Enantioselective Total Synthesis of Aplyviolene

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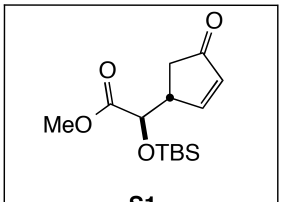
Chemical Materials and Methods.

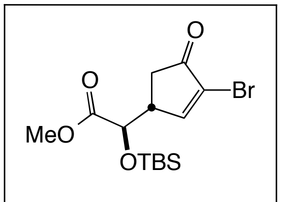
Unless stated otherwise, reactions were conducted in oven- dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). Titanium(IV) chloride and methylene bromide were purified by distillation. TMEDA, HMPA, and bromine 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).

Synthetic Experimental Procedures



S1
$C_{14}H_{24}O_4Si$
Mol. Wt. 284.42

***R*)-Methyl 2-(*tert*-butyldimethylsilyloxy)-2-((*R*)-4-oxocyclopent-2-enyl)ethanoate (S1):** Alcohol **10** (1.90 g, 11.2 mmol)[1] was dissolved in CH_2Cl_2 (32 mL) at 0 °C. DMAP (4.09 g, 33.5 mmol) and TBSCl (5.03 g, 33.5 mmol) were added, the solution was allowed to warm rt. After 1h, the solution was added to 100 mL of saturated NH_4Cl (100 mL) and CH_2Cl_2 (50 mL) and the layers were separated. The aqueous layer was washed with additional CH_2Cl_2 (2 × 50 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (5→15% EtOAc/hexanes) gave **S1** (2.63 g, 83%) as a clear oil: R_f: 0.56 (2:1 hexane:EtOAc); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.57 (dd, J = 5.7, 2.5 Hz, 1H), 6.22 (dd, J = 5.7, 1.9 Hz, 1H), 4.18 (d, J = 5.9 Hz, 1H), 3.74 (s, 3H), 3.34 (m, 1H), 2.44 (dd, J = 19, 6.8 Hz, 1H), 2.22 (dd, J = 19, 2.4 Hz, 1H), 0.85 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) ∂ 208.6, 172.6, 163.6, 135.9, 73.7, 52.3, 45.6, 37.4, 25.8, 25.6, 18.4, −4.8, −5.3; IR (thin film) 2954, 1754, 1717, 1254 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{24}O_4SiNa$ (M+Na): 307.1342, observed: 307.1341; $[\alpha]_D^{25}$ +167, $[\alpha]_{577}^{25}$+ 175, $[\alpha]_{546}^{25}$ +199, $[\alpha]_{435}^{25}$ +347, $[\alpha]_{405}^{25}$ +416, (c = 1.0, $CHCl_3$).



9
$C_{14}H_{23}BrO_4Si$
Mol. Wt. 363.32

(*R*)-Methyl 2-((*R*)-3-bromo-4-oxocyclopent-2-enyl)-2-(*tert*-butyldimethylsilyloxy)ethanoate (9): Freshly distilled bromine (200 µL, 3.8 mmol) in CH_2Cl_2 (5 mL) was added slowly over 10 min to a solution of enone **SI** (1.00 g, 3.47 mmol) in CH_2Cl_2 (40 mL) at 0 °C. After 5 minutes the reaction was complete by TLC and was concentrated. Purification of the resulting oil by silica gel chromatography gave **21** (1.05 g, 84%) as a colorless oil: R_f 0.26 (15% EtOAc)/hexanes); ^1H NMR ($CDCl_3$, 500 MHz) ∂ 7.63 (d, J = 2.8 Hz, 1H), 4.20 (d, J = 5.4 Hz, 1H), 3.75 (s, 3H), 3.30 (m, 1H), 2.62 (dd, J = 19, 6.7 Hz, 1H), 2.37 (dd, J = 19, 2.1 Hz, 1H), 0.84 (s, 9H), 0.04 (s, 3H),

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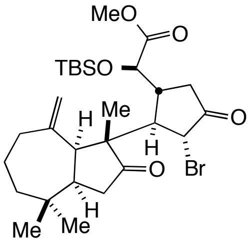
[1] (a) Schnermann, M. J.; Beaudry, C. M.; Egovora, A. V.; Polishchuk, R. S.; Sütterlin, C.; Overman. L. E. *Proc. Nat. Acad. Sci. USA* **2010**, *107,* 6158. (b) submitted for publication

0.02 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 200.1, 172.1, 160.6, 127.4, 77.3, 52.4, 44.7, 36.0, 25.7, 18.3, –4.8, –5.4; IR 1754, 1727 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_4SiBrNa$ (M+Na): 385.0447, observed: 385.0449; $[\alpha]_D^{25}$+99, $[\alpha]_{577}^{25}$+105, $[\alpha]_{546}^{25}$ +118, $[\alpha]_{435}^{25}$+209, $[\alpha]_{405}^{25}$+255, (c = 1.0, CHCl$_3$).



7

$C_{28}H_{45}BrO_5Si$
Mol. Wt. 569.6434

Bromide 7: Both **8** and **9** were dried azeotropically by dissolving in benzene (3mL) and concentrating. To a solution of **8** (200 mg, 0.97 mmol)[2] in THF (2 mL) and HMPA (2 mL) at rt was added dropwise a freshly prepared solution 0.6 M LDA in THF (1.3 mL, 0.78 mmol). The bright yellow solution was maintained at rt for 4 h and then cooled to −78 °C. Syringe pump addition of **9** (220 mg, 0.60 mmol) in THF (2 mL) over 25 min formed a red solution. After 30 min at −78 °C, the solution was added to saturated NH$_4$Cl (100 mL) and Et$_2$O (50 mL) and the layers were separated. The aqueous layer was washed with additional Et$_2$O (2 × 50 mL). The organic phases were combined, dried over Na$_2$SO$_4$, filtered, and concentrated. Purification of the residue by pH 7 buffered silica gel chromatography[3] (1→2% EtOAc/hexanes) gave **7** (275 mg, 81%) as a white solid: m.p. 135–136 °C; R$_f$: 0.50 (20% EtOAc/hexanes); ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 4.67 (m, 2H), 4.52 (s, 1H), 4.04 (d, J = 4.9 Hz, 1H), 3.35 (s, 3h), 3.09 (d, J = 4.9 Hz, 1H), 2.64 (m, 3H), 2.30 (m, 2H), 2.00 (m, 2H), 1.88 (d, J = 17.9 Hz, 1H), 1.47 (m, 1H), 1.25 (m, 2H), 1.11 (m, 2H), 1.10 (s, 3H), 1.00 (s, 9H), 0.69 (s, 3H), 0.58 (s, 3H), 0.15 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (C$_6$D$_6$, 125 Mhz) δ 218.5, 205.7, 172.7, 152.6, 114.2, 76.8, 56.4, 54.9, 51.6, 49.7, 47.8, 43.1, 41.2, 40.9, 38.3, 36.6, 36.5, 34.7, 34.0, 29.0, 26.2, 25.2, 18.9, 14.5, −4.7, −5.0; IR (thin film) 2931, 1759, 1730, 1257, 1141 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{28}H_{45}O_5SiBrNa$ (M+Na)$^+$ 591.2117, observed 591.2107; $[\alpha]_D^{25}$ +56.5, $[\alpha]_{577}^{25}$ +58.6, $[\alpha]_{546}^{25}$ +64.9, $[\alpha]_{435}^{25}$ +114.7°, $[\alpha]_{405}^{25}$ +133.7°, (c = 1, CH$_2$Cl$_2$); X-ray quality crystals were obtained via vapour diffusion by dissolving **7** in EtOAc and exposing to hexanes vapour.

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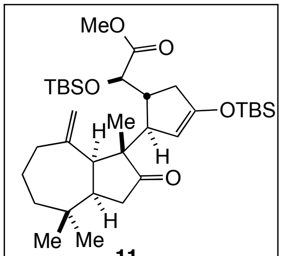
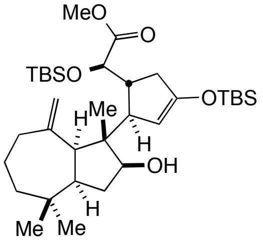
[2] Lebsack, A. D.; Overman, L. E.; Valentekovich, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 4851.

[3] Deactivated silica gel can be prepared by adding 10% (by weight) pH 7, 0.2 M phosphate buffer to silica gel and mixing until homogenous. A convenient method for mixing is to let the mixture tumble on a spinning rotovap, without applying a vacuum. This procedure has been used to facilitate the purification of guanidine containing compounds, see: Coffey, D. S.; Overman, L. E.; Stappenbeck, F. *J. Am. Chem. Soc.* **2000**, *122*, 4904. In this case, its use avoided the formation of the α-hydroxy ketone byproduct.



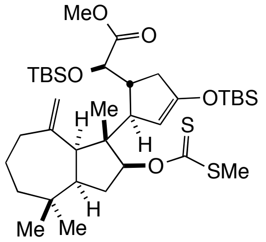
11
$C_{34}H_{60}O_5Si_2$
Mol. Wt. 605.0082

Enol Silane 11: A 0.5 M solution of $Me_2CuCNLi$ in Et_2O (~10 mL) was prepared by addition of 1.5 M MeLi in Et_2O (2.7 mL, 4.0 mmol) to a stirred mixture of CuCN (180 mg, 2.0 mmol) in Et_2O (7.5 mL) at 0 °C to form a clear homogenous solution. To a flask at −78 °C containing TBSCl (1.0 g, 6.8 mmol) was added THF (4.5 mL), HMPA (1 mL), and 0.2 M $Me_2CuCNLi$ in Et_2O (4.6 mL, 0.92 mmol) to form a clear homogenous solution. A solution of **7** (260 mg, 0.46 mmol) in THF (4.5 mL) was added by syringe pump over 30 min to generate a persistent yellow solution. After 10 min, the solution was added to 10:1 saturated NH_4Cl/NH_4OH (100 mL) and Et_2O (100 mL) and the layers were separated. The aqueous layer was washed with additional Et_2O (2 × 50 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (1→5% EtOAc/hexanes) gave **11** (240 mg, 86%) as a clear oil: R_f: 0.44 (5% EtOAc/hexanes); ^1H NMR (C_6D_6, 500 MHz) δ 4.73 (m, 2H), 4.68 (s, 1H), 4.28 (d, *J* = 4.1 Hz, 1H), 3.50 (s, 3H), 3.25 (bs, 1H), 2.88 (d, *J* = 8.2 Hz, 1H), 2.67 (m, 1H), 2.58 (m, 2H), 2.32 (d, *J* = 16.4 Hz, 1H), 2.20 (d, *J* = 11.6 Hz, 1H), 2.01 (dd, *J* = 12.8, 5.7 Hz, 1H), 1.49 (m, 1H), 1.33 (m, 4H), 1.22 (m, 1H), 1.20 (s, 3H), 1.00 (s, 9H), 0.99 (s, 9H), 0.96 (s, 3H), 0.79 (s, 3H), 0.32 (s, 3H), 0.24 (s, 3H), 0.14 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (C_6D_6, 125 Mhz) δ 219.2, 173.0, 155.3, 153.5, 113.7, 102.2, 77.0, 58.8, 55.0, 51.4, 48.9, 44.2, 42.0, 38.45, 38.4, 36.8, 36.6, 35.0 34.4, 29.1, 26.1, 25.9, 25.4, 18.7, 18.2, 15.0, −4.3, −4.5, −4.7, −5.1; IR (thin film) 2929, 2857, 1755, 1730, 1253, 839 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{34}H_{60}O_5Si_2Na$ $(M+Na)^+$ 627.3877, observed 627.3862; $[\alpha]_D^{25}$ +6.0, $[\alpha]_{577}^{25}$ +5.4, $[\alpha]_{546}^{25}$ +6.9, $[\alpha]_{435}^{25}$ +6.7, $[\alpha]_{405}^{25}$+20.1, (*c* = 0.33, CH_2Cl_2).



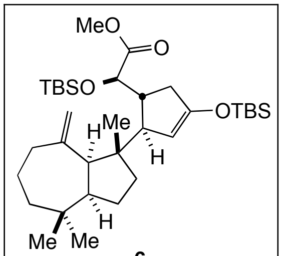
12
$C_{34}H_{62}O_5Si_2$
Mol. Wt. 607.0241

Alcohol 12: To a stirred solution of **11** (240 mg, 0.39 mmol) in EtOH (4 mL) at 0°C was added $CeCl_3$-$7H_2O$ (29 mg, 0.078 mmol) and $NaBH_4$ (120 mg, 3.1 mmol). After 2h at 0 °C, saturated aqueous NH_4Cl (10 mL) and CH_2Cl_2 (5 mL). The biphasic mixture was stirred vigorously for 4 h and the layers were separated. The aqueous layer was washed with additional 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 (1→5% EtOAc/hexanes) gave **12** (167 mg, 71%) as a clear oil: R_f: 0.38 (20% EtOAc/hexanes); ^1H NMR (C_6D_6, 500 MHz) δ 5.09 (s, 1H), 4.94 (d, *J* = 2.4 Hz, 1H), 4.85 (s, 1H), 4.19 (d, *J* = 7.8 Hz, 1H), 3.82 (m, 1H), 3.37 (s, 3H), 2.95 (m, 2H), 2.87 (m, 1H), 2.66 (m, 1H), 2.29 (m, 2H), 1.87 (apt t, *J* = 12.7 Hz, 1H), 1.75 (m, 2H), 1.64 (m, 1H), 1.52 (m, 3H), 1.19 (m, 1H), 1.11 (s, 3H), 1.04 (s, 9H), 1.01 (s, 9H), 0.98 (s, 3H), 0.95 (s, 3H), 0.23 (s, 6H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (C_6D_6, 125 Mhz) δ 173.3, 155.9, 154.9, 115.2, 103.4, 78.5, 76.8, 56.7, 55.8, 51.5, 51.2, 48.2, 40.5, 38.5, 37.5, 37.1, 36.9, 36.1, 34.9, 29.2, 26.1, 25.9, 18.6, 18.3, 14.4, −4.2, −4.4, −4.8, −4.9; IR (thin film) 2952, 2858, 1651, 1252, 839 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{34}H_{62}O_5Si_2Na$ $(M+Na)^+$ 629.4034, observed 629.4038; $[\alpha]_D^{25}$ +57.2, $[\alpha]_{577}^{25}$ +59.4, $[\alpha]_{546}^{25}$ +65.6, $[\alpha]_{435}^{25}$ +118.5, $[\alpha]_{405}^{25}$ +141.9, (*c* = 0.5, CH_2Cl_2).



S2
$C_{36}H_{64}O_5S_2Si_2$
Mol. Wt. 697.1914

Xanthate ester S2: To a solution of **12** (210 mg, 0.34 mmol) in THF (3.4 mL) at −78 °C was added CS_2 (0.13 mL, 1.7 mmol) and 1 M NaHMDS in THF (1.1 mL, 1.1 mmol). After 5 min, MeI (0.10 mL, 1.7 mmol) was added. The solution was maintained at −78 °C for 10 min and then added to saturated aqueous ammonium chloride (30 mL) and Et_2O (20 mL) and the layers were separated. The aqueous layer was washed with additional Et_2O (2 × 10 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (0→4% EtOAc/hexanes) gave **S2** (220 mg, 93%) as a clear oil: R_f: 0.51 (5% EtOAc/hexanes); ^{1}H NMR (C_6D_6, 500 MHz) δ 6.09 (dd, *J* = 9.4, 6.6 Hz, 1H), 5.01 (s, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 4.23 (d, *J* = 6.5 Hz, 1H), 3.36 (s, 3H), 3.09 (bs, 1H), 2.97 (d, 1H), 2.71 (m, 2H), 2.41 (m, 1H), 2.31 (d, *J* = 11.2 Hz, 1H), 2.27 (dd, *J* = 12.0, 4.8 Hz, 1H), 2.21 (s, 3H), 1.98 (m, 1H), 1.86 (m, 1H), 1.75 (m, 1H), 1.62 (m, 1H), 1.39 (m, 2H), 1.13 (s, 3H), 1.10 (m, 1H), 1.08 (s, 3H), 0.98 (s, 9H), 0.97 (s, 9H), 0.87 (s, 3H), 0.26 (s, 3H), 0.25 (s, 3H), 0.12 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (C_6D_6, 125 Mhz) δ 215.9, 173.0, 156.9, 154.0, 115.8, 102.5, 89.6, 76.9, 56.0, 55.9, 52.0, 51.3, 48.3, 41.0, 38.0, 37.3, 37.0, 36.2, 34.5, 33.0, 29.1, 26.1, 25.9, 25.8, 18.7, 18.6, 18.3, 16.0, −4.2, −4.4, −4.8, −4.9; IR (thin film) 2953, 2929, 2857, 1754, 1650, 1252, 1227 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{36}H_{64}O_5Si_2S_2Na$ $(M+Na)^+$ 719.3632, observed 719.3612; $[\alpha]_D^{25}$ +29.8, $[\alpha]_{577}^{25}$ +30.3, $[\alpha]_{546}^{25}$ +28.5, $[\alpha]_{435}^{25}$ +8.2, $[\alpha]_{405}^{25}$ −37.3, (*c* = 0.5, CH_2Cl_2).

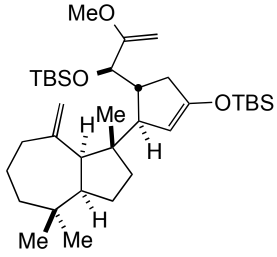


6

$C_{34}H_{62}O_4Si_2$

591.0247

Ester 6: To a solution of **S2** (210 mg, 0.30 mmol) in toluene (6 mL) was added Bu_3SnH (0.40 mL, 1.5 mmol) and the solution was degassed with Ar for 10 min. AIBN (14 mg, 0.090 mmol) was added to the solution and the yellow solution was placed in a 100 °C oil bath. After 5 min, the now clear solution was allowed to cool to r.t. and concentrated. Purification of the residue by silica gel chromatography (0→4% EtOAc/hexanes) gave **6** (150 mg, 85%) as a clear oil: R_f: 0.53 (5% EtOAc/hexanes); ^{1}H NMR (C_6D_6, 500 MHz) δ 5.07 (d, *J* = 2.2 Hz, 1H), 4.93 (d, *J* = 2.2 Hz, 1H), 4.79 (s, 1H), 4.22 (d, *J* = 7.5 Hz, 1H), 3.38 (s, 3H), 2.95 (d, 1H), 2.75 (m, 1H), 2.60 (m, 1H), 2.32 (m, 2H), 2.04 (m, 1H), 1.82 (t, *J* = 12.6 Hz, 1H), 1.55 (m, 7H), 1.20 (m, 1H), 1.14 (s, 3H), 1.02 (s, 9H), 1.00 (s, 3H), 0.98 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (C_6D_6, 125 Mhz) δ 173.2, 155.7, 155.4, 114.6, 103.8, 76.9, 56.2, 55.8, 55.1, 51.2, 50.5, 41.3, 38.6, 38.4, 37.6, 37.1, 36.4, 34.9, 29.3, 27.2, 26.2, 26.1, 25.9, 20.9, 18.6, 18.3, −4.2, −4,4, −4.8, −4.9; IR (thin film) 2930, 1652, 1252, 838 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{34}H_{62}O_4Si_2Na$ $(M+Na)^+$ 613.4084, observed 613.4083; $[\alpha]_D^{25}$ +39.0, $[\alpha]_{577}^{25}$ +36.7, $[\alpha]_{546}^{25}$ +43.7, $[\alpha]_{435}^{25}$ +82.7, $[\alpha]_{405}^{25}$+102.0, (*c* = 0.5, CH_2Cl_2).



S3

$C_{35}H_{64}O_3Si_2$

Mol. Wt. 589.0519

Enol Ether S3: The general procedure of Rainer was followed.[4] A stirring solution of $TiCl_4$ (0.19 mL, 1.70 mmol) in CH_2Cl_2 (5 mL) was cooled to 0 °C and THF (0.5 mL) was added dropwise to generate a yellow solution. After 5 min, TMEDA (1.5 mL, 10 mmol) was added dropwise to form a red mixture. After 15 min, the solution was allowed to warm to rt and a mixture of Zn (230 mg, 3.5 mmol) and $PbCl_2$ (55 mg, 0.20 mmol) was added. The resulting mixture became a blue solution. After 15 min, a solution of ester **6** (150 mg, 0.25 mmol) and CH_2Br_2 (0.12 mL, 1.7 mmol) in CH_2Cl_2 (0.5 mL) was added. The solution became a dark mixture while 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 (0→4% EtOAc/hexanes) gave **S3** (145 mg, 97%): R_f: 0.8 (5% EtOAc/hexanes); ^{1}H NMR (C_6D_6, 500 MHz) δ 5.14 (d, *J* = 2.4 Hz, 1H), 4.97 (d, *J* = 2.4 Hz, 1H), 4.82 (s, 1H), 4.20 (d, *J* = 1.7 Hz, 1H), 4.01 (d, *J* = 7.7 Hz, 1H), 3.93 (d, *J* = 1.7 Hz, 1H),

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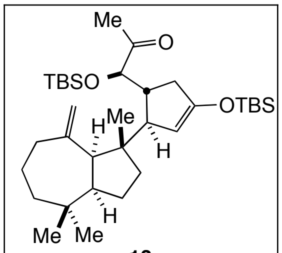
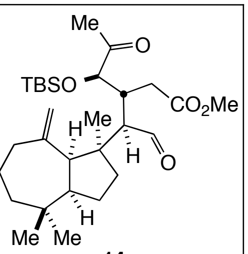
[4]. Roberts, S.W.; Rainier, J. D. *Org. Lett.* **2007**, *9*, 2227.

3.18 (s, 3H), 3.04 (d, J = 9.1 Hz, 1H), 2.96 (bs, 1H), 2.72 (apt t, J = 8.0 Hz, 1H), 2.60 (m, 1H), 2.35 (dd, J = 12.0, 4.4 Hz, 1H), 2.23 (d, J = 16.5 Hz, 1H), 2.07 (m, 1H), 1.87 (apt t, J = 12.8 Hz, 1H), 1.63 (m, 5H), 1.50 (m, 2H), 1.23 (m, 1H), 1.22 (s, 3H), 1.04 (s, 9H), 1.01 (s, 6H), 0.97 (s, 9H), 0.21 (s, 3H), 0.205 (s, 3H), 0.19 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 165.0, 155.9, 155.7, 114.5, 104.3, 83.4, 78.3, 56.4, 55.4, 55.2, 54.4, 50.7, 41.2, 39.0, 38.5, 38.0, 37.7, 36.5, 35.1, 29.4, 27.3, 26.4, 25.9, 21.0, 18.7, 18.3, −4.1 (2C), −4.4 (2C); IR(thin film) 2954, 1756, 1738, 1651, 1252 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{35}H_{64}O_3Si_2Na$ $(M+Na)^+$ 611.4292, observed 611.4269; $[\alpha]_D^{25}$ +37.1, $[\alpha]_{577}^{25}$ +44.2, $[\alpha]_{546}^{25}$ +46.2, $[\alpha]_{435}^{25}$ +79.6, $[\alpha]_{405}^{25}$ +90.5 (c = 0.5, CH_2Cl_2).



13
$C_{34}H_{62}O_3Si_2$
Mol. Wt. 575.0253

Ketone 13: To a solution of enol ether **S3** (100 mg, 0.17 mmol) in *t*-BuOH (1.7 mL) and H_2O (0.75 mL) at 0 °C was added oxalic acid (24 mg, 0.22 mmol) and the solution was allowed to warm to rt. After 2 h, saturated aqueous $NaHCO_3$ (10 mL) and Et_2O (10 mL) were added to the solution. The layers were separated and the aqueous layer was washed with additional Et_2O (10 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (1→2% EtOAc/hexanes) gave ketone **13** (56 mg, 57%) as a colorless oil: R_f: 0.53 (5% EtOAc/hexanes); ^{1}H NMR (C_6D_6, 500 MHz) δ 4.96 (d, J = 2.4 Hz, 1H), 4.88 (d, J = 2.3 Hz, 1H), 4.76 (s, 1H), 3.86 (d, J = 8.5 Hz, 1H), 2.97 (d, J = 9.1 Hz, 1H), 2.87 (bs, 1H), 2.45 (m, 2H), 2.30 (dd, J = 12.1, 4.2 Hz, 1H), 2.20 (m, 1H), 2.06 (s, 3H), 2.00 (m, 1H), 1.82 (apt t, J = 12.4 Hz, 1H), 1.68 (m, 1H), 1.59 (m, 3H), 1.48 (m, 2H), 1.39 (m, 1H), 1.23 (m, 1H), 1.16 (s, 3H), 1.00 (s, 3H), 0.95 (s, 12H), 0.94 (s, 9H), 0.19 (s, 6H), 0.23 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (C_6D_6, 125 Mhz) δ 209.1, 156.0, 155.9, 114.3, 103.7, 82.9, 56.6, 56.1, 55.3, 50.6, 40.1, 38.9, 38.4, 37.6, 36.4, 36.1, 35.0, 29.4, 27.2, 26.2, 26.1, 25.9, 24.6, 20.7, 18.4, 18.3, −4.3, −4.4, −4.7, −4.8; IR (thin film) 2953, 2930, 1714, 1649, 1253 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{34}H_{62}O_3Si_2Na$ $(M+Na)^+$ $C_{34}H_{62}O_3Si_2$ 597.4135, observed 597.4137; $[\alpha]_D^{25}$ +59.9, $[\alpha]_{577}^{25}$ +62.2, $[\alpha]_{546}^{25}$ +70.8, $[\alpha]_{435}^{25}$ +141.8, $[\alpha]_{405}^{25}$ +181.3 (c = 1.0, CH_2Cl_2).

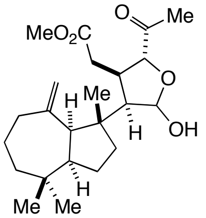


14

$C_{29}H_{50}O_5Si$

Mol. Wt. 506.7898

Tricarbonyl 14: To a mixture of **13** (16 mg, 0.028 mmol) in THF (0.3 mL) and H_2O (30 μL) at 0 °C was added NMO (4.9 mg, 0.042 mmol). The mixture was stirred for 5 min until the NMO dissolved. A 2.5% solution of OsO_4 in *t*-BuOH (27 μL, 0.0028 mmol) was added and the mixture was allowed to warm to rt. After 8 h, solid sodium sulfite (5 mg) was added and the mixture was stirred for an additional 5 min. The mixture was diluted with H_2O (2 mL) and Et_2O (2 mL). The layers were separated and the aqueous layer was washed with additional Et_2O (2 mL) to afford the crude α-hydroxy-ketone. To a solution of crude α-hydroxy-ketone in MeOH (0.015 mL) and benzene (0.015 mL) at 0 °C was added $Pb(OAc)_4$ (23 mg, 0.054 mmol). After 10 min, saturated aqueous $NaHCO_3$ (0.3 mL) was added to the yellow solution, and a brown precipitate was formed. After being stirred for 5 min, the mixture was diluted with Et_2O (2 mL) and passed through a glass pipette contained $NaSO_4$ on top of a short layer (~1 cm) of SiO_2 using Et_2O as an eluent. The resulting light yellow solution was concentrated. Rapid purification of the residue by silica gel chromatography (1→5% EtOAc/hexanes) gave tricarbonyl **14** (11 mg, 81%) as a colorless oil: Rf: 0.46 (10% EtOAc/hexanes); ^{1}H NMR (C_6D_6, 500 MHz) δ 9.94 (d, *J* = 2.7 Hz, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 4.32 (d, *J* = 2.7 Hz, 1H), 3.30 (s, 3H), 3.16 (m, 1H), 2.88 (dd, *J* = 17.8, 1.8 Hz, 1H), 2.82 (d, *J* = 2.4 Hz, 1H), 2.79 (d, *J* = 10.2 Hz, 1H), 2.73 (dd, *J* = 17.8, 10.2 Hz, 1H), 2.17 (s, 3H), 2.16 (m, 1H), 1.94 (m, 1H), 1.47 (m, 8H), 1.15 (m, 1H), 1.10 (s, 3H), 1.05 (s, 3H), 0.95 (s, 9H), 0.93 (s, 3H), −0.01 (s, 6H); ^{13}C NMR (C_6D_6, 125 MHz) δ 208.7, 204.1, 173.2, 153.4, 115.3, 81.6, 56.9, 56.6, 53.3, 51.4, 49.3, 39.2, 38.4, 38.0, 37.2, 36.2, 34.5, 33.9, 29.2, 26.5, 26.0, 25.9, 25.8, 22.9, 18.4, −4.7, −5.3; IR (thin film) 2952, 2848, 1732, 1695, 1254, 839 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{29}H_{50}O_5Si$ $(M+Na)^+$ 529.3325, observed 529.3323; $[\alpha]_D^{25}$ +19.8, $[\alpha]_{577}^{25}$ +22.6, $[\alpha]_{546}^{25}$ +24.4, $[\alpha]_{435}^{25}$ +46.2, $[\alpha]_{405}^{25}$ +62.5 (*c* = 0.2, $CHCl_3$).



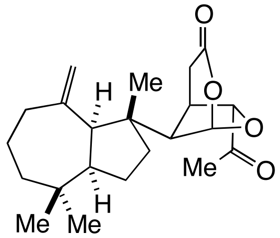
15

$C_{23}H_{36}O_5$

Mol. Wt. 392.5289

Lactol 15: To a solution of aldehyde **14** (13 mg, 0.026 mmol) in THF (0.25 mL) at 0 °C was added 1M TBAF in THF (28 μL, 0.028 mmol). The solution was maintained at 0 °C for 30 min and then SiO_2 (~200 mg) was added. The mixture was stirred for 5 min, loaded onto an SiO_2 column, and eluted with 20–40% EtOAc/hexanes to afford **15** (7.0 mg, 69%) as a clear oil and a ~10:1 mixture of unassigned lactol diastereomers: R_f: 035 (30% EtOAc/hexanes); ^{1}H NMR (C_6D_6, 500 MHz, for major isomer) δ 5.43 (bs, 1H), 4.76 (d, *J* = 2.1 Hz, 1H), 4.71 (s, 1H), 4.45 (bs, 1H), 4.38 (s, 1H), 3.43 (s, 3H), 2.89 (m, 1H), 2.59 (dd, *J* =

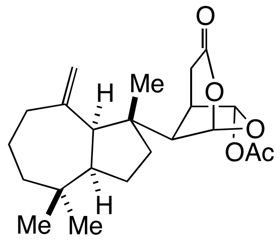
16.5, 2.8 Hz, 1H), 2.40 (dd, *J* = 10.2, 5.6 Hz, 1H), 2.25 (t, *J* = 5.3 Hz, 1H), 2.20 (dd, *J* = 12.3, 5.0 Hz, 1H), 1.91 (s, 3H), 1.83 (m, 1H), 1.50 (m, 9H), 1.23 (m, 1H), 1.04 (s, 3H), 0.94 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 210.2, 172.9, 154.1, 114.7, 101.4, 88.1, 58.9, 55.4, 54.1, 51.3, 46.6, 42.1, 38.1, 38.0, 37.7, 36.2, 34.6, 34.4, 28.9, 27.3, 25.9, 25.7, 24.2; IR (thin film) 2954, 2848, 1736, 1437, 1260 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{23}H_{36}O_5Na$ $(M+Na)^+$ 415.2460, observed 415.2458; $[\alpha]_D^{25}$ +20.6, $[\alpha]_{577}^{25}$ +17.6, $[\alpha]_{546}^{25}$ +18.8, $[\alpha]_{435}^{25}$ +29.3, $[\alpha]_{405}^{25}$ +35.4 (*c* = 0.3, $CHCl_3$).



17
$C_{22}H_{32}O_4$
Mol. Wt. 360.4871

6-acyl-2,7-dioxabicyclo[3.2.1]octan-3-one (17) To a solution of **15** (4.5 mg, 0.011 mmol) in CH_2Cl_2 (200 μL) at −78 °C was added DAST (3.0 μL, 0.017 mmol). After 10 min, saturated aqueous $NaHCO_3$ (1 mL) and CH_2Cl_2 (1 mL) were added and the layers were separated. The layers were separated and the aqueous layer was washed with additional CH_2Cl_2 (2 × 2 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated to yield crude **16** as clear oil and a ~5:1 mixture of unassigned lactol diastereomers. Characteristic ^{1}H-NMR and M.S. data for **16**: R_f: 0.37, 0.44 (30% EtOAc/hexanes); ^{1}H NMR (C_6D_6, 500 MHz, for major isomer) δ 5.96 (dd, *J* = 57, 2.4 Hz, 1H), 4.68 (s, 1H), 4.66 (s, 1H), 4.52 (s, 1H), 3.29 (s, 3H), 3.00 (m, 1H), 2.86 (d, *J* = 8.0 Hz, 1H), 2.85 (s, 1H), 2.72 (m, 2H), 2.20 (m, 2H), 1.96 (s, 3H), 1.86 (m, 2H), 1.44 (m, 6H), 1.13 (m, 2H), 0.94 (s, 3H), 0.91 (s, 3H), 0.86 (s, 3H); HRMS (ESI/TOF) calculated for $C_{23}H_{34}O_4F$ $(M+Na)^+$ 383.2198, observed 383.2202. Crude **16** was dissolved in EtOH (200 μL) and 1N NaOH was added (22 μL, 0.022 mmol). The mixture was stirred for 1 h at r.t. and 1N HCl (4 mL) and CH_2Cl_2 (2 mL) was added The layers were separated and the aqueous layer was washed with additional CH_2Cl_2 (5 × 2 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated to yield the crude carboxylic acid, which was used without further purification. The crude acid was dissolved in benzene and concentrated (3×). The acid was then dissolved in DMF (300 μL) and $SnCl_2$ (3.0 mg, 0.017 mmol) was added. The mixture was stirred at rt during which time a clear solution was formed. After 18 h, saturated aqueous $NaHCO_3$ (2 mL) and CH_2Cl_2 (2 mL) were added. The layers were separated and the aqueous layer was washed with additional CH_2Cl_2 (2 × 2 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (20→30% EtOAc/hexanes) gave ketone **17** (3.5 mg, 76%) as a film: R_f: 0.46 (30% EtOAc/hexanes); ^{1}H

NMR (C_6D_6, 500 MHz) δ 5.53 (d, *J* = 1.8 Hz, 1H), 4.77 (d, *J* = 1.9 Hz, 1H), 4.50 (d, *J* = 1.9 Hz, 1H), 3.62 (s, 1H), 2.73 (m, 1H), 2.66 (dd, *J* = 18.9, 5.0 Hz, 1H), 2.61 (d, *J* = 9.4 Hz, 1H), 2.25 (m, 1H), 2.21 (d, *J* = 19.2 Hz, 1H), 1.88 (s, 3H), 1.79 (m, 2H), 1.67 (m, 3H), 1.46 (m, 4H), 1.25 (m, 2H), 1.06 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 205.4, 167.2, 153.2, 114.7, 100.9, 89.2, 57.8, 53.9, 51.3, 45.7, 38.2, 37.7, 36.0, 35.9, 35.2, 34.3, 30.2, 28.5, 26.9, 26.4, 26.1, 23.8; IR (thin film) 2922, 1755, 1712, 1377, 945 cm^{-1}; HRMS (ESI/TOF) calculated for $C_{22}H_{32}O_4$ $(M+Na)^+$ 383.2198, observed 383.2202; $[\alpha]_D^{25}$ −6.8, $[\alpha]_{577}^{25}$ −5.8, $[\alpha]_{546}^{25}$ −13.4, $[\alpha]_{435}^{25}$ −17.2, $[\alpha]_{405}^{25}$ −26.6. (*c* = 0.23, CH_2Cl_2).



1

$C_{22}H_{32}O_5$

Mol. Wt. 376.4865

Aplyviolene (1): To a stirred mixture of **17** (3.0 mg, 0.0083 mmol) and $NaHCO_3$ (17 mg, 0.21 mmol) in CH_2Cl_2 (150 μL) at 0 °C was added *m*-CPBA (1.8 mg, 0.012 mmol) in CH_2Cl_2 (150 μL). The stirred mixture was maintained at 0 °C. After 18 h, saturated aqueous sodium thiosulfate was added and the mixture was stirred at rt for 30 min. The mixture was diluted with H_2O (0.5 mL) and CH_2Cl_2 (1 mL) and the layers were separated. The aqueous layer was washed with additional CH_2Cl_2 (2 × 2 mL). The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated. Purification of the residue by silica gel chromatography (1→2% EtOAc/hexanes) gave **1** (1.9 mg, 61%) as a film. The NMR and IR data was good match for published data.[5] However, we found a slight frame shift between the published ^{1}H NMR data and our own suggesting a slightly different benzene solvent reference value was used. The carbon data matched almost exactly (Table S1), however it was found that to observe the C20 carbon (δ 34.3), the sample had to be heated to 40 °C. Our ^{1}H-NMR spectra matched precisely with that obtained by the Gerwick lab when they kindly purified a small sample (~30 μg) for us from the original sample from the Faulkner isolation studies (Figure S1).[6] The NMR data we obtained at 40°C follows: ^{1}H NMR (C_6D_6, 500 MHz, 40 °C) δ 6.05 (s, 1H), 5.48 (d, *J* = 1.6 Hz, 1H), 4.69 (d, *J* = 2.1 Hz, 1H), 4.41 (d, *J* = 2.1 Hz, 1H), 2.51 (d, *J* = 9.3 Hz, 1H), 2.47 (dd, *J* = 19.5, 5.8 Hz, 1H), 2.29 (m, 1H), 2.15 (m, 1H), 2.12 (d, *J* = 19.5 Hz, 1H), 2.02 (m, 1H), 1.71 (m, 1H), 1.57 (m, 3H), 1.53 (s, 3H), 1.37 (m, 4H), 1.15 (m, 2H), 0.92 (s, 3H), 0.83 (s, 3H), 0.80 (s, 3H); ^{13}C NMR

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[5] Hambley, T.W.; Poiner, A.; Taylor, W. *Aus. J. Chem.* **1990**, *43*, 1861.

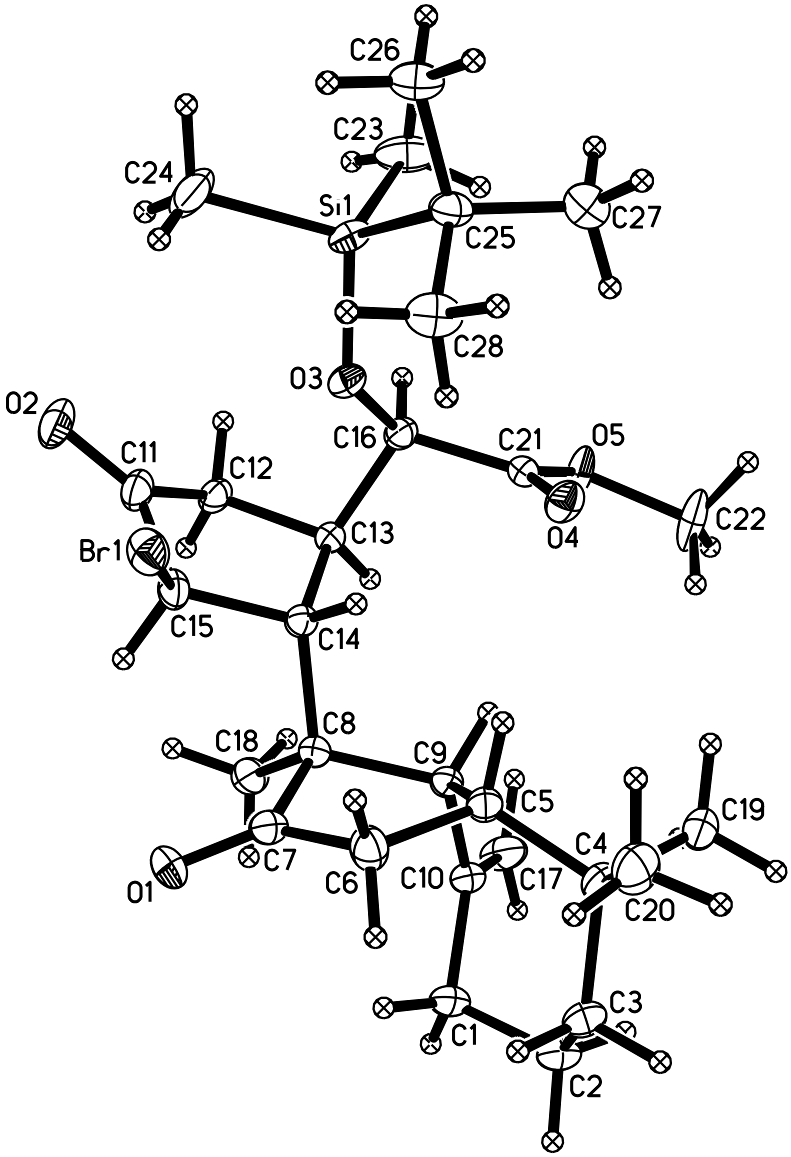
[6] Bobzin, S. C.; Faulkner, D. J. *J. Nat. Prod.* **1991**, *54*, 225.

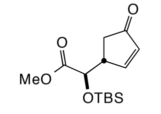
(C_6D_6, 125 MHz) δ 168.5, 166.4, 153.5, 114.7, 101.1, 100.6, 58.1, 54.3, 49.6, 45.8, 38.7, 38.5, 38.2, 37.8, 36.1, 34.3, 33.3, 28.6, 27.0, 26.1, 23.9, 20.5.

Table S1. Comparison of published and synthetic C^{13} spectra

carbon #	Published[5]	Synthetic
CO**Me**	21.1	20.5
18	23.8	23.9
19	26.0	26.1
6	26.9	27.0
2	28.3	28.6
12	33.1	33.3
20	34.3	34.3
4	36.0	36.1
1	37.6	37.8
3	38.0	38.2
13	38.2	38.5
7	38.5	38.7
8	45.5	45.8
14	49.2	49.6
5	54.1	54.3
9	57.8	58.1
15	100.8	100.6
16	100.9	101.1
17	114.7	114.7
10	153.1	153.5
11	167.7	166.4
CO	169.5	168.5

X-ray structure of 7 (CCDC-840473)





S1

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DE                  6.00 usec
TE                 298.0 K
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MCWRK         0.01500000 sec

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PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
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WDW                   EM
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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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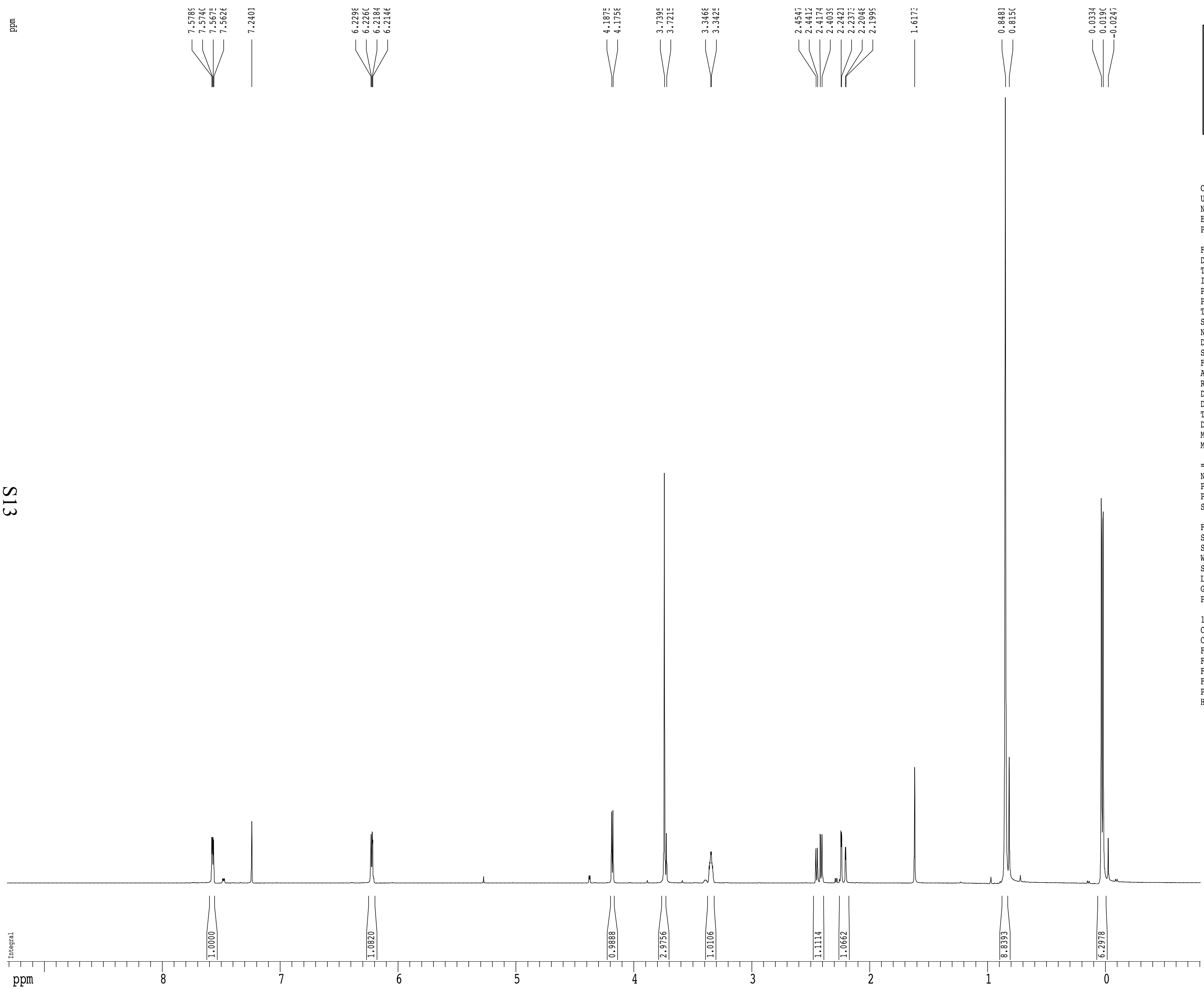
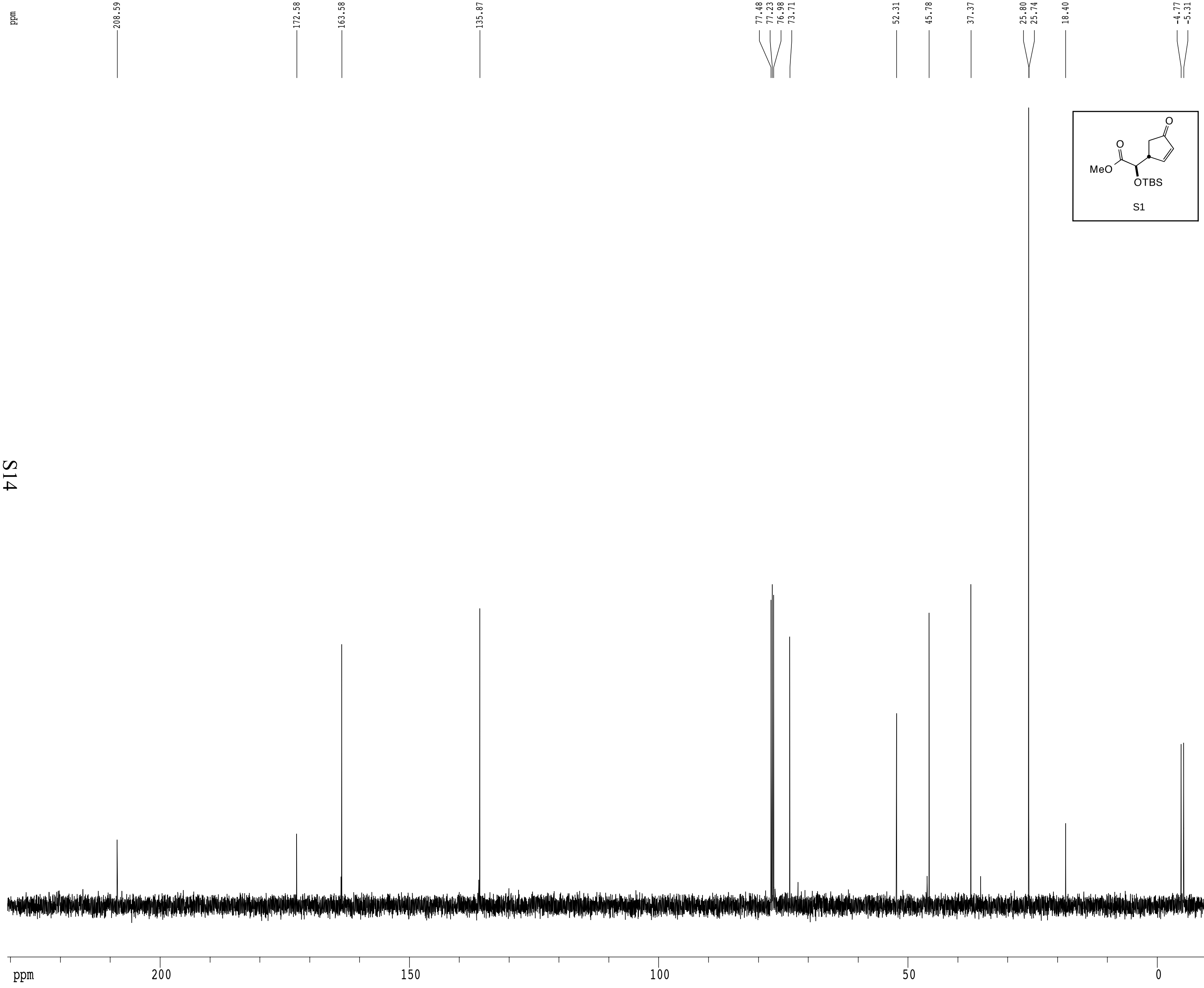


Z-restored spin-echo 13C spectrum with 1H decoupling



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DS                    16
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DE                  6.00 usec
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MCWRK         0.01500000 sec
P2                 31.00 usec

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P12              2000.00 usec
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PL1                -1.00 dB
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SP1                 3.20 dB
SP2                 3.20 dB
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SPOFF2              0.00 Hz

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

====== GRADIENT CHANNEL =====
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GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
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GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
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1D NMR plot parameters
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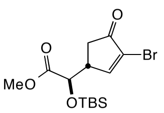

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DS                     2
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FIDRES          0.098043 Hz
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RG                     4
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
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MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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

F2 - Processing parameters
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SF           500.2200415 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
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CY                 15.00 cm
F1P                8.997 ppm
F1               4500.55 Hz
F2P               -0.518 ppm
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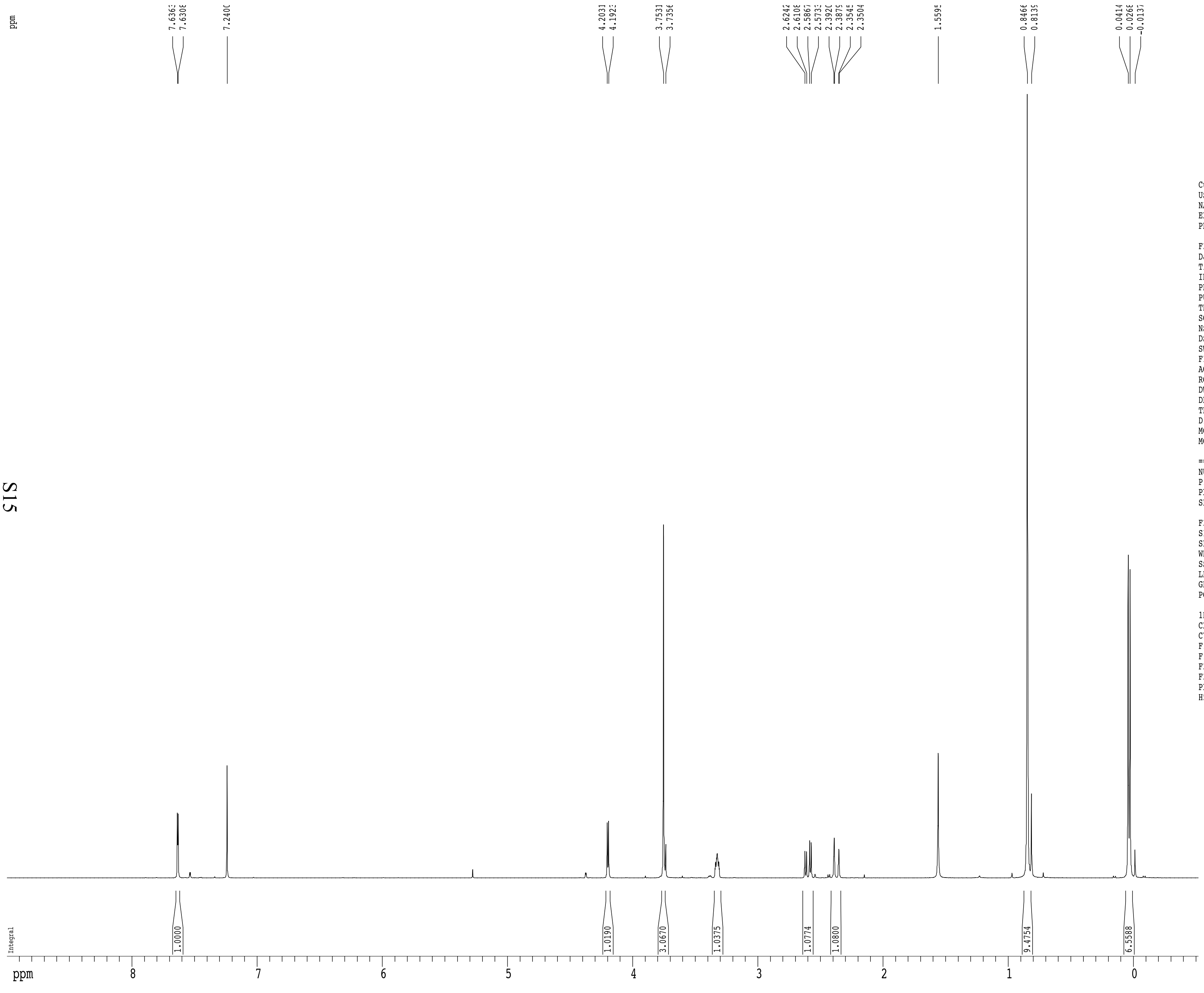
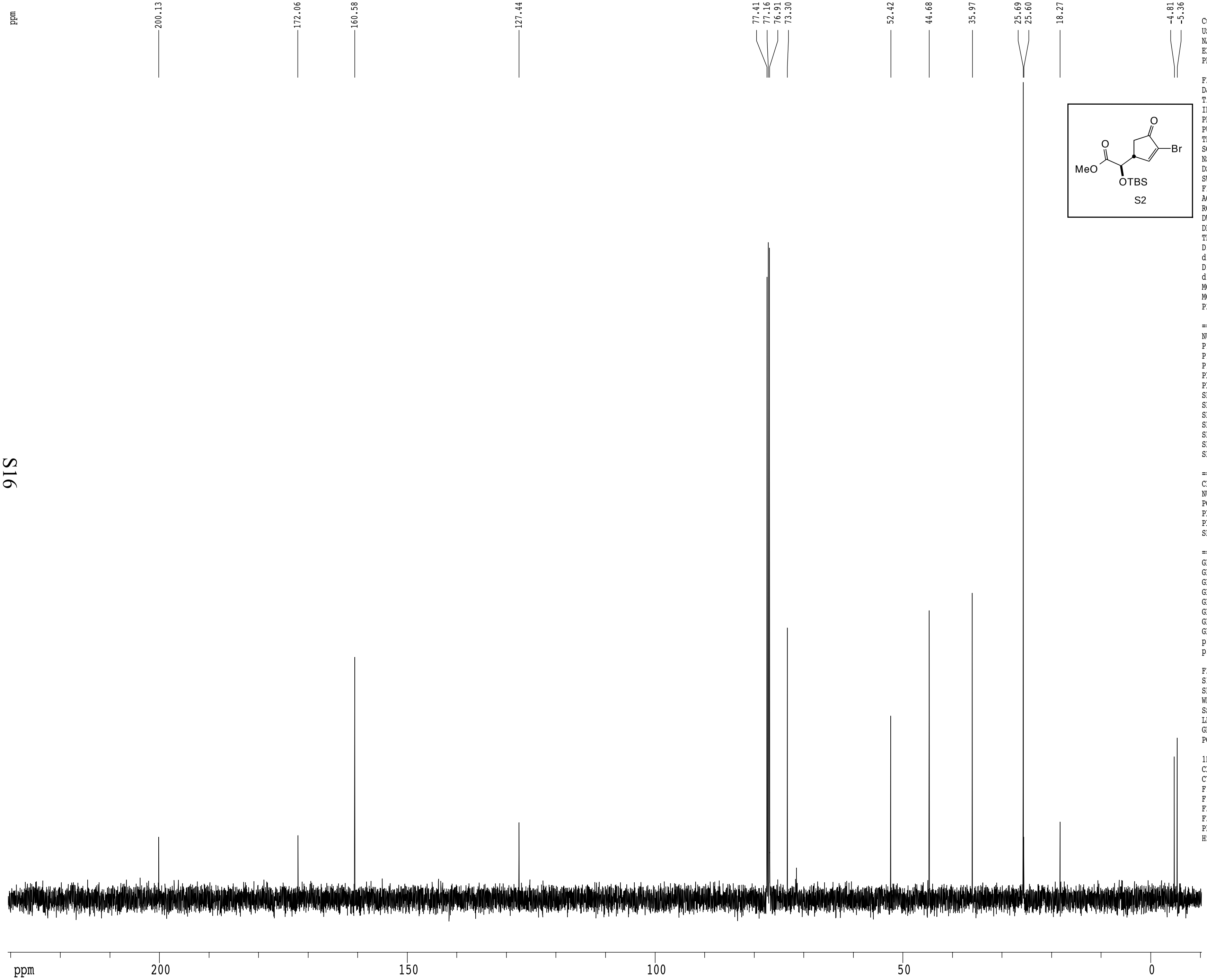


Z-restored spin-echo 13C spectrum with 1H decoupling



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NS                   123
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
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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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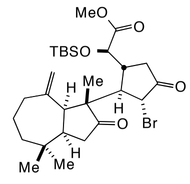
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

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              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



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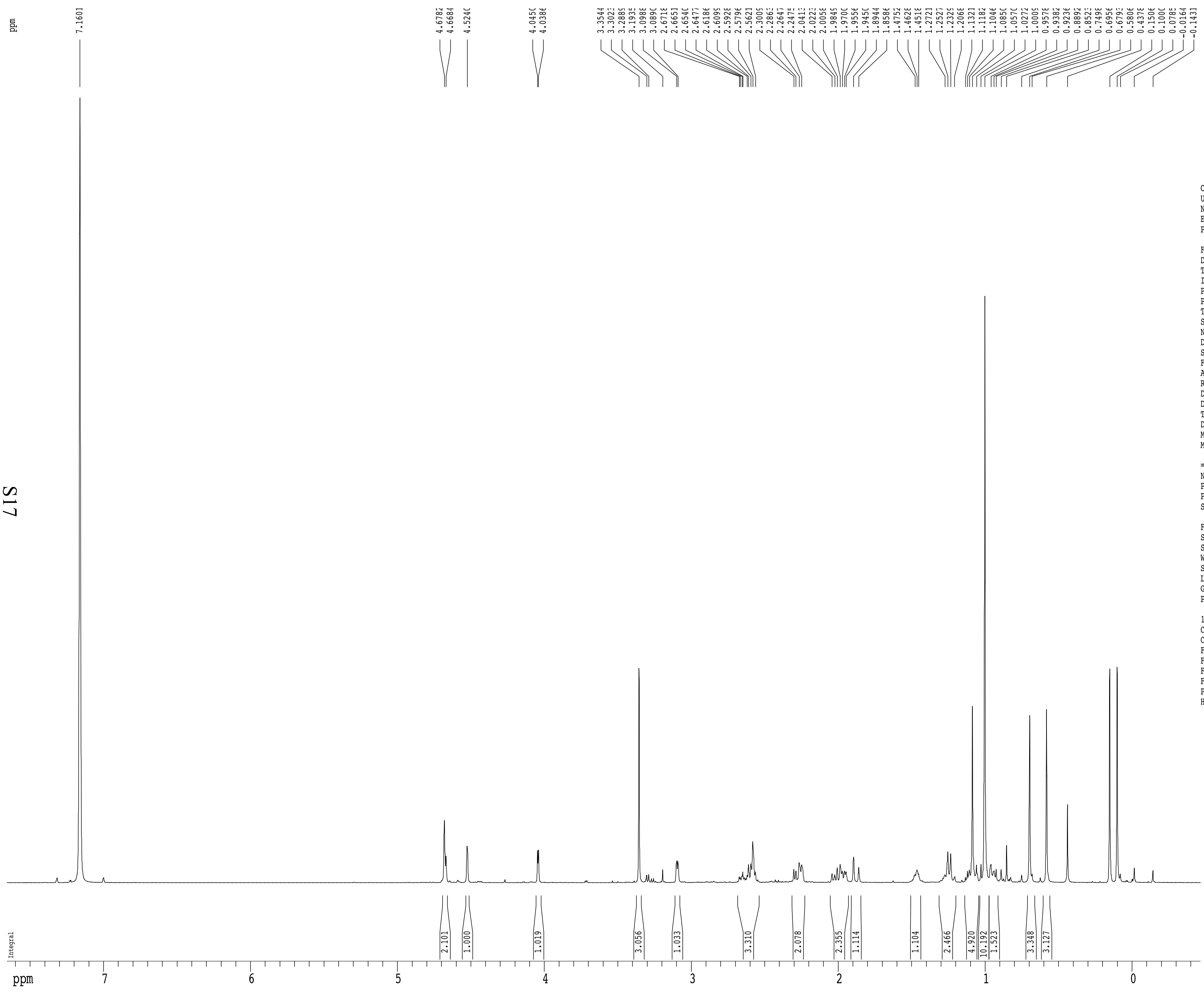
```
Current Data Parameters
USER              schner
NAME         mjs4-70-3-3c13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110511
Time               14.35
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

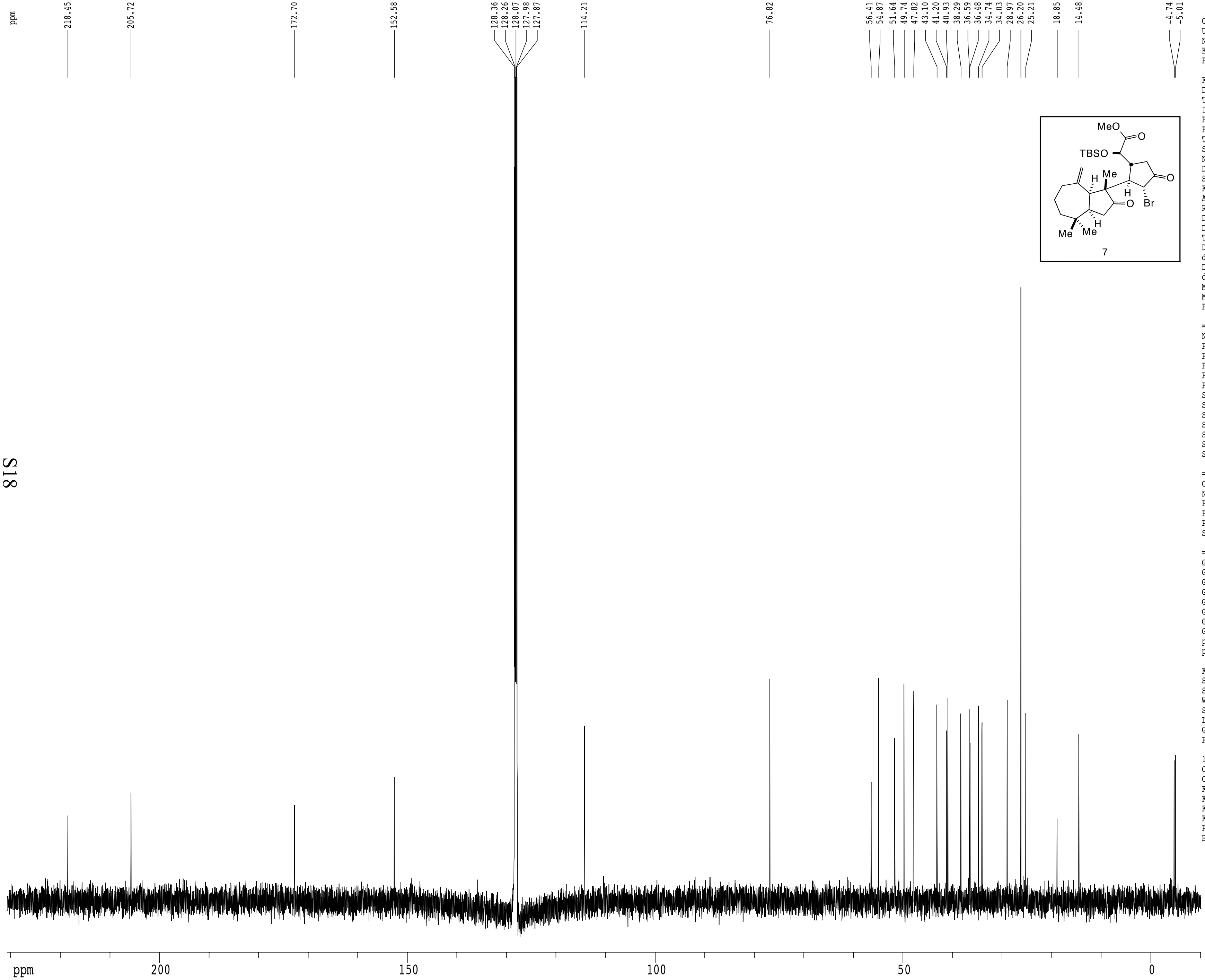
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200013 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                7.656 ppm
F1               3829.45 Hz
F2P               -0.466 ppm
F2               -233.16 Hz
PPMCM            0.35621 ppm/cm
HZCM           178.18475 Hz/cm
```



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



```
Current Data Parameters
USER                schner
NAME       mjs4-70-3-3cl3
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110511
Time                 14.36
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     209
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

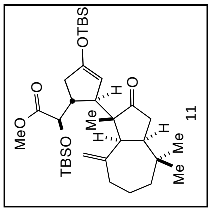
======== CHANNEL f1 ========
NUC1                   13C
P1                   15.50 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   3.20 dB
SP2                   3.20 dB
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             125.7803747 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                  200.00 cm
F1P                230.637 ppm
F1                29009.67 Hz
F2P                -10.287 ppm
F2                -1293.96 Hz
PPMCM             10.56688 ppm/cm
HZCM            1329.10657 Hz/cm
```



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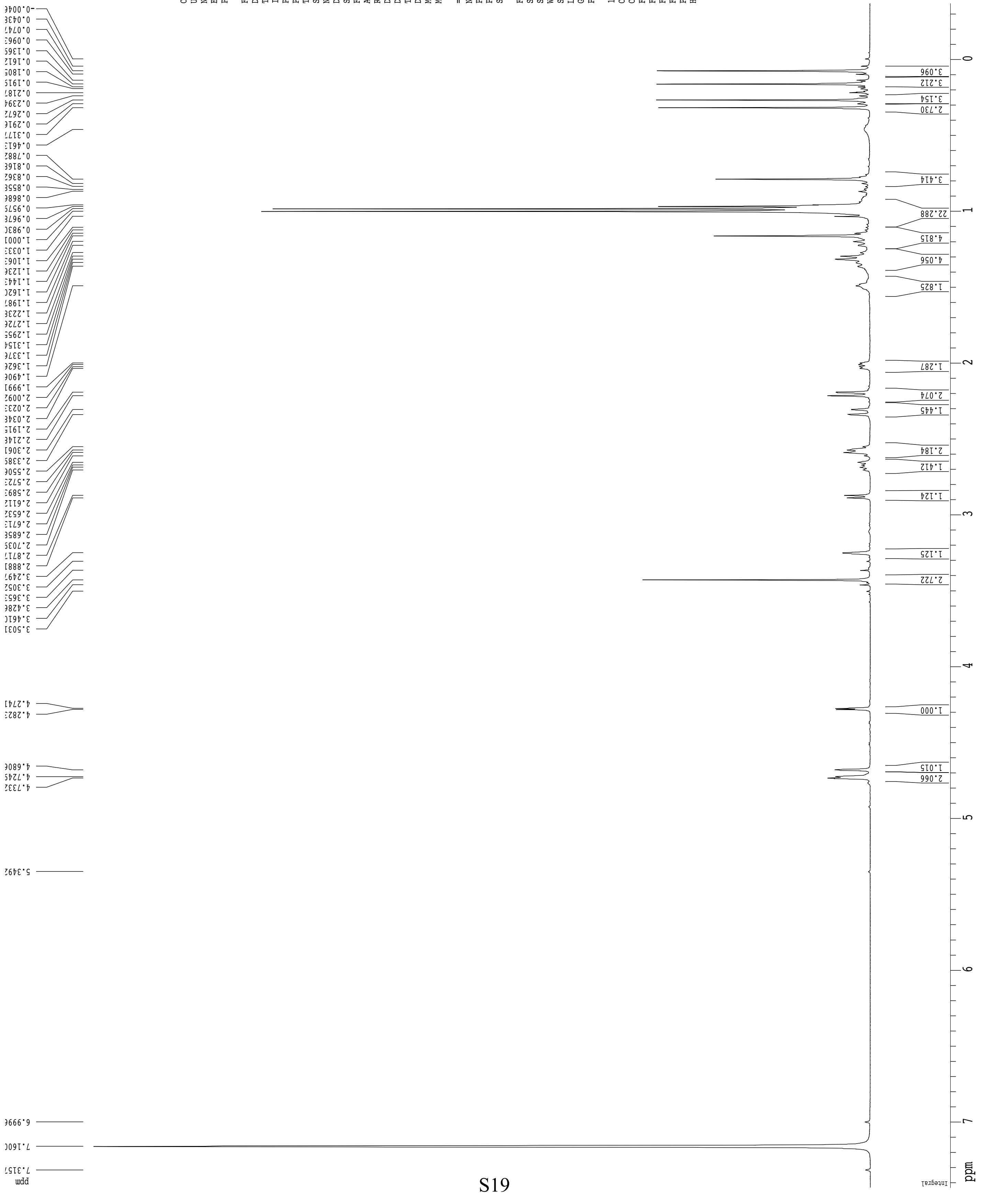
```
Current Data Parameters
USER              schner
NAME            mjs4-47-3
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110427
Time                11.45
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                    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

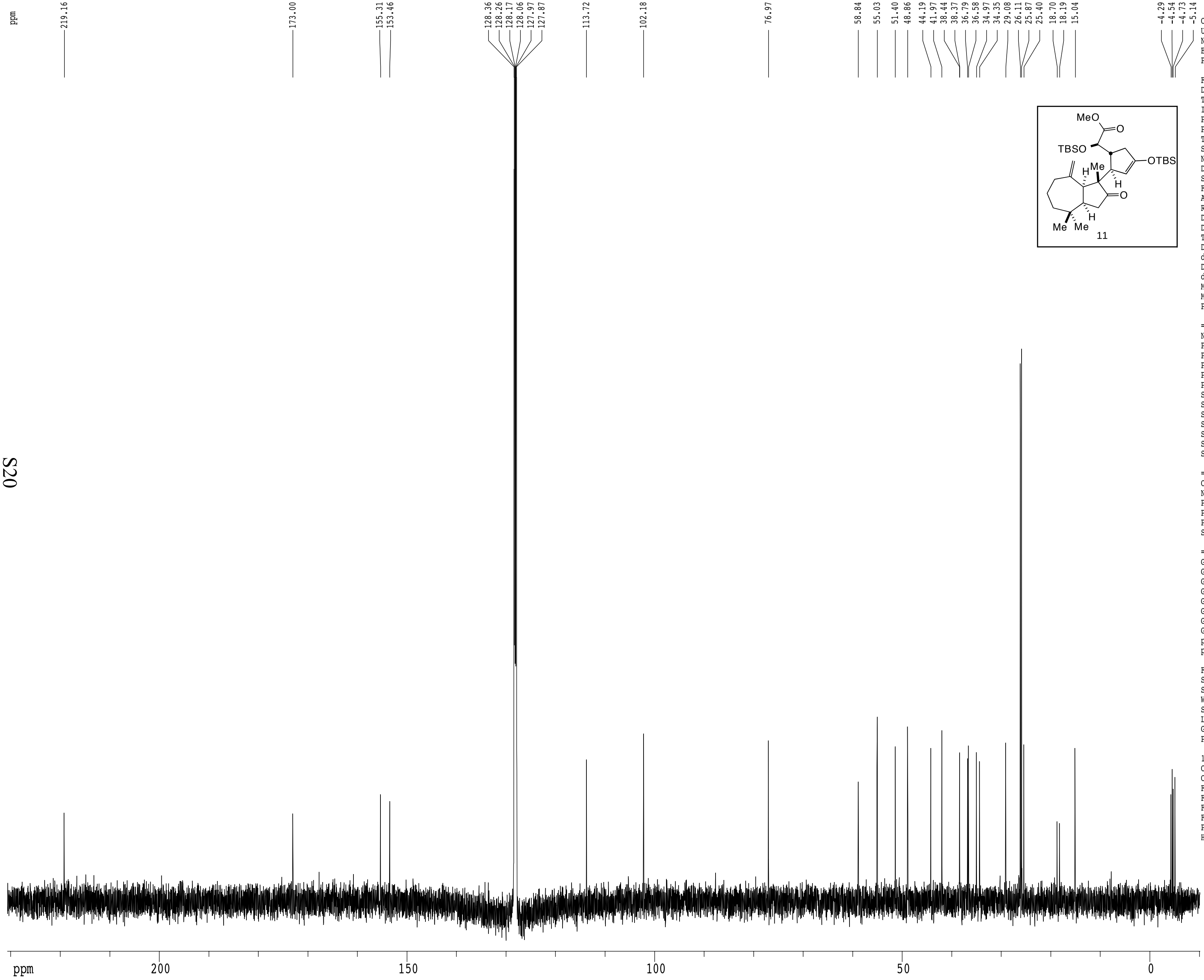
======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200012 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                 7.431 ppm
F1                3717.17 Hz
F2P                -0.370 ppm
F2                -184.86 Hz
PPMCM             0.34213 ppm/cm
HZCM            171.14188 Hz/cm
```



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



```
Current Data Parameters
USER              schner
NAME           mjs4-47-3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110427
Time               11.48
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   141
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  2048
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

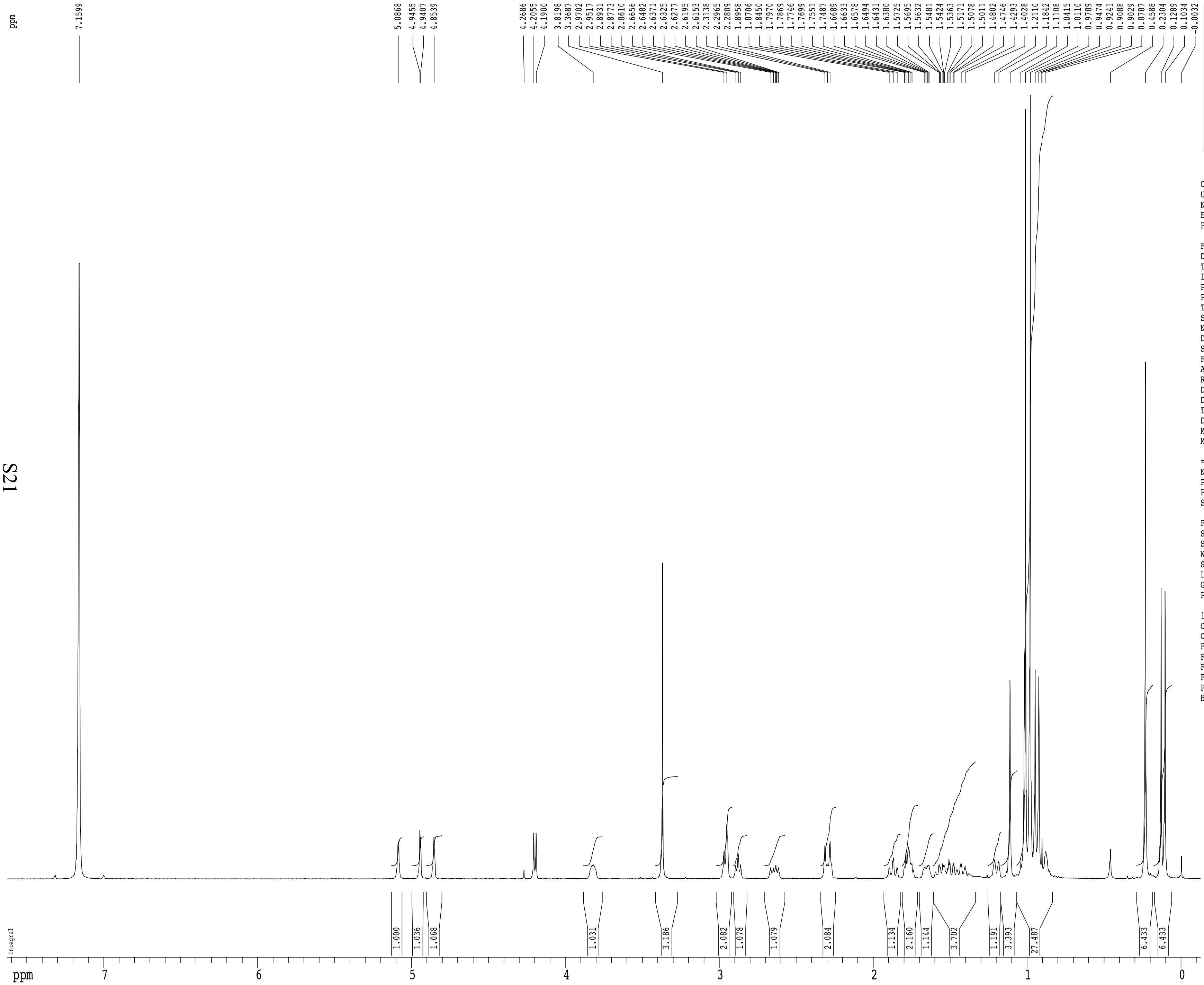
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2        500.2225011 MHz

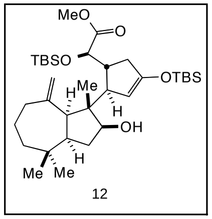
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803747 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                200.00 cm
F1P              230.637 ppm
F1              29009.67 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10657 Hz/cm
```

1H spectrum





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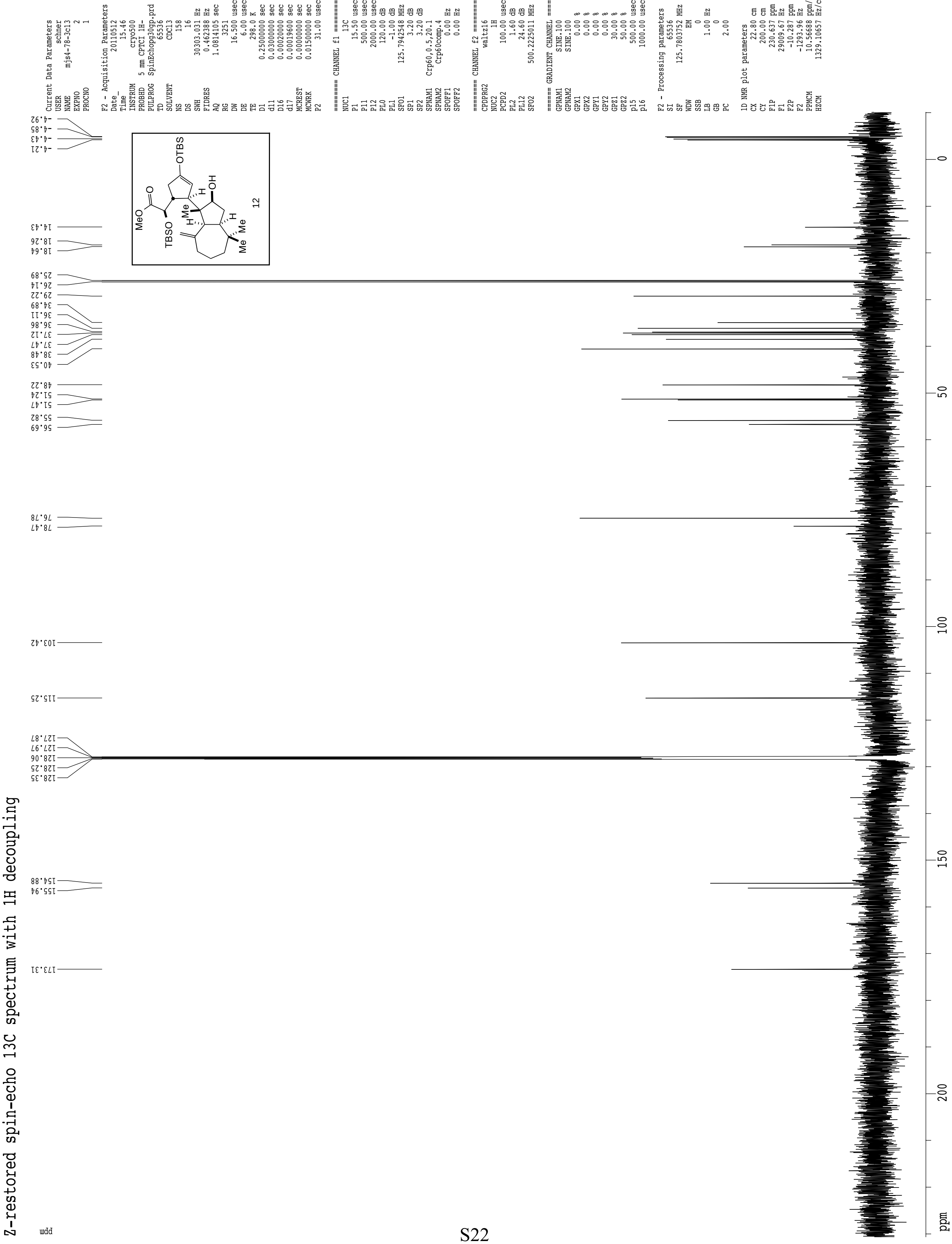
```
Current Data Parameters
USER               schner
NAME          mjs4-78-3c13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110512
Time                15.45
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT              C6D6
NS                      5
DS                      2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 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

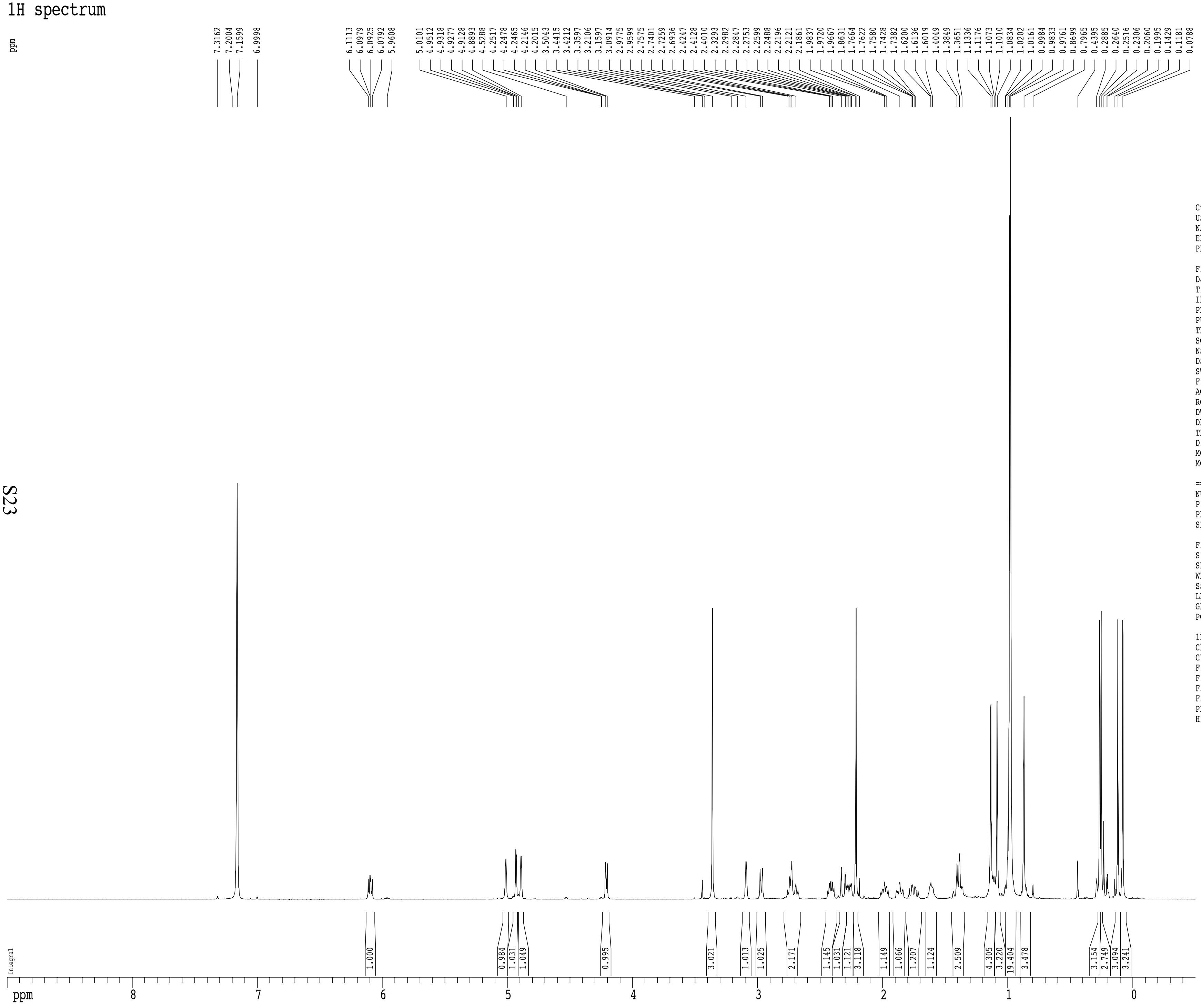
F2 - Processing parameters
SI                  65536
SF            500.2200012 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

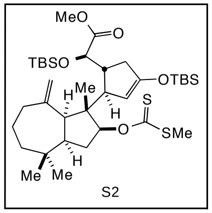
1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 7.627 ppm
F1                3815.39 Hz
F2P                -0.126 ppm
F2                 -63.05 Hz
PPMCM             0.34006 ppm/cm
HZCM            170.10709 Hz/cm
```



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

1H spectrum





S2

```
Current Data Parameters
USER              schner
NAME            mjs4-62-3
EXPNO                  1
PROCNO                 1

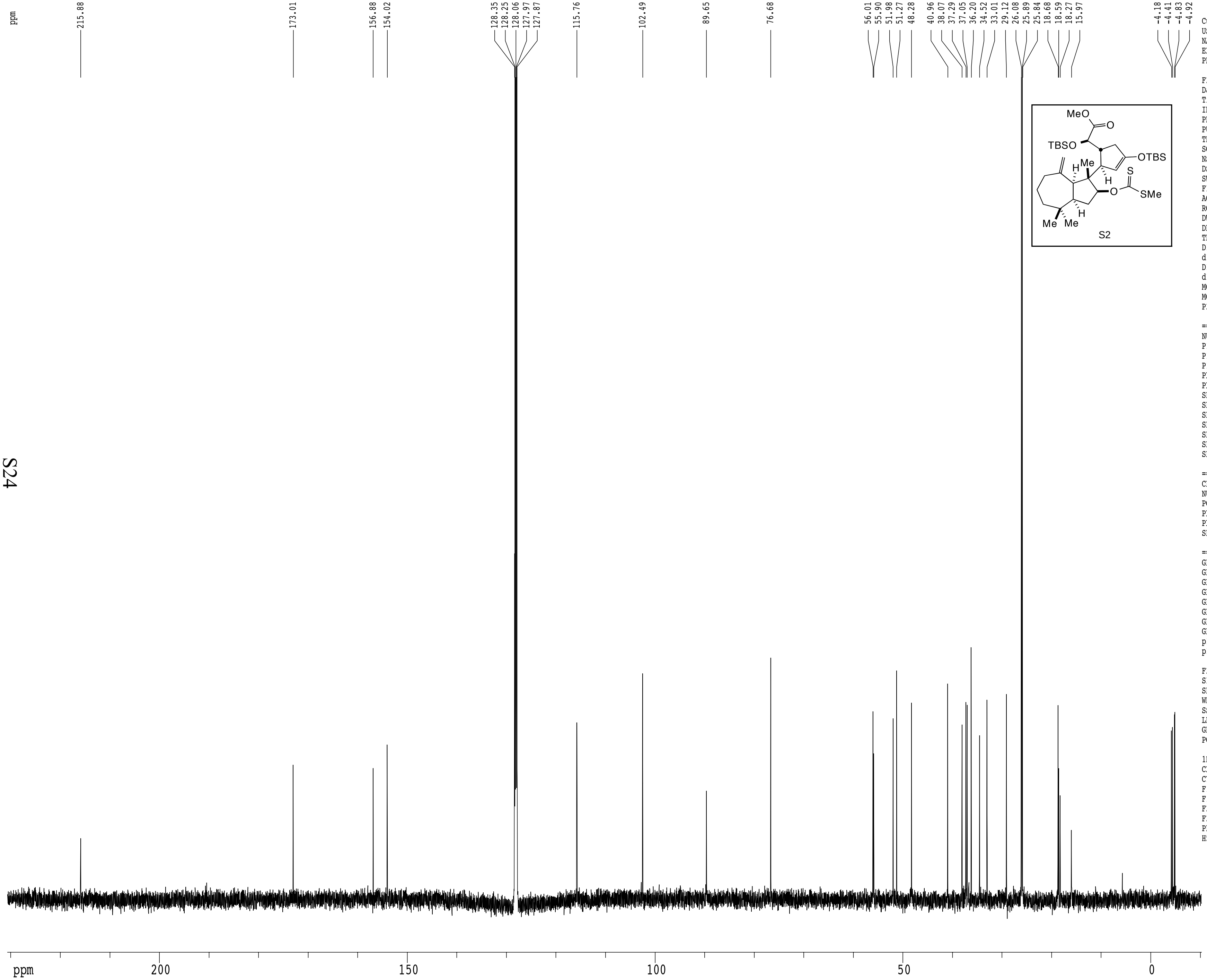
F2 - Acquisition Parameters
Date_           20110504
Time               11.38
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   3.2
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          500.2200558 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  0.25

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42503 Hz/cm
```

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



```
Current Data Parameters
USER              schner
NAME           mjs4-62-3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110504
Time               11.41
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   131
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                2580.3
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

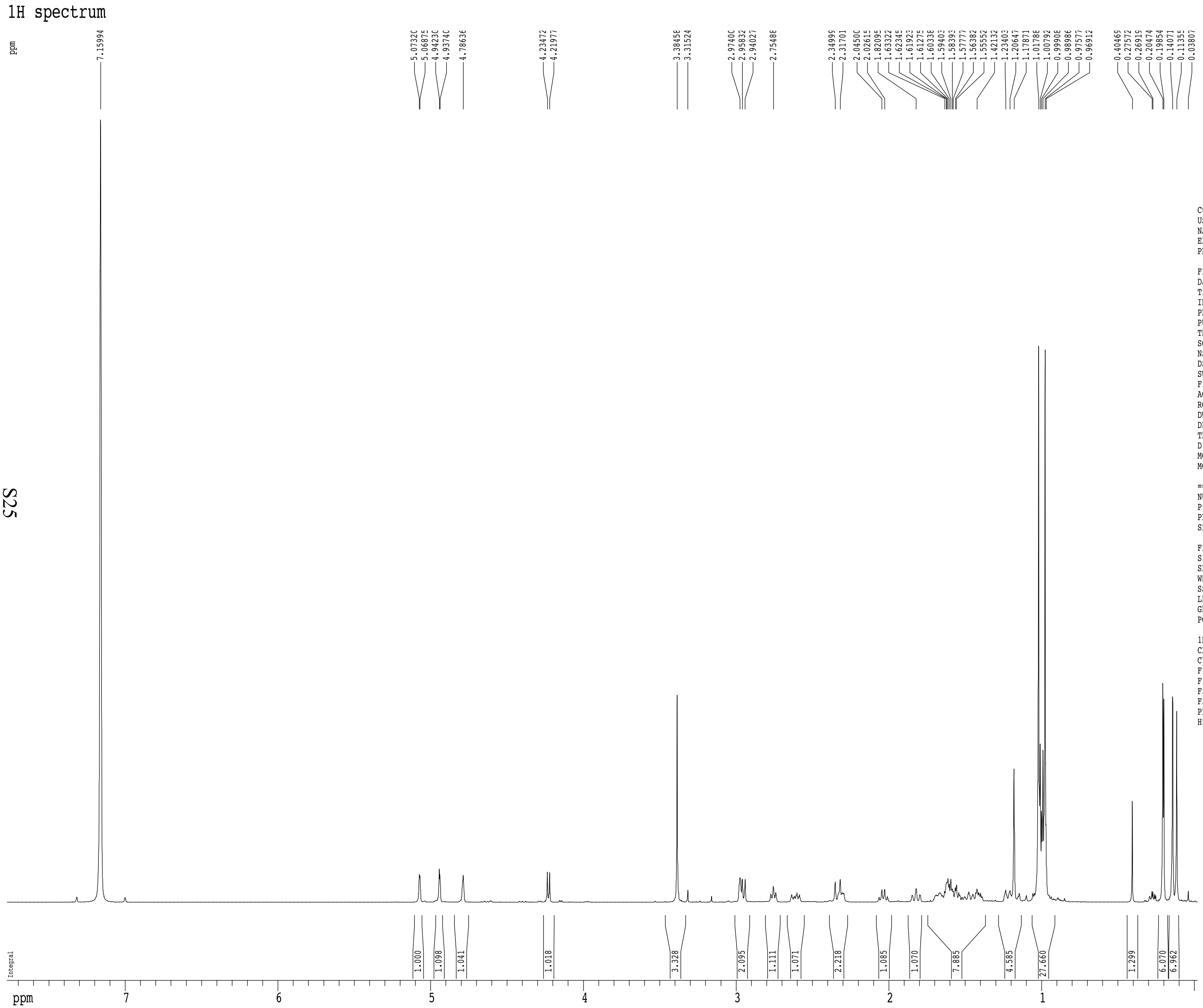
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

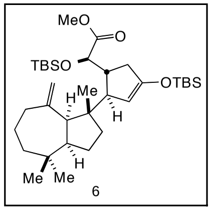
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803891 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              230.637 ppm
F1              29009.67 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10669 Hz/cm
```

1H spectrum





6

```
Current Data Parameters
USER              schner
NAME         mjs4-80-3c13
EXPNO                  1
PROCNO                 1

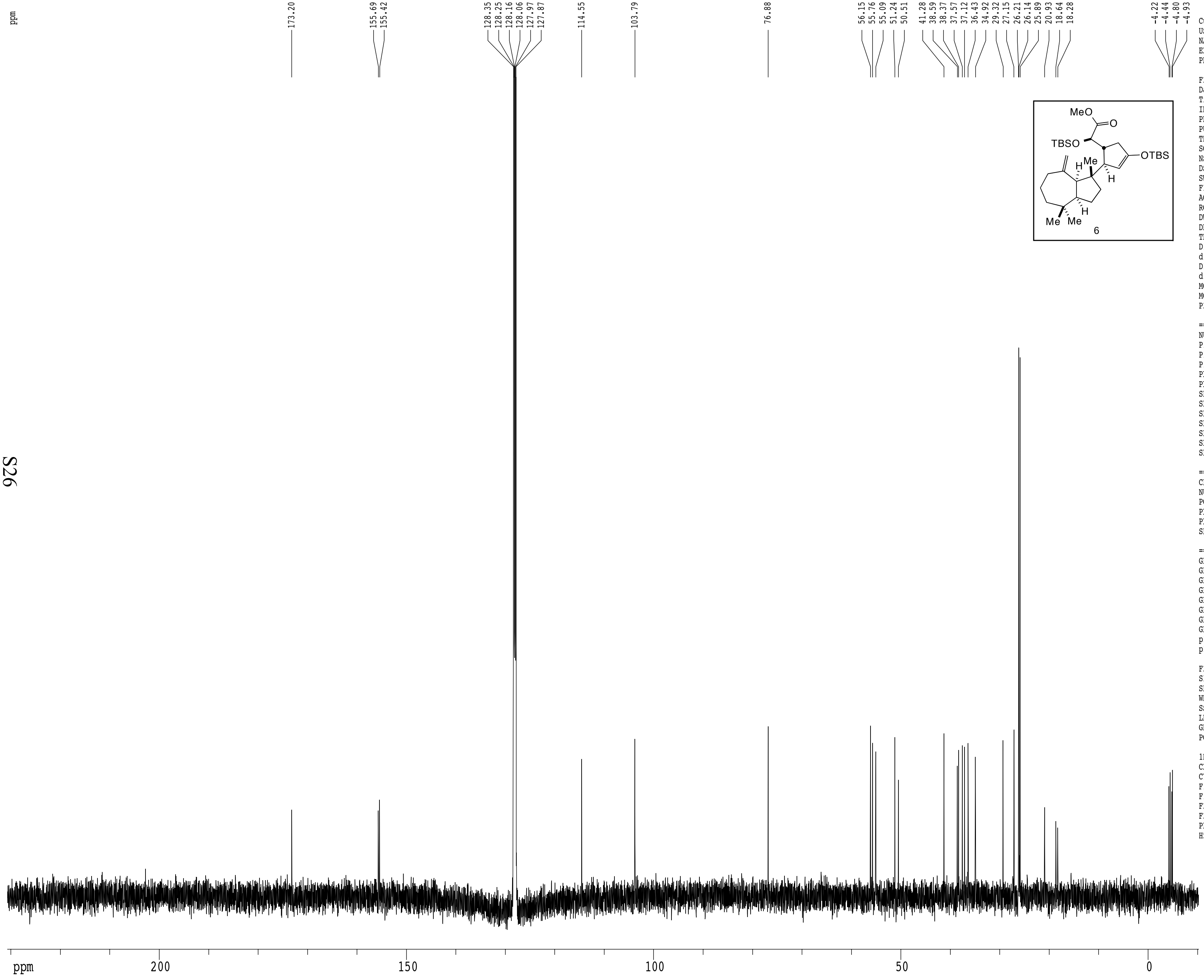
F2 - Acquisition Parameters
Date_           20110517
Time                8.01
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 sec
RG                  71.8
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           500.2200563 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                7.773 ppm
F1               3888.22 Hz
F2P               -0.020 ppm
F2                 -9.91 Hz
PPMCM            0.34179 ppm/cm
HZCM           170.97058 Hz/cm
```

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



```
Current Data Parameters
USER              schner
NAME         mjs4-80-3c13
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110517
Time                8.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   197
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0814105 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                 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

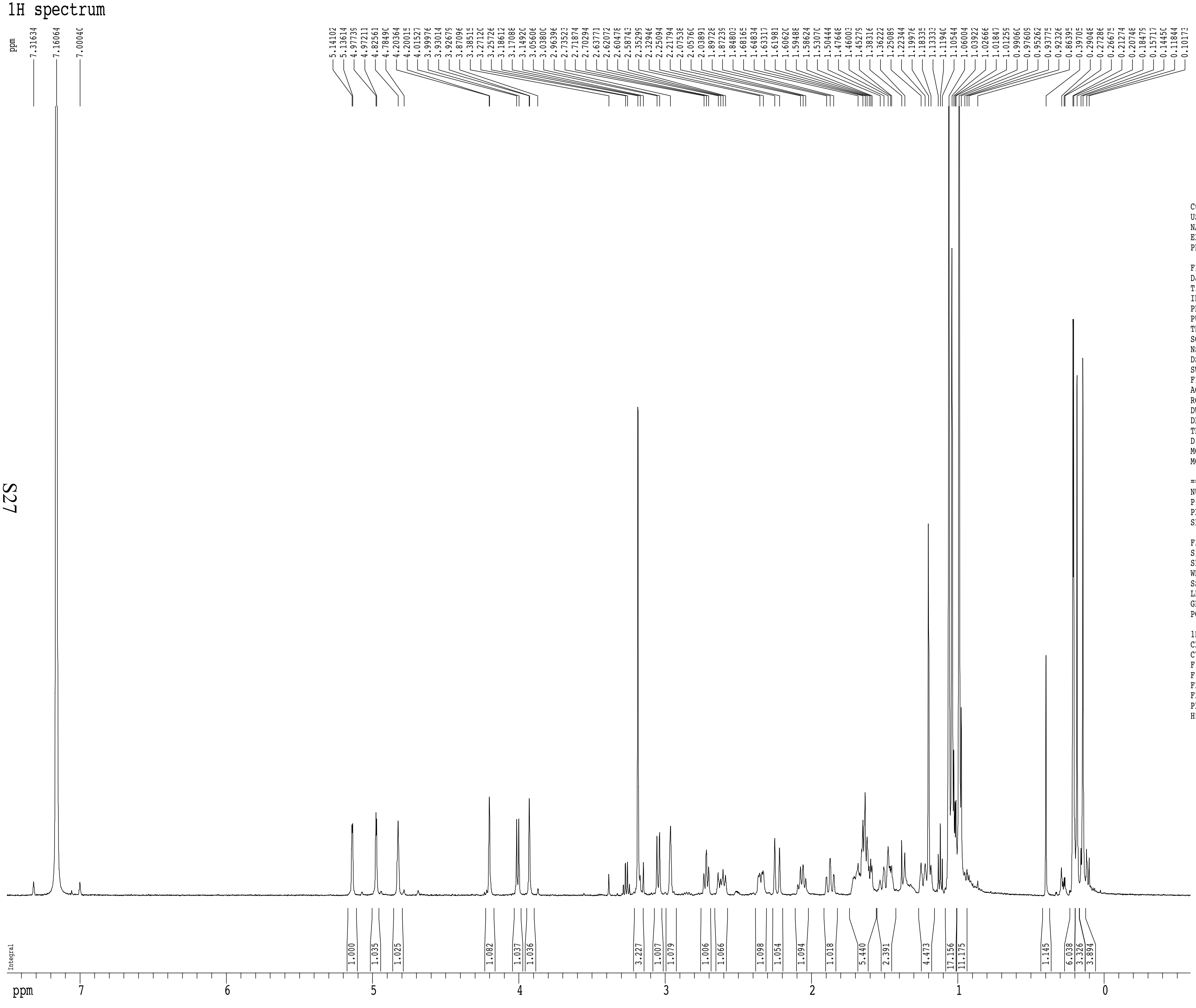
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

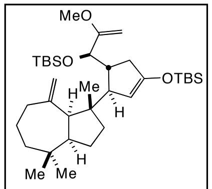
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803891 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                200.00 cm
F1P              230.698 ppm
F1              29017.29 Hz
F2P              -10.222 ppm
F2              -1285.73 Hz
PPMCM           10.56667 ppm/cm
HZCM          1329.08032 Hz/cm
```

1H spectrum





S3

```
Current Data Parameters
USER              schner
NAME          mjs4-81-3
EXPNO                  1
PROCNO                 1

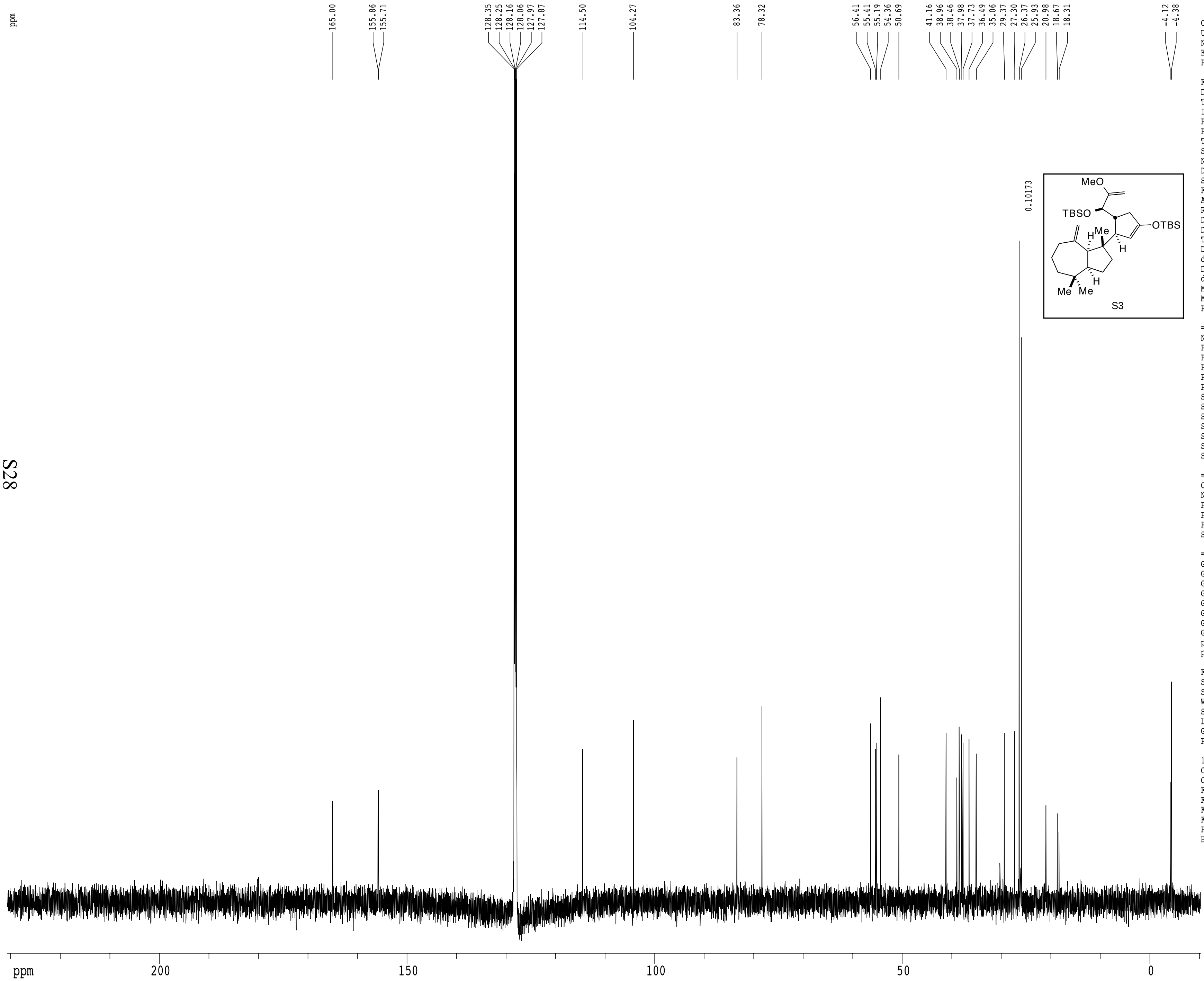
F2 - Acquisition Parameters
Date_           20110517
Time               13.20
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    15
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 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           500.2200560 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                7.498 ppm
F1               3750.65 Hz
F2P               -0.590 ppm
F2               -295.13 Hz
PPMCM            0.35474 ppm/cm
HZCM           177.44673 Hz/cm
```

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



```
Current Data Parameters
USER                schner
NAME             mjs4-81-3
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110517
Time                 13.24
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     199
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0814105 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                   31.00 usec

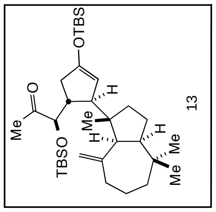
======== CHANNEL f1 ========
NUC1                   13C
P1                   15.50 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   3.20 dB
SP2                   3.20 dB
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             125.7803891 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                  200.00 cm
F1P                230.637 ppm
F1                29009.67 Hz
F2P                -10.287 ppm
F2                -1293.96 Hz
PPMCM             10.56688 ppm/cm
HZCM            1329.10669 Hz/cm
```



13

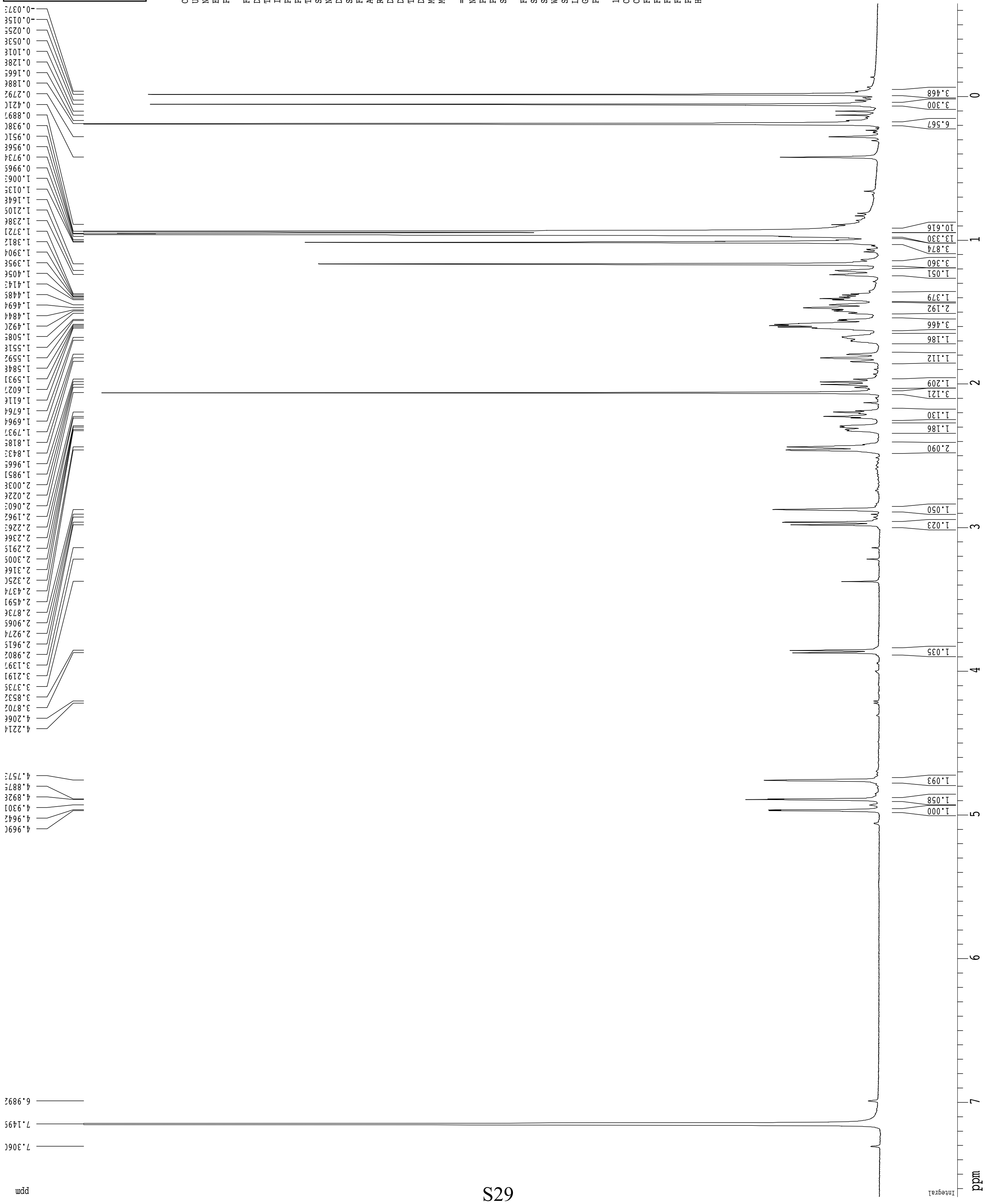
```
Current Data Parameters
USER              schner
NAME            mjs4-82-3
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110518
Time                9.36
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             5.0999398 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

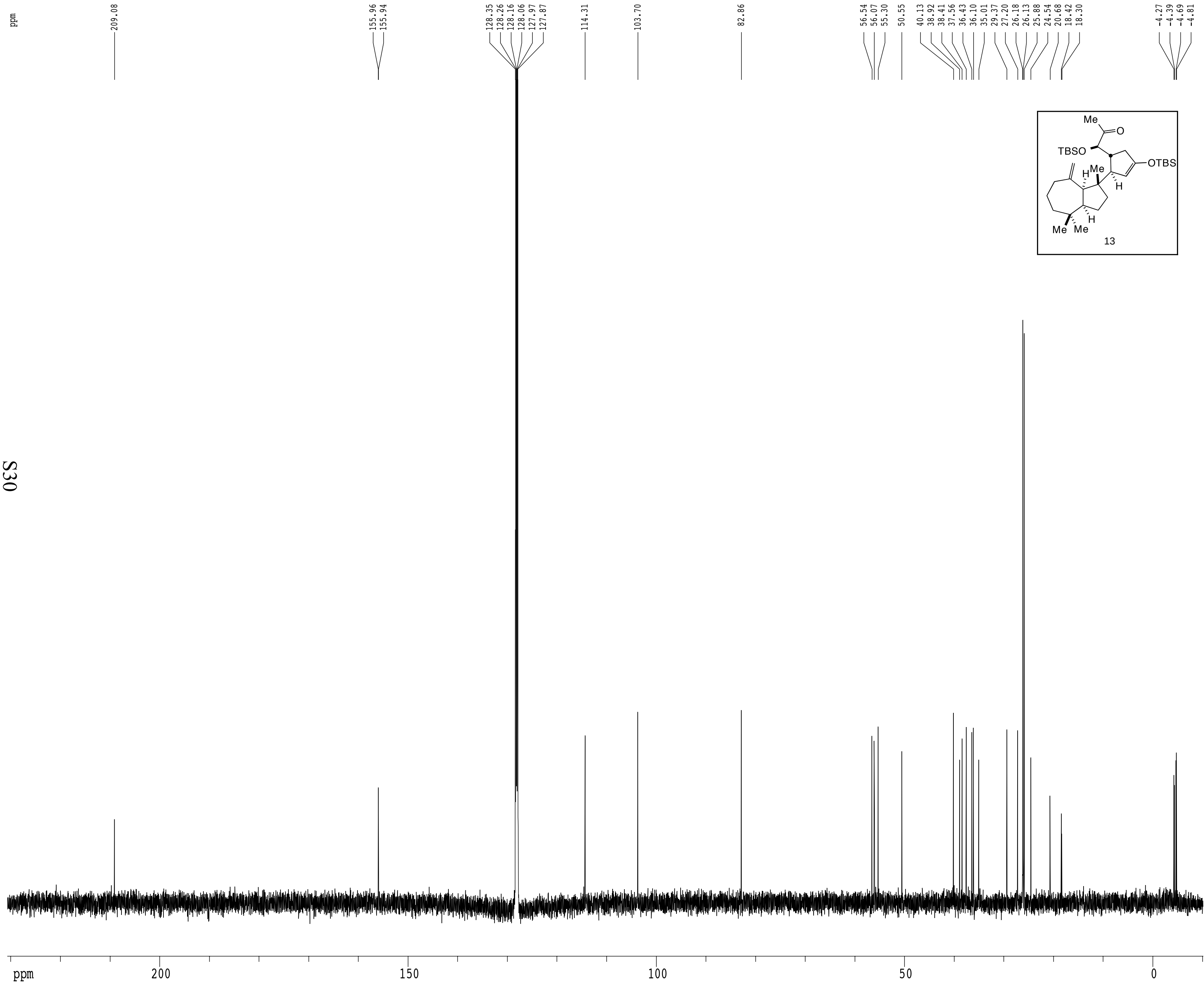
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200063 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                7.657 ppm
F1               3829.95 Hz
F2P               -0.648 ppm
F2               -324.11 Hz
PPMCM            0.36423 ppm/cm
HZCM           182.19592 Hz/cm
```



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



13

```
Current Data Parameters
USER              schner
NAME           mjs4-82-3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110518
Time                9.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   138
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0814105 sec
RG                4597.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

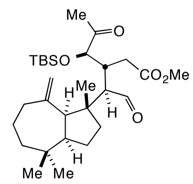
======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1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

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

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

F2 - Processing parameters
SI                 65536
SF           125.7803747 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              230.637 ppm
F1              29009.67 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10657 Hz/cm
```



14

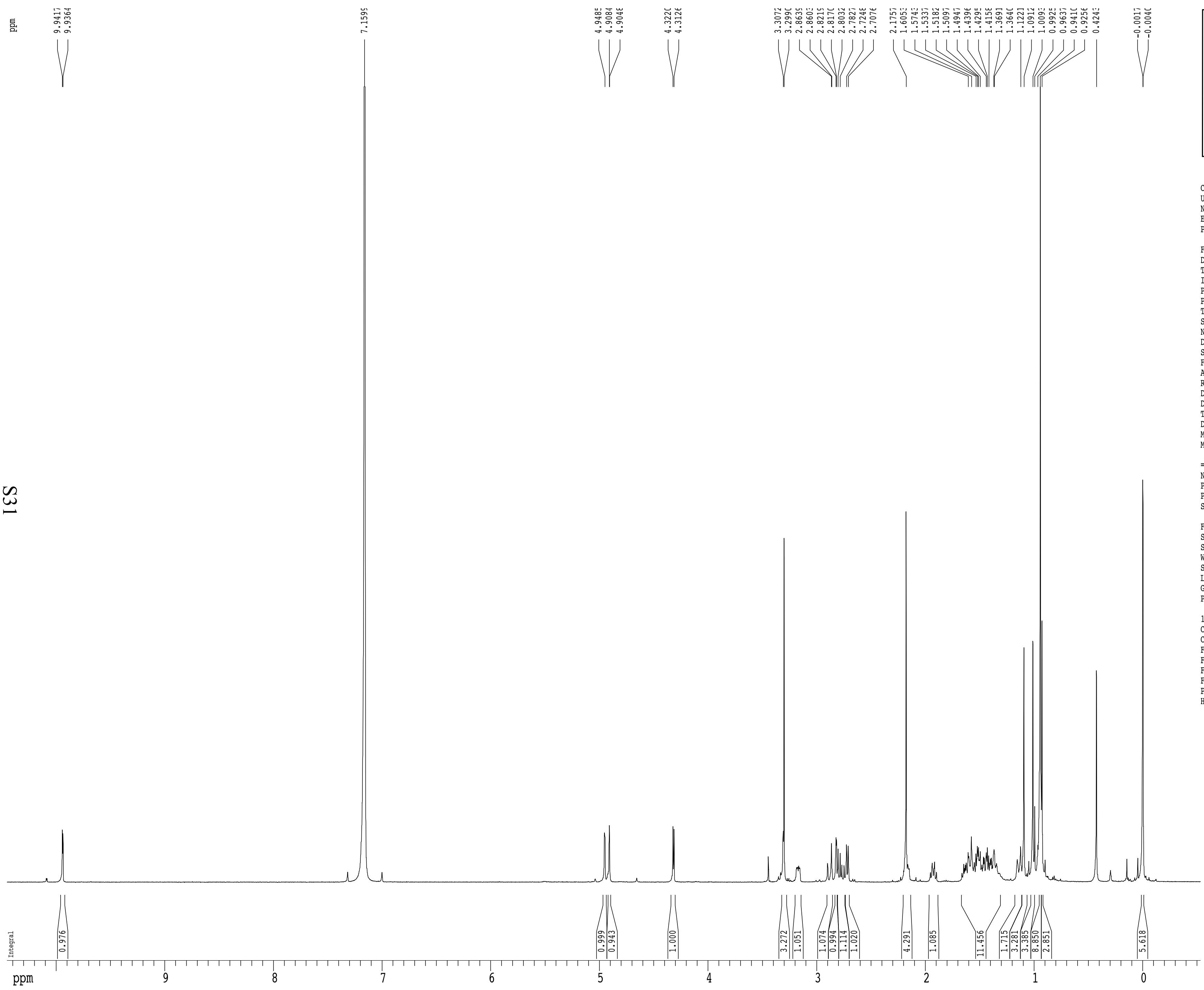
```
Current Data Parameters
USER              schner
NAME         mjs4-85-3real
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110523
Time               13.36
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT             C6D6
NS                     7
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

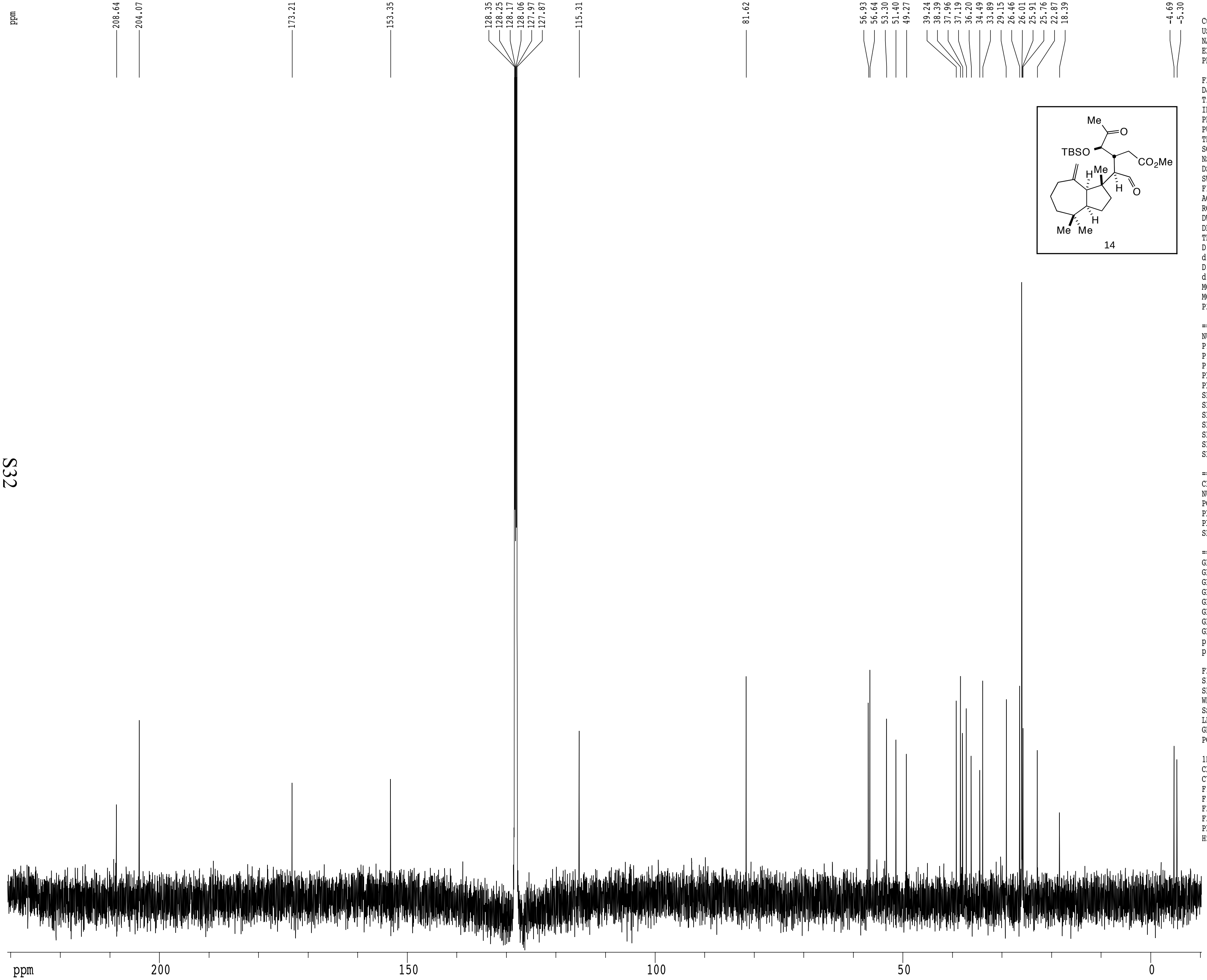
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200562 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               10.451 ppm
F1               5227.69 Hz
F2P               -0.531 ppm
F2               -265.68 Hz
PPMCM            0.48166 ppm/cm
HZCM           240.93716 Hz/cm
```



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



```
Current Data Parameters
USER              schner
NAME         mjs4-85-3real
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110523
Time               13.37
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   180
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                 31.00 usec

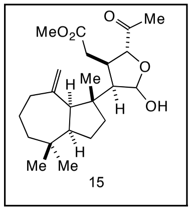
======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
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           125.7803891 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                300.00 cm
F1P              230.637 ppm
F1              29009.67 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10669 Hz/cm
```



15

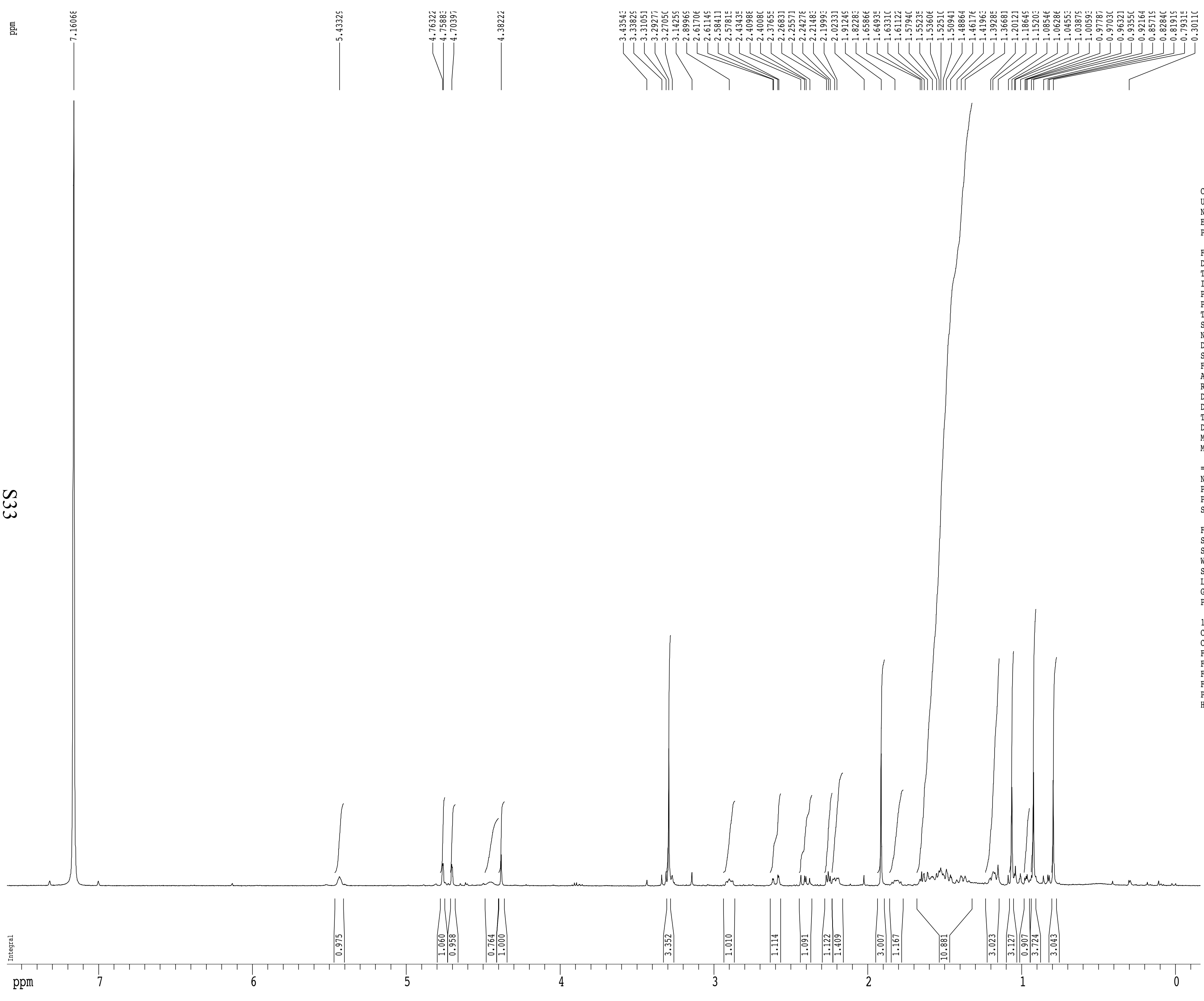
```
Current Data Parameters
USER            schner
NAME          mjs4-93-3
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20110603
Time              15.04
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT            C6D6
NS                   11
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0999398 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

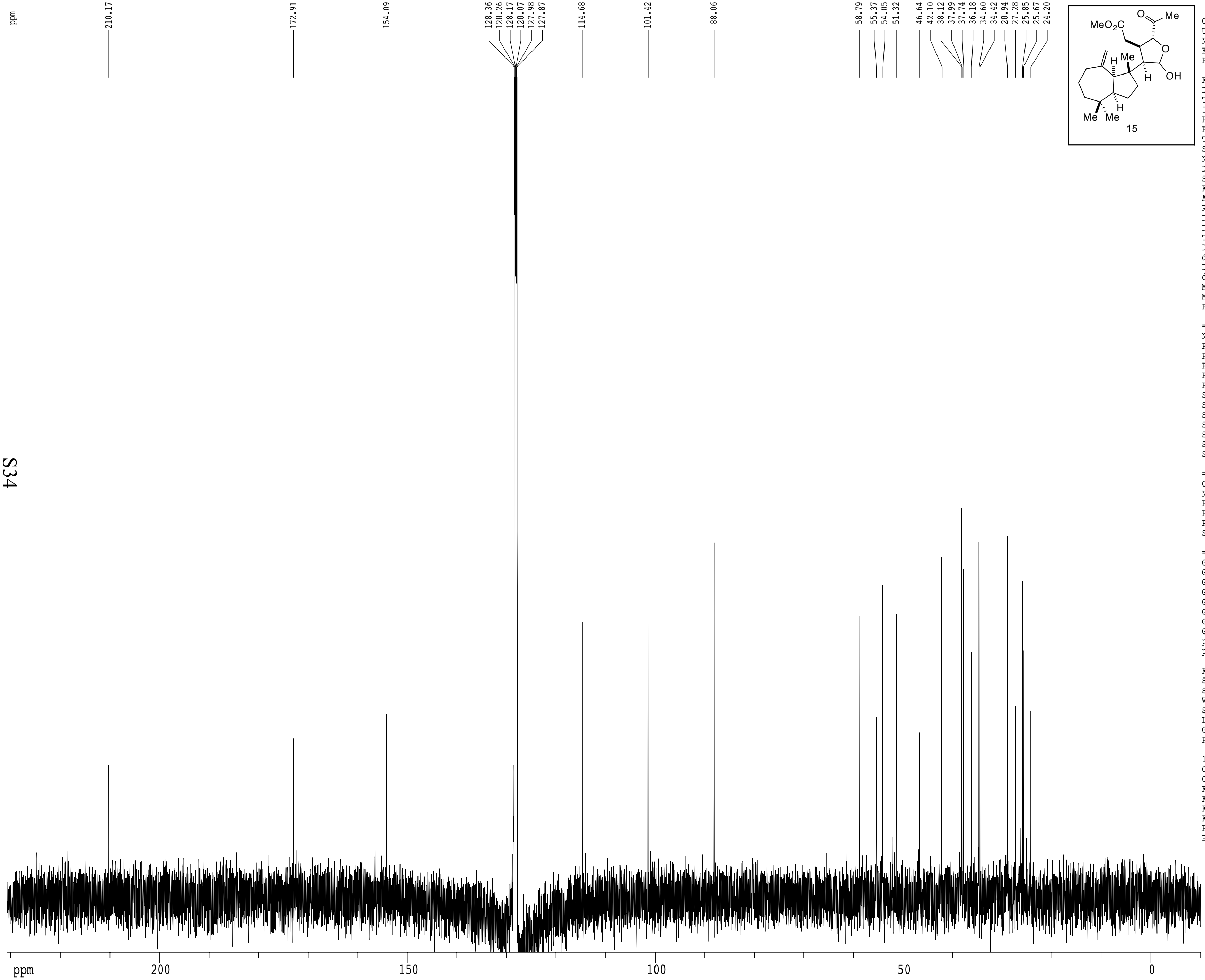
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200005 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               7.595 ppm
F1              3799.08 Hz
F2P              -0.162 ppm
F2               -81.02 Hz
PPMCM           0.34021 ppm/cm
HZCM          170.18004 Hz/cm
```



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



```
Current Data Parameters
USER              schner
NAME           mjs4-93-3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110603
Time               15.09
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   344
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                31.00 usec

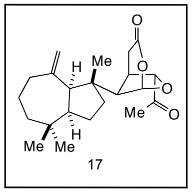
======== CHANNEL f1 ========
NUC1                 13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM1   Crp60,0.5,20.1
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          125.7803747 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                500.00 cm
F1P              230.637 ppm
F1              29009.67 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10657 Hz/cm
```



17

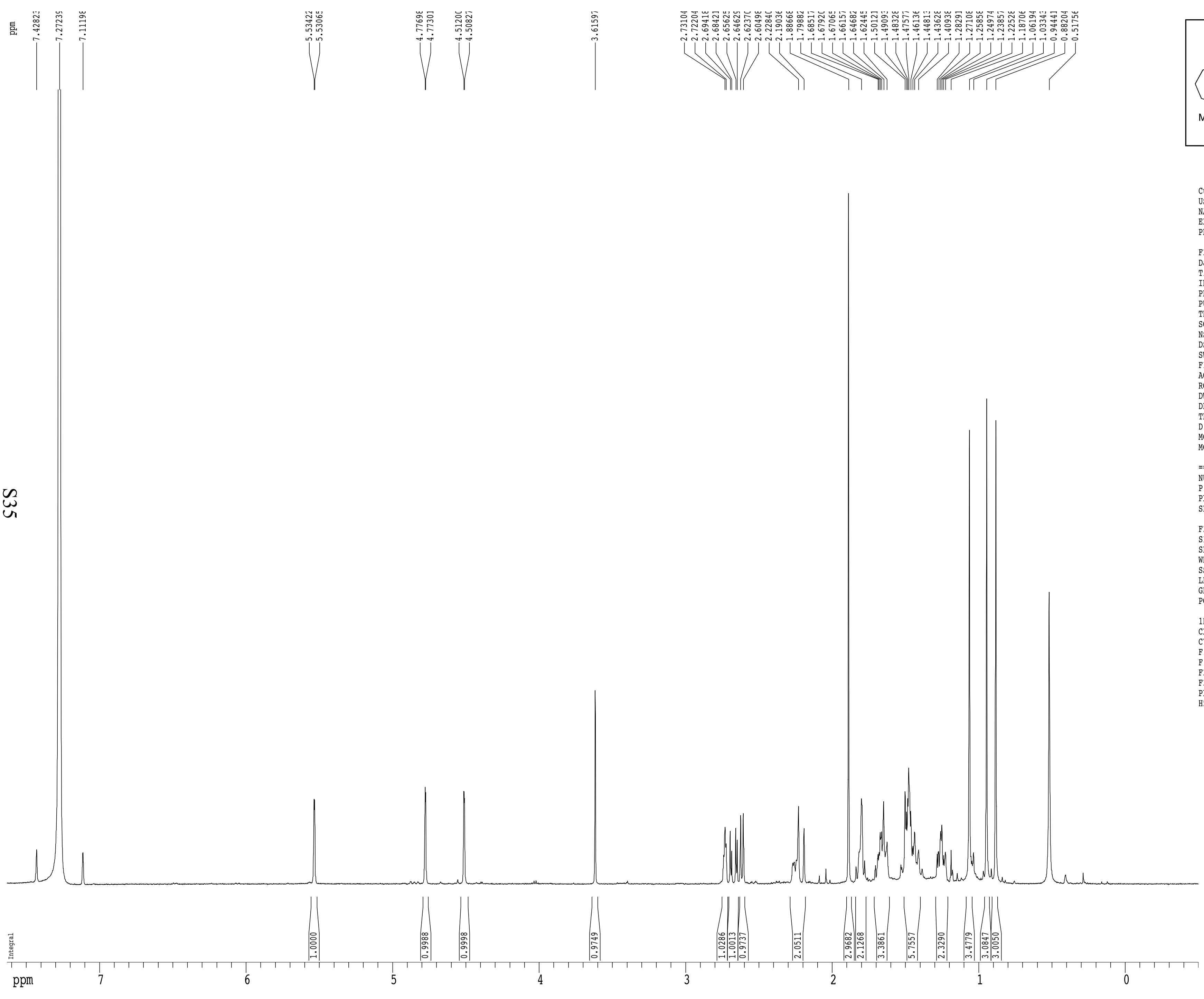
```
Current Data Parameters
USER          schner
NAME      mjs4-95-3c13
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20110608
Time             7.07
INSTRUM       cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG          zg30
TD              81728
SOLVENT          c6d6
NS                 20
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

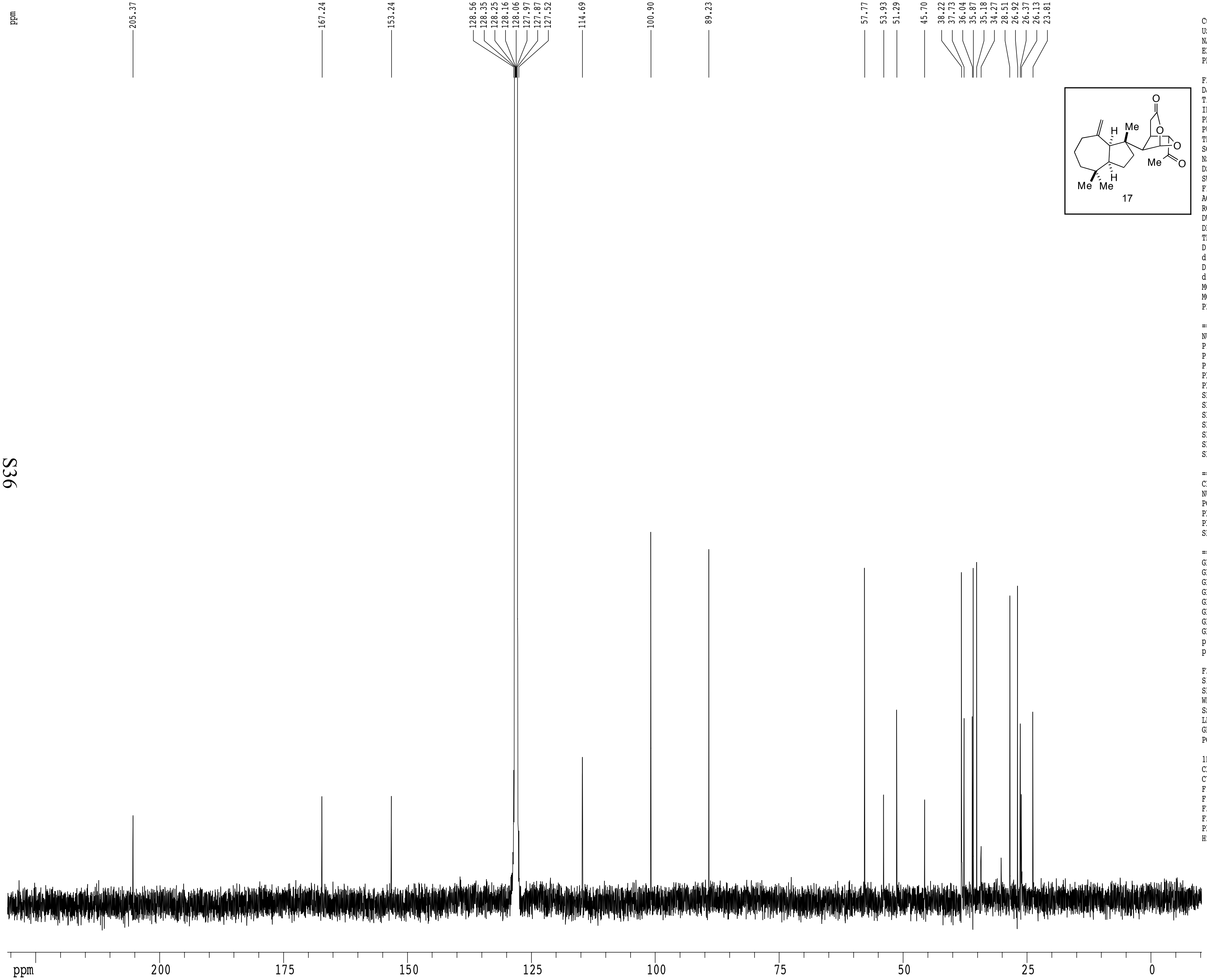
======== CHANNEL f1 ========
NUC1               1H
P1               7.50 usec
PL1              1.60 dB
SFO1      500.2235015 MHz

F2 - Processing parameters
SI              65536
SF        500.2200000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               4.00

1D NMR plot parameters
CX              22.80 cm
CY             100.00 cm
F1P             7.630 ppm
F1            3816.47 Hz
F2P            -0.500 ppm
F2            -250.11 Hz
PPMCM         0.35656 ppm/cm
HZCM        178.35895 Hz/cm
```



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



17

```
Current Data Parameters
USER              schner
NAME         mjs4-95-3c13
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110608
Time                7.10
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  4583
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  2048
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

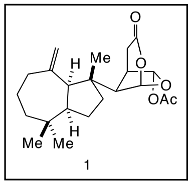
======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
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           125.7803891 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY               1000.00 cm
F1P              230.698 ppm
F1              29017.28 Hz
F2P              -10.222 ppm
F2              -1285.75 Hz
PPMCM           10.56667 ppm/cm
HZCM          1329.08044 Hz/cm
```



1

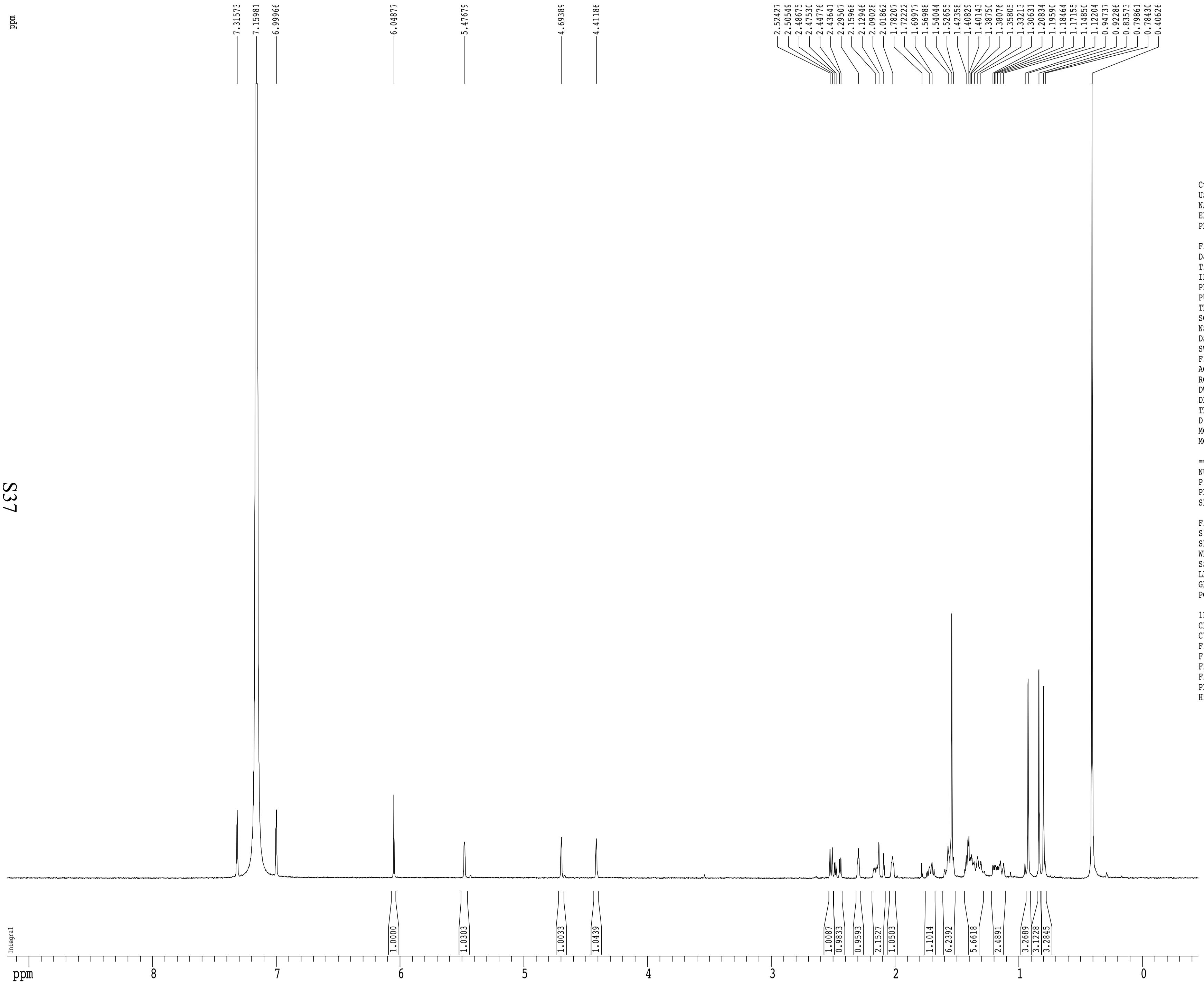
```
Current Data Parameters
USER               schner
NAME         mjs4-101-3dg
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110822
Time                10.13
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT              c6d6
NS                     50
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                  313.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

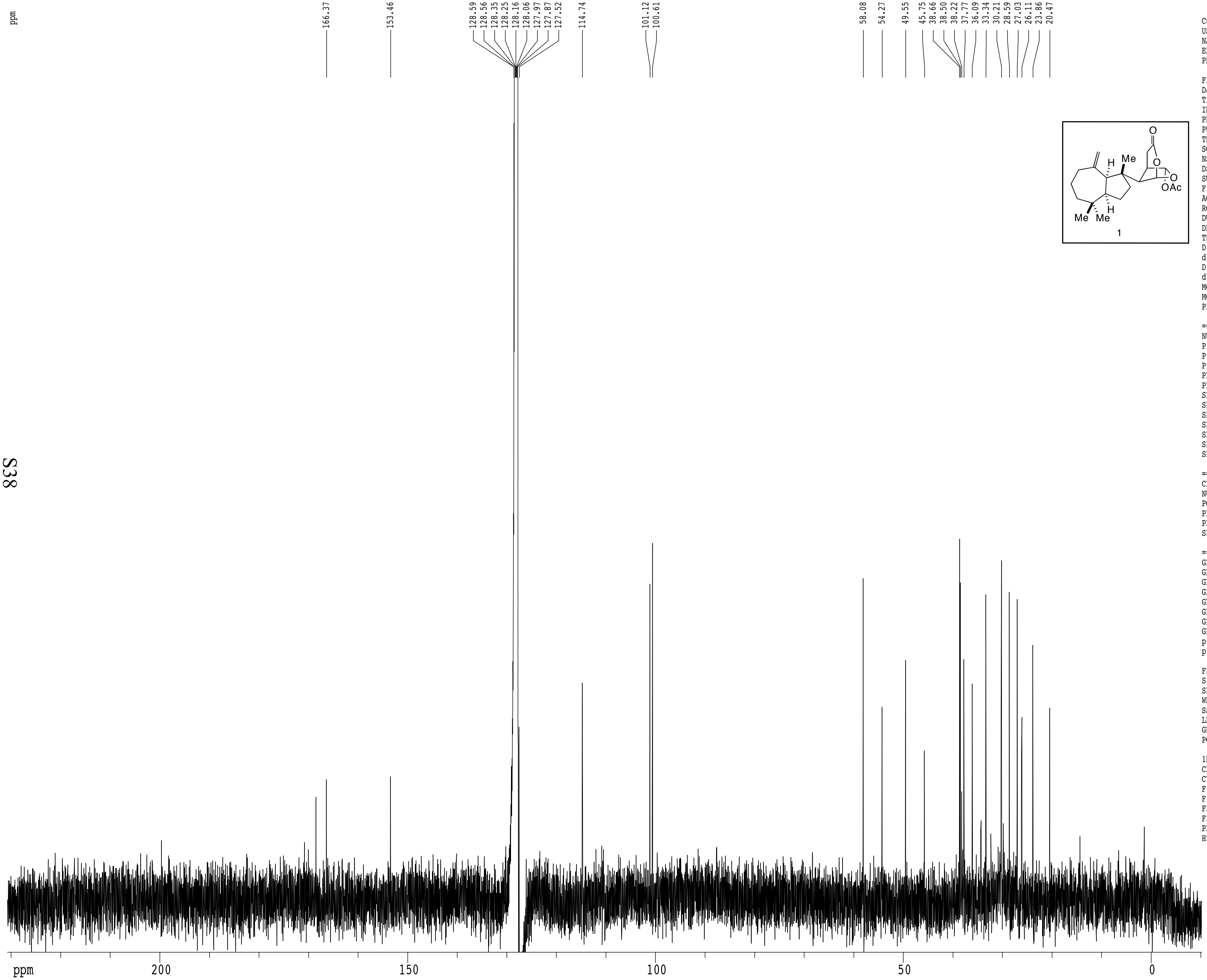
======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00

1D NMR plot parameters
CX                  22.80 cm
CY                 200.00 cm
F1P                 9.176 ppm
F1                4589.85 Hz
F2P                -0.451 ppm
F2                -225.81 Hz
PPMCM             0.42224 ppm/cm
HZCM            211.21341 Hz/cm
```



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



```
Current Data Parameters
USER              schner
NAME     mjs4-101-3varitc13
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110621
Time               18.56
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                 17768
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                 313.0 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           125.7803831 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY               5000.00 cm
F1P              230.746 ppm
F1              29023.30 Hz
F2P              -10.174 ppm
F2              -1279.73 Hz
PPMCM           10.56667 ppm/cm
HZCM          1329.08032 Hz/cm
```

Figure S1. Comparison H1 NMR of synthetic and natural aplyviolene (1)