Revisiting a Classic Approach to the *Aspidosperma* Alkaloids: An Intramolecular Schmidt Reaction-Mediated Synthesis of (+)-Aspidospermidine

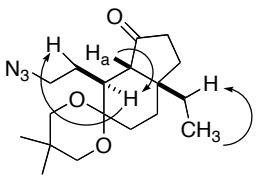
Rajesh Iyengar, Klaas Schildknegt, Martha Morton, and Jeffrey Aubé*

Department of Medicinal Chemistry, 1251 Wescoe Hall Drive, Room 4070, Malott Hall, University of Kansas, Lawrence, Kansas 66045-7582; jaube@ku.edu

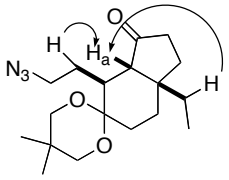
Supporting Information

Details on Characterization of Selected Compounds

Compound 28. In **28**, the CH_3 of the ethyl group appeared as a triplet at 0.88 ppm (J = 7.5 Hz) in its ^{1}H NMR (Figure 1). ^{1}H–^{1}H COSY then allowed the determination of the positions of the CH_2 of the ethyl group as being buried in the multiplets at 1.65 and 1.80 ppm. The ring fusion proton H_a was again distinctive, appearing as a doublet at 1.81 ppm (J = 5.1 Hz, the only proton expected to appear as a doublet in the molecule). That in turn coupled into the proton on the carbon bearing the side chain at 2.55 ppm. Using similar correlations, the protons on the side chain were identified. In order to determine the relative stereochemistry of the major isomer in **28**, the compound was subjected to 2D-NOE experiments, which revealed that the azide-containing side chain, H_a, and the ethyl group were cis to each other. Hence the major isomer was determined as the one in which the side chain occupies a β-orientation as depicted.

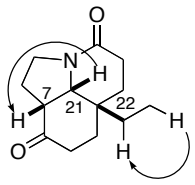


^{1}H-^{1}H COSY in **28**

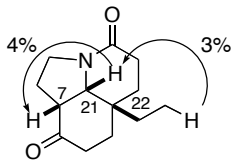


NOESY in **28**

Compound 6. The point of entry for establishing the proton signals in **6** was the CH_3 (triplet at 1.0 ppm) of the ethyl group (Figure 2). COSY data then unambiguously established the positions of the CH_2 of the ethyl group (1.50 ppm), and protons at C-7 (triplet, J = 5.9 Hz, 2.86 ppm) and C-21 (doublet, J = 5.0 Hz, 3.63 ppm, furthest downfield). The protons at C-7, C-21 and the ethyl group at C-22 in **6** were determined to be *cis* to one other (^{1}H NOE data, aspidospermidine numbering), thus establishing the stereochemistry of **6** as shown.

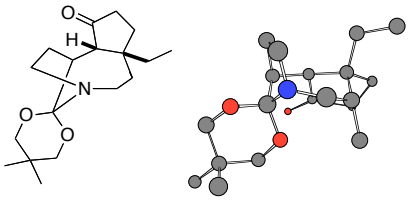


COSY correlations in **6**

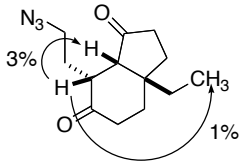


^{1}H NOE data for **6**

Compound 29 was subjected to X-ray crystallographic analysis. The cif file of this structure is included as a separate piece of Supporting Information.



Compound 7. Selected ^{1}H NOE correlations in **7** are shown below.



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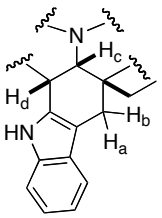
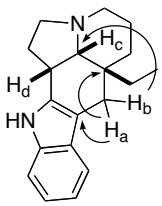
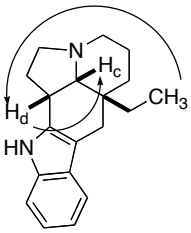
Compound 31. The molecular weight of 31 was determined to be 280 and thus having the probable molecular formula $C_{19}H_{24}N_2$ (2 protons fewer than aspidospermidine). Also apparent from the ^{13}C NMR of the compound was the presence of 8 aromatic signals indicating an intact indole ring system. DEPT analysis indicated the presence of 7 methylenes, 2 methines, 4 aromatic protons, and 1 methyl group in the molecule. In addition to the more routine signals, a key feature of the proton spectrum was 2 geminal protons (H_a and H_b, 2.51 and 2.79 ppm, J = 15.0 Hz) that were coupled only to each other (Figure 5). HMQC (single-bond 1H–13C correlations) assigned all the protons to their respective carbons and HMBC data (2,3-bond 1H–13C correlations) showed that Ha and Hb correlated into the indole system, the carbon bearing the ethyl group, and the carbon of Hc. Hc was coupled to Hd as determined by 1H-1H COSY experiments. These results set up **32** to be the probable partial structure. Stereochemical assignments were then deduced by 1D and 2D NOE experiments as depicted.



32



HMBC data in **31**



NOE data in **31**

Additional Experimental Details

General. ^1H and ^{13}C NMR spectra were recorded at the field strengths noted for particular compounds. All NMR samples were dissolved in $CDCl_3$, and the chemical shifts are expressed in parts per million (□) relative to tetramethylsilane as an internal reference. Abbreviations are s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. Melting points are uncorrected. All mass spectra measurements were carried out in-house. Optical rotations were taken on at ambient temperature; the concentrations are reported in g/100 mL. Elemental analyses were performed in-house. All chromatography was performed using silica gel (32-63 mesh) with the indicated solvent mixtures. Tetrahydrofuran was distilled from sodium benzophenone ketyl, dichloromethane and triethylamine were distilled from calcium hydride, and all other solvents were used without further purification. Reaction flasks were flame-dried and cooled under argon, and all reactions were conducted under a positive pressure of dry argon.

4-Benzyloxy-1-butanol.[1] 1,4-Butanediol (20.3 g, 226 mmol) was added dropwise to an ice-cooled suspension of sodium hydride (4.33 g, 180 mmol) in DMF (200 mL). The resulting mixture was warmed to rt, treated with benzyl bromide (30.9 g, 180 mmol), and allowed to react for 20 h. The reaction mixture was then poured into H_2O, and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo to yield a light yellow oil (27.9 g, 86%). IR (film) 3390 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) □ 1.72 (m, 4H), 2.40 (br s, 1H), 3.54 (t, *J* = 5.6 Hz, 2H), 3.66 (t, *J* = 5.7 Hz, 2H), 4.55 (s, 2H), 7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) □ 27.1, 30.5, 63.1, 70.8, 73.5, 128.1, 128.2, 128.8, 138.6; CIMS *m/z* (relative intensity) 181 (MH^+, 100), 136 (50), 91 (95).

4-Benzyloxybutyraldehyde.[1] PCC (40.5 g, 188 mmol) was added in a single portion to a solution of the above alcohol (22.5 g, 125 mmol) in CH_2Cl_2 (300 mL)

maintained at rt. After 3 h, the reaction mixture was diluted with Et_2O (300 mL) and filtered through a silica gel plug. The filtrate was concentrated to approximately 50 mL and the resulting solution was distilled under high vacuum to yield 12.9 g (58%) of the title compound (bp 115–118 °C/1.0 Torr) as a clear liquid. IR (film) 1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.95 (m, 2H), 2.55 (t, J = 7.1 Hz, 2H), 3.50 (t, J = 6.1 Hz, 2H), 4.50 (s, 2H), 7.30 (m, 5H), 9.78 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6, 40.9, 69.2, 72.9, 127.6, 128.4, 138.3, 202.2; CIMS *m/z* (relative intensity) 179 (MH^+, 60), 91 (100).

6-Benzyloxy-1-hexen-3-ol. A solution of the above aldehyde (10.9 g, 61.0 mmol) in THF (20 mL) was added dropwise to a rt solution of vinyl magnesium bromide (1 M in THF, 80.0 mL, 80.0 mmol). The reaction mixture was stirred for an additional 30 min before it was carefully poured over ice-cold 1 M HCl and extracted with Et_2O. The combined organic layers were washed successively with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The resulting oil was distilled under high vacuum to yield 11.1 g (88%) of the title compound (bp 145-155 °C/1.0 Torr) as a clear thin oil. IR (film) 3400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.82-1.60 (m, 4H), 2.50 (br s, 1H), 3.54 (t, J = 5.9 Hz, 2H), 4.16 (q, J = 5.9 Hz, 1H), 4.54 (s, 2H), 5.12 (d, J = 10.4 Hz, 1H), 5.25 (d, J = 17.2 Hz, 1H), 5.90 (ddd, J = 17.0, 10.6, 6.1 Hz, 1H), 7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 34.7, 70.8, 73.1, 73.4, 114.9, 128.06, 128.12, 128.8, 138.6, 141.5; CIMS *m/z* (relative intensity) 207 (MH^+, 15), 189 (100), 171 (50). Anal. calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79, found: C, 75.57; H, 9.00.

7a*R*-Ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (9). A solution of 2-ethylcyclopentanone[2] (5.36 g, 47.9 mmol), (*S*)-α-methylbenzylamine (5.22 g, 43.1 mmol) and *p*-TsOH (0.01 g) in benzene (50 mL) was thoroughly degassed and then allowed to reflux for 24 h using a Dean-Stark trap to remove H_2O. After the theoretical amount of H_2O had been removed, the remaining benzene was distilled off at atmospheric pressure and the crude imine pot residue was cooled to rt and used directly in the next step. Methyl vinyl ketone (3.93 g, 56 mmol) and hydroquinone (ca. 0.025 g) were added to the imine and the resulting solution was heated at 60 °C for 44 h, cooled to rt, diluted with aqueous acetic acid (10%, 30 mL) and MeOH (15 mL), and the resulting biphasic solution was stirred vigorously for 2 h. The mixture was then poured over 1 M HCl and extracted with Et_2O. The combined organic layers were successively washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was added to a solution of sodium methoxide (3.0 g, 86.2 mmol) in methanol (70 mL) and allowed to reflux for 24 h. After this time, the reaction mixture was cooled to rt and 1N HCl was added in a dropwise manner until the pH was adjusted to 2.0 and the reaction mixture stirred for an additional 15 min. The aqueous layer was extracted with Et_2O (6 $\times$ 100 mL) and the organic layer washed with a saturated aqueous solution of $NaHCO_3$ (3 $\times$ 100 mL), H_2O (1 $\times$ 100 mL), brine (1 $\times$ 100 mL), dried over $MgSO_4$, concentrated and purified by distillation to afford 2.2 g (31%) of **9** (R_f = 0.72, 30% EtOAc/hexanes) as a clear oil. IR (neat) 2968, 2881, 1675 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3H), 1.20-1.32 (m, 1H), 1.38-1.52 (m, 2H), 1.63 (dt, J = 13.7, 5.2 Hz, 1H), 1.75-1.90 (m, 2H), 1.96-2.00 (m, 1H), 2.17-2.32 (m, 2H), 2.38-2.50 (m, 2H), 2.60-2.72 (m, 1H), 5.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 20.9, 25.4,

30.8, 31.2, 33.2, 35.7, 45.8, 120.9, 179.2, 199.4; CIMS *m/z* (relative intensity) 165 (MH^+, 100), 136 (16), 122 (18); HRMS calcd for $C_{11}H_{17}O$: 165.1279, found: 165.1267.

7a*R*-Ethyl-3*R*-hydroxy-1,2,3,6,7,7a-hexahydroinden-5-one. The enone **9** (0.039 g, 0.24 mmol) and *p*-TsOH (0.011 g, 0.06 mmol) were added to isopropenylacetate (5 mL) and the reaction mixture heated at 105 °C for 1.5 h. After this time the reaction mixture was cooled to room temperature and diluted with Et_2O (50 mL). The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (10 mL), H_2O (10 mL), dried over $MgSO_4$, concentrated to a light brown oil that was used in the next step without purification.

The crude dienol acetate was dissolved in acetone (3 mL), followed by the addition of H_2O (1 mL), a saturated aqueous solution of $NaHCO_3$ (1 mL) and Oxone (0.40 g). The resulting reaction mixture was stirred at rt for 45 min. The reaction mixture was diluted with H_2O (5 mL) and the aqueous layer was extracted with EtOAc (2 × 20 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated to give the title compound (R_f = 0.28, 30% EtOAc/hexanes) as a colorless oil that was used in the next step without purification. $[\alpha]_D$ = –66.2 (*c* 1.7, CH_2Cl_2); IR (neat) 3405, 2960, 1666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.43-1.64 (m, 4H), 1.75-1.87 (m, 3H), 2.17 (ddd, *J* = 2.0, 5.0, 15.0 Hz, 1H), 2.25-2.29 (m, 1H), 2.35 (m, 1H), 2.42-2.46 (m, 1H), 4.78 (dt, *J* = 2.0, 8.0 Hz, 1H), 5.94 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.1, 29.1, 32.2, 32.5, 33.0, 33.7, 43.2, 73.2, 119.2, 178.9, 199.6; CIMS *m/z* (relative intensity) 181 (MH^+, 100), 124 (14); HRMS calcd for $C_{11}H_{17}O_2$: 181.1228, found: 181.1231.

6-Benzyloxy-1-hexen-3-one (10).[3] Jones reagent (8 M in H_2O, 21.0 mL, 168 mmol) was added dropwise to a 0 °C solution of the above alcohol (11.1 g, 53.8 mmol) dissolved in 20 mL of acetone. After the addition was complete the reaction was poured over H_2O and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was treated with ca. 200 mg of hydroquinone and distilled under high vacuum to yield 8.80 g (80%) of **10** (bp 135-145 °C/1.0 Torr) as a light yellow oil. IR (film) 1690, 1670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (m, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 4.55 (s, 2H), 5.84 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.25 (dd, *J* = 17.7, 1.2 Hz, 1H), 6.38 (dd, *J* = 17.7, 10.4 Hz, 1H), 7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 36.6, 69.6, 69.7, 73.3, 116.5, 128.0, 128.1, 128.5, 128.8, 137.0, 138.8, 201.0; CIMS *m/z* (relative intensity) 205 (MH^+, 20), 97 (90).

3a*S*-Ethyl-3,3a,4,5-tetrahydro-2H-inden-1,6-dione (15). The above alcohol (1.52 mmol) was dissolved in CH_2Cl_2 (7 mL) and PCC (0.65 g, 3.04 mmol) was added in one portion. The reaction mixture was stirred at rt for 1.5 h after which time the organic layer was filtered through a pad of silica gel, concentrated and purified by chromatography (10% EtOAc/hexanes) to afford 0.226 g of **15** (84% from **9**) as a yellow solid. Mp = 107-109 °C; $[\alpha]_D$ = –289.2 (*c* 0.204, $CHCl_3$); IR (neat) 2960, 2881, 1728, 1684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, *J* = 7.4 Hz, 3H), 1.53-1.64 (m, 3H), 1.84 (dt, *J* = 13.7, 5.5 Hz, 1H), 2.28-2.39 (m, 2H), 2.47-2.55 (m, 4H), 6.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.3, 26.8, 30.5, 32.8, 33.7, 36.0, 42.9, 122.7, 161.7, 200.1,

207.6; CIMS *m/z* (relative intensity) 179 (MH^+, 100), 150 (37), 137 (28), 121 (16), 107 (11), 93 (11), 79 (15), 65 (12); HRMS calcd for $C_{13}H_{20}BrO$ (M^++H): 271.0698, found: 271.0710.

4-(2´-Bromoethyl)-7a*R*-ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (16a). Boron tribromide (1 M in CH_2Cl_2, 1.34 mL, 1.34 mmol) was added dropwise to a -78 °C solution of benzyl ether **8** (0.20 g, 0.67 mmol) in CH_2Cl_2 (2 mL). The reaction was then allowed to stir without external cooling for 3 h before it was poured over saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product residue was purified by chromatography (20% Et_2O/hexanes) to yield 0.10 g (55%) of **16a** (R_f = 0.30, 20% Et_2O/hexanes) as a clear oil. $[\alpha]_D$ = –27.4 (*c* 1.2, CH_2Cl_2); IR (film) 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3H), 1.30 (m, 1H), 1.46 (q, *J* = 7.5 Hz, 2H), 1.66 (td, *J* = 13.8, 5.4 Hz, 1H), 1.84 (m, 2H), 2.05 (m, 1H), 2.18 (ddd, J = 13.3, 5.3, 1.9 Hz, 1H), 2.34 (ddd, *J* = 18.2, 5.4, 1.9 Hz, 1H), 2.49 (ddd, *J* = 18.3, 14.2, 5.3 Hz, 1H), 2.58-2.84 (m, 4H), 3.48 (td, *J* = 7.0, 0.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.6, 22.0, 26.0, 30.5, 30.6, 31.2, 32.6, 33.8, 36.8, 47.0, 128.6, 176.5, 198.7; CIMS *m/z* (relative intensity) 273 (MH_2^+, 100), 271 (M^+, 100), 191 (25); HRMS calcd for $C_{13}H_{19}O$: 271.0698, found: 271.0710.

4-(2´-Chloroethyl)-7a*R*-ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (16b). Boron trichloride (1 M solution in CH_2Cl_2, 3.40 mL, 3.40 mmol) was added dropwise to a -78 °C solution of benzyl ether **8** (0.60 g, 2.01 mmol) in CH_2Cl_2 (6 mL). The reaction was then allowed to stir without external cooling for 45 min before it was poured over saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product residue was purified by chromatography (20% Et_2O/hexanes), to yield 0.38 g (84%) of the chloride **16b** (R_f = 0.30, 20% Et_2O/hexanes) as a light yellow oil. $[\alpha]_D$ = –30.2 (*c* 4.1, CH_2Cl_2); IR (film) 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.30 (td, *J* = 12.4, 10.0 Hz, 1H), 1.47 (q, *J* = 7.4 Hz, 2H), 1.66 (td, *J* = 13.8, 5.3 Hz, 1H), 1.84 (m, 2H), 2.01 (dt, *J* = 12.5, 4.0 Hz, 1H), 2.18 (ddd, *J* = 13.3, 5.3, 1.9 Hz, 1H), 2.35 (ddd, *J* = 18.3, 5.4, 1.9 Hz, 1H), 2.49 (ddd, *J* = 18.3, 14.2, 5.3 Hz, 1H), 2.65 (m, 4H), 3.61 (td, *J* = 6.9, 2.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.6, 22.0, 26.0, 30.48, 30.55, 31.2, 33.8, 36.8, 44.0, 46.9, 127.8, 176.7, 198.8; CIMS *m/z* (relative intensity) 227 (MH^+, 90), 191 (50), 161 (15), 91 (15). Anal. calcd for $C_{13}H_{19}ClO$: C, 68.86; H, 8.45, found: C, 68.98; H, 8.50.

7-(2´-Chloroethyl)-3a*S*-ethyl-3,3a,4,5-tetrahydro-2H-indene-1,6-dione (17). A solution of chloride **16b** (0.70 g, 3.1 mmol) and isopropenyl acetate (12 mL) was treated with *p*-TsOH (0.30 g) and heated at reflux for 1.5 h. The reaction was then cooled to rt, diluted with Et_2O, washed successively with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. The resulting solution was concentrated in vacuo to yield 0.83 g (100%) of dienol acetate as a light yellow oil. $[\alpha]_D$ = +23.4 (*c* 2.3, CH_2Cl_2); IR (film) 1750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.5 Hz, 3H), 1.58-1.31 (m, 4H), 1.95 (dd, *J* = 12.9, 6.3 Hz, 1H), 2.00 (dd, *J* = 12.6, 7.5 Hz, 1H), 2.12 (m, 1H), 2.20 (s, 3H), 2.33 (m, 1H), 2.48 (m, 2H), 2.60 (m, 1H), 2.67 (ddd, *J* = 13.5, 9.8, 7.1 Hz, 1H), 3.49 (m, 2H), 5.58 (s, 1H).

This sensitive material was directly dissolved in a mixture of acetone (20 mL), saturated aqueous $NaHCO_3$ (10 mL), and H_2O (5 mL), and treated with 3.5 g of Oxone. After 30 min the reaction was poured over H_2O and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo, and the resulting residue was purified by chromatography (50% Et_2O/hexanes), to yield 0.60 g (80%) of the allylic alcohol (R_f = 0.20, 50% Et_2O/hexanes) as a clear oil. $[\alpha]_D$ = –16.4 (*c* 1.8, CH_2Cl_2); IR (film) 3400, 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.42 (m, 2H), 1.63 (m, 1H), 1.76 (m, 1H), 1.83 (m, 1H), 1.92 (m, 1H), 2.04 (m, 1H), 2.14 (m, 1H), 2.21 (m, 1H), 2.42 (m, 1H), 2.48 (m, 1H), 2.80 (m, 1H), 2.98 (m, 1H), 3.70 (m, 2H), 4.97 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.8, 27.7, 30.4, 31.3, 33.6, 33.7, 33.9, 44.3, 46.6, 72.9, 130.5, 175.5, 199.9; CIMS *m/z* (relative intensity) 243 (MH^+, 90), 207 (50), 180 (25).

A solution of allylic alcohol (0.67 g, 2.8 mmol) in CH_2Cl_2 (30 mL), maintained at rt, was treated with PCC (1.2 g, 5.5 mmol) and stirred for 3 h. The reaction was then diluted with Et_2O and filtered through a silica gel plug. The filtrate was concentrated in vacuo and the resulting crude product residue was purified by chromatography (30% Et_2O/hexanes), to yield 0.45 g (68%) of **17** (R_f = 0.20, 30% Et_2O/hexanes) as a yellow solid: mp = 54-55 °C; $[\alpha]_D$ = –211.6 (*c* 1.4, CH_2Cl_2); IR (film) 1705, 1665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.4 Hz, 3H), 1.57 (m, 3H), 1.86 (td, *J* = 13.6, 6.0 Hz, 1H), 2.25 (ddd, *J* = 13.0, 7.9, 2.3 Hz, 1H), 2.31 (ddd, *J* = 13.5, 5.1, 2.3 Hz, 1H), 2.41-2.62 (m, 4H), 3.13 (m, 1H), 3.29 (dt, *J* = 12.5, 7.2 Hz, 1H), 3.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 27.7, 30.5, 32.5, 33.7, 37.0, 43.6, 44.3, 135.6, 156.6, 200.3, 209.5; CIMS *m/z* (relative intensity) 241 (MH^+, 30), 240 (M^+, 50), 211 (40), 175 (100).

7-(2´-Chloroethyl)-3a*S*-ethyl-7a*R*-hexahydroindene-1,6-dione (18). Concentrated HCl (12 M, 0.91 mL, 11.0 mmol) and sodium iodide (1.64 g, 11.0 mmol) were added to a solution of enedione **17** (0.33 g, 1.37 mmol) in acetone (50 mL) maintained at rt. After 15 min the reaction was diluted with Et_2O and washed successively with 10% aqueous $Na_2S_2O_3$ (until the organic layer remained colorless), H_2O, and brine. The resulting organic layer was dried over Na_2SO_4 and concentrated in vacuo to give a crude product residue that was purified by chromatography (30% Et_2O/hexanes), to yield 0.31 g (93%) of a ~1:1 diastereomeric mixture of **18** (R_f = 0.15) as a clear oil. IR (film) 1725, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.4 Hz, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 1.35-1.42 (sextet, *J* = 7.4 Hz, 1H), 1.49-1.53 (sextet, *J* = 7.4 Hz, 1H), 1.55-1.65 (m, 1H), 1.70-1.80 (m, 2H), 1.83-2.10 (m, 9H), 2.05-2.10 (m, 1H), 2.10-2.20 (m, 1H), 2.20-2.35 (m, 4H), 2.35-2.47 (m, 4H), 2.65-2.75 (m, 2H), 2.83 (q, *J* = 6.5 Hz, 1H), 3.50-3.58 (m, 1H), 3.61-3.67 (m, 3H); CIMS *m/z* (relative intensity) 243 (MH^+, 30), 207 (50), 180 (90); HRMS calcd for $C_{13}H_{19}O_2$ (M^++H): 207.1385, found: 207.1385.

Cyclopropane (19). A solution of **18** (0.31 g, 1.28 mmol) in THF (18 mL) was treated with 14 drops of DBU and stirred overnight at rt. After 18 h the reaction was diluted with Et_2O, washed successively with 1M HCl and brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by chromatography (30% Et_2O/hexanes) to yield 0.20 g (76%) of **19** (R_f = 0.10) as a clear oil. $[\alpha]_D$ = –100 (*c* 0.66,

CH_2Cl_2); IR (film) 1730, 1685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.68 (ddd, J = 9.1, 7.1, 3.3 Hz, 1H), 0.94 (m, 1H), 1.02 (t, J = 7.5 Hz, 3H), 1.08 (ddd, J = 9.0, 7.2, 4.6 Hz, 1H), 1.60 (m, 1H), 1.69-1.93 (m, 6H), 2.01 (m, 1H), 2.24-2.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.6, 12.4, 20.7, 25.8, 29.3, 31.1, 31.11, 35.2, 36.2, 42.8, 61.3, 209.4, 217.3; CIMS *m/z* (relative intensity) 207 (MH^+, 50), 150 (100).

Cyclopropane (20). To **16b** (0.277 g, 0.12 mmol) in THF (2 mL) was added DBU (0.036 g, 0.24 mmol) and the reaction mixture was heated under reflux for 5 h. After this time the reaction mixture was cooled to rt, diluted with H_2O (5 mL) and extracted with Et_2O (3 x 15 mL). The organic layer was dried over $MgSO_4$, concentrated in vacuo and the resulting oil was purified by chromatography (10% EtOAc/hexanes) to afford 18 mg (78%) of **20** (R_f = 0.86, 20% EtOAc/hexanes) as a clear oil. IR (neat) 1693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.4 Hz, 3H), 0.89 (buried m, 1H), 1.23 (m, 1H), 1.36 (m, 1H), 1.54-1.62 (m, 3H), 1.66-1.78 (m, 2H), 2.01-2.06 (m, 2H), 2.28 (m, 2H), 2.44 (m, 2H), 5.06 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 16.8, 27.1, 28.5, 29.5, 30.8, 33.3, 36.1, 36.3, 49.8, 117.7, 149.0, 210.4; CIMS *m/z* (relative intensity) 191 (MH^+, 100), 162 (42), 91 (11); HRMS calcd for $C_{13}H_{19}O$: 191.1436, found: 191.1460.

4-(2´-Azidoethyl)-7a*R*-ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (21). Cyclopropane **20** (0.030 g, 0.16 mmol), $TMSN_3$ (0.168 mL, 0.64 mmol) and Bu_4NF (0.64 mL, 0.64 mmol) were combined and heated at 66 °C for 25 h. The reaction mixture was cooled to rt and quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL). The aqueous layer was extracted with Et_2O (3 x 25 mL), and the organic layer washed with a saturated solution of $NaHCO_3$ (5 mL), and H_2O (5 mL). The organic layer was dried over $MgSO_4$, concentrated in vacuo and the resulting oil was purified by chromatography (10% EtOAc/hexanes) to afford 30 mg (81%) of **21** (R_f = 0.59, 20% EtOAc/hexanes) as a clear oil. IR (neat) 2968, 2872, 2095, 1666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.4 Hz, 3H), 1.22-1.32 (m, 1H), 1.44 (q, J = 7.4 Hz, 2H), 1.64 (dt, J = 13.8, 9.6 Hz, 1H), 1.80-1.88 (m, 2H), 1.97-2.04 (m, 1H), 2.17 (ddd, J = 1.6, 5.1, 13.3 Hz, 1H), 2.33 (ddd, J = 1.6, 5.2, 12.0 Hz, 1H), 2.40-2.58 (m, 3H), 2.64 (q, J = 8.3 Hz, 2H), 3.25-3.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 21.4, 25.3, 26.7, 29.8, 30.6, 33.3, 36.1, 46.4, 50.1, 127.2, 175.8, 198.3; CIMS *m/z* (relative intensity) 234 (MH^+, 100), 206 (54), 149 (16); HRMS calcd for $C_{13}H_{19}N_3O$: 234.1606, found: 234.1594.

4-(2´-Azidoethyl)-7a*R*-ethyl-3*S*-hydroxy-1,2,3,6,7,7a-hexahydroinden-5-one (22). Enone **21** (0.019 g, 0.08 mmol) and *p*-TsOH (0.003 g, 0.016 mmol) were placed in isopropenyl acetate (5 mL) and the reaction mixture heated at 105 °C for 1.5 h. After this time the reaction mixture was cooled to room temperature and diluted with Et_2O (50 mL). The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (10 mL), H_2O (10 mL), dried over $MgSO_4$, concentrated to a light brown oil that was used in the next step without purification.

The crude dienol acetate was dissolved in acetone (3 mL), followed by the addition of H_2O (1 mL), a saturated aqueous solution of $NaHCO_3$ (1 mL) and Oxone (0.40 g) and the resulting reaction mixture was stirred at rt for 45 min. The reaction mixture was diluted with H_2O (5 mL) and the aqueous layer was extracted with EtOAc (2 x 20

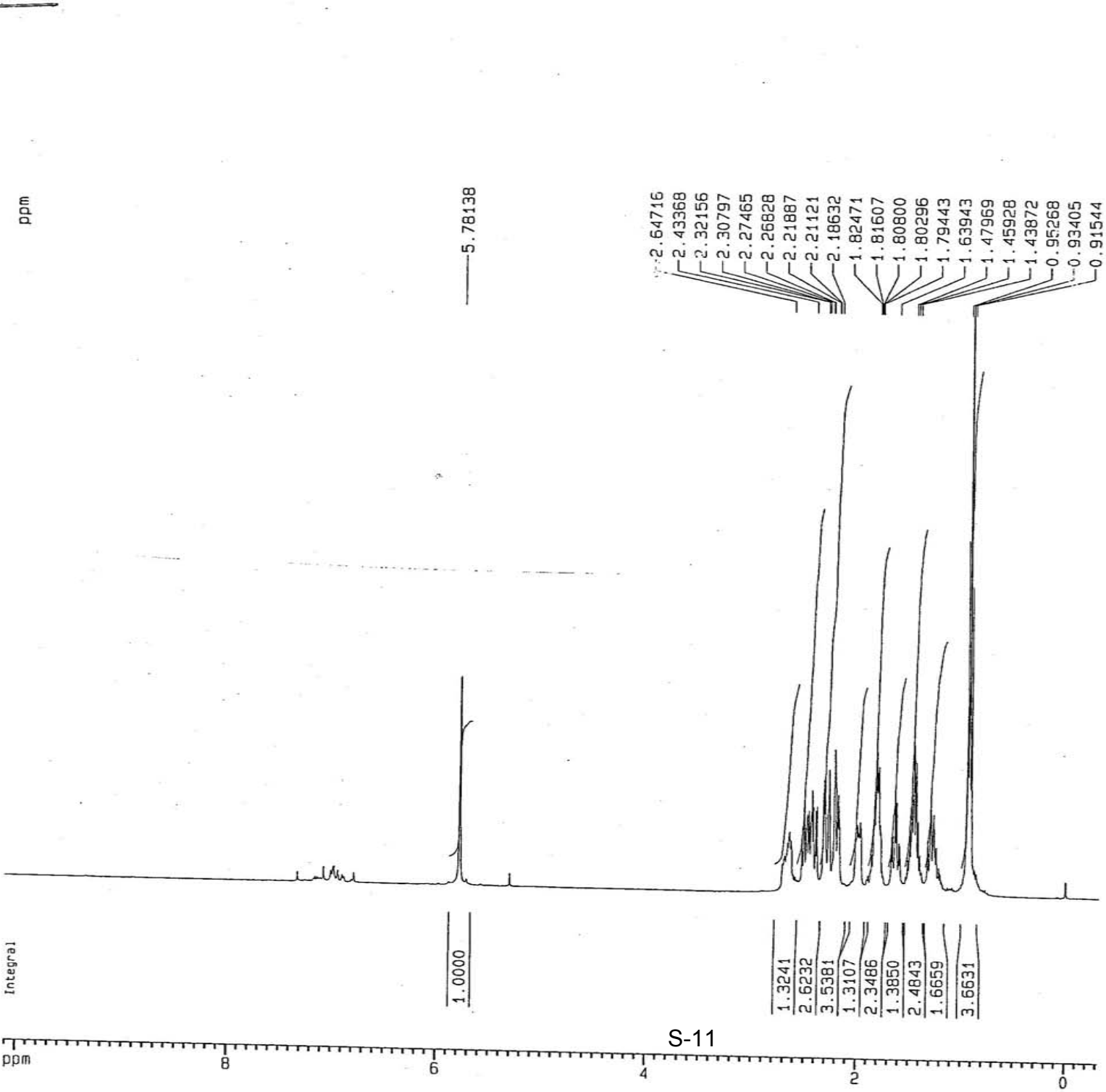
mL). The organic layer was washed with brine, dried over $MgSO_4$, concentrated, and purified by chromatography (50% EtOAc/hexanes) to afford 13 mg of **32** (65%) as a clear oil (R_f = 0.28, 20% EtOAc/hexanes). IR (neat) 3432, 2942, 2103, 1658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 0.90 (t, *J* = 7.4 Hz, 3H), 1.34-1.40 (m, 2H), 1.61-1.75 (m, 2H), 1.77-1.91 (m, 2H), 2.00-2.08 (m, 2H), 2.20 (ddd, *J* = 2.0, 5.0, 13.3 Hz, 1H), 2.38-2.53 (m, 3H), 2.77 (td, *J* = 4.3, 13.8 Hz, 1H), 3.07 (br s, 1H), 3.48-3.57 (m, 2H), 4.84 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 9.4, 26.9, 27.2, 30.7, 32.8, 33.1, 33.5, 46.2, 50.0, 71.8, 129.5, 175.8, 199.4; CIMS *m/z* (relative intensity) 250 (MH^+, 27), 222 (29), 204 (100); HRMS calcd for $C_{13}H_{20}O_2N_3$: 250.1555, found: 250.1567.

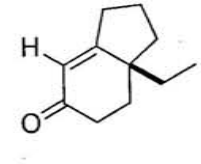
5a*S*-Ethyl-8a*S*-decahydro-3-oxa-indacen-8-one (24). $NaBH_4$ (0.49 g, 13.0 mmol) was added to a solution of **18** (4.32 mmol) in MeOH (25 mL) at 0 °C. After stirring the reaction mixture for 5 min it was allowed to warm to rt, stirred for an additional 20 min, quenched with acetone (2 mL), and poured into H_2O (50 mL). The aqueous layer was extracted with Et_2O (2 x 100 mL) and the organic layer was washed with H_2O (50 mL), dried over $MgSO_4$, and concentrated to **23** which was a thick oil that was used in the next step without purification.

NaN_3 (2.45 g, 37.7 mmol) was added to crude **23** (0.93 g, 3.77 mmol) in DMF (30 mL), and the reaction mixture heated at 78 °C for 17 h. The reaction was allowed to cool to rt and poured into H_2O (100 mL) and the aqueous layer was extracted with Et_2O (3 x 100 mL). The organic layer was washed with brine, dried over $MgSO_4$, and concentrated to afford 0.87 g of a clear oil that was reacted with PCC (2.97 g, 13.7 mmol). After stirring for 2 h at rt the reaction mixture was treated with silica gel (2 g) and diluted with Et_2O (100 mL). The reaction mixture was then filtered through a pad of silica gel and the organic layer was concentrated to a pale yellow oil. The crude product was purified by chromatography (30% EtOAc/hexanes) to afford **7** and **24** (4:1 mixture). For **24**: IR (neat) 2922, 1727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 0.85-0.95 (m, 3H), 1.15-2.15 (m, 8H), 2.22-2.33 (m, 3H), 2.45-2.52 (m, 1H), 2.72-2.80 (m, 1H), 3.02-3.20 (m, 1H), 3.70-3.80 (m, 1H), 3.85-4.00 (m, 2H); CIMS *m/z* (relative intensity) 209 (MH^+, 95), 191 (100).

References

(1) Parker, K. A.; Iqbal, T. *J. Org. Chem.* **1987**, *52*, 4369-4377.
(2) Bernady, K. F.; Poletto, J. F.; Nocera, J.; Mirando, P.; Schaub, R. E.; Weiss, M. J. *J. Org. Chem.* **1980**, *45*, 4702-4715.
(3) Yadav, J. S.; Prahlad, V.; Muralidhar, B. *Synth. Commun.* **1997**, *27*, 3415-3418.





9

Current Data Parameters

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PROCNO	1

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F2 - Processing parameters

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1D NMR plot parameters

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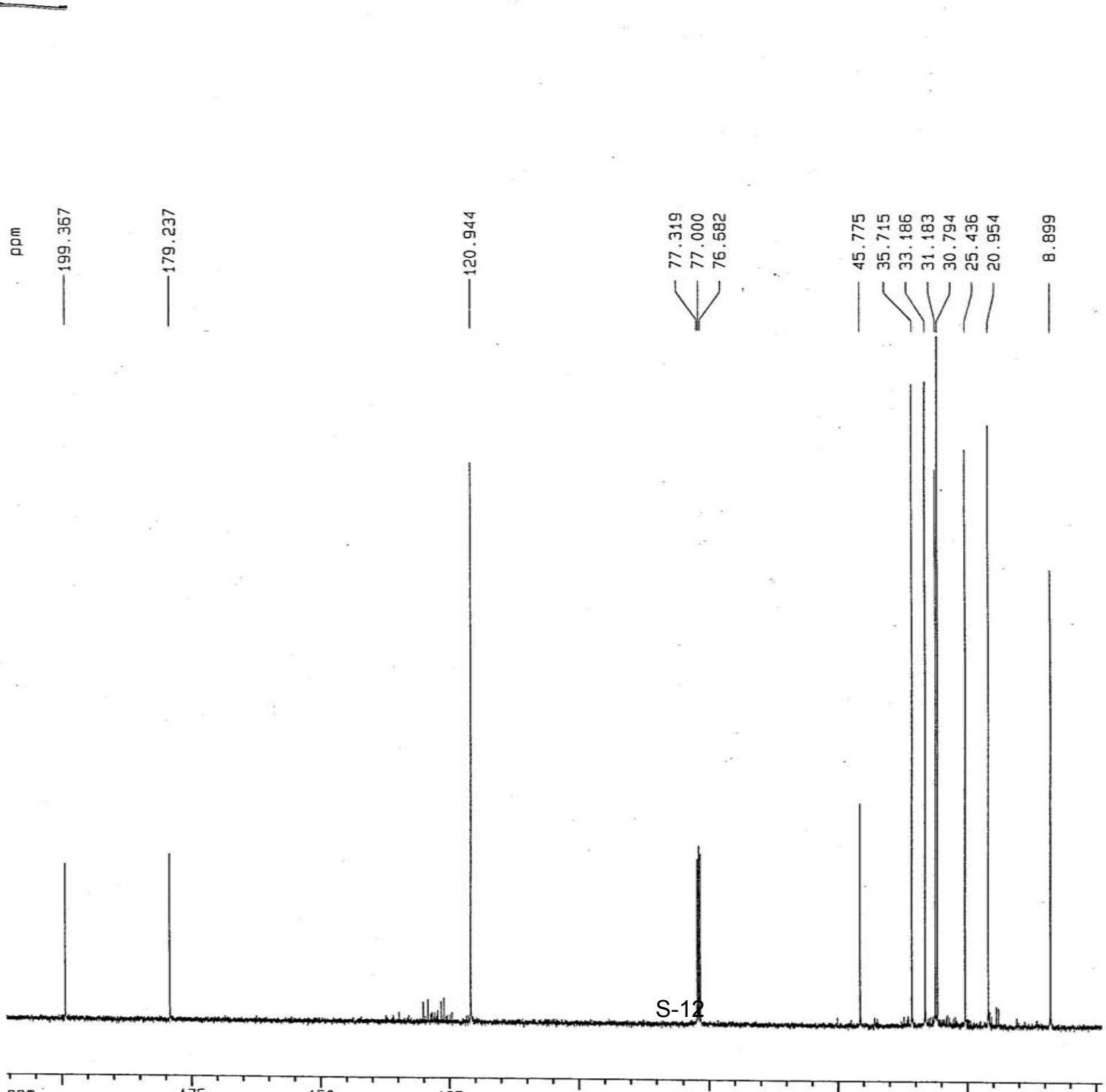

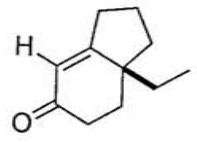

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Current Data Parameters

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PROCNO	1

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F2 - Processing parameters

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1D NMR plot parameters

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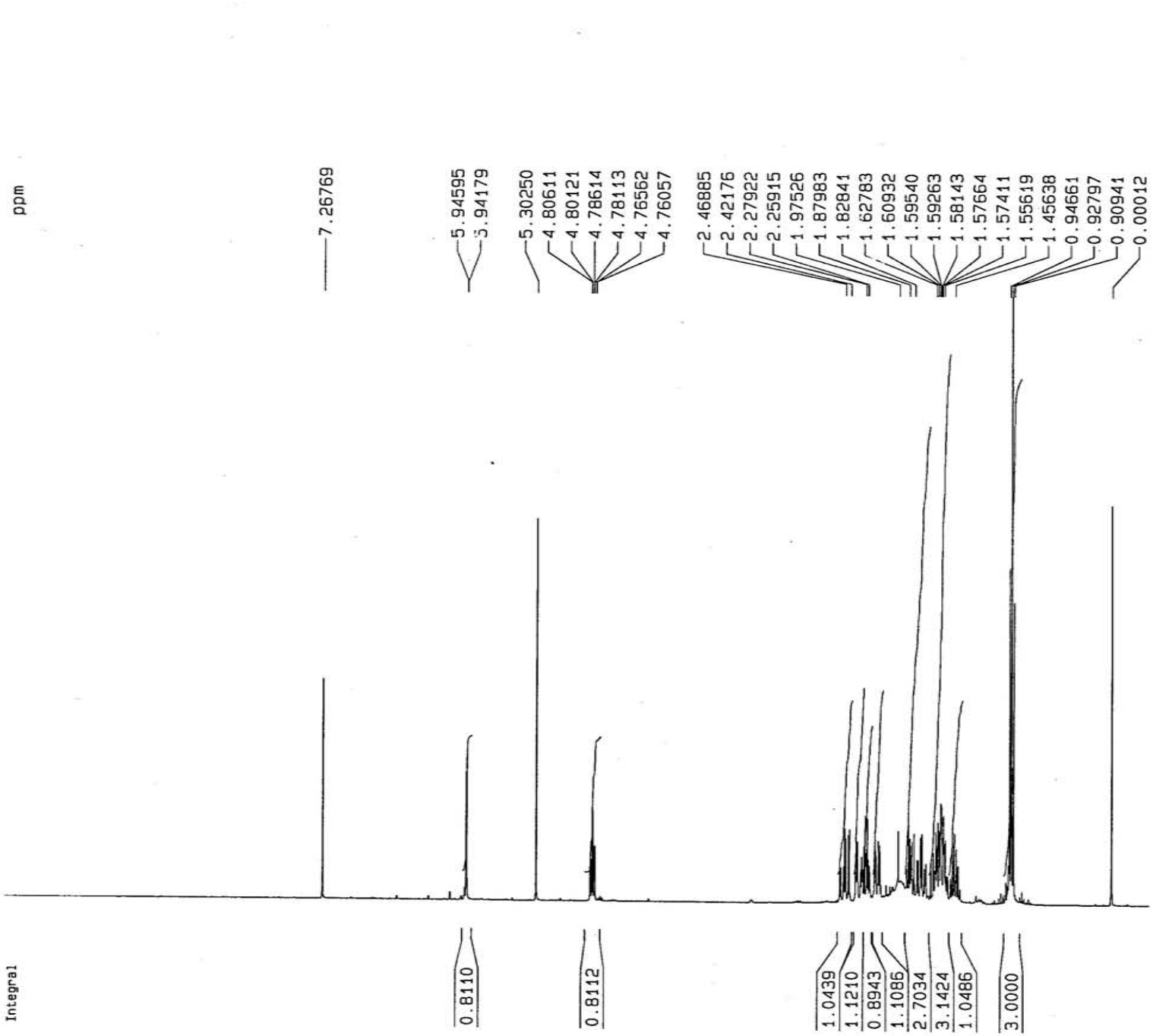

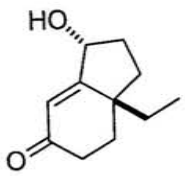

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PROCNO 1

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NUC1	1H
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F2 - Processing parameters

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1D NMR plot parameters

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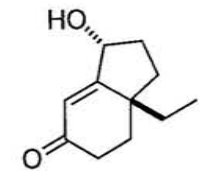

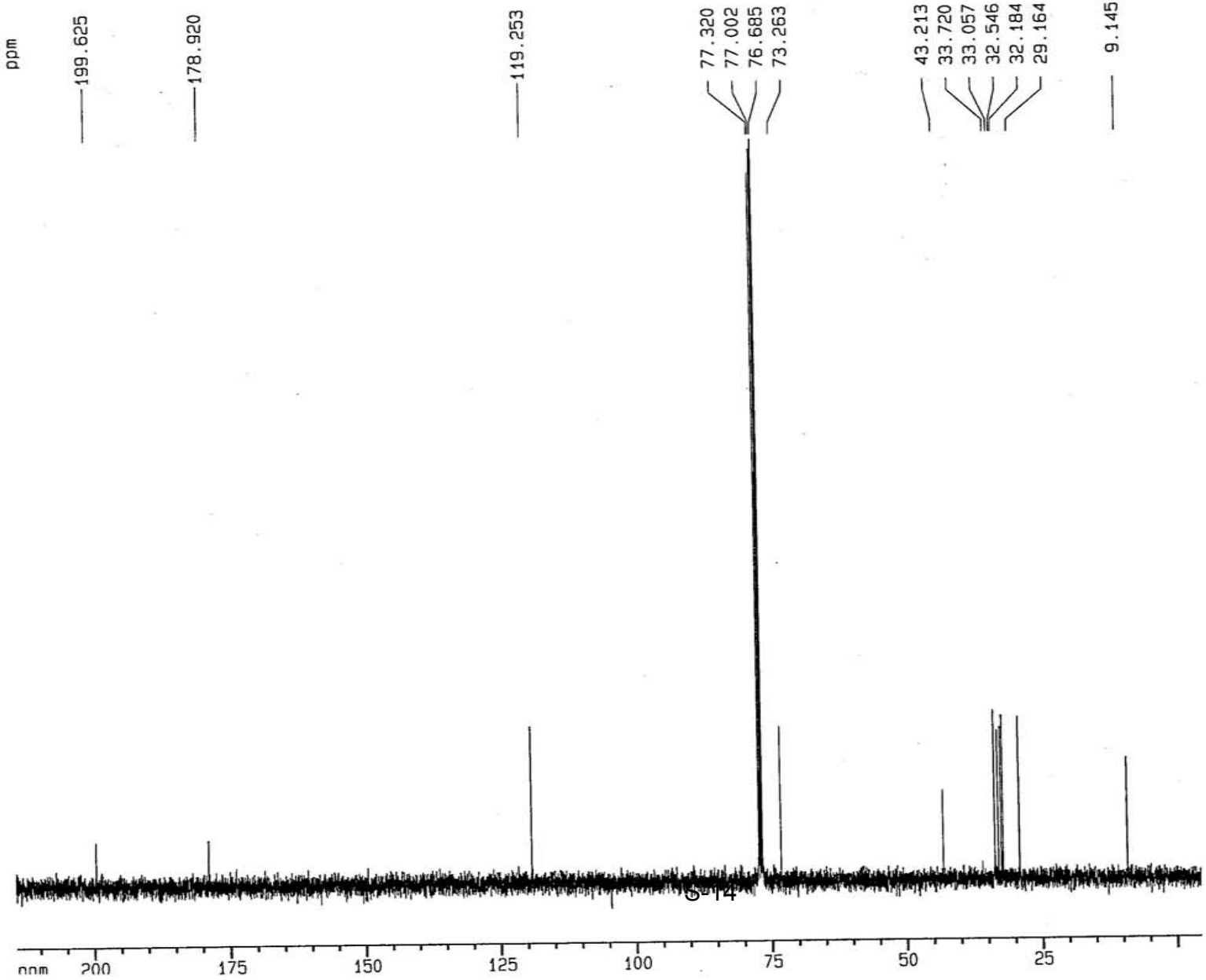

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PROCNO	1

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NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

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1D NMR plot parameters

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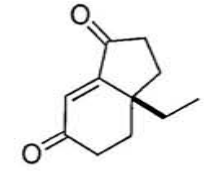

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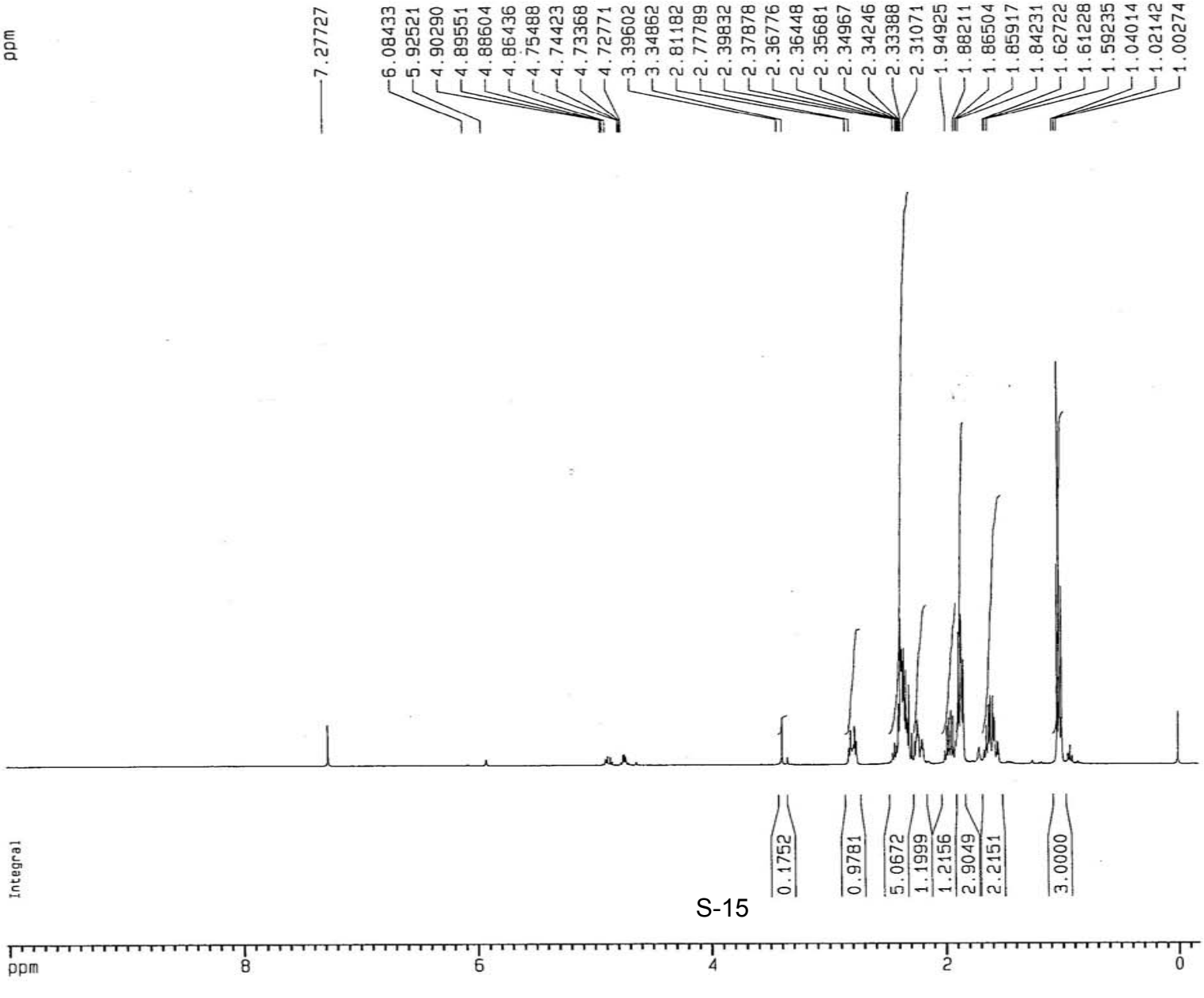

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PROCNO 1

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DS 2
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FIDRES 0.146157 Hz
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RG 128
DW 104.400 usec
DE 4.50 usec
TE 300.0 K
D1 1.00000000 sec
P1 7.70 usec
DE 4.50 usec
SFO1 400.1320007 MHz
NUC1 1H
PL1 -6.00 dB

F2 - Processing parameters
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LB 0.30 Hz
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1D NMR plot parameters
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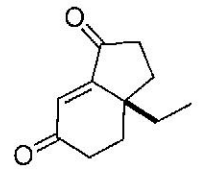

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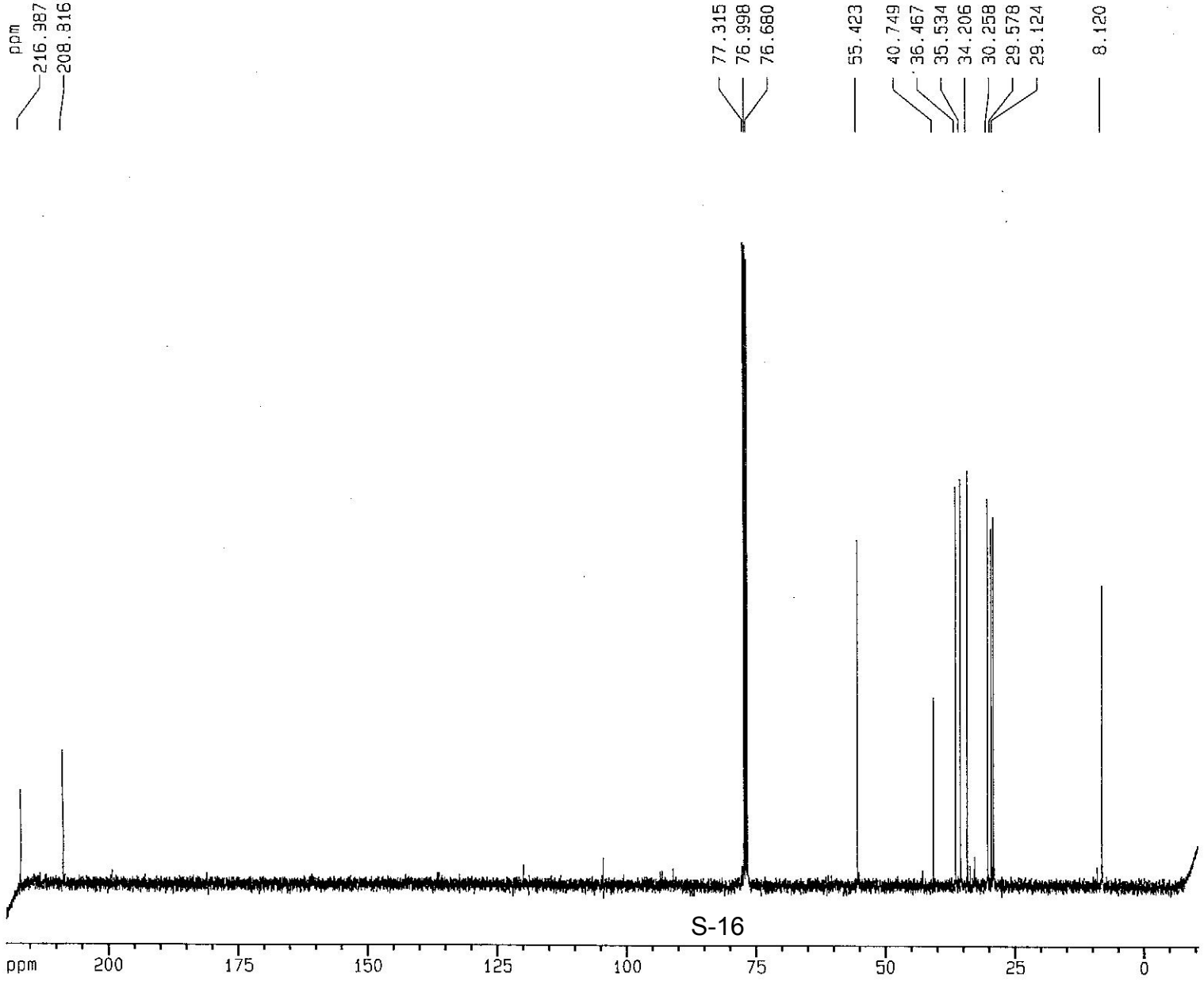

S-16

Current Data Parameters

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PROCNO	1

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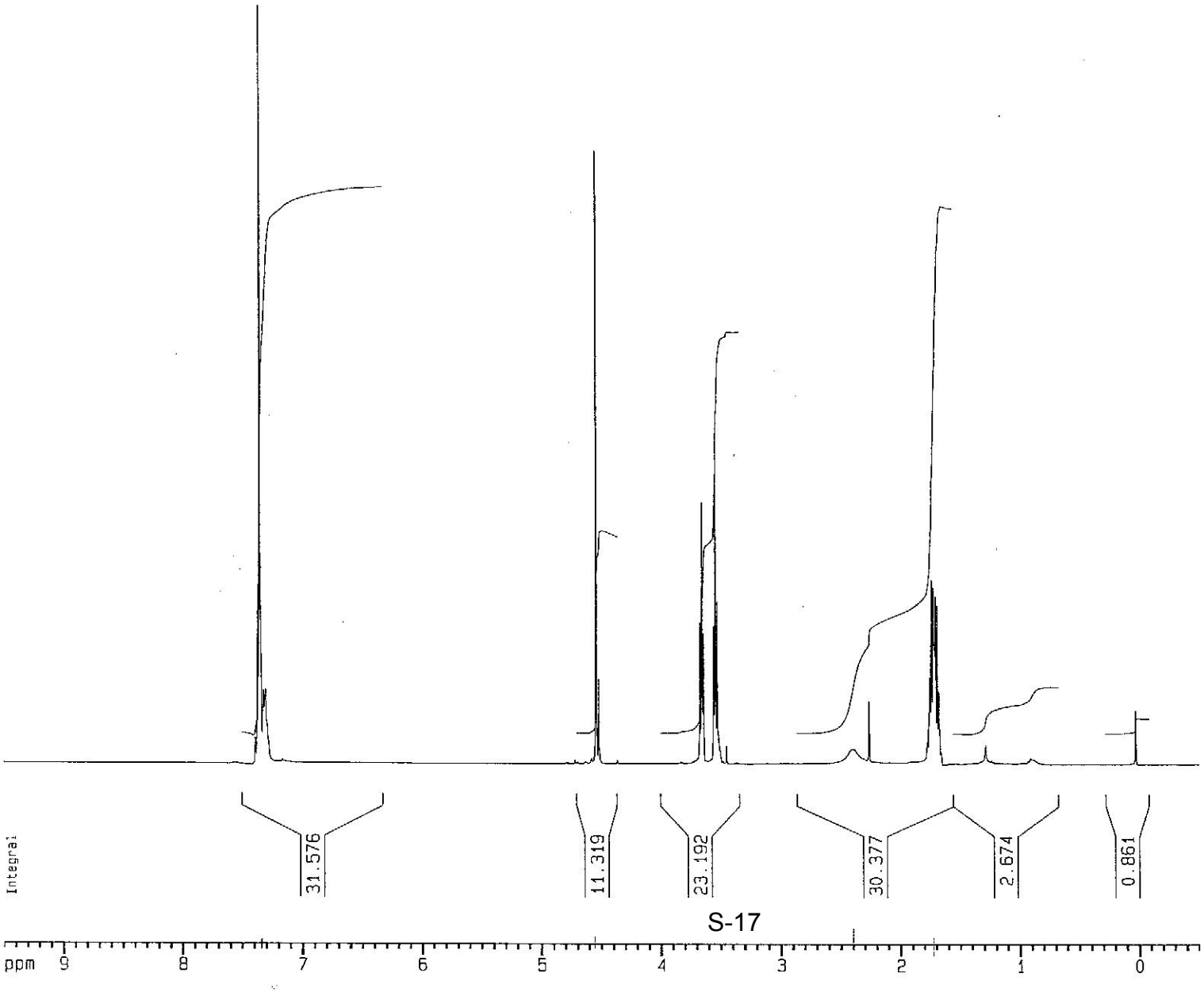
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	1024
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

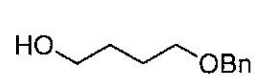
F2 - Processing parameters

SI	32768
SF	100.6127741 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	219.587 ppm
F1	22093.27 Hz
F2P	-10.485 ppm
F2	-1054.88 Hz
PPMCM	11.50358 ppm/c
HZCM	1157.40747 Hz/cm





Current Data Parameters

NAME	ks3.100
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

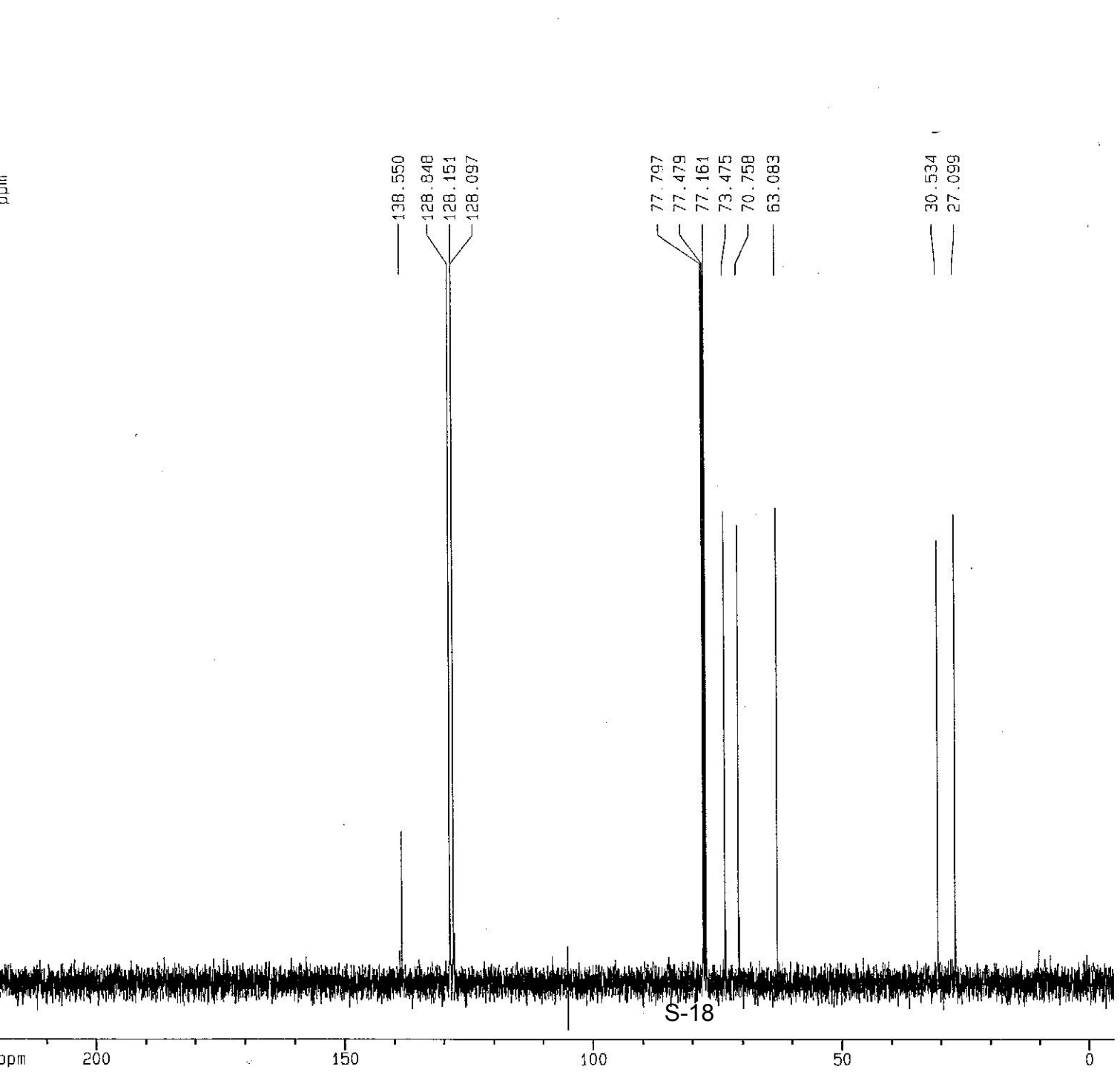
Date_	961226
Time	9.16
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

F2 - Processing parameters

SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm



Current Data Parameters

NAME	ks3.100
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

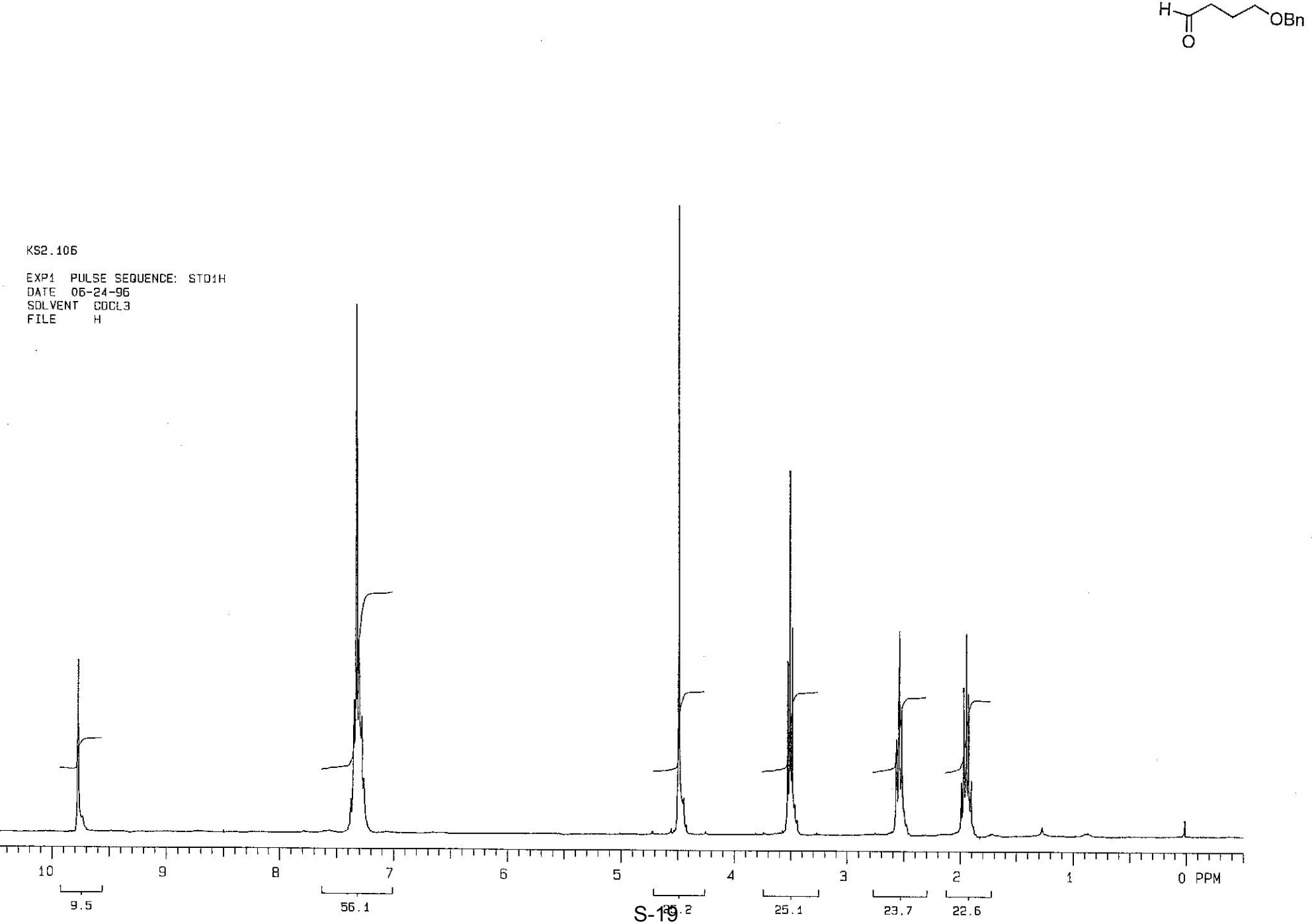
Date_	961226
Time	9.26
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

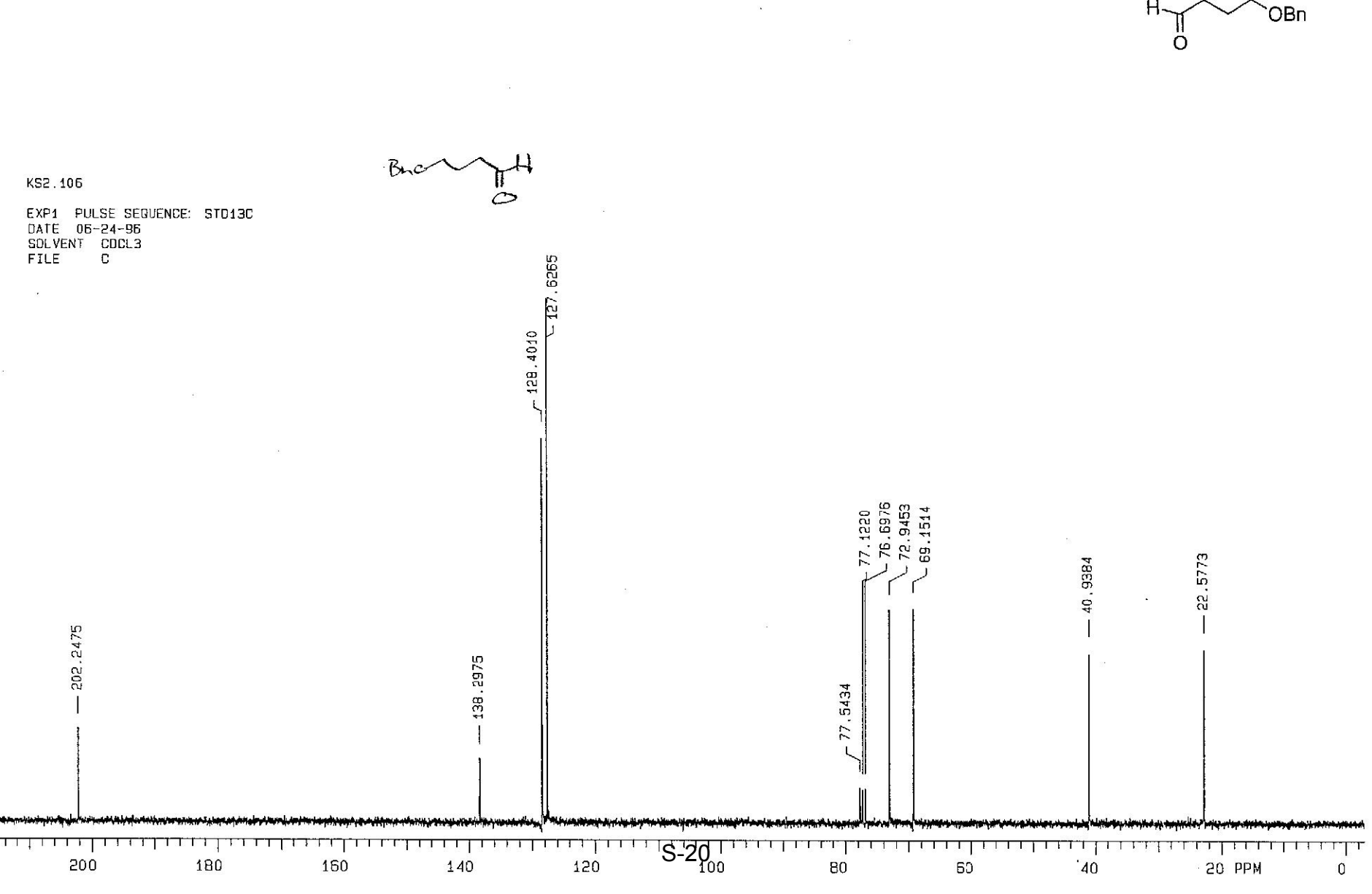
F2 - Processing parameters

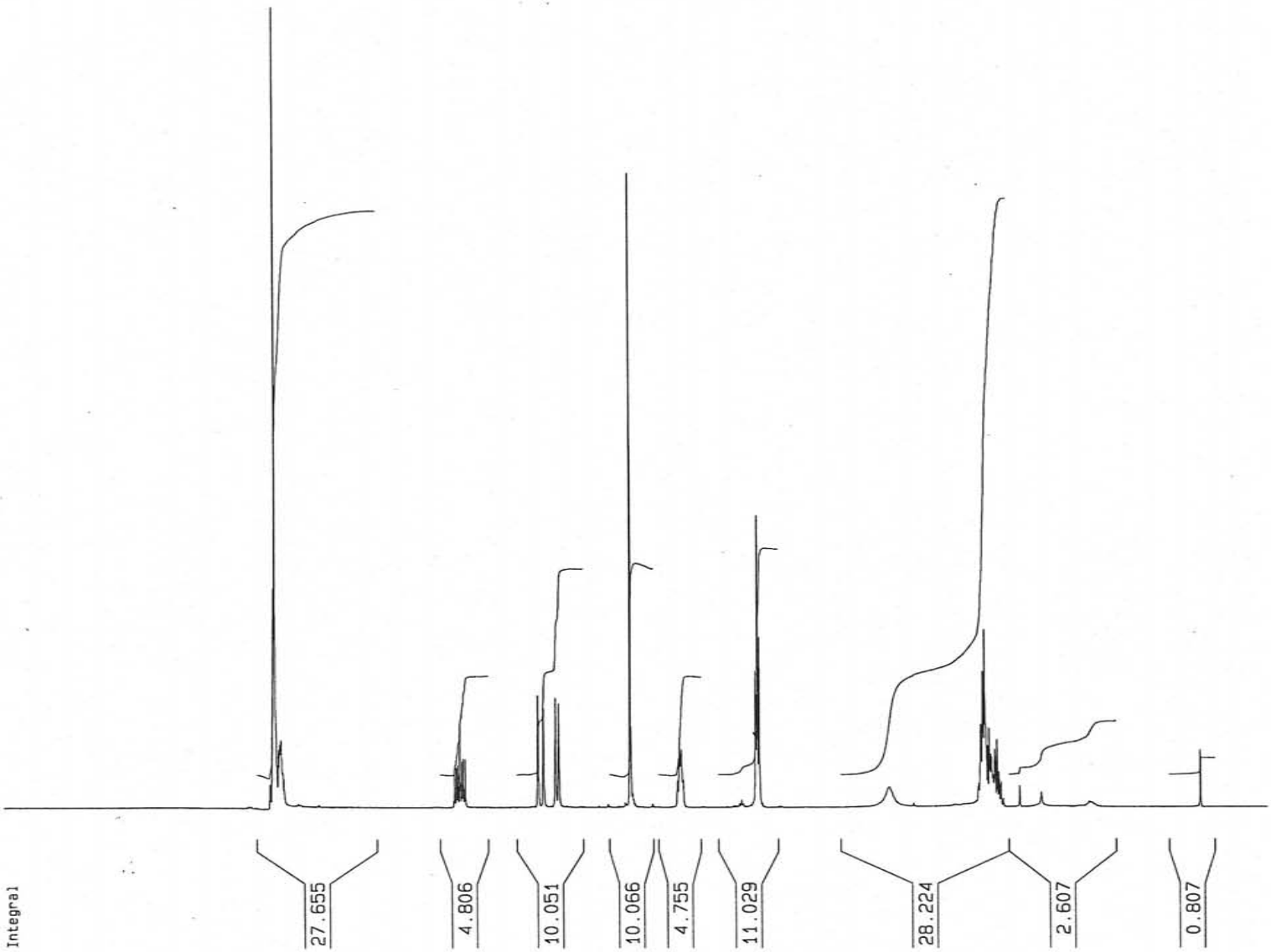
SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	4.00

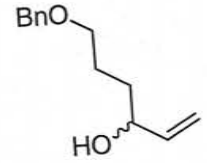
1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	22134.80 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/c
HZCM	1131.89319 Hz/cm


H
O
OBn
KS2.106
EXP1 PULSE SEQUENCE: STD1H
DATE 06-24-96
SOLVENT CDCL3
FILE H
10
9
8
7
6
5
4
3
2
1
0 PPM
9.5
56.1
25.1
23.7
22.6


KS2.106
EXP1 PULSE SEQUENCE: STD13C
DATE 06-24-96
SOLVENT CDCL3
FILE C
202.2475
138.2975
128.4010
127.6265
77.5434
77.1220
76.6976
72.9453
69.1514
40.9384
22.5773
200
180
160
140
120
100
80
60
40
20 PPM
0





Current Data Parameters

NAME	ks3.065
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

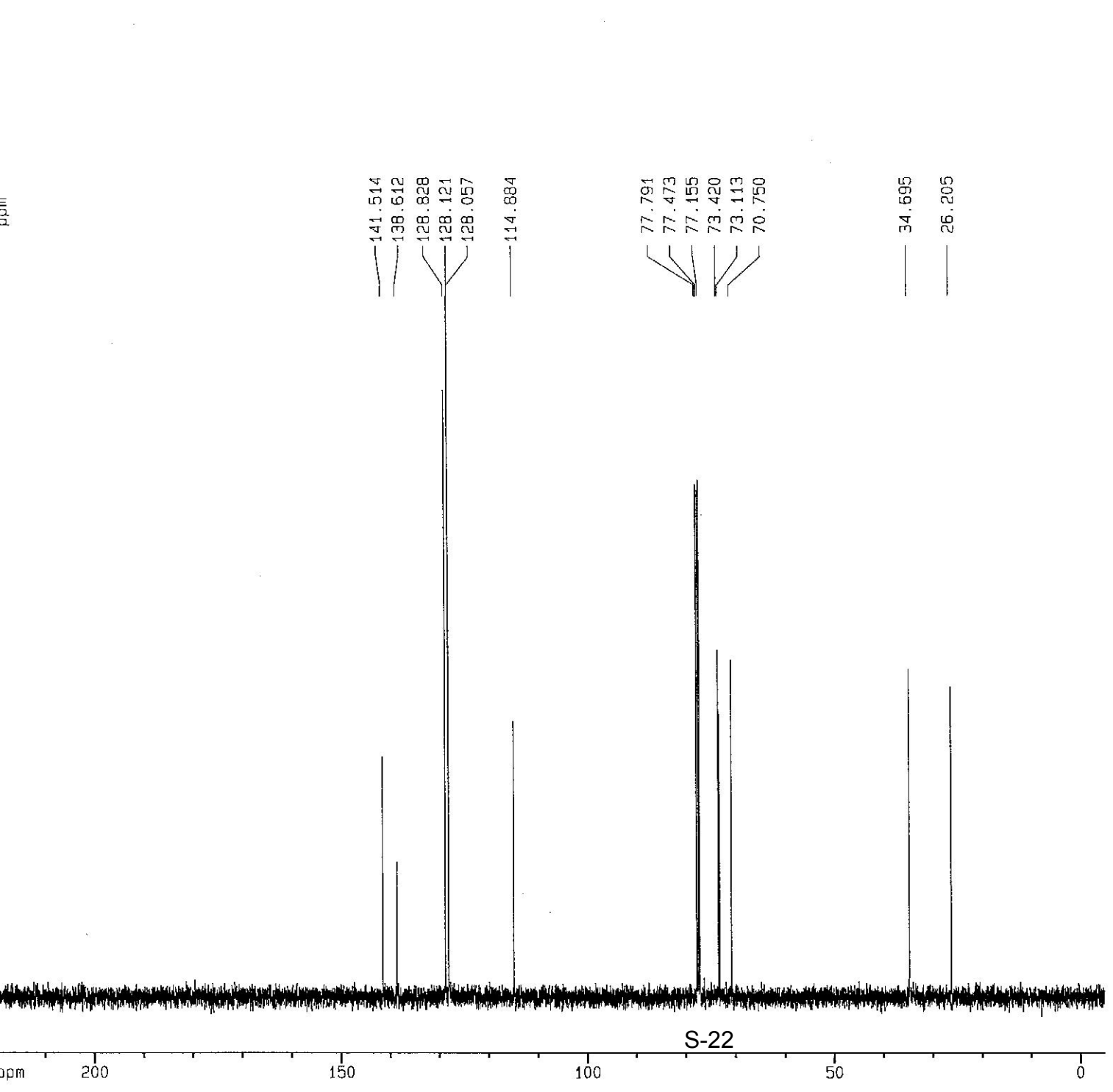
Date_	961223
Time	10.03
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

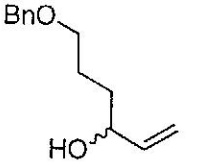
F2 - Processing parameters

SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm





Current Data Parameters

NAME	ks3.065
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

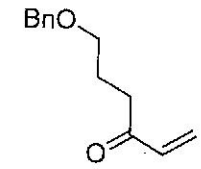
Date_	961223
Time	10.16
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
O1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	22134.80 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/cm
HZCM	1131.89319 Hz/cm



10

Current Data Parameters

NAME	ks2.267
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

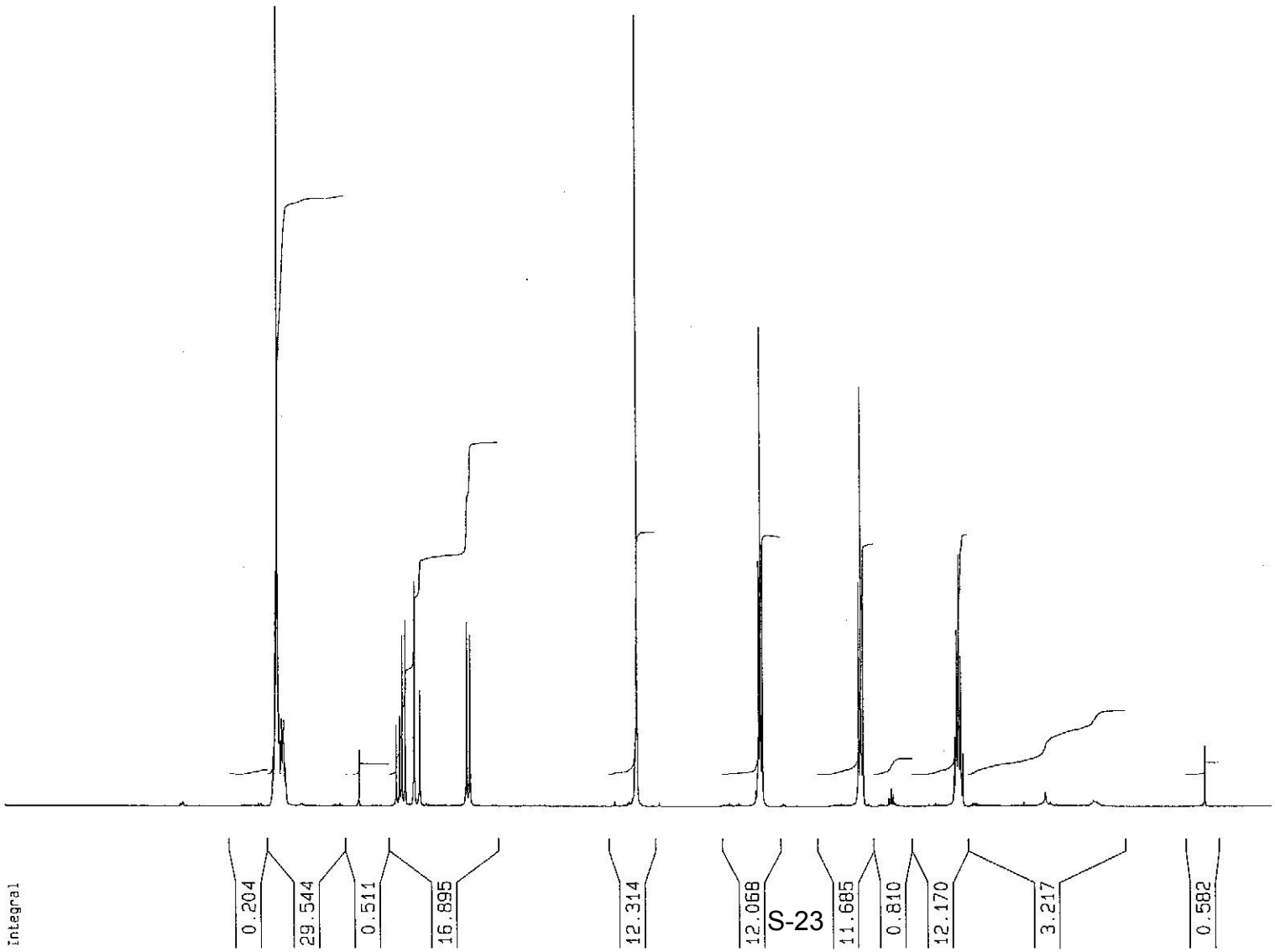
Date_	961218
Time	16.13
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

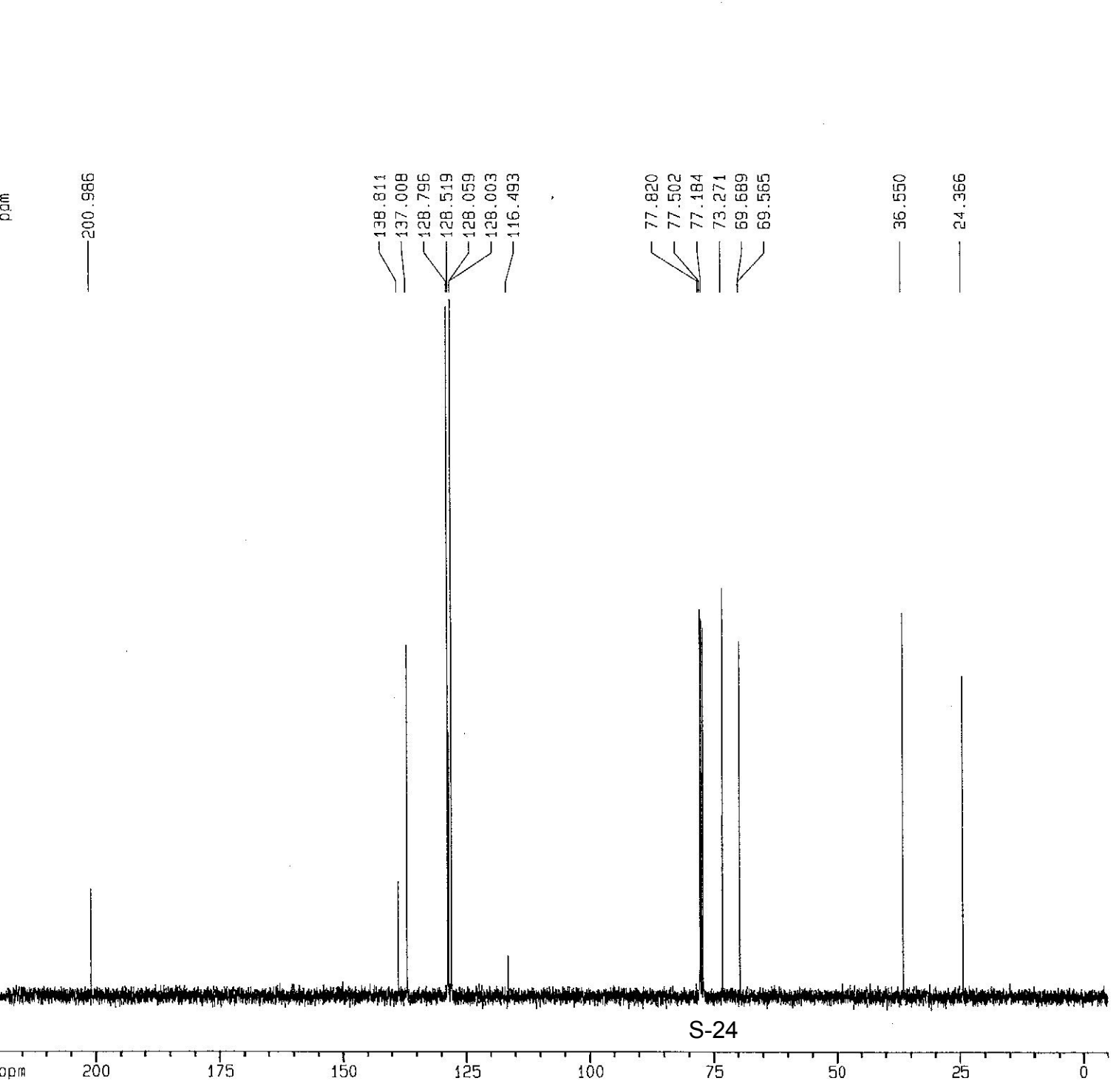
F2 - Processing parameters

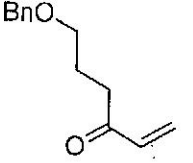
SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm







Current [**10** rameters

NAME	ks2.267
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

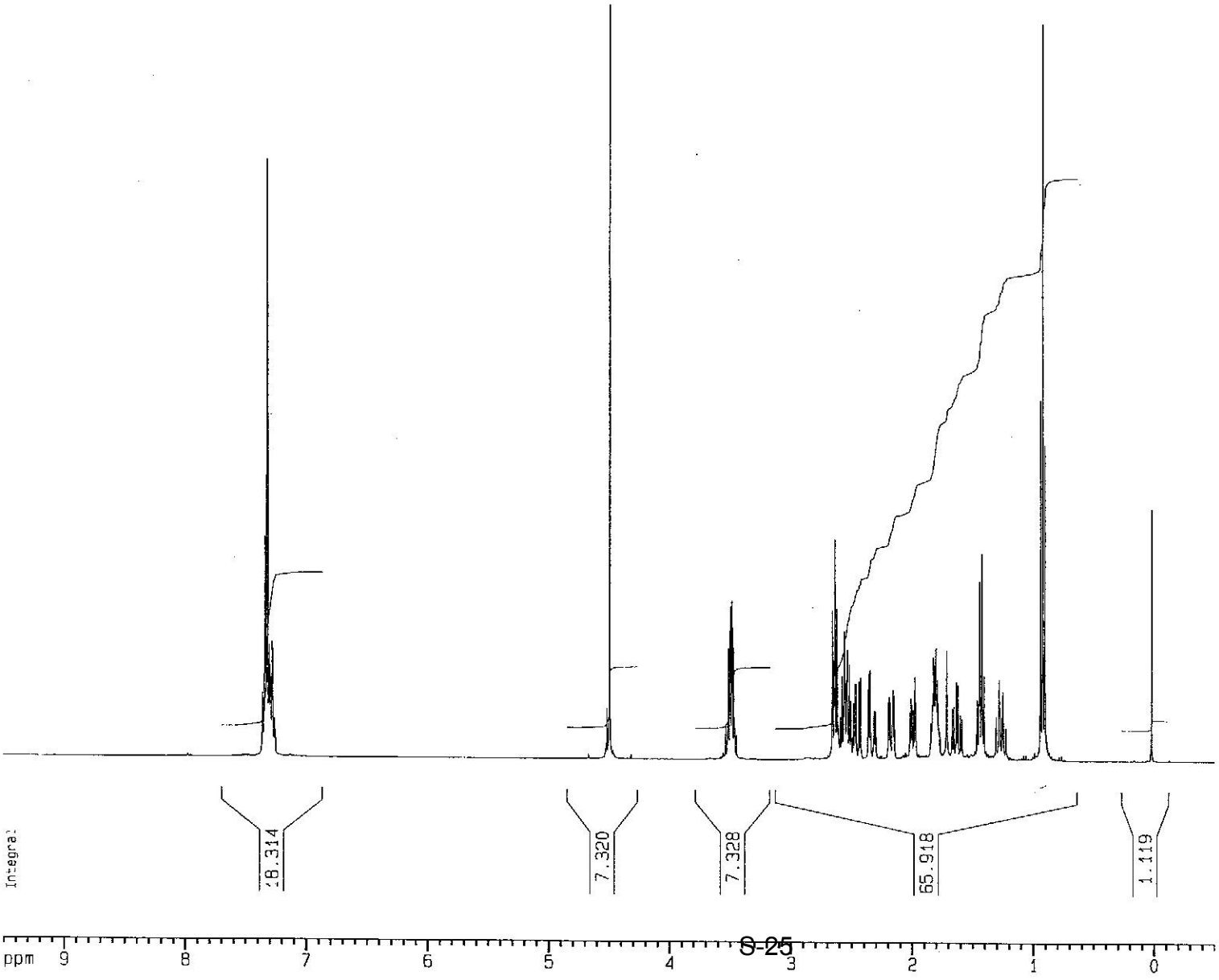
Date_	961218
Time	16.24
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

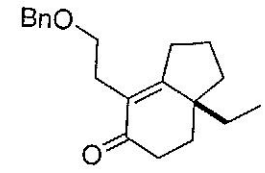
F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	22134.60 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/cm
HZCM	1131.89319 Hz/cm





8

Current Data Parameters

NAME	ks3.032
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

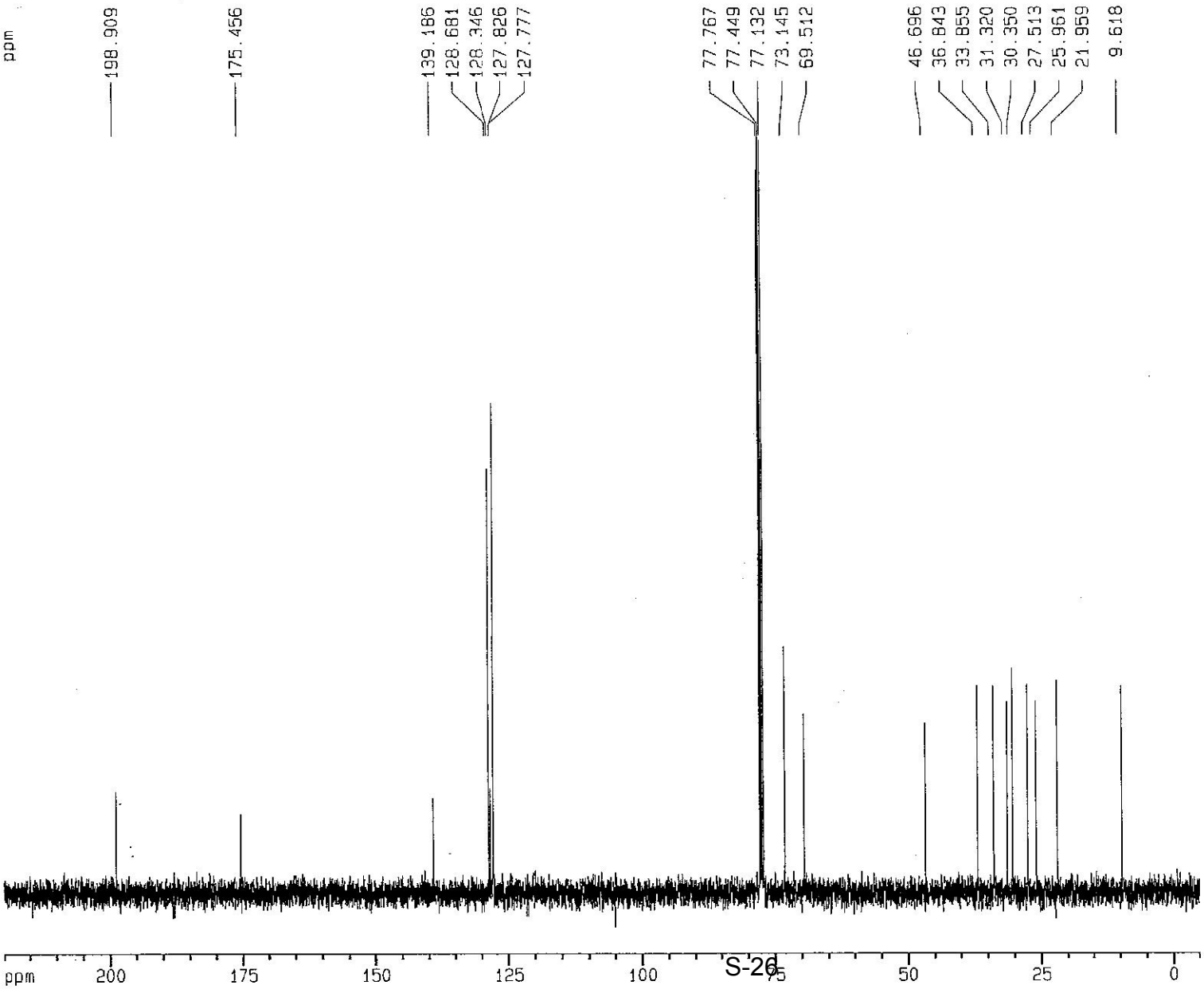
Date_	961216
Time	7.12
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	114
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

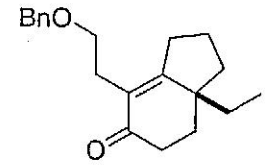
F2 - Processing parameters

SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm





8

Current Data Parameters

NAME	ks3.032
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

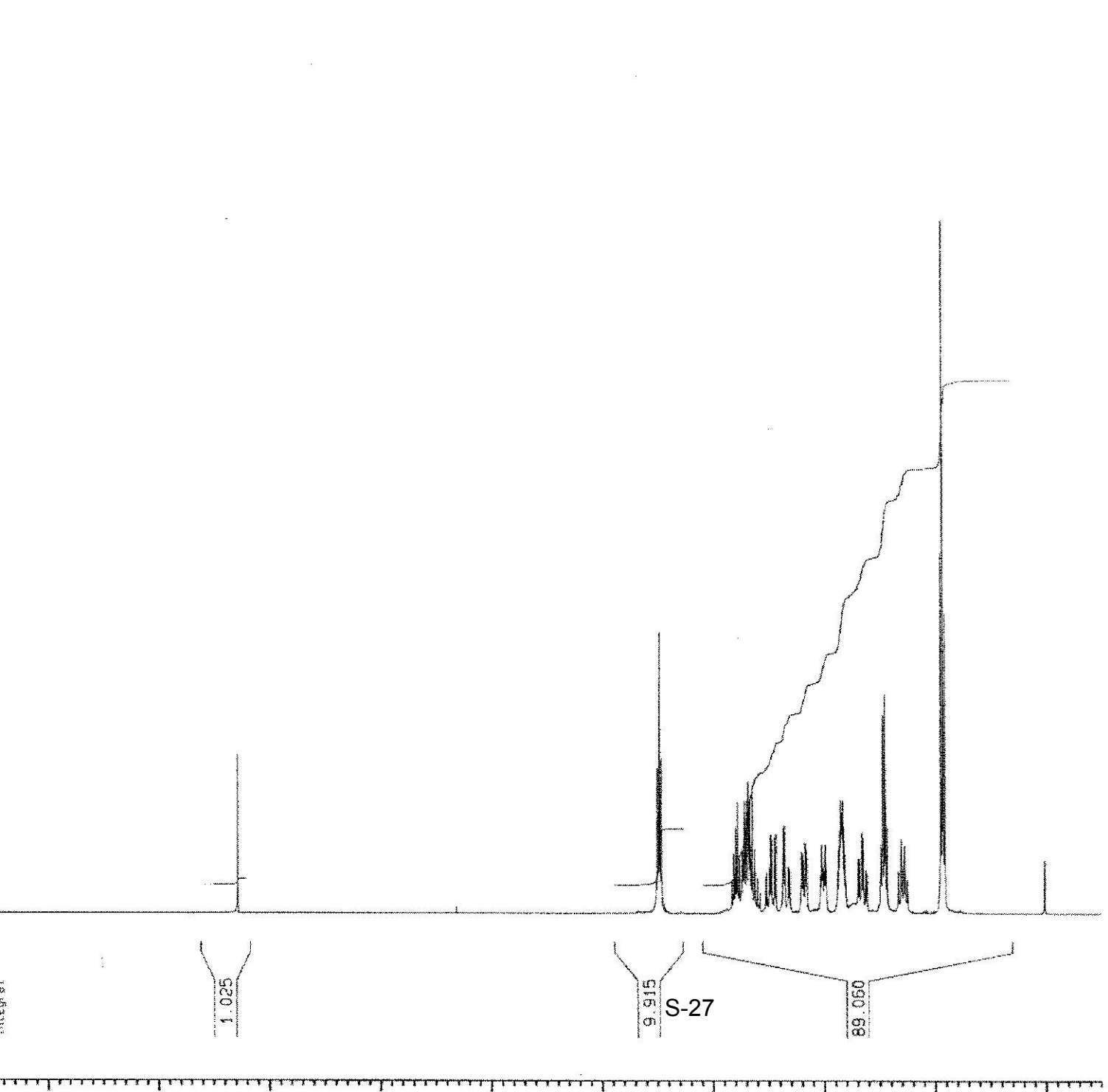
Date_	961216
Time	7.34
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

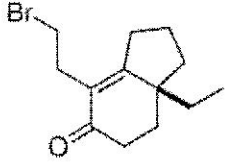
F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	22134.80 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/cm
HZCM	1131.89319 Hz/cm





16a

```
Current Data Parameters
NAME                  ks2.193
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_                  970430
Time                    13.08
INSTRUM                 drx400
PROBHD     5 mm Multinu
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                         16
DS                          2
SWH                 4789.272 Hz
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                        114
DW                  104.400 usec
DE                    4.50 usec
TE                    300.0 K
D1                  1.00000000 sec
P1                    7.70 usec
DE                    4.50 usec
SFO1              400.1320007 MHz
NUC1                      1H
PL1                   -6.00 dB

F2 - Processing parameters
SI                        16384
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                    0.30 Hz
GB                          0
PC                     1.00

1D NMR plot parameters
CX                    20.00 cm
F1P                   9.500 ppm
F1                  3801.24 Hz
F2P                  -0.500 ppm
F2                   -200.07 Hz
PPMCM                0.50000 ppm/cm
HZCM               200.06500 Hz/cm
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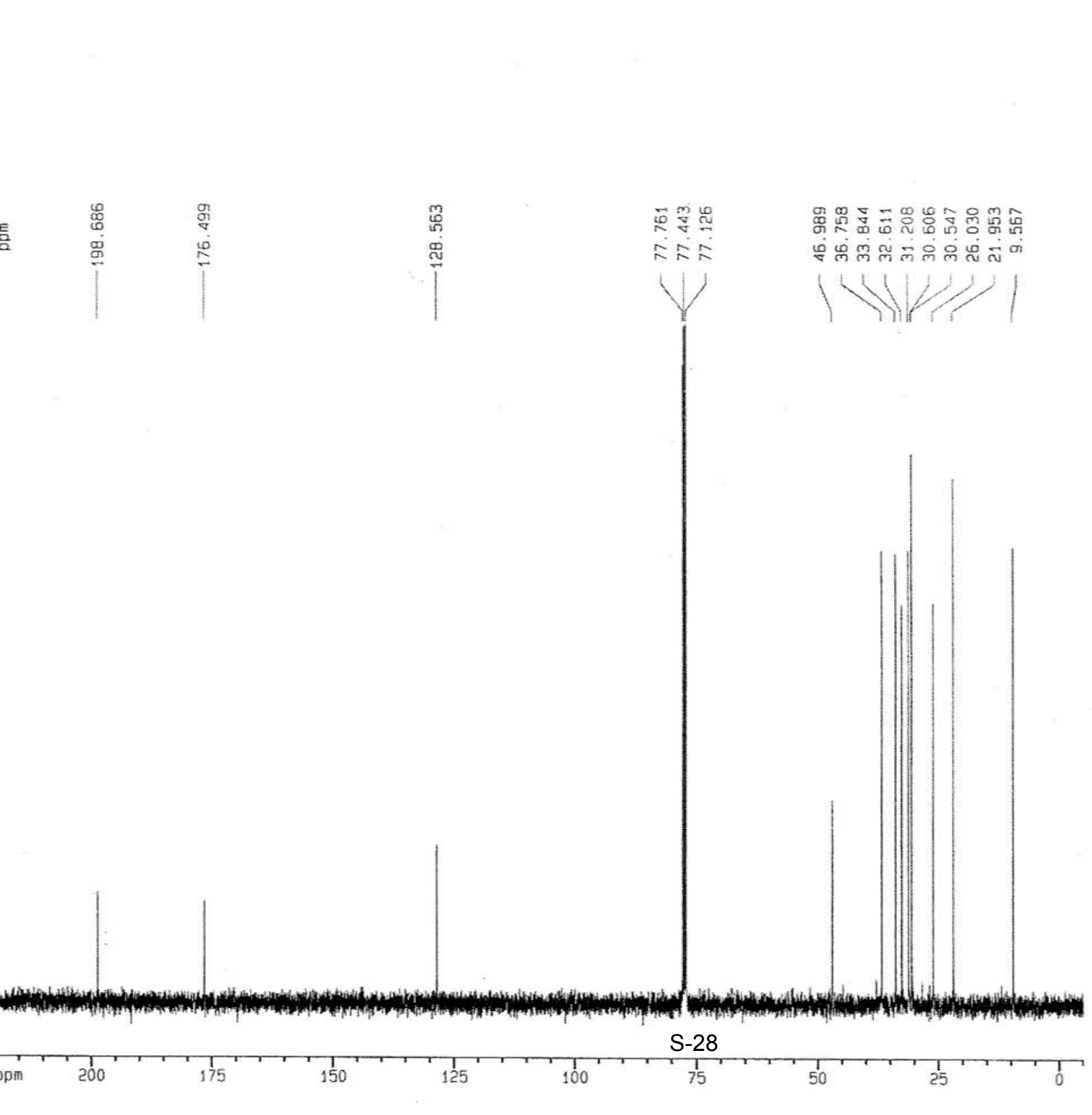
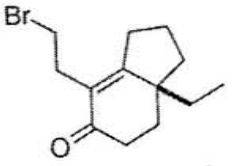




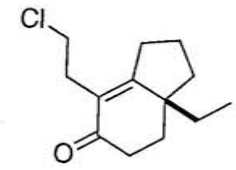
16a

Current Data Parameters	
NAME	ks2.193
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	970430
Time	13.31
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters	
SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
F1P	220.000 ppm
F1	22134.80 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/cm
HZCM	1131.68319 Hz/cm



16b

Current Data Parameters

NAME	ks3.057
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

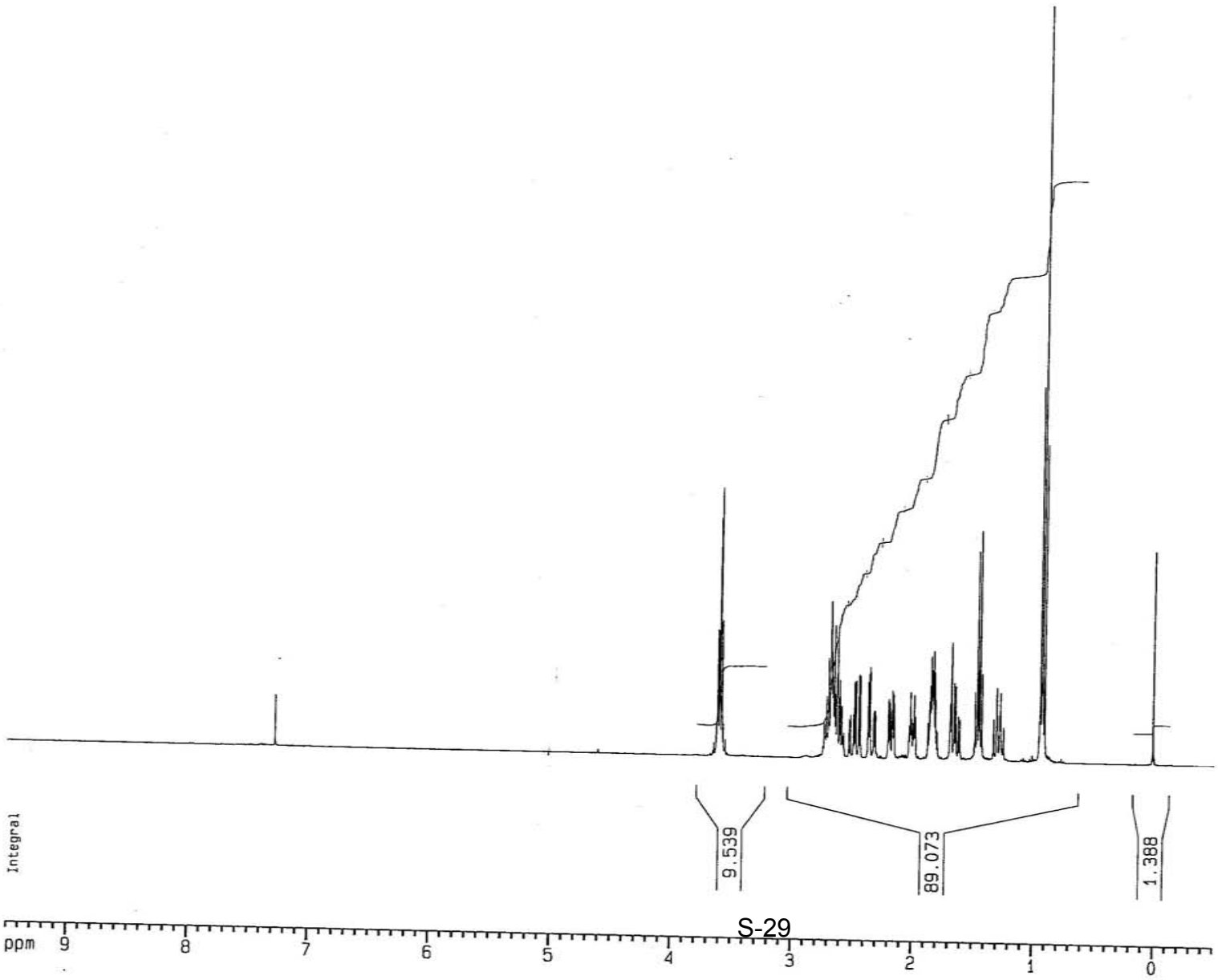
Date_	961216
Time	12.55
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	114
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

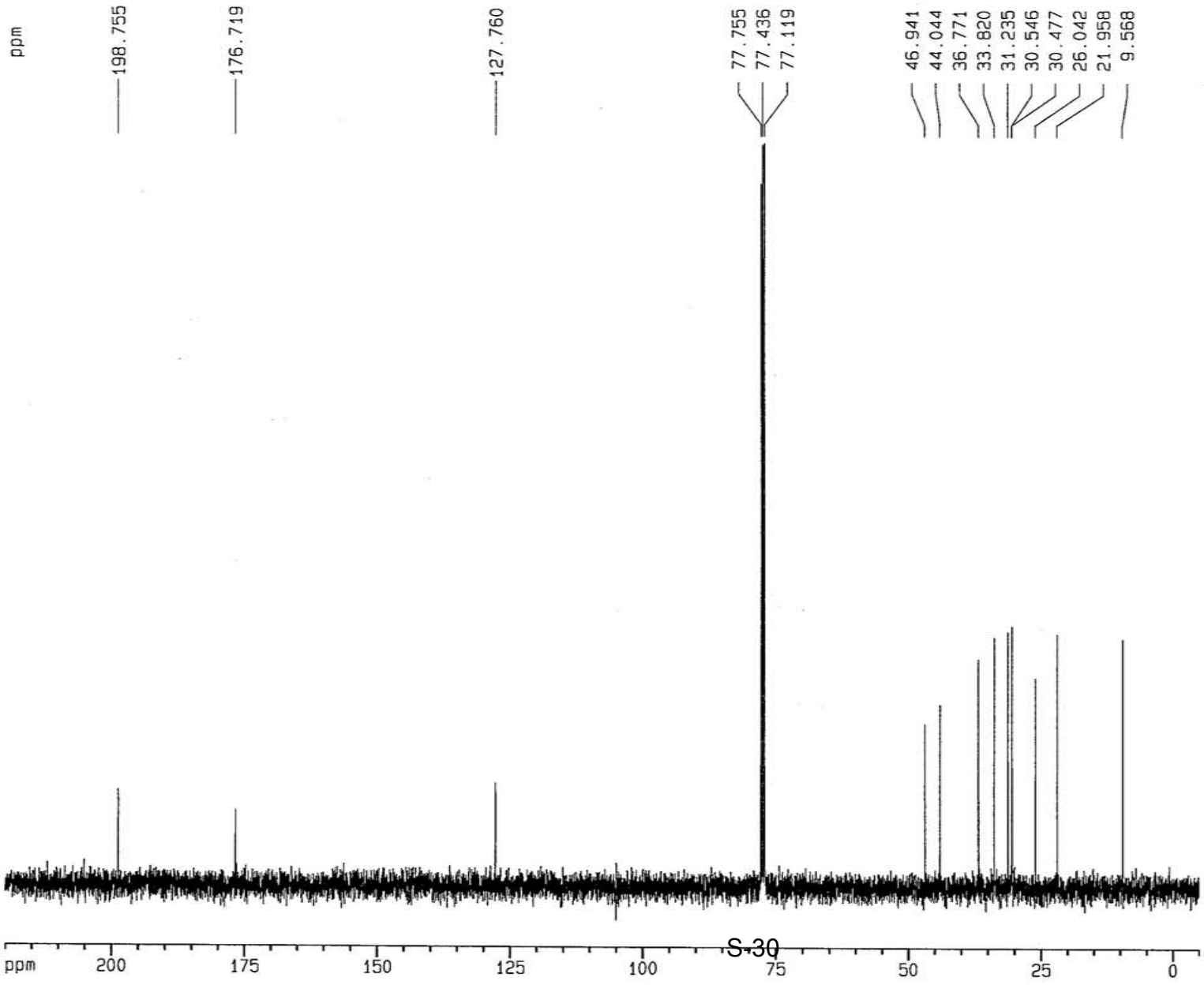
F2 - Processing parameters

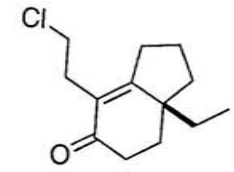
SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm

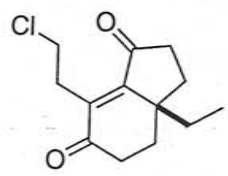






16b

Current Data Parameters	
NAME	ks3_057
EXPNO	2
PROCNO	1
F2 - Acquisition Parameters	
Date_	961216
Time	13.23
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB
F2 - Processing parameters	
SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
1D NMR plot parameters	
CX	20.00 cm
F1P	220.000 ppm
F1	22134.80 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/cm
HZCM	1131.89319 Hz/cm



17

Current Data Parameters

NAME	ks3.274
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

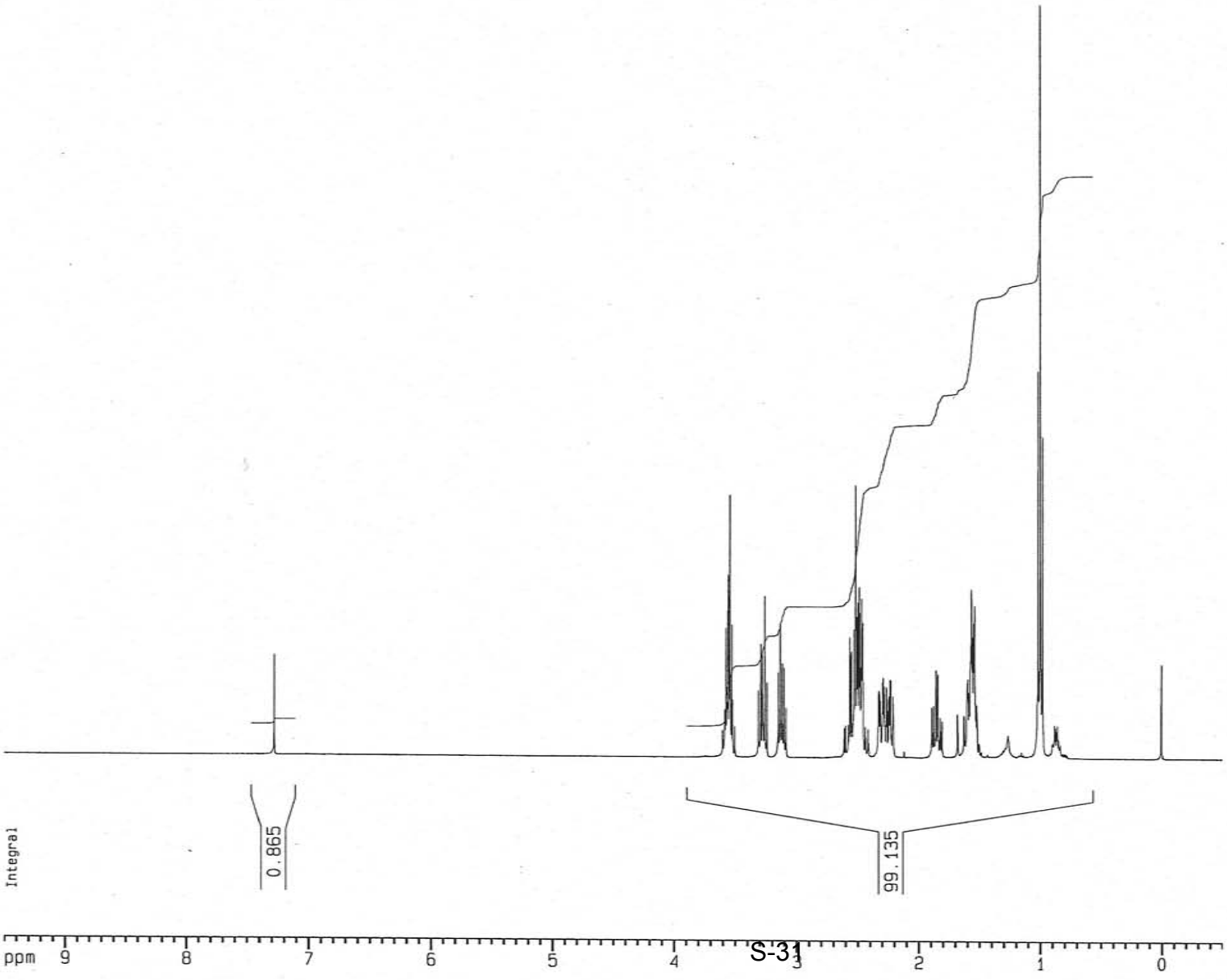
Date_	970422
Time	15.07
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	90.5
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

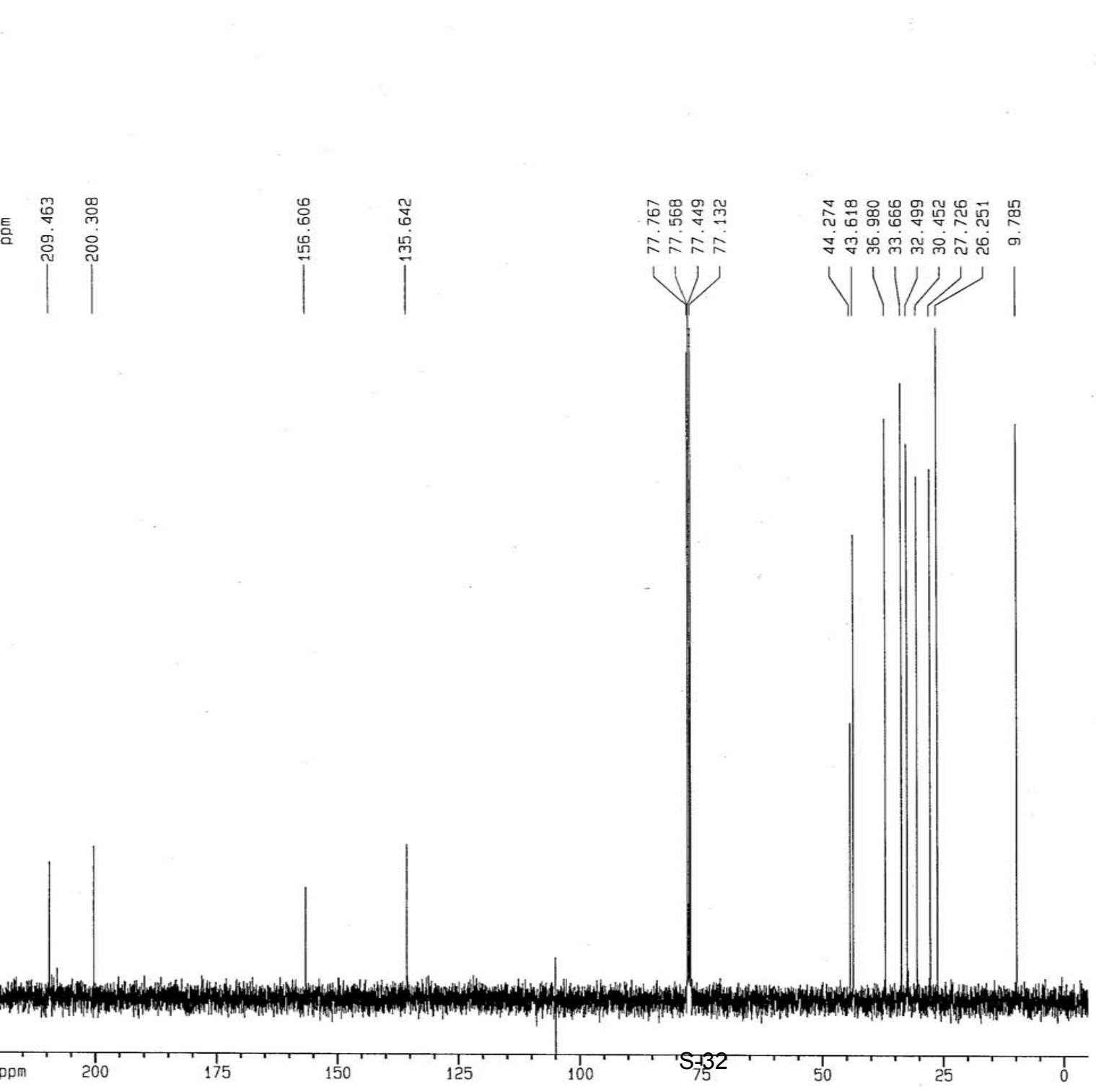
F2 - Processing parameters

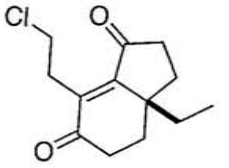
SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm







17

Current Data Parameters

NAME	ks3.274
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

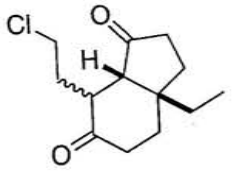
Date_	970422
Time	15.28
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

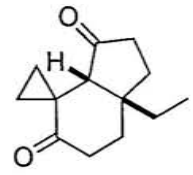
1D NMR plot parameters

CX	20.00 cm
F1P	220.036 ppm
F1	22138.41 Hz
F2P	-5.000 ppm
F2	-503.06 Hz
PPMCM	11.25179 ppm/cm
HZCM	1132.07385 Hz/cm



18

GE NMR
QE PLUS
KSIII 083
11JAN96
RESUBMITTED
OPERATOR: KEF



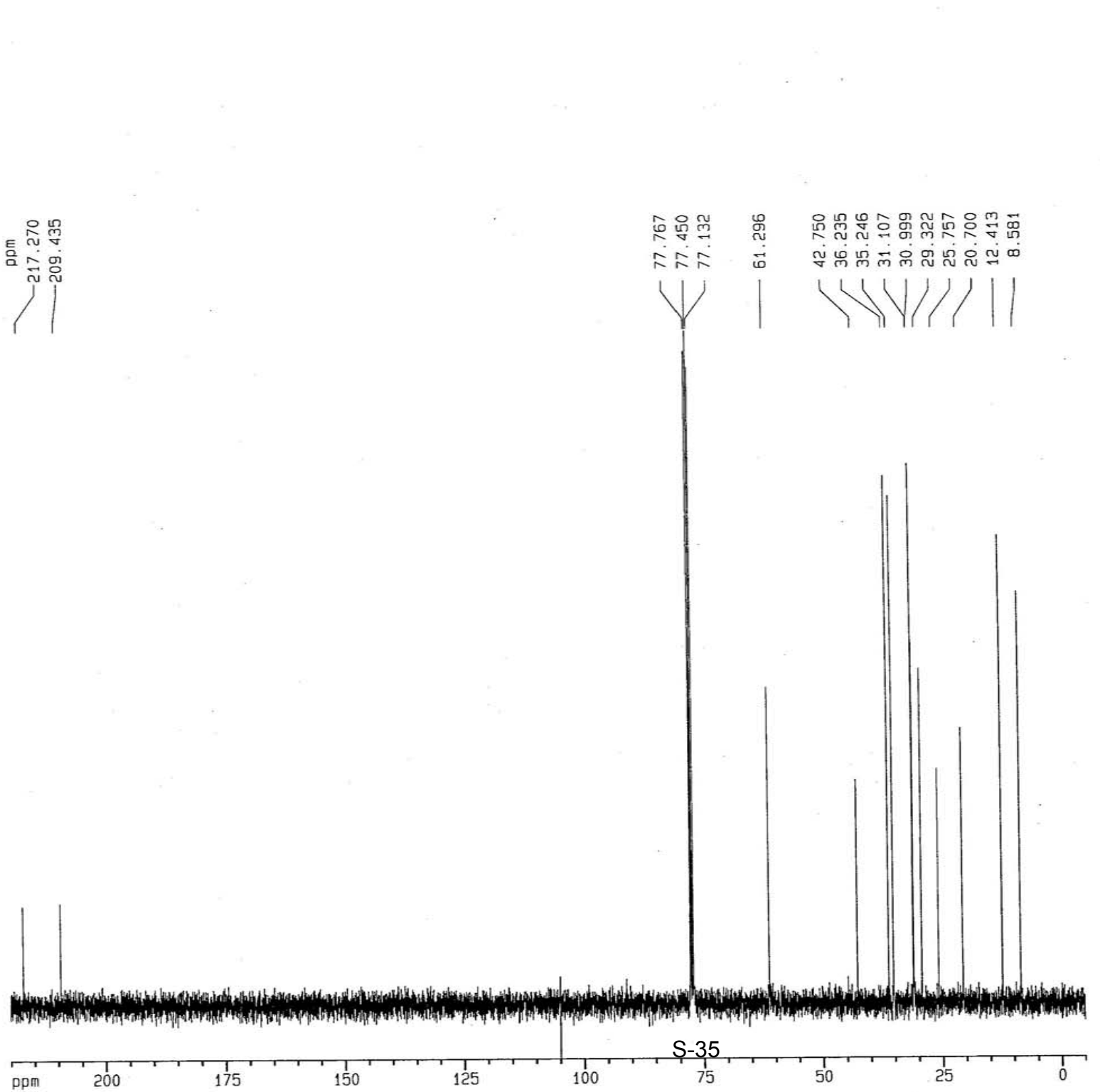
19

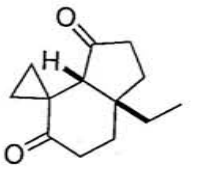
Current Data Parameters	
NAME	ks3.097
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters	
Date_	970423
Time	12.34
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	114
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

F2 - Processing parameters	
SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters	
CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm





19

Current Data Parameters

NAME	ks3.097
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

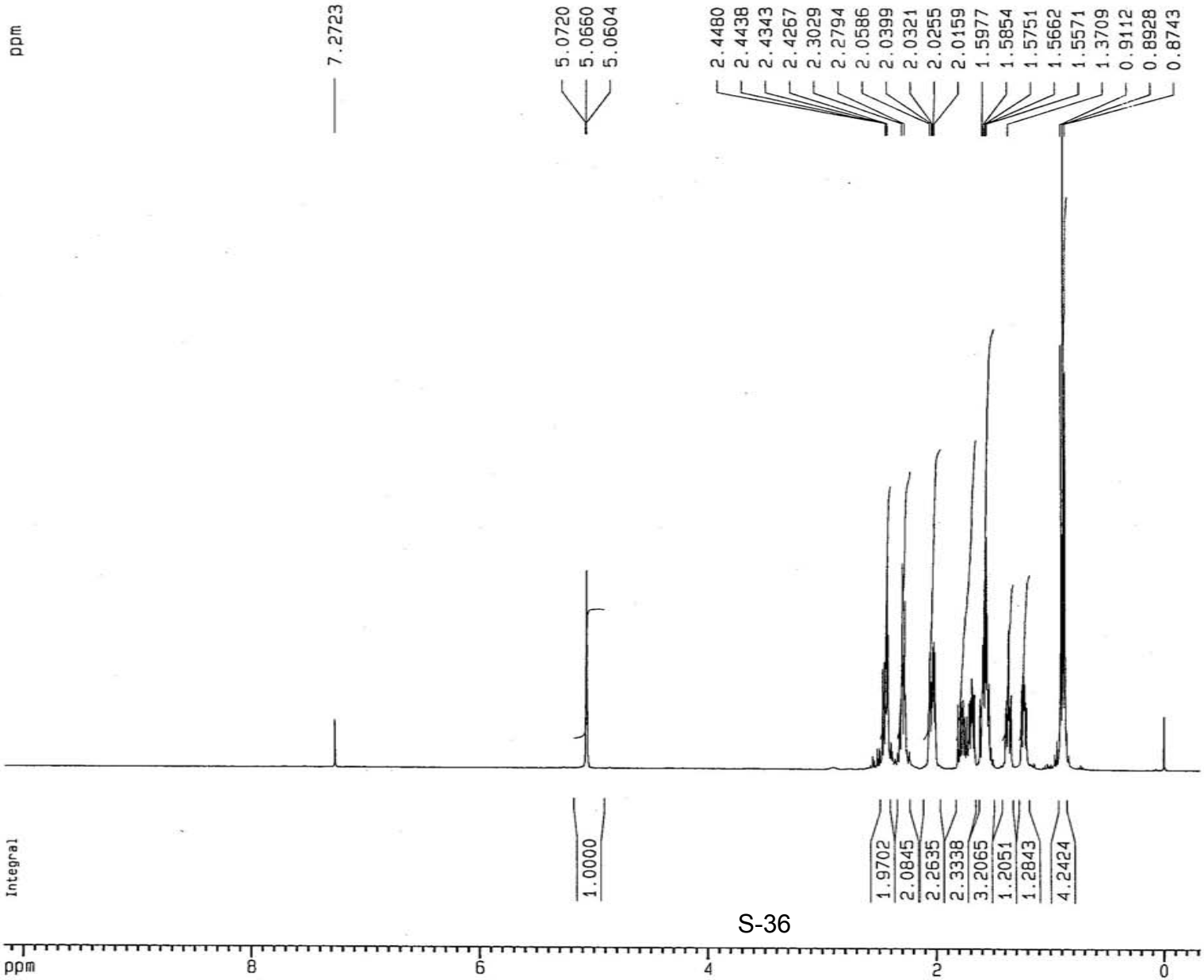
Date_	970423
Time	12.45
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	2
SWH	23640.662 Hz
FIDRES	0.360728 Hz
AQ	1.3861364 sec
RG	32768
DW	21.150 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

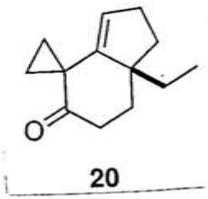
F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	22134.80 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/cm
HZCM	1131.89319 Hz/cm





20

Current Data Parameters

NAME	raj-3-84-prdt
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

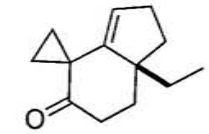
Date_	1000217
Time	16.12
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

F2 - Processing parameters

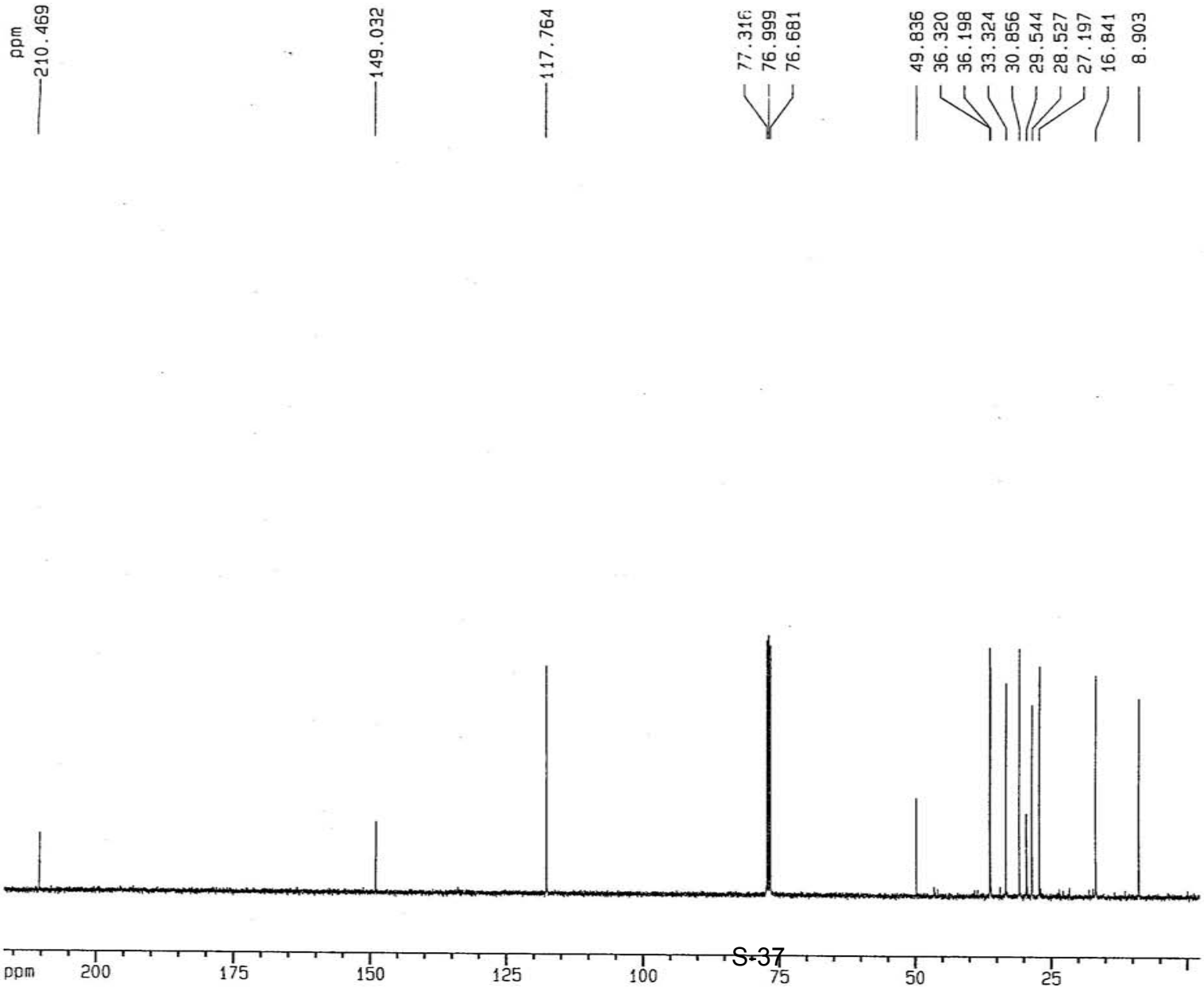
SI	16384
SF	400.1300047 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.167 ppm
F1	4068.20 Hz
F2P	-0.317 ppm
F2	-127.02 Hz
PPMCM	0.52423 ppm/cm
HZCM	209.76091 Hz/cm



20

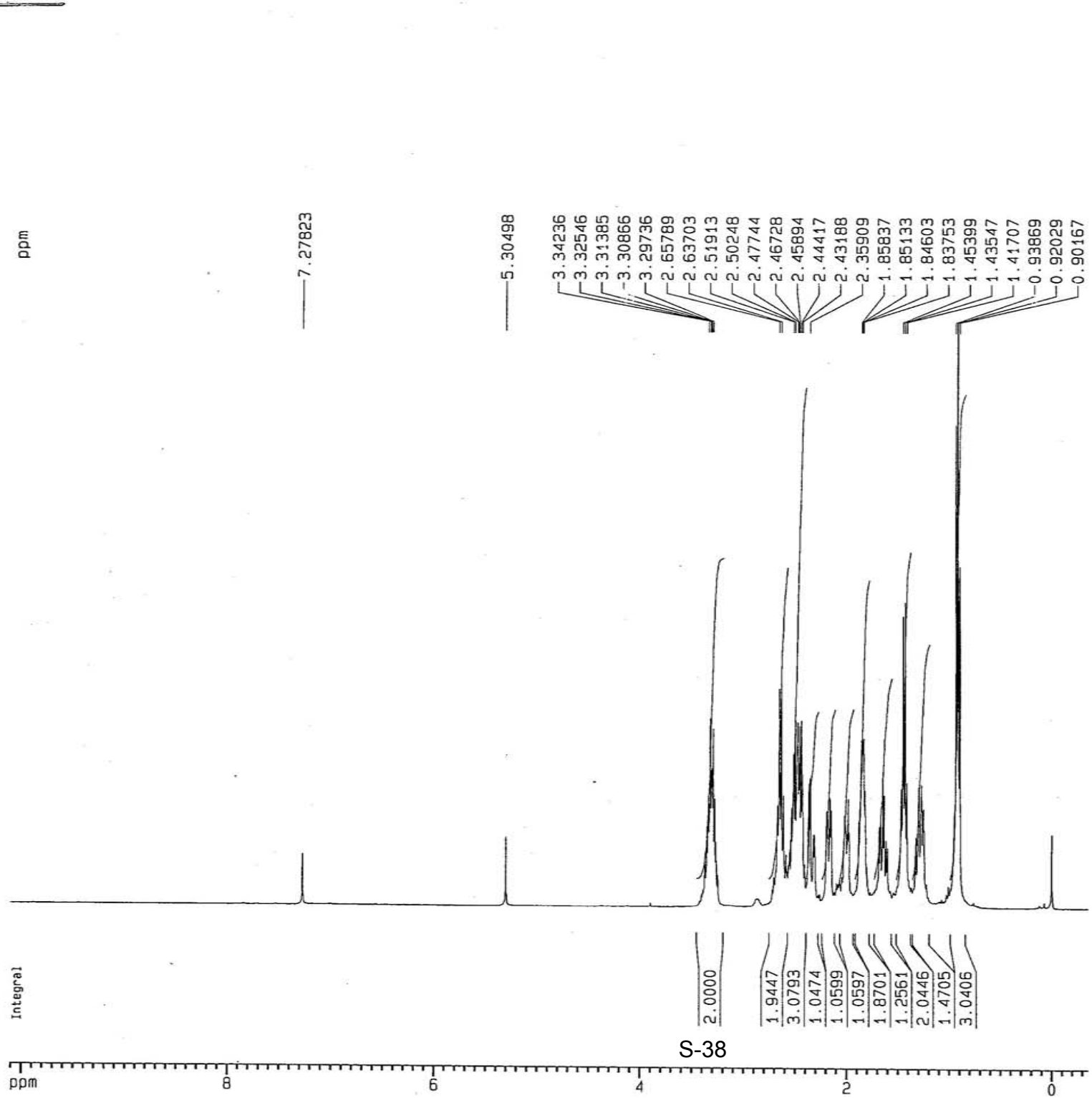


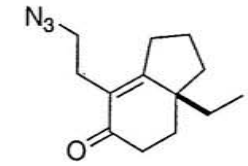
Current Data Parameters	
NAME	raj-3-84-prdt
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	1000217
Time	16.06
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	1024
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters	
SI	32768
SF	100.6127727 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
F1P	216.725 ppm
F1	21805.33 Hz
F2P	-2.285 ppm
F2	-229.92 Hz
PPMCM	10.95053 ppm/cm
HZCM	1101.76270 Hz/cm





21

Current Data Parameters

NAME	raj-3-80-crd
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

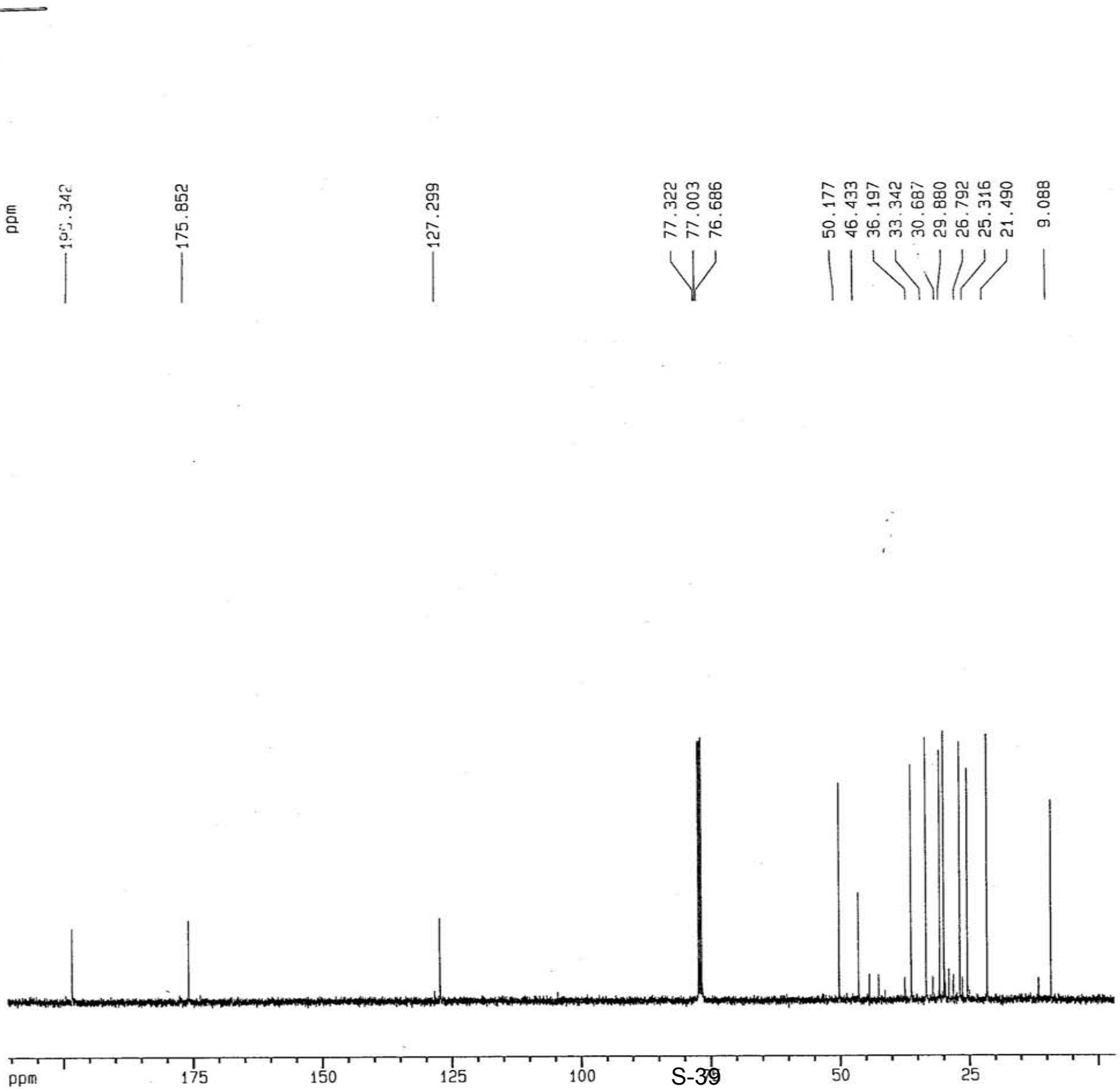
Date_	1000204
Time	12.52
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

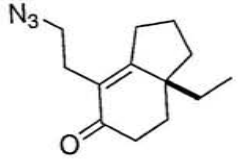
F2 - Processing parameters

SI	16384
SF	400.1300021 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.108 ppm
F1	4044.36 Hz
F2P	-0.354 ppm
F2	-141.54 Hz
PPMCM	0.52307 ppm/cm
HZCM	209.29495 Hz/cm





21

Current Data Parameters

NAME	raj-3-80-crd
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

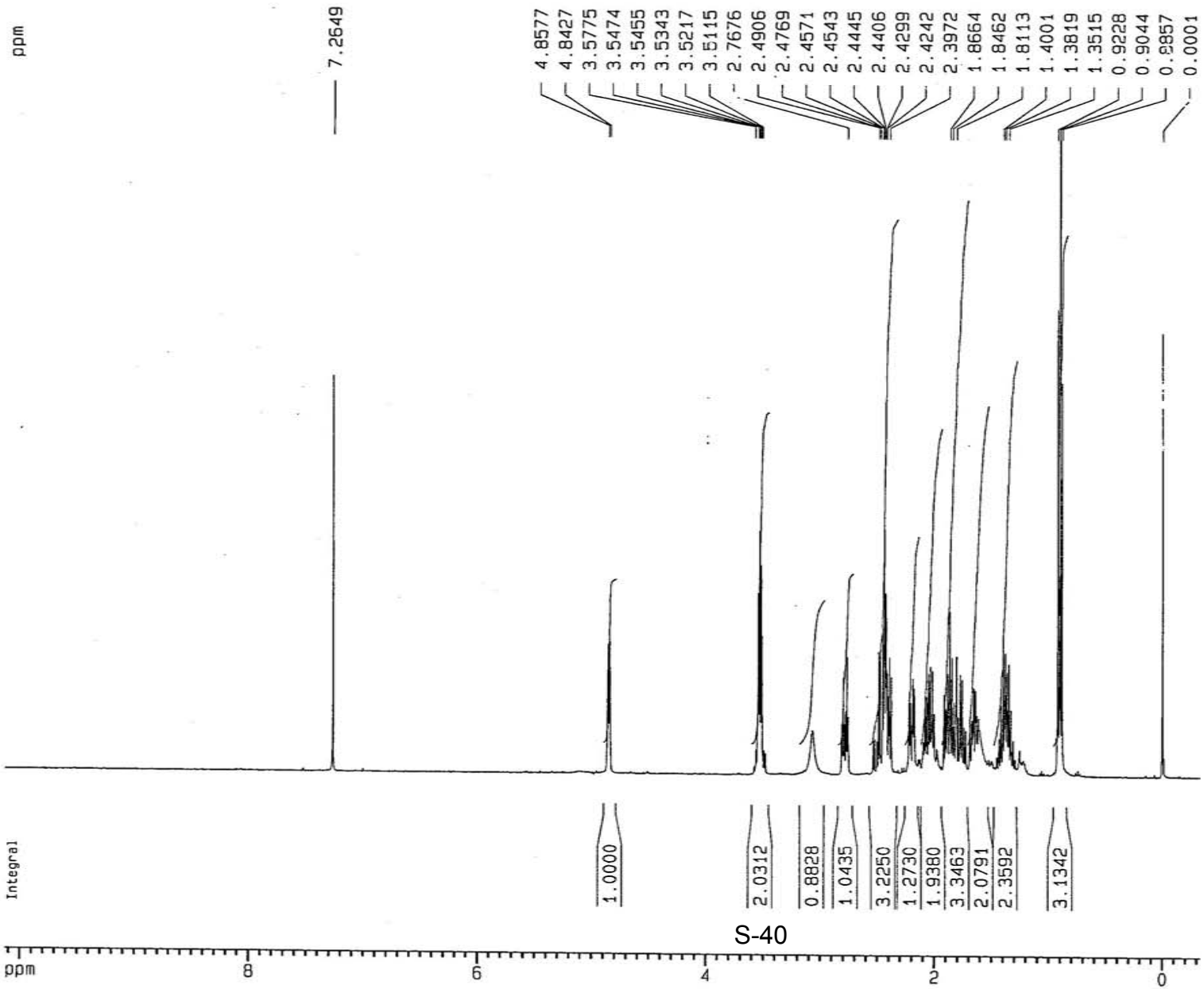
Date_	1000204
Time	15.19
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	802
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	512
DW	21.600 usec
DE	4.50 usec
TE	3[illegible].0 K
d11	0.03000000 sec
d12	0.00002000 sec
PL13	16.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

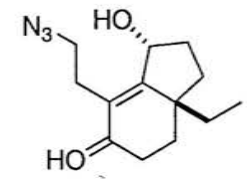
F2 - Processing parameters

SI	32768
SF	100.6127741 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	210.702 ppm
F1	21199.33 Hz
F2P	-3.236 ppm
F2	-325.62 Hz
PPMCM	10.69693 ppm/cm
HZCM	1076.24780 Hz/cm





22

Current Data Parameters

NAME	raj-3-83-prdt
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

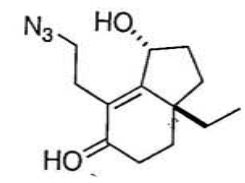
Date_	1000209
Time	17.39
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	456.1
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

F2 - Processing parameters

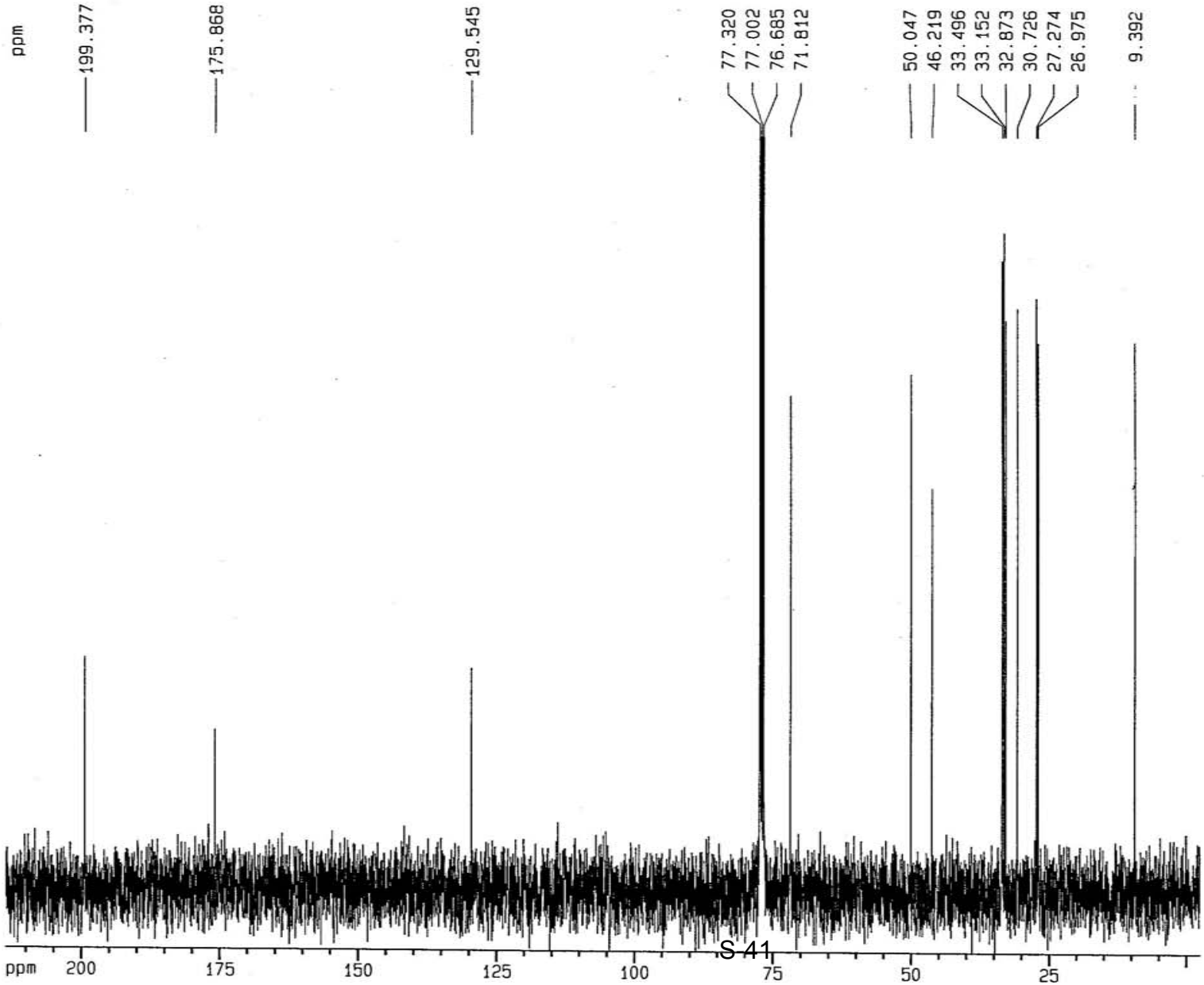
SI	16384
SF	400.1300074 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.129 ppm
F1	4052.86 Hz
F2P	-0.333 ppm
F2	-133.29 Hz
PPMCM	0.52310 ppm/cm
HZCM	209.30728 Hz/cm



22

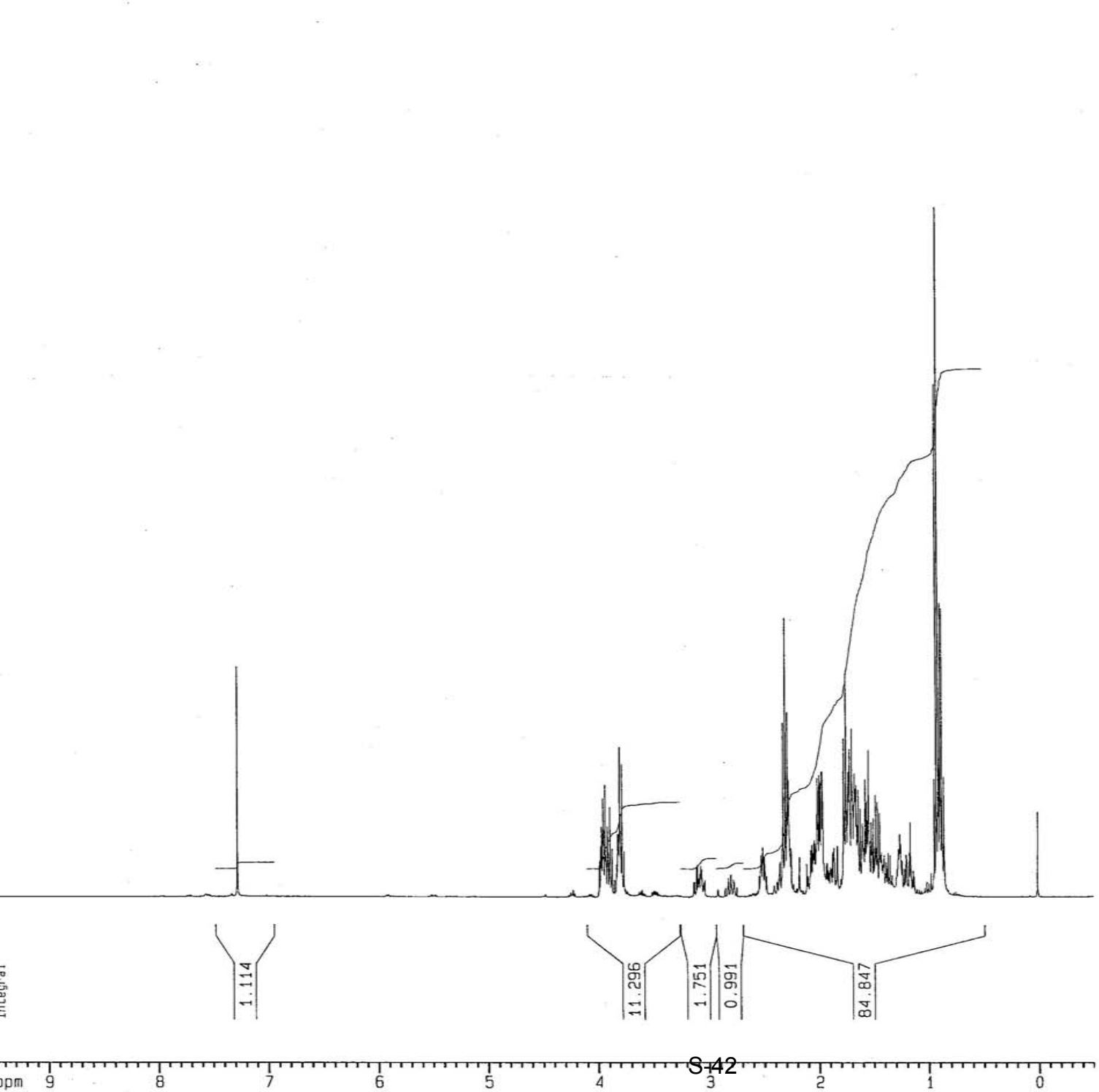


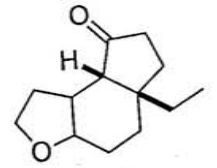
Current Data Parameters	
NAME	raj-3-83-prdt
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	1000209
Time	18.06
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	4096
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	--6.00 dB

F2 - Processing parameters	
SI	32768
SF	100.6127706 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
F1P	213.613 ppm
F1	21492.19 Hz
F2P	-2.508 ppm
F2	-252.39 Hz
PPMCM	10.80607 ppm/cm
HZCM	1087.22876 Hz/cm





24

Current Data Parameters

NAME	ks3.266
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

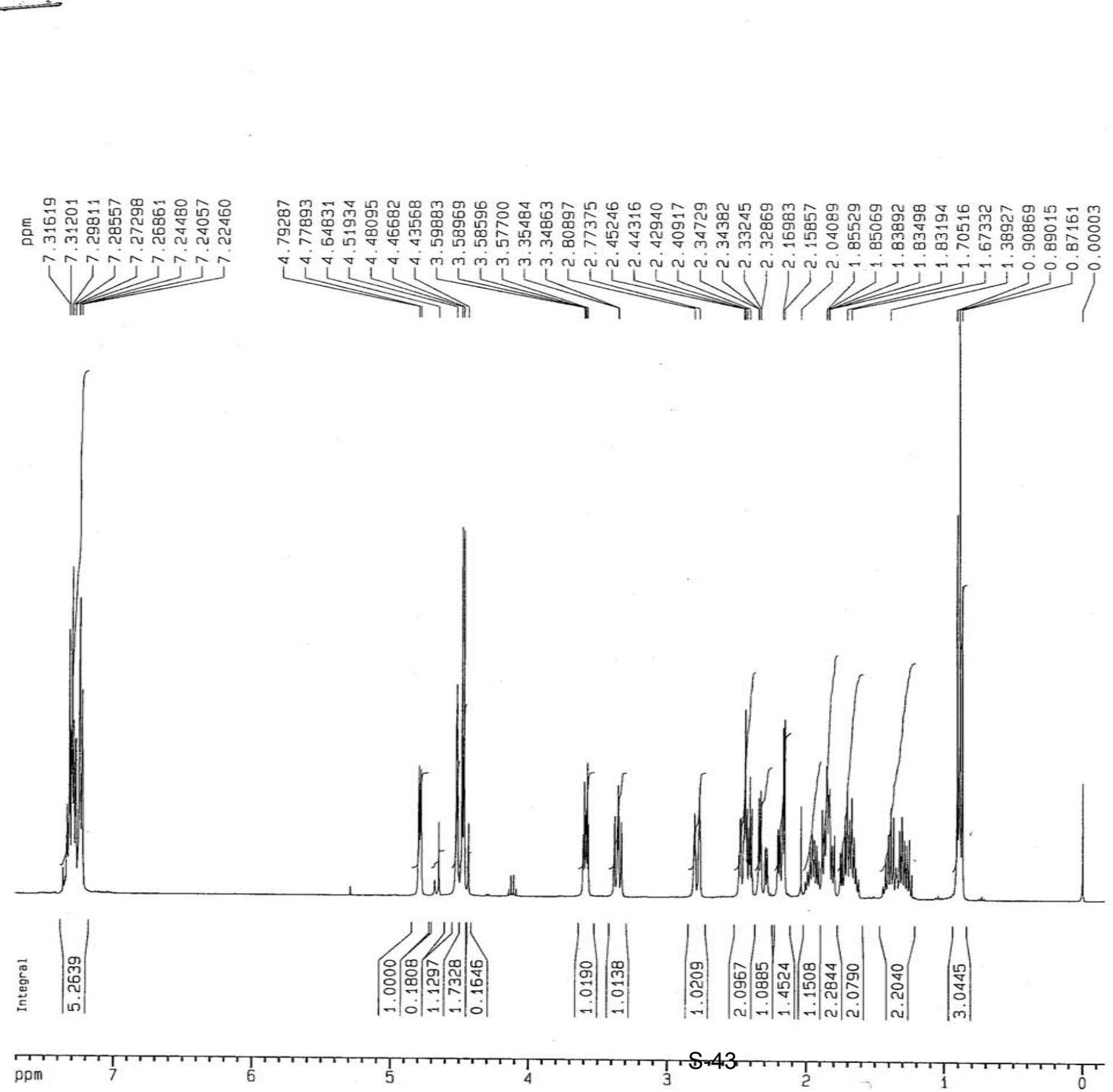
Date_	970414
Time	11.58
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	128
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

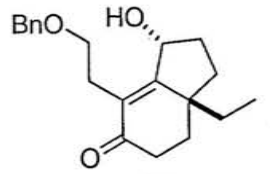
F2 - Processing parameters

SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm





25

Current Data Parameters

NAME	raj-2-218-prot
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

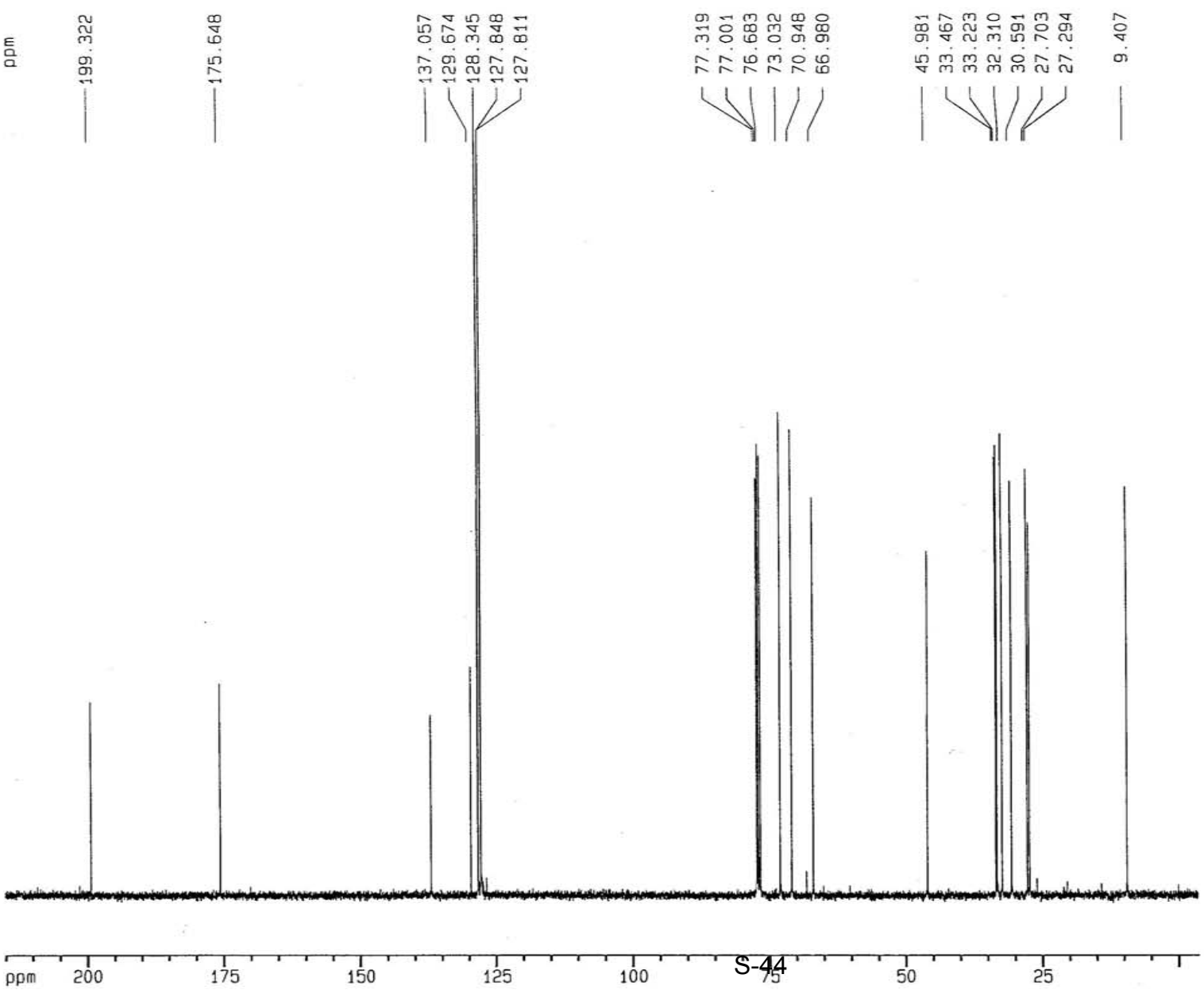
Date_	990715
Time	11.09
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

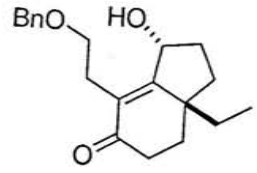
F2 - Processing parameters

SI	16384
SF	400.1300041 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	7.708 ppm
F1	3084.14 Hz
F2P	-0.161 ppm
F2	-64.53 Hz
PPMCM	0.39346 ppm/cm
HZCM	157.43359 Hz/cm





25

Current Data Parameters

NAME	raj-2-218-prdt
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

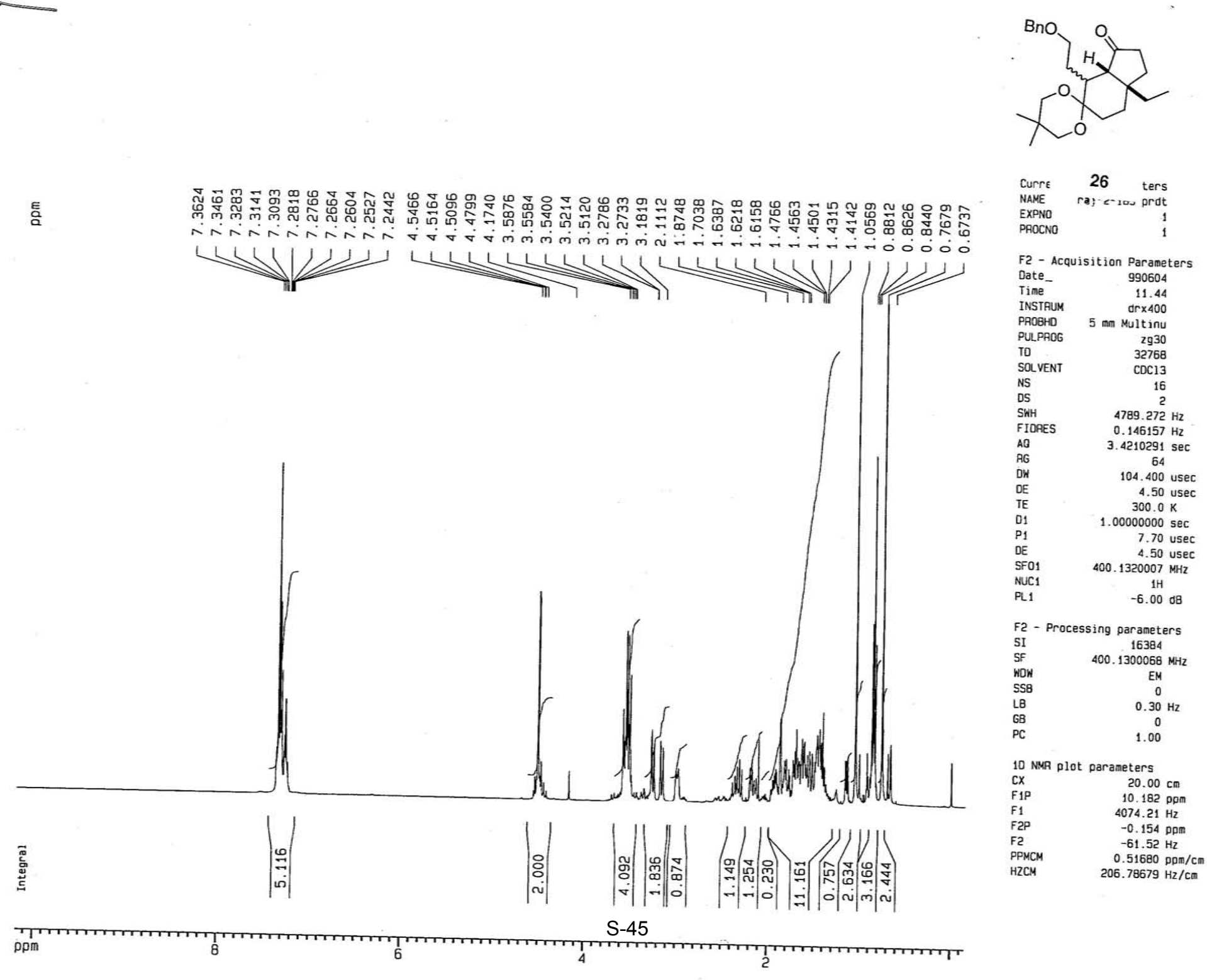
Date_	990715
Time	16.30
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	512
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	32768
SF	100.6127777 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	215.161 ppm
F1	21647.98 Hz
F2P	-3.714 ppm
F2	-373.68 Hz
PPMCM	10.94377 ppm/cm
HZCM	1101.08313 Hz/cm



Curre ters
NAME ra) prdt
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

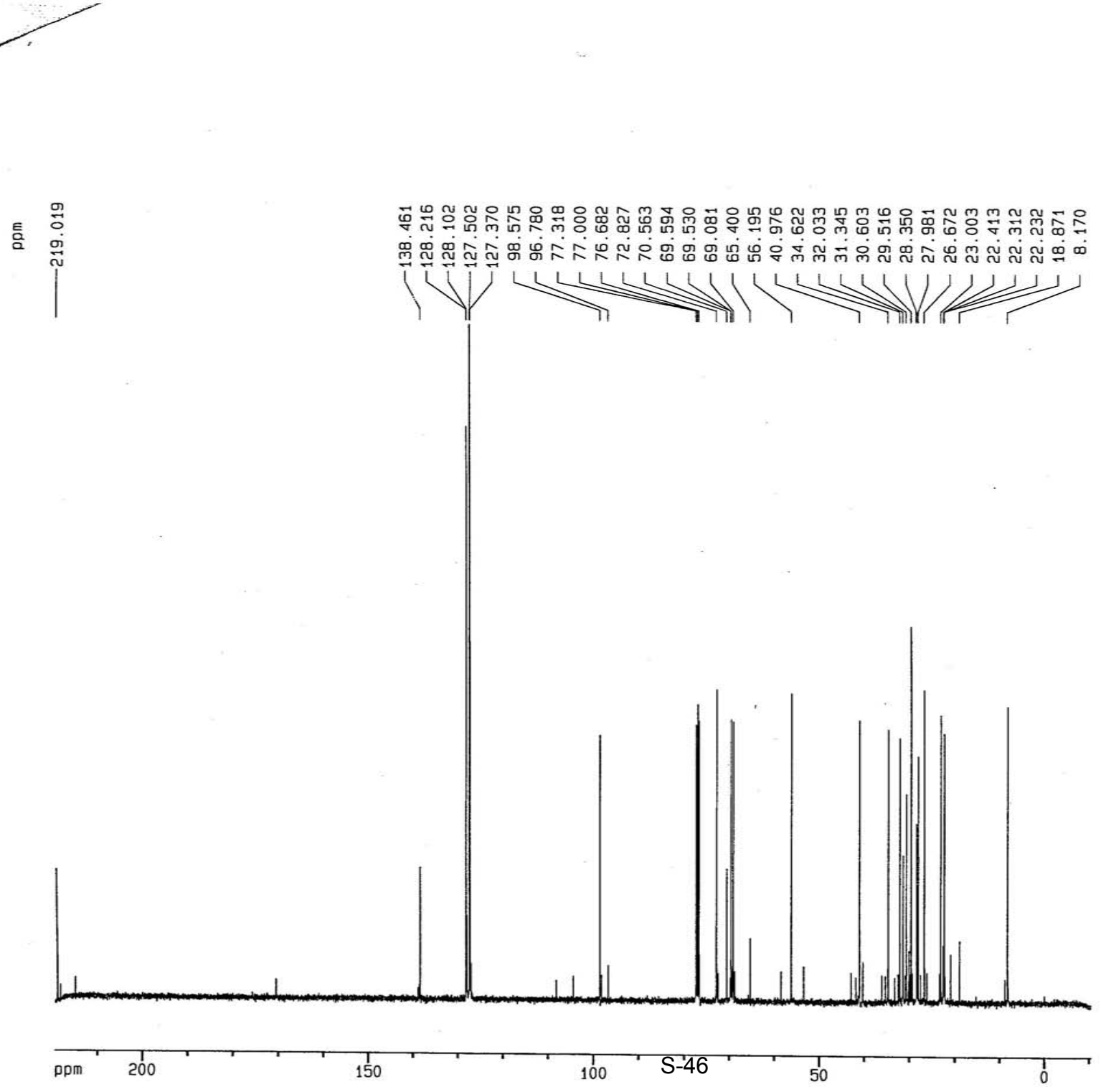
Date_	990604
Time	11.44
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

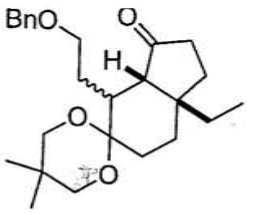
F2 - Processing parameters

SI	16384
SF	400.1300068 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.182 ppm
F1	4074.21 Hz
F2P	-0.154 ppm
F2	-61.52 Hz
PPMCM	0.51680 ppm/cm
HZCM	206.78679 Hz/cm





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Currer	s
NAME	raj-2-254-prdt
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

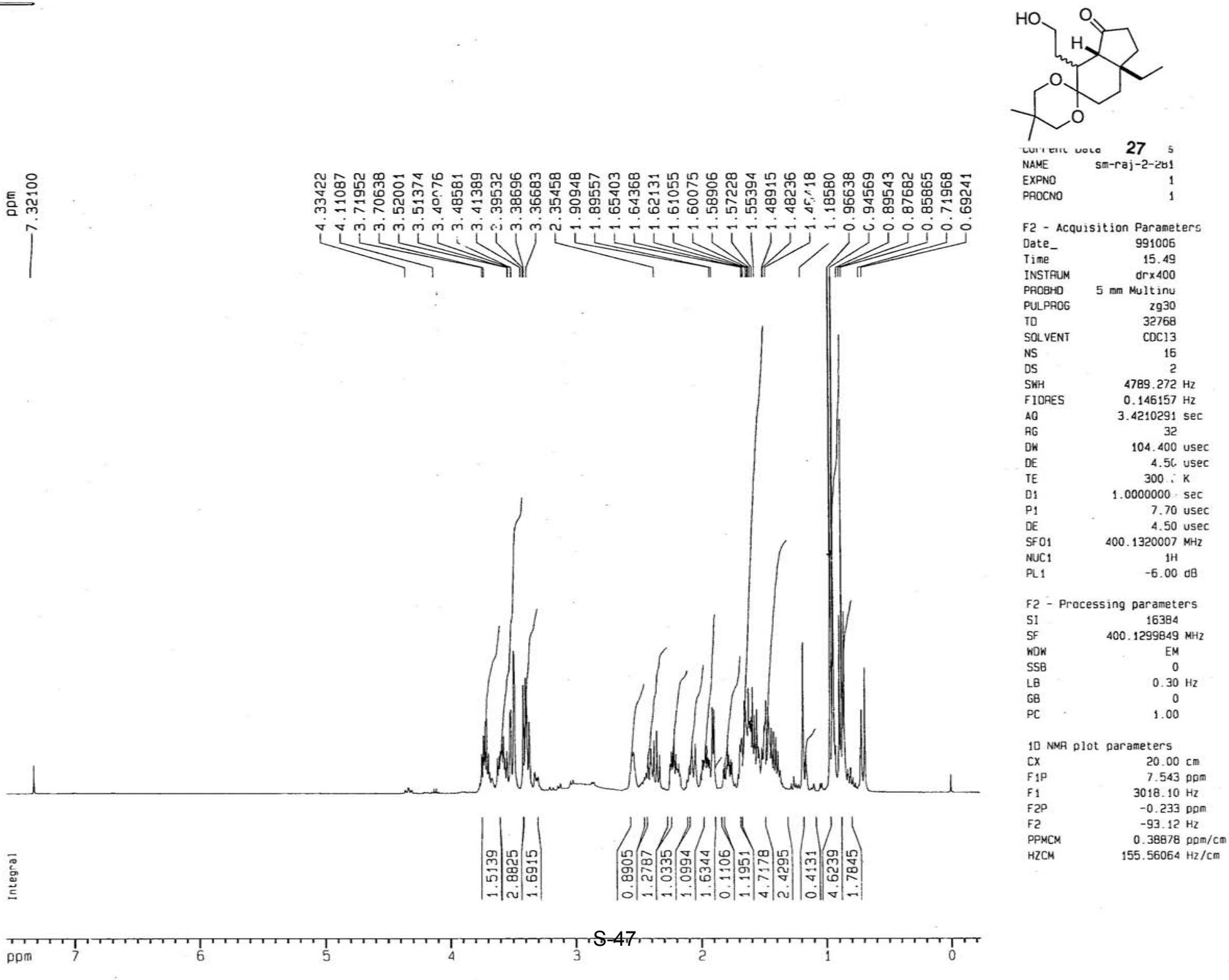
Date_	990827
Time	7.40
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	4096
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	32768
SF	100.6127791 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	230.000 ppm
F1	23140.94 Hz
F2P	-10.534 ppm
F2	-1059.82 Hz
PPMCM	12.02668 ppm/cm
HZCM	1210.03796 Hz/cm



Current Data 27 s

NAME	sm-raj-2-261
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	991006
Time	15.49
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	32
DW	104.400 usec
DE	4.50 usec
TE	300.[illegible] K
D1	1.0000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

F2 - Processing parameters

SI	16384
SF	400.1299849 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	7.543 ppm
F1	3018.10 Hz
F2P	-0.233 ppm
F2	-93.12 Hz
PPMCM	0.38878 ppm/cm
HZCM	155.56064 Hz/cm

RAJ-2-255

PPM

219.940

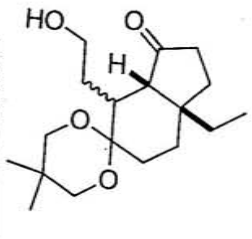
98.479

77.254
77.000
76.746
69.751
69.622

61.981
57.313

41.034
34.651
32.298
30.202
29.674
28.804
27.154
25.697
22.862
22.700

8.090



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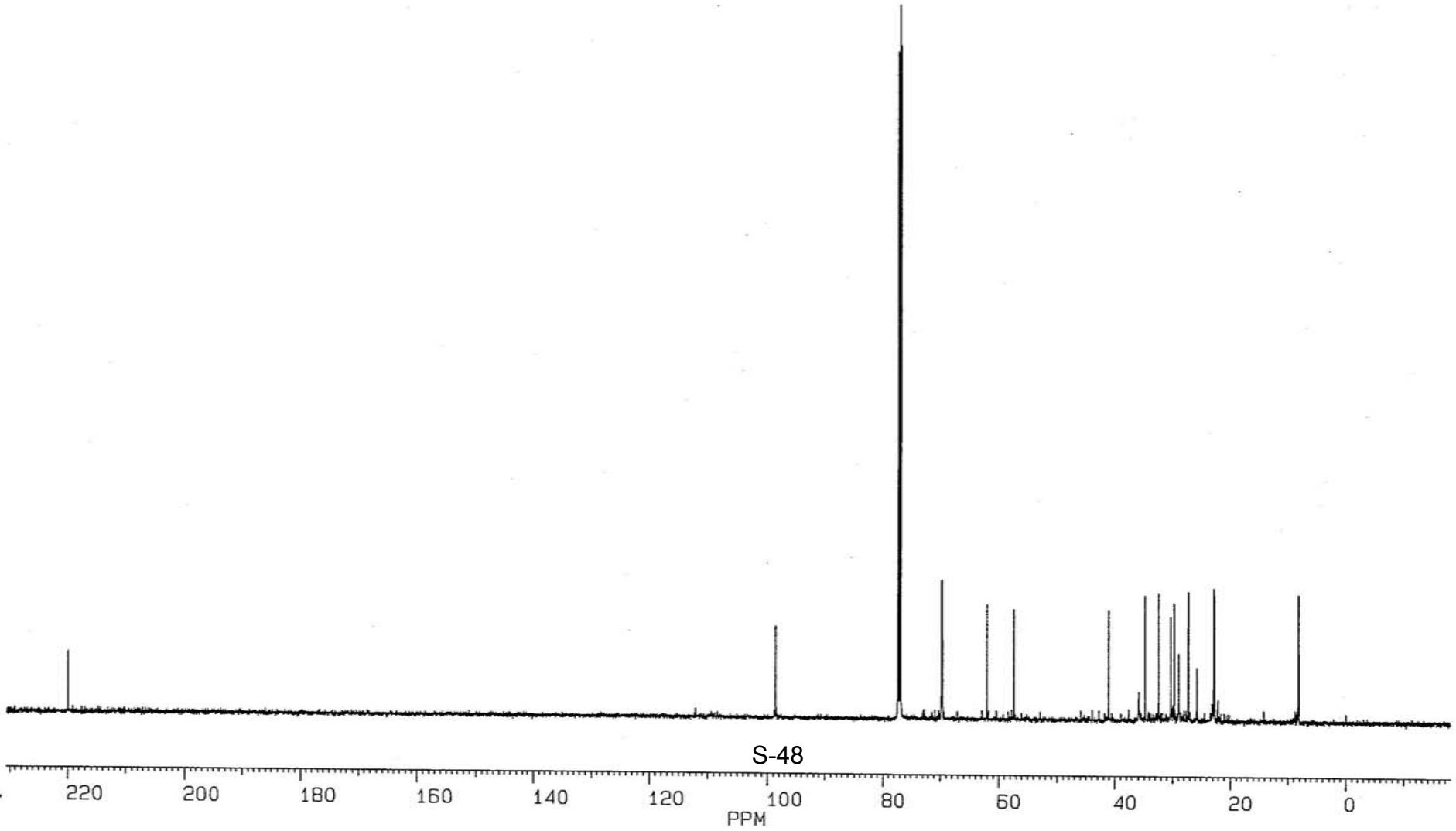
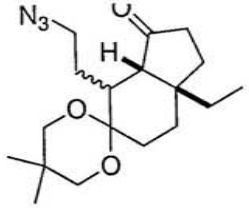
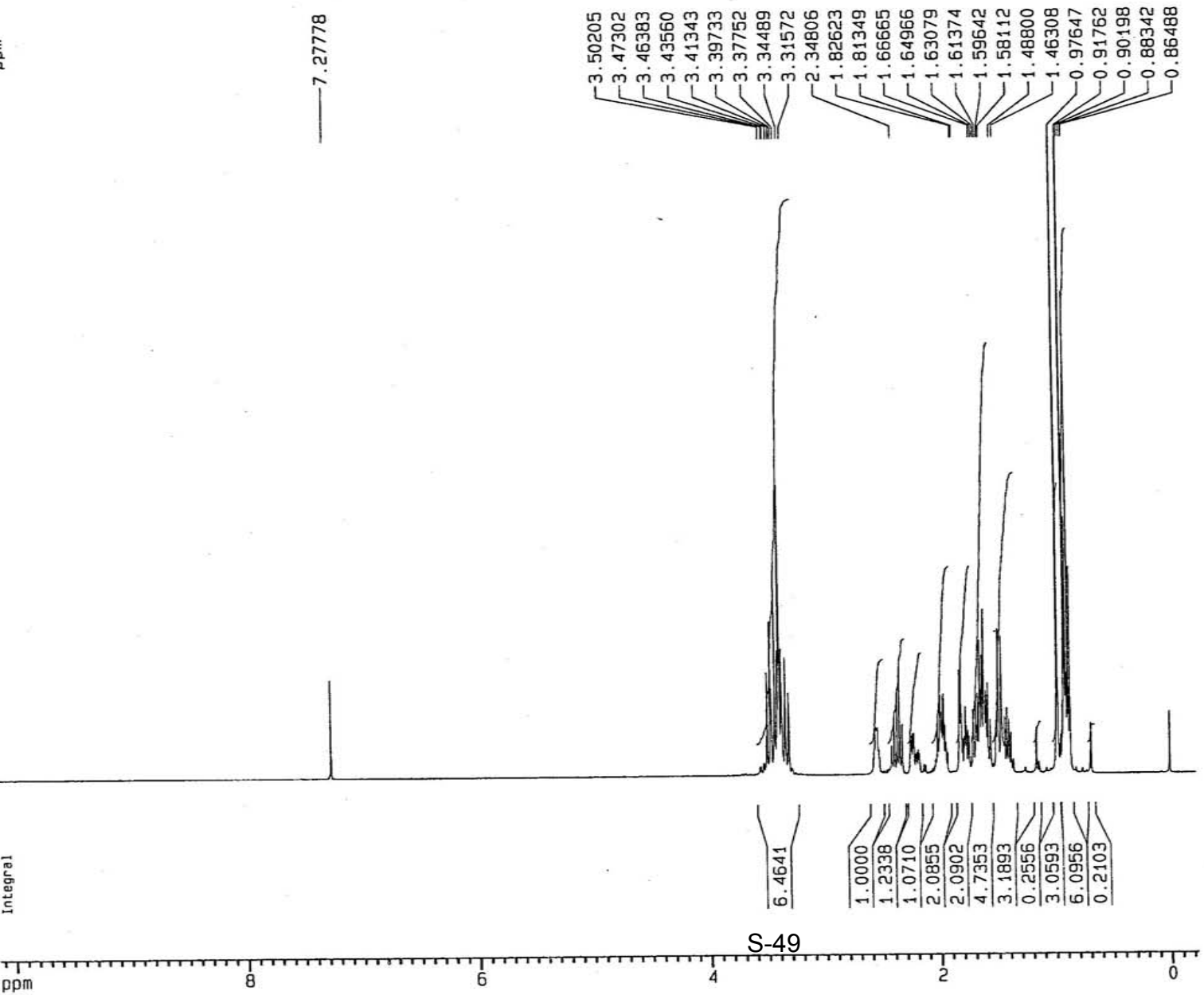




28



NAME	raj-2-231-prdt
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

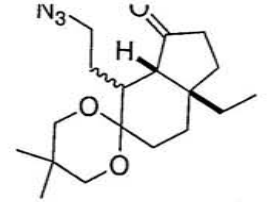
Date_	990729
Time	23.44
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	64
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

F2 - Processing parameters

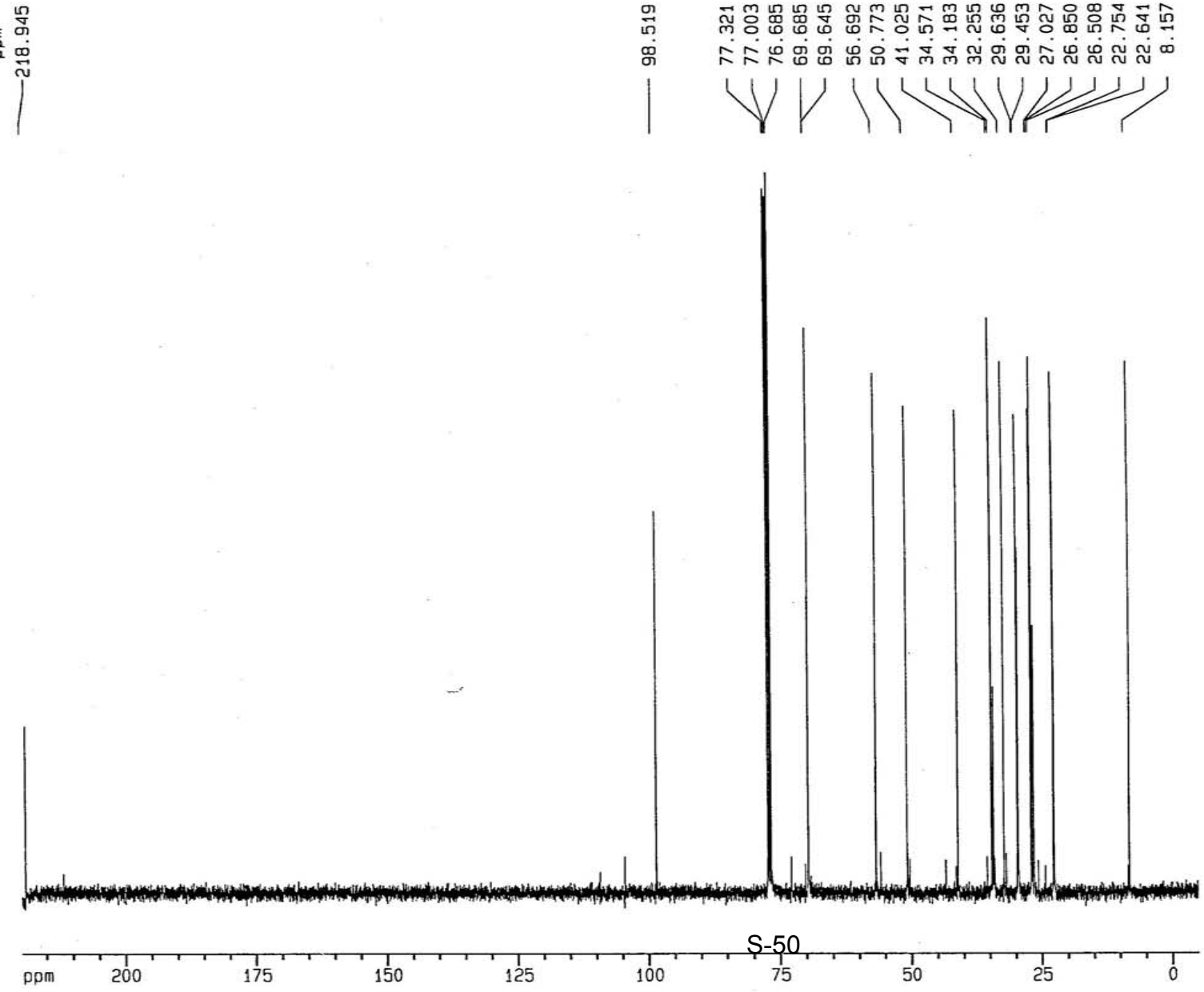
SI	16384
SF	400.1300024 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.145 ppm
F1	4059.29 Hz
F2P	-0.225 ppm
F2	-90.19 Hz
PPMCM	0.51852 ppm/cm
HZCM	207.47418 Hz/cm



28

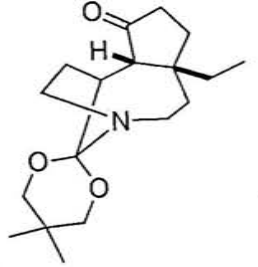



```
Current Data Parameters
NAME      raj-2-231-prdt
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_             990730
Time                0.14
INSTRUM          drx400
PROBHD     5 mm Multinu
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH          23148.148 Hz
FIDRES        0.353213 Hz
AQ           1.4156276 sec
RG                 1024
DW              21.600 usec
DE               4.50 usec
TE               300.0 K
d11           0.0300000 sec
d12           0.0000200 sec
PL13             18.00 dB
D1            0.05000000 sec
CPDPRG2         waltz16
PCPD2          100.00 usec
SFO2        400.1316005 MHz
NUC2                1H
PL2              -6.00 dB
PL12             18.00 dB
P1                6.90 usec
DE               4.50 usec
SFO1        100.6232933 MHz
NUC1                13C
PL1              -6.00 dB

F2 - Processing parameters
SI                32768
SF          100.6127734 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
F1P             225.000 ppm
F1             22637.87 Hz
F2P              -5.000 ppm
F2              -503.06 Hz
PPMCM          11.50000 ppm/cm
HZCM        1157.04688 Hz/cm
```



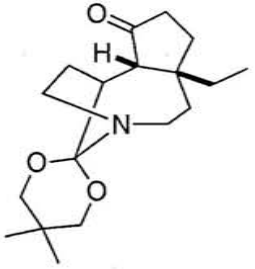
Curre
NAME 29
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 991021
Time 12.10
INSTRUM drx400
PROBHD 5 mm Multinu
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 64
DW 104.400 usec
DE 4.50 usec
TE 300.0 K
D1 1.0000000 sec
P1 7.70 usec
DE 4.50 usec
SFO1 400.1320007 MHz
NUC1 1H
PL1 -6.00 dB

F2 - Processing parameters
SI 16384
SF 400.1300003 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

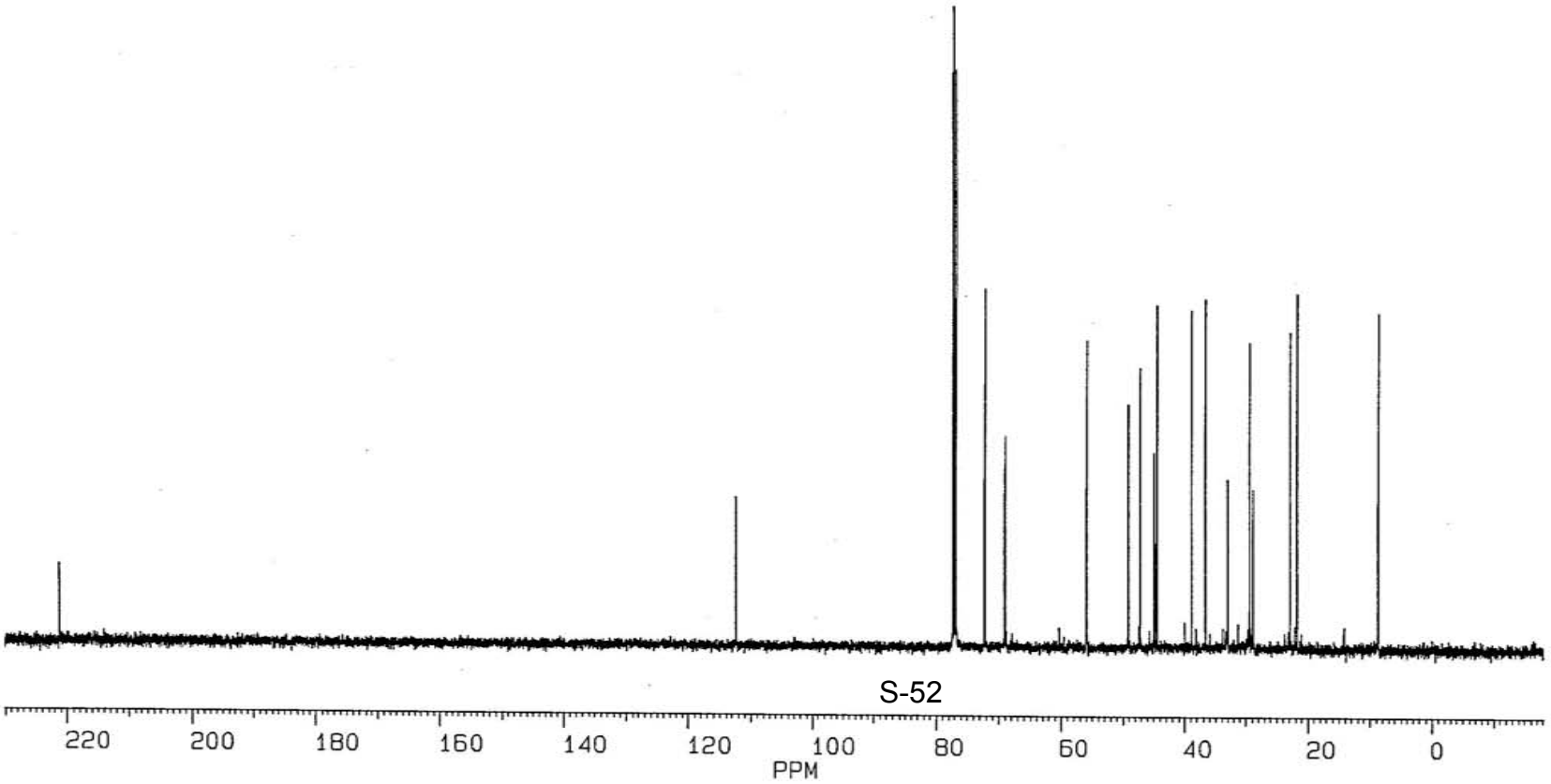
1D NMR plot parameters
CX 20.00 cm
F1P 10.063 ppm
F1 4026.53 Hz
F2P -0.168 ppm
F2 -67.37 Hz
PPMCM 0.51157 ppm/cm
HZCM 204.69534 Hz/cm

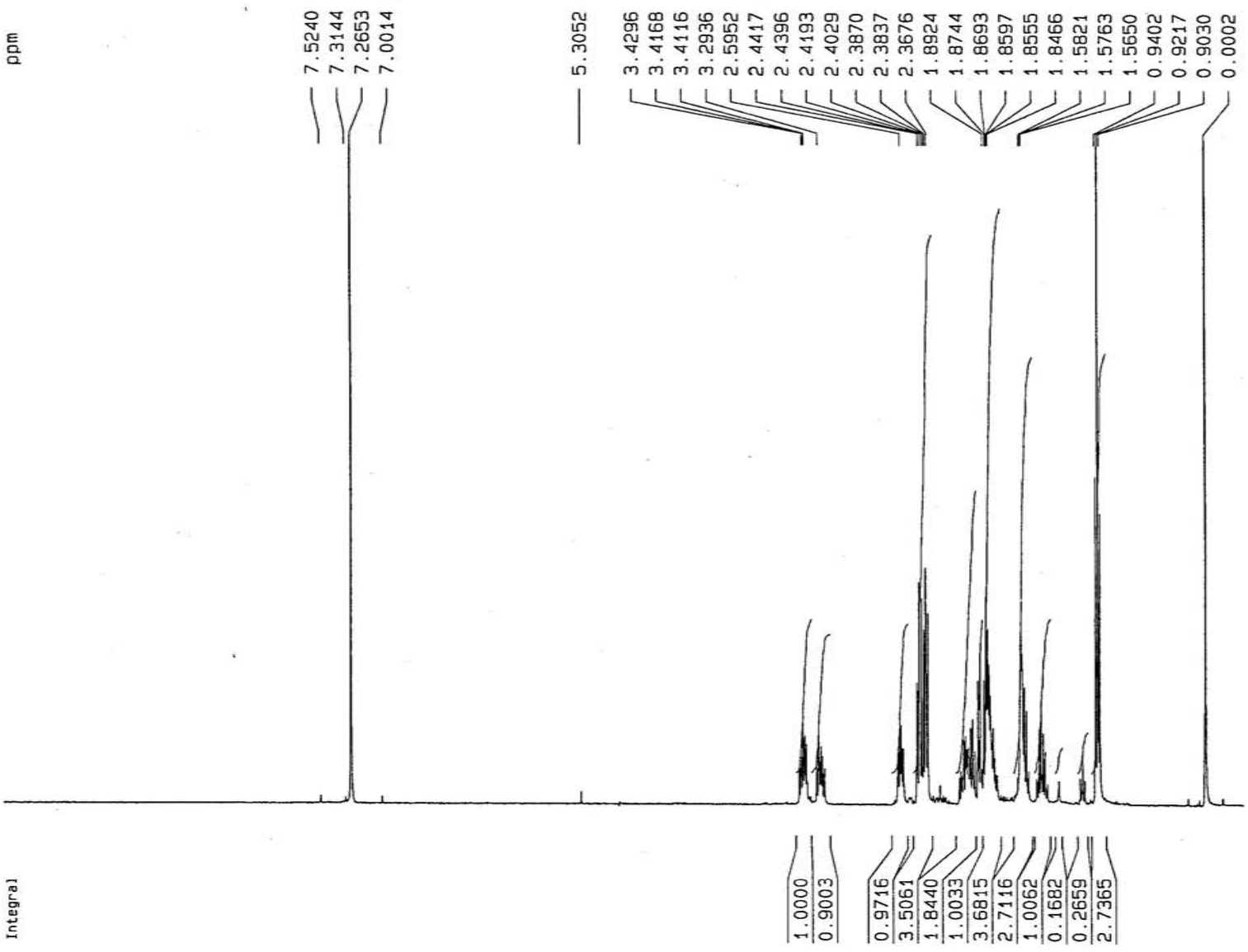
RAJ-2-285

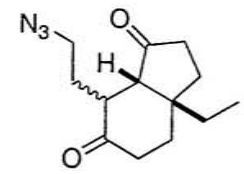


29

SF	125.759
SY	93.0
O1	2500.000
SI	65536
TD	65536
SW	31250.000
HZ/PT	.954
PW	2.0
RD	1.000
AQ	1.049
RG	200
NS	806
TE	297
FW	39100
O2	7500.000
DP	15H DO
LB	1.000
GB	0.0
CX	22.00
CY	0.0
F1	230.115
F2	-18.125
HZ/CM	1.419E3
PPM/CM	11.284
SR	-10844.61







7

Current Data Parameters

NAME	raj-2-261-prdt
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

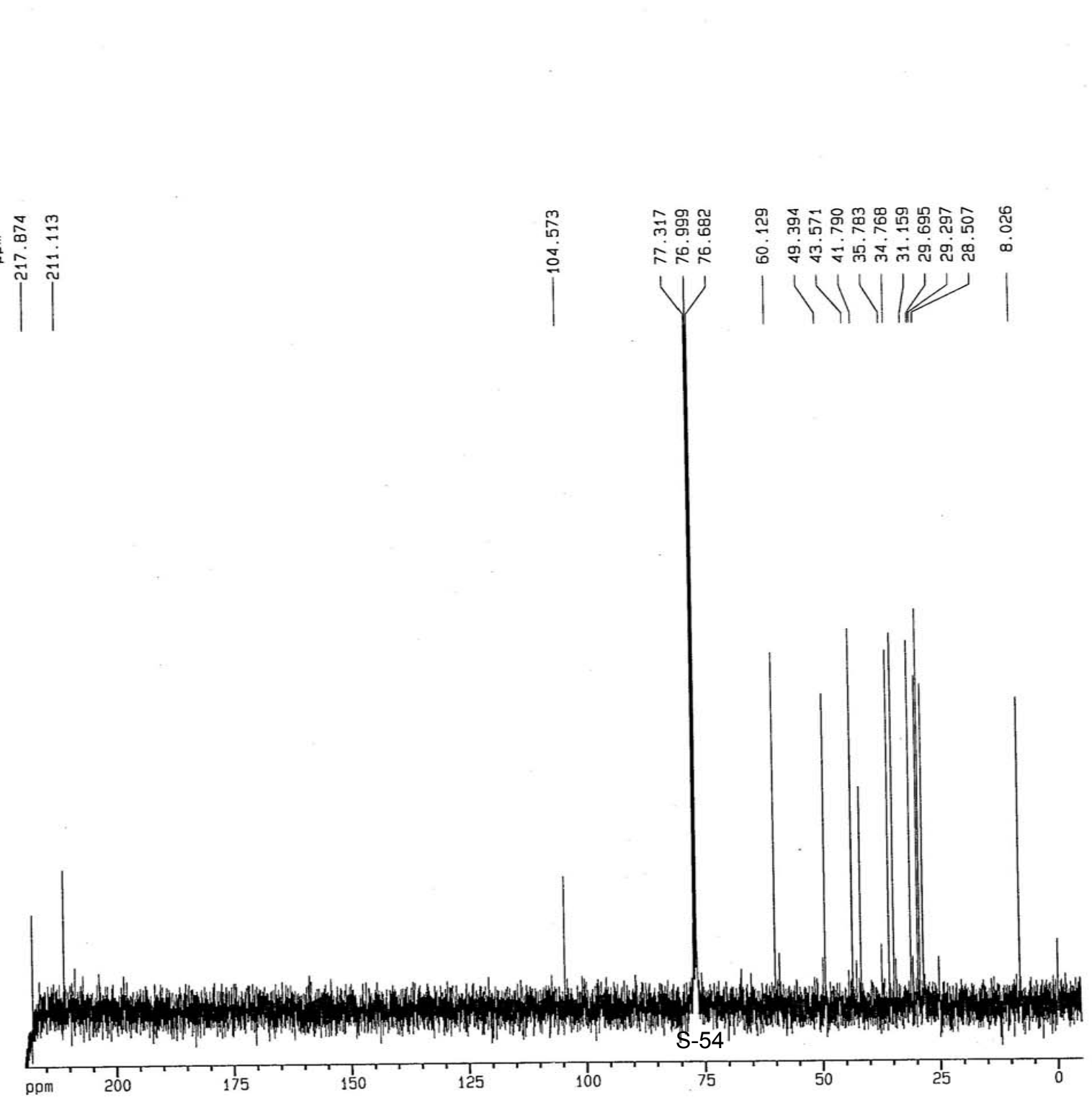
Date_	990913
Time	14.29
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	812.7
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

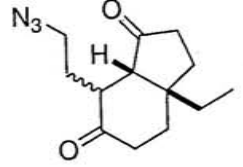
F2 - Processing parameters

SI	16384
SF	400.1300077 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.217 ppm
F1	4088.30 Hz
F2P	-0.325 ppm
F2	-129.94 Hz
PPMCM	0.52711 ppm/cm
HZCM	210.91219 Hz/cm





7

Current Data Parameters

NAME	raj-2-233-prdt
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

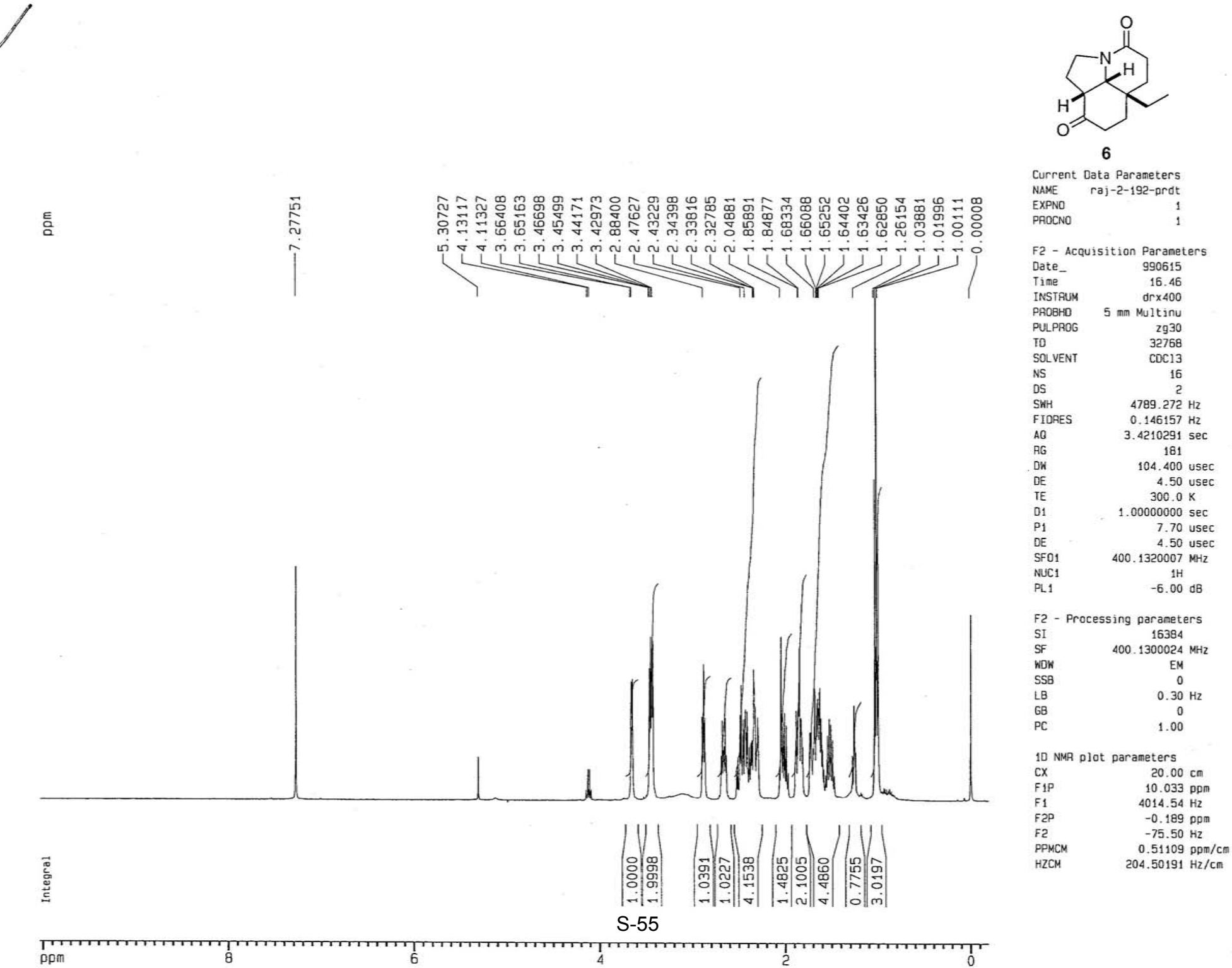
Date_	990801
Time	19.08
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	1024
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	32768
SF	100.6127720 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	225.000 ppm
F1	22637.87 Hz
F2P	-5.000 ppm
F2	-503.06 Hz
PPMCM	11.50000 ppm/cm
HZCM	1157.04688 Hz/cm



6

Current Data Parameters

NAME	raj-2-192-prdt
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

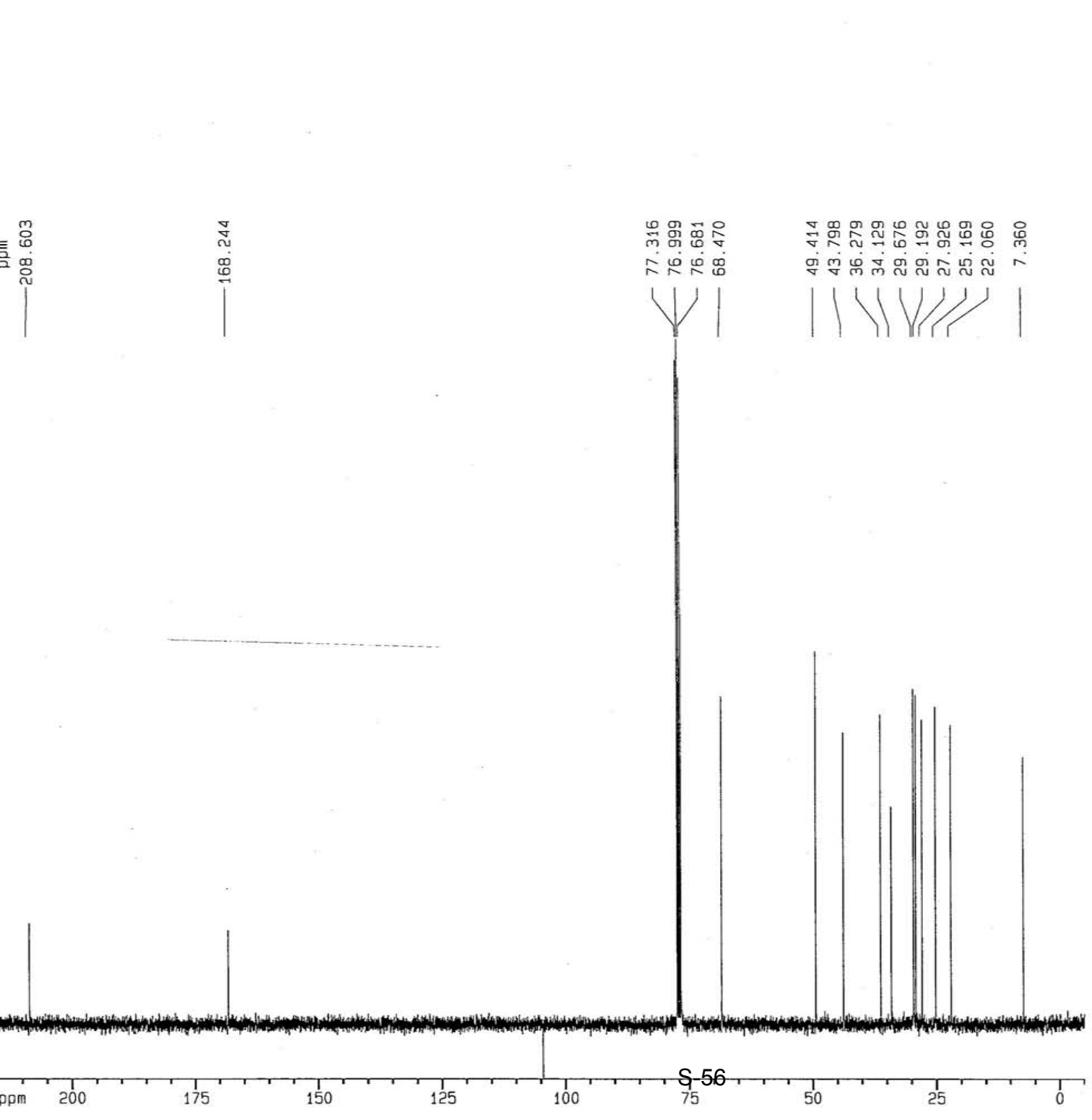
Date_	990615
Time	16.46
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	181
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

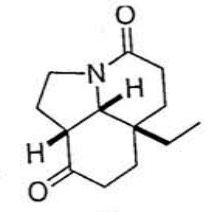
F2 - Processing parameters

SI	16384
SF	400.1300024 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.033 ppm
F1	4014.54 Hz
F2P	-0.189 ppm
F2	-75.50 Hz
PPMCM	0.51109 ppm/cm
HZCM	204.50191 Hz/cm





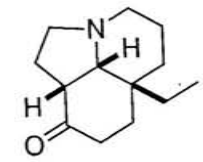
6

Current Data Parameters	
NAME	ks2.240
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters	
Date_	961018
Time	13.34
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	1024
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters	
SI	32768
SF	100.6127741 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
F1P	215.000 ppm
F1	21631.75 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.00000 ppm/cm
HZCM	1106.74060 Hz/cm



3

Current Data Parameters

NAME	ks3.287
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

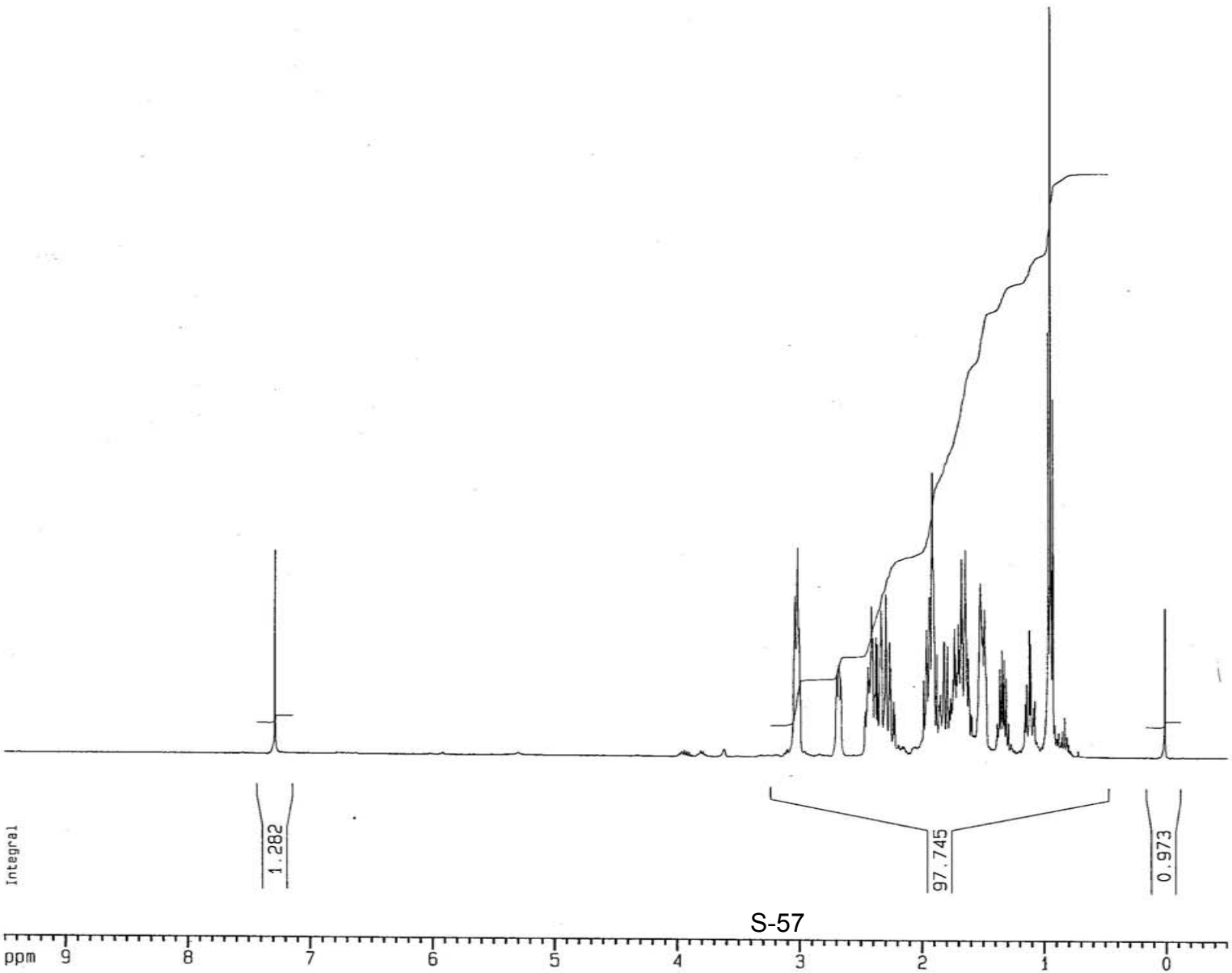
Date_	970501
Time	15.05
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	90.5
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

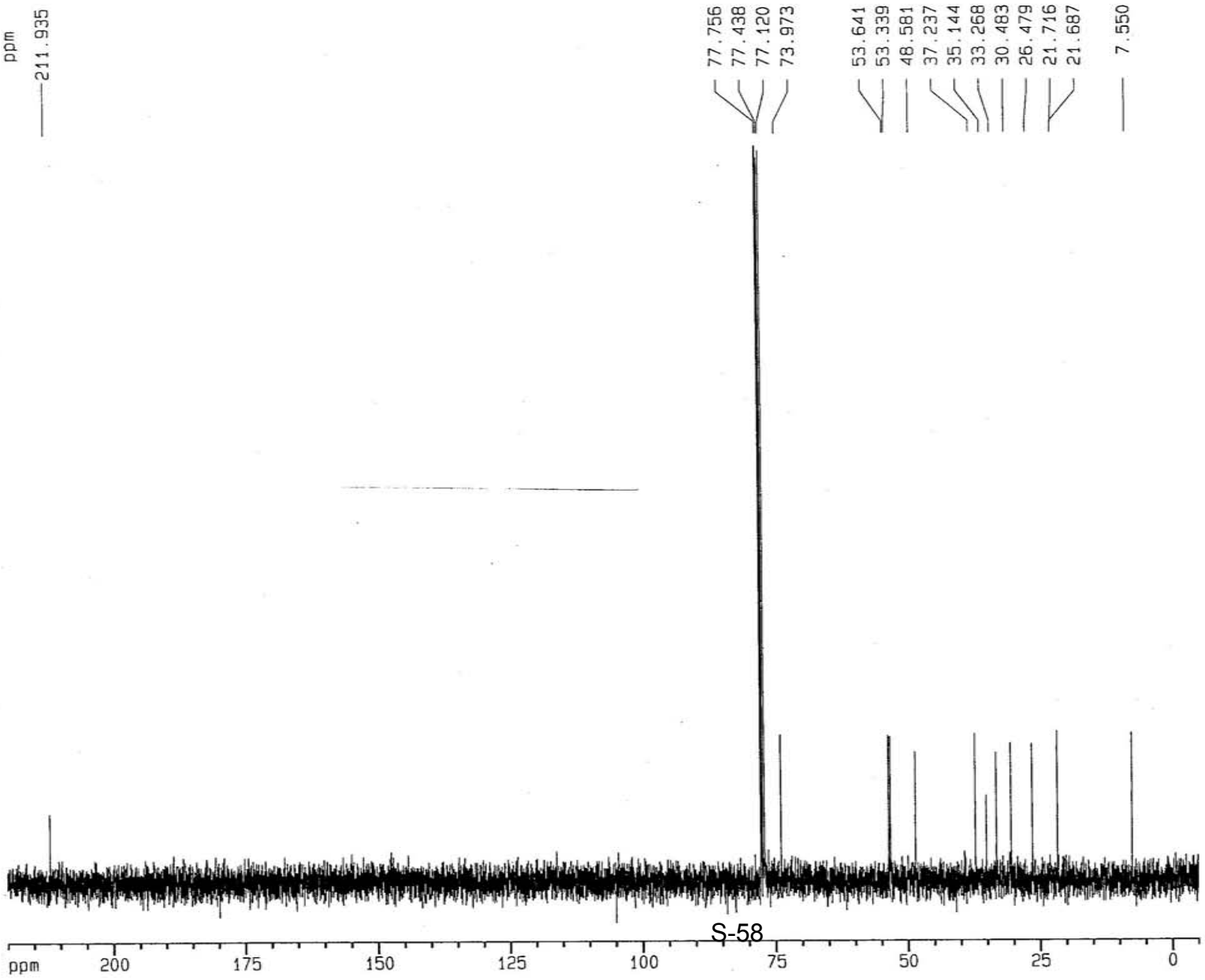
F2 - Processing parameters

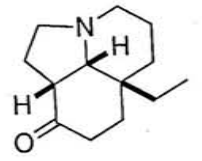
SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	9.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPMCM	0.50000 ppm/cm
HZCM	200.06500 Hz/cm







3

Current Data Parameters

NAME	ks3.287
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

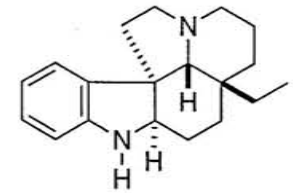
Date_	970501
Time	15.25
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	32768
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	22134.80 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	11.25000 ppm/cm
HZCM	1131.89319 Hz/cm



(+)-Aspidospermidine (**1**)

EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

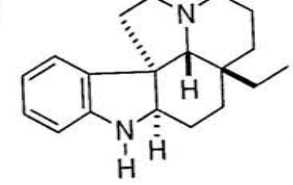
Date_	500000
Time	15.22
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	256
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

F2 - Processing parameters

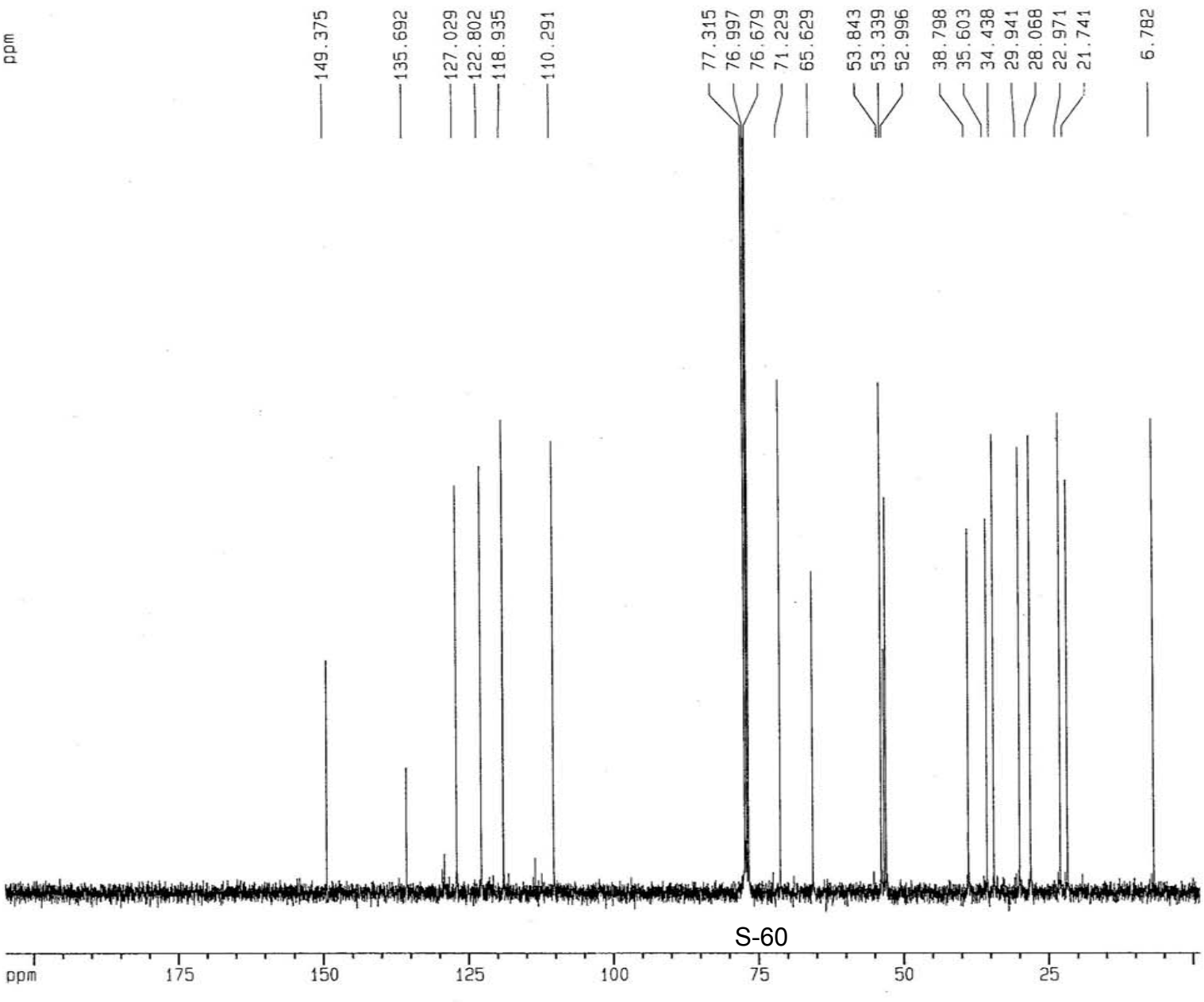
SI	16384
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

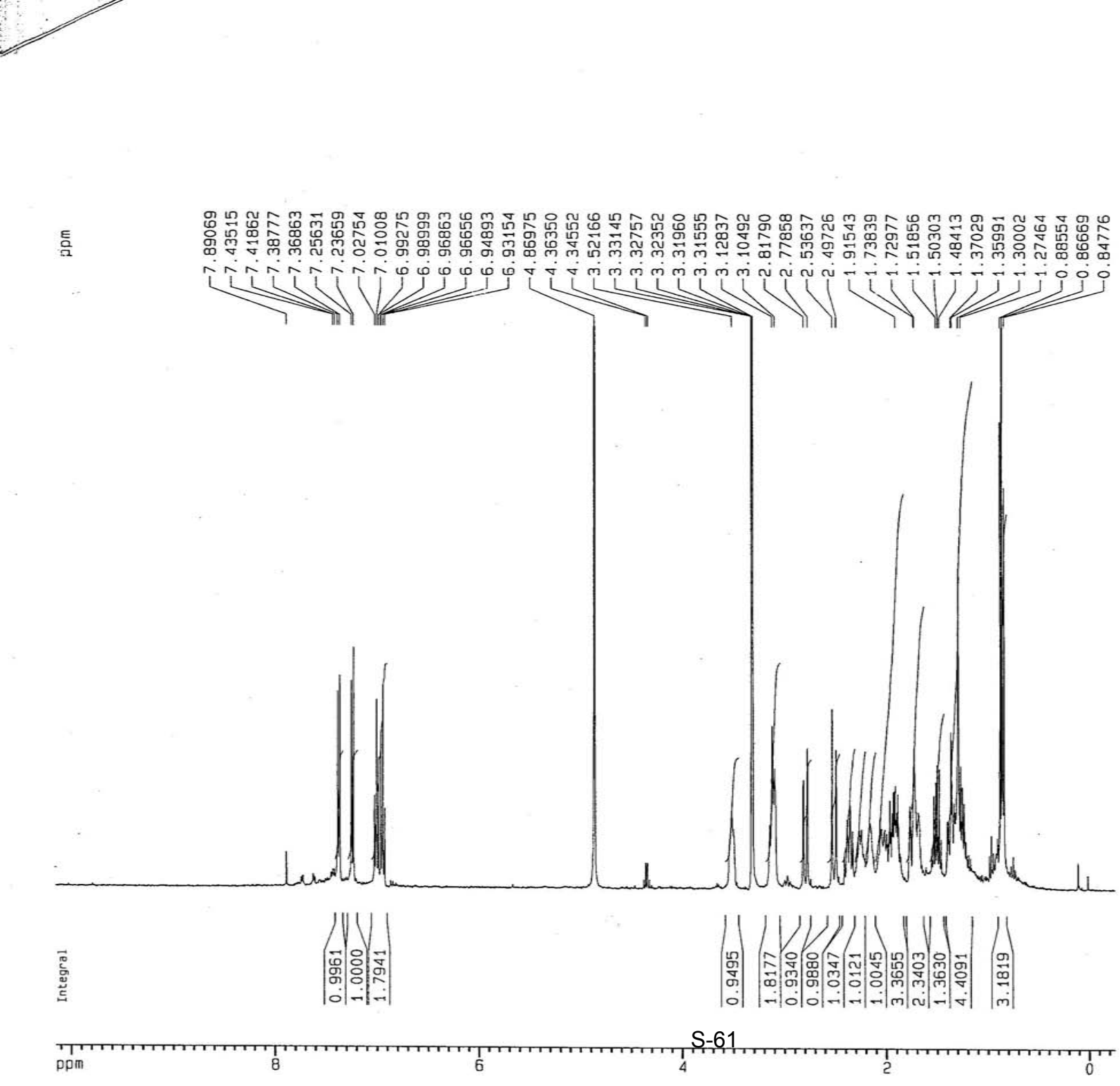
CX	20.00 cm
F1P	10.166 ppm
F1	4067.84 Hz
F2P	-0.272 ppm
F2	-108.74 Hz
PPMCM	0.52190 ppm/cm
HZCM	208.82909 Hz/cm

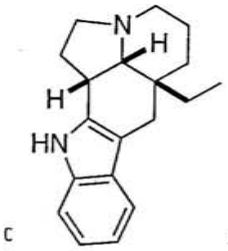


(+)-Aspidospermidine (**1**)



Current Data Parameters	
NAME	raj-3-71-pndt
EXPNO	2
PROCNO	1
F2 - Acquisition Parameters	
Date_	500000
Time	17.29
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	4096
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB
F2 - Processing parameters	
SI	32768
SF	100.6127741 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
1D NMR plot parameters	
CX	20.00 cm
F1P	204.851 ppm
F1	20610.64 Hz
F2P	-1.215 ppm
F2	-122.26 Hz
PPMCM	10.30331 ppm/cm
HZCM	1036.64478 Hz/cm





31

F2 - Acquisition Parameters

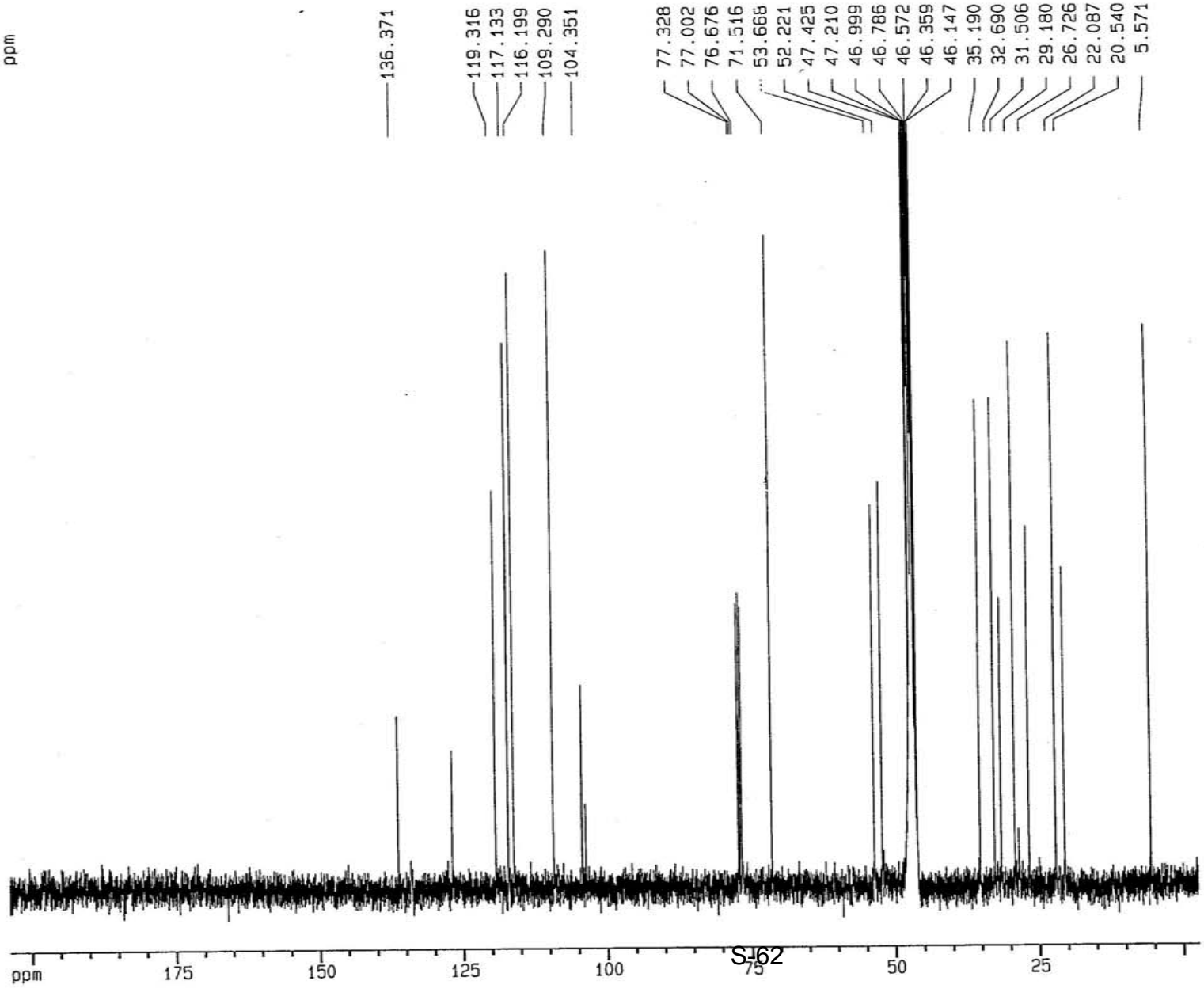
Date_	1000210
Time	8.49
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zg30
TD	32768
SOLVENT	MeOH
NS	16
DS	2
SWH	4789.272 Hz
FIDRES	0.146157 Hz
AQ	3.4210291 sec
RG	574.7
DW	104.400 usec
DE	4.50 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.70 usec
DE	4.50 usec
SFO1	400.1320007 MHz
NUC1	1H
PL1	-6.00 dB

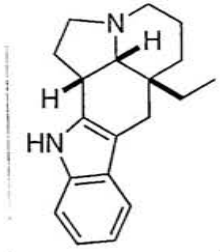
F2 - Processing parameters

SI	16384
SF	400.1300020 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.151 ppm
F1	4061.69 Hz
F2P	-0.253 ppm
F2	-101.29 Hz
PPMCM	0.52020 ppm/cm
HZCM	208.14912 Hz/cm





31

PROCNO	1

F2 - Acquisition Parameters

Date_	1000219
Time	8.38
INSTRUM	drx400
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	20493
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	2048
DW	21.600 usec
DE	4.50 usec
TE	300.0 K
d11	0.0300000 sec
d12	0.0000200 sec
PL13	18.00 dB
D1	0.05000000 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1316005 MHz
NUC2	1H
PL2	-6.00 dB
PL12	18.00 dB
P1	6.90 usec
DE	4.50 usec
SFO1	100.6232933 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	32768
SF	100.6128554 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	203.834 ppm
F1	20508.32 Hz
F2P	-2.687 ppm
F2	-270.33 Hz
PPMCM	10.32604 ppm/cm
HZCM	1038.93262 Hz/cm