Antimalarial Properties of Simplified Kalihinol Analogues

Mary Elisabeth Daub,[a] Jacques Prudhomme,[b] Choukri Ben Mamoun,[c] Karine Le Roch,[b] and Christopher D. Vanderwal[a]

[a]*Department of Chemistry, University of California, Irvine, 1102 Natural Sciences II, Irvine, California 92697, United States*

[b]*Department of Cell Biology & Neuroscience, University of California, Riverside, 900 University Avenue, Riverside, California 92521, United States*

[c]*Department of Internal Medicine, Section of Infectious Diseases, Yale School of Medicine, New Haven, Connecticut 06520, United States*

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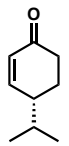
II. General Experimental Methods

All reactions were performed under an inert atmosphere of argon using oven-dried or flame-dried glassware and Teflon® coated stir bars. Solvents were dried by passage through columns of activated alumina, and *tert*-butyl alcohol was distilled from calcium hydride prior to use. Trimethylsilyl cyanide and methyl vinyl ketone were purified by distillation prior to use. Commercial reagents were used as received unless noted otherwise, and all other reagents were prepared using known literature procedures. Reactions were monitored by thin-layer chromatography (TLC) performed on 250 μm silica gel 60 plates with 254 nm fluorescent indicator from EMD Chemicals using UV light as a visualizing agent and $KMnO_4/H_2SO_4$, *p*-anisaldehyde or ceric ammonium molybdate and heat as developing agents. Flash chromatography was performed on EMD Chemicals (40-63 μm) silica gel. NMR spectra were recorded on a Bruker 500 MHz or a Bruker 600 MHz spectrometer. Chemical shifts are reported in parts per million using residual non-deuterated solvent as an internal standard ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant(s) in Hz, integration. NMR spectra were obtained at 298 K unless otherwise noted. FT-IR spectra were recorded on a Varian 640-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-1010 polarimeter operating on the sodium D-line (589 nm) using a 50 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent). Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC using a Chiralpak AD-H column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries Ltd. with visualization at 254 nm. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier spectrometer using ESI-TOF

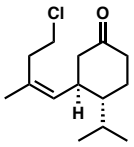
(electrospray ionization-time of flight) or CI-TOF (chemical ionization-time of flight). Melting points (mp) are uncorrected and were measured on a Mel-Temp II melting point apparatus.

III. Experimental Procedures and Characterization Data



9: (±)-cryptone

(±)-Cryptone (9). The title compound was prepared according to the literature procedure using a two-step Robinson annulation sequence.[1] The spectral data for this compound are consistent with those reported in the literature.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.89 (dt, J = 10.5, 2.0 Hz, 1H), 6.00 (dd, J = 10.5, 2.5 Hz, 1H), 2.50 (dt, J = 16.5, 4.0 Hz, 1H), 2.38 – 2.32 (m, 1H), 2.32 – 2.25 (m, 1H), 2.04 – 1.96 (m, 1H), 1.86 – 1.71 (m, 1H), 0.96 (t, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2, 154.5, 129.8, 42.6, 37.5, 31.6, 25.4, 19.8, 19.6.

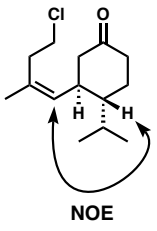


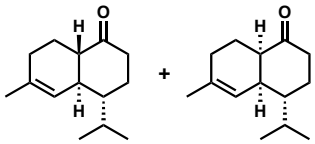
(±)-10

Ketone 10. To a solution of (*Z*)-4-chloro-1-iodo-2-methylbut-1-ene[3] (0.346 g, 1.50 mmol) in Et_2O (6 mL, previously sparged with argon gas for 20 min) at –78 ˚C was added *tert*-butyllithium (2.1 mL, 1.45 M in pentane, 3.01 mmol) dropwise *via* syringe. After 20 min, freshly prepared $MgBr_2$•OEt_2 (2.2 mL, ~1 M suspension in Et_2O, 2.15 mmol) was added dropwise *via* syringe. After 20 min, CuBr•DMS (0.155 g, 0.752 mmol) was added in one portion. TMEDA

[1] Chen, K.; Ishihara, Y.; Galán, M. M.; Baran, P. S. *Tetrahedron* **2010**, *66*, 4738–4744.
[2] Hawley, R. C.; Schreiber, S. L. *Synth. Commun.* **1990**, *20*, 1159–1165.
[3] (*Z*)-4-chloro-1-iodo-2-methylbut-1-ene was prepared according to the previously reported procedure: Daub, M. E.; Prudhomme, J.; Le Roch, K.; Vanderwal, C. D. *J. Am. Chem. Soc.* **2015**, *137*, 4912–4915.

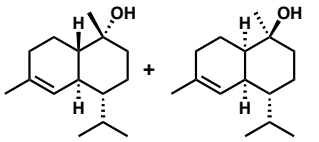
(0.11 mL, 0.752 mmol) was added dropwise *via* syringe immediately afterwards. After 30 min at –78 ˚C, TMSCl (0.11 mL, 0.859 mmol) was added dropwise *via* syringe followed by a solution of (±)-cryptone (**9**) (98.9 mg, 0.716 mmol) in Et_2O (0.5 mL). The transfer was completed with an additional portion of Et_2O (0.5 mL). After allowing the reaction mixture to stir for 2 h at –78 ˚C, the reaction was quenched with 9:1 saturated NH_4Cl solution/NH_4OH (15 mL). After warming to room temperature, the reaction mixture was extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with 1 M HCl (15 mL), saturated $NaHCO_3$ solution (15 mL), and brine (15 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 5% EtOAc/hexanes) to afford the title compound (138.2 mg, 80%) as a white solid (mp 55–57 ˚C). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.10 (d, J = 9.6 Hz, 1H), 3.54 (t, J = 7.2 Hz, 2H), 2.61 – 2.50 (m, 2H), 2.50 – 2.43 (m, 2H), 2.42 – 2.31 (m, 2H), 2.14 (ap t, J = 13.2 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.73 (s, 3H), 1.52 – 1.40 (m, 2H), 0.96 (d, J = 7.0 Hz, 3H), 0.73 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.4, 131.8, 131.6, 47.9, 47.1, 42.4, 41.2, 40.6, 35.2, 27.9, 24.5, 22.9, 21.9, 16.1; IR (thin film) ν 2957, 2870, 1714, 1455, 1368, 1259, 1202, 1066 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{14}H_{23}ClONa$ $(M + Na)^+$ 265.1335, found 265.1329. ^{1}H-NOESY-2D (500 MHz, $CDCl_3$) spectra were obtained for ketone **10** and selected NOE interactions are shown.





Decalones 11 and 12. To a solution of alkyl chloride **10** (0.292 g, 1.20 mmol) in *tert*-butyl alcohol (6.0 mL) at 30 ˚C was added potassium *tert*-butoxide (1.10 mL, 1.6 M in THF, 1.81 mmol) dropwise *via* syringe. After stirring for 6 h at 30 ˚C, the reaction was quenched with saturated NH_4Cl solution (6 mL). The aqueous layer was extracted with pentane (3 x 15 mL), and the combined organic extracts were washed with water (3 x 10 mL) and with brine (10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 5% Et_2O/pentane) to afford a 1.1:1 mixture of *trans*- and *cis*-decalones (176.4 mg, 71%) as a colorless oil, which was characterized as a mixture. The spectral data for these compounds are consistent with those reported in the literature.[4,5] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.55 (s, 1H), 5.32 (s, 1H), 2.52 (br s, 1H), 2.49 – 2.11 (m, 7H), 2.11 – 1.95 (m, 8H), 1.95 – 1.85 (m, 1H), 1.85 – 1.78 (m, 1H), 1.68 (s, 3H), 1.64 (s, 3H), 1.62 – 1.38 (m, 6H), 1.00 (d, J = 5.0 Hz, 3H), 0.99 (d, J = 5.0 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H), 0.77 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.8, 213.1, 136.0, 135.1, 124.4, 121.6, 51.2, 46.9, 46.1, 45.2, 44.4, 41.2, 39.0, 38.4, 29.8, 28.6, 26.9, 26.5, 25.5, 24.0, 23.9, 23.8, 23.1, 22.0, 21.70, 21.65, 17.9, 15.1.

[4] Nishikawa, K.; Nakahara, H.; Shirokura, Y.; Nogata, Y.; Yoshimura, E.; Umezawa, T.; Okino, T.; Matsuda, F. *J. Org. Chem.* **2011**, *76*, 6558–6573.
[5] Taber, D. F.; Gunn, B. P. *J. Am. Chem. Soc.* **1979**, *101*, 3992–3993.



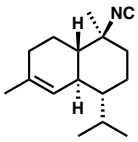
13: *(±)-cedrelanol* **14**: *(±)-torreyol*

(±)-Cedrelanol (13) and (±)-torreyol (14). Methylmagnesium bromide (1.9 mL, 2.25 M in Et_2O, 4.27 mmol) was added dropwise to a solution of a mixture of decalones **11** and **12** (0.176 g, 0.855 mmol) in THF (8.6 mL) cooled to 0 ˚C. The reaction mixture was allowed to warm to room temperature for 30 min, and the reaction was quenched with saturated aqueous NH_4Cl solution (10 mL) at 0 ˚C. The aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10% EtOAc/hexanes), yielding (±)-cedrelanol (**13**) (0.106 g, 55%) as a colorless oil and (±)-torreyol (**14**) (0.084 g, 44%) as a white solid (mp 109–110 ˚C, lit.[5] mp 108.5–109 ˚C). The spectral data for these compounds are consistent with those reported in the literature.[5,6,7]

(±)-Cedrelanol (**13**): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.55 (br s, 1H), 2.22 – 2.15 (m, 1H), 2.04 – 1.89 (m, 4H), 1.74 (dt, *J* = 13.1, 2.9 Hz, 1H), 1.67 (s, 3H), 1.50 – 1.45 (m, 1H), 1.45 – 1.29 (m, 3H), 1.22 (s, 3H), 1.09 (t, *J* = 10.3 Hz, 1H), 1.01 (tt, *J* = 11.4, 3.2 Hz, 1H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5, 122.8, 70.8, 48.1, 46.8, 40.4, 37.9, 31.0, 28.6, 26.3, 23.9, 22.7, 21.5, 19.9, 15.3.

(±)-Torreyol (**14**): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.52, (d, *J* = 4.3 Hz, 1 H), 2.06 – 1.92 (m, 4H), 1.92 – 1.86 (m, 1H), 1.66 (s, 3H), 1.63 – 1.47 (m, 6H), 1.35 – 1.24 (m, 2H), 1.30 (s, 3H), 1.15 – 1.05 (m, 1H) 0.89 (d, *J* = 6.9 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5, 124.7, 72.7, 45.6, 44.2, 36.9, 35.4, 31.3, 28.1, 26.5, 23.8, 21.8, 21.7, 18.6, 15.4.

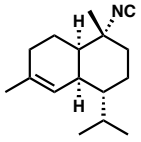
[6] Pronin, S. V; Reiher, C. A.; Shenvi, R. A. *Nature* **2013**, *501*, 195–199.
[7] Borg-Karlson, A.-K.; Norin, T.; Talvitie, A. *Tetrahedron* **1981**, *37*, 425–430.



15: *(±)-10-isocyano-4-cadinene*

(±)-10-Isocyano-4-cadinene (15). The title compound was prepared according to the literature procedure.[6] A mixture of (±)-cedrelanol (**13**) (28.3 mg, 0.127 mmol) and pyridine (50 μL, 0.508 mmol) in CH_2Cl_2 (1.3 mL) at 0 ˚C was treated with trifluoroacetic anhydride (40 μL, 0.255 mmol). After 15 minutes, the reaction was quenched with 1 M HCl (2 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were washed with water (5 mL), washed with saturated $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. A portion of the crude trifluoroacetate (15.9 mg, 0.0499 mmol) was dissolved in TMSCN (50 μL), and a solution of scandium(III) trifluoromethanesulfonate (~0.7 mg, 0.0015 mmol) in TMSCN (50 μL) was added. After 4 h at room temperature, the reaction was quenched with TMEDA (20 μL) and the volatiles were removed under reduced pressure. The crude residue was dissolved in hexanes (5 mL), washed with saturated aqueous $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 30% CH_2Cl_2/hexanes) to afford the title compound (3.9 mg, 34%) as a thin film along with a mixture of diastereomers (1.1 mg, 9%). The spectral data for this compound are consistent with those reported in the literature.[6] ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.46, (s, 1 H), 2.22 – 2.13 (m, 1H), 2.12 – 1.94 (m, 4H), 1.82 (td, *J* = 13.3, 4.0 Hz, 1H), 1.73 (t, *J* = 10.8 Hz, 1H), 1.68 (s, 3H), 1.59 (dq, *J* = 13.3, 3.3 Hz, 1H), 1.50 (t, *J* = 11.0 Hz, 1H), 1.34 (dd, *J* = 12.3, 5.8 Hz, 1H), 1.30 (s, 3H), 1.12 (qd, *J* = 13.0, 3.5 Hz, 1H), 1.06 (tt, *J* = 12.0, 3.0 Hz, 1H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

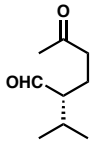
152.1 (br t, J = 4.3 Hz), 135.5, 121.4, 60.9 (br t, J = 5.1 Hz), 48.1, 46.3, 40.7, 38.0, 30.8, 26.0, 23.9, 23.8, 21.5, 20.3, 20.1, 15.2.



(±)-**16**

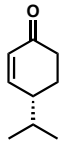
Isocyanide 16. The following procedure was adopted from Pronin *et al*.[6] A mixture of (±)-torreyol (**14**) (30.8 mg, 0.139 mmol) and pyridine (50 μL, 0.556 mmol) in CH_2Cl_2 (1.4 mL) at 0 ˚C was treated with trifluoroacetic anhydride (40 μL, 0.278 mmol). After 15 minutes, the reaction was quenched with 1 M HCl (2 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were washed with water (5 mL), washed with saturated $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude trifluoroacetate was dissolved in TMSCN (0.14 mL), and a solution of scandium(III) trifluoromethanesulfonate (3.4 mg, 0.0695 mmol) in TMSCN (0.14 mL) was added. After 3 h at room temperature, the reaction was quenched with TMEDA (20 μL) and the volatiles were removed under reduced pressure. The crude residue was dissolved in hexanes (5 mL), washed with saturated aqueous $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 30% CH_2Cl_2/hexanes) to afford the title compound (10.4 mg, 33%) as a thin film. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.56 (d, J = 1.0 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.07 – 1.93 (m, 3H), 1.83 (d, J = 13.0 Hz, 1H), 1.74 (d, J = 11.0 Hz, 1H), 1.65 (s, 3H), 1.61 – 1.54 (m, 1H), 1.54 – 1.37 (m, 4H), 1.42 (s, 3H), 1.31 – 1.21 (m, 1H), 0.90 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3 (t, J = 4.5 Hz), 133.6, 124.4, 62.2 (t, J = 4.4 Hz), 44.6, 43.6, 35.0, 33.6, 31.0, 27.9, 26.7, 23.6, 21.7, 20.0, 19.4, 15.4; IR (thin film) ν 2956, 2893, 2872, 2832, 2126,

1452, 1384, 1154, 884 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{16}H_{25}NNa$ $(M + Na)^+$ 254.1885, found 254.1880.



S1

(*R*)-2-Isopropyl-5-oxohexanal (S1). The title compound was prepared according to the literature procedure.[1] The spectral data for this compound are consistent with those reported in the literature.[8,9] $[\alpha]_D^{24}$ = –33.7 (c = 1.0, $CHCl_3$), lit.[9] $[\alpha]_D$ = +40 (c = 1.72, $CDCl_3$) for the (*S*)-form; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (d, *J* = 3.0 Hz, 1H), 2.50 (ddd, *J* = 17.5, 8.8, 5.8 Hz, 1H), 2.36 (ddd, *J* = 17.8, 8.0, 6.8 Hz, 1H), 2.12 (s, 3H), 2.09 – 1.98 (m, 2H), 1.88 – 1.71 (m, 2H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 205.5, 57.7, 41.4, 30.2, 28.5, 20.4, 19.6, 19.5.

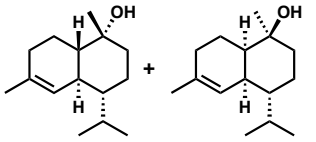


9: *(–)-cryptone*

(–)-Cryptone (9). To a solution of (*R*)-2-isopropyl-5-oxohexanal (**S1**) (0.731 mg, 4.68 mmol) in 2-propanol (15.6 mL) was added a solution of lithium isopropoxide (0.35 mL, 0.66 M in THF, 0.234 mmol). After 1 h, the reaction was quenched with saturated NH_4Cl solution (16 mL). The aqueous phase was extracted with ether (3 x 40 mL). The combined organic extracts were washed with water (2 x 20 mL), brine (1 x 20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10% Et_2O/pentane) to afford (–)-cryptone (0.435 g, 66%) as a colorless oil. The spectral data for this compound are

[8] Hagiwara, H.; Komatsubara, N.; Ono, H.; Okabe, T.; Hoshi, T.; Suzuki, T.; Ando, M.; Kato, M. *J. Chem. Soc. Perkin Trans. 1* **2001**, 316–322.
[9] Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691–6707.

consistent with those reported in the literature.[2] $[\alpha]_D^{24}$ = –80.8 (c = 1.04, $CHCl_3$), lit.[10] $[\alpha]_D^{21}$ = –90 (c = 1.38, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (dt, *J* = 10.0, 2.0 Hz, 1H), 6.01 (dd, *J* = 10.0, 2.5 Hz, 1H), 2.51 (dt, *J* = 17.0, 4.0 Hz, 1H), 2.38 – 2.32 (m, 1H), 2.32 – 2.25 (m, 1H), 2.04 – 1.96 (m, 1H), 1.86 – 1.71 (m, 1H), 0.97 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2, 154.5, 129.8, 42.6, 37.5, 31.6, 25.4, 19.8, 19.6. The enantiomeric excess of (–)-cryptone was determined to be 88% using chiral HPLC (Chiralpak AD-H column, 2% *i*PrOH in hexanes, flow rate of 0.5 mL/min).



13: *(+)-cedrelanol* **14**: *(+)-torreyol*

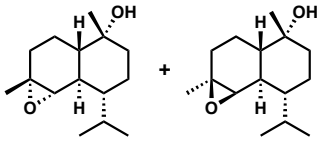
(+)-Cedrelanol (13) and (+)-torreyol (14). The title compounds were prepared from (–)-cryptone according to the three-step sequence described above. The spectral data for these compounds are consistent with those reported in the literature.[5–7]

(+)-Cedrelanol (**13**): $[\alpha]_D^{24}$ = +2.2 (c = 1.0, $CHCl_3$), lit.[7] $[\alpha]_D$ = +3.4 (c = 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.55 (br s, 1H), 2.22 – 2.15 (m, 1H), 2.04 – 1.89 (m, 4H), 1.74 (dt, *J* = 13.1, 2.9 Hz, 1H), 1.67 (s, 3H), 1.50 – 1.45 (m, 1H), 1.45 – 1.29 (m, 3H), 1.22 (s, 3H), 1.09 (t, *J* = 10.3 Hz, 1H), 1.01 (tt, *J* = 11.4, 3.2 Hz, 1H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5, 122.8, 70.8, 48.1, 46.8, 40.4, 37.9, 31.0, 28.6, 26.3, 23.9, 22.7, 21.5, 19.9, 15.3.

(+)-Torreyol (**14**): mp 109–110 ˚C, lit.[5] mp 108.5–109 ˚C; $[\alpha]_D^{24}$ = +95.4 (c = 1.0, $CHCl_3$), lit.[7] $[\alpha]_D$ = –100.4 (c = 1.2, $CHCl_3$) for (–)-torreyol; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.52, (d, *J* = 4.3 Hz, 1 H), 2.06 – 1.92 (m, 4H), 1.92 – 1.86 (m, 1H), 1.66 (s, 3H), 1.63 – 1.47 (m, 6H), 1.35 – 1.24

[10] Gillespie, D. T. C.; Macbeth, A. K.; Mills, J. A. *J. Chem. Soc.* **1948**, 996–999.

(m, 2H), 1.30 (s, 3H), 1.15 – 1.05 (m, 1H) 0.89 (d, J = 6.9 Hz, 3H), 0.77 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5, 124.7, 72.7, 45.6, 44.2, 36.9, 35.4, 31.3, 28.1, 26.5, 23.8, 21.8, 21.7, 18.6, 15.4.

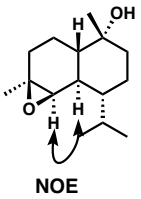


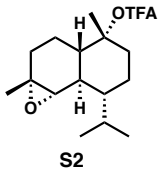
17 18

Epoxides 17 and 18. To a solution of (+)-cedrelanol (**13**) (0.188 g, 0.845 mmol) in acetone (42 mL) was added saturated aqueous $NaHCO_3$ (28 mL). The resulting mixture was cooled to 0 ˚C and a solution of Oxone® (0.571 g, 0.930 mmol) in H_2O (2 mL) was added dropwise over 5 minutes. The reaction mixture was stirred vigorously for 30 min at 0 ˚C, diluted with H_2O (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic extracts were diluted with hexanes until cloudy, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10 → 30% EtOAc/hexanes) to afford β-epoxide **18** (77.1 mg, 38%) as a white solid (mp 90–93 ˚C) and α-epoxide **17** (120.4 mg, 60%) as a colorless oil. The hydroxylic peaks in the ^{1}H NMR spectra for epoxides **17** and **18** could not be unambiguously identified.

Epoxide **17**: $[\alpha]_D^{24}$ = +22.6 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.94 (s, 1H), 2.32 – 2.20 (m, 1H), 2.09 (dd, J = 14.3, 3.8 Hz, 1H), 1.73 – 1.46 (m, 5H), 1.46 – 1.32 (m, 2H), 1.30 (s, 3H), 1.27 – 1.11 (m, 2H), 1.17 (s, 3H), 0.96 (d, J = 7 Hz, 3H), 0.88 (d, J = 7 Hz, 3H), 0.90 – 0.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.5, 61.5, 58.2, 47.5, 44.7, 39.9, 38.7, 30.8, 28.0, 26.4, 23.8, 21.6, 20.1, 19.7, 15.7; IR (thin film) ν 3459 (br), 2957, 2937, 2871, 2849, 1463, 1453, 1368, 1135, 1003, 876 cm^{-1}; HRMS (ESI) m / z calcd for $C_{15}H_{26}O_2Na$ $(M + Na)^+$ 261.1830, found 261.1838. ^{1}H-NOESY-2D (500 MHz, $CDCl_3$) spectra were obtained for epoxide **17**.

Epoxide **18**: $[\alpha]_D^{24}$ = +10.7 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.08 (s, 1H), 2.29 – 2.19 (m, 1H), 1.91 – 1.80 (m, 2H), 1.80 – 1.72 (m, 1H), 1.72 – 1.66 (m, 1H), 1.64 – 1.57 (m, 1H), 1.54 – 1.49 (m, 1H), 1.44 – 1.33 (m, 3H), 1.31 (s, 3H), 1.19 – 1.08 (m, 2H), 1.16 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.9, 61.9, 58.7, 44.3, 42.4, 40.3, 38.4, 29.2, 29.1, 26.6, 25.0, 21.8, 21.4, 20.0, 15.6; IR (thin film) ν 3463 (br), 2956, 2934, 2872, 1464, 1375, 1209, 1142, 1022, 907, 845 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{15}H_{26}O_2Na$ $(M + Na)^+$ 261.1830, found 261.1838. ^{1}H-NOESY-2D (500 MHz, $CDCl_3$) spectra were obtained for epoxide **18** and selected NOE interactions are shown.

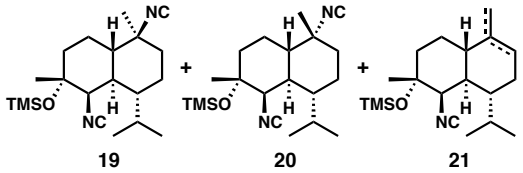




S2

Trifluoroacetate S2. A mixture of epoxide **17** (0.120 g, 0.505 mmol) and pyridine (0.16 mL, 2.02 mmol) in CH_2Cl_2 (5.1 mL) at 0 ˚C was treated with trifluoroacetic anhydride (0.14 mL, 1.01 mmol). After 30 minutes, the reaction was quenched with 1 M HCl (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were washed with water (10 mL), washed with saturated $NaHCO_3$ solution (10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 50% CH_2Cl_2/hexanes) to afford the title compound (0.114 g, 67%) as a colorless oil. $[\alpha]_D^{24}$ = –7.0 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.91 (s, 1H), 2.75 (dt, *J* = 15.0, 3.0 Hz, 1H), 2.29 – 2.22 (m, 1H), 2.12 (dd, *J* = 13.8, 4.8 Hz, 1H), 1.76 (t, *J* = 11.7 Hz, 1H), 1.67 – 1.54 (m, 3H), 1.57 (s, 3H), 1.40 – 1.24 (m, 3H), 1.31 (s, 3H), 1.14 (qd, *J* = 13.8, 3.3 Hz, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.92 (t, *J* = 11.7 Hz, 1H), 0.85 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2 (q,

J = 41.0 Hz), 114.6 (q, J = 285.4 Hz), 88.3, 61.4, 57.9, 48.6, 43.9, 38.4, 34.3, 30.7, 26.4, 23.8, 23.7, 21.5, 19.8, 19.6, 15.2; IR (thin film) ν 2960, 2873, 1778, 1453, 1373, 1218, 1155 cm^{-1}; HRMS (ESI) m / z calcd for $C_{17}H_{25}F_3O_3Na$ $(M + Na)^+$ 357.1653, found 357.1647.



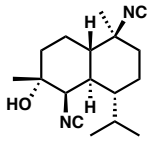
Isocyanides 19, 20, and 21. The following procedure was adopted from Pronin *et al*.[6] A solution of trifluoroacetate **S2** (62.3 mg, 0.186 mmol) in TMSCN (0.19 mL) was cooled to 0 ˚C. A solution of scandium(III) trifluoromethanesulfonate (9.2 mg, 0.0186 mmol) in TMSCN (0.37 mL) was added, and the reaction mixture was allowed to warm to room temperature after 1 h. After 24 h at room temperature, the reaction was quenched with TMEDA (30 μL) and the volatiles were removed under reduced pressure. The crude residue was dissolved in hexanes (10 mL), washed with saturated aqueous $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 2% EtOAc/hexanes) to afford a 6.3:1 mixture of elimination products **21** (18.9 mg, 32%) as a thin film and a 1.9:1 mixture of isocyanides **19** and **20** (8.0 mg, 12%) as a thin film. Isocyanides **19** and **20** were separated by column chromatography (SiO_2, 80% CH_2Cl_2/hexanes). The 6.3:1 mixture of alkene isomers (**21**) was characterized as a mixture; only the resonances in the ^1H and ^{13}C NMR spectra for the major Δ^9-isomer are listed.

Diisocyanide **19**: $[\alpha]_D^{22}$ = +14.9 (c = 0.66, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.55 (s, 1H), 2.06 (dt, J = 13.0, 3.3 Hz, 1H), 1.94 – 1.60 (m, 8H), 1.54 – 1.40 (m, 2H), 1.45 (s, 3H), 1.30 (s, 3H), 1.11 (qd, J = 13.3, 3.5 Hz, 1H), 0.95 (d, J = 7.0 Hz, 3H), 0.72 (d, J = 7.0 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5 (br t, J = 4.9 Hz), 153.1 (br t, J = 4.4 Hz), 73.4, 61.6

(br t, J = 5.2 Hz), 60.3 (br t, J = 5.3 Hz), 42.6, 42.1, 40.4, 35.9, 32.6, 27.5, 25.5, 21.4, 21.2, 20.6, 19.2, 14.9, 2.3; IR (thin film) ν 2956, 2874, 2131, 1456, 1384, 1252, 1184, 1038, 842 cm^{-1}; HRMS (ESI) m / z calcd for $C_{20}H_{34}N_2OSiNa$ $(M + Na)^+$ 369.2338, found 369.2343.

Diisocyanide **20**: $[\alpha]_D^{24}$ = –7.7 (c = 0.34, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.59 (s, 1H), 2.10 – 2.01 (m, 1H), 1.97 (ap d, J = 13.5 Hz, 1H), 1.92 (quin of d, J = 6.8, 3.0 Hz, 1H) 1.75 – 1.65 (m, 5H), 1.54 – 1.34 (m, 2H), 1.44 (s, 3H), 1.41 (br s, 3H), 1.34 – 1.24 (m, 2H), 0.96 (d, J = 6.5 Hz, 3H), 0.79 (d, J = 6.5 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8 (br t), 155.3 (br t), 72.9, 61.6 (br t, J = 5.3 Hz), 61.5 (br t, J = 4.9 Hz), 42.3, 42.0, 39.1, 36.0, 32.3, 27.8, 27.6, 25.7, 21.3, 21.1, 19.1, 15.0, 2.4; IR (thin film) ν 2957, 2874, 2127, 1454, 1379, 1252, 1184, 1043, 869, 841 cm^{-1}; HRMS (ESI) m / z calcd for $C_{20}H_{34}N_2OSiNa$ $(M + Na)^+$ 369.2338, found 369.2332.

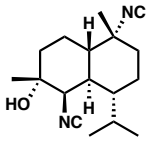
Isocyanide **21**: $[\alpha]_D^{23}$ = +25.3 (c = 0.90, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.42 (s, 1H), 3.56 (s, 1H), 2.10 – 1.50 (m, 9H) 1.64 (s, 3H), 1.45 (s, 3H), 1.28 – 1.16 (m, 1H), 0.94 (d, J = 6.9 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3 (br t, J = 4.8 Hz), 135.1, 121.8, 73.7, 61.7 (br t, J = 5.2 Hz), 38.9, 38.4, 37.6, 34.4, 27.7, 25.6, 25.3, 23.8, 21.2, 21.0, 14.6, 2.5; IR (thin film) ν 2959, 2894, 2872, 2133, 1455, 1379, 1251, 1052, 842 cm^{-1}; HRMS (ESI) m / z calcd for $C_{19}H_{33}NOSiNa$ $(M + Na)^+$ 342.2229, found 342.2215.



22

Diisocyanide 22. To a solution of TMS ether **19** (6.6 mg, 0.0190 mmol) in THF (0.2 mL) was added TBAF (40 μL, 1.0 M in THF, 0.0381 mmol). After 1 h, the reaction was quenched with water (1 mL). The aqueous layer was extracted with ether (3 x 2 mL). The combined organic

extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 20% EtOAc/hexanes) to afford diisocyanide **22** (3.5 mg, 67%) as a thin film. The spectral data for this compound are consistent with those reported in the literature.[11] $[\alpha]_D^{23}$ = +23.3 (c = 0.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.63 (s, 1H), 2.07 (dt, *J* = 13.0, 3.3 Hz, 1H), 1.95 – 1.60 (m, 8H), 1.58 – 1.43 (m, 2H), 1.45 (s, 3H), 1.33 (br t, *J* = 2.0 Hz, 3H), 1.26 (s, 1H), 1.13 (qd, *J* = 12.8, 3.3 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7 (br t, *J* = 4.5 Hz), 153.1 (br t, *J* = 4.6 Hz), 70.5, 60.9 (br t, *J* = 5.4 Hz), 60.3 (br t, *J* = 5.1 Hz), 42.8, 42.4, 40.4, 36.2, 32.8, 28.9, 25.5, 21.4, 21.2, 20.9, 19.2, 15.2; IR (thin film) ν 3414 (br), 2955, 2873, 2133, 1452, 1386, 1267, 1180, 1126, 1002, 760 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{17}H_{26}N_2ONa$ $(M + Na)^+$ 297.1943, found 297.1949.

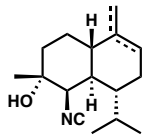


23

Diisocyanide 23. To a solution of TMS ether **20** (3.4 mg, 0.0098 mmol) in THF (0.2 mL) was added TBAF (20 μL, 1.0 M in THF, 0.0196 mmol). After 1 h, the reaction was quenched with water (1 mL). The aqueous layer was extracted with ether (3 x 2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 15% EtOAc/hexanes) to afford diisocyanide **23** (1.9 mg, 70%) as a thin film. $[\alpha]_D^{23}$ = –5.9 (c = 0.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.68 (s, 1H), 2.04 – 1.88 (m, 3H), 1.87 – 1.60 (m, 5H), 1.57 – 1.28 (m, 5H), 1.44 (s, 3H), 1.43 (br s, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.81 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1 (br t, *J* =

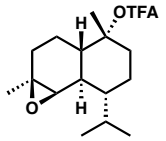
[11] White, R. D.; Wood, J. L. *Org. Lett.* **2001**, *3*, 1825–1827.

5.5 Hz), 155.4 (br t, J = 4.4 Hz), 70.1, 61.3 (br t, J = 4.4 Hz), 60.9 (br t, J = 5.2 Hz), 42.5, 42.1, 39.2, 36.4, 32.4, 28.6, 27.9, 25.7, 21.4, 21.0, 19.1, 15.2; IR (thin film) ν 3428 (br), 2957, 2874, 2133, 1455, 1377, 1276, 1181, 1001, 833 cm^{-1}; HRMS (ESI) m / z calcd for $C_{17}H_{26}N_2ONa$ $(M + Na)^+$ 297.1943, found 297.1934.



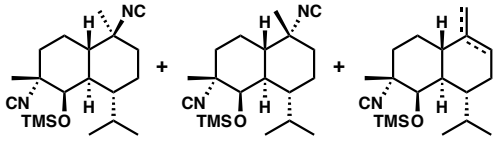
24

Isocyanide 24. To a solution of TMS ether **21** (9.0 mg, 0.0282 mmol) in THF (0.28 mL) was added TBAF (60 μL, 1.0 M in THF, 0.0563 mmol). After 1 h, the reaction was quenched with water (1 mL). The aqueous layer was extracted with ether (3 x 2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 2.5:47.5:50 EtOAc/CH_2Cl_2/hexanes) to afford a 7:1 mixture of isocyanides **24** (5.0 mg, 71%) as a thin film. The alkene isomers were characterized as a mixture; only the resonances in the ^1H and ^{13}C NMR spectra for the major Δ^9-isomer are listed. $[\alpha]_D^{24}$ = +64.4 (c = 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.43 (s, 1H), 3.63 (s, 1H), 2.15 – 1.78 (m, 8H), 1.71 – 1.51 (m, 2H), 1.65 (s, 3H), 1.45 (s, 3H), 1.24 (qd, J = 13.2, 4.0 Hz, 1H), 0.95 (d, J = 6.9 Hz, 3H), 0.77 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6 (br t, J = 4.4 Hz), 134.6, 122.0, 70.9, 60.8 (br t, J = 5.4 Hz), 39.2, 38.6, 37.6, 34.0, 28.5, 25.6, 25.1, 23.8, 21.2, 20.9, 14.9; IR (thin film) ν 3422 (br), 2960, 2934, 2892, 2871, 2153, 2134, 1450, 1378, 1207, 1012 cm^{-1}; HRMS (ESI) m / z calcd for $C_{16}H_{25}NONa$ $(M + Na)^+$ 270.1834, found 270.1833.



S3

Trifluoroacetate S3. A mixture of epoxide **18** (77.1 mg, 0.323 mmol) and pyridine (0.10 mL, 0.647 mmol) in CH_2Cl_2 (3.2 mL) at 0 ˚C was treated with trifluoroacetic anhydride (90 µL, 0.647 mmol). After 30 minutes, the reaction was quenched with 1 M HCl (3 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were washed with water (10 mL), washed with saturated $NaHCO_3$ solution (10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 40% CH_2Cl_2/hexanes) to afford the title compound (70.1 mg, 65%) as a white solid (mp 86–88 ˚C). $[\alpha]_D^{24}$ = –12.5 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.11 (s, 1H), 2.75 (dt, *J* = 15.0, 3.0 Hz, 1H), 2.25 (quin of d, *J* = 6.9, 3.3 Hz, 1H), 1.92 – 1.80 (m, 3H), 1.69 – 1.64 (m, 1H), 1.61 – 1.55 (m, 1H), 1.56 (s, 3H), 1.45 (tt, *J* = 11.7, 3.3 Hz, 1H), 1.38 (td, *J* = 14.4, 4.2 Hz, 1H), 1.33 (s, 3H), 1.30 – 1.20 (m, 2H), 1.13 (qd, *J* = 13.2, 3.6 Hz, 1H), 0.95 (d, *J* = 7.2 Hz, 3H), 0.83 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0 (q, *J* = 40.8 Hz), 114.5 (q, *J* = 285.6 Hz), 89.5, 61.5, 58.6, 43.8, 43.4, 37.9, 34.4, 28.8, 26.5, 24.9, 24.1, 21.5, 21.3, 19.6, 15.1; IR (thin film) ν 2957, 2868, 1777, 1452, 1372, 1207, 1162 cm^{-1}; HRMS (CI) *m* / z calcd for $C_{15}H_{25}O$ (M – $C_2O_2F_3$)$^+$ 221.1905, found 221.1907.



25 26 27

Isocyanides 25, 26, and 27. The following procedure was adopted from Pronin *et al*.[6] A solution of trifluoroacetate **S3** (18.5 mg, 0.0553 mmol) in TMSCN (50 µL) was cooled to 0 ˚C. A

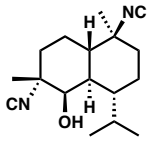
solution of scandium(III) trifluoromethanesulfonate (2.7 mg, 0.00553 mmol) in TMSCN (0.11 mL) was added, and the reaction mixture was allowed to warm to room temperature after 1 h. After 24 h at room temperature, the reaction was quenched with TMEDA (20 μL) and the volatiles were removed under reduced pressure. The crude residue was dissolved in hexanes (5 mL), washed with saturated aqueous $NaHCO_3$ solution (3 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 3% EtOAc/hexanes) to afford a 5.7:1 mixture of elimination products **27** (6.8 mg, 38%) as a thin film, diisocyanide **25** (4.3 mg, 22%) as thin film, and diisocyanide **26** (3.8 mg, 20%) as a thin film. The 5.7:1 mixture of alkene isomers (**27**) was characterized as a mixture; only the resonances in the ^1H and ^{13}C NMR spectra for the major Δ^9-isomer are listed.

Diisocyanide **25**: $[\alpha]_D^{23}$ = –3.3. (c = 0.73, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.83 (s, 1H), 2.04 (dt, *J* = 13.0, 3.3 Hz, 1H), 1.95 – 1.79 (m, 3H), 1.79 – 1.64 (m, 4H), 1.63 – 1.48 (m, 2H), 1.40 (br s, 3H), 1.33 (br s, 3H), 1.30 (dt, *J* = 11.5, 3.8 Hz, 1H), 1.11 (qd, *J* = 13.5, 3.3 Hz, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0 (br t, *J* = 4.6 Hz), 152.5 (br t, *J* = 4.6 Hz), 73.2, 61.5 (br t, *J* = 5.1 Hz), 60.5 (br t, *J* = 5.1 Hz), 41.4, 40.44, 40.37, 38.7, 31.4, 27.5, 25.7, 22.2, 21.3, 20.7, 18.9, 15.0, 1.1; IR (thin film) ν 2957, 2900, 2875, 2127, 1456, 1385, 1252, 1131, 1114, 883, 841 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{34}N_2OSiNa$ $(M + Na)^+$ 369.2338, found 369.2338.

Diisocyanide **26**: $[\alpha]_D^{24}$ = –13.4 (c = 0.51, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.89 (s, 1H), 1.99 – 1.88 (m, 3H), 1.80 – 1.66 (m, 4H), 1.63 – 1.46 (m, 3H), 1.40 (br s, 6H), 1.37 – 1.20 (m, 2H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6 (br t, *J* = 4.9 Hz), 155.6 (br t, *J* = 4.7), 73.3, 61.2 (br t, *J* = 4.6 Hz), 60.9 (br t, *J* = 5.3 Hz), 40.9, 40.7, 39.1, 38.9, 31.3, 28.1, 27.7, 25.9, 22.1, 21.2, 18.8, 15.1, 1.1; IR (thin film) ν

2957, 2930, 2898, 2875, 2132, 1451, 1370, 1252, 1134, 1058, 840 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{34}N_2OSiNa$ $(M + Na)^+$ 369.2338, found 369.2331.

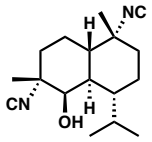
Isocyanide **27**: $[\alpha]_D^{23}$ = –20.5 (c = 1.27, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.40 (s, 1H), 3.89 (s, 1H), 2.17 (t, *J* = 11.3 Hz, 1H), 1.98 – 1.03 (complex, 9H), 1.64 (s, 3H), 1.40 (s, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2 (br t, *J* = 4.9 Hz), 135.4, 121.6, 73.3, 61.7 (br t, *J* = 5.1 Hz), 41.5, 37.4, 36.1, 33.1, 27.6, 26.03, 25.99, 23.6, 21.1, 21.0, 14.7, 0.96; IR (thin film) ν 2959, 2907, 2127, 1452, 1368, 1252, 1127, 887, 841 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{19}H_{33}NOSiNa$ $(M + Na)^+$ 342.2229, found 342.2240.



28

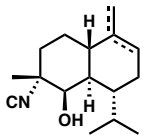
Diisocyanide 28. To a solution of TMS ether **25** (7.3 mg, 0.0211 mmol) in THF (0.21 mL) was added TBAF (40 μL, 1.0 M in THF, 0.0421 mmol). After 1 h, the reaction was quenched with water (1 mL). The aqueous layer was extracted with ether (3 x 2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 15% EtOAc/hexanes) to afford diisocyanide **28** (3.3 mg, 57%) as a thin film. $[\alpha]_D^{23}$ = +37.5 (c = 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.79 (d, *J* = 4.7 Hz, 1H), 2.06 (dt, *J* = 12.8, 3.3 Hz, 1H), 1.99 – 1.89 (m, 2H), 1.84 – 1.51 (m, 8H), 1.48 (br t, *J* = 1.8 Hz, 3H), 1.44 (ap tt, *J* = 12.0, 3.3 Hz, 1H), 1.35 (br s, 3H), 1.15 (qd, *J* = 13.5, 3.5 Hz, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.70 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8 (br t), 152.7 (br t), 71.0, 61.0 (br t, *J* = 5.3 Hz), 60.5 (br t, *J* = 5.3 Hz), 41.8, 41.5, 40.6, 38.1, 31.1, 26.6, 25.8, 22.0, 21.5, 20.6, 19.4, 15.3; IR (thin film) ν 3394 (br), 2955, 2873, 2128,

1455, 1386, 1127, 1032, 759 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{17}H_{26}N_2ONa$ $(M + Na)^+$ 297.1943, found 297.1954.



29

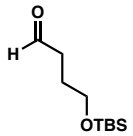
Diisocyanide 29. To a solution of TMS ether **26** (5.1 mg, 0.0147 mmol) in THF (0.2 mL) was added TBAF (30 μL, 1.0 M in THF, 0.0294 mmol). After 1 h, the reaction was quenched with water (1 mL). The aqueous layer was extracted with ether (3 x 2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 20% EtOAc/hexanes) to afford diisocyanide **29** (2.9 mg, 73%) as a thin film. $[\alpha]_D^{24}$ = –22.6 (c = 0.29, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.86 (s, 1H), 2.01 – 1.90 (m, 3H), 1.83 – 1.60 (m, 6H), 1.59 – 1.50 (m, 1H), 1.48 (br t, *J* = 1.8 Hz, 3H), 1.43 – 1.33 (m, 3H), 1.41 (br t, *J* = 1.8 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5 (br t), 155.8 (br t), 71.1, 61.2 (br t, *J* = 4.4 Hz), 60.4 (br t, *J* = 5.4 Hz), 41.7, 41.2, 39.3, 38.4, 31.1, 28.0, 26.8, 26.0, 21.8, 21.5, 19.3, 15.4; IR (thin film) ν 3391 (br), 2956, 2939, 2873, 2151, 2128, 1454, 1386, 1179, 1130, 1032 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{17}H_{26}N_2ONa$ $(M + Na)^+$ 297.1943, found 297.1931.



30

Isocyanide 30. To a solution of TMS ether **27** (12.7 mg, 0.0397 mmol) in THF (0.40 mL) was added TBAF (80 μL, 1.0 M in THF, 0.0795 mmol). After 1 h, the reaction was quenched with water (1 mL). The aqueous layer was extracted with ether (3 x 3 mL). The combined organic

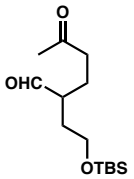
extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 1:49:50 EtOAc/CH_2Cl_2/hexanes) to afford a 5.6:1 mixture of isocyanides **30** (5.8 mg, 59%) as a thin film. The alkene isomers were characterized as a mixture; only the resonances in the ^1H and ^{13}C NMR spectra for the major Δ^9-isomer are listed. $[\alpha]_D^{24}$ = –4.1 (c = 0.58, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.42 (s, 1H), 3.86 (d, *J* = 4.5 Hz, 1H), 2.11 – 1.51 (m, 10H), 1.65 (s, 3H), 1.49 (t, *J* = 1.8 Hz, 3H), 1.36 (qd, *J* = 13.0, 4.0 Hz, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0 (br t, *J* = 4.4 Hz), 134.9, 122.0, 71.6, 61.1 (br t, *J* = 5.2 Hz), 41.0, 38.5, 36.5, 32.9, 26.7, 26.1, 25.7, 24.1, 21.3, 21.0, 15.3; IR (thin film) ν 3412 (br), 2957, 2932, 2870, 2151, 2128, 1451, 1387, 1367, 1038 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{16}H_{25}NONa$ $(M + Na)^+$ 270.1834, found 270.1841.



S4

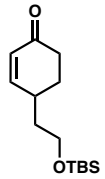
Aldehyde S4. The title compound was prepared according to the literature procedure.[12] The spectral data for this compound are consistent with those reported in the literature.[12] ^1H NMR (500 MHz, $CDCl_3$) δ 9.78 (t, *J* = 1.8 Hz, 1H), 3.64 (t, *J* = 6.0 Hz, 2H), 2.49 (td, *J* = 7.0, 1.5 Hz, 2H), 1.85 (quin, *J* = 6.6 Hz, 2H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 62.2, 40.9, 26.0, 25.6, 18.4, –5.3.

[12] Kwan, E. E.; Scheerer, J. R.; Evans, D. A. *J. Org. Chem.* **2013**, *78*, 175–203.



S5

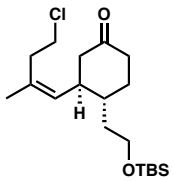
Keto-aldehyde S5. The following procedure was adapted from Hagiwara *et al*.[8] Diethylamino(trimethyl)silane (90 μL, 0.473 mmol) was added to a solution of aldehyde **S4** (0.478 g, 2.36 mmol) in MeCN (7.9 mL). The reaction mixture was cooled to 0 ˚C and methyl vinyl ketone (0.29 mL, 3.54 mmol) was added dropwise *via* syringe. The reaction mixture was heated at reflux for 24 h, cooled to room temperature, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10% EtOAc/hexanes) to afford the title compound (0.561 g, 87%) as a colorless oil. The spectral data for this compound are consistent with those reported in the literature.[18] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.57 (d, J = 2.5 Hz, 1H), 3.68 – 3.59 (m, 2H), 2.56 – 2.32 (m, 3H), 2.13 (s, 3H), 1.96 – 1.84 (m, 2H), 1.77 – 1.65 (m, 2H), 0.86 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.1, 204.4, 60.6, 48.7, 40.9, 32.7, 30.2, 26.0, 22.3, 18.4, –5.4.



S6

Enone S6. To a solution of keto-aldehyde **S5** (2.43 g, 8.92 mmol) in Et_2O (83 mL) and THF (28 mL) was added aqueous KOH solution (89 mL, 0.3 N) and nBu$_4$NOH (2.9 mL, 40% aq) in one portion. The reaction mixture was heated at reflux for 8 h and cooled to room temperature, at which point additional KOH (1.50 g, 26.7 mmol) was added in one portion. The reaction mixture was heated at reflux for 15 h, and cooled to room temperature. The biphasic reaction mixture was separated, and the aqueous layer was extracted with Et_2O (2 x 100 mL). The combined organic

extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10% EtOAc/hexanes) to afford the title compound (1.48 g, 65%) as a colorless oil. The spectral data for this compound are consistent with those reported in the literature.[13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.90 (ddd, *J* = 10.0, 2.8, 1.3 Hz, 1H), 5.97 (ddd, *J* = 10.0, 2.5, 0.75 Hz, 1H), 3.79 – 3.67 (m, 2H), 2.68 – 2.57 (m, 1H), 2.49 (dt, *J* = 16.8, 4.8 Hz, 1H), 2.36 (ddd, *J* = 17.0, 12.3, 5.0 Hz, 1H), 2.17 – 2.08 (m, 1H), 1.79 – 1.66 (m, 2H), 1.66 – 1.56 (m, 1H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.0, 155.4, 129.0, 60.5, 37.4, 37.0, 33.1, 28.7, 26.0, 18.4, –5.21, –5.24.

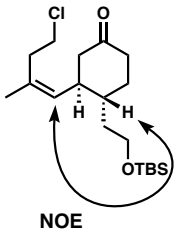


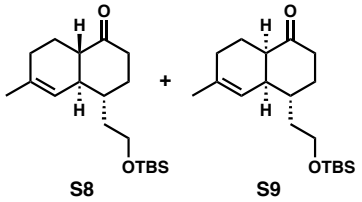
S7

Ketone S7. To a solution of (*Z*)-4-chloro-1-iodo-2-methylbut-1-ene[3] (0.313 g, 1.36 mmol) in Et_2O (2.3 mL, previously sparged with argon gas for 20 min) at –78 ˚C was added *tert*-butyllithium (1.70 mL, 1.60 M in pentane, 2.72 mmol) dropwise *via* syringe. After 20 min, lithium 2-thienylcyanocuprate solution (5.43 mL, 0.25 M in THF, 1.36 mmol) was added dropwise *via* syringe. The reaction mixture was allowed to stir for 1 h at –78 ˚C. A solution of enone **S6** (0.230 g, 0.905 mmol) in Et_2O (1.0 mL) was added dropwise *via* syringe. The transfer was completed with additional portions of Et_2O (2 x 0.5 mL). After allowing the reaction mixture to warm to –40 ˚C and stir for 1 h, the reaction was quenched with 9:1 saturated NH_4Cl solution/NH_4OH (10 mL). After warming to room temperature, the solution turned a deep blue color. The aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with 9:1 saturated NH_4Cl solution/NH_4OH (2 x 10 mL), washed with brine (10

[13] Houjeiry, T. I.; Poe, S. L.; McQuade, D. T. *Org. Lett.* **2012**, *14*, 4394–4397.

mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 5% EtOAc/hexanes) to afford the title compound (0.298 g, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.09 (d, J = 9.5 Hz, 1H), 3.71 – 3.60 (m, 2H), 3.56 – 3.48 (m, 2H), 2.55 – 2.24 (m, 6H), 2.24 – 2.10 (m, 2H), 1.88 – 1.79 (m, 1H), 1.73 (s, 3H), 1.69 – 1.59 (m, 1H), 1.39 (qd, J = 13.0, 4.8 Hz, 1H), 1.22 – 1.13 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.0, 132.0, 131.7, 61.2, 47.6, 43.4, 42.4, 41.0, 38.1, 36.3, 35.3, 31.1, 26.1, 23.0, 18.4, –5.1, –5.2; IR (thin film) ν 2954, 2930, 2897, 2857, 1717, 1255, 1096, 835, 775 cm^{-1}; HRMS (CI) *m* / z calcd for $C_{19}H_{35}ClO_2SiNH_4$ (M + NH_4)$^+$ 376.2439, found 376.2437. ^{1}H-NOESY-2D (500 MHz, $CDCl_3$) spectra were obtained for ketone **S7** and selected NOE interactions are shown.

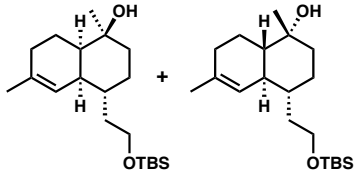




S8 S9

Decalones S8 and S9. To a solution of alkyl chloride **S7** (0.298 g, 0.829 mmol) in *tert*-butyl alcohol (8.3 mL) at 30 ˚C was added potassium *tert*-butoxide (0.62 mL, 1.6 M in THF, 0.995 mmol) dropwise *via* syringe. After stirring for 6 h at 30 ˚C, the reaction was quenched with saturated NH_4Cl solution (16 mL). The aqueous layer was extracted with pentane (3 x 20 mL), and the combined organic extracts were washed with water (4 x 20 mL) and brine (20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 5% EtOAc/hexanes) to afford a 1:1 mixture of *trans*- and *cis*-decalones (176.4 mg, 71%) as a colorless oil, which was characterized as a mixture. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.54 (s, 1H), 5.30 (s, 1H), 3.78 – 3.62 (m, 4H), 2.51 – 2.34 (m, 4H), 2.33 – 2.25 (m, 2H), 2.22 – 1.77 (m, 14H), 1.70 – 1.29 (m, 6H), 1.67 (s, 3H), 1.63 (s, 3H), 0.897

(s, 9H), 0.895 (s, 9H), 0.059 (s, 6H), 0.058 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.0, 212.8, 135.7, 124.5, 122.3, 61.6, 61.1, 51.2, 47.1, 46.1, 42.2, 41.1, 38.1, 38.0, 35.9, 35.3, 34.9, 32.7, 39.8, 28.2, 28.1, 26.1, 23.81, 23.80, 23.0, 21.9, 18.4, –5.12, –5.14, –5.17. IR (thin film) ν 2953, 2928, 2857, 1713, 1472, 1254, 1100, 836, 776 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{19}H_{34}O_2SiNa$ $(M + Na)^+$ 345.2226, found 345.2226.



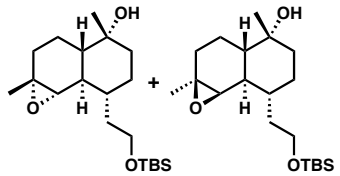
S10 31

***cis*-Decalin S10 and *trans*-decalin 31.** Methylmagnesium bromide (1.54 mL, 3.0 M in Et_2O, 4.62 mmol) was added dropwise to a solution of a mixture of decalones **S8** and **S9** (0.213 g, 0.923 mmol) in THF (9.2 mL) cooled to 0 ˚C. The reaction mixture was allowed to warm to room temperature for 30 min, and the reaction was quenched with saturated aqueous NH_4Cl solution (12 mL) at 0 ˚C. The aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 5 → 10% EtOAc/hexanes), yielding *trans*-decalin **31** (0.103 g, 46%) and *cis*-decalin **S10** (0.101 g, 45%) as colorless oils.

cis-Decalin **S10**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.57 (d, *J* = 4.0 Hz, 1H), 3.71 – 3.64 (m, 1H), 3.63 – 3.56 (m, 1H), 2.03 – 1.94 (m, 2H), 1.91 – 1.81 (m, 3H), 1.72 – 1.36 (m, 6H), 1.65 (s, 3H), 1.35 – 1.22 (m, 2H), 1.30 (s, 3H), 1.10 (qd, *J* = 13.0, 4.0 Hz, 1H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 124.9, 72.6, 61.7, 45.5, 40.1, 36.4, 36.2, 35.3, 31.2, 29.4, 28.0, 26.1, 23.7, 18.7, –5.08, –5.12; IR (thin film) ν 3380 (br), 2956, 2929, 2893, 2857, 1462, 1254,

1095, 835, 774 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{38}O_2SiNa$ $(M + Na)^+$ 361.2539, found 361.2547.

trans-Decalin **31**: ^1H NMR ($CDCl_3$, 500 MHz) δ 5.53 (s, 1H), 3.74 – 3.67 (m, 1H), 3.67 – 3.59 (m, 1H), 2.06 – 1.86 (m, 4H), 1.85 – 1.76 (m, 1), 1.72 – 1.60 (m, 2H), 1.66 (s, 3H), 1.47 – 1.28 (m, 4H), 1.22 (s, 3H), 1.17 – 1.00 (m, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3, 123.5, 70.7, 61.5, 47.8, 40.5, 40.1, 38.5, 36.1, 31.0, 28.6, 27.9, 26.1, 23.8, 22.6, 18.5, –5.07, –5.11; IR (thin film) ν 3455 (br), 2954, 2928, 2857, 1462, 1375, 1255, 1096, 835, 774 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{38}O_2SiNa$ $(M + Na)^+$ 361.2539, found 361.2544.



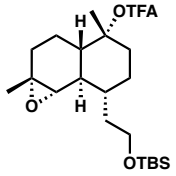
32 33

Epoxides 32 and 33. To a solution of *trans*-decalin **31** (0.109 g, 0.321 mmol) in acetone (16.1 mL) was added saturated aqueous $NaHCO_3$ (10.7 mL). The resulting mixture was cooled to 0 ˚C and a solution of Oxone® (0.217 g, 0.353 mmol) in H_2O (2 mL) was added dropwise over 5 minutes. The reaction mixture was stirred vigorously for 30 min at 0 ˚C, diluted with H_2O (20 mL) and extracted with EtOAc (4 x 20 mL). The combined organic extracts were diluted with hexanes until cloudy, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10 → 20% EtOAc/hexanes) to afford β-epoxide **33** (25.7 mg, 23%) and α-epoxide **32** (72.4 mg, 64%) as colorless oils.

Epoxide **33**: ^1H NMR ($CDCl_3$, 500 MHz) δ 3.78 – 3.71 (m, 1H), 3.71 – 3.63 (m, 1H), 3.17 (s, 1H), 2.02 – 1.93 (m, 1H), 1.90 – 1.78 (m, 2H), 1.69 – 1.56 (m, 4H), 1.55 – 1.38 (m, 4H), 1.30 (s, 3H), 1.20 – 1.06 (m, 2H), 1.16 (s, 3H), 0.99 (s, 1H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.8, 62.1, 61.3, 58.5, 41.9, 41.1, 40.1, 36.2, 35.9, 29.1, 29.0, 27.7, 26.1, 24.9,

21.7, 18.5, –5.12, –5.16; IR (thin film) ν 3480 (br), 2929, 2857, 1462, 1377, 1255, 1096, 836, 775 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{38}O_3SiNa$ $(M + Na)^+$ 377.2488, found 377.2488.

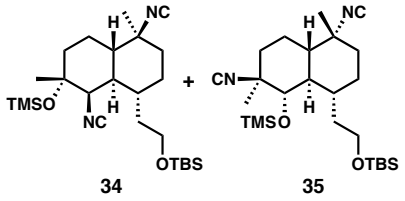
Epoxide **32**: ^1H NMR ($CDCl_3$, 500 MHz) δ 3.78 – 3.70 (m, 1H), 3.70 – 3.61 (m, 1H), 2.90 (s, 1H), 2.13 – 2.01 (m, 2H), 1.78 – 1.70 (m, 1H), 1.68 – 1.54 (m, 3H), 1.52 – 1.44 (m, 1H), 1.41 – 1.32 (m, 4H), 1.29 (s, 3H), 1.18 (s, 3H), 1.17 – 1.06 (m, 1H), 1.04 (s, 1H), 0.89 (s, 9H), 0.85 (t, *J* = 11.8 Hz, 1H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.4, 62.4, 61.1, 58.2, 47.3, 41.4, 39.7, 36.4, 36.3, 30.8, 28.6, 28.2, 26.1, 23.7, 19.6, 18.4, –5.11, –5.18; IR (thin film) ν 3481 (br), 2954, 2928, 2856, 1450, 1378, 1255, 1095, 836, 775 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{38}O_3SiNa$ $(M + Na)^+$ 377.2488, found 377.2483.



S11

Trifluoroacetate S11. A mixture of epoxide **32** (79.3 mg, 0.224 mmol) and pyridine (60 µL, 0.672 mmol) in CH_2Cl_2 (2.2 mL) at 0 ˚C was treated with trifluoroacetic anhydride (50 µL, 0.335 mmol). After 30 minutes, the reaction was quenched with 1 M HCl (3 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic extracts were washed with water (5 mL), washed with saturated $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 5% EtOAc/hexanes) to afford the title compound (82.3 mg, 82%) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 3.76 – 3.69 (m, 1H), 3.67 – 3.59 (m, 1H), 2.88 (s, 1H), 2.70 (dt, *J* = 14.8, 3.3 Hz, 1H), 2.15 – 2.02 (m, 2H), 1.86 – 1.79 (m, 1H), 1.68 – 1.52 (m, 3H), 1.57 (s, 3H), 1.49 – 1.21 (m, 4H), 1.30 (s, 3H), 1.05 (qd, *J* = 14.0, 3.5 Hz, 1H), 0.91 (t, *J* = 11.0 Hz, 1H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2 (q, *J* = 41 Hz), 114.5 (q, *J* = 285.4 Hz),

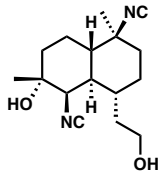
88.2, 62.0, 60.7, 58.0, 48.6, 41.2, 36.2, 35.7, 34.3, 30.8, 27.7, 26.1, 23.73, 23.65, 19.6, 18.4, –5.17, –5.24; IR (thin film) ν 2956, 2930, 2859, 1779, 1452, 1374, 1255, 1157, 1092, 837, 777 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{22}H_{37}F_3O_4SiNa$ $(M + Na)^+$ 473.2311, found 473.2301.



Diisocyanides 34 and 35. The following procedure was adopted from Pronin *et al.*[6] A solution of trifluoroacetate **S11** (50.7 mg, 0.113 mmol) in TMSCN (0.11 mL) was cooled to 0 ˚C. A solution of scandium(III) trifluoromethanesulfonate (5.5 mg, 0.0113 mmol) in TMSCN (0.23 mL) was added, and the reaction mixture was allowed to warm to room temperature after 1 h. After 24 h at room temperature, the reaction was quenched with TMEDA (30 μL) and the volatiles were removed under reduced pressure. The crude residue was dissolved in hexanes (5 mL), washed with saturated aqueous $NaHCO_3$ solution (3 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 3 → 6% EtOAc/hexanes) to afford diisocyanide **34** (5.0 mg, 10%) as thin film and diisocyanide **35** (6.0 mg, 11%) as a 4:1 mixture of C10 epimers.

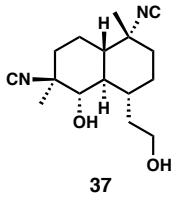
Diisocyanide **34**: ^1H NMR ($CDCl_3$, 500 MHz) δ 3.71 – 3.57 (m, 3H), 2.02 (dt, *J* = 13.5, 4.0 Hz, 1H), 1.90 – 1.09 (m, 12H), 1.45 (s, 3H), 1.31 (br s, 3H), 0.90 (s, 9H), 0.13 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0 (br t), 153.3 (br t), 73.5, 61.9 (br t, *J* = 5.1 Hz), 60.7, 60.2 (br t, *J* = 4.9 Hz), 42.6, 40.4, 38.7, 34.8, 34.6, 32.6, 27.6, 26.8, 26.1, 21.1, 20.5, 18.5, 2.4, –5.16, –5.19; IR (thin film) ν 2952, 2935, 2857, 2130, 1462, 1384, 1252, 1103, 1039, 840 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{25}H_{46}N_2O_2Si_2Na$ $(M + Na)^+$ 485.2996, found 485.2990.

Diisocyanide **35**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.71 (d, *J* = 9.0 Hz, 1H), 3.69 – 3.56 (m, 2H), 2.39 – 2.29 (m, 1H), 2.13 (dt, *J* = 10.0, 3.5 Hz, 1H), 1.98 – 1.73 (m, 4H), 1.51 – 1.06 (m, 7H), 1.41 (s, 3H), 1.40 (s, 3H), 0.88 (s, 9H), 0.28 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1 (br t), 155.5 (br t), 81.0, 63.0 (br t, *J* = 5.1 Hz), 60.8, 60.6 (br t, *J* = 4.3 Hz), 47.8, 44.4, 38.4, 38.0, 37.9, 37.3, 28.5, 26.7, 26.1, 21.8, 20.6, 18.4, 1.5, –5.2, –5.3; IR (thin film) ν 2952, 2930, 2897, 2858, 2127, 1463, 1384, 1253, 1104, 840, 775 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{25}H_{46}N_2O_2Si_2Na$ $(M + Na)^+$ 485.2996, found 485.3009.



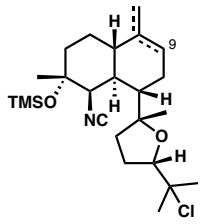
36

Diisocyanide 36. To a solution of silyl ether **34** (7.8 mg, 0.0169 mmol) in THF (0.2 mL) was added TBAF (90 μL, 1.0 M in THF, 0.0845 mmol). After 24 h, the reaction was quenched with saturated $NaHCO_3$ solution (1 mL). The reaction mixture was extracted with ether (3 **x** 2 mL). The combined organic extracts were washed with water (5 mL), washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 2 → 3% MeOH/CH_2Cl_2) to afford diisocyanide **36** (2.7 mg, 57%) as a thin film. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 – 3.64 (s, 3H), 2.05 (dt, *J* = 13.0, 3.3 Hz, 1H), 1.96 – 1.59 (m, 9H), 1.59 – 1.31 (m, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.29 – 1.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0 (br t), 153.2 (br t), 70.5, 61.2 (br t, *J* = 5.4 Hz), 60.21, 60.17 (br t, *J* = 5.3 Hz), 42.8, 40.2, 38.8, 34.8, 34.3, 32.7, 28.8, 26.6, 21.1, 20.8; IR (thin film) ν 3390 (br), 2937, 2871, 2134, 1451, 1384, 1122, 1036, 1003, 733 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{16}H_{24}N_2O_2Na$ $(M + Na)^+$ 299.1736, found 299.1733.



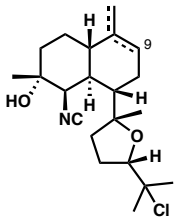
37

Diisocyanide 37. To a solution of silyl ether **35** (8.5 mg, 0.0184 mmol) in THF (0.2 mL) was added TBAF (0.10 mL, 1.0 M in THF, 0.0918 mmol). After 24 h, the reaction was quenched with saturated $NaHCO_3$ solution (1 mL). The reaction mixture was extracted with ether (3 x 2 mL). The combined organic extracts were washed with water (5 mL), washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 3% MeOH/CH_2Cl_2) to afford diisocyanide **37** (3.9 mg, 76%) as a 4:1 mixture of C10 epimers. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.67 (br s, 1H), 3.90 (td, *J* = 10.0, 3.0 Hz, 1H), 3.76 (ddd, *J* = 10.0, 6.5, 4.0 Hz, 1H), 3.55 (d, *J* = 10.0 Hz, 1H), 2.56 (br s, 1H), 2.29 – 2.19 (m, 1H), 2.12 (dt, *J* = 13.5, 3.8 Hz, 1H), 2.06 – 1.17 (m, 10H), 1.42 (br s, 3H), 1.40 (br s, 3H), 1.06 (t, *J* = 12.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3 (br t), 153.1 (br t), 79.7, 62.8 (br t, *J* = 5.6 Hz), 60.8 (br t, *J* = 4.6 Hz), 60.1, 48.7, 42.1, 39.4, 39.1, 36.8, 36.3, 28.8, 28.2, 21.6, 19.3; IR (thin film) ν 3357 (br), 2938, 2870, 2130, 1448, 1384, 1116, 1041, 731 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{16}H_{24}N_2O_2Na$ $(M + Na)^+$ 299.1736, found 299.1727.



S12

Isocyanide S12. The title compound was isolated as a side product in our previous synthesis of kalihinol B.[14] The crude product was fully characterized after fluoride-mediated removal of the silyl ether.



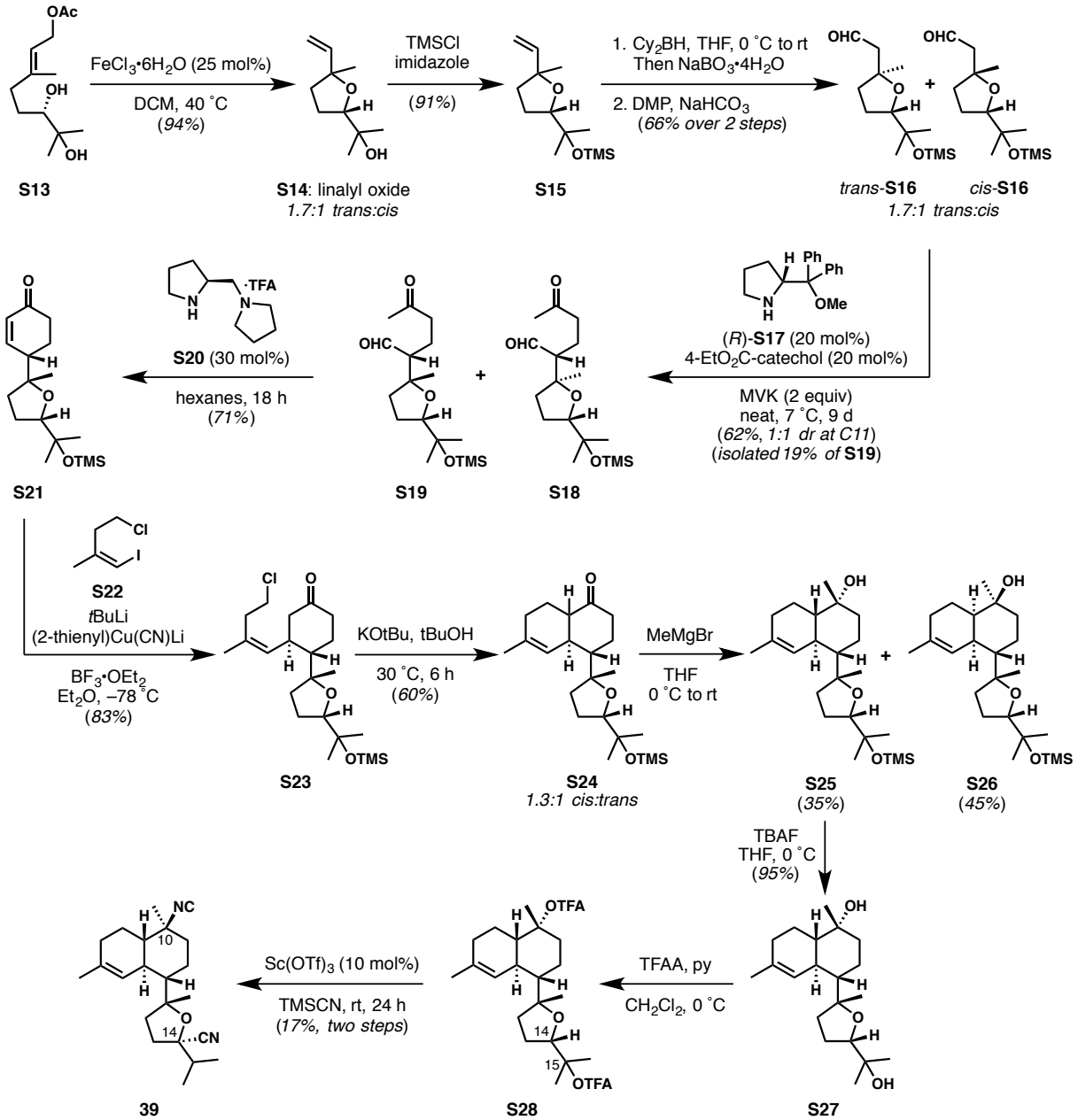
38 *(3:1 favoring Δ^9 isomer)*

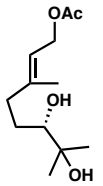
Isocyanide 38. To a solution of isocyanide **S12** (20.0 mg, 0.0456 mmol) in THF (0.5 mL) was added TBAF (0.10 mL, 1.0 M in THF, 0.100 mmol). After 1 h, the reaction was quenched with water (1 mL). The aqueous phase was extracted with ether (3 x 2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 2.5:55:45 EtOAc/CH_2Cl_2/hexanes) to afford a 3:1 mixture of **38** (8.3 mg, 50%) favoring the Δ^9 isomer as a thin film. The mixture of alkene isomers complicated the ^{1}H and ^{13}C NMR spectra. $[\alpha]_D^{22}$ = +14.7 (c = 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.35 (d, *J* = 4.0 Hz, 1H), 4.73 (s, 1H), 4.63 (s, 1H), 4.40 (s, 1H), 4.24 (s, 1H), 4.09 (dd, *J* = 9.0, 4.5 Hz, 1H), 4.07 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.33 (dt, *J* = 12.8, 3.3 Hz, 1H), 2.20 (t, *J* = 11.2 Hz, 1H), 2.12 – 1.50 (complex), 1.65 (s, 6H), 1.62 (s, 3H), 1.57 (s, 3H), 1.53 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.34 – 1.13 (complex), 1.06 (m, 3H), 1.02 (m, 3H); ^{13}C NMR (125 MHz,

[14] Daub, M. E.; Prudhomme, J.; Le Roch, K.; Vanderwal, C. D. *J. Am. Chem. Soc.* **2015**, *137*, 4912–4915.

$CDCl_3$) δ 157.1 (br t), 151.1, 134.9, 120.7, 105.8, 87.8, 87.5, 84.9, 84.8, 71.7, 71.5, 71.1, 70.8, 63.7 (t, J = 5.8 Hz), 63.4 (t, J = 5.6 Hz), 47.6, 43.4, 42.0, 38.9, 38.8, 38.2, 37.8, 36.9, 36.0, 34.2, 32.8, 31.2, 30.7, 30.3, 29.8, 28.79, 28.76, 28.7, 26.0, 25.9, 25.7, 25.6, 24.1, 20.9, 17.9, 17.1; IR (thin film) ν 3418 (br), 2971, 2933, 2892, 2852, 2156, 2139, 1457, 1382, 1122, 1025, 758 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{21}H_{32}ClNO_2Na$ $(M + Na)^+$ 388.2019, found 388.2006.

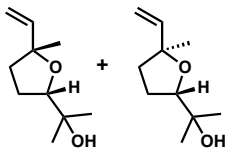
Scheme S1. Synthesis of C14-nitrile **39**.





S13

(*S,E*)-6,7-Dihydroxy-3,7-dimethyloct-2-enyl acetate (S13). (*S,E*)-6,7-Dihydroxy-3,7-dimethyloct-2-enyl acetate (**S13**) was prepared according to the literature procedure using a Sharpless dihydroxylation of geranyl acetate.[15] The spectral data for this compound are consistent with those reported in the literature.[15] $[\alpha]_D^{24}$ = –22.5 (c = 1.0, $CHCl_3$), lit.[15] $[\alpha]_D^{23}$ = +26.8 (c = 1.0, $CHCl_3$) for the (*R*)-form; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.39 (t, *J* = 7.0 Hz, 1H), 4.58 (d, *J* = 7.5 Hz, 2H), 3.34 (ddd, *J* = 10.5, 4.5, 1.5 Hz, 1H), 2.37 – 2.28 (m, 1H), 2.25 (d, J = 4.5 Hz, 1H), 2.15 – 2.06 (m, 1H), 2.05 (s, 3H), 1.98 (s, 1H), 1.72 (s, 3H), 1.64 – 1.56 (m, 1H), 1.49 – 1.39 (m, 1H), 1.21 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 142.2, 118.9, 78.2, 73.2, 61.5, 36.7, 29.6, 26.6, 23.4, 21.2, 16.6. The enantiomeric excess of **S13** was determined as 90% by ^{1}H NMR analysis of its corresponding mono-(*R*)-MTPA ester. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 ppm (t, 1H) for the *S* enantiomer; δ 5.23 ppm (t, 1H) for the *R* enantiomer, corresponding to the methyl group on the methoxy group of the ester.



cis-**S14** *trans*-**S14**

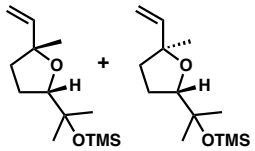
***cis*- and *trans*-Linalyl oxides (S14).** The following procedure was adapted from Guérinot *et al*.[16] To a solution of diol **S13** (4.23 g, 18.37 mmol) in CH_2Cl_2 (184 mL) was added $FeCl_3$•$6H_2O$ (1.24 g, 4.59 mmol) in one portion. After stirring at 40 ˚C for 5 h, the reaction mixture was cooled to

[15] Surendra, K.; Corey, E. J. *J. Am. Chem. Soc.* **2008**, *130*, 8865–8869.
[16] Guérinot, A.; Serra-Muns, A.; Gnamm, C.; Bensoussan, C.; Reymond, S.; Cossy, J. *Org. Lett.* **2010**, *12*, 1808–1811.

room temperature and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 25 → 30% Et2O/pentane) to afford a 1:1.7 mixture of *cis*- and *trans*-linalyl oxides (3.06 g, 97%) as a colorless oil. The *cis*- and *trans*-THFs were separated for analytical purposes, and the spectral data for these compounds are consistent with those reported in the literature.[17,18,19,20]

trans-**S14**: $[\alpha]_D^{23}$ = +5.7 (c = 0.95, $CHCl_3$), lit.[17] $[\alpha]_D^{25}$ = +4.73 (c = 2.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.88 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.19 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.00 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.79 (t, *J* = 7.3 Hz, 1H), 2.16 (s, 1H), 1.94 – 1.80 (m, 3H), 1.76 – 1.69 (m, 1H), 1.31 (s, 3H), 1.23 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 111.5, 85.7, 83.2, 71.3, 37.6, 27.4, 27.0, 26.4, 24.3.

cis-**S14**: $[\alpha]_D^{23}$ = –3.8 (c = 0.72, $CHCl_3$), lit.[17] $[\alpha]_D^{25}$ = –2.94 (c = 2.14, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.97 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.20 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.01 (dd, *J* = 10.5, 1.0 Hz, 1H), 3.86 (t, *J* = 7.3 Hz, 1H), 2.07 (s, 1H), 1.96 – 1.74 (m, 4H), 1.32 (s, 3H), 1.23 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 111.7, 85.7, 82.9, 71.3, 38.1, 27.6, 26.6, 26.2, 24.5.



cis-**S15** *trans*-**S15**

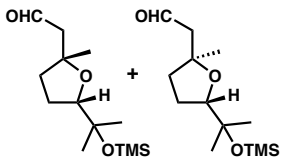
***cis*- and *trans*-Silyl ethers S15.** Imidazole (1.21 g, 17.8 mmol) was added in one portion to a solution of *cis*- and *trans*-linalyl oxides (**S14**) (1.01 g, 5.92 mmol) in CH_2Cl_2 (12 mL). Chlorotrimethylsilane (1.13 mL, 8.88 mmol) was added dropwise *via* syringe. After 30 min,

[17] Méou, A.; Bouanah, N.; Archelas, A.; Zhang, X. M.; Guglielmetti, R.; Furstoss, R. *Synthesis* **1990**, 752–753.
[18] Howell, A. R.; Pattenden, G. *J. Chem. Soc. Perkin Trans. 1* **1990**, 2715–2720.
[19] Fournier-Nguefack, C.; Lhoste, P.; Sinou, D. *Tetrahedron* **1997**, *53*, 4353–4362.
[20] Wan, K. K.; Litz, J. P.; Vosburg, D. A. *Tetrahedron: Asymmetry* **2010**, *21*, 2425–2428.

saturated $NaHCO_3$ solution (15 mL) was added to the reaction mixture. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (10 mL). The biphasic mixture was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phases were washed with water (30 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 2.5% Et_2O/pentane) to afford a 1:1.7 mixture of *cis*-**S15** and *trans*-**S15** (1.30 g, 91%) as a colorless oil. The diastereomers were separated for analytical purposes.

trans-**S15**: $[\alpha]_D^{23}$ = +7.1 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.86 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.16 (dd, *J* = 17.3, 1.8 Hz, 1H), 4.97 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.74 (t, *J* = 6.5 Hz, 1H), 1.94 – 1.75 (m, 3H), 1.71 – 1.62 (m, 1H), 1.30 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 111.2, 86.4, 83.4, 75.2, 37.4, 27.9, 26.7, 26.4, 25.5, 2.7; IR (thin film) ν 2972, 2873, 1465, 1365, 1249, 1171, 1044, 839 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{13}H_{26}O_2SiNa$ $(M + Na)^+$ 265.1600, found 265.1604.

cis-**S15**: $[\alpha]_D^{23}$ = –0.27 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.97 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.20 (dd, *J* = 17.3, 1.8 Hz, 1H), 4.95 (dd, *J* = 11.0, 1.5 Hz, 1H), 3.78 (t, *J* = 7.0 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.85 – 1.78 (m, 1H), 1.74 – 1.65 (m, 1H), 1.28 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 111.3, 86.3, 83.1, 75.2, 38.0, 27.9, 26.6, 25.73, 25.70, 2.7; IR (thin film) ν 2972, 2872, 1459, 1365, 1250, 1172, 1045, 840 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{13}H_{26}O_2SiNa$ $(M + Na)^+$ 265.1600, found 265.1597.



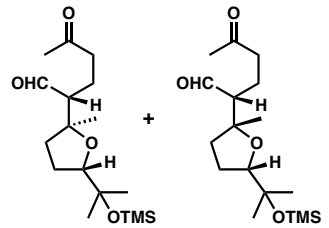
cis-**S16** *trans*-**S16**

***cis*- and *trans*-Aldehydes S16.** A solution of BH_3•DMS (0.60 mL, 6.31 mmol) in THF (10.5 mL) was cooled to 0 ˚C. Cyclohexene (1.28 mL, 12.62 mmol) was added dropwise *via* syringe over 2 min. After 20 min, the reaction mixture was allowed to warm to room temperature. After 2 h, the reaction mixture was cooled to 0 ˚C and a 1:1.7 mixture of *cis*- and *trans*-**S15** (1.02 g, 4.21 mmol) was added as a solution in THF (10.5 mL). The transfer was completed with additional portions of THF (2 x 2 mL). The reaction mixture was allowed to stir at 0 ˚C for one hour before allowing to warm to room temperature. After 3 h, the reaction was quenched with water (30 mL) and $NaBO_3$•$4H_2O$ (3.24 g, 21.04 mmol) was added in one portion. The reaction mixture was allowed to stir vigorously for 16 h. The reaction mixture was diluted with water (30 mL) and extracted with Et_2O (3 x 60 mL). The combined organic extracts were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 20% EtOAc/hexanes) to afford a mixture of *cis*- and *trans*-THFs contaminated with cyclohexanol. ^{1}H NMR and ^{13}C NMR spectra were complicated by the mixture of tetrahydrofuran diastereomers and cyclohexanol contaminant. Sodium bicarbonate (2.12 g, 25.18 mmol) was added to a solution of DMP (4.27 g, 10.07 mmol) in CH_2Cl_2 (40 mL) in one portion. A solution of *cis*- and *trans*-THFs contaminated with cyclohexanol (1.312 g, 5.036 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 2 min. The transfer was completed with additional portions of CH_2Cl_2 (2 x 2.5 mL). After 2 h, the reaction was quenched with a 1:1 mixture of saturated $NaHCO_3$ solution and saturated $Na_2S_2O_3$ solution (50 ml), and allowed to stir until bubbling ceased (20 min). The phases were separated, and the

aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with 1 M NaOH (1 x 50 mL) and water (1 x 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 8.5% Et_2O/pentane) to afford a 1:1.7 mixture of *cis*-**S16** and *trans*-**S16** (0.714 g, 66% over two steps) as a colorless oil. The diastereomers were separated for analytical purposes using flash chromatography (SiO_2, 100% CH_2Cl_2).

trans-**S16**: $[\alpha]_D^{22}$ = +11.2 (c = 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.82 (t, *J* = 3.0 Hz, 1H), 3.73 (t, *J* = 7.3 Hz, 1H), 2.58 (dd, *J* = 14.8, 2.8 Hz, 1H), 2.52 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.00 – 1.72 (m, 4H), 1.31 (s, 3H), 1.21 (s, 3H), 1.17 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 87.0, 81.4, 74.8, 54.4, 38.0, 27.7, 27.5, 26.4, 25.9, 2.7; IR (thin film) ν 2972, 2898, 2873, 2736, 1724, 1458, 1380, 1250, 1175, 1068, 1044, 840 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{13}H_{26}O_3SiNa$ $(M + Na)^+$ 281.1549, found 281.1554.

cis-**S16**: $[\alpha]_D^{22}$ = –49.4 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.86 (dd, *J* = 3.5, 2.5 Hz, 1H), 3.77 (t, *J* = 7.3 Hz, 1H), 2.65 (dd, *J* = 15.0, 2.5 Hz, 1H), 2.46 (dd, *J* = 15.0, 3.5 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.87 – 1.80 (m, 1H), 1.79 – 1.72 (m, 1H), 1.29 (s, 3H), 1.24 (s, 3H), 1.16 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 86.8, 81.4, 74.9, 54.4, 38.0, 27.3, 27.0, 26.6, 26.2, 2.6; IR (thin film) ν 2970, 2873, 2736, 1723, 1456, 1380, 1250, 1177, 1040, 840 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{13}H_{26}O_3SiNa$ $(M + Na)^+$ 281.1549, found 281.1539.



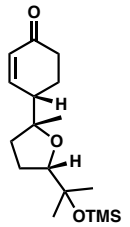
S18 S19

Keto-aldehydes S18 and S19. The following procedure was adapted from Peelen *et al.*[21] A 2-dram vial was charged with a mixture of *cis*- and *trans*-aldehydes **S16** (0.714 g, 2.76 mmol), prolinol catalyst **S17**[22] (0.148 g, 0.553 mmol), and 4-EtO_2C-catechol (0.101 g, 0.553 mmol). The vial was sealed with a septum, the headspace was purged with argon, and the reaction mixture was cooled to 0 ˚C. Methyl vinyl ketone (0.45 mL, 5.53 mmol) was added *via* syringe. The reaction mixture was allowed to stir at 0 ˚C until the solution became homogenous (30 min) before being placed in a 7 ˚C refrigerator for 9 days. The reaction mixture was purified directly using flash chromatography (SiO_2, 12.5% EtOAc/hexanes) to afford keto-aldehyde **S19** (0.177 g, 19%) as a colorless oil and keto-aldehyde **S18** (0.318 g, 35%) containing ca. 25% other diastereomers.

Keto-aldehyde **S18**: $[\alpha]_D^{22}$ = –48.6 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.70 (d, *J* = 3.0 Hz, 1H), 3.59 (dd, *J* = 8.5, 6.5 Hz, 1H), 2.51 (ddd, *J* = 18.0, 8.5, 5.8 Hz, 1H), 2.45 – 2.34 (m, 2H), 2.11 (s, 3H), 1.97 – 1.77 (m, 6H), 1.74 – 1.59 (m, 1H), 1.20 (s, 5H), 1.14 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 205.1, 87.3, 83.8, 74.4, 60.6, 41.7, 35.9, 30.1, 27.5, 26.2, 26.0, 25.7, 19.0, 2.7; IR (thin film) ν 2972, 2896, 2873, 2730, 1718, 1455, 1363, 1249, 1175, 1041, 839 cm^{-1}; HRMS (CI) *m* / z calcd for $C_{17}H_{32}O_4SiH$ $(M + H)^+$ 329.2148, found 329.2133.

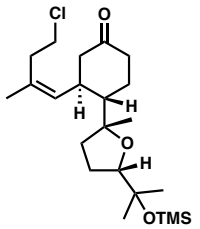
[21] Peelen, T. J.; Chi, Y.; Gellman, S. H. *J. Am. Chem. Soc.* **2005**, *127*, 11598–11599.
[22] Enders, D.; Kipphardt, H.; Gerdes, P.; Breña Valle, L. J.; Bhushan, V. *Bull. Soc. Chim. Belg.* **1988**, *97*, 691–704.

Keto-aldehyde **S19**: $[\alpha]_D^{22}$ = –92.7 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.90 (br s, 1H), 3.77 (t, *J* = 7.3 Hz, 1H), 2.56 (ddd, *J* = 18.0, 8.0, 5.5 Hz, 1H), 2.50 (dt, *J* = 11.0, 1.8 Hz, 1H), 2.33 (dt, *J* = 18.0, 7.5 Hz, 1H), 2.09 (s, 3H), 2.06 – 1.77 (m, 4H), 1.70 – 1.63 (m, 1H), 1.61 – 1.52 (m, 1H), 1.23 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 207.1, 87.0, 85.0, 74.9, 59.5, 41.9, 37.2, 30.1, 27.2, 26.8, 25.8, 23.4, 19.5, 2.6; IR (thin film) ν 2970, 2873, 2730, 1718, 1449, 1364, 1250, 1176, 1038, 840 cm^{-1}; HRMS (CI) *m* / z calcd for $C_{17}H_{32}O_4SiH$ $(M + H)^+$ 329.2148, found 329.2138.



S21

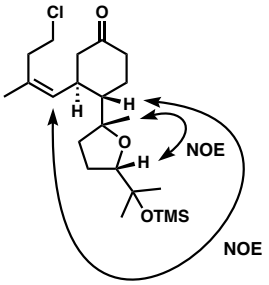
Enone S21. A solution of keto-aldehyde **S19** (0.177 g, 0.539 mmol) and catalyst **S20**[13] (43.4 mg, 0.162 mmol) in hexanes (5.4 mL, previously sparged with argon gas for 20 min) was stirred at room temperature for 21 h. The reaction mixture was concentrated *in vacuo*, and the resulting crude residue was purified using flash chromatography (SiO_2, 7.5% EtOAc/hexanes) to afford the title compound (0.119 g, 71%) as a colorless oil. $[\alpha]_D^{23}$ = –54.0 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.22 (dt, *J* = 10.5, 1.5 Hz, 1H), 6.06 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.77 (t, *J* = 7.0 Hz, 1H), 2.67 – 2.60 (m, 1H), 2.50 (dt, *J* = 16.3, 3.8 Hz, 1H), 2.33 (td, *J* = 15.5, 5.0 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.97 – 1.81 (m, 3H), 1.75 – 1.58 (m, 2H), 1.23 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1, 154.2, 129.9, 86.4, 84.3, 74.9, 46.4, 37.8, 35.9, 27.3, 26.6, 26.3, 25.6, 22.7, 2.6; IR (thin film) ν 2969, 2872, 1683, 1452, 1380, 1249, 1178, 1042, 839 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{17}H_{30}O_3SiNa$ $(M + Na)^+$ 333.1862, found 333.1850.

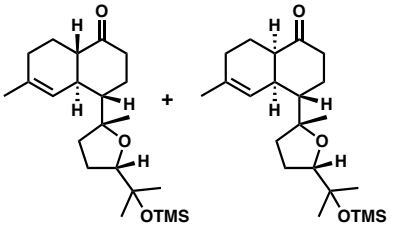


S23

Ketone S23. To a solution of (*Z*)-4-chloro-1-iodo-2-methylbut-1-ene (**S22**)[3] (0.154 g, 0.669 mmol) in Et_2O (1.1 mL, previously sparged with argon gas for 20 min) at –78 ˚C was added *tert*-butyllithium (0.84 mL, 1.59 M in pentane, 1.34 mmol) dropwise *via* syringe. After 20 min, lithium 2-thienylcyanocuprate solution (2.70 mL, 0.25 M in THF, 0.669 mmol) was added dropwise *via* syringe. The reaction mixture was allowed to stir for 1 h at –78 ˚C. A solution of enone **S21** (0.139 g, 0.446 mmol) in Et_2O (0.5 mL) was added dropwise *via* syringe. The transfer was completed with additional portions of Et_2O (2 x 0.25 mL). Immediately following this addition, BF_3•OEt_2 (75 μL, 0.580 mmol) was added dropwise *via* syringe. After allowing the reaction mixture to stir for 3 h at –78 ˚C, the reaction was quenched with 9:1 saturated NH_4Cl solution/NH_4OH (12 mL). After warming to room temperature, the solution turned a deep blue color. The aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with 9:1 saturated NH_4Cl solution/NH_4OH (2 x 15 mL), washed with brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 7.5% EtOAc/hexanes) to afford the title compound (0.150 g, 81%) as a white solid (mp 56–58 ˚C). $[\alpha]_D^{23}$ = –4.3 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.37 (d, *J* = 9.5 Hz, 1H), 3.69 (t, *J* = 6.8 Hz, 1H), 3.61 – 3.48 (m, 2H), 2.76 (ddd, *J* = 18.5, 9.8, 4.5 Hz, 1H), 2.58 (quin, *J* = 5.9 Hz, 1H), 2.47 – 2.35 (m, 3H), 2.29 (td, *J* = 15.0, 5.5 Hz, 1H), 2.15 (dd, *J* = 14.5, 10.0 Hz, 1H), 2.11 – 2.05 (m, 1H), 1.86 (dt, *J* = 9.5, 6.5 Hz, 1H), 1.79 (ddd, *J* = 11.8, 8.5, 3.8 Hz, 1H), 1.72 – 1.62 (m, 1H), 1.68 (s, 3H), 1.62 – 1.51 (m, 3H), 1.19

(s, 3H), 1.17 (s, 3H), 1.07 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.9, 133.9, 127.4, 85.6, 85.1, 75.3, 50.7, 47.7, 42.5, 40.4, 38.4, 36.7, 35.2, 28.1, 27.2, 25.5, 23.0, 21.8, 2.8; IR (thin film) ν 2964, 2873, 1718, 1454, 1378, 1249, 1174, 1043, 839 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{22}H_{39}ClO_3SiNa$ $(M + Na)^+$ 437.2255, found 437.2252. ^{1}H-NOESY-2D (500 MHz, $CDCl_3$) spectra were obtained for ketone **S23** and selected NOE interactions are shown.

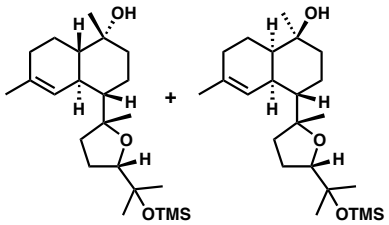




trans-**S24** *cis*-**S24**

***cis*- and *trans*-Decalones S24.** To a solution of alkyl chloride **S23** (0.150 g, 0.362 mmol) in *tert*-butyl alcohol (1.81 mL) at 30 ˚C was added potassium *tert*-butoxide (0.27 mL, 1.6 M in THF, 0.434 mmol) dropwise *via* syringe. After stirring for 6 h at 30 ˚C, the reaction was quenched with saturated NH_4Cl solution (12 mL). The aqueous layer was extracted with pentane (4 x 10 mL), and the combined organic extracts were washed with water (3 x 10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 5% EtOAc/hexanes) to afford a 1.3:1 mixture of *cis*- and *trans*-decalones (99.7 mg, 73%) as a colorless oil, which was characterized as a mixture. $[\alpha]_D^{22}$ = –79.2 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.27

(s, 1H), 5.38 (s, 1H), 3.80 (t, J = 6.3 Hz, 1H), 3.73 (dd, J = 7.9, 5.5 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.68 – 2.61 (m, 1H), 2.44 – 2.34 (m, 3 H), 2.26 – 2.15 (m, 4H), 2.13 – 1.38 (m, 21H), 1.64 (s, 3H), 1.58 (s, 3H), 1.20 (s, 3H), 1.18 (s, 9H), 1.17 (s, 3H), 1.07 (s, 3H), 0.11 (s, 9H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.2, 213.1, 133.1, 133.0, 127.7, 125.5, 86.4, 86.1, 85.4, 85.2, 75.6, 75.4, 51.4, 50.8, 50.0, 45.6, 44.4, 41.0, 38.8, 38.6, 36.5, 36.4, 29.9, 29.6, 28.0, 27.9, 27.2, 26.0, 25.7, 25.1, 24.8, 24.2, 23.84, 23.77, 22.7, 22.2, 22.0, 19.4, 2.77, 2.74; IR (thin film) ν 2963, 2875, 1714, 1454, 1378, 1249, 1172, 1041, 839 cm^{-1}; HRMS (ESI) m / z calcd for $C_{22}H_{38}O_3SiNa$ $(M + Na)^+$ 401.2488, found 401.2474.



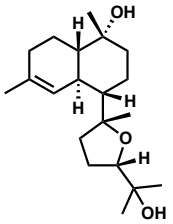
S25 **S26**

Decalins S25 and S26. Methylmagnesium bromide (0.44 mL, 3.0 M in Et_2O, 1.32 mmol) was added dropwise to a solution of a mixture of *cis*- and *trans*-decalones **S24** (99.7 mg, 0.263 mmol) in THF (2.63 mL) cooled to 0 ˚C. The reaction mixture was allowed to warm to room temperature for 30 min, and the reaction was quenched with saturated aqueous NH_4Cl solution (6 mL) at 0 ˚C. The aqueous layer was extracted with Et_2O (3 x 6 mL). The combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10% EtOAc/hexanes), yielding *trans*-decalin **S25** (36.5 mg, 35%) as a colorless oil and *cis*-decalin **S26** (47.1 mg, 45%) as a white solid (mp 82–84 ˚C).

cis-Decalin **S26**: $[\alpha]_D^{22}$ = +62.4 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.74, (d, J = 5.0 Hz, 1 H), 3.71 (t, J = 6.3 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.00 – 1.80 (m, 5H), 1.66 – 1.44 (m, 9H),

1.61 (s, 3H), 1.31 (s, 3H), 1.28 – 1.10 (m, 1H), 1.13 (s, 3 H), 1.11 (s, 3H), 1.08 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.2, 128.1, 86.2, 85.4, 75.7, 72.5, 49.1, 46.2, 38.2, 36.9, 35.3, 31.0, 28.2, 28.0, 26.8, 25.10, 25.07, 23.6, 19.9, 18.7, 2.7; IR (thin film) ν 3370 (br), 2963, 2940, 2894, 2872, 1458, 1376, 1249, 1043, 839 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{23}H_{42}O_3SiNa$ $(M + Na)^+$ 417.2801, found 417.2801.

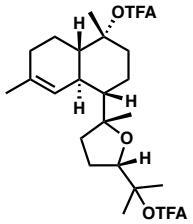
trans-Decalin **S25**: $[\alpha]_D^{22}$ = –22.3 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.31 (s, 1H), 3.79 (dd, *J* = 7.0, 5.5 Hz, 1H), 2.17 (ap t, *J* = 10.3 Hz, 1H), 2.06 – 1.89 (m, 3H), 1.87 – 1.78 (m, 2H), 1.73 – 1.67 (m, 1H), 1.66 – 1.11 (m, 9H), 1.62 (s, 3H), 1.21 (s, 3H), 1.19 (s, 3H), 1.14 (s, 3H), 1.09 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.7, 126.6, 87.1, 85.1, 75.7, 70.7, 52.3, 47.8, 40.7, 38.7, 38.5, 30.9, 28.6, 28.1, 25.6, 24.8, 24.7, 23.8, 22.9, 19.1, 2.8; IR (thin film) ν 3464 (br), 2962, 2871, 1453, 1377, 1249, 1171, 1083, 1043, 839 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{23}H_{42}O_3SiNa$ $(M + Na)^+$ 417.2801, found 417.2801.



S27

Diol S27. To a solution of *trans*-decalin **S25** (36.5 mg, 0.0925 mmol) in THF (0.93 mL) cooled to 0 ˚C was added TBAF (0.19 mL, 1.0 M in THF, 0.185 mmol). After 1 h, added additional TBAF (0.19 mL, 1.0 M in THF, 0.185). After 20 min, the reaction was quenched with water (5 mL). The reaction mixture was extracted with ether (4 x 5 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 15% EtOAc/hexanes) to afford diol **S27** (28.2 mg, 95%) as a white solid (mp 98–100 ˚C). $[\alpha]_D^{23}$ = –21.1 (c = 0.77, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ

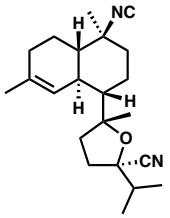
6.25, (s, 1H), 3.85 (dd, *J* = 7.8, 6.8 Hz, 1H), 2.27 – 2.18 (m, 1H), 2.17 – 1.88 (m, 4H), 1.85 – 1.60 (m, 6H), 1.64 (s, 3H), 1.52 – 1.40 (m, 3H), 1.35 (ddd, *J* = 24.5, 12.3, 5.8 Hz, 1H), 1.28 – 1.12 (m, 2H), 1.24 (s, 3H), 1.22 (s, 3H), 1.15 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.8, 125.9, 87.1, 84.4, 71.4, 70.7, 52.3, 47.9, 40.7, 38.7, 38.5, 30.7, 28.7, 27.7, 25.8, 24.5, 24.3, 24.0, 22.8, 19.2; IR (thin film) ν 3436 (br), 2965, 2936, 2870, 1453, 1375, 1147, 1078, 892, 756 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{34}O_3Na$ $(M + Na)^+$ 345.2406, found 345.2415.



S28

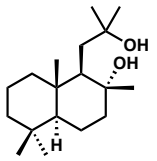
Bis(trifluoroacetate) S28. A mixture of diol **S27** (10.2 mg, 0.0316 mmol) and pyridine (30 μL, 0.371 mmol) in CH_2Cl_2 (0.32 mL) at 0 ˚C was treated with trifluoroacetic anhydride (20 μL, 0.144 mmol). After 20 min, added additional pyridine (20 μL, 0.247 mmol) and trifluoroacetic anhydride (20 μL, 0.144 mmol). After 20 min, the reaction was quenched with 1 M HCl (2 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic extracts were washed with water (5 mL), washed with saturated $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was used directly in the subsequent reaction. $[\alpha]_D^{23}$ = –30.0 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.20 (s, 1H), 4.07 (dd, *J* = 9.3, 3.8 Hz, 1H), 2.75 (dt, *J* = 14.8, 3.3 Hz, 1H), 2.33 (ap t, *J* = 10.3 Hz, 1H), 2.08 – 1.92 (m, 4H), 1.86 – 1.78 (m, 1H), 1.73 – 1.49 (m, 7H), 1.62 (s, 3H), 1.57 (s, 3H), 1.53 (s, 3H), 1.44 (td, *J* = 14.3, 3.8 Hz, 1H), 1.33 (td, *J* = 12.5, 2.8 Hz, 1H), 1.19 (t, *J* = 11.8 Hz, 1H), 1.16 – 1.06 (m, 1H), 1.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3 (q, *J* = 36.3 Hz), 156.2 (q, *J* = 40.8 Hz), 132.5, 125.3, 114.6 (q, *J* = 285.6 Hz), 114.5 (q, *J* = 285.3 Hz), 89.9, 89.0, 87.6, 82.9, 51.2,

48.8, 38.2, 37.8, 34.9, 30.5, 25.1, 25.0, 23.72, 23.70, 22.6, 21.2, 21.3, 18.7; IR (thin film) ν 2962, 2931, 2877, 1779, 1456, 1375, 1220, 1156 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{24}H_{32}F_6O_5Na$ $(M + Na)^+$ 537.2051, found 537.2051.



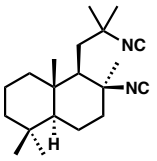
39

C14-Nitrile 39. The following procedure was adopted from Pronin *et al*.[6] Trifluoroacetate **S28** (10.2 mg, 0.0316 mmol) was dissolved in TMSCN (60 µL) and cooled to 0 ˚C. A solution of scandium(III) trifluoromethanesulfonate (1.6 mg, 0.00316 mmol) in TMSCN (0.11 mL) was added to the reaction mixture dropwise *via* syringe. After 30 min, the reaction mixture was allowed to warm to room temperature. After 4 h, the reaction was quenched with TMEDA (20 µL) and the volatiles were removed under reduced pressure. The crude residue was dissolved in hexanes (6 mL), washed with saturated aqueous $NaHCO_3$ solution (6 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 3 → 5% EtOAc/hexanes) to afford the title compound (2.0 mg, 19%) as a thin film. $[\alpha]_D^{22}$ = +32.1 (c = 0.20, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.02 (s, 1H), 2.28 – 2.20 (m, 1H), 2.20 – 2.02 (m, 4H), 2.02 – 1.77 (m, 7H), 1.72 – 1.48 (m, 3H), 1.65 (s, 3H), 1.39 – 1.27 (m, 1H), 1.31 (br s, 3H), 1.15 (d, *J* = 6.5 Hz, 3H), 1.08 (s, 3H), 1.05 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6 (br t), 133.8, 123.8, 120.8, 88.9, 85.0, 60.6 (br t, *J* = 5.1 Hz), 51.9, 47.5, 40.6, 38.9, 38.7, 37.9, 35.5, 30.4, 25.3, 24.0, 21.8, 20.3, 18.2, 17.9; IR (thin film) ν 2965, 2933, 2875, 2128, 1453, 1384, 1063 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{22}H_{32}N_2ONa$ $(M + Na)^+$ 363.2412, found 363.2417.



41

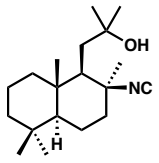
Diol 41. Methylmagnesium bromide (0.47 mL, 3.0 M in Et_2O, 1.40 mmol) was added dropwise to a solution of (3a*R*)-(+)-sclareolide (**40**) (70.0 mg, 0.280 mmol) in THF (2.8 mL) cooled to 0 ˚C. The reaction mixture was allowed to warm to room temperature for 30 min, and the reaction was quenched with saturated aqueous NH_4Cl solution (5 mL) at 0 ˚C. The aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 25% EtOAc/hexanes), yielding diol **41** (69.4 mg, 88%) as a white solid (mp 166–168 ˚C). $[\alpha]_D^{23}$ = +8.1 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.06 (s, 2H), 1.88 (dt, *J* = 12.5, 3.0 Hz, 1H), 1.74 – 1.32 (m, 7H), 1.30 – 1.07 (m, 3H), 1.27 (s, 3H), 1.22 (s, 3H), 1.19 (s, 3H), 0.98 – 0.82 (m, 3H), 0.87 (s, 3H), 0.78 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.4, 69.8, 56.3, 54.8, 44.4, 42.0, 40.1, 38.9, 38.5, 33.6, 33.3, 28.5, 25.1, 21.8, 20.4, 18.7, 15.6; IR (thin film) ν 3230 (br), 2964, 2934, 2868, 1467, 2128, 1451, 1386, 1155, 1124, 940, 756 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{18}H_{34}O_2Na$ $(M + Na)^+$ 305.2456, found 305.2451.



43

Diisocyanide 43. The following procedure was adopted from Pronin *et al*.[6] A mixture of diol (**41**) (25.8 mg, 0.0913 mmol) and pyridine (40 µL, 0.383 mmol) in CH_2Cl_2 (0.91 mL) at 0 ˚C was treated with trifluoroacetic anhydride (0.1 mL, 1.92 M in CH_2Cl_2, 0.192 mmol). After 15

minutes, the reaction was quenched with 1 M HCl (2 mL). The aqueous layer was extracted with hexanes (2 x 3 mL). The combined organic extracts were washed with water (5 mL), washed with saturated $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude trifluoroacetate was dissolved in TMSCN (0.1 mL) and cooled to 0 ˚C. A solution of scandium(III) trifluoromethanesulfonate (1.3 mg, 0.00274 mmol) in TMSCN (0.1 mL) was added. After 30 min, the reaction mixture was placed in a 3˚C refrigerator for 18 h. The reaction was quenched with TMEDA (20 μL) and the volatiles were removed under reduced pressure. The crude residue was suspended in hexanes (5 mL), washed with saturated aqueous $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 2.5% EtOAc/hexanes) to afford the title compound (6.3 mg, 23%) as a thin film. $[\alpha]_D^{24}$ = +17.1 (c = 0.60, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.13 (dt, *J* = 14.0, 3.0 Hz, 1H), 1.87 – 1.31 (m, 7H), 1.53 (s, 3H), 1.50 (s, 3H), 1.48 (s, 3H), 1.29 – 1.11 (m, 3H), 1.09 – 1.75 (m, 3H), 1.04 (s, 3H), 0.90 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0 (br t), 156.4 (br t), 61.4 (br t, *J* = 4.4 Hz), 57.4 (br t, *J* = 4.8 Hz), 55.4, 52.5, 42.0, 41.6, 40.9, 39.4, 37.9, 33.6, 33.5, 33.1, 32.6, 32.1, 21.9, 18.7, 18.1, 15.4; IR (thin film) ν 2929, 2841, 2133, 1465, 1444, 1392, 1367, 1156, 1131 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{20}H_{32}N_2Na$ $(M + Na)^+$ 323.2463, found 323.2456.



44

Isocyanide 44. The following procedure was adopted from Pronin *et al*.[6] A mixture of diol (**41**) (69.4 mg, 0.246 mmol) and pyridine (80 μL, 1.03 mmol) in CH_2Cl_2 (2.5 mL) at 0 ˚C was treated with trifluoroacetic anhydride (70 μL, 0.516 mmol). After 15 minutes, the reaction was quenched

with 1 M HCl (3 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were washed with water (5 mL), washed with saturated $NaHCO_3$ solution (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude trifluoroacetate was dissolved in TMSCN (0.25 mL) and cooled to 0 ˚C. A solution of scandium(III) trifluoromethanesulfonate (2.4 mg, 0.00492 mmol) in TMSCN (0.16 mL) was added. After 2 h at 0 ˚C, the reaction was quenched with pyridine (50 μL) and the volatiles were removed under reduced pressure. The crude residue was dissolved in MeOH (2 mL) and cooled to 0 ˚C. Potassium carbonate (68.0 mg, 0.492 mmol) was added in one portion. After 15 min, the reaction mixture was filtered and concentrated *in vacuo*. The crude residue was purified using flash chromatography (SiO_2, 10% EtOAc/hexanes) to afford the title compound (14.8 mg, 21%) as a solid (mp 156–158 ˚C). $[\alpha]_D^{21}$ = +27.3 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.10 (ap d, *J* = 14.0 Hz, 1H), 1.77 – 1.54 (m, 6H), 1.54 – 1.33 (m, 3H), 1.40 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H), 1.22 – 1.04 (m, 3H), 1.03 (s, 3H), 0.95 – 0.86 (m, 2H), 0.88 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0 (br t, *J* = 4.9 Hz), 70.3, 61.7 (br t, *J* = 4.3 Hz), 55.6, 51.7, 42.3, 41.8, 40.6, 39.4, 38.9, 33.57, 33.55, 32.8, 32.3, 31.7, 21.9, 18.8, 18.2, 15.1; IR (thin film) ν 3486 (br), 2950, 2919, 2839, 2134, 1466, 1442, 1389, 1365, 1154, 1129 cm^{-1}; HRMS (ESI) *m* / z calcd for $C_{19}H_{33}NONa$ $(M + Na)^+$ 314.2460, found 314.2469.

IV. Evaluation of Inhibition of *P. falciparum* Growth

Method: Drug sensitive and resistant strains of *P.* falciparum malaria (BEI Resources, MR4/ATCC, Manassas, VA) were cultured in human type O+ erythrocytes in complete medium consisting of RPMI 1640 (Gibco), 0.043 mg/mL gentamicin (Gibco), 0.014 mg/mL hypoxanthine (Acros), 38.5 mM HEPES (Sigma), 0.18% sodium bicarbonate (Cellgro), 0.20% glucose (MP Biomedical), 0.003 mM NaOH (Sigma), 0.2% Albumax (Gibco), and 5% human serum as previously described.[23] Briefly, cultures were maintained in 25-cm^2 flasks (Corning) at a volume of 10 mL, gassed for 30 s with 3% CO_2, 1% O_2, and 96% N_2, and were finally incubated at 37 ˚C. The antiplasmodial activity was determined with an SYBR Green based parasite proliferation assay as previously described.[24] After 72 h of incubation in the presence of serial dilutions of compounds, the increase of parasite DNA contained in human red blood cells was evaluated. The relative fluorescence values were measured using a Molecular Devices SpectraMAX Gemini EM fluorimeter (excitation 495 nm, and emission 525 nm). Data were analyzed using Microsoft Excel and were plotted using SigmaPlot 10 (Systat).

[23] Le Roch, K. G.; Zhou, Y.; Blair, P. L.; Grainger, M.; Moch, J. K.; Haynes, J. D.; De La Vega, P.; Holder, A. A.; Batalov, S.; Carucci, D. J. *Science* **2003**, *301*, 1503–1508.

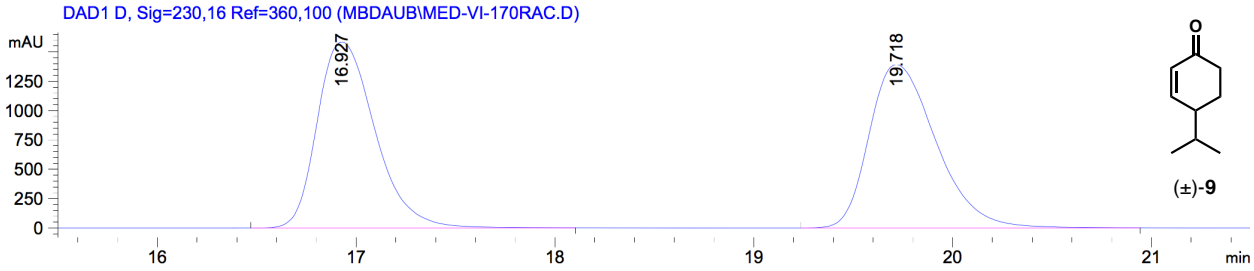
[24] Prudhomme, J.; McDaniel, E.; Ponts, N.; Bertani, S.; Fenical, W.; Jensen, P.; Le Roch, K. *PLoS One* **2008**, *3*, e2335.

Table S1. Activity of synthetic ICTs against wild-type (3D7) and chloroquine-resistant (Dd2) *P. falciparum*.

Compound	Pf strain[a]	IC50 [nM]	IC50 [μg/mL]	std error[b]	*R*	hillslope	Chloroquine[c] IC50 [μM]	std error
2	**3D7**	8.4	0.0033	0.0007	0.9914	1.342	0.0063	0.002
2	**Dd2**	4.6	0.0018	0.0002	0.9938	2.937	0.0399	0.0035
38	**3D7**	139	0.0508	0.0072	0.9952	2.3689	0.0052	0.0001
38	**Dd2**	144	0.0526	0.0093	0.9959	1.4242	0.0275	0.0086
39	**3D7**	175	0.0596	0.0117	0.9903	1.4691	0.0066	0.0004
39	**Dd2**	123	0.0418	0.0188	0.9808	0.6601	0.0413	0.0037
(±)-15	**3D7**	705	0.1631	0.0894	0.9899	0.5629	0.0059	0.0009
(±)-15	**Dd2**	247	0.057	0.0234	0.9961	0.5342	0.0322	0.0039
(±)-16[d]	**3D7**	180	0.0417	0.0191	0.9748	0.8015	0.0091	0.0007
(±)-16[d]	**Dd2**	45	0.0104	0.0073	0.9882	0.2933	0.0337	0.0031
22	**3D7**	12	0.0034	0.0006	0.9963	7.3863	0.0089	0.0018
22	**Dd2**	16	0.0043	0.0001	0.9979	4.6016	0.0497	0.0157
23	**3D7**	2.9	0.0008	0.0002	0.984	1.3984	0.0089	0.0018
23	**Dd2**	31	0.0084	0.0016	0.9917	1.5004	0.0497	0.0157
24	**3D7**	138	0.0342	0.0037	0.9935	2.6747	0.0089	0.0018
24	**Dd2**	200	0.0495	0.0089	0.9939	1.3615	0.0497	0.0157
28	**3D7**	15	0.0041	0.0006	0.9954	1.6148	0.0089	0.0018
28	**Dd2**	17	0.0047	0.0003	0.9983	3.1883	0.0497	0.0157
(±)-28[e]	**3D7**	27	0.0074	0.0013	0.9927	--	0.0058	0.0005
(±)-28[e]	**Dd2**	46	0.0127	0.0016	0.9918	--	0.0521	0.0274
29	**3D7**	1150	0.3155	0.0179	0.9989	2.0297	0.0089	0.0018
29	**Dd2**	958	0.2628	0.0427	0.9962	1.0929	0.0497	0.0157
30	**3D7**	312	0.0771	0.0032	0.9995	2.1804	0.0089	0.0018
30	**Dd2**	529	0.1308	0.0057	0.999	2.8612	0.0497	0.0157
(±)-36[f]	**3D7**	302	0.0836	0.018	0.9773	4.7837	0.0091	0.0007
(±)-36[f]	**Dd2**	205	0.0566	0.007	0.9833	3.2312	0.0337	0.0031
(±)-37[g]	**3D7**	27	0.0075	0.0009	0.9831	2.043	0.0091	0.0007
(±)-37[g]	**Dd2**	24	0.0065	0.0009	0.9879	1.2806	0.0337	0.0031
43	**3D7**	1.9	0.0006	0.0002	0.9833	1.7569	0.0059	0.0009
43	**Dd2**	1.6	0.0005	0.0002	0.9903	0.7528	0.0322	0.0039
44	**3D7**	244	0.0745	0.0083	0.997	1.4462	0.0061	0.0005
44	**Dd2**	416	0.1271	0.0438	1.2621	1.2721	0.0419	0.0905

[a]3D7 is a chloroquine-sensitive strain of *P. falciparum*. Dd2 is a chloroquine-resistant strain of *P. falciparum*. [b]n = 3. [c]Chloroquine was used as the antimalarial standard. [d]Precipitate at 33.3 μg/mL. [e]Average of three separate assays. [f]Precipitate at 11.1 μg/mL. [g]Precipitate at 3.7 μg/mL.

Determination of enantiomeric excess of (*R*)-cryptone (**9**)
Chiralpak AD-H column, 2% *i*PrOH in hexanes, flow rate of 0.5 mL/min



Signal 3: DAD1 D, Sig=230,16 Ref=360,100

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2	19.718	BB	0.3625	3.25110e4	1391.95129	50.4496
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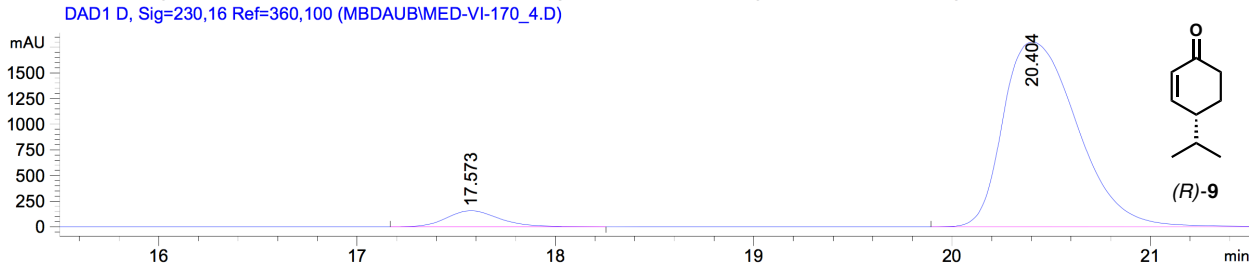

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

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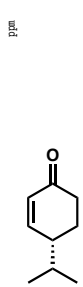
Totals :				4.96805e4	1956.46533	

1H spectrum



9: (±)-cryptone

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DE 6.00 usec
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MCWRK 0.01500000 sec

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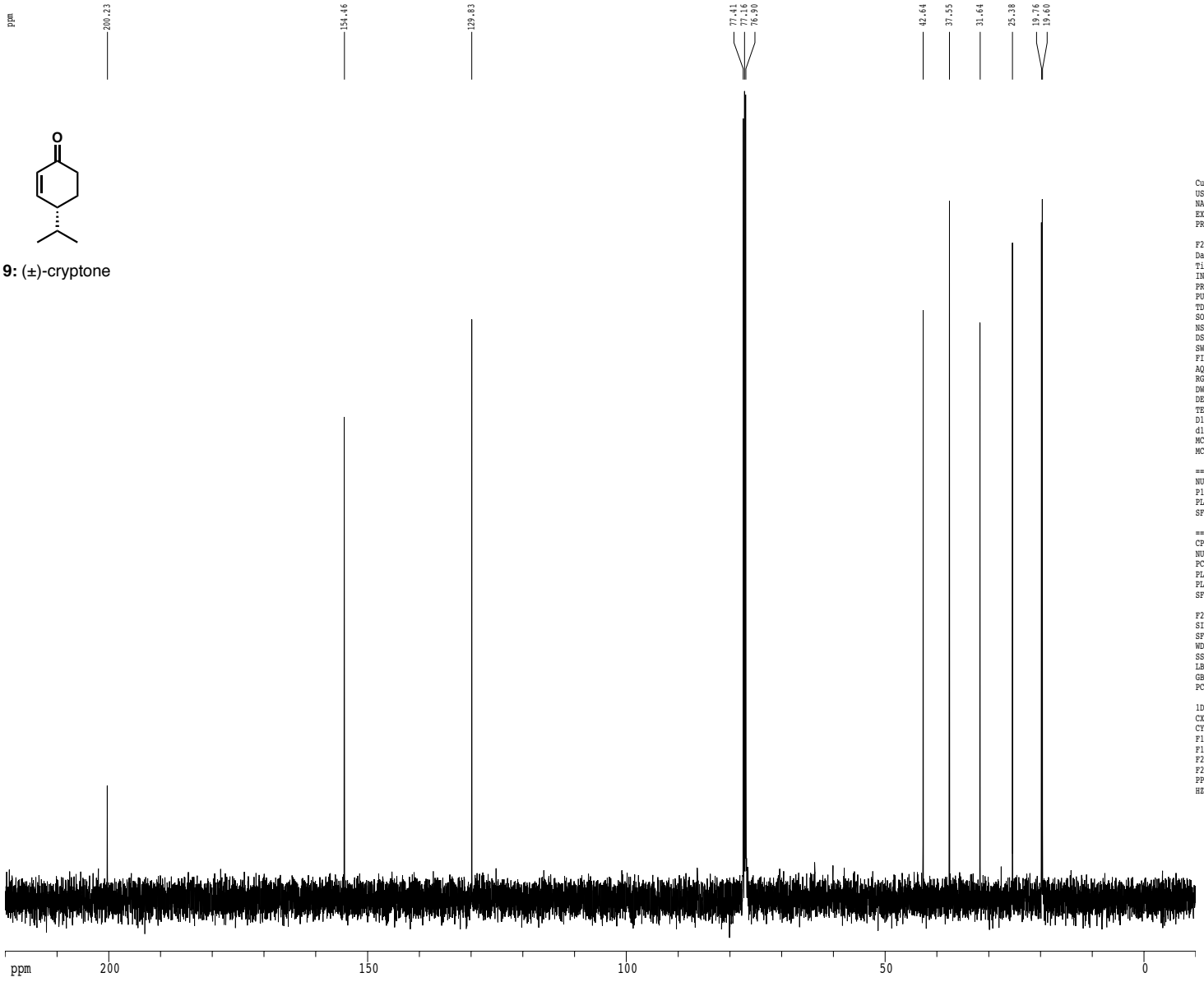
13C spectrum with 1H decoupling



9: (±)-cryptone

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SFO1         125.5327181 MHz

======== CHANNEL f2 ========
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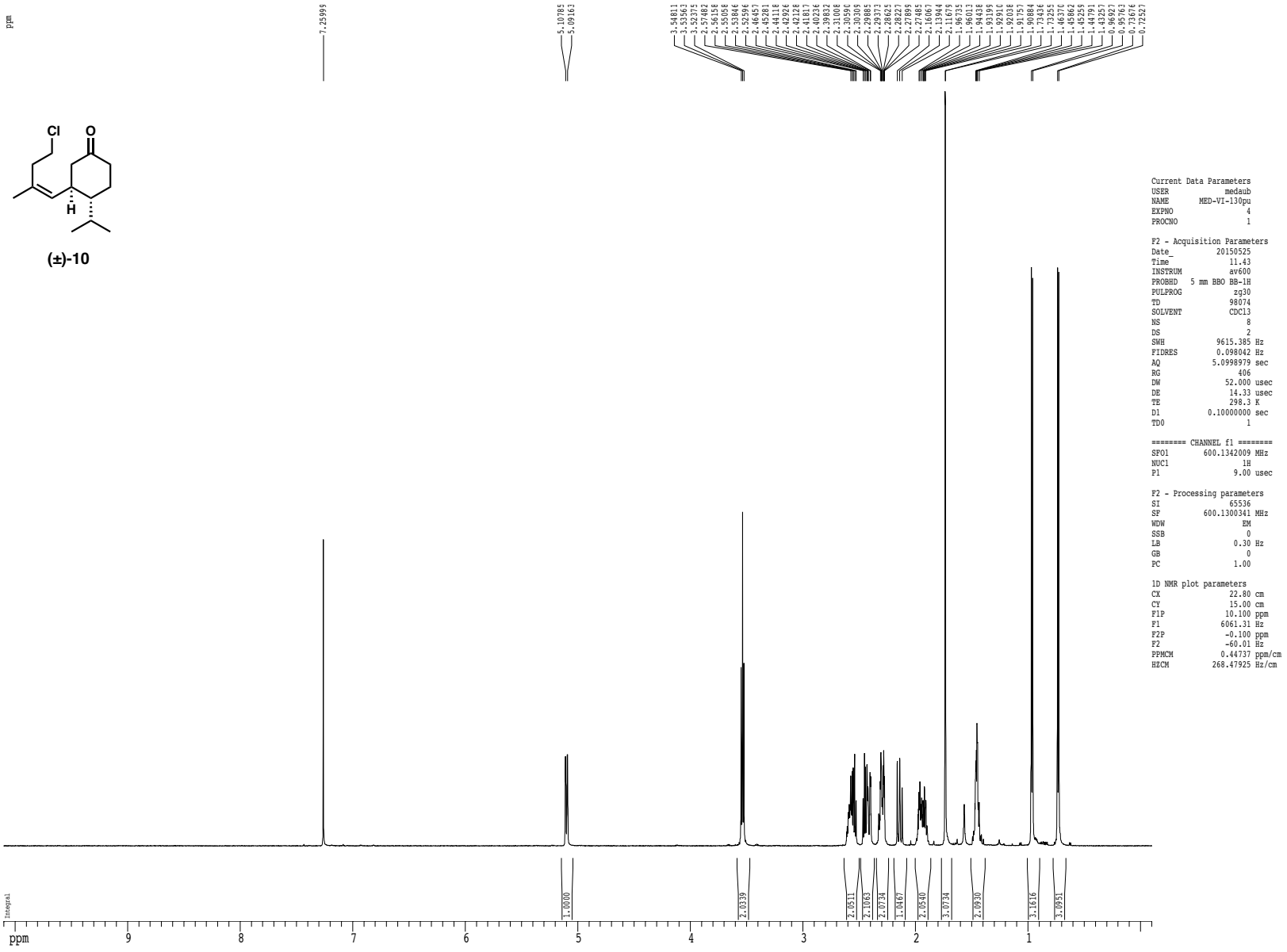
PL2                -3.00 dB
PL12               12.80 dB
SFO2         499.1824959 MHz

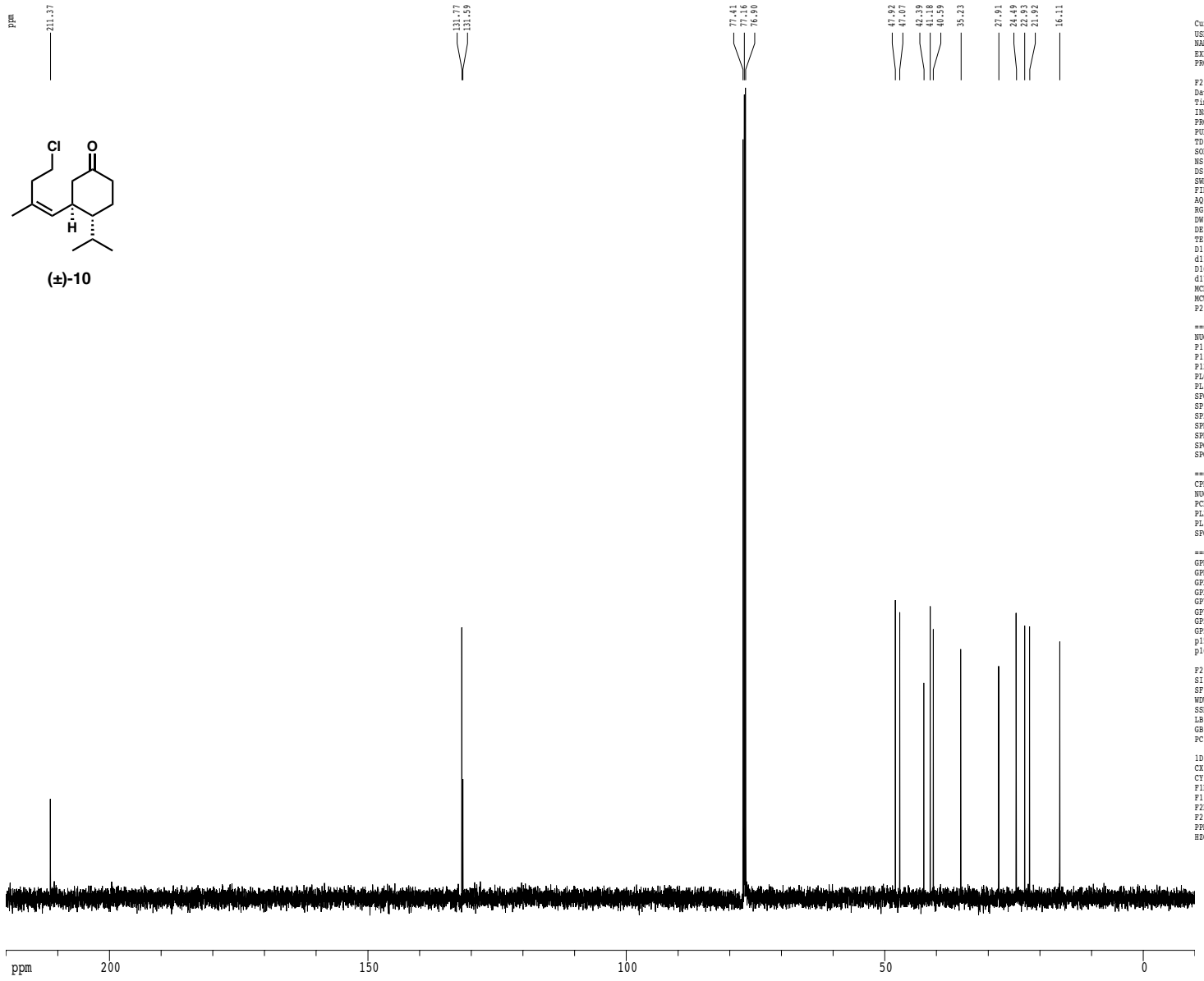
F2 - Processing parameters
SI                65536
SF           125.5188998 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P              220.000 ppm
F1             27614.16 Hz
F2P              -10.000 ppm
F2             -1255.19 Hz
PPMCM          10.08772 ppm/cm
HZCM         1266.19946 Hz/cm
```

1H spectrum


ppm
7.25999
5.10785
5.09163
3.54811
3.53563
3.52375
3.57482
2.56158
2.55058
2.53846
2.52596
2.46457
2.45281
2.44118
2.42826
2.42128
2.41817
2.40236
2.39832
2.31008
2.30590
2.30309
2.29885
2.29371
2.28625
2.28277
2.27899
2.27485
2.16067
2.13944
2.11679
1.96735
1.96013
1.94438
1.93199
1.92916
1.92038
1.91375
1.90884
1.73436
1.73255
1.46370
1.45862
1.45259
1.44791
1.43257
0.96927
0.95761
0.73876
0.72327
Cl
O
H
(±)-10
Current Data Parameters
USER medaub
NAME MED-VI-130pu
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150525
Time 11.43
INSTRUM av600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 98074
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 406
DW 52.000 usec
DE 14.33 usec
TE 298.3 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.1342009 MHz
NUC1 1H
P1 9.00 usec
F2 - Processing parameters
SI 65536
SF 600.1300341 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 10.100 ppm
F1 6061.31 Hz
F2P -0.100 ppm
F2 -60.01 Hz
PPMCM 0.44737 ppm/cm
HZCM 268.47925 Hz/cm
Integral
1.0000
2.0339
2.0511
2.1063
2.0734
1.0467
2.0540
3.0734
2.0930
3.1616
3.0951
ppm
9
8
7
6
5
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME         MED-VI-130pu
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20150525
Time              11.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  128
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1            0.00 Hz
SPOFF2            0.00 Hz

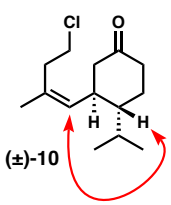
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2        500.2225011 MHz

====== 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          125.7804085 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         1268.83752 Hz/cm
```

noesygp



(±)-10

NOE


```
Current Data Parameters
NAME         MED-VI-130pu
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150525
Time                11.46
INSTRUM              av-600
PROBHD    5 mm BBO BB-1H
PULPROG        noesygpph
TD                   2048
SOLVENT              CDCl3
NS                      2
DS                      4
SWH              4930.966 Hz
FIDRES           2.407698 Hz
AQ               0.2076672 sec
RG                    912
DW                101.400 usec
DE                 13.47 usec
TE                298.2 K
D0             0.00008994 sec
D1             2.00000000 sec
D8             1.00000000 sec
D16            0.00020000 sec
IN0            0.00020280 sec

-------- CHANNEL f1 --------
SFO1          600.1323929 MHz
NUC1                    1H
P1                   9.00 usec
P2                  18.00 usec
PLW1          60.25600052 W

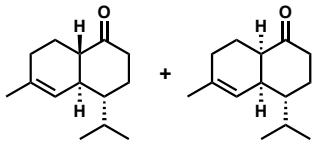
------ GRADIENT CHANNEL -----
GPNAM[1]       SMSQ10.100
GPZ1                40.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    113
SFO1             600.1324 MHz
FIDRES          43.636871 Hz
SW                  8.216 ppm
FnMODE        States-TPPI

F2 - Processing parameters
SI                    1024
SF            600.1300341 MHz
WDW                   QSINE
SSB                       2
LB          0 Hz
GB          0
PC                    4.00

F1 - Processing parameters
SI                    1024
MC2           States-TPPI
SF            600.1300341 MHz
WDW                   QSINE
SSB                       2
LB          0 Hz
GB          0
```

1H spectrum



(±)-11 + (±)-12


```
Current Data Parameters
USER                medaub
NAME          MED-VI-132pu
EXPNO                   1
PROCNO                  1

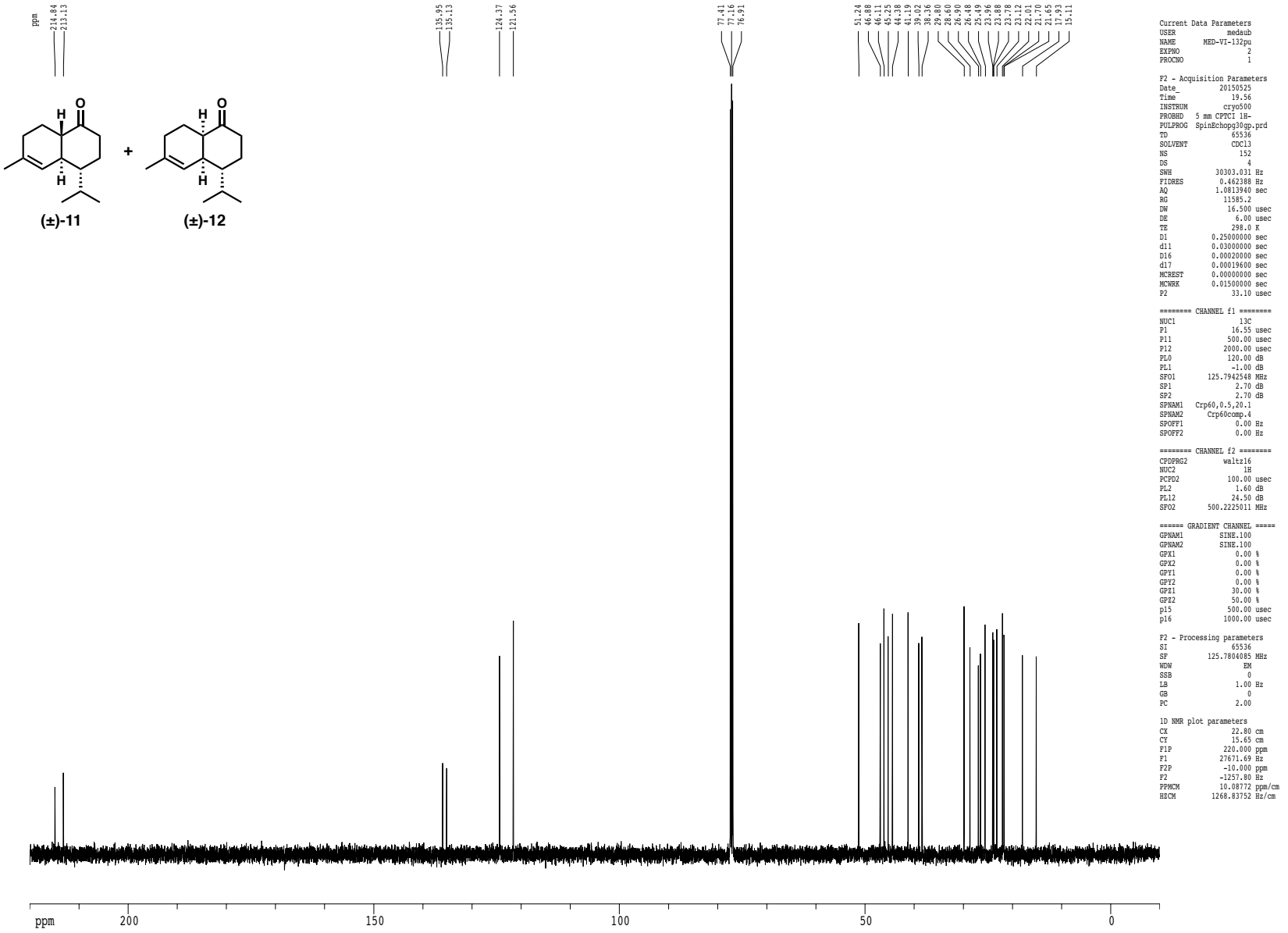
F2 - Acquisition Parameters
Date_            20150525
Time                19.53
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           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                  7.50 usec
PL1                 1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200316 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                10.100 ppm
F1               5052.22 Hz
F2P                -0.100 ppm
F2                -50.02 Hz
PPMCM             0.44737 ppm/cm
HZCM            223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME        MED-VI-132pu
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20150525
Time              19.56
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 152
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             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

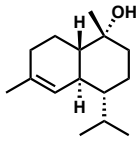
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2               1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== 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          125.7804085 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                2.00

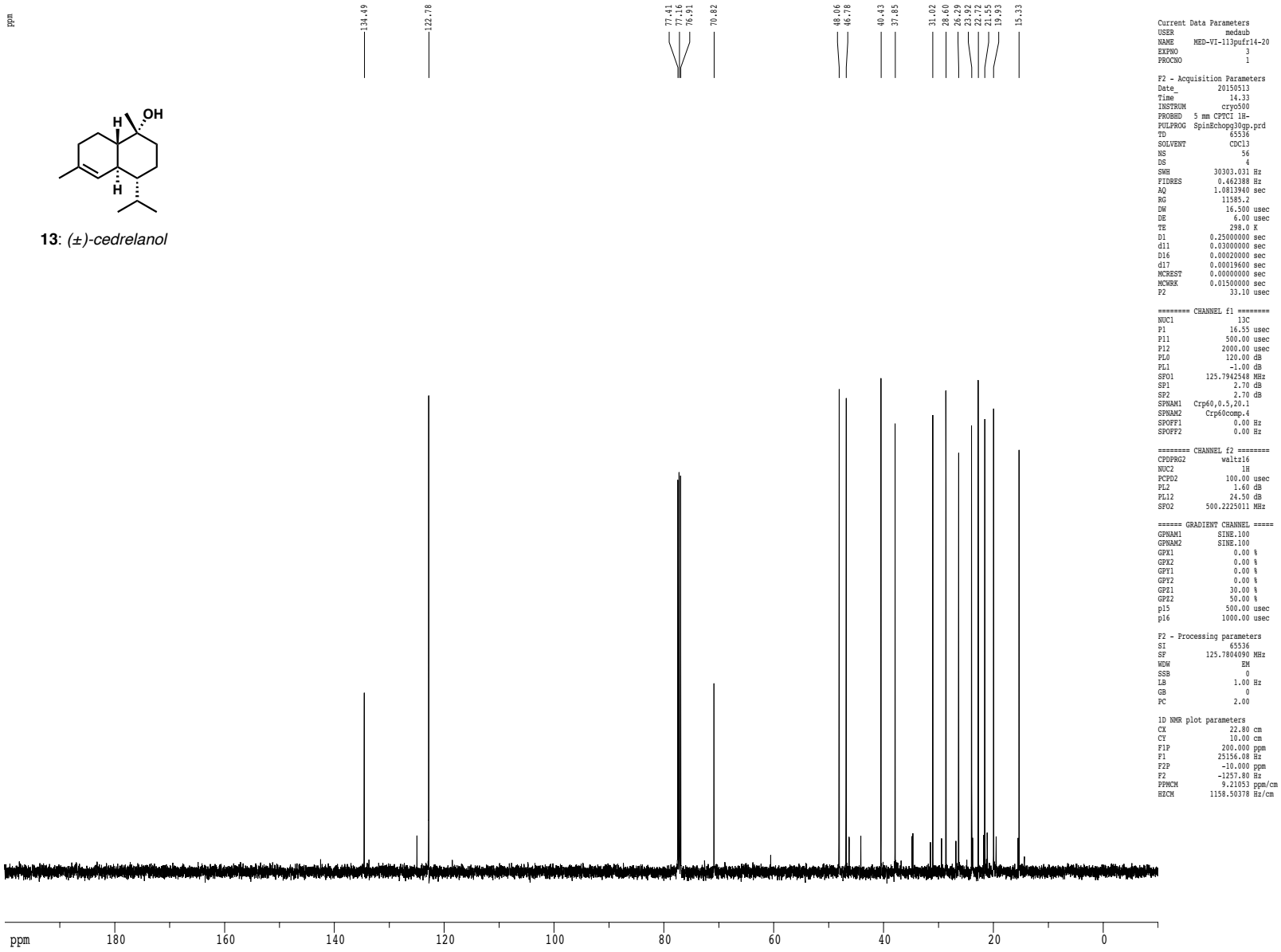
1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P              220.000 ppm
F1             27671.69 Hz
F2P              -10.000 ppm
F2             -1257.80 Hz
PPMCM           10.08772 ppm/cm
HZCM          1268.83752 Hz/cm
```

1H spectrum



13: *(±)-cedrelanol*

Z-restored spin-echo 13C spectrum with 1H decoupling



13: *(±)-cedrelanol*

```
Current Data Parameters
USER                medaub
NAME       MED-VI-113pufr14-20
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150513
Time                14.33
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     56
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

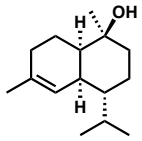
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== 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           125.7804090 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  10.00 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



14: *(±)-torreyol*

Current Data Parameters
USER medaub
NAME MED-VI-113pufr22-30
EXPNO 1
PROCNO 1

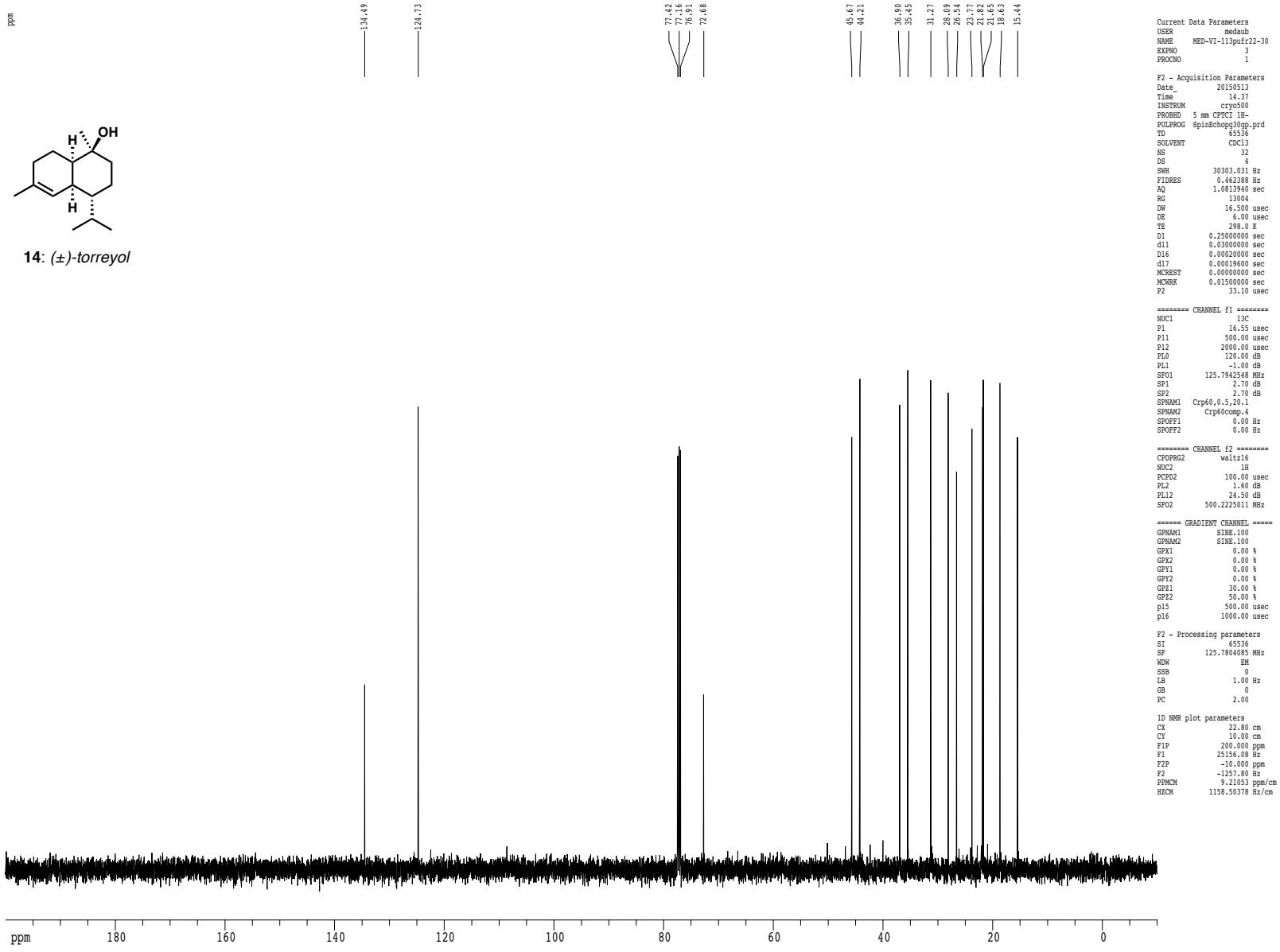
F2 - Acquisition Parameters
Date_ 20150513
Time 13.57
INSTRUM av600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 98074
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 645
DW 52.000 usec
DE 14.33 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1342009 MHz
NUC1 1H
P1 9.00 usec

F2 - Processing parameters
SI 65536
SF 600.1300341 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 10.100 ppm
F1 6061.31 Hz
F2P -0.100 ppm
F2 -60.01 Hz
PPMCM 0.44737 ppm/cm
HZCM 268.47925 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



14: *(±)-torreyol*

```
Current Data Parameters
USER                medaub
NAME        MED-VI-113pufr22-30
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150513
Time                14.37
INSTRUM          cryo500
PROBHD    5 mm CPPCI 1H-
PULPROG   SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      4
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                  13004
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                 33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1                0.00 Hz
SPOFF2                0.00 Hz

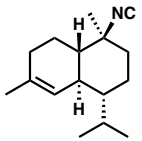
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2         500.2225011 MHz

====== 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           125.7804085 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  10.00 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



(±)-**15**: *10-isocyano-4-cadinene*


```
Current Data Parameters
USER              medaub
NAME      MED-VI-152pu2fr9-13
EXPNO                    2
PROCNO                   1

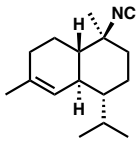
F2 - Acquisition Parameters
Date_          20150609
Time_             17.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ              5.0998774 sec
RG                   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          500.2200313 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               10.100 ppm
F1                5052.22 Hz
F2P               -0.100 ppm
F2                -50.02 Hz
PPMCM           0.44737 ppm/cm
HZCM          223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



(±)-**15**: *10-isocyano-4-cadinene*


```
Current Data Parameters
USER              medaub
NAME      MED-VI-152pu2fr9-13
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150609
Time              17.34
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopq30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   696
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
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

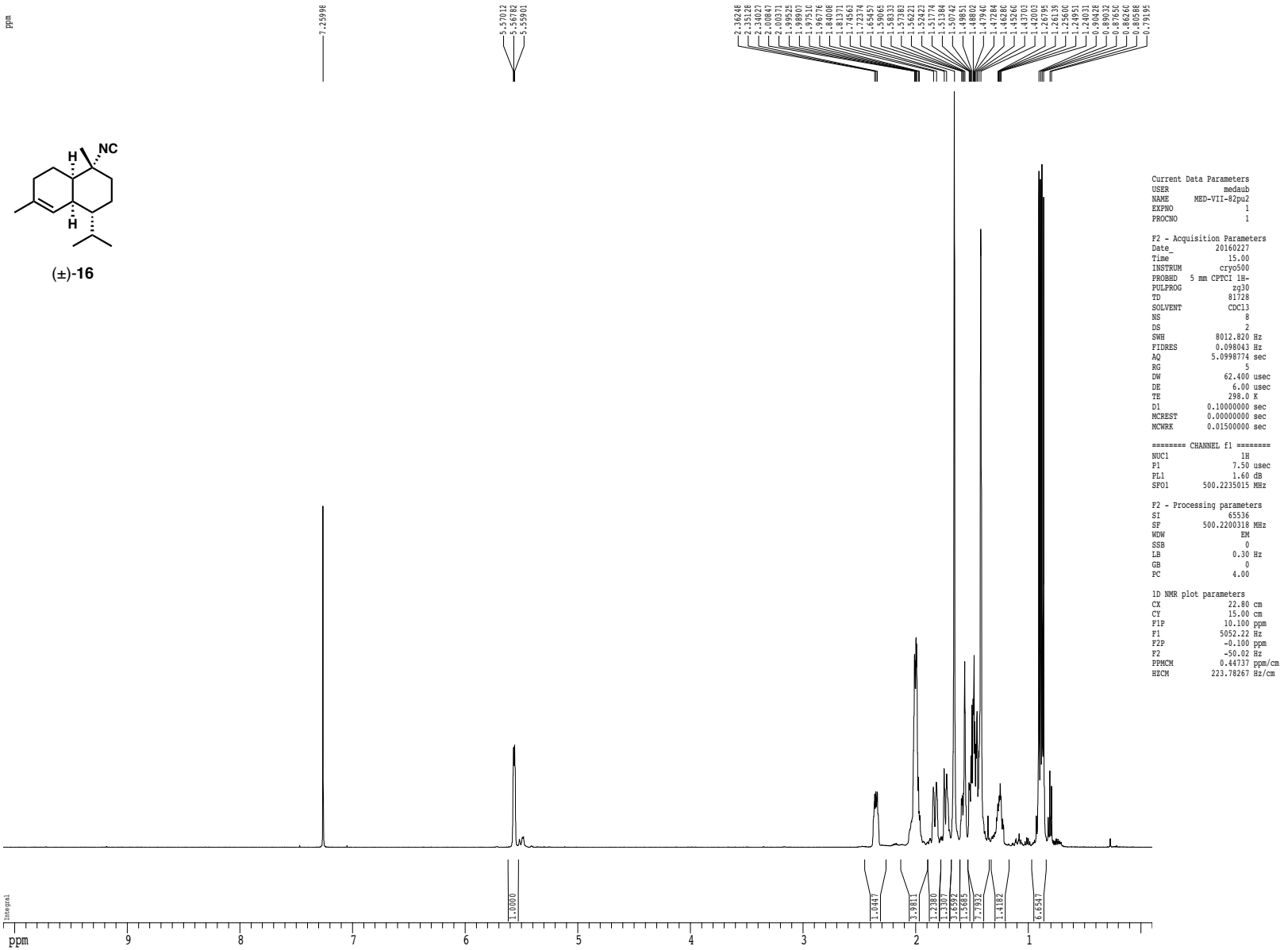
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== 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

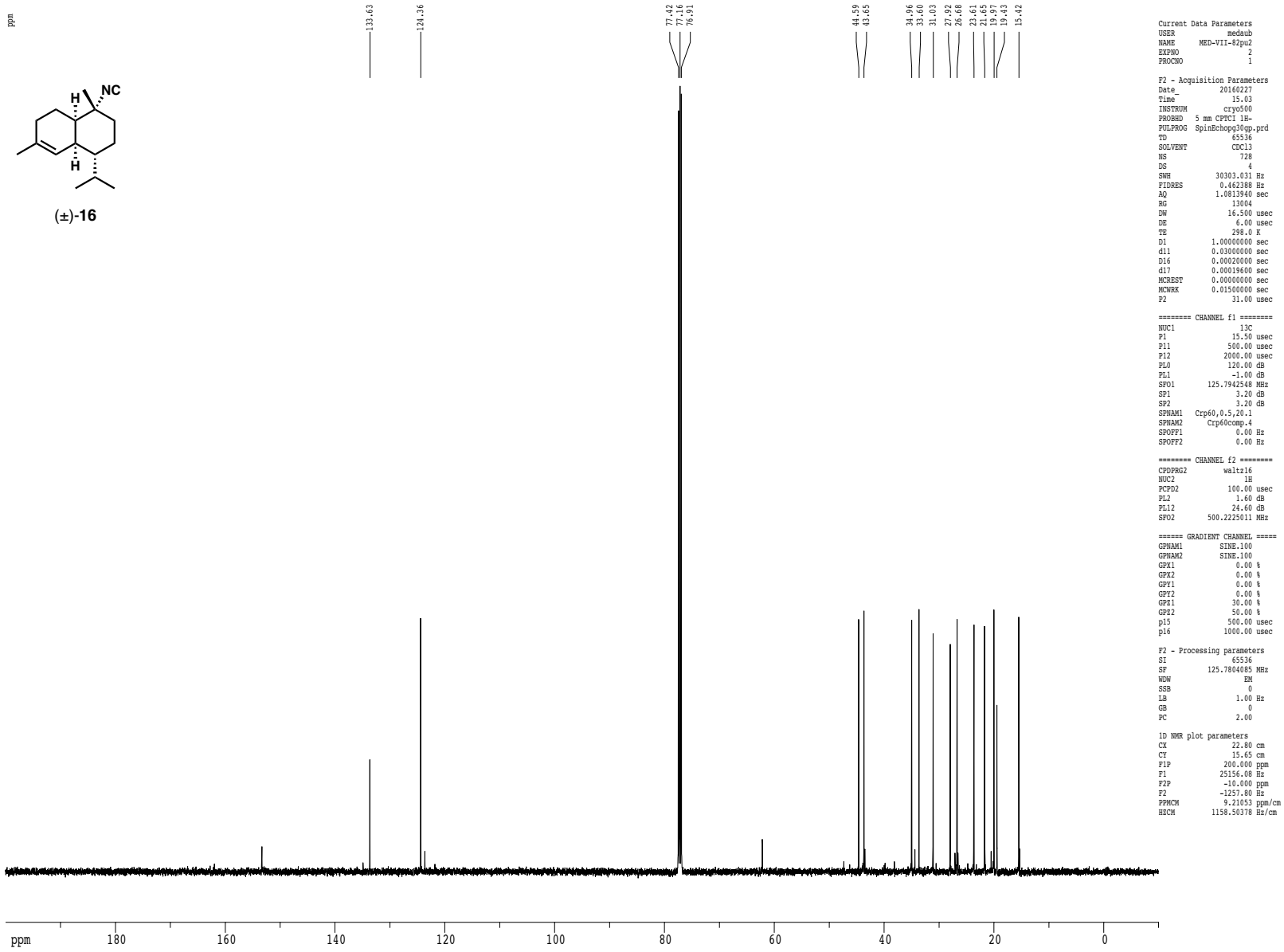
F2 - Processing parameters
SI                 65536
SF          125.7804075 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 0.50

1D NMR plot parameters
CX                22.80 cm
CY                30.00 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


ppm
7.25998
5.57012
5.56782
5.55901
2.36248
2.35128
2.34027
2.00847
2.00571
1.99935
1.99807
1.97510
1.96776
1.84008
1.81371
1.74563
1.72374
1.65457
1.59065
1.58333
1.57386
1.56223
1.54774
1.51384
1.50742
1.49851
1.48802
1.47940
1.47284
1.46286
1.45266
1.43703
1.42001
1.26196
1.25638
1.25600
1.24951
1.24031
0.90428
0.89032
0.87656
0.86266
0.80588
0.79195
H
NC
H
(±)-16
Current Data Parameters
USER medaub
NAME MED-VII-82pu2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160227
Time 15.00
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 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200318 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 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm
Integral
1.0000
1.0447
3.0811
1.2380
1.1430
3.5692
1.5685
7.7932
1.4182
6.6547
ppm
9
8
7
6
5
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VII-82pu2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160227
Time 15.03
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 728
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 13004
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 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

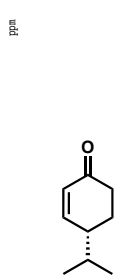
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== 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 125.7804085 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



9: *(–)-cryptone*

Current Data Parameters
USER medaub
NAME MED-VI-170pu2
EXPNO 1
PROCNO 1

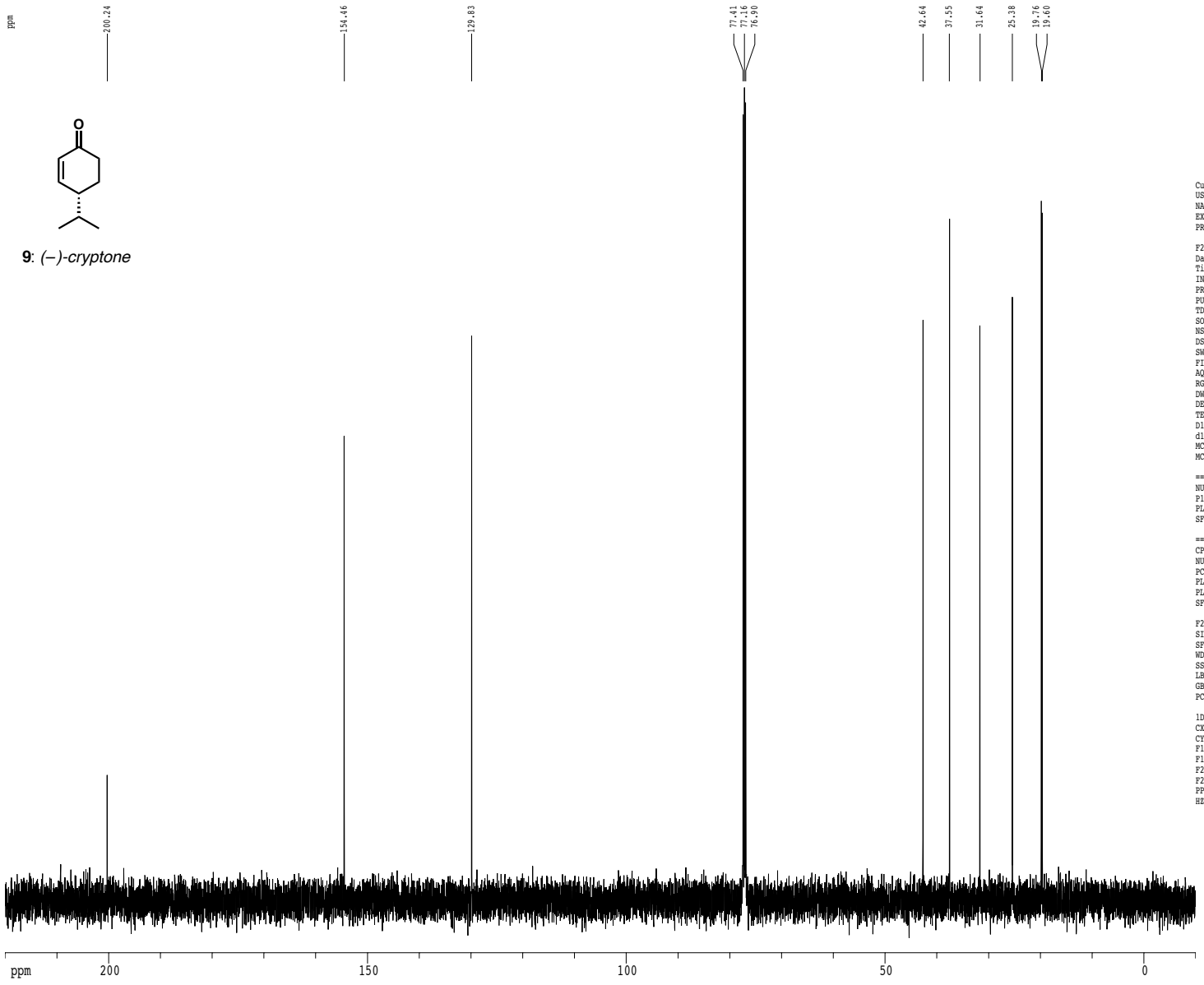
F2 - Acquisition Parameters
Date_ 20150629
Time 11.34
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 1824.6
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.1834943 MHz

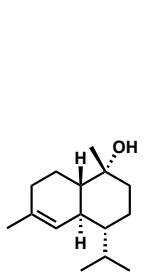
F2 - Processing parameters
SI 65536
SF 499.1800272 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 30.00 cm
F1P 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm

13C spectrum with 1H decoupling



1H spectrum



13: *(+)-cedrelanol*


```
Current Data Parameters
USER                medaub
NAME      MED-VI-191pufr17-26
EXPNO                    1
PROCNO                   1

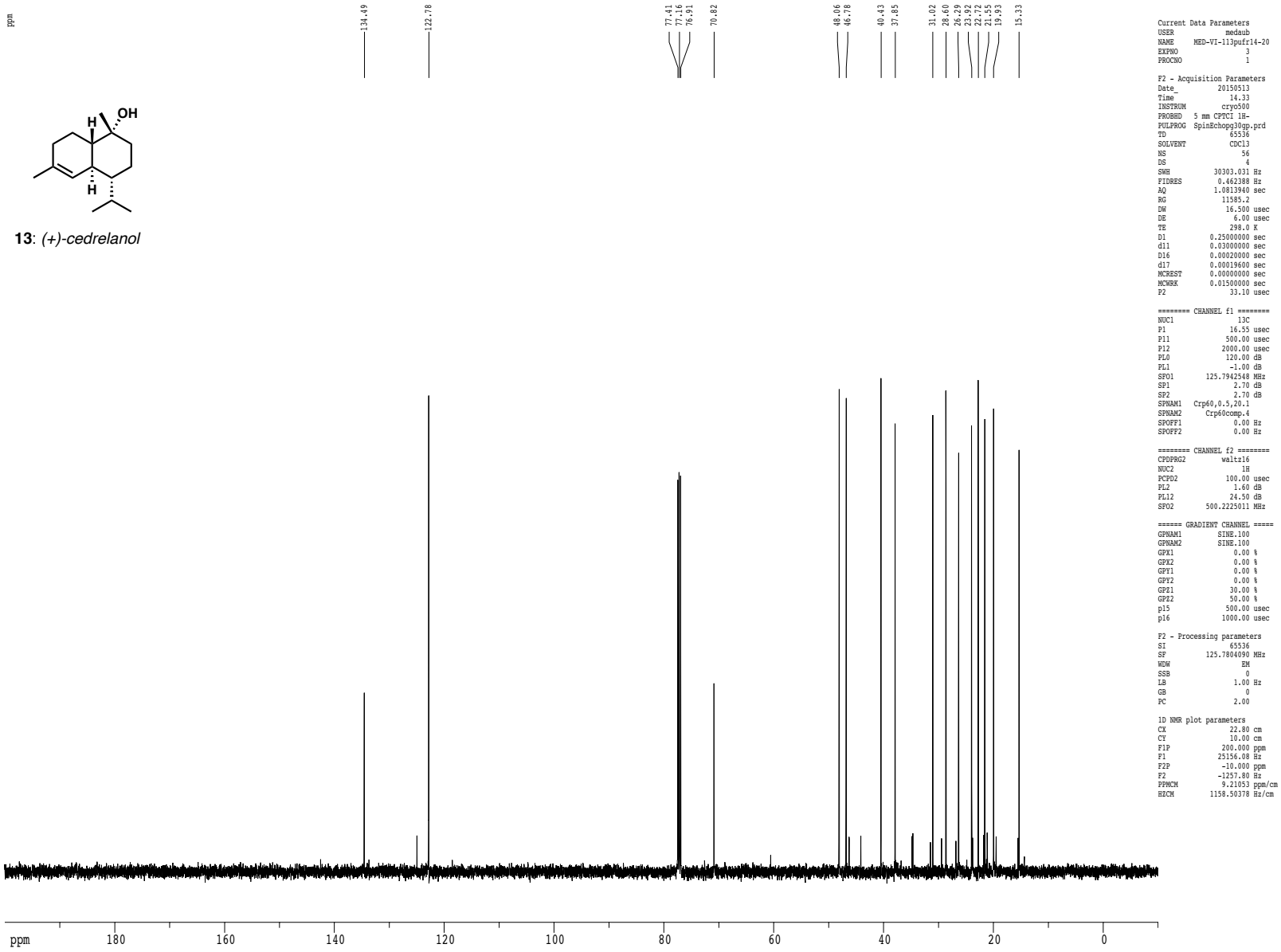
F2 - Acquisition Parameters
Date_            20150720
Time                18.12
INSTRUM           av600
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  98074
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ               5.0998979 sec
RG                    203
DW                 52.000 usec
DE                 14.33 usec
TE                 294.7 K
D1              0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                   1H
P1                  9.00 usec

F2 - Processing parameters
SI                    65536
SF            600.1300346 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                 10.100 ppm
F1                6061.31 Hz
F2P                -0.100 ppm
F2                 -60.01 Hz
PPMCM             0.44737 ppm/cm
HZCM            268.47925 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



13: *(+)-cedrelanol*

```
Current Data Parameters
USER                medaub
NAME       MED-VI-113pufr14-20
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150513
Time                14.33
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     56
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

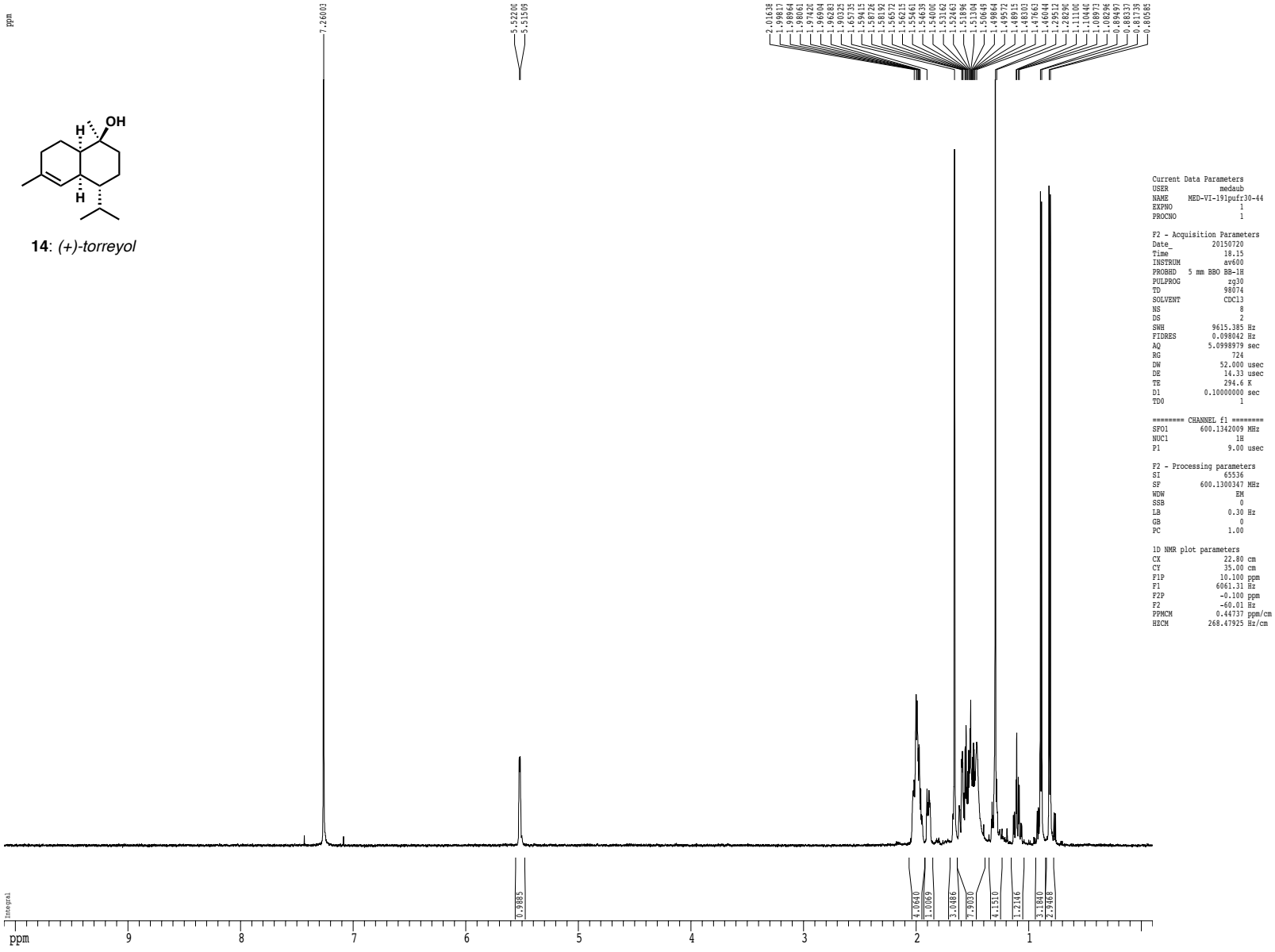
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== 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           125.7804090 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  10.00 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



14: *(+)-torreyol*

```
Current Data Parameters
USER              medaub
NAME     MED-VI-191pufr30-44
EXPNO                    1
PROCNO                   1

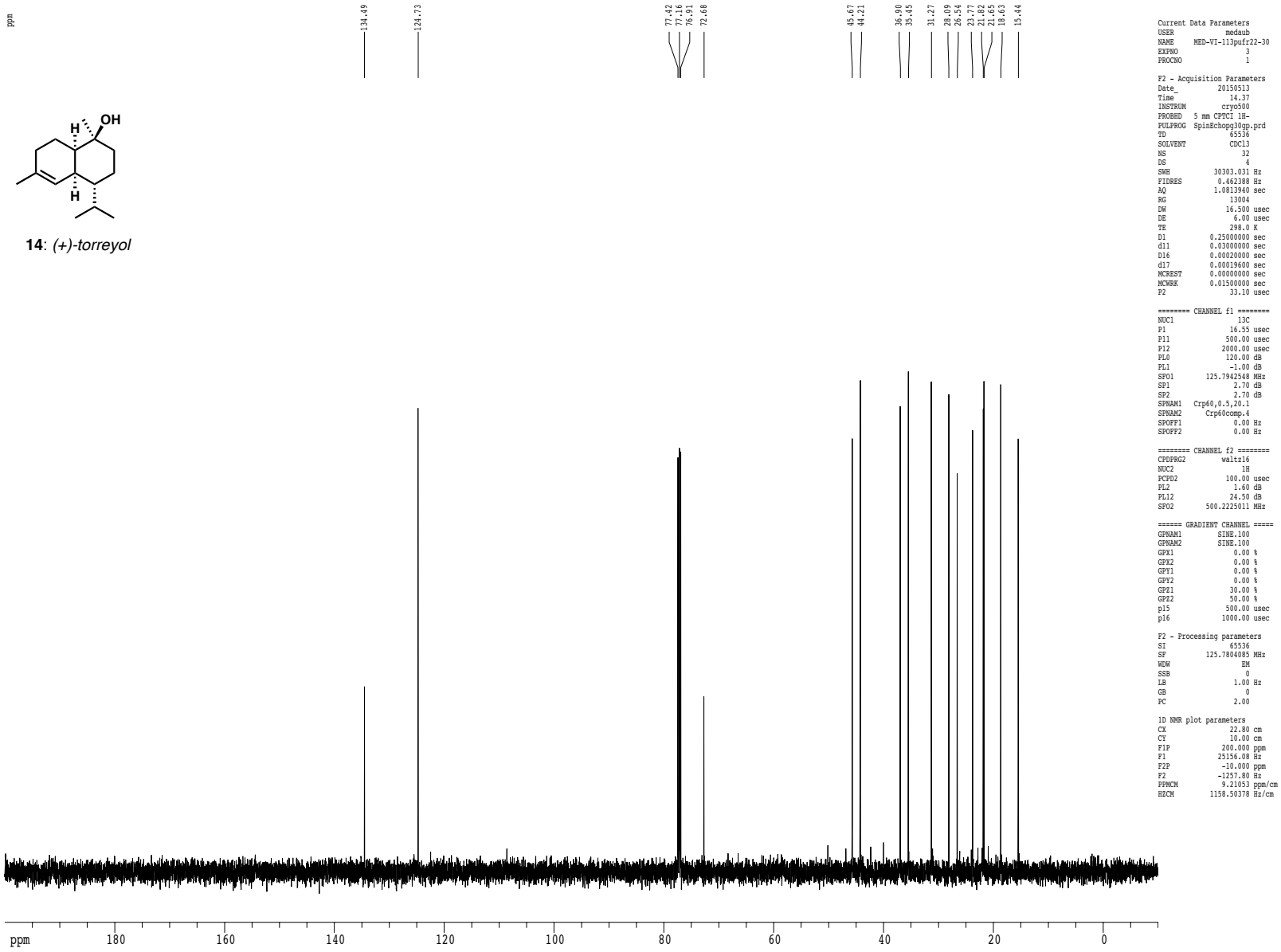
F2 - Acquisition Parameters
Date_          20150720
Time              18.15
INSTRUM           av600
PROBHD   5 mm BBO BB-1H
PULPROG           zg30
TD                98074
SOLVENT           CDCl3
NS                   8
DS                   2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ             5.0998979 sec
RG                 724
DW              52.000 usec
DE              14.33 usec
TE                294.6 K
D1           0.10000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1               1H
P1               9.00 usec

F2 - Processing parameters
SI                65536
SF          600.1300347 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               35.00 cm
F1P             10.100 ppm
F1             6061.31 Hz
F2P             -0.100 ppm
F2              -60.01 Hz
PPMCM          0.44737 ppm/cm
HZCM         268.47925 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



14: *(+)-torreyol*

```
Current Data Parameters
USER                medaub
NAME       MED-VI-113pufr22-30
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150513
Time              14.37
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                13004
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               33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1        125.7942548 MHz
SP1              2.70 dB
SP2              2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

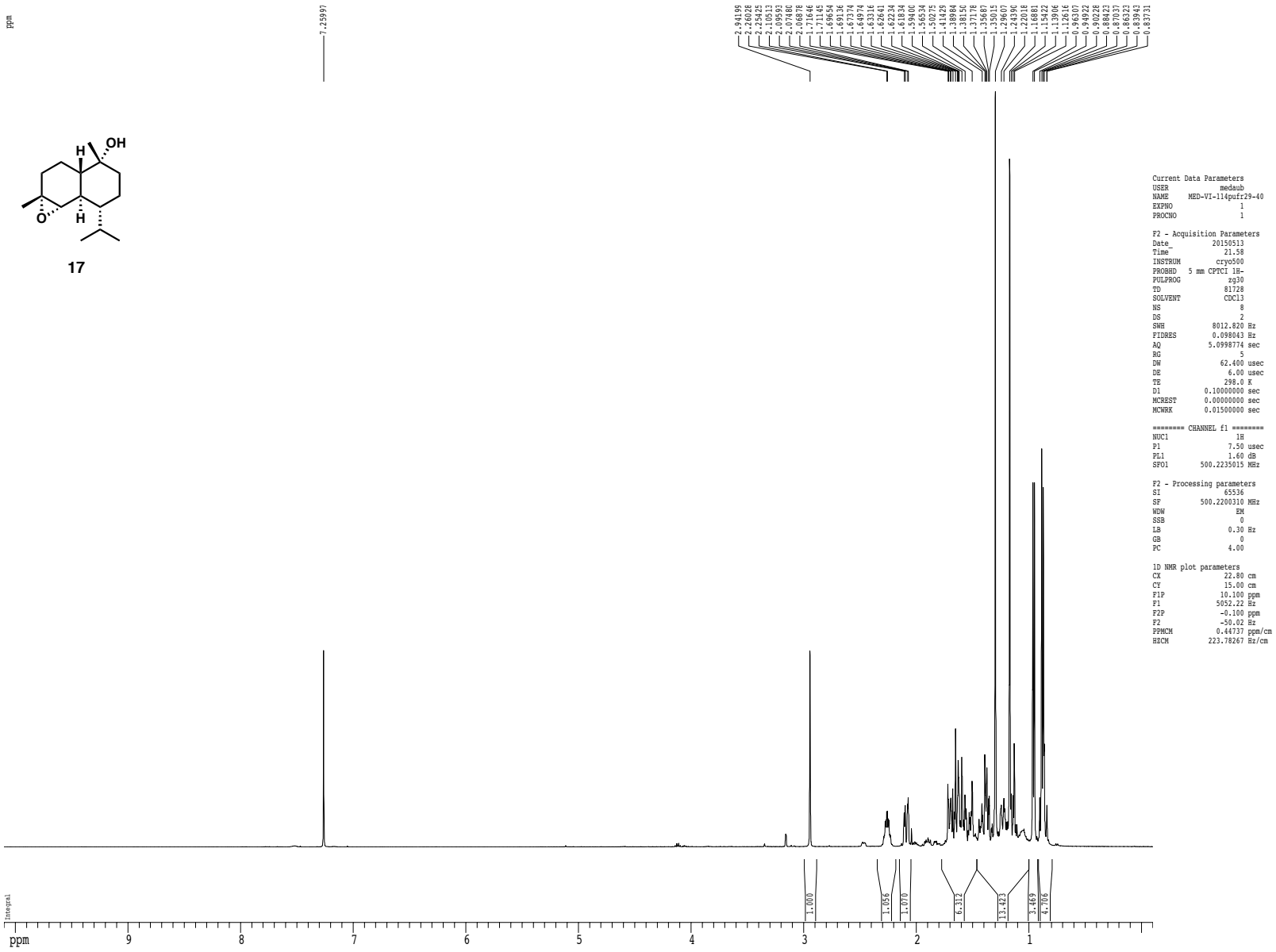
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              1.60 dB
PL12            24.50 dB
SFO2        500.2225011 MHz

====== 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

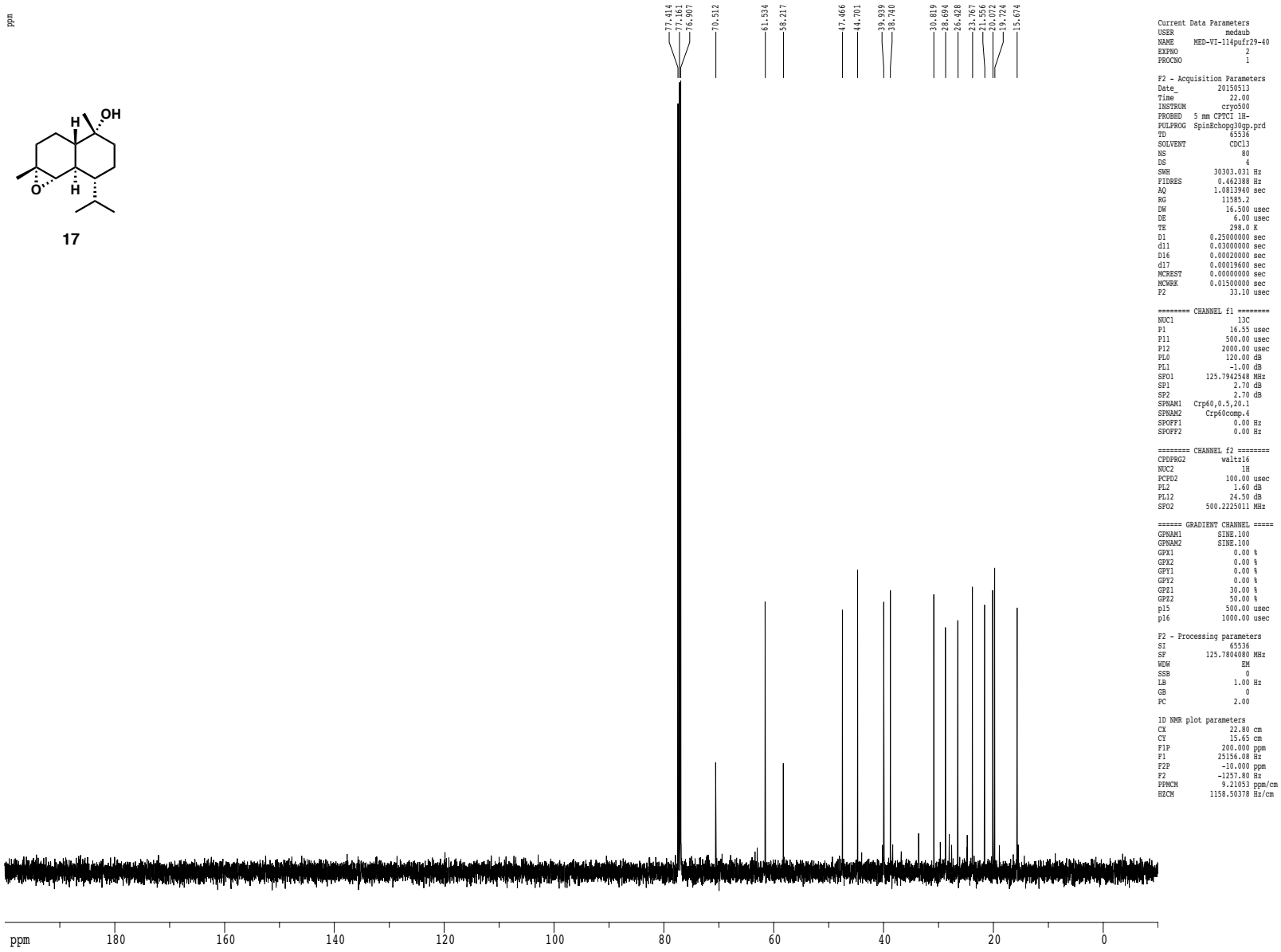
F2 - Processing parameters
SI                  65536
SF          125.7804085 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  10.00 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


ppm
7.25997
2.94198
2.76928
2.54425
2.10513
2.09593
2.07486
2.06878
1.71646
1.71145
1.69654
1.69136
1.67374
1.64974
1.63516
1.62641
1.62234
1.61834
1.59400
1.56534
1.50275
1.41429
1.38984
1.38156
1.37178
1.35687
1.35015
1.34670
1.24390
1.22018
1.16881
1.15422
1.13906
1.12616
0.96307
0.94922
0.90228
0.88423
0.87037
0.85523
0.85043
0.83731
H
OH
O
H
17
Current Data Parameters
USER medaub
NAME MED-VI-114pufr29-40
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150513
Time_ 21.58
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 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200310 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 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm
Integral
1.000
1.056
1.070
6.312
15.423
3.469
4.706
ppm
9
8
7
6
5
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME       MED-VI-114pufr29-40
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150513
Time              22.00
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  80
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

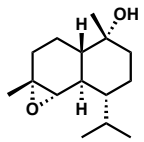
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== 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           125.7804080 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
```

gnoesy



17


```
Current Data Parameters
NAME      MED-VI-114pufr29-40
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_           20150513
Time                22.08
INSTRUM          cryo400
PROBHD   5 mm CPTCI 1H-
PULPROG       noesygptp
TD                 2048
SOLVENT           CDCl3
NS                    2
DS                    4
SWH            4006.410 Hz
FIDRES         1.956255 Hz
AQ             0.2555904 sec
RG                  128
DW               124.800 usec
DE                 6.00 usec
TE               298.0 K
D0            0.00000300 sec
D1            2.00000000 sec
D8            0.80000001 sec
D16           0.00020000 sec
d20           0.39880002 sec
IN0           0.00012480 sec

-------- CHANNEL f1 --------
NUC1                  1H
P1                 7.50 usec
P2                15.00 usec
PL1                1.60 dB
SFO1        500.2219426 MHz

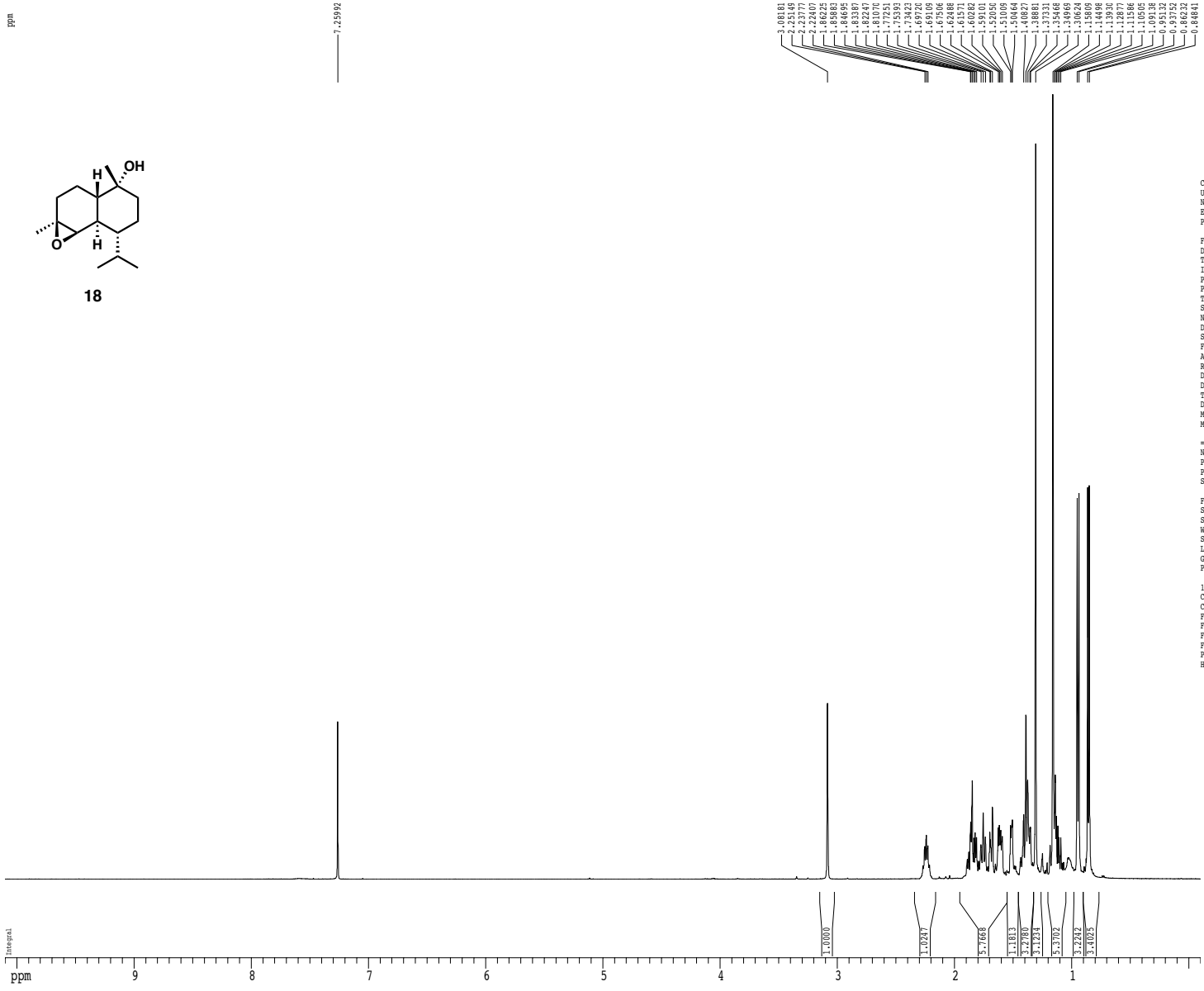
------ GRADIENT CHANNEL -----
GPNAM[1]        sine.100
GPNAM[2]        sine.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               40.00 %
GPZ2              -40.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   632
SFO1            500.2219 MHz
FIDRES        63.593815 Hz
SW                8.009 ppm
FnMODE        undefined

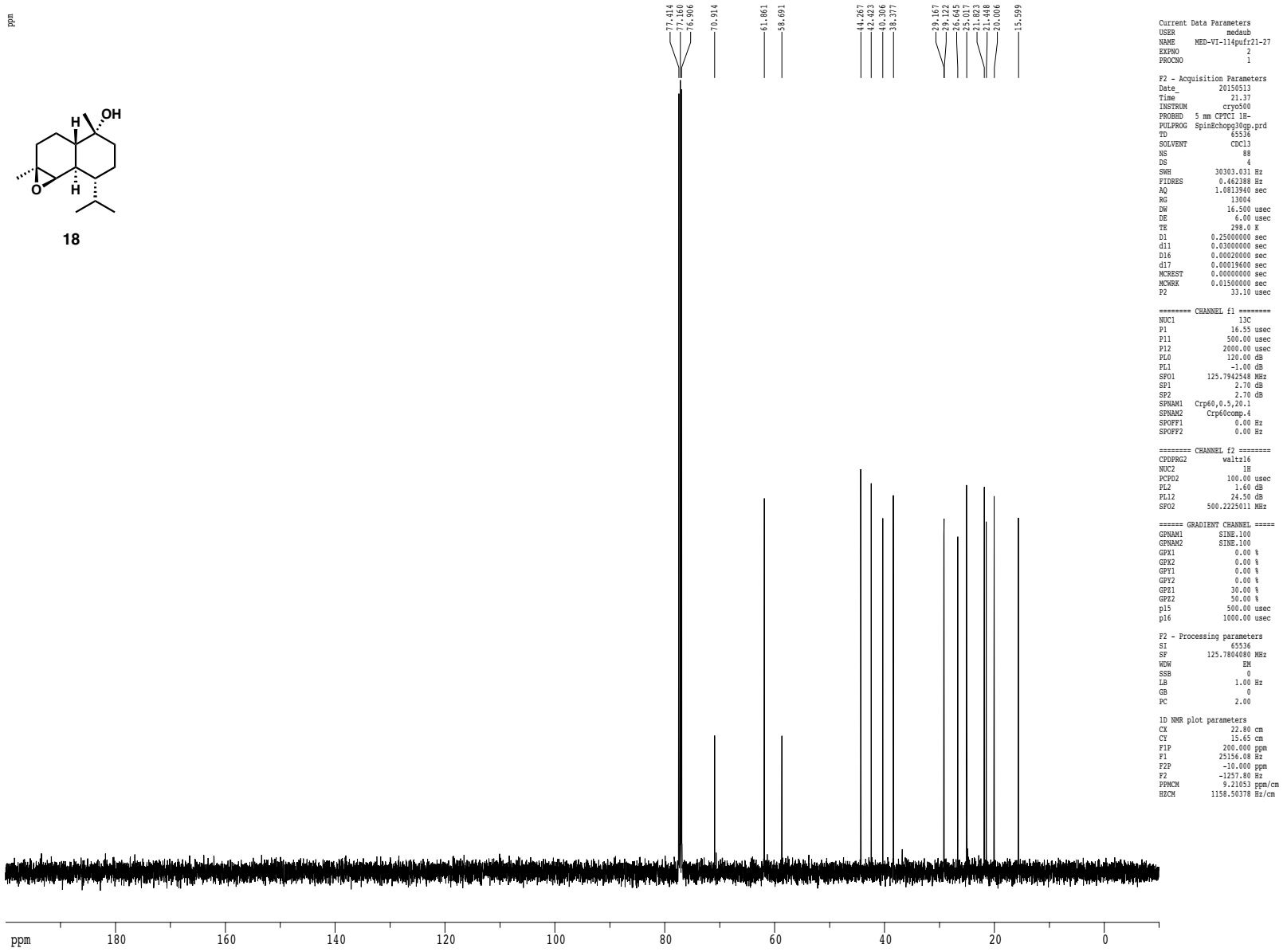
F2 - Processing parameters
SI                   1024
SF          500.2200310 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                   1024
MC2                  TPPI
SF          500.2200310 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

1H spectrum


ppm
7.25992
3.08181
2.25149
2.23777
2.22407
1.86225
1.85613
1.84695
1.83397
1.82247
1.81070
1.77251
1.75393
1.73423
1.69720
1.69109
1.67506
1.62488
1.61571
1.60282
1.59101
1.52050
1.51009
1.50464
1.40827
1.38881
1.37331
1.35468
1.34969
1.30624
1.18896
1.14498
1.13930
1.12877
1.11586
1.10505
1.09138
0.95132
0.93752
0.86232
0.84841
H
OH
O
H
18
Current Data Parameters
USER medaub
NAME MED-VI-114pafr21-27
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150513
Time 21.34
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 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200308 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 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm
Integral
1.0000
1.0247
5.7668
1.1813
3.2780
3.1234
5.3702
3.2242
3.4025
ppm
9
8
7
6
5
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME       MED-VI-114pufr21-27
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_            20150513
Time                21.37
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     88
DS                      4
SWH            30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                  13004
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                33.10 usec

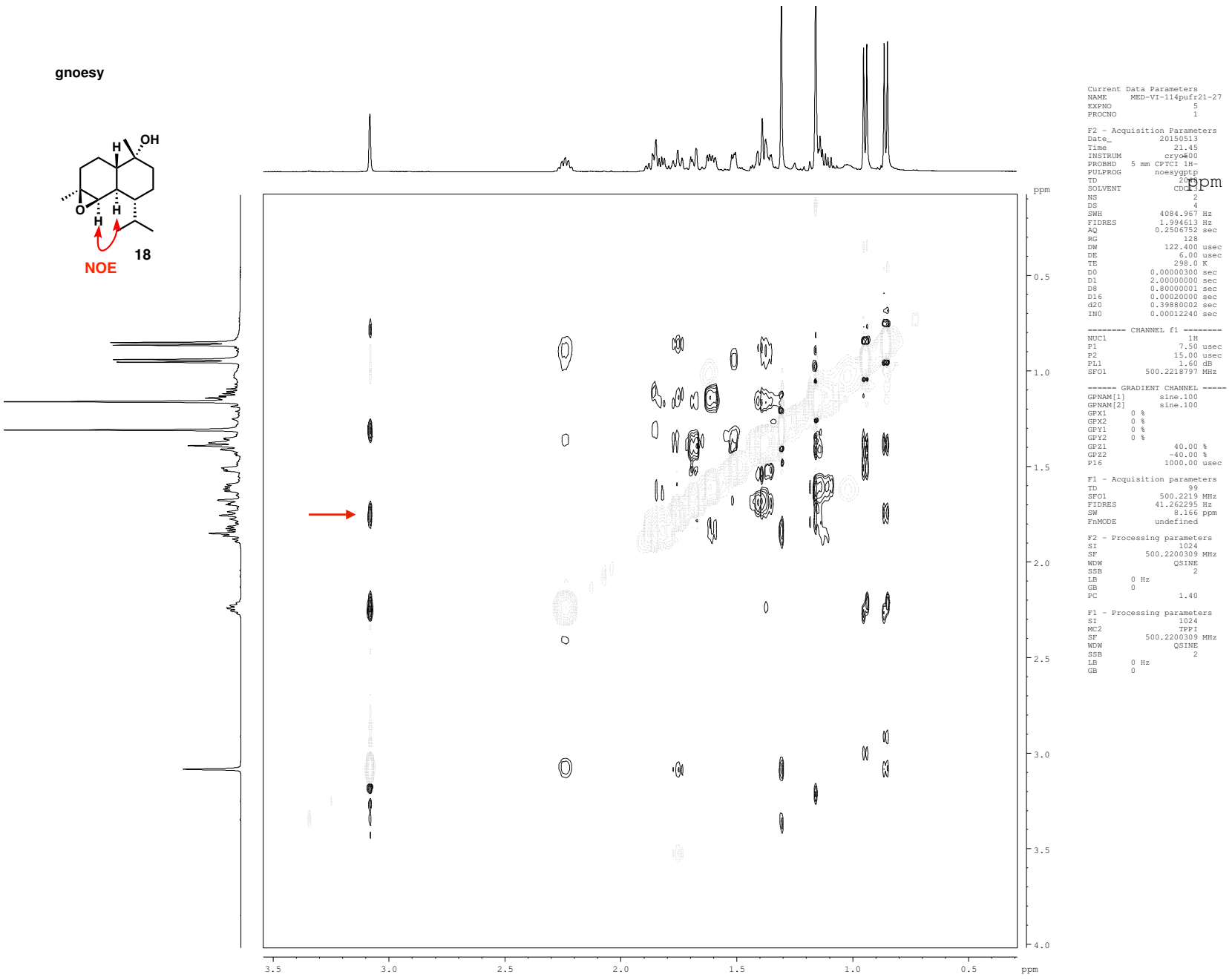
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1    Crp60,0.5,20.1
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              24.50 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           125.7804080 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
```




```
Current Data Parameters
NAME      MED-VI-114pufr21-27
EXPNO                       5
PROCNO                      1

F2 - Acquisition Parameters
Date_           20150513
Time                21.45
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG        noesygptp
TD                  2048
SOLVENT            CDCl3
NS                     2
DS                     4
SWH             4084.967 Hz
FIDRES          1.994613 Hz
AQ              0.2506752 sec
RG                   128
DW                122.400 usec
DE                  6.00 usec
TE                298.0 K
D0             0.00000300 sec
D1             2.00000000 sec
D8             0.80000001 sec
D16            0.00020000 sec
d20            0.39880002 sec
IN0            0.00012240 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
P2                   15.00 usec
PL1                   1.60 dB
SFO1         500.2218797 MHz

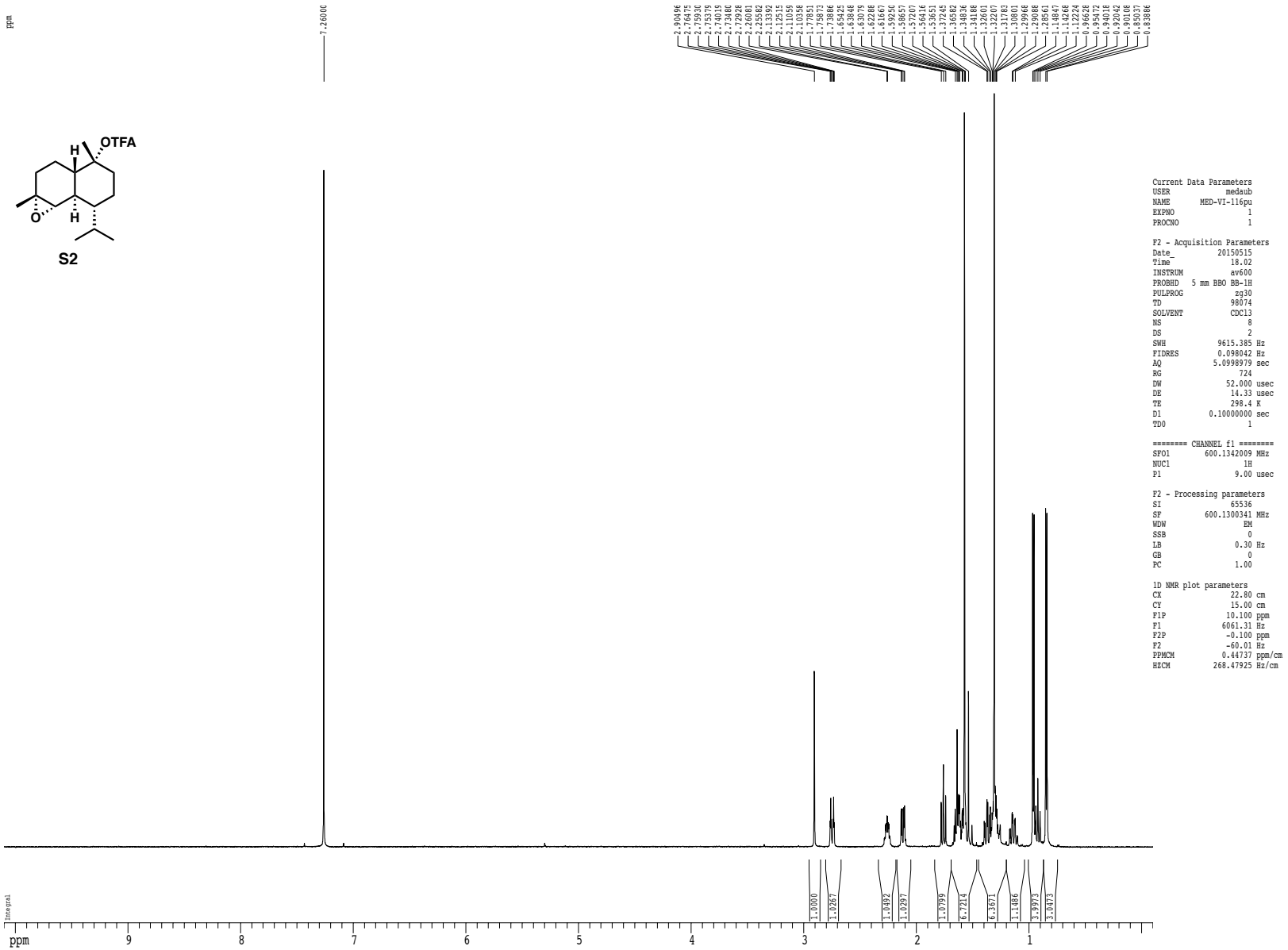
====== GRADIENT CHANNEL =====
GPNAM[1]         sine.100
GPNAM[2]         sine.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                 40.00 %
GPZ2                -40.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                     99
SFO1            500.2219 MHz
FIDRES         41.262295 Hz
SW                 8.166 ppm
FnMODE         undefined

F2 - Processing parameters
SI                   1024
SF            500.2200309 MHz
WDW                  QSINE
SSB                      2
LB         0 Hz
GB         0
PC                    1.40

F1 - Processing parameters
SI                   1024
MC2                  TPPI
SF            500.2200309 MHz
WDW                  QSINE
SSB                      2
LB         0 Hz
GB         0
```

1H spectrum



Current Data Parameters
USER medaub
NAME MED-VI-116pu
EXPNO 1
PROCNO 1

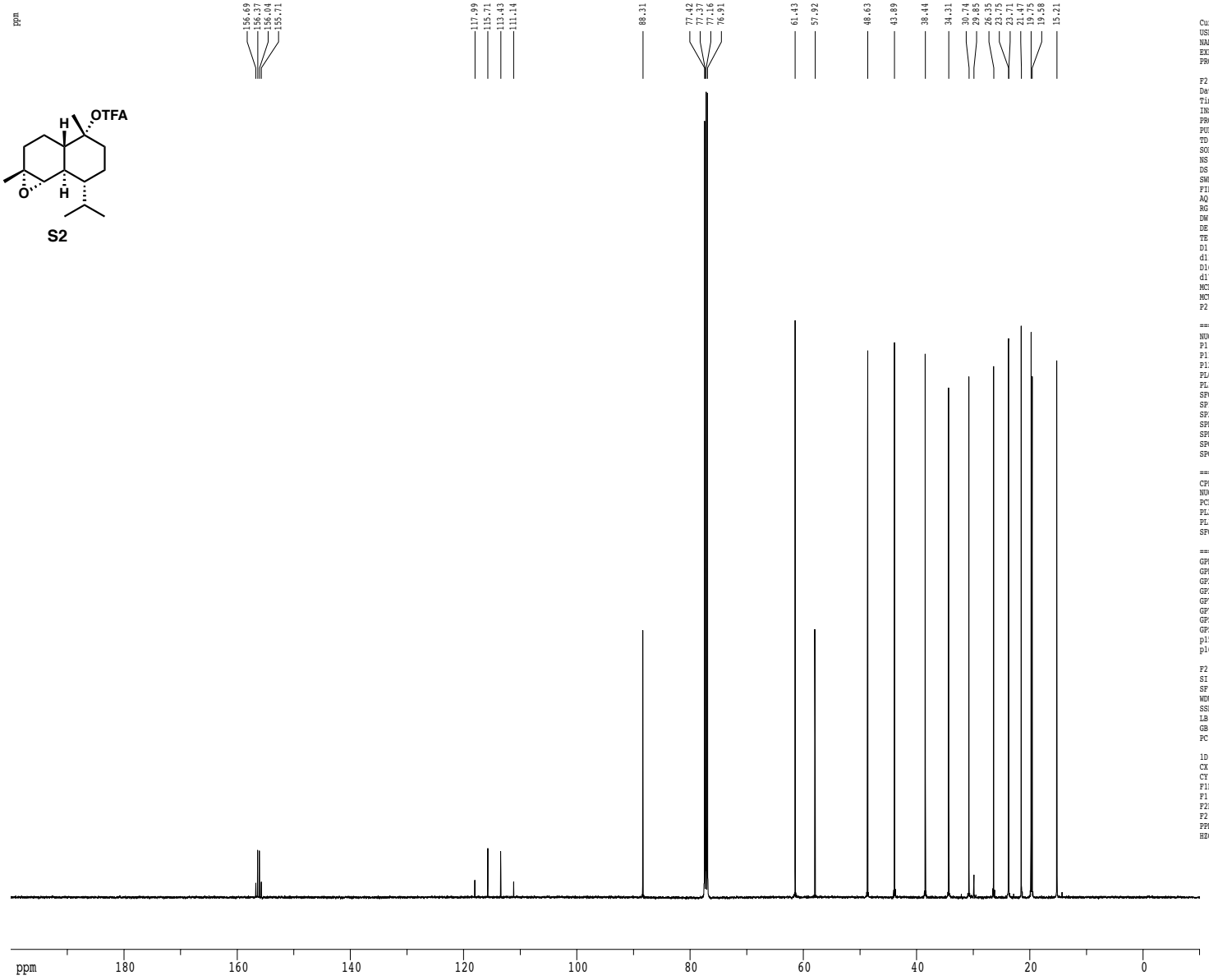
F2 - Acquisition Parameters
Date_ 20150515
Time 18.02
INSTRUM av600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 98074
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.0998979 sec
RG 724
DW 52.000 usec
DE 14.33 usec
TE 298.4 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1342009 MHz
NUC1 1H
P1 9.00 usec

F2 - Processing parameters
SI 65536
SF 600.1300341 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 10.100 ppm
F1 6061.31 Hz
F2P -0.100 ppm
F2 -60.01 Hz
PPMCM 0.44737 ppm/cm
HZCM 268.47925 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME        MED-VI-116pu
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20150515
Time             21.59
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                12056
DS                    4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 sec
RG                13004
DW               16.500 usec
DE                6.00 usec
TE              298.0 K
D1            1.50000000 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

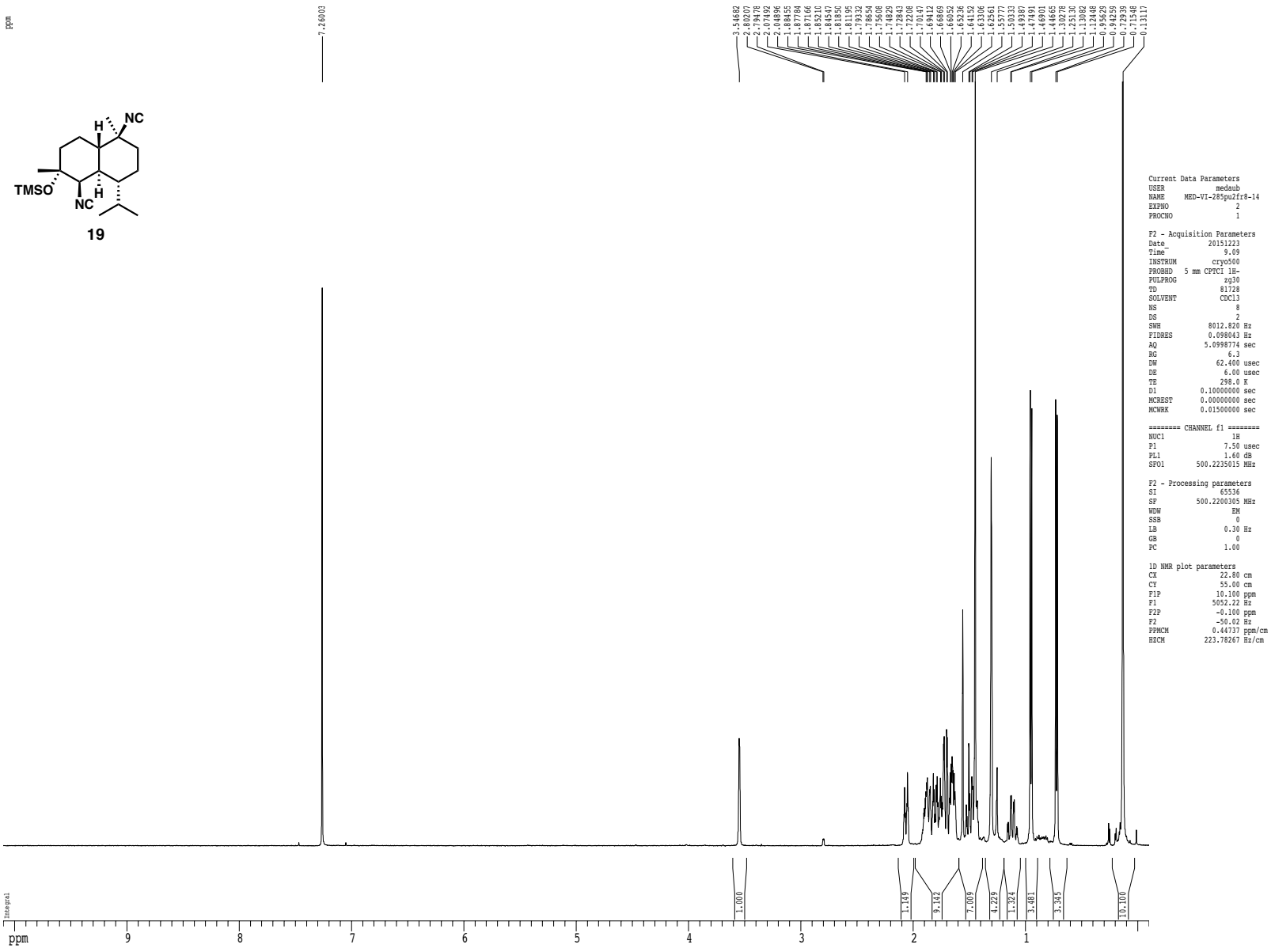
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            100.00 usec
PL2               1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== 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          125.7804076 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



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```
Current Data Parameters
USER              medaub
NAME      MED-VI-285pu2fr8-14
EXPNO                    2
PROCNO                   1

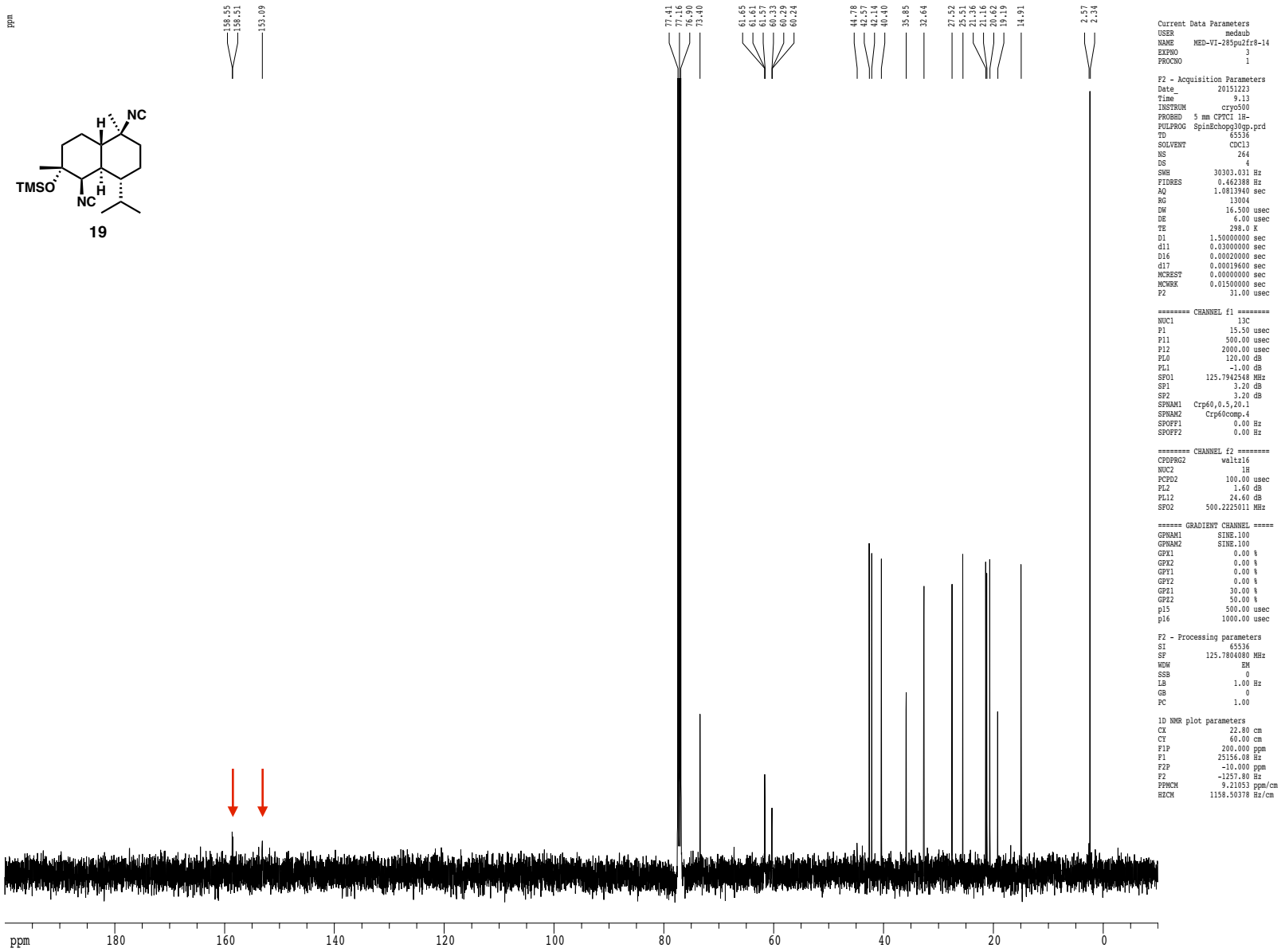
F2 - Acquisition Parameters
Date_           20151223
Time                9.09
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 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           500.2200305 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                55.00 cm
F1P              10.100 ppm
F1             5052.22 Hz
F2P              -0.100 ppm
F2              -50.02 Hz
PPMCM           0.44737 ppm/cm
HZCM          223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME      MED-VI-285pu2fr8-14
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151223
Time                9.13
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   264
DS                     4
SWH            30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                 13004
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             1.50000000 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

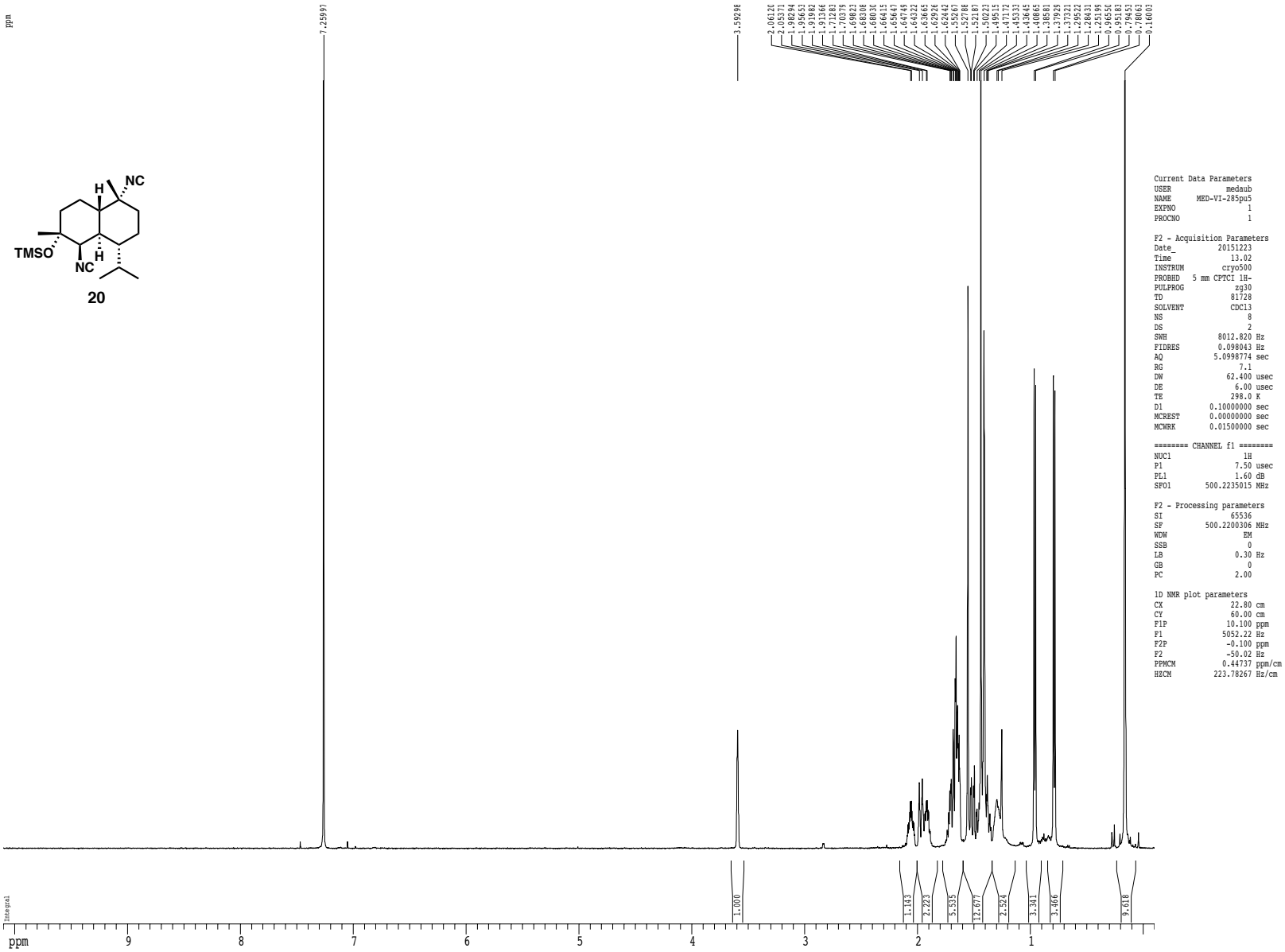
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2         500.2225011 MHz

====== 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           125.7804080 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                60.00 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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```
Current Data Parameters
USER                medaub
NAME          MED-VI-285pu5
EXPNO                   1
PROCNO                  1

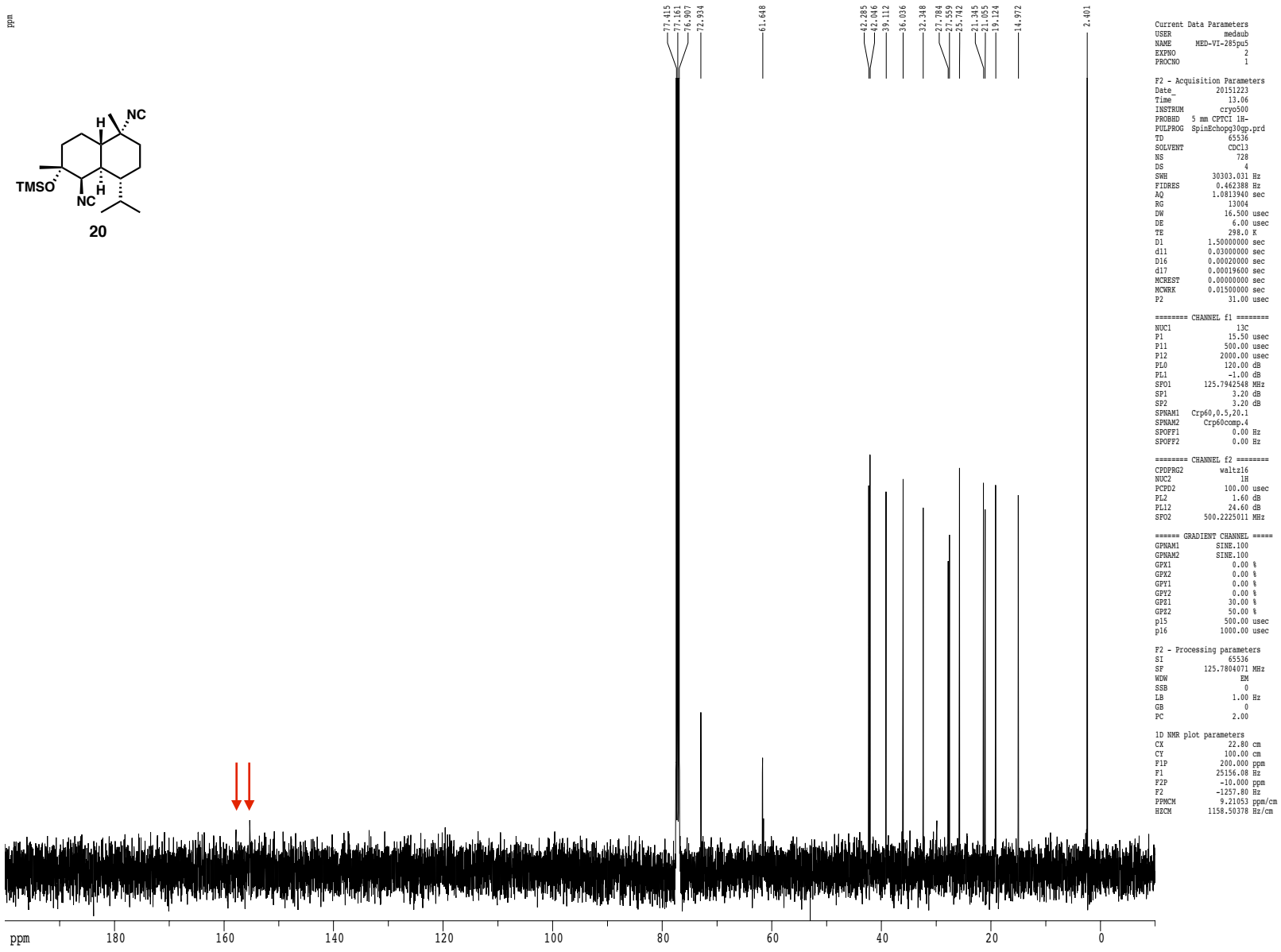
F2 - Acquisition Parameters
Date_            20151223
Time                13.02
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.098043 Hz
AQ              5.0998774 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            500.2200306 MHz
WDW                    EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  60.00 cm
F1P                10.100 ppm
F1               5052.22 Hz
F2P                -0.100 ppm
F2                -50.02 Hz
PPMCM              0.44737 ppm/cm
HZCM             223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME      MED-VI-285pu5
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20151223
Time              13.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  728
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                13004
DW               16.500 usec
DE                6.00 usec
TE                298.0 K
D1           1.50000000 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

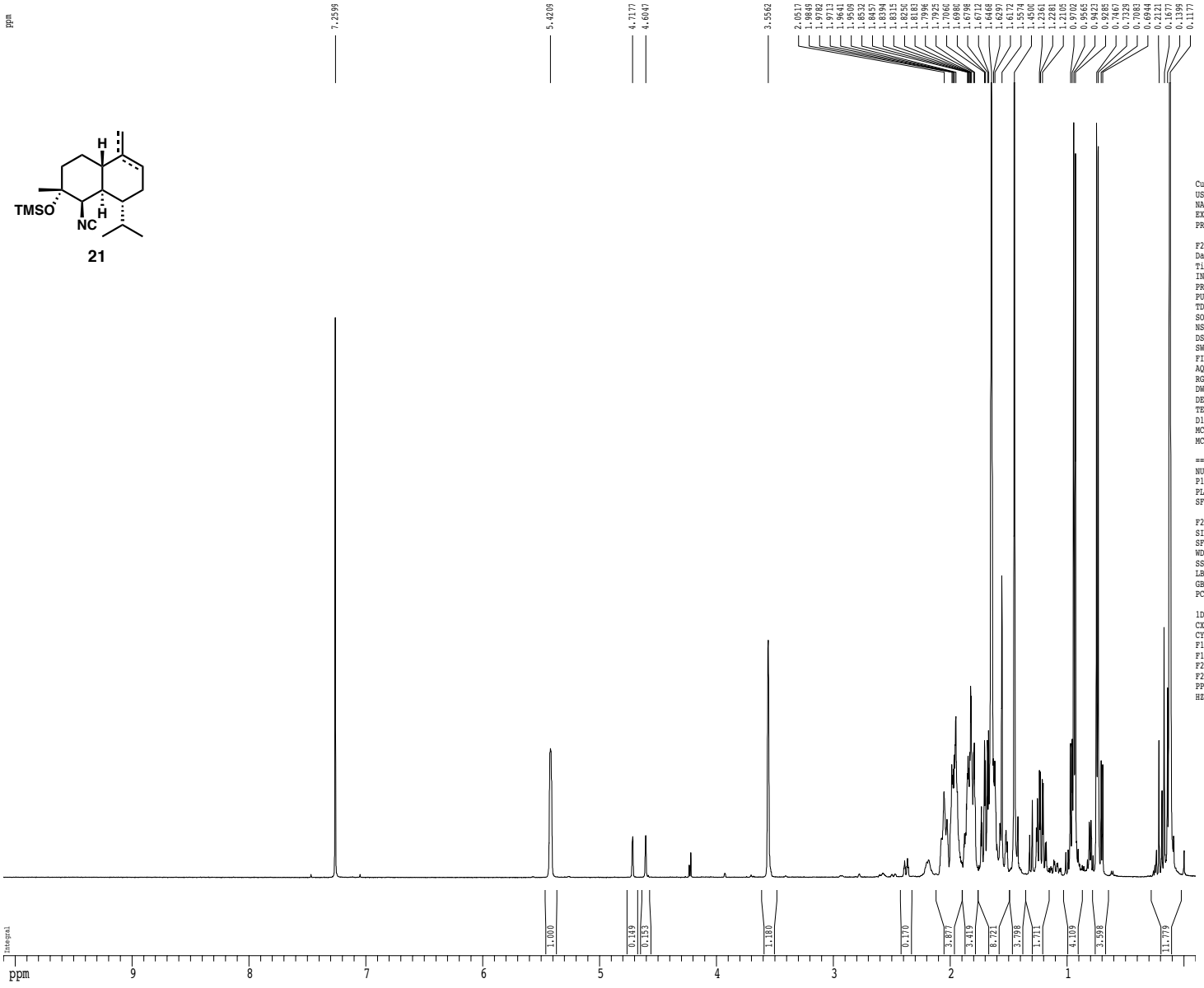
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== 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          125.7804071 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY               100.00 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 Parameters

USER	medaub
NAME	MED-VI-285pu4
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20151223
Time	9.24
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	9
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

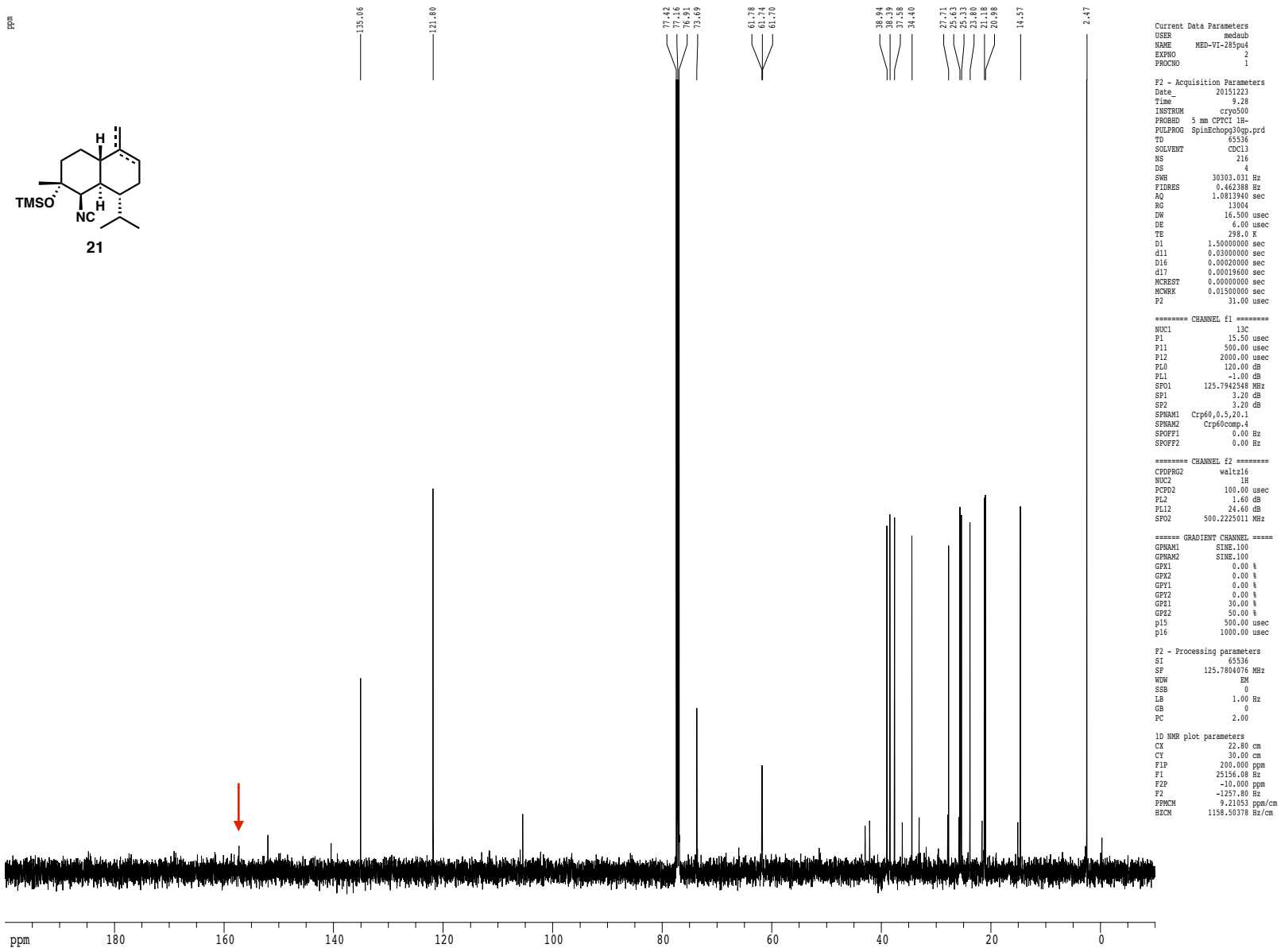
F2 - Processing parameters

SI	65536
SF	500.2200305 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	15.00

1D NMR plot parameters

CX	22.80 cm
CY	80.00 cm
F1P	10.100 ppm
F1	5052.22 Hz
F2P	-0.100 ppm
F2	-50.02 Hz
PPMCM	0.44737 ppm/cm
HZCM	223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME          MED-VI-285pu4
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151223
Time                9.28
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    216
DS                      4
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                  13004
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1              1.50000000 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

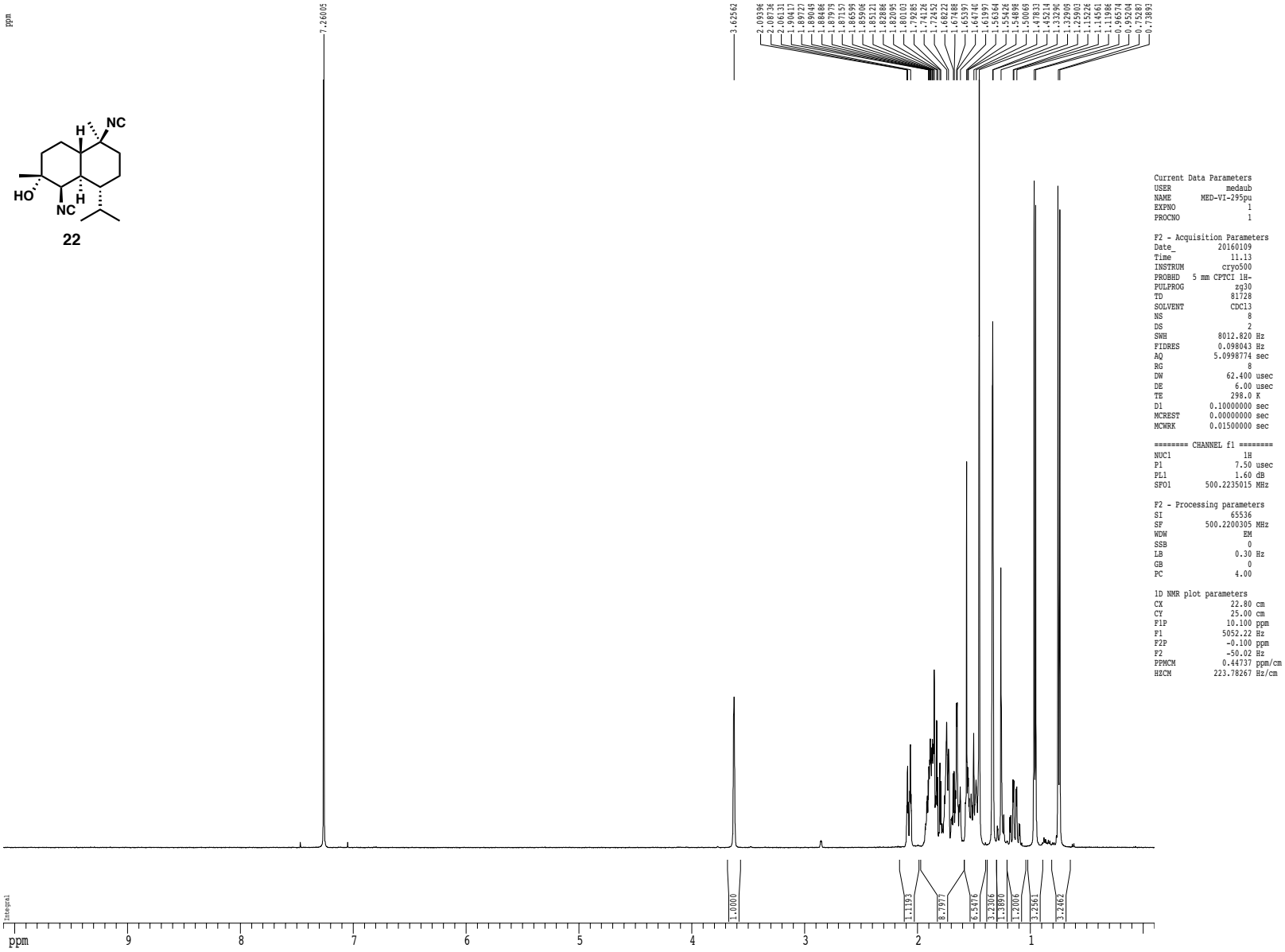
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2         500.2225011 MHz

====== 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           125.7804076 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 30.00 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


ppm
7.26005
3.62562
2.09396
2.08736
2.06131
1.90411
1.89727
1.89049
1.88486
1.87979
1.87157
1.86599
1.85906
1.85121
1.82886
1.82095
1.80103
1.79285
1.74126
1.72452
1.67822
1.67488
1.65397
1.64740
1.61997
1.56364
1.55426
1.54898
1.50069
1.47833
1.45214
1.33296
1.32908
1.25903
1.15226
1.14561
1.11986
0.96574
0.95204
0.75287
0.73893
HO
NC
H
NC
H
22
Current Data Parameters
USER medaub
NAME MED-VI-295pu
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160109
Time 11.13
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 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 parameters
SI 65536
SF 500.2200305 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 25.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm
Integral
1.0000
1.1193
8.7977
6.5476
1.2006
3.2561
3.2462
ppm
9
8
7
6
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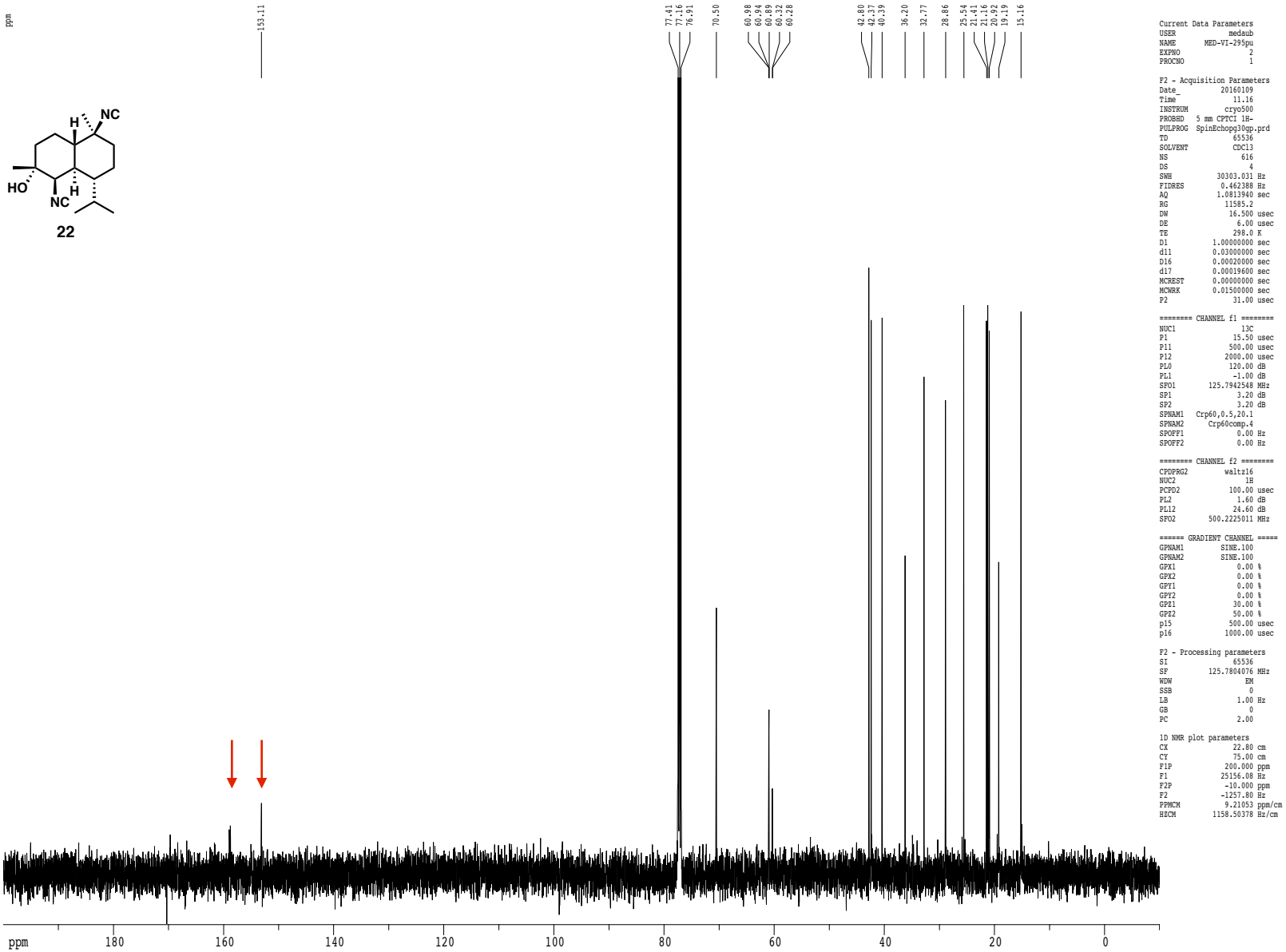
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME          MED-VI-295pu
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_            20160109
Time                11.16
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    616
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
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

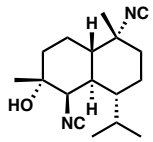
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2         500.2225011 MHz

====== 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           125.7804076 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 75.00 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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Current Data Parameters
USER medaub
NAME MED-VI-296pu
EXPNO 1
PROCNO 1

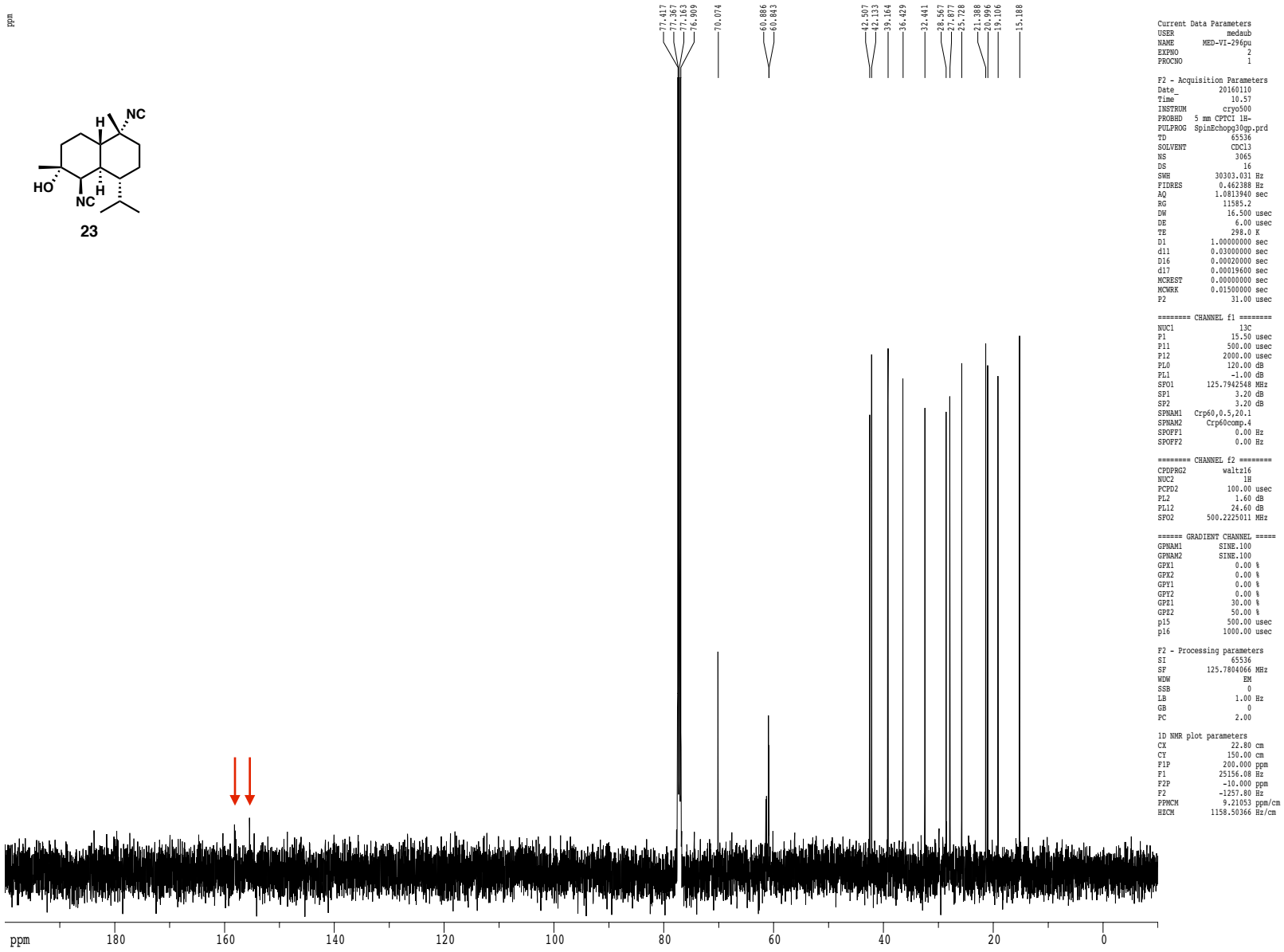
F2 - Acquisition Parameters
Date_ 20160110
Time 10.54
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200305 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VI-296pu
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160110
Time 10.57
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 3065
DS 16
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
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

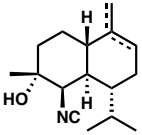
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== 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 125.7804066 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 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



24

7:1 favoring Δ^9-isomer

Current Data Parameters
USER medaub
NAME MED-VI-299pu
EXPNO 1
PROCNO 1

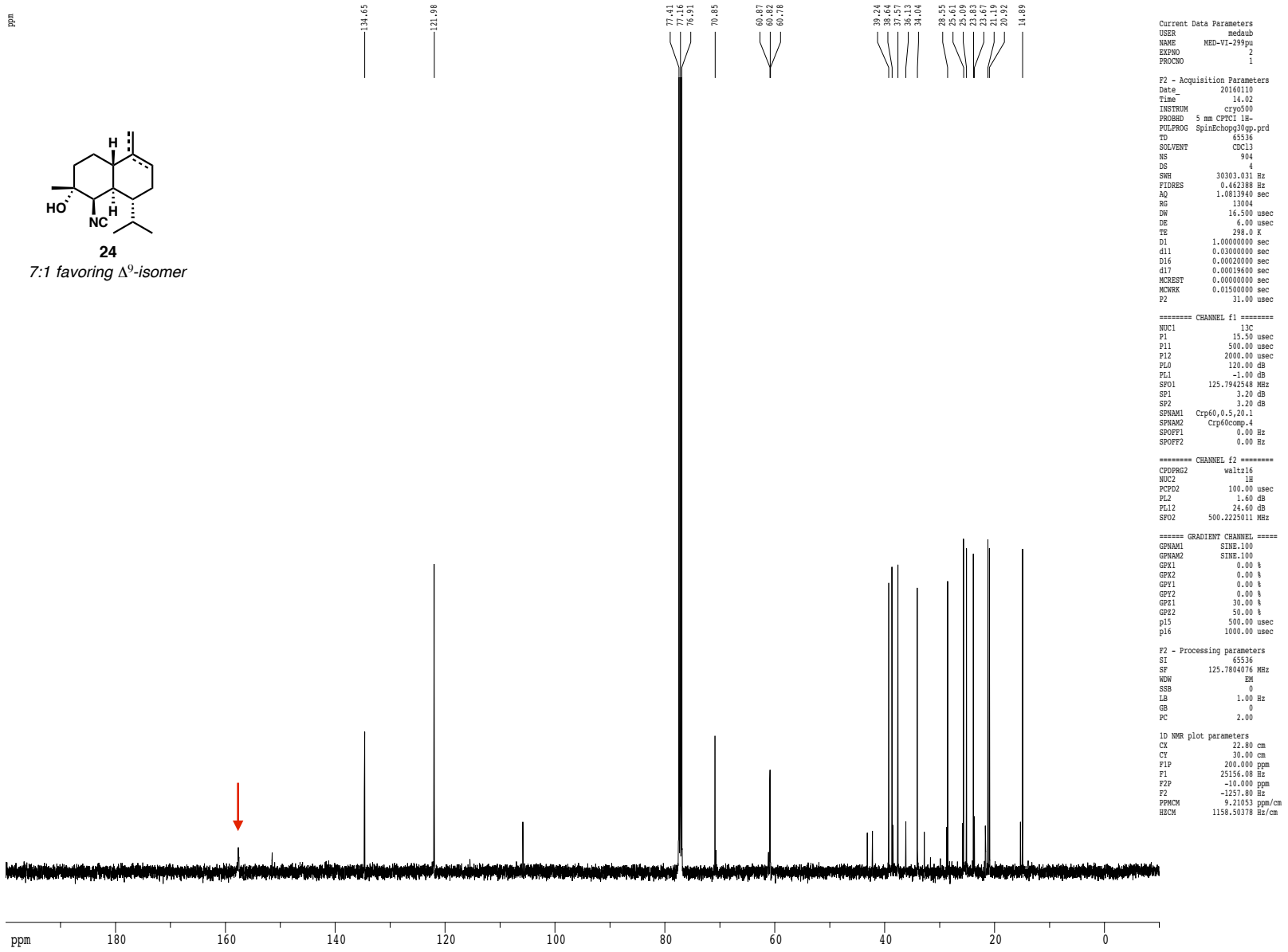
F2 - Acquisition Parameters
Date_ 20160110
Time 13.30
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

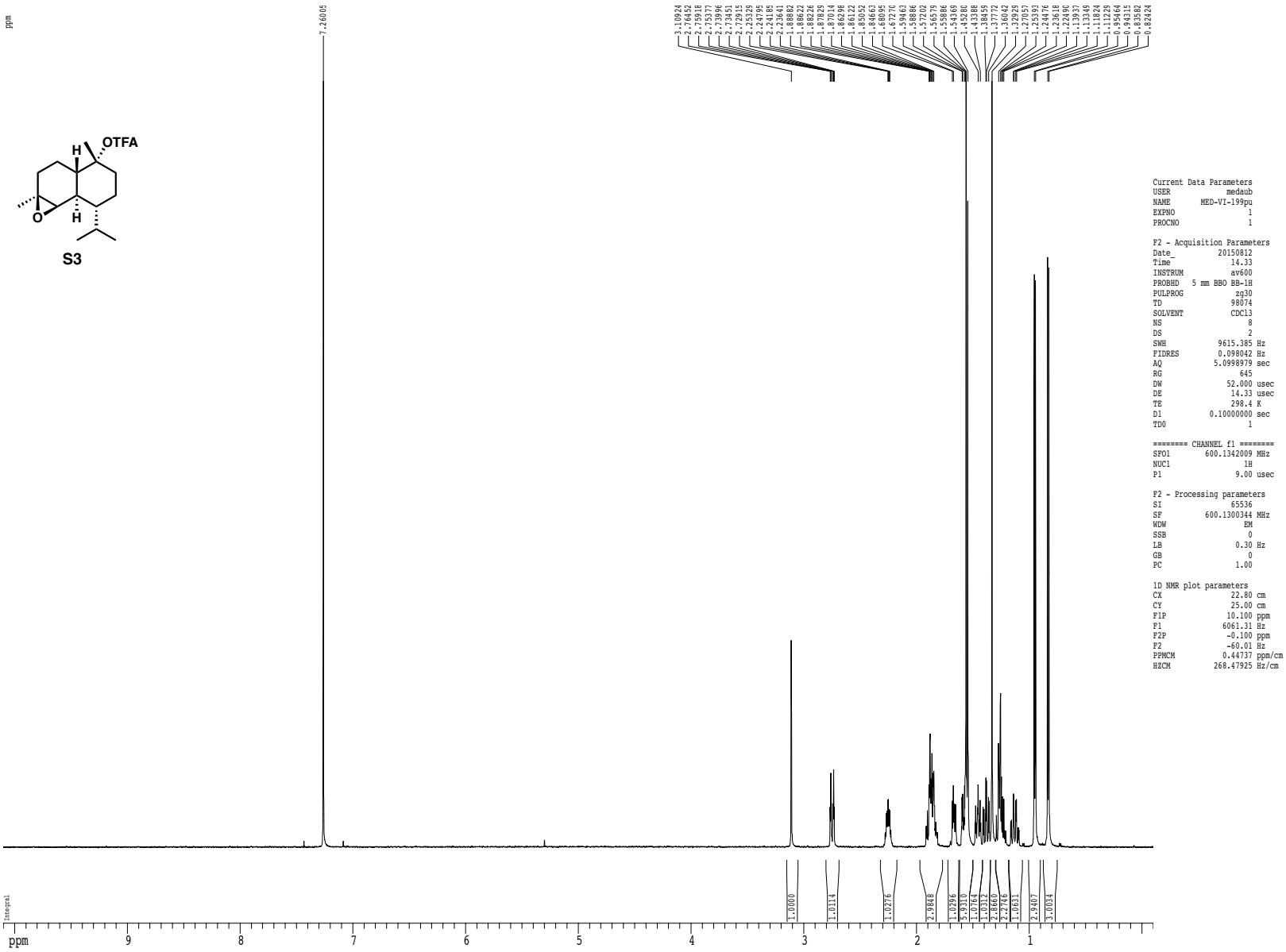
F2 - Processing parameters
SI 65536
SF 500.2200306 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 35.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum




```
Current Data Parameters
USER                medaub
NAME          MED-VI-199pu
EXPNO                    1
PROCNO                   1

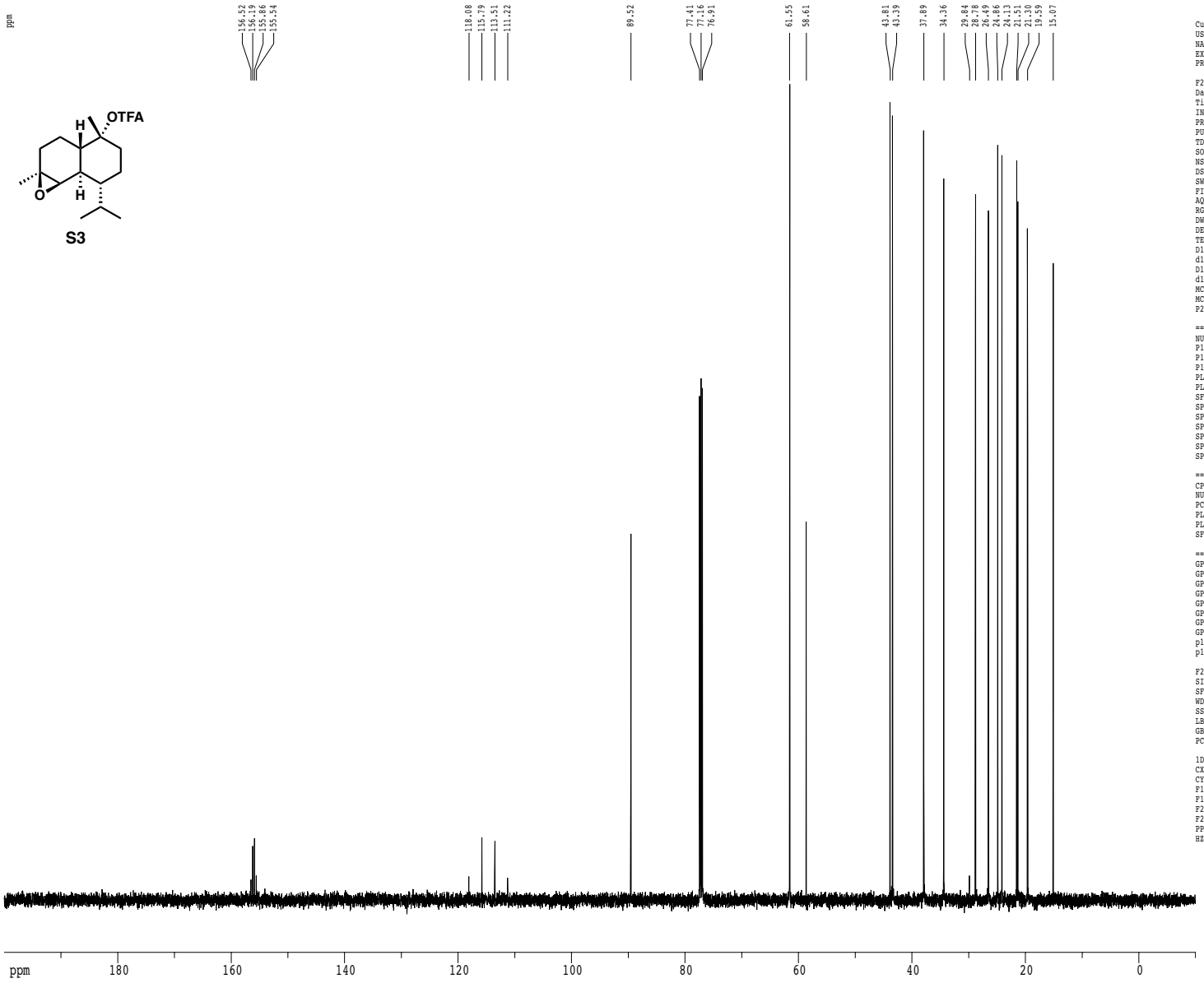
F2 - Acquisition Parameters
Date_            20150812
Time                14.33
INSTRUM             av600
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  98074
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ               5.0998979 sec
RG                    645
DW                 52.000 usec
DE                 14.33 usec
TE                 298.4 K
D1              0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                    1H
P1                   9.00 usec

F2 - Processing parameters
SI                   65536
SF            600.1300344 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  25.00 cm
F1P                10.100 ppm
F1                 6061.31 Hz
F2P                -0.100 ppm
F2                 -60.01 Hz
PPMCM             0.44737 ppm/cm
HZCM           268.47925 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VI-199pu
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150812
Time 16.33
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 112
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 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

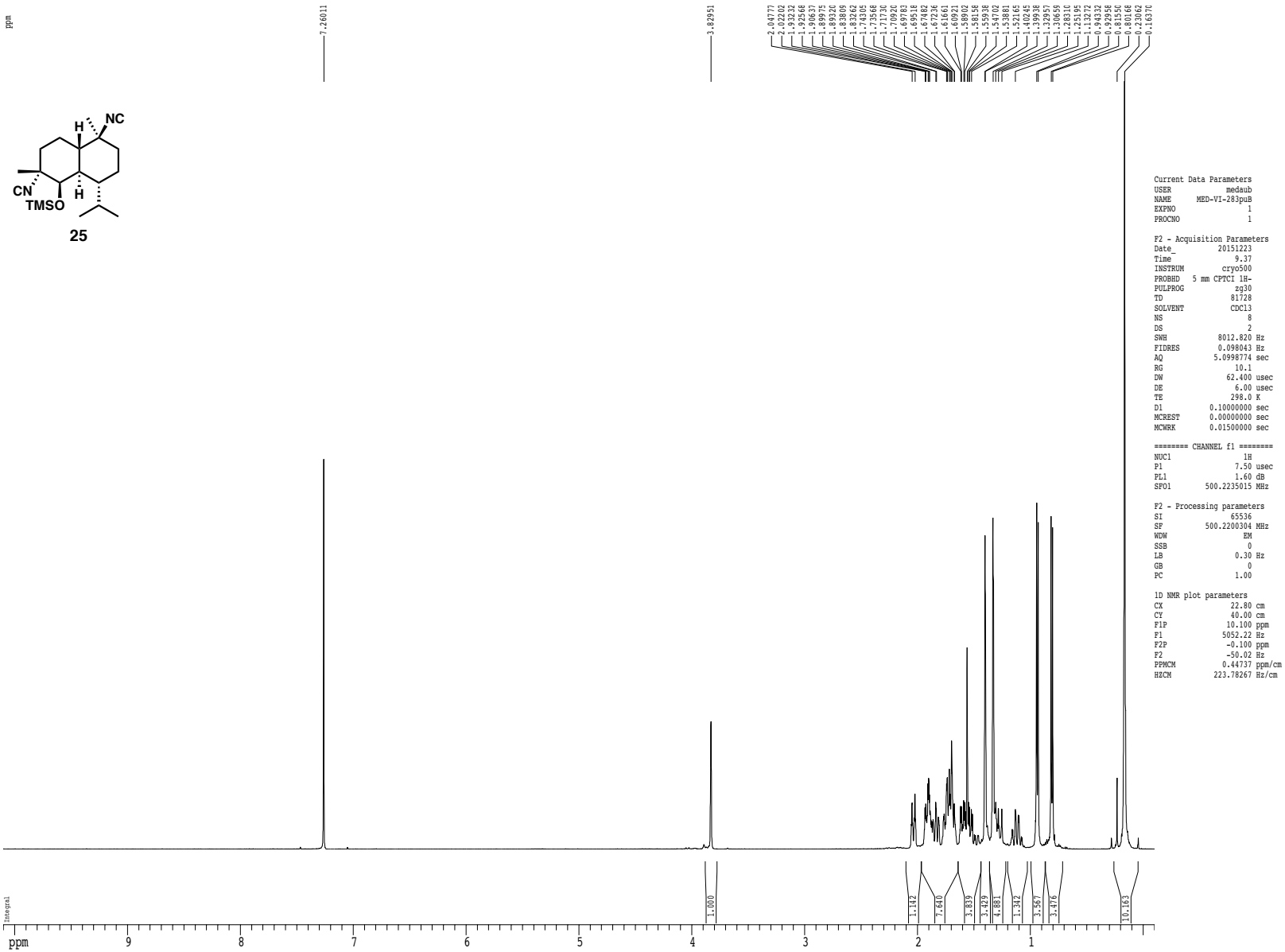
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== 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

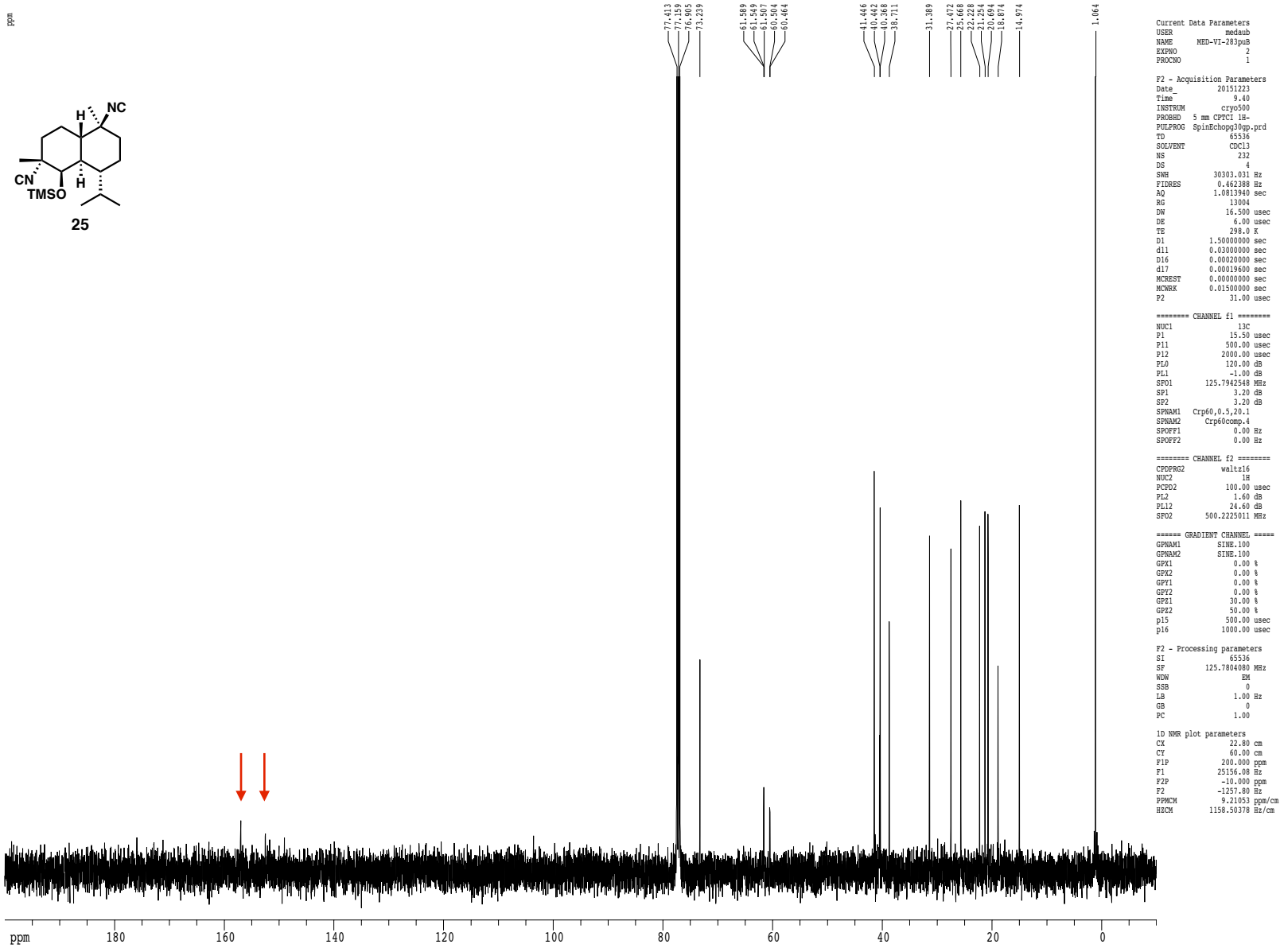
F2 - Processing parameters
SI 65536
SF 125.7804078 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

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


ppm
7.26011
3.82951
2.04777
2.02202
1.93232
1.92566
1.90617
1.89975
1.89326
1.83809
1.83262
1.74305
1.73568
1.71730
1.70926
1.69783
1.69518
1.67456
1.67236
1.61661
1.60921
1.58002
1.58158
1.55938
1.54702
1.53881
1.52165
1.40245
1.39938
1.39357
1.38655
1.28310
1.25195
1.13272
0.94332
0.92958
0.81556
0.80168
0.23062
0.16370
H
NC
CN
TMSO
H
25
Current Data Parameters
USER medaub
NAME MED-VI-283puB
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151223
Time 9.37
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 parameters
SI 65536
SF 500.2200304 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 40.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm
Integral
1.000
1.142
7.640
3.839
3.429
4.881
1.342
3.567
3.476
10.163
ppm
9
8
7
6
5
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling

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Current Data Parameters
USER              medaub
NAME      MED-VI-283puB
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20151223
Time               9.40
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 232
DS                   4
SWH          30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG               13004
DW              16.500 usec
DE               6.00 usec
TE              298.0 K
D1           1.50000000 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

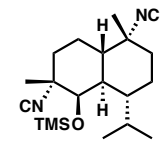
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2          100.00 usec
PL2              1.60 dB
PL12            24.60 dB
SFO2       500.2225011 MHz

====== 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         125.7804080 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.00

1D NMR plot parameters
CX              22.80 cm
CY              60.00 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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Current Data Parameters
USER medaub
NAME MED-VI-285puC
EXPNO 1
PROCNO 1

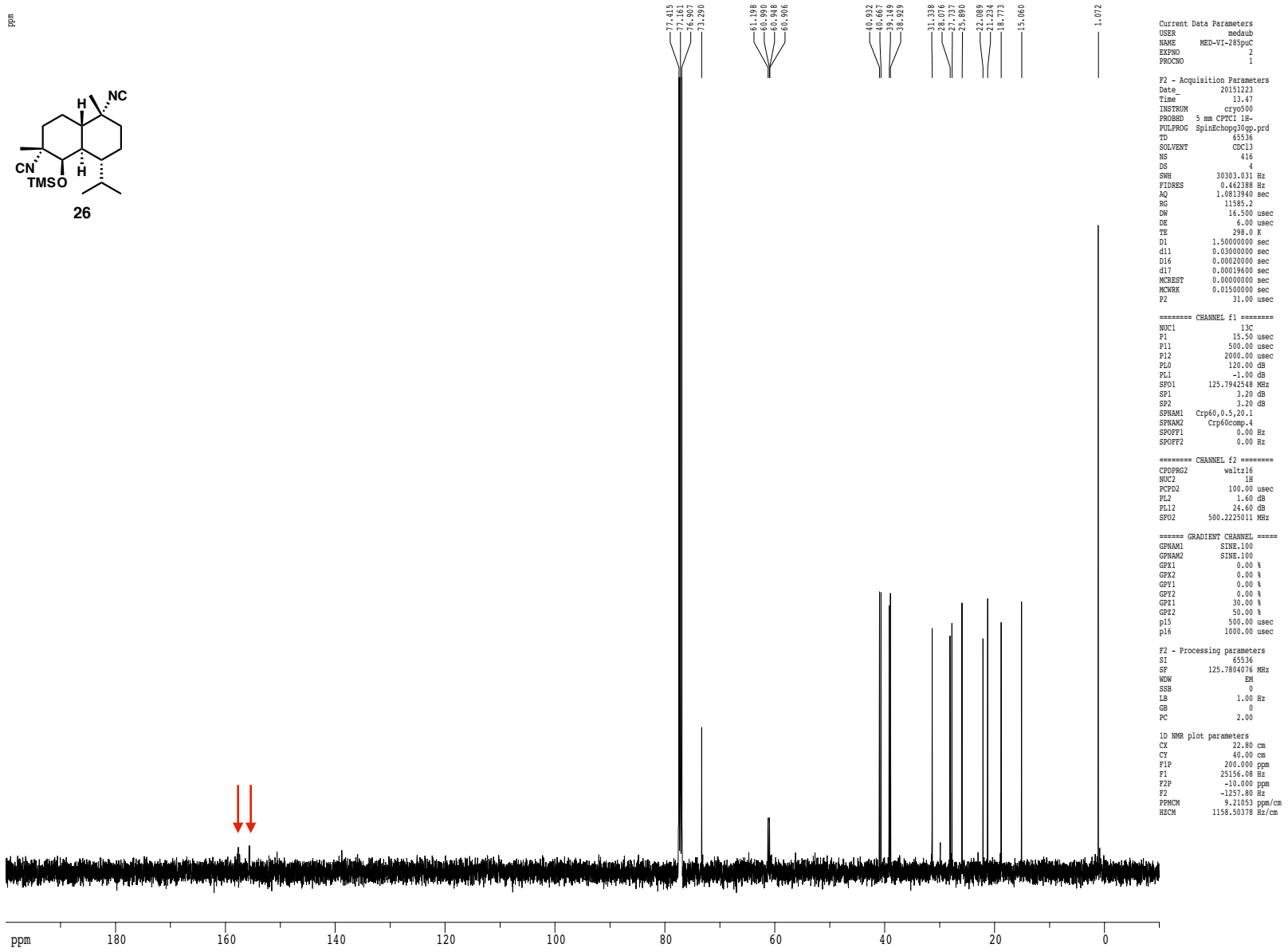
F2 - Acquisition Parameters
Date_ 20151223
Time 13.38
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

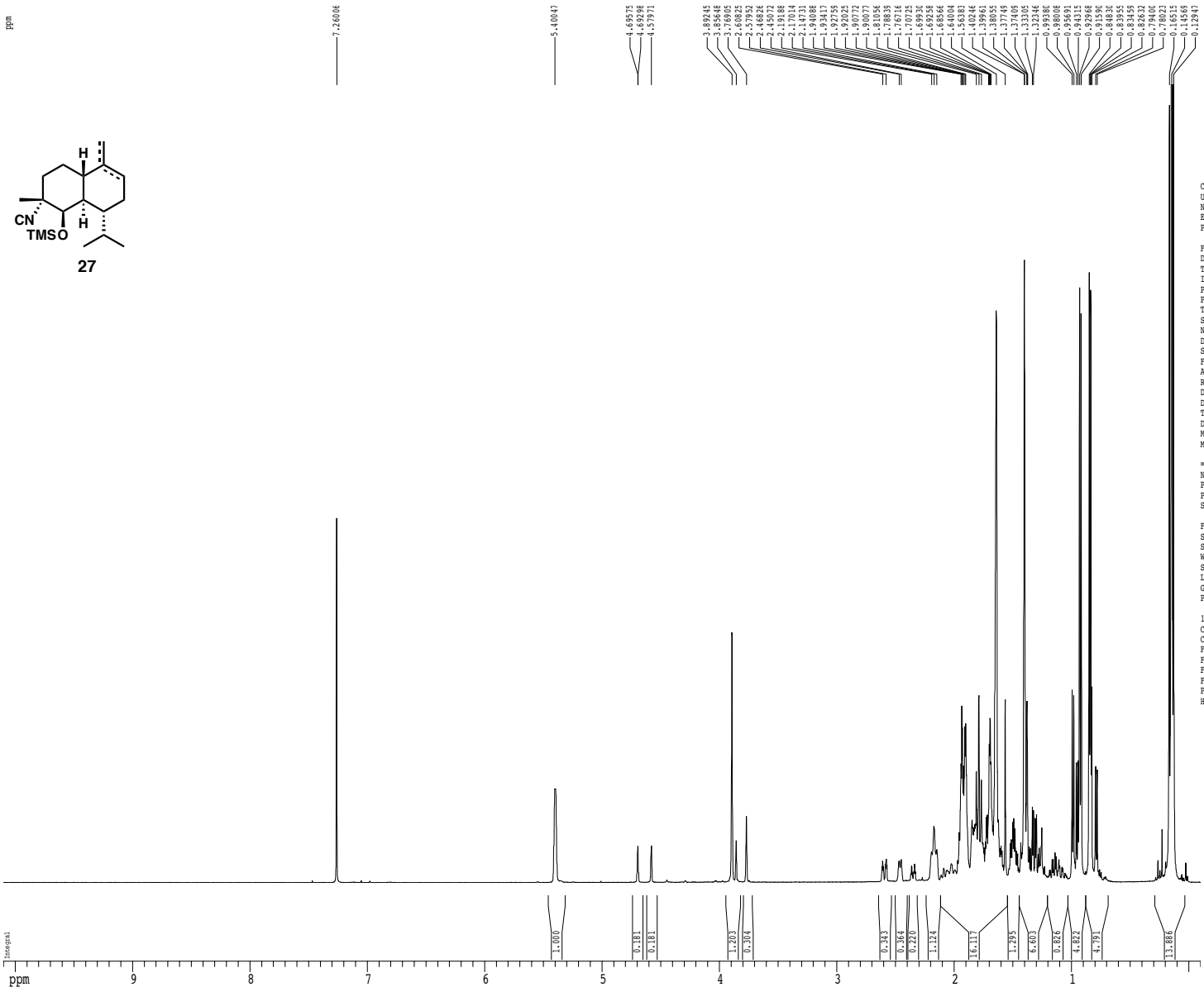
F2 - Processing parameters
SI 65536
SF 500.2200305 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

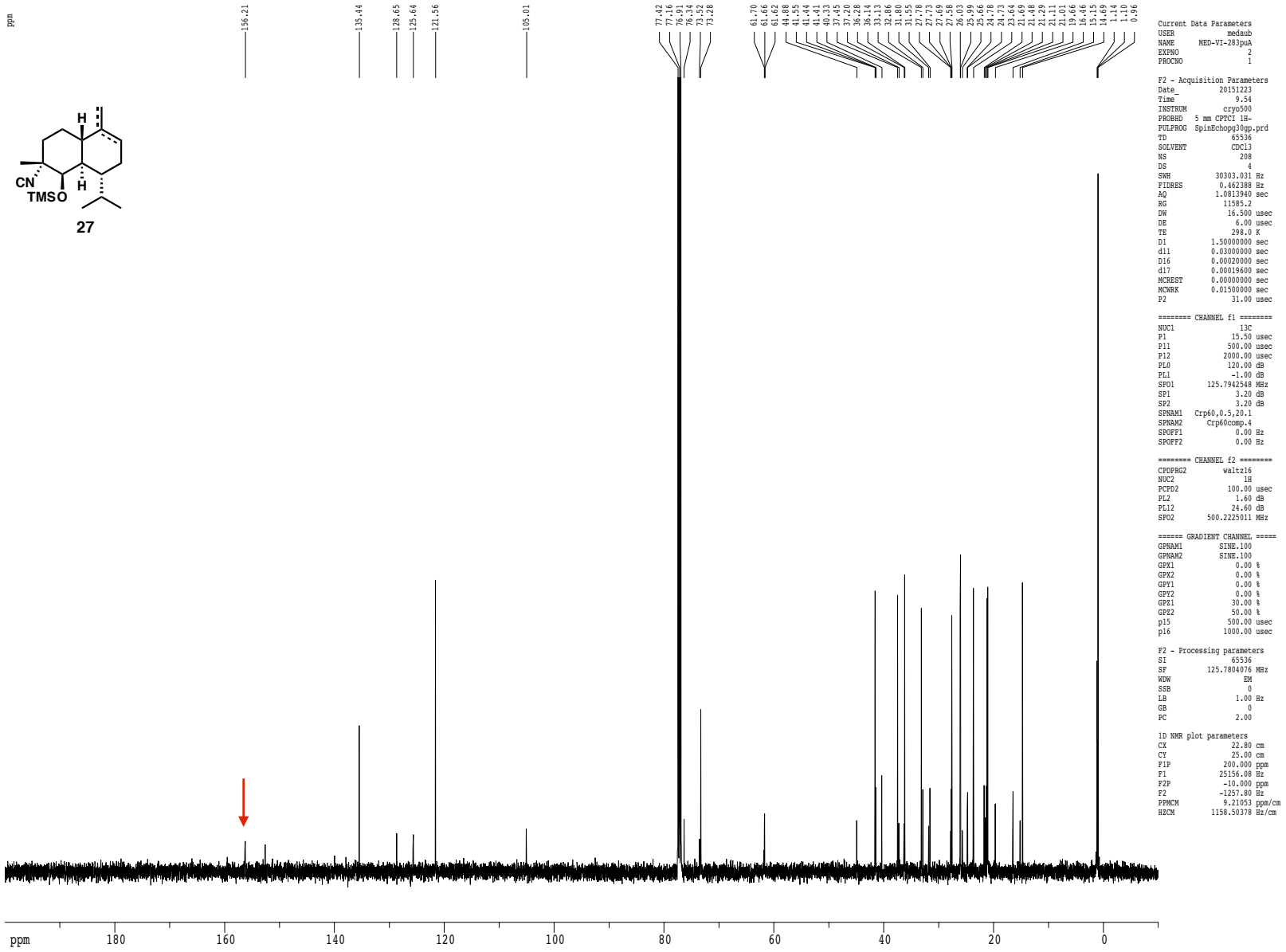
Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum


ppm
7.26006
5.40047
4.69575
4.69298
4.57971
3.89245
3.85648
3.76905
2.60825
2.57952
2.46826
2.45072
2.19188
2.17014
2.14731
1.94088
1.93417
1.92755
1.91025
1.90772
1.90077
1.81056
1.78839
1.76716
1.70725
1.69930
1.69258
1.68566
1.64004
1.63682
1.62046
1.39961
1.38055
1.37749
1.37409
1.33305
1.32346
0.99380
0.98008
0.93691
0.94315
0.92966
0.91596
0.84830
0.83955
0.83459
0.82632
0.79400
0.78023
0.16515
0.14569
0.12947
H
CN
TMSO
H
27
Current Data Parameters
USER medaub
NAME MED-VI-283puA
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151223
Time 9.51
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 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 parameters
SI 65536
SF 500.2200305 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm
Integral
1.000
0.181
0.181
1.203
0.304
0.343
0.364
0.220
1.124
16.117
1.295
6.803
0.826
4.822
4.791
13.886
ppm
9
8
7
6
5
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VI-283puA
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151223
Time 9.54
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 208
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 1.50000000 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

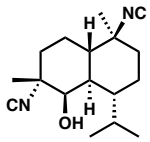
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== 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 125.7804076 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 25.00 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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Current Data Parameters
USER medaub
NAME MED-VI-297pu
EXPNO 1
PROCNO 1

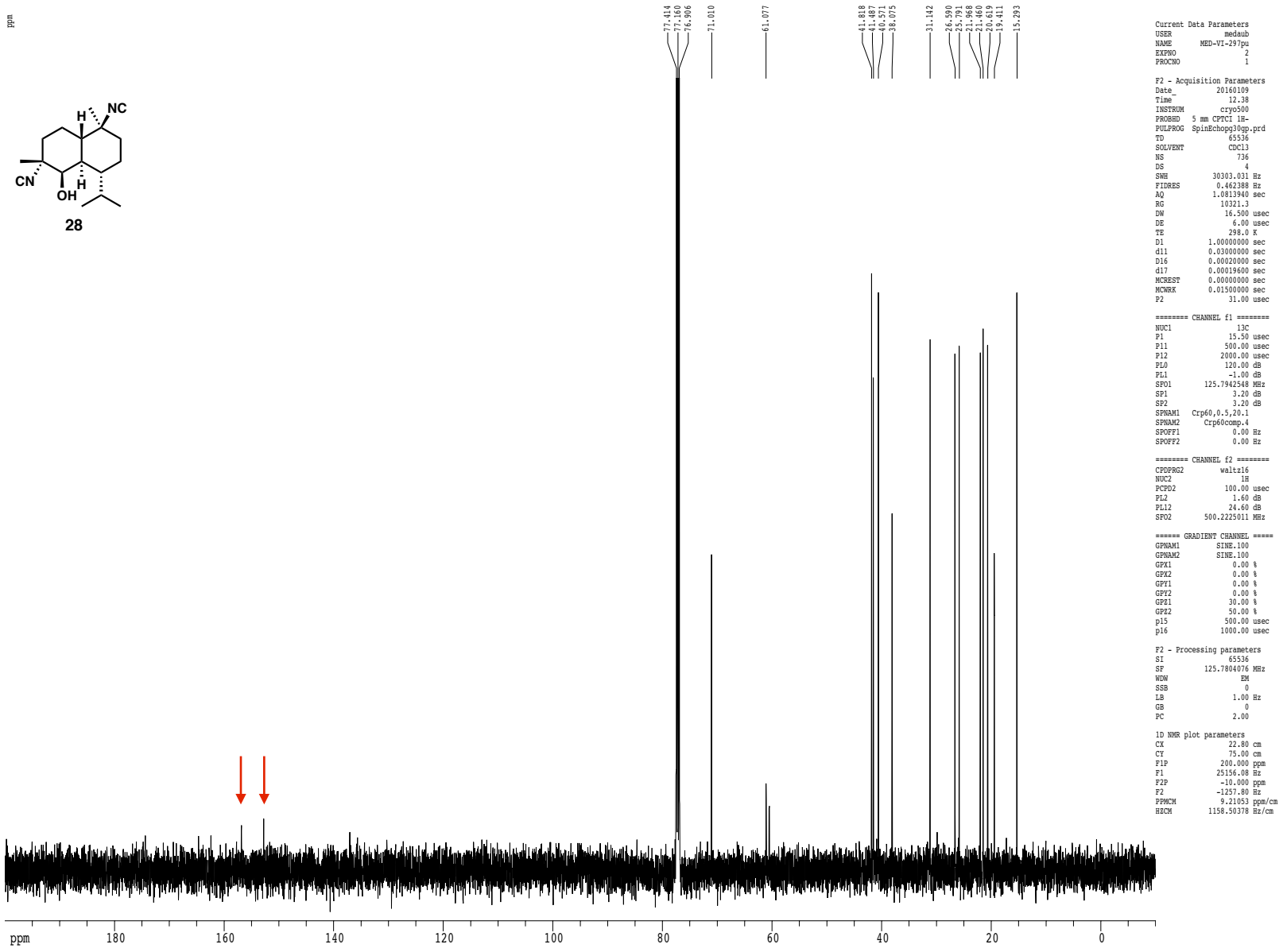
F2 - Acquisition Parameters
Date_ 20160109
Time 12.12
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200306 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 25.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VI-297pu
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160109
Time 12.38
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 736
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 10321.3
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 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

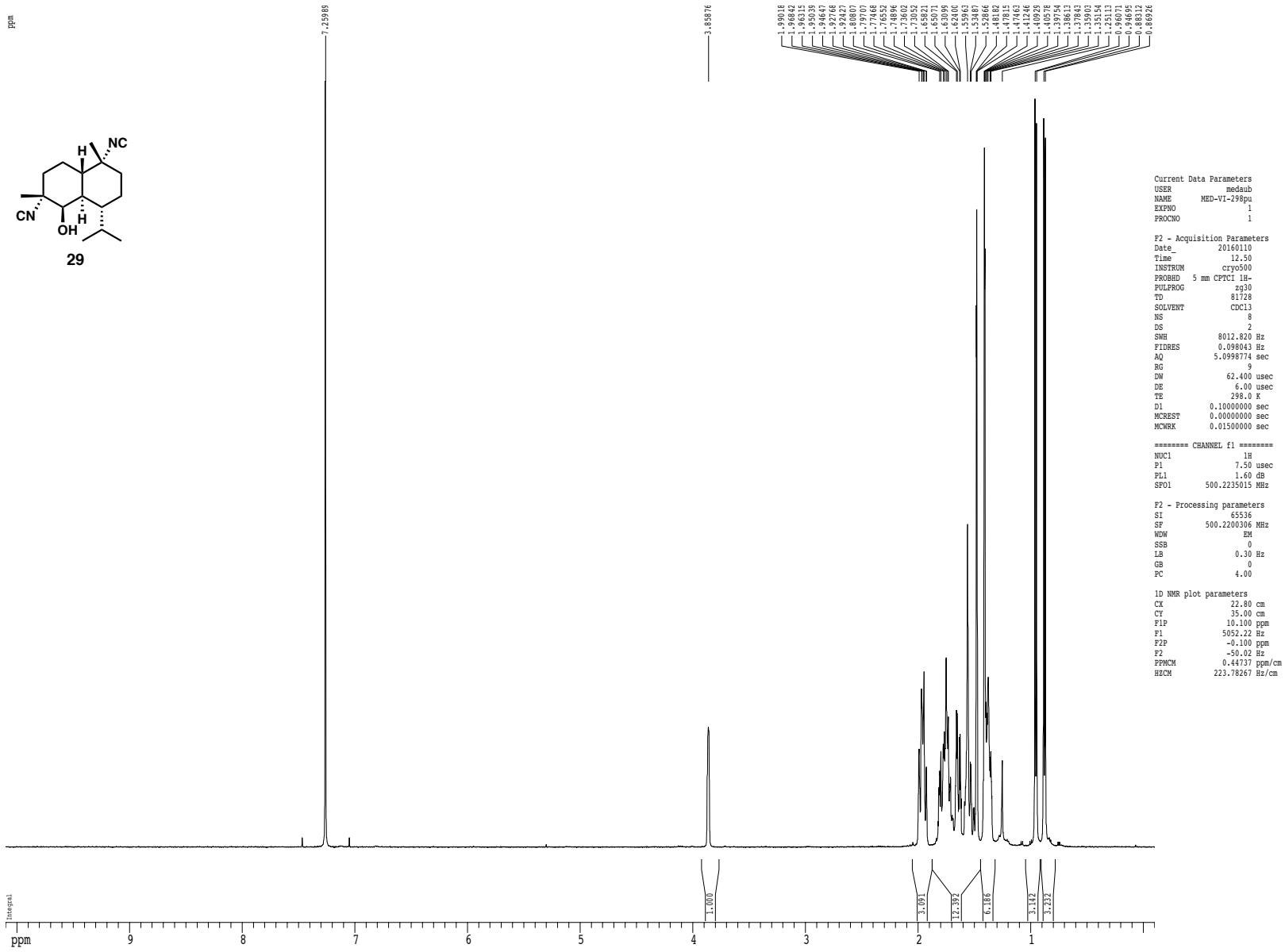
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== 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

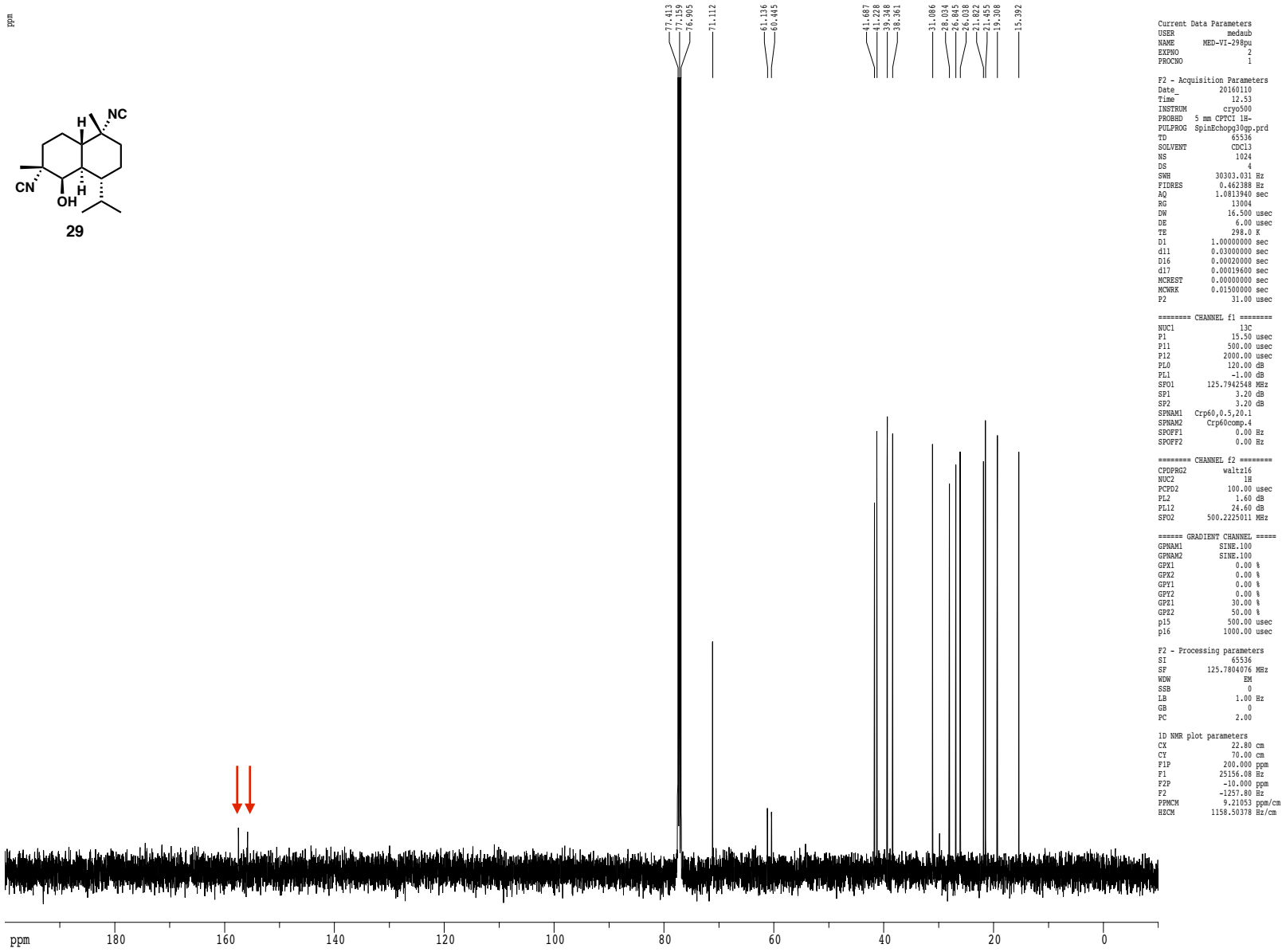
F2 - Processing parameters
SI 65536
SF 125.7804076 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 75.00 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

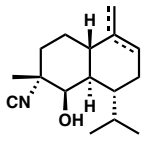
1H spectrum


ppm
7.25989
3.85876
1.99018
1.96842
1.96315
1.95039
1.94647
1.92768
1.92427
1.80807
1.79707
1.77466
1.76956
1.76096
1.73602
1.73052
1.65821
1.65071
1.63099
1.62400
1.55963
1.53487
1.52866
1.46182
1.47015
1.41745
1.41246
1.40929
1.40578
1.39754
1.38613
1.37843
1.35903
1.35154
1.25113
0.96071
0.94695
0.88521
0.86926
H
NC
CN
H
OH
29
Integral
1.000
3.091
12.392
6.186
3.142
3.232
ppm
9
8
7
6
5
4
3
2
1
Current Data Parameters
USER medaub
NAME MED-VI-298pu
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160110
Time 12.50
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 9
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 500.2200306 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 35.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



30

5.6:1 favoring Δ^9-isomer

Current Data Parameters
USER medaub
NAME MED-VI-300pu
EXPNO 1
PROCNO 1

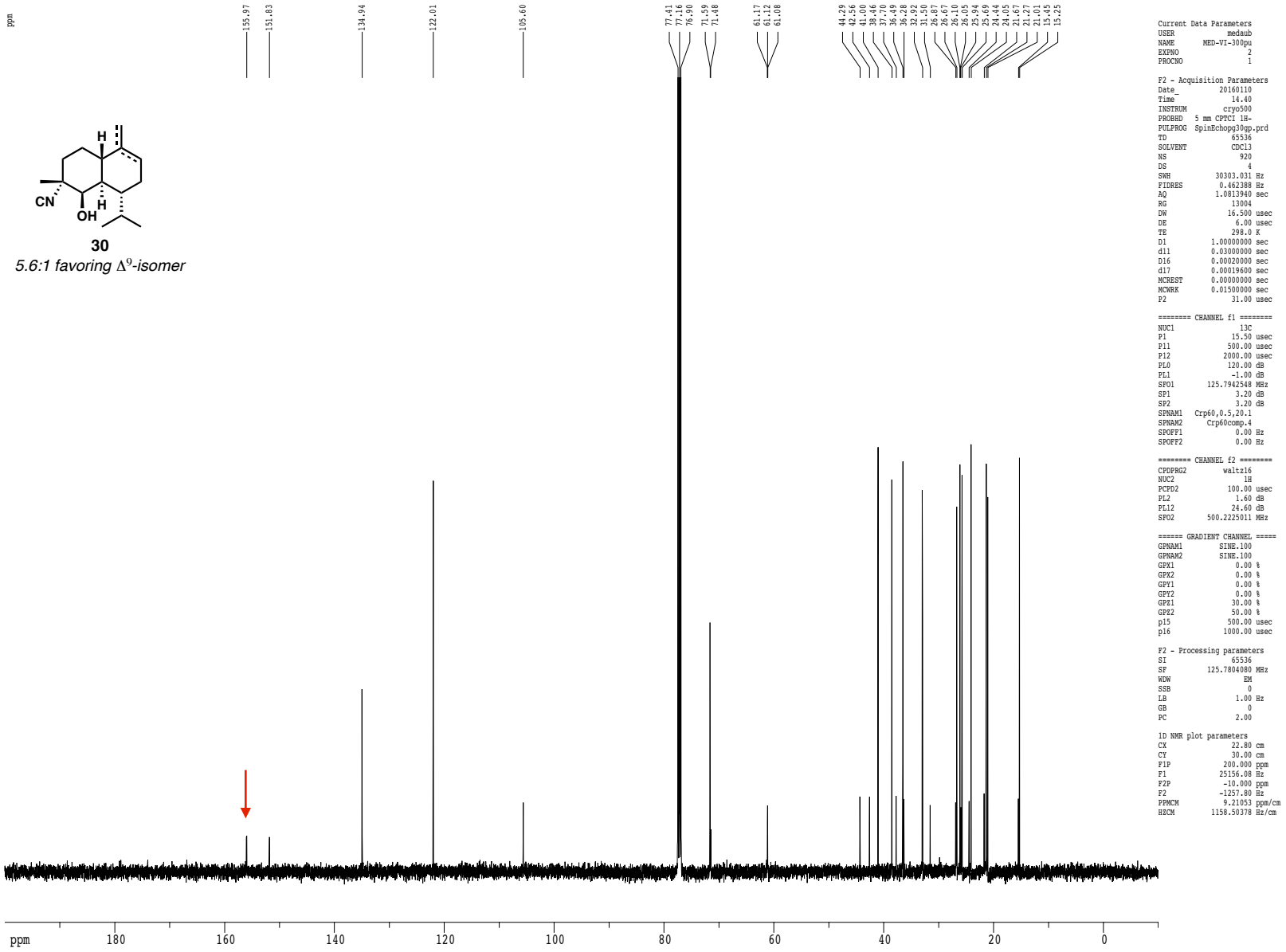
F2 - Acquisition Parameters
Date_ 20160110
Time 14.07
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 8
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200307 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 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



30

5.6:1 favoring Δ^9-isomer

```
Current Data Parameters
USER              medaub
NAME        MED-VI-300pu
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20160110
Time              14.40
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT           CDCl3
NS                 920
DS                   4
SWH          30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                13004
DW               16.500 usec
DE                6.00 usec
TE              298.0 K
D1             1.00000000 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

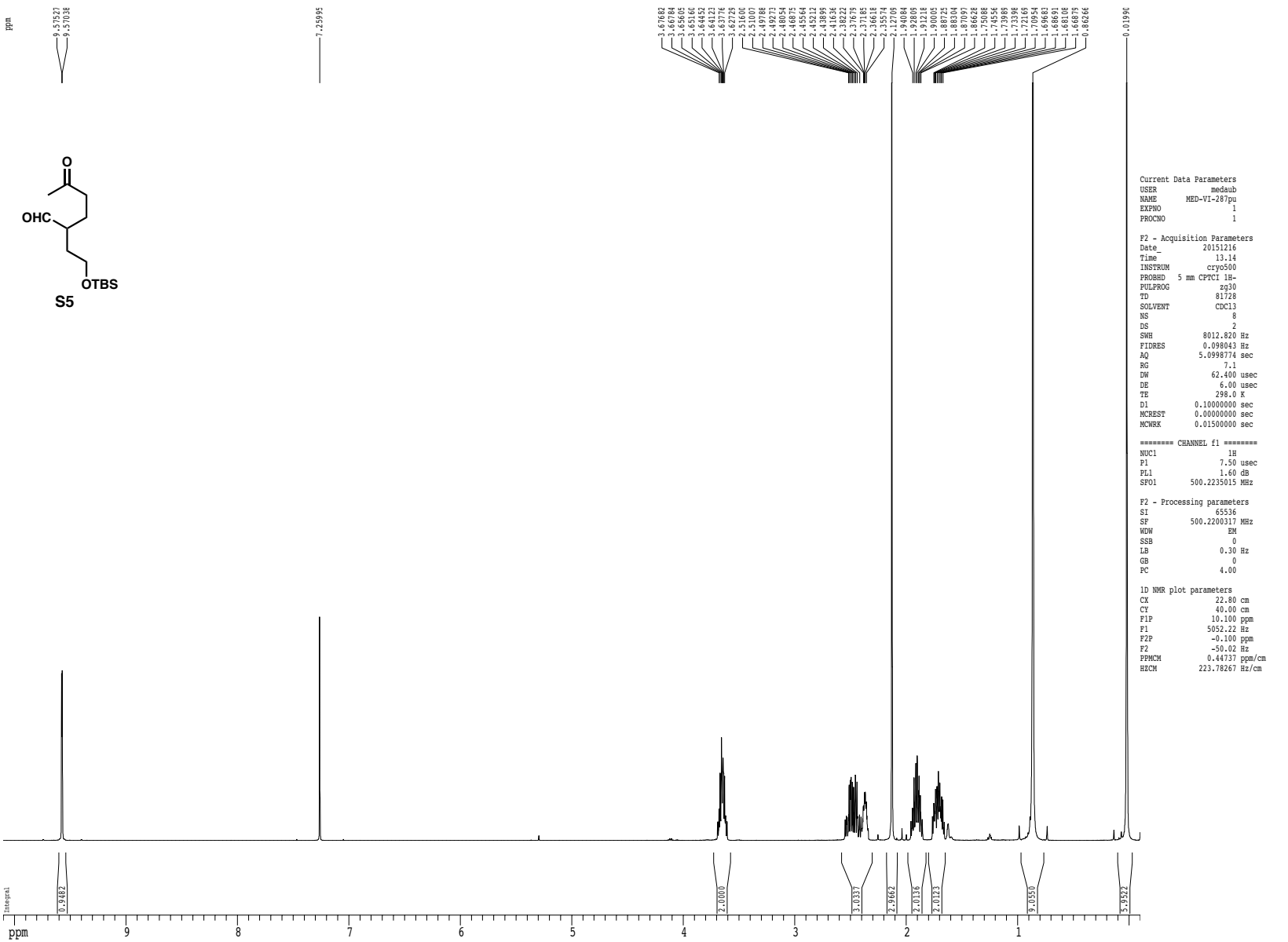
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             100.00 usec
PL2               1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== 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          125.7804080 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                30.00 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 Parameters
USER              medaub
NAME       MED-VI-287pu
EXPNO                1
PROCNO               1

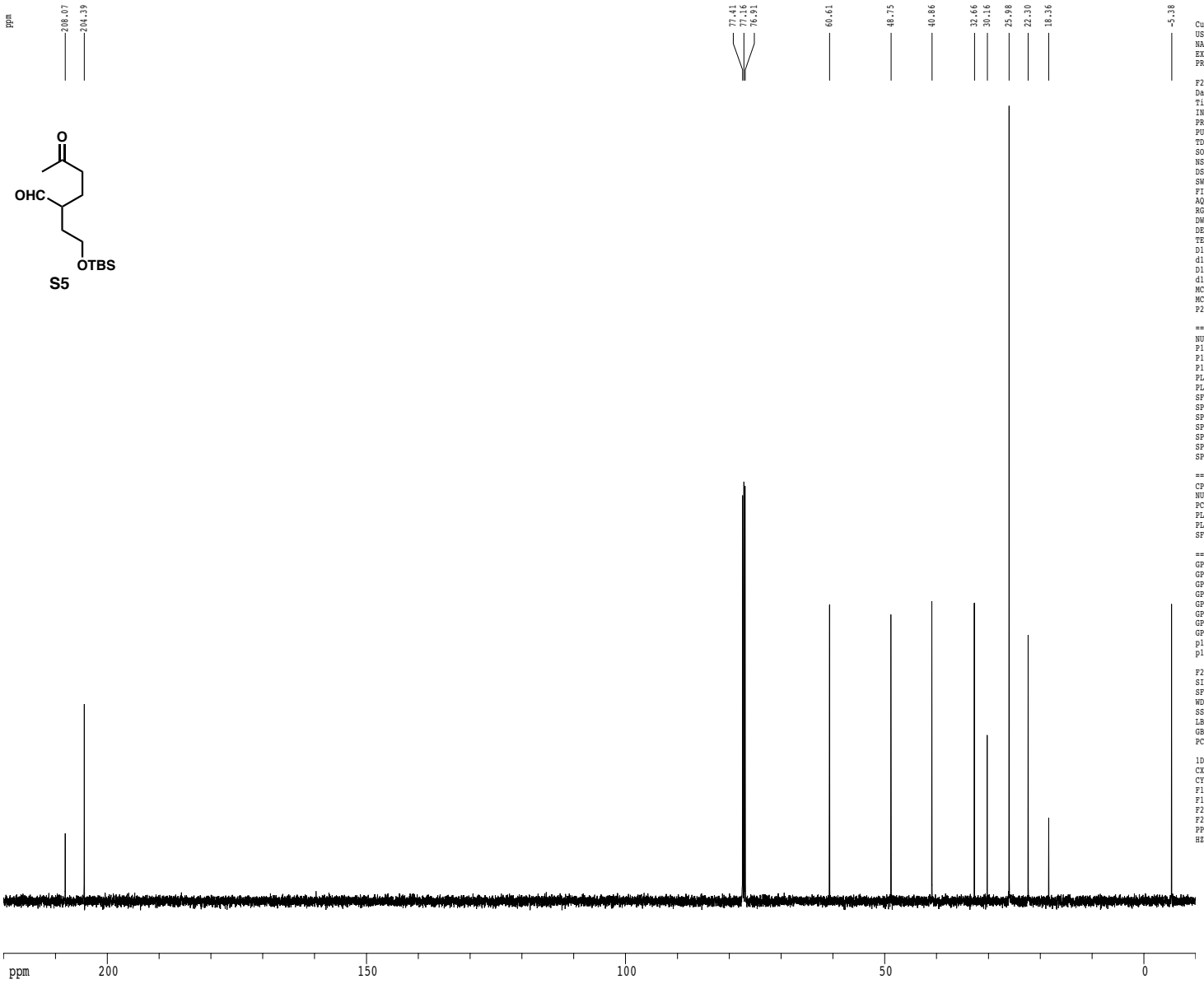
F2 - Acquisition Parameters
Date_          20151216
Time              13.14
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ             5.0998774 sec
RG                  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         500.2200317 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00

1D NMR plot parameters
CX                22.80 cm
CY                40.00 cm
F1P               10.100 ppm
F1              5052.22 Hz
F2P               -0.100 ppm
F2               -50.02 Hz
PPMCM          0.44737 ppm/cm
HZCM         223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME          MED-VI-287pu
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151216
Time                13.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      4
SWH            30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                  13004
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                33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

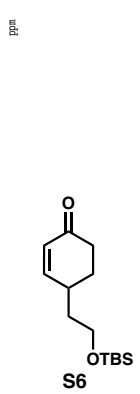
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== 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           125.7804085 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          1268.83752 Hz/cm
```

1H spectrum



S6


```
Current Data Parameters
USER                medaub
NAME          MED-VI-288pu
EXPNO                   1
PROCNO                  1

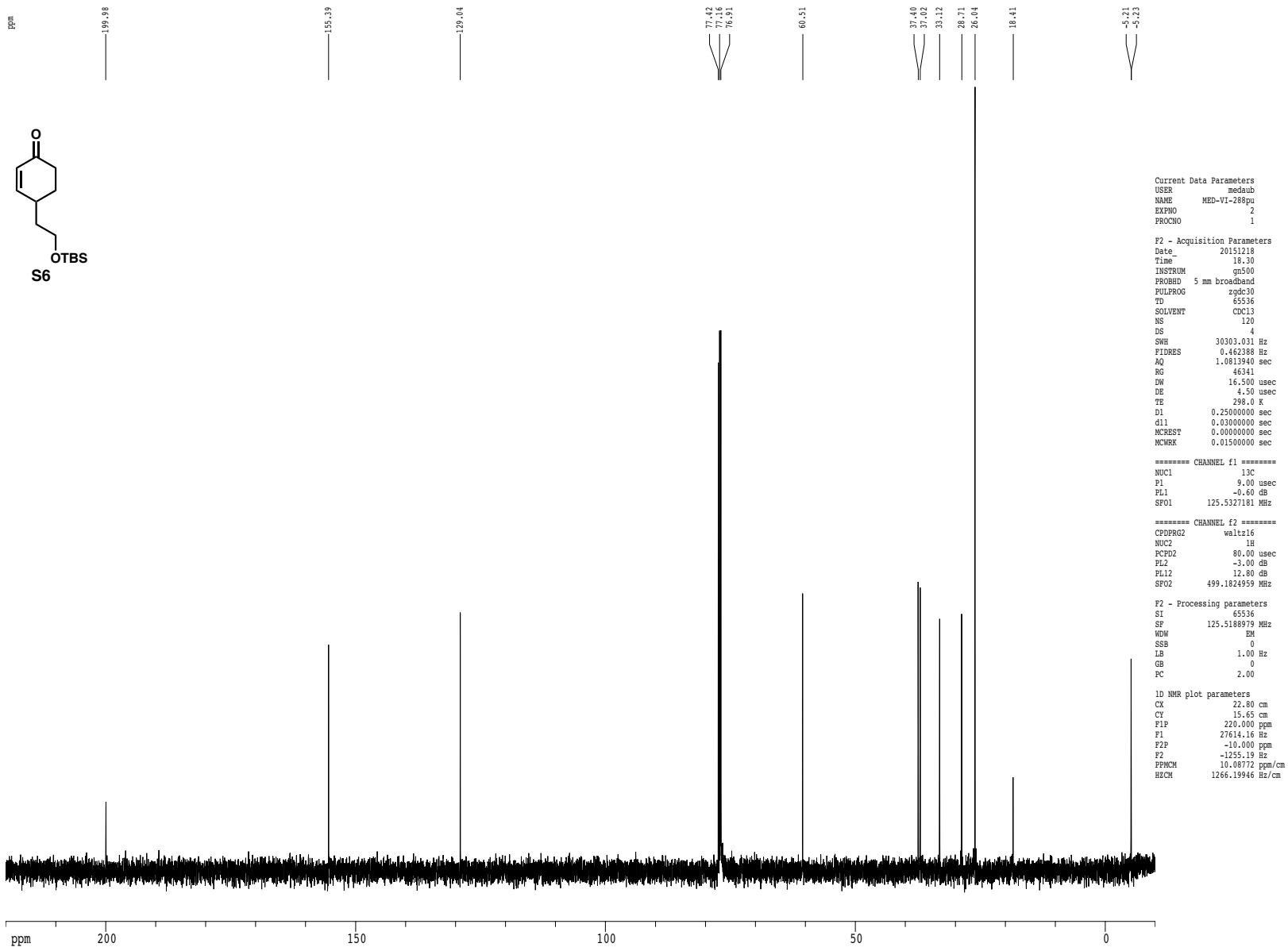
F2 - Acquisition Parameters
Date_            20151218
Time                18.27
INSTRUM             qn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                    114
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                -5.80 dB
SFO1          499.1834943 MHz

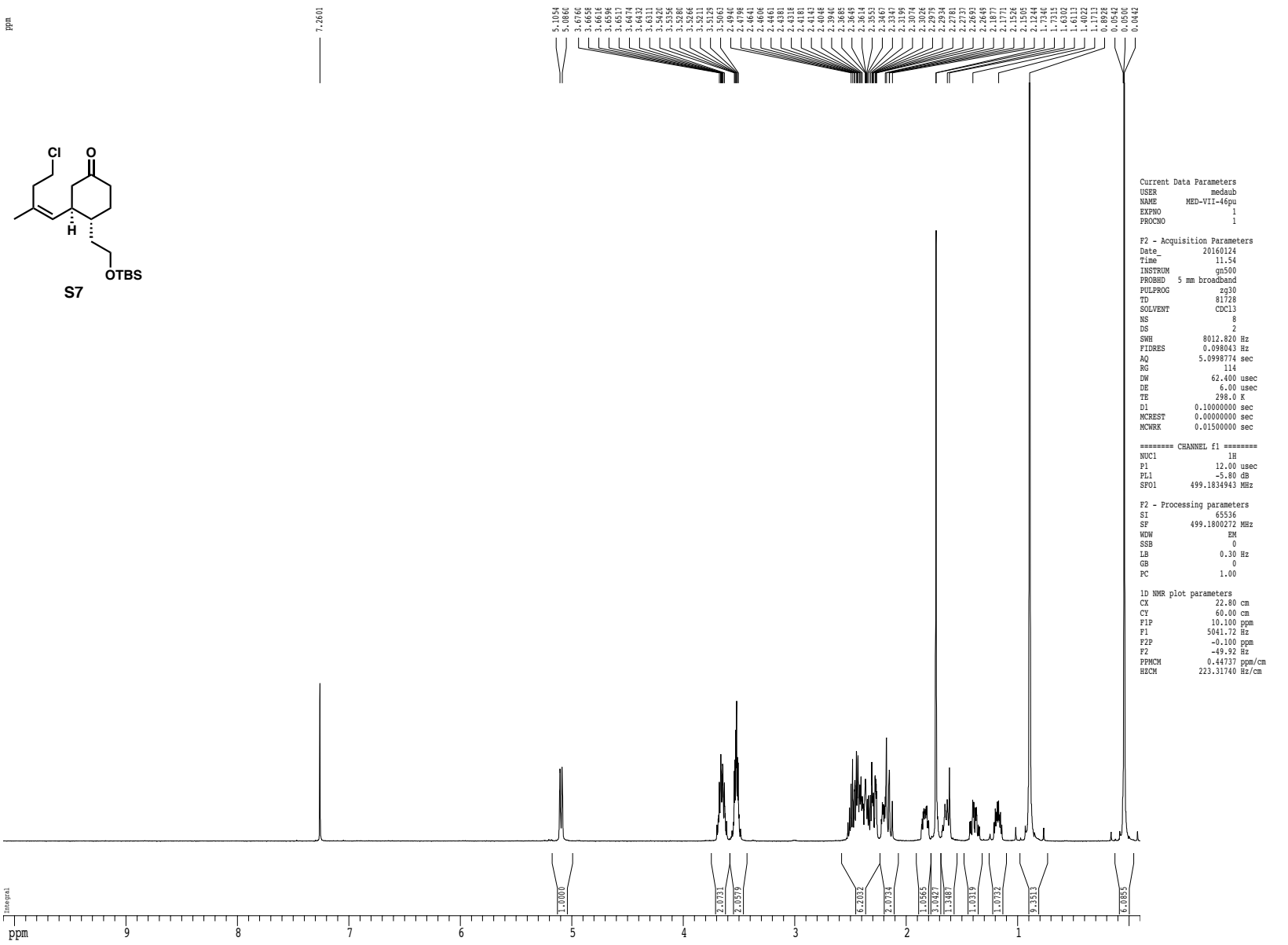
F2 - Processing parameters
SI                 65536
SF            499.1800268 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                100.00 cm
F1P               10.100 ppm
F1              5041.72 Hz
F2P               -0.100 ppm
F2               -49.92 Hz
PPMCM            0.44737 ppm/cm
HZCM           223.31740 Hz/cm
```

13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER medaub
NAME MED-VII-46pu
EXPNO 1
PROCNO 1

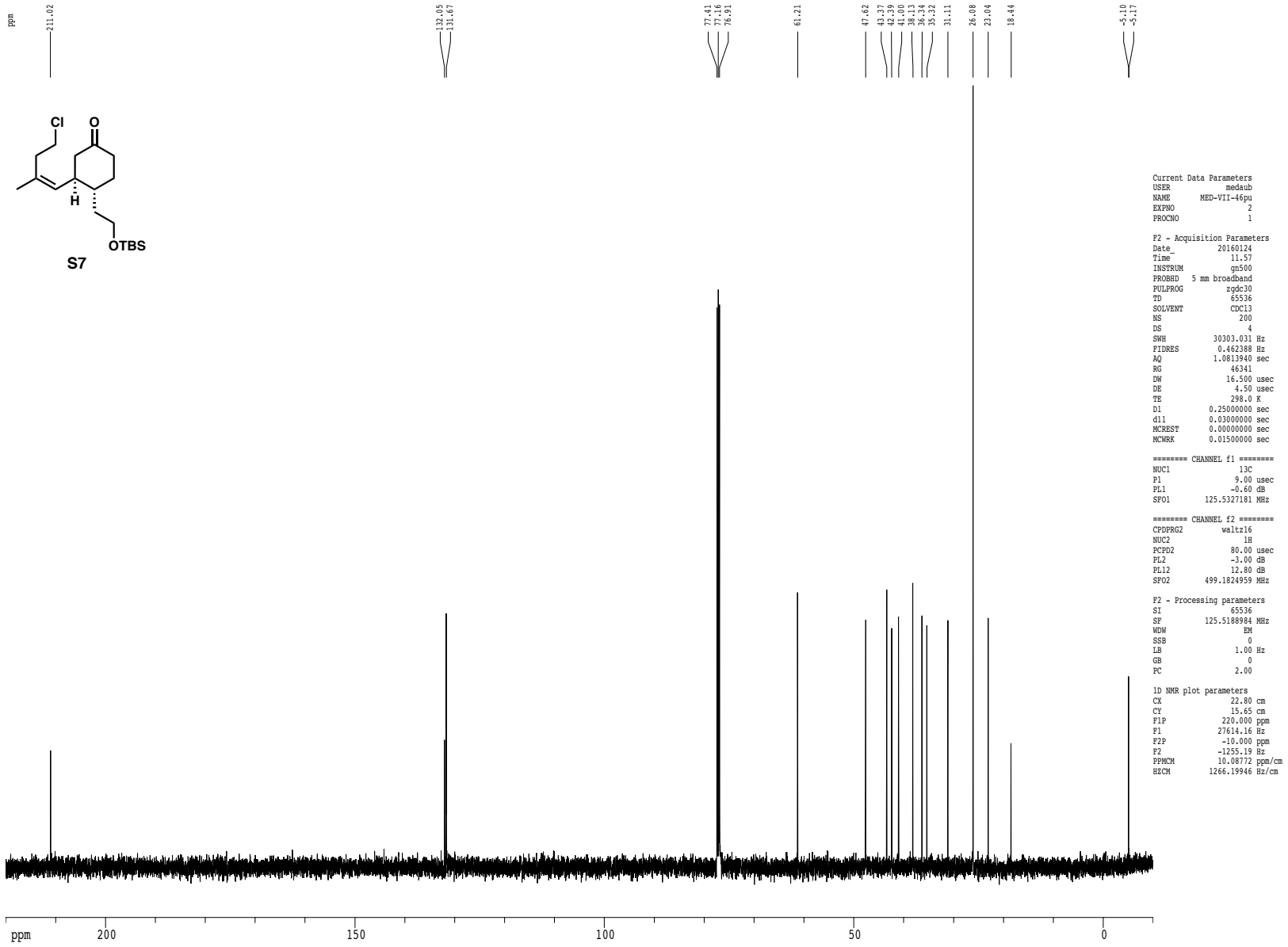
F2 - Acquisition Parameters
Date_ 20160124
Time 11.54
INSTRUM qn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 114
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.1834943 MHz

F2 - Processing parameters
SI 65536
SF 499.1800272 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VII-46pu
EXPNO 2
PROCNO 1

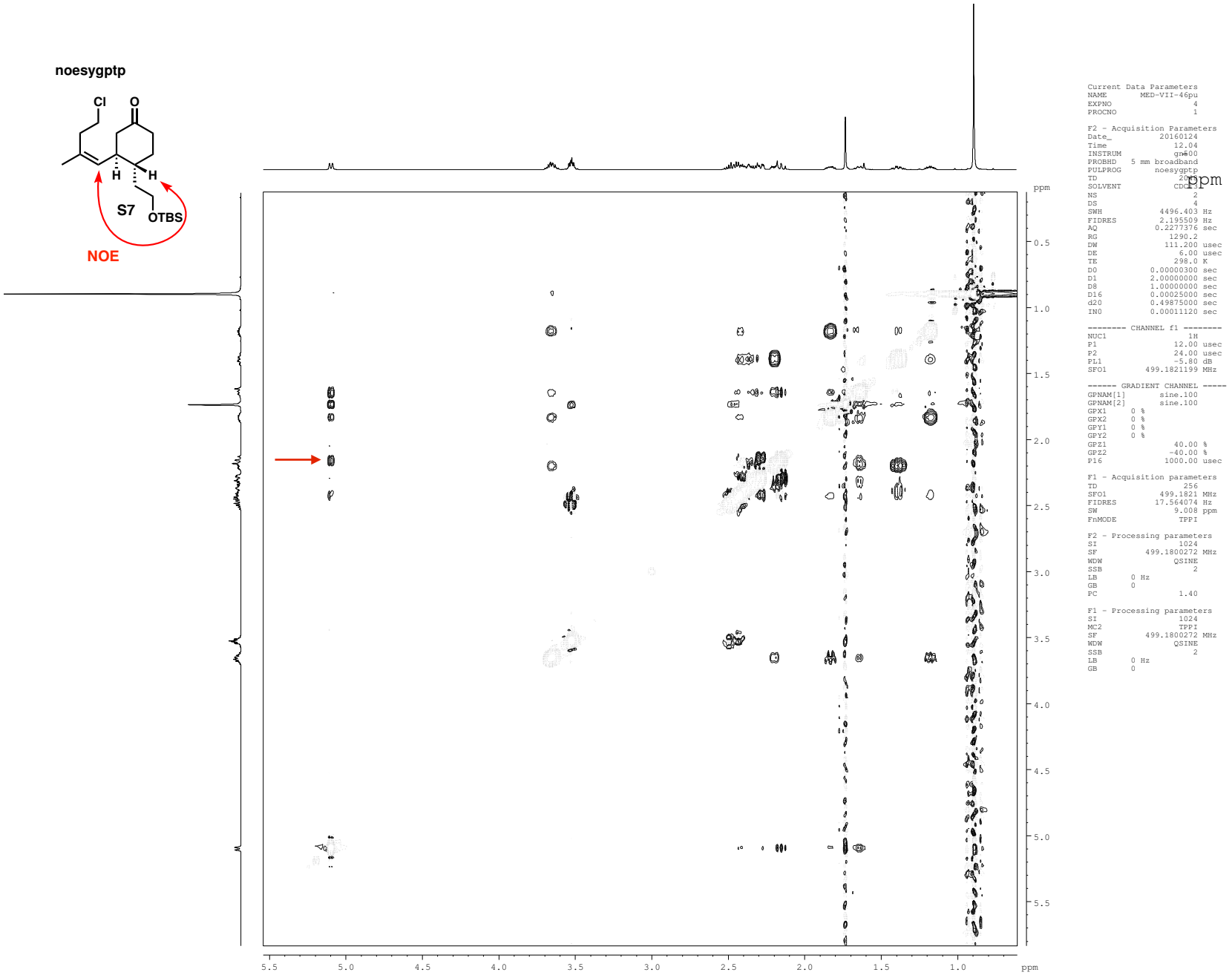
F2 - Acquisition Parameters
Date_ 20160124
Time 11.57
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 46341
DW 16.500 usec
DE 4.50 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -0.60 dB
SFO1 125.5327181 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.80 dB
SFO2 499.1824959 MHz

F2 - Processing parameters
SI 65536
SF 125.5188984 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 27614.16 Hz
F2P -10.000 ppm
F2 -1255.19 Hz
PPMCM 10.08772 ppm/cm
HZCM 1266.19946 Hz/cm



Current Data Parameters
NAME MED-VII-46pu
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160124
Time 12.04
INSTRUM spect
PROBHD 5 mm broadband
PULPROG noesygptp
TD 2048
SOLVENT CDCl3
NS 2
DS 4
SWH 4496.403 Hz
FIDRES 2.195509 Hz
AQ 0.2277376 sec
RG 1290.2
DW 111.200 usec
DE 6.00 usec
TE 298.0 K
D0 0.00000300 sec
D1 2.00000000 sec
D8 1.00000000 sec
D16 0.00025000 sec
d20 0.49875000 sec
IN0 0.00011120 sec

-------- CHANNEL f1 --------
NUC1 1H
P1 12.00 usec
P2 24.00 usec
PL1 -5.80 dB
SFO1 499.1821199 MHz

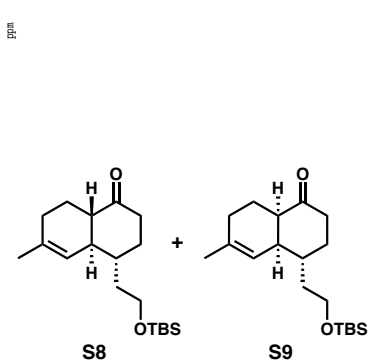
------ GRADIENT CHANNEL -----
GPNAM[1] sine.100
GPNAM[2] sine.100
GPX1 0 %
GPX2 0 %
GPY1 0 %
GPY2 0 %
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 499.1821 MHz
FIDRES 17.564074 Hz
SW 9.008 ppm
FnMODE TPPI

F2 - Processing parameters
SI 1024
SF 499.1800272 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 TPPI
SF 499.1800272 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

1H spectrum



Current Data Parameters
USER medaub
NAME MED-VII-45pu
EXPNO 1
PROCNO 1

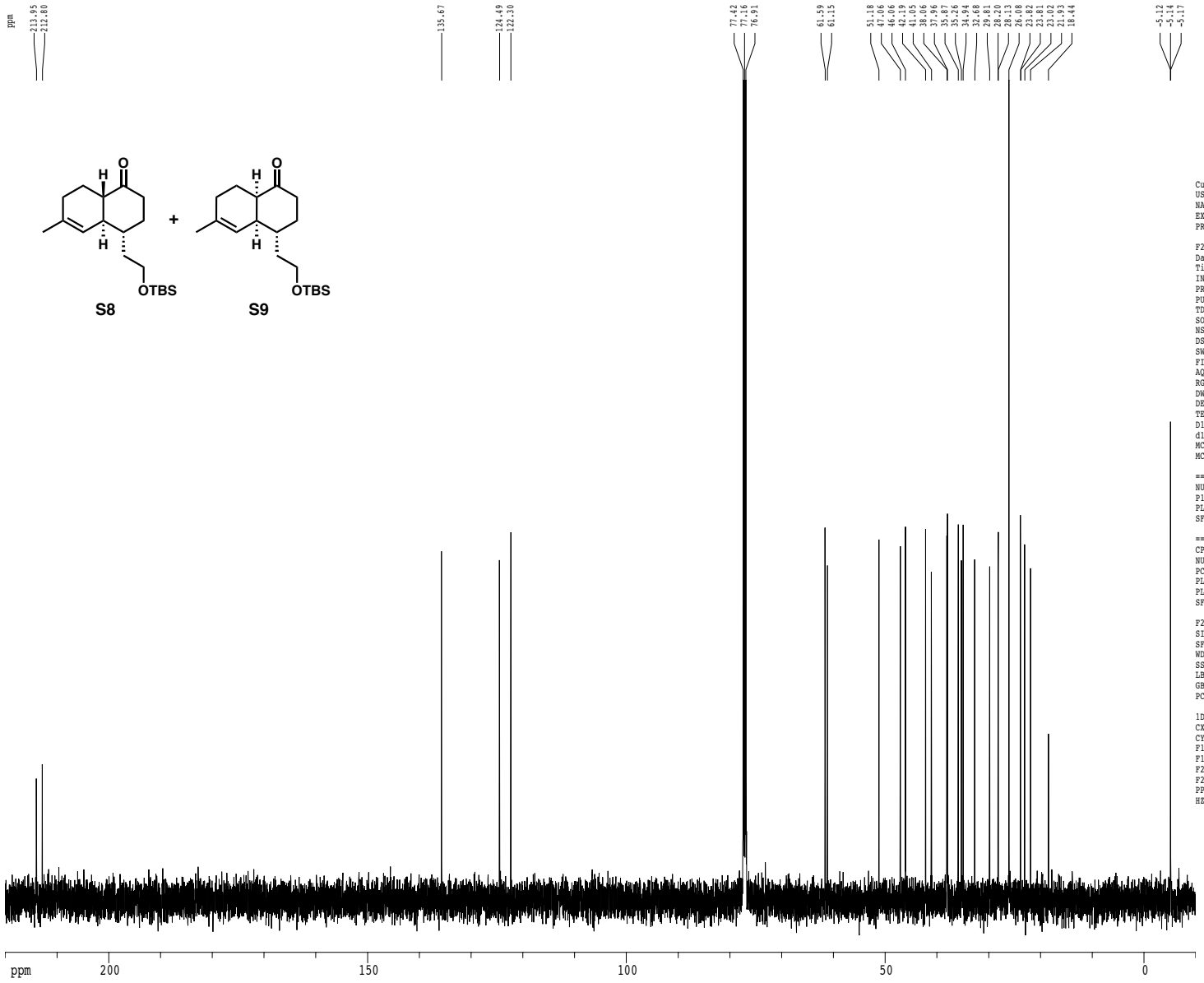
F2 - Acquisition Parameters
Date_ 20160124
Time 11.40
INSTRUM qn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 114
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.1834943 MHz

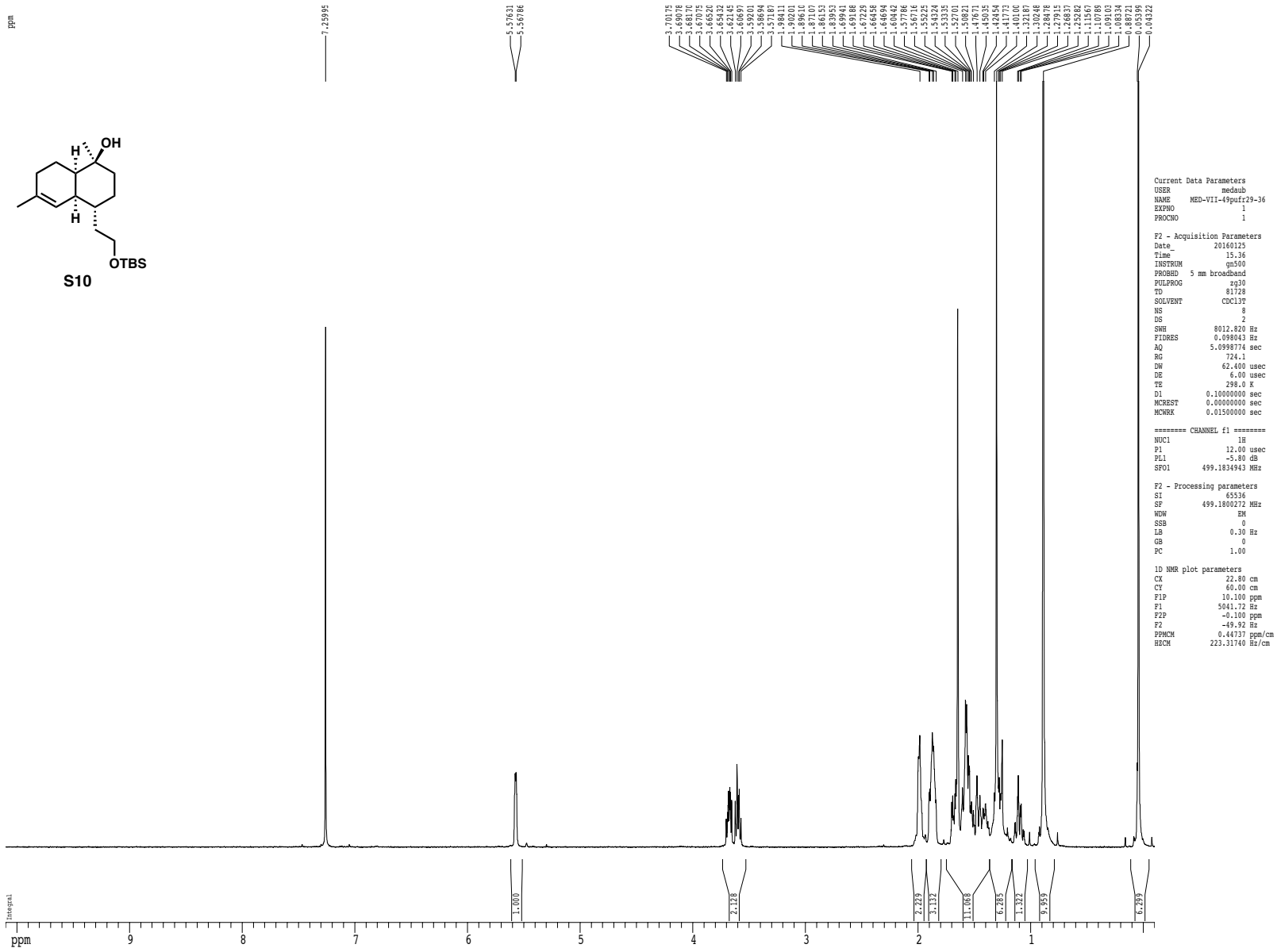
F2 - Processing parameters
SI 65536
SF 499.1800271 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm

13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER medaub
NAME MED-VII-49pufr29-36
EXPNO 1
PROCNO 1

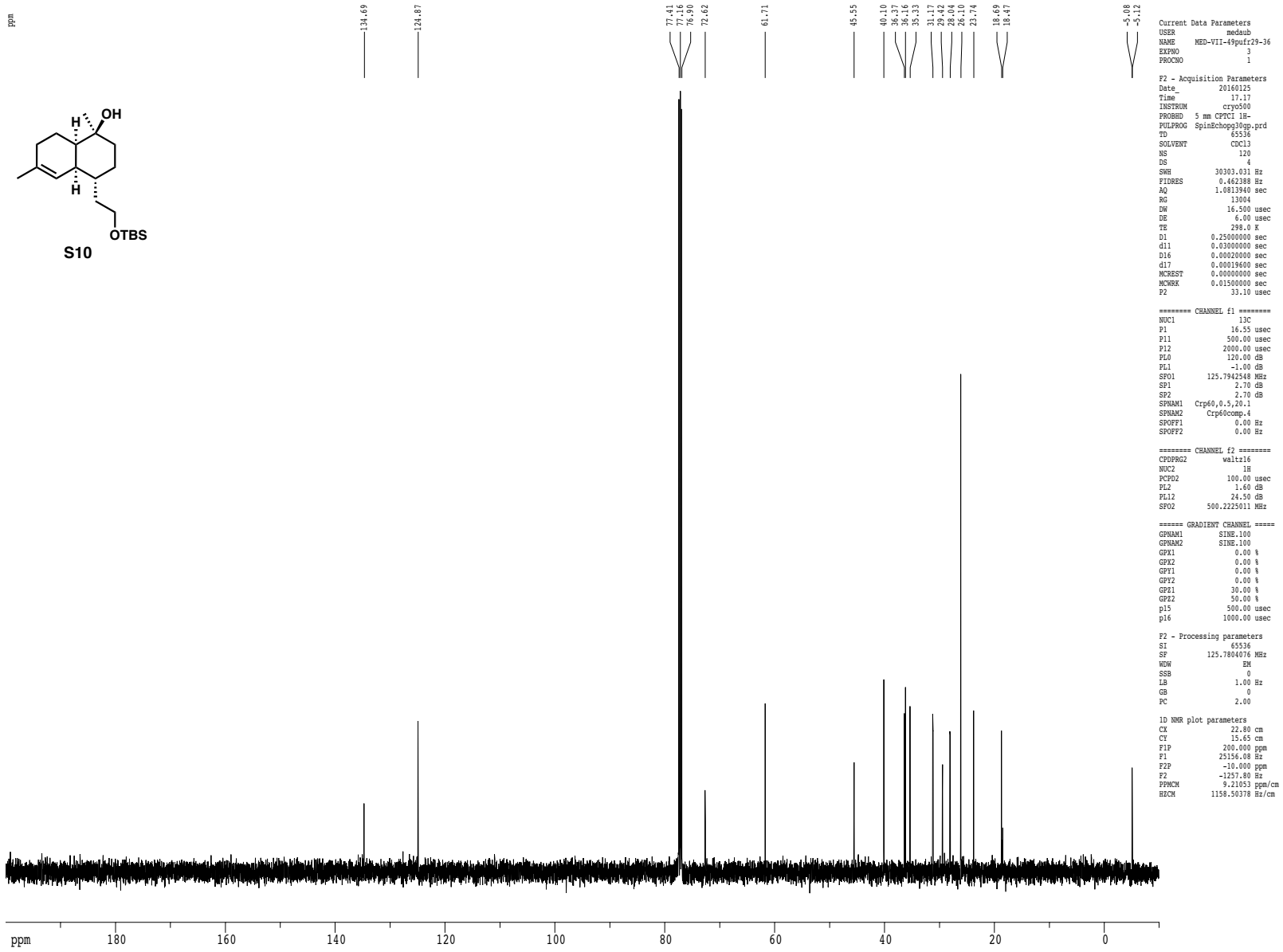
F2 - Acquisition Parameters
Date_ 20160125
Time 15.36
INSTRUM qn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3P
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 724.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.1834943 MHz

F2 - Processing parameters
SI 65536
SF 499.1800272 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME       MED-VII-49pufr29-36
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_            20160125
Time                17.17
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    120
DS                      4
SWH            30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                  13004
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                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

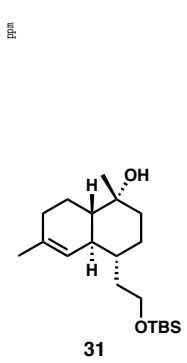
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

====== 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           125.7804076 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



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Current Data Parameters
USER medaub
NAME MED-VII-49pufr18-24
EXPNO 1
PROCNO 1

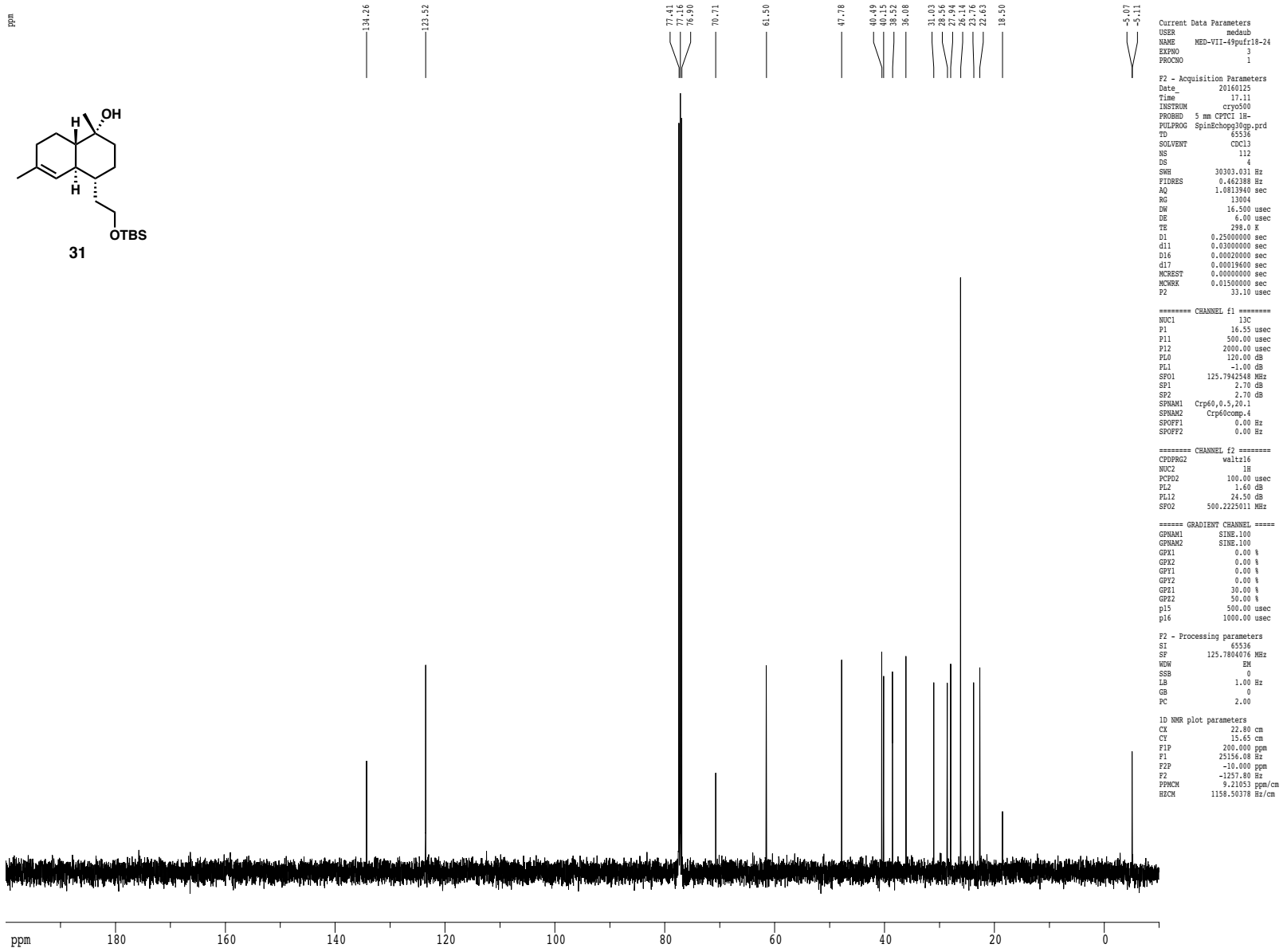
F2 - Acquisition Parameters
Date_ 20160125
Time 15.33
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 574.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.1834943 MHz

F2 - Processing parameters
SI 65536
SF 499.1800271 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 45.00 cm
F1P 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VII-49pufr18-24
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160125
Time 17.11
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30qp.prd
TD 65536
SOLVENT CDCl3
NS 112
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 13004
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 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

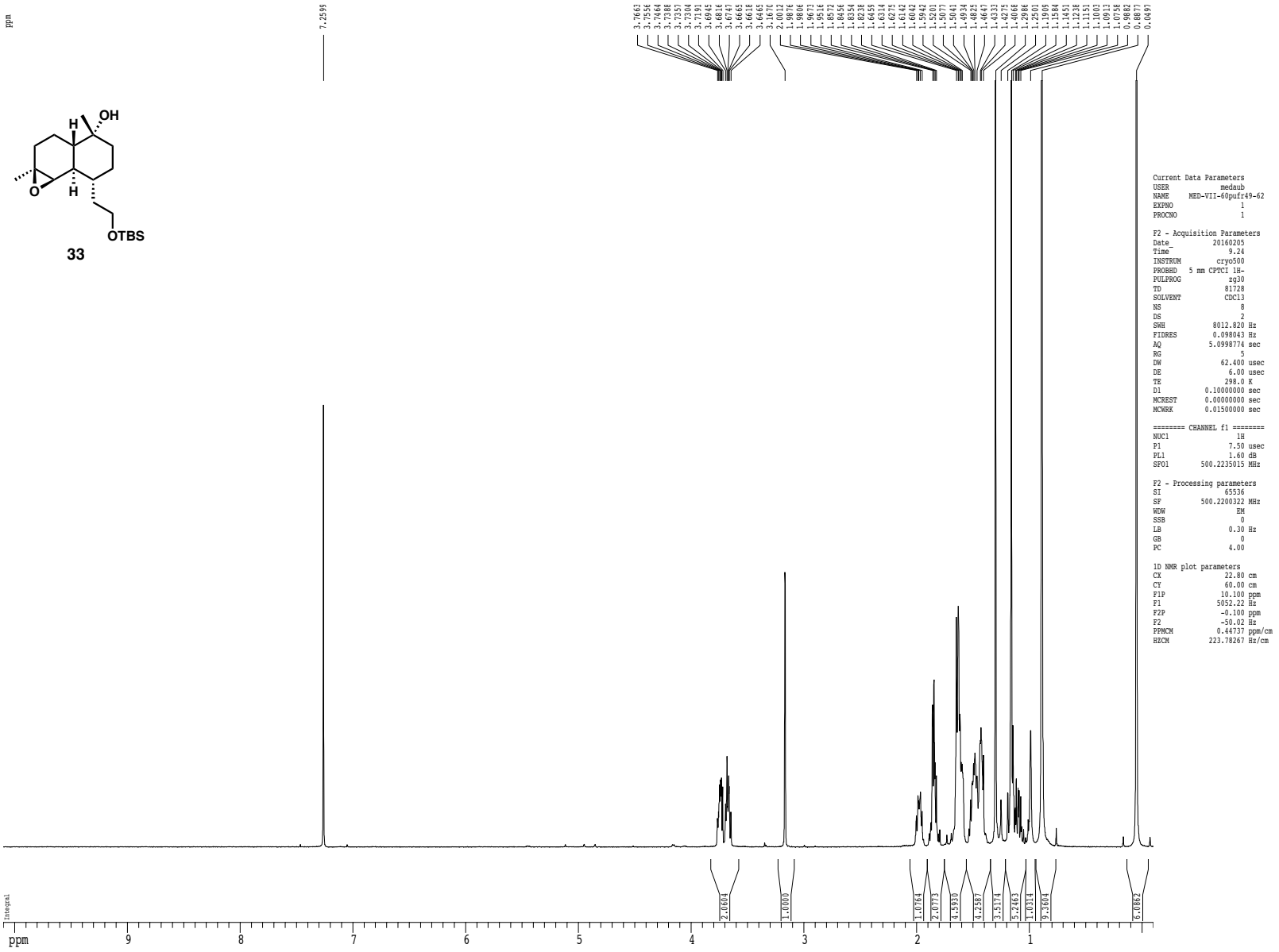
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== 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 125.7804076 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



Current Data Parameters
USER medaub
NAME MED-VII-60pafr49-62
EXPNO 1
PROCNO 1

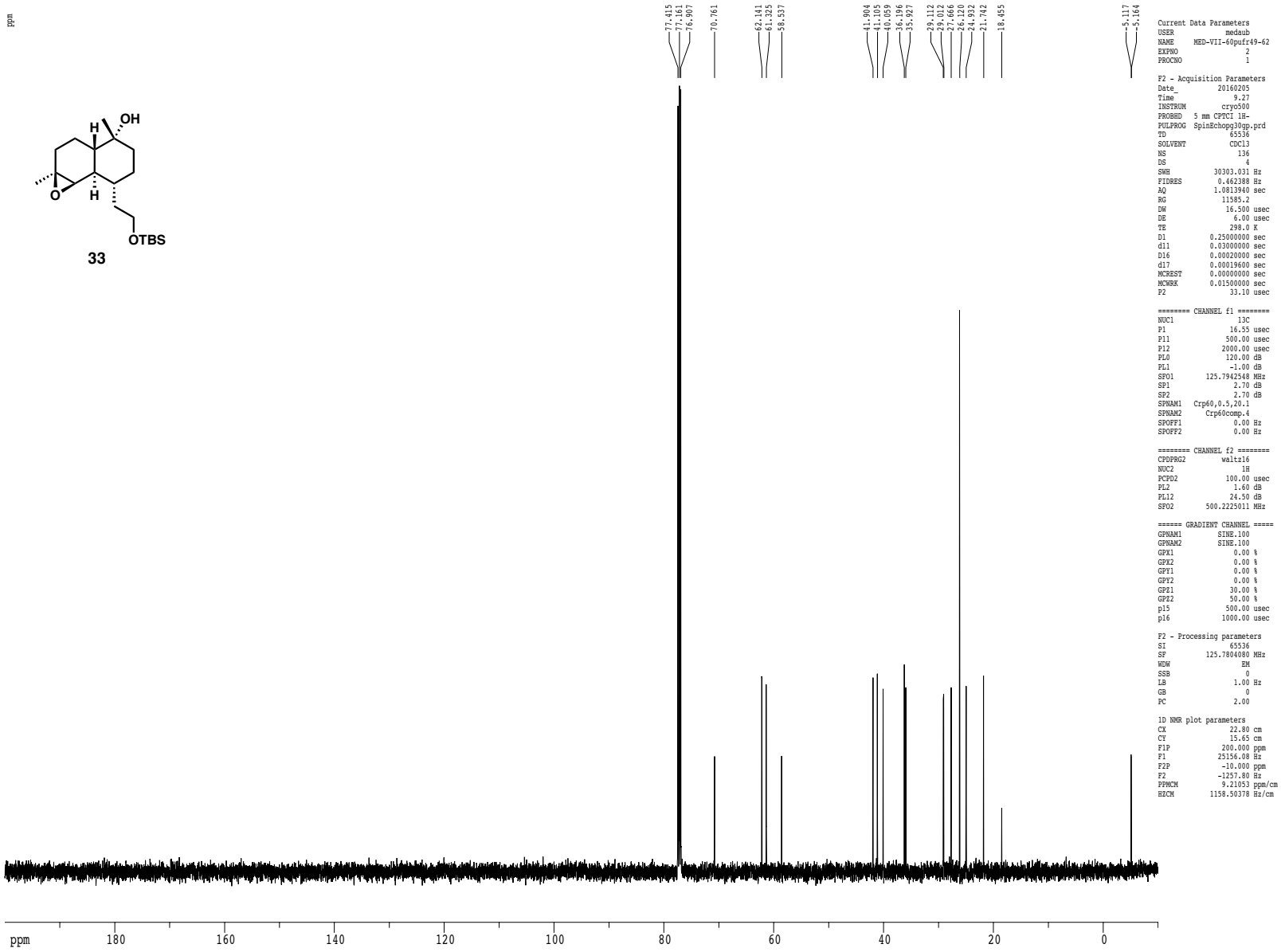
F2 - Acquisition Parameters
Date_ 20160205
Time 9.24
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

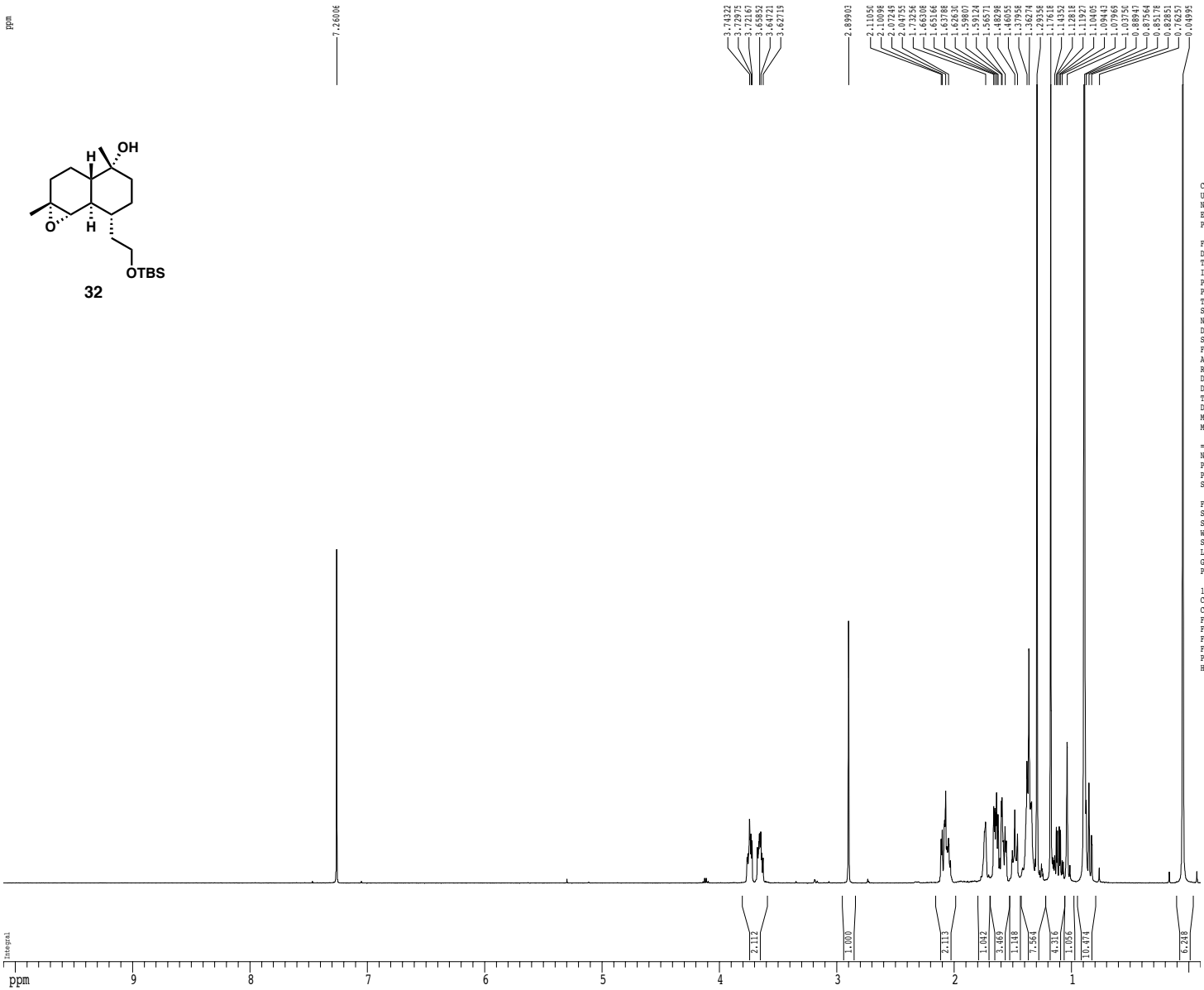
F2 - Processing parameters
SI 65536
SF 500.2200322 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.60 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum




```
Current Data Parameters
USER                medaub
NAME      MED-VII-60pufr64-80
EXPNO                    1
PROCNO                   1

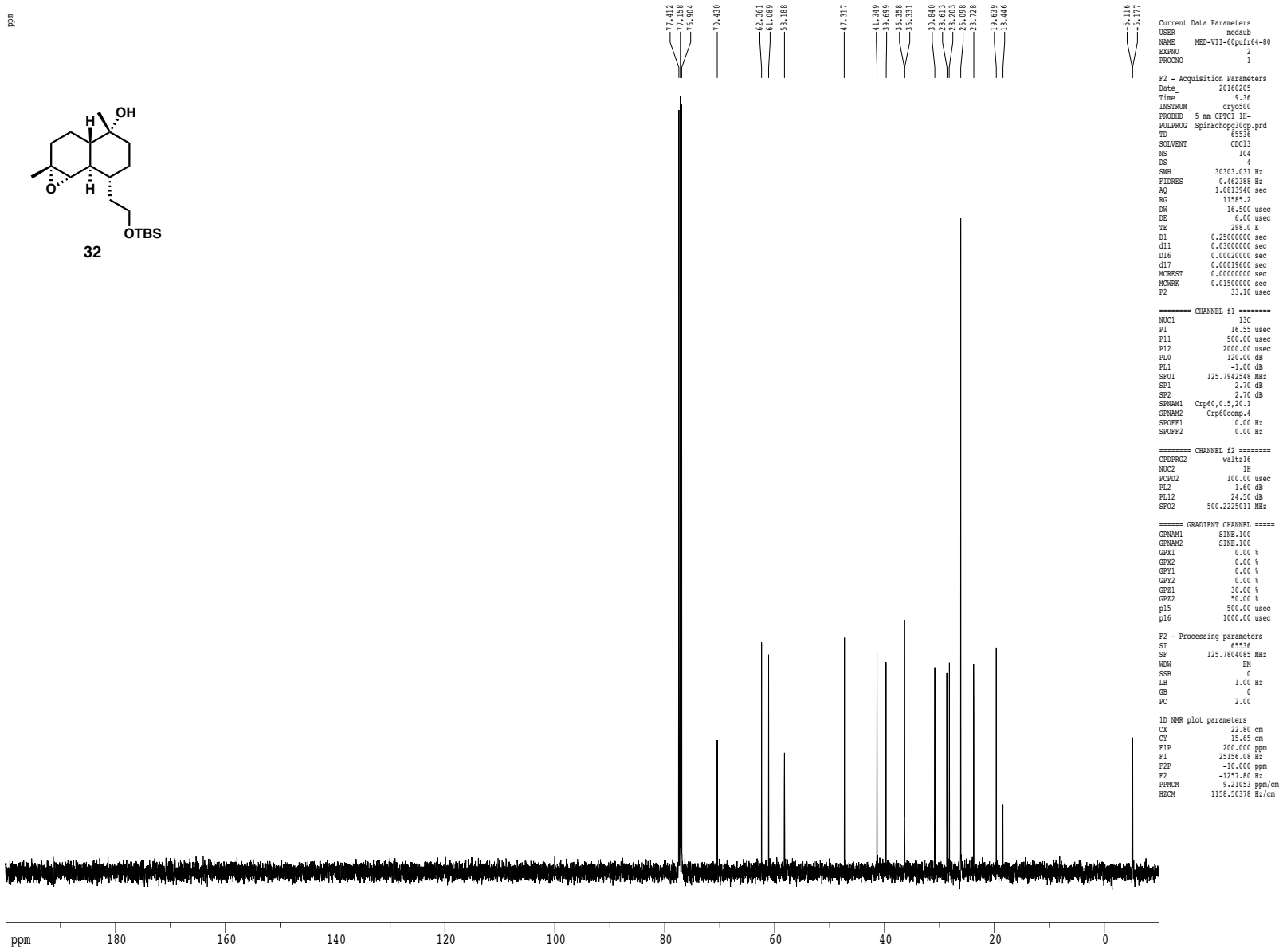
F2 - Acquisition Parameters
Date_              20160205
Time                  9.33
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES               0.098043 Hz
AQ                5.0998774 sec
RG                       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

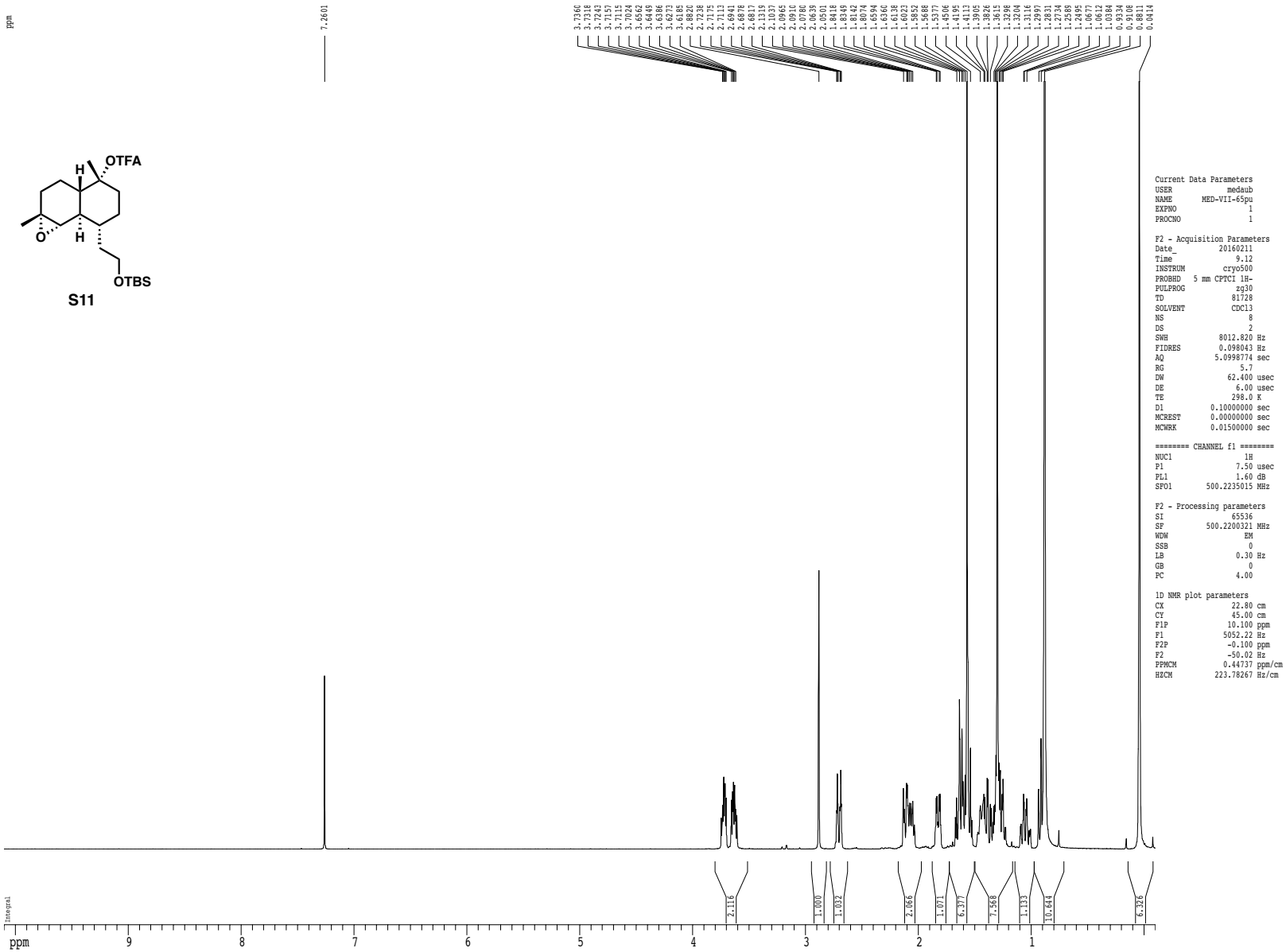
F2 - Processing parameters
SI                   65536
SF             500.2200321 MHz
WDW                      EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   45.00 cm
F1P                 10.100 ppm
F1                5052.22 Hz
F2P                 -0.100 ppm
F2                  -50.02 Hz
PPMCM              0.44737 ppm/cm
HZCM             223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



S11

```
Current Data Parameters
USER                medaub
NAME         MED-VII-65pu
EXPNO                  1
PROCNO                 1

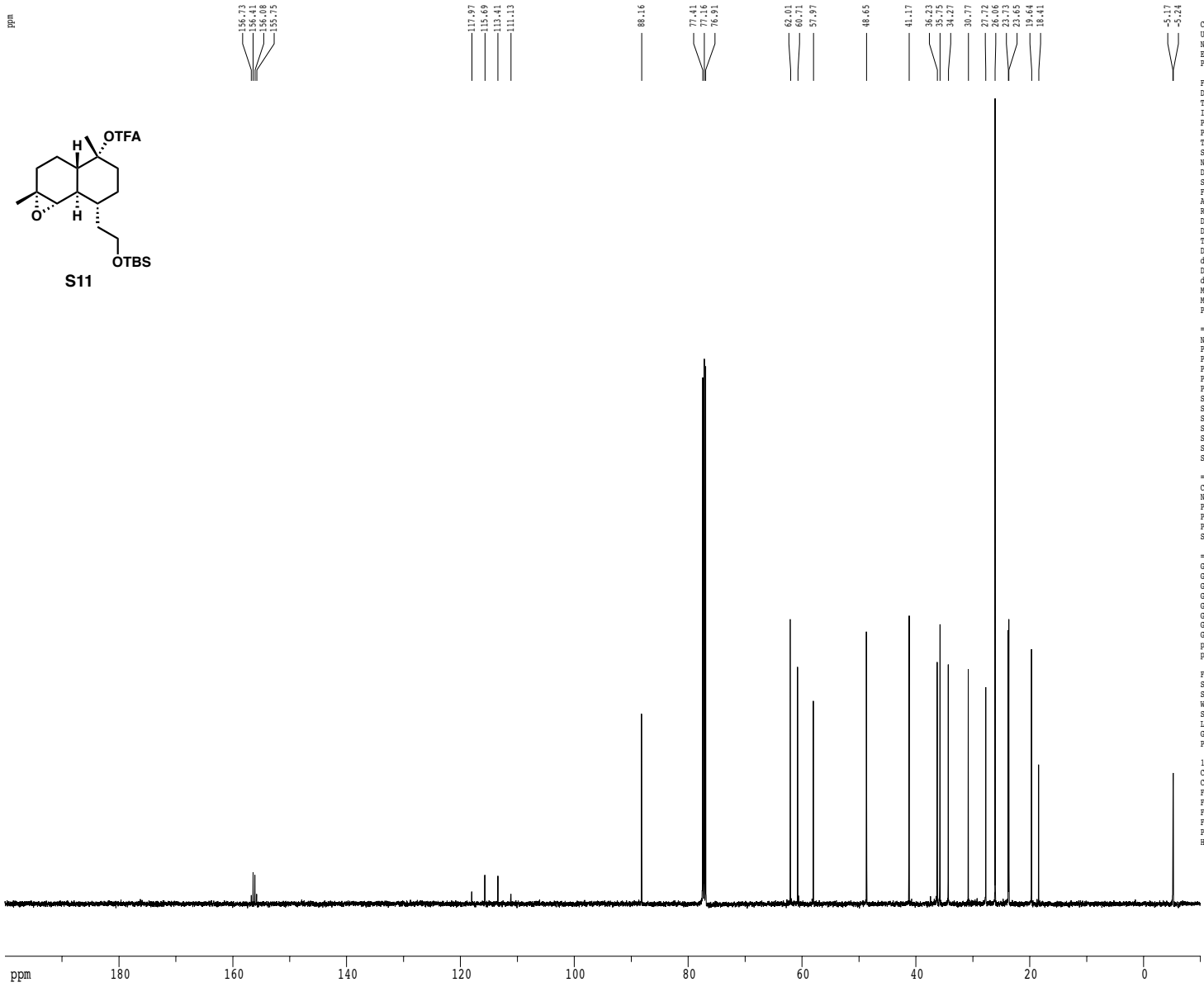
F2 - Acquisition Parameters
Date_           20160211
Time               9.12
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 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                 7.50 usec
PL1                1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200321 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 45.00 cm
F1P               10.100 ppm
F1                5052.22 Hz
F2P               -0.100 ppm
F2                 -50.02 Hz
PPMCM           0.44737 ppm/cm
HZCM          223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME         MED-VII-65pu
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160211
Time                9.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   440
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
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

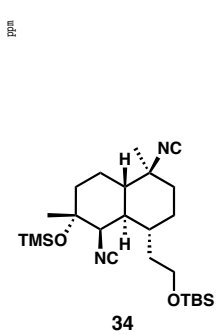
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2         500.2225011 MHz

====== 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           125.7804080 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



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```
Current Data Parameters
USER                medaub
NAME       MED-VII-74puA
EXPNO                   1
PROCNO                  1

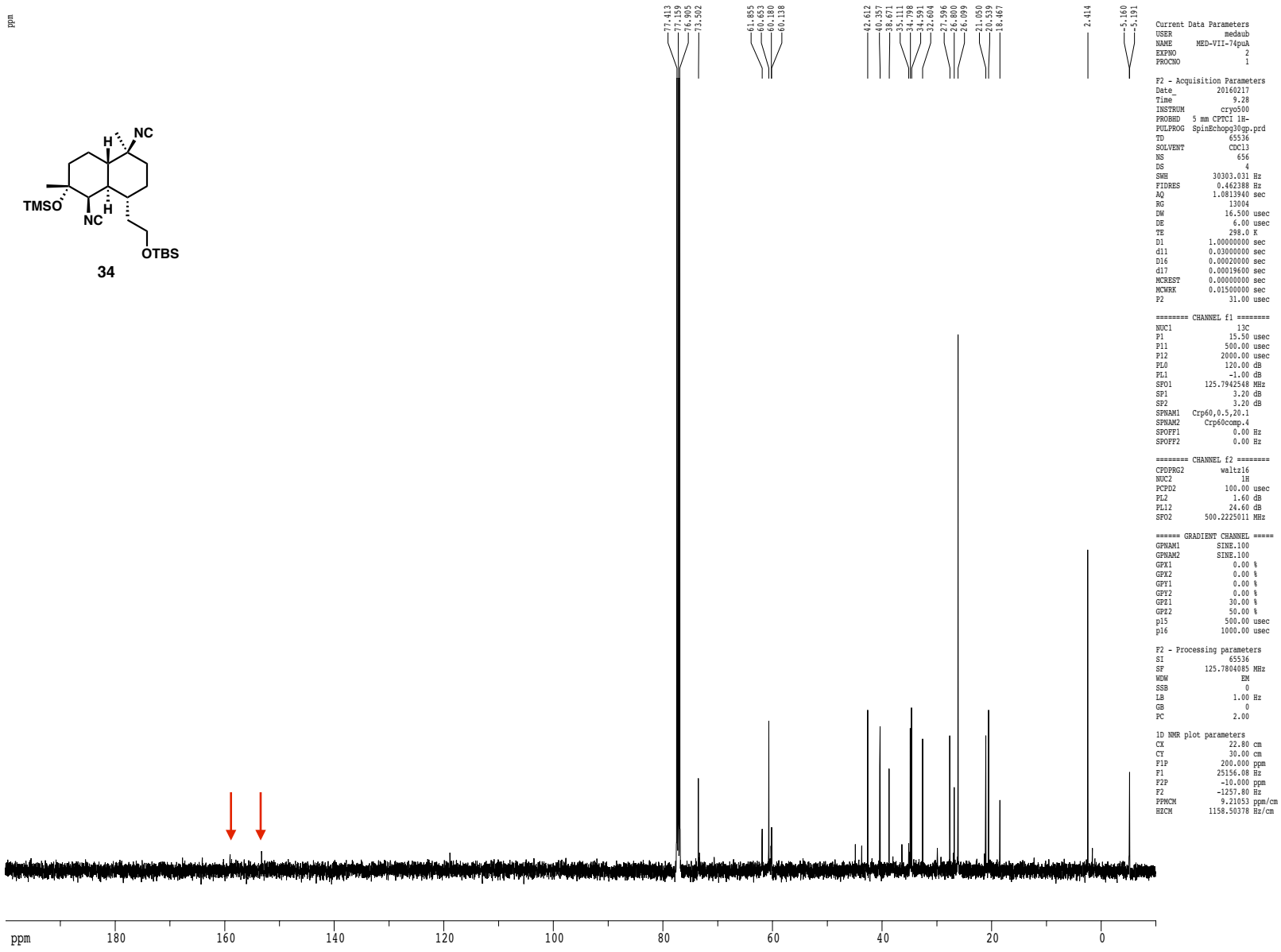
F2 - Acquisition Parameters
Date_            20160217
Time                9.23
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 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

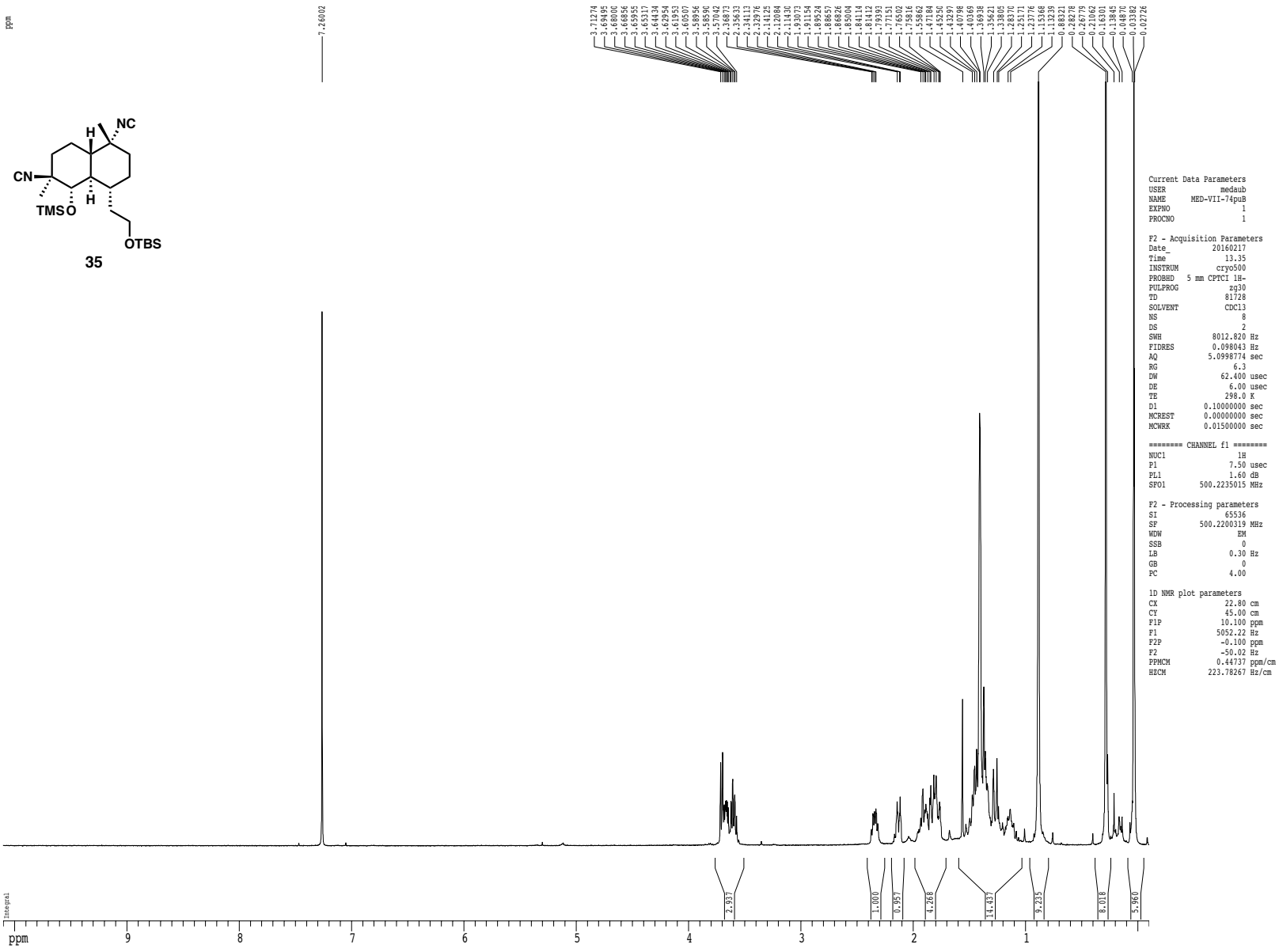
F2 - Processing parameters
SI                 65536
SF          500.2200321 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 45.00 cm
F1P               10.100 ppm
F1               5052.22 Hz
F2P               -0.100 ppm
F2                -50.02 Hz
PPMCM           0.44737 ppm/cm
HZCM          223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



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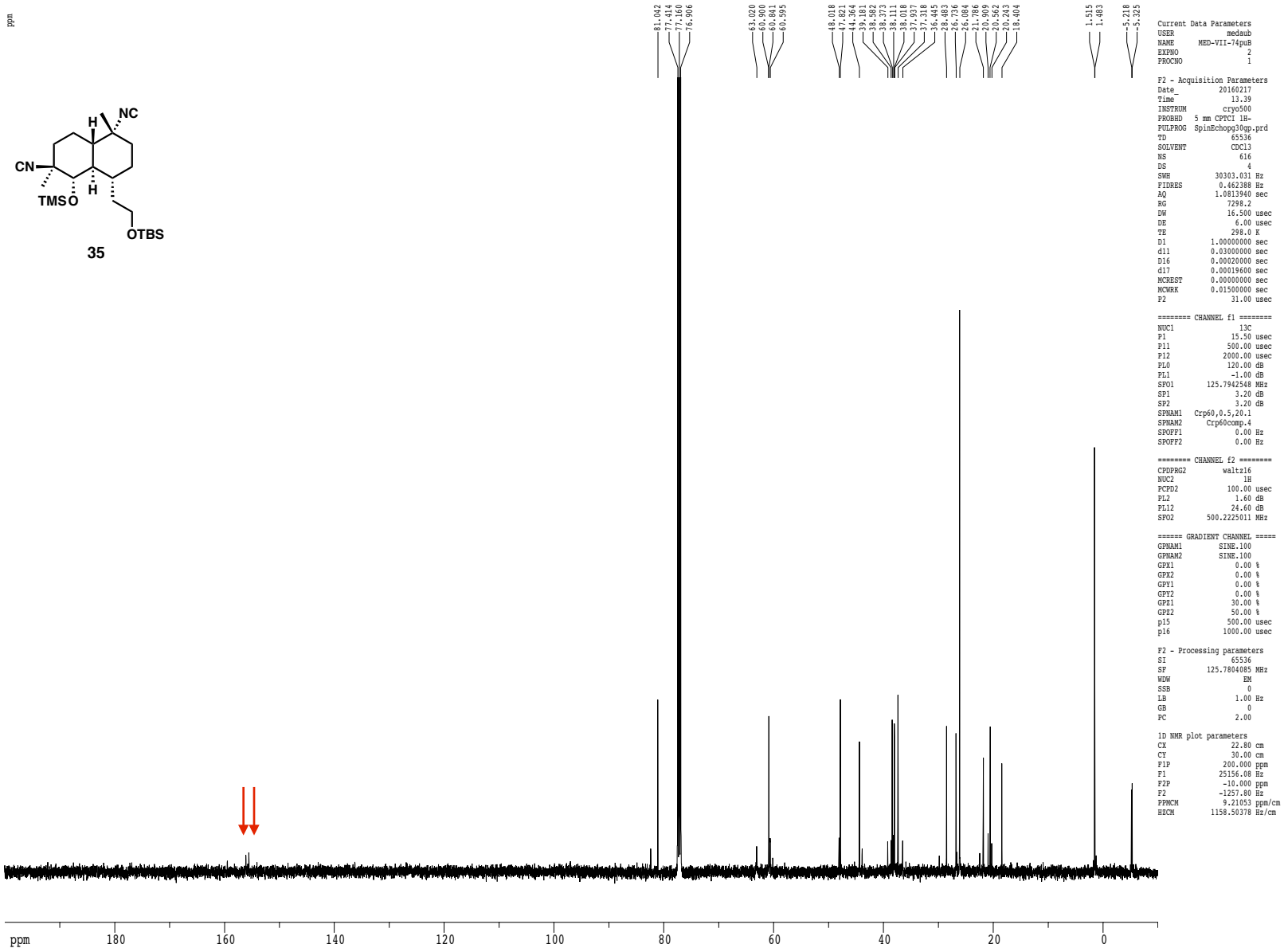
Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VII-74puB
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160217
Time 13.39
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 616
DS 4
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 1.00000000 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

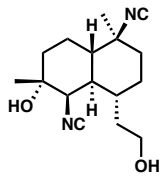
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz

====== 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 125.7804085 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 30.00 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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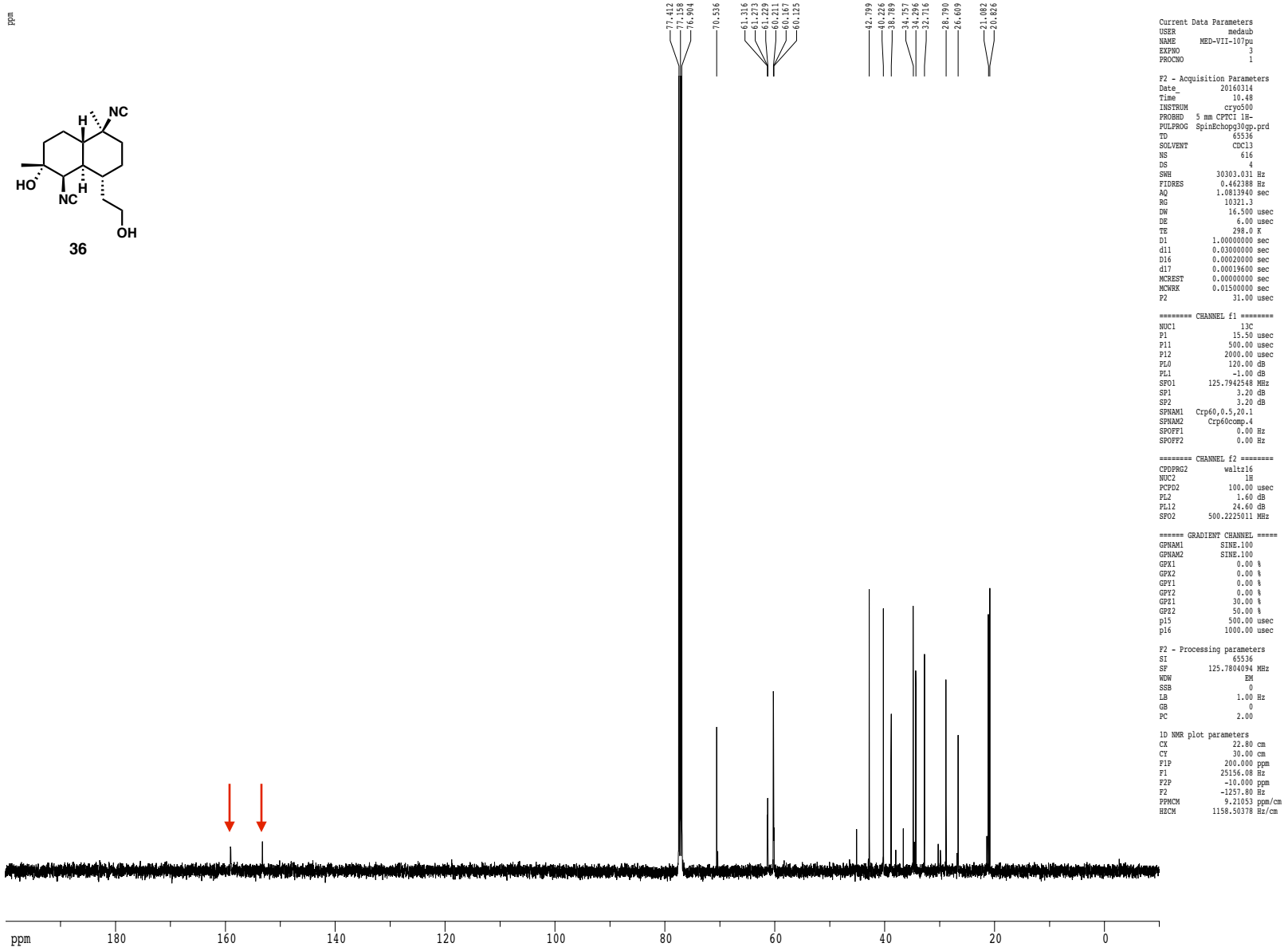
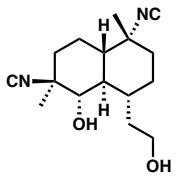
Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



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Current Data Parameters
USER medaub
NAME MED-VII-108pu
EXPNO 2
PROCNO 1

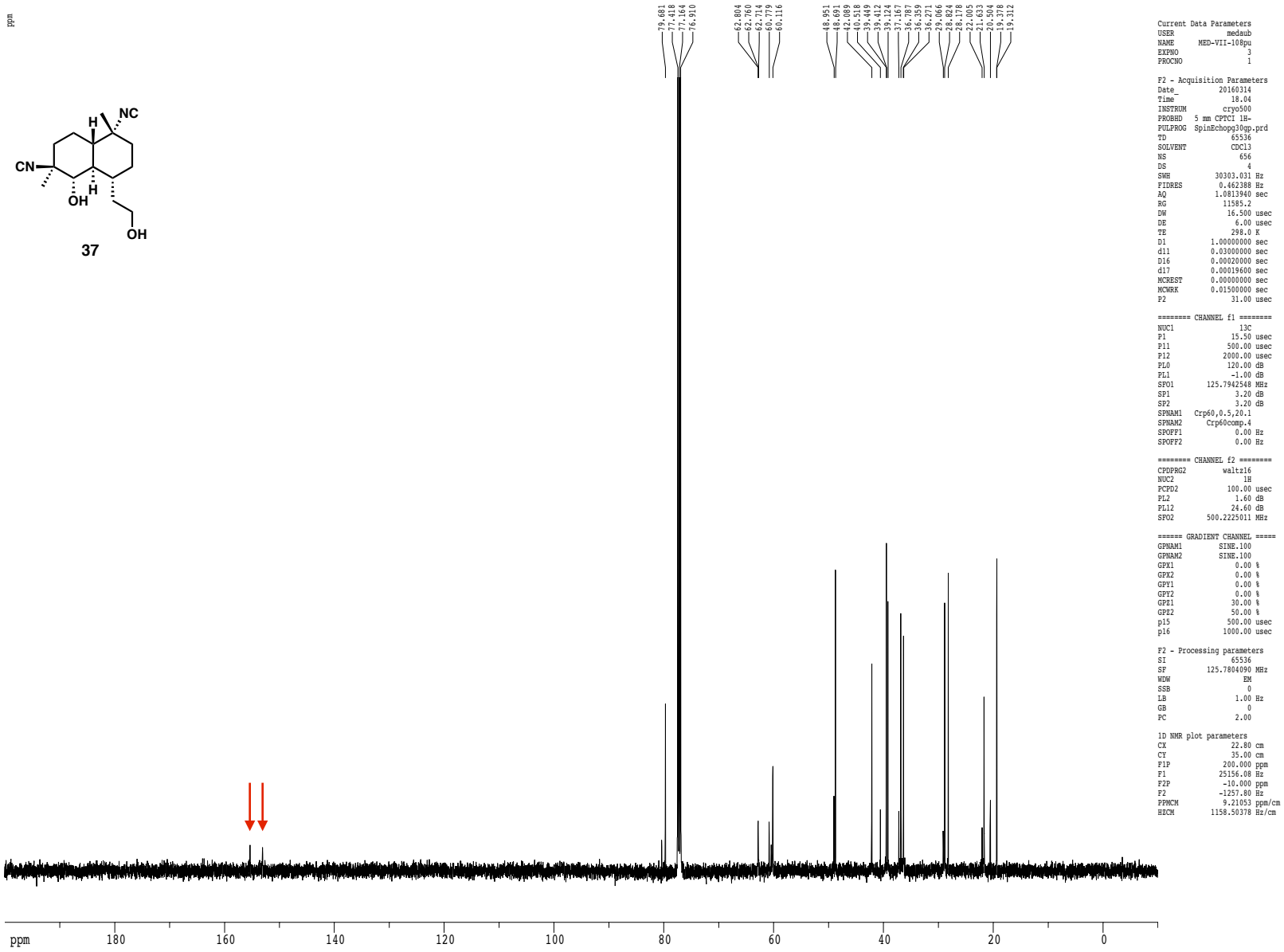
F2 - Acquisition Parameters
Date_ 20160314
Time 18.01
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200317 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 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME        MED-VII-108pu
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160314
Time                18.04
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    656
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
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

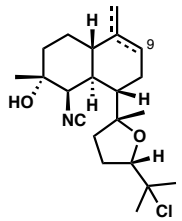
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2         500.2225011 MHz

====== 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           125.7804090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  35.00 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



38 *(3:1 favoring Δ^9 isomer)*


```
Current Data Parameters
USER                medaub
NAME      MED-VI-260pafr13-16
EXPNO                   2
PROCNO                  1

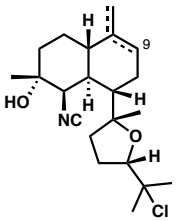
F2 - Acquisition Parameters
Date_            20151017
Time                9.52
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           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            500.2200315 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   0.50

1D NMR plot parameters
CX                  22.80 cm
CY                  25.00 cm
F1P                10.100 ppm
F1                 5052.22 Hz
F2P                -0.100 ppm
F2                  -50.02 Hz
PPMCM             0.44737 ppm/cm
HZCM            223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



38 *(3:1 favoring Δ^9 isomer)*


```
Current Data Parameters
USER                medaub
NAME       MED-VI-260pufr13-16
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20151017
Time                9.54
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    752
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
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

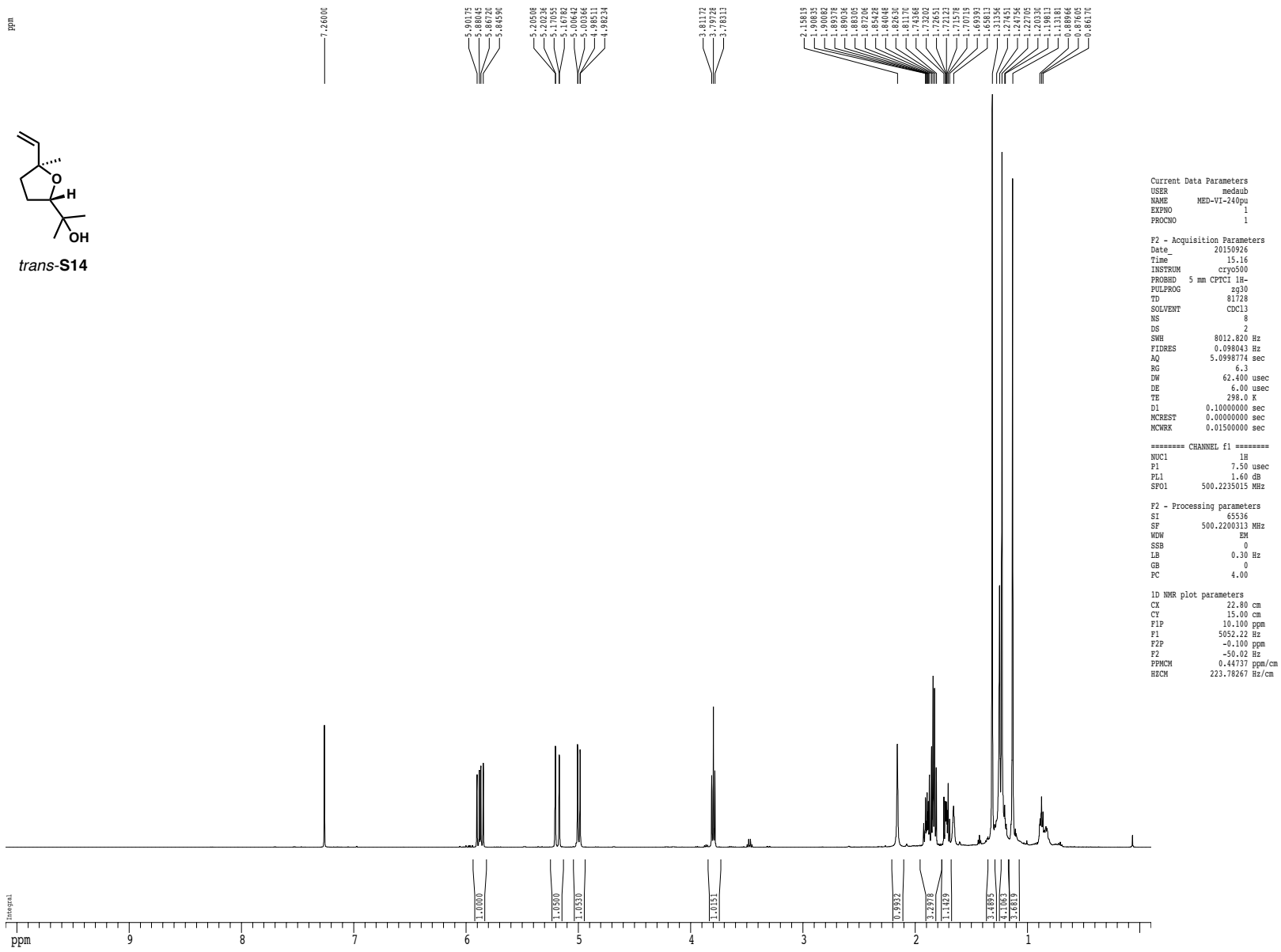
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== 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           125.7804082 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  30.00 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



trans-**S14**

```
Current Data Parameters
USER                medaub
NAME         MED-VI-240pu
EXPNO                   1
PROCNO                  1

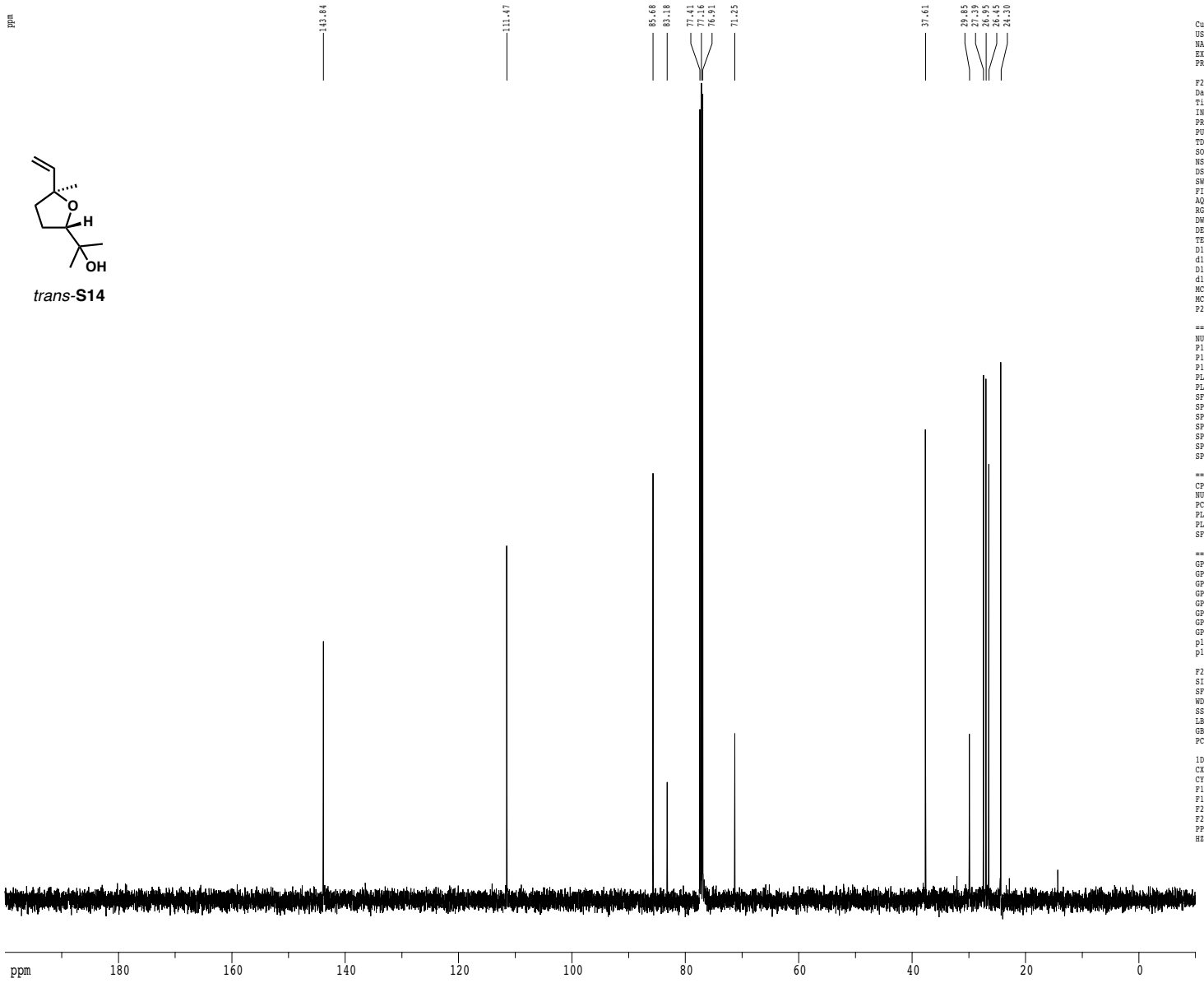
F2 - Acquisition Parameters
Date_            20150926
Time                15.16
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            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          500.2200313 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                 10.100 ppm
F1                 5052.22 Hz
F2P                -0.100 ppm
F2                 -50.02 Hz
PPMCM             0.44737 ppm/cm
HZCM            223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



trans-**S14**

Current Data Parameters
USER medaub
NAME MED-VI-240pu
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150926
Time 15.19
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 104
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 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

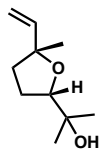
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== 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 125.7804080 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



cis-**S14**

Current Data Parameters
USER medaub
NAME MED-VI-241pu
EXPNO 1
PROCNO 1

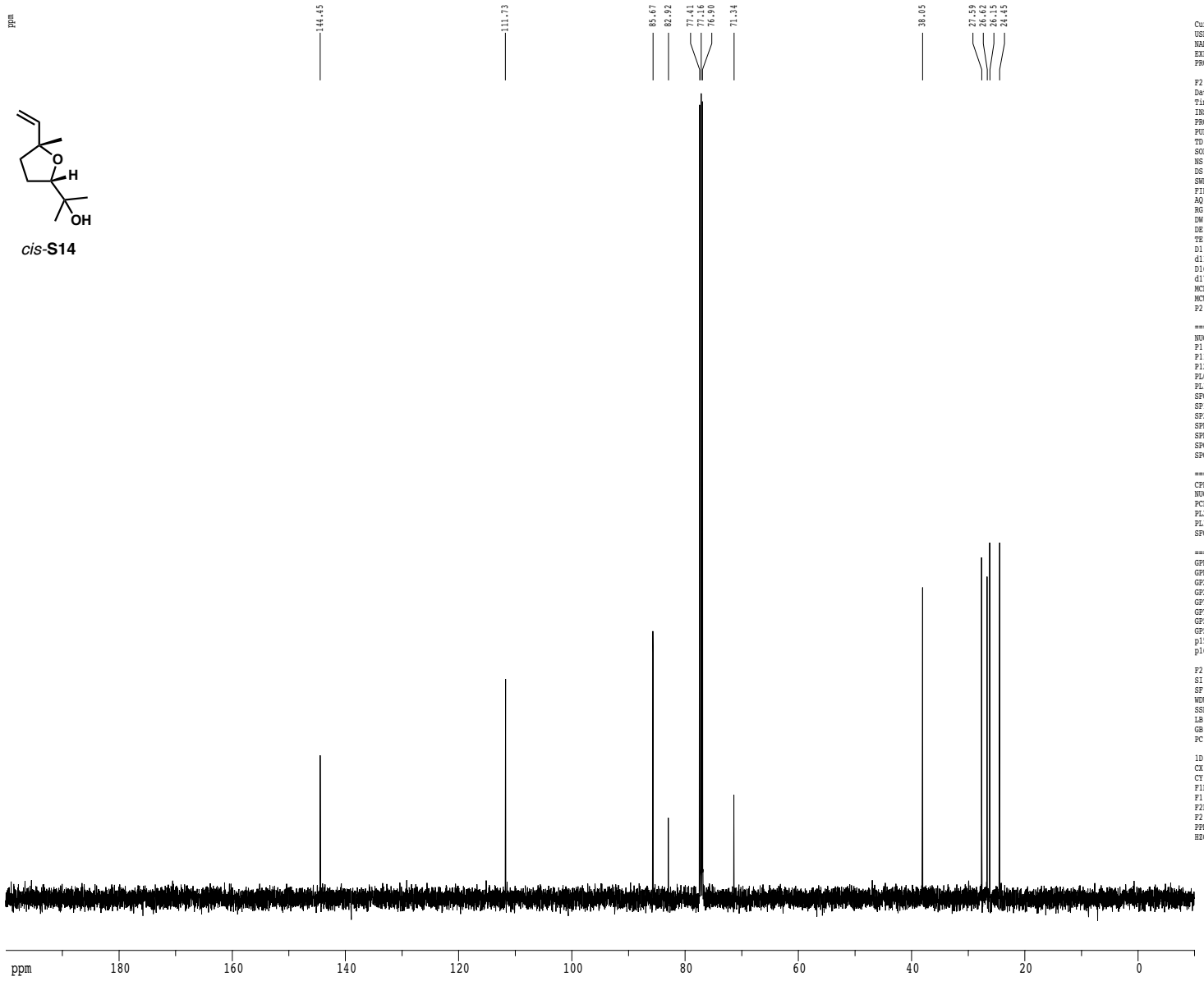
F2 - Acquisition Parameters
Date_ 20150926
Time 15.25
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 7.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200313 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 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



cis-**S14**

```
Current Data Parameters
USER              medaub
NAME        MED-VI-241pu
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20150926
Time              15.27
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   88
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

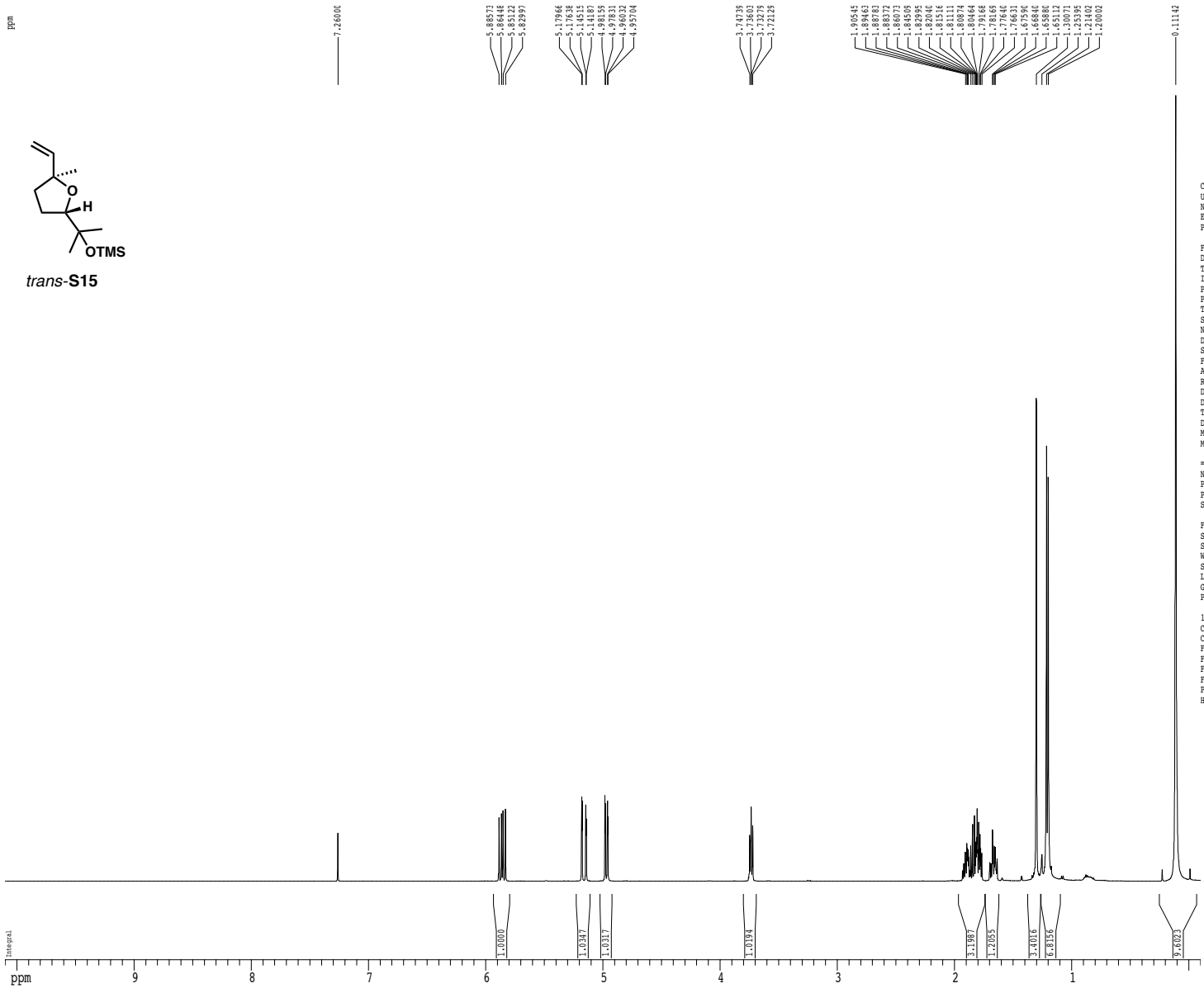
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            100.00 usec
PL2               1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== 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          125.7804080 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




```
Current Data Parameters
USER                medaub
NAME      MED-VI-227pufr7
EXPNO                    1
PROCNO                   1

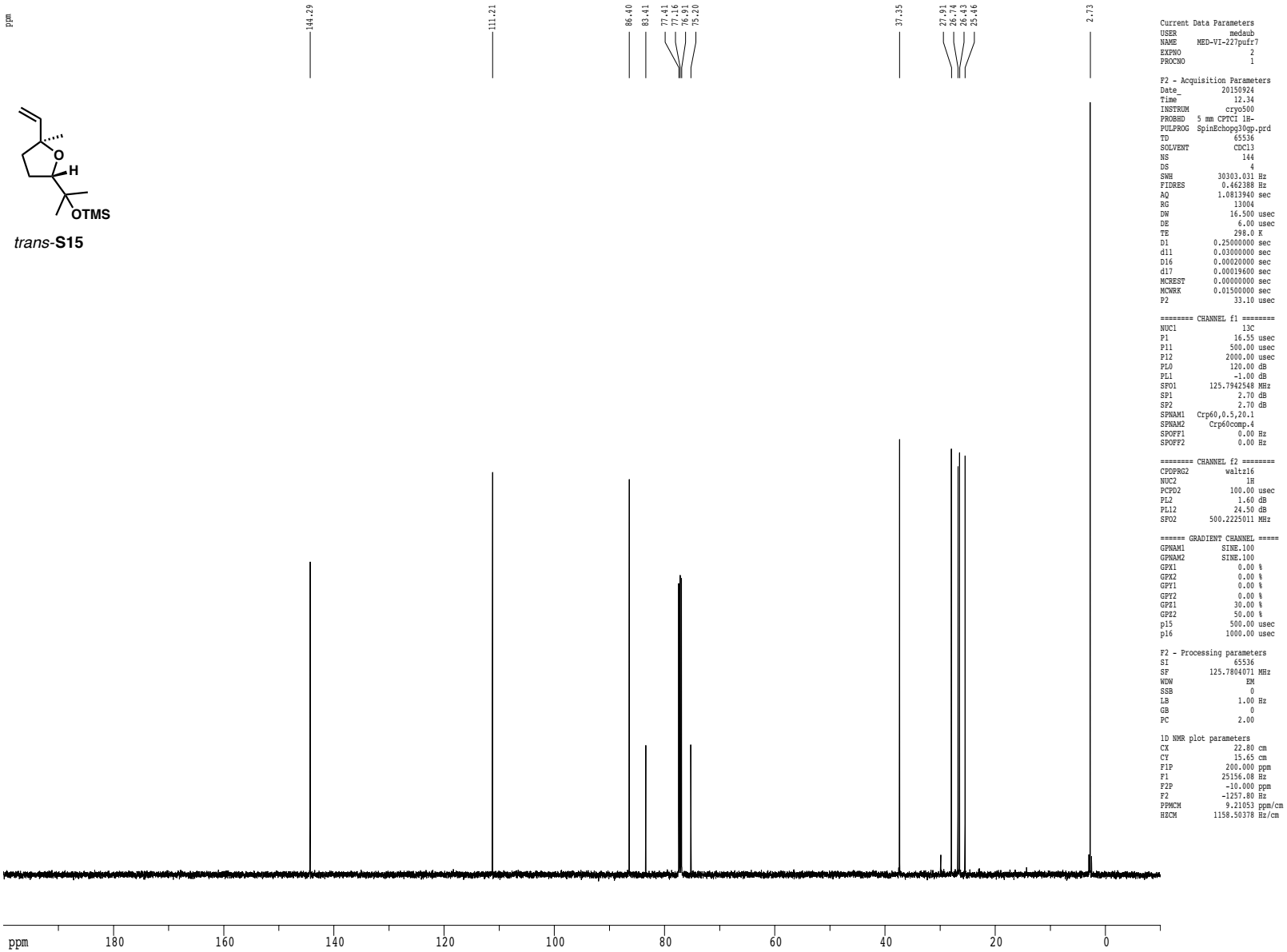
F2 - Acquisition Parameters
Date_            20150924
Time                12.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH               8012.820 Hz
FIDRES            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                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200312 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                 10.100 ppm
F1                5052.22 Hz
F2P                -0.100 ppm
F2                 -50.02 Hz
PPMCM             0.44737 ppm/cm
HZCM            223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



trans-**S15**

Current Data Parameters
USER medaub
NAME MED-VI-227pufr7
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150924
Time 12.34
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 144
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 13004
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 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

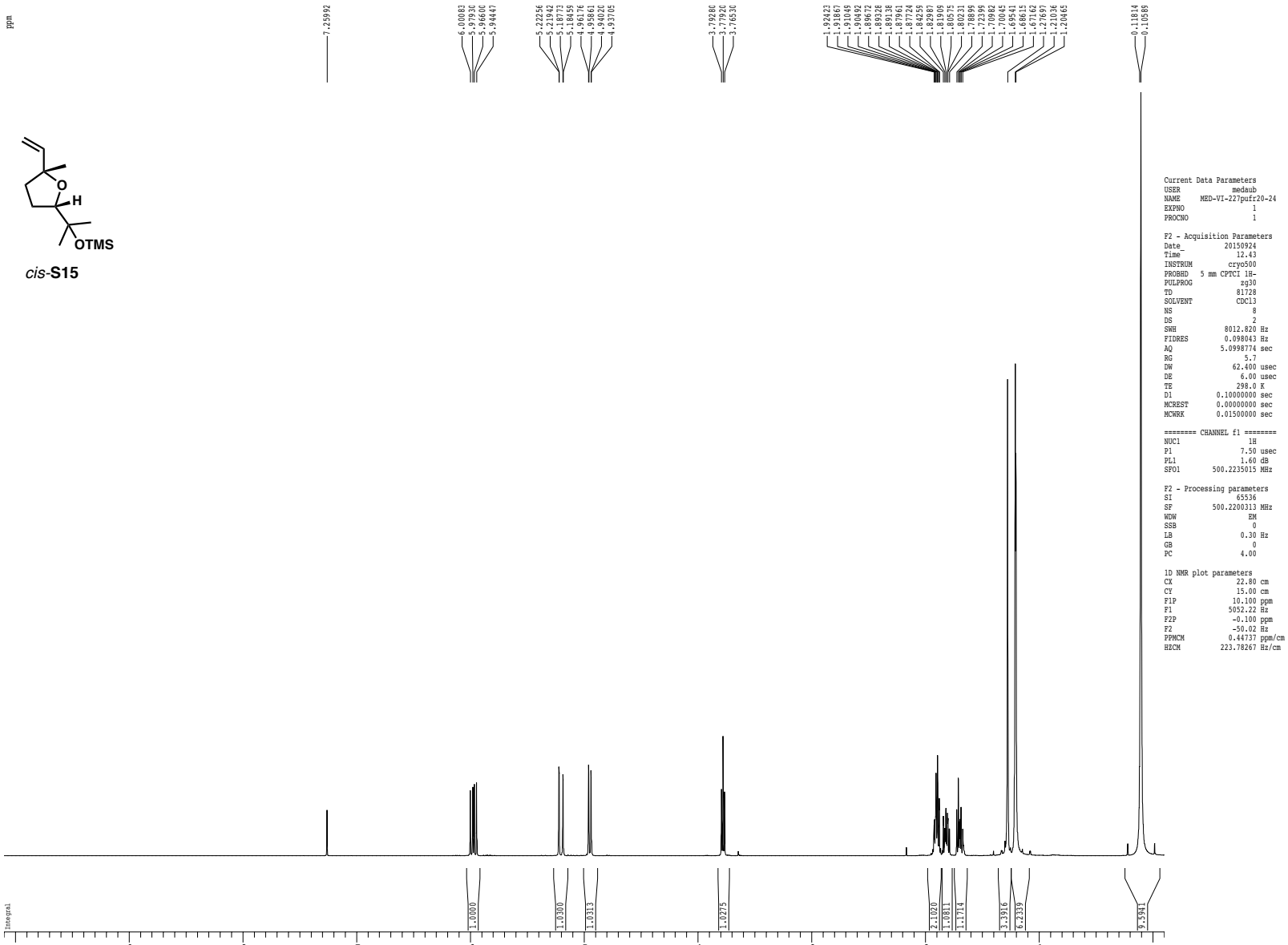
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== 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 125.7804071 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



cis-**S15**

```
Current Data Parameters
USER                medaub
NAME      MED-VI-227pufr20-24
EXPNO                    1
PROCNO                   1

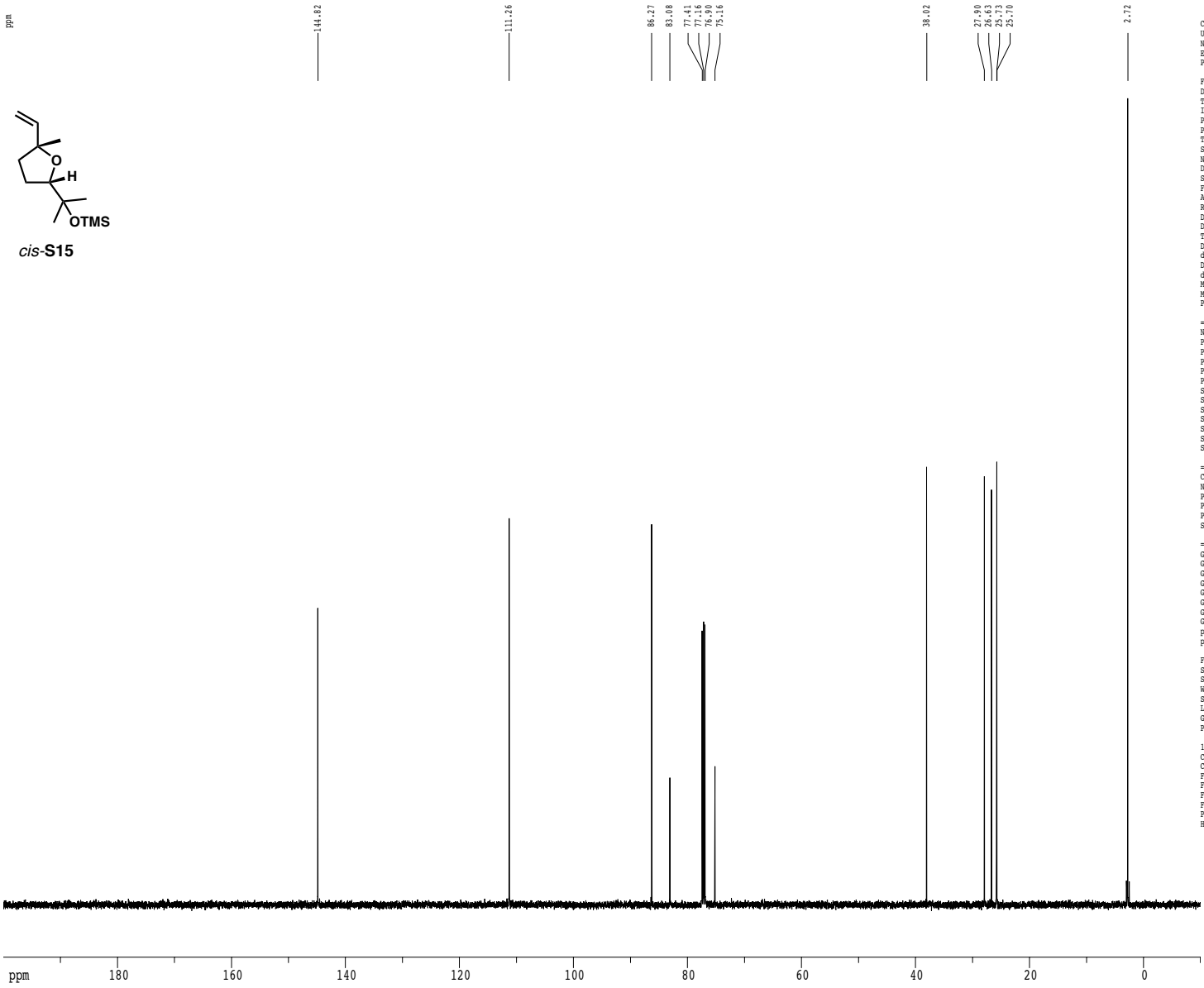
F2 - Acquisition Parameters
Date_            20150924
Time_               12.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH              8012.820 Hz
FIDRES           0.098043 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                  7.50 usec
PL1                 1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200313 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               10.100 ppm
F1               5052.22 Hz
F2P               -0.100 ppm
F2                -50.02 Hz
PPMCM            0.44737 ppm/cm
HZCM           223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



cis-**S15**

```
Current Data Parameters
USER                medaub
NAME       MED-VI-227pufr20-24
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150924
Time                12.46
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     96
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

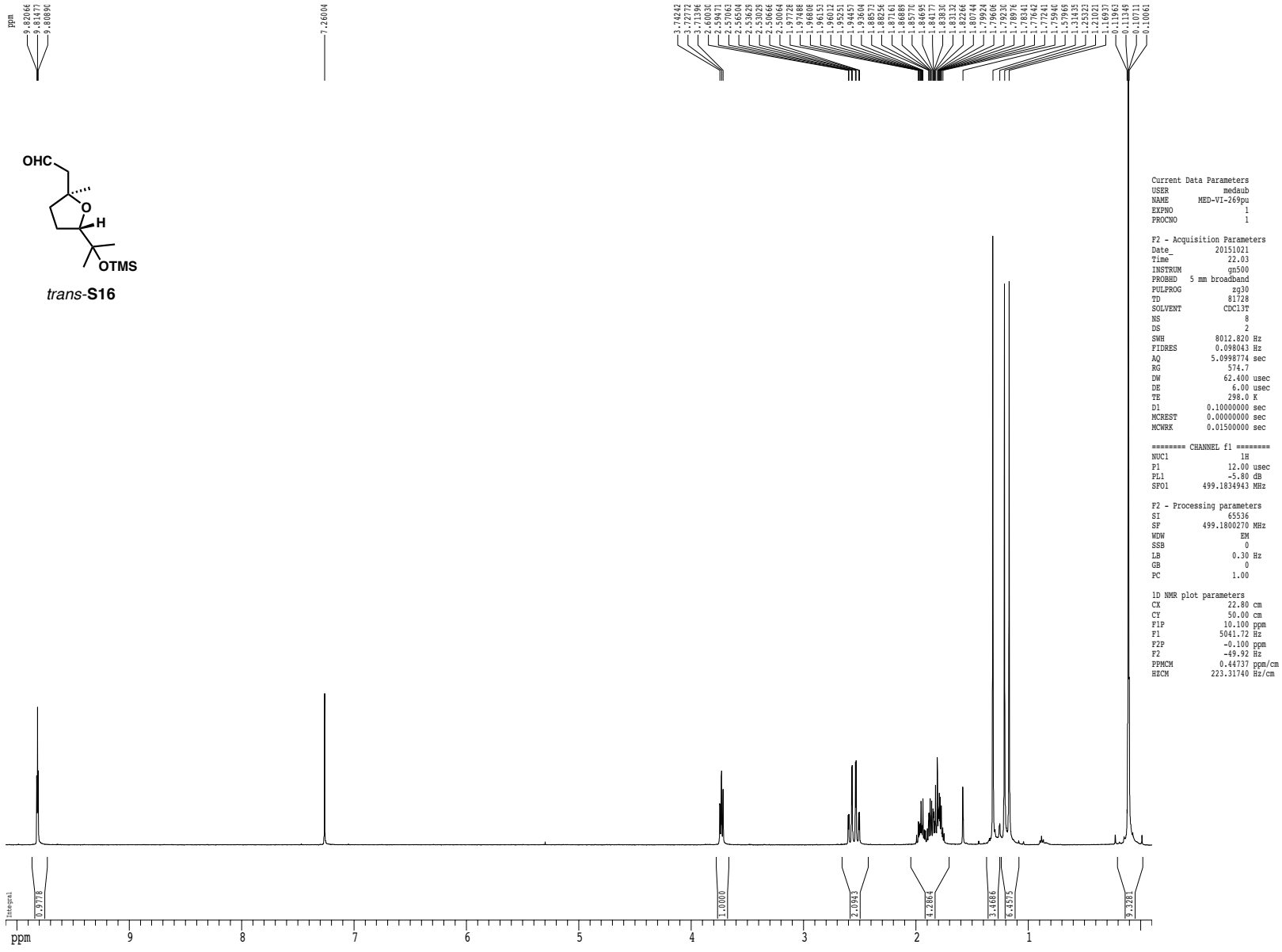
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== 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           125.7804076 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

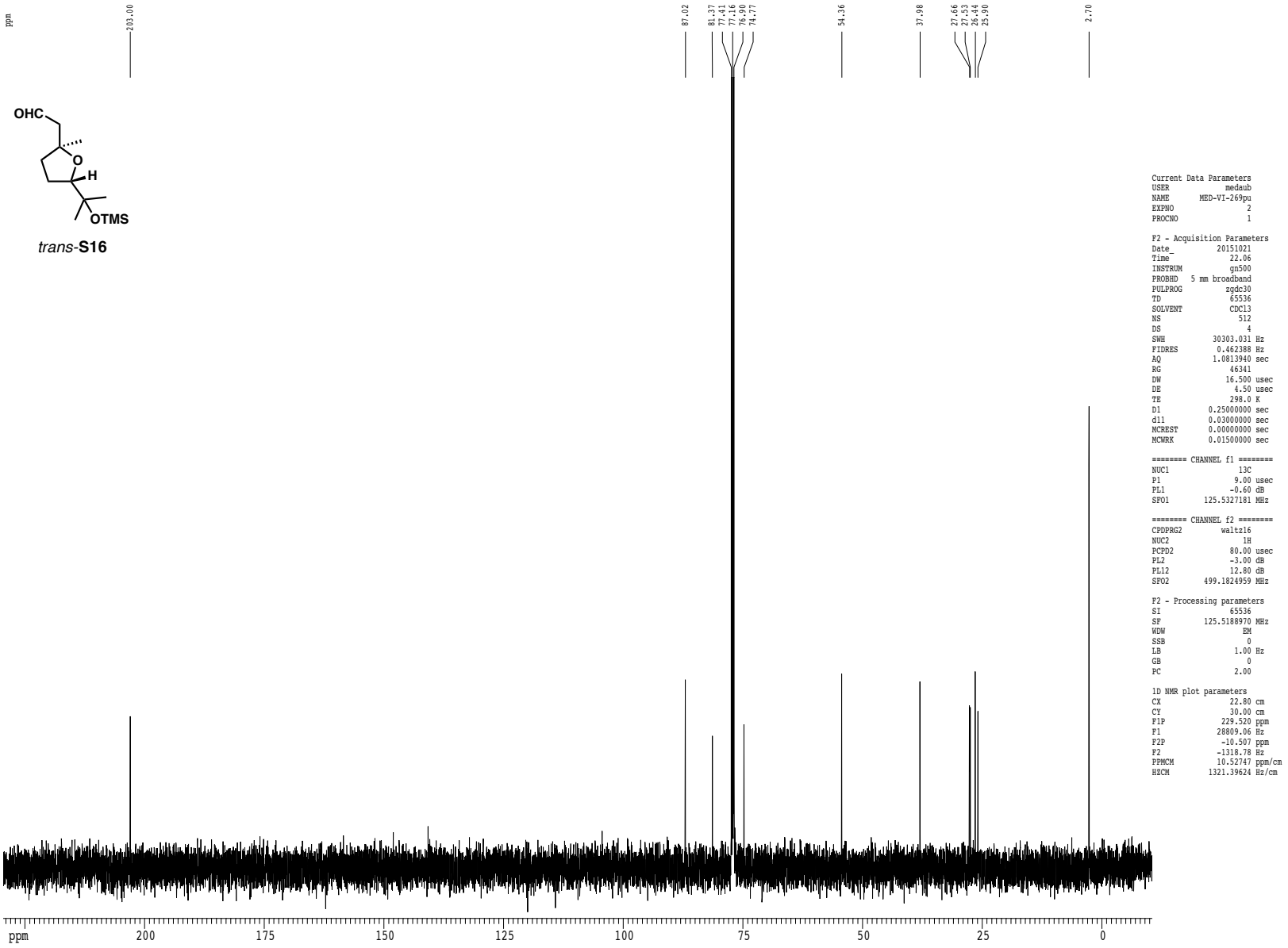
1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               200.000 ppm
F1               25156.08 Hz
F2P               -10.000 ppm
F2              -1257.80 Hz
PPMCM            9.21053 ppm/cm
HZCM          1158.50378 Hz/cm
```

1H spectrum



trans-**S16**

13C spectrum with 1H decoupling



trans-**S16**

```
Current Data Parameters
USER                medaub
NAME          MED-VI-269pu
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_            20151021
Time                22.06
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                 46341
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

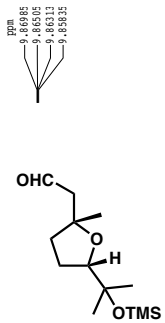
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.00 usec
PL1                -0.60 dB
SFO1         125.5327181 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               12.80 dB
SFO2         499.1824959 MHz

F2 - Processing parameters
SI                 65536
SF           125.5188970 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 30.00 cm
F1P              229.520 ppm
F1              28809.06 Hz
F2P              -10.507 ppm
F2              -1318.78 Hz
PPMCM           10.52747 ppm/cm
HZCM          1321.39624 Hz/cm
```

1H spectrum



cis-**S16**

Current Data Parameters
USER medaub
NAME MED-VI-270pu
EXPNO 1
PROCNO 1

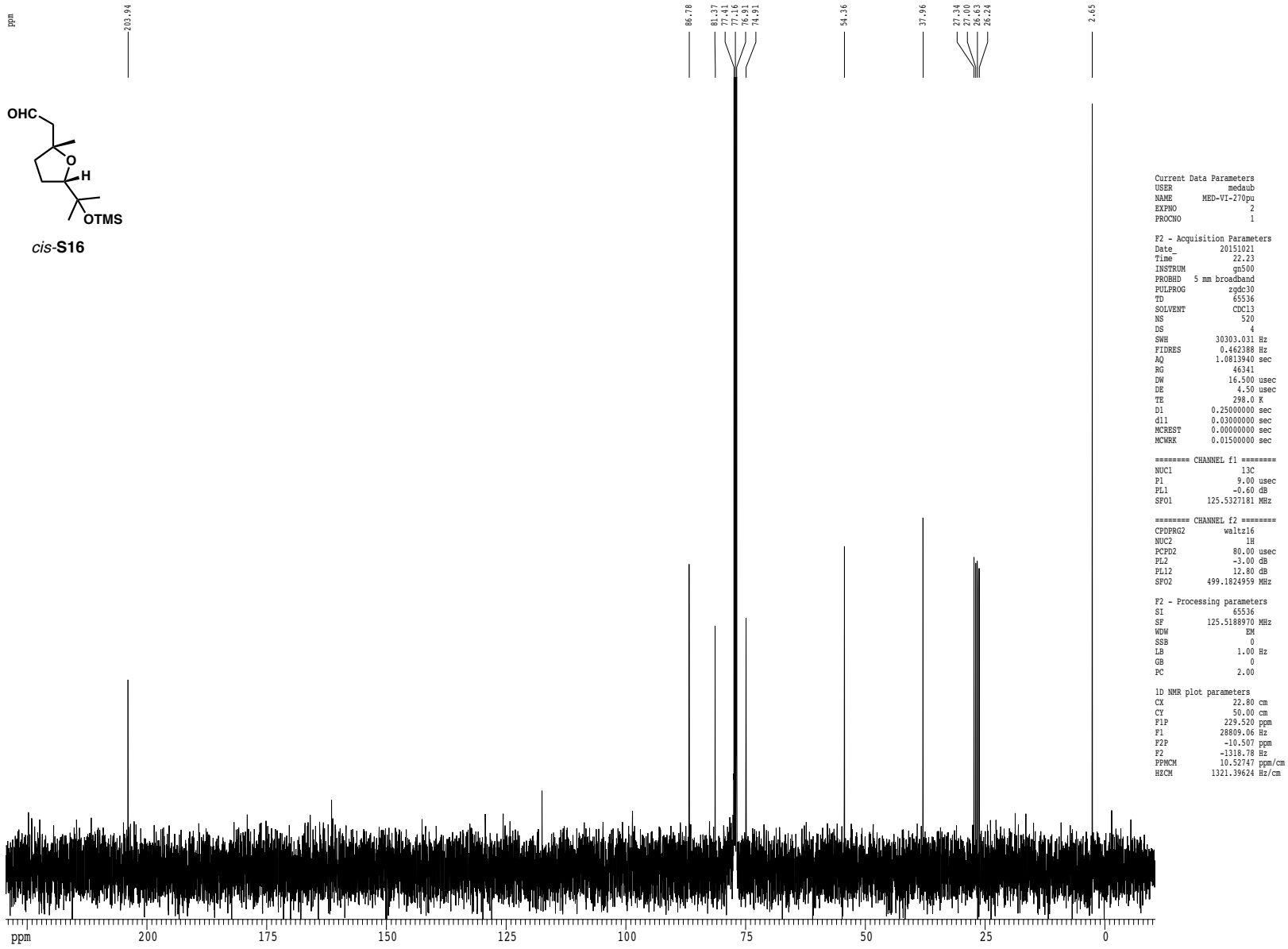
F2 - Acquisition Parameters
Date_ 20151021
Time 22.19
INSTRUM qn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 181
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.1834943 MHz

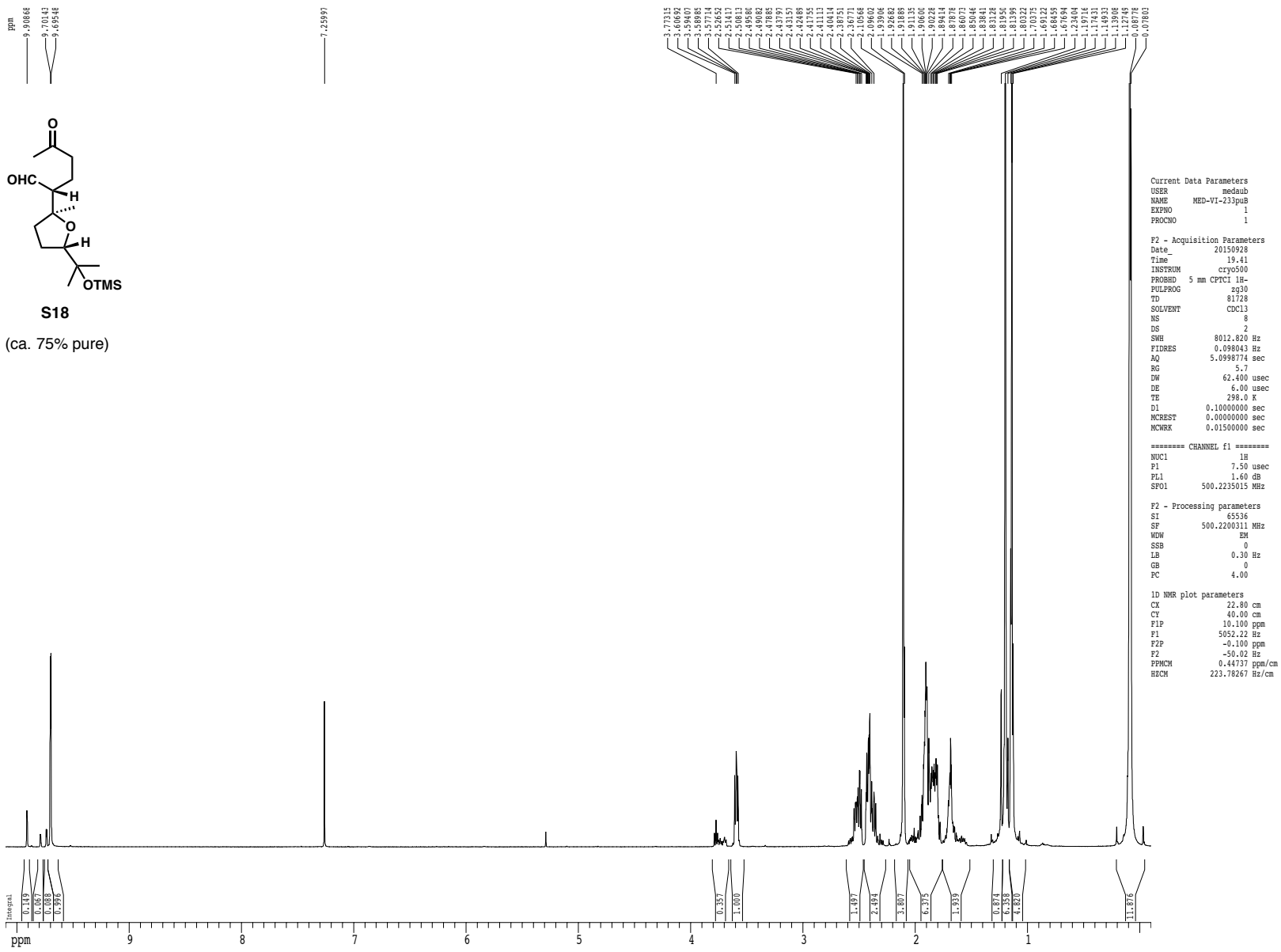
F2 - Processing parameters
SI 65536
SF 499.1800271 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm

13C spectrum with 1H decoupling



1H spectrum



S18

(ca. 75% pure)

```
Current Data Parameters
USER                medaub
NAME        MED-VI-233puB
EXPNO                   1
PROCNO                  1

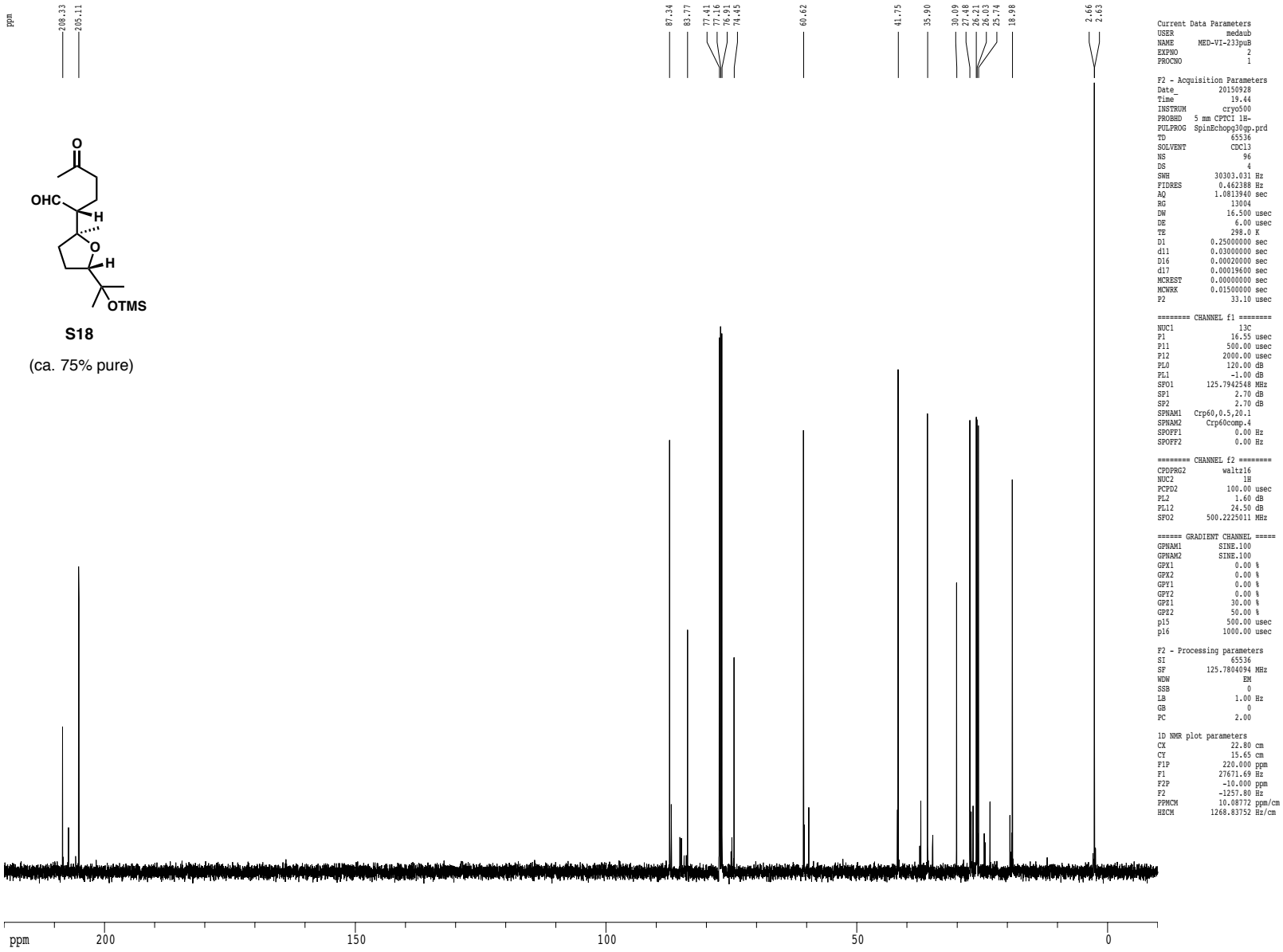
F2 - Acquisition Parameters
Date_            20150928
Time                19.41
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            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                  7.50 usec
PL1                 1.60 dB
SFO1          500.2235015 MHz

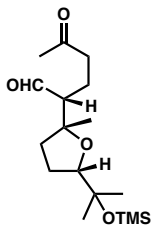
F2 - Processing parameters
SI                   65536
SF            500.2200311 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                  22.80 cm
CY                  40.00 cm
F1P                10.100 ppm
F1                 5052.22 Hz
F2P                -0.100 ppm
F2                 -50.02 Hz
PPMCM            0.44737 ppm/cm
HZCM           223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



1H spectrum



S19

Current Data Parameters
USER medaub
NAME MED-VI-233puA
EXPNO 1
PROCNO 1

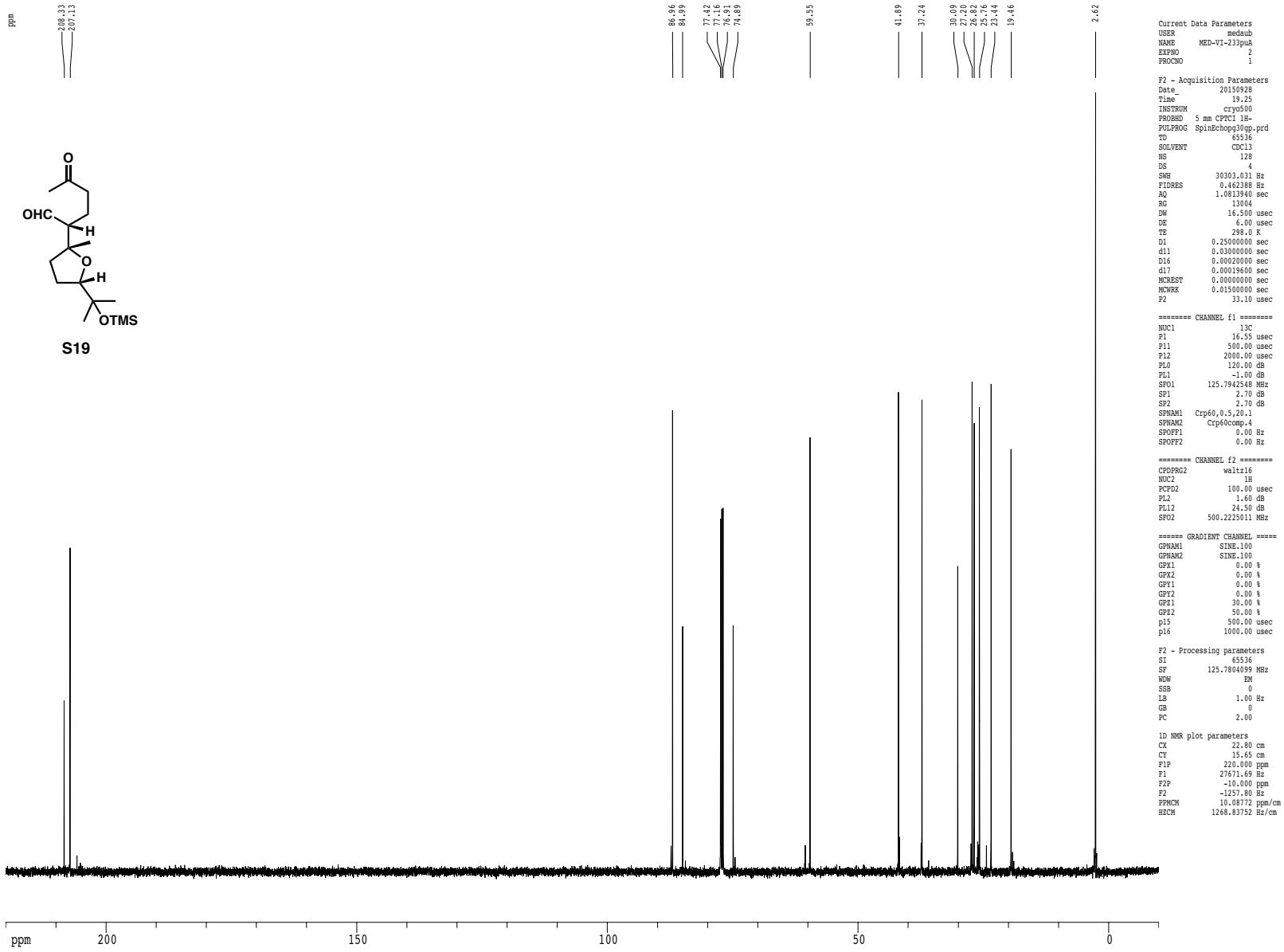
F2 - Acquisition Parameters
Date_ 20150928
Time 19.22
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200311 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 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VI-233puA
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150928
Time 19.25
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 13004
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 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

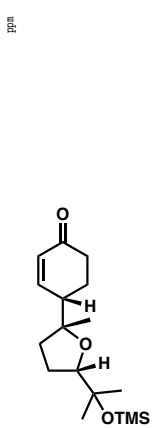
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== 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 125.7804099 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 1268.83752 Hz/cm

1H spectrum



S21

Current Data Parameters
USER medaub
NAME MED-VI-242pafr26-34
EXPNO 2
PROCNO 1

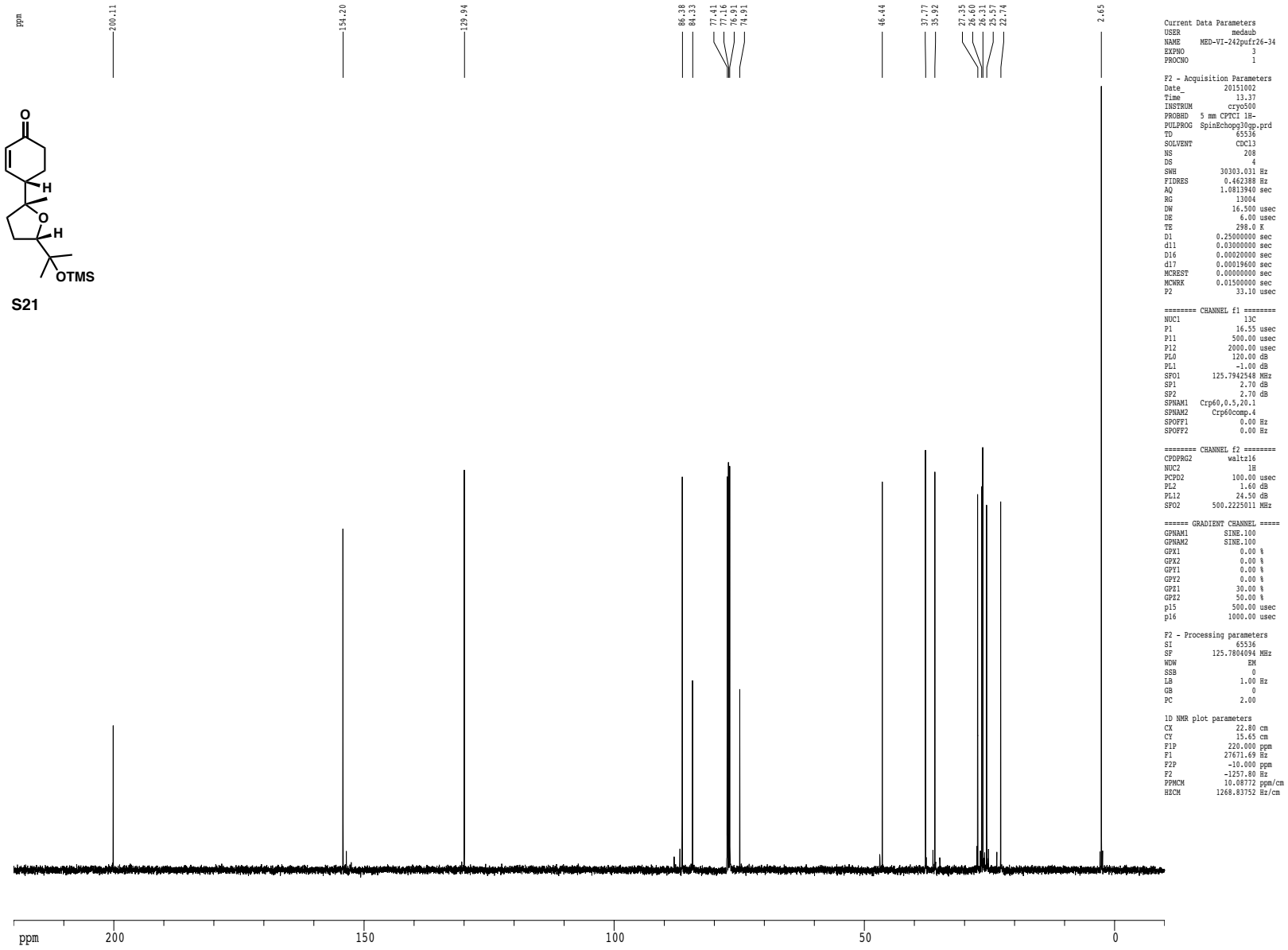
F2 - Acquisition Parameters
Date_ 20151002
Time 13.33
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200311 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.60 cm
CY 30.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



S21

```
Current Data Parameters
USER              medaub
NAME      MED-VI-242pufr26-34
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_          20151002
Time              13.37
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            CDCl3
NS                   208
DS                     4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 sec
RG                 13004
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               33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1        125.7942548 MHz
SP1              2.70 dB
SP2              2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2     Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

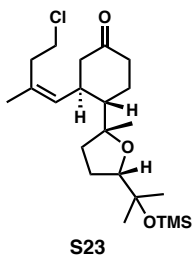
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2        500.2225011 MHz

====== 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          125.7804094 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          1268.83752 Hz/cm
```

1H spectrum



S23

Current Data Parameters
USER medaub
NAME MED-VI-244pu
EXPNO 1
PROCNO 1

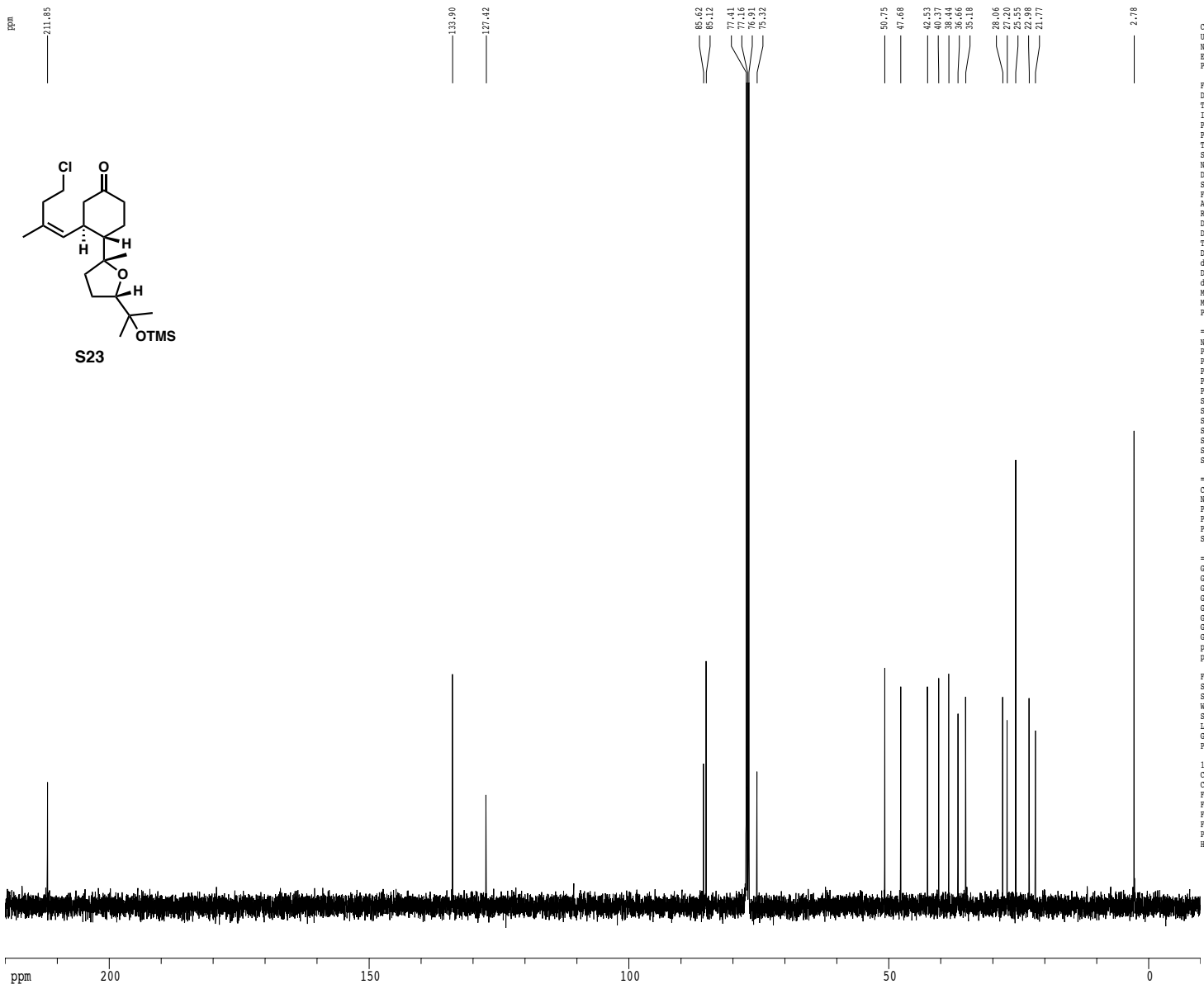
F2 - Acquisition Parameters
Date_ 20151006
Time 10.32
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 7.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200312 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME         MED-VI-244pu
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151006
Time              10.36
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  392
DS                    4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 sec
RG                13004
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              33.10 usec

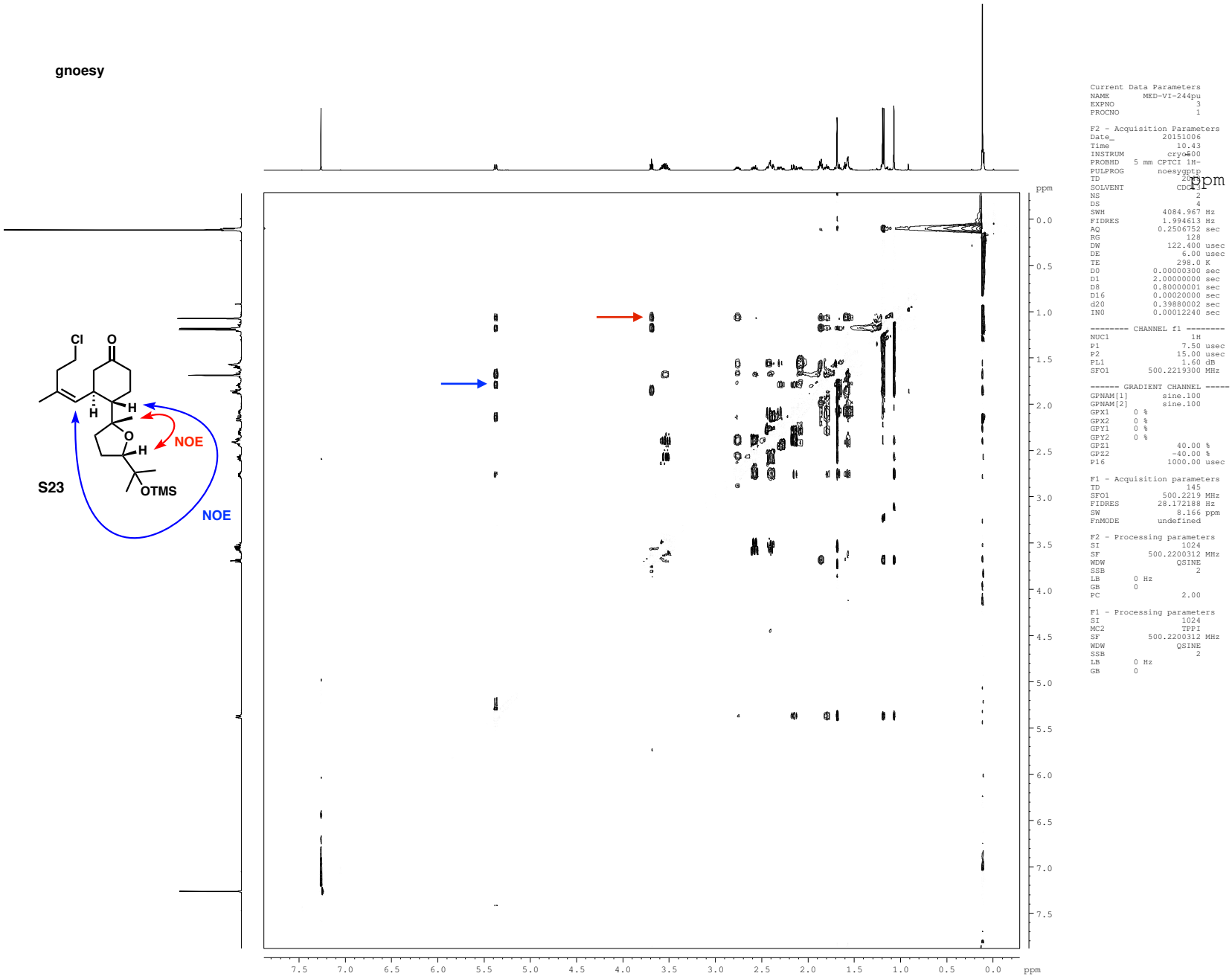
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      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             24.50 dB
SFO2        500.2225011 MHz

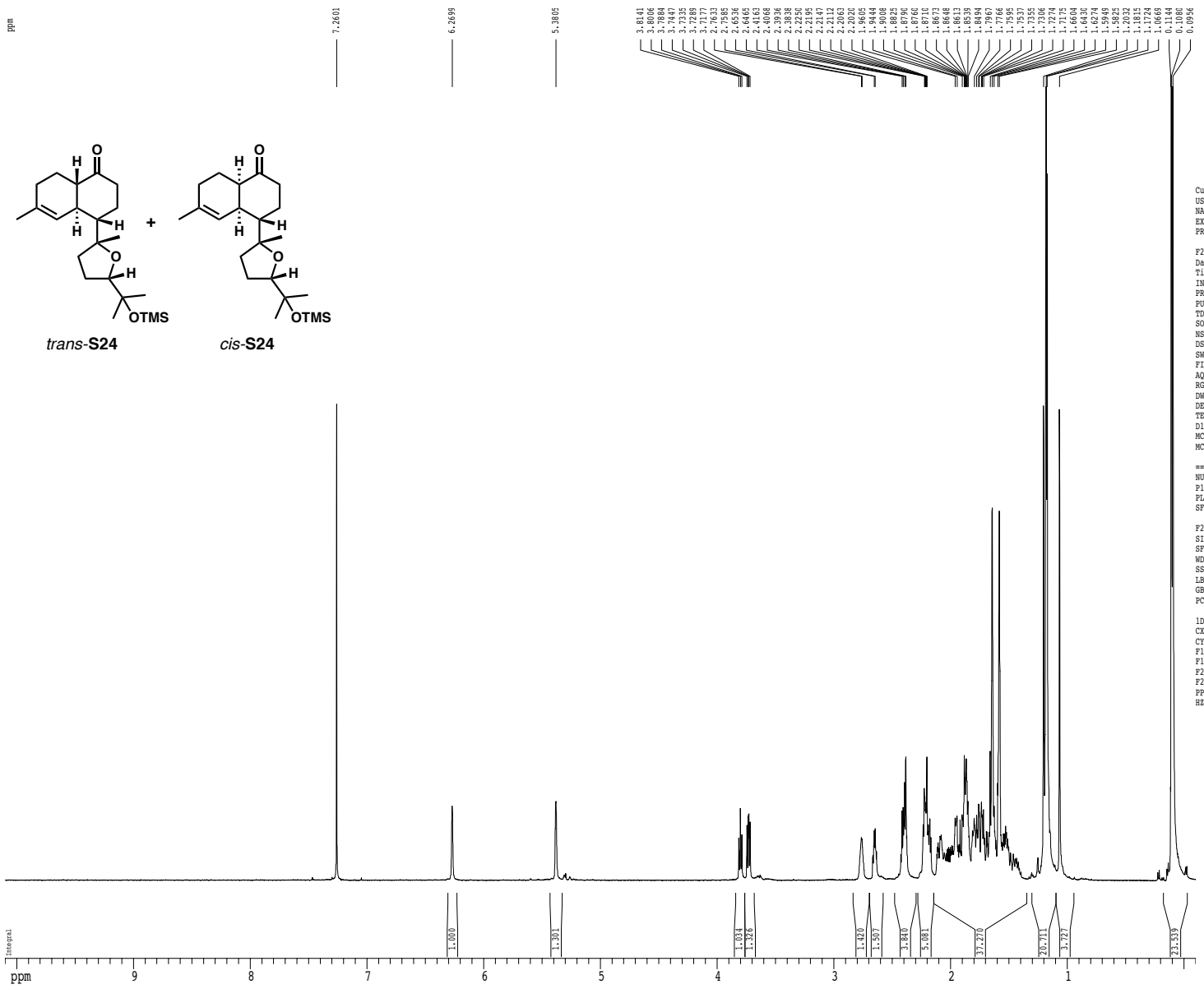
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                  65536
SF          125.7804076 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

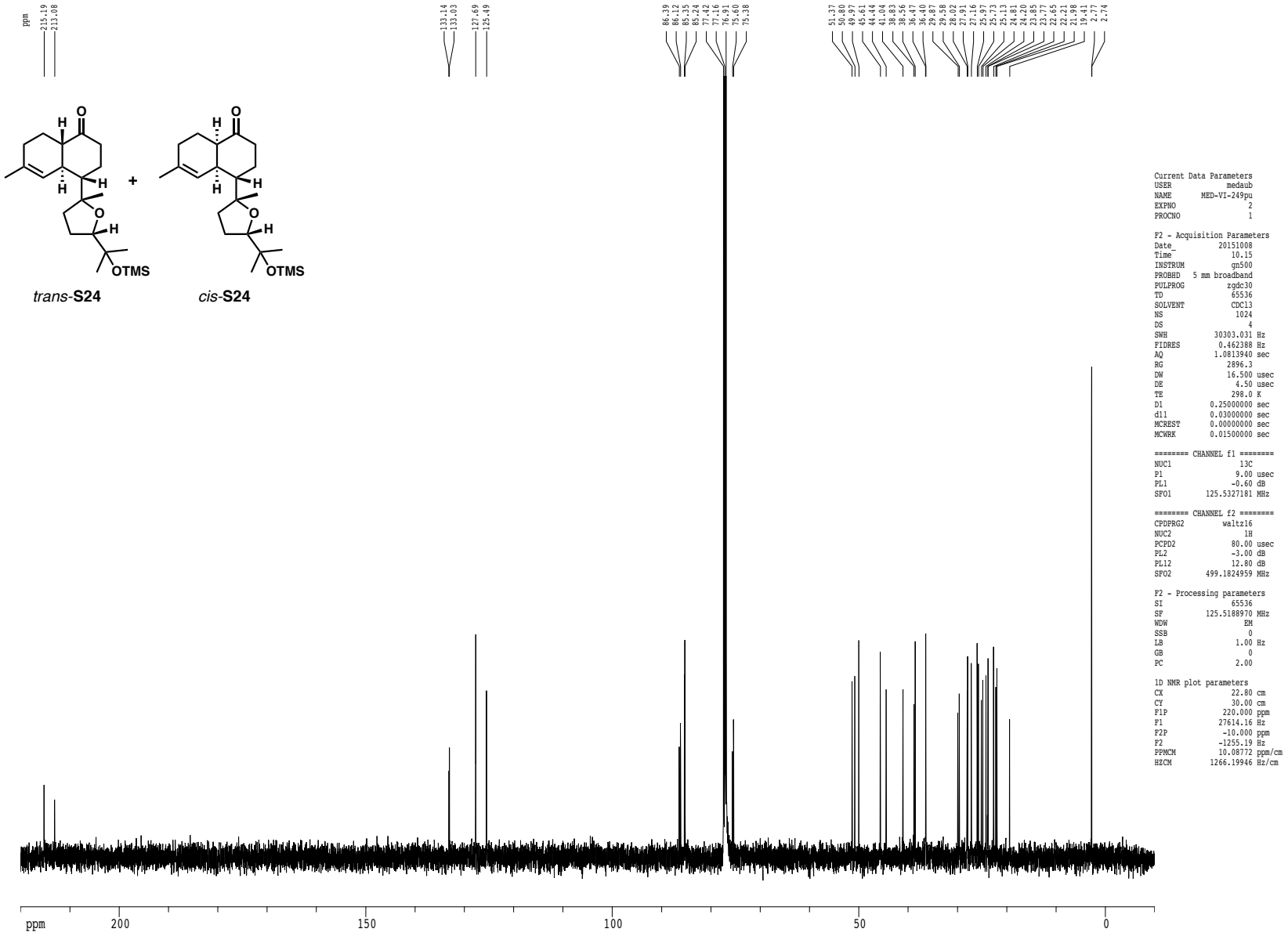
1D NMR plot parameters
CX                 22.80 cm
CY                 30.00 cm
F1P               220.000 ppm
F1              27671.69 Hz
F2P               -10.000 ppm
F2              -1257.80 Hz
PPMCM           10.08772 ppm/cm
HZCM          1268.83752 Hz/cm
```


gnoesy
Cl
O
H
H
O
H
NOE
S23
OTMS
NOE
ppm
ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Current Data Parameters
NAME MED-VI-244pu
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151006
Time 10.43
INSTRUM cryo600
PROBHD 5 mm CPTCI 1H-
PULPROG noesygptp
TD 2048
SOLVENT CDCl3
NS 2
DS 4
SWH 4084.967 Hz
FIDRES 1.994613 Hz
AQ 0.2506752 sec
RG 128
DW 122.400 usec
DE 6.00 usec
TE 298.0 K
D0 0.00000300 sec
D1 2.00000000 sec
D8 0.80000001 sec
D16 0.00020000 sec
d20 0.39880002 sec
IN0 0.00012240 sec
-------- CHANNEL f1 --------
NUC1 1H
P1 7.50 usec
P2 15.00 usec
PL1 1.60 dB
SFO1 500.2219300 MHz
------ GRADIENT CHANNEL -----
GPNAM[1] sine.100
GPNAM[2] sine.100
GPX1 0 %
GPX2 0 %
GPY1 0 %
GPY2 0 %
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec
F1 - Acquisition parameters
TD 145
SFO1 500.2219 MHz
FIDRES 28.172188 Hz
SW 8.166 ppm
FnMODE undefined
F2 - Processing parameters
SI 1024
SF 500.2200312 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 2.00
F1 - Processing parameters
SI 1024
MC2 TPPI
SF 500.2200312 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

1H spectrum


ppm
7.2601
6.2699
5.3805
3.8141
3.8006
3.7884
3.7447
3.7335
3.7269
3.7177
3.7633
2.7585
2.6536
2.6465
2.4163
2.4068
2.3936
2.3838
2.2250
2.2195
2.2147
2.2113
2.2063
2.2020
1.9605
1.9444
1.9008
1.8825
1.8796
1.8766
1.8710
1.8673
1.8644
1.8613
1.8539
1.8494
1.7967
1.7766
1.7595
1.7537
1.7355
1.7306
1.7274
1.7175
1.6604
1.6470
1.6274
1.5949
1.5825
1.2032
1.1815
1.1724
1.0669
0.1144
0.1086
0.0956
H
O
H
H
O
H
OTMS
+
H
O
H
H
O
H
OTMS
trans-S24
cis-S24
Current Data Parameters
USER medaub
NAME MED-VI-249pu
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151008
Time 10.11
INSTRUM qn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 181
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 -5.80 dB
SFO1 499.1834943 MHz
F2 - Processing parameters
SI 65536
SF 499.1800271 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm
Integral
1.000
1.301
1.034
1.326
1.420
1.507
3.840
5.081
37.270
20.711
3.727
23.539
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



trans-**S24** *cis*-**S24**

Current Data Parameters
USER medaub
NAME MED-VI-249pu
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151008
Time 10.15
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2896.3
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

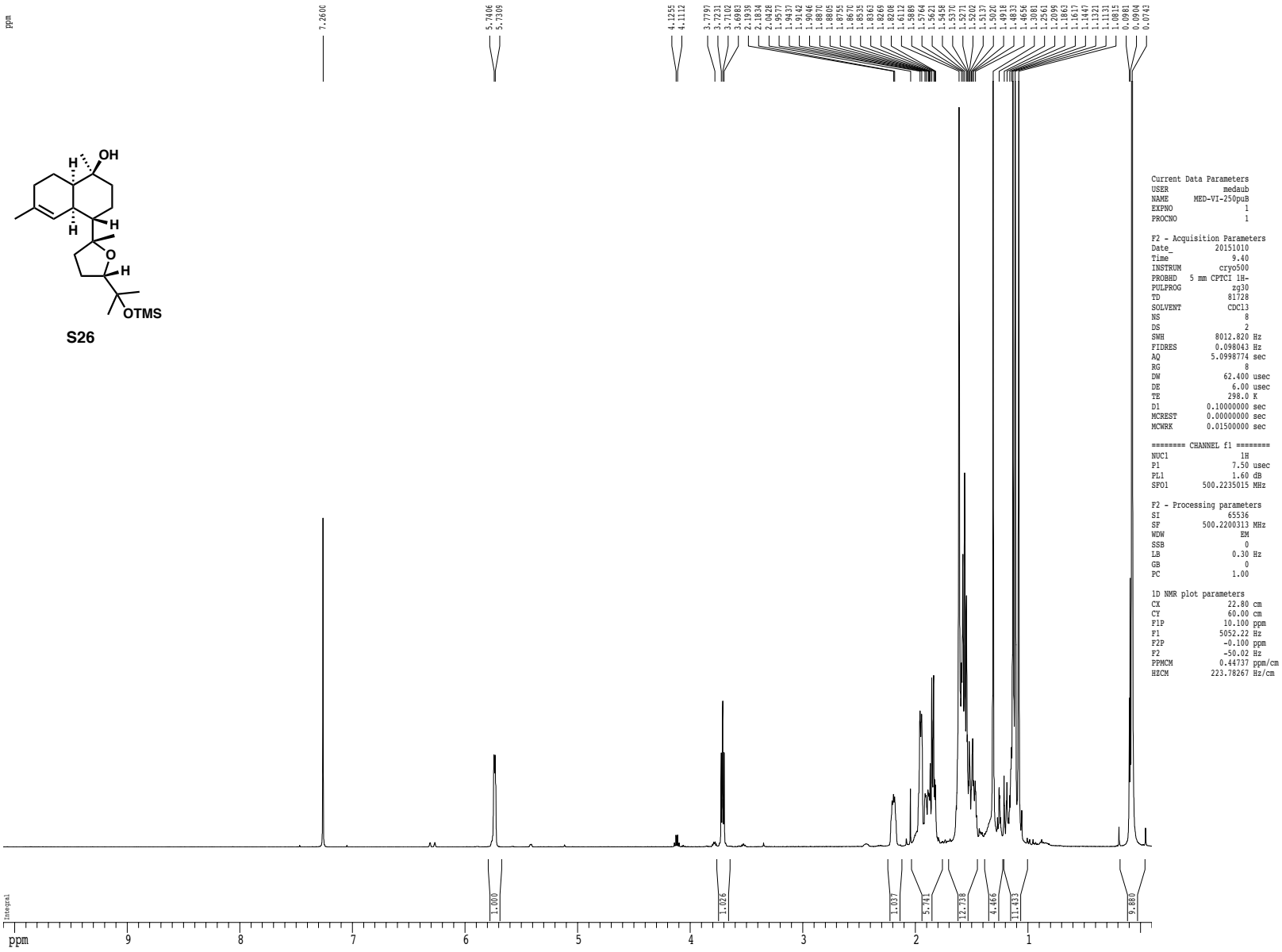
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -0.60 dB
SFO1 125.5327181 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.80 dB
SFO2 499.1824959 MHz

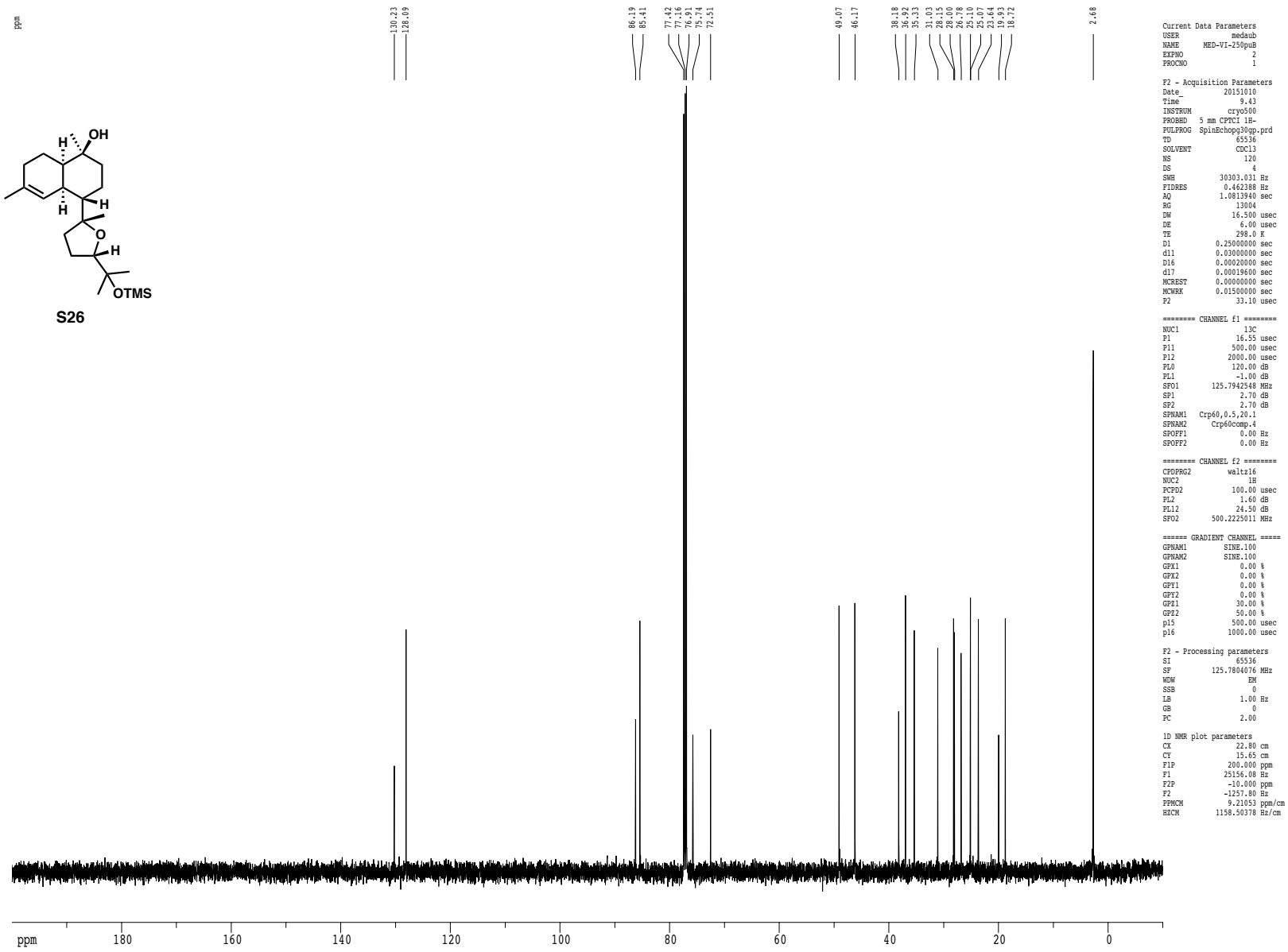
F2 - Processing parameters
SI 65536
SF 125.5188970 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 30.00 cm
F1P 220.000 ppm
F1 27614.16 Hz
F2P -10.000 ppm
F2 -1255.19 Hz
PPMCM 10.08772 ppm/cm
HZCM 1266.19946 Hz/cm

1H spectrum


ppm
7.2600
5.7406
5.7309
4.1255
4.1112
3.7797
3.7231
3.7102
3.6983
2.1939
2.1834
2.0428
1.9577
1.9437
1.9142
1.9046
1.8870
1.8805
1.8755
1.8670
1.8535
1.8363
1.8269
1.8208
1.6112
1.5869
1.5764
1.5621
1.5458
1.5370
1.5271
1.5202
1.5137
1.5026
1.4918
1.4833
1.4656
1.3061
1.2556
1.2099
1.1863
1.1617
1.1447
1.1321
1.1131
1.0815
0.0981
0.0904
0.0743
H
OH
H
H
O
H
OTMS
S26
Current Data Parameters
USER medaub
NAME MED-VI-250puB
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151010
Time 9.40
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 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 parameters
SI 65536
SF 500.2200313 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 60.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm
Integral
1.000
1.026
1.037
5.741
12.738
4.466
11.433
9.860
ppm
9
8
7
6
5
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME       MED-VI-250puB
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20151010
Time              9.43
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  120
DS                    4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 sec
RG                13004
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               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

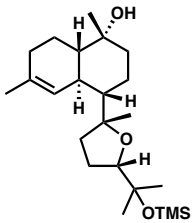
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            100.00 usec
PL2               1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== 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          125.7804076 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



S25

Current Data Parameters
USER medaub
NAME MED-VI-250puA
EXPNO 1
PROCNO 1

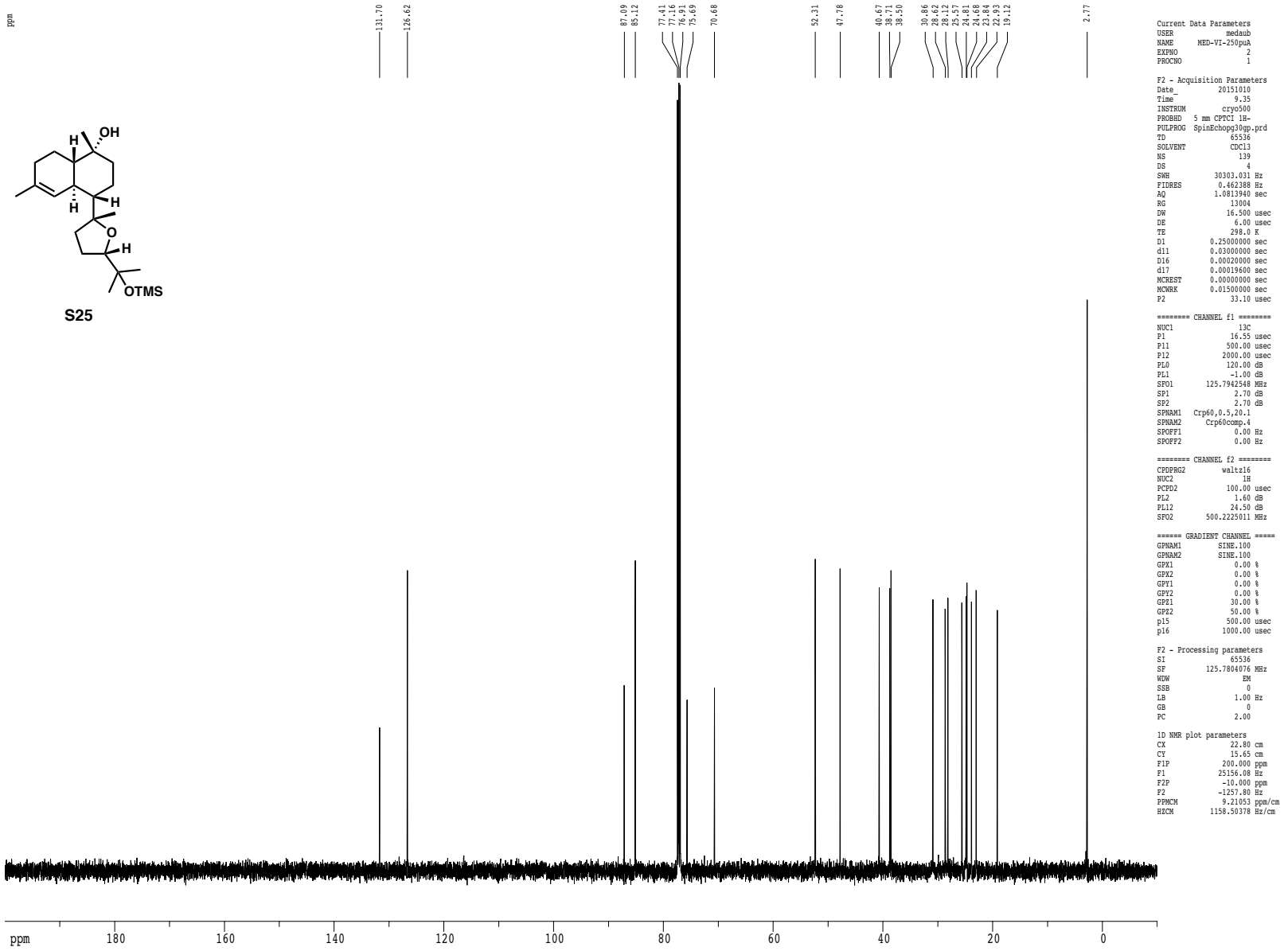
F2 - Acquisition Parameters
Date_ 20151010
Time 9.33
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200313 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 40.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



Current Data Parameters
USER medaub
NAME MED-VI-250puA
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151010
Time 9.35
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 139
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 13004
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 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

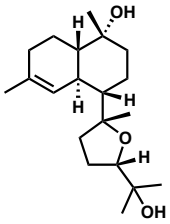
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== 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 125.7804076 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

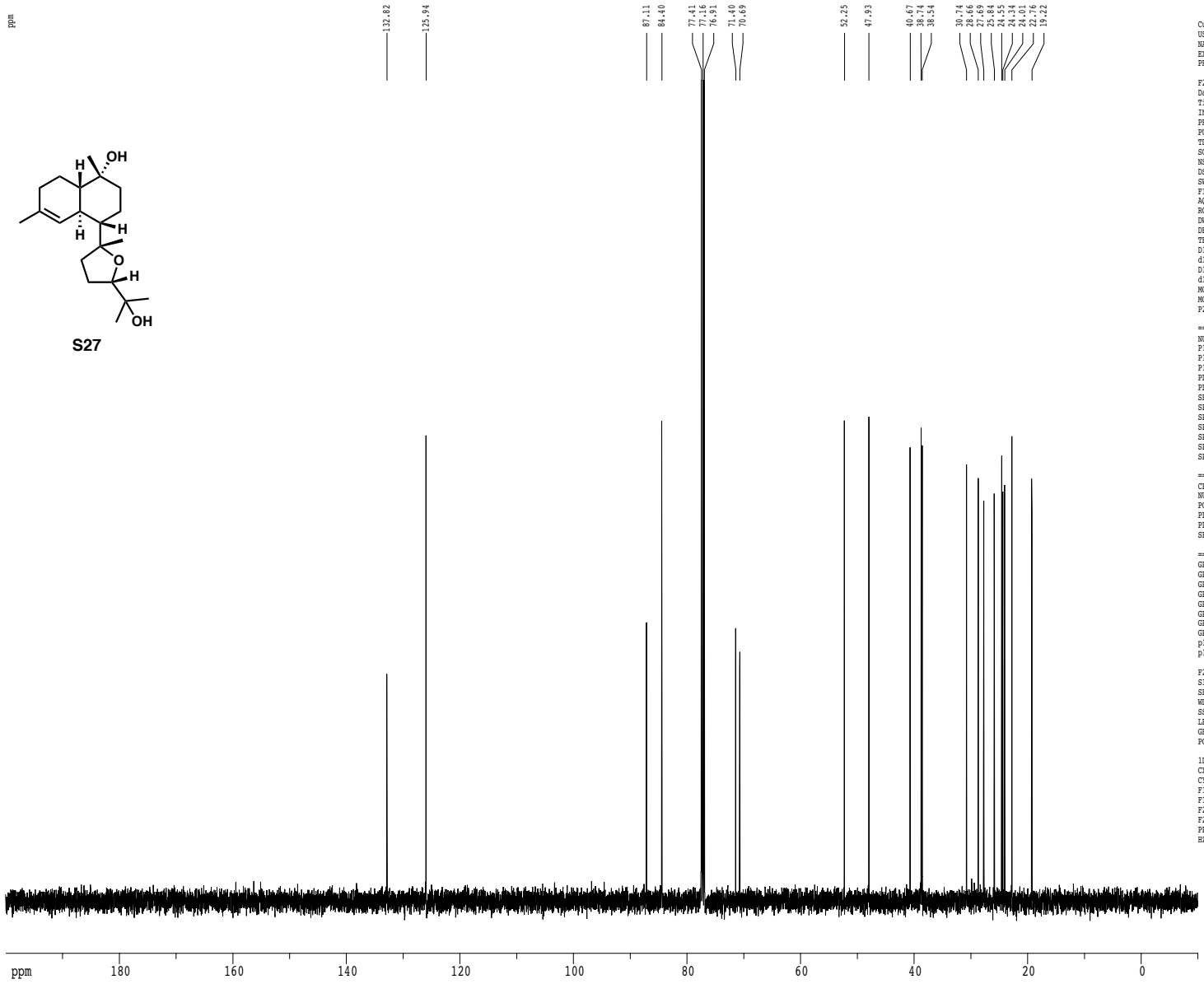
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



S27

Z-restored spin-echo 13C spectrum with 1H decoupling



S27

```
Current Data Parameters
USER              medaub
NAME        MED-VI-252pu
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20151010
Time              17.54
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   80
DS                    4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 sec
RG                13004
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               33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2       Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

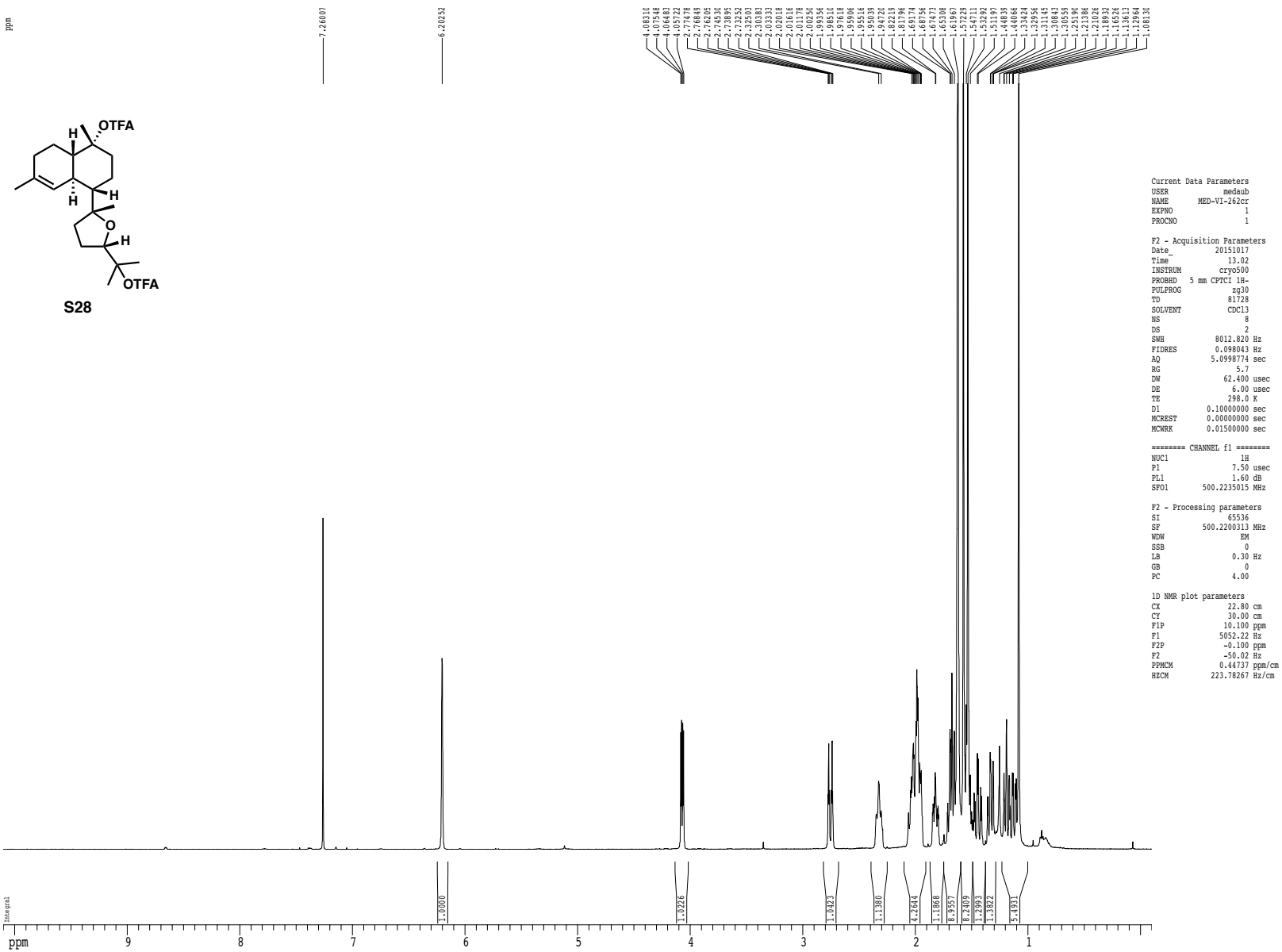
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2        500.2225011 MHz

====== 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          125.7804090 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                16.00 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 Parameters
USER                medaub
NAME        MED-VI-262cr
EXPNO                  1
PROCNO                 1

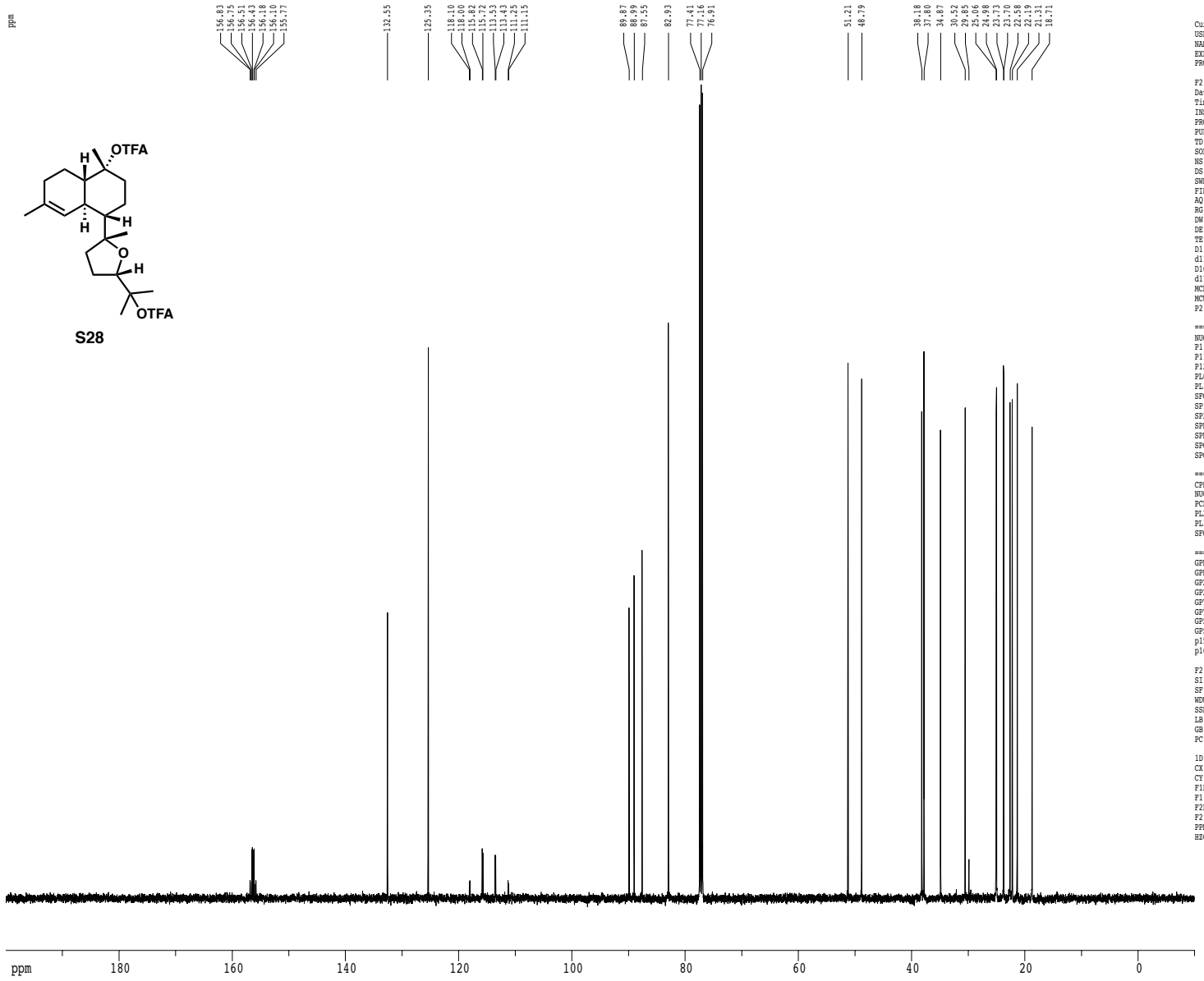
F2 - Acquisition Parameters
Date_           20151017
Time                13.02
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 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                 7.50 usec
PL1                1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200313 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                10.100 ppm
F1               5052.22 Hz
F2P                -0.100 ppm
F2                 -50.02 Hz
PPMCM            0.44737 ppm/cm
HZCM           223.78267 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER              medaub
NAME         MED-VI-262cr
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20151017
Time              13.05
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT            CDCl3
NS                 944
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1            0.00 Hz
SPOFF2            0.00 Hz

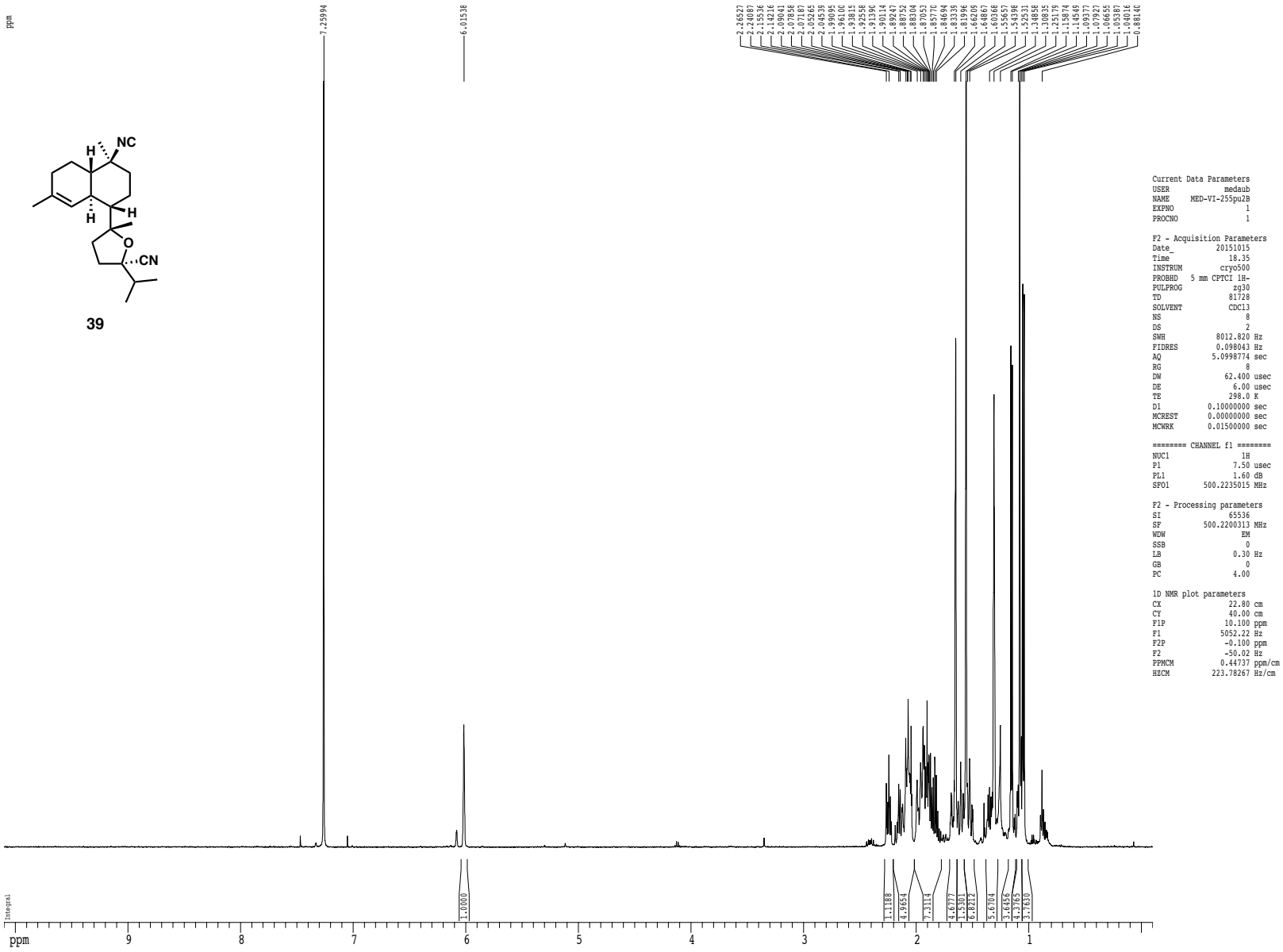
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2        500.2225011 MHz

====== 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          125.7804071 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



Current Data Parameters
USER medaub
NAME MED-VI-255pu2B
EXPNO 1
PROCNO 1

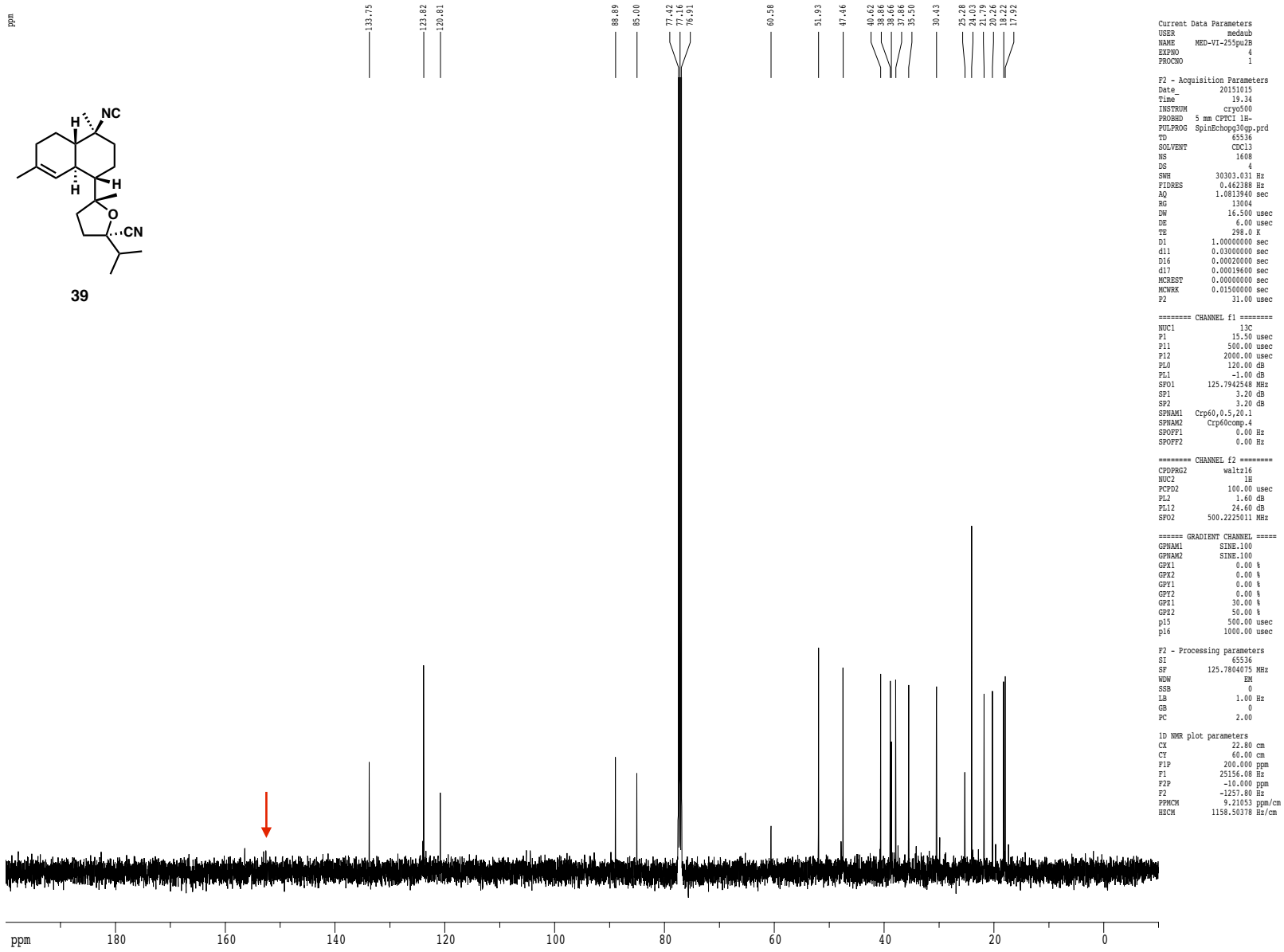
F2 - Acquisition Parameters
Date_ 20151015
Time 18.35
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 8
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200313 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
CY 40.00 cm
F1P 10.100 ppm
F1 5052.22 Hz
F2P -0.100 ppm
F2 -50.02 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.78267 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling




```
Current Data Parameters
USER                medaub
NAME       MED-VI-255pu2B
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151015
Time                19.34
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                   1608
DS                      4
SWH            30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                  13004
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 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

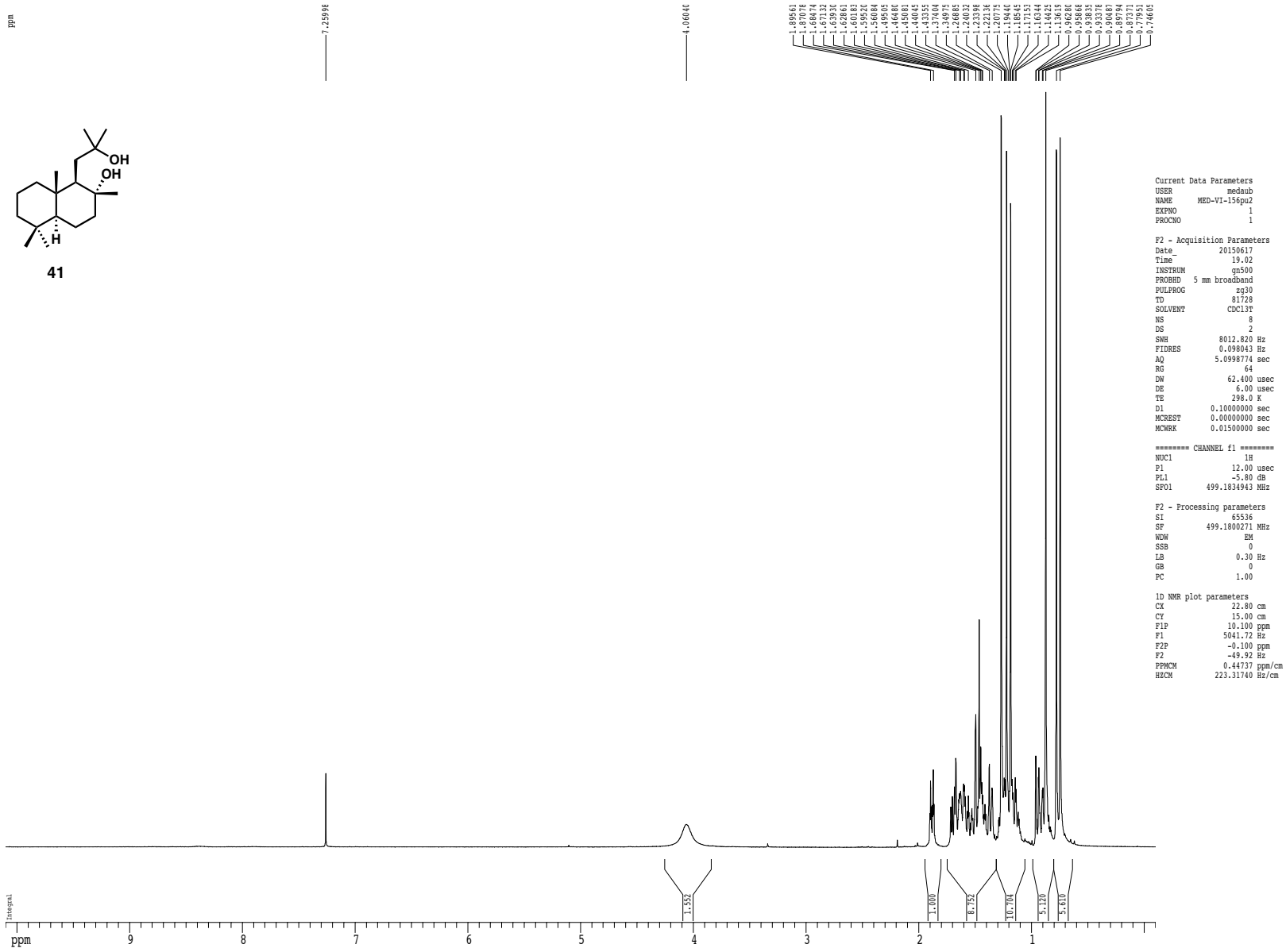
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== 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           125.7804075 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               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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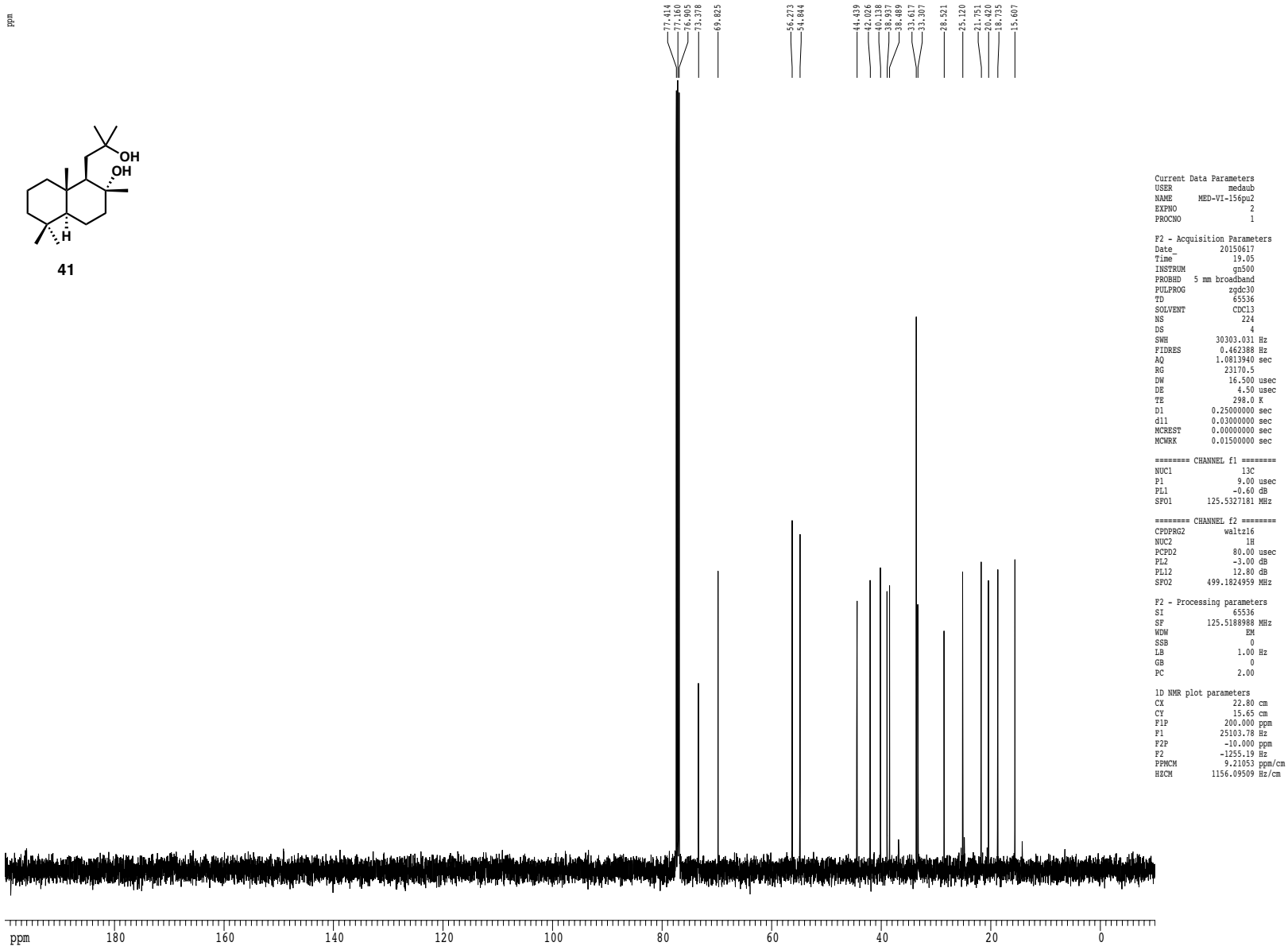
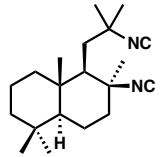
4.06040
1.89561
1.87078
1.68474
1.67132
1.63930
1.62861
1.60183
1.59520
1.56084
1.49505
1.46460
1.45081
1.44045
1.43355
1.37404
1.34975
1.26885
1.24032
1.23398
1.22136
1.20775
1.19440
1.19145
1.17153
1.16344
1.14425
1.13619
0.96280
0.95868
0.93835
0.93378
0.90487
0.89794
0.87371
0.77951
0.74605
OH
OH
H
41
Current Data Parameters
USER medaub
NAME MED-VI-156pu2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150617
Time 19.02
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 64
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 -5.80 dB
SFO1 499.1834943 MHz
F2 - Processing parameters
SI 65536
SF 499.1800271 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 10.100 ppm
F1 5041.72 Hz
F2P -0.100 ppm
F2 -49.92 Hz
PPMCM 0.44737 ppm/cm
HZCM 223.31740 Hz/cm
Integral
1.552
1.000
8.752
10.704
5.120
5.610
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



1H spectrum



43

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NAME MED-VI-159pufr22-32
EXPNO 2
PROCNO 1

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SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 912.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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PL1 -5.80 dB
SFO1 499.1834943 MHz

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GB 0
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1D NMR plot parameters
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CY 15.00 cm
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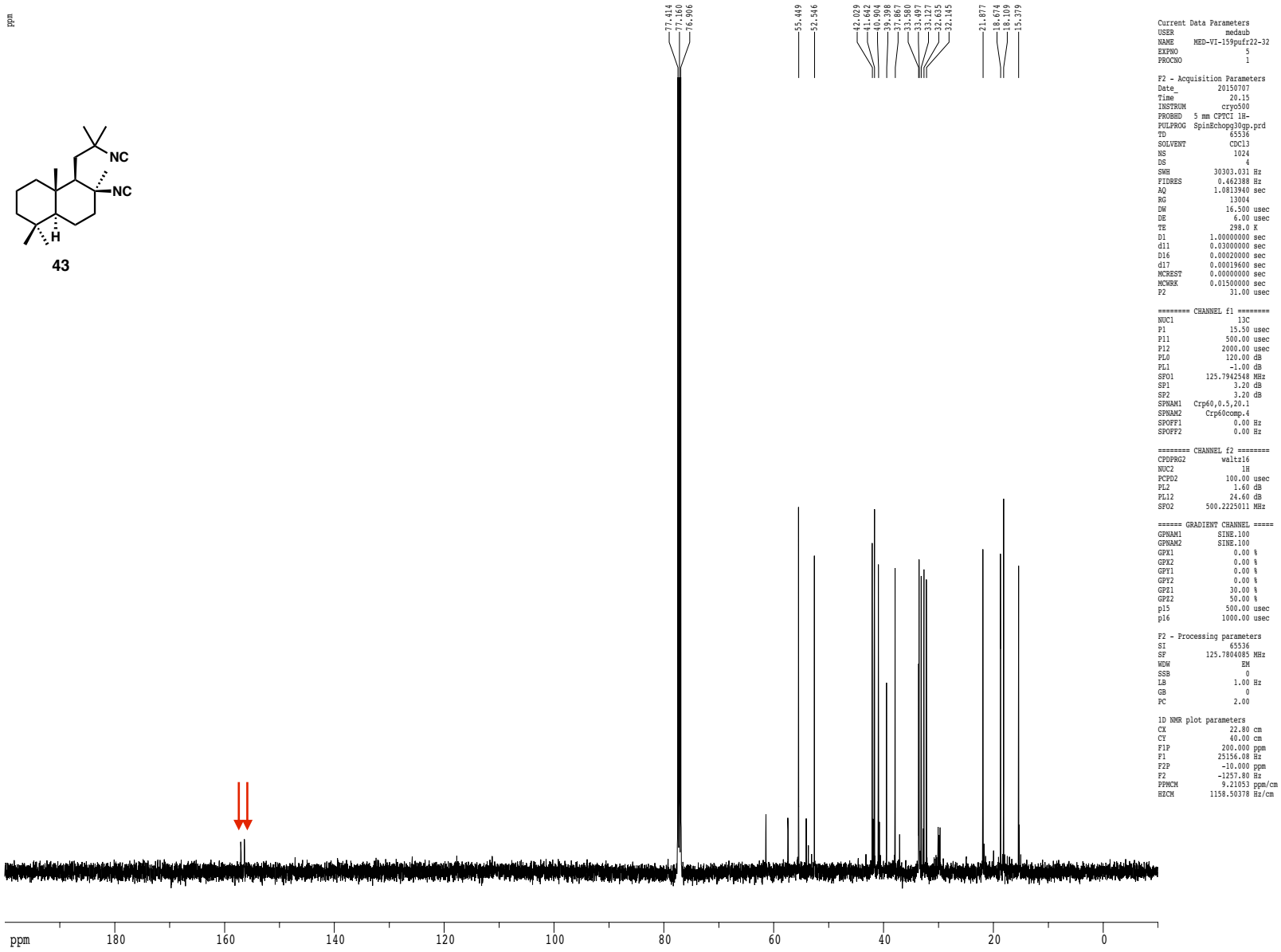
Z-restored spin-echo 13C spectrum with 1H decoupling



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NAME MED-VI-159pufr22-32
EXPNO 5
PROCNO 1

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SOLVENT CDCl3
NS 1024
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 13004
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 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 ========
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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
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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 =====
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GPNAM2 SINE.100
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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
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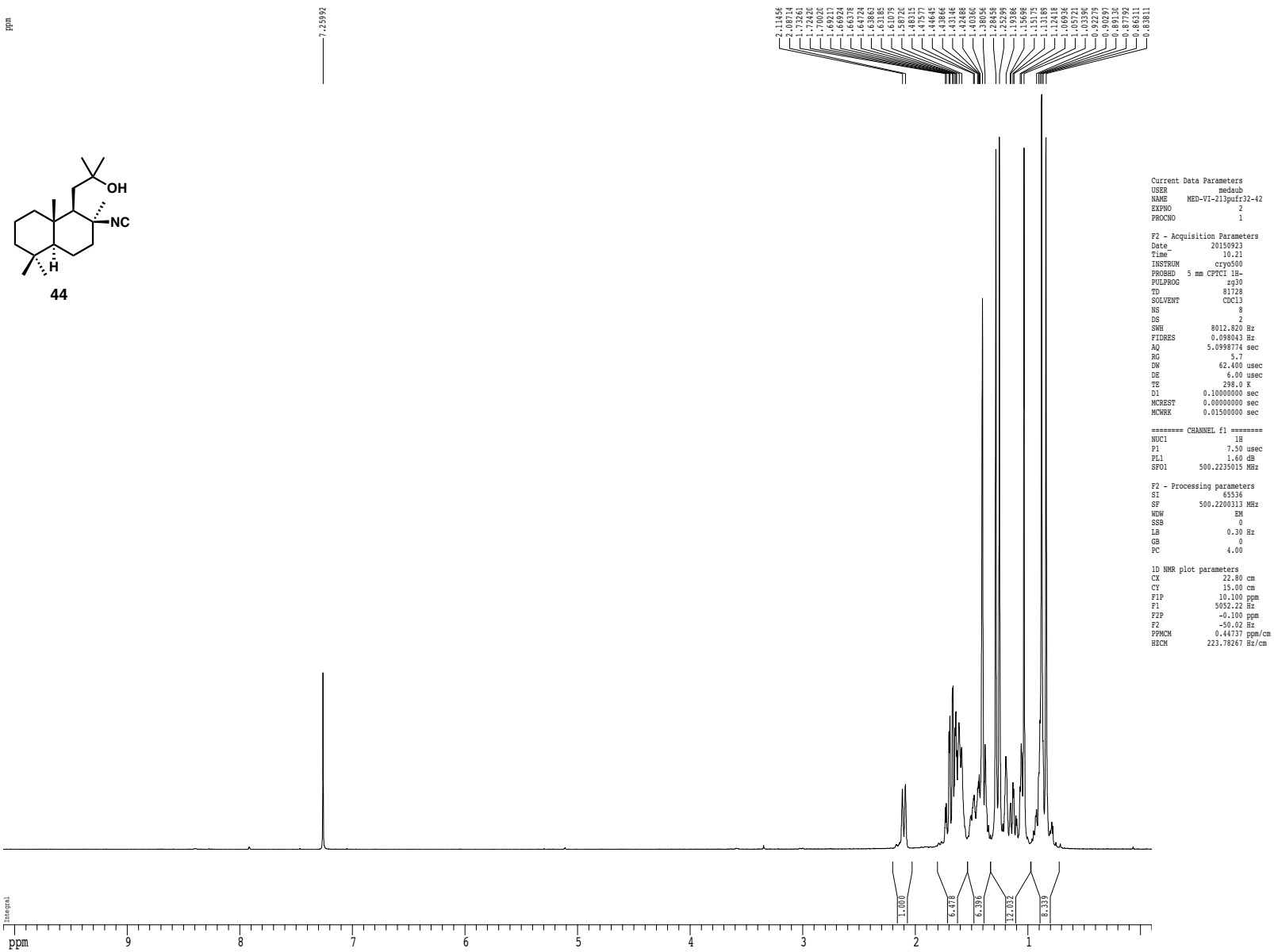
SF 125.7804085 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 40.00 cm
F1P 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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H
44
Current Data Parameters
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PROCNO 1
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TD 81728
SOLVENT CDCl3
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DS 2
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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 ========
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F2 - Processing parameters
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WDW EM
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LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
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CY 15.00 cm
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F1 5052.22 Hz
F2P -0.100 ppm
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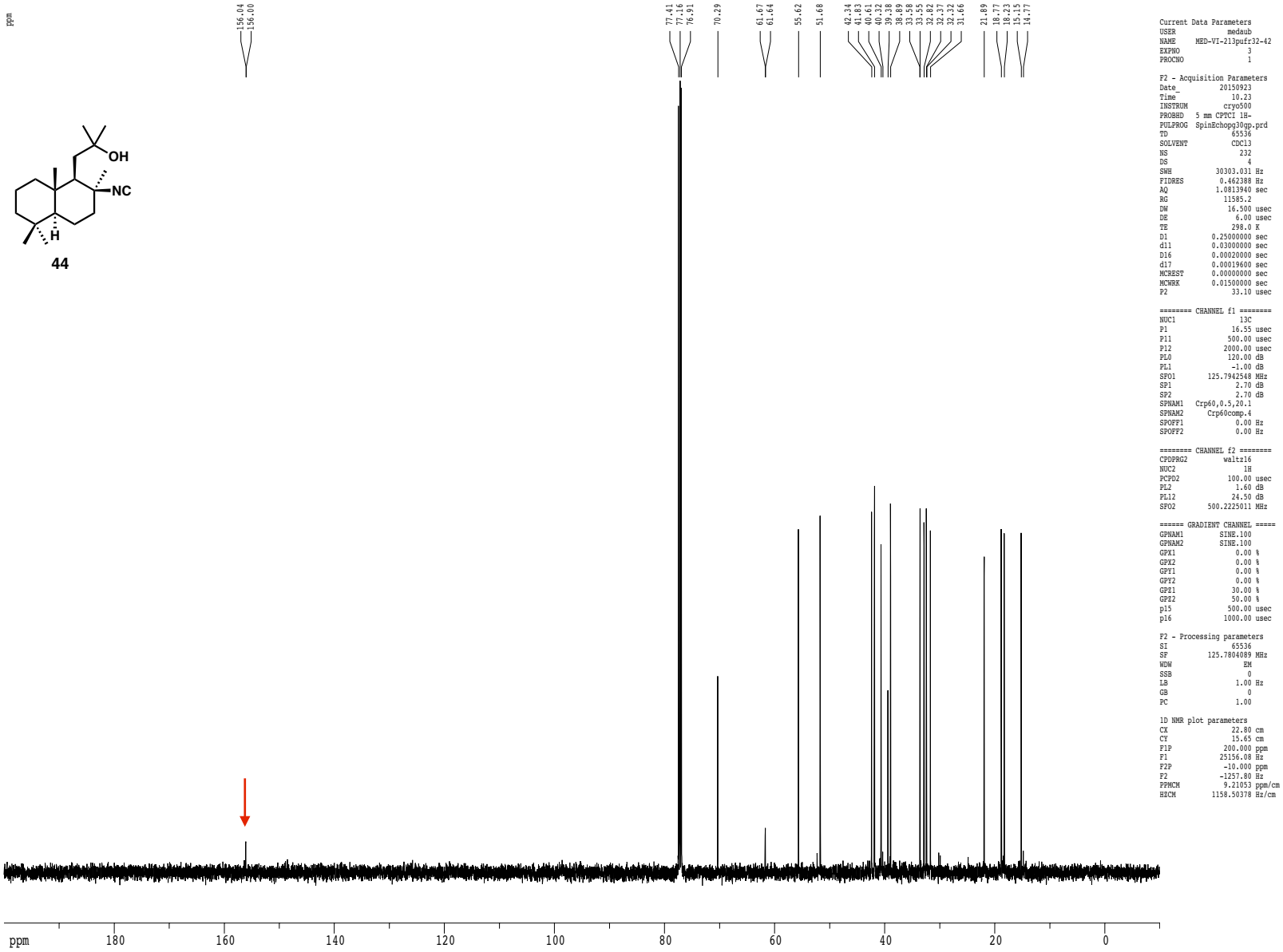
4
3
2
1

Z-restored spin-echo 13C spectrum with 1H decoupling

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Current Data Parameters
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EXPNO                    3
PROCNO                   1

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PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  232
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            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1        125.7942548 MHz
SP1              2.70 dB
SP2              2.70 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            24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
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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          125.7804089 MHz
WDW                 EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.00

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
```

Study details

Test concentration	1 μM
Reference compound	Ketanserin
Test systems	human, mouse liver microsomes (from BD Gentest) with final liver microsomal protein concentration of 0.5 mg/mL
Incubation condition	0, 5, 15, 30, 45 min at 37°C
Sample size	Duplicates (n=2)
Bioanalytical method	LC-MS/MS

Calculations

$T_{1/2}$ = 0.693/K (K is the rate constant from a plot of ln [concentration] vs. incubation time)

Cl_{int} = (0.693/$T_{1/2}$) × (1/(microsomal protein concentration (0.5 mg/mL))) × Scaling Factors (Table 1)

Table 1 Scaling Factors for Intrinsic Clearance Prediction in the Mouse, Rat, Dog, Monkey, and Human Microsomes

Species	Microsomal Protein per Gram of Liver	Liver Weight per Kilogram of Body Weight	Scaling Factor[a]	Hepatic Blood Flow (mL/min/kg)
Mouse	45	87.5	3937.5	90
Rat	44.8	40	1792	55.2
Dog	77.9	32	2492.8	30.9
Monkey	45	32.5	1462.5	44
Human	48.8	25.7	1254.2	20.7

[a]Scaling Factor = (microsomal protein per gram of liver) × (liver weight per kilogram of body weight)

Table 2a: Summary Data

Test Article	Species		Percent Remaining (%)					$T_{1/2}$ (minute)	Cl_{int} (mL/min/kg)
			0 min	5 min	15 min	30 min	45 min		
ketanserin	human	Mean	100.00	88.36	76.98	62.54	47.28	43.44	40.02
		RSD of Area Ratio	0.02	0.02	0.00	0.00	0.05		
	mouse	Mean	100.00	79.90	55.49	32.89	21.72	20.44	266.94
		RSD of Area Ratio	0.01	0.03	0.01	0.02	0.02		
MED-VII-108	human	Mean	100.00	82.25	73.80	91.55	69.01	142.48	12.20
		RSD of Area Ratio	0.17	0.25	0.15	0.17	0.14		
	mouse	Mean	100.00	100.00	86.70	77.93	71.54	87.26	62.54
		RSD of Area Ratio	0.12	0.21	0.04	0.18	0.06		

Note: Some compounds in liver microsomes showed biphasic metabolic kinetics, an initial fast disappearance followed by a slow disappearance.
The data points marked in red in column "F ~ H" represented the slow disappearance rates and were excluded from half-life calculation.

Comments:

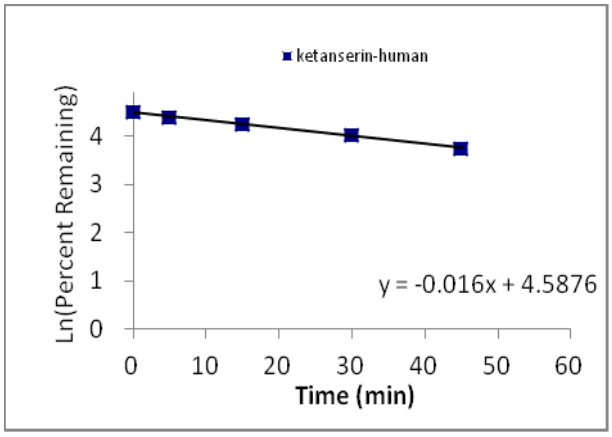
1. Historic data of ketanserin:

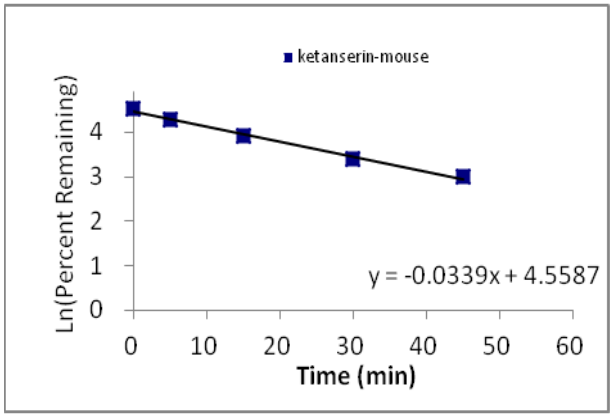
$T_{1/2}$ (Human) =	39.69 ± 6.36	min
$T_{1/2}$ (Mouse) =	18.27 ± 3.89	min

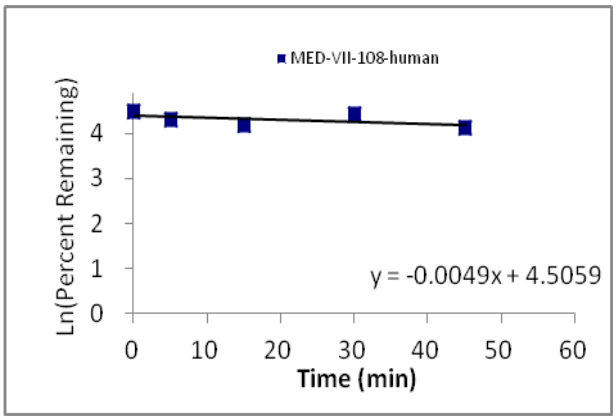
2. In this study, half lives of Ketanserin were consistent with historical results.

3. If percent remaining at 45 min was higher than 50 %, then $T_{1/2}$ was calculated using extrapolation method; If percentage remaining at 45 min was near 100% and the value $T_{1/2}$ <0 by Excel default, then $T_{1/2}$ and Cl_{int} were reported as "∞" and "0", respectively.

4. As summarized in table 2 (summary table), $T_{1/2}$ values marked in green suggested these compounds were stable in liver microsomes ($T_{1/2}$ > 120 min);
$T_{1/2}$ values marked in orange suggested these compounds showed moderate metabolism in liver microsomes ($T_{1/2}$ = 30-120 min);
$T_{1/2}$ values marked in red suggested these compounds were susceptible to metabolism in liver microsomes ($T_{1/2}$ < 30 min).


ketanserin-human
Ln(Percent Remaining)
y = -0.016x + 4.5876
Time (min)


ketanserin-mouse
Ln(Percent Remaining)
y = -0.0339x + 4.5587
Time (min)


MED-VII-108-human
Ln(Percent Remaining)
y = -0.0049x + 4.5059
Time (min)

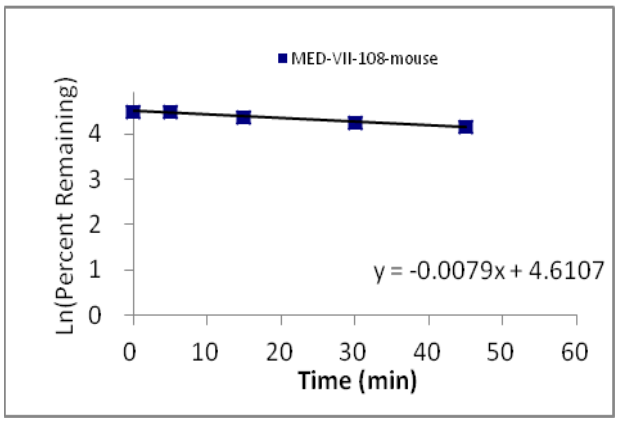

MED-VII-108-mouse
Ln(Percent Remaining)
y = -0.0079x + 4.6107
Time (min)

Table 3a: Raw data of reference and test compounds in human liver microsome

Cpd	Species	Time(min)	Raw Data					
			Analyte Peak Area (counts)	Analyte Peak Area (counts)	IS Peak Area (counts)	IS Peak Area (counts)	Area Ratio	Area Ratio
ketanserin	human	0	7620000	7540000	#######	#######	1.140	1.180
		5	6620000	6620000	#######	#######	1.040	1.010
		15	5640000	5650000	#######	#######	0.891	0.895
		30	4510000	4470000	#######	#######	0.723	0.728
		45	2950000	3550000	#######	#######	0.531	0.566
MED-VII-108	human	0	17600	13700	#######	#######	0.002	0.002
		5	11000	15100	#######	#######	0.001	0.002
		15	10500	12900	#######	#######	0.001	0.001
		30	12100	15300	#######	#######	0.001	0.002
		45	11400	9330	#######	#######	0.001	0.001

Table 3b: Raw data of reference and test compounds in mouse liver microsome

Cpd	Species	Time(min)	Raw Data					
			Analyte Peak Area (counts)	Analyte Peak Area (counts)	IS Peak Area (counts)	IS Peak Area (counts)	Area Ratio	Area Ratio
ketanserin	mouse	0	6460000	6490000	#######	#######	1.010	1.030
		5	5130000	5220000	#######	#######	0.795	0.835
		15	3500000	3570000	#######	#######	0.570	0.562
		30	1960000	2030000	#######	#######	0.340	0.331
		45	1140000	1290000	#######	#######	0.224	0.219
MED-VII-108	mouse	0	15500	17800	#######	#######	0.002	0.002
		5	19100	14200	#######	#######	0.002	0.002
		15	15200	14200	#######	#######	0.002	0.002
		30	10500	13300	#######	#######	0.001	0.002
		45	10700	11100	#######	#######	0.001	0.001

Detection method	UPLC-MS/MS-29(API6500+)				
Matrix	liver microsomes				
Internal standard (s)	Osalmid, imipramine				
MS conditions	Positive ion, ESI				
Mobile phase	A: 0.025%FA/1mM NH4OAc/H2O B: 0.025%FA/1mM NH4OAc/MeOH				
Column	ACQUITY-BEH-C18 (2.1*50 mm, 1.7 um)				
LC conditions	0.60 mL/min Time (min) Pump B (%) 0.2 2 0.4 98 1.4 98 1.41 2 2.5 stop				
Detection & Retention time (RT)	compound	Analyte Mass Ranges (Da)	Analyte RT (min)	IS Mass Ranges (Da)	IS RT (min)
	ketanserin	396.300/189.000 Da	0.99	281.100/193.100	1.06
	MED-VII-108	277.500/205.200 Da	0.96	230.100/121.300	0.96

Experimental procedure:

1. Buffer A: 1.0 L of 0.1 M monobasic Potassium Phosphate buffer containing 1.0 mM EDTA
   Buffer B: 1.0 L of 0.1 M Dibasic Potassium Phosphate buffer containing 1.0 mM EDTA
   Buffer C: 0.1 M Potassium Phosphate buffer, 1.0 mM EDTA, pH 7.4 by titrating 700 mL of buffer B with buffer A while monitoring with the pH meter.

2. Reference compouds(Ketanserin) and test compounds spiking solution:
   500 μM spiking solution: add 10 μL of 10 mM DMSO stock solution into 190 μL ACN.

   1.5 μM spiking solution in microsomes (0.75 mg/mL): add 1.5 μL of 500 μM spiking solution and 18.75 μL of 20 mg/mL liver microsomes into 479.75 μL of Buffer C on ice.

3. Prepare NADPH stock solution (6 mM) by dissolving NADPH into buffer C.

4. Dispense 30 μL of 1.5 μM spiking solution containing 0.75 mg/mL microsomes solution to the assay plates designated for different time points (0-, 5-, 15-, 30-, 45-min) on ice.

5. For 0-min, add 135 μL of ACN containing IS to the wells of 0-min plate and then add 15 μL of NADPH stock solution (6 mM).

6. Pre-incubate all other plates at 37 °C for 5 minutes.

7. Add 15 μL of NADPH stock solution (6 mM) to the plates to start the reaction and timing.

8. At 5-min, 15-min, 30-min, and 45-min, add 135 μL of ACN containing IS to the wells of corresponding plates, respectively, to stop the reaction.

9. After quenching, shake the plates at the vibrator (IKA, MTS 2/4) for 10 min (600 rpm/min) and then centrifuge at 5594 g for 15 min (Thermo Multifuge × 3R).

10. Transfer 50 μL of the supernatant from each well into a 96-well sample plate containing 50 μL of ultra pure water (Millipore, ZMQS50F01) for LC/MS analysis.