Asymmetric Construction of Rings A–D of Daphnicyclidin Type Alkaloids

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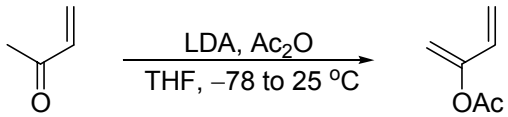
Supporting Information – Table of Contents

Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless additional purification is stated in the procedure. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 25 ºC). Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with ceric ammonium molybdate or potassium permanganate. Flash column chromatography was performed using normal phase silica gel (60 Å, 230-240 mesh, Merck KGA). ^{1}H NMR spectra were recorded on Bruker spectrometers (at 500 or 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (at 125 or 150 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on an Applied System REACT-IR 1000 spectrometer or a Varian 640-IR FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Optical

rotations were measured with a Jasco P-1010 polarimeter. High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility.

Experimental Procedures



S-1

1-Methyleneprop-2-enyl acetate (S-1).[1] A solution of *n*-butyllithium (145 mL, 276 mmol, 1.9 M in hexanes) was added dropwise to a solution of diisopropylamine (42.0 mL, 300 mmol) in THF (190 mL) over 40 min at –78 °C, ensuring that the temperature did not rise above –60 °C (internal measure). The cooling bath was removed, and the solution was allowed to warm to –25 °C over 15 min. The solution was then recooled to –78 °C. A solution of freshly distilled methyl vinyl ketone (20.8 mL, 250 mmol) in THF (20 mL) was added over 30 min. After maintaining the reaction for 15 min at –78 °C, acetic anhydride (30.7 mL, 325 mmol) was added over 20 min, resulting in a viscous yellow suspension. The cooling bath and the reaction mixture were allowed to slowly warm to rt and then stirred at rt for 15 h. Pentane (225 mL) was then added, along with saturated aqueous sodium bisulfate (300 mL). The layers were separated, and the aqueous layer was extracted with pentane (225 mL). The combined organic extracts were washed with brine (2 × 100 mL), dried over $MgSO_4$, filtered, and then concentrated to a volume of ~120 mL in vacuo. The mixture was then further concentrated by short path distillation (1 atm) to ~60 mL total volume. Distillation of this residue under partial vacuum (~40 torr, 55 °C at thermometer head) afforded **S-1** (13.2 g, 47%) as a colorless oil, contaminated with THF and *N*,*N*-diisopropylacetamide (approximately 85% pure by ^{1}H NMR analysis). This material was used in the subsequent Diels-Alder reaction without further purification:[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (ddd, J = 17.2, 10.9, 0.3 Hz, 1H), 5.29 (dq, J = 17.2, 1.5, 0.6 Hz, 1H), 5.18 (dddd, J = 10.9, 1.5, 0.8, 0.8 Hz, 1H), 5.03 (m, 1H), 4.94 (ddd, J = 1.6, 1.6, 0.6 Hz, 1H), 2.23 (s, 3H).

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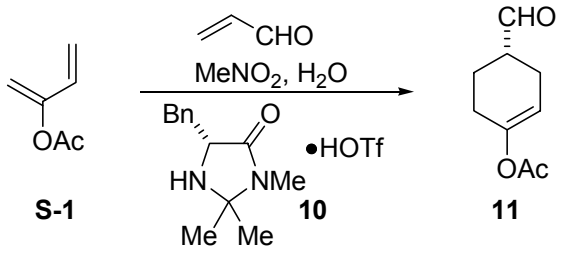
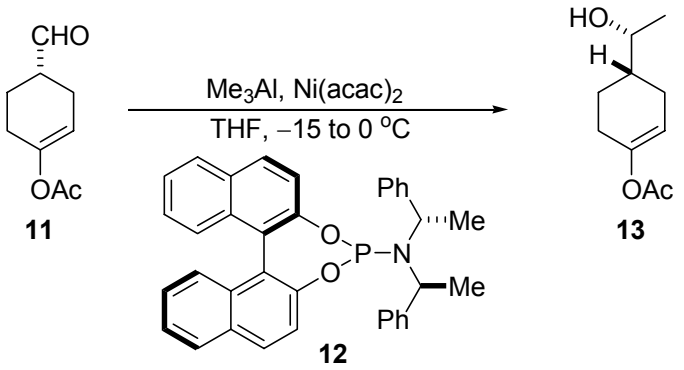
[1] Kowalski, M. D. Studies Toward the Enantioselective Total Synthesis of Manzamine A. Ph.D. Dissertation, University of California, Irvine, CA 2008.

[2] For an alternative preparation of **S-1**, see: Hagemeyer, H. J.; Hull, D. C. *Ind. Eng. Chem.* **1949**, *41*, 2920–2924.



(*S*)-4-Formylcyclohex-1-enyl acetate (11). Prepared by the general method of MacMillan.[3b] Freshly distilled acrolein (1.2 mL, 18 mmol) was added to a solution of acetoxydiene **S-1** (1.2 g, ~85% pure, 9 mmol) and catalyst **10**[3] (0.082 g, 0.22 mmol) in water-saturated nitromethane (9 mL). Aliquots of the reaction mixture were diluted with $CDCl_3$ and analyzed directly by ^{1}H NMR spectroscopy, with no starting material detected after 21 h. The reaction mixture was then filtered through a plug of silica gel (3 x 9 cm) and eluted with 100 mL each of 20%, 30%, and 50% ethyl acetate in hexanes. The product-containing fractions were concentrated in vacuo to give a solution of the Diels-Alder product and nitromethane. The nitromethane was removed in vacuo at approximately 10 torr pressure. The residue was purified by flash column chromatography (silica gel, gradient: 1.5:1 to 1:1 hexanes:Et_2O), which separated the desired product from a slightly faster-eluting impurity. Aldehyde **11** (1.17 g, 77%) was isolated as a colorless oil: $[\alpha]^{27}_{589}$ –60, $[\alpha]^{27}_{577}$ –63, $[\alpha]^{27}_{546}$ –71, $[\alpha]^{27}_{435}$ –130, $[\alpha]^{27}_{405}$ –162 (*c* 1.85, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 (s, 1H), 5.41 (s, 1H), 2.57–2.52 (m, 1H), 2.37–2.35 (m, 2H), 2.34–2.28 (m, 1H), 2.22–2.15 (m, 1H), 2.13–2.10 (m, 1H), 2.11 (s, 3H), 1.85–1.79 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1 (CH), 169.2 (C), 148.1 (C), 111.9 (CH), 45.2 (CH), 25.4 (CH_2), 23.0 (CH_2), 22.2 (CH_2), 20.9 (CH_3); IR (film) 2931, 2848, 2719, 1748, 1721, 1692, 1553, 1439, 1366, 1218, 1119, 1040, 909 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_9H_{13}O_3$ [$(M+H)^+$]: 169.0864; found: 169.0866. The ee of the enantiomeric product **ent-11**, prepared using catalyst **ent-10**, was previously determined to be 91% by ^{1}H NMR analysis of a Mosher ester derivative.[1]

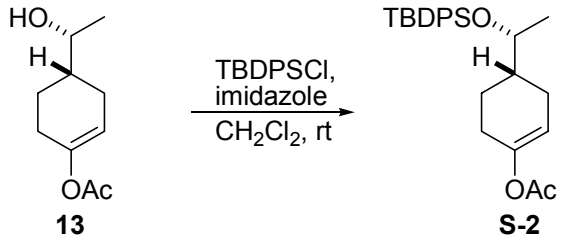
[3] Catalyst **10** was prepared from its hydrochloride salt by a literature procedure: a) Jen, W. S.; Wiener, J. J. M.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2000**, *122*, 9874–9875. The hydrochloride salt of **10** was in turn prepared from (*R*)-phenylalanine methyl ester hydrochloride by a literature procedure: b) Ahrendt, K. A.; Borths, C. J.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244.



4-((1*R*)-1-Hydroxyethyl)(4*S*)cyclohex-1enyl acetate (13). Prepared by the general procedure of Woodward.[4] Phosphoramidite ligand **12**[5] (0.361 g, 0.669 mmol), $Ni(acac)_2$ (0.086 g, 0.34 mmol) and THF (105 mL) were combined in a round-bottomed flask. The solution was cooled to 0 °C and stirred for 10 min at 0 °C. Aldehyde **11** (5.63 g, 33.5 mmol) was added, along with a THF rinse (5 mL). The solution was cooled to –20 °C, and trimethylaluminum (34 mL, 67 mmol, 2.0 M in toluene) was added dropwise by addition funnel, maintaining a temperature below –8 °C (internal measure). The solution was warmed to 0 °C and stirred for 1.5 h at 0 °C. The reaction mixture was then transferred through a wide-bored cannula into a stirring, biphasic mixture of aqueous 3 N HCl (110 mL) and Et_2O (160 mL), keeping the temperature below 12 °C. The mixture was then allowed to warm to rt and stirred at rt for 30 min. The layers were separated and the aqueous portion was extracted with Et_2O (160 mL). The combined organic portions were diluted with hexanes (120 mL) and washed with 1 N HCl (120 mL) and brine (120 mL). The combined aqueous washes were then extracted with Et_2O (2 × 160 mL). The combined organic portions were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, gradient: 3:7 EtOAc:hexanes to 1:1 EtOAc:hexanes) to give **13** (5.80 g, 94%, 5.7:1 dr as determined by ^1H NMR analysis) as a colorless oil. Because the diastereomeric alcohols were not separable at this stage, the mixture was characterized, with only the signals for the major isomer reported:[6] ^1H NMR (500 MHz, $CDCl_3$) δ 5.39–5.38 (m, 1H), 3.74 (appt quint, J = 6.0 Hz, 1H), 2.32–2.22 (m, 2H), 2.14–2.10 (m, 1H), 2.12 (s, 3H), 2.05–1.99 (m, 1H), 1.83–1.79 (m, 1H), 1.65–1.59 (m, 1H), 1.59–1.50 (m, 1H), 1.32 (br s, 1H), 1.22 (d, J= 6.5

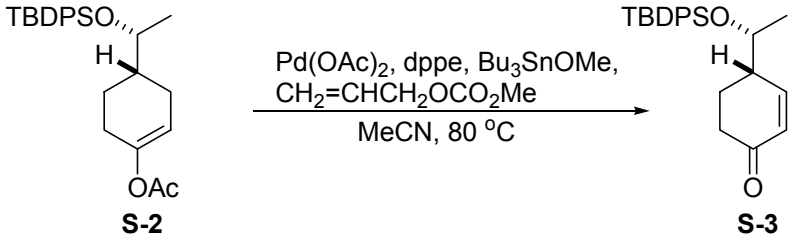
[4] Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2232–2234.
[5] Prepared by a literature procedure: Rimkus, A.; Sewald, N. *Synthesis* **2004**, 135–146.
[6] Optical rotation not determined because this product is a mixture of epimers.

Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5 (C), 148.1 (C), 113.2 (CH), 70.9 (CH), 40.3 (CH), 26.6 (CH_2), 25.1 (CH_2), 25.0 (CH_2), 21.1 (CH_3), 20.9 (CH_3); IR (film) 3400, 2971, 2929, 2896, 1752, 1694, 1439, 1370, 1223, 1113, 913 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{16}O_3Na$ [(M+Na)$^+$]: 207.0997; found: 207.1003.



13 **S-2**

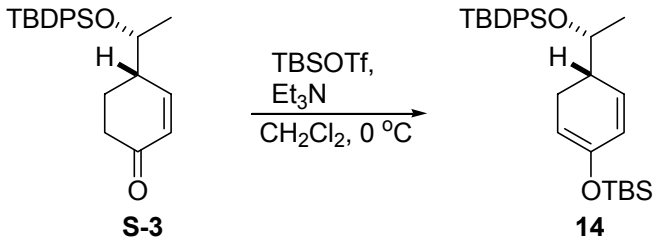
4-[(1*R*)-1-(2,2-Dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](4*S*)cyclohex-1-enyl acetate (S-2). *tert*-Butyldiphenylsilyl chloride (14.0 mL, 54.0 mmol) was added to a solution of secondary alcohol **13** (9.28 g, 51.5 mmol) and imidazole (7.20 g, 106 mmol) in CH_2Cl_2 (100 mL), resulting in the formation of a precipitate. The suspension was stirred for 16 h at rt, then diluted with CH_2Cl_2 (100 mL) and quenched with saturated aqueous ammonium chloride (100 mL). The layers were separated, and the aqueous portion was extracted with CH_2Cl_2 (2 × 200 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. Purification of the residue by silica gel flash column chromatography (gradient: 1:49 EtOAc:hexanes to 1:9 EtOAc:hexanes) gave **S-2** (21.8 g, 100%) as a colorless oil and a 5.7:1 mixture of diastereomers. Because these stereoisomers were not separable at this stage, the mixture was characterized, with only the signals for the major isomer being reported:[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 4H), 7.46–7.37 (m, 6H), 5.37–5.35 (m, 1H), 3.84–3.80 (m, 1H), 2.26–2.24 (m, 1H), 2.17–1.99 (m, 3H), 2.13 (s, 3H), 1.82–1.78 (m, 1H), 1.71–1.64 (m, 1H), 1.57 (qd, *J* = 12.0, 5.5 Hz, 1H), 1.06 (s, 9H), 1.01 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5 (C), 148.2 (C), 135.92 (CH), 135.89 (CH), 134.9 (C), 134.1 (C), 129.5 (CH), 129.4 (CH), 127.5 (CH), 127.3 (CH), 113.5 (CH), 72.3 (CH), 40.9 (CH), 27.03 (CH_3), 26.99 (CH_2), 25.1 (CH_2), 24.8 (CH_2), 21.1 (CH_3), 20.4 (CH_3), 19.4 (C); IR (film) 3072, 2960, 2933, 2894, 2858, 1756, 1694, 1428, 1362, 1223, 1208, 1034, 1007 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{34}O_3SiNa$ [(M+Na)$^+$]: 445.2175; found: 445.2164.



S-2 **S-3**

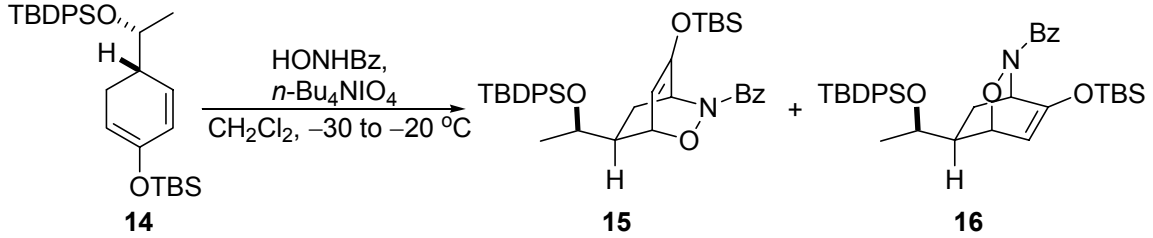
4-[(1*R*)-1-(2,2-Dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](4*S*)cyclohex-2-en-1-one (S-3). Prepared by the general procedure of Tsuji.[7] Allyl methyl carbonate (8.39 mL, 73.8 mmol), 1,2-bis(diphenylphosphino)ethane (1.47 g, 3.69 mmol), and palladium (II) acetate (0.829 g, 3.69 mmol) were added to a solution of enol acetate **S-2** (15.6 g, 36.9 mmol) in MeCN (185 mL). The resultant suspension was stirred for 10 min at rt. Tributyltin methoxide (3.2 mL, 11 mmol) was added and the suspension was heated at 80 °C for 3 h. The suspension was allowed to cool to rt and was filtered through a silica gel plug, eluting with EtOAc. The organic solution was concentrated in vacuo and the residue was purified by silica gel flash column chromatography (gradient: 1:9 EtOAc:hexanes to 1:3 EtOAc:hexanes) to give enone **S-3** (12.7 g, 91%) as a colorless oil and a 5.7:1 mixture of diastereomers. Because these stereoisomers were not separable at this stage, the mixture was characterized, with only the signals for the major isomer being reported:[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70–7.67 (m, 4H), 7.46–7.38 (m, 6H), 6.95 (dt, J = 10.0, 2.0 Hz, 1H), 6.01 (dd, J = 10.0, 2.5 Hz, 1H), 3.94 (appt quint, J = 6.0 Hz, 1H), 2.53–2.48 (m, 2H), 2.32 (ddd, J = 17.0, 14.0, 5.0 Hz, 1H), 2.07–2.04 (m, 1H), 1.89–1.81 (m, 1H), 1.09 (d, J = 6.0 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9 (C), 151.7 (CH), 135.85 (CH), 135.78 (CH), 134.2 (C), 133.7 (C), 129.8 (CH), 129.71 (CH), 129.68 (CH), 127.7 (CH), 127.5 (CH), 71.5 (CH), 44.1 (CH), 37.3 (CH_2), 27.0 (CH_3), 24.5 (CH_2), 20.5 (CH_3), 19.3 (C); IR (film) 3072, 3049, 2960, 2933, 2889, 2858, 1683, 1472, 1428, 1389, 1362, 1187, 1136, 1106, 1084, 1009 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{30}O_2SiNa$ [$(M+Na)^+$]: 401.1913; found: 401.1911.

[7] Minami, I.; Takahashi, K.; Shimizu, I.; Kimura, T.; Tsuji, J. *Tetrahedron* **1986**, *42*, 2971–2977.



S-3 **14**

1-{(1*R*)-1-[(1*S*)-4-(1,1,2,2-Tetramethyl-1-silapropoxy)cyclohexa-2,4-dienyl]ethoxy}-2,2-dimethyl-1,1-diphenyl-1-silapropane (14). Triethylamine (6.6 mL, 47 mmol) was added to a solution of enone **S-3** (8.98 g, 23.7 mmol) in CH_2Cl_2 (120 mL) at 0 °C, followed by dropwise addition of *tert*-butyldimethylsilyl trifluoromethanesulfonate (5.99 mL, 26.1 mmol). The solution was maintained at 0 °C for 1 h, then methanol (1.5 mL) was added and the solution was concentrated in vacuo. The oily residue was extracted with pentane (4 × 25 mL), and decanted, and subsequent concentration of the combined organic extracts in vacuo afforded **14** (11.9 g, 102%) as a yellow oil and a 5.7:1 mixture of diastereomers. The material was used in the subsequent reaction without further purification. The mixture was characterized, with only the signals for the major isomer being reported:[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 4H), 7.44–7.36 (m, 6H), 5.72 (dd, *J* = 10.0, 3.0 Hz, 1H), 5.67 (dt, *J* = 10.0, 2.0 Hz, 1H), 4.85 (br s, 1H), 3.87 (appt quint, *J* = 6.0 Hz, 1H), 2.47–2.42 (m, 1H), 2.26 (ddd, *J* = 16.5, 14.0, 3.5 Hz, 1H), 2.17 (ddd, *J* = 16.5, 9.0, 5.5 Hz, 1H), 1.06 (s, 9H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.93 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 135.88, 135.85, 134.7, 134.2, 130.1, 129.5, 129.4, 127.5, 127.4, 126.3, 102.0, 71.7, 41.4, 27.0, 25.7, 22.9, 20.3, 19.4, 18.1, –4.47, –4.52; IR (film) 3072, 3051, 2958, 2931, 2889, 2858, 1652, 1590, 1472, 1463, 1428, 1362, 1254, 1111, 1086, 1007 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{45}O_2Si_2$ [$(M+H)^+$]: 493.2958; found: 493.2961.



14 **15** **16**

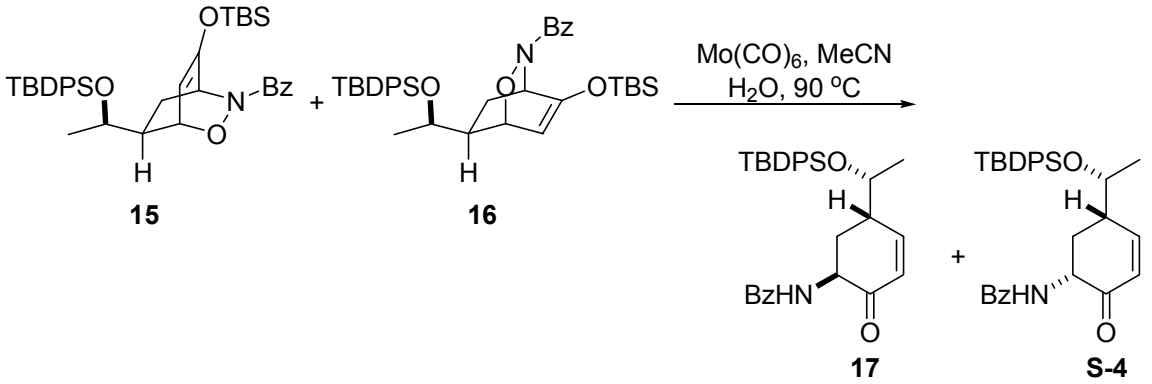
8-[(1*R*)-1-(2,2-Dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](1*S*,4*S*,8*S*)-2-aza-3-oxa-6-(1,1,2,2-tetramethyl-1-silapropoxy)bicyclo[2.2.2]oct-5-en-2-yl phenyl ketone (15) and

8-[(1*R*)-1-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](8*S*,1*R*,4*R*)-2-aza-3-oxa-6-(1,1,2,2-tetramethyl-1-silapropoxy)bicyclo[2.2.2]oct-5-en-2-yl phenyl ketone (16). Benzohydroxamic acid (3.58 g, 26.1 mmol) was added to a solution of dienoxysilane **14** (11.7 g, 23.7 mmol) in CH_2Cl_2 (130 mL) and the resultant yellow suspension was cooled to –35 °C. A solution of tetra-*n*-butylammonium periodate (11.3 g, 26.1 mmol) in CH_2Cl_2 (30 mL) was added dropwise by syringe, maintaining a temperature below –30 °C (internal measure), resulting in an orange solution. The reaction was maintained at –30 to –20 °C for 2.5 h, then the mixture was poured into a biphasic mixture of Et_2O (300 mL) and 2 M aqueous sodium thiosulfate (150 mL). The layers were separated and the aqueous portion was extracted with Et_2O (300 mL). The combined organic extracts were washed with 2 M aqueous sodium thiosulfate (150 mL) and water (2 × 225 mL). The organic layer was then diluted with hexanes (500 mL), washed with brine (2 × 225 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:9 EtOAc:hexanes to 1:4 EtOAc:hexanes) to give **15** and **16** (9.55 g, 64%, 6:1 dr) as a colorless foam. The isomers were chromatographically separable for characterization purposes. The undesired diastereomer from the Ni-catalyzed methylation step was also separated chromatographically at this stage. **16** elutes first, followed by **15**, which is then followed by the undesired diastereomer.

15: $[\alpha]^{27}_{589}$ +37, $[\alpha]^{27}_{577}$ +39, $[\alpha]^{27}_{546}$ +44, $[\alpha]^{27}_{435}$ +73, $[\alpha]^{27}_{405}$ +89 (*c* 1.67, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 8.10 (br d, *J* = 7.0 Hz, 2H), 7.71–7.69 (m, 4H), 7.24–7.18 (m, 6H), 7.11–7.06 (m, 3H), 5.28 (br s, 1H), 5.22 (dd, *J* = 6.0, 3.5 Hz, 1H), 4.93 (dd, *J* = 6.0, 2.5 Hz, 1H), 3.27 (dq, *J* = 10.0, 6.0 Hz, 1H), 2.44–2.39 (m, 1H), 1.90 (ddd, *J* = 13.0, 9.0, 4.0 Hz, 1H), 1.05 (s, 9H), 0.99 (s, 9H), 0.75 (d, *J* = 6.0 Hz, 3H), 0.65 (ddd, *J* = 13.0, 5.0, 2.0 Hz, 1H), 0.21 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6, 323 K) δ 171.1 (C), 157.1 (C,broad at rt), 136.3 (CH), 136.2 (CH), 135.1 (C), 134.9 (C), 134.1 (C), 130.9 (CH), 130.1 (CH), 129.94 (CH), 129.92 (CH), 100.3 (CH), 75.9 (CH), 73.1 (CH) 53.5 (CH, broad at rt), 46.2 (CH), 27.2 (CH_3), 26.2 (CH_2), 25.8 (CH_3), 20.6 (CH_3), 19.5 (C), 18.2 (C), –4.3 (CH_3), –4.5 (CH_3), 3 missing carbons attributed to overlap with solvent; IR (film) 3072, 2958, 2931, 2896, 2860, 1638, 1472, 1428, 1376, 1341, 1254, 1233, 1219,

1104, 1077 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{37}H_{49}O_4Si_2Na$ [$(M+Na)^+$]: 650.3098; found: 650.3110.

16: $[\alpha]^{29}_{589}$ +28, $[\alpha]^{29}_{577}$ +28, $[\alpha]^{29}_{546}$ +32, $[\alpha]^{29}_{435}$ +60, $[\alpha]^{29}_{405}$ +73 (*c* 1.10, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 8.12 (br d, *J* = 7.0 Hz, 2H), 7.87–7.81 (m, 4H), 7.28–7.14 (m, 9H), 5.31 (d, *J* = 7.0 Hz, 1H), 5.19 (br s, 1H), 5.13 (dd, *J* = 7.0, 2.5 Hz, 1H), 4.08 (dq, *J* = 10.0, 6.0 Hz, 1H), 1.55 (ddd, *J* = 10.0, 10.0, 4.0 Hz, 1H), 1.38 (ddd, *J* = 13.0, 11.0, 3.0 Hz, 1H), 1.15 (s, 9H), 1.03–1.09 (m, 1H), 0.99 (s, 9H), 0.84 (d, *J* = 6.0 Hz, 3H), 0.20 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6, 323 K) δ 170.7 (C), 157.4 (C,broad at rt), 136.3 (CH), 136.2 (CH), 135.5 (C), 135.0 (C), 134.1 (C), 131.0 (CH), 130.1 (CH), 129.8 (CH), 128.5 (CH), 102.7 (CH), 74.4 (CH), 71.8 (CH) 53.5 (CH, broad at rt), 46.9 (CH), 27.3 (CH_3), 25.8 (CH_3), 25.1 (CH_2), 22.1 (CH_3), 19.8 (C), 18.2 (C), –4.4 (CH_3), –4.6 (CH_3), 3 missing carbons attributed to overlap with solvent; IR (film) 3072, 2958, 2931, 2896, 2860, 1642, 1472, 1428, 1389, 1378, 1362, 1254, 1237, 1136, 1111 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{37}H_{49}O_4Si_2Na$ [$(M+Na)^+$]: 650.3098; found: 650.3093.



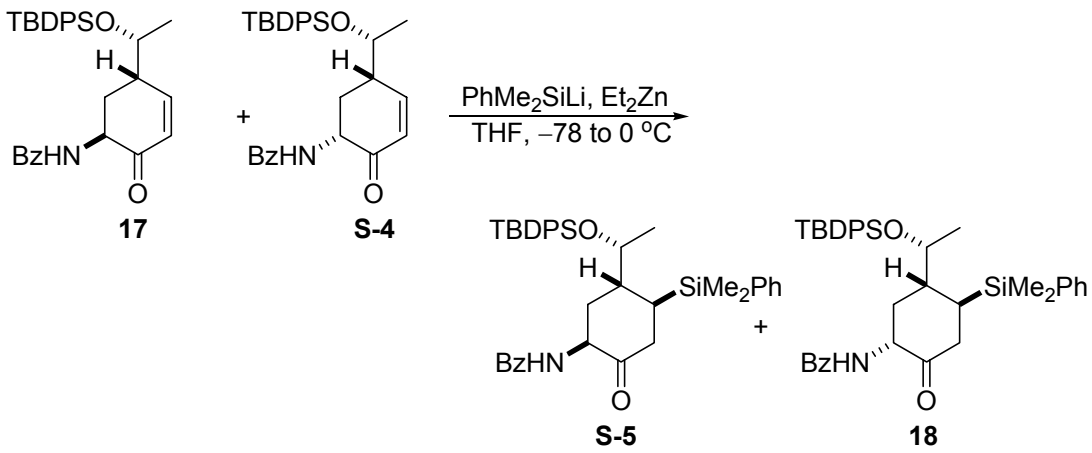
***N*-{5-[(1*R*)-1-(2,2-Dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](1*S*,5*S*)-2-oxocyclohex-3-enyl}benzamide (17) and *N*-{5-[(1*R*)-1-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](5*S*,1*R*)-2-oxocyclohex-3-enyl}benzamide (S-4).** Prepared by the general procedure of Ghosez.[8] Molybdenum hexacarbonyl (1.59 g, 6.04 mmol) was added to a mixture of **15** and **16** (3.79 g, 6.04 mmol) in acetonitrile (60 mL) and water (6 mL), resulting in a cloudy suspension. The flask containing the mixture was lowered into an oil bath that had been pre-heated to 90 °C and the solution was vigorously stirred. The

[8] Cabanal–Duvillard, I.; Berrien, J.–F.; Ghosez, L.; Husson, H.–P.; Royer, J. *Tetrahedron* **2000**, *56*, 3763–3769.

cloudy suspension became a yellow solution within 9 min. After 38 min at 90 °C, the yellow solution became dark brown and analysis of the reaction mixture by TLC indicated that no starting material remained. The reaction was removed from the oil bath and allowed to cool to rt. The mixture was then filtered through a silica gel plug, eluting with 1:1 EtOAc:hexanes. The filtrate was then concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 3:17 EtOAc:hexanes to 1:3 EtOAc:hexanes) to give the diastereomeric enones **17** (elutes first) and **S-4** (elutes second) (2.44 g, 81%, 5:1 dr) as a brown foam.

17: $[\alpha]^{24}_{589}$ –46, $[\alpha]^{24}_{577}$ –47, $[\alpha]^{24}_{546}$ –54, $[\alpha]^{24}_{435}$ –79, $[\alpha]^{24}_{405}$ –74 (*c* 0.91, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.73–7.71 (m, 4H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.46–7.38 (m, 8H), 7.07 (d, *J* = 4.0 Hz, 1H), 7.04 (dd, *J* = 10.0, 5.0 1H), 5.99 (d, *J* = 10.0 Hz, 1H), 4.64 (dt, *J* = 13.5, 5.0 Hz, 1H), 4.32 (appt quint, *J* = 6.0 Hz, 1H), 2.85 (dd, *J* = 13.5, 5.0 Hz, 1H), 2.70–2.67 (m, 1H), 1.92 (td, *J* = 13.5, 6.5 Hz, 1H), 1.40 (d, *J* = 6.0 Hz, 3H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6 (C), 167.3 (C), 153.1 (CH), 135.9 (CH), 135.8 (CH), 134.0 (C), 133.9 (C), 133.4 (C), 131.7 (CH), 129.9 (CH), 129.7 (CH), 128.5 (CH), 127.7 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 71.6 (CH), 52.6 (CH), 44.1 (CH), 30.6 (CH_2), 27.0 (CH_3), 22.5 (CH_3), 19.3 (C); IR (film) 3344, 3072, 3054, 2962, 2933, 2894, 2858, 1690, 1648, 1532, 1486, 1474, 1428, 1329, 1111, 1028 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{31}H_{36}NO_3Si$ $[(M+H)^+]$: 498.2465; found: 498.2466.

S-4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.69–7.67 (m, 4H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.48–7.38 (m, 8H), 7.15–7.11 (m, 2H), 6.17 (d, *J* = 10.5, 3.0 Hz, 1H), 4.65 (dt, *J* = 13.5, 5.0 Hz, 1H), 3.88 (appt quint, *J* = 6.0 Hz, 1H), 2.83–2.80 (m, 1H), 2.77–2.73 (m, 1H), 1.68 (appt quart, *J* = 12.5 Hz, 1H), 1.12 (d, *J* = 6.0 Hz, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9 (C), 167.3 (C), 152.5 (CH), 135.85 (CH), 135.81 (CH), 134.1 (C), 134.0 (C), 133.4 (C), 131.7 (CH), 129.9 (CH), 129.7 (CH), 128.6 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.1 (CH), 71.5 (CH), 55.6 (CH), 44.7 (CH), 32.8 (CH_2), 27.0 (CH_3), 20.9 (CH_3), 19.4 (C); IR (film) 3359, 3072, 2962, 2931, 2892, 2858, 1690, 1656, 1543, 1509, 1484, 1428, 1324, 1218, 1136, 1111, 1067 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{31}H_{36}NO_3Si$ $[(M+H)^+]$: 498.2465; found: 498.2471.



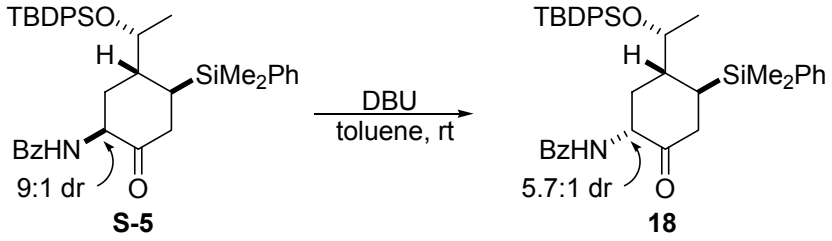
Preparation of phenyldimethylsilyllithium.[9] Lithium wire (295 mg, 42.5 mmol) was cut into BB-sized pieces, washed with pentane, and placed into a Schlenk flask, along with a magnetic stir bar. THF (25 mL) was added, and the mixture was cooled to 0 °C. Phenyldimethylsilyl chloride (2.10 mL, 12.5 mmol) was added and the mixture was sonicated for 2 h at 0 °C. After 1 h, the mixture became deep red. The mixture was then stirred overnight at 0 °C, then allowed to warm to rt. The prepared reagent was titrated by a total base method by adding the $PhMe_2SiLi$ solution (1.0 mL) to a solution of phenolphthalein (3 mg) in water (10 mL), followed by aqueous HCl (8.0 mL, 0.80 mmol, 0.10 M). Aqueous NaOH (3.4 mL, 0.34 mmol, 0.10 M) was then added dropwise to the solution until a pink color persisted, indicating a concentration of 0.46 M for the $PhMe_2SiLi$ solution.

***N*-{5-[(1*R*)-1-(2,2-Dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](4*S*,1*S*,5*R*)-4-(1-methyl-1-phenyl-1-silaethyl)-2-oxocyclohexyl}benzamide (S-5) and *N*-{5-[(1*R*)-1-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](4*S*,1*R*,5*R*)-4-(1-methyl-1-phenyl-1-silaethyl)-2-oxocyclohexyl}benzamide (18).** Prepared by the general procedure of Fleming.[10] A solution of diethylzinc (6.4 mL, 9.6 mmol, 1.5 M in toluene) was added to THF (40 mL) and the resultant solution was cooled to 0 °C. The previously prepared solution of phenyldimethylsilyllithium (21 mL, 9.6 mmol, 0.46 M in THF) was then added, and the solution was maintained for 15 min at 0 °C, then cooled to –78 °C. A solution of enones **17** and **S-4** (3.00 g, 6.03 mmol) in THF (15 mL with a 5 mL rinse) was added dropwise at –78 °C. The solution was maintained for 15 min at –78 °C, then

[9] Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527–2532.
[10] Crump, R. A. N. C.; Fleming, I.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 701–706.

allowed to slowly warm to 0 °C over 30 min. The reaction was then maintained at 0 °C for 30 min. Saturated aqueous NH_4Cl (60 mL) was then added to the solution, and the mixture was extracted with Et_2O (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:9 EtOAc:hexanes to 1:4 EtOAc:hexanes) to give the ketones **S-5** (elutes first) and **18** (elutes second) (3.09 g, 81%, 9:1 dr) as a colorless foam, along with approximately 0.260 g (approximated by ^{1}H NMR integration) of dimethylphenylsilanol that co-eluted with **S-5**.

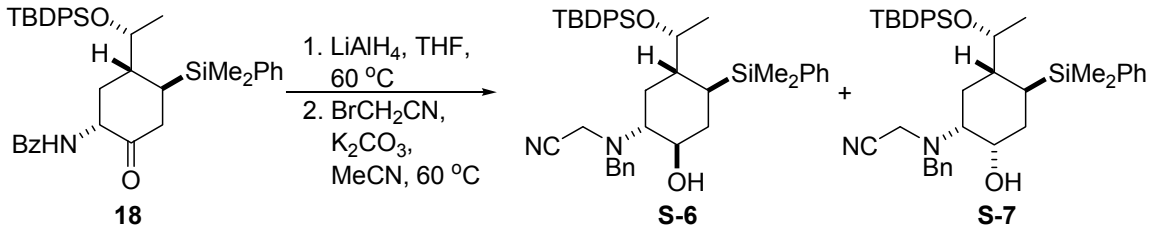
S-5:[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.52–7.31 (m, 14H), 7.01 (br d, *J* = 5.0 Hz, 1H), 4.36 (ddd, *J* = 12.5, 6.0, 5.5 Hz, 1H), 4.25 (dq, *J* = 8.0, 6.0 Hz, 1H), 2.70–2.67 (m, 1H), 2.13–2.07 (m, 2H), 2.02 (br m, 1H), 1.96 (dd, *J* = 14.5, 8.0 Hz, 1H), 1.50 (td, *J* = 13.5, 5.0 Hz, 1H), 1.42 (d, *J* = 6.0 Hz, 3H), 1.08 (s, 9H), 0.29 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3 (C), 166.8 (C), 137.0 (C), 136.1 (CH), 135.9 (CH), 134.0 (C), 133.9 (CH), 133.8 (C), 133.7 (C), 131.7 (CH), 129.8 (CH), 129.7 (CH), 129.2 (CH), 128.5 (CH), 127.83 (CH), 127.78 (CH), 127.5 (CH), 127.0 (CH), 69.1 (CH), 54.7 (CH), 42.6 (CH), 37.1 (CH_2), 33.6 (CH_2), 27.1 (CH_3), 25.1 (CH), 21.4 (CH_3), 19.5 (C), –3.4 (CH_3), –3.5 (CH_3); IR (film) 3346, 3072, 3051, 2958, 2933, 2894, 2858, 1717, 1648, 1511, 1484, 1428, 1378, 1364, 1316, 1252, 1111, 1079 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{39}H_{48}NO_3Si_2$ [$(M+H)^+$]: 634.3173; found: 634.3178.



***N*-{5-[(1*R*)-1-(2,2-Dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](4*S*,1*R*,5*R*)-4-(1-methyl-1-phenyl-1-silaethyl)-2-oxocyclohexyl}benzamide (18).** A solutio of enones **S-5** and **18** (5.29 g, 8.34 mmol) in toluene (55 mL) was cooled to 0 °C and DBU (0.19 mL, 1.3 mmol) was added dropwise. The solution was allowed to warm to rt and maintained at rt for 15 h. The reaction mixture was then filtered through a silica gel plug, eluting

with 1:3 EtOAc:hexanes. The filtrate was concentrated in vacuo and the residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give the ketones **18** and **S-5** (5.22 g, 99%, 5.7:1 dr) as a colorless foam.

18: $[\alpha]^{28}_{589}$ +53, $[\alpha]^{28}_{577}$ +57, $[\alpha]^{28}_{546}$ +65, $[\alpha]^{28}_{435}$ +131, $[\alpha]^{29}_{405}$ +173 (*c* 0.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.79–7.77 (m, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.53–7.44 (m, 7H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.0 Hz, 2H), 7.03 (br d, *J* = 6.0 Hz, 1H), 4.72 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H), 4.04–4.01 (m, 1H), 3.21 (ddd, *J* = 12.5, 6.0, 2.5 Hz, 1H), 2.35 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.22–2.16 (m, 2H), 1.44 (q, *J* = 12.5 Hz, 1H), 1.17 (ddd, *J* = 15.0, 12.0, 3.5 Hz, 1H), 1.06 (s, 9H), 0.68 (d, *J* = 6.0 Hz, 3H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.1 (C), 166.7 (C), 137.0 (C), 136.0 (CH), 135.8 (CH), 134.4 (C), 134.2 (C), 134.0 (C), 133.5 (CH), 131.5 (CH), 129.8 (CH), 129.6 (CH), 129.2 (CH), 128.5 (CH), 127.9 (CH), 127.6 (CH), 127.1 (CH), 69.5 (CH), 57.7 (CH), 44.4 (CH), 41.7 (CH_2), 36.7 (CH_2), 30.8 (CH), 27.0 (CH_3), 19.1 (C), 16.6 (CH_3), –3.8 (CH_3), –4.7 (CH_3); IR (film) 3415, 3328, 3072, 3051, 2960, 2933, 2894, 2860, 1717, 1661, 1534, 1513, 1486, 1428, 1362, 1252, 1111, 1069 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{39}H_{47}NO_3Si_2Na$ [$(M+Na)^+$]: 656.2992; found: 656.2994.



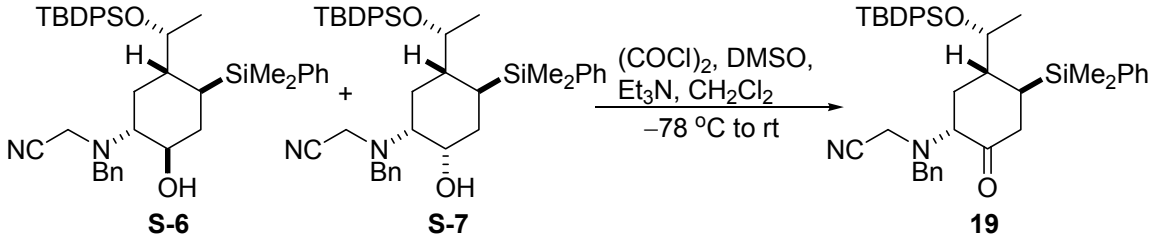
2-({5-[(1*R*)-1-(2,2-Dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](4*S*,1*R*,2*R*,5*R*)-2-hydroxy-4-(1-methyl-1-phenyl-1-silaethyl)cyclohexyl}benzylamino)ethanenitrile (S-6) and 2-({5-[(1*R*)-1-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl](2*S*,4*S*,1*R*,5*R*)-2-hydroxy-4-(1-methyl-1-phenyl-1-silaethyl)cyclohexyl}benzylamino)ethanenitrile (S-7).

Lithium aluminum hydride (9.2 mL, 9.2 mmol, 1.0 M in Et_2O) was added dropwise to a solution of ketone **18** (1.94 g, 3.06 mmol) in THF (20 mL) at 0 °C. The solution was allowed to warm to rt and then heated at 60 °C for 3.5 h. The reaction was then cooled to

0 °C and benzene (10 mL) and sodium fluoride (1.93 g, 45.9 mmol) were added. Water (777 μL, 43.1 mmol) was then added dropwise 0 °C. The mixture was allowed to warm to rt, then stirred vigorously at rt for 3 h. The suspension was filtered through celite, rinsing with THF (100 mL), and the filtrate was concentrated in vacuo. The resultant amino alcohols were used in the subsequent reaction without further purification. The crude mixture of amino alcohols was dissolved in MeCN (12 mL). Potassium carbonate (1.27 g, 9.18 mmol) was added, followed by bromoacetonitrile (0.62 μL, 8.9 mmol), and the resultant mixture was heated at 60 °C for 4.5 h. The mixture was then allowed to cool to rt, and water (30 mL) and Et_2O (60 mL) were added. The layers were separated and the aqueous portion was extracted with Et_2O (2 × 60 mL). The combined organic extracts were diluted with hexanes (50 mL) and washed with saturated aqueous sodium carbonate (20 mL), brine (20 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:9 acetone:hexanes to 1:4 acetone:hexanes) to give the nitriles **S-6** and **S-7** (1.94 g, 96%, 4:1 dr) as a colorless solid.

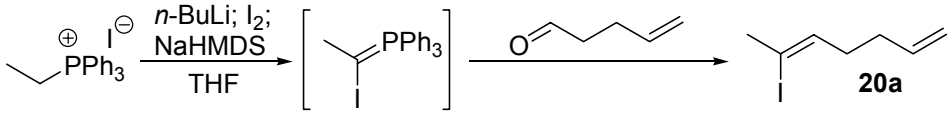
S-6: $[\alpha]^{27}_{589}$ –2.0, $[\alpha]^{27}_{577}$ –2.2, $[\alpha]^{27}_{546}$ –3.2, $[\alpha]^{28}_{435}$ –8.4, $[\alpha]^{28}_{405}$ –12.6 (*c* 1.36, $CHCl_3$); ^{1}H NMR (600 MHz, C_6D_6) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.28–7.24 (m, 6H), 7.18–7.06 (m, 10H), 4.11–4.08 (m, 1H), 3.75 (d, *J* = 13.0 Hz, 1H), 3.50 (d, *J* = 13.0 Hz, 1H), 3.15 (ddd, *J* = 10.0, 10.0, 4.5 Hz, 1H), 2.95 (br s, 1H), 2.86 (d, *J* = 17.5 Hz, 1H), 2.76 (br d, *J* = 12.0 Hz, 1H), 2.63 (d, *J* = 17.5 Hz, 1H), 2.33 (ddd, *J* = 12.5, 9.5, 3.0 Hz, 1H), 2.14–2.11 (m, 1H), 1.70–1.64 (m, 1H), 1.25–1.19 (m, 1H), 1.23 (s, 9H), 1.07 (q, *J* = 12.0 Hz, 1H), 0.78 (d, *J* = 6.0 Hz, 3H), 0.49 (ddd, *J* = 14.0, 11.0, 3.0 Hz, 1H), 0.00 (s, 3H), –0.01 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 138.7 (C), 137.7 (C), 136.35 (CH), 136.29 (CH), 134.9 (C), 134.8 (C), 133.9 (CH), 130.0 (CH), 129.9 (CH), 129.7 (CH), 129.1 (CH), 129.0 (CH), 128.5 (CH), 116.9 (C), 70.75 (CH), 70.64 (CH), 69.2 (CH), 53.3 (CH_2), 46.7 (CH), 38.2 (CH_2), 35.5 (CH_2), 27.3 (CH_3), 25.8 (CH), 24.2 (CH_2), 19.4 (C), 17.1 (CH_3), –3.1 (CH_3), –4.4 (CH_3), 3 missing carbons attributed to overlap with solvent and/or accidental equivalence; IR (film) 3500, 3070, 2952, 2931, 2898, 2858, 1590, 1462, 1428, 1382, 1362, 1250, 1111, 1082, 1023 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{41}H_{52}N_2O_2Si_2Na$ $[(M+Na)^+]$: 683.3465; found: 683.3471.

S-7:[6] ^{1}H NMR (500 MHz, C_6D_6) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.77–7.75 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31–7.07 (m, 14H), 4.18–4.15 (m, 1H), 3.77 (s, 1H), 3.76 (d, *J* = 13.5 Hz, 1H), 3.50 (d, *J* = 13.5 Hz, 1H), 2.98 (d, *J* = 18.0 Hz, 1H), 2.90 (d, *J* = 18.0 Hz, 1H), 2.43 (br d, *J* = 12.0 Hz, 1H), 2.37 (br d, *J* = 12.0 Hz, 1H), 2.23 (s, 1H), 1.95 (br d, *J* = 14.0 Hz, 1H), 1.68 (br t, *J* = 12.0 Hz, 1H), 1.41 (q, *J* = 12.0 Hz, 1H), 1.23 (s, 9H), 1.23–1.20 (m, 1H), 1.00 (t, *J* = 14.0 Hz, 1H), 0.87 (d, *J* = 6.0 Hz, 3H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 139.2, 137.9, 136.4, 136.2, 134.85, 134.76, 134.0, 130.1, 129.9, 129.2, 129.0, 128.9, 115.2, 70.9, 64.7, 62.9, 54.8, 45.8, 37.3, 33.4, 27.3, 23.3, 19.6, 19.4, 17.2, –3.1, –4.5, 4 missing carbons attributed to overlap with solvent; IR (film) 3494, 3070, 2958, 2933, 2896, 2858, 1428, 1382, 1250, 1111, 1082, 1052 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{41}H_{52}N_2O_2Si_2Na$ [$(M+Na)^+$]: 683.3465; found: 683.3461.



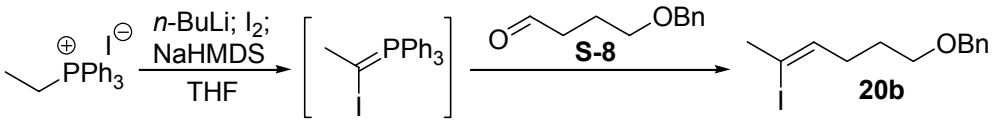
2-(Benzyl((1*R*,4*S*,5*R*)-5-((*R*)-1-(*tert*-butyldiphenylsilyloxy)ethyl)-4-(dimethyl(phenyl)silyl)-2-oxocyclohexyl)amino)acetonitrile (19). A solution of oxalyl chloride (410 μL, 4.70 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of dimethyl sulfoxide (833 μL, 11.7 mmol) in CH_2Cl_2 (14 mL) at –78 °C, maintaining an internal temperature below –70 °C. The solution was stirred for 10 min at –78 °C, and then a solution of amino alcohols **S-6** and **S-7** (1.94 g, 2.93 mmol) in CH_2Cl_2 (14 mL with a 2 mL rinse) was added dropwise, maintaining an internal temperature below –68 °C. The reaction was stirred 15 min at –78 °C and then triethylamine (2.9 mL, 21 mmol) was added dropwise. The reaction was then allowed to warm to –10 °C and saturated aqueous sodium bicarbonate (20 mL) was added. The layers were separated and the organic portion was washed with water (20 mL). The combined aqueous layers were extracted with CH_2Cl_2 (2 × 40 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give ketone **19** (1.80 g, 93%) as a colorless foam: $[\alpha]^{24}_{589}$ +51.4, $[\alpha]^{24}_{577}$ +53.6, $[\alpha]^{24}_{546}$ +61.7,

$[\alpha]^{24}_{435}$ +120 (*c* 2.82, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.0 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.50–7.28 (m, 12H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 4.04–4.00 (m, 1H), 3.90 (d, *J* = 13.5 Hz, 1H), 3.86 (d, *J* = 13.5 Hz, 1H), 3.71 (d, *J* = 18.0 Hz, 1H), 3.67 (d, *J* = 18.0 Hz, 1H), 3.42 (dd, *J* = 13.0, 5.5 Hz, 1H), 2.93–2.90 (m, 1H), 2.25 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.04 (t, *J* = 13.5 Hz, 1H), 2.01–1.96 (m, 1H), 1.65 (q, *J* = 12.5 Hz, 1H), 1.12 (ddd, *J* = 15.0, 11.5, 3.5 Hz, 1H), 1.07 (s, 9H), 0.69 (d, *J* = 6.0 Hz, 3H), 0.02 (s, 3H), –0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.3 (C), 137.4 (C), 137.1 (C), 135.9 (CH), 135.8 (CH), 134.09 (C), 134.07 (C), 133.5 (CH), 129.8 (CH), 129.7 (CH), 129.1 (CH), 128.8 (CH), 128.6 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.7 (CH), 116.8 (C), 69.7 (CH), 67.9 (CH), 55.6 (CH_2), 45.4 (CH), 42.7 (CH_2), 38.7 (CH_2), 31.9 (CH_2), 30.0 (CH), 26.9 (CH_3), 19.2 (C), 16.7 (CH_3), –3.8 (CH_3), –5.0 (CH_3); IR (film) 3070, 2960, 2931, 2894, 2858, 1717, 1590, 1428, 1383, 1252, 1111, 1079 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{41}H_{50}N_2O_2Si_2Na$ [$(M+Na)^+$]: 681.3309; found: 681.3324.



(*Z*)-6-Iodohepta-1,5-diene (20a). A solution of *n*-butyllithium (9.70 mL, 23.8 mmol, 2.45 M in hexanes) was added dropwise to a suspension of ethyltriphenylphosphonium iodide (9.94 g, 23.8 mmol) in THF (50 mL), ensuring that the temperature remained below 35 °C (internal measure). The resultant red solution was stirred 30 min at rt. In a separate flask, a solution of iodine (6.03 g, 23.8 mmol) in THF (140 mL) was cooled to –78 °C. The red solution of ylide was then transferred into the iodine solution by cannula over 25 min, maintaining a temperature below –65 °C (internal measure). The reaction was then allowed to warm to –10 °C and then recooled to –45 °C. A solution of sodium hexamethyldisilazide (23.8 mL, 23.8 mmol, 1.0 M in THF) was added dropwise over 15 min, resulting in a red solution. After 10 min at –40 °C, 4-pentenal (1.18 mL, 11.9 mmol) was quickly added, and the solution was allowed to warm to –10 °C. The reaction was quenched with methanol (1.5 mL), resulting in a brown suspension, and silica gel (90 mL) was added. The suspension was concentrated in vacuo, and the residue was dry loaded onto a silica gel column and eluted with pentane:Et_2O (49:1) to provide **20a**, contaminated with triphenylphosphine. The mixture was repurified by silica flash column

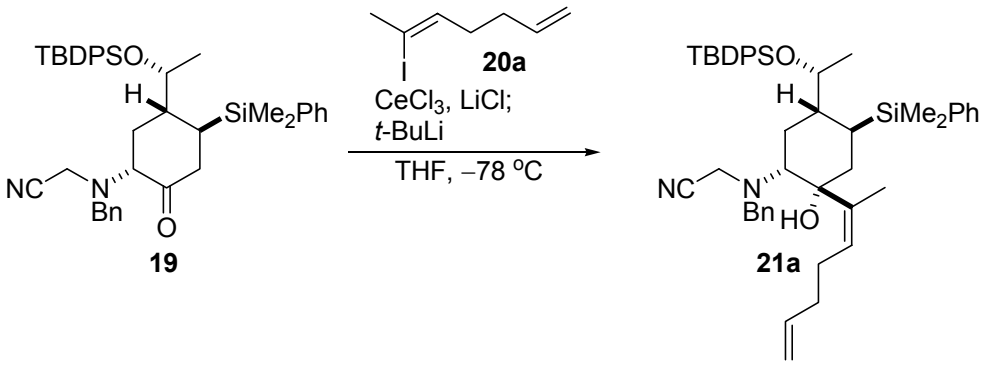
chromatography (49:1 pentane:Et_2O) to provide **20a** (0.980 g, 37%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (dddd, *J* = 16.3, 12.1, 5.9, 5.9 Hz, 1H), 5.44 (t, *J* = 6.3 Hz, 1H), 5.05 (d, *J* = 17.2 Hz, 1H), 5.00 (d, *J* = 10.3 Hz, 1H), 2.51 (s, 3H), 2.24–2.11 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7 (CH), 134.6 (CH), 115.1 (CH_2), 101.3 (C), 35.8 (CH_2), 33.5 (CH_3), 32.4 (CH_2); IR (film): 2921 cm^{-1}; attempts to obtain HRMS data were unsuccessful, presumably due to poor ionization of the molecule.



(*Z*)-1-((5-Iodohex-4-enyloxy)methyl)benzene (20b). A solution of *n*-butyllithium (38.2 mL, 61.0 mmol, 1.60 *M* in hexanes) was added dropwise over 45 min to a suspension of ethyltriphenylphosphonium iodide (25.5 g, 61.0 mmol) in THF (140 mL), maintaining a temperature below 35 °C (internal measure). The resultant red solution was stirred 30 min at rt. In a separate flask, a solution of iodine (15.5 g, 61.0 mmol) in THF (340 mL) was cooled to –78 °C. The red solution of ylide was transferred by cannula into the flask containing the iodine solution over 50 min, maintaining a temperature below –65 °C (internal measure), resulting in the formation of a yellow precipitate. The suspension was allowed to warm to –10 °C, then recooled to –45 °C. A solution of sodium hexamethyldisilazide (61 mL, 61 mmol, 1.0 M in THF) was added over 20 min, resulting in a red solution. After 10 min at –40 °C, a solution of aldehyde **S-8**[11] (5.44 g, 30.5 mmol) in THF (15 mL) was quickly added, and the solution was allowed to warm to –15 °C. Methanol (3 mL) was then added, resulting in a brown suspension, and silica gel was added. The suspension was concentrated in vacuo, and the crude material was dry loaded onto a silica gel column and eluted with hexanes:Et_2O (49:1) to provide slightly impure **20b** as a 7:1 mixture of *Z* and *E* isomers. The 7:1 mixture of olefin isomers was repurified by silver nitrate impregnated silica gel flash column chromatography (49:1 hexanes:Et_2O) to give **20b** (2.04 g, 21%) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5H), 5.44 (t, *J* = 7.0 Hz, 1H), 4.52 (s, 2H), 3.50 (t, *J* = 6.5 Hz, 2H), 2.50 (s, 3H), 2.20 (q, *J* = 7.0 Hz, 2H), 1.73 (quint, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5,

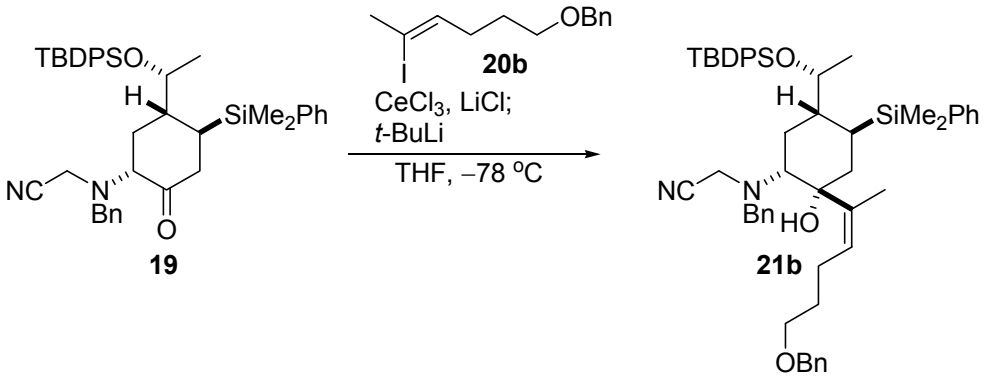
[11] Moreau, B.; Ginisty, M.; Alberico, D.; Charette, A. B. *J. Org. Chem.* **2007**, *72*, 1235–1240.

134.8, 128.3, 127.7, 127.5, 101.3, 72.9, 69.6, 33.5, 33.4, 28.4; IR (film) 3064, 3029, 2943, 2916, 2858, 1495, 1455, 1426, 1364, 1272, 1024 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}OINa$ [$(M+Na)^+$]: 339.0222; found: 339.0220.



2-(Benzyl((1*R*,2*S*,4*S*,5*R*)-5-((*R*)-1-(*tert*-butyldiphenylsilyloxy)ethyl)-4-(dimethyl(phenyl)silyl)-2-((*Z*)-hepta-2,6-dien-2-yl)-2-hydroxycyclohexyl)amino)acetonitrile (21a). Note: THF used in this reaction was freshly distilled from sodium/benzophenone. Lithium chloride (95 mg, 2.2 mmol) and anhydrous cerium (III) trichloride (275 mg, 1.12 mmol) were added to a round-bottomed flask in a glove box. The flask was removed from the glove box, THF (10 mL) was added, and the suspension was stirred vigorously for 2 h at rt, producing a near colorless solution. A solution of ketone **19** (480 mg, 0.744 mmol) in THF (8 mL with a 2 mL rinse) was added by cannula. The solution was stirred 2 h at rt, then a solution of iodide **20a** (413 mg, 1.86 mmol) in THF (4 mL with a 1 mL rinse) was added. The solution was cooled to –78 °C, and a solution of *tert*-butyllithium (1.4 mL, 2.1 mmol, 1.5 M in pentane) was added dropwise in two portions. The progress of the reaction was monitored by thin layer chromatography after the addition of each portion. Methanol (1.5 mL) was then added at –78 °C, the cold bath was removed, and 10% aqueous AcOH (5 mL), saturated aqueous sodium thiosulfate (5 mL), and Et_2O (30 mL) were added sequentially. After the mixture warmed to rt, Et_2O (30 mL) and water (30 mL) were added, and the layers were separated. The aqueous portion was extracted with Et_2O (60 mL). The combined organic extracts were diluted with hexanes (30 mL), and washed sequentially with saturated aqueous sodium thiosulfate (40 mL), saturated aqueous sodium bicarbonate (40 mL), and brine (40 mL). The organic portion was dried over Na_2SO_4,

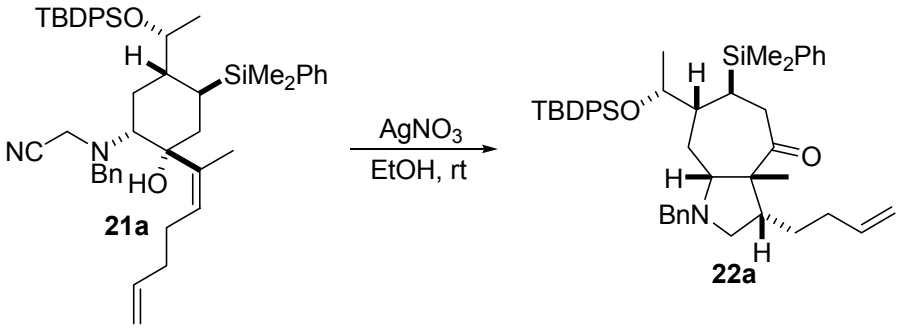
filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give **21a** (410 mg, 73%) as a pale yellow foam, along with the product derived from *tert*-butyl addition to ketone **19** (36 mg, 7%): $[\alpha]^{24}_{589}$ +39, $[\alpha]^{24}_{577}$ +42, $[\alpha]^{24}_{546}$ +47, $[\alpha]^{24}_{435}$ +76 (*c* = 0.63, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (m, 2H), 7.64 (m, 2H), 7.46 (m, 2H), 7.42 (m, 4H), 7.35–7.26 (m, 6H), 7.19 (m, 2H), 7.14 (m, 2H), 5.77 (dddd, *J* = 16.9, 10.2, 6.7, 6.7 Hz, 1H), 5.19 (ddd, *J* = 6.4, 6.4, 1.0 Hz, 1H), 5.00 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.95 (dd, *J* = 10.2, 0.8 Hz, 1H), 4.06 (d, *J* = 13.3 Hz, 1H), 4.01 (m, 1H), 3.91 (d, *J* = 17.5 Hz, 1H), 3.82 (d, *J* = 13.3 Hz, 1H), 3.50 (d, *J* = 17.4 Hz, 1H), 2.84 (dd, *J* = 12.2, 3.1 Hz, 1H), 2.46 (m, 1H), 2.29 (m, 2H), 2.06 (ddd, *J* = 7.1, 7.1, 7.1 Hz, 2H), 1.96 (s, 1H), 1.69 (s, 3H), 1.66 (ddd, *J* = 12.1, 12.1, 12.1 Hz, 1H), 1.49 (d, *J* = 8.3 Hz, 3H), 1.08 (s, 9H), 0.97 (m, 1H), 0.76 (d, *J* = 6.2 Hz, 3H), 0.00 (s, 3H), –0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6 (C), 138.4 (CH), 138.1 (C), 136.03 (CH), 135.98 (CH), 134.7 (C), 134.5 (C), 133.6 (CH), 129.7 (CH), 129.6 (CH), 129.0 (CH), 128.8 (CH), 128.6 (CH), 127.8 (CH), 127.6 (CH), 117.7 (C), 115.1 (CH_2), 70.5 (CH), 64.8 (CH), 56.7 (CH_2), 46.2 (CH), 40.1 (CH_2), 39.0 (CH_2), 34.5 (CH_2), 28.7 (CH_2), 27.1 (CH_3), 23.4 (CH_3), 21.8 (CH), 21.6 (C), 19.3 (C), 16.9 (CH_3), –3.3 (CH_3), –4.5 (CH_3), 5 missing carbons attributed to accidental equivalence and/or broadening; IR (film) 3512, 2930 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{48}H_{63}N_2O_2Si_2$ [$(M+H)^+$]: 755.4428; found: 755.4431.



2-(Benzyl((1*R*,2*S*,4*S*,5*R*)-2-((*Z*)-6-(benzyloxy)hex-2-en-2-yl)-5-((*R*)-1-(*tert*-butyldiphenylsilyloxy)ethyl)-4-(dimethyl(phenyl)silyl)-2-hydroxycyclohexyl)amino)acetonitrile (21b). Note: THF used in this reaction was freshly distilled from sodium/benzophenone. Anhydrous cerium (III) trichloride (93 mg,

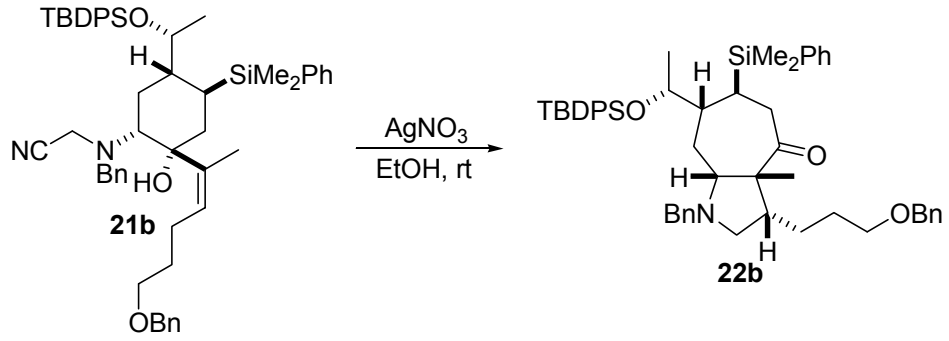
0.38 mmol) and lithium chloride (32 mg, 0.76 mmol) were added to a round-bottomed flask in a glove box. The flask was removed from the glove box, THF (1.6 mL) was added, and the suspension was stirred vigorously and heated at 45 °C for 3 h. The suspension was allowed to cool to rt, and a solution of ketone **19** (165 mg, 0.250 mmol) in THF (1.5 mL with a 0.5 mL rinse) was added by cannula. The suspension was stirred 2.5 h at rt, then a solution of iodide **20b** (151 mg, 0.501 mmol) in THF (3.4 mL) was added. The suspension was cooled to –78 °C, and a solution of *tert*-butyllithium (0.60 mL, 0.90 mmol, 1.5 M in pentane) was added dropwise in three portions. The progress of the reaction was monitored by thin layer chromatography after the addition of each portion. Methanol (0.5 mL) was then added at –78 °C, the cold bath was removed, and 10% aqueous AcOH (1 mL), saturated aqueous sodium thiosulfate (1 mL), and Et_2O (5 mL) were added sequentially. After allowing the mixture to warm to rt, Et_2O (10 mL) and water (10 mL) were added, and the layers were separated. The aqueous portion was extracted with Et_2O (10 mL). The combined organic extracts were diluted with hexanes (10 mL), and the resultant solution was washed sequentially with saturated aqueous sodium thiosulfate (7 mL), saturated aqueous sodium bicarbonate (7 mL), and brine (7 mL). The organic portion was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 EtOAc:hexanes to 1:9 EtOAc:hexanes) to give **21b** (151 mg, 71%) as a pale yellow foam, along with the product derived from *tert*-butyl addition to ketone **19** (14 mg, 8%): $[\alpha]^{25}_{589}$ +35.5, $[\alpha]^{26}_{577}$ +36.8, $[\alpha]^{25}_{546}$ +41.9, $[\alpha]^{26}_{435}$ +68.5 (*c* 2.13, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.0 Hz, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.47–7.23 (m, 17H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.0 Hz, 2H), 5.20 (t, *J* = 8.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.09 (d, *J* = 13.5 Hz, 1H), 4.02 (d, *J* = 17.0 Hz, 1H), 4.00–3.94 (m, 1H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.55 (d, *J* = 17.0 Hz, 1H), 3.50–3.45 (m, 1H), 3.44–3.40 (m, 1H), 3.01 (br s, 1H), 2.85–2.70 (br m, 1H), 2.74 (br d, *J* = 12.0 Hz, 1H), 2.41 (br d, *J* = 12.0 Hz, 1H), 2.19–2.14 (m, 1H), 1.81–1.74 (m, 1H), 1.77 (q, *J* = 12.0 Hz, 1H), 1.63 (s, 3H), 1.52–1.46 (m, 3H), 1.39 (dd, *J* = 14.0, 2.5 Hz, 1H), 1.09 (s, 9H), 1.00 (ddd, *J* = 14.0, 11.0, 3 Hz, 1H), 0.75 (d, *J* = 6.0 Hz, 3H), –0.05 (s, 3H), –0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2 (C), 138.7 (C), 138.3 (C), 137.9 (C), 135.93 (CH), 135.89 (CH), 134.60 (C), 134.52 (C), 133.6 (CH), 129.56 (CH), 129.44 (CH), 128.97

(CH), 128.56 (CH), 128.40 (CH), 128.36 (CH), 127.64 (CH), 127.62 (CH), 127.56 (CH), 127.49 (CH), 127.36 (CH), 126.8 (CH), 118.1 (C), 79.7 (C), 72.3 (CH_2), 70.5 (CH), 68.6 (CH_2), 64.2 (CH), 56.9 (CH_2), 46.4 (CH), 40.7 (CH_2), 38.6 (CH_2), 28.9 (CH_2), 27.0 (CH_3), 24.8 (CH_2), 23.1 (CH_3), 21.3 (CH), 20.1 (CH_2), 19.2 (C), 16.8 (CH_3), –3.5 (CH_3), –4.5 (CH_3), missing carbon attributed to accidental equivalence; IR (film) 3400, 3070, 3031, 2956, 2931, 2858, 1455, 1428, 1382, 1250, 1111, 1088 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{54}H_{68}N_2O_3Si_2Na$ [$(M+Na)^+$]: 871.4666; found: 871.4675.



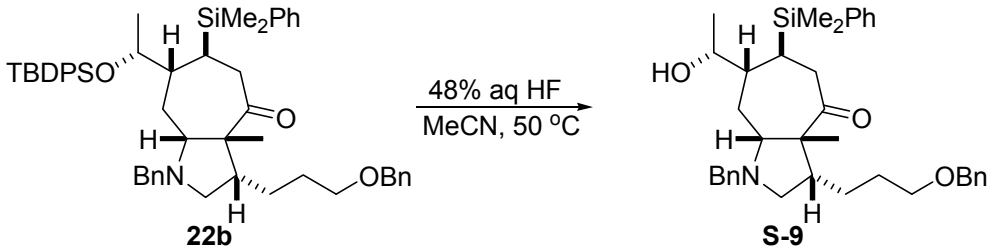
(3*S*,3a*R*,6*S*,7*R*,8a*R*)-1-Benzyl-3-(but-3-enyl)-7-((*R*)-1-(*tert*-butyldiphenylsilyloxy)ethyl)-6-(dimethyl(phenyl)silyl)-3a-methyl-octahydrocyclohepta[*b*]pyrrol-4(5*H*)-one (22a). Silver nitrate (0.191 g, 1.12 mmol) was added to a solution of tertiary allylic alcohol **21a** (0.707 g, 0.936 mmol) in ethanol (10 mL), resulting in a brown suspension. The flask was covered with aluminum foil and the reaction was stirred for 3.5 h at rt. Saturated aqueous ammonium hydroxide (20 mL) was then added, followed by water (20 mL). The mixture was extracted with a 1:3 mixture of hexanes:EtOAc (2 × 100 mL). The combined organic extracts were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (1:19 acetone:hexanes) to give **22a** (0.605 g, 89%) as a colorless foam: $[\alpha]^{23}_{589}$ +1.18, $[\alpha]^{23}_{577}$ +1.23, $[\alpha]^{23}_{546}$ +1.75, $[\alpha]^{23}_{435}$ +9.32, $[\alpha]^{23}_{405}$ +16.8 (*c* = 1.77, CH_2Cl_2); ^{1}H NMR (500 MHz, CDCl3) δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.44 (m, 2H), 7.40–7.29 (m, 8H), 7.25 (m, 2H), 7.18 (m, 4H), 5.78 (m, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.2 Hz, 1H), 4.08 (d, *J* = 13.7 Hz, 1H), 3.95 (br s, 1H), 3.65 (d, *J* = 13.7 Hz, 1H), 2.77–2.68 (m, 4H), 2.61 (d, *J* = 10.3 Hz, 1H), 2.42 (dd, *J* = 10.2, 10.2 Hz, 1H), 2.08–1.94 (m, 2H), 1.91 (m, 1H), 1.80 (br s, 2H), 1.43 (m, 2H), 1.19 (s, 3H), 1.05 (s, 10H), 0.66 (d, *J* = 6.1 Hz, 3H), 0.13 (s,

3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.3 (C), 139.6 (CH), 138.9 (C), 138.7 (C), 136.0 (CH), 134.6 (C), 134.4 (C), 133.8 (CH), 129.8 (CH), 129.7 (CH), 128.9 (CH), 128.7 (CH), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 126.9 (CH), 114.6 (CH_2), 70.72 (CH), 70.67 (CH), 61.5 (C), 57.9 (CH_2), 55.4 (CH_2), 47.4 (CH), 47.3 (CH), 42.6 (CH_2), 34.4 (CH_2), 33.9 (CH_2), 29.6 (CH_2), 29.0 (CH), 27.9 (CH_3), 27.1 (CH_3), 19.3 (C), 16.9 (CH_3), –2.4 (CH_3), –3.9 (CH_3), missing carbon attributed to accidental equivalence; IR (film) 2930, 1693 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{47}H_{62}NO_2Si_2$ [$(M+H)^+$]: 728.4319; found: 728.4316.



(3*S*,3a*R*,6*S*,7*R*,8a*R*)-1-Benzyl-3-(3-(benzyloxy)propyl)-7-((*R*)-1-(*tert*-butyldiphenylsilyloxy)ethyl)-6-(dimethyl(phenyl)silyl)-3a-methyl-octahydrocyclohepta[*b*]pyrrol-4(5*H*)-one (22b). Silver nitrate (0.108 g, 0.637 mmol) was added to a solution of tertiary allylic alcohol **21b** (0.451 g, 0.531 mmol) in ethanol (5 mL), resulting in a brown suspension. The flask was covered with aluminum foil and the reaction was stirred for 4 h at rt. Saturated aqueous ammonium hydroxide (10 mL) was added, followed by water (10 mL). The mixture was extracted with 1:3 hexanes:EtOAc (2 × 50 mL). The combined organic extracts were washed with water (10 mL), brine (30 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (1:19 acetone:hexanes) to give **22b** (0.395 g, 90%) as a colorless foam: $[\alpha]^{24}_{589}$ –2.3, $[\alpha]^{24}_{577}$ –2.3, $[\alpha]^{24}_{546}$ –2.2, $[\alpha]^{24}_{435}$ +2.4 (*c* 2.28, EtOH); ^{1}H NMR (600 MHz, C_6D_6) δ 7.74–7.69 (m, 4H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.25–7.08 (m, 17H), 4.29 (s, 2H), 4.17 (d, *J* = 13.5 Hz, 1H), 4.10–4.02 (br m, 1H), 3.57 (d, *J* = 13.5 Hz, 1H), 3.30–3.25 (m, 2H), 2.97–2.92 (m, 1H), 2.81 (dd, *J* = 11.0, 4.0 Hz, 1H), 2.77–2.73 (m, 2H), 2.57 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.42 (dd, *J* = 11.0, 8.5 Hz, 1H), 2.25–2.17 (m, 1H), 1.96–1.91 (m, 1H), 1.81–1.78 (m, 1H), 1.70–1.53 (m, 3H), 1.47–

1.43 (m, 1H), 1.20 (s, 3H), 1.14 (s, 9H), 1.05–1.00 (m, 1H), 0.69 (d, J = 6.0 Hz, 3H), 0.18 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 213.7 (C), 140.2 (C), 139.6 (C), 139.1 (C), 136.3 (CH), 134.9 (C), 134.7 (C), 134.0 (CH), 130.0 (CH), 129.9 (CH), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 127.4 (CH), 127.2 (CH), 72.7 (CH_2), 71.5 (CH), 71.0 (CH), 70.5 (CH_2), 61.4 (C), 58.4 (CH_2), 56.0 (CH_2), 48.6 (CH), 47.1 (CH), 42.5 (CH_2), 34.3 (br, CH_2), 30.2 (CH_2), 28.8 (br, CH), 28.0 (CH_3), 27.7 (CH_2), 27.2 (CH_3), 19.4 (C), 16.9 (br, CH_3), –2.2 (CH_3), –4.0 (CH_3), 4 missing carbons attributed to overlap with solvent and/or accidental equivalence; IR (film) 3068, 2958, 2931, 2858, 2800, 1698, 1455, 1428, 1382, 1362, 1258, 1111, 1079 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{53}H_{68}NO_3Si_2$ [(M+H)$^+$]: 822.4738; found: 822.4721.

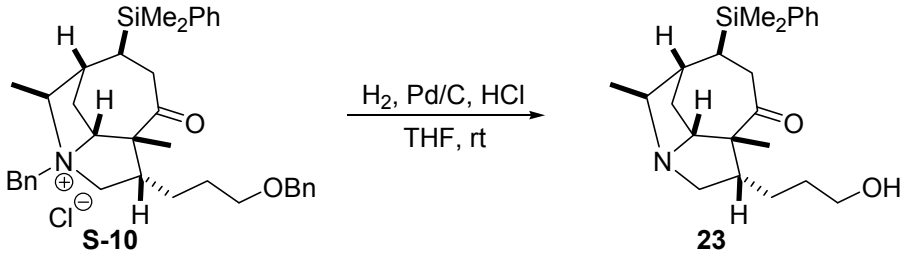


(3*S*,3a*R*,6*S*,7*R*,8a*R*)-1-Benzyl-3-(3-(benzyloxy)propyl)-6-(dimethyl(phenyl)silyl)-7-((*R*)-1-hydroxyethyl)-3a-methyl-octahydrocyclohepta[*b*]pyrrol-4(5*H*)-one (S-9).. Hydrogen fluoride (0.5 mL, 48% aq) was added to a solution of silyl ether **22b** (0.162 g, 0.197 mmol) in MeCN (2.0 mL) in a Nalgene vial. The solution was heated at 50 °C for 19 h. Additional hydrogen fluoride (0.5 mL, 48% aq) was added and the reaction was maintained at 50 °C for another 7 h. The solution was then cooled to rt and poured into a stirring, biphasic mixture of Et_2O (50 mL) and aq 1 N NaOH (50 mL). The mixture was stirred for 20 min at rt, and then the layers were separated. The aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic extracts were washed with water (10 mL), brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give **S-9** (92 mg, 80%) as a colorless foam, along with recovered starting material **22b** (25 mg, 15%): $[\alpha]^{25}_{589}$ –43, $[\alpha]^{25}_{577}$ –44, $[\alpha]^{25}_{546}$ –50, $[\alpha]^{25}_{435}$ –83 (*c* 0.74, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.53 (m, 2H), 7.37–7.27 (m, 13H), 7.00 (br s, 1H), 4.44 (s, 2H), 4.11 (d, J = 13.0 Hz, 1H), 3.93 (q,

J = 6.0 Hz, 1H), 3.54 (d, *J* = 13.0 Hz, 1H), 3.35 (t, *J* = 6.0 Hz, 2H), 3.15 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.01 (dd, *J* = 11.5, 9.0 Hz, 1H), 2.86–2.81 (m, 2H), 2.54 (dd, *J* = 11.0, 6.0 Hz, 1H), 2.00–1.94 (m, 1H), 1.85 (br dd, *J* = 15.0, 5.0 Hz, 1H), 1.80–1.72 (m, 2H), 1.70–1.66 (m, 1H), 1.48–1.40 (m, 3H), 1.02 (s, 3H), 1.02–0.94 (m, 1H), 0.90 (d, *J* = 6.0 Hz, 3H), 0.40 (s, 3H), 0.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.5 (C), 138.3 (C), 138.0 (C), 136.8 (C), 134.3 (CH), 129.6 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 127.62 (CH), 127.55 (CH), 127.54 (CH), 127.48 (CH), 73.2 (CH), 72.9 (CH_2), 71.6 (br, CH), 70.0 (CH_2), 61.8 (C), 60.8 (CH_2), 56.5 (CH_2), 47.3 (CH), 43.3 (CH_2), 42.1 (CH), 32.9 (br, CH_2), 29.0 (CH_2), 25.9 (CH_2), 24.0 (CH_3), 21.5 (CH), 20.7 (br, CH_3), –3.3 (CH_3), –4.2 (CH_3); IR (film) 3382, 3068, 3029, 2966, 2931, 2860, 1690, 1455, 1428, 1372, 1250, 1111, 1077 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{37}H_{50}NO_3Si$ [$(M+H)^+$]: 584.3560; found: 584.3555.

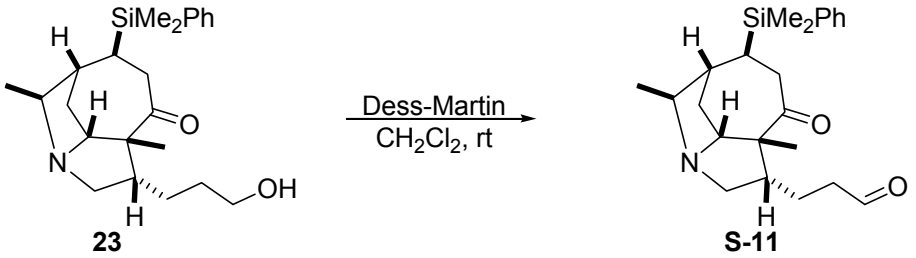
(3*S*,3a*R*,6*S*,7*R*,8a*R*,9*S*)-Octahydro-1-benzyl-3-(3-(benzyloxy)propyl)-3a,9-dimethyl-6-(dimethyl(phenyl)silyl)-1,7-methanocyclohepta[*b*]pyrrolium-4(5*H*)-one chloride (S-10). Triethylamine (45 μL, 0.32 mmol) and methanesulfonyl chloride (16 μL, 0.21 mmol) were added sequentially to a solution of alcohol **S-9** (0.110 g, 0.188 mmol) in CH_2Cl_2 (1.9 mL) at 0 °C. The solution was stirred for 30 min at 0 °C, then concentrated in vacuo to give **S-10**, which was used in the subsequent reaction without further purification: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.0 Hz, 2H), 7.52–7.50 (m, 2H), 7.41–7.23 (m, 11H), 5.10 (d, *J* = 12.5 Hz, 1H), 4.91 (d, *J* = 12.5 Hz, 1H), 4.47 (dd, *J* = 13.0, 9.0 Hz, 1H), 4.38 (s, 2H), 3.55 (d, *J* = 7.0 Hz, 1H), 3.33–3.28 (m, 4H), 3.08 (ddd, *J* = 16.0, 9.0, 7.0 Hz, 1H), 2.83 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.58 (t, *J* = 12.0 Hz, 1H), 2.25 (dd, *J* = 12.0, 5.0 Hz, 1H), 1.96–1.90 (m, 1H), 1.72 (br d, *J* = 16.0 Hz, 1H), 1.70 (d, *J* = 7.0 Hz, 3H), 1.66–1.60 (m, 1H), 1.49–1.43 (m, 1H), 1.25–1.18 (m, 1H), 1.09 (dd, *J* = 12.0, 5.0 Hz, 1H), 0.98–0.92 (m, 1H), 0.96 (s, 3H), 0.39 (s, 3H), 0.37 (s, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 212.9 (C), 138.2 (C), 134.9 (C), 133.9 (CH), 133.0 (CH), 130.4 (C), 129.9 (CH), 129.2 (CH), 128.36 (CH), 128.30 (CH), 128.27 (CH), 127.7 (CH), 127.6 (CH), 87.7 (CH), 79.6 (CH), 72.9 (CH_2), 69.5 (CH_2), 66.2 (CH_2), 58.4 (CH_2), 56.4 (C), 49.6 (CH), 42.6 (CH), 37.7 (CH_2), 30.4 (CH), 29.3 (CH_2), 24.2 (CH_2), 23.3 (CH_2), 19.8 (CH_3), 14.9 (CH_3), –4.8 (CH_3), –4.9 (CH_3); HRMS (ESI) *m/z* calcd for $C_{37}H_{48}NO_2Si$ [M^+]: 566.3455; found: 566.3438.



(3*S*,3a*R*,6*S*,7*R*,8a*R*,9*S*)-Octahydro-3-(3-hydroxypropyl)-3a,9-dimethyl-6-(dimethyl(phenyl)silyl)-1,7-methanocyclohepta[*b*]pyrrol-4(5*H*)-one (23). Concentrated HCl (47 μL, 0.57 mmol, 12.1 N) was added to a solution of benzylammonium salt **S-10** (0.113 g, 0.188 mmol) in THF (4 mL). Palladium on carbon (0.040 g, 0.038 mmol) was then added and the flask was purged thoroughly with hydrogen. The suspension was stirred at rt under an atmosphere of hydrogen (balloon pressure) for 15 h. The reaction mixture was then filtered through celite, rinsing with methanol (50 mL). The filtrate was concentrated in vacuo and the resultant oil was dissolved in CH_2Cl_2 (30 mL) and stirred vigorously with saturated aqueous sodium carbonate (15 mL) for 20 min. The layers were separated and the aqueous layer was extracted with a 1:9 mixture of MeOH:CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:5:95 NH_4OH:MeOH:CH_2Cl_2 to 1:10:90 NH_4OH:MeOH:CH_2Cl_2) to give **23** (0.064 g, 88% over two steps) as a colorless oil: $[\alpha]^{23}_{589}$ +30, $[\alpha]^{23}_{577}$ +31, $[\alpha]^{23}_{546}$ +40, $[\alpha]^{23}_{435}$ +130 (*c* 0.83, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.38–7.37 (m, 3H), 3.71 (dd, *J* = 10.5, 9.0 Hz, 1H), 3.62–3.55 (m, 2H), 3.36 (br d, *J* = 8.0 Hz, 1H), 2.80 (appt t, *J* = 10.5 Hz, 1H), 2.68 (appt q, *J* = 6.5 Hz, 1H), 2.53 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.40 (dd, *J* = 12.0, 7.0 Hz, 1H), 2.22–2.14 (m, 2H), 2.09 (br d, *J* = 6.0 Hz, 1H), 1.7–1.5 (br s,

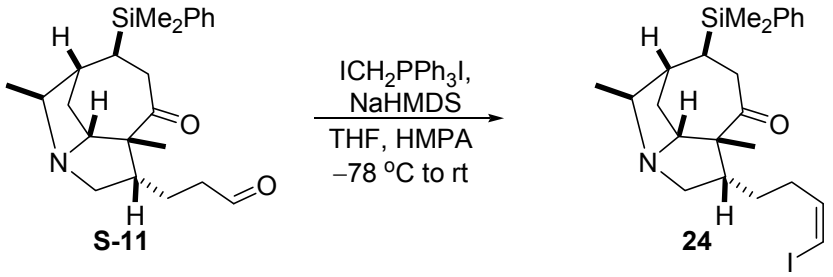
1H), 1.57–1.43 (m, 4H), 1.32–1.26 (m, 1H), 1.24–1.22 (m, 1H), 1.10 (d, J = 6.5 Hz, 3H), 1.03 (s, 3H), 0.36 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.0 (C), 137.9 (C), 134.0 (CH), 129.1 (CH), 127.8 (CH), 75.0 (CH), 73.9 (CH), 62.8 (CH_2), 60.9 (CH_2), 60.3 (C), 52.7 (CH), 44.7 (CH), 41.3 (CH_2), 32.1 (CH_2), 31.9 (CH), 29.8 (CH_2), 24.8 (CH_2 and CH_3), 21.1 (CH_3), –3.0 (CH_3), –3.2 (CH_3), missing carbon attributed to accidental equivalence; IR (film) 3400, 3070, 3049, 2956, 2929, 2865, 1684, 1457, 1387, 1374, 1320, 1250, 1111, 1081, 1063 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{36}NO_2Si$ [$(M+H)^+$]: 386.2515; found: 386.2502.



3-((3*S*,3a*R*,6*S*,7*R*,8a*R*,9*S*)-Octahydro-3a,9-dimethyl-6-(dimethyl(phenyl)silyl)-4(5*H*)-oxo-1,7-methanocyclohepta[*b*]pyrrol-3-yl)propanal (S-11). Dess–Martin periodinane[12] (0.048 g, 0.11 mmol) was added to a solution of alcohol **23** (0.022 g, 0.057 mmol) in water-saturated CH_2Cl_2 (1 mL). The resultant suspension was stirred at rt for 30 min. A solution of 1:9 MeOH:CH_2Cl_2 (2 mL), followed by a solution of sodium thiosulfate (0.28 g) in 80% saturated aqueous sodium bicarbonate (2 mL) were added. The layers were separated and the aqueous portion was extracted with a 1:9 mixture of MeOH:CH_2Cl_2 (3 x 3 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (eluted with acetone) to give aldehyde **S-11** (0.018 g, 82%) as a colorless oil: $[\alpha]^{24}_{589}$ +38, $[\alpha]^{24}_{577}$ +40, $[\alpha]^{24}_{546}$ +50, $[\alpha]^{24}_{435}$ +154 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.55–7.53 (m, 2H), 7.38–7.37 (m, 3H), 3.63 (dd, J = 11.0, 9.0 Hz, 1H), 3.32 (d, J = 8.0 Hz, 1H), 2.78 (appt t, J = 11.0 Hz, 1H), 2.64 (appt q, J = 6.5 Hz, 1H), 2.55 (dd, J = 12.0, 4.5 Hz, 1H), 2.41 (t, J = 7.0 Hz, 2H), 2.35 (dd, J = 12.0, 7.0 Hz, 1H), 2.18 (ddd, J = 14.0, 8.0, 8.0 Hz, 1H), 2.16–2.10 (m, 1H), 2.08 (br d, J = 7.0 Hz, 1H), 1.78–1.72 (m, 1H), 1.70–1.63 (m, 1H), 1.53 (d, J = 14.0 Hz, 1H), 1.26–

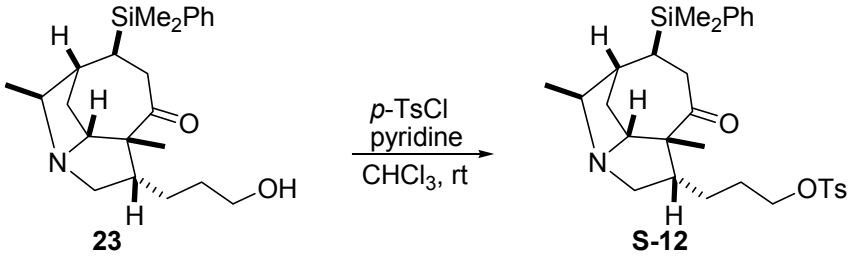
[12] Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155–4156.

1.20 (m, 1H), 1.08 (d, J = 6.5 Hz, 3H), 1.05 (s, 3H), 0.355 (s, 3H), 0.346 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.8 (C), 201.5 (C), 137.7 (C), 134.0 (CH), 129.1 (CH), 127.8 (CH), 75.2 (CH), 74.2 (CH), 60.5 (CH_2), 60.0 (C), 52.3 (CH), 44.6 (CH), 43.0 (CH_2), 41.0 (CH_2), 31.9 (CH), 29.5 (CH_2), 24.9 (CH_3 + CH_2), 20.9 (CH_3), –3.1 (CH_3), –3.2 (CH_3), missing carbon attributed to accidental equivalence; IR (film) 3070, 2956, 2929, 2865, 2721, 1725, 1683, 1457, 1445, 1428, 1389, 1372, 1320, 1250, 1221, 1150, 1111, 1081 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{34}NO_2Si$ [$(M+H)^+$]: 384.2359; found: 384.2366.

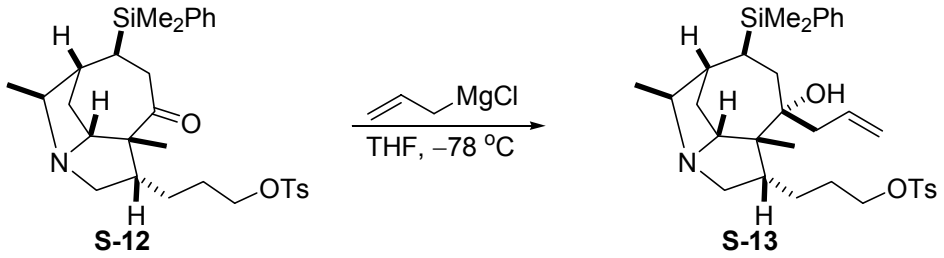


(3*S*,3a*R*,6*S*,7*R*,8a*R*,9*S*,*Z*)-Octahydro-3-(4-iodobut-3-enyl)-3a,9-dimethyl-6-(dimethyl(phenyl)silyl)-1,7-methanocyclohepta[*b*]pyrrol-4(5*H*)-one (24). A solution of sodium hexamethyldisilazide (0.16 mL, 0.16 mmol, 1.0 M in THF) was added dropwise to a suspension of iodomethyltriphenylphosphonium iodide (0.104 g, 0.196 mmol) in THF (1.5 mL). The suspension was cooled to –78 °C and HMPA (0.3 mL) was added, followed by a solution of aldehyde **S-11** (0.030 g, 0.078 mmol) in THF (1.5 mL). The mixture was stirred for 15 min at –78 °C and then allowed to warm to rt over 30 min. Water (0.75 mL) was added and the mixture was extracted with Et_2O (4 × 5 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (1:19 acetone:hexanes) to give **24** (0.024 g, 60%) as a pale yellow oil: $[\alpha]^{25}_{589}$ +3.5, $[\alpha]^{25}_{577}$ +4.7, $[\alpha]^{25}_{546}$ +5.8, $[\alpha]^{25}_{435}$ +31 (c = 0.64, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.38 (m, 3H), 6.20 (d, J = 7.3 Hz, 1H), 6.08 (dd, J = 14.0, 6.9 Hz, 1H), 3.75 (dd, J = 8.8, 8.8 Hz, 1H), 3.34 (d, J = 8.0 Hz, 1H), 2.82 (dd, J = 10.6, 10.6 Hz, 1H), 2.68 (dd, J = 12.9, 6.3 Hz, 1H), 2.53 (dd, J = 11.9, 3.8 Hz, 1H), 2.39 (dd, J = 11.9, 7.2 Hz, 1H), 2.25– 2.01 (m, 5H), 1.59–1.48 (m, 2H), 1.36 (m, 1H), 1.24 (m, 1H), 1.10 (d, J = 6.5 Hz, 3H), 1.01 (s, 3H), –0.35 (s, 3H), –0.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.0 (C),

140.4 (CH), 137.9 (C), 134.1 (CH), 129.2 (CH), 127.9 (CH), 83.2 (CH), 75.0 (CH), 74.0 (CH), 60.9 (CH_2), 60.3 (C), 52.4 (CH), 44.8 (CH), 41.3 (CH_2), 34.1 (CH_2), 32.0 (CH), 29.8 (CH_2), 26.9 (CH_2), 25.0 (CH_3), 21.0 (CH_3), –2.9 (CH_3), –3.1 (CH_3); IR (film): 2931, 1684 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{35}INOSi$ [$(M+H)^+$]: 508.1533; found: 508.1526.

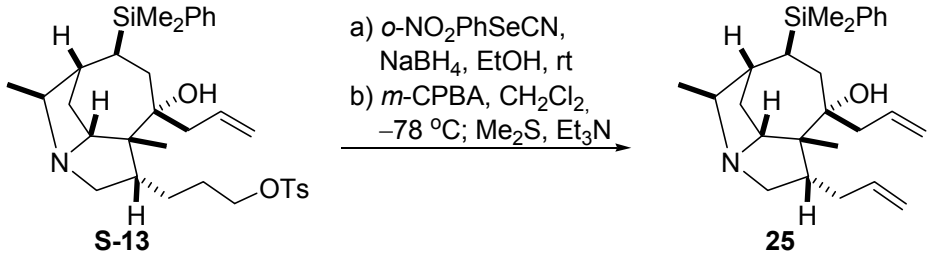


Tosylate S-12. Pyridine (17 μL, 0.22 mmol) and *p*-toluenesulfonyl chloride (0.021 g, 0.11 mmol) were added sequentially to a solution of alcohol **23** (0.021 g, 0.054 mmol) in chloroform (0.5 mL) at rt. The resultant red solution was stirred for 17 h at rt. Saturated aqueous $NaHCO_3$ (1 mL) was added and the mixture was extracted with CH_2Cl_2 (4 x 2 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was dissolved in heptane (3 mL) and concentrated in vacuo (x 2) to remove pyridine by azeotropic distillation. The residue was purified by silica gel flash column chromatography (1:10:90 NH_4OH (aq):MeOH:CH_2Cl_2) to give **S-12** (0.025 g, 84%) as a pink oil: $[\alpha]^{24}_{589}$ +24, $[\alpha]^{24}_{577}$ +25, $[\alpha]^{24}_{546}$ +33, $[\alpha]^{24}_{435}$ +91 (*c* = 0.99, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3, 2H), 7.51 (m, 2H), 7.42–7.35 (m, 3H), 7.33 (d, *J* = 8.2, 2H), 3.96 (dd, *J* = 11.3, 4.7, 2H), 3.75 (dd, *J* = 9.4, 9.4, 1H), 3.52 (br s, 1H), 2.76–2.67 (m, 2H), 2.52 (dd, *J* = 11.9, 5.6, 1H), 2.44 (s, 3H), 2.28 (dd, *J* = 12.0, 6.6, 1H), 2.22 (m, 1H), 2.16 (d, *J* = 7.7, 1H), 2.07 (ddd, *J* = 16.1, 8.6, 8.6, 1H), 1.64–1.51 (m, 3H), 1.51–1.40 (m, 2H), 1.2 (m, 1H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.03 (s, 3H), 0.35 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3 (C), 144.9 (C), 134.0 (CH), 133.0 (C), 130.03 (CH), 129.95 (CH), 129.5 (C), 128.0 (CH), 127.9 (CH), 75.3 (CH_2), 70.1 (CH_2), 59.7 (CH_2), 59.1 (C), 51.6 (CH), 44.6 (CH), 40.2 (CH_2), 31.7 (CH_3), 28.8 (CH), 28.4 (CH_2), 24.1 (CH_2), 23.2 (CH), 21.7 (CH_3), 20.3 (CH_3), –3.4 (CH_3), –3.7 (CH_3), missing carbon attributed to accidental equivalence; IR (film): 2957, 1685 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{42}NO_4SSi$ [$(M+H)^+$]: 540.2604; found: 5402606.



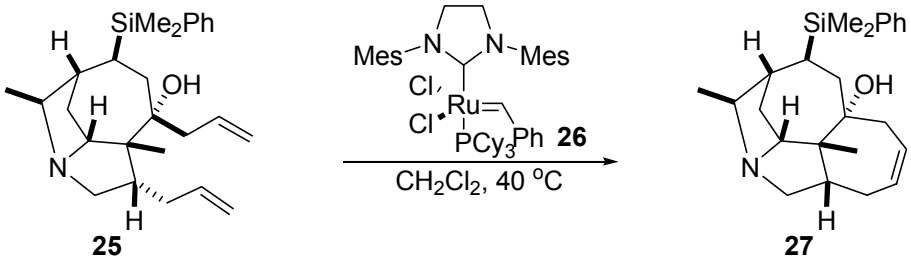
S-12 **S-13**

Allyl addition product S-13. A solution of allylmagnesium chloride (87 μL, 0.17 mmol, 2.0 M in THF) was added to a solution of tosylate **S-12** (0.023 g, 0.043 mmol) in THF (1.5 mL) at –78 °C. After 15 min at –78 °C, additional allylmagnesium chloride solution (43 μL, 0.086 mmol, 2.0 M in THF) was added. The reaction was maintained 20 min at –78 °C, and then water (1 mL) was added and the mixture was allowed to warm to rt. The mixture was extracted with Et_2O (5 x 3 mL). The combined extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:10:90 NH_4OH (aq):MeOH:CH_2Cl_2 to 2:20:80 NH_4OH (aq):MeOH:CH_2Cl_2) to give **S-13** (0.020 g, 78%) as a colorless oil: $[\alpha]^{24}_{589}$ –20, $[\alpha]^{24}_{577}$ –10, $[\alpha]^{24}_{546}$ +3.4, $[\alpha]^{24}_{435}$ +11 (*c* = 0.47, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 5.5 Hz, 2H), 7.43–7.32 (m, 5H), 5.59 (dddd, *J* = 16.8, 9.0, 9.0, 9.0 Hz, 1H), 5.31 (d, *J* = 9.9 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 4.03 (dd, *J* = 11.9, 5.9 Hz, 2H), 3.59–3.39 (m, 3H), 3.00 (m, 1H), 2.48 (m, 1H), 2.45 (s, 3H), 2.13–1.99 (m, 3H), 1.98–1.79 (m, 3H), 1.70–1.40 (m, 5H), 1.33–1.12 (m, 4H), 0.93 (s, 3H), 0.29 (s, 3H), 0.28 (s, 3H), missing H attributed to deuterium exchange with solvent; ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.9 (C), 133.8 (CH), 133.1 (C), 132.1 (CH), 130.0 (CH), 129.4 (CH), 128.0 (CH), 127.9 (CH), 126.0 (C), 123.5 (CH_2), 80.1 (CH), 76.7 (C), 75.6 (CH), 70.6 (CH_2), 58.0 (CH_2), 53.4 (CH), 49.3 (C), 44.2 (CH_2), 43.6 (CH), 31.9 (CH_2), 29.8 (CH), 28.6 (CH_2), 27.4 (CH_3), 26.4 (CH_2), 25.1 (CH_2), 21.7 (CH_3), 21.4 (CH_3), –4.5 (CH_3), –4.7 (CH_3); IR (film): 3417, 2954 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{33}H_{48}NO_4SSi$ [$(M+H)^+$]: 582.3073; found: 582.3083.

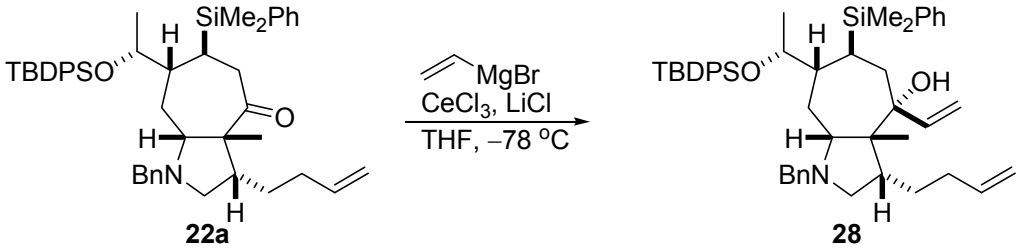


Diene 25. Sodium borohydride (4.7 mg, 0.12 mmol) was added to a suspension of 2-nitrophenyl selenocyanate (0.028 g, 0.12 mmol) in ethanol (0.5 mL) at 0 °C. After 10 min at 0 °C, a solution of tosylate **S-13** (0.024 g, 0.041 mmol) in ethanol (1 mL) was added and the suspension was allowed to warm to rt. The mixture was stirred at rt for 14 h, and then water (1 mL) was added to the deep red solution. The mixture was extracted with CH_2Cl_2 (4 x 3 mL) and the combined extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (1:10:90 NH_4OH (aq):MeOH:CH_2Cl_2) to give the selenide (0.018 g, 69%) as a yellow oil, which was immediately used in the subsequent elimination step. The selenide (8.5 mg, 0.014 mmol) was dissolved in CH_2Cl_2 (0.7 mL) and the resultant yellow solution was cooled to –78 °C. A solution of *m*-chloroperoxybenzoic acid (3.8 mg, 0.017 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise by syringe. The solution was maintained for 1.5 h at –78 °C, then dimethyl sulfide (51 μL, 0.70 mmol) was added, followed by triethylamine (48 μL, 0.35 mmol). The solution was allowed to warm to rt and stirred at rt for 17 h. Saturated aqueous sodium bicarbonate (1 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 x 3 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (1:10:90 NH_4OH (aq):MeOH:CH_2Cl_2) to give diene **25** (4.6 mg, 81%) as a colorless oil: $[\alpha]^{24}_{589}$ +4.6, $[\alpha]^{24}_{577}$ +4.9, $[\alpha]^{24}_{546}$ +4.7, $[\alpha]^{24}_{435}$ +7.5 (*c* = 0.53, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 3.9 Hz, 2H), 7.36 (m, 3H), 5.74 (m, 1H), 5.63 (m, 1H), 5.25 (d, *J* = 9.9 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 3.37 (m, 1H), 3.28–3.15 (m, 2H), 2.91 (dd, *J* = 10.4 Hz, 10.4, 1H), 2.59–2.50 (m, 2H), 2.09 (dd, *J* = 13.0, 6.4 Hz, 1H), 2.01–1.90 (m, 3H), 1.64–1.53 (m, 2H), 1.46 (m, 1H), 1.37 (m, 1H), 1.28–1.23 (m, 2H), 1.09 (d, *J* = 15.7 Hz, 3H), 0.92 (s, 3H), 0.29 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (CH), 137.8 (C), 133.8 (CH), 133.0 (CH), 129.1 (CH), 127.9 (CH), 122.4 (CH_2), 115.4

(CH_2), 80.8 (CH), 77.3 (C), 75.1 (CH), 59.1 (CH_2), 54.0 (CH), 48.9 (C), 44.5 (CH_2), 43.4 (CH), 33.9 (CH_2), 31.8 (CH_2), 27.6 (CH), 26.8 (CH_2), 23.8 (CH_3), 21.6 (CH_3), –4.4 (CH_3), –4.6 (CH_3); IR (film): 3320, 2954 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{40}NOSi$ [$(M+H)^+$]: 410.2879; found: 410.2877.

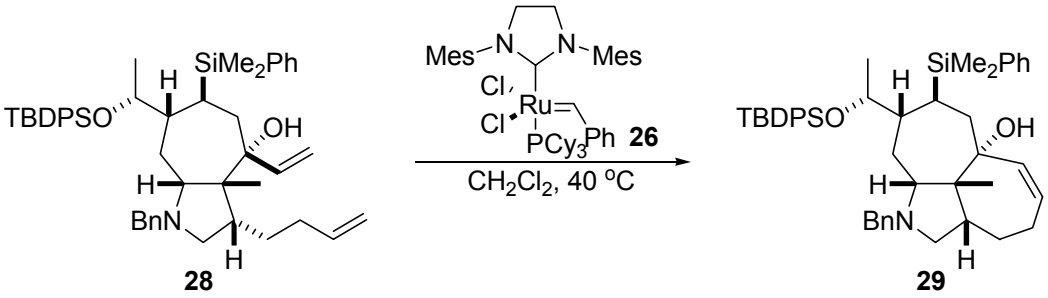


Tetracyclic alcohol 27. The Grubbs second generation catalyst (**26)** (benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium) (3.5 mg, 4.1 μmol) was added to a solution of diene **25** (0.017 g, 0.041 mmol) in CH_2Cl_2 (1.5 mL), and the resultant brown solution was heated at reflux for 3 h. The solution was allowed to cool to rt and then concentrated in vacuo. The residue was purified by silica gel flash column chromatography (1:10:90 NH_4OH (aq):MeOH:CH_2Cl_2) to give **27** (4.6 mg, 81%) as a purple oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.38 (m, 3H), 5.67 (m, 1H), 5.47 (m, 1H), 4.09 (d, *J* = 6.7 Hz, 1H), 3.99 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.71 (s, 1H), 3.10 (dd, *J* = 10.3, 10.3 Hz, 1H), 2.60 (s, 1H), 2.52 (d, *J* = 19.5 Hz, 1H), 2.41– 2.27 (m, 2H), 2.21–2.13 (m, 2H), 2.05 (d, *J* = 19.8 Hz, 1H), 1.97 (s, 1H), 1.84 (dd, *J* = 14.1, 14.1 Hz, 1H), 1.59 (d, *J* = 13.2 Hz, 1H), 1.53 (dd, *J* = 13.1, 3.6 Hz, 1H), 1.39 (d, *J* = 7.0 Hz, 3H), 1.37 (dd, *J* = 15.0, 3.5 Hz, 1H), 1.14 (s, 3H), 0.32 (s, 3H), 0.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7 (C), 133.8 (CH), 129.6 (CH), 128.1 (CH), 128.0 (CH), 125.0 (CH), 79.0 (CH), 78.0 (C), 76.4 (CH), 60.1 (CH_2), 49.4 (C), 48.3 (CH), 47.5 (CH_2), 44.2 (CH), 35.9 (CH_2), 28.8 (CH_2), 27.1 (CH), 25.8 (CH_2), 24.7 (CH_3), 19.5 (CH_3), –4.2 (CH_3), –4.9 (CH_3); IR (film): 3320, 2954 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{36}NOSi$ [$(M+H)^+$]: 382.2566; found: 382.2563.



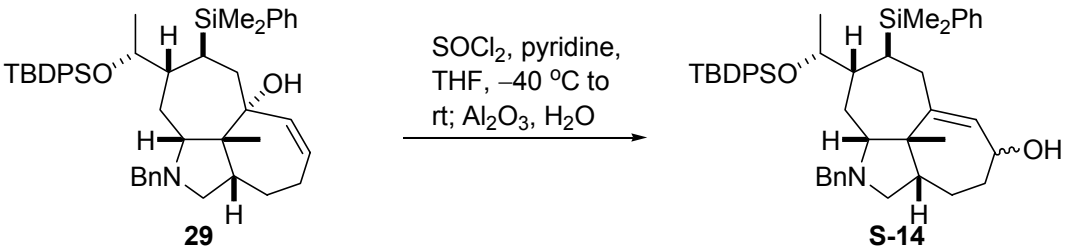
(3*S*,3a*R*,4*R*,6*S*,7*R*,8a*R*)-1-Benzyl-3-(but-3-enyl)-7-((*R*)-1-(*tert*-butyldiphenylsilyloxy)ethyl)-6-(dimethyl(phenyl)silyl)-3a-methyl-4-vinyl-decahydrocyclohepta[*b*]pyrrol-4-ol (28). Lithium chloride (0.199 g, 4.70 mmol) and anhydrous cerium (III) trichloride (0.579 g, 2.35 mmol) were added to a round-bottomed flask in a glove box. The flask was removed from the glove box, THF (3 mL) was added, and the suspension was stirred vigorously for 2.5 h at rt, producing a near colorless solution. This solution was added to ketone **22a** (0.171 g, 0.235 mmol) by cannula with a THF (2 mL) rinse. The solution was stirred for 2.5 h at rt, then cooled to –78 °C. A solution of vinylmagnesium bromide (1.7 mL, 2.4 mmol, 1.4 M in THF) was quickly added. After 20 min at –78 °C, methanol (2 mL) was added. The cold bath was removed, and 10% aqueous AcOH (6 mL) and Et_2O (20 mL) were added sequentially. After the solution had warmed to rt, the layers were separated. The aqueous layer was extracted with Et_2O (30 mL). The combined organic layers were washed sequentially with saturated aqueous sodium bicarbonate (30 mL) and brine (30 mL). The organic portion was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give **28** (0.129 g, 72%) as a colorless foam: $[\alpha]^{23}_{589}$ –14, $[\alpha]^{23}_{577}$ –16, $[\alpha]^{23}_{546}$ –17, $[\alpha]^{23}_{435}$ –32 (*c* = 1.2, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.49–7.44 (m, 2H), 7.44–7.30 (m, 9H), 7.22 (m, 1H), 7.11 (m, 4H), 6.04 (dd, *J* = 17.0, 10.7 Hz, 1H), 5.73 (m, 1H), 5.24 (d, *J* = 16.9 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 4.92 (d, *J* = 9.1 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.24 (d, *J* = 13.0 Hz, 1H), 3.94 (dd, *J* = 5.6, 3.8 Hz, 1H), 3.27 (d, *J* = 13.3 Hz, 1H), 2.84 (dd, *J* = 13.0, 7.9 Hz, 1H), 2.65 (m, 2H), 2.51 (dd, *J* = 9.1, 9.1 Hz, 1H), 2.14 (dd, *J* = 8.2, 8.2 Hz, 1H), 1.94 (m, 2H), 1.78–1.55 (m, 6H), 1.35 (ddd, *J* = 12.9, 12.9, 4.3 Hz, 1H), 1.17 (s, 3H), 1.04 (s, 9H), 0.94 (m, 1H), 0.52 (d, *J* = 5.9 Hz, 3H), 0.01 (s, 3H), –0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3 (CH), 139.7 (C), 138.8 (C), 138.7 (CH), 135.9 (CH), 135.9

(CH), 134.6 (C), 134.5 (C), 133.6 (CH), 129.6 (CH), 129.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.6 (CH), 127.5 (CH), 127.0 (CH), 114.5 (CH_2), 109.8 (CH_2), 80.5 (C), 73.2 (CH), 71.5 (CH), 57.3 (CH_2), 56.4 (CH_2), 51.5 (CH), 50.5 (CH), 42.1 (CH_2), 40.9 (CH), 36.6 (C), 33.9 (CH_2), 30.9 (CH_2), 28.4 (CH_2), 27.0 (CH_3), 25.5 (CH_3), 23.3 (CH), 19.2 (C), 16.1 (CH_3), –1.4 (CH_3), –4.9 (CH_3); IR (film): 3270, 2930, 2359 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{49}H_{66}NO_2Si_2$ [$(M+H)^+$]: 756.4632; found: 756.4639.

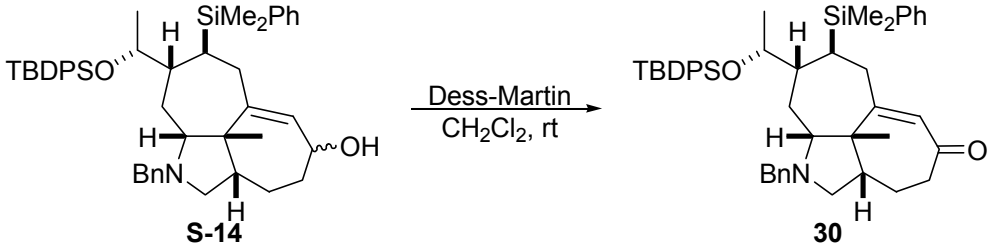


Alcohol 29. The Grubbs second generation catalyst (**26**) (benzylidene[1,3- bis(2,4,6-trimethylphenyl)-2- imidazolidinylidene] dichloro(tricyclohexylphosphine)ruthenium) (8.5 mg, 10 μmol) was added to a solution of diene **28** (0.151 g, 0.200 mmol) in CH_2Cl_2 (20 mL). The resultant brown solution was heated at reflux for 2.5 h. The solution was then cooled to rt and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give **29** (0.139 g, 96%) as a brown oil: $[\alpha]^{23}_{589}$ –22, $[\alpha]^{24}_{577}$ –23, $[\alpha]^{24}_{546}$ –26 (*c* = 0.84, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.62 (d, *J* = 6.8 Hz, 2H), 7.48– 7.35 (m, 8H), 7.30 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.26–7.21 (m, 2H), 7.17 (m, 4H), 5.54 (m, 1H), 5.37 (d, *J* = 11.8 Hz, 1H), 4.24 (d, *J* = 13.3 Hz, 1H), 3.97 (dd, *J* = 5.8, 3.3 Hz, 1H), 2.99 (d, *J* = 13.3 Hz, 1H), 2.94 (m, 1H), 2.68 (dd, *J* = 12.4, 5.1 Hz, 1H), 2.59 (d, *J* = 8.9 Hz, 1H), 2.42–2.29 (m, 2H), 2.21–2.03 (m, 2H), 1.89–1.71 (m, 3H), 1.68–1.62 (m, 1H), 1.58 (dd, *J* = 15.0, 4.1 Hz, 1H), 1.49 (m, 1H), 1.35–1.25 (m, 2H), 1.08 (s, 3H), 1.05 (s, 9H), 0.61 (d, *J* = 5.9 Hz, 3H), 0.02 (s, 3H), –0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4 (CH), 140.2 (C), 139.9 (C), 136.1 (CH), 136.0 (CH), 134.7 (C), 134.6 (C), 133.6 (CH), 131.4 (CH), 129.61 (CH), 129.57 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 127.7 (CH), 127.6 (CH), 126.6 (CH), 79.1 (C), 77.6 (CH), 71.7 (CH), 61.0 (CH_2), 58.4 (CH_2), 54.2 (C), 50.2 (CH), 43.3 (CH_2), 42.8 (CH), 32.0 (CH_2), 31.1 (CH_3), 30.6

(CH_2), 29.4 (CH_2), 27.2 (CH), 27.1 (CH_3), 19.3 (C), 16.5 (CH_3), –2.3 (CH_3), –3.8 (CH_3), missing carbon attributed to accidental equivalence; IR (film): 3440, 2929 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{47}H_{62}NO_2Si_2$ [$(M+H)^+$]: 728.4319; found: 728.4333.

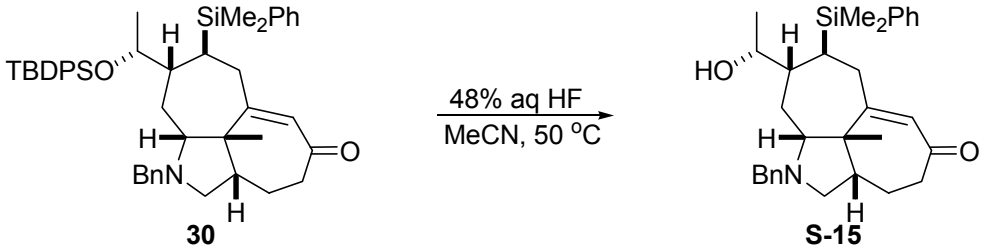


Alcohol S-14. Pyridine (34 μL, 0.42 mmol) and thionyl chloride (24 μL, 0.34 mmol) were added sequentially to a solution of allylic alcohol **29** (0.122 g, 0.168 mmol) in THF (4 mL) at –40 °C. After 30 min at –40 °C, aluminum oxide (2 g), water (2 mL), and THF (6 mL) were added, and the mixture was allowed to warm to rt. The suspension was stirred vigorously for 18 h at rt, then filtered through celite, washing with CH_2Cl_2 (50 mL). The filtrate was concentrated in vacuo and the residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give alcohol **S-14** (0.081 g, 66%) as a colorless foam and a 1.1:1 mixture of diastereomers. This compound was not characterized because it was obtained as a mixture. A copy of the ^1H NMR spectrum of the mixture is included in the spectral section for reference purposes. Satisfactory low-resolution mass spectral data were obtained: LRMS (ESI) *m/z* for $C_{47}H_{62}NO_2Si_2$ [$(M+H)^+$]: 728.4.



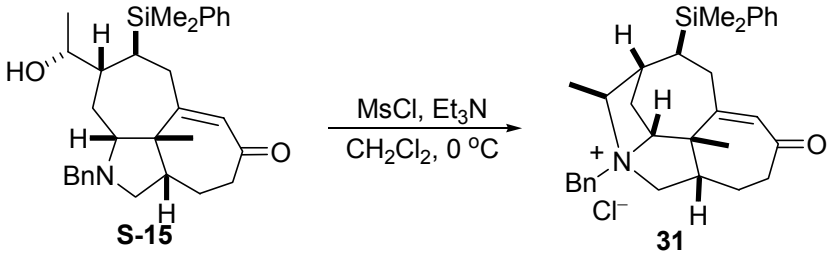
Enone 30. Pyridine (19 μL, 0.24 mmol) and Dess–Martin periodinane (44 mg, 0.10 mmol) were added sequentially to a solution of alcohols **S-14** (0.069 g, 0.095 mmol) in water-saturated CH_2Cl_2 (5 mL). The resultant suspension was stirred for 1 h at rt. A solution of sodium thiosulfate (4 g) in 80% saturated aqueous sodium bicarbonate (20

mL) was then added. The layers were separated, and the aqueous portion was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give **30** (0.047 g, 68%) as a colorless oil: $[\alpha]^{23}_{589}$ +13, $[\alpha]^{23}_{577}$ +15, $[\alpha]^{23}_{546}$ +19, $[\alpha]^{23}_{435}$ +65 (*c* = 0.70, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.46–7.16 (m, 16H), 5.69 (s, 1H), 3.96 (m, 1H), 3.82 (d, *J* = 13.8 Hz, 1H), 3.72 (d, *J* = 13.6 Hz, 1H), 3.09 (dd, *J* = 8.1, 8.1 Hz, 1H), 2.79 (d, *J* = 10.0 Hz, 1H), 2.67–2.59 (m, 2H), 2.50 (dd, *J* = 8.9, 5.0 Hz, 1H), 2.44 (m, 1H), 2.30 (d, *J* = 12.8 Hz, 1H), 2.12 (m, 1H), 2.02 (m, 2H), 1.72 (dd, *J* = 9.6, 9.6 Hz, 1H), 1.64 (d, *J* = 13.9 Hz, 1H), 1.56 (br s, 1H), 1.34 (s, 3H), 1.04 (s, 9H), 0.86 (dd, *J* = 11.7, 11.7 Hz, 1H), 0.73 (d, *J* = 16.1 Hz, 3H), 0.05 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8 (C), 166.9 (C), 139.6 (C), 138.5 (C), 135.94 (CH), 125.86 (CH), 134.5 (C), 134.3 (C), 133.4 (CH), 129.63 (CH), 129.59 (CH), 129.1 (CH), 128.9 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 127.5 (CH), 126.7 (CH), 73.5 (CH), 70.6 (CH), 58.2 (CH_2), 56.3 (C), 55.9 (CH_2), 49.5 (CH), 49.1 (CH), 43.0 (CH_2), 39.2 (CH_2), 35.2 (CH_2), 32.9 (CH_2), 29.4 (CH_2), 27.4 (CH), 27.0 (CH_3), 19.1 (C), 16.9 (CH_3), –3.3 (CH_3), –3.4 (CH_3); IR (film) 2927, 1651 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{47}H_{60}NO_2Si_2$ [$(M+H)^+$]: 726.4163; found: 726.4157.



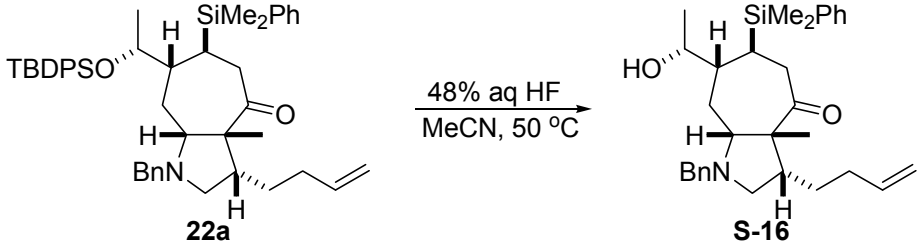
Alcohol S-15. Hydrogen fluoride (0.4 mL, 48% aq) was added to a solution of silyl ether **30** (0.021 g, 0.028 mmol) in MeCN (1.6 mL) in a Nalgene vial and the solution was heated at 50 °C for 17.5 h. Additional hydrogen fluoride (0.4 mL, 48% aq) was added and the solution was maintained for another 9 h at 50 °C. The solution was then cooled to rt and poured into a stirring, biphasic mixture of Et_2O (70 mL) and aqueous 1 N NaOH solution (60 mL). The mixture was stirred for 20 min at rt, then the layers were separated.

The aqueous layer was extracted with Et_2O (2 x 70 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (gradient: 1:19 acetone:hexanes to 1:9 acetone:hexanes) to give **S-15** (0.011 g, 80%) as a colorless foam, along with recovered starting material (**30**) (1 mg, 5%): $[\alpha]^{23}_{589}$ +2.16, $[\alpha]^{23}_{577}$ +3.98, $[\alpha]^{23}_{546}$ +7.03 (*c* = 1.14, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.43–722 (m, 8H), 5.79 (s, 1H), 3.94 (m, 1H), 3.79 (d, *J* = 13.3 Hz, 1H), 3.65 (d, *J* = 13.3 Hz, 1H), 3.11 (dd, *J* = 7.1, 7.1 Hz, 1H), 2.72–2.61 (m, 2H), 2.52 (m, 1H), 2.47 (m, 1H), 2.38 (d, *J* = 12.7 Hz, 1H), 2.19 (d, *J* = 12.7 Hz, 1H), 2.14–2.00 (m, 3H), 1.66 (m, 1H), 1.48 (dd, *J* = 11.5, 11.5 Hz, 1H), 1.35 (s, 3H), 1.25 (m, 1H), 0.94 (dd, *J* = 11.8, 11.8 Hz, 1H), 0.84 (d, *J* = 6.3 Hz, 3H), 0.36 (s, 3H), 0.34 (s, 3H), missing H attributed to deuterium exchange with solvent; ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7 (C), 166.5 (C), 139.4 (C), 138.5 (C), 133.4 (CH), 129.3 (CH), 129.2 (CH), 128.6 (CH), 128.2 (CH), 128.0 (CH), 126.8 (CH), 72.5 (CH), 69.0 (CH), 58.8 (CH_2), 56.2 (C), 55.9 (CH2), 49.3 (CH), 49.0 (CH), 42.9 (CH_2), 39.3 (CH_2), 34.7 (CH), 32.8 (CH_3), 28.5 (CH_2), 27.4 (CH_2), 16.3 (CH_3), –2.8 (CH_3), –3.1 (CH_3); IR (film): 3429, 2924, 1637 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{31}H_{42}NO_2Si$ [$(M+H)^+$]: 488.2985; found: 488.2977.



Benzylammonium salt 31. Triethylamine (4 μL, 0.03 mmole) and methanesulfonyl chloride (2 μL, 0.02 mmole) were added sequentially to a solution of alcohol **S-15** (9.1 mg, 0.019 mmole) in CH_2Cl_2 (1 mL) at 0 °C. The cold bath was removed and the solution was stirred at rt for 24 h. Additional triethylamine (5 μL) and methanesulfonyl chloride (3 μL) were added and the solution was stirred for 24 h at rt. The reaction mixture was loaded directly onto a silica gel column that had been pretreated with sodium bromide as

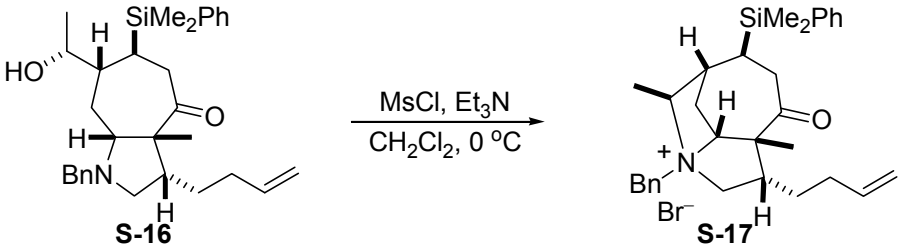
per the literature method.[13] The product was eluted with a 9:1 mixture of CH_2Cl_2:MeOH and the product-containing fractions were concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with a 1:1 mixture of brine:saturated $NaHCO_3$ solution (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give **31** as a colorless solid: $[\alpha]^{24}_{589}$ +55, $[\alpha]^{24}_{577}$ +58, $[\alpha]^{24}_{546}$ +68, $[\alpha]^{24}_{435}$ +153, $[\alpha]^{24}_{405}$ +204 (*c* = 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.5 Hz, 2H), 7.52-7.50 (m, 2H), 7.48-7.42 (m, 6H), 6.00 (s, 1H), 5.61 (d, *J* = 12.7 Hz, 1H), 4.66 (dd, *J* = 13.6, 9.1 Hz, 1H), 4.19 (d, *J* = 12.7 Hz, 1H), 3.99 (dd, *J* = 13.6, 13.6 Hz, 1H), 3.78 (m, 1H), 3.58 (d, *J* = 6.5 Hz, 1H), 2.76 (m, 1H), 2.54 (m, 2H), 2.42 (m, 2H), 2.31 (dd, *J* = 13.9, 4.3 Hz, 1H), 1.97 (m, 1H), 1.85 (d, *J* = 7.0 Hz, 3H), 1.81 (m, 2H), 1.62 (m, 1H), 1.12 (m, 1H), 1.10 (s, 3H), 0.40 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8 (C), 155.2 (C), 135.1 (C), 133.7 (CH), 132.9 (CH), 132.8 (CH), 130.8 (CH), 130.1 (CH), 129.6 (CH), 128.4 (CH), 127.9 (C), 87.1 (CH), 81.3 (CH), 62.3 (CH_2), 57.6 (CH_2), 50.7 (C), 47.3 (CH), 41.9 (CH), 37.7 (CH_2), 35.0 (CH_2), 33.6 (CH), 25.4 (CH_3), 24.0 (CH_2), 18.7 (CH_2), 14.8 (CH_3), -4.8 (CH_3), -4.9 (CH_3); IR (film) 2953, 2924, 1648 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{31}H_{40}NOSi$ [$(M)^+$]: 470.2879; found: 470.2877.



(3*S*,3a*R*,6*S*,7*R*,8a*R*)-1-Benzyl-3-(but-3-enyl)-6-(dimethyl(phenyl)silyl)-7-((*R*)-1-hydroxyethyl)-3a-methyl-octahydrocyclohepta[*b*]pyrrol-4(5*H*)-one (S-16). Hydrogen fluoride (0.3 mL, 48% aq) was added to a solution of silyl ether **22a** (0.031 g, 0.043 mmol) in MeCN (2.5 mL) in a Nalgene vial at rt. The solution was then heated at 50 °C for 24 h. Additional hydrogen fluoride (0.4 mL, 48% aq) was added and the solution was maintained for 21 h at 50 °C. The solution was then cooled to rt and added to a stirring, biphasic mixture of Et_2O (70 mL) and aqueous 1 N NaOH solution (60 mL). The mixture was stirred for 20 min at rt, then the layers were separated and the aqueous layer was

[13] Bluhm, L. H.; Li, T. *Tetrahedron Lett.* **1998**, *39*, 3623–3626.

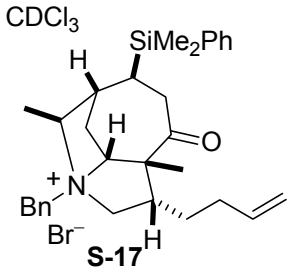
extracted with Et_2O (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (5:1 hexanes:acetone) to give **S-16** (15.5 mg, 74%) as a colorless oil: $[\alpha]^{24}_{589}$ −68, $[\alpha]^{24}_{577}$ −75, $[\alpha]^{24}_{546}$ −86, $[\alpha]^{24}_{435}$ −158, $[\alpha]^{24}_{405}$ −190 (*c* = 0.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.38-7.29 (m, 8H), 5.70-5.61 (m, 1H), 4.95-4.90 (m, 2H), 4.10 (d, *J* = 13.2 Hz, 1H), 3.93-3.90 (m, 1H), 3.55 (d, *J* = 13.2 Hz, 1H), 3.14 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.01 (dd, *J* = 11.6, 8.8 Hz, 1H), 2.84-2.80 (m, 2H), 2.53 (dd, *J* = 11.3, 6.1 Hz, 1H), 1.97-1.93 (m, 2H), 1.86-1.71 (m, 4H), 1.67-1.65 (m, 1H), 1.47-1.41 (m, 1H), 1.02-0.99 (m, 1H), 1.01 (s, 3H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.88-0.85 (m, 1H), 0.38 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.8 (C), 138.3 (C), 138.0 (CH), 137.1 (C), 134.6 (CH), 129.9 (CH), 129.2 (CH), 128.7 (CH), 127.8 (CH), 115.2 (CH_2), 73.5 (CH), 71.7 (CH), 62.0 (C), 61.0 (CH_2), 56.6 (CH_2), 47.5 (CH), 43.6 (CH_2), 42.4 (CH), 33.2 (CH_2), 32.9 (CH_2), 28.6 (CH_2), 24.2 (CH_3), 21.8 (CH), 21.0 (CH_3), -3.1 (CH_3), -4.0 (CH_3), missing carbon atttributed to accidental equivalence; IR (film) 2965, 1691, 1455 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{31}H_{44}NO_2Si$ [$(M+H)^+$]: 490.3141; found: 490.3135.



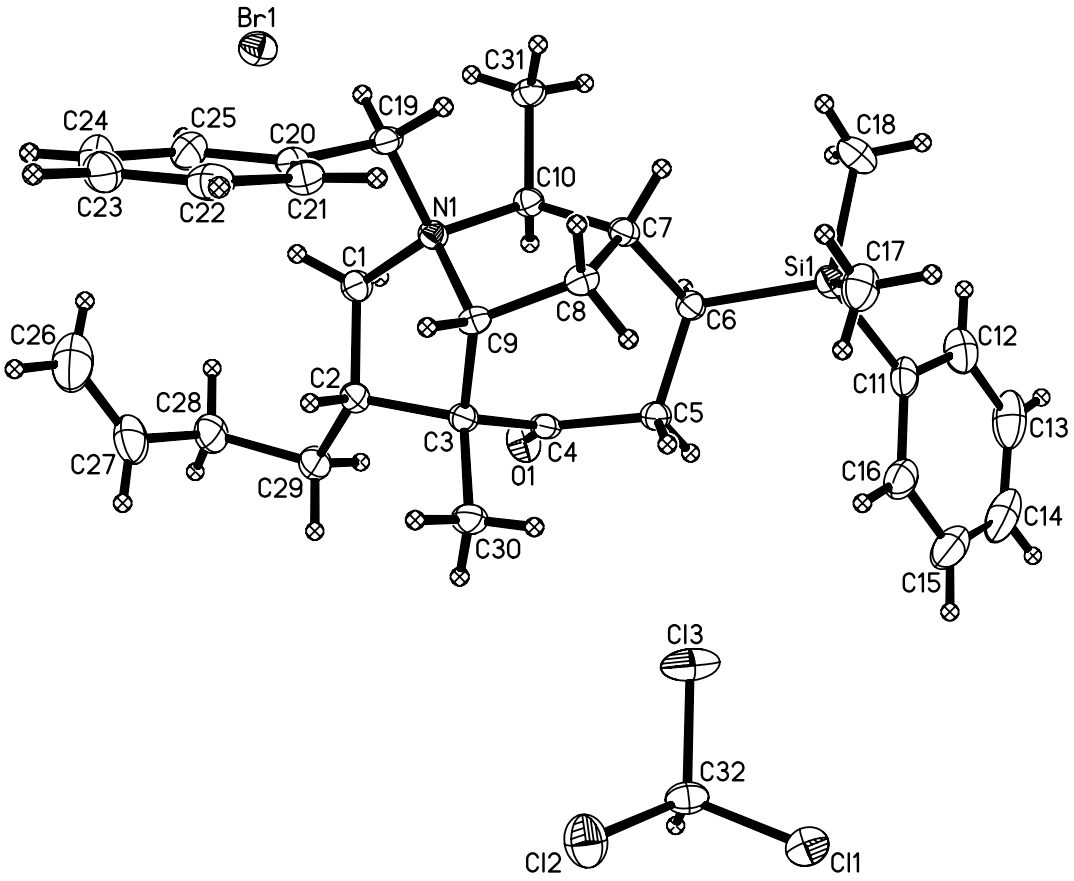
(3*S*,3a*R*,6*S*,7*R*,8a*R*,9*S*)-Octahydro-1-benzyl-3-(but-3-enyl)-3a,9-dimethyl-6-(dimethyl(phenyl)silyl)-1,7-methanocyclohepta[*b*]pyrrolium-4(5*H*)-one bromide (S-17). Triethylamine (7 μL, 0.05 mmole) and methanesulfonyl chloride (3 μL, 0.04 mmole) were added sequentially to a solution of alcohol **S-16** (15 mg, 0.031 mmole) in CH_2Cl_2 (1 mL) at 0 °C. The solution was stirred at 0 °C for 30 min, then diluted with CH_2Cl_2 (3 mL) and saturated aqueous $NaHCO_3$ solution (3 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 1 mL). The combined organic extracts were concentrated in vacuo and the residue was purified on a silica gel column that had been pretreated with sodium bromide as per the literature method.[13] The product was

eluted with a 9:1 mixture of CH_2Cl_2:MeOH and the product-containing fractions were concentrated in vacuo. The residue was dissolved in CH_2Cl_2, washed with a 1:1 mixture of dilute aqueous NaBr solution:saturated $NaHCO_3$ solution, dried over Na_2SO_4, filtered, and concentrated in vacuo to give **S-17** (15.0 mg, 89%) as a colorless solid. Slow diffusion of diethyl ether into a solution of **S-17** in $CDCl_3$ (0.2 mL) provided crystals suitable for X-ray analysis: $[\alpha]^{24}_{589}$ +27, $[\alpha]^{24}_{577}$ +31, $[\alpha]^{24}_{546}$ +38, $[\alpha]^{24}_{435}$ +111, $[\alpha]^{24}_{405}$ +167 (*c* = 0.41, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.0 Hz, 2H), 7.57-7.55 (m, 2H), 7.44-7.43 (m, 3H), 7.41-7.35 (m, 3H), 5.58-5.50 (m, 1H), 5.02 (d, *J* = 13.0 Hz, 1H), 4.99 (d, *J* = 13.0 Hz, 1H), 4.93-4.89 (m, 2H), 4.45 (dd, *J* = 13.0, 9.0 Hz, 1H), 3.50 (d, *J* = 6.7 Hz, 1H), 3.32-3.25 (m, 2H), 3.14-3.08 (m, 1H), 3.00-2.97 (m, 1H), 2.59 (dd, *J* = 12.2, 12.2 Hz, 1H), 2.27 (dd, *J* = 11.9, 5.1 Hz, 1H), 2.17-2.09 (m, 1H), 2.00-1.93 (m, 1H), 1.80-1.70 (m, 5H), 1.62-1.56 (m, 1H), 1.09 (dd, *J* = 12.5, 5.0 Hz, 1H), 1.05-1.01 (m, 1H), 0.99 (s, 3H), 0.43 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.4 (C), 137.2 (CH), 135.1 (C), 134.3 (CH), 133.2 (CH), 130.7 (CH), 130.1 (CH), 129.6 (CH), 128.5 (CH), 128.3 (C), 116.5 (CH_2), 87.9 (CH), 79.6 (CH), 66.1 (CH_2), 58.5 (CH_2), 56.7 (C), 49.0 (CH), 42.4 (CH), 37.8 (CH_2), 33.5 (CH_2), 30.7 (CH), 25.9 (CH_2), 24.5 (CH_2), 20.0 (CH_3), 15.0 (CH_3), -4.56 (CH_3), -4.60 (CH_3); IR (film) 2923, 1698, 1454 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{31}H_{42}NOSi$ [$(M)^+$]: 472.3036; found: 472.3019.

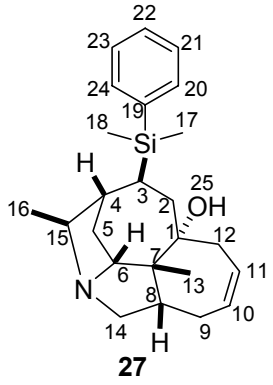
X-ray structure of S-17[14]



S-17



[14] The thermal ellipsoid plot is shown at the 50% probability level.

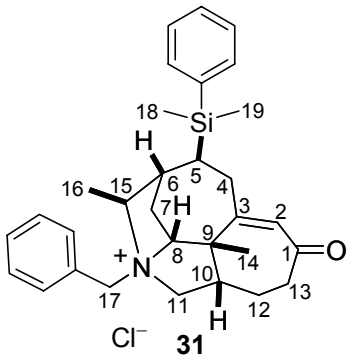


27

Table S1. NMR data for **27** in $CDCl_3$.

Atom	^{1}H shift (ppm)	^{1}H mult.	*J* value(s) (Hz)	^{13}C shift (ppm)	^{13}C mult.	HMBC	COSY	NOESY
1				78.0	C			
2a	1.84	dd	14.1,14.1	35.9	CH_2	3,7	2b,3	2b,5b,12a,13
2b	1.37	dd	15.0,3.5	35.9	CH_2	1,3,4,7,12	2a,3	3,12a,12b
3	1.53	dd	13.1,3.6	27.1	CH	4,5,10	2a,2b	2b,15
4	2.21-2.13	m		44.2	CH	2,3,5	5a	5b,15,16
5a	2.21-2.13	m		25.8	CH_2	6,7	4,5b	5b,6
5b	1.59	d	13.2	25.8	CH_2	3,4,6,15	5a	2a,4,5a,6,13
6	3.71	s		79.0	CH	1,4,15	5a,5b	5a,5b,8,13
7				49.4	C			
8	2.41-2.27	m		48.3	CH	1,7,9	9a,9b	6,13,14a
9a	2.41-2.27	m		28.8	CH_2	8	8,9b	9b,10
9b	2.60	s		28.8	CH_2	4	8,9a	9a,10,14b
10	5.67	m		125.0	CH		9a,11	9a,9b,11
11	5.48	m		128.0	CH		10,12a,12b	10,12a,12b
12a	2.52	d	19.5	47.5	CH_2		12b	2a,11,12b,13

12b	2.05	d	19.8	47.5	CH_2		12a	2b,11,12a
13	1.14	s		24.7	CH_3	1,6,7,8		2a,5b,6,8,12a
14a	3.99	dd	9.2,9.2	60.1	CH_2		8,14b	8,14b
14b	3.10	dd	10.3,10.3	60.1	CH_2	8,9,15	8,14a	9b,14a,15
15	4.09	d	6.7	76.4	CH	3,4,14	4,16	3,4,14b,16
16	1.39	d	7.0	19.5	CH_3	4,15	15	4,15
17	0.31	s		-4.9	CH_3			2a,2b,3,4,5a,5b,20,24
18	0.32	s		-4.2	CH_3			2a,2b,3,4,5a,5b,20,24
19				136.7	C	20,21,23,24		
20	7.45	m		133.8	CH	19,21,22	21	2a,3,4
21	7.42-7.33	m		128.1	CH	19,20,22	20,22	
22	7.42-7.33	m		129.6	CH	20,21,23,24	21,23	
23	7.42-7.33	m		128.1	CH	19,22,24	22,24	
24	7.45	m		133.8	CH	19,22,23	23	2a,3,4
25	1.97	s			OH			



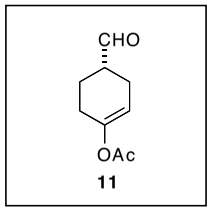
31

Table S2. NMR data for **31** in $CDCl_3$.

Atom	^{1}H shift (ppm)	^{1}H mult.	*J* value(s) (Hz)	^{13}C shift (ppm)	^{13}C mult.	HMBC	COSY
1				199.8	C		
2	6.00	s		132.8	CH	1, 3, 9, 4	4a,4b,13b
3				155.2	C		
4a	2.42	m		35.0	CH_2	2,3,5,6,9	2,4b,5
4b	2.31	dd	13.9, 4.3	35.0	CH_2	2,3,5,6,9	2,4a,5
5	1.12	m		33.6	CH	3,4,6,7,15	4a,4b
6	2.54	m		41.9	CH	4,7,8,16	7a,7b,15
7a	2.42	m		24.0	CH_2	5,6,8,9	6,7b,8
7b	1.81	m		24.0	CH_2	5,6,9	6,7a
8	3.58	d	6.5	81.3	CH	3,6,7,9,10,14,15,17	7a
9				50.7	C		
10	1.62	m		47.3	CH	3	11a,11b,12a,12b
11a	4.66	dd	13.6,9.1	62.3	CH_2	8,9,10,12,15,17	10,11b
11b	3.99	dd	13.6,13.6	62.3	CH_2	10,12,15,17	10,11a
12a	1.97	m		18.7	CH_2	9	10,12b,13a,13b
12b	1.81	m		18.7	CH_2	1,9,10,13	10,12a,13a,13b

13a	2.76	m		37.7	CH_2	1,10,12	12a,12b,13b
13b	2.54	m		37.7	CH_2	1,10,12	12a,12b,13a
14	1.10	s		25.4	CH_3	3,8,9,10	
15	3.78	m		87.1	CH	5,6,11,16,17	6,16
16	1.85	d	7.0	14.8	CH_3	6,15	15
17a	5.61	d	12.7	57.6	CH_2	8,11,15	17b
17b	4.19	d	12.7	57.6	CH_2	8,11,15	17a
18	0.40	s		-4.8	CH_3		
19	0.39	s		-4.9	CH_3		

1H spectrum



11

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1D NMR plot parameters

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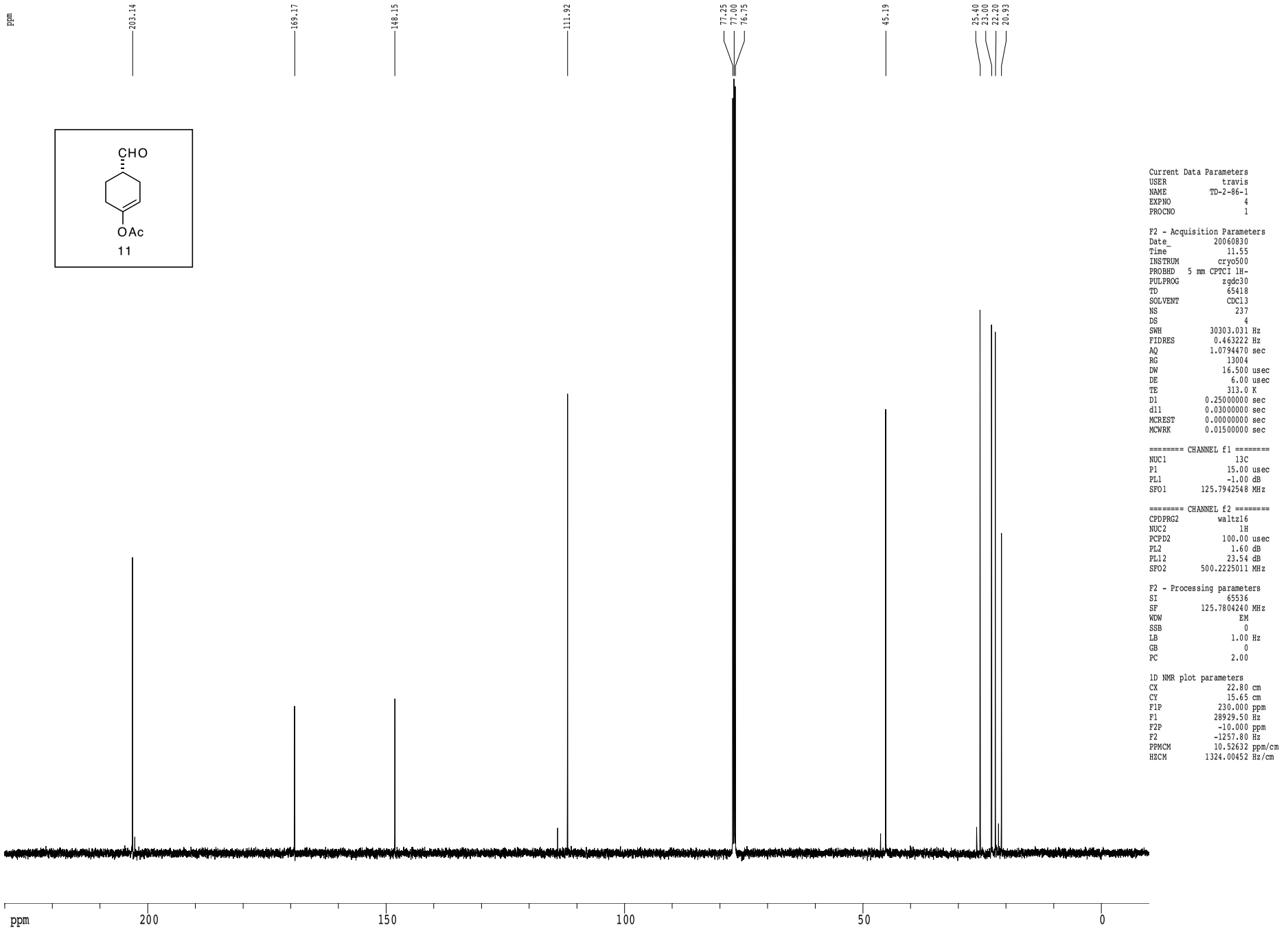
13C spectrum with 1H decoupling



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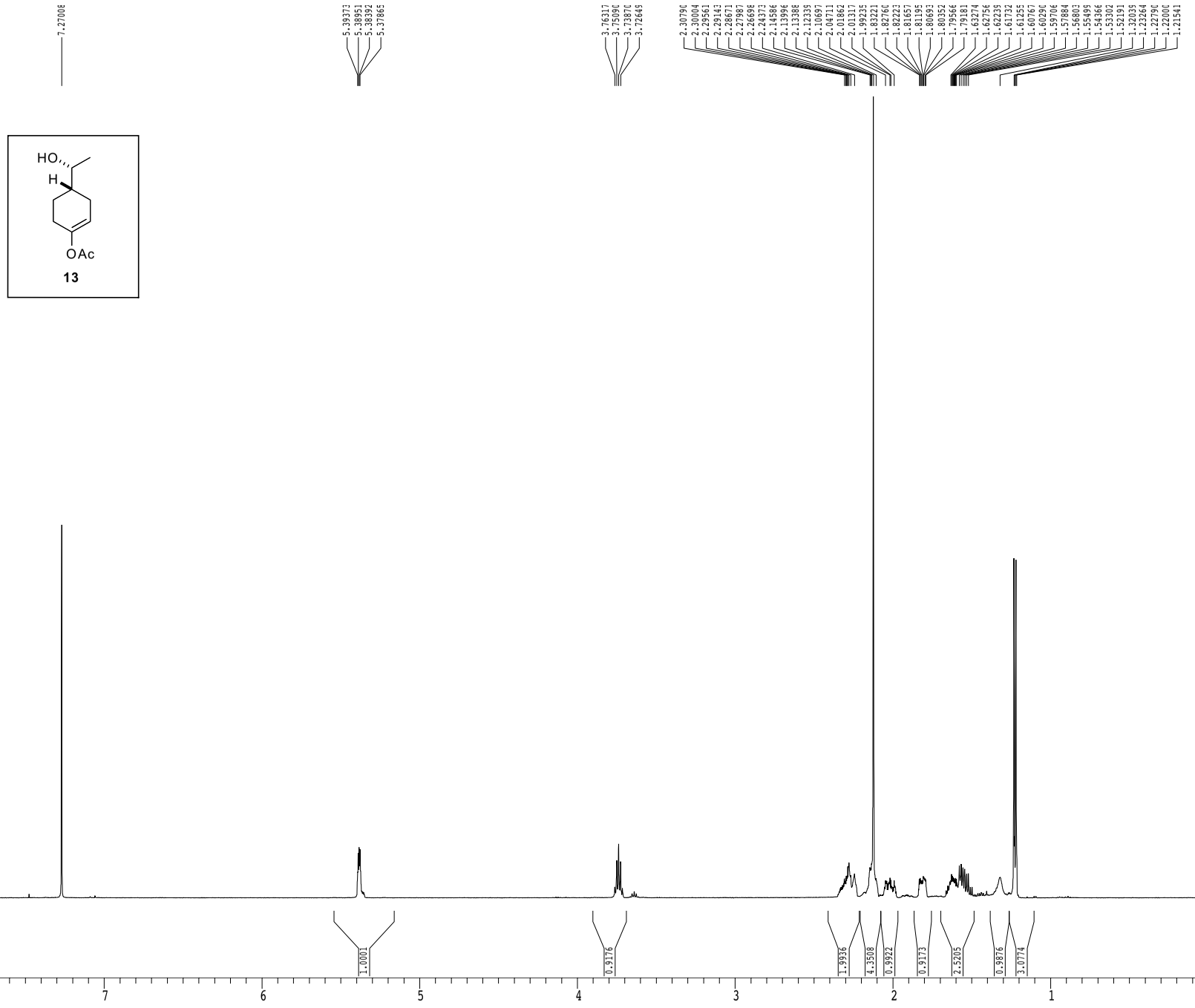
1H spectrum



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PROCNO 1

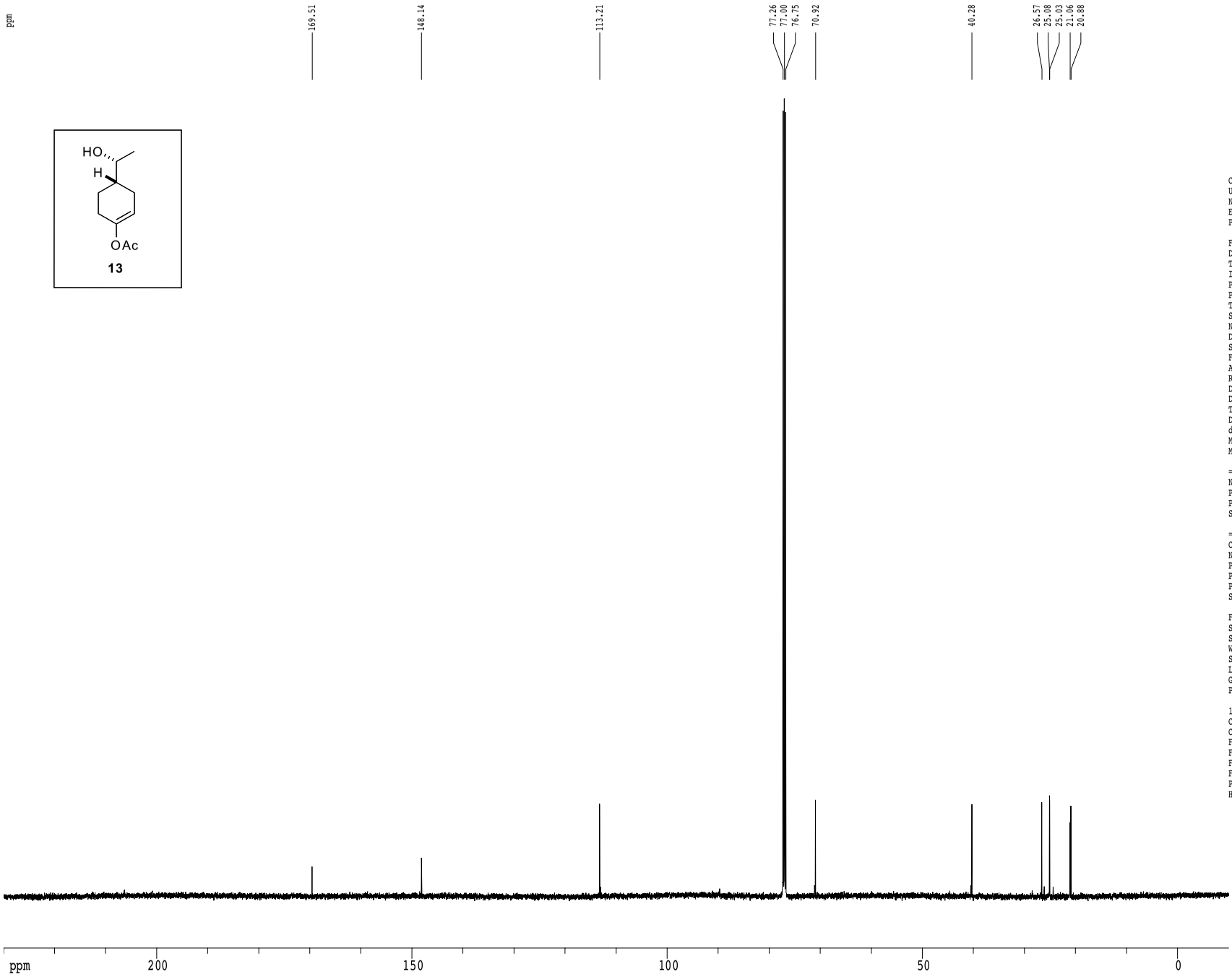
F2 - Acquisition Parameters
Date_ 20060928
Time 14.06
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.000 ppm
F1 4001.76 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.35088 ppm/cm
HZCM 175.51581 Hz/cm

13C spectrum with 1H decoupling

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Current Data Parameters
USER              travis
NAME          TD-2-119-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20060928
Time              15.29
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  426
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG               18390.4
DW               16.500 usec
DE                6.00 usec
TE               298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

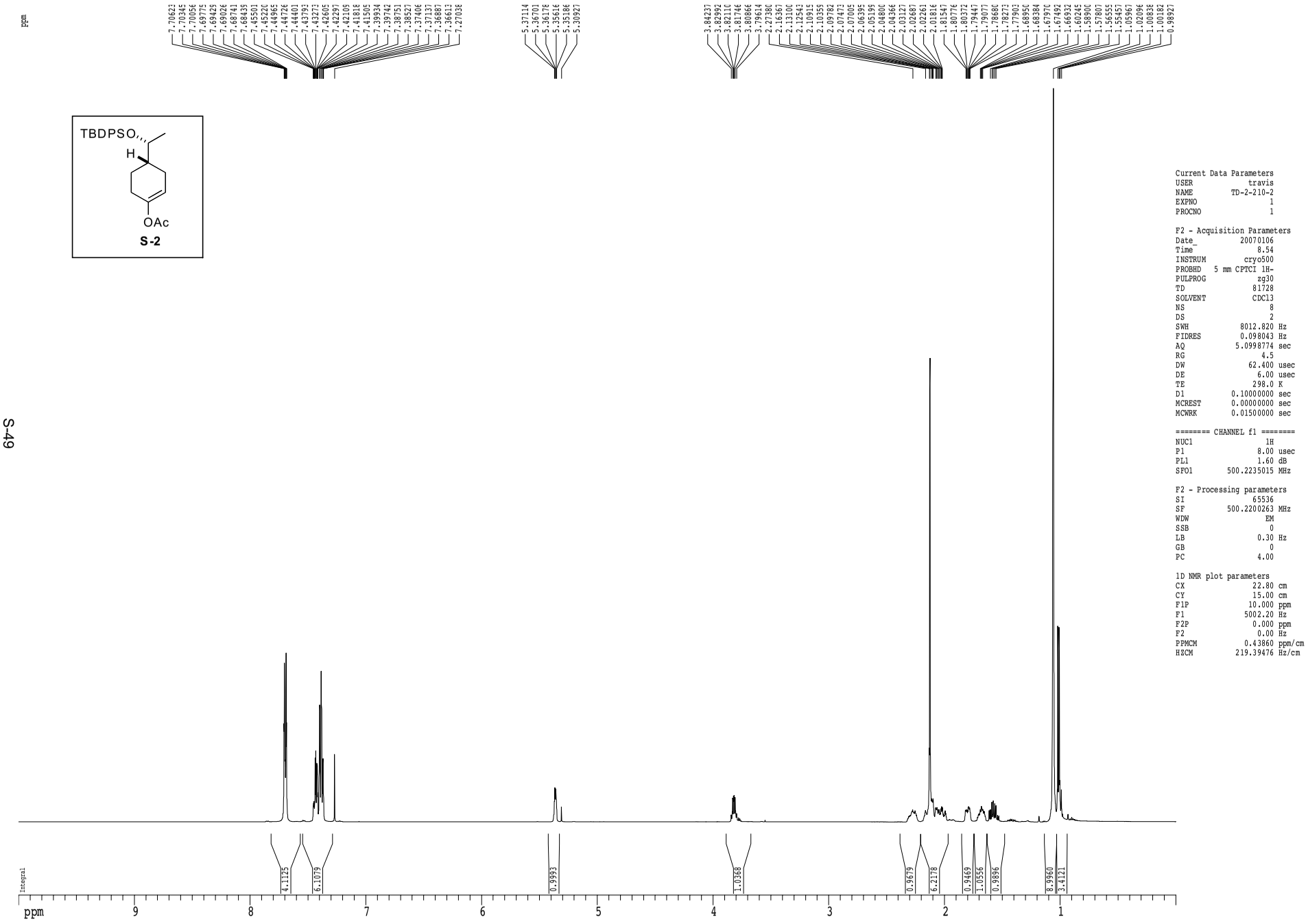
======= CHANNEL f1 =======
NUC1               13C
P1               15.00 usec
PL1              -1.00 dB
SFO1        125.7942548 MHz

======= CHANNEL f2 =======
CPDPRG2         waltz16
NUC2               1H
PCPD2            100.00 usec
PL2               1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

F2 - Processing parameters
SI                65536
SF          125.7804277 MHz
WDW                EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.000 ppm
F1              28929.50 Hz
F2P              -10.000 ppm
F2             -1257.80 Hz
PPMCM           10.52632 ppm/cm
HZCM         1324.00452 Hz/cm
```

1H spectrum



Current Data Parameters
USER travis
NAME TD-2-210-2
EXPNO 1
PROCNO 1

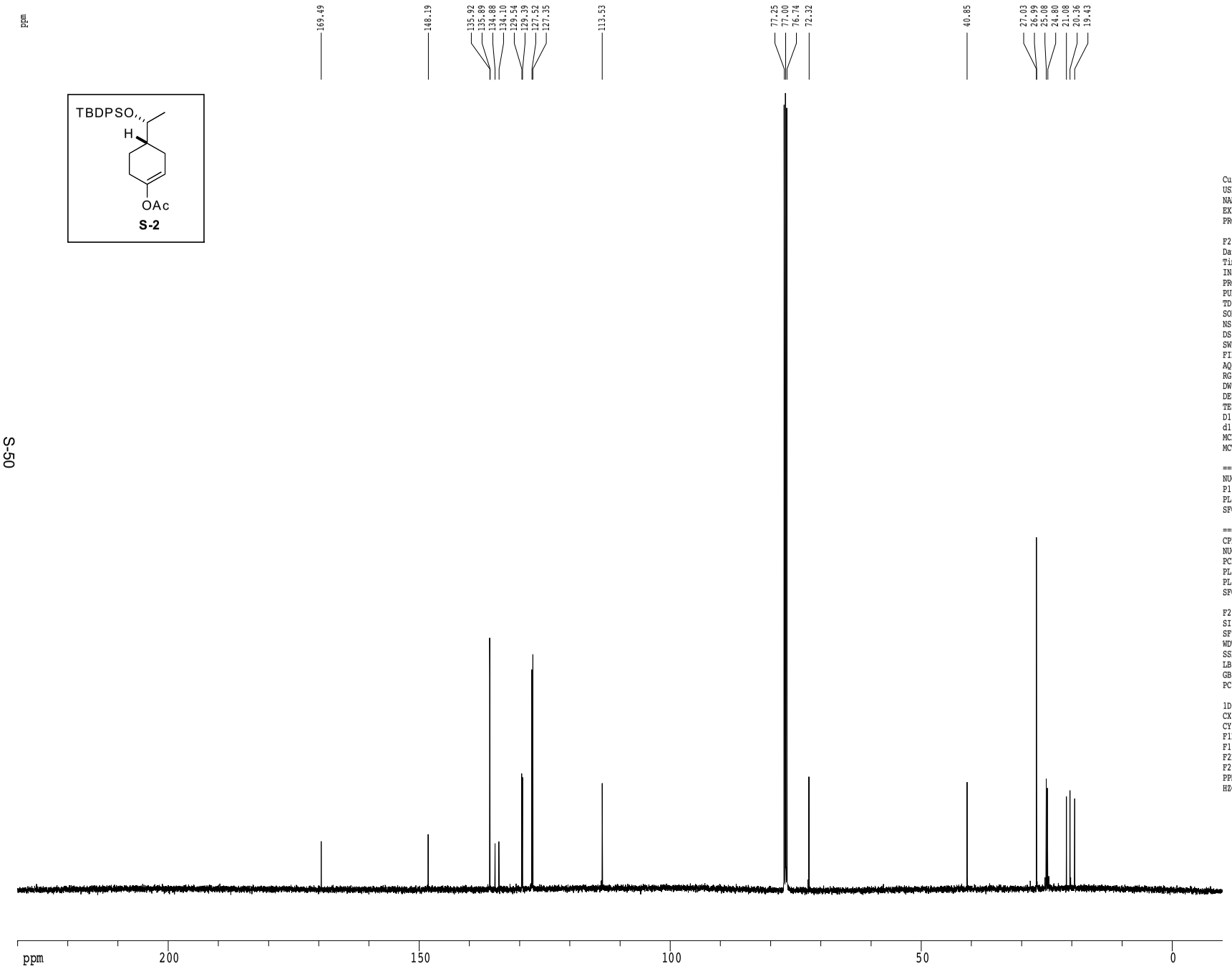
F2 - Acquisition Parameters
Date_ 20070106
Time 8.54
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4.5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200263 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER travis
NAME TD-2-210-2
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070221
Time 14.35
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 146
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 9195.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

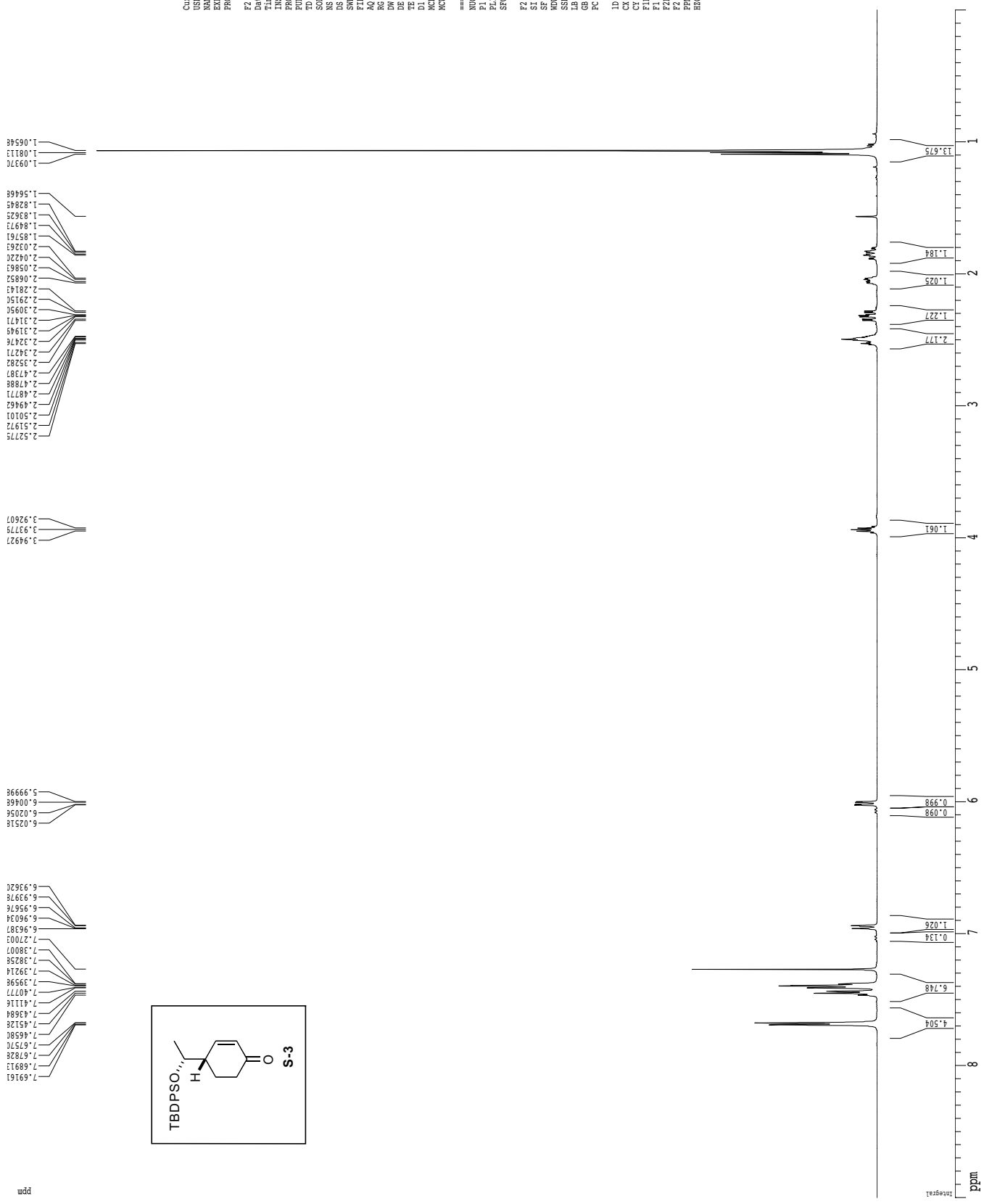
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

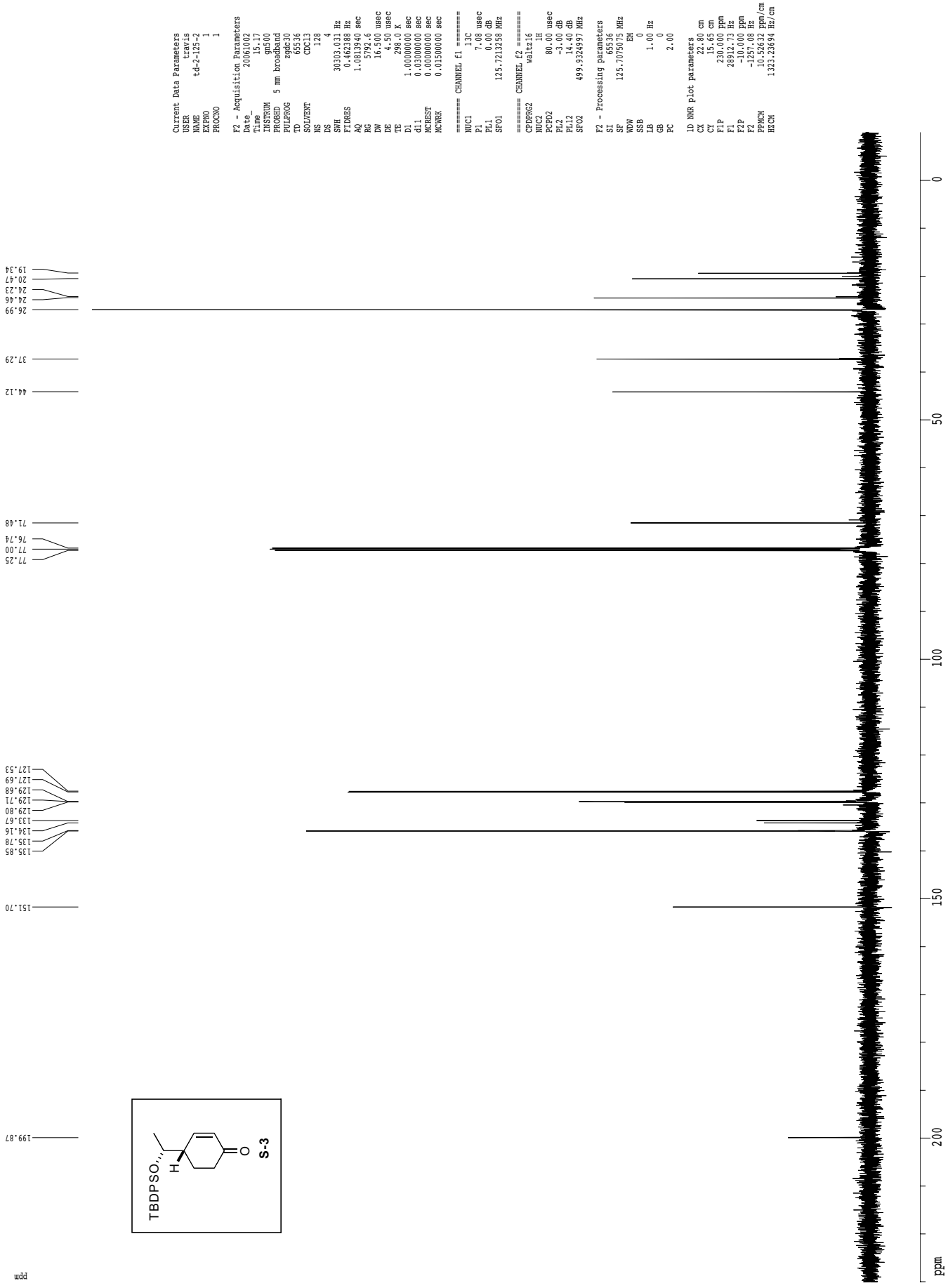
F2 - Processing parameters
SI 65536
SF 125.7804286 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 230.000 ppm
F1 28929.50 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 10.52632 ppm/cm
HZCM 1324.00452 Hz/cm

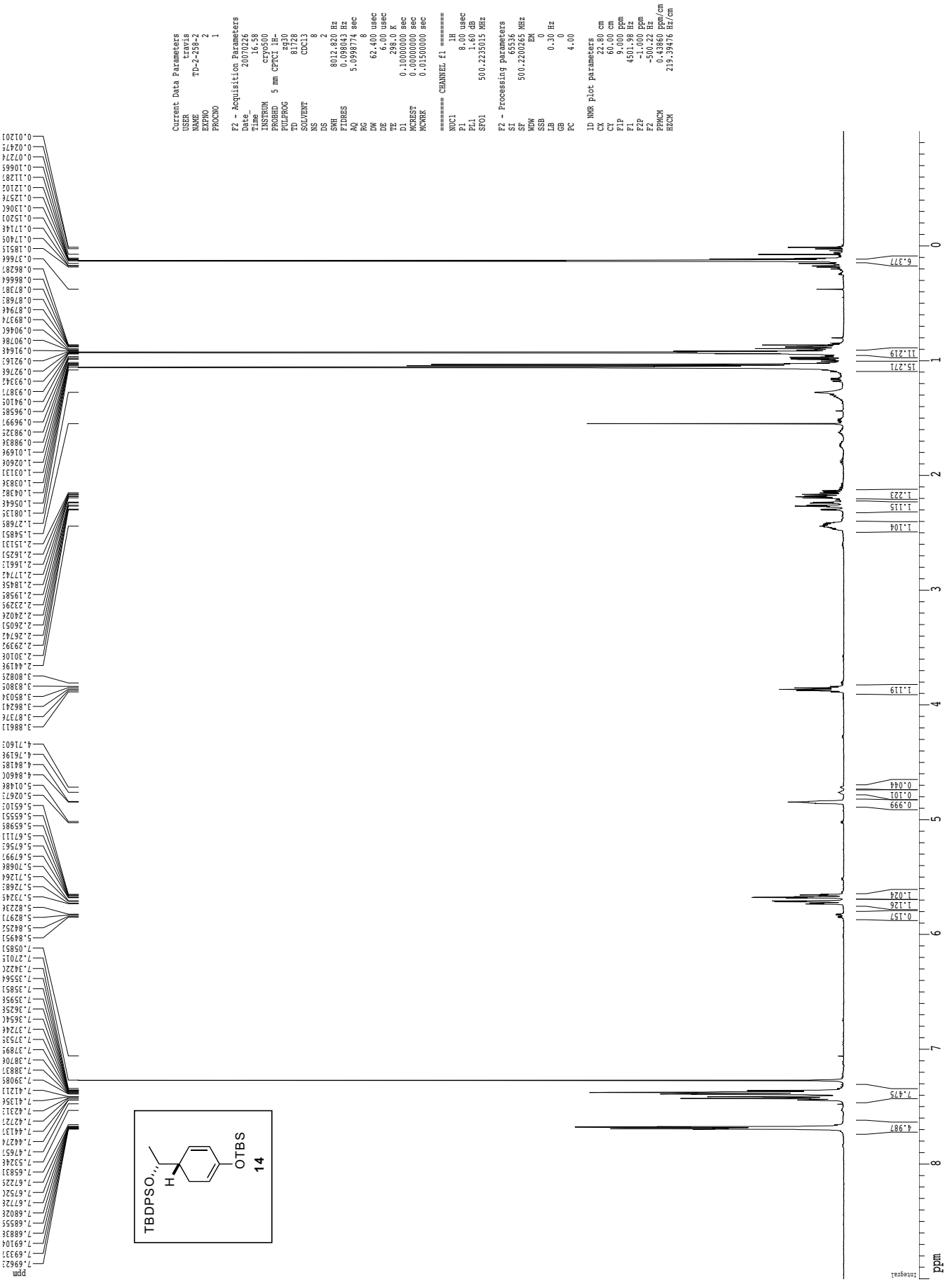
1H spectrum


Current Data Parameters
USER travis
NAME TD-2-211-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070102
Time_ 14.21
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200266 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.39474 ppm/cm
HZCM 197.45528 Hz/cm
TBDPSO
H
O
S-3
ppm
Integral

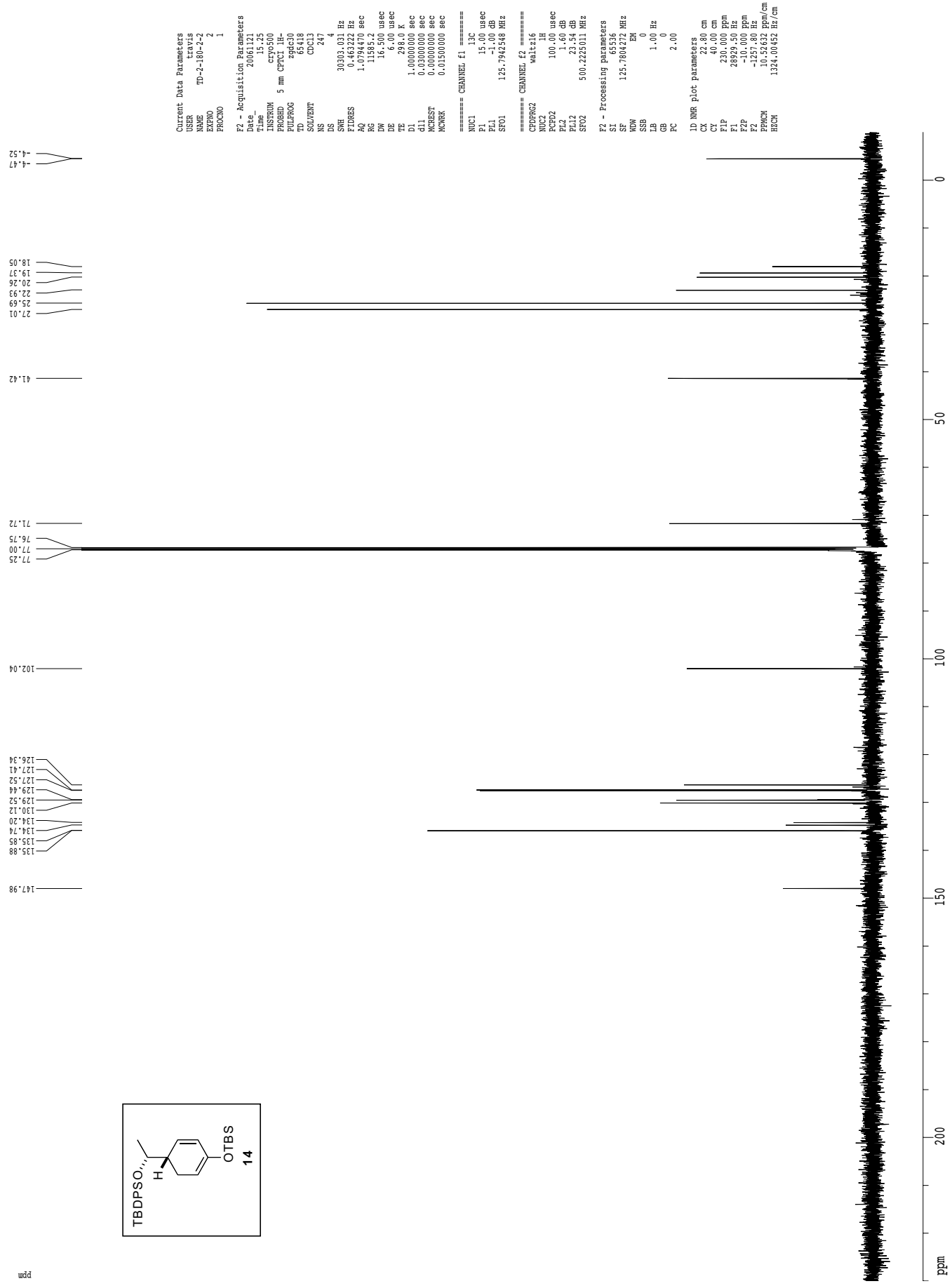
13C spectrum with 1H decoupling



1H spectrum



13C spectrum with 1H decoupling



Current Data Parameters
USER travis
NAME TD-2-180-2-2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061121
Time 15.25
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 247
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794470 sec
RG 11585.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

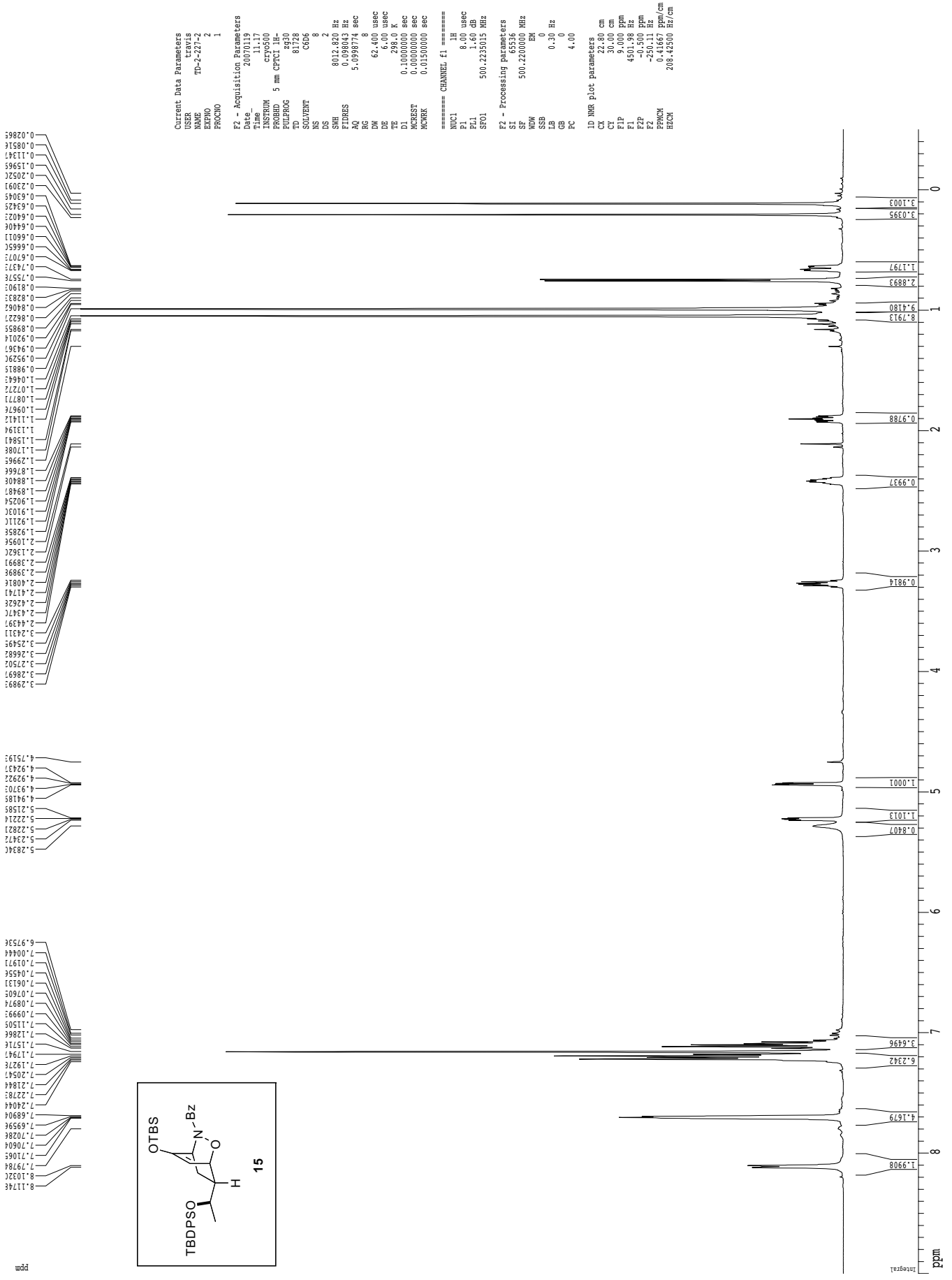
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

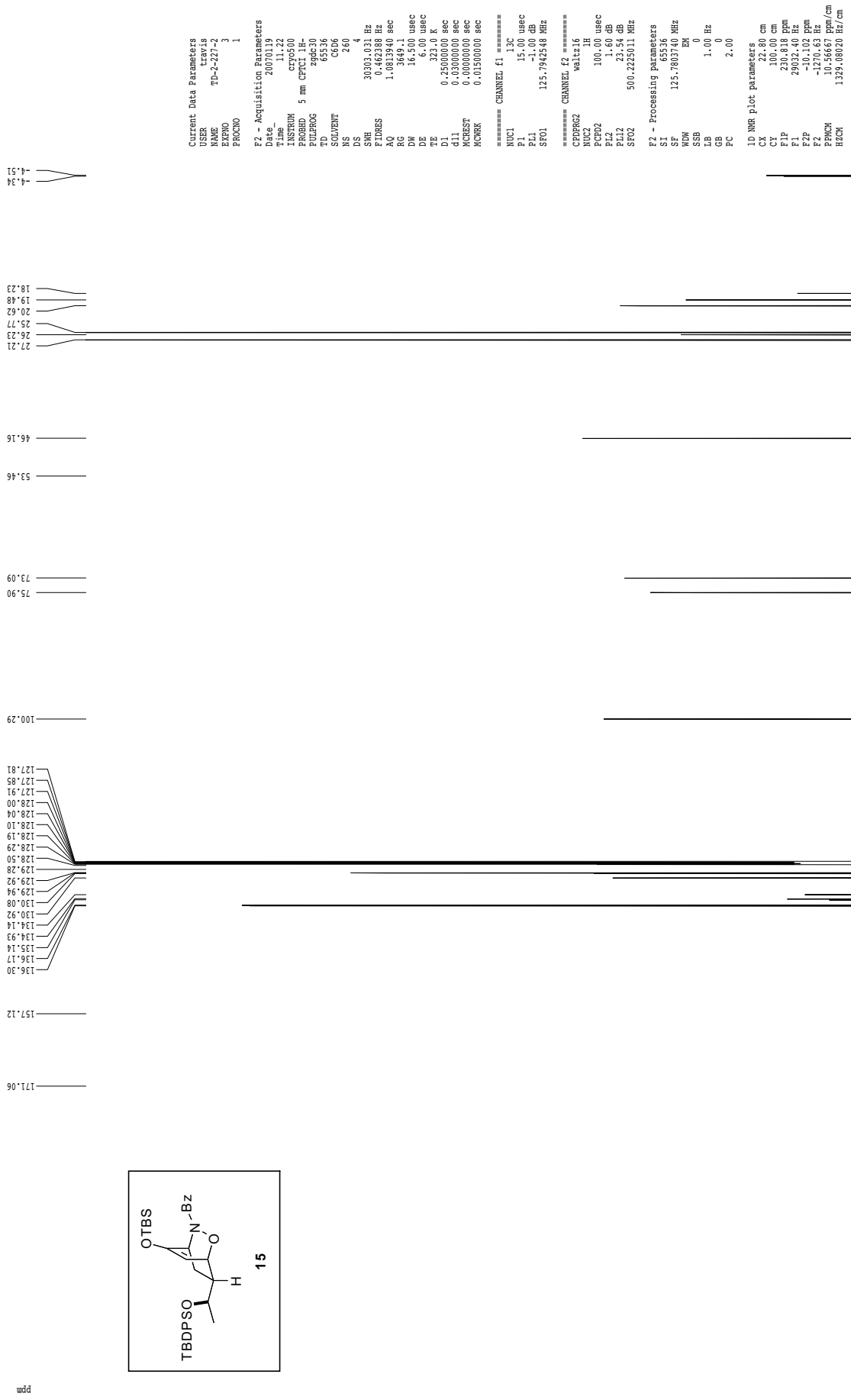
F2 - Processing parameters
SI 65536
SF 125.7804272 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

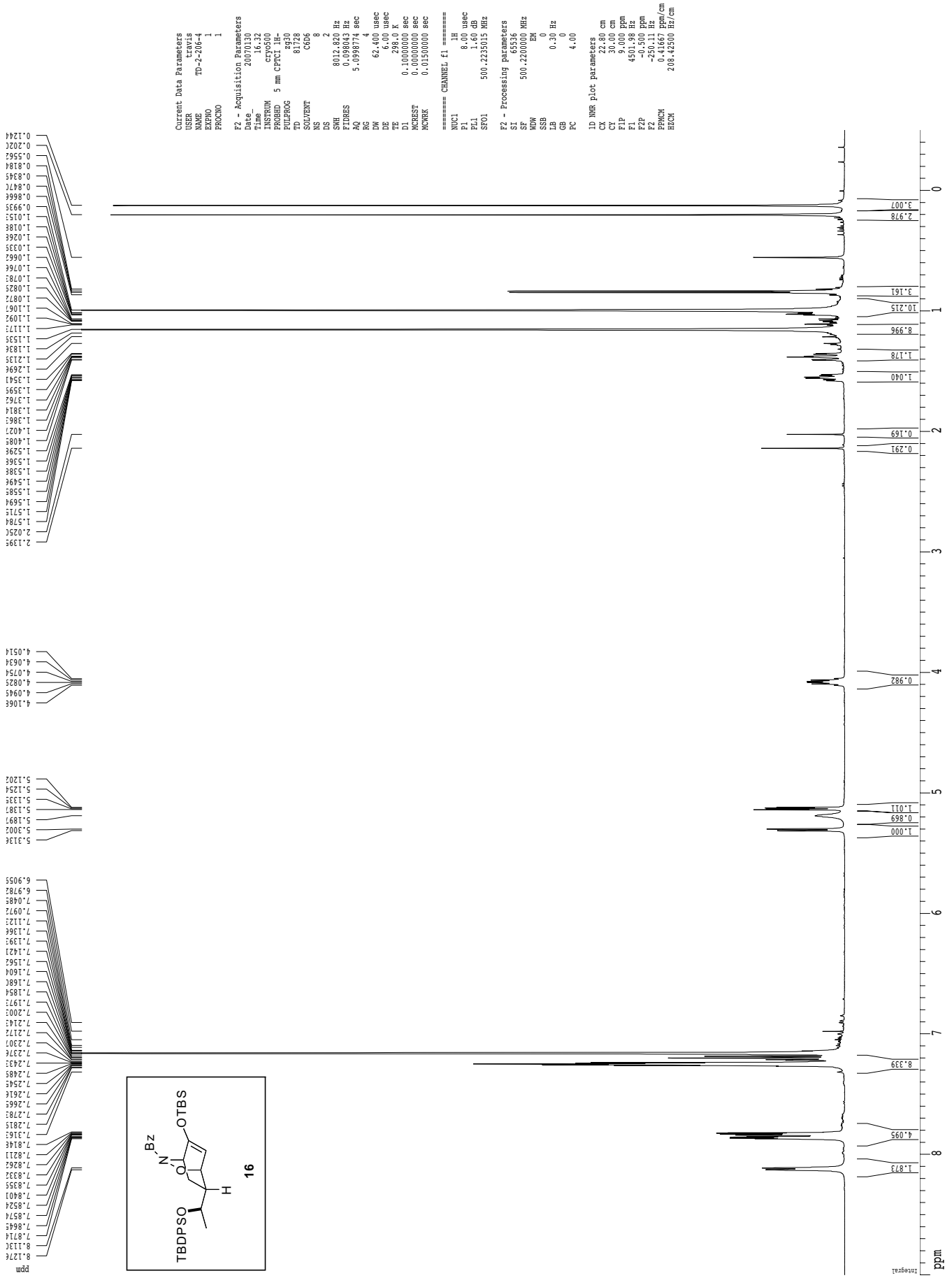
1D NMR plot parameters
CX 22.80 cm
CY 40.00 cm
F1P 230.000 ppm
F1 28929.50 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 10.52632 ppm/cm
HZCM 1324.00452 Hz/cm

1H spectrum

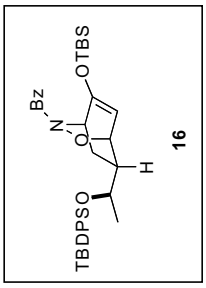


13C spectrum with 1H decoupling

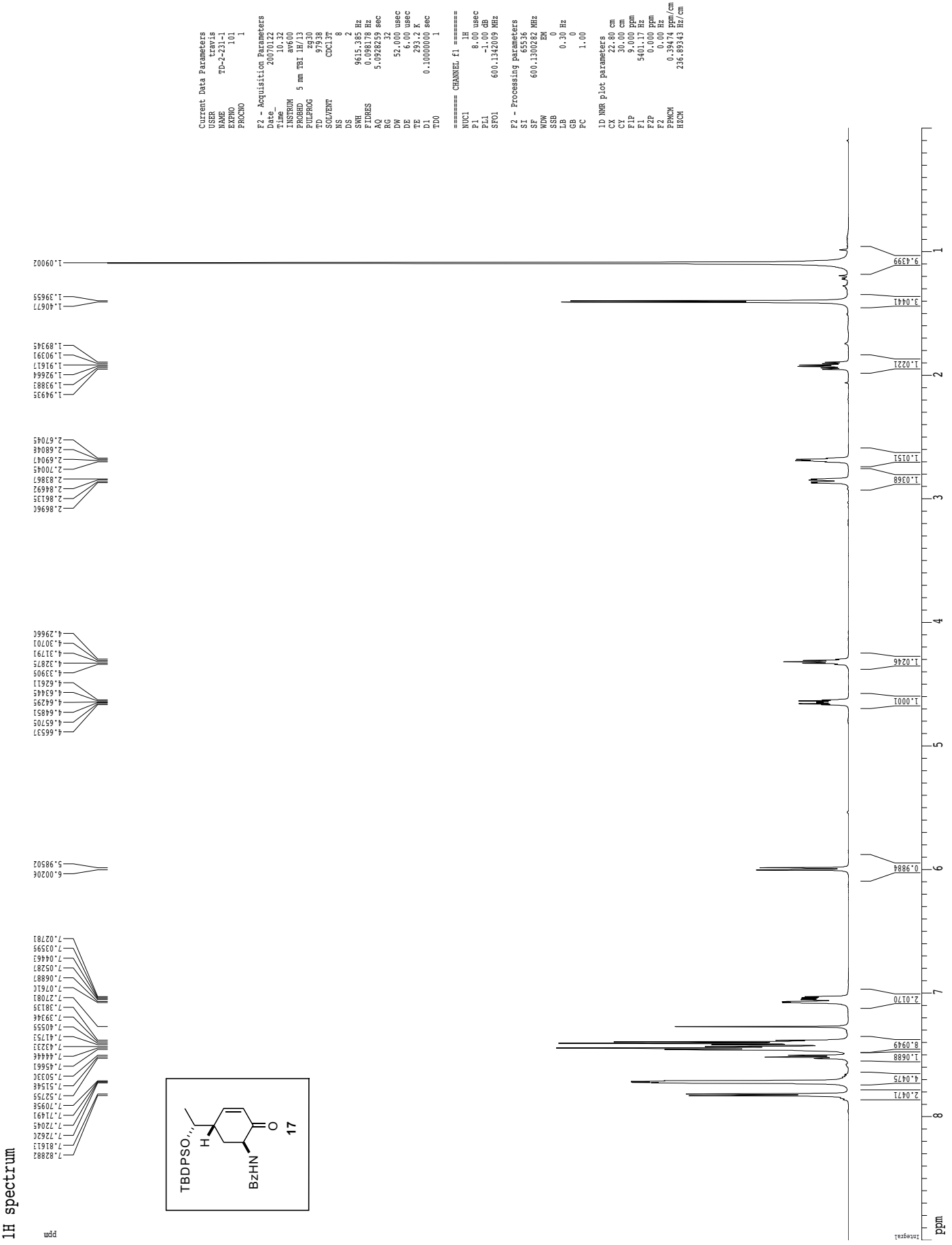



1H spectrum
TBDPSO
OTBS
Bz
N
O
H
16
Current Data Parameters
USER travis
NAME TD-2-206-4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070130
Time 16.32
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT C6D6
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 30.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm
ppm
Integral

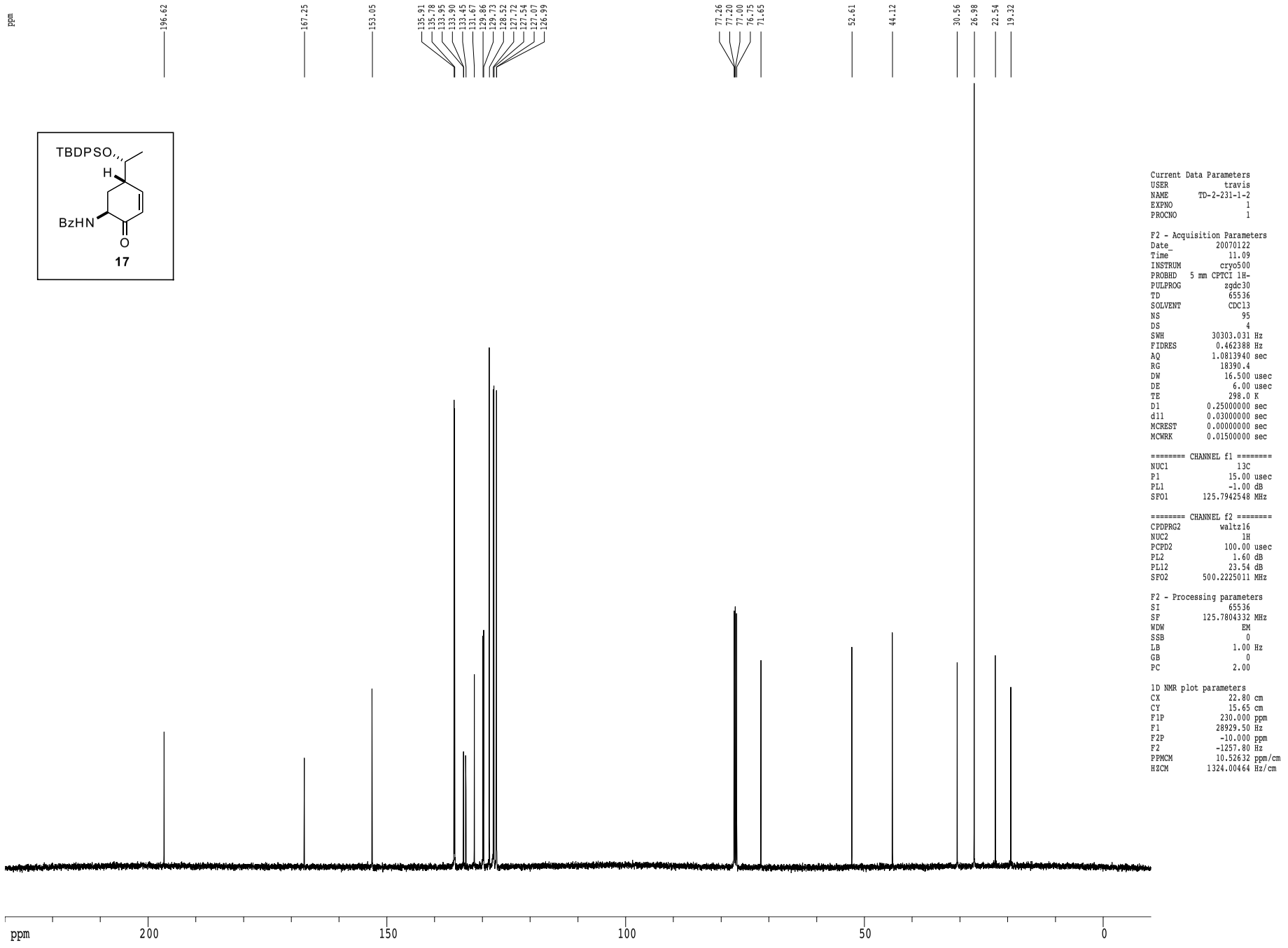
13C spectrum with 1H decoupling



1H spectrum


TBDPSO
H
BzHN
O
17
ppm
Integral
Current Data Parameters
USER travis
NAME TD-2-231-1
EXPNO 101
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070122
Time 10.32
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 97938
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098178 Hz
AQ 5.0938259 sec
RG 32
DW 52.000 usec
DE 6.00 usec
TE 293.2 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1300282 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 30.00 cm
F1P 9.000 ppm
F1 5401.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.39474 ppm/cm
HZCM 236.89343 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER travis
NAME TD-2-231-1-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070122
Time 11.09
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 95
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 18390.4
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

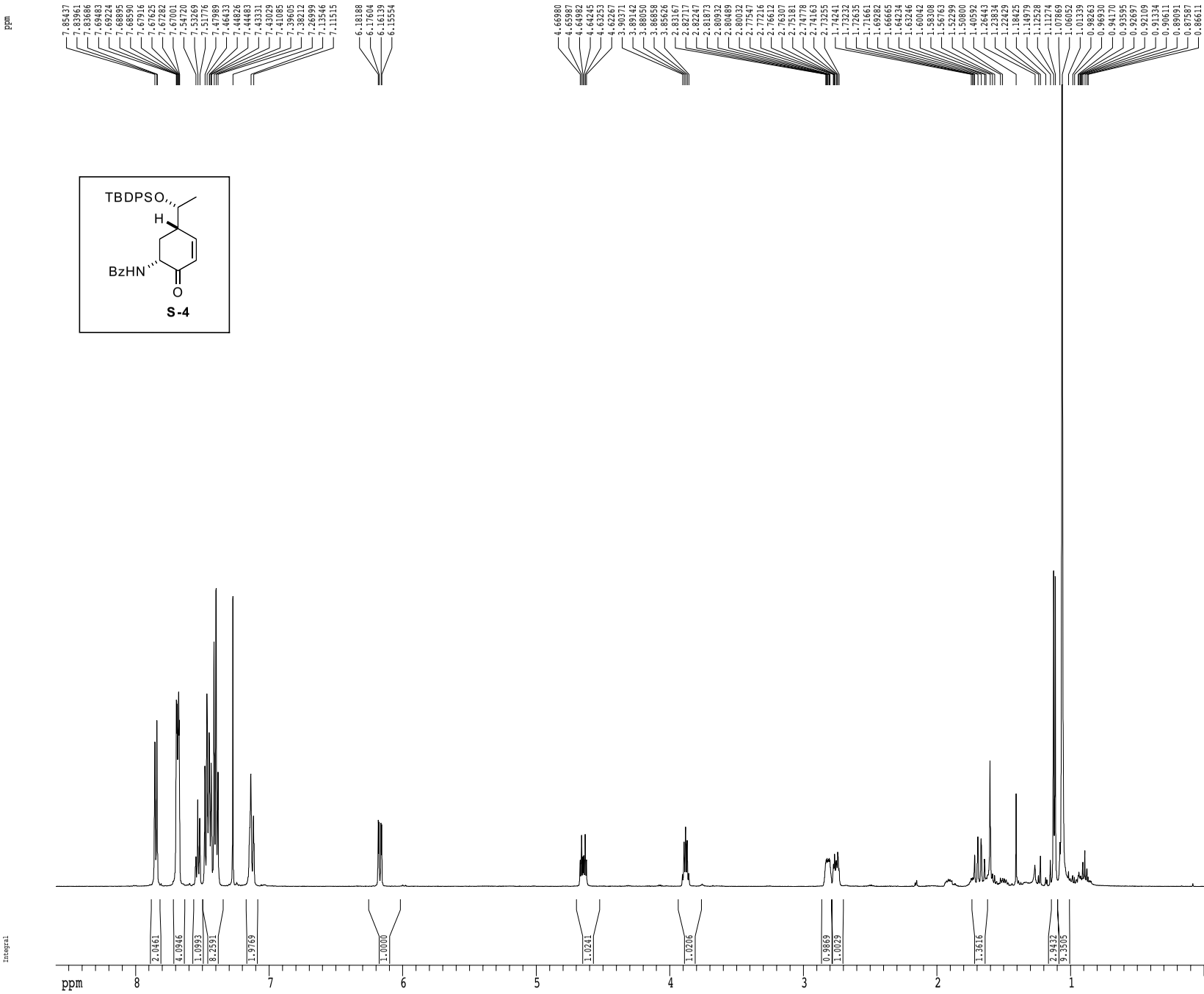
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804332 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 230.000 ppm
F1 28929.50 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 10.52632 ppm/cm
HZCM 1324.00464 Hz/cm

1H spectrum



Current Data Parameters

USER	travis
NAME	TD-2-192-3-2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20061206
Time	10.56
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	81728
SOLVENT	CDCl3
NS	8
DS	2
SWH	4310.345 Hz
FIDRES	0.052740 Hz
AQ	9.4804983 sec
RG	4.5
DW	116.000 usec
DE	6.00 usec
TE	298.0 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	1H
P1	8.00 usec
PL1	1.60 dB
SFO1	500.2221708 MHz

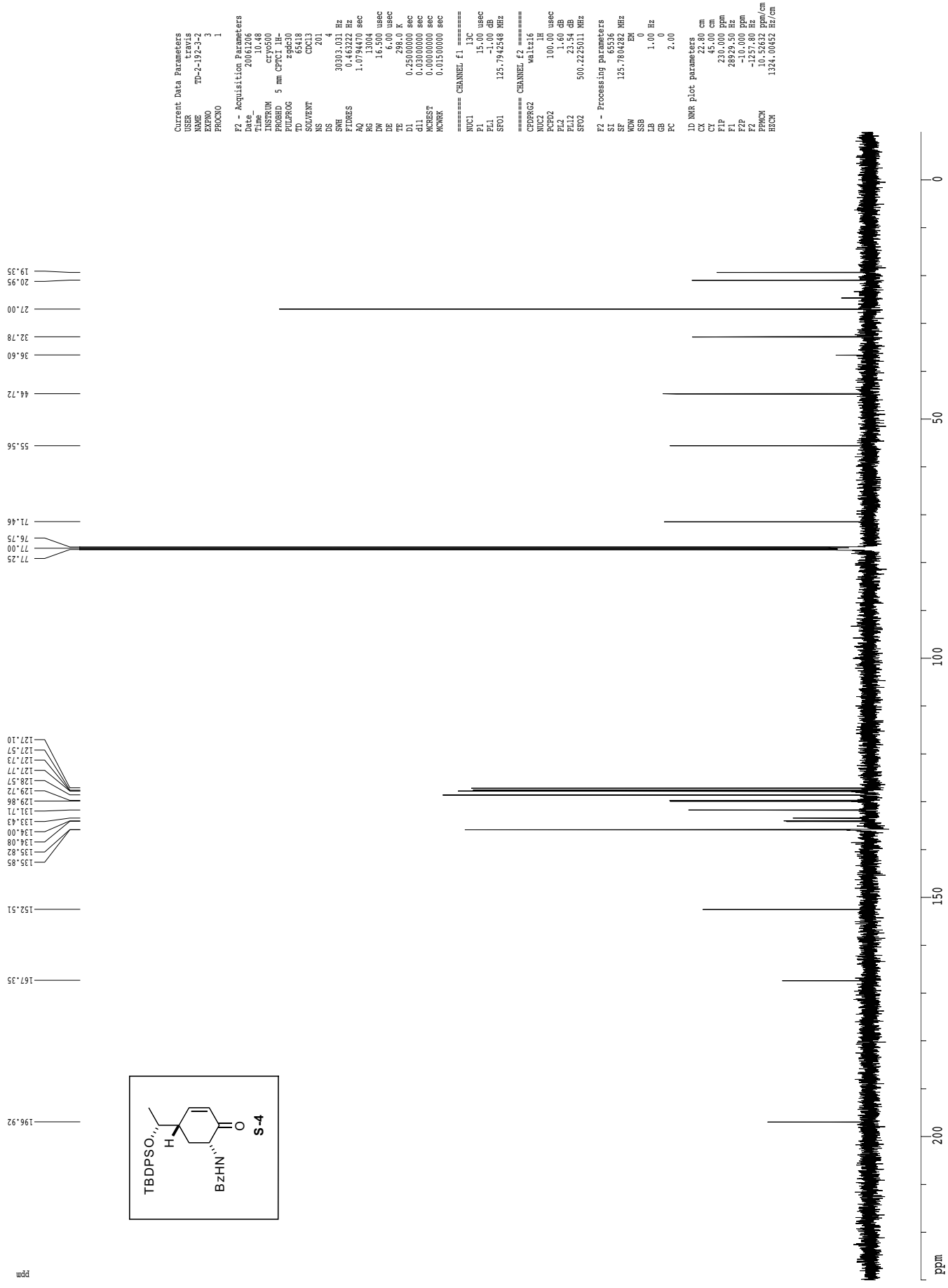
F2 - Processing parameters

SI	65536
SF	500.2200263 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	4.00

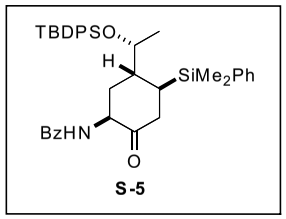
1D NMR plot parameters

CX	22.80 cm
CY	30.00 cm
F1P	9.000 ppm
F1	4501.98 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.39474 ppm/cm
HZCM	197.45528 Hz/cm

13C spectrum with 1H decoupling

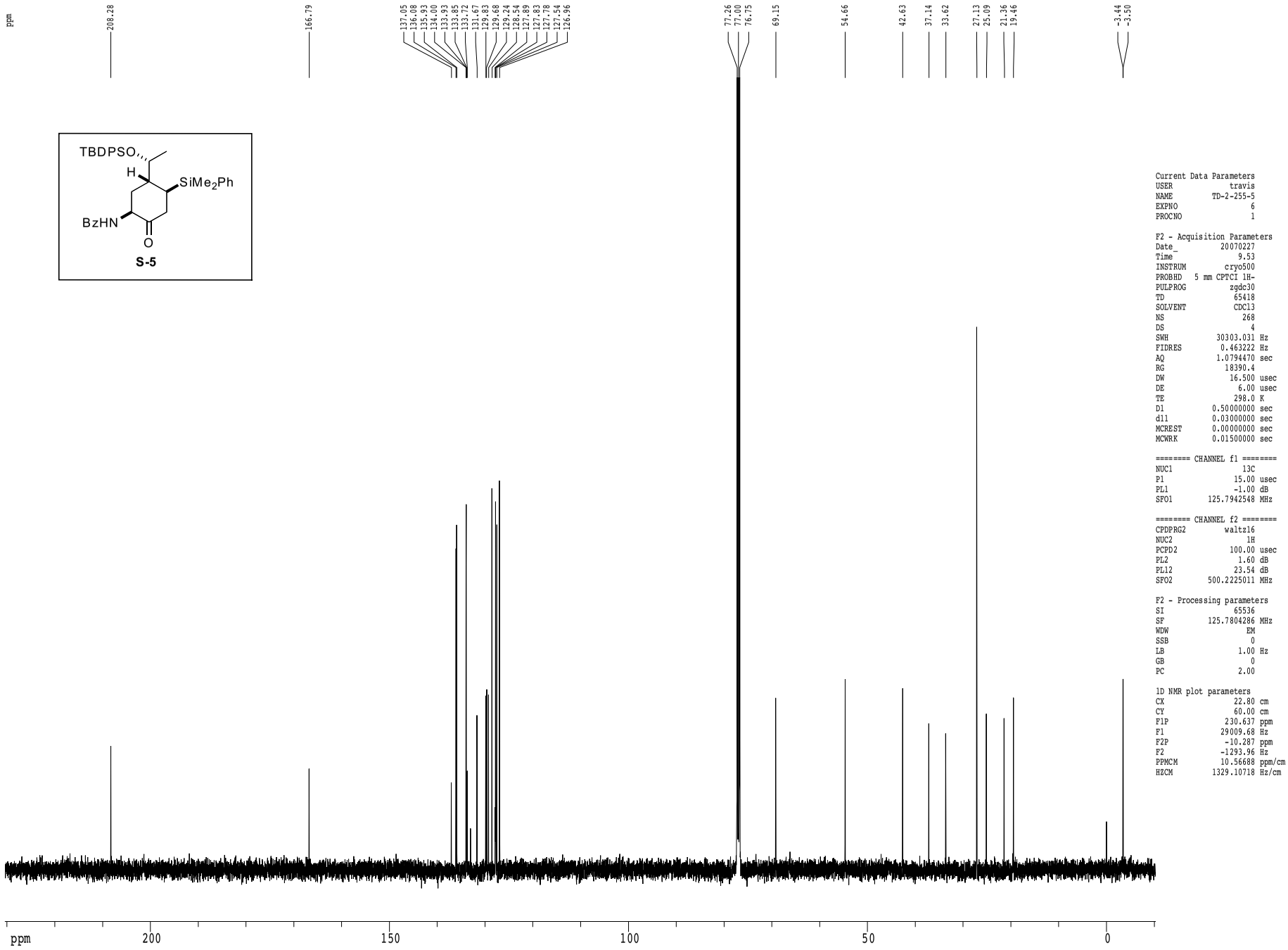


1H spectrum



S-5

13C spectrum with 1H decoupling



Current Data Parameters

USER	travis
NAME	TD-2-255-5
EXPNO	6
PROCNO	1

F2 - Acquisition Parameters

Date_	20070227
Time	9.53
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	65418
SOLVENT	CDCl3
NS	268
DS	4
SWH	30303.031 Hz
FIDRES	0.463222 Hz
AQ	1.0794470 sec
RG	18390.4
DW	16.500 usec
DE	6.00 usec
TE	298.0 K
D1	0.50000000 sec
d11	0.03000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

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

======== CHANNEL f2 ========

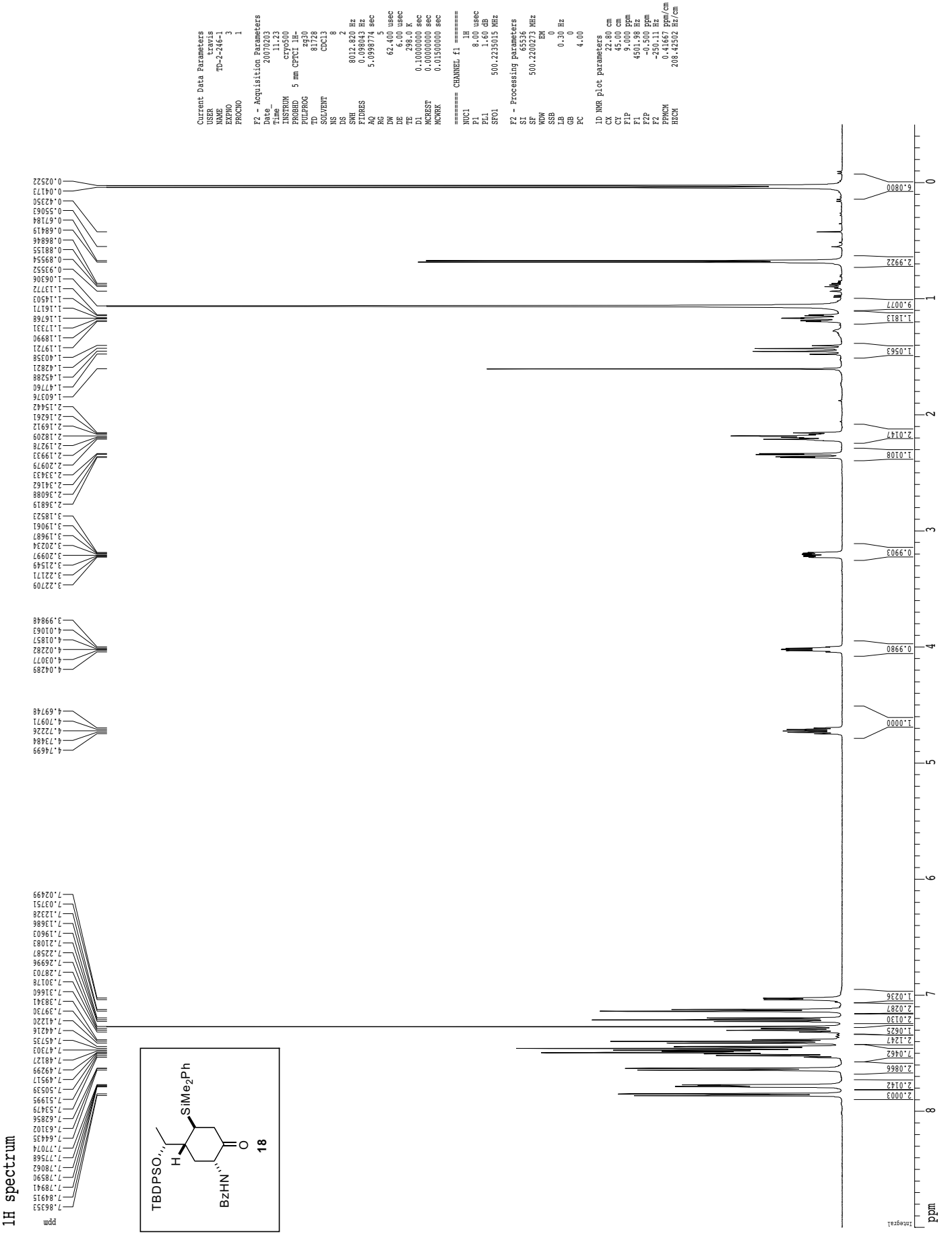
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	1.60 dB
PL12	23.54 dB
SFO2	500.2225011 MHz

F2 - Processing parameters

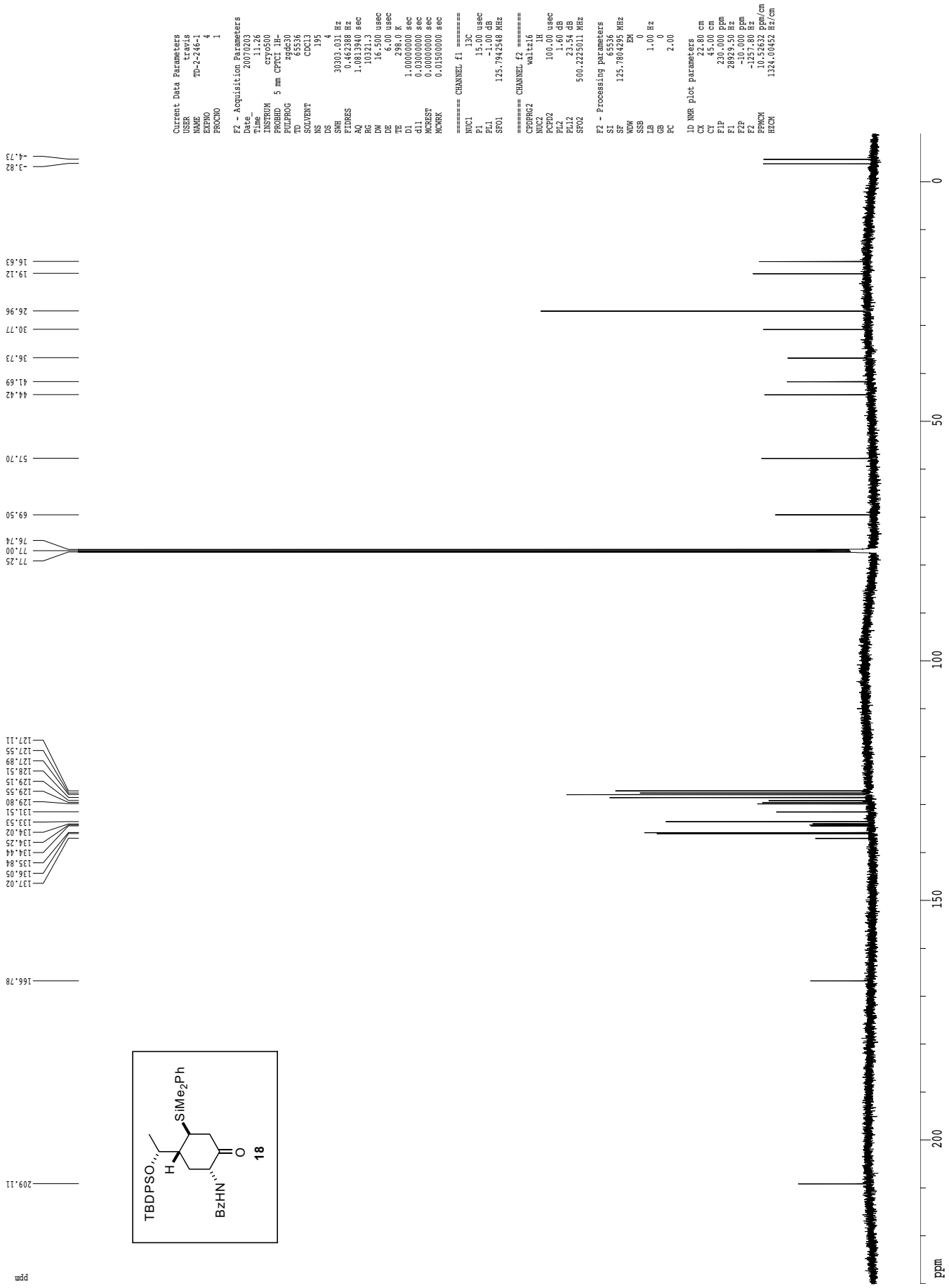
SI	65536
SF	125.7804286 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

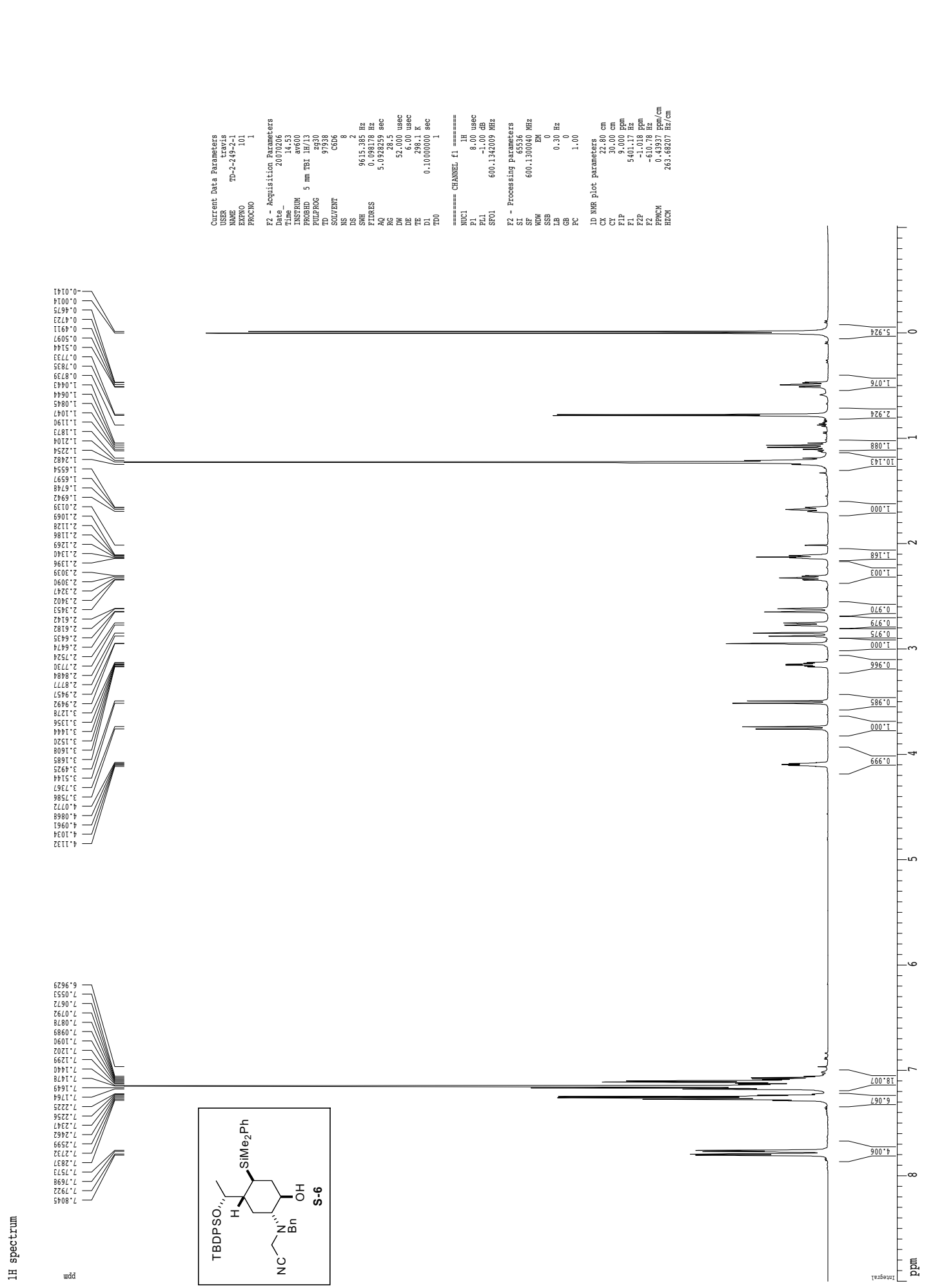
1D NMR plot parameters

CX	22.80 cm
CY	60.00 cm
F1P	230.637 ppm
F1	29009.68 Hz
F2P	-10.287 ppm
F2	-1293.96 Hz
PPMCM	10.56688 ppm/cm
HZCM	1329.10718 Hz/cm

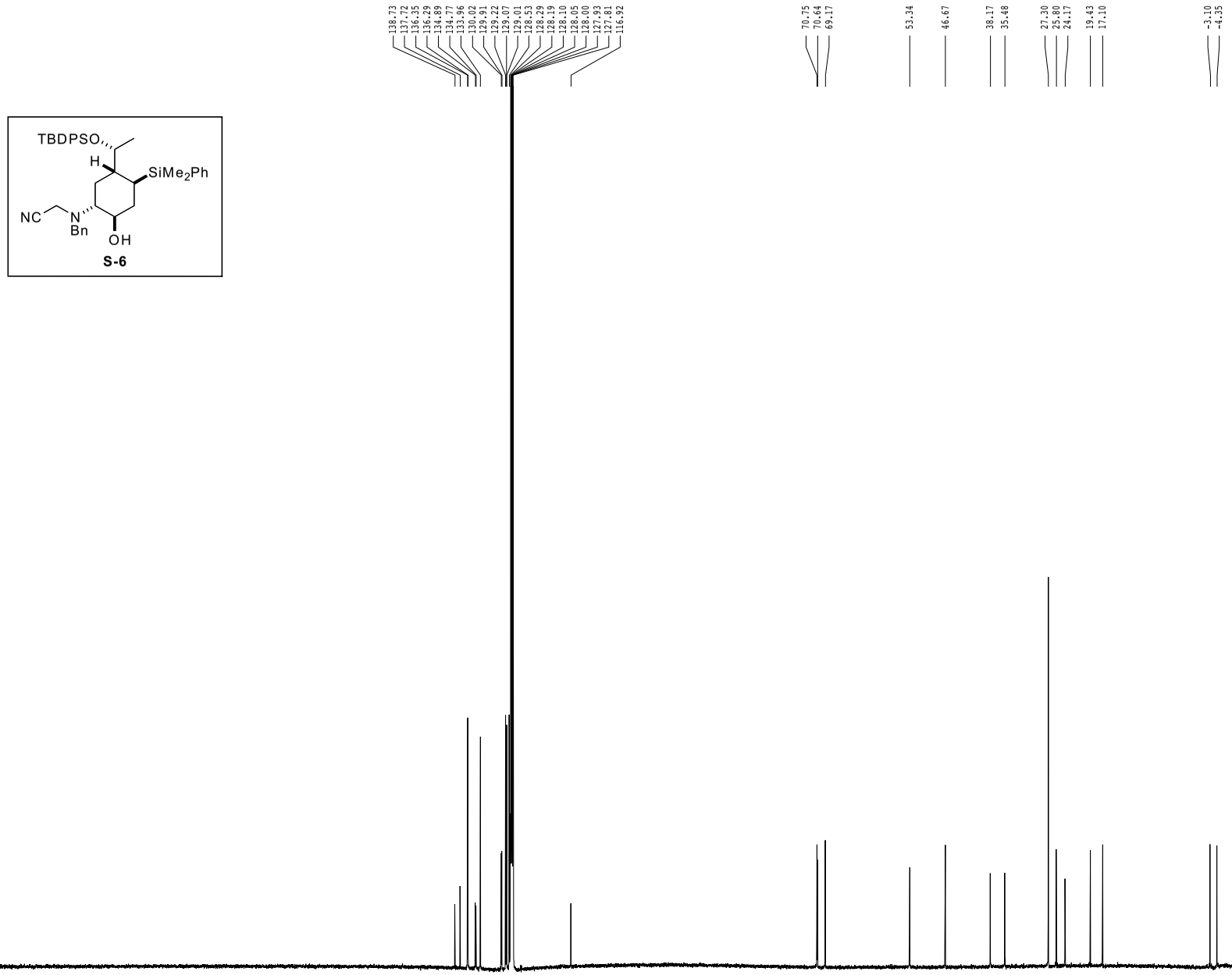

1H spectrum
TBDPSO
H
SiMe2Ph
BzHN
O
18
ppm
Integral

13C spectrum with 1H decoupling




1H spectrum
TBDPSO
H
SiMe2Ph
OH
S-6
N
Bn
NC
Current Data Parameters
USER travis
NAME TD-2-249-2-1
EXPNO 101
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070206
Time_ 14.53
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 97938
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098178 Hz
AQ 5.0928259 sec
RG 28.5
DW 52.000 usec
DE 6.00 usec
TE 298.1 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1300040 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 30.00 cm
F1P 9.000 ppm
F1 5401.17 Hz
F2P -1.018 ppm
F2 -610.78 Hz
PPMCM 0.43937 ppm/cm
HZCM 263.68207 Hz/cm
Integral
ppm

13C spectrum with 1H decoupling



Current Data Parameters
USER travis
NAME TD-2-249-2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070206
Time 14.05
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65536
SOLVENT C6D6
NS 213
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 3251
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.50000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

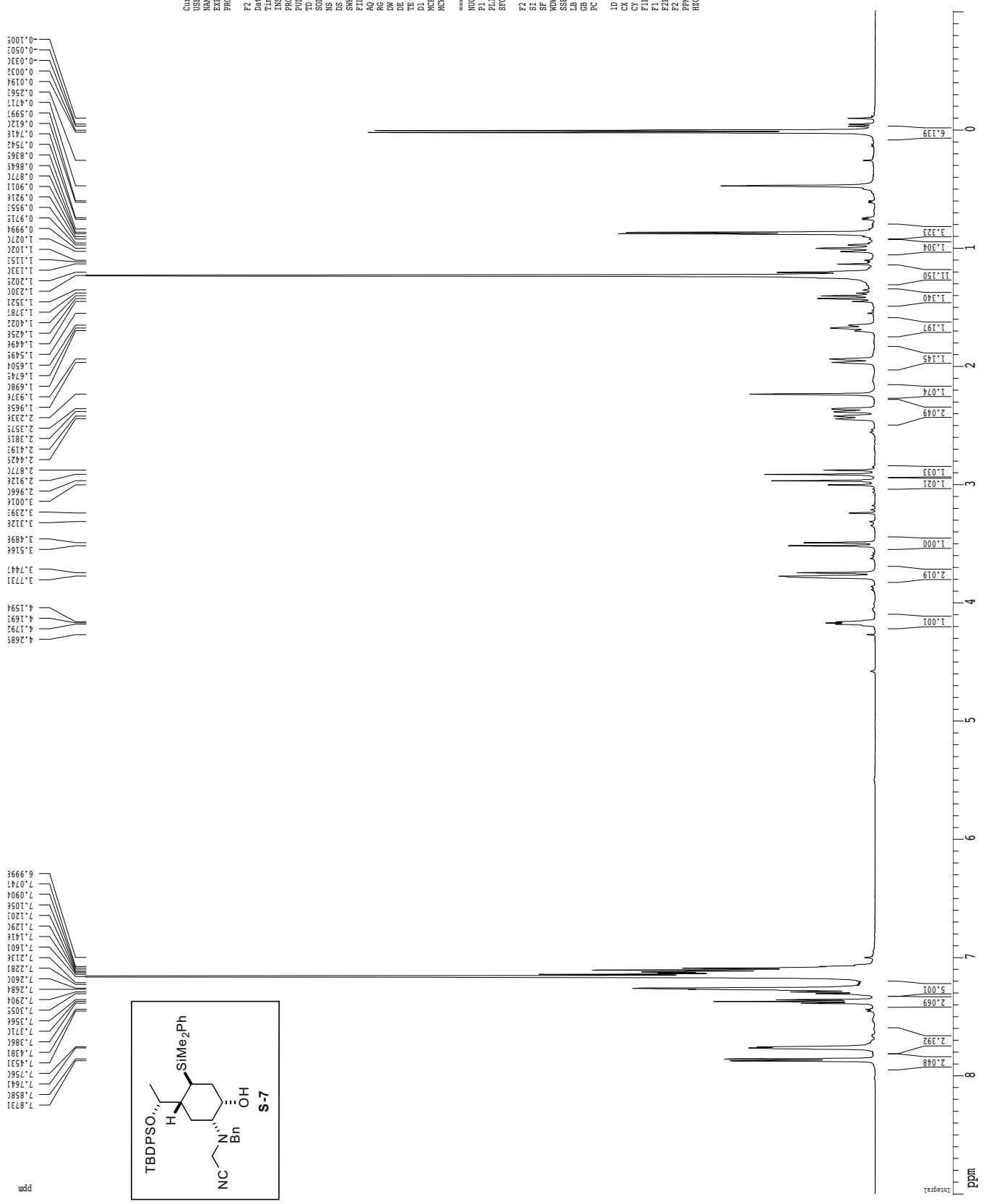
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

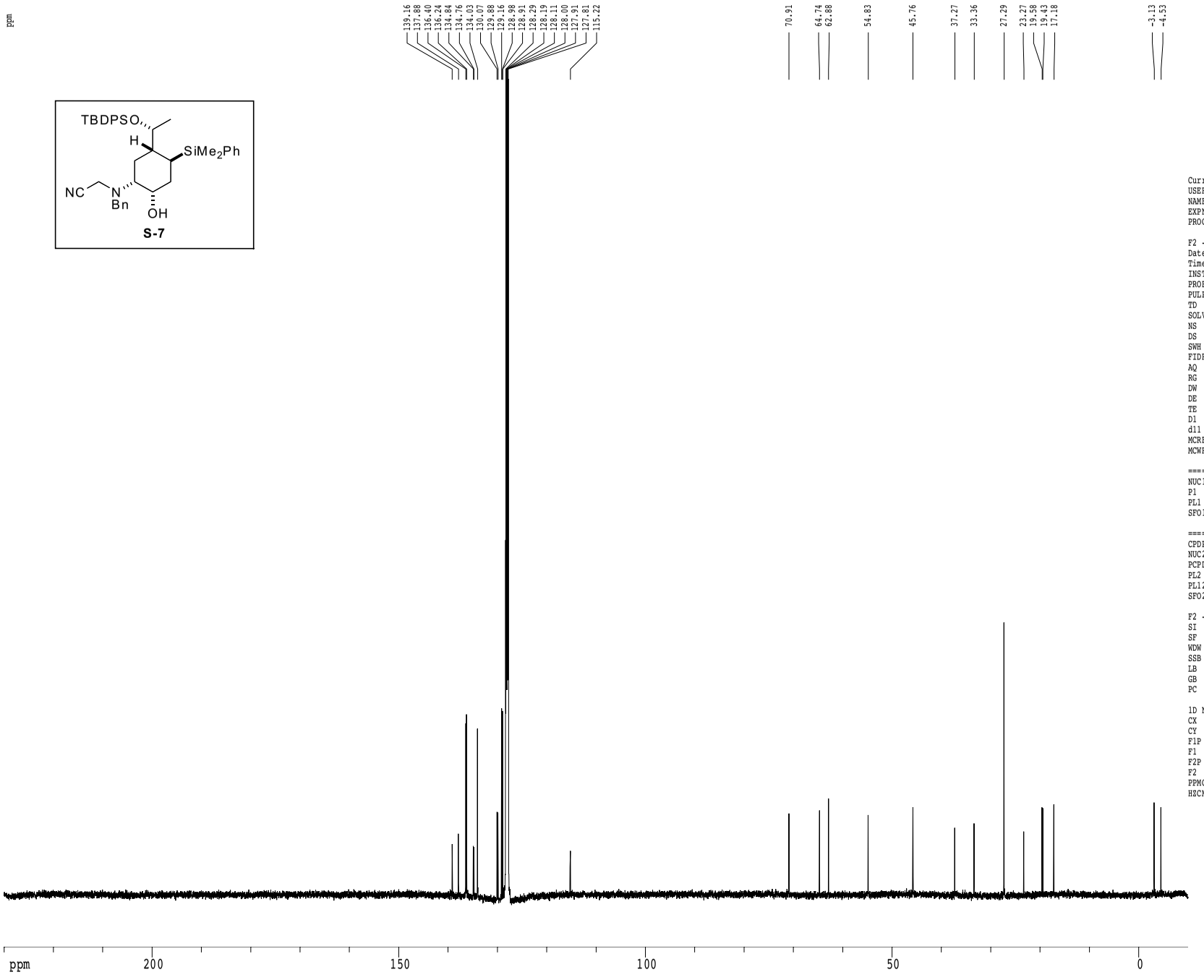
F2 - Processing parameters
SI 65536
SF 125.7803837 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 45.00 cm
F1P 230.000 ppm
F1 28929.49 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 10.52632 ppm/cm
HZCM 1324.00403 Hz/cm

1H spectrum



13C spectrum with 1H decoupling



Current Data Parameters

USER	travis
NAME	TD-3-102-2
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20070709
Time	22.50
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	65418
SOLVENT	C6D6
NS	362
DS	4
SWH	30303.031 Hz
FIDRES	0.463222 Hz
AQ	1.0794470 sec
RG	3251
DW	16.500 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
d11	0.03000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

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

======== CHANNEL f2 ========

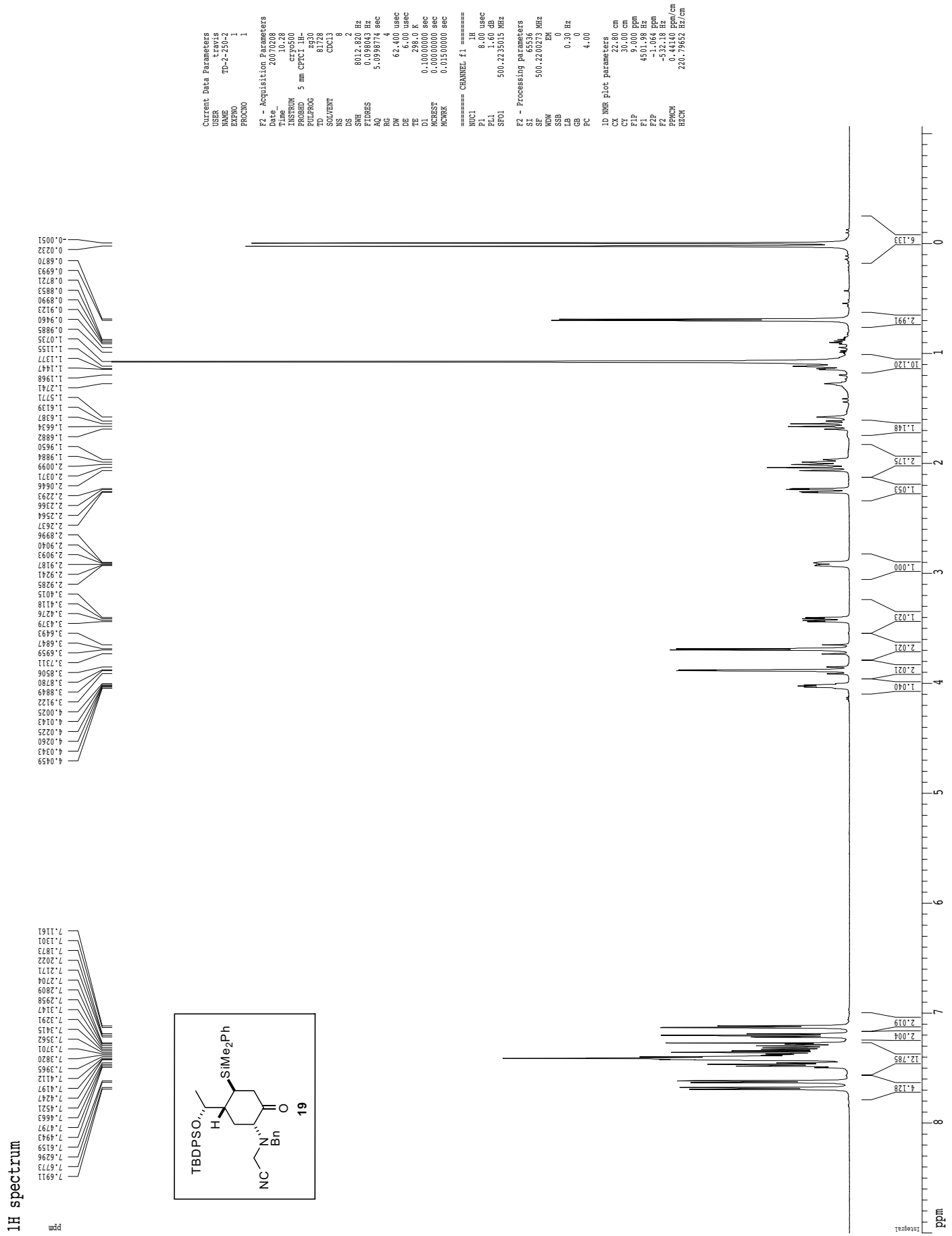
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	1.60 dB
PL12	23.54 dB
SFO2	500.2225011 MHz

F2 - Processing parameters

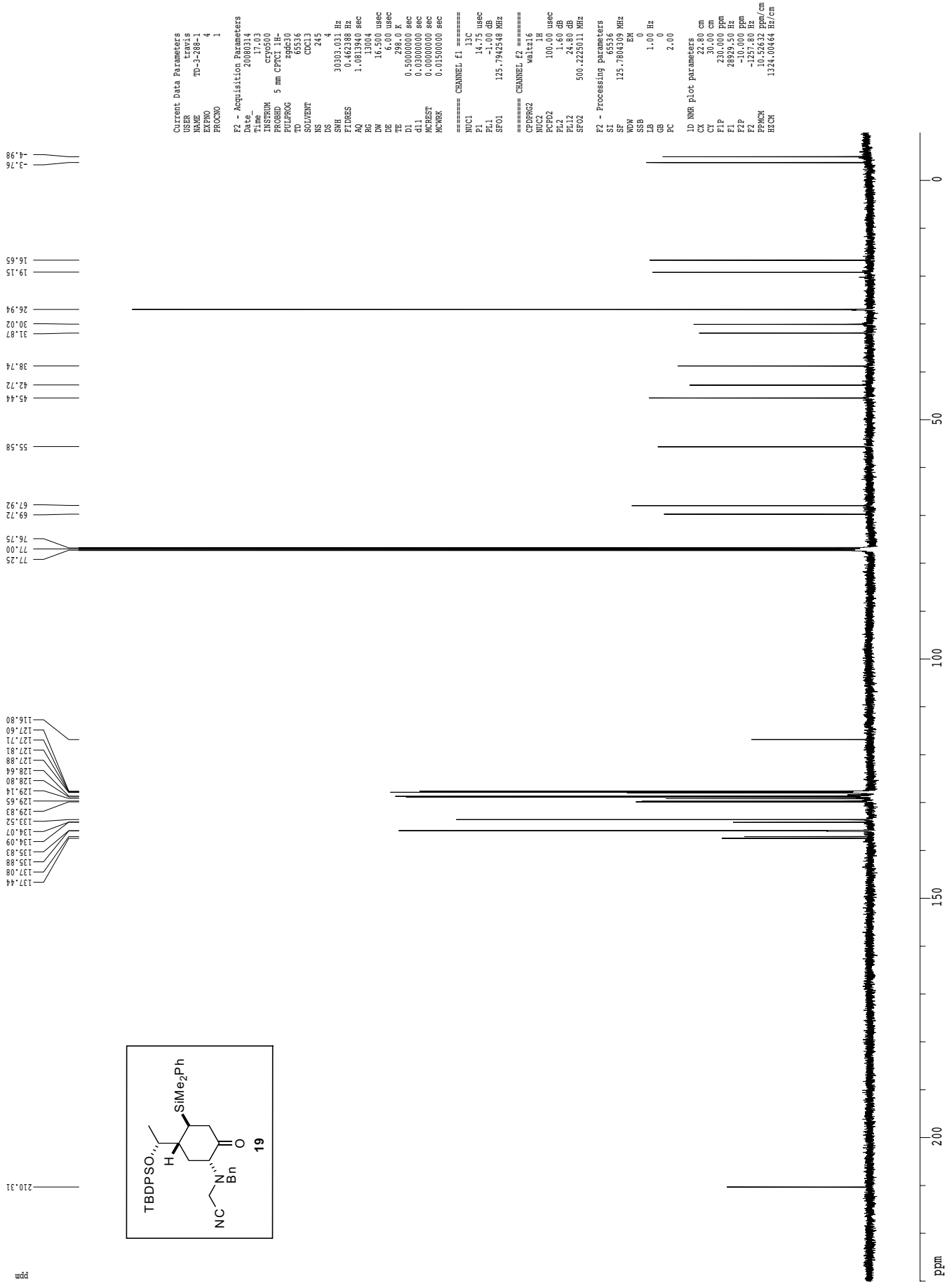
SI	65536
SF	125.7803823 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

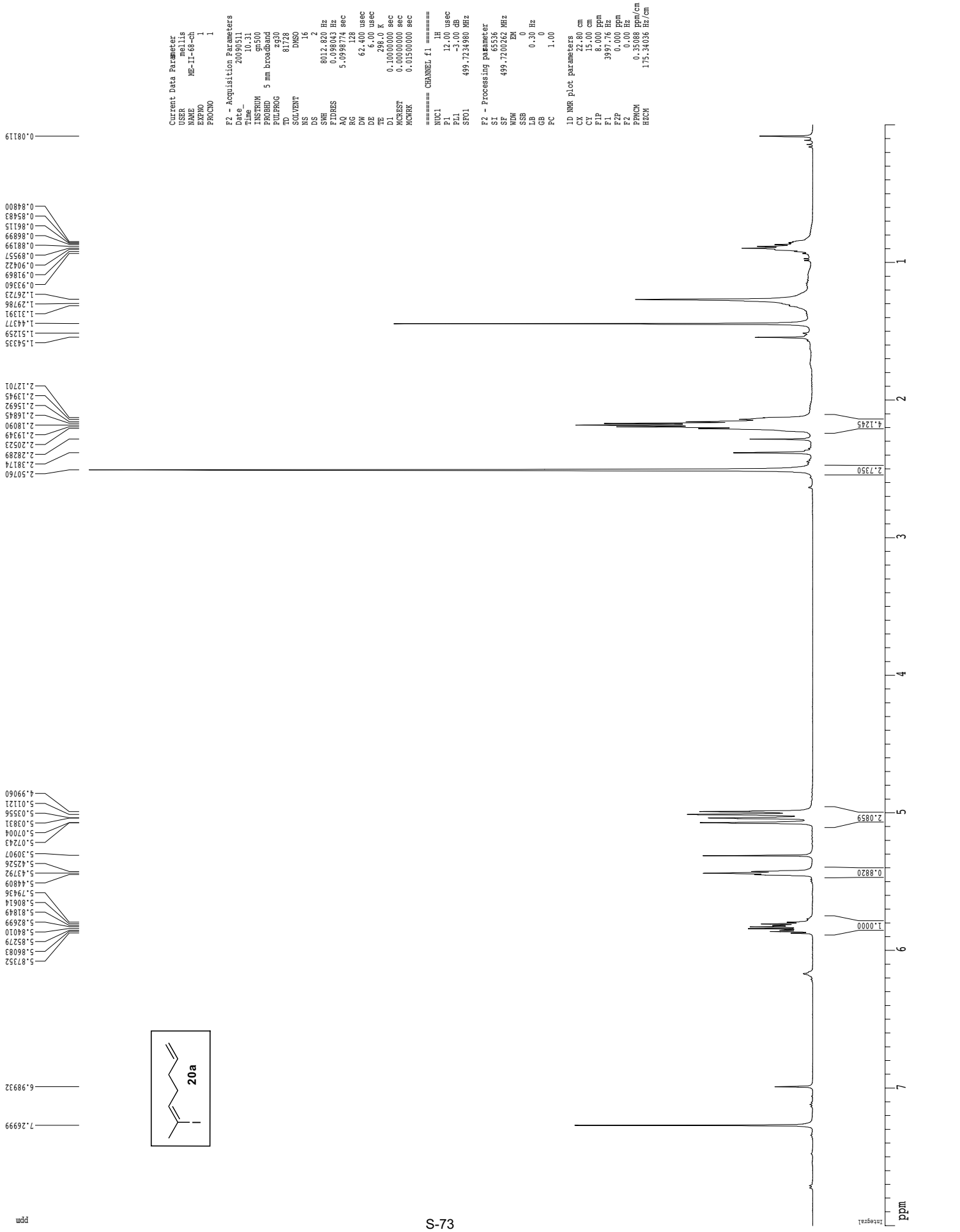
CX	22.80 cm
CY	150.00 cm
F1P	230.000 ppm
F1	28929.49 Hz
F2P	-10.000 ppm
F2	-1257.80 Hz
PPMCM	10.52632 ppm/cm
HZCM	1324.00403 Hz/cm


1H spectrum
TBDPSO
SiMe2Ph
H
N
Bn
NC
O
19
ppm
integral
Current Data Parameters
USER travis
NAME TD-2-250-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070208
Time_ 10.28
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200273 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 16.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -1.061 ppm
F2 -531.08 Hz
PPMCM 0.44140 ppm/cm
HZCM 220.79652 Hz/cm
6.133
2.991
10.120
1.148
2.175
1.053
1.000
1.023
2.021
2.021
1.040
2.019
2.004
12.785
4.128

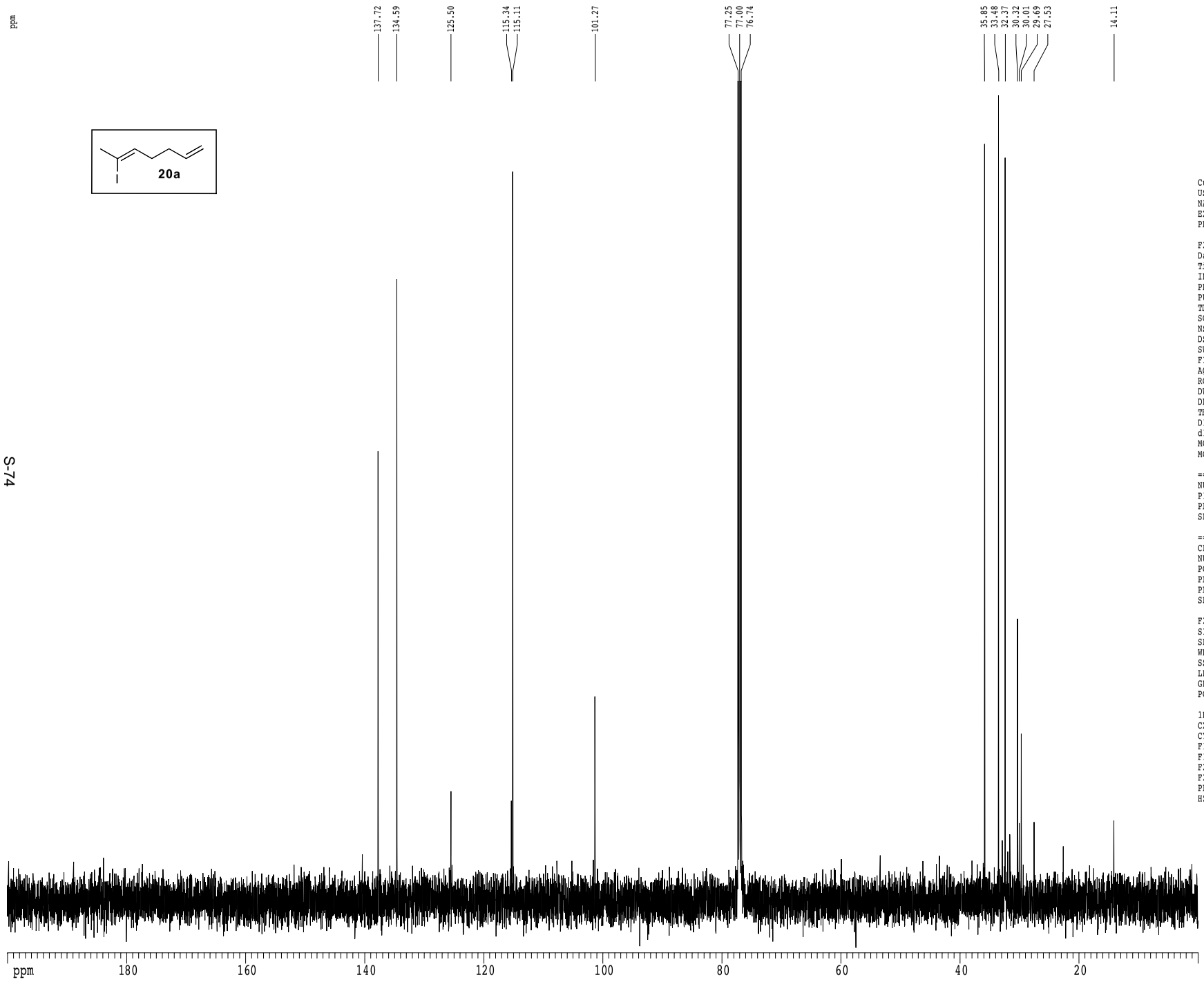
13C spectrum with 1H decoupling



1H spectrum


Current Data Parameter
USER mellis
NAME MS-II-68-ch
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090511
Time_ 10.31
INSTRUM qn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.09988774 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -3.00 dB
SFO1 499.7234980 MHz
F2 - Processing parameter
SI 65536
SF 499.7200262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.000 ppm
F1 3997.76 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.35088 ppm/cm
HZCM 175.34036 Hz/cm
0.08119
0.84800
0.85483
0.86115
0.86899
0.88199
0.89557
0.90422
0.91869
0.93360
1.26723
1.29786
1.31391
1.44377
1.51259
1.54335
2.12701
2.13945
2.15692
2.16845
2.18090
2.19349
2.20523
2.28289
2.38174
2.50760
4.99060
5.01121
5.03556
5.03831
5.07004
5.07243
5.30907
5.42526
5.43792
5.44809
5.79436
5.80614
5.81849
5.82699
5.84010
5.85279
5.86083
5.87352
6.98932
7.26999
20a
4.1245
2.7350
2.0859
0.8820
1.0000
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER mellis
NAME ME-II-68-ch
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090511
Time 10.38
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 331
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 6502
DW 16.500 usec
DE 4.50 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

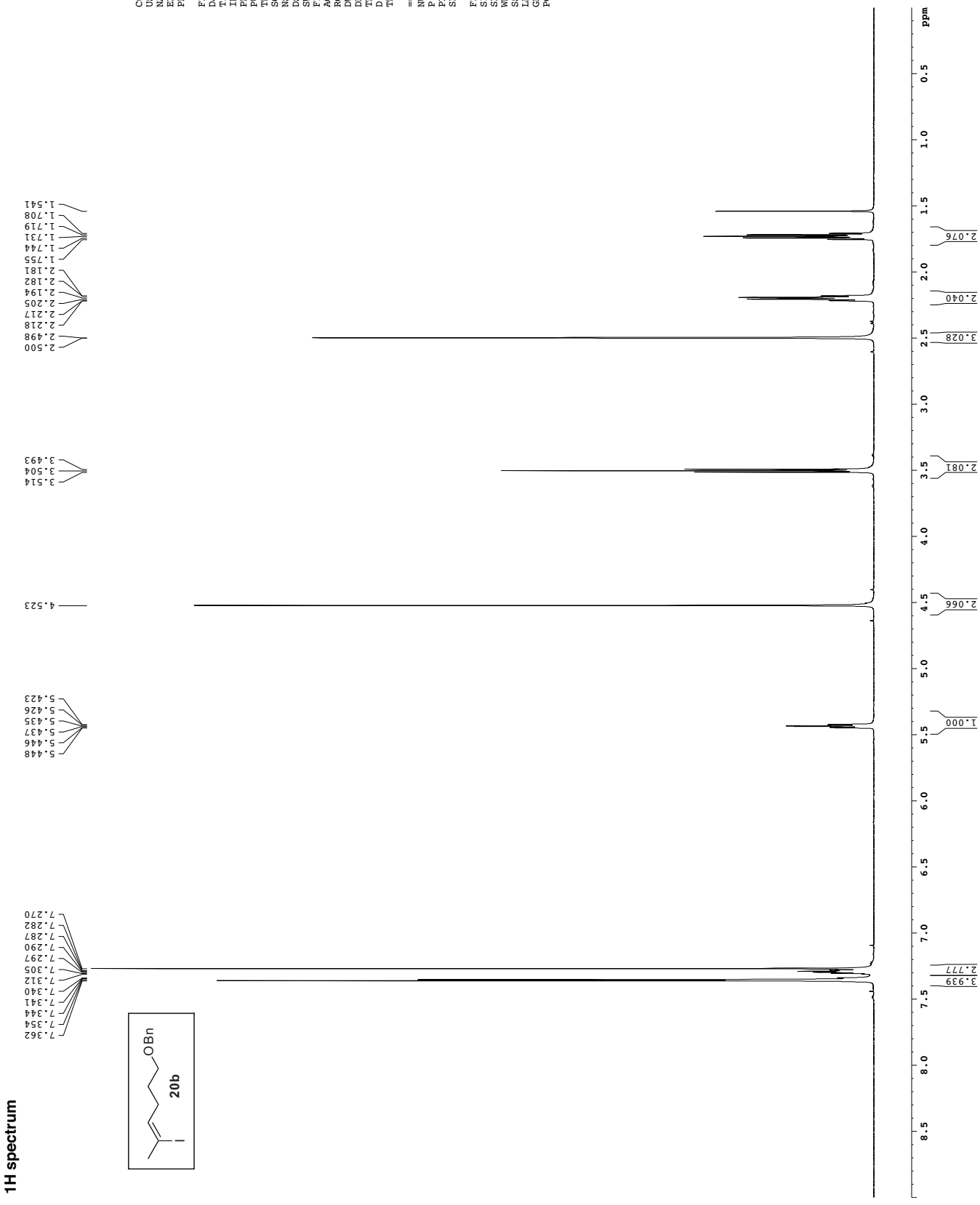
======== CHANNEL f1 ========
NUC1 13C
P1 7.08 usec
PL1 0.00 dB
SFO1 125.6685160 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 14.70 dB
SFO2 499.7224986 MHz

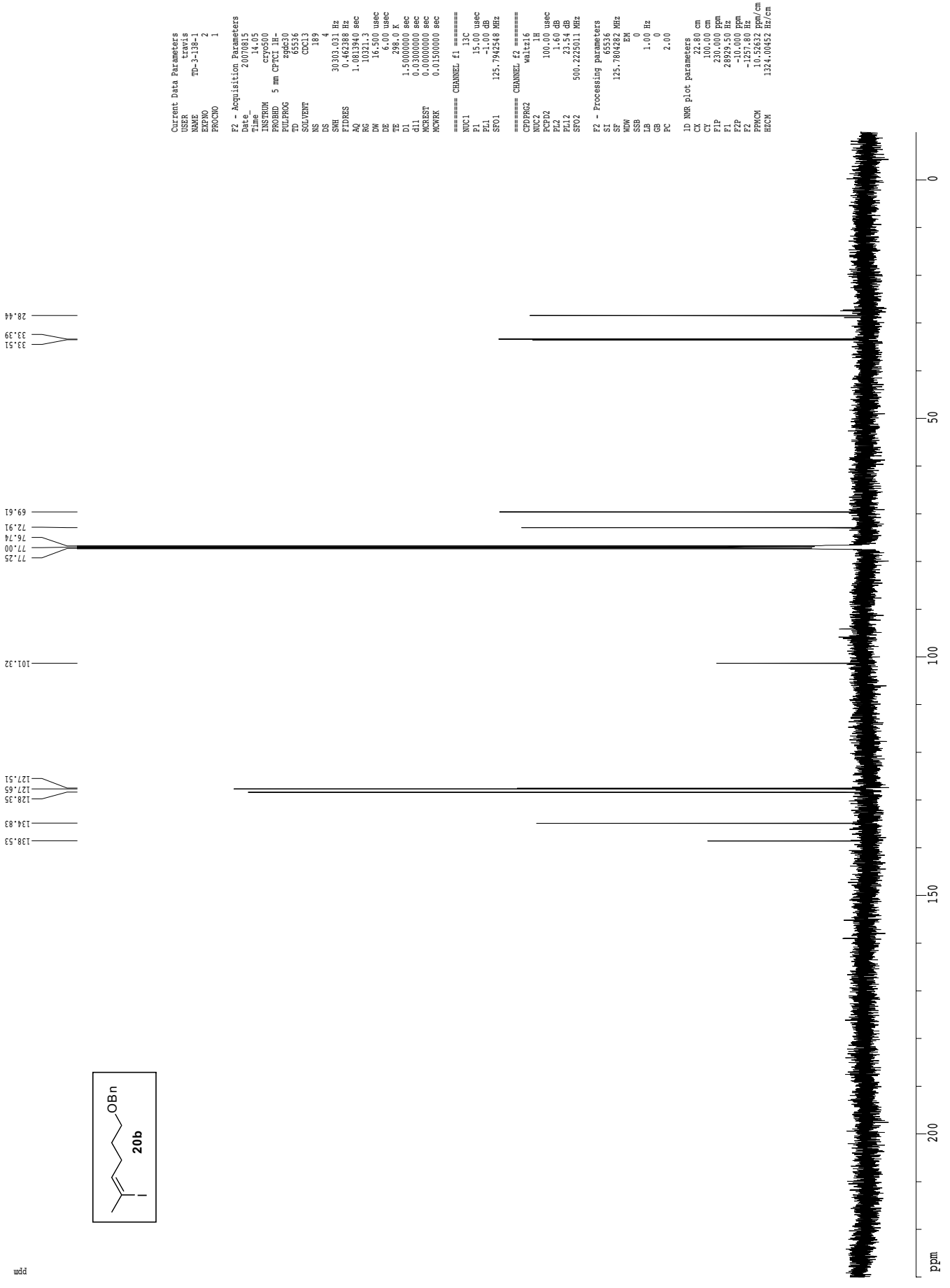
F2 - Processing parameter
SI 65536
SF 125.6547018 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25130.94 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1102.23425 Hz/cm

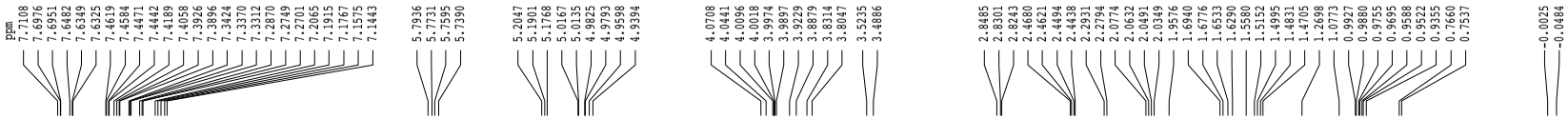
1H spectrum

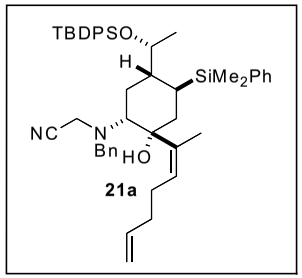


13C spectrum with 1H decoupling



1H spectrum





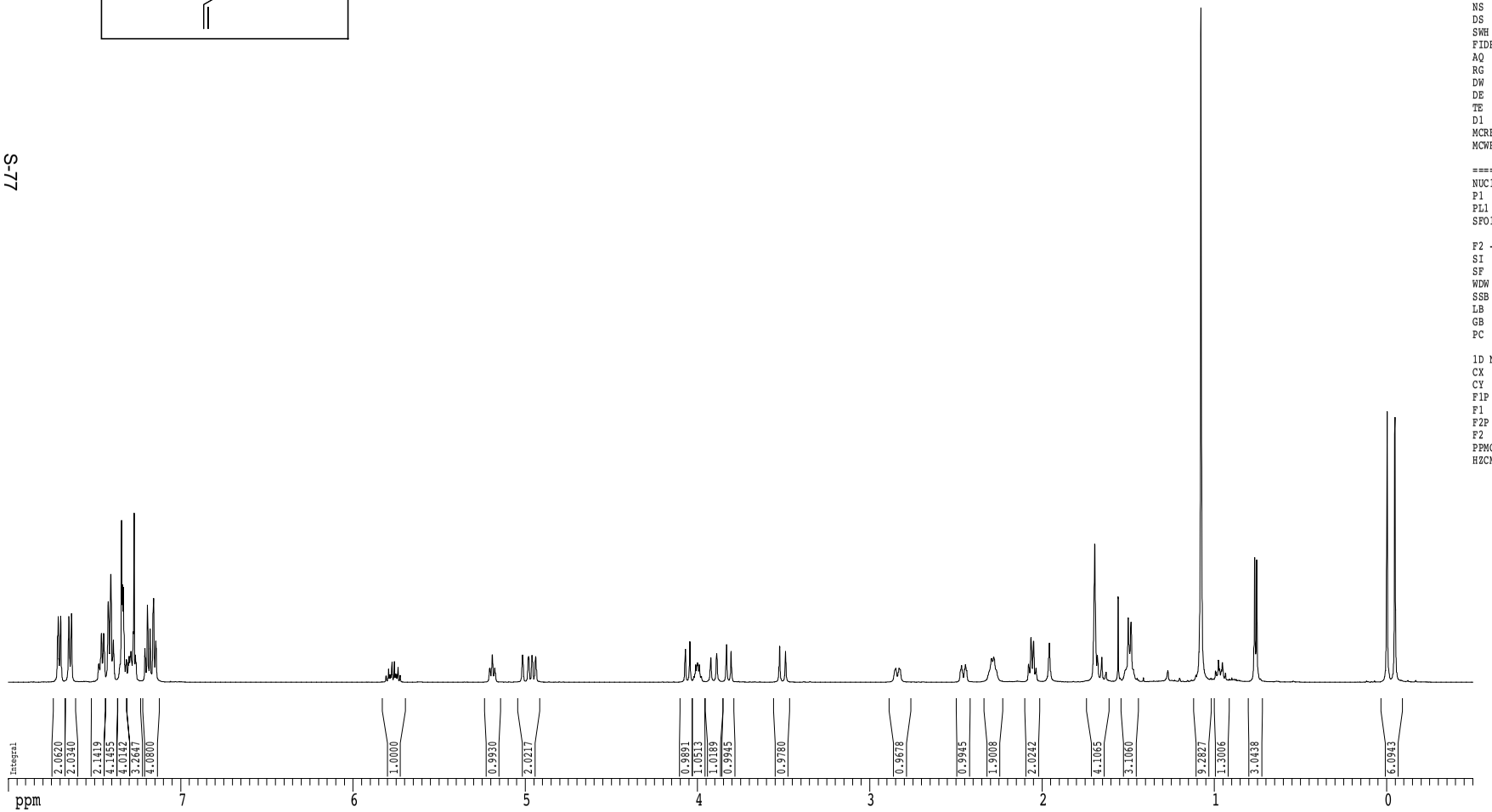

```
Current Data Parameter
USER                mellis
NAME            kh-1-123d
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090306
Time                11.04
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998774 sec
RG                  10.1
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

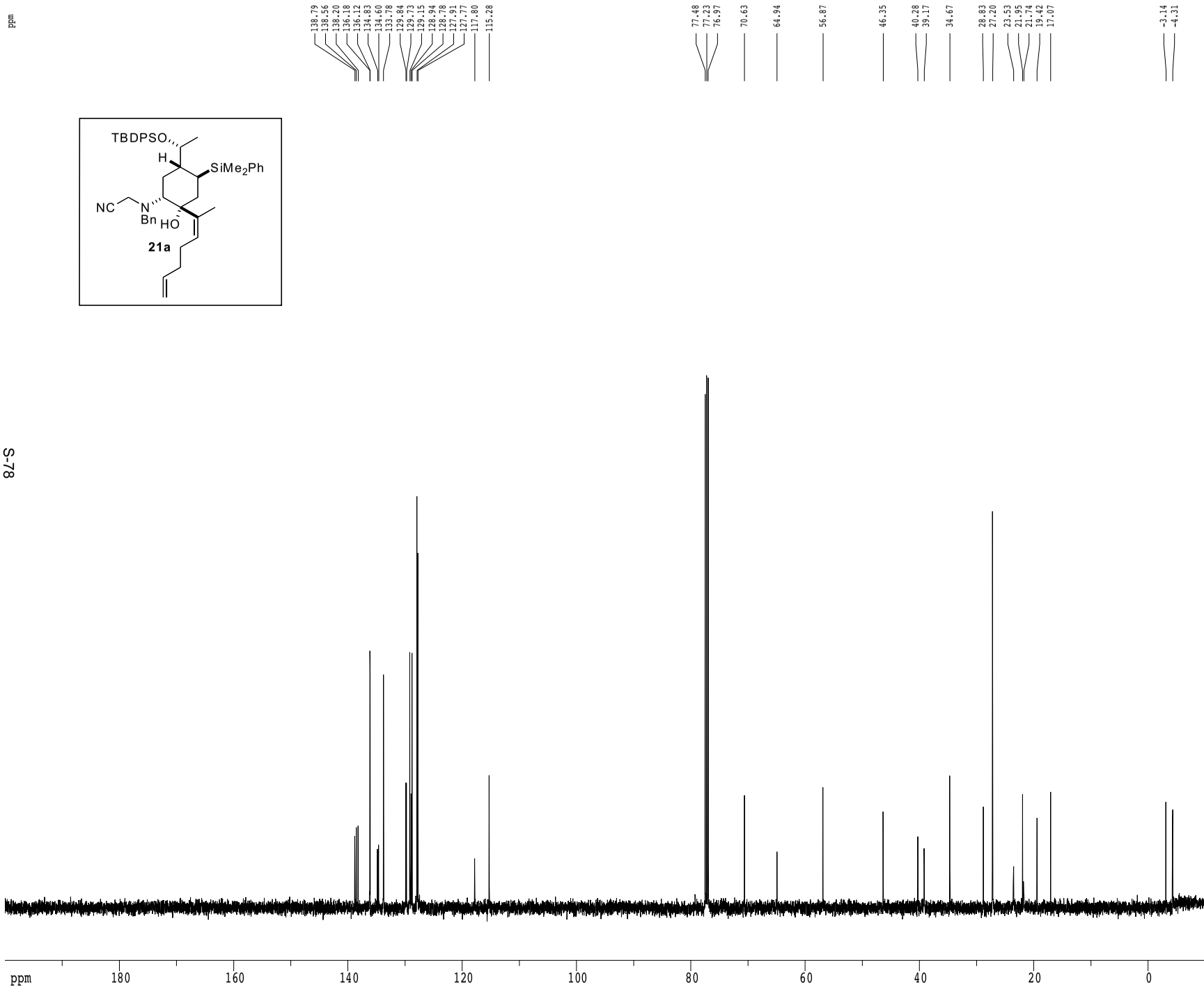
======== CHANNEL f1 ========
NUC1                   1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameter
SI                 65536
SF          500.2200269 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 10.51 cm
F1P                8.000 ppm
F1               4001.76 Hz
F2P                -0.500 ppm
F2               -250.11 Hz
PPMCM            0.37281 ppm/cm
HZCM           186.48555 Hz/cm
```



13C spectrum with 1H decoupling



Current Data Parameters
USER mellis
NAME kh-1-123d
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090306
Time 11.08
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 160
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 29.70 usec

======== CHANNEL f1 =======
NUC1 13C
P1 14.85 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.60 dB
SP2 3.60 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

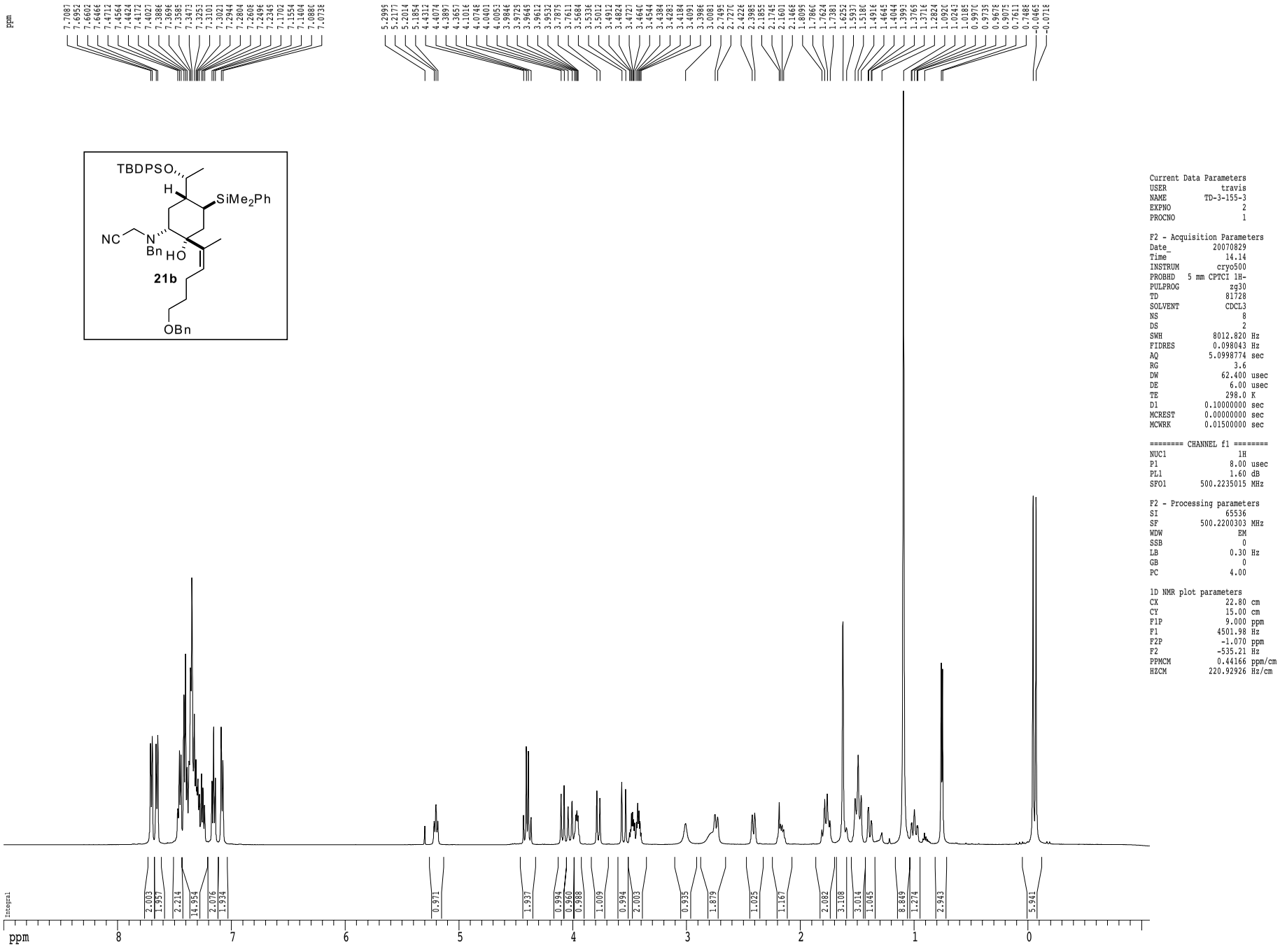
======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804002 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 10.21 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50366 Hz/cm

1H spectrum



Current Data Parameters
USER travis
NAME TD-3-155-3
EXPNO 2
PROCNO 1

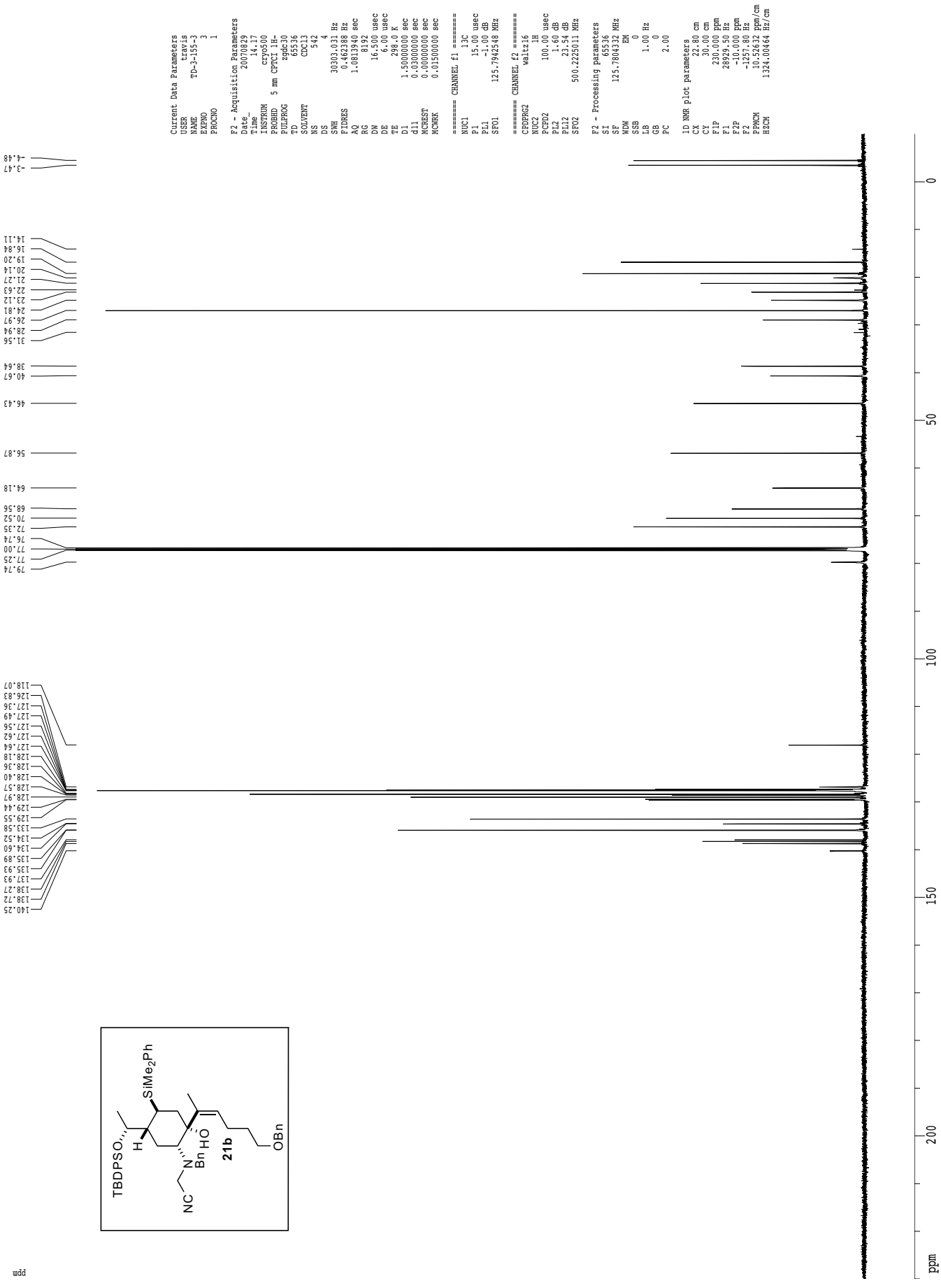
F2 - Acquisition Parameters
Date_ 20070829
Time 14.14
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCL3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 3.6
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

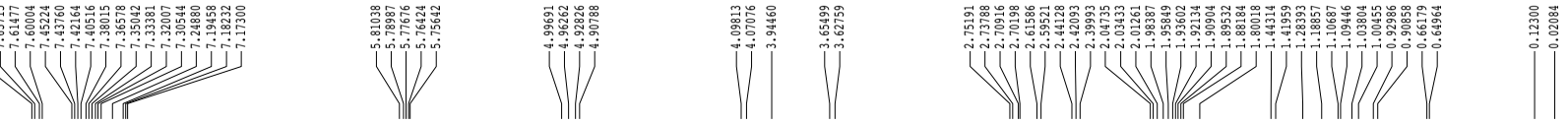
F2 - Processing parameters
SI 65536
SF 500.2200303 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

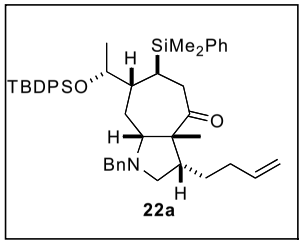
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -1.070 ppm
F2 -535.21 Hz
PPMCM 0.44166 ppm/cm
HZCM 220.92926 Hz/cm

13C spectrum with 1H decoupling



1H spectrum






```
Current Data Parameter
USER                 mellis
NAME              ME-II-22
EXPNO                    1
PROCNO                   1

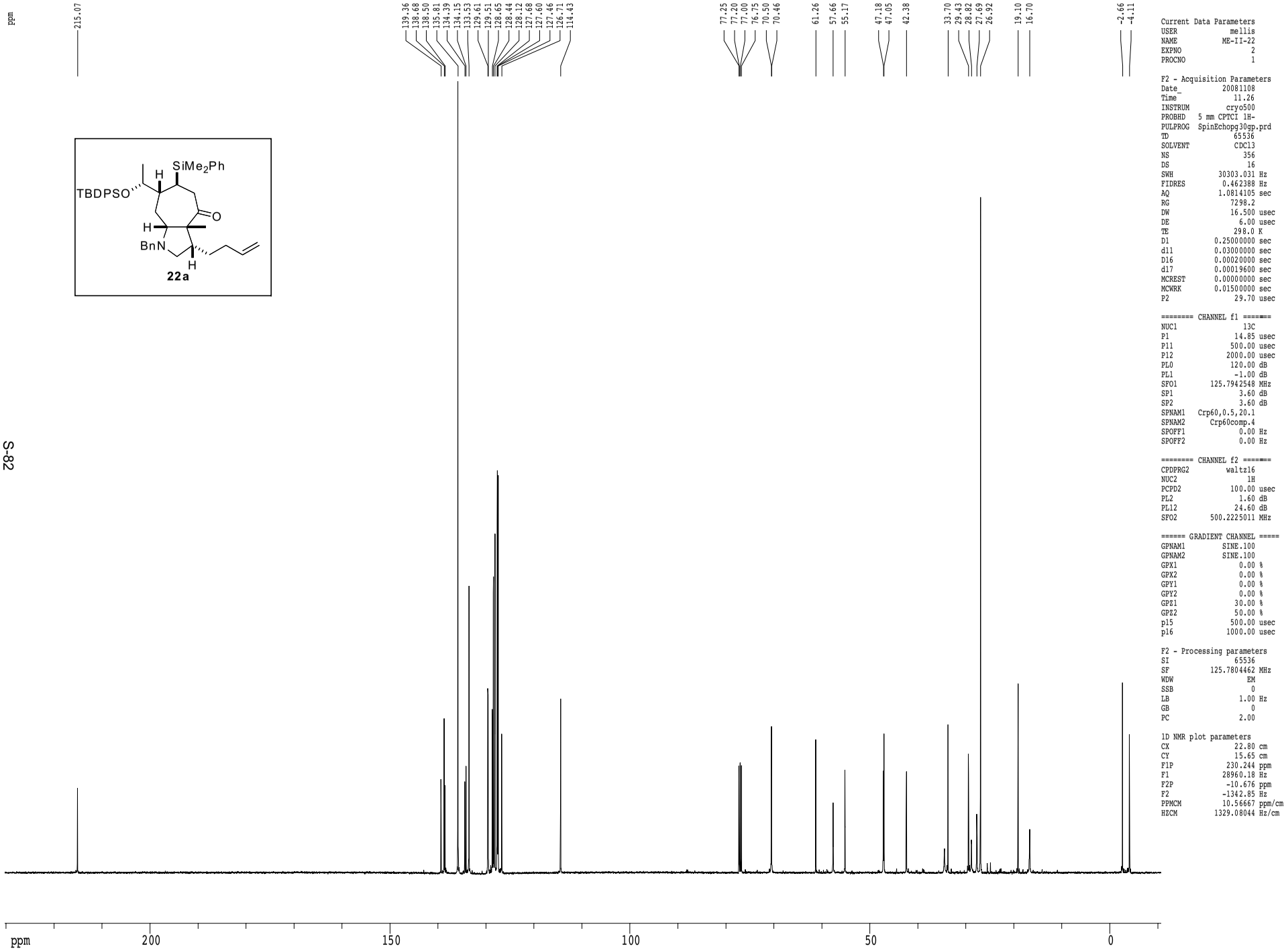
F2 - Acquisition Parameters
Date_             20081108
Time                11.17
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0999398 sec
RG                     1.8
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameter
SI                   65536
SF            500.2200606 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 8.000 ppm
F1                4001.76 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.37281 ppm/cm
HZCM            186.48555 Hz/cm
```

13C spectrum with 1H decoupling



Current Data Parameters
USER mellis
NAME ME-II-22
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20081108
Time 11.26
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 356
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0814105 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 29.70 usec

======== CHANNEL f1 =======
NUC1 13C
P1 14.85 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.60 dB
SP2 3.60 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

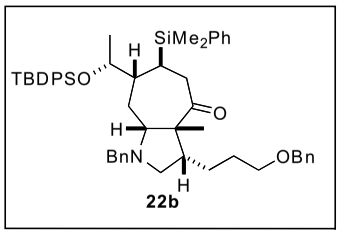
======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

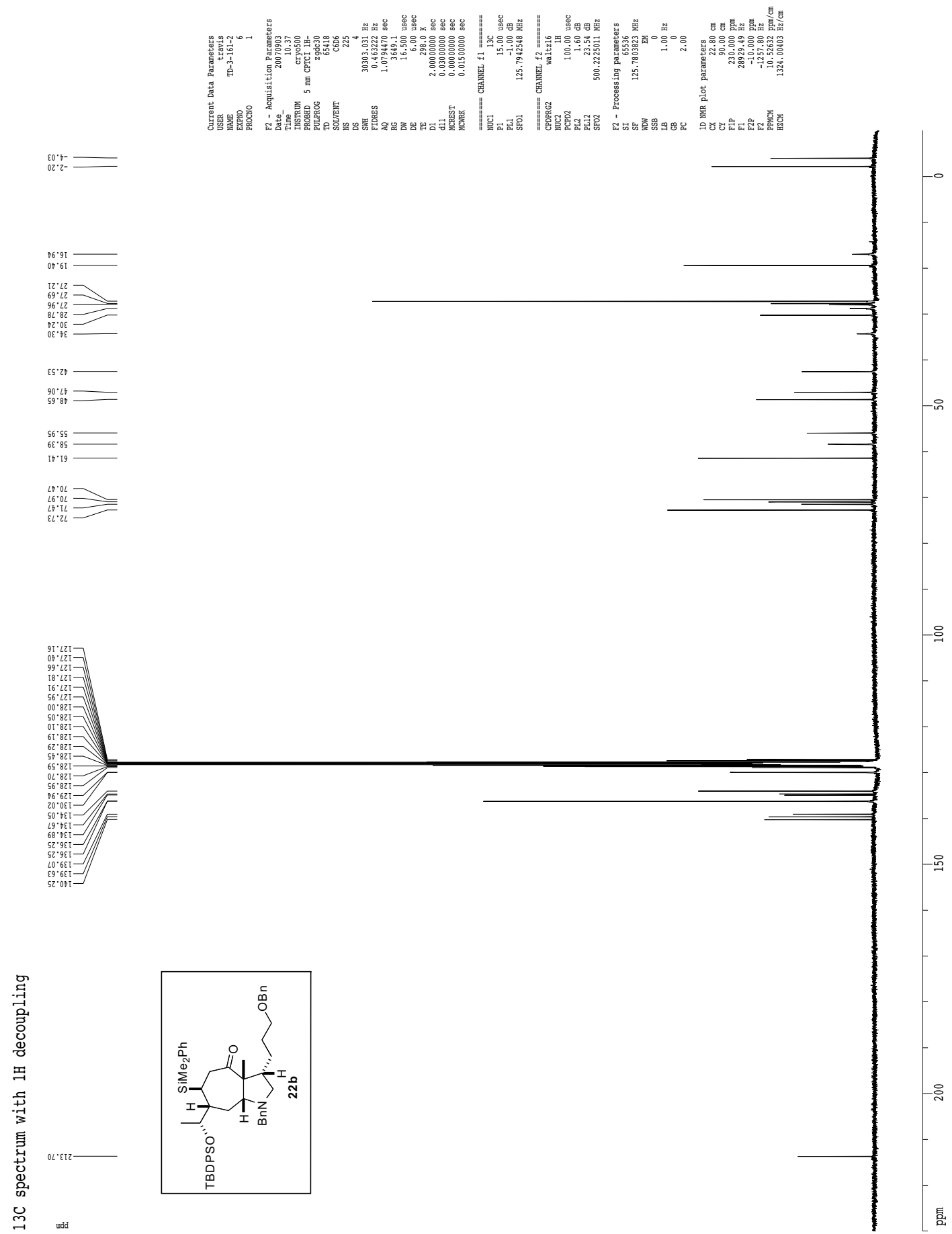
F2 - Processing parameters
SI 65536
SF 125.7804462 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 230.244 ppm
F1 28960.18 Hz
F2P -10.676 ppm
F2 -1342.85 Hz
PPMCM 10.56667 ppm/cm
HZCM 1329.08044 Hz/cm

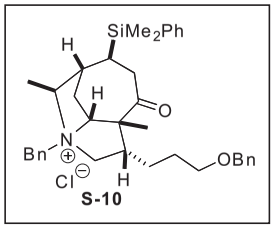
1H spectrum



13C spectrum with 1H decoupling



1H spectrum



S-10

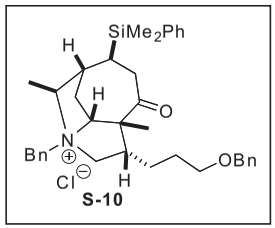

```
Current Data Parameters
USER                travis
NAME            TD 4 43 1
EXPNO                 101
PROCNO                  1

F2   Acquisition Parameter
Date_            20080308
Time                16.38
INSTRUM             av600
PROBHD   5 mm BBO BB 1H
PULPROG              zg30
TD                  97938
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098178 Hz
AQ               5.0928259 se
RG                    128
DW                 52.000 us
DE                  6.00 us
TE                 298.0 K
D1              0.10000000 se
TD0                     1

======== CHANNEL f1 ======
NUC1                   1H
P1                  9.00 us
PL1                 5.30 dB
SFO1          600.1342009 MH

F2   Processing parameters
SI                  65536
SF            600.1300283 MH
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

13C spectrum with 1H decoupling



S-10


```
Current Data Parameters
USER              travis
NAME          TD 3 300 2
EXPNO                 2
PROCNO                1

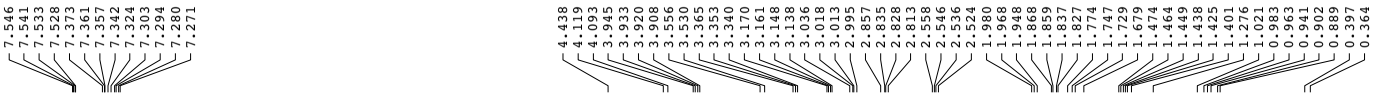
F2   Acquisition Parameter
Date_          20080204
Time              12.49
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  130
DS                    4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 se
RG              11585.2
DW               16.500 us
DE                6.00 us
TE               298.0 K
D1           1.00000000 se
d11          0.03000000 se
MCREST       0.00000000 se
MCWRK        0.01500000 se

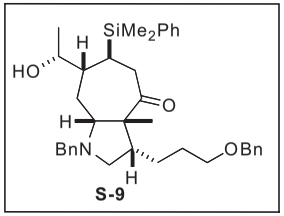
======== CHANNEL f1 ======
NUC1                13C
P1               15.00 us
PL1               1.00 dB
SFO1        125.7942548 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 us
PL2               1.60 dB
PL12             23.54 dB
SFO2        500.2225011 MH

F2   Processing parameters
SI                65536
SF          125.7804346 MH
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                2.00
```

1H spectrum



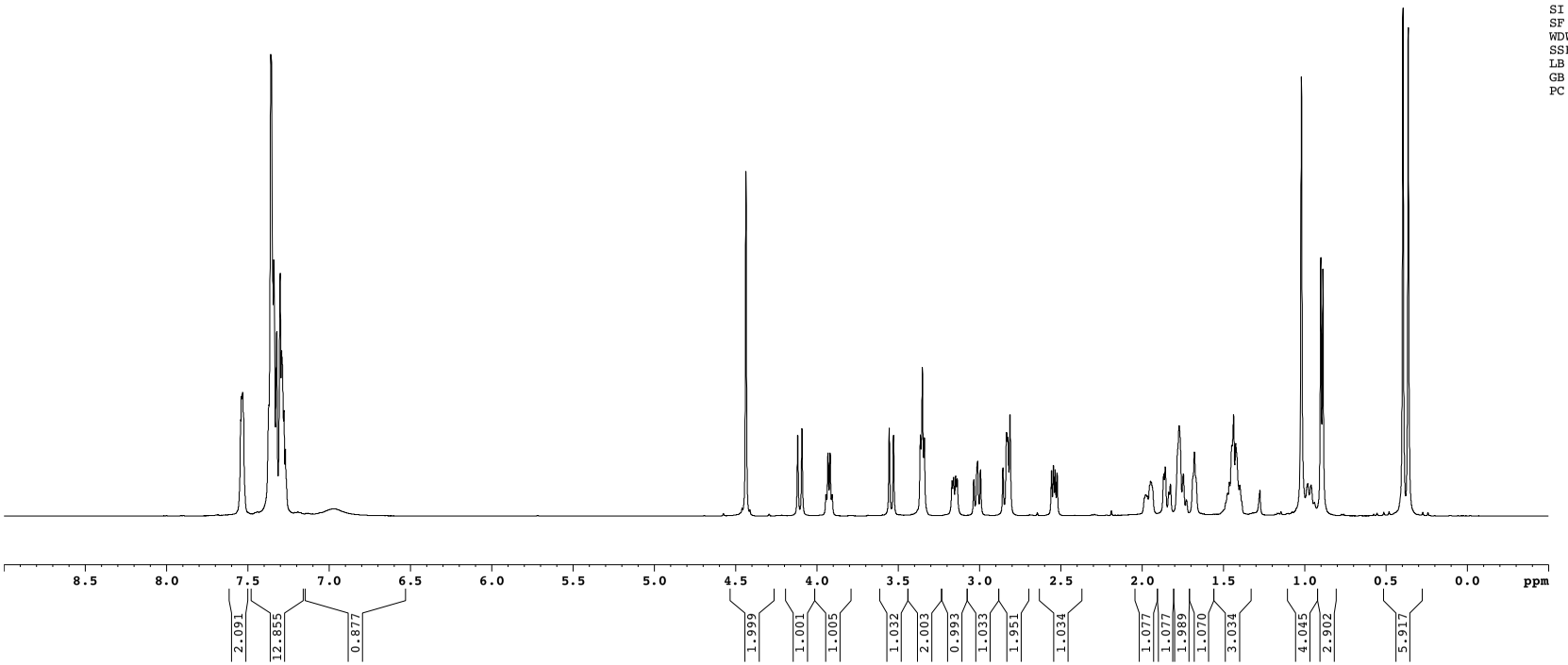



```
Current Data Parameters
USER                travis
NAME            TD 4 33 2
EXPNO                   2
PROCNO                  1

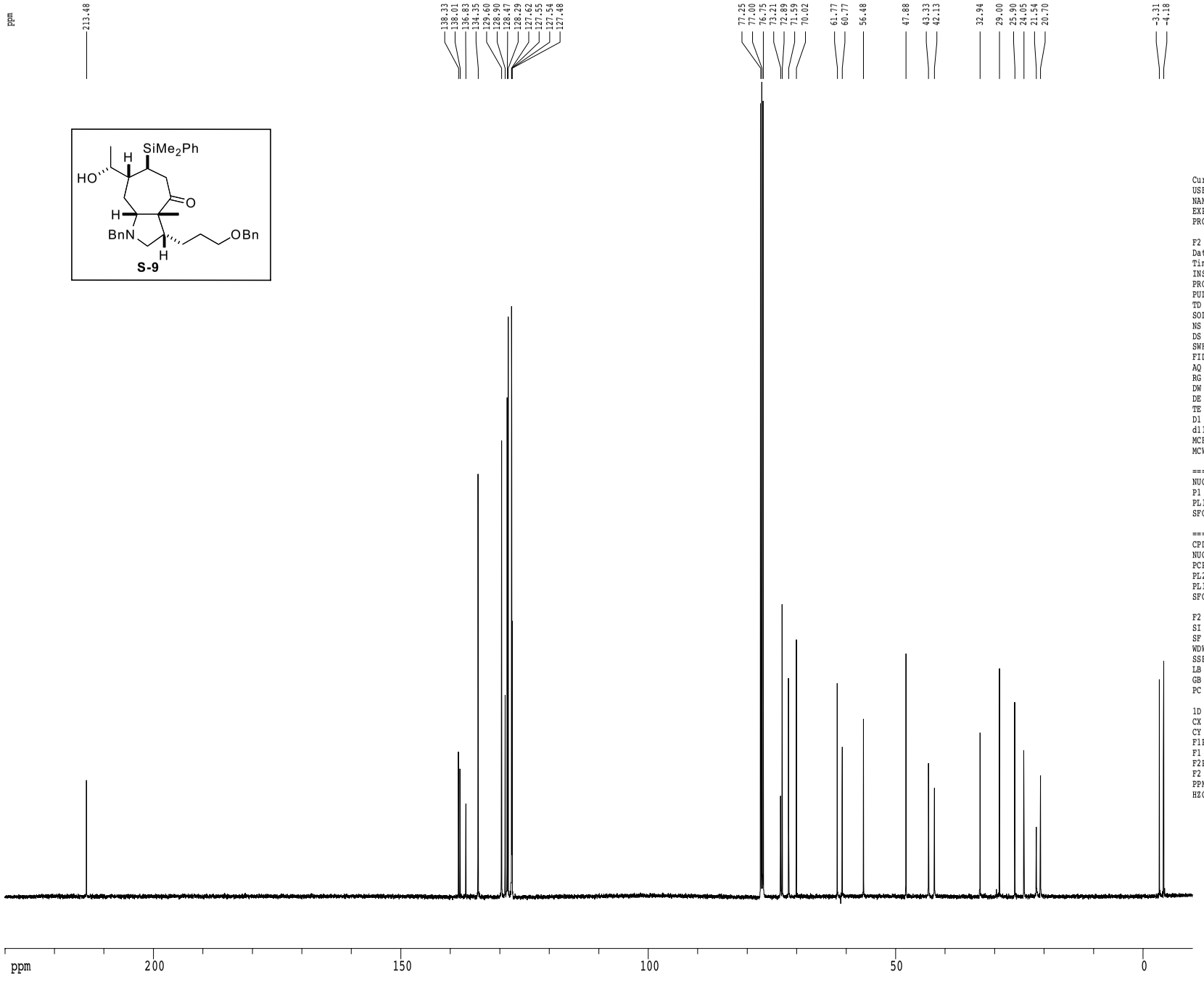
F2   Acquisition Parameter
Date_             20080308
Time                  9.38
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ                5.0998774 se
RG                      3.2
DW                   62.400 us
DE                    6.00 us
TE                   298.0 K
D1              0.10000000 se
MCREST          0.00000000 se
MCWRK           0.01500000 se

======== CHANNEL f1 =======
NUC1                    1H
P1                   7.38 us
PL1                  1.60 dB
SFO1          500.2235015 MH

F2   Processing parameters
SI                    65536
SF            500.2200251 MH
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



13C spectrum with 1H decoupling



Current Data Parameters
USER travis
NAME TD-4-33-2
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080308
Time 9.39
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 255
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 8192
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

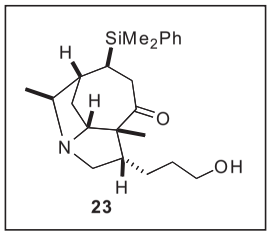
======== CHANNEL f1 ========
NUC1 13C
P1 14.75 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.80 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804356 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 230.000 ppm
F1 28929.50 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 10.52632 ppm/cm
HZCM 1324.00464 Hz/cm

1H spectrum



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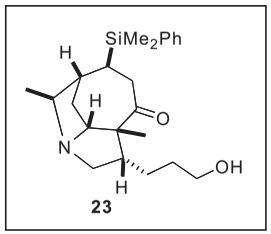
```
Current Data Parameters
USER                travis
NAME              TD 4 20 3
EXPNO                   101
PROCNO                    1

F2   Acquisition Parameter
Date_              20080211
Time                 20.48
INSTRUM              av600
PROBHD   5 mm TBI 1H/13
PULPROG               zg30
TD                   97938
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               9615.385 Hz
FIDRES            0.098178 Hz
AQ                5.0928259 se
RG                     256
DW                  52.000 us
DE                   6.00 us
TE                  298.0 K
D1              0.10000000 se
TD0                      1

======== CHANNEL f1 ======
NUC1                    1H
P1                   8.00 us
PL1                  1.00 dB
SFO1          600.1342009 MH

F2   Processing parameters
SI                   65536
SF            600.1300282 MH
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

13C spectrum with 1H decoupling



23

213.957
137.864
134.031
129.089
127.799
77.255
77.001
76.747
75.025
73.933
62.776
60.896
60.303
52.749
44.749
41.284
32.063
31.947
29.762
24.806
21.092
2.991
3.172

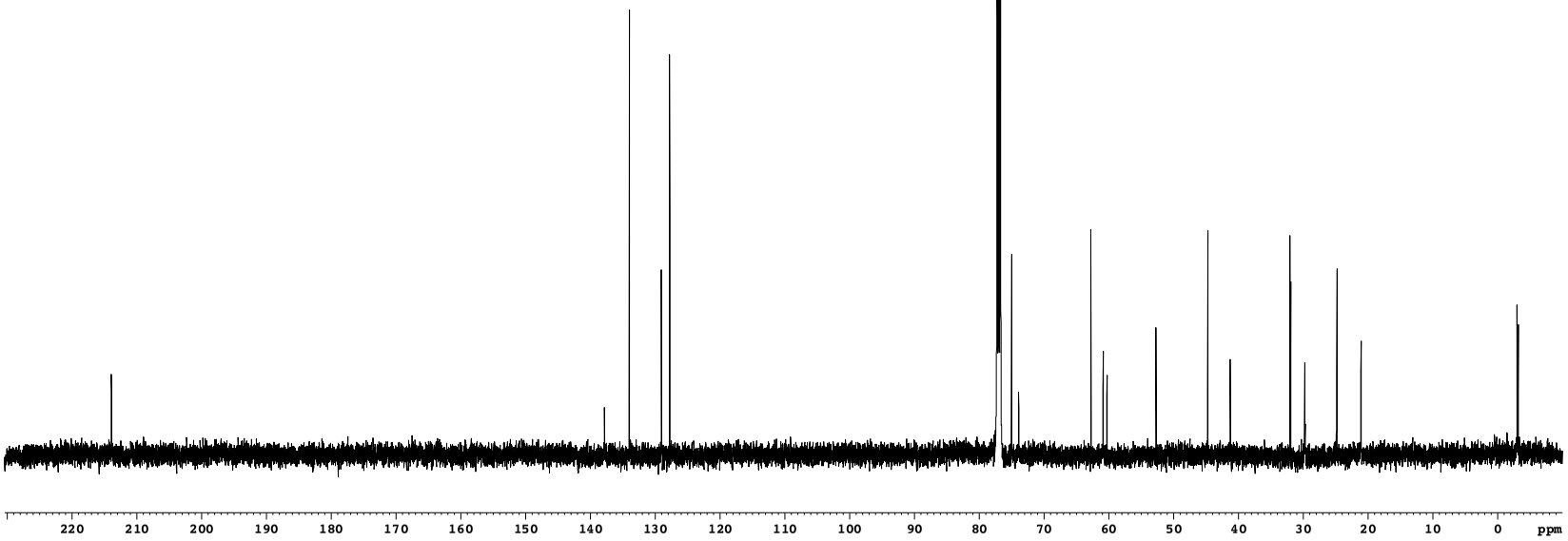
```
Current Data Parameters
USER                travis
NAME            TD 4 20 3
EXPNO                   5
PROCNO                  1

F2   Acquisition Parameter
Date_             20080211
Time                 21.30
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H
PULPROG           zgdc30
TD                 65418
SOLVENT            CDCl3
NS                   794
DS                     4
SWH            30303.031 Hz
FIDRES          0.463222 Hz
AQ             1.0794470 se
RG                11585.2
DW                 16.500 us
DE                  6.00 us
TE                298.0 K
D1           1.00000000 se
d11          0.03000000 se
MCREST       0.00000000 se
MCWRK        0.01500000 se

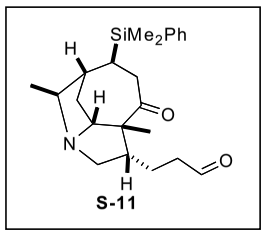
======== CHANNEL f1 ======
NUC1                13C
P1                14.75 us
PL1                1.00 dB
SFO1        125.7942548 MH

======== CHANNEL f2 ======
CPDPRG2         waltz16
NUC2                1H
PCPD2             100.00 us
PL2                1.60 dB
PL12               24.80 dB
SFO2        500.2225011 MH

F2   Processing parameters
SI                 65536
SF          125.7804272 MH
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  2.00
```



1H spectrum



S-11

Current Data Parameters
USER travis
NAME TD-4-36-3
EXPNO 1
PROCNO 1

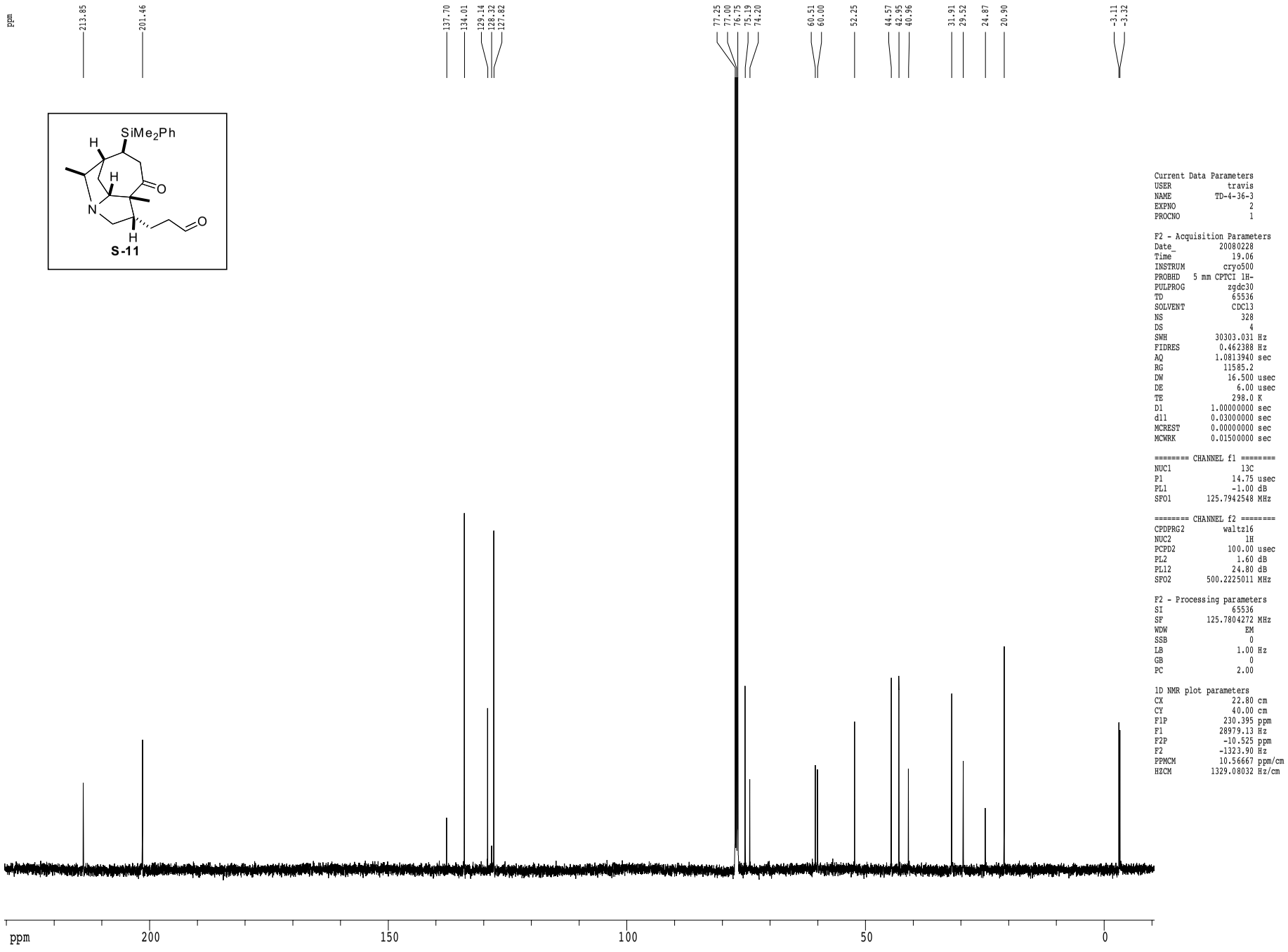
F2 - Acquisition Parameters
Date_ 20080228
Time 19.04
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200258 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 12.000 ppm
F1 6002.64 Hz
F2P -1.000 ppm
F2 -500.22 Hz
PPMCM 0.57018 ppm/cm
HZCM 285.21320 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters

USER	travis
NAME	TD-4-36-3
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20080228
Time	19.06
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	328
DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	11585.2
DW	16.500 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
d11	0.03000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	14.75 usec
PL1	-1.00 dB
SFO1	125.7942548 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	1.60 dB
PL12	24.80 dB
SFO2	500.2225011 MHz

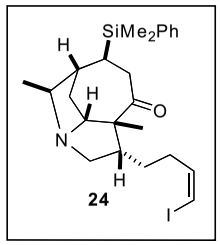
F2 - Processing parameters

SI	65536
SF	125.7804272 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
CY	40.00 cm
F1P	230.395 ppm
F1	28979.13 Hz
F2P	-10.525 ppm
F2	-1323.90 Hz
PPMCM	10.56667 ppm/cm
HZCM	1329.08032 Hz/cm

1H spectrum




```
Current Data Parameter
USER                 mellis
NAME          ME-I-204-ch
EXPNO                   1
PROCNO                  1

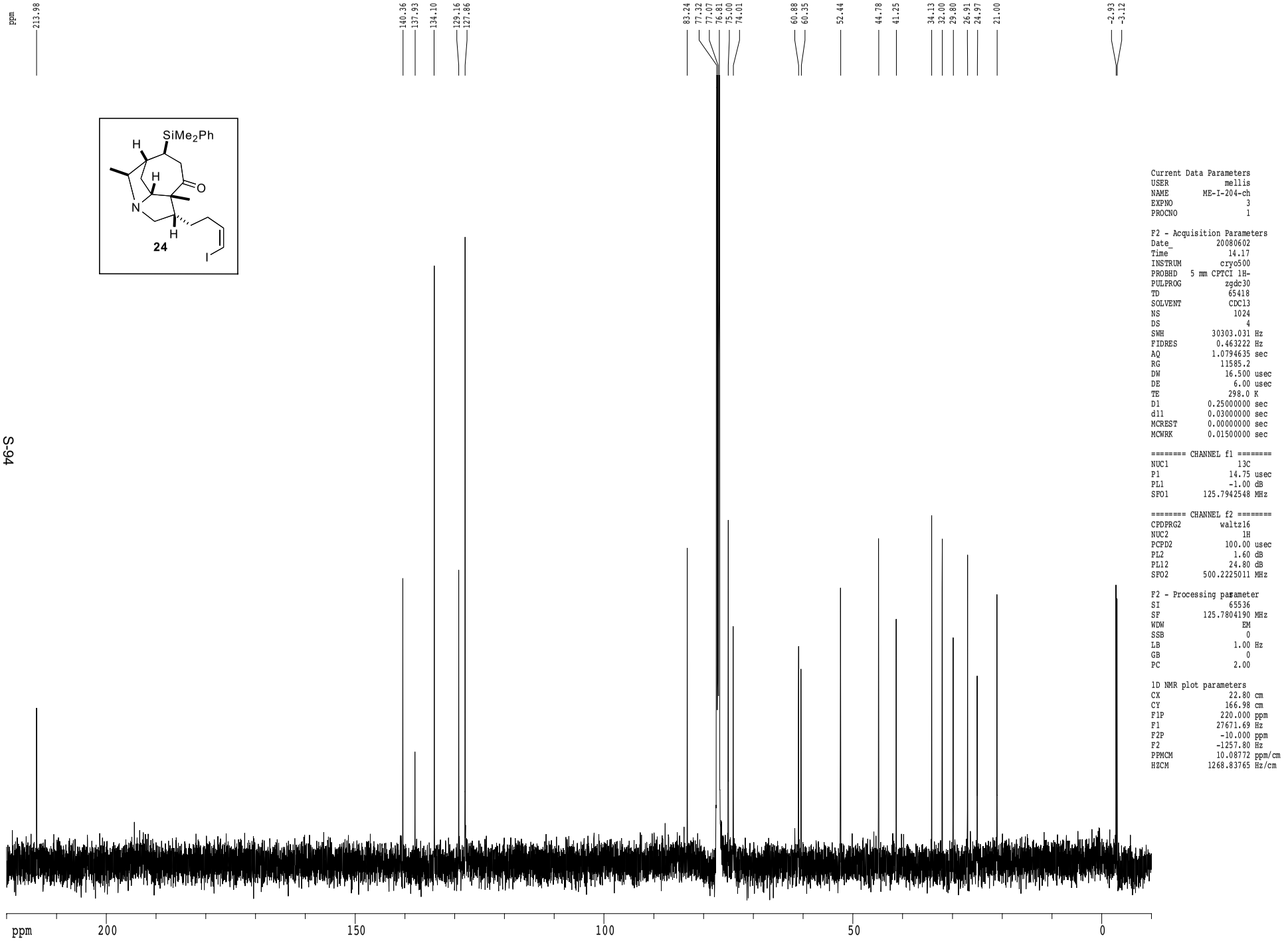
F2 - Acquisition Parameters
Date_             20080602
Time                14.02
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ                5.0999398 sec
RG                     4.5
DW                  62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.38 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameter
SI                   65536
SF            500.2200261 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  8.000 ppm
F1                4001.76 Hz
F2P                 -1.000 ppm
F2                -500.22 Hz
PPMCM             0.39474 ppm/cm
HZCM            197.45528 Hz/cm
```

13C spectrum with 1H decoupling



Current Data Parameters
USER mellis
NAME ME-I-204-ch
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080602
Time 14.17
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 1024
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 11585.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

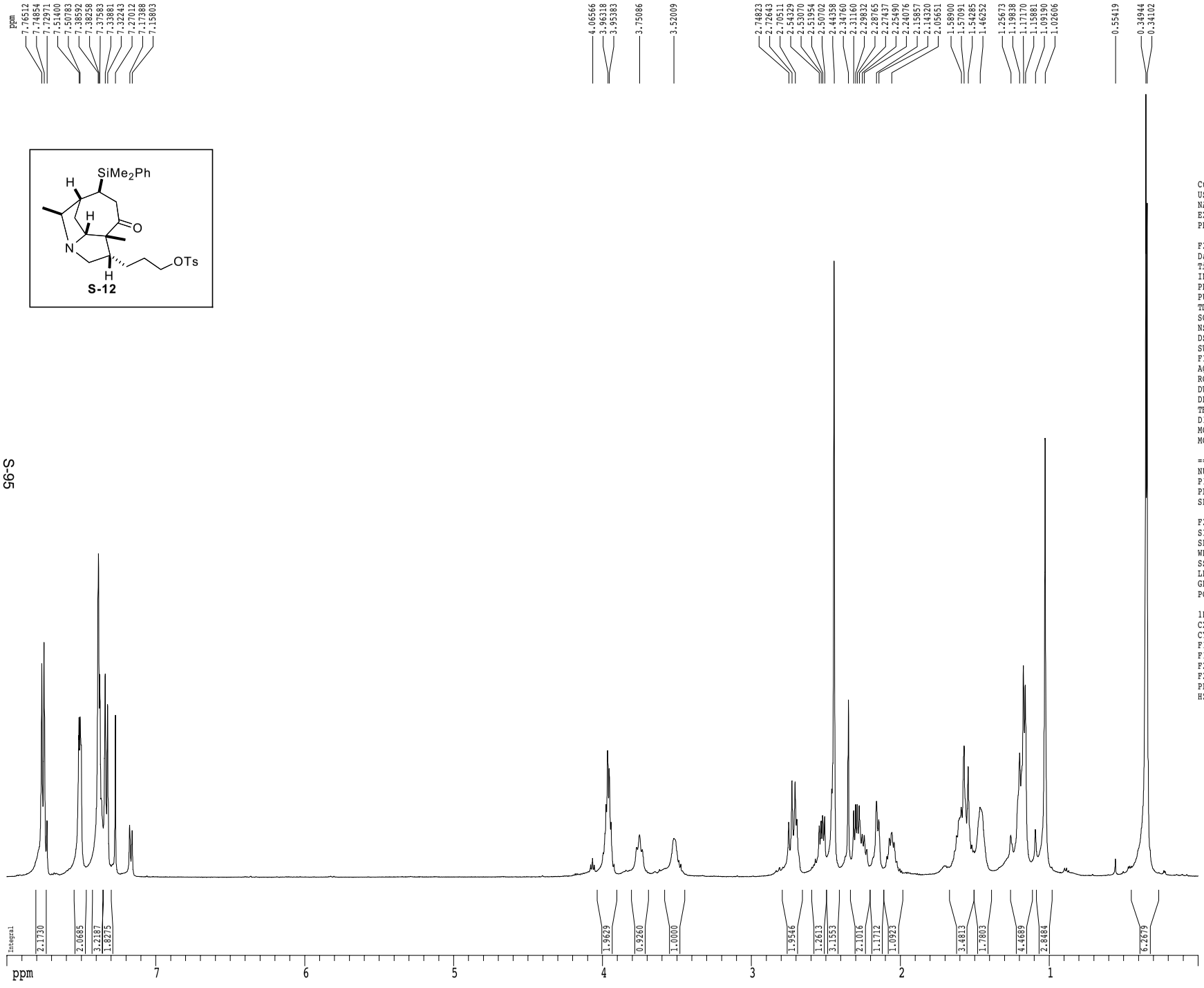
======== CHANNEL f1 ========
NUC1 13C
P1 14.75 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.80 dB
SFO2 500.2225011 MHz

F2 - Processing parameter
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 166.98 cm
F1P 220.000 ppm
F1 27671.69 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 10.08772 ppm/cm
HZCM 1268.83765 Hz/cm

1H spectrum



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```
Current Data Parameter
USER                 mellis
NAME           ME-I-258-ch
EXPNO                   1
PROCNO                  1

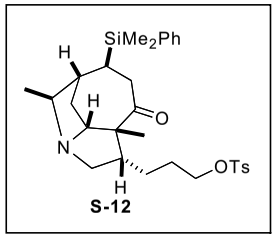
F2 - Acquisition Parameters
Date_              20080710
Time                  13.39
INSTRUM             cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    81728
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8012.820 Hz
FIDRES             0.098043 Hz
AQ                 5.0999398 sec
RG                      4.5
DW                   62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1                0.10000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    7.38 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameter
SI                    65536
SF              500.2200252 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                   8.000 ppm
F1                 4001.76 Hz
F2P                   0.000 ppm
F2                    0.00 Hz
PPMCM              0.35088 ppm/cm
HZCM             175.51581 Hz/cm
```

13C spectrum with 1H decoupling



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```
Current Data Parameters
USER                mellis
NAME          ME-I-258-ch
EXPNO                  3
PROCNO                 1

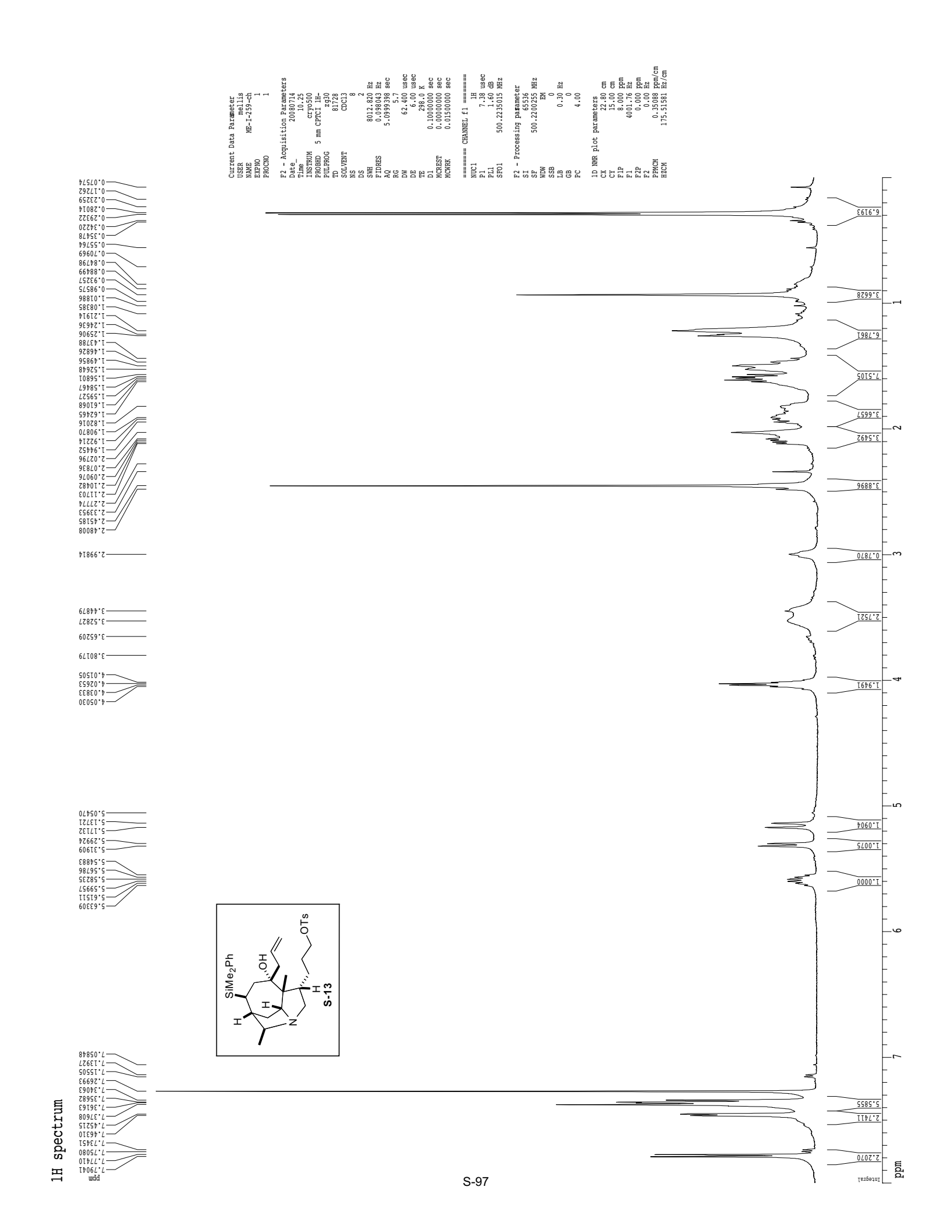
F2 - Acquisition Parameters
Date_           20080710
Time              13.53
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG          zgdc30
TD               65418
SOLVENT           CDCl3
NS                 824
DS                   4
SWH          30303.031 Hz
FIDRES        0.463222 Hz
AQ           1.0794635 sec
RG            11585.2
DW             16.500 usec
DE              6.00 usec
TE             298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1              14.75 usec
PL1             -1.00 dB
SFO1       125.7942548 MHz

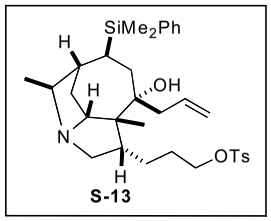
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2          100.00 usec
PL2              1.60 dB
PL12             24.80 dB
SFO2       500.2225011 MHz

F2 - Processing parameter
SI                65536
SF          125.7804190 MHz
WDW                EM
SSB                0
LB              1.00 Hz
GB                 0
PC              2.00

1D NMR plot parameters
CX              22.80 cm
CY              15.65 cm
F1P            230.637 ppm
F1            29009.68 Hz
F2P            -10.287 ppm
F2            -1293.96 Hz
PPMCM         10.56688 ppm/cm
HZCM        1329.10706 Hz/cm
```


1H spectrum
Current Data Parameter
USER mellis
NAME MB-I-259-ch
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180714
Time_ 10.25
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0999398 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameter
SI 65536
SF 500.2200255 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.000 ppm
F1 4001.76 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.35088 ppm/cm
HZCM 175.51581 Hz/cm
SiMe2Ph
OH
OTs
H
H
H
N
S-13
ppm
Integral
6.9193
3.6628
6.7861
7.5105
3.6657
3.5492
3.8896
0.7870
2.7521
1.9491
1.0904
1.0075
1.0000
5.5855
2.7411
2.2070
7.7904
7.7741
7.7508
7.7451
7.4631
7.4521
7.3768
7.3616
7.3568
7.3406
7.2699
7.1555
7.1392
7.0584
5.6330
5.6151
5.5995
5.5823
5.5678
5.5488
5.3190
5.2992
5.1713
5.1372
5.0547
4.0503
4.0383
4.0265
4.0150
3.8017
3.6520
3.5282
3.4487
2.9981
2.4800
2.4518
2.3395
2.2771
2.1170
2.1048
2.0907
2.0783
2.0279
1.9445
1.9221
1.9087
1.8201
1.6243
1.6106
1.5952
1.5846
1.5680
1.5264
1.4985
1.4682
1.4378
1.2590
1.2463
1.2191
1.0838
1.0188
0.9857
0.9325
0.8849
0.8479
0.7096
0.5576
0.3547
0.3422
0.2932
0.2801
0.2325
0.1726
0.0757

13C spectrum with 1H decoupling



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Current Data Parameters
USER mellis
NAME ME-I-259-ch
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080714
Time 10.33
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 1370
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 11585.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

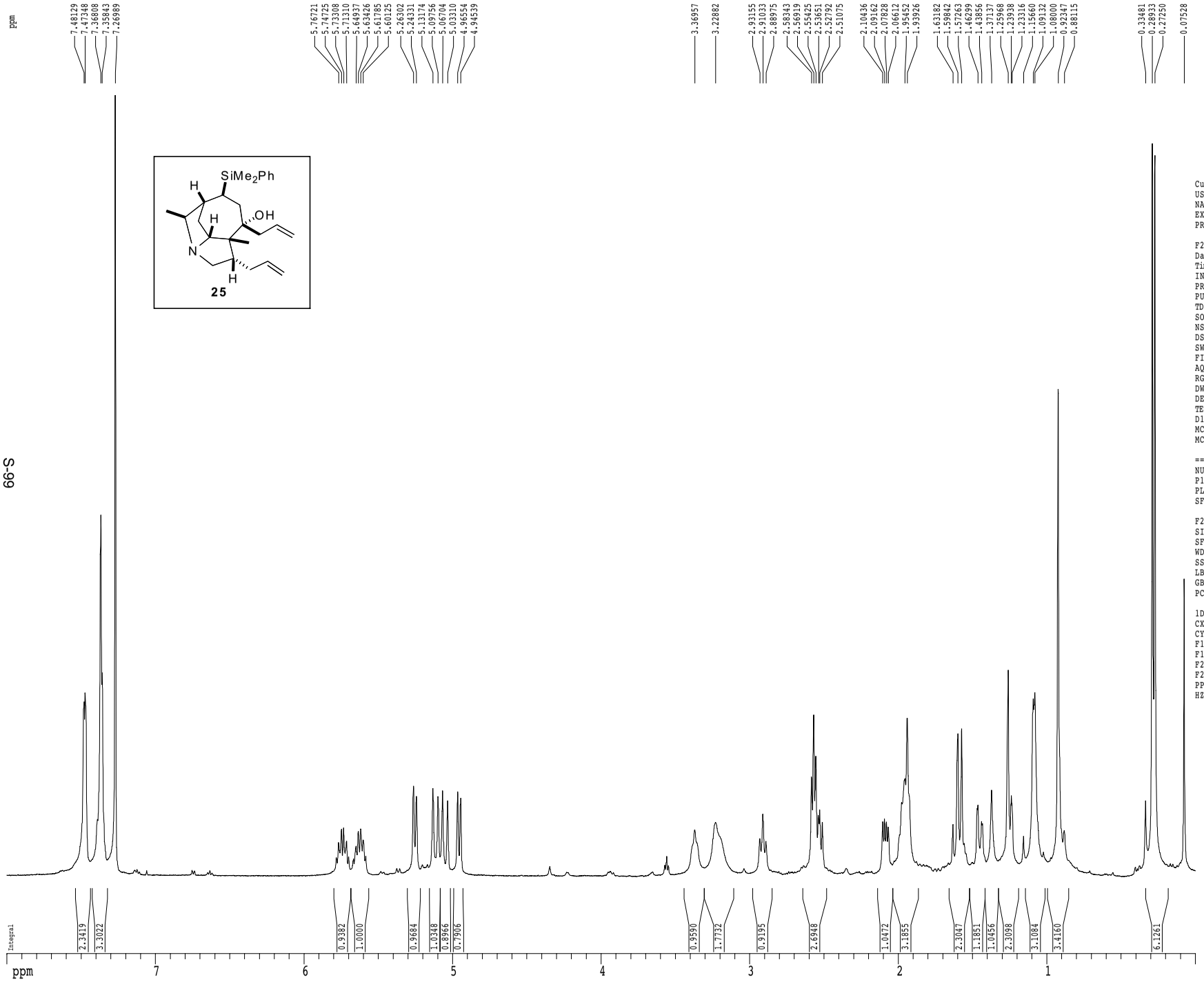
======== CHANNEL f1 ========
NUC1 13C
P1 14.75 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.80 dB
SFO2 500.2225011 MHz

F2 - Processing parameter
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 143.06 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum




```
Current Data Parameter
USER                mellis
NAME          ME-I-266-ch
EXPNO                  1
PROCNO                 1

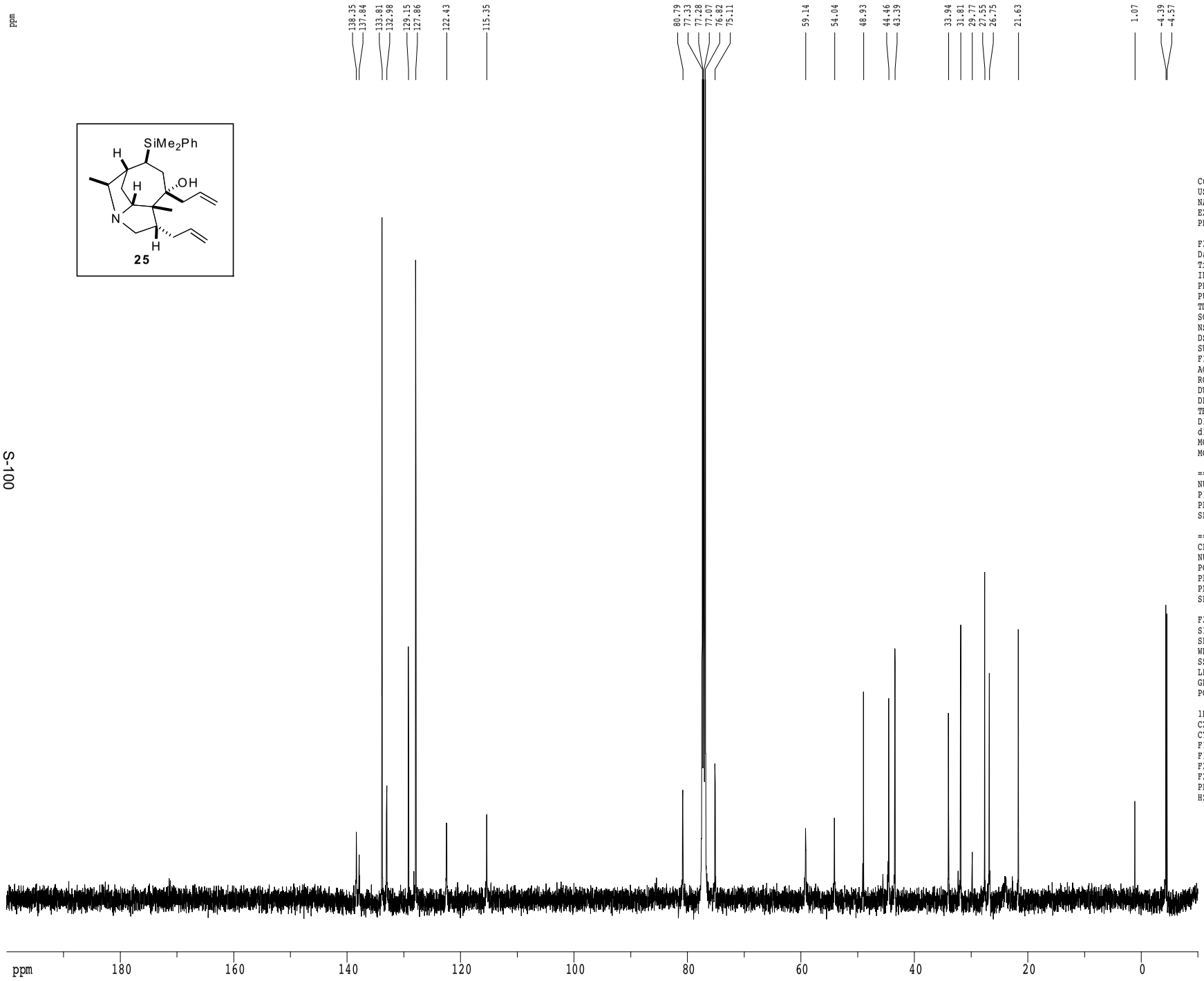
F2 - Acquisition Parameters
Date_           20080726
Time                13.03
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                     8
DS                     2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0999398 sec
RG                     5
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  7.38 usec
PL1                 1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameter
SI                  65536
SF            500.2200256 MHz
WDW                    EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 8.000 ppm
F1                4001.76 Hz
F2P                 0.000 ppm
F2                  0.00 Hz
PPMCM            0.35088 ppm/cm
HZCM           175.51581 Hz/cm
```

13C spectrum with 1H decoupling



S-100

Current Data Parameters
USER mellis
NAME ME-I-266-ch
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080726
Time 13.12
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 1024
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 11585.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

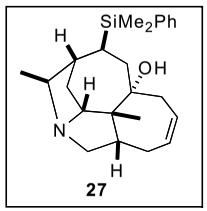
======== CHANNEL f1 ========
NUC1 13C
P1 14.75 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.80 dB
SFO2 500.2225011 MHz

F2 - Processing parameter
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 73.99 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



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S-101

Current Data Parameter
USER mellis
NAME ME-I-295-old
EXPNO 1
PROCNO 1

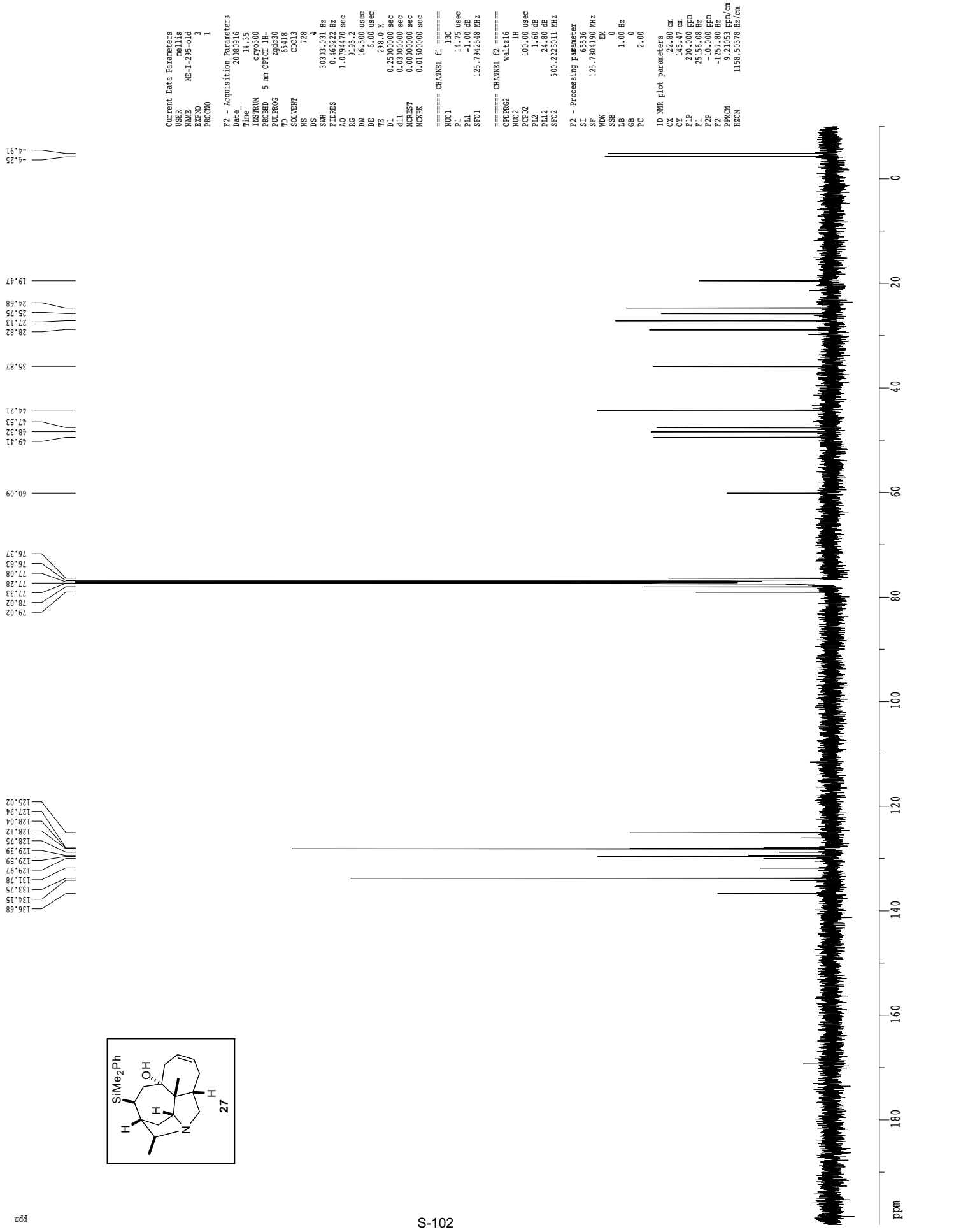
F2 - Acquisition Parameters
Date_ 20080916
Time 14.31
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 7.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

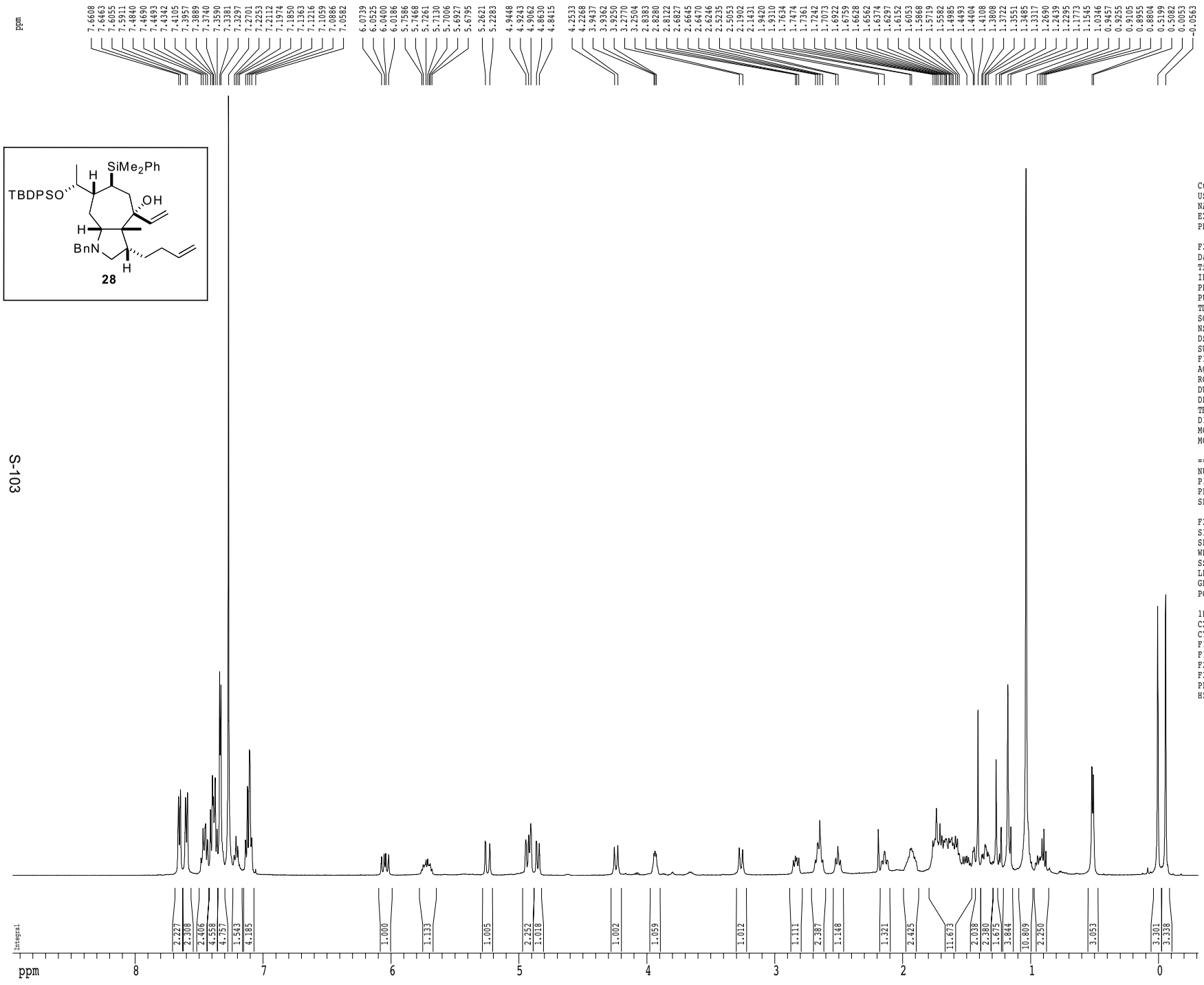
F2 - Processing parameter
SI 65536
SF 500.2200261 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 36.94 cm
F1P 8.000 ppm
F1 4001.76 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.35088 ppm/cm
HZCM 175.51581 Hz/cm

13C spectrum with 1H decoupling



1H spectrum




```
Current Data Parameter
USER                mellis
NAME             ME-II-24
EXPNO                   1
PROCNO                  1

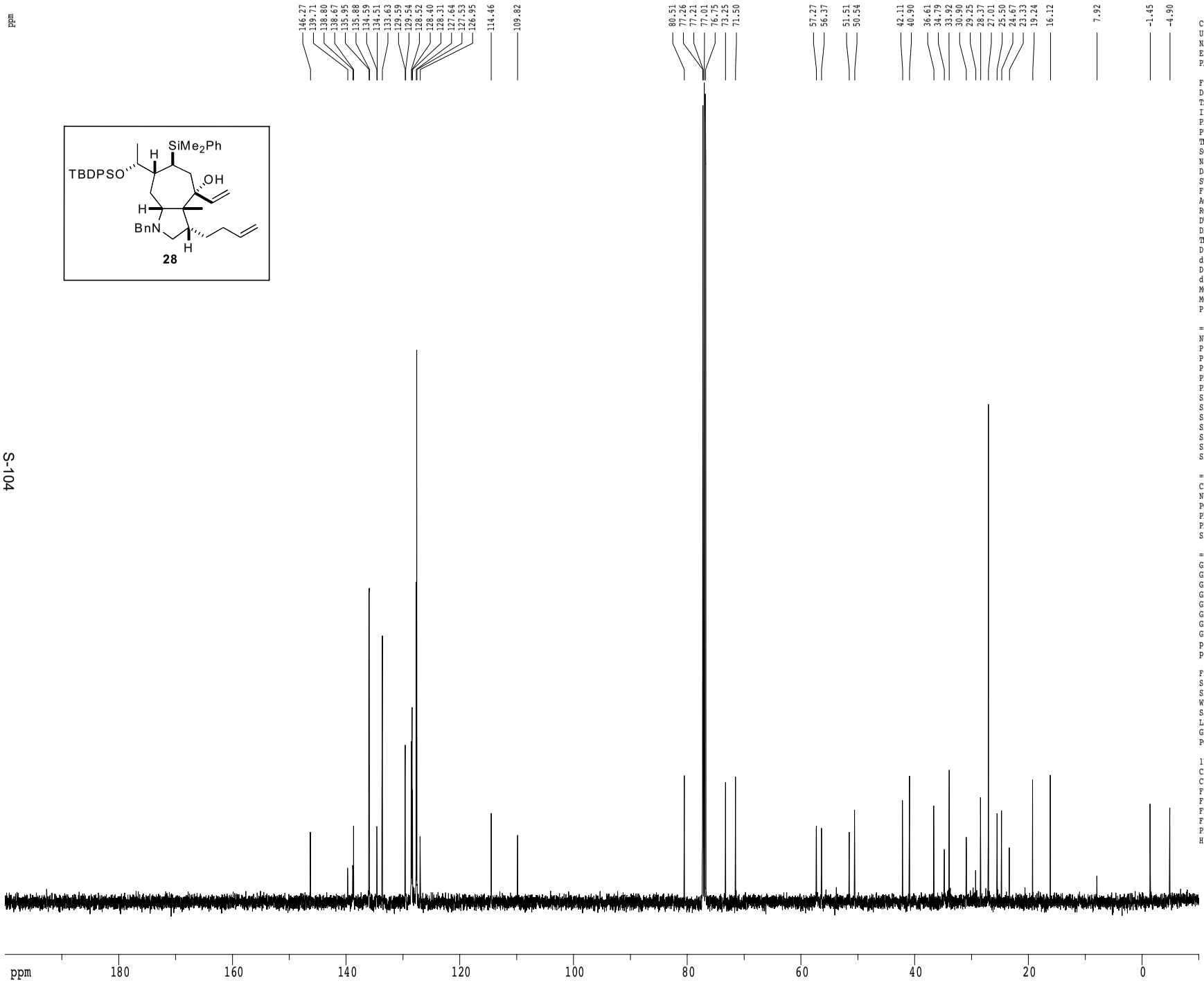
F2 - Acquisition Parameters
Date_            20081107
Time                16.04
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0999398 sec
RG                    4.5
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameter
SI                    65536
SF            500.2200246 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  8.955 ppm
F1                 4479.51 Hz
F2P                 -0.309 ppm
F2                 -154.62 Hz
PPMCM             0.40632 ppm/cm
HZCM             203.25117 Hz/cm
```

13C spectrum with 1H decoupling



S-104

```
Current Data Parameters
USER              mellis
NAME           ME-II-24
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20081107
Time              16.11
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  420
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0814105 sec
RG                 4096
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                29.70 usec

======== CHANNEL f1 =======
NUC1                13C
P1                14.85 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               3.60 dB
SP2               3.60 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

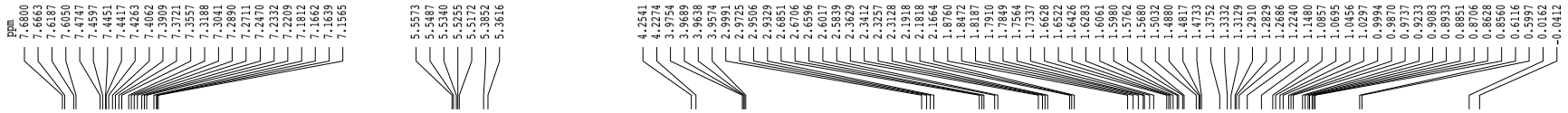
======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2               1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

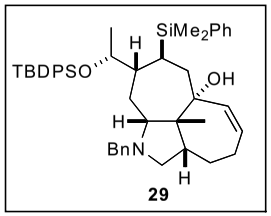
====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                 65536
SF          125.7804268 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P              -10.000 ppm
F2             -1257.80 Hz
PPMCM            9.21053 ppm/cm
HZCM          1158.50391 Hz/cm
```

1H spectrum





29

S-105

Current Data Parameter
USER mellis
NAME ME-II-25
EXPNO 1
PROCNO 1

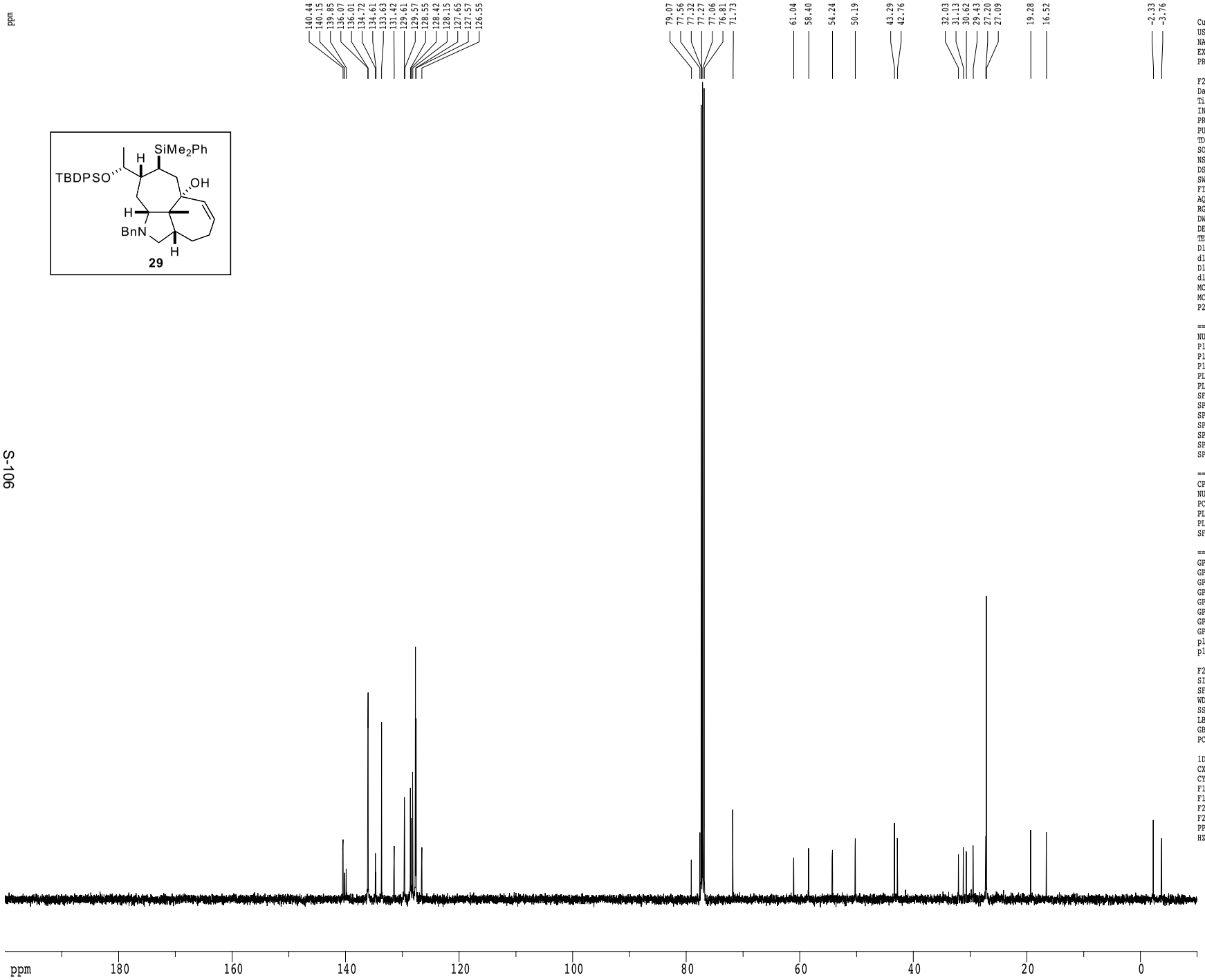
F2 - Acquisition Parameters
Date_ 20081117
Time 8.15
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0999398 sec
RG 11.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

F2 - Processing parameter
SI 65536
SF 500.2200239 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.000 ppm
F1 4001.76 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.37281 ppm/cm
HZCM 186.48555 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER mellis
NAME ME-II-25
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20081117
Time 8.23
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 1002
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0814105 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 29.70 usec

======== CHANNEL f1 =======
NUC1 13C
P1 14.85 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.60 dB
SP2 3.60 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

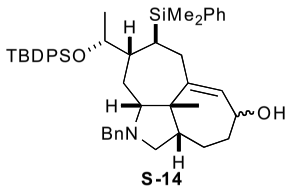
======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



S-14

S-107

```
Current Data Parameters
USER                 mellis
NAME              ME-II-95
EXPNO                    1
PROCNO                   1

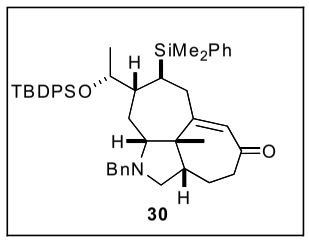
F2 - Acquisition Parameters
Date_             20090227
Time                 11.17
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                     7.1
DW                  62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF            500.2200269 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                 10.000 ppm
F1                5002.20 Hz
F2P                 -1.000 ppm
F2                -500.22 Hz
PPMCM             0.48246 ppm/cm
HZCM            241.33423 Hz/cm
```

1H spectrum



30


```
Current Data Parameter
USER                 mellis
NAME              ME-II-51
EXPNO                    1
PROCNO                   1

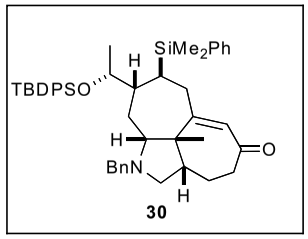
F2 - Acquisition Parameters
Date_             20090110
Time                 13.14
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                      28
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ                5.0998774 sec
RG                     4.5
DW                  62.400 usec
DE                   6.00 usec
TE                   298.0 K
D1                0.10000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameter
SI                    65536
SF             500.2200258 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00

1D NMR plot parameters
CX                    22.80 cm
CY                    15.00 cm
F1P                   8.000 ppm
F1                 4001.76 Hz
F2P                  -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.37281 ppm/cm
HZCM             186.48555 Hz/cm
```

13C spectrum with 1H decoupling



30

ppm 204.83 166.87 139.58 138.55 135.94 135.86 134.45 134.29 133.39 129.63 129.59 129.09 128.87 128.30 128.16 127.87 127.61 127.52 126.68 77.25 77.20 77.00 76.75 73.55 70.58 58.17 56.28 55.87 49.48 49.13 43.03 39.20 35.23 32.88 29.70 29.37 27.42 26.98 19.14 16.90 -3.28 -3.41

```
Current Data Parameters
USER                 mellis
NAME              ME-II-51
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090110
Time                 13.23
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     964
DS                      16
SWH              30303.031 Hz
FIDRES           0.462388 Hz
AQ               1.0813940 sec
RG                  9195.2
DW                  16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                  29.70 usec

======== CHANNEL f1 =======
NUC1                   13C
P1                  14.85 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  3.60 dB
SP2                  3.60 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

======== CHANNEL f2 =======
CPDPRG2            waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.60 dB
SFO2          500.2225011 MHz

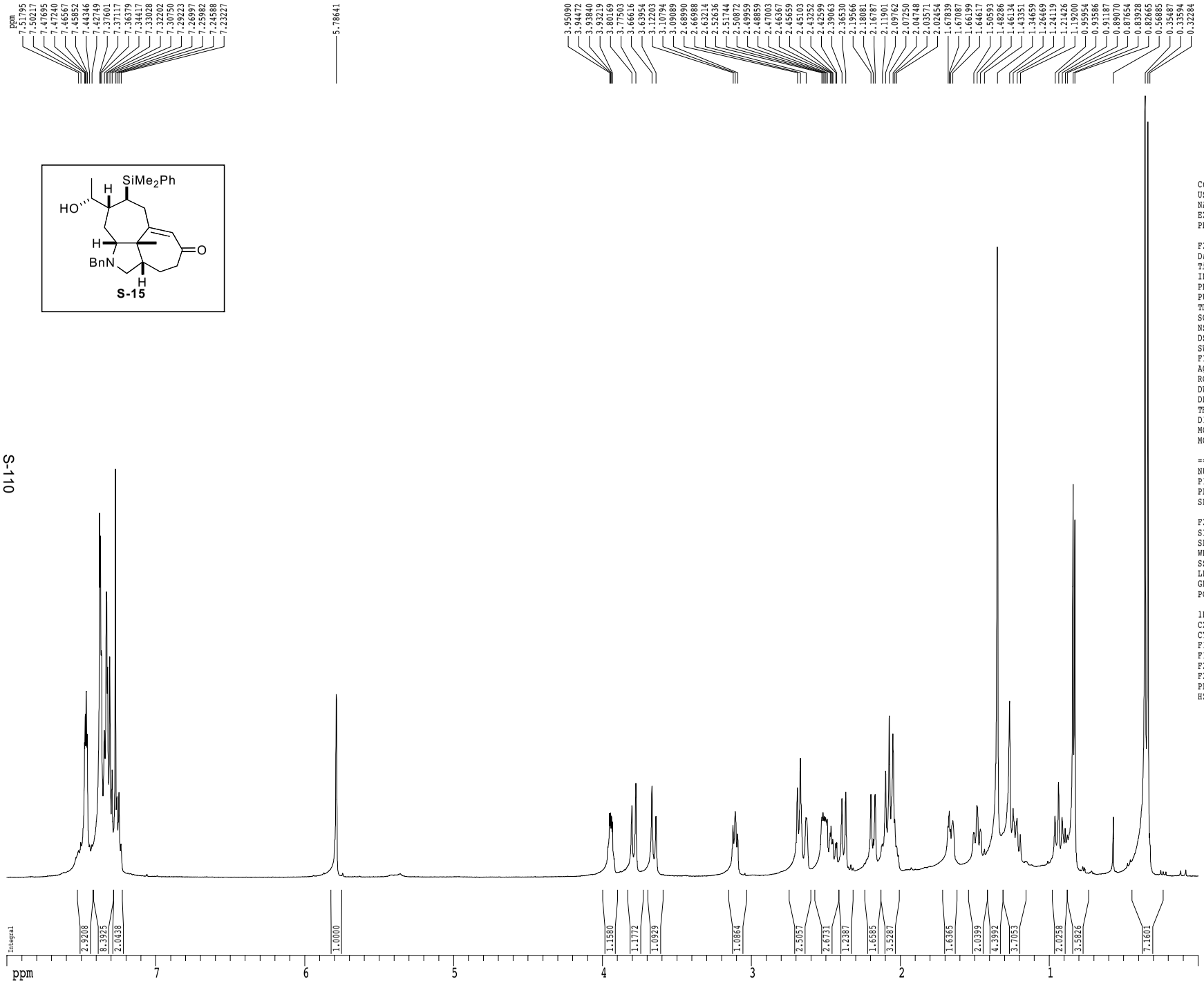
====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                   65536
SF            125.7804272 MHz
WDW                     EM
SSB                      0
LB                   1.00 Hz
GB                       0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P                210.000 ppm
F1                26413.89 Hz
F2P                -10.000 ppm
F2               -1257.80 Hz
PPMCM              9.64912 ppm/cm
HZCM           1213.67078 Hz/cm
```

ppm 200 180 160 140 120 100 80 60 40 20 0

1H spectrum




```
Current Data Parameter
USER                mellis
NAME        ME-II-100-ch
EXPNO                  1
PROCNO                 1

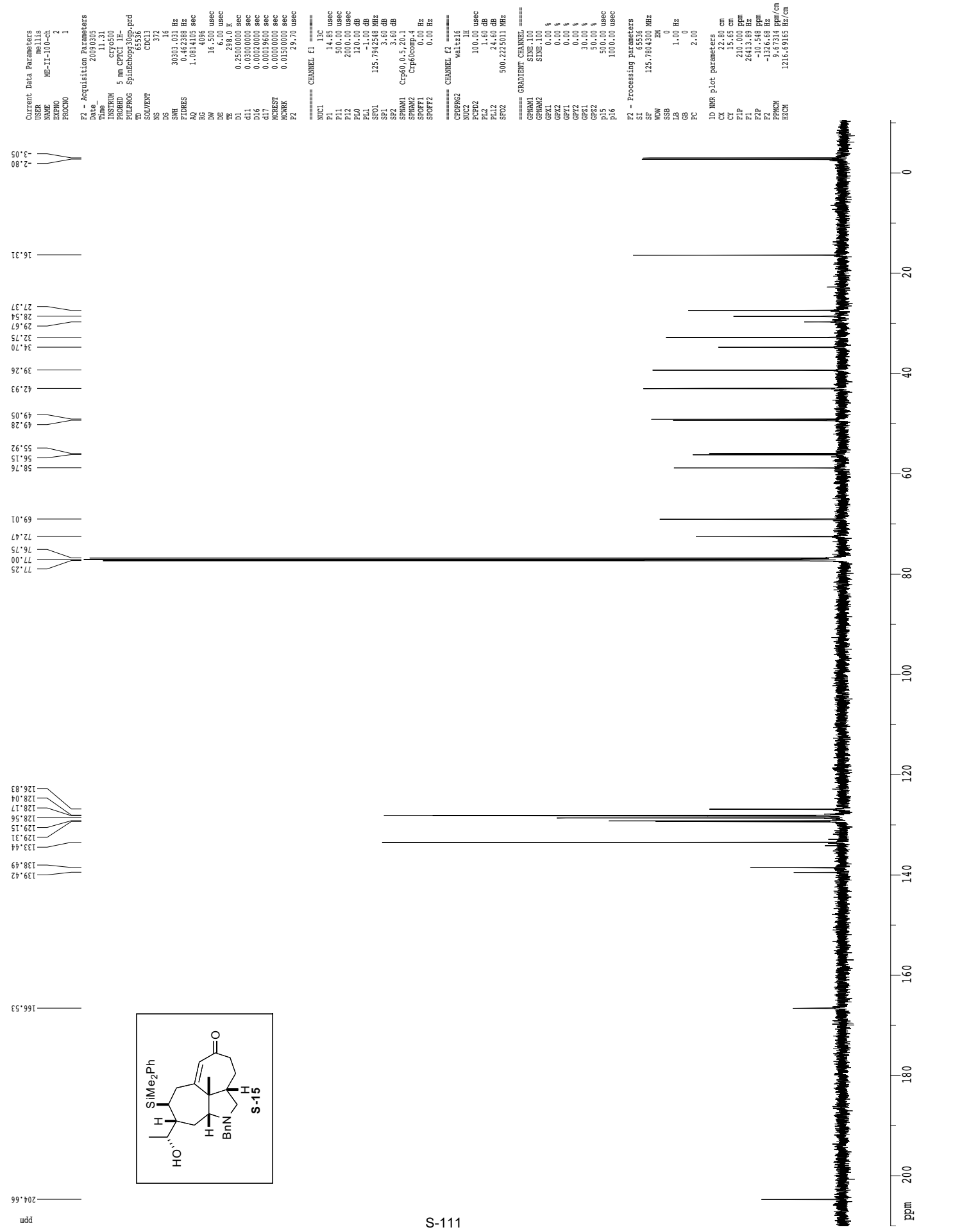
F2 - Acquisition Parameters
Date_           20090305
Time                11.27
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0999398 sec
RG                    6.3
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

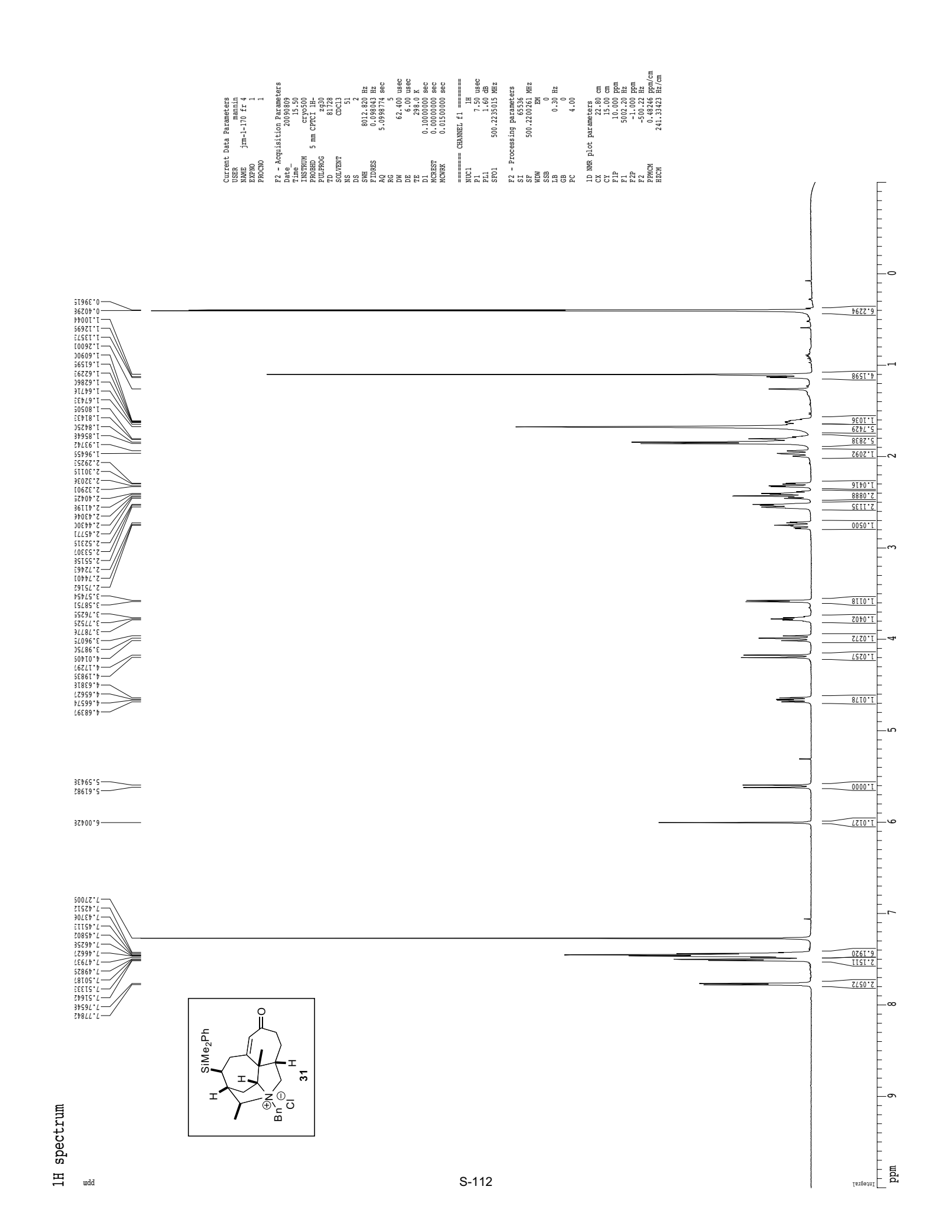
======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameter
SI                  65536
SF            500.2200268 MHz
WDW                    EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

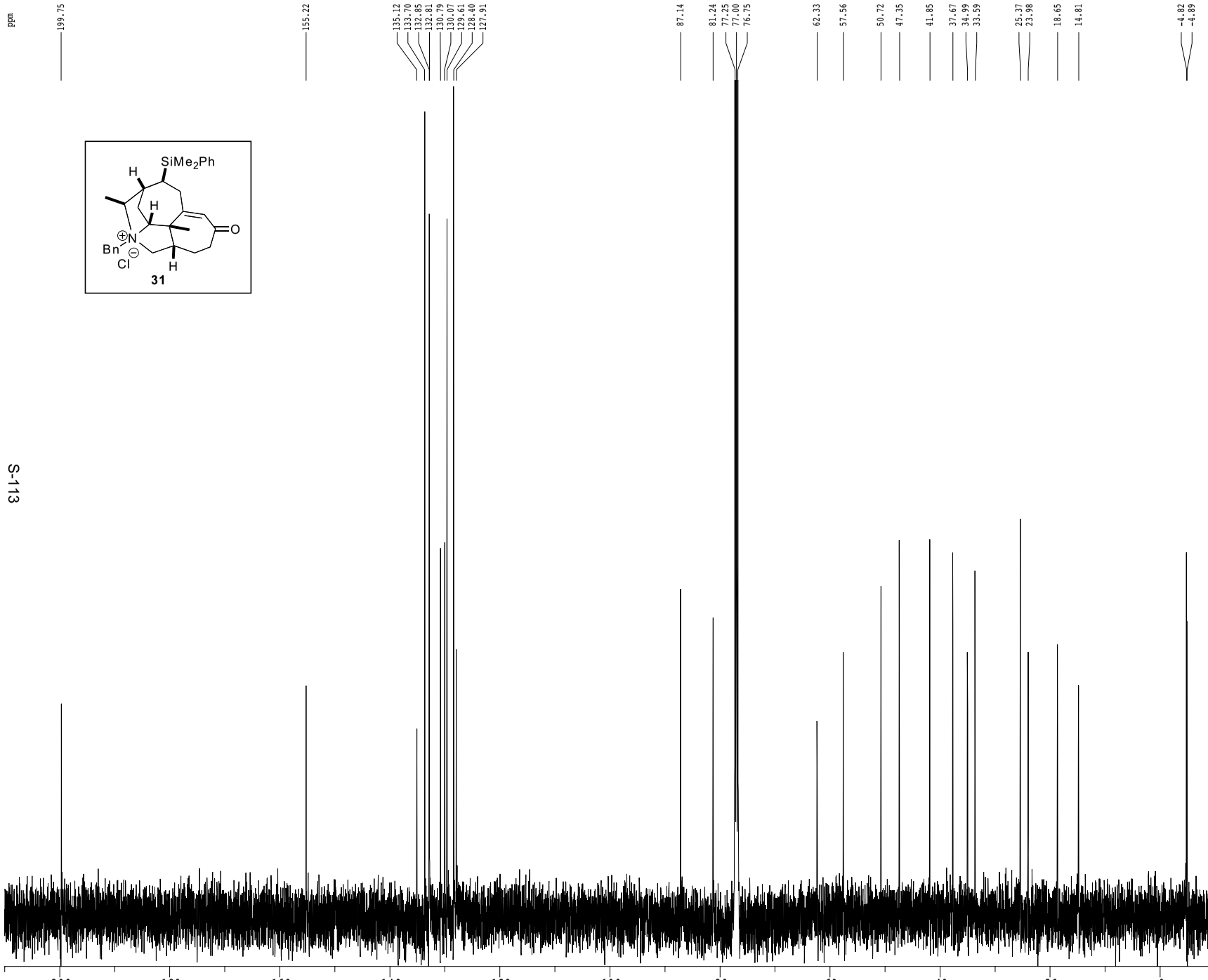
1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 8.000 ppm
F1                4001.76 Hz
F2P                 0.000 ppm
F2                  0.00 Hz
PPMCM            0.35088 ppm/cm
HZCM           175.51581 Hz/cm
```

13C spectrum with 1H decoupling




1H spectrum
Current Data Parameters
USER mannin
NAME jzm-1-170 fr 4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090809
Time 15.50
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 51
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200261 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P -1.000 ppm
F2 -500.22 Hz
PPMCM 0.48246 ppm/cm
HZCM 241.33423 Hz/cm
SiMe2Ph
Bn
Cl
31
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER mannin
NAME jrm-1-170 fr 4
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090809
Time 16.31
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 2429
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 29.70 usec

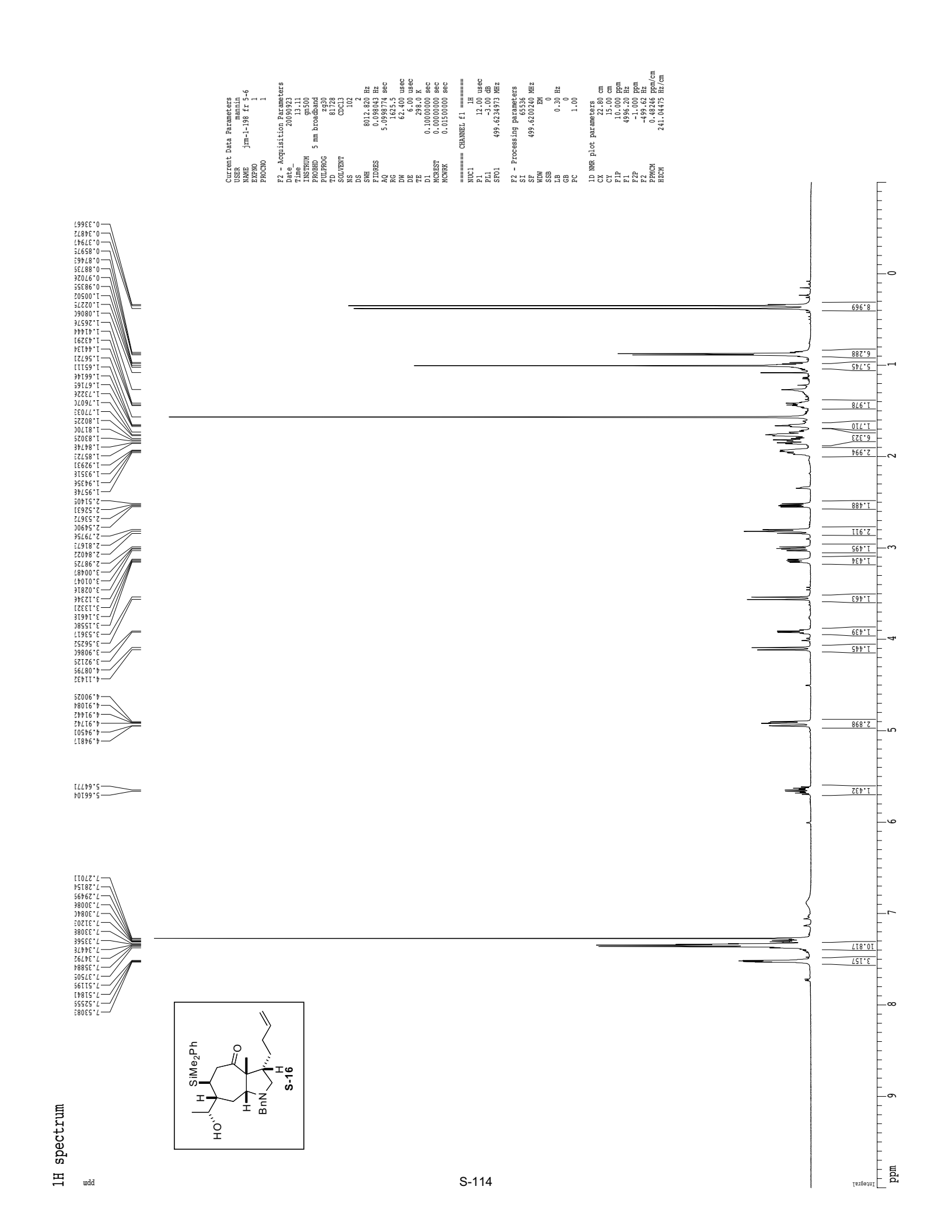
======== CHANNEL f1 ========
NUC1 13C
P1 14.85 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.60 dB
SP2 3.60 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

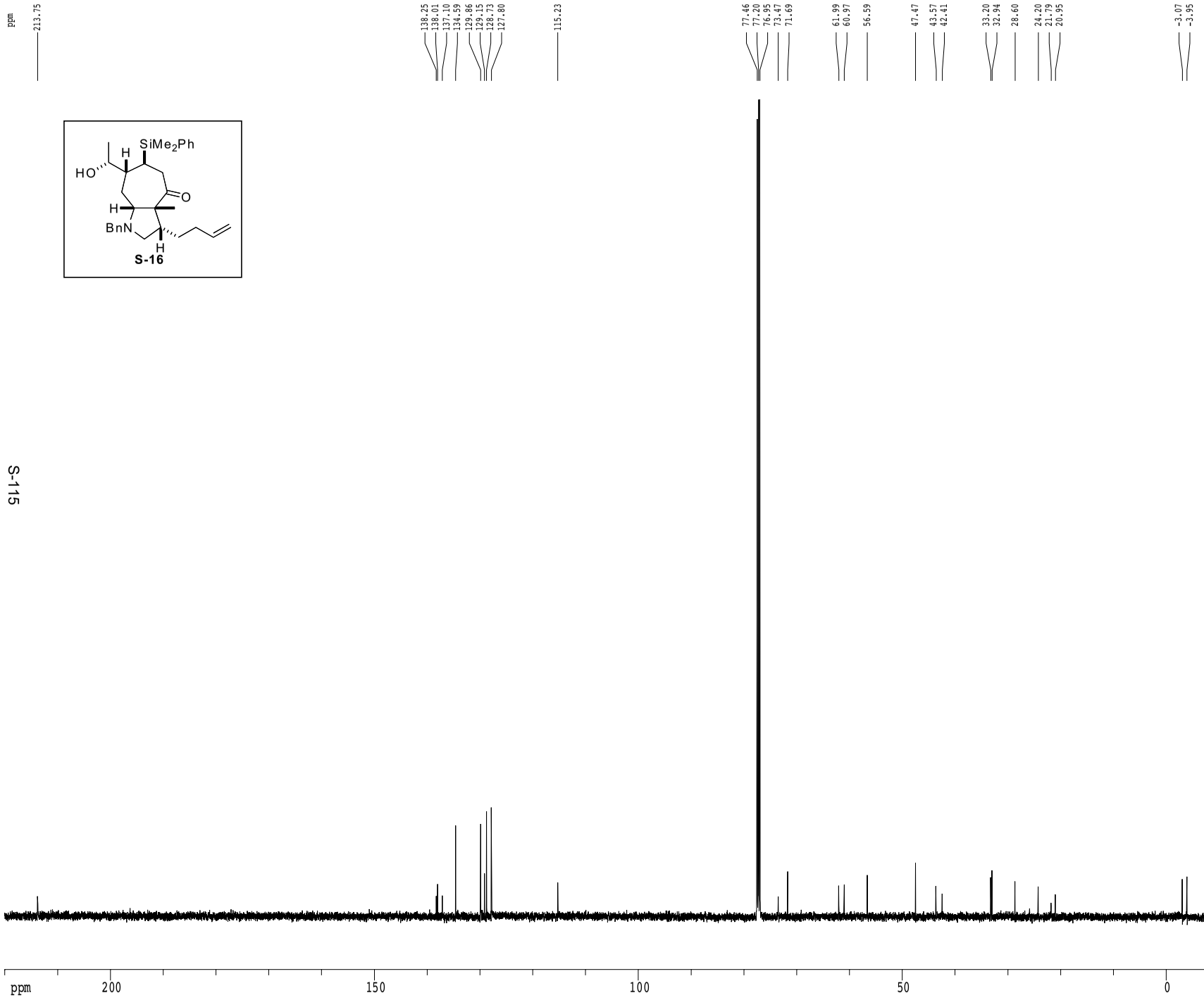
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804277 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 210.000 ppm
F1 26413.89 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.64912 ppm/cm
HZCM 1213.67078 Hz/cm


1H spectrum
Current Data Parameters
USER manlin
NAME jcm-1-198 ff 5-6
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090923
Time 13.11
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 102
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 1625.5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -3.00 dB
SFO1 499.6234973 MHz
F2 - Processing parameters
SI 65536
SF 499.6200240 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 10.000 ppm
F1 4996.20 Hz
F2P -1.000 ppm
F2 -499.62 Hz
PPMCM 0.48246 ppm/cm
HZCM 241.04475 Hz/cm
SiMe2Ph
HO
BnN
S-16
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER mannin
NAME jrm-1-198 fr 5-6
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090923
Time 13.26
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 816
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 4597.6
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 31.00 usec

======== CHANNEL f1 ========
NUC1 13C
P1 15.50 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.20 dB
SP2 3.20 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

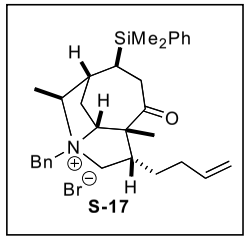
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804021 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 220.000 ppm
F1 27671.69 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 10.08772 ppm/cm
HZCM 1268.83740 Hz/cm

1H spectrum



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```
Current Data Parameters
USER                mannin
NAME              jrm-1-200
EXPNO                     1
PROCNO                    1

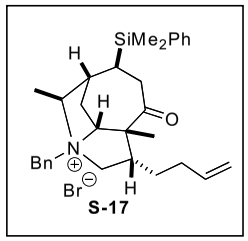
F2 - Acquisition Parameters
Date_              20090924
Time                   7.22
INSTRUM             cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    81728
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8012.820 Hz
FIDRES                0.098043 Hz
AQ                 5.0998774 sec
RG                        6.3
DW                   62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1                 0.10000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.50 usec
PL1                    1.60 dB
SFO1            500.2235015 MHz

F2 - Processing parameters
SI                     65536
SF              500.2200263 MHz
WDW                       EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00

1D NMR plot parameters
CX                    22.80 cm
CY                    15.00 cm
F1P                  10.000 ppm
F1                 5002.20 Hz
F2P                  -1.000 ppm
F2                 -500.22 Hz
PPMCM                 0.48246 ppm/cm
HZCM               241.33423 Hz/cm
```

13C spectrum with 1H decoupling



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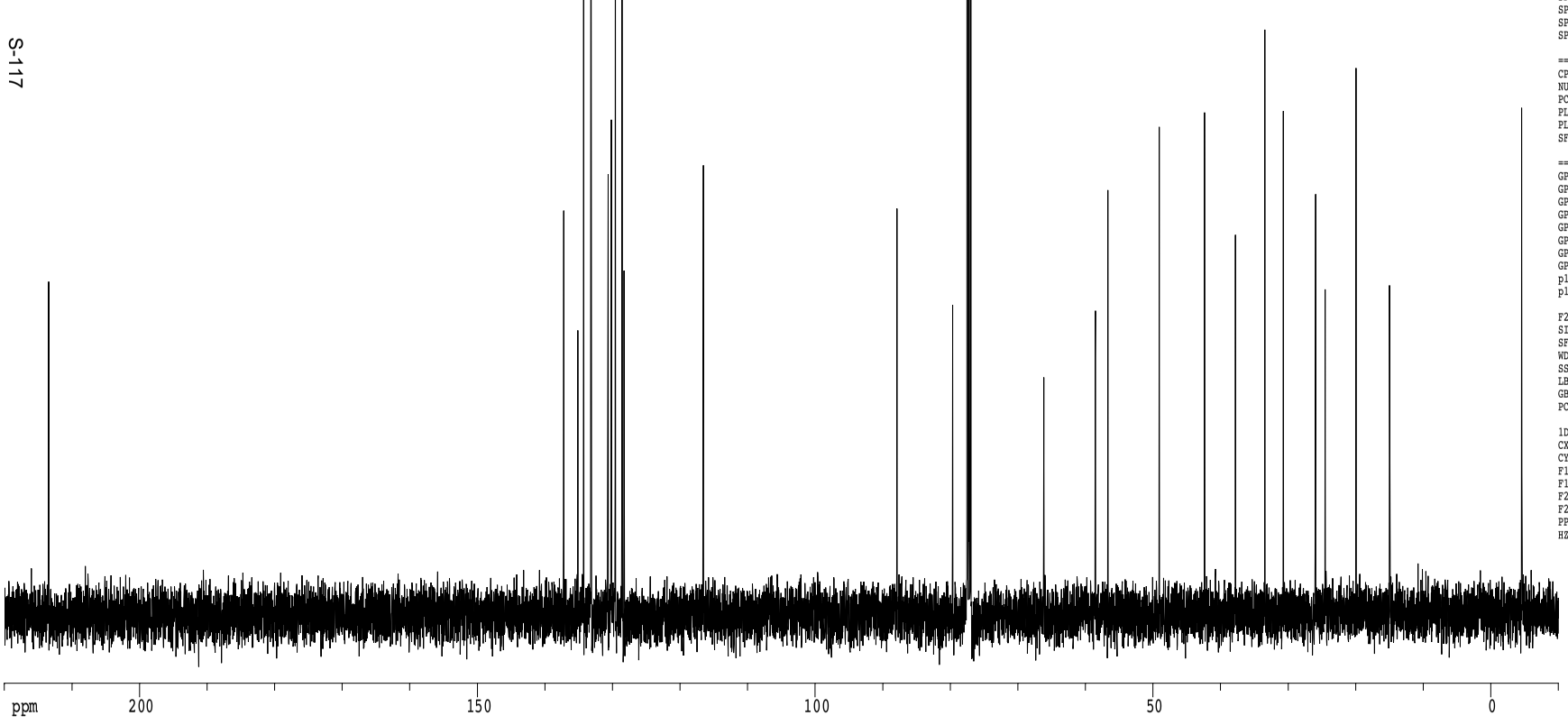
ppm 213.37 | 137.20 135.08 134.26 133.15 130.65 130.14 129.55 128.54 128.26 | 116.51 | 87.85 | 79.62 77.45 77.20 76.94 | 66.12 | 58.50 56.67 | 49.04 | 42.36 | 37.81 | 33.46 | 30.68 | 25.93 24.50 | 19.94 | 14.95 | -4.56 -4.61




```
Current Data Parameters
USER              mannin
NAME          jrm-1-200
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20090924
Time               7.27
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  329
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW              16.500 usec
DE               6.00 usec
TE              298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2              31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1               15.50 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1        125.7942548 MHz
SP1              3.20 dB
SP2              3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              1.60 dB
PL12            24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                  65536
SF          125.7804044 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               220.000 ppm
F1              27671.69 Hz
F2P               -10.000 ppm
F2              -1257.80 Hz
PPMCM            10.08772 ppm/cm
HZCM          1268.83740 Hz/cm
```