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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 solvent were reagent grade. Solvents for dry reactions (DCM, DMF, THF, toluene, acetonitrile, Et_2O) 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.

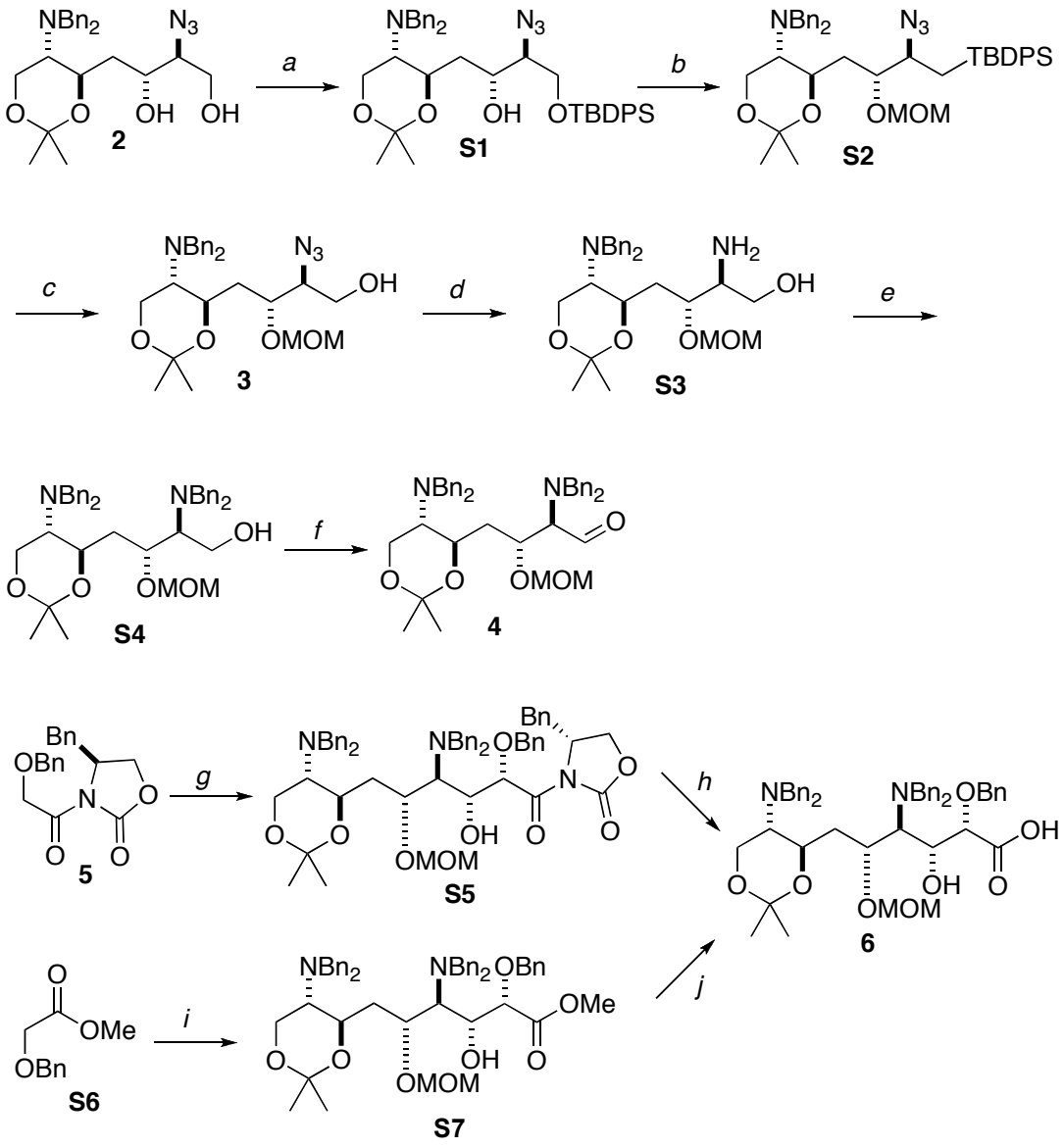
NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) using either a Varian Mercury-400 (400 MHz) or a Varian Unity-500 (500 MHz). Residual solvent signals were used for reference ($CHCl_3$ at δ 7.26 ppm for ^1H, δ 77.16 for ^{13}C NMR). HRMS measurements were measured at the University of 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[19] by derivatization with 2,4-dinitrophenyl-5-fluoro-L-leucinamide under standard conditions followed by analysis (C_{18} 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 30ºC 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_2O 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 2×10^3 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 $10^3/10^4$ cells per mL. Four wells containing the drug-free medium, H_2O and inoculum were used as controls. The inoculated plates were incubated at 30ºC for 24 h (*Candida* sp.). All fungal strains were tested in deuplicate 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.

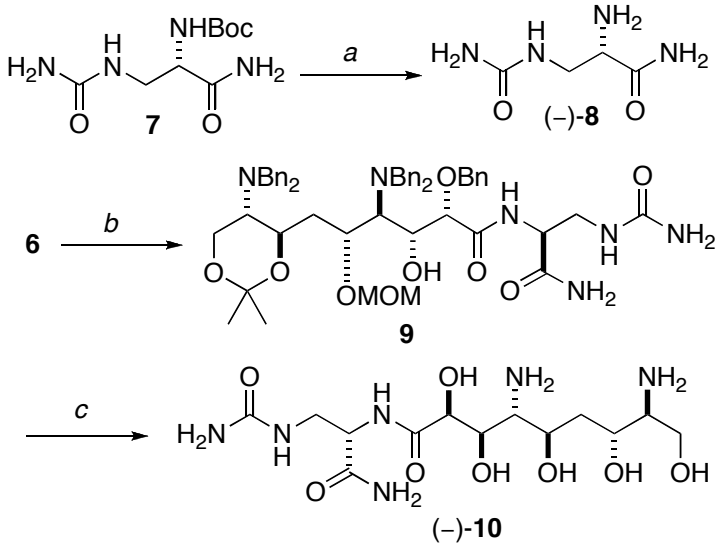
[19] P. Marfey, *Carlsberg Res. Commun.* **1984**, *49*, 591-596.

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



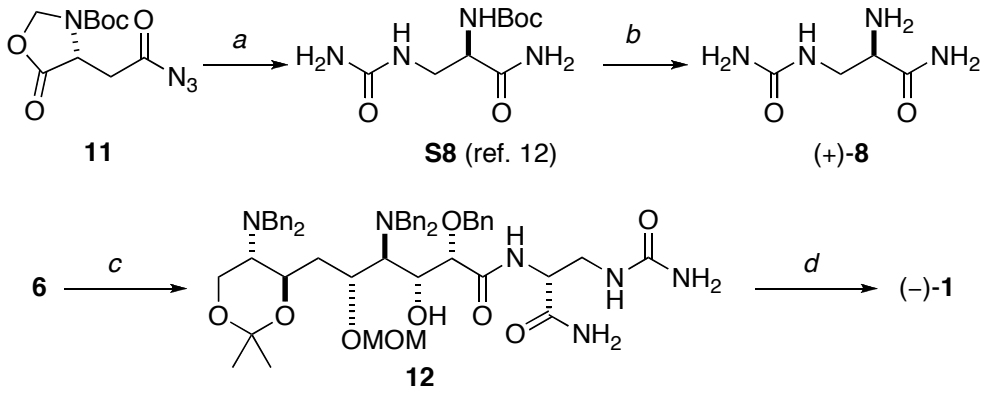
(a) TBDPSCl, imidazole, DMF, 0 ˚C-rt, 4 h, 91%; (b) $MeOCH_2Cl$, Hünig's base, CH_2Cl_2, 0 ˚C-rt, 56 h, 98%; (c) TBAF, THF, –10 ˚C, 4 h, 95%; (d) Lindlar's cat., H_2, (1 atm), EtOH, 14 h, 98%; (e) BnBr, K_2CO_3, CH_3CN, 31 h, 91%; (f) (*i*) $(COCl)_2$, DMSO, CH_2Cl_2, –78 ˚C, (*ii*) Et_3N, 94%; (g) (*i*) *n*-Bu_2BOTf, Et_3N, CH_2Cl_2, –78 to 0 ˚C, 3 h, (*ii*) **4**, –78 to 0 ˚C, 2.5 h, 77%, dr 24:1; (h) H_2O_2, LiOH, 0 ˚C, 30 min, 96%; (i) (*i*) *n*-Bu_2BOTf, Hünig's base, Et_2O, –78 ˚C, 1.5 h, (*ii*) **4**, –78 to 0 ˚C, 2 h, 44%, 37% de; (j) LiOH, H_2O: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*) EDCI, HOBt, DMF, 0 ˚C, 10 min, (*ii*) (–)-**8**, Et_3N, 0 ˚C-rt, 1 h, 81%; (c) (*i*) HCl, MeOH, H_2 (5 atm), Pd/C, 1 h, (*ii*) HCl, H_2O, H_2 (5 atm), Pd/C, 1 h, 76%.

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



(a) (*i*) μW, toluene, 110 ˚C, 15 min, (*ii*) THF, NH_3, 30 min, (*iii*) 2M NH_3, MeOH, 5 h, (*iv*) 1*N* NaOH, MeOH, 4.5 h, 62%; (b) TFA, 0 ˚C, 1 h, 99%; (c) (*i*) EDCI, HOBt, DMF, 0 ˚C, 10 min, (*ii*) (+)-**8**, Et_3N, 0 ˚C-rt, 1 h, 88%; (d) (*i*) HCl, MeOH, H_2 (5 atm), Pd/C, 1 h, (*ii*) HCl, H_2O, H_2 (5 atm), Pd/C, 1 h, 75%.

Experimental:

(2*R*,3*S*)-3-azido-4-(*tert*-butyldiphenylsilyloxy)-1-((4*R*,5*S*)-5-(dibenzylamino)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-ol (S1). *tert*-Butyldiphenylchlorosilane (492 µL, 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 ºC. 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 × 50 mL) and combined extracts washed with brine (100 mL), dried over Na_2SO_4 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) ν 3500, 3070, 2929, 2859, 2101, 1791, 1460, 1429, 1374, 1265, 1225, 1100, 819 cm^{-1}; $[\alpha]_D^{23}$ +42.3º ($CHCl_3$, *c* 9.52); ^1H NMR (500 MHz, $CDCl_3$) δ 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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_2), 58.0 (CH_2), 57.3 (CH), 54.8 (CH_2), 35.4 (CH_2), 26.9 (CH_3), 26.8 (CH_3), 21.4 (CH_3), 19.2 (C); HREIMS *m/z* 678.3586 $[M]^+$, calcd. for $C_{40}H_{50}N_4O_4Si_1$ 678.3596.

(4*R*,5*S*)-4-((2*R*,3*S*)-3-azido-4-(*tert*-butyldiphenylsilyloxy)-2-(methoxymethoxy)butyl)-*N*,*N*-dibenzyl-2,2-dimethyl-1,3-dioxan-5-amine (S2). Chloromethyl methyl ether (628 µL, 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 ºC. The mixture was warmed to room temperature and stirred for 56 hours then quenched by addition of saturated aqueous NH_4Cl (50 mL). The mixture was extracted with ethyl ether (3 × 50 mL) and combined extracts washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4 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) ν 3067, 3034, 3001, 2944, 2894, 2861, 2110, 1508, 1475, 1458, 1433, 1392, 1277, 1235, 1128, 1037, 831, 757, 724 cm^{-1}; $[\alpha]_D^{24}$ +30.8º ($CHCl_3$, *c*

6.68); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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 (CH_2) 75.6 (CH), 67.5 (CH), 66.4 (CH), 63.6 (CH_2), 58.3 (CH_2), 57.8 (CH), 55.9 (CH_3), 54.7 (CH_2), 34.2 (CH_2), 27.3 (CH_3), 26.8 (CH_3), 21.2 (CH_3), 19.2 (C); HRESIMS *m/z* 723.3939 $[M+H]^+$, calcd. for $C_{42}H_{55}N_4O_5Si_1$ 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 ºC. The mixture was stirred for 4 hours then quenched by addition of water (125 mL). The mixture was extracted with ethyl ether (3 × 75 mL) and combined extracts washed with brine (50 mL), dried over Na_2SO_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) ν 3458, 2985, 2929, 2812, 2101, 1444, 1374, 1265, 1225, 1140, 1108, 1022, 913 cm^{-1}; mp 74 ºC; $[\alpha]_D^{23}$ +28.8º ($CHCl_3$, *c* 2.01); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 139.5 (C), 129.0 (CH), 128.5 (CH), 127.3 (CH), 99.1 (C), 97.8 (CH_2) 76.2 (CH), 66.9 (CH), 66.8 (CH), 62.0 (CH_2), 58.2 (CH_2), 57.9 (CH), 56.2 (CH_3), 54.9 (CH_2), 35.2 (CH_2), 27.3 (CH_3), 21.4 (CH_3); HREIMS *m/z* 484.2682 $[M]^+$, calcd. for $C_{26}H_{36}N_4O_5$ 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 µmol). The mixture was placed under hydrogen (1 atm) at room temperature and stirred for 14 hours. The solution was filtered through a 0.45 µm 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) ν 3467, 3362, 3292, 3030, 2986, 2934, 2882, 2829, 1597, 1492, 1457, 1387, 1230, 1160, 1108, 1038, 977, 916, 758, 706 cm^{-1}; $[\alpha]_D^{21}$ +24.5º ($CHCl_3$, *c* 3.82); ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 139.5 (C), 128.9 (CH), 128.3 (CH), 127.2 (CH), 99.0 (C), 97.9 (CH_2) 79.4 (CH), 66.8 (CH), 63.1 (CH_2), 58.1 (CH_2), 58.0 (CH), 56.0 (CH_2), 55.9 (CH_3), 54.7 (CH), 35.4 (CH_2), 27.1 (CH_3), 21.4 (CH_3); HREIMS *m/z* 458.2781 $[M]^+$, calcd. for $C_{26}H_{38}N_2O_5$ 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 μL, 5.37 mmol) was added dropwise to a stirred solution of amine **S3** (547 mg, 1.19 mmol) and K_2CO_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 × 50 mL) and combined extracts washed with brine (75 mL), dried over Na_2SO_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) ν 3476, 3065, 3030, 2995, 2943, 2882, 2812, 1597, 1492, 1457, 1379, 1265, 1221, 1151, 1108, 1029, 977, 916, 758, 706 cm^{-1}; $[\alpha]_D^{20}$ +28.8º ($CHCl_3$, *c* 6.48); ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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 (CH_2), 58.0 (CH), 57.9 (CH_2), 56.4 (CH_3), 54.9 (CH_2), 54.8 (CH_2), 38.6 (CH_2), 27.9 (CH_3), 20.9 (CH_3); HRMS *m/z* 639.3973 $[M+H]^+$, calcd. for $C_{40}H_{51}N_2O_5$ 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 μL, 152 mg, 1.94 mmol) in CH_2Cl_2 (138 μL) was added dropwise to a stirred solution of oxalyl chloride (82.6 μL, 122 mg, 939 μmol) in anhydrous CH_2Cl_2 (800 μL) at –78 ºC. The mixture was stirred for 15 minutes then a solution of alcohol **S4** (200 mg, 313 μmol) in CH_2Cl_2 (800 μL) was added dropwise. The mixture was stirred for 1.25 hours at –78 ºC then triethylamine (393 μL, 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 × 60 mL) and combined extracts washed with 1% HCl solution (100 mL), water (2 × 100 mL), saturated $NaHCO_3$ solution (50 mL), brine (50 mL), dried over Na_2SO_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) ν 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 cm^{-1}; $[\alpha]_D^{22}$ +47.6º ($CHCl_3$, *c* 10.3); ^1H NMR (400 MHz, $CDCl_3$) *δ* 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}C NMR (100 MHz, $CDCl_3$) *δ* 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_2) 74.8 (CH), 68.9 (CH), 66.6 (CH), 58.4 (CH_2), 57.9 (CH), 56.1 (CH_3), 55.0 (CH_2), 54.8 (CH_2), 37.5 (CH_2), 27.8 (CH_3), 20.9 (CH_3); HREIMS *m/z* 636.3562 $[M]^+$, calcd. for $C_{40}H_{48}N_2O_5$ 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 μL, 206 μmol) and triethylamine (32,7 μL, 235 μmol) was added to a stirred solution of **5** (31.8 mg, 176 μmol) in dichloromethane (250 μL) at –78 ºC. The mixture was warmed to 0 ºC and stirred for 3 hours then cooled to –78 ºC and aldehyde **4** (93.0 mg, 147 μmol) in dichloromethane (150 μL) was added dropwise. The mixture was stirred for 10 minutes then warmed to 0 ºC and stirred a further 2.5 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_2O_2 (620 μL) at 0 ºC. This mixture was stirred at 0 ºC for 1 hour then 5% $NaHCO_3$ 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_2SO_4 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^{-1}; $[\alpha]_D^{21}$ +86.5º ($CHCl_3$, *c* 3.45); ^1H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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_2), 80.1 (CH), 74.6 (CH), 73.2 (CH_2), 70.3 (CH), 67.3 (CH), 66.6 (CH_2), 60.9 (CH), 58.5 (CH_2), 58.0 (CH), 56.2 (CH), 56.1 (CH_3), 54.7 (CH_2), 38.3 (CH_2), 37.7 (CH_2), 28.0 (CH_3), 20.5 (CH_3); HRESIMS *m/z* 962.4959 $[M+H]^+$, calcd. for $C_{59}H_{68}N_3O_9$ 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 ºC. 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 ºC 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_2O_2 (620 μL) at 0 ºC. This mixture was stirred at 0 ºC for 1 hour then 5% $NaHCO_3$ 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_2SO_4 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) ν 3432, 3065, 3030, 2986, 2934, 2890, 2838, 1754, 1597, 1492, 1449, 1379, 1265, 1213, 1151, 1082, 1029, 916, 819, 758, 706 cm^{-1}; $[\alpha]_D^{24}$ −31.0º ($CHCl_3$, *c* 4.81); ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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 (CH_2), 78.5 (CH), 74.5 (CH), 72.3 (CH_2), 69.9 (CH), 67.6 (CH), 60.9 (CH), 58.3 (CH_2), 58.2 (CH), 56.3 (CH_3), 55.3 (CH_2), 54.7 (CH_2), 52.2 (CH), 39.5 (CH_2), 27.5 (CH_3), 21.5 (CH_3); HRMS *m/z* 817.4438 $[M+H]^+$, calcd. for $C_{50}H_{61}N_1O_8N_2$ 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 H_2O_2 (12.7 μL, 125 μmol) and lithium hydroxide monohydrate (1.74 mg, 41.6 μmol) was added to a stirred solution of **S5** (21.0 mg, 21.8 μmol) in 1:3 H_2O:THF (430 μL) at 0 ºC. The mixture was stirred for 30 minutes then quenched by addition of 1.5 N Na_2SO_3 solution (94 μL) and the mixture stirred for 10 minutes at 0 ºC 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 × 15 mL), and brine (10 mL), dried over Na_2SO_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 μmol) was added to a stirred solution of ester **S7** (6.50 mg, 7.96 μmol) in 3:2:2 MeOH:H_2O:THF (350 μL) 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 × 5 mL) and combined extracts washed with brine (5 mL), dried over Na_2SO_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) ν 3450, 3065, 3021, 2925, 2847, 1728, 1492, 1449, 1379, 1265, 1213, 1108, 1073, 1029, 968, 916, 750, 697 cm^{-1}; $[\alpha]_D^{21}$ +7.7º ($CHCl_3$, *c* 4.03); ^1H NMR (400 MHz, $CDCl_3$) *δ* 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}C NMR (100 MHz, $CDCl_3$) *δ* 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_2), 78.5 (CH), 75.3 (CH), 72.9 (CH_2), 71.5 (CH), 67.9 (CH), 60.8 (CH), 58.4 (CH_2), 57.9 (CH), 56.5 (CH_3), 55.1 (CH_2), 54.9 (CH_2), 39.6 (CH_2), 27.5 (CH_3), 20.9 (CH_3); HRMS *m/z* 803.4267 $[M+H]^+$, calcd. for $C_{49}H_{59}N_2O_8$ 803.4271.

(*S*)-2-amino-3-ureidopropanamide ((–)-8). CF_3COOH (600 μL) was added dropwise to **7** (14.5 mg, 58.9 μmol, neat) with stirring at 0 ºC. The mixture was stirred 1 hour at 0 ºC then warmed to room temperature and stirred for 2.5 hours. The reaction mixture was blown to dryness with a stream of N_2 and then dried under azeotropic distillation with 1:1 MeOH:toluene (2 × 1 mL) to provided (–)-**8** (14.9 mg, 98%, 94% ee by Marfey's analysis[1]) as a viscous oil: $[\alpha]_D^{21}$ −15.1º (CH_3OH, *c* 6.63); ^1H NMR (400 MHz, CD_3OD) *δ* 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}C NMR (100 MHz, CD_3OD) *δ* 170.4 (C), 162.6 (C), 55.4 (CH), 42.3 (CH_2); HRMS *m/z* 147.0882 $[M+H]^+$, calcd. for $C_4H_{11}N_4O_2$ 147.0877.

(2*S*,3*R*,4*S*,5*R*)-*N*-((*S*)-1-amino-1-oxo-3-ureidopropan-2-yl)-2-(benzyloxy)-4-(dibenzylamino)-6-((4*R*,5*S*)-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 μmol) in DMF (100 μL) was cooled to 0 ºC under nitrogen and treated with EDCI (5.12 mg, 26.7 μmol) and HOBt (3.89 mg, 28.8 μmol). After 10 minutes, amine **17** (6.0 mg, 23.1 μmol) in DMF (50 μL) and triethylamine (2.86 μL, 20.6 μmol) 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 × 3 mL). The organic phase was dried over Na_2SO_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) ν 3450, 3362, 2065, 3030, 2986, 2934, 2838, 2523, 2418, 1658, 1606, 1492, 1449, 1379, 1221, 1151, 1099, 1064, 1029, 916, 750, 697

cm^{-1}; $[\alpha]_D^{20}$ +4.3º ($CHCl_3$, *c* 5.66); ^{1}H NMR (400 MHz, CD_3OD) δ 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); ^{13}C NMR (100 MHz, CD_3OD) δ 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_2), 81.9 (CH), 76.9 (CH), 74.3 (CH_2), 72.3 (CH), 69.4 (CH), 62.0 (CH), 59.5 (CH_2), 58.9 (CH), 56.7 (CH_3), 56.1 (CH_2), 55.6 (CH_2), 54.7 (CH), 43.1 (CH_2), 40.1 (CH_2), 28.3 (CH_3), 21.2 (CH_3); HRMS *m/z* 931.4951 $[M+H]^+$, calcd. for $C_{53}H_{67}N_6O_9$ 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 µL, 12.7 mg, 120 µmol) was added to **9** (11.5 mg, 12.4 µmol) in dry MeOH (1.5 mL) at 0 ºC. The mixture was warmed to room temperature over 5 minutes with agitation. 10% Pd/C (13.1 mg, 12.4 µmol, 100 mol % Pd) was added and the mixture placed under H_2 (5 atm) and agitated for 1 hour on a Parr shaker. The mixture was filtered through a 0.45 µm 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 µmol, 100 mol % Pd) added. The mixture was placed under H_2 (5 atm) and agitated for 1 hour on a Parr shaker. Filtration through a 0.45 µm 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 × 250 mm column, 1.3 MeOH: 0.1 CF_3COOH: 98.6 H_2O, 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: $[\alpha]_D^{21}$ –23.0º (H_2O, *c* 1.49); ^{1}H NMR (400 MHz, 0.2% acetonitrile:D_2O (ref δ 2.06)) δ 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); ^{13}C NMR (100 MHz, 0.2% acetonitrile:D_2O (ref δ 1.47)) δ

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_2), 57.3 (CH), 55.0 (CH), 41.4 (CH_2), 35.6 (CH_2); HRMS *m/z* 419.1871 $[M+Na]^+$, calcd. for $C_{13}H_{28}N_6O_8Na_1$ 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 ºC in a microwave reactor for 15 minutes. The mixture was cooled to room temperature and NH_3 (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_3 in MeOH (4.6 mL, 9.25 mM) and stirred for 5 hours. The reaction mixture was dried and redisolved 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 $MgSO_4$, flitered and dried. Flash chromatography (silica, 20% MeOH in dichloromethane) provided **S8** (316 mg, 62%) as a crystalline solid (mp 141.5 ºC). Compound **S8** matched literature values (Ref. 12).

(*R*)-2-amino-3-ureidopropanamide ((+)-8). CF_3COOH (1.0 mL) was added dropwise to **9** (24.8 mg, 101 μmol, neat) with stirring at 0 ºC. The mixture was stirred 1 hour at 0 ºC. The reaction mixture was blown to dryness with a stream of N_2 at 0 ºC 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[1]) as a viscous oil: $[\alpha]_D^{20}$ +15.7º (CH_3OH, *c* 9.91); ^{1}H NMR (400 MHz, CD_3OD) 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); ^{13}C NMR (100 MHz, CD_3OD) δ 170.5 (C), 162.7 (C), 55.4 (CH), 42.2 (CH_2); HRMS *m/z* 147.0882 $[M+H]^+$, calcd. for $C_4H_{11}N_4O_2$ 147.0877.

(2*S*,3*R*,4*S*,5*R*)-*N*-((*R*)-1-amino-1-oxo-3-ureidopropan-2-yl)-2-(benzyloxy)-4-(dibenzylamino)-6-((4*R*,5*S*)-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 ºC 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_2SO_4 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) ν 3361, 3061, 3026, 2932, 1666, 1602, 1540, 1453, 1377, 1147, 1103, 1070, 1027, 749, 699 cm^{-1}; $[\alpha]_D^{20}$ +7.0º ($CHCl_3$, *c* 8.34); ^1H NMR (500 MHz, CD_3OD) δ 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); ^{13}C NMR (100 MHz, CD_3OD) δ 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_2), 82.0 (CH), 77.0 (CH), 74.4 (CH_2), 73.1 (CH), 69.2 (CH), 61.8 (CH), 59.2 (CH_2), 58.6 (CH), 56.7 (CH_3), 56.1 (CH_2), 55.7 (CH), 55.6 (CH_2), 42.3 (CH_2), 39.7 (CH_2), 28.4 (CH_3), 21.2 (CH_3); HRMS *m/z* 931.4949 $[M+H]^+$, calcd. for $C_{53}H_{67}N_6O_9$ 931.4964.

(2*S*,3*R*,4*R*,5*R*,7*R*,8*S*)-4,8-diamino-*N*-((*R*)-1-amino-1-oxo-3-ureidopropan-2-yl)-2,3,5,7,9-pentahydroxynonanamide ((–)-1). TMSCl (15.0 µL, 12.7 mg, 120 µmol) was added to **12** (16.0 mg, 17.2 µmol) in dry MeOH (1.5 mL) at 0 ºC. The mixture was warmed to room temperature over 5 minutes with agitation. 10% Pd/C (18.3 mg, 17.2 µmol, 100 mol % Pd) was added and the mixture placed under H_2 (5 atm) and agitated for 1 hour on a Parr shaker. The mixture was filtered through a 0.45 µm 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 µmol, 100 mol % Pd) added. The mixture was placed under H_2 (5 atm) and agitated for 1 hour on a Parr shaker. Filtration through a 0.45 µm 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 × 250 mm column, 1.3 MeOH: 0.1 CF_3COOH: 98.6 H_2O, 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: $[\alpha]_D^{21}$ –7.9º (H_2O, *c* 2.39); ^1H NMR (400 MHz, 0.2% acetonitrile:D_2O (ref δ 2.06)) δ 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}C NMR (100 MHz, 0.2% acetonitrile:D_2O (ref δ 1.47)) δ 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* $[M+H]^+$ 397.2054, calcd. for $C_{13}H_{29}N_6O_8$ 397.2047.

IEP2S1-23606, EWR_VI

exp2 std1h

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	fid	dmm	c
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bs	4	wexp	
ss	2	wbs	
tpwr	55	wnt	
pw	7.0		
d1	1.000		
tof	0		
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
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wp	6005.6		
vs	156		
sc	0		
wc	250		
hzmm	24.02		
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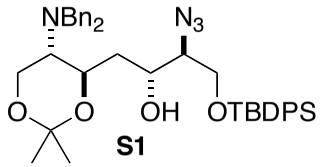
nm	ph		



S1

IEP2S1-23606, EWR_VI

exp2 std13c

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ss	4	wexp	
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dp	y		
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vs	143		
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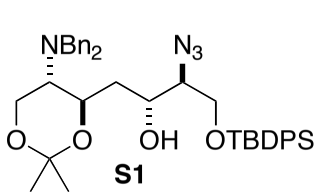
nm	ph		



S1

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IMP7S06707, EWR_VII

exp1  std1h

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                  d   dmm                c
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sfrq        399.911        PROCESSING
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np            24024   proc              ft
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fb         not used
bs                4   werr
ss                2   wexp
tpwr             55   wbs
pw              7.0   wnt
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tof               0
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alock             n
gain       not used
      FLAGS
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in                n
dp                y
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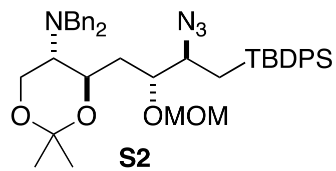
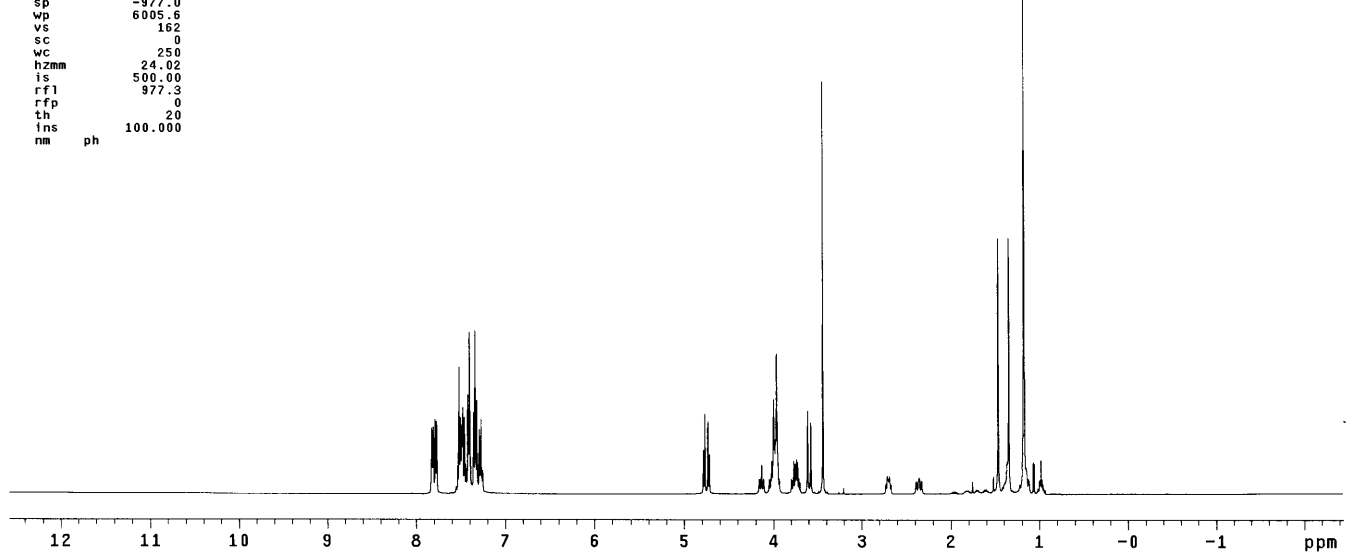
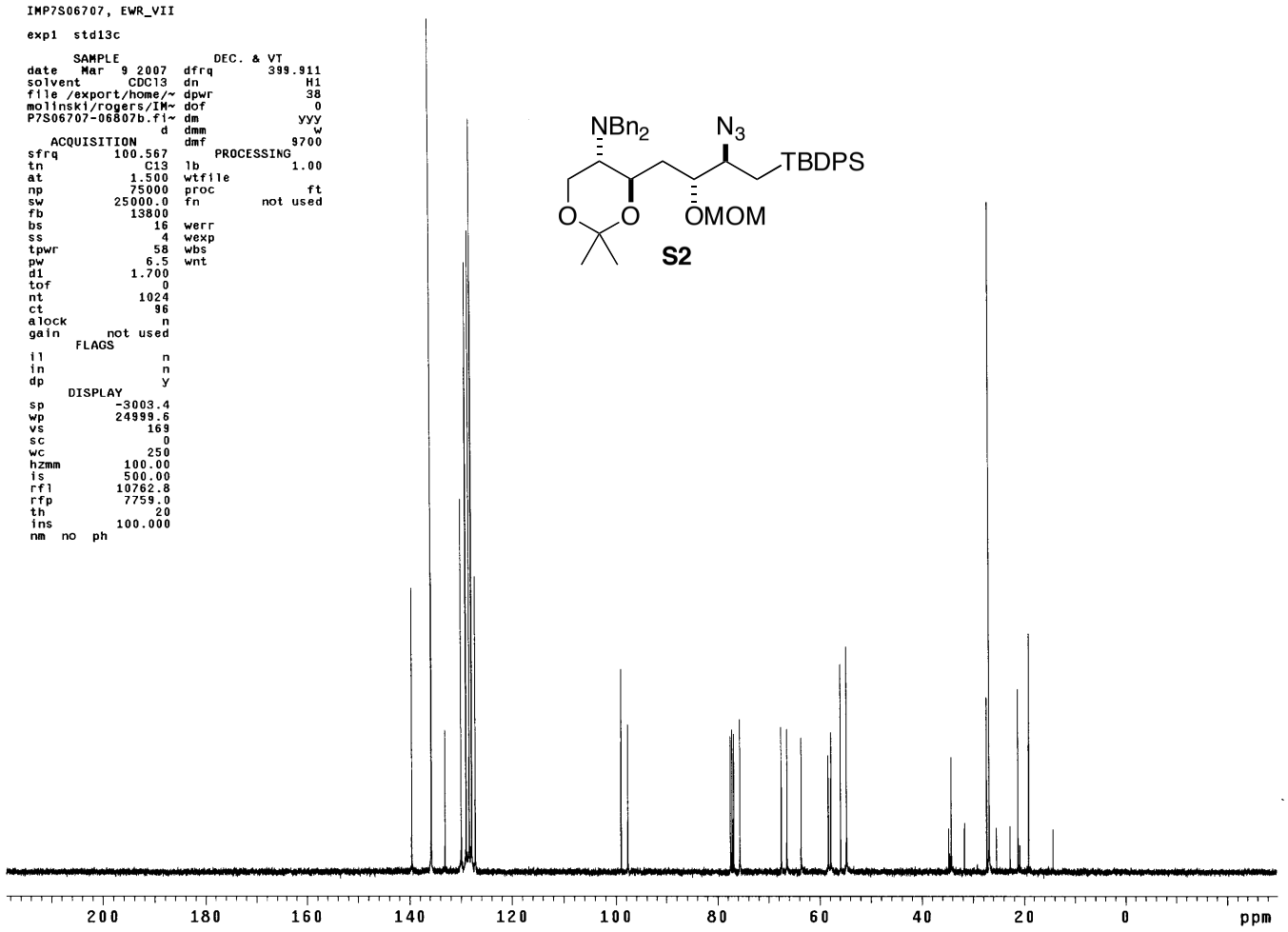


S2

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date Mar 9 2007
solvent CDCl3
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P7S06707-06807b.fi~
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sw 25000.0
fb 13800
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tpwr 58
pw 6.5
d1 1.700
tof 0
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ct 96
alock n
gain not used
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dp y
DISPLAY
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wp 24999.6
vs 169
sc 0
wc 250
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is 500.00
rfl 10762.8
rfp 7759.0
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ins 100.000
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DEC. & VT
dfrq 399.911
dn H1
dpwr 38
dof 0
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PROCESSING
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proc ft
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wexp
wbs
wnt
NBn2
N3
TBDPS
O
O
OMOM
S2
200
180
160
140
120
100
80
60
40
20
0
ppm

IMA5S08707, EWR_VII

exp1 std1h

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	A5S08707-08707a.fi~	dm	nnn
	d	dmm	c
ACQUISITION		dmf	200
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ss	2	wexp	
tpwr	57	wbs	
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ct	16		
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gain	not used		
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in	n		
dp	y		
DISPLAY			
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wp	6005.6		
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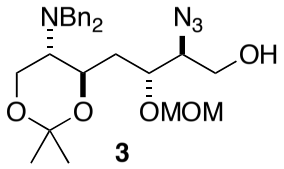
nm	ph		



3

IMA5S08707, EWR_VII

exp1 std13c

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	d	dmm	w
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ss	4	wexp	
tpwr	55	wbs	
pw	7.5	wnt	
d1	1.700		
tof	0		
nt	1024		
ct	48		
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in	n		
dp	y		
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sp	-3009.0		
wp	24999.6		
vs	130		
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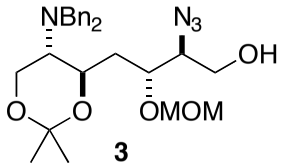
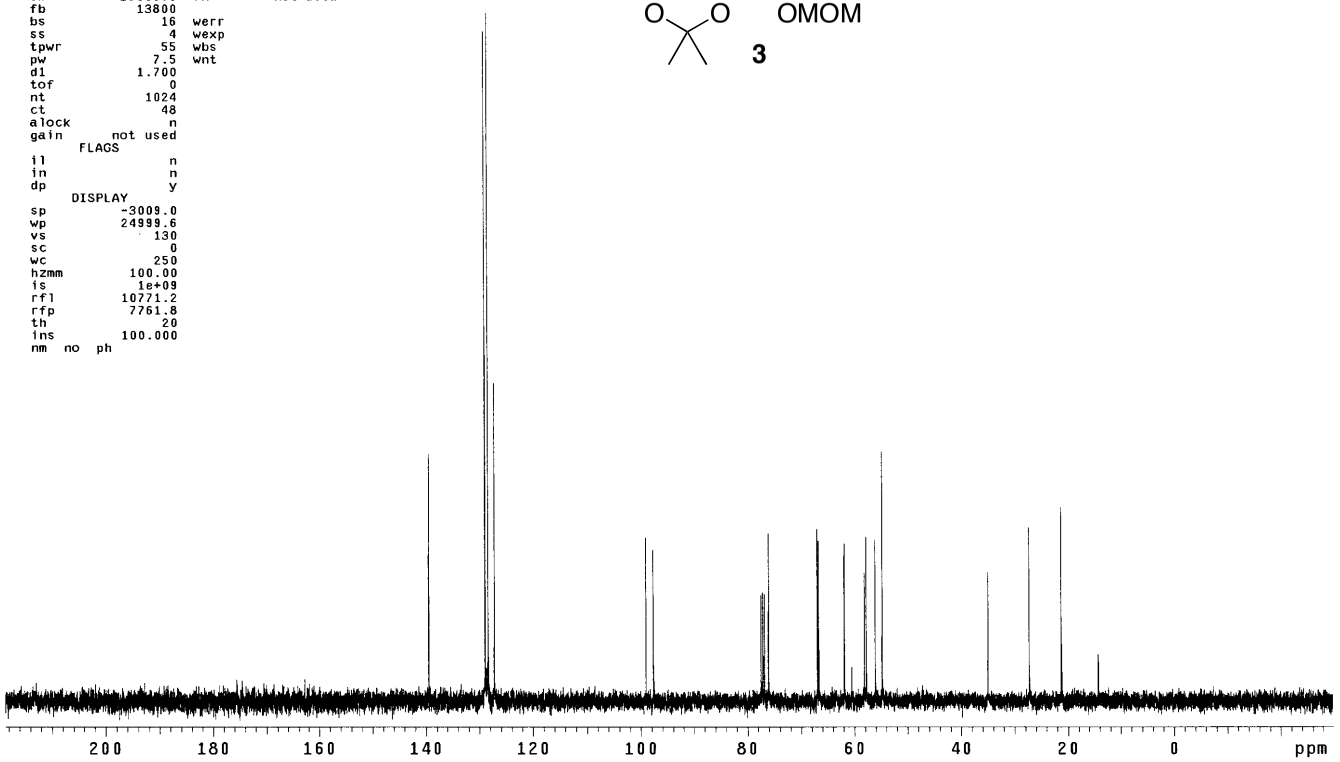
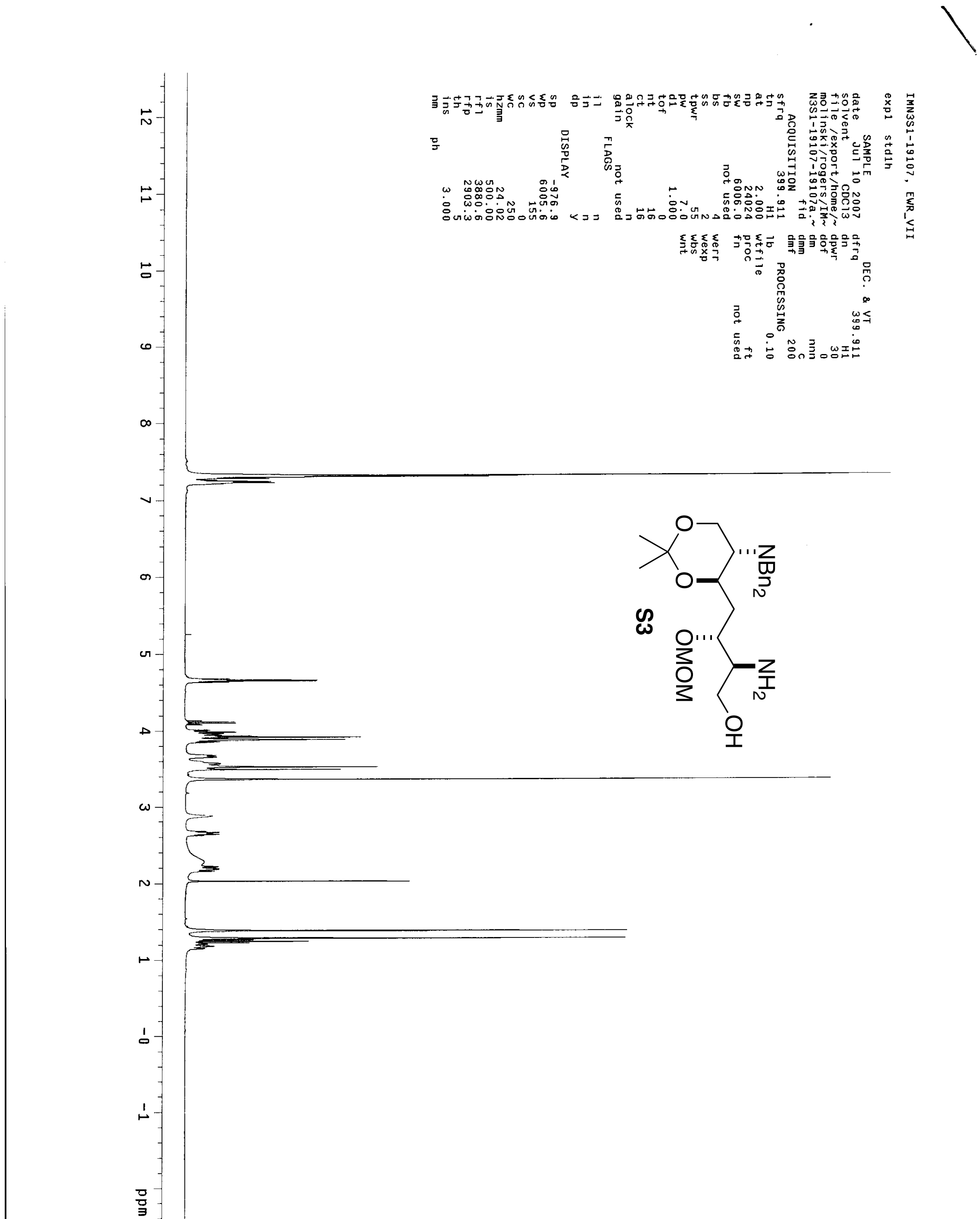
nm no ph



3




IMN3S1-19107, EWR_VII
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solvent CDCl3
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N3S1-19107-19107a.~
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pw 7.0
d1 1.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
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wp 6005.6
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sc 0
wc 250
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is 500.00
rfl 3880.6
rfp 2903.3
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ins 3.000
nm ph
DEC. & VT
dfrq 399.911
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dof 0
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dmm c
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PROCESSING
lb 0.10
wtfile
proc ft
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werr
wexp
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wnt
NBn2
NH2
OH
O
O
OMOM
S3
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10
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8
7
6
5
4
3
2
1
-0
-1
ppm

IMN3S1-19107, EWR_VII

exp1 std13c

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	fid	dmm	w
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sfrq	100.567	PROCESSING	
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at	1.500	wtfile	
np	75000	proc	ft
sw	25000.0	fn	not used
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bs	16	werr	
ss	4	wexp	
tpwr	58	wbs	
pw	6.5	wnt	
d1	1.700		
tof	0		
nt	1024		
ct	96		
alock	n		
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il	n		
in	n		
dp	y		
DISPLAY			
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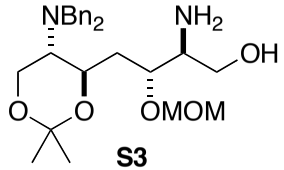

S3

IMNB4S1-19707, EWR_VII

exp1 std1h

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	.fid	dmm	c
ACQUISITION		dmf	200
sfrq	399.911	PROCESSING	
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np	24024	proc	ft
sw	6006.0	fn	not used
fb	not used		
bs	4	werr	
ss	2	wexp	
tpwr	55	wbs	
pw	7.0	wnt	
d1	1.000		
tof	0		
nt	16		
ct	16		
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wp	6005.6		
vs	151		
sc	0		
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is	500.00		
rfl	977.3		
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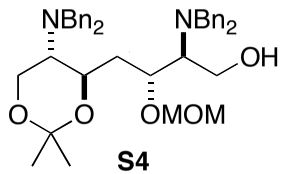
nm	ph		



S4

IMNB4S1-19707, EWR_VII

exp1 std13c

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NB4S1-19707-19707b~		dm	yyy
	.fid	dmm	w
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sfrq	100.567	PROCESSING	
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at	1.500	wtfile	
np	75000	proc	ft
sw	25000.0	fn	not used
fb	13800		
bs	16	werr	
ss	4	wexp	
tpwr	58	wbs	
pw	6.5	wnt	
d1	1.700		
tof	0		
nt	1024		
ct	64		
alock	n		
gain	not used		
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in	n		
dp	y		
DISPLAY			
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wp	24999.6		
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wc	250		
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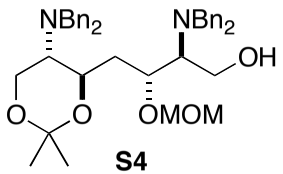
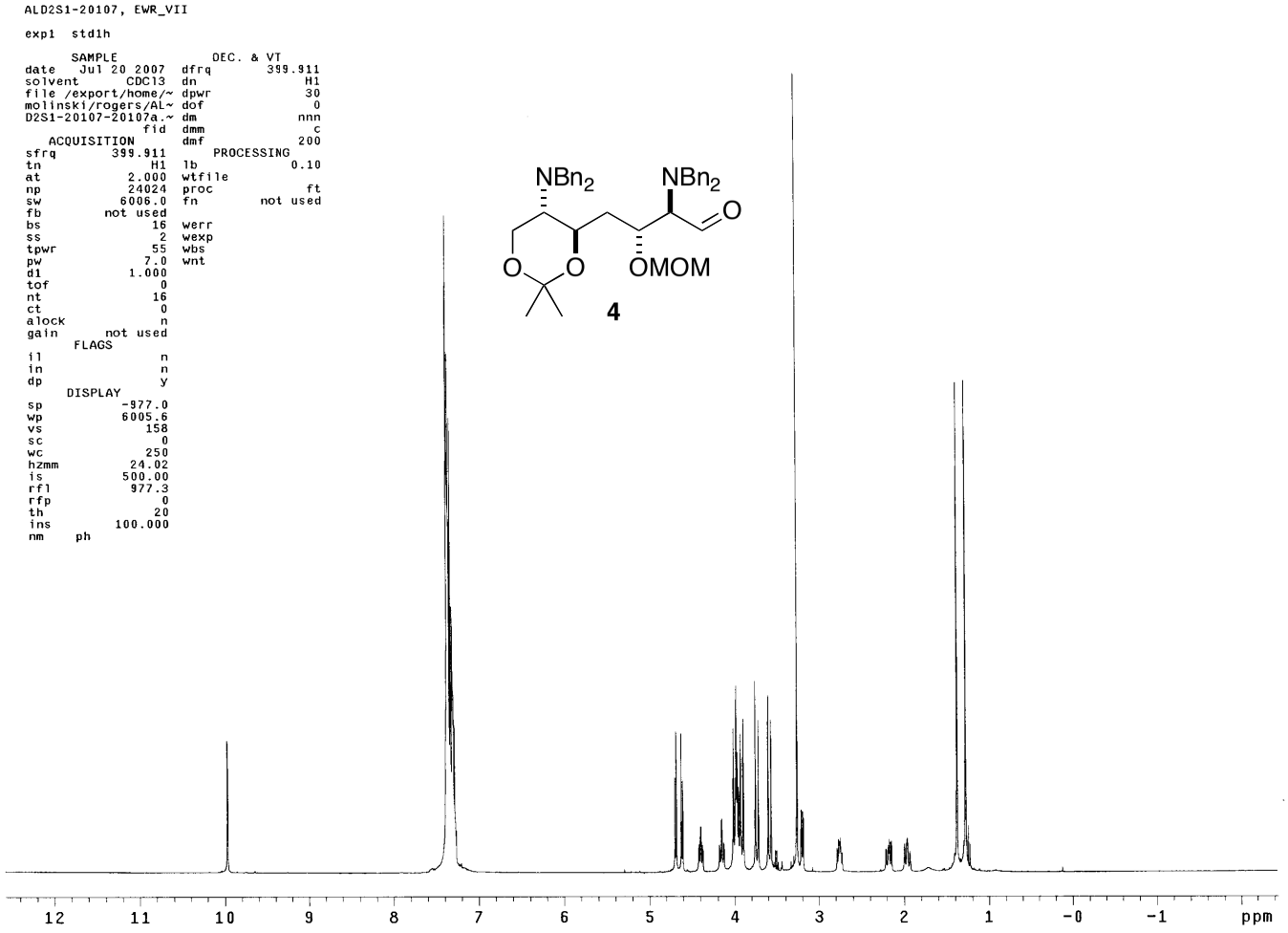
nm no ph			



S4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solvent CDCl3
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molinski/rogers/AL~
D2S1-20107-20107a.~
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sw 6006.0
fb not used
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ss 2
tpwr 55
pw 7.0
d1 1.000
tof 0
nt 16
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -977.0
wp 6005.6
vs 158
sc 0
wc 250
hzmm 24.02
is 500.00
rfl 977.3
rfp 0
th 20
ins 100.000
nm ph
DEC. & VT
dfrq 399.911
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2
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O
O
OMOM
4
12
11
10
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8
7
6
5
4
3
2
1
-0
-1
ppm

ALD2S1-20107, EWR_VII

exp1 std13c

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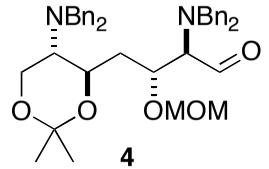
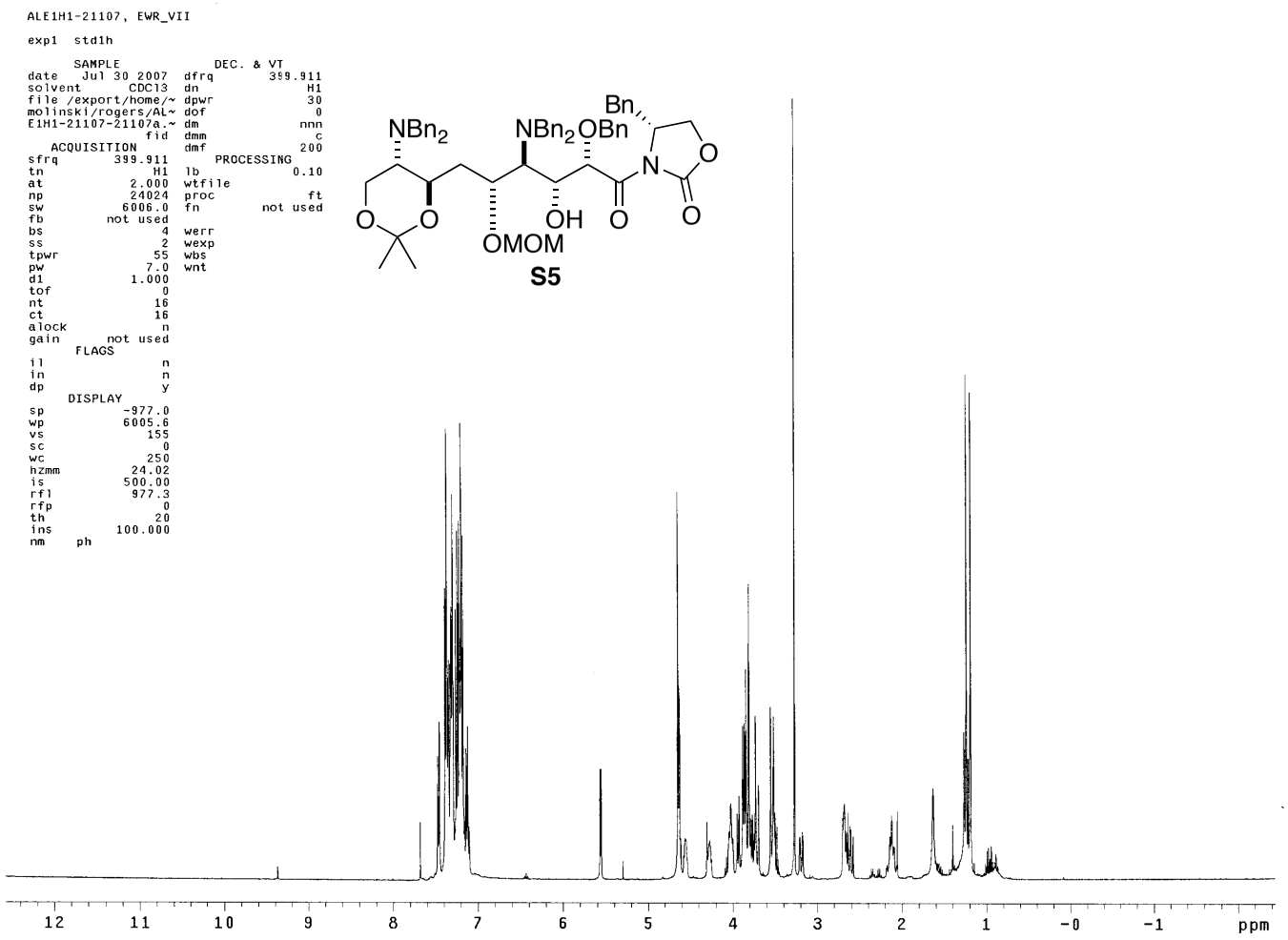
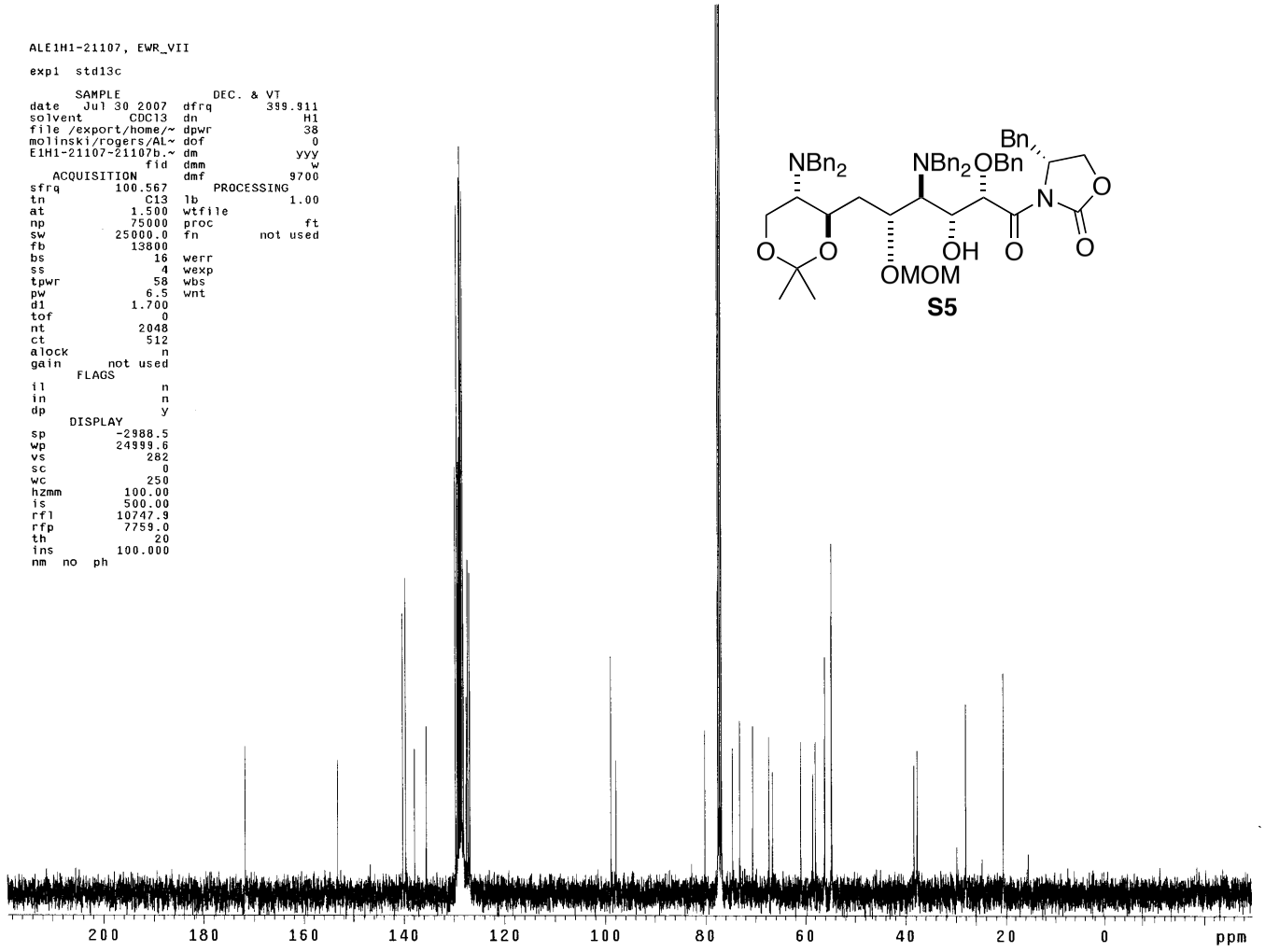
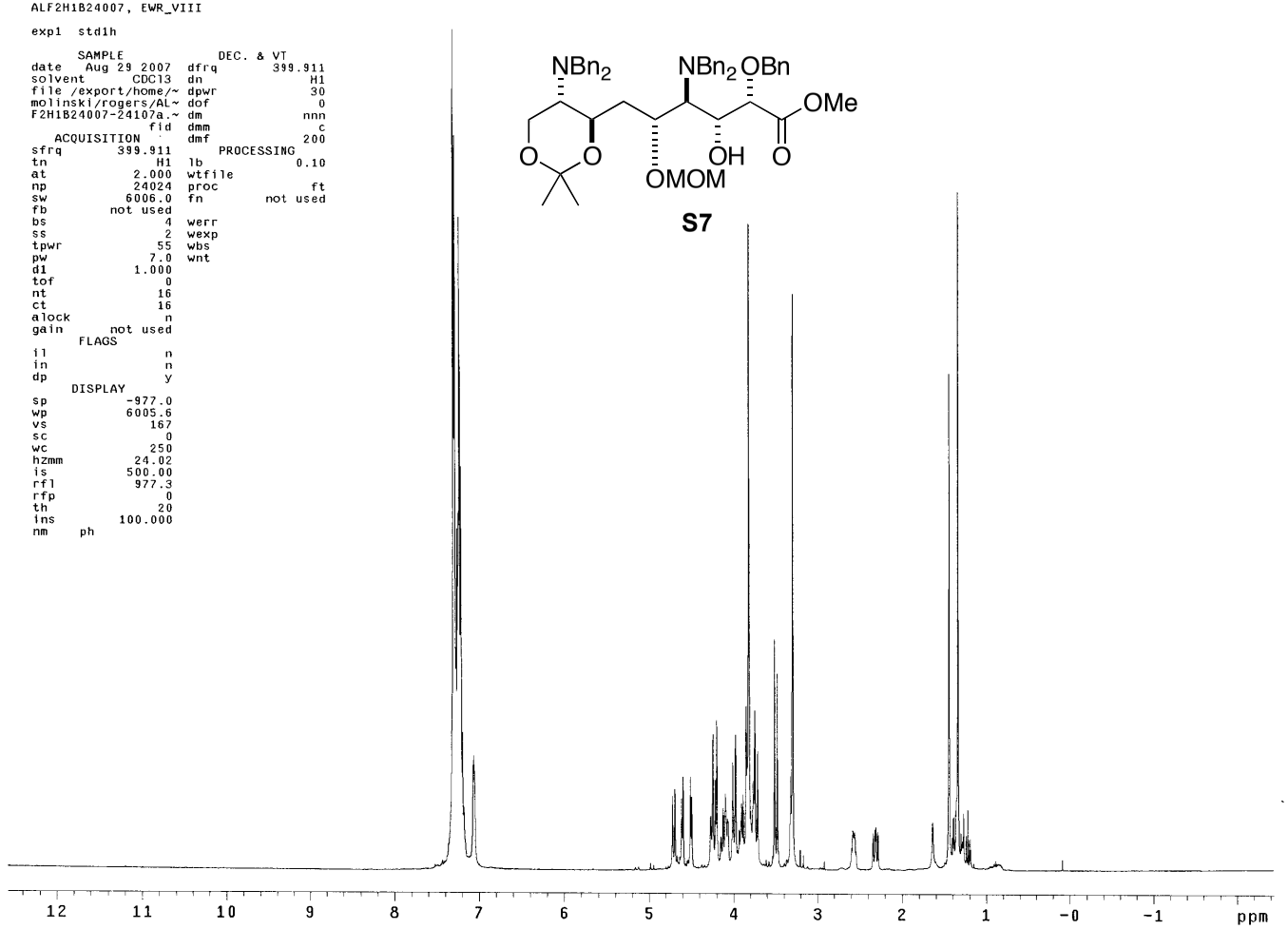
tn	C13	lb	1.00
at	1.500	wtfile	
np	75000	proc	ft
sw	25000.0	fn	not used
fb	13800		
bs	16	werr	
ss	4	wexp	
tpwr	58	wbs	
pw	6.5	wnt	
d1	1.700		
tof	0		
nt	1024		
ct	0		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-2994.3		
wp	24999.6		
vs	163		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	10753.6		
rfp	7759.0		
th	20		
ins	100.000		
nm no ph			



4


ALE1H1-21107, EWR_VII
exp1 std1h
SAMPLE
date Jul 30 2007
solvent CDCl3
file /export/home/~
molinski/rogers/AL~
E1H1-21107-21107a.~
fid
ACQUISITION
sfrq 399.911
tn H1
at 2.000
np 24024
sw 6006.0
fb not used
bs 4
ss 2
tpwr 55
pw 7.0
d1 1.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -977.0
wp 6005.6
vs 155
sc 0
wc 250
hzmm 24.02
is 500.00
rfl 977.3
rfp 0
th 20
ins 100.000
nm ph
DEC. & VT
dfrq 399.911
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2
OBn
Bn
N
O
O
O
O
O
OH
OMOM
S5
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

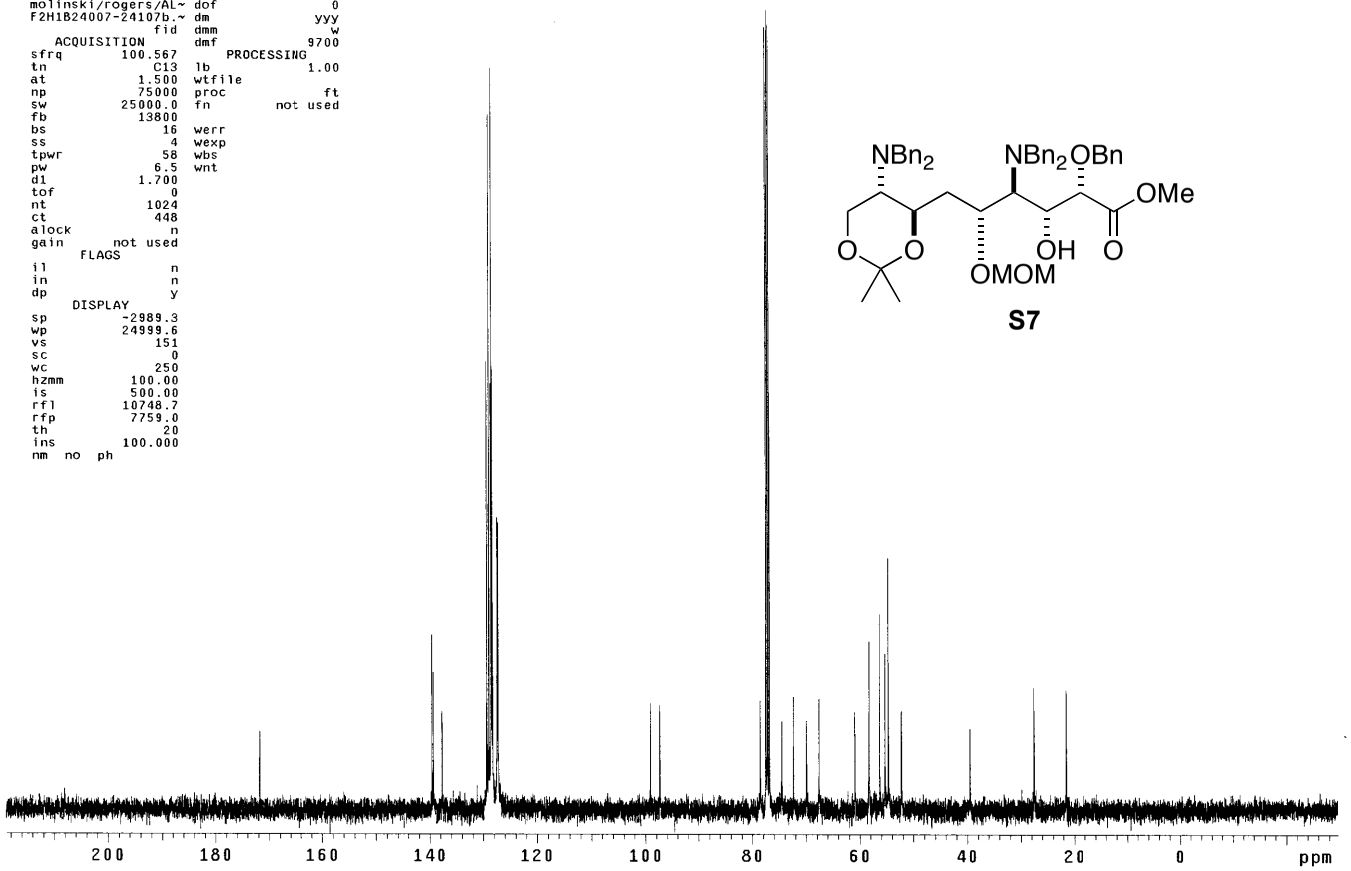

ALE1H1-21107, EWR_VII
exp1 std13c
SAMPLE
date Jul 30 2007
solvent CDCl3
file /export/home/~
molinski/rogers/AL~
E1H1-21107-21107b.~
fid
ACQUISITION
sfrq 100.567
tn C13
at 1.500
np 75000
sw 25000.0
fb 13800
bs 16
ss 4
tpwr 58
pw 6.5
d1 1.700
tof 0
nt 2048
ct 512
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2988.5
wp 24999.6
vs 282
sc 0
wc 250
hzmm 100.00
is 500.00
rfl 10747.9
rfp 7759.0
th 20
ins 100.000
nm no ph
DEC. & VT
dfrq 399.911
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 9700
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2OBn
Bn
O
N
O
O
O
OH
O
OMOM
S5
200
180
160
140
120
100
80
60
40
20
0
ppm


ALF2H1B24007, EWR_VIII
exp1 std1h
SAMPLE
date Aug 29 2007
solvent CDCl3
file /export/home/~
molinski/rogers/AL~
F2H1B24007-24107a.~
fid
ACQUISITION
sfrq 399.911
tn H1
at 2.000
np 24024
sw 6006.0
fb not used
bs 4
ss 2
tpwr 55
pw 7.0
d1 1.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -977.0
wp 6005.6
vs 167
sc 0
wc 250
hzmm 24.02
is 500.00
rfl 977.3
rfp 0
th 20
ins 100.000
nm ph
DEC. & VT
dfrq 399.911
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2
OBn
OMe
O
O
OH
O
OMOM
S7
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

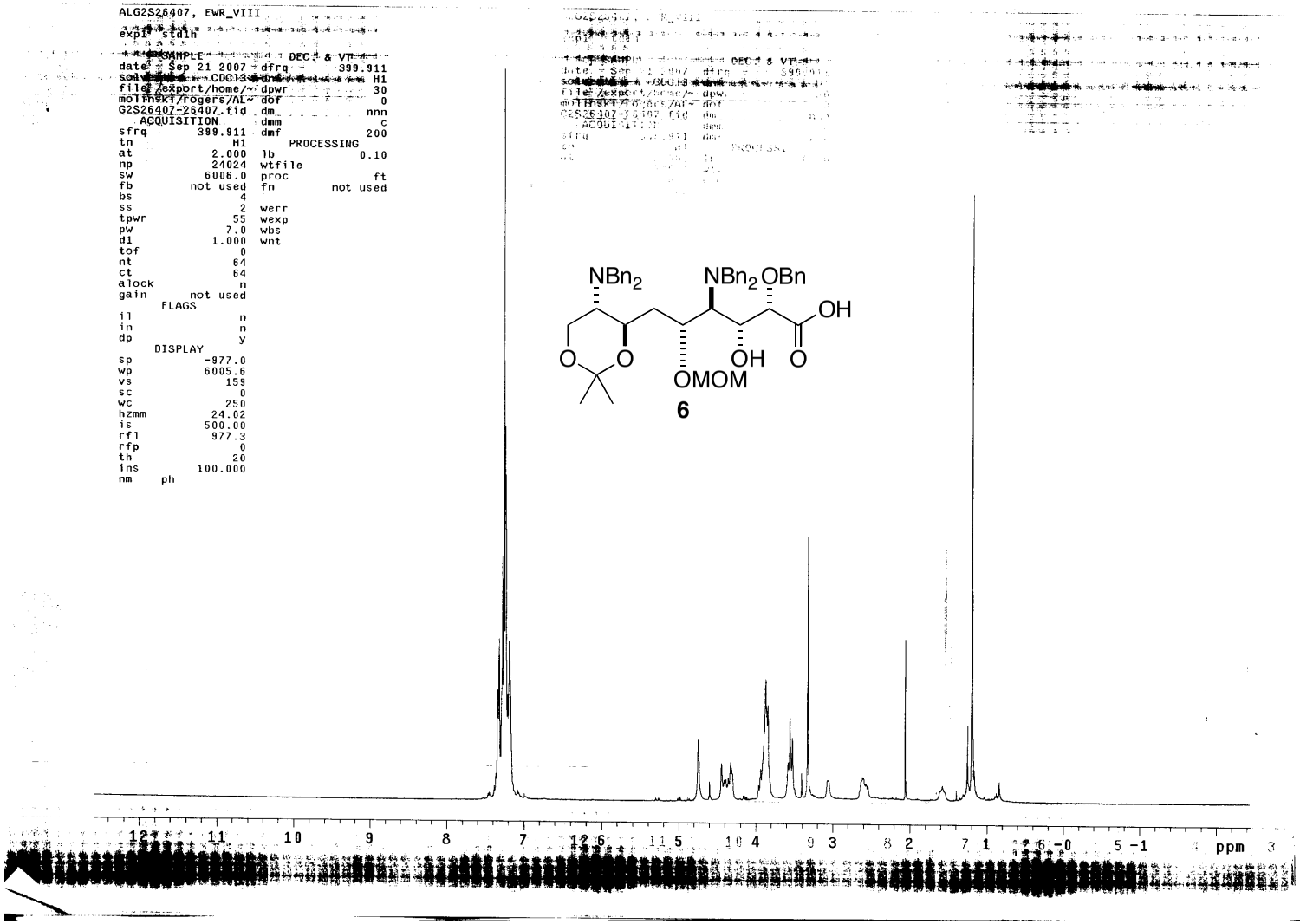
ALF2H1B24007, EWR_VIII

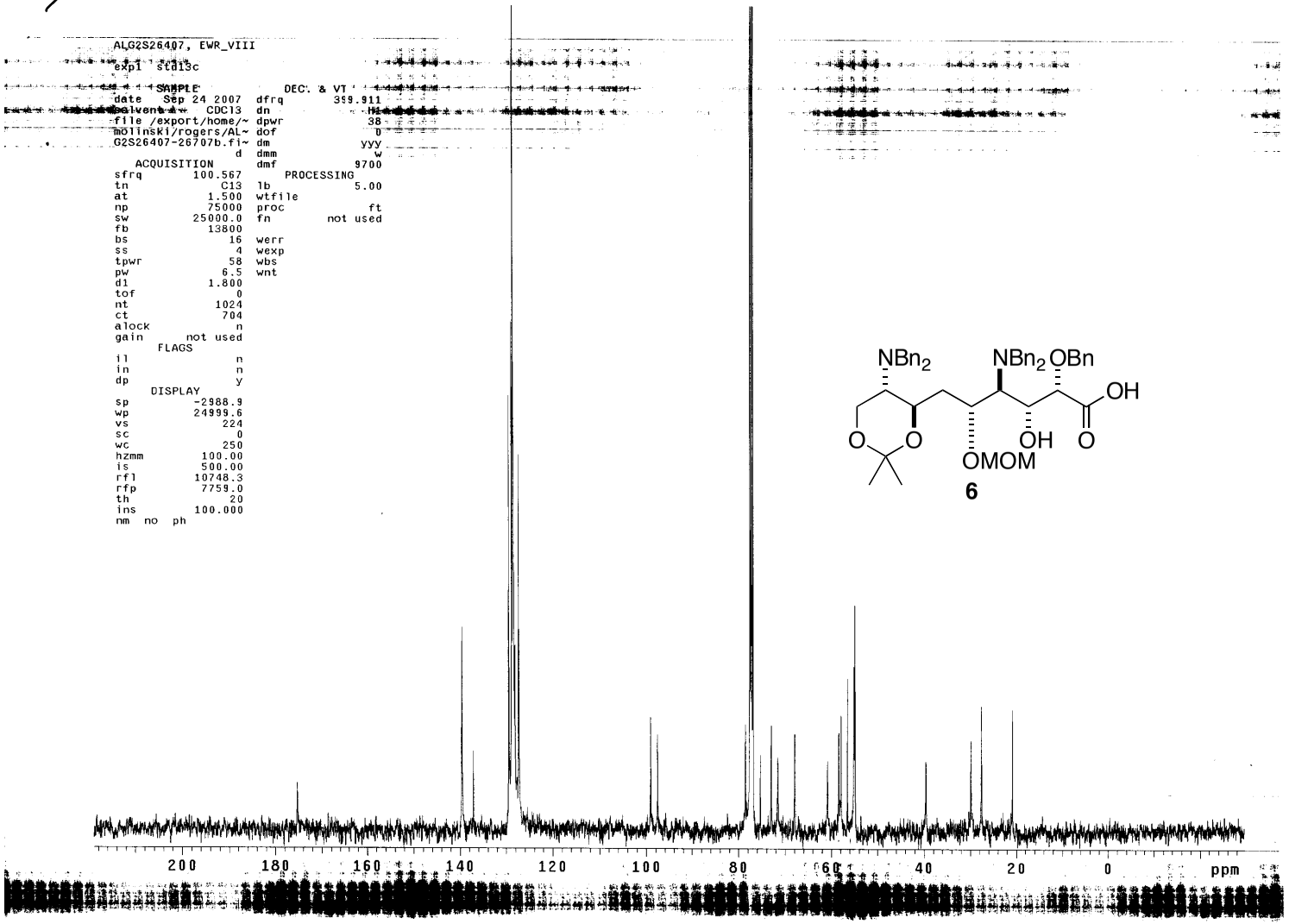
exp1 std13c

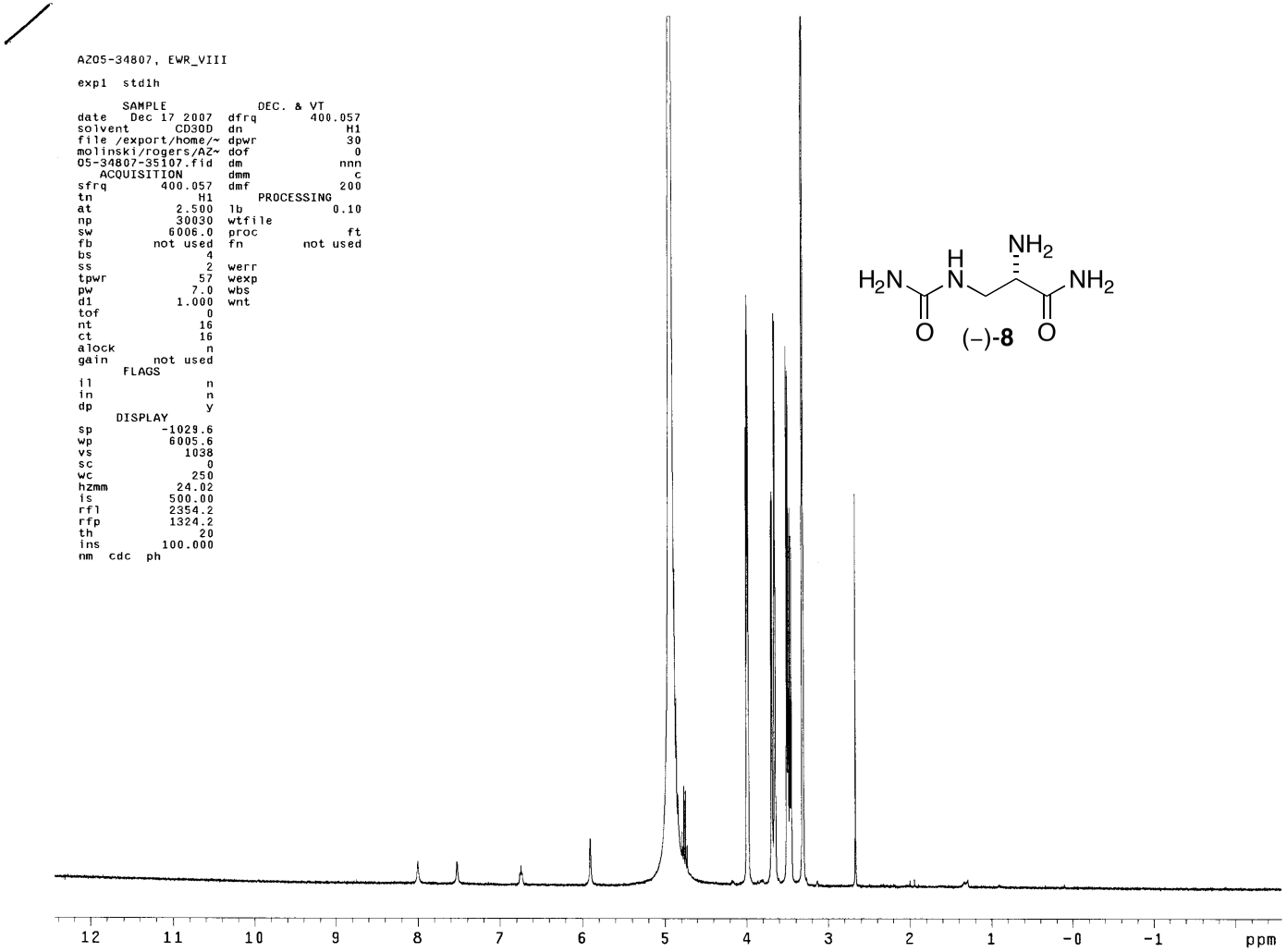
SAMPLE		DEC. & VT	
date	Aug 29 2007	dfrq	399.911
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	38
molinski/rogers/AL~		dof	0
F2H1B24007-24107b.~		dm	yyy
	fid	dmm	w
ACQUISITION		dmf	9700
sfrq	100.567	PROCESSING	
tn	C13	lb	1.00
at	1.500	wtfile	
np	75000	proc	ft
sw	25000.0	fn	not used
fb	13800		
bs	16	werr	
ss	4	wexp	
tpwr	58	wbs	
pw	6.5	wnt	
d1	1.700		
tof	0		
nt	1024		
ct	448		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-2989.3		
wp	24999.6		
vs	151		
sc	0		
wc	250		
hzmm	100.00		
is	500.00		
rfl	10748.7		
rfp	7759.0		
th	20		
ins	100.000		
nm no ph			

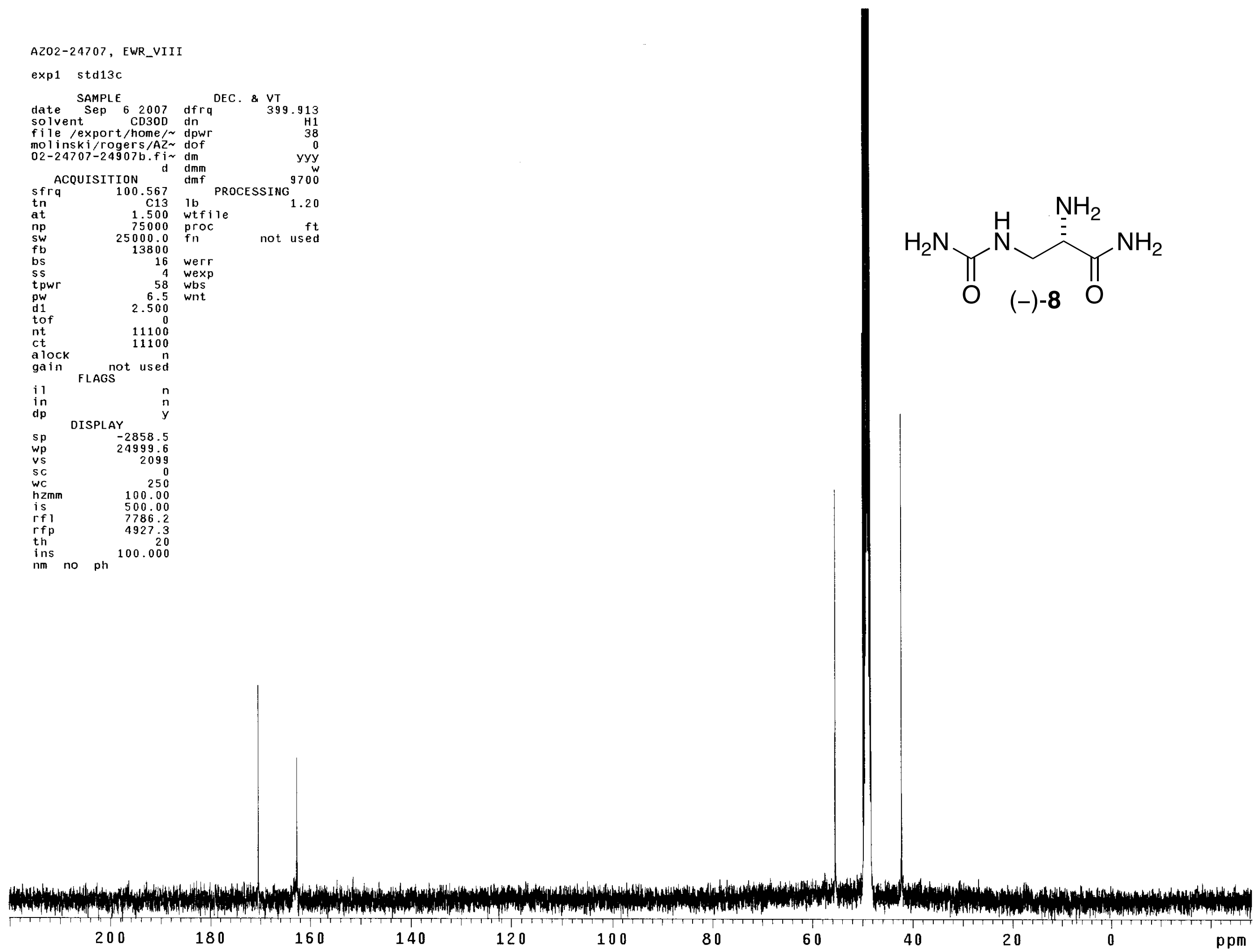


S7

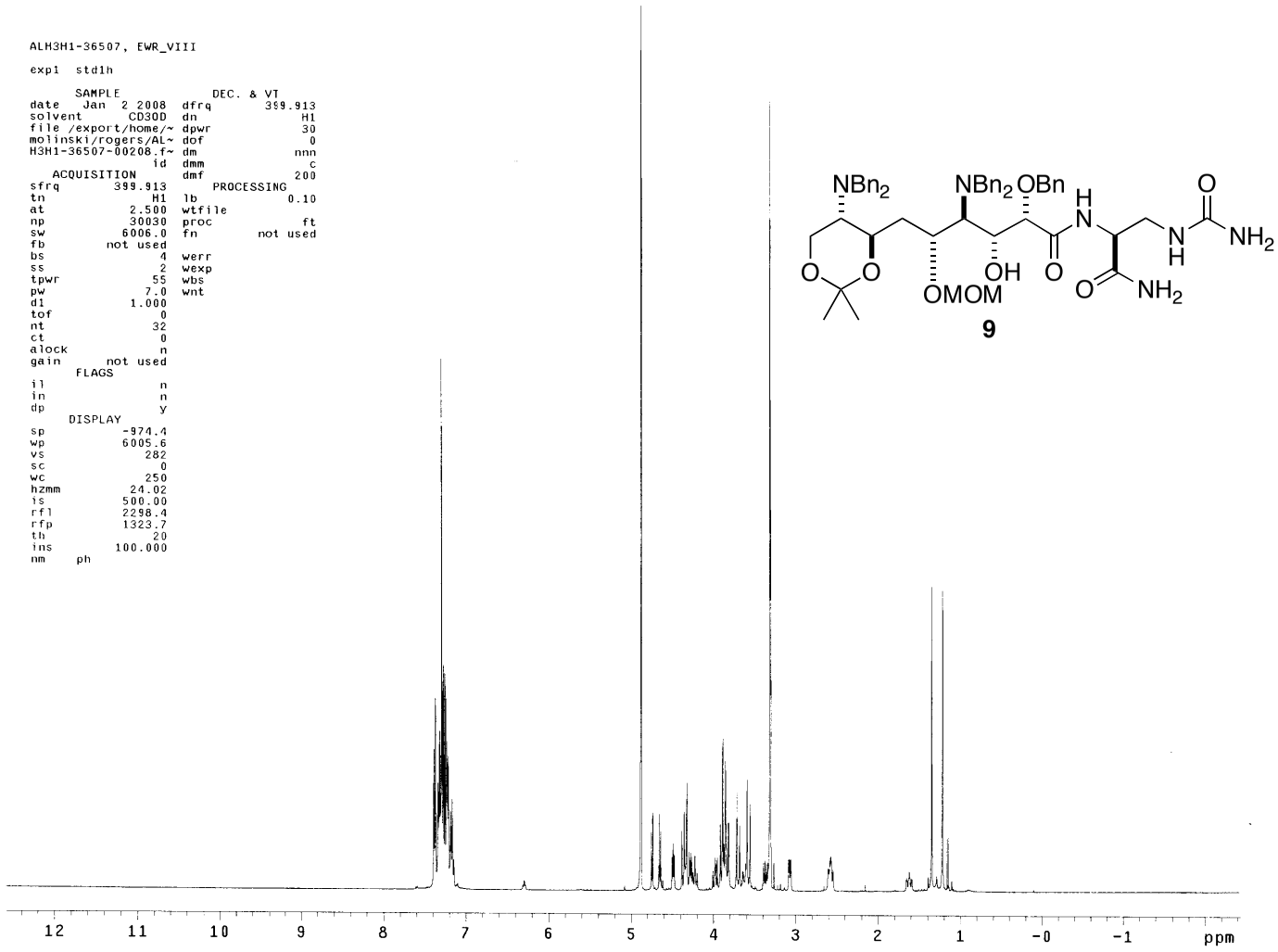

ALG2S26407, EWR_VIII
expl stuin
SAMPLE
date Sep 21 2007
sol CDCl3
file /export/home/
molinski/rogers/AL
G2S26407-26407.fid
ACQUISITION
sfrq 399.911
tn H1
at 2.000
np 24024
sw 6006.0
fb not used
bs 4
ss 2
tpwr 55
pw 7.0
d1 1.000
tof 0
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -977.0
wp 6005.6
vs 159
sc 0
wc 250
hzmm 24.02
is 500.00
rfl 977.3
rfp 0
th 20
ins 100.000
nm ph
DEC 1 & VT
dfrq 399.911
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2
OBn
OH
O
O
OH
O
OMOM
6
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

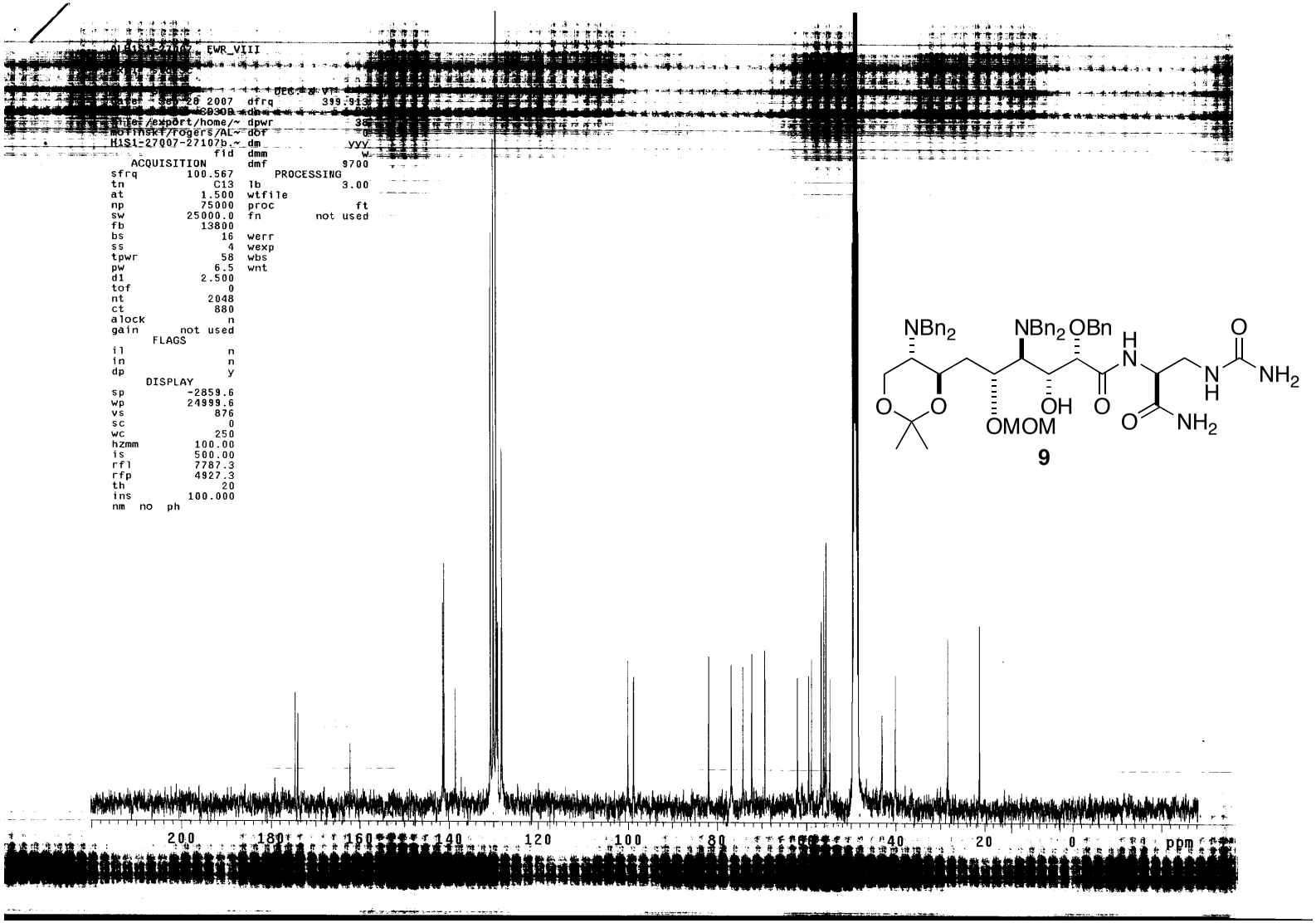

ALG2S26407, EWR_VIII
exp1 std13c
SAMPLE
date Sep 24 2007
solvent CDCl3
file /export/home/molinski/rogers/ALG2S26407-26707b.fid
ACQUISITION
sfrq 100.567
tn C13
at 1.500
np 75000
sw 25000.0
fb 13800
bs 16
ss 4
tpwr 58
pw 6.5
d1 1.800
tof 0
nt 1024
ct 704
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2988.9
wp 24999.6
vs 224
sc 0
wc 250
hzmm 100.00
is 500.00
rfl 10748.3
rfp 7759.0
th 20
ins 100.000
nm no ph
DEC. & VT
dfrq 399.911
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 9700
PROCESSING
lb 5.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2
OBn
OH
O
O
OH
O
OMOM
6
200
180
160
140
120
100
80
60
40
20
0
ppm


AZ05-34807, EWR_VIII
exp1 std1h
SAMPLE
date Dec 17 2007
solvent CD3OD
file /export/home/~
molinski/rogers/AZ~
05-34807-35107.fid
ACQUISITION
sfrq 400.057
tn H1
at 2.500
np 30030
sw 6006.0
fb not used
bs 4
ss 2
tpwr 57
pw 7.0
d1 1.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -1029.6
wp 6005.6
vs 1038
sc 0
wc 250
hzmm 24.02
is 500.00
rfl 2354.2
rfp 1324.2
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.057
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
H2N
H
N
NH2
NH2
O
O
(–)-8
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


A202-24707, EWR_VIII
exp1 std13c
SAMPLE
date Sep 6 2007
solvent CD3OD
file /export/home/~
molinski/rogers/AZ~
02-24707-24907b.fi~
d
ACQUISITION
sfrq 100.567
tn C13
at 1.500
np 75000
sw 25000.0
fb 13800
bs 16
ss 4
tpwr 58
pw 6.5
d1 2.500
tof 0
nt 11100
ct 11100
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2858.5
wp 24999.6
vs 2099
sc 0
wc 250
hzmm 100.00
is 500.00
rfl 7786.2
rfp 4927.3
th 20
ins 100.000
nm no ph
DEC. & VT
dfrq 399.913
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 9700
PROCESSING
lb 1.20
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
200
180
160
140
120
100
80
60
40
20
0
ppm
H2N
H
N
NH2
NH2
O
O

(–)-**8**

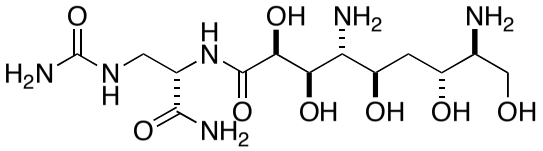

ALH3H1-36507, EWR_VIII
exp1 std1h
SAMPLE
date Jan 2 2008
solvent CD3OD
file /export/home/~
molinski/rogers/AL~
H3H1-36507-00208.f~
id
ACQUISITION
sfrq 399.913
tn H1
at 2.500
np 30030
sw 6006.0
fb not used
bs 4
ss 2
tpwr 55
pw 7.0
d1 1.000
tof 0
nt 32
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -974.4
wp 6005.6
vs 282
sc 0
wc 250
hzmm 24.02
is 500.00
rfl 2298.4
rfp 1323.7
th 20
ins 100.000
nm ph
DEC. & VT
dfrq 399.913
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2
OBn
OH
OMOM
H
N
N
H
O
O
O
O
O
NH2
NH2
9
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


EWR_VIII
CDCl3
20 2007
/export/home/~
H1S1-27007-27107b.~
fid
ACQUISITION
sfrq 100.567
tn C13
at 1.500
np 75000
sw 25000.0
fb 13800
bs 16
ss 4
tpwr 58
pw 6.5
d1 2.500
tof 0
nt 2048
ct 880
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -2859.6
wp 24999.6
vs 876
sc 0
wc 250
hzmm 100.00
is 500.00
rfl 7787.3
rfp 4827.3
th 20
ins 100.000
nm no ph
dfrq 399.91
dpwr 38
dof 0
dm yyy
dmm w
dmf 9700
PROCESSING
lb 3.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
NBn2
NBn2
OBn
OMOM
OH
H
N
O
NH2
9
200
180
160
140
120
100
80
40
20
0
ppm

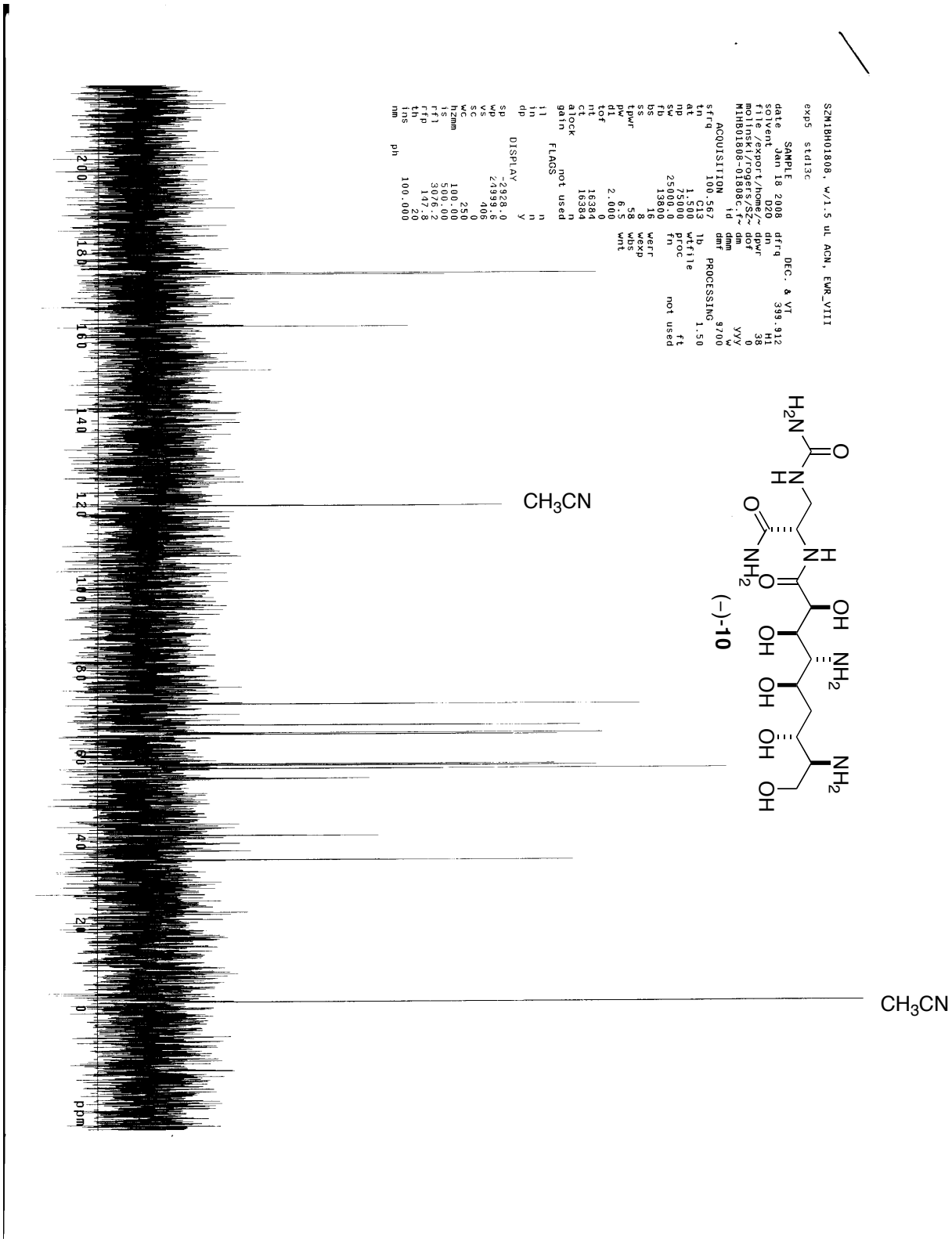
SZM1HB01808, w/1.5 uL ACN, EWR_VIII

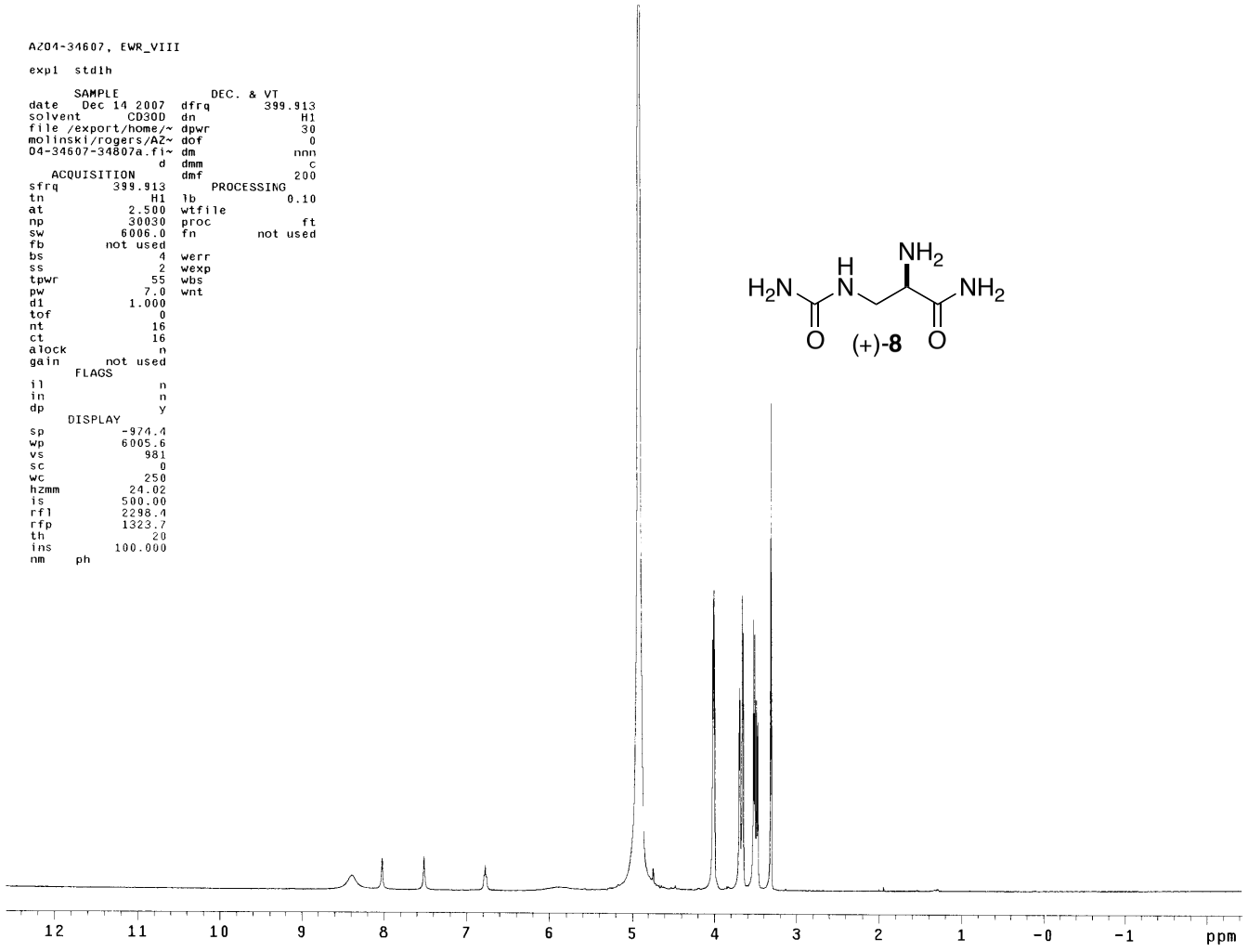
Pulse Sequence: s2pul
Solvent: D2O
Ambient temperature
File: SZM1HB01808-01808b
Mercury-400BB "hg402"

Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 2.000 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 399.9099585 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 59 sec



(–)-**10**


SZM1BH01808, w/1.5 uL ACN, EWR_VIII
exp5 std13c
CH3CN
(–)-10
CH3CN
ppm

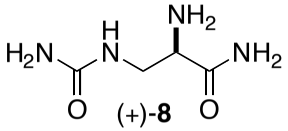

AZ04-34607, EWR_VIII
exp1 std1h
SAMPLE
date Dec 14 2007
solvent CD3OD
file /export/home/~
molinski/rogers/AZ~
04-34607-34807a.fi~
d
ACQUISITION
sfrq 399.913
tn H1
at 2.500
np 30030
sw 6006.0
fb not used
bs 4
ss 2
tpwr 55
pw 7.0
d1 1.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -974.4
wp 6005.6
vs 981
sc 0
wc 250
hzmm 24.02
is 500.00
rfl 2298.4
rfp 1323.7
th 20
ins 100.000
nm ph
DEC. & VT
dfrq 399.913
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
H2N
H
N
NH2
NH2
O
O
(+)-8
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

AZ04-34607, EWR_VIII

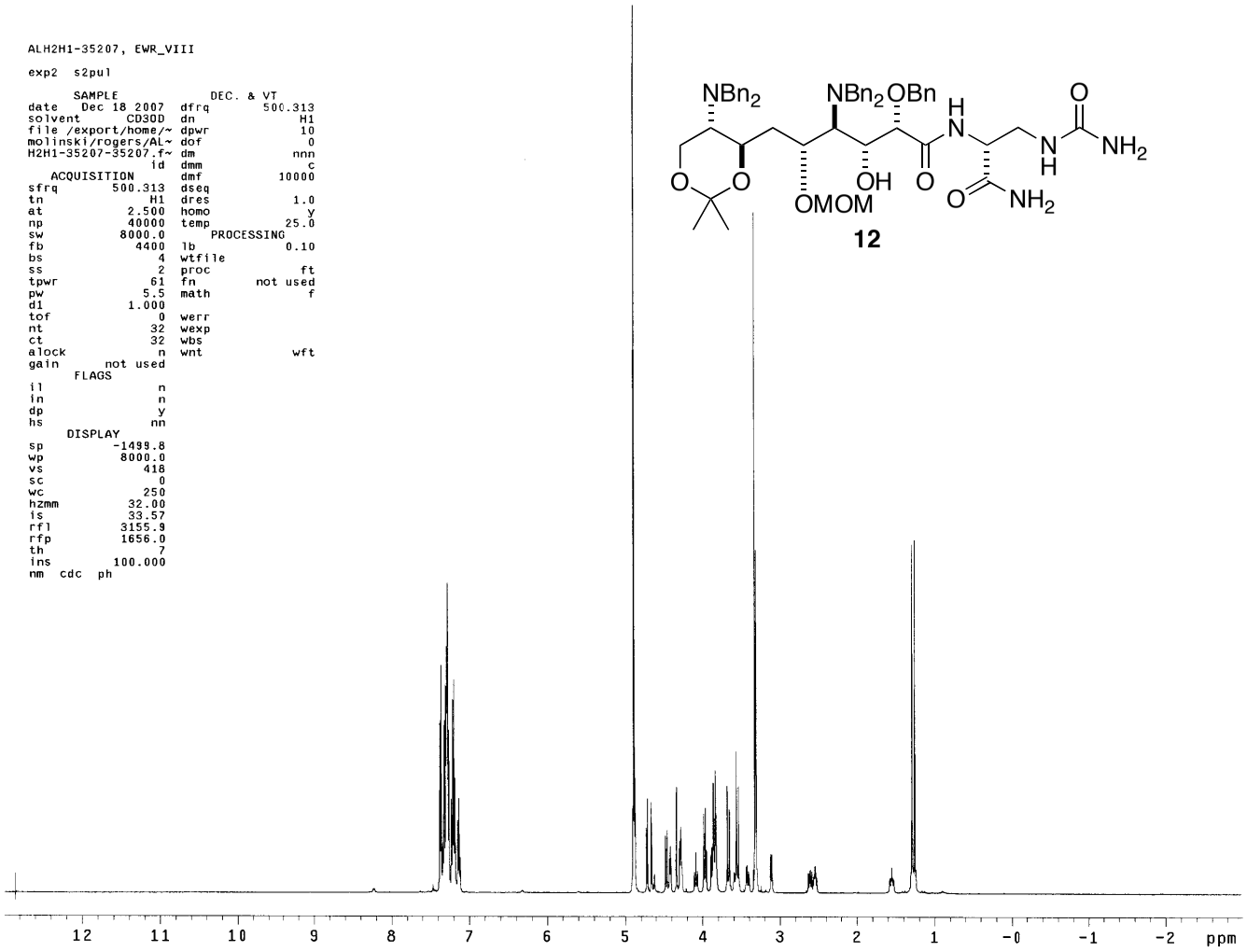
Pulse Sequence: s2pul

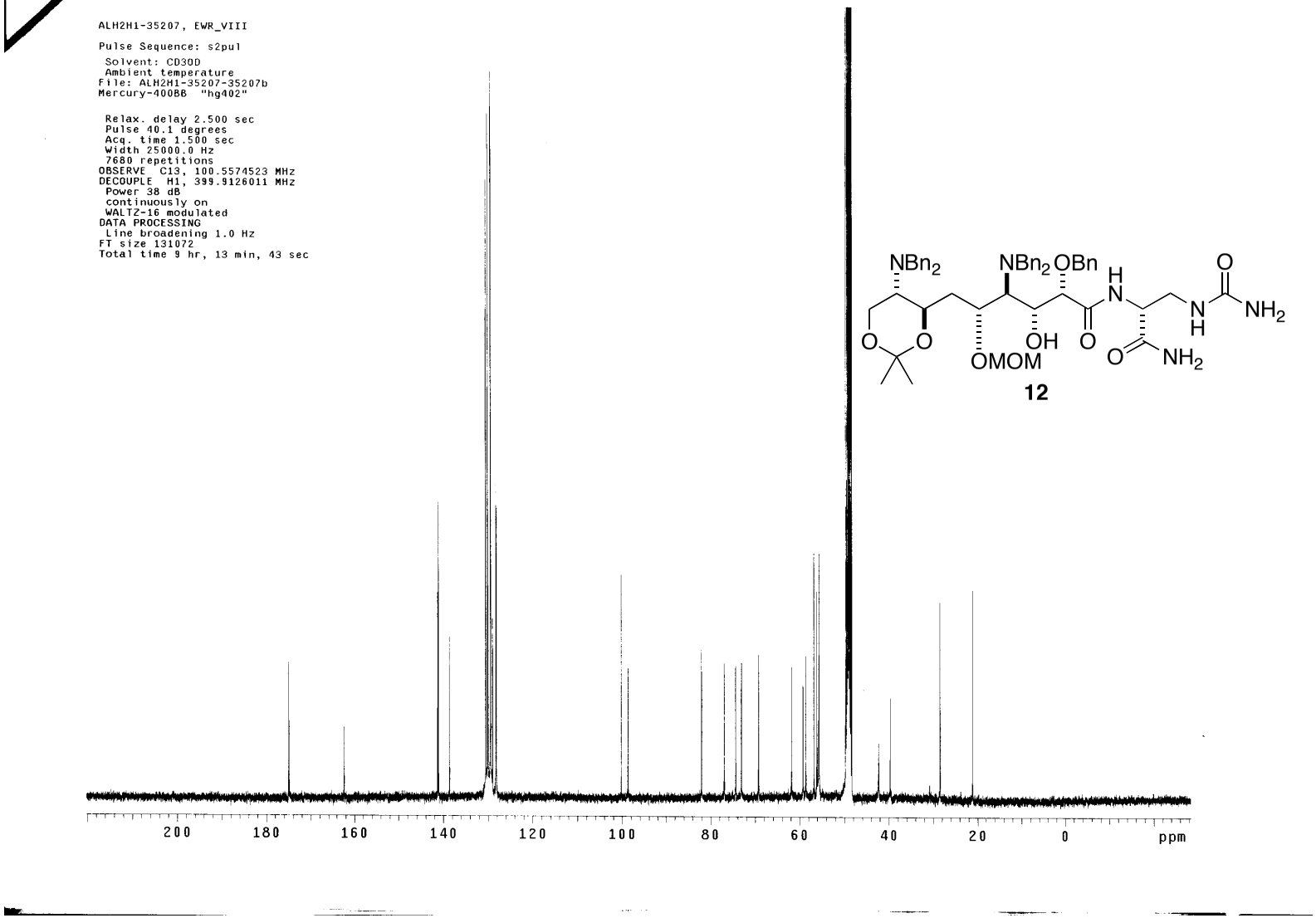
Solvent: CD3OD
Ambient temperature
File: AZ04-34607-34807b
Mercury-400BB "hg402"

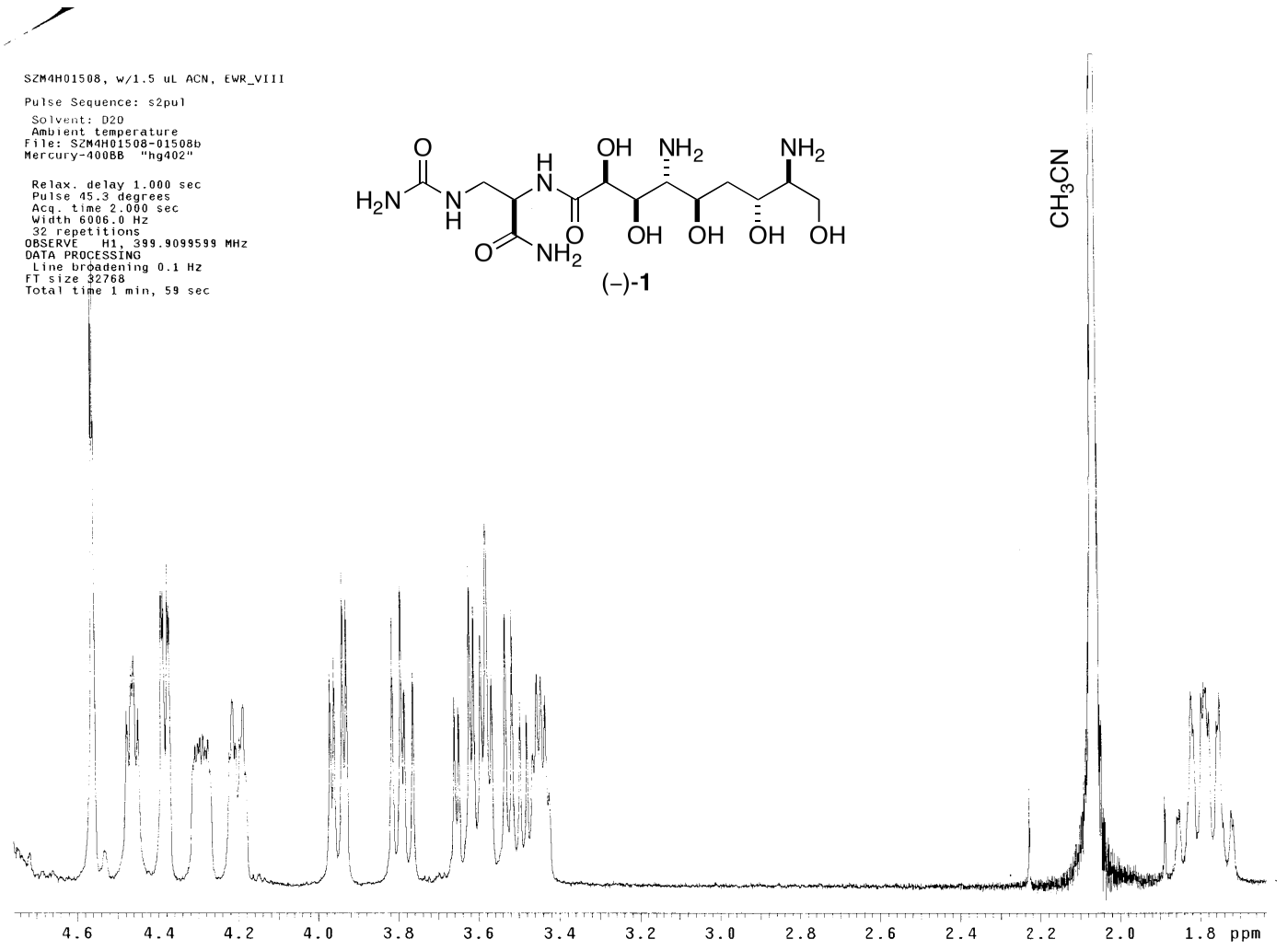
Relax. delay 2.200 sec
Pulse 40.1 degrees
Acq. time 1.500 sec
Width 25000.0 Hz
656 repetitions
OBSERVE C13, 100.5574538 MHz
DECOUPLE H1, 399.9126011 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 26 min, 21 sec



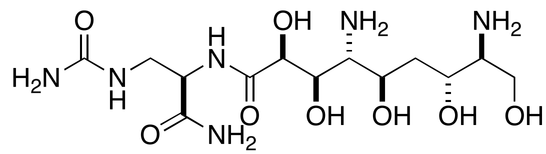
(+)-**8**


ALH2H1-35207, EWR_VIII
exp2 s2pul
SAMPLE
date Dec 18 2007
solvent CD3OD
file /export/home/~
molinski/rogers/AL~
H2H1-35207-35207.f~
id
ACQUISITION
sfrq 500.313
tn H1
at 2.500
np 40000
sw 8000.0
fb 4400
bs 4
ss 2
tpwr 61
pw 5.5
d1 1.000
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1499.8
wp 8000.0
vs 418
sc 0
wc 250
hzmm 32.00
is 33.57
rfl 3155.9
rfp 1656.0
th 7
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.313
dn H1
dpwr 10
dof 0
dm nnn
dmm c
dmf 10000
dseq
dres 1.0
homo y
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
NBn2
NBn2OBn
OMOM
OH
12
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 -2 ppm

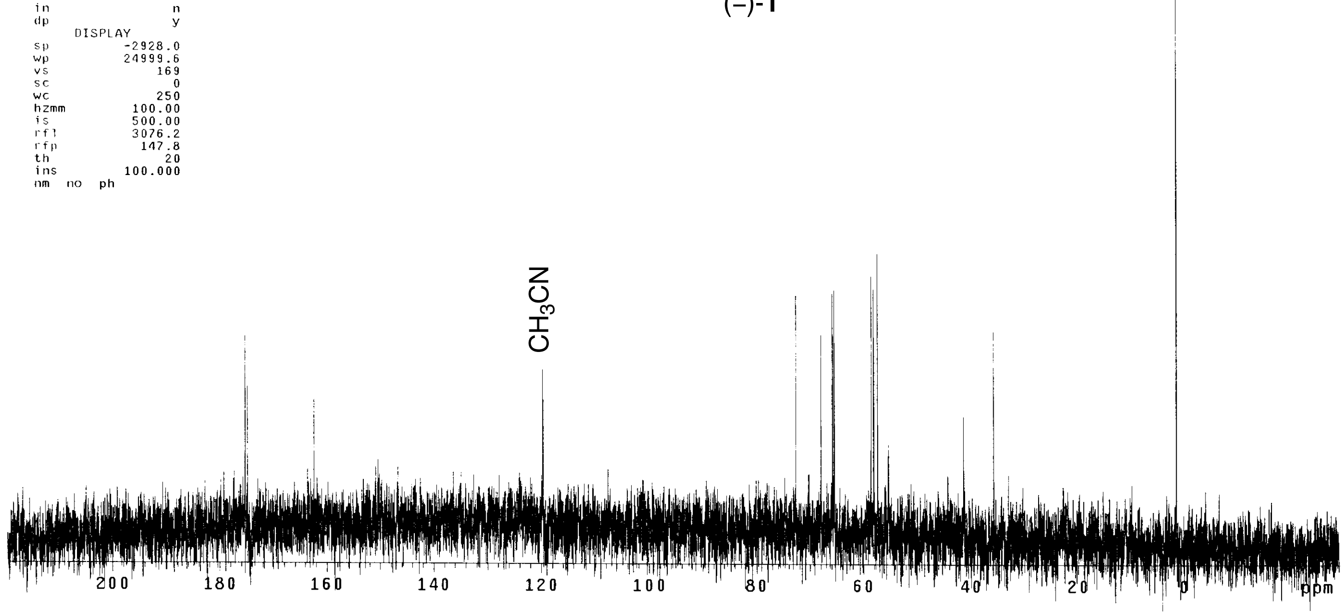

ALH2H1-35207, EWR_VIII
Pulse Sequence: s2pul
Solvent: CD3OD
Ambient temperature
File: ALH2H1-35207-35207b
Mercury-400BB "hg402"
Relax. delay 2.500 sec
Pulse 40.1 degrees
Acq. time 1.500 sec
Width 25000.0 Hz
7680 repetitions
OBSERVE C13, 100.5574523 MHz
DECOUPLE H1, 399.9126011 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 13 min, 43 sec
NBn2
NBn2
OBn
OH
OMOM
12
200
180
160
140
120
100
80
60
40
20
0
ppm


SZM4H01508, w/1.5 uL ACN, EWR_VIII
Pulse Sequence: s2pul
Solvent: D2O
Ambient temperature
File: SZM4H01508-01508b
Mercury-400BB "hg402"
Relax. delay 1.000 sec
Pulse 45.3 degrees
Acq. time 2.000 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 399.9099599 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 59 sec
(–)-1
CH3CN
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8 ppm

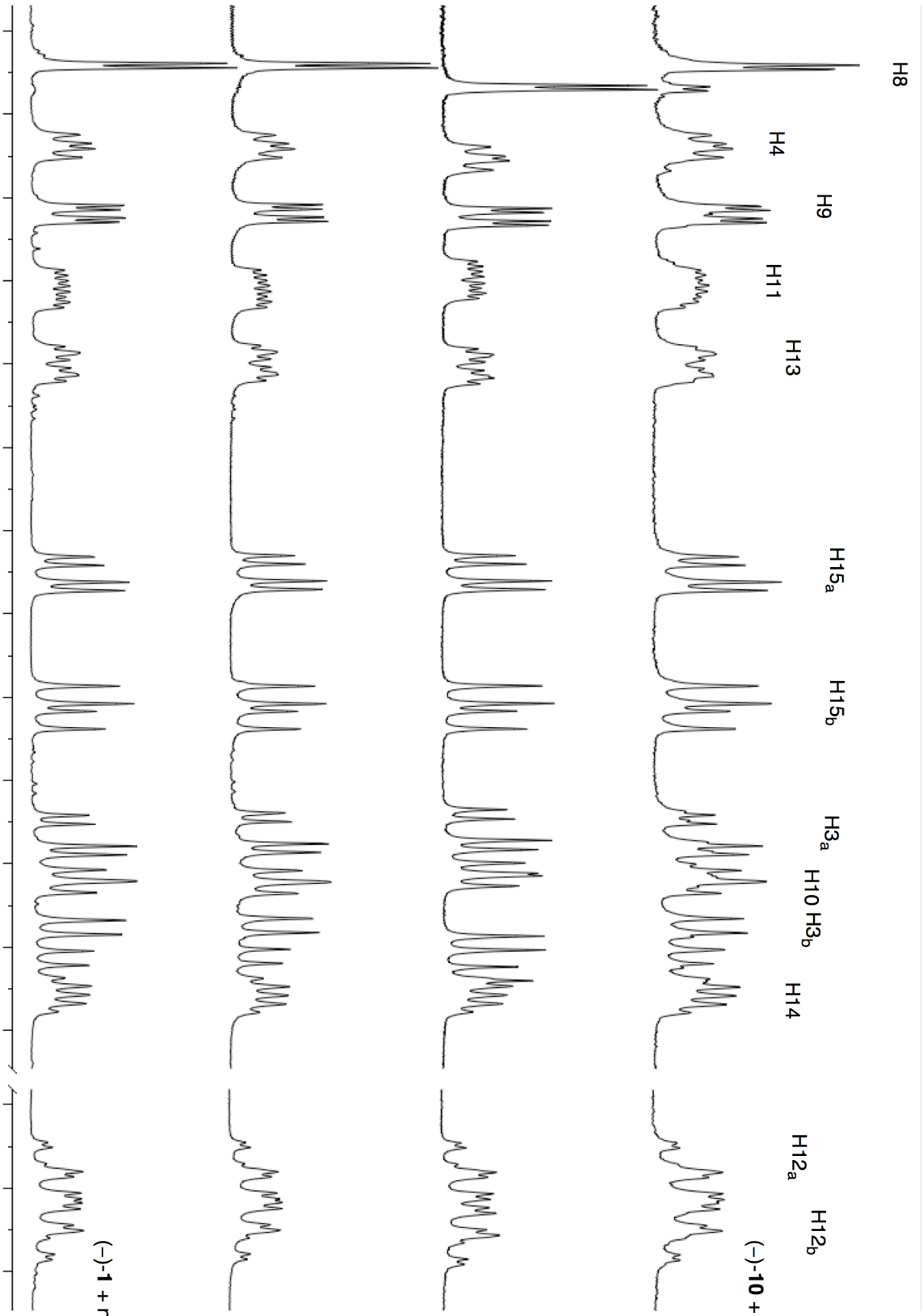
```
SZM4H01508, w/1.5 uL ACN, EWR_VIII

exp5  std13c

      SAMPLE              DEC. & VT
date   Jan 15 2008  dfrq        399.912
solvent         D20  dn               H1
file /export/home/~ dpwr              38
molinski/rogers/SZ~ dof                0
M4H01508-01508c.fi~ dm               yyy
                  d  dmm               w
   ACQUISITION       dmf            9700
sfrq        100.567       PROCESSING
tn              C13  lb             1.50
at            1.500  wtfile
np            75000  proc             ft
sw          25000.0  fn         not used
fb            13800
bs               16  werr
ss                4  wexp
tpwr             58  wbs
pw              6.5  wnt
d1            2.000
tof               0
nt            10240
ct                0
alock             n
gain       not used
       FLAGS
il                n
in                n
dp                y
      DISPLAY
sp          -2928.0
wp          24999.6
vs              169
sc                0
wc              250
hzmm         100.00
is           500.00
rfl          3076.2
rfp           147.8
th               20
ins         100.000
nm  no  ph
```



(–)-**1**



^{1}H NMR (400 MHz, D_2O) comparison of (–)-**1**, (+)-**1** and (–)-**10**.



^{13}C NMR (100 MHz, D_2O) comparisons (a) of (–)-**1** and (b) 1;2 mol ratio of (–)-**1** and (+)-**1**.