An Effective Enantioselective Route to the Platensimycin Core

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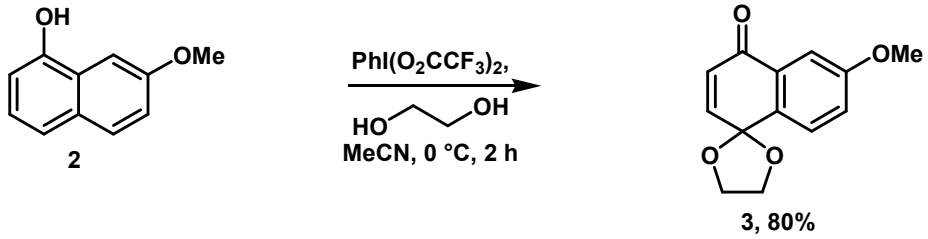
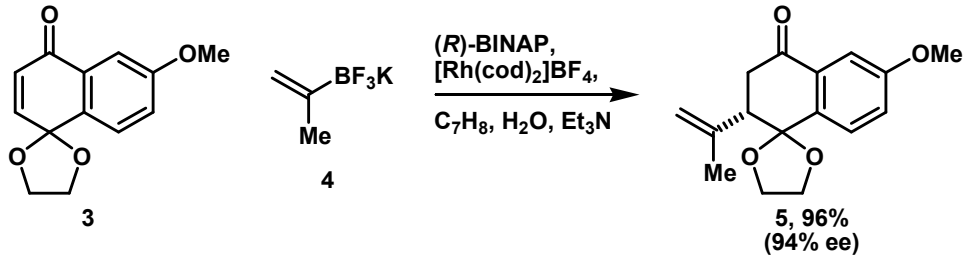
Supplementary Materials

Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled dry solvents. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 μm). Flash chromatography was performed using Baker silica gel (40 μm particle size) and a Biotage SP1. NMR spectra were recorded on Varian Inova-500, or Inova-600 instruments and calibrated using residual undeuterated solvent as an internal reference. IR spectra were recorded on Avatar 360 FTIR spectrometer. Low-resolution and high-resolution mass spectral analyses were performed at the Harvard University Mass Spectrometry Center. Analytical high performance liquid chromatography (HPLC) was performed on an Isco 2350 Series or a Waters 626 HPLC using the indicated chiral column. Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane was distilled from CaH_2. Toluene, Et_2O and THF were purified by Seco Solvent Systems.

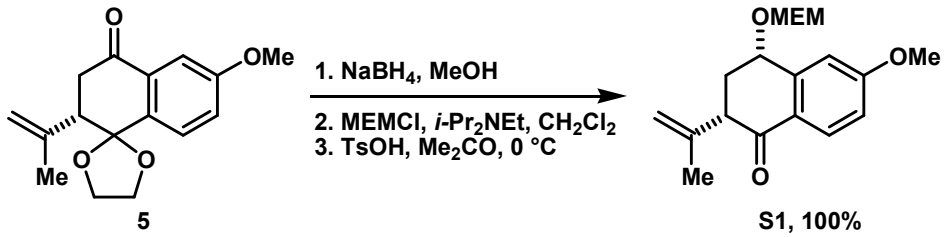


Enone 3: A solution of known phenol **2**[1] (7.90 g, 1.00 equiv, 45.3 mmol) in 150 mL of MeCN was added over a two hour period to a solution of $PhI(O_2CCF_3)_2$ (42.9 g, 2.20 equiv, 99.6 mmol) in ethyleneglycol (350 mL) and MeCN (100 mL) at 0 °C. After the addition was completed, aq. $NaHCO_3$ was added to the reaction mixture. The product was extracted with ether, and the extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (7% to 60% EtOAc in hexane) to yield **3** (7.9 g, 80% yield) as a yellow amorphous powder; FT-IR (thin film): 2961, 2891, 1670, 1313, 1288, 1108, 1023, 944 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.07 (dd, $J_1 = 9$ Hz, $J_2 = 3$ Hz, 1H), 6.73 (dd, $J_1 = 10$ Hz, $J_2 = 0.5$ Hz, 1H), 6.24 (dd, $J_1 = 10$ Hz, $J_2 = 0.5$ Hz, 1H), 4.27-4.24 (m, 2H), 4.17-4.14 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 160.7, 143.1, 133.3, 132.4, 128.8, 128.5, 121.5, 108.9, 100.4, 66.0, 55.9; LRMS (ESI^+) *m/z* calc'd $C_{13}H_{13}O_4^+$ $[M+H]^+$: 233.08, found 233.08.



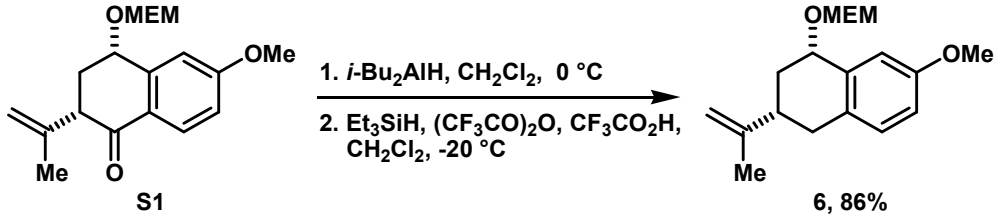
Ketone 5: To a Schlenk tube were added potassium trifluoroborate **4**[2] (5.30 g, 2.00 equiv, 36.2 mmol), **3** (4.20 g, 1.00 equiv, 18.08 mmol), (*S*)-BINAP (0.248 g, 0.022 equiv, 0.398 mmol) and $Rh(cod)_2BF_4$ (0.147 g, 0.02 equiv, 0.362 mmol). The tube was evacuated and filled with nitrogen three times. To the mixture was then added Et_3N (10.1 mL, 4.00 equiv, 72.3 mmol), followed by toluene (65 mL) and degassed H_2O (16 mL). The Schlenk tube was sealed with a

teflon stopper and the reaction mixture was stirred at room temperature. After 36 h, the reaction mixture was poured to a mixture of ether and sat. aq. NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (4% to 30% EtOAc in hexane) to yield product **5** as a colorless oil (4.76 g, 96% yield, 94 % ee); HPLC (Chiralpac AD column, 3% *i*-PrOH/hexanes, 1.0 mL/min, 230 nm, t_{major} = 14.8 min, t_{minor} = 11.9 min; ee = 94%); $[\alpha]_D^{23}$ = +8.3 (*c* = 1.01, $CHCl_3$); FT-IR (thin film): 3076, 2953, 1683, 1282, 1249, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.48-7.45 (m, 2H), 7.13 (dd, J_1 = 8 Hz, J_2 = 3 Hz, 1H), 4.98-4.97 (m, 1H), 4.84 (s, 1H), 4.23-4.21 (m, 1H), 4.15-4.02 (m, 3H), 3.84 (s, 3H), 3.11-3.07 (m, 2H), 2.93-2.88 (m, 1H), 1.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 160.3, 143.4, 136.5, 133.2, 126.6, 121.8, 115.6, 109.4, 108.1, 66.5, 65.4, 55.8, 50.4, 41.9, 23.6; HRMS (ESI^+) *m/z* calc'd $C_{16}H_{19}O_4^+$ $[M+H]^+$: 275.1283, found 275.1281.



Ketone S1: To a solution of **5** (4.96 g, 1.00 equiv, 18.08 mmol) in MeOH (50 mL) was added $NaBH_4$ (0.68 g, 1.00 equiv, 18.08 mmol). After 1 h, the reaction mixture was concentrated under reduced pressure. To the residue was added sat. aq. NH_4Cl solution and the product was extracted with ether. The organic extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude alcohol was dissolved in CH_2Cl_2 (60 mL) and was added to a Schlenk tube containing TBAI (0.67 g, 0.10 equiv, 1.81 mmol). To the resulting solution was added Hünig's base (12.6 mL, 4.00 equiv, 72.3 mmol), followed by MEMCl (4.10 mL, 2.00 equiv, 36.2 mmol). The tube was sealed and placed into an oil bath at 80 °C. After 2 h, the reaction mixture was poured in to a separatory funnel containing 0.1 M HCl, and the product was extracted with ether. The organic layer was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was dissolved in acetone (150 mL) and to the resulting solution was added p–TsOH (6.60 g, 1.90 equiv, 34.7 mmol). The reaction mixture was stirred at room temperature and after

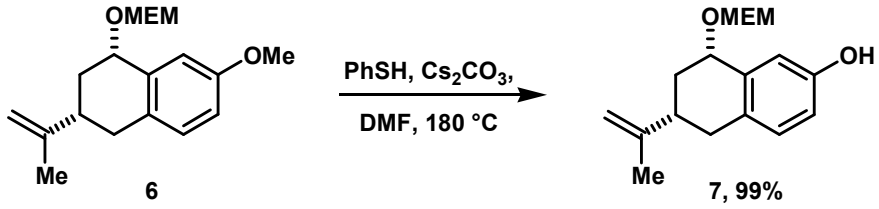
10 min saturated aq. $NaHCO_3$ was added. Acetone was removed from the reaction mixture under reduced pressure and the product was extracted with ether. The organic extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield crude ketone **S1** in quantitative yield. The crude product was used without further purification in the next step while a small portion of the material was purified by column chromatography to yield ketone **S1** as a white amorphous powder. FT-IR (thin film): 2927, 2877, 1675, 1597, 1237, 1101, 1021 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 9 Hz, 1H), 7.12 (d, J = 1.5 Hz, 1H), 6.88 (dd, J_1 = 9 Hz, J_2 = 1.5 Hz, 1H), 5.10 (d, J = 7 Hz, 1H), 5.00-4.97 (m, 3H), 4.87 (s, 1H), 3.88-3.85 (m, 5H), 3.61-3.60 (m, 2H), 3.39 (s, 3H), 3.21 (dd, J_1 = 14 Hz, J_2 = 4 Hz, 1H), 2.55-2.52 (m, 1H), 2.22-2.12 (m, 1H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 164.2, 147.4, 143.5, 130.3, 125.2, 114.8, 114.2, 110.1, 95.1, 74.0, 72.0, 67.8, 59.3, 55.7, 54.5, 36.2, 20.3; HRMS (ESI^+) *m/z* calc'd $C_{18}H_{25}O_5^+$ $[M+H]^+$: 321.1696, found 321.1684.



MEM-Ether 6: To a solution of **S1** (5.80 g, 1.00 equiv, 18.08 mmol) in CH_2Cl_2 (120 mL) was added 1M solution of *i*-Bu_2AlH (36.2 mL, 2.00 equiv, 36.2 mmol) in hexane, at 0 °C. The appearance of the reaction mixture during the addition changes from colorless, to yellow, to colorless and the addition was stopped after the first drop that makes the reaction mixture colorless. The reaction was then quenched with a saturated aqueous solution of sodium potassium tartarate (200 mL) and the biphasic mixture was vigorously stirred for 2 hours at room temperature. The product was extracted from the reaction mixture with ether and the extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield 5.40 g (92% yield) of the crude alcohol that was used in the following step without further purification.

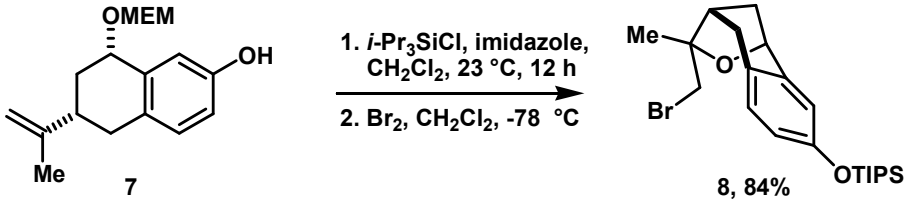
To a cooled solution (–20 °C) of the alcohol (5.40 g, 1.00 equiv, 16.8 mmol) in CH_2Cl_2 (85 mL) was added triethylsilane (21.4 mL, 8.00 equiv, 134 mmol), and trifluoroacetic anhydride (3.03 mL, 1.30 equiv, 21.8 mmol), followed by a slow addition of trifluoroacetic acid (0.65 mL,

0.50 equiv, 8.37 mmol). After 3 h at –20 °C, the reaction mixture was warmed to 0 °C and after an additional 0.5 hours sat. aq. $NaHCO_3$ solution was added. The product was extracted from the reaction mixture with ether and the extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (5% to 30% EtOAc in hexane) to yield **6** (4.41 g, 86% yield) as a colorless oil; $[\alpha]_D^{23}$ = +61.1 (*c* = 1.20, $CHCl_3$); FT-IR (thin film): 2953, 1262, 1104, 1033 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, *J* = 3 Hz, 1H), 7.00 (d, *J* = 8 Hz, 1H), 6.76 (dd, J_1 = 7 Hz, J_2 = 3 Hz, 1H), 5.06 (d, *J* = 7 Hz, 1H), 4.93 (d, *J* = 7 Hz, 1H), 4.85-4.79 (m, 3H), 3.89-3.85 (m, 2H), 3.84 (s, 3H), 3.62-3.60 (m, 2H), 3.41 (s, 3H), 2.76-2.67 (m, 2H), 2.45-2.40 (m, 2H), 1.80 (s, 3H), 1.66-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 148.9, 138.6, 129.9, 129.2, 113.9, 111.8, 109.7, 95.0, 76.1, 72.1, 67.5, 59.3, 55.5, 40.8, 35.4, 34.5, 20.8; HRMS (ESI^+) *m/z* calc'd for $C_{18}H_{26}KO_4^+$ $[M+K]^+$: 345.1468, found 345.1449.

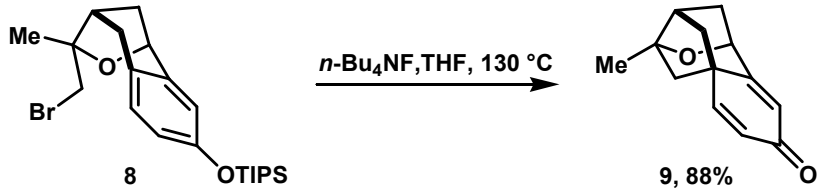


Phenol 7: To a Schlenk tube was added Cs_2CO_3 (5.32 g, 2.50 equiv, 16.3 mmol) and **6** (2.00 g, 1.00 equiv, 6.53 mmol) as a solution in degassed anhydrous DMF (25 mL). To the resulting suspension was added thiophenol (1.34 mL, 2.00 equiv, 13.1 mmol), and the reaction mixture was placed in the oil bath preheated to 180 °C. After evolution of CO_2 stopped, the tube was sealed with a teflon stopper and the reaction mixture was stirred at the same temperature. After 12 h, the reaction mixture was cooled to room temperature and sat. aq. NH_4Cl was added. The product was extracted with ether and the organic extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (10% to 50% EtOAc in Hexane) to yield phenol **7** (1.90 g, 99% yield) as a colorless oil. $[\alpha]_D^{23}$ = +60.3 (*c* = 1.00, $CHCl_3$); FT-IR (thin film): 3364 (br), 2922, 2884, 1091, 1033 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, *J* = 2.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.68 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H), 5.60 (s, 1H), 5.03 (d, *J* = 7.5 Hz, 1H), 4.90 (d, *J* = 8.5 Hz, 1H), 4.80-4.78 (m, 3H), 3.95-3.92 (m, 1H), 3.79-3.77 (m, 1H), 3.65-3.63 (m, 2H),

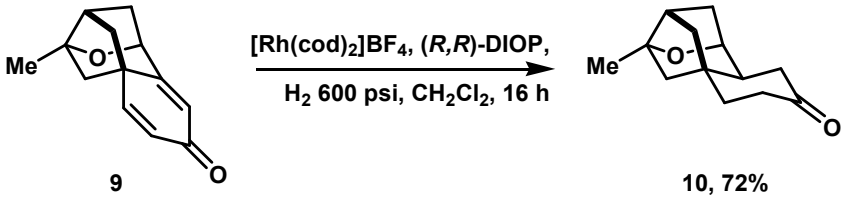
3.49 (s, 3H), 2.78-2.68 (m, 1H), 2.66-2.62 (m, 1H), 2.40-2.37 (m, 2H), 1.79 (s, 3H), 1.63-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 148.9, 138.6, 130.0, 128.9, 114.9, 113.9, 109.7, 95.3, 76.8, 72.3, 67.6, 59.4, 40.9, 35.5, 34.5, 20.8; HRMS (ESI^+) *m/z* calc'd for $C_{17}H_{28}NO_4^+$ $[M+NH_4]^+$: 310.2013, found 310.2023.



Bromo ether 8: To a solution of **7** (1.79 g, 1.00 equiv, 6.13 mmol) and imidazole (0.773 g, 2.00 equiv, 12.3 equiv) in CH_2Cl_2 (15 mL) was added TIPSCl (1.44 mL, 1.10 equiv, 6.74 mmol) at room temperature. After 16 h, the reaction mixture was diluted with ether and was washed with 0.1 M HCl, sat. aq. $NaHCO_3$, and brine. The organic extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude reaction product was dissolved in CH_2Cl_2 (60 mL) and to the resulting solution, cooled to –78 °C, was slowly added a solution of Br_2 in CH_2Cl_2 (10% v/v). After the addition was completed sat. aq. $Na_2S_2O_3$ was added and the reaction mixture was warmed to room temperature. The resulting solution was extracted with ether and the organic extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (2% to 12% EtOAc in hexane) to yield **8** as an inseparable mixture of diastereoisomers (>10:1) (2.25 g, 84% yield). $[\alpha]_D^{23} = +113.1$ (*c* = 1.01, $CHCl_3$); FT-IR (thin film): 2943, 2866, 1272, 880 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): δ 6.76-6.77 (m, 2H), 6.70 (t, *J* = 1.5 Hz, 1H), 4.59 (d, *J* = 4.5 Hz, 1H), 3.19-3.21 (m, 2H), 3.16 (d, *J* = 17.5 Hz, 1H), 2.66 (dd, J_1 = 17.5 Hz, J_2 = 4 Hz, 1H), 2.13-2.17 (m, 1H), 2.04-2.11 (m, 1H), 1.55 (d, *J* = 11.5 Hz 1H), 1.34 (s, 3H), 1.12-1.20 (m, 3H), 1.12-1.04 (m, 18H); ^{13}C NMR (100 MHz, C_6D_6): δ 154.4, 142.3, 129.8, 126.7, 119.8, 118.7, 84.2, 78.5, 41.7, 38.6, 35.1, 31.5, 26.3, 18.1, 13.0; HRMS (ESI^+) *m/z* calc'd for $C_{22}H_{36}BrO_2Si^+$ $[M+H]^+$: 439.1662, found 439.1669.

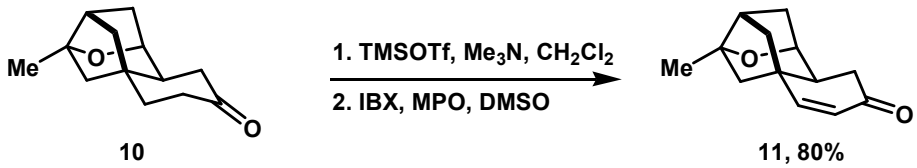


Dienone 9: To a solution of **8** (3.77 g, 1.00 equiv, 8.58 mmol) in THF (60 mL) in a Schlenk flask was added 1M solution of TBAF in THF (10.3 mL, 1.20 equiv, 10.3 mmol) at room temperature. The flask was sealed and placed in a 130 °C oil bath. After 4 h, the reaction mixture was cooled to room temperature, diluted with EtOAc, and washed with sat. aq. NH_4Cl and brine. The aqueous phase was extracted with EtOAc, and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (10% to 80% EtOAc in hexane) to yield **9** as a white amorphous powder (1.53 g, 88% yield). $[\alpha]_D^{23}$ = +33.7 (*c* = 1.25, $CHCl_3$); FT-IR (thin film): 2963, 1655, 1626, 1147 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.66 (d, *J* = 10 Hz, 1H), 6.31 (dd, J_1 = 10 Hz, J_2 = 2 Hz, 1H), 6.11 (d, *J* = 10 Hz, 1H), 4.71 (d, *J* = 5 Hz, 1H), 2.58 (t, *J* = 6 Hz, 1H), 2.26-2.20 (m, 1H), 2.14-2.19 (m, 1H), 1.92-1.99 (m, 2H), 1.77 (d, *J* = 11.5 Hz, 1H), 1.72-1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 160.4, 150.9, 130.0, 121.8, 87.1, 80.0, 54.8, 49.9, 48.6, 44.4, 42.5, 22.2; LRMS (ESI^+) *m/z* calc'd for $C_{13}H_{15}O_2^+$ $[M+H]^+$: 203.11, found 203.11.



Ketone 10: To a flask containing **9** (0.60 g, 1.00 equiv, 2.97 mmol), $[Rh(cod)_2]BF_4$ (0.24 g, 0.20 equiv, 0.59 mmol) and (4*R*,5*R*)-DIOP (0.30 g, 0.20 equiv, 0.59 mmol) was added CH_2Cl_2 (60 mL). The flask was quickly transferred to a hydrogenation apparatus. The hydrogenation apparatus was flushed with hydrogen three times and filled with 600 psi of hydrogen. After 12 h the reaction mixture was placed under a nitrogen atmosphere and Dess-Martin reagent was added in small portions until all of the alcohol byproduct (less than 0.1 equiv) disappeared. To the resulting reaction mixture was added silica gel (3 g) and the solvent was removed under reduced pressure. The desired product **10** was obtained after the column chromatography (5% to 60% Et_2O in hexane) as a white amorphous powder (0.44 g, 72% yield). $[\alpha]_D^{23}$ = -10.8 (*c* = 0.84,

$CHCl_3$); FT-IR (thin film): 2944, 1709, 1040 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.07 (t, J = 10 Hz, 1H), 2.40-2.29 (m, 3H), 2.26-2.22 (m, 2H), 2.12-2.02 (m, 2H), 1.90-1.78 (m, 3H), 1.68 (dd, J_1 = 11 Hz, J_2 = 3 Hz, 1H), 1.65-1.59 (m, 1H), 1.52 (d, J = 11 Hz, 1H), 1.43-1.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 86.0, 79.2, 52.6, 45.1, 44.9, 44.3, 41.5, 39.9, 39.2, 37.0, 35.0, 23.1; HRMS (ESI^+) *m/z* calc'd for $C_{13}H_{19}O_2^+$ $[M+H]^+$: 207.1385, found 207.1380.

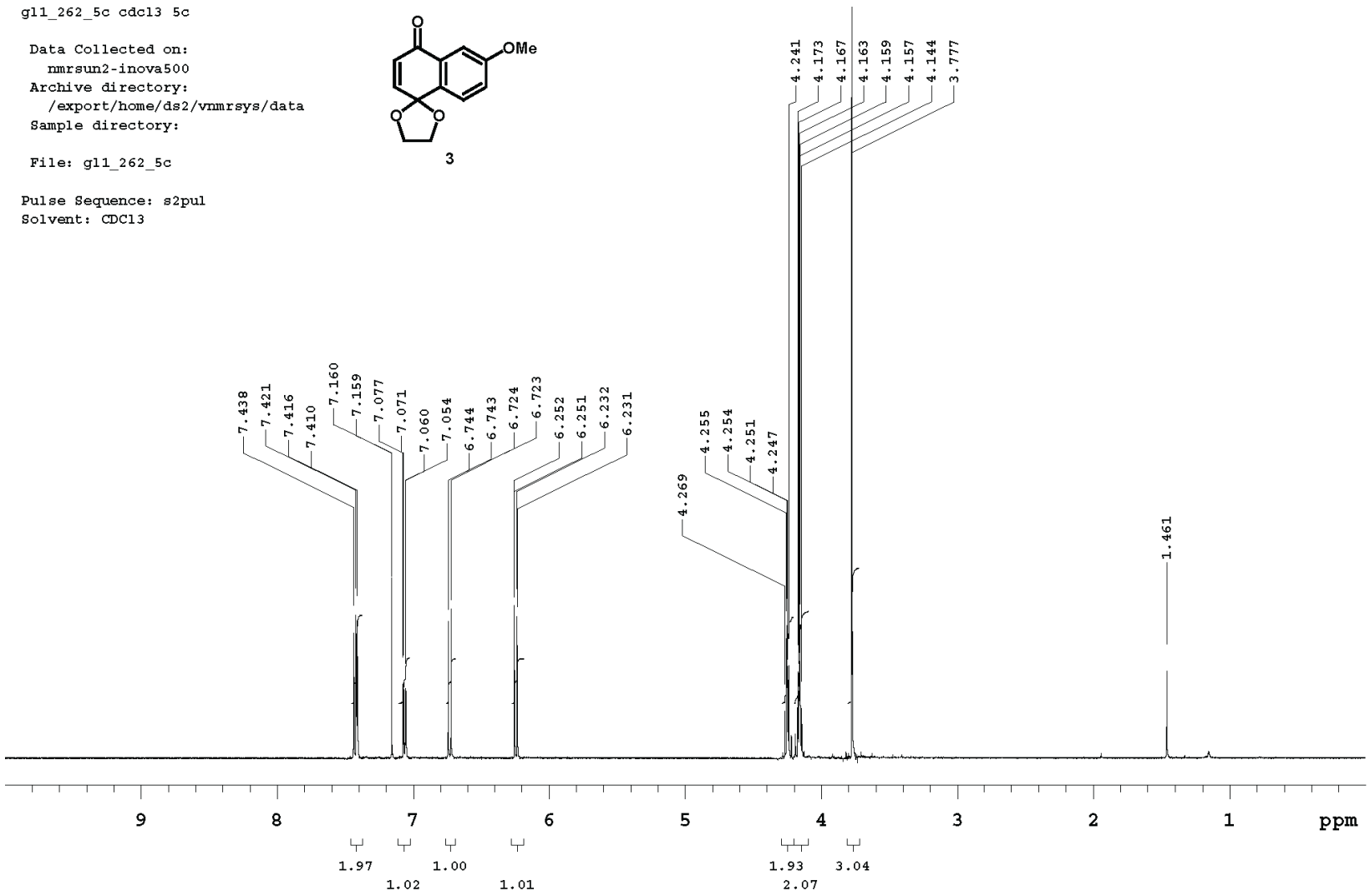


Enone 11: To a solution of **10** (0.054 g, 1.00 equiv, 0.262 mmol) and Me_3N (0.15 mL, 6.00 equiv, 1.57 mmol) in CH_2Cl_2 (2.6 mL) at 0 °C was added TMSOTf (0.14 mL, 3.00 equiv, 0.78 mmol). After 1.5 h pentane was added and the resulting mixture was extracted with aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was dissolved in DMSO (0.10 mL) and 0.4 M solution of IBX and MPO (4-Methoxy pyridine-*N*-oxide) in DMSO (0.98 mL, 1.5 equiv, 0.39 mmol) was added at room temperature. After 1.5 h, to the reaction mixture was added sat. aq. $NaHCO_3$ and the resulting solution was extracted with EtOAc. The organic extracts were combined and were extracted with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product obtained as a 7.2:1 mixture of regioisomers was purified by column chromatography (4% to 60% EtOAc in benzene) to yield **11** (0.043 g, 80% yield, 98% ee) as a white solid. HPLC (Chiralpac AD-H column, 2% *i*-PrOH/hexanes, 1.0 mL/min, 230 nm, t_{major} = 16.3 min, t_{minor} = 18.4 min; ee = 98%); $[\alpha]_D^{23}$ = -16.6 (*c* = 1.00, $CHCl_3$); FT-IR (thin film): 2948, 1674, 1137, 1082, 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.62 (d, J = 10.0 Hz, 1H), 5.94 (d, J = 10.0 Hz, 1H), 4.16 (dd, J_1 = 3.4 Hz, J_2 = 3.4 Hz, 1H), 2.44-2.27 (m, 4H), 1.97-1.92 (m, 2H), 1.89 (d, J= 11.5 Hz, 1H), 1.78-1.73 (m, 2H), 1.66 (d, J = 11 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR (120 MHz, $CDCl_3$): δ = 199.1, 155.2, 128.9, 87.0, 79.0, 51.7, 46.2, 44.1, 42.7, 42.2, 37.9, 37.5, 23.1; LRMS (ESI^+) *m/z* calc'd for $C_{13}H_{17}O_2^+$ $[M+H]^+$: 205.12, found 205.12.

References:

(1) Hulme, A. N.; Henry, S. S.; Meyers, A. I. *J. Org. Chem.* **1995**, *60*, 1265-1270.

(2) Molander, G. A.; Ribagorda, M. *J. Org. Chem.* **2003**, *125*, 11148-11149.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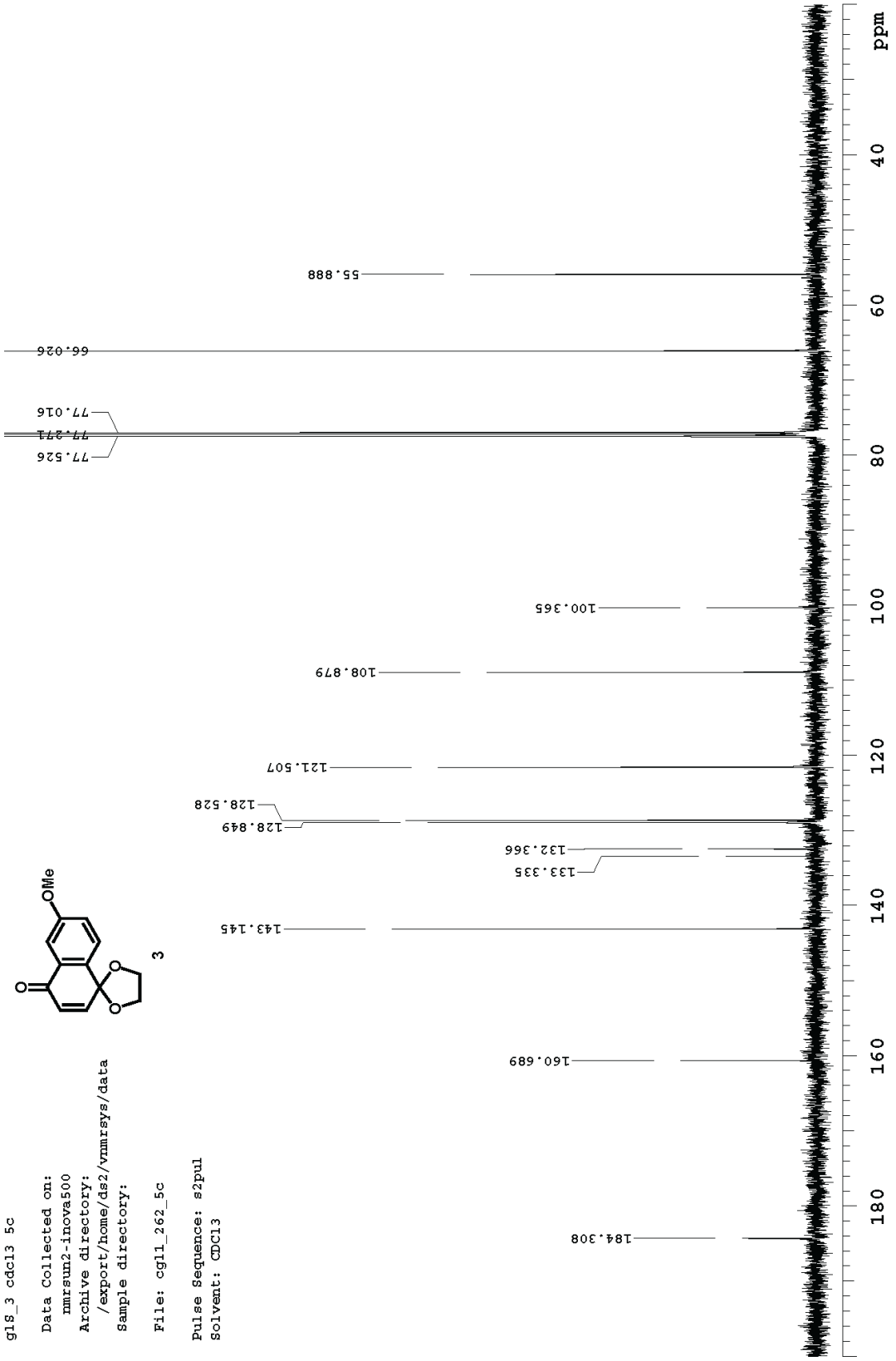
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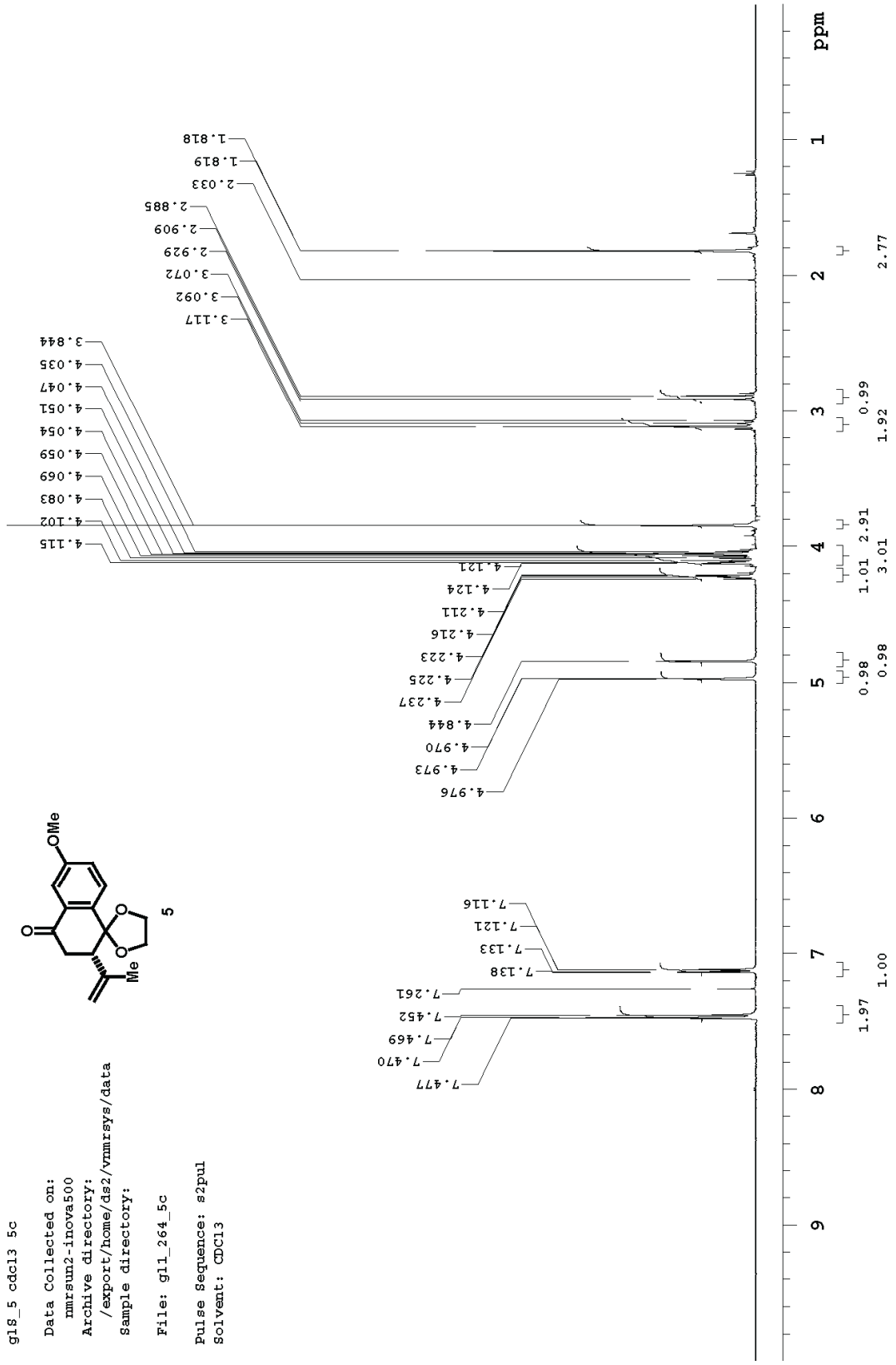
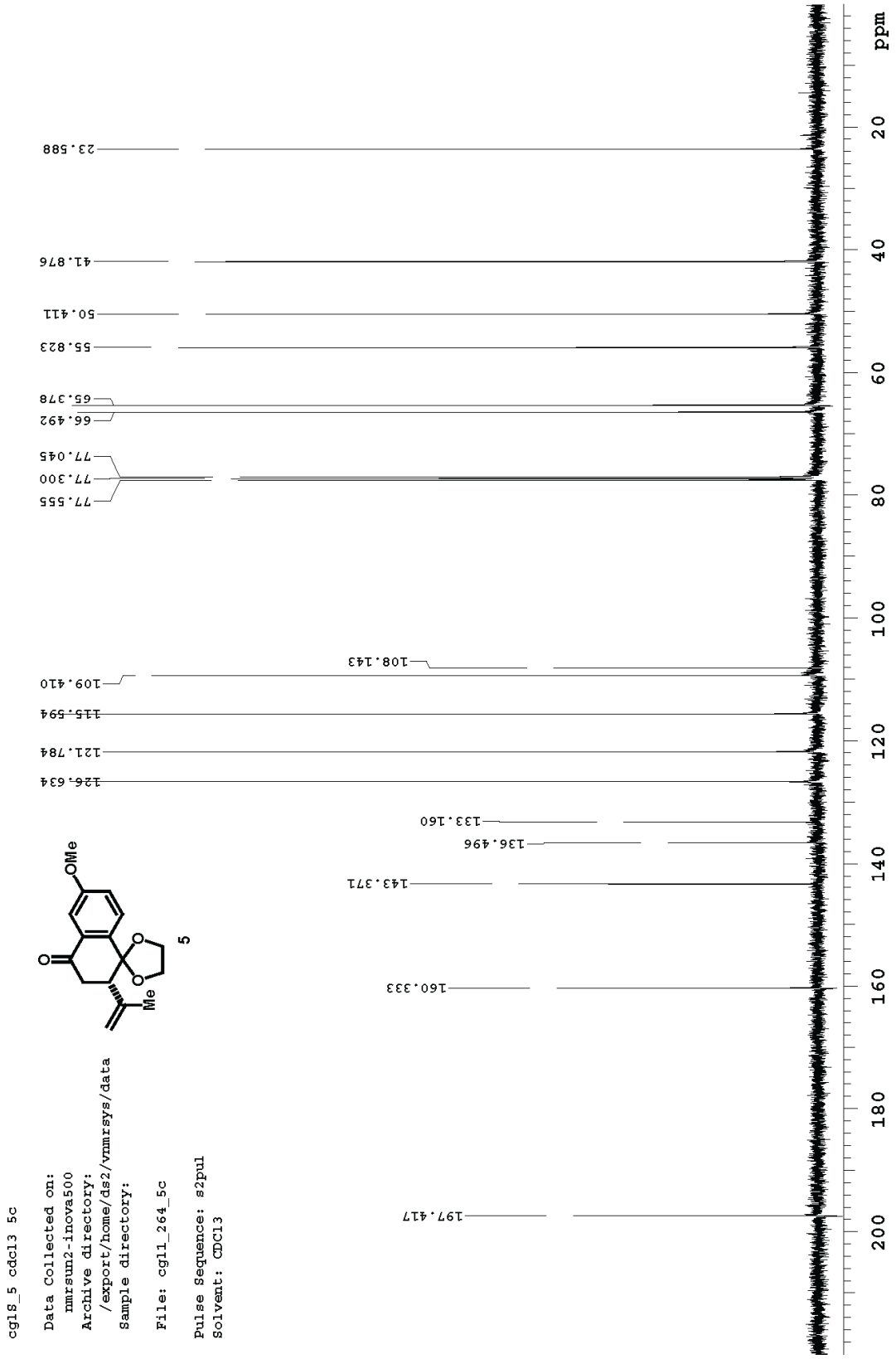
/export/home/ds2/vnmrsys/data
Sample directory:
File: cgl1_262_5c
Pulse Sequence: s2pul
Solvent: CDCl3
OMe
O
O
O
3
184.308
160.689
143.145
133.335
132.366
128.849
128.528
121.507
108.879
100.365
77.526
77.371
77.016
66.026
55.888
ppm
180
160
140
120
100
80
60
40

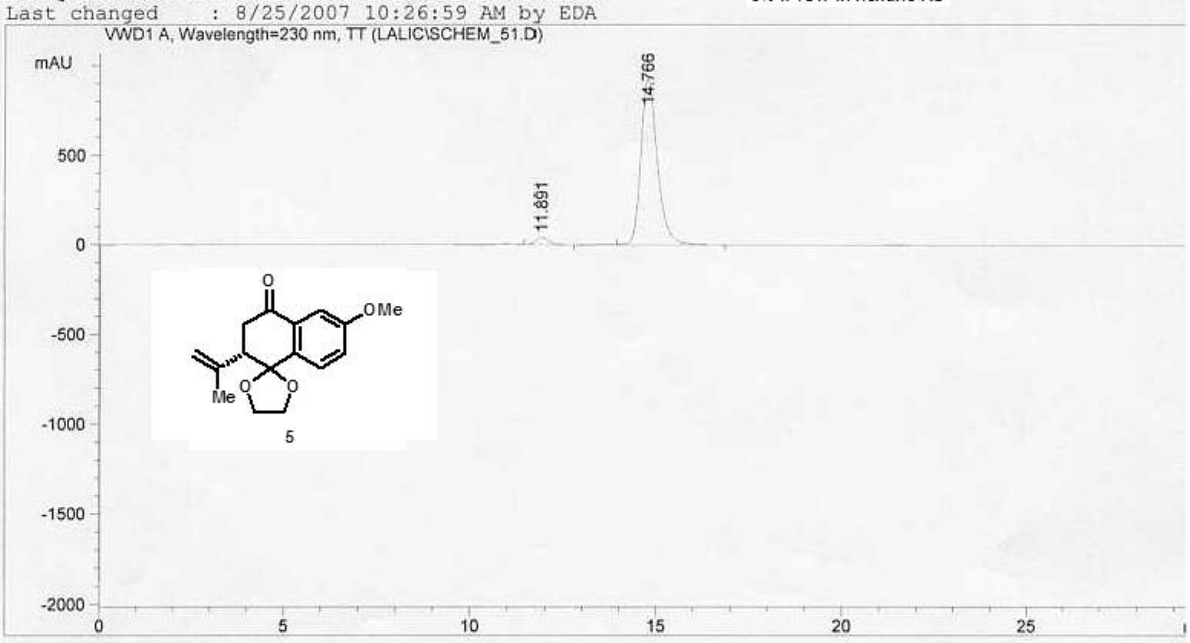

gl8_5 cdcl3 5c
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: gl1_264_5c
Pulse Sequence: s2pul
Solvent: CDCl3
OMe
O
O
O
Me
5
7.477
7.470
7.469
7.452
7.261
7.138
7.133
7.121
7.116
4.976
4.973
4.970
4.844
4.237
4.225
4.223
4.216
4.211
4.124
4.121
4.115
4.102
4.083
4.069
4.059
4.054
4.051
4.047
4.035
3.844
3.117
3.092
3.072
2.929
2.909
2.885
2.033
1.819
1.818
ppm
1
2
3
4
5
6
7
8
9
2.77
0.99
1.92
1.01
2.91
3.01
0.98
0.98
1.97
1.00


cgl8_5 cdcl3 5c
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: cgl1_264_5c
Pulse Sequence: s2pul
Solvent: CDCl3
OMe
O
O
O
Me
5
197.417
160.333
143.371
136.496
133.160
126.634
121.784
115.594
109.410
108.143
77.555
77.300
77.045
66.492
65.378
55.823
50.411
41.876
23.588
ppm
20
40
60
80
100
120
140
160
180
200

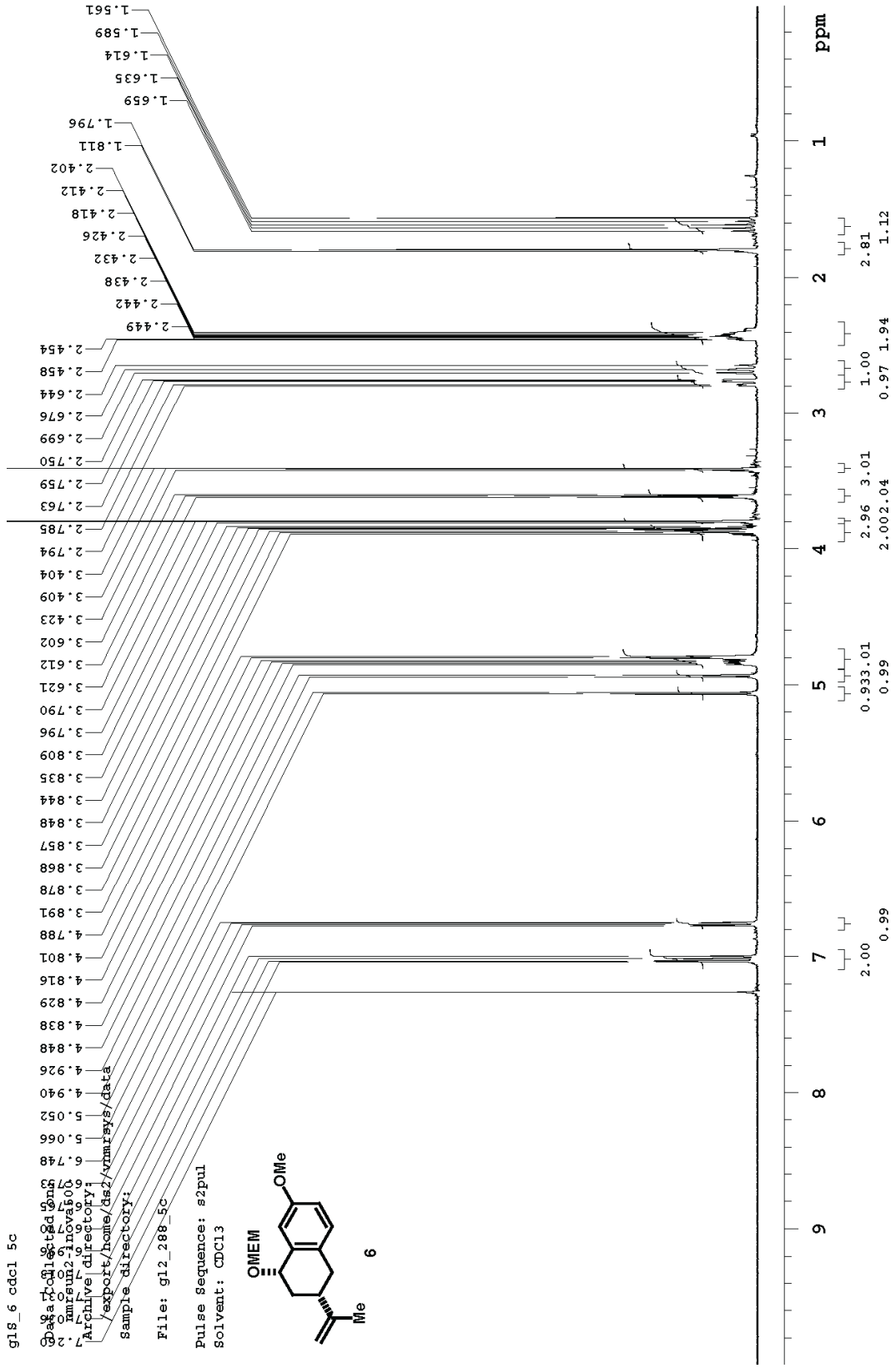
Data File C:\HPCHEM\1\DATA\LALIC\SCHEM_51.D Sample Name: Scheme

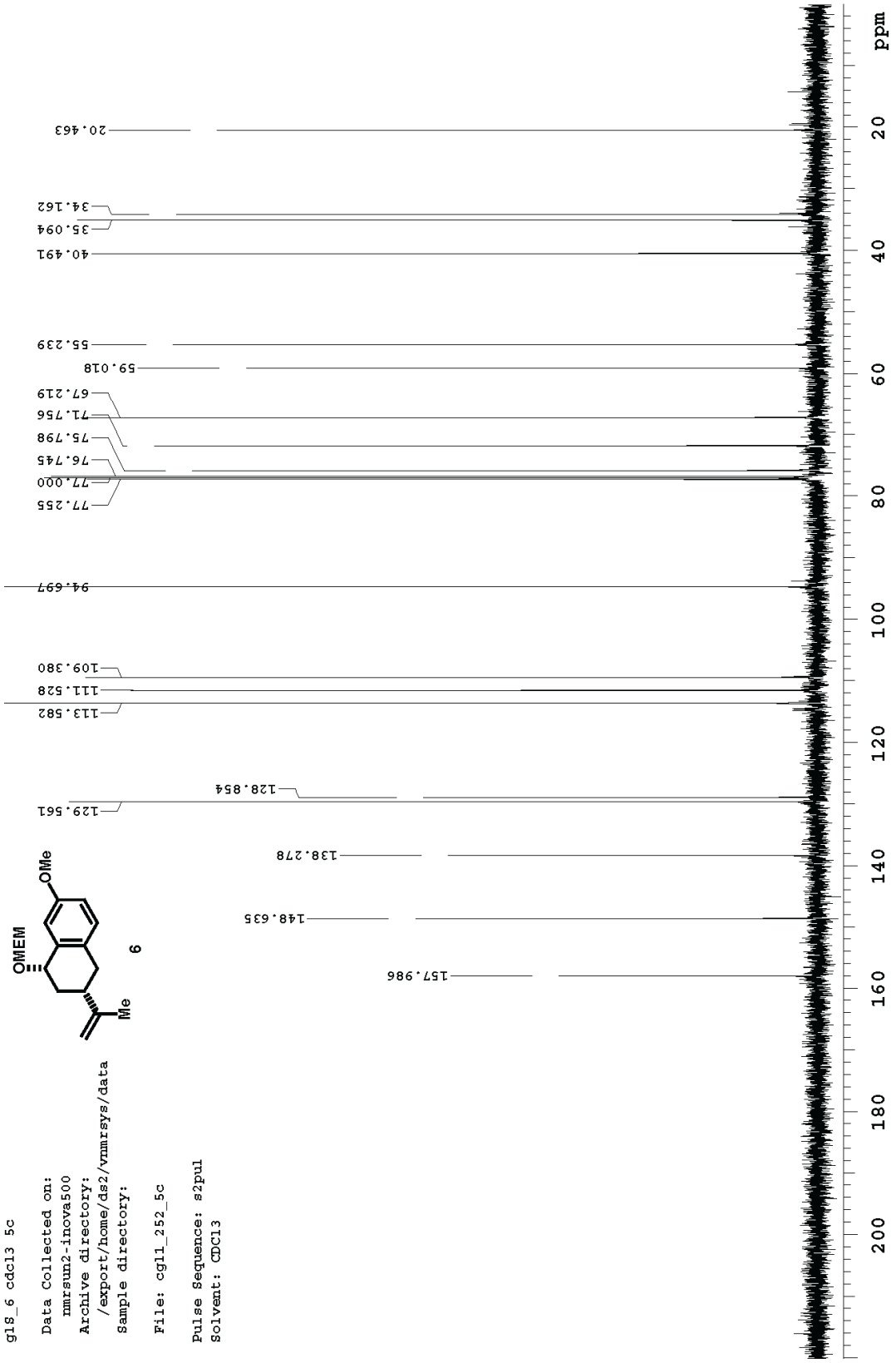
```
Injection Date  : 8/7/2007 4:04:14 PM          Seq. Line :   1
Sample Name     : Scheme_5                     Location : Vial 1
Acq. Operator   : Gl                               Inj :   1
Acq. Instrument : Instrument 1
Acq. Method     : C:\HPCHEM\1\METHODS\LALIC\SCHEME5.M
Last changed    : 8/7/2007 4:02:00 PM by Gl
Analysis Method : C:\HPCHEM\1\DATA\BRIAN\WASH.M
Last changed    : 8/25/2007 10:26:59 AM by EDA
```

3% iPrOH in hexane AD




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.891 VP    0.3536  988.25433   42.59863   3.3048
   2  14.766 VB    0.4717 2.89153e4   930.59106  96.6952

Totals :                  2.99035e4   973.18969

 Results obtained with enhanced integrator!

                        *** End of Report ***
```


gls_6 cdcl 5c
Pulse Sequence: s2pul
Solvent: CDCl3
File: gl2_288_5c
Sample directory:
/export/home/ds2/nmrsys/data
Archive directory:
nmrsun2.inova400
OMEM
OMe
Me
6
ppm

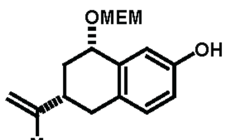

gl8_6 cdcl3 5c
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: cgl1_252_5c
Pulse Sequence: s2pul
Solvent: CDCl3
OMe
OMEM
Me
6
157.986
148.635
138.278
129.561
128.854
113.582
111.528
109.380
94.697
77.255
77.000
76.745
75.798
71.756
67.219
59.018
55.239
40.491
35.094
34.162
20.463
ppm
200
180
160
140
120
100
80
60
40
20

S7 cdcl3 5

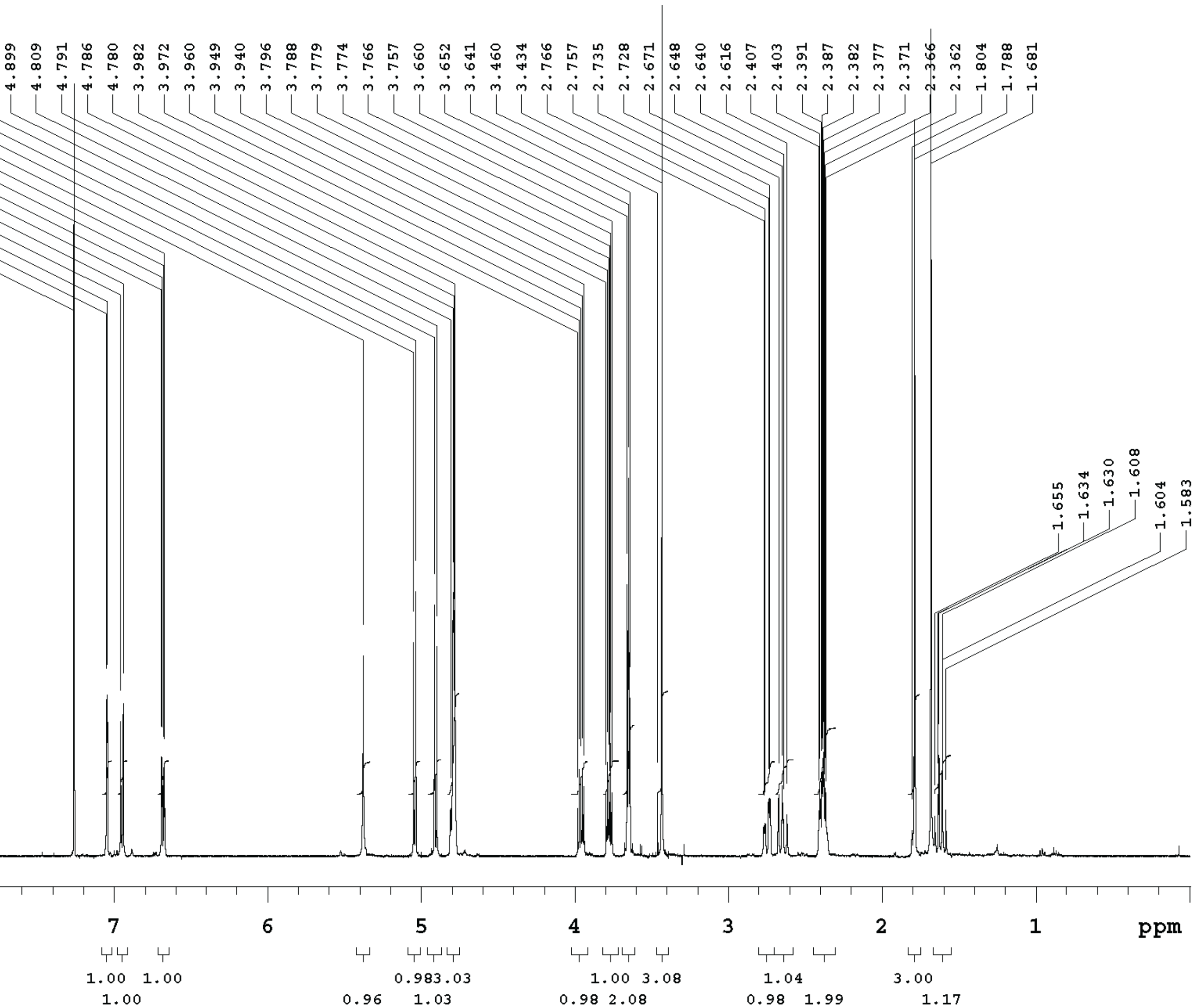
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:

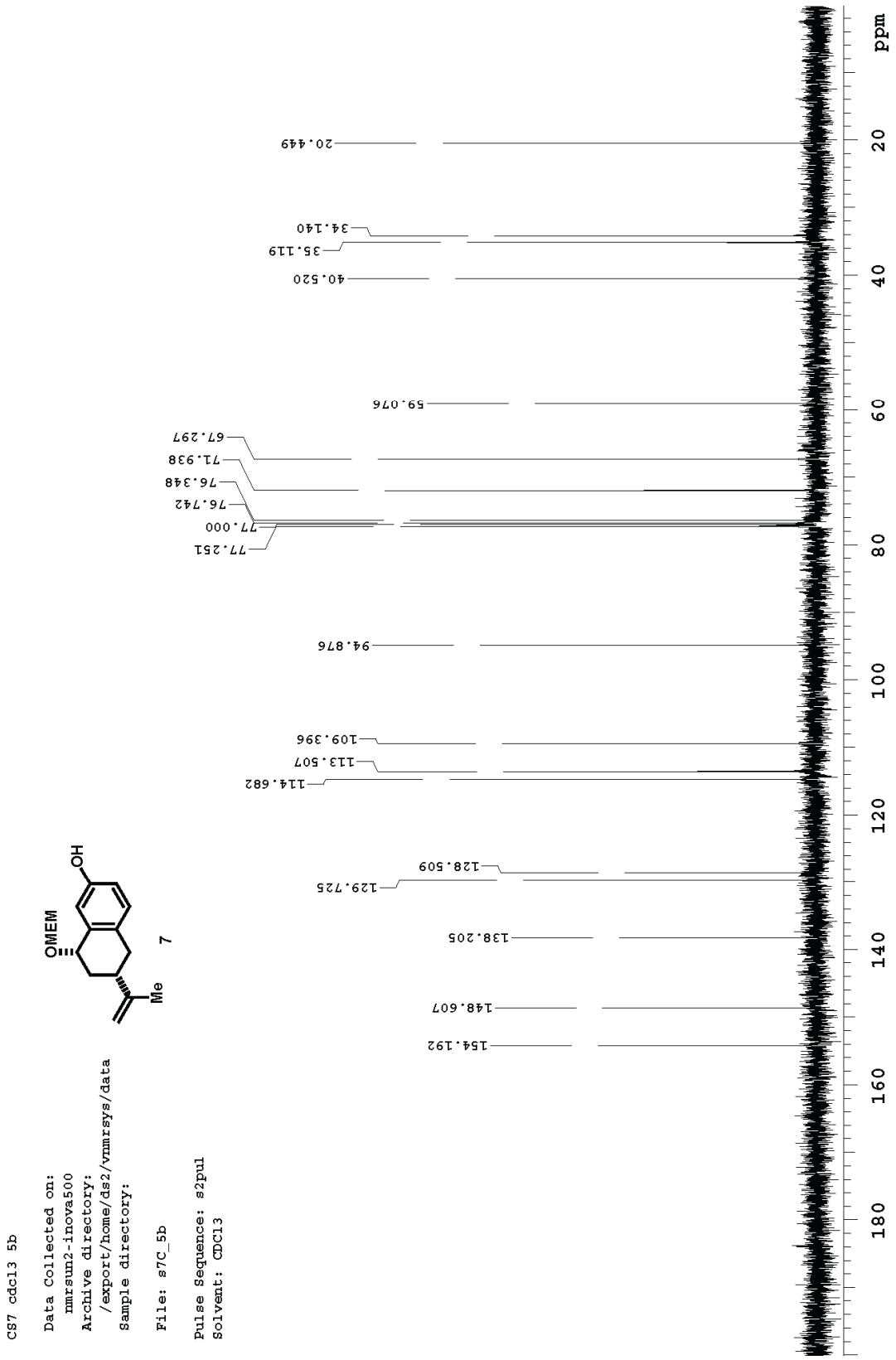
File: s7_5b

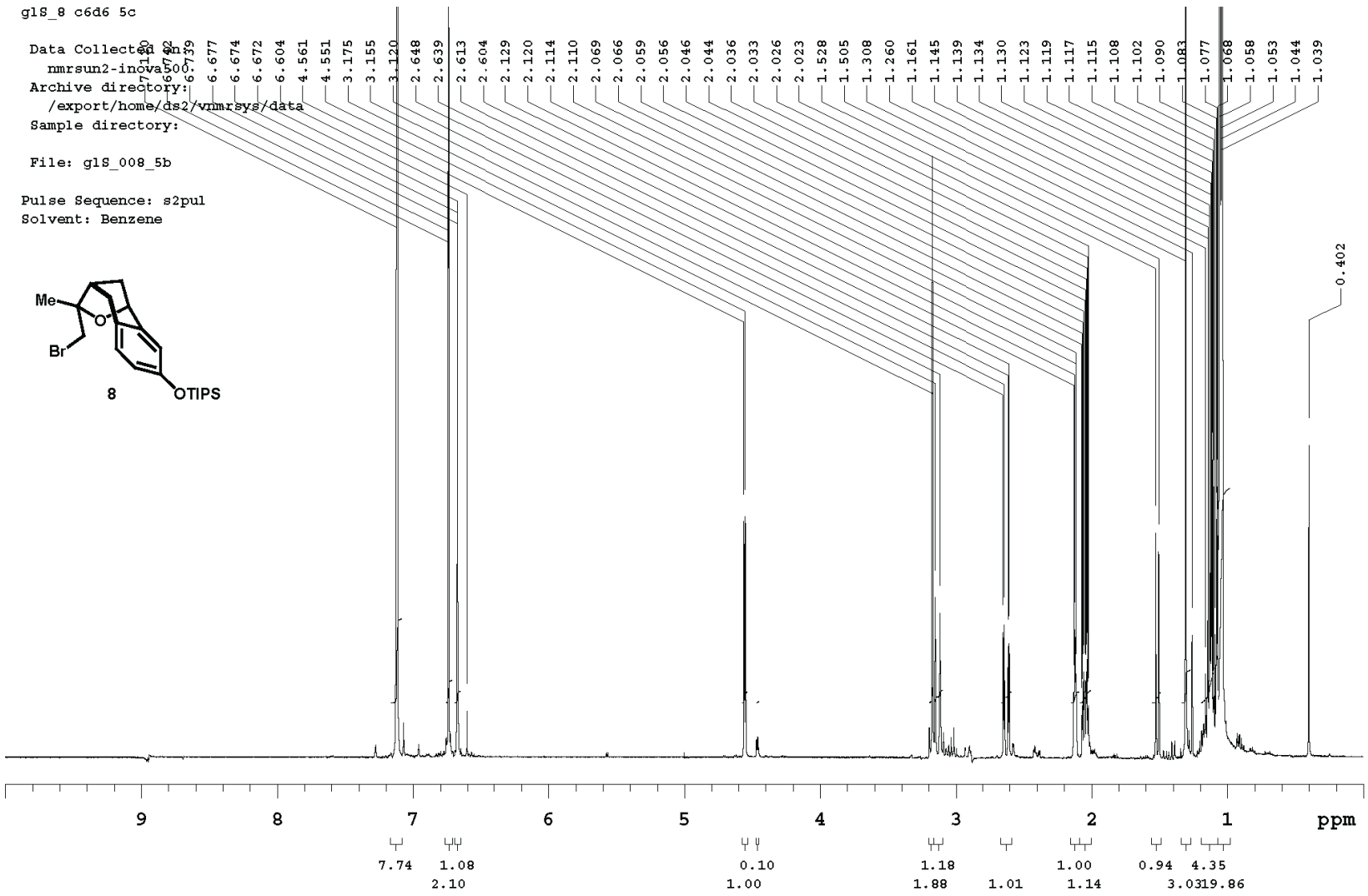
Pulse Sequence: s2pul
Solvent: CDCl3

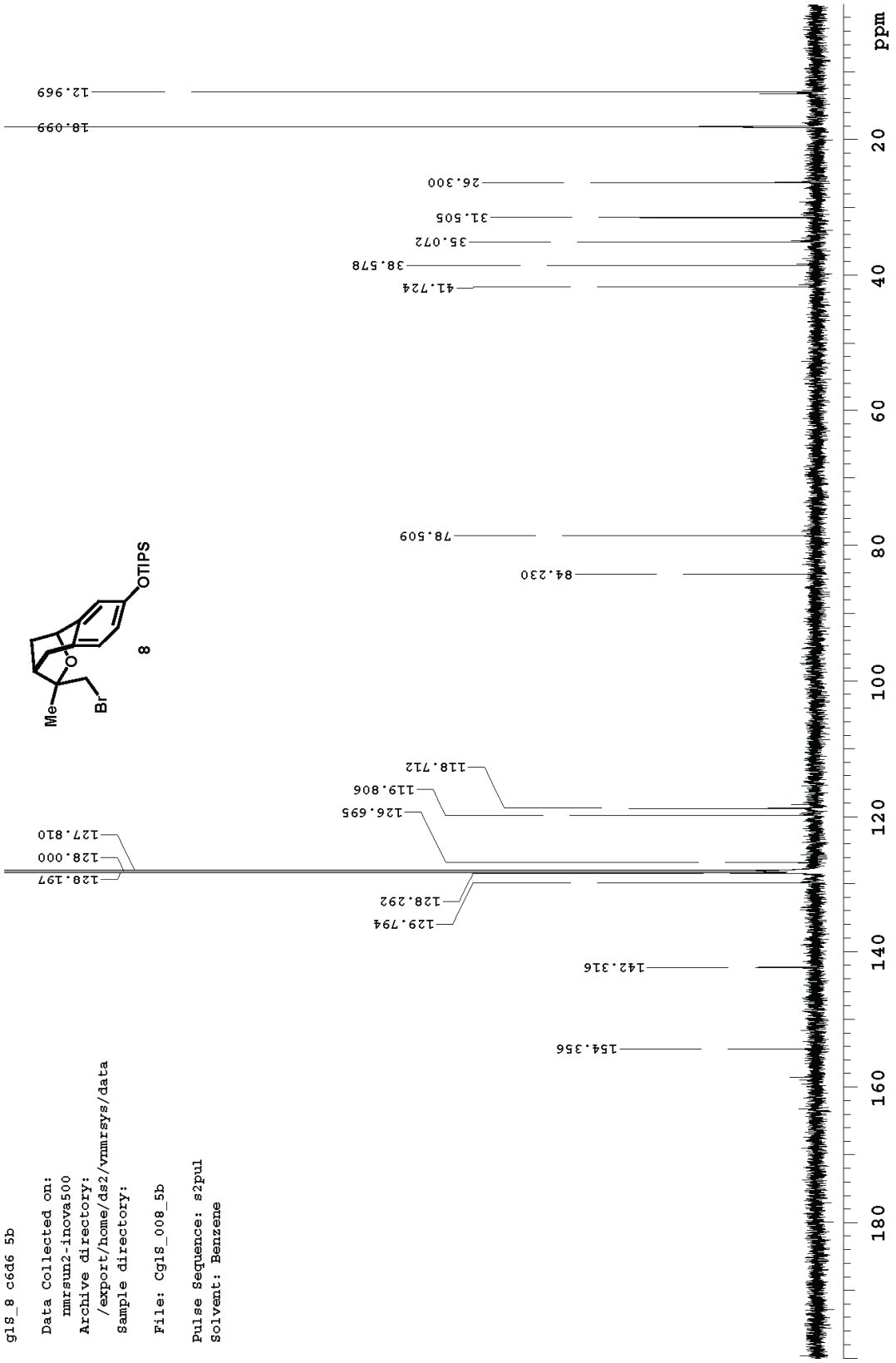


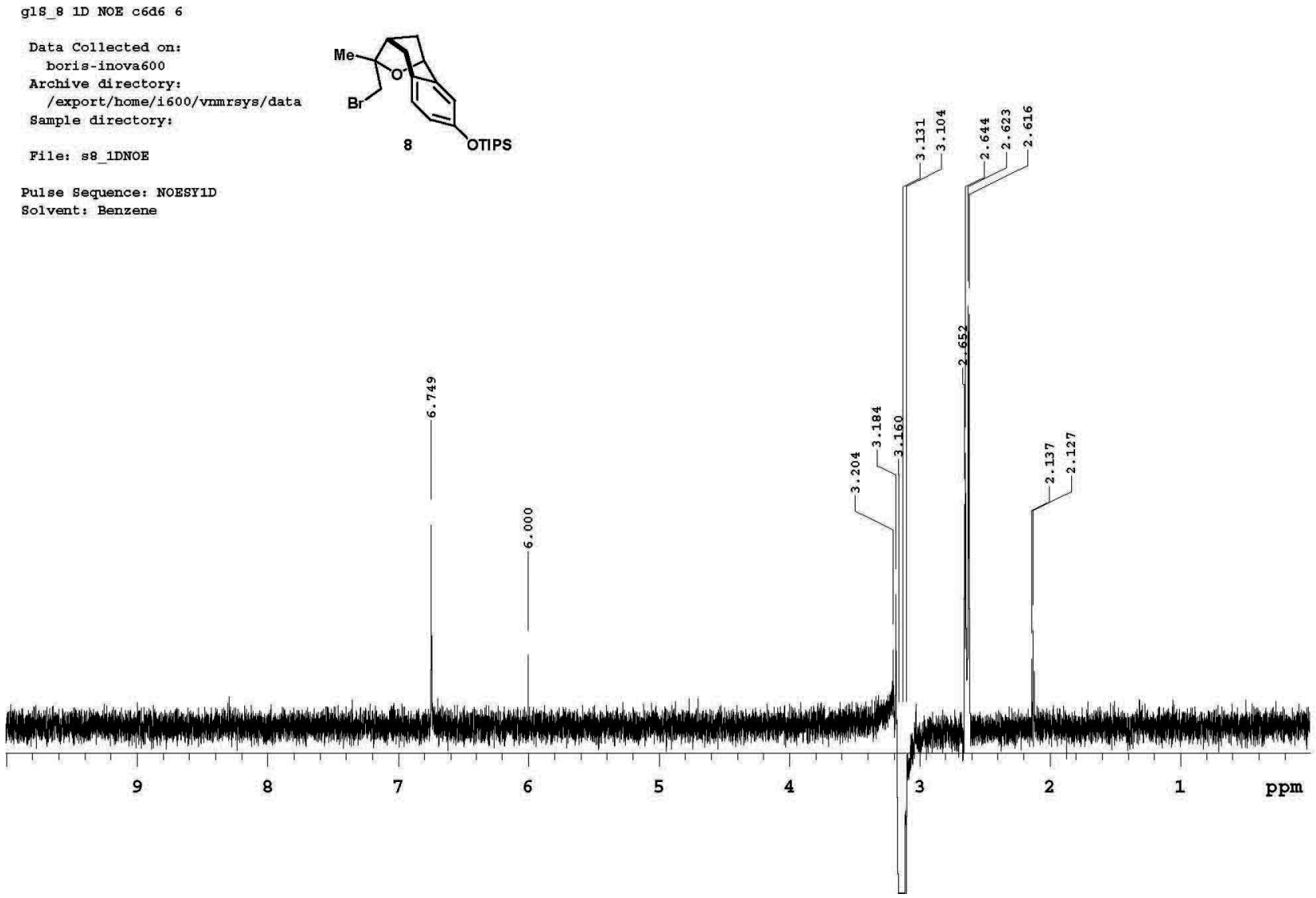
7




CS7 cdcl3 5b
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: s7C_5b
Pulse Sequence: s2pul
Solvent: CDCl3
OMEM
OH
Me
7
154.192
148.607
138.205
129.725
128.509
114.682
113.507
109.396
94.876
77.251
77.000
76.742
76.348
71.938
67.297
59.076
40.520
35.119
34.140
20.449
ppm
180
160
140
120
100
80
60
40
20


gls_8 c6d6 5c
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: gls_008_5b
Pulse Sequence: s2pul
Solvent: Benzene
Me
O
Br
8
OTIPS
0.402
9
8
7
6
5
4
3
2
1
ppm
7.74
1.08
2.10
0.10
1.00
1.18
1.88
1.01
1.00
1.14
0.94
4.35
3.03
19.86


gls_8 c6d6 5b
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: Cgls_008_5b
Pulse Sequence: s2pul
Solvent: Benzene
12.969
18.099
26.300
31.505
35.072
38.578
41.724
78.509
84.230
118.712
119.806
126.695
127.810
128.000
128.197
128.292
129.794
142.316
154.356
ppm
20
40
60
80
100
120
140
160
180
OTIPS
Me
Br
O
8

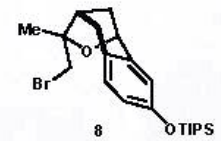

gls_8 1D NOE c6d6 6
Data Collected on:
boris-inova600
Archive directory:
/export/home/i600/vnmrsys/data
Sample directory:
File: s8_1DNOE
Pulse Sequence: NOESY1D
Solvent: Benzene
Me
O
Br
8
OTIPS
6.749
6.000
3.204
3.184
3.160
3.131
3.104
2.652
2.644
2.623
2.616
2.137
2.127
9
8
7
6
5
4
3
2
1
ppm

STANDARD PROTON PARAMETERS

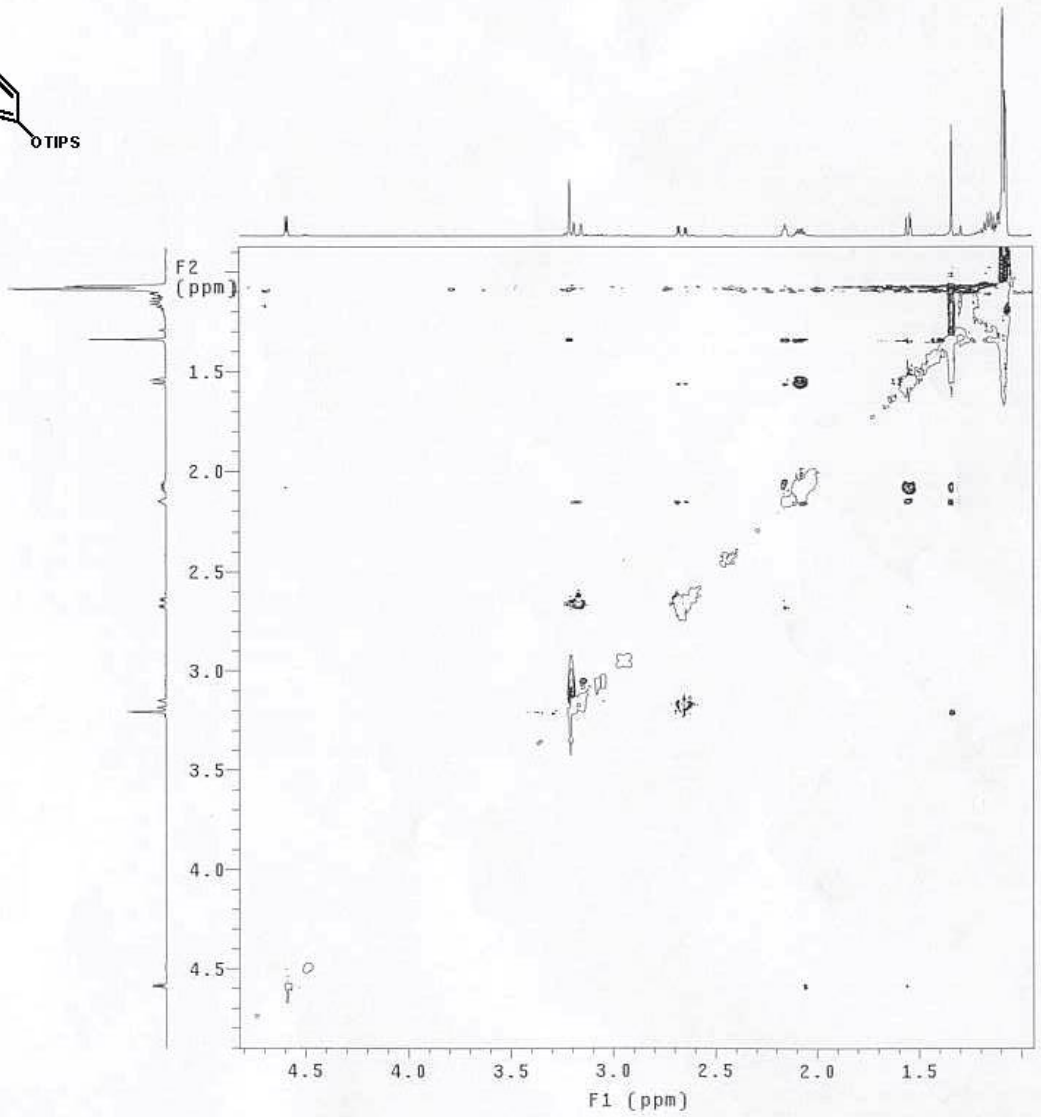
Pulse Sequence: NOESY

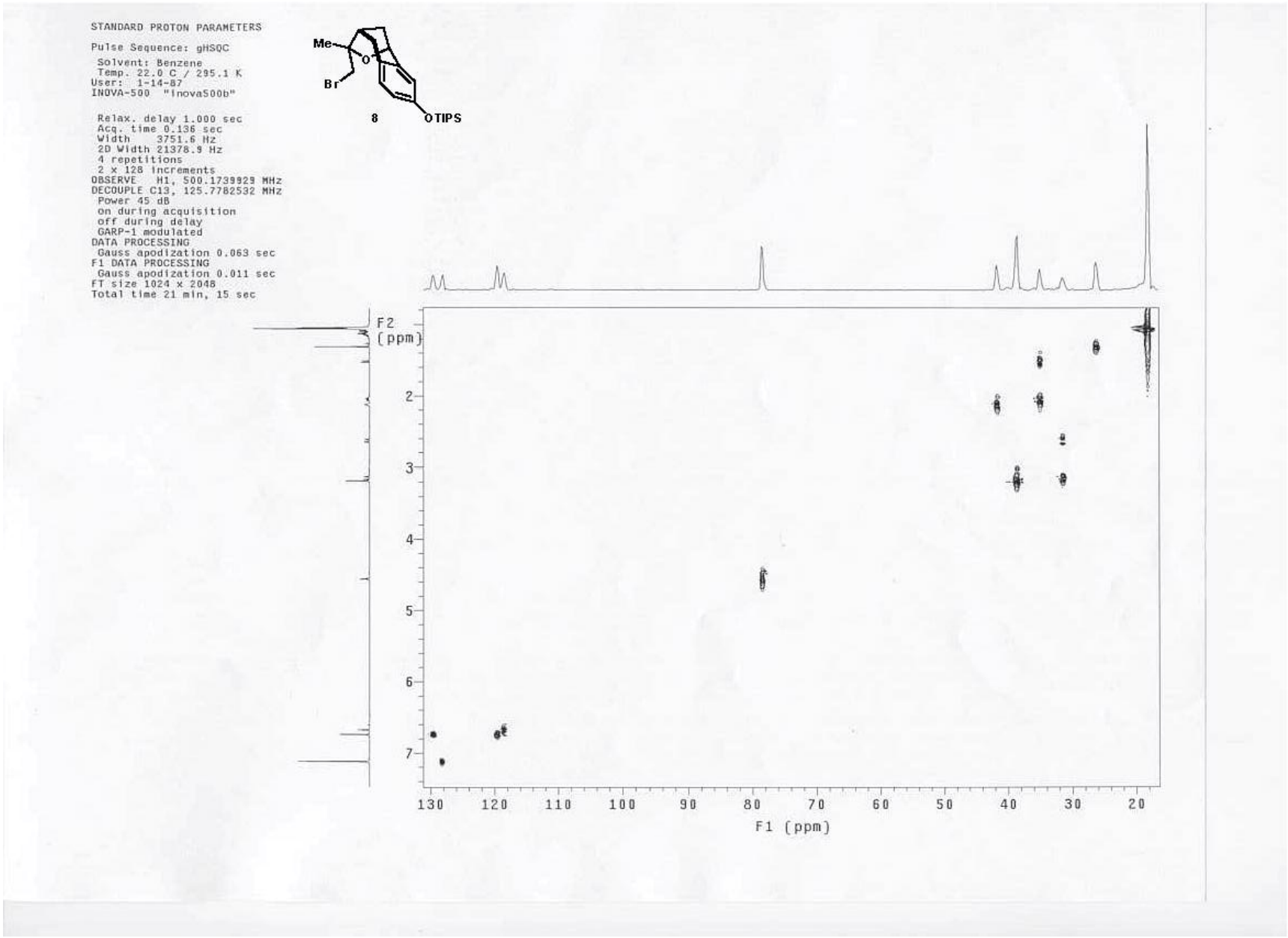
Solvent: Benzene
Temp. 22.0 C / 295.1 K
INOVA-500 "inova500b"

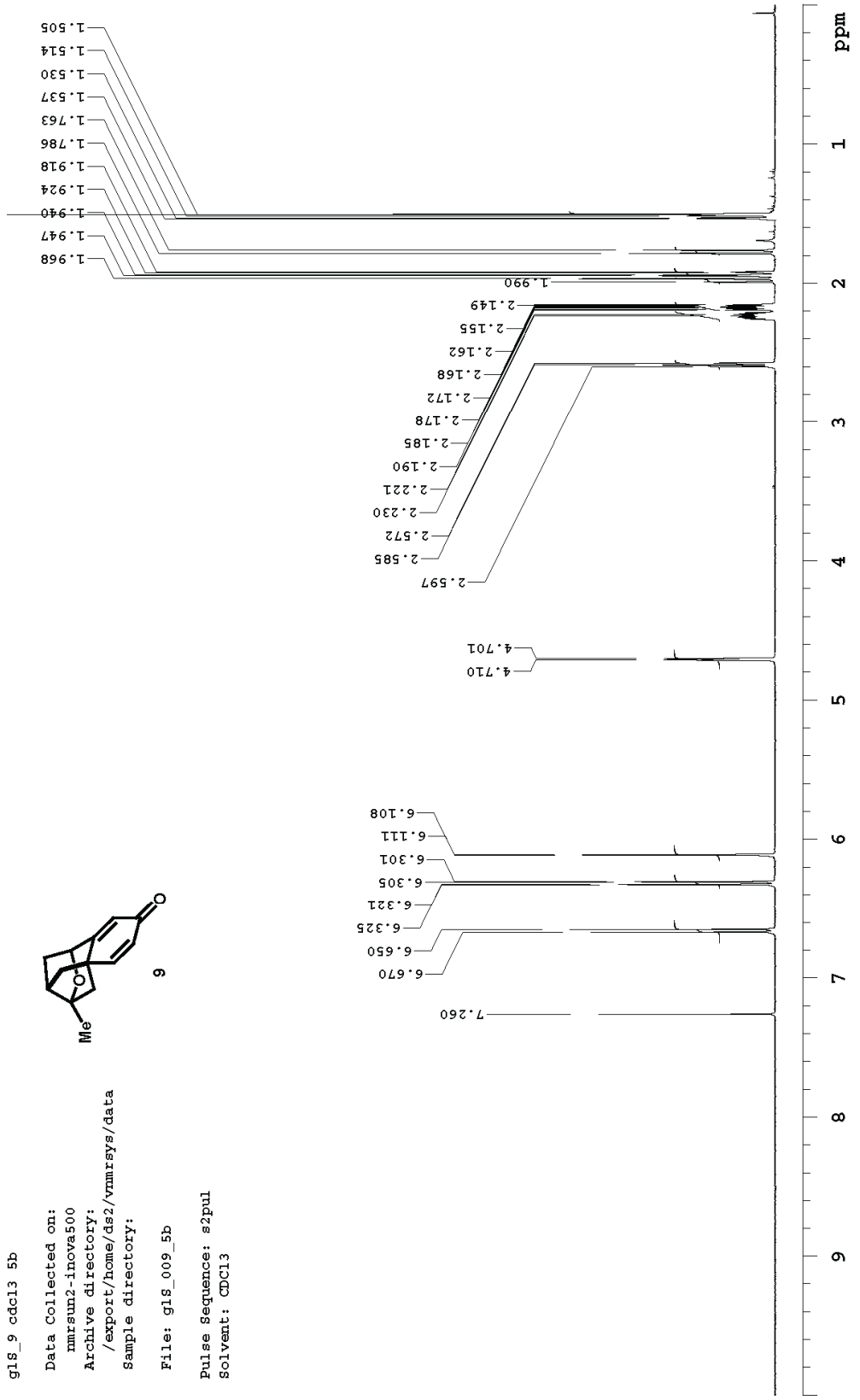
Relax. delay 1.000 sec
Mixing 0.500 sec
Acq. time 0.142 sec
Width 3603.8 Hz
2D Width 3603.8 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 500.1739780 MHz
DATA PROCESSING
Gauss apodization 0.066 sec
F1 DATA PROCESSING
Gauss apodization 0.051 sec
FT size 2048 x 2048
Total time 1 hr, 30 min, 39 sec

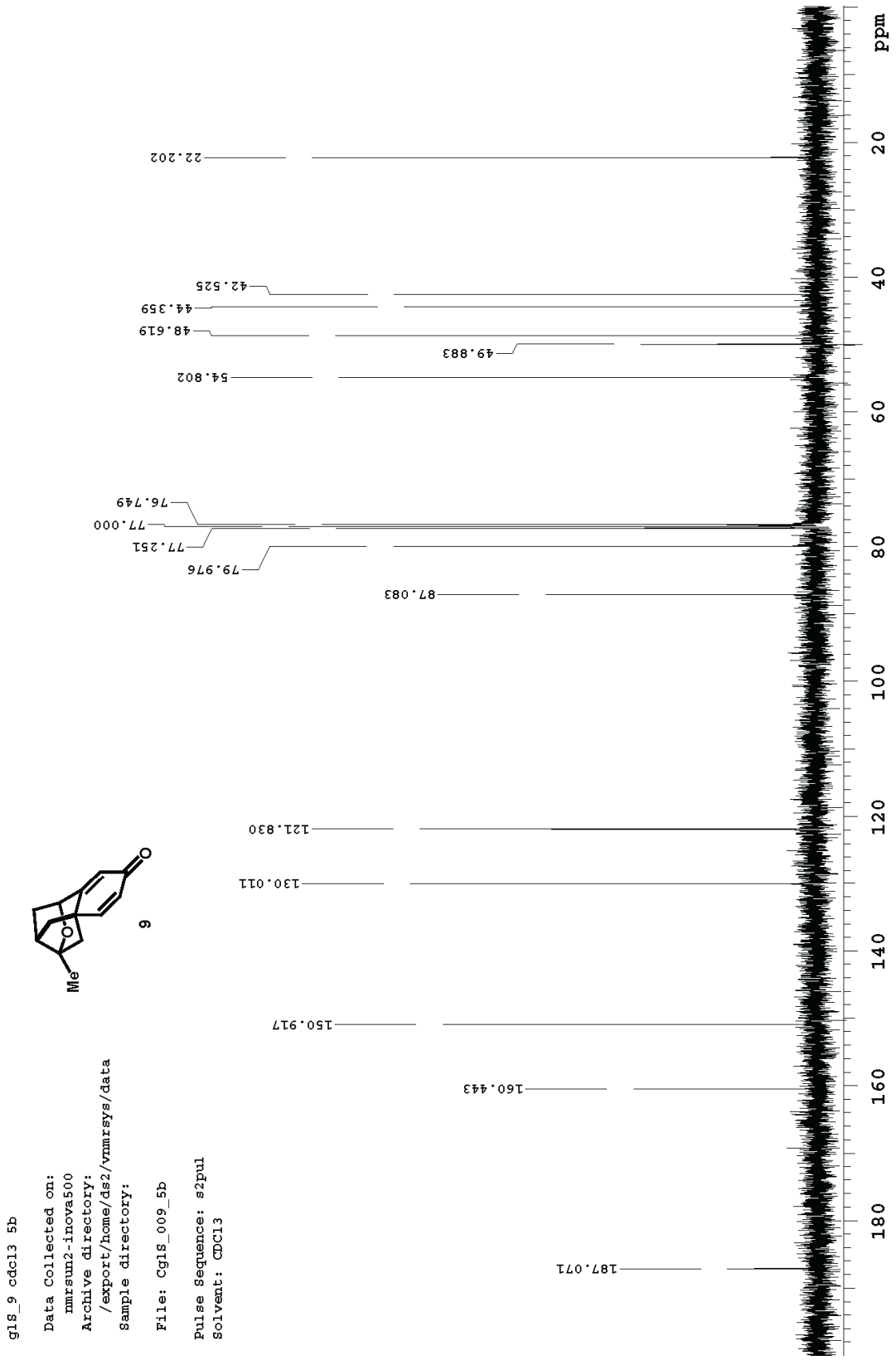


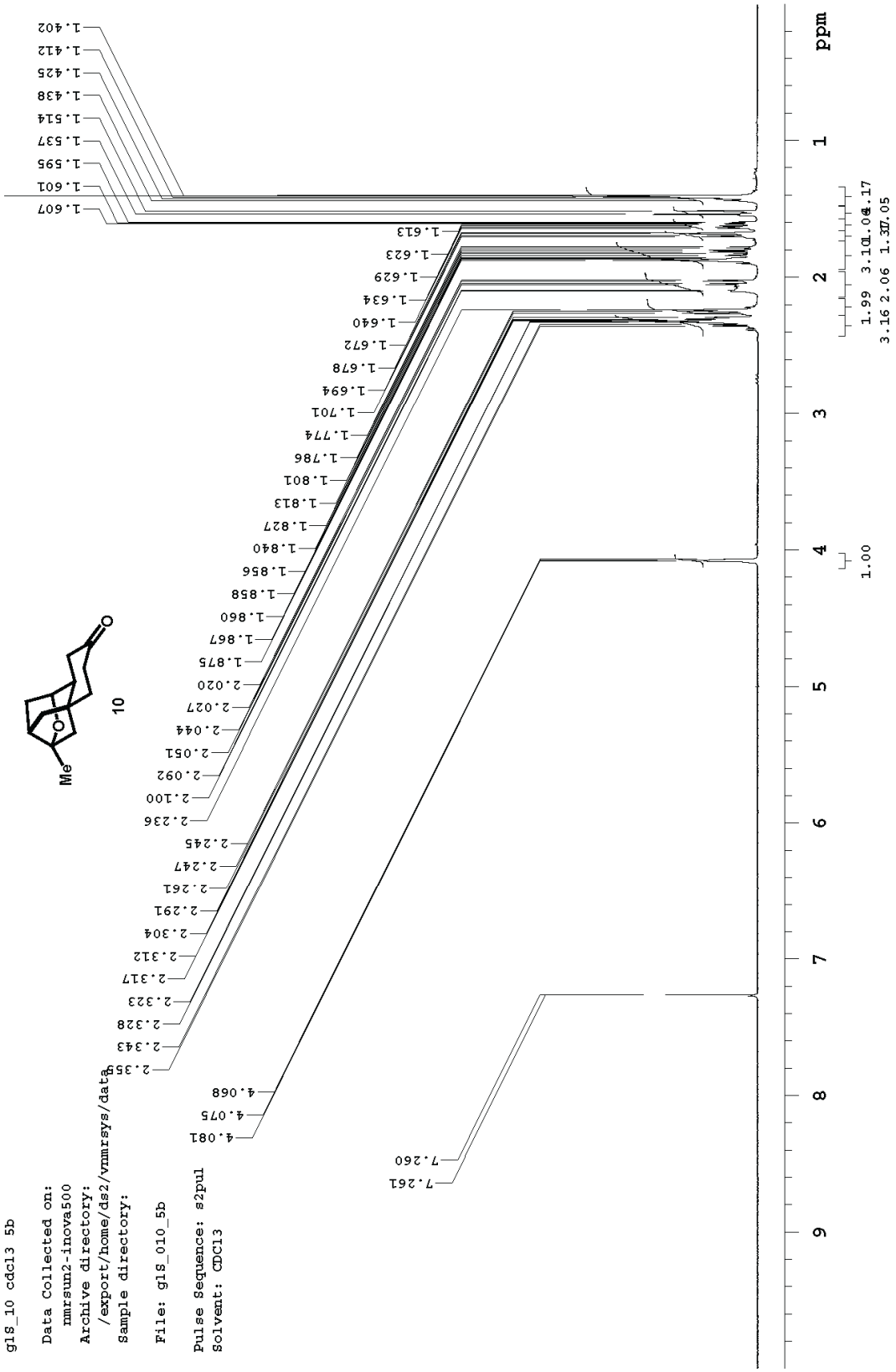
8

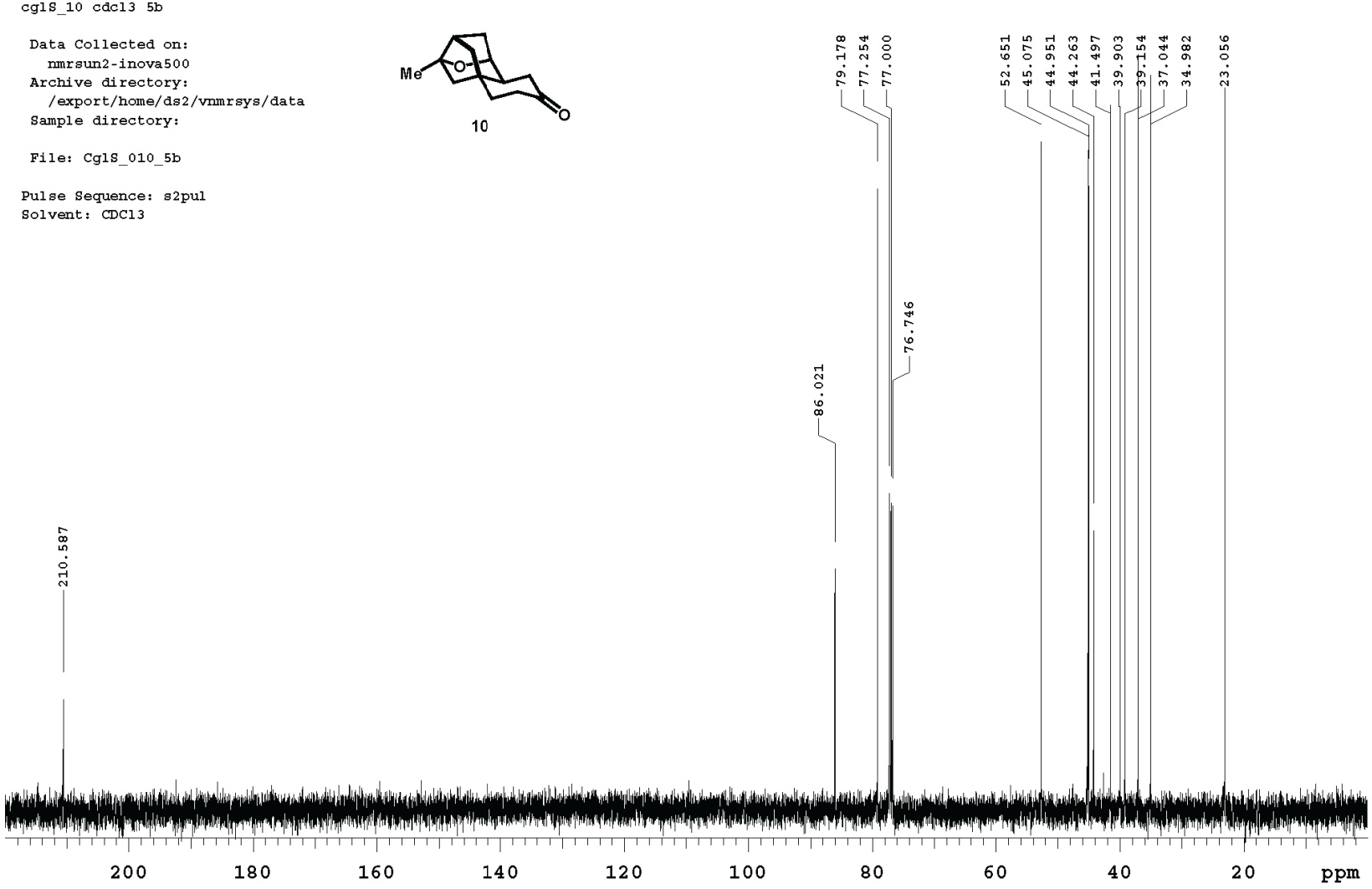


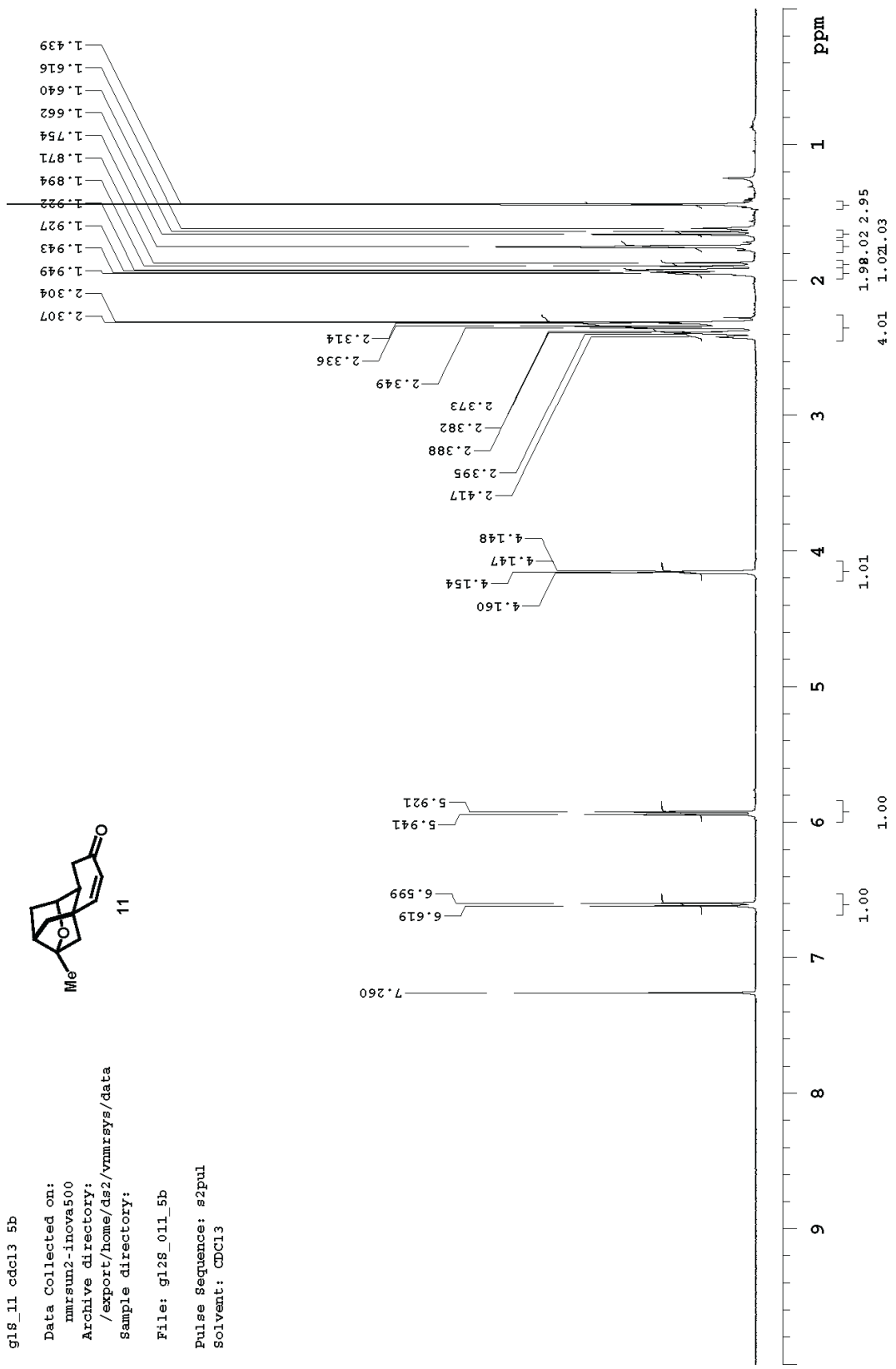

STANDARD PROTON PARAMETERS
Pulse Sequence: gHSQC
Solvent: Benzene
Temp. 22.0 C / 295.1 K
User: 1-14-87
INOVA-500 "Inova500b"
Relax. delay 1.000 sec
Acq. time 0.136 sec
Width 3751.6 Hz
2D Width 21378.9 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 500.1739929 MHz
DECOUPLE C13, 125.7782532 MHz
Power 45 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.063 sec
F1 DATA PROCESSING
Gauss apodization 0.011 sec
FT size 1024 x 2048
Total time 21 min, 15 sec
Me
O
Br
8
OTIPS
F2 (ppm)
F1 (ppm)

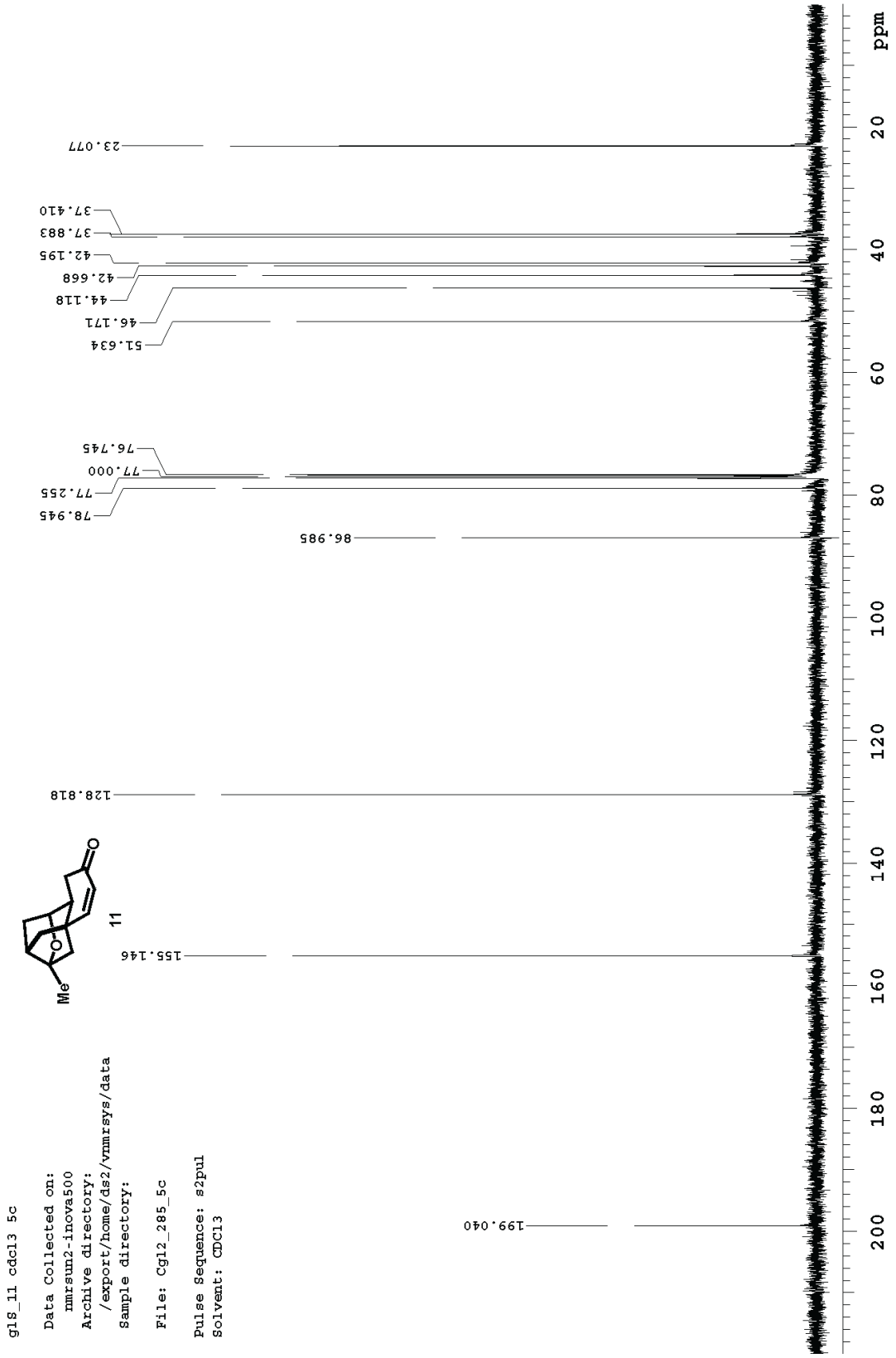

gls_9 cdcl3 5b
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: gls_009_5b
Pulse Sequence: s2pul
Solvent: CDCl3
Me
O
O
9
ppm
1
2
3
4
5
6
7
8
9
1.505
1.514
1.530
1.537
1.763
1.786
1.918
1.924
1.940
1.947
1.968
1.990
2.149
2.155
2.162
2.168
2.172
2.178
2.185
2.190
2.221
2.230
2.572
2.585
2.597
4.710
4.701
6.108
6.111
6.301
6.305
6.321
6.325
6.650
6.670
7.260


gls_9 cdcl3 5b
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: Cgls_009_5b
Pulse Sequence: s2pul
Solvent: CDCl3
Me
O
O
9
187.071
160.443
150.917
130.011
121.830
87.083
79.976
77.251
77.000
76.749
54.802
49.883
48.619
44.359
42.525
22.202
ppm
180
160
140
120
100
80
60
40
20


gls_10 cdcl3 5b
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: gls_010_5b
Pulse Sequence: s2pul
Solvent: CDCl3
ppm
1.607
1.601
1.595
1.537
1.514
1.438
1.425
1.412
1.402
1.613
1.623
1.629
1.634
1.640
1.672
1.678
1.694
1.701
1.774
1.786
1.801
1.813
1.827
1.840
1.856
1.858
1.860
1.867
1.875
2.020
2.027
2.044
2.051
2.092
2.100
2.236
2.245
2.247
2.261
2.291
2.304
2.312
2.317
2.323
2.328
2.343
2.355
4.068
4.075
4.081
7.260
7.261
1.00
1.99
3.16
2.06
1.37
10
Me
O
O


cg1S_10 cdcl3 5b
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: Cg1S_010_5b
Pulse Sequence: s2pul
Solvent: CDCl3
Me
O
O
10
79.178
77.254
77.000
76.746
86.021
210.587
52.651
45.075
44.951
44.263
41.497
39.903
39.154
37.044
34.982
23.056
200
180
160
140
120
100
80
60
40
20
ppm


gl8_11 cdcl3 5b
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: gl2S_011_5b
Pulse Sequence: s2pul
Solvent: CDCl3
11
Me
O
O
7.260
6.619
6.599
5.941
5.921
4.160
4.154
4.147
4.148
2.417
2.395
2.388
2.382
2.373
2.349
2.336
2.314
2.307
2.304
1.949
1.943
1.927
1.922
1.894
1.871
1.754
1.662
1.640
1.616
1.439
1.00
1.00
1.01
4.01
1.98
1.02
2.95
1.02
1.03
ppm

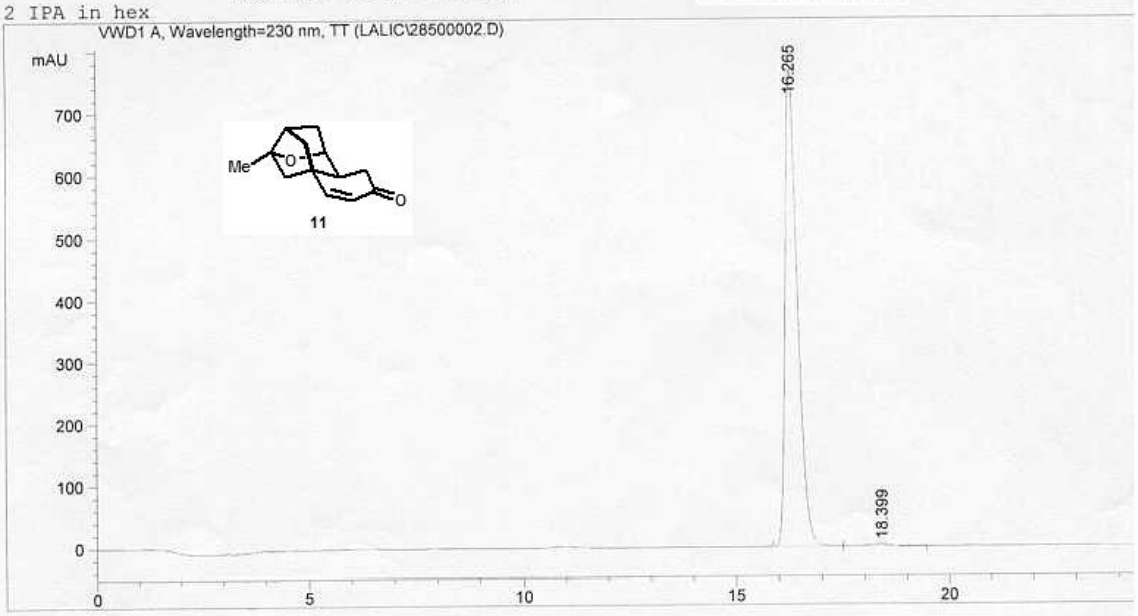

gl8_11 cdcl3 5c
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: Cgl2_285_5c
Pulse Sequence: s2pul
Solvent: CDCl3
Me
11
199.040
155.146
128.818
86.985
78.945
77.255
77.000
76.745
51.634
46.171
44.118
42.668
42.195
37.883
37.410
23.077
ppm

Data File C:\HPCHEM\1\DATA\LALIC\28500002.D Sample Name: 228

```
Injection Date  : 8/2/2007 3:40:47 PM          Seq. Line :   1
Sample Name     : 2285_                       Location : Vial 1
Acq. Operator   : Gl                             Inj :   1
Acq. Instrument : Instrument 1
Acq. Method     : C:\HPCHEM\1\METHODS\LALIC\FINALINT.M
Last changed    : 8/2/2007 2:58:46 PM by Gl
Analysis Method : C:\HPCHEM\1\METHODS\LALIC\FINALINT.M
Last changed    : 8/2/2007 4:15:16 PM by Gl
                  (modified after loading)
```

2% iPrOH in hexane AD-H

2 IPA in hex



Area Percent Report

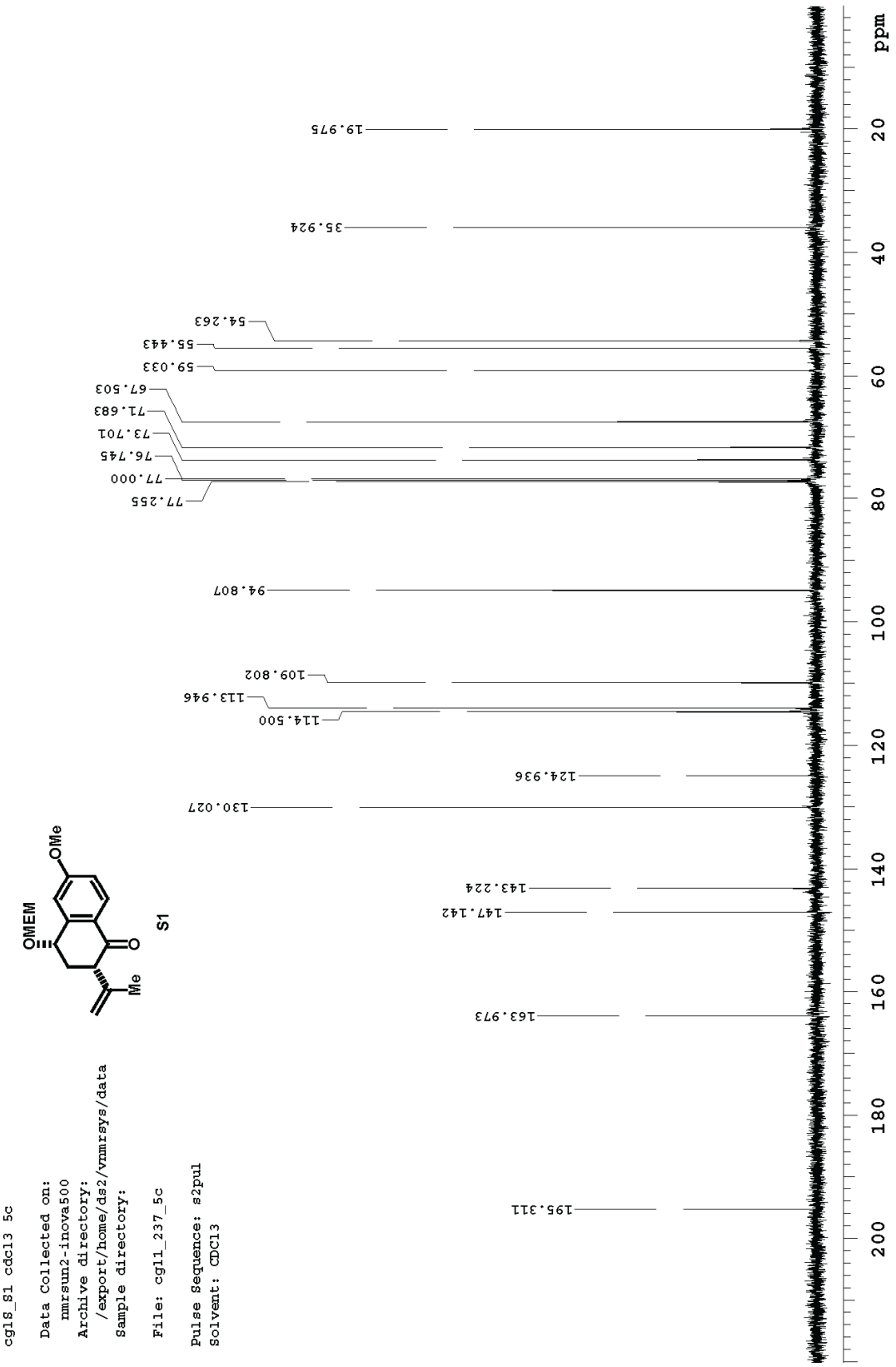
```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

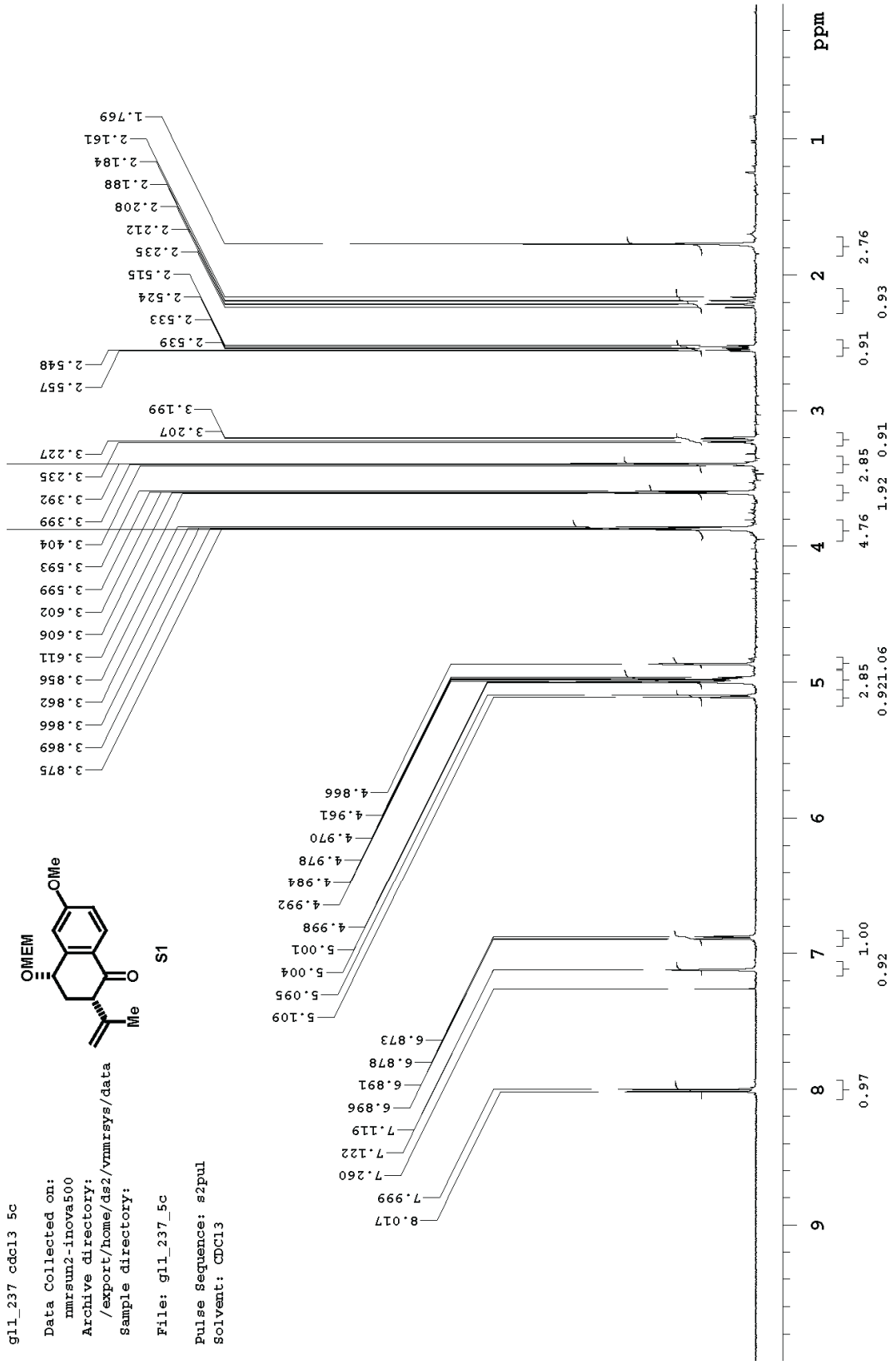
Signal 1: VWD1 A, Wavelength=230 nm, TT

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.265	BB	0.3013	1.52692e4	769.94861	99.1367
2	18.399	BB	0.5009	132.96970	3.63604	0.8633
Totals :				1.54022e4	773.58465	

Results obtained with enhanced integrator!

*** End of Report ***


cgl8_S1 cdcl3 5c
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: cgl1_237_5c
Pulse Sequence: s2pul
Solvent: CDCl3
OMe
OMEM
O
Me
S1
195.311
163.973
147.142
143.224
130.027
124.936
114.500
113.946
109.802
94.807
77.255
77.000
76.745
73.701
71.683
67.503
59.033
55.443
54.263
35.924
19.975
ppm
200
180
160
140
120
100
80
60
40
20


gl1_237 cdcl3 5c
Data Collected on:
nmrsun2-inova500
Archive directory:
/export/home/ds2/vnmrsys/data
Sample directory:
File: gl1_237_5c
Pulse Sequence: s2pul
Solvent: CDCl3
OMe
OMEM
O
Me
S1
ppm
1
2
3
4
5
6
7
8
9
1.769
2.161
2.184
2.188
2.208
2.212
2.235
2.515
2.524
2.533
2.539
2.548
2.557
3.199
3.207
3.227
3.235
3.392
3.399
3.404
3.593
3.599
3.602
3.606
3.611
3.856
3.862
3.866
3.869
3.875
4.866
4.961
4.970
4.978
4.984
4.992
4.998
5.001
5.004
5.095
5.109
6.873
6.878
6.891
6.896
7.119
7.122
7.260
7.999
8.017
0.97
1.00
0.92
2.85
0.921.06
4.76
2.85
1.92
0.91
0.91
2.76
0.93