

# Construction of Epidithiodioxopiperazines by Directed Oxidation of Hydroxyproline-Derived Dioxopiperazines

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## Supporting Information

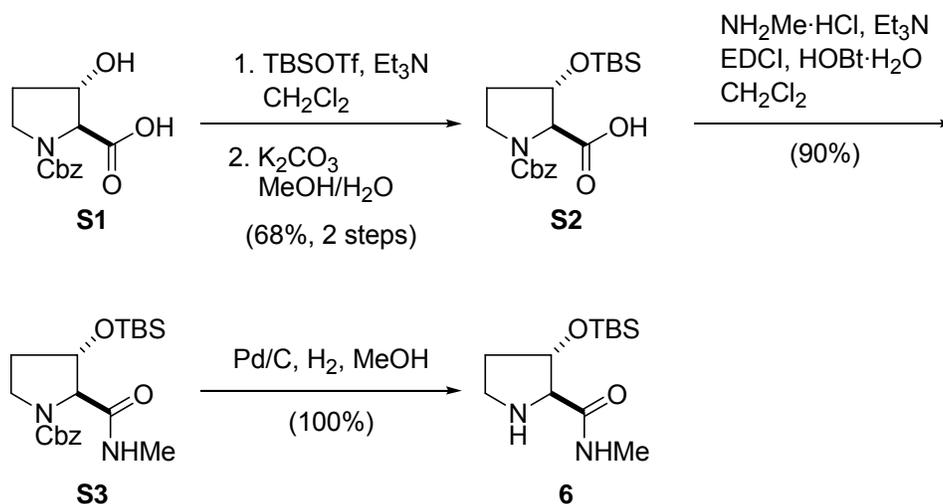
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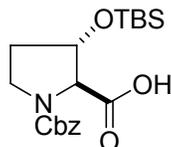
### A. Experimental Procedures

**General Details.** Reactions were performed in oven-dried glassware fitted with rubber septa under an argon atmosphere.  $\text{CH}_2\text{Cl}_2$  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,  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  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).  $^1\text{H}$  NMR spectra were recorded at 500 or 600 MHz and  $^{13}\text{C}$  NMR spectra at 125 MHz or 150 MHz with Bruker Avance spectrometers. Chemical shifts are reported in ppm with reference to solvent signals [ $^1\text{H}$ -NMR:  $\text{CHCl}_3$  (7.27),  $\text{C}_6\text{HD}_5$  (7.16),  $\text{CD}_2\text{HOD}$  (3.31);  $^{13}\text{C}$ -NMR:  $\text{CDCl}_3$  (77.23),  $\text{C}_6\text{D}_6$  (128.40),  $\text{CD}_3\text{CN}$  (118.69)  $\text{CD}_3\text{OD}$  (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**)

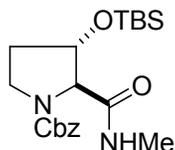


To a solution of *N*-Cbz-2-hydroxy-*L*-proline **S1**<sup>1</sup> (8.10 g, 30.5 mmol), Et<sub>3</sub>N (21 mL, 150 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL), was added TBSOTf (25 mL, 110 mmol) at room temperature. The resulting solution was maintained for 30 min at room temperature, quenched with H<sub>2</sub>O (100 mL), and acidified with citric acid (11.7 g) to pH 3. This mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL), then EtOAc (300 mL). The combined organic extracts were washed with brine (100 mL), dried over MgSO<sub>4</sub>, and concentrated. The residue was dissolved in MeOH (68 mL) and H<sub>2</sub>O (34 mL), and K<sub>2</sub>CO<sub>3</sub> (4.22 g, 30.5 mmol) was added. This solution was maintained for 3 h at room temperature and diluted with H<sub>2</sub>O (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<sub>4</sub>, 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 °C; [α]<sub>D</sub><sup>26</sup> 20.6 (c 1.07, CH<sub>3</sub>OH); IR (film) 3359, 2925, 1679, 1428 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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,

<sup>1</sup> 1. Adams, E. *Int. J. Pept. Prot. Res.* **1976**, 8, 503–516.

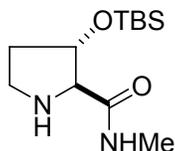
3/5H), 5.13 (d,  $J = 12.6$  Hz, 2/5H), 5.17 (d,  $J = 12.6$  Hz, 2/5H), 5.21 (s, 6/5H), 7.33 (m, 5H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  -4.88, -4.85, 18.1, 18.1, 25.7, 25.8, 33.0, 33.7, 45.0, 45.2, 67.2, 67.7, 68.1, 68.7, 74.4, 76.0, 127.6, 127.9, 128.2, 128.5, 128.6, 136.2, 136.6, 154.6, 156.4, 174.0, 176.1; HRMS (ESI), calcd for  $\text{C}_{19}\text{H}_{29}\text{O}_5\text{NSiNa}^+$  ( $\text{M}+\text{Na}$ ) $^+$  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),  $\text{Et}_3\text{N}$  (870  $\mu\text{L}$ , 6.2 mmol), *N*-hydroxybenzotriazole monohydrate (HOBt· $\text{H}_2\text{O}$ , 504 mg, 3.73 mmol) and  $\text{CH}_2\text{Cl}_2$  (31 mL) at room temperature. This mixture was stirred for 1 d at room temperature and quenched with  $\text{H}_2\text{O}$  (30 mL). The mixture was extracted with EtOAc (2x 50 mL). The combined organic layers were washed with brine (30 mL), dried over  $\text{MgSO}_4$ , 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;  $[\alpha]_{\text{D}}^{27} -34.7$  ( $c$  1.11,  $\text{CHCl}_3$ ); IR (film) 3332, 2954, 2931, 2894, 2858, 1708, 1663  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  -4.73 ( $\text{CH}_3$ ), -4.67 ( $\text{CH}_3$ ), 18.1 (C), 25.9 ( $\text{CH}_3$ ), 26.2 ( $\text{CH}_3$ ), 32.7 ( $\text{CH}_2$ ), 33.8 ( $\text{CH}_2$ ), 45.4 ( $\text{CH}_2$ ), 45.7 ( $\text{CH}_2$ ), 67.4 ( $\text{CH}_2$ ), 67.5 ( $\text{CH}_2$ ), 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  $\text{C}_{20}\text{H}_{32}\text{O}_4\text{N}_2\text{SiNa}^+$  ( $\text{M}+\text{Na}$ ) $^+$  415.2029, found 415.2019.

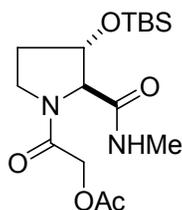
**(2*S*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-*N*-methylpyrrolidine-2-carboxamide (**6**)**



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

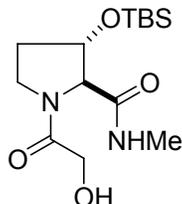
room temperature. The mixture was filtered through Celite, and the filter cake was washed with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (20:1, 400 mL), and the filtrate was concentrated to give 10.7 g of **6** (100%); colorless oil;  $[\alpha]_D^{25} -9.4$  ( $c$  1.28,  $\text{CHCl}_3$ ); IR (film) 3327, 2954, 2931, 2887, 2858, 1659  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  -4.6 ( $\text{CH}_3$ ), 18.2 (C), 25.8 ( $\text{CH}_3$ ), 26.0 ( $\text{CH}_3$ ), 34.5 ( $\text{CH}_2$ ), 45.2 ( $\text{CH}_2$ ), 70.2 (CH), 76.5 (CH), 173.2 (C); HRMS (ESI), calcd for  $\text{C}_{12}\text{H}_{27}\text{O}_2\text{N}_2\text{Si}^+$  ( $\text{M}+\text{H}$ ) $^+$  259.1842, found 259.1843.

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



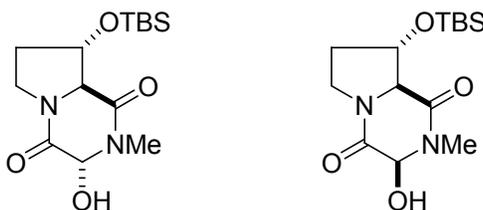
1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 341 mg, 1.78 mmol) was added to a solution of **6** (369 mg, 1.43 mmol), acetylglycolic acid **7** (211 mg, 1.78 mmol),  $\text{Et}_3\text{N}$  (250  $\mu\text{L}$ , 1.8 mmol), 1-hydroxy-7-azabenzotriazole (HOAt, 242 mg, 1.78 mmol) and THF (14 mL) at room temperature. This mixture was stirred for 16 h at room temperature, and quenched with  $\text{H}_2\text{O}$  (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  $\text{MgSO}_4$ , and concentrated. The residue was purified by silica gel column chromatography (EtOAc to  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  20:1) to give 513 mg of **8** (100%); colorless oil;  $[\alpha]_D^{26} -62.2$  ( $c$  0.94,  $\text{CHCl}_3$ ); IR (film) 3327, 2956, 2933, 2892, 2860, 1752, 1659  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 10:1 mixture of rotamers, signals of the major isomer are reported)  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 10:1 mixture of rotamers, signals of the major isomer are reported)  $\delta$  -4.64 ( $\text{CH}_3$ ), -4.62 ( $\text{CH}_3$ ), 18.2 (C), 20.8 ( $\text{CH}_3$ ), 25.9 ( $\text{CH}_3$ ), 26.4 ( $\text{CH}_3$ ), 34.2 ( $\text{CH}_2$ ), 44.6 ( $\text{CH}_2$ ), 61.8 ( $\text{CH}_2$ ), 69.2 (CH), 72.7 (CH), 167.7 (C), 169.9 (C), 170.9 (C); HRMS (ESI), calcd for  $\text{C}_{16}\text{H}_{30}\text{O}_5\text{N}_2\text{SiNa}^+$  ( $\text{M}+\text{Na}$ ) $^+$  381.1822, found 381.1809.

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



LiOH·H<sub>2</sub>O (1.09 g, 26.0 mmol) was added to a solution of **8** (8.21 g, 22.9 mmol), THF (115 mL) and H<sub>2</sub>O (115 mL) at room temperature. This solution was maintained for 10 min at room temperature, cooled to 0 °C, and quenched after 5 min with 1M NaHSO<sub>4</sub> in H<sub>2</sub>O (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<sub>4</sub>, and concentrated. The residue was purified with silica gel column chromatography (EtOAc to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 20:1) to give 7.25 g of **9** (100%, two rotamers, dr=12:1 in CDCl<sub>3</sub>): colorless amorphous solid; [ $\alpha$ ]<sub>D</sub><sup>27</sup> -62.0 (*c* 0.93, CHCl<sub>3</sub>); IR (film) 3321, 2954, 2931, 2890, 2858, 1652 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 12:1 mixture of rotamers, signals of the major isomer are reported)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 12:1 mixture of rotamers, signals of the major isomer are reported)  $\delta$  -4.7 (CH<sub>3</sub>), -4.6 (CH<sub>3</sub>), 18.2 (C), 25.9 (CH<sub>3</sub>), 26.4 (CH<sub>3</sub>), 34.1 (CH<sub>2</sub>), 43.8 (CH<sub>2</sub>), 60.7 (CH<sub>2</sub>), 69.3 (CH), 72.8 (CH), 169.9 (C), 172.5 (C); HRMS (ESI), calcd for C<sub>14</sub>H<sub>28</sub>O<sub>4</sub>N<sub>2</sub>SiNa (M+Na)<sup>+</sup> 339.1716, found 339.1710.

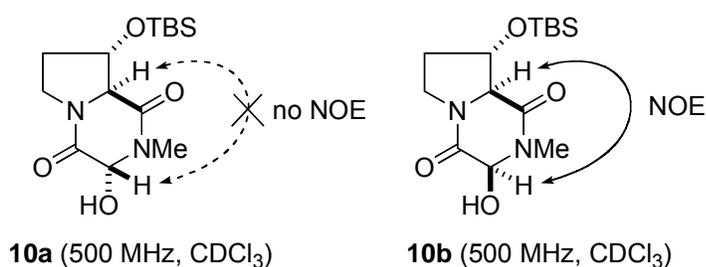
**(3*R*,8*S*,8*aS*)-8-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2-methylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione (**10a**) and (3*S*,8*S*,8*aS*)-8-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2-methylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione (**10b**)**



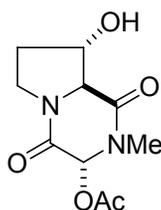
Sulfur trioxide pyridine complex (5.06 g, 31.8 mmol) was added to a solution of **9** (3.34 g, 10.6 mmol), Et<sub>3</sub>N (8.9 mL, 64.0 mmol), DMSO (18 mL) and CH<sub>2</sub>Cl<sub>2</sub> (88 mL) at room temperature. This solution was maintained for 2.5 h at room temperature, and quenched with saturated aqueous NaHCO<sub>3</sub> (100 mL). The

mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and then EtOAc (200 mL). The combined organic layers were washed with H<sub>2</sub>O (100 mL) and brine (100 mL), dried over MgSO<sub>4</sub>, 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<sub>2</sub>Cl<sub>2</sub>/MeOH 20:1) to give 520 mg of **10a** (16%) and 173 mg of **10b** (5%): **10a**: colorless crystals, mp 149–150 °C;  $[\alpha]_D^{25}$  -65.8 (*c* 1.05, CHCl<sub>3</sub>); IR (film) 3311, 2954, 2931, 2892, 2858, 1663 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ -4.7 (CH<sub>3</sub>), -4.6 (CH<sub>3</sub>), 18.2 (C), 25.9 (CH<sub>3</sub>), 32.3 (CH<sub>3</sub>), 33.2 (CH<sub>2</sub>), 43.3 (CH<sub>2</sub>), 65.1 (CH), 73.6 (CH), 83.1 (CH), 164.5 (C), 167.9 (C); HRMS (ESI), calcd for C<sub>14</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>SiNa<sup>+</sup> (M+Na)<sup>+</sup> 337.1559, found 337.1558. **10b**: colorless oil;  $[\alpha]_D^{23}$  -13.3 (*c* 1.19, CHCl<sub>3</sub>); IR (film) 3346, 2954, 2931, 2890, 2858, 1671 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ -4.7 (CH<sub>3</sub>), -4.6 (CH<sub>3</sub>), 18.2 (C), 25.9 (CH<sub>3</sub>), 28.1 (CH<sub>3</sub>), 33.5 (CH<sub>2</sub>), 44.1 (CH<sub>2</sub>), 67.3 (CH), 73.6 (CH), 76.7 (CH), 165.2 (C), 165.5 (C); HRMS (ESI), calcd for C<sub>14</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>SiNa<sup>+</sup> (M+Na)<sup>+</sup> 337.1559, found 337.1555.

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



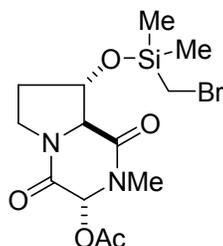
**(3*R*,8*S*,8*a**S*)-8-hydroxy-2-methyl-1,4-dioxooctahydropyrrolo[1,2-*a*]pyrazin-3-yl ethanoate (11)**



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<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>O (2x 200 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO<sub>4</sub>, 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; [ $\alpha$ ]<sub>D</sub><sup>24</sup> -9.2 (*c* 0.96, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 2956, 2939, 2982, 2860, 1756, 1694 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  -4.7 (CH<sub>3</sub>), -4.6 (CH<sub>3</sub>), 18.2 (C), 20.9 (CH<sub>3</sub>), 25.9 (CH<sub>3</sub>), 33.2 (CH<sub>2</sub>), 33.7 (CH<sub>3</sub>), 43.2 (CH<sub>2</sub>), 65.2 (CH), 73.6 (CH), 81.9 (CH), 160.3 (C), 168.7 (C), 170.1 (C); HRMS (ESI), calcd for C<sub>16</sub>H<sub>28</sub>O<sub>5</sub>N<sub>2</sub>SiNa<sup>+</sup> (M+Na)<sup>+</sup> 379.1665, found 379.1655.

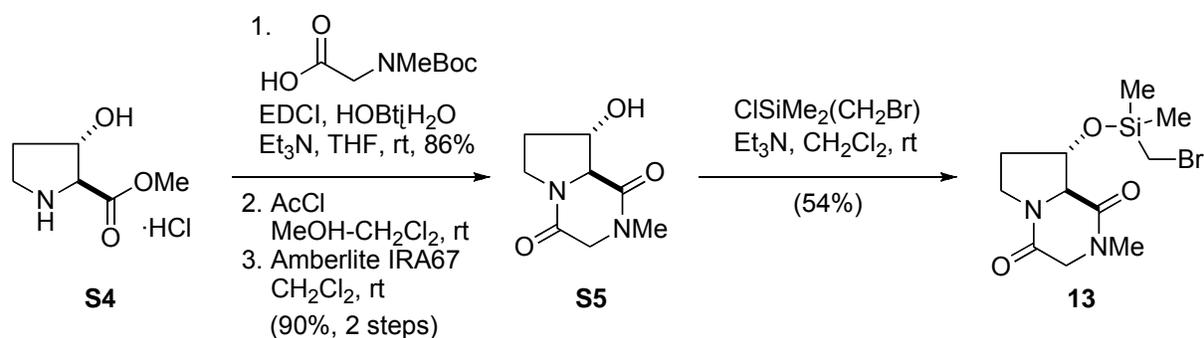
Tetrabutylammonium fluoride (1M in THF, 6.5 mL, 6.5 mmol) was added to a solution of this acetate derivative (774 mg, 2.17 mmol), AcOH (1.5 mL, 26 mmol) and THF (22 mL) at room temperature. This solution was heated to 60 °C, stirred for 1.5 h, cooled to room temperature, and concentrated. The residue was purified by silica gel column chromatography (EtOAc) to give 404 mg of **11** (77%): colorless crystals, mp 111–112 °C; [ $\alpha$ ]<sub>D</sub><sup>24</sup> -45.1 (*c* 1.13, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3436, 2983, 2954, 2896, 1752, 1671 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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); <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  20.2 (CH<sub>3</sub>), 30.0 (CH<sub>2</sub>), 32.6 (CH<sub>3</sub>), 42.1 (CH<sub>2</sub>), 62.9 (CH), 72.9 (CH), 82.0 (CH), 159.8 (C), 170.0 (C), 170.1 (C); HRMS (ESI), calcd for C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>N<sub>2</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 265.0800, found 265.0806.

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

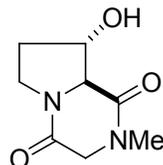


(Bromomethyl)chlorodimethylsilane (450  $\mu$ L, 3.3 mmol) was added to a solution of **11** (198 mg, 817  $\mu$ mol), triethylamine (910  $\mu$ L, 6.50 mmol) and  $\text{CH}_2\text{Cl}_2$  (8.2 mL) at room temperature. This solution was maintained for 10 min at room temperature, and quenched with pH 7 phosphate buffer (10 mL). The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ /hexane (1:1, 15 mL), and then  $\text{Et}_2\text{O}$  (20 mL). The combined organic layers were washed with brine (10 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated. Triethylamine was removed azeotropically from toluene (2x 5 mL) under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ $\text{EtOAc}$  3:1 to 1:1) to give 306 mg of **12** (98%): colorless oil;  $[\alpha]_D^{24}$   $-19.2$  ( $c$  1.09,  $\text{CH}_2\text{Cl}_2$ ); IR (film) 2960, 2898, 1756, 1686  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  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);  $^{13}\text{C}$  NMR (150 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$   $-2.4$  ( $\text{CH}_3$ ),  $-2.2$  ( $\text{CH}_3$ ), 16.8 ( $\text{CH}_2$ ), 20.2 ( $\text{CH}_3$ ), 32.5 ( $\text{CH}_2$ ), 33.0 ( $\text{CH}_3$ ), 42.7 ( $\text{CH}_2$ ), 64.2 (CH), 73.9 (CH), 82.3 (CH), 160.1 (C), 168.7 (C), 170.0 (C); HRMS (ESI), calcd for  $\text{C}_{13}\text{H}_{21}\text{O}_5\text{N}_2\text{SiBrNa}^+$  ( $\text{M}+\text{Na}$ ) $^+$  415.0301, found 415.0290.

### Synthesis of $\alpha$ -Bromomethyl Silyl Ether **13**



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



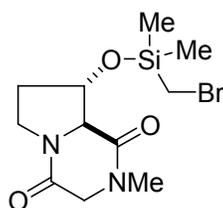
Triethylamine (3.3 mL, 23.7 mmol) and *N*-hydroxybenzotriazole monohydrate (HOBt $\cdot$ H $_2$ O, 1.71 g, 12.7 mmol) were added to a mixture of **S4**<sup>2</sup> (2.00 g, 11.0 mmol), *N*-Boc-sarcosine (2.30 g, 12.1 mmol) and THF

<sup>2</sup> 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<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>Cl<sub>2</sub>/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<sub>2</sub>Cl<sub>2</sub> (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; [ $\alpha$ ]<sub>D</sub><sup>25</sup> -75.2 (*c* 1.06, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3415, 2954, 2896, 1648 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  29.8 (CH<sub>2</sub>), 33.2 (CH<sub>3</sub>), 41.7 (CH<sub>2</sub>), 53.3 (CH<sub>2</sub>), 62.7 (CH), 72.5 (CH), 162.6 (C), 167.2 (C); HRMS (ESI), calcd for C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub>Na<sup>+</sup> (M+Na)<sup>+</sup>, 207.0746, found 207.0754.

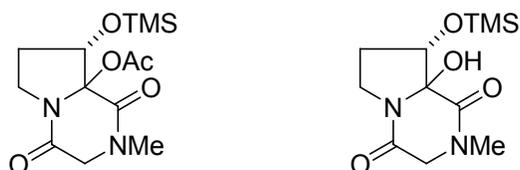
**(8*S*,8*aS*)-8-((bromomethyl)dimethylsilyloxy)-2-methylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione (13)**



(Bromomethyl)chlorodimethylsilane (770  $\mu$ L, 5.7 mmol) was added to a solution of **S5** (299 mg, 1.62 mmol), triethylamine (1.58 ml, 11.3 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>O (30 mL). The organic layer was washed with brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> 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;  $[\alpha]_D^{25}$   $-31.0$  (*c* 1.14, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 2958, 2896, 1663 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$   $-2.22$  (CH<sub>3</sub>),  $-2.15$  (CH<sub>3</sub>), 17.1 (CH<sub>2</sub>), 32.8 (CH<sub>2</sub>), 33.1 (CH<sub>3</sub>), 42.5 (CH<sub>2</sub>), 53.4 (CH<sub>2</sub>), 64.6 (CH), 74.1 (CH), 162.7 (C), 166.3 (C); HRMS (ESI), calcd for C<sub>11</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>SiBrNa<sup>+</sup> (M+Na)<sup>+</sup>, 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  $\mu$ mol), Cu(OAc)<sub>2</sub> (72.7 mg, 400  $\mu$ mol), AIBN (120  $\mu$ mol), a mediator (120  $\mu$ mol) and solvent (2.0 mL) was heated to 80 °C 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<sub>2</sub>O (2x 15 mL). The combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc 2:1) to give acetate **14** and hemiaminal **15** in the amounts reported in Table 1: Acetate **14**: colorless oil;  $[\alpha]_D^{24}$  144.0 (*c* 0.80, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 2962, 2906, 1744, 1683 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.44 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 29.7 (CH<sub>2</sub>), 33.2 (CH<sub>3</sub>), 44.7 (CH<sub>2</sub>), 54.2 (CH<sub>2</sub>), 77.2 (CH), 93.5 (C), 162.7 (c), 165.4 (C), 169.8 (C); HRMS (ESI), calcd for C<sub>13</sub>H<sub>22</sub>O<sub>5</sub>N<sub>2</sub>SiNa<sup>+</sup> (M+Na)<sup>+</sup>, 337.1196, found 337.1187. Hemiaminal **15**: colorless oil;  $[\alpha]_D^{25}$   $-50.6$  (*c* 1.12, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3309, 2960, 2904, 1667 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.45 (CH<sub>3</sub>), 29.9 (CH<sub>2</sub>), 33.0 (CH<sub>3</sub>), 41.3 (CH<sub>2</sub>), 53.1 (CH<sub>2</sub>), 73.7 (CH), 84.3 (C), 165.5 (C), 166.3 (C); HRMS (ESI), calcd for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>SiNa<sup>+</sup> (M+Na)<sup>+</sup>, 295.1090, found 295.1078.

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

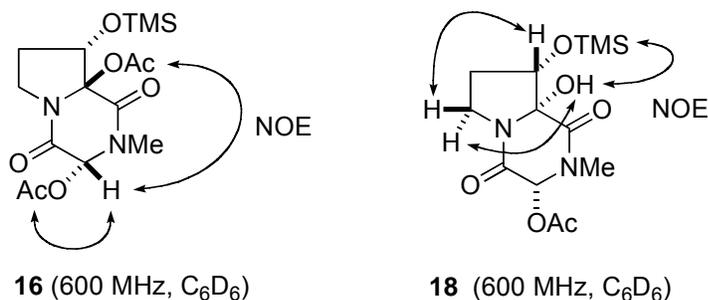


A solution of AIBN (744 mg, 4.53 mmol), (TMS)<sub>3</sub>SiH (1.39 mL, 4.53 mmol) and (CH<sub>2</sub>Cl)<sub>2</sub> (16 mL) was added over 1 h using a syringe pump to a stirring mixture of **12** (14.8 mg, 38.9 μmol), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (1.68 mg, 8.41 mmol) and (CH<sub>2</sub>Cl)<sub>2</sub> (16 mL) at 80 °C, and the resulting mixture was stirred for an additional 30 min at 80 °C. 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<sub>4</sub> 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)<sub>3</sub>SiH (84 μL, 273 μmol) and (CH<sub>2</sub>Cl)<sub>2</sub> (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)<sub>2</sub>·H<sub>2</sub>O (54.4 mg, 273 μmol) and (CH<sub>2</sub>Cl)<sub>2</sub> (1.0 mL) at 80 °C, and the resulting mixture was stirred for an additional 30 min at 80 °C. 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<sub>4</sub> 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; [α]<sub>D</sub><sup>25</sup> 79.7 (*c* 1.03, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 2960, 1760, 1748, 1694 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>) 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); <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.35 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 29.7 (CH<sub>2</sub>), 30.4 (CH<sub>3</sub>), 44.8 (CH<sub>2</sub>), 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.  $\beta$ -Hemiaminal **17**: amorphous solid;  $[\alpha]_D^{25}$  10.8 (*c* 0.68,  $CH_2Cl_2$ ); IR (film) 3344, 2960, 2925, 2856, 1760, 1671  $cm^{-1}$ ;  $^1H$  NMR (600 MHz,  $C_6D_6$ )  $\delta$  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,  $C_6D_6$ )  $\delta$  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.  $\alpha$ -Hemiaminal **18**: amorphous solid;  $[\alpha]_D^{25}$  -33.6 (*c* 1.32,  $CH_2Cl_2$ ); IR (film) 3436, 2960, 2904, 1756, 1698  $cm^{-1}$ ;  $^1H$  NMR (600 MHz,  $C_6D_6$ )  $\delta$  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,  $C_6D_6$ )  $\delta$  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;  $[\alpha]_D^{25}$  -18.8 (*c* 0.84,  $CH_2Cl_2$ ); IR (film) 2958, 2898, 1756, 1686  $cm^{-1}$ ;  $^1H$  NMR (600 MHz,  $C_6D_6$ )  $\delta$  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,  $C_6D_6$ )  $\delta$  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  $\beta$ -acetate **16** and  $\alpha$ -hemiaminal **18**

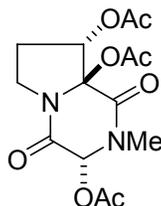


**(3*S*,8*S*,8*a**S*)-2-methyl-1,4-dioxo-8-(trimethylsilyloxy)octahydropyrrolo[1,2-*a*]pyrazine-3,8*a*-diyl diethanoate (**16**)**

Acetic anhydride (190  $\mu$ L, 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%).

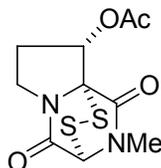
**(3*S*,8*S*,8*aS*)-2-methyl-1,4-dioxooctahydropyrrolo[1,2-*a*]pyrazine-3,8,8*a*-triyl triethanoate (**20**)**



Tetrabutylammonium fluoride (1M in THF, 120  $\mu$ L, 120  $\mu$ mol) was added to a solution of **16** (43.4 mg, 117  $\mu$ mol), 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  $^{\circ}$ C,  $[\alpha]_D^{25}$  98.3 (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3427, 1746, 1698, 1210  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN)  $\delta$  21.3 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 29.4 (CH<sub>2</sub>), 31.0 (CH<sub>3</sub>), 44.9 (CH<sub>2</sub>), 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<sub>12</sub>H<sub>16</sub>O<sub>7</sub>N<sub>2</sub>Na<sup>+</sup> (*M*+Na)<sup>+</sup> 323.0855, found 323.0846.

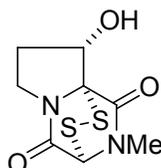
Acetic anhydride (58  $\mu$ L, 610  $\mu$ mol) was added to a solution of the this alcohol (87.3 mg, 291  $\mu$ mol), DMAP (89.6 mg, 734  $\mu$ mol) and CH<sub>2</sub>Cl<sub>2</sub> (5.8 mL) at room temperature. This resulting solution was maintained for 50 min at room temperature, and quenched with 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<sub>2</sub>SO<sub>4</sub>, 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;  $[\alpha]_D^{23}$  85.1 (*c* 1.05, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 2931, 1748, 1698, 1202  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  20.5 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 27.0 (CH<sub>2</sub>), 30.6 (CH<sub>3</sub>), 44.4 (CH<sub>2</sub>), 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<sub>14</sub>H<sub>18</sub>O<sub>8</sub>N<sub>2</sub>Na<sup>+</sup> (*M*+Na)<sup>+</sup> 365.0961, found 365.0960.

### Acetoxy Epidithiodioxopiperazine (**22**)



A solution of **20** (52.7 mg, 154  $\mu\text{mol}$ ) and MeCN (4.0 mL) in a sealed vial was degassed using the freeze-pump-thaw technique (3x) and cooled to  $-78\text{ }^\circ\text{C}$ . Hydrogen sulfide (bp  $-60\text{ }^\circ\text{C}$ , 3 mL) was condensed at  $-78\text{ }^\circ\text{C}$ , and added via cannula to the solution of **20** at  $-78\text{ }^\circ\text{C}$ . Then a solution of scandium triflate (15.2 mg, 30.8  $\mu\text{mol}$ ) 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  $-78\text{ }^\circ\text{C}$ , 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  $\text{H}_2\text{S}$  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  $206\text{--}207\text{ }^\circ\text{C}$  dec;  $[\alpha]_{\text{D}}^{25} -81.3$  (*c* 0.34,  $\text{CH}_2\text{Cl}_2$ ); IR (film) 2993, 1752, 1698, 1221  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  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);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  21.1 ( $\text{CH}_3$ ), 30.2 ( $\text{CH}_2$ ), 32.1 ( $\text{CH}_3$ ), 43.8 ( $\text{CH}_2$ ), 69.0 (CH), 74.8 (CH), 78.6 (C), 162.9 (C), 166.0 (C), 170.3 (C); HRMS (ESI), calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2\text{S}_2\text{Na}^+$  ( $\text{M}+\text{Na}$ ) $^+$  311.0136, found 311.0127.

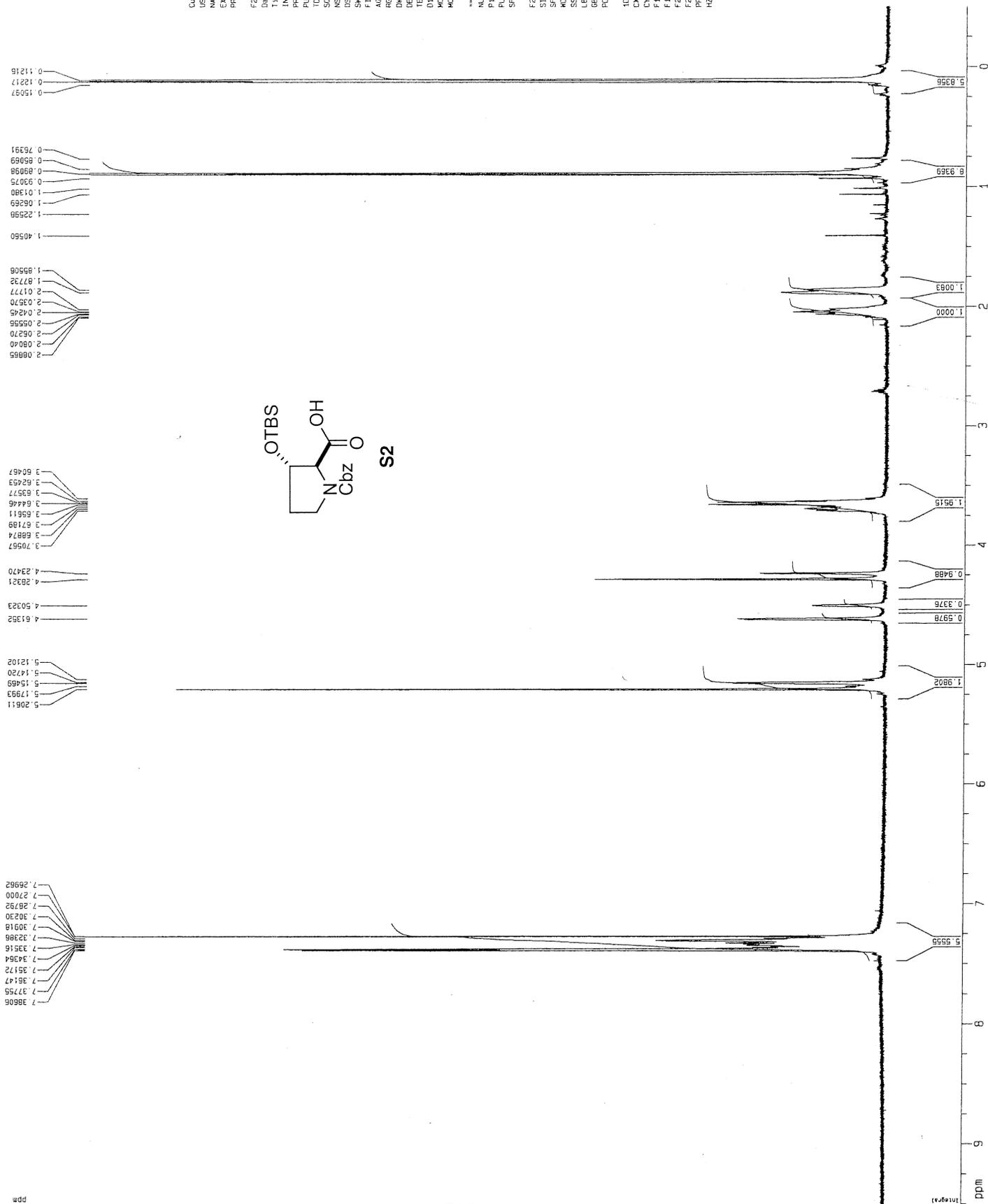
### Hydroxy Epidithiodioxopiperazine (**23**)



Scandium triflate (28.0 mg, 56.9  $\mu\text{mol}$ ) was added to a solution of **22** (16.4 mg, 56.9  $\mu\text{mol}$ ), 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  $\text{Na}_2\text{SO}_4$ , 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<sub>2</sub>Cl<sub>2</sub>: mp 198–199 °C dec;  $[\alpha]_D^{24}$  –46.5 (*c* 0.31, CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3042, 2991, 2925, 1671 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD) 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); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) δ 31.7 (CH<sub>3</sub>), 32.3 (CH<sub>2</sub>), 43.4 (CH<sub>3</sub>), 68.7 (CH), 73.7 (CH), 81.5 (C), 164.6 (C), 167.8 (C); HRMS (ESI), calcd for C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub>S<sub>2</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 269.0031, found 269.0026.

1H spectrum



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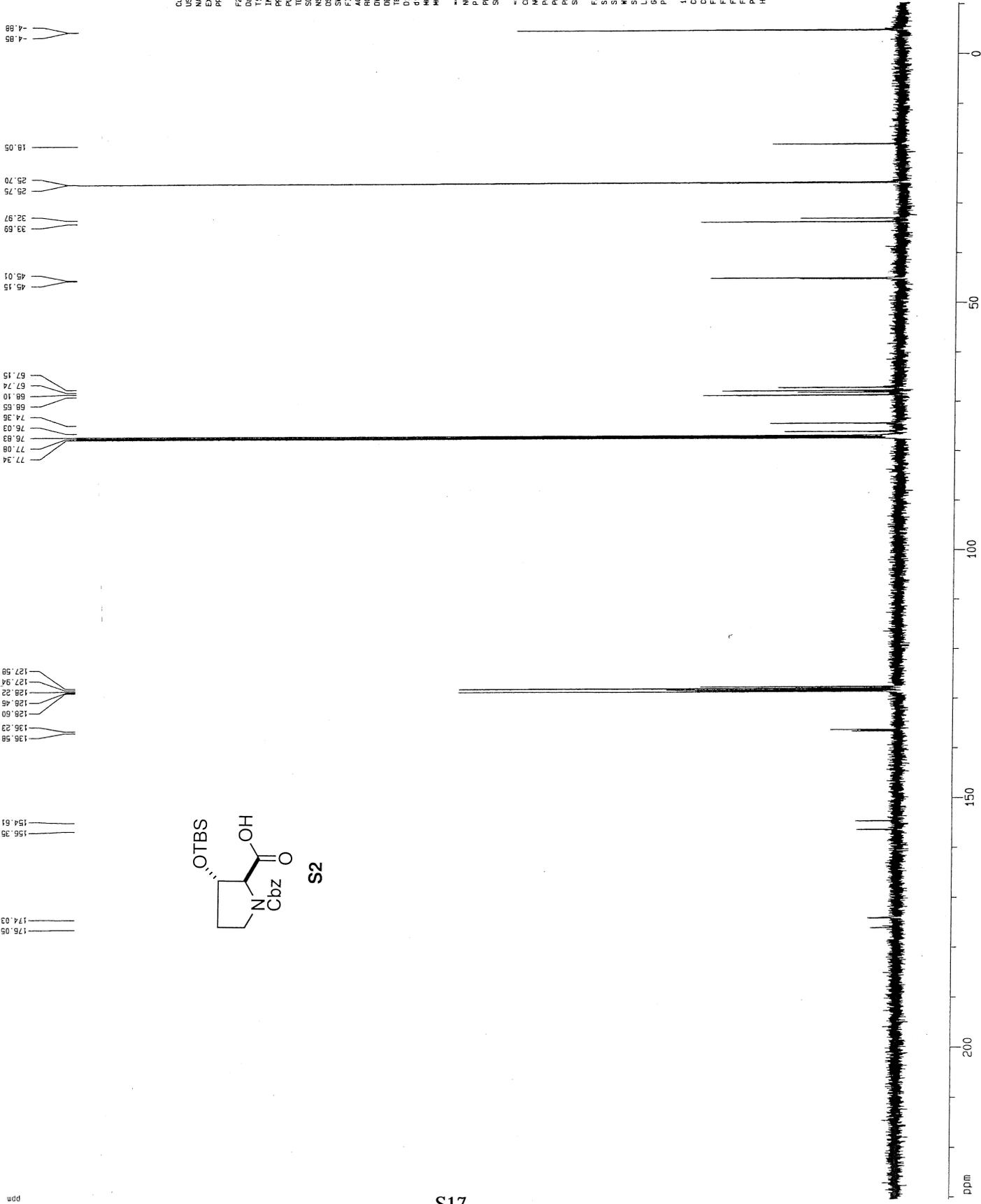
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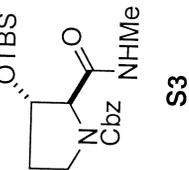
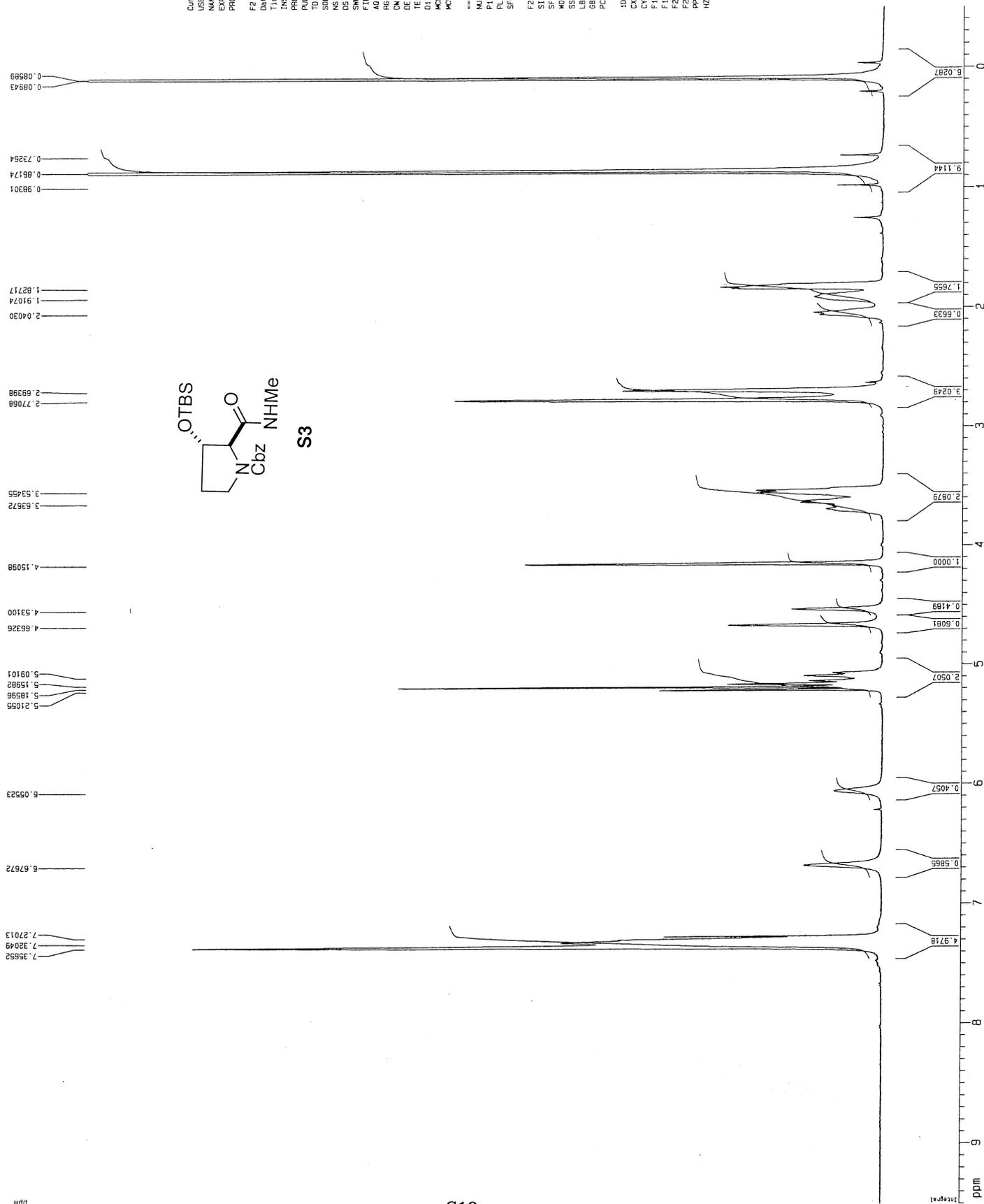
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13C spectrum with 1H decoupling



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1H spectrum



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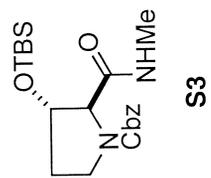
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13C spectrum with 1H decoupling



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\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
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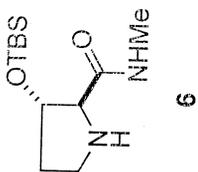
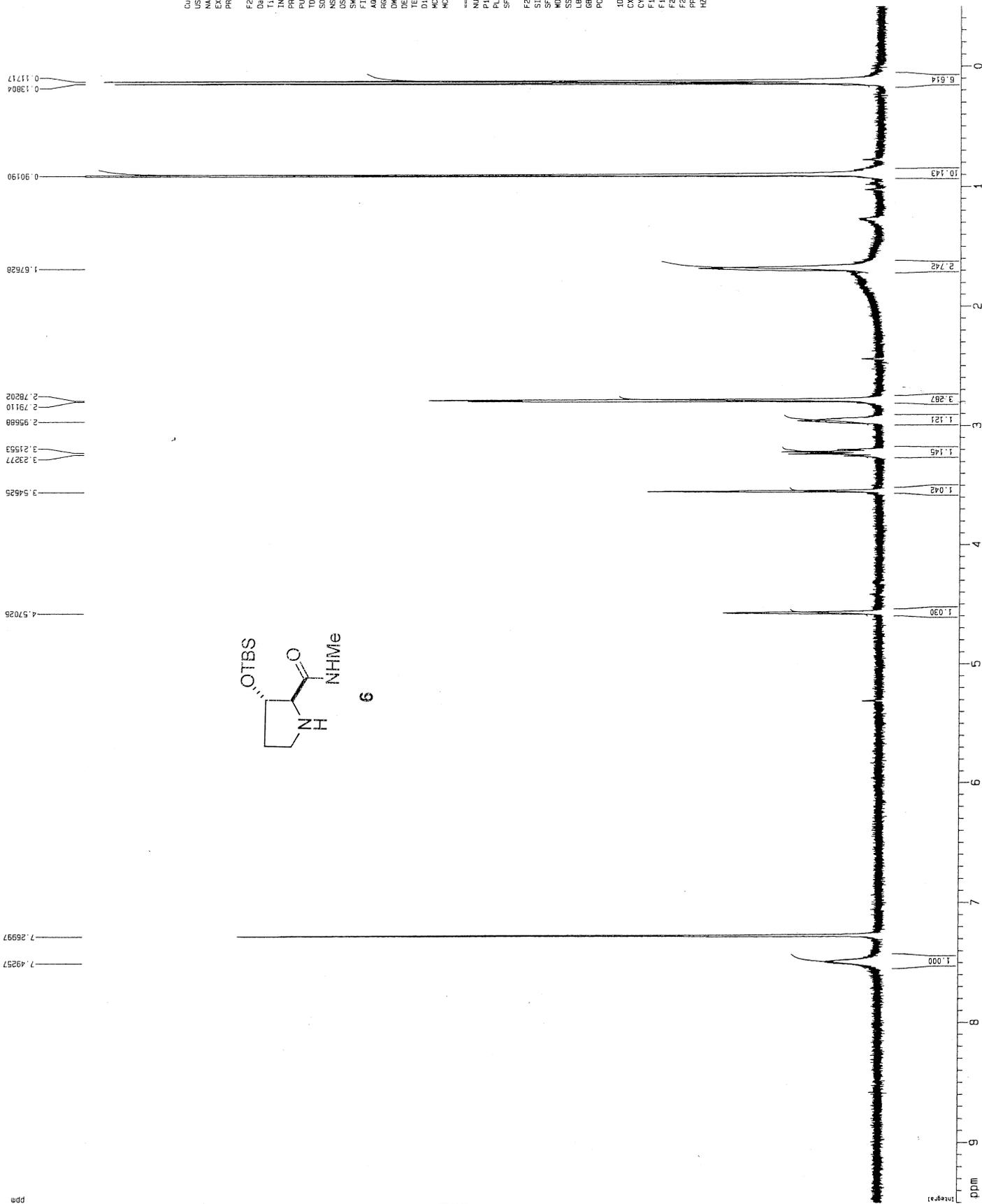
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 CY 14.71 cm  
 F1P 230.637 ppm  
 F1 29009.68 Hz  
 F2P -10.287 ppm  
 F2 -1293.95 Hz  
 PPMCH 10.56668 ppm/cm  
 HZCM 1329.10693 Hz/cm



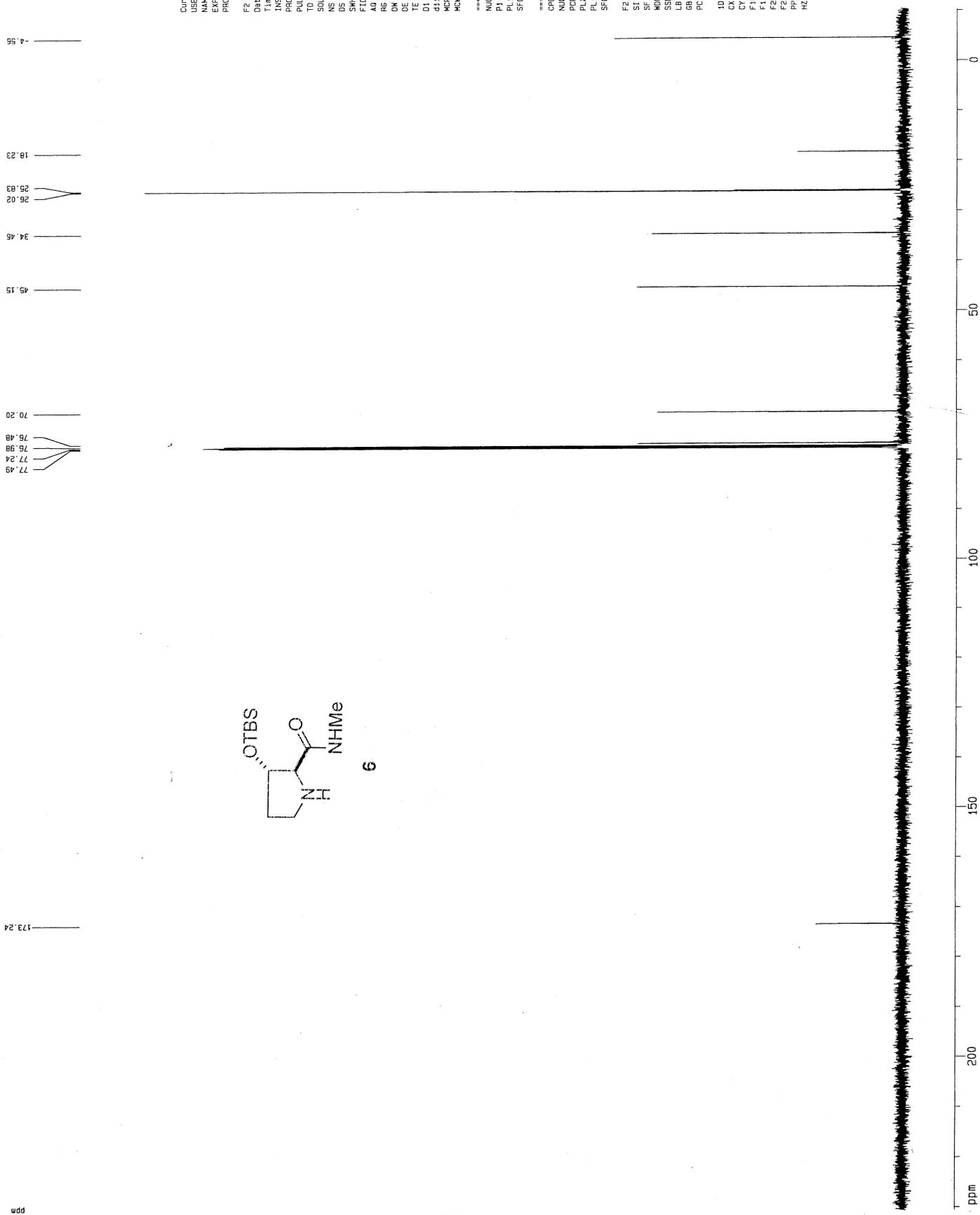
1H spectrum

ppm



Current Data Parameters  
 USER: [unreadable]  
 NAME: TS-1-301  
 EXPNO: 1  
 PROCNO: 1  
 F2 - Acquisition Parameters  
 Date\_: 20070211  
 Time: 16.55  
 INSTRUM: gnm500  
 PROBHD: 5 mm broadband  
 PULPROG: zg30  
 TD: 65536  
 SOLVENT: CDCl3  
 CS: 2  
 SFO1: 601.2820 MHz  
 FIDRES: 0.098043 Hz  
 AQ: 0.098043 Hz  
 RG: 645.1  
 DM: 62.400 usec  
 DE: 6.00 usec  
 TE: 298.0 K  
 D1: 0.10000000 sec  
 MCREST: 0.00000000 sec  
 MCHK: 0.01500000 sec  
 ===== CHANNEL f1 =====  
 NUC1: 1H  
 P1: 12.00 usec  
 PL1: -3.00 dB  
 SFO1: 499.9334995 MHz  
 F2 - Processing parameters  
 SI: 65536  
 SF: 499.9300251 MHz  
 MCH: no  
 SSB: 0  
 LB: 0.00 Hz  
 GB: 0  
 PC: 4.00  
 1D NMR plot parameters  
 CX: 22.80 cm  
 CY: 44.57 cm  
 F1P: 9.500 ppm  
 F1: 4749.34 Hz  
 F2P: -0.500 ppm  
 F2: -249.97 Hz  
 PPMCH: 0.43860 ppm/cm  
 HZCM: 219.26756 Hz/cm

13C spectrum with 1H decoupling



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

F2 - Acquisition Parameters  
 Date\_ 20070211  
 Time 17.15  
 INSTRUM crys000  
 PROBO 5 mm CPD1 1H-  
 PULPROG zgpg30  
 TO 28.00  
 SOLVENT CDCl3  
 NS 22  
 DS 4  
 SWH 30303.031 Hz  
 FIDRES 0.463222 Hz  
 AQ 1.0794635 sec  
 RG 8192  
 DM 16.500 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.25000000 sec  
 d11 0.03000000 sec  
 ACQRES 0.00000000 sec  
 MCWK 0.01500000 sec

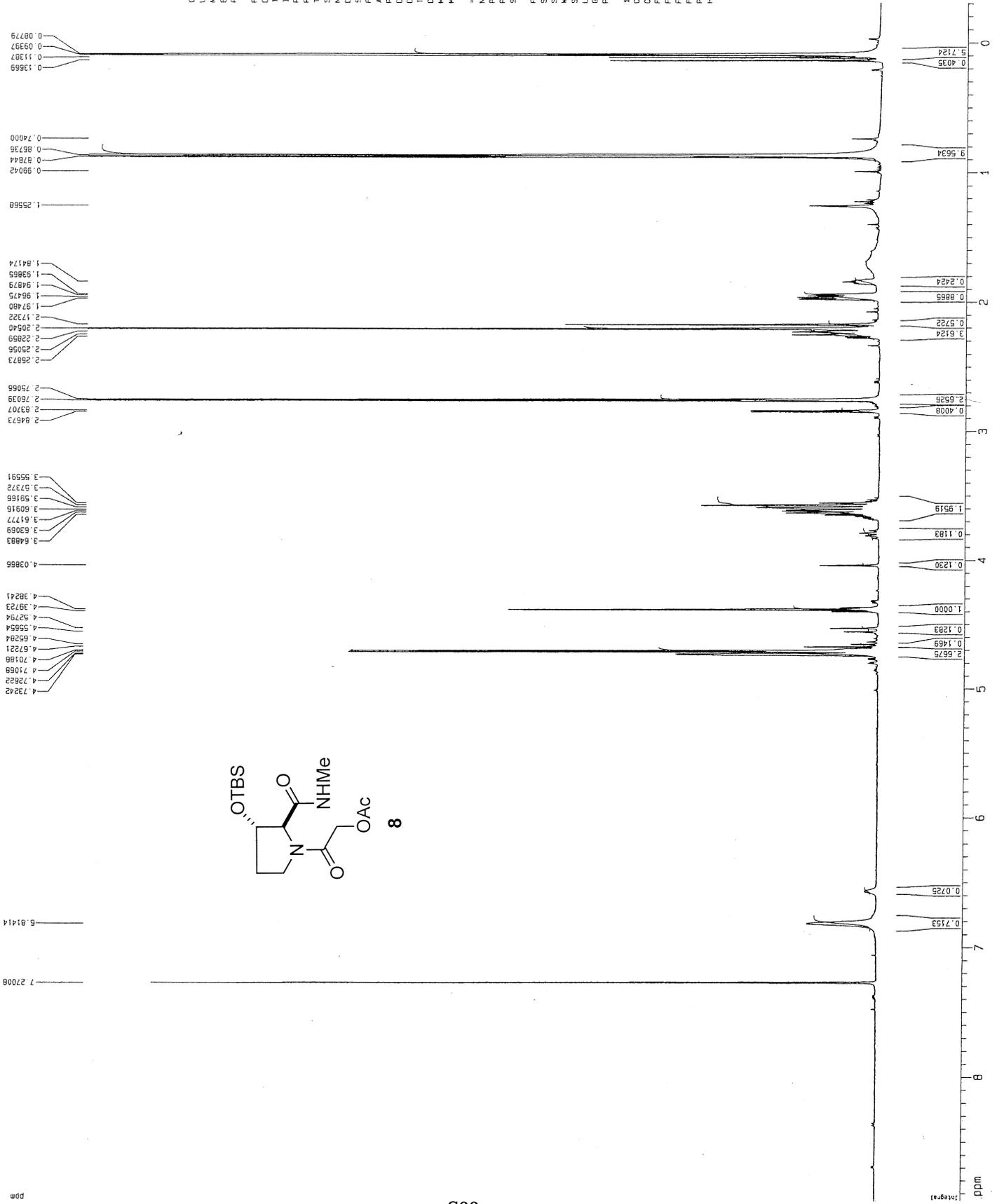
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 15.00 usec  
 PL1 -1.00 dB  
 SFO1 125.7542548 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 P2 100.00 usec  
 PL2 1.60 dB  
 PL12 23.54 dB  
 SFO2 500.2625011 MHz

F2 - Processing parameters  
 SI 65536  
 SF 125.7504006 MHz  
 EQ  
 SSF 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



Current Data Parameters  
 USER Lab40  
 NAME TS-1\_302H  
 EXPNO 1  
 PROCNO 1

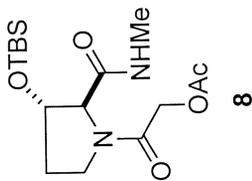
F2 - Acquisition Parameters  
 Date\_ 20070212  
 Time 16.44  
 INSTRUM cryo500  
 PROBHD 5 mm CPCLP 1H  
 PULPROG zgpg30  
 TD 6728  
 SOLVENT CDCl3  
 NS 12  
 DS 2  
 SMH 8032.820 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.0958774 sec  
 RG 5.7  
 DW 62.400 usec  
 DE 6.00 usec  
 TE 298.0 K  
 0.1000000 sec  
 0.1000000 sec  
 0.1000000 sec  
 0.1000000 sec  
 MCRXX

\*\*\*\*\* 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  
 ID  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 4.00

1D NMR Plot parameters  
 CX 22.60 cm  
 CY 89.54 cm  
 F1P 8.955 ppm  
 F1 4479.51 Hz  
 F2P -0.305 ppm  
 F2 -154.62 Hz  
 PPHOM 0.40632 ppm/cm  
 HZCM 203.25117 Hz/cm

13C spectrum with 1H decoupling



```

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

F2 - Acquisition Parameters
Date_     20070212
Time      16.46
INSTRUM   cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   zgpg30
TD         65488
SOLVENT    CDCl3
NS         99
DS         4
AQ         30093.03 Hz
FIDRES     0.463222 Hz
AQ         1.0754635 sec
RG         8192
DM         16.500 uSFC
DE         6.00 uSFC
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 uSFC
PL1        -1.00 dB
SFO1       125.7604002 MHz

***** CHANNEL f2 *****
COPPRG2    waltz16
NUC2        1H
P2PD2      100.00 uSFC
PL2         1.60 dB
PL12       23.54 dB
SFO2       500.2250111 MHz

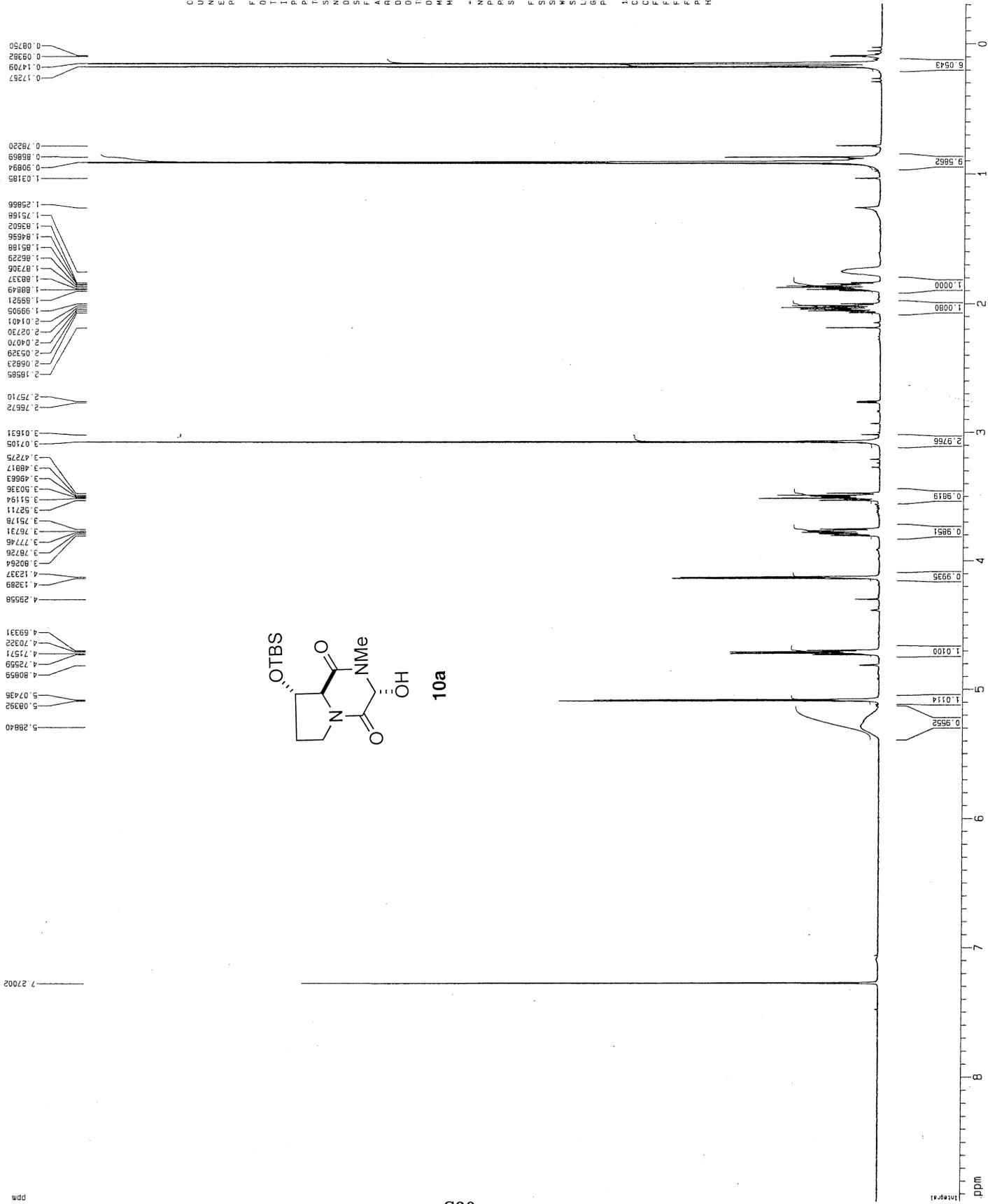
F2 - Processing parameters
SI         65536
SF         125.7604002 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00

ID NMR plot parameters
CX         22.20 cm
CY         22.65 cm
CZ         0.00 cm
FIP        230.637 mm
F1         28009.68 Hz
F2P        -10.287 ppm
F2         -1283.95 Hz
PPMCM      10.56688 ppm/cm
HZCM       1329.10693 Hz/cm
    
```





1H spectrum



Current Data Parameters  
 USER Lasato  
 NAME TS-2-013down  
 EXPNO 1  
 PROCNO 1

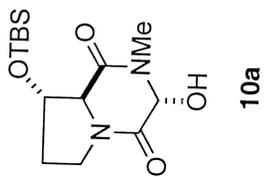
F2 - Acquisition Parameters  
 Date\_ 20070216  
 Time 18.27  
 INSTRUM cryo500  
 PROBHD 5 mm CPCL1 1H-  
 PULPROG zg30  
 01728  
 SOLVENT DMS  
 NS 11  
 DS 2  
 SMH 8012.820 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.0398774 sec  
 RG 6.3  
 DM 62.400 usec  
 DE 6.00 usec  
 TE 299.0 K  
 D1 0.1000000 sec  
 MICHEST 0.0000000 sec  
 MCORR 0.0750000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 8.00 usec  
 PL1 1.60 dB  
 SFO1 500.2635015 MHz

F2 - Processing parameters  
 SI 65536  
 SF 500.260274 MHz  
 WDW no  
 SSB 0  
 GB 0  
 PC 4.00

1D NMR plot parameters  
 CX 22.80 cm  
 CY 76.63 cm  
 F1 8.955 ppm  
 F2 4479.51 Hz  
 F3 -0.309 ppm  
 F4 -154.62 Hz  
 PPMCH 0.40632 ppm/cm  
 HZCM 203.25117 Hz/cm

13C spectrum with 1H decoupling



```

Current Data Parameters
USER          basilo
NAME          TS-2-01300m13C
EXPNO        1
PROCNO       1

F2 - Acquisition Parameters
Date_        20070216
Time         18.47
INSTRUM     cryo500
PROBHD      5 mm CPYCI 1H-
PULPROG     zgpg30
TD           65536
SOLVENT     DMS-d6
NS           49
DS           4
SWH          30393.031 Hz
FIDRES       0.462388 Hz
AQ           1.1091588 sec
RG           13004
DW           16.500 uSBC
DE           6.00 uSBC
TE           298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
d12          0.03000000 sec
d13          0.03000000 sec
d14          0.03000000 sec
d15          0.03000000 sec
d16          0.03000000 sec
d17          0.03000000 sec
d18          0.03000000 sec
d19          0.03000000 sec
d20          0.03000000 sec
d21          0.03000000 sec
d22          0.03000000 sec
d23          0.03000000 sec
d24          0.03000000 sec
d25          0.03000000 sec
d26          0.03000000 sec
d27          0.03000000 sec
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d29          0.03000000 sec
d30          0.03000000 sec
d31          0.03000000 sec
d32          0.03000000 sec
d33          0.03000000 sec
d34          0.03000000 sec
d35          0.03000000 sec
d36          0.03000000 sec
d37          0.03000000 sec
d38          0.03000000 sec
d39          0.03000000 sec
d40          0.03000000 sec
d41          0.03000000 sec
d42          0.03000000 sec
d43          0.03000000 sec
d44          0.03000000 sec
d45          0.03000000 sec
d46          0.03000000 sec
d47          0.03000000 sec
d48          0.03000000 sec
d49          0.03000000 sec
d50          0.03000000 sec
d51          0.03000000 sec
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d73          0.03000000 sec
d74          0.03000000 sec
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d78          0.03000000 sec
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d80          0.03000000 sec
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d92          0.03000000 sec
d93          0.03000000 sec
d94          0.03000000 sec
d95          0.03000000 sec
d96          0.03000000 sec
d97          0.03000000 sec
d98          0.03000000 sec
d99          0.03000000 sec
d100         0.03000000 sec

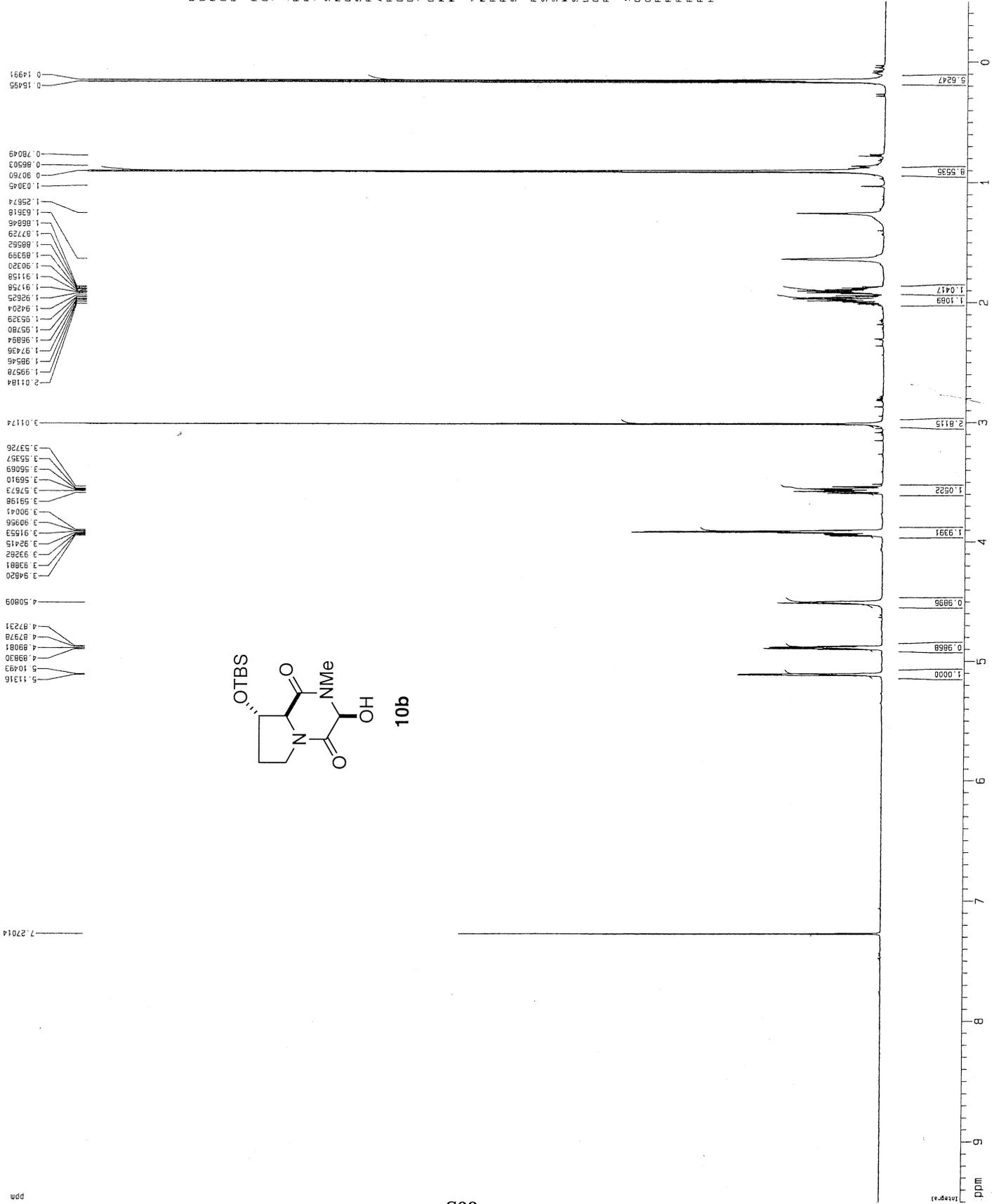
===== CHANNEL f1 =====
NUC1         13C
P1           15.00 uSBC
PL1          -1.00 dB
SF01         125.7942548 MHz

===== CHANNEL f2 =====
COPROG2     waltz16
NUC2         1H
P2           100.00 uSBC
PL2          0.00 dB
PL12         23.54 dB
SF02         500.2250011 MHz

F2 - Processing parameters
SI           65536
SF           125.7894011 MHz
WDW          no
SSB          0
LB           0.00 Hz
GB           0
PC           2.00

1D NMR plot parameters
CX           22.80 cm
CY           14.76 cm
F1           230.637 ppm
F2           290.000 ppm
F3           14.260 ppm
F4           -1283.96 Hz
PRGCM       10 56688 ppm/cm
HZCM        1328.10683 Hz/cm
    
```

1H spectrum



Current Data Parameters  
 USER Lasaro  
 NAME 18-2-013UD  
 EXPNO 2  
 PROCNO 1

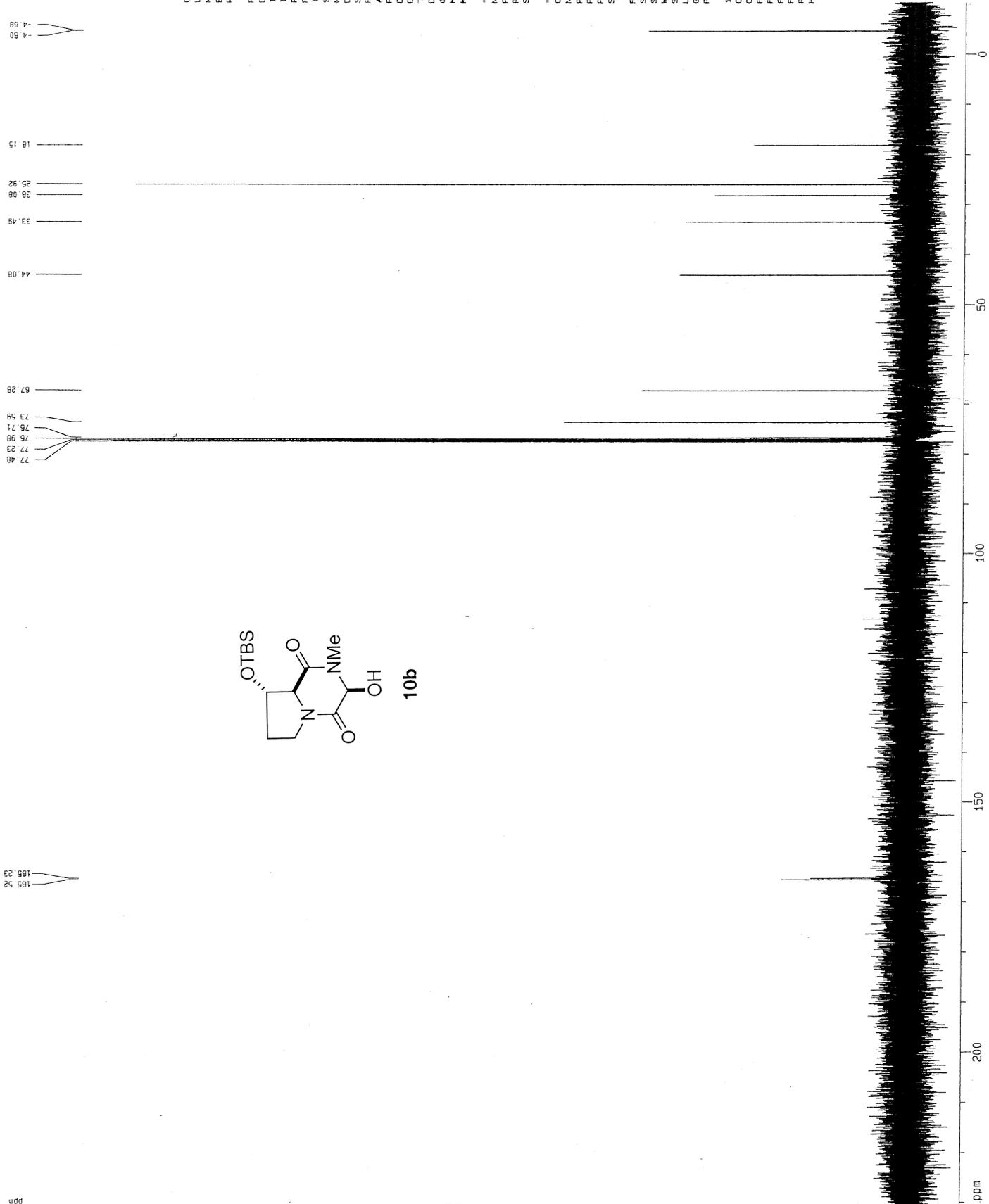
F2 - Acquisition Parameters  
 Date\_ 20070216  
 Time 18.17  
 INSTRUM cryo500  
 PROBHD 5 mm CP1CI 1H-  
 PULPROG zg30  
 0 8128  
 SOLVENT DMS  
 NS 0013  
 DS 2  
 SMH 8012.820 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.0958774 sec  
 RG 6.3  
 DM 62.400 usec  
 DE 6.00 usec  
 TE 299.0 K  
 D1 0.1000000 sec  
 MCHST 0.0000000 sec  
 MCHPK 0.0150000 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  
 MDW no  
 SSB no  
 GB 0  
 PC 4.00

1D NMR plot parameters  
 CX 22.60 cm  
 CY 68.39 cm  
 F1P 9.500 ppm  
 F1 4752.09 Hz  
 F2P -0.500 ppm  
 F2 -250.11 Hz  
 PPMCH 0.43860 ppm/cm  
 HZCH 219.38476 Hz/cm

<sup>13</sup>C spectrum with <sup>1</sup>H decoupling



Current Data Parameters  
 USER Lasato  
 NAME 1S-2-01sup13C  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070216  
 Time 18.19  
 INSTRUM cryo500  
 PROBHD 5 mm QNP1H-  
 PULPROG zgpg30  
 TO 65536  
 SOLVENT CDCl3  
 NS 122  
 DS 4  
 SWH 30303.051 Hz  
 FIDRES 0.46288 Hz  
 AQ 1.01852 sec  
 RG 31585.2  
 DM 15.500 usec  
 DE 5.00 usec  
 TE 298.0 K  
 D1 0.25000000 sec  
 d11 0.03000000 sec  
 MCHRG1 0.00000000 sec  
 MCHRG2 0.01500000 sec

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

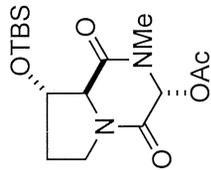
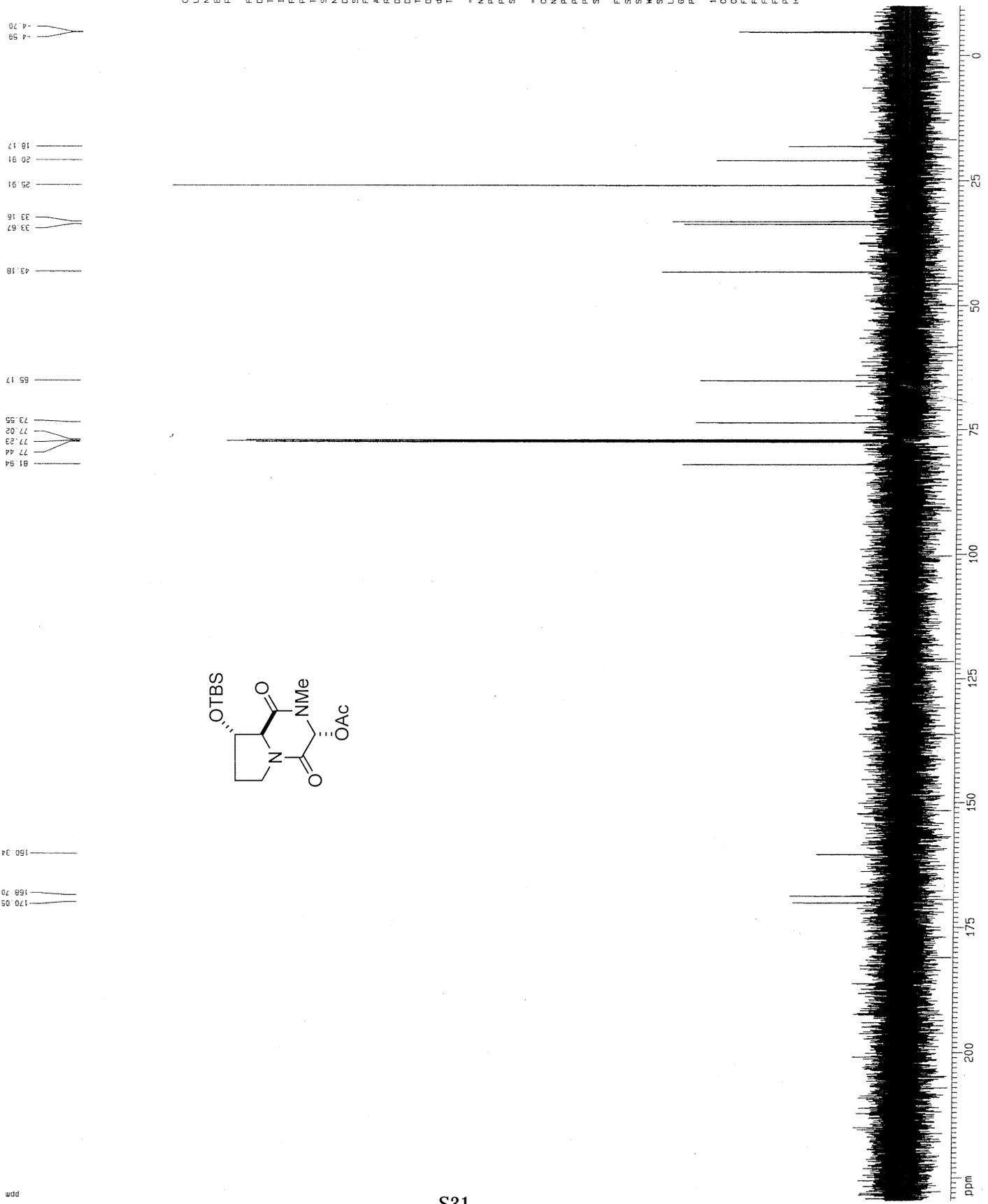
===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 <sup>1</sup>H  
 P2 100.00 usec  
 PL2 1.60 dB  
 PL12 23.54 dB  
 SFO2 500.225011 MHz

F2 - Processing parameters  
 SI 65536  
 SF 125.7804002 MHz  
 NDM no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 2.00

10 NMR plot parameters  
 CX 22.80 cm  
 F1 1.23 cm  
 F2 240.00 mm  
 F3 28009.66 Hz  
 F4 -10.287 ppm  
 F5 -1293.56 Hz  
 PPHCM 10.56688 ppm/cm  
 HZCM 1329.10693 Hz/cm



13C spectrum with 1H decoupling



```

Current Data Parameters
USER          Lasato
NAME          15-2-0143C
EXPNO        1
PROCNO       1

F2 - Acquisition Parameters
Date_        20070217
Time         20.58
INSTRUM      av600
PROBHD      5 mm 1H13
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           212
DS           4
SWH          36231.863 Hz
AQ           0.3526855 Hz
RG           0.3044499 sec
WDW          EM
SSB          0
LB           13.800 usec
GB           0
PC           1.00
TE           298.2 K
DE           6.00 usec
d1           0.40000001 sec
d11          0.03000000 sec
TD0          1

***** CHANNEL f1 *****
NUC1         13C
P1           15.00 usec
PL1          0.00 dB
SFO1         150.9194000 MHz

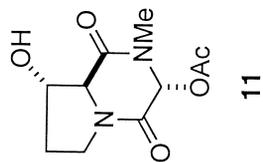
***** CHANNEL f2 *****
CPDPRG2      waltz16
NUC2         13C
P2           60.00 usec
PL2          120.00 dB
PL12         18.80 dB
SFO2         600.1330010 MHz

F2 - Processing parameters
SI           65536
SF           150.9027836 MHz
WDW          EM
SSB          0
LB           0.00 Hz
GB           0
PC           1.00

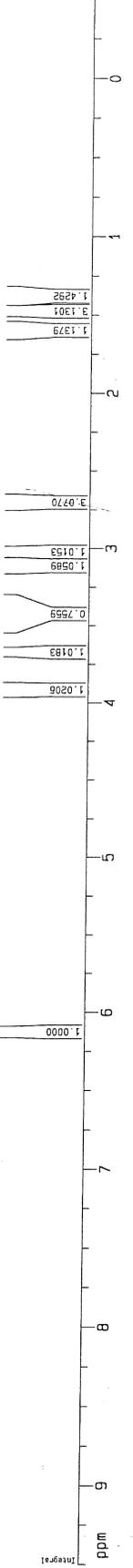
1D NMR plot parameters
CX           22.80 cm
CT           14.38 cm
FTIP         265.260 ppm
F1           34638.00 Hz
F2           -10.507 ppm
F2F          -1585.47 Hz
PPHQM        10.52747 ppm/cm
HZCM         1588.62439 Hz/cm
    
```

1H spectrum

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0.6834  
0.6618  
0.6618  
0.6402  
0.6402  
0.6186  
0.6186  
0.5970  
0.5970  
0.5754  
0.5754  
0.5538  
0.5538  
0.5322  
0.5322  
0.5106  
0.5106  
0.4890  
0.4890  
0.4674  
0.4674  
0.4458  
0.4458  
0.4242  
0.4242  
0.4026  
0.4026  
0.3810  
0.3810  
0.3594  
0.3594  
0.3378  
0.3378  
0.3162  
0.3162  
0.2946  
0.2946  
0.2730  
0.2730  
0.2514  
0.2514  
0.2298  
0.2298  
0.2082  
0.2082  
0.1866  
0.1866  
0.1650  
0.1650  
0.1434  
0.1434  
0.1218  
0.1218  
0.1002  
0.1002  
0.0786  
0.0786  
0.0570  
0.0570  
0.0354  
0.0354  
0.0138  
0.0138  
0.0000  
0.0000



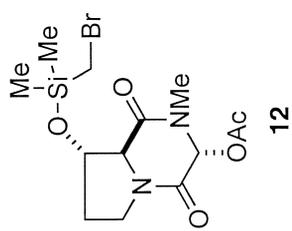
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 USER Labato  
 NAME TS-2-017  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20070220  
 Time 10:55  
 INSTRUM spect  
 PROBHD 5 mm TBI 1H/13  
 PULPROG zgpg30  
 TO 98074  
 SOLVENT CDCl3  
 NS 12  
 DS 2  
 SWH 9615.385 Hz  
 FIDRES 0.098042 Hz  
 AQ 5.098979 sec  
 RG 203  
 DM 52.000 usec  
 DE 6.00 usec  
 TE 298.1 K  
 D1 0.1000000 sec  
 T00 1  
 ===== CHANNEL f1 =====  
 NUC1 1H  
 P1 8.00 usec  
 PL1 -1.00 dB  
 SF01 600.1342009 MHz  
 F2 - Processing parameters  
 S1 655.36  
 SF 600.1299944 MHz  
 MVM no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 4.00  
 ID NMR plot parameters  
 CX 32.80 cm  
 CY 54.71 cm  
 CZ 0.00 cm  
 F1 5701.23 Hz  
 F2 -0.500 GHz  
 F3 -300.07 Hz  
 PPMCM 0.43860 ppm/cm  
 HZCM 283.21484 Hz/cm





1H spectrum

ppm



Current Data Parameters  
 USER Labato  
 NAME TS-2-018  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070220  
 Time 15:03  
 INSTRUM spect  
 PROBHD 5 mm BBI 1H/13  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 9  
 DS 2  
 SWH 9645.365 Hz  
 FIDRES 0.098042 Hz  
 AD 5.0988979 sec  
 RE 161  
 DM 52.000 usec  
 DE 6.00 usec  
 TE 299.0 K  
 D1 0.10000000 sec  
 T00 1

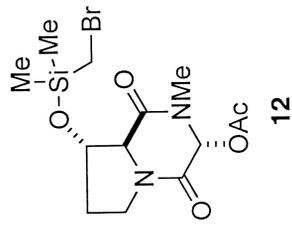
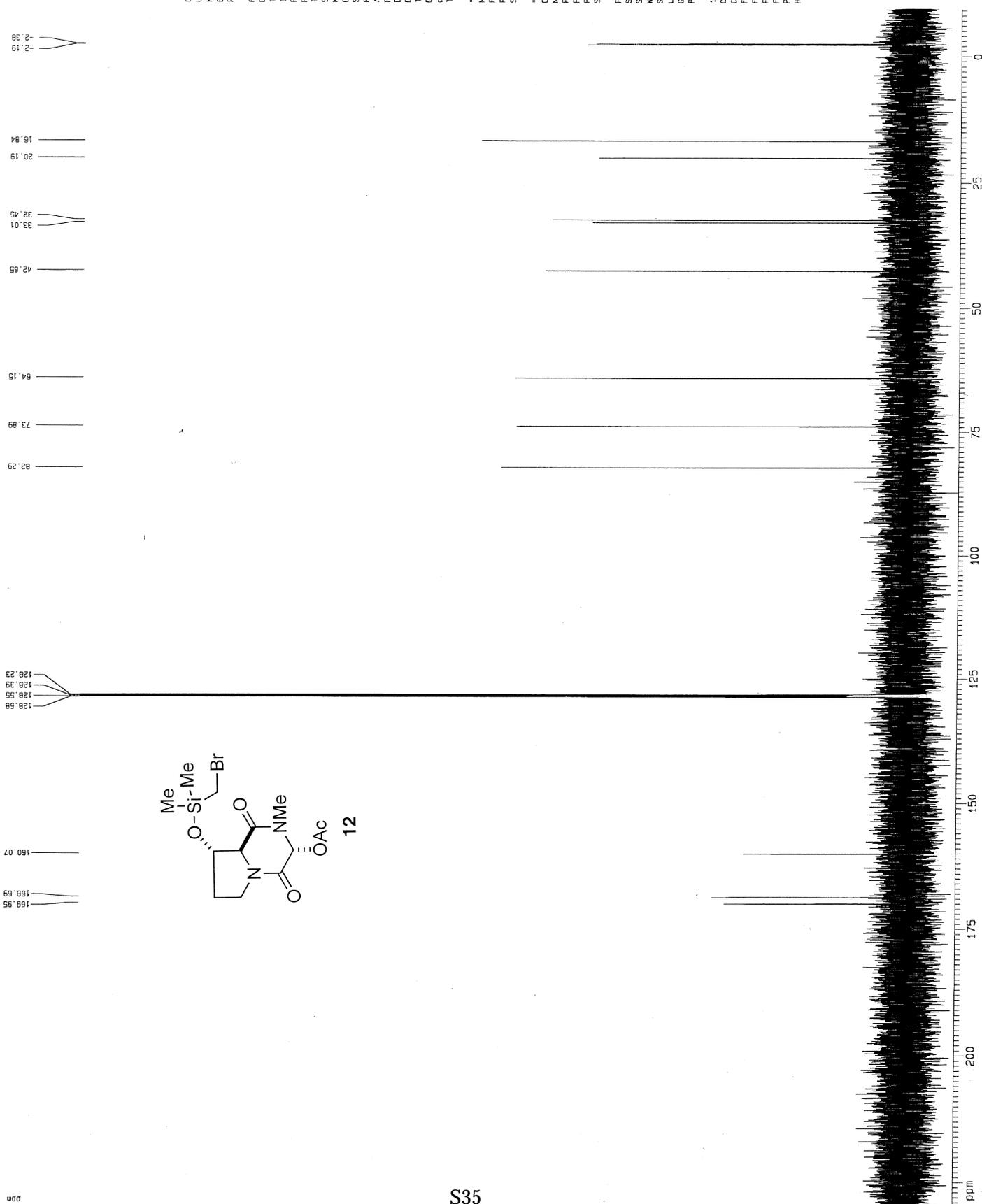
===== CHANNEL f1 =====  
 NUC1 13  
 P1 6.00 usec  
 PL1 -1.00 dB  
 SFO1 600.1342009 MHz

F2 - Processing parameters  
 S1 65536  
 SF 600.1299956 MHz  
 MDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

IG NMR plot parameters  
 CX 600.000 MHz  
 CY 52.780 MHz  
 F1 9.500 ppm  
 F2 5701.23 Hz  
 F3 -0.500 ppm  
 F4 -300.07 Hz  
 PPMCM 0.43950 ppm/cm  
 HZCM 263.21494 Hz/cm

<sup>13</sup>C spectrum with <sup>1</sup>H decoupling

ppm



Current Data Parameters  
 USER CAS910  
 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 zgpg30  
 TD 65536  
 SOLVENT water  
 NS 333  
 DS 4  
 SWH 36231.893 Hz  
 FIDRES 0.3528255 Hz  
 AQ 0.3074469 sec  
 RG 655  
 DW 13.600 usec  
 DE 6.000 usec  
 TE 298.1 K  
 O1 0.40000001 sec  
 O11 0.03000000 sec  
 TDO 1

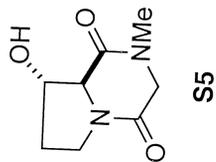
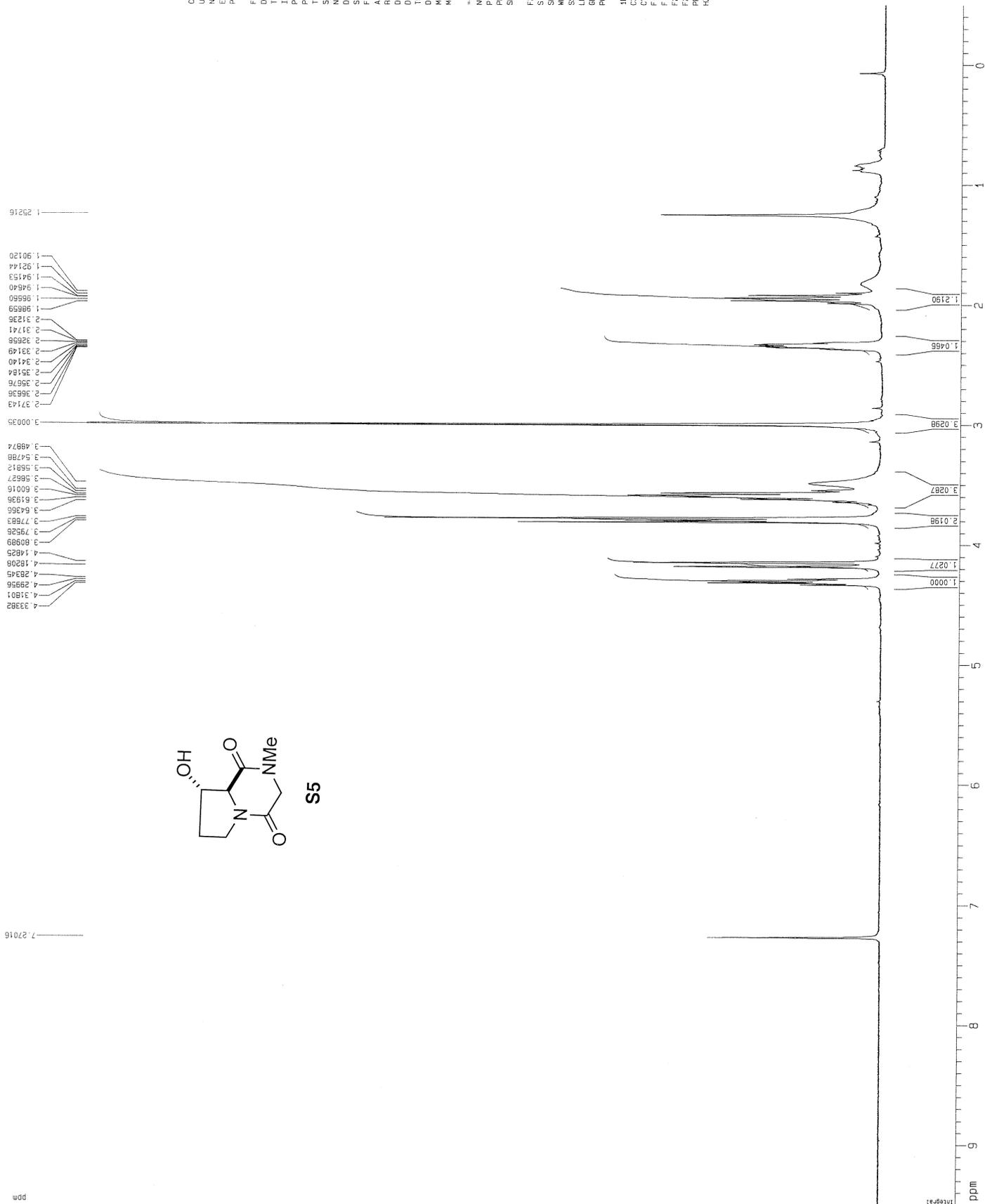
===== CHANNEL f1 =====  
 NUC1 <sup>13</sup>C  
 P1 15.00 usec  
 PL1 0.00 dB  
 SF01 150.9194080 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 <sup>1</sup>H  
 P2 60.00 usec  
 PL2 130.00 dB  
 PL12 18.80 dB  
 SF02 600.1330010 MHz

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

1D NMR plot parameters  
 CX 22.80 cm  
 F1 64.91 cm  
 F1P 325.520 ppm  
 F2 300.000 MHz  
 F2P 150.000 ppm  
 F2 -1385.47 Hz  
 PPMCM 10.52347 ppm/cm  
 HZCM 1588.62384 Hz/cm

1H spectrum



Current Data Parameters  
 USER Lasako  
 NAME TS-1-21  
 EXPNO 1  
 PROCNO 1

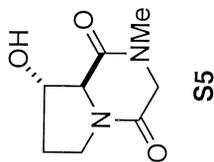
F2 - Acquisition Parameters  
 Date\_ 20060511  
 Time 15.32  
 INSTRUM cryo500  
 PROBHD 5 mm bncsdband  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 19  
 DS 2  
 SWH 8012.820 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.0398774 sec  
 RG 143.7  
 DW 62.400 usec  
 DE 6.00 usec  
 TE 299.0 K  
 MCHYST 0.100000 sec  
 MCHRSK 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 500.220262 MHz  
 WTW 0  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.80 cm  
 CY 37.74 cm  
 FIP 9.500 ppm  
 F1 4752.09 Hz  
 F2 -0.500 ppm  
 F3 0.000 Hz  
 PRNCHA 0.4386 Hz/cm  
 HZCM 219.38476 Hz/cm

13C spectrum with 1H decoupling



```

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      zgpg30
TD           65536
SOLVENT      CDCl3
NS           536
DS           4
SWH          30303.031 Hz
FIDRES       0.462368 Hz
AQ           1.0813940 sec
RG           18380.4
DM           18.500 usec
DE           6.00 usec
TE           298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
ACQRES       0.00000000 sec
RGCRK        0.03000000 sec

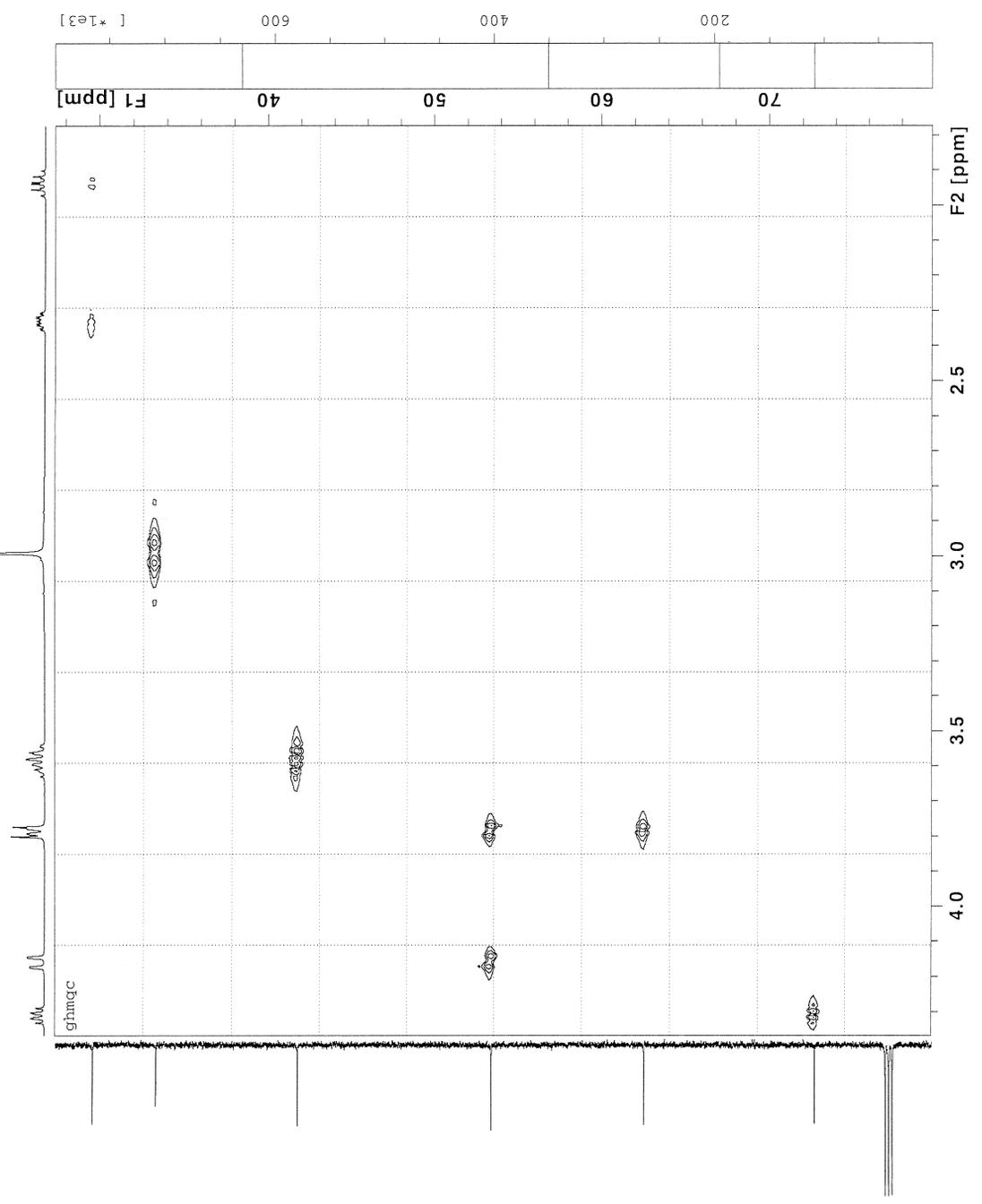
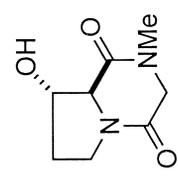
===== CHANNEL f1 =====
NUC1         13C
P1           8.50 usec
PL1          0.00 dB
SFO1         125.7942548 MHz

===== CHANNEL f2 =====
CPOPRG2      waltz16
NUC2         1H
P2           100.00 usec
PL2          1.60 dB
PL12         13.40 dB
SFO2         500.225011 MHz

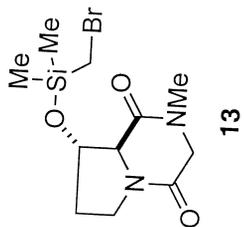
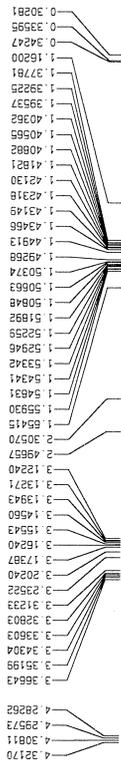
F2 - Processing parameters
SF           125.7604158 MHz
SI           65536
RG           65536
WDW          no
SSB          0
LB           0.00 Hz
GB           0
PC           2.00

ID NMR plot parameters
CX           22.80 cm
CY           7.49 cm
F1           230.637 ppm
F2           -10.267 ppm
Z            1293.96 Hz
GAMMA1      0.36688 ppm/cm
RECVM       1325.10706 Hz/cm
    
```

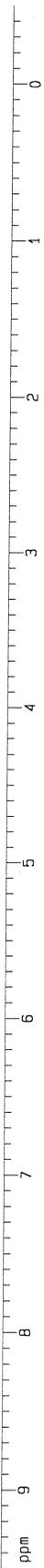
TS-1-229 15 1 /v tasato



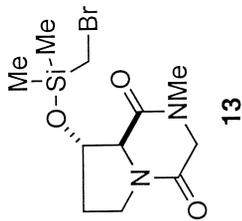
1H spectrum



Current Data Parameters  
 USER Lasato  
 NAME 15-1-100column1  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20060715  
 Time\_ 0.29  
 INSTRUM gn500  
 PROBHD 5 mm broadband  
 PULPROG zg30  
 TO 81728  
 SOLVENT CDCl3  
 NS 9  
 DS 2  
 SWH 8013.822 Hz  
 FIDRES 0.098843 Hz  
 AQ 5.0988774 sec  
 RG 128  
 DM 62.400 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.1000000 sec  
 MCREST 0.0000000 sec  
 MCWRR 0.0150000 sec  
 ----- CHANNEL f1 -----  
 NUC1 1H  
 P1 11.50 usec  
 PL1 -3.00 dB  
 SF01 499.9334955 MHz  
 F2 - Processing parameters  
 SI 65536  
 SF 499.9299967 MHz  
 WDM 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 -245.96 Hz  
 PPMCM 0.43860 ppm/cm  
 HZCM 219.26755 Hz/cm



13C spectrum with 1H decoupling

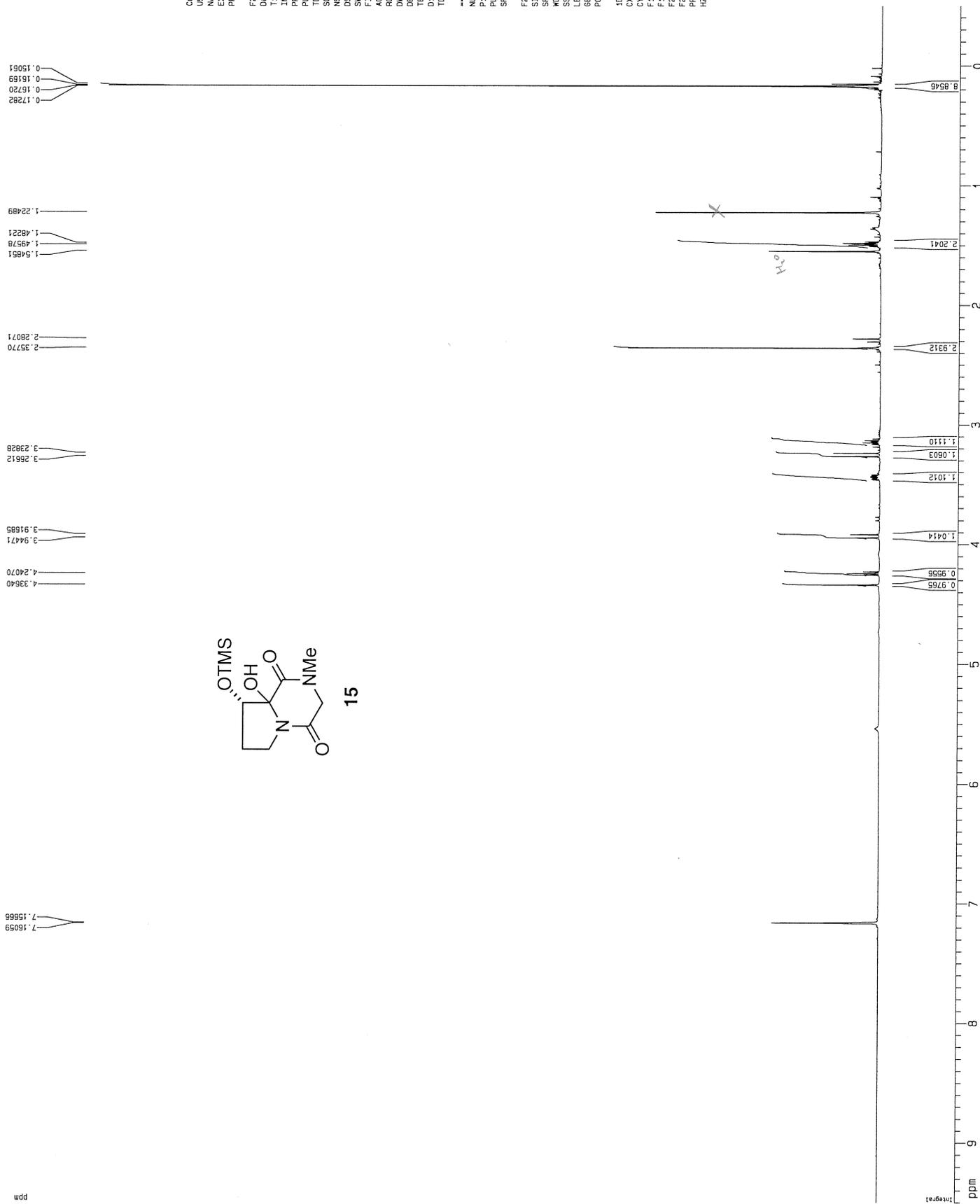


Current Data Parameters  
 USER tasato  
 NAME TS-1-100-13C  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20060717  
 Time 21.01  
 INSTRUM cryo500  
 PROBHD 5 mm broadband  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 135  
 DS 4  
 SWH 30303.031 Hz  
 FIDRES 0.462388 Hz  
 AQ 1.0914105 sec  
 RG 4096  
 DW 16.500 usec  
 DE 6.00 usec  
 TE 300.2 K  
 D1 0.2500000 sec  
 d11 0.0300000 sec  
 MCREST 0.0000000 sec  
 MCMRK 0.01500000 sec  
 \*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 8.90 usec  
 PL1 0.00 dB  
 SF01 125.7942548 MHz  
 \*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 P2 100.00 usec  
 PL2 1.80 dB  
 PL12 13.40 dB  
 SF02 500.2225011 MHz  
 F2 - Processing parameters  
 SI 65536  
 SF 125.7803323 MHz  
 WDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 2.00  
 1D NMR plot parameters  
 CX 22.80 cm  
 F1 174.61 cm  
 F2 231.46 cm  
 E1 28074.06 Hz  
 E2 -91.771 ppm  
 F2 -1228.97 Hz  
 PPMCM 10.56668 ppm/cm  
 HZCM 1329.08032 Hz/cm





1H spectrum



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

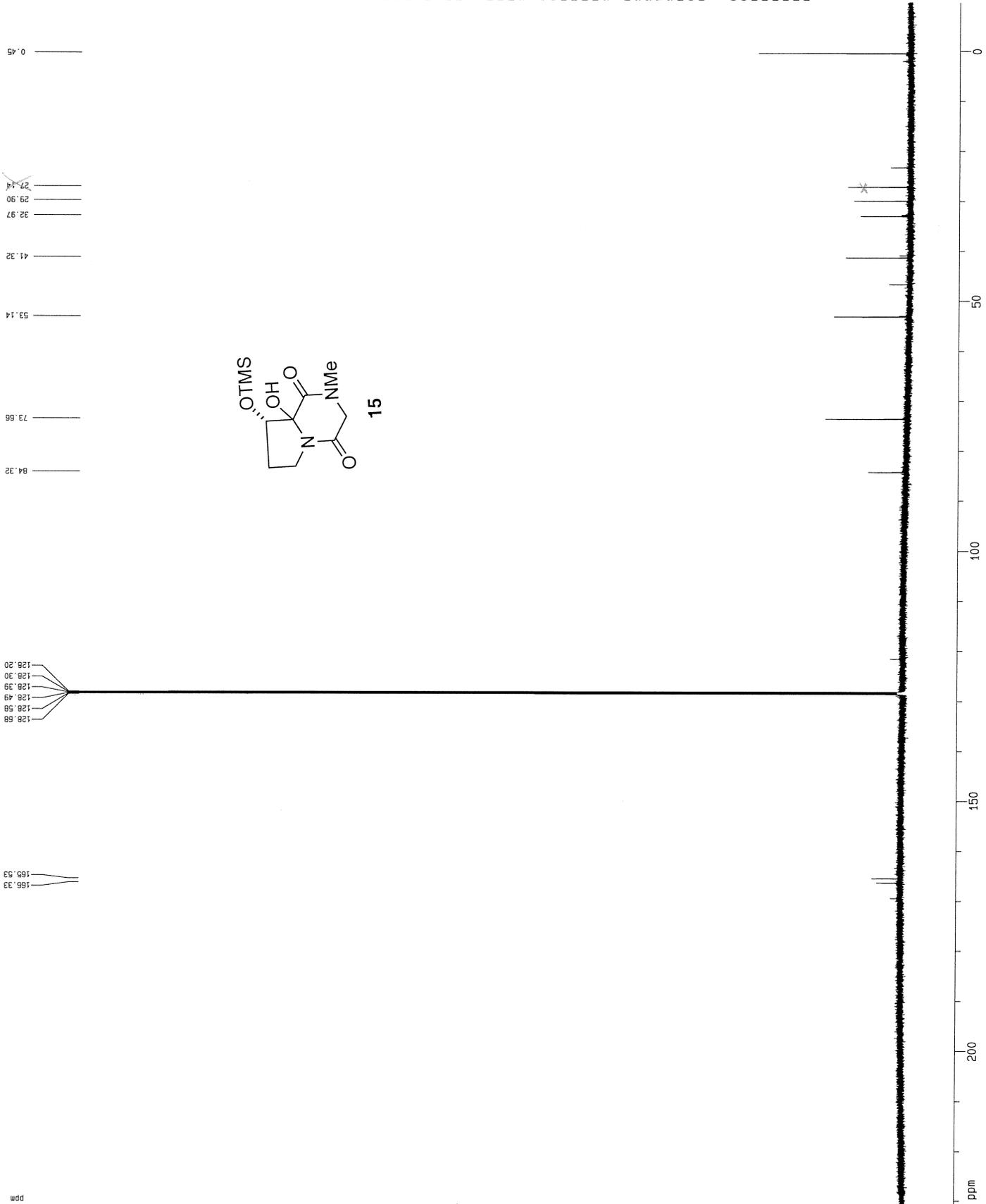
F2 - Acquisition Parameters  
 Date\_ 20070524  
 Time 17:28  
 INSTRUM r4600  
 PROBHD 5 mm TBI H4/L3  
 PULPROG zg30  
 SOLVENT dmsd  
 TD 66074  
 NS 10  
 DS 2  
 SWH 9615.385 Hz  
 FIDRES 0.080042 Hz  
 AQ 5.0988979 sec  
 RG 80.6  
 DM 52.000 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 1.00  
 TDD 0.10000000 sec

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

F2 - Processing parameters  
 SI 65536  
 SF 600.1299569 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

13C spectrum with 1H decoupling



Current Data Parameters  
 USER tasato  
 NAME TS-2-0670\data  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070904  
 Time 19:38  
 INSTRUM cryo  
 PROBRD 5 mm CPYCH 1H-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT DMSO-d6  
 NS 76  
 DS 4  
 SWH 30303.031 Hz  
 FIDRES 0.462368 Hz  
 AQ 1.0813940 sec  
 RG 3251  
 DM 16.500 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.2500000 sec  
 D11 0.0300000 sec  
 SFO1 125.7603332 MHz  
 ACQRES 0.1500000 sec  
 MCHNK 0.1500000 sec

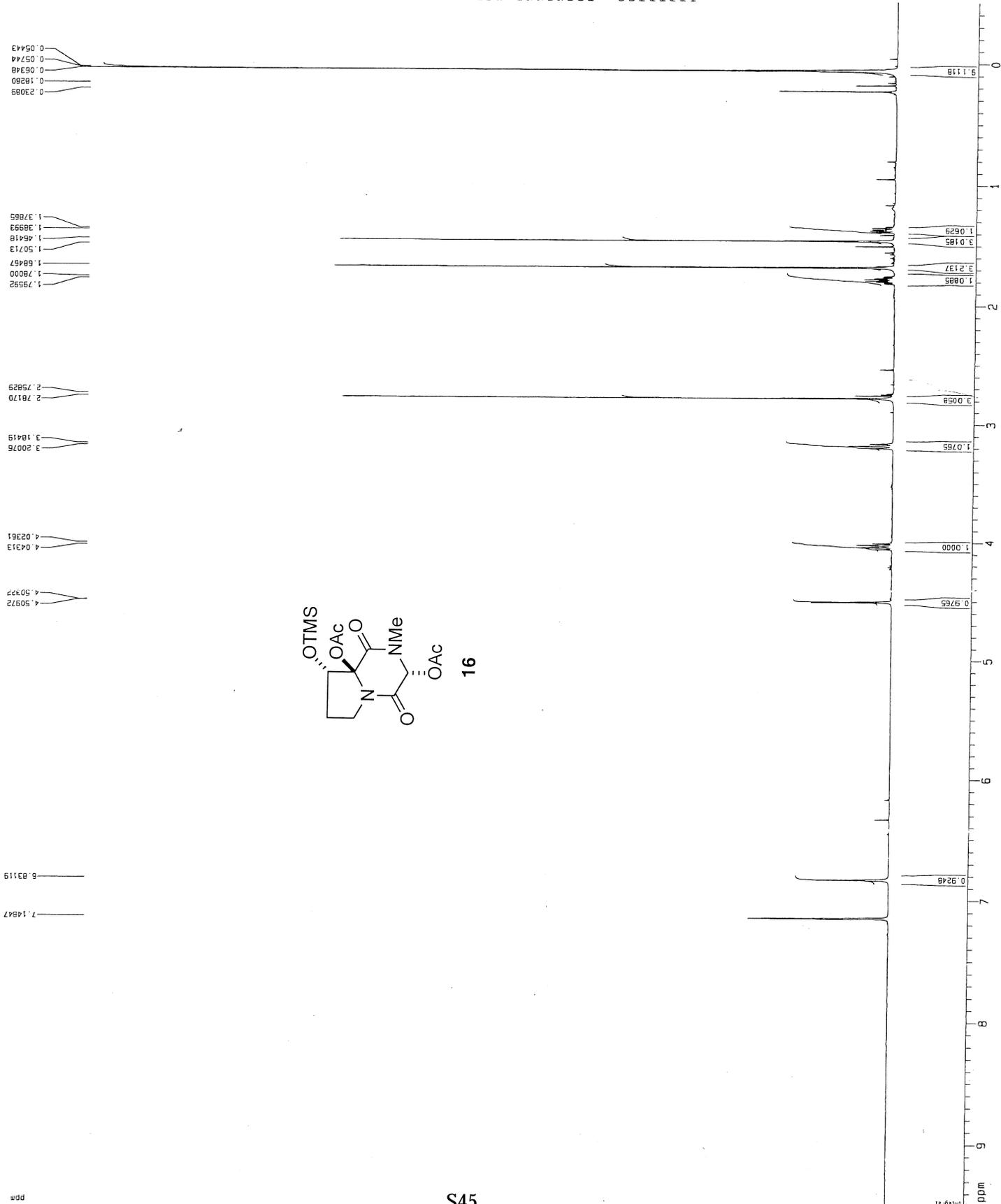
==== CHANNEL f1 =====  
 NUC1 13C  
 P1 15.00 usec  
 PL1 -1.00 dB  
 SFO1 125.7603332 MHz

==== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 P2 100.00 usec  
 PL2 1.00 dB  
 PL12 23.54 dB  
 SFO2 500.225011 MHz

F2 - Processing Parameters  
 SI 65536  
 SF 125.7603332 MHz  
 KW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 2.00

1D NMR plot parameters  
 CX 22.60 cm  
 CY 20.19 cm  
 F1 230.637 ppm  
 F2 29009.66 Hz  
 F3 -10.267 ppm  
 F4 1283.96 Hz  
 PRGCM 10.5860 ppm/cm  
 HZCM 1325.16625 Hz/cm

1H spectrum



Current Data Parameters  
 USER Lasato  
 NAME 15-2-049acetate1H  
 EXPNO 1  
 PROCNO 1

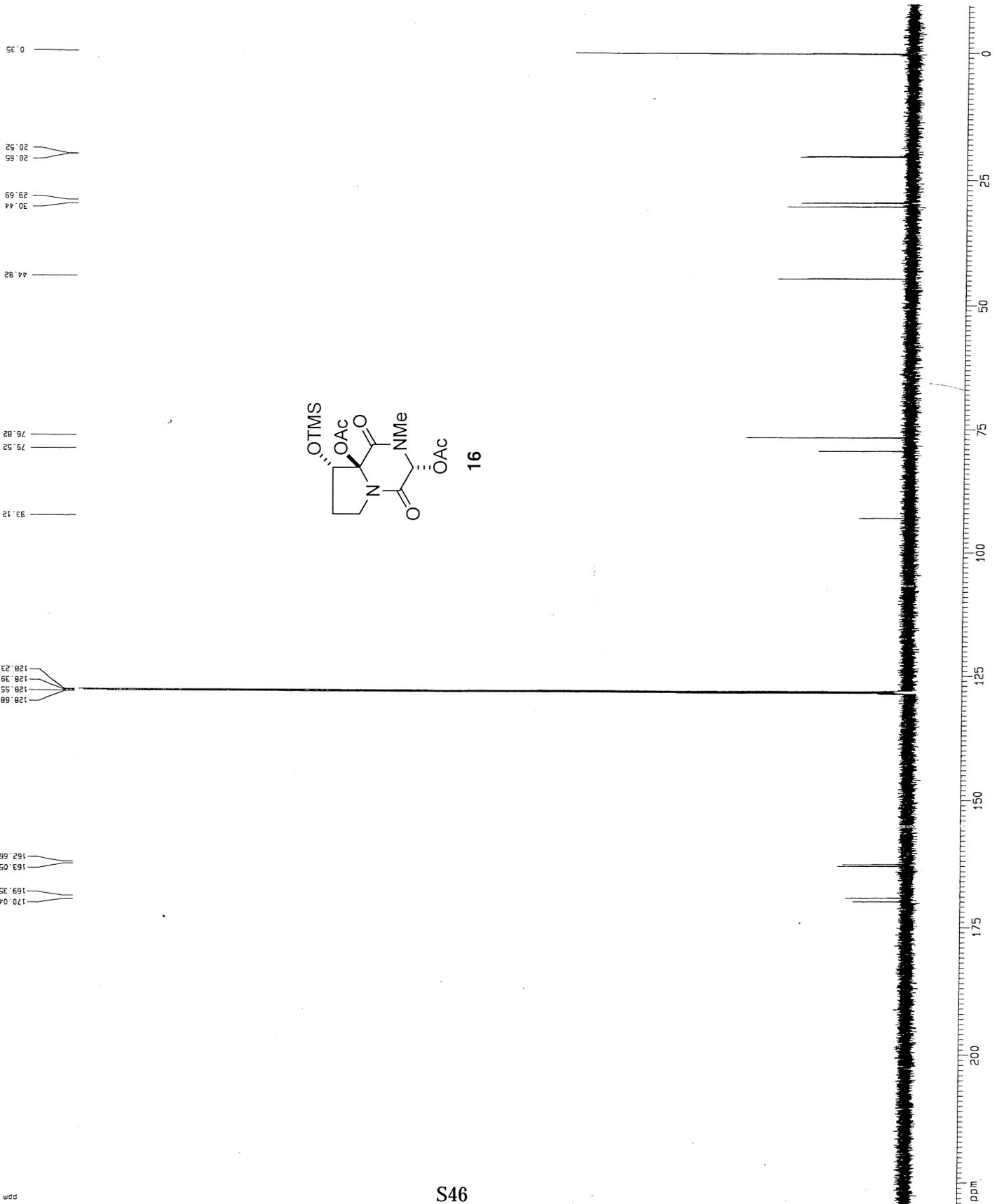
F2 - Acquisition Parameters  
 Date\_ 20070329  
 Time 13.45  
 Date\_ 0500  
 Program 5 mm 1H1  
 PULPROG zgpg30  
 TO 98074  
 SOLVENT CDCl3  
 NS 13  
 DS 2  
 SWH 5615.365 Hz  
 FIDRES 0.098042 Hz  
 AQ 5.0988979 sec  
 RG 32  
 RW 52.000 usec  
 DE 6.00 usec  
 TE 298.6  
 D1 0.10000000 sec  
 TDO 1

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

F2 - Processing parameters  
 F1 50536  
 CF 600.1300040 MHz  
 RG 0  
 SSF 0  
 LB 0.00 Hz  
 GB 0  
 PC 10.00

1D NMR plot parameters  
 CX 25.80 cm  
 CY 23.68 cm  
 F1P 9.500 ppm  
 F1 5701.23 Hz  
 F2P -0.500 ppm  
 F2 -3.500 ppm  
 PPM0 0.43860 usec/cm  
 HZCM 263.21694 Hz/cm

<sup>13</sup>C spectrum with <sup>1</sup>H decoupling



Current Data Parameters  
 USER esato  
 NAME TS-2-OAcacetate  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070329  
 Time 13.27  
 INSTRUM av600  
 PROBHD 5 mm TBI 1H/13  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 186  
 DS 4  
 SWH 36231.863 Hz  
 FIDRES 0.3526955 Hz  
 AQ 0.3044468 sec  
 RG 652  
 DM 13.800 usec  
 DE 6.00 usec  
 TE 298.1 K  
 O1 0.40000001 sec  
 O11 0.03000000 sec  
 TDO 1

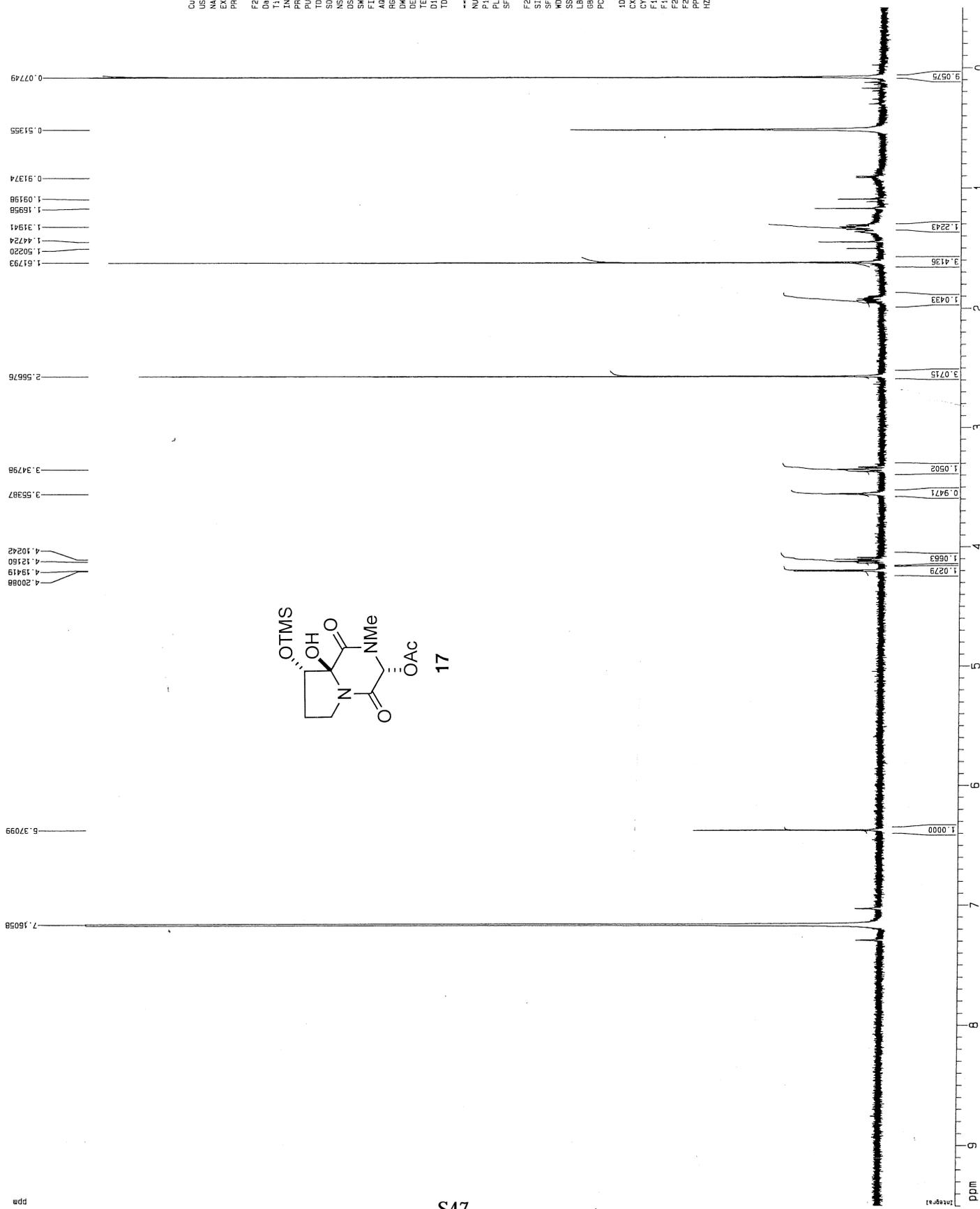
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 15.00 usec  
 PL1 0.00 dB  
 SFO1 150.9194080 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 P2 80.00 usec  
 PL2 120.00 dB  
 PL12 18.00 dB  
 SFO2 600.1330710 MHz

F2 - Processing parameters  
 SI 65536  
 SF 150.9027033 MHz  
 MDW 0  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

10 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 1585.62354 Hz/cm

1H spectrum



Current Data Parameters  
USER tsato  
NAME TS-2-117down  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20070604  
Time 19:42  
INSTRUM spect  
PROBHD 5 mm TBI HX30  
PULPROG zgpg30  
TD 66024  
SOLVENT CDCl3  
NS 32  
DS 2  
SMH 9615.385 Hz  
FIDRES 0.058042 Hz  
AQ 5.0958975 sec  
RG 2050  
DM 52.000 usec  
DE 6.00 usec  
TE 294.5 K  
D1 0.1000000 sec  
TDD 1

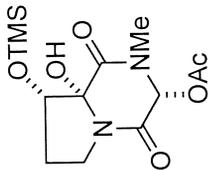
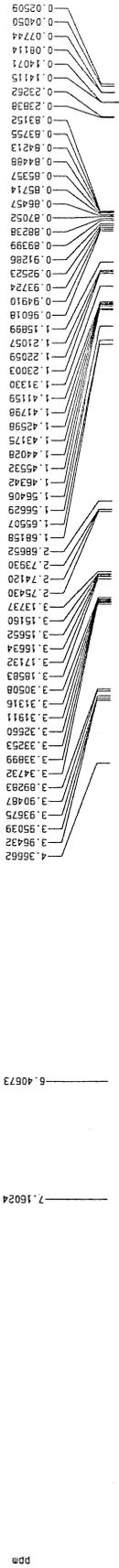
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
NUC1 1H  
P1 8.00 usec  
PL1 -1.00 dB  
SFO1 600.1342000 MHz

F2 - Processing parameters  
SI 65536  
SF 600.1258971 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  
F1 670.300 ppm  
F2 0.000 Hz  
F3 -300.07 Hz  
PRCM 0.43850 ppm/cm  
HZCM 263.21484 Hz/cm



1H spectrum



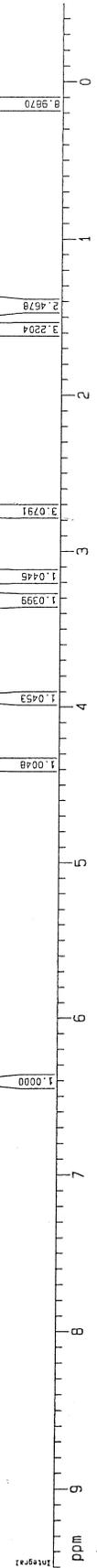
Current Data Parameters  
 USER kasato  
 NAME TS-2-16HPLCB  
 EXPNO 100  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070803  
 Time 20.48  
 INSTRUM av600  
 PROBNM 5 mm TBI 1H/13  
 PULPROG zg30  
 ID 97938  
 SOLVENT water  
 NS 5  
 DS 2  
 SWH 9515.365 Hz  
 FIDRES 0.098178 Hz  
 AQ 5.032255 sec  
 RG 405  
 DM 52.000 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.10000000 sec  
 TDO 1

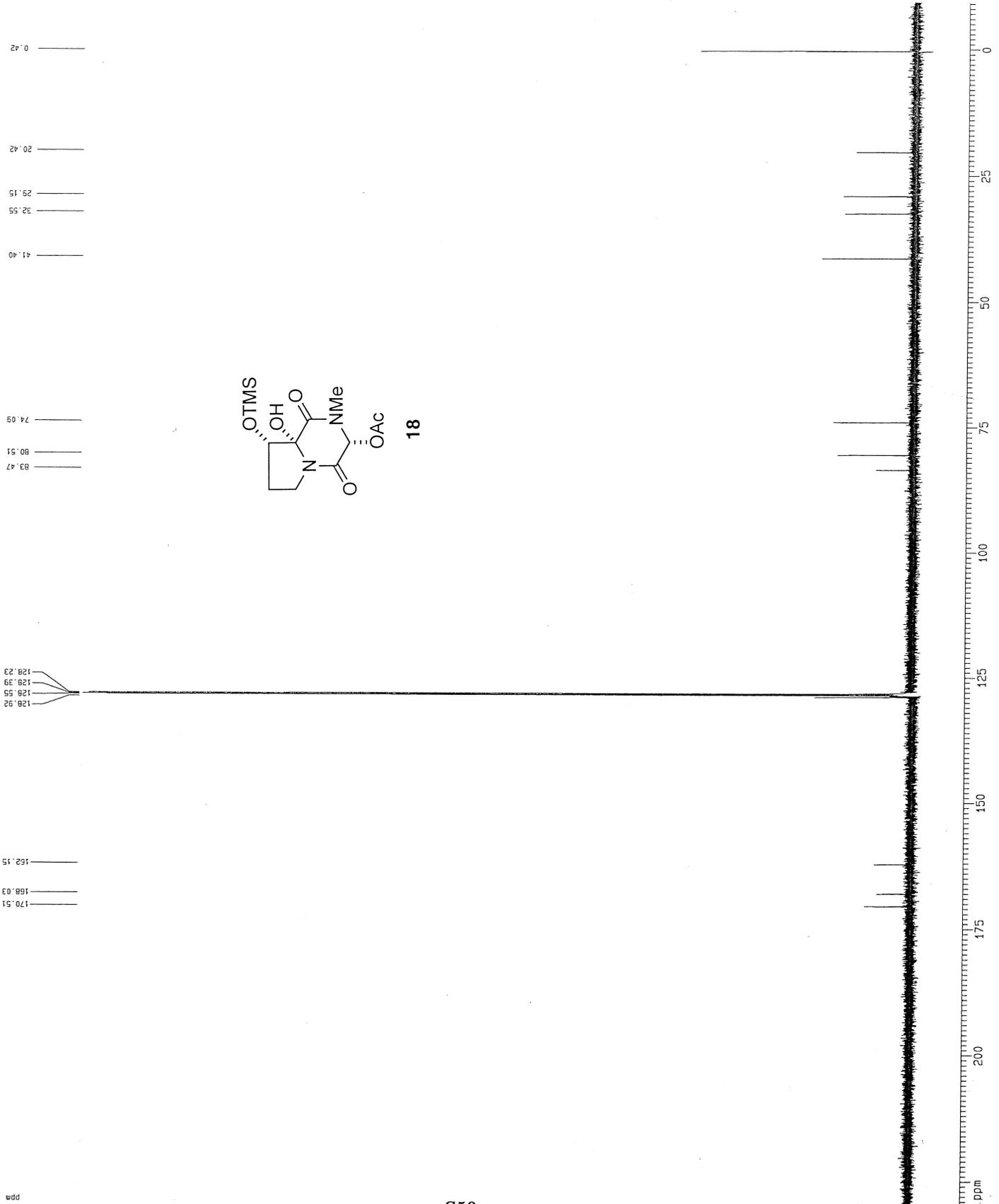
----- CHANNEL f1 -----  
 NUC1 1H  
 P1 8.00 usec  
 PL1 -1.00 dB  
 SFO1 600.1342009 MHz

F2 - Processing parameters  
 SI 658536  
 SF 600.1269869 MHz  
 WDW PC  
 SSF 0  
 GB 0  
 BF 0.00 Hz  
 SC 1.00

ID NMR plot parameters  
 CX 22.50 cm  
 CY 45.28 cm  
 F1P 9.500 ppm  
 F2 5701.23 Hz  
 F2P -0.500 ppm  
 ZF 300.07 Hz  
 PPGM 0.43860 ppm/cm  
 MCH 263.21454 Hz/cm



<sup>13</sup>C spectrum with <sup>1</sup>H decoupling



Current Data Parameters  
 USER Laszlo  
 NAME 1S-2-161HPLC/3C  
 EXPNO 5  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070803  
 Time 22.10  
 INSTRUM av600  
 PROBHD 5 mm TBI 1H/13  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT acet  
 NS 4096  
 DS 4  
 SFO1 150.9194680 MHz  
 FIDRES 0.5528955 Hz  
 AQ 0.9044468 sec  
 RG 575  
 DM 13.800 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.40000001 sec  
 d11 0.03000000 sec  
 TDO 1

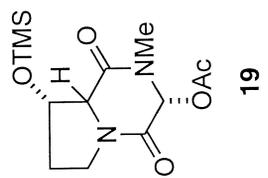
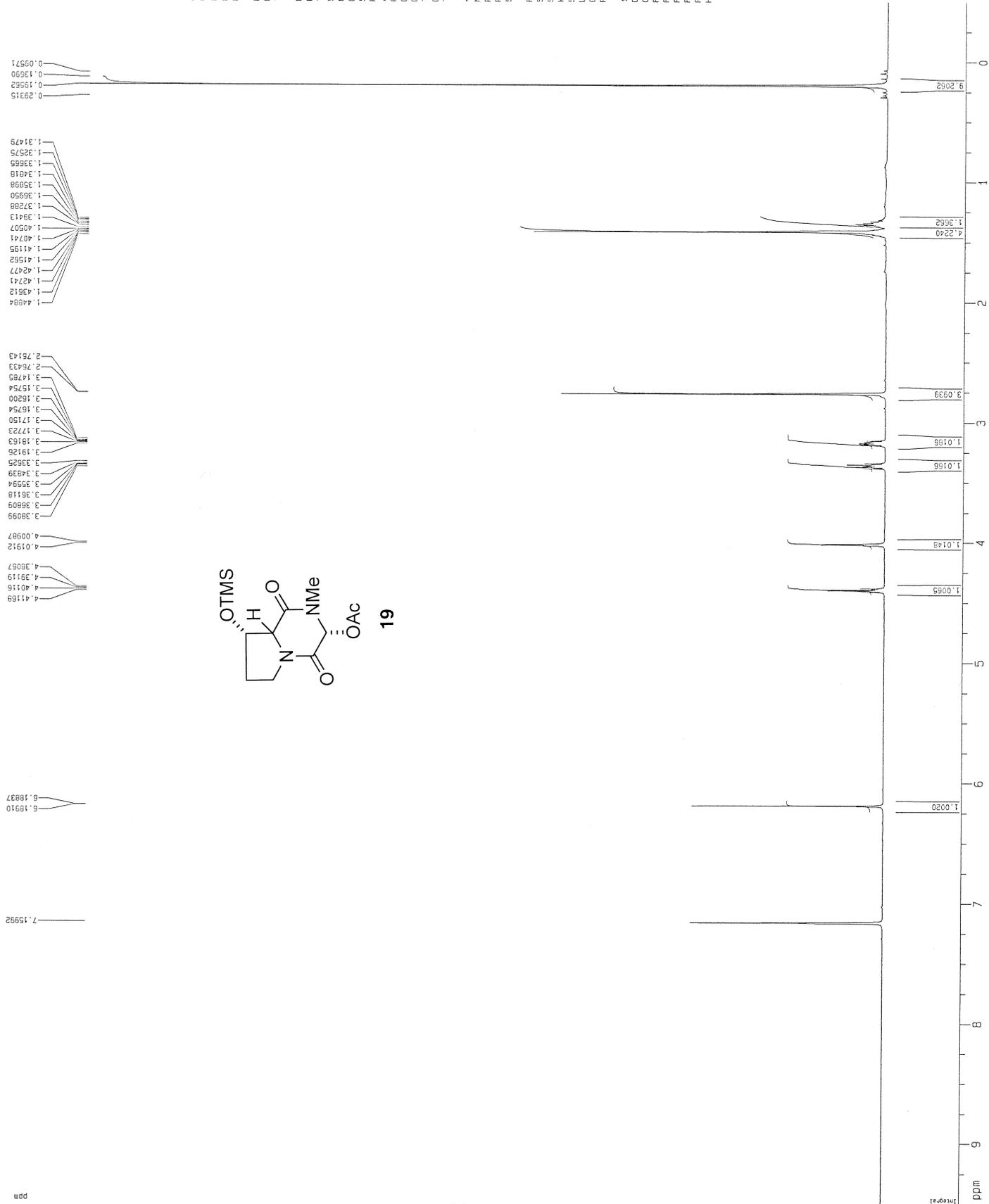
===== CHANNEL f1 =====  
 NUC1 <sup>13</sup>C  
 P1 15.00 usec  
 PL1 0.00 dB  
 SFO1 150.9194680 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 <sup>1</sup>H  
 PPR2 80.00 usec  
 PL2 120.00 dB  
 PL12 18.80 dB  
 SFO2 600.1300010 MHz

F2 - Processing parameters  
 SI 32768  
 SF 150.9027033 MHz  
 WDW 0  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

10 NMR plot parameters  
 CX 22.80 cm  
 CY 15.65 cm  
 FIP 289.520 ppm  
 F1 34835.14 Hz  
 F2 -10.507 ppm  
 F3 15577.00 Hz  
 PRACH 10.82742 Hz/cm  
 HZCM 1588.62354 Hz/cm

1H spectrum



Current Data Parameters  
 USER Lasata  
 NAME TS-2-161HPLCC  
 EXPNO 1  
 PROCNO 1

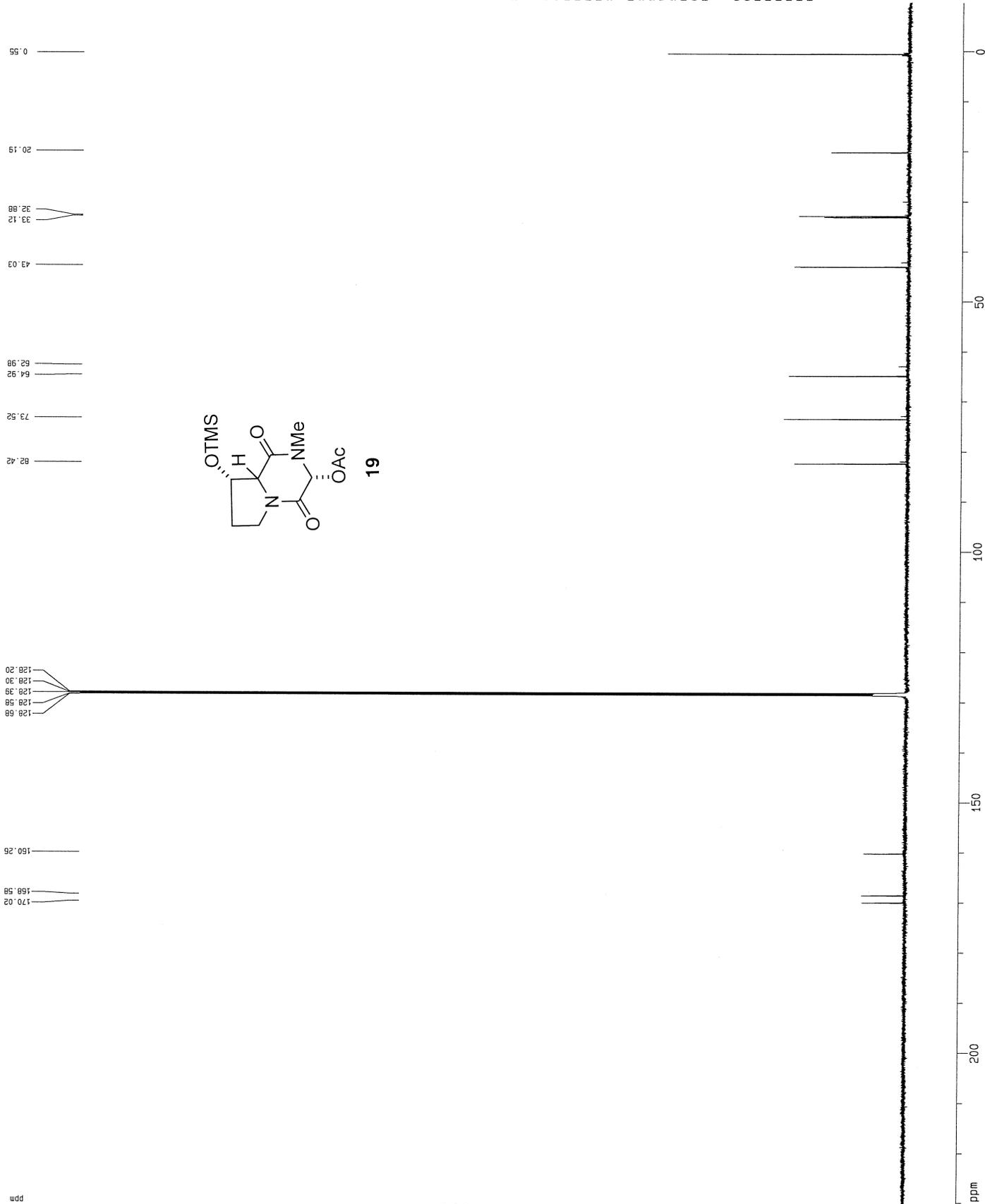
F2 - Acquisition Parameters  
 Date\_ 20070803  
 Time 20.53  
 INSTRUM av600  
 PROBHD 5 mm TBI 1H/13  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6515.30 Hz  
 FIDRES 0.000023 Hz  
 AQ 5.0998979 sec  
 RG 322  
 DM 52.000 usec  
 DE 6.00 usec  
 TE 299.1 K  
 D1 0.10000000 sec  
 TDD 1

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 8.00 usec  
 PL1 -1.00 dB  
 SFO1 600.136009 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.1269970 MHz  
 MDK no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.80 cm  
 CY 32.75 cm  
 FIP 9.500 ppm  
 F1 9701.23 Hz  
 F2 -0.500 ppm  
 F3 996.07 Hz  
 PRGM 0.4000 ppm/cm  
 HZCM 263.21484 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters  
 USER Tabato  
 NAME TS-2-16reddata  
 EXPNO 102  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070918  
 Time 13.39  
 INSTRUM cryo500  
 PROBH0 5 mm CPTCI 1H-  
 PULPROG zgpg30  
 TD 65418  
 SOLVENT CDCl3  
 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 298.2 K  
 D1 0.25000000 sec  
 d11 0.03000000 sec  
 MCHRG 0.00000000 sec  
 MCMRK 0.01500000 sec

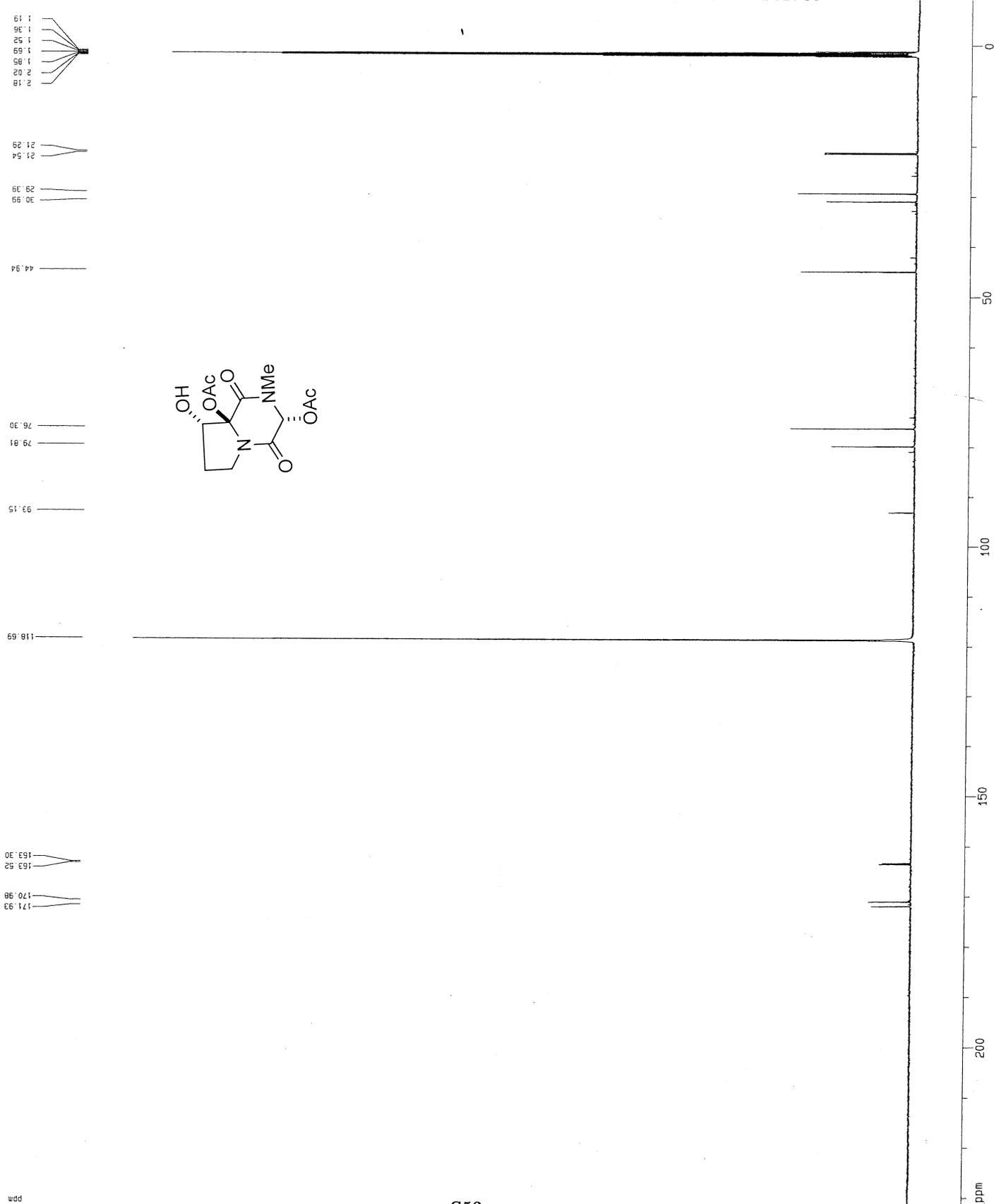
===== CHANNEL f1 =====  
 NUC1 13C  
 P1 15.00 usec  
 PL1 -1.00 dB  
 SFO1 125.7942548 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 13C  
 P2 10.00 usec  
 PL2 1.60 dB  
 PL12 23.54 dB  
 SFO2 500.225011 MHz

F2 - Processing parameters  
 SI 65536  
 SF 125.7803228 MHz  
 MDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 2.00

10 NMR plot parameters  
 CX 22.80 cm  
 CY 27.95 cm  
 F1P 230.628 MHz  
 F1 28009.656 Hz  
 F2P -10.207 ppm  
 F2 -1293.96 Hz  
 PPMCM 10.56688 ppm/cm  
 HZCM 1329.10620 Hz/cm

<sup>13</sup>C spectrum with <sup>1</sup>H decoupling



Current Data Parameters  
 USER Tasato  
 NAME TS-2-10813C  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070928  
 Time 17.16  
 INSTRUM crys500  
 PROBHD 5 mm CP1CI 1H-  
 PULPROG zgpg30  
 SOLVENT DMSO-d6  
 NS 50418  
 DS 4  
 SWH 30303.031 Hz  
 FIDRES 0.463222 Hz  
 AQ 1.0794470 sec  
 RG 5160.6  
 DM 16.500 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.25000000 sec  
 d11 0.03000000 sec  
 ACQRES 0.00000000 sec  
 PCPRG2 0.01500000 sec

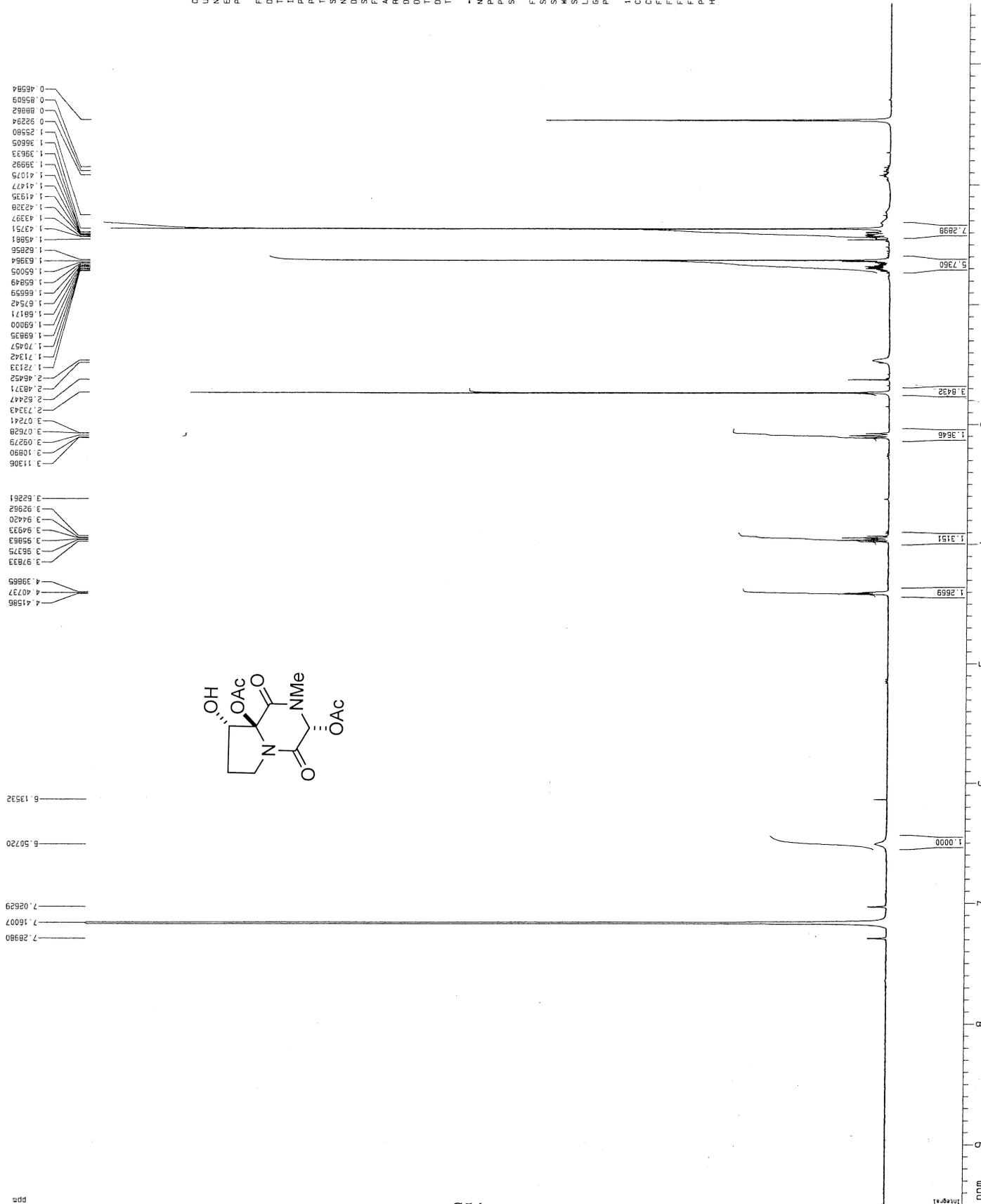
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 <sup>13</sup>C  
 P1 15.00 usec  
 PL1 -1.00 dB  
 SFO1 125.7942546 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 <sup>1</sup>H  
 PCPD2 100.00 usec  
 PL2 1.60 dB  
 PL12 23.54 dB  
 SFO2 500.225011 MHz

F2 - Processing parameters  
 S1 65536  
 SF 125.7602335 MHz  
 EN 0  
 US6 1.00 Hz  
 GB 0  
 PC 2.00

1D NMR plot parameters  
 CX 22.60 cm  
 CY 14.76 cm  
 F1P 231.776 ppm  
 F1 29162.63 Hz  
 F2P -9.145 ppm  
 F2 -1150.20 Hz  
 PPMCH 10.56666 ppm/cm  
 HZCM 1389.08032 Hz/cm

1H spectrum



Current Data Parameters  
 USER Labato  
 NAME TS-2-106  
 EXPNO 1  
 PROCNO 1

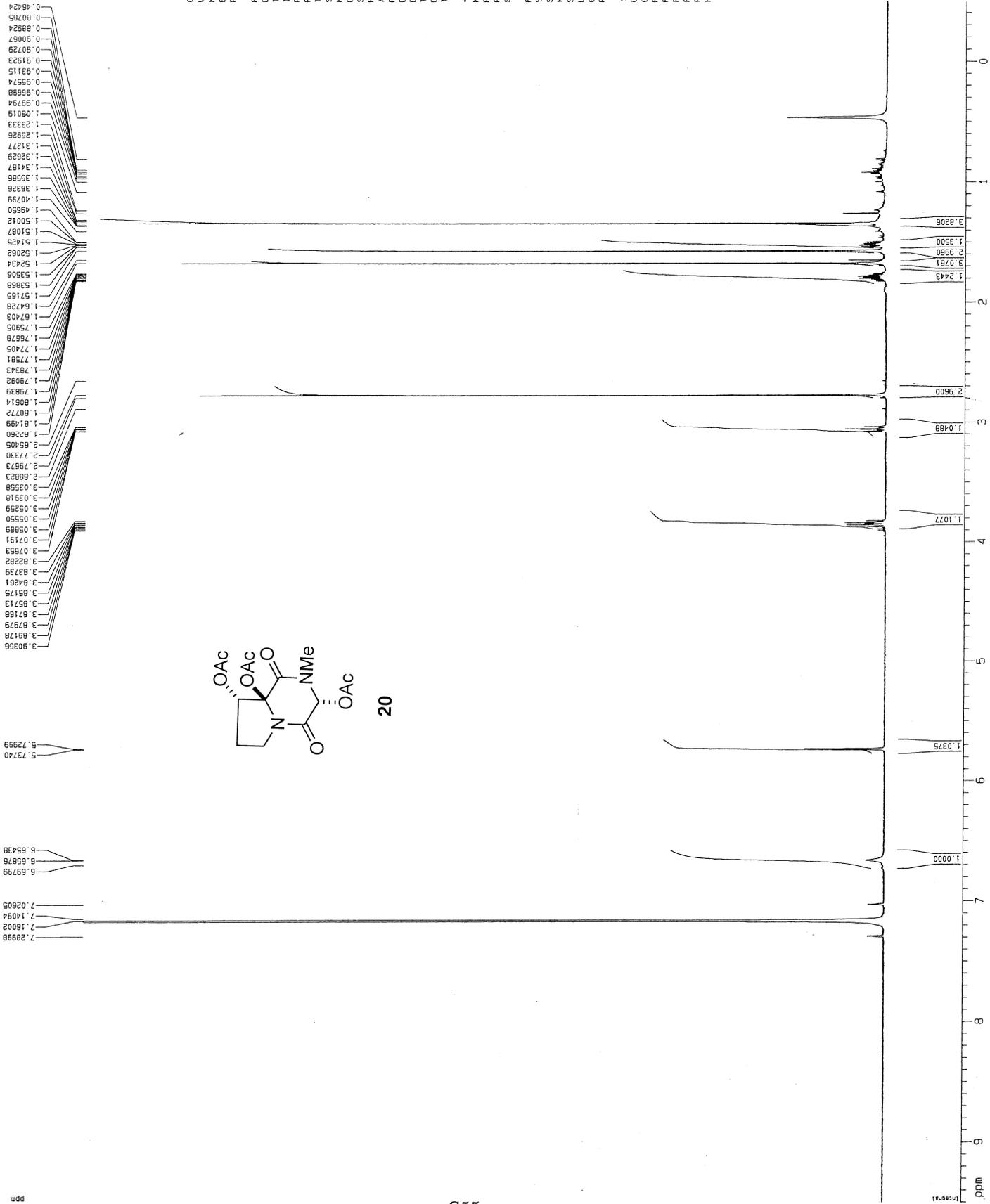
F2 - Acquisition Parameters  
 Date\_ 20070525  
 Time 16.41  
 INSTRUM av600  
 PROBDW 5 mm TBI 1H/13  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT DMSO  
 NS 14  
 DS 2  
 SMH 9615.365 Hz  
 FIDRES 0.096042 Hz  
 AQ 5.0398979 sec  
 RG 362  
 DN 52.000 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.1000000 sec  
 TDO 1

----- CHANNEL f1 -----  
 NUCL1 1H  
 P1 8.00 usec  
 PL1 0.00 dB  
 SFO1 600.1342009 MHz

F2 - Processing parameters  
 S1 65536  
 SF 600.1299774 MHz  
 MDW 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  
 F2P 570.123 Hz  
 F3P 0.000 ppm  
 FZP -300.00 ppm  
 PRMCM 0.43860 ppm/cm  
 HZCM 263.21494 Hz/cm

1H spectrum



Current Data Parameters  
 USER Lasato  
 NAME TS-2-035  
 EXPNO 100  
 PROCNO 1

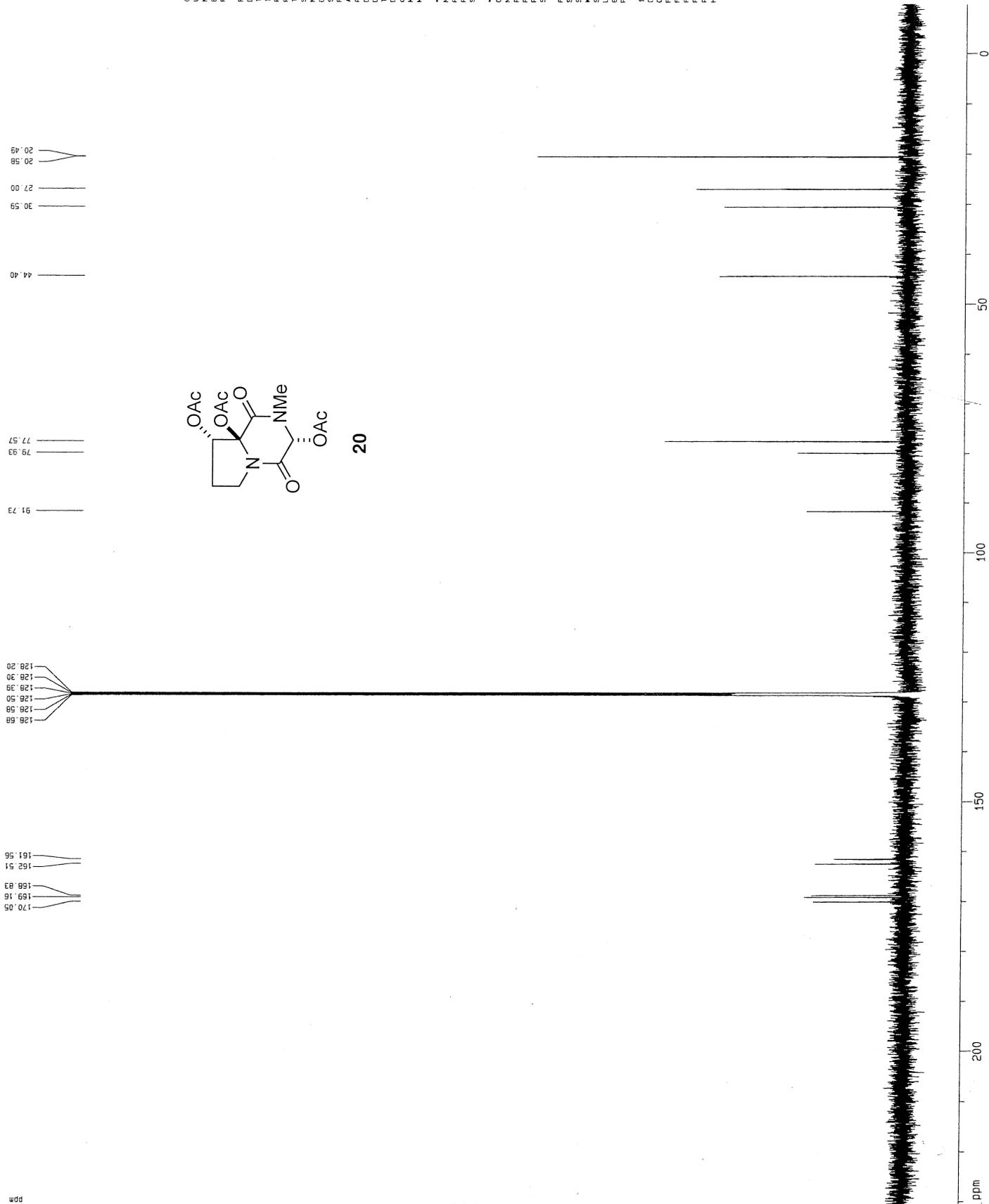
F2 - Acquisition Parameters  
 Date\_ 20070310  
 Time 20.30  
 INSTRUM av600  
 PULPROG zgpg30  
 TO 9258  
 SOLVENT DMSO  
 NS 6  
 DS 2  
 SMH 9615.365 Hz  
 FIDRES 0.098178 Hz  
 AQ 5.0928259 sec  
 RG 287  
 DM 52.000 USEC  
 DE 6.00 USEC  
 TE 283.9 K  
 D1 0.10000000 sec  
 T00 1

----- CHANNEL f1 -----  
 NUC1 1H  
 P1 9.00 USEC  
 PL1 -1.00 dB  
 SF01 600.1342009 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.1298973 MHz  
 MDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

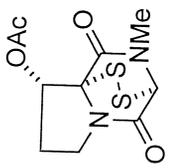
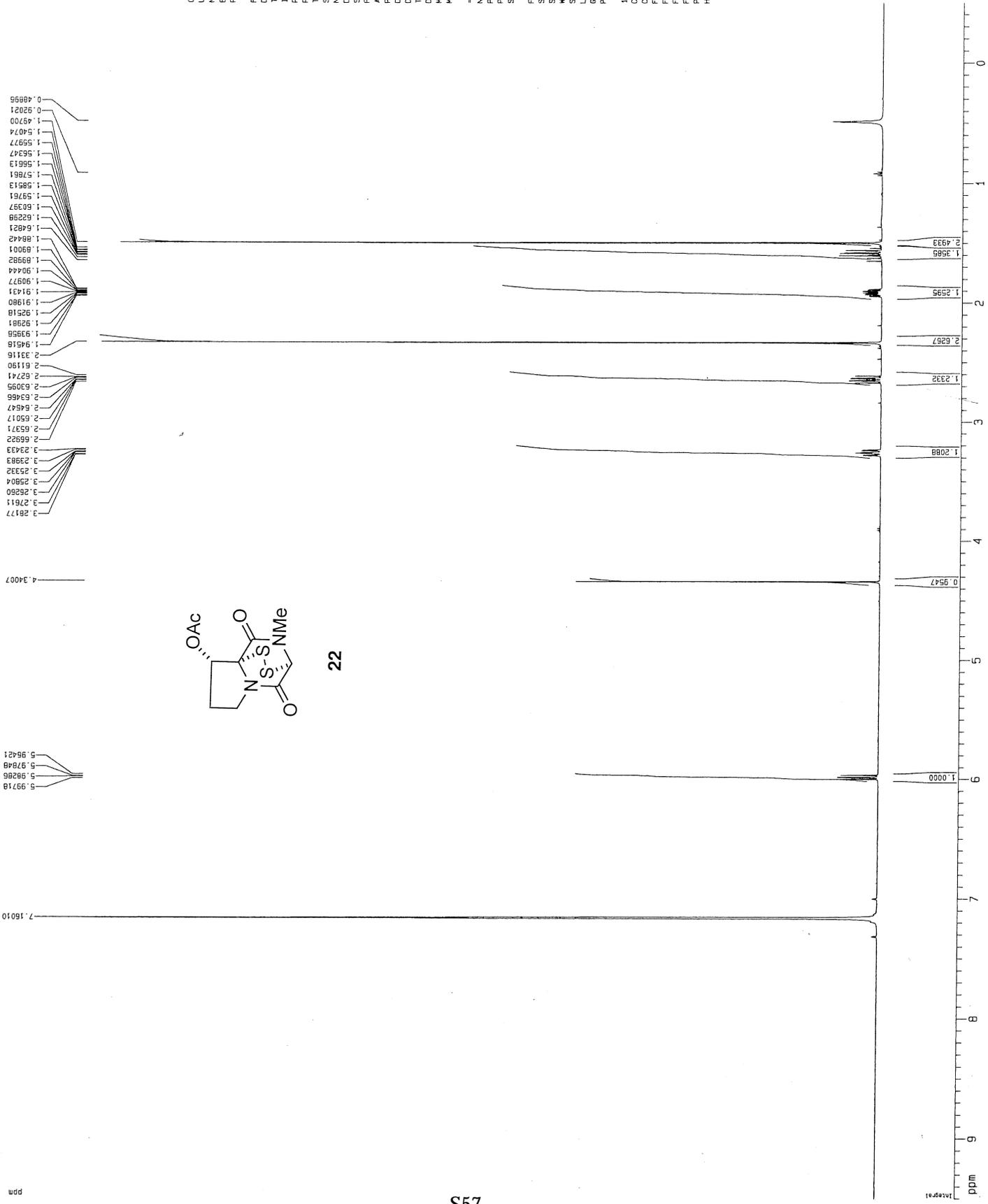
1D NMR plot parameters  
 CX 22.60 cm  
 CY 37.46 cm  
 F1 5704.253 ppm  
 F2 -0.500 ppm  
 F3 -300.07 Hz  
 PPHUM 0.43860 ppm/cm  
 HZCM 263.21494 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters  
 Date\_ 15-2-1025M08  
 NAME\_ 15-2-1025M08acetate13C  
 EXPNO\_ 2  
 PROCNO\_ 1  
 F2 - Acquisition Parameters  
 Date\_ 20070528  
 Time\_ 19:21  
 INSTRUM\_ crys500  
 PROBRD\_ 5 mm CPXI 1H  
 PULPROG\_ zgpg30  
 TO SOLVENT\_ DMSO-d6  
 NS\_ 19  
 DS\_ 4  
 SWH\_ 30393.074 Hz  
 FIDRES\_ 0.46322 Hz  
 AQ\_ 1.0794470 sec  
 RG\_ 3281  
 DM\_ 16.2900 usec  
 DE\_ 1.00 usec  
 TE\_ 298.2 K  
 D1\_ 0.25000000 sec  
 d11\_ 0.03000000 sec  
 ACQRES\_ 0.00000000 sec  
 FWHM\_ 0.03000000 sec  
 \*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1\_ 13C  
 P1\_ 12.00 usec  
 PL1\_ -1.00 dB  
 SFO1\_ 125.7645618 MHz  
 \*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 NUC2\_ 1H  
 P2\_ 100.00 usec  
 PL2\_ 1.60 dB  
 SFO2\_ 500.1364550 MHz  
 F2 - Processing parameters  
 SI\_ 65536  
 SF\_ 125.760337 MHz  
 SN\_ 0  
 LB\_ 1.00 Hz  
 GB\_ 0  
 SB\_ 0  
 PL\_ 2.00  
 ID NH1 plot parameters  
 CX\_ 22.86 cm  
 CY\_ 137.37 cm  
 F1P\_ 250.637 ppm  
 F2P\_ -10.267 ppm  
 F2\_ -1263.96 Hz  
 PP4MCH\_ 10.56868 ppm/cm  
 HZCM\_ 1326.10250 Hz/cm

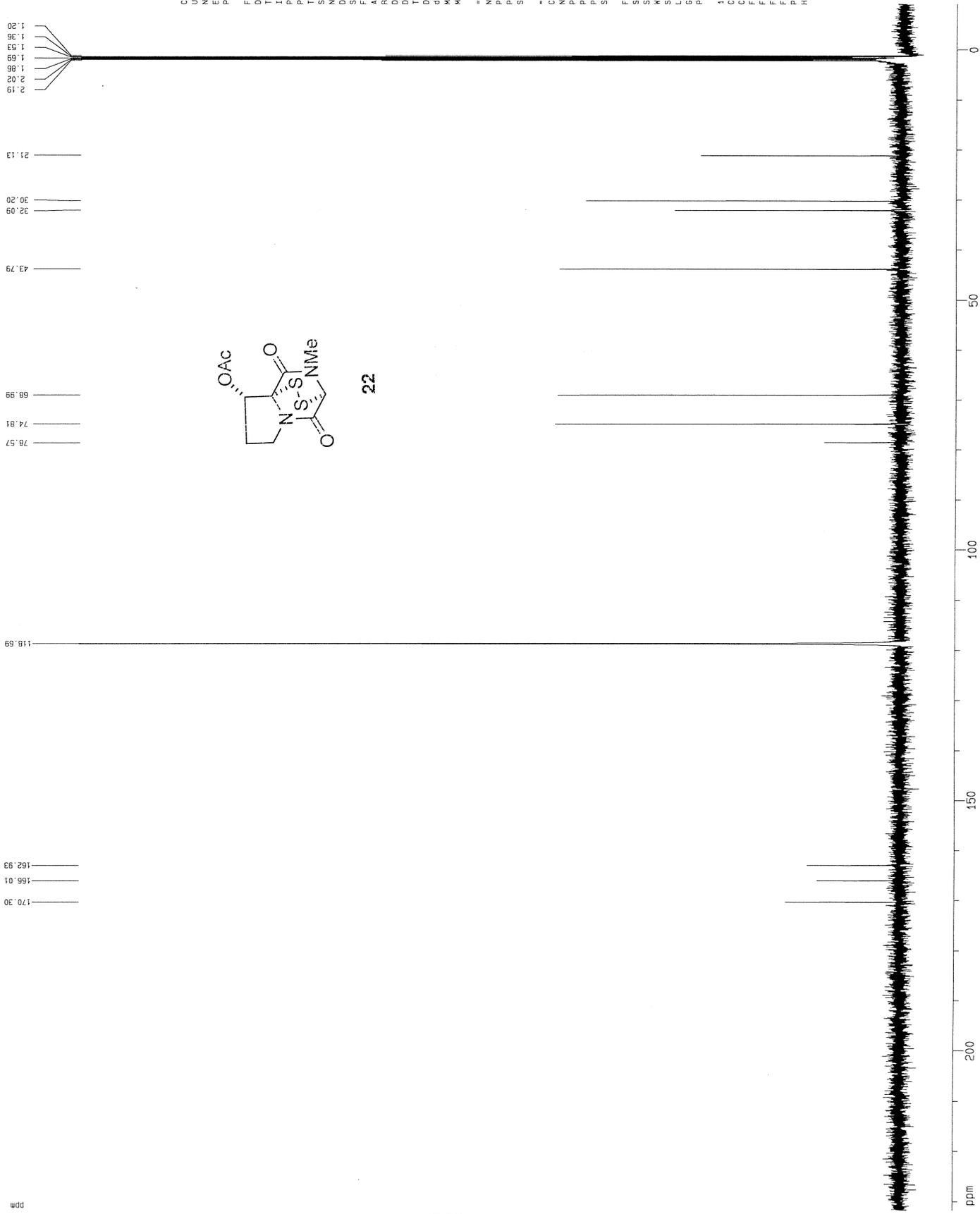
1H spectrum



22

Current Data Parameters  
 USER kaaabo  
 NAME TS-2-128HPLCS2  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20070818  
 Time 20.50  
 INSTRUM crys500  
 PROBHD 5 mm QNP1H  
 PULPROG zg30  
 TO 81728  
 SOLVENT acet  
 NS 20  
 DS 2  
 SWH 8012.920 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.098774 sec  
 RG 327.50  
 DE 62.400 usec  
 TE 298.0 K  
 D1 0.10000000 sec  
 MCREST 0.00000000 sec  
 MCMRK 0.01500000 sec  
 \*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 6.00 usec  
 PL1 1.60 dB  
 SFO1 500.2235015 MHz  
 F2 - Processing parameters  
 SI 65536  
 SF 500.2200008 MHz  
 NDM no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 4.00  
 ID NMR plot parameters  
 CX 22.80 cm  
 CY 13.84 cm  
 F1 4752.00 mm  
 F2 -0.500 mm  
 F3 -250.11 Hz  
 PPMCM 0.43860 ppm/cm  
 HZCM 219.33474 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters  
 USER tasato  
 NAME TS-2-16data  
 EXPNO 102  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 2007002  
 Time 0.23  
 INSTRM cp130  
 PROBRD 5 mm CP130  
 PULPROG zgpg30  
 TD 65418  
 SOLVENT DMSO-d6  
 NS 38  
 DS 4

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

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 P2 100.00 usec  
 PL2 1.80 dB  
 PL12 1.80 dB  
 SFO2 500.225011 MHz

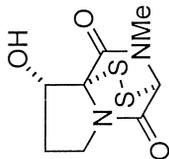
F2 - Processing parameters  
 SI 65536  
 SF 125.7802535 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 2.00

1D NMR plot parameters  
 CX 22.80 cm  
 CY 71.61 cm  
 F1P 231.776 ppm  
 F1 29.8282 MHz  
 F2P 11.272 ppm  
 F2 -1150.21 Hz  
 PPMCK 10.56669 DDM/cm  
 HZCM 1329.08932 Hz/cm

1H spectrum

ppm

5.8752  
 5.1787  
 5.1670  
 5.1503  
 4.8347  
 3.8194  
 3.8081  
 3.7547  
 3.7240  
 3.7027  
 3.7706  
 3.7731  
 3.4491  
 3.4343  
 3.4286  
 3.4206  
 3.4170  
 3.4154  
 3.4173  
 3.3913  
 3.3157  
 3.3128  
 3.3107  
 3.3075  
 3.3044  
 3.0728  
 2.9732  
 2.8885  
 2.8523  
 2.8590  
 2.8715  
 2.8806  
 2.8543  
 2.8600  
 2.8562  
 2.8516  
 2.8437  
 2.4408  
 2.2504  
 2.2185  
 2.2109  
 2.2020  
 2.1795  
 2.1852  
 2.1898  
 2.1688  
 2.2905



23

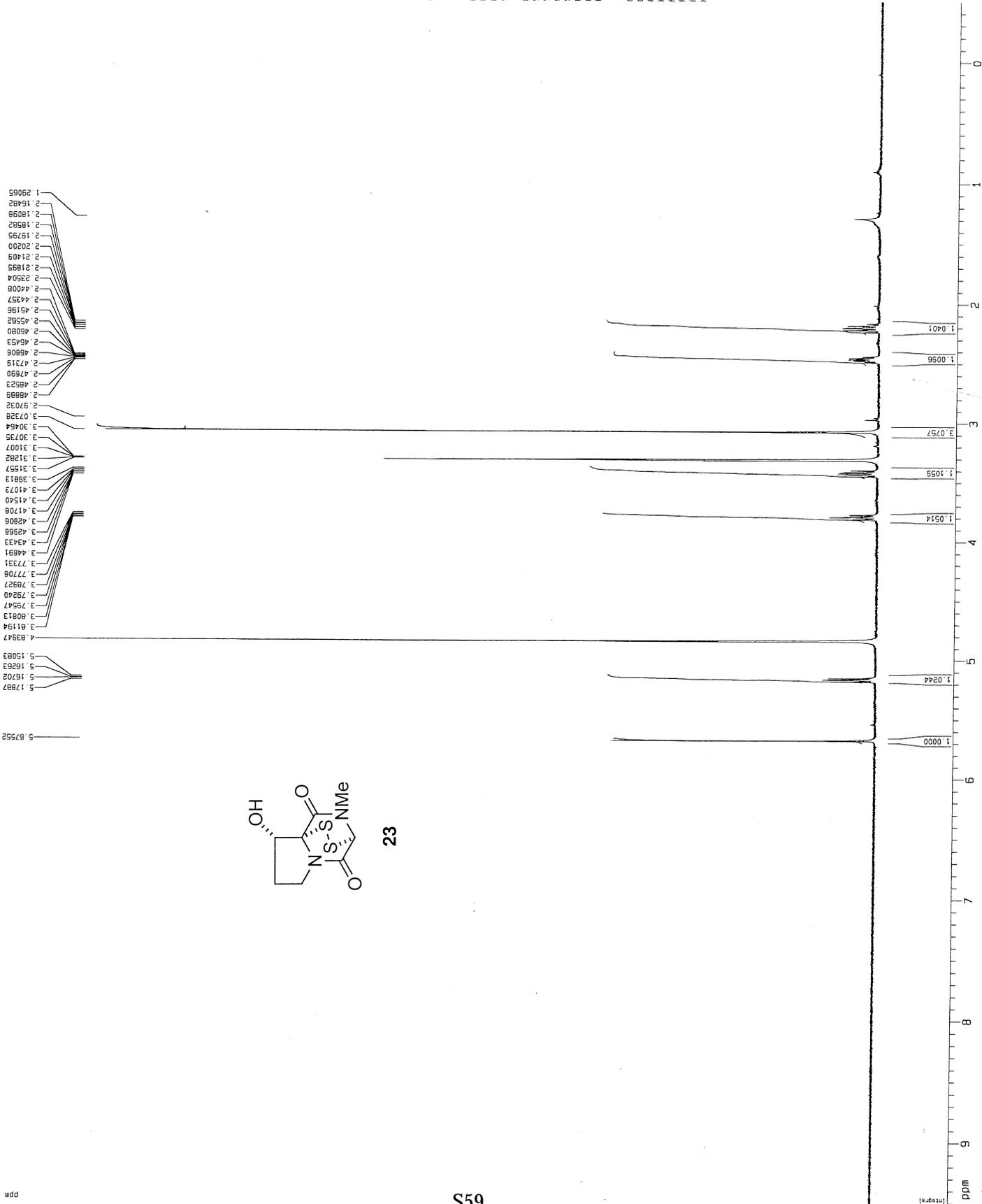
Current Data Parameters  
 USER: asac  
 NAME: TS-2-150601  
 EXPNO: 1  
 PROCNO: 1

F2 - Acquisition Parameters  
 Date\_: 20070914  
 Time: 13.26  
 INSTRUM: av600  
 PROBH0: 5 mm 1H/13  
 PULPROG: zg30  
 TD: 98074  
 SOLVENT: CD300  
 NS: 19  
 DS: 2  
 SWH: 9615.385 Hz  
 FIDRES: 0.038062 Hz  
 AQ: 0.020000 sec  
 RG: 320  
 DM: 52.000 usec  
 DE: 6.00 usec  
 TE: 299.0 K  
 D1: 0.10000000 sec  
 TDO: 1

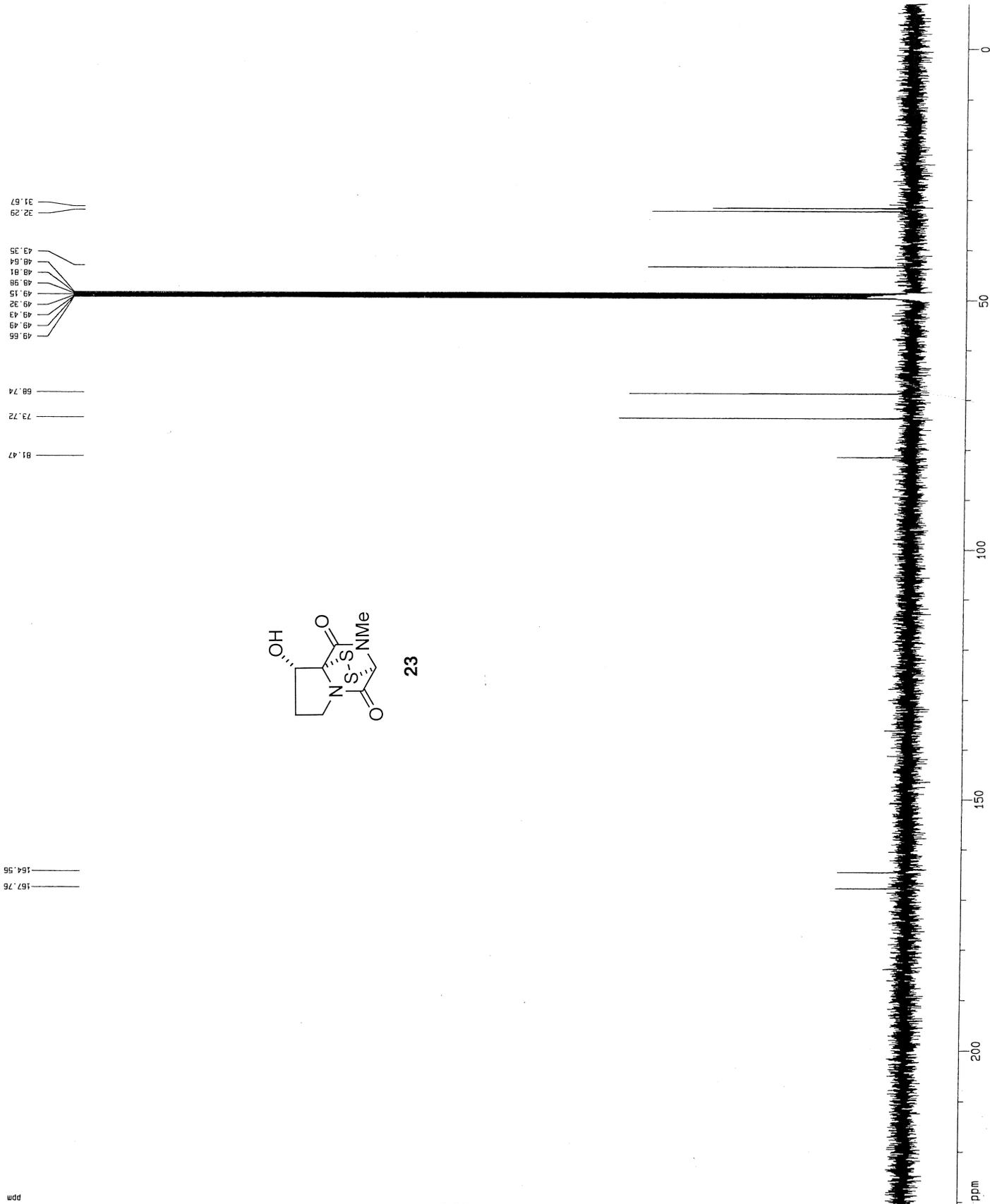
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1: 1H  
 P1: 8.00 usec  
 PL1: -1.00 dB  
 SFO1: 600.1342009 MHz

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

10 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: 263.21484 Hz/cm



13C spectrum with 1H decoupling



Current Data Parameters  
 USER tassato  
 NAME TS-2-16CD0013C  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070814  
 Time 13.05  
 INSTRUM crys500  
 PROBHD 5 mm CPTCL H-  
 PULPROG zgpg30  
 TD 65418  
 SOLVENT CD300  
 NS 89  
 DS 4  
 SMH 30303.031 Hz  
 FIDRES 0.463222 Hz  
 AQ 1.0794635 sec  
 RG 10221.3  
 CM 16.500 USEC  
 CO 2.00 USEC  
 TE 300.2 K  
 DE 1.00 USEC  
 DI 0.25000000 sec  
 d11 0.03000000 sec  
 d12 0.03000000 sec  
 d13 0.03000000 sec  
 d14 0.03000000 sec  
 d15 0.03000000 sec  
 d16 0.03000000 sec  
 d17 0.03000000 sec  
 d18 0.03000000 sec  
 d19 0.03000000 sec  
 d20 0.03000000 sec  
 d21 0.03000000 sec  
 d22 0.03000000 sec  
 d23 0.03000000 sec  
 d24 0.03000000 sec  
 d25 0.03000000 sec  
 d26 0.03000000 sec  
 d27 0.03000000 sec  
 d28 0.03000000 sec  
 d29 0.03000000 sec  
 d30 0.03000000 sec  
 d31 0.03000000 sec  
 d32 0.03000000 sec  
 d33 0.03000000 sec  
 d34 0.03000000 sec  
 d35 0.03000000 sec  
 d36 0.03000000 sec  
 d37 0.03000000 sec  
 d38 0.03000000 sec  
 d39 0.03000000 sec  
 d40 0.03000000 sec  
 d41 0.03000000 sec  
 d42 0.03000000 sec  
 d43 0.03000000 sec  
 d44 0.03000000 sec  
 d45 0.03000000 sec  
 d46 0.03000000 sec  
 d47 0.03000000 sec  
 d48 0.03000000 sec  
 d49 0.03000000 sec  
 d50 0.03000000 sec  
 d51 0.03000000 sec  
 d52 0.03000000 sec  
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 d61 0.03000000 sec  
 d62 0.03000000 sec  
 d63 0.03000000 sec  
 d64 0.03000000 sec  
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 d66 0.03000000 sec  
 d67 0.03000000 sec  
 d68 0.03000000 sec  
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 d70 0.03000000 sec  
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 d72 0.03000000 sec  
 d73 0.03000000 sec  
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 d75 0.03000000 sec  
 d76 0.03000000 sec  
 d77 0.03000000 sec  
 d78 0.03000000 sec  
 d79 0.03000000 sec  
 d80 0.03000000 sec  
 d81 0.03000000 sec  
 d82 0.03000000 sec  
 d83 0.03000000 sec  
 d84 0.03000000 sec  
 d85 0.03000000 sec  
 d86 0.03000000 sec  
 d87 0.03000000 sec  
 d88 0.03000000 sec  
 d89 0.03000000 sec  
 d90 0.03000000 sec  
 d91 0.03000000 sec  
 d92 0.03000000 sec  
 d93 0.03000000 sec  
 d94 0.03000000 sec  
 d95 0.03000000 sec  
 d96 0.03000000 sec  
 d97 0.03000000 sec  
 d98 0.03000000 sec  
 d99 0.03000000 sec  
 d100 0.03000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 15.00 USEC  
 PL1 -1.00 dB  
 SF01 125.7542548 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 P2 100.00 USEC  
 PL2 1.50 dB  
 PL12 23.54 dB  
 SF02 500.2225011 MHz

F2 - Processing parameters  
 SI 65536  
 SF 125.7802274 MHz  
 MDW 0  
 EHQ 0  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 2.00

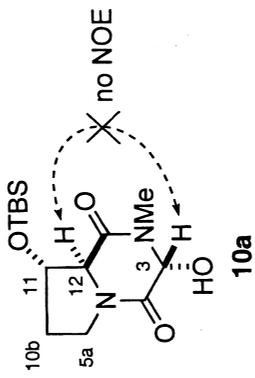
1D NMR plot parameters  
 CX 22.80 cm  
 CY 124.60 cm  
 F1P 230.637 ppm  
 F1 23009.63 Hz  
 F2P -10.267 ppm  
 F2 -1293.96 Hz  
 PPMCM 10.56688 ppm/cm  
 HZCM 1329.10510 Hz/cm

0.9594  
0.9578

3.11972

12

3



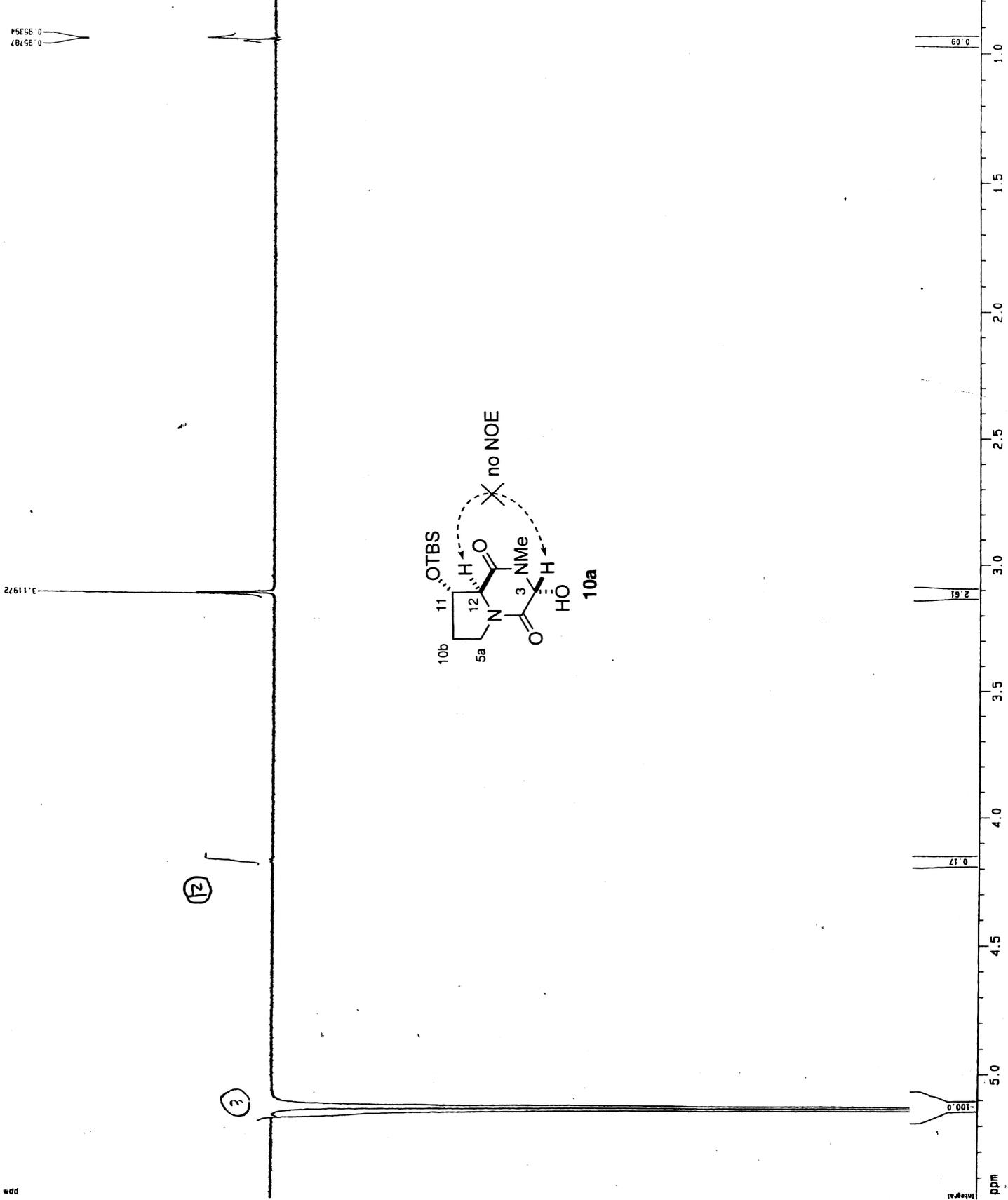
Current Data Parameters  
 USP tasato  
 NAME 15-2-43001arnue2  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20070512  
 Time 23 38  
 INSTRUM gn500  
 PROBHD 5 mm broadband  
 PULPROG zgpg30  
 TO gaoctc wu  
 SOLVENT CDCl3  
 NS 128  
 DS 4  
 SWH 5482.465 Hz  
 FIDRES 0.08355 Hz  
 AQ 5.977326 sec  
 RG 1625.5  
 DW 91.200 usec  
 DE 16.00 usec  
 TE 298.0 K  
 O1 1.0000000 sec  
 D1 0.5000000 sec  
 D16 0.0002000 sec  
 D21 0.3337499 sec  
 D22 0.1639959 sec  
 P2 24.00 usec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 12.00 usec  
 D3 36.00 usec  
 P4 48.00 usec  
 D5 32.00 usec  
 P12 40000.00 usec  
 SFO 499.9326563 MHz  
 SFO 52.30 MHz  
 SFO 98.91512 MHz  
 SFOFF1 0.00 Hz

\*\*\*\*\* GRADIENT CHANNEL \*\*\*\*\*  
 GPMN1 line 100  
 GPMN2 line 100  
 GPMN3 line 100  
 GPMN4 line 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 0.00 %  
 GPZ2 0.00 %  
 GPZ3 0.00 %  
 GPZ4 0.00 %  
 P16 1000.00 usec

F2 - Processing Parameters  
 S1 65536  
 SF 499.9300000 MHz  
 MDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

10 NMR plot parameters  
 CA 2.00 cm  
 CB 50.00 cm  
 CIP 5.482 cm  
 F1 2740.718 Hz  
 F2 0.779 ppm  
 F2 389.51 Hz  
 PPMCH 0.20628 ppm/cm  
 MZCH 103.12856 Hz/cm



Current Data Parameters  
 USER casato  
 NAME TS-2-043186D01ARNUESY  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters

Date\_ 20070513  
 Time 1.13  
 INSTRUM gr500  
 PROBHD 5 mm broadband  
 PULPROG noesygptp  
 TD 2048  
 SOLVENT CDC13  
 NS 28  
 DS 16  
 SWH 2026.051 Hz  
 FIDRES 1.292251 Hz  
 AQ 0.3698882 sec  
 RG 101.5  
 DM 180.400 uSBC  
 DE 6.00 uSBC  
 TE 298.0 K  
 D0 0.00000000 sec  
 D1 2.00000000 sec  
 D2 0.00025000 sec  
 D3 1.00025000 sec  
 D4 0.49875000 sec  
 INO 0.00049040 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*

NUC1 1H  
 P1 12.00 uSBC  
 P2 24.00 uSBC  
 PL1 -3.00 dB  
 SFO1 499.9313078 MHz

\*\*\*\*\* GRADIENT CHANNEL \*\*\*\*\*

GPMA1 0.00 %  
 GPMX1 0.00 %  
 GPMY1 0.00 %  
 GPMZ1 0.00 %  
 GPMX2 0.00 %  
 GPMY2 0.00 %  
 GPMZ2 -40.00 %  
 P18 1000.00 uSBC

F1 - Acquisition parameters

NU0 2  
 TD 256  
 SFO1 499.9313 MHz  
 FIDRES 10.259010 Hz  
 SW 5.253 ppm  
 FMODE unrefined

F2 - Processing parameters

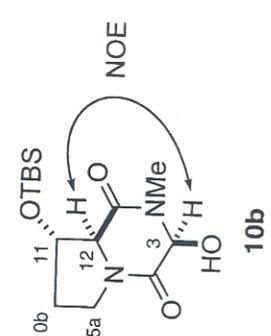
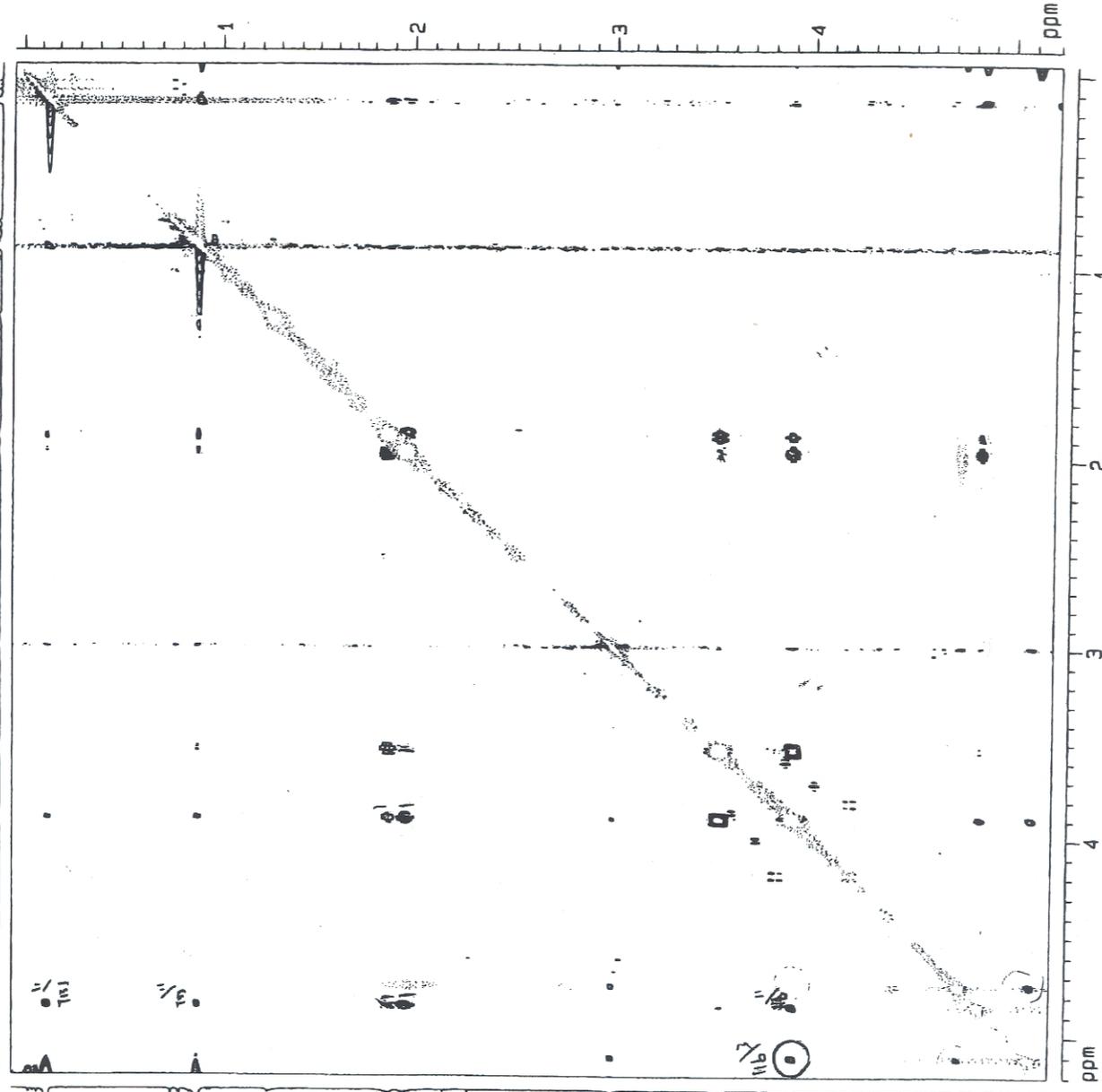
SI 1024  
 SF 499.9300204 MHz  
 WDW 0.5TINE  
 SSB 2  
 LB 0.00 Hz  
 GB 0  
 PC 1.40

F1 - Processing parameters

SI 1024  
 MC2 TPPI  
 SF 499.9300204 MHz  
 WDW 0.5TINE  
 SSB 2  
 LB 0.00 Hz  
 GB 0

2D NMR plot parameters

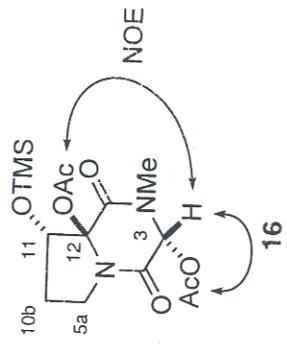
CX2 15.00 cm  
 CX1 15.00 cm  
 F2PL0 5.202 ppm  
 F2L0 2600.51 Hz  
 F2PM1 -0.051 ppm  
 F2H1 -25.54 Hz  
 F1PL0 5.202 ppm  
 F1L0 2600.51 Hz  
 F1PM1 -0.051 ppm  
 F1H1 -25.54 Hz  
 F2PMCM 0.35019 ppm/cm  
 F2H2CM 175.07002 Hz/cm  
 F1PMCM 0.35019 ppm/cm  
 F1H2CM 175.07002 Hz/cm



noesygptp

noesygp

S63



Current Data Parameters  
 USER labtdc  
 NAME TS-2-043NDESY  
 CAPND 102  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20070526  
 Time 20.57  
 INSTRUM av600  
 PROBHD 5 mm TBI 1H/13  
 PULPROG noesygph  
 TO 1912  
 SOLVENT CDCl3  
 NS 4  
 DS 16  
 SWH 9615.365 Hz  
 FIDRES 5.026967 Hz  
 AQ 0.0594740 sec  
 RG 57  
 DW 52.000 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D0 0.00044161 sec  
 D1 2.00000000 sec  
 D8 1.00000000 sec  
 D16 0.00020000 sec  
 INO 0.00010400 sec  
 STICHT 128  
 TAU 0.49680001 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 8.00 usec  
 P2 16.00 usec  
 PL1 -1.00 dB  
 SFO1 600.1342009 MHz

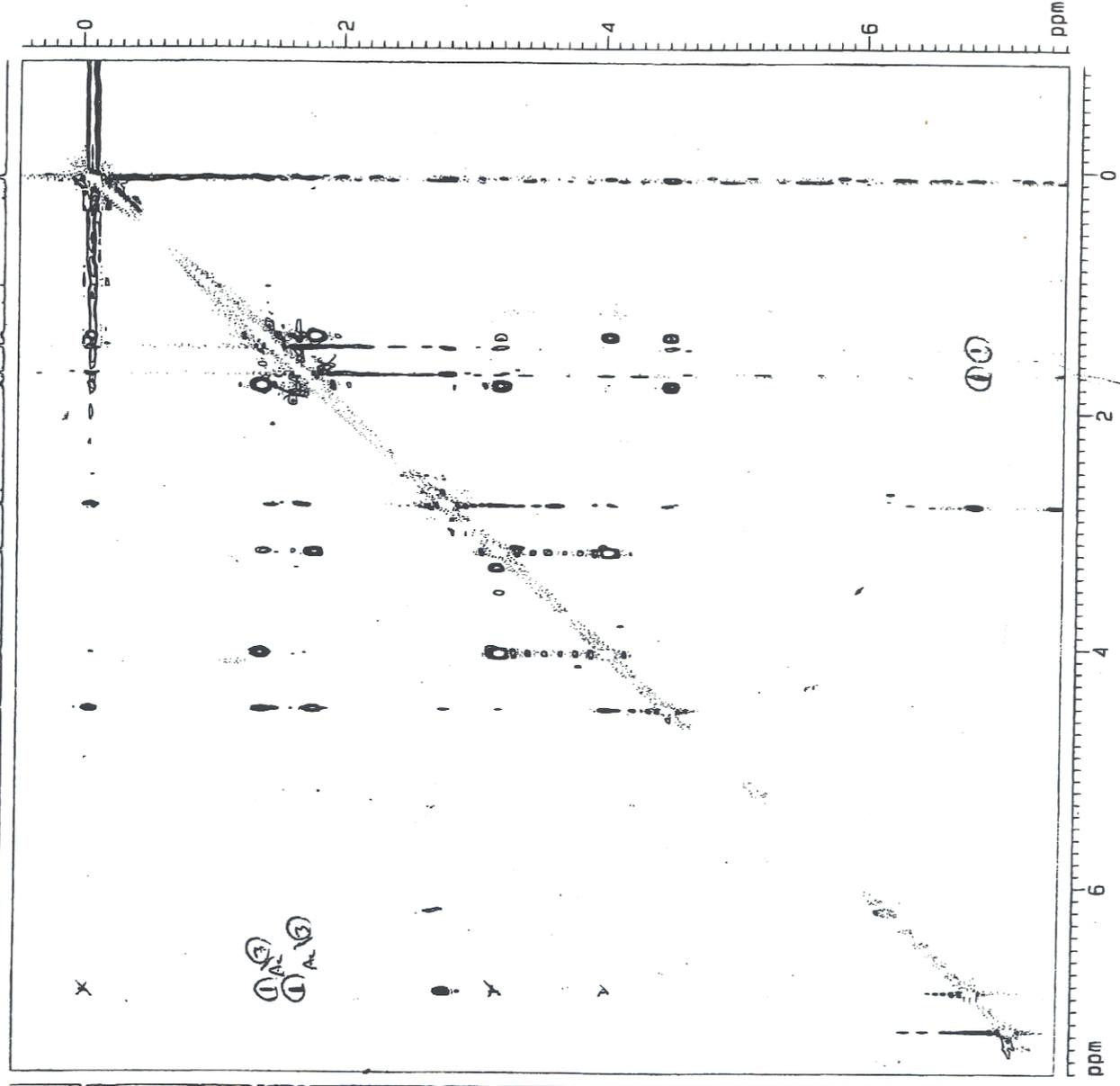
\*\*\*\*\* GRADIENT CHANNEL \*\*\*\*\*  
 GPNAM1 SINE.100  
 GPNAM2 SINE.100  
 GPZ1 40.00 %  
 GPZ2 -40.00 %  
 P16 1000.00 usec

F1 - Acquisition parameters  
 ND0 1  
 TO 256  
 SFO1 600.1342 MHz  
 FIDRES 37.560097 Hz  
 SN 16.022 dB  
 FMODE States-TPT1

F2 - Processing parameters  
 SI 1024  
 SF 600.1259573 MHz  
 WDW 0.5SINE  
 SSB 2  
 LB 0.00 Hz  
 GB 0  
 PC 1.00

F1 - Processing parameters  
 SI 1024  
 MC2 States-TPT1  
 SF 600.1259573 MHz  
 WDW 0.5SINE  
 SSB 2  
 LB 0.00 Hz  
 GB 0

2D NMR plot parameters  
 CN2 15.00 cm  
 CN1 15.00 cm  
 F2PL0 7.505 ppm  
 F2L0 4504.30 Hz  
 F2PHI -0.866 ppm  
 F2H1 -519.56 Hz  
 F1PL0 7.521 ppm  
 F1L0 4513.49 Hz  
 F1PHI -0.475 ppm  
 F1H1 -284.81 Hz  
 F2PRICH 0.56806 ppm/cm  
 F2MZN 334.91086 Hz/cm  
 F1PRICH 0.53303 ppm/cm  
 F1MZN 319.88681 Hz/cm



Current Data Parameters  
 USER tsasto  
 NAME TS-2-16 HPLC/NOESY  
 EXPNO 3101  
 PROCNO 1

F2 - Acquisition Parameters

Date\_ 20070803  
 Time 22:35  
 INSTRUM av600  
 PROBO 5 mm TBI 1H/13  
 PULPROG noesygdph  
 TD 1312  
 SOLVENT DMSO  
 NS 36  
 DS 16  
 SWH 4201.681 MHz  
 FIDRES 2.197532 MHz  
 AQ 0.2275780 sec  
 RG 57  
 DM 119.000 usec  
 DE 5.00 usec  
 TE 298.0 K  
 D0 0.0004181 sec  
 D1 2.0000000 sec  
 D8 1.0000000 sec  
 D16 0.0002000 sec  
 INO 0.0001000 sec  
 ST1CNT 128  
 TAU 0.49860001 sec

\*\*\*\*\* CHANNEL F1 \*\*\*\*\*

NUC1 1H  
 P1 8.00 usec  
 PL1 -1.00 dB  
 SF01 600.1321005 MHz  
 \*\*\*\*\* GRADIENT CHANNEL \*\*\*\*\*  
 GPNAM1 SINE 100  
 GPNAM2 SINE 100  
 GPZ1 40.00 %  
 GPZ2 -40.00 %  
 P16 1000.00 usec

F1 - Acquisition Parameters

NUC 1  
 TD 256  
 SF01 600.1321 MHz  
 FIDRES 37.560097 MHz  
 SM 16.022 ppm  
 FMODE States-TPI

F2 - Processing parameters

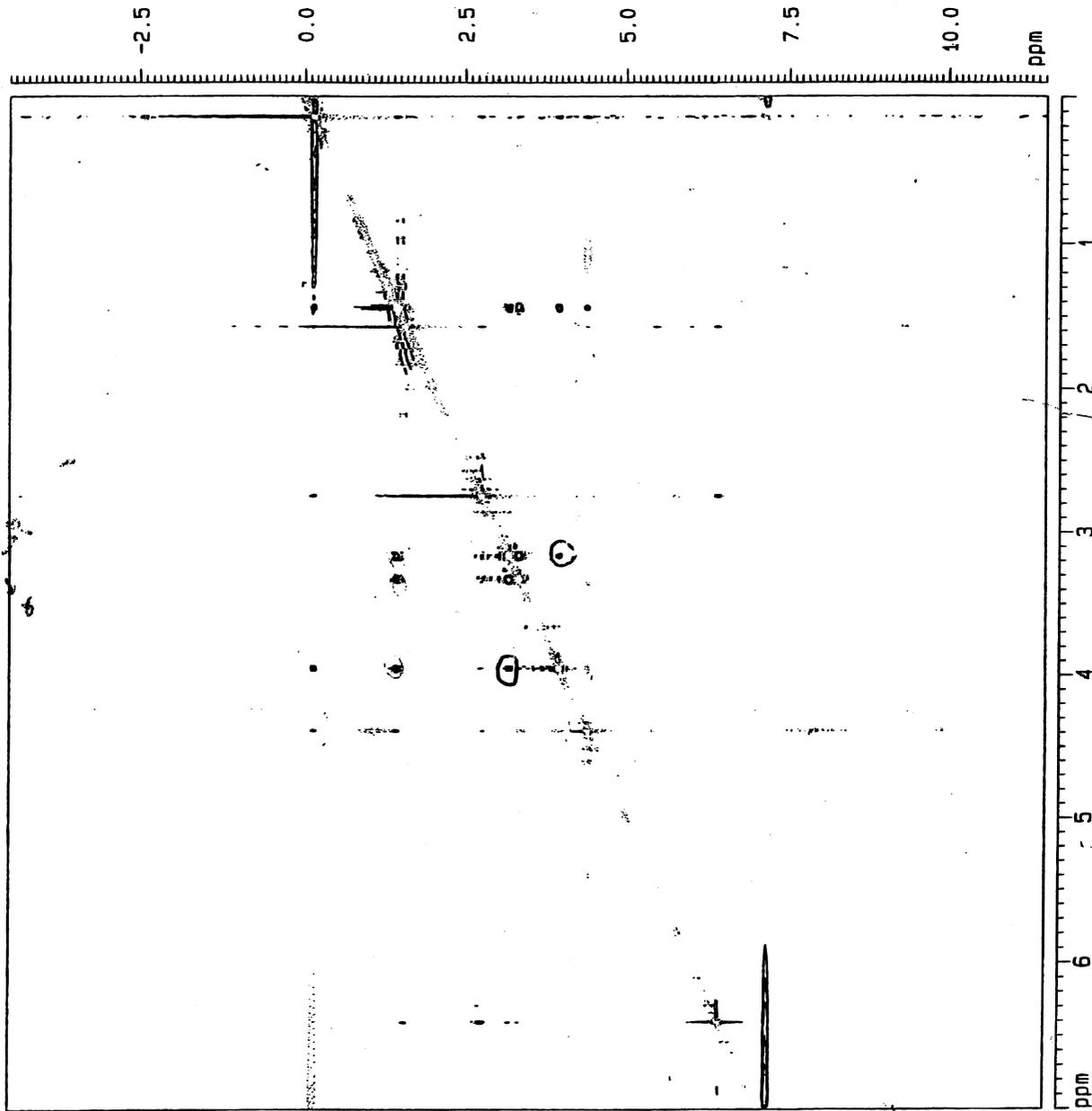
SI 1024  
 SF 600.1300000 MHz  
 USINE  
 MDM 2  
 SSB 2  
 LB 0.00 MHz  
 GB 0  
 PC 1.00

F1 - Processing parameters

SI 1024  
 MC2 States-TPI  
 SF 600.1300000 MHz  
 USINE  
 SSB 2  
 LB 0.00 MHz  
 GB 0

2D NMR plot parameters

CX2 15.00 cm  
 CX1 15.00 cm  
 FSRLO 7.001 ppm  
 FZLO 4201.30 MHz  
 FZHI -0.001 ppm  
 F1LO 11.511 ppm  
 F1HI 6908.14 MHz  
 F1HI -4.511 ppm  
 F1HI -2707.24 MHz  
 F2PPOCM 0.46675 ppm/cm  
 F2RZCM 280.11203 Hz/cm  
 F1PPOCM 1.06816 ppm/cm  
 F1RZCM 641.02563 Hz/cm



noesygd

