

Novel Carboxylated Pyrrole- and Carbazole-Based Monomers.

Synthesis and Electro-Oxidation Features

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Supporting Information

Content

General Information.....	S1
Characterization Data of All New Compounds.....	S1-S9
Electrochemical Data for Compounds 9b & 6b	S10
Copies of NMR Spectra for All New Compounds.....	S11-S45

General Information:

Flash chromatography was performed on Merck silica gel (40-60 mesh) at medium pressure (200 mbar). TLC was done on Merck silica gel plates (60F₂₅₄) with a fluorescent indicator. 3 & 4 Å molecular sieves (Aldrich, for solvent dehydration) were activated before use by drying at 300 °C (18 h, 0.1 mm Hg). Infrared spectra were recorded on a FT-IR Bruker Tensor 27 spectrometer using either neat samples (KBr cell) or as 1 % weight KBr dispersion pellets. ¹H and ¹³C-NMR spectra were recorded on a Bruker DPX 300 or DRX 600 Fourier transform spectrometers at the Department of Chemistry (Bar-Ilan University). ¹H-NMR (300 or 600 MHz, reference: internal Me₄Si) and ¹³C-NMR (75 MHz) spectra were obtained exclusively in CDCl₃. NMR data are presented in the following order: chemical shift, assignment, peak multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constant, proton number/integration. Depending on samples, mass spectra were obtained on several apparatuses, - a Q-TOF MS Micro (Micromass, electrospray mode), a Finnigan Low/High Resolution Mass Spectrometer (DCI, CH₄), or a VG AutoSpec (Fisons Instruments, FAB) in *m*-nitrobenzyl alcohol or glycerol matrices -.

Characterization Data of All New Compounds:

(S)-2-Pyrrol-1-yl-pentanedioic acid 1-benzyl ester (1a). Pale yellow mobile oil; FT-IR (neat, ν in cm⁻¹): 698 (w), 733 (w), 1093 (w), 1174 (w), 1385 (w), 1456 (w), 1489 (w), 1541 (m), 1558 (m), 1716 (s), 1734 (s), 2939 (w), 3676-3649 (m); ¹H-NMR (300 MHz, CDCl₃,) δ 2.18-2.48 (m, 4H), 4.73-4.80 (dd, J = 9.8 and 5.6 Hz, 1H), 5.16 (s, 2H), 6.21 (t, J = 2.1 Hz, 2H), 6.73 (t, J = 2.3 Hz, 2H), 7.27-7.65 (m, 5H); ¹³C-NMR (75 MHz, CDCl₃) δ 27.6, 29.5, 60.5, 67.3, 109.1, 120.0, 128.0, 128.4, 128.6, 135.1, 169.9, 178.4; MS (DCI, CH₄): *m/z* 287 [MH⁺, 100%], 152 (64%), 106

(49.1%), 91 (48.1%); HRMS (DCI, CH₄): *m/z* Calcd. for C₁₆H₁₇NO₄ [MH⁺] = 287.1157, found 287.1123 (3.4 mDa); $[\alpha]_D^{25} = -4.1^\circ$ (C = 5.56, CH₂Cl₂ (DCM))

(S)-2-Carbazol-9-yl-pentanedioic acid 1-benzyl ester (1b). Off-white solid (mp: 97-99 °C); FT-IR (KBr pellet, ν in cm⁻¹): 697 (w), 724 (w), 751 (w), 1157 (w), 1237 (w), 1329 (w), 1453 (w), 1483 (w), 1535 (w), 1597 (w), 1647 (s), 1734 (s), 2931 (w), 3061 (w), 3319 (w); ¹H-NMR (300 MHz, CDCl₃) δ 2.30-2.42 (m, 2H), 2.79-3.02 (m, 2H), 5.30 (s, 2H), 5.67 (dd, *J* = 9.6 and 6.0 Hz, 1H), 7.19-7.24 (m, 2H), 7.35-7.60 (m, 9H), 8.28 (d, *J* = 7.8 Hz, 2H), 10.89 (bs, 1H); ¹³C-NMR (75 MHz, CDCl₃) δ 24.5, 29.7, 55.6, 67.3, 109.4, 119.8, 120.5, 123.5, 126.0, 128.1, 128.2, 128.4, 135.0, 139.9, 170.1, 178.8; MS (DCI, CH₄): *m/z* 387 [MH⁺, 58%], 252 (100%), 206 (36%), 91 (26%); HRMS (DCI, CH₄): *m/z* Calcd. for C₂₄H₂₁NO₄ [MH⁺] = 387.1470, found 387.1440 (3.1 mDa); $[\alpha]_D^{25} = -35.0^\circ$ (C = 3.0, DCM)

4-{2-[2-((S)-4-Benzoyloxycarbonyl-4-carbazol-9-yl-butryrylamino)-ethylamino]-ethylcarbamoyl}-(S)-2-carbazol-9-yl-butyric acid benzyl ester (3b). Pale yellow viscous oil, FT-IR (KBr, ν in cm⁻¹): 750 (s), 997 (m), 1091 (m), 1232 (s), 1337 (s), 1450 (s), 1655 (s), 1738 (s), 2931 (s), 3053 (s), 3255 (s); ¹H-NMR (300 MHz, CDCl₃) δ 1.57-1.62 (m, 4H), 1.84 (dt, *J* = 15.9 and 6.0 Hz, 4H), 2.30 (bs, 3H), 2.32-2.35 (m, 4H), 2.54-2.63 (m, 4H), 2.93-3.01 (m, 4H), 5.04-5.05 (s, 4H), 5.46-5.49 (m, 2H), 6.98 (d, *J* = 2.1 Hz, 2H), 7.00 (m, 2H), 7.17-7.30 (m, 28H), 8.01-8.03 (d, *J* = 7.8 Hz, 4H); ¹³C-NMR (75 MHz, CDCl₃) δ 24.9, 31.0, 38.6, 47.9, 55.6, 67.2, 109.7, 119.7, 120.3, 123.3, 125.9, 128.1, 128.3, 128.4, 135.2, 140.0, 170.2, 171.8; FAB-MS: 842 [MH⁺, 100%], 206 (61%), 193 (17%), 180 (26%), FAB-HRMS (positive mode ionization, *m*-nitrobenzyl alcohol matrix): *m/z* Calcd. for C₅₂H₅₂N₅O₆ [MH⁺] = 842.39176, found 842.39126 (0.5 mDa); $[\alpha]_D^{25} = -33.5^\circ$ (C = 4.92, DCM)

4-{[2-[(S)-4-Benzylloxycarbonyl-4-carbazol-9-yl-butyrylamino)-ethyl]-[4-{bis-[2-((S)-4-benzylloxycarbonyl-4-carbazol-9-yl-butyrylamino)-ethyl]-carbamoyl}-benzoyl]-amino}-ethylcarbamoyl}-(S)-2-carbazol-9-yl-butrylic acid benzyl ester (4b). Pale yellow foamy solid (mp: 109-111 °C); FT-IR (KBr, ν in cm^{-1}): 621 (w), 750 (w), 804 (s), 1025 (s), 1101 (w), 1261 (s), 1453 (m), 1653 (m), 1738 (m), 2891 (m), 2964 (m); $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.26-1.40 (m, 2H), 1.42-1.58 (m, 2H), 1.76-1.90 (m, 2H), 1.92-2.08 (m, 2H), 2.30-2.45 (m, 4H), 2.45-2.61 (m, 4H), 2.59-2.83 (m, 8H), 3.10-3.40 (m, 8H), 5.05 (s, 8H), 5.18 (t, $J = 8.1$ Hz, 2H), 5.58 (dd, $J = 10.8, 5.4$ Hz, 2H), 6.24 (bs, 2H), 6.57 (bs, 2H), 6.64 (s, 4H), 6.98 (t, $J = 5.4$ Hz, 8H), 7.06-7.23 (m, 28H), 7.31 (s, 8H), 8.00 (dd, $J = 12.6$ and 7.5 Hz, 8H); $^1\text{H-NMR}$ (600 MHz, CDCl_3 , 280 °K) δ 1.24 (bs, 2H), 1.40 (bs, 2H), 1.79-1.82 (m, 2H), 1.91-1.94 (m, 2H), 2.35 (s, 4H), 2.49 (s, 2H), 2.56 (s, 2H), 2.66 (bs, 6H), 2.74 (s, 2H), 3.19 (s, 2H), 3.26 (s, 6H), 5.05 (s, 8H), 5.18 (s, 2H), 5.58 (s, 2H), 6.24 (bs, 2H), 6.57 (bs, 2H), 6.64 (s, 4H), 6.98 (t, $J = 5.4$ Hz, 8H), 7.06-7.21 (m, 28H), 7.31 (s, 8H), 8.00 (dd, $J = 13.0, 8.0$ Hz, 8H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 25.2, 31.4, 31.7, 37.6, 38.8, 46.0, 49.0, 55.8, 56.0, 67.3, 67.4, 109.5, 109.7, 119.7, 119.8, 120.4, 123.3, 123.4, 126.0, 126.3, 128.1, 128.2, 128.4, 128.5, 135.1, 135.2, 136.6, 140.1, 170.0, 170.4, 171.8, 172.5; EI-MS: m/z 1814 [MH^+ , 54%], 1352 (41%), 1341 (83%), 927 (12%), 609 (20%), 447 (47%), 431 (100%); FAB-HRMS (positive mode ionization, *m*-nitrobenzyl alcohol matrix): m/z Calcd. for $\text{C}_{112}\text{H}_{104}\text{N}_{10}\text{O}_{14}$ [M^+] = 1812.773, found 1812.747 (-26.7 mDa); $[\alpha]_D^{25} = -66.3^\circ$ ($C = 1.3$, THF)

4-{(3,5-Bis-{bis-[2-((S)-4-benzylloxycarbonyl-4-pyrrol-1-yl-butyrylamino)-ethyl]-carbamoyl}-benzoyl)-[2-((S)-4-benzylloxycarbonyl-4-pyrrol-1-yl-butyrylamino)-ethyl]-amino}-ethylcarbamoyl}-(S)-2-pyrrol-1-yl-butrylic acid benzyl ester (5a). Pale yellow oil, FT-IR (KBr, ν in cm^{-1}): 621 (w), 698 (m), 730 (m), 803 (w), 1025 (m), 1093 (s), 1169 (m), 1261 (s), 1455 (m), 1490 (m), 1544 (m), 1653 (s), 1741 (s), 2927 (m), 2961 (w), 3307 (w); $^1\text{H-NMR}$ (300 MHz,

CDCl_3) δ 1.92 (m, 12H), 2.14-2.50 (m, 12H), 3.11-3.52 (m, 24H), 4.70 (bs, 6H), 5.10 (s, 12H), 6.12 (s, 12H), 6.46 (bs, 2H), 6.72 (s, 12H), 6.73 (bs, 2H), 7.20-7.35 (m, 33H); $^1\text{H-NMR}$ (600 MHz, CDCl_3 , 280 °K) δ 1.90-1.91 (m, 12H), 2.10-2.80 (m, 6H), 2.25-2.26 (m, 3H), 2.39-2.41 (m, 3H), 3.10 (bs, 6H), 3.23 (bs, 6H), 3.38 (bs, 6H), 3.51 (bs, 6H), 4.69 (dd, $J = 10.4$ Hz, 3H), 4.71 (dd, $J = 10.4$ Hz, 3H), 5.10 (s, 12H), 6.11 (s, 12H), 6.66 (s, 12H), 7.22-7.26 (m, 12H), 7.30-7.33 (m, 12H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 24.7, 25.0, 30.7, 31.1, 37.8, 45.5, 49.1, 55.7, 67.2, 109.7, 119.7, 120.4, 123.3, 126.0, 127.2, 128.0, 128.3, 128.4, 135.1, 136.3, 140.0, 170.4, 170.5, 172.3; TOF-MS (ES, positive mode ionization): 2081 [MH^+ , 100%]; FAB-HRMS (positive mode ionization, *m*-nitrobenzyl alcohol matrix): *m/z* Calcd. for $\text{C}_{117}\text{H}_{129}\text{N}_{15}\text{O}_{21}$ [M^+] = 2080.952, found 2080.933 (18.3 mDa); $[\alpha]_D^{25} = -13.3^\circ$ (C = 0.7, THF)

4-(2-{(3,5-Bis-{bis-[2-((S)-4-benzyloxycarbonyl-4-carbazol-9-yl-butryrylamino)-ethyl]-carbamoyl}-benzoyl)-[2-((S)-4-benzyloxycarbonyl-4-carbazol-9-yl-butryrylamino)-ethyl]-amino}-ethyl-carbamoyl)-(S)-2-carbazol-9-yl-butryric acid benzyl ester (5b). Pale yellow solid (mp : 104-106 °C); FT-IR (KBr, ν in cm^{-1}): 699 (w), 750 (m), 804 (s), 1024 (s), 1095 (s), 1161 (s), 1261 (s), 1337 (w), 1452 (m), 1485 (w), 1542 (w), 1653 (m), 1737 (m), 2963 (w), 3300 (w); $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.40-1.55 (m, 6H), 1.50-1.85 (m, 6H), 2.22-2.41 (m, 6H), 2.38-2.63 (m, 6H), 2.62-2.87 (m, 12H), 3.05-3.25 (m, 12H), 4.87-5.02 (m, 12H), 5.27-5.39 (m, 6H), 5.68 (bs, 2H), 6.15 (bs, 2H), 6.57 (bs, 2H), 6.89 (t, $J = 8.1$ Hz, 12H), 7.02-7.27 (m, 54H), 7.92 (dd, $J = 16.2, 7.5$ Hz, 12H); $^1\text{H-NMR}$ (600 MHz, CDCl_3 , 280 °K) δ 1.45 (bs, 6H), 1.62 (bs, 3H), 1.72 (bs, 3H), 2.31 (bs, 6H), 2.5-2.87 (m, 24H), 3.1-3.26 (m, 12H), 4.91-4.95 (m, 6H), 5.01 (bs, 12H), 5.37-5.41 (m, 6H), 6.15 (bs, 2H), (bs, 2H), 6.57 (bs, 2H), 6.91 (d, $J = 9.0$ Hz, 6H), 6.99 (d, $J = 9.0$ Hz, 6H), 7.1-7.35 (m, 54H), 7.92 (s, 12H), 7.99 (d, $J = 9.0$ Hz, 6H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 27.9, 28.1, 31.3, 31.6, 37.9, 38.1, 45.5, 49.2, 60.9, 67.2, 108.9, 109.2, 120.3, 126.9,

128.0, 128.3, 128.5, 128.7, 135.3, 136.7, 140.0, 170.4, 170.6, 172.4; TOF-MS (ES +): *m/z* 2681 [M-H⁺, 30%], 1912 (100%), 1341 (10%), 868 (13%), 494 (50%), 431 (97%); FAB-HRMS (positive mode ionization, *m*-nitrobenzyl alcohol matrix): *m/z* Calcd. for C₁₆₅H₁₅₃N₁₅O₂₁ [M⁺] = 2682.15065, found 2682.1535 (-2.9 mDa); $[\alpha]_D^{25} = -83.9^\circ$ (C = 1.9, THF)

4-(2-{(4-{Bis-[2-((S)-4-carboxy-4-pyrrol-1-yl-butyrylamino)-ethyl]-carbamoyl}-benzoyl)-[2-((S)-4-carboxy-4-pyrrol-1-yl-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-pyrrol-1-yl-butrylic acid (6a). Pale yellow foamy solid (mp : 80-82 °C); FT-IR (KBr pellet, ν in cm⁻¹): 734 (m), 860 (w), 1093 (w), 1195 (m), 1263 (m), 1373 (w), 1431 (w), 1551 (m), 1631 (s), 1732 (s), 2941 (w), 3098 (w), 3372 (s); ¹H-NMR (300 MHz, CDCl₃) δ 1.77-2.03 (m, 16H), 3.05-3.45 (m, 16H), 4.72-4.83 (bs, 4H), 6.00 (s, 8H), 6.77 (s, 8H), 7.31 (m, 4H), 7.86-8.02 (m, 4H); ¹³C-NMR (75 MHz, CDCl₃) δ 28.0, 31.0, 31.3, 36.4, 36.9, 44.4, 48.3, 60.2, 60.5, 61.1, 107.8, 108.1, 120.2, 126.4, 137.3, 170.5, 171.2, 171.3, 171.95, 172.02; FAB-MS (negative mode, *m*-nitrobenzyl alcohol matrix): *m/z* 1051 [M-H, 64%], 729 (15%), 639 (29%), 460 (100%), 183 (92%); FAB-HRMS (negative mode, *m*-nitrobenzyl alcohol matrix): *m/z* Calcd. for C₅₂H₆₃N₁₀O₁₄ [M-H] = 1051.4507, found 1051.4510 (5.0 mDa); $[\alpha]_D^{25} = -12.8^\circ$ (C = 2.2, DMF).

4-(2-{(3,5-Bis-{bis-[2-((S)-4-carboxy-4-pyrrol-1-yl-butyrylamino)-ethyl]-carbamoyl}-benzoyl)-[2-((S)-4-carboxy-4-pyrrol-1-yl-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-pyrrol-1-yl-butrylic acid (7a). Pale yellow foam; FT-IR (KBr pellet, ν in cm⁻¹): 733 (m), 806 (w), 904 (w), 952 (w), 1091 (w), 1195 (m), 1262 (s), 1370 (w), 1431 (w), 1484 (w), 1548 (m), 1638 (s), 1734 (m), 2962 (w), 3100 (w), 3370 (m); ¹H-NMR (300 MHz, CDCl₃) δ 1.86-2.30 (m, 24H), 3.05-3.55 (m, 24H), 4.66-4.71 (m, 6H), 6.00 (bs, 12H), 6.76 (m, 12H), 6.45 (bs, 1H), 7.29-7.39 (m, 3H), 7.83-8.04 (m, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ 28.6, 30.9, 31.2, 31.7, 36.9, 37.6, 45.3, 48.9, 61.1, 108.2, 108.6, 120.6, 125.9, 128.2, 128.9, 137.3, 170.0, 171.6, 171.8, 172.5;

FAB-MS (negative mode, *m*-nitrobenzyl alcohol matrix): *m/z* 1538 [M-H, 63%], 518 (72%); FAB-HRMS (negative mode, *m*-nitrobenzyl alcohol matrix): *m/z* Calcd. for C₈₀H₉₂N₁₃O₁₉ [M-H] = 1538.6632, found 1538.6617 (5.0 mDa); $[\alpha]_D^{25} = -13.1^\circ$ (C = 2.4, DMF).

4-(2-{(3,5-Bis-{bis-[2-((S)-4-carbazol-9-yl-4-carboxy-butyrylamino)-ethyl]-carbamoyl}-benzoyl)-[2-((S)-4-carbazol-9-yl-4-carboxy-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-carbazol-9-yl-butrylic acid (7b). Pale yellow foamy solid (mp: 231-233 °C); FT-IR (KBr pellet, ν in cm⁻¹): 724 (w), 753 (m), 1076 (m), 1238 (m), 1332 (s), 1380 (m), 1453 (w), 1629 (s), 1726 (m), 2946 (w), 3057 (w), 3396 (s); ¹H-NMR (300 MHz, CDCl₃) δ 1.73-1.95 (m, 10H), 2.22-2.55 (m, 8H), 2.87-3.25 (m, 30H), 5.54-5.59 (m, 6H), 7.09-7.18 (m, 12H), 7.26-7.53 (m, 28H), 7.81 (bs, 2H), 8.07-8.14 (m, 12H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 25.2, 30.5, 31.1, 31.4, 36.3, 37.0, 44.8, 48.4, 55.8, 67.1, 110.0, 119.0, 120.2, 122.4, 125.0, 125.7, 136.6, 139.3, 139.8, 169.4, 171.4, 171.8; TOF-MS (ES, positive mode ionization): 2141 [M⁺, 94%], 1091 (15%), 641 (46%), 342 (53%); FAB-HRMS (negative mode ionization, *p*-nitrobenzyl alcohol matrix): Calcd. for C₁₂₂H₁₁₆N₁₅O₂₁ [M-H⁺] = 2139.8503, found 2139.8673 (-16.9 mDa); $[\alpha]_D^{25} = -78.5^\circ$ (C = 1.5, THF)

4-(2-{((S)-4-Benzylloxycarbonyl-4-pyrrol-1-yl-butyryl)-[2-((S)-4-benzylloxycarbonyl-4-pyrrol-1-yl-butyrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-pyrrol-1-yl-butrylic acid benzyl ester (8a). Colorless viscous oil; FT-IR (KBr pellet, ν in cm⁻¹): 700 (w), 732 (w), 804 (s), 1024 (s), 1094 (s), 1167 (w), 1262 (s), 1451 (w), 1490 (w), 1541 (w), 1653 (s), 1741 (s), 2963 (m), 3416 (m); ¹H-NMR (300 MHz, CDCl₃) δ 1.82-1.98 (m, 4H), 2.04-2.14 (m, 2H), 2.14-2.28 (m, 3H), 2.32-2.47 (m, 3H), 3.13 (s, 4H), 3.30 (m, 4H), 4.71-4.76 (m, 3H), 5.14 (s, 4H), 6.14-6.18 (m, 6H), 6.66-6.72 (m, 6H), 7.26-7.35 (m, 15H); ¹³C-NMR (75 MHz, CDCl₃) δ 27.9, 28.0, 28.1, 31.0, 31.4, 38.0, 38.6, 45.9, 47.9, 60.4, 60.6, 67.0, 108.8, 109.0, 120.0, 120.1, 127.9, 128.3,

128.5, 135.1, 170.1, 170.2, 171.9, 172.0, 172.6; FAB-MS: 911 [MH⁺, 41%], 642 (15%), 270 (100%), 184 (12%); FAB-HRMS (positive mode ionization, *p*-nitrobenzyl alcohol matrix): Calcd. for C₅₂H₅₉N₆O₉ [MH⁺] = 911.4344, found 911.4378 (-3.5 mDa); $[\alpha]_D^{25} = -25.2^\circ$ (C = 2.4, THF)

4-(2-{{(S)-4-Benzoyloxycarbonyl-4-carbazol-9-yl-butryryl}-[2-((S)-4-benzoyloxycarbonyl-4-carbazol-9-yl-butryrylamino)-ethyl]-amino}-ethylcarbamoyl)-2-carbazol-9-yl-butryric acid benzyl ester (8b). Pale yellow viscous oil; FT-IR (KBr pellet, ν in cm⁻¹): 751 (m), 805 (s), 1024 (s), 1094 (s), 1261 (s), 1337 (w), 1453 (m), 1486 (m), 1523 (m), 1652 (s), 1738 (s), 2963 (s); ¹H-NMR (300 MHz, CDCl₃) δ 1.82-1.98 (m, 4H), 2.04-2.14 (m, 2H), 2.14-2.28 (m, 3H), 2.32-2.47 (m, 3H), 3.09 (s, 4H), 3.23-3.33 (m, 4H), 4.66-4.78 (m, 3H), 5.08 (s, 2H), 5.09 (s, 4H), 6.11-6.14 (m, 6H), 6.36 (bs, 1H), 6.45 (bs, 1H), 6.65-6.67 (m, 6H), 7.20-7.32 (m, 15H), 8.05 (m, 4H); ¹³C-NMR (75 MHz, CDCl₃) δ 24.3, 24.5, 25.0, 27.8, 30.5, 31.2, 38.0, 38.6, 46.5, 47.4, 55.0, 55.4, 55.7, 67.3, 109.7, 119.7, 119.8, 120.4, 123.1, 123.4, 126.0, 128.1, 128.3, 128.5, 135.2, 140.1, 170.2, 170.3, 171.8, 172.1, 172.7; TOF-MS (ES, positive mode ionization): 1211 [M+H⁺, 100%]; FAB-HRMS (positive mode ionization, glycerol matrix): Calcd. for C₇₆H₇₀N₆O₉ [M⁺] = 1211.5267, found 1211.5191 (7.5 mDa); $[\alpha]_D^{25} = -79.0^\circ$ (C = 1.9, THF)

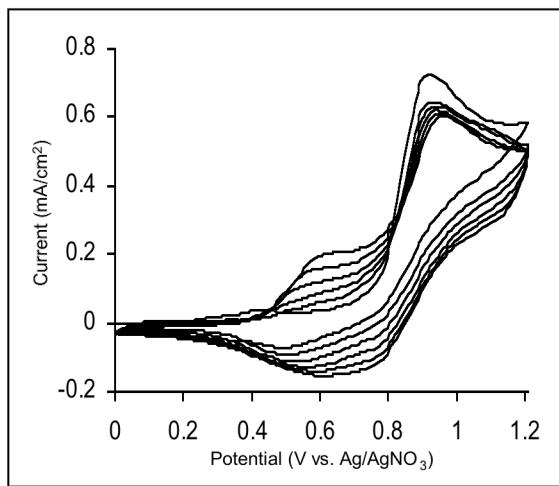
4-(2-{{(S)-4-Carboxy-4-pyrrol-1-yl-butryryl}-[2-((S)-4-carboxy-4-pyrrol-1-yl-butryrylamino)-ethyl]-amino}-ethylcarbamoyl)-(S)-2-pyrrol-1-yl-butryric acid (9a). Pale yellow light foam (turns brown on prolonged storage); FT-IR (KBr pellet, ν in cm⁻¹): 733 (m), 896 (w), 1067 (w), 1093 (w), 1200 (m), 1264 (m), 1369 (w), 1432 (w), 1487 (w), 1550 (w), 1628 (s), 1731 (s), 2577 (s), 2945 (s), 3101 (w), 3366 (s); ¹H-NMR (300 MHz, DMSO-*d*₆) δ 1.75-2.26 (m, 12H), 3.10-3.21 (m, 8H), 4.71 (bs, 3H), 6.00 (s, 6H), 6.76 (s, 6H), 7.86-8.01 (m, 2H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 28.1, 30.5, 31.2, 31.3, 36.8, 37.2, 45.2, 47.0, 60.4, 60.5, 67.1, 107.9, 120.2, 171.3,

171.4, 172.1; EI-MS: 641 [MH⁺, 100%], 623 (16%), 528 (20%), 462 (36%); FAB-HRMS (positive mode ionization, glycerol matrix): Calcd. for C₃₁H₄₀N₆O₉ [M⁺] = 640.2856, found 640.2785 (7.2 mDa); $[\alpha]_D^{25} = -21.6^\circ$ (C = 2.0, THF)

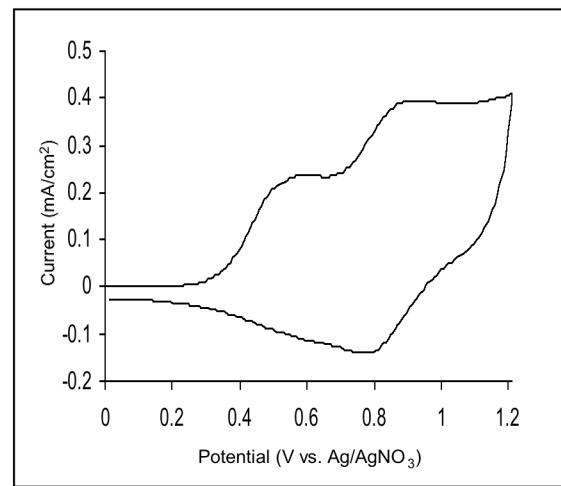
(S)-2-Carbazol-9-yl-4-(2-{{(S)-4-carbazol-9-yl-4-carboxy-butryl)-[2-((S)-4-carbazol-9-yl-4-carboxy-butryl)amino}-ethylcarbamoyl)-butyric acid (9b). Pale yellow solid (mp : 204-206 °C); FT-IR (KBr pellet, ν in cm⁻¹): 722 (m), 752 (s), 886 (w), 1056 (w), 1129 (w), 1159 (s), 1229 (m), 1452 (s), 1484 (m), 1539 (w), 1600 (s), 1627 (s), 1729 (s), 2575 (w), 2876 (w), 2942 (m), 3052 (w), 3393 (m); ¹H-NMR (300 MHz, DMSO-d₆) δ 1.68-2.00 (m, 12H), 2.40-3.00 (m, 8H), 3.60-3.62 (s, 8H), 5.56-5.58 (bs, 3H), 7.13-7.21 (s, 6H), 7.32-7.49 (m, 15H), 8.09-8.15 (m, 4H); ¹³C-NMR (75 MHz, DMSO-d₆) δ 25.1, 28.1, 30.4, 31.2, 34.4, 36.3, 36.7, 45.1, 46.7, 55.4, 55.7, 67.0, 109.9, 119.0, 120.2, 122.5, 124.2, 124.9, 125.6, 139.8, 170.7, 171.1, 171.3, 171.7; FAB-MS (negative mode ionization, *p*-nitrobenzyl alcohol matrix): 939 [M-H, 70%], 473 (100%), 283 (33%), 166 (83%); FAB-HRMS (negative mode ionization, *p*-nitrobenzyl alcohol matrix): Calcd. for C₅₅H₅₁N₆O₉ [M-H] = 939.3717, found 939.3692 (2.5 mDa); $[\alpha]_D^{25} = -96.5^\circ$ (C = 2.1, THF)

Cyclic Voltammograms for the Electropolymerization of Carboxylated Tri/TetraCbz-based Monomers 9b & 6b (5 mm Ø Pt Disk Electrode) Including Voltammetric Responses of Resulting Conducting PolyCbz-Films Poly(9b) & Poly(6b) in Supporting Electrolyte (without monomer)

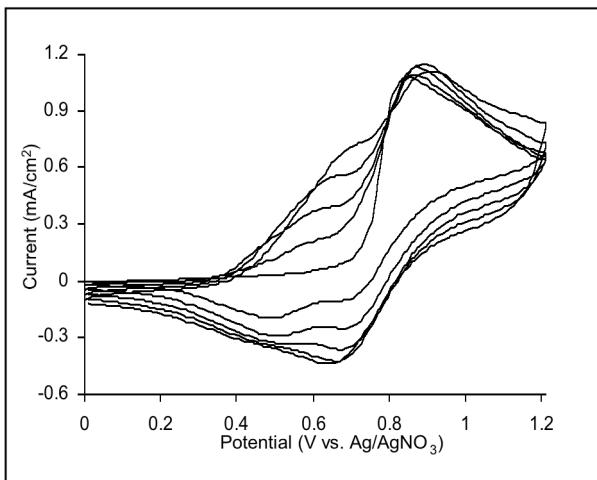
Voltamogramm for the electropolymerization of monomer 9b



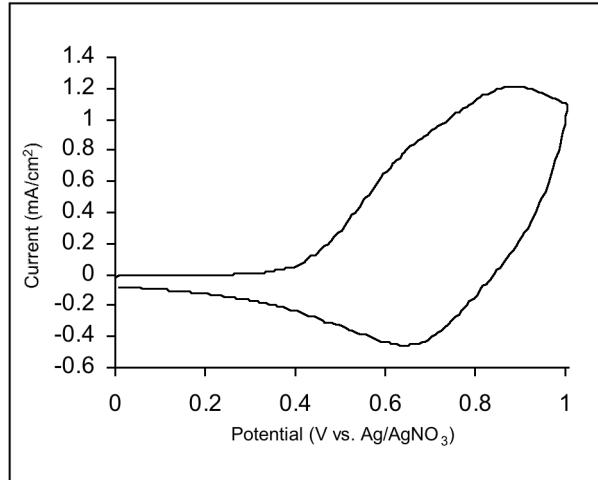
Voltammetric response of the polyCbz-film poly(9b)



Voltamogramm for the electropolymerization of monomer 6b

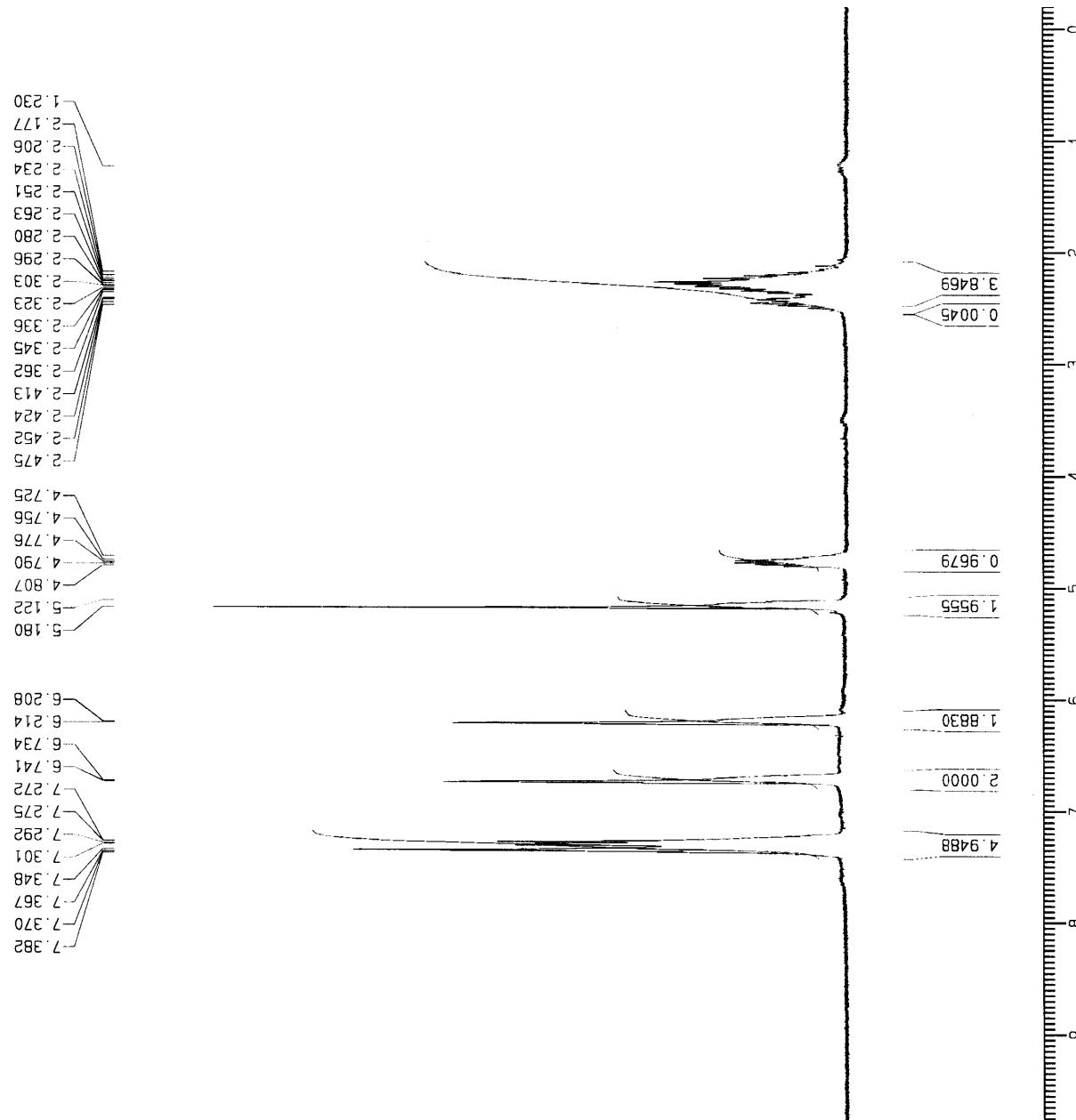


Voltammetric response of the polyCbz-film poly(6b)

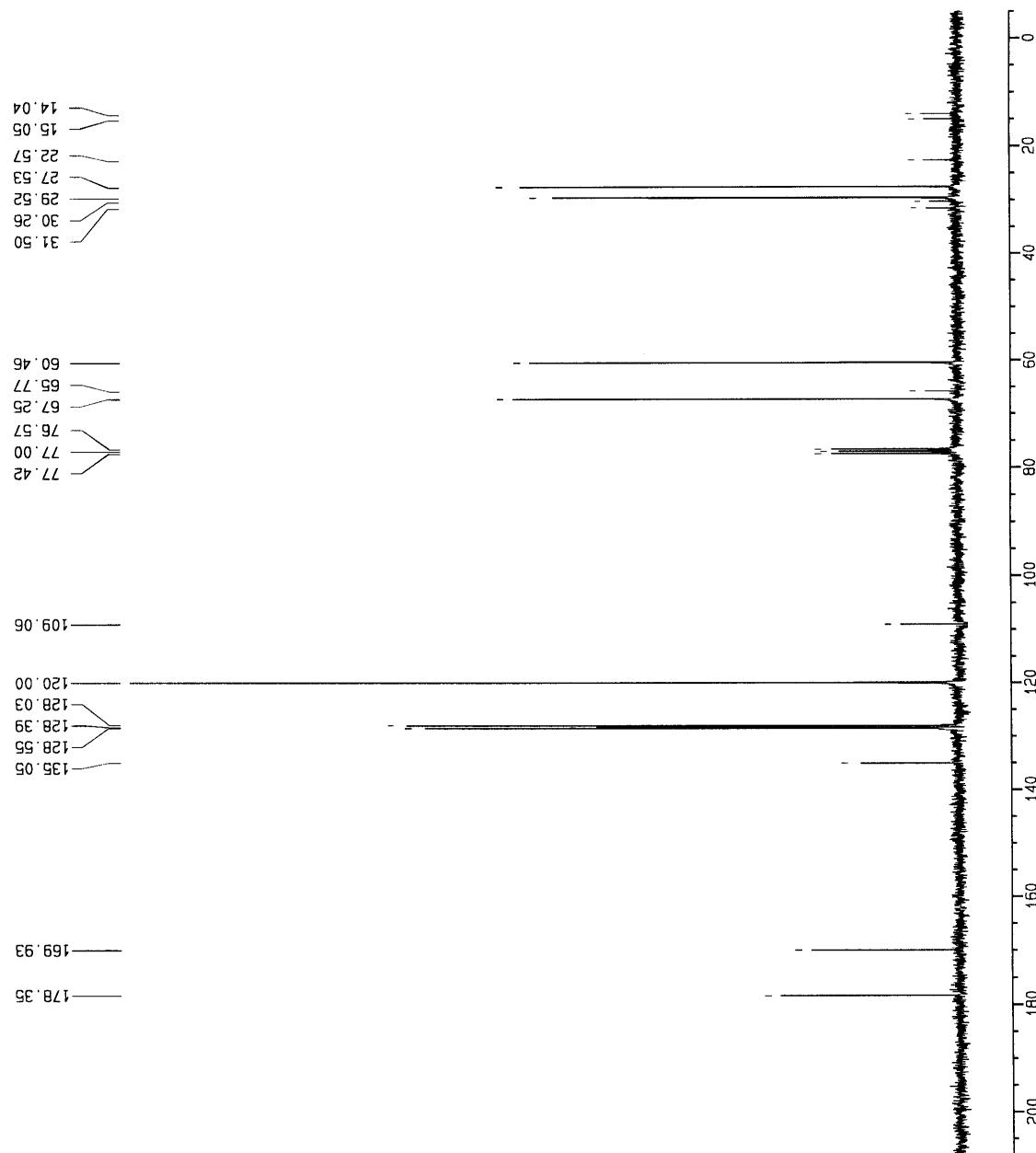


Copies of ^1H - & ^{13}C -NMR Spectra of All New Compound.

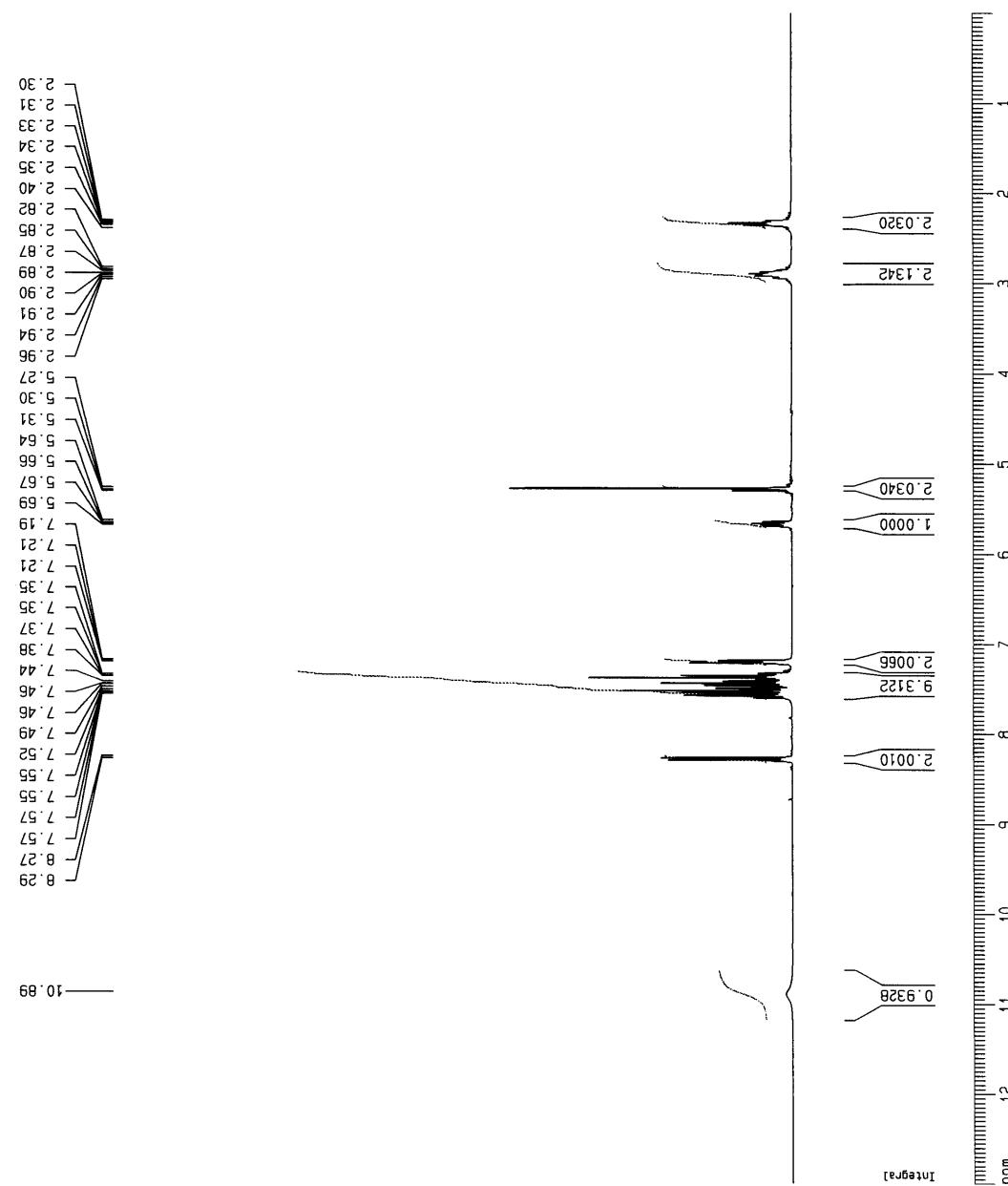
1a $^1\text{H-NMR}$



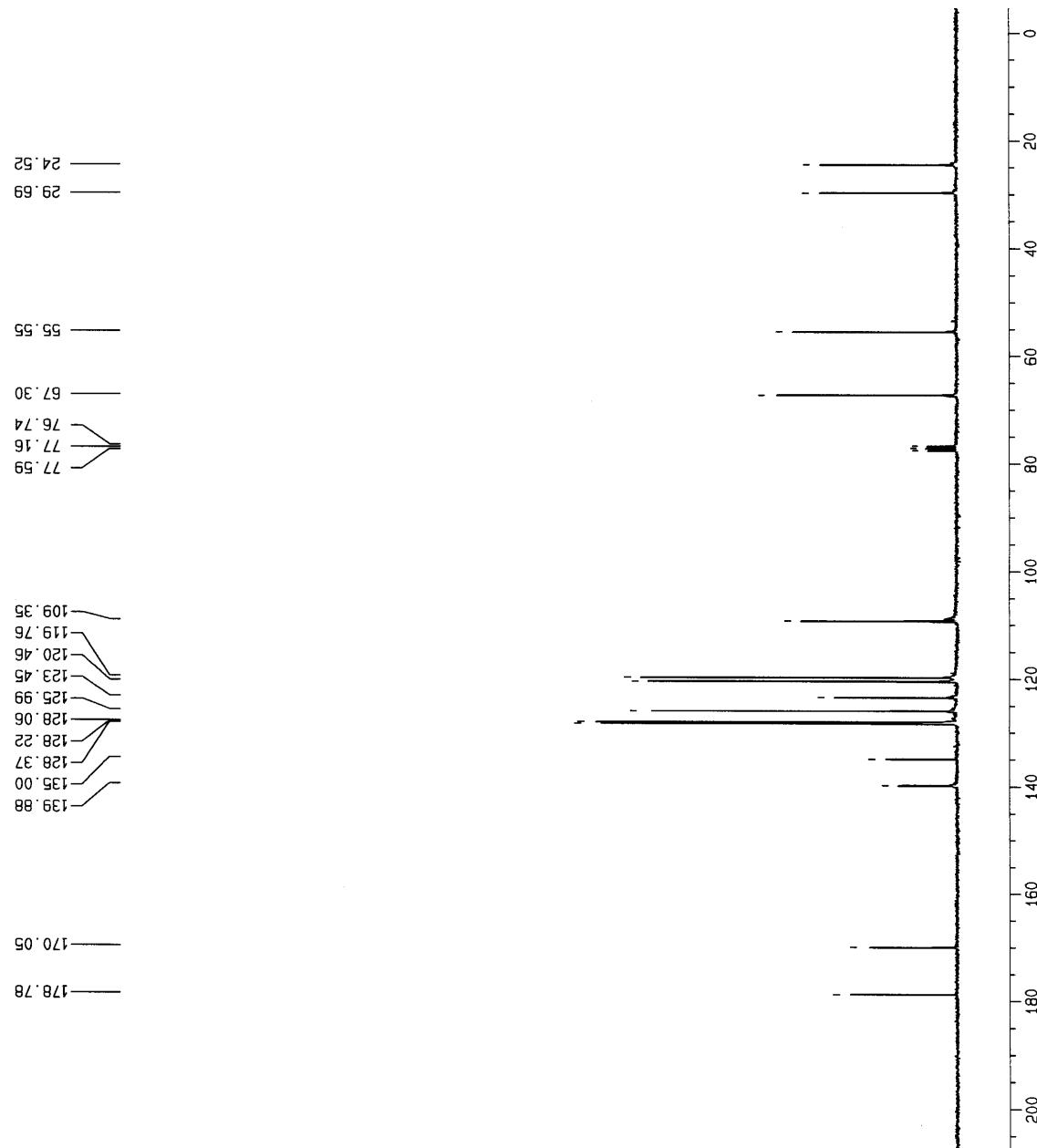
1a ^{13}C -NMR



1b $^1\text{H-NMR}$



1b ^{13}C -NMR



3a $^1\text{H-NMR}$

Current Data Parameters
NAME *121*
EXPNO *1*
PROCNO *1*

F2 - Acquisition Parameters
Date 20031120

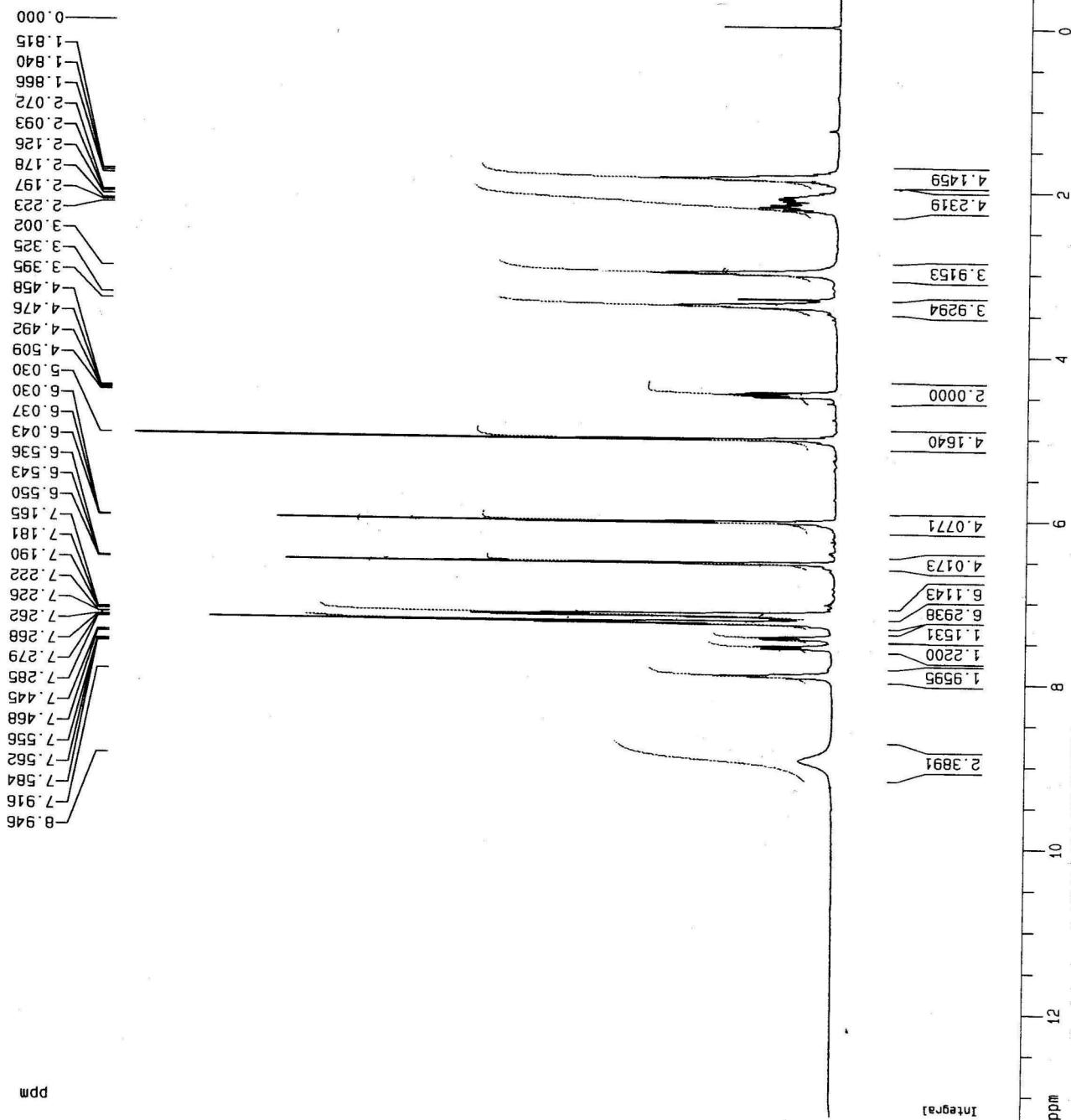
16..49	0	4194.31 Hz
spect		0.128010 Hz
Dua1 13C/		3.9059956 sec
29	4	
32768		
CDC13 ✓		

28.5	
119.200	usec
4.50	usec
300.0	K
0.00100000	sec

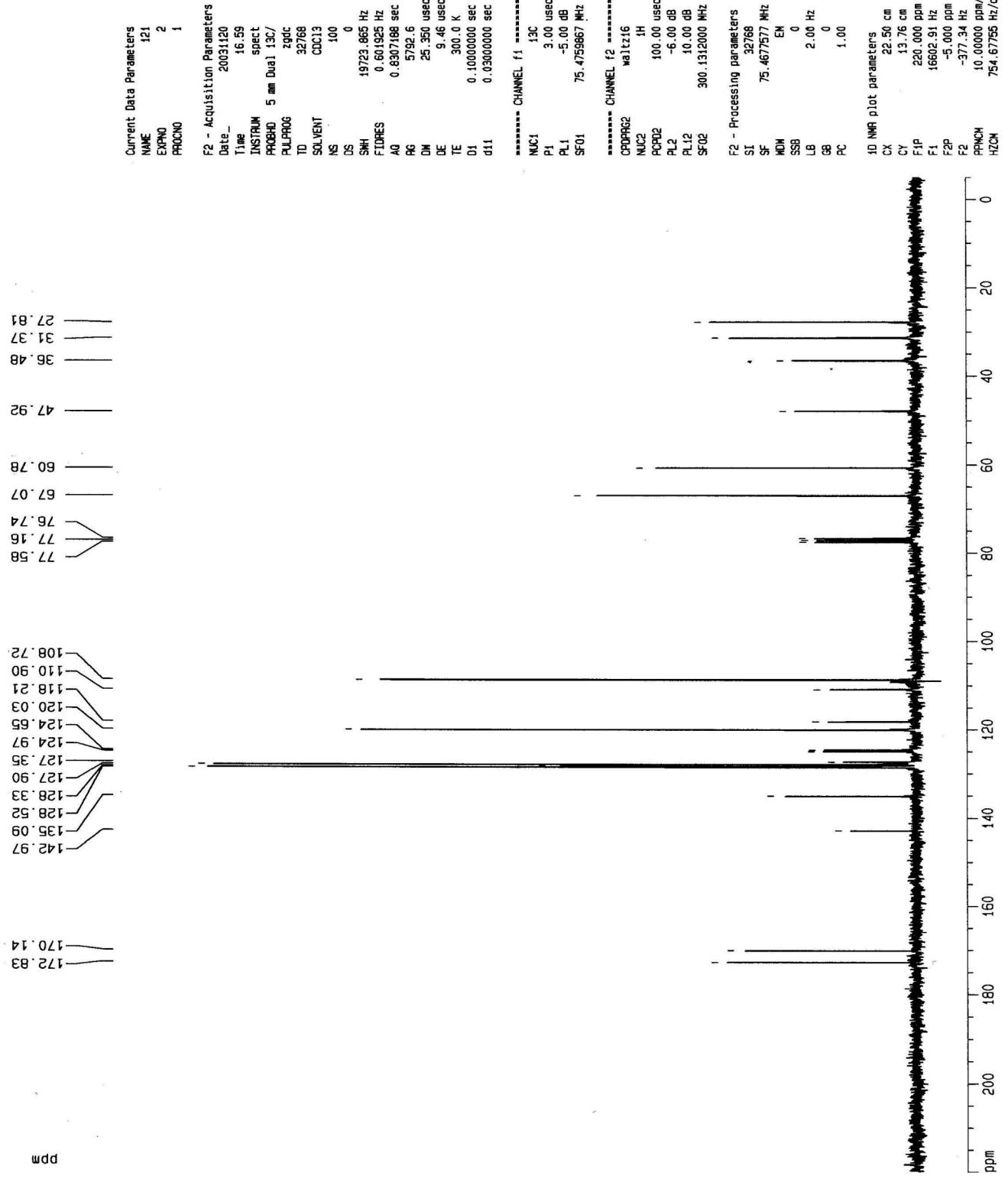
CHANNEL f1 ======
1H 9.00 usec
-3.00 dB

ing parameters

parameters	22.50 cm	12.58 cm	13.262 ppm	3980.34 Hz	-0.714 ppm	-214.29 Hz	0.62116 ppm/cm	186.42004 Hz/cm
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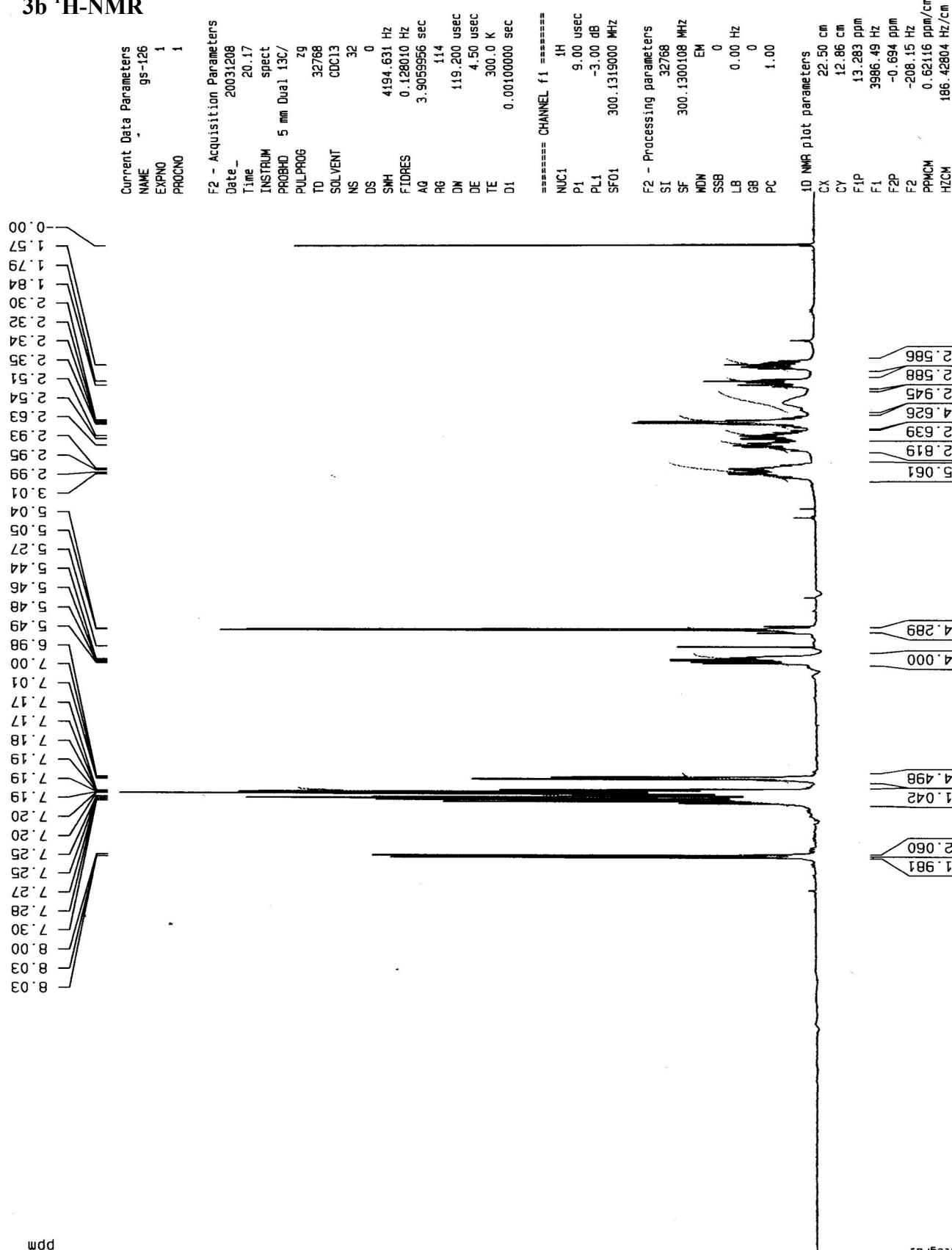


3a ^{13}C -NMR

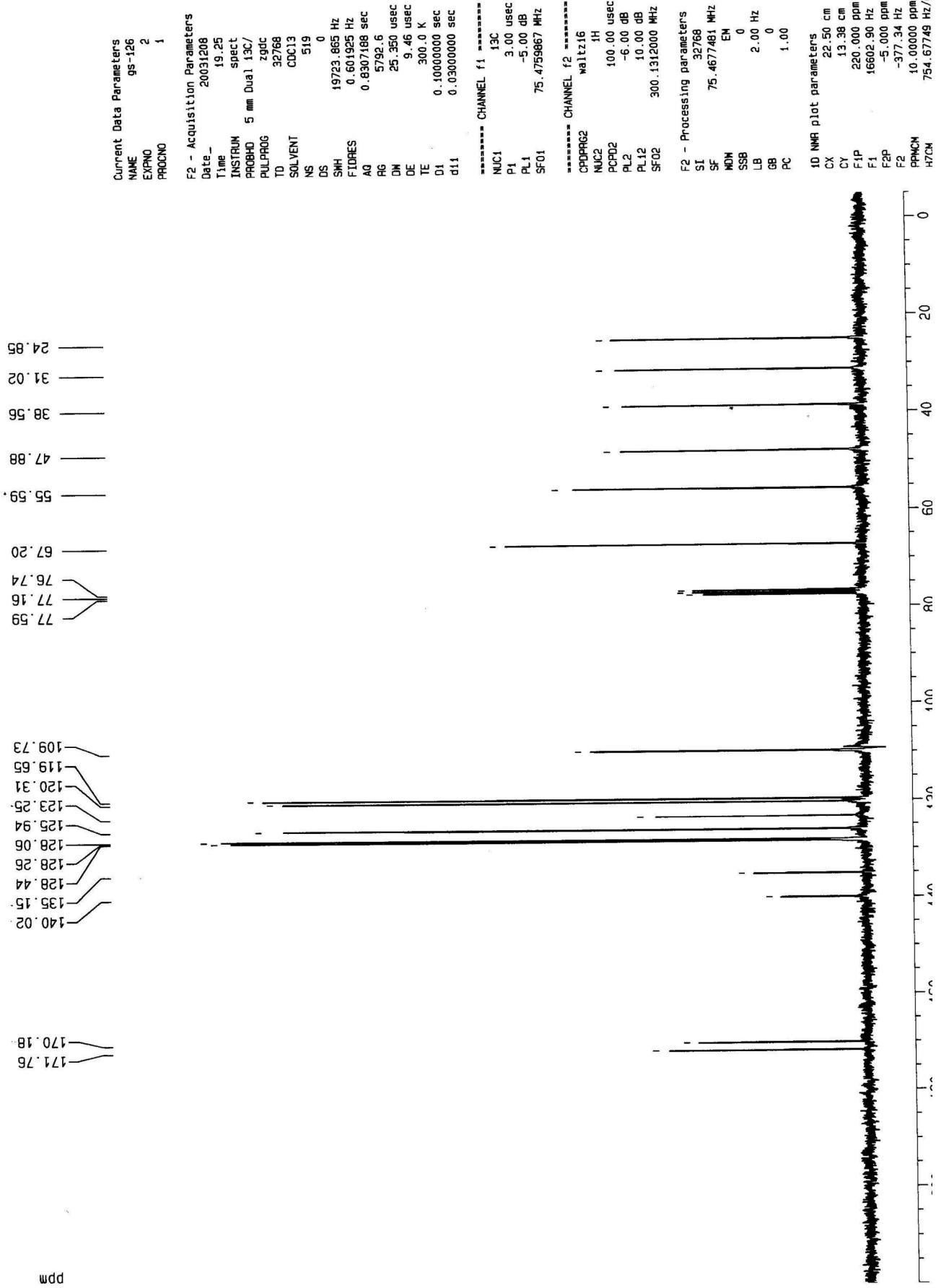


ppm

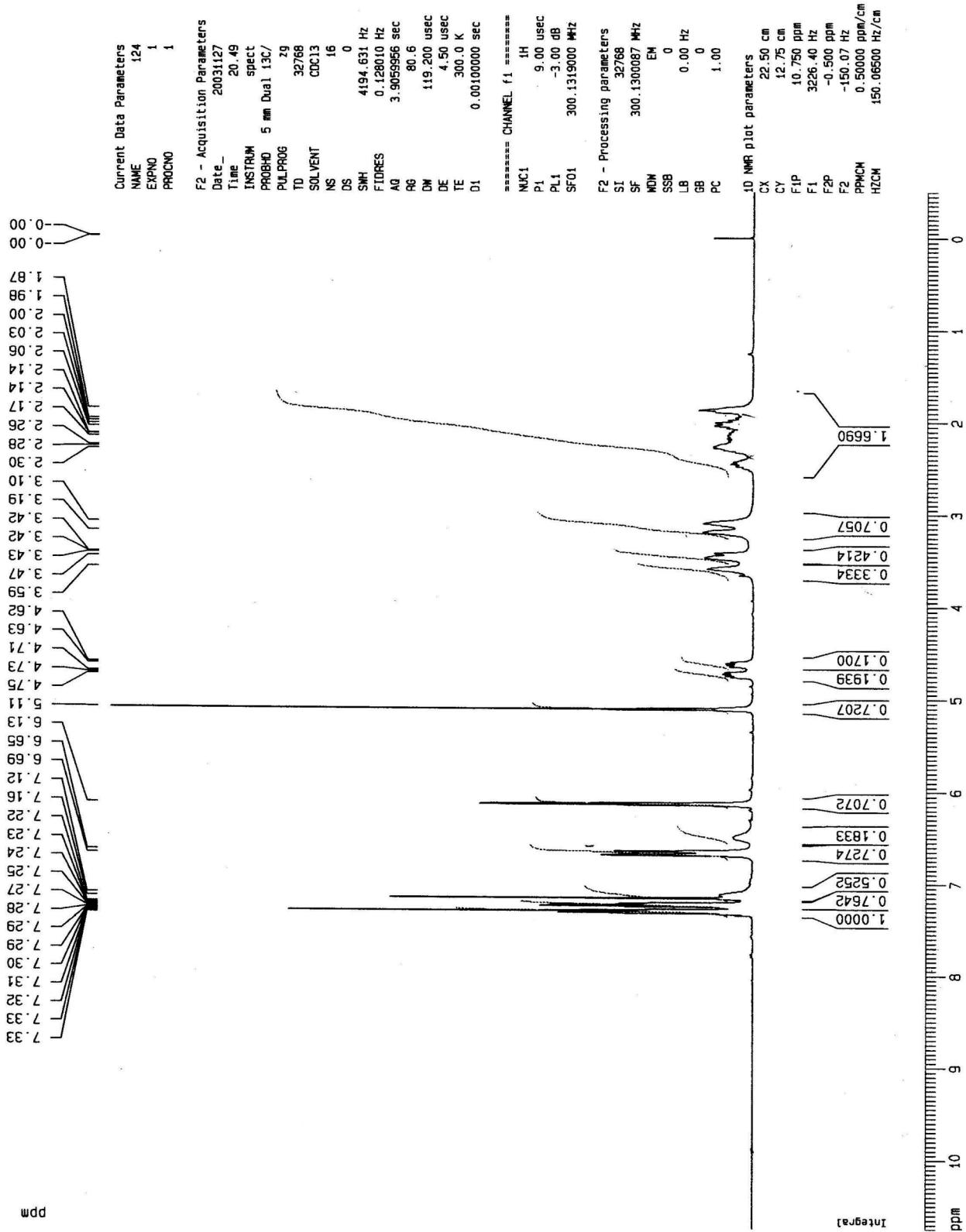
3b $^1\text{H-NMR}$



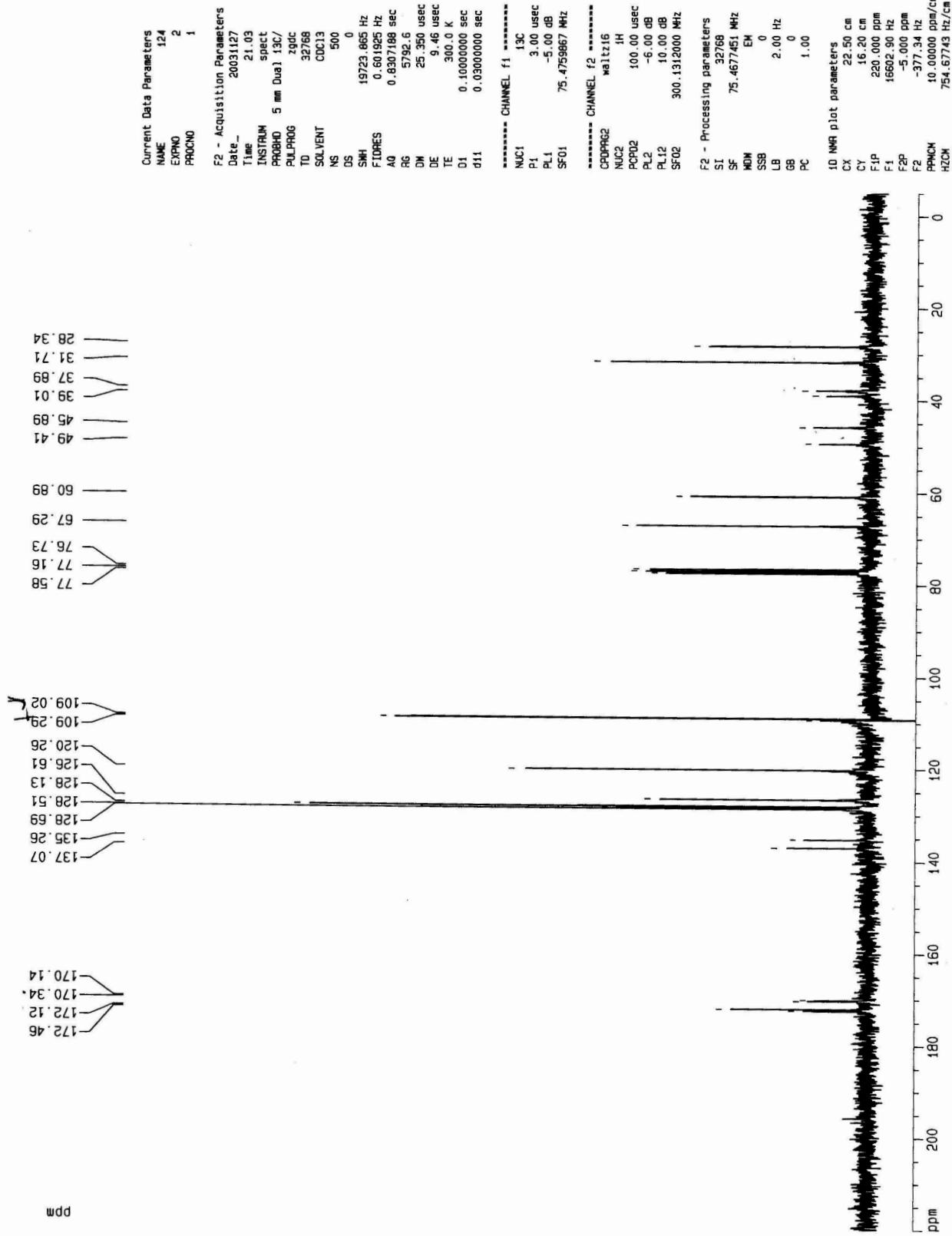
3b ^{13}C -NMR



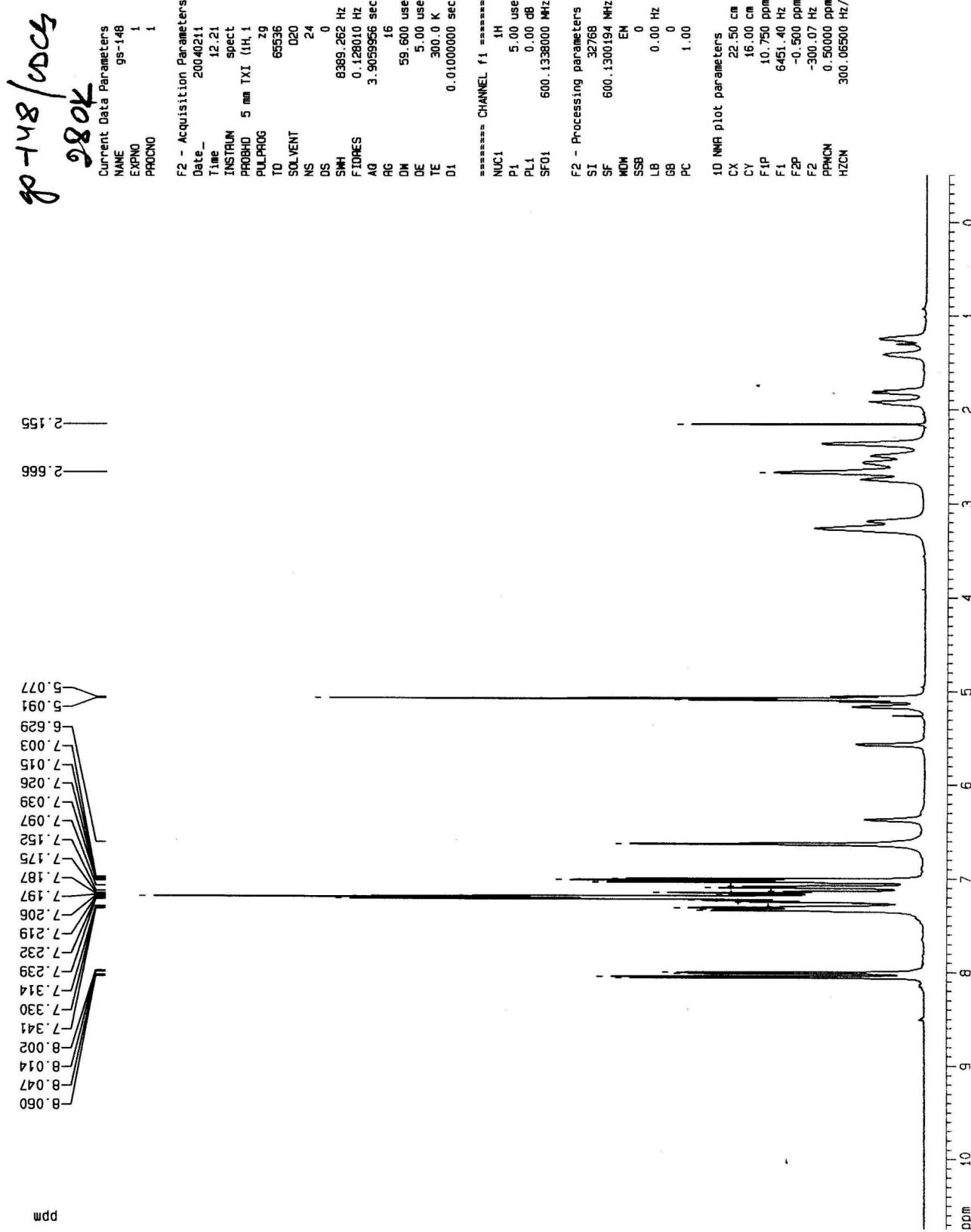
4a $^1\text{H-NMR}$



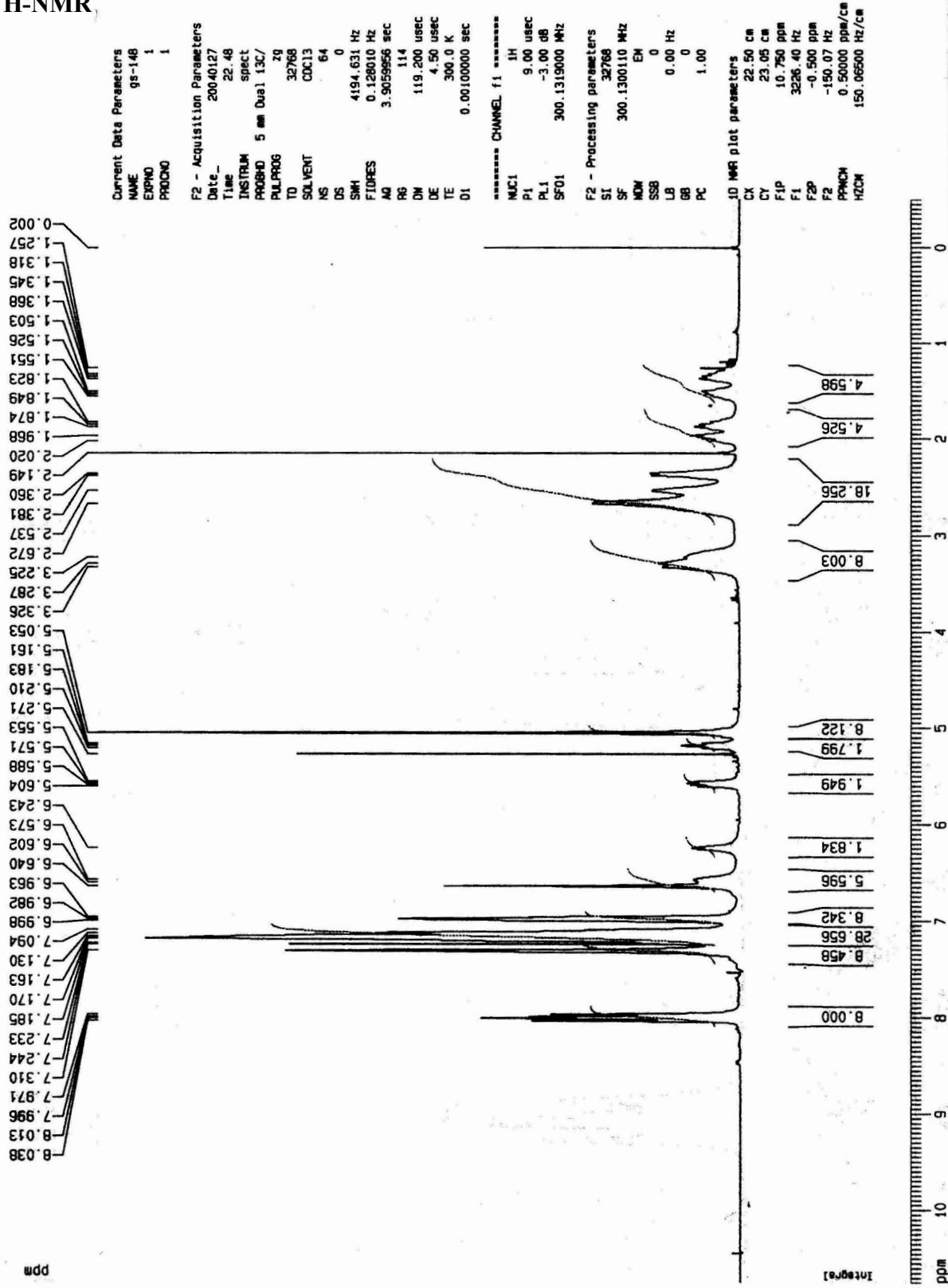
4a ^{13}C -NMR



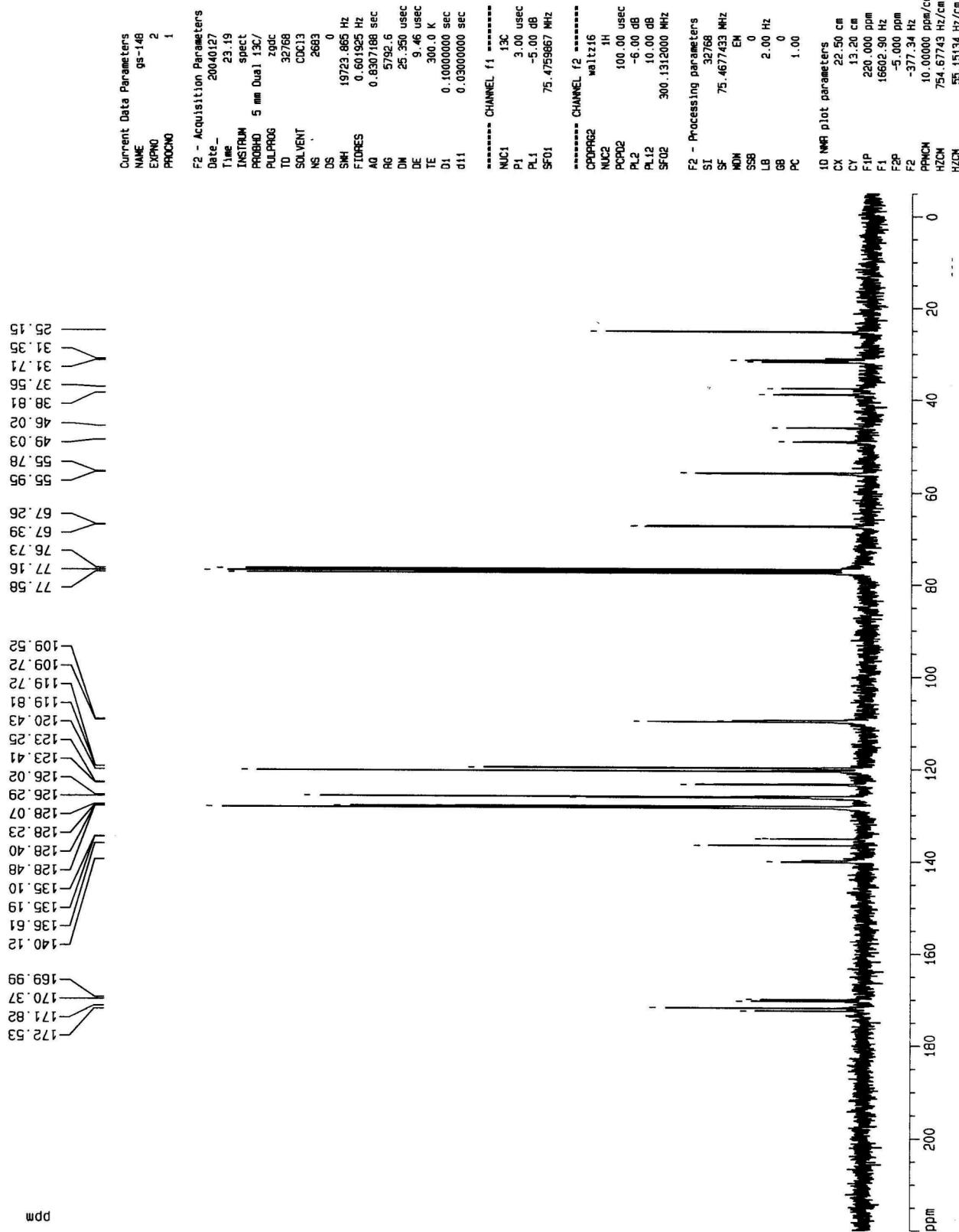
4b ^1H -NMR 600 MHz



4b $^1\text{H-NMR}$



4b ^{13}C -NMR



ppm

St-gs143/aq

5a ^1H -NMR 600 MHz

Current Data Parameters

NAME

St-gs143

EXPN0

2

PROCNO

1

F2 - Acquisition Parameters

Date	20040122
Time	13:20
INSTRUM	spect
PROBHD	5 mm TXI (1H, 1
PULPROG	29
TD	65536
SOLVENT	D2O
NS	40
DS	0
SWH	8389.262 Hz
ETDRES	0.128010 Hz
RG	3.9059956 sec
ACQ	256
DM	59.600 usec
DE	5.00 usec
TE	300.0 K
DT	0.01000000 sec

F2 - CHANNEL f1

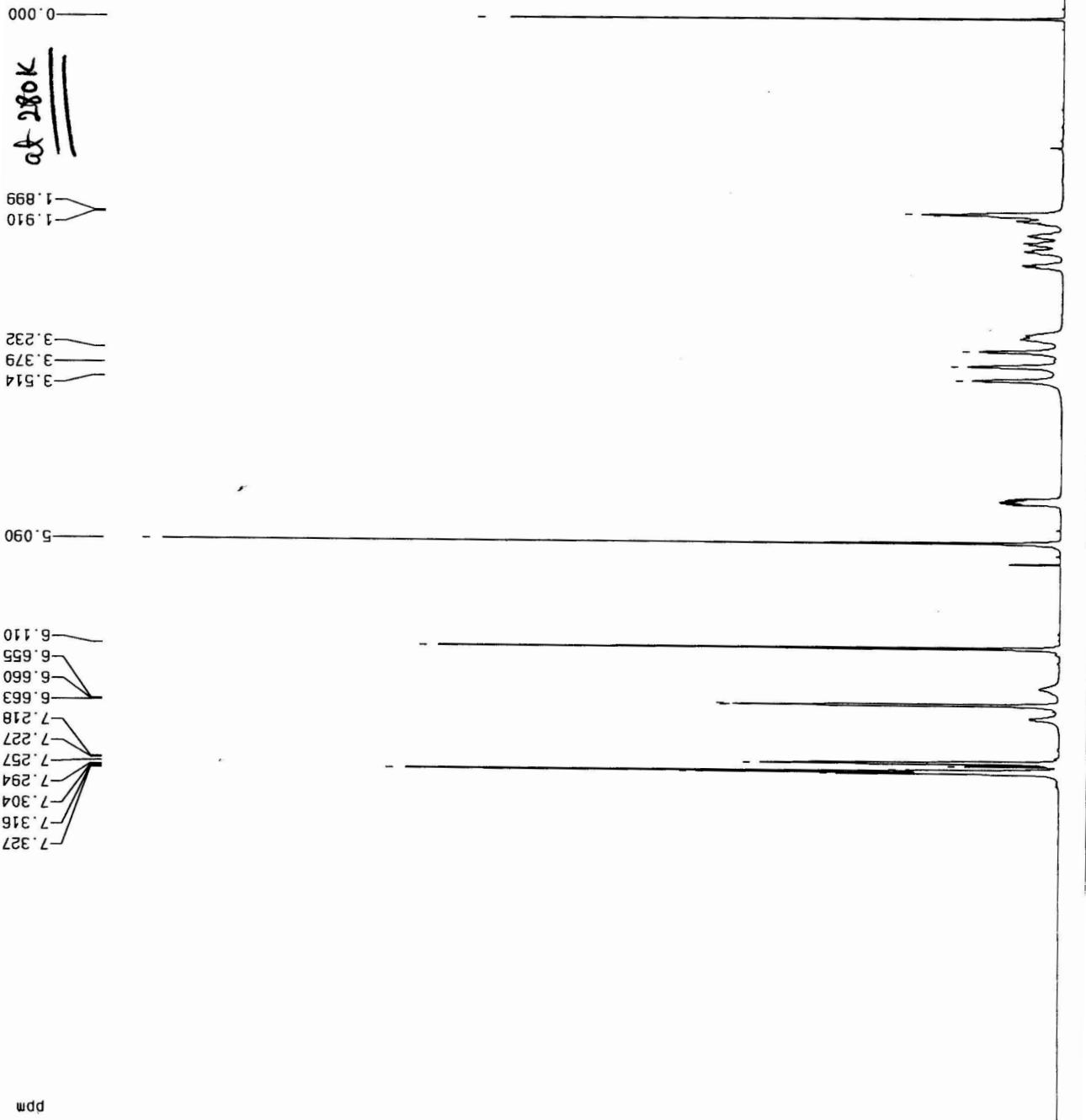
NUC1	^1H
P1	5.00 usec
PL1	0.00 dB
SFO1	600.1338000 MHz

F2 - Processing parameters

SI	32768
SF	600.1330186 MHz
NDW	EN
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

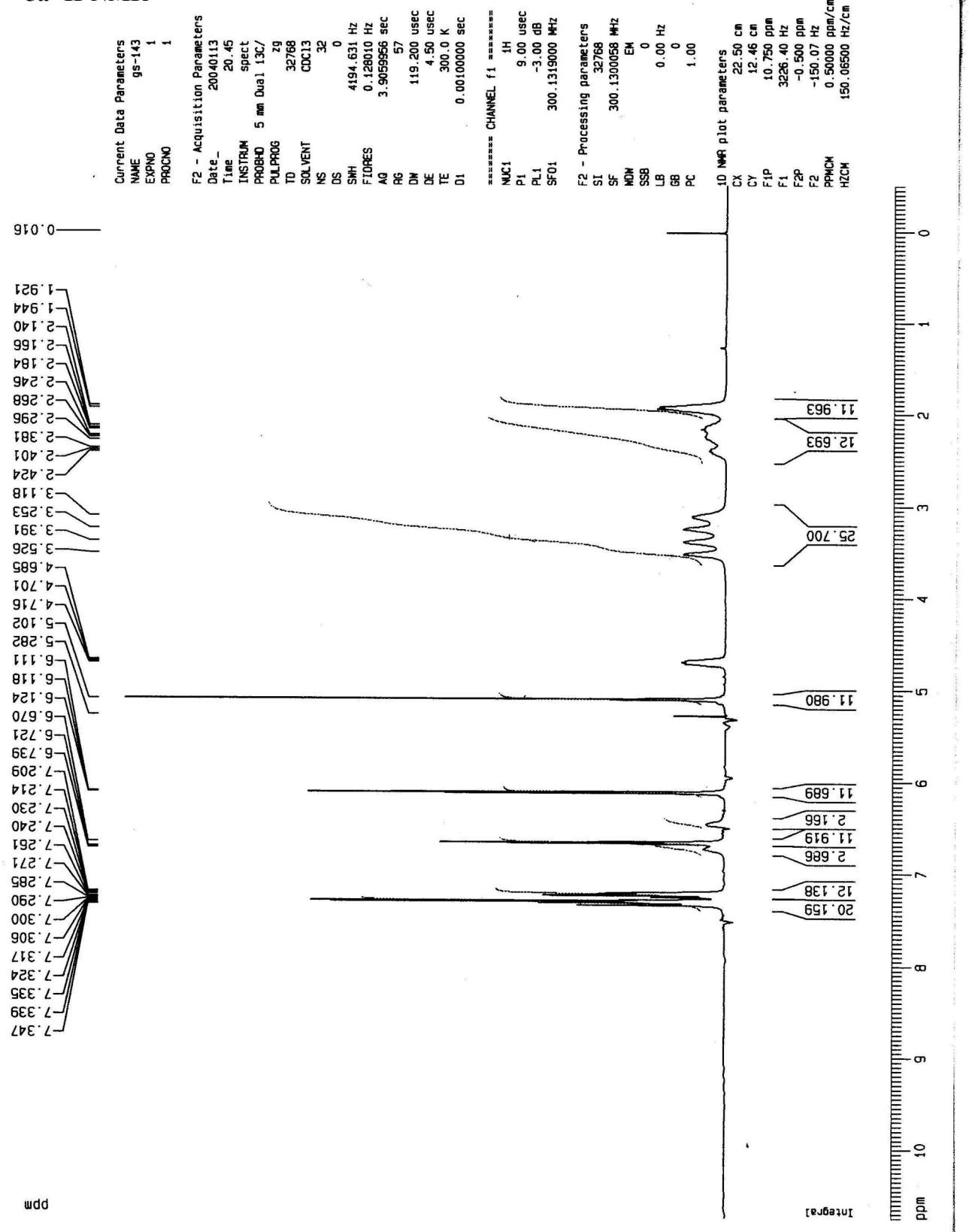
1D NMR plot parameters

CX	22.50 cm
CY	16.00 cm
F1P	10.750 ppm
F1	6451.40 Hz
F2P	-0.500 ppm
F2	-300.07 Hz
PPCM	0.50000 ppm/cm
HZCN	300.06500 Hz/cm

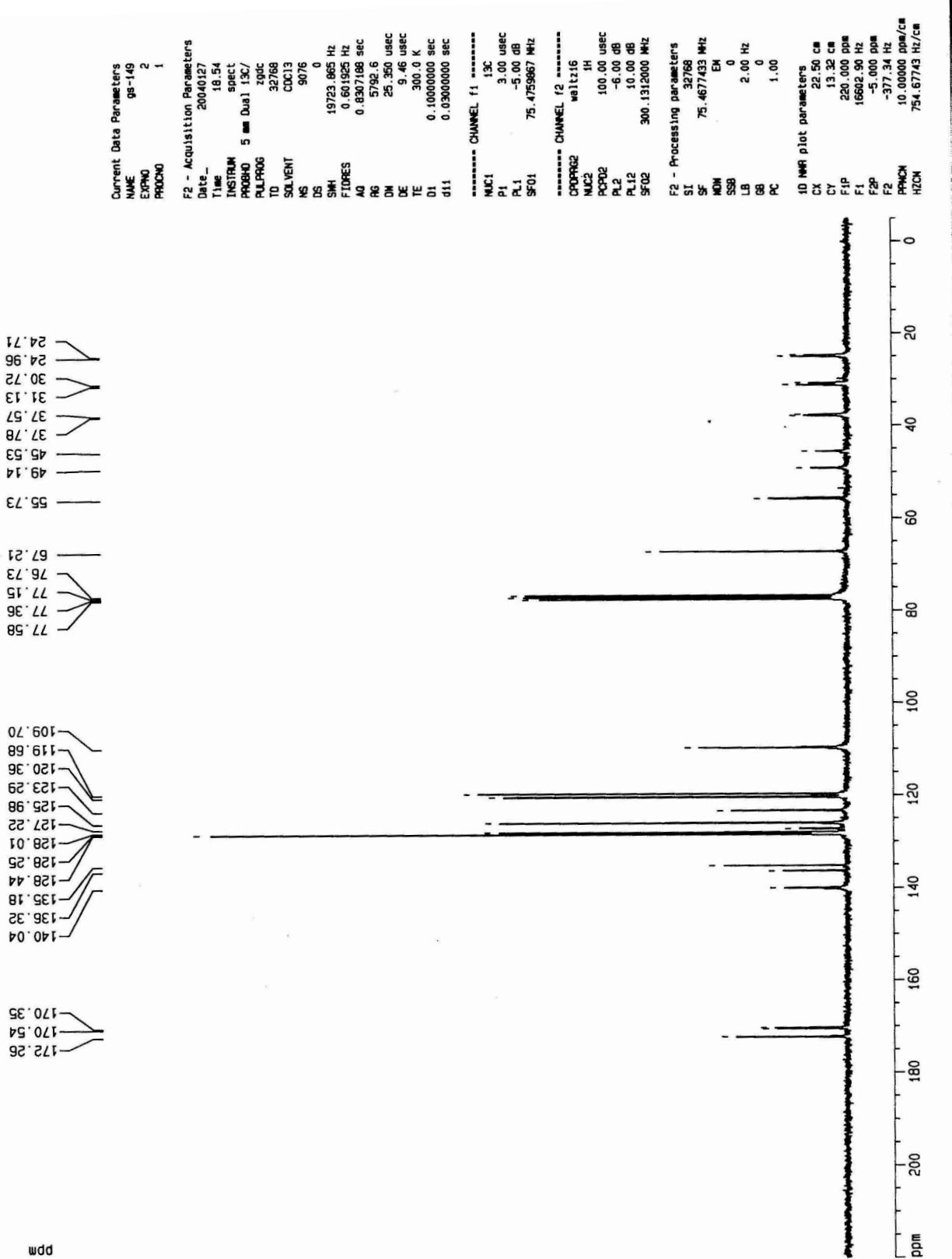


ppm

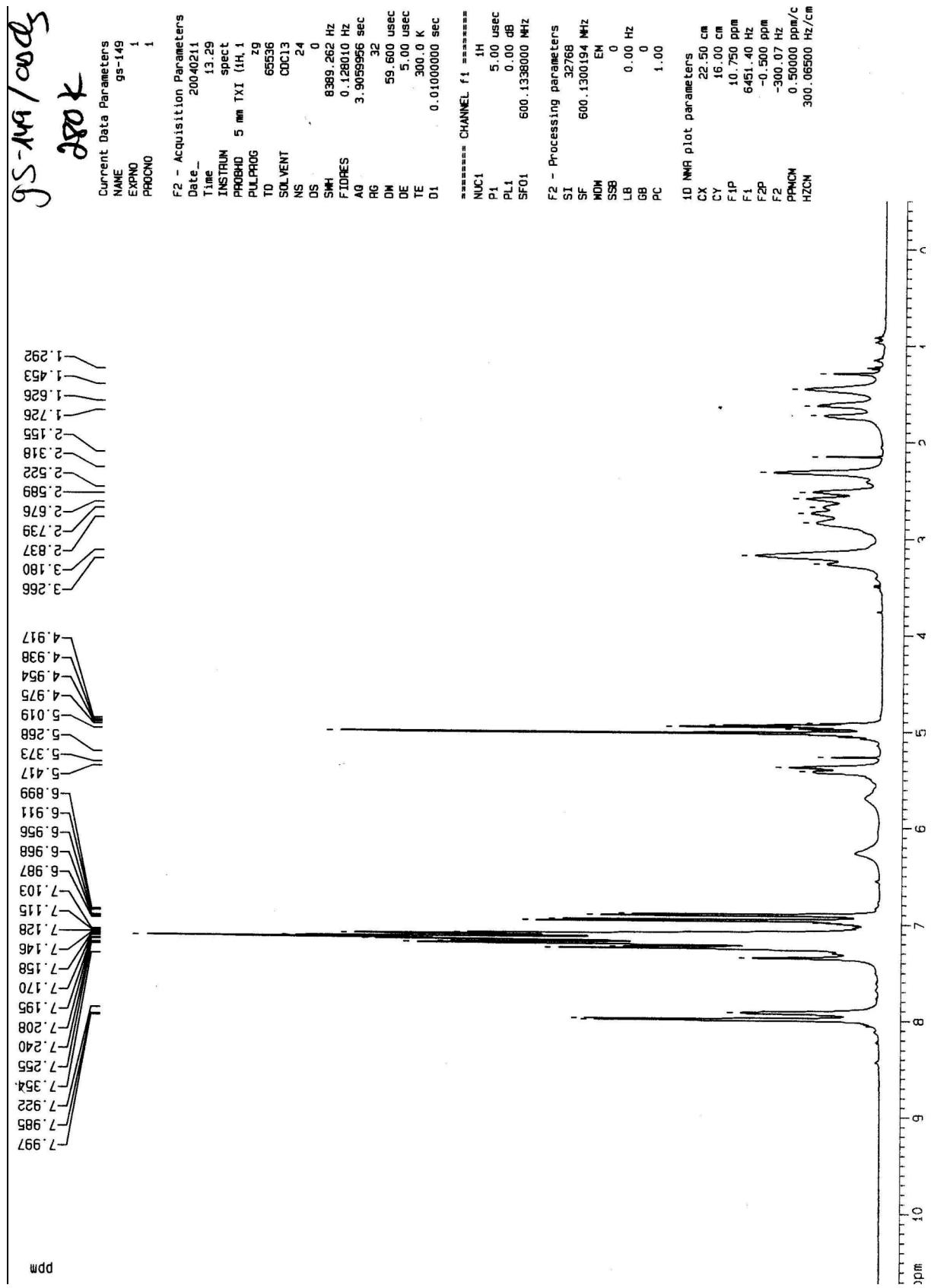
5a $^1\text{H-NMR}$



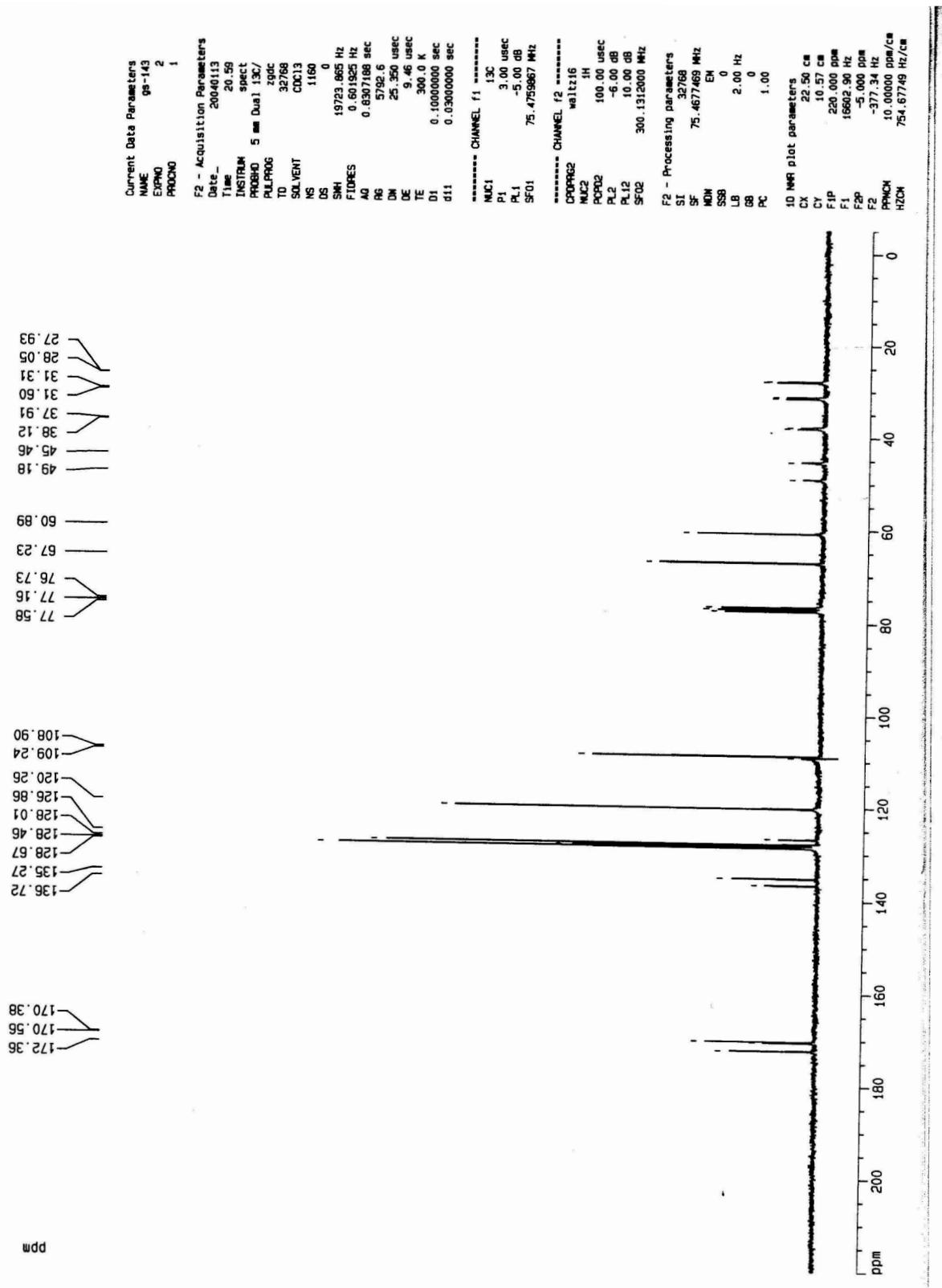
5a ^{13}C -NMR



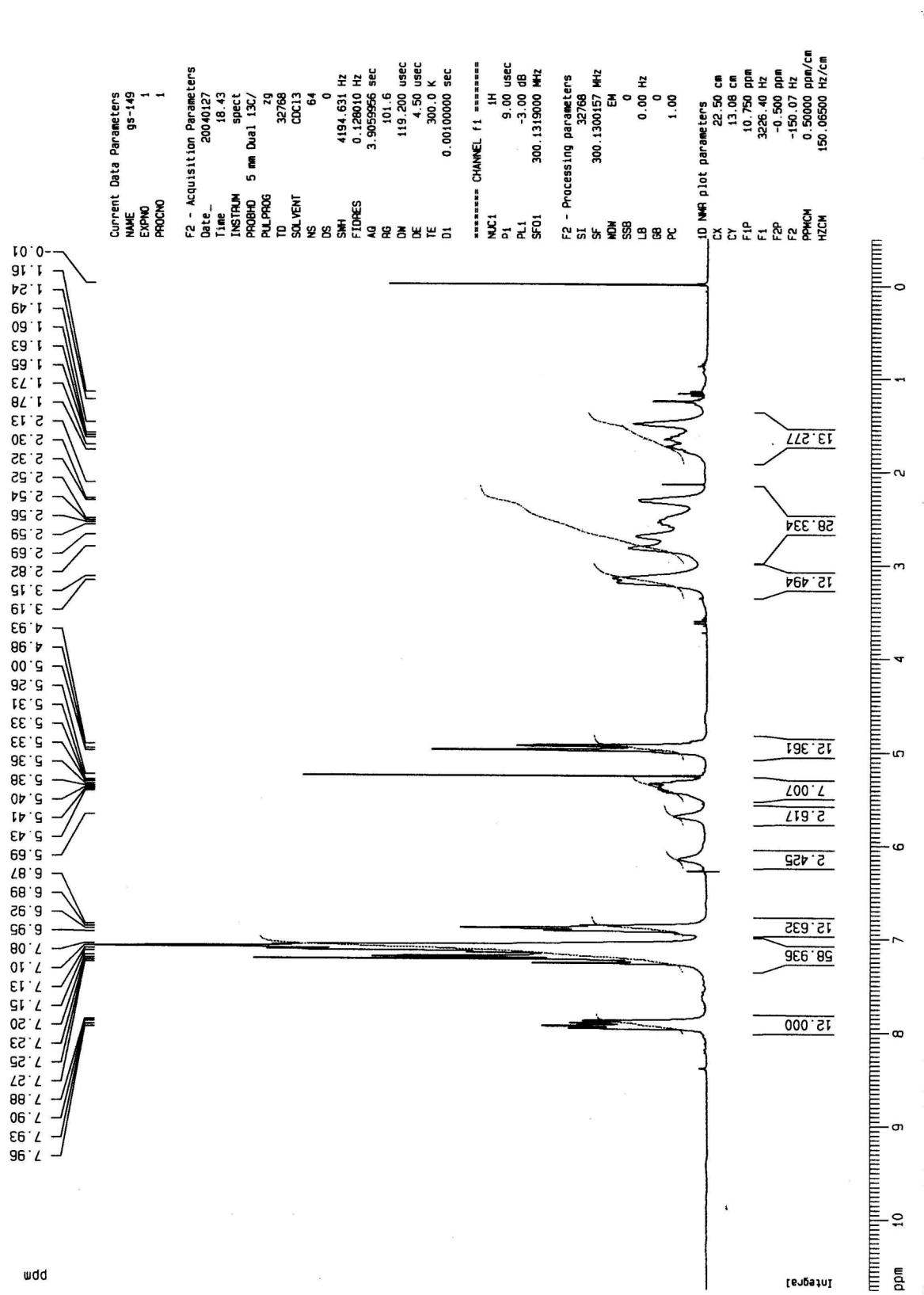
5b ^1H -NMR 600MHz



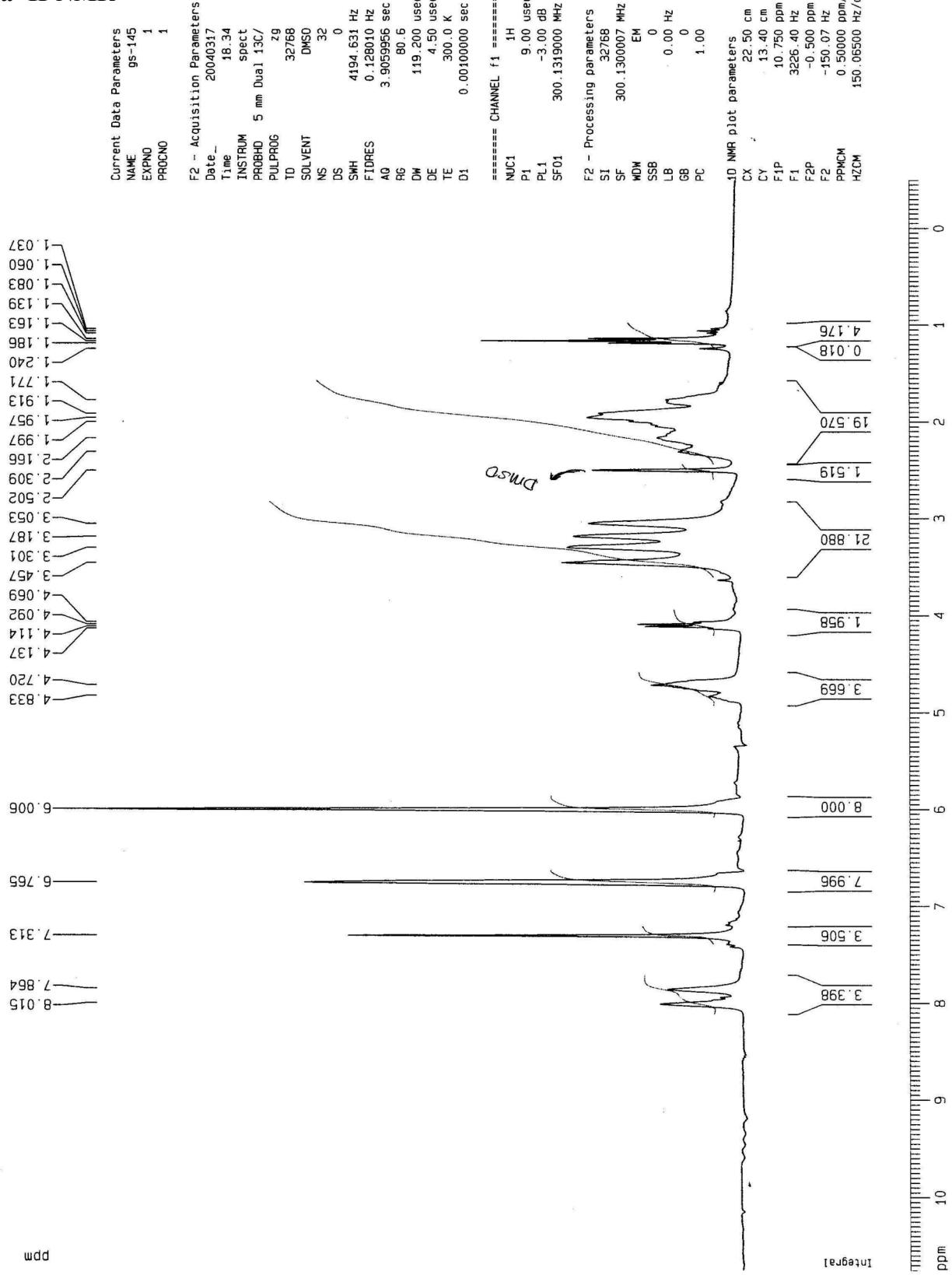
5b ^{13}C -NMR



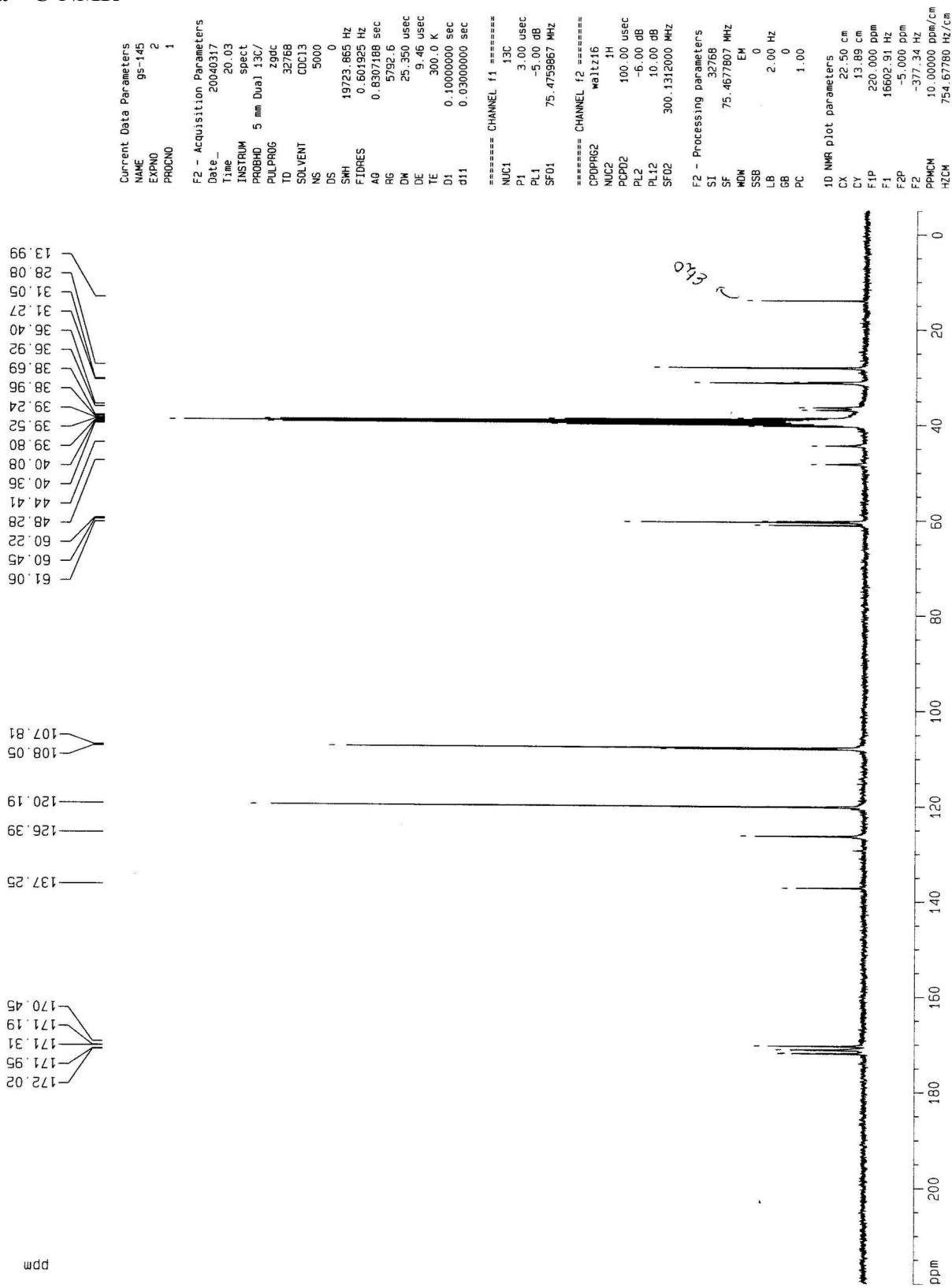
5b $^1\text{H-NMR}$



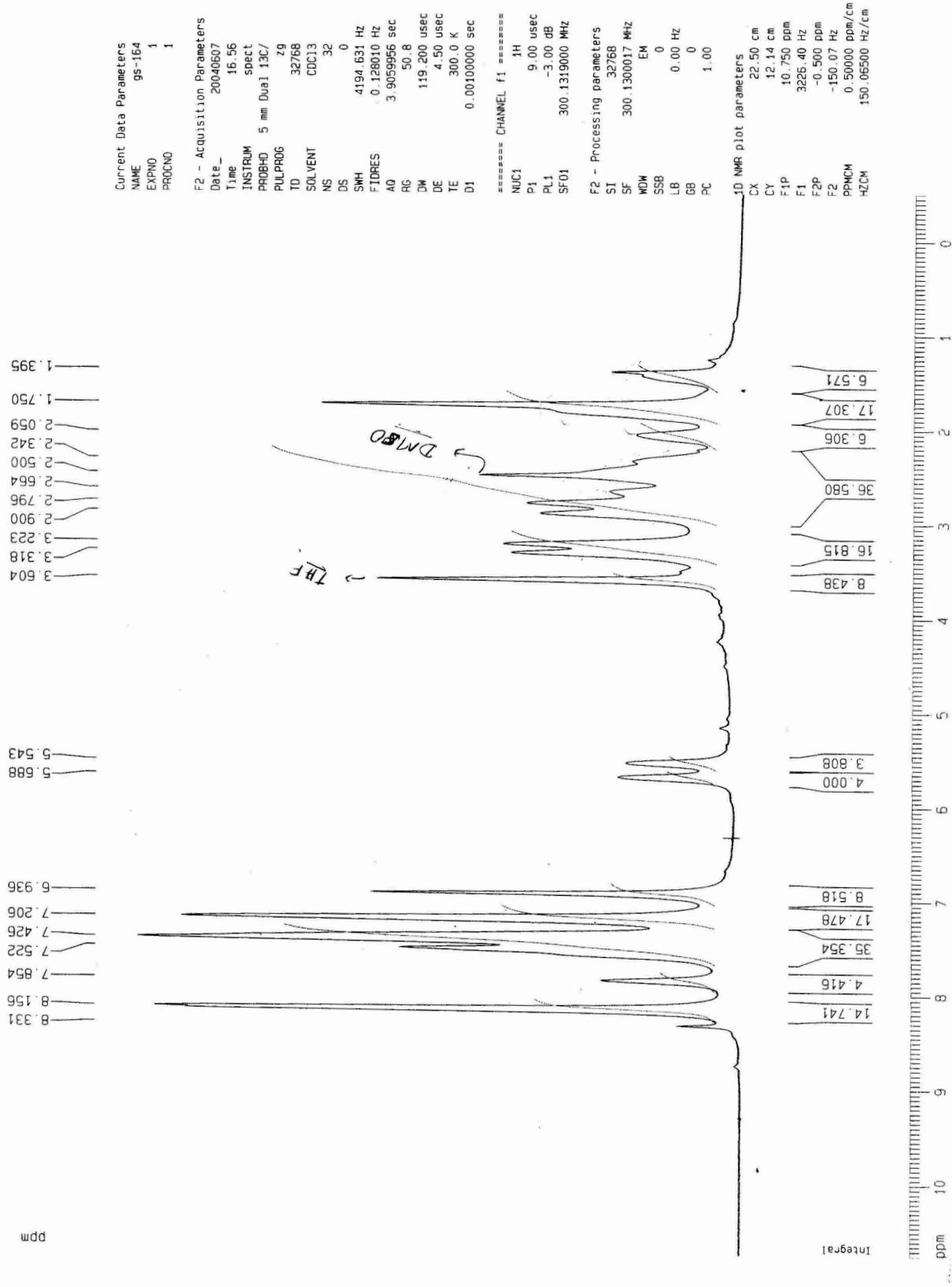
6a $^1\text{H-NMR}$



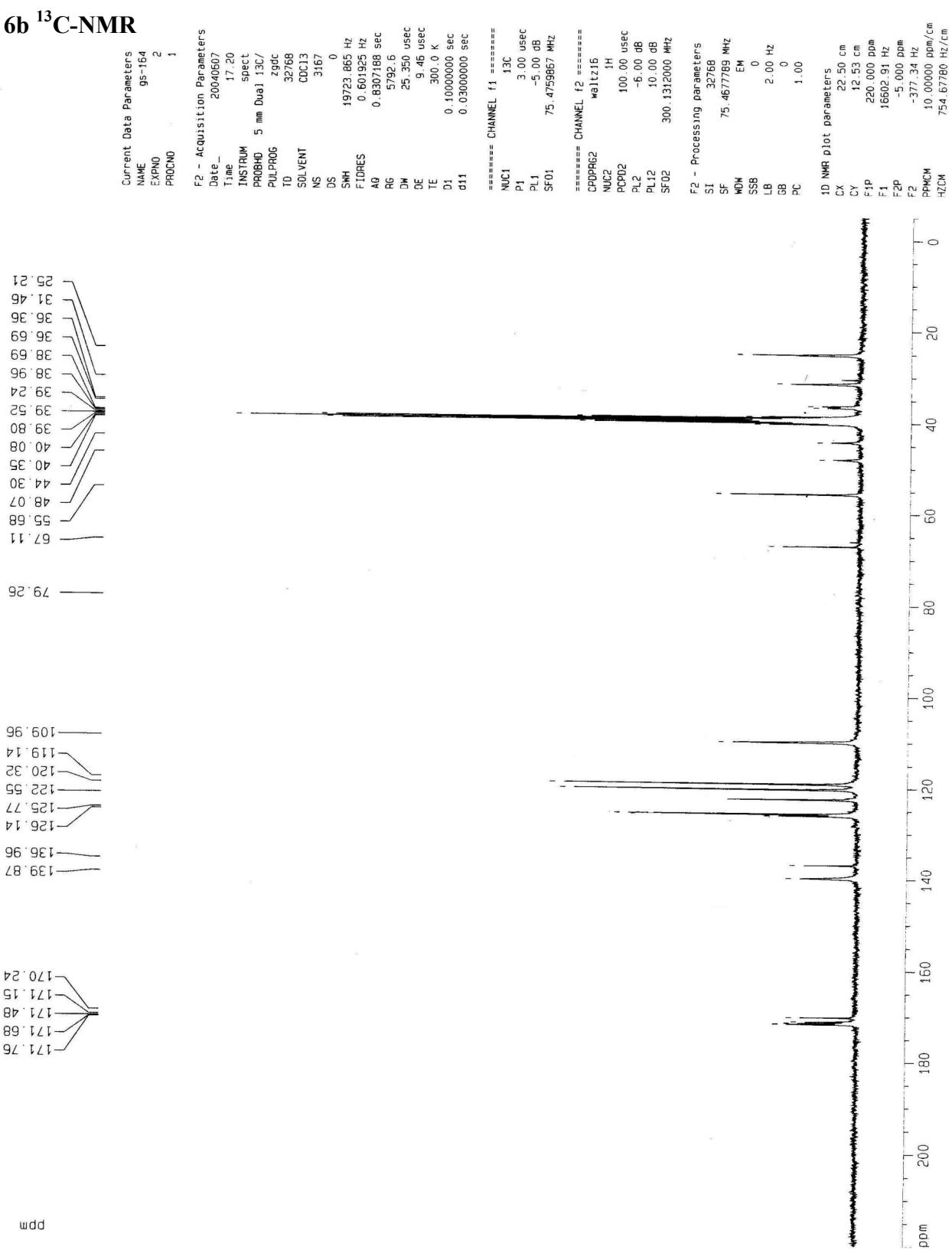
6a ^{13}C -NMR



6b $^1\text{H-NMR}$

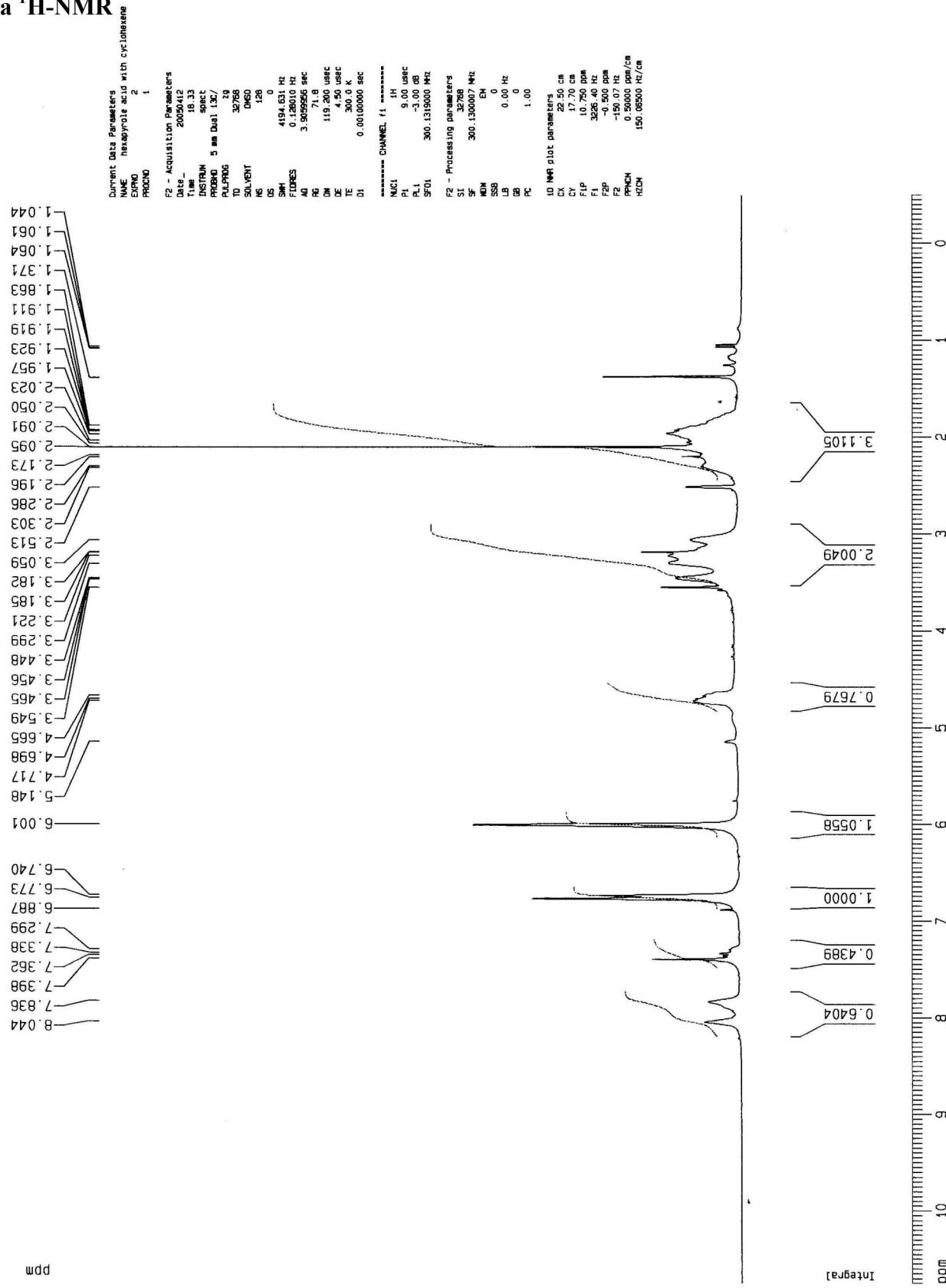


6b ^{13}C -NMR

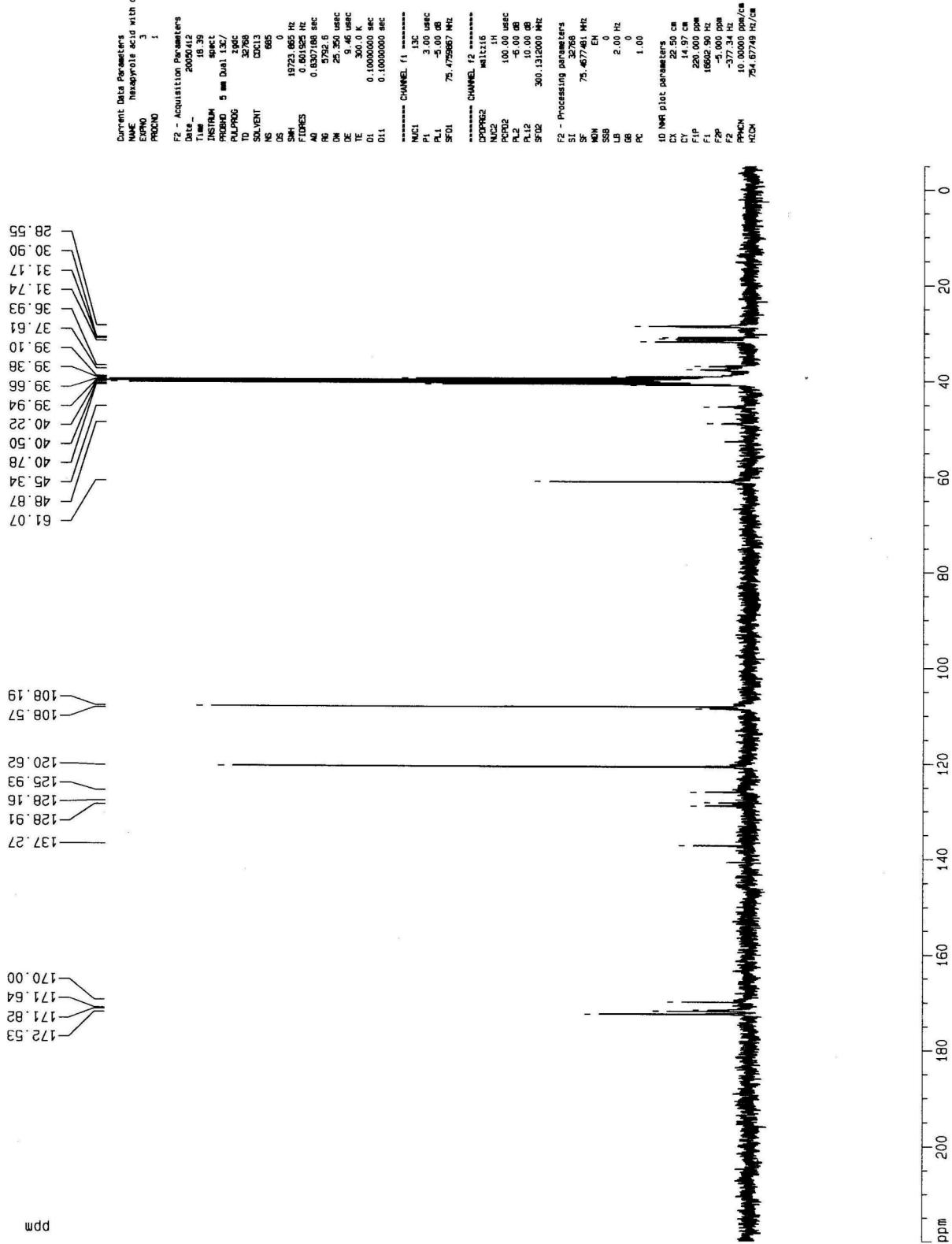


ppm

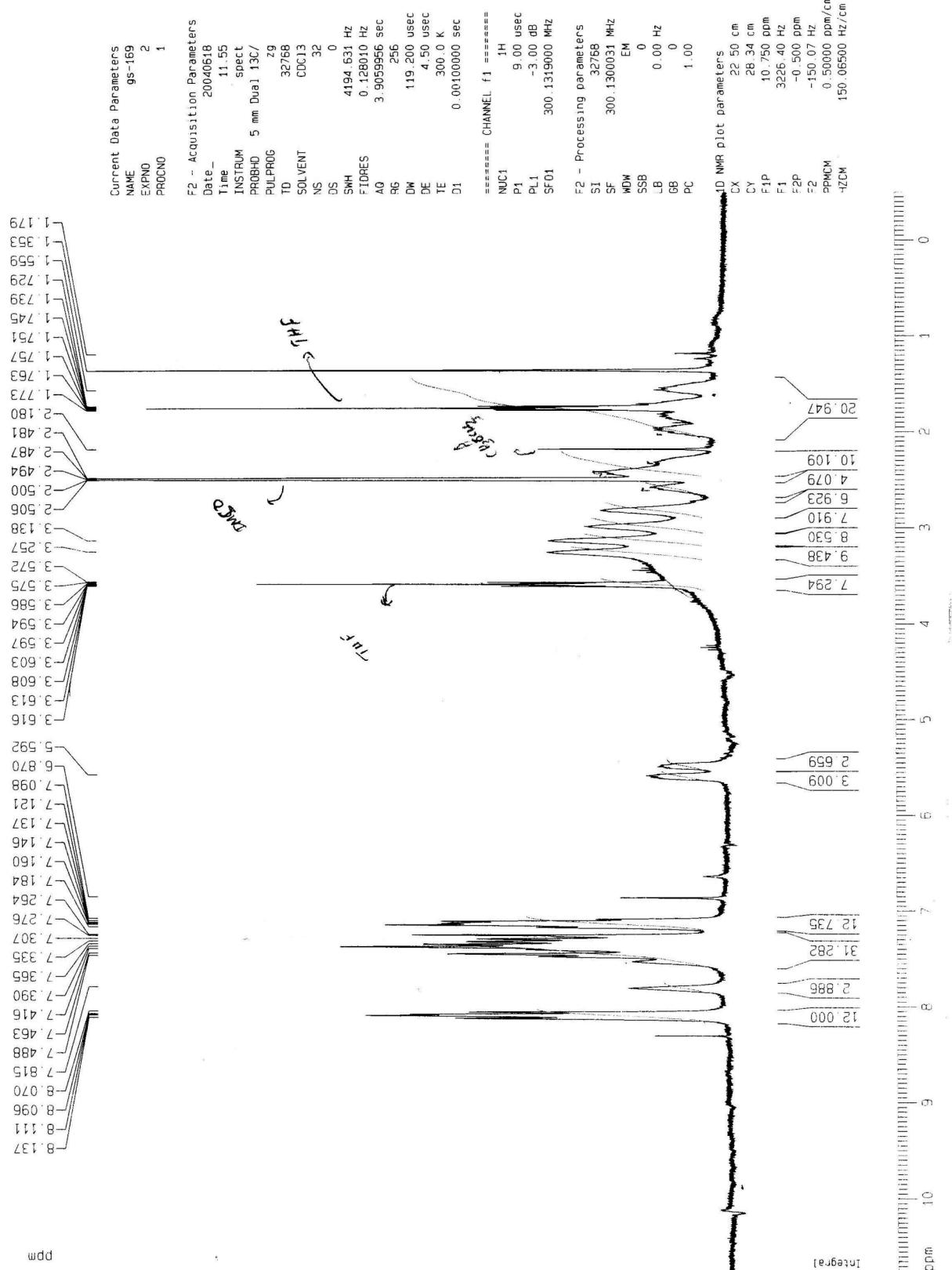
7a $^1\text{H-NMR}$



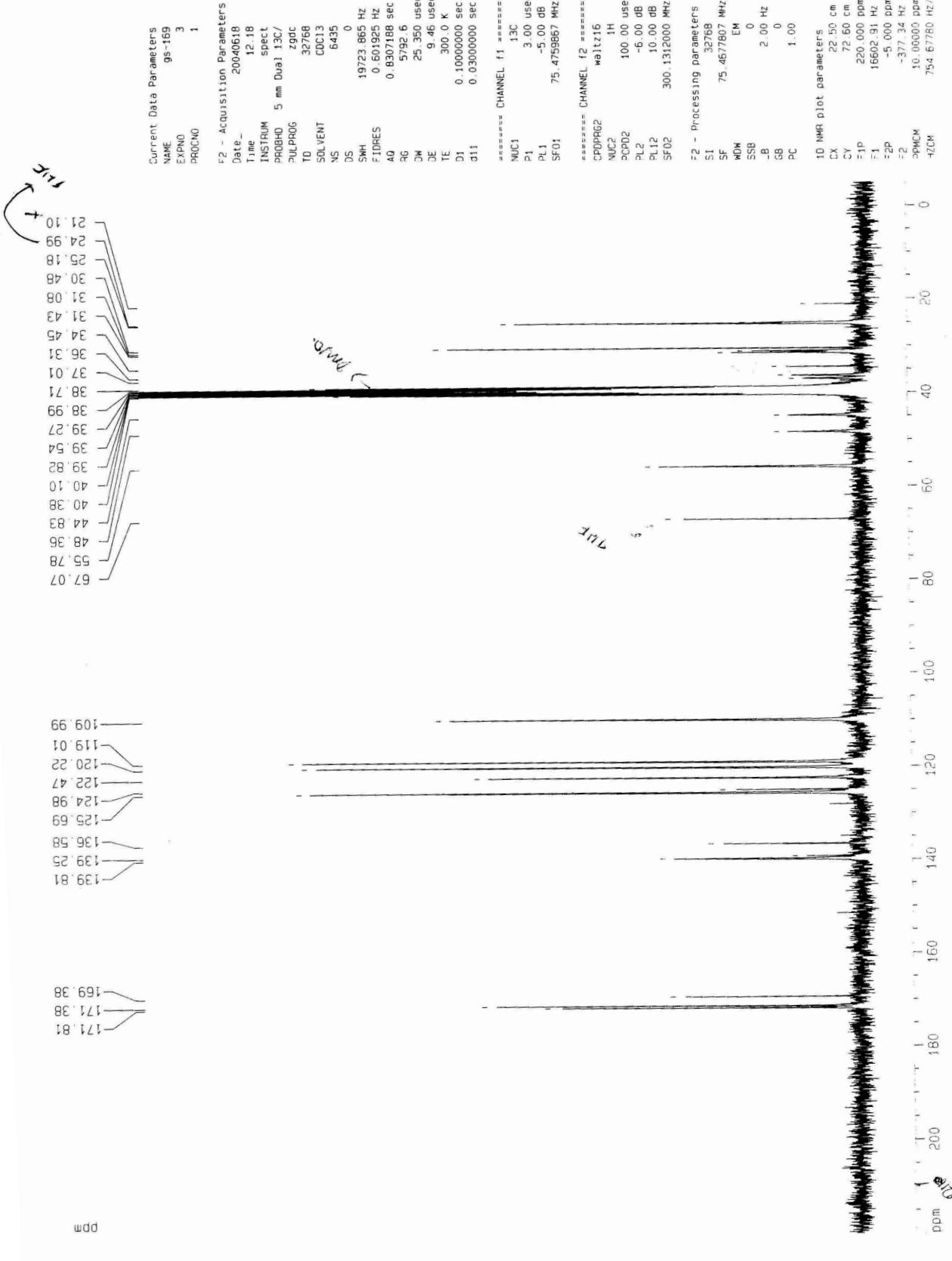
7a ^{13}C -NMR



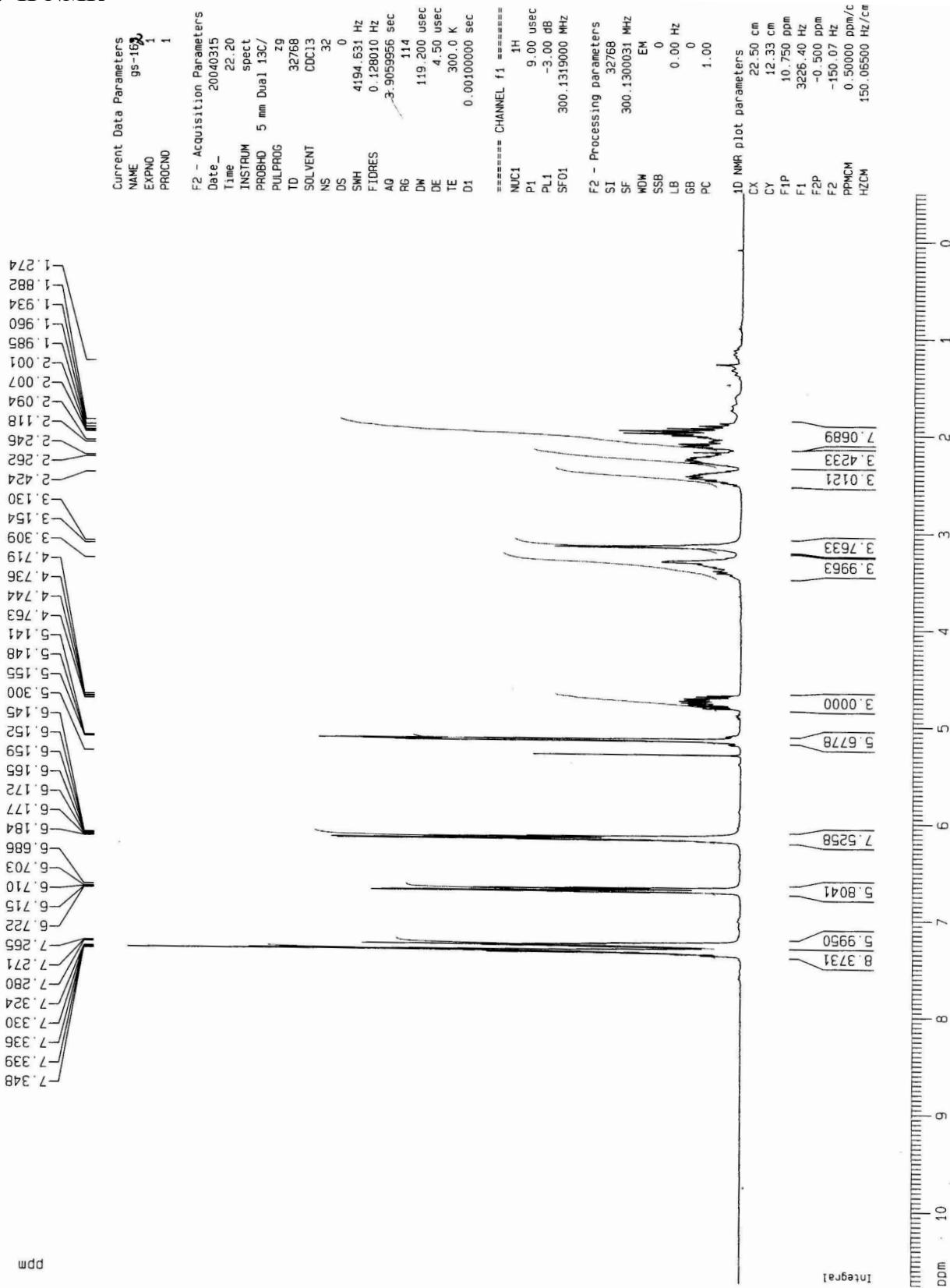
7b ¹H-NMR



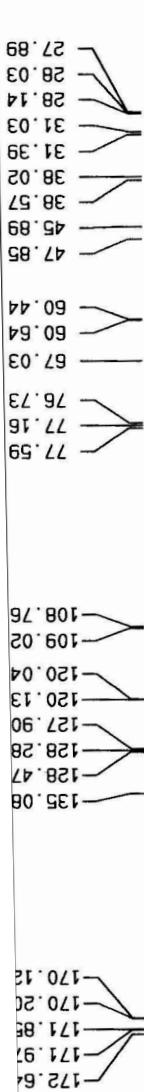
7b ^{13}C -NMR



8a $^1\text{H-NMR}$



8a ^{13}C -NMR



Current Data Parameters
NAME: 122
ECHO: 2
PROCNO: 1

F2 - Acquisition Parameters

Date: 20031130
Time: 18.44
INSTRUM: spect
PROBHD: 5 mm Dual 13C/
PULPROG: zgdc
TD: 32768
SOLVENT: CDCl₃
NS: 60
DS: 0
SWH: 19723.865 Hz
FIDRES: 0.601925 Hz
AQ: 0.8307188 sec
RG: 5792.6
DW: 25.350 usec
DE: 9.46 usec
TE: 300.0 K
D1: 0.1000000 sec
d11: 0.0300000 sec

***** CHANNEL f1 *****

MUC1: 13C
P1: 3.00 usec
RL1: -5.00 dB
SF01: 75.4759867 MHz

***** CHANNEL f2 *****

CPDPRG2: 13C
NUC2: 1H
PCPD2: 100.00 usec
PL2: -6.00 dB
PL12: 10.00 dB
SF02: 300.1312000 MHz

F2 - Processing parameters

SI: 32768
SF: 75.4677649 MHz
WDW: EH
SSB: 0
LB: 2.00 Hz
GB: 0
PC: 1.00

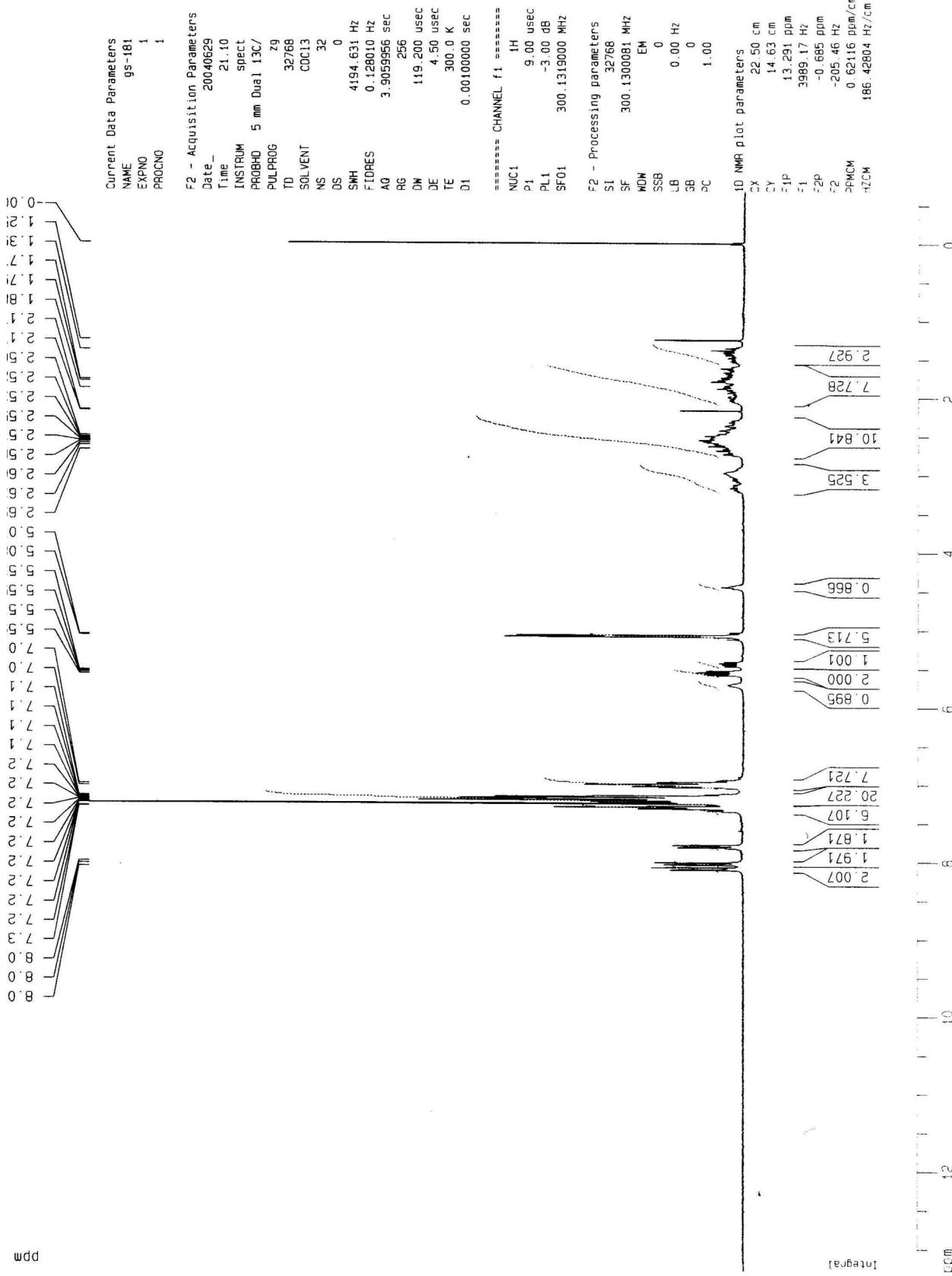
1D NMR plot parameters

CX: 22.50 cm
CY: 14.37 cm
F1P: 220.000 ppm
F1: 166.02.91 Hz
F2P: -5.000 ppm
F2: -37.34 Hz
PPMCH: 10.00000 ppm/cm
HZCM: 754.67767 Hz/cm

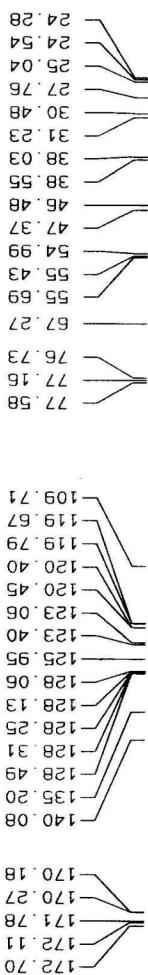
ppm



8b $^1\text{H-NMR}$



8b ^{13}C -NMR



ppm

Current Data Parameters
NAME gs-181
EXPO 3
PRONO 1

F2 - Acquisition Parameters
Date 20140707
Time 22:59

INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG 29dc
TD 32768
SOLVENT CDCl3
NS 633
DS 0
SWH 19723.865 Hz
ETDRES 0.60/1925 Hz
AQ 0.8307188 sec
RG 5732.6
DM 25.350 usec
DE 9.46 usec
TE 300.0 K
D1 0.1000000 sec
TDZ 0.0300000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 3.00 usec
PL1 -5.00 dB
SF01 75.4759867 MHz

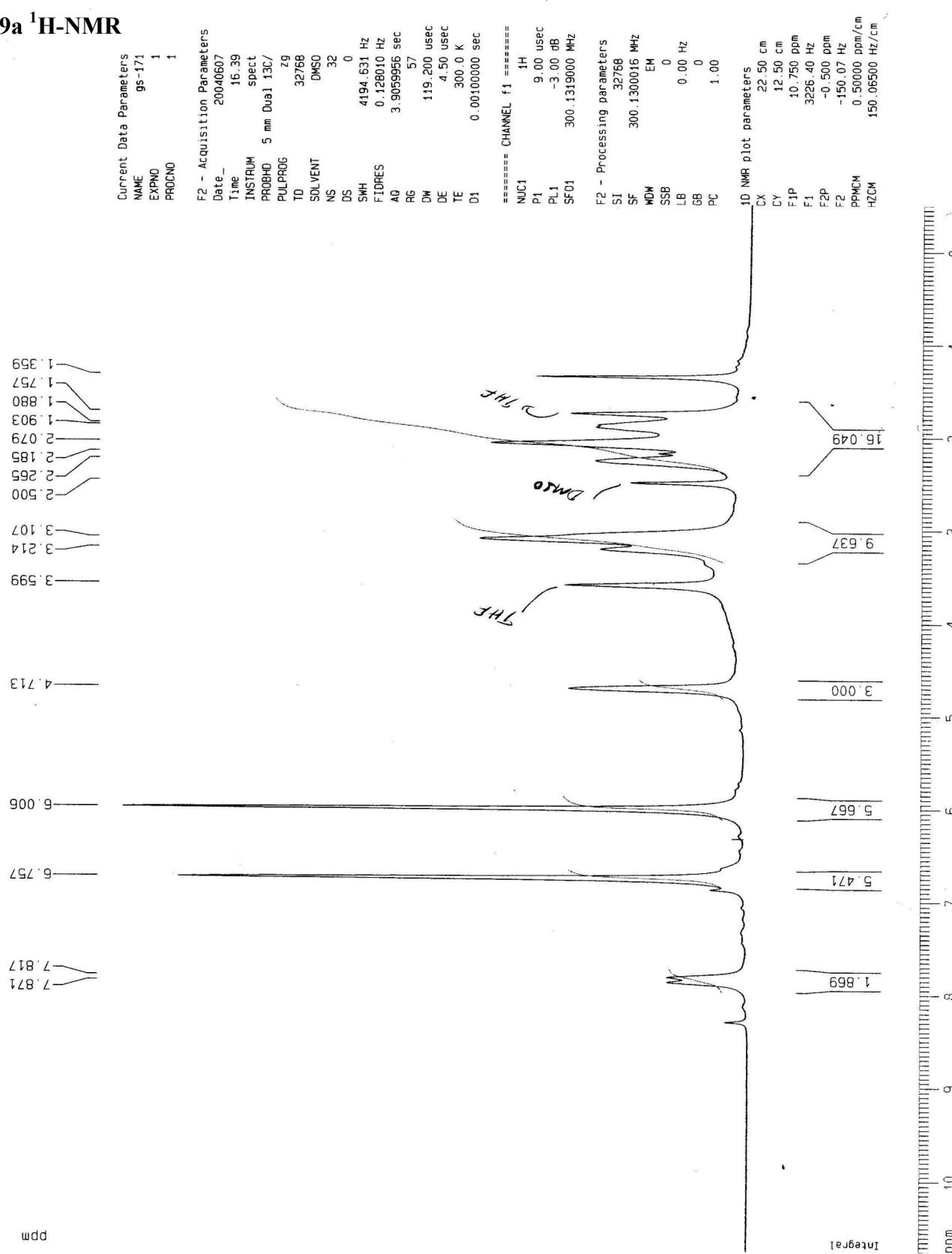
***** CHANNEL f2 *****
CPDPRG2 WALT216
NUC2 1H
PCD2 100.00 usec
PL2 -6.00 dB
R12 10.00 dB
SF02 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 75.4677445 MHz
WDW EH
SSB 0
LB 2.00 Hz
SB 0
PC 1.00

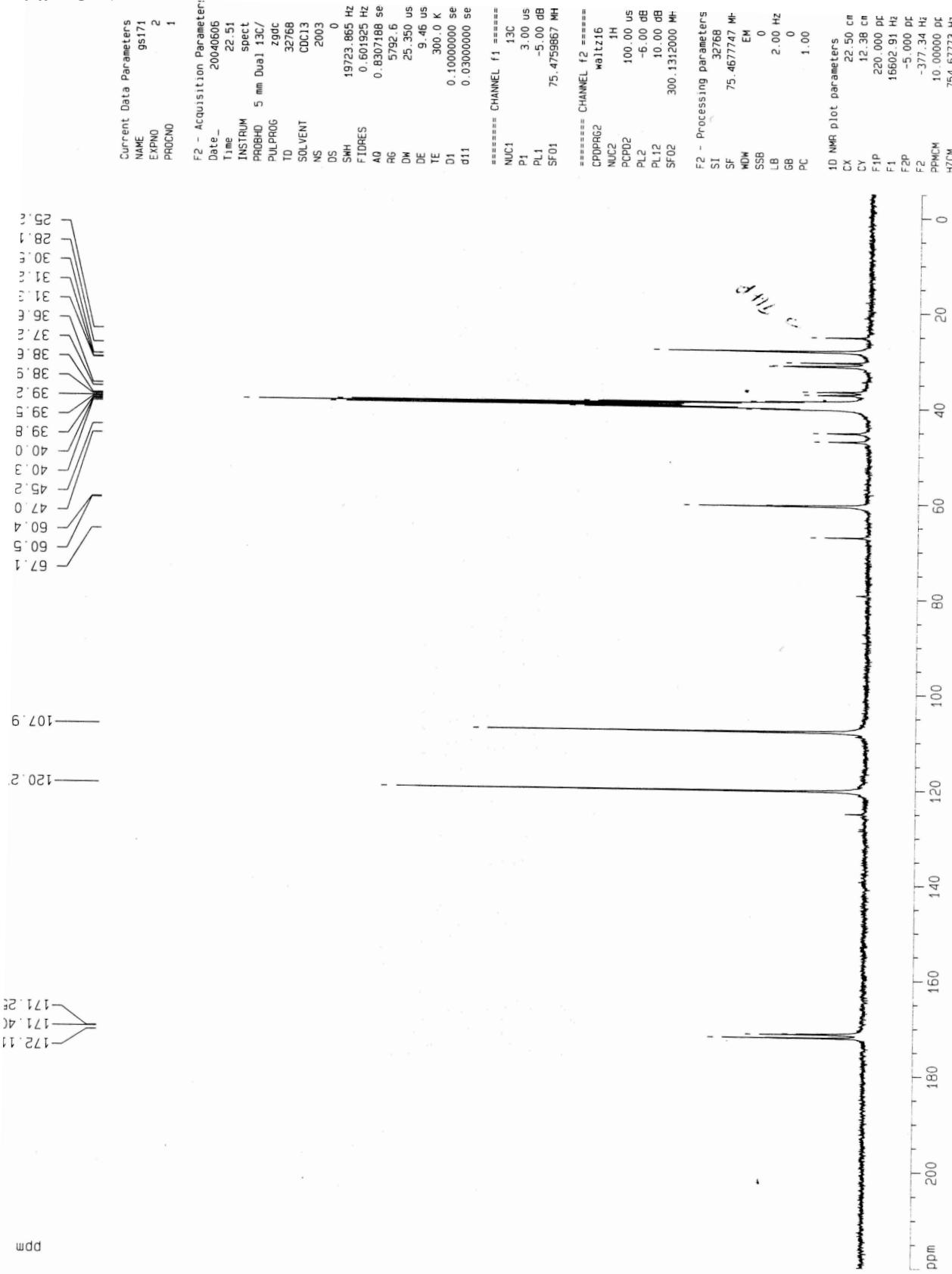
1D NMR pilot parameters
CX 22.50 cm
CY 12.24 cm
F1P 220.000 ppm
F1 16602.90 Hz
F2P -5.000 ppm
F2 -377.34 Hz
DPM 10.00000 ppm/c
TCDM 754.67743 Hz/cm



9a $^1\text{H-NMR}$

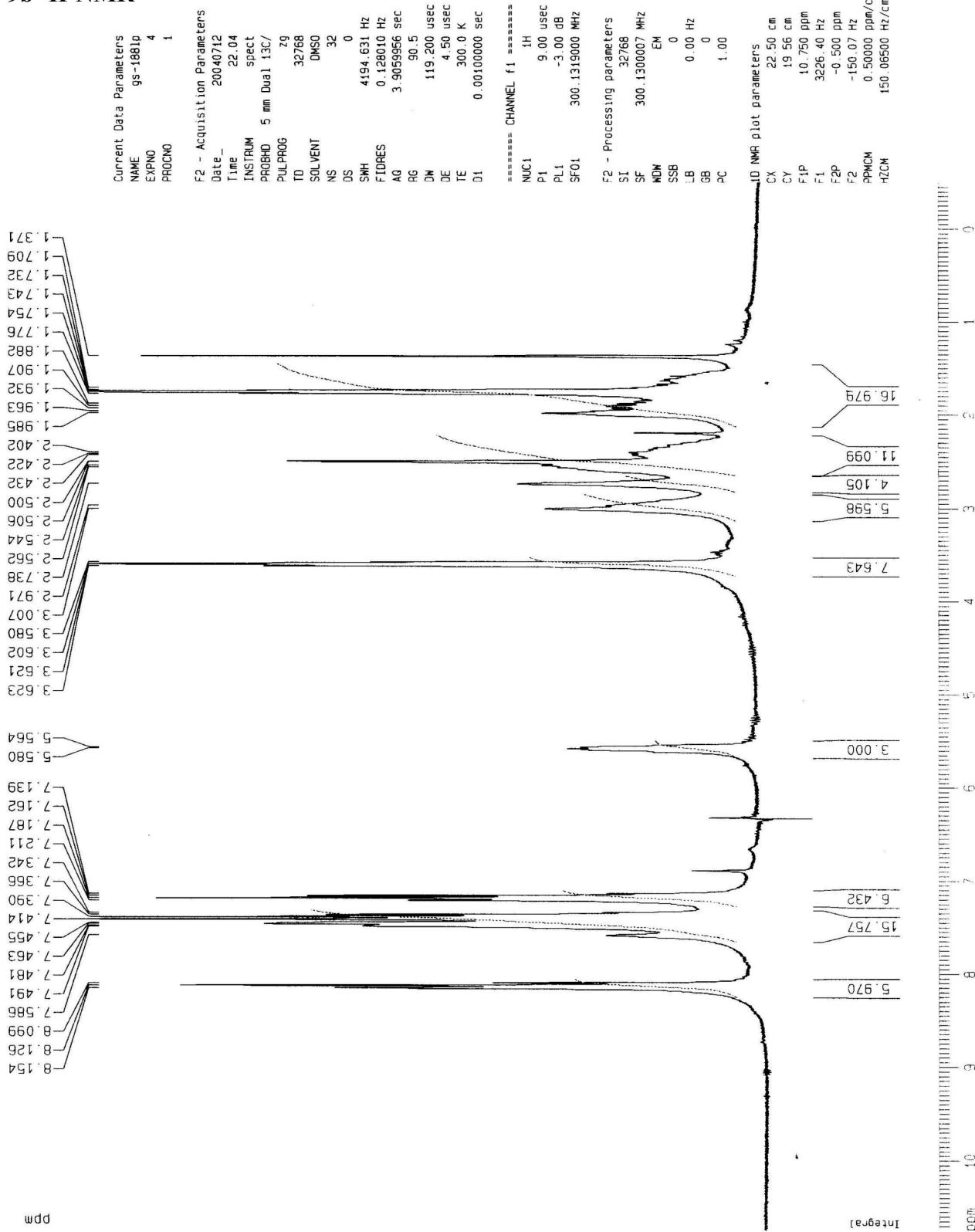


9a ^{13}C -NMR

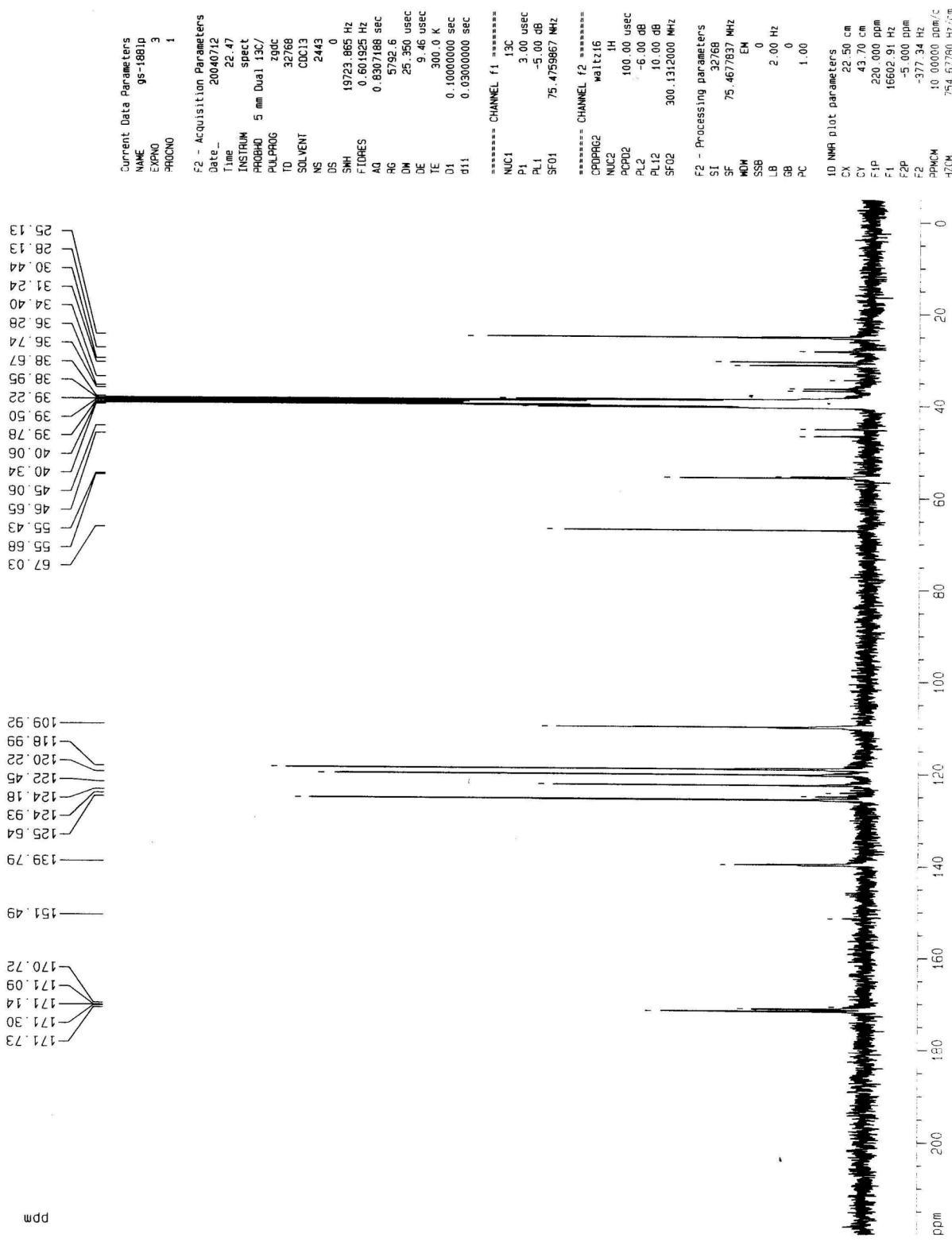


ppm

9b $^1\text{H-NMR}$



9b ^{13}C -NMR



ppm