



Supporting Information

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## Supporting Information

# **(+)-Zwittermicin A (ZwA). Complete Configuration and Implication of D-Serine in its Biosynthesis by Total Synthesis of (–)-ZwA.**

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**General Procedures:** All non-aqueous reactions were carried out in oven-dried glassware under a nitrogen atmosphere, unless otherwise noted. All solvents were reagent grade. Solvents for dry reactions (DCM, DMF, THF, toluene, acetonitrile, Et<sub>2</sub>O) were passed through twin alumina columns (J. C. Myer, Glass Contour). DMSO was distilled from calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Dry MeOH was prepared and stored over 4 Å molecular sieves. Triethylamine and pyridine were distilled from calcium hydride. All other commercially available reagents were used as received. Reactions were monitored by thin layer chromatography (TLC) using 0.25-mm E. Merck per-coated silica gel plates.

NMR spectra were recorded in CDCl<sub>3</sub> (unless otherwise stated) using either a Varian Mercury-400 (400 MHz) or a Varian Unity-500 (500 MHz). Residual solvent signals were used for reference (CHCl<sub>3</sub> at δ 7.26 ppm for <sup>1</sup>H, δ 77.16 for <sup>13</sup>C NMR). HRMS measurements were measured at the University of California, Riverside or University of California, San Diego mass spectrometry facilities. Optical rotations were obtained using a Jasco P-1010 or a Jasco P-2000 polarimeters in cells of 10 mm pathlength (concentrations, *c*, expressed in g/100 mL). IR spectra were recorded on a Nicolet Magna IR 550 FTIR spectrometer as thin films (deposited on KBr plates) or on a Jasco 4100 FTIR using ATR (ZnSe plate). The ee analysis for diaminopropionamides (–)-**8** and (+)-**8** were conducted using Marfey's method<sup>[19]</sup> by derivatization with 2,4-dinitrophenyl-5-fluoro-L-leucinamide under standard conditions followed by analysis (C<sub>18</sub> HPLC-MS).

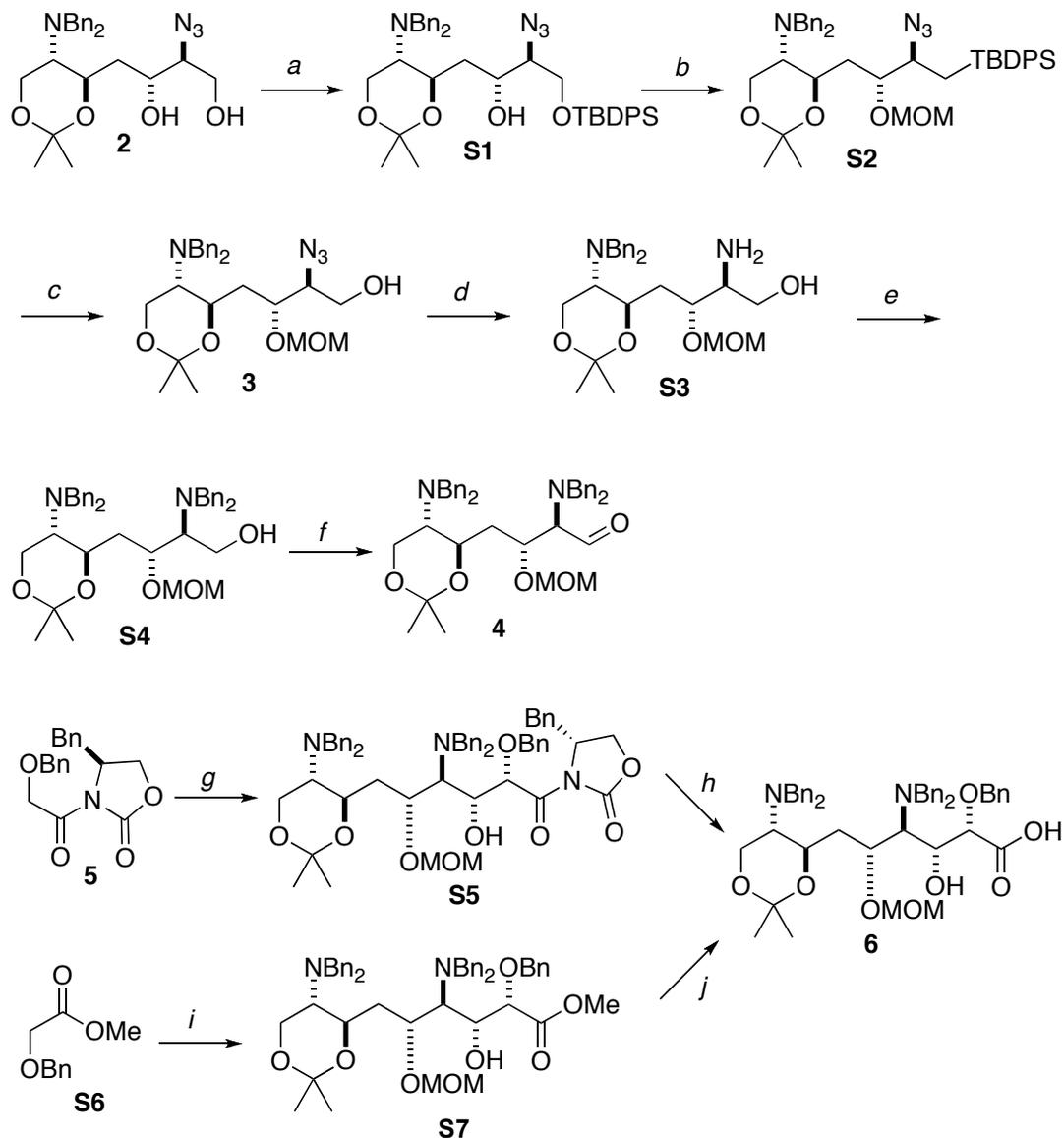
#### **Biological Evaluation of (+)- and (–)-Zwittermicin A: Fungal Strains and Culture conditions**

The fungal isolates used in this study were strains of *Candida albicans* (2 clinical isolates which are fluconazole-resistant, strain UCDFR1 and 96-489 and a reference strain, ATCC 14503), clinical isolates of *Candida glabrata* and *Candida krusei*. The fungi were grown and maintained in Sabouraud dextrose agar, SDA plates (BBL, 211584) and incubated at 30°C for 24 h (*Candida* sp.). The *in vitro* susceptibility of each compound was determined by the broth micro dilution method according to the guidelines National Committee for Clinical Laboratory Standards (NCCLS; National Committee for Clinical Laboratory Standards, 2002 . Reference method for broth dilution antifungal susceptibility testing of yeast, 2nd ed. Approved standard M27-A2. National Committee for Clinical Laboratory Standards, Wayne, Pennsylvania, USA) Briefly, 2-fold serial dilutions of compounds were prepared in 96-well microtiter plates (Corning Incorporated, 3595) from stock solutions in an RPMI-1640 broth medium (Sigma) buffered to a final pH of 7.5 with 0.165 M morpholinepropane-sulfonic acid (MOPS; Sigma) to a final volume of 100 μL. A stock solution was prepared in sterile H<sub>2</sub>O for the various zwittermicin compounds and for amphotericin B (Sigma) which was used as control. The final drug concentrations tested were from 0.5 to 128 μg/mL and from 0.03 to 8 μg/mL for amphotericin B .

Fungal inocula were prepared from 24-h (*Candida* sp.) cultures on SDA plates. The inocula were harvested by harvesting a single colony of yeast into a sterile saline tube and diluted into RPMI-1640 broth medium to yield a final inoculum concentration of 2 × 10<sup>3</sup> cells per mL. The micro dilution wells, which contained 100 μL of the serially diluted drug, were inoculated with 100 μL of the resulting fungal suspension. The final inoculum concentration after dilution with the drug suspension was 10<sup>3</sup>/10<sup>4</sup> cells per mL. Four wells containing the drug-free medium, H<sub>2</sub>O and inoculum were used as controls. The inoculated plates were incubated at 30°C for 24 h (*Candida* sp.). All fungal strains were tested in duplicate in each run of the experiments. The growth was determined by the OD at 600 nm using a Spectramax Plus 384 microplate reader (Molecular Devices, CA). The MIC endpoint was defined as the lowest concentration with complete (90%) growth inhibition.

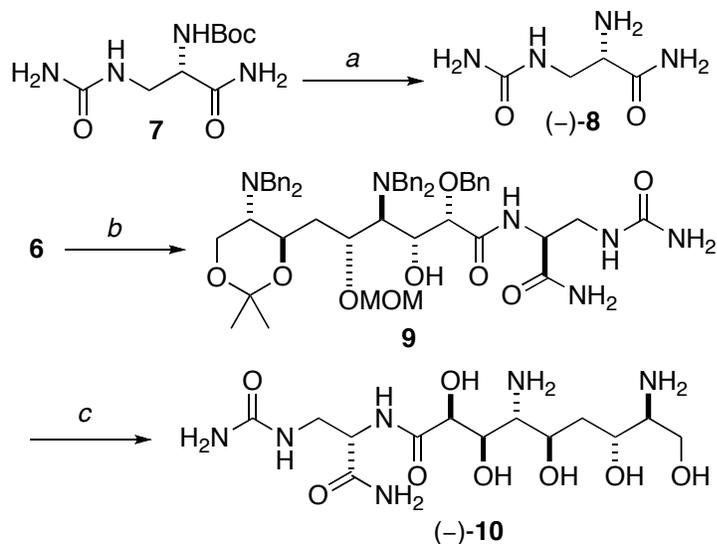
[19] P. Marfey, *Carlsberg Res. Commun.* **1984**, *49*, 591-596.

**Scheme S1:** Synthesis of carboxylic acid **6**.



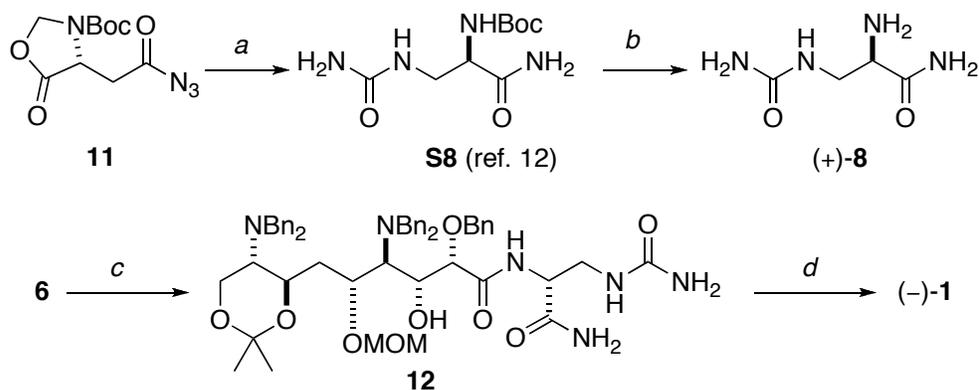
(a) TBDPSCl, imidazole, DMF, 0 °C-rt, 4 h, 91%; (b) MeOCH<sub>2</sub>Cl, Hünig's base, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C-rt, 56 h, 98%; (c) TBAF, THF, -10 °C, 4 h, 95%; (d) Lindlar's cat., H<sub>2</sub>, (1 atm), EtOH, 14 h, 98%; (e) BnBr, K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, 31 h, 91%; (f) (i) (COCl)<sub>2</sub>, DMSO, CH<sub>2</sub>Cl<sub>2</sub>, -78 °C, (ii) Et<sub>3</sub>N, 94%; (g) (i) *n*-Bu<sub>2</sub>BOTf, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, -78 to 0 °C, 3 h, (ii) **4**, -78 to 0 °C, 2.5 h, 77%, dr 24:1; (h) H<sub>2</sub>O<sub>2</sub>, LiOH, 0 °C, 30 min, 96%; (i) (i) *n*-Bu<sub>2</sub>BOTf, Hünig's base, Et<sub>2</sub>O, -78 °C, 1.5 h, (ii) **4**, -78 to 0 °C, 2 h, 44%, 37% de; (j) LiOH, H<sub>2</sub>O:MeOH:THF (2:3:2), rt, 4.5 h, 81%.

**Scheme S2:** Synthesis of proposed zwittermicin A structure **10**.



(a) TFA, 0 °C, 1 h, 98%; (b) (i) EDCl, HOBT, DMF, 0 °C, 10 min, (ii) **(-)-8**, Et<sub>3</sub>N, 0 °C-rt, 1 h, 81%; (c) (i) HCl, MeOH, H<sub>2</sub> (5 atm), Pd/C, 1 h, (ii) HCl, H<sub>2</sub>O, H<sub>2</sub> (5 atm), Pd/C, 1 h, 76%.

**Scheme S3:** Synthesis of (-)-zwittermicin A.



(a) (i)  $\mu$ W, toluene, 110 °C, 15 min, (ii) THF, NH<sub>3</sub>, 30 min, (iii) 2M NH<sub>3</sub>, MeOH, 5 h, (iv) 1N NaOH, MeOH, 4.5 h, 62%; (b) TFA, 0 °C, 1 h, 99%; (c) (i) EDCl, HOBT, DMF, 0 °C, 10 min, (ii) **(+)-8**, Et<sub>3</sub>N, 0 °C-rt, 1 h, 88%; (d) (i) HCl, MeOH, H<sub>2</sub> (5 atm), Pd/C, 1 h, (ii) HCl, H<sub>2</sub>O, H<sub>2</sub> (5 atm), Pd/C, 1 h, 75%.

## Experimental:

**(2R,3S)-3-azido-4-(tert-butylidiphenylsilyloxy)-1-((4R,5S)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-ol (S1).** *tert*-Butylidiphenylchlorosilane (492  $\mu$ L, 1.90 mmol) was added to a stirred solution of alcohol **2** (760 mg, 1.73 mmol) and imidazole (311 mg, 4.31 mmol) in dimethylformamide (8.6 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 4 hours then quenched by addition of water (175 mL). The mixture was extracted with ethyl ether (3  $\times$  50 mL) and combined extracts washed with brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Flash chromatography (Analogix 40 g silica cartridge, 1.5%, 2.5% and 5% ethyl acetate in hexane, 34 mL/min flow rate) provided **S1** (1.07 g, 91%) as a viscous oil: IR (neat)  $\nu$  3500, 3070, 2929, 2859, 2101, 1791, 1460, 1429, 1374, 1265, 1225, 1100, 819 cm<sup>-1</sup>; [ $\alpha$ ]<sub>D</sub><sup>23</sup> +42.3° (CHCl<sub>3</sub>, *c* 9.52); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.78-7.71 (m, 4H), 7.50-7.40 (m, 6H), 7.34-7.21 (m, 10H), 4.17 (ddd, *J* = 10.0, 7.5, 4.0 Hz, 1H), 3.98-3.86 (m, 5H), 3.81 (dd, *J* = 11.0, 7.5 Hz, 1H), 3.64 (m, 1H), 3.52 (d, *J* = 13.5 Hz, 2H), 3.43 (ddd, *J* = 7.5, 7.5, 3.3 Hz, 1H), 3.35 (d, *J* = 5.0 Hz, 1H), 2.80 (dt, *J* = 9.5, 6.3 Hz, 1H), 1.99 (ddd, *J* = 14.8, 9.0, 3.5 Hz, 1H), 1.65 (ddd, *J* = 14.8, 7.5, 2.0 Hz, 1H), 1.40 (s, 3H), 1.29 (s, 3H), 1.12 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.1 (C), 135.73 (CH), 135.71 (CH), 133.1 (C), 133.0 (C), 129.9 (CH), 129.0 (CH), 128.5 (CH), 127.9 (CH), 127.4 (CH), 99.4 (C), 68.3 (CH), 68.2 (CH), 67.5 (CH), 64.6 (CH<sub>2</sub>), 58.0 (CH<sub>2</sub>), 57.3 (CH), 54.8 (CH<sub>2</sub>), 35.4 (CH<sub>2</sub>), 26.9 (CH<sub>3</sub>), 26.8 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 19.2 (C); HREIMS *m/z* 678.3586 [M]<sup>+</sup>, calcd. for C<sub>40</sub>H<sub>50</sub>N<sub>4</sub>O<sub>4</sub>Si<sub>1</sub> 678.3596.

**(4R,5S)-4-((2R,3S)-3-azido-4-(tert-butylidiphenylsilyloxy)-2-(methoxymethoxy)butyl)-N,N-dibenzyl-2,2-dimethyl-1,3-dioxan-5-amine (S2).** Chloromethyl methyl ether (628  $\mu$ L, 8.27 mmol) was added to a stirred solution of alcohol **S1** (936 mg, 1.38 mmol) and Hünig's base (2.30 mL, 13.8 mmol) in dichloromethane (6.9 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 56 hours then quenched by addition of saturated aqueous NH<sub>4</sub>Cl (50 mL). The mixture was extracted with ethyl ether (3  $\times$  50 mL) and combined extracts washed with water (2  $\times$  50 mL), brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Flash chromatography (silica, 3-7% ethyl acetate in hexane) provided **S2** (977.4 mg, 98%) as a viscous oil: IR (neat)  $\nu$  3067, 3034, 3001, 2944, 2894, 2861, 2110, 1508, 1475, 1458, 1433, 1392, 1277, 1235, 1128, 1037, 831, 757, 724 cm<sup>-1</sup>; [ $\alpha$ ]<sub>D</sub><sup>24</sup> +30.8° (CHCl<sub>3</sub>, *c*

6.68);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.75 (m, 4H), 7.54-7.43 (m, 6H), 7.41 (d,  $J = 7.2$  Hz, 4H), 7.34 (t,  $J = 7.2$  Hz, 4H), 7.27 (t,  $J = 7.2$  Hz, 2H), 4.77 (d,  $J = 6.6$  Hz, 1H), 4.72 (d,  $J = 6.6$  Hz, 1H), 4.13 (t,  $J = 9.8$  Hz, 1H), 4.06-3.92 (m, 6H), 3.80-3.64 (m, 2H), 3.59 (d,  $J = 13.6$  Hz, 2H), 3.44 (s, 3H), 2.70 (dt,  $J = 9.6$ , 6.8 Hz, 1H), 3.35 (dd,  $J = 14.4$ , 10.8 Hz, 1H), 1.47 (s, 3H), 1.35 (s, 3H), 1.17 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6 (C), 135.7 (CH), 133.1 (C), 133.0 (C), 129.9 (CH), 129.0 (CH), 128.3 (CH), 127.9 (CH), 127.2 (CH), 98.9 (C), 97.7 ( $\text{CH}_2$ ) 75.6 (CH), 67.5 (CH), 66.4 (CH), 63.6 ( $\text{CH}_2$ ), 58.3 ( $\text{CH}_2$ ), 57.8 (CH), 55.9 ( $\text{CH}_3$ ), 54.7 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ), 27.3 ( $\text{CH}_3$ ), 26.8 ( $\text{CH}_3$ ), 21.2 ( $\text{CH}_3$ ), 19.2 (C); HRESIMS  $m/z$  723.3939  $[\text{M}+\text{H}]^+$ , calcd. for  $\text{C}_{42}\text{H}_{55}\text{N}_4\text{O}_5\text{Si}_1$  723.3942.

**(2*S*,3*R*)-2-azido-4-((4*R*,5*S*)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-**

**(methoxymethoxy)butan-1-ol (3).** Tetrabutylammonium fluoride (TBAF, 1M in THF, 1.69 mL, 1.69 mmol) was added to a stirred solution of azide **S2** (977 mg, 1.35 mmol) in THF (5.0 mL) at  $-10$  °C. The mixture was stirred for 4 hours then quenched by addition of water (125 mL). The mixture was extracted with ethyl ether ( $3 \times 75$  mL) and combined extracts washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Flash chromatography (silica, 1:3 ethyl acetate:hexane) provided **3** (620 mg, 95%) as a crystalline solid (needles): IR (neat)  $\nu$  3458, 2985, 2929, 2812, 2101, 1444, 1374, 1265, 1225, 1140, 1108, 1022, 913  $\text{cm}^{-1}$ ; mp 74 °C;  $[\alpha]_{\text{D}}^{23} +28.8^\circ$  ( $\text{CHCl}_3$ ,  $c$  2.01);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.29 (m, 8H), 7.27-7.22 (m, 2H), 4.71 (d,  $J = 6.8$  Hz, 1H), 4.69 (d,  $J = 6.8$  Hz, 1H), 4.01 (td,  $J = 10.0$ , 1.2 Hz, 1H), 3.98-3.83 (m, 5H), 3.67 (bs, 3H), 3.52 (d,  $J = 13.2$  Hz, 2H), 3.41 (s, 3H), 2.65 (m, 1H), 2.41 (bs, 1H), 2.33 (ddd,  $J = 14.8$ , 9.6, 2.0 Hz, 1H), 1.39 (s, 3H), 1.29 (s, 1H), 1.21 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5 (C), 129.0 (CH), 128.5 (CH), 127.3 (CH), 99.1 (C), 97.8 ( $\text{CH}_2$ ) 76.2 (CH), 66.9 (CH), 66.8 (CH), 62.0 ( $\text{CH}_2$ ), 58.2 ( $\text{CH}_2$ ), 57.9 (CH), 56.2 ( $\text{CH}_3$ ), 54.9 ( $\text{CH}_2$ ), 35.2 ( $\text{CH}_2$ ), 27.3 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ); HREIMS  $m/z$  484.2682  $[\text{M}]^+$ , calcd. for  $\text{C}_{26}\text{H}_{36}\text{N}_4\text{O}_5$  484.2680.

**(2*S*,3*R*)-2-amino-4-((4*R*,5*S*)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-**

**(methoxymethoxy)butan-1-ol (S3).** To a solution of alcohol **3** (600 mg, 1.24 mmol) in ethanol (90 mL) was added Lindlar's catalyst (395 mg, 190  $\mu\text{mol}$ ). The mixture was placed under hydrogen (1 atm) at room temperature and stirred for 14 hours. The solution was filtered through a 0.45  $\mu\text{m}$  syringe filter and

concentrated under reduced pressure. Flash chromatography (silica, 10% MeOH in dichloromethane) provided recovered starting material **S3** (558 mg, 98%) as a viscous oil: IR (neat)  $\nu$  3467, 3362, 3292, 3030, 2986, 2934, 2882, 2829, 1597, 1492, 1457, 1387, 1230, 1160, 1108, 1038, 977, 916, 758, 706  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}}^{21} +24.5^\circ$  ( $\text{CHCl}_3$ ,  $c$  3.82);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.20 (m, 10H), 4.67 (d,  $J = 7.2$  Hz, 1H), 4.64 (d,  $J = 7.2$  Hz, 1H), 4.02-3.84 (m, 5H), 3.70 (bd,  $J = 9.6$  Hz, 1H), 3.57 (m, 1H), 3.50 (d,  $J = 14.0$  Hz, 2H), 3.36 (s, 3H), 2.87 (bs, 1H), 2.65 (dt,  $J = 9.6, 6.0$  Hz, 1H), 2.28 (bs, 2H), 2.19 (dd,  $J = 13.6, 9.6$  Hz, 1H), 1.38 (s, 3H), 1.29 (s, 3H), 1.18 (ddd,  $J = 14.4, 11.6, 2.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5 (C), 128.9 (CH), 128.3 (CH), 127.2 (CH), 99.0 (C), 97.9 ( $\text{CH}_2$ ), 79.4 (CH), 66.8 (CH), 63.1 ( $\text{CH}_2$ ), 58.1 ( $\text{CH}_2$ ), 58.0 (CH), 56.0 ( $\text{CH}_2$ ), 55.9 ( $\text{CH}_3$ ), 54.7 (CH), 35.4 ( $\text{CH}_2$ ), 27.1 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ); HREIMS  $m/z$  458.2781  $[\text{M}]^+$ , calcd. for  $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_5$  458.2775.

**(2*S*,3*R*)-2-(dibenzylamino)-4-((4*R*,5*S*)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-**

**(methoxymethoxy)butan-1-ol (S4).** Benzylbromide (642  $\mu\text{L}$ , 5.37 mmol) was added dropwise to a stirred solution of amine **S3** (547 mg, 1.19 mmol) and  $\text{K}_2\text{CO}_3$  (2.47 g, 17.9 mmol) in anhydrous acetonitrile (5.96 mL) at room temperature. The mixture was stirred for 31 hours then quenched by addition of water (75 mL). The mixture was extracted with ethyl acetate (3  $\times$  50 mL) and combined extracts washed with brine (75 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Flash chromatography (silica, step gradient of 3% and 10% ethyl ether in hexane then 25% ethyl acetate in hexane) provided **S4** (690 mg, 91%) as an amorphous solid: IR (neat)  $\nu$  3476, 3065, 3030, 2995, 2943, 2882, 2812, 1597, 1492, 1457, 1379, 1265, 1221, 1151, 1108, 1029, 977, 916, 758, 706  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}}^{20} +28.8^\circ$  ( $\text{CHCl}_3$ ,  $c$  6.48);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.23 (m, 20H), 4.77 (d,  $J = 6.4$  Hz, 1H), 4.68 (d,  $J = 6.4$  Hz, 1H), 4.15 (m, 1H), 4.02 (t,  $J = 9.6$  Hz, 1H), 4.00-3.88 (m, 6H), 3.84 (d,  $J = 13.6$  Hz, 2H), 3.70 (d,  $J = 13.6$  Hz, 2H), 3.59 (d,  $J = 14.0$  Hz, 2H), 3.40 (s, 3H), 3.31 (bs, 1H), 2.78-2.70 (m, 2H), 2.14 (dd,  $J = 13.6, 9.6$  Hz, 1H), 1.90 (ddd,  $J = 14.8, 10.8, 2.4$  Hz, 1H), 1.36 (s, 3H), 1.33 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0 (C), 139.6 (C), 129.1 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 127.2 (CH), 127.0 (CH), 98.8 (CH), 98.7 (C), 76.2 (CH), 67.0 (CH), 62.6 (CH), 58.5 ( $\text{CH}_2$ ), 58.0 (CH), 57.9 ( $\text{CH}_2$ ), 56.4 ( $\text{CH}_3$ ), 54.9 ( $\text{CH}_2$ ), 54.8 ( $\text{CH}_2$ ), 38.6 ( $\text{CH}_2$ ), 27.9 ( $\text{CH}_3$ ), 20.9 ( $\text{CH}_3$ ); HRMS  $m/z$  639.3973  $[\text{M}+\text{H}]^+$ , calcd. for  $\text{C}_{40}\text{H}_{51}\text{N}_2\text{O}_5$  639.3793.

**(2*R*,3*R*)-2-(dibenzylamino)-4-((4*R*,5*S*)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-**

**(methoxymethoxy)butanal (4).** DMSO (138  $\mu$ L, 152 mg, 1.94 mmol) in  $\text{CH}_2\text{Cl}_2$  (138  $\mu$ L) was added dropwise to a stirred solution of oxalyl chloride (82.6  $\mu$ L, 122 mg, 939  $\mu$ mol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (800  $\mu$ L) at  $-78^\circ\text{C}$ . The mixture was stirred for 15 minutes then a solution of alcohol **S4** (200 mg, 313  $\mu$ mol) in  $\text{CH}_2\text{Cl}_2$  (800  $\mu$ L) was added dropwise. The mixture was stirred for 1.25 hours at  $-78^\circ\text{C}$  then triethylamine (393  $\mu$ L, 285 mg, 2.82 mmol) was added dropwise and the solution was allowed to warm to room temperature. Water (100 mL) was added and the mixture was extracted with ethyl ether ( $3 \times 60$  mL) and combined extracts washed with 1% HCl solution (100 mL), water ( $2 \times 100$  mL), saturated  $\text{NaHCO}_3$  solution (50 mL), brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Flash chromatography (silica, 10% then 25% ethyl acetate in hexane) provided **4** (188 mg, 94%) as a viscous oil: IR (neat)  $\nu$  3091, 3065, 3039, 2995, 2934, 2890, 2820, 27824, 1955, 1719, 1606, 1492, 1449, 1379, 1265, 1230, 1204, 1151, 1108, 1029, 977, 924, 819, 750, 706, 514, 461  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}}^{22} +47.6^\circ$  ( $\text{CHCl}_3$ ,  $c$  10.3);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.97 (d,  $J = 3.2$  Hz, 1H), 7.39-7.26 (m, 20H), 4.68 (d,  $J = 6.6$  Hz, 1H), 4.61 (d,  $J = 6.6$  Hz, 1H), 4.39 (ddd,  $J = 9.2, 9.2, 2.0$  Hz, 1H), 4.15 (t,  $J = 9.6$  Hz, 1H), 4.02-3.93 (m, 4H), 3.92 (d,  $J = 13.6$  Hz, 2H), 3.73 (d,  $J = 13.6$  Hz, 2H), 3.58 (d,  $J = 14.0$  Hz, 2H), 3.26 (s, 3H), 3.20 (dd,  $J = 8.4, 3.2$  Hz, 1H), 2.76 (m, 1H), 2.18 (ddd,  $J = 14.8, 9.6, 1.6$  Hz, 1H), 1.37 (s, 3H), 1.27 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.6 (CH), 139.6 (C), 139.1 (C), 129.1 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 127.3 (CH), 127.2 (CH), 98.8 (C), 98.2 (CH<sub>2</sub>) 74.8 (CH), 68.9 (CH), 66.6 (CH), 58.4 (CH<sub>2</sub>), 57.9 (CH), 56.1 (CH<sub>3</sub>), 55.0 (CH<sub>2</sub>), 54.8 (CH<sub>2</sub>), 37.5 (CH<sub>2</sub>), 27.8 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>); HREIMS  $m/z$  636.3562  $[\text{M}]^+$ , calcd. for  $\text{C}_{40}\text{H}_{48}\text{N}_2\text{O}_5$  636.3563.

**(*R*)-4-benzyl-3-((2*S*,3*R*,4*S*,5*R*)-2-(benzyloxy)-4-(dibenzylamino)-6-((4*R*,5*S*)-5-(dibenzylamino)-2,2-**

**dimethyl-1,3-dioxan-4-yl)-3-hydroxy-5-(methoxymethoxy)hexanoyl)oxazolidin-2-one (S5).** Freshly distilled *n*-BuBOTf (51.9  $\mu$ L, 206  $\mu$ mol) and triethylamine (32.7  $\mu$ L, 235  $\mu$ mol) was added to a stirred solution of **5** (31.8 mg, 176  $\mu$ mol) in dichloromethane (250  $\mu$ L) at  $-78^\circ\text{C}$ . The mixture was warmed to  $0^\circ\text{C}$  and stirred for 3 hours then cooled to  $-78^\circ\text{C}$  and aldehyde **4** (93.0 mg, 147  $\mu$ mol) in dichloromethane (150  $\mu$ L) was added dropwise. The mixture was stirred for 10 minutes then warmed to  $0^\circ\text{C}$  and stirred a further 2.5 hours. The mixture was quenched with addition of pH 7 phosphate buffer (206  $\mu$ L), MeOH (620  $\mu$ L)

and 2:1 MeOH:30% v/v H<sub>2</sub>O<sub>2</sub> (620 μL) at 0 °C. This mixture was stirred at 0 °C for 1 hour then 5% NaHCO<sub>3</sub> solution (50 mL) added and the mixture extracted with ethyl ether (3 × 50 mL) and combined extracts washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Flash chromatography (Analogix 12 g silica cartridge, 5%, 10%, and 20% ethyl acetate in hexane, 24 mL/min flow rate) provided **S5** (109 mg, 77%, dr 24:1) as a viscous oil: IR (neat) ν 3432, 3065, 3039, 2917, 1798, 1702, 1501, 1457, 1387, 1274, 1204, 1117, 1073, 1038, 924, 872, 758, 706 cm<sup>-1</sup>; [α]<sub>D</sub><sup>21</sup> +86.5° (CHCl<sub>3</sub>, *c* 3.45); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.40-7.15 (m, 26H), 7.11 (d, *J* = 7.2 Hz, 2H), 5.56 (d, *J* = 6.0 Hz, 1H), 4.64 (s, 2H), 4.62 (m, 2H), 4.55 (m, 1H), 4.27 (m, 1H), 4.02 (m, 2H), 3.93 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.87 (d, *J* = 6.8 Hz, 2H), 3.82 (d, *J* = 14.0 Hz, 4H), 3.77 (t, *J* = 8.0 Hz, 1H), 3.71 (d, *J* = 14.0 Hz, 2H), 3.57-3.50 (m, 3H), 3.27 (s, 3H), 3.19 (dd, *J* = 12.0, 2.8 Hz, 1H), 2.70-2.66 (m, 2H), 2.61 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.12 (m, 2H), 1.24 (s, 3H), 1.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.8 (C), 153.2 (C), 140.2 (C), 139.6 (C), 137.8 (C), 135.5 (C), 129.6 (CH), 129.3 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.5 (C), 127.2 (C), 126.8 (C), 98.9 (C), 97.9 (CH<sub>2</sub>), 80.1 (CH), 74.6 (CH), 73.2 (CH<sub>2</sub>), 70.3 (CH), 67.3 (CH), 66.6 (CH<sub>2</sub>), 60.9 (CH), 58.5 (CH<sub>2</sub>), 58.0 (CH), 56.2 (CH), 56.1 (CH<sub>3</sub>), 54.7 (CH<sub>2</sub>), 38.3 (CH<sub>2</sub>), 37.7 (CH<sub>2</sub>), 28.0 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>); HRESIMS *m/z* 962.4959 [M+H]<sup>+</sup>, calcd. for C<sub>59</sub>H<sub>68</sub>N<sub>3</sub>O<sub>9</sub> 962.4956.

**(2*S*,3*R*,4*S*,5*R*)-methyl-2-(benzyloxy)-4-(dibenzylamino)-6-((4*R*,5*S*)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-hydroxy-5-(methoxymethoxy)hexanoate (S7)**. Freshly distilled *n*-BuBOTf (51.9 μL, 206 μmol) and Hünig's base (40.9 μL, 235 μmol) was added to a stirred solution of **S6** (31.8 mg, 176 μmol) in ethyl ether (250 μL) at -78 °C. The mixture was stirred for 1.5 hours then aldehyde **4** (93.0 mg, 147 μmol) in ethyl ether (150 μL) was added dropwise. The mixture was stirred for 15 minutes then warmed to 0 °C and stirred a further 2 hours. The mixture was quenched with addition of pH 7 phosphate buffer (206 μL), MeOH (620 μL) and 2:1 MeOH:30% v/v H<sub>2</sub>O<sub>2</sub> (620 μL) at 0 °C. This mixture was stirred at 0 °C for 1 hour then 5% NaHCO<sub>3</sub> solution (50 mL) added and the mixture extracted with ethyl ether (3 × 50 mL) and combined extracts washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Flash chromatography (Analogix 4 g silica cartridge, 5% ethyl acetate in hexane, 13 mL/min flow rate) provided **S7** (52.6 mg, 44%, 37% de by NMR). Further HPLC purification (silica 10 ×

250 mm column, 3% IPA in hexane, 4 mL/min) provided pure **S7** (28.4 mg) as a viscous oil: IR (neat)  $\nu$  3432, 3065, 3030, 2986, 2934, 2890, 2838, 1754, 1597, 1492, 1449, 1379, 1265, 1213, 1151, 1082, 1029, 916, 819, 758, 706  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}}^{24}$   $-31.0^{\circ}$  ( $\text{CHCl}_3$ ,  $c$  4.81);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.18 (m, 23H), 7.06 (m, 2H), 4.70 (d,  $J$  = 11.2 Hz, 1H), 4.60 (d,  $J$  = 6.4 Hz, 1H), 4.50 (d,  $J$  = 6.4 Hz, 1H), 4.28-4.18 (m, 3H), 4.16-4.05 (m, 2H), 4.00 (d,  $J$  = 13.4 Hz, 2H), 3.94-3.75 (m, 9H), 3.73 (d,  $J$  = 13.4 Hz, 2H), 3.49 (d,  $J$  = 14.0 Hz, 2H), 3.32 (m, 1H), 3.30 (s, 3H), 2.57 (m, 1H), 2.31 (dd,  $J$  = 13.2, 9.6 Hz, 1H), 1.44 (s, 3H), 1.34 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.7 (C), 139.6 (C), 139.3 (C), 137.7 (C), 129.3 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 99.0 (C), 97.3 ( $\text{CH}_2$ ), 78.5 (CH), 74.5 (CH), 72.3 ( $\text{CH}_2$ ), 69.9 (CH), 67.6 (CH), 60.9 (CH), 58.3 ( $\text{CH}_2$ ), 58.2 (CH), 56.3 ( $\text{CH}_3$ ), 55.3 ( $\text{CH}_2$ ), 54.7 ( $\text{CH}_2$ ), 52.2 (CH), 39.5 ( $\text{CH}_2$ ), 27.5 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ); HRMS  $m/z$  817.4438  $[\text{M}+\text{H}]^+$ , calcd. for  $\text{C}_{50}\text{H}_{61}\text{N}_1\text{O}_8\text{N}_2$  817.4422.

**(2*S*,3*R*,4*S*,5*R*)-2-(benzyloxy)-4-(dibenzylamino)-6-((4*R*,5*S*)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-hydroxy-5-(methoxymethoxy)hexanoic acid (6).** Method a) A mixture of 30% v/v  $\text{H}_2\text{O}_2$  (12.7  $\mu\text{L}$ , 125  $\mu\text{mol}$ ) and lithium hydroxide monohydrate (1.74 mg, 41.6  $\mu\text{mol}$ ) was added to a stirred solution of **S5** (21.0 mg, 21.8  $\mu\text{mol}$ ) in 1:3  $\text{H}_2\text{O}$ :THF (430  $\mu\text{L}$ ) at 0  $^{\circ}\text{C}$ . The mixture was stirred for 30 minutes then quenched by addition of 1.5 N  $\text{Na}_2\text{SO}_3$  solution (94  $\mu\text{L}$ ) and the mixture stirred for 10 minutes at 0  $^{\circ}\text{C}$  then warmed to room temperature and stirred a further 5 minutes. The mixture was diluted with ethyl acetate (50 mL) and washed with 1% HCl (20 mL), water ( $2 \times 15$  mL), and brine (10 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Flash chromatography (silica saturated with AcOH, 1% AcOH + 25% ethyl acetate in hexane) provided **6** (16.8 mg, 96%) as a viscous oil.

Method b) Lithium hydroxide monohydrate (0.33 mg, 7.96  $\mu\text{mol}$ ) was added to a stirred solution of ester **S7** (6.50 mg, 7.96  $\mu\text{mol}$ ) in 3:2:2 MeOH: $\text{H}_2\text{O}$ :THF (350  $\mu\text{L}$ ) at room temperature. The mixture was stirred for 8 hours then diluted with water (2 mL) and the pH adjusted to 2 with 1 N HCl. The mixture was extracted with ethyl acetate ( $3 \times 5$  mL) and combined extracts washed with brine (5 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Flash chromatography (silica, 25% then 50% ethyl acetate in hexane then 5% AcOH + 20% MeOH in dichloromethane) provided **6** (5.2 mg, 81%) as a viscous

oil: IR (neat)  $\nu$  3450, 3065, 3021, 2925, 2847, 1728, 1492, 1449, 1379, 1265, 1213, 1108, 1073, 1029, 968, 916, 750, 697  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}}^{21} +7.7^\circ$  ( $\text{CHCl}_3$ ,  $c$  4.03);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.14 (m, 25H), 4.74 (m, 2H), 4.45-4.30 (m, 4H), 3.98-3.80 (m, 8H), 3.60-3.50 (m, 4H), 3.33 (s, 3H), 3.06 (m, 1H), 2.63-2.54 (m, 2H), 1.57 (m, 1H), 1.20 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2 (C), 139.6 (C), 139.5 (C), 137.1 (C), 129.4 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 127.3 (CH), 99.0 (C), 97.6 (CH<sub>2</sub>), 78.5 (CH), 75.3 (CH), 72.9 (CH<sub>2</sub>), 71.5 (CH), 67.9 (CH), 60.8 (CH), 58.4 (CH<sub>2</sub>), 57.9 (CH), 56.5 (CH<sub>3</sub>), 55.1 (CH<sub>2</sub>), 54.9 (CH<sub>2</sub>), 39.6 (CH<sub>2</sub>), 27.5 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>); HRMS  $m/z$  803.4267  $[\text{M}+\text{H}]^+$ , calcd. for  $\text{C}_{49}\text{H}_{59}\text{N}_2\text{O}_8$  803.4271.

**(S)-2-amino-3-ureidopropanamide ((-)-8)**.  $\text{CF}_3\text{COOH}$  (600  $\mu\text{L}$ ) was added dropwise to **7** (14.5 mg, 58.9  $\mu\text{mol}$ , neat) with stirring at 0  $^\circ\text{C}$ . The mixture was stirred 1 hour at 0  $^\circ\text{C}$  then warmed to room temperature and stirred for 2.5 hours. The reaction mixture was blown to dryness with a stream of  $\text{N}_2$  and then dried under azeotropic distillation with 1:1 MeOH:toluene ( $2 \times 1$  mL) to provided (-)-**8** (14.9 mg, 98%, 94% ee by Marfey's analysis<sup>1</sup>) as a viscous oil:  $[\alpha]_{\text{D}}^{21} -15.1^\circ$  ( $\text{CH}_3\text{OH}$ ,  $c$  6.63);  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  3.99 (dd,  $J = 6.4, 3.6$  Hz, 1H), 3.67 (dd,  $J = 15.0, 3.6$  Hz, 1H), 3.48 (dd,  $J = 15.0, 6.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  170.4 (C), 162.6 (C), 55.4 (CH), 42.3 (CH<sub>2</sub>); HRMS  $m/z$  147.0882  $[\text{M}+\text{H}]^+$ , calcd. for  $\text{C}_4\text{H}_{11}\text{N}_4\text{O}_2$  147.0877.

**(2S,3R,4S,5R)-N-((S)-1-amino-1-oxo-3-ureidopropan-2-yl)-2-(benzyloxy)-4-(dibenzylamino)-6-((4R,5S)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-hydroxy-5-**

**(methoxymethoxy)hexanamide (9)**. A solution of **6** (16.5 mg, 20.6  $\mu\text{mol}$ ) in DMF (100  $\mu\text{L}$ ) was cooled to 0  $^\circ\text{C}$  under nitrogen and treated with EDCI (5.12 mg, 26.7  $\mu\text{mol}$ ) and HOBt (3.89 mg, 28.8  $\mu\text{mol}$ ). After 10 minutes, amine **17** (6.0 mg, 23.1  $\mu\text{mol}$ ) in DMF (50  $\mu\text{L}$ ) and triethylamine (2.86  $\mu\text{L}$ , 20.6  $\mu\text{mol}$ ) was added. The mixture was warmed to room temperature and stirred for 1 hour. A solution of 10% isopropyl alcohol in chloroform (15 mL) was added, and the mixture washed with water ( $5 \times 3$  mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Flash chromatography (silica, 2.5-10% MeOH in dichloromethane) provided **9** (15.0 mg, 81%) as a amorphous solid: IR (neat)  $\nu$  3450, 3362, 2065, 3030, 2986, 2934, 2838, 2523, 2418, 1658, 1606, 1492, 1449, 1379, 1221, 1151, 1099, 1064, 1029, 916, 750, 697

cm<sup>-1</sup>; [ $\alpha$ ]<sub>D</sub><sup>20</sup> +4.3° (CHCl<sub>3</sub>, *c* 5.66); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  7.40-7.13 (m, 25H), 4.74 (d, *J* = 6.8 Hz, 1H), 4.64 (d, *J* = 6.8 Hz, 1H), 4.49 (dd, *J* = 7.2, 4.4 Hz, 1H), 4.39-4.31 (m, 3H), 4.28 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.22 (t, *J* = 10.0 Hz, 1H), 3.97 (dd, *J* = 12.0, 8.8 Hz, 1H), 3.92-3.80 (m, 6H), 3.69 (d, *J* = 13.2 Hz, 2H), 3.62 (m, 1H), 3.57 (d, *J* = 13.6 Hz, 2H), 3.36 (m, 1H), 3.32 (s, 3H), 3.07 (dd, *J* = 8.4, 3.6 Hz, 1H), 2.61-2.53 (m, 2H), 1.62 (ddd, *J* = 14.0, 11.6, 2.6 Hz, 1H), 1.34 (s, 3H), 1.22 (s, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  174.5 (C), 174.0 (C), 162.2 (C), 141.4 (C), 141.1 (C), 138.6 (C), 130.6 (CH), 130.0 (CH), 129.9 (CH), 129.4 (CH), 129.3 (CH), 129.0 (CH), 128.2 (CH), 128.1 (CH), 100.1 (C), 98.9 (CH<sub>2</sub>), 81.9 (CH), 76.9 (CH), 74.3 (CH<sub>2</sub>), 72.3 (CH), 69.4 (CH), 62.0 (CH), 59.5 (CH<sub>2</sub>), 58.9 (CH), 56.7 (CH<sub>3</sub>), 56.1 (CH<sub>2</sub>), 55.6 (CH<sub>2</sub>), 54.7 (CH), 43.1 (CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 28.3 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>); HRMS *m/z* 931.4951 [M+H]<sup>+</sup>, calcd. for C<sub>53</sub>H<sub>67</sub>N<sub>6</sub>O<sub>9</sub> 931.4970.

**(2*S*,3*R*,4*R*,5*R*,7*R*,8*S*)-4,8-diamino-*N*-((*S*)-1-amino-1-oxo-3-ureidopropan-2-yl)-2,3,5,7,9-**

**pentahydroxynonanamide ((-)-10).** TMSCl (15.0  $\mu$ L, 12.7 mg, 120  $\mu$ mol) was added to **9** (11.5 mg, 12.4  $\mu$ mol) in dry MeOH (1.5 mL) at 0 °C. The mixture was warmed to room temperature over 5 minutes with agitation. 10% Pd/C (13.1 mg, 12.4  $\mu$ mol, 100 mol % Pd) was added and the mixture placed under H<sub>2</sub> (5 atm) and agitated for 1 hour on a Parr shaker. The mixture was filtered through a 0.45  $\mu$ m syringe filter and concentrated under reduced pressure at room temperature or below. The crude material was resuspended in 1% HCl in water (1.5 mL) and 10% Pd/C (13.1 mg, 12.4  $\mu$ mol, 100 mol % Pd) added. The mixture was placed under H<sub>2</sub> (5 atm) and agitated for 1 hour on a Parr shaker. Filtration through a 0.45  $\mu$ m syringe filter and concentration under reduced pressure at or below room temperature provided the hydrochloride salt of (-)-**10** (5.9 mg, (76% purity by NMR)). Further HPLC purification (Synergi Hydro-RP 10  $\times$  250 mm column, 1.3 MeOH: 0.1 CF<sub>3</sub>COOH: 98.6 H<sub>2</sub>O, 3.5 mL/min, (product converted to HCl salt by resuspending in 1% HCl and re-drying)) provided pure (-)-**10** (2.3 mg) as a white solid: [ $\alpha$ ]<sub>D</sub><sup>21</sup> -23.0° (H<sub>2</sub>O, *c* 1.49); <sup>1</sup>H NMR (400 MHz, 0.2% acetonitrile:D<sub>2</sub>O (ref  $\delta$  2.06))  $\delta$  4.53 (d, *J* = 2.0 Hz, 1H), 4.45 (dd, *J* = 6.4, 4.4 Hz, 1H), 4.38 (dd, *J* = 6.0, 2.0 Hz, 1H), 4.30 (ddd, *J* = 10.0, 3.6, 2.0 Hz, 1H), 4.20 (ddd, *J* = 10.0, 2.8, 3.2 Hz, 1H), 3.95 (dd, *J* = 12.2, 4.0 Hz, 1H), 3.79 (dd, *J* = 12.2, 8.4 Hz, 1H), 3.64 (dd, *J* = 14.6, 4.4 Hz, 1H), 3.59 (dd, *J* = 5.6, 5.6 Hz, 1H), 3.48 (dd, *J* = 14.6, 2.4 Hz, 1H), 3.44 (m, 1H), 1.79 (ddd, *J* = 14.4, 12.0, 2.0 Hz, 1H), 1.72 (ddd, *J* = 14.4, 12.0, 2.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, 0.2% acetonitrile:D<sub>2</sub>O (ref  $\delta$  1.47))  $\delta$

175.1 (C), 174.7 (C), 162.3 (C), 72.7 (CH), 67.6 (CH), 65.8 (CH), 65.5 (CH), 58.4 (CH), 58.1 (CH<sub>2</sub>), 57.3 (CH), 55.0 (CH), 41.4 (CH<sub>2</sub>), 35.6 (CH<sub>2</sub>); HRMS  $m/z$  419.1871 [M+Na]<sup>+</sup>, calcd. for C<sub>13</sub>H<sub>28</sub>N<sub>6</sub>O<sub>8</sub>Na<sub>1</sub> 419.1866.

**(R)-tert-butyl 1-amino-1-oxo-3-ureidopropan-2-ylcarbamate (S8).** Compound **11** (500 mg, 1.85 mmol) in dry toluene (5 mL) was heated to 110 °C in a microwave reactor for 15 minutes. The mixture was cooled to room temperature and NH<sub>3</sub> (11.1 mL, 5.55 mmol, 0.5 M in dioxane) was added. The mixture was stirred for 30 minutes. The reaction dried then dissolved in 2 M NH<sub>3</sub> in MeOH (4.6 mL, 9.25 mM) and stirred for 5 hours. The reaction mixture was dried and redissolved in MeOH (15 mL) and NaOH (0.9 mL of 1 N solution, 0.9 mmol) added. The mixture stirred for 4.5 hours and then diluted with THF (1 L), dried with MgSO<sub>4</sub>, filtered and dried. Flash chromatography (silica, 20% MeOH in dichloromethane) provided **S8** (316 mg, 62%) as a crystalline solid (mp 141.5 °C). Compound **S8** matched literature values (Ref. 12).

**(R)-2-amino-3-ureidopropanamide ((+)-8).** CF<sub>3</sub>COOH (1.0 mL) was added dropwise to **9** (24.8 mg, 101 μmol, neat) with stirring at 0 °C. The mixture was stirred 1 hour at 0 °C. The reaction mixture was blown to dryness with a stream of N<sub>2</sub> at 0 °C and then dried under azeotropic distillation with 1:1 MeOH:toluene (2 × 1 mL) to provided **(+)-8** (25.8 mg, 99%, 87% ee by Marfey's analysis<sup>1</sup>) as a viscous oil: [α]<sub>D</sub><sup>20</sup> +15.7° (CH<sub>3</sub>OH, *c* 9.91); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 3.99 (dd, *J* = 6.4, 3.6 Hz, 1H), 3.67 (dd, *J* = 15.0, 3.6 Hz, 1H), 3.49 (dd, *J* = 15.0, 6.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 170.5 (C), 162.7 (C), 55.4 (CH), 42.2 (CH<sub>2</sub>); HRMS  $m/z$  147.0882 [M+H]<sup>+</sup>, calcd. for C<sub>4</sub>H<sub>11</sub>N<sub>4</sub>O<sub>2</sub> 147.0877.

**(2S,3R,4S,5R)-N-((R)-1-amino-1-oxo-3-ureidopropan-2-yl)-2-(benzyloxy)-4-(dibenzylamino)-6-((4R,5S)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)-3-hydroxy-5-(methoxymethoxy)hexanamide (12).** A solution of **6** (21.0 mg, 26.1 μmol) in DMF (150 μL) was cooled to 0 °C under nitrogen and treated with EDCI (6.52 mg, 34.0 μmol) and HOBt (4.95 mg, 36.6 μmol). After 10 minutes amine **(+)-8** (7.48 mg, 28.8 μmol) in DMF (50 μL) and triethylamine (4.0 μL, 29 μmol) was added. The mixture was warmed to room temperature and stirred for 20 minutes. A solution of 10% isopropyl alcohol in chloroform (20 mL) was added, and the mixture washed with water (5 × 4 mL). The

organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Flash chromatography (silica, 2.5%, 5%, and 10% MeOH in dichloromethane) provided **12** (21.5 mg, 88%) as an amorphous solid: IR (neat)  $\nu$  3361, 3061, 3026, 2932, 1666, 1602, 1540, 1453, 1377, 1147, 1103, 1070, 1027, 749, 699 cm<sup>-1</sup>; [ $\alpha$ ]<sub>D</sub><sup>20</sup> +7.0° (CHCl<sub>3</sub>, *c* 8.34); <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta$  7.40-7.11 (m, 25H), 4.72 (d, *J* = 7.0 Hz, 1H), 4.66 (d, *J* = 7.0 Hz, 1H), 4.46 (d, *J* = 11.0 Hz, 1H), 4.41 (dd, *J* = 6.0, 3.5 Hz, 1H), 4.33 (d, *J* = 2.5 Hz, 1H), 4.27 (m, 2H), 4.08 (t, *J* = 10.0 Hz, 1H), 4.00-3.94 (m, 2H), 3.90-3.81 (m, 5H), 3.67 (d, *J* = 14.0 Hz, 2H), 3.56 (m, 1H), 3.55 (d, *J* = 14.0 Hz, 2H), 3.42 (dd, *J* = 14.0, 6.5 Hz, 1H), 3.33 (s, 3H), 3.11 (dd, *J* = 8.5, 3.0 Hz, 1H), 2.61 (dd, *J* = 14.8, 8.5 Hz, 1H), 2.54 (m, 1H), 1.55 (ddd, *J* = 14.8, 10.4, 4.0 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  175.0 (C), 174.8 (C), 162.4 (C), 141.3 (C), 141.0 (C), 138.6 (C), 130.5 (CH), 130.1 (CH), 130.0 (CH), 129.4 (CH), 129.3 (CH), 129.3 (CH), 129.0 (CH), 128.2 (CH), 128.1 (CH), 100.2 (C), 98.7 (CH<sub>2</sub>), 82.0 (CH), 77.0 (CH), 74.4 (CH<sub>2</sub>), 73.1 (CH), 69.2 (CH), 61.8 (CH), 59.2 (CH<sub>2</sub>), 58.6 (CH), 56.7 (CH<sub>3</sub>), 56.1 (CH<sub>2</sub>), 55.7 (CH), 55.6 (CH<sub>2</sub>), 42.3 (CH<sub>2</sub>), 39.7 (CH<sub>2</sub>), 28.4 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>); HRMS *m/z* 931.4949 [M+H]<sup>+</sup>, calcd. for C<sub>53</sub>H<sub>67</sub>N<sub>6</sub>O<sub>9</sub> 931.4964.

**(2S,3R,4R,5R,7R,8S)-4,8-diamino-N-((R)-1-amino-1-oxo-3-ureidopropan-2-yl)-2,3,5,7,9-pentahydroxynonanamide ((-)-1)**. TMSCl (15.0  $\mu$ L, 12.7 mg, 120  $\mu$ mol) was added to **12** (16.0 mg, 17.2  $\mu$ mol) in dry MeOH (1.5 mL) at 0 °C. The mixture was warmed to room temperature over 5 minutes with agitation. 10% Pd/C (18.3 mg, 17.2  $\mu$ mol, 100 mol % Pd) was added and the mixture placed under H<sub>2</sub> (5 atm) and agitated for 1 hour on a Parr shaker. The mixture was filtered through a 0.45  $\mu$ m syringe filter and concentrated under reduced pressure at room temperature or below. The crude material was resuspended in 1% HCl in water (1.5 mL) and 10% Pd/C (18.3 mg, 17.2  $\mu$ mol, 100 mol % Pd) added. The mixture was placed under H<sub>2</sub> (5 atm) and agitated for 1 hour on a Parr shaker. Filtration through a 0.45  $\mu$ m syringe filter and concentration under reduced pressure at or below room temperature provided the hydrochloride salt of (-)-1 (7.9 mg, (75% purity by NMR)). Further HPLC purification (Synergi Hydro-RP 10  $\times$  250 mm column, 1.3 MeOH: 0.1 CF<sub>3</sub>COOH: 98.6 H<sub>2</sub>O, 3.5 mL/min, (product converted to HCl salt by resuspending in 1% HCl and re-drying)) provided pure (-)-1 (4.4 mg) as a white solid: [ $\alpha$ ]<sub>D</sub><sup>21</sup> -7.9° (H<sub>2</sub>O, *c* 2.39); <sup>1</sup>H NMR (400 MHz, 0.2% acetonitrile:D<sub>2</sub>O (ref  $\delta$  2.06))  $\delta$  4.56 (d, *J* = 2.0 Hz, 1H), 4.46 (dd, *J* = 6.4, 4.0 Hz, 1H), 4.38 (dd, *J* = 5.8, 2.0 Hz, 1H), 4.29 (ddd, *J* = 10.0, 4.8, 2.4 Hz, 1H), 4.20 (ddd, *J* = 10.0, 3.2, 2.8 Hz, 1H),

3.95 (dd,  $J = 12.2, 4.0$  Hz, 1H), 3.79 (dd,  $J = 12.2, 8.6$  Hz, 1H), 3.64 (dd,  $J = 14.8, 4.4$  Hz, 1H), 3.58 (dd,  $J = 5.4, 5.4$  Hz, 1H), 3.51 (dd,  $J = 14.8, 6.4$  Hz, 1H), 3.45 (m, 1H), 1.82 (ddd,  $J = 14.0, 11.6, 2.0$  Hz, 1H), 1.75 (ddd,  $J = 14.0, 11.6, 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, 0.2% acetonitrile:D<sub>2</sub>O (ref  $\delta$  1.47))  $\delta$  175.3 (C7), 174.8 (C5), 162.4 (C1), 72.7 (C8), 67.9 (C9), 65.8 (C13), 65.5 (C11), 58.5 (C10), 58.1 (C15), 57.3 (C14), 55.2 (C4), 41.3 (C3), 35.7 (C12); HRMS  $m/z$  [M+H]<sup>+</sup> 397.2054, calcd. for C<sub>13</sub>H<sub>29</sub>N<sub>6</sub>O<sub>8</sub> 397.2047.



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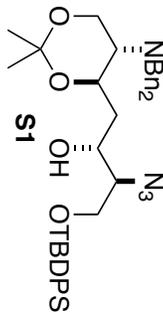
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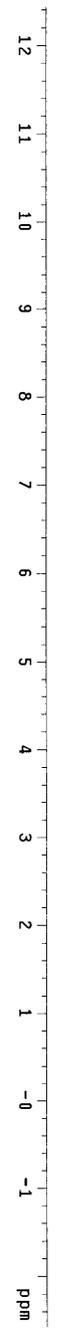
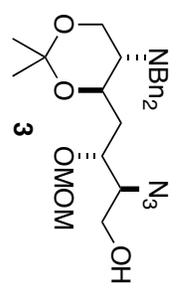






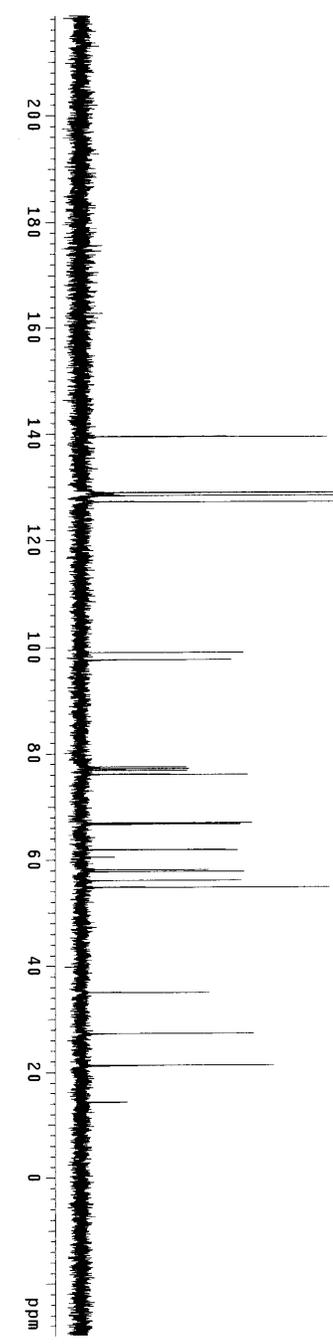
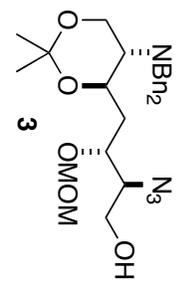
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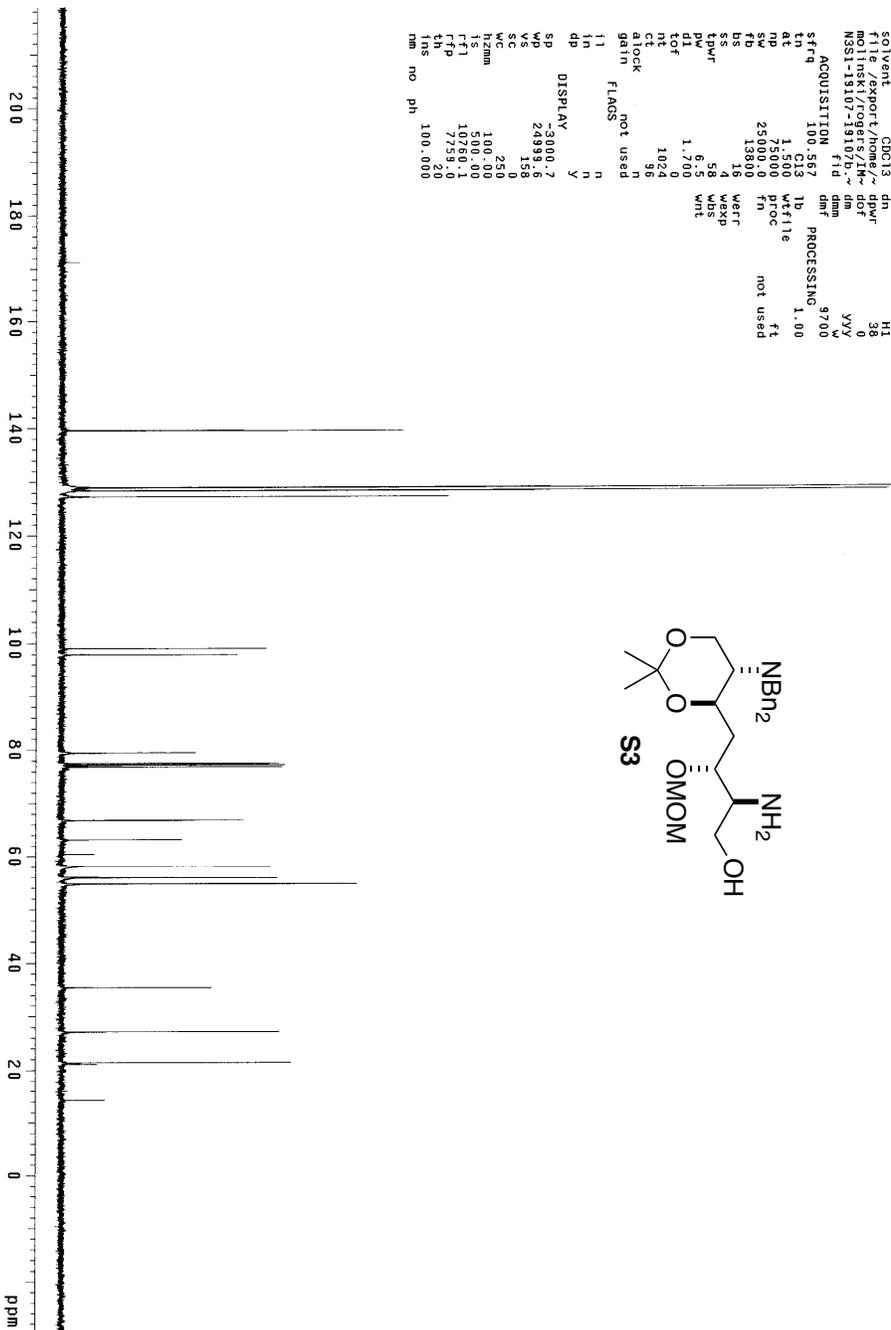
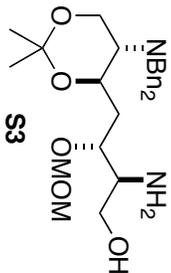




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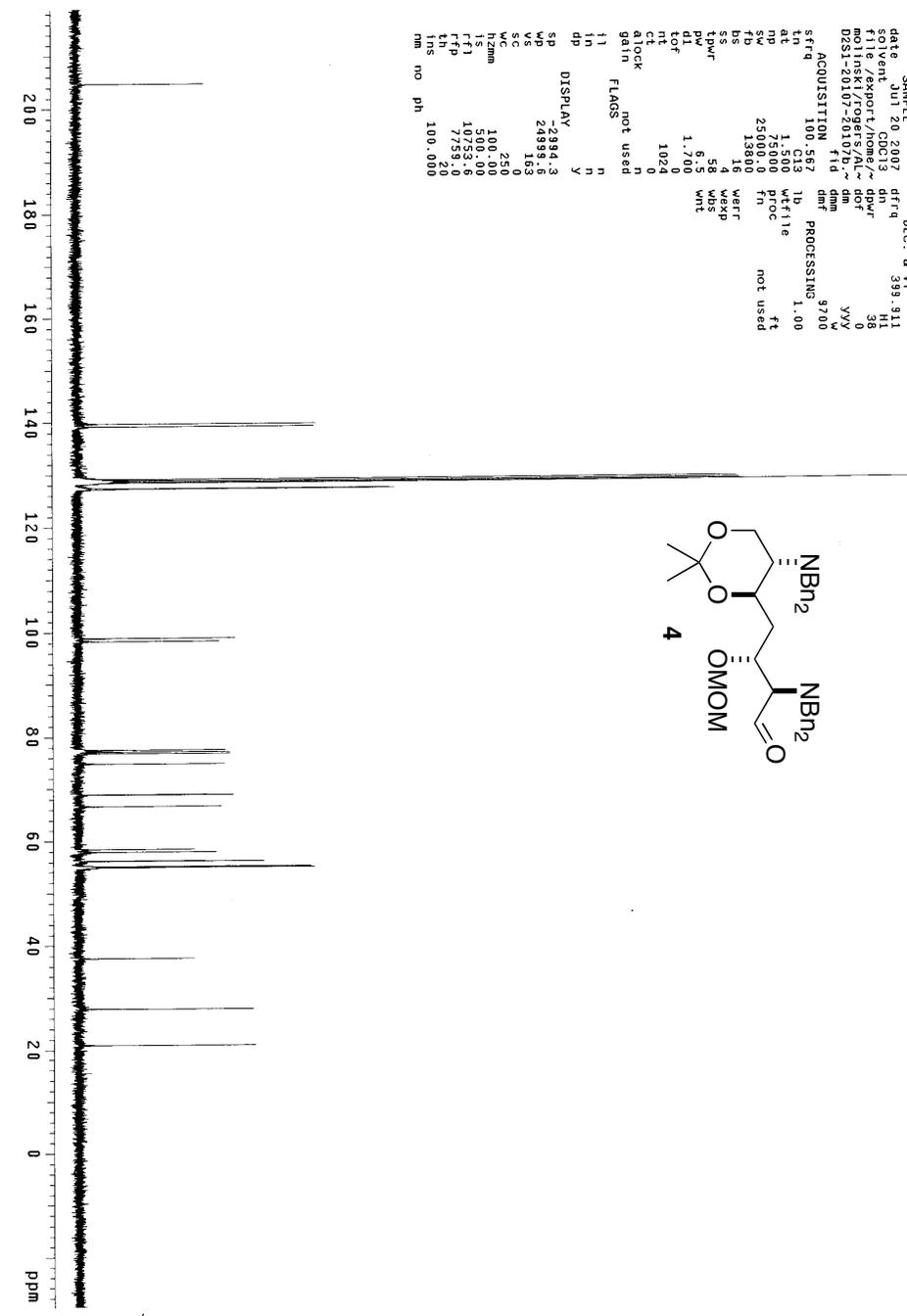
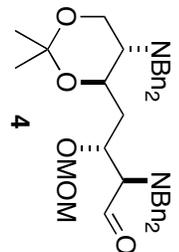
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l1469 n  
l1470 n  
l1471 n  
l1472 n  
l1473 n  
l1474 n  
l1475 n  
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l1487 n  
l1488 n  
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l1490 n  
l1491 n  
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l1494 n  
l1495 n  
l1496 n  
l1497 n  
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l1499 n  
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l1637 n  
l1638 n  
l1639 n  
l1640 n  
l1641 n  
l1642 n

ALD2S1-20107, EMR\_V11

exp1 std13c

SAMPLE DEC: & VT  
date Jun 20 2007 399.911  
f01vent export/home2 dmwr 38  
molinski/rogers/Alc~ dof 0  
D2S1-20107-20107b~ dm yyy  
ACQUISITION f1d dm 9700  
sfrq 100.567 C13 lb PROCESsing 1.00  
tn 1.500 wffile  
at 250000 Proc not used  
sp 13800 f1  
fb 16 werr  
bs 4 wexp  
ss 5 wnt  
dmwr 6.25 wnt  
p1 1.700  
d1 1024  
tof 0  
nt 1024  
atlock n  
gain not used  
flags n  
l1 n  
l2 n  
l3 n  
dp y  
DISPLAY  
sp -2494.2  
ve 2493.169  
sc 0  
wc 250  
n2mm 100.00  
rf1 10753.6  
rfp 7759.0  
th 100.000  
ms no ph





ALEIHI-21107, EWR.VII

exp1 std13c

SAMPLE DEC. & VI

date exp1 Jul 30 2002 dfreq 359.911

file export/home/~ dnr

molinski/rogers/AL~ dof

EIHI-21107-21107b.~ dm yyy

ACQUISITION 100.567 1b dm PROCESSING 9700

ln C13 1b dm

at 1.500 wffile 1.00

pd 25000 proc not used

fb 13800

bs 18 werr

sswf 54 wexp

pw 6.5 wnt

d1 1.700

lof 20.0

rf 512

atlock n

gain not used

l1 n

in n

dp y

DISPLAY

sp 2988.5

vs 243.282

sc 0

wcmm 250

wcmm 100.00

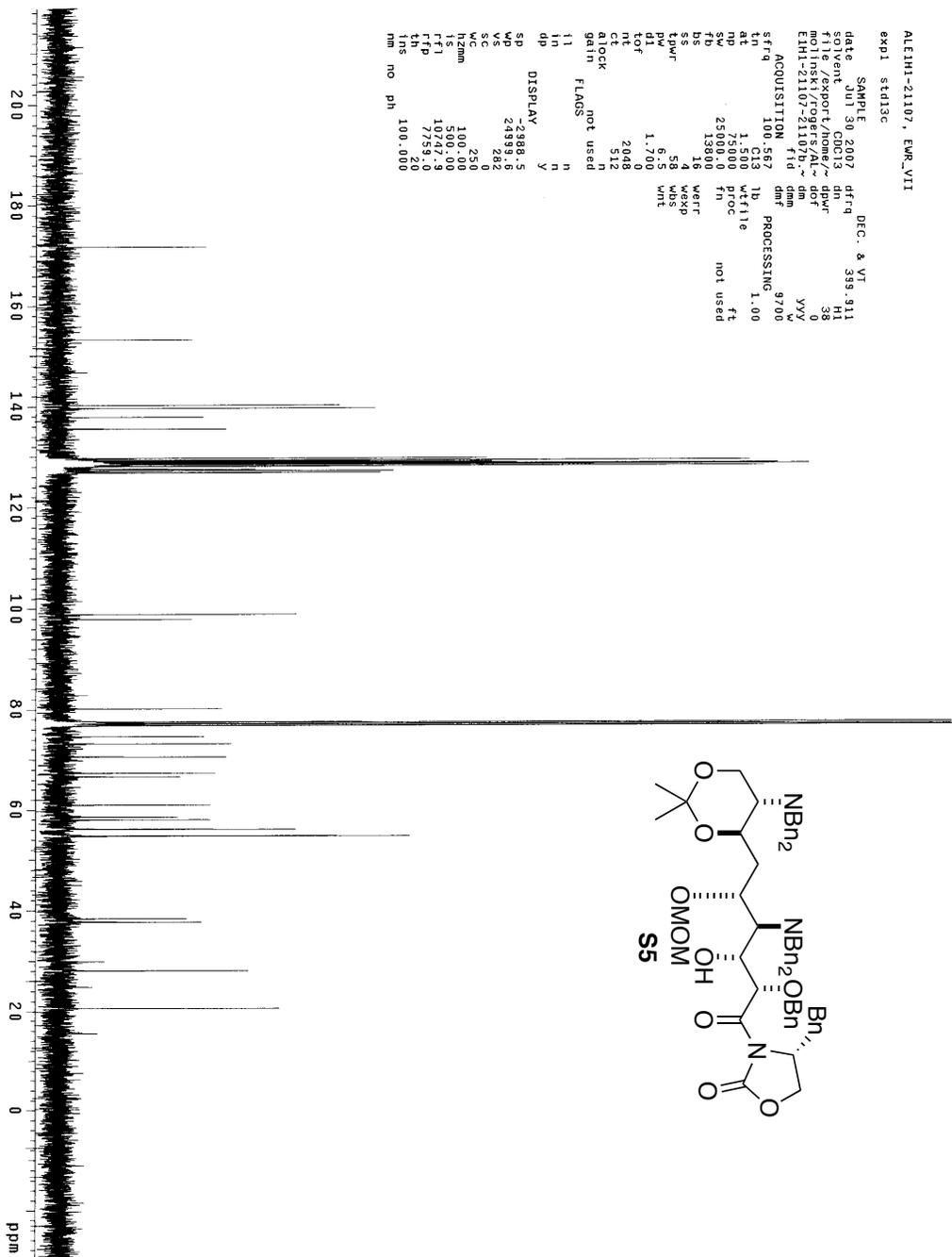
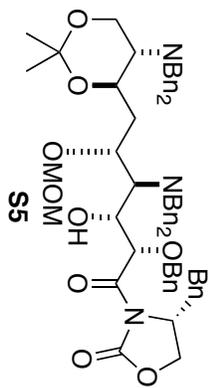
rf1 500.00

rfp 10747.9

rfp 7759.0

th 20

ms 100.000

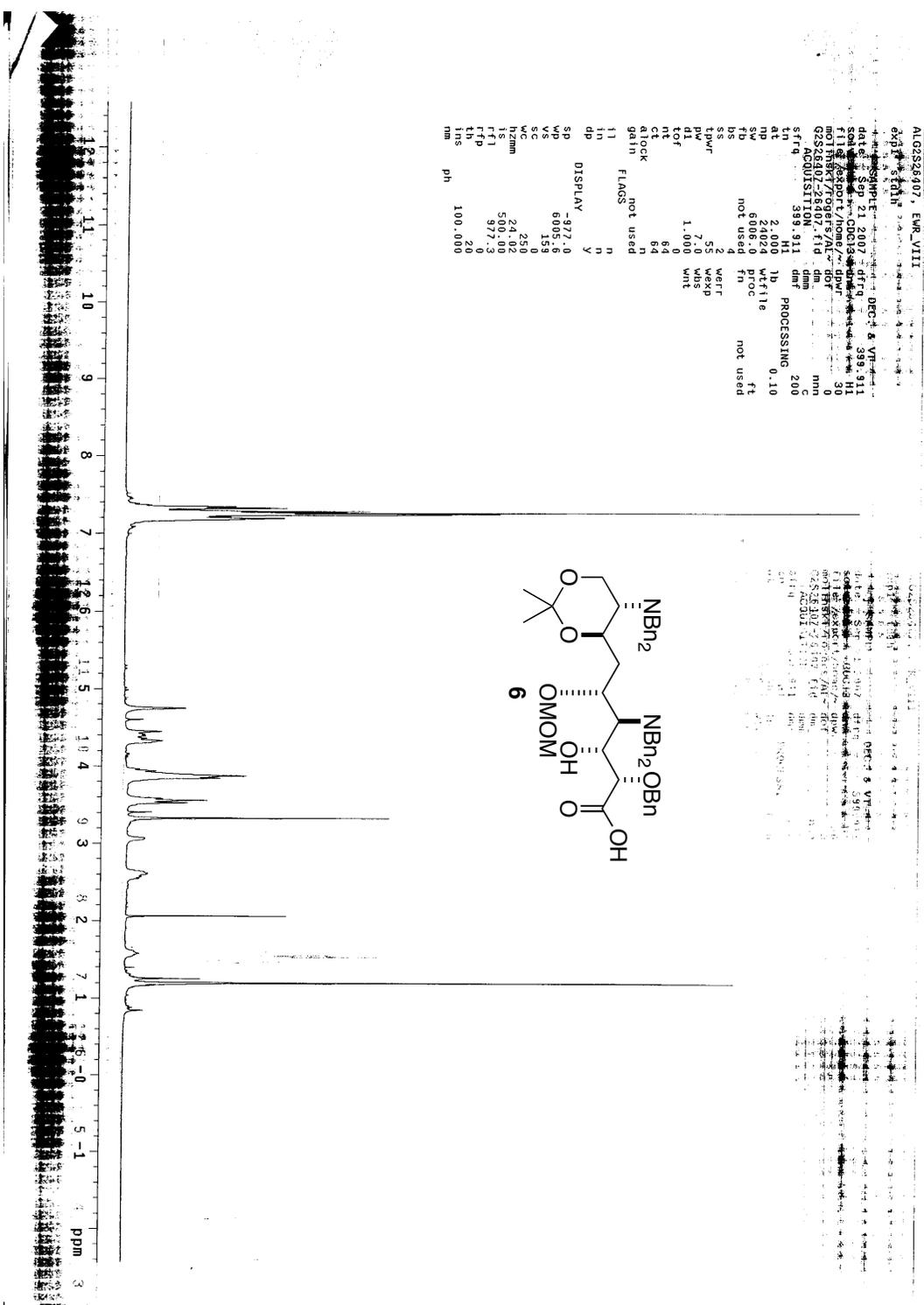
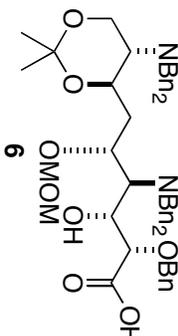






ALG226407, EMR VIII  
 6/21/2007 11:51:11  
 SAMPLE: 20070921-001  
 DATE: Sep 21 2007 09:11  
 SOLVENT: CDCl3  
 MOT: F1H3/1000/1000/1000  
 G226407-26407.fid dm  
 ACQUISITION: 399.911 dm  
 F1: 2.000 lb PROCESSING: 200  
 NP: 24024 wflite 0.10  
 SW: 6008.0 proc ft  
 BS: not used fn not used  
 SS: 2 weft  
 TDWR: 55 wexp  
 PW: 7.00 wds  
 FWHM: 1.000 wht  
 TOF: 0  
 NT: 64  
 CT: 64  
 GAIN: not used  
 11: not used  
 10: not used  
 9: not used  
 8: not used  
 7: not used  
 6: not used  
 5: not used  
 4: not used  
 3: not used  
 2: not used  
 1: not used  
 0: not used  
 -1: not used  
 -2: not used  
 -3: not used  
 -4: not used  
 -5: not used  
 -6: not used  
 -7: not used  
 -8: not used  
 -9: not used  
 -10: not used  
 -11: not used  
 -12: not used  
 -13: not used  
 -14: not used  
 -15: not used  
 -16: not used  
 -17: not used  
 -18: not used  
 -19: not used  
 -20: not used  
 100.000  
 mm

ALG226407, EMR VIII  
 6/21/2007 11:51:11  
 SAMPLE: 20070921-001  
 DATE: Sep 21 2007 09:11  
 SOLVENT: CDCl3  
 MOT: F1H3/1000/1000/1000  
 G226407-26407.fid dm  
 ACQUISITION: 399.911 dm  
 F1: 2.000 lb PROCESSING: 200  
 NP: 24024 wflite 0.10  
 SW: 6008.0 proc ft  
 BS: not used fn not used  
 SS: 2 weft  
 TDWR: 55 wexp  
 PW: 7.00 wds  
 FWHM: 1.000 wht  
 TOF: 0  
 NT: 64  
 CT: 64  
 GAIN: not used  
 11: not used  
 10: not used  
 9: not used  
 8: not used  
 7: not used  
 6: not used  
 5: not used  
 4: not used  
 3: not used  
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 -6: not used  
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 -9: not used  
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 -12: not used  
 -13: not used  
 -14: not used  
 -15: not used  
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 -17: not used  
 -18: not used  
 -19: not used  
 -20: not used  
 100.000  
 mm

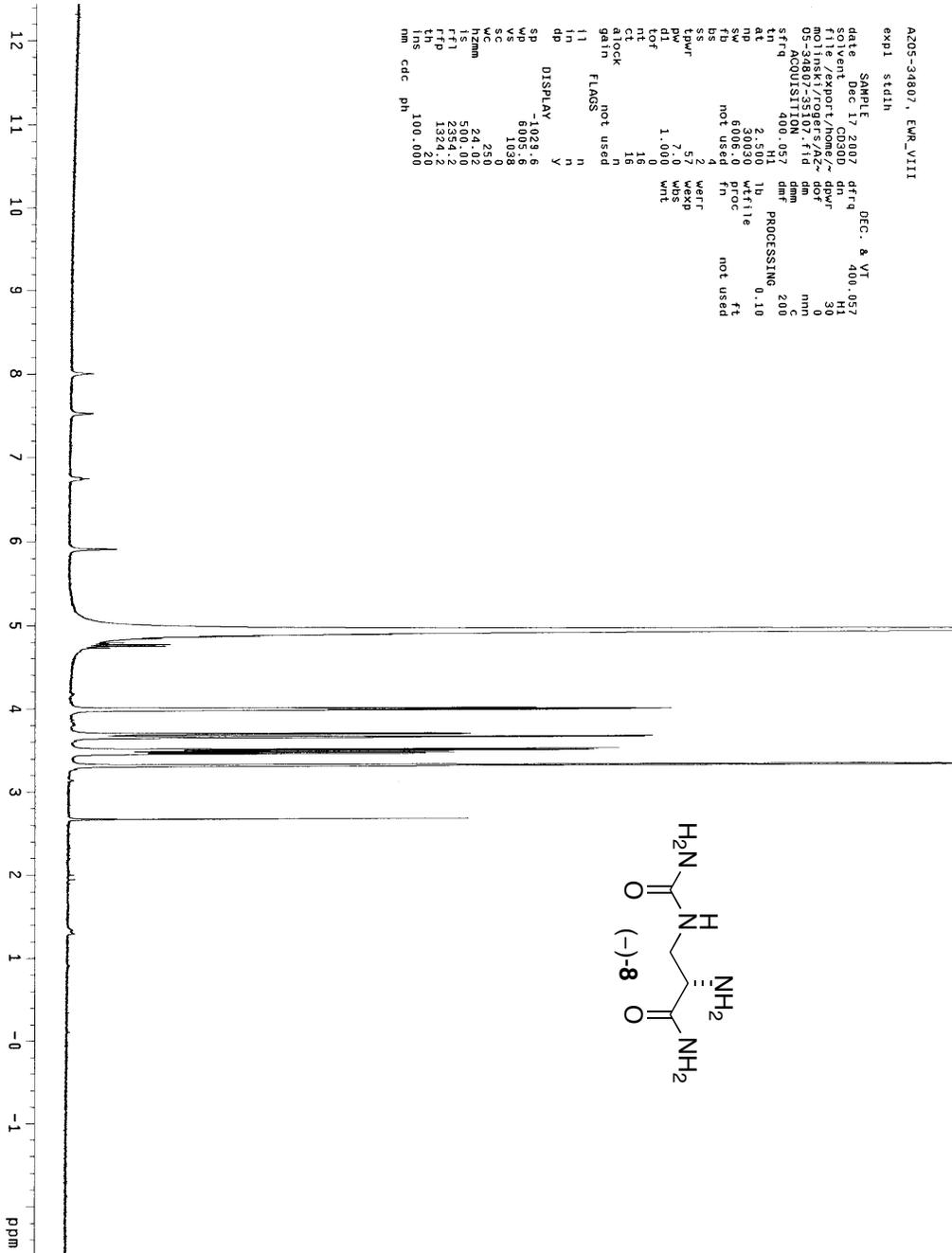




A205-34807, EWR\_VIII

exp1 std1h

```
date SAMPLE Dec 17 2007 dfrq DEC. & VI
sfreq 400.057 dfrq 400.057
file /export/home/~
molinski/rogers/AZ- dpr 30
05-34807-35107.fid dm 30
sfreq 400.057 dm 30
tn 400.057 dm 200
at 2.500 H1 1b dm PROCESSING 200
np 30000 Wf11e 0.10
fb 63000 not used ft
bs not used f1 not used
ss 2 werr
dpr 57 wesp
d1 77 wsc
d2 1.000 wnt
tof 0
nt 16
atlock 1 n
gain not used
flags not used
11 n
11 n
dp y
DISPLAY y
SP -1023.6
VP 8003.8
WC 1000
SC 0
hZnm 250
f1 24.02
f2 239.42
f3 1324.2
th 20
ms cdc phi 100.000
```



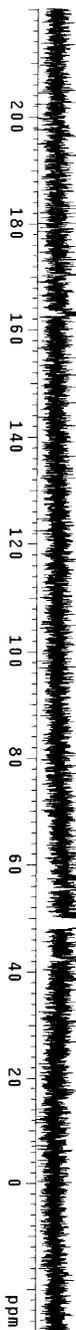
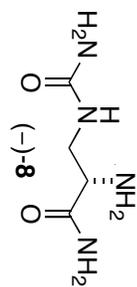
A202-24707, EWR\_VIII

exp1 std13c

SAMPLE DEC. & VT 399.913  
date Sep 6 2007 dfrq 399.913  
s1 8 020807 dnm H1  
s1 8 020807 dnm H1  
molinski/rogers/AZ dof 0  
02-24707-24807b-ft~ dm yyy  
w

ACQUISITION d dnm  
sfrq 100.567 dnm PROCESSING 9700  
tn C13 1b 1.20  
at 1.500 wfttle  
np 250.000 ft not used  
fb 13800  
bs 16 werr  
ss 54 wexp  
dw 6 wds  
d1 2.500 msl  
tof 11.00  
nt 11.00  
atlock 11.00  
gain not used  
flags not used  
i1 n  
i2 n  
dp y

DISPLAY  
sp -2858.5  
sd 2858.5  
vs 249.2098  
sc 0  
wc 250  
ncmm 100.00  
fzmm 100.00  
rf1 7786.2  
rfp 4927.3  
th 20  
ms no ph 100.000

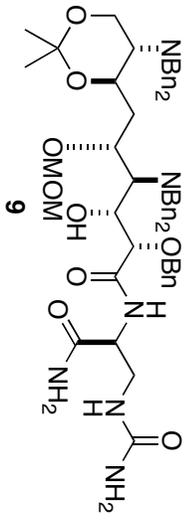
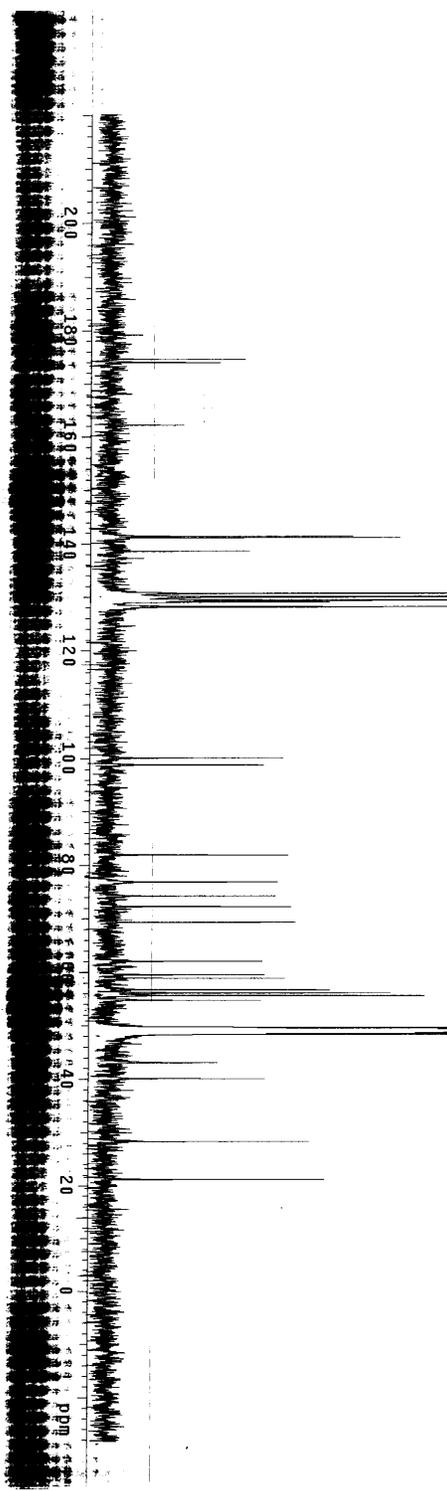


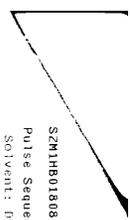


```

EMR VIII
Date: 12/06/07
Time: 16:50
User:
Host: /opt/ft/rogers/AL-100
P1: 1.00
P2: 0.00
P3: 0.00
P4: 0.00
P5: 0.00
P6: 0.00
P7: 0.00
P8: 0.00
P9: 0.00
P10: 0.00
P11: 0.00
P12: 0.00
P13: 0.00
P14: 0.00
P15: 0.00
P16: 0.00
P17: 0.00
P18: 0.00
P19: 0.00
P20: 0.00
P21: 0.00
P22: 0.00
P23: 0.00
P24: 0.00
P25: 0.00
P26: 0.00
P27: 0.00
P28: 0.00
P29: 0.00
P30: 0.00
P31: 0.00
P32: 0.00
P33: 0.00
P34: 0.00
P35: 0.00
P36: 0.00
P37: 0.00
P38: 0.00
P39: 0.00
P40: 0.00
P41: 0.00
P42: 0.00
P43: 0.00
P44: 0.00
P45: 0.00
P46: 0.00
P47: 0.00
P48: 0.00
P49: 0.00
P50: 0.00
P51: 0.00
P52: 0.00
P53: 0.00
P54: 0.00
P55: 0.00
P56: 0.00
P57: 0.00
P58: 0.00
P59: 0.00
P60: 0.00
P61: 0.00
P62: 0.00
P63: 0.00
P64: 0.00
P65: 0.00
P66: 0.00
P67: 0.00
P68: 0.00
P69: 0.00
P70: 0.00
P71: 0.00
P72: 0.00
P73: 0.00
P74: 0.00
P75: 0.00
P76: 0.00
P77: 0.00
P78: 0.00
P79: 0.00
P80: 0.00
P81: 0.00
P82: 0.00
P83: 0.00
P84: 0.00
P85: 0.00
P86: 0.00
P87: 0.00
P88: 0.00
P89: 0.00
P90: 0.00
P91: 0.00
P92: 0.00
P93: 0.00
P94: 0.00
P95: 0.00
P96: 0.00
P97: 0.00
P98: 0.00
P99: 0.00
P100: 0.00

```





SZMH01808, w/1.5 ul ACN, EWR\_VIII

Pulse Sequence: szpu1

Solvent: D2O

Acq. temperature: 300.2

File: SZMH01808-020

Reference: 40088 19.902

Relax. delay: 1.000 sec

Pulse: 49.3 degrees

Acq. time: 2.000 sec

Width: 6006.0 Hz

Offset: 399.9099585 MHz

OBSERVED: 399.9099585 MHz

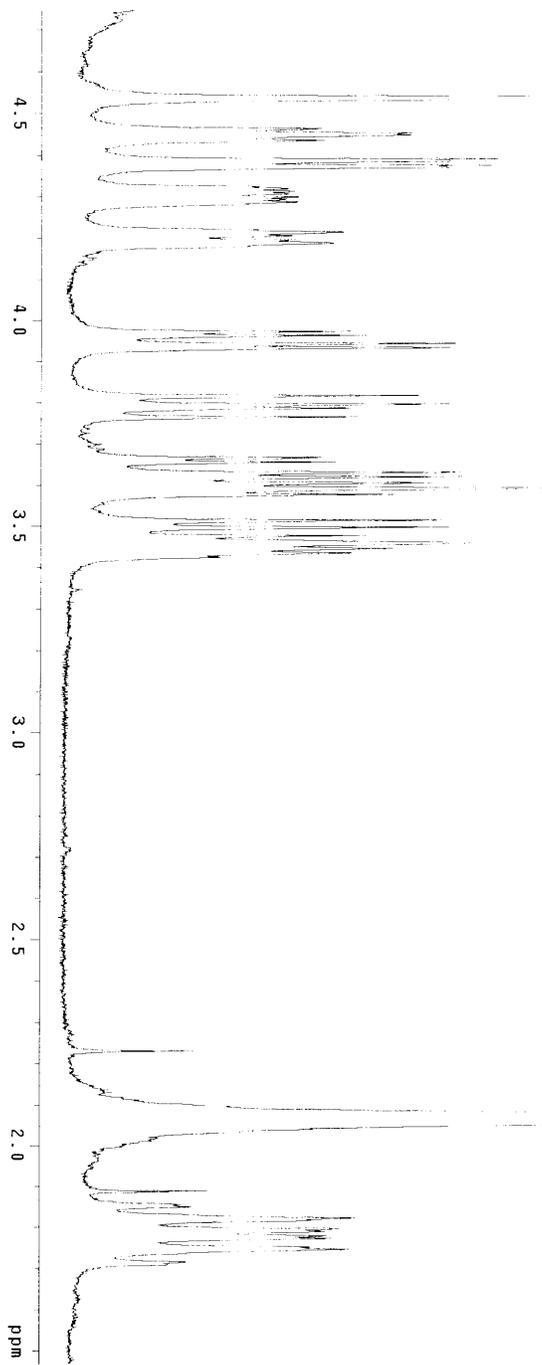
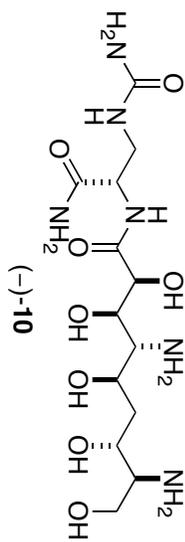
DATA PROCESSING

Line broadening: 0.1 Hz

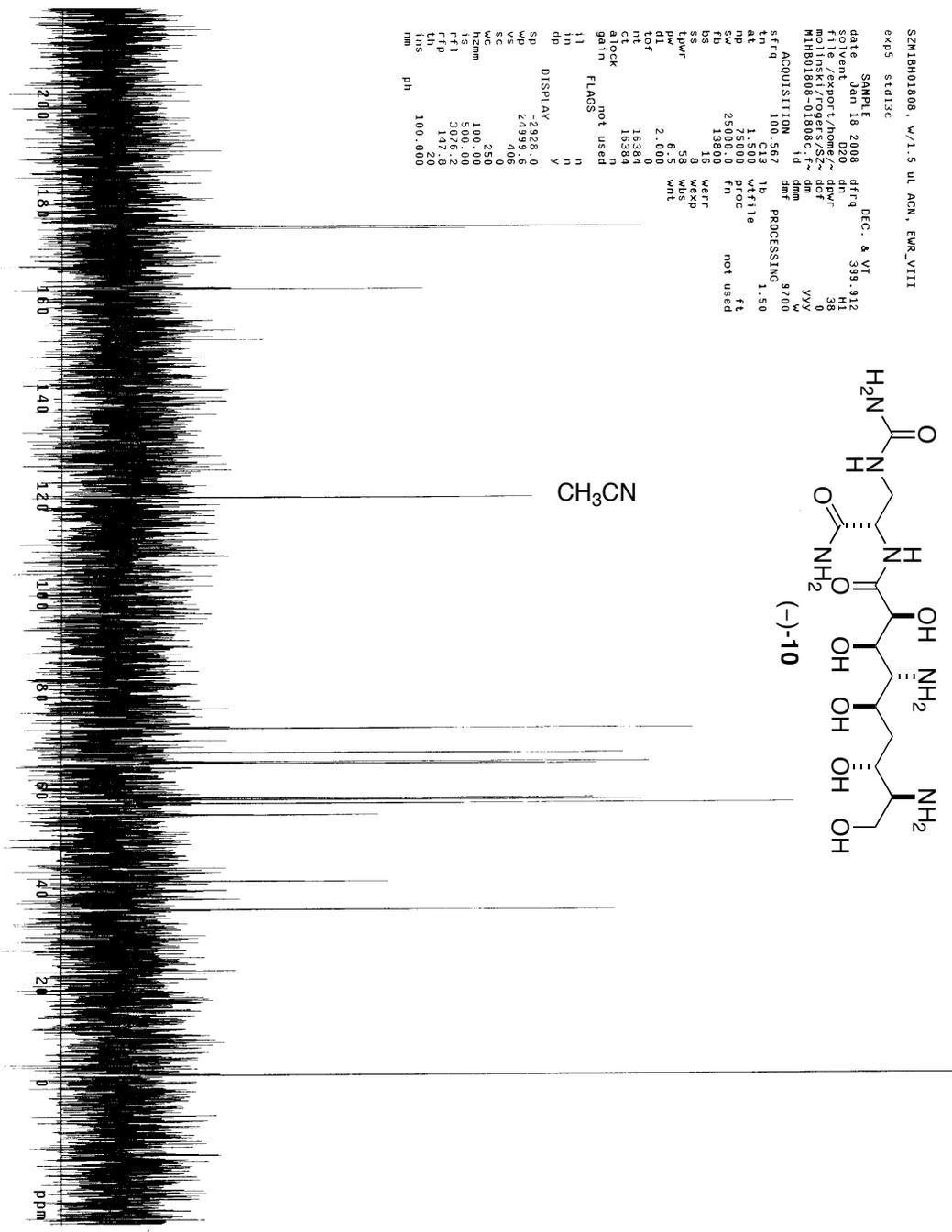
FT size: 32768

Total time: 1 min, 59 sec

CH<sub>3</sub>CN



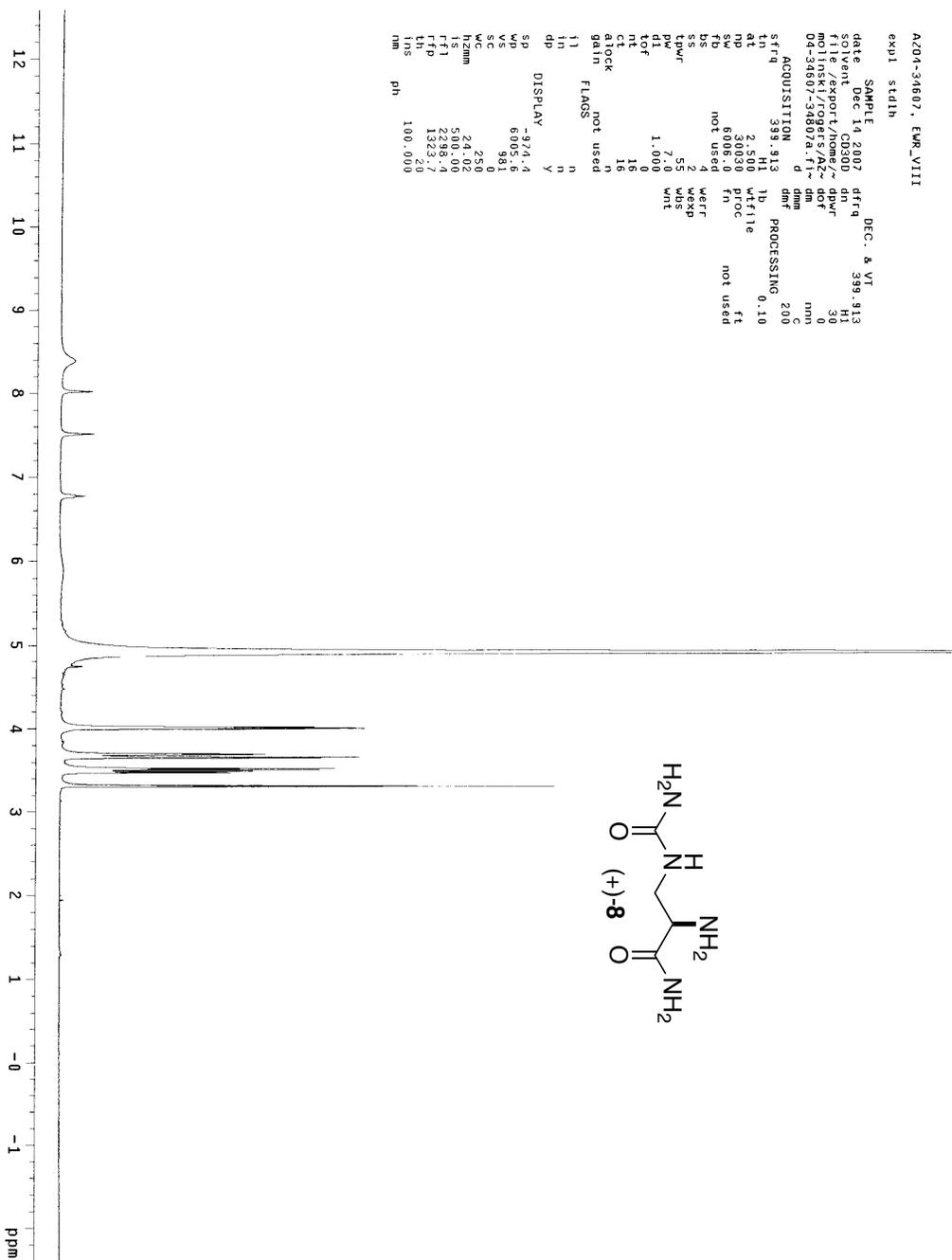
S2M18H01808, w/1.5 ul ACN, EWR\_VIII  
 exp5 std13c  
 date Jan 18 2008 DEC: & VT  
 time 11:30:00 399.912  
 file /export/home/~ molinski/r/rogers/SZ~ dof 38  
 molinski/r/rogers/SZ~ dof 0  
 M18H01808-01808c.f~ dm yyy  
 ACQUISITION 18 dm 9700  
 sffrq 100.567 dm PROCESSING 1.50  
 tn C13 1b wf file  
 at 1.300 wf file ft  
 sw 25000.0 fn not used  
 fb 13800  
 ds 18 werr  
 ts 48 wexp  
 tswr 6.5 wnt  
 dl 2.000  
 lof 16380  
 ct 16384  
 alock n  
 gain not used  
 ll n  
 ln n  
 dp y  
 DISPLAY 24828.0  
 sp 24849.0  
 vs 408  
 sc 2.0  
 wcm 100.250  
 ls 500.00  
 rff1 3976.2  
 rffp 147.8  
 th 100.000  
 nm pH



A204-34607, EWR-VIII

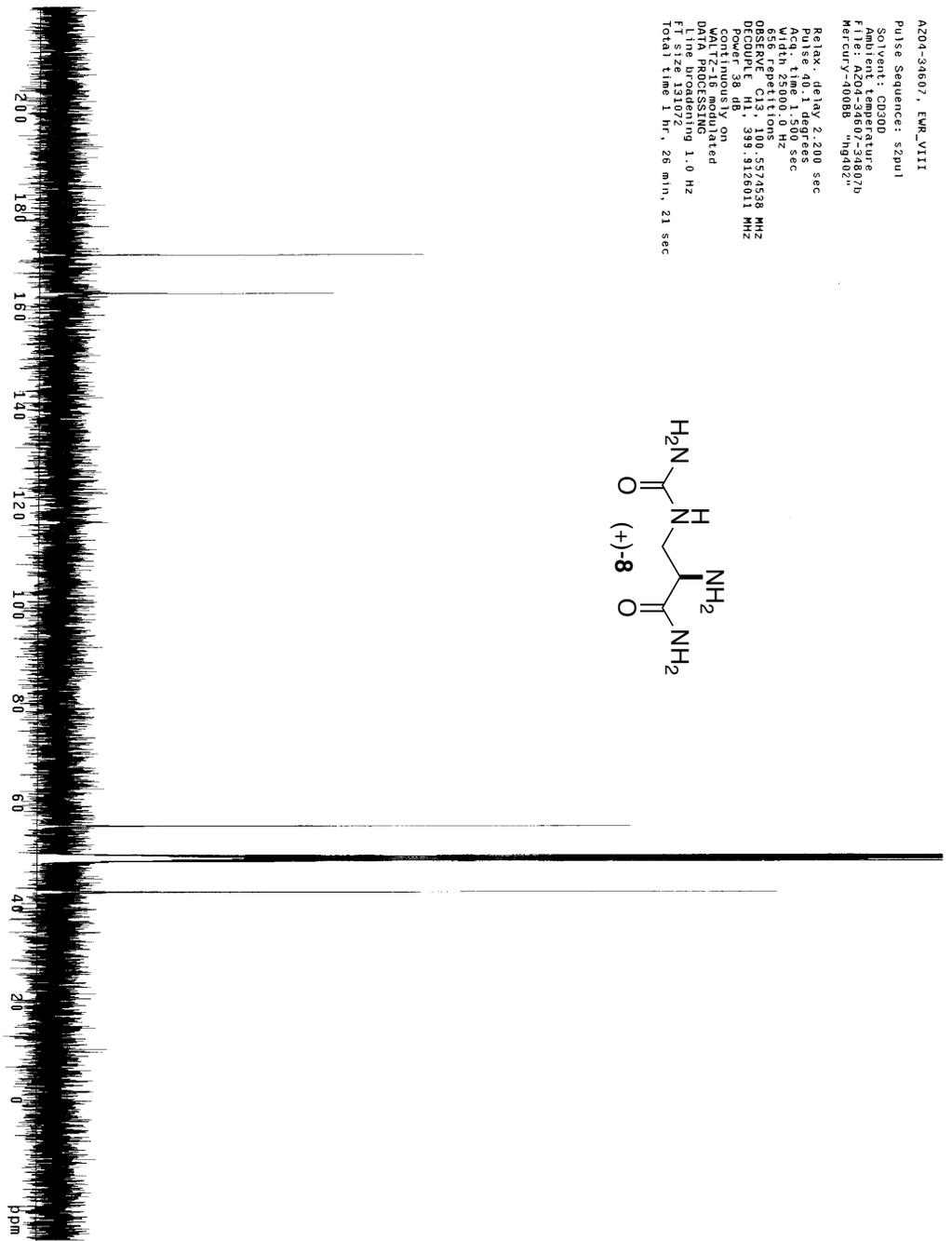
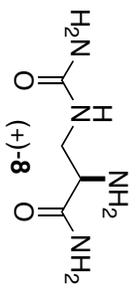
ex01 std1h

DATE Dec 14 2007 DEC. 8 VT 399.913  
TIME 12:00:00  
FILE /export/home/moliniski/rogers/AZ~  
04-34607-34607a.f1~  
ACQUISITION d mmf PROCESSING 200  
sfrq 399.913  
in HI 1b  
at 2.500 wf file  
sp 6.008 f1  
fb not used  
bs 4 werr  
ss 52 wexp  
pw 7.0 wnt  
dl 1.000  
lof 0  
ct 16  
c 15  
atlock n  
gain not used  
flags n  
in n  
dp Y  
SP DISPLAY -824.4  
VS 681.4  
VC 981  
SC 0  
WC 250  
I 24.00  
I 50.00  
RFI 2299.4  
RFP 1323.7  
THS 100.000  
nm  
ph





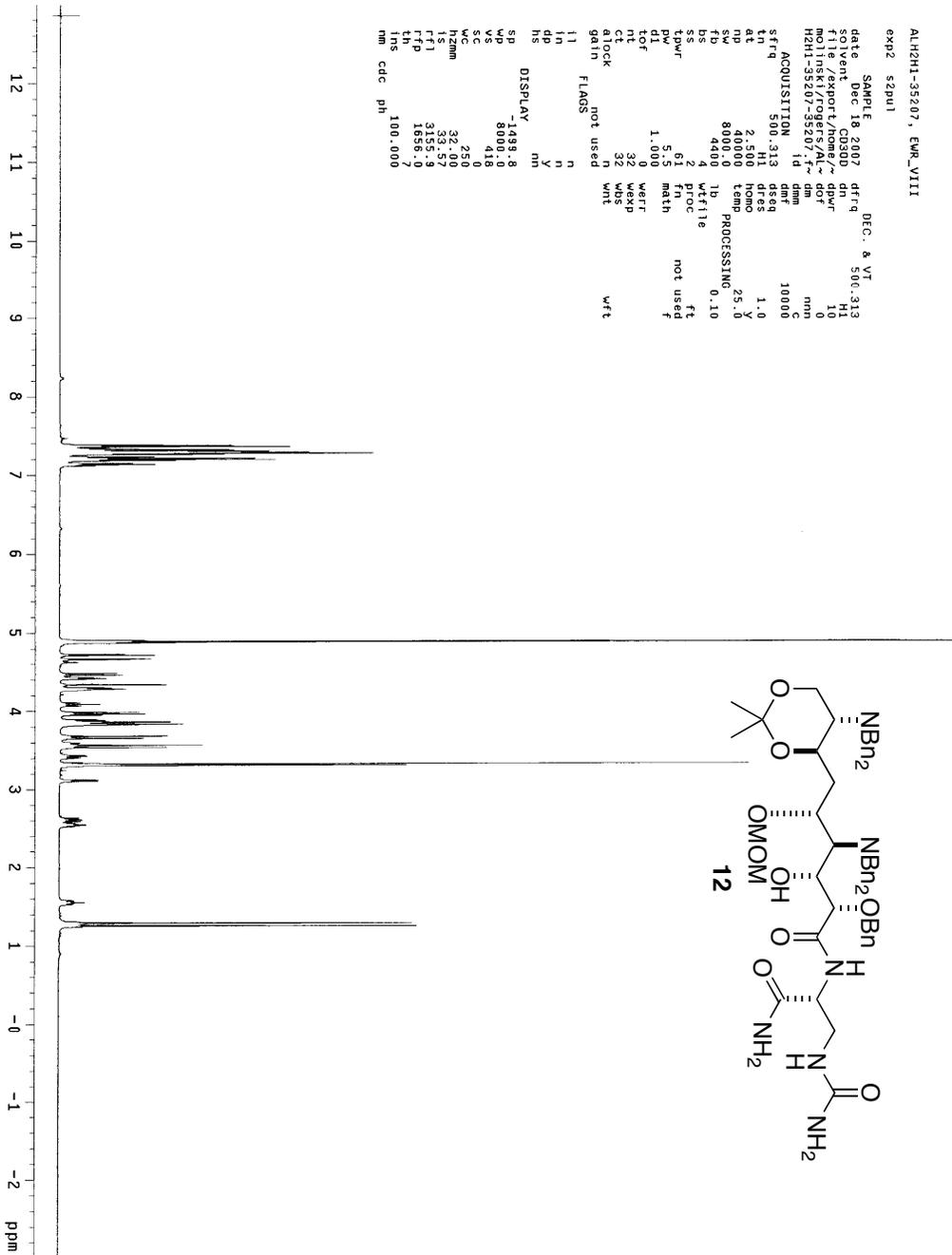
AZ04-34607, EWR\_VIII  
Pulse Sequence: szpu1  
Solvent: CD300  
Ambient Temperature  
File: AZ04-34607-34807p  
Mercury--00085 mg/02  
Pulse delay 2.200 sec  
Pulse 40.1 degrees  
Acq. time 1.500 sec  
Width 25000.0 Hz  
Observed C13  
Frequency 5574538 MHz  
Decouple H1: 399.9126011 MHz  
Power 38 dB  
Continuously on  
Data Processing  
Line broadening 1.0 Hz  
FT size 131072  
Total time 1 hr, 26 min, 21 sec



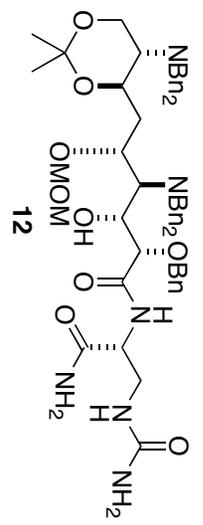
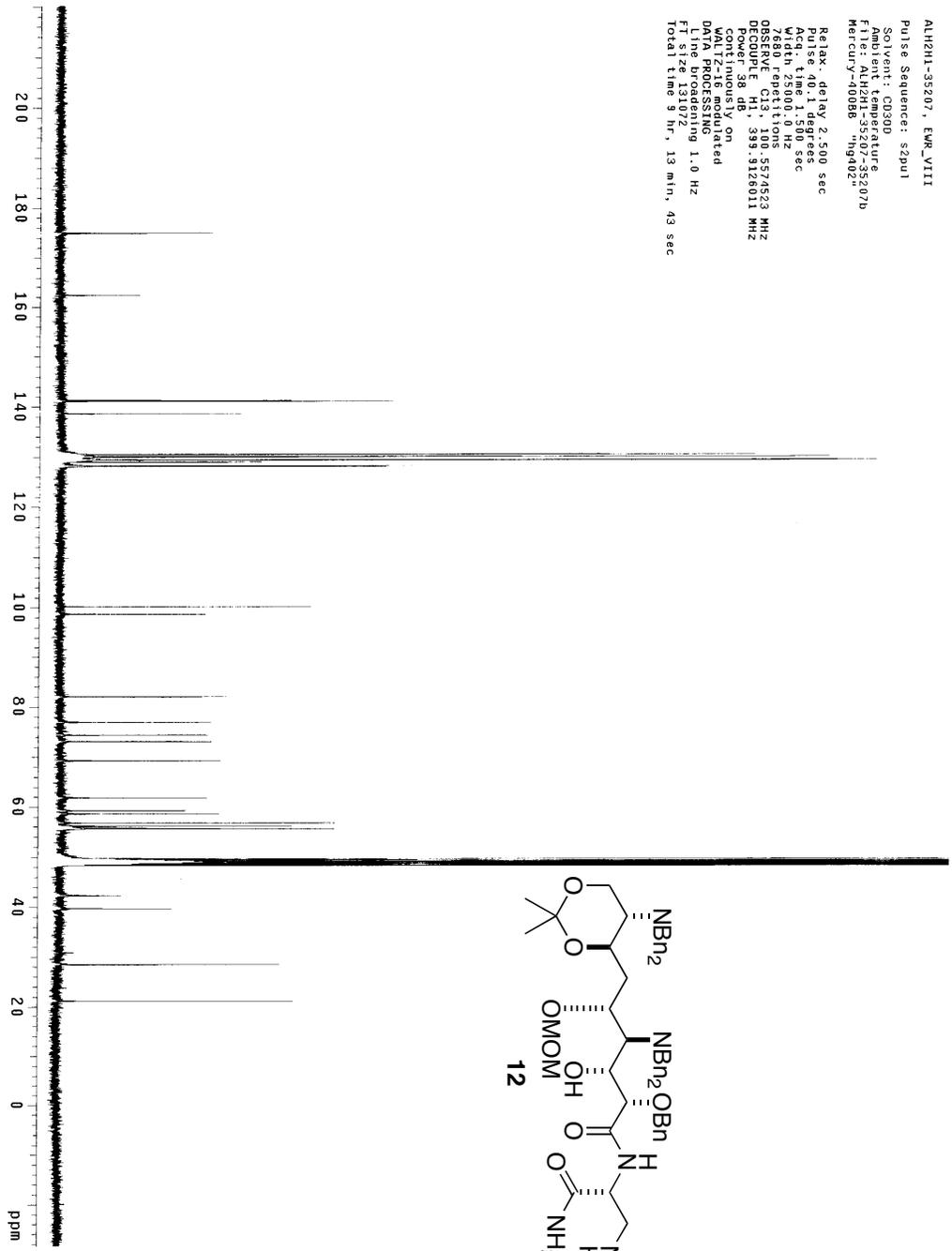
ALH2H1-35207, EMR\_VIII

exp2 s2pu1

SAMPLE DEC. & VI 500.313  
date Dec 18 2007 dfreq H1  
solvent export/homol dn H1  
molski/rogers/AL-2 dof 0  
H2H1-35207-35207-f~ dm nmh  
ACQUISITION: id dnm 10000  
sfrq 500.313 dses 1.0  
tn H1 dres 1.0  
at 2.500 homo 25.0  
np 8000 temp PROCESSING 0.10  
fb 4400 lb wfile  
bs 4 wfile  
ss 2 proc ft  
pwr 5.5 math not used  
di 1.000  
tof 0 wefr  
rt 32 wek  
atlock n wnt  
gain not used wft  
} }  
in n  
dp y  
hs mh  
DISPLAY  
sp 1499.8  
wp 8000.0  
vs 418  
sc 0  
asc 25.0  
wctmm 32.80  
ls 33.57  
rfi 3155.9  
rfp 1656.0  
lms 100.000  
nm cdc ph



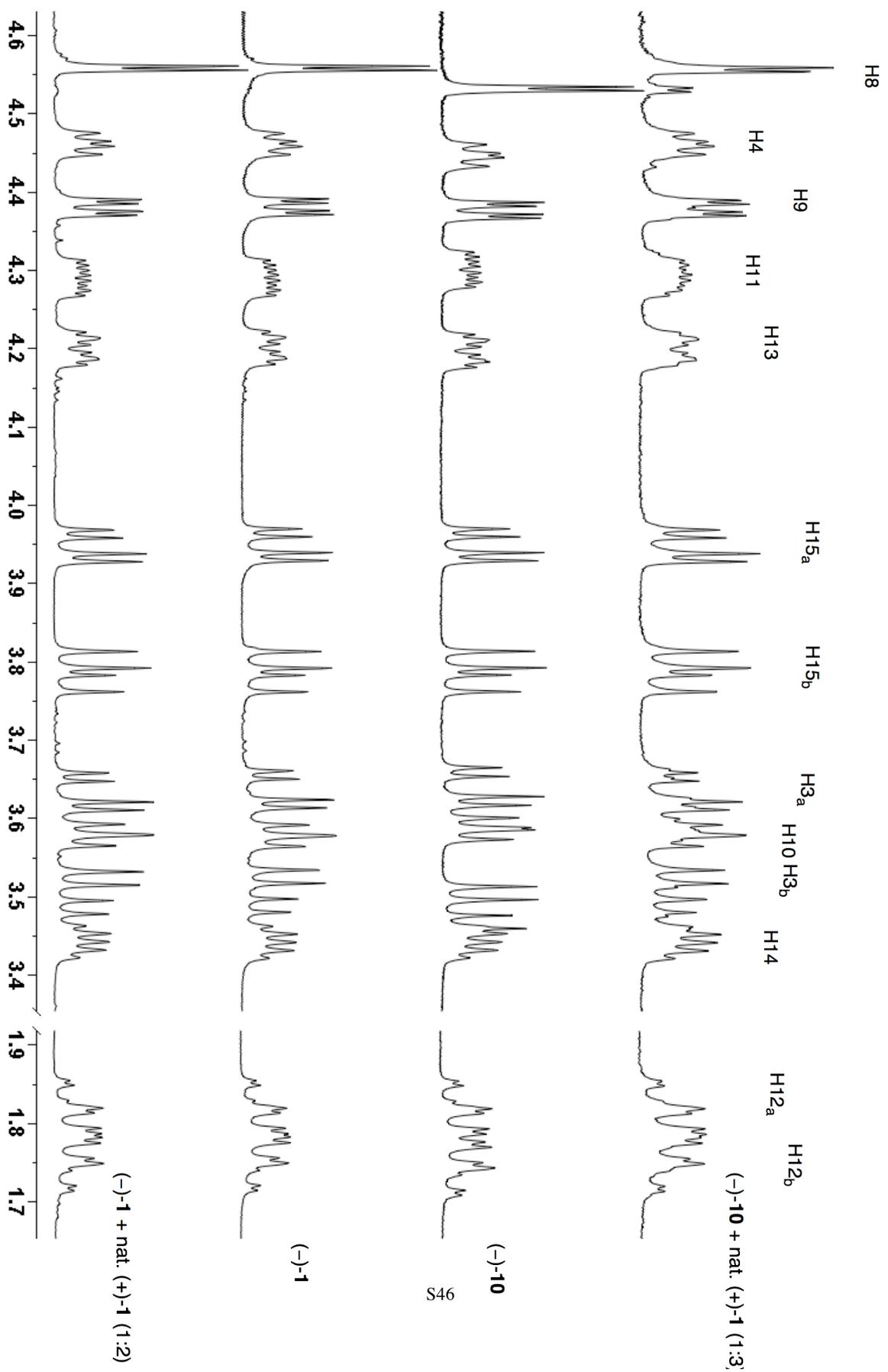
ALH2H1-35207, EWR\_VIII  
 Pulse Sequence: szpu1  
 Solvent: CD300  
 Ambient Temperature  
 File: ALH2H1-35207-35207b  
 Mercury--0086 7hg402  
 R1Prk delay 2.500 sec  
 Pulse 40.1 degree  
 Acq. time 1.500 sec  
 Width 25000.0 Hz  
 Observed F1 F2 5574523 MHz  
 DECOUPLE H1 339.9128011 MHz  
 Power 38 dB  
 Continuously on  
 Continuously on  
 Data processing  
 Line broadening 1.0 Hz  
 FT size 131072  
 Total time 9 hr, 13 min, 43 sec







<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) comparison of (-)-**1**, (+)-**1** and (-)-**10**.



$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ) comparisons (a) of (-)-1 and (b) 1;2 mol ratio of (-)-1 and (+)-1.

