Construction of Epidithiodioxopiperazines by Directed Oxidation of Hydroxyproline-Derived Dioxoxpiperazines

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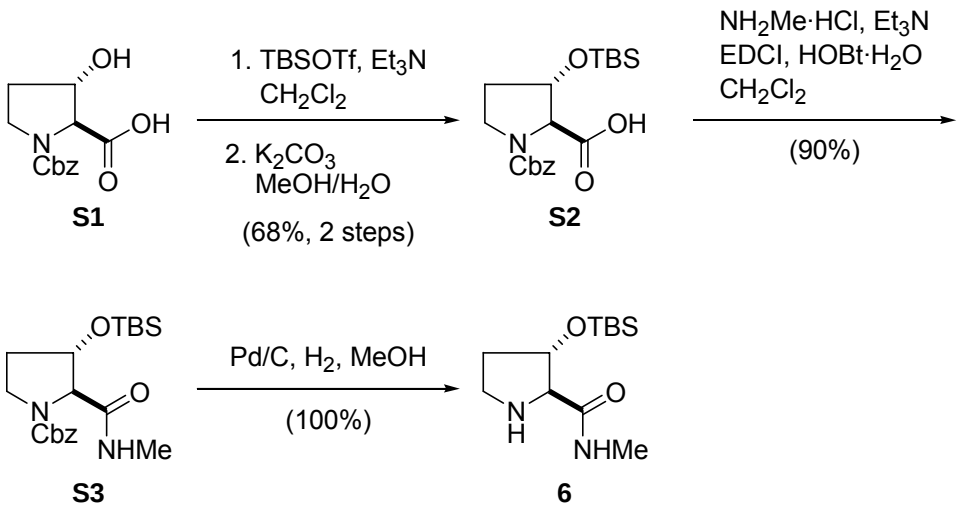
Supporting Information

Table of Contents

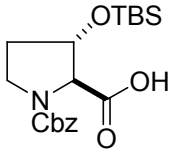
A. Experimental Procedures

General Details. Reactions were performed in oven-dried glassware fitted with rubber septa under an argon atmosphere. CH_2Cl_2 and THF were dried by passage through a bed of activated alumina. Commercial reagents were used without further purification. Thin-layer chromatography was performed on Merck 60 F254 precoated silica gel plates, which were visualized by exposure to UV (254 nm) or stained by submersion in *p*-anisaldehyde solution, $KMnO_4/H_2SO_4$ or ethanolic phosphomolybdic acid solution followed by heating on a hot plate. Flash column chromatography was performed on silica gel (230-400 mesh, Merck KGA). ^{1}H NMR spectra were recorded at 500 or 600 MHz and ^{13}C NMR spectra at 125 MHz or 150 MHz with Brucker Avance spectrometers. Chemical shifts are reported in ppm with reference to solvent signals [^{1}H-NMR: $CHCl_3$ (7.27), C_6HD_5 (7.16), CD_2HOD (3.31); ^{13}C-NMR: $CDCl_3$ (77.23), C_6D_6 (128.40), CD_3CN (118.69) CD_3OD (49.15)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared spectra were recorded using an ASI ReactIR™ 1000 spectrometer. Mass spectra were measured with a Waters LCT Premier. Optical rotations were measured with a Jasco P-1010 polarimeter.

Synthesis of Secondary Amine 6



(2*S*,3*S*)-1-(benzyloxycarbonyl)-3-(*tert*-butyldimethylsilyloxy)pyrrolidine-2-carboxylic acid (S2)

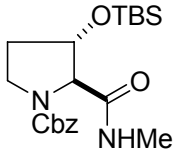


To a solution of *N*-Cbz-2-hydroxy-*L*-proline **S1**[1] (8.10 g, 30.5 mmol), Et_3N (21 ml, 150 mmol) and CH_2Cl_2 (100 mL), was added TBSOTf (25 mL, 110 mmol) at room temperature. The resulting solution was maintained for 30 min at room temperature, quenched with H_2O (100 mL), and acidified with citric acid (11.7 g) to pH 3. This mixture was extracted with CH_2Cl_2 (200 mL), then EtOAc (300 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, and concentrated. The residue was dissolved in MeOH (68 mL) and H_2O (34 mL), and K_2CO_3 (4.22 g, 30.5 mmol) was added. This solution was maintained for 3 h at room temperature and diluted with H_2O (100 mL). The aqueous solution was washed with hexane/EtOAc (9:1, 2x 100 ml), and acidified with citric acid (14.6 g) to pH 3. The acidified aqueous layer was extracted with EtOAc (2x 200 mL). The organic layer was washed with brine (100 mL), dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 3:1 to 1:2) to give 7.87 g of **S2** (68%): colorless crystals, mp 98–99 ºC; $[\alpha]^{26}_D$ 20.6 (*c* 1.07, CH_3OH); IR (film) 3359, 2925, 1679, 1428 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.12 (m, 6H), 0.89 (s, 9H), 1.87 (m, 1H), 2.05 (m, 1H), 3.66 (m, 2H), 4.23 (s, 2/5H), 4.28 (s, 3/5H), 4.50 (m, 2/5H), 4.61 (m,

[1] 1. Adams, E. *Int. J. Pept. Prot. Res.* **1976**, *8*, 503–516.

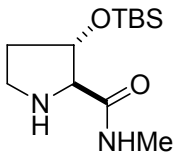
3/5H), 5.13 (d, *J* = 12.6 Hz, 2/5H), 5.17 (d, *J* = 12.6 Hz, 2/5H), 5.21 (s, 6/5H), 7.33 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.88, –4.85, 18.1, 18.1, 25.7, 25.8, 33.0, 33.7, 45.0, 45.2, 67.2, 67.7, 68.1, 68.7, 74.4, 76.0, 127.6, 127.9, 127.9, 128.2, 128.5, 128.6, 136.2, 136.6, 154.6, 156.4, 174.0, 176.1; HRMS (ESI), calcd for $C_{19}H_{29}O_5NSiNa^+$ $(M+Na)^+$ 402.1713, found 402.1697.

(2*S*,3*S*)-benzyl 3-(*tert*-butyldimethylsilyloxy)-2-(methylcarbamoyl)pyrrolidine-1-carboxylate (S3)



1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 715 mg, 3.73 mmol) was added to a mixture of **S2** (1.18 g, 3.11 mmol), methylamine hydrochloride (420 mg, 6.22 mmol), Et_3N (870 μL, 6.2 mmol), *N*-hydroxybenzotriazole monohydrate ($HOBt{\cdot}H_2O$, 504 mg, 3.73 mmol) and CH_2Cl_2 (31 mL) at room temperature. This mixture was stirred for 1 d at room temperature and quenched with H_2O (30 mL). The mixture was extracted with EtOAc (2x 50 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 1:1) to give 1.10 g of **S3** (90%): yellow oil; $[\alpha]^{27}_D$ –34.7 (*c* 1.11, $CHCl_3$); IR (film) 3332, 2954, 2931, 2894, 2858, 1708, 1663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.86 (s, 9H), 1.93 (m, 2H), 2.69 (s, 6/5H), 2.77 (s, 9/5H), 3.63 (m, 2H), 4.15 (s, 1H), 4.53 (s, 2/5H), 4.66 (s, 3/5H), 5.12 (d, *J* = 12.2 Hz, 2/5H), 5.15 (d, *J* = 12.7 Hz, 3/5H), 5.22 (d, *J* = 12.2 Hz, 2/5H), 5.22 (d, *J* = 12.7 Hz, 3/5H), 6.06 (s, 2/5H), 6.68 (s, 3/5H), 7.31 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.73 (CH_3), –4.67 (CH_3), 18.1 (C), 25.9 (CH_3), 26.2 (CH_3), 32.7 (CH_2), 33.8 (CH_2), 45.4 (CH_2), 45.7 (CH_2), 67.4 (CH_2), 67.5 (CH_2), 69.7 (CH), 70.5 (CH), 73.9 (CH), 75.8 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 128.7 (CH), 136.5 (C), 155.6 (C), 156.7 (C), 170.5 (C), 170.8 (C); HRMS (ESI), calcd for $C_{20}H_{32}O_4N_2SiNa^+$ $(M+Na)^+$ 415.2029, found 415.2019.

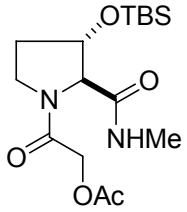
(2*S*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-*N*-methylpyrrolidine-2-carboxamide (6)



Palladium on carbon (10 wt%, 415 mg) was added to a solution of **S3** (16.3 g, 41.5 mmol) and MeOH (210 mL) at room temperature. This reaction mixture was stirred under hydrogen atmosphere for 1d at

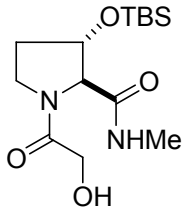
room temperature. The mixture was filtered through Celite, and the filter cake was washed with CH_2Cl_2/MeOH (20:1, 400 mL), and the filtrate was concentrated to give 10.7 g of **6** (100%); colorless oil; $[\alpha]^{25}_D$ –9.4 (*c* 1.28, $CHCl_3$); IR (film) 3327, 2954, 2931, 2887, 2858, 1659 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.12 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 1.68 (m, 2H), 2.79 (d, *J* = 4.5 Hz, 3H), 2.95 (m, 1H), 3.22 (ddd, *J* = 8.6, 8.6, 8.6 Hz, 1H), 3.55 (s, 1H), 4.57 (s, 1H), 7.49 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.6 (CH_3), 18.2 (C), 25.8 (CH_3), 26.0 (CH_3), 34.5 (CH_2), 45.2 (CH_2), 70.2 (CH), 76.5 (CH), 173.2 (C); HRMS (ESI), calcd for $C_{12}H_{27}O_2N_2Si^+$ $(M+H)^+$ 259.1842, found 259.1843.

2-((2*S*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-2-(methylcarbamoyl)pyrrolidin-1-yl)-2-oxoethylethanoate (8)



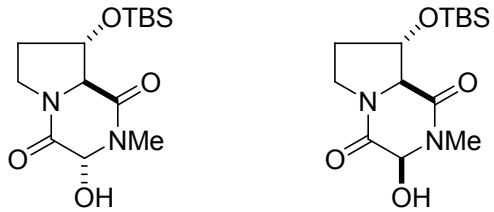
1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 341 mg, 1.78 mmol) was added to a solution of **6** (369 mg, 1.43 mmol), acetylglycolic acid **7** (211 mg, 1.78 mmol), Et_3N (250 μL, 1.8 mmol), 1-hydroxy-7-azabenzotriazole (HOAt, 242 mg, 1.78 mmol) and THF (14 mL) at room temperature. This mixture was stirred for 16 h at room temperature, and quenched with H_2O (15 mL). The aqueous solution was extracted with hexane/THF (1:1, 30 mL), and then EtOAc (2x 30 mL). The combined organic extracts were washed with brine (40 mL), dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (EtOAc to CH_2Cl_2/MeOH 20:1) to give 513 mg of **8** (100%): colorless oil; $[\alpha]^{26}_D$ –62.2 (*c* 0.94, $CHCl_3$); IR (film) 3327, 2956, 2933, 2892, 2860, 1752, 1659 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 10:1 mixture of rotamers, signals of the major isomer are reported) δ 0.088 (s, 3H), 0.094 (s, 3H), 0.87 (s, 9H), 1.96 (ddd, *J* = 12.9, 6.4, 1.5 Hz, 1H), 2.21 (s, 3H), 2.24 (dddd, *J* = 12.9, 11.3, 9.0, 3.8 Hz, 1H), 2.76 (d, *J* = 4.9 Hz, 3H), 3.61 (m, 2H), 4.38 (s, 1H), 4.69 (d, *J* = 14.9 Hz, 1H), 4.73 (d, *J* = 14.9 Hz, 1H), 4.73 (d, *J* = 3.8 Hz, 1H), 6.81 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 10:1 mixture of rotamers, signals of the major isomer are reported)δ –4.64 (CH_3), –4.62 (CH_3), 18.2 (C), 20.8 (CH_3), 25.9 (CH_3), 26.4 (CH_3), 34.2 (CH_2), 44.6 (CH_2), 61.8 (CH_2), 69.2 (CH), 72.7 (CH), 167.7 (C), 169.9 (C), 170.9 (C); HRMS (ESI), calcd for $C_{16}H_{30}O_5N_2SiNa^+$ $(M+Na)^+$ 381.1822, found 381.1809.

(2*S*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-1-(2-hydroxyethanoyl)-*N*-methylpyrrolidine-2-carboxamide (9)



$LiOH{\cdot}H_2O$ (1.09 g, 26.0 mmol) was added to a solution of **8** (8.21 g, 22.9 mmol), THF (115 mL) and H_2O (115 mL) at room temperature. This solution was maintained for 10 min at room temperature, cooled to 0 ºC, and quenched after 5 min with 1M $NaHSO_4$ in H_2O (46 mL). The aqueous solution was extracted with EtOAc (2x 300 ml). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, and concentrated. The residue was purified with silica gel column chromatography (EtOAc to CH_2Cl_2/MeOH 20:1) to give 7.25 g of **9** (100%, two rotamers, dr=12:1 in $CDCl_3$): colorless amorphous solid; $[\alpha]^{27}_D$ –62.0 (*c* 0.93, $CHCl_3$); IR (film) 3321, 2954, 2931, 2890, 2858, 1652 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 12:1 mixture of rotamers, signals of the major isomer are reported) δ 0.089 (s, 3H), 0.093 (s, 3H), 0.87 (s, 9H), 1.95 (ddd, *J* = 13.0, 7.0, 1.3 Hz, 1H), 2.26 (dddd, *J* = 13.0, 9.5, 8.8, 3.9 Hz, 1H), 2.78 (d, *J* = 4.9 Hz, 3H), 3.29 (s, 1H), 3.44 (ddd, *J* = 9.5, 8.8, 1.3 Hz, 1H), 3.51 (ddd, *J* = 9.5, 9.5, 7.0 Hz, 1H), 4.20 (s, 2H), 4.36 (s, 1H), 4.72 (d, *J* = 3.9 Hz, 1H), 6.81 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 12:1 mixture of rotamers, signals of the major isomer are reported)δ –4.7 (CH_3), –4.6 (CH_3), 18.2 (C), 25.9 (CH_3), 26.4 (CH_3), 34.1 (CH_2), 43.8 (CH_2), 60.7 (CH_2), 69.3 (CH), 72.8 (CH), 169.9 (C), 172.5 (C); HRMS (ESI), calcd for $C_{14}H_{28}O_4N_2SiNa$ $(M+Na)^+$ 339.1716, found 339.1710.

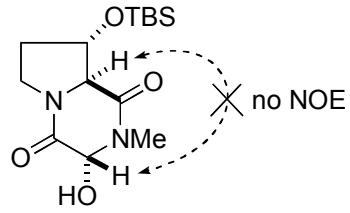
(3*R*,8*S*,8a*S*)-8-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2-methylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione (10a) and (3*S*,8*S*,8a*S*)-8-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2-methylhexahydro pyrrolo[1,2-*a*]pyrazine-1,4-dione (10b)



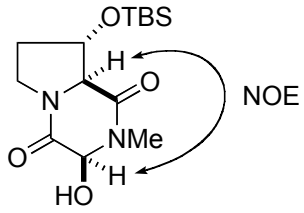
Sulfur trioxide pyridine complex (5.06 g, 31.8 mmol) was added to a solution of **9** (3.34 g, 10.6 mmol), Et_3N (8.9 mL, 64.0 mmol), DMSO (18 mL) and CH_2Cl_2 (88 mL) at room temperature. This solution was maintained for 2.5 h at room temperature, and quenched with saturated aqueous $NaHCO_3$ (100 mL). The

mixture was extracted with CH_2Cl_2 (200 mL) and then EtOAc (200 mL). The combined organic layers were washed with H_2O (100 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated. The resulting solid was crystallized from hexane/EtOAc to give 1.44 g of **10a** (43%). The mother liquid was concentrated and the residue purified by silica gel column chromatography (EtOAc to CH_2Cl_2/MeOH 20:1) to give 520 mg of **10a** (16%) and 173 mg of **10b** (5%): **10a**: colorless crystals, mp 149–150 ºC; $[\alpha]^{25}_D$ –65.8 (*c* 1.05, $CHCl_3$); IR (film) 3311, 2954, 2931, 2892, 2858, 1663 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 1.87 (dddd, *J* = 13.1, 7.5, 5.8, 5.3 Hz, 1H), 2.03 (dddd, *J* = 13.1, 7.5, 7.5, 5.6 Hz, 1H), 3.07 (s, 3H), 3.50 (ddd, *J* = 11.9, 7.5, 7.5 Hz, 1H), 3.78 (ddd, *J* = 11.9, 7.5, 5.8 Hz, 1H), 4.13 (d, *J* = 4.9 Hz, 1H), 4.71 (ddd, *J* = 5.6, 5.3, 4.9 Hz, 1H), 5.08 (d, *J* = 4.8 Hz, 1H), 5.29 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.7 (CH_3), –4.6 (CH_3), 18.2 (C), 25.9 (CH_3), 32.3 (CH_3), 33.2 (CH_2), 43.3 (CH_2), 65.1 (CH), 73.6 (CH), 83.1 (CH), 164.5 (C), 167.9 (C); HRMS (ESI), calcd for $C_{14}H_{26}O_4N_2SiNa^+$ $(M+Na)^+$ 337.1559, found 337.1558. **10b**: colorless oil; $[\alpha]^{23}_D$ –13.3 (*c* 1.19, $CHCl_3$); IR (film) 3346, 2954, 2931, 2890, 2858, 1671 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 3H), 0.16 (s, 3H), 0.91 (s, 9H), 1.90 (dddd, *J* = 13.0, 7.3, 4.7, 3.7 Hz, 1H), 1.98 (dddd, *J* = 13.0, 8.1, 7.7, 5.5 Hz, 1H), 3.01 (s, 3H), 3.56 (ddd, *J* = 12.0, 8.1, 7.3 Hz, 1H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.92 (ddd, *J* = 12.0, 7.7, 4.7 Hz, 1H), 4.50 (d, *J* = 4.1 Hz, 1H), 4.89 (ddd, *J* = 5.5, 3.7, 3.0 Hz, 1H), 5.11 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.7 (CH_3), –4.6 (CH_3), 18.2 (C), 25.9 (CH_3), 28.1 (CH_3), 33.5 (CH_2), 44.1 (CH_2), 67.3 (CH), 73.6 (CH), 76.7 (CH), 165.2 (C), 165.5 (C); HRMS (ESI), calcd for $C_{14}H_{26}O_4N_2SiNa^+$ $(M+Na)^+$ 337.1559, found 337.1555.

NOE experiment for **10a** and NOESY experiment for **10b**

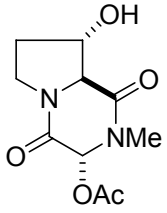


10a (500 MHz, $CDCl_3$)



10b (500 MHz, $CDCl_3$)

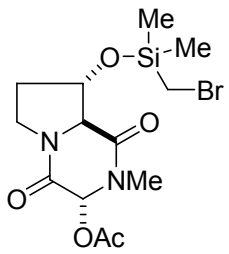
(3*R*,8*S*,8a*S*)-8-hydroxy-2-methyl-1,4-dioxooctahydropyrrolo[1,2-*a*]pyrazin-3-yl ethanoate (11)



Acetic anhydride (1.8 mL, 19 mmol) was added to a solution of **10a** (3.88 g, 12.3 mmol), pyridine (2.00 mL, 25 mmol), DMAP (150 mg, 1.23 mmol) and CH_2Cl_2 (82 mL) at room temperature. This solution was maintained for 1 h at room temperature, and quenched with pH 7 phosphate buffer (50 mL). The mixture was extracted with Et_2O (2x 200 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 1:1) to give 4.18 g of the corresponding acetate (95%): colorless oil; $[\alpha]^{24}_D$ –9.2 (*c* 0.96, CH_2Cl_2); IR (film) 2956, 2939, 2982, 2860, 1756, 1694 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.15 (s, 3H), 0.18 (s, 3H), 0.92 (s, 9H), 1.90 (dddd, *J* = 13.0, 8.0, 7.3, 5.7 Hz, 1H), 2.08 (dddd, *J* = 13.0, 7.3, 6.5, 5.7 Hz, 1H), 2.15 (s, 3H), 3.07 (s, 3H), 3.56 (ddd, *J* = 12.0, 8.0, 6.5 Hz, 1H), 3.75 (ddd, *J* = 12.0, 7.3, 7.3 Hz, 1H), 4.20 (d, *J* = 5.0 Hz, 1H), 4.70 (ddd, *J* = 5.7, 5.7, 5.0 Hz, 1H), 6.10 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ –4.7 (CH_3), –4.6 (CH_3), 18.2 (C), 20.9 (CH_3), 25.9 (CH_3), 33.2 (CH_2), 33.7 (CH_3), 43.2 (CH_2), 65.2 (CH), 73.6 (CH), 81.9 (CH), 160.3 (C), 168.7 (C), 170.1 (C); HRMS (ESI), calcd for $C_{16}H_{28}O_5N_2SiNa^+$ $(M+Na)^+$ 379.1665, found 379.1655.

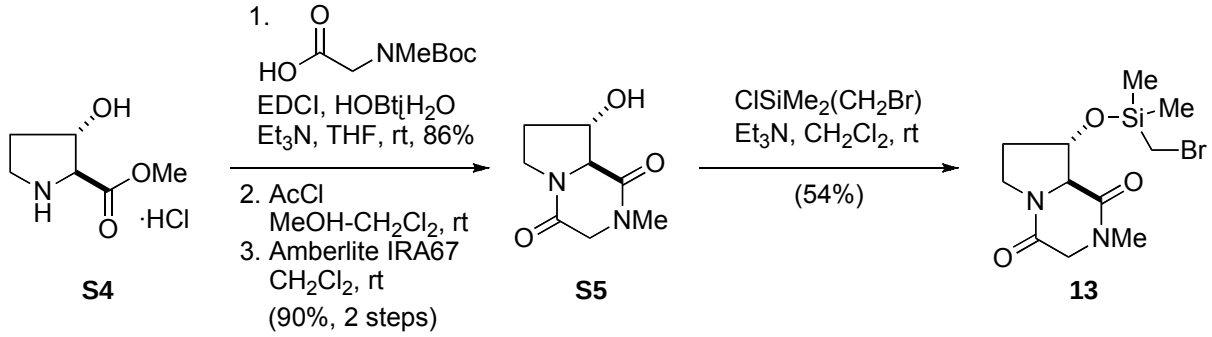
Tetrabutylammonium fluoride (1M in THF, 6.5 mL, 6.5 mmol) was added to a solution of this acetate derivative (774 mg, 2.17 mmol), AcOH (1.5 mL, 26 mmol) and THF (22 mL) at room temperature. This solution was heated to 60 ºC, stirred for 1.5 h, cooled to room temperature, and concentrated. The residue was purified by silica gel column chromatography (EtOAc) to give 404 mg of **11** (77%): colorless crystals, mp 111–112 ºC; $[\alpha]^{24}_D$ –45.1 (*c* 1.13, CH_2Cl_2); IR (film) 3436, 2983, 2954, 2896, 1752, 1671 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 1.39 (dddd, *J* = 12.5, 9.8, 9.8, 9.8 Hz, 1H), 1.47 (s, 3H), 1.60 (dddd, *J* = 12.5, 7.5, 7.5, 2.5 Hz, 1H), 2.71 (s, 1H), 3.03 (ddd, *J* = 12.1, 9.8, 2.5 Hz, 1H), 3.11 (ddd, *J* = 12.1, 9.8, 7.5 Hz, 1H), 3.44 (bs, 1H), 3.68 (d, *J* = 7.9 Hz, 1H), 3.91 (ddd, *J* = 9.8, 7.9, 7.5 Hz, 1H), 6.13 (s, 1H); ^{13}C NMR (150 MHz, C_6D_6) δ 20.2 (CH_3), 30.0 (CH_2), 32.6 (CH_3), 42.1 (CH_2), 62.9 (CH), 72.9 (CH), 82.0 (CH), 159.8 (C), 170.0 (C), 170.1 (C); HRMS (ESI), calcd for $C_{10}H_{14}O_5N_2Na^+$ $(M+Na)^+$ 265.0800, found 265.0806.

(3*R*,8*S*,8a*S*)-8-((bromomethyl)dimethylsilyloxy)-2-methyl-1,4-dioxooctahydropyrrolo[1,2-*a*] pyrazin-3-yl ethanoate (12)

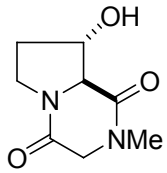


(Bromomethyl)chlorodimethylsilane (450 μL, 3.3 mmol) was added to a solution of **11** (198 mg, 817 μmol), triethylamine (910 μL, 6.50 mmol) and CH_2Cl_2 (8.2 mL) at room temperature. This solution was maintained for 10 min at room temperature, and quenched with pH 7 phosphate buffer (10 mL). The mixture was extracted with CH_2Cl_2/hexane (1:1, 15 mL), and then Et_2O (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated. Triethylamine was removed azeotropically from toluene (2x 5 mL) under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc 3:1 to 1:1) to give 306 mg of **12** (98%): colorless oil; $[\alpha]^{24}_D$ –19.2 (*c* 1.09, CH_2Cl_2); IR (film) 2960, 2898, 1756, 1686 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.26 (s, 3H), 0.30 (s, 3H), 1.35 (dddd, *J* = 12.9, 9.0, 8.4, 6.9 Hz, 1H), 1.43 (s, 3H), 1.50 (dddd, *J* = 12.9, 8.4, 6.9, 4.7 Hz, 1H), 2.39 (d, *J* = 13.1 Hz, 1H), 2.43 (d, *J* = 13.1 Hz, 1H), 2.73 (s, 3H), 3.13 (ddd, *J* = 12.4, 9.0, 4.7 Hz, 1H), 3.25 (ddd, *J* = 12.4, 8.4, 8.4 Hz, 1H), 3.93 (d, *J* = 6.3 Hz, 1H), 4.04 (ddd, *J* = 6.9, 6.9, 6.3 Hz, 1H), 6.16 (s, 1H); ^{13}C NMR (150 MHz, C_6D_6) δ –2.4 (CH_3), –2.2 (CH_3), 16.8 (CH_2), 20.2 (CH_3), 32.5 (CH_2), 33.0 (CH_3), 42.7 (CH_2), 64.2 (CH), 73.9 (CH), 82.3 (CH), 160.1 (C), 168.7 (C), 170.0 (C); HRMS (ESI), calcd for $C_{13}H_{21}O_5N_2SiBrNa^+$ $(M+Na)^+$ 415.0301, found 415.0290.

Synthesis of α-Bromomethyl Silyl Ether 13



(8*S*,8a*S*)-8-hydroxy-2-methylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione (S5)



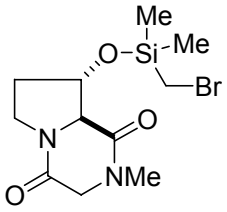
Triethylamine (3.3 mL, 23.7 mmol) and *N*-hydroxybenzotriazole monohydrate (HOBt·H_2O, 1.71 g, 12.7 mmol) were added to a mixture of **S4**[2] (2.00 g, 11.0 mmol), *N*-Boc-sarcosine (2.30 g, 12.1 mmol) and THF

[2] 2. Demange, L.; Cluzeau, J.; Ménez, A.; Dugave, C. *Tetrahedron Lett.* **2001**, *42*, 651–653.

(220 mL) at room temperature. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 2.43 g, 12.7 mmol) was divided into four portions and added to the reaction mixture every hour at room temperature. The resulting mixture was stirred overnight at room temperature and quenched with saturated aqueous sodium bicarbonate (200 mL). The mixture was extracted with THF/hexane (1:1, 400 mL) and then EtOAc (300 mL). The combined organic layers were washed with brine (200 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 3:1 to EtOAc) to give 3.00 g of the corresponding dipeptide (86%).

Acetyl chloride (5.0 mL) was added to a solution of the this dipeptide (3.12 g, 9.86 mmol) and CH_2Cl_2/MeOH (1:1, 100 mL) at 0 °C. This solution was maintained for 2.5 h at room temperature, and concentrated. The residue was dissolved in CH_2Cl_2 (100 mL), and Amberlite IRA 67 (6.24 g) was added to the solution at room temperature. This mixture was stirred overnight at room temperature and filtered through a pad of silica gel to give 1.64 g of **S5** (90% over 2 steps): colorless crystals, mp 112–113 °C; $[\alpha]^{25}_D$ –75.2 (*c* 1.06, CH_2Cl_2); IR (film) 3415, 2954, 2896, 1648 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.95 (dddd, *J* = 12.8, 10.0, 10.0, 10.0 Hz, 1H), 2.34 (dddd, *J* = 12.8, 7.3, 7.3, 2.7 Hz, 1H), 3.00 (s, 3H), 3.48 (s, 1H), 3.60 (m, 2H), 3.79 (dd, *J* = 9.6, 1.3 Hz, 1H), 3.79 (dd, *J* = 16.9, 1.3 Hz, 1H), 4.18 (dd, *J* = 16.9, 2.1 Hz, 1H), 4.31 (ddd, *J* = 10.0, 9.6, 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.8 (CH_2), 33.2 (CH_3), 41.7 (CH_2), 53.3 (CH_2), 62.7 (CH), 72.5 (CH), 162.6 (C), 167.2 (C); HRMS (ESI), calcd for $C_8H_{12}O_3N_2Na^+$ $(M+Na)^+$, 207.0746, found 207.0754.

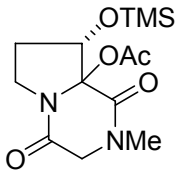
(8*S*,8a*S*)-8-((bromomethyl)dimethylsilyloxy)-2-methylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione (13)

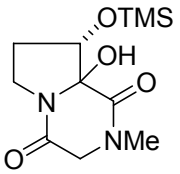


(Bromomethyl)chlorodimethylsilane (770 μL, 5.7 mmol) was added to a solution of **S5** (299 mg, 1.62 mmol), triethylamine (1.58 ml, 11.3 mmol) and CH_2Cl_2 (16 mL) at room temperature. This solution was maintained for 30 min at room temperature and quenched with pH 7 phosphate buffer (2x 20 mL). The mixture was extracted with Et_2O (30 mL). The organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated. Triethylamine was removed azeotropically from toluene (2x 5 mL) under reduced pressure. The residue was purified with flash column chromatography (hexane/EtOAc 3:1 to

EtOAc) to give 292 mg of **13** (54%), together with 22.4 mg of recovered **S5** (7%): **13**: colorless oil; $[\alpha]^{25}_{D}$ –31.0 (*c* 1.14, CH_2Cl_2); IR (film) 2958, 2896, 1663 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 0.30 (s, 3H), 0.34 (s, 3H), 1.41 (dddd, *J* = 13.0, 9.0, 7.2, 6.7 Hz, 1H), 1.53 (dddd, *J* = 13.0, 7.9, 7.0, 5.7 Hz, 1H), 2.31 (s, 3H), 2.50 (s, 2H), 3.14 (d, *J* = 16.5 Hz, 1H), 3.15 (ddd, *J* = 11.6, 9.0, 5.7 Hz, 1H), 3.22 (dd, *J* = 16.5, 1.3 Hz, 1H), 3.34 (ddd, *J* = 11.6, 7.9, 6.7 Hz, 1H), 3.35 (dd, *J* = 7.0, 1.3 Hz, 1H), 4.30 (ddd, *J* = 7.2, 7.0, 7.0 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ –2.22 (CH_3), –2.15 (CH_3), 17.1 (CH_2), 32.8 (CH_2), 33.1 (CH_3), 42.5 (CH_2), 53.4 (CH_2), 64.6 (CH), 74.1 (CH), 162.7 (C), 166.3 (C); HRMS (ESI), calcd for $C_{11}H_{19}N_2O_3SiBrNa^+$ $(M+Na)^+$, 357.0246, found 357.0240.

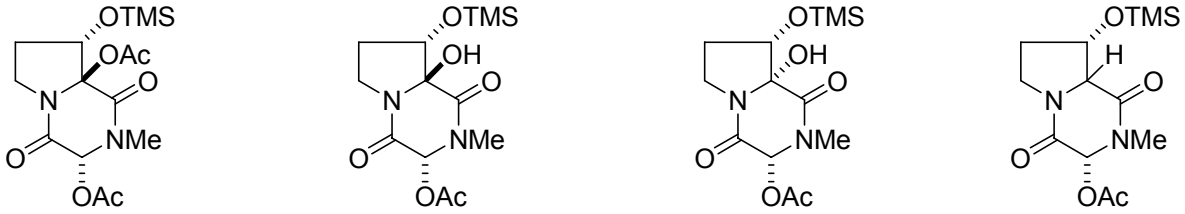
General Procedure for Radical-Promoted C-H Bond Oxidation of 13





A stirring mixture of **13** (13.4 mg, 40 μmol), $Cu(OAc)_2$ (72.7 mg, 400 μmol), AIBN (120 μmol), a mediator (120 μmol) and solvent (2.0 mL) was heated to 80 ºC and maintained at this temperature for 40 min. After cooling to room temperature, the reaction mixture was quenched with pH 7 phosphate buffer (10 mL). The mixture was extracted with Et_2O (2x 15 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 2:1) to give acetate **14** and hemiaimnal **15** in the amounts reported in Table 1: Acetate **14**: colorless oil; $[\alpha]^{24}_{D}$ 144.0 (*c* 0.80, CH_2Cl_2); IR (film) 2962, 2906, 1744, 1683 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 0.10 (s, 9H), 1.39 (ddd, *J* = 13.3, 8.3, 1.5 Hz, 1H), 1.48 (s, 3H), 1.83 (dddd, *J* = 13.3, 10.1, 9.7, 3.9 Hz, 1H), 2.48 (s, 3H), 3.28 (ddd, *J* = 11.5, 10.1, 1.5 Hz, 1H), 3.51 (d, *J* = 16.7 Hz, 1H), 4.09 (ddd, *J* = 11.5, 9.7, 8.3 Hz, 1H), 4.23 (d, *J* = 16.7 Hz, 1H), 4.55 (d, *J* = 3.9 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.44 (CH_3), 20.8 (CH_3), 29.7 (CH_2), 33.2 (CH_3) 44.7 (CH_2), 54.2 (CH_2), 77.2 (CH), 93.5 (C), 162.7 (c), 165.4 (C), 169.8 (C); HRMS (ESI), calcd for $C_{13}H_{22}O_5N_2SiNa^+$ $(M+Na)^+$, 337.1196, found 337.1187. Hemiaminal **15**: colorless oil; $[\alpha]^{25}_{D}$ –50.6 (*c* 1.12, CH_2Cl_2); IR (film) 3309, 2960, 2904, 1667 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.17 (s, 9H), 1.49 (m, 2H), 2.36 (s, 3H), 3.14 (ddd, *J* = 11.6, 8.2, 8.2 Hz, 1H), 3.25 (d, *J* = 16.7 Hz, 1H), 3.44 (ddd, *J* = 11.6, 8.0, 5.4 Hz, 1H), 3.93 (d, *J* = 16.7 Hz, 1H), 4.24 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.34 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.45 (CH_3), 29.9 (CH_2), 33.0 (CH_3), 41.3 (CH_2), 53.1 (CH_2), 73.7 (CH), 84.3 (C), 165.5 (C), 166.3 (C); HRMS (ESI), calcd for $C_{11}H_{20}N_2O_4SiNa^+$ $(M+Na)^+$, 295.1090, found 295.1078.

(3*S*,8*S*,8a*S*)-2-methyl-1,4-dioxo-8-(trimethylsilyloxy)octahydropyrrolo[1,2-*a*]pyrazine-3,8a-diyl diethanoate (16), (3*S*,8*S*,8a*S*)-8a-hydroxy-2-methyl-1,4-dioxo-8-(trimethylsilyloxy)octahydro pyrrolo[1,2-*a*]pyrazin-3-yl ethanoate (17), (3*S*,8*S*,8a*R*)-8a-hydroxy-2-methyl-1,4-dioxo-8-(trimethylsilyloxy)octahydropyrrolo[1,2-*a*]pyrazin-3-yl ethanoate (18), and (3*S*,8*S*)-2-methyl-1,4-dioxo-8-(trimethylsilyloxy)octahydropyrrolo[1,2-*a*]pyrazin-3-yl ethanoate (19)

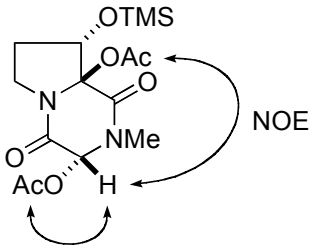


A solution of AIBN (744 mg, 4.53 mmol), $(TMS)_3SiH$ (1.39 mL, 4.53 mmol) and $(CH_2Cl)_2$ (16 mL) was added over 1 h using a syringe pump to a stirring mixture of **12** (14.8 mg, 38.9 μmol), $Cu(OAc)_2{\cdot}H_2O$ (1.68 mg, 8.41 mmol) and $(CH_2Cl)_2$ (16 mL) at 80 ºC, and the resulting mixture was stirred for an additional 30 min at 80 ºC. After cooling to room temperature, the reaction mixture was quenched with pH 7 phosphate buffer (30 mL). The mixture was extracted with EtOAc (3x 50 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 4:1 to 1:2) to give 98.8 mg of β-acetate **16** (41%), 68.4 mg of β-hemiaminal **17** (32%), 25.7 mg of α-hemiaminal **18** (12%), and 12.2 mg of reduced product **19** (6%).

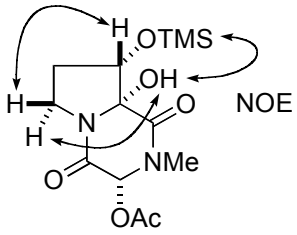
An improved procedure was developed, which is detailed below. A solution of AIBN (19.2 mg, 117 μmol), $(TMS)_3SiH$ (84 μL, 273 μmol) and $(CH_2Cl)_2$ (1.0 mL) was added over 1 h using a syringe pump to a stirring mixture of **12** (14.8 mg, 38.9 μmol), $Cu(OAc)_2{\cdot}H_2O$ (54.4 mg, 273 μmol) and $(CH_2Cl)_2$ (1.0 mL) at 80 ºC, and the resulting mixture was stirred for an additional 30 min at 80 ºC. After cooling to room temperature, the reaction mixture was quenched with pH 7 phosphate buffer (15 mL). The mixture was extracted with EtOAc (3x 15 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 4:1 to 1:2) to give 6.1 mg of β-acetate **16** (42%), 3.2 mg of β-hemiaminal **17** (25%), 0.8 mg of α-hemiaminal **18** (6%), and 0.7 mg of reduced product **19** (6%): β-Acetate **16**: amorphous solid; $[\alpha]^{25}_D$ 79.7 (*c* 1.03, CH_2Cl_2); IR (film) 2960, 1760, 1748, 1694 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.06 (s, 9H), 1.37 (ddd, *J* = 13.5, 8.3, 1.5 Hz, 1H), 1.46 (s, 3H), 1.68 (s, 3H), 1.79 (dddd, *J* = 13.5, 9.7, 9.7, 4.0 Hz, 1H), 2.78 (s, 3H), 3.18 (ddd, *J* = 11.6, 9.7, 1.5 Hz, 1H), 4.03 (ddd, *J* = 11.6, 9.7, 8.3 Hz, 1H), 4.51 (d, *J* = 4.0 Hz, 1H), 6.83 (s, 1H); ^{13}C NMR (150 MHz, C_6D_6) δ 0.35 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 29.7 (CH_2), 30.4 (CH_3), 44.8 (CH_2), 76.8 (CH), 79.5 (CH), 93.1 (C), 162.7 (C), 163.1 (C), 169.4 (C), 170.0 (C);

HRMS (ESI), calcd for $C_{15}H_{24}O_7N_2SiNa^+$ $(M+Na)^+$ 395.1251, found 395.1244. β-Hemiaminal **17**: amorphous solid; $[\alpha]^{25}_D$ 10.8 (*c* 0.68, CH_2Cl_2); IR (film) 3344, 2960, 2925, 2856, 1760, 1671 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.08 (s, 9H), 1.33 (ddd, *J* = 12.9, 8.5, 2.4 Hz, 1H), 1.62 (s, 3H), 1.92 (dddd, *J* = 12.9, 9.7, 8.5, 4.0 Hz, 1H), 2.57 (s, 3H), 3.35 (ddd, *J* = 11.5, 9.7, 2.4 Hz, 1H), 3.55 (s, 1H), 4.11 (ddd, *J* = 11.5, 8.5, 8.5 Hz, 1H), 4.20 (d, *J* = 4.0 Hz, 1H), 6.37 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.48 (CH_3), 20.4 (CH_3), 29.9 (CH_2), 30.7 (CH_3), 44.3 (CH_2), 77.0 (CH), 78.3 (CH), 90.6 (C), 162.0 (C), 166.4 (C), 170.0 (C); HRMS (ESI), calcd for $C_{13}H_{22}O_6N_2SiNa^+$ $(M+Na)^+$ 353.1145, found 353.1140. α-Hemiaminal **18**: amorphous solid; $[\alpha]^{25}_D$ –33.6 (*c* 1.32, CH_2Cl_2); IR (film) 3436, 2960, 2904, 1756, 1698 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.14 (s, 9H), 1.43 (m, 2H), 1.56 (s, 3H), 2.74 (s, 3H), 3.16 (ddd, *J* = 9.9, 7.3, 7.3 Hz, 1H), 3.33 (ddd, *J* = 9.9, 7.4, 4.2 Hz, 1H), 3.95 (dd, *J* = 7.0, 7.0 Hz, 1H), 4.37 (s, 1H), 6.41 (s, 1H); ^{13}C NMR (150 MHz, C_6D_6) δ 0.42, 20.4, 29.2, 32.6, 41.4, 74.1, 80.5, 83.5, 162.2, 168.0, 170.5; HRMS (ESI), calcd for $C_{13}H_{22}O_6N_2SiNa^+$ $(M+Na)^+$ 353.1145, found 353.1135. Reduced products **19**: colorless oil; $[\alpha]^{25}_D$ –18.8 (*c* 0.84, CH_2Cl_2); IR (film) 2958, 2898, 1756, 1686 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.20 (s, 9H), 1.38 (m, 2H), 1.42 (s, 3H), 2.76 (s, 3H), 3.17 (ddd, *J* = 11.9, 8.4, 5.8 Hz, 1H), 3.36 (ddd, *J* = 11.9, 7.7, 7.7 Hz, 1H), 4.01 (d, *J* = 5.6 Hz, 1H), 4.40 (ddd, *J* = 6.3, 6.3, 6.3 Hz, 1H), 6.19 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.55 (CH_3), 20.2 (CH_3), 32.9 (CH_2), 33.1 (CH_3), 43.0 (CH_2), 64.9 (CH), 73.5 (CH), 82.4 (CH), 160.3 (C), 168.6 (C), 170.0 (C); $C_{13}H_{22}O_5N_2SiNa^+$ $(M+Na)^+$ 337.1196, found 337.1191.

NOESY experiments for β-acetate **16** and α-hemiaminal **18**



16 (600 MHz, C_6D_6)



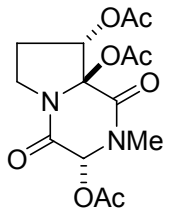
18 (600 MHz, C_6D_6)

(3*S*,8*S*,8a*S*)-2-methyl-1,4-dioxo-8-(trimethylsilyloxy)octahydropyrrolo[1,2-*a*]pyrazine-3,8a-diyl diethanoate (16)

Acetic anhydride (190 μL, 2.1 mmol) was added to a solution of **17** (452 mg, 1.37 mmol), DMAP (302 mg, 2.47 mmol) and CH_2Cl_2 (27 mL) at room temperature. This solution was maintained for 10 min at room temperature, and quenched by adding pH 7 phosphate buffer (30 mL). The mixture was extracted with Et_2O (2x 50 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4,

and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 1:1) to give 391 mg of **16** (77%).

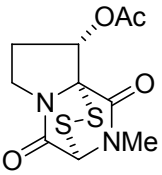
(3*S*,8*S*,8a*S*)-2-methyl-1,4-dioxooctahydropyrrolo[1,2-*a*]pyrazine-3,8,8a-triyl triethanoate (20)



Tetrabutylammonium fluoride (1M in THF, 120 μL, 120 μmol) was added to a solution of **16** (43.4 mg, 117 μmol), AcOH (67 ml, 1.2 mmol) and THF (2.3 mL) at room temperature. This solution was maintained for 1.5 h at room temperature, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 1.5:1 to EtOAc) to give 33.6 mg of the corresponding secondary alcohol (96%): colorless crystals, mp 181–182 °C, $[\alpha]^{25}_D$ 98.3 (*c* 1.00, CH_2Cl_2); IR (film) 3427, 1746, 1698, 1210 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 1.37 (s, 3H), 1.42 (ddd, *J* = 13.6, 8.7, 2.1 Hz, 1H), 1.63 (s, 3H), 1.69 (dddd, *J* = 13.6, 10.3, 8.7, 4.7 Hz, 1H), 2.46 (bs, 1H), 2.73 (s, 3H), 3.09 (ddd, *J* = 11.8, 10.3, 2.1 Hz, 1H), 3.95 (ddd, *J* = 11.8, 8.7, 8.7 Hz, 1H), 4.41 (dd, *J* = 8.5, 4.7 Hz, 1H), 6.51 (s, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 21.3 (CH_3) , 21.5 (CH_3), 29.4 (CH_2), 31.0 (CH_3), 44.9 (CH_2), 76.3 (CH), 79.8 (CH), 93.2 (C), 163.3 (C), 163.5 (C), 171.0 (C), 171.9 (C); HRMS (ESI), calcd for $C_{12}H_{16}O_7N_2Na^+$ $(M+Na)^+$ 323.0855, found 323.0846.

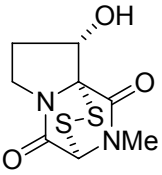
Acetic anhydride (58 μL, 610 μmol) was added to a solution of the this alcohol (87.3 mg, 291 mmol), DMAP (89.6 mg, 734 μmol) and CH_2Cl_2 (5.8 mL) at room temperature. This resulting solution was maintained for 50 min at room temperature, and quenched with pH 7 phosphate buffer (10 mL). The mixture was extracted with EtOAc (2x 20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 1:1 to hexane/EtOAc 1:2) to give 99.7 mg of **20** (100%): colorless amorphous solid; $[\alpha]^{23}_D$ 85.1 (*c* 1.05, CH_2Cl_2); IR (film) 2931, 1748, 1698, 1202 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 1.34, (s, 3H), 1.52 (ddd, *J* = 14.7, 8.7, 2.2 Hz, 1H), 1.57 (s, 3H), 1.67 (s, 3H), 1.79 (dddd, *J* = 14.7, 10.1, 8.7, 4.4 Hz, 1H), 2.77 (s, 3H), 3.06 (ddd, *J* = 12.0, 10.1, 2.2 Hz, 1H), 3.85 (ddd, *J* = 12.0, 8.7, 8.7 Hz, 1H), 5.73 (d, *J* = 4.4 Hz, 1H), 6.65 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 20.5 (CH_3), 20.5 (CH_3), 20.6 (CH_3), 27.0 (CH_2), 30.6 (CH_3), 44.4 (CH_2), 77.6 (CH), 79.9 (CH), 91.7 (C), 161.6 (C), 162.5 (C), 168.8 (C), 169.2 (C), 170.1 (C); HRMS (ESI), calcd for $C_{14}H_{18}O_8N_2Na^+$ $(M+Na)^+$ 365.0961, found 365.0960.

Acetoxy Epidithiodioxopiperazine (22)



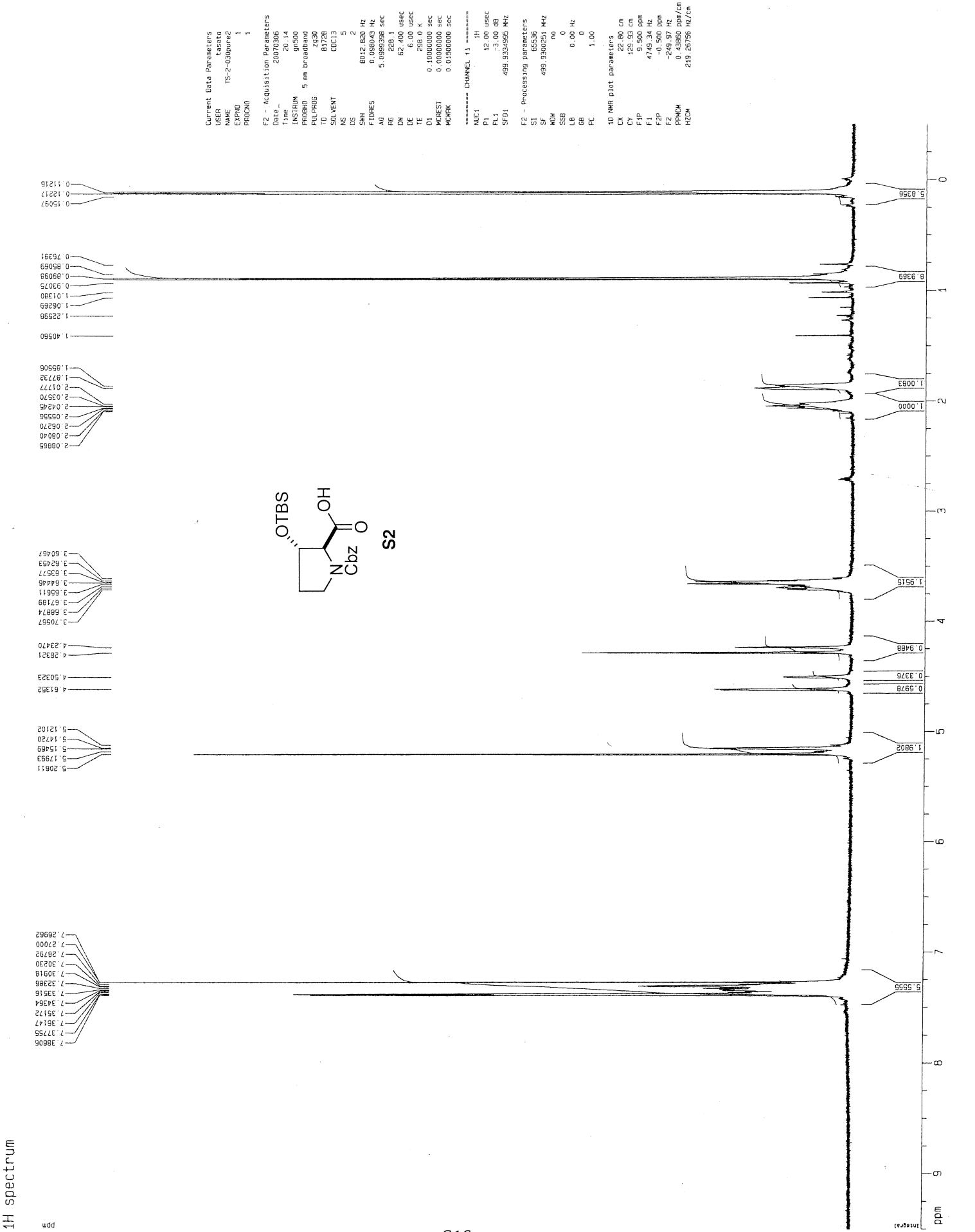
A solution of **20** (52.7 mg, 154 μmol) and MeCN (4.0 mL) in a sealed vial was degassed using the freeze-pump-thaw technique (3x) and cooled to –78 ºC. Hydrogen sulfide (bp –60 ºC, 3 mL) was condensed at –78 ºC, and added via cannula to the solution of **20** at –78 ºC. Then a solution of scandium triflate (15.2 mg, 30.8 μmol) and MeCN (4 mL), which had been degassed by the freeze-pump-thaw technique (3x), was then added via cannula to the solution of **20**. The sealed vial was then allowed to warm to room temperature behind a blast shield, stirred for 13 h at room temperature, cooled to –78 ºC, sealed vial stopper was replaced with a rubber septa containing a bleed needle. The cooling bath was removed, and the solution was allowed to warm to room temperature. Once the solution was at room temperature, residual H_2S and MeCN were removed under reduced pressure by connecting a vacuum manifold mounted in the fume hood. The resulting residue was dissolved in MeOH (20 mL), and oxygen was slowly bubbled through the solution for 12 h at room temperature. After concentration. The residue was purified by silica gel column chromatography (hexane/EtOAc 1:1 to EtOAc) to give 16.5 mg of **22** (37%): yellow crystals, mp 206–207 ºC dec; $[\alpha]^{25}_{D}$ –81.3 (*c* 0.34, CH_2Cl_2); IR (film) 2993, 1752, 1698, 1221 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 1.50 (s, 3H), 1.58 (dddd, *J* = 12.7, 9.5, 9.5, 9.5 Hz, 1H), 1.91 (dddd, *J* = 12.7, 7.8, 7.2, 2.8 Hz, 1H), 2.33 (s, 3H), 2.64 (ddd, *J* = 11.4, 9.5, 7.8 Hz, 1H), 3.26 (ddd, *J* = 11.4, 9.5, 2.8 Hz, 1H), 4.34 (s, 1H) 5.98 (dd, *J* = 9.5, 7.2 Hz, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 21.1 (CH_3), 30.2 (CH_2), 32.1 (CH_3), 43.8 (CH_2), 69.0 (CH), 74.8 (CH), 78.6 (C), 162.9 (C), 166.0 (C), 170.3 (C); HRMS (ESI), calcd for $C_{10}H_{12}O_4N_2S_2Na^+$ $(M+Na)^+$ 311.0136, found 311.0127.

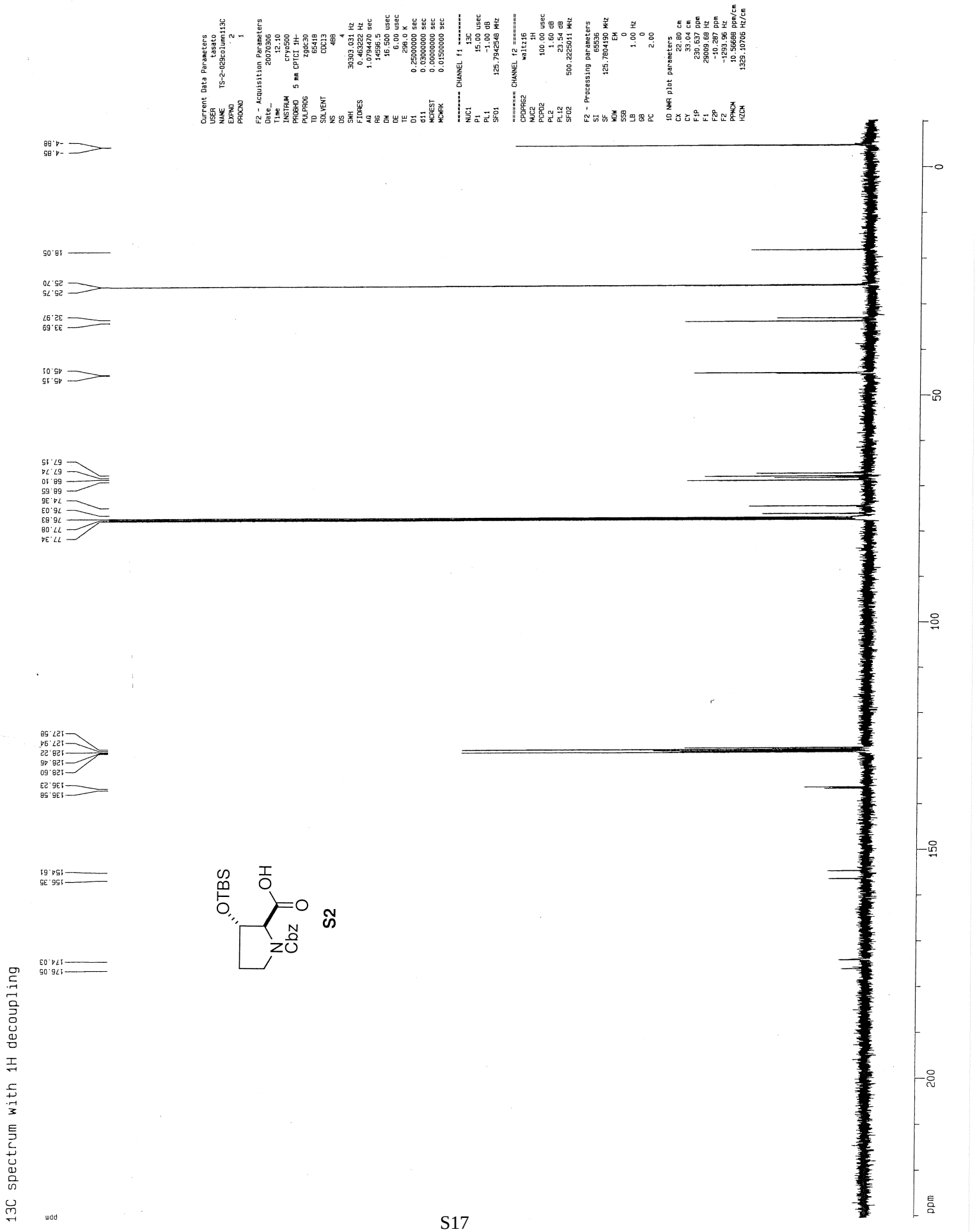
Hydroxy Epidithiodioxopiperazine (23)



Scandium triflate (28.0 mg, 56.9 μmol) was added to a solution of **22** (16.4 mg, 56.9 μmol), MeCN (1.9 mL) and MeOH (0.1 mL) at room temperature. This solution was maintained for 7 h at room temperature, and quenched with pH 7 phosphate buffer (5 mL). The mixture was extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The

residue was purified by silica gel column chromatography (hexane/EtOAc 3:1 to EtOAc) to afford 14.0 mg of **23** (100%) as a crystalline solid. Single crystals were obtained by recrystallization from CH_2Cl_2: mp 198–199 ºC dec; $[\alpha]^{24}_D$ –46.5 (*c* 0.31, CH_2Cl_2); IR (film) 3042, 2991, 2925, 1671 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 2.20 (dddd, *J* = 12.6, 9.9, 9.7, 8.6 Hz, 1H), 2.46 (dddd, *J* = 12.6, 7.5, 7.1, 2.3 Hz, 1H), 3.07 (s, 3H), 3.42 (ddd, *J* = 11.3, 8.6, 7.5 Hz, 1H), 3.79 (ddd, *J* = 11.3, 9.9, 2.3 Hz, 1H), 5.16 (dd, *J* = 9.7, 7.1 Hz, 1H), 5.68 (s, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 31.7 (CH_3), 32.3 (CH_2), 43.4 (CH_3), 68.7 (CH), 73.7 (CH), 81.5 (C), 164.6 (C), 167.8 (C); HRMS (ESI), calcd for $C_8H_{10}O_3N_2S_2Na^+$ $(M+Na)^+$ 269.0031, found 269.0026.


1H spectrum
S2
OTBS
OH
O
Cbz
N
ppm


13C spectrum with 1H decoupling
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-4.85
18.05
25.70
25.75
32.97
33.69
45.01
45.15
67.15
67.74
68.10
68.65
74.36
76.03
76.83
77.08
77.34
127.58
127.94
128.22
128.46
128.60
136.23
136.58
154.61
156.35
174.03
176.05
OTBS
OH
O
N
Cbz
S2
Current Data Parameters
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NAME TS-2-029column113C
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PROCNO 1
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PULPROG zgdc30
TD 65418
SOLVENT CDCl3
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SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794472 sec
RG 14596.5
DW 16.500 usec
DE 6.00 usec
TE 298.1 K
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d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz
======== CHANNEL f2 ========
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NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz
F2 - Processing parameters
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SF 125.7604190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
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CY 33.04 cm
F1P 230.637 ppm
F1 29009.68 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10706 Hz/cm
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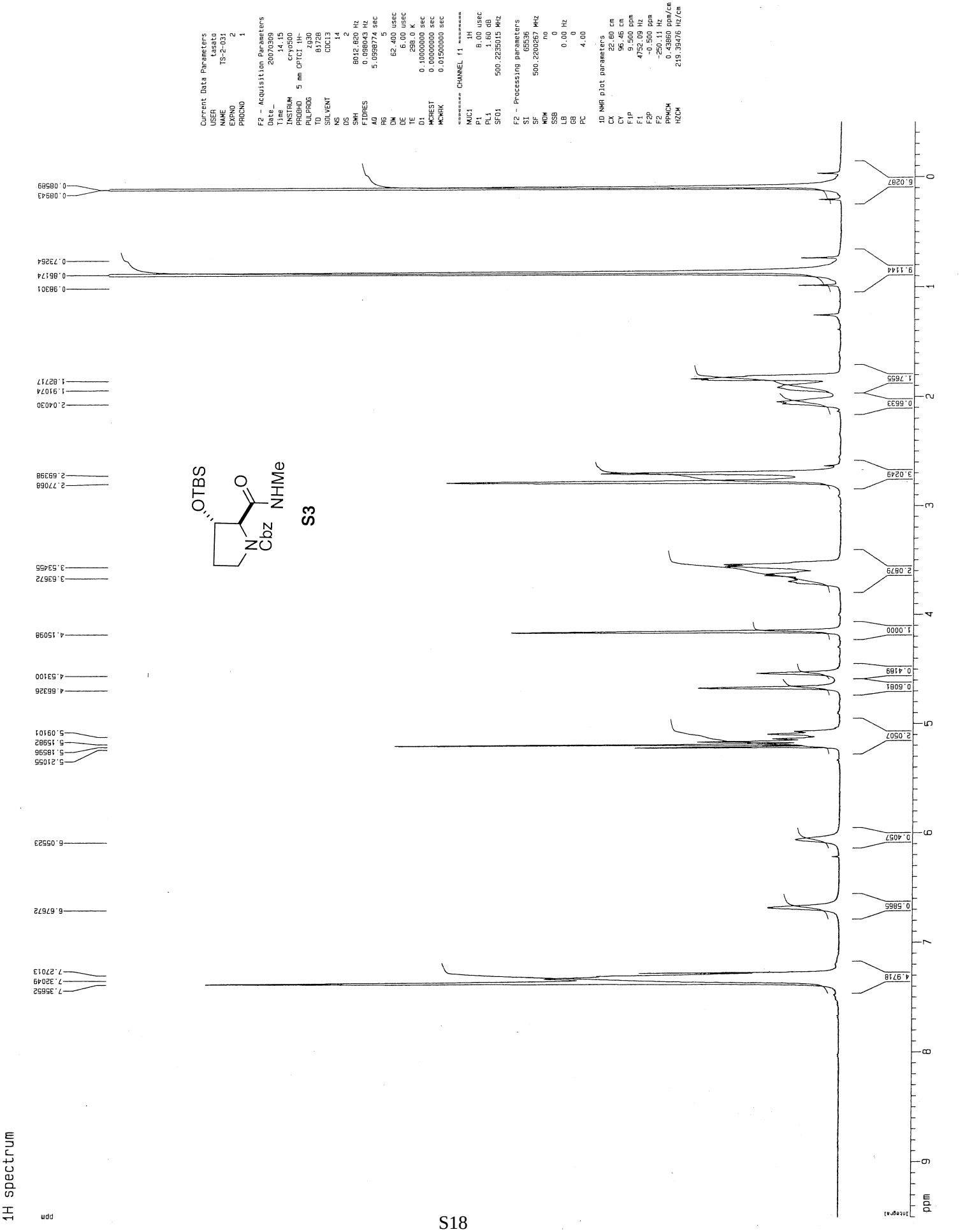
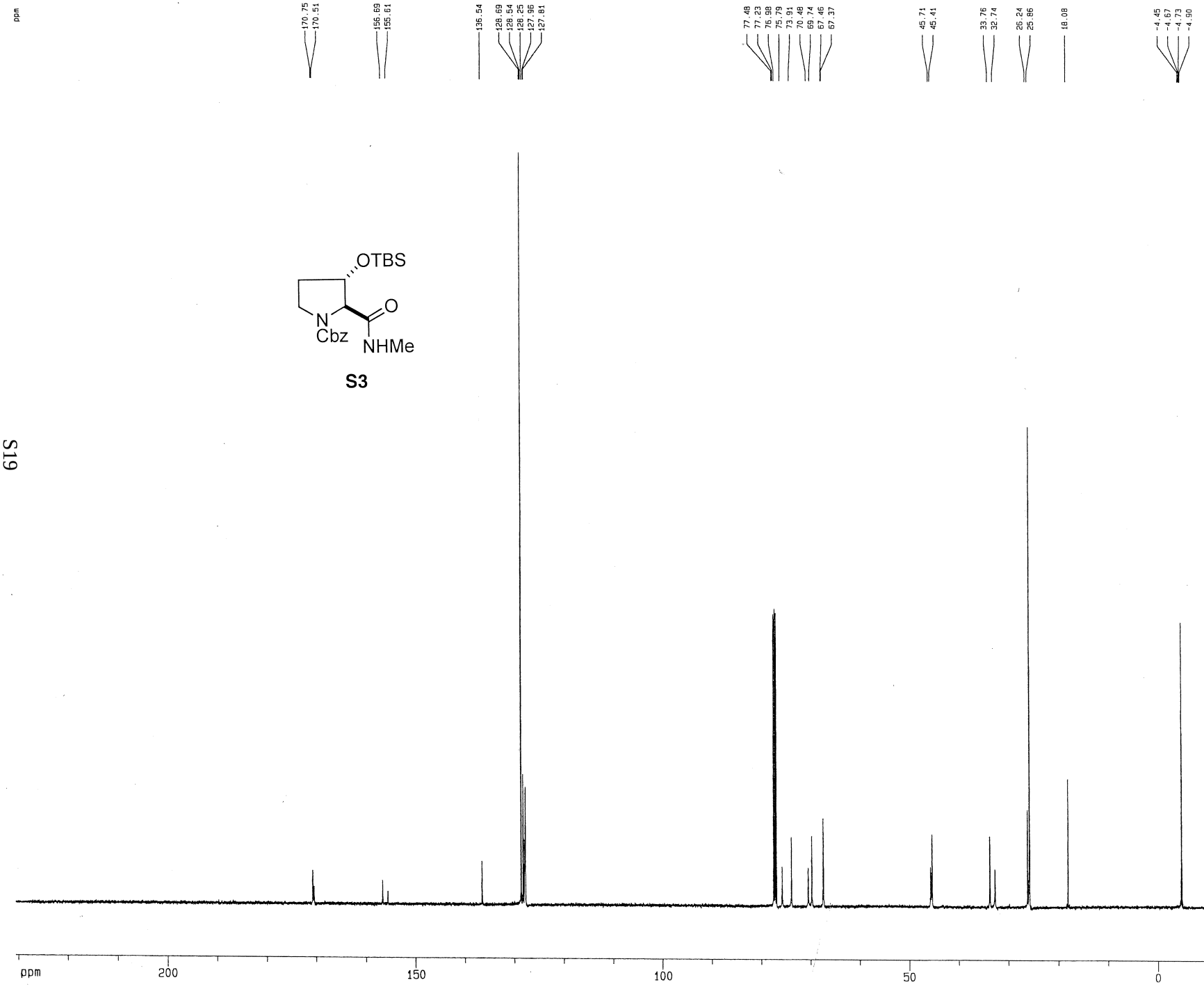
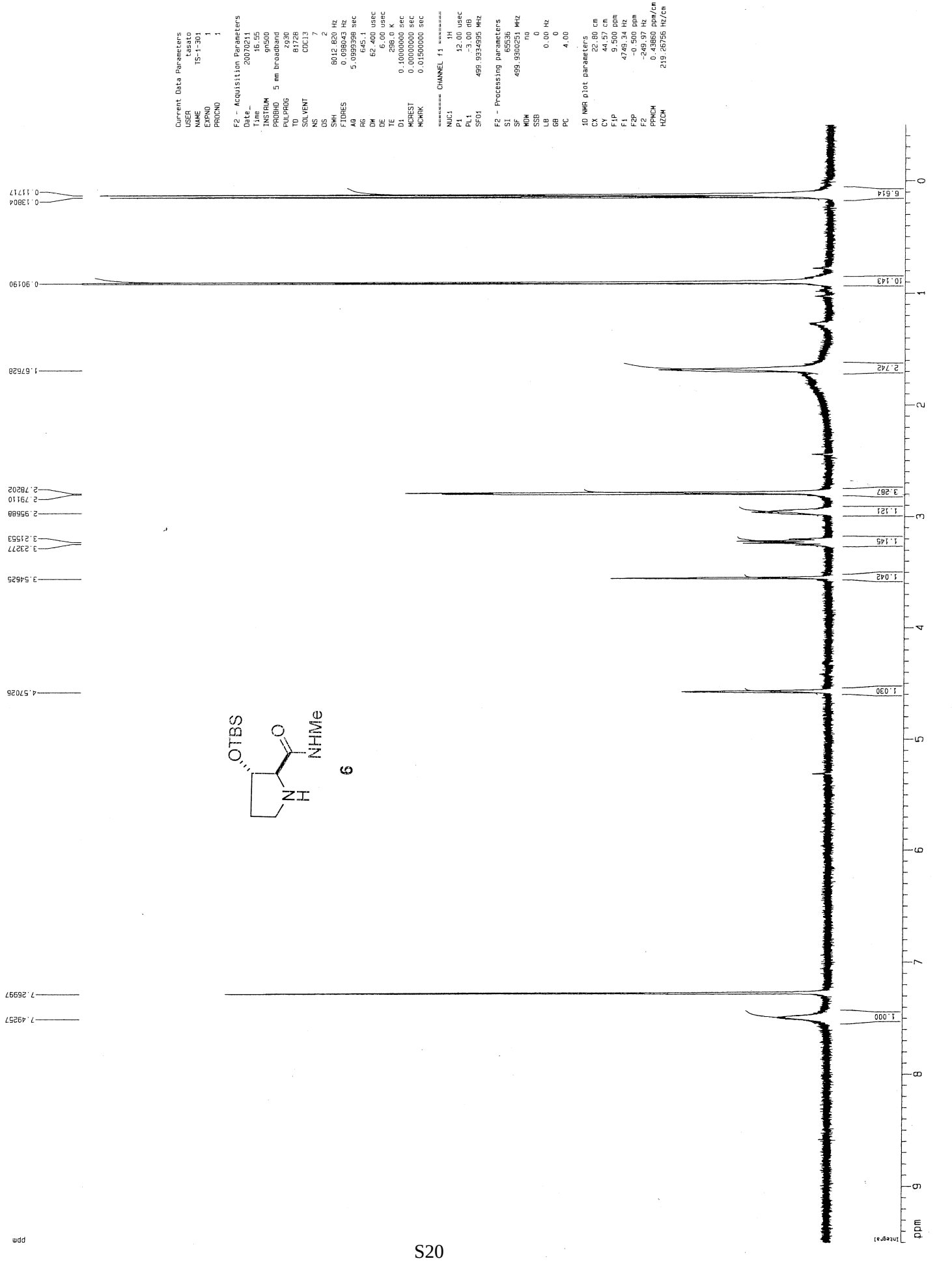
50
100
150
200
ppm


1H spectrum
S3
OTBS
NHMe
Cbz
ppm

13C spectrum with 1H decoupling

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PROCNO 1
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Time 16.55
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PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 7
DS 2
SWH 6012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0999398 sec
RG 645.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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P1 12.00 usec
PL1 -3.00 dB
SF01 499.9334995 MHz
F2 - Processing parameters
SI 65536
SF 499.9300251 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
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CY 44.57 cm
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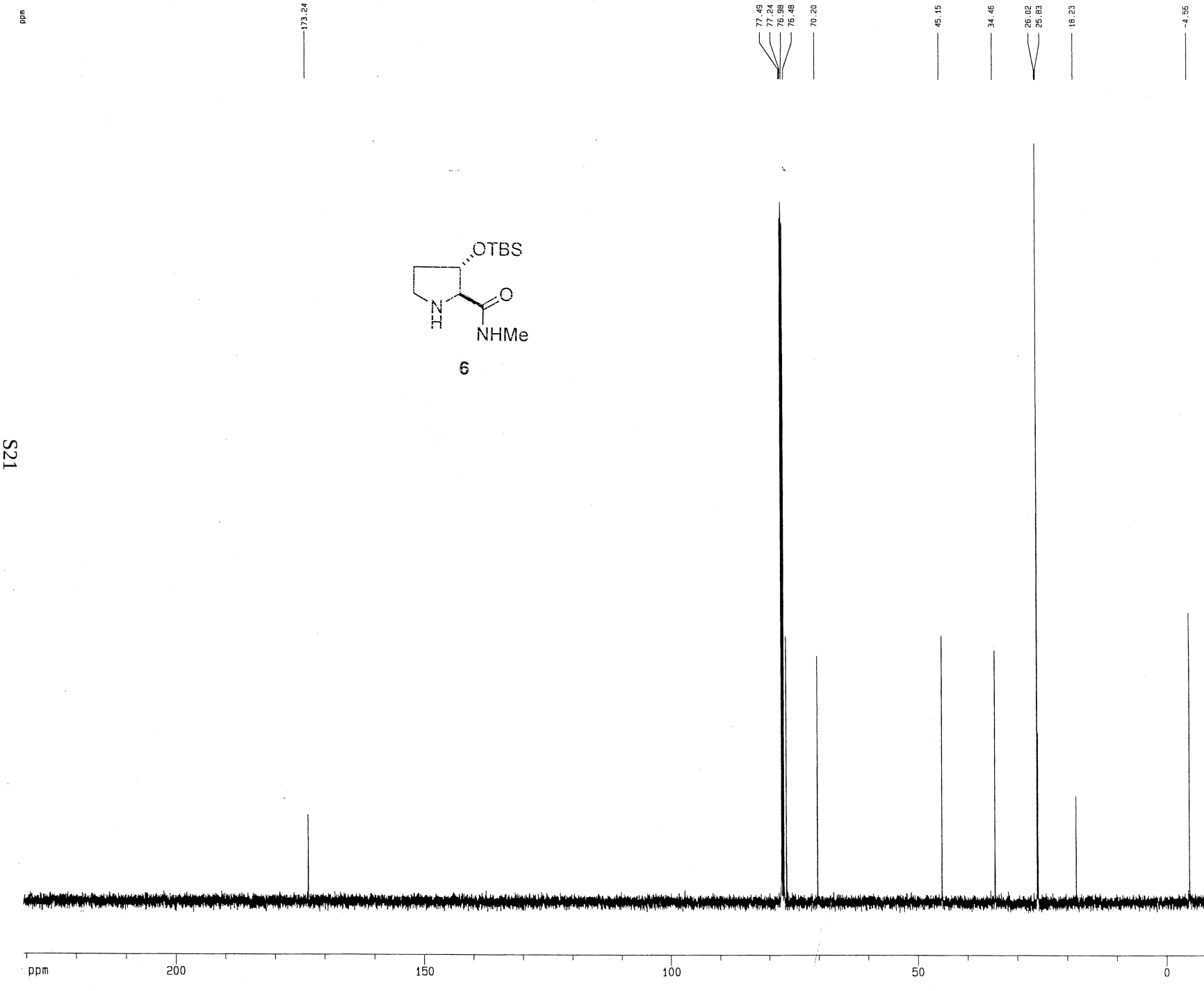
F1 4749.34 Hz
F2P -0.500 ppm
F2 -249.97 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.26756 Hz/cm
0.11717
0.13804
0.90190
1.67628
2.78202
2.79110
2.95588
3.21553
3.23277
3.54625
4.57026
7.26997
7.49257
6.614
10.143
2.742
3.287
1.121
1.145
1.042
1.030
1.000
OTBS
NHMe
6
ppm
integral

13C spectrum with 1H decoupling



Current Data Parameters
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NAME TS-1-30113C
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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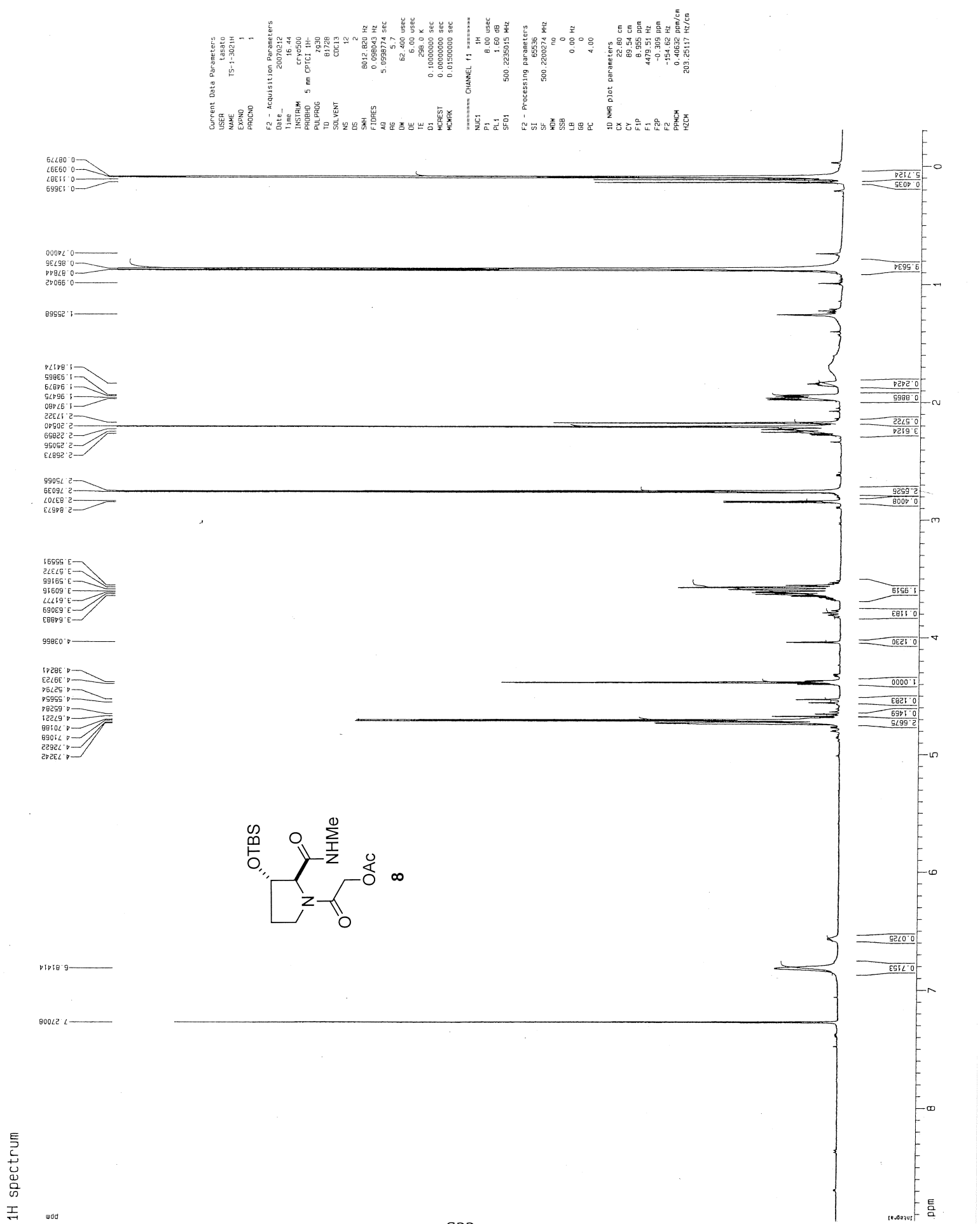
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 22
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 8192
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

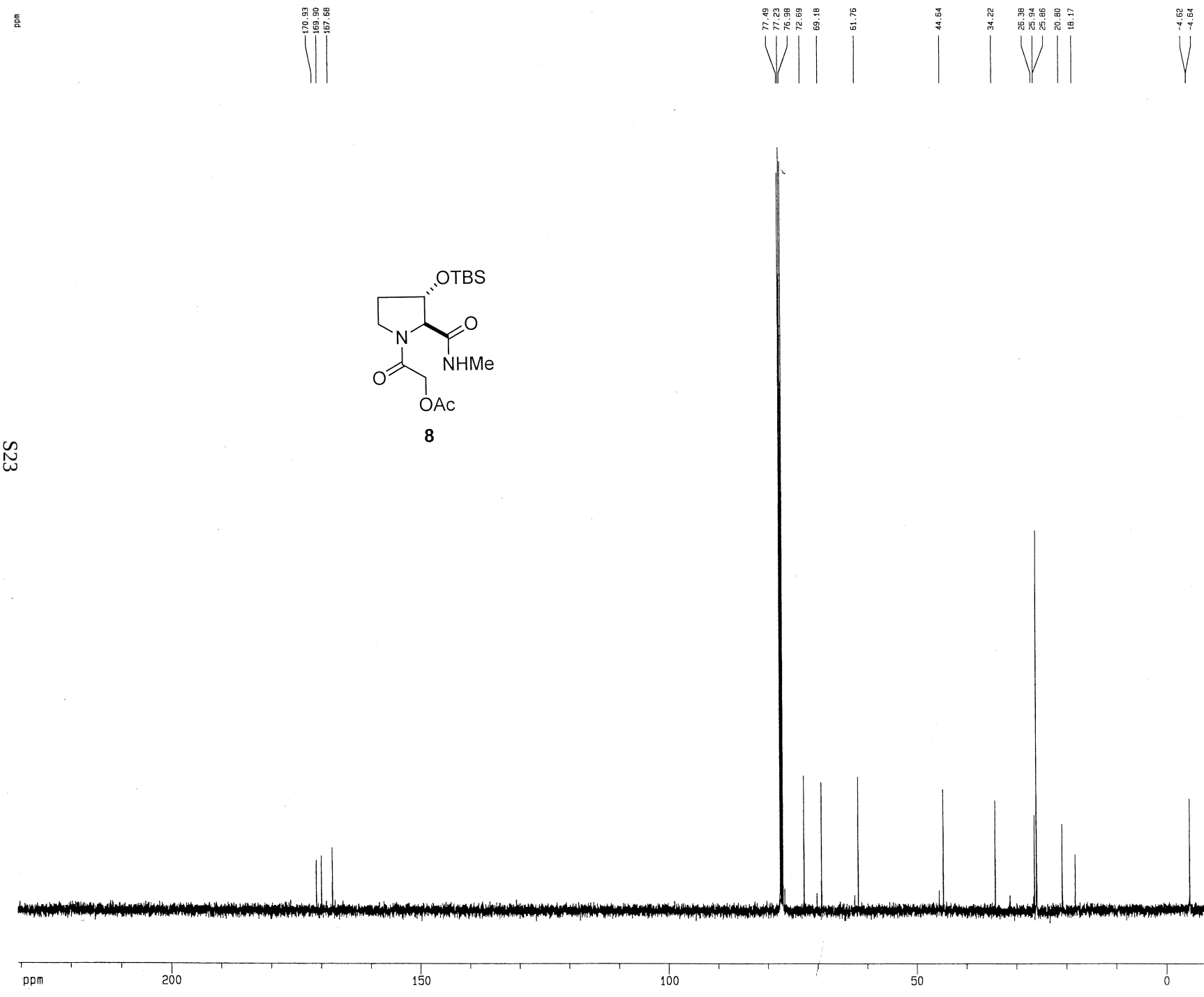
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804006 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 14.54 cm
F1P 230.637 ppm
F1 29009.68 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10693 Hz/cm


1H spectrum
OTBS
NHMe
OAc
8
ppm

13C spectrum with 1H decoupling



Current Data Parameters
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NAME TS-1-30213C
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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Time 16.46
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PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 99
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 8192
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804002 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 14.65 cm
F1P 230.637 ppm
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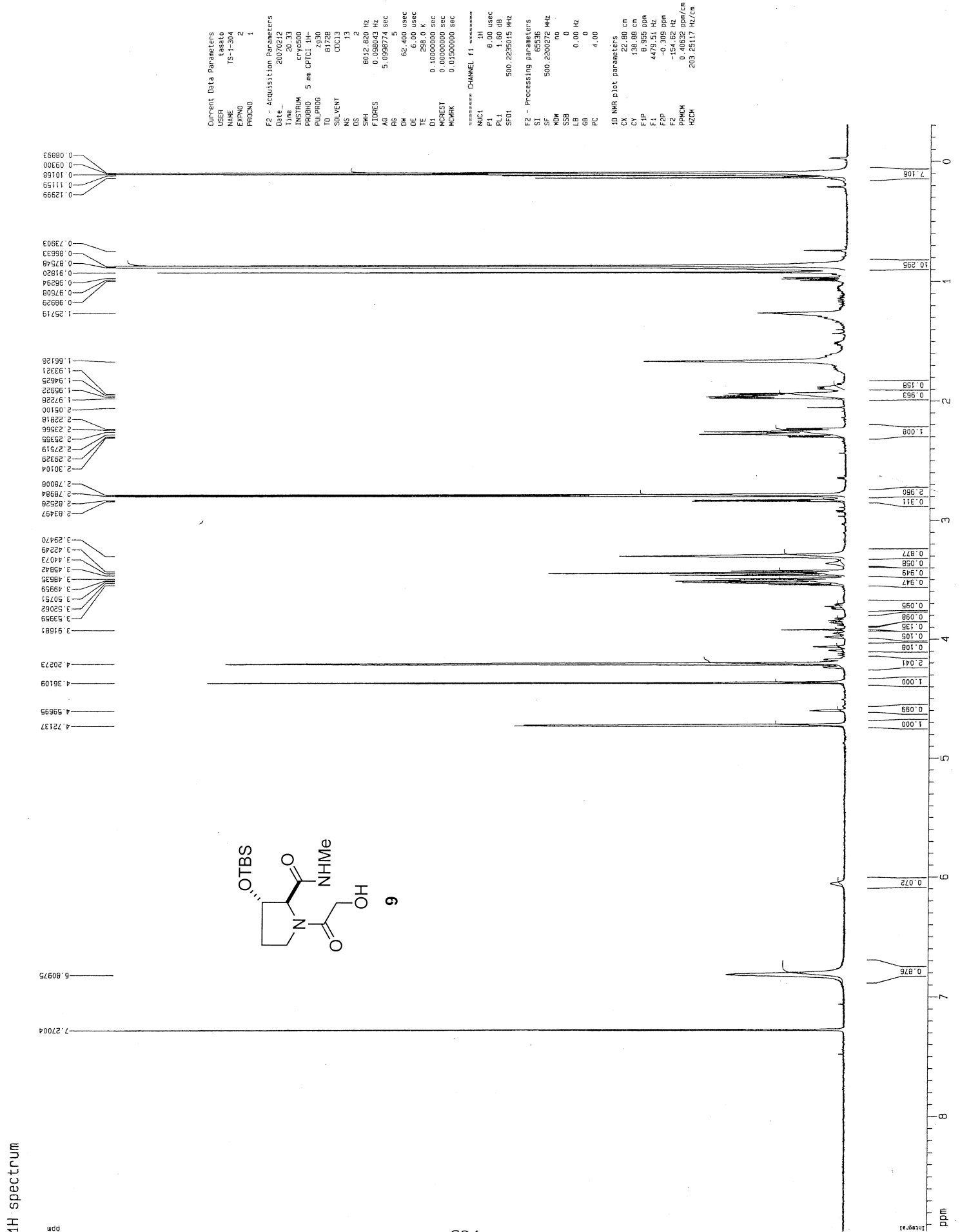
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10693 Hz/cm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PROCNO 1
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PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 13
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SF01 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200272 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 138.88 cm
F1P 8.955 ppm
F1 4479.51 Hz
F2P -0.309 ppm
F2 -154.62 Hz
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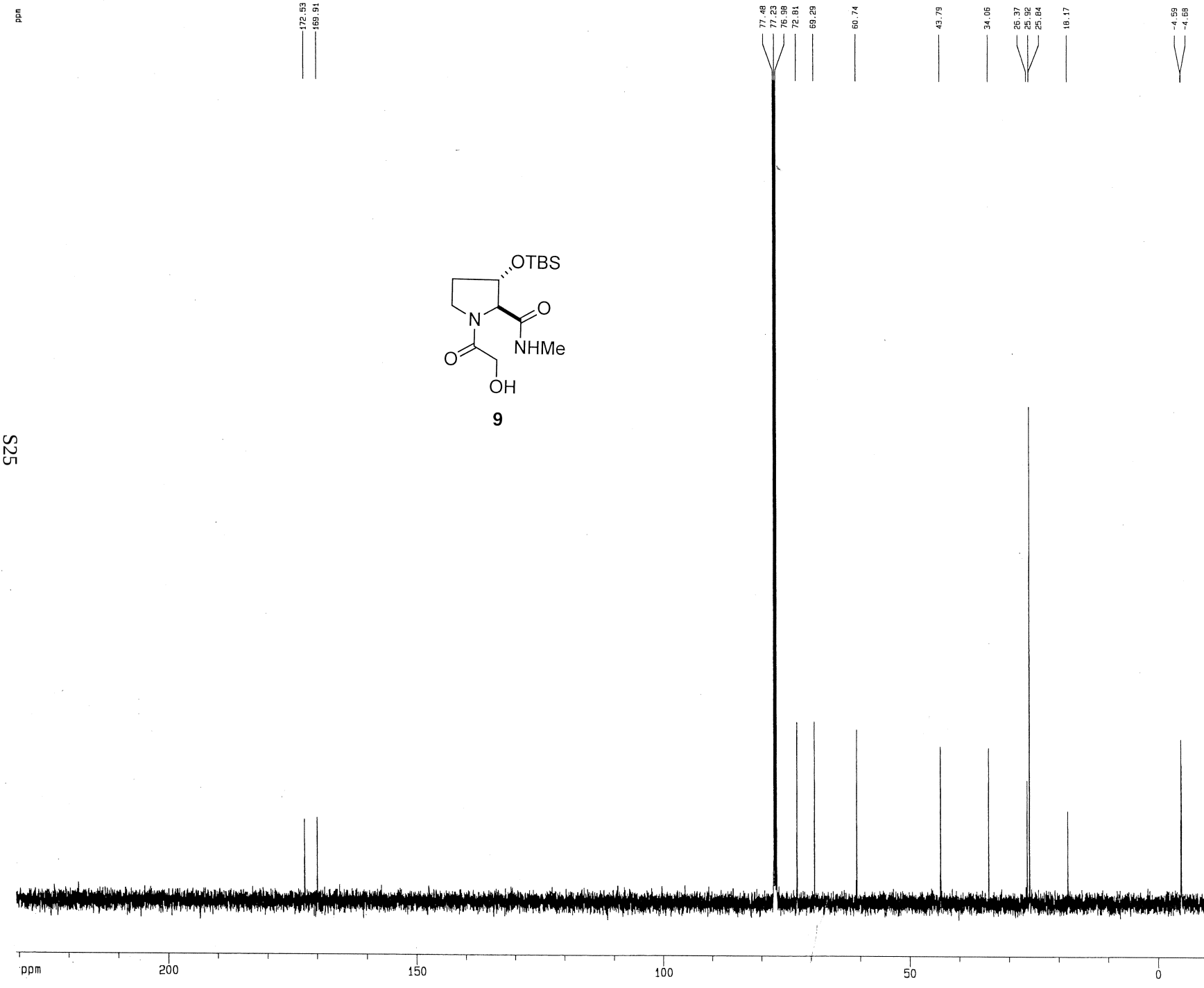
HZCM 203.25117 Hz/cm
OTBS
NHMe
OH
9
ppm
Integral

1H spectrum

13C spectrum with 1H decoupling



Current Data Parameters

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EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

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PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	65418
SOLVENT	CDCl3
NS	57
DS	4
SWH	30303.031 Hz
FIDRES	0.463222 Hz
AQ	1.0794635 sec
RG	13004
DW	16.500 usec
DE	6.00 usec
TE	298.0 K
D1	0.25000000 sec
d11	0.03000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	15.00 usec
PL1	-1.00 dB
SFO1	125.7942548 MHz

======== CHANNEL f2 ========

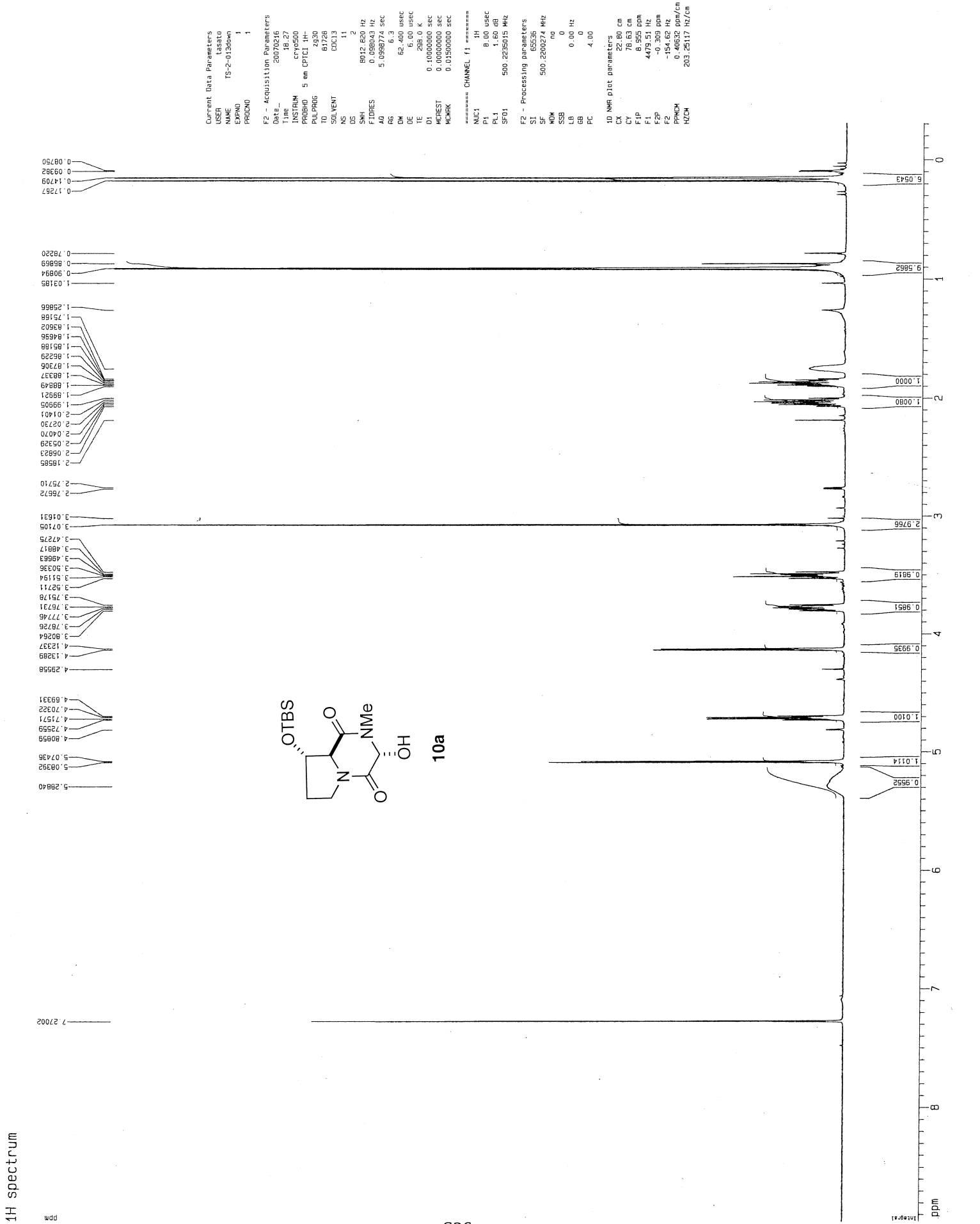
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	1.60 dB
PL12	23.54 dB
SFO2	500.2225011 MHz

F2 - Processing parameters

SI	65536
SF	125.7804002 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
CY	38.47 cm
F1P	230.637 ppm
F1	29009.68 Hz
F2P	-10.287 ppm
F2	-1293.96 Hz
PPMCM	10.56688 ppm/cm
HZCM	1329.10693 Hz/cm


1H spectrum
Current Data Parameters
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NAME TS-2-013down
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 18.27
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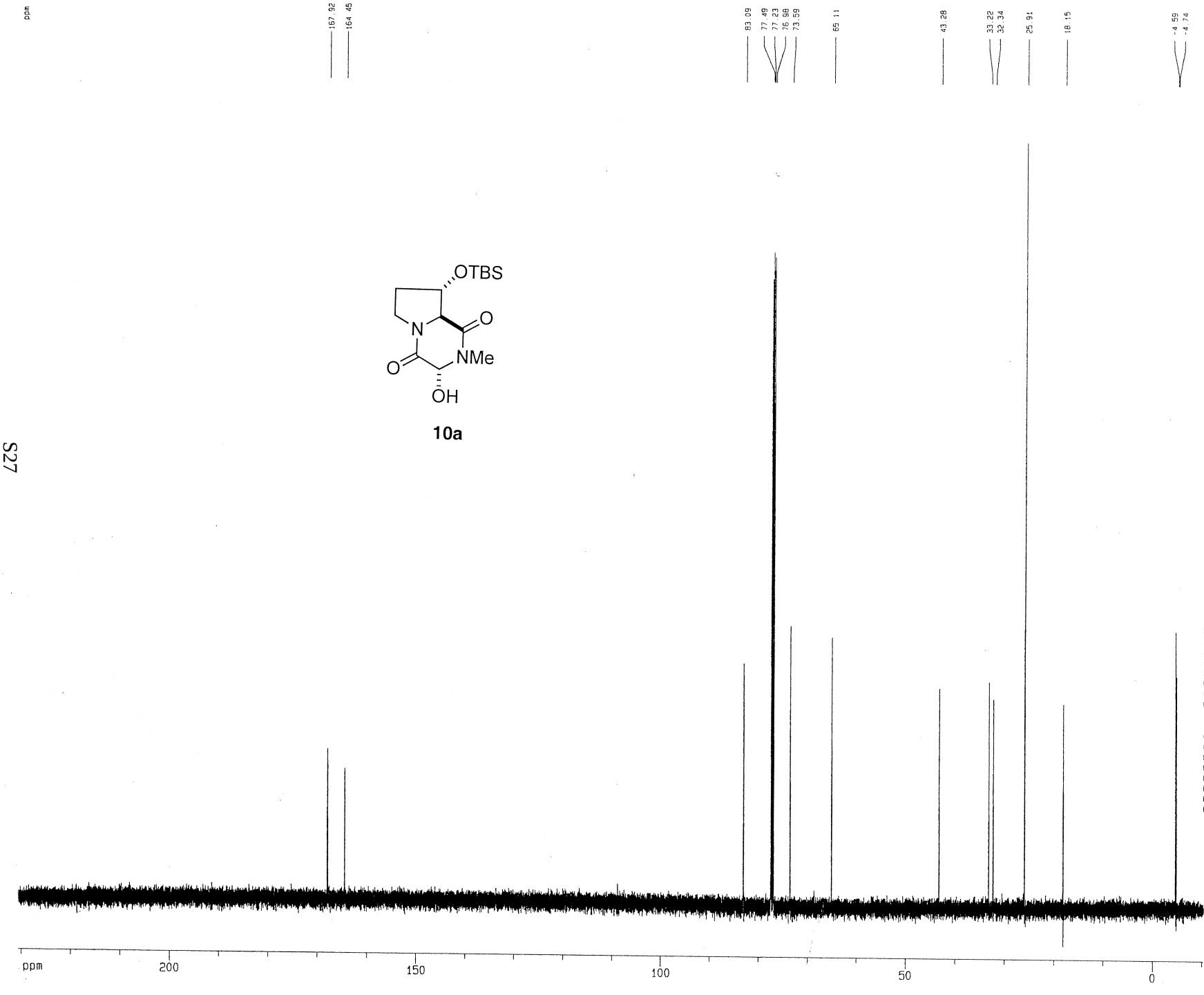
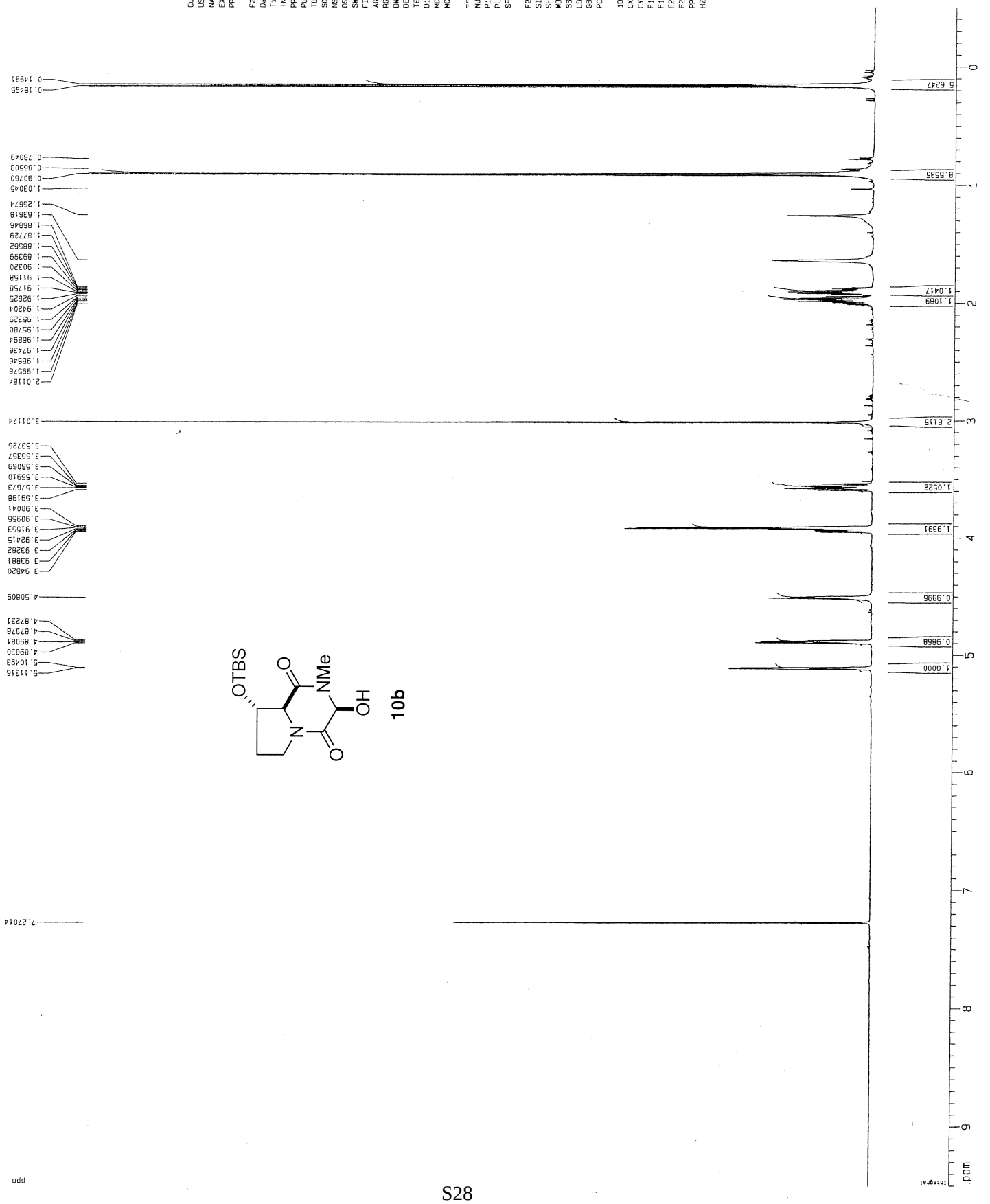
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 61726
SOLVENT CDCl3
NS 11
DS 2
SWH 8012.820 Hz
FIDRES 0.129804 Hz
AQ 5.098774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200274 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 78.63 cm
F1P 8.955 ppm
F1 4479.51 Hz
F2P -0.309 ppm
F2 -154.62 Hz
PPMCM 0.40632 ppm/cm
HZCM 203.25117 Hz/cm
OTBS
NMe
OH
10a
ppm
Integral

13C spectrum with 1H decoupling

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EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
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Time 18.17
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PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 10
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 290.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200273 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
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CY 68.39 cm
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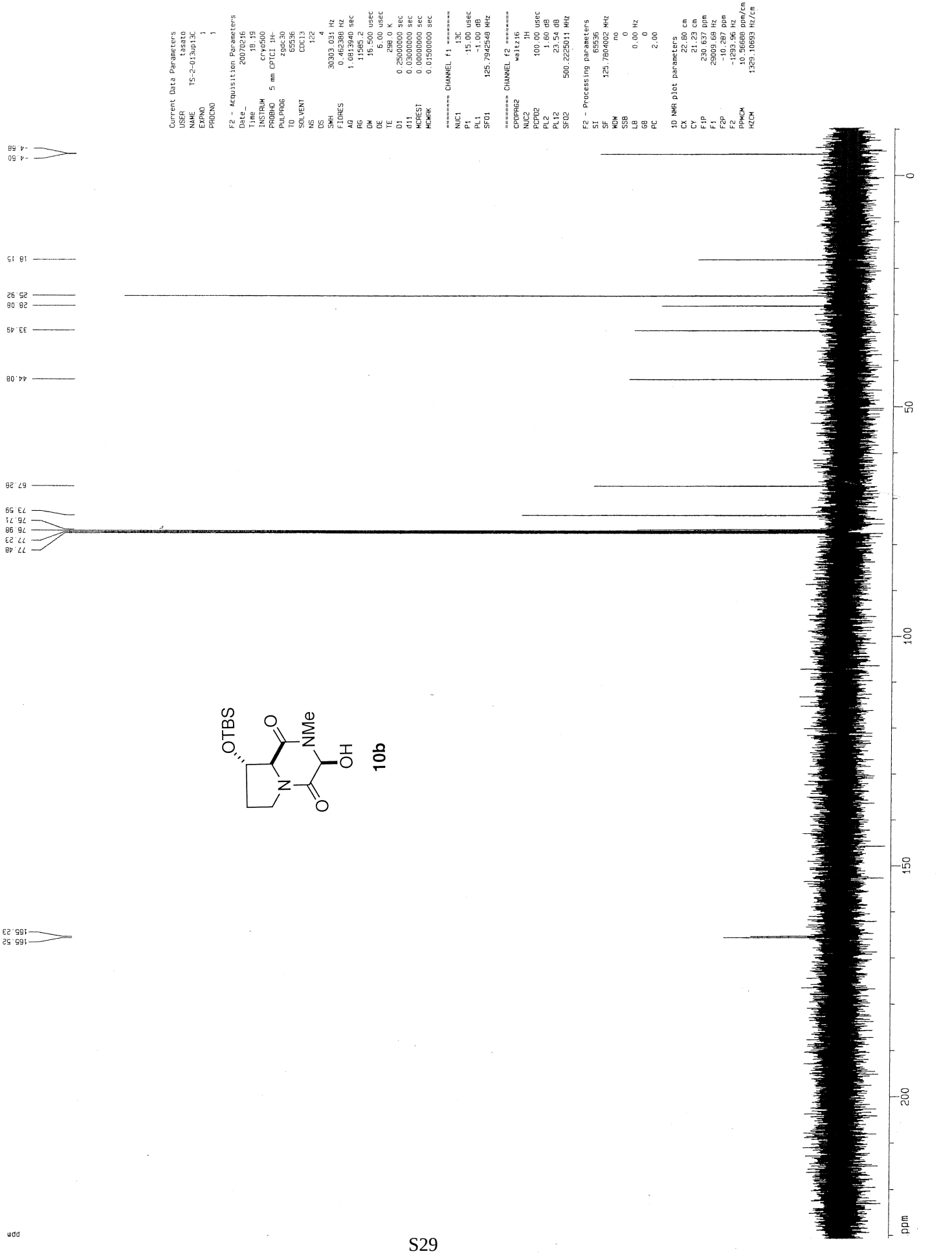
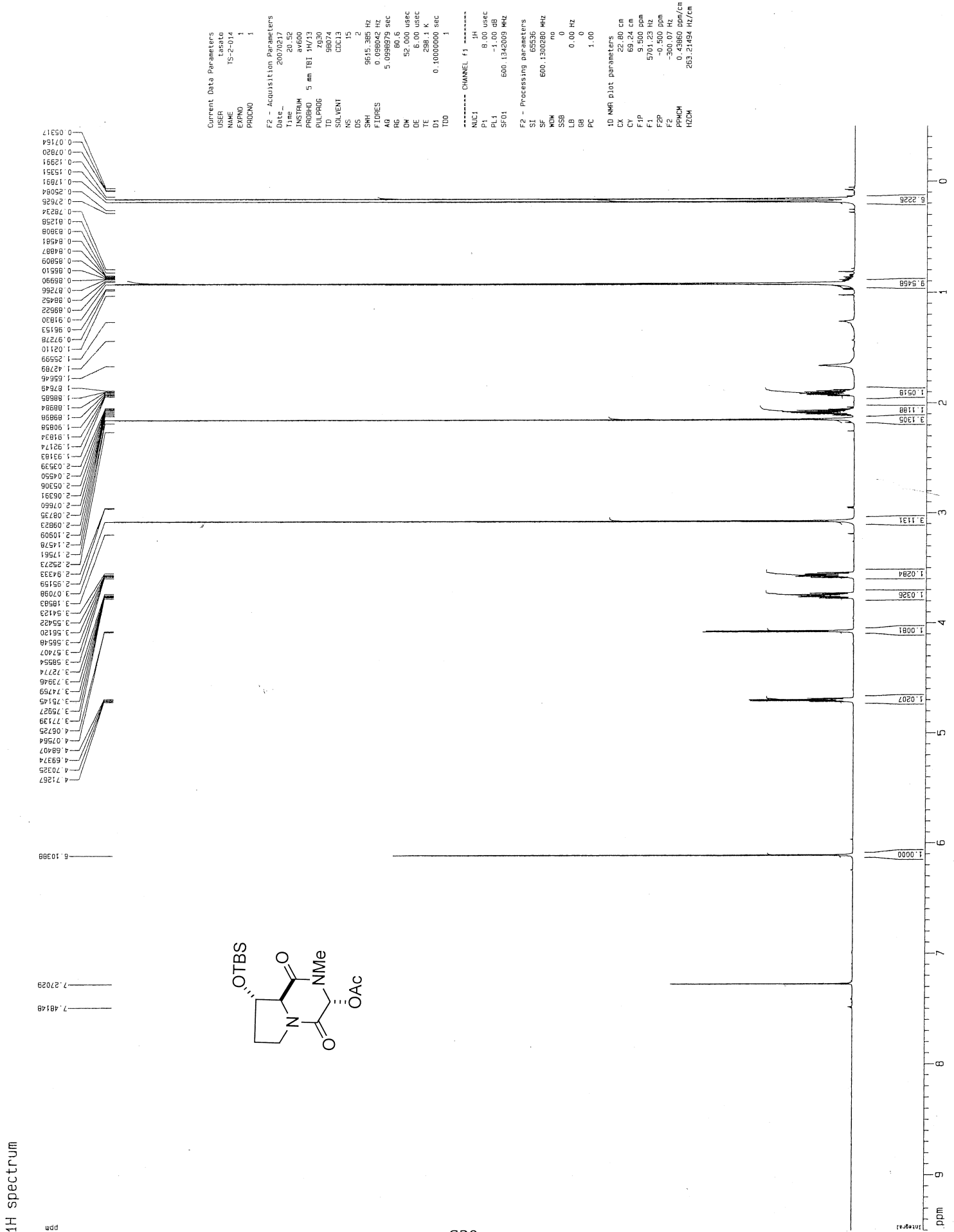
F1 4752.09 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.43660 ppm/cm
HZCM 219.39476 Hz/cm
OTBS
NMe
OH
10b
ppm
Integral

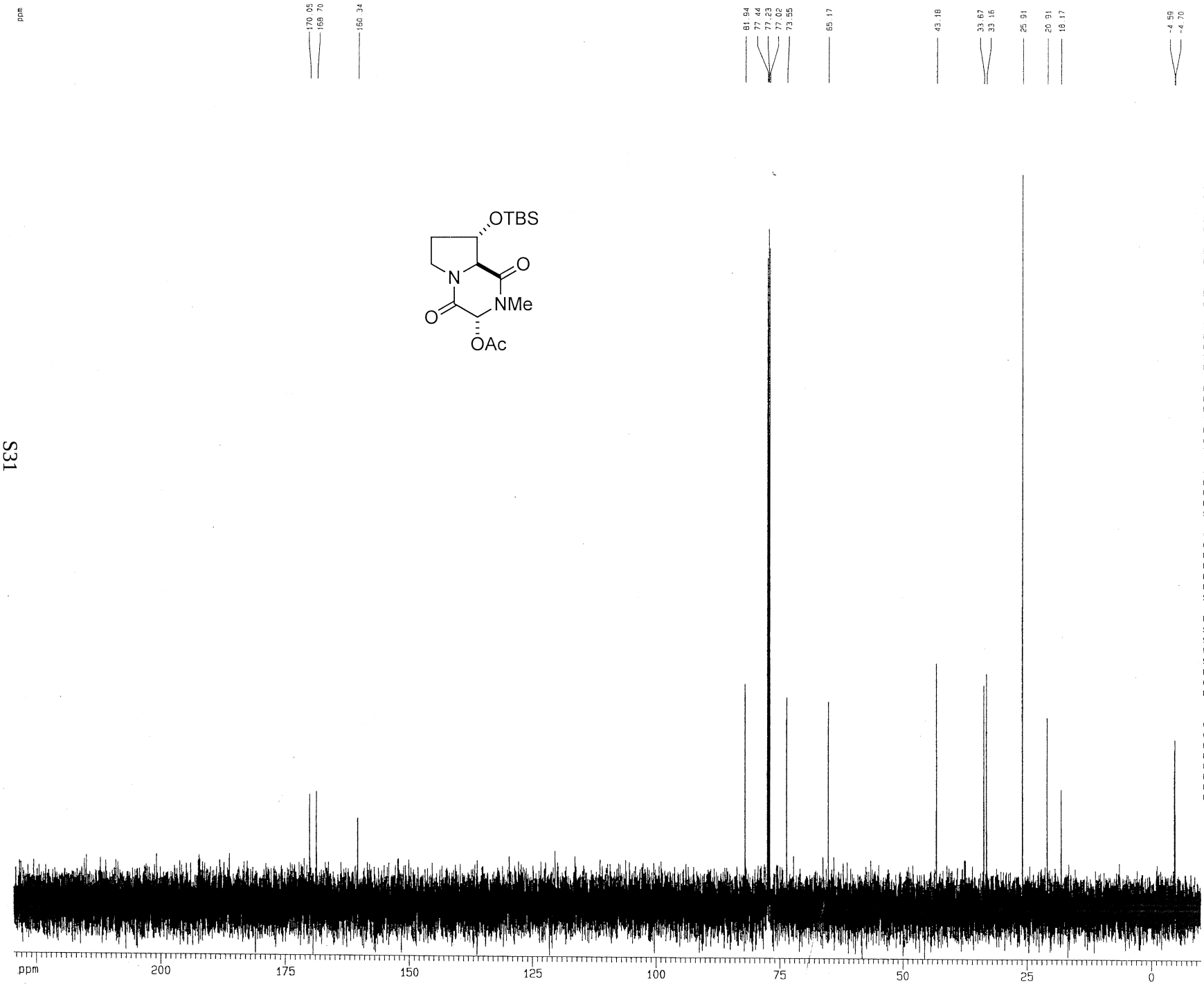
1H spectrum

13C spectrum with 1H decoupling

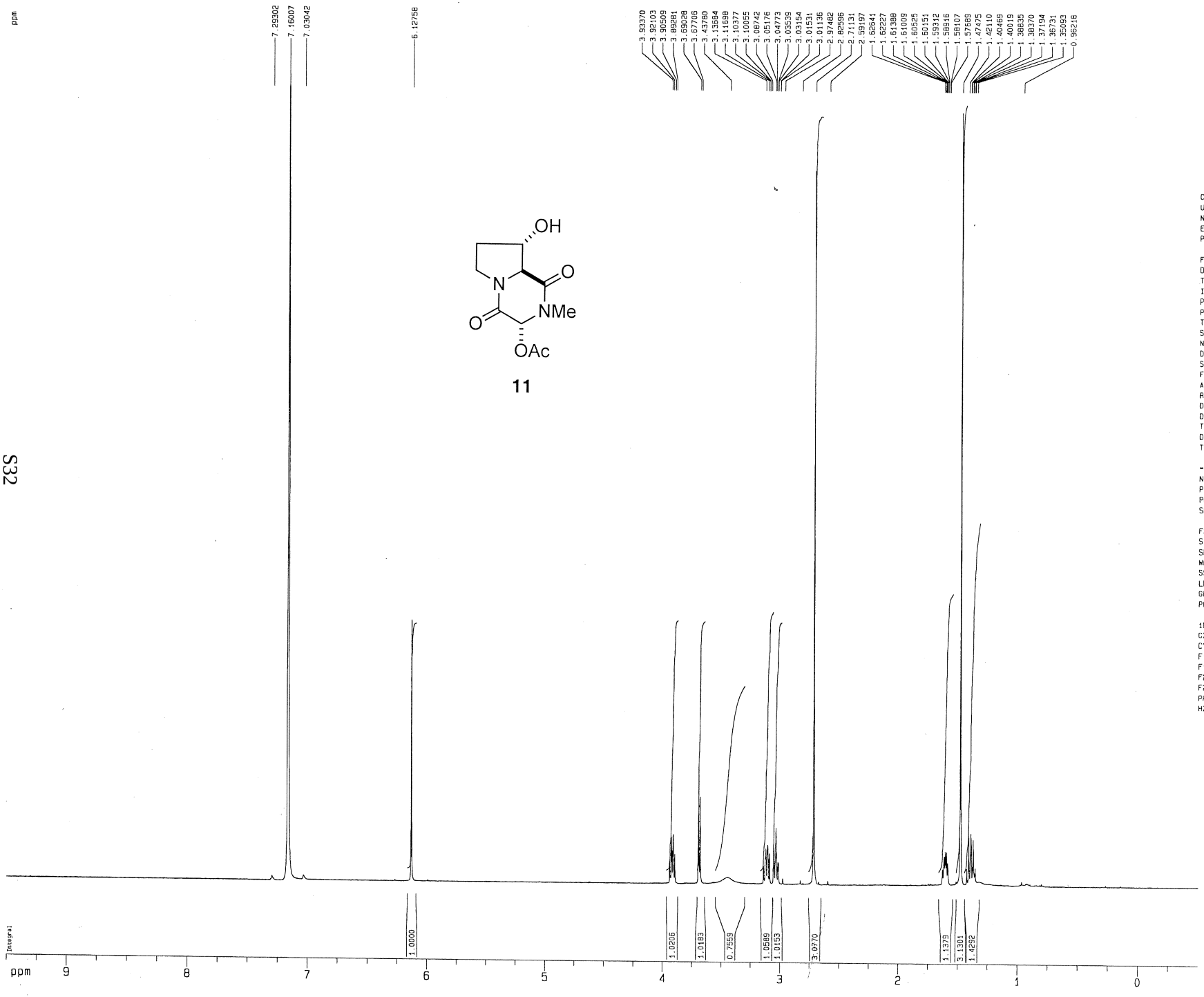



1H spectrum
ppm
integral
OTBS
NMe
OAc
N
O
O
O

13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters

USER	tasato
NAME	TS-2-017
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070220
Time	10.55
INSTRUM	av600
PROBHD	5 mm TBI 1H/13
PULPROG	zg30
TD	98074
SOLVENT	C6D6
NS	12
DS	2
SWH	9615.385 Hz
FIDRES	0.098042 Hz
AQ	5.0998979 sec
RG	203
DW	52.000 usec
DE	6.00 usec
TE	298.1 K
D1	0.10000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	8.00 usec
PL1	-1.00 dB
SFO1	600.1342009 MHz

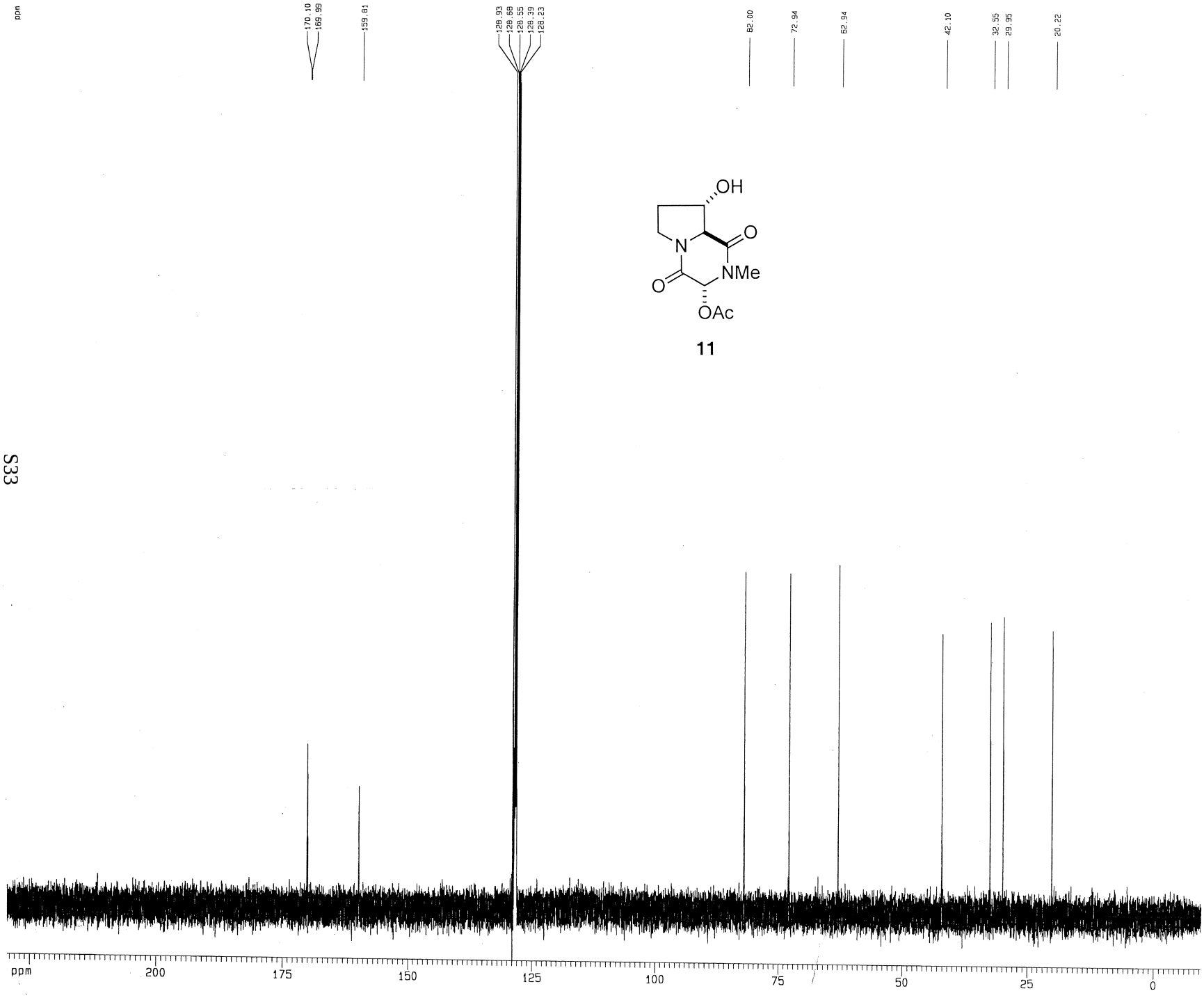
F2 - Processing parameters

SI	65536
SF	600.1299944 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	4.00

1D NMR plot parameters

CX	22.80 cm
CY	51.71 cm
F1P	9.500 ppm
F1	5701.23 Hz
F2P	-0.500 ppm
F2	-300.07 Hz
PPMCM	0.43860 ppm/cm
HZCM	263.21494 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters

USER	tasato
NAME	TS-2-01713C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070220
Time	11.00
INSTRUM	av600
PROBHD	5 mm TBI 1H/13
PULPROG	zgdc30
TD	65536
SOLVENT	~~CDCl3~~ C6D6
NS	499
DS	4
SWH	36231.883 Hz
FIDRES	0.552855 Hz
AQ	0.9044468 sec
RG	322
DW	13.800 usec
DE	6.00 usec
TE	298.0 K
D1	0.40000001 sec
d11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	15.00 usec
PL1	0.00 dB
SFO1	150.9194080 MHz

======== CHANNEL f2 ========

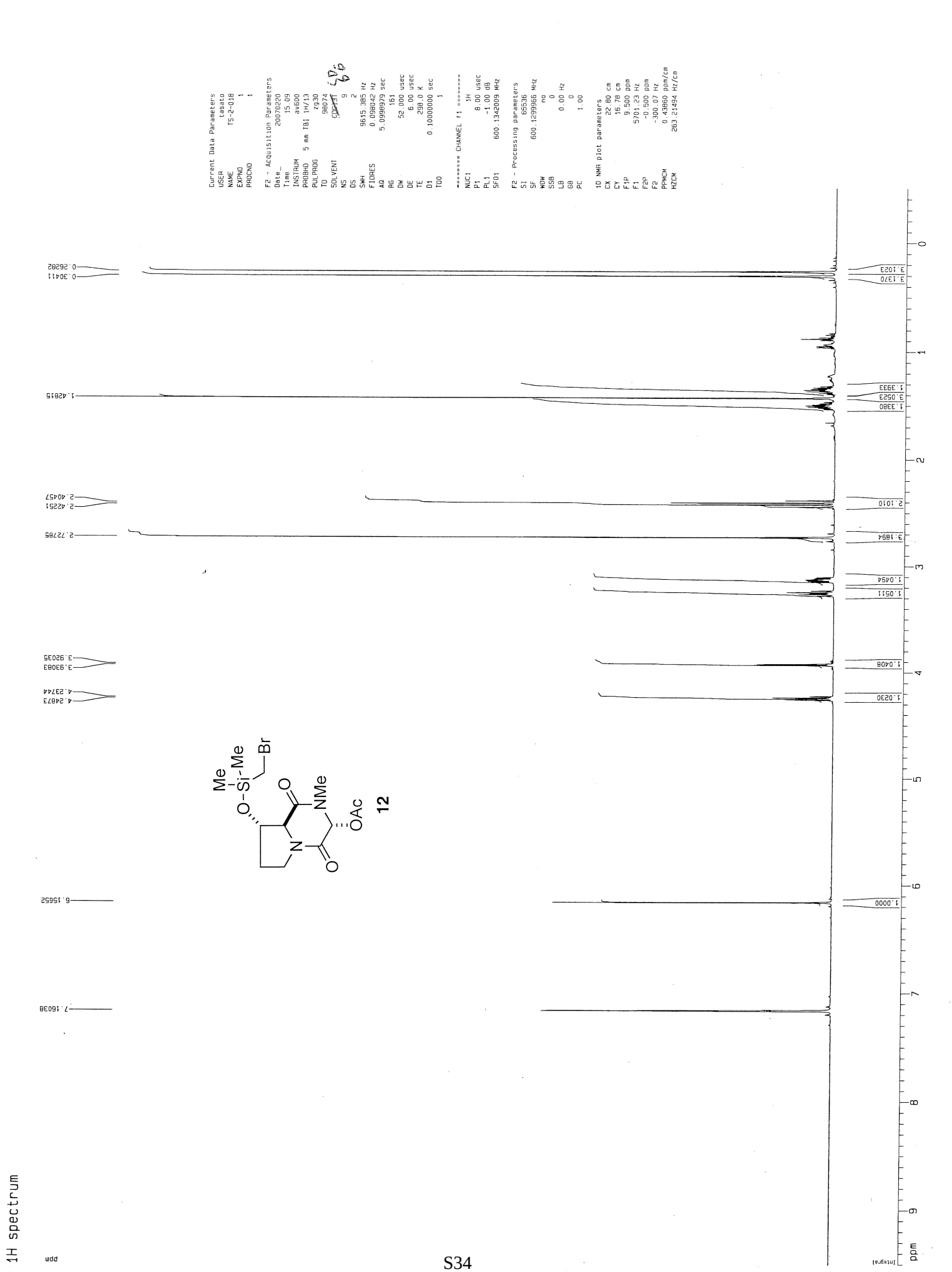
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	18.80 dB
SFO2	600.1330010 MHz

F2 - Processing parameters

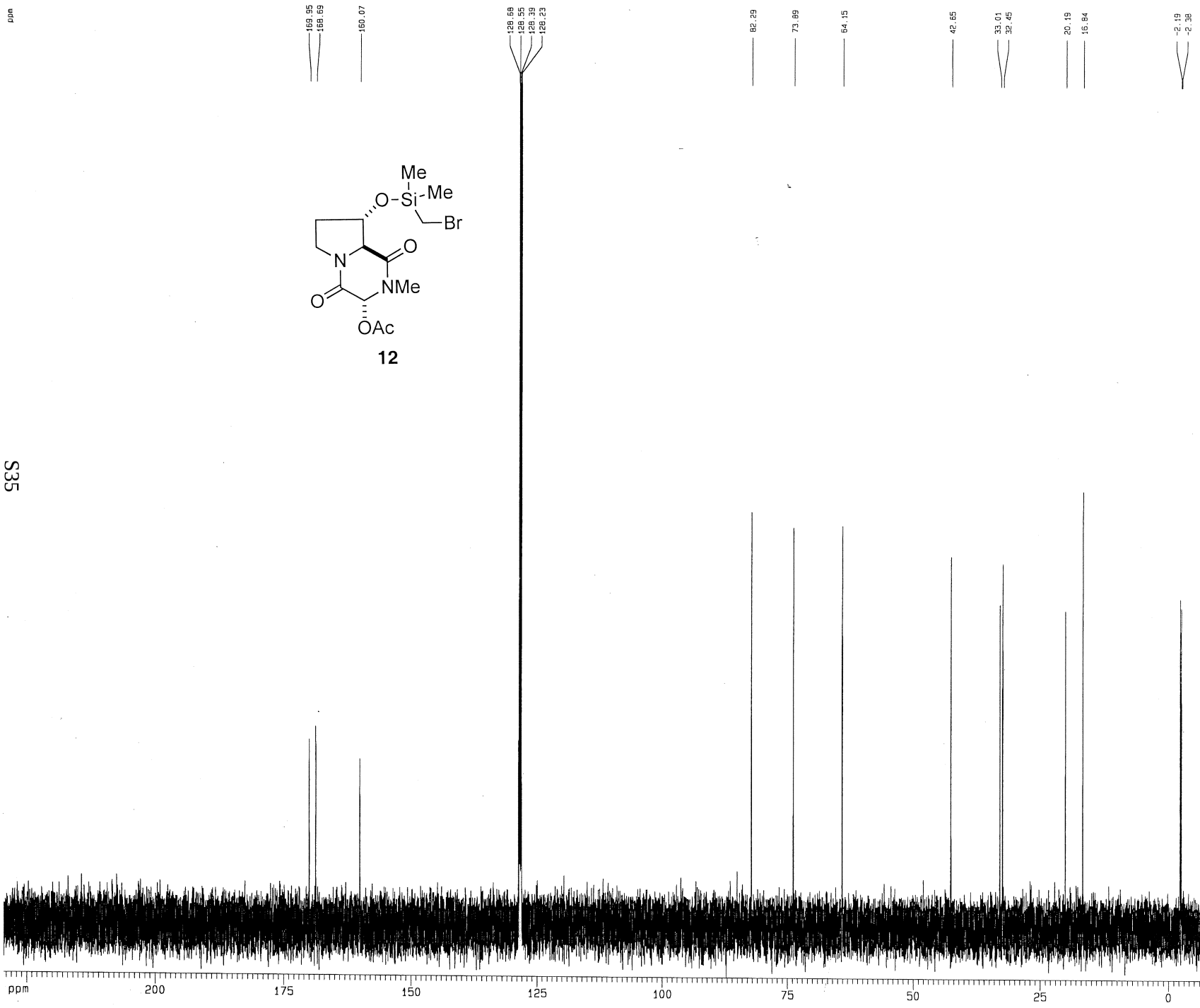
SI	65536
SF	150.9027033 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
CY	67.40 cm
F1P	229.520 ppm
F1	34635.14 Hz
F2P	-10.507 ppm
F2	-1585.47 Hz
PPMCM	10.52747 ppm/cm
HZCM	1588.62354 Hz/cm


1H spectrum
Current Data Parameters
USER tasato
NAME TS-2-018
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070220
Time 15.09
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT CDCl3
NS 9
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 161
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1299968 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 16.78 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm
0.26282
0.30411
1.42815
2.40457
2.42551
2.72785
3.92035
3.93083
4.23744
4.24873
6.15652
7.16038
1.0230
1.0408
1.0511
1.0454
3.1884
2.1010
1.3380
3.0523
1.3933
1.1370
1.1023
1.0000
Integral
ppm
Me
Si
Me
O
Br
NMe
OAc
N
12

13C spectrum with 1H decoupling



Current Data Parameters
USER tasato
NAME TS-2-01813C
EXPNO 1
PROCNO 1

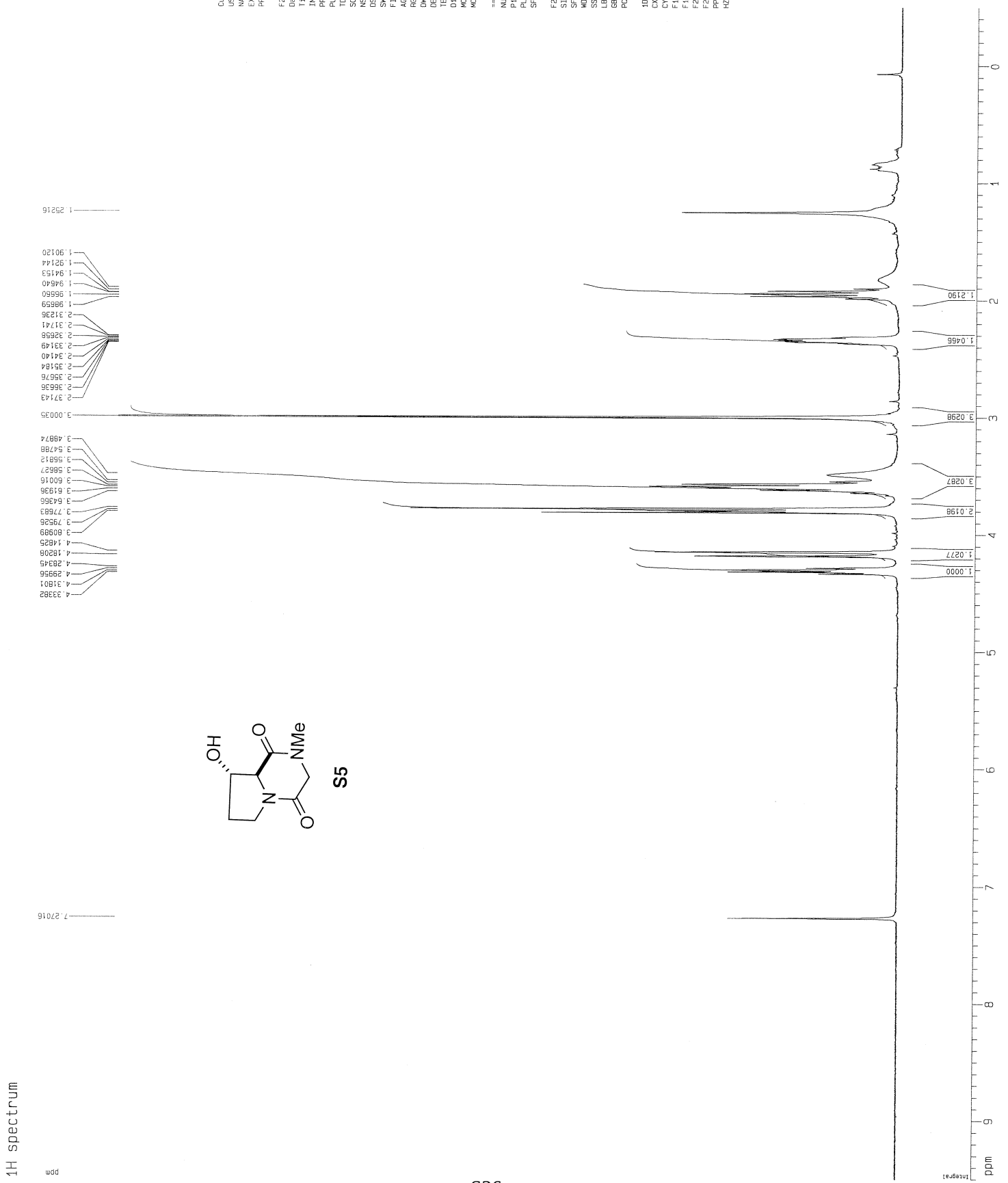
F2 - Acquisition Parameters
Date_ 20070220
Time 14.59
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zgdc30
TD 65536
SOLVENT ~~CDCl3~~ C_6D_6
NS 333
DS 4
SWH 36231.883 Hz
FIDRES 0.552855 Hz
AQ 0.9044468 sec
RG 2050
DW 13.800 usec
DE 6.00 usec
TE 298.1 K
D1 0.40000001 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 0.00 dB
SFO1 150.9194080 MHz

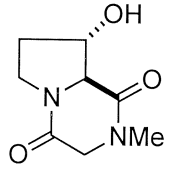
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 18.80 dB
SFO2 600.1330010 MHz

F2 - Processing parameters
SI 65536
SF 150.9027033 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

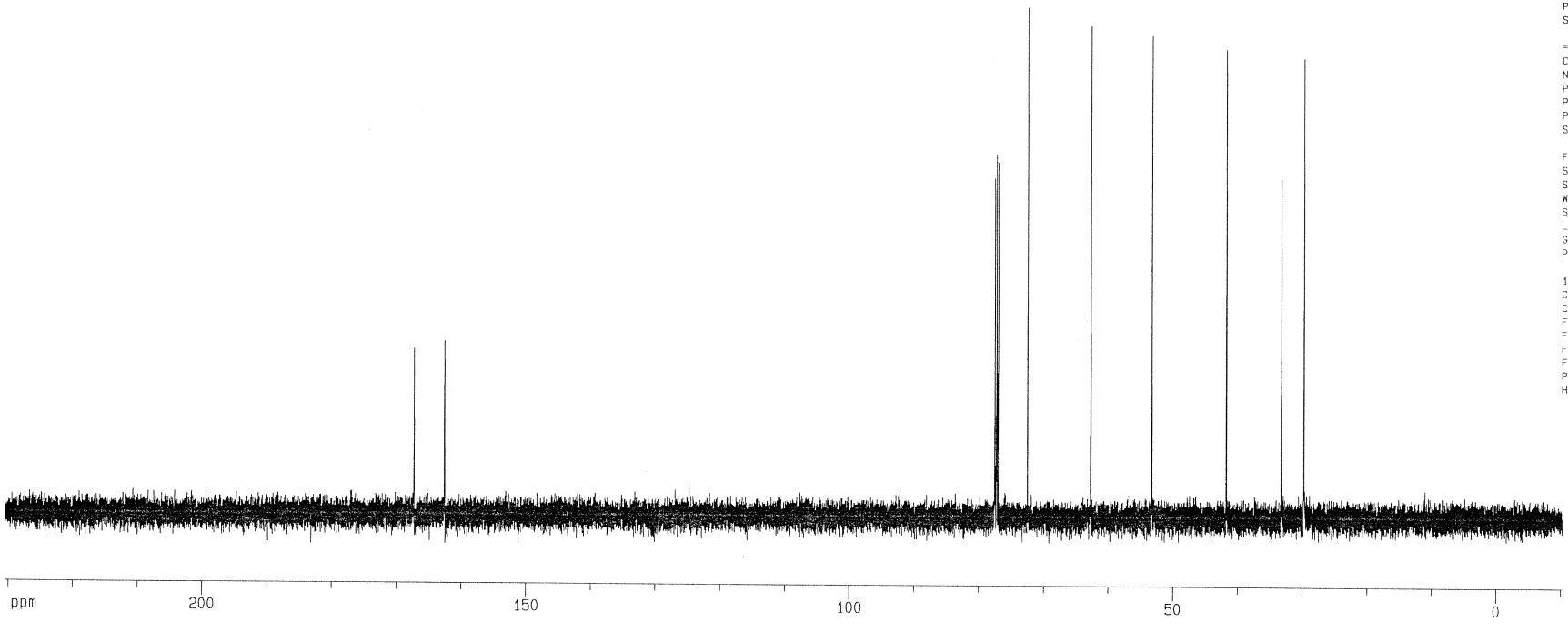
1D NMR plot parameters
CX 22.80 cm
CY 64.91 cm
F1P 229.520 ppm
F1 34635.14 Hz
F2P -10.507 ppm
F2 -1585.47 Hz
PPMCM 10.52747 ppm/cm
HZCM 1588.62354 Hz/cm


1H spectrum
Current Data Parameters
USER tasato
NAME TS-1-21
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060511
Time 15.32
INSTRUM cryo500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 19
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 143.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200262 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.60 cm
CY 37.74 cm
F1P 9.500 ppm
F1 4752.09 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
7.27016
4.33382
4.31801
4.29956
4.28345
4.18208
4.14825
3.80989
3.79526
3.77683
3.64366
3.61936
3.60016
3.58627
3.56812
3.54788
3.48874
3.00035
2.37143
2.36636
2.35676
2.35184
2.34140
2.33149
2.32656
2.31741
2.31236
1.98659
1.96560
1.94640
1.94153
1.92144
1.90120
1.25216
1.2190
1.0466
3.0298
3.0287
2.0198
1.0277
1.0000
OH
O
NMe
N
O
S5
ppm
Integral

13C spectrum with 1H decoupling



S5



Current Data Parameters

USER	tasato
NAME	TS-1-21-13C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20060511
Time	19.46
INSTRUM	cryo500
PROBHD	5 mm broadband
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	96
DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	18390.4
DW	16.500 usec
DE	6.00 usec
TE	298.0 K
D1	0.25000000 sec
d11	0.03000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	8.90 usec
PL1	0.00 dB
SFO1	125.7942548 MHz

======== CHANNEL f2 ========

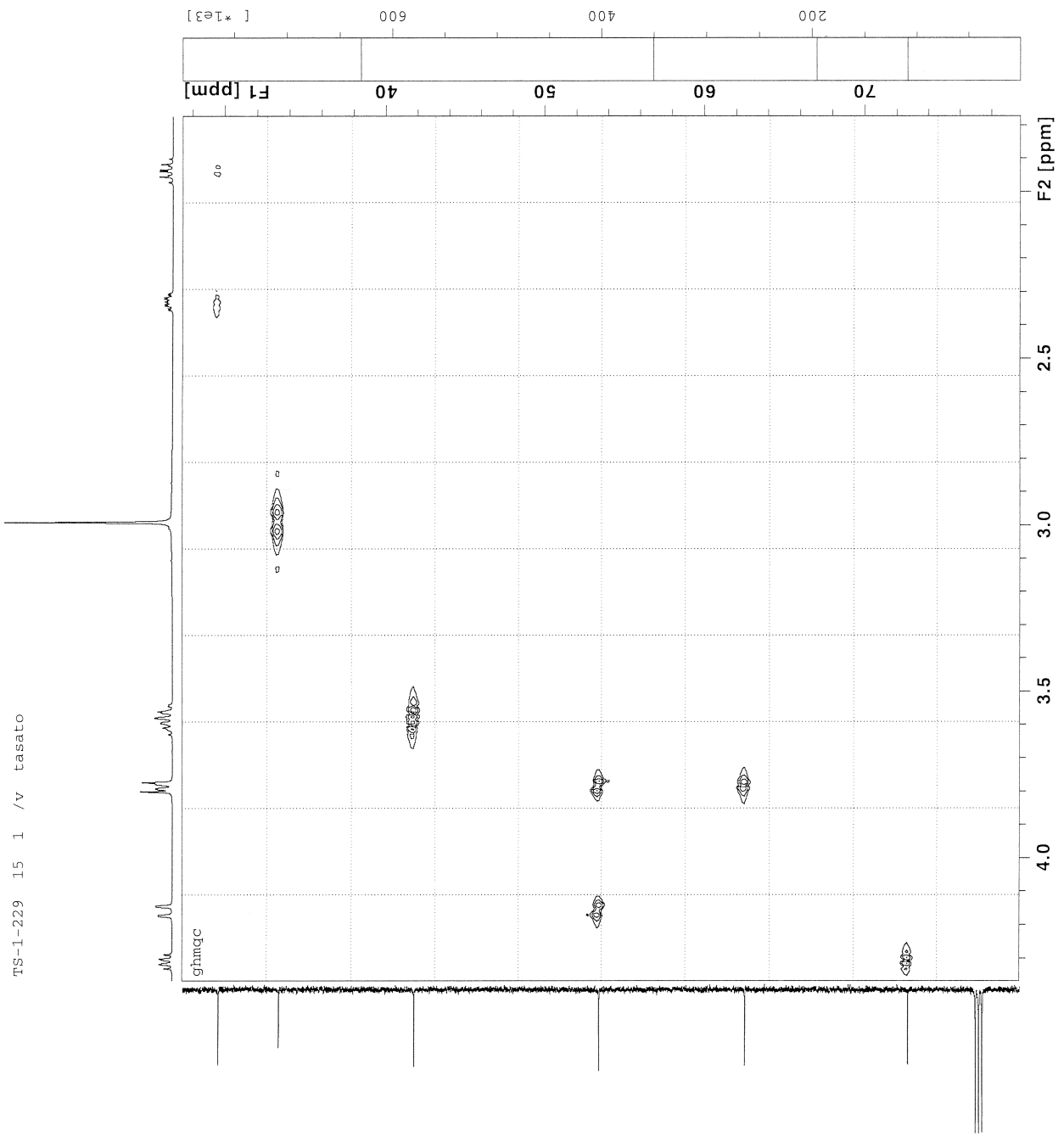
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	1.60 dB
PL12	13.40 dB
SFO2	500.2225011 MHz

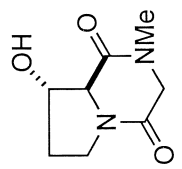
F2 - Processing parameters

SI	65536
SF	125.7804159 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

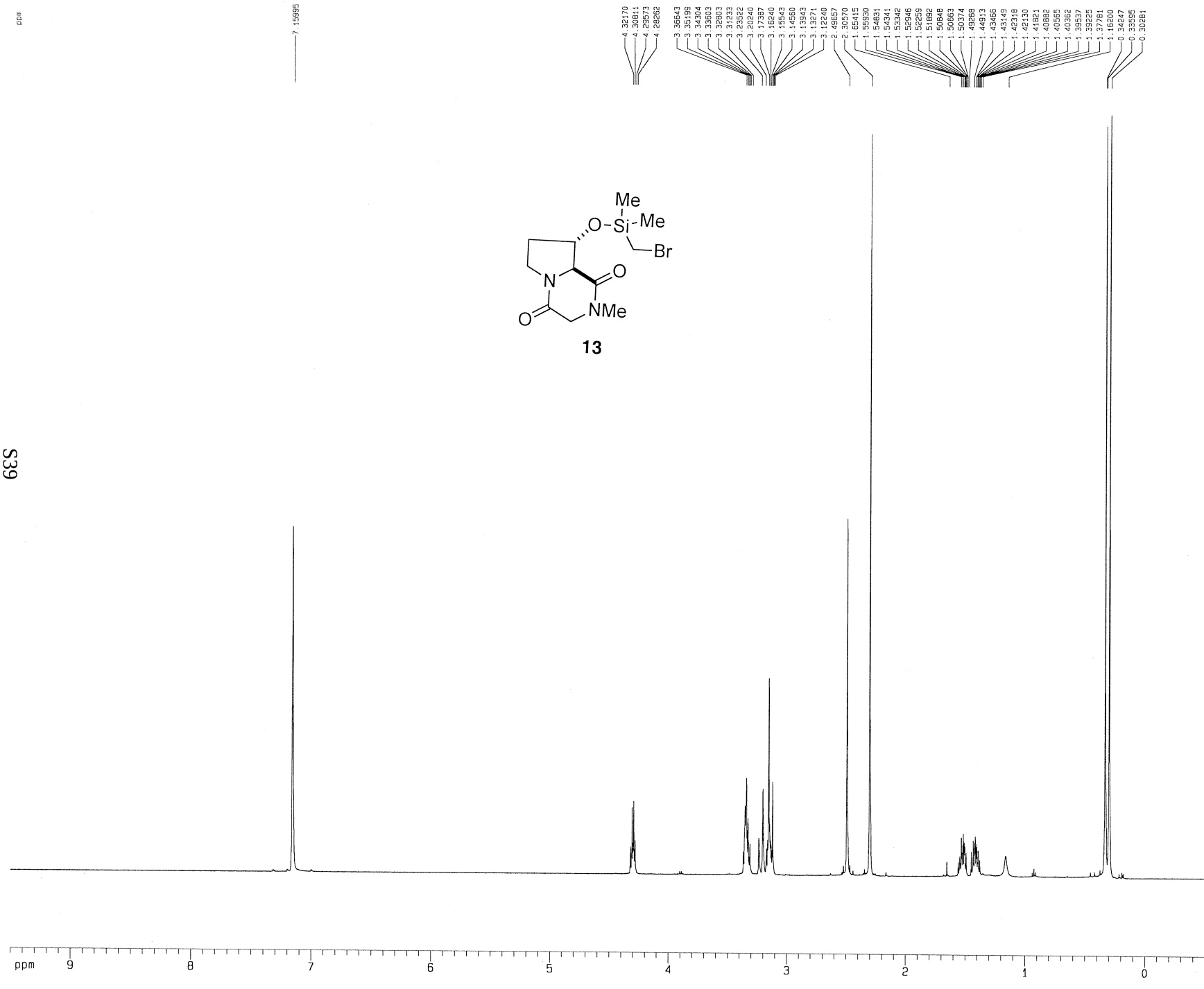
CX	22.80 cm
CY	7.49 cm
F1P	230.637 ppm
F1	29009.68 Hz
F2P	-10.287 ppm
F2	-1293.96 Hz
PPMCM	10.56688 ppm/cm
HZCM	1329.10706 Hz/cm


TS-1-229 15 1 /v tasato
gHmqc
F1 [ppm]
F2 [ppm]
70
60
50
40
2.5
3.0
3.5
4.0
200
400
600
[*1e3]


OH
O
NMe
N
O

S5

1H spectrum



Current Data Parameters
USER tasato
NAME TS-1-100column1
EXPNO 1
PROCNO 1

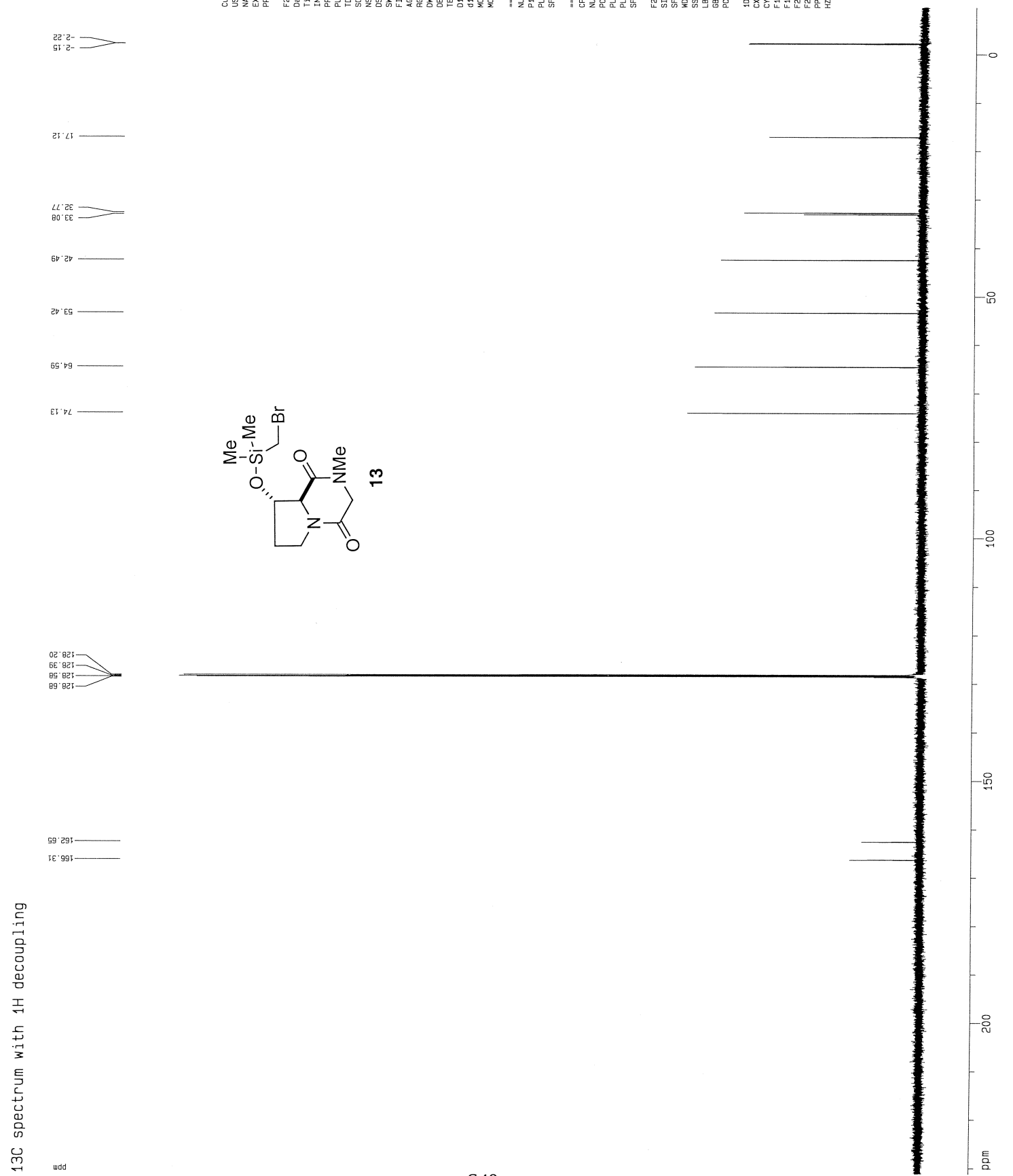
F2 - Acquisition Parameters
Date_ 20060715
Time 0.29
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT C6D6
NS 9
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

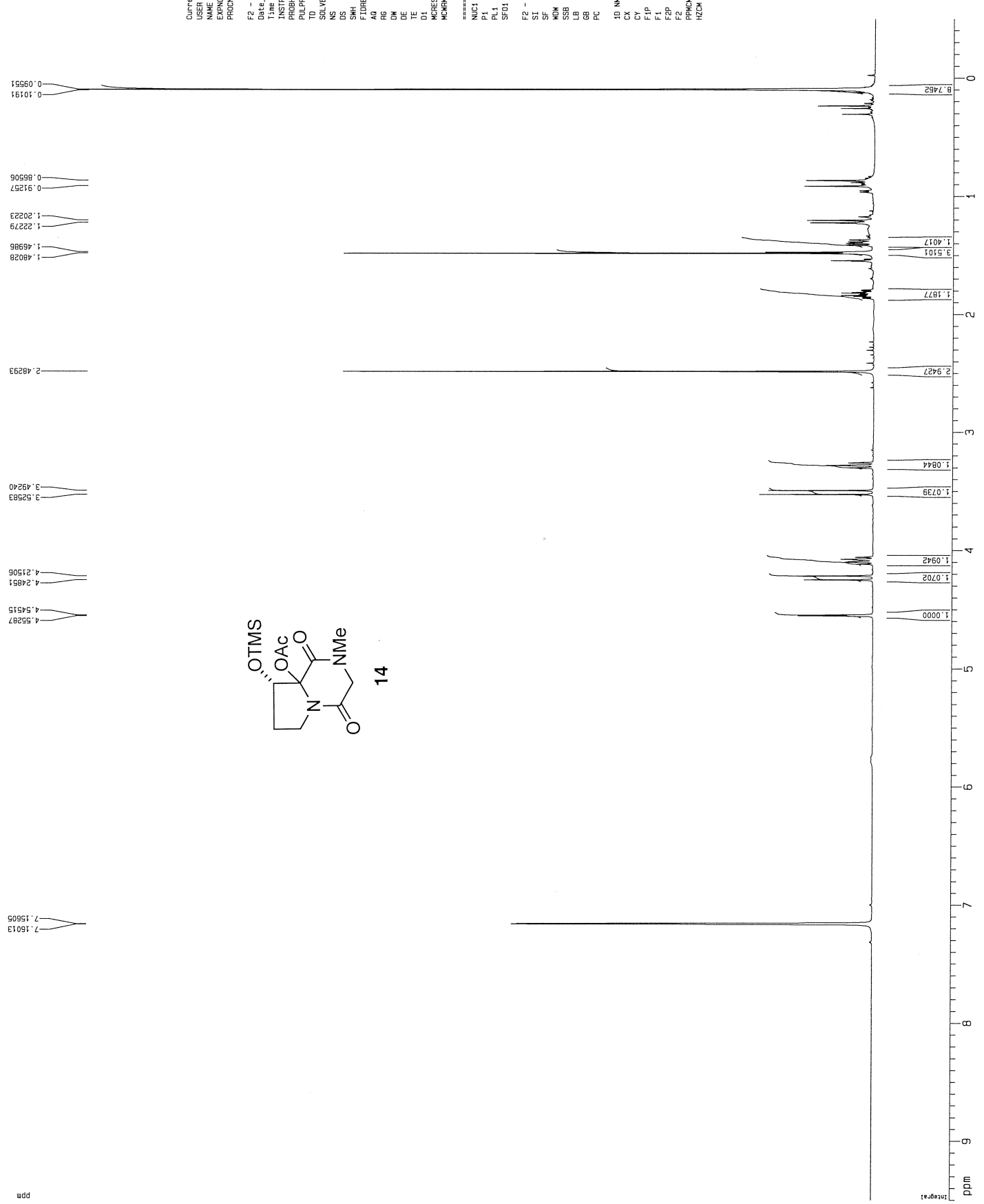
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -3.00 dB
SFO1 499.9334995 MHz

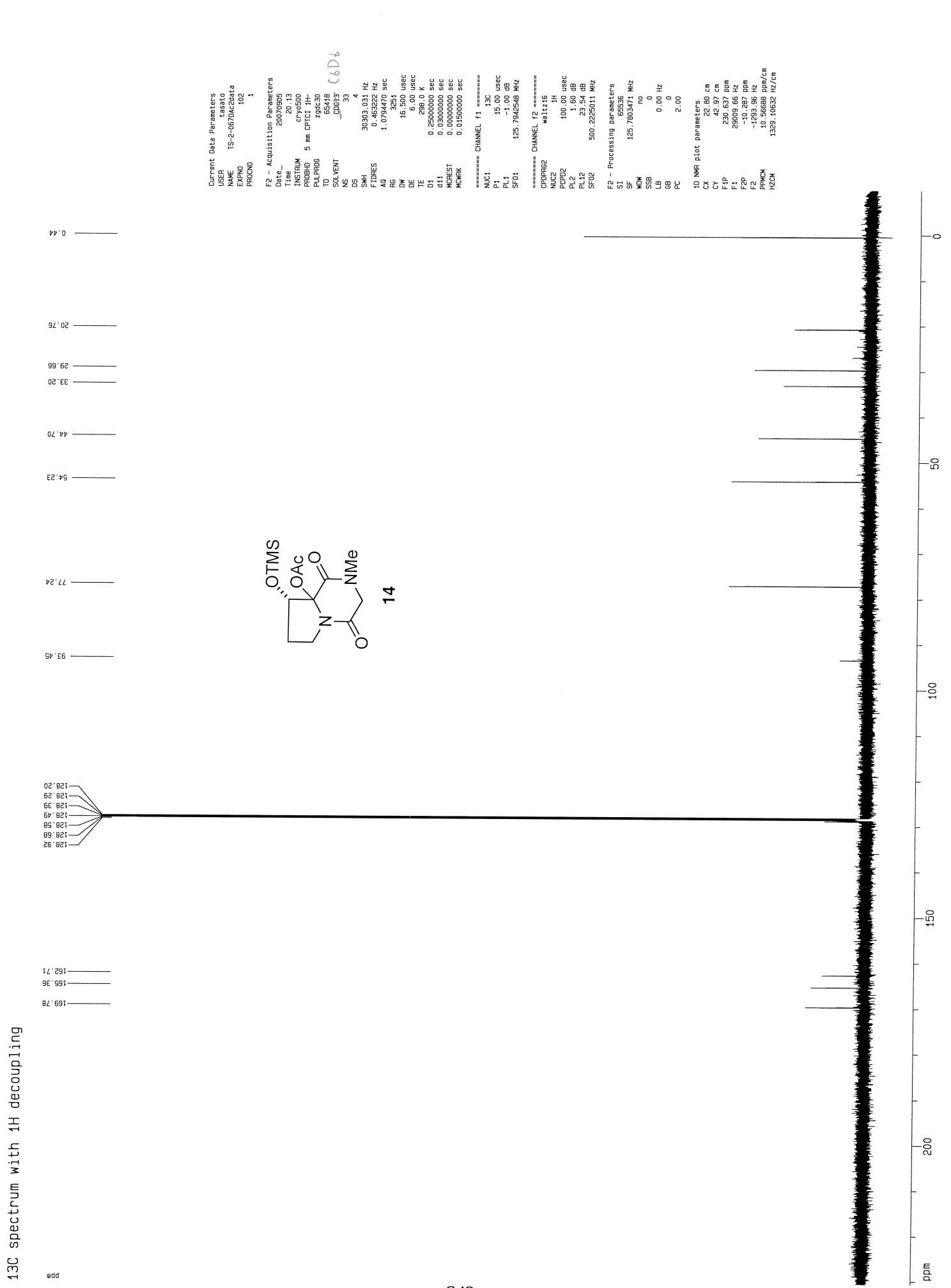
F2 - Processing parameters
SI 65536
SF 499.9299987 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

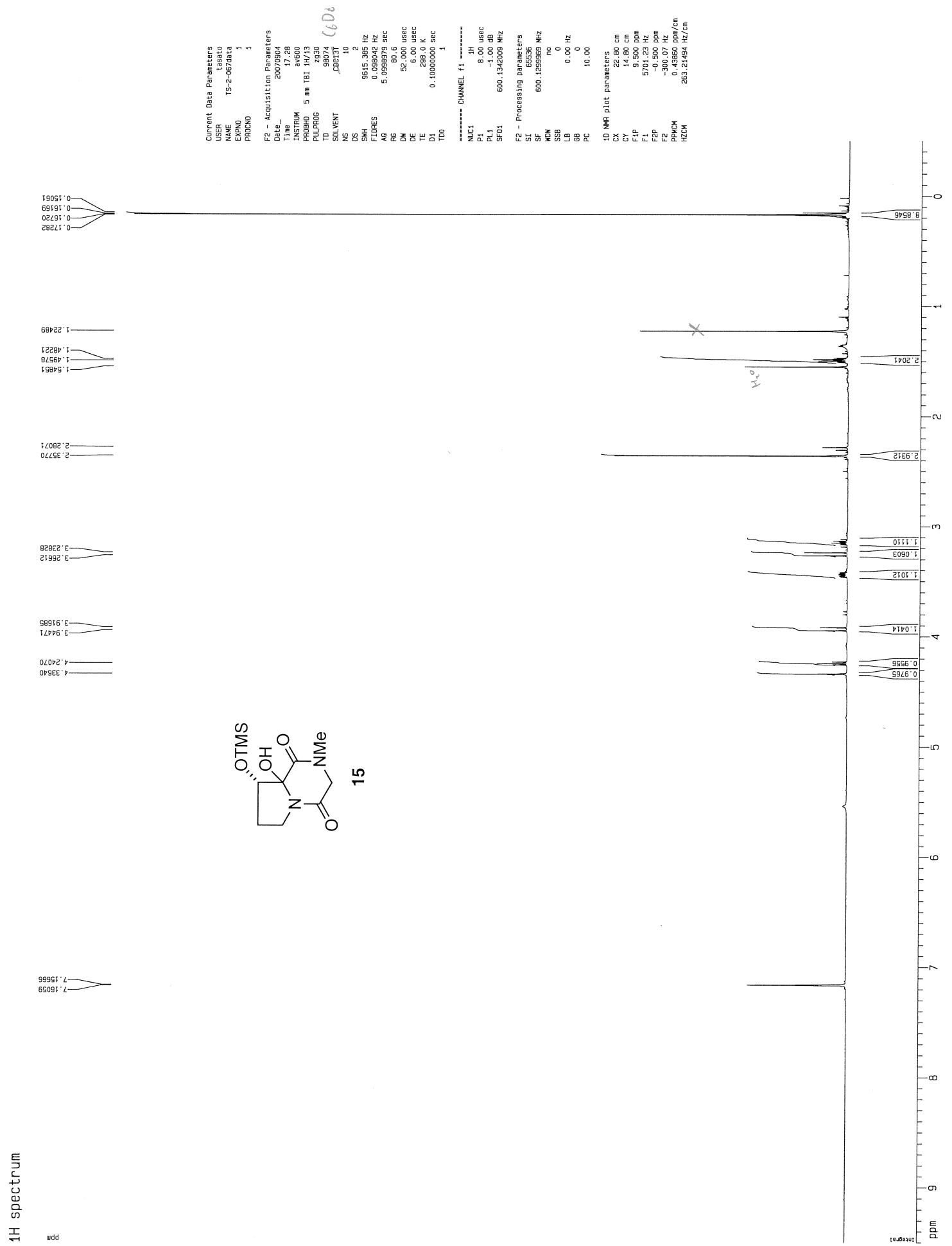
1D NMR plot parameters
CX 22.80 cm
CY 14.69 cm
F1P 9.500 ppm
F1 4749.33 Hz
F2P -0.500 ppm
F2 -249.96 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.26755 Hz/cm

13C spectrum with 1H decoupling

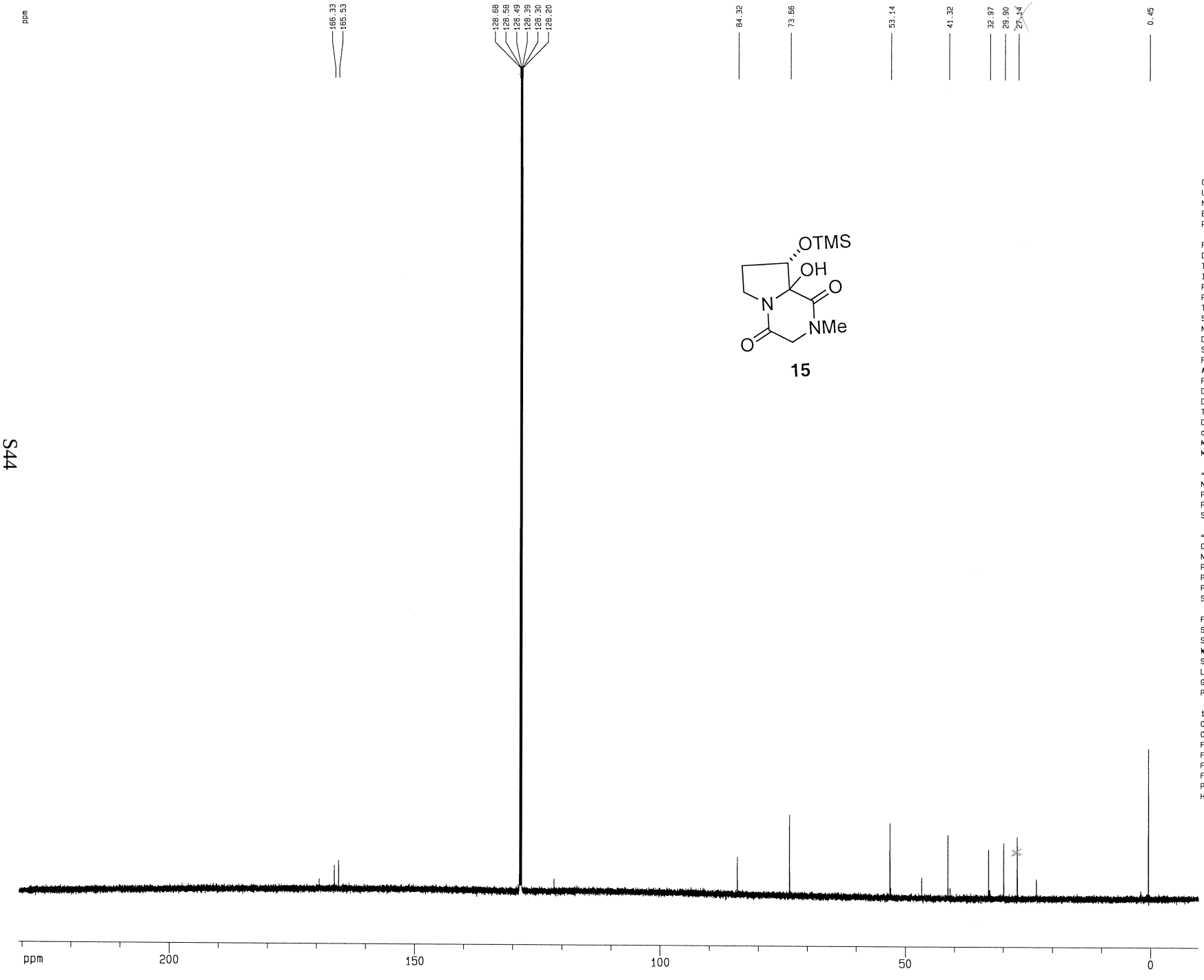



1H spectrum
Current Data Parameters
USER tasato
NAME TS-2-057OAc2data
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070905
Time 20.10
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 10
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200545 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 22.32 cm
F1P 9.500 ppm
F1 4752.09 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39478 Hz/cm
CDCl3
0.09551
0.10191
0.86506
0.91257
1.20223
1.22279
1.46986
1.48028
2.48293
3.49240
3.52583
4.21506
4.24851
4.54515
4.55287
7.15605
7.16013
OTMS
OAc
NMe
14
8.7462
1.4017
3.5101
1.1877
2.9427
1.0844
1.0739
1.0942
1.0702
1.0000
integral
ppm


13C spectrum with 1H decoupling
Current Data Parameters
USER tasato
NAME TS-2-067OAc2data
EXPNO 102
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070905
Time 20.13
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 33
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 3251
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz
F2 - Processing parameters
SI 65536
SF 125.7803471 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 42.97 cm
F1P 230.637 ppm
F1 29009.66 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56668 ppm/cm
HZCM 1329.10632 Hz/cm
OTMS
OAc
NMe
14
ppm


1H spectrum
Current Data Parameters
USER tasato
NAME TS-2-067data
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070904
Time 17.28
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT CDCl3T
NS 10
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 80.6
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
======= CHANNEL f1 =======
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1299969 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 10.00
1D NMR plot parameters
CX 22.80 cm
CY 14.80 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm
(CDCl3)
OTMS
OH
NMe
15
ppm
integral

13C spectrum with 1H decoupling



15

Current Data Parameters
USER tasato
NAME TS-2-067OHdata
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070904
Time 19.38
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65536
SOLVENT ~~CDCl3~~ (6D6
NS 76
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 3251
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

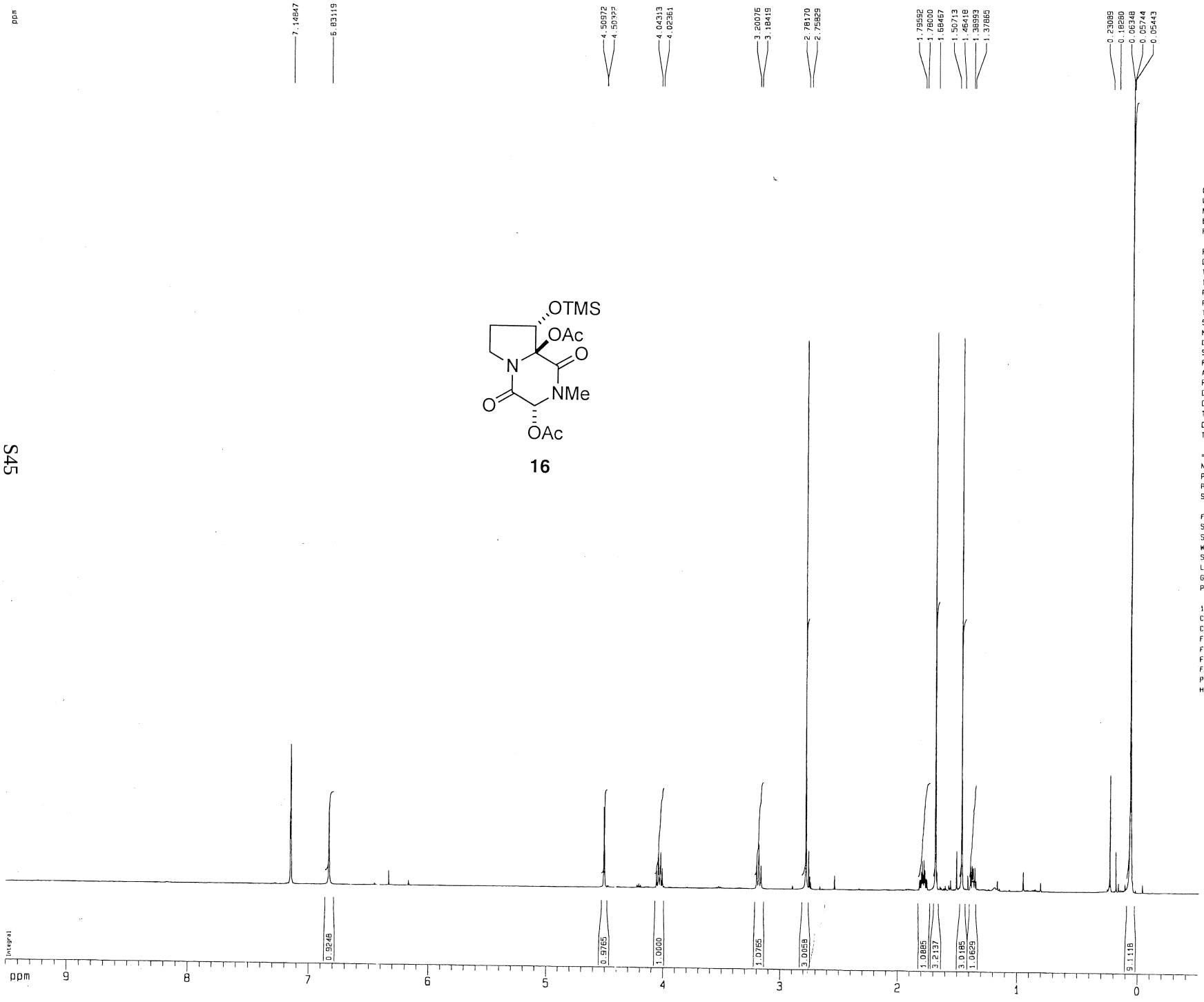
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7803332 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 20.19 cm
F1P 230.637 ppm
F1 29009.66 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10620 Hz/cm

1H spectrum



16

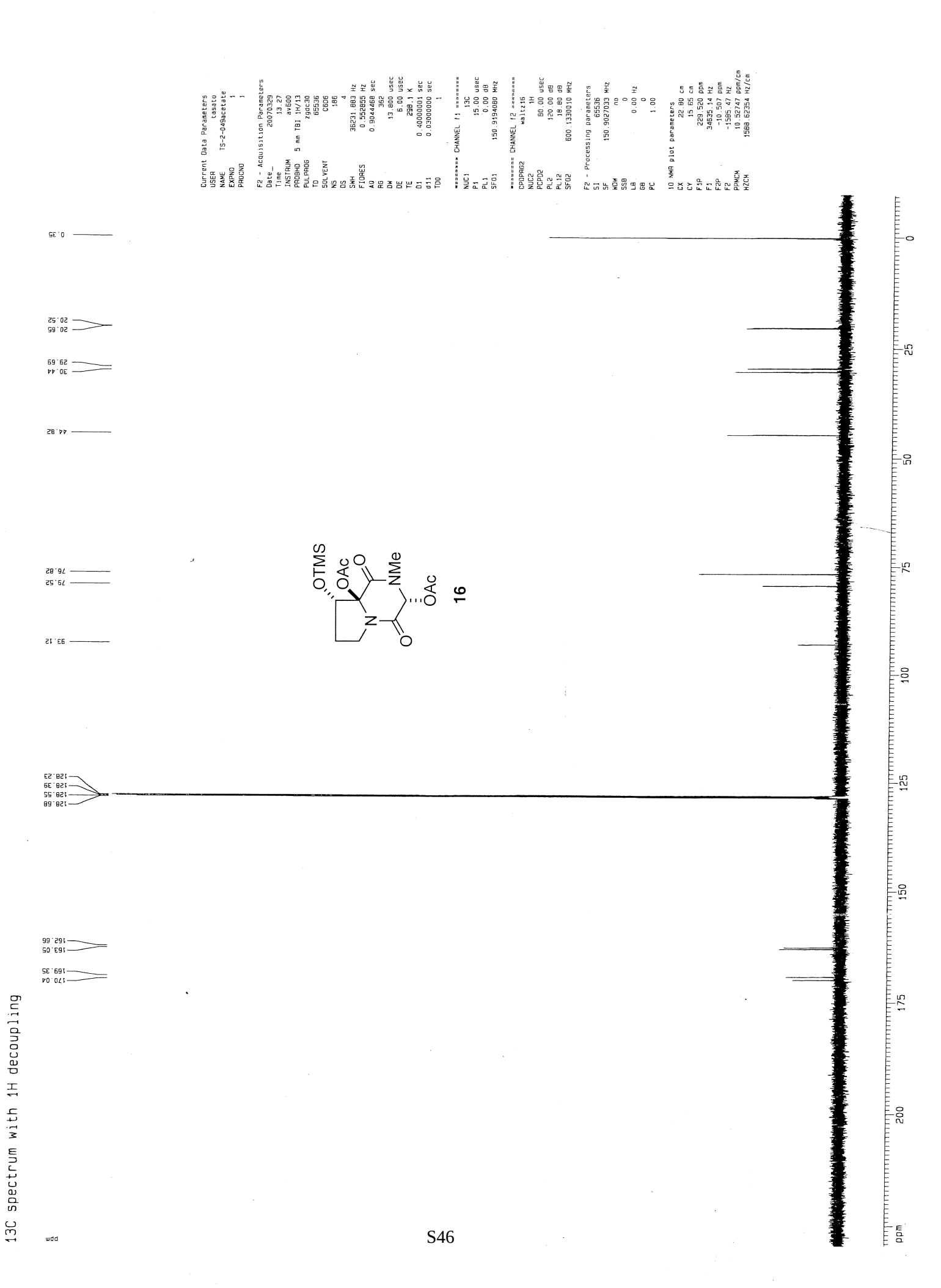
Current Data Parameters
USER tasato
NAME TS-2-049acetate1H
EXPNO 1
PROCNO 1

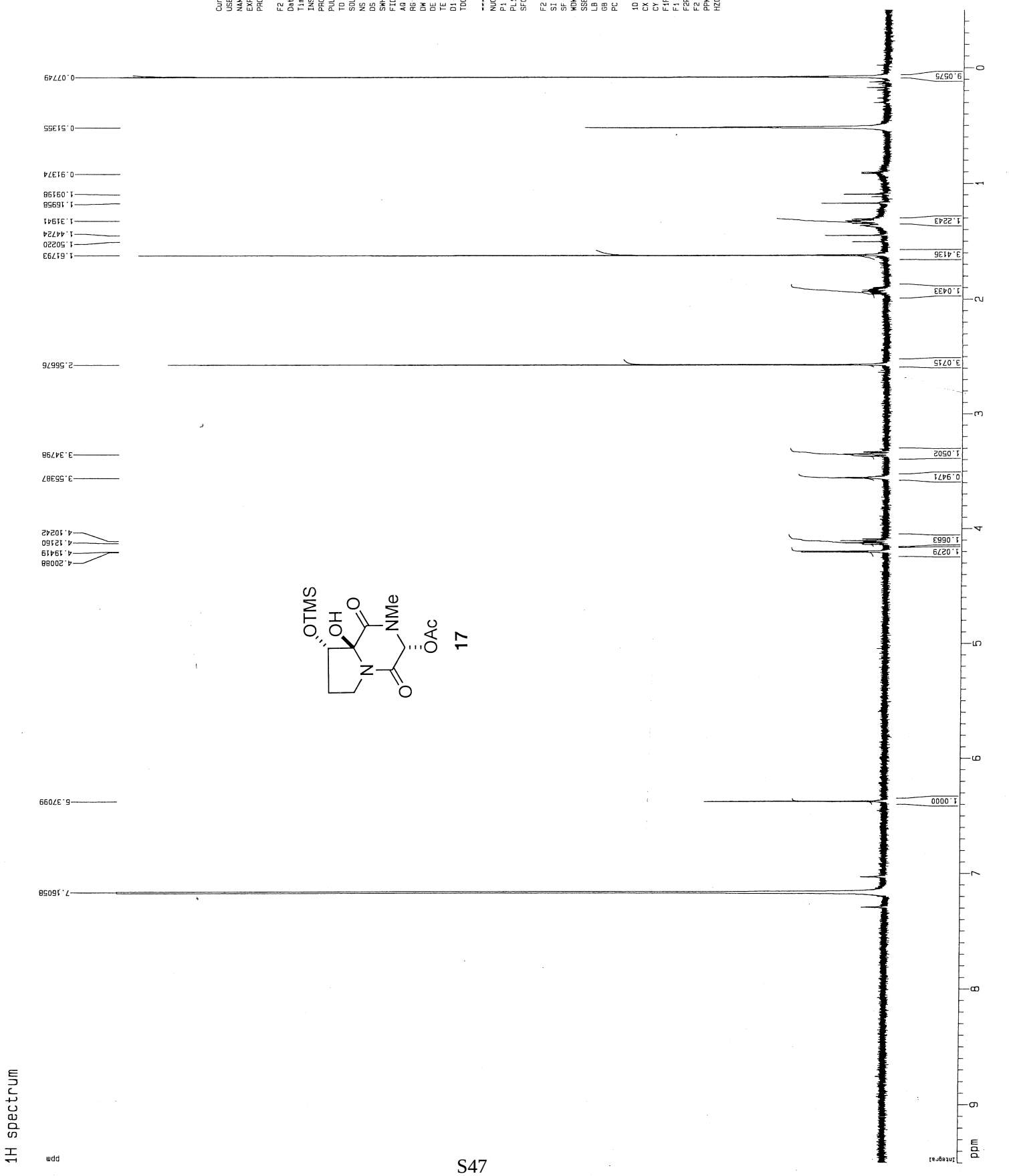
F2 - Acquisition Parameters
Date_ 20070329
Time 13.45
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT C6D6
NS 13
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 32
DW 52.000 usec
DE 6.00 usec
TE 298.1 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz

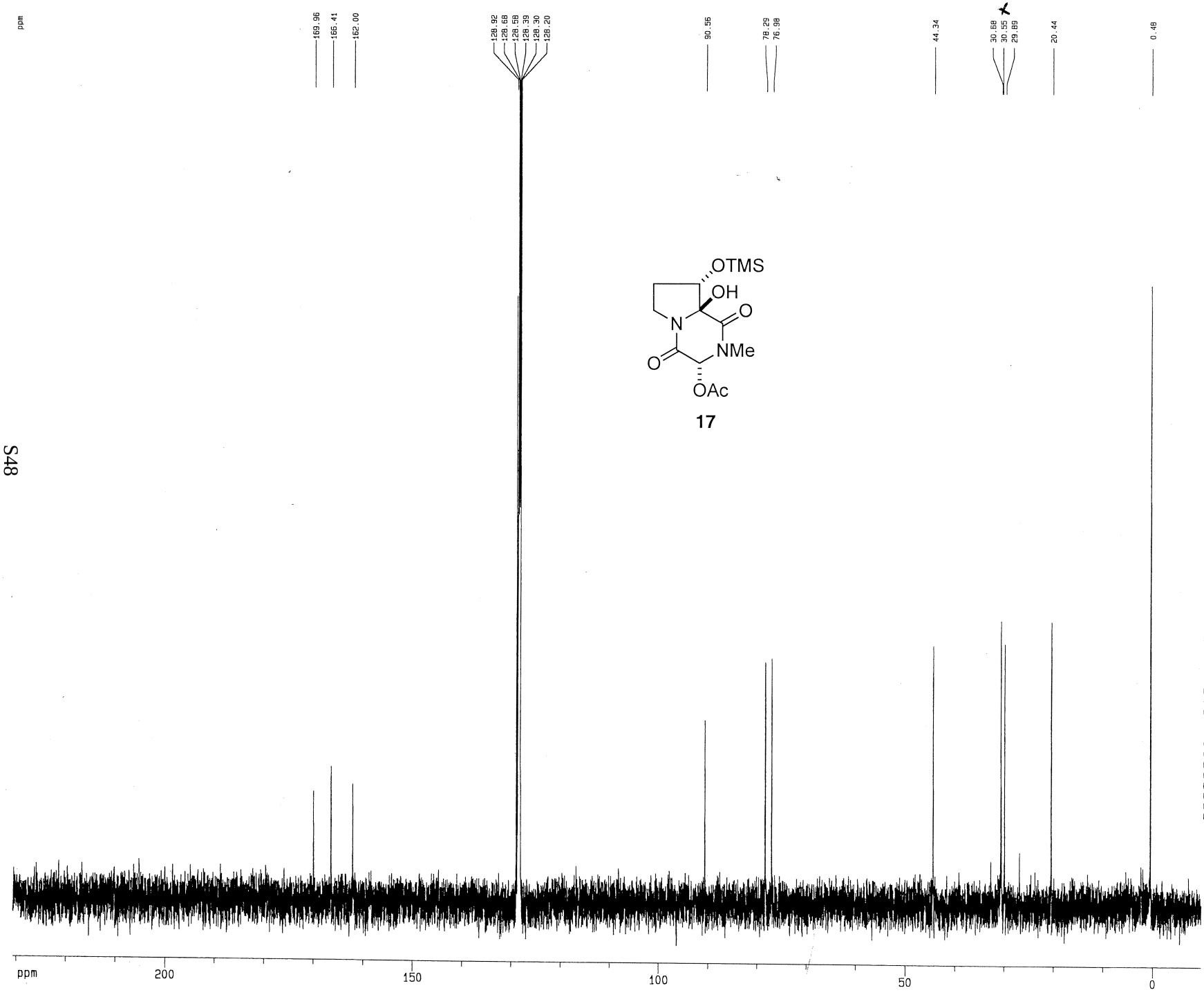
F2 - Processing parameters
SI 65536
SF 600.1300040 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 10.00

1D NMR plot parameters
CX 22.80 cm
CY 23.68 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm


13C spectrum with 1H decoupling
Current Data Parameters
USER casatu
NAME TS-2-049acetate
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070329
Time 13.27
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zgdc30
TD 65536
SOLVENT C606
NS 186
DS 4
SWH 36231.883 Hz
FIDRES 0.552855 Hz
AQ 0.9044468 sec
RG 362
DW 13.800 usec
DE 6.00 usec
TE 298.1 K
D1 0.40000001 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 0.00 dB
SF01 150.9194080 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 18.80 dB
SF02 600.1330010 MHz
F2 - Processing parameters
SI 65536
SF 150.9027033 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 229.520 ppm
F1 34635.14 Hz
F2P -10.507 ppm
F2 -1585.47 Hz
PPMCM 10.52747 ppm/cm
HZCM 1588.62354 Hz/cm
OTMS
OAc
O
NMe
N
O
OAc
16
0.35
20.52
20.65
29.69
30.44
44.82
76.82
79.52
93.12
128.23
128.39
128.55
128.68
162.66
163.05
169.35
170.04
ppm
0
25
50
75
100
125
150
175
200
ppm


Current Data Parameters
USER tasato
NAME TS-2-117down
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070604
Time 19.42
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT CDCl3
NS 32
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 2050
DW 52.000 usec
DE 6.00 usec
TE 294.5 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1299971 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 85.93 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm
0.07749
0.51355
0.91374
1.09198
1.16958
1.31941
1.44724
1.50220
1.61793
2.56576
3.34798
3.55387
4.10242
4.12160
4.19419
4.20088
5.37099
7.16058
9.0575
1.2243
3.4136
1.0433
3.0715
1.0502
0.9471
1.0663
1.0279
1.0000
OTMS
OH
O
NMe
OAc
N
O
17
1H spectrum
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER tasato
NAME TS-2-122b-OH13C
EXPNO 2
PROCNO 1

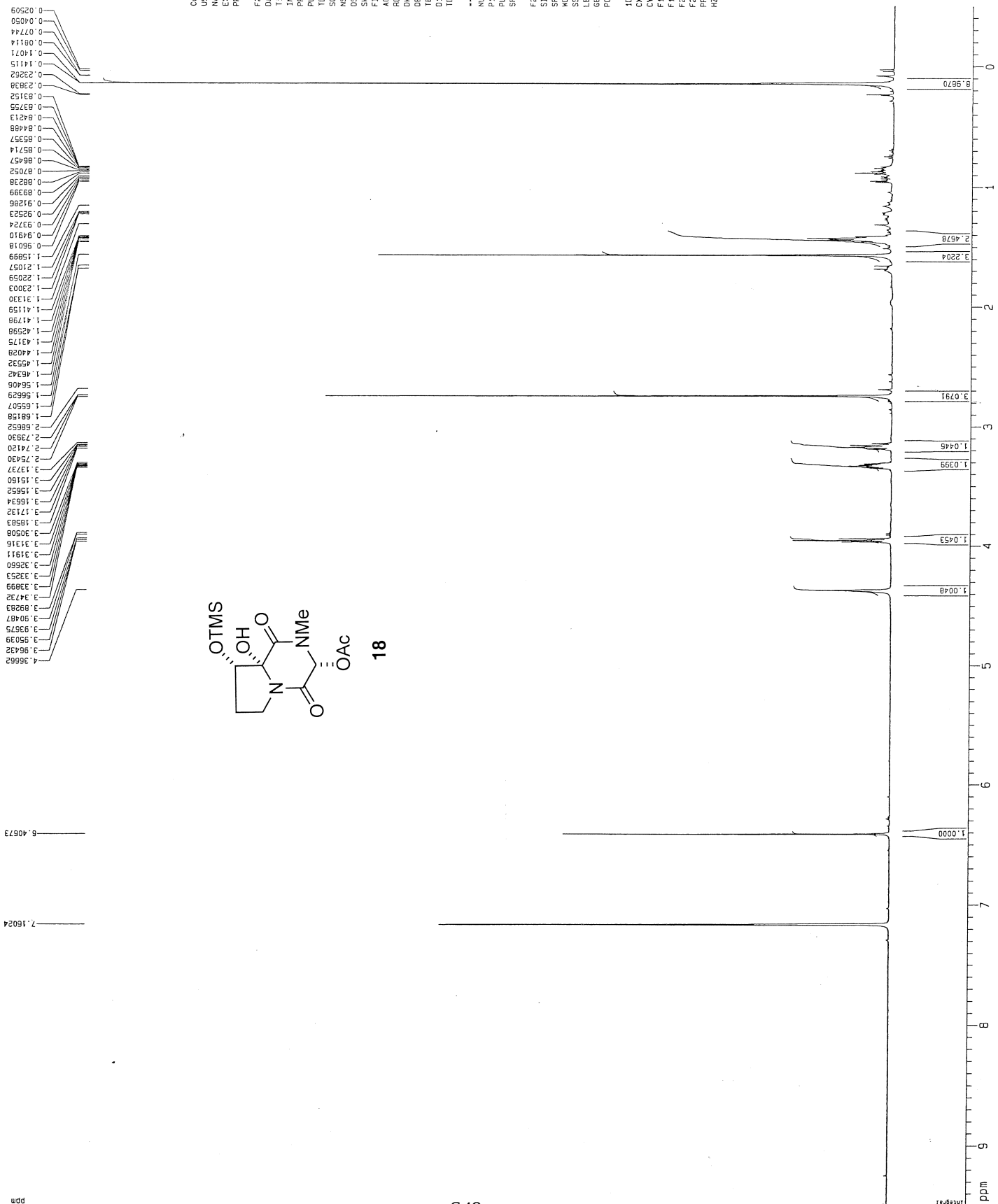
F2 - Acquisition Parameters
Date_ 20070608
Time 20.18
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT ~~CDCl3~~ C6D6
NS 40
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 3251
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

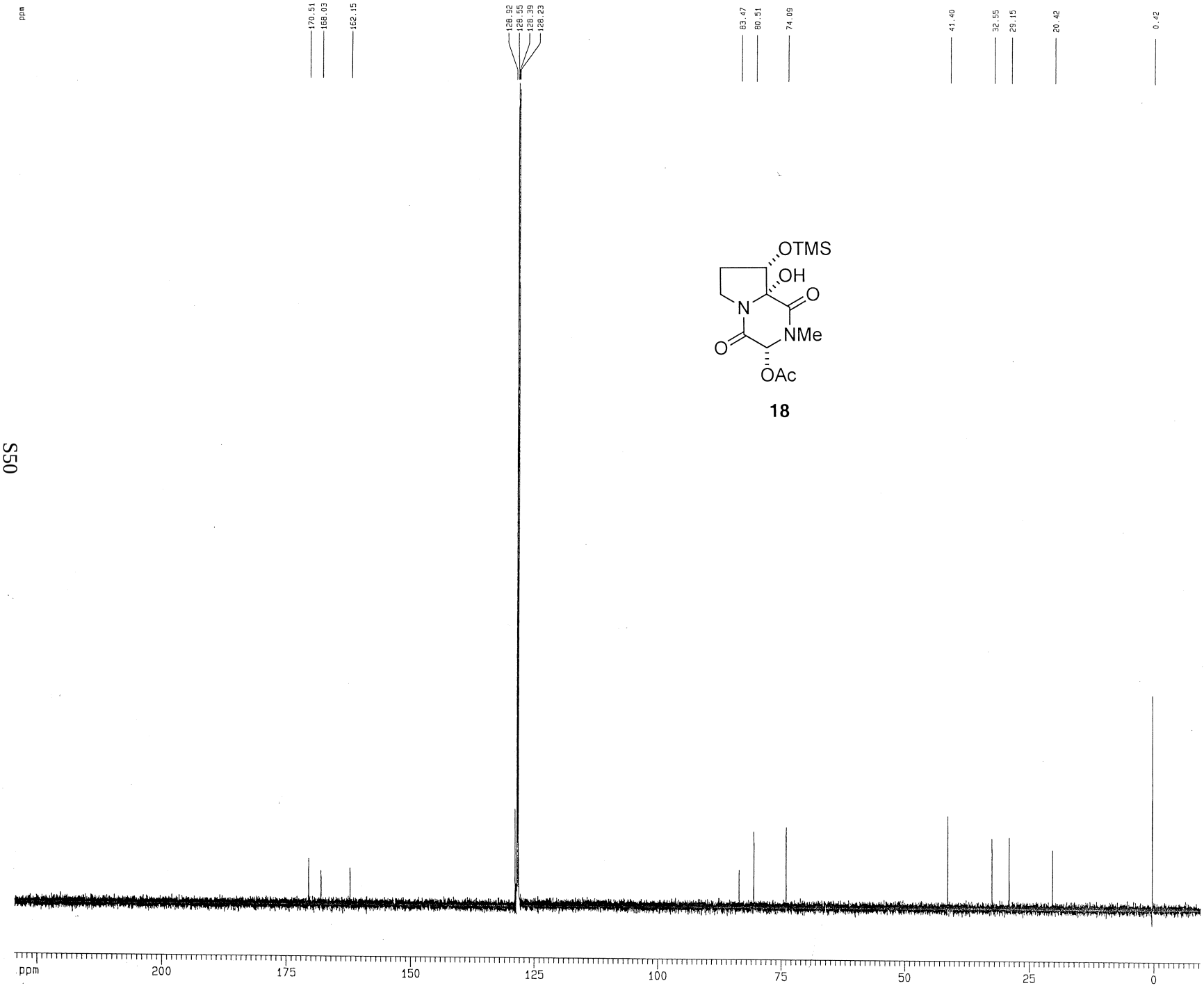
F2 - Processing parameters
SI 65536
SF 125.7803337 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 273.15 cm
F1P 230.637 ppm
F1 29009.66 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10620 Hz/cm


Current Data Parameters
USER tasato
NAME TS-2-161HPLC8
EXPNO 100
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070803
Time 20.48
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 97938
SOLVENT CDCl3
NS 5
DS 2
SWH 9615.385 Hz
FIDRES 0.098178 Hz
AQ 5.0928259 sec
RG 406
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1299969 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 45.28 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm
OTMS
OH
NMe
OAc
N
O
O
18
8.9870
2.4678
3.2204
3.0791
1.0446
1.0399
1.0453
1.0048
1.0000
ppm
Integral

1H spectrum

13C spectrum with 1H decoupling



18

Current Data Parameters
USER tasato
NAME TS-2-161HPLC_13C
EXPNO 5
PROCNO 1

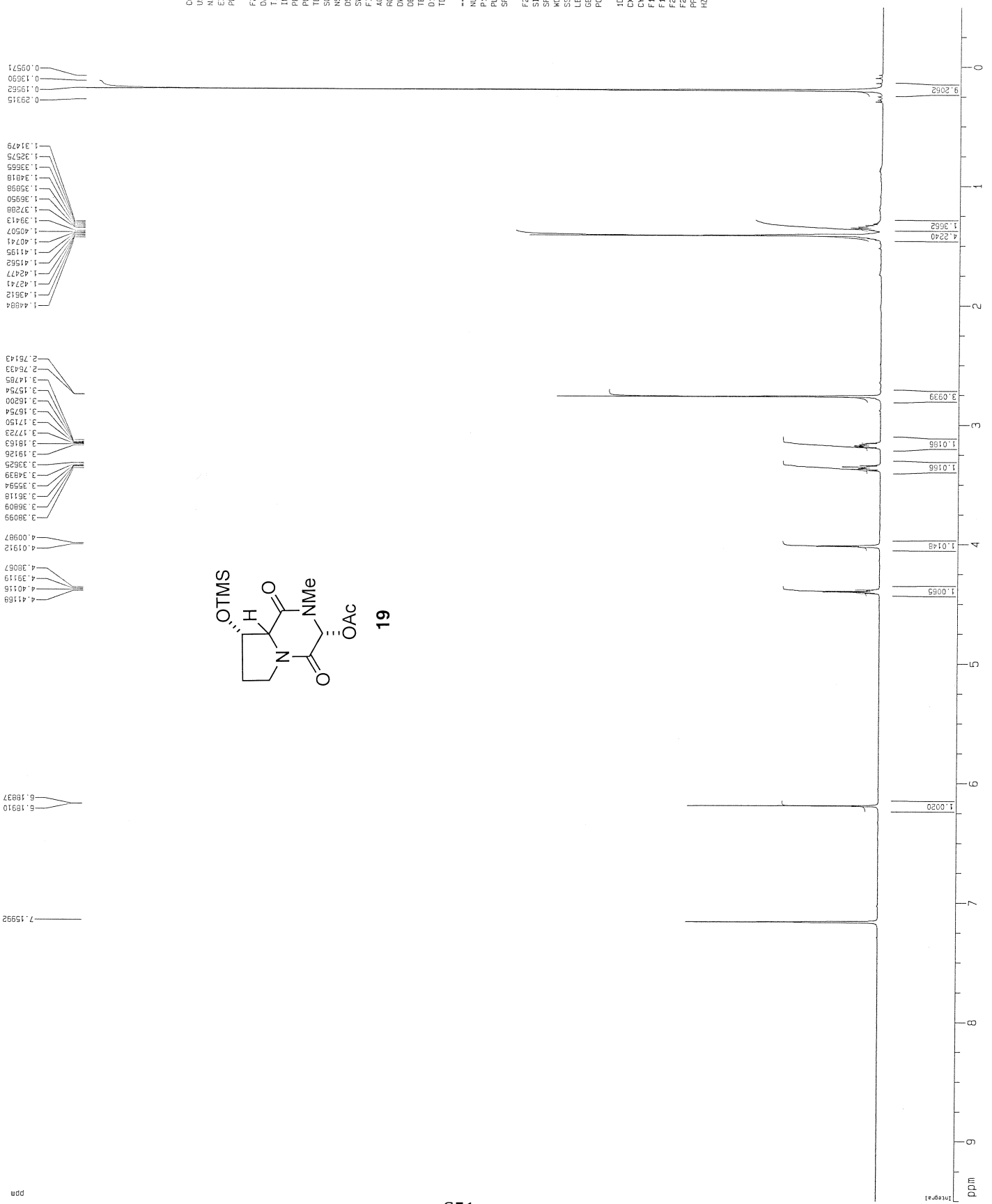
F2 - Acquisition Parameters
Date_ 20070803
Time 22.10
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zgdc30
TD 65536
SOLVENT ~~CDCl3~~ C6D6
NS 471
DS 4
SWH 36231.883 Hz
FIDRES 0.552855 Hz
AQ 0.9044468 sec
RG 575
DW 13.800 usec
DE 6.00 usec
TE 298.0 K
D1 0.40000001 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 0.00 dB
SFO1 150.9194080 MHz

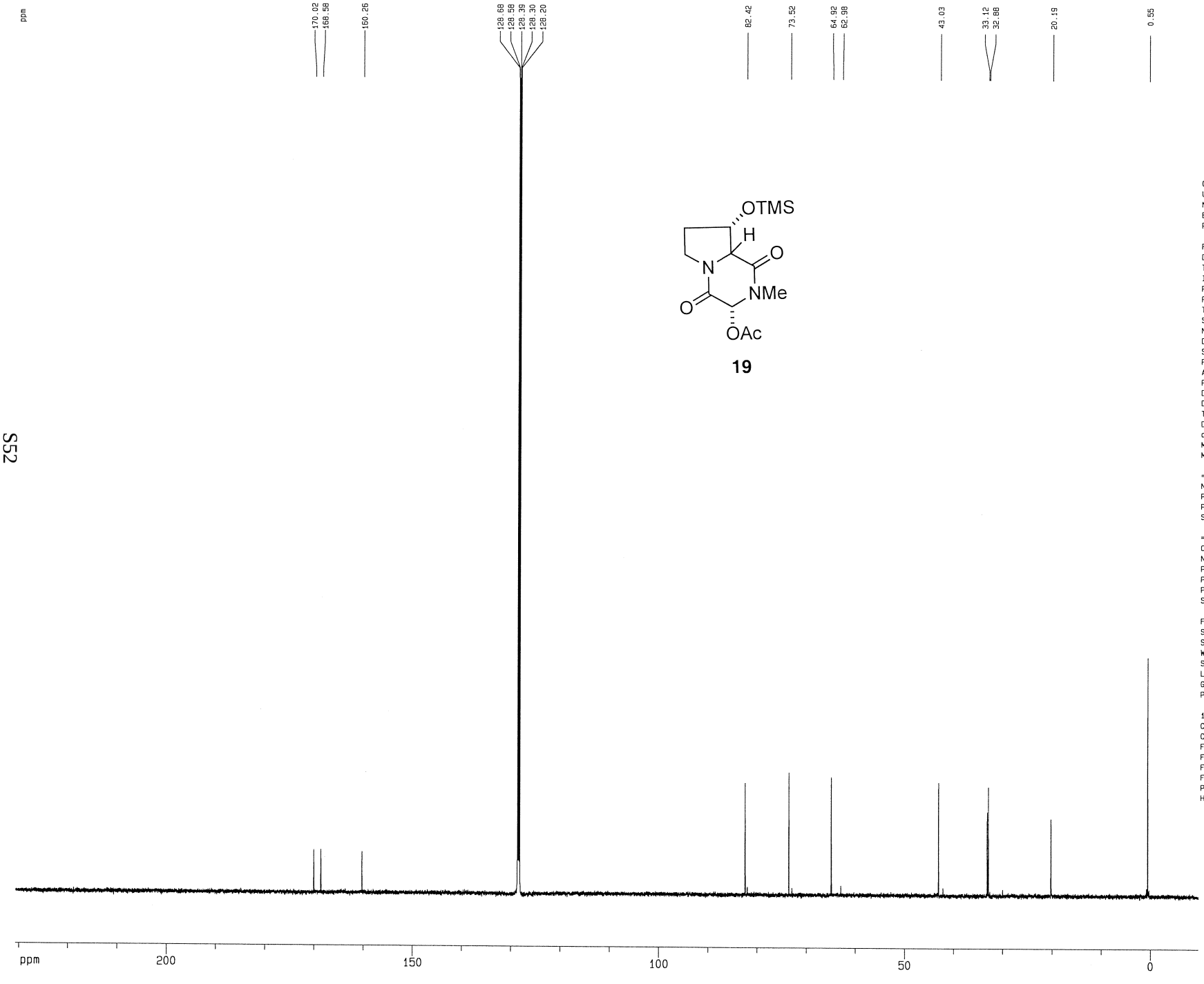
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 18.80 dB
SFO2 600.1330010 MHz

F2 - Processing parameters
SI 65536
SF 150.9027033 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 229.520 ppm
F1 34635.14 Hz
F2P -10.507 ppm
F2 -1585.47 Hz
PPMCM 10.52747 ppm/cm
HZCM 1588.62354 Hz/cm


1H spectrum
Current Data Parameters
USER tasato
NAME TS-2-161HPLCC
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070803
Time 20.53
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT CDCl3T
NS 16
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 322
DW 52.000 usec
DE 6.00 usec
TE 298.1 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1299970 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 32.75 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm
OTMS
H
O
NMe
OAc
N
O
19
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER tasato
NAME TS-2-161reddata
EXPNO 102
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070918
Time 13.39
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT ~~CDCl3~~ C6D6
NS 34
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 3251
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

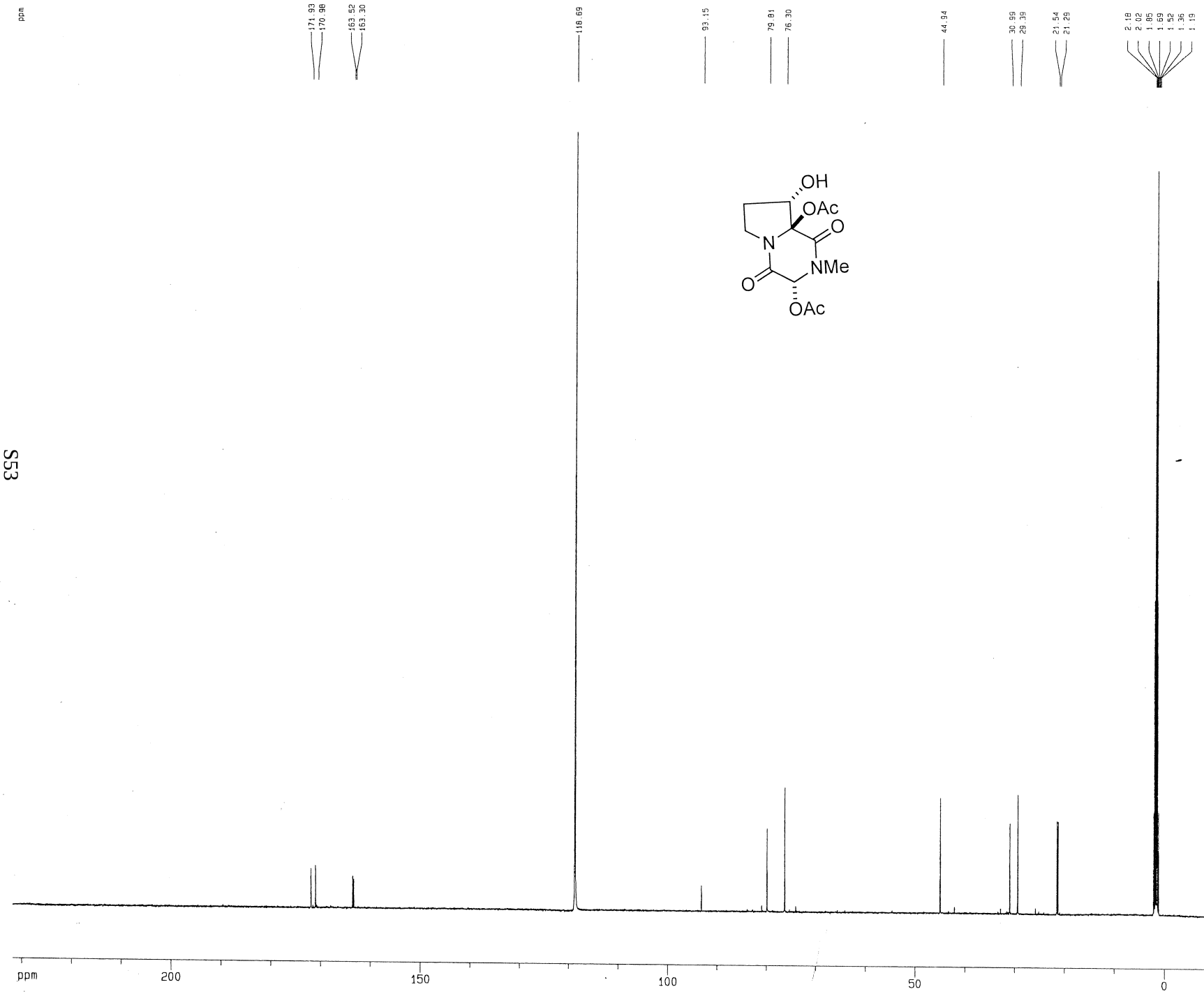
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

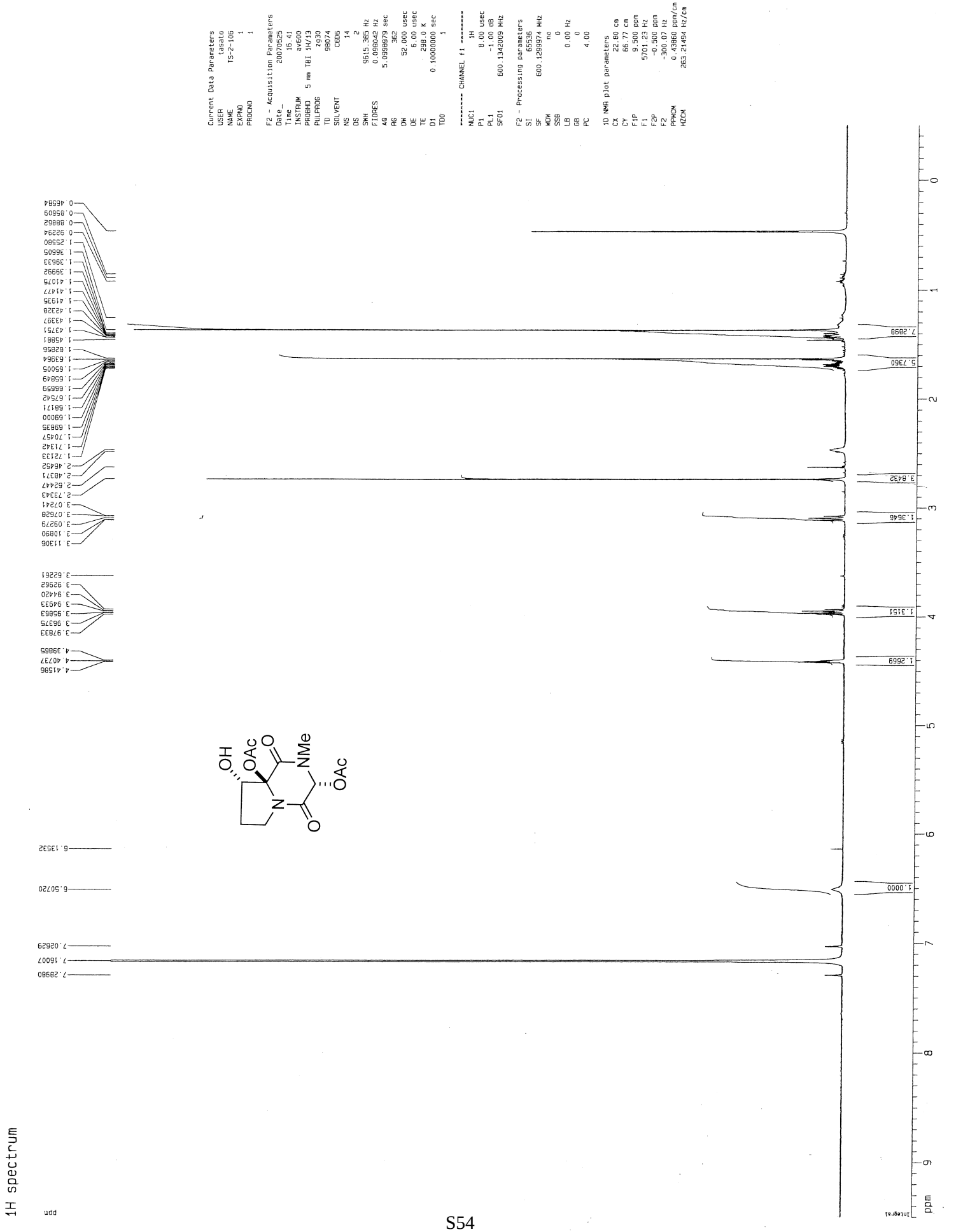
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

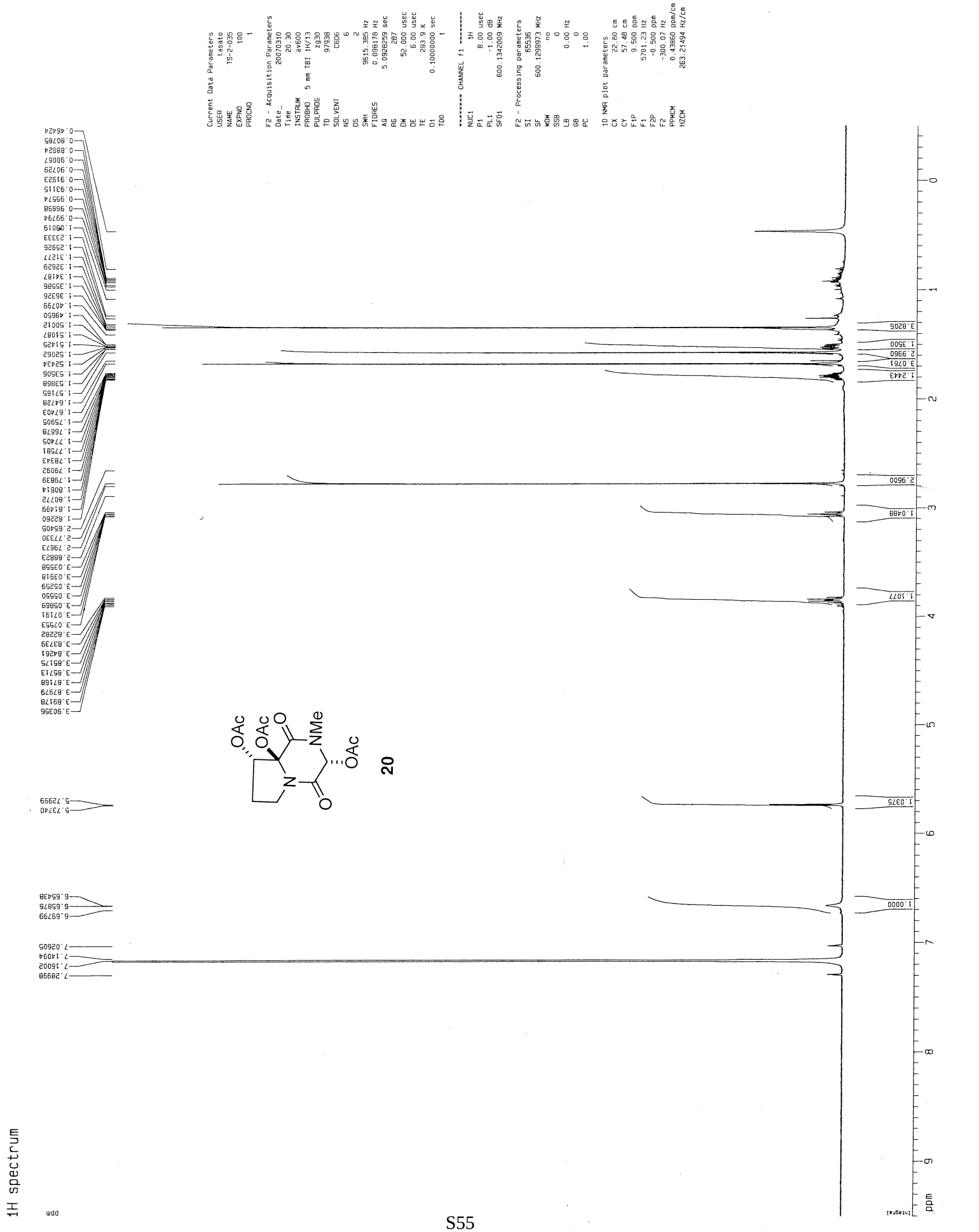
F2 - Processing parameters
SI 65536
SF 125.7803328 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 27.59 cm
F1P 230.637 ppm
F1 29009.66 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10620 Hz/cm

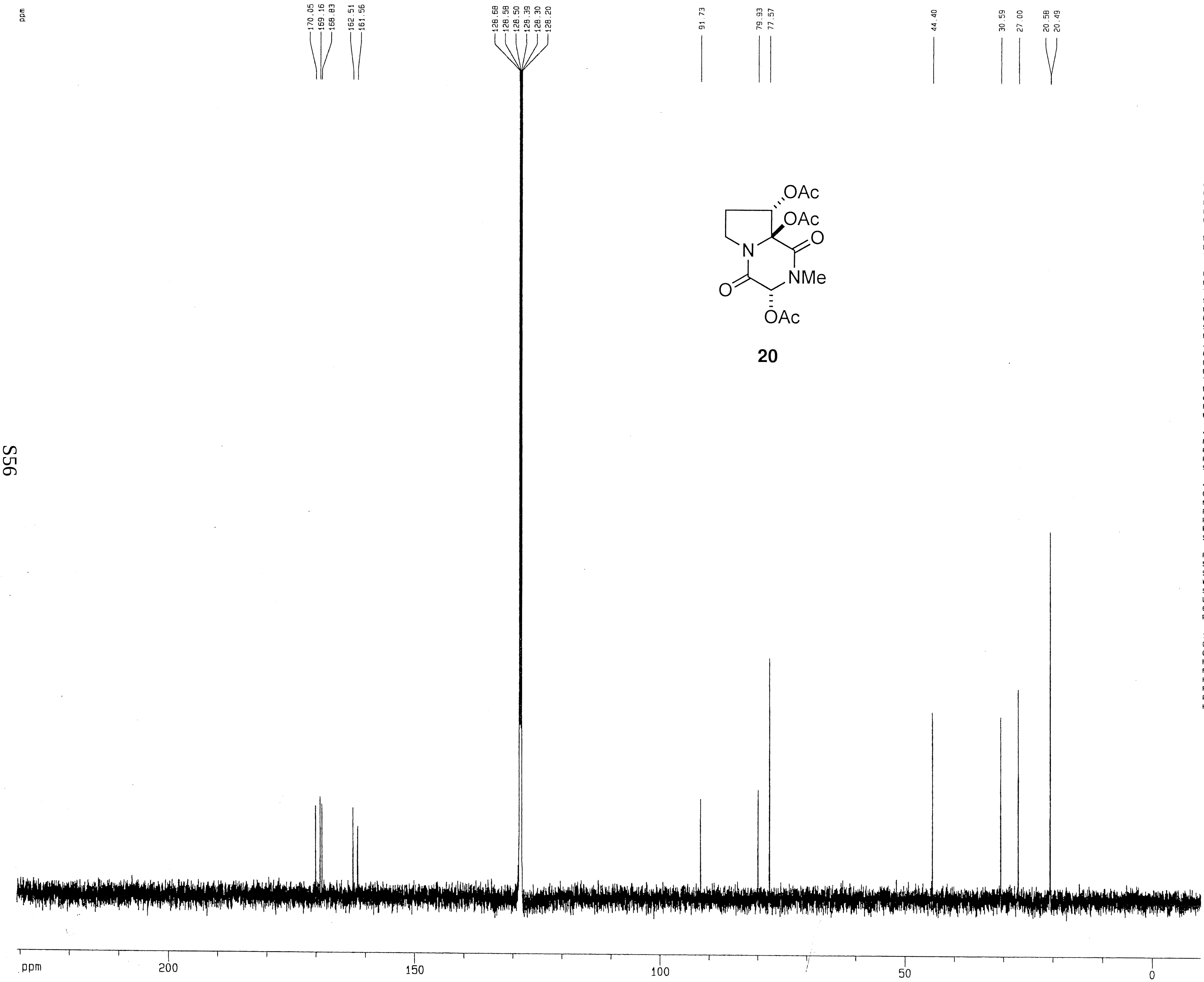
13C spectrum with 1H decoupling




1H spectrum
Current Data Parameters
USER tasato
NAME TS-2-106
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070525
Time 16.41
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT CDCl3
NS 14
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 362
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1299974 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 66.77 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm
OH
OAc
NMe
OAc
N
O
O
O
7.2898
5.7360
3.8432
1.3646
1.3151
1.2669
1.0000
ppm
Integral


1H spectrum
Current Data Parameters
USER tasato
NAME TS-2-035
EXPNO 100
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070310
Time 20.30
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 97938
SOLVENT C6D6
NS 6
DS 2
SWH 9615.385 Hz
FIDRES 0.098178 Hz
AQ 5.0928259 sec
RG 287
DW 52.000 usec
DE 6.00 usec
TE 293.9 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SF01 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1299973 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 57.48 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm
OAc
OAc
O
NMe
OAc
N
O
20
ppm
Integral

13C spectrum with 1H decoupling



20

Current Data Parameters
USER tasato
NAME TS-2-102SMtriacetate13C
EXPNO 2
PROCNO 1

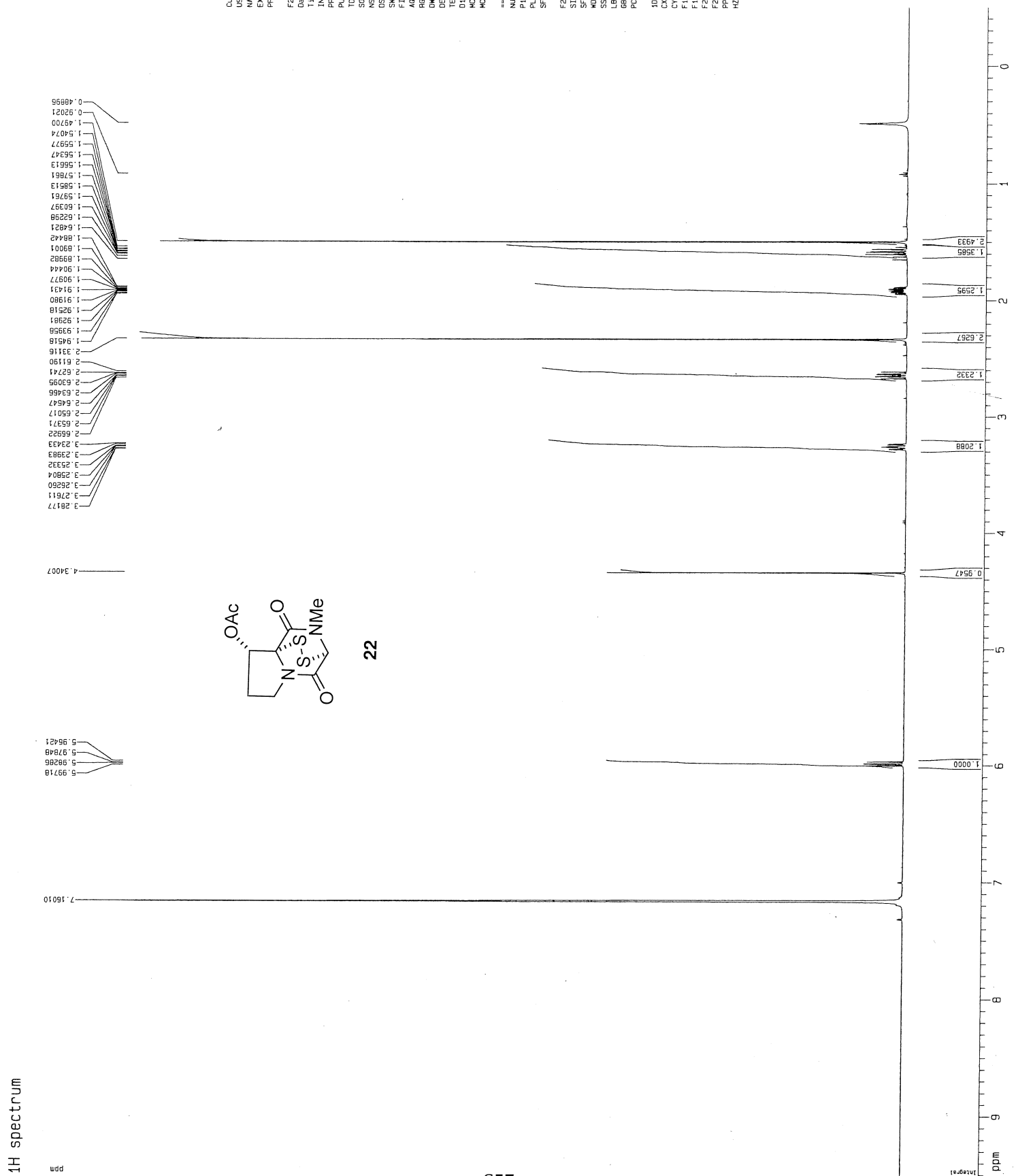
F2 - Acquisition Parameters
Date_ 20070522
Time 19.21
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3 C6D6
NS 19
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 3251
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

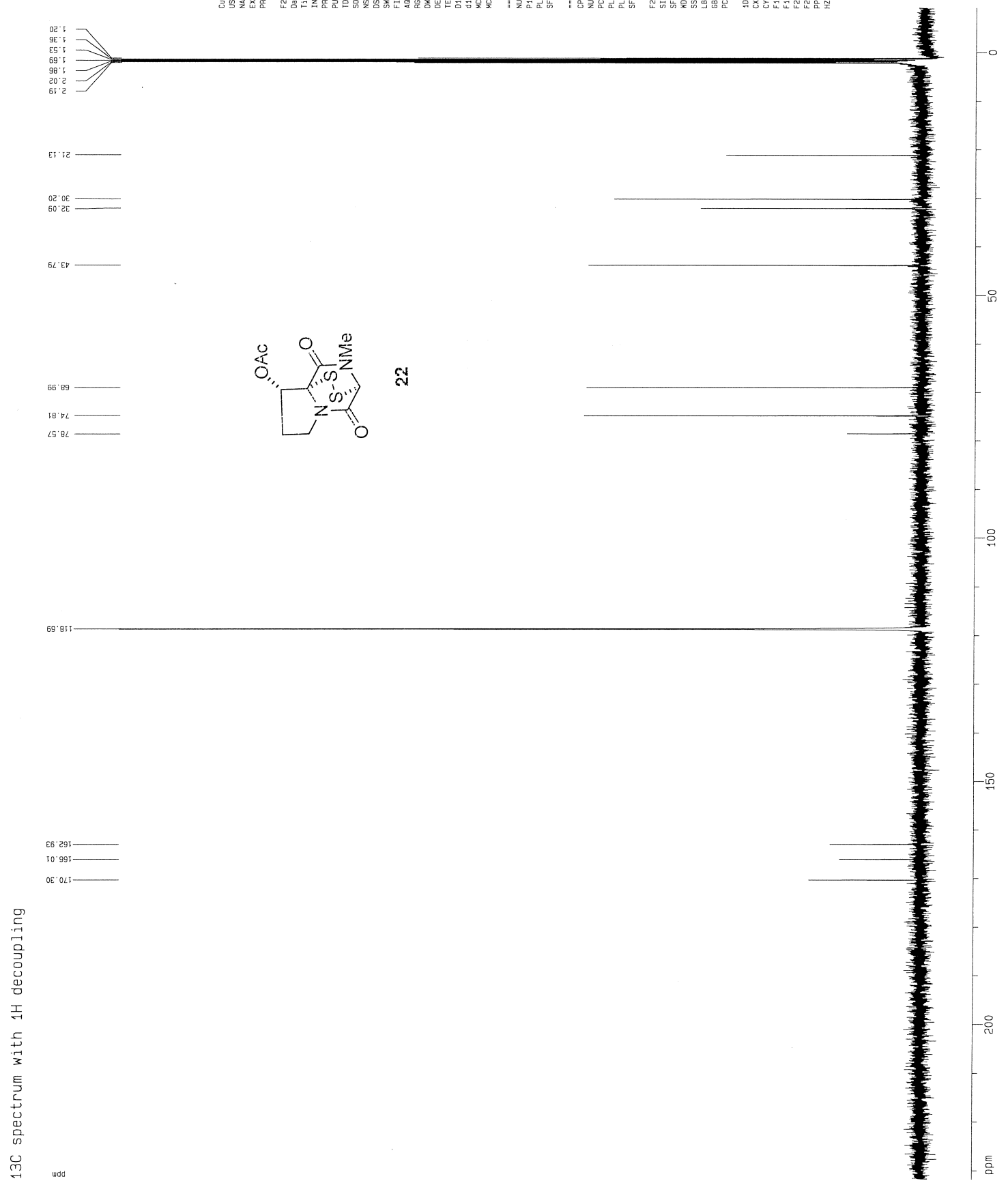
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

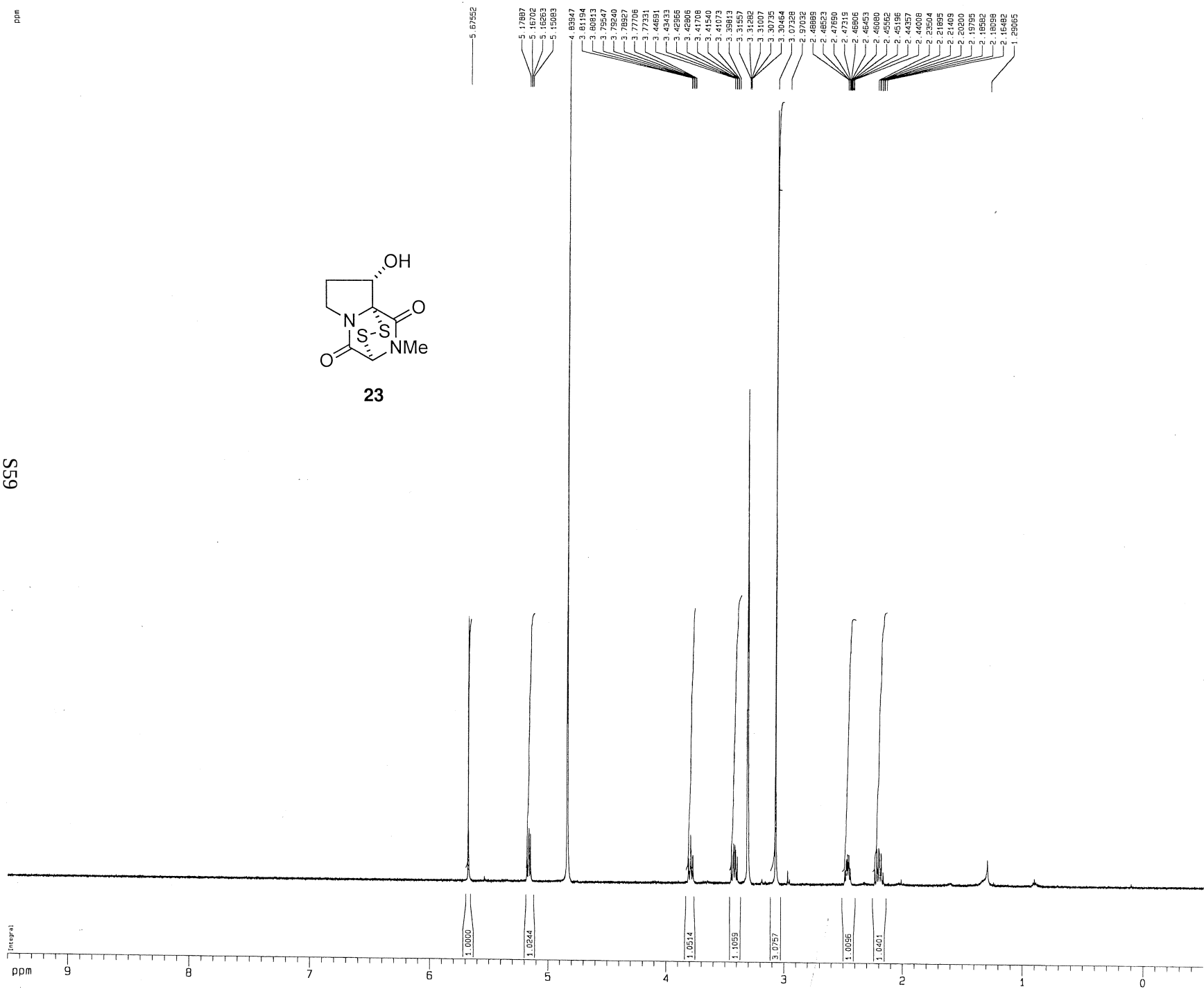
F2 - Processing parameters
SI 65536
SF 125.7803337 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 137.37 cm
F1P 230.637 ppm
F1 29009.66 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10620 Hz/cm


1H spectrum
Current Data Parameters
USER tasato
NAME TS-2-129HPLC52
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070618
Time 20.50
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 20
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200008 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.84 cm
F1P 9.500 ppm
F1 4752.09 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39474 Hz/cm
OAc
O
S
S
NMe
N
O
22
ppm
Integral


13C spectrum with 1H decoupling
ppm
Current Data Parameters
USER tasato
NAME TS-2-166data
EXPNO 102
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071002
Time 0.23
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 38
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 7296.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz
F2 - Processing parameters
SI 65536
SF 125.7802535 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 71.61 cm
F1P 231.776 ppm
F1 29152.82 Hz
F2P -9.145 ppm
F2 -1150.21 Hz
PPMCM 10.56668 ppm/cm
HZCM 1329.08032 Hz/cm
OAc
NMe
22
1.20
1.36
1.53
1.69
1.86
2.02
2.19
21.13
30.20
32.09
43.79
68.99
74.81
78.57
118.69
162.93
166.01
170.30
0
50
100
150
200
ppm

1H spectrum



Current Data Parameters
USER tasato
NAME TS-2-168MeOH
EXPNO 1
PROCNO 1

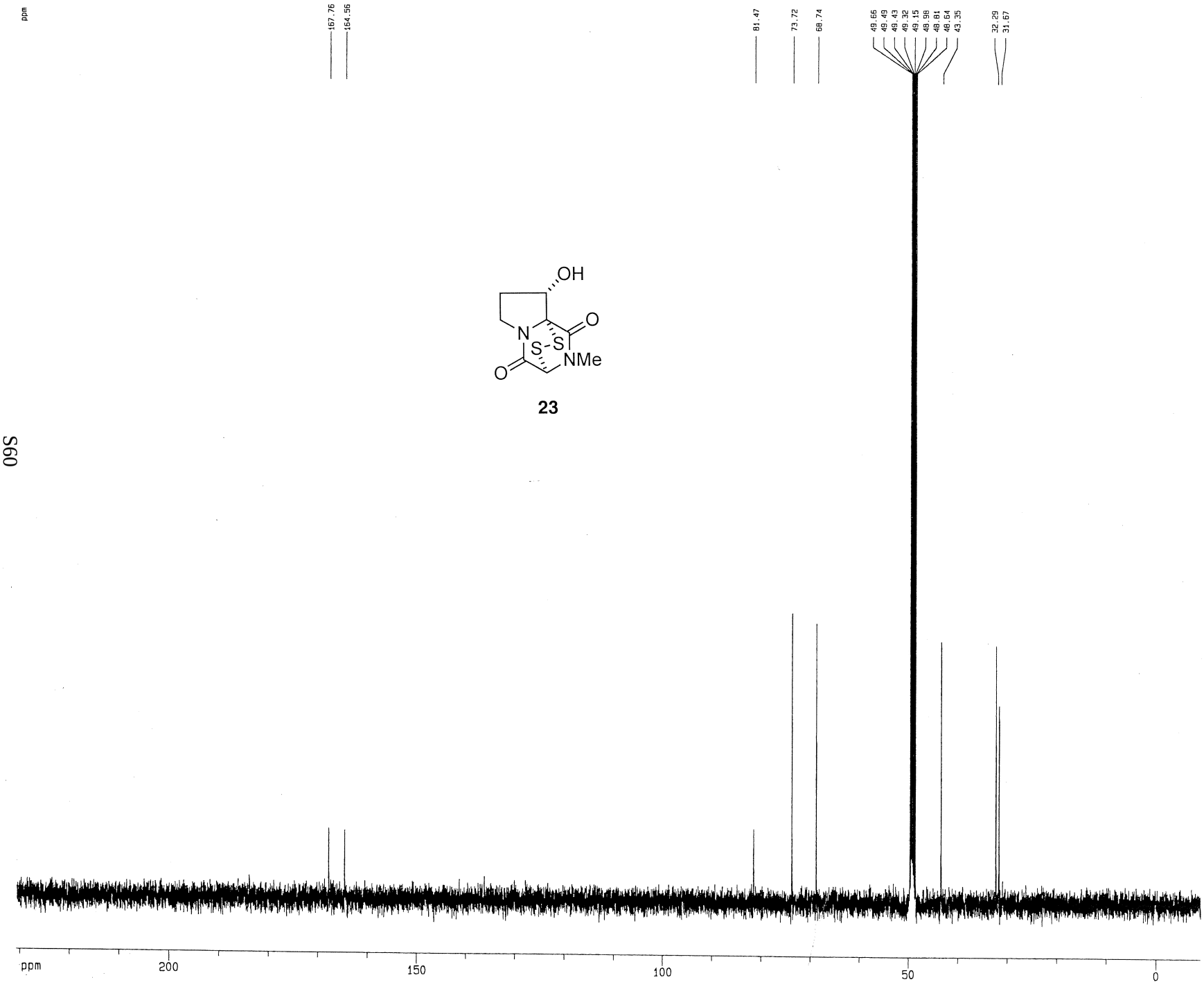
F2 - Acquisition Parameters
Date_ 20070814
Time 13.26
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT CD3OD
NS 19
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 1290
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SF01 600.1342009 MHz

F2 - Processing parameters
SI 65536
SF 600.1300199 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 16.22 cm
F1P 9.500 ppm
F1 5701.23 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.43860 ppm/cm
HZCM 263.21494 Hz/cm

13C spectrum with 1H decoupling



23

S60

Current Data Parameters

USER	tasato
NAME	TS-2-168C030C13C
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20070814
Time	16.13
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	65418
SOLVENT	CD3OD
NS	89
DS	4
SWH	30303.031 Hz
FIDRES	0.463222 Hz
AQ	1.0794635 sec
RG	10321.3
DW	16.500 usec
DE	6.00 usec
TE	298.0 K
D1	0.25000000 sec
d11	0.03000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	15.00 usec
PL1	-1.00 dB
SFO1	125.7942548 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	1.60 dB
PL12	23.54 dB
SFO2	500.2225011 MHz

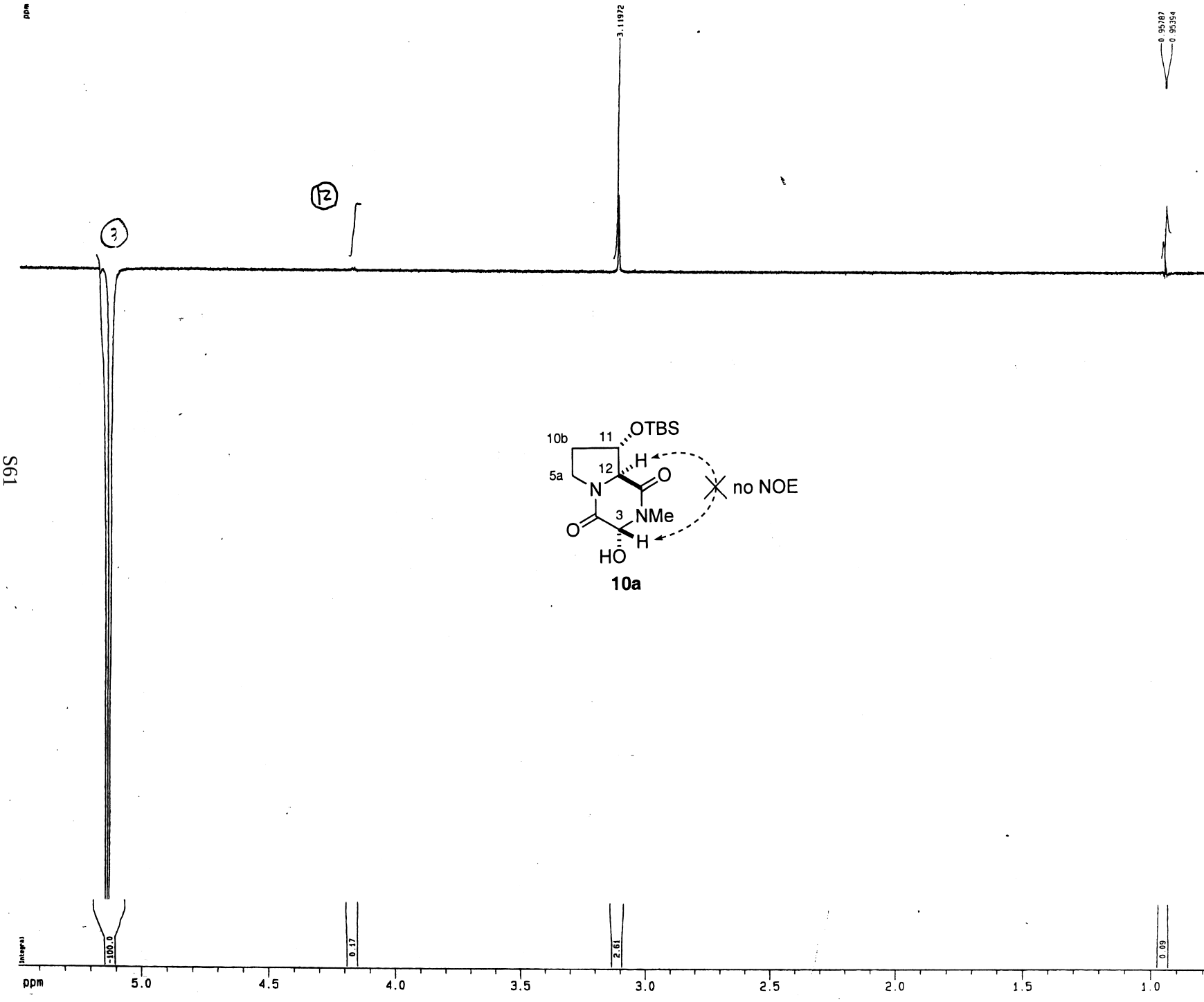
F2 - Processing parameters

SI	65536
SF	125.7802274 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
CY	124.60 cm
F1P	230.637 ppm
F1	29009.63 Hz
F2P	-10.287 ppm
F2	-1293.96 Hz
PPMCM	10.56688 ppm/cm
HZCM	1329.10510 Hz/cm

gnoe



10a

Current Data Parameters

USER	tasato
NAME	TS-2-43oolarnue2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070512
Time	23.38
INSTRUM	qn500
PROBHD	5 mm broadband
PULPROG	gnoeicc wu
TD	65536
SOLVENT	CDCl3
NS	128
DS	8
SWH	5482.456 Hz
FIDRES	0.083656 Hz
AQ	5.9770246 sec
RG	1625.5
DW	91.200 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
DB	0.50000000 sec
D16	0.00020000 sec
d21	0.33374399 sec
d22	0.16399899 sec
p2	24.00 usec

======== CHANNEL f1 ========

NUC1	1H
P1	12.00 usec
p3	36.00 usec
p4	48.00 usec
p5	32.00 usec
P12	40000.00 usec
PL1	-3.00 dB
SFO1	499.9325630 MHz
SP1	55.20 dB
SPNAM1	gauss1.512
SPOFF1	0.00 Hz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPNAM3	sine.100
GPNAM4	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPX3	0.00 %
GPX4	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPY3	0.00 %
GPY4	0.00 %
GPZ1	7.00 %
GPZ2	3.00 %
GPZ3	2.30 %
GPZ4	-2.30 %
P16	1000.00 usec

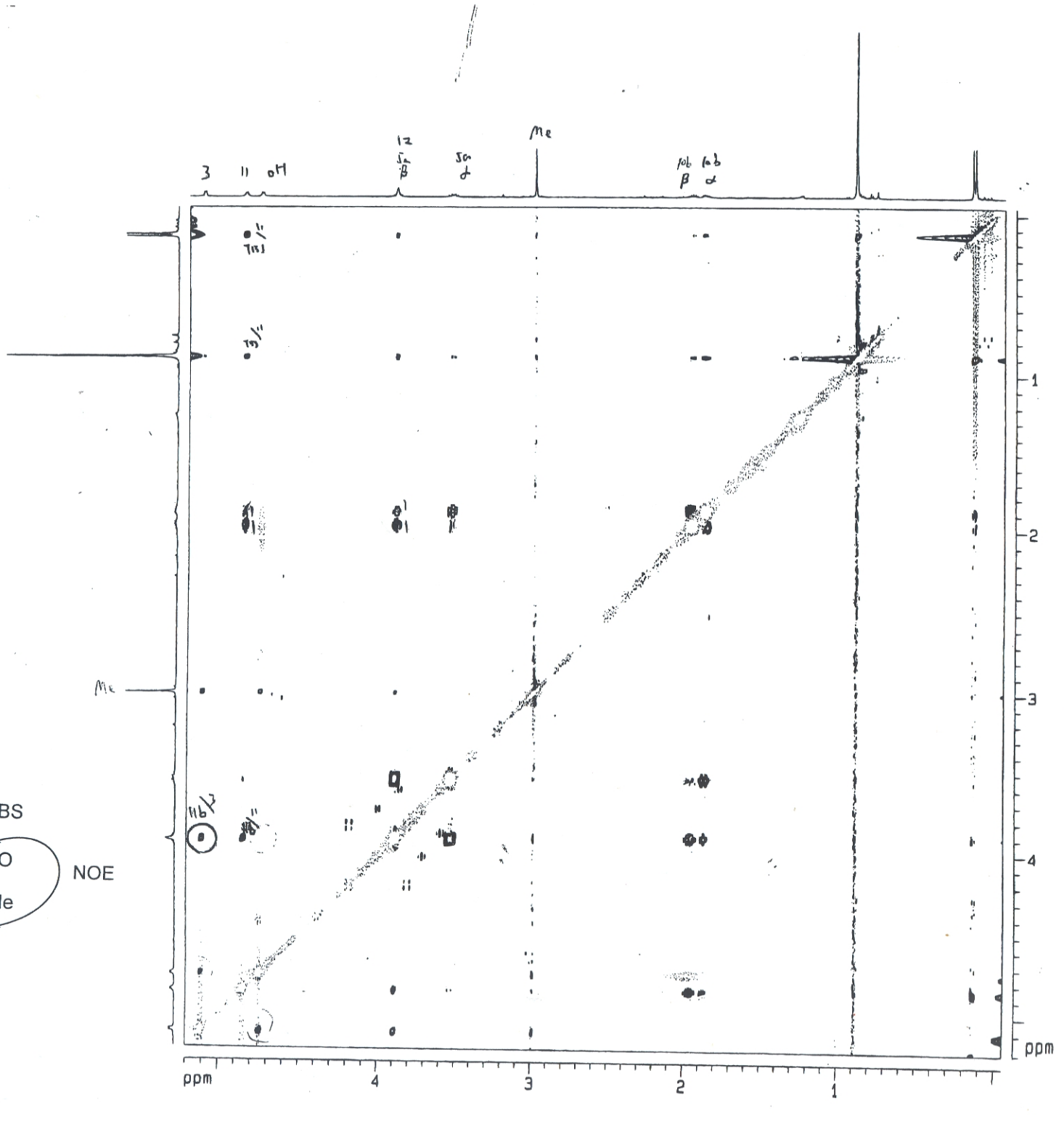
F2 - Processing parameters

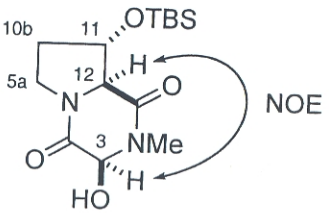
SI	65536
SF	499.9300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
CY	50.00 cm
F1P	5.482 ppm
F1	2740.78 Hz
F2P	0.779 ppm
F2	389.51 Hz
PPMCM	0.20628 ppm/cm
HZCM	103.12556 Hz/cm

noesygptp

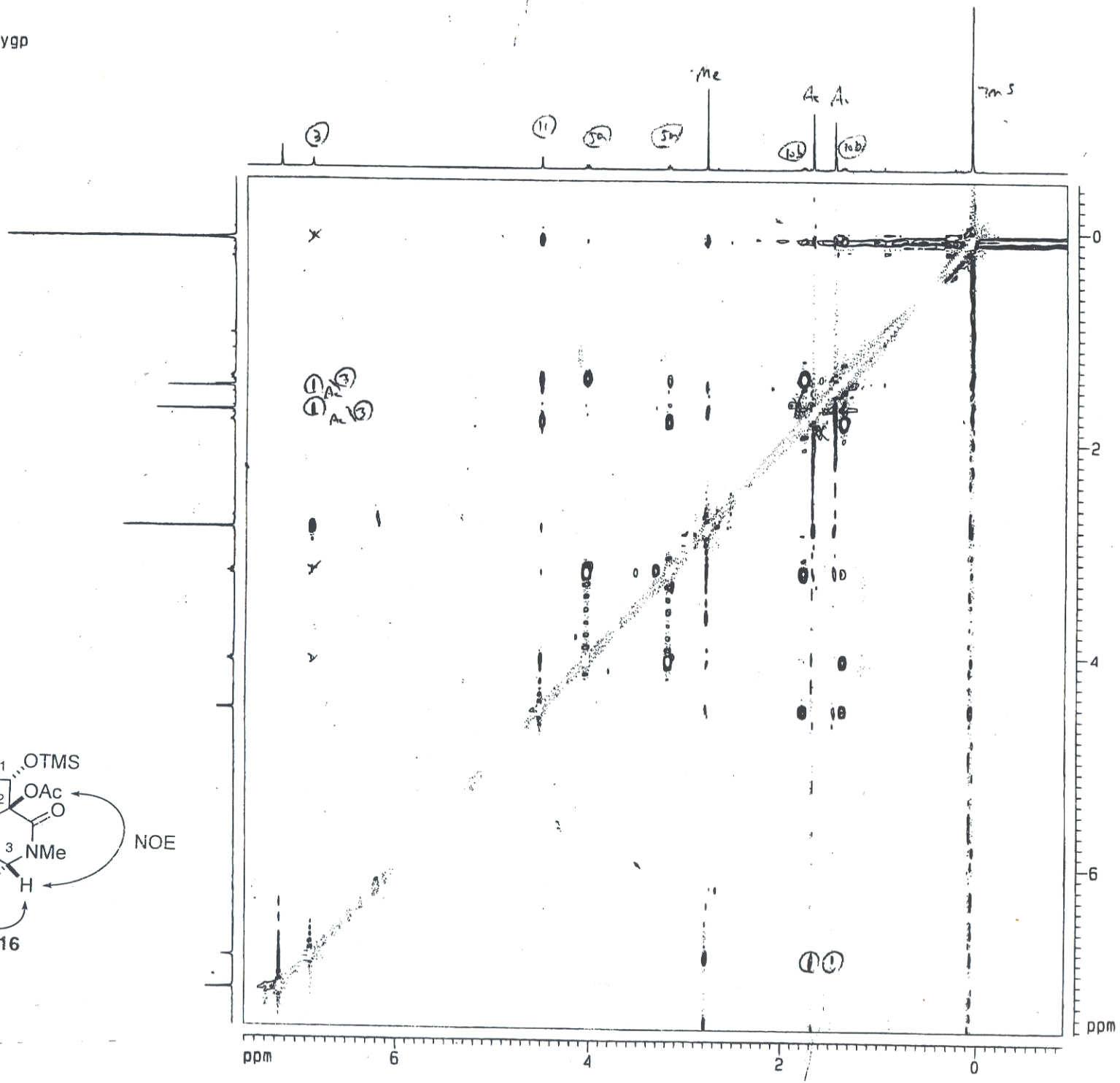




10b


```
                Current Data Parameters
   USER                 tasato
NAME          TS-2-043lesspolarNOESY
   EXPNO                   3
   PROCNO                  1

            F2 - Acquisition Parameters
   Date_             20070513
   Time                 1.13
   INSTRUM             qn500
   PROBHD   5 mm broadband
   PULPROG          noesygptp
   TD                   2048
   SOLVENT             CDCl3
   NS                     28
   DS                     16
   SWH              2826.051 Hz
   FIDRES           1.282251 Hz
   AQ               0.3899882 sec
   RG                  101.6
   DW                180.400 usec
   DE                  6.00 usec
   TE                298.0 K
   D0               0.00000300 sec
   D1               2.00000000 sec
   D8               1.00000000 sec
   D16              0.00025000 sec
   d20              0.49875000 sec
   INO              0.00019040 sec

   ======== CHANNEL f1 ========
   NUC1                 1H
   P1                12.00 usec
   P2                24.00 usec
   PL1               -3.00 dB
   SFO1         499.9313078 MHz

   ====== GRADIENT CHANNEL =====
   GPNAM1          sine.100
   GPNAM2          sine.100
   GPX1              0.00 %
   GPX2              0.00 %
   GPY1              0.00 %
   GPY2              0.00 %
   GPZ1             40.00 %
   GPZ2            -40.00 %
   P16            1000.00 usec

            F1 - Acquisition parameters
   ND0                  2
   TD                 256
   SFO1          499.9313 MHz
   FIDRES        10.258010 Hz
   SW             5.253 ppm
   FnMODE        undefined

            F2 - Processing parameters
   SI                1024
   SF          499.9300204 MHz
   WDW               QSINE
   SSB                  2
   LB                0.00 Hz
   GB                   0
   PC                1.40

            F1 - Processing parameters
   SI                1024
   MC2               TPPI
   SF          499.9300204 MHz
   WDW               QSINE
   SSB                  2
   LB                0.00 Hz
   GB                   0

            2D NMR plot parameters
   CX2              15.00 cm
   CX1              15.00 cm
   F2PLO             5.202 ppm
   F2LO           2600.51 Hz
   F2PHI            -0.051 ppm
   F2HI             -25.54 Hz
   F1PLO             5.202 ppm
   F1LO           2600.51 Hz
   F1PHI            -0.051 ppm
   F1HI             -25.54 Hz
   F2PPMCM       0.35019 ppm/cm
   F2HZCM      175.07002 Hz/cm
   F1PPMCM       0.35019 ppm/cm
   F1HZCM      175.07002 Hz/cm
```

noesygp



S63

16

Current Data Parameters

USER	tasato
NAME	TS-2-043NOESY
EXPNO	102
PROCNO	1

F2 - Acquisition Parameters

Date_	20070526
Time	20.57
INSTRUM	av600
PROBHD	5 mm TBI 1H/13
PULPROG	noesygpph
TD	1912
SOLVENT	C6D6
NS	4
DS	16
SWH	9615.385 Hz
FIDRES	5.028967 Hz
AQ	0.0994740 sec
RG	57
DW	52.000 usec
DE	6.00 usec
TE	298.0 K
d0	0.00004181 sec
D1	2.00000000 sec
D8	1.00000000 sec
D16	0.00020000 sec
IN0	0.00010400 sec
ST1CNT	128
TAU	0.49880001 sec

======== CHANNEL f1 ========

NUC1	1H
P1	8.00 usec
p2	16.00 usec
PL1	-1.00 dB
SFO1	600.1342009 MHz

====== GRADIENT CHANNEL =====

GPNAM1	SINE.100
GPNAM2	SINE.100
GPZ1	40.00 %
GPZ2	-40.00 %
P16	1000.00 usec

F1 - Acquisition parameters

NDO	1
TD	256
SFO1	600.1342 MHz
FIDRES	37.560097 Hz
SW	16.022 ppm
FnMODE	States-TPPI

F2 - Processing parameters

SI	1024
SF	600.1299973 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

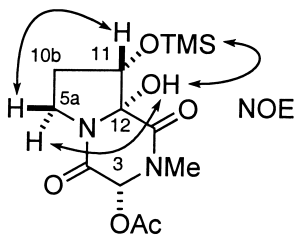
F1 - Processing parameters

SI	1024
MC2	States-TPPI
SF	600.1299973 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	7.505 ppm
F2LO	4504.10 Hz
F2PHI	-0.866 ppm
F2HI	-519.56 Hz
F1PLO	7.521 ppm
F1LO	4513.49 Hz
F1PHI	-0.475 ppm
F1HI	-284.81 Hz
F2PPMCM	0.55806 ppm/cm
F2HZCM	334.91086 Hz/cm
F1PPMCM	0.53303 ppm/cm
F1HZCM	319.88681 Hz/cm

noesygp



18

S64

Current Data Parameters

USER	tasato
NAME	TS-2-161HPLC NOESY
EXPNO	101
PROCNO	1

F2 - Acquisition Parameters

Date_	20070803
Time	22.33
INSTRUM	av600
PROBHD	5 mm TBI 1H/13
PULPROG	noesygpph
TD	1912
SOLVENT	~~CDCl3~~ C6D6
NS	36
DS	16
SWH	4201.681 Hz
FIDRES	2.197532 Hz
AQ	0.2275780 sec
RG	57
DW	119.000 usec
DE	6.00 usec
TE	298.0 K
d0	0.00004181 sec
D1	2.00000000 sec
D8	1.00000000 sec
D16	0.00020000 sec
IN0	0.00010400 sec
ST1CNT	128
TAU	0.49880001 sec

======== CHANNEL f1 ========

NUC1	1H
P1	8.00 usec
p2	16.00 usec
PL1	-1.00 dB
SFO1	600.1321005 MHz

====== GRADIENT CHANNEL =====

GPNAM1	SINE.100
GPNAM2	SINE.100
GPZ1	40.00 %
GPZ2	-40.00 %
P16	1000.00 usec

F1 - Acquisition parameters

NDO	1
TD	256
SFO1	600.1321 MHz
FIDRES	37.560097 Hz
SW	15.022 ppm
FnMODE	States-TPPI

F2 - Processing parameters

SI	1024
SF	600.1300000 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

SI	1024
MC2	States-TPPI
SF	600.1300000 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	7.001 ppm
F2LO	4201.30 Hz
F2PHI	-0.001 ppm
F2HI	-0.39 Hz
F1PLO	11.511 ppm
F1LO	6908.14 Hz
F1PHI	-4.511 ppm
F1HI	-2707.24 Hz
F2PPMCM	0.46875 ppm/cm
F2HZCM	280.11203 Hz/cm
F1PPMCM	1.06814 ppm/cm
F1HZCM	641.02563 Hz/cm