Total Synthesis and Biological Investigation of Neopeltolide Leading to a Structural Reassignment and Analog Evaluations

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Supporting Information

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General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF was purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain, anisaldehyde, or potassium permangenate stain followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. Optical rotations were measured on a Perkin Elmer Model 341 polarimeter with a sodium lamp and are reported as follows: $[\alpha]_{\lambda T}{}^{\circ}C$ (c = g/100 mL, solvent). ^{1}H NMR spectra were recorded on a Varian INOVA 500 (500 MHz) or a Bruker AVANCEIII 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. All coupling constant(s) are reported in Hz. Proton-decoupled ^{13}C NMR spectra were recorded on Varian INOVA 500 (125 MHz), INOVA 400 (100 MHz), or Bruker AVANCEIII 500 (125 MHz) spectrometers and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

Cell culture. MCF-7 cells were a generous gift from Anton Bennett (Yale University, New Haven, CT) and were grown in RPMI 1640 medium supplemented with 10% heat-inactivated fetal bovine serum. PC12 cells were a gift from Randy Pittman (University of Pennsylvania, Philadelphia, PA) and were grown in RPMI 1640 medium supplemented with 10% heat-inactivated horse serum and 5% heat-inactivated fetal bovine serum. A549 and P-388 cells were obtained from the Yale Cancer Center: A549 cells were cultured in Ham's F-12K medium supplemented with 10% heat-inactivated fetal bovine serum, and P-388 cells were grown in RPMI 1640 medium supplemented with 10% heat-inactivated fetal bovine serum. HeLa and KB cells were purchased from ATCC (Manassas, VA): HeLa cells were grown in high glucose Dulbecco's Modified Eagle Medium supplemented with 10% heat-inactivated fetal bovine serum and KB cells were cultivated in minimal essential medium supplemented with Earle's salts, 2 mM glutamine, 1 mM sodium pyruvate and 0.1 mM non-essential amino acids. All culture medium was supplemented with 100 units/ml penicillin G and 100 μg/ml streptomycin sulfate. All cells were grown at 37°C in an atmosphere of 5% CO_2 and 95% O_2.

[^{3}H]-thymidine incorporation. Cells were seeded into 96 well plates in growth medium at a density of 4000 cells/well (10,000 cells/well for PC12 cells). After an overnight incubation to allow for cell attachment, the growth medium was removed and replaced with fresh medium containing serum and neopeltolide or the analog of interest at the specified concentration(s). In the case of P-388 cells, which are not adherent, the existing growth medium was rather overlayed with an equal volume of growth medium containing 2X the desired final concentration of neopeltolide or neopeltolide analog. After 20 hr, each well of cells received another 20 μl of

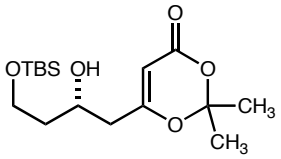
1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organomet.* **1996**, *15*, 1518-1520.
2. Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals;* 3rd Ed., Pergamon Press, Oxford. 1988.

medium containing 2 μCi of [^{3}H]-thymidine (Perkin-Elmer, Boston, MA). Following another 4 h, the cells were harvested from the wells and passed through glass fiber filters using a Ska-Tron cell harvestor (Molecular Devices, Sunnyvale, CA). The filters were transferred to vials, scintillant was added and the amount of radioactivity incorporated into the cells in the filters was quantified by scintillation counting. The resulting data was analyzed using PRISM software (GraphPad Software, Sand Diego, CA).

Trypan blue-exclusion quantitation of cell density. Following neopeltolide treatment as described above, a small 90 μl aliquot of cells was withdrawn from each culture, combined with 10 μl of 0.4% trypan blue in PBS and mixed. The density of cells per ml for each treatment group was then directly counted using a hemocytometer and light microscope.

Cytotoxicity assay. Following neopeltolide treatment as indicated, medium was supplemented with 330 μg/ml MTS (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium)(Promega Corp.) and 25 μM phenazine methosulfate and incubated at 37°C protected from light. Metabolic reduction of MTS to the colored formazan derivative was monitored by measuring the absorbance at 490 nm.

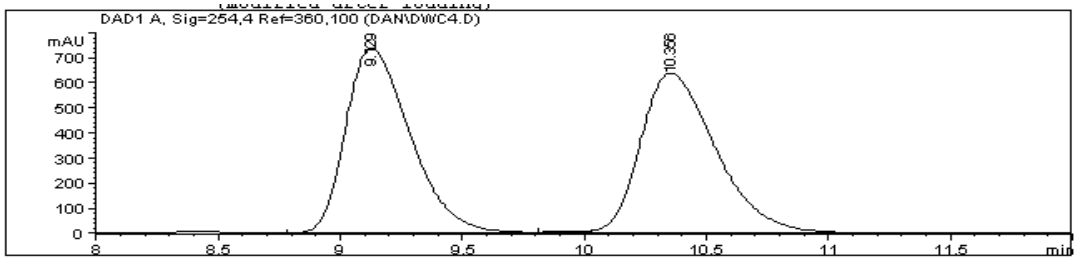
Experimental Procedures and Characterization Data for Synthesis of Proposed Structure



(*S*)-6-(4-(*tert*-butyldimethylsilyloxy)-2-hydroxybutyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (15): A mixture of (*R*)-BINOL (0.26 g, 0.9 mmol), Ti(*i*-OPr)$_4$ (271 µL, 0.9 mmol), 4Å molecular sieves (2.11 g), and THF (11 mL) was stirred vigorously at room temperature under N_2 for 60 minutes to yield a heterogeneous orange solution. The mixture was cooled to –78 °C and a solution of aldehyde **13** (1.14 g, 6.0 mmol) in THF (24 mL) was added via cannula and the resulting solution stirred for 30 min. Enol silane **14** (2.61 g, 12.2 mmol) was added dropwise to the solution and the mixture was stirred vigoursly for 2 h at –78 °C. The mixture was then warmed to 23 °C and allowed to stir for 12 h. Trifluoroacetic acid (2.5 mL) was added at –78 °C and the solution was allowed to warm to 23 °C. Stirring continued for 1 h. The reaction mixture was diluted with EtOAc (60 mL) and saturated $NaHCO_3$ was added dropwise until gas evolution ceased. The mixture was added to a separatory funnel containing brine (60 mL). The aqueous layer was extracted with EtOAc (3 x 20 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (50% Et_2O/hexanes) to afford β-hydroxy-dioxinone **15** (1.25 g, 63%, 88% ee) as a colorless oil. Analytical data for **15**: IR (film); 3462, 2953, 2857, 1728, 1635, 1386, 1255, 1205, 1091, 1012, 1091 ^{1}H NMR, (500 MHz, $CDCl_3$) δ 5.34 (s, 1H), 4.15 (bs, 1H), 3.93-3.89 (m, 1H), 3.85-3.83 (m, 1H), 2.43 (dd, *J* = 14.2, 7.81 Hz, 1H), 2.34 (dd, *J* = 14.6, 4.88 Hz, 1H), 1.8-1.65 (m, 2H), 1.70 (s, 3H), 1.69 (s, 3H), 0.89 (s, 9H), 0.08 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 161.4, 106.7, 95.3, 69.332, 62.6, 41.8, 38.0, 26.0, 25.5, 24.9, 18.3, –5.3; LRMS (ESI): Mass calculated for $C_{16}H_{30}O_5SiNa$ $[M+Na]^+$, 353. Found $[M+Na]^+$, 353. $[\alpha]_D^{25}$ = +17.5 ($CHCl_3$, c = 1.0,

er = 94:6). Enantiomeric ratio was measured by HPLC (Chiralcel OD-H, 5% IPA/Hexanes, Rt_1 = 9.00, Rt_2 = 10.17).

HPLC data for Racemic 15

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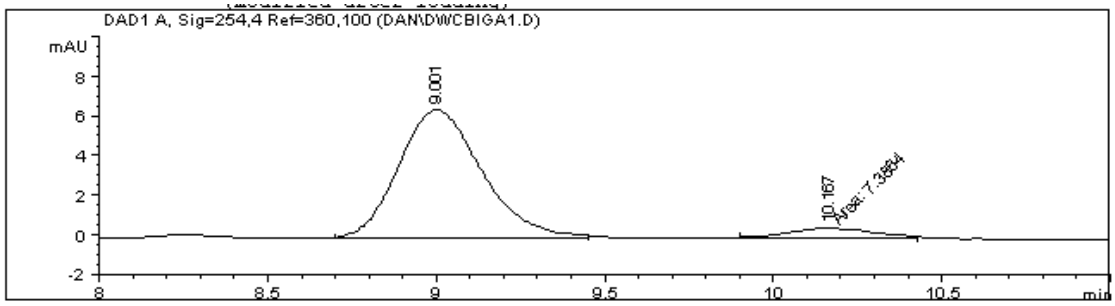


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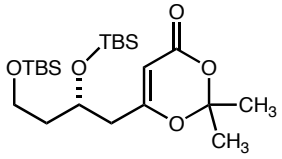
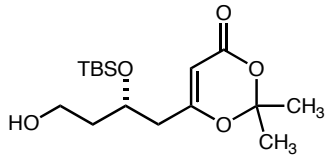
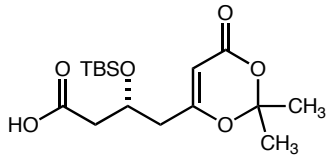


(*S*)-6-(2,4-bis(*tert*-butyldimethylsilyloxy)butyl)-2-hydroxybutyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (46): To a 0 °C solution of **15** (1.63 g, 4.9 mmol) in CH_2Cl_2 (52 mL) was added 2,6-lutidine (1.7 mL, 14.8 mmol) and TBSOTf (2.0 mL, 8.9 mmol). The resulting solution was stirred at 0 °C for 1 h and quenched by the addition of saturated $NaHCO_3$ (80 mL). The aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography (40% Et_2O/hexanes) to afford silyl ether **46** (1.98 g, 91%) as a clear oil. Analytical data for **46**: IR (film) 2955, 2932, 2858, 1734, 1636, 1386, 1254, 836, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1H), 4.15-4.13 (m, 1H), 3.68 (dd, *J* = 6.3, 5.8 Hz, 2H), 2.40 (ddd, *J* = 20.0, 14.1, 5.86 Hz, 2H), 1.72-1.66 (m, 2H), 1.70 (s, 3H), 1.68 (s, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 161.4, 106.5, 95.6, 66.8, 59.3, 42.4, 40.3, 26.1, 26.0, 25.9, 24.7, 18.4, 18.2, –4.3, –5.1; LRMS (ESI): Mass calculated for $C_{22}H_{44}O_5Si_2Na$ $[M+Na]^+$, 468. Found [M+Na], 468. $[\alpha]_D^{25}$ = +3.1 ($CHCl_3$, c = 0.3).

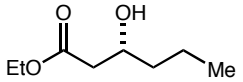


(*S*)-6-(2-(*tert*-butyldimethylsilyloxy)-4-hydroxybutyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (16): To a 23 ºC solution of **46** (1.82 g, 4.1 mmol) in EtOH (178 mL) was added pPTs (2.48 g, 9.8 mmol). The resulting mixture was stirred vigorously for 24 h. Brine (4 mL) was added to the reaction mixture and the solvent was removed *in vacuo* and the resulting residue was diluted with EtOAc (100 mL) and added to a separatory funnel containing brine (100 mL). The aqueous layer was extracted with EtOAc (4 x 15 mL). The organic layers were combined and dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography (50% Et_2O/hexanes) to afford **16** (1.28 g, 83%) as a clear oil. Analytical data for **16**: IR (film) 3452, 2932, 2858, 1728, 1633, 1388, 1205, 1015, 835, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.29 (s, 1H), 4.23-4.18 (m, 1H), 3.83-3.73 (m, 1H), 2.45 (dddd, *J* = 22.9, 20.0, 14.1, 5.85, 2H), 1.98 (bs, 1H), 1.88-1.81 (m, 1H), 1.75-1.65 (m, 2H), 1.71 (s, 3H), 1.69 (s, 3H), 0.89 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 161.3, 128.6, 106.7, 95.7, 68.2, 59.6, 42.1, 38.9, 25.9, 24.7, 18.2, –4.5; LRMS (ESI): Mass calculated for $C_{16}H_{30}O_5SiNa$ $[M+Na]^+$, 353 Found [M+Na] 353. $[\alpha]_D^{25}$ = –2.7 ($CHCl_3$, c = 1.0).



(*R*)-3-(*tert*-butyldimethylsilyloxy)-4-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)butanoic acid (7): To a 23 °C solution of **16** (0.45 g, 1.36 mmol) in DMF (21 mL) was added PDC (2.61 g, 12.3 mmol). The resulting mixture was stirred vigorously for 3 h. The reaction mixture was then diluted with Et_2O (20 mL) and then passed through a short plug of $MgSO_4$ (eluting with Et_2O). H_2O (450 mL) was then added to the filtrate and the aqueous layer was extracted with Et_2O (5 x 20 mL). The combined organic layers were combined and dried with anhydrous

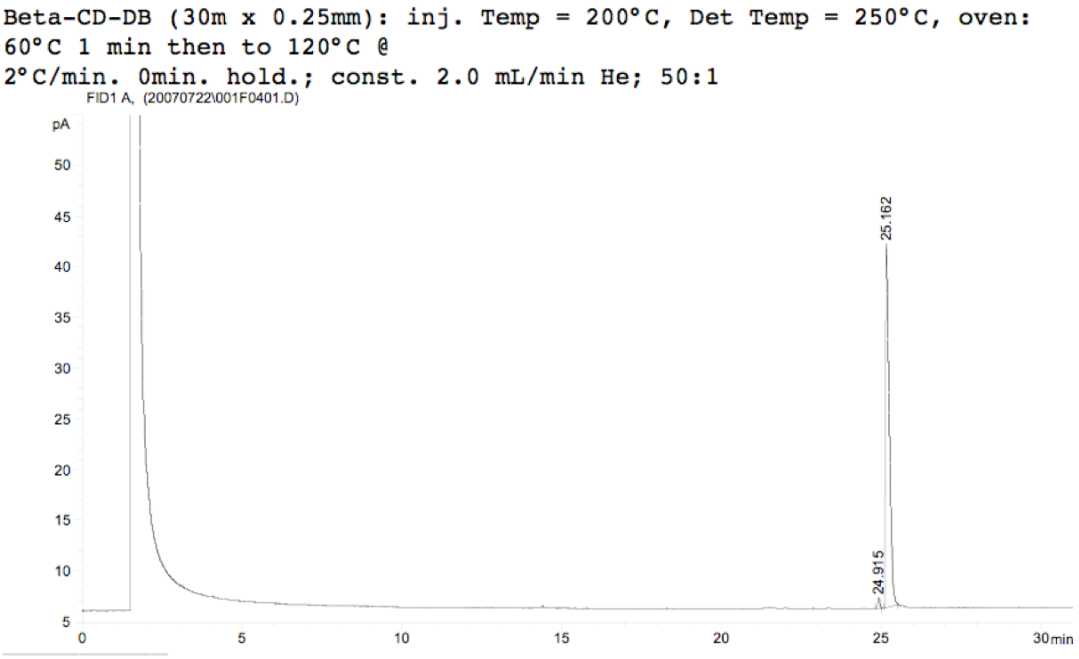
Na_2SO_4, filtered and concentrated to afford carboxylic acid **7** (44 mg, 97%) as a colorless oil. Carboxylic acid **7** was used directly in the next step. Analytical data: IR (film) 3101, 2931, 2857, 1734, 1635, 1388, 1205, 1092, 1015, 833, 777 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.32 (s, 1H), 4.42-4.40 (m, 1H), 2.59 (d, *J* = 5.86, 2H), 2.49 (d, *J* = 5.86 Hz, 2H), 1.72 (s, 3H), 1.70 (s, 3H), 1.26 (s, 1H), 0.88 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz) δ 176.3, 168.2, 161.1, 106.8, 96.1, 66.5, 42.2, 41.9, 29.9, 25.9, 25.8, 24.7, 18.1, -4.7; LRMS (ESI): Mass calculated for $C_{16}H_{28}O_6SiNa$ $[M+Na]^+$, 367. Found [M+Na] 367. $[\alpha]_D^{25}$ = +3.3 ($CHCl_3$, c = 0.6).

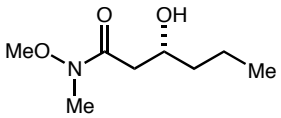


(*R*)-Ethyl 3-hydroxyhexanoate. A stainless steel stirred autoclave was charged with $[RuCl_2(benzene)]_2$ (402 mg, 0.80 mmol) and (*R*)-tol-BINAP (1145 mg, 1.69 mmol). The vessel was sealed and repeatedly pressure purged with argon (ca. 20 × 30 psig). Argon sparged absolute ethanol (950 mL) and ethyl 3-oxohexanoate (109.35 g, 682.6 mmol) were then added via cannula into the reaction vessel under argon. The vessel was sealed and pressure purged with argon and then hydrogen. The reactor was pressurized to and maintained at about 50 psig using a pressure regulator fed by a small high-pressure reservoir of hydrogen. The reaction mixture was vigorously stirred and heated to 100 °C. Hydrogen uptake was complete within about 30 min. of reaching 100 °C after which heating continued for an additional 1 h. After cooling and release of pressure, the orange product mixture was filtered and the filtrate was evaporated. Chiral GC (FID) analysis of the unpurified product mixture revealed 97% ee. Vacuum distillation at about 125-130 °C/90 mmHg afforded 102.9 g (94%) of a clear, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H) 4.01 (m, 1H) 3.23 (s, 1H) 2.48 (dd, *J* = 16.2, 3.6 Hz, 1H) 2.40 (dd, *J* = 16.2, 8.6 Hz, 1H) 1.32-1.58 (m, 4H) 1.27 (dd, *J* = 7.1, 7.1 Hz, 3H) 0.93 (dd, *J* = 7.1, 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 67.6, 60.4, 41.5, 38.7, 18.8, 14.3, 14.1.

Chiral GC analysis was performed using an Agilent 6850 gas chromatograph equipped with an FID detector, Chiraldex β-cyclodextrin-DB (30m x 0.25 mm) column, and a split injection port (50:1). Helium was used as the carrier gas at a constant 2 mL/min. The column oven was initially held at 60 °C for 1 min then ramped to 120 °C at 2 °C/min. The chromatographic separation was checked using racemic ethyl 3-hydroxyhexanoate prepared analogously using racemic BINAP. The predominant isomer eluted second after about 25.2 min and was assigned to the *R*-configuration based upon literature precedent[3] and Mosher ester analysis.

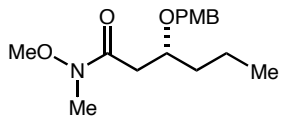
3. (a) Kitamura, M.; Tokunaga, M.; Ohkuma, T.; Noyori, R. *Org. Synth.* **1993**, *71*, 1. (b) Deng, L. S.; Huang, X. P.; Zhao, G. *J. Org. Chem.* **2006**, *71*, 4625.



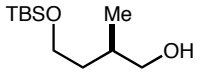


(*R*)-3-hydroxy-*N*-methoxy-*N*-methylhexanamide (47): Weinreb's amine[4] (MeONHMe·HCl) (4.00 g, 41.0 mmol) was azeotroped with benzene 3 times, dried *in vacuo* for 30 min, and dissolved in THF (20 mL). (*R*)-Ethyl-3-hydroxyhexanoate (2.12 g, 13.2 mmol) was then added and the mixture was cooled to –20 °C (dry ice/benzyl alcohol). *i*-PrMgCl (2.0 M solution in THF, 39.7 mL) was then added dropwise over 30 min via cannula, and the mixture was stirred for an additional 45 min at –20 °C. The bath was then removed and the mixture stirred for 1 h at 23 °C. The reaction was quenched with the dropwise addition of 20% aqueous NH_4Cl (40 mL). The aqueous layer was then extracted with EtOAc (3 x 40 mL), the organic layers combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (20%-40% gradient EtOAc/hexanes) to afford amide **47** (1.97 g, 85%) as a colorless oil. Analytical data for **47**: IR (film) 3448, 2958, 2936, 2874, 1647, 1420, 1388, 1122, 1178, 1000 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.00 (m, 1H), 3.78 (s, 1H), 3.66 (s, 3H), 3.16 (s, 3H), 2.63 (d, *J* = 16.5 Hz, 1H), 2.42 (dd, *J* = 17.0, 9.5 Hz, 1H), 1.56-1.44 (m, 2H), 1.38 (dddd, *J* = 22.0, 15.5, 15.5, 4.0 Hz, 2H), 0.90 (dd, *J* = 7.5, 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 67.7, 61.4, 38.8, 38.3, 31.9, 18.9, 14.2; LRMS (ESI): Mass calculated for $C_{16}H_{34}N_2O_6Na$ $[2M+Na]^+$, 373. Found [2M+Na], 373; $[\alpha]_D^{25}$ = –42.4 ($CHCl_3$, c = 0.79).

4. Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815-3818.



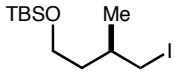
(*R*)-3-(4-methoxybenzyloxy)-*N*-methoxy-*N*-methylhexanamide (18): Amide **47** (1.40 g, 8.00 mmol) was dissolved in cyclohexane (7 mL) and CH_2Cl_2 (3 mL) and cooled to 0 °C. Freshly prepared PMB-imidate (2.71 g, 9.60 mmol) was dissolved in CH_2Cl_2 (2 mL) and added dropwise, followed by the addition of pPTs (0.10 g, 0.40 mmol) in one portion. The mixture was then warmed to 23 °C and stirred for 8 h after which an additional portion of pPTs was added (0.10 g, 0.40 mmol). This mixture was stirred for an additional 7 h, and then plug filtered through a pad of silica (20% EtOAc/hexanes), and the filtrate washed with saturated aqueous $NaHCO_3$ and brine then dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (15%-30% gradient EtOAc/hexanes) to afford amide **18** (1.87 g, 80%) as a yellow oil. Analytical data for **18**: IR (film) 3287, 2960, 2872, 1732, 1661, 1614, 1515, 1462, 1385, 1249, 1175, 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 7.5 Hz, 2 H), 4.45 (A of ABq, J_{AB} = 10.5 Hz, 1H), 4.41 (B of ABq, J_{AB} = 10.5 Hz, 1H), 3.92 (ddd, J = 11.5, 5.5, 5.5 Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 3.14 (s, 3H), 2.80 (dd, J = 14.5, 6.5 Hz, 1H), 2.41 (dd, J = 15.5, 4.5 Hz, 1H), 1.58-1.39 (m, 3 H), 1.33 (dddd, J = 23.5, 13.5, 13.5, 6.5 Hz, 1H), 0.87 (dd, J = 7.5, 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 159.0, 130.8, 129.3, 113.6, 75.7, 71.5, 61.2, 55.1, 37.2, 37.1, 32.0, 18.6, 14.1; LRMS (ESI): Mass calculated for $C_{32}H_{50}N_2O_8Na$ $[2M+Na]^+$, 614. Found [2M + Na], 613; $[\alpha]_D^{25}$ = +8.5 ($CHCl_3$, c = 1.0).



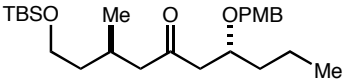
(*R*)-4-(*tert*-butyldimethylsilyloxy)-2-methylbutan-1-ol (48): Diisopropylamine (23.8 g, 32.9 mL, 234 mmol), was dissolved in THF (200 mL) and cooled to –78 °C. A solution of *n*-butyllithium (1.59 M in hexanes, 137 mL) was added dropwise by syringe and the solution was stirred for 10 min at –78 °C, then warmed to 0 °C and stirred for an additional 15 min. Ammonia-borane complex (6.90 g, 224 mmol) was then added in one portion and the mixture stirred for 15 min at 0 °C, then warmed to 23 °C and stirred for an additional 15 min. The mixture was then cooled back down to 0 °C and [1*S*(*R*),2*S*]-*N*-(2-Hydroxy-1-methyl-2-phenylethyl)-4-(*tert*-butyldimethylsilyloxy)-*N*,2-dimethylbutanamide[5] (21.2 g, 55.9 mmol) dissolved in THF (120 mL) was added via cannula, and the mixture was warmed to 23 °C and stirred for 2 h. The mixture was then cooled to 0 °C and quenched with the addition of 0.01 M HCl (500 mL). This mixture was then extracted with EtOAc (3 x 200 mL) and the organic layers were combined, washed with 0.1 M HCl (100 mL), 1 M NaOH (100 mL), brine (100 ML) then dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (10% EtOAc/hexanes) to afford alcohol **48** (11.3 g, 90%) as a colorless oil. Analytical data for **48**: IR (film) 3352, 2930, 2859, 1464, 1389, 1253, 1095, 1085, 1044, 1001, 835, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.72 (ddd, J = 10.5, 6.0, 6.0 Hz, 1H), 3.62 (ddd, J = 7.5, 7.5, 4.0Hz, 1H), 3.45 (ddd, J = 16.5, 5.5, 5.5 Hz, 1H), 3.37 (ddd, J =15.0, 4.0, 4.0 Hz, 1H), 3.29 (s 1H), 1.75 (ddd, J = 12.5, 12.5, 6.5, 1H), 1.56-1.44 (m, 2H), 0.88 (d, J = 7.0 Hz,

5. Myers, A. G.; McKinstry, L. *J. Org. Chem.* **1996**, *61*, 2428-2440.

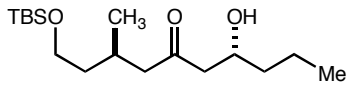
3H), 0.86 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 68.2, 61.9, 37.6, 34.4, 26.0, 18.4, 17.5, –5.3; LRMS (ESI): Mass calculated for $C_{11}H_{26}O_2Si$ $[M]^+$, 218. Found [M], 218; $[\alpha]_D^{25}$ = +9.8 ($CHCl_3$, c = 1.0).



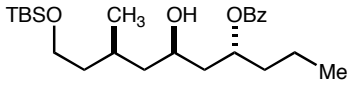
((*R*)-4-iodo-3-methylbutoxy)(*tert*-butyl)dimethylsilane (19): Triphenylphosphine (8.21 g, 31.3 mmol) was dissolved in CH_2Cl_2 (130 mL and imidazole (2.66 g, 39.2 mmol) was added in one portion followed by I_2 (9.27 g, 36.5 mmol). A solution of alcohol **48** in CH_2Cl_2 (50 mL) was then added via cannula and the mixture stirred for 15 min at 23 °C. The solvent was removed *in vacuo* and the residue was purified by flash column chromatography (5% Et_2O/hexanes) to afford iodide **19** (6.02 g, 70%) as a tan oil. Analytical data for **19**: IR (film) 3746, 2929, 2857, 2362, 1652, 1464, 1253, 1099, 834, 775 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.63 (dddd, *J* = 16.5, 10.5, 10.5, 6.0 Hz, 2H), 3.27 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.19 (dd, *J* = 10.0, 6.0 Hz, 1H), 1.67-1.56 (m, 2H), 1.42 (ddd, *J* = 13.0, 13.0, 6.5 Hz, 1H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.8, 39.9, 31.5, 26.1, 20.8, 18.4, 18.4, –5.1; $[\alpha]_D^{25}$ = –4.9 ($CHCl_3$, c = 1.0).



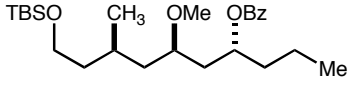
(3*R*,7*R*)-1-(*tert*-butyldimethylsilyloxy)-7-(4-methoxybenzyloxy)-3-methyldecan-5-one (20): Iodide **19** (2.04 g, 6.20 mmol) was azeotroped with benzene 3 times then dissolved in pentane (freshly distilled from CaH_2, 35 mL) and ether (25 mL) and cooled to –78 °C. A solution of *t*-butyllithium (1.7 M in pentane, 7.30 mL) was added dropwise and the mixture was stirred at –78 °C for 15 min, then warmed to 0 °C for 20 min (after which a white precipitate was generated). The solution was cooled back down to –78 °C and a solution of amide **18** (1.02 g, 3.45 mmol) in THF was cooled to –78 °C and added via cannula (dripped along the side of the cooled reaction flask). This mixture was stirred for 15 min at –78 °C. The reaction was quenched at low temperature with the addition of saturated aqueous NH_4Cl (50 mL). Upon warming to ambient temperature, the mixture was extracted with EtOAc (3 x 50 mL), the organic layers combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (3%-10% gradient EtOAc/hexanes) to afford ketone **20** (0.74 g, 50%) as a colorless oil. Analytical data for **20**: IR (film) 2957, 2860, 2362, 1713, 1614, 1514, 1465, 1362, 1302, 1250, 1094, 1039, 835 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.42 (s. 2H), 3.92 (ddd, *J* = 11.5, 6.0, 6.0 Hz, 1H), 3.77 (s, 3H), 3.62 (dddd, *J* = 7.5, 7.5, 7.5, 6.0 Hz, 2H), 2.71 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.43 (dddd, *J* = 25.0, 9.0, 9.0, 9.0 Hz, 2H), 2.24 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.15 (ddd, *J* = 13.5, 13.5, 6.5 Hz, 1H), 1.55-1.44 (m, 4H), 1.43-1.33 (m, 2H), 0.95-0.86 (m, 6H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.8, 159.4, 131.0, 129.6, 113.9, 75.3, 71.5, 61.3, 55.5, 51.8, 48.3, 39.8, 37.0, 26.4, 26.2, 20.1, 18.8, 18.5, 14.4, –5.1; LRMS (ESI): Mass calculated for $C_{50}H_{88}O_8Si_2Na$ $[2M + Na]^+$, 896. Found [2M + Na], 897; $[\alpha]_D^{25}$ = –5.0 ($CHCl_3$, c = 1.0).



(3*R*,7*R*)-1-(*tert*-butyldimethylsilyloxy)-7-hydroxy-3-methyldecan-5-one (49): Ketone **20** (0.52 g, 1.2 mmol) was dissolved in CH_2Cl_2 (110 mL), pH 7 phosphate buffer added (10 mL) and the mixture cooled to 0 °C. DDQ added (0.32 g, 1.4 mmol) and the mixture stirred for 3 h at 0 °C. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (50 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (3%-5% gradient EtOAc/hexanes) to afford ketone **49** (0.32 g, 84%) as a colorless oil. Analytical data for **49**: IR (film) 3463, 2957, 2860, 1701, 1465, 1254, 1096, 837, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.02 (m, 1H), 3.62 (dddd, *J* = 10.5, 10.5, 10.5, 6.5 Hz, 2H), 3.07 (d, *J* = 3.5 Hz, 1H), 2.55 (dd, *J* = 17.5, 2.0 Hz, 1H), 2.50-2.43 (m, 2H), 2.24 (dd, *J* = 16.0, 8.5 Hz, 1H), 2.15 (dddd, *J* = 13.0, 13.0, 13.0, 6.0, 1H), 1.52-1.43 (m, 3H), 1.41-1.29 (m, 3H), 0.92-0.87 (m, 6H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.4, 67.4, 61.1, 51.3, 49.5, 39.7, 38.7, 26.3, 26.1, 20.1, 18.8, 18.4, 14.2, –5.1; LRMS (ESI): Mass calculated for $C_{34}H_{72}O_6Si_2Na$ $[2M + Na]^+$, 656. Found [2M + Na], 655; $[\alpha]_D^{25}$ = +23.4 ($CHCl_3$, c = 0.82).



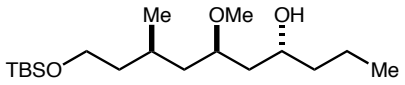
(4*R*,6*R*,8*R*)-10-(*tert*-butyldimethylsilyloxy)-6-hydroxy-8-methyldecan-4-yl benzoate (21): Ketone **49** (0.32g, 1.0 mmol) and benzaldehyde (0.53 g, 0.51 mL, 5.0 mmol) were dissolved in THF (4 mL) that was freshly distilled over benzophenone and sodium, then cooled to –10 °C (ice/salt water). A freshly prepared 0.1 M solution of SmI_2 (10.1 mL)[6] was added dropwise and the mixture stirred at –10 °C for 12 h. The reaction was quenched at low temperature by the addition of saturated aqueous $NaHCO_3$ (5 mL), and the aqueous layer was extracted with Et_2O (3 x 20 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (5%-7.5% gradient EtOAc/hexanes) to afford alcohol **21** (0.39 g, 91%) as a colorless oil. Analytical data for **21**: IR (film) 3519, 2957, 2930, 2858, 2362, 1700, 1459, 1277, 1097, 837 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.57 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.36 (m, 1H), 3.66-3.55 (m, 3H), 3.26 (d, *J* = 3.5 Hz, 1H), 1.80-1.71 (m, 3H), 1.66-1.50 (m, 3H), 1.47-1.24 (m, 5H), 0.93 (t, *J* = 7.5 Hz, 3 H), 0.86 (d, *J* = 6.5 Hz, 3 H), 0.85 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 133.4, 130.3, 128.7, 72.5, 65.4, 61.6, 44.7, 43.5, 39.7, 37.5, 26.6, 26.2, 20.7, 19.0, 18.5, 14.2, –5.0; LRMS (ESI): Mass calculated for $C_{48}H_{84}O_8Si_2Na$ $[2M + Na]^+$, 868. Found [2M + Na], 867; $[\alpha]_D^{25}$ = +4.1 ($CHCl_3$, c = 0.70).



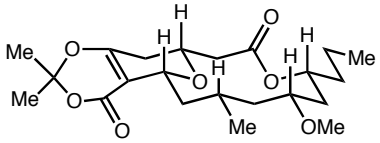
(4*R*,6*R*,8*R*)-10-(*tert*-butyldimethylsilyloxy)-6-methoxy-8-methyldecan-4-yl benzoate (50): Alcohol **21** (0.098 g, 0.23 mmol) was dissolved in CH_2Cl_2 (1 mL) and 2,6-di-*tert*-butyl-4-

6. Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693-2698.

methylpyridne (0.238 g, 1.16 mmol) was added. This solution was cooled to 0 °C and freshly prepared MeOTf (0.190 g, 0.13 mL, 1.16 mmol) added dropwise. The ice bath was then removed and the mixture stirred for 12 h at 23 °C (formation of a white precipitate observed). After 12 h, a second portion of MeOTf (0.190 g, 0.13 mL, 1.16 mmol) was added and the mixture was allowed to stir for an additional 8 h. The mixture was then concentrated *in vacuo* and the residue was purified by flash column chromatography (3%-5% gradient EtOAc/hexanes) to afford methylated alcohol **50** (0.088 g, 88%) as a colorless oil. Analytical data for **50**: IR (film) 2931, 2858, 2362, 1273, 1096, 836, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.55 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.44 (dd, *J* = 7.5, 7.5 Hz, 2H), 5.38 (ddd, *J* = 12.0, 9.0, 3.0 Hz, 1H), 3.63 (dddd, *J* = 17.0, 10.5, 10.5, 6.5 Hz, 2H), 3.28 (m, 3H), 3.24 (m, 1H), 1.85 (m, 1H), 1.74-1.60 (m, 4H), 1.55 (ddd, *J* = 13.0, 7.0, 7.0, 1H), 1.48-1.30 (m, 5H) 0.92 (t, *J* = 7.0 Hz, 3H), 0.88 (s, 9H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 132.9, 130.9, 129.7, 128.5, 76.3, 72.3, 61.2, 57.2, 41.6, 40.5, 39.9, 37.5, 26.3, 26.2, 20.0, 18.7, 18.5, 14.3, –5.0; LRMS (ESI): Mass calculated for $C_{25}H_{44}O_4Si$ $[M]^+$, 437. Found [M], 437; $[\alpha]_D^{25}$ = – 14.5 ($CHCl_3$, c = 0.75).

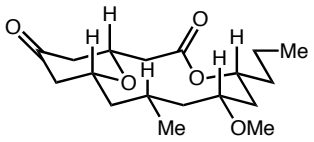


(4*R*,6*R*,8*R*)-10-(*tert*-butyldimethylsilyloxy)-6-methoxy-8-methyldecan-4-ol (8): Methylated alcohol **50** (0.078 g, 0.180 mmol) was dissolved in MeOH (2 mL) and K_2CO_3 (1.24 g, 8.98 mmol) added. This slurry was stirred at 23 °C for 20 h. The mixture was then concentrated *in vacuo* and the residue was diluted with water, and extracted with Et_2O (3 x 15 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (5%-10% gradient EtOAc/hexanes) to afford alcohol **8** (0.052 g, 86%) as a colorless oil. Analytical data for **8**: IR (film) 3454, 2955, 2932, 1464, 1253, 1094, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.89 (m, 1H), 3.64 (ddd, *J* = 24.5, 10.0, 6.0 Hz, 2H), 3.56 (ddd, *J* = 10.0, 10.0, 6.5 Hz, 1H), 3.36 (s, 3H), 3.06 (d, *J* = 3.0 Hz, 1H), 1.72 (m, 1H), 1.65-1.31 (m, 10H), 0.95 (d, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 3.0 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.3, 68.7, 61.2, 56.9, 40.6, 40.5, 40.2, 39.0, 26.6, 26.2, 20.0, 19.1, 18.5, 14.4, –5.0; LRMS (ESI): Mass calculated for $C_{36}H_{82}O_7Si$ $[2M + H_2O]^+$, 683. Found $[2M + H_2O]$, 682; $[\alpha]_D^{25}$ = – 14.8 ($CHCl_3$, c = 0.62).

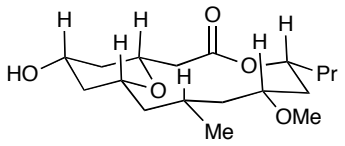


Tricyclic Dioxinone (30): To a round bottom charged with aldehyde **5** (21.6 mg, 0.05 mmol), $CaSO_4$ (20.6 mg, 1.52 mmol), and $Sc(OTf)_3$ (4.9 mg, 0.01 mmol) was added MeCN (5.0 mL). The reaction stirred for 45 min and then brine (0.5 mL) was added and the reaction mixture was filtered through a short pad of Celite eluting with CH_2Cl_2. The layers were separated and the aqueous layer was extracted with EtOAc (4 X 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography (30% EtOAc:hexanes) to afford tricyclic dioxinone **30** (5.0 mg, 25%) as a colorless oil. Analytical data for **30**: ^1H NMR (500 MHz, $CDCl_3$) δ 5.21 (m, 1H), 4.44 (d, *J* = 10.0, 1H), 4.04 (m, 1H), 3.35 (s, 3H), 3.22 (m, 1H), 2.53 (dd, *J* = 12., 2.5 Hz, 1H), 2.47 (dd, *J* =

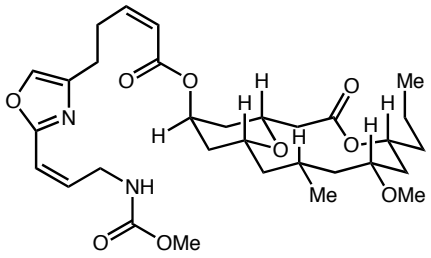
11.0, 11.0, 1H), 2.35-2.11 (m, 4H), 1.82 (d, *J* = 7.5 Hz, 1H),1.70 (s, 6H), 1.59-1.48 (m, 4H), 1.35 (ddd, *J* = 14.0, 9.5, 6.0 Hz, 2H), 1.22-1.17 (m, 2H), 1.03 (d, *J* = 7.5 Hz, 3H), 0.93 (dd, *J* = 7.5, 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 162.2, 159.5, 106.0, 105.9, 82.5, 76.0, 75.1, 71.0, 56.9, 44.9, 42.5, 41.9, 40.5, 37.9, 33.6, 33.3, 27.7, 25.3, 22.1, 18.7, 14.1; LRMS (ESI): Mass calculated for $C_{44}H_{68}O_{14}Na$ [2M+Na]$^+$, 843. Found [2M+Na]$^+$, 843.



(1R,5R,7R,9S,11R)-7-methoxy-9-methyl-5-propyl-4,15-dioxabicylo[9.3.1]penta-decane-3,12-dione (51): To a one-dram vial charged with tricyclic dioxinone **30** (4.1 mg, 0.01 mmol) was added DMSO (0.18 mL) and H_2O (0.5 mL). The reaction was then submerged into a preheated oil bath at 130 ºC. The reaction stirred for 12 h and was then diluted with EtOAc (2 mL) and added to a separatory funnel containing brine (120 mL). The layers were separated and the aqueous layer was extracted with EtOAc (5 X 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography (30% EtOAc:hexanes) to afford pyranone **51** (3.2 mg, 99%) as a colorless oil. Analytical data for **51**: IR (film) 2918, 2872, 1724, 1651, 1558, 1369, 1100 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (dddd, *J* = 11.0, 5.5, 5.5, 5.5, 1H), 4.01 (dd, *J* = 11.0, 11.0, 1H), 3.71 (dd, *J* = 10.5, 10.5, 1H), 3.33 (s, 3H), 3.21 (dd, *J* = 8.5, 8.5, 1H), 2.55 (dd, *J* = 11.5, 11.5, 1H), 2.45 (d, *J* = 13.5, 2H), 2.36 (d, *J* = 14.0, 2H), 2.26 (ddd, *J* = 16.0, 16.0, 12.5, 2H), 1.84 (d, *J* = 15.0, 1H), 1.65-1.53 (m, 3H), 1.51-1.46 (m, 2H), 1.38-1.32 (m, 3H), 1.18 (ddd, *J* = 14.5, 9.5, 6.5, 1H), 1.03 (d, *J* = 6.0, 3H), 0.93 (dd, *J* = 8.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 171.9, 83.3, 79.5, 75.4, 75.0, 56.5, 48.6, 47.5, 44.8, 44.7, 42.7, 39.9, 38.0, 34.5, 24.6, 18.8, 14.1; LRMS (ESI): Mass calculated for $C_{36}H_{60}O_{10}Na$ [2M+Na]$^+$, 676. Found [2M+Na]$^+$, 676. $[\alpha]_D^{25}$ = +20.6 ($CHCl_3$, c = 0.1).

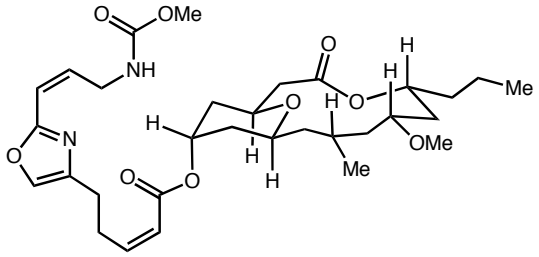


(1*R*,5*R*,7*R*,9*S*,11*R*,13*S*)-13-hydroxy-7-methoxy-9-methyl-5-propyl-4,15-dioxabicyclo[9.3.1]pentadecan-3-one (3): To a one-dram vial charged with pyranone **51** (4.2 mg, 0.013 mmol) was added MeOH (0.26 mL). The reaction mixture was cooled to 0 ºC and $NaBH_4$ (1.0 mg, 0.026 mmol) was added. After 10 min, AcOH (8.0 μL) was added and the reaction was concentrated in vacuo. The resulting residue was purified by flash column chromatography (50% EtOAc:hexanes) to afford alcohol **3** (2.9 mg, 96%) as a colorless oil. Analytical data for **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.25 (m, 1H), 3.84 (dddd, *J* = 5.8, 5.8, 5.8, 5.8, 1H), 3.74 (apt, *J* = 10.9, 1H), 3.43 (apt, *J* = 10.6, 1H), 3.43 (s, 3H), 3.21 (apt, *J* = 8.4, 1H), 2.43 (ddd, *J* = 14.7, 3.6, 3.6, 2H), 2.29 (d, *J* = 14.4, 1H), 2.02 (dd, *J* = 9.8, 2.0, 1H), 1.95 (dd, *J* = 4.2, 2.0, 1H), 1.82 (d, *J* = 14.8, 1H), 1.63-1.44 (m, 6H), 1.43-1.13 (m, 6H), 1.00 (d, *J* = 6.7, 3H), 0.93 (dd, *J* = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 83.3, 78.3, 74.7, 74.2, 68.0, 56.5, 45.1, 44.5, 42.6, 41.9, 40.9, 40.0, 38.0, 34.5, 24.8, 18.8, 14.1.



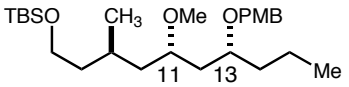
Originally proposed structure (2): To a one-dram vial charged with alcohol **3** (2.0 mg, 0.006 mmol), oxazole **4** (6.1 mg, 0.022 mmol) and PPh_3 (6.22 mg, 0.024 mmol) to which was added benzene (0.33 mL). To the reaction mixture was added diisopropyl azodicarboxylate (4.7 μL, 0.024 mmol). After five min the reaction was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (30% EtOAc:hexanes) to afford **2** (2.6 mg, 73%) as a colorless oil. Analytical data for **2**: IR (film) 3361, 2922, 2871, 1718, 1649, 1520, 1459, 1248, 1159, 1106 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.65 (s, 1H), 6.39 (ddd, *J* = 11.5, 7.4, 7.4, 1H), 6.33 (ddd, *J* = 11.8, 2.0, 2.0, 1H), 6.05 (ddd, *J* = 12.1, 6.1, 6.1, 1H), 5.89 (ddd, 11.5, 1.5, 1.5, 1H), 5.26-5.23 (m, 1H), 5.21 (dddd, *J* = 2.9, 2.9, 2.9, 2.9, 1H), 4.32 (d, *J* = 4.8, 2H), 4.03 (ddd, *J* = 13.2, 4.5, 2.1, 1H), 3.71 (dd, *J* = 11.4, 1H), 3.6 (s, 3H), 3.3 (s, 3H), 3.24 (dd, *J* = 8.1, 8.1, 1H), 3.02 (ddd, *J* = 7.5, 7.5, 2H), 2.73 (dd, *J* = 8.0, 8.0, 2H), 2.37 (dd, *J* = 12.3, 2.9, 1H), 2.33 (dd, *J* = 17.3, 6.5, 1H), 1.85-1.81 (m, 2H), 1.72 (apdd, *J* = 14.3, 2.7, 1H), 1.58-1.47 (m, 6H), 1.39-1.20 (m, 6H), 1.06 (ddd, *J* = 14.5, 10.1, 6.6, 1H), 0.96 (d, *J* = 6.9, 3H), 0.93 (dd, *J* = 7.3, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 173.4, 165.6, 160.6, 158.4, 148.8, 141.0, 137.9, 134.7, 120.4, 114.7, 83.2, 75.2, 74.4, 71.5, 67.7, 55.3, 51.3, 44.8, 44.3, 41.9, 40.0, 39.7, 37.5, 35.8, 34.8, 34.3, 27.7, 25.1, 23.9, 18.4, 12.9; LRMS (ESI): Mass calculated for $C_{31}H_{47}N_2O_9$ $[M+H]^+$, 591. Found $[M+H]^+$, 591. $[\alpha]_D^{25}$ = +19.0 (CH_3OH), c = 0.03).

Characterization Data for Diastereomer 34



Analytic data for **34:** ^1H NMR (500 MHz, CD_3OD) δ 6.34 (ddd, *J* = 11.7, 7.6, 7.6, 1H), 6.25 (apd, *J* = 11.7, 1H), 6.02 (ddd, *J* = 11.7, 5.8, 5.8, 1H), 5.86 (apd, *J* = 11.7, 1H), 5.21 (m, 1H), 5.11 (m, 1H), 4.28 (d, *J* = 5.2, 2H), 4.01 (m, 1H), 3.74 (apt, *J* = 10.5, 1H), 3.63 (s, 3H), 3.32 (s, 3H), 2.99 (ddd, *J* = 7.0, 7.0, 7.0, 2H), 2.69 (dd, *J* = 7.6, 2H), 2.65 (ddd, *J* = 4.1, 4.1, 4.1, 1H), 2.24 (ddd, *J* = 14.0, 8.7, 1H), 1.90-1.74 (m, 4H), 1.67-1.50 (m, 7H), 1.34-1.09 (m, 7H), 0.91 (d, *J* = 7.6, 3H), 0.88 (dd, *J* = 7.0, 3H); LRMS (ESI): Mass calculated for $C_{31}H_{47}N_2O_9$ $[M+1]^+$, 591. Found $[M+H]^+$, 591.

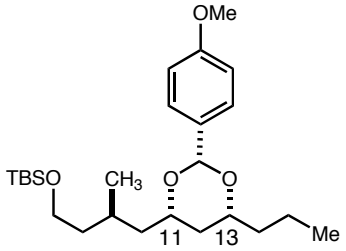
Experimental Procedures and Characterization Data for Synthesis of Revised Structure



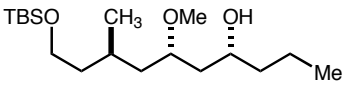
***tert*-Butyl((3*R*,5*S*,7*R*)-5-methoxy-7-(4-methoxybenzyloxy)-3-methyldecyloxy) dimethylsilane (39):** Iodide **19** (0.126 g, 0.385 mmol) was azeotroped with benzene 3 times then dissolved in pentane (freshly distilled from CaH_2, 3 mL) and ether (2 mL) and cooled to –78 °C. A solution of *t*-butyllithium (2.7 M in heptane, 0.30 mL) was added dropwise and the mixture was stirred at –78 °C for 15 min, then warmed to 0 °C for 20 min (after which a white precipitate was noticed). The solution was cooled back down to –78 °C and a solution of (*R*)-3-(4-methoxybenzyloxy)hexanal (derived from the DIBAL reduction of amide **18**) (0.091 g, 0.39 mmol) in THF was cooled to –78 °C and added via cannula (dripped along the side of the cooled reaction flask). This mixture was stirred for 15 min at –78 °C. The reaction was quenched at low temperature with the addition of saturated aqueous NH_4Cl (50 mL). Upon warming to ambient temperature, the mixture was extracted with EtOAc (3 x 50 mL), the organic layers combined, dried over anhydrous Na_2SO_4, filtered and concentrated. This mixture of C11/C13 *syn-* and *anti*-addition products proved difficult to separate and was carried forward without exhaustive separation.

The alcohol (1:1 mixture of diastereomers, 0.300 g, 0.685 mmol) was dissolved in CH_2Cl_2 (2 mL) and 2,6-di-*tert*-butyl-4-methylpyridne (0.703 g, 3.42 mmol) was added. This solution was cooled to 0 °C and freshly prepared MeOTf (0.37 mL, 3.42 mmol) added dropwise. The ice bath was then removed and the mixture stirred for 12 h at 23 °C (formation of a white precipitate observed). After 12 h, a second portion of MeOTf (0.37 mL, 3.42 mmol) was added and the mixture was allowed to stir for an additional 8 h. The mixture was then concentrated *in vacuo* and the residue was purified by flash column chromatography (5% EtOAc/hexanes) to afford methyl ether **39** (0.093 g, 30%) as a colorless oil. Analytical data for **39**: IR (film) 2931, 2859, 2362, 1614, 1514, 1465, 1249, 1095, 835, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 4.45 (A of ABq, J_{AB} = 11.0 Hz, 1H), 4.39 B of ABq, J_{AB} = 11.5 Hz, 1H), 3.80 (s, 3H), 3.63 (ddd, J = 18.5, 18.5, 6.0 Hz, 2H), 3.45 (dddd, J = 11.0, 5.0, 5.0, 5.0 Hz, 1H), 3.37 (m, 1H), 3.29 (s, 3H), 1.90 (ddd, J = 13.5, 6.0, 6.0 Hz, 1H), 1.74 (m, 1H), 1.57-1.46 (m, 5H), 1.45-1.25 (m, 3H) 1.19 (ddd, J = 13.0, 8.5, 4.0 Hz, 1H), 0.92 (d, J = 7.5 Hz, 3H), 0.90-0.87 (m, 3H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 131.2, 129.6, 113.9, 76.3, 75.8, 70.5, 61.6, 56.3, 55.5, 42.3, 40.8, 39.0, 36.6, 26.4, 26.2, 19.9, 18.7, 18.5, 14.5, –5.0; LRMS (ESI): Mass calculated for $C_{26}H_{48}O_4SiNa$ $[M+Na]^+$, 476. Found [M+Na], 476; $[\alpha]_D^{25}$ = –16.3 ($CHCl_3$, c = 0.49).

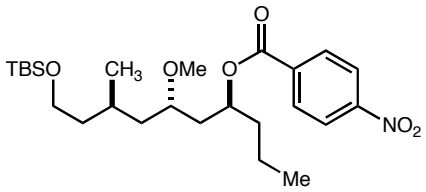
Stereochemical proof of C11/C13 cis relationship of 39



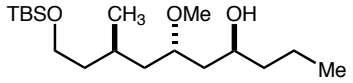
***tert*-butyl((*R*)-4-((2*R*,4*S*,6*R*)-2-(4-methoxyphenyl)-6-propyl-1,3-dioxan-4-yl)-3-methylbutoxy)dimethylsilane (52):** The cis alcohol from the addition above was separated after multiple purifications by column chromatography. A pure sample of this material (0.0150 g, 0.0355 mmol) was dissolved in CH_2Cl_2 (0.5 mL), activated 4Å molecular sieves (0.0249 g) and the mixture cooled to 0 °C. DDQ (0.0121 g, 0.533 mmol) added and the mixture stirred for 2 h while warming to 23 °C. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (3 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (5% acetone/hexanes) to afford acetal **52** (0.011 g, 75%) as a colorless oil. Analytical data for **52**: IR (film) 2928, 2856, 2362, 2336, 1650, 1514, 1464, 1249, 1094, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 5.46 (s, 1H), 3.88 (m, 1H), 3.79 (m, 4H), 3.65 (dddd, *J* = 13.0, 9.5, 9.5, 6.0, 2H), 1.73-1.57 (m, 6H), 1.53-1.34 (m, 4H), 1.29-1.24 (m, 2H), 0.95-0.92 (m, 5H), 0.87 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 132.0, 127.5, 113.6, 100.5, 76.8, 74.8, 61.5, 55.5, 43.7, 40.5, 38.4, 37.7, 26.2, 25.7, 19.8, 18.6, 18.6, 14.3, –5.1; LRMS (ESI): Mass calculated for $C_{25}H_{44}O_4Si$ $[M]^+$, 437. Found $[M]^+$, 437; $[\alpha]_D^{25}$ = –5.0 ($CHCl_3$, c = 0.14).



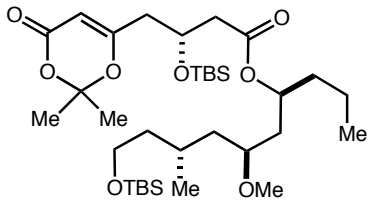
(4*R*,6*S*,8*R*)-10-(*tert*-butyldimethylsilyloxy)-6-methoxy-8-methyldecan-4-ol (53): PMB ether **39** (0.0967 g, 0.214 mmol) was dissolved in CH_2Cl_2 (20 mL), pH 7 phosphate buffer added (2 mL) and the mixture cooled to 0 °C. DDQ was added (0.0582 g, 0.26 mmol) and the mixture stirred for 3 h at 0 °C. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (6%-8% gradient EtOAc/hexanes) to afford alcohol **53** (0.059 g, 83%) as a colorless oil. Analytical data for **53**: IR (film) 3447, 2956, 2932, 2864, 2362, 2336, 1465, 1380, 1253, 1095, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.77 (m, 1H), 3.68-3.60 (m, 2H), 3.57 (s, 1H), 3.51 (m, 1H), 3.35 (s, 3H), 1.69 (m, 1H), 1.63-1.52 (m, 4H), 1.49-1.42 (m, 2H), 1.39-1.28 (m, 3H), 1.25 (ddd, *J* = 21.0, 14.0, 7.0 Hz, 1H), 0.93-0.92 (m, 6H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 80.4, 71.8, 61.2, 56.2, 41.6, 41.4, 40.2, 40.1, 26.3, 26.2, 20.5, 18.9, 18.5, 14.4, –5.2; LRMS (ESI): Mass calculated for $C_{18}H_{40}O_3Si$ $[M]^+$, 333. Found $[M]^+$, 333; $[\alpha]_D^{25}$ = +16.3 ($CHCl_3$, c = 0.27).



(4*S*,6*S*,8*R*)-10-(*tert*-butyldimethylsilyloxy)-6-methoxy-8-methyldecan-4-yl-4-nitrobenzoate (54): To a round bottom charged with alcohol **53** (59 mg, 0.118 mmol) was added benzene (2.0 mL) followed by addition of PPh_3 (24 mg, 0.90 mmol), 4-nitrobenzoic acid (135 mg, 0.81 mmol) and diethyl azodicarboxylate (141 μL, 0.90 mmol). The reaction stirred for 3 h and was diluted with EtOAc (10 mL). The mixture was then washed with water (10 mL) and then brine (10 mL). The combined aqueous layers were extracted with EtOAc (2 X 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography (5% EtOAc:hexanes) to afford ester **54** (63 mg, 73%) of a colorless oil. Analytical data for **54**: IR (film) 2930, 2858, 1724, 1530, 1724, 1530, 1274, 1097, 836, 717 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 9.0, 2H), 8.23 (d, *J* = 9.0, 2H), 5.41 (dddd, *J* = 8.5, 8.5, 8.5, 8.5, 1H), 3.63 (ddd, *J* = 13.0, 13.0, 10.5, 2H), 3.34-3.32 (m, 1H), 3.29 (s, 3H), 1.87 (ddd, *J* = 14.5, 9.0, 3.5, 1H), 1.81-1.60 (m, 5H), 1.56 (ddd, *J* = 13.0, 13.0, 7.0, 1H), 1.46-1.37 (m, 2H), 1.28 (ddd, *J* = 20.5, 14.0, 7.0, 1H), 1.22 (ddd, *J* = 13.5, 6.0, 6.0, 1H), 0.95 (dd, *J* = 7.5, 7.5, 3H), 0.91 (d, *J* = 6.0, 3H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 150.6, 136.3, 130.8, 123.7, 84.3, 75.9, 74.1, 73.7, 61.2, 57.0, 42.1, 40.2, 39.7, 37.4, 26.4, 26.1, 20.2, 18.7, 18.5, 14.2, –5.0; LRMS (ESI): Mass calculated for $C_{25}H_{43}NO_5Si$ $[M]^+$, 482. Found $[M]^+$, 482. $[\alpha]_D^{25}$ = +19.1 ($CHCl_3$, c = 0.83).

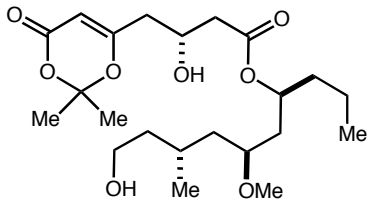


(4S,6S,8R)-10-(*tert*-butyldimethylsilyloxy)-6-methoxy-8-methyldecan-4-ol (36): To a round bottom flask charged with ester **54** (63 mg, 0.13 mmol) was added MeOH (2 mL) followed by K_2CO_3 (898 mg, 6.5 mmol). The reaction mixture stirred for 3 h and was then concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (10% EtOAc:hexanes) to afford alcohol **36** (30 mg, 70%) as a colorless oil. Analytical data for **36**: IR (film) 3446, 2931, 2860, 1650, 1461, 1253, 1094, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.91 (m, 1H), 3.66 (m, 2H), 3.60 (dddd, *J* = 6.0, 6.0, 6.0, 6.0, 1H), 1.77-1.69 (m, 3H), 1.63-1.44 (m, 6H), 1.40-1.31 (m, 4H), 1.24 (ddd, *J* = 15.5, 9.0, 5.0, 2H), 0.96-0.93 (m, 6H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.0, 68.7, 61.3, 56.9, 47.6, 41.2, 40.2, 39.4, 26.6, 26.2, 20.2, 19.1, 18.5, 14.4, –5.1; LRMS (ESI): Mass calculated for $C_{18}H_{40}O_3Si$ $[M]^+$, 333. Found $[M]^+$, 333. $[\alpha]_D^{25}$ = +10.9 ($CHCl_3$, c = 0.3).

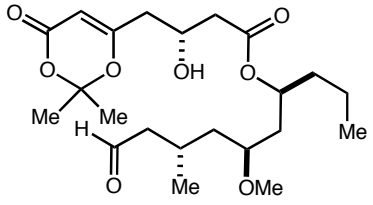


(*R*)-((4*S*,6*S*,8*R*)-10-(*tert*-butyldimethylsilyloxy)-6-methoxy-8-methyldecan-4-yl)-3-(*tert*-butyldimethylsilyloxy)-4-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)butanoate (55): To a

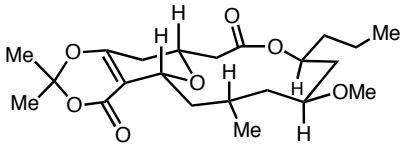
solution of carboxylic acid **7** (53.9 mg, 0.156 mmol) in THF (2.8 mL) was added Et_3N (23 μL, 0.166 mmol) followed by 2,4,6-trichlorobenzoyl chloride (25 μL, 0.156 mmol). The reaction mixture was allowed to stir for 1 h and a mixture of alcohol **36** (52 mg, 0.156 mmol), DMAP (21 mg, 0.166 mmol) in THF (0.8 mL) was added via cannula. The reaction was allowed to stir for 18 h and was then quenched by the addition of saturated aqueous NH_4Cl. The aqueous layer was separated and extracted with EtOAc (4 X 2 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography to afford **55** (81.5 mg, 82%) as a clear oil. Analytical data for **55**: IR (film) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.30 (s, 1H), 5.10 (dddd, *J* = 12.5, 6.0, 6.0, 6.0, 1H), 4.41 (dddd, *J* = 12.0, 6.0, 6.0, 6.0, 1H), 3.65 (ddd, *J* = 17.5, 17.5, 10.0, 2H), 3.29 (s, 3H), 3.25 (m, 1H), 2.58-2.45 (m, 3H), 2.44 (ddd, *J* = 12.0, 12.0, 5.0, 1H), 1.75-1.66 (m, 2H), 1.71 (s, 3H), 1.69 (s, 3H), 1.61-1.48 (m, 4H), 1.41-1.22 (m, 4H), 1.18 (ddd, *J* = 13.5, 7.5, 5.5, 1H), 0.94-0.91 (m, 6H), 0.90 (s, 9H), 0.87 (s, 9H), 0.09 (s, 6H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6. 168.7. 161.5. 106.7. 96.0. 75.9. 72.0. 66.4. 61.3. 56.9. 42.6. 42.2. 41.9. 40.5. 39.5. 37.2. 26.4. 26.2. 26.0. 25.9. 24.6. 20.1. 18.6. 18.5. 18.1. 14.2. –4.5, –4.9; LRMS (ESI): Mass calculated for $C_{34}H_{67}O_8Si_2$ $[M+H]^+$, 660. Found [M+H] 660 $[\alpha]_D^{25}$ = +5.3 ($CHCl_3$, c = 0.5).



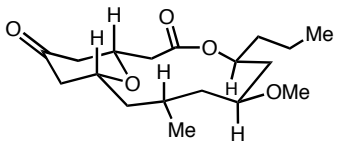
(*R*)-((4*S*,6*S*,8*R*)-10-hydroxy-6-methoxy-8-methyldecan-4-yl)-4-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-3-hydroxybutanoate (56): To a 0 ºC solution of silyl ether **55** (81.5 mg, 0.124 mmol) in THF (2.5 mL) was added HF•pyridine (0.22 mL, 2.48 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. At this time, the reaction was then cooled to 0 ºC and diluted with EtOAc (2 mL) and quenched with saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was separated and extracted with EtOAc (5 X 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography to afford **56** (49.7 mg, 93%) as a clear oil. Analytical data for **56**: IR (film) 3421, 2927, 1726, 1386, 1273, 1201, 1012 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.37 (s, 1H), 5.20 (m, 1H), 4.33 (m, 1H), 4.032 (bs, 1H), 3.37-3.31 (m, 1H), 3.33, (s, 3H), 2.57 (dd, *J* = 16.0, 3.0, 1H), 2.47 (ddd, *J* = 20.5, 9.0, 9.0, 2H), 2.38 (dd, *J* = 14.5, 4.5, 1H), 2.053 (bs, 1H), 1.85 (ddd, *J* = 13.5, 10.0, 2.5, 1H), 1.75-1.49 (m, 5H), 1.71 (s, 6H), 1.43 (ddd, *J* = 13.5, 6.5, 6.5, 2H), 1.35-1.26 (m, 2H), 1.14 (ddd, *J* = 13.0, 5.5, 5.5, 1H), 0.96-0.91 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 168.6, 161.3, 106.9, 95.5, 76.4, 72.0, 65.1, 60.5, 56.9, 42.2, 40.8, 39.8, 38.3, 37.4, 26.0, 25.4, 25.0, 20.5, 18.7, 14.1; LRMS (ESI): Mass calculated for $C_{22}H_{39}O_8Si$ $[M+H]^+$, 431. Found $[M+H]^+$ 431. $[\alpha]_D^{25}$ = +2.8 ($CHCl_3$, c = 1.0).



(*R*)-((4*S*,6*S*,8*S*)-6-methoxy-8-methyl-10-oxodecan-4-yl)-4-(2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-yl)-3-hydroxybutanoate (40): To a solution of diol **56** (49.7 mg, 0.116 mmol) in CH_2Cl_2 (1.9 mL) was added TEMPO (1.8 mg, 0.012 mmol) and bisacetoxy iodobenzene (41.0 mg, 0.13 mmol). The reaction mixture stirred for 4 h and was then diluted with CH_2Cl_2 (5 mL) and quenched with saturated $Na_2S_2O_3$ (20 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (5 X 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated to afford aldehyde **40** (49.2 mg, 99%) as a colorless oil. Aldehyde **40** was used directly in the next step. Analytical data for: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, 1H), 5.37 (s, 1H), 5.16 (m, 1H), 4.33 (m, 1H), 3.58 (m, 1H), 3.38-3.26 (m, 1H), 3.32 (s, 3H), 2.57 (dd, *J* = 16.0, 3.0, 1H), 2.51-2.37 (m, 2H), 2.32 (dd, *J* = 7.5, 2.0, 1H), 2.29 (dd, *J* = 9.5, 4.5, 1H), 2.22 (ddd, *J* = 13.5, 13.5, 7.0, 1H), 1.82-1.74 (m, 1H), 1.72 (s, 3H), 1.71 (s, 3H), 1.67-1.65 (m, 2H), 1.64-1.56 (m, 1H), 1.55-1.48 (m, 2H), 1.38-1.23 (m, 3H), 1.02 (d, *J* = 6.5, 3H), 0.93 (dd, *J* = 7.5, 7.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 171.6, 168.5, 161.2, 106.9, 95.7, 76.2, 72.1, 65.1, 56.8, 51.6, 41.8, 41.2, 40.7, 38.4, 37.3, 29.9, 25.6, 24.9, 20.7, 18.8, 14.1; LRMS (ESI): Mass calculated for $C_{22}H_{36}O_8Na$ $[M+Na]^+$, 451. Found $[M+Na]^+$, 451.

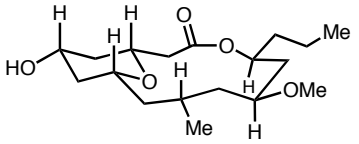


Tricyclic Dioxinone (41): To round bottom charged with aldehyde **40** (21.6 mg, 0.05 mmol), $CaSO_4$ (20.6 mg, 1.52 mmol), and $Sc(OTf)_3$ (4.9 mg, 0.01 mmol) was added MeCN (5.0 mL). The reaction stirred for 45 min and then brine (0.5 mL) was added and the reaction mixture was filtered through a short pad of Celite eluting with CH_2Cl_2. The layers were separated and the aqueous layer was extracted with EtOAc (4 X 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography (30% EtOAc:hexanes) to afford tricyclic dioxinone **41** (5.0 mg, 25%) as a colorless oil. Analytical data for **41**: IR (film) 2922, 1726, 1648, 1406, 1269, 1207, 1090, 999 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.25 (dddd, *J* = 9.0, 4.0, 4.0, 4.0, 1H), 4.44-4.42 (d, *J* = 11.0, 1H), 3.96 (dddd, *J* = 12.5, 9.0, 5.0, 2.0, 1H), 3.34 (m, 1H), 3.30 (s, 3H), 2.91-2.84 (m, 2H), 2.35 (dd, *J* = 12.5, 2.5, 1H), 2.15 (d, *J* = 18.5, 1H), 2.00 (m, 1H), 1.75-1.71 (m, 1H), 1.70 (s, 3H), 1.69 (s, 3H), 1.63-1.49 (m, 4H), 1.44 (m, 1H), 1.40-1.32 (m, 2H), 1.28-1.23 (m, 2H), 1.06 (d, *J* = 7.5, 3H), 0.93 (dd, *J* = 7.5, 7.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 163.2, 159.6, 106.3, 105.1, 76.9, 73.6, 72.3, 68.4, 56.2, 43.5, 42.3, 42.1, 39.8, 37.6, 32.1, 27.7, 27.2, 23.7, 22.5, 18.9, 14.1;LRMS (ESI): Mass calculated for $C_{44}H_{68}O_{14}Na$ $[2M+Na]^+$, 843. Found $[2M+Na]^+$, 843. $[\alpha]_D^{25}$ = +198.6 ($CHCl_3$, c = 0.9).

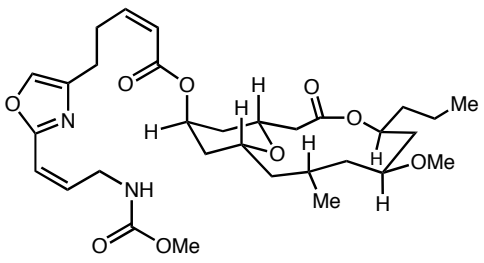


(1*R*,5*S*,7*S*,9*S*,11*R*)-7-methoxy-9-methyl-5-propyl-4,15-dioxabicyclo[9.3.1]penta decane-3,13-dione (42): To a one-dram vial charged with tricyclic dioxinone **41** (5.0 mg, 0.01 mmol) was added DMSO (0.25 mL) and H_2O (0.6 mL). The reaction was then submerged into a preheated oil bath of 130 °C. The reaction stirred for 12 h and was then diluted with EtOAc (2 mL) and

added to a separatory funnel containing brine (125 mL). The layers were separated and the aqueous layer was extracted with EtOAc (5 X 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash column chromatography (30% EtOAc:hexanes) to afford pyranone **42** (3.0 mg, 82%) as a colorless oil. Analytical data for **42**: IR (film) 2958, 2920, 1725, 1651, 1558, 1273, 1249, 1091 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.25-5.20 (m, 1H), 4.05 (apt, *J* = 10.2, 1H), 3.59 (apt, *J* = 9.72, 1H), 3.51 (apt, *J* = 9.7, 1H), 3.344 (s, 3H), 2.72 (dd, *J* = 15.1, 4.34, 1H), 2.53 (dd, *J* = 14.6, 10.7, 1H), 2.44 (d, *J* = 14.1, 1H), 2.35-2.22 (m, 2H), 1.86 (apt, *J* = 12.2, 1H), 1.73-1.60 (m, 3H), 1.55-1.45 (m, 2H), 1.43-1.35 (m, 4H), 1.20 (apt, *J* = 12.1, 2H), 1.01 (d, *J* = 6.8, 3H), 0.93 (dd, *J* = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 170.2, 79.2, 77.5, 75.9, 73.5, 56.5, 49.0, 47.2, 44.4, 42.7, 40.2, 37.1, 31.3, 25.7, 19.1, 14.1; LRMS (ESI): Mass calculated for $C_{36}H_{62}O_{11}$ $[2M+H_2O]^+$, 670. Found $[2M+H_2O]^+$, 670. $[\alpha]_D^{25}$ = +32.6 ($CHCl_3$, c = 0.1).

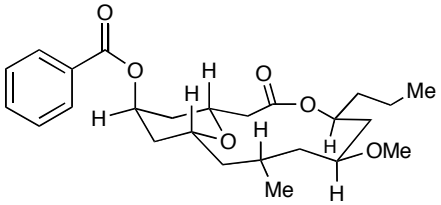


Alcohol (43): To a one-dram vial charged with pyranone **42** (3.0 mg, 0.01 mmol) was added MeOH (0.2 mL). The reaction mixture was cooled to 0 ºC and $NaBH_4$ (0.5 mg, 0.02 mmol) was added. After 10 min, AcOH (7.0 μL) was added and the reaction was concentrated in vacuo. The resulting residue was purified by flash column chromatography (50% EtOAc:hexanes) to afford pyran **43** (2.9 mg, 96%) as a colorless oil. Analytical data for **43**: IR (film) 3416, 2918, 2871, 1730, 1650, 1459, 1087 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.18-5.16 (m, 1H), 3.81-3.77 (m, 1H), 3.75 (apt, *J* = 11.2, 1H), 3.68 (apt, *J* = 10.2, 1H), 3.32 (s, 3H), 3.18 (apt, *J* = 10.2, 1H), 2.63 (dd, *J* = 14.6, 3.9, 1H), 2.43 (dd, *J* = 14.1, 11.2, 1H), 1.98 (apd, *J* = 12.2, 1H), 1.86 (apt, *J* = 11.2, 2H), 1.70 (dddd, *J* = 5.8, 5.8, 5.8, 5.8, 1H), 1.59 (apt, *J* = 12.7, 2H), 1.51-1.50 (m, 3H), 1.50-1.42 (m, 1H), 1.37-1.33 (m, 4H), 1.30-1.12 (m, 2H), 0.99 (d, *J* = 6.35 3H), 0.92 (t, *J* = 7.32, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 78.8, 75.7, 73.4, 72.5, 68.3, 56.5, 44.3, 42.5, 42.4, 42.1, 40.9, 40.2, 37.1, 31.4, 25.8, 19.2, 14.1; LRMS (ESI): Mass calculated for $C_{36}H_{64}O_{10}Na$ $[2M+Na]^+$, 328.44. Found $[2M+Na]^+$, 679.9. $[\alpha]_D^{25}$ = +18.1 ($CHCl_3$, c = 0.1).

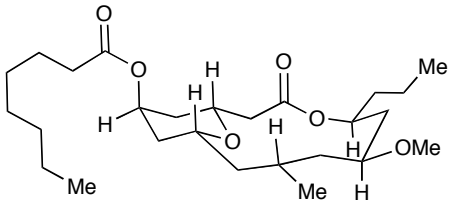


Neopeltolide (1): To a one-dram vial charged with pyran **43** (2.9 mg, 0.009 mmol), oxazole **4** (8.6 mg, 0.032 mmol) and PPh_3 (6.84 mg, 0.027 mmol) was added benzene (0.36 mL). To the reaction mixture was added diisopropyl azodicarboxylate (5.2 μL, 0.027 mmol). After five min the reaction was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (30% EtOAc:hexanes) to afford **1** (4.2 mg, 79%) as a colorless oil. Analytical data for **1**: IR (film) 3356, 3132, 2921, 2497, 1718, 1645, 1458, 1394, 1273, 1167, 1084, 1026,

777 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.67 (s, 1H), 6.40 (ddd, *J* = 11.5, 7.4, 7.4, 1H), 6.29 (ddd, *J* = 11.9, 4.2, 2.1, 1H), 6.05 (ddd, *J* = 11.9, 6.0, 6.0, 1H), 5.90 (ddd, *J* = 13.1, 3.3, 1.6, 1H), 5.22—5.21 (m, 1H), 5.19-5.16 (m, 1H), 4.32 (d, *J* = 4.94, 2H), 4.09 (dddd, *J* = 11.3, 11.3, 4.2, 2.1, 1H), 3.68 (dd, *J* = 9.5, 9.5, 1H), 3.66 (s, 3H), 3.56 (t, *J* = 9.88, 1H), 3.29 (s, 3H), 3.03 (ddd, *J* = 7.5, 7.5, 7.5, 2H), 2.74 (dd, *J* = 7.3, 7.3, 2H), 2.72 (dd, *J* = 10.8, 3.7, 1H), 2.32 (dd, *J* = 14.7, 10.8, 1H), 1.89 (ddd, *J* = 14.2, 10.8, 1H), 1.85-1.83 (m, 1H), 1.75-1.71 (m, 1H), 1.71-1.68 (m, 1H), 1.61-1.50 (m, 4H), 1.44-1.29 (m, 7H), 1.12 (ddd, *J* = 12.9, 10.9, 1.9, 1H), 1.00 (d, *J* = 6.7, 3H), 0.96 (dd, *J* = 14.8, 7.4, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 173.2, 166.9, 162.0, 159.0, 150.1, 142.4, 139.3, 136.0, 121.8, 116.0, 77.2, 77.1, 74.0, 71.4, 69.3, 56.5, 52.7, 45.3, 43.6, 43.3, 41.1, 38.0, 37.5, 36.3, 32.7, 29.1, 26.5, 26.1, 20.1, 14.2; HRMS (ESI): Exact mass calculated for $C_{31}H_{47}N_2O_9$ $[M+H]^+$, 591.3282. Found $[M+H]^+$, 591.3277 $[\alpha]_D^{25}$ = +23.8 (CH_3OH), c = 0.24). Reported $[\alpha]_D^{25}$ for natural neopeltolide = +24 (CH_3OH), c = 0.24).[7]



Analytic data for **44:** IR (film) 2956, 2917, 1851, 1719, 1653, 1559, 1456, 1273, 1115, 1087, 1071, 1026, 713 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5, 2H), 7.52 (dd, *J* = 7.5, 7.5, 1H), 7.42 (dd, *J* = 7.5, 7.5, 2H), 3.35 (app tt, *J* = 3, 1H), 5.07 (dddd, *J* = 14.5, 5, 5, 5, 1H), 4.11 (dddd, *J* = 6.5, 6.5, 2, 2, 1H), 3.68 (app tt, *J* = 10, 1H), 3.53 (app tt, *J* = 7.5, 1H), 3.26 (s, 3H), 2.55 (ddd, *J* = 14.5, 4.5, 1H), 2.32 (ddd, *J* = 14.5, 10.5, 1H), 1.88 (dd, *J* = 13.5, 11, 1H), 1.75 (m, 2H), 1.59-1.36 (m, 6H), 1.35-1.28 (m, 4H), 1.09 (ddd, *J* =13, 11, 2, 2H), 0.92 (d, *J* = 6.5, 3H), 0.86 (dd, *J* = 6.5, 3H); ^{13}C NMR ($CDCl_3$) d 169.8, 164.7, 132.1, 129.4, 128.6, 127.4, 74.6, 74.5, 72.6, 68.9, 67.6, 55.2, 43.0, 41.5, 41.2, 38.9, 35.9, 35.3, 34.5, 29.9, 28.7, 24.5, 18.0, 12.9; LRMS (ESI): Mass calculated for $C_{25}H_{36}O_6Na$ $[M+23]^+$, 455. Found $[M+23]^+$, 455. $[\alpha]_D^{25}$ = +26.4 (CH_2Cl_2), c = 0.09).

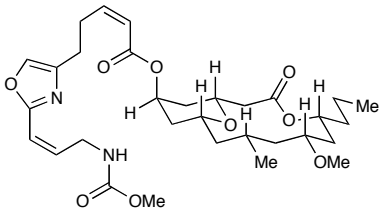


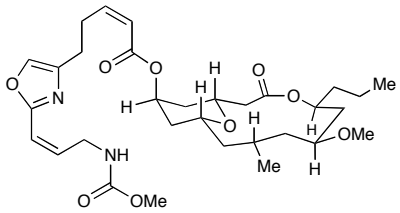
Analytic data for **45:** IR (film) 2951, 2922, 2852, 1731, 1459, 1372, 1268, 1245, 1163, 1088, 1062, 1033, 993 cm^{-1}, ^1H NMR (500 MHz, CD_3OD) δ 5.19 (ddd, *J* = 9.5, 4.5, 4.5, 1H), 5.14 (app tt, *J* = 2.5, 1H), 4.07 (dddd, *J* = 5.5, 5.5, 1.5, 1.5, 1H), 3.68 (app tt, *J* = 10.5, 1H), 3.27 (s, 3H), 2.69 (ddd, *J* = 15, 4.5, 1H), 2.37 (dd, *J* = 7.5, 2H), 2.29 (ddd, *J* = 14.5, 11, 1H), 1.89 (dd, *J* = 11, 7, 1H), 1.80 (dd, *J* = 14.5, 2, 1H), 1.75-1.70 (m, 5H), 1.56-1.46 (m, 4H), 1.39-1.23 (m, 13H),

7. Wright, A. E.; Botelho, J. C.; Guzman, E.; Harmody, D.; Linley, P.; McCarthy, P. J.; Pitts, T. P.; Pomponi, S. A.; Reed, J. K. *J. Nat. Prod.* **2007**, *70*, 412-416.

1.13 (ddd, *J* = 12.5, 11, 1.5, 1H), 0.99 (d, *J* = 7, 3H), 0.95-0.89 (m, 6H); ^{13}C NMR (CD_3OD) δ 174.6, 173.9, 77.1, 76.9, 73.7, 71.2, 62.3, 56.3, 45.1, 43.4, 43.1, 41.0, 37.9, 37.3, 36.1, 35.3, 32.8, 32.6, 30.1, 30.0, 26.1, 25.9, 23.6, 19.9, 14.4, 14.0; LRMS (ESI): Mass calculated for $C_{26}H_{46}O_6Na$ $[M+23]^+$, 477. Found $[M+23]^+$, 477. $[\alpha]_D^{25}$ = +28.6 (CH_2Cl_2), c = 0.43).

Comparison of ^{13}C Spectral Data of Neopeltolide, 1, and 2





neopeltolide[7] *isolated*	*Synthetic* ***2*** *(proposed structure)*	*Synthetic* ***1*** *(actual structure)*
14.1	12.9	14.2
20.0	18.4	20.1
26.0	23.9	26.1
26.4	25.1	26.5
29.0	27.7	29.1
32.6	34.3	32.7
36.2	34.8	36.3
37.4	35.8	37.5
37.9	37.5	38.0
41.0	39.7	41.1
41.0	40.0	41.1
43.2	41.9	43.3
43.5	44.3	43.6
45.2	44.8	45.3
52.6	51.3	52.7
56.4	55.3	56.5
69.2	67.7	69.3
71.3	71.5	71.4
73.9	74.4	74.0
77.0	75.2	77.1
77.1	83.2	77.2
115.7	114.7	116.2
121.7	120.4	121.8
135.9	134.7	136.0
139.2	137.9	139.3
142.3	141.0	142.4
150.0	148.8	150.1
159.6	158.4	159.0
161.9	160.6	162.0
166.9	165.6	166.9
173.0	173.4	173.2

Comparison of ^{1}H Spectral Data of Natural Neopeltolide and Synthetic Neopeltolide

Isolated neopeltolide	Synthetic neopeltolide (**1**)
0.92, t (7.6)	0.96, dd (7.4, 7.4)
0.94, d (6.9)	1.00, d (6.7)
1.08, m	1.12, ddd (12.9, 10.9, 1.9)
1.25, m	1.25, m
1.28, m	1.29, m
1.33, m	1.29-1.44, m
1.36, m	1.33, m
1.38, m	1.36, m
1.46, m	1.38, m
1.48, m	1.48, m
1.49, m	1.50-1.61, m
1.54, m	1.54, m
1.64, m	1.68-1.71, m
1.68, m	1.73, m
1.78, m	1.84, m
1.83, m	1.89, ddd (14.2, 10.8)
2.26, dd (15.1, 11.0)	2.32, dd (14.7, 10.8)
2.66, dd (15.1, 4.1)	2.72, dd (10.8, 3.7)
2.68, dd (7.6, 7.6)	2.74, dd (7.3, 7.3)
2.98, m	3.03, ddd (7.5, 7.5, 7.5)
3.23, s	3.29, s
3.55, bt (10.3)	3.56, dd (9.8, 9.8)
3.62, s	3.66 (s)
3.64, m	3.68, dd (9.5, 9.5)
4.04, ddt (4.1, 2.1)	4.09, dddd (11.3, 11.3, 4.2, 2.1)
4.28, bd (4.8)	4.32, d (4.9)
5.14, dt (4.8, 9.6)	5.16, m
5.17, m	5.21, m
5.86, dt (11.7, 1.4)	5.90, ddd (13.1, 3.3, 1.6)
6.02, dt (11.7, 6.2)	6.05, ddd (11.9, 6.0, 6.0)
6.24, dt (11.7, 6.2)	6.29, ddd (11.9, 4.2, 2.1)
6.33, dt (11.7, 7.6)	6.40, ddd (11.5, 7.4, 7.4)
7.64, s	7.67, s

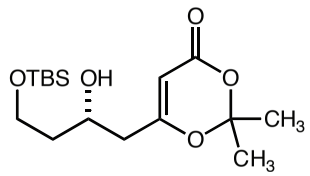
Selected NMR Spectra (^{1}H, ^{13}C, NOE, NOESY)

H1_std P-inova500 H/C probe RT

Date: Wed Oct 31 09:48:07 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3

Spectrometer: Inova500
Nucleus: H1

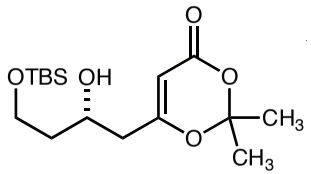
INDEX	FREQUENCY	PPM	HEIGHT
1	2670.429	5.344	15.8
2	850.005	1.701	54.4
3	845.611	1.692	51.3
4	449.590	0.900	151.2
5	44.292	0.089	86.2



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:22:30 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-aldolCS
Spectrometer: Inova500
Nucleus: C13

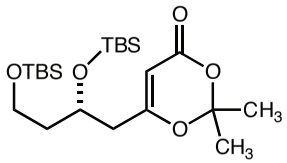
INDEX	FREQUENCY	PPM	HEIGHT
1	-4911.401	-39.085	0.0



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:24:12 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-realbissilyletherHS
Spectrometer: Inova500
Nucleus: H1

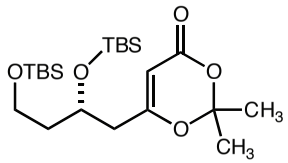
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:25:11 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-bissilyletherC
Spectrometer: Inova500
Nucleus: C13

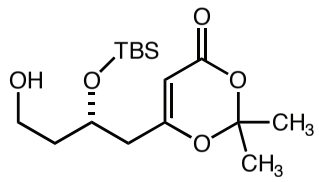
INDEX	FREQUENCY	PPM	HEIGHT
1	9740.993	77.518	396.9
2	9708.995	77.263	404.7
3	9677.530	77.013	400.8



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:26:53 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-alcoholHS
Spectrometer: Inova500
Nucleus: H1

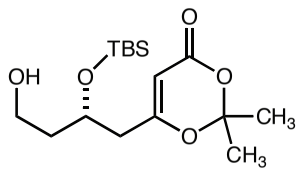
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0

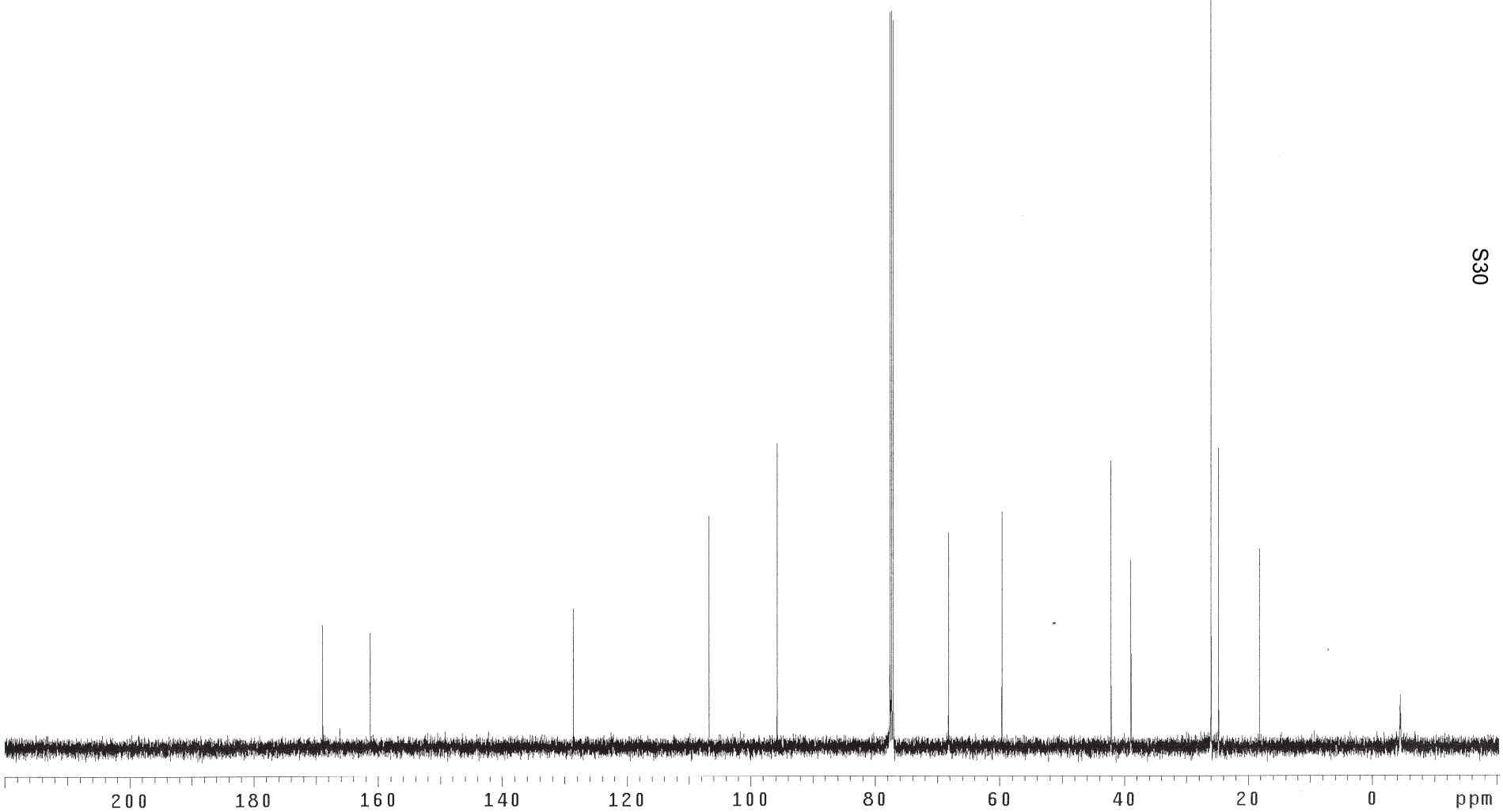


C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:27:54 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-alcoholC
Spectrometer: Inova500
Nucleus: C13

INDEX	FREQUENCY	PPM	HEIGHT
1	-4911.401	-39.085	0.0

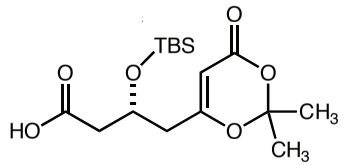




H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:28:49 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-carboxylicacidH
Spectrometer: Inova500
Nucleus: H1

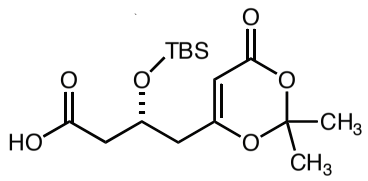
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:29:56 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-carboxylicC2
Spectrometer: Inova500
Nucleus: C13

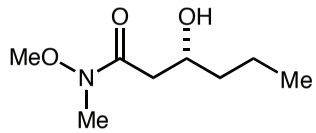
INDEX	FREQUENCY	PPM	HEIGHT
1	9742.059	77.526	445.2
2	9710.061	77.272	456.6
3	9678.063	77.017	448.7



H1_std P-inova500 H/C probe RT

Date: Mon Nov 5 16:15:46 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1

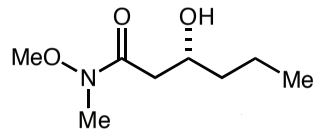
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

INDEX	FREQUENCY	PPM	HEIGHT
1	-4922.527	-39.173	0.0

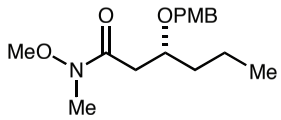
Date: Mon Nov 5 16:16:11 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13



TZ:1-188

Date: Mon Nov 5 16:12:31 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1

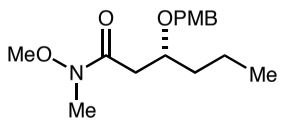
INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0



C13 std p-500 H/C probe RT

Date: Mon Nov 5 16:14:08 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13

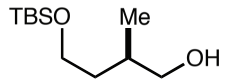
INDEX	FREQUENCY	PPM	HEIGHT
1	-4946.524	-39.364	0.0



TZ:1-229,f11

Date: Mon Nov 5 16:06:19 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1

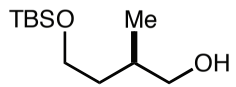
INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0



TZ:1-229

Date: Mon Nov 5 16:04:31 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13

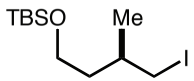
INDEX	FREQUENCY	PPM	HEIGHT
1	-4920.394	-39.156	0.0



TZ:1-230

INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0

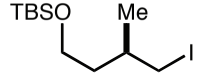
Date: Mon Nov 5 16:09:24 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1



C13 std p-500 H/C probe RT

Date: Mon Nov 5 16:10:35 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13

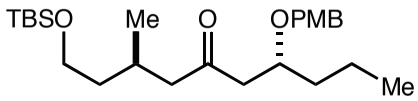
INDEX	FREQUENCY	PPM	HEIGHT
1	-4920.394	-39.156	0.0



TZ:1-232

Date: Mon Nov 5 16:20:10 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1

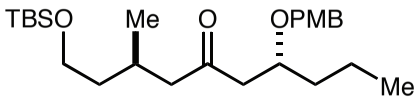
INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0



C13 std p-500 H/C probe RT

Date: Mon Nov 5 16:22:10 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13

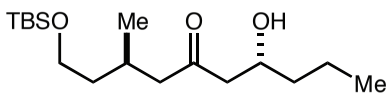
INDEX	FREQUENCY	PPM	HEIGHT
1	-4911.401	-39.085	0.0



TZ:1-233

Date: Mon Nov 5 16:25:10 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1

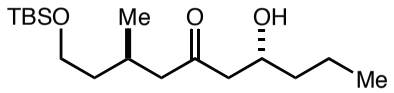
INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0



C13 std p-500 H/C probe RT

Date: Mon Nov 5 16:26:18 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13

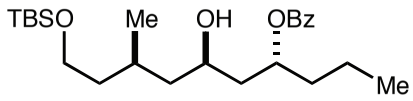
INDEX	FREQUENCY	PPM	HEIGHT
1	-4917.728	-39.135	0.0



TZ:1-234,f29-33

Date: Mon Nov 5 16:27:29 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1

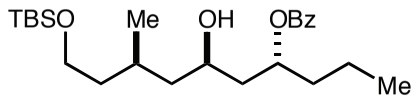
INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0

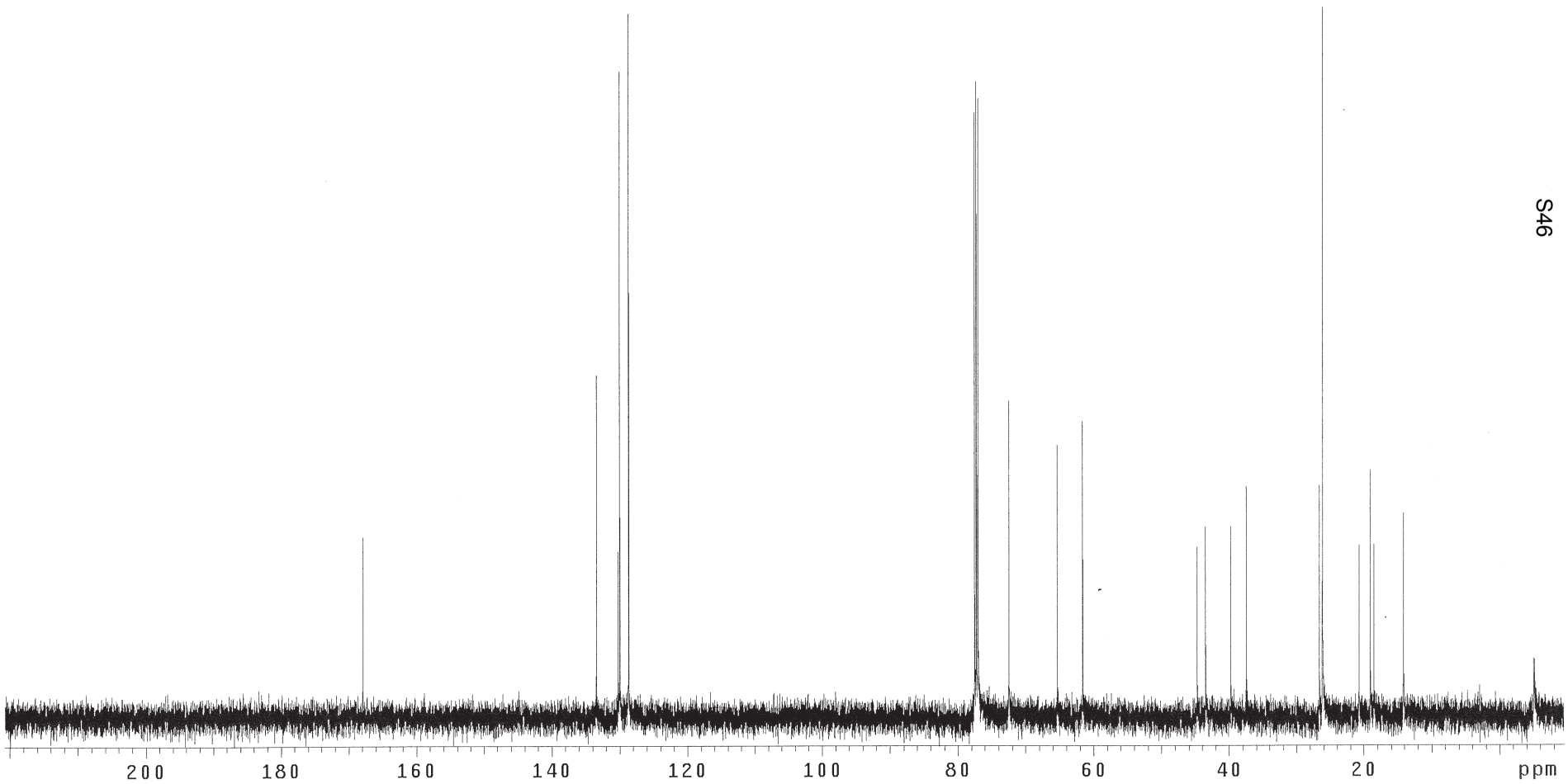


C13 std p-500 H/C probe RT

Date: Mon Nov 5 16:28:22 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13

INDEX	FREQUENCY	PPM	HEIGHT
1	-4911.401	-39.085	0.0

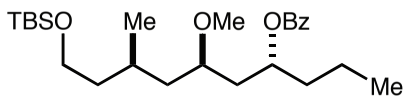




TZ:1-235

Date: Mon Nov 5 16:32:58 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: H1

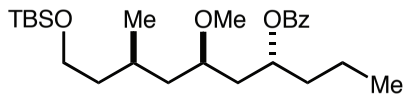
INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0



TZ:1-235

Date: Mon Nov 5 16:33:24 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13

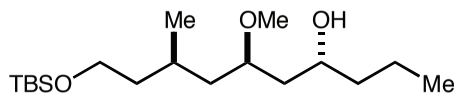
INDEX	FREQUENCY	PPM	HEIGHT
1	-4916.128	-39.122	0.0



C13 std p-500 H/C probe RT

INDEX	FREQUENCY	PPM	HEIGHT
1	-4911.401	-39.085	0.0

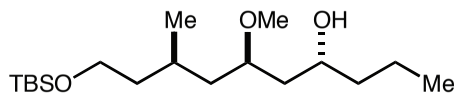
Date: Mon Nov 5 16:30:48 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1
Spectrometer: Inova500
Nucleus: C13



H1_std P-inova500 H/C probe RT

Date: Mon Nov 5 16:30:21 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: TZ:1-239
Spectrometer: Inova500
Nucleus: H1

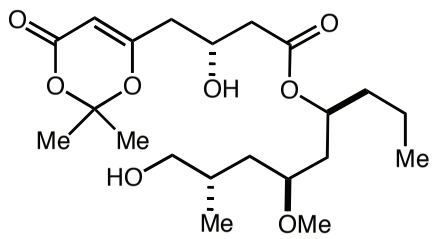
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:14:46 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-deprotection
Spectrometer: Inova500
Nucleus: H1

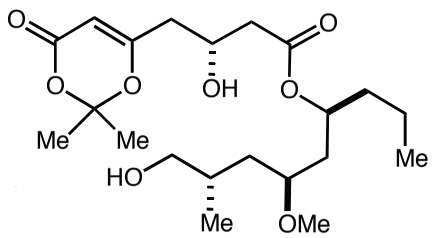
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:15:46 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-deprotectionC
Spectrometer: Inova500
Nucleus: C13

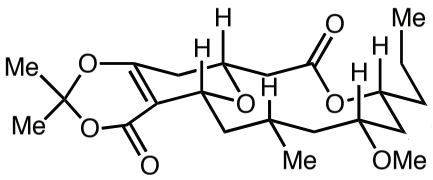
INDEX	FREQUENCY	PPM	HEIGHT
1	9743.659	77.539	247.8
2	9711.661	77.285	255.2
3	9679.663	77.030	249.2



H1_std P-inova500 H/C probe RT

Date: Thu Sep 20 17:16:35 CDT 2007
Pulse Sequence: s2pul
Solvent: CDCl3

Spectrometer: Inova500
Nucleus: H1

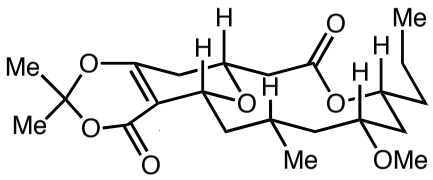


INDEX FREQUENCY PPM HEIGHT

C13 std p-500 H/C probe RT

Date: Thu Sep 20 19:37:59 CDT 2007
Pulse Sequence: s2pul
Solvent: CDCl3

Spectrometer: Inova500
Nucleus: C13

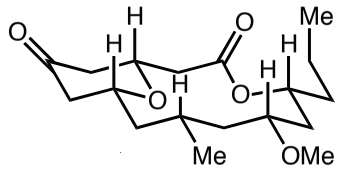


INDEX	FREQUENCY	PPM	HEIGHT
1	21576.501	171.704	49.6
2	20391.510	162.274	44.0
3	20048.599	159.545	48.6
4	13325.830	106.046	63.1
5	13308.764	105.910	49.9
6	12563.212	99.977	-24.1
7	10369.219	82.517	83.8
8	9740.459	77.514	802.6
9	9708.461	77.259	817.3
10	9676.997	77.009	822.4
11	9551.138	76.007	74.1
12	9442.345	75.141	73.6
13	8926.645	71.037	67.2
14	7159.292	56.973	86.0
15	5648.988	44.954	48.6
16	5342.341	42.514	37.6
17	5276.746	41.992	49.0
18	5097.557	40.566	42.9
19	4767.445	37.939	63.0
20	4228.813	33.653	64.2
21	4184.549	33.300	56.3
22	3489.660	27.770	64.6
23	3186.746	25.360	42.1
24	2781.439	22.134	73.2
25	2361.199	18.790	65.8
26	1780.436	14.169	60.3

H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:30:54 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-pyranonediasterH
Spectrometer: Inova500
Nucleus: H1

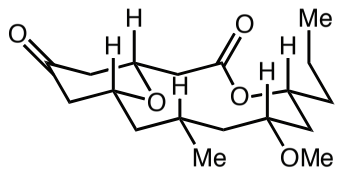
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:32:11 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-pyranonediastC
Spectrometer: Inova500
Nucleus: C13

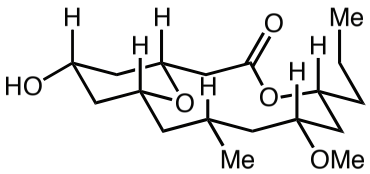
INDEX	FREQUENCY	PPM	HEIGHT
1	9740.993	77.518	379.1
2	9708.995	77.263	386.7
3	9676.997	77.009	377.5



H1 stdpar RT idpfg_5mm inova500

Date: Sun Sep 23 15:48:03 CDT 2007
Pulse Sequence: s2pul
Solvent: CDCl3

Spectrometer: Inova500
Nucleus: H1



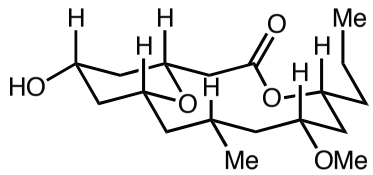
INDEX	FREQUENCY	PPM	HEIGHT
1	3640.207	7.289	56.8
2	1664.877	3.334	151.2
3	1062.194	2.127	45.1
4	769.363	1.541	36.9
5	650.766	1.303	38.0
6	637.955	1.277	40.9
7	508.743	1.019	84.7
8	502.154	1.006	87.7
9	473.054	0.947	57.6
10	465.916	0.933	93.2
11	458.596	0.918	50.2

C13 std p-500 H/C probe RT

Date: Sun Sep 23 18:28:24 CDT 2007
Pulse Sequence: s2pul
Solvent: CDCl3

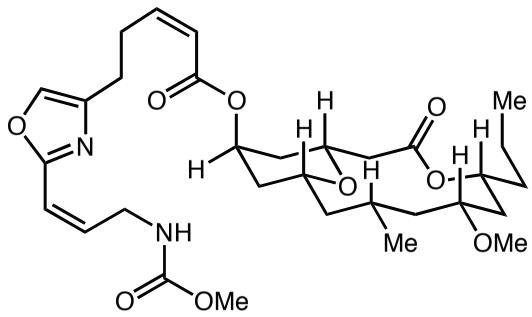
Spectrometer: Inova500
Nucleus: C13

INDEX FREQUENCY PPM HEIGHT



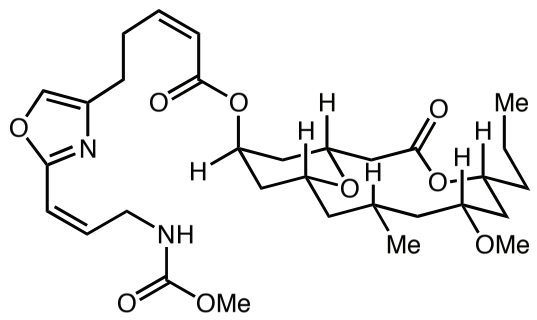
1H LINESHAPE
1% CHCL3 (89)
Date: Thu Dec 6 16:11:54 CST 2007
Solvent: CDCl3
Pulse Sequence: s2pul
File: dan_custar_1d_2nd_110507
Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	3126.824	5.212	183.9
2	3123.711	5.207	2036.4
3	2199.679	3.666	661.9
4	2198.398	3.664	779.4
5	2196.750	3.662	995.7
6	2195.102	3.659	666.2
7	2193.546	3.656	336.0



inova400 DB_5mm RT non-spin
C13 std
Date: Thu Dec 6 16:43:55 CST 2007
Solvent: cdcl3
File: dwc5-neodiastC
Spectrometer: Mercury400
Nucleus: C13

INDEX	FREQUENCY	PPM	HEIGHT
1	4877.864	48.423	383.3
2	4856.501	48.211	1131.8
3	4835.138	47.999	2249.5
4	4813.775	47.787	2666.5
5	4792.412	47.575	2305.4
6	4771.049	47.363	1140.7
7	4748.923	47.143	386.5

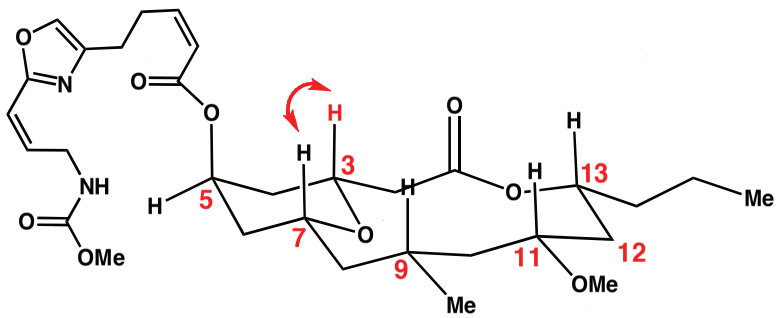


H1 stdpar RT idpfg_5mm inova500

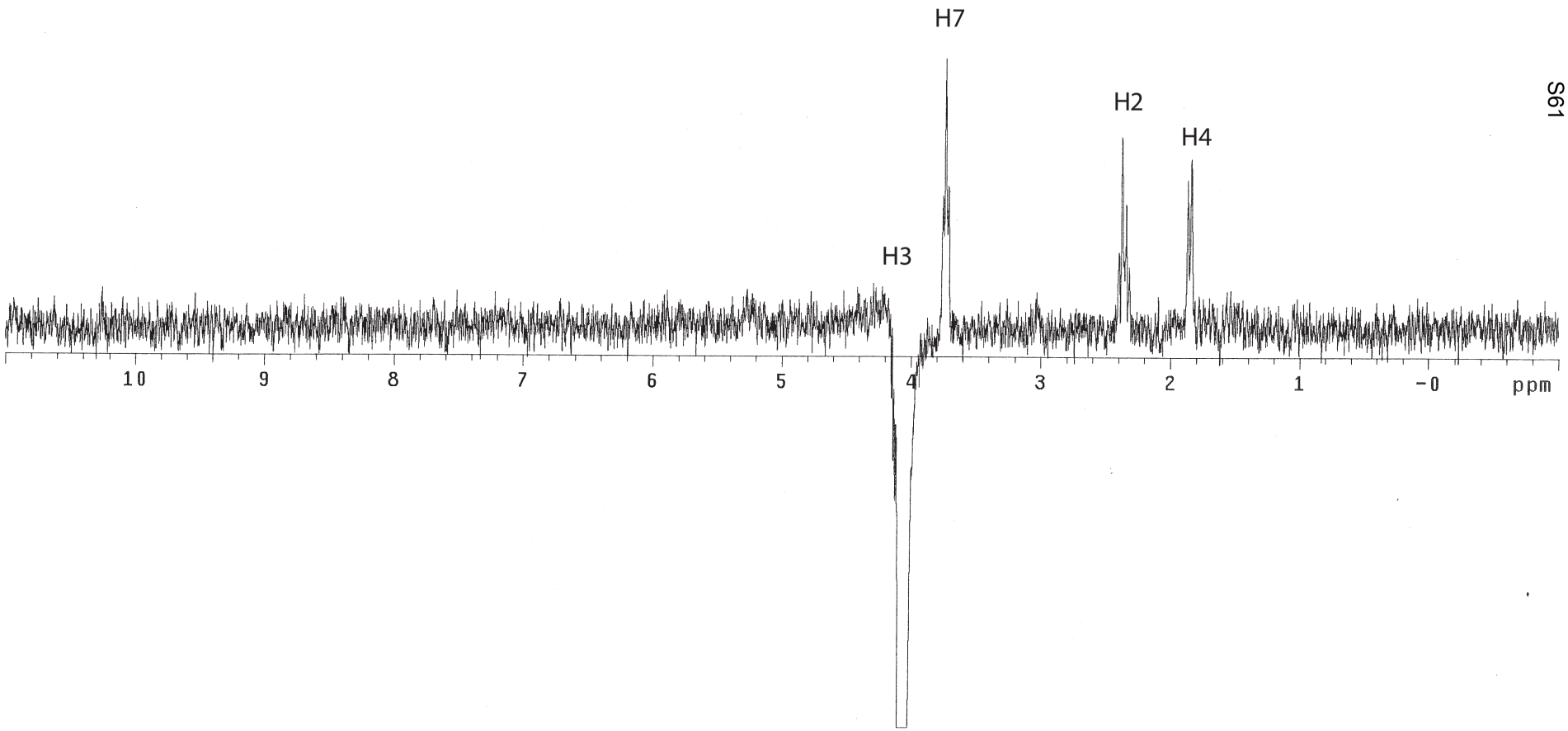
Date: Mon Sep 24 08:51:00 CDT 2007
Pulse Sequence: NOESY1D
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2036.354	4.078	-604.1
2	2025.739	4.056	-1171.8
3	2014.941	4.035	-651.0
4	1864.682	3.734	42.6



H3 Irradiation

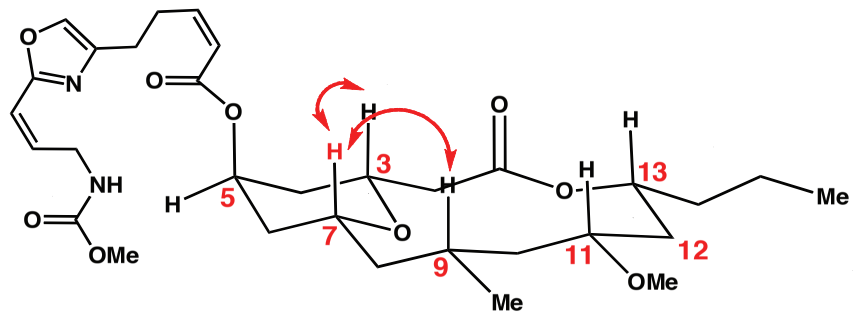


H1 stdpar RT idpfg_5mm inova500

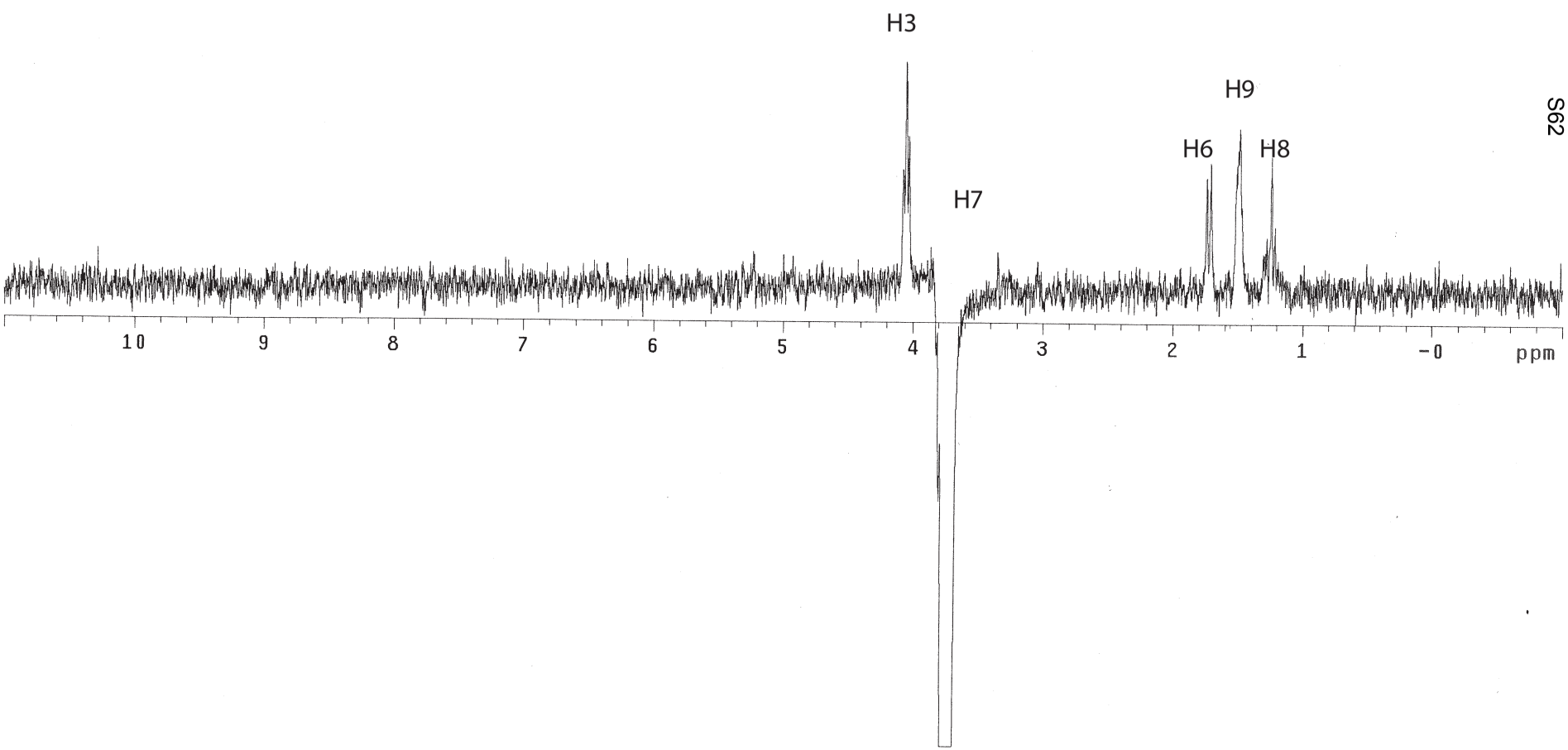
Date: Mon Sep 24 10:04:15 CDT 2007
Pulse Sequence: NOESYID
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2026.471	4.058	36.6
2	1893.233	3.791	-33.7
3	1875.114	3.755	-506.0
4	1864.682	3.734	-936.9
5	1853.518	3.711	-577.2
6	1837.961	3.680	-133.7



H7 Irradiation



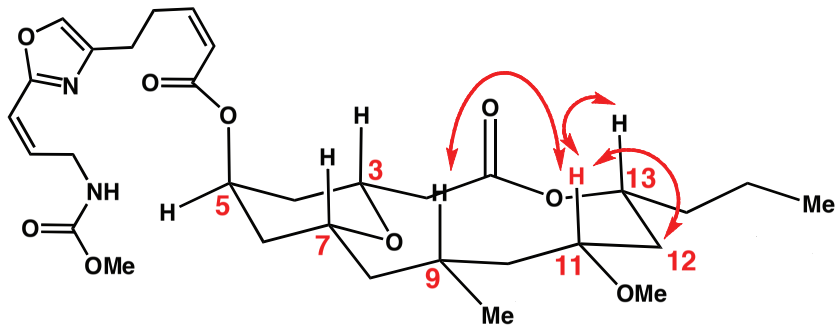
S62

H1 stdpar RT idpfg_5mm inova500

Date: Mon Sep 24 08:55:11 CDT 2007
Pulse Sequence: NOESYID
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2620.919	5.248	33.5
2	1668.668	3.341	132.2
3	1649.268	3.302	-409.0
4	1638.287	3.280	-1004.1
5	1630.417	3.265	-1527.4
6	1622.547	3.249	-1053.9
7	743.870	1.490	34.6

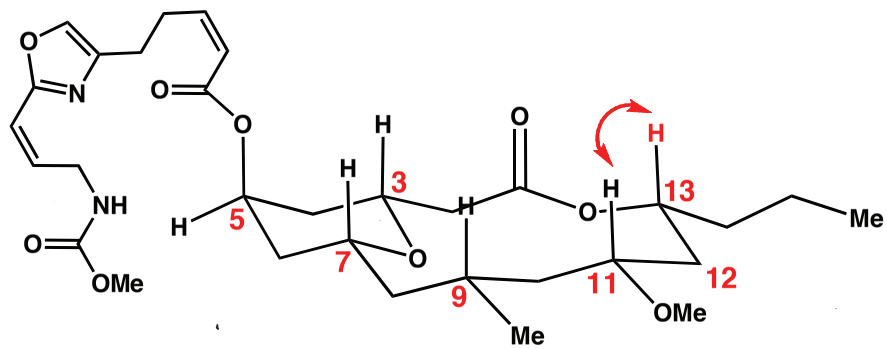


H1 stdpar RT idpfg_5mm inova500

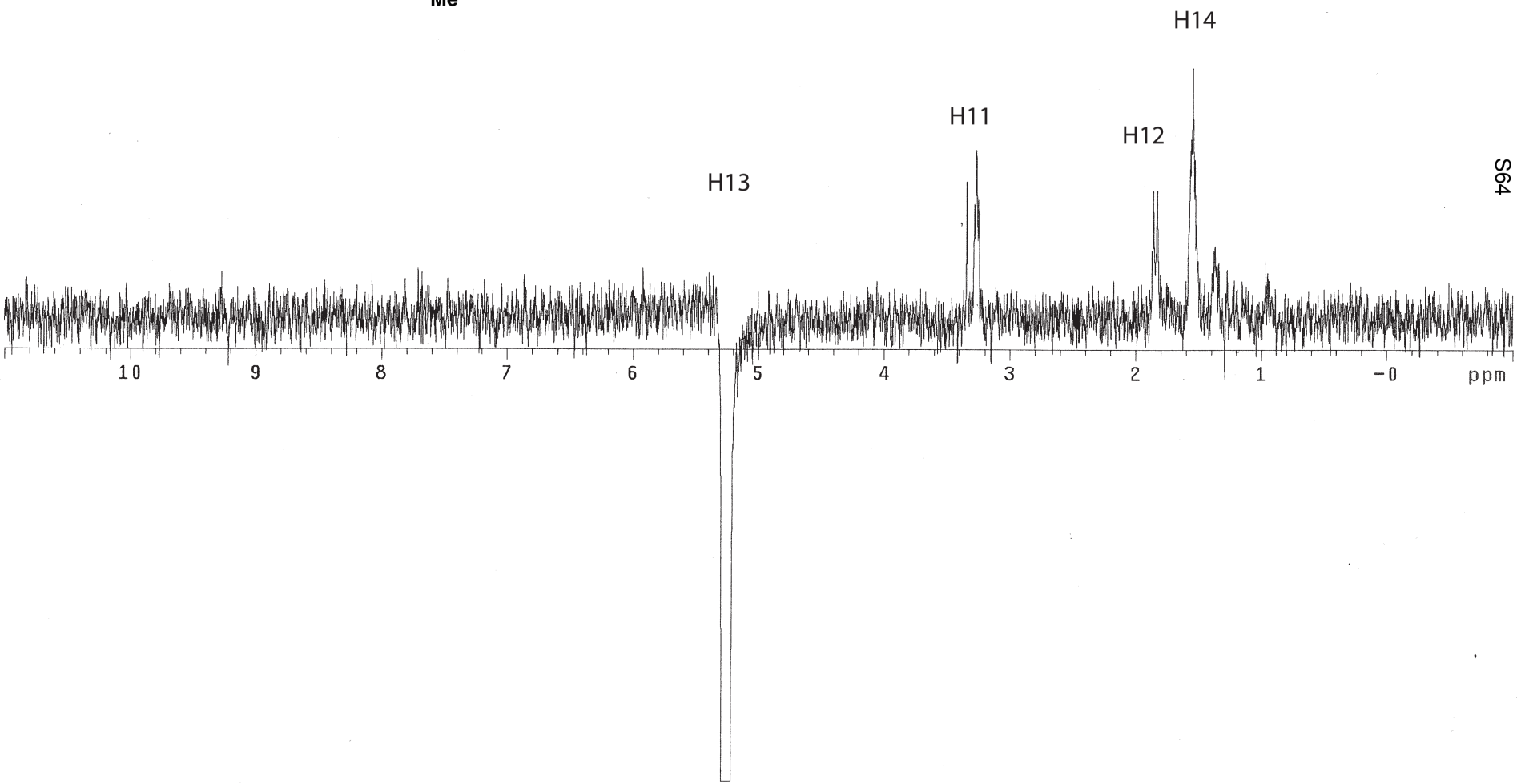
Date: Mon Sep 24 10:08:13 CDT 2007
Pulse Sequence: NOESY1D
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2631.168	5.269	-789.8
2	2625.860	5.258	-913.3
3	2621.102	5.248	-891.7
4	2614.696	5.236	-665.8
5	771.323	1.544	41.3



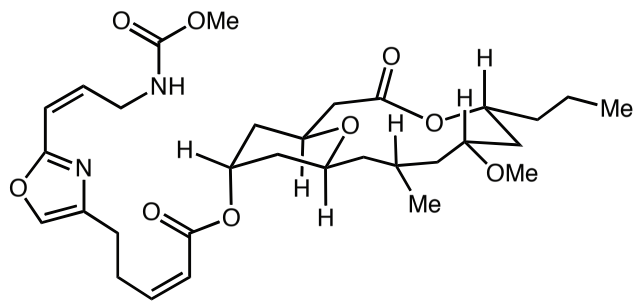
H13 Irradiation



H1 std RT spin=0 INOVA-400 DB_5mm

Date: Thu Dec 6 16:53:00 CST 2007
Sample Directory: tamaP_08jun1999
Solvent: cd3od
Pulse Sequence: s2pul
File: aw99-he8sdfa_H
Spectrometer:Mercury400
Nucleus: H1

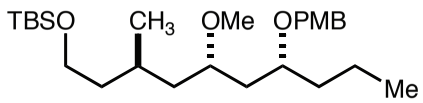
INDEX	FREQUENCY	PPM	HEIGHT
1	1953.851	4.877	209.5
2	1317.534	3.289	247.2



TZ:1-236

Date: Thu Dec 6 20:39:24 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1-236
Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0

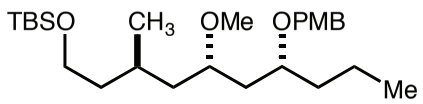


S66

C13 std p-500 H/C probe RT

Date: Thu Dec 6 20:40:11 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1-236C13
Spectrometer: Inova500
Nucleus: C13

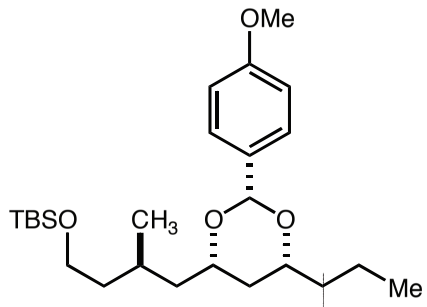
INDEX	FREQUENCY	PPM	HEIGHT
1	9736.799	77.485	456.2
2	9704.801	77.230	467.1
3	9672.803	76.975	459.0



TZ:1-225

INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0

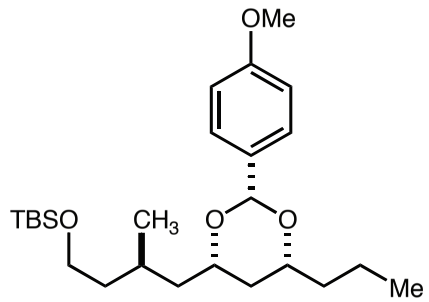
Date: Thu Dec 6 20:48:13 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1-225
Spectrometer: Inova500
Nucleus: H1



C13 std p-500 H/C probe RT

Date: Thu Dec 6 20:36:40 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1-225C13
Spectrometer: Inova500
Nucleus: C13

INDEX	FREQUENCY	PPM	HEIGHT
1	9740.993	77.518	1182.5
2	9708.995	77.263	1218.2
3	9676.997	77.009	1206.3

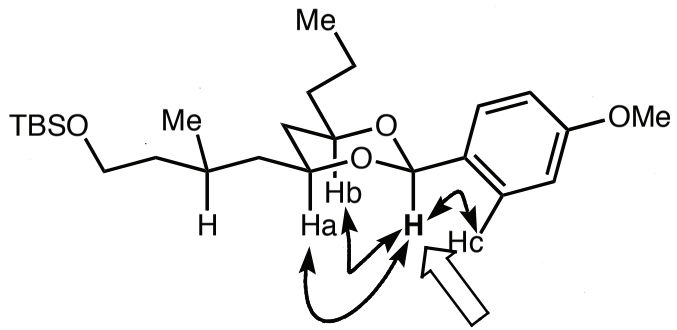


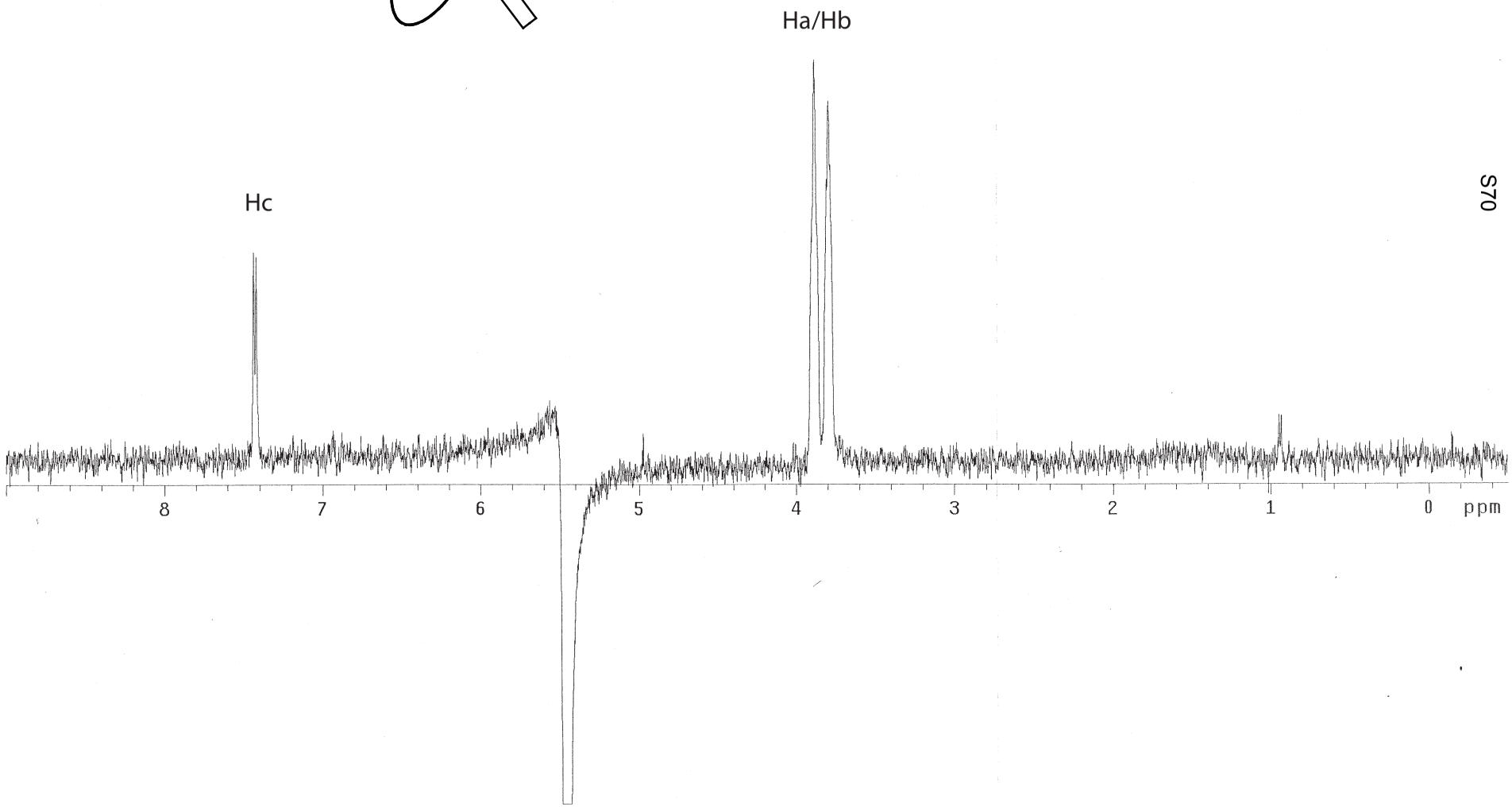
TZ:1-225,f7-8

Date: Tue Oct 23 10:18:37 CDT 2007
Pulse Sequence: NOESYTD
Solvent: CDCl3

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	3713.468	7.436	33.8
2	3705.049	7.419	33.0
3	2726.993	5.460	-5031.0
4	1939.276	3.883	65.6
5	1895.901	3.796	58.6

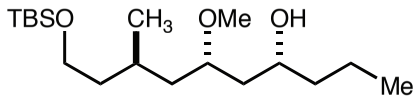




TZ:1-238

Date: Thu Dec 6 20:37:49 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1-238
Spectrometer: Inova500
Nucleus: H1

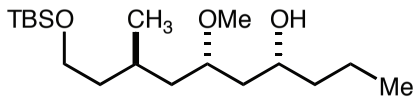
INDEX	FREQUENCY	PPM	HEIGHT
1	-1510.020	-3.022	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 20:38:17 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: 1-238C13
Spectrometer: Inova500
Nucleus: C13

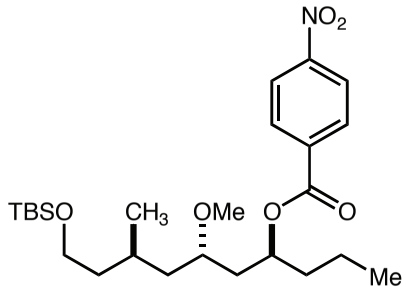
INDEX	FREQUENCY	PPM	HEIGHT
1	9736.799	77.485	303.3
2	9704.801	77.230	313.4
3	9672.803	76.975	305.5



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:34:54 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-mitsunobuH
Spectrometer: Inova500
Nucleus: H1

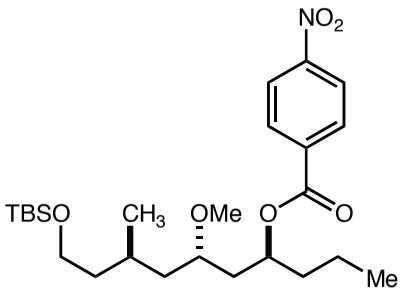
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:36:39 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-mitsunobuC
Spectrometer: Inova500
Nucleus: C13

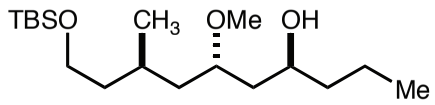
INDEX	FREQUENCY	PPM	HEIGHT
1	9741.526	77.522	198.1
2	9709.528	77.268	197.8
3	9678.063	77.017	195.3



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:37:40 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-hydrolysisH
Spectrometer: Inova500
Nucleus: H1

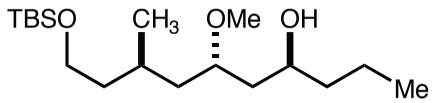
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:38:45 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-hydrolysisC
Spectrometer: Inova500
Nucleus: C13

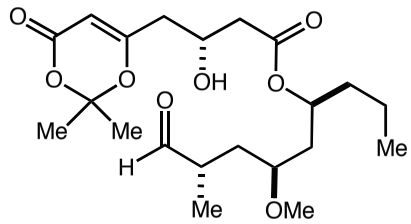
INDEX	FREQUENCY	PPM	HEIGHT
1	9740.993	77.518	200.7
2	9708.995	77.263	207.1
3	9676.997	77.009	203.7



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:03:10 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-aldhydeH
Spectrometer: Inova500
Nucleus: H1

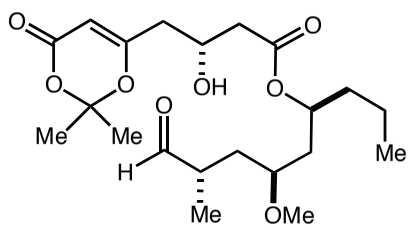
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:13:53 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-aldehydeC
Spectrometer: Inova500
Nucleus: C13

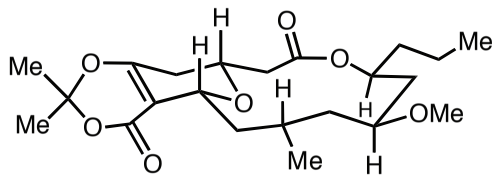
INDEX	FREQUENCY	PPM	HEIGHT
1	9747.392	77.569	507.5
2	9715.394	77.314	520.0
3	9683.396	77.060	512.1



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:39:53 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-cyclizationH
Spectrometer: Inova500
Nucleus: H1

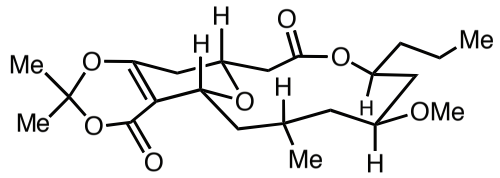
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:40:52 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-cyclizationC
Spectrometer: Inova500
Nucleus: C13

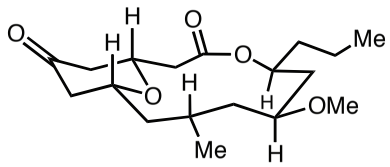
INDEX	FREQUENCY	PPM	HEIGHT
1	9741.526	77.522	387.2
2	9709.528	77.268	400.7
3	9677.530	77.013	394.7



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:17:00 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-pyranoneH
Spectrometer: Inova500
Nucleus: H1

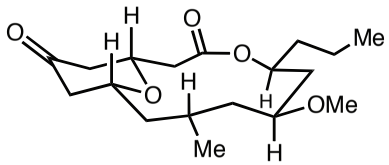
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

Date: Thu Dec 6 16:17:56 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-pyranoneC
Spectrometer: Inova500
Nucleus: C13

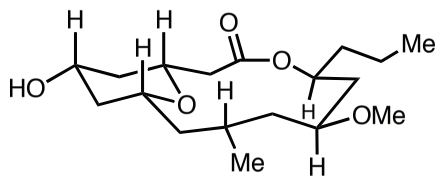
INDEX	FREQUENCY	PPM	HEIGHT
1	9741.526	77.522	331.7
2	9710.061	77.272	341.9
3	9678.063	77.017	339.3



H1_std P-inova500 H/C probe RT

Date: Thu Dec 6 16:18:50 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-pyranH
Spectrometer: Inova500
Nucleus: H1

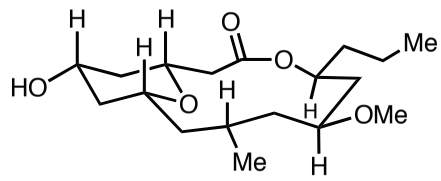
INDEX	FREQUENCY	PPM	HEIGHT
1	-1501.212	-3.004	0.0



C13 std p-500 H/C probe RT

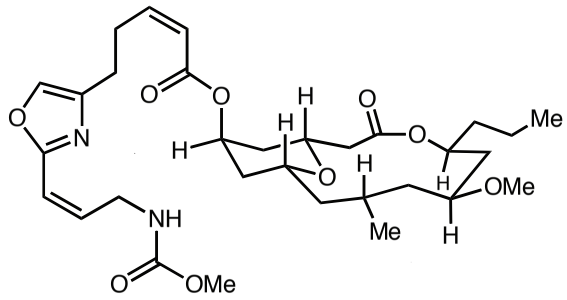
Date: Thu Dec 6 16:19:40 CST 2007
Pulse Sequence: s2pul
Solvent: CDCl3
File: dwc5-pyranC
Spectrometer: Inova500
Nucleus: C13

INDEX	FREQUENCY	PPM	HEIGHT
1	9740.993	77.518	656.7
2	9708.995	77.263	671.9
3	9676.997	77.009	665.6

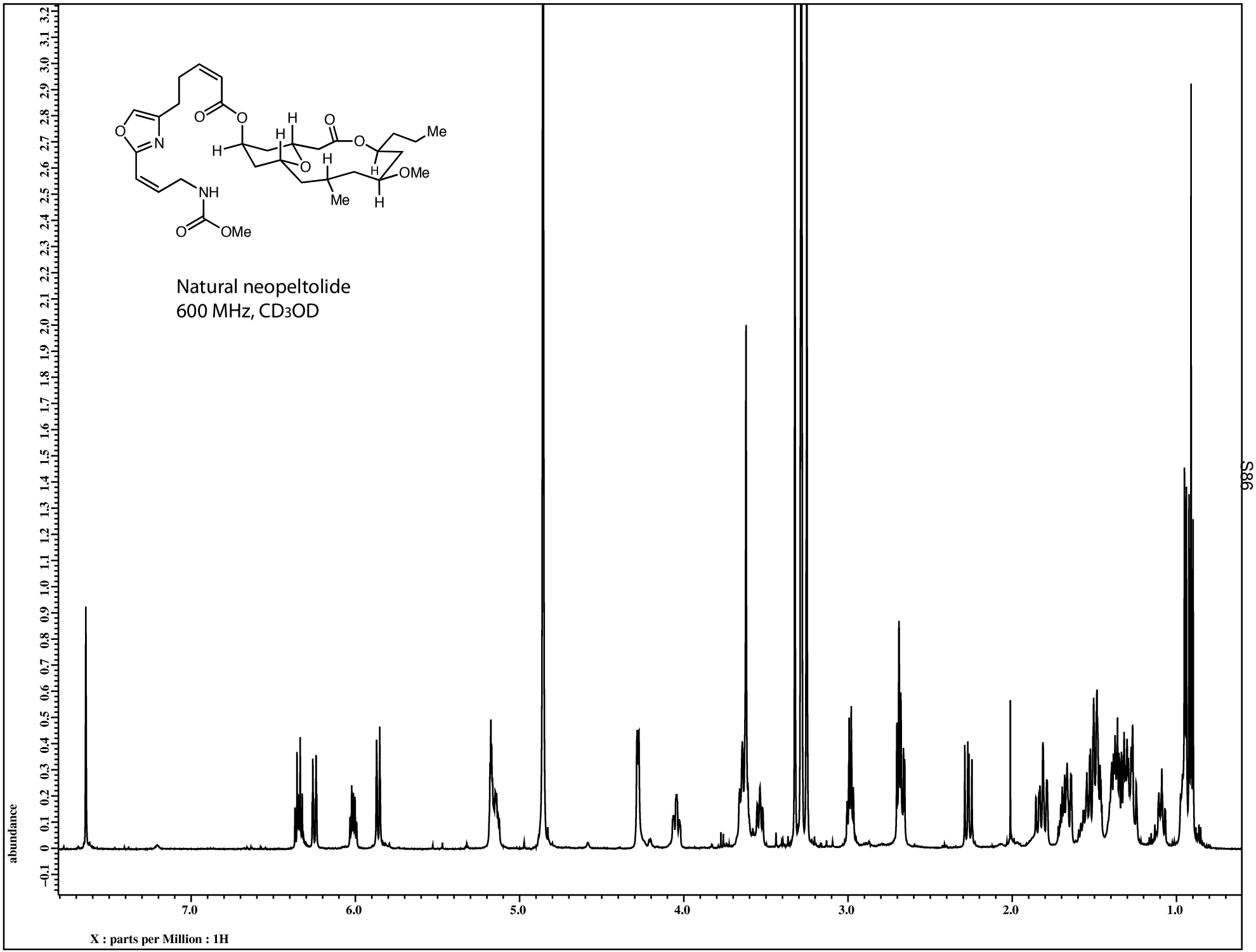


1H LINESHAPE
1% CHCL3 (89)
Date: Thu Dec 6 16:51:38 CST 2007
Solvent: CD3OD
Pulse Sequence: s2pul
File: dwc5-neopeltolide600
Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2920.935	4.870	190.9
2	1974.750	3.292	203.8

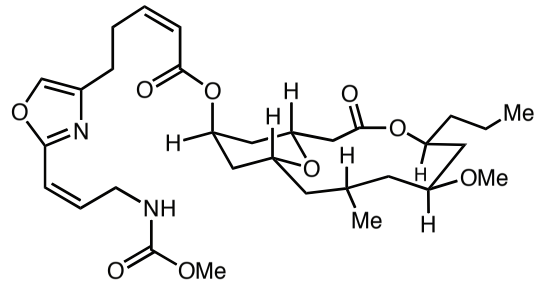


synthetic neopeltolide (1)
600 MHz, CD3OD


Natural neopeltolide
600 MHz, CD3OD
abundance
X : parts per Million : 1H
7.0
6.0
5.0
4.0
3.0
2.0
1.0
S86

1H LINESHAPE
1% CHCL3 (89)
Date: Fri Dec 7 17:49:13 CST 2007
Solvent: CD3OD
Pulse Sequence: s2pul
File: dwc5-neopeltolide600
Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	-201.952	-0.337	0.0

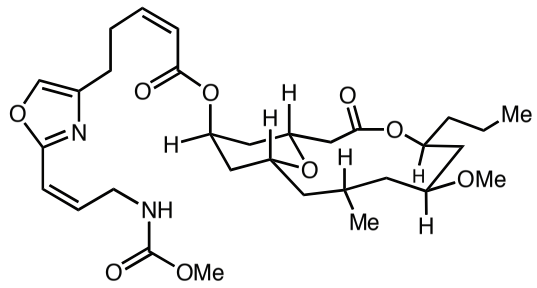


Synthetic neopeltolide (1)
600 MHz, CD_3OD

Natural neopeltolide
600 MHz, CD_3OD

1H LINESHAPE
1% CHCL3 (89)
Date: Fri Dec 7 17:51:10 CST 2007
Solvent: CDCL3
Pulse Sequence: s2pul
File: dwc5-neopeltolide600
Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	1996.720	3.329	290.3
2	1995.072	3.326	383.7
3	1993.425	3.324	261.4
4	1974.750	3.292	500.3

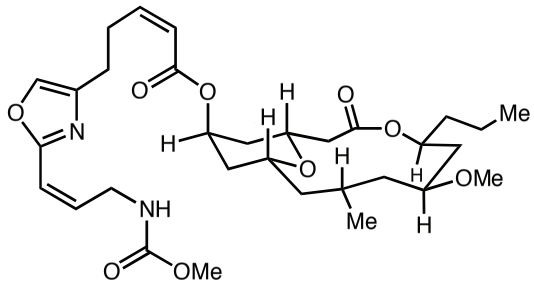


Synthetic neopeltolide (1)
600 MHz, CD_3OD

Natural neopeltolide
600 MHz, CD_3OD

1H LINESHAPE
1% CHCL3 (89)
Date: Fri Dec 7 17:50:14 CST 2007
Solvent: CDCl3
File: dwc5-neopeltolide600
Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	571.309	0.953	246.0

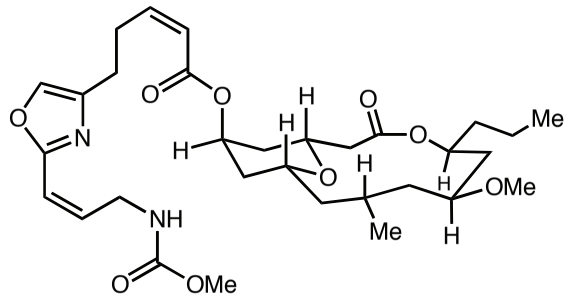


Synthetic neopeltolide (1)
600 MHz, CD_3OD

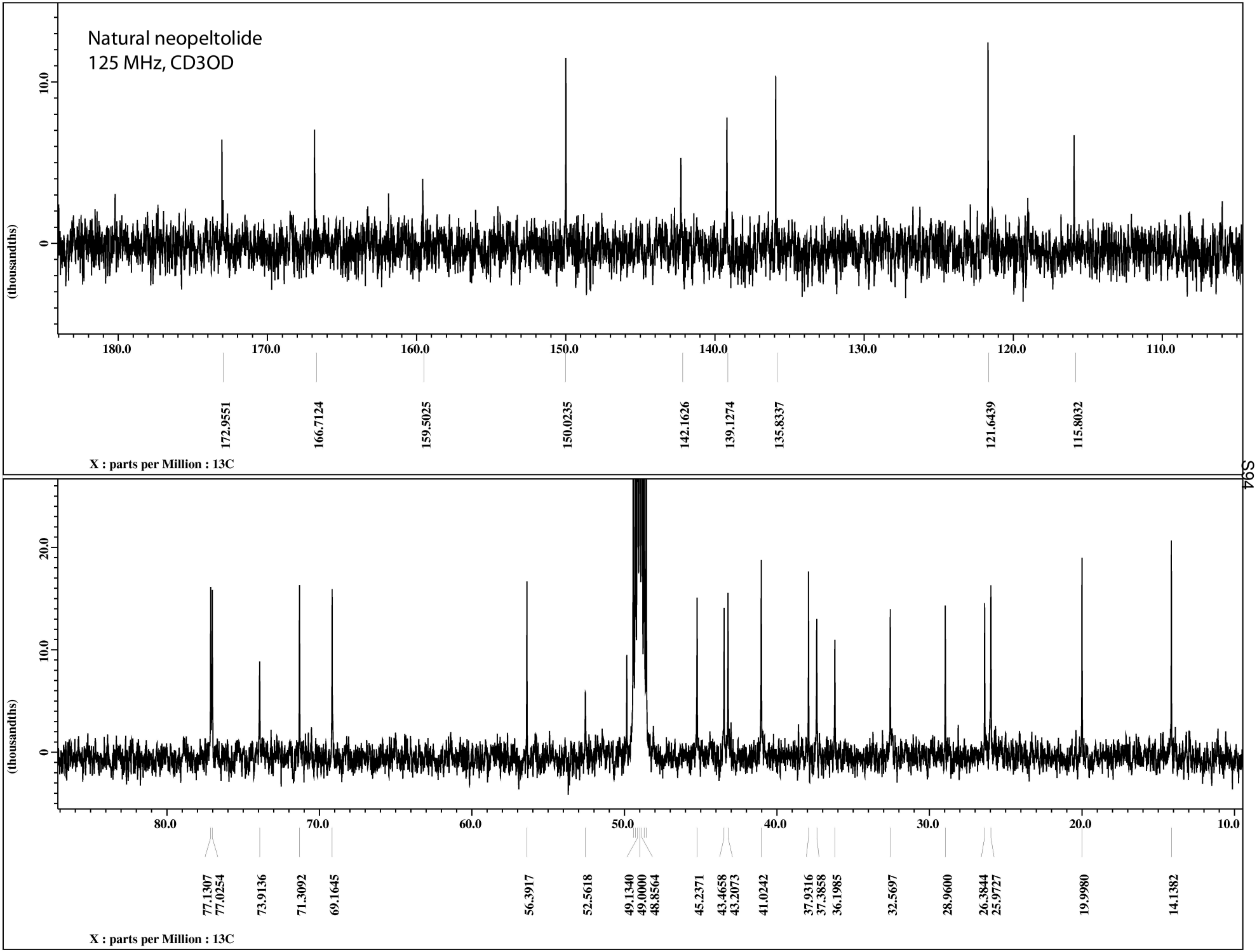
Natural neopeltolide
600 MHz, CD_3OD

inova400 DB_5mm RT non-spin
C13 std
Date: Thu Dec 6 16:45:47 CST 2007
Solvent: CD3OD
File: dwc5-neoC
Spectrometer: Mercury400
Nucleus: C13

INDEX	FREQUENCY	PPM	HEIGHT
1	5015.189	49.786	223.9
2	4993.826	49.574	660.2
3	4972.463	49.362	1295.8
4	4951.100	49.150	1512.5
5	4929.737	48.938	1300.9
6	4908.374	48.726	660.1
7	4887.011	48.514	218.4



synthetic neopeltolide
100 MHz, CD3OD

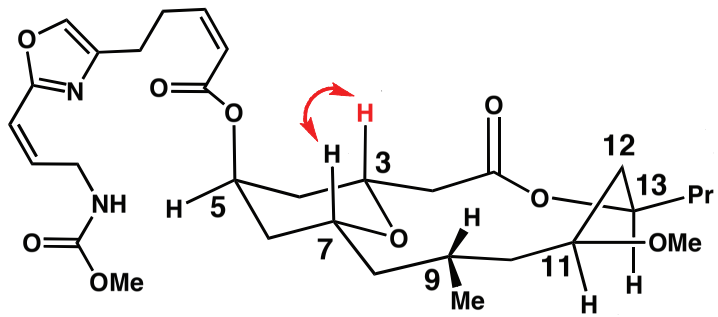

Natural neopeltolide
125 MHz, CD3OD
(thousandths)
10.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
172.9551
166.7124
159.5025
150.0235
142.1626
139.1274
135.8337
121.6439
115.8032
X : parts per Million : 13C
(thousandths)
20.0
10.0
0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
77.1307
77.0254
73.9136
71.3092
69.1645
56.3917
52.5618
49.1340
49.0000
48.8564
45.2371
43.4658
43.2073
41.0242
37.9316
37.3858
36.1985
32.5697
28.9600
26.3844
25.9727
19.9980
14.1382
X : parts per Million : 13C

H1 stdpar RT idpfg_5mm inova500

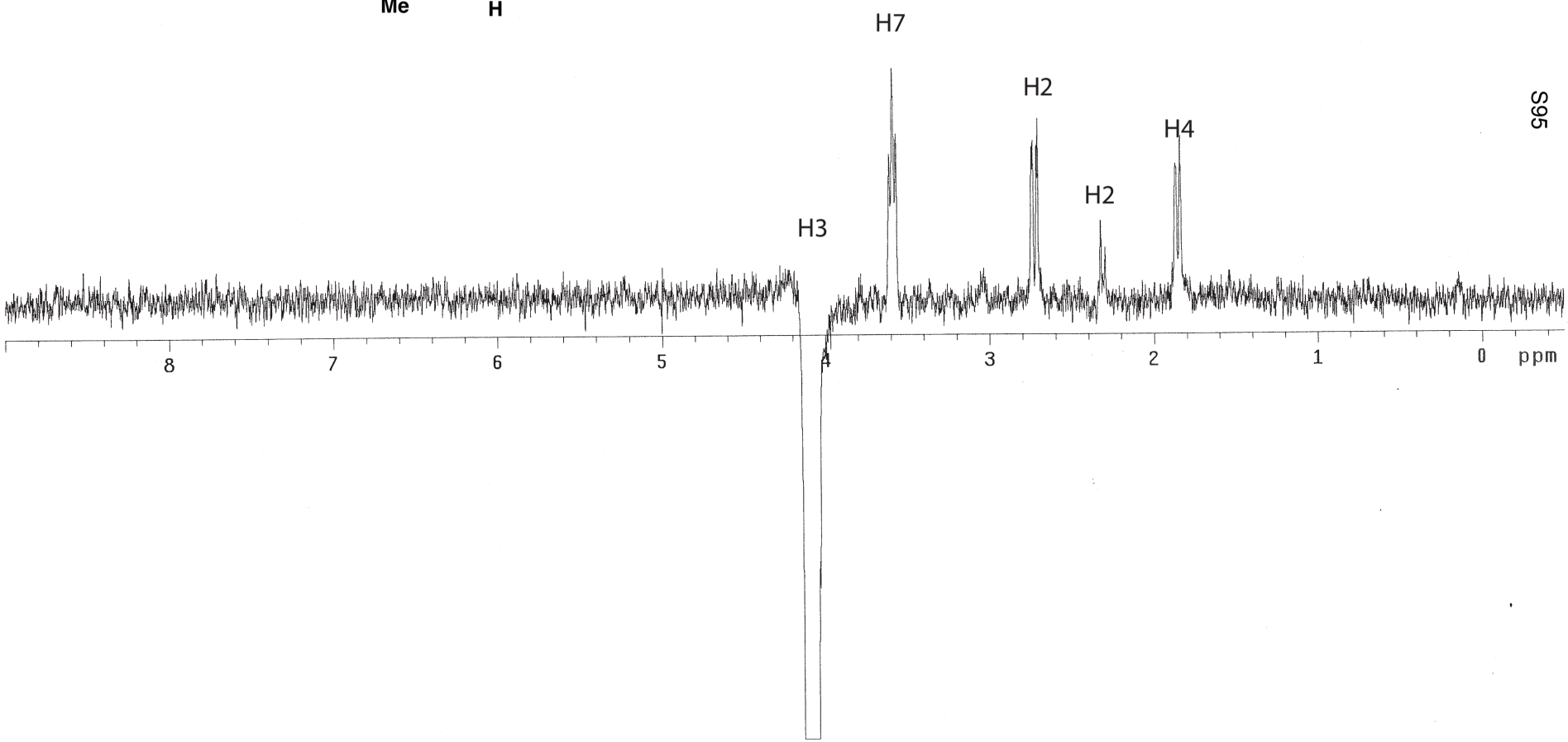
Date: Sat Nov 3 15:08:35 CST 2007
Pulse Sequence: NOESYTD
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2056.486	4.118	-429.2
2	2046.969	4.099	-844.1
3	2035.988	4.077	-503.3
4	1803.370	3.611	23.7
5	1793.487	3.591	37.6
6	1782.689	3.570	26.9
7	1366.137	2.736	25.8
8	1351.678	2.707	29.5
9	1161.338	2.325	13.2
10	933.295	1.869	22.1
11	919.386	1.841	26.5



H3 Irradiation of 1

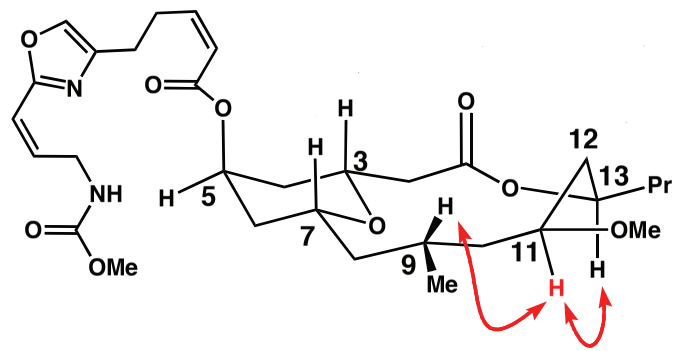


H1 stdpar RT idpfg_5mm inova500

Date: Sat Nov 3 15:38:54 CST 2007
Pulse Sequence: NOESY1D
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2597.675	5.202	14.0
2	1856.263	3.717	-548.2
3	1846.563	3.698	-1037.8
4	1837.229	3.679	-597.7
5	1649.817	3.304	120.7
6	955.258	1.913	9.5
7	940.250	1.883	11.6
8	798.410	1.599	17.4
9	785.965	1.574	12.6
10	724.104	1.450	16.9
11	677.617	1.357	9.0
12	661.694	1.325	9.4



H11 Irradiation of 1

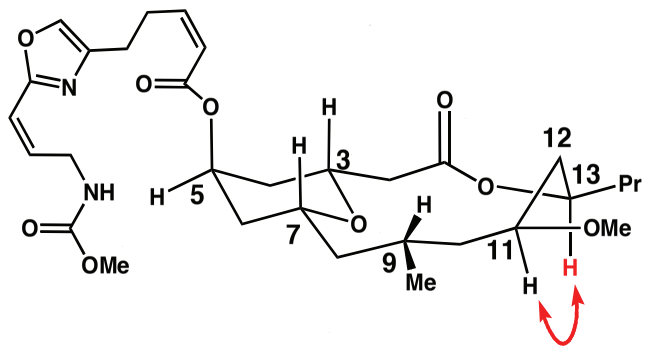
S96

H1 stdpar RT idpfg_5mm inova500

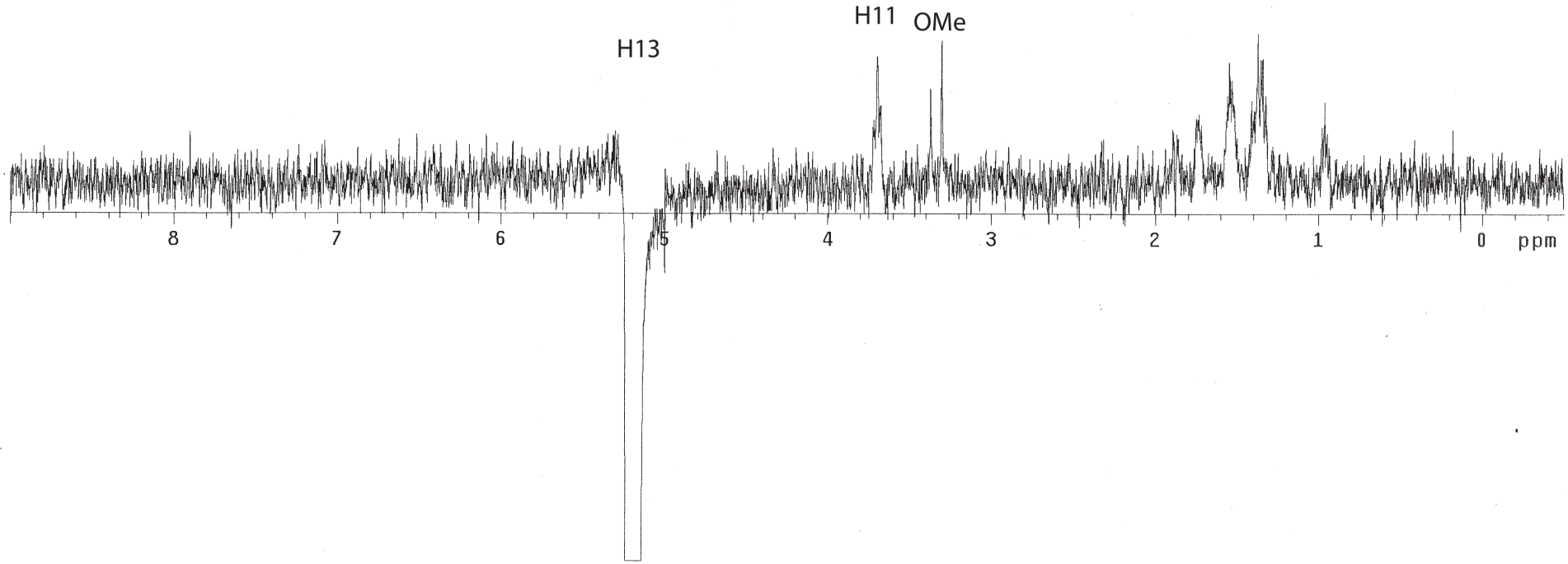
Date: Sat Nov 3 15:26:34 CST 2007
Pulse Sequence: NOESY1D
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2607.558	5.221	-732.1
2	2603.349	5.213	-871.9
3	2597.858	5.202	-1202.5
4	2594.198	5.195	-1197.0
5	2588.707	5.184	-815.8
6	2584.498	5.175	-694.5
7	2574.432	5.155	-832.8
8	1846.380	3.697	20.3
9	1684.042	3.372	15.2
10	1649.634	3.303	22.9
11	865.578	1.733	11.2
12	773.336	1.549	19.5
13	686.036	1.374	24.1
14	480.871	0.963	13.1



H13 Irradiation of 1

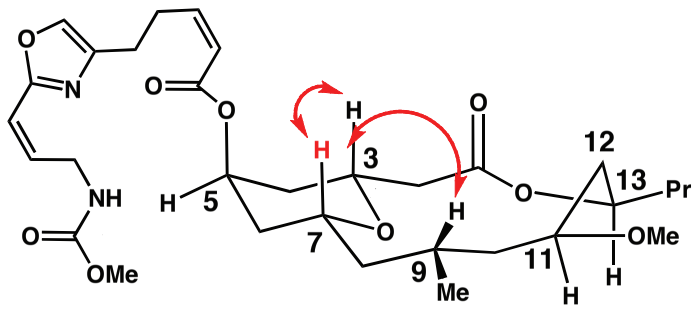


H1 stdpar RT idpfg_5mm inova500

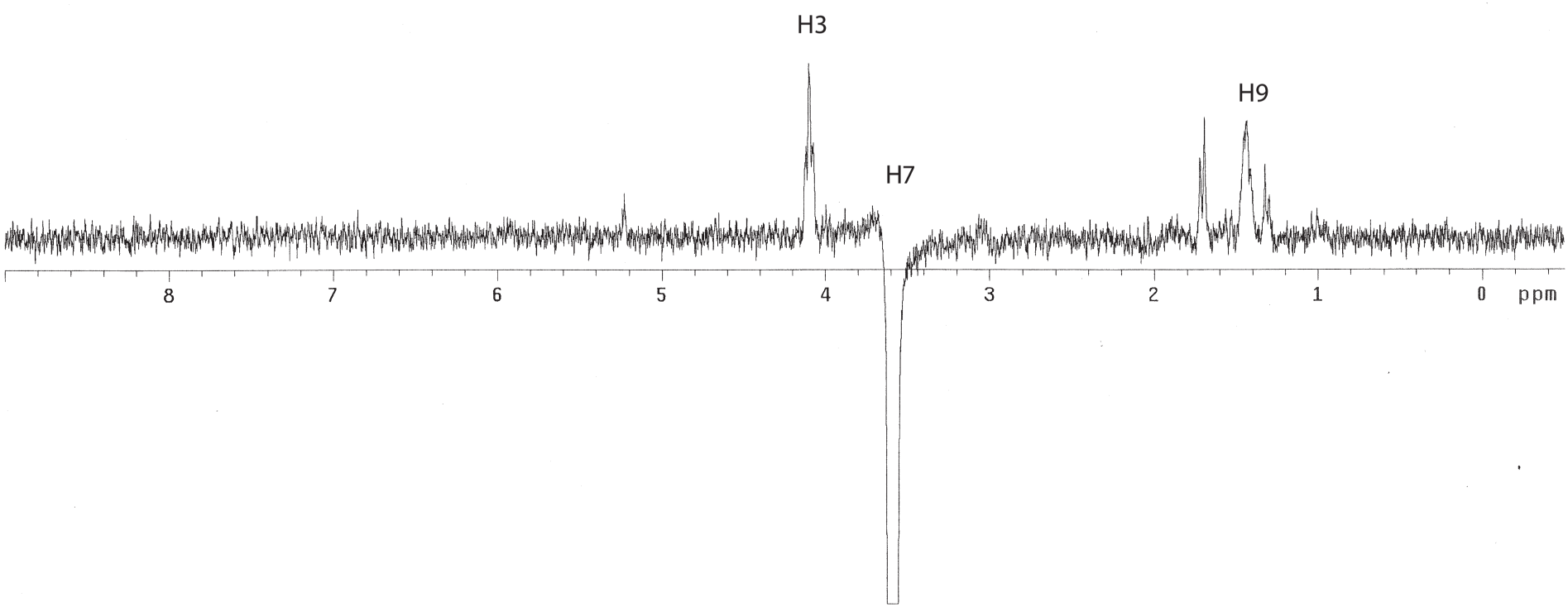
Date: Sat Nov 3 15:12:34 CST 2007
Pulse Sequence: NOESY1D
Solvent: cd3od

Spectrometer: Inova500
Nucleus: H1

INDEX	FREQUENCY	PPM	HEIGHT
1	2048.251	4.101	27.8
2	1802.821	3.610	-362.6
3	1792.938	3.590	-604.4
4	1783.055	3.570	-399.8
5	845.995	1.694	19.4
6	716.966	1.436	18.8



H7 Irradiation of 1

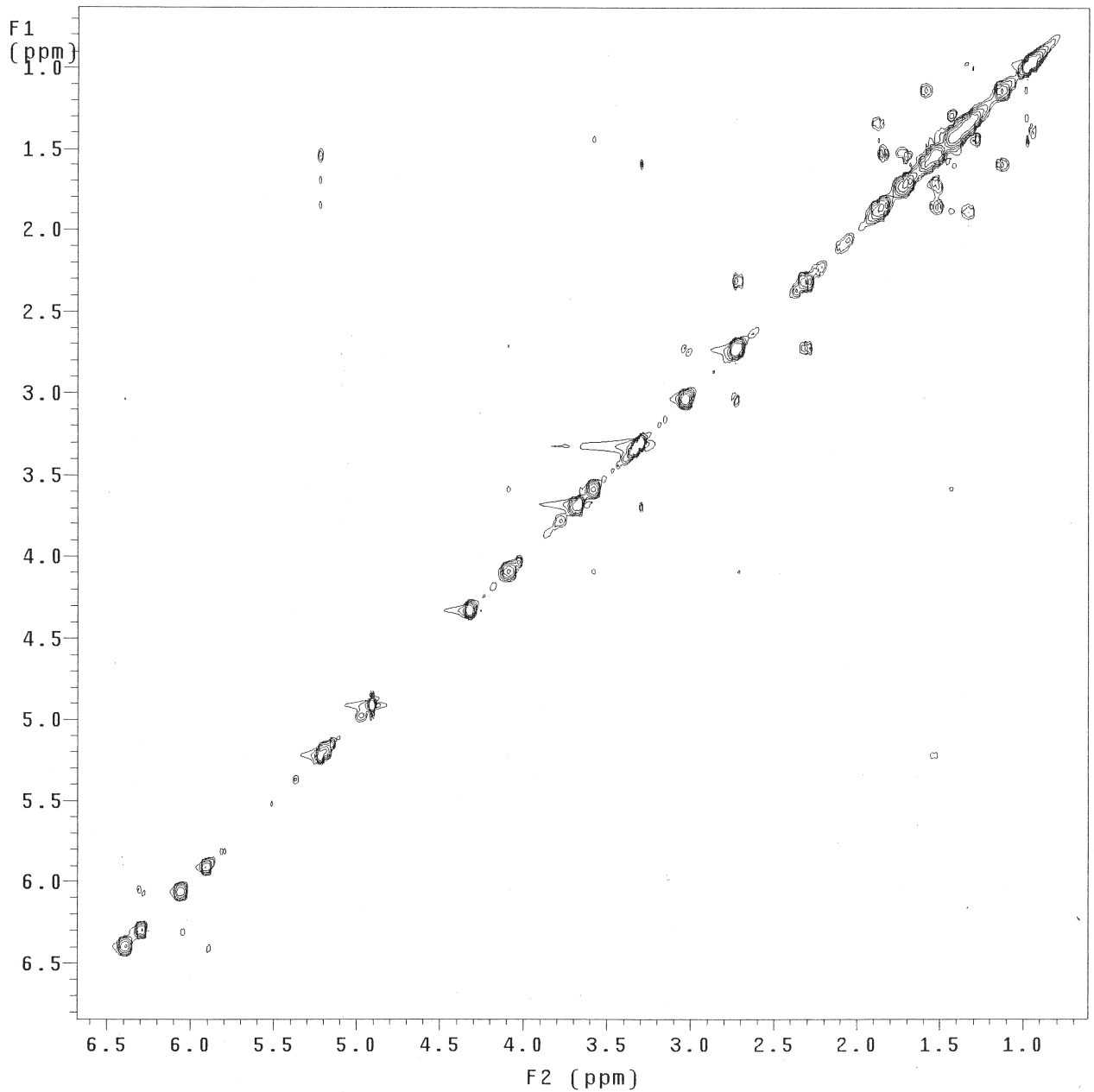


H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	306.3
pw	10.800	wp	3026.7
NOESY		sp1	313.9
mix	0.400	wp1	3102.9
PRESATURATION		rf1	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai	ph

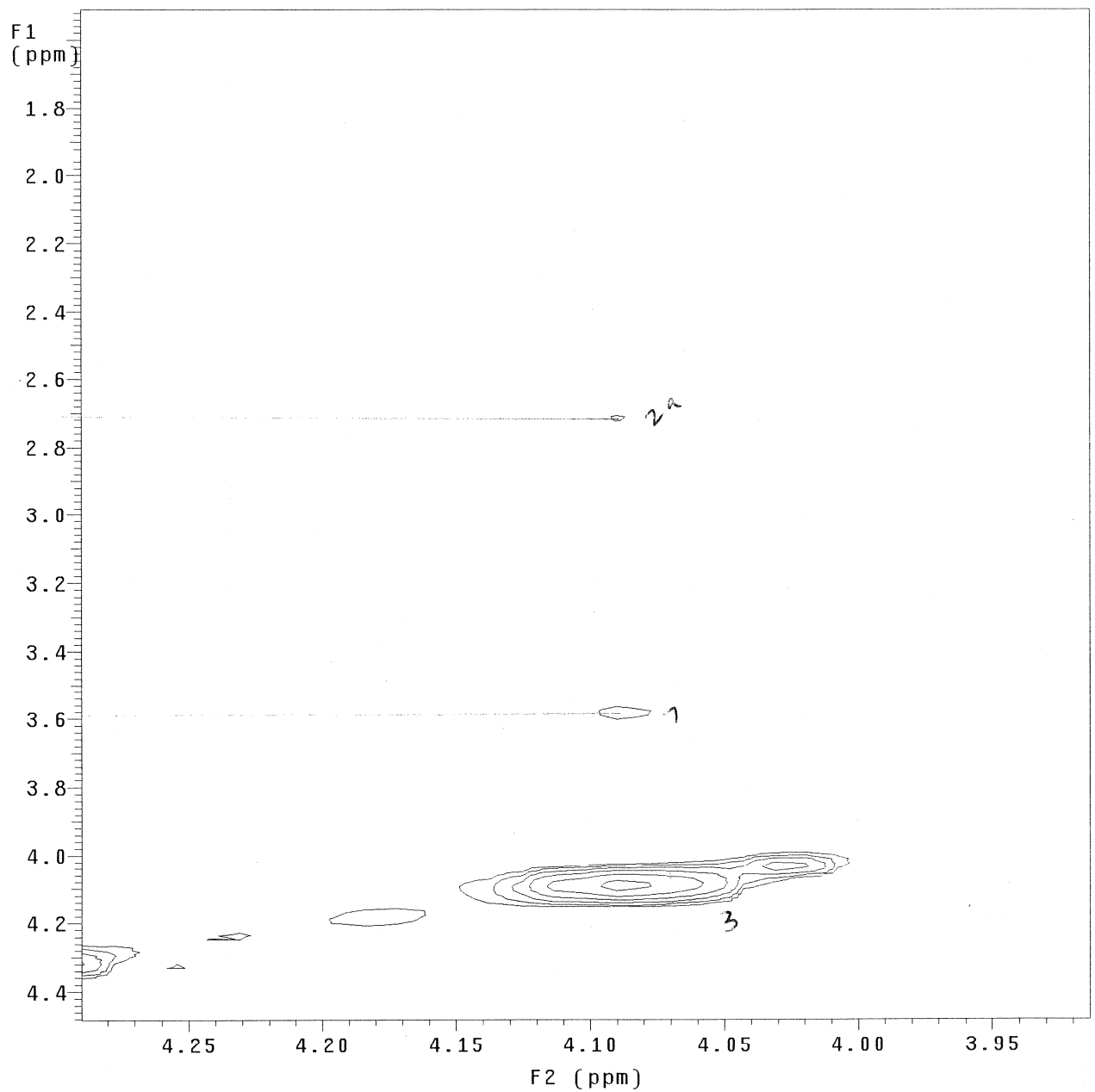
NOESY for synthetic neopeltolide (1) Next eight pages



H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

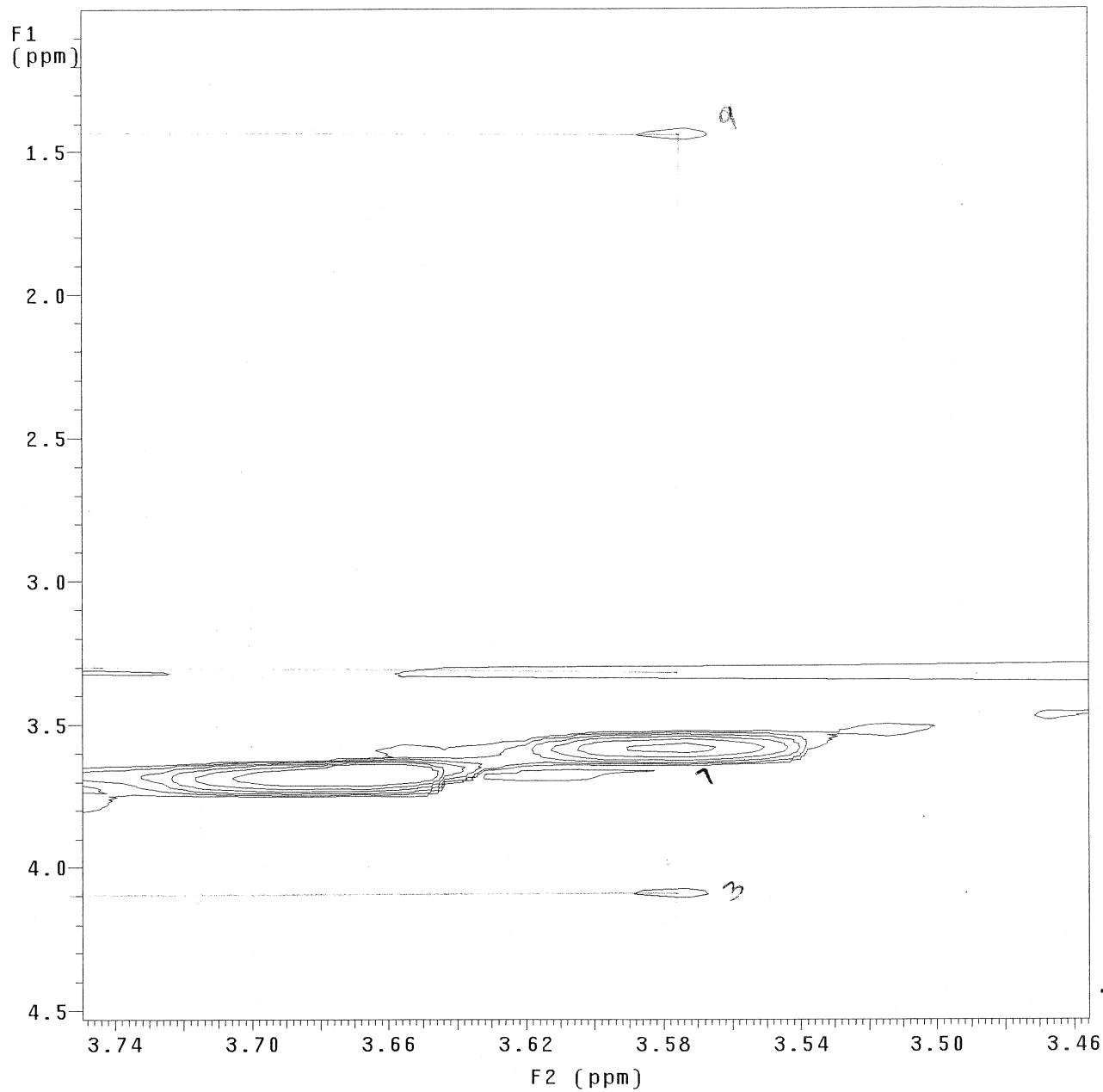
SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	1954.5
pw	10.800	wp	187.7
NOESY		sp1	753.9
mix	0.400	wp1	1484.0
PRESATURATION		rfl	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai ph	



H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

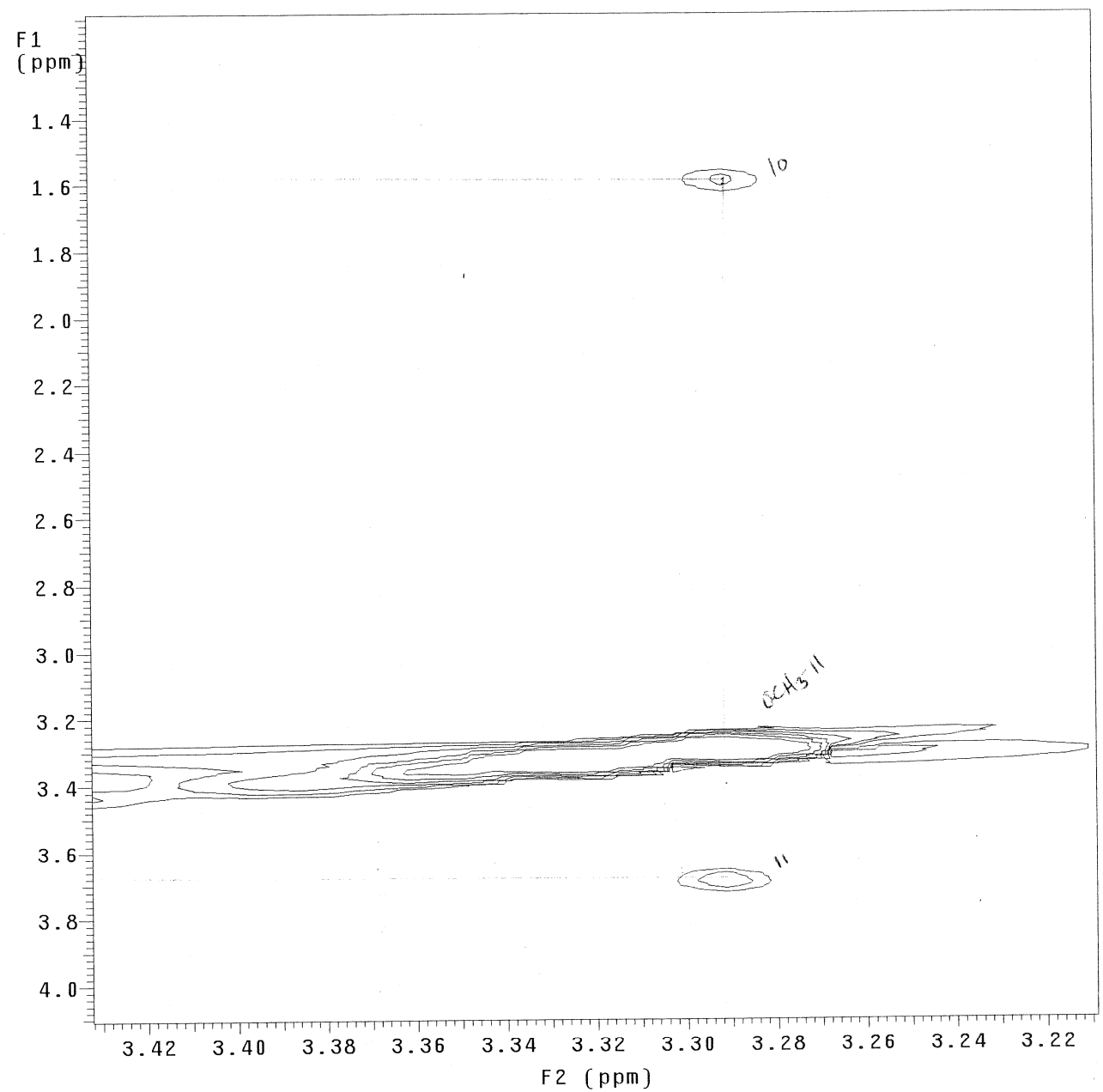
SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	1725.8
pw	10.800	wp	146.6
NOESY		sp1	501.6
mix	0.400	wp1	1759.7
PRESATURATION		rfl	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai	ph



H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

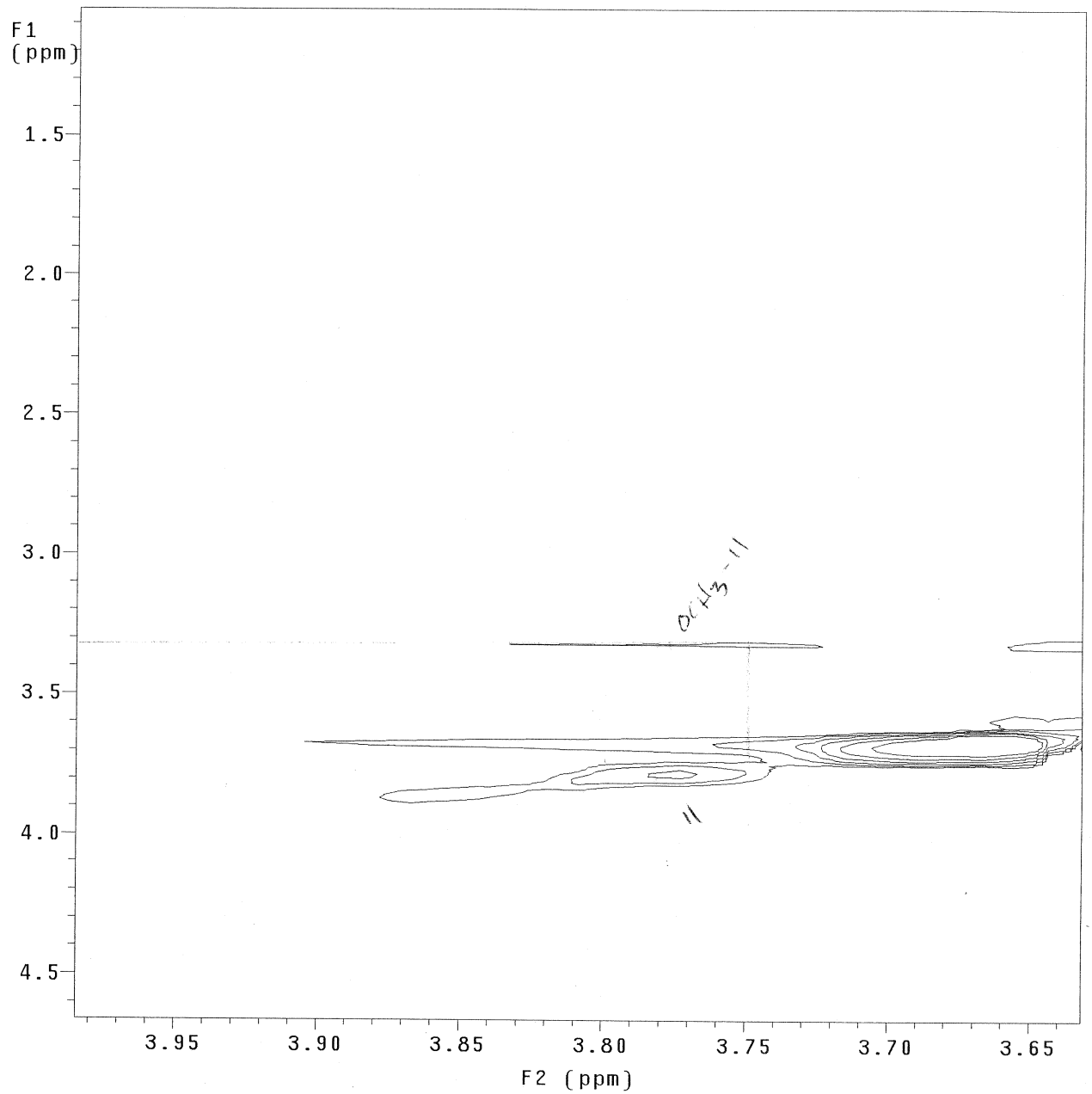
SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	1602.6
pw	10.800	wp	111.4
NOESY		sp1	542.7
mix	0.400	wp1	1507.5
PRESATURATION		rfl	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai ph	



H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

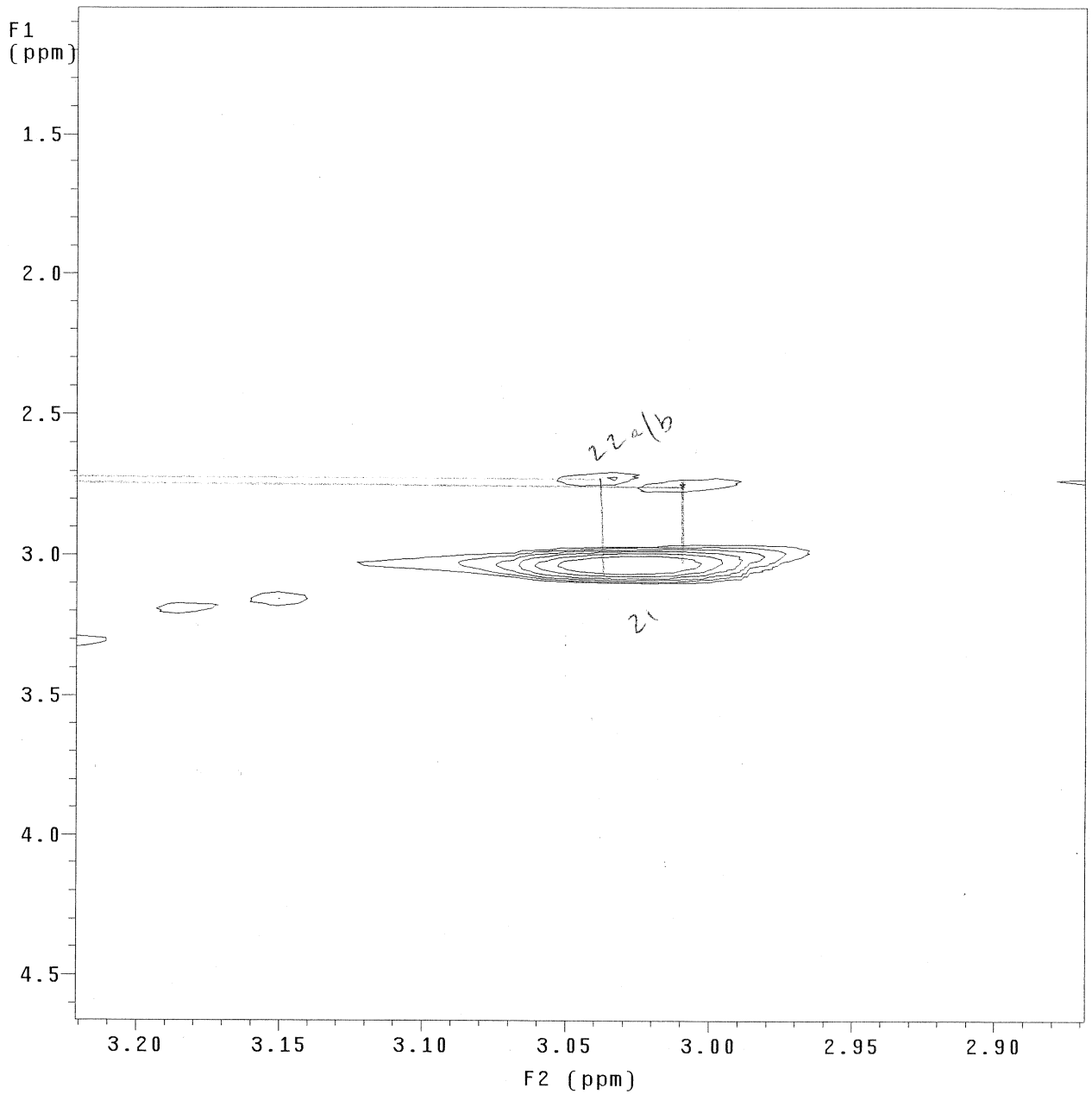
SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	1813.8
pw	10.800	wp	176.0
NOESY		sp1	525.1
mix	0.400	wp1	1800.8
PRESATURATION		rfl	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai ph	



H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

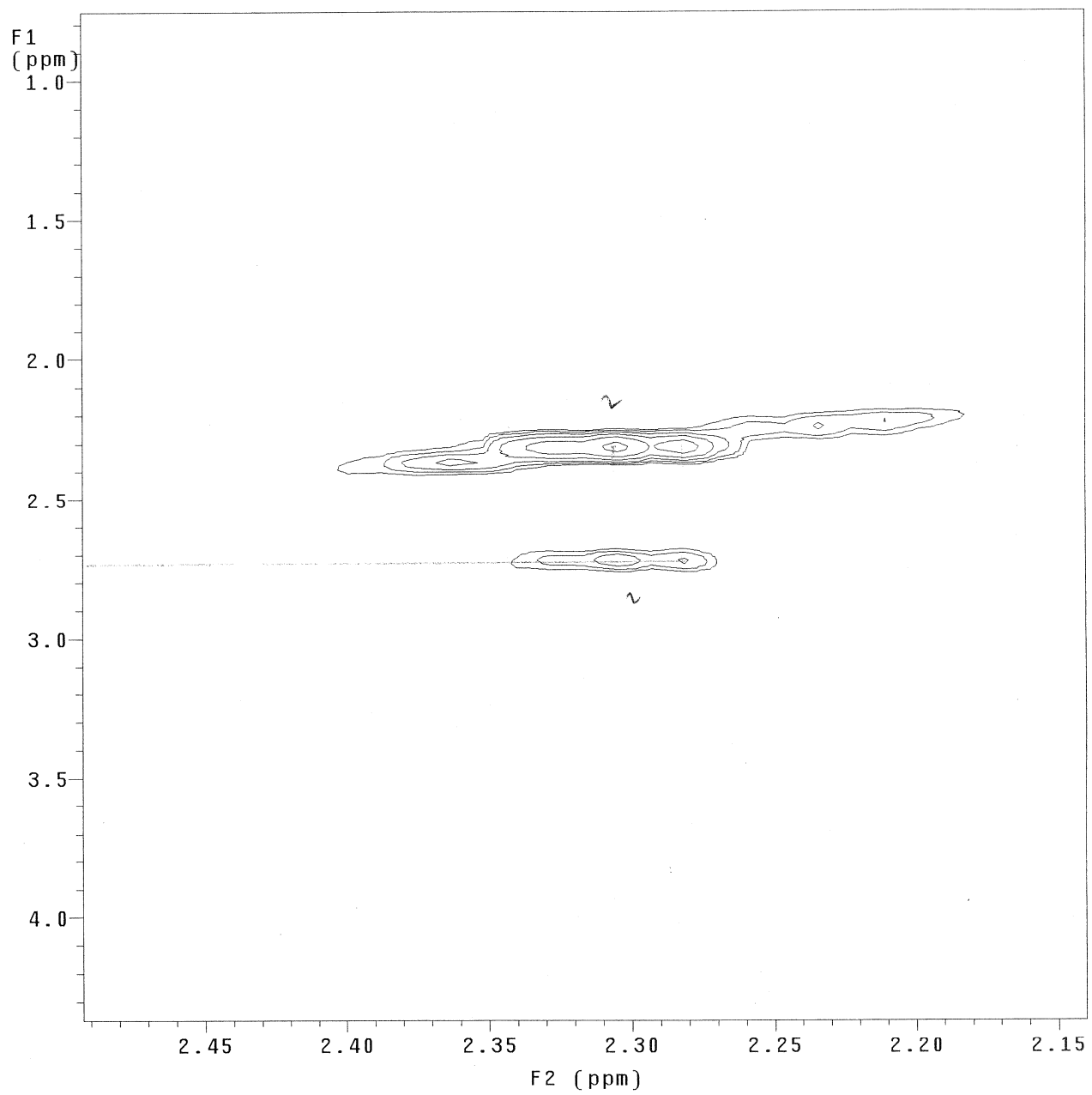
SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	1432.5
pw	10.800	wp	176.0
NOESY		sp1	525.1
mix	0.400	wp1	1800.8
PRESATURATION		rfl	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai ph	



H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	1068.8
pw	10.800	wp	176.0
NOESY		sp1	378.5
mix	0.400	wp1	1800.8
PRESATURATION		rf1	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai	ph



H1 stdpar RT idpfg_5mm inova500

exp8 NOESY

SAMPLE		FLAGS	
date	Nov 2 2007	hs	n
solvent	CD3OD	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvl	2000
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	32
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	192	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.410	fn1	2048
tof	0	DISPLAY	
tpwr	52	sp	2511.8
pw	10.800	wp	211.2
NOESY		sp1	525.1
mix	0.400	wp1	2387.3
PRESATURATION		rfl	503.2
satmode	nnnn	rfp	0
satpwr	0	rfl1	501.4
satdly	0	rfp1	0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	567
		th	1
		ai	ph

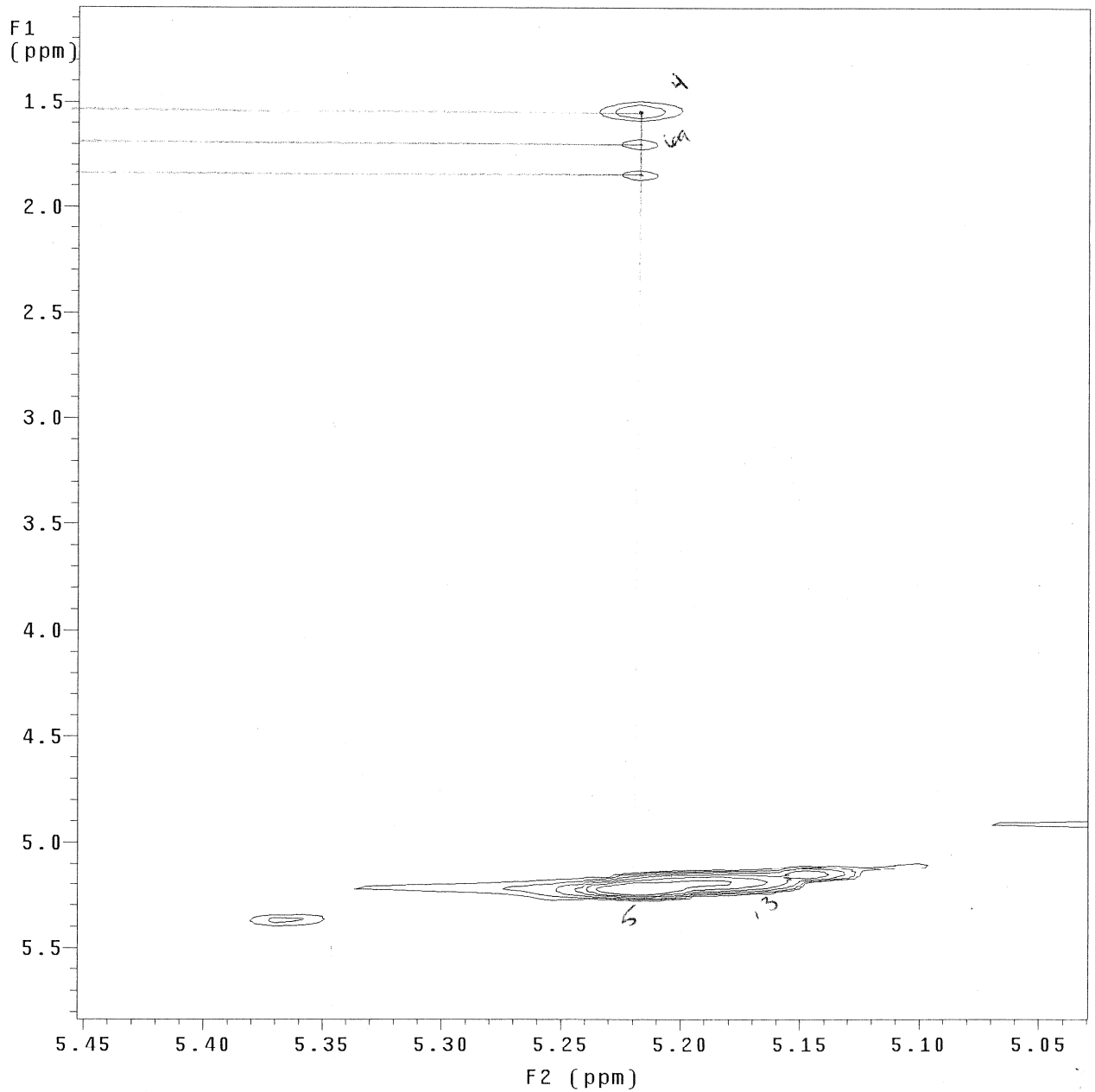


Table Window Report

MS Formula Results: + Scan (0.360-0.457 min) - NeoPelt.d

Mz	Species	Formula	Abundance
591.32772	(M+H)+	C31H47N2O9	160605

Best	Formula	Score	Mass	Calc. Mass	Diff (ppm)	Abs Diff (ppm)	DBE
☑	C31H46N2O9	100	590.32044	590.32033	-0.18	0.18	10

Isotope	Abund %	Calc Abund %	m/z	Calculated m/z	Diff (ppm)
1	100	100	591.32772	591.32761	-0.18
2	29.13	35.14	592.33123	592.33088	-0.58
3	4.74	7.84	593.33173	593.33362	3.18
4	0.67	1.31	594.33161	594.33629	7.88

Best	Formula	Score	Mass	Calc. Mass	Diff (ppm)	Abs Diff (ppm)	DBE
☐	C27H50N2O10Si	69.47	590.32044	590.32347	5.14	5.14	5

Isotope	Abund %	Calc Abund %	m/z	Calculated m/z	Diff (ppm)
1	100	100	591.32772	591.33075	5.13
2	29.13	35.98	592.33123	592.3335	3.83
3	4.74	11.59	593.33173	593.33358	3.11
4	0.67	2.62	594.33161	594.33474	5.27

Mz	Species	Formula	Abundance
613.30954	(M+Na)+	C31H46N2O9Na	110371

Best	Formula	Score	Mass	Calc. Mass	Diff (ppm)	Abs Diff (ppm)	DBE
☑	C31H46N2O9	100	590.32032	590.32033	0.02	0.02	10

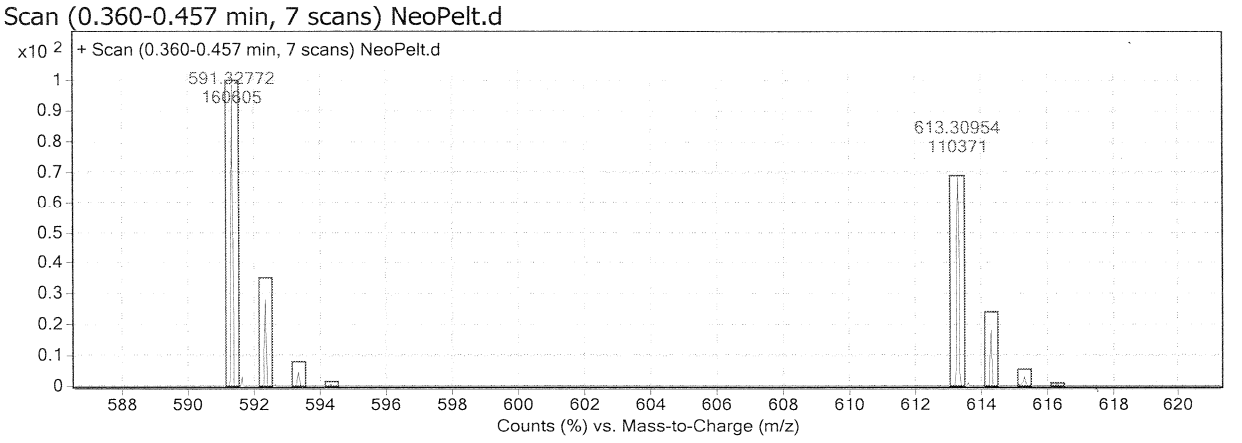
Isotope	Abund %	Calc Abund %	m/z	Calculated m/z	Diff (ppm)
1	100	100	613.30954	613.30955	0.02
2	27.1	35.13	614.31359	614.31283	-1.25
3	4.43	7.84	615.3117	615.31556	6.27
4	0.73	1.31	616.30731	616.31823	17.72

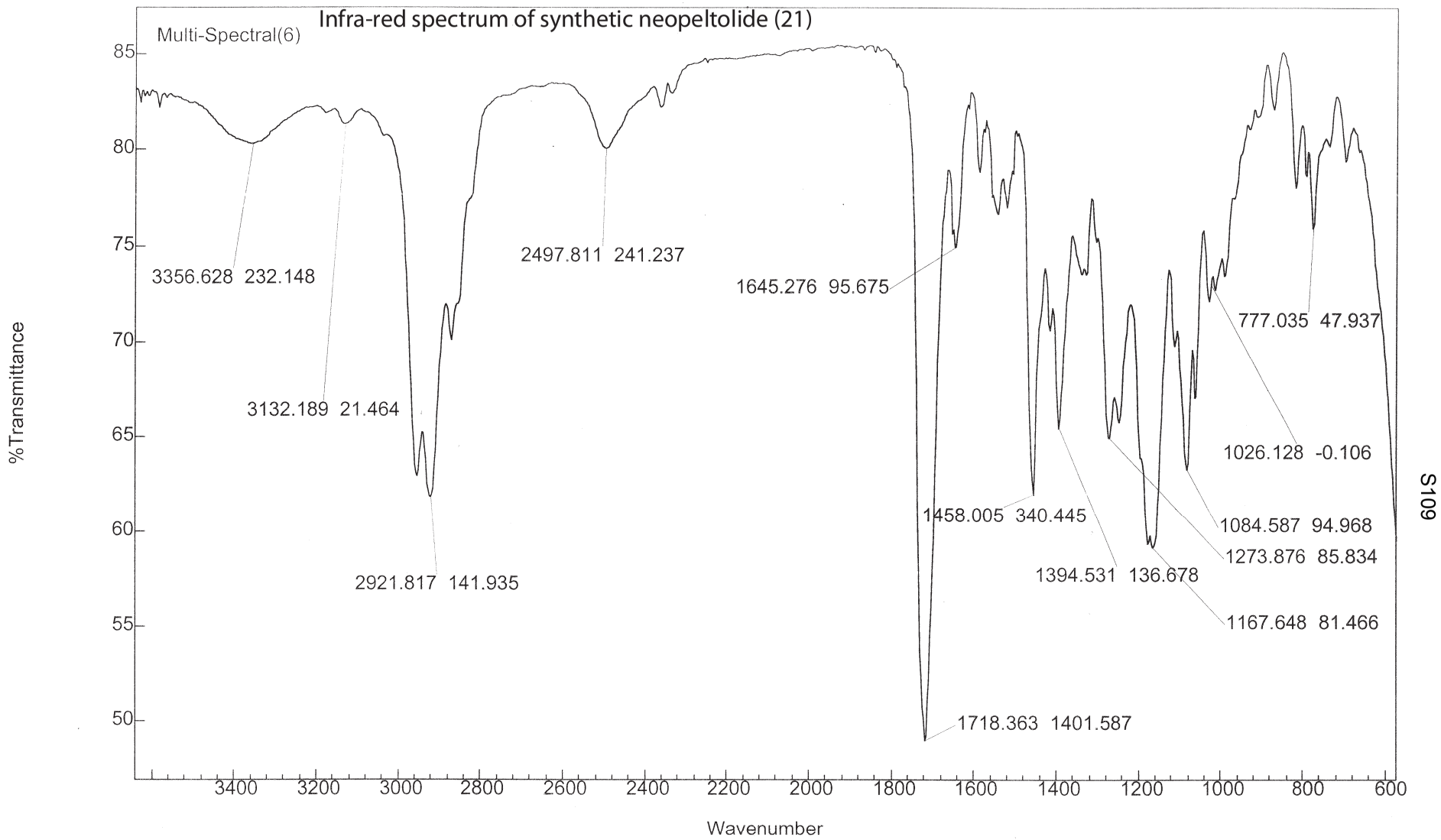
Best	Formula	Score	Mass	Calc. Mass	Diff (ppm)	Abs Diff (ppm)	DBE
☐	C27H50N2O10Si	71.25	590.32032	590.32347	5.35	5.35	5

Isotope	Abund %	Calc Abund %	m/z	Calculated m/z	Diff (ppm)
1	100	100	613.30954	613.31269	5.14
2	27.1	35.97	614.31359	614.31544	3.01
3	4.43	11.59	615.3117	615.31552	6.21
4	0.73	2.62	616.30731	616.31668	15.2

Plot Window Report

+ Scan (0.360-0.457 min, 7 scans) NeoPelt.d




Infra-red spectrum of synthetic neopeltolide (21)
Multi-Spectral(6)
%Transmittance
Wavenumber
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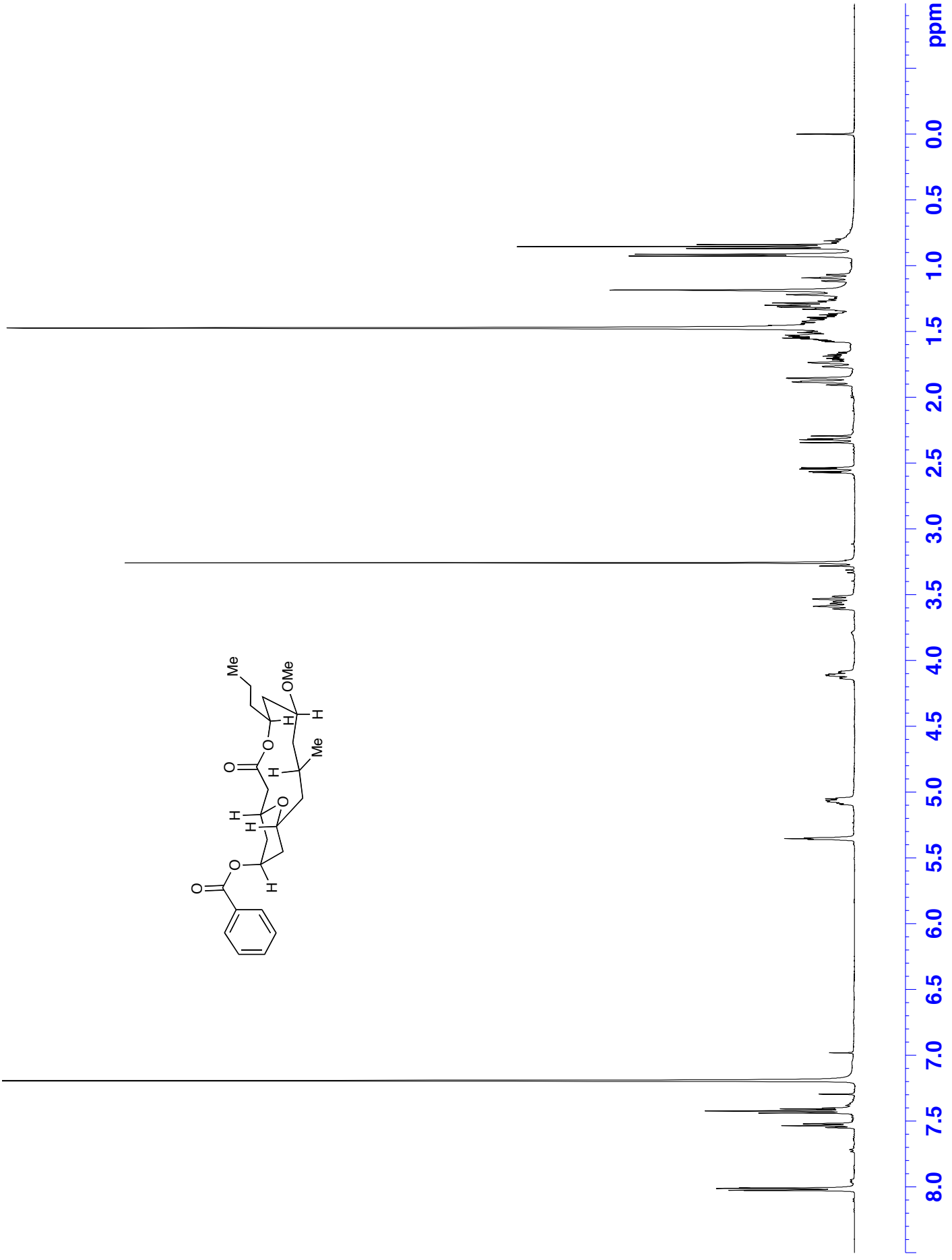
3132.189 21.464
2921.817 141.935
2497.811 241.237
1645.276 95.675
1718.363 1401.587
1458.005 340.445
1394.531 136.678
1273.876 85.834
1167.648 81.466
1084.587 94.968
1026.128 -0.106
777.035 47.937
Name
Multi-Spectral(6)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H
Me
O
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H
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H
H
O
O
H
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6.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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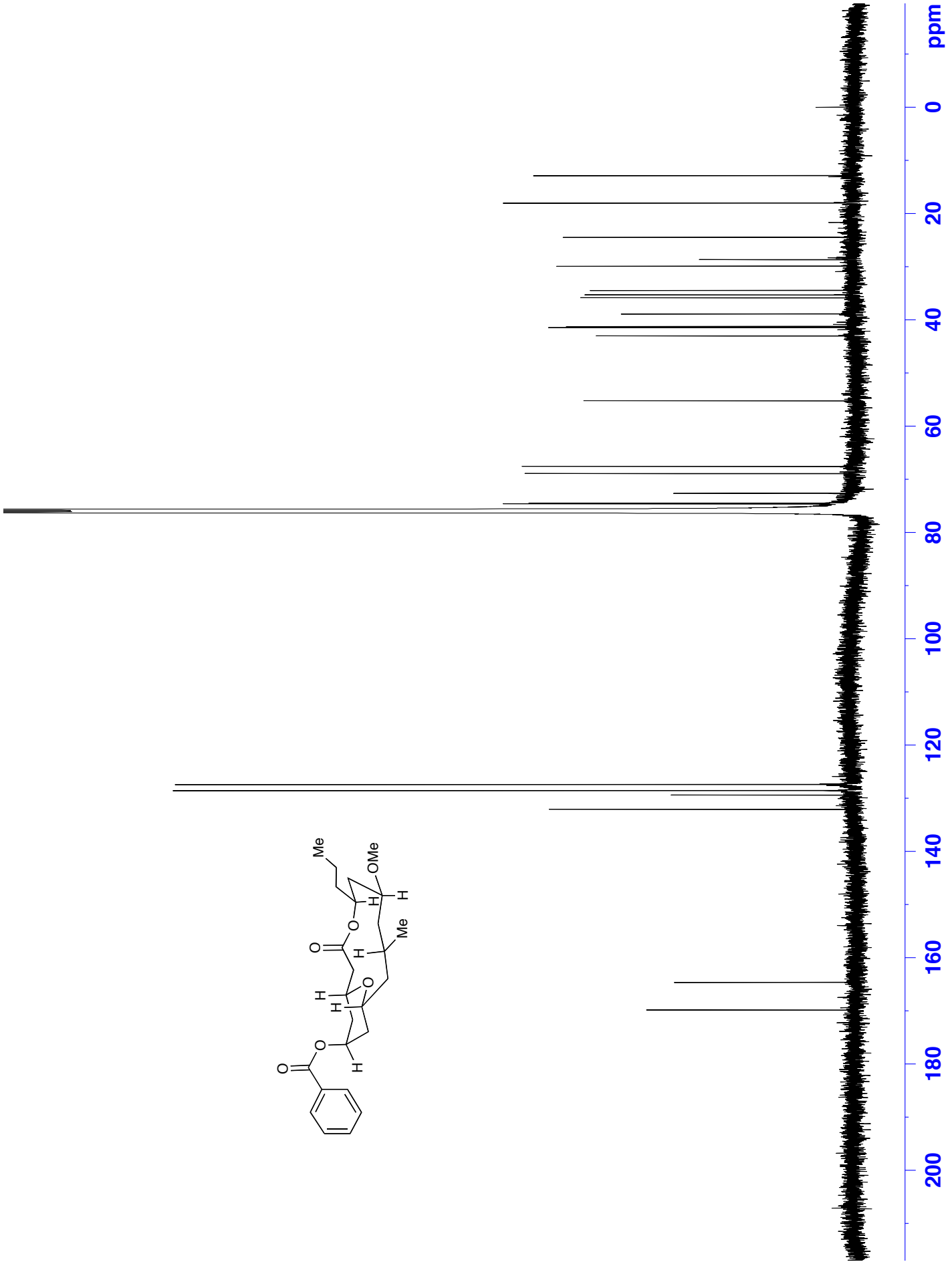
ppm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H
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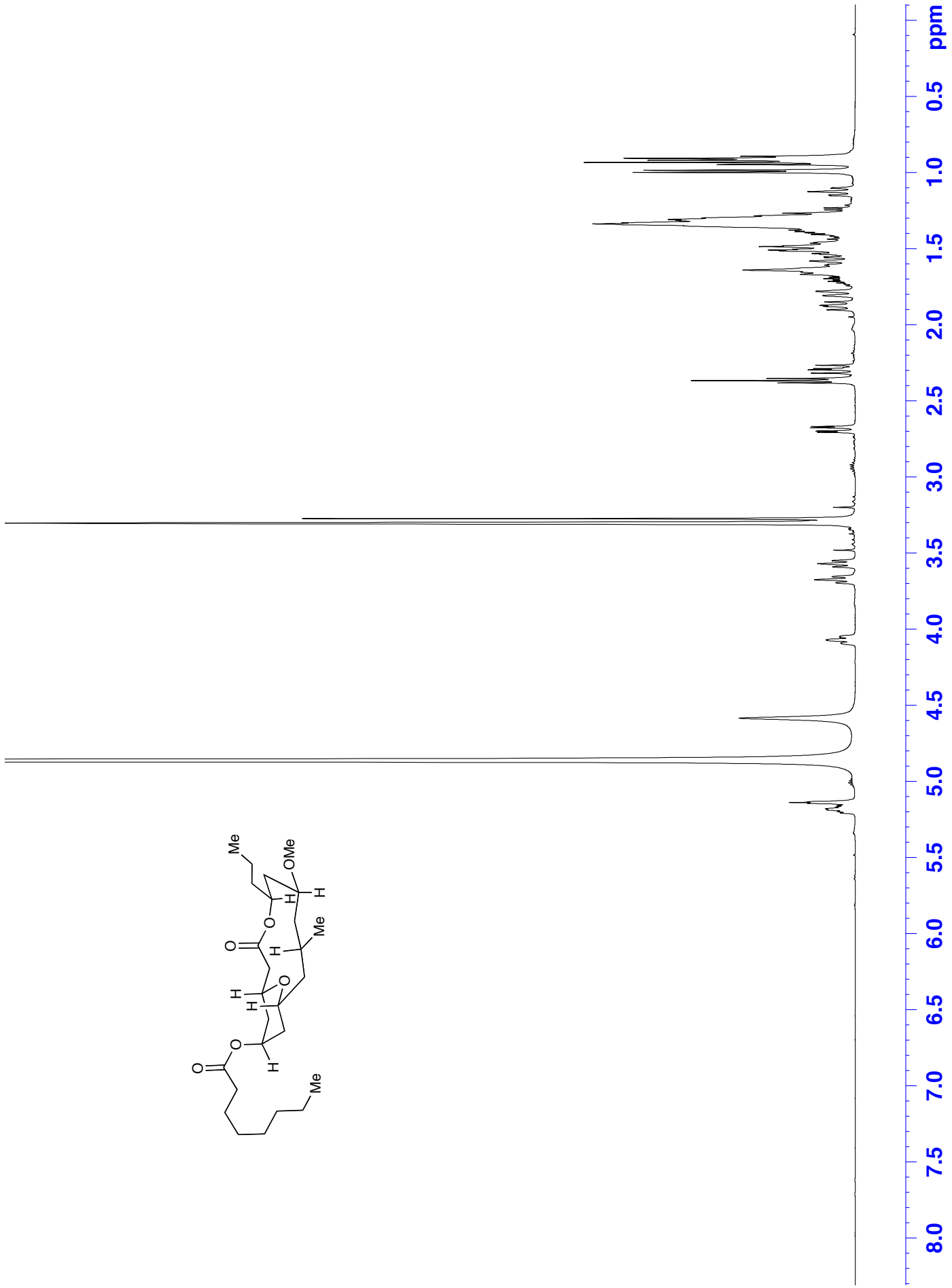
O
O
H
O
H
H
O
O
H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Me
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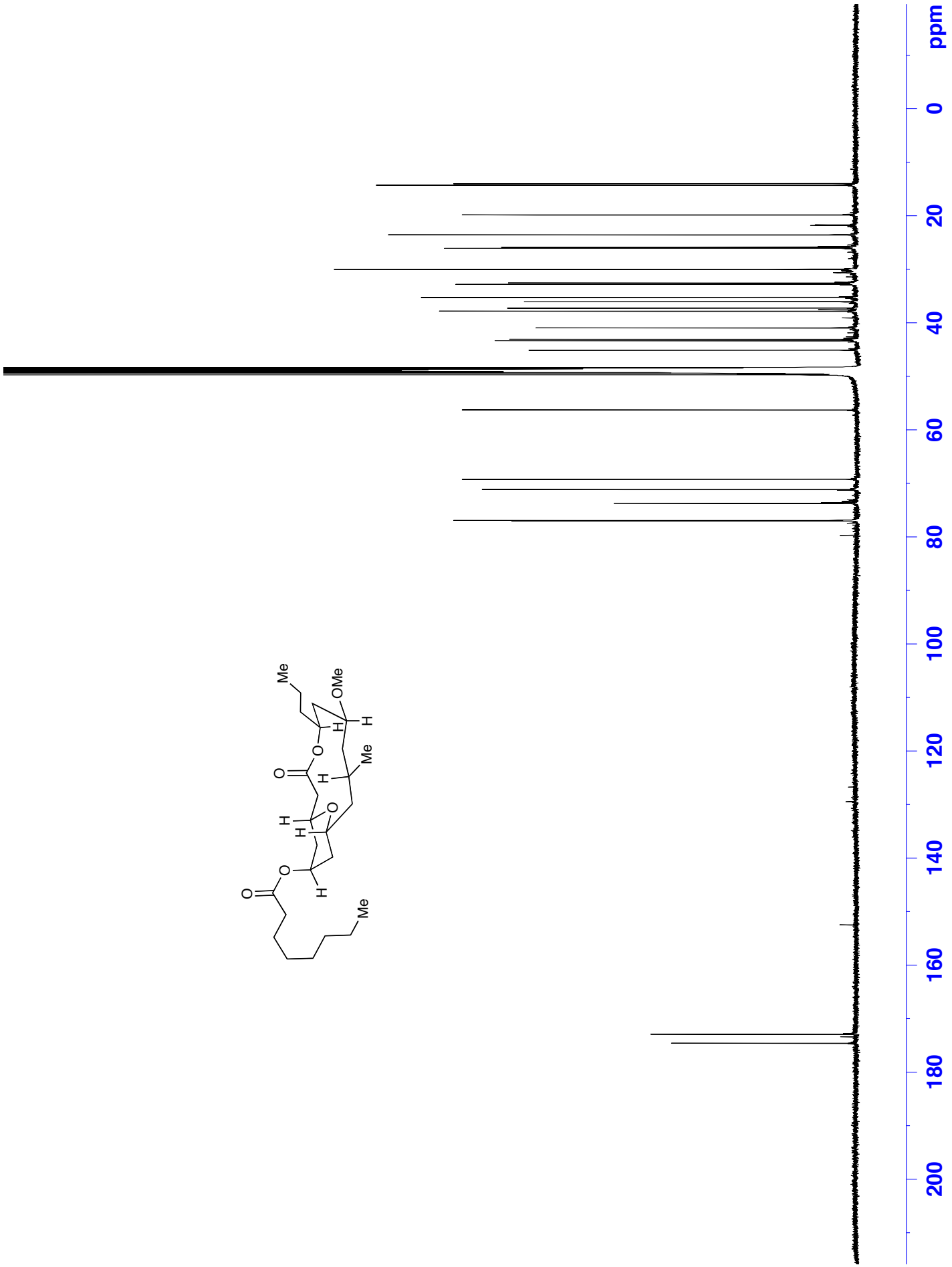
2.0
1.5
1.0
0.5
ppm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40
60
80
100
120
140
160
180
200
Me
OMe
H
H
O
Me
O
H
O
H
H
O
H
O
Me