

Supporting Information

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

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Experimental section

General experimental. Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Methylene chloride was distilled from calcium hydride, while CDCl_3 was dried over 3 Å 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*-butyldiphenylsilyloxyethyl)-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 ($\text{M}^+ - \text{CH}_2\text{O}$), 121, 104 (100), 103, 91, 77; Anal. calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3$: C, 66.65; H, 6.71. Found: C, 66.61; H, 6.74.

3-(2-*t*-Butyldiphenylsilyloxyethyl)-1,4-dihydroxy-4-methylpentan-2-one (2b). A solution of 3-(2-*t*-butyldiphenylsilyloxyethyl)-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 ($\text{M}^+-\text{CH}_2\text{OH}$), 281, 221, 199, 181, 139, 135, 83 (100), 77, 59, 43; Anal. calcd for $\text{C}_{24}\text{H}_{34}\text{SiO}_4$: 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,

CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 208.6, 126.3, 67.2, 62.7, 58.6, 28.3; MS (EI) *m/z* 162 (M⁺ - C₄H₉), 160, 146 (M⁺ - C₄H₉O), 133, 104, 60, 57 (100); Anal. calcd for C₉H₁₇NO₅: 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 (CDCl₃) 3457, 2966, 2880, 1719, 1460, 1389, 1127, 1026 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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⁺ - CH₂O), 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 (CDCl₃) 3466, 3077, 2967, 2880, 1760, 1722, 1640, 1498, 1447, 1121, 1051 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (m, 2H), 7.31 (m, 1H), 7.20 (m, 2H), 5.71 (dd, *J* = 17.1, 10.1, 7.3, 7.3 Hz, 1H), 5.19 (dd, *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 ($\text{M}^+ - \text{CH}_2\text{O}$), 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} ; ^1H 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 ($\text{M}^+ - \text{CH}_2\text{O}$), 162 ($\text{M}^+ - \text{AcOH}$), 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 ($\text{CHCl}_3/\text{MeOH}$ 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, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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⁺ - CH₂O), 91 (100), 82, 81(M⁺ - CH₂C₄H₃N₂), 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 CDCl₃ (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⁺ - CH₂O), 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 Et₂O (20 mL), and then quenched with saturated NH₄Cl (1 mL). The organic layer was separated, dried (Na₂SO₄), 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 (CDCl₃) 3442, 3057, 3025, 2928, 2875, 1699, 1576, 1485, 1389, 1089, 1046 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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⁺ - CH₂O), 151(PhSCH₂CO⁺), 132, 123 (PhSCH₂⁺), 109 (PhS⁺), 91 (100), 77, 65, 51; Anal calcd for C₁₆H₁₆O₂S: 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 Et₂O (3 mL) was added dropwise to a stirred suspension of LiAlH₄ (37 mg, 0.93 mmol) in dry Et₂O (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 Et₂O (20 mL) and stirred (10 min). H₂SO₄ (2 M, 2 mL) was added dropwise, followed by saturated NaCl (10 mL). The mixture was extracted with Et₂O (3 x 10 mL). The combined organic extracts were dried (Na₂SO₄), 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 (CDCl₃) 3422, 3030, 2973, 1455, 1375 cm⁻¹; Major diastereomer: ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 129.2, 128.8, 127.3, 68.9, 64.4, 54.9, 21.0. Minor diastereomer: ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 128.8, 128.2, 127.1, 72.9, 67.2, 55.3, 22.7; MS (EI) *m/z* 148 (M⁺ - H₂O), 133 (M⁺ - H₂O - CH₃), 104 (100), 91, 78, 65, 51.

2-(Hydroxymethyl)-3-phenyloxetane (3a). Diisobutylaluminum hydride (1.10 mL, 1 M in CH₂Cl₂, 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 CH₂Cl₂ (3 mL) at -78 °C. The mixture was left to stir for 1 h at -78 °C. It was diluted with Et₂O (15 mL) and warmed to 0 °C. H₂O (0.04 mL) was added dropwise and the mixture stirred (15 min). NaOH (15 %, 0.04 mL) and H₂O (0.08 mL) was added and the mixture stirred at RT (15 min). The mixture was dried (MgSO₄), 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 (CDCl₃) 3406 (br), 3023, 2956, 2877, 1595, 1488, 1449, 1179, 1027 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 136.5, 128.6, 127.7, 127.2, 84.7, 73.0, 63.3, 41.2; MS (EI) *m/z* 133 (M⁺ - CH₂OH), 115, 104 (100), 91, 78, 77, 63, 51.

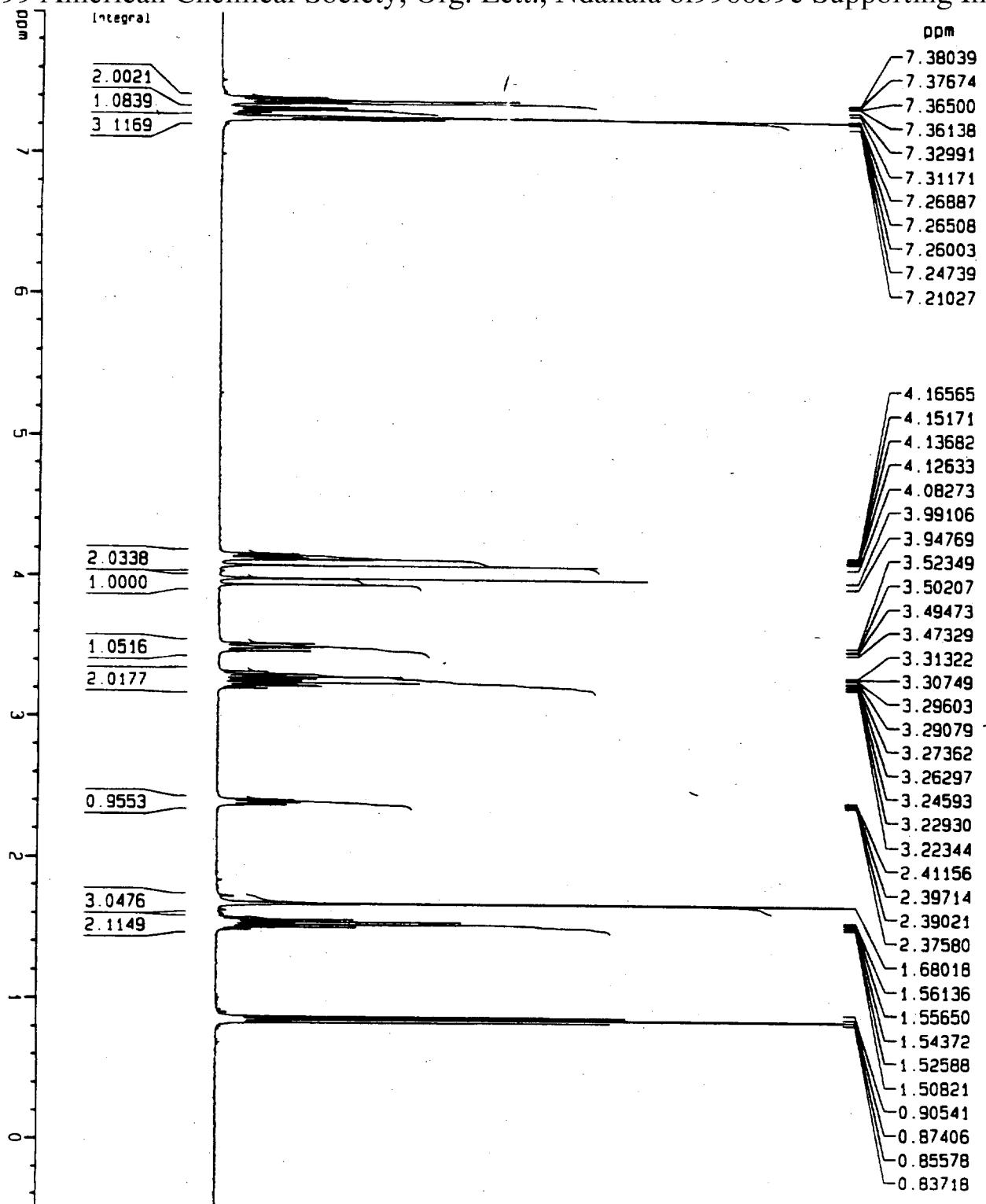
2-Azido-2-(hydroxymethyl)-3-phenyloxetane (3b). TMSN₃ (0.22 g, 1.85 mmol) was added to a stirred solution of 3-phenyl-1,5-dioxaspiro[3.2]hexane (**1a**) (0.20 g, 1.23 mmol) in dry ether (2 mL). The reaction mixture was left to stir overnight at RT. It was then concentrated to provide a colorless oil, 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 (CDCl₃) 3441, 3062, 3031, 2971, 2903, 2116, 1590, 1493, 1452, 1257, 1048, 946 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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 ($\text{M}^+ - \text{N}_2$), 159 ($\text{M}^+ - \text{N}_2 - \text{CH}_2\text{O}$), 129, 120, 117 (100), 103, 90, 89, 77, 63, 51; Anal. calcd for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2$: 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 ($\text{M}^+ - \text{H}_2\text{O}$), 147 ($\text{M}^+ - \text{CH}_2\text{OH}$), 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.

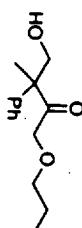


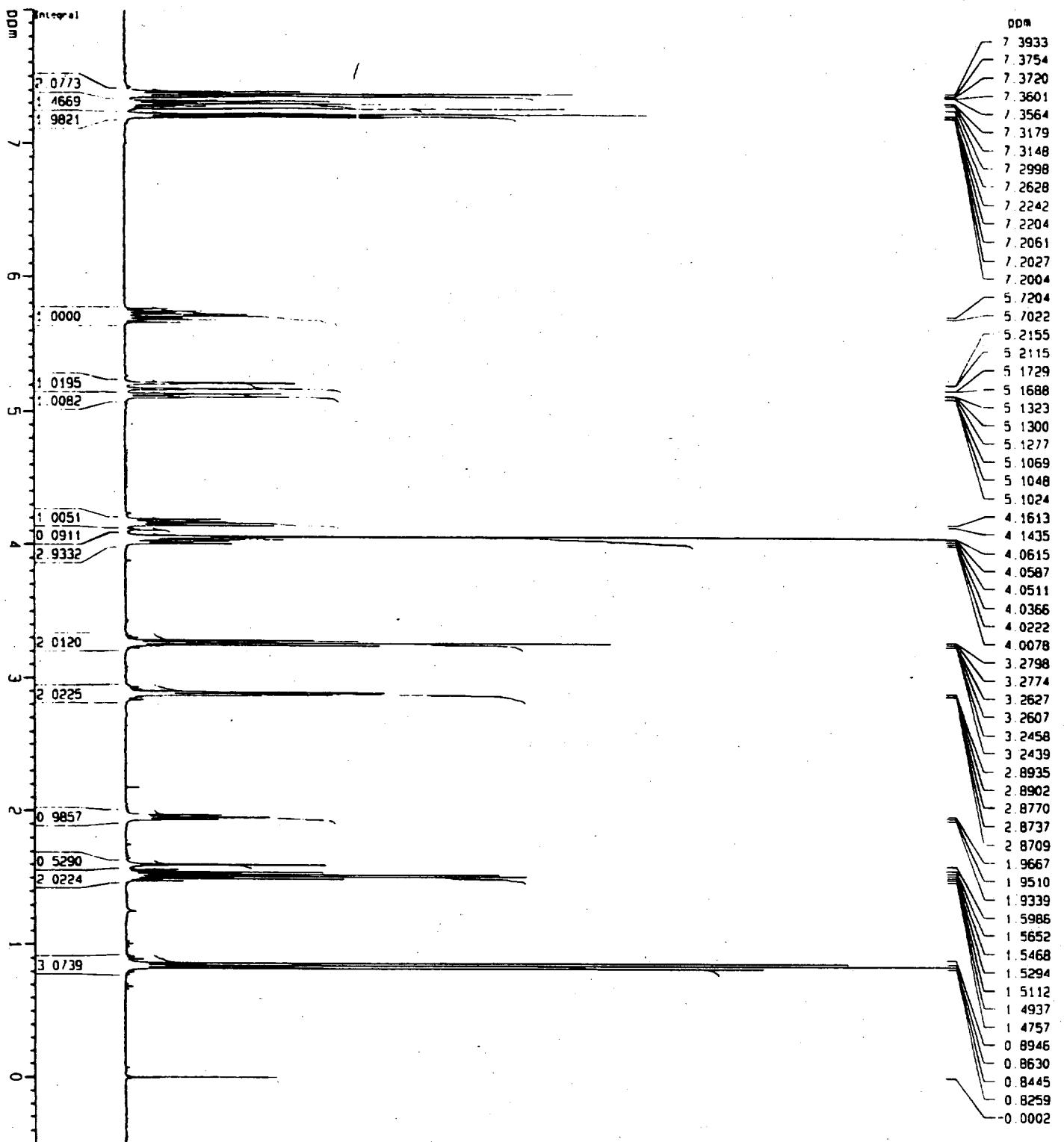
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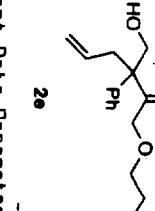
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PULPROG: zg30

TD: 65536

SOLVENT: CDCl3

NS: 0

DS: 32

SWH: 8012.820 Hz

FIDRES: 0.122266 Hz

AQ: 4.0884966 sec

RG: 574.7

DM: 62 400 use

DE: 7.14 use

TE: 240.0 K

D1: 5.0000000 sec

P1: 7.40 use

SF: 400.1320340 MHz

NUC1: 1H

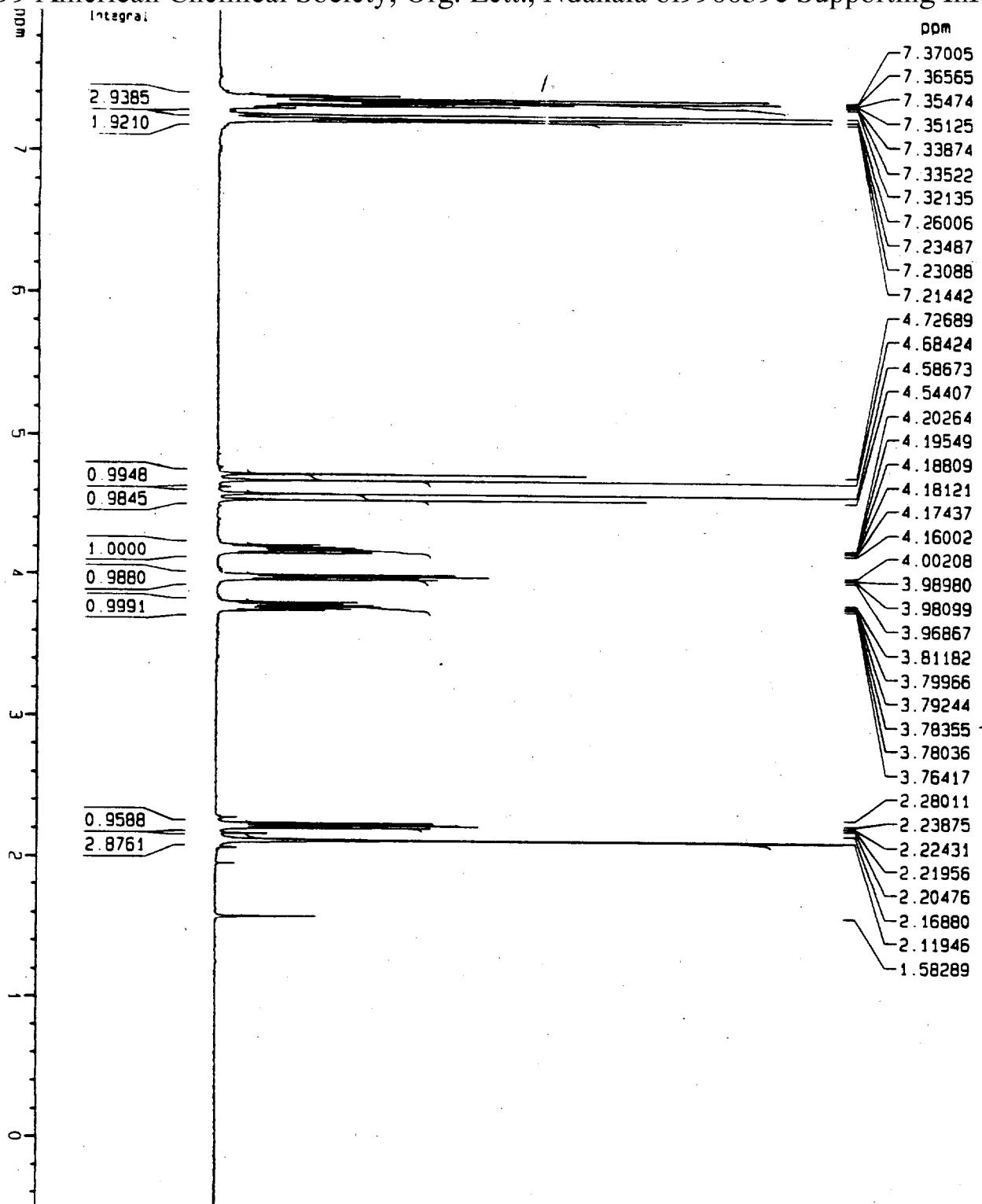
PL1: 0.00 dB

F2 - Processing parameters

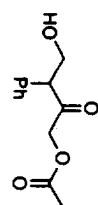
SI: 32768
SF: 400.1300081 MHz
WDW: EM
SSB: 0
LB: 0.00 Hz
GB: 0
PC: 4.00

1D NMR plot parameters

CX: 20.00 ppm
F1P: 8.000 ppm
F1: 320.04 Hz
F2P: -0.500 ppm
F2: -200.07 Hz
PPMCM: 0.42500 ppm
HZCM: 0.05525 Hz



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Current Data Parameters
 NAM 8JN4-041-1
 EXPNO 2
 PROCN 1

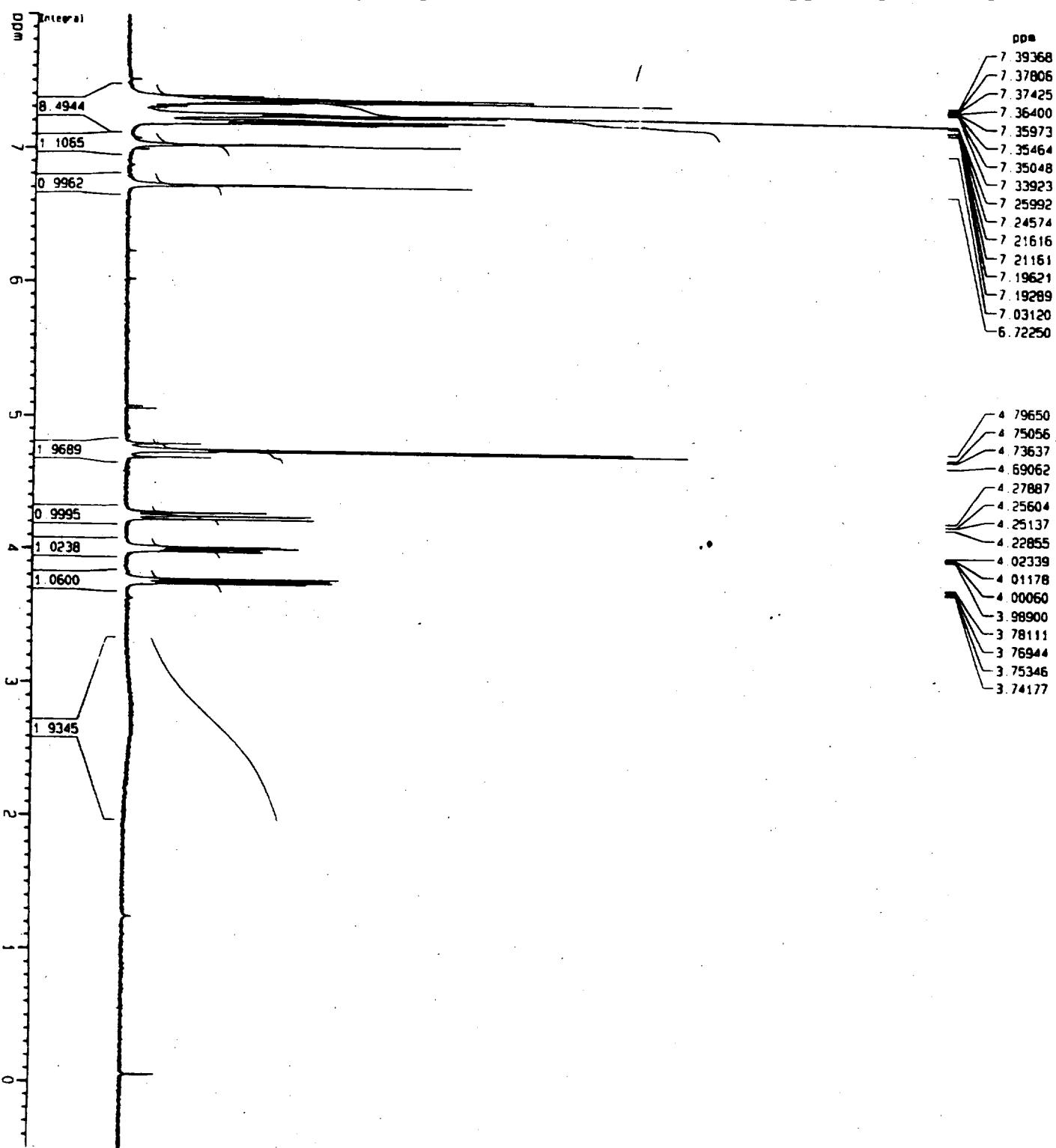
F2 - Acquisition Parameters

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 TIME 13.02
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 PROBD 5 mm QNP 1H
 PULPROG 2930
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 8223.685 Hz
 FIDRES 0.250567 Hz
 A0 1.982344 sec
 RG 812.7
 DM 60.800 usec
 DE 4.50 usec
 TE 300.0 K
 D1 4.0000000 sec
 P1 8.70 usec
 PR 4.50 usec
 SP01 400.1324710 Hz
 NUC1 1H
 PL1 1.00 dB

F2 - Processing parameters

S1 16384
 SF 400.1300092 MHz
 MDW 16M
 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
 PR1W 0.42500 ppm/cm
 HZCM 1.0 0.05525 Hz/cm



Current Data Parameters

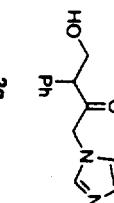
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EXPNO		1
PROCNO		1

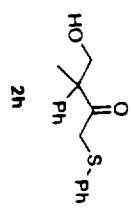
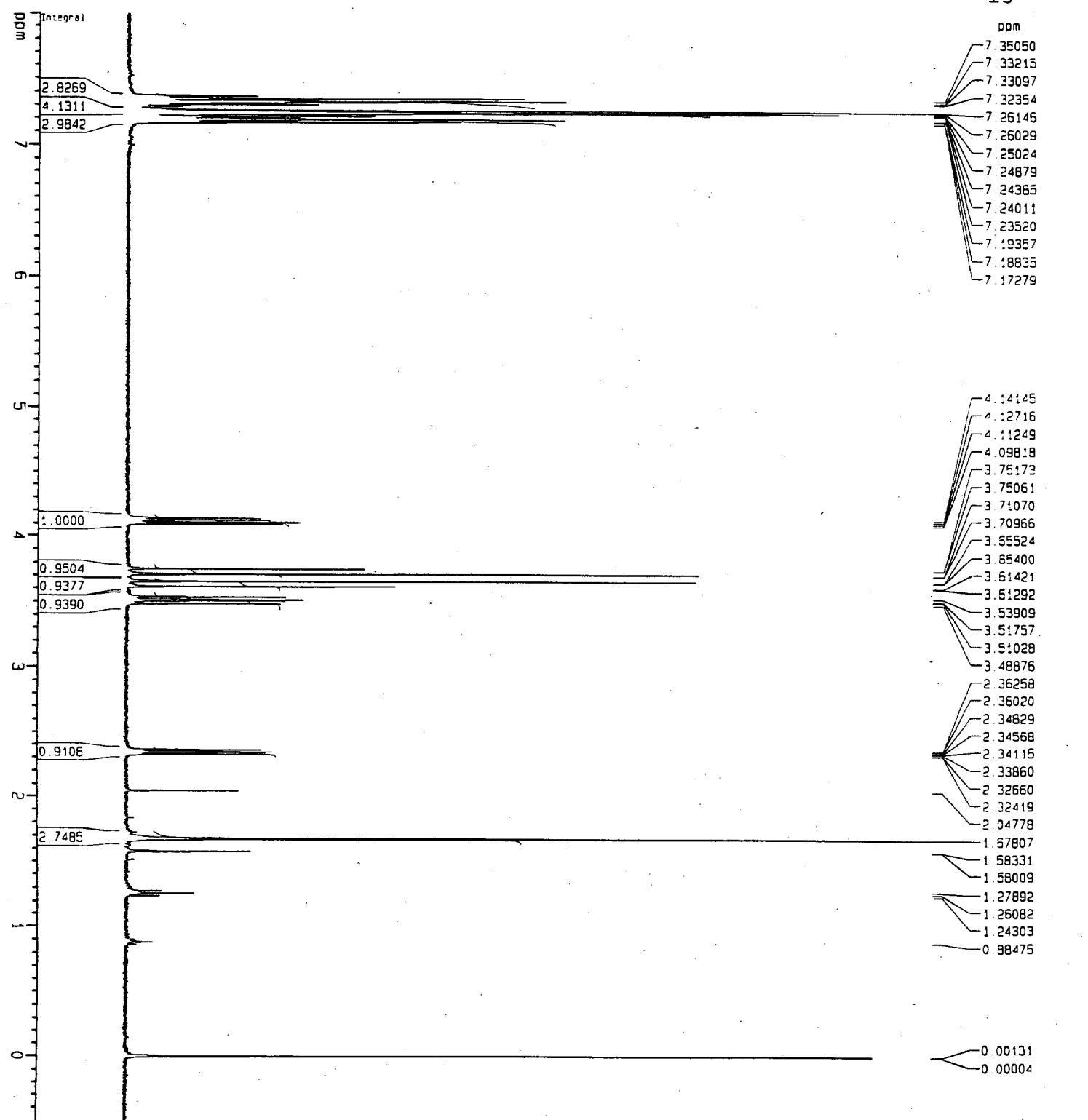
F2 - Acquisition Parameters

Date	980813
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INSTRUM	drx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDC13
NS	8
DS	0
SWH	8012.820 Hz
FTORES	0.122265 Hz
AQ	4.0894966 sec
RG	574.7
DW	62.400 use
DE	7.14 use
TE	240.0 K
D1	5.0000000 sec
P1	7.40 use
DE	7.14 use
NUC1	400.1320340 MHz
PL1	1H

F2 - Processing parameters

CX	20.00 cm
CP	8.000 ppm
C1	3201.04 Hz
C2P	-0.500 ppm
C2	-200.07 Hz
CPCM	42500 ppm
CPM	0.0525 Hz





F2 - Acquisition Parameters

NAME	bjn5-015-1
EXPT	1
PROCND	1

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

FORES 0.122266 Hz

AQ 4.0894966 sec

RG 574.7

DD 62.400 use

DE 7.14 use

D1 240.0 K

P1 7.40 use

DE 7.14 use

D1 5.0000000 sec

P1 7.40 use

DE 7.14 use

D1 400.1320340 MHz

P1 1H

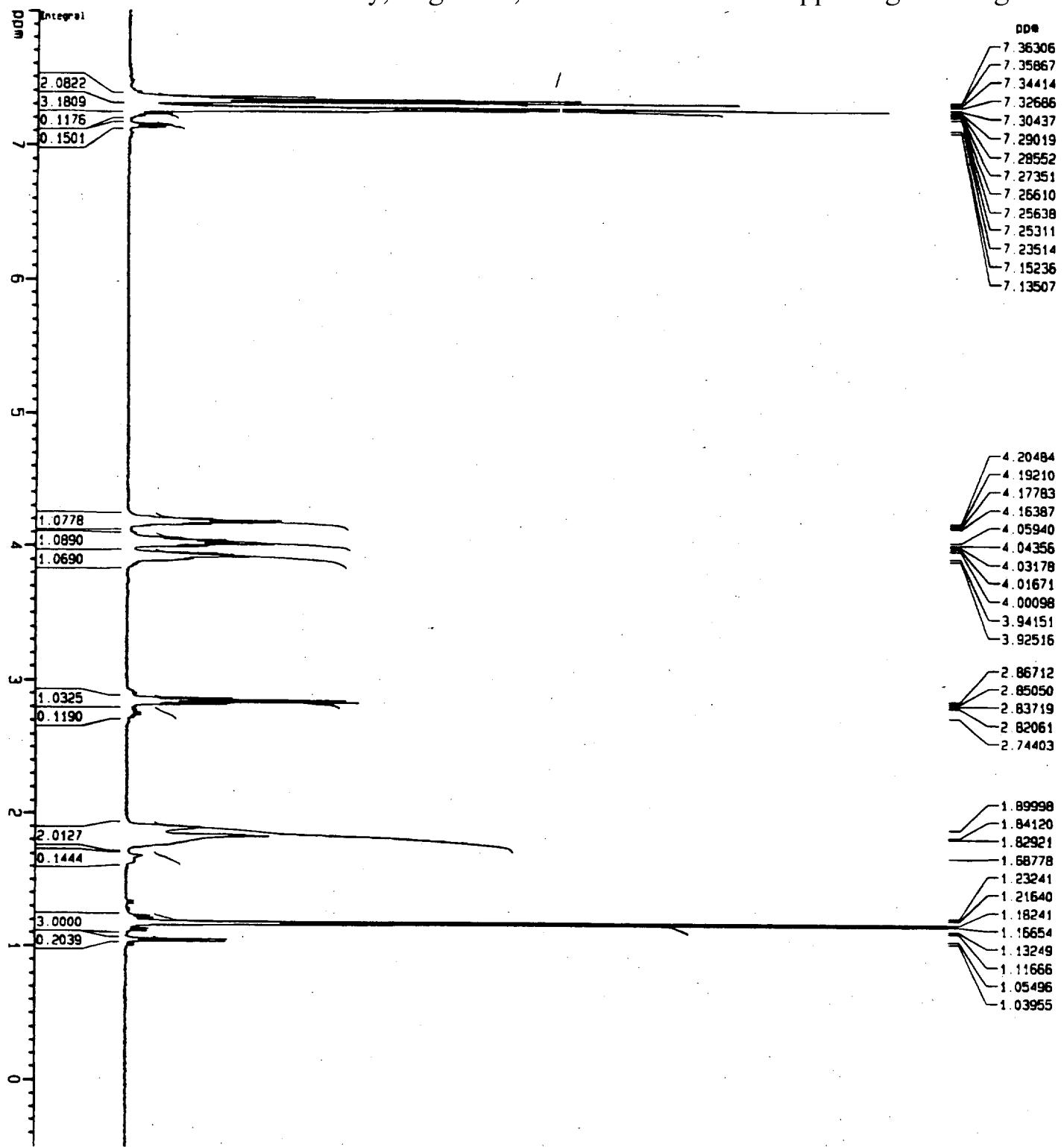
PL1 0.00 dB

F2 - Processing parameters

CX	20.00 cm
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
PPCM	0.42500 ppm
Hz/cm) 05525 Hz/

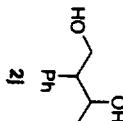


Current Data Parameters

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EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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TIME	8.54
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ID	65536
SOLVENT	CDCl ₃
NS	16
DS	0
SWH	8012.820 Hz
FORES	0.122266 Hz
AQ	4.0894966 sec
RG	574.7
DM	62.400 use
DE	7.14 use
TE	240.0 K
D1	5.0000000 sec
P1	7.40 use
DE	7.14 use
SFO1	400.1320340 MHz
NUC1	¹ H
PL1	0.00 dB



F2 - Processing 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
PC	4.00

1D NMR plot parameters

SI	32768
SF	400.1300120 MHz
WDW	EM
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PC	4.00



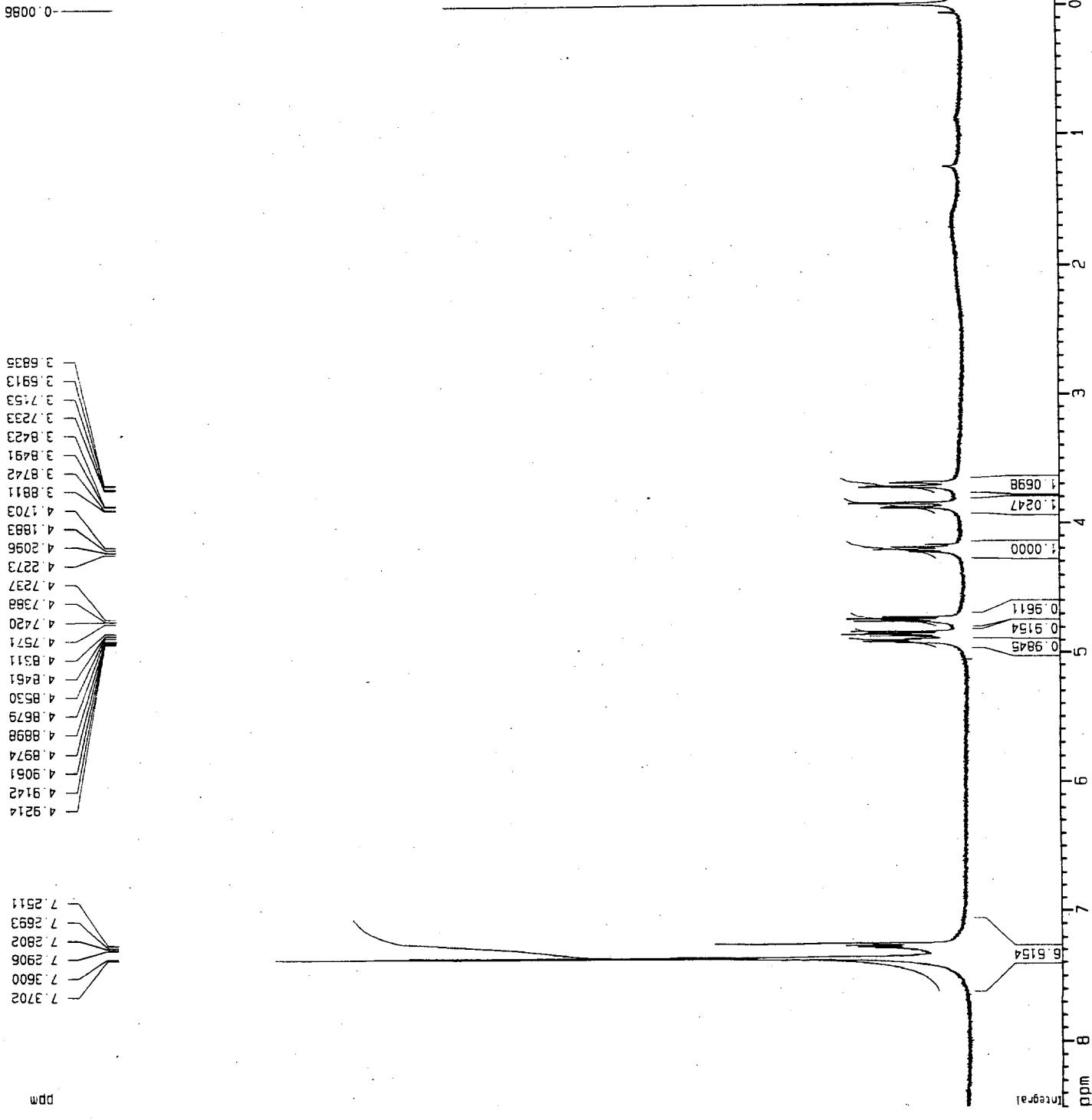
8

Current Data Parameters

NAME EXPNO PROCN0
gg0-2-091-1

EE2 = Acquisition Parameters

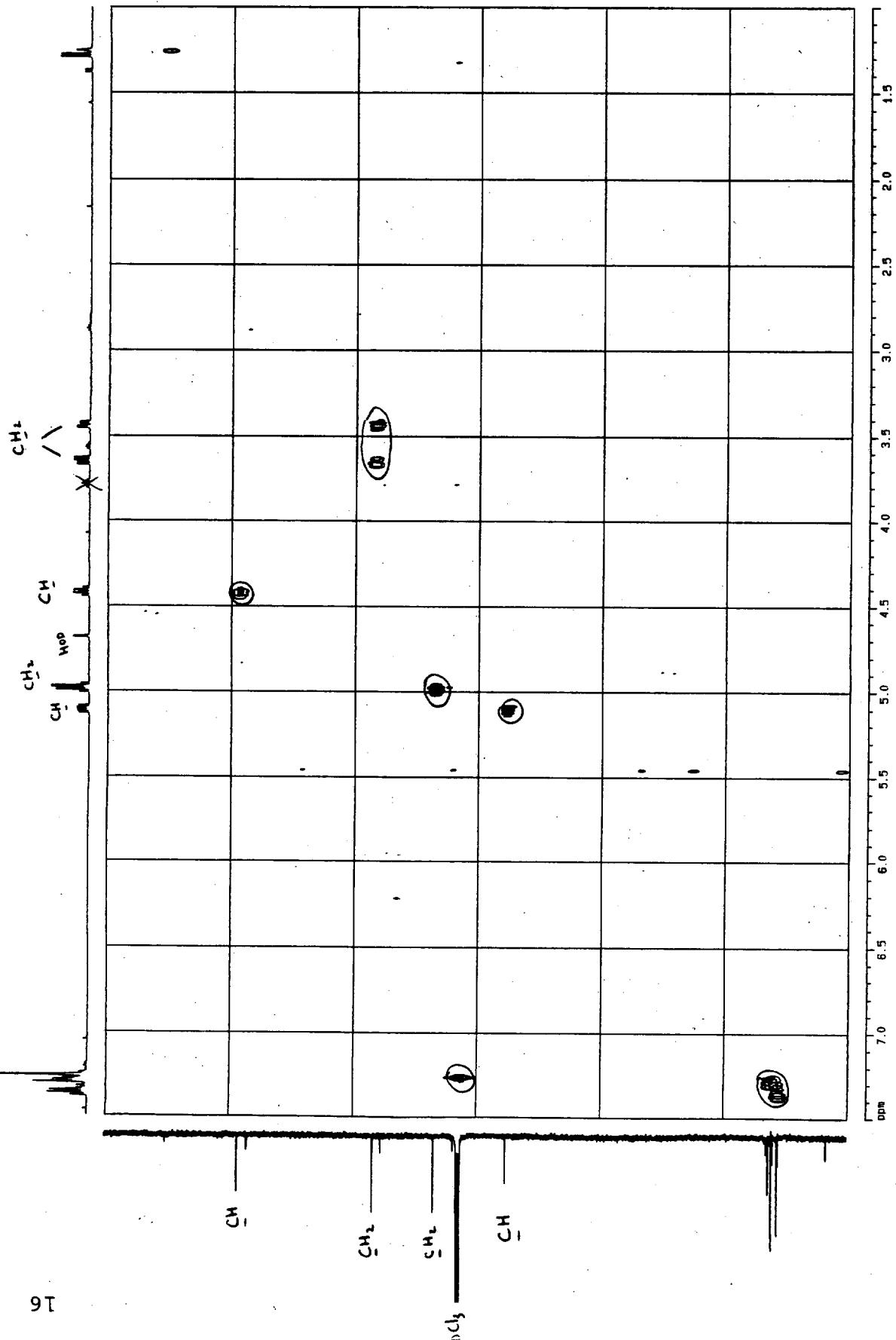
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INSTRUM	drx400
PROBHD	5 mm QNP 1H
PULPROG	2930
TD	65536
SOLVENT	CDC13



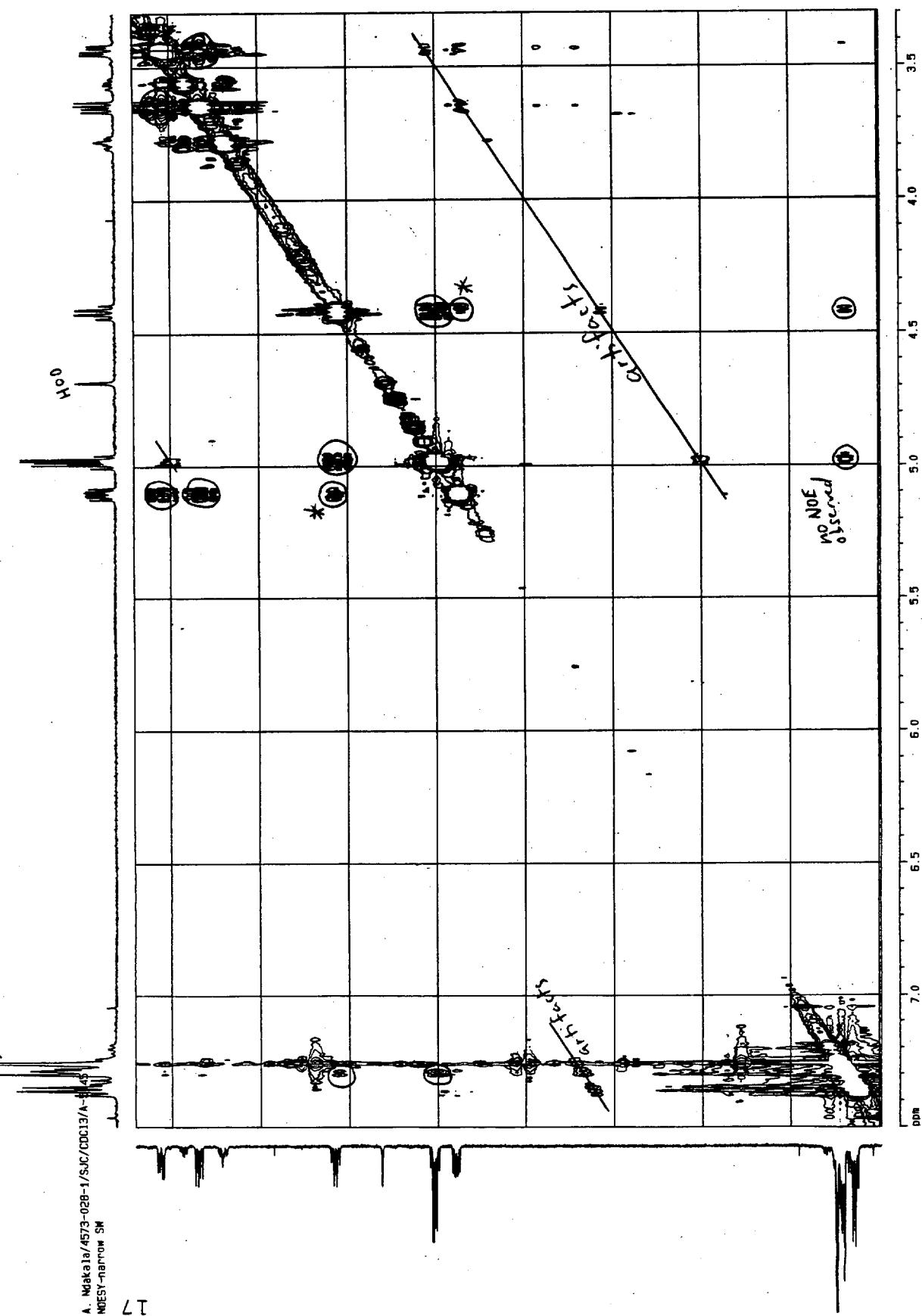
51

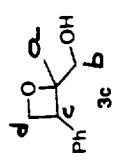
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EDATE	1
PRODNO	

R2 - Acquisition Page#1



F2 - Acquisition Parameter		F3 - Processing parameter		F4 - Output parameter	
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FILPROB	0			3.200	mm
TO	2048			1024.00	mm
SOLVENT	CDC13			512.00	mm
NG	16			256.00	mm
SBH	300.800	Hz		128.00	mm
FUTURES	1.471511	Hz		64.00	mm
SPW1	0.348207	Hz		32.00	mm
SPW2	0.100000	Hz		16.00	mm
SPW3	0.033333	Hz		8.00	mm
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Current Data Parameters
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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PULPROG PULPROG
T0 65536
SOLVENT CDCl₃
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec.
RG 256
DW 62.400 us
DE 7.14 us
TE 240.0 K
D1 5.0000000 sec
P1 7.40 us
DE 7.14 us
SF01 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
HzCM 180.05850 Hz

