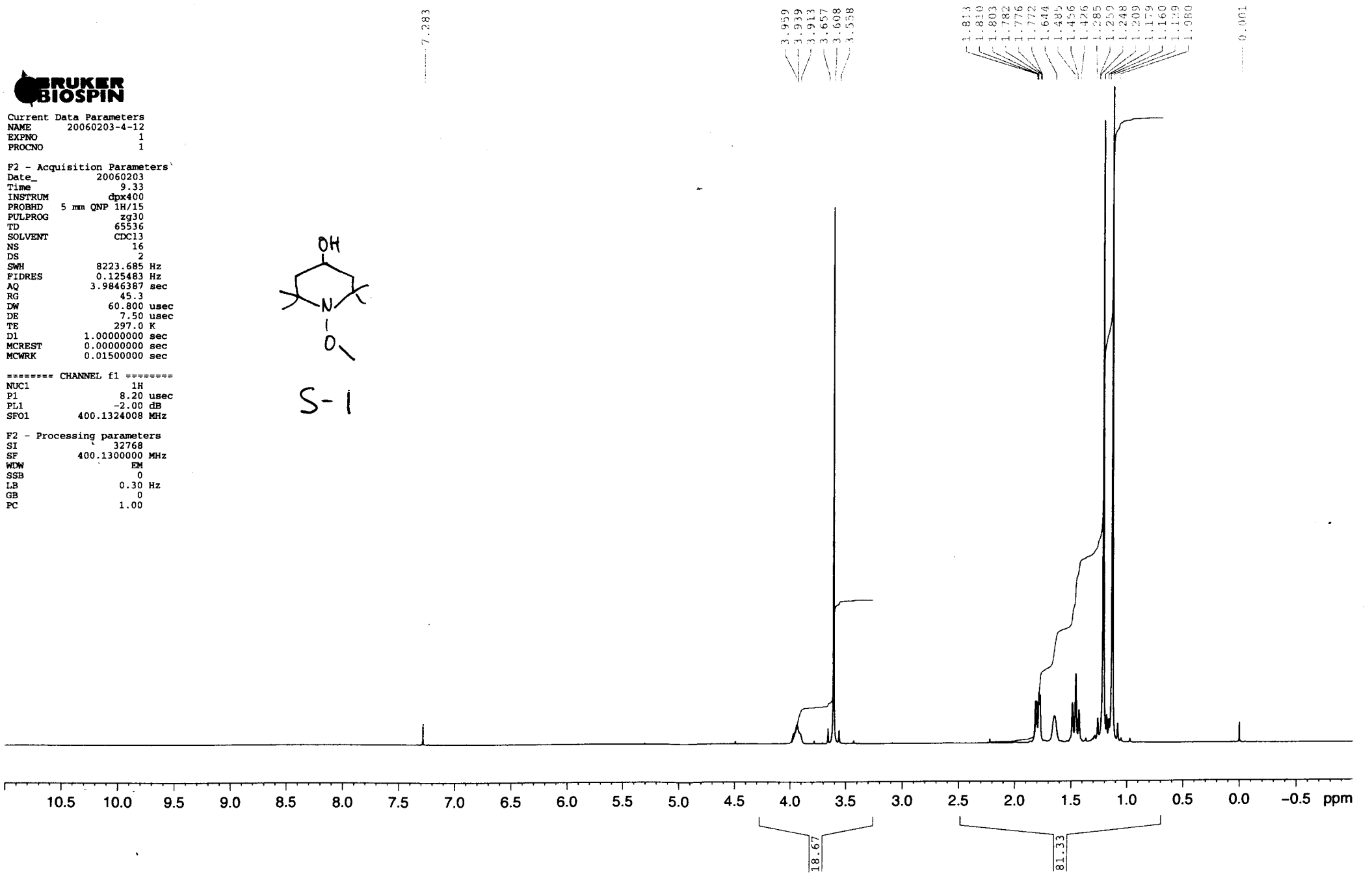
2,2,6,6-Tetramethyl-1-(2,2,2-trifluoro-ethoxy)-piperidin-4-ol (S-24). To a solution of 0.50 g (2.9 mmol) 4-hydroxy-TEMPO in 4 ml *tert*-butanol/water (1:1) was added CuCl (10 mg, 3.5 mol%) and 3,3,3-trifluoropropanal (0.32 ml, 3.75 mmol). 0.30 g (4.35 mmol) 50 % H_2O_2 was added over a period of 30 min while keeping the temperature below 30 °C. After 72 h of stirring at rt, the mixture was extracted with MTBE. The combined organic layers were washed with 10% ascorbic acid solution, 1 N NaOH, water, and brine. After drying over Na_2SO_4, the organic phase was concentrated *in vacuo* to leave a yellow oil which was purified by column chromatography (80 g silica gel, hexane/ethyl acetate 1:1) to give **S-24** (0.55 g, 2.15 mmol, 74%) as a colourless oil, which quickly solidified into a white wax. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.15 (dd, $^{2}J_{H,H}$ = 8.7 Hz, $^{3}J_{H,F}$ = 17.5 Hz, 2H), 3.97 (m, 1H), 1.82 (ddd, *J* = 5.4, 4.2, 1.8 Hz, 2H), 1.46 (ps t, *J* = 12.0 Hz, 2H), 1.22 (s, 6H), 1.19 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 123.1 (d, $^{1}J_{C,F}$ = 278.7 Hz), 73.8 (q, $^{2}J_{C,F}$ = 31.7 Hz), 62.8, 60.7, 48.1, 32.7, 20.8; ^{19}F-NMR (282 MHz, $CDCl_3$, d CF_3COOH = - 76.0 ppm): d -73.12; IR (neat): ν max 3231, 2976, 3005, 2932, 1364, 1264, 1165, 1090, 1040, 1050 cm^{-1}; HRMS (+ESI) calcd. $[C_{11}H_{20}F_3NO_2]^+$ $[M+H]^+$ MS: 256.1524 found 256.1533.

1-(2-Hydroxy-2-methyl-propoxy)-2,2,6,6-tetramethylpiperidin-4-ol (S-25). To a solution of 215.9 mg (1.25 mmol) 4-hydroxy-TEMPO and 160 mg (1.57 mmol) 3-hydroxy-3-methylbutanal in 1 ml *tert*-butanol/water (1:1) was added CuCl (5 mg, 3.5 mol%). 178 mg (1.57 mmol) 30 % H_2O_2 was added and the reaction mixture was stirred at rt over night. The green solution was diluted with MTBE and the organic phase was washed with 10 % ascorbic acid solution, 1 N

NaOH, water, and brine. After drying over $MgSO_4$, the organic phase was concentrated *in vacuo* to provide a pale yellow oil which solidified upon standing at rt. The crude product was recrystallized from hexane/ethyl acetate (10:1) to afford 210.3 mg (0.86 mmol, 69%) of **S-25**. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.96 (m, 1H), 3.65 (s, 2H), 2.15 (br s, 1H), 1.81 (dd, *J* = 12.3, 4.2 Hz, 2H), 1.47 (ps t, *J* = 12.0 Hz, 2H), 1.25 (2s, 6H), 1.22 (2s, 6H), 1.19 (2s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 84.0 (q), 70.7 (s), 63.1 (t), 60.5 (2q), 48.3 (2s), 33.2 (2p), 26.5 (2P), 21.2 (2p); IR (neat): ν max 3342, 2966, 1488, 1376, 1166, 1047 cm^{-1}. MS: m/z = 264 $[M+H]^+$. Anal. Calcd. for $C_{13}H_{27}NO_3$: C, 63.64; H, 11.09; N, 5.71. Found: C, 63.43; H, 11.17; N, 5.73.

4-(4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy)-butane-1,2,3-triol (S-26). 1.00 g (7.46 mmol) 2-deoxy-D-ribose was dissolved in 3.5 ml acetic acid/water (3:1), and 2.0 g (11.6 mmol) 4-hydroxy-TEMPO and CuCl (20 mg, 0.20 mmol) were added. 0.6 g (8.82 mmol) 50 % H_2O_2 were added over a period of 2.5 h, and the reaction mixture was stirred over night at 30 °C. The reaction mixture was concentrated *in vacuo* at 35 °C. The residue was subjected to reversed phase column chromatography (25 g RP8 silica gel, methanol) to yield 1.22 g (4.40 mmol, 38%) **S-26** as a viscous, pale yellow oil. ^{1}H-NMR (300 MHz, MeOD): δ 4.00 (m, 1H), 3.91 (m, 2H), 3.72 (m, 2H), 3.59 (m, 2H), 1.70 (dd, *J* = 12.3, 3.6 Hz, 2H), 1.44 (m, 2H), 1.30 (s, 3H), 1.27 (s, 3H), 1.24 (s, 3H), 1.21 (s, 3H). ^{13}C-NMR (75 MHz, MeOD): δ 79.8, 73.9, 72.5, 64.7, 63.5, 63.1, 62.3, 61.5, 61.4, 48.3, 48.1, 33.7, 31.6, 21.7, 21.2; IR (neat): ν max 3334, 2973, 2931, 1736, 1593, 1456, 1362, 1046 cm^{-1}; HRMS (+ESI) calcd. $[C_{13}H_{27}NO_5]^+$ $[M+H]^+$ MS: 278.1962 found 278.1959.

1-Hydroxy-2,2,6,6-tetramethyl-4-piperidinol (**S-27**). 2.00 g (11.6 mmol) 4-hydroxy-TEMPO was dissolved in 6 ml 20 % formalin. CuCl (10 mg, 0.10 mmol) and 1.18 g (17.4 mmol) 50 % H_2O_2 were added and the reaction mixture was stirred at 30 °C until complete disappearance of the nitroxide radical. The reaction mixture was concentrated in vacuo, and the crude product was subsequently recrystallized from ethanol under inert gas. **S-27** was obtained as white crytals (1.75 g, 10.1 mmol, 87%). ^{1}H-NMR (300 MHz, DMSO-d6): δ 7.00 (s, 1H), 4.37 (d, *J* = 4.8 Hz, 1H), 3.74 (m, 1H), 1.71 (dd, *J* = 12.0, 4.2 Hz, 2H), 1.24 (ps t, *J* = 11.8, 2H), 1.04 (2s, 6H), 1.01 (2s, 6H). ^{13}C-NMR (75 MHz, DMSO-d6): δ 62.0, 58.8, 49.0, 33.6, 21.1; MS: m/z = 174 $[M+H]^+$.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TD 65536
SOLVENT CDCl3
NS 16
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SWH 8223.685 Hz
FIDRES 0.125483 Hz
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RG 45.3
DW 60.800 usec
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O
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3.558
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1.782
1.776
1.772
1.644
1.485
1.456
1.426
1.285
1.259
1.248
1.209
1.179
1.160
1.129
1.080
0.001
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
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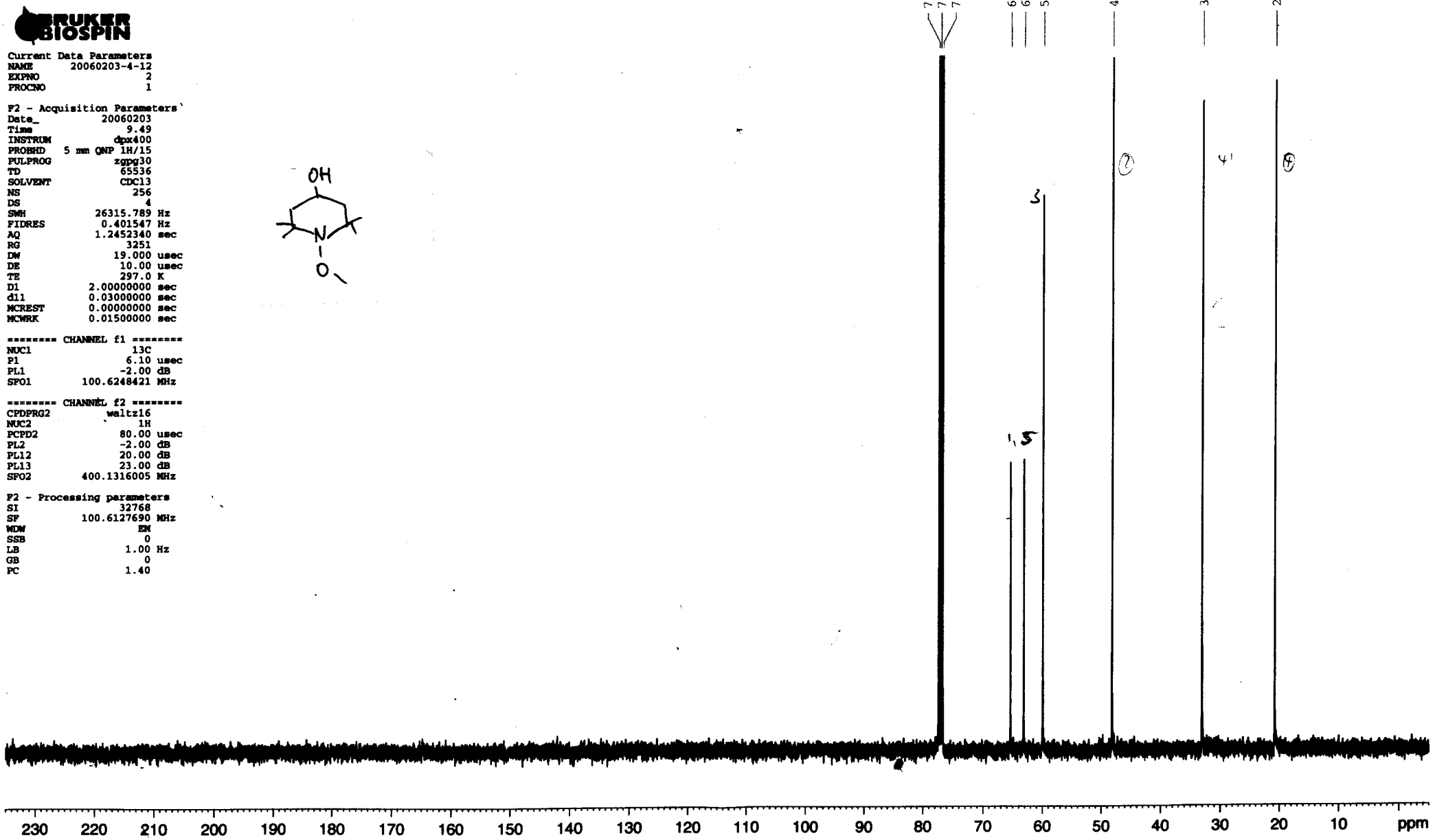
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TD 65536
SOLVENT CDCl3
NS 256
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FIDRES 0.401547 Hz
AQ 1.2452340 sec
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DE 10.00 usec
TE 297.0 K
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MCWRK 0.01500000 sec
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NUC1 13C
P1 6.10 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz
======== CHANNEL f2 ========
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NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 dB
PL13 23.00 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
OH
N
O
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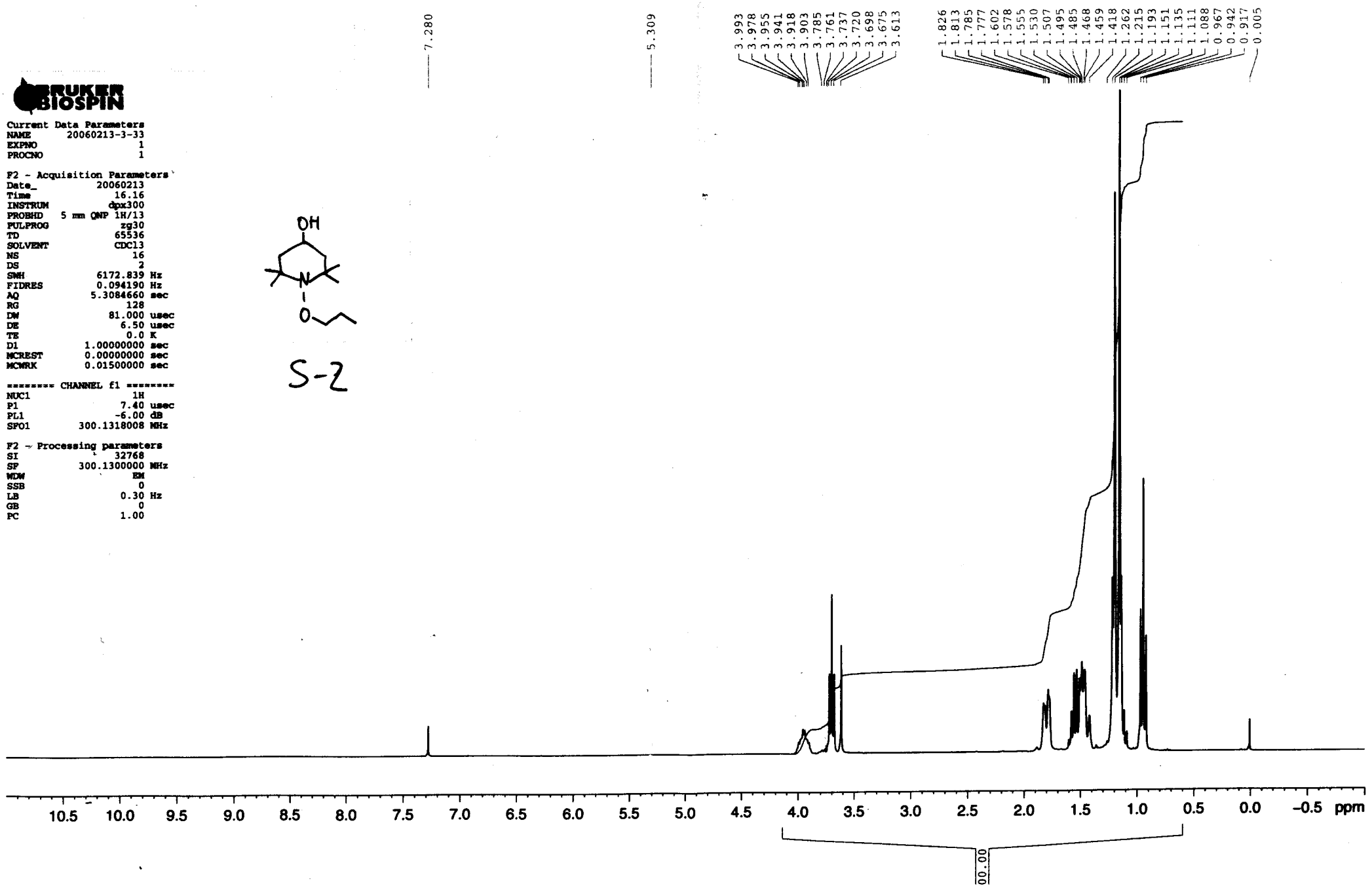

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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.40 usec
PL1 -6.00 dB
SFO1 300.1318008 MHz

F2 - Processing parameters
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SF 300.1300000 MHz
WDW EM
SSB 0
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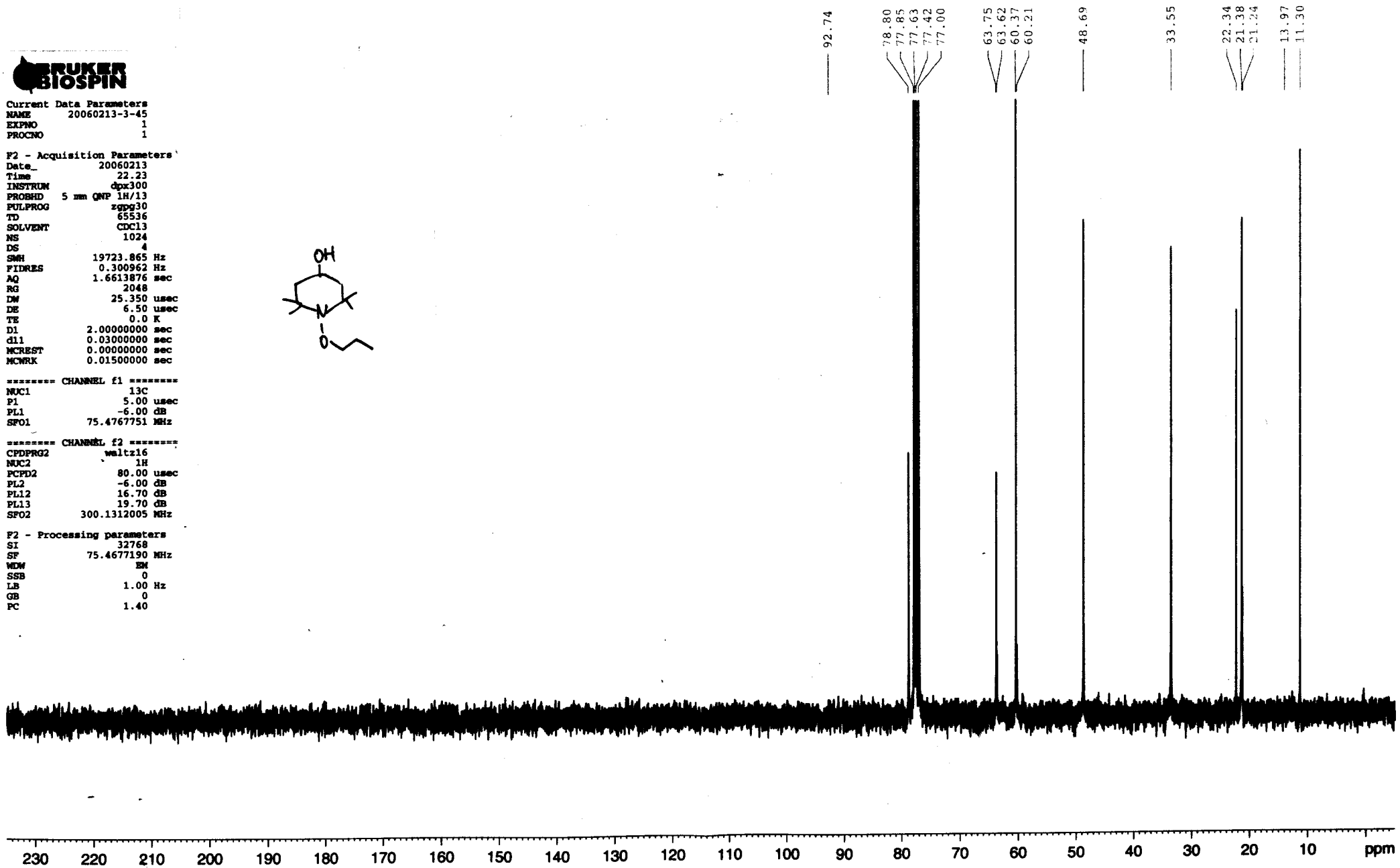
S-2



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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 19723.865 Hz
FIDRES 0.300962 Hz
AQ 1.6613876 sec
RG 2048
DW 25.350 usec
DE 6.50 usec
TE 0.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SFO1 75.4767751 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 16.70 dB
PL13 19.70 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
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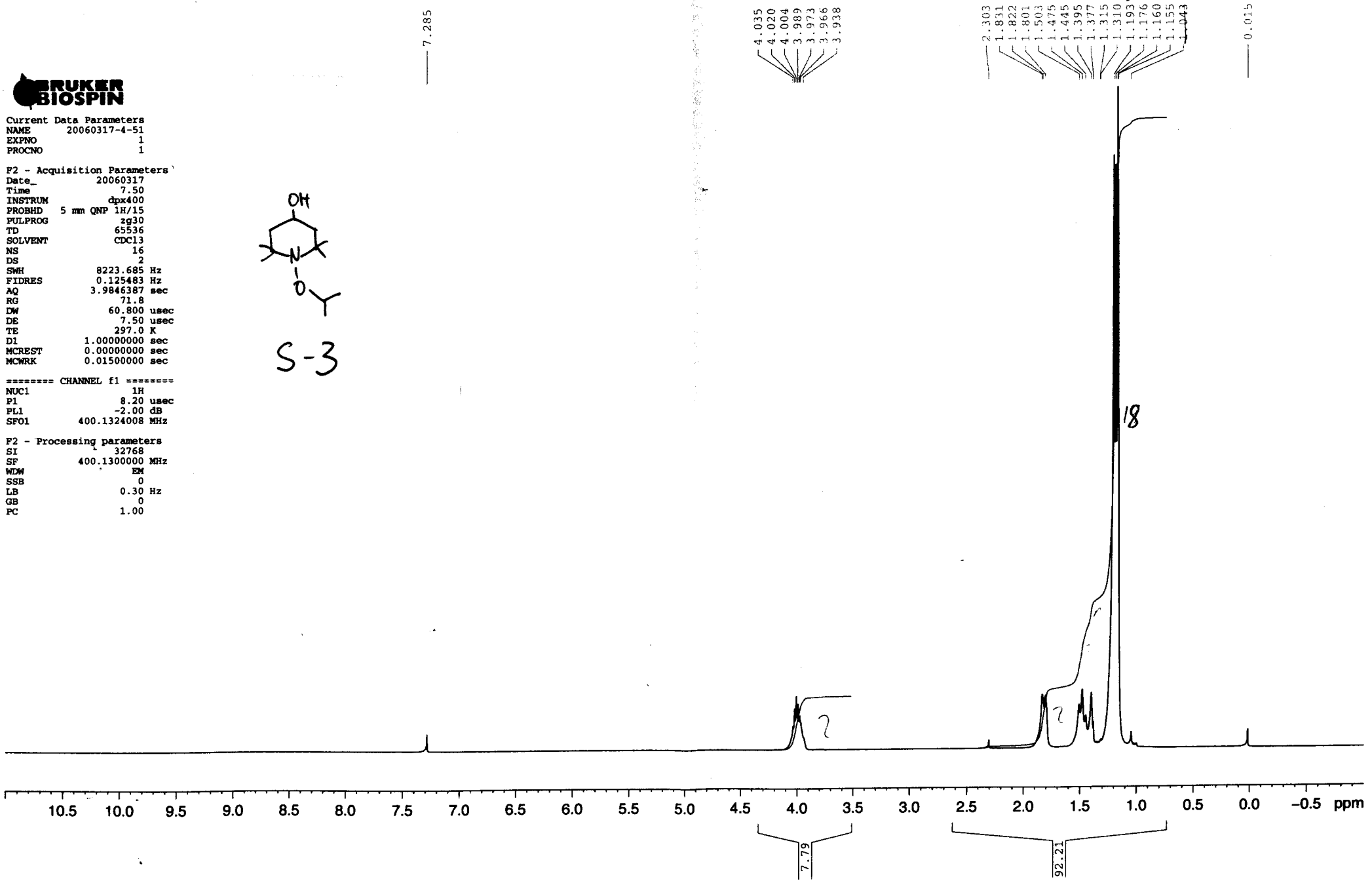
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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EXPNO 1
PROCNO 1

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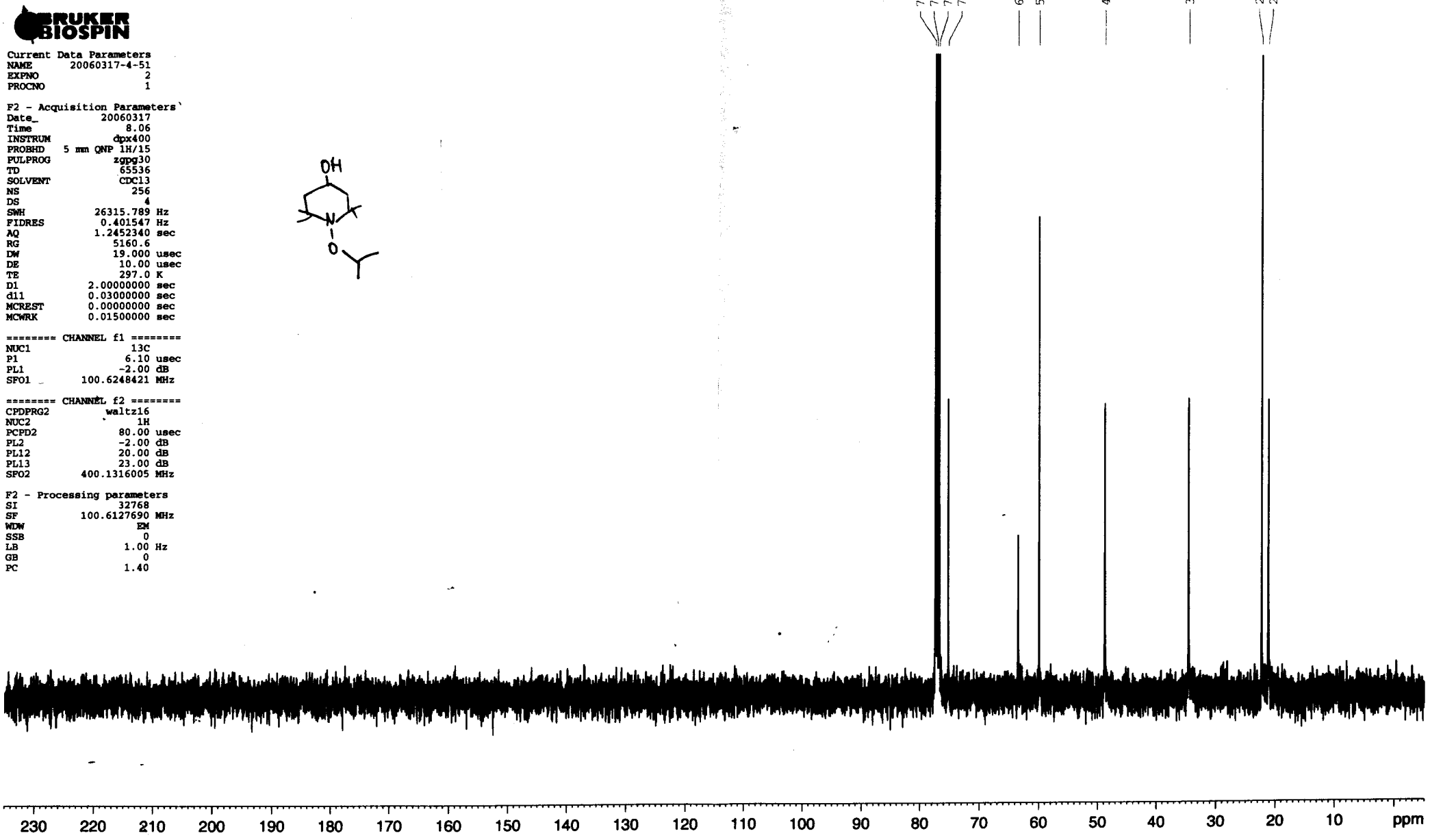
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 71.8
DW 60.800 usec
DE 7.50 usec
TE 297.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 -2.00 dB
SFO1 400.1324008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

p24



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TD 65536
SOLVENT CDCl3
NS 256
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SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 5160.6
DW 19.000 usec
DE 10.00 usec
TE 297.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 dB
PL13 23.00 dB
SFO2 400.1316005 MHz

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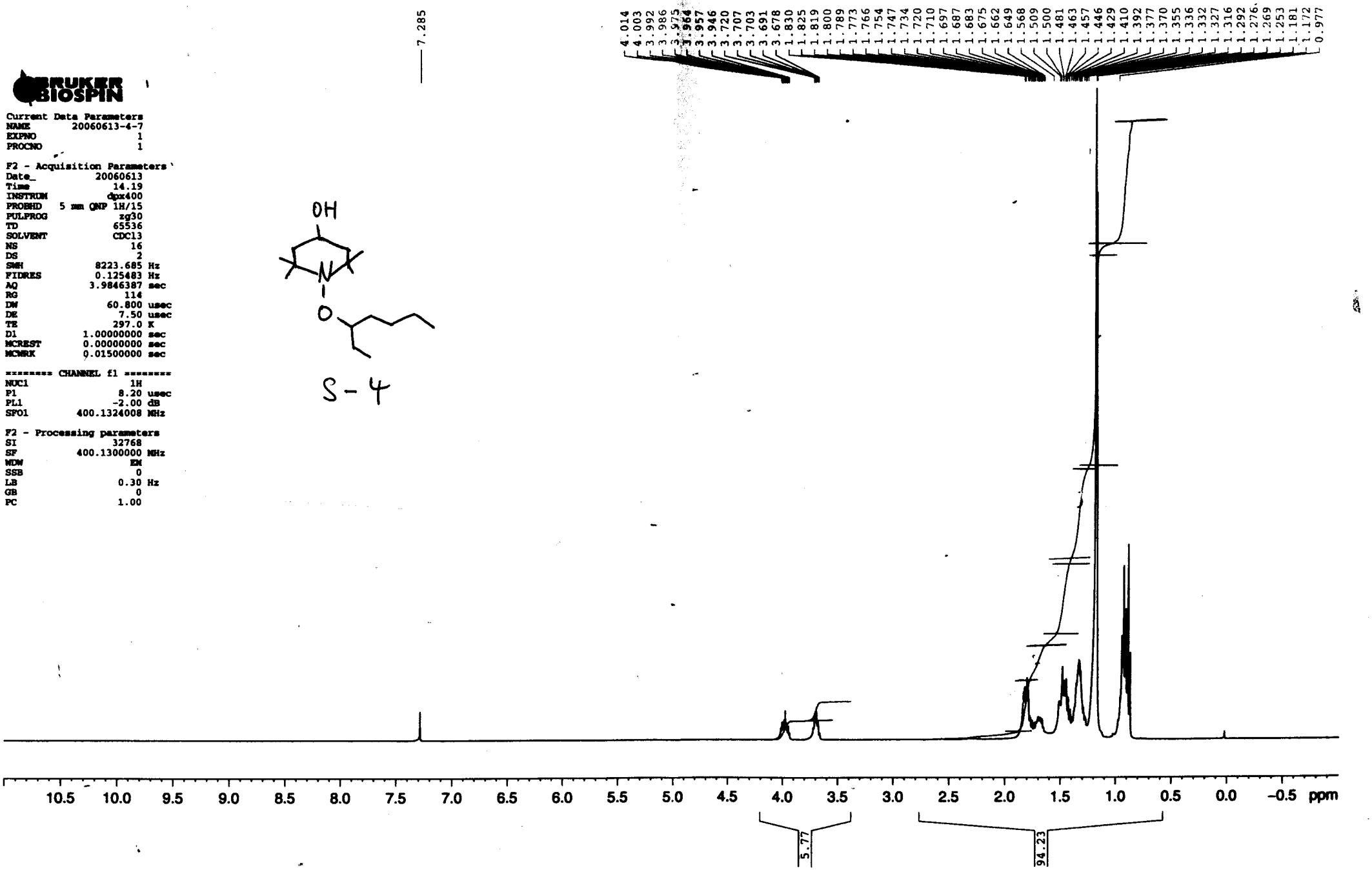
PC 1.40

p25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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 114
DW 60.800 usec
DE 7.50 usec
TE 297.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 -2.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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S-4
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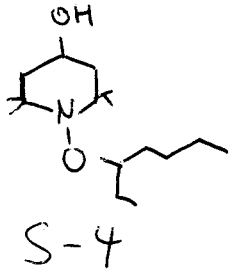

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PROCNO 1

F2 - Acquisition Parameters
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 1824.6
DW 19.000 usec
DE 10.00 usec
TE 298.4 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 dB
PL13 23.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
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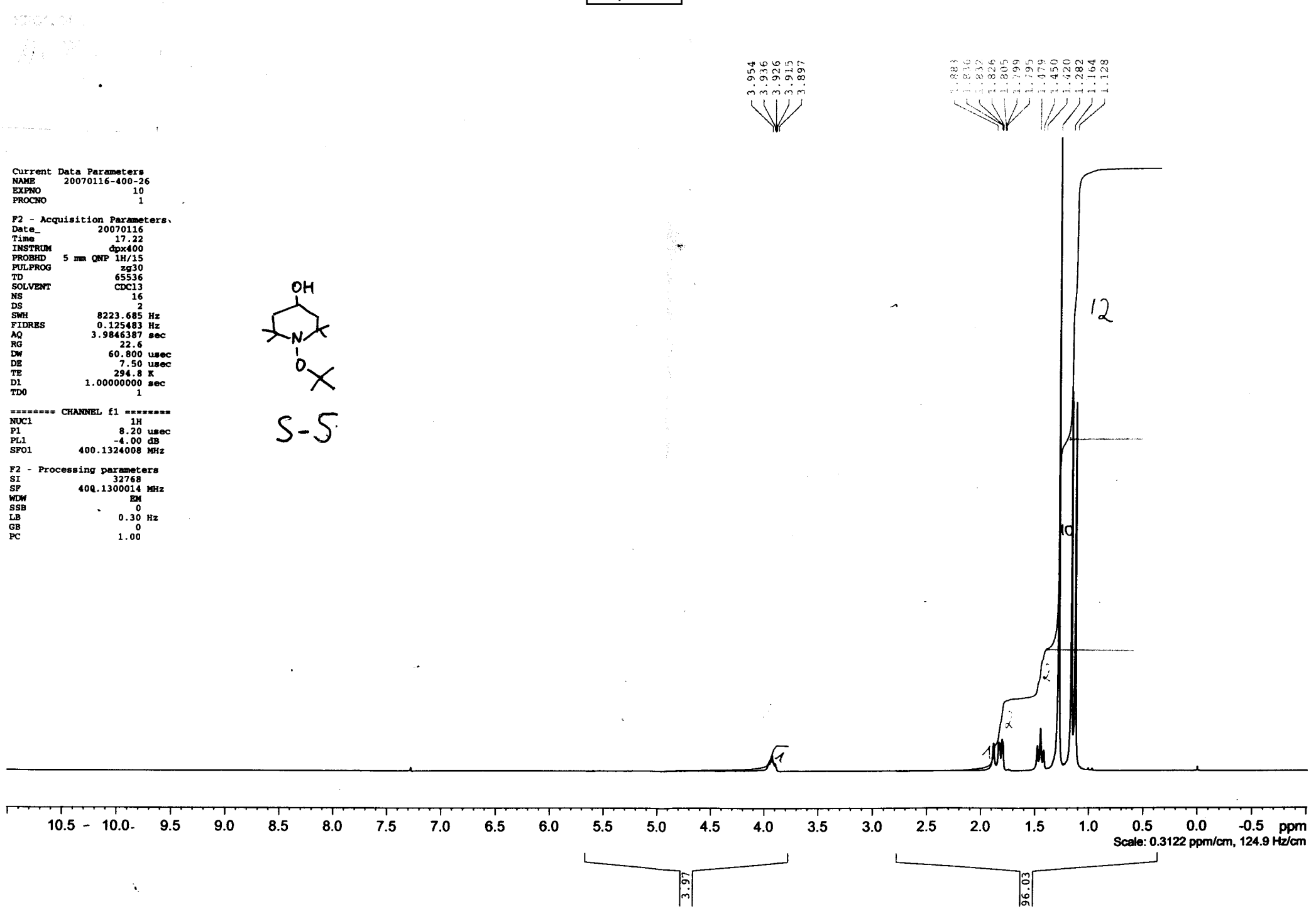
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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PROCNO 1
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INSTRUM dpx400
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 22.6
DW 60.800 usec
DE 7.50 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 -4.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300014 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
N
O
S-5
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3.926
3.915
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1.164
1.128
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10
1
3.97
96.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
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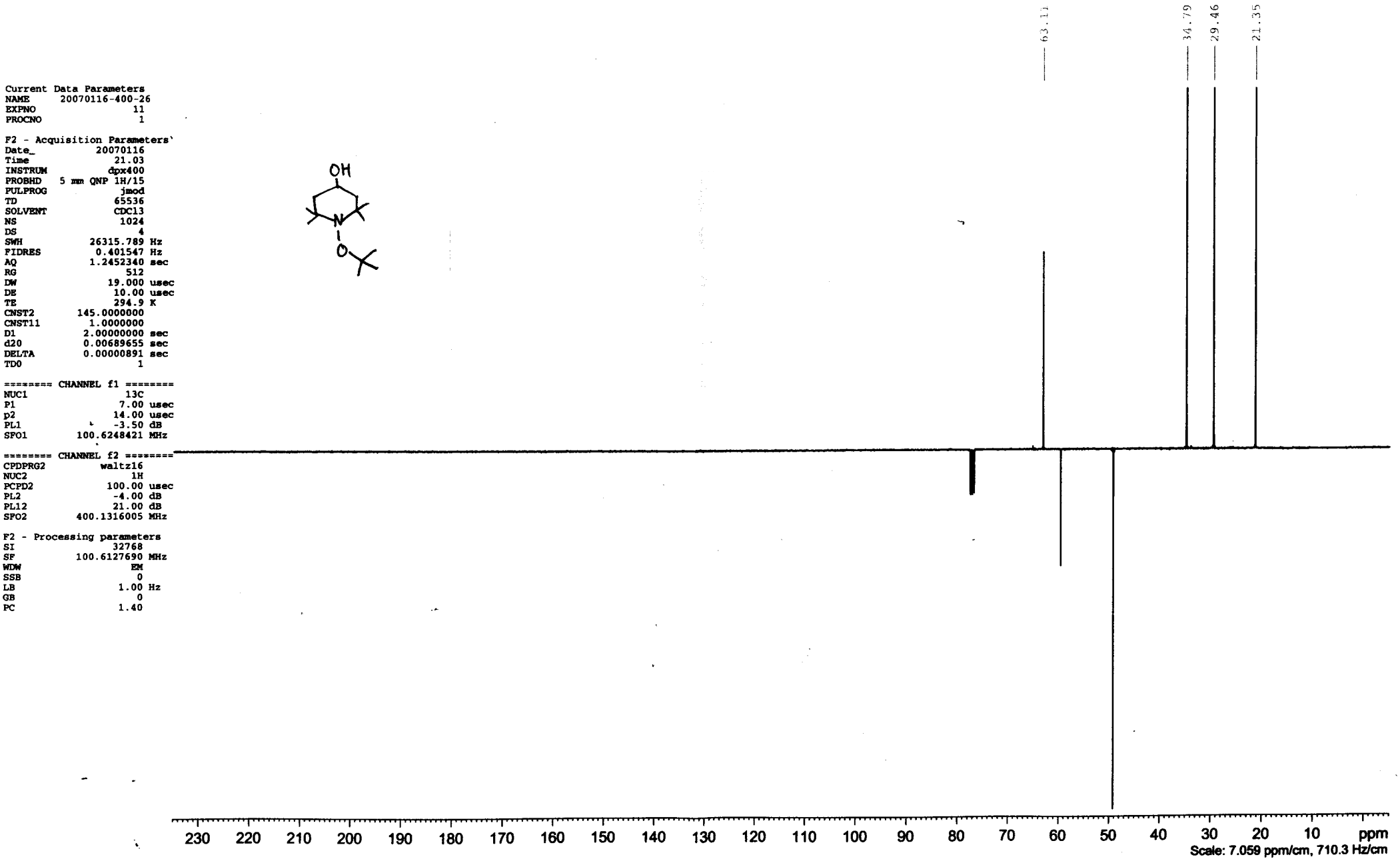


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PROCNO                  1

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TD                 65536
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DS                     4
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FIDRES             0.401547 Hz
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RG                   512
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DE                  10.00 usec
TE                  294.9 K
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D1              2.00000000 sec
d20             0.00689655 sec
DELTA           0.00000891 sec
TD0                    1

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P1                   7.00 usec
p2                  14.00 usec
PL1                 -3.50 dB
SFO1          100.6248421 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               100.00 usec
PL2                  -4.00 dB
PL12                 21.00 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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Ciba

BRUKER dpx 400

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EXPNO                 10
PROCNO                 1

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Time                9.24
INSTRUM            spect
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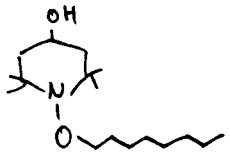
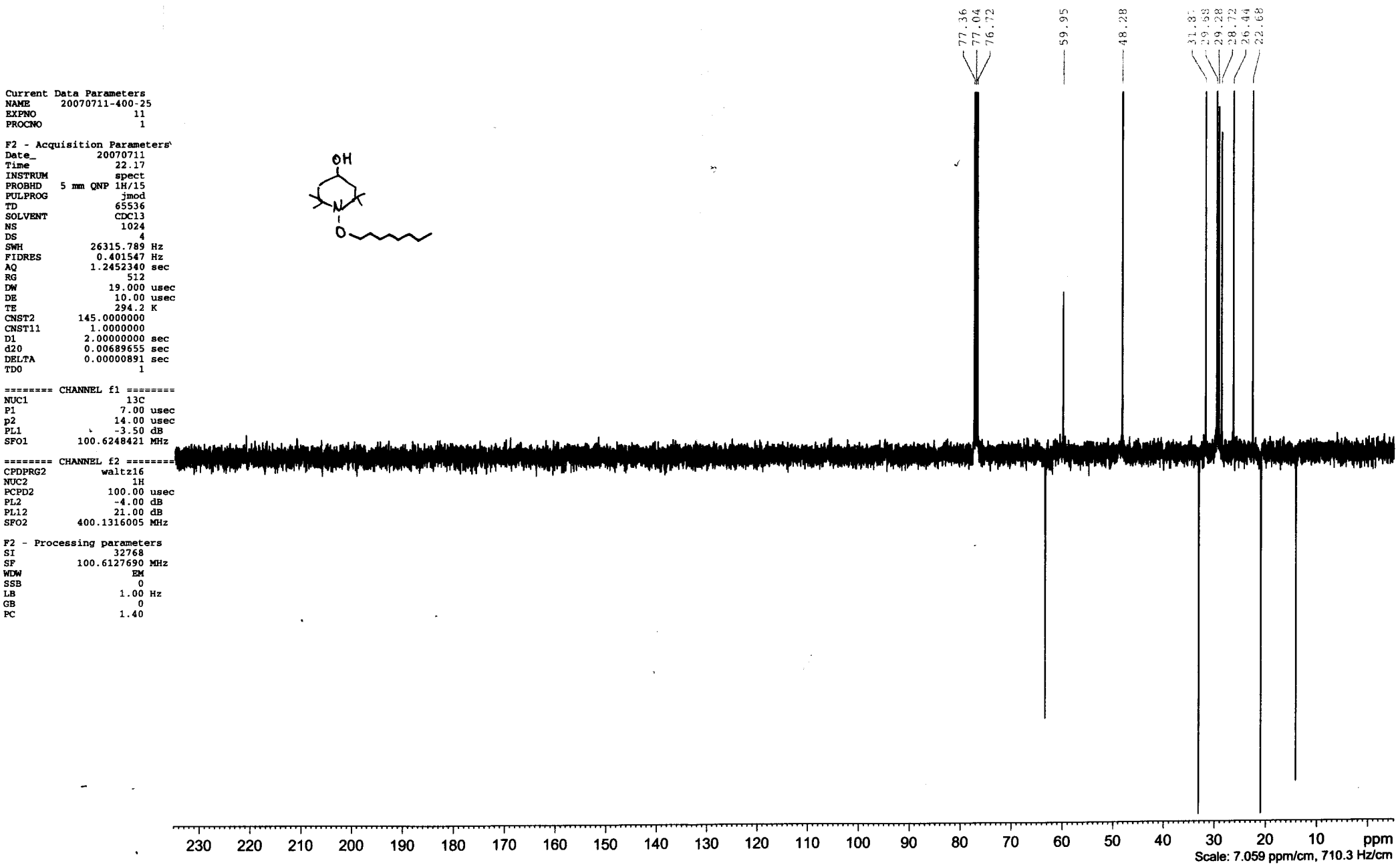
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   128
DW                60.800 usec
DE                 7.50 usec
TE                293.8 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.20 usec
PL1               -4.00 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300071 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



S-6




```
Current Data Parameters
NAME      20070711-400-25
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070711
Time                22.17
INSTRUM             spect
PROBHD   5 mm QNP 1H/15
PULPROG              jmod
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH            26315.789 Hz
FIDRES          0.401547 Hz
AQ             1.2452340 sec
RG                    512
DW                 19.000 usec
DE                 10.00 usec
TE                 294.2 K
CNST2         145.0000000
CNST11          1.0000000
D1              2.00000000 sec
d20             0.00689655 sec
DELTA           0.00000891 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  7.00 usec
p2                 14.00 usec
PL1                -3.50 dB
SFO1         100.6248421 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -4.00 dB
PL12               21.00 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
```

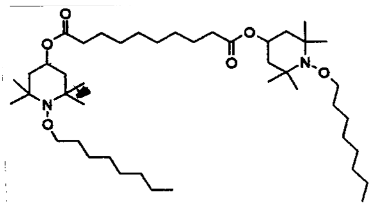
p31

```
Current Data Parameters
NAME      20070308-400-45
EXPNO                  10
PROCNO                  1

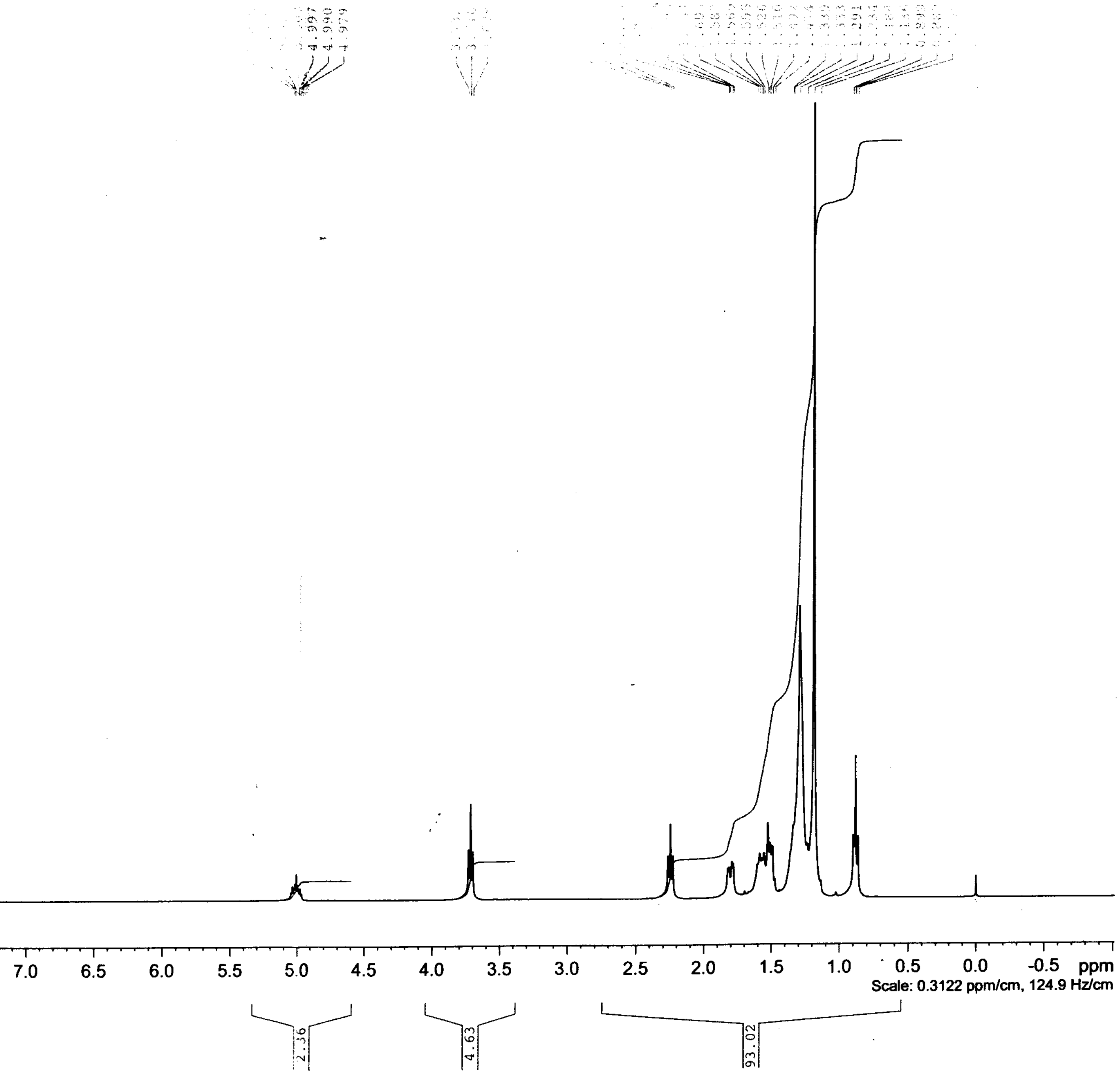
F2 - Acquisition Parameters
Date_            20070308
Time                16.12
INSTRUM            dpx400
PROBHD    5 mm QNP 1H/15
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                     57
DW                 60.800 usec
DE                   7.50 usec
TE                  296.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.20 usec
PL1                 -4.00 dB
SFO1          400.1324008 MHz

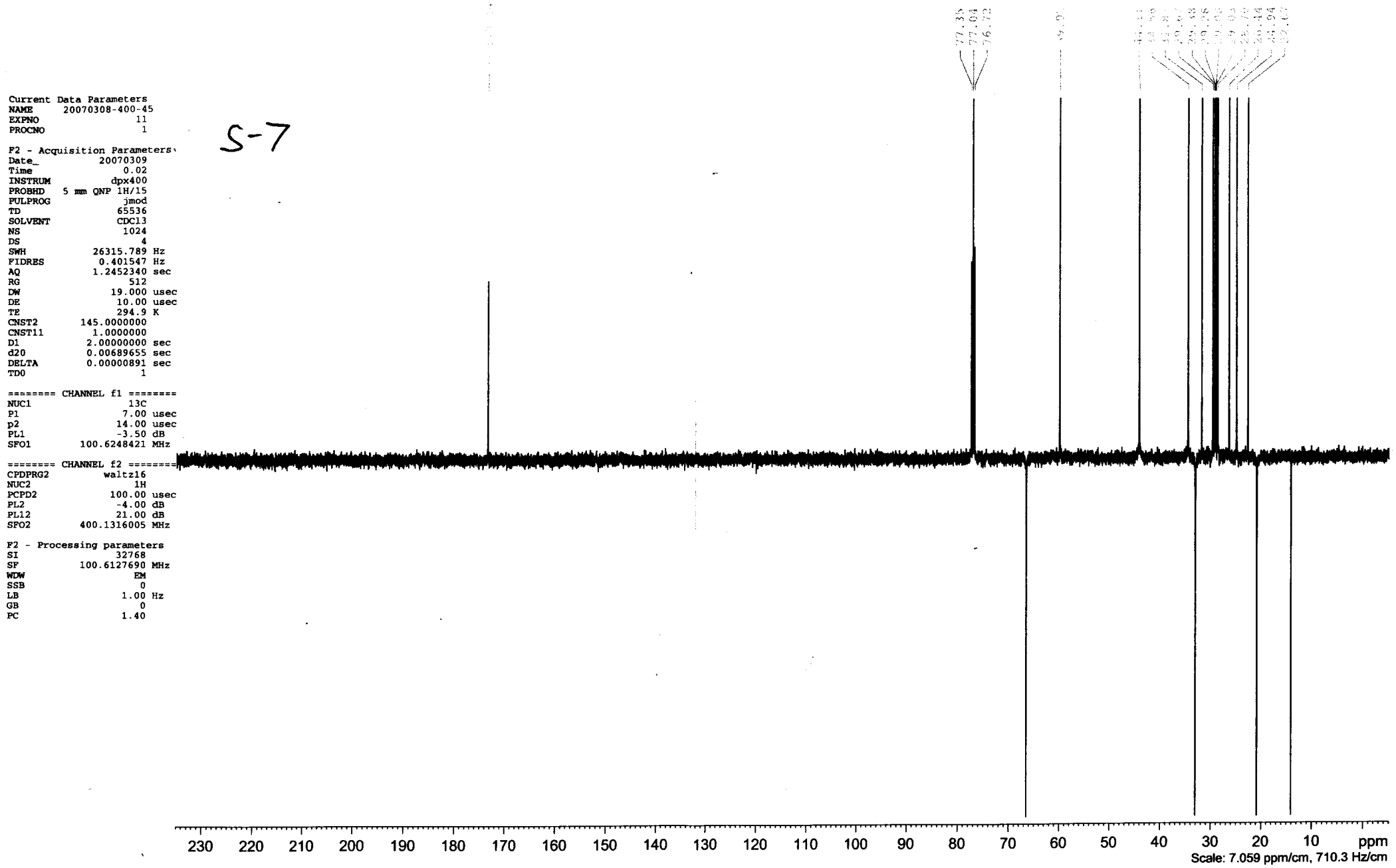
F2 - Processing parameters
SI                  32768
SF            400.1300057 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



S-7



S-7



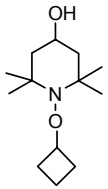

```
Current Data Parameters
NAME      20070308-400-45
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070309
Time                0.02
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/15
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            26315.789 Hz
FIDRES         0.401547 Hz
AQ             1.2452340 sec
RG                   512
DW              19.000 usec
DE              10.00 usec
TE                294.9 K
CNST2         145.0000000
CNST11          1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00000891 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.00 usec
p2                14.00 usec
PL1               -3.50 dB
SFO1         100.6248421 MHz

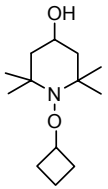
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -4.00 dB
PL12              21.00 dB
SFO2         400.1316005 MHz

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



^{1}H-NMR:
S-8: 1-Cyclobutoxy-2,2,6,6-tetramethyl-piperidin-4-ol

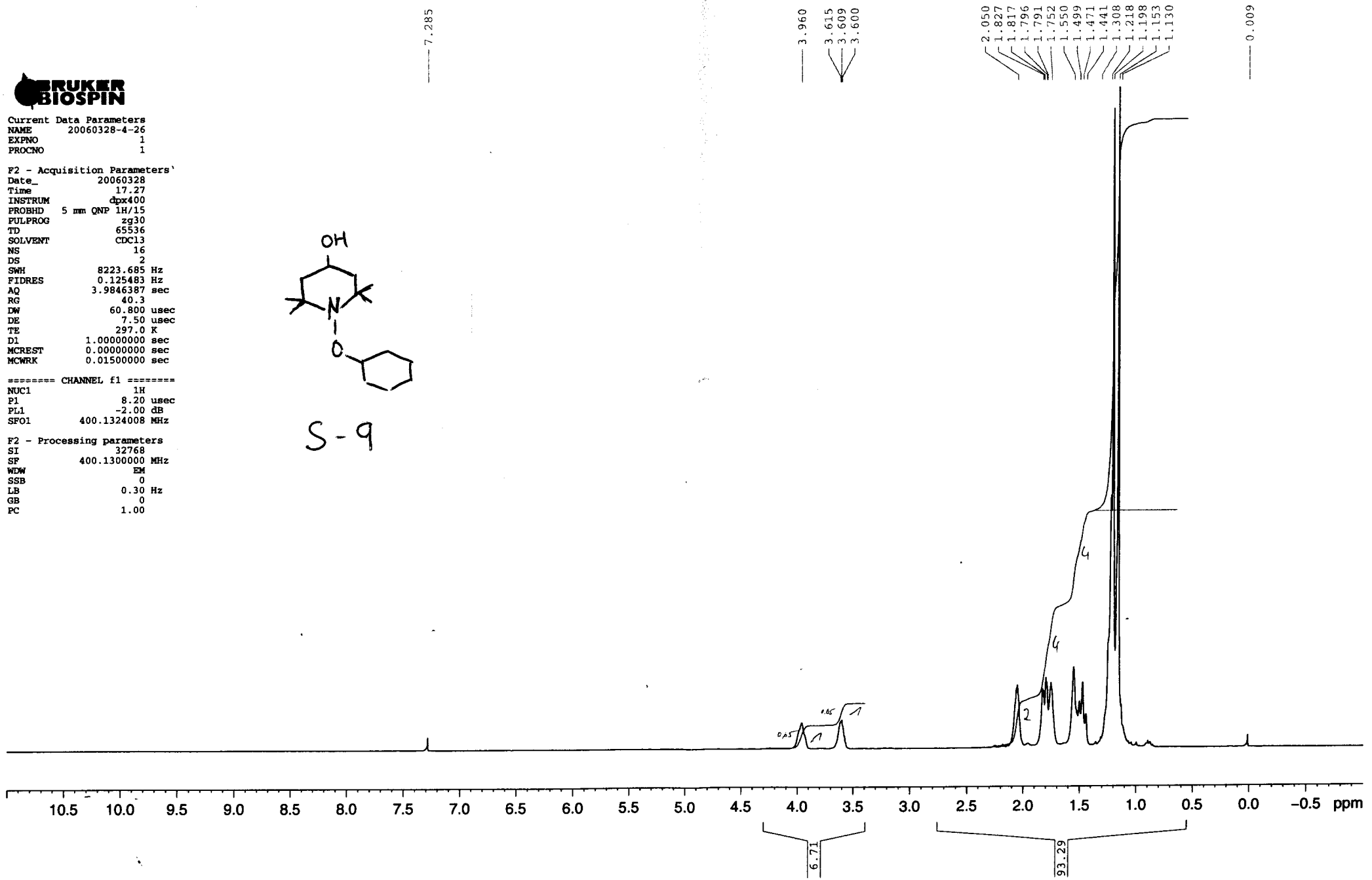
Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	21.900



^{13}C-NMR

S-8: 1-Cyclobutoxy-2,2,6,6-tetramethyl-piperidin-4-ol

Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	256
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	21.400



BRUKER BIOSPIN

Current Data Parameters
NAME 20060328-4-26
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060328
Time 17.27
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 40.3
DW 60.800 usec
DE 7.50 usec
TE 297.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 -2.00 dB
SFO1 400.1324008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

AD_C13PD2k CDCl3 x

BRUKER BIOSPIN

Current Data Parameters
NAME 20060328-4-26
EXPNO 2
PROCNO 1

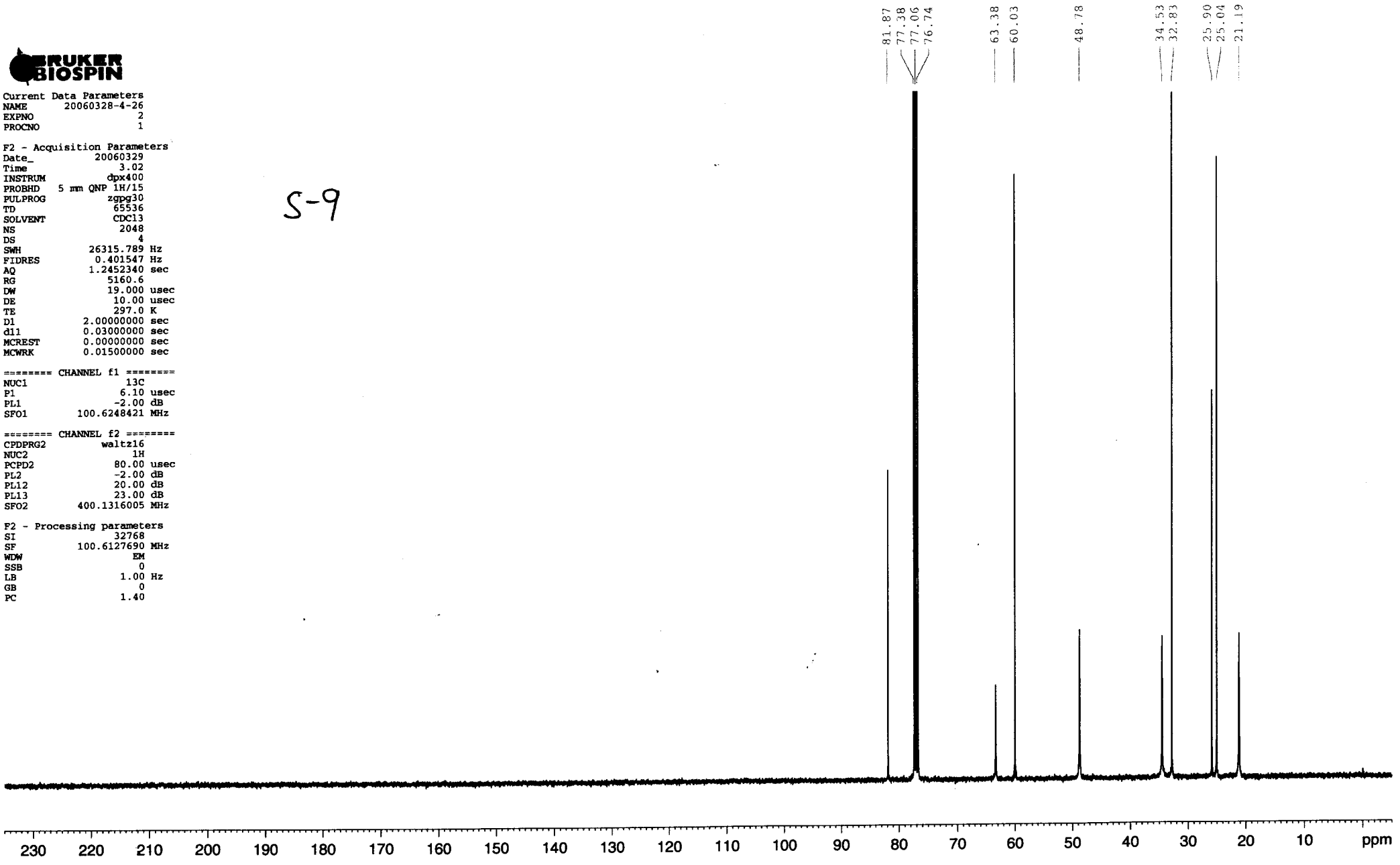
F2 - Acquisition Parameters
Date_ 20060329
Time 3.02
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 5160.6
DW 19.000 usec
DE 10.00 usec
TE 297.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

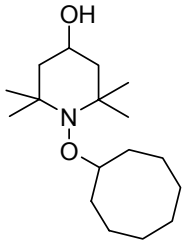
======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 dB
PL13 23.00 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

S-9

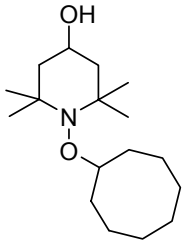




^{1}H-NMR

S-10: 1-Cyclooctyloxy-2,2,6,6-tetramethyl-piperidin-4-ol

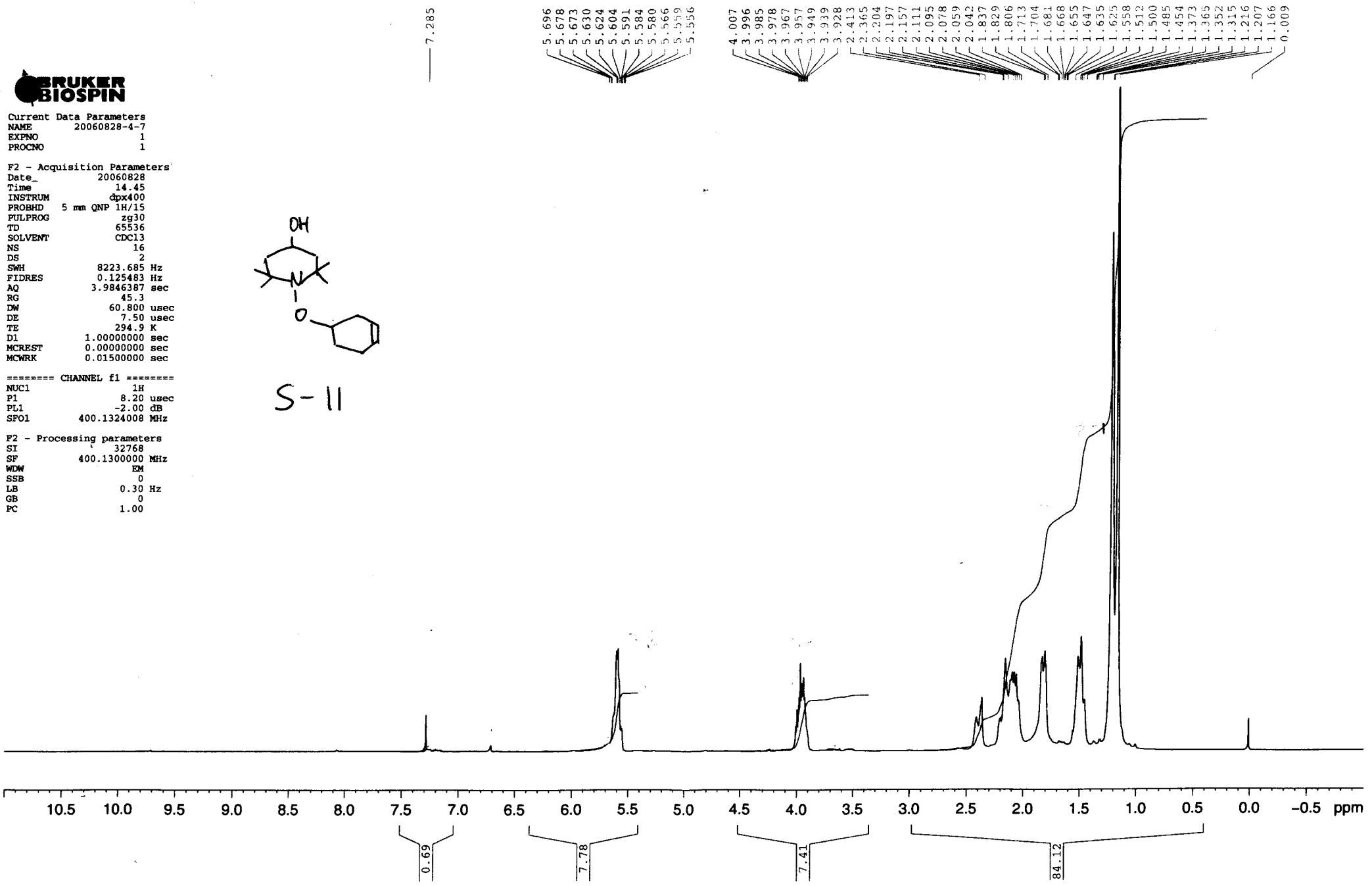
Parameter	Value
Acquisition Time (sec)	2.6542
Frequency (MHz)	300.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	6172.84
Temperature (degree C)	27.000



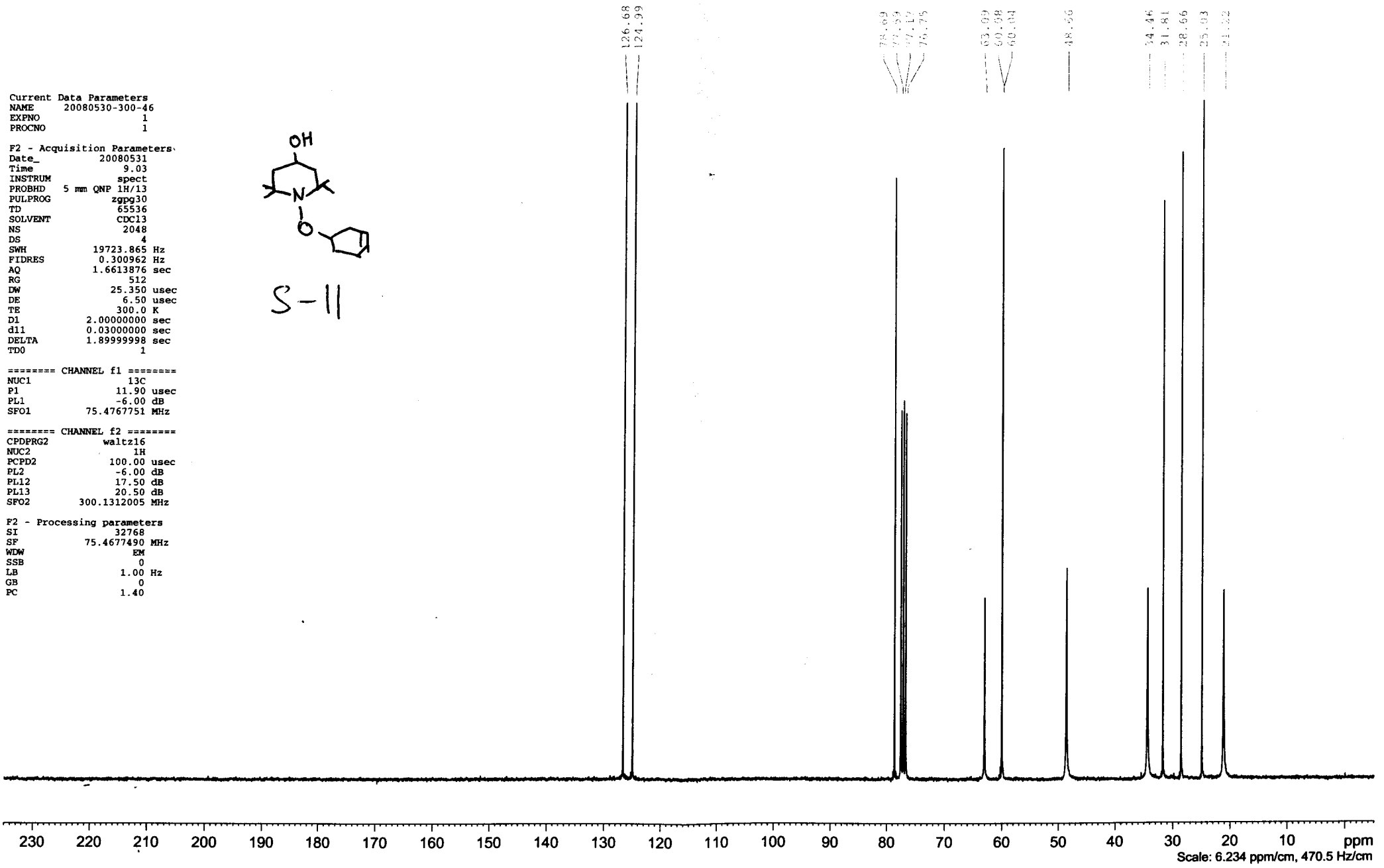
^{13}C-NMR

S-10: 1-Cyclooctyloxy-2,2,6,6-tetramethyl-piperidin-4-ol

Parameter	Value
Acquisition Time (sec)	0.8307
Frequency (MHz)	75.47
Nucleus	13C
Number of Transients	1024
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	19723.87
Temperature (degree C)	27.000


BRUKER BIOSPIN
Current Data Parameters
NAME 20060828-4-7
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060828
Time 14.45
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 45.3
DW 60.800 usec
DE 7.50 usec
TE 294.9 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 -2.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
O
S-11
7.285
5.696
5.678
5.673
5.630
5.624
5.604
5.591
5.584
5.580
5.566
5.559
5.556
4.007
3.996
3.985
3.978
3.967
3.957
3.949
3.939
3.928
2.413
2.365
2.204
2.197
2.157
2.111
2.095
2.078
2.059
2.042
1.837
1.829
1.806
1.713
1.704
1.681
1.668
1.655
1.647
1.635
1.625
1.558
1.512
1.500
1.485
1.454
1.373
1.365
1.352
1.315
1.216
1.207
1.166
0.009
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
0.69
7.78
7.41
84.12

AD_C13PD2K CDCl3 D:




```
Current Data Parameters
NAME      20080530-300-46
EXPNO                   1
PROCNO                  1

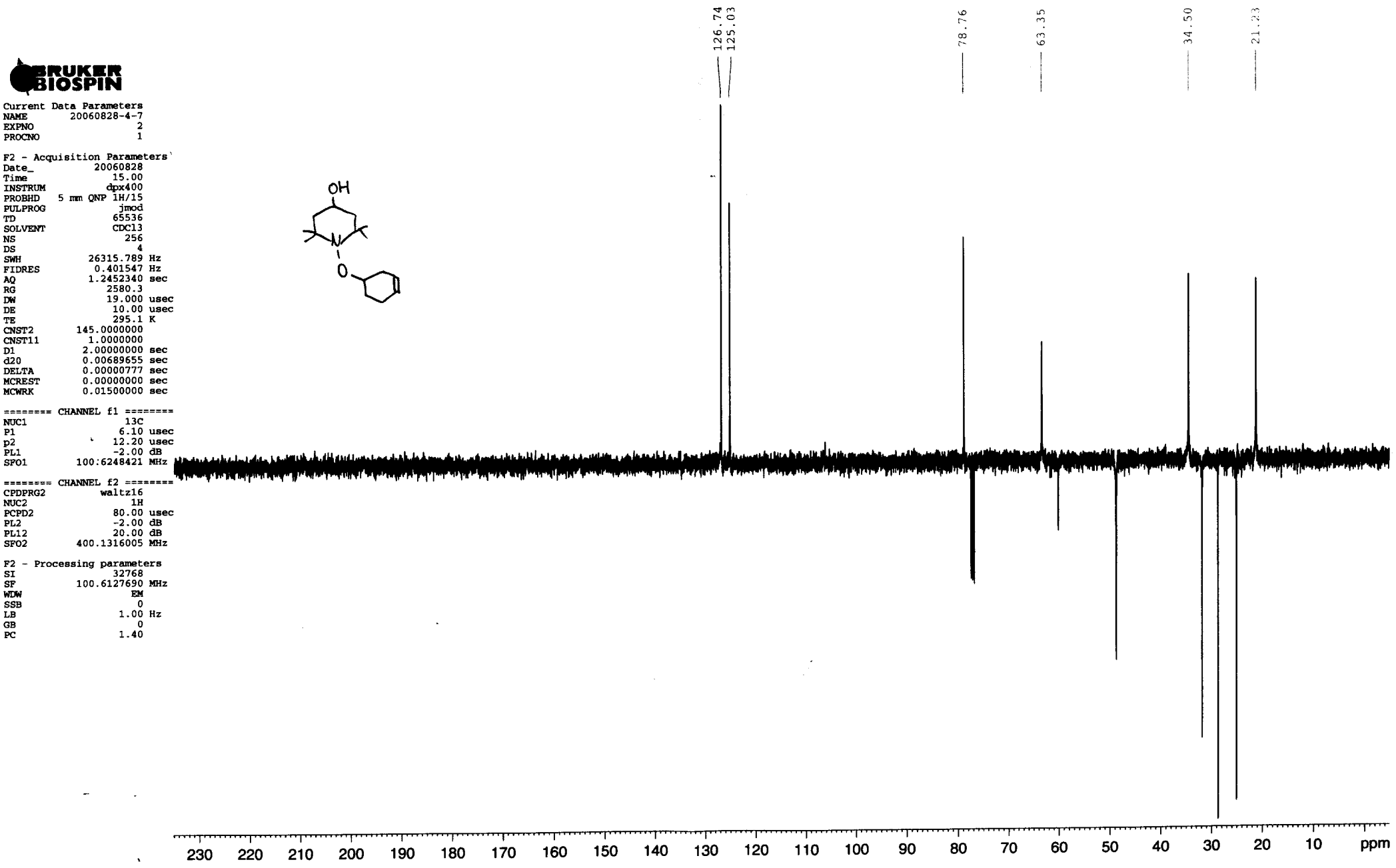
F2 - Acquisition Parameters
Date_            20080531
Time                9.03
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH           19723.865 Hz
FIDRES         0.300962 Hz
AQ            1.6613876 sec
RG                   512
DW                25.350 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.90 usec
PL1                 -6.00 dB
SFO1          75.4767751 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -6.00 dB
PL12               17.50 dB
PL13               20.50 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


S-11



BRUKER BIOSPIN

Current Data Parameters
NAME 20060828-4-7
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060828
Time 15.00
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 2580.3
DW 19.000 usec
DE 10.00 usec
TE 295.1 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00000777 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
p2 12.20 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 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

AD_PROT16 CDCl3 D:

Ciba

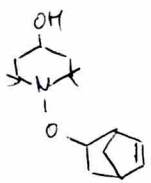
BRUKER dpx 300

```
Current Data Parameters
NAME      20081003-300-25
EXPNO                   1
PROCNO                  1

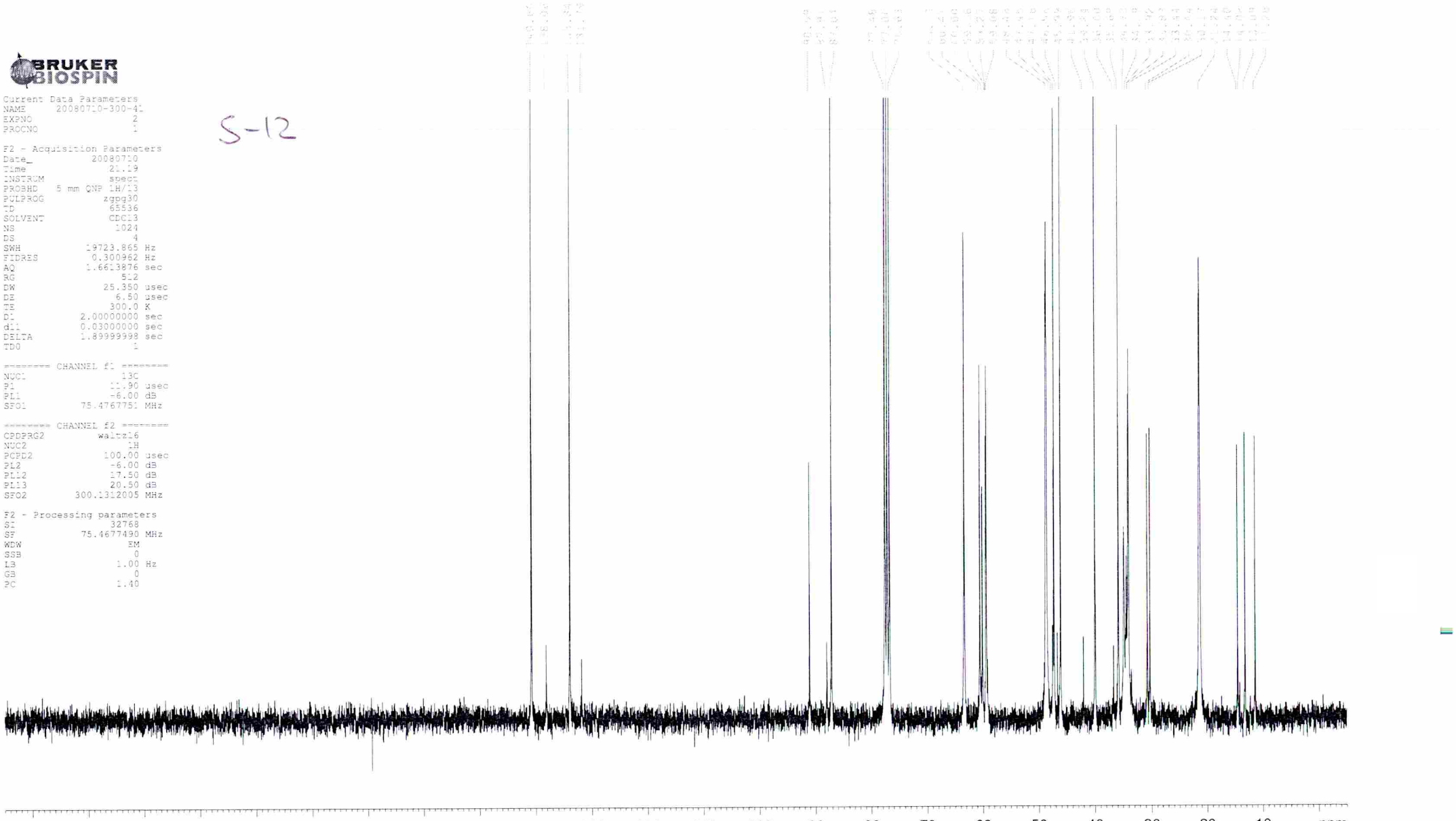
F2 - Acquisition Parameters
Date_           20081003
Time               14.39
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                 228.1
DW                81.000 usec
DE                 6.50 usec
TE                300.0 K
D1             1.00000000 sec
TD0                    1

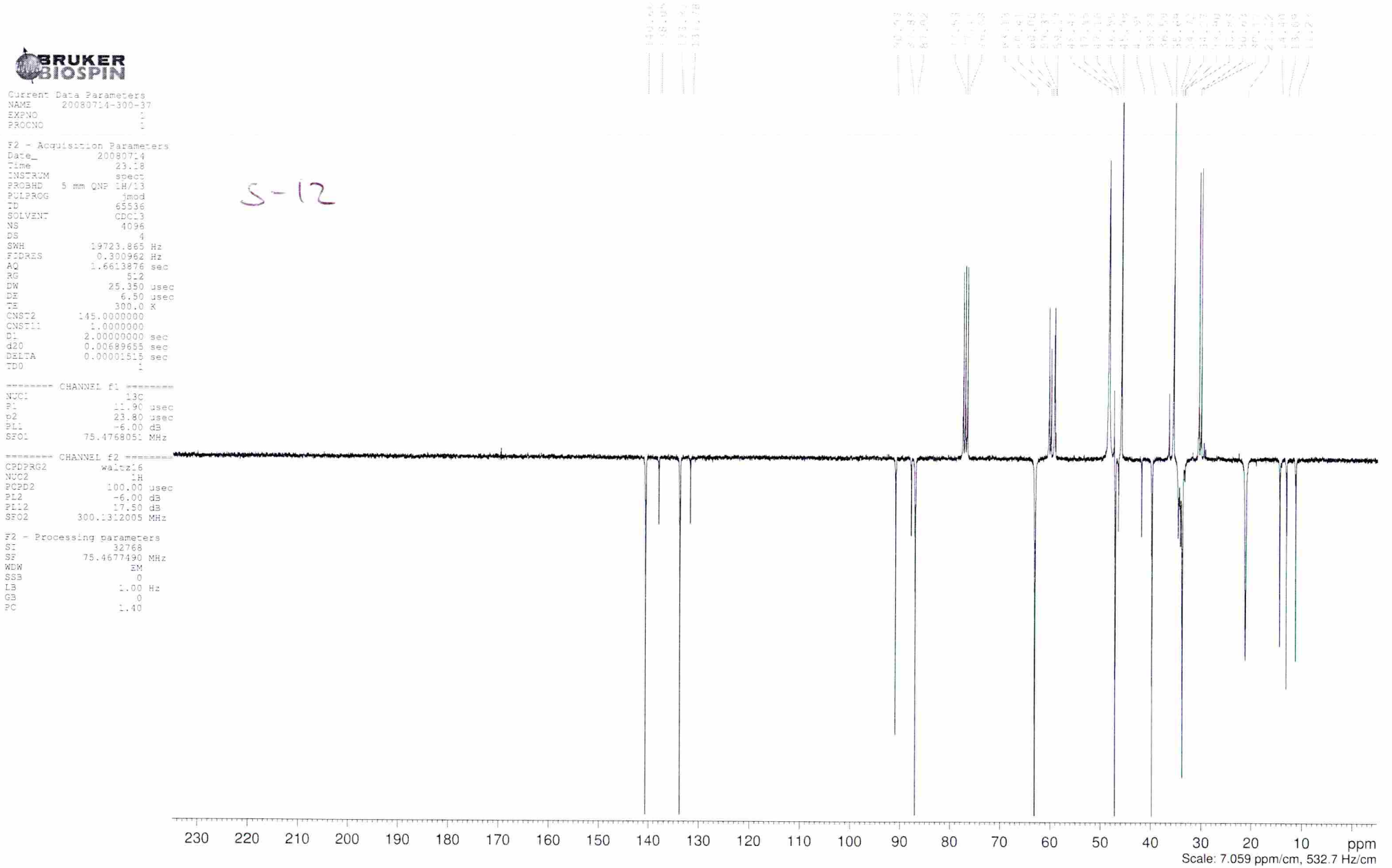
======== CHANNEL f1 ========
NUC1                  1H
P1                 8.30 usec
PL1               -6.00 dB
SFO1         300.1318008 MHz

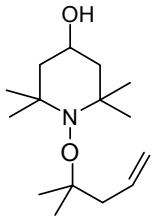
F2 - Processing parameters
SI                 32768
SF          300.1300043 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



S-12


BRUKER BIOSPIN
Current Data Parameters
NAME 20080710-300-41
EXPNO 2
PROCNO 1
S-12
F2 - Acquisition Parameters
Date_ 20080710
Time 21.19
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 19723.865 Hz
FIDRES 0.300962 Hz
AQ 1.6613876 sec
RG 512
DW 25.350 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.90 usec
PL1 -6.00 dB
SFO1 75.4767751 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 17.50 dB
PL13 20.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

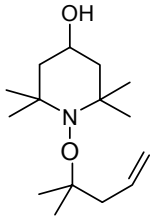

BRUKER BIOSPIN
Current Data Parameters
NAME 20080714-300-37
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080714
Time 23.18
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 4096
DS 4
SWH 19723.865 Hz
FIDRES 0.300962 Hz
AQ 1.6613876 sec
RG 512
DW 25.350 usec
DE 6.50 usec
TE 300.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001515 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.90 usec
p2 23.80 usec
PL1 -6.00 dB
SFO1 75.4768051 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
S-12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Scale: 7.059 ppm/cm, 532.7 Hz/cm



^{1}H-NMR

S-13: 1-(1,1-Dimethyl-but-3-enyloxy)-2,2,6,6-tetramethyl-piperidin-4-ol

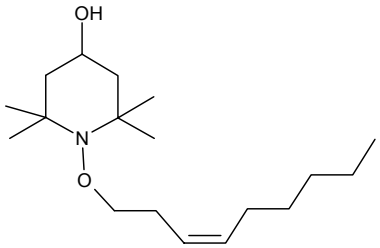
Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	22.000



^{13}C-NMR

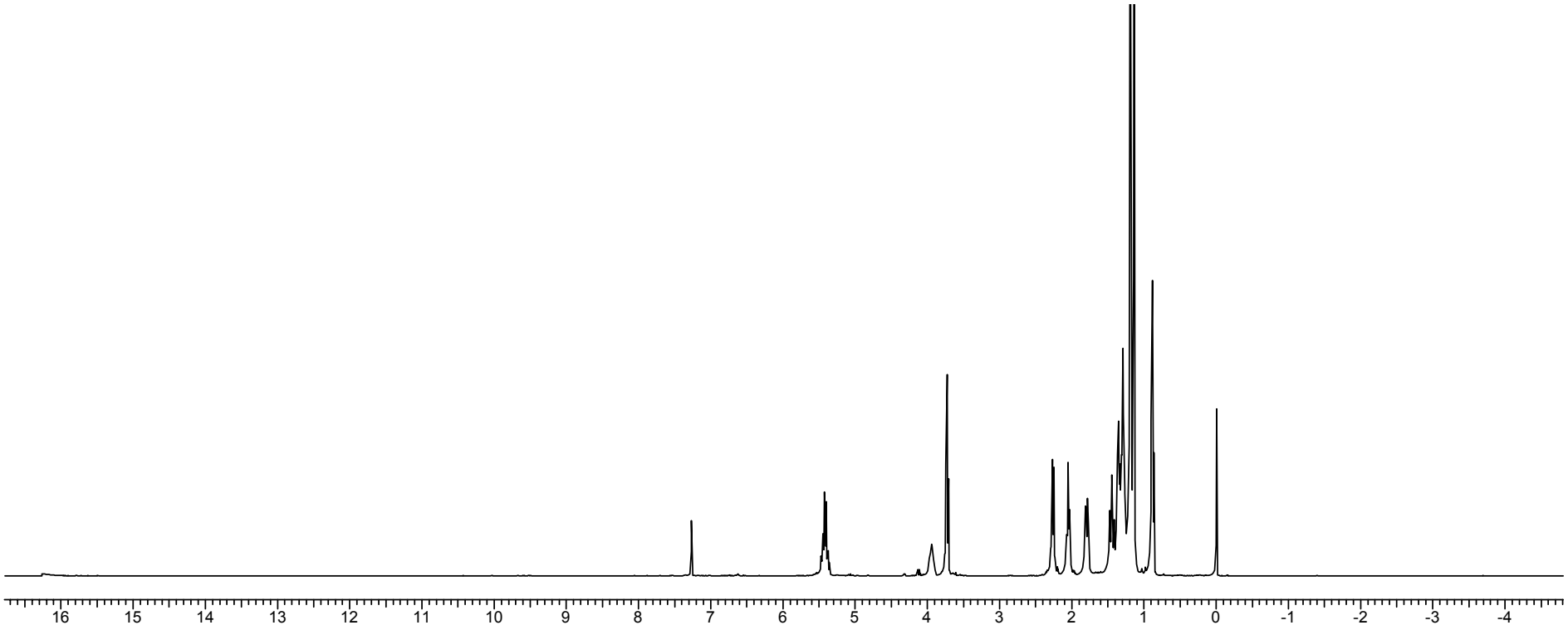
S-13: 1-(1,1-Dimethyl-but-3-enyloxy)-2,2,6,6-tetramethyl-piperidin-4-ol

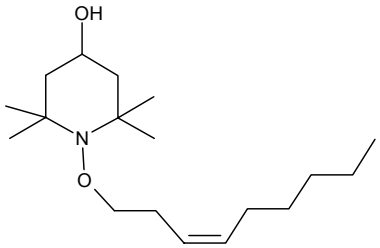
Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	1024
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	22.000



^{1}H-NMR
S-14:

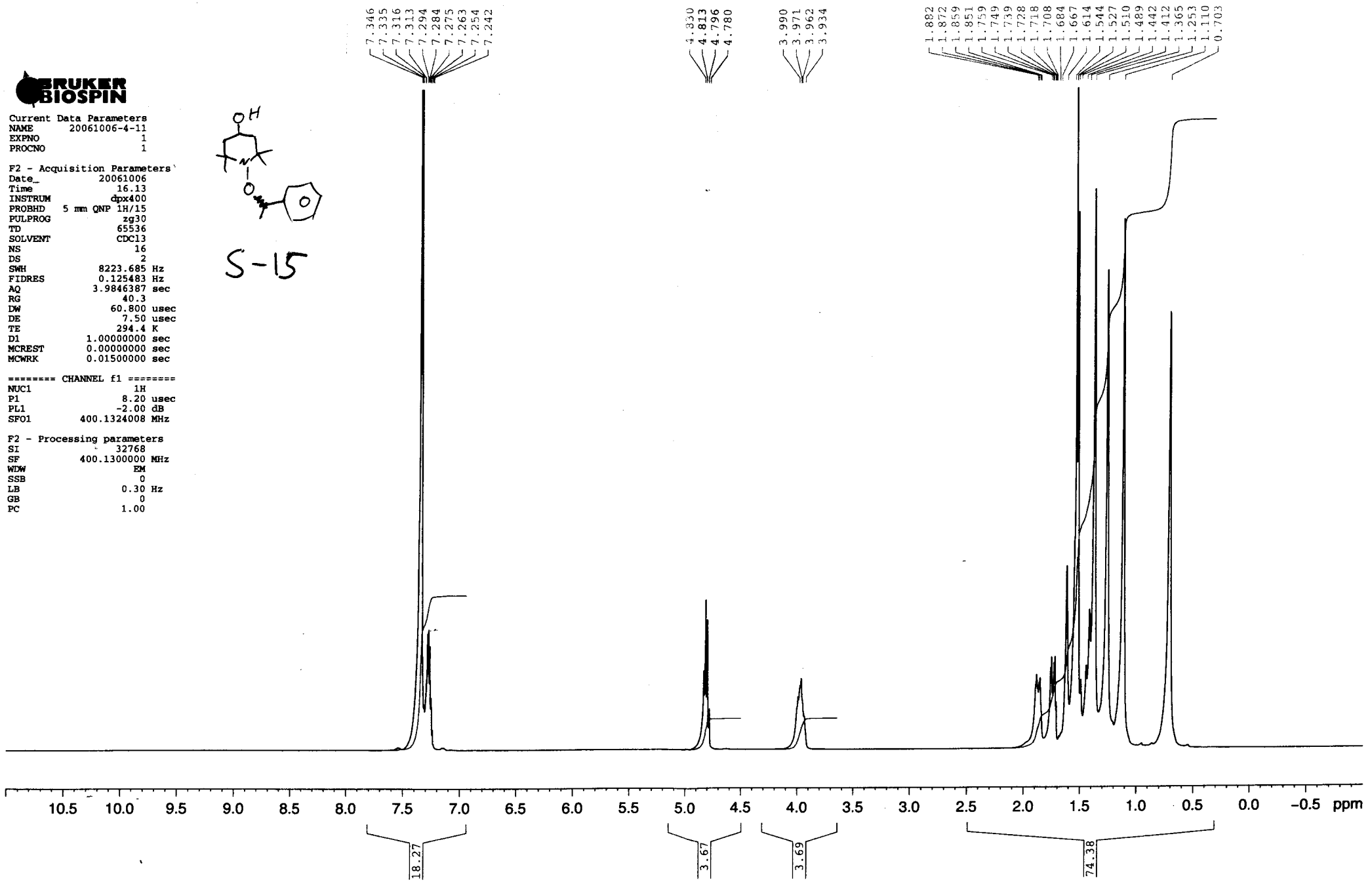
Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	22.000



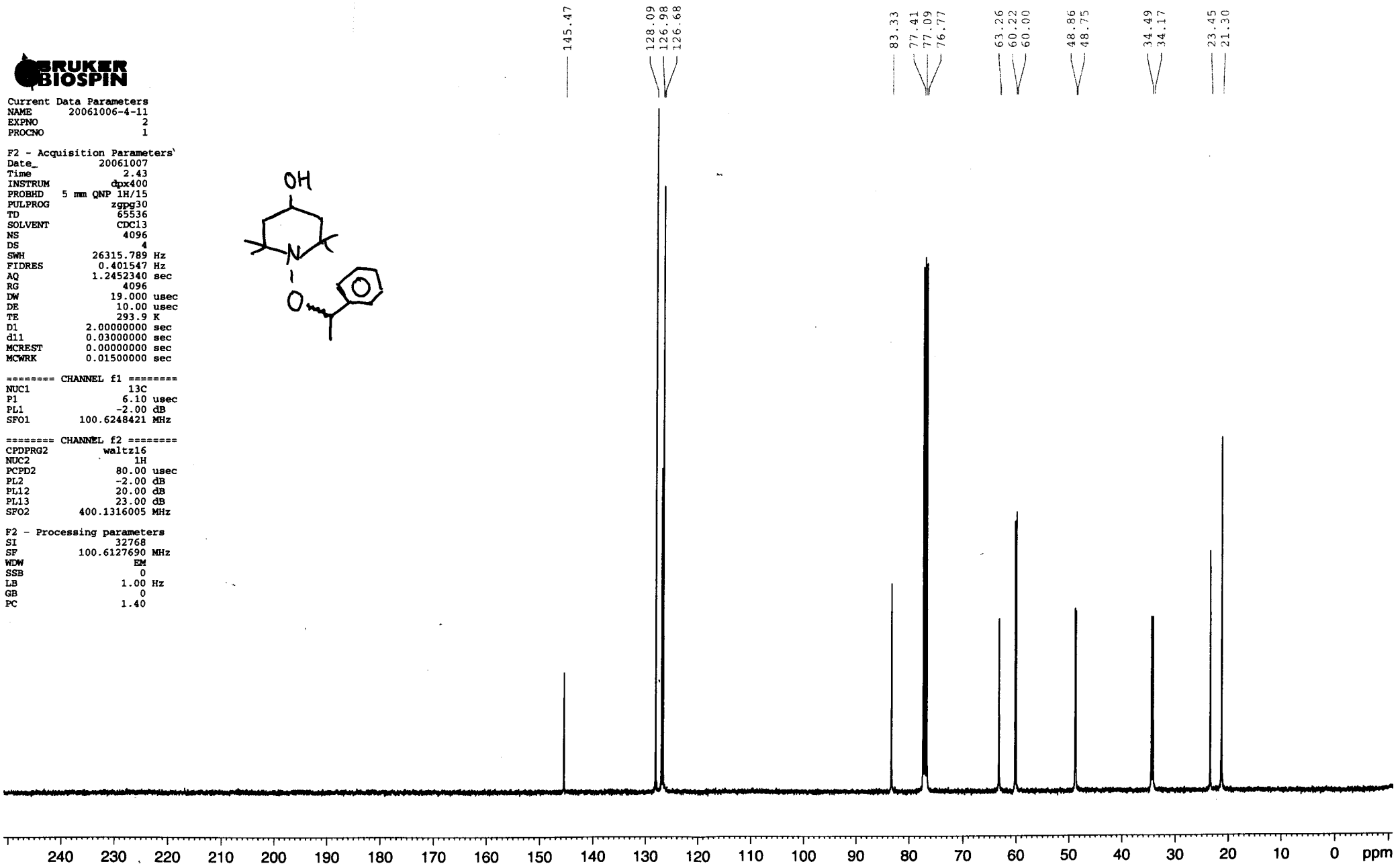


^{13}C-NMR
S-14:

Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	256
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	22.000


BRUKER BIOSPIN
Current Data Parameters
NAME 20061006-4-11
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20061006
Time 16.13
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 40.3
DW 60.800 usec
DE 7.50 usec
TE 294.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 -2.00 dB
SFO1 400.1324008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
S-15
7.346
7.335
7.316
7.313
7.294
7.284
7.275
7.263
7.254
7.242
4.830
4.813
4.796
4.780
3.990
3.971
3.962
3.934
1.882
1.872
1.859
1.851
1.759
1.749
1.739
1.728
1.718
1.708
1.684
1.667
1.614
1.544
1.527
1.510
1.489
1.442
1.412
1.365
1.253
1.110
0.703
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
18.27
3.67
3.69
74.38

p50



BRUKER BIOSPIN

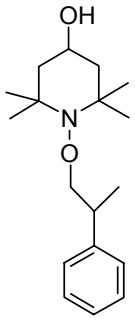
Current Data Parameters
NAME 20061006-4-11
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061007
Time 2.43
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4096
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 4096
DW 19.000 usec
DE 10.00 usec
TE 293.9 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz

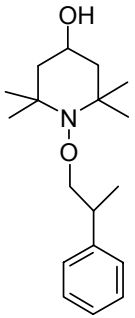
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 dB
PL13 23.00 dB
SFO2 400.1316005 MHz

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



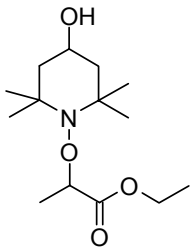
^{1}H-NMR:
S-16: 2,2,6,6-Tetramethyl-1-(2-phenyl-propoxy)-piperidin-4-ol

Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	22.000



^{13}C-NMR:
S-16: 2,2,6,6-Tetramethyl-1-(2-phenyl-propoxy)-piperidin-4-ol

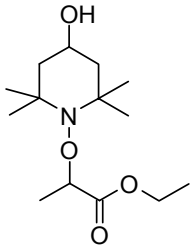
Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	256
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	22.000



^{1}H-NMR

S-17: 2-(4-Hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid ethyl ester

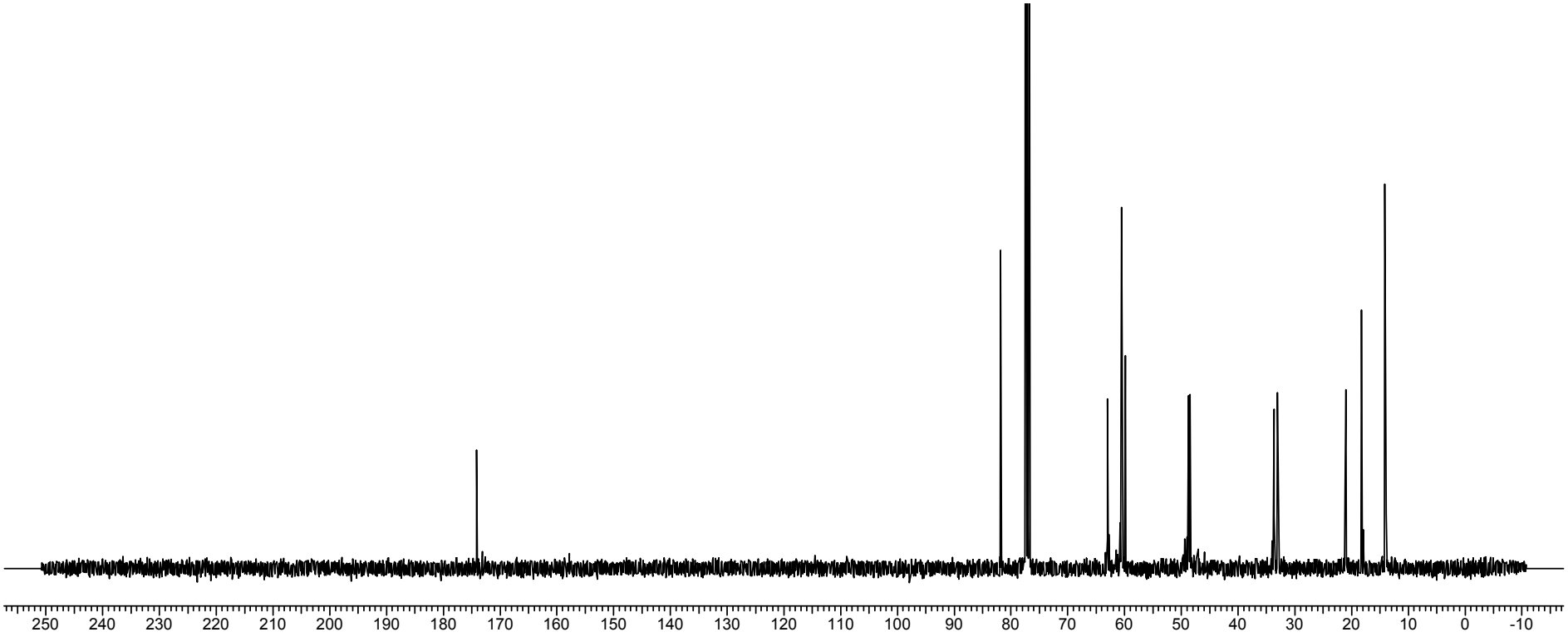
Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	21.800

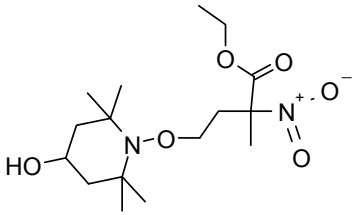


^{13}C-NMR

S-17: 2-(4-Hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid ethyl ester

Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	256
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	22.800

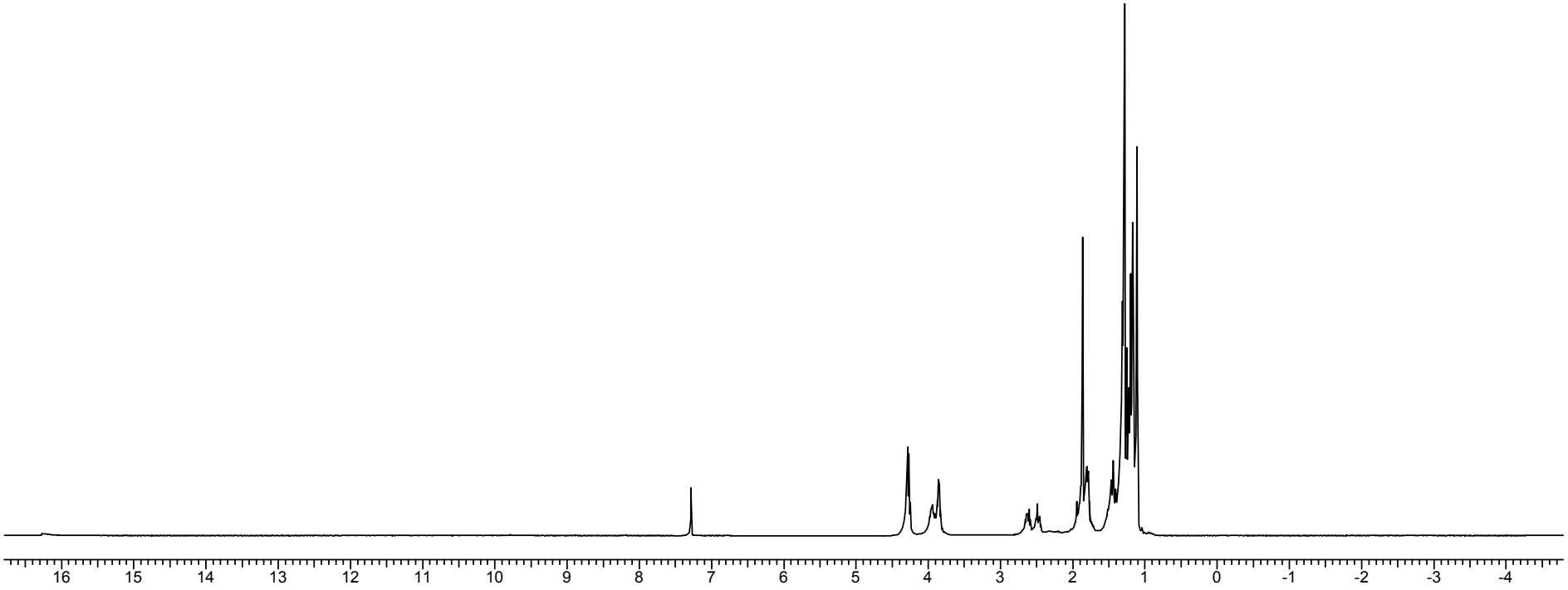


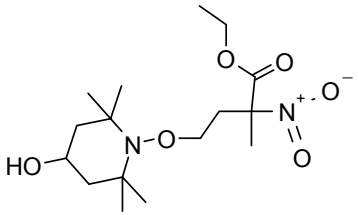


^{1}H-NMR

S-18: 4-(4-Hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxy)-2-methyl-2-nitro-butyric acid ethyl ester

Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	22.000

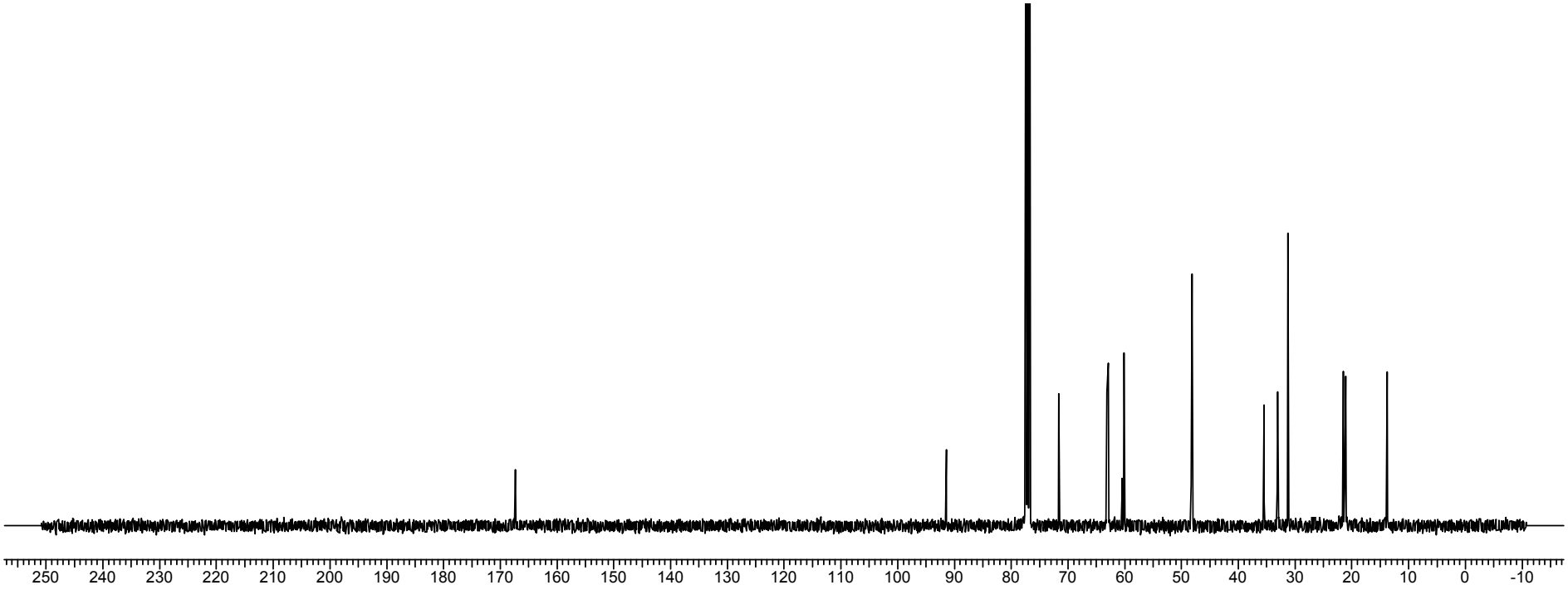




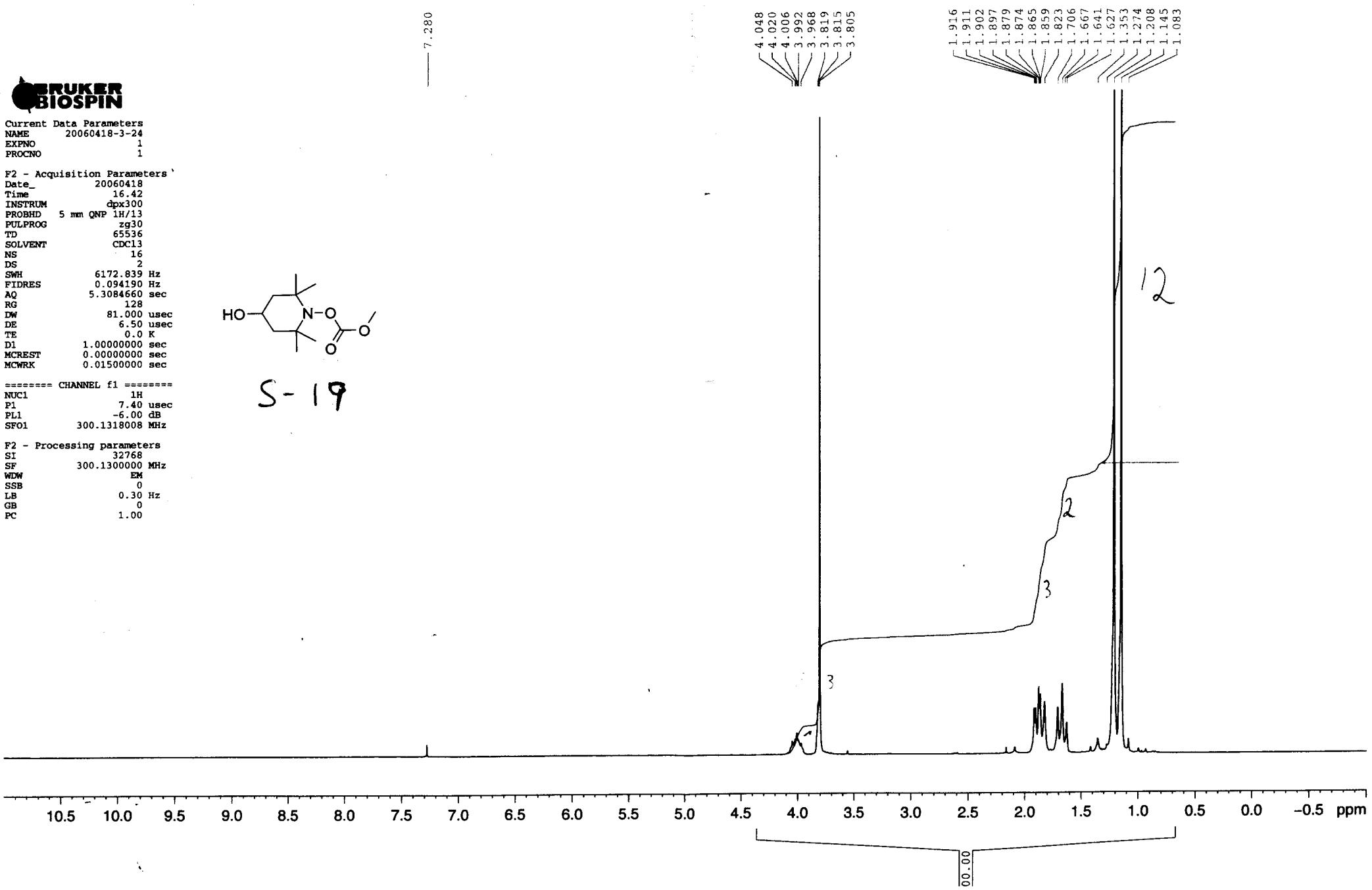
^{13}C-NMR

S-18: 4-(4-Hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxy)-2-methyl-2-nitro-butyric acid ethyl ester

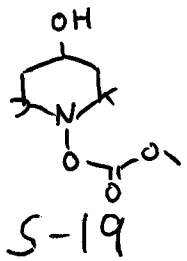
Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	1024
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	22.000



AD_PROT16 CDCl3



AD_C13PD2k CDCl3 :



BRUKER BIOSPIN

Current Data Parameters
NAME 20060418-3-24
EXPNO 2
PROCNO 1

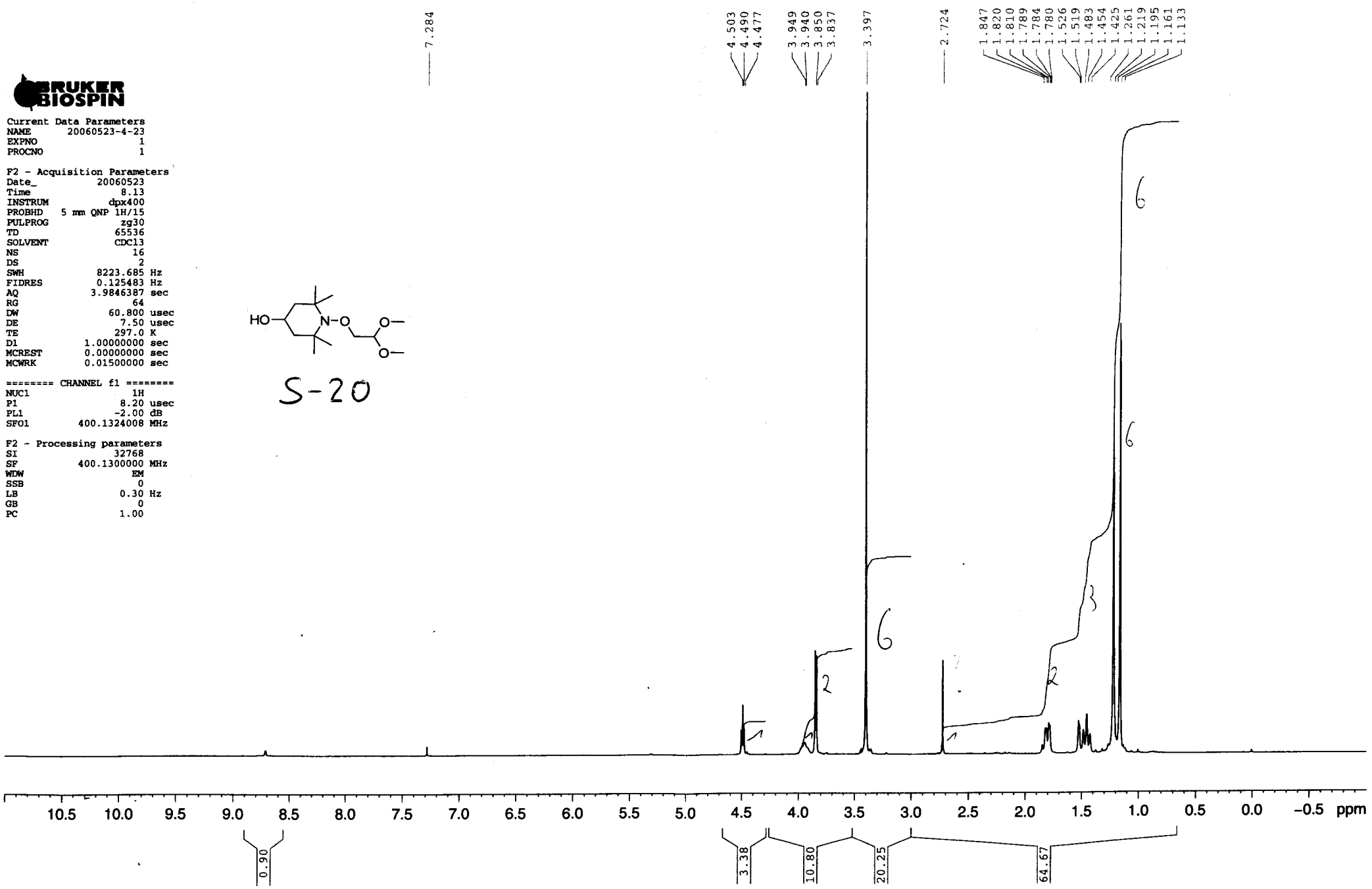
F2 - Acquisition Parameters
Date_ 20060418
Time 23.29
INSTRUM dpx300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 19723.865 Hz
FIDRES 0.300962 Hz
AQ 1.6613876 sec
RG 812.7
DW 25.350 usec
DE 6.50 usec
TE 0.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SFO1 75.4767751 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 16.70 dB
PL13 19.70 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

AD_PROT16 CDCl3 :



AD_C13PD256 CDCl3 x

BRUKER BIOSPIN

Current Data Parameters
NAME 20060523-4-23
EXPNO 2
PROCNO 1

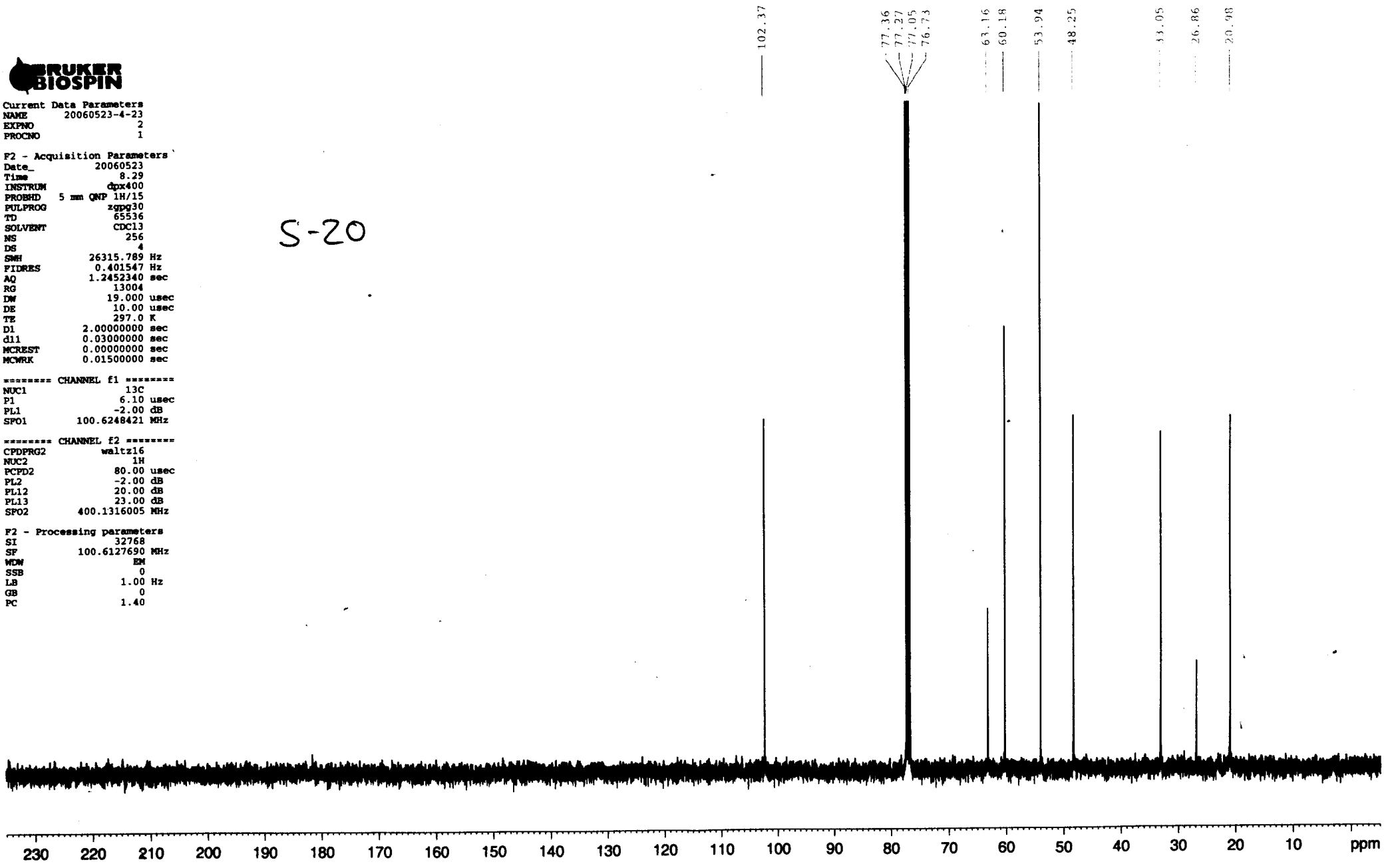
F2 - Acquisition Parameters
Date_ 20060523
Time 8.29
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 13004
DW 19.000 usec
DE 10.00 usec
TE 297.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz

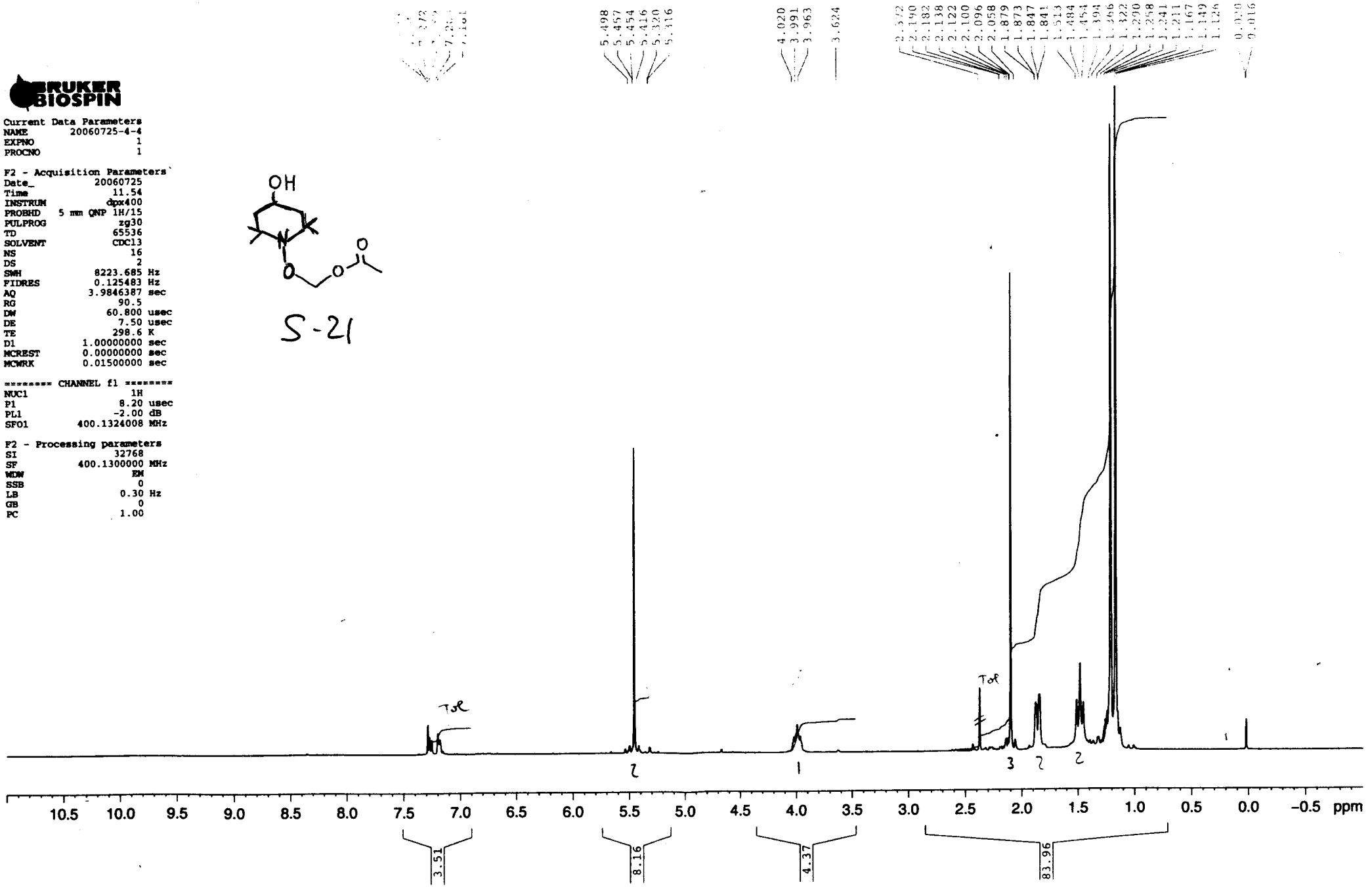
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 dB
PL13 23.00 dB
SFO2 400.1316005 MHz

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

S-20



AD_PROT16 CDCl3 x



AD_APTa CDCl3 x

BRUKER BIOSPIN

Current Data Parameters
NAME 20060725-4-7
EXPNO 1
PROCNO 1

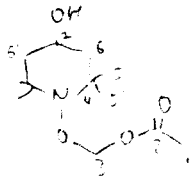
F2 - Acquisition Parameters
Date_ 20060725
Time 14.22
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 2580.3
DW 19.000 usec
DE 10.00 usec
TE 299.4 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00000777 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

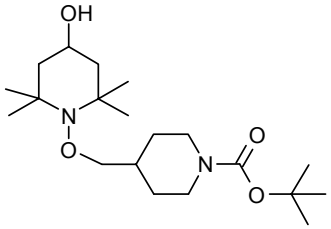
======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
p2 12.20 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 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

S-21

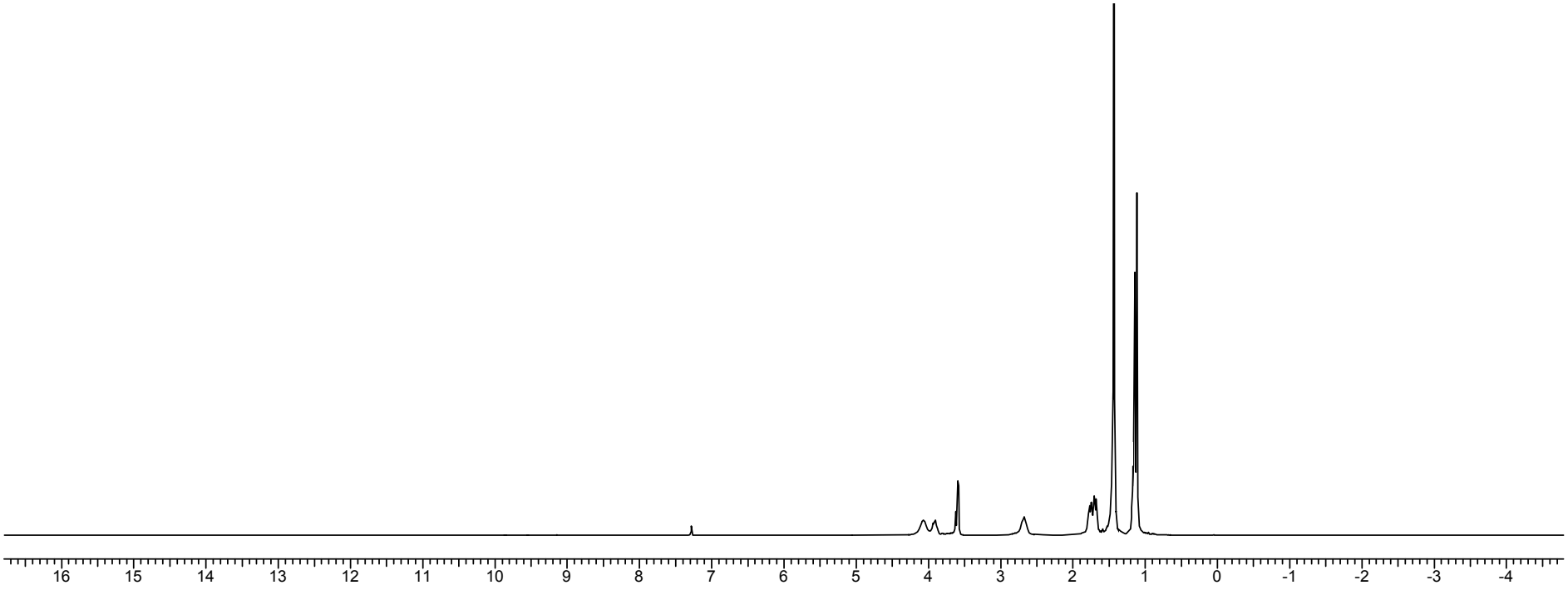


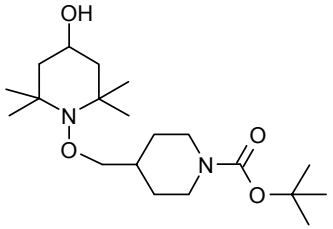


^{1}H-NMR

S-22: 4-(4-Hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxymethyl)-piperidine-1-carboxylic acid tert-butyl ester

Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	22.000

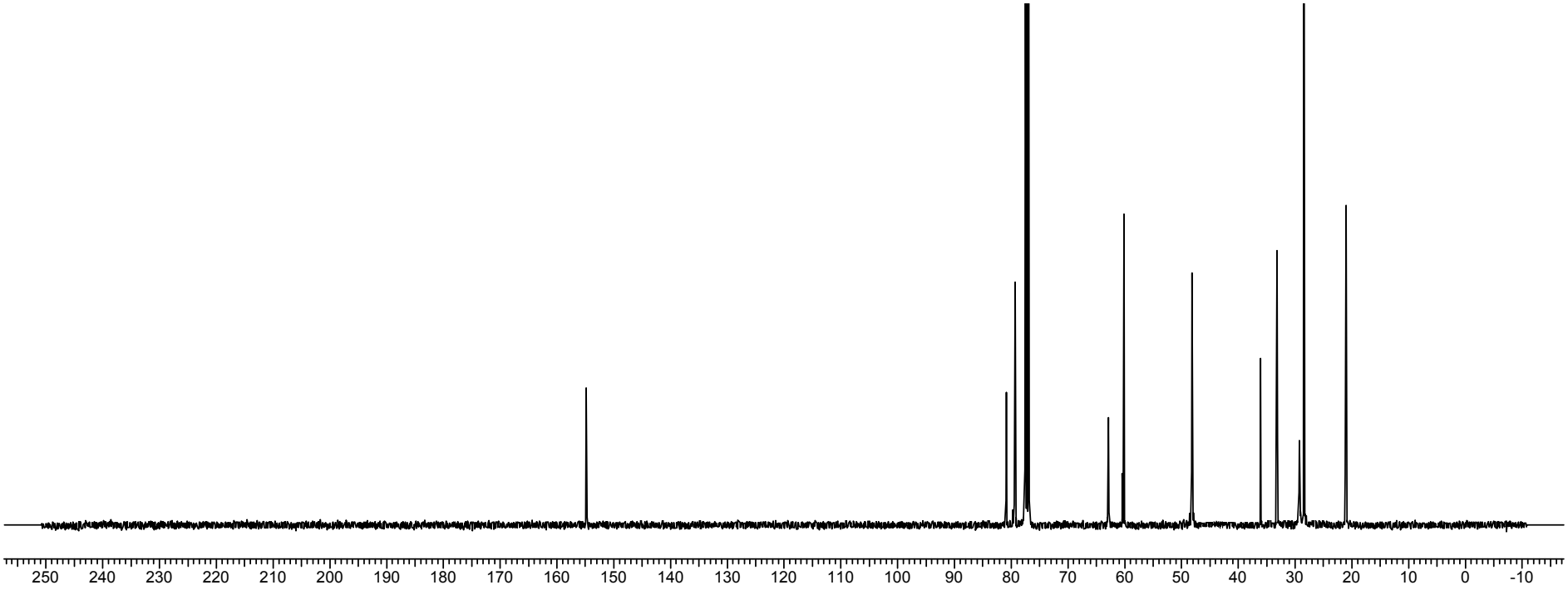


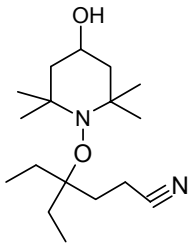


^{13}C-NMR

S-22: 4-(4-Hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxymethyl)-piperidine-1-carboxylic acid tert-butyl ester

Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	1024
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	22.000

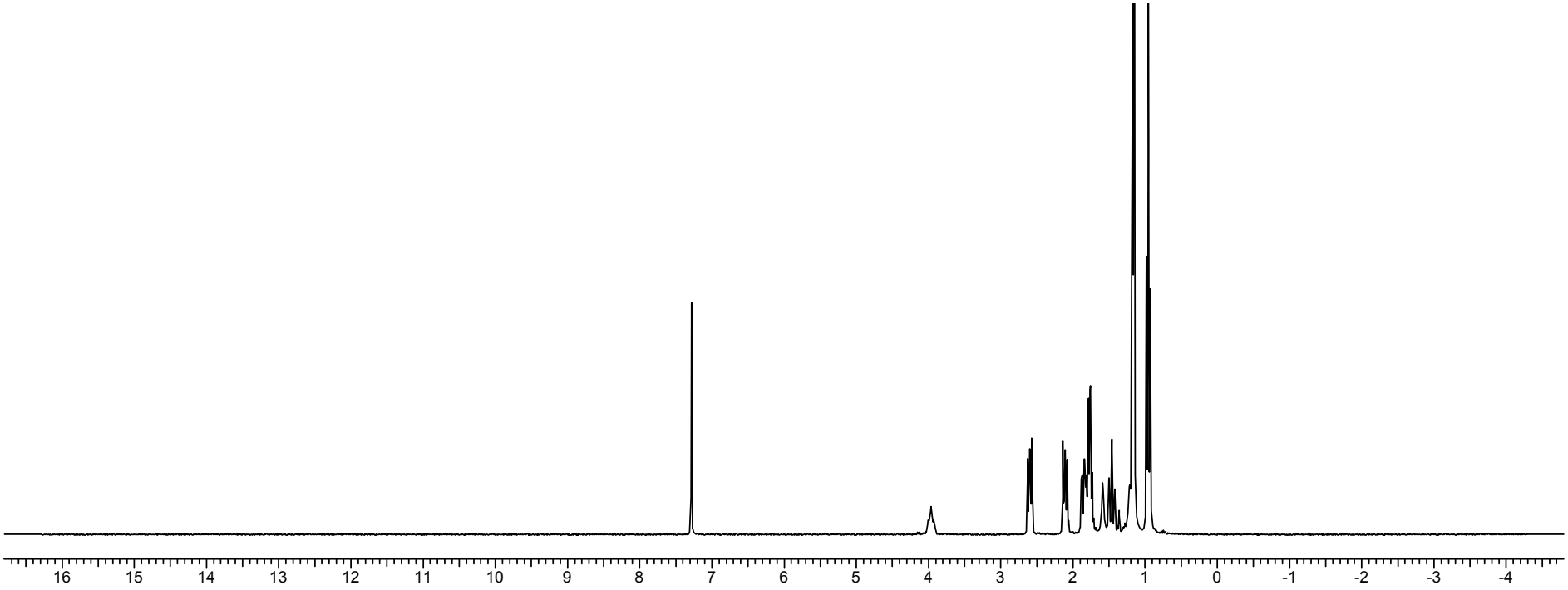


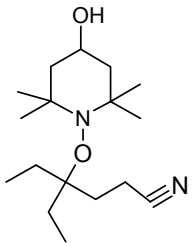


^{1}H-NMR

S-23: 4-Ethyl-4-(4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxy)-hexanenitrile

Parameter	Value
Acquisition Time (sec)	2.6542
Frequency (MHz)	300.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	6172.84
Temperature (degree C)	27.000

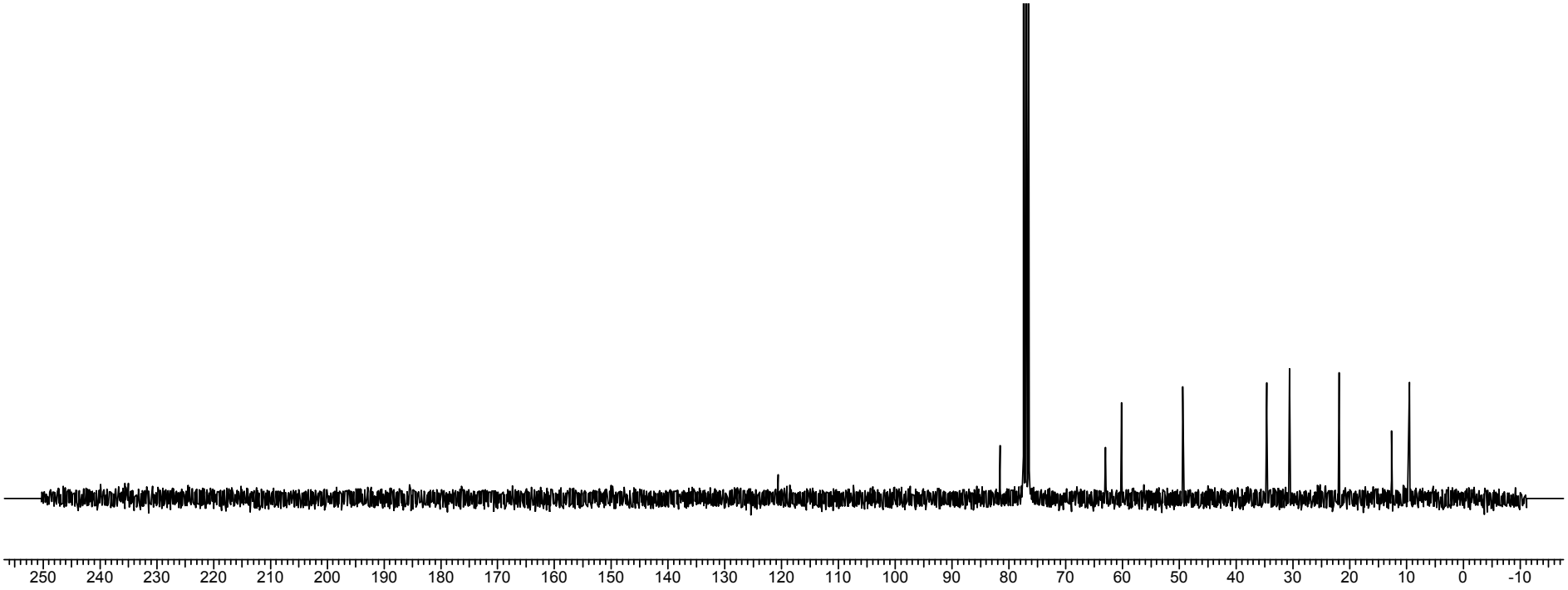


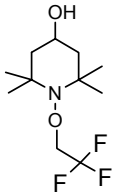


^{13}C-NMR

S-23: 4-Ethyl-4-(4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-yloxy)-hexanenitrile

Parameter	Value
Acquisition Time (sec)	0.8307
Frequency (MHz)	75.47
Nucleus	13C
Number of Transients	1024
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	19723.87
Temperature (degree C)	27.000

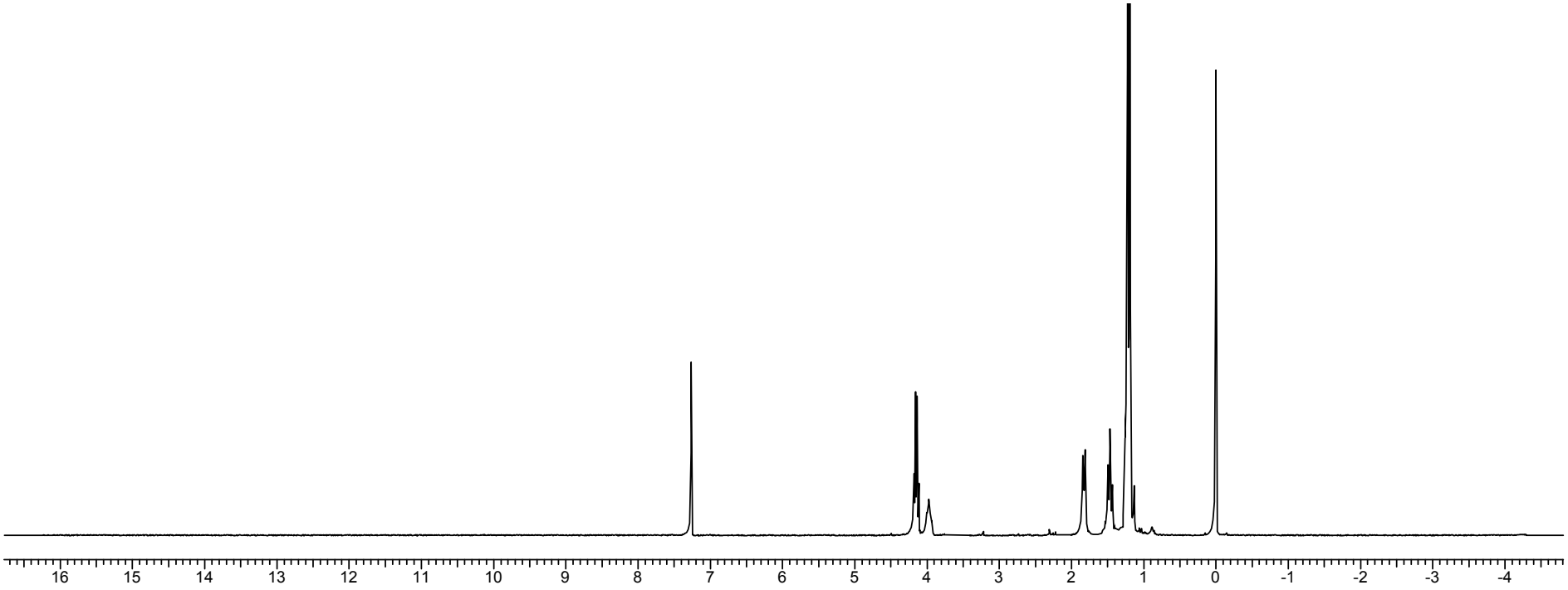


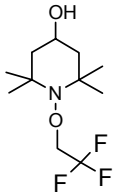


^{1}H-NMR

S-24: 2,2,6,6-Tetramethyl-1-(2,2,2-trifluoro-ethoxy)-piperidin-4-ol

Parameter	Value
Acquisition Time (sec)	1.9923
Frequency (MHz)	400.13
Nucleus	1H
Number of Transients	16
Original Points Count	32768
Points Count	32768
Pulse Sequence	zg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	8223.68
Temperature (degree C)	22.000

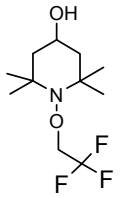




^{13}C-NMR

S-24: 2,2,6,6-Tetramethyl-1-(2,2,2-trifluoro-ethoxy)-piperidin-4-ol

Parameter	Value
Acquisition Time (sec)	0.6226
Frequency (MHz)	100.61
Nucleus	13C
Number of Transients	256
Original Points Count	32768
Points Count	32768
Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D
Sweep Width (Hz)	26315.79
Temperature (degree C)	22.000

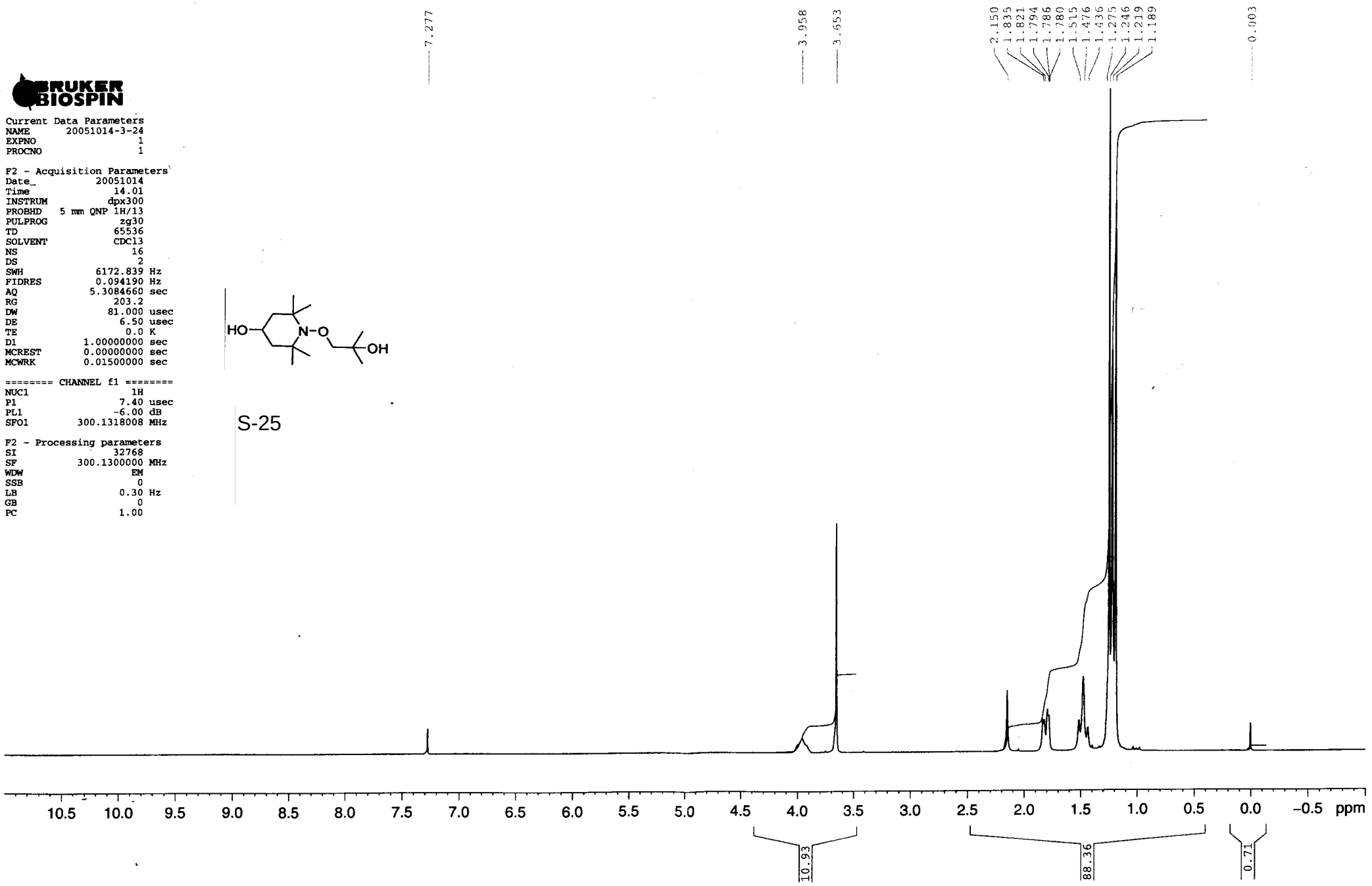


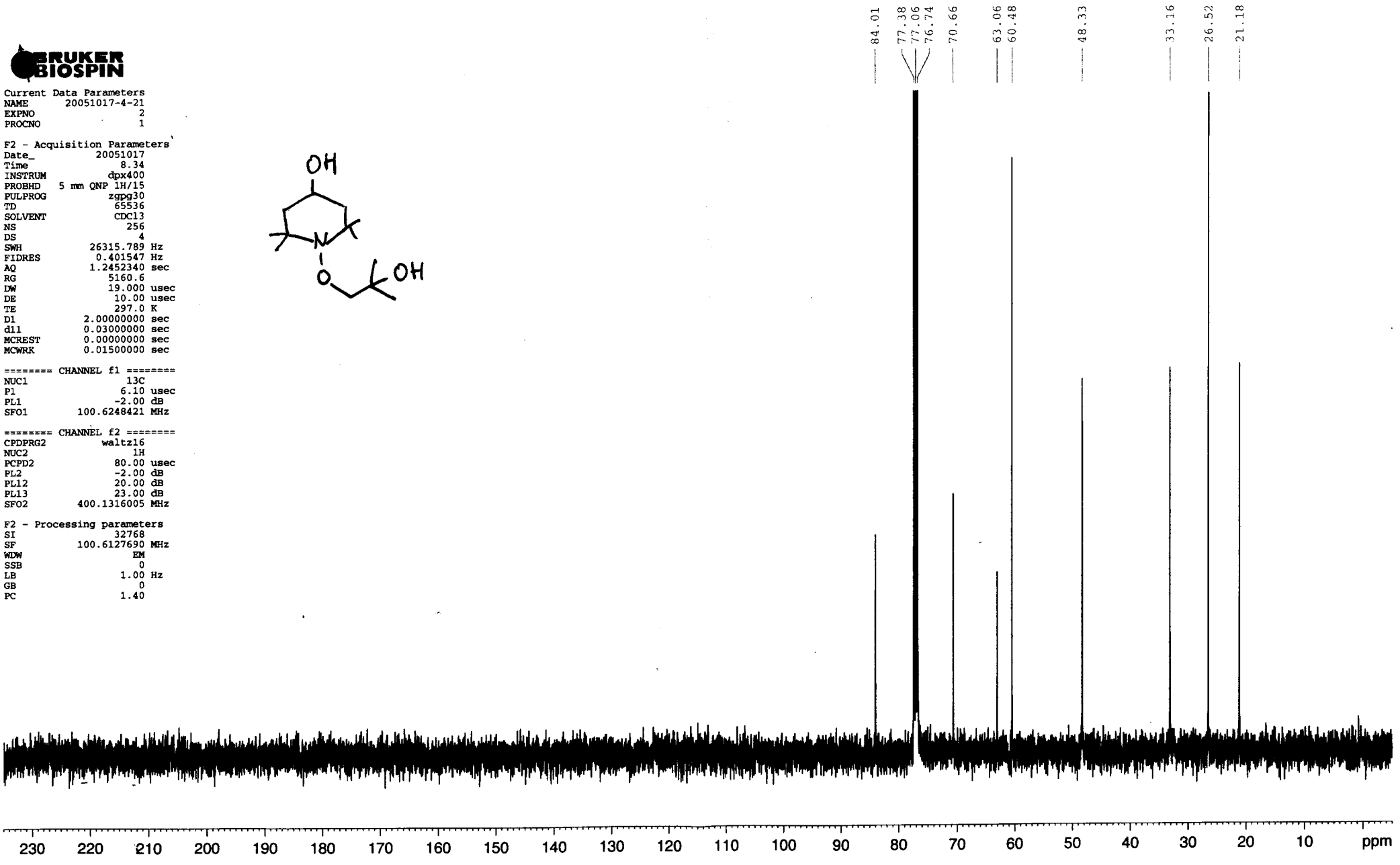
^{19}F-NMR

S-24: 2,2,6,6-Tetramethyl-1-(2,2,2-trifluoro-ethoxy)-piperidin-4-ol

(Reference: CF_3COOH: $\delta = -76$ ppm)

Parameter	Value
Acquisition Time (sec)	0.4456
Frequency (MHz)	282.40
Nucleus	19F
Number of Transients	32
Original Points Count	65536
Points Count	65536
Pulse Sequence	zgfhigqn
Solvent	CHLOROFORM-D
Sweep Width (Hz)	73529.41
Temperature (degree C)	27.000


7.277
3.958
3.653
2.150
1.835
1.821
1.794
1.786
1.780
1.515
1.476
1.436
1.275
1.246
1.219
1.189
0.003
BRUKER BIOSPIN
Current Data Parameters
NAME 20051014-3-24
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051014
Time 14.01
INSTRUM dpx300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 203.2
DW 81.000 usec
DE 6.50 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.40 usec
PL1 -6.00 dB
SFO1 300.1318008 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
N-O
OH
S-25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
10.93
88.36
0.71


BRUKER BIOSPIN
Current Data Parameters
NAME 20051017-4-21
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051017
Time 8.34
INSTRUM dpx400
PROBHD 5 mm QNP 1H/15
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 5160.6
DW 19.000 usec
DE 10.00 usec
TE 297.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 6.10 usec
PL1 -2.00 dB
SFO1 100.6248421 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 20.00 dB
PL13 23.00 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
OH
N
O
OH
84.01
77.38
77.06
76.74
70.66
63.06
60.48
48.33
33.16
26.52
21.18
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

AD_PROT16 MeOD D:

p72

Ciba

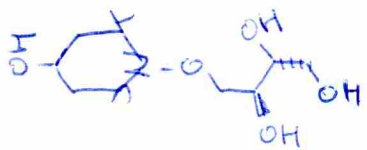
dpx 300

```
Current Data Parameters
NAME      20080807-300-21
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20080807
Time               17.04
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                 228.1
DW                81.000 usec
DE                 6.50 usec
TE                300.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.30 usec
PL1                -6.00 dB
SFO1         300.1318008 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



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AD_C13PD4k MeOD I

```
Current Data Parameters
NAME      20080807-300-15
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20080807
Time               23.18
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                  4096
DS                     4
SWH           19723.865 Hz
FIDRES         0.300962 Hz
AQ            1.6613876 sec
RG                   512
DW              25.350 usec
DE               6.50 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.90 usec
PL1                -6.00 dB
SFO1         75.4767751 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -6.00 dB
PL12               17.50 dB
PL13               20.50 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4676418 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

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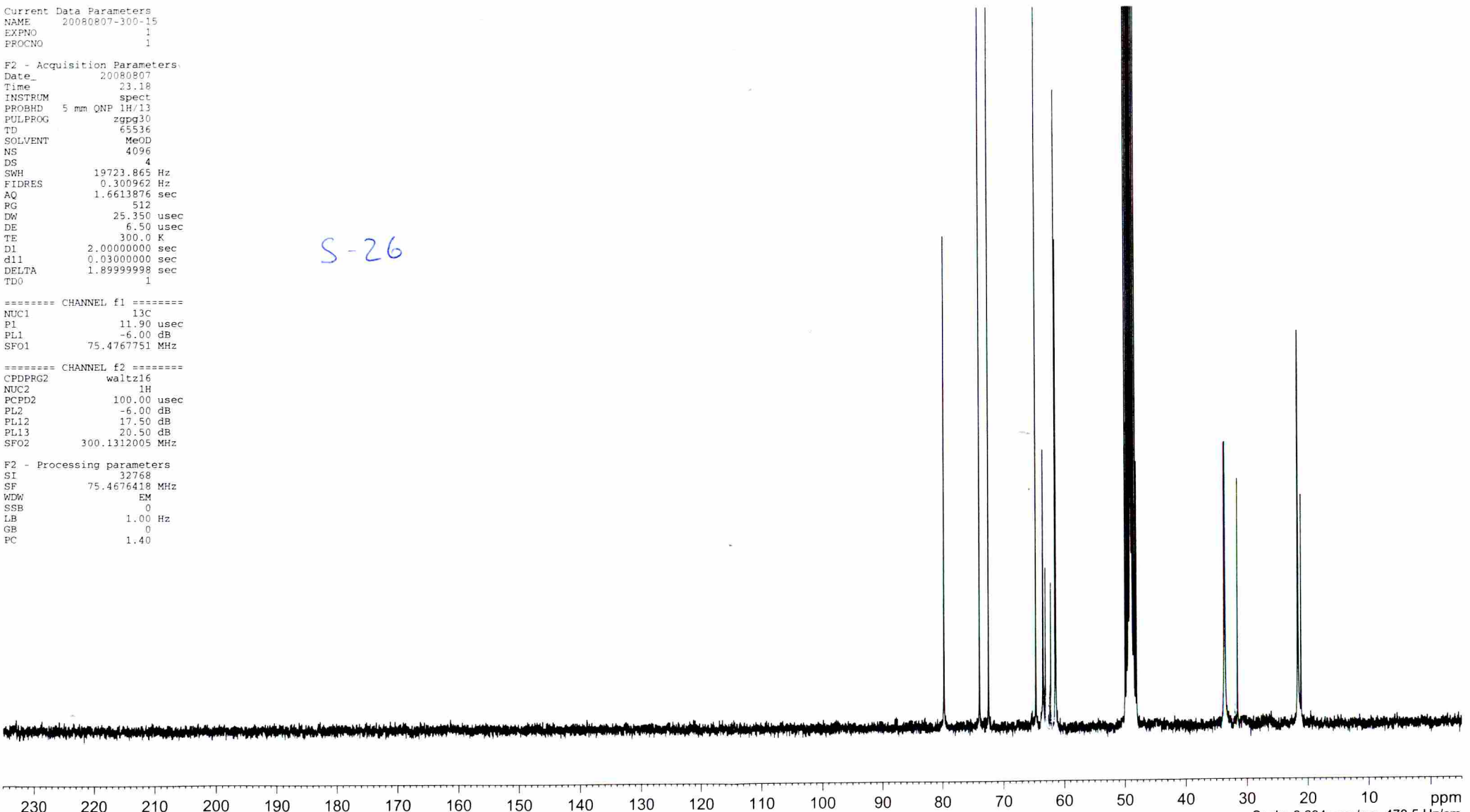


AD_PROT16 DMSO ›

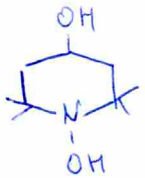
BRUKER BIOSPIN

Current Data Parameters
NAME 20050826-3-11
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050826
Time 10.29
INSTRUM dpx300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 287.4
DW 81.000 usec
DE 6.50 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.40 usec
PL1 -6.00 dB
SFO1 300.1318008 MHz

F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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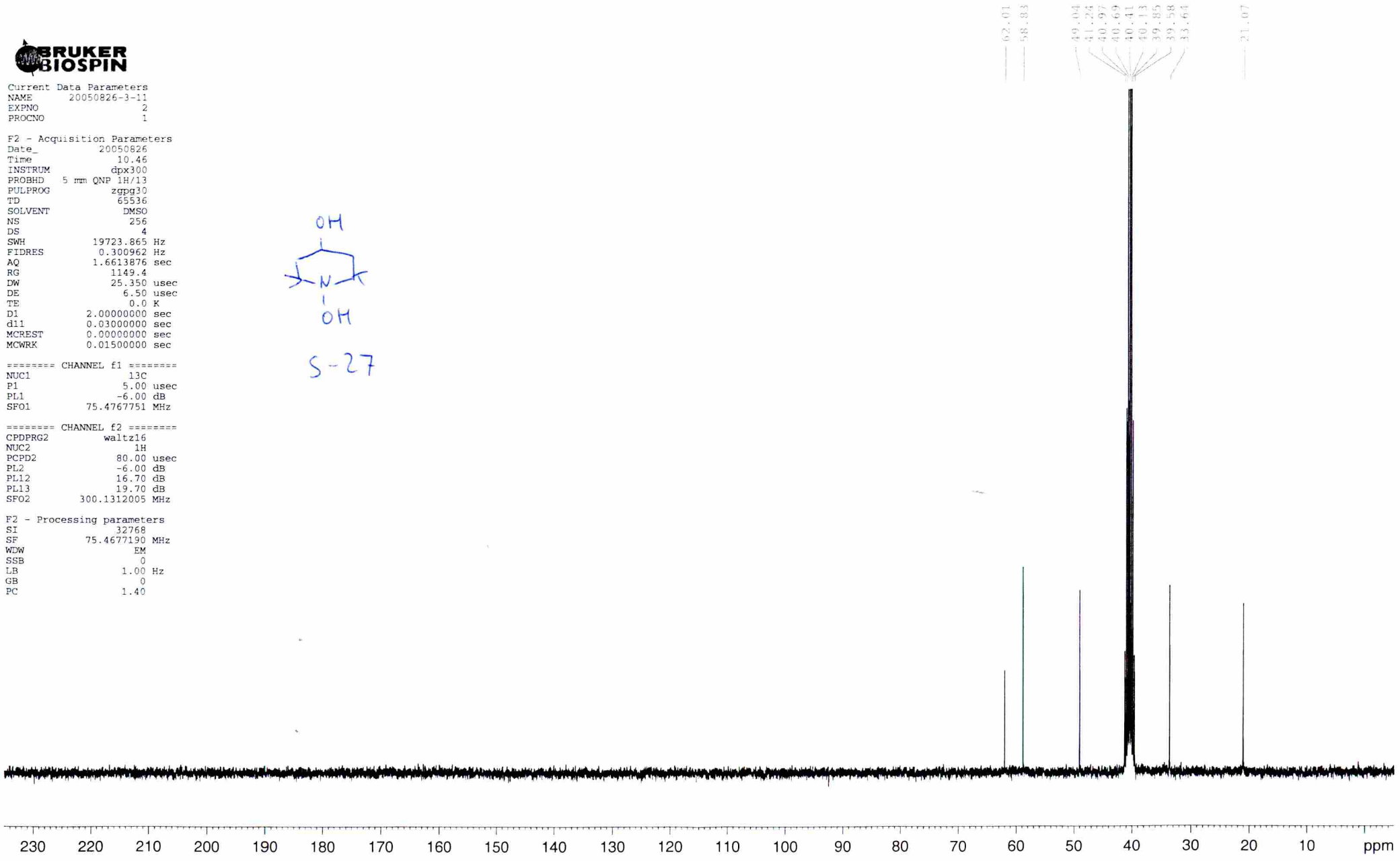
BRUKER BIOSPIN
Current Data Parameters
NAME 20050826-3-11
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050826
Time 10.46
INSTRUM dpx300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 256
DS 4
SWH 19723.865 Hz
FIDRES 0.300962 Hz
AQ 1.6613876 sec
RG 1149.4
DW 25.350 usec
DE 6.50 usec
TE 0.0 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SFO1 75.4767751 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 16.70 dB
PL13 19.70 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OH
N
OH
S-27
62.01
58.83
49.04
41.24
40.97
40.69
40.41
40.13
39.85
39.58
33.61
21.07
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm