Supporting Information

Ring-opening of 1,5-Dioxaspiro[3.2]hexanes: Selective Preparation of α-Heterofunctionalized-β'-hydroxy Ketones or 2,2-Disubstituted Oxetanes

Amy R. Howell* and Albert J. Ndakala

Department of Chemistry, University of Connecticut, Storrs, CT 06269-3060

Experimental section

General experimental. Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Methylene chloride was distilled from calcium hydride, while $CDCl_3$ was dried over 3Å molecular sieves. All reagents were purchased from Aldrich and used without further purification. 3-Phenyl-1,5-dioxaspiro[3.2]hexane (**1a**), 3-(2-*t*-butyldiphenylsilyoxyethyl)-2,2-dimethyl-1,5-dioxaspiro[3.2]hexane (**1b**), (S)-(N-*t*-butoxycarbonyl)-3-amino-1,5-dioxaspiro[3.2]hexane (**1c**), 3-methyl-3-phenyl-1,5-dioxaspiro[3.2]hexane (**1d**), and 3-allyl-3-phenyl-1,5-dioxaspiro[3.2]hexane (**1e**) were prepared as described in the literature.[1]

1,4-Dihydroxy-3-phenylbutan-2-one (2a). A solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (0.16 g, 0.99 mmol) in a mixture of THF (4 mL) and H_2O (0.5 mL) was stirred at RT for 2 d. The reaction mixture was diluted with $CHCl_3$ (15 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc 7:3 to 1:1). A white solid (0.11 g, 61%) was obtained. Recrystallization from EtOAc/petroleum ether yielded white, needle-like crystals: mp 73-74 °C; IR ($CDCl_3$) 3466, 3066, 2933, 1722, 1602, 1494, 1451, 1274, 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.23 (m, 2H), 4.26 (dd, J = 11.0, 8.6 Hz, 1H), 4.25 (s, 2H), 3.95 (dd, J = 8.6, 5.1 Hz, 1H), 3.83 (dd, J = 11.0,

5.1 Hz, 1H), 2.90 (br, 1H), 2.05 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 134.4, 129.3, 128.4, 128.3, 67.9, 63.8, 57.2; MS (EI) *m/z* 150 (M^+ - CH_2O), 121, 104 (100), 103, 91, 77; Anal. calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.61; H, 6.74.

3-(2-*t*-Butyldiphenylsilyoxyethyl)-1,4-dihydroxy-4-methylpentan-2-one (2b). A solution of 3-(2-*t*-butyldiphenylsilyoxyethyl)-2,2-dimethyl-1,5-dioxaspiro[3.2]-hexane (**1b**) (0.13 g, 0.33 mmol) in a mixture of THF (3 mL) and water (0.5 mL) was stirred overnight at RT. The reaction mixture was diluted with CH_2Cl_2 (5 mL), dried ($MgSO_4$), filtered, and concentrated. The crude material was purified by flash chromatography on silica gel (petroleum ether/EtOAc 9:1) to provide white, plate-like crystals (0.13 g, 97%): mp 115-116 °C; IR ($CDCl_3$) 3508, 2933, 2860, 1714, 1472, 1428, 1389, 1274, 1112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 4H), 7.41 (m, 6H), 4.36 (dd, *J* = 19.4, 4.8 Hz, 1H), 4.28 (dd, *J* = 19.4, 4.8 Hz, 1H), 3.66 (ddd, *J* = 10.7, 5.4, 5.4 Hz, 1H), 3.54 (ddd, *J* = 10.7, 8.4, 4.3 Hz, 1H), 3.11 (dd, *J* = 4.8, 4.8 Hz, 1H), 2.87 (dd, *J* = 10.5, 3.2 Hz, 1H), 2.24 (s, 1H), 1.97 (m, 1H), 1.79 (m, 1H), 1.26 (s, 3H), 1.20 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 135.5, 135.5, 133.3, 133.1, 129.8, 127.8, 127.7, 72.2, 70.8, 62.5, 54.2, 31.2, 29.4, 26.8, 26.7, 19.1; MS (EI) *m/z* 383 (M^+-CH_2OH), 281, 221, 199, 181, 139, 135, 83 (100), 77, 59, 43; Anal. calcd for $C_{24}H_{34}SiO_4$: C, 69.53; H, 8.27. Found: C, 69.56; H, 8.48.

(S)-(N-*t*-Butoxycarbonyl)-3-amino-1,4-dihydroxybutan-2-one (2c). A solution of (S)-(N-*t*-butoxycarbonyl)-3-amino-1,5-dioxaspiro[3.2]hexane (**1c**) (0.13 g, 0.62 mmol) in a mixture of THF (3.5 mL) and H_2O (0.5 mL) was stirred at RT for 2 d. The reaction mixture was diluted with CH_2Cl_2 (20 mL), dried ($MgSO_4$), filtered, and the solvent evaporated *in vacuo*. A white solid (0.11 g, 77%) was obtained. Recrystallization from EtOAc/petroleum ether yielded white prisms: mp 104-105 °C; ^1H NMR (400 MHz,

$CDCl_3$) δ 5.50 (s, 1H), 4.47 (m, 3H), 4.06 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.86 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.01 (br, 1H), 2.18 (br, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 126.3, 67.2, 62.7, 58.6, 28.3; MS (EI) *m/z* 162 ($M^+ - C_4H_9$), 160, 146 ($M^+ - C_4H_9O$), 133, 104, 60, 57 (100); Anal. calcd for $C_9H_{17}NO_5$: C, 49.31; H, 7.82; N, 6.39. Found: C, 49.45; H, 7.86; N, 6.33.

4-Hydroxy-3-methyl-3-phenyl-1-propoxybutan-2-one (2d). A solution of 3-methyl-3-phenyl-1,5-dioxaspiro[3.2]hexane (**1d**) (80 mg, 0.46 mmol) in anhydrous propanol (3 mL) was stirred for 2 d at RT. The solvent was removed *in vacuo* , and the yellow oil purified by flash chromatography on silica gel (petroleum ether/EtOAc 19:1 to 17:3 to 7:3) to provide a colorless oil (77 mg, 87%): IR ($CDCl_3$) 3457, 2966, 2880, 1719, 1460, 1389, 1127, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.31 (m, 1H), 7.26 (m, 2H), 4.14 (dd, *J* = 11.5, 5.6 Hz, 1H), 4.10 (d, *J* = 17.3 Hz, 1H), 3.97 (d, *J* = 17.3 Hz, 1H), 3.50 (dd, *J* = 11.5, 8.6 Hz, 1H), 3.30 (m, 1H), 3.24 (m, 1H), 2.39 (dd, *J* = 8.5, 5.8 Hz, 1H), 1.68 (s, 3H), 1.56 (ddq, *J* = 7.3, 7.3, 7.3 Hz, 1H), 1.51 (dd, *J* = 7.3, 7.3 Hz, 1H), 0.86 (dd, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 139.0, 129.0, 127.7, 126.4, 73.3, 72.4, 69.6, 56.0, 22.7, 18.4, 10.3; MS (EI) *m/z* 206 ($M^+ - CH_2O$), 148, 120, 105 (100), 73.

3-Allyl-4-hydroxy-3-phenyl-1-propoxybutan-2-one (2e). A solution of 3-allyl-3-phenyl-1,5-dioxaspiro[3.2]hexane (**1e**) (0.20 g, 0.99 mmol) in anhydrous propanol (3 mL) was stirred at RT for 2 d. The solvent was removed *in vacuo*, and the resultant colorless, viscous oil was purified by flash chromatography on silica gel (petroleum ether/EtOAc 9:1) to provide a colorless oil (0.20 g, 78%): IR ($CDCl_3$) 3466, 3077, 2967, 2880, 1760, 1722, 1640, 1498, 1447, 1121, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.31 (m, 1H), 7.20 (m, 2H), 5.71 (dddd, *J* = 17.1, 10.1, 7.3, 7.3 Hz, 1H), 5.19 (dddd, *J* = 17.1, 1.5, 1.5, 1.5 Hz, 1H), 5.11 (m, 1H), 4.17 (dd, *J*

= 11.5, 7.2 Hz, 1H), 4.06 (s, 2H), 4.03 (dd, *J* = 11.5, 5.8 Hz, 1H), 3.26 (dd, *J* = 6.8, 6.8 Hz, 2H), 2.88 (m, 2H), 1.95 (dd, *J* = 6.3, 6.3 Hz, 1H), 1.52 (ddq, *J* = 7.4, 7.4, 7.4 Hz, 2H), 0.84 (dd, *J* = 7.4, 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 138.6, 133.3, 129.0, 127.6, 126.8, 119.1, 73.4, 73.2, 65.6, 59.1, 37.1, 22.7, 10.3; MS (EI) *m/z* 232 (M^+ - CH_2O), 174, 144, 131 (100), 129, 121, 115, 91, 73.

1-Acetoxy-4-hydroxy-3-phenylbutan-2-one (2f). A solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (0.15 g, 0.93 mmol) in dry THF (4 mL) was added at once to a stirred mixture of Bu_4NOAc (0.56 g, 1.85), acetic acid (79 mg, 1.31 mmol) and 4 Å molecular sieves (2 g) in dry THF (8 mL) at 0 °C. The mixture was stirred (15 min) and then left to warm to RT overnight. It was diluted with Et_2O (25 mL) and washed with saturated $NaHCO_3$ (2 x 10 mL). The organic layer was dried (K_2CO_3), filtered, and concentrated. The orange oil was purified by flash chromatography on silica gel (petroleum ether/EtOAc 9:1 to 4:1 to 3:2). A colorless oil (0.17 g, 81 %) was obtained. IR ($CDCl_3$) 3494, 3031, 2933, 1748, 1732, 1494, 1375, 1231, 1048 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.22 (m, 2H), 4.71 (d, *J* = 17.1 Hz, 1H), 4.57 (d, *J* = 17.1 Hz, 1H), 4.19 (ddd, *J* = 11.4, 8.5, 5.8 Hz, 1H), 3.99 (dd, *J* = 8.5, 4.9 Hz, 1H), 3.78 (ddd, *J* = 11.4, 7.8, 4.9 Hz, 1H), 2.22 (dd, *J* = 7.8, 5.8 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 170.1, 134.3, 129.3, 128.5, 128.2, 67.6, 64.0, 57.7, 20.3; MS (EI) *m/z* 192 (M^+ - CH_2O), 162 (M^+ - AcOH), 150, 131, 121, 104 (100), 103, 91, 78, 73, 65, 51.

4-Hydroxy-1-imidazol-1-yl-3-phenylbutan-2-one (2g). Imidazole (34 mg, 0.50 mmol) was added to a stirred solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (81 mg, 0.50 mmol) in dry THF (2 mL). The mixture was stirred at RT for 1 h and then concentrated. The orange residue was purified by flash chromatography on silica gel ($CHCl_3$/MeOH 49:1 to 19:1). A colorless oil (27 mg, 23 %) was obtained. IR ($CDCl_3$)

3346, 3121, 3035, 2918, 2843, 1731, 1598, 1507, 1447, 1238, 1063 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 3H), 7.25 (m, 2H), 7.20 (m, 1H), 7.03 (s, 1H), 6.72 (s, 1H), 4.77 (d, *J* = 18.4 Hz, 1H), 4.71 (d, *J* = 18.3 Hz, 1H), 4.25 (dd, *J* = 11.0, 9.1 Hz, 1H), 4.01 (dd, *J* = 9.1, 4.6 Hz, 1H), 3.76 (dd, *J* = 11.1, 4.7 Hz, 1H), 2.95 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 138.0, 134.1, 129.4, 129.3, 128.4, 120.0, 63.8, 58.5, 55.1; MS (EI) *m/z* 200 (M^+ - CH_2O), 91 (100), 82, 81(M^+ - $CH_2C_4H_3N_2$), 65, 59.

1-Hydroxy-2-methyl-2-phenyl-4-(phenylsulfanyl)butan-3-one (2h). A solution of 3-methyl-3-phenyl-1,5-dioxaspiro[3.2]hexane (**1d**) (45 mg, 0.26 mmol) and benzenethiol (31 mg, 0.28 mmol) in dry $CDCl_3$ (0.5 mL) was stirred at RT. **1d** was consumed in 10 d as observed by ^1H NMR. The solvent was removed *in vacuo*. The clear oil was purified by flash chromatography on silica gel (petroleum ether/EtOAc 9:1 to 4:1 to 1:1). A colorless oil (23 mg, 31 %) was obtained. ^1H NMR (400 MHz) δ 7.37 (m, 4H), 7.22 (m, 6H), 4.12 (dd, *J* = 11.5, 5.2 Hz, 1H), 3.74 (dd, *J* = 16.4, 0.6 Hz, 1H), 3.64 (dd, *J* = 16.4, 0.6 Hz, 1H), 3.53 (dd, *J* = 11.5, 8.2 Hz, 1H), 2.38 (dd, *J* = 8.1, 5.9 Hz, 1H), 1.68 (s, 3H); MS (EI) *m/z* 256 (M^+ - CH_2O), 214, 165, 147, 123, 105 (100), 79, 77, 51.

4-Hydroxy-3-phenyl-1-(phenylsulfanyl)butan-2-one (2i). n-BuLi (1.6 M in hexane, 0.46 mL, 0.62 mmol) was added to a stirred solution of benzenethiol (68mg, 0.62 mmol) in dry THF (2 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 30 min, and then a solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (0.10 g, 0.62 mmol) in dry THF (1 mL) was added at once. The mixture was stirred at -78 °C for 3 h, diluted with Et_2O (20 mL), and then quenched with saturated NH_4Cl (1 mL). The organic layer was separated, dried (Na_2SO_4), and filtered. The filtrate was concentrated and purified by flash chromatography on silica (petroleum ether/EtOAc 17:3 to 7:3). A white solid (0.14 g, 79%) was obtained. Recrystallization from EtOAc/petroleum ether yielded

white, needle-like crystals: mp 50-51 °C. IR ($CDCl_3$) 3442, 3057, 3025, 2928, 2875, 1699, 1576, 1485, 1389, 1089, 1046 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 8H), 7.18 (m, 2H), 4.32 (dd, *J* = 8.5, 4.9 Hz, 1H), 4.14 (dd, *J* = 11.3, 8.6 Hz, 1H), 3.75 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.65 (d, *J* = 1.6 Hz, 2H), 2.08 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 134.8, 134.3, 130.1, 129.2, 129.0, 128.7, 128.0, 127.0, 64.0, 58.5, 43.3; MS (EI) *m/z* 242 (M^+ - CH_2O), 151($PhSCH_2CO^+$), 132, 123 ($PhSCH_2^+$), 109 (PhS^+), 91 (100), 77, 65, 51; Anal calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.44; H, 5.76; S, 12.09.

2-Phenyl-1,3-butanediol (2j).[2] A solution of 3-phenyl-1,5-dioxaspiro-[3.2]hexane (**1a**) (0.15 g, 0.93 mmol) in dry Et_2O (3 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (37 mg, 0.93 mmol) in dry Et_2O (8 mL) at 0 °C. The mixture was stirred at 0 °C (10 min) and then warmed to RT (1h). It was diluted with wet Et_2O (20 mL) and stirred (10 min). H_2SO_4 (2 M, 2 mL) was added dropwise, followed by saturated NaCl (10 mL). The mixture was extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. The colorless oil was purified by flash chromatography on silica gel (petroleum ether/EtOAc 17:3 to 7:3). A colorless oil (0.14 g, 93 %) was obtained as a mixture of diastereomers (15:1). IR ($CDCl_3$) 3422, 3030, 2973, 1455, 1375 cm^{-1}; Major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 5H), 4.20 (m, 1H), 4.05 (m, 1H), 3.96 (m, 1H), 2.86 (q, *J* = 5.4 Hz, 1H), 1.65 (m, 2H), 1.19 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 129.2, 128.8, 127.3, 68.9, 64.4, 54.9, 21.0. Minor diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 3H), 7.17 (m, 2H), 4.22 (m, 1H), 4.10 (m, 1H), 3.91 (m, 1H), 2.78 (ddd, *J* = 8.6, 8.6, 4.5 Hz, 1H), 2.67 (m, 1H), 2.51 (m, 1H), 1.07 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 128.8, 128.2, 127.1, 72.9, 67.2, 55.3, 22.7; MS (EI) *m/z* 148 (M^+ - H_2O), 133 (M^+ - H_2O - CH_3), 104 (100), 91, 78, 65, 51.

2-(Hydroxymethyl)-3-phenyloxetane (3a). Diisobutylaluminum hydride (1.10 mL, 1 M in CH_2Cl_2, 1.10 mmol) was added dropwise to a stirred solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (150 mg, 0.93 mmol) in CH_2Cl_2 (3 mL) at -78 °C. The mixture was left to stir for 1 h at -78 °C. It was diluted with Et_2O (15 mL) and warmed to 0 °C. H_2O (0.04 mL) was added dropwise and the mixture stirred (15 min). NaOH (15 %, 0.04 mL) and H_2O (0.08 mL) was added and the mixture stirred at RT (15 min). The mixture was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc 7:3 to 1:1). A colorless oil (104 mg, 68 %) was obtained. IR ($CDCl_3$) 3406 (br), 3023, 2956, 2877, 1595, 1488, 1449, 1179, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.27 (m, 3H), 5.09 (ddd, J = 8.5, 7.1, 4.7 Hz, 1H), 4.99 (dd, J = 8.4, 6.4 Hz, 1H), 4.96 (dd, J = 8.4, 6.5 Hz, 1H), 4.40 (ddd, J = 8.2, 8.2, 8.2 Hz, 1H), 3.65 (m, 1H), 3.43 (m, 1H), 1.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 128.6, 127.7, 127.2, 84.7, 73.0, 63.3, 41.2; MS (EI) *m/z* 133 (M^+ - CH_2OH), 115, 104 (100), 91, 78, 77, 63, 51.

2-Azido-2-(hydroxymethyl)-3-phenyloxetane (3b). $TMSN_3$ (0.22 g, 1.85 mmol) was added to a stirred solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (0.20 g, 1.23 mmol) in dry ether (2 mL). The reaction mixture was left to stir overnight at RT. It was then concentrated to provide a colorless oil, which was then dissolved in dry THF (5 mL). The mixture was cooled to 0 °C and TBAF (1.85 mL, 1 M in THF, 1.85 mmol) was added dropwise. The mixture was stirred at 0 °C for 2 h and then concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc 9:1 to 4:1). A white solid (0.14 g, 56 %) was obtained. Recrystallization from EtOAc/petroleum ether yielded white prisms: mp 37-38 °C; IR ($CDCl_3$) 3441, 3062, 3031, 2971, 2903, 2116, 1590, 1493, 1452, 1257, 1048, 946 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.29 (m, 3H), 4.86 (dd, J = 7.7, 6.2 Hz, 1H), 4.80 (dd, J = 8.8, 6.2 Hz, 1H), 4.49 (dd, J = 8.3, 8.3 Hz, 1H), 3.53 (dd, J = 12.5, 7.1 Hz, 1H), 3.40 (dd,

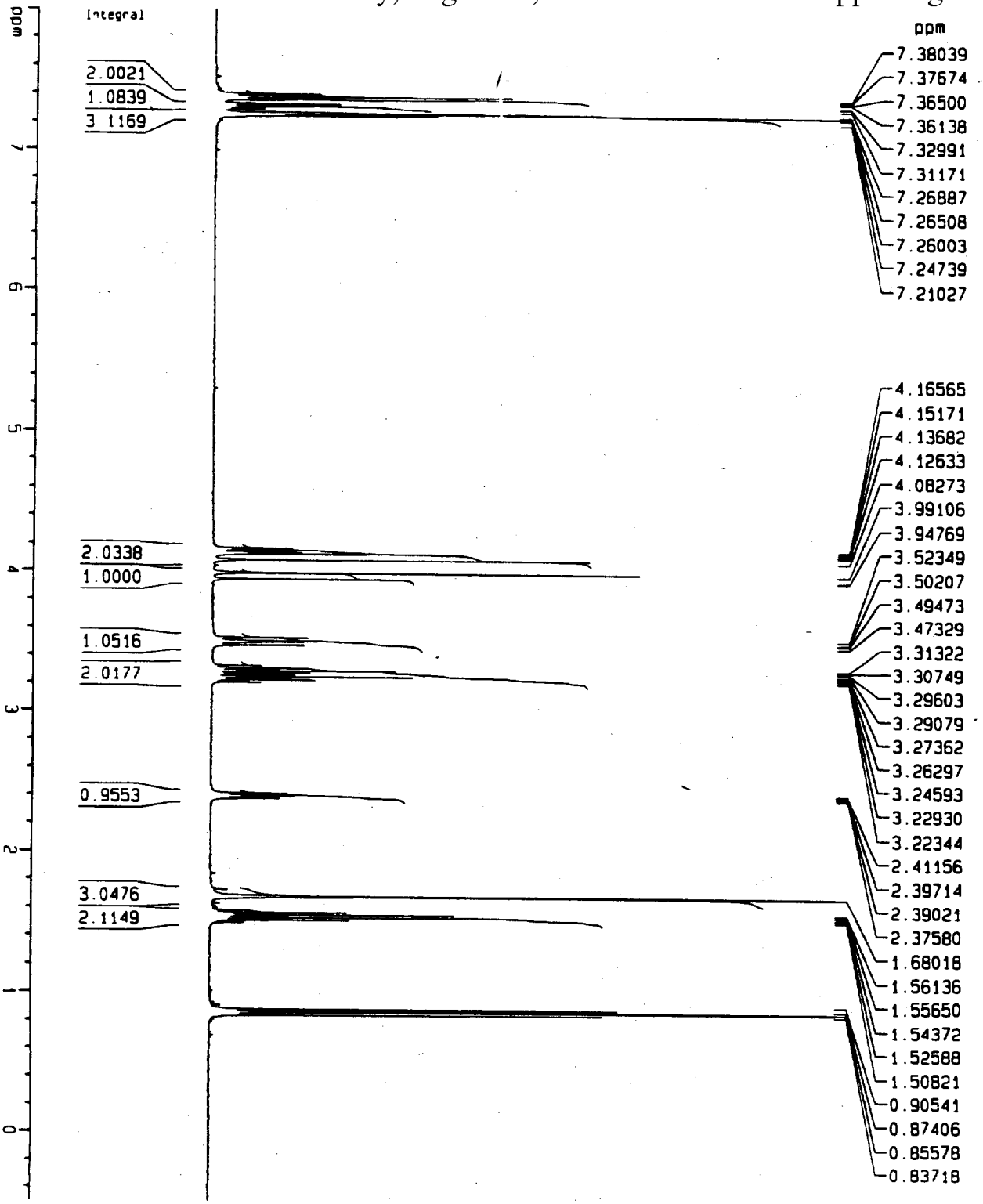
J = 12.4, 6.8 Hz, 1H), 1.52 (dd, J = 7.0, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 133.8, 128.8, 127.9, 127.6, 100.9, 67.2, 64.1, 48.3; MS (EI) *m/z* 177 ($M^+ - N_2$), 159 ($M^+ - N_2 - CH_2O$), 129, 120, 117 (100), 103, 90, 89, 77, 63, 51; Anal. calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.82; H, 5.09; N, 20.11.

2-(Hydroxymethyl)-2-methyl-3-phenyloxetane (3c). Trimethylaluminum (0.37 mL, 2 M in hexane, 0.74 mmol) was added to a stirred solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (100 mg, 0.62 mmol) in CH_2Cl_2 (3 mL) at -78 °C. The reaction mixture was left to stir for 1 h at -78 °C. It was diluted with Et_2O (15 mL) and warmed to 0 °C. H_2O (0.03 mL) was added dropwise and the mixture stirred (15 min). NaOH (15 %, 0.03 mL) and H_2O (0.07 mL) was added and the mixture stirred at RT (15 min). The cloudy organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc 7:3). A colorless oil (87 mg, 79 %) was obtained. IR ($CDCl_3$) 3421, 3014, 2960, 2886, 1491, 1448, 1373, 1100, 1046, 1030, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.25 (m, 3H), 4.95 (dd, J = 8.3, 6.4 Hz, 1H), 4.76 (dd, J = 8.8, 6.4 Hz, 1H), 4.14 (dd, J = 8.6, 8.6 Hz, 1H), 3.54 (d, J = 12.0 Hz, 1H), 3.32 (d, J = 12.0 Hz, 1H), 1.60 (s, 3H), 1.55 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 136.4, 128.6, 127.4, 127.1, 88.8, 68.5, 66.0, 48.1, 25.8; MS (EI) *m/z* 160 ($M^+ - H_2O$), 147 ($M^+ - CH_2OH$), 129, 105, 104 (100), 91, 78, 51.

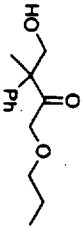
REFERENCES

1) Ndakala, A. J.; Howell, A. R. *J. Org. Chem.* **1998**, *63*, 6098-6099.

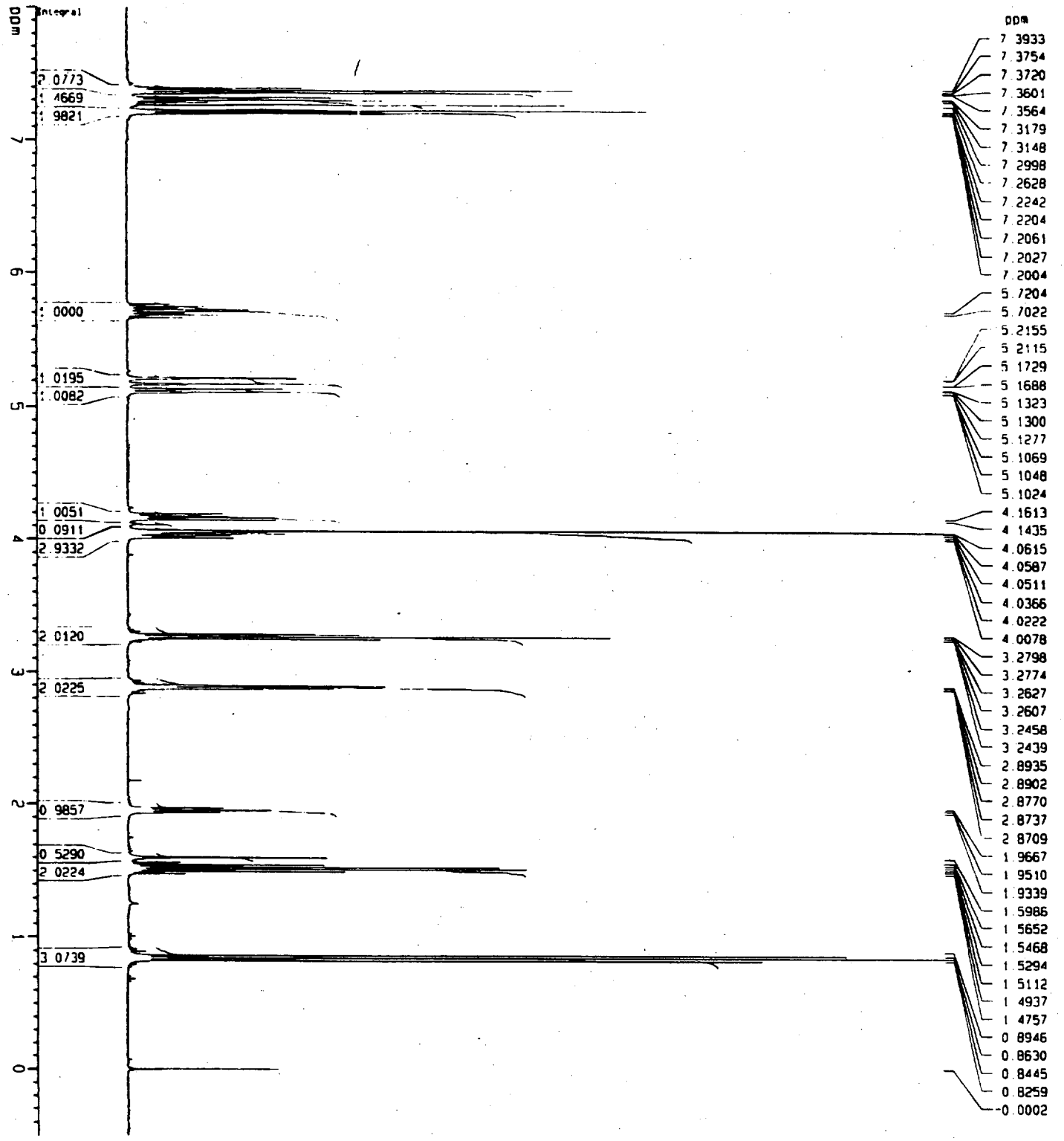
2) Pelter, A.; Vaughan-Williams, G. F.; Rosser, R. M. *Tetrahedron* **1993**, *49*, 3007-3034.



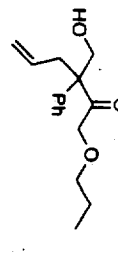

```
Current Data Parameters
NAME                  ajn2-191-1
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_               981226
Time                    12.37
INSTRUM               drx400
PROBHD     5 mm QNP 1H
PULPROG               zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8223.685 Hz
FIDRES             0.250967 Hz
AQ                 1.9923444 sec
RG                      1024
DW                 60.800 usec
DE                  4.50 usec
TE                  300.0 K
D1                 4.00000000 sec
P1                    8.70 usec
DE                    4.50 usec
SFO1           400.1324710 MHz
NUC1                      1H
PL1                  -4.00 dB

F2 - Processing parameters
SI                       16384
SF             400.1300092 MHz
WDW                        EM
SSB                         0
LB                   0.30 Hz
GB                          0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                8.000 ppm
F1                3201.04 Hz
F2P                0.500 ppm
F2                 200.07 Hz
PPMCM             0.42500 ppm/cm
HZCM              170.05525 Hz/cm
```



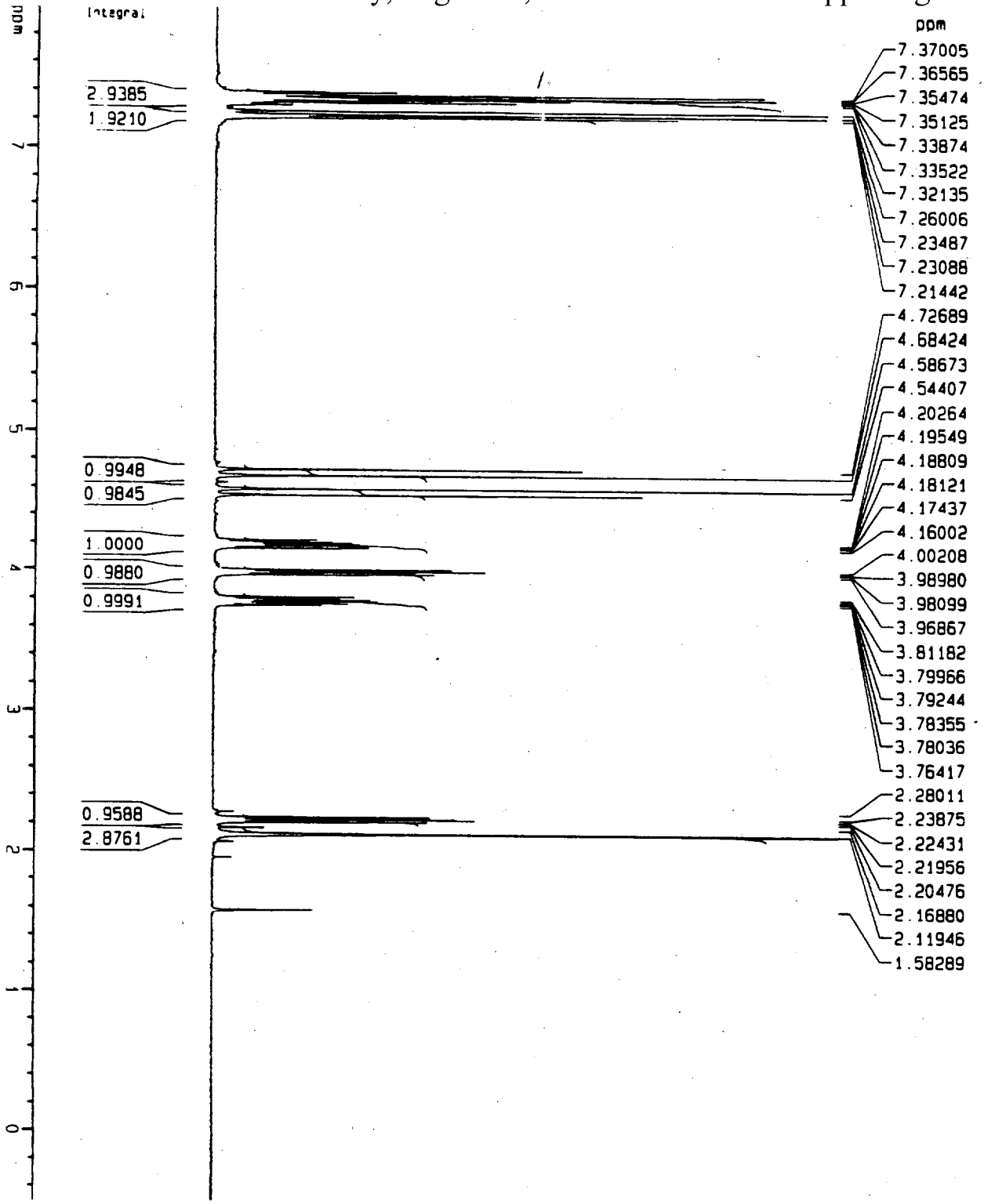
2d



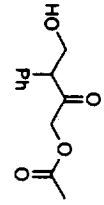

```
Current Data Parameters
NAME                  ajn2-141rechr
EXPNO                            1
PROCNO                           1

F2 - Acquisition Parameters
Date_                     971113
Time                       19.54
INSTRUM                  drx400
PROBHD     5 mm QNP 1H
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          32
DS                           0
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                         574.7
DW                        62.400 usec
DE                         7.14 usec
TE                        240.0 K
D1                    5.00000000 sec
P1                         7.40 usec
DE                         7.14 usec
SFO1                400.1320340 MHz
NUC1                         1H
PL1                       0.00 dB

F2 - Processing parameters
SI                        32768
SF                400.1300081 MHz
WDW                          EM
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         4.00

1D NMR plot parameters
CX                        20.00 cm
F1P                        8.000 ppm
F1                      3201.04 Hz
F2P                       -0.500 ppm
F2                      -200.07 Hz
PPMCM                  0.42500 ppm/
HZCM                   0.05525 Hz/
```



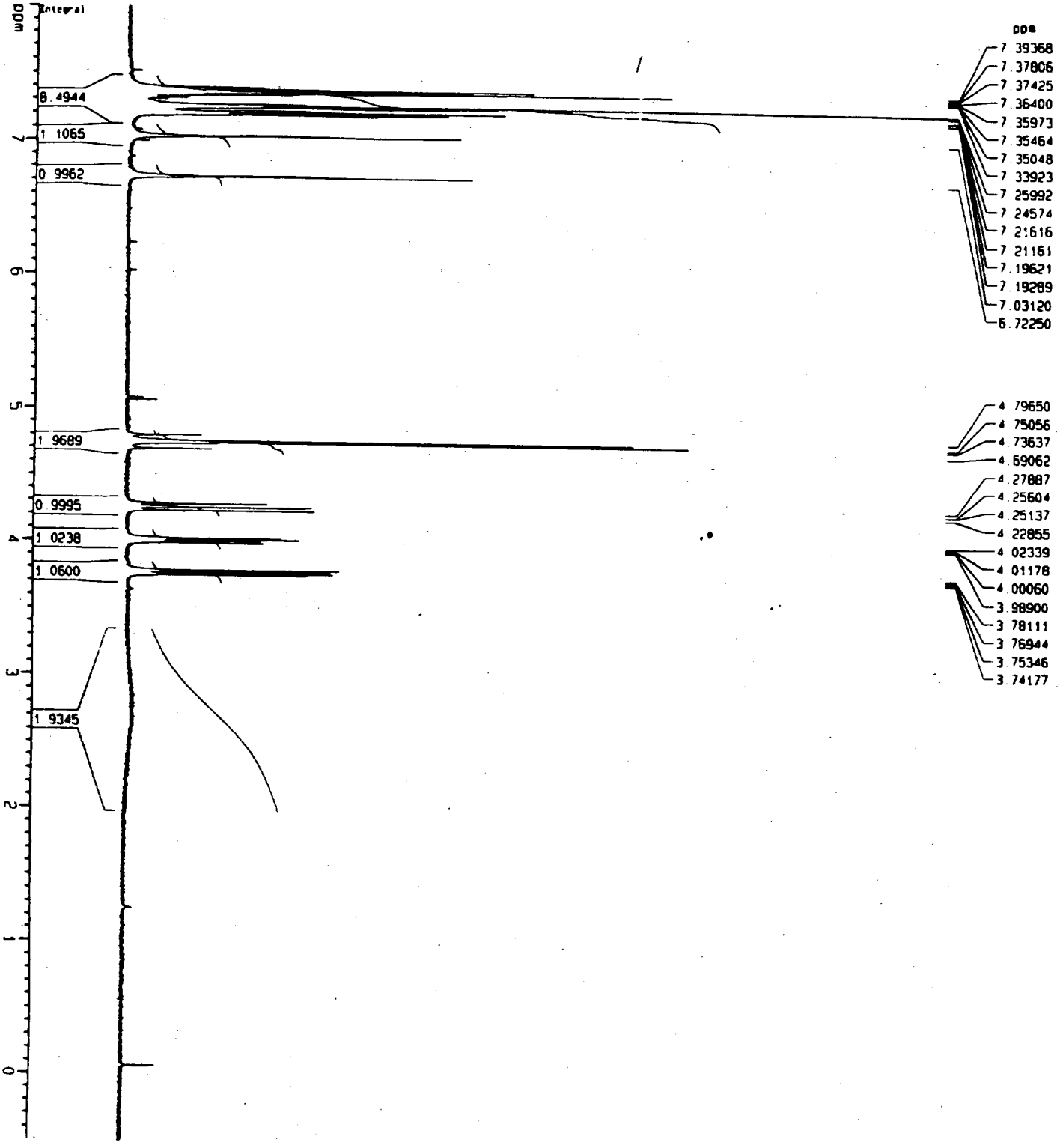
2e

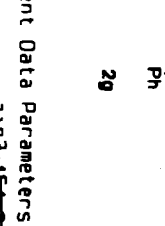



```
Current Data Parameters
NAME                  ajm4-041-1
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_               981226
Time                    13.02
INSTRUM                 drx400
PROBHD     5 mm QNP 1H
PULPROG                 zg30
TD                      32768
SOLVENT                 CDCl3
NS                          8
DS                          0
SWH                 8223.685 Hz
FIDRES              0.250967 Hz
AQ                  1.992344 sec
RG                      812.7
DW                     60.800 usec
DE                      4.50 usec
TE                     300.0 K
D1                  4.00000000 sec
P1                      8.70 usec
DE                      4.50 usec
SFO1               400.1324710 MHz
NUC1                        1H
PL1                    -4.00 dB

F2 - Processing parameters
SI                      16384
SF                 400.1300092 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
F1P                   8.000 ppm
F1                 3201.04 Hz
F2P                   0.500 ppm
F2                  200.07 Hz
PPMCM              0.42500 ppm/cm
HZCM               170.05525 Hz/cm
```



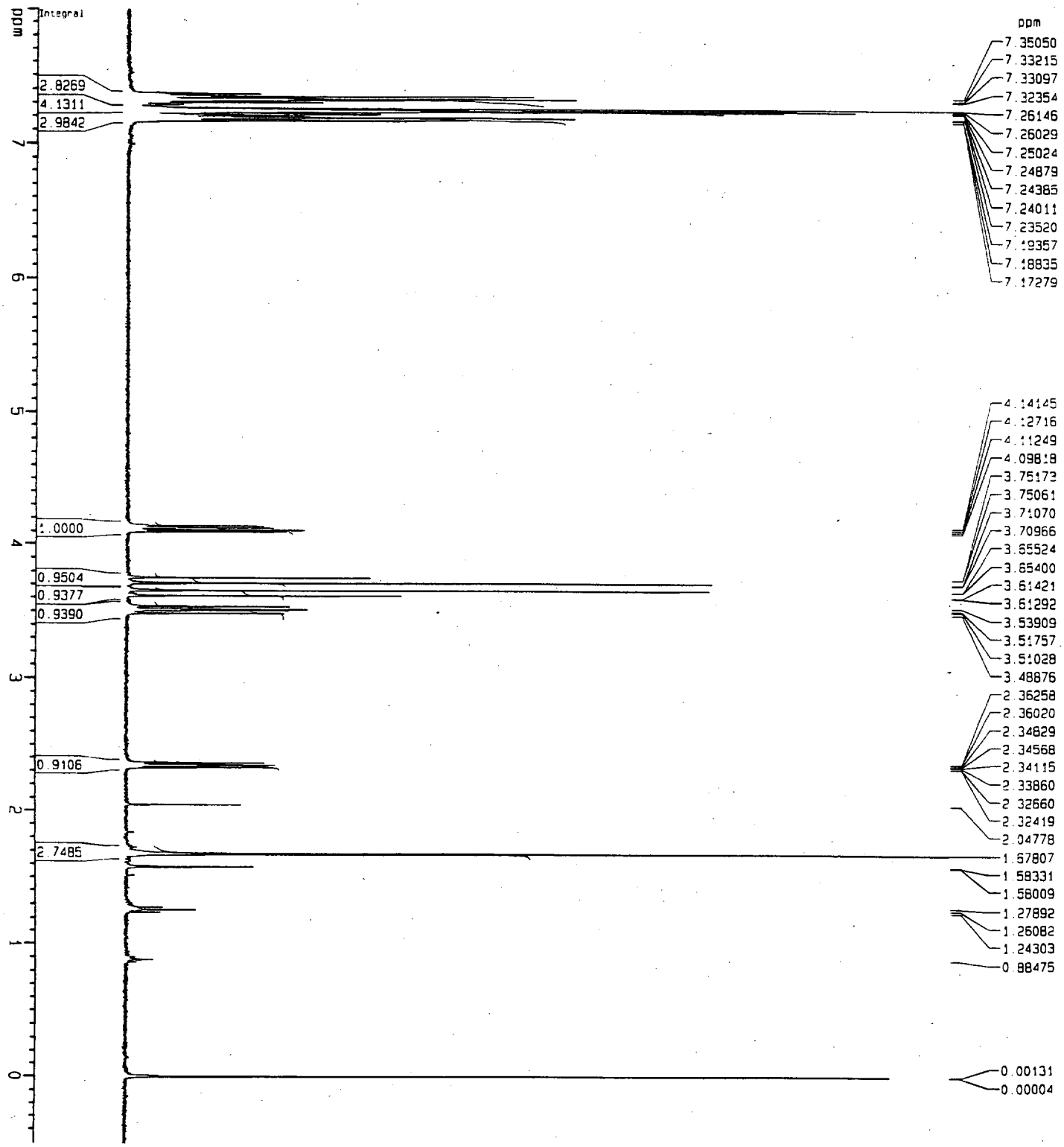
21

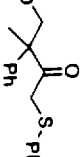




2g

```
Current Data Parameters
NAME                  ajn3-15
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               980813
Time                19.08
INSTRUM             drx400
PROBHD     5 mm QNP 1H
PULPROG             zg30
TD                  65536
SOLVENT             CDCl3
NS                  8
DS                  0
SWH                 8012.820 Hz
FIDRES              0.122866 Hz
AQ                  4.0894966 sec
RG                  574.7
DW                  62.400 use
DE                  7.14 use
TE                  240.0 K
D1                  5.00000000 sec
P1                  7.40 use
DE                  7.14 use
SFO1                400.1320340 MHz
NUC1                1H
PL1                 0.00 dB

F2 - Processing parameters
SI                  32768
SF                  400.1300094 MHz
WDW                 EM
SSB                 0
LB                  0.00 Hz
GB                  0
PC                  4.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 8.000 ppm
F1                  3201.04 Hz
F2P                 -0.500 ppm
F2                  -200.07 Hz
PPMCM               42500 ppm
HZCM                .05525 Hz/
```





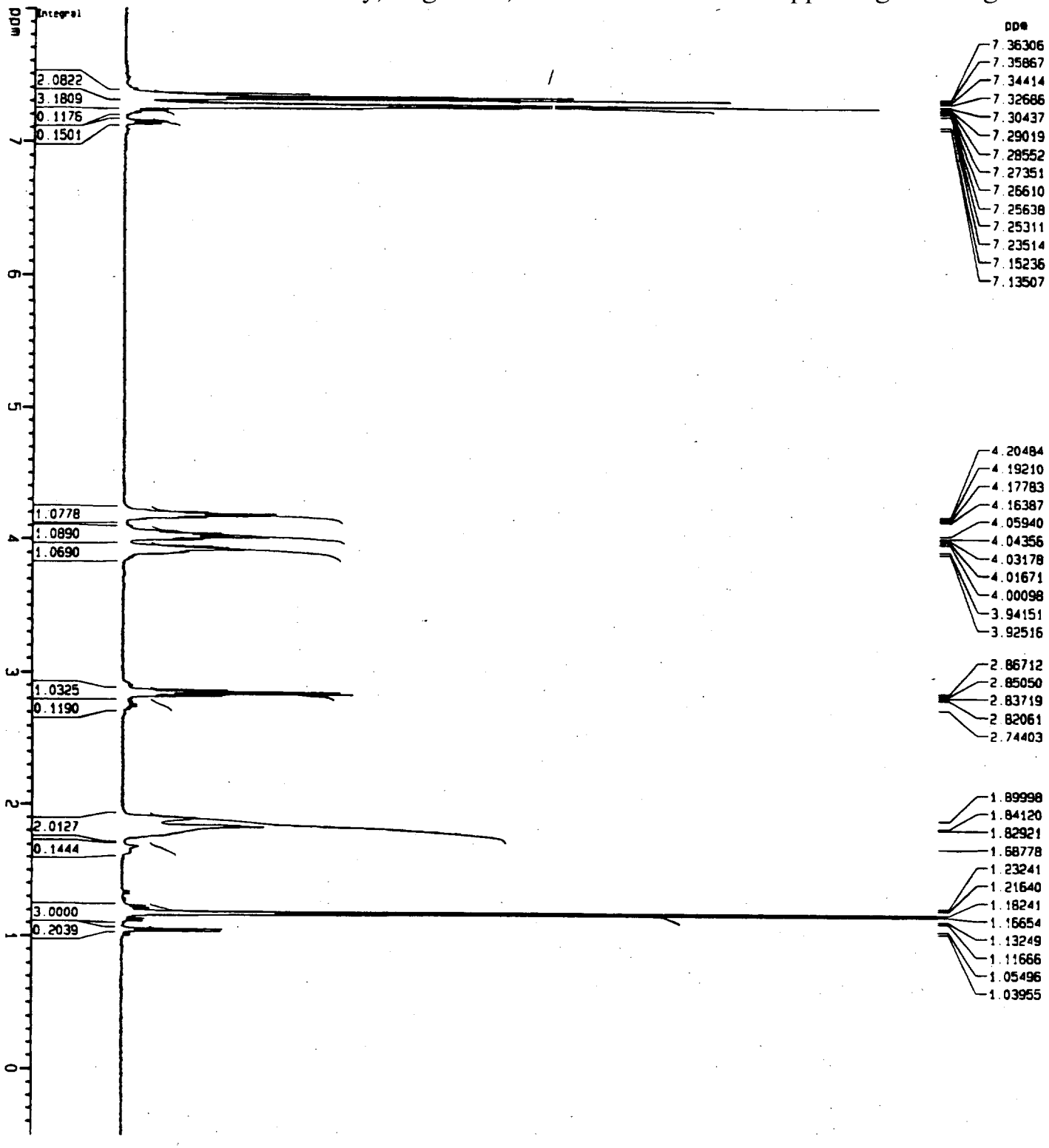
2h

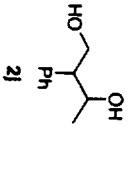
Current Data Parameters
NAME ajn5-015-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 990413
Time 7.48
INSTRUM drx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 574.7
DW 62.400 use
DE 7.14 use
TE 240.0 K
D1 5.00000000 sec
P1 7.40 use
DE 7.14 use
SFO1 400.1320340 MHz
NUC1 1H
PL1 0.00 dB

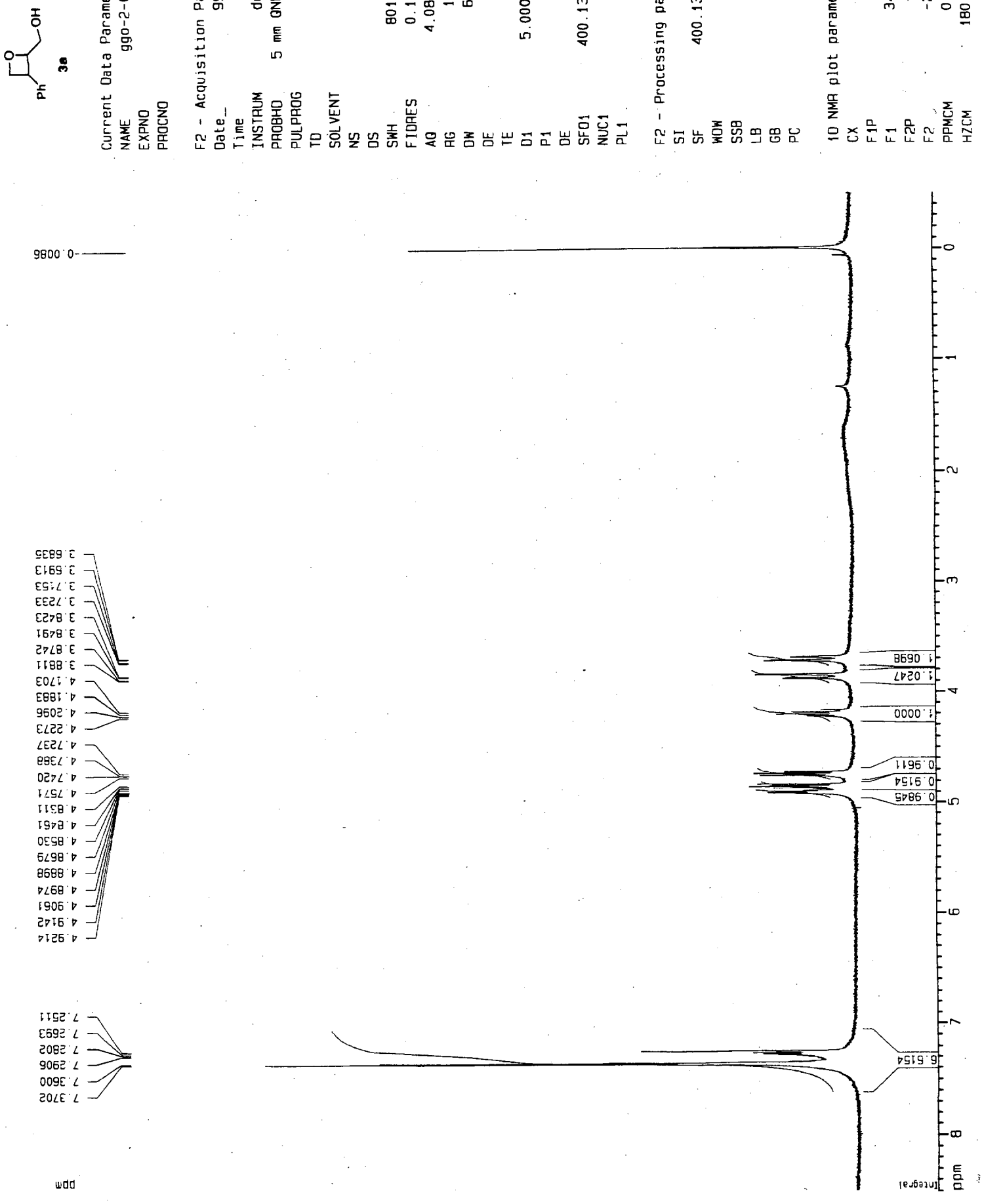
F2 - Processing parameters
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

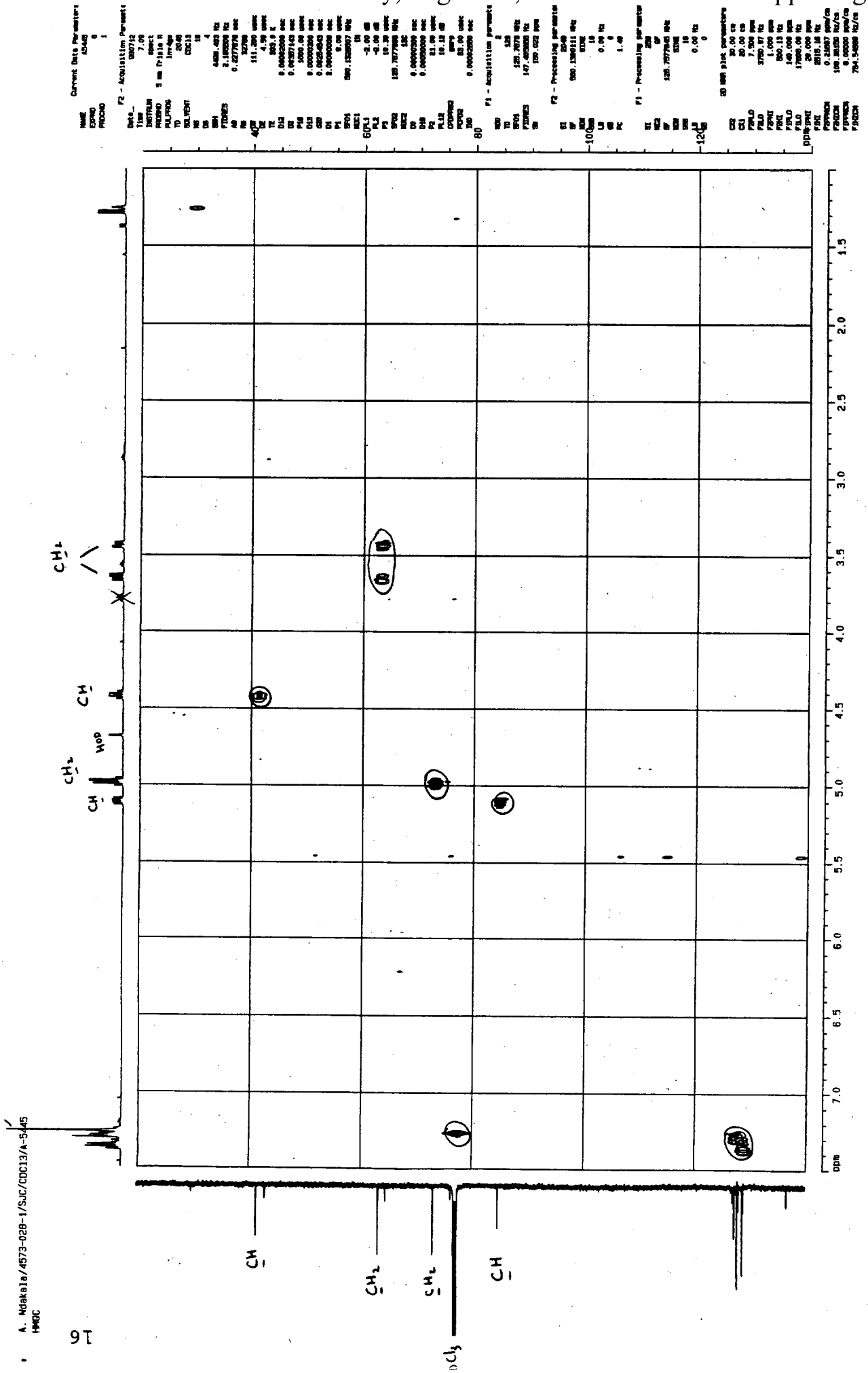
1D NMR plot parameters
CX 20.00 cm
F1P 8.000 ppm
F1 3201.04 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.42500 ppm
HZCM 1.05525 Hz/

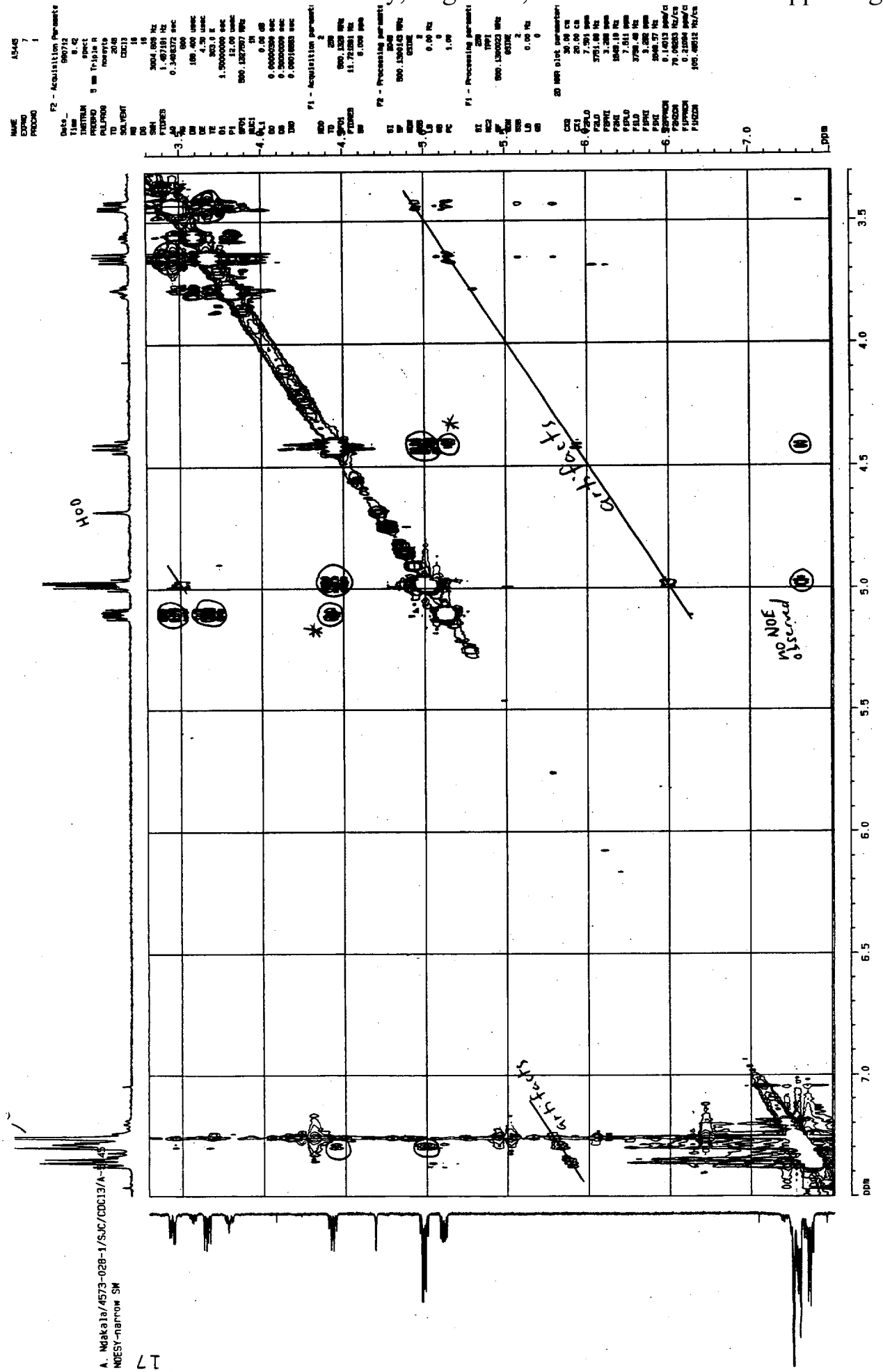


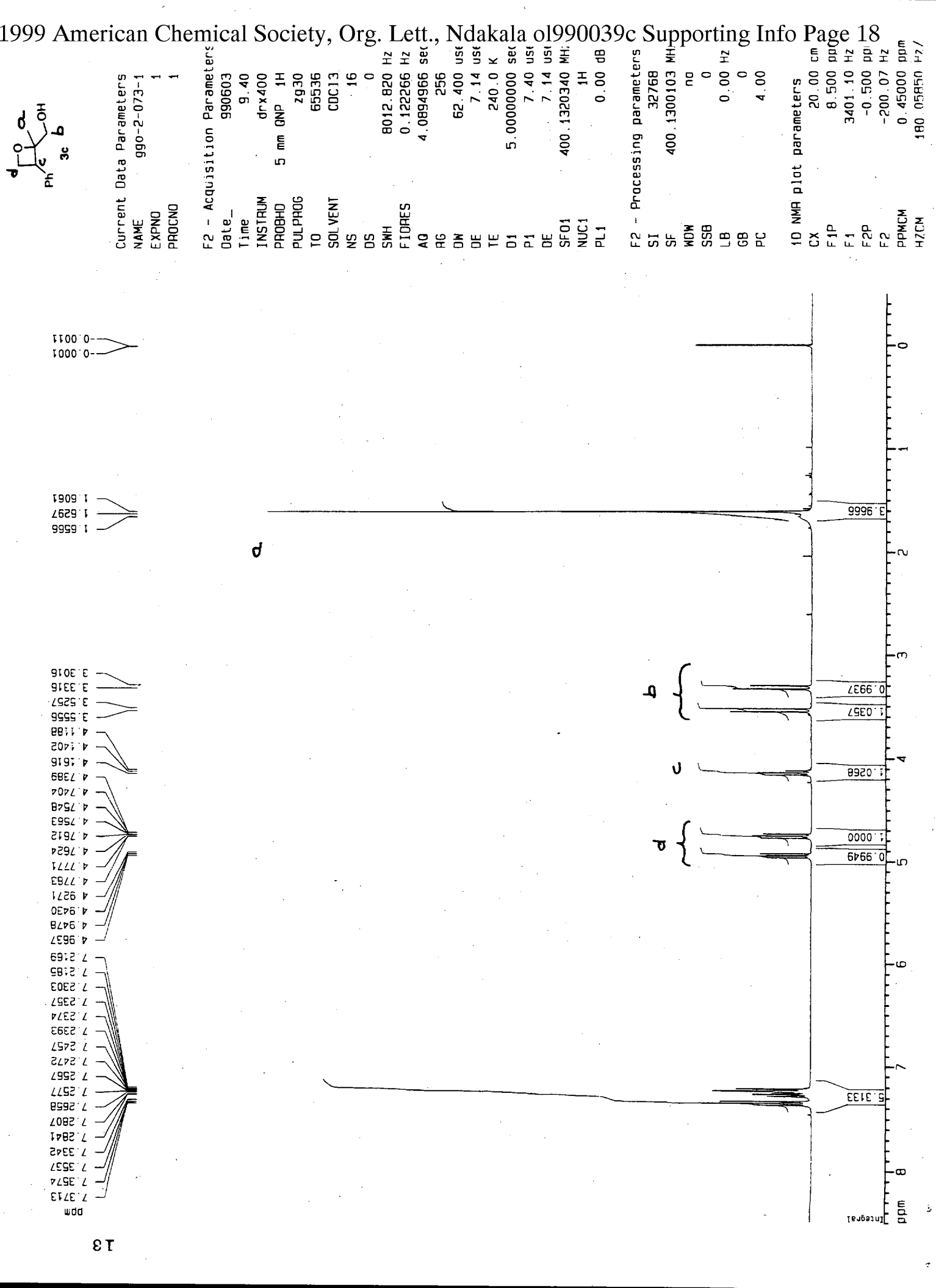



```
Current Data Parameters
NAME                  ajn4-039-1
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_               990315
Time                     8.54
INSTRUM                drx400
PROBHD     5 mm QNP 1H
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         0
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                       574.7
DW                      62.400 usec
DE                       7.14 usec
TE                      240.0 K
D1                5.00000000 sec
P1                      7.40 usec
DE                      7.14 usec
SFO1              400.1320340 MHz
NUC1                       1H
PL1                     0.00 dB

F2 - Processing parameters
SI                        32768
SF                400.1300120 MHz
WDW                        EM
SSB                         0
LB                      0.00 Hz
GB                          0
PC                      4.00

1D NMR plot parameters
CX                     20.00 cm
F1P                     8.000 ppm
F1                   3201.04 Hz
F2P                    -0.500 ppm
F2                   -200.07 Hz
PPMCM                  0.42500 ppm/
HZCM                 170.05525 Hz/
```

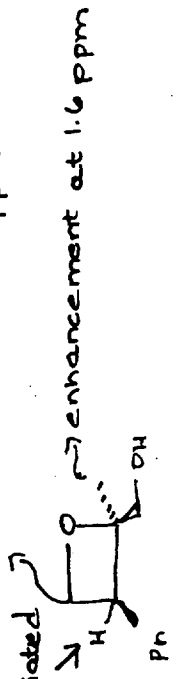

OH
O
Ph
3a
Current Data Parameters
NAME ggo-2-091-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 990612
Time 19.30
INSTRUM drx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 se
RG 1149.4
DW 62.400 us
DE 7.14 us
TE 240.0 K
D1 5.00000000 se
P1 7.40 us
DE 7.14 us
SFO1 400.1320340 MH
NUC1 1H
PL1 0.00 dB
F2 - Processing parameters
SI 32768
SF 400.1300120 MH
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 20.00 cm
F1P 8.500 pp
F1 3401.10 Hz
F2P -0.500 pp
F2 -200.07 Hz
PPMCM 0.45000 ppm
HZCM 180.05850 Hz/
7.3702
7.3600
7.2906
7.2802
7.2693
7.2511
4.9214
4.9142
4.9061
4.8974
4.8898
4.8679
4.8530
4.8461
4.8511
4.7571
4.7420
4.7388
4.7237
4.2273
4.2096
4.1883
4.1703
3.8811
3.8742
3.8491
3.8423
3.7233
3.7153
3.6913
3.6835
1.0698
1.0247
1.0000
0.9611
0.9154
0.9845
6.5154
integral
ppm
ppm

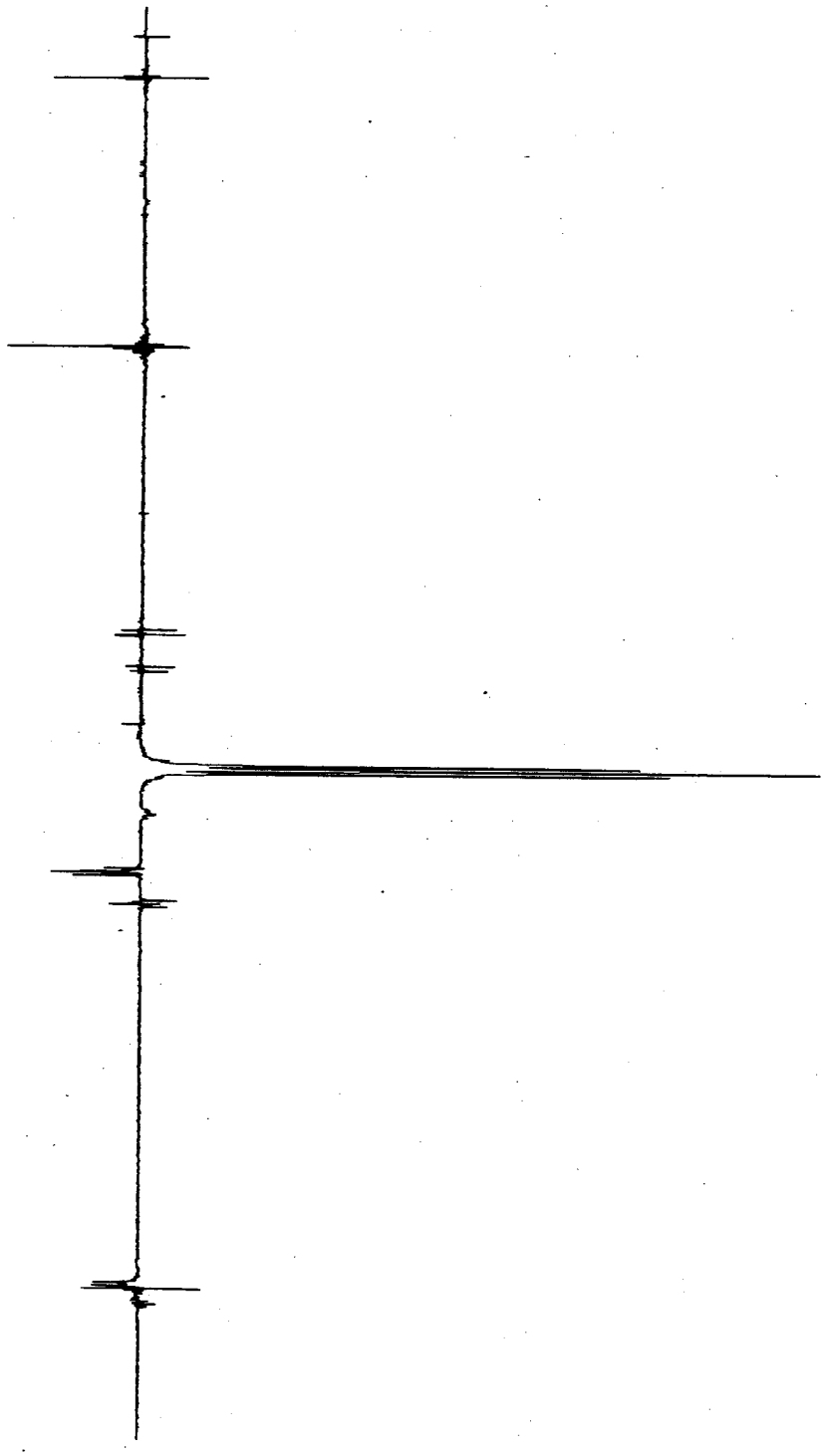





Current Data Parameters
NAME ggo-2-073-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 990603
Time 9.40
INSTRUM drx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 256
DW 62.400 usec
DE 7.14 usec
TE 240.0 K
D1 5.00000000 sec
P1 7.40 usec
DE 7.14 usec
SFO1 400.1320340 MHz
NUC1 1H
PL1 0.00 dB
F2 - Processing parameters
SI 32768
SF 400.1300103 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 20.00 cm
F1P 8.500 ppm
F1 3401.10 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45000 ppm/cm
HZCM 180.05850 Hz/cm
d
b
c
d
3.9666
0.9937
1.0357
1.0268
1.0000
0.9949
5.3133
Integral
ppm
13

NOE Difference for compound 3c





```
Current Data Parameters
NAME                  amy
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              691231
Time                16.00
INSTRUM
PROBHD                 06
PULPROG          zgf2pr.tk1
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      4
SWH              3434.066 Hz
FIDRES              0.052400 Hz
AQ                9.5420914 sec
RG                    128
DW                145.600 usec
DE                  4.50 usec
TE                  300.0 K
d11               0.0300000 sec
d13               0.0000030 sec
PL17                76.00 dB
D1               15.00000000 sec
SFO2            400.1299124 MHz
NUC2                   1H
PL2                 -3.00 dB
P1                   8.70 usec
DE                   4.50 usec
SFO1            400.1315605 MHz
NUC1                   1H
PL1                 -4.00 dB

F2 - Processing parameters
SI                    65536
SF              400.1300000 MHz
WDW                    no
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 8.500 ppm
F1                 3401.10 Hz
F2P                -0.500 ppm
F2                -200.07 Hz
PPMCM            0.45000 ppm/cm
HZCM             180.05850 Hz/cm
```