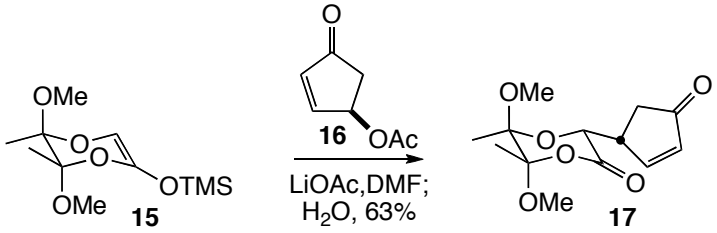
Golgi Modifying Properties of Macfarlandin E and the Synthesis and Evaluation of its Dioxabicyclo[3.2.1]octanone Core

Supporting Information – Table of Contents

Chemical Materials and Methods. Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). Titanium(IV) chloride and methylene bromide were purified by distillation. TMEDA, benzylamine, BF_3OEt_2 were purified by distillation over CaH_2. All other commercially obtained reagents were used as received. Reaction temperatures were controlled using an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, ceric ammonium molybdate, potassium permanganate and iodine. Flash column chromatography was performed using normal phase silica gel (60 Å, 230-240 mesh, Merck KGA). ^{1}H NMR spectra were recorded on Bruker spectrometers (at 500 or 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (at 125 or 150 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on 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. High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility with a Micromass LCT spectrometer. See *JOC Standard Abbreviations and Acronyms* for abbreviations (available at http://pubs.acs.org/userimages/ContentEditor/1218717864819/joceah_abbreviations.pdf).

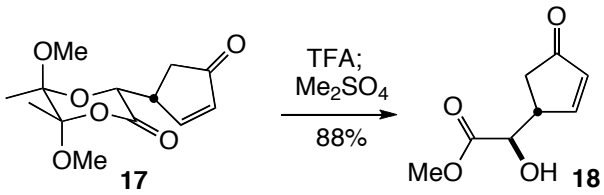
Experimental Procedures



5,6-Dimethoxy-5,6-dimethyl-3-((*R*)-4-oxocyclopent-2-enyl)-1,4-dioxan-2-one (17): A solution of silyl ketene acetal **15**[1] (91 g, 0.347 mol) in DMF (50 mL) was added to a stirring mixture of

1. Ley SV, Dixon DJ, Guy RT, Rodriguez F, Sheppard TD (2005) Michael, Michael-aldol and Michael-Michael reactions of enolate equivalents of butane-2,3-diacetal protected glycolic acid derivatives. *Org. Biomol. Chem.* 3:4095-4107.

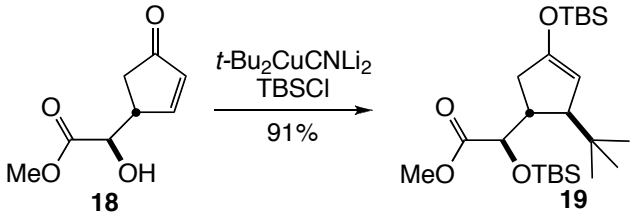
enone **16**[2] (19.5 g, 0.139 mol) and LiOAc (27.5 g, 0.416 mol) in DMF (700 mL) at 0 °C.[3] After 5 min, TLC analysis showed the consumption of **16**. The reaction mixture was allowed to warm to rt, H_2O (3.0 mL, 190 mmol) was added, and the mixture was stirred for an additional hour. The mixture was partitioned between EtOAc (500 mL) and 1 M HCl (500 mL). The aqueous phase was extracted with EtOAc (2 × 400 mL). The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue by silica gel chromatography (50% Et_2O/hexanes) followed by recrystallization (50% Et_2O/hexanes, 4 crops) gave **17** (23.7 g, 63%) as a colorless solid: R_f 0.21 (60% EtOAc/hexanes); mp 64-67 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (dd, J = 5.7, 2.3 Hz, 1H), 6.22 (dd, J = 5.7, 2.1 Hz, 1H), 4.21 (d, J = 5.2 Hz, 1H), 3.58 (m, 1H), 3.42 (s, 3H), 3.28 (s, 3H), 2.52 (dd, J = 18.7, 6.7 Hz, 1H), 2.42 (dd, J = 18.7, 2.9 Hz, 1H), 1.48 (s, 3H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 208.6, 168.5, 163.0, 135.5, 105.6, 98.5, 71.3, 50.2, 49.3, 43.9, 37.3, 17.8, 17.0; IR (thin film) 1744, 1713, 1270 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{19}O_6$ (M+H) 271.1182, observed 271.1181; $[\alpha]_D^{23}$ +246°, $[\alpha]_{577}^{23}$ +258°, $[\alpha]_{546}^{24}$ +291°, $[\alpha]_{435}^{25}$ +484°, $[\alpha]_{405}^{24}$ +569° (c = 1.0, $CHCl_3$). Crystals obtained by the above isolation procedure were suitable for X-ray diffraction crystal analysis.



(*R*)-Methyl 2-hydroxy-2-((*R*)-4-oxocyclopent-2-enyl)ethanoate (18): A flask was charged with **17** (13.7 g, 50.7 mmol) at rt. A solution of TFA (170 mL) and H_2O (17 mL) was added and the mixture was stirred for 5 min with a yellow homogenous solution being obtained.[4] This solution was concentrated *in vacuo* (<3 torr) for 18 h with stirring to give the crude hydroxy acid. The acid was dissolved in acetone (250 mL) and K_2CO_3 (17.5 g, 127 mmol) and dimethyl sulfate (7.2 mL, 76.1 mmol) were added and the resulting mixture was vigorously stirred and heated to 50 °C for 30 min. Acetic acid (2 mL) was added and the mixture was allowed to cool to rt. The crude mixture was passed through a pad of silica gel (90% EtOAc/hexanes) to afford **18** (7.56 g, 88%)

2. Hughes CC, Miller AK, Trauner D (2005) An electrochemical approach to the guanacastepenes. *Org. Lett.* 7:3425-3428.
3. Nakagawa T, Fujisawa H, Yuzo NI, Mukaiyama T (2004) Lithium acetate-catalyzed Michael reaction between trimethylsilyl enolate and α,β-unsaturated carbonyl compound. *Chem. Lett.* 33:1016-1017.
4. Ley SV, *et al.* (1998) Total synthesis of the protein phosphatase inhibitor okadaic acid *J. Chem. Soc. Perkin Trans. 1* 3907-3911.

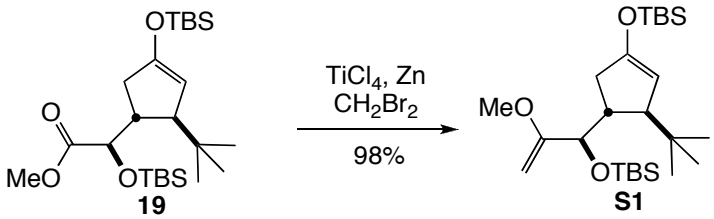
as a tan oil: R_f 0.23 (60% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (dd, J = 5.7, 2.4 Hz, 1H), 6.28 (dd, J = 5.7, 2.0 Hz, 1H), 4.25 (t, J = 5.8 Hz, 1H), 3.83 (s, 3H), 3.35 (m, 1H), 2.78 (d, J = 6.2 Hz, 1H), 2.48 (dd, J = 18.7, 6.6 Hz, 1H), 2.37 (dd, J = 18.7, 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 208.5, 173.9, 162.3, 136.6, 71.6, 53.1, 45.3, 37.3; IR (thin film) 3423, 1706, 1675 cm^{-1}; HRMS (ESI) calculated for $C_8H_{11}O_4$ (M+H) 171.0657, observed 171.0652; $[\alpha]_D^{24}$ +157°, $[\alpha]_{577}^{24}$ +164°, $[\alpha]_{546}^{24}$ +188°, $[\alpha]_{435}^{24}$ +329°, $[\alpha]_{405}^{24}$ +396° (c = 1.0, $CHCl_3$).



(*R*)-Methyl 2-((1*R*,2*S*)-2-*tert*-butyl-4-(*tert*-butyldimethylsilyloxy)cyclopent-3-enyl)-2-(*tert*-butyldimethylsilyloxy)acetate (19): The general procedure of Corey was followed.[5,6] A hexane solution of *t*-BuLi (119 mL, 1.7 M, 203 mmol) was added to a stirring suspension of CuCN (9.11 g, 101 mmol) in Et_2O (400 mL) at –78 °C, and the resulting solution was stirred for 30 min. The solution was warmed to –40 °C for 15 min, then cooled to –78 ºC. A solution of TBSCl (15.3 g, 101 mmol) in THF (40 mL) was added via cannula transfer and the solution was stirred for an additional 5 min. A solution of hydroxy enone **18** (6.89 g, 40.5 mmol) in THF (40 mL) was added via cannula transfer and the resulting solution was allowed to gradually warm to rt over 10 h as a dark heterogeneous mixture was formed. This mixture was poured into a separatory funnel containing a mixture of saturated aqueous NH_4Cl and NH_4OH (9:1, 500 mL) and EtOAc (500 mL). The layers were separated and the organic phase was washed with additional NH_4Cl/NH_4OH solution (500 mL). The combined aqueous layers were extracted with EtOAc (2 × 400 mL). The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue by silica gel chromatography (10% EtOAc/hexanes) gave **19** (16.8 g, 91%) as a colorless oil: R_f 0.45 (5% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.49 (s, 1H), 3.98 (d, J = 6.4 Hz, 1H), 3.67 (s, 3H), 2.38 (apt ddt, J = 16.4, 9.0, 2.5 Hz, 1H), 2.32 (m, 1H), 2.27 (m, 1H), 1.96 (app dt, J = 17.5, 1.3 Hz, 1H), 0.92 (s, 9H), 0.90 (s, 9H), 0.82 (s, 9H), 0.50 (s, 3H), 0.40 (s, 3H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.7, 154.0, 103.2, 76.3,

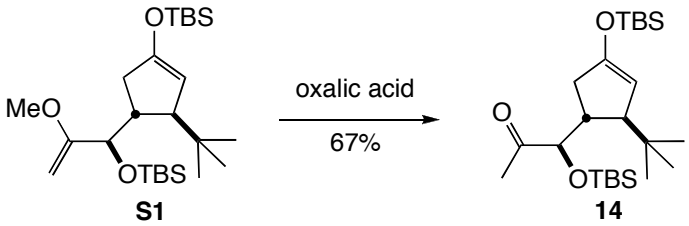
5. Corey EJ, Kang M, Desai MC, Ghosh AK, Houpis JN (1988) Total synthesis of (+/-)-Ginkgolide-B. *J. Am. Chem. Soc.* 110:649-651.
6. Corey EJ, Boaz NW (1985) The reactions of combined organocuprate chlorotrimethylsilane reagents with conjugated carbonyl-compounds. *Tetrahedron Lett.* 26:6019-6022.

54.1, 51.7, 40.9, 36.4, 34.5, 27.3, 25.9, 25.85, 18.4, 18.2, –4.3, –4.6, –4.9, –5.0; IR (thin film) 1758, 1652, 1252 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{48}O_4Si_2Na$ (M+Na) 479.2989, observed 479.2980; $[\alpha]_D^{24}$ +10.0°, $[\alpha]_{577}^{25}$ +10.8°, $[\alpha]_{546}^{25}$ +11.5°, $[\alpha]_{435}^{25}$ +20.4°, $[\alpha]_{405}^{25}$ +22.1° (*c* = 1.0, $CHCl_3$).



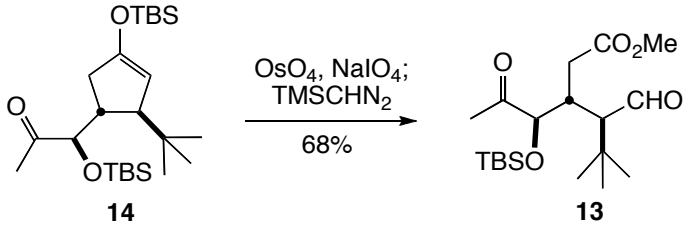
***tert*-butyl((3*S*,4*R*)-3-*tert*-butyl-4-((*R*)-1-(*tert*-butyldimethylsilyloxy)-2-methoxyallyl) cyclopent-1-enyloxy)dimethylsilane (S1):** The general procedure of Rainer was followed.[7] A stirring solution of $TiCl_4$ (7.68 mL, 69.9 mmol) in CH_2Cl_2 (300 mL) was cooled to 0 °C and THF (30.0 mL) was added dropwise to generate a yellow solution. After 5 min, TMEDA (62.0 mL, 412 mmol) was added dropwise to form a red solution. After 15 min, the solution was allowed to warm to rt and a mixture of Zn (9.24 g, 142 mmol) and $PbCl_2$ (2.3 g, 8.24 mmol) was added. The resulting mixture turned blue. After 15 min, a solution of ester **19** (4.70 g, 10.3 mmol) and CH_2Br_2 (4.80 mL, 68.0 mmol) in CH_2Cl_2 (30 mL) was added via cannula. The resulting mixture was gently refluxed for 1.5 h. The reaction mixture was cooled to rt and saturated aqueous K_2CO_3 (10 mL) was very slowly added. The dark colored heterogenous mixture was filtered through a pad of silica with Et_2O and the eluent was concentrated *in vacuo*. Purification of the residue by silica gel chromatography (2% EtOAc/hexanes) gave **S1** (4.60 g, 98%) as a colorless oil: R_f 0.63 (2.5% Et_2O/hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.52 (s, 1H), 4.09 (d, *J* = 1.8 Hz, 1H), 3.99 (s, 1H), 3.76 (d, *J* = 7.4 Hz, 1H), 3.48 (s, 3H), 2.33 (m, 2H), 2.18 (m, 1H), 1.88 (d, *J* = 15.9 Hz, 1H), 0.90 (s, 9H), 0.86 (s, 9H), 0.79 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H), 0.02 (s, 3H), –0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.4, 154.2, 103.9, 83.5, 77.7, 54.7, 54.1, 40.8, 36.9, 34.7, 27.5, 26.2, 26.0, 18.5, 18.3, –4.1, –4.4, –4.5, –4.6; IR(thin film) 1715, 1658 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{50}O_3Si_2Na$ (M+Na) 477.3196, observed 477.3192; $[\alpha]_D^{24}$ +13.6°, $[\alpha]_{577}^{24}$ +14.3°, $[\alpha]_{546}^{24}$ +16.4°, $[\alpha]_{435}^{24}$ +28.2°, $[\alpha]_{405}^{24}$ +33.2° (*c* = 1.0, $CHCl_3$).

7. Roberts SW, Rainier JD (2007) Synthesis of an A-E gambieric acid subunit with use of a C-glycoside centered strategy. *Org. Lett.* 9:2227-2230.



S1 **14**

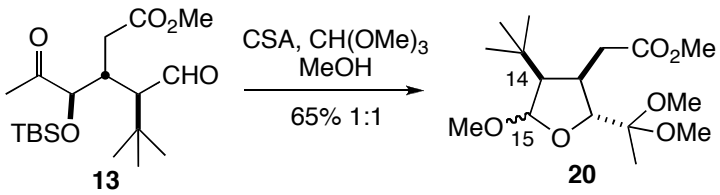
(*R*)-1-((1*R*,2*S*)-2-*tert*-butyl-4-(*tert*-butyldimethylsilyloxy)cyclopent-3-enyl)-1-(*tert*-butyldimethylsilyloxy)propan-2-one (14): To a solution of enol ether **S1** (4.3 g, 9.47 mmol) in *i*PrOH (40 mL) and H_2O (10 mL) at 0 °C was added oxalic acid (1.79 g, 14.2 mmol) and the solution was allowed to warm to rt. After 1.5 h, 10% aqueous K_2CO_3 (250 mL) and 50% EtOAc/hexanes (200 mL) were added to the solution. The layers were separated and the aqueous layer was washed with additional 50% EtOAc/hexanes (200 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (2→5% Et_2O/hexanes) gave ketone **14** (2.80 g, 67%) as a colorless oil: R_f 0.52 (7% Et_2O/hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.49 (s, 1H), 3.63 (d, J = 8.6 Hz, 1H), 2.32 (m, 2H), 2.12 (m, 4H), 1.87 (d, J = 16.7 Hz, 1H), 0.88 (s, 9H), 0.86 (s, 9H), 0.77 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.03 (s, 3H), –0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 211.5, 154.2, 103.1, 82.4, 54.0, 40.3, 35.5, 34.7, 27.4, 26.0, 25.9, 25.3, 18.3, 18.25, –4.3, –4.55, –4.6, –4.8; IR (thin film) 1715, 1650, 1254 cm^{-1}; HRMS (ESI) calculated for $C_{24}H_{48}O_3Si_2Na$ (M+Na) 463.3040, observed 463.3048; $[\alpha]_D^{25}$ +41.5°, $[\alpha]_{577}^{25}$ +43.0°, $[\alpha]_{546}^{25}$ –50.5°, $[\alpha]_{435}^{25}$ +105°, $[\alpha]_{405}^{25}$ +143° (*c* = 1.0, $CHCl_3$).



14 **13**

(3*R*,4*R*)-Methyl 3-((*R*)-1-(*tert*-butyldimethylsilyloxy)-2-oxopropyl)-4-formyl-5,5-dimethylhexanoate (13): To a stirred mixture of enoxy silane **14** (1.20 g, 2.72 mmol) in THF (11 mL) and H_2O (3.0 mL), $NaIO_4$ (1.74 g, 8.2 mmol) and OsO_4 (1.4 mL, 2.5 wt% in *t*BuOH, 0.136 mmol) were added. The mixture was stirred with a large stir bar for 16 h. The reaction mixture was diluted with MeOH (20 mL) and filtered through a plug of cotton. The filtrate was stirred and cooled to 0 °C and $TMSCHN_2$ (2.0 M in Et_2O) was added until the color of the mixture was a persistent yellow (~15 mL). The excess $TMSCHN_2$ was destroyed by slow addition of AcOH (30% in MeOH, ~1 mL). The mixture was then filtered through a plug of cotton and the

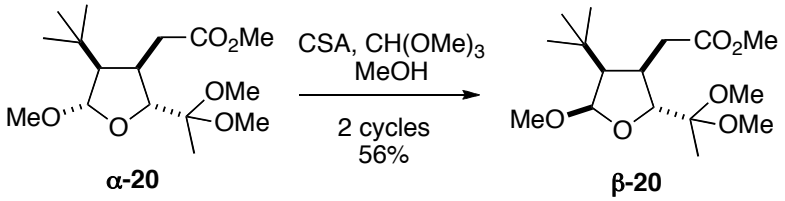
filtrate was concentrated. Purification of the residue by silica gel chromatography (10% hexanes/EtOAc) gave tricarbonyl **13** (690 mg, 68%) as a colorless oil: R_f 0.27 (10% hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.81 (d, J = 3.0 Hz, 1H), 4.15 (d, J = 3.0 Hz, 1H), 3.67 (s, 3H), 2.80 (m, 2H), 2.48 (dd, J = 17.9, 11.2 Hz, 1H), 2.32 (d, J = 3.0 Hz, 1H), 2.15 (s, 3H), 0.94 (s, 9H), 0.87 (s, 9H), –0.02 (s, 3H), –0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 209.3, 204.9, 173.7, 81.0, 56.9, 52.0, 37.8, 34.1, 33.7, 28.7, 26.3, 25.9, 18.4, –4.5, –5.3; IR (thin film) 1729, 1254, 1173 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{36}O_5SiNa$ (M+Na) 395.2230, observed 395.2222; $[\alpha]_D^{25}$ +0.1°, $[\alpha]_{577}^{25}$ –0.6°, $[\alpha]_{546}^{25}$ –2.0°, $[\alpha]_{435}^{25}$ –22.8°, $[\alpha]_{405}^{25}$ –40.5° (c = 1.0, $CHCl_3$).



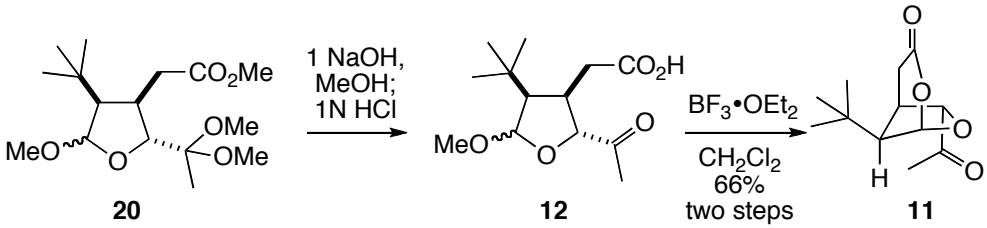
13 **20**

Methyl 2-((2*R*,3*R*,4*R*)-4-*tert*-butyl-2-(1,1-dimethoxyethyl)-5-methoxytetrahydrofuran-3-yl) ethanoate (20): To a solution of **13** (548 mg, 1.47 mmol) in MeOH (30 mL) at 0 °C was added $CH(OMe)_3$ (1.6 mL, 2.6 mmol) and camphorsulfonic acid (514 mg, 2.20 mmol) and the solution was allowed to warm to rt. After 18 h, saturated aqueous $NaHCO_3$ (50 mL) and CH_2Cl_2 (100 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel chromatography (2–10% Et_2O/CH_2Cl_2) afforded the more non-polar β-**20** (154 mg, 33%) as a yellow oil and α-**20** (148 mg, 32%) as a yellow oil. Data for β-**20**: R_f 0.5 (4% Et_2O/CH_2Cl_2); ^{1}H NMR (C_6D_6, 500 MHz) δ 4.85 (d, J = 3.9 Hz, 1H), 4.42 (d, J = 2.8 Hz, 1H), 3.44 (s, 3H), 3.21 (s, 3H), 3.14 (s, 3H), 3.07 (s, 3H), 2.95 (dd, J = 10.3, 3.3 Hz, 1H), 2.79 (m, 2H), 1.87 (dd, J = 8.2, 3.9 Hz, 1H), 1.25 (s, 3H), 1.02 (s, 9H); 1D-NOE studies, irradiation of the anomeric C14 CH(δ 4.85) showed a 3.4% NOE (mixing time – 1.0 sec) to the C14 CH (δ 1.87); ^{13}C NMR (C_6D_6, 125 MHz) δ 173.2, 106.5, 102.5, 84.2, 57.0, 54.6, 51.3, 48.9, 48.6, 39.9, 38.6, 32.0, 30.6, 17.3; IR (thin film) 2953, 1741, 1469, 1164 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{30}O_6$ (M+Na) 341.1940, observed 341.1938; $[\alpha]_D^{25}$ –28.4; $[\alpha]_{577}^{25}$ –30.7; $[\alpha]_{546}^{25}$ –34.9; $[\alpha]_{435}^{25}$ –51.0; $[\alpha]_{405}^{25}$ –57.3 (c = 1.0, CH_2Cl_2). Data for α-**20**: R_f 0.40 (4% Et_2O/ CH_2Cl_2); ^{1}H NMR (C_6D_6, 500 MHz) δ 4.88 (s, 1H), 4.11 (d, J = 9.9 Hz, 1H), 3.79 (m, 4H), 3.26 (s, 3H), 3.24 (s, 3H), 3.00 (m, 4H), 2.70 (dd, J = 17.0, 8.9 Hz, 1H), 2.33 (d, J = 7.4 Hz, 1H), 1.47 (s, 3H), 0.91 (s, 9H); 1D-NOE studies, irradiation of the anomeric C14 CH(δ 4.88) resulted in a 0.85% NOE (mixing time – 1.0 sec) to the tert-butyl group (δ 1.02); ^{13}C NMR (C_6D_6, 125 MHz) δ 173.1, 108.0, 103.3,

83.3, 58.1, 55.0, 51.4, 48.2, 48.1, 39.5, 34.8, 32.9, 29.9, 17.6; IR (thin film) 1741, 1383, 1134 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{30}O_6$ (M+Na) 341.1940, observed 341.1943; $[\alpha]_D^{25}$ +49.0°, $[\alpha]_{577}^{25}$ +50.1°, $[\alpha]_{546}^{25}$ +56.3°, $[\alpha]_{435}^{25}$ +93.7°, $[\alpha]_{405}^{25}$ +112.3° (*c* = 1.0, $CHCl_3$).

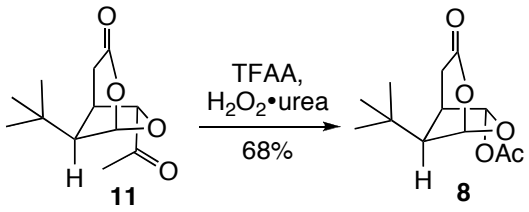


Equilibration of 20: A solution of α-**20** (95 mg) was submitted to reaction conditions and isolation procedures discussed above and after two cycles 53 mg (56%) of β-**20** was isolated.

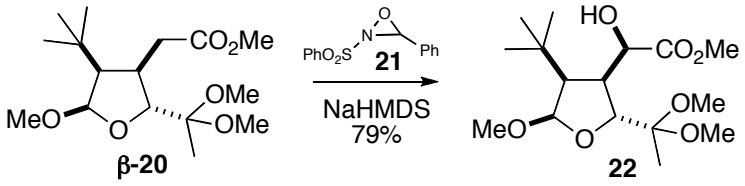


(1*S*,5*R*,6*R*,8*R*)-8-*tert*-butyl-6-ethanoyl-2,7-dioxabicyclo[3.2.1]octan-3-one (11): To a solution of ester **20** (105 mg, 0.33 mmol) in MeOH (13.9 mL) at rt was added 1N NaOH (1.4 mL, 1M in H_2O, 1.39 mmol) and the mixture was stirred for 18 h. The resulting mixture was cooled to 0 °C and 1 N HCl (5 mL) was added and the mixture was stirred for 30 min. To the resulting solution, CH_2Cl_2 (5 mL) was added and the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to give the crude acid **12** as a clear oil that was sufficiently pure for use in the subsequent transformation. The crude acid **12** was dissolved in CH_2Cl_2 (2.6 mL), cooled to 0 °C, and boron-trifluoride etherate (BF_3•OEt_2) (34 μL, 0.33 mmol) was added. After 1 h, saturated aqueous $NaHCO_3$ (4 mL) was added and the layers were separated and the aqueous phase was washed with additional CH_2Cl_2 (2 × 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (30→50% EtOAc/hexanes) gave **11** (49 mg, 66% from **20**) as a colorless oil: R_f 0.43 (50% hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.73 (d, *J* = 2.4 Hz, 1H), 4.30 (s, 1H), 3.00 (m, 2H), 2.67 (d, *J* = 18.9 Hz, 1H), 2.22 (s, 3H), 1.68 (app t, *J* = 3.1 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.2, 168.4, 101.2, 90.7, 52.2, 36.5, 35.4, 30.6, 29.9, 27.2; IR (thin film)

1748, 1719 cm^{-1}; HRMS (ESI) calculated for $C_{12}H_{19}O_4$ (M+H) 227.1283, observed 227.1290; $[\alpha]_D^{25}$ –32.0°, $[\alpha]_{577}^{25}$ –32.0°, $[\alpha]_{546}^{25}$ –37.0°, $[\alpha]_{435}^{25}$ –59.5°, $[\alpha]_{405}^{25}$ –69.4° (*c* = 0.4, $CHCl_3$).



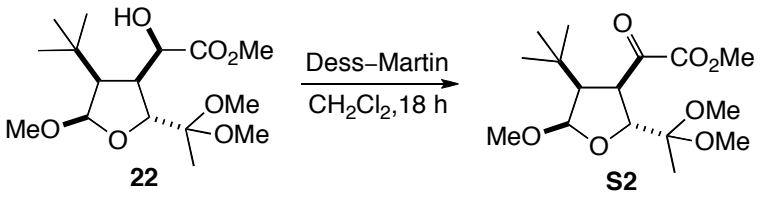
(1*S*,5*R*,6*R*,8*R*)-8-*tert*-butyl-3-oxo-2,7-dioxabicyclo[3.2.1]octan-6-yl ethanoate (8): To a solution of methyl ketone **11** (85 mg, 0.38 mmol) in CH_2Cl_2 (4.7 mL) at 0 °C was added urea•H_2O_2 complex (354 mg, 3.76 mmol) and TFAA (210 μL, 1.50 mmol).[8] The mixture was stirred for 30 min and then allowed to warm to rt and stirred for 30 min. To the resulting mixture, saturated aqueous $NaHCO_3$ (10 mL) and CH_2Cl_2 (5 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (50% hexanes/EtOAc) gave **8** (62 mg, 68%) as a clear oil: R_f 0.27 (66% hexanes/Et_2O); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.11 (s, 1H), 5.67 (d, *J* = 2.3 Hz, 1H), 2.95 (dd, *J* = 19.7, 6.0 Hz, 1H), 2.69 (d, *J* = 19.7 Hz, 1H), 2.64 (m, 1H), 2.22 (m, 1H), 2.08 (s, 3H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.7, 167.7, 101.6, 100.8, 49.8, 37.8, 33.6, 30.8, 30.0, 21.3; IR (thin film) 1750 cm^{-1}; HRMS (ESI) calculated for $C_{12}H_{18}O_5Na$ (M+Na): 265.1052, observed: 265.1042; $[\alpha]_D^{27}$ –92.6°, $[\alpha]_{577}^{27}$ –97.1°, $[\alpha]_{546}^{28}$ –109°, $[\alpha]_{435}^{28}$ –185°, $[\alpha]_{405}^{27}$ –220° (*c* = 1.0, $CHCl_3$).



(*R*)-methyl 2-((2*R*,3*S*,4*R*,5*R*)-4-*tert*-butyl-2-(1,1-dimethoxyethyl)-5-methoxytetrahydrofuran-3-yl)-2-hydroxyethanoate (22): A solution of **β-20** (80 mg, 0.25 mmol) in THF (2 mL) was cooled to 0 °C and a solution of 1 M NaHMDS in THF (0.52 mmol, 520 μL) was added. After 1 h, the solution was cooled to – 78 °C and a solution of (+/-)-trans-2-(phenylsulfonyl)-3-

8. Cooper MS, Heaney H, Newbold, AJ, Sanderson WR (1990) Oxidation reactions using urea-hydrogen peroxide; a safe alternative to anhydrous hydrogen peroxide *Synlett* 533-535.

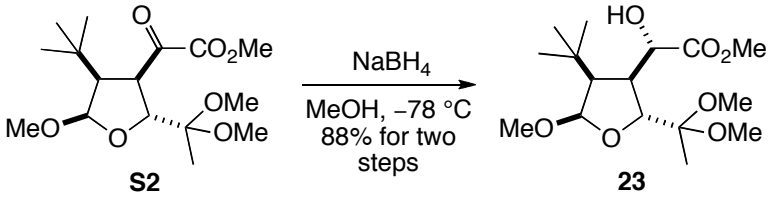
phenyloxaziridine (**21**)[9] (101 mg, 0.39 mmol) in THF (300 μL) was added. After 2 h, saturated aqueous $NaHCO_3$ (5 mL) and CH_2Cl_2 (5 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (5 × 3 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel chromatography (30% EtOAc/hexanes) afforded a solid mixture. Trituration of this mixture to remove byproducts derived from **21** by stirring in 20% EtOAc/hexanes, filtration, and the concentration of the filtrate afforded **22** as a white solid (69 mg, 79%): R_f 0.15 (40% EtOAc/hexanes); m.p. 109-110 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.19 (s, 1H), 4.96 (d, *J* = 3.9 Hz, 1 H), 4.64 (s, 1H), 4.41 (d, *J* = 3.4 Hz, 1H), 3.72 (s, 3H), 3.44 (s, 3H), 3.22 (s, 3H), 3.16 (s, 3H), 2.68 (dd, *J* = 9.8, 3.4 Hz, 1 H), 2.02 (dd, *J* = 3.9, 9.8 Hz, 1H), 1.17 (s, 3H), 1.10 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.1, 104.6, 101.8, 76.6, 68.9, 56.3, 54.6, 52.1, 48.8, 48.6, 44.0, 31.6, 29.9, 16.4; IR (thin film) 3352, 1759, 1372, 1063 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{30}O_7$ (M+Na) 357.1889, observed 357.1884; $[\alpha]_D^{25}$ –34.9; $[\alpha]_{577}^{25}$ –36.9; $[\alpha]_{546}^{25}$ –42.0; $[\alpha]_{435}^{25}$ –67.2; $[\alpha]_{405}^{25}$ –78.4 (*c* = 0.4, CH_2Cl_2).



Methyl 2-((2*R*,3*R*,4*R*,5*R*)-4-*tert*-butyl-2-(1,1-dimethoxyethyl)-5-methoxytetrahydrofuran-3-yl)-2-oxoethanoate (S2): A solution of **22** (69 mg, 0.21 mmol) was dissolved in CH_2Cl_2 (2.1 mL) and $NaHCO_3$ (84 mg, 1.0 mmol) and Dess–Martin periodinane (140 mg, 0.33 mmol) were added and the mixture allowed to stir for 18 h at 25 °C. To the resulting mixture, 10% aqueous sodium thiosulfate (3 mL) and saturated sodium bicarbonate (3 mL) were added and the mixture was stirred for 20 min. The mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated to afford material of sufficient purity for use in the next reaction. For characterisation purposes the residue could be further purified by silica gel chromatography (10→30% EtOAc/hexanes) to afford **22** as a colorless oil: R_f 0.49 (40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.95 (d, *J* = 3.9 Hz, 1H), 4.72 (d, *J* = 5.2 Hz, 1H), 4.01 (dd, *J* = 10.9, 5.2 Hz, 1H), 3.86 (s, 3H), 3.36 (s, 3H), 3.23 (s, 3H), 3.13 (s, 3H), 2.22 (dd, *J* = 3.9, 10.9, 1H), 1.24 (s, 3H), 0.97 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.4, 162.6, 106.4, 101.8, 82.3, 61.5, 54.6, 53.3, 48.9, 48.8, 46.4, 32.2, 30.2, 16.6; IR (thin film) 2954, 1731, 1369, 1265, 1145 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{28}O_7$ (M+Na) 355.1733, observed

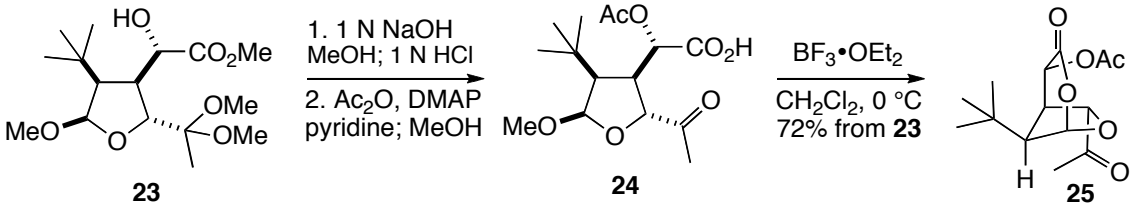
9. Vishwakarma LC, Stringer OD, Davis FA (1988) (+/-)-Trans-2-(Phenylsulfonyl)-3-Phenyloxaziridine. *Org. Synth.* 66:203-210.

355.1729; $[\alpha]_{D}^{25}$ –49.8; $[\alpha]_{577}^{25}$ –61.0; $[\alpha]_{546}^{25}$ –66.4; $[\alpha]_{435}^{25}$ –104.3; $[\alpha]_{405}^{25}$ –136.1 (*c* = 0.15, CH_2Cl_2).



S2 **23**

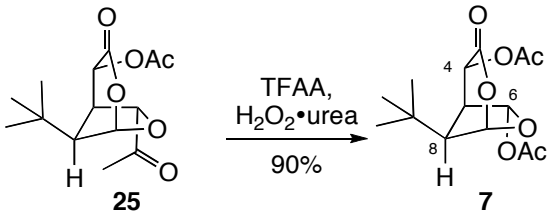
Methyl 2-((2*R*,3*S*,4*R*,5*R*)-4-*tert*-butyl-2-(1,1-dimethoxyethyl)-5-methoxytetrahydrofuran-3-yl)-2-hydroxyethanoate (23): A solution of crude **S2** from above in MeOH (2.1 mL) was cooled to –78 °C and $NaBH_4$ (23 mg, 0.62 mmol) was added. After 30 min, saturated aqueous $NaHCO_3$ (3 mL) and CH_2Cl_2 (3 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel chromatography (20→30% EtOAc/hexanes) afforded **23** as a colorless oil (61 mg, 88% from **22**): R_f 0.41 (40% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.95 (d, *J* = 3.5 Hz, 1H), 4.68 (d, *J* = 6.5 Hz, 1H), 4.33 (d, *J* = 4.1 Hz, 1H), 4.30 (dd, *J* = 6.5, 3.1 Hz, 1H), 3.74 (s, 3H), 3.40 (s, 3H), 3.27 (s, 3H), 3.24 (s, 3H), 2.85 (m, 1H), 1.93 (dd, *J* = 9.5, 3.5 Hz, 1H), 1.24 (s, 3H), 1.01 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.3, 105.1, 102.4, 81.5, 72.7, 58.1, 54.4, 52.2, 48.9, 48.6, 43.7, 31.2, 30.0, 16.3; IR (thin film) 2951, 1732, 1211, 1179 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{30}O_7$ (M+Na) 357.1889 observed 357.1881; $[\alpha]_{D}^{25}$ –31.3; $[\alpha]_{577}^{25}$ –33.6; $[\alpha]_{546}^{25}$ –33.8; $[\alpha]_{435}^{25}$ –53.1; $[\alpha]_{405}^{25}$ –54.3 (*c* = 0.2, CH_2Cl_2).



23 **24** **25**

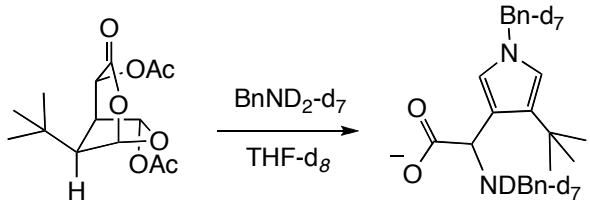
8-*tert*-Butyl-6-ethanoyl-3-oxo-2,7-dioxabicyclo[3.2.1]octan-4-yl ethanoate (25): To a solution of **23** (61 mg, 0.18 mmol) in MeOH (1 mL), 1N aqueous NaOH (300 μL) was added. The mixture was stirred for 18 h, cooled to 0 °C, and 1N HCl (5.0 mL) was added and the stirred mixture was allowed to warm to rt after 5 min. After 1 h, CH_2Cl_2 (3 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (10 × 2 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated to yield the crude acid that was used without further purification. Diagnostic data for crude acid: ^{1}H NMR (600 MHz, C_6D_6) δ

4.68 (d, *J* = 3.6 Hz, 1H), 4.19 (m, 2H), 3.35 (m, 1H), 2.96 (s, 3H), 1.80 (s, 3H), 1.75 (dd, *J* = 7.8, 4.0 Hz, 1H), 0.91 (s, 9H), 0.88 (t, 1H, *J* = 6.0 Hz); MS (ESI) calculated for $C_{13}H_{22}O_6$ (M–H) 273.14, observed 273.13. The crude acid was dissolved in CH_2Cl_2 (2 mL) and pyridine (134 μL, 1.44 mmol), Ac_2O (101 μL, 1.08 mmol), and DMAP (1.18 mg, 0.009 mmol) were added. After 3 h at 25 °C, MeOH (2 mL) was added and after 20 min and the solution was concentrated. The residue was dissolved in heptane (1 mL) and the solution was concentrated. This was repeated with heptane (2 × 1 mL) and benzene (2 × 1 mL) to yield the crude acetylated acid **24** that was used without further purification. Diagnostic data for crude **24**: ^{1}H NMR (600 MHz, C_6D_6) δ 5.78 (d, *J* = 6.8 Hz, 1H), 5.03 (s, 1H), 4.88 (d, *J* = 3.9 Hz, 1H), 3.24 (m, 1H), 3.13 (s, 3H), 1.96 (s, 3H), 1.74 (s, 3H), 1.23 (m, 1H), 1.02 (s, 9H); MS (ESI) calculated for $C_{15}H_{24}O_7$ (M–H) 315.14, observed 315.13. The crude acid was dissolved in CH_2Cl_2 (2 mL) and cooled to 0 °C and BF_3•OEt_2 (25 μL, 0.042 mmol) in CH_2Cl_2 (100 μL) was added. After 10 min, saturated aqueous $NaHCO_3$ (2 mL) and CH_2Cl_2 (2 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 2 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel chromatography (30% EtOAc/hexanes) **25** as a white solid (36.0 mg, 72%): R_f 0.34 (40% EtOAc/hexanes); m.p. 98–99 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.92 (d, *J* = 4.9 Hz, 1H), 5.71 (d, *J* = 1.8 Hz, 1H), 4.72 (s, 1H), 3.15 (apt t, *J* = 4.5 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 3H), 1.83 (m, 1H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.4, 169.3, 166.5, 101.6, 83.6, 66.9, 54.8, 41.4, 30.8, 30.3, 27.2, 20.9; IR (thin film) 2958, 1767, 1372, 1223 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{20}O_6$ (M+Na) 307.1158, observed 307.1154; $[\alpha]_D^{24}$ –110.3; $[\alpha]_{577}^{24}$ –112.1; $[\alpha]_{546}^{24}$ –126.4; $[\alpha]_{435}^{24}$ –211.3; $[\alpha]_{405}^{24}$ –249.3 (*c* = 0.3, CH_2Cl_2).



***tert*-Bu-MacE (7):** To a solution of methyl ketone **25** (36 mg, 0.13 mmol) in CH_2Cl_2 (1.3 mL) at 0 °C was added urea•H_2O_2 complex (97 mg, 1.04 mmol) followed by TFAA (72 μL, 0.51 mmol) in CH_2Cl_2 (200 μL). The mixture was stirred for 30 min and then allowed to warm to rt and stirred for 30 min. To the resulting mixture, saturated aqueous $NaHCO_3$ (2 mL) and CH_2Cl_2 (2 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated.

Purification of the residue by silica gel chromatography (30% hexanes/EtOAc) gave **7** (35 mg, 90%) as a white solid: R_f 0.34 (40% EtOAc/ hexanes); m.p. 103–105 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.48 (s, 1H), 5.88 (d, *J* = 5.3 Hz, 1H), 5.67 (d, *J* = 1.8 Hz, 1H), 2.85 (apt. t, *J* = 4.3 Hz, 1H), 2.43 (apt. t, *J* = 3.2 Hz, 1H), 2.19 (s, 3H), 2.08 (s, 3H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6 (2 carbons), 165.9, 101.1, 96.4, 66.2, 52.7, 44.4, 30.8, 30.3, 21.3, 20.8; IR (thin film) 2916, 1749, 1370, 1214 cm; HRMS (ESI) calculated for $C_{14}H_{20}O_7$ (M+Na) 323.1107, observed 323.1112; $[\alpha]_D^{25}$ –82.1; $[\alpha]_{577}^{25}$ –85.3; $[\alpha]_{546}^{25}$ –95.3; $[\alpha]_{435}^{25}$ –149.7; $[\alpha]_{405}^{25}$ –179.1 (*c* = 0.15, CH_2Cl_2). X-ray quality crystals were obtained via vapour diffusion by dissolving **7** in benzene and exposing to hexanes vapour.



7 **26**

In situ observation of 26: To a solution of **7** (3 mg, 0.010 mmol) in THF-d_8 (400 μL) in a 5 mm NMR tube, $C_6D_5CD_2ND_2$[10] (10 μL) was added. The solution was allowed to stand for 36 h and compound **26**[11], $AcO^-ND_3Bn\text{-}d_7^+$, and Bn-d_7N(H,D)Ac were observed as the major new products. Key spectral data for **26**: ^{1}H NMR (THF-d_8, 500 MHz) δ 6.77 (bs, 1H) 6.37 (bs, 1H), 4.48 (s, 1H), 1.25 (s, 9H); ^{13}C NMR (THF-d_8, 125 MHz) δ 177.3, 133.4, 122.0, 121.6, 117.5, 60.0, 53.0, 52.1, 32.4, 32.2; HRMS (ESI) calculated for $C_{24}H_{14}D_{14}N_2O_2$ (M+Na) 389.2946, observed 389.2951. Key spectral data for $AcO^-ND_3Bn\text{-}d_7^+$: ^{1}H NMR (THF-d_8, 500 MHz) δ 1.86; ^{13}C NMR (THF-d_8, 125 MHz) δ 172.8, 21.0. Key spectral data for Bn-d_7NHAc: ^{1}H NMR (THF-d_8, 500 MHz) δ 1.85; ^{13}C (THF-d_8, 500 MHz) δ 169.35, 22.86. Key spectral data for Bn-d_7NDAc: ^{1}H NMR δ 1.85; ^{13}C (THF-d_8, 500 MHz) δ 169.27, 22.81.[12]

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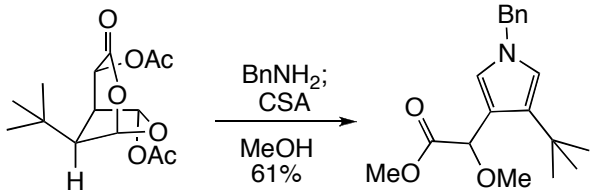
10. Prepared from $C_6D_5CD_2NH_2$ (Sabine L, Grehl M (1994) Diastereoselective Synthesis of α-Hydroxy and α-Aminoindolizidines and Quinolizidines. Evidence for a Novel Cyclization/ Hydride Migration Mechanism in the $TiCl_4$-Induced Reaction of Prolinal Benzylamines by Deuterium Labeling Studies. *Chem. Ber.* 127:2023-2034). A solution of $BnNH_2\text{-}d_7$ (0.2 mL) in D_2O (0.5 mL) was stirred for 5 min and CH_2Cl_2 (0.5 mL) was added and the layers were separated. The organic layer was concentrated and D_2O (0.5 mL) was added. After 5 min, CH_2Cl_2 (0.5 mL) was added and the layers were separated. The organic layer was dried (Na_2SO_4) and concentrated to yield clean $C_6D_5CD_2ND_2$ by H_1-NMR.

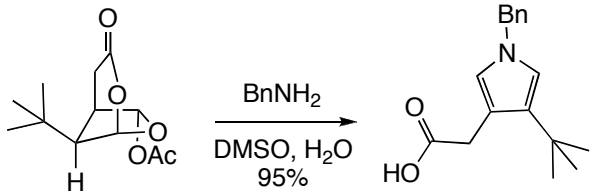
11. See page 18 for full NMR assignment.

12. Bn-d_7NHAc and Bn-d_7NDAc were prepared independently.



7 27

Methyl 2-(1-benzyl-4-*tert*-butyl-1*H*-pyrrol-3-yl)-2-methoxyethanoate (27): $BnNH_2$ (3.5 μL, 0.03 mmol) was added to a solution of **7** (4 mg, 0.013 mmol) in MeOH (0.65 mL). After 18 h at rt CSA (12 mg, 0.052 mmol) was added and the solution was stirred for an additional 18 h. To the resulting solution, saturated aqueous $NaHCO_3$ (2 mL) and CH_2Cl_2 (2 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel chromatography (10→20% hexanes/EtOAc) gave **27**[13] (2.5 mg, 61%) as a clear oil: R_f 0.24 (20% EtOAc/ hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.28 (m, 3H), 7.10 (apt. d, 1H, J = 7.0 Hz), 6.69 (d, 1H, J = 2.5 Hz), 6.34 (d, 1H, J = 2.5 Hz), 5.05 (s, 1H), 4.90 (s, 2H), 3.71 (s, 3H), 3.37 (s, 3H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.9, 137.7, 133.2, 128.9, 127.9, 127.6, 122.3, 117.8, 116.8, 76.3, 57.2, 53.7, 52.2, 31.9, 31.5; IR (thin film) 2916, 1747, 1099 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{25}NO_3$ (M+Na) 338.1732, observed 338.1730.



8 28

2-(1-benzyl-4-*tert*-butyl-pyrrol-3-yl)ethanoic acid (28): To a solution of **8** (4 mg, 0.016 mmol) in H_2O (0.72 mL) and DMSO (80 μL), $BnNH_2$ (9 μL, 0.082 mmol) was added. The

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Bn-d_7NHAc: To a solution of Bn-d_7NH_2 (50 mg, 0.43 mmol) in CH_2Cl_2 (0.9 mL), TEA (136 μL, 0.47 mmol) and Ac_2O (43 μL, 0.47 mmol) were added. The solution was allowed to stand for 18 h and then 1 N HCl (1 mL) was added and the layers were separated. The organic layer was extracted with 1 N NaOH (1 mL) and the organic layer was dried (Na_2SO_4) and concentrated to yield Bn-d_7NHAc.

Bn-d_7NDAc: Bn-d_7NHAc (25 mg) in $CDCl_3$ (1 mL) was stirred with 40% NaOD in D_2O for 5 min. The layers were separated and the organic layer was dried (Na_2SO_4) and concentrated to afford Bn-d_7NDAc.

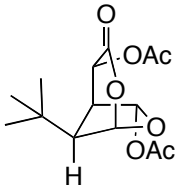
Clean ^{13}C spectra (in THF-d_8) were obtained for each compound and then the solutions were mixed and a mixed ^{13}C spectra was obtained in which doubled signals were observed with chemical shifts within 0.1 ppm of those listed above. This result demonstrates that the ^{13}C doubling observed with d_7-benzyl acetamide is consistent with an isotopic shift reflecting the presence of a mixture of deutero and protio d_7-benzyl acetamide species.

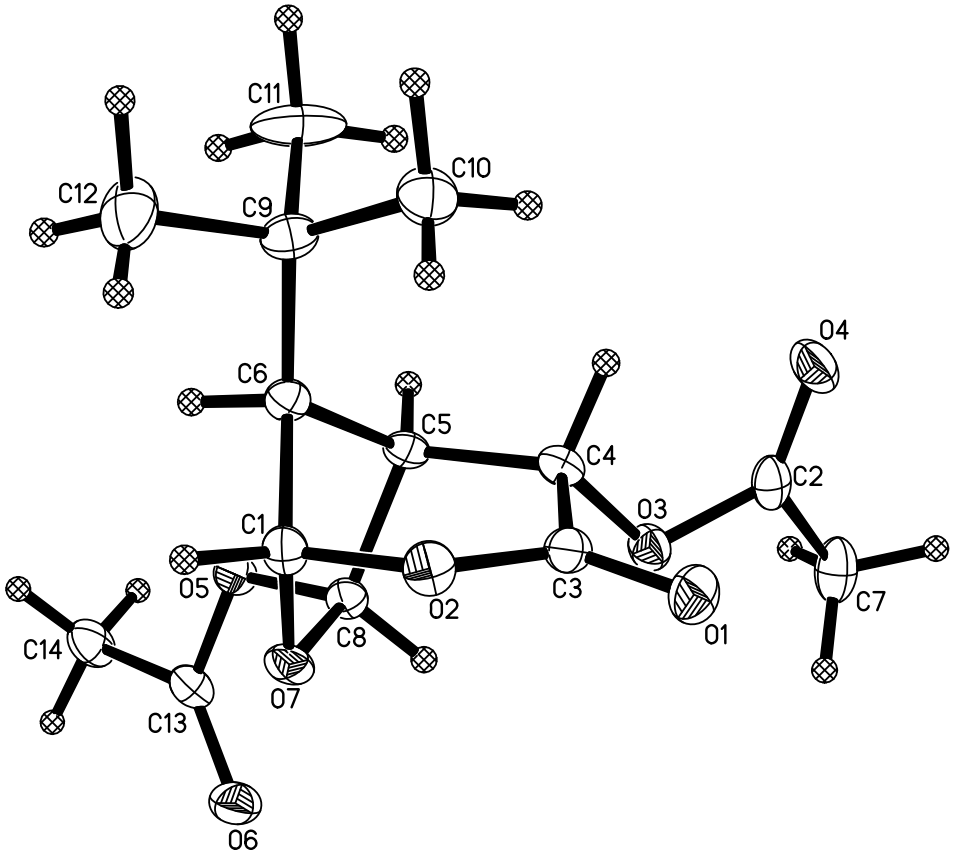
13. See page 18 for full NMR assignment.

solution was stirred at rt for 36 h. To the resulting solution, saturated aqueous NH_3Cl (2 mL) and CH_2Cl_2 (2 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel chromatography (50→100% hexanes/ EtOAc) gave **28**[14] (4.2 mg, 95%) as a clear oil: R_f 0.28 (20% EtOAc/ hexanes); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.95 (bs, 1H), 7.32 (m, 2H), 7.27 (m, 1H), 7.21 (m, 2H), 6.59 (d, 1H, *J* = 2.4 Hz), 6.49 (d, 1H, *J* = 2.4 Hz), 4.94 (s, 2H), 3.40 (s, 2H), 1.18 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 173.7, 138.9, 131.0, 128.5, 127.5, 127.3, 121.4, 116.8, 113.2, 52.1, 32.9, 31.1, 30.9; IR (thin film) 2959, 1708, 1150 cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{21}NO_2$ (M+Na) 294.1470, observed 294.1478.

14. See page 19 for full assignment.

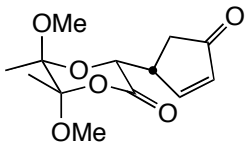
X-ray structure of 7[15]

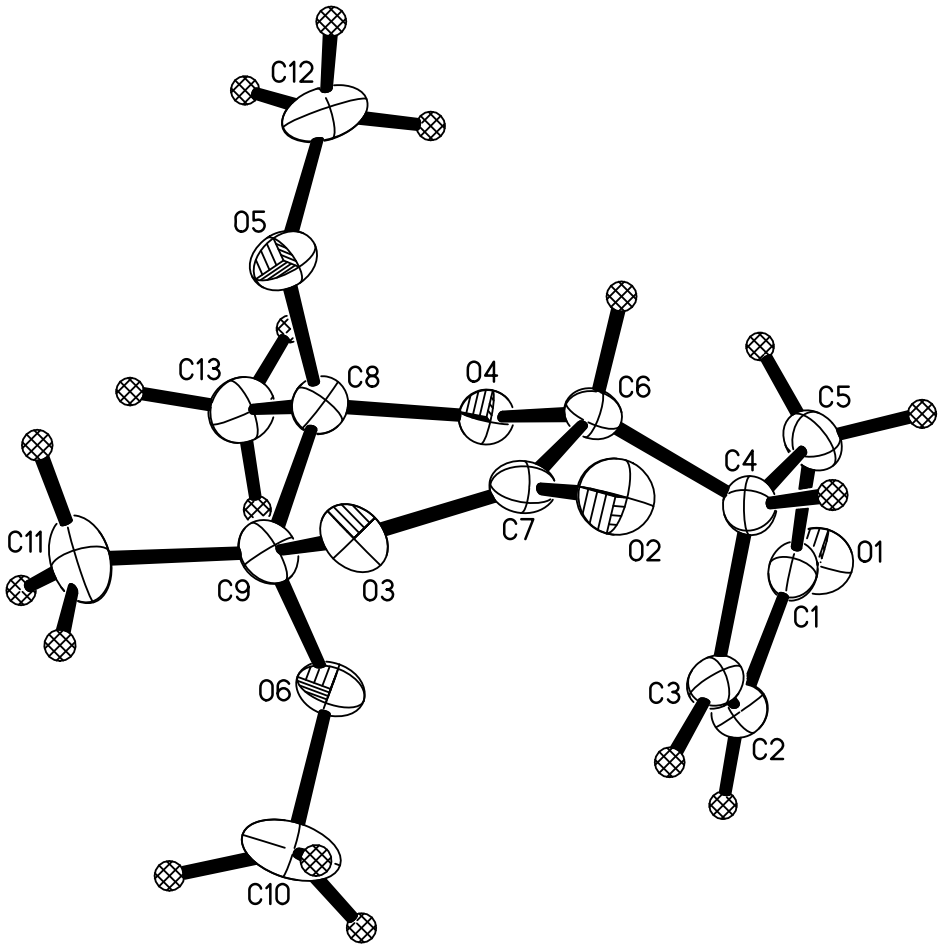




[15] The thermal ellipsoid plot is shown at the 50% probability level.

X-ray structure of 17[16]

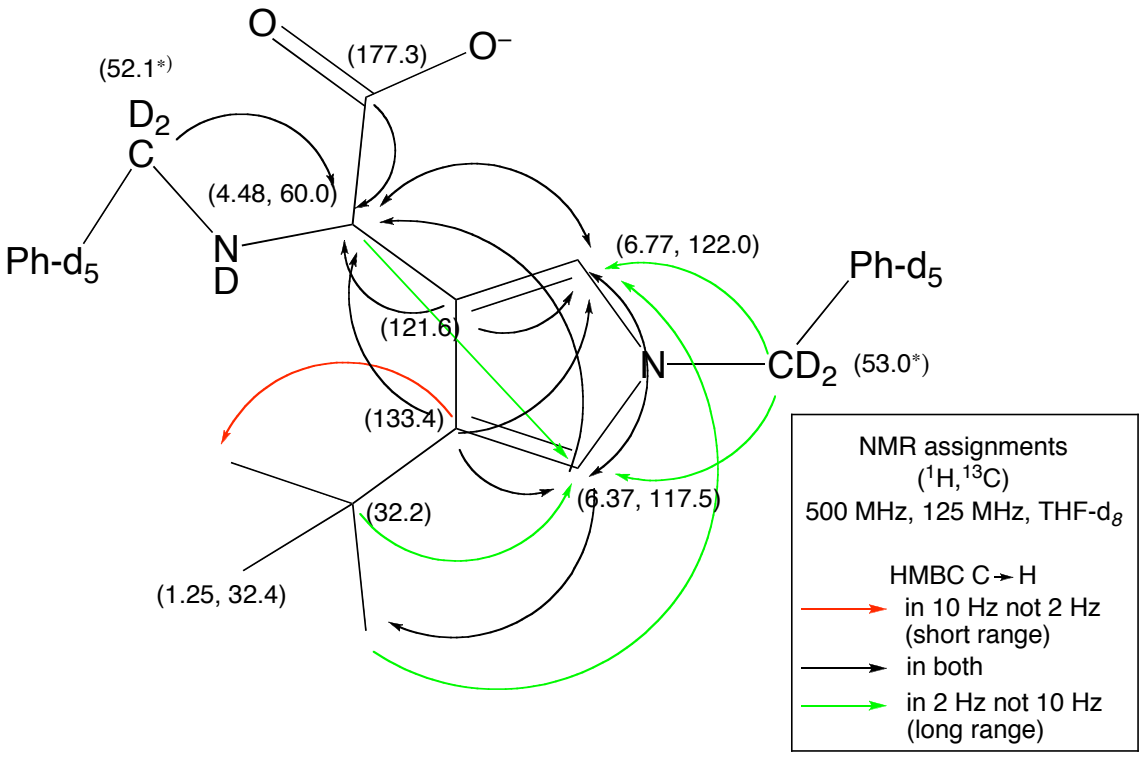




[16] The thermal ellipsoid plot is shown at the 50% probability level.

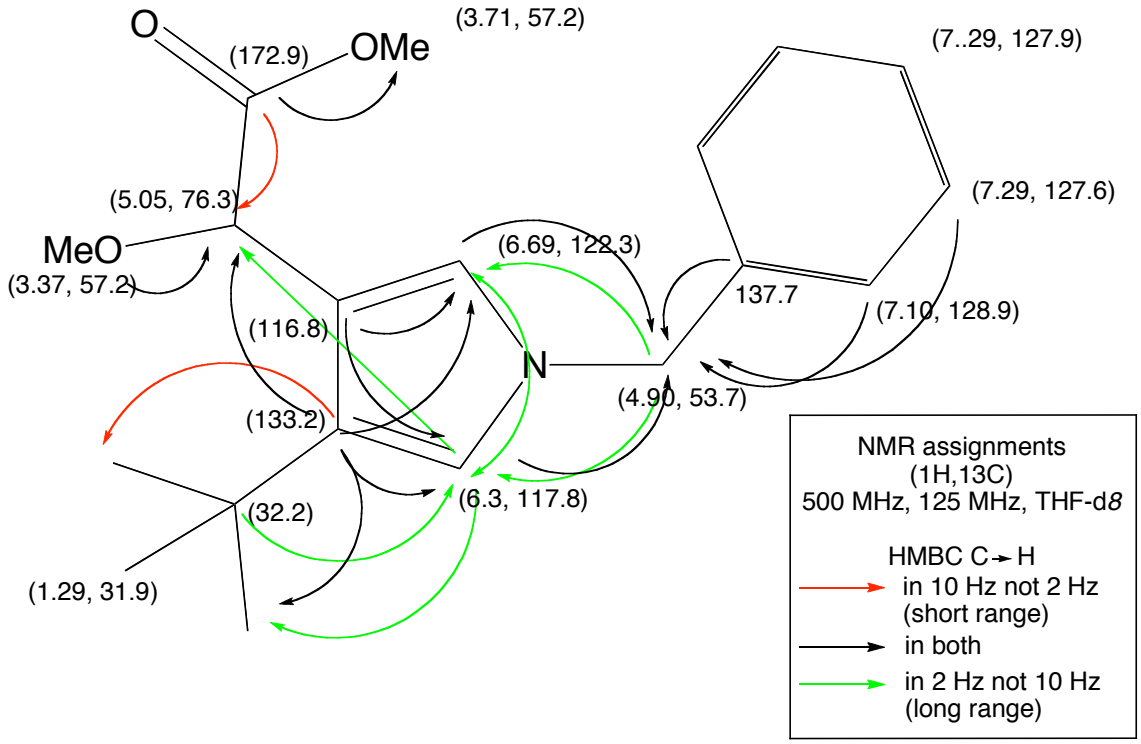
NMR Assignment of 26, 27, and 28

Assignment of **26**

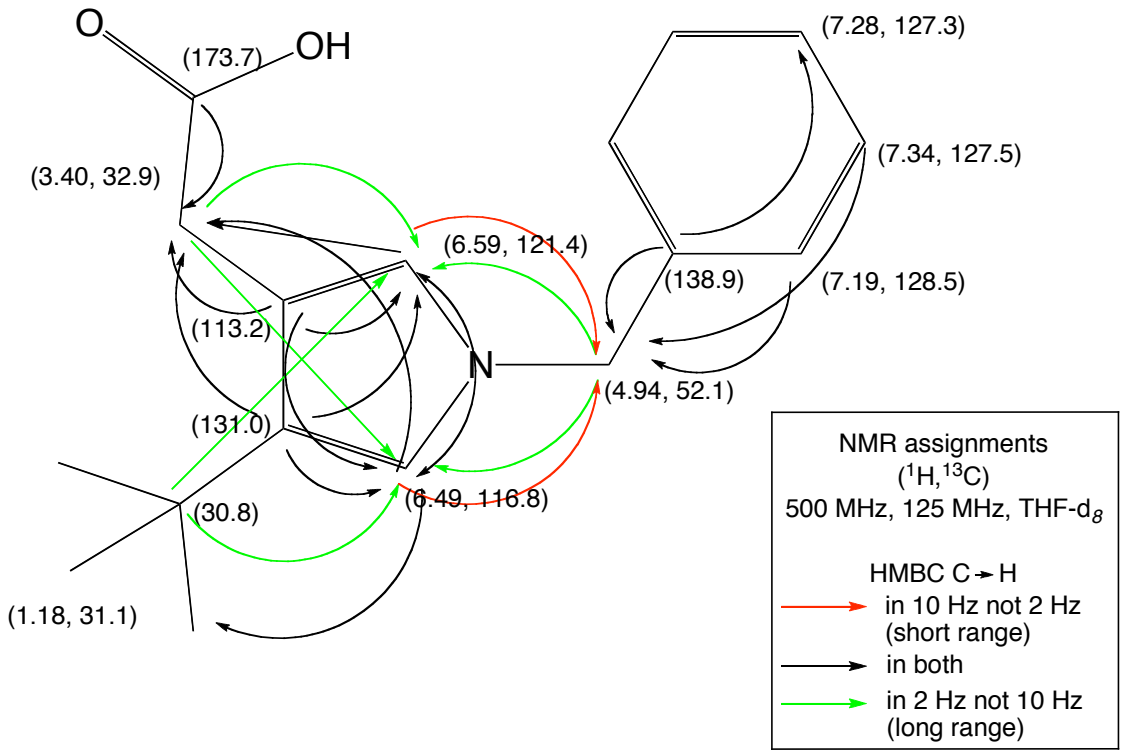


* CD_2 not observed in C_{13} spectra because of C-D splitting, only observed in HMBC

Assignment of **27**



Assignment of **28**



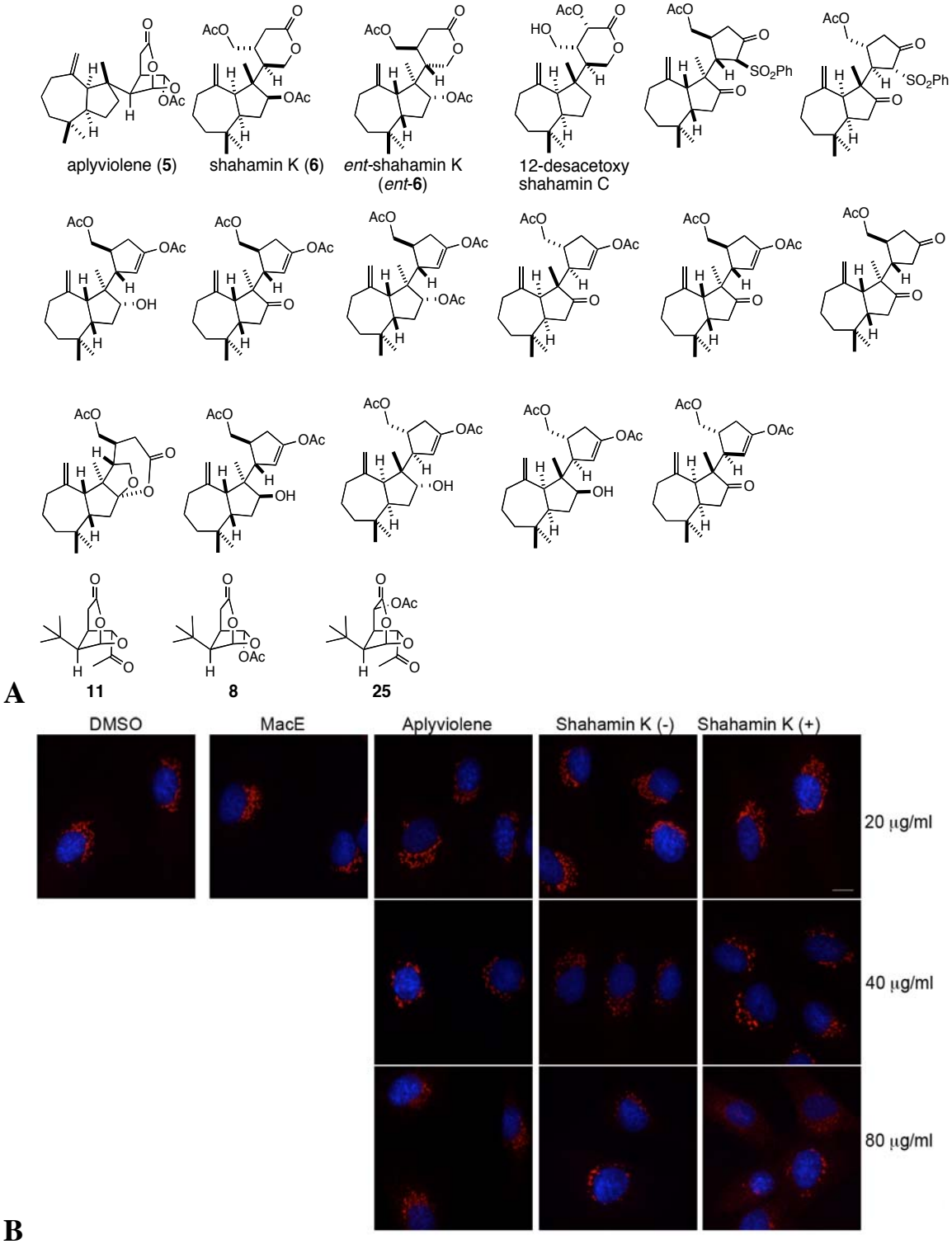


Fig. S1. Structurally related compounds screened for macfarlandin E-type Golgi activity
NRK cells on coverslips were treated with compounds (A) for 60 min at 37 °C, fixed and processed for immunofluorescence analysis with an antibody to the Golgi protein, giantin, and the DNA dye Hoechst 33342. Representative images for aplyviolene (**5**), *ent*-(-)-shahamin K (***ent*-6**), and (+)-shahamin K (**6**), is shown (B)**.**

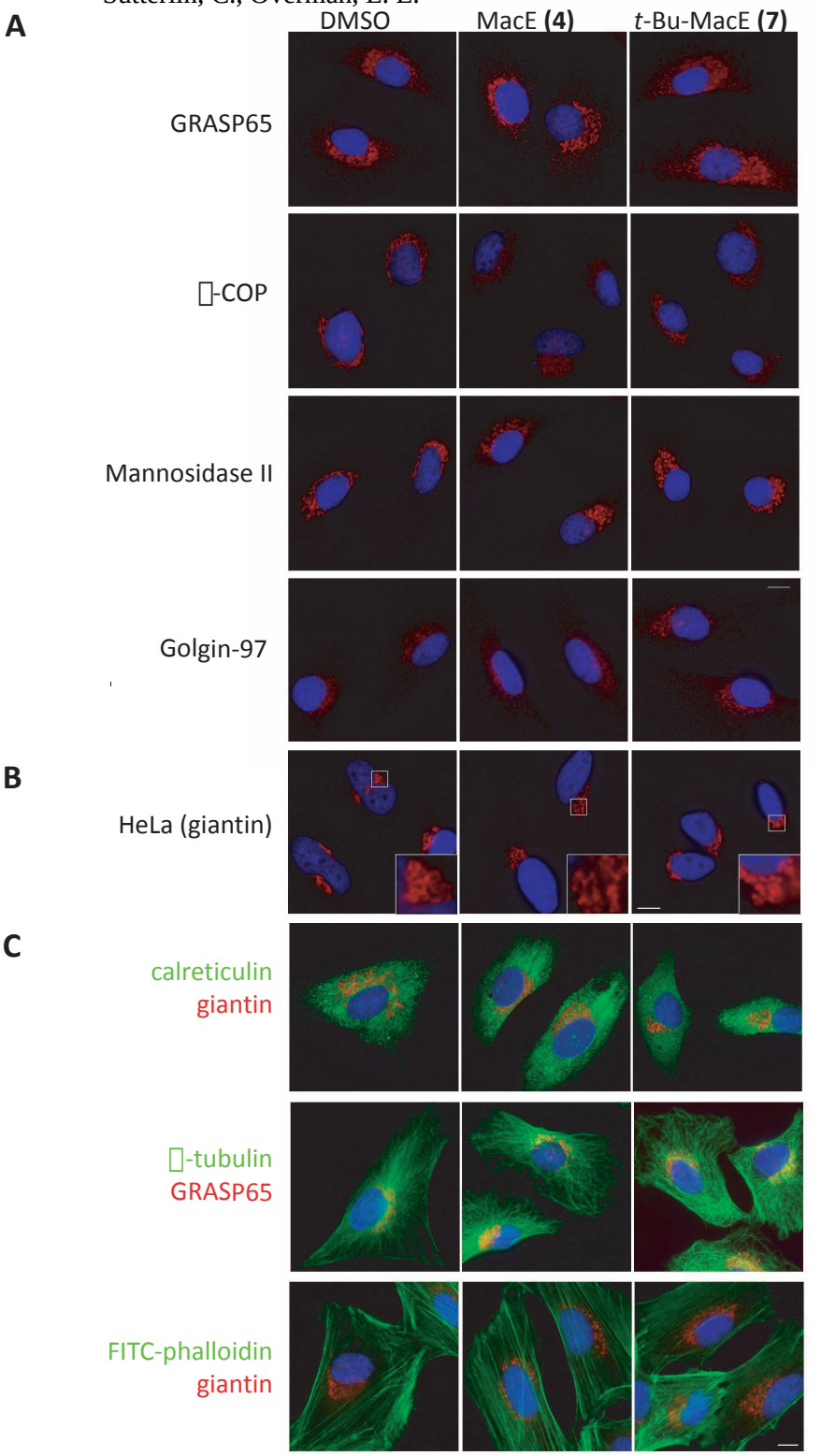


Fig. S2: The effect of MacE and *t*-Bu-MacE on other Golgi markers, HeLa cells, and other cellular structures
(A) NRK cells on coverslips were treated with DMSO, 20 g/mL MacE and 40 g/mL *t*-Bu-MacE for 60 min, fixed and analyzed by immunofluorescence using antibodies to GRASP65, -COP, mannosidase-II, and golgin-97 and the DNA dye Hoechst 33342. (B) HeLa cells on coverslips were treated with DMSO, 20 g/mL MacE and 40 g/mL *t*-Bu-MacE for 60 min, fixed and analyzed by immunofluorescence using an antibody to giantin and the DNA dye Hoechst 33342. (C) NRK cells on coverslips were treated with DMSO, 20 g/mL MacE and 40 g/mL *t*-Bu-MacE for 60 min. The cells were fixed and processed for immunofluorescence with antibodies to calreticulin and giantin to visualize the ER or the Golgi, respectively (top panel). Cells were also stained with antibodies to ±-tubulin and the Golgi protein, GRASP65, to reveal the organization of the microtubule cytoskeleton and the Golgi (middle panel). FITC-coupled phalloidin was used to visualize the organization of the actin cytoskeleton (bottom panel).

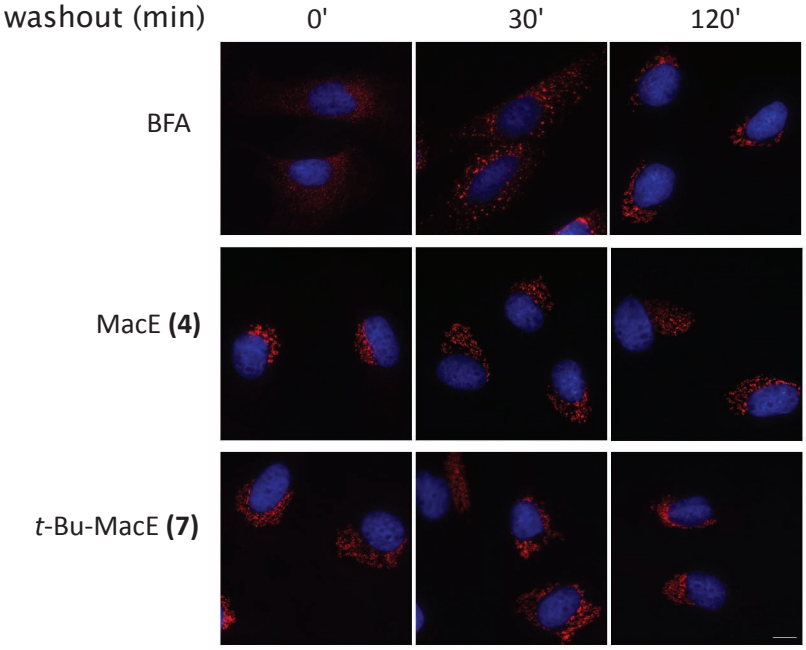


Fig S3. The effect of MacE and *t*-Bu-MacE on the Golgi is irreversible
NRK cells were treated with 3 μg/mL BFA, 20 μg/mL MacE and *t*-Bu-MacE 40 μg/mL, followed by washout of the compounds and incubation in fresh medium for 30 or 120 minutes. Cells were then fixed and stained with an antibody to giantin and the DNA dye Hoechst 33342.

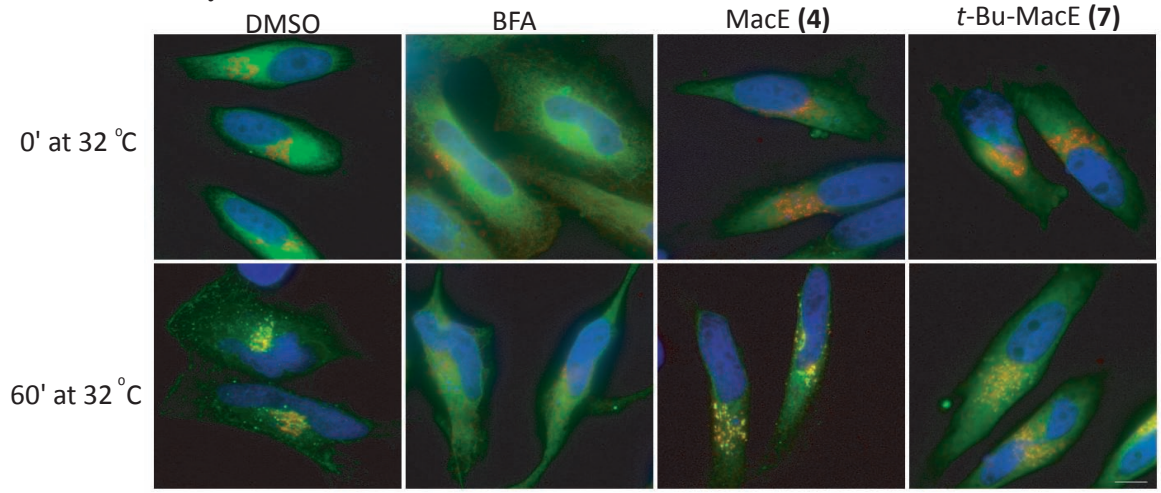


Fig. S4. MacE and *t*-Bu-MacE block transport between the Golgi and the plasma membrane
HeLa cells expressing GFP-tagged VSV-G^{tsO45} were shifted to the non-permissive temperature of 40 °C for 6 hrs, of which the last 1 hr was in the presence of DMSO, 3 μg/mL BFA, 20 μg/mL MacE or 40 μg/mL *t*-Bu-MacE. Cells were then shifted to 32 °C to allow transport from the ER to the Golgi to the plasma membrane. Cells were fixed and stained with an antibody to giantin and the DNA dye Hoechst 33342. Representative images are shown for each experimental condition.

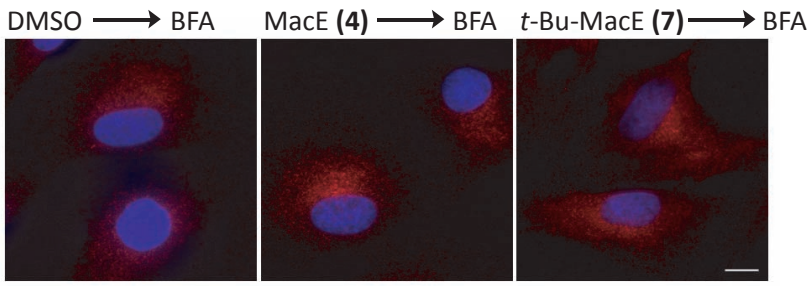
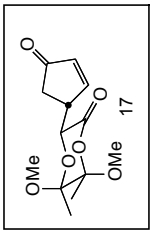


Fig S5. MacE and *t*-Bu-MacE does not block BFA induced relocalization of Golgi proteins to the ER
NRK cells were treated with DMSO, 20 μg/mL MacE and *t*-Bu-MacE 40 μg/mL for 1 hour, followed by replacement with media containing the same agent and 3 μg/mL BFA for 45 minutes. Cells were fixed and stained with an antibody to giantin and the DNA dye Hoechst 33342.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OMe
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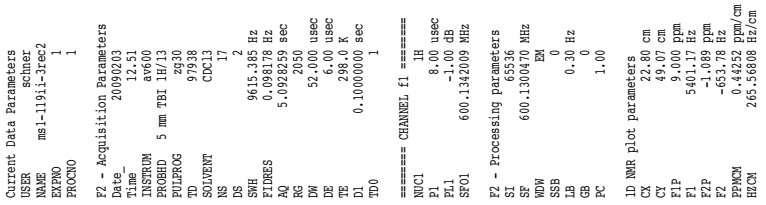
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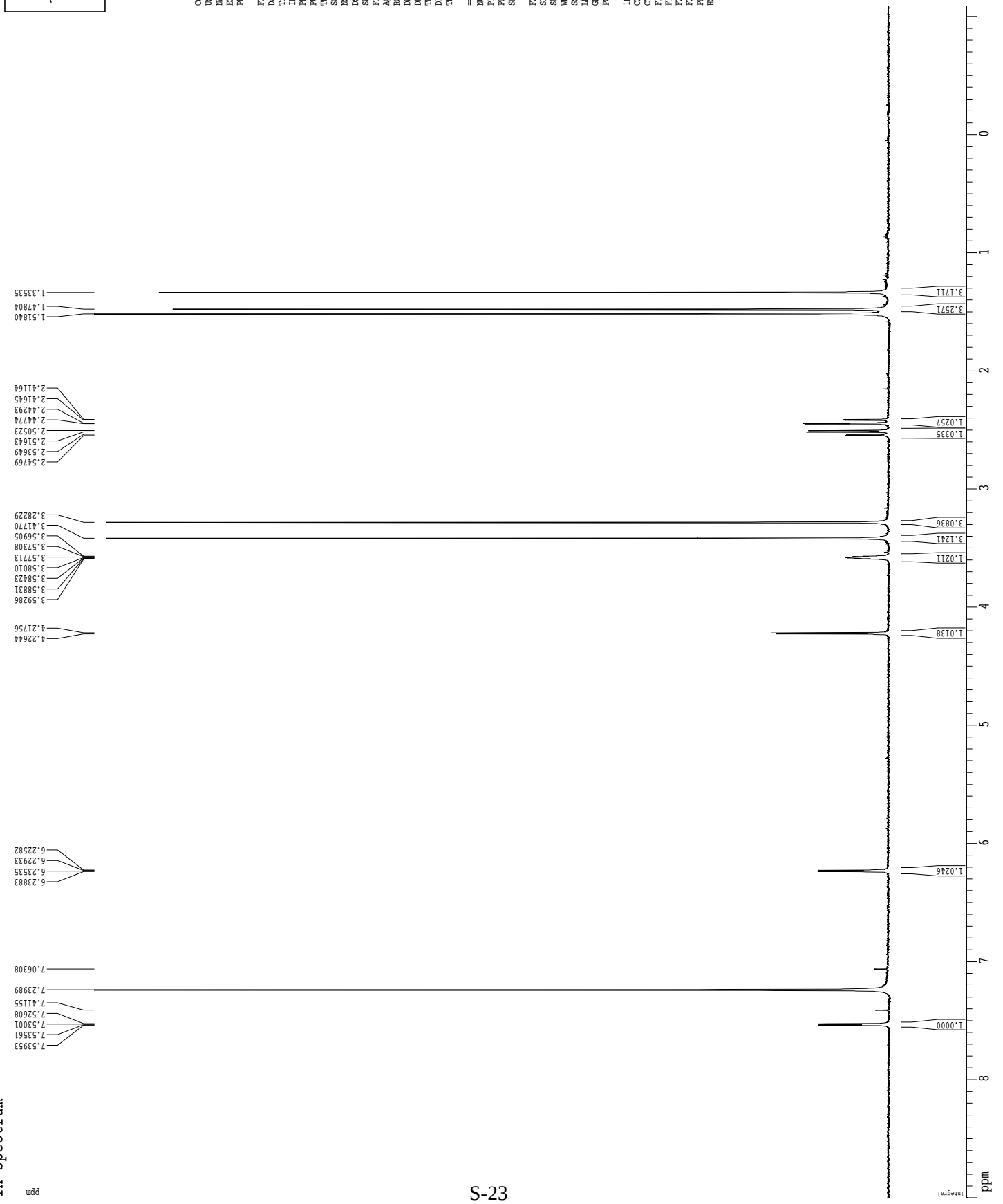
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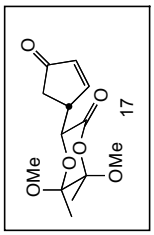
1H spectrum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MCWRK 0.01500000 sec
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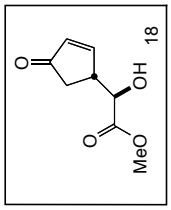
13C spectrum with 1H decoupling
ppm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O
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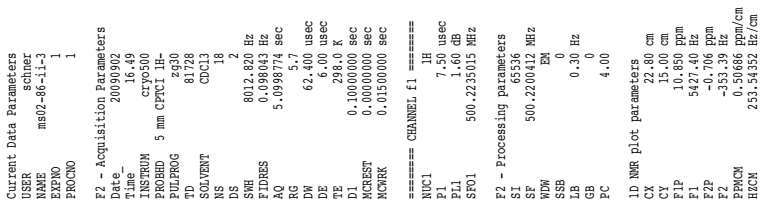
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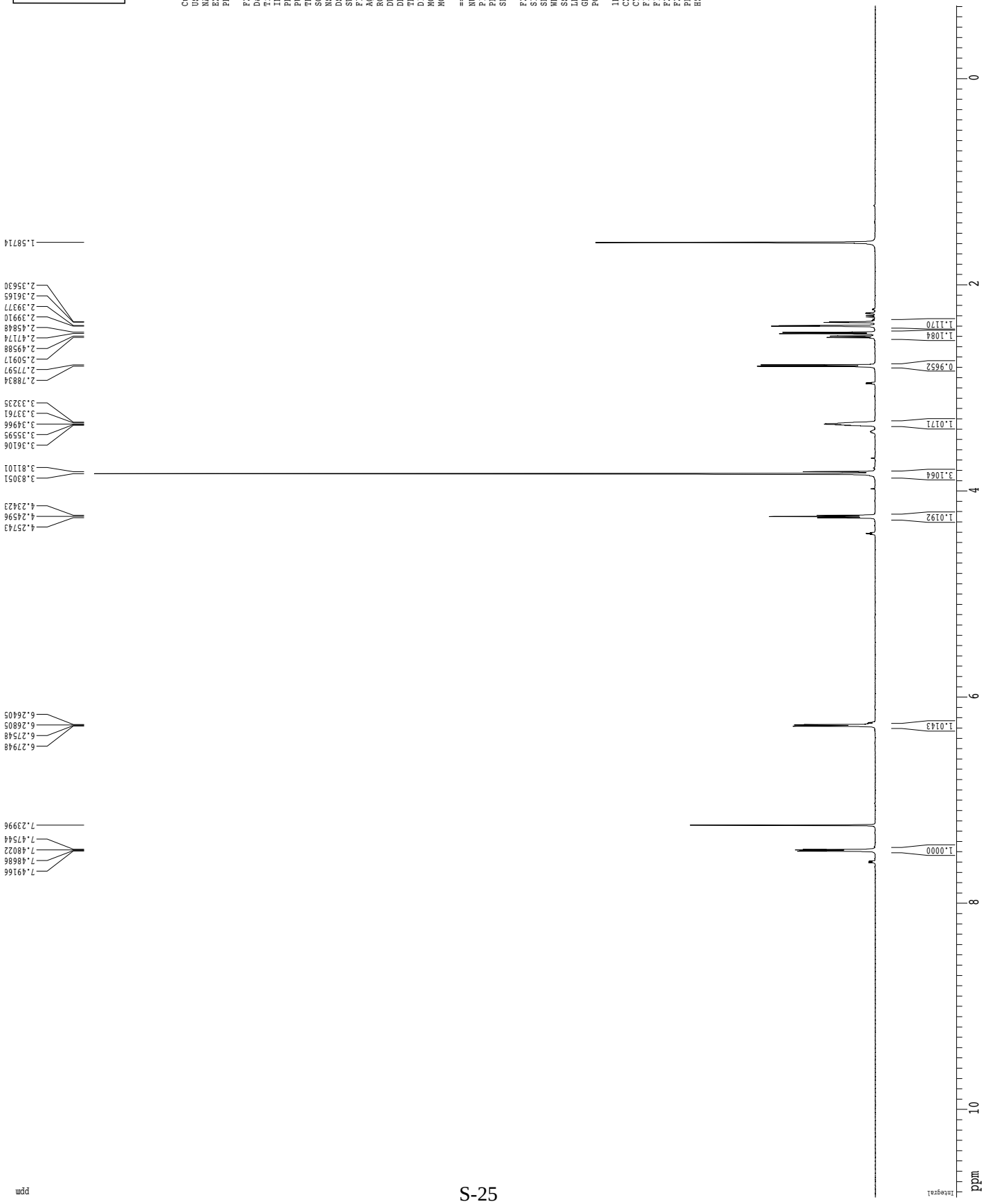
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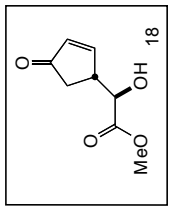
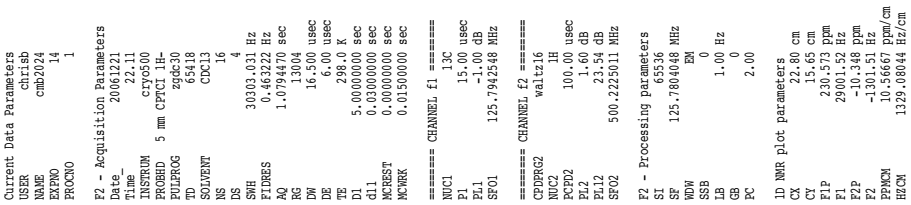
1H spectrum





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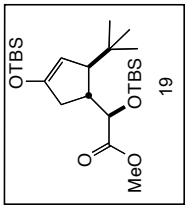
13C spectrum with 1H decoupling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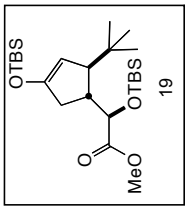
1H spectrum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19

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RG 9195.2
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TE 298.0 K
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MCWRK 0.01500000 sec
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150
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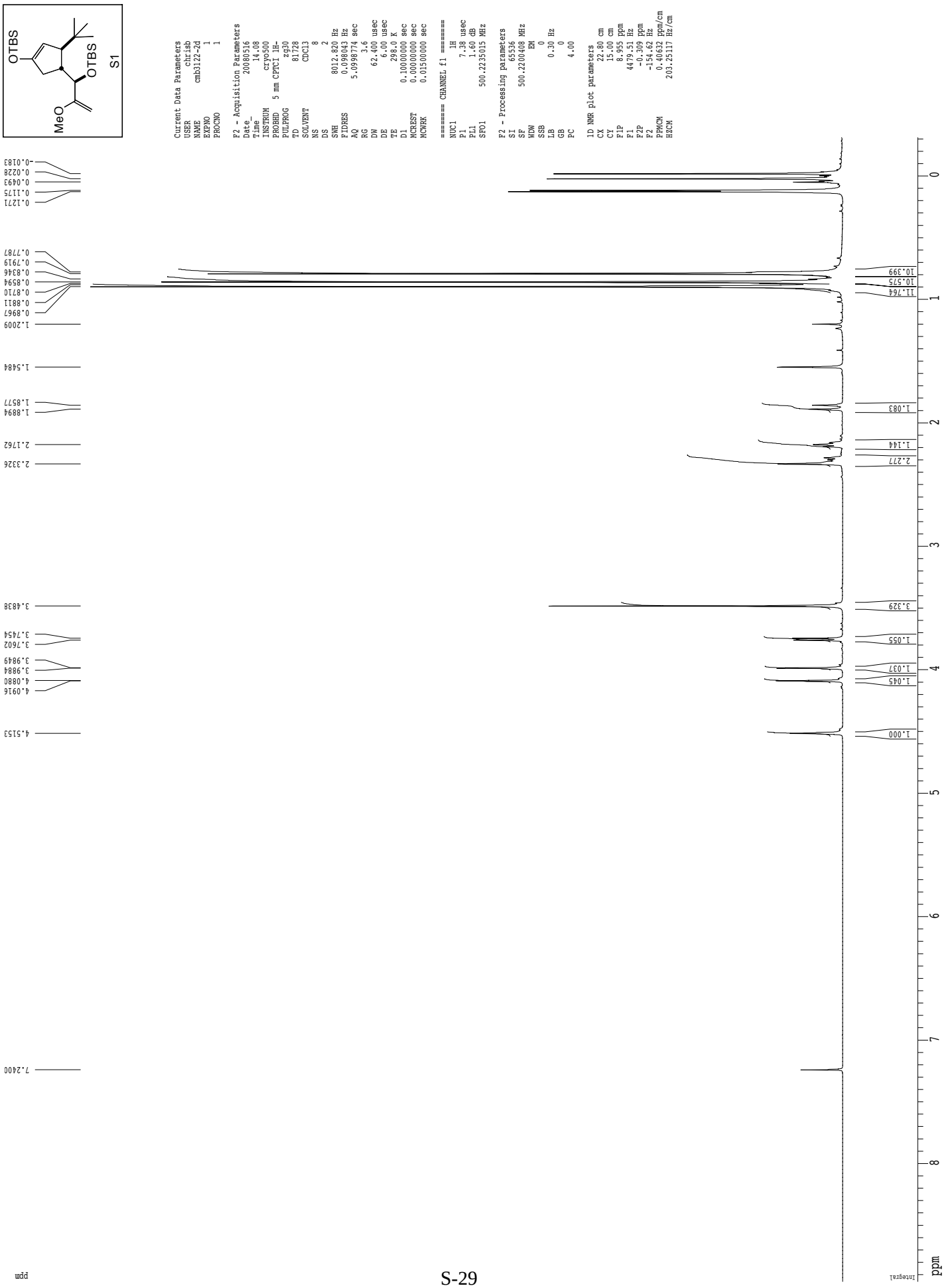
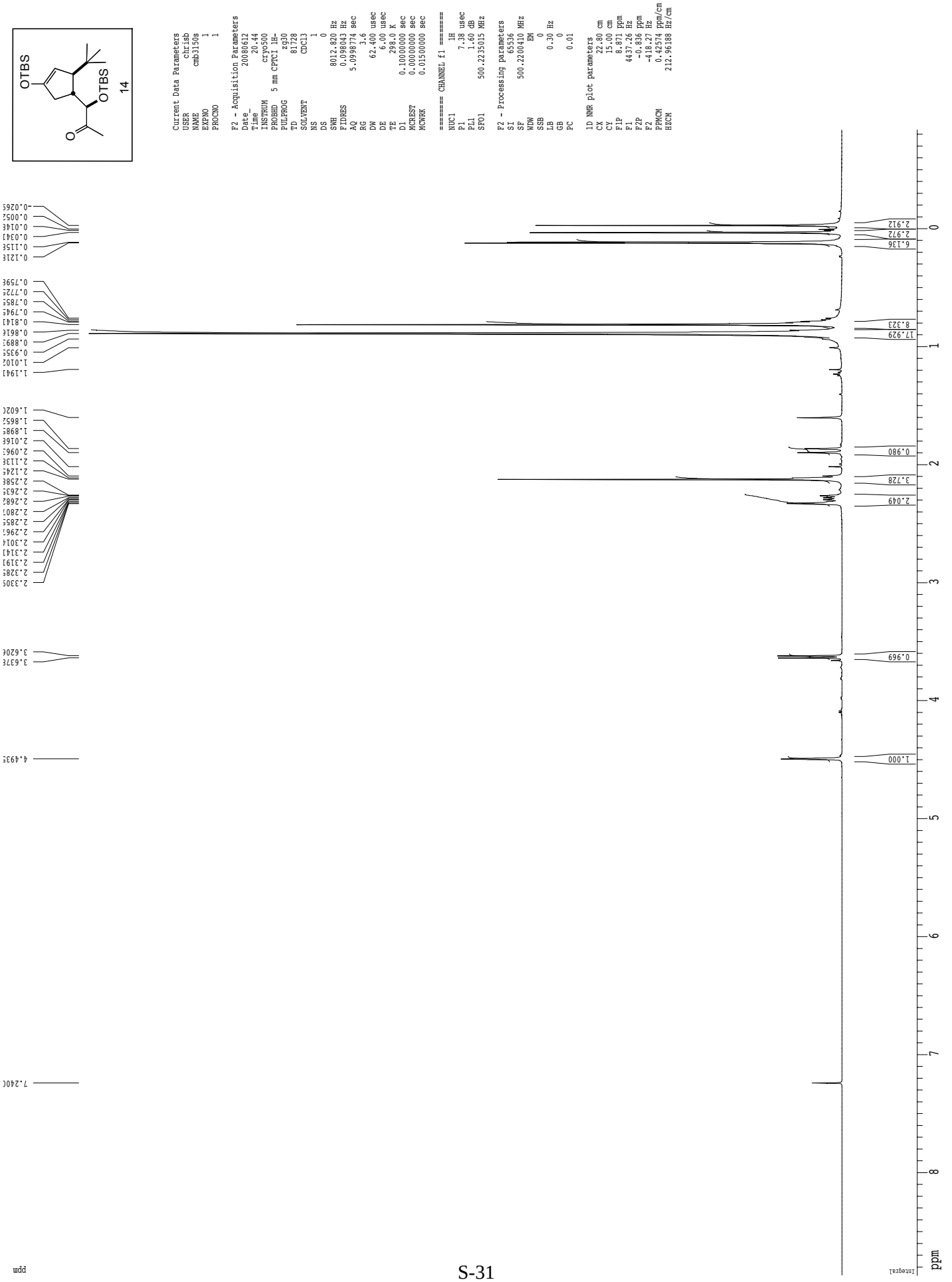
ppm
13C spectrum with 1H decoupling
ppm


OTBS
OTBS
MeO
S1
Current Data Parameters
USER chris5b
NAME cmb3122-2d
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080516
Time 14.08
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 3.6
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200408 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.955 ppm
F1 4479.51 Hz
F2P -0.309 ppm
F2 -154.62 Hz
PPMCM 0.40632 ppm/cm
HZCM 203.25117 Hz/cm
-0.0183
0.0228
0.0493
0.1175
0.1271
0.7787
0.7919
0.8346
0.8594
0.8710
0.8811
0.8967
1.2009
1.5484
1.8577
1.8894
2.1762
2.3326
3.4838
3.7454
3.7602
3.9849
3.9884
4.0880
4.0916
4.5153
7.2400
10.399
10.575
11.764
1.083
1.144
2.277
3.329
1.055
1.037
1.045
1.000
1H spectrum
ppm
Integral

13C spectrum with 1H decoupling


OTBS
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14
Current Data Parameters
USER chris5b
NAME cmb03150s
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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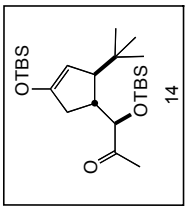
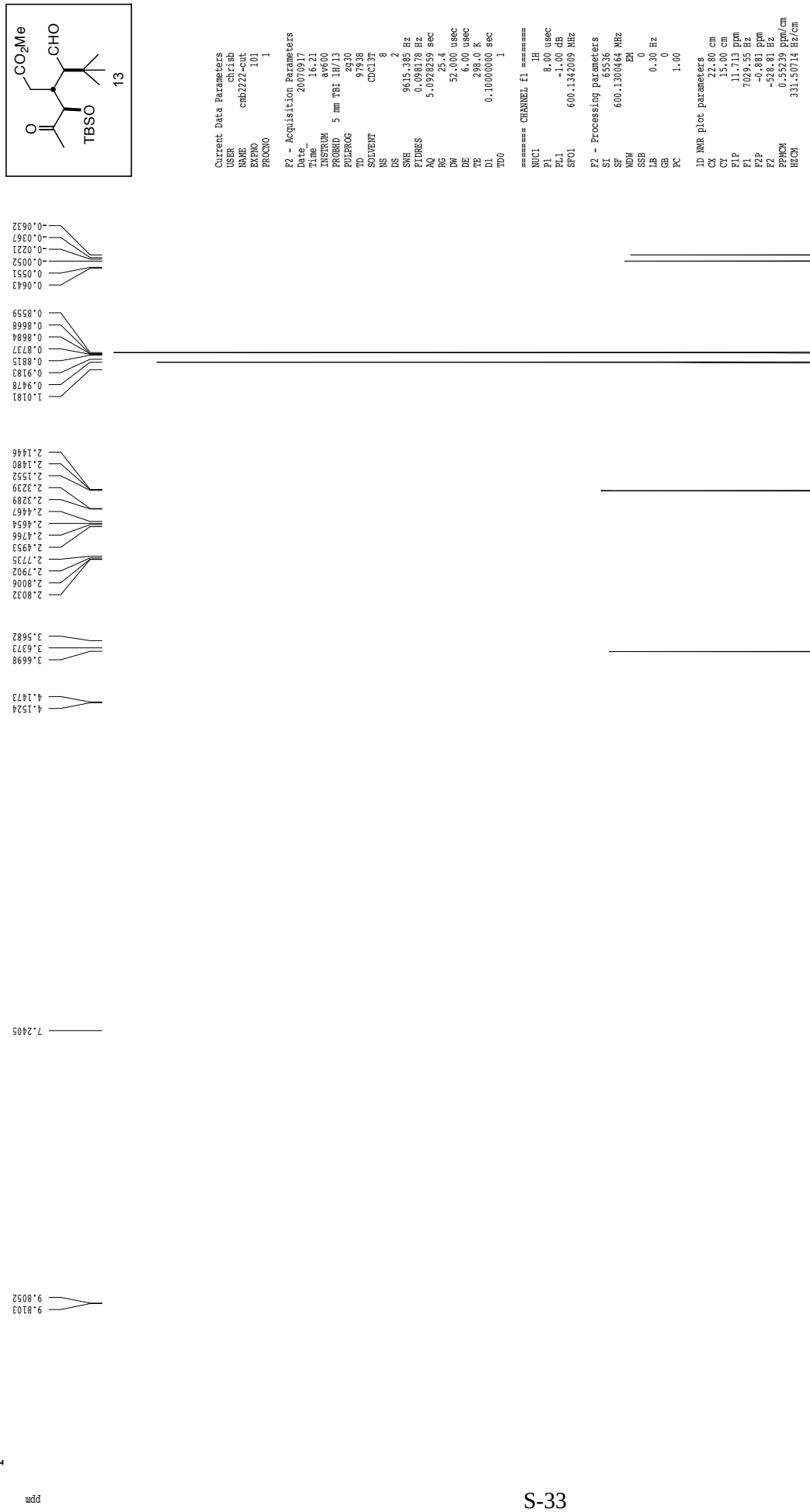
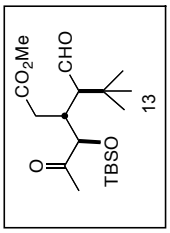
Time 20.44
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 1
DS 0
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 3.6
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.38 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200410 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.01
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.871 ppm
F1 4437.26 Hz
F2P -0.836 ppm
F2 -418.27 Hz
PPMCM 0.42574 ppm/cm
HZCM 212.96188 Hz/cm
0.0265
0.0052
0.0146
0.0343
0.1156
0.1218
0.7596
0.7725
0.7856
0.7945
0.8143
0.8616
0.8883
0.9356
1.0102
1.1943
1.6026
1.8652
1.8986
2.0166
2.0963
2.1136
2.1245
2.2586
2.2639
2.2682
2.2807
2.2856
2.2961
2.3014
2.3143
2.3193
2.3286
2.3305
3.6206
3.6378
4.4935
7.2400
2.912
2.972
6.136
8.323
17.929
0.980
3.728
2.049
0.969
1.000
ppm
Integral

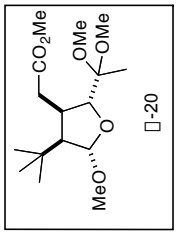

OTBS
OTBS
O
14

Current Data Parameters
USER chrisb
NAME cmb3150s
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080612
Time_ 20.45
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
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
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 13C
P1 14.75 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz
======= CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.80 dB
SFO2 500.2225011 MHz
F2 - Processing parameters
SI 65536
SF 125.7803983 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 230.637 ppm
F1 29009.67 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10681 Hz/cm
-4.78
-4.63
-4.55
-4.31
18.25
18.26
25.25
25.88
26.03
27.42
34.71
35.46
40.28
54.04
76.97
77.23
77.48
82.38
103.13
154.17
211.50
0
50
100
150
200
ppm
13C spectrum with 1H decoupling
ppm

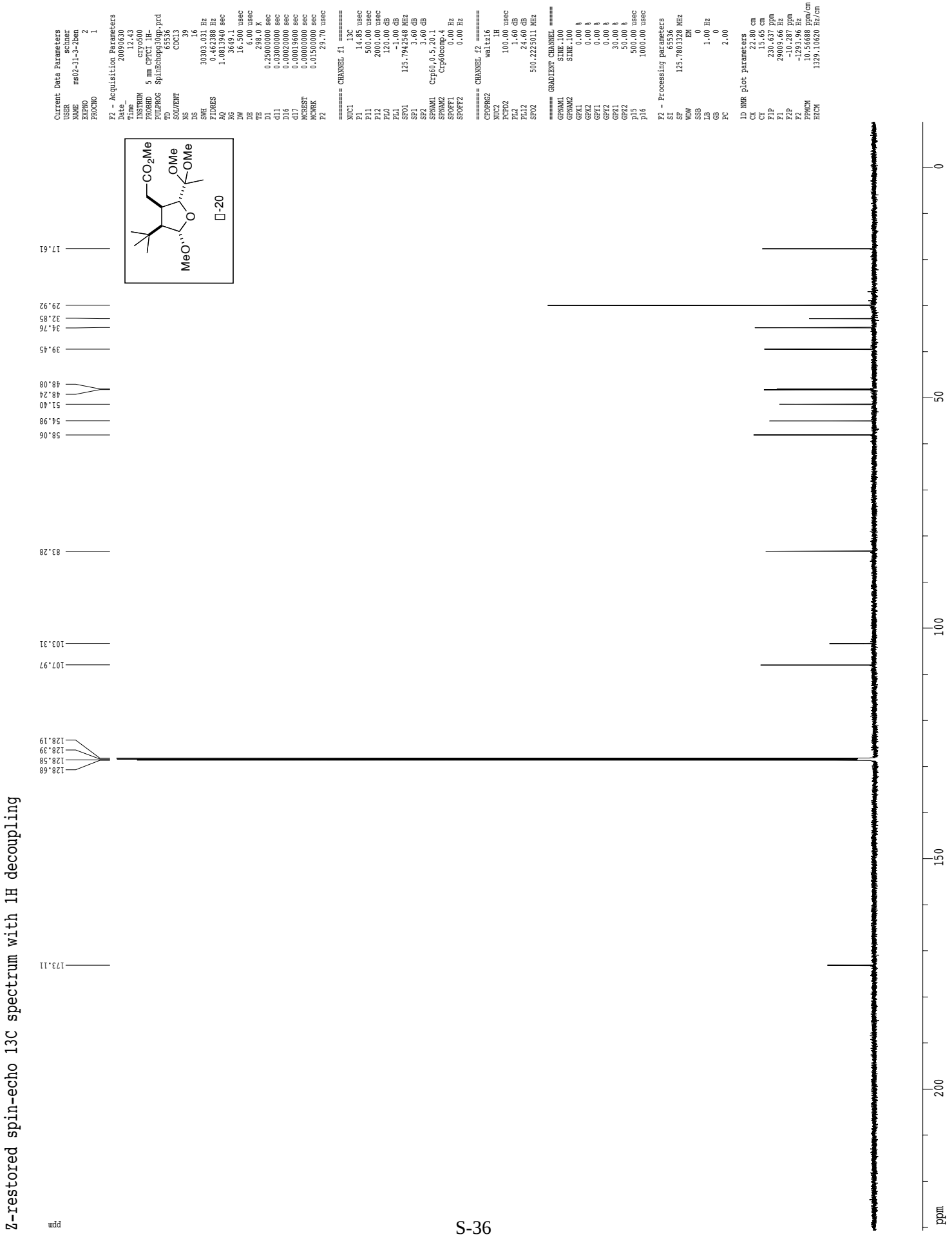

CO2Me
CHO
TBSO
O
13
Current Data Parameters
USER chrisb
NAME cmb2222-cut
EXPNO 101
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070917
Time_ 16.21
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 97938
SOLVENT CDCl3T
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098178 Hz
AQ 5.0928259 sec
RG 25.4
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1300464 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 11.713 ppm
F1 7029.55 Hz
F2P -0.881 ppm
F2 -528.01 Hz
PPMCM 0.55239 ppm/cm
HZCM 331.50714 Hz/cm
0.0632
0.0367
0.0221
0.0052
0.0551
0.0643
0.8559
0.8668
0.8684
0.8737
0.8815
0.9183
0.9478
1.0181
2.1446
2.1480
2.1552
2.3239
2.3289
2.4467
2.4654
2.4766
2.4953
2.7735
2.7902
2.8006
2.8032
3.5682
3.6373
3.6698
4.1473
4.1524
7.2405
9.8052
9.8103
3.091
3.331
10.842
9.830
3.456
1.019
1.068
2.176
3.098
1.038
1.000
1H spectrum
ppm
Integral


CO2Me
CHO
O
TBSO
13

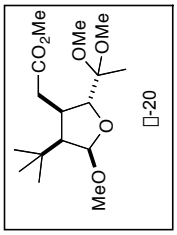
Current Data Parameters
USER chrisb
NAME cmb2222-cut
EXPNO 113
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070917
Time_ 16.24
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zgdc30
TD 65400
SOLVENT CDC13
NS 32
DS 0
SWH 36231.883 Hz
FIDRES 0.554004 Hz
AQ 0.9025700 sec
RG 512
DW 13.800 usec
DE 6.00 usec
TE 298.0 K
D1 5.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 0.00 dB
SFO1 150.9194080 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 18.80 dB
SFO2 600.1330010 MHz
F2 - Processing parameters
SI 65536
SF 150.9027820 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 229.520 ppm
F1 34635.16 Hz
F2P -10.507 ppm
F2 -1585.47 Hz
PPMCM 10.52747 ppm/cm
HZCM 1588.62439 Hz/cm
-5.30
-4.54
18.40
25.91
26.31
28.71
33.66
34.13
37.77
51.99
56.94
77.02
77.23
77.45
80.99
173.70
204.86
209.31
0
25
50
75
100
125
150
175
200
ppm
13C spectrum with 1H decoupling
ppm


CO2Me
OMe
OMe
O
MeO
-20

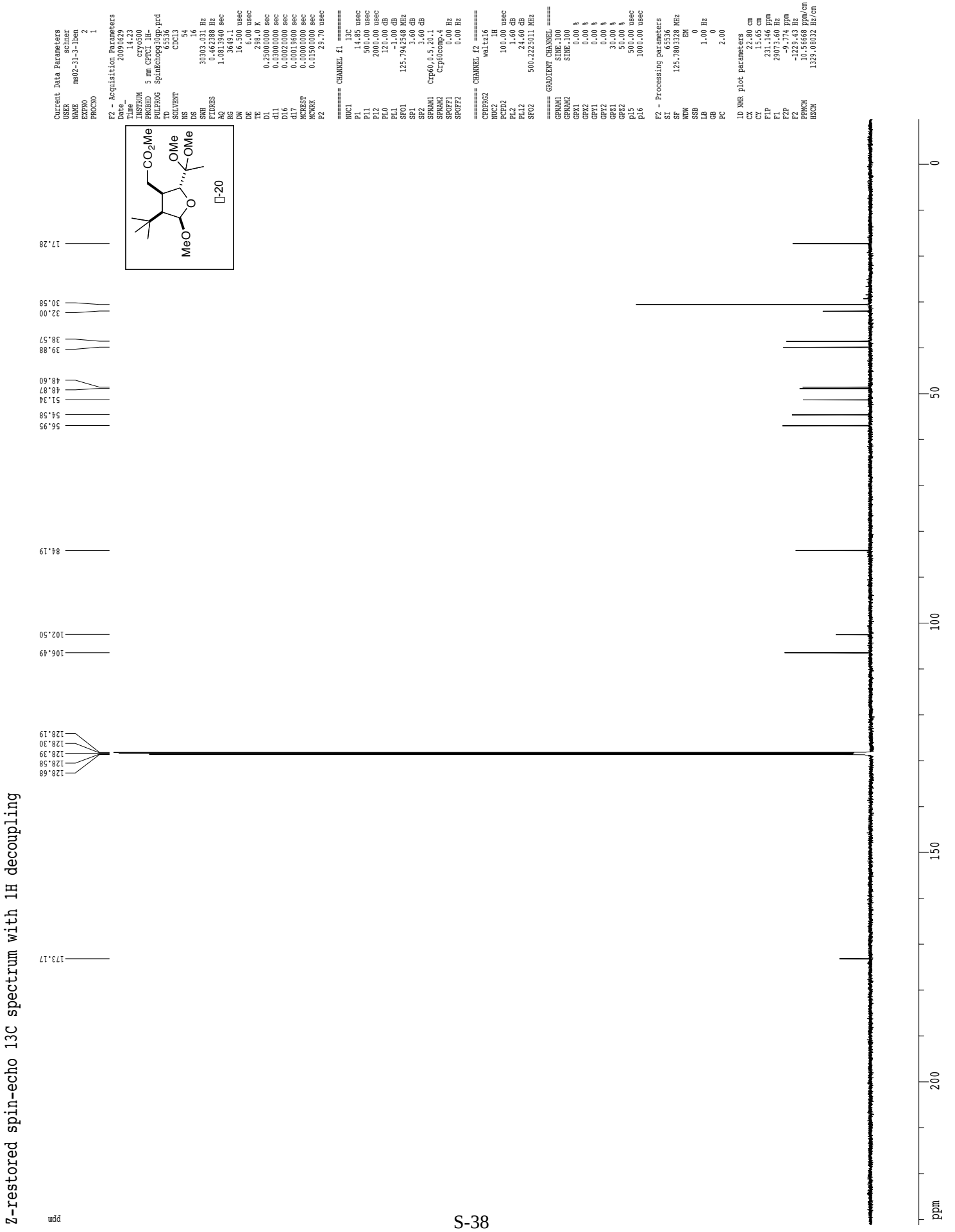
Current Data Parameters
USER schner
NAME ms02-31-3-2ben
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090630
Time_ 12.42
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT C6D6
NS 6
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 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 500.2199998 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 7.502 ppm
F1 3752.88 Hz
F2P -0.850 ppm
F2 -424.94 Hz
PPMCM 0.36632 ppm/cm
HZCM 183.23811 Hz/cm
0.90728
1.47089
2.32460
2.33950
2.67521
2.69295
2.70924
2.72698
2.95323
2.96637
2.98830
3.00022
3.24378
3.26566
3.37934
4.10802
4.12779
4.87690
7.15995
9.0945
2.9996
1.0371
1.0332
4.0274
6.0317
4.0293
1.0143
1.0139
ppm
Integral
1H spectrum

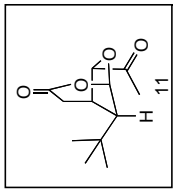


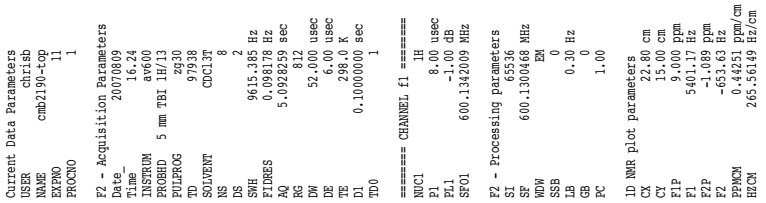
Z-restored spin-echo 13C spectrum with 1H decoupling

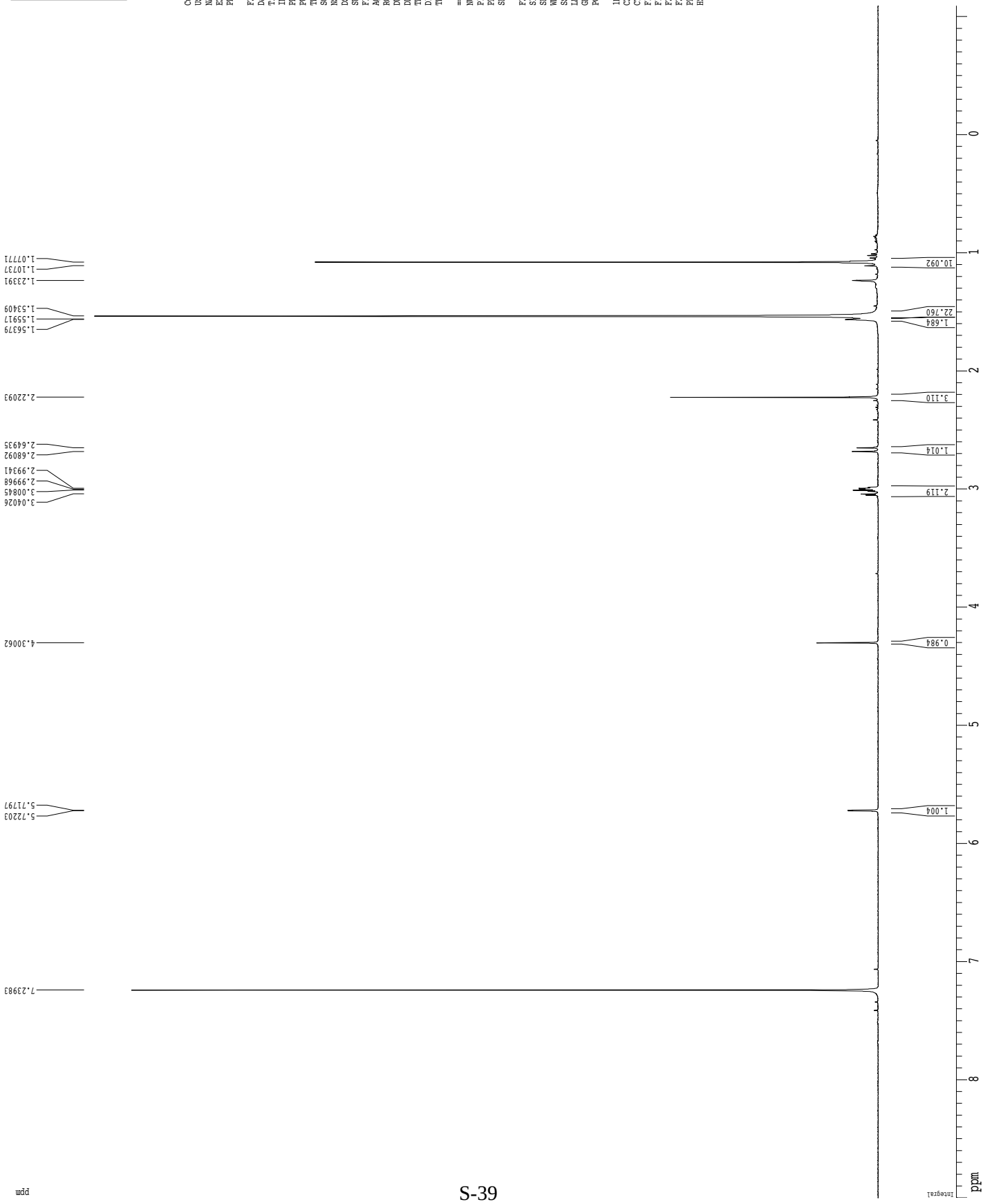

CO2Me
OMe
OMe
MeO
O
-20

Current Data Parameters
USER schner
NAME ms02-31-3-1ben
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090629
Time 14.19
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT C6D6
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 57
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 500.2199998 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 7.805 ppm
F1 3904.37 Hz
F2P -0.945 ppm
F2 -472.78 Hz
PPMCM 0.38379 ppm/cm
HZCM 191.98038 Hz/cm
1.01345
1.02686
1.25424
1.85991
1.86766
1.87615
1.88396
2.75966
2.78335
2.79490
2.94820
2.95442
2.97167
2.97830
3.07506
3.14036
3.21206
3.43522
4.41981
4.42545
4.84605
4.85383
7.16005
9.9233
3.1809
1.0546
2.0780
1.1804
3.2304
3.1108
3.0852
3.0572
1.0296
1.0287
ppm
Integral


Z-restored spin-echo 13C spectrum with 1H decoupling
ppm
173.17
128.68
128.58
128.39
128.30
128.19
106.49
102.50
84.19
56.95
54.58
51.34
48.87
48.60
39.88
38.57
32.00
30.58
17.28
CO2Me
OMe
OMe
MeO
O
-20
Current Data Parameters
USER schner
NAME ms02-31-3-1ben
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090629
Time 14.23
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 54
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 3649.1
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 29.70 usec
======== CHANNEL f1 ========
NUC1 13C
P1 14.85 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.60 dB
SP2 3.60 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
P15 500.00 usec
P16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 125.7803328 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 231.146 ppm
F1 29073.60 Hz
F2P -9.774 ppm
F2 -1229.43 Hz
PPMCM 10.56668 ppm/cm
HZCM 1329.08032 Hz/cm
0
50
100
150
200
ppm


O
O
O
O
H
11


Current Data Parameters
USER chrisb
NAME cmb2190-top
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070809
Time_ 16.24
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 97938
SOLVENT CDCl3T
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098178 Hz
AQ 5.0928259 sec
RG 812
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SFO1 600.1342009 MHz
F2 - Processing parameters
SI 65536
SF 600.1300468 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 9.000 ppm
F1 5401.17 Hz
F2P -1.089 ppm
F2 -653.63 Hz
PPMCM 0.44251 ppm/cm
HZCM 265.56149 Hz/cm


1.07771
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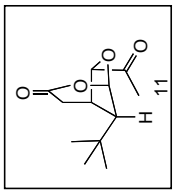
1.23391
1.53409
1.55917
1.56379
2.22093
2.64935
2.68092
2.99341
2.99968
3.00845
3.04026
4.30062
5.71797
5.72203
7.23983
10.092
22.760
1.684
3.110
1.014
2.119
0.984
1.004
ppm
Integral

1H spectrum

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Current Data Parameters
USER            chrisb
NAME          cmb2190-top
EXPNO              15
PROCNO              1

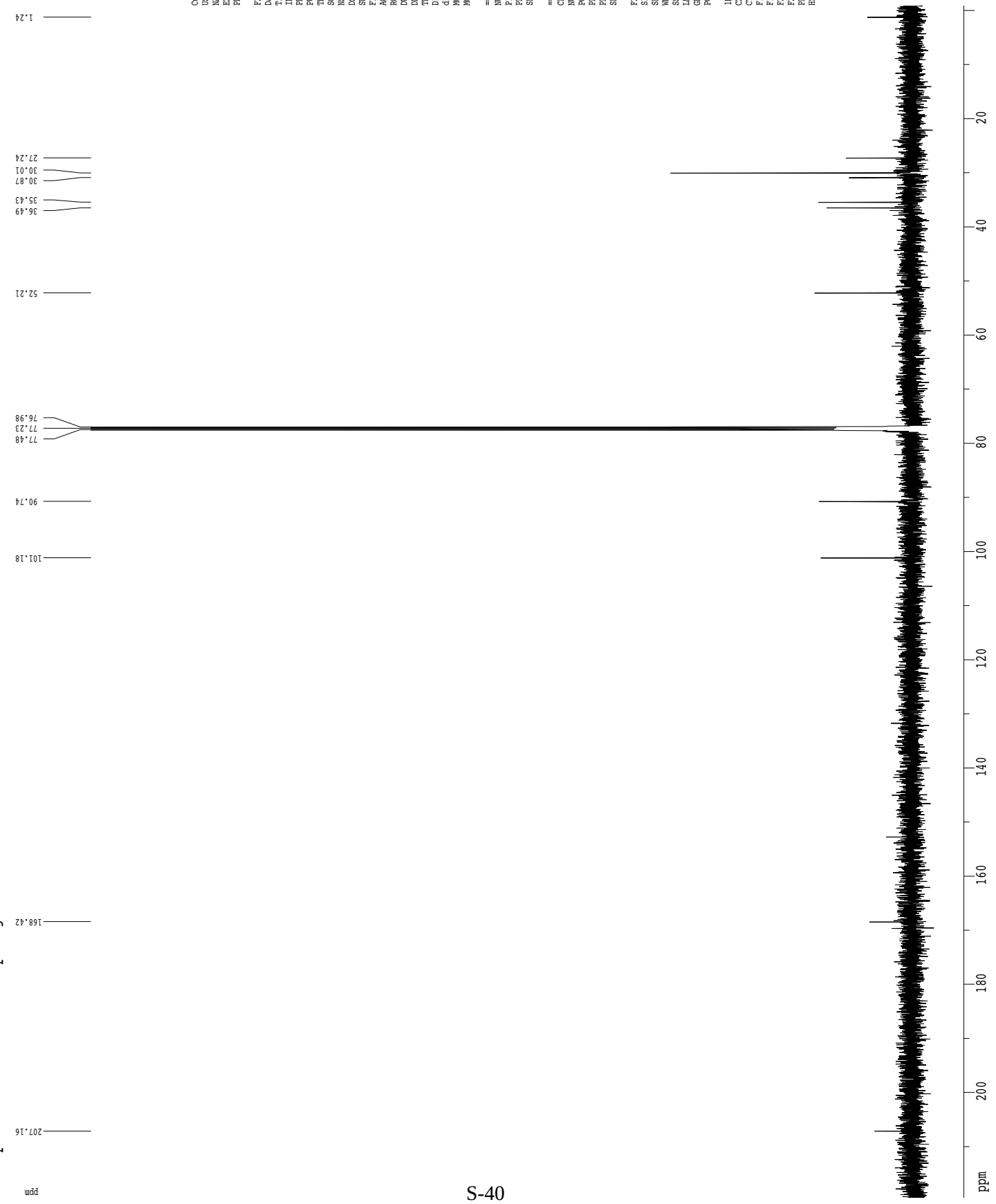
F2 - Acquisition Parameters
Date_         20070810
Time_             10.46
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG         zgdc30
TD               65418
SOLVENT          CDCl3
NS                 731
DS                   4
SWH          30303.031 Hz
FIDRES        0.463222 Hz
AQ            1.07794470 sec
RG               91.95.2
DW               16.500 usec
DE                6.00 usec
TE              298.0 K
D1              2.00000000 sec
d11             0.03000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

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

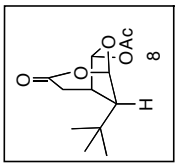
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2        500.2225011 MHz

F2 - Processing parameters
SI                65536
SF          125.7803988 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.20

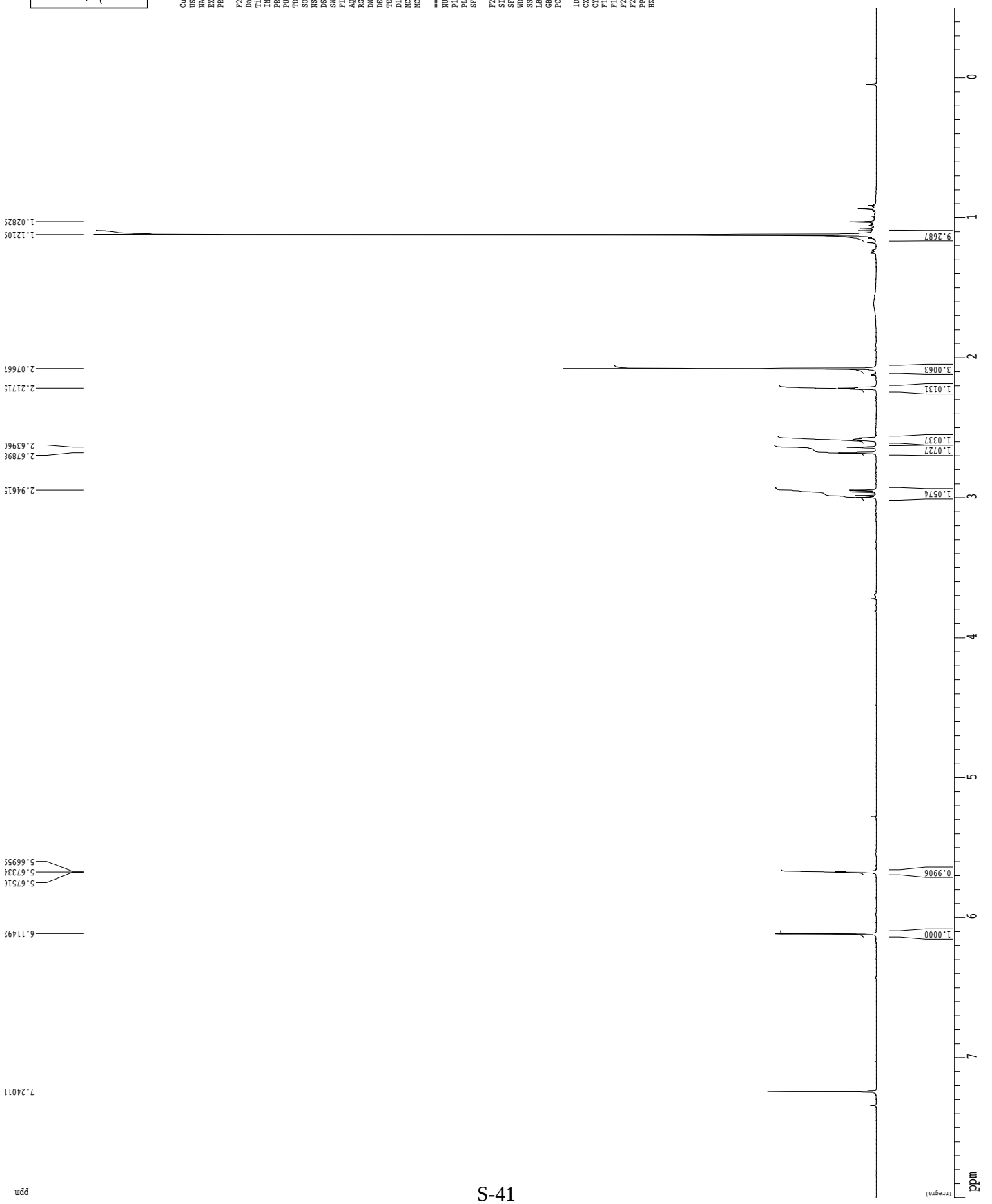
1D NMR plot parameters
CX              22.80 cm
CY             100.00 cm
F1P            219.444 ppm
F1           27601.79 Hz
F2P             -0.861 ppm
F2            -108.30 Hz
PPMCM        9.66251 ppm/cm
HZCM      1215.35486 Hz/cm
```



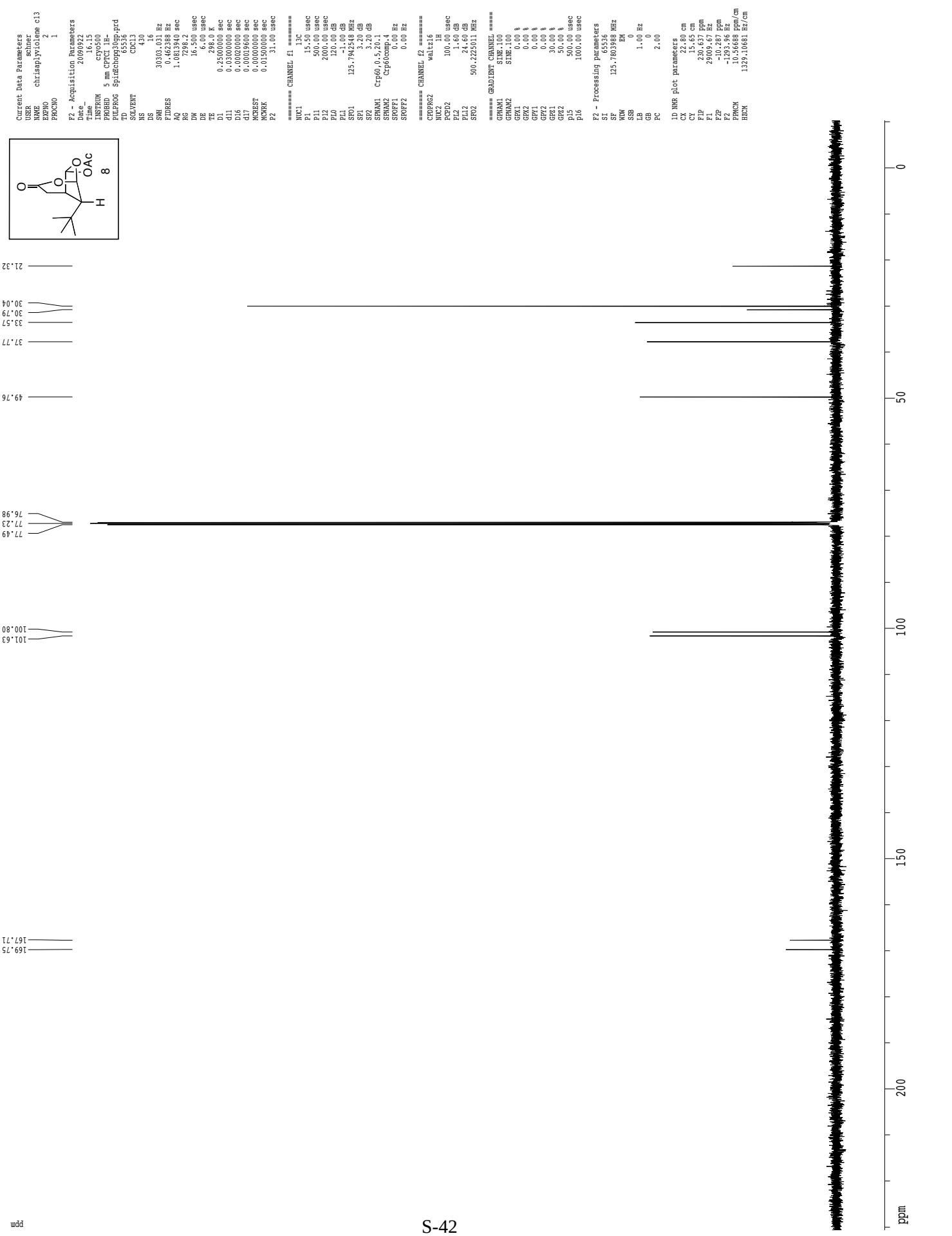
13C spectrum with 1H decoupling

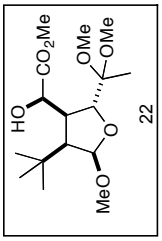

O
O
O
OAc
H
8

Current Data Parameters
USER schner
NAME chrisaplyviolene c13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090922
Time_ 16.05
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 9
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 500.2200411 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.000 ppm
F1 4001.76 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.37281 ppm/cm
HZCM 186.48555 Hz/cm

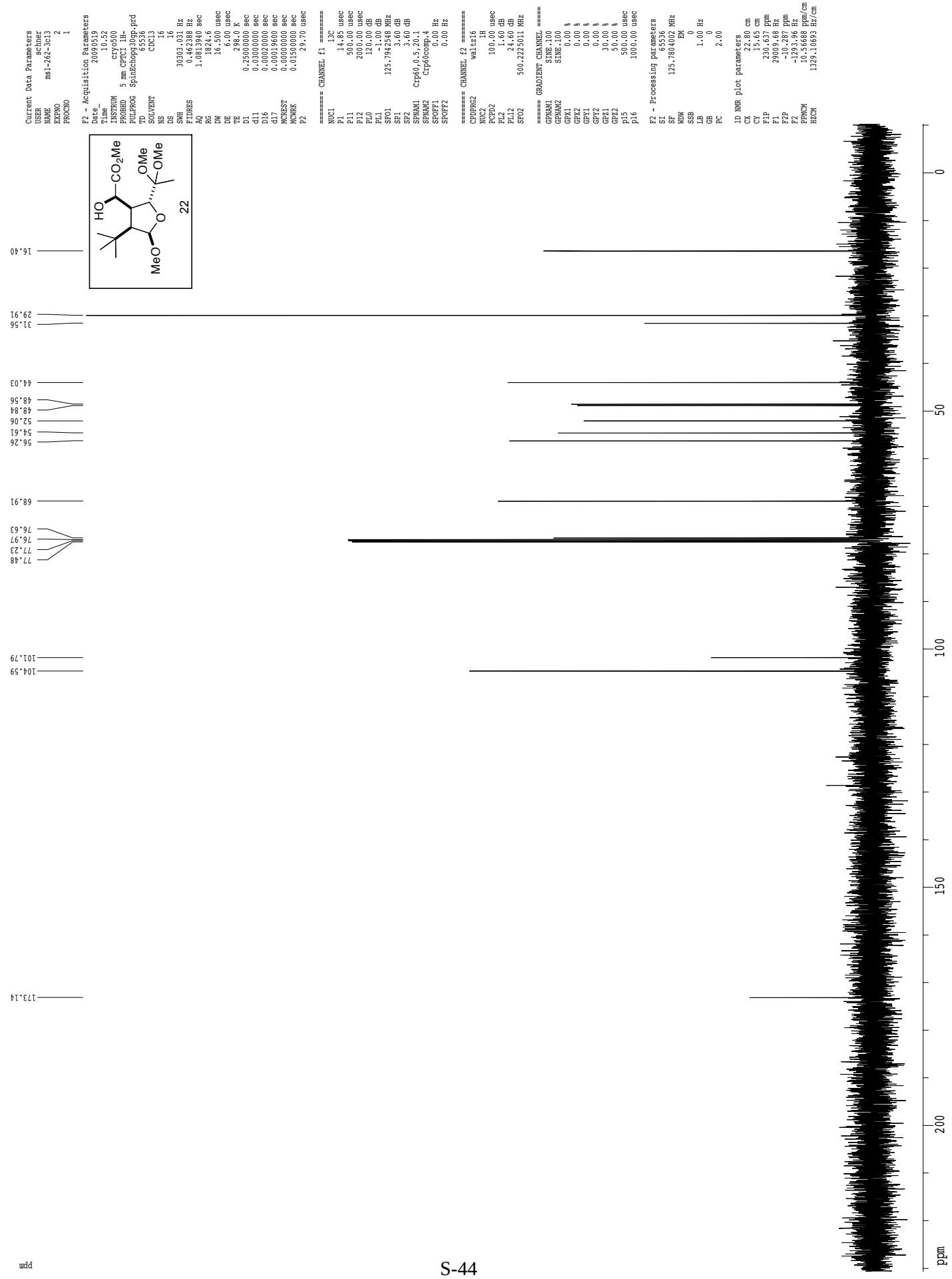

1.02825
1.12105
2.07665
2.21715
2.63966
2.67898
2.94615
5.66955
5.67334
5.67516
6.11492
7.24011
9.2687
3.0063
1.0131
1.0337
1.0727
1.0574
0.9906
1.0000
ppm
Integral

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

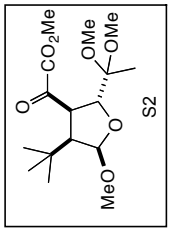



HO
CO2Me
OMe
OMe
O
MeO
22

Current Data Parameters
USER schner
NAME ms1-262-3conc
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090520
Time 18.55
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 14
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 500.2200412 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.937 ppm
F1 4970.53 Hz
F2P -0.709 ppm
F2 -354.71 Hz
PPMCM 0.46692 ppm/cm
HZCM 233.56311 Hz/cm
0.0463
1.1075
1.1705
1.2311
1.5371
2.0150
2.0229
2.0346
2.0425
2.6731
2.6790
2.6927
2.6987
3.1589
3.2215
3.4419
3.7195
4.4119
4.4188
4.6397
4.9595
4.9675
5.1882
7.2400
7.3409
9.0089
3.1454
2.7733
1.1152
0.9928
2.9593
2.9582
2.9150
2.9423
0.9851
0.9673
0.9886
1.0000
ppm
Integral

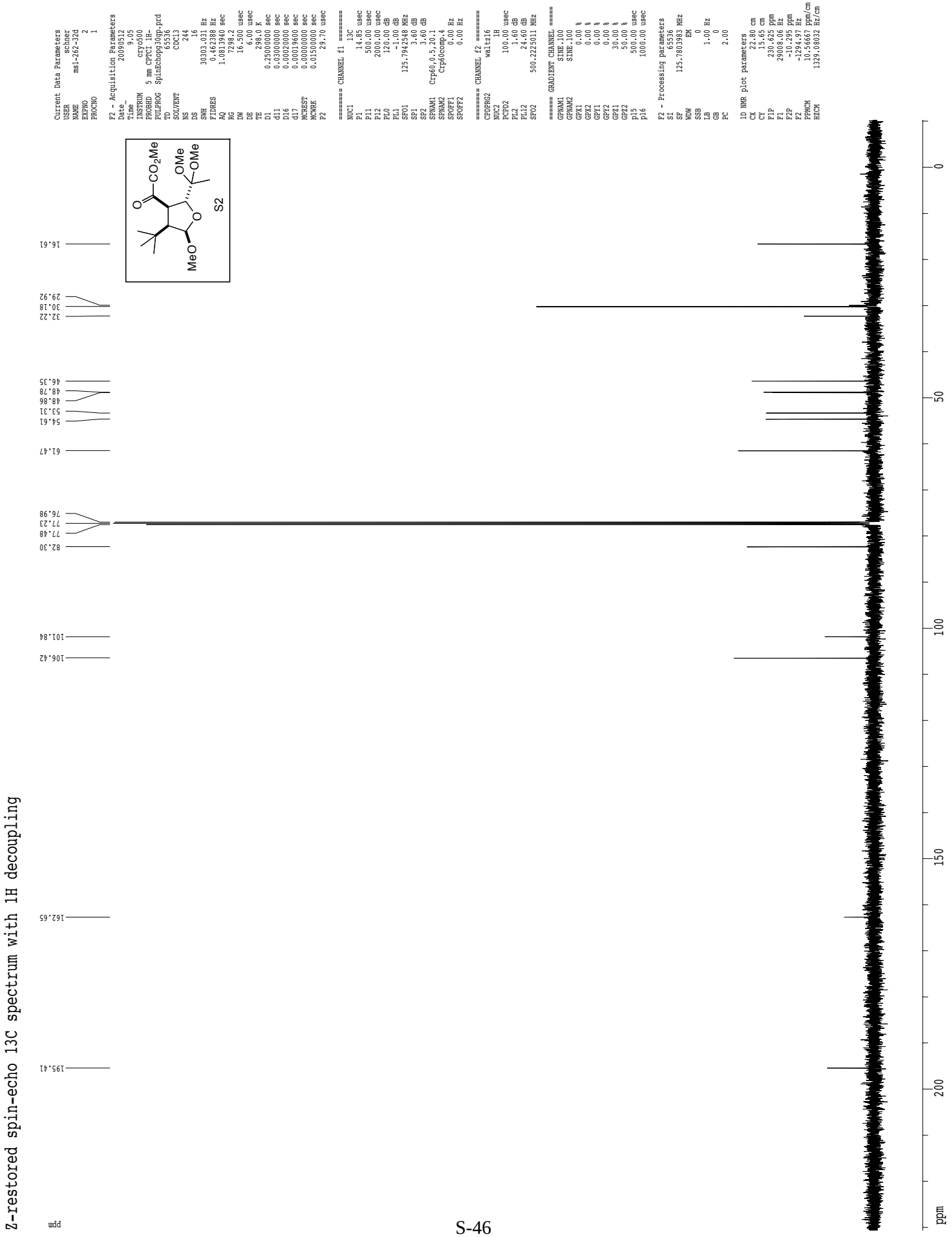


Z-restored spin-echo 13C spectrum with 1H decoupling


CO2Me
OMe
OMe
O
O
MeO
S2

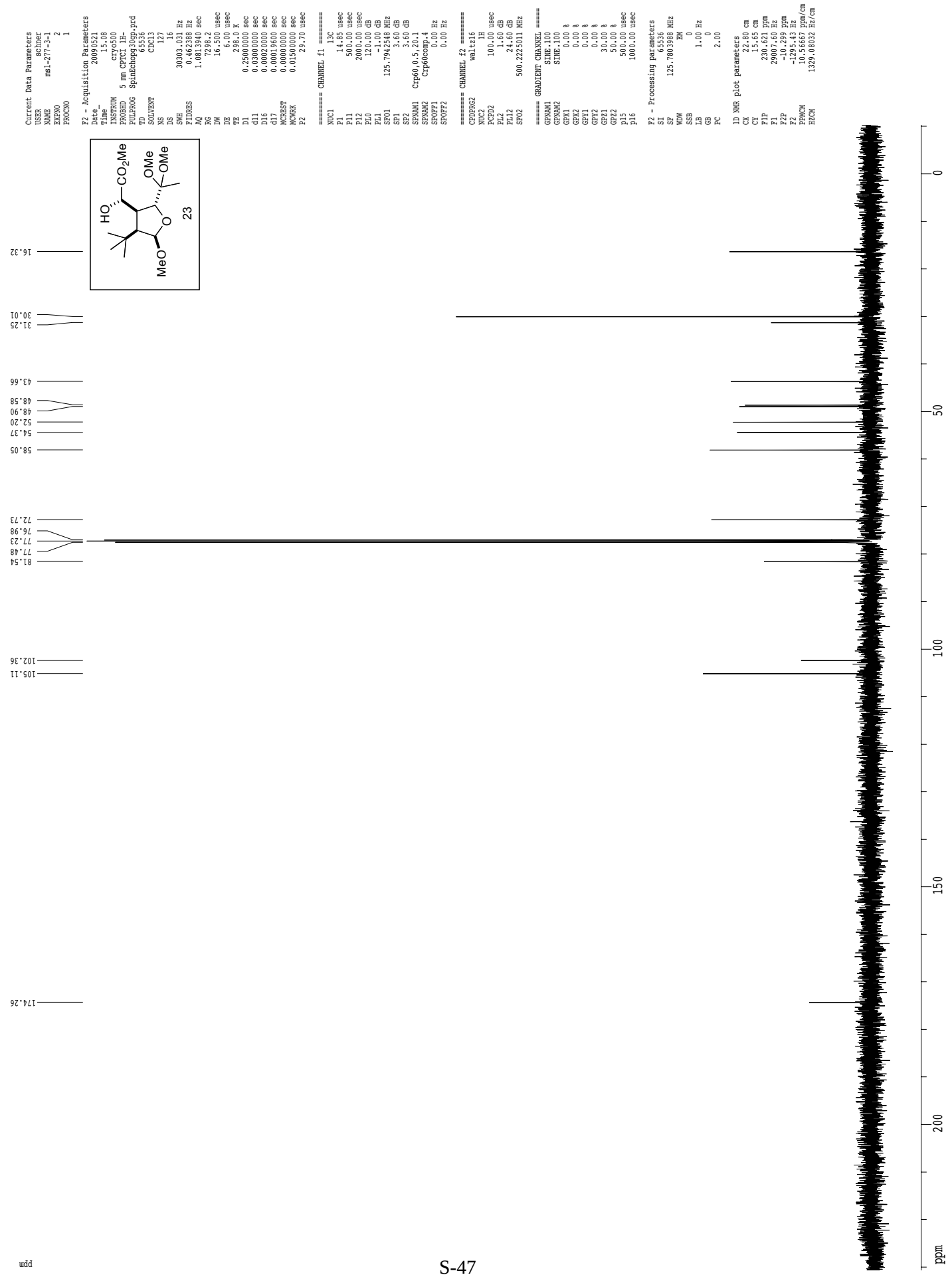
Current Data Parameters
USER schner
NAME ms1-262-32d
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090512
Time_ 9.00
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 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 500.2200412 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.100 cm
F1P 10.170 ppm
F1 5087.102 Hz
F2P -0.543 ppm
F2 -271.50 Hz
PPMCM 0.46984 ppm/cm
HZCM 235.02289 Hz/cm
0.96020
1.23062
1.25542
1.54107
2.14461
2.22234
2.23637
2.24412
3.12856
3.23386
3.36234
3.86040
3.99821
4.00862
4.01997
4.03041
4.71705
4.72744
4.94336
4.95109
7.24002
9.1941
3.2809
2.0410
1.0143
3.0139
3.0527
3.0460
3.0159
1.0073
0.9820
1.0000
ppm
Integral

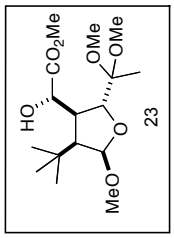
1H spectrum



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

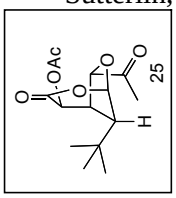
Z-restored spin-echo 13C spectrum with 1H decoupling




HO
CO2Me
OMe
OMe
O
MeO
23

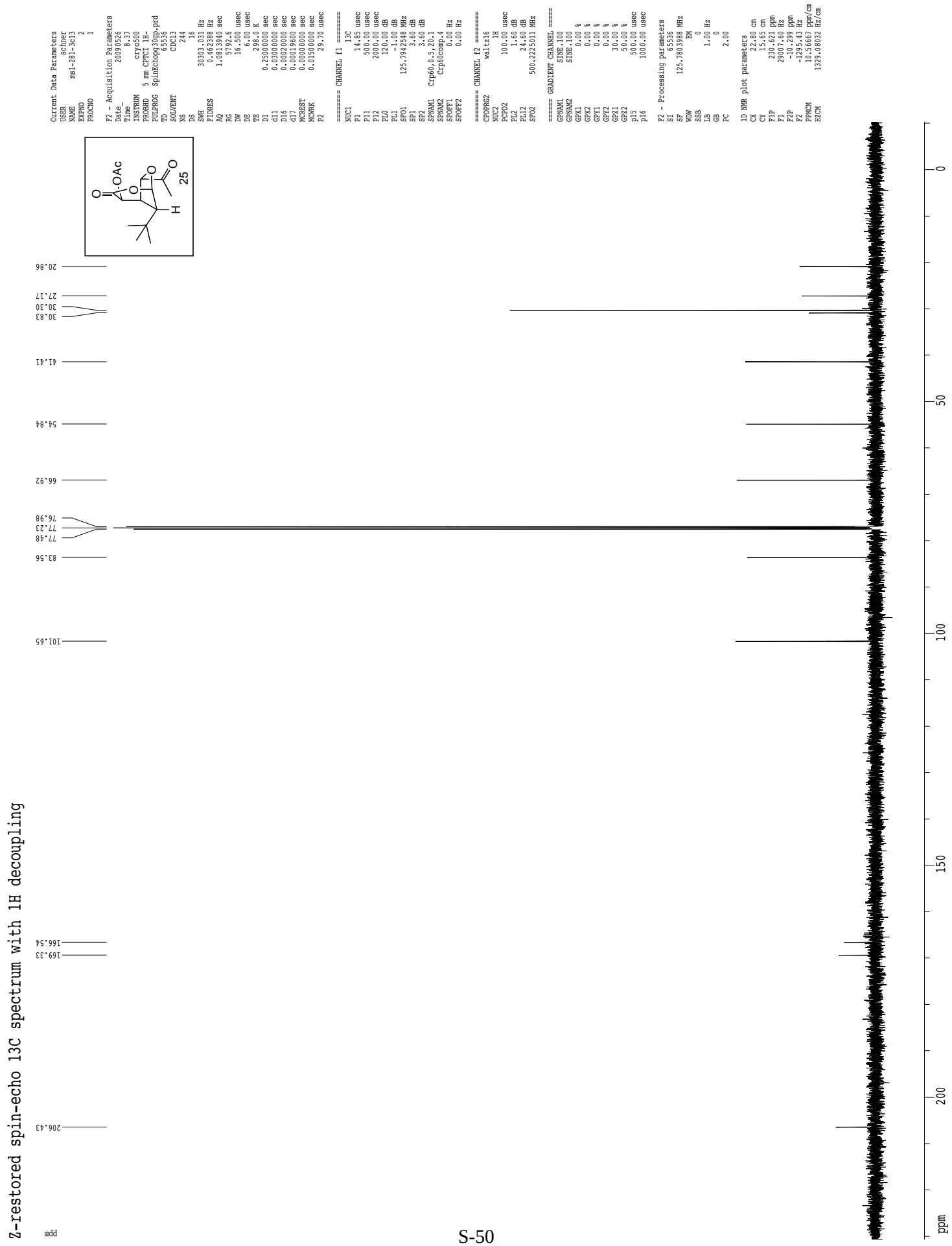
Current Data Parameters
USER schner
NAME ms1-277-3-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090521
Time_ 15.06
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 11
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 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 500.2200410 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.021 ppm
F1 4912.53 Hz
F2P -0.941 ppm
F2 -470.95 Hz
PPMCM 0.47203 ppm/cm
HZCM 236.11771 Hz/cm
1.01306
1.23039
1.24700
1.56327
1.92669
1.93563
1.94557
1.95253
2.83881
2.84588
2.85332
2.85686
2.86472
2.87177
3.23708
3.26511
3.39857
3.74343
4.29020
4.29625
4.30294
4.30904
4.32971
4.33781
4.67739
4.69029
4.95084
4.95786
7.24009
8.8243
3.1189
2.7055
1.0250
1.0114
3.0937
3.0420
3.0961
3.0501
1.0309
1.0115
0.9810
1.0000
ppm
Integral

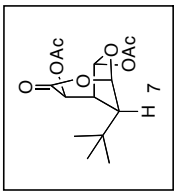
1H spectrum

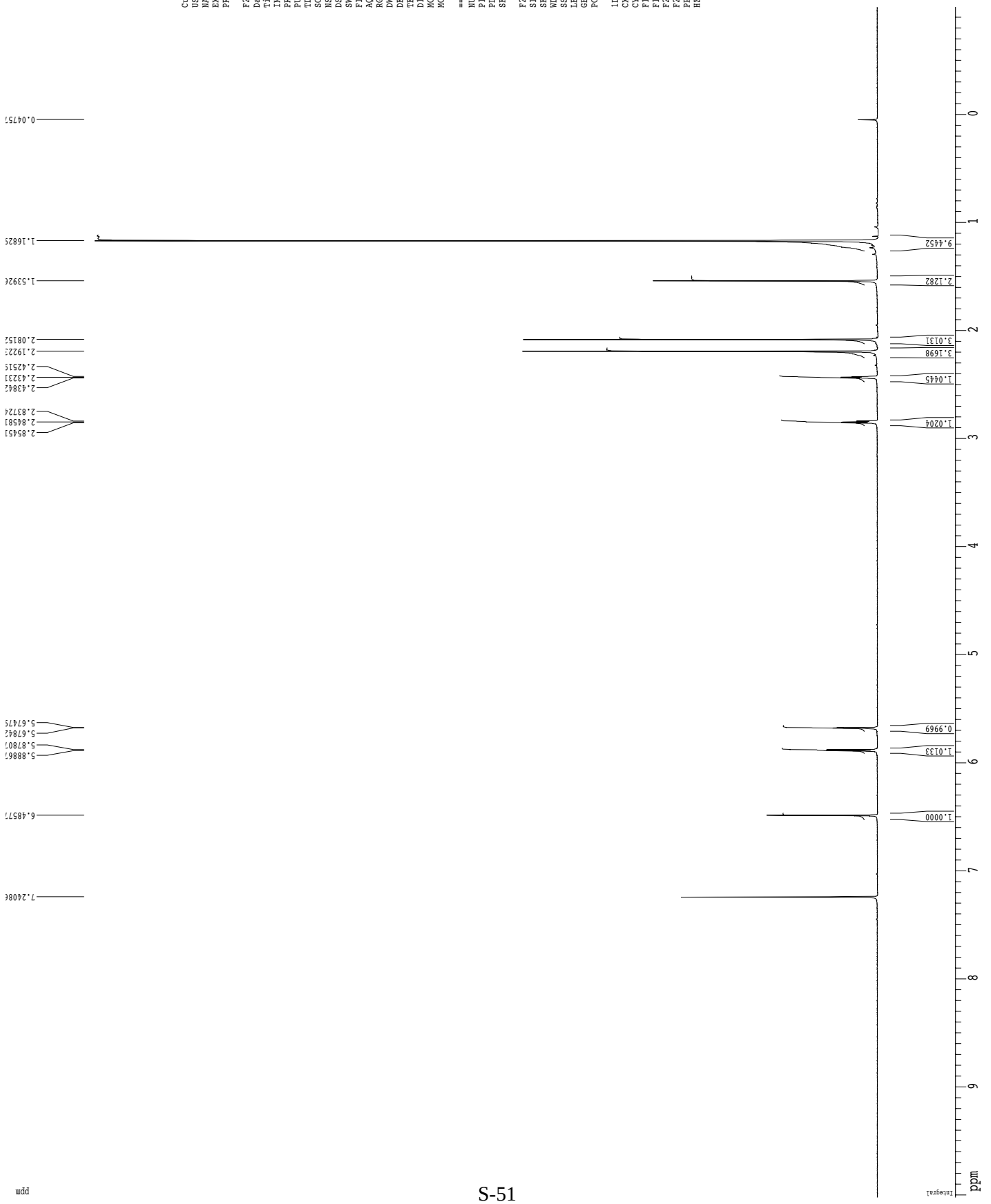

O
OAc
O
O
O
H
25

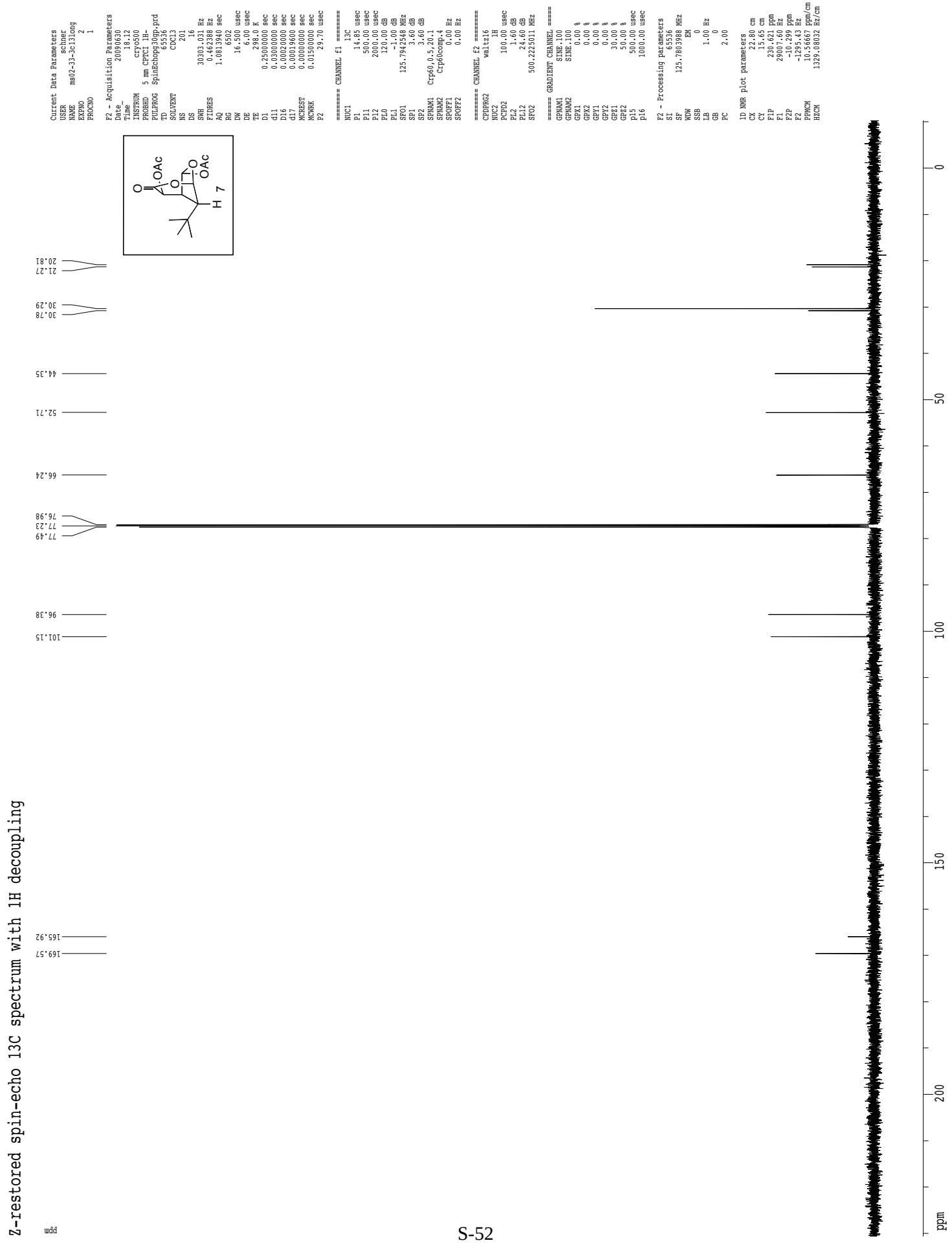
Current Data Parameters
USER schner
NAME msl-281-3c13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090526
Time_ 8.43
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 2
DS 7
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 10.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 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 500.2200413 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 10.552 ppm
F1 5178.42 Hz
F2P -0.926 ppm
F2 -463.00 Hz
PPMCM 0.49464 ppm/cm
HZCM 247.43095 Hz/cm
1.12685
1.23086
1.53976
1.82393
1.82928
1.83214
1.83731
2.17901
2.22797
3.13927
3.14836
3.15727
4.72072
5.71547
5.71912
5.91523
5.92502
7.24000
9.2545
1.0177
3.0146
3.0871
1.0070
0.9772
0.9867
1.0000
ppm
Integral

1H spectrum

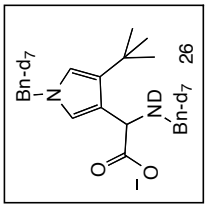

Current Data Parameters
USER schner
NAME ms1-281-3c13
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090526
Time_ 8.37
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30rp.prd
TD 65536
SOLVENT CDCl3
NS 244
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 5792.6
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 29.70 usec
======== CHANNEL f1 ========
NUC1 13C
P1 14.85 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.60 dB
SP2 3.60 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz
======== CHANNEL f2 ========
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 125.7803988 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 230.621 ppm
F1 29007.60 Hz
F2P -10.299 ppm
F2 -1295.43 Hz
PPMCM 10.56667 ppm/cm
HZCM 1329.08032 Hz/cm
O
OAc
O
O
O
H
25
20.86
27.17
30.30
30.83
41.41
54.84
66.92
76.98
77.23
77.48
83.56
101.65
166.54
169.33
206.43
ppm
0
50
100
150
200
wdd
Z-restored spin-echo 13C spectrum with 1H decoupling

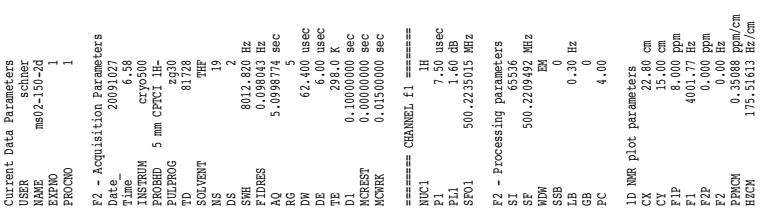

OAc
OAc
H 7

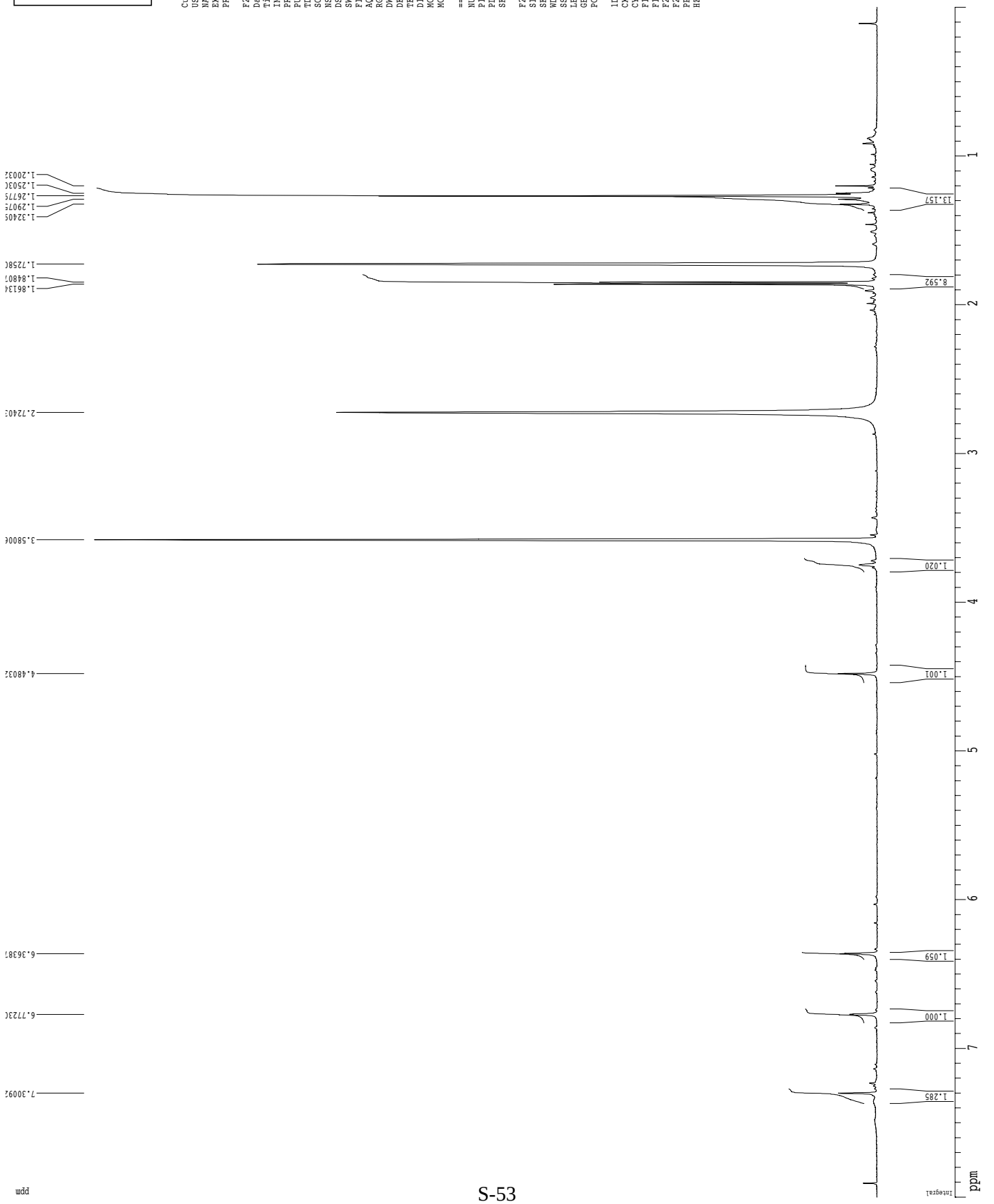

Current Data Parameters
USER schnei
NAME ms02-33-3c1long
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090630
Time 18.07
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 4
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 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 500.2200409 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 10.021 ppm
F1 5012.50 Hz
F2P -0.991 ppm
F2 -495.80 Hz
PPMCM 0.48297 ppm/cm
HZCM 241.59184 Hz/cm
0.04751
1.16825
1.53924
2.08152
2.19223
2.42515
2.43231
2.43842
2.83724
2.84581
2.85451
5.67475
5.67842
5.87801
5.88867
6.48571
7.24086
9.4452
2.1282
3.0131
3.1698
1.0445
1.0204
0.9969
1.0133
1.0000
ppm
Integral



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


Bn-d7
N
ND
Bn-d7
26
O
O


Current Data Parameters
USER schner
NAME ms02-150-2d
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091027
Time 6.58
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT THF
NS 19
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 500.2209492 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.000 ppm
F1 4001.77 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.35088 ppm/cm
HZCM 175.51613 Hz/cm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1.26775
1.29075
1.32405
1.72580
1.84801
1.86134
2.72403
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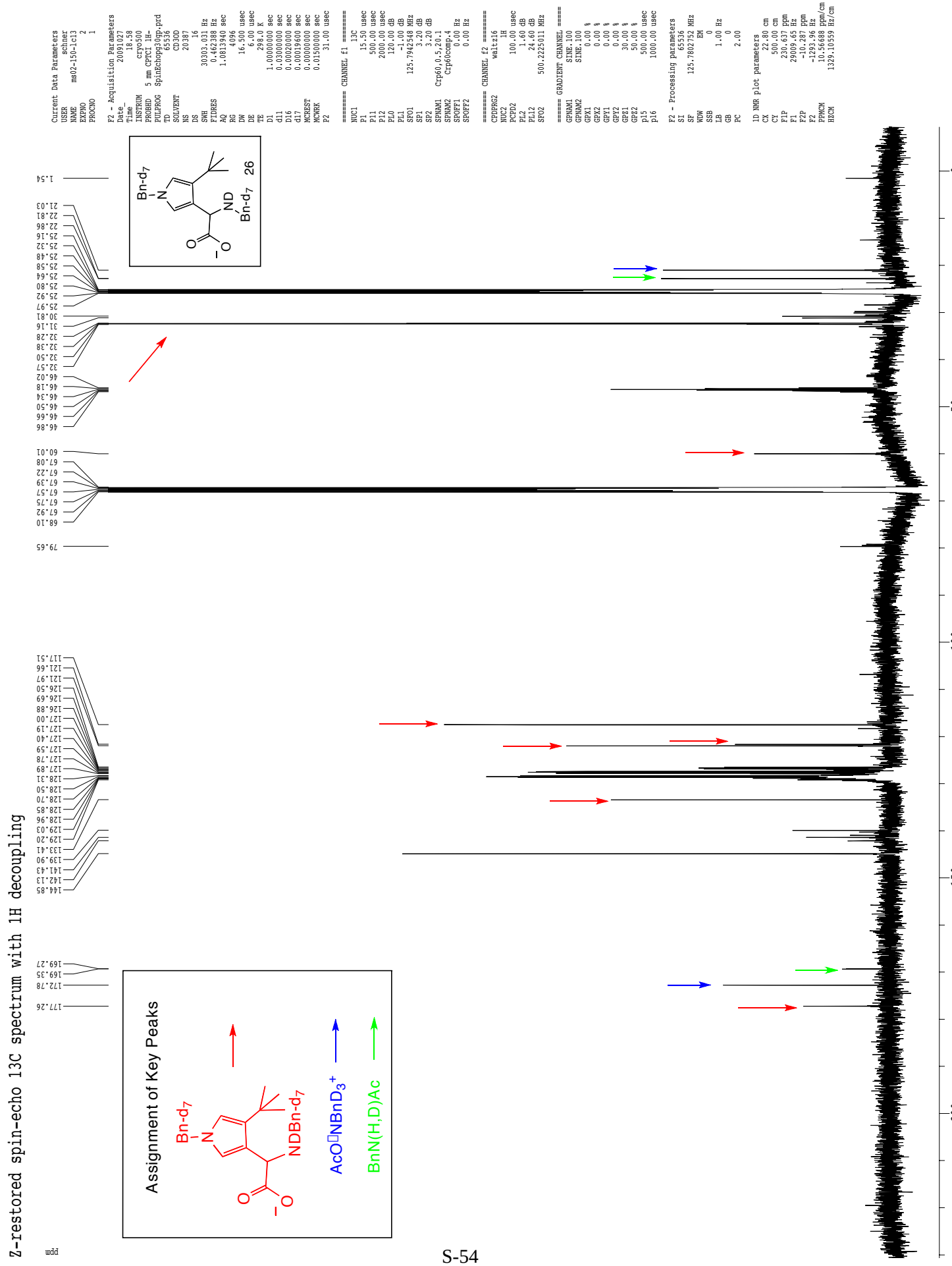
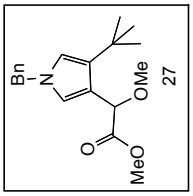
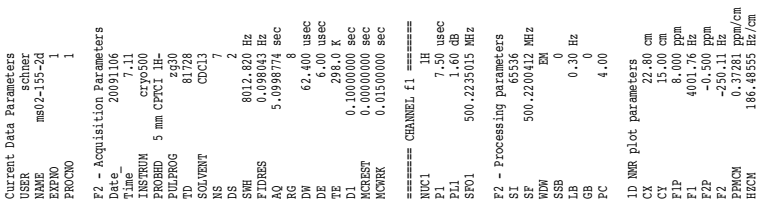
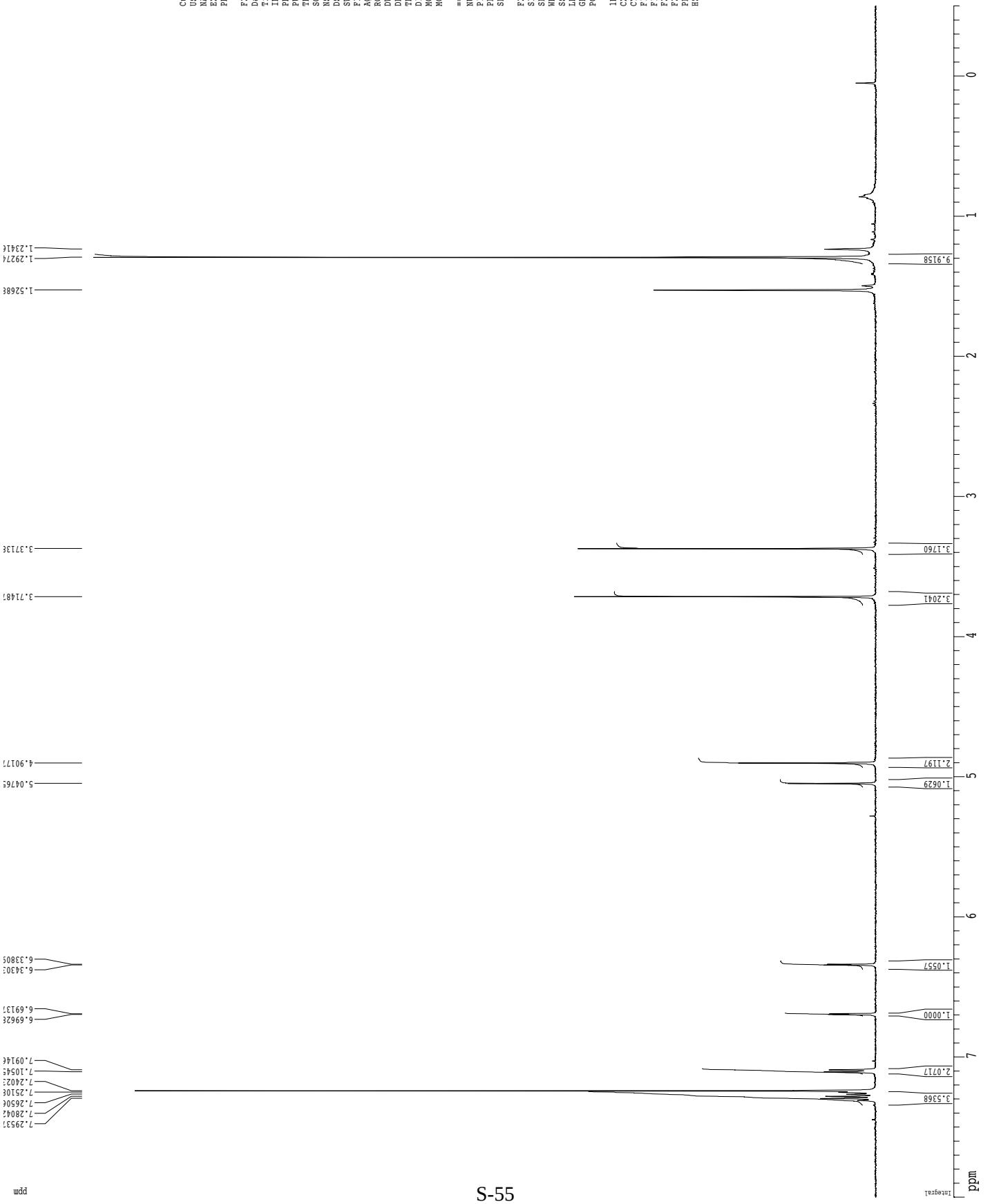
4.48032
6.36381
6.77230
7.30092
13.157
8.592
1.020
1.001
1.059
1.000
1.285
ppm
Integral


Z-restored spin-echo 13C spectrum with 1H decoupling
Assignment of Key Peaks
Bn-d7
NDBn-d7
AcO⁻NBnD3+
BnN(H,D)Ac
Bn-d7
ND
Bn-d7
26
ppm


Bn
N
OMe
27
O
MeO


Current Data Parameters
USER schner
NAME ms02-155-2d
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091106
Time 7.11
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 7
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 500.2200412 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.000 ppm
F1 4001.76 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.37281 ppm/cm
HZCM 186.48555 Hz/cm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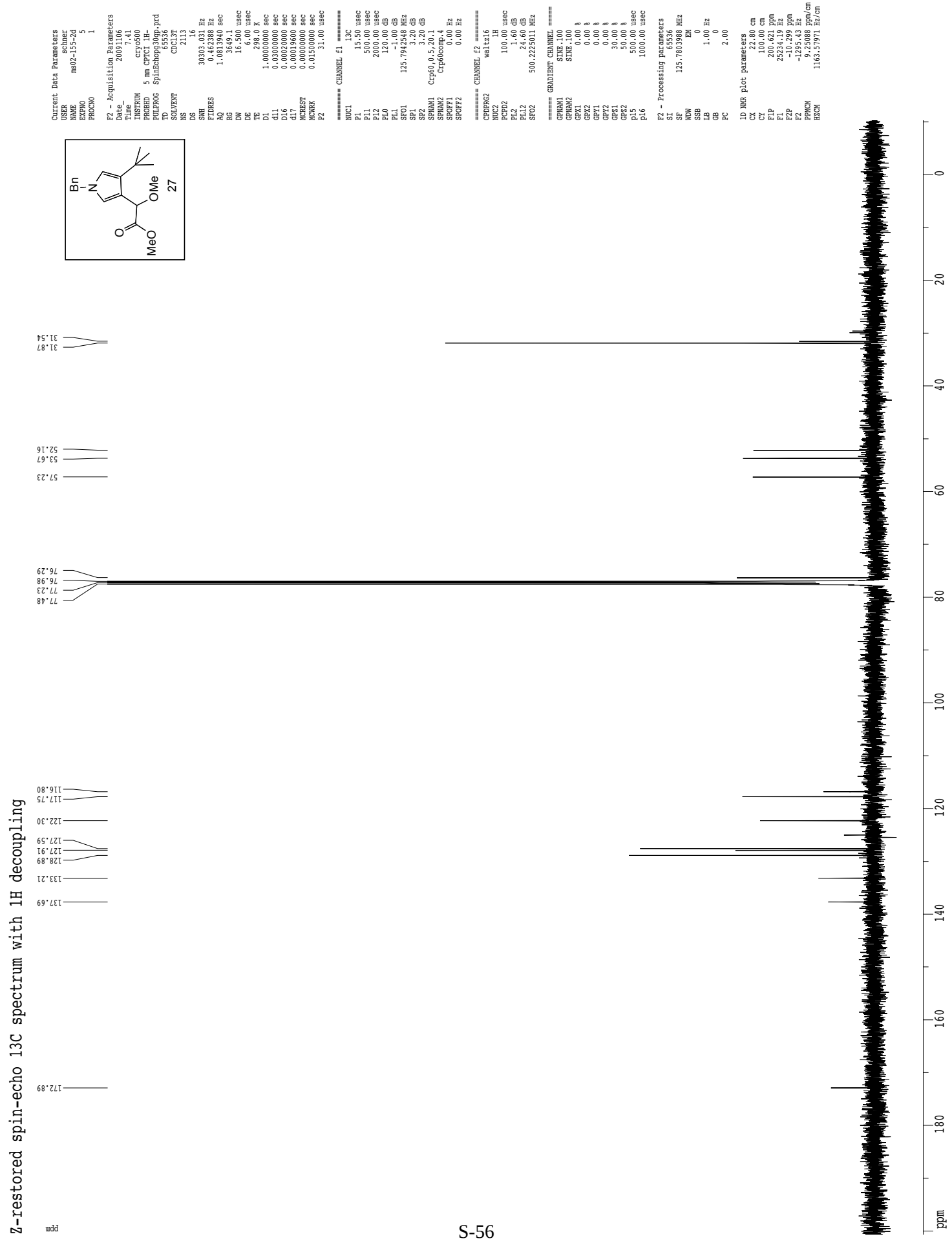
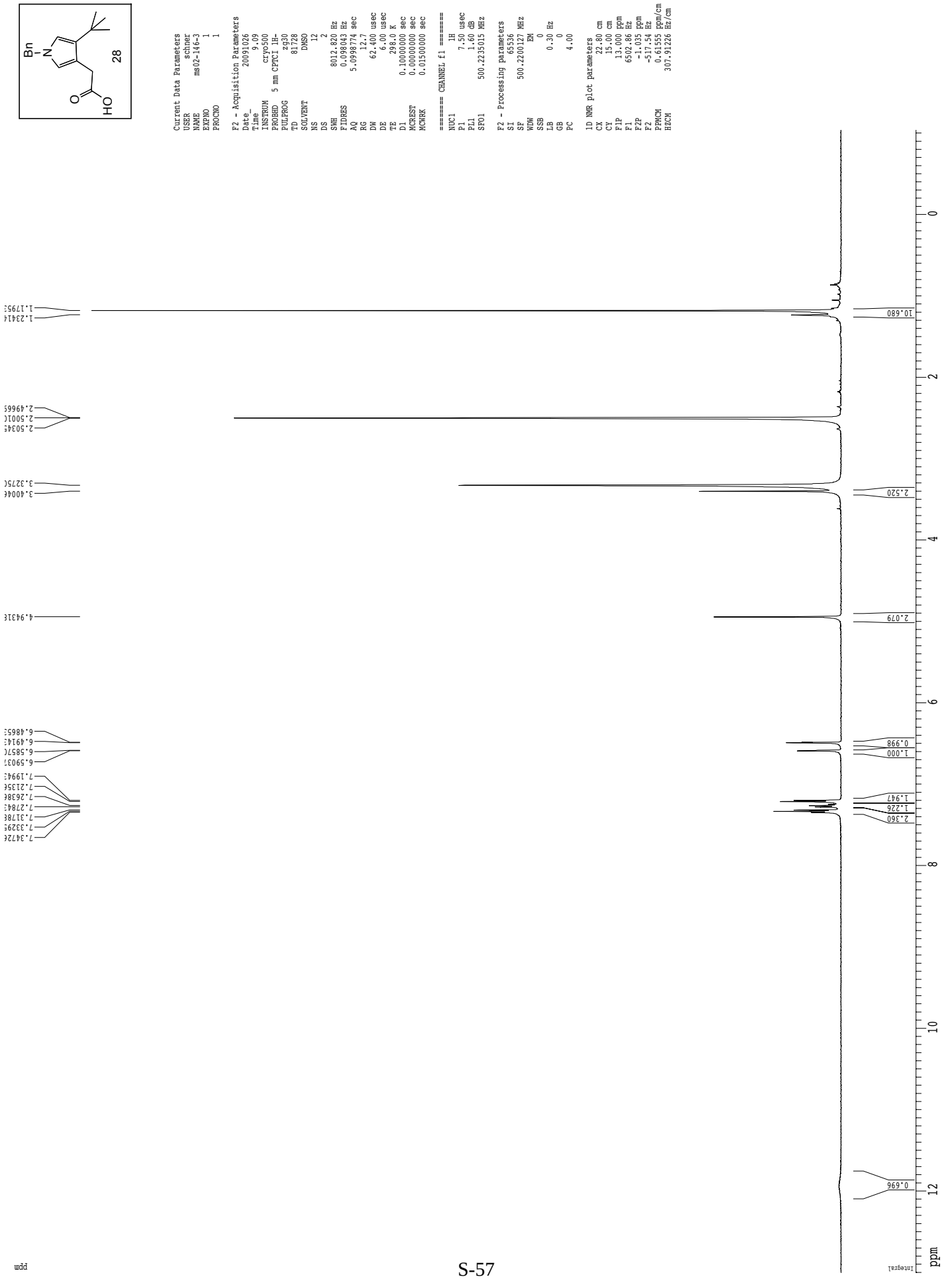
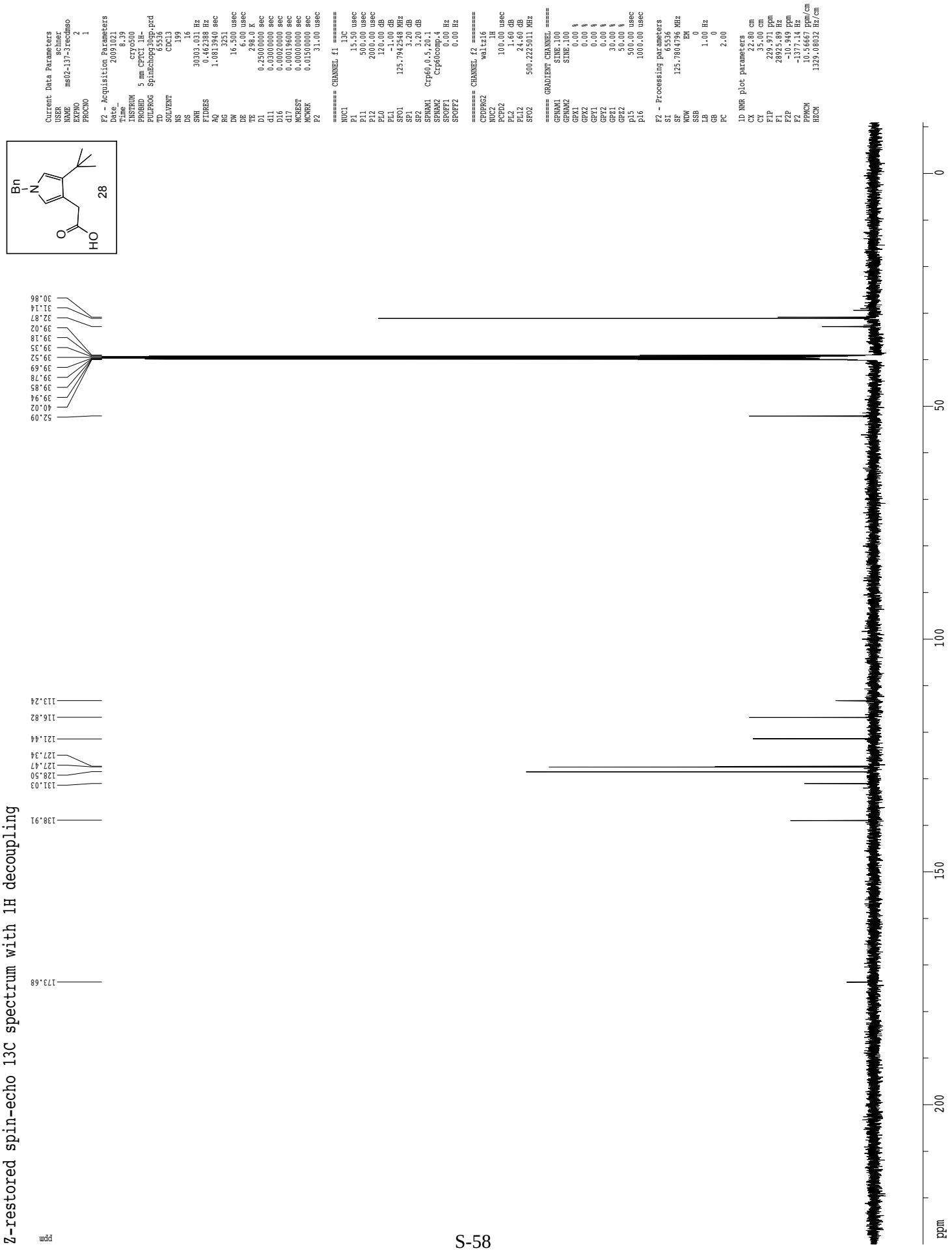
1.52686
3.37136
3.71487
4.90177
5.04769
6.33805
6.34303
6.69628
6.69137
7.09146
7.10549
7.24023
7.25108
7.26506
7.28042
7.29537
9.9158
3.1760
3.2041
2.1197
1.0629
1.0557
1.0000
2.0717
3.5368
ppm
Integral


Z-restored spin-echo 13C spectrum with 1H decoupling
Current Data Parameters
USER schner
NAME ms02-155-2d
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091106
Time_ 7.41
INSTRUM cryo500
PROBHD 5 mm CPDCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 2113
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 3649.1
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 ========
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 125.7803988 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 200.621 ppm
F1 25234.19 Hz
F2P -10.299 ppm
F2 -1295.43 Hz
PPMCM 9.25088 ppm/cm
HZCM 1163.57971 Hz/cm
Bn
N
OMe
27
O
MeO
31.54
31.87
52.16
53.67
57.23
76.29
76.98
77.23
77.48
116.80
117.75
122.30
127.59
127.91
128.89
133.21
137.69
172.89
wdd
ppm
0
20
40
60
80
100
120
140
160
180


Bn
N
O
HO
28
Current Data Parameters
USER schner
NAME ms02-146-3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091026
Time 9.09
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT DMSO
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 12.7
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 500.2200127 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 13.000 ppm
F1 6502.86 Hz
F2P -1.035 ppm
F2 -517.54 Hz
PPMCM 0.61555 ppm/cm
HZCM 307.91226 Hz/cm
1.17953
1.23414
2.49665
2.50010
2.50349
3.32750
3.40046
4.94316
6.48653
6.49143
6.58570
6.59037
7.19943
7.21356
7.26386
7.27843
7.31786
7.33295
7.34726
10.680
2.520
2.079
0.998
1.000
1.947
1.226
2.360
0.696
ppm
Integral


Current Data Parameters
USER schner
NAME ms02-137-3recdmso
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091021
Time_ 8.39
INSTRUM cryo500
PROBHD 5 mm CPDCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 199
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 3251
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 31.00 usec
======== CHANNEL f1 ========
NUC1 13C
P1 15.50 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 3.20 dB
SP2 3.20 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.60 dB
SFO2 500.2225011 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 125.7804796 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 229.971 ppm
F2P 28925.89 Hz
F1 -10.949 ppm
F2 -1377.14 Hz
PPMCM 10.56667 ppm/cm
HZCM 1329.08032 Hz/cm
Bn
N
O
HO
28
30.86
31.14
32.87
39.02
39.18
39.35
39.52
39.69
39.78
39.85
39.94
40.02
52.09
113.24
116.82
121.44
127.34
127.47
128.50
131.03
138.91
173.68
Z-restored spin-echo 13C spectrum with 1H decoupling
wdd
ppm
0
50
100
150
200