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Permuting Diels-Alder and Robinson Annulation Stereopatterns

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Supplementary Information

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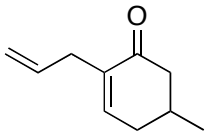
General information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. Toluene, hexanes and CH_2Cl_2 were distilled over CaH_2. THF and Et_2O were distilled over sodium/benzophenone ketyl. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatography (TLC) was performed on Silica Gel 60 F254 plates and was visualized with UV light and $KMnO_4$ stain. Preparative thin layer chromatography was performed with Merck silica gel 60-F254 coated 0.50 mm plates. Flash chromatography was performed with Sorbent Tech. silica gel 60. Yields reported are for isolated, spectroscopically pure compounds. NMR spectra were recorded on 300, 400 or 500 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass spectra were recorded by the Columbia University Mass Spectrometry Core facility on a JEOL HX110 spectrometer. Infrared spectra were taken on an Perkin-Elmer 1600 FT-IR spectrometer using thin neat film deposition on NaCl plates.

Preparation of enone **22**, **25**, **28**.

These ketones were prepared according to a reported procedure. [1]



Enone **28**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.81-6.55 (m, 1H), 5.98-5.59 (m, 1H), 5.03 (ddd, J = 12.7, 2.8, 1.6 Hz, 2H), 2.94 (ddd, J = 3.2, 1.9, 0.9 Hz, 2H), 2.55-2.47 (m, 1H),

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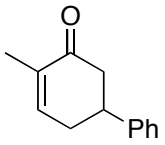
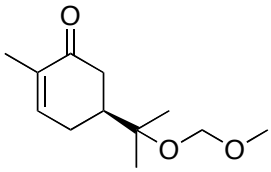
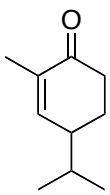
2.46-2.37 (m, 1H), 2.24-1.98 (m, 3H), 1.05 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 144.9, 137.6, 135.8, 116.1, 46.5, 34.33, 33.2, 30.5, 21.1; IR (neat): cm^{-1} 2959, 2929, 1717, 1680, 1370, 1154; HRMS (EI, *m/z*) calcd for $C_{10}H_{14}O$ $[M]^+$ 150.1045, found 150.1035.



Enone **25**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 4H), 6.78-6.76 (m, 1H), 3.33-3.26 (m, 1H), 2.74-2.1.84 (m, 4H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 144.2, 143.2, 135.4, 128.4, 126.6, 126.4, 44.7, 41.1, 33.7, 15.5; IR (neat): cm^{-1} 2930, 1715, 1660, 1148; HRMS (EI, *m/z*) calcd for $C_{13}H_{14}O$ $[M]^+$ 186.1045, found 186.1038.



Enone **19**: Enone 19 was prepared from commercial available enone (*5s*)-carvone hydrate (98%) by MOM ether protection.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80-6.57 (m, 1H), 4.68 (s, 2H), 3.33 (s, 3H), 2.58 (ddd, J = 16.1, 3.4, 1.4 Hz, 1H), 2.40 (dtd, J = 18.2, 4.7, 1.4 Hz, 1H), 2.31-2.18 (m, 2H), 2.13-2.03 (m, 1H), 1.74 (s, 3H), 1.19 (s, 3H), 1.18(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 145.0, 135.1, 90.8, 76.5, 55.2, 45.7, 39.4, 27.1, 23.6, 23.6, 15.5; IR (neat): cm^{-1} 2980, 2892, 1728, 1673, 1143, 1038; HRMS (EI, *m/z*) calcd for $C_{12}H_{21}O_3$ $[M+H]^+$ 213.1491, found 213.1487.



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Enone **44**: At room temperature, to a mixture of ethyl vinyl ketone (1.14 mL, 11 mmol) and isovaleraldehyde (0.81 mL 7.5 mmol) was added 2-(methoxydiphenylmethyl) pyrrolidine (50 mg, 0.19 mmol) and ethyl 3, 4-dihydroxy benzoate (136 mg, 0.75 mmol). The reaction mixture was stirred at room temperature for 3 days and diluted with 100 mL of ether. The ether solution was washed with water and transferred to a 250 mL flash. To this ether solution was added 20 mL of THF, 41 mL of KOH solution (0.1 N), and n-Bu_4NOH (1 mL). The reaction mixture was stirred at 42 ^oC for 24 h.[2] Upon cooling down, the mixture was extracted with ether. The combined organic solvent was washed with brine, dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified using flash chromatography and yielded the enone **44** as a light yellow oil. (820 mg, 72%) ^1H NMR (400 MHz, $CDCl_3$) δ 6.65 (dt, J = 2.7, 1.4 Hz, 1H), 2.52 (dt, J = 16.5, 4.1 Hz, 1H), 2.38-2.19 (m, 2H), 1.96 (dqd, J = 13.4, 4.7, 1.6 Hz, 1H), 1.78 (dd, J = 2.4, 1.4 Hz, 3H), 1.77-1.66 (m, 2H), 0.96 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 149.5, 135.4, 77.3, 77.0, 76.7, 42.8, 37.6, 31.7, 25.6, 19.7, 19.4, 16.2. IR (neat): cm^{-1} 2985, 1725, 1676, 1050; HRMS (EI, *m/z*) calcd for $C_{10}H_{17}O$ $[M+H]^+$ 153.1297, found 153.1292.

General Experimental Procedure for the Diels-Alder/Isomerization/Oxidation Sequence:

Diels-Alder reaction between silyloxy dienes and enones: To a stirred solution of enone(1 mmol) in anhydrous DCM (5 mL) was added $EtAlCl_2$ (1M in hexane, 0.5 mL). The mixture was stirred at 0 ^oC for 3 min and 2-silyloxy diene (2 mmol) was added. The resultant reaction mixture was slowly warmed up to room temperature, stirred for additional 2 h (or until TLC indicated disappearance of enone), and quenched with saturated sodium bicarbonate at -78 ^oC. After the ice melted, the mixture was extracted with diethyl ether. The organic extracts were dried over MgSO4, filtered and concentrated. The residue was purified using flash chromatograph. Compound **11**, **32**, **34** were obtained directly after column purification.

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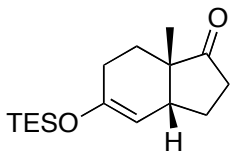
Silica gel-catalyzed isomerization of DA adducts: To a stirred solution of DA adduct (0.5 mmol) in anhydrous toluene (20 mL) was added oven-activated silica gel (200-300 mesh, 500 mg). The resultant mixture was stirred at 110 ^{o}C for 20 h. After cooled down to room temperature, the silica gel was filtered and the toluene was removed under reduced pressure and the residue was used without further purification. Compound **15**, **16** were purified using flash chromatography.

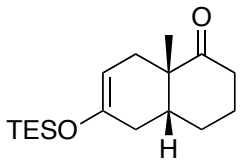
Saegusa Oxidation(Method A): To a stirred solution of isomerized silyl enol ether (0.5 mmol) in anhydrous CH_3CN (5 mL) was added $Pd(OAc)_2$ (0.55 mmol) at room temperature. The reaction was stirred at room temperature until TLC indicated disappearance of starting material. The reaction mixture was then filtered through a pad of Celite and concentrated. The residue was purified using flash chromatography.

Saegusa Oxidation(Method B): To a stirred solution of isomerized sily enol ether (0.5 mmol) in anhydrous acetonitrile was added 2, 6-di-tert-butyl- 4-methylpyridine (4 mmol) and DDQ (2mmol).[3] The resultant mixture was stirred at room temperature for about 12 h. Then the mixture was quenched with saturated $Na_2S_2O_3$ and extracted with diethyl ether. The extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified using flash chromatography.

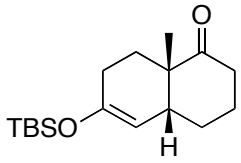


Silyl enol ether **11**: Flash chromatography (hexanes) yielded a colorless oil (235 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.81 (d, J = 3.5 Hz, 1H), 2.52 (brs, 1H), 2.33-2.14 (m, 4H), 1.97-1.94 (m, 2H), 1.88-1.83 (m, 1H), 1.65-1.60 (m, 1H),; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 222.9, 151.2, 106.3, 47.1, 43.2, 35.7, 28.1, 26.9, 26.5, 21.5, 6.7, 5.0; IR

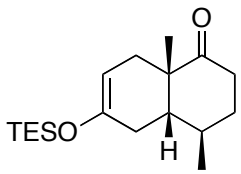
(neat): cm^{-1} 2956, 1708, 1674, 1192; HRMS (EI, *m/z*) calcd for $C_{16}H_{28}O_2Si$ $[M]^+$ 280.1859, found 280.1845.



Diels-Alder adduct: Flash chromatography (hexanes) yielded a colorless oil (256 mg, 88%). ^1H NMR ($CDCl_3$, 400 MHz): δ 4.76-4.74 (m, 1H), 2.64-2.50 (m, 2H), 2.33-2.24 (m, 2H), 2.03-1.97 (m, 1H), 1.80-1.58 (m, 6H), 1.10 (s, 3H), 0.99-0.95 (m, 9H), 0.68-0.62 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.3, 147.7, 99.5, 47.4, 42.3, 37.2, 32.8, 30.8, 28.1, 25.2, 19.9, 6.6, 5.0; IR (neat): cm^{-1} 2954, 1705, 1675, 1195;HRMS (ESP) calcd for $C_{17}H_{31}O_2Si$: 295.2093; found: 295.2102.



Silyl enol ether **12**: Flash chromatography (hexanes) yielded a colorless oil (226 mg, 90%). ^1H NMR ($CDCl_3$, 400 MHz): δ 4.60 (s, 1H), 2.47 (s, 1H), 2.45-2.33 (m, 1H), 2.26 (dd, *J* = 15.5, 4.5 Hz, 1H), 2.22-2.11 (m, 2H), 2.04 (td, *J* = 13.6, 7.5 Hz, 1H), 1.92 (dd, *J* = 15.0, 6.2 Hz, 1H), 1.78 (dt, *J* = 8.7, 5.0 Hz, 2H), 1.64-1.44 (m, 2H), 1.37-1.21 (m, 1H), 1.16 (s, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 215.3, 151.8, 108.0, 46.8, 42.9, 38.6, 31.3, 28.2, 27.2, 25.6, 24.3, 22.9, 17.9, -4.3, -4.4; IR (neat): cm^{-1} 2954, 1705, 1675, 1195; HRMS (EI, *m/z*) calcd for $C_{17}H_{31}O_2Si$ $[M+H]^+$ 295.2093, found 295.2092.



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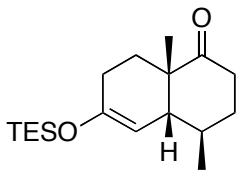
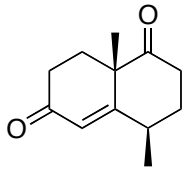
Diels-Alder adduct: Flash chromatography (hexanes) yielded a colorless oil (274 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94-4.52 (m, 1H), 2.74 (td, *J* = 14.5, 6.6 Hz, 1H), 2.49 (d, *J* = 16.7 Hz, 1H), 2.34-2.14 (m, 2H), 2.07 (d, *J* = 18.1 Hz, 1H), 2.01-1.93 (m, 1H), 1.88-1.76 (m, 1H), 1.77-1.58 (m, 1H), 1.36 (ddd, *J* = 18.5, 12.6, 5.8 Hz, 2H), 1.11 (s, 3H), 0.98 (dd, *J* = 8.8, 7.2 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.5, 147.6, 99.6, 48.6, 46.9, 37.2, 34.9, 31.5, 34.9, 31.5, 29.9, 28.8, 20.2, 19.8, 6.7, 5.0; IR (neat): cm^{-1} 2955, 1707, 1675, 1185; HRMS (EI, *m/z*) calcd for $C_{18}H_{32}O_2Si$ $[M]^+$ 308.2172, found 308.2161.



Silyl enol ether **15**: Flash chromatography (hexanes) yielded a colorless oil (245 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (d, *J* = 4.2 Hz, 1H), 2.62-2.46 (m, 1H), 2.32 (ddd, *J* = 14.8, 4.1, 3.2 Hz, 1H), 2.16-1.95 (m, 3H), 1.92-1.82 (m, 1H), 1.75-1.63 (m, 2H), 1.35 (ddd, *J* = 18.5, 11.3, 5.2 Hz, 2H), 1.11 (s, 3H), 1.03 (d, *J* = 6.0 Hz, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.6, 149.1, 105.9, 50.0, 46.7, 38.2, 36.6, 33.7, 28.7, 26.4, 19.8, 19.6, 6.7, 5.1; IR (neat): cm^{-1} 2953, 1705, 1674, 1183; HRMS (EI, *m/z*) calcd for $C_{18}H_{32}O_2Si$ $[M]^+$ 308.2172, found 308.2169.



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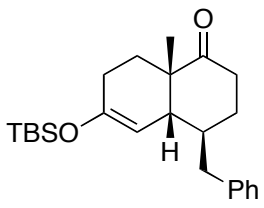
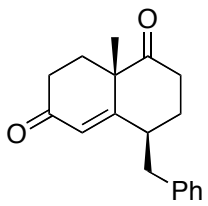
Enone **17a**: Flash chromatography yielded a light yellow oil (65 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (s, 1H), 2.81 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.72 (ddd, *J* = 16.6, 7.0, 4.6 Hz, 1H), 2.57-2.44 (m, 2H), 2.40-2.28 (m, 1H), 2.18 (ddd, *J* = 13.9, 5.0, 2.6 Hz, 1H), 2.13-2.03 (m, 1H), 1.98 (td, *J* = 13.9, 5.6 Hz, 1H), 1.91-1.78 (m, 1H), 1.47 (s, 3H), 1.36 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.8, 198.5, 170.1, 127.1, 48.9, 36.2, 33.2, 31.5, 27.4, 24.1, 22.4; IR (neat): cm^{-1} 2928, 1712, 1671, 1611; HRMS (EI, *m/z*) calcd for $C_{12}H_{17}O_2[M+H]^+$ 193.1229, found 193.1221.



Silyl enol ether **16**: Flash chromatography (hexanes) yielded a colorless oil (214 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-6.89 (m, 5H), 4.85 (d, *J* = 4.9 Hz, 1H), 3.15 (dd, *J* = 13.3, 3.5 Hz, 1H), 2.60-2.50 (m, 2H), 2.38-1.38 (m, 8H), 1.28 (dd, *J* = 11.4, 4.9 Hz, 1H), 1.18 (s, 3H), 0.98 (s, 9H), 0.23 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.4, 147.6, 140.1, 129.2, 128.3, 126.0, 100.1, 47.0, 46.9, 40.2, 36.8, 36.3, 31.4, 31.1, 28.7, 25.8, 25.7, 20.0, 18.0, -4.1, -4.3; IR (neat): cm^{-1} 2930, 1708, 1674, 1176; HRMS (EI, *m/z*) calcd for $C_{24}H_{37}O_2Si$ $[M+H]^+$ 385.2563, found 385.1535.



Enone **18**: Flash chromatography yielded a light yellow oil (87 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-6.90 (m, 5H), 5.92 (s, 1H), 3.04 (dd, *J* = 11.8, 4.2 Hz, 1H), 2.99-

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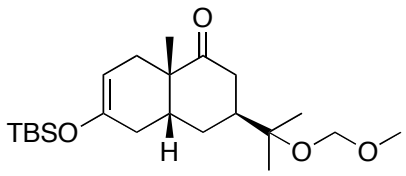
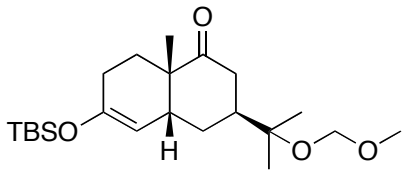
2.85 (m, 2H), 2.72 (ddd, *J* = 16.2, 7.7, 4.6 Hz, 1H), 2.60-2.41 (m, 2H), 2.37-2.26 (m, 1H), 2.20 (ddd, *J* = 13.9, 4.9, 2.7 Hz, 1H), 2.01 (dd, *J* = 13.8, 5.6 Hz, 1H), 1.97-1.77 (m, 2H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.6, 198.2, 167.4, 138.6, 129.0, 128.6, 128.1, 126.8, 48.9, 43.8, 42.7, 36.0, 33.2, 31.7, 24.6, 23.9; IR (neat): cm^{-1} 2925, 1716, 1674, 1230; HRMS (EI, *m/z*) calcd for $C_{18}H_{21}O_2$ $[M+H]^+$ 269.1542, found 269.1544.

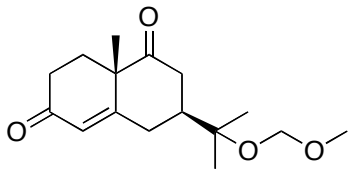


Diels-Alder adduct: Flash chromatography yielded a colorless oil (376 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (dd, *J* = 4.3, 3.4 Hz, 1H), 4.70 (d, *J* = 0.8 Hz, 2H), 3.35 (s, 3H), 2.66-2.45 (m, 2H), 2.41-2.30 (m, 1H), 2.26-2.19 (m, 1H), 2.12-1.97 (m, 3H), 1.91-1.80 (m, 1H), 1.73 (ddd, *J* = 17.0, 5.2, 2.7 Hz, 1H), 1.68-1.58 (m, 1H), 1.24 (s, 3H), 1.21 (s, 6H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 147.6, 101.6, 91.0, 77.4, 55.3, 46.1, 43.7, 39.0, 38.0, 32.3, 31.1, 26.0, 25.7, 24.2, 24.2, 24.0, 17.9, -4.4, -4.5; IR (neat): cm^{-1} 2954, 2931, 1708, 1194, 1040; HRMS (EI, *m/z*) calcd for $C_{22}H_{39}O_4Si$ $[M+H]^+$ 395.2618, found 395.2625.

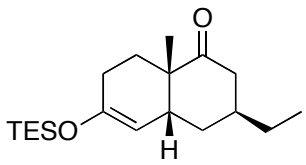


Silyl enol ether **20**: Flash chromatography yielded a colorless oil (356 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84-4.64 (m, 2H), 4.53 (s, 1H), 3.35 (s, 3H), 2.60 (d, *J* = 2.9 Hz, 1H), 2.35 (dd, *J* = 6.2, 4.6 Hz, 1H), 2.25-2.15 (m, 2H), 2.04-1.83 (m, 4H), 1.67 (d, *J* = 10.6 Hz, 1H), 1.28 (ddd, *J* = 18.8, 9.9, 6.2 Hz, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 1.16 (s, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 152.3, 108.3, 90.8, 76.9, 55.2, 45.9, 44.2, 41.7, 39.7, 31.8, 28.2, 27.2, 25.6, 25.5, 24.1, 23.9,

17.9, -4.2, -4.4; IR (neat): cm^{-1} 2931, 2857, 1704, 1196, 1041; HRMS (EI, *m/z*) calcd for $C_{22}H_{39}O_4Si$ $[M+H]^+$ 395.2618, found 395.2612.



Enone **21**: Flash chromatography (hexanes) yielded a colorless oil (224 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (d, *J* = 1.6 Hz, 1H), 4.76-4.69 (m, 2H), 3.37 (s, 3H), 2.75-2.53 (m, 4H), 2.49-2.42 (m, 2H), 2.14-2.07 (m, 2H), 1.85 (tt, *J* = 12.4, 4.4 Hz, 1H), 1.44 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 198.3, 165.4, 126.4, 91.1, 76.4, 55.4, 49.8, 45.5, 39.1, 33.6, 32.9, 29.7, 24.1, 23.8, 23.2; IR (neat): cm^{-1} 2927, 1712, 1673, 1037; HRMS (EI, *m/z*) calcd for $C_{16}H_{24}O_4$ $[M]^+$ $C_{16}H_{24}O_4$: 280.1675; found: 280.1683.



Silyl enol ether **23**: Flash chromatography yielded a colorless oil (272 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.55 (s, 1H), 2.55 (d, *J* = 1.4 Hz, 1H), 2.38-2.14 (m, 3H), 2.07 (dd, *J* = 15.1, 12.0 Hz, 1H), 1.93-1.81 (m, 1H), 1.83-1.69 (m, 2H), 1.44-1.21 (m, 4H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.61 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.8, 151.8, 108.0, 46.1, 44.7, 42.0, 36.1, 34.0, 31.8, 29.3, 27.1, 25.3, 11.2, 6.6, 5.0; IR (neat): cm^{-1} 2952, 1707, 1195; HRMS (EI, *m/z*) calcd for $C_{19}H_{34}O_2Si$ $[M]^+$ 322.2328, found 322.2325.

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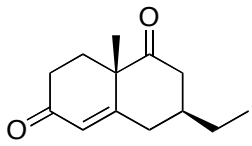
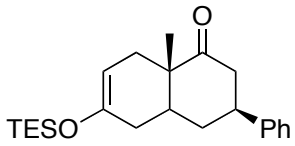
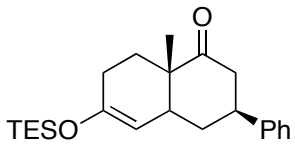


Enone **24**: Flash chromatography yielded a colorless oil (80 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) d 5.86 (s, 1H), 2.63-2.35 (m, 6H), 2.20-2.03 (m, 2H), 1.70 (m, 1H), 1.55-1.45 (m, 2H), 1.43 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 210.8, 198.5, 165.1, 125.9, 50.0, 43.8, 38.4, 37.3, 33.6, 29.6, 29.5, 23.3, 10.9; IR (neat): cm^{-1} 2950, 1710, 1192; HRMS (EI, *m/z*) calcd for $C_{13}H_{19}O_2$ $[M+H]^+$ 207.1385, found 207.1399.

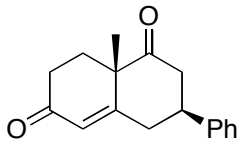


Diels-Alder adduct: Flash chromatography yielded a colorless oil (334 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-6.89 (m, 5H), 4.80 (s, 1H), 3.47 (dd, *J* = 12.0, 6.1 Hz, 1H), 2.78 (dd, *J* = 6.4, 3.1 Hz, 2H), 2.64 (d, *J* = 16.2 Hz, 1H), 2.37-1.95 (m, 4H), 1.82 (dd, *J* = 28.5, 10.4 Hz, 2H), 1.24 (s, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.5, 147.7, 144.6, 128.5, 127.1, 126.4, 100.3, 47.0, 42.0, 39.7, 37.6, 34.2, 32.4, 31.2, 22.2, 6.7, 5.0; IR (neat): cm^{-1} 2968, 1709, 1650; HRMS (EI, *m/z*) calcd for $C_{23}H_{34}O_2Si$ $[M]^+$ 370.2328, found 370.2356.

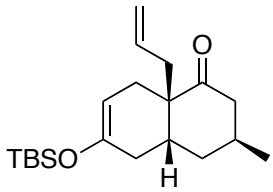


Silyl enol ether **26 :** Flash chromatography (hexanes) yielded a colorless oil (305 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.32 (m, 2H), 7.24-7.21 (m, 3H), 4.65 (br s,

1H), 3.13 (dddd, *J* = 12.8, 12.8, 3.6, 3.6 Hz, 1H), 2.69 (br s, 1H), 2.64 (dd, *J* = 15.3, 13.2, 1H), 2.46 (ddd, *J* = 15.2, 4, 2 Hz, 1H), 2.36-2.25 (m, 3H), 1.96-1.91 (m, 1H), 1.82-1.78 (m, 1H), 1.40-1.32 (m, 1H), 1.27 (s, 3H), 0.98 (t, *J* = 8 Hz, 9H), 0.68 (q, *J* = 8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.7, 152.6, 144.6, 128.7, 126.6, 107.5, 46.0, 45.7, 42.3, 40.0, 35.1, 31.9, 27.2, 25.6, 6.6, 5.1; IR (neat): cm^{-1} 2954, 1705, 1640; HRMS (EI, *m/z*) calcd for $C_{23}H_{35}O_2Si$ $[M+H]^+$ 371.2406, found 371.2388.



Enone **27**: Flash chromatography (20% EtOAc/Hexane) yielded a colorless oil (90 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.36 (m, 2H), 7.30-7.24 (m, 3H), 5.92 (s, 1H), 3.00-2.95 (m, 3H), 2.73-2.70 (m, 2H), 2.53-2.48 (m, 2H), 2.20-2.18 (m, 2H), 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 209.9, 198.2, 164.1, 142.2, 129.0, 127.4, 126.5, 126.4, 49.9, 45.1, 41.1, 39.8, 33.6, 29.6, 23.4; IR (neat): cm^{-1} 2953, 1713, 1670, 1620, 1167; HRMS (EI, *m/z*) calcd for $C_{17}H_{19}O_2$ $[M+H]^+$ 255.1385, found 255.1383.



Diels-Alder adduct: Flash chromatography (20% EtOAc/Hexane) yielded a colorless oil (267 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (dddd, *J* = 16.8, 10.1, 8.1, 6.6 Hz, 1H), 5.12-4.95 (m, 2H), 4.76 (dd, *J* = 4.6, 3.2 Hz, 1H), 2.56 (dd, *J* = 14.6, 5.8 Hz, 2H), 2.46-2.39 (m, 2H), 2.34-2.23 (m, 2H), 2.15 (dd, *J* = 14.1, 7.2 Hz, 2H), 1.89-1.58 (m, 4H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.8, 147.8, 133.9, 117.6, 100.7, 50.2, 45.0, 39.8, 34.9, 33.7, 31.9, 29.5, 29.3, 25.6, 21.2, 17.9, -4.3, -4.4; IR (neat): cm^{-1} 2955, 2929, 2857, 1707, 1193; HRMS (EI, *m/z*) calcd for $C_{20}H_{35}O_2Si$ $[M+H]^+$ 335.2406, found 335.2390.

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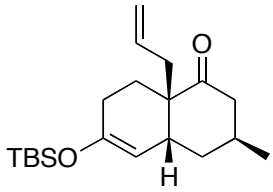
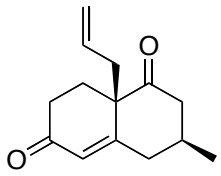


Silyl enol ether **29 :** Flash chromatography (hexanes) yielded a colorless oil (240 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (ddt, *J* = 17.6, 10.4, 7.4 Hz, 1H), 5.09-4.93 (m, 2H), 4.55 (s, 1H), 2.65 (br s, 2H), 2.45 (dd, *J* = 14.0, 7.2 Hz, 2H), 2.27-1.39 (m, 8H), 1.00 (d, *J* = 6.2 Hz, 3H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 151.8, 132.8, 118.1, 108.2, 49.3, 47.4, 41.6, 40.0, 36.0, 29.4, 28.4, 26.9, 25.7, 25.6, 22.1, -4.3, -4.4; IR (neat): cm^{-1} 2954, 1707, 1194; HRMS (EI, *m/z*) calcd for $C_{20}H_{35}O_2Si$ $[M+H]^+$ 335.2406, found 335.2390.



Enone **27**: Flash chromatography (20% EtOAc/Hexane) yielded a colorless oil (77 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (s, 1H), 5.58 (ddt, *J* = 17.5, 10.5, 7.4 Hz, 1H), 5.22-5.02 (m, 2H), 2.64 (dd, *J* = 14.9, 6.5 Hz, 1H), 2.57-2.36 (m, 7H), 2.24 (dt, *J* = 14.5, 4.4 Hz, 1H), 2.03 (dt, *J* = 14.5, 9.8 Hz, 1H), 1.91 (ddt, *J* = 19.6, 13.1, 6.6 Hz, 1H), 1.13 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 198.3, 164.0, 131.5, 126.5, 119.4, 53.5, 46.7, 40.6, 39.8, 33.3, 31.3, 29.7, 26.0, 22.0; IR (neat): cm^{-1} 2925, 1710, 1675; HRMS (EI, *m/z*) calcd for $C_{14}H_{18}O_2$ $[M]^+$ 218.1307, found 218.1299.

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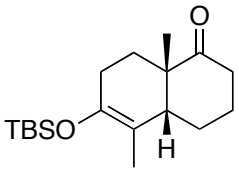
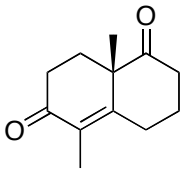
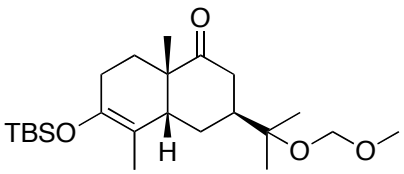


Silyl enol ether **32**: Flash chromatography (hexanes) yielded a colorless oil (262 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43-2.29 (m, 2H), 2.16-1.93 (m, 5H), 1.87-1.72 (m, 1H), 1.69-1.61 (m, 2H), 1.26 (dt, *J* = 6.8, 3.8 Hz, 1H), 1.12 (s, 3H), 0.93 (s, 9H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9, 143.6, 113.1, 48.5, 47.7, 38.4, 29.5, 27.1, 26.8, 25.8, 23.6, 21.8, 18.1, 14.7, -3.8, -3.8; IR (neat): cm^{-1} 2932, 2858, 1703, 1682, 1173; HRMS (EI, *m/z*) calcd for $C_{18}H_{32}O_2Si$ $[M]^+$ 308.2172, found 308.2176.

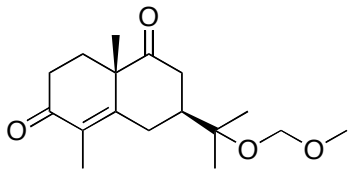


Enone **33**: Flash chromatography (20% EtOAc/Hexane) yielded a colorless oil (77 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (dt, *J* = 16.0, 4.8 Hz, 1H), 2.67 (ddd, *J* = 16.1, 10.4, 6.0 Hz, 1H), 2.57-2.37 (m, 4H), 2.20-2.01 (m, 3H), 1.80 (d, *J* = 1.0 Hz, 3H), 1.79-1.70 (m, 1H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.1, 197.6, 158.1, 130.8, 50.6, 37.3, 33.3, 29.6, 27.2, 23.3, 21.5, 11.3; IR (neat): cm^{-1} 2951, 1710, 1666, 1611; HRMS (EI, *m/z*) calcd for $C_{12}H_{16}O_2$ $[M]^+$ 192.1150, found 192.1156.

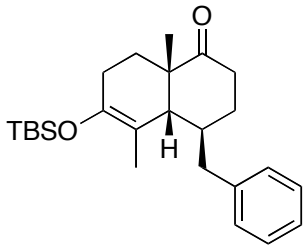


Silyl enol ether **34**: Flash chromatography (hexanes) yielded a colorless oil (385 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (s, 2H), 3.35 (s, 3H), 2.45 (s, 1H), 2.35 (d, *J* = 8.8 Hz, 2H), 2.26-2.09 (m, 2H), 1.99 (dd, *J* = 13.9, 3.7 Hz, 1H), 1.94-1.80 (m, 2H), 1.68-

1.60 (m, 1H), 1.57 (s, 3H), 1.32-1.23 (m, 1H), 1.21 (s, 3H), 1.21 (s, 2H), 1.16 (s, 3H), 0.92 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.5, 145.9, 112.3, 90.8, 76.8, 55.1, 46.7, 45.9, 43.2, 39.7, 31.2, 27.7, 25.9, 25.8, 24.9, 23.8, 23.7, 18.2, 13.4, -3.8, -4.0; IR (neat): cm^{-1} 2932, 1704, 1196, 1042; HRMS (EI, *m/z*) calcd for $C_{23}H_{42}O_4Si$ $[M]^+$ 410.2852, found 410.2846.

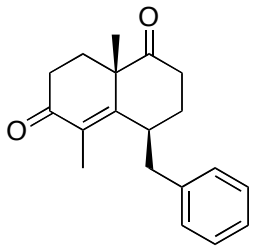


Enone **35**: Flash chromatography (20% EtOAc/Hexane) yielded a colorless oil (117 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (d, *J* = 1.5 Hz, 2H), 3.38 (s, 3H), 3.05 (ddd, *J* = 14.1, 3.5, 2.0 Hz, 1H), 2.65 (dd, *J* = 15.1, 11.5 Hz, 1H), 2.59-2.45 (m, 3H), 2.30 (t, *J* = 13.5 Hz, 1H), 2.13-1.98 (m, 2H), 1.84 (s, 3H), 1.83-1.76 (m, 1H), 1.41 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.4, 197.7, 157.9, 130.8, 91.0, 76.8, 55.4, 50.5, 44.9, 38.8, 33.4, 29.6, 28.3, 23.9, 23.6, 23.1, 11.3; IR (neat): cm^{-1} 2973, 1710, 1664, 1140; HRMS (EI, *m/z*) calcd for $C_{17}H_{27}O_4$ $[M+H]^+$ 295.1909, found 295.1898.

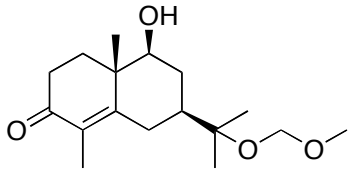


Silyl enol ether **36**: Flash chromatography (hexanes) yielded a colorless oil (318 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 14.0, 6.4 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 2H), 3.17 (dd, *J* = 12.9, 3.7 Hz, 1H), 2.43 (ddd, *J* = 15.2, 12.9, 6.3 Hz, 1H), 2.32-2.12 (m, 5H), 2.08-1.96 (m, 1H), 1.85 (d, *J* = 9.7 Hz, 1H), 1.79 (s, 3H), 1.73 (ddd, *J* = 13.3, 6.4, 3.3 Hz, 1H), 1.41 (dd, *J* = 10.8, 6.8 Hz, 1H), 1.27 (ddd, *J* = 24.6, 13.0, 5.0 Hz, 1H), 1.14 (s, 3H), 1.01 (s, 9H), 0.22 (s, 3H), 0.20 (s, 3H).

; ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.2, 144.2, 141.0, 129.0, 128.3, 125.9, 113.4, 55.2, 48.3 43.6, 41.1, 37.1, 29.2, 28.9, 26.8, 25.9, 19.9, 19.6, 18.3, -3.6, -3.7.; IR (neat): cm^{-1} 2955, 1708, 1672, 1176; HRMS (EI, *m/z*) calcd for $C_{18}H_{32}O_2Si$ $[M]^+$ 308.2172, found 308.2176.

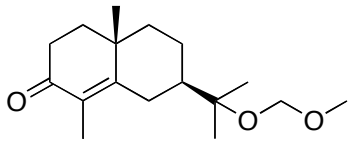


Enone **36**: Flash chromatography (20% EtOAc/Hexane) yielded a colorless oil (80 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.23 (d, *J* = 7.2 Hz, 2H), 3.34-3.23 (m, 1H), 3.05 (dd, *J* = 13.6, 3.7 Hz, 1H), 2.70 (dd, *J* = 13.4, 11.4 Hz, 1H), 2.66-2.50 (m, 3H), 2.26 (ddd, *J* = 15.5, 11.1, 4.6 Hz, 1H), 2.19-2.12 (m, 1H), 1.98 (s, 3H), 1.96-1.92 (m, 1H), 1.91-1.84 (m, 1H), 1.82-1.70 (m, 1H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 198.0, 160.7, 139.7, 133.3, 128.8, 128.7, 126.8, 49.3, 40.9, 40.7, 36.2, 33.1, 31.4, 24.5, 23.9, 11.7. IR (neat): cm^{-1} 2926, 1712, 1674; HRMS (EI, *m/z*) calcd for $C_{19}H_{22}O_2$ $[M]^+$ 282.1620, found 282.1619.



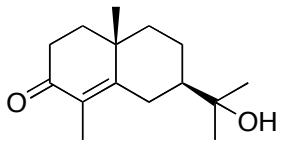
Enone **39**: To a solution of enone **35** (52 mg, 0.18 mmol) in ethanol (5 mL) at 0 °C was added $NaBH_4$ (3.8 mg, 0.1 mmol). 1 hour later, the reaction was quenched with saturated NH_4Cl solution and extracted with ether. The combined organic solution was dried over $MgSO_4$ and concentrated. The residue was purified using flash chromatography (20% EtOAc/Hexane) and yielded a colorless oil (49 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (d, *J* = 1.5 Hz, 2H), 3.45-3.41 (m, 1H), 3.38 (s, 3H), 2.81 (dd, *J* = 14.1, 2.8 Hz, 1H),

2.46-2.42 (m, 2H), 2.12 (ddd, *J* = 13.2, 13.2, 4.4 Hz, 1H), 1.98-1.92 (m, 2H), 1.80 (s, 3H), 1.84-1.76 (m, 1H), 1.60-1.54 (m, 2H), 1.26 (s, 3H), 1.25 (s, 3H), 1.16 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 160.3, 130.5, 90.8, 78.4, 55.2, 44.6, 41.4, 33.4, 33.3, 31.1, 27.9, 24.0, 23.4, 15.7, 11.3; IR (neat): cm^{-1} 3437, 2948, 1654, 1610, 1369, 1144, 1039; HRMS (EI, *m/z*) calcd for $C_{17}H_{29}O_4$ $[M+H]^+$ 297.2066, found 297.2061.



Compound **40**: To a solution of enone **39 (**10 mg, 0.03 mmol) in dichloroethane (3 mL) was added TCDI (32 mg, 0.18 mmol) and DMAP (3mg, 0.03mmol). The reaction mixture was stirred at 50 ^{o}C for 4 h and cooled down to room temperature. Then dichloroethane was removed under reduced pressure. To this residue was added anhydrous toluene (3 mL), tributyltin hydride (10 mL) and AIBN (1 mg) under argon. The reaction mixture was stirred at 90 ^{o}C for 3 h and cooled down to room temperature. The mixture was purified using flash chromatography directly and yielded a colorless oil. (6 mg, 65%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82-4.54 (m, 2H), 3.38 (s, 3H), 2.86 (d, *J* = 14.4 Hz, 1H), 2.60-2.45 (m, 1H), 2.44-2.32 (m, 1H), 1.92 (t, *J* = 13 Hz, 1H), 1.78 (s, 3H), 1.77-1.65 (m, 4H), 1.48-1.32 (m, 4H), 1.25 (s, 3H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 162.9, 128.8, 90.8, 77.8, 55.2, 48.7, 42.0, 37.4, 35.9, 33.8, 29.7, 28.6, 24.1, 23.3, 22.5, 10.9; IR (neat): cm^{-1} 2924, 1662, 1461, 1141, 1040; HRMS (EI, *m/z*) calcd for $C_{17}H_{19}O_3$ $[M+H]^+$ 281.2117, found 281.2110.



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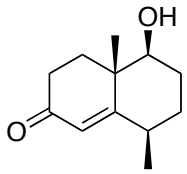
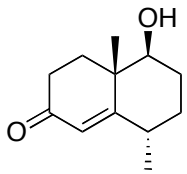
(+)-carissone **41**: To a solution of compound **40** (6 mg, 0.02 mmol) in anhydrous dichloromethane (2 mL) at -78 ^{o}C was added Me_2BBr (2 mL). 5 mins later, the reaction mixture was quenched with saturated $NaHCO_3$. Upon warming up to room temperature, the mixture was extracted with ether, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified using flash chromatography and yielded a colorless oil. (4.3 mg, 90%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90-2.82 (m, 1H), 2.52 (ddd, *J* = 16.9, 12.9, 6.8 Hz, 1H), 2.39 (dt, *J* = 16.9, 4.2 Hz, 1H), 1.90 (t, *J* = 13.5 Hz, 1H), 1.78 (d, *J* = 1.1 Hz, 3H), 1.78-1.68 (m, 4H), 1.54-1.33 (m, 4H), 1.26 (s, 3H), 1.25 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 162.6, 128.9, 72.5, 49.6, 41.9, 37.4, 35.8, 33.8, 28.7, 27.5, 26.8, 22.6, 22.5, 10.9; IR (neat): cm^{-1} 3408, 2928, 1652, 1607, 1378, 1148; HRMS (EI, *m/z*) calcd for $C_{15}H_{25}O_2$ $[M+H]^+$ 237.1855, found 237.1865; $[\alpha]_D^{22}$ = + 89 ^{o} (c 0.00075 $CHCl_3$).



Procedure was the same as the preparation of compound 39.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (s, 1H), 3.44 (d, *J* = 11.8 Hz, 1H), 2.69-2.57 (m, 1H), 2.57-2.47 (m, 1H), 2.42 (d, *J* = 17.5 Hz, 1H), 2.29-2.13 (m, 1H), 2.00-1.87 (m, 1H), 1.86-1.62 (m, 3H), 1.51 (d, *J* = 7.9 Hz, 1H), 1.29 (s, 3H), 1.24 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 173.2, 126.5, 78.7, 41.2, 37.4, 36.5, 33.9, 28.8, 25.9, 22.5, 17.8; IR (neat): cm^{-1} 3401, 2937, 1659, 1606, 1455, 1076; HRMS (EI, *m/z*) calcd for $C_{12}H_{19}O_2$$[M+H]^+$ 195.1385, found 195.1378.



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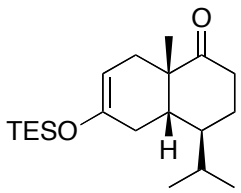
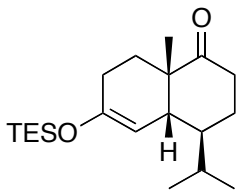
to a solution of compound in DCM (2 mL) was added HClO4 (0.2 mL). the mixture was stirred at room temperature for 12 h and quenched with water. The mixture was extracted with DCM and dried over MgSO4. The solution was concentrated in vacuo and purified using chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (d, *J* = 1.7 Hz, 1H), 3.45 (dd, *J* = 11.5, 4.4 Hz, 1H), 2.60-2.33 (m, 3H), 2.17 (dt, *J* = 13.5, 4.7 Hz, 1H), 1.93-1.67 (m, 4H), 1.21 (s, 3H), 1.08 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 171.1, 123.2, 78.2, 41.7, 34.5, 33.5, 33.4, 32.1, 30.3, 17.7, 16.3; IR (neat): cm^{-1} 3402, 2920, 1659, 1610, 1458, 1054; HRMS (EI, *m/z*) calcd for $C_{12}H_{19}O_2[M+H]^+$ 195.1385, found 195.1393.



^{1}H NMR (400 MHz, $CDCl_3$) d 4.82-4.61 (m, 1H), 2.65 (ddd, *J* = 14.8, 13.7, 6.4 Hz, 1H), 2.48 (d, *J* = 17.1 Hz, 1H), 2.31 (ddd, *J* = 15.0, 4.5, 3.3 Hz, 1H), 2.19-2.08 (m, 2H), 2.01 (dtd, *J* = 13.8, 6.9, 3.4 Hz, 1H), 1.92 (ddt, *J* = 13.2, 6.5, 3.3 Hz, 1H), 1.79-1.66 (m, 2H), 1.61 (dd, *J* = 11.4, 4.2 Hz, 1H), 1.35 (ddd, *J* = 25.1, 13.4, 4.8 Hz, 1H), 1.13 (s, 4H), 0.97 (t, *J* = 7.9 Hz, 11H), 0.72 (d, *J* = 6.9 Hz, 3H), 0.66 (q, *J* = 7.9 Hz, 6H).
; ^{13}C NMR (101 MHz, $CDCl_3$) d 215.6, 147.7, 99.7, 46.9, 44.1, 39.1, 37.2, 31.5, 27.6, 27.4, 24.2, 21.5, 20.2, 14.5, 6.7, 5.0; IR (neat): cm^{-1} 2954, 1707, 1674, 1183; HRMS (EI, *m/z*) calcd for $C_{20}H_{36}O_2Si$ $[M]^+$ 336.2485, found 336.2486.



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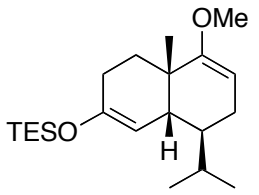
^{1}H NMR (400 MHz, $CDCl_3$) d 4.99 (d, *J* = 5.6 Hz, 1H), 2.68-2.27 (m, 4H), 2.22-1.92 (m, 4H), 1.91-1.78 (m, 1H), 1.69 -1.50 (m, 1H), 1.36 (dt, *J* = 9.5, 6.3 Hz, 1H), 1.12 (s, 3H), 1.04-0.90 (m, 11H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.67 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) d 216.7, 149.3, 105.5, 46.7, 46.6, 45.1, 37.9, 28.5, 27.2, 26.3, 23.4, 21.7, 20.0, 15.2, 6.6, 5.0; IR (neat): cm^{-1} 2952, 1706, 1675, 1184; HRMS (EI, *m/z*) calcd for $C_{20}H_{36}O_2Si$ $[M]^+$ 336.2485, found 336.2489.



Compound **50**: To a solution of diisopropylamine (84 mL, 0.62 mmol) in anhydrous THF (5 mL) at 0 ^{o}C was added n-BuLi (1M in hexane, 240 mL). The solution was stirred for 5 mins and cooled down to -78 ^{o}C. To this reaction mixture was injected a solution of compound **47** (40 mg, 0.12 mL) in anhydrous THF (1 mL). The reaction reacture was stirred at -78 ^{o}C for 40 mins and was then treated with HMPA (300 mL). 5 min later, dimethylsulfate (70 mL) was injected slowly into the reaction mixture. While stirring, the reaction mixture was slowly warmed up to 0 ^{o}C in 30 min, quenched with satuated NH4Cl solution and extracted with ether. The combined organic solution was dried over MgSO4, concentrated in vacuo and the residue was purified using flash chromatography. (33 mg, 80%)

^{1}H NMR (400 MHz, $CDCl_3$) d 4.92 (dd, *J* = 5.5, 1.4 Hz, 1H), 4.55 (dd, *J* = 6.2, 1.9 Hz, 1H), 3.46 (s, 3H), 2.15-1.97 (m, 2H), 1.95-1.87 (m, 2H), 1.85-1.73 (m, 3H), 1.69-1.58 (m, 1H), 1.49-1.29 (m, 1H), 1.08 (s, 3H), 1.04-0.94 (m, 9H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.67 (dt, *J* = 8.1, 6.8 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) d 161.4, 149.9, 105.2, 91.3, 54.2, 43.8, 43.1, 36.8, 28.9, 26.9, 22.0, 21.6, 14.9, 6.7, 5.1; IR (neat): cm^{-1} 2956, 2926, 1670, 1199; HRMS (EI, *m/z*) calcd for $C_{21}H_{38}O_2Si$ $[M]^+$ 350.2641, found 350.2632.

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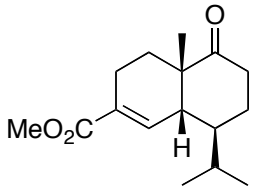
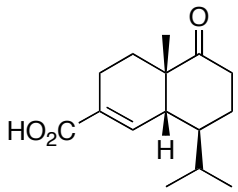


To a solution of compound **50** (33 mg, 0.09 mmol) in anhydrous THF (2 mL) at 0 ^{o}C was injected slowly n-BuLi (1M in hexane, 100 mL). The reaction mixture was stirred under argon for additional 30 mins and then treated with Comin's reagent (60 mg, 0.1 mmol). 2 hour later the reaction was quenched with water, extracted with ether and dried over $MgSO_4$. After filtration, the solution was concentrated in vacuo. To the residue was added Pd(OAc)2 (3.4 mg 0.015 mmol), PPh3 (8 mg, 0.03 mmol), triethylamine (21 mL, 0.15 mmol), anhydrous DMF (1.5 mL) and anhydrous MeOH (0.5 mL). The reaction mixture was then degassed with CO and stirred for additional 12 h at room temperature under a balloon pressure of CO. The reaction was cooled down to 0 ^{o}C and 1N HCl solution (2 mL) and THF (1 mL) were added to the reaction mixture. The mixture was then stirred at 0 ^{o}C for 6 hour, extracted with ether and dried over MgSO4. The solution was concentrated in vacuo and the residue was purified using flash chromatography. (16 mg, 65% yield)

^{1}H NMR (400 MHz, $CDCl_3$) d 7.08 (dd, J = 3.5, 1.8 Hz, 1H), 3.76 (s, 3H), 2.53-2.38 (m, 2H), 2.33-2.13 (m, 1H), 2.11-1.87 (m, 3H), 1.54 (m, 5H), 1.04 (s, 3H), 0.98 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H).

; ^{13}C NMR (101 MHz, $CDCl_3$) d 215.6, 140.4, 128.8, 51.7, 46.2, 45.9, 37.8, 29.7, 27.7, 27.5, 23.7, 21.6, 21.2, 20.2, 15.6; IR (neat): cm^{-1} 2922, 1711, 1650, 1259; HRMS (EI, *m/z*) calcd for $C_{16}H_{25}O_3$ $[M+H]^+$ 265.1804, found 265.1815.



To a solution of compound **53** (16 mg, 0.06 mmol) in 1 mL of THF was added 1 ml of LiOH aqueous solution (0.2 M). The reaction mixture was stirred at room temperature for

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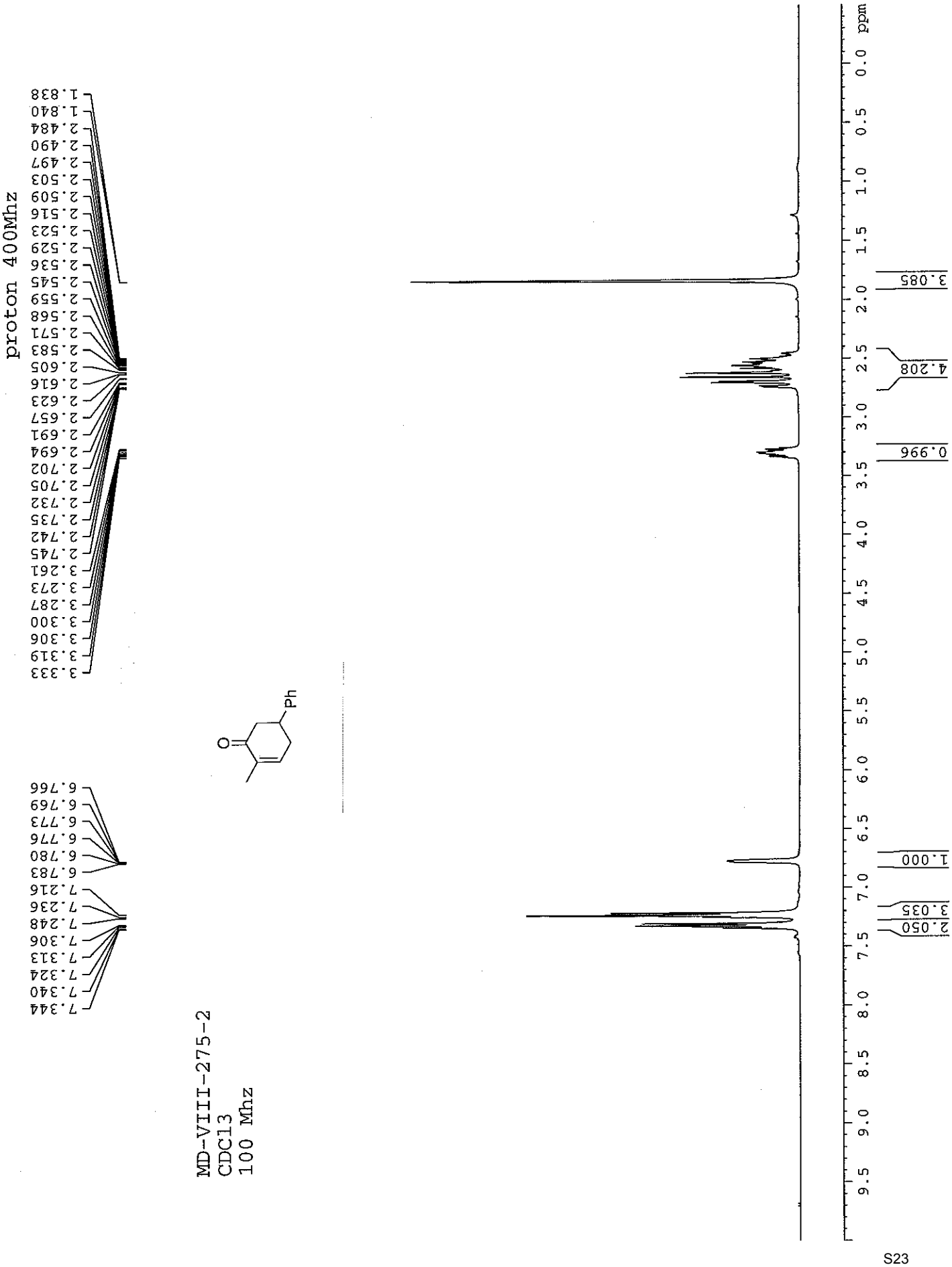
12 h and extracted with ethyl acetate. The combined solution was dried over MgSO4 and concentrated in vacuo. The residue was purified using flash chromatography. (14.3 mg, 90%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 5.3 Hz, 1H), 2.58-2.36 (m, 2H), 2.22 (dd, *J* = 10.1, 6.5 Hz, 1H), 2.12-1.87 (m, 3H), 1.78-1.38 (m, 5H), 1.05 (s, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.4, 169.9, 142.9, 128.0, 46.2, 46.1, 46.0, 37.8, 27.6, 27.5, 23.7, 21.5, 20.9, 20.3, 15.6; IR (neat): cm^{-1} 2925, 1708, 1692, 1650, 1275; HRMS (EI, *m/z*) calcd for $C_{15}H_{23}O_3$ $[M+H]^+$ 251.1647, found 251.1644.

^{13}C comparison:

Isolated cosmosoic acid	Synthetic cosmosoic acid
212.2	215.4
171.0	169.9
151.4	142.9
132.9	128.0
59.4	46.2
55.8	46.1
52.8	46.0
39.4	37.8
34.9	27.6
32.8	27.5
27.0	23.7
25.0	21.5
22.6	20.9
21.9	20.3
19.8	15.6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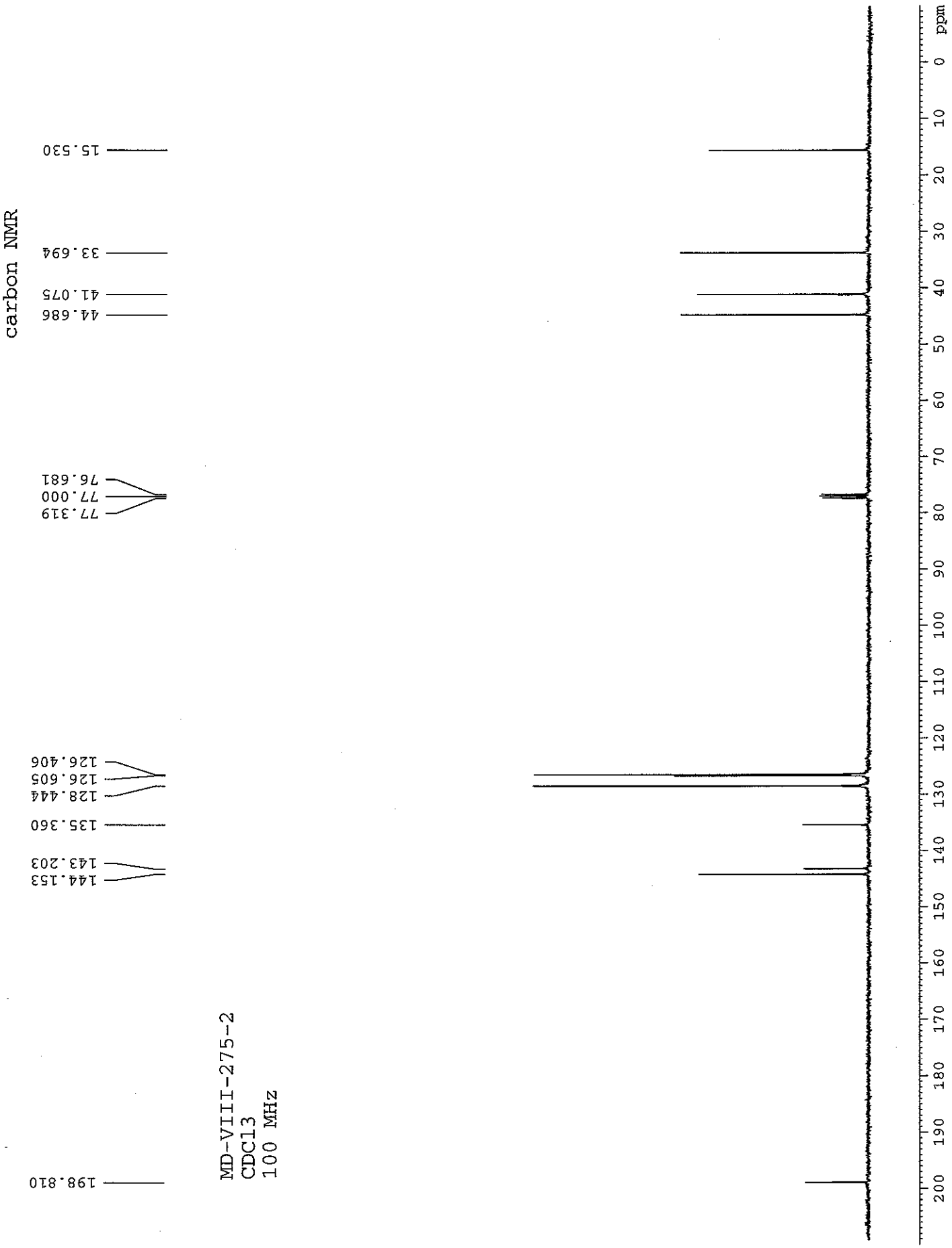

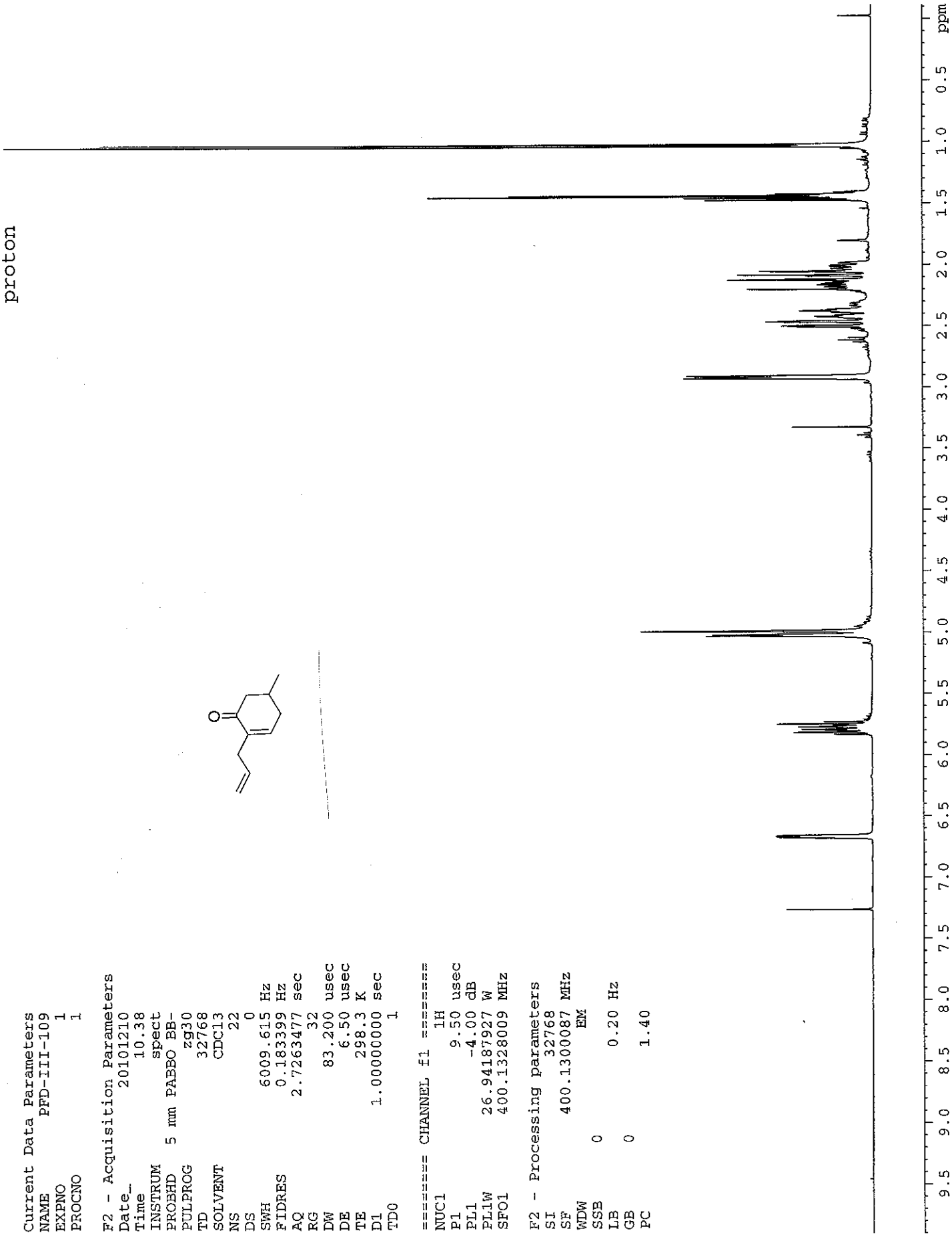
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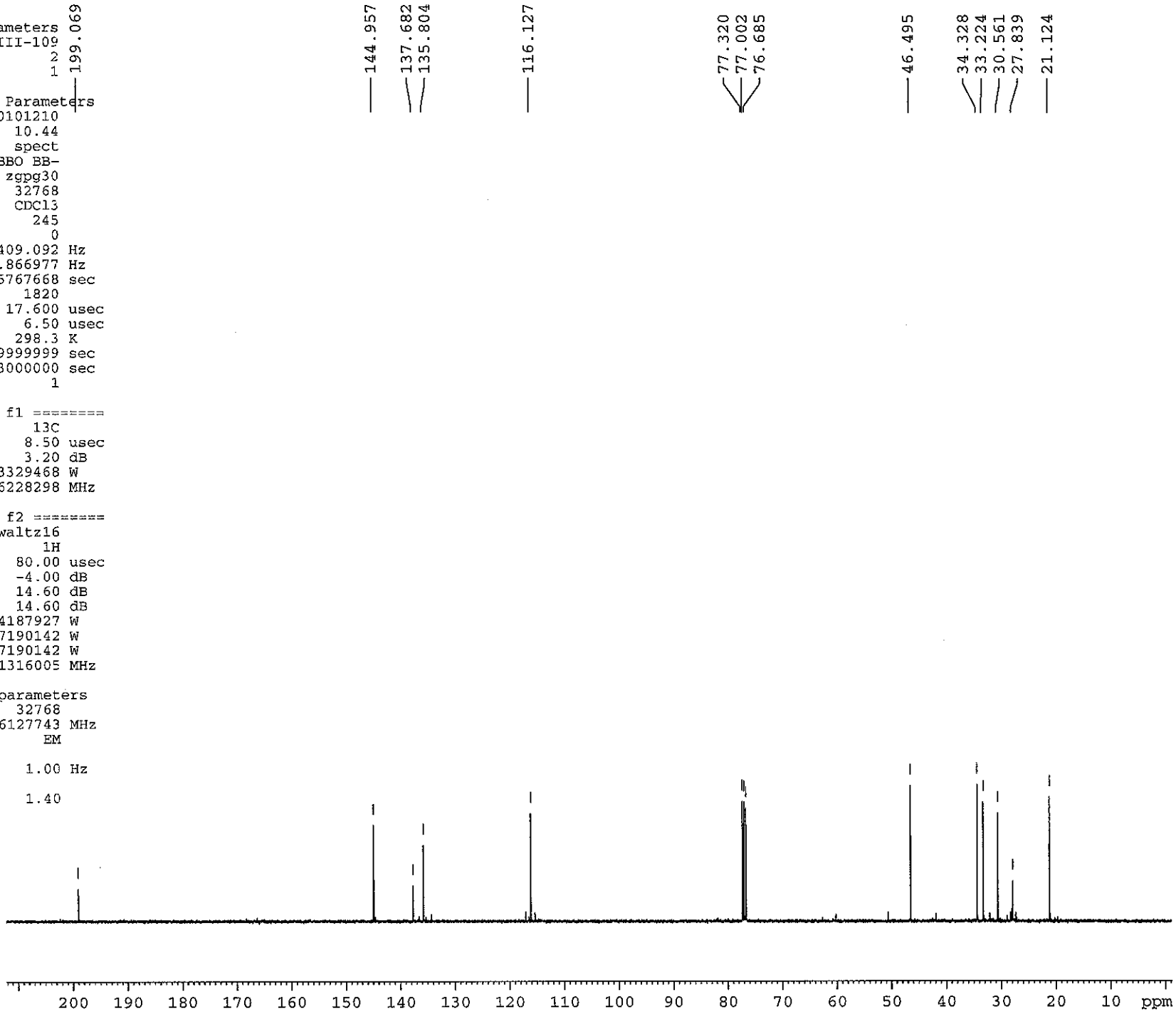

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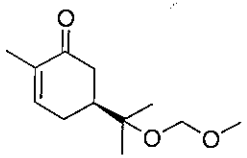

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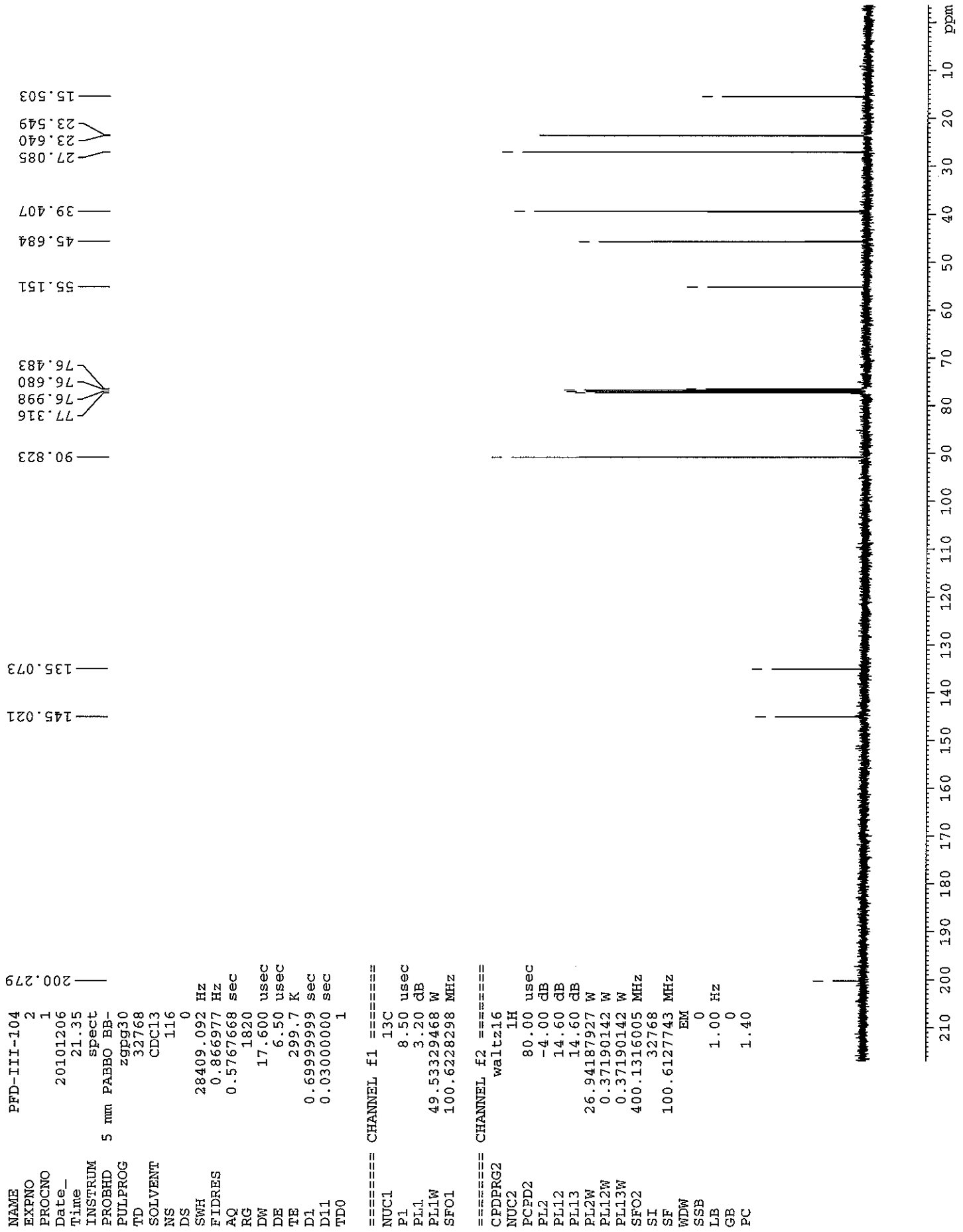

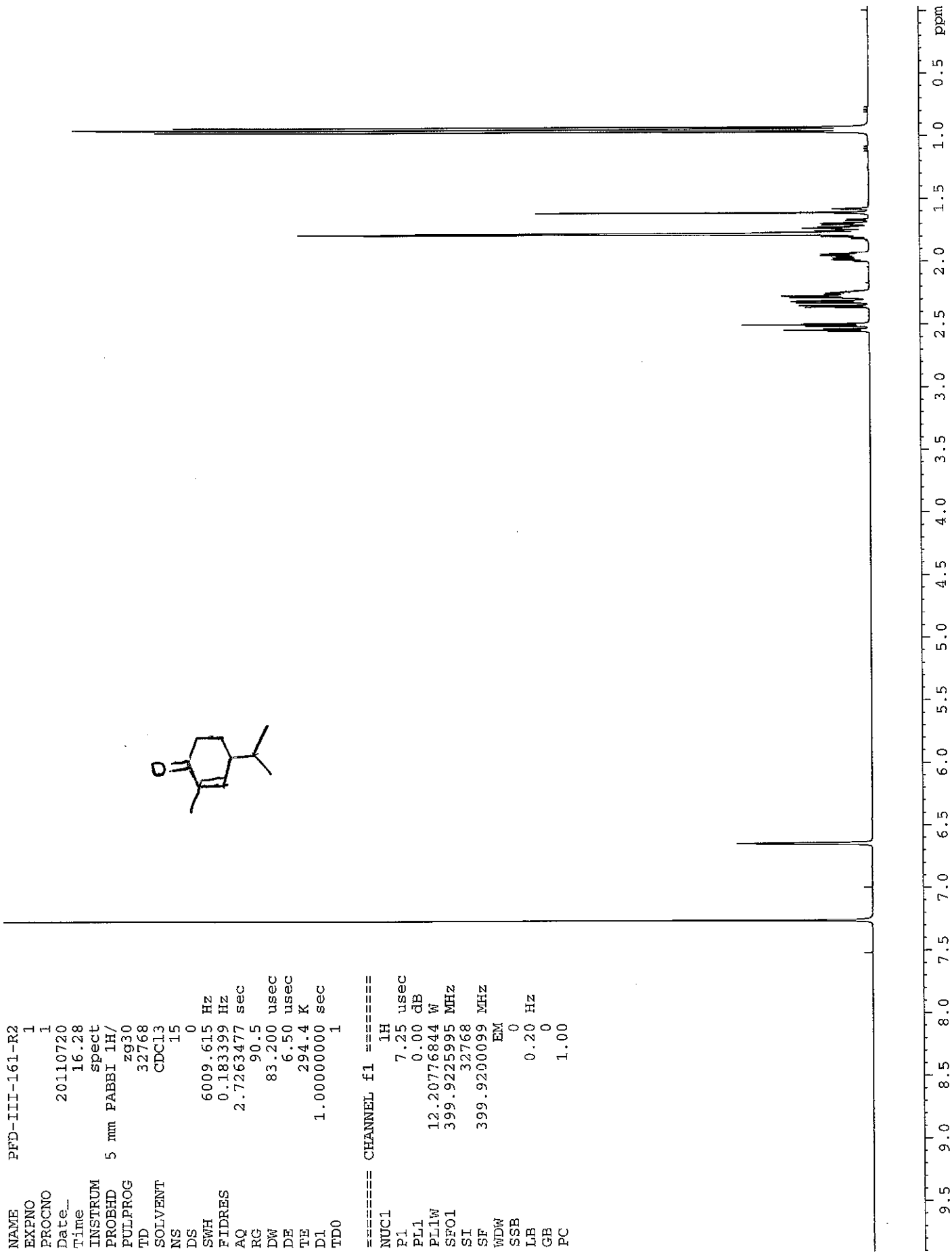
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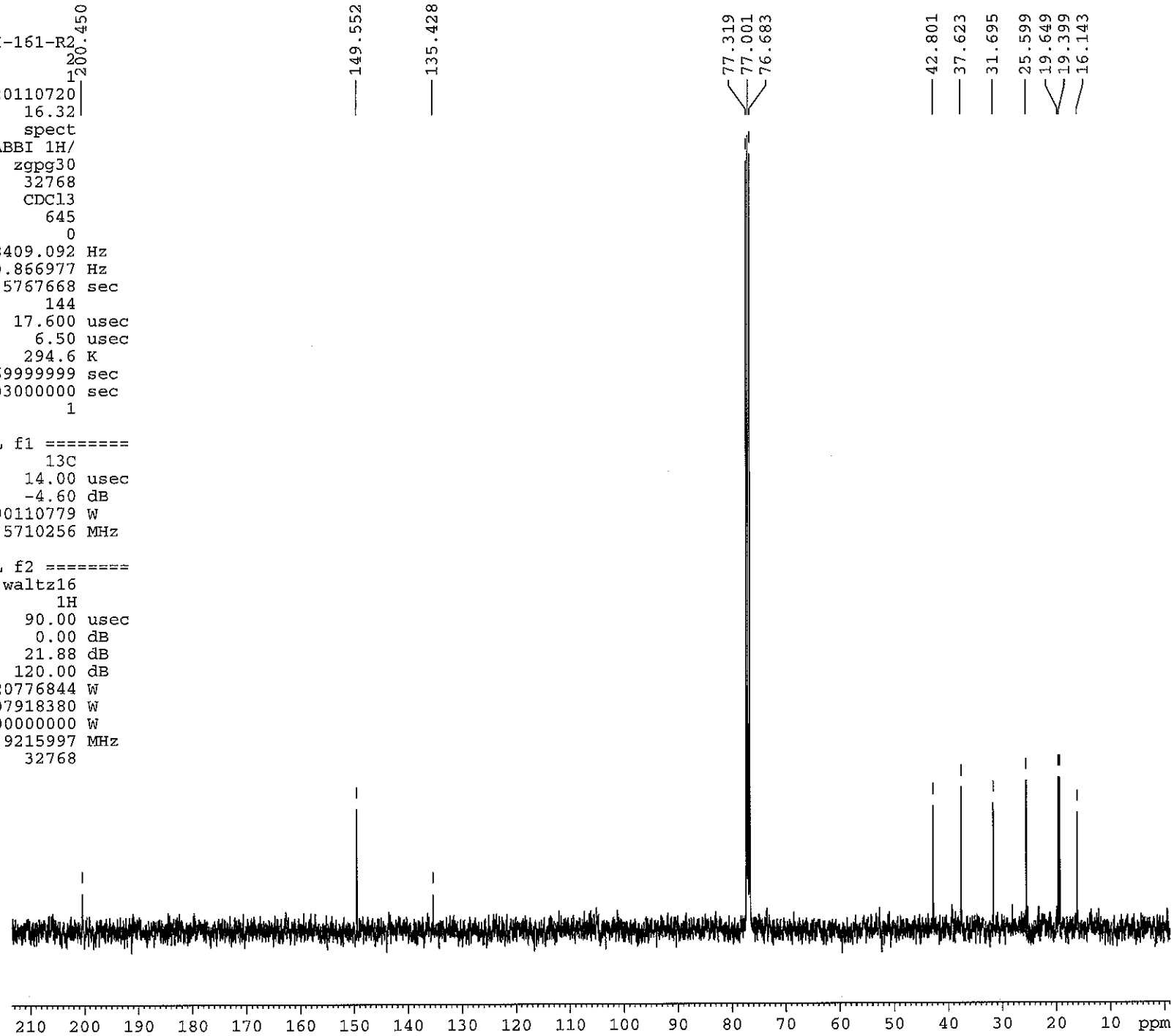

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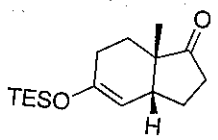
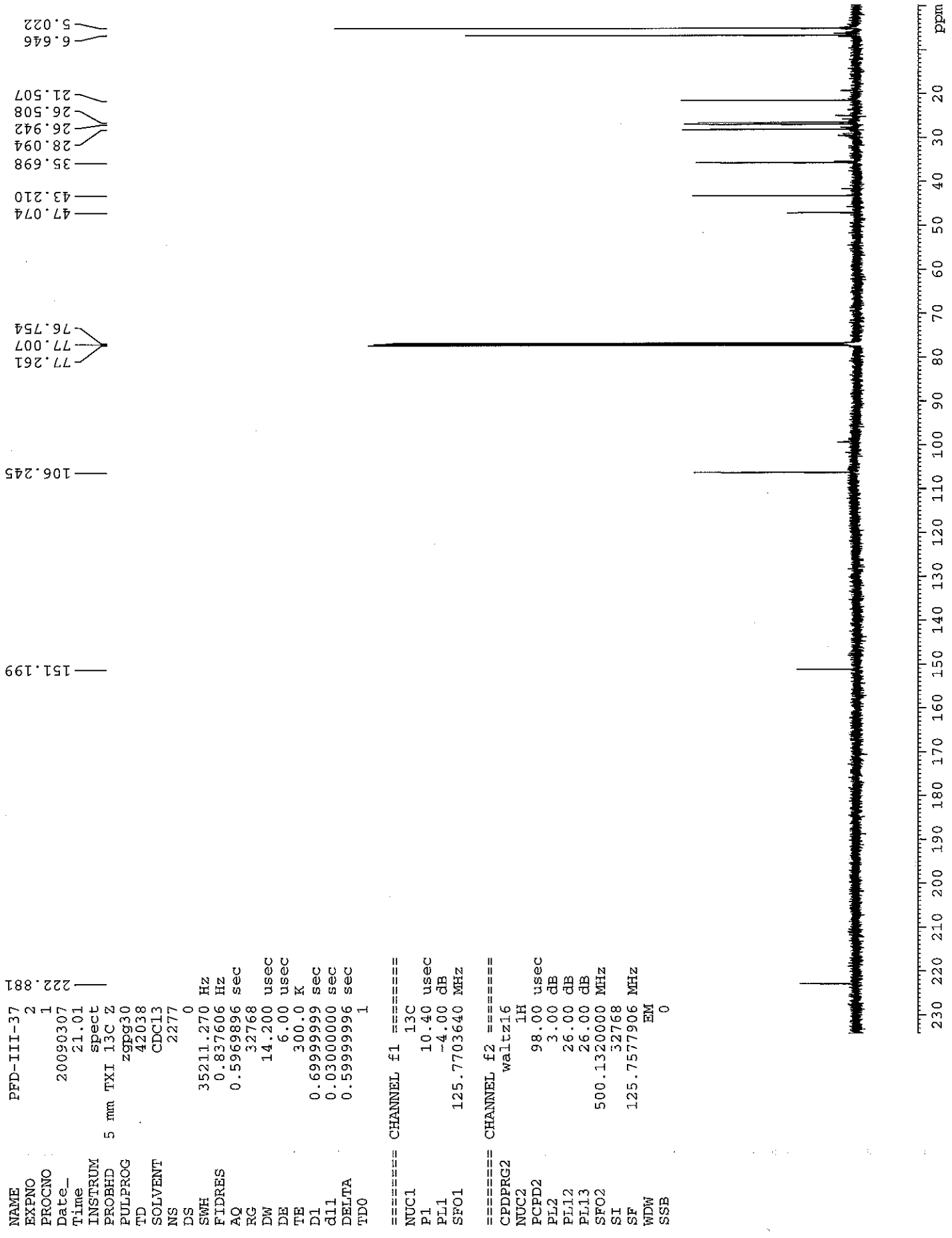
NAME	PFD-III-37
EXPNO	1
PROCNO	1
Date_	20090307
Time	20.49
INSTRUM	spect
PROBHD	5 mm TXI 13C Z
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	16
DW	83.200 usec
DE	5.50 usec
TE	300.0 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	3.00 usec
PL1	3.00 dB
SFO1	500.1325006 MHz
SI	16384
SF	500.1300126 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00






```
NAME                PFD-III-37
EXPNO                        2
PROCNO                       1
Date_                20090307
Time                    21.01
INSTRUM                  spect
PROBHD  5 mm TXI 13C Z
PULPROG                 zgpg30
TD                       42038
SOLVENT                  CDC13
NS                        2277
DS                           0
SWH                  35211.270 Hz
FIDRES                0.837606 Hz
AQ                    0.5969896 sec
RG                         32768
DW                      14.200 usec
DE                       6.00 usec
TE                      300.0 K
D1                    0.69999999 sec
d11                   0.03000000 sec
DELTA                 0.59999996 sec
TD0                          1

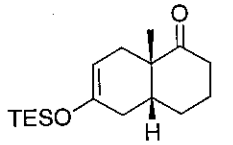
======== CHANNEL f1 ========
NUC1                        13C
P1                        10.40 usec
PL1                       -4.00 dB
SFO1                 125.7703640 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     98.00 usec
PL2                        3.00 dB
PL12                      26.00 dB
PL13                      26.00 dB
SFO2                 500.1320000 MHz
SI                         32768
SF                   125.7577906 MHz
WDW                           EM
SSB                            0
```

NAME	PFD-III-50
EXPNO	1
PROCNO	1
Date_	20090921
Time	22.49
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	299.9 K
D1	1.00000000 sec
TD0	1

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

NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200109 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



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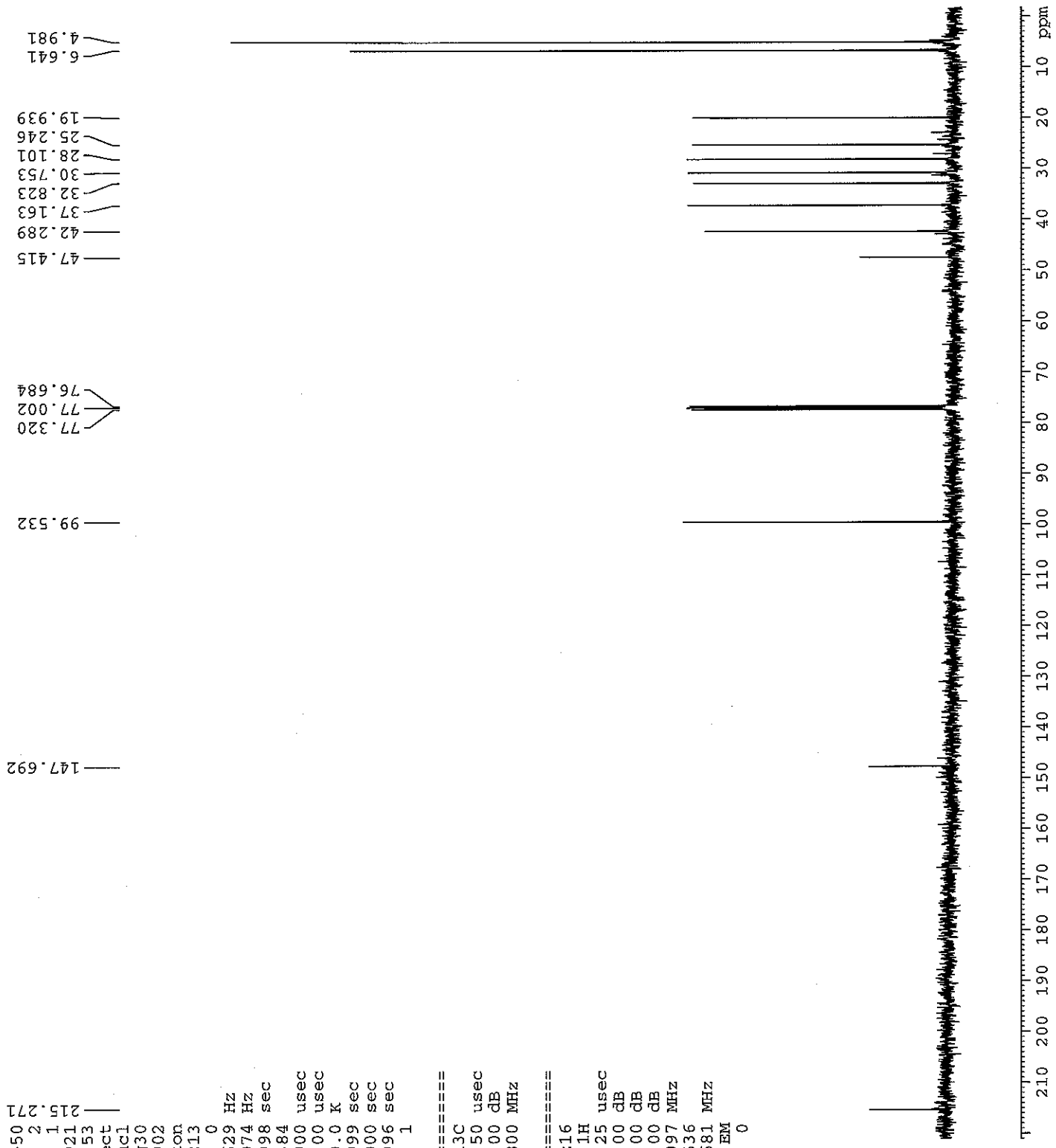
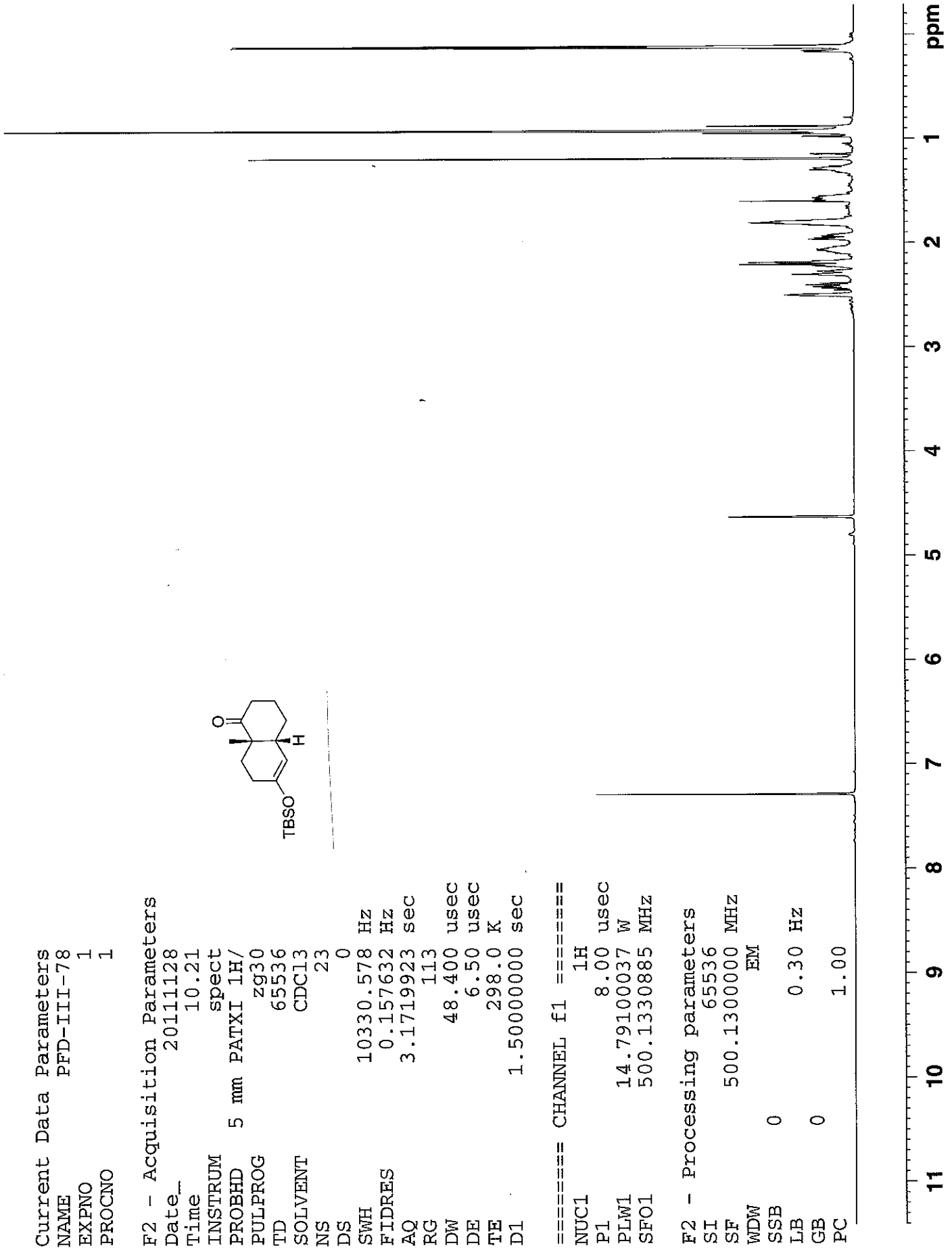



```
NAME                 PFD-III-500
EXPNO                          2
PROCNO                         1
Date_                20090921
Time                       22.53
INSTRUM                     spect
PROBHD     5 mm Multinucl
PULPROG                 zgpg30
TD                       30902
SOLVENT                 Aceton
NS                         213
DS                           0
SWH                  25125.629 Hz
FIDRES                0.813074 Hz
AQ                    0.6149998 sec
RG                         16384
DW                        19.900 usec
DE                         6.00 usec
TE                        300.0 K
D1                    0.69999999 sec
d11                   0.03000000 sec
DELTA                 0.59999996 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                         17.50 usec
PL1                        -1.00 dB
SFO1                 100.5699800 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                      96.25 usec
PL2                         0.00 dB
PL12                       23.00 dB
PL13                       23.00 dB
SFO2                 399.9215997 MHz
SI                         65536
SF                   100.5599681 MHz
WDW                           EM
SSB                            0
```


Current Data Parameters
NAME PFD-III-78
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111128
Time 10.21
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 23
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 113
DW 48.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.50000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
H
TBSO
11
10
9
8
7
6
5
4
3
2
1
ppm

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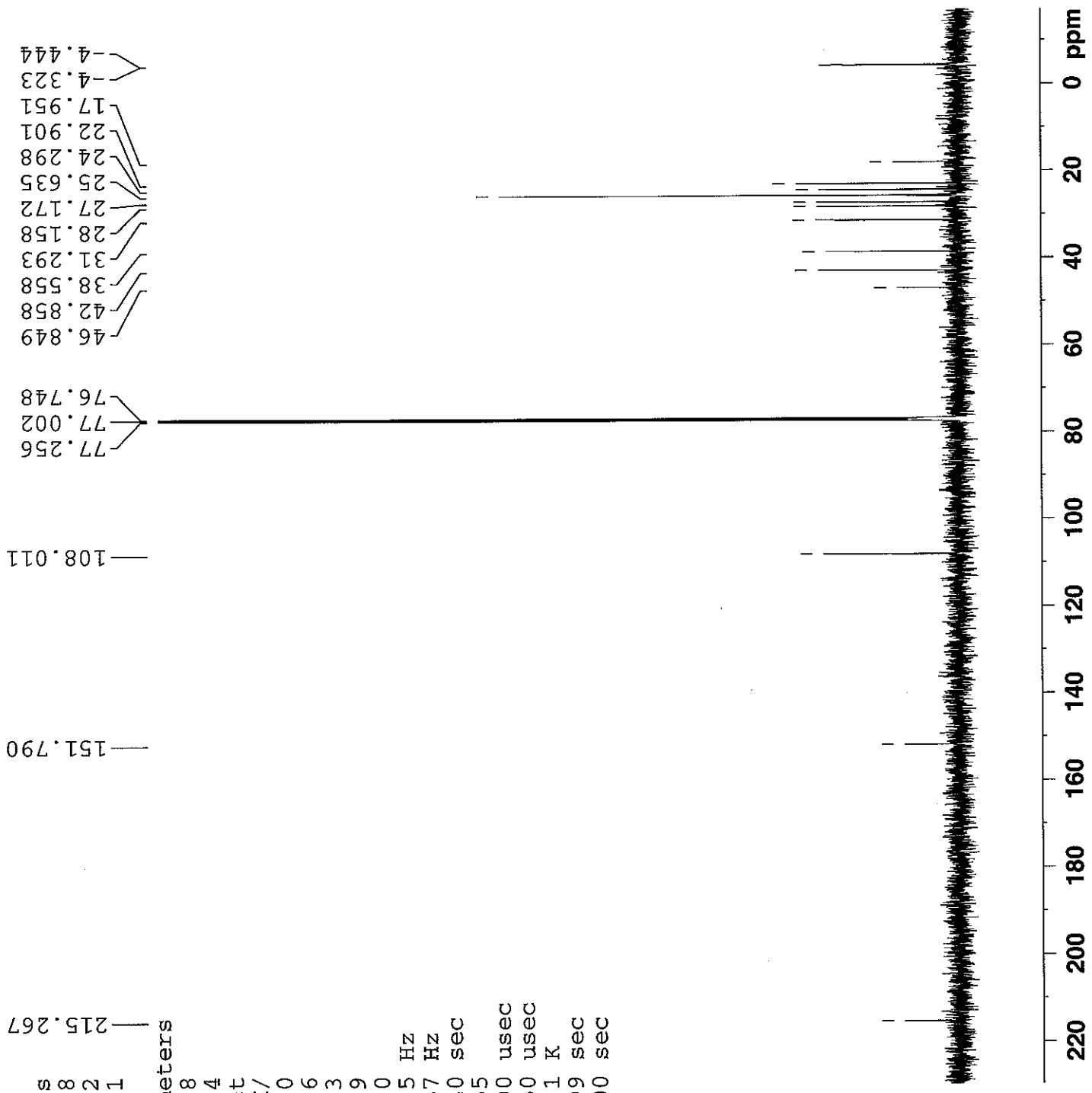
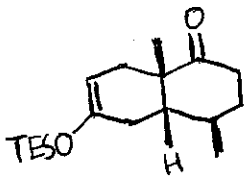



```
Current Data Parameters
NAME       PFD-III-78
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_        20111128
Time             10.24
INSTRUM          spect
PROBHD   5 mm PATXI 1H/
PULPROG         zgpg30
TD               65536
SOLVENT          CDC13
NS                 289
DS                   0
SWH          35714.285 Hz
FIDRES        0.544957 Hz
AQ            0.9175540 sec
RG                73.55
DW               14.000 usec
DE                6.50 usec
TE                298.1 K
D1            0.69999999 sec
D11           0.03000000 sec
```

NAME	PFD-III-57
EXPNO	1
PROCNO	1
Date_	20090922
Time	0.35
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200109 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



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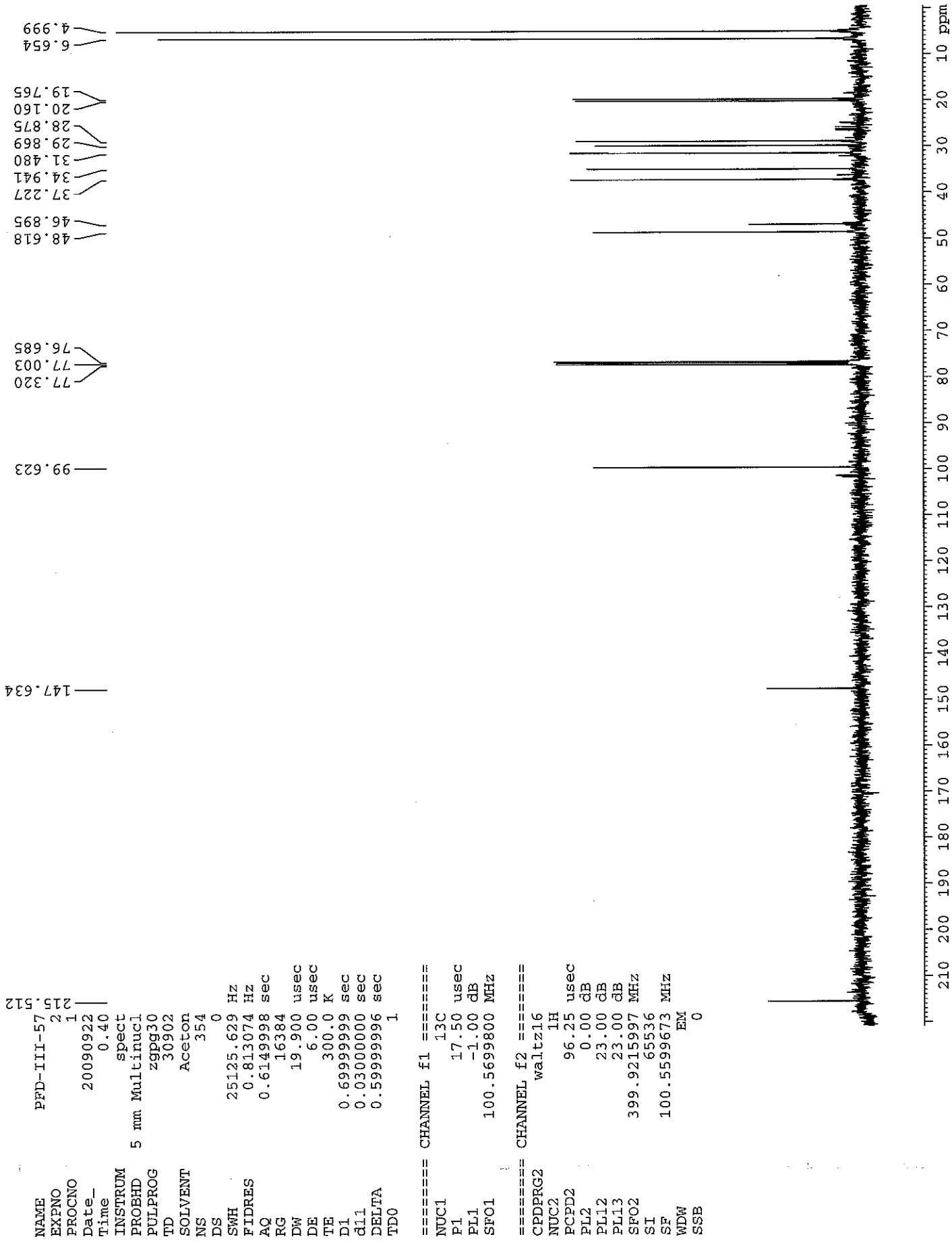


```
NAME          PFD-III-57
EXPNO                  2
PROCNO                 1
Date_           20090922
Time                0.40
INSTRUM            spect
PROBHD  5 mm Multinucl
PULPROG            zgpg30
TD                  30902
SOLVENT            Aceton
NS                     354
DS                       0
SWH             25125.629 Hz
FIDRES          0.813074 Hz
AQ              0.6149998 sec
RG                   16384
DW                19.900 usec
DE                 6.00 usec
TE                 300.0 K
D1              0.69999999 sec
d11             0.03000000 sec
DELTA           0.59999996 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                   13C
P1                 17.50 usec
PL1                -1.00 dB
SFO1          100.5699800 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2              96.25 usec
PL2                 0.00 dB
PL12               23.00 dB
PL13               23.00 dB
SFO2          399.9215997 MHz
SI                   65536
SF            100.5599673 MHz
WDW                    EM
SSB                     0
```

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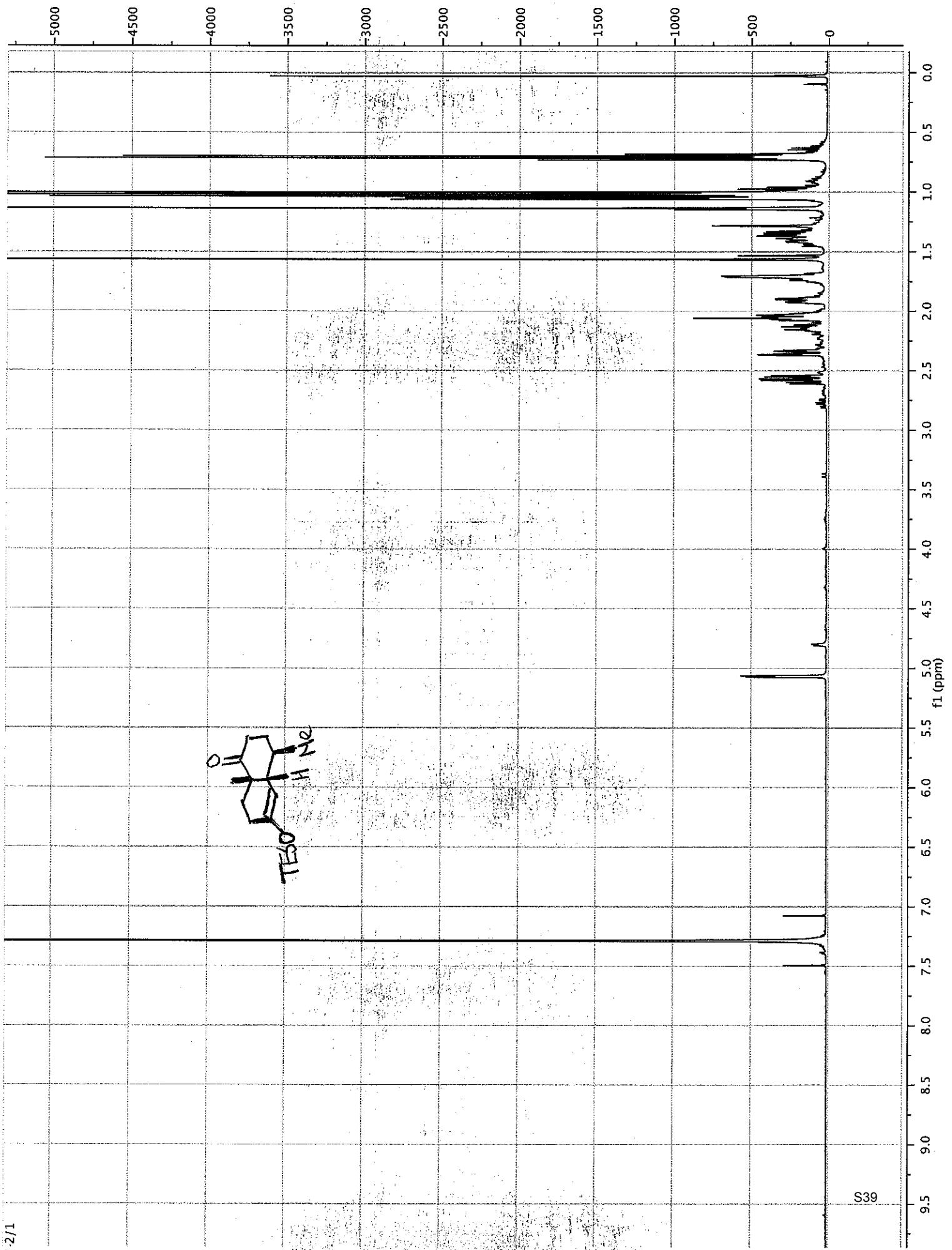

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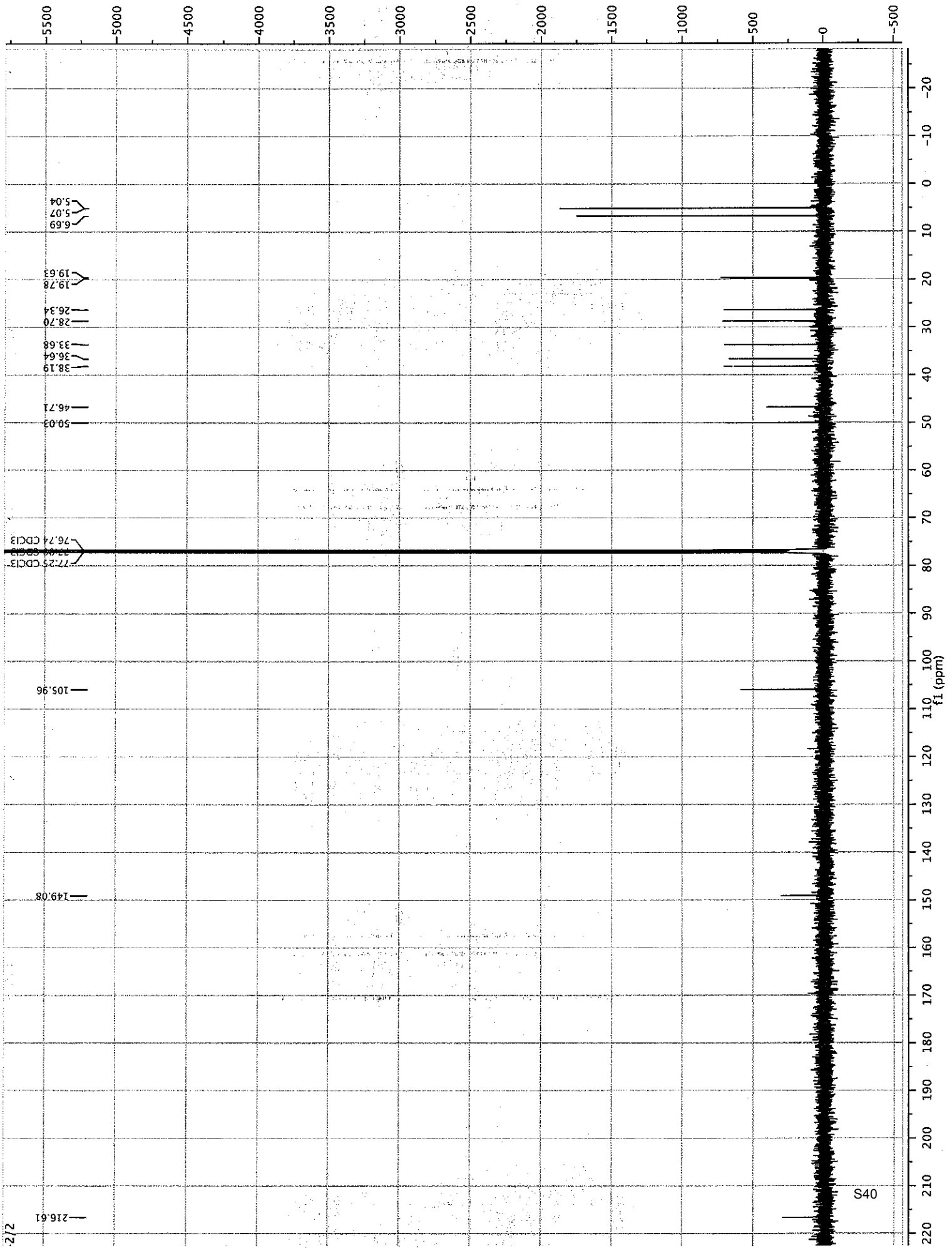

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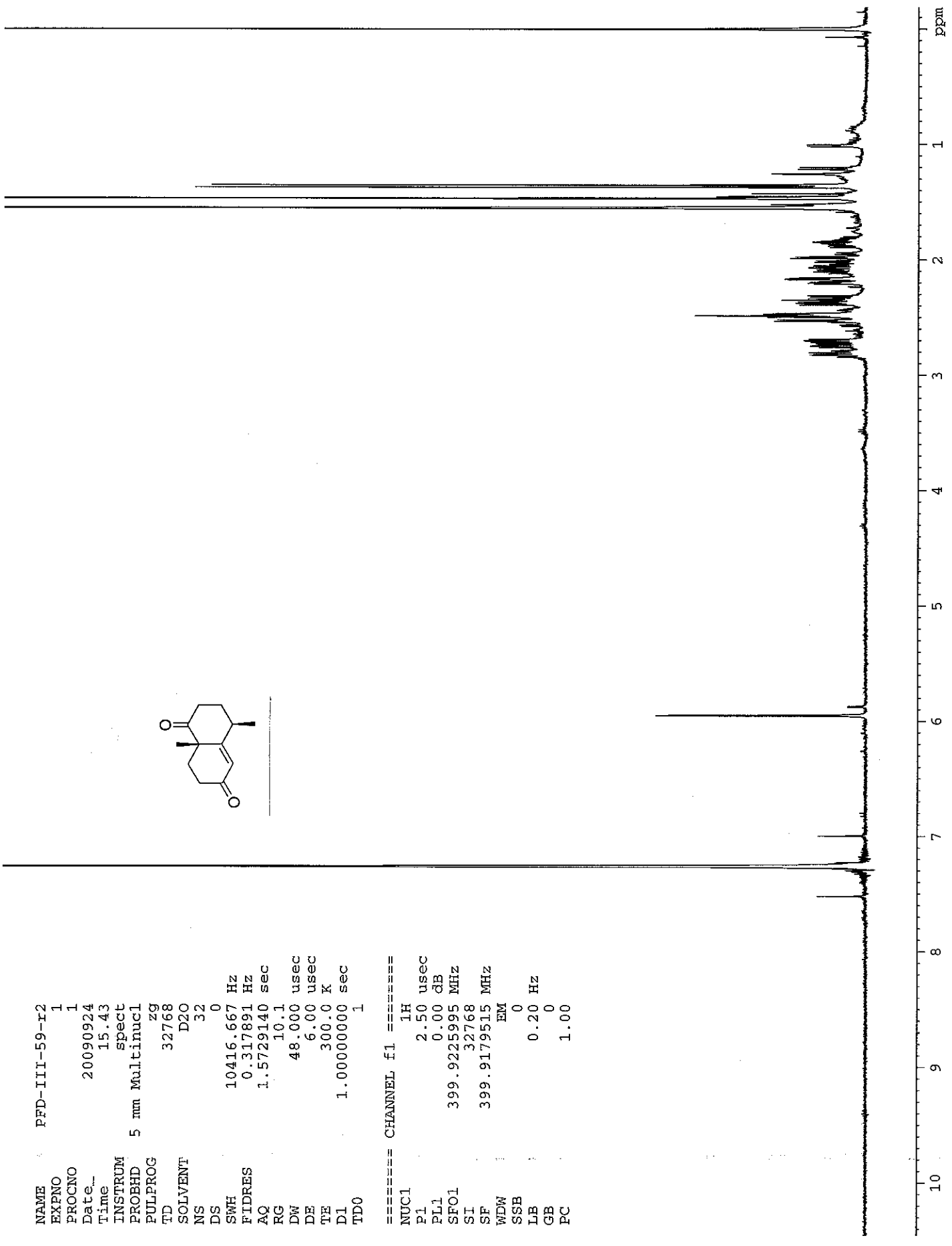

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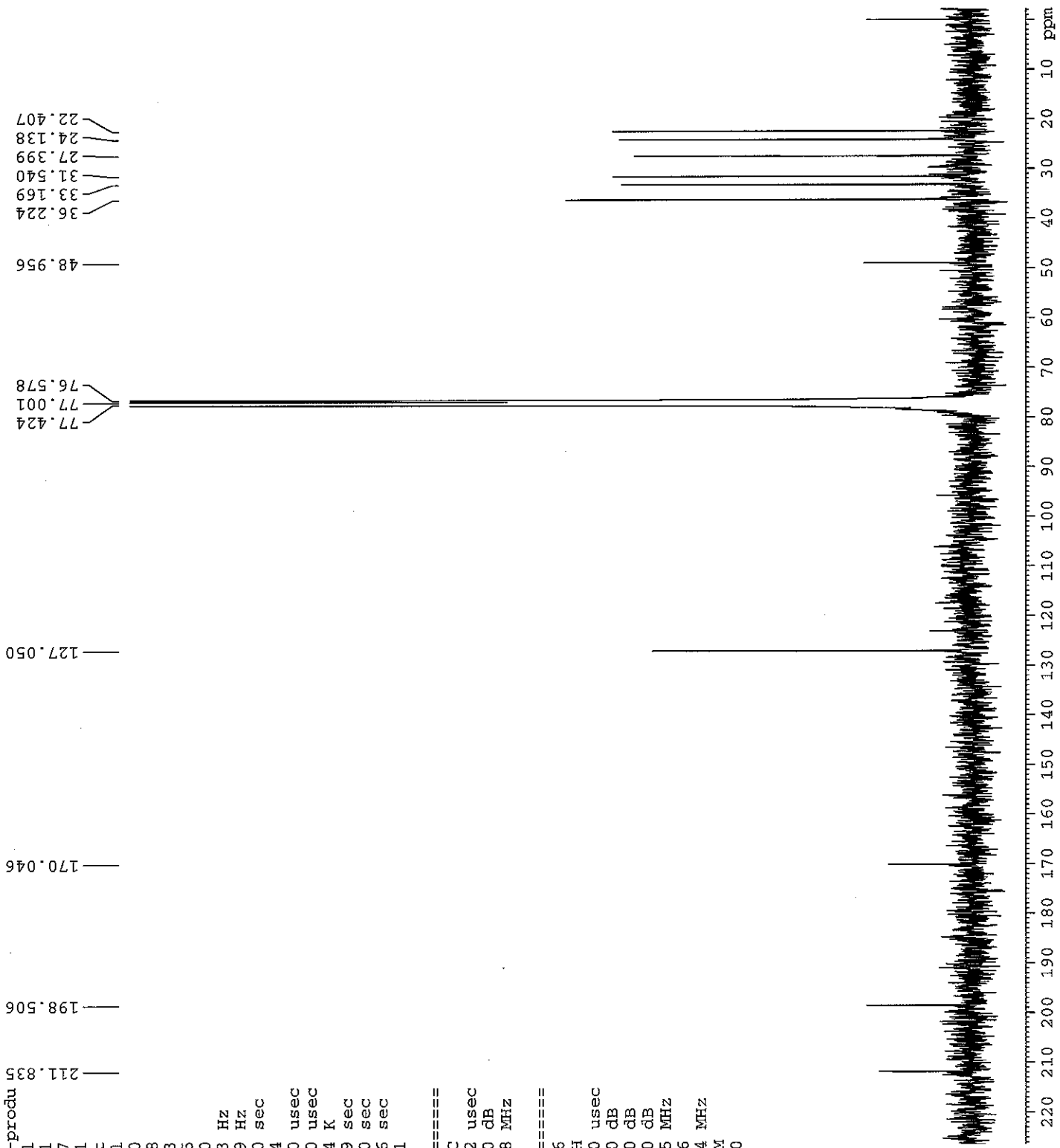
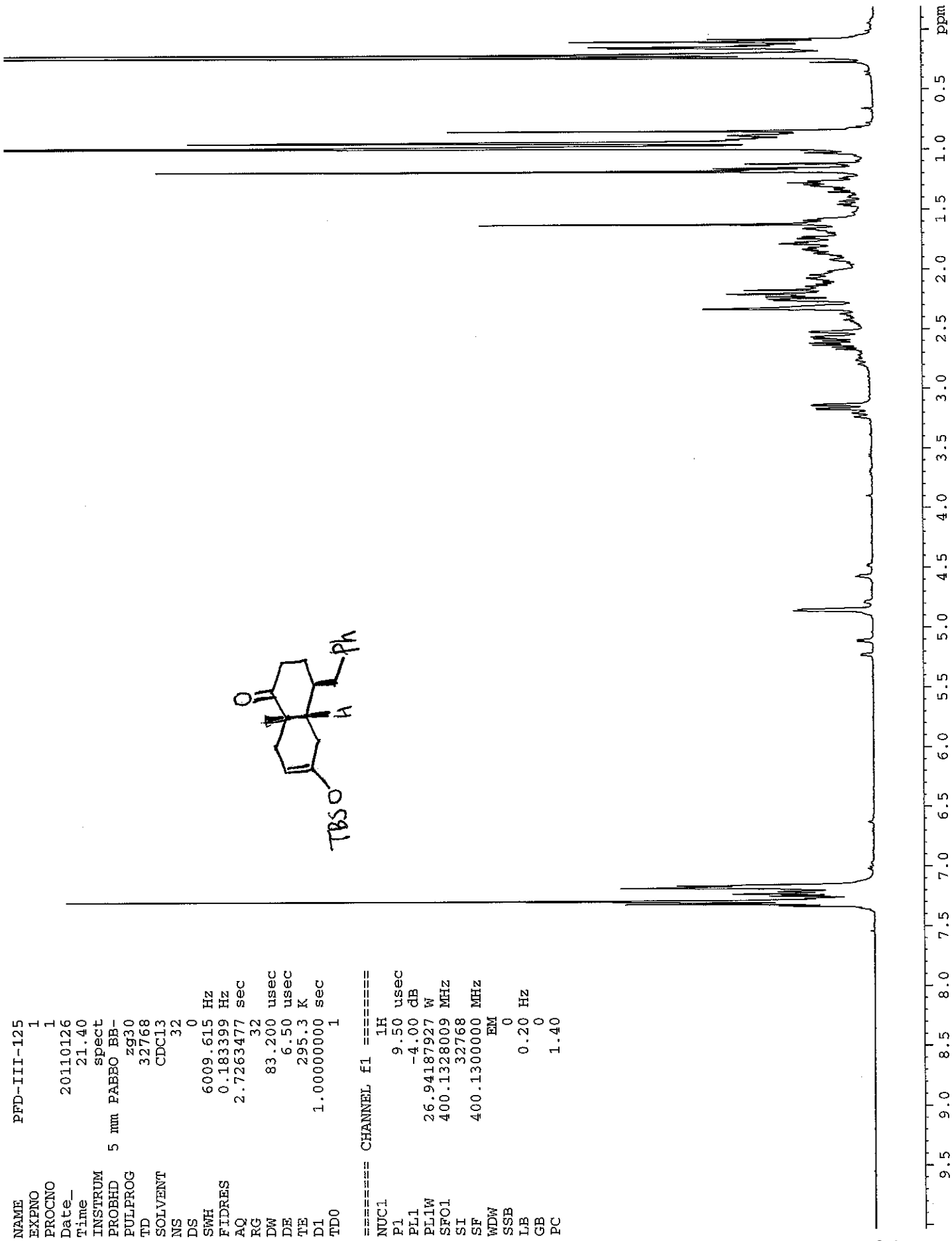
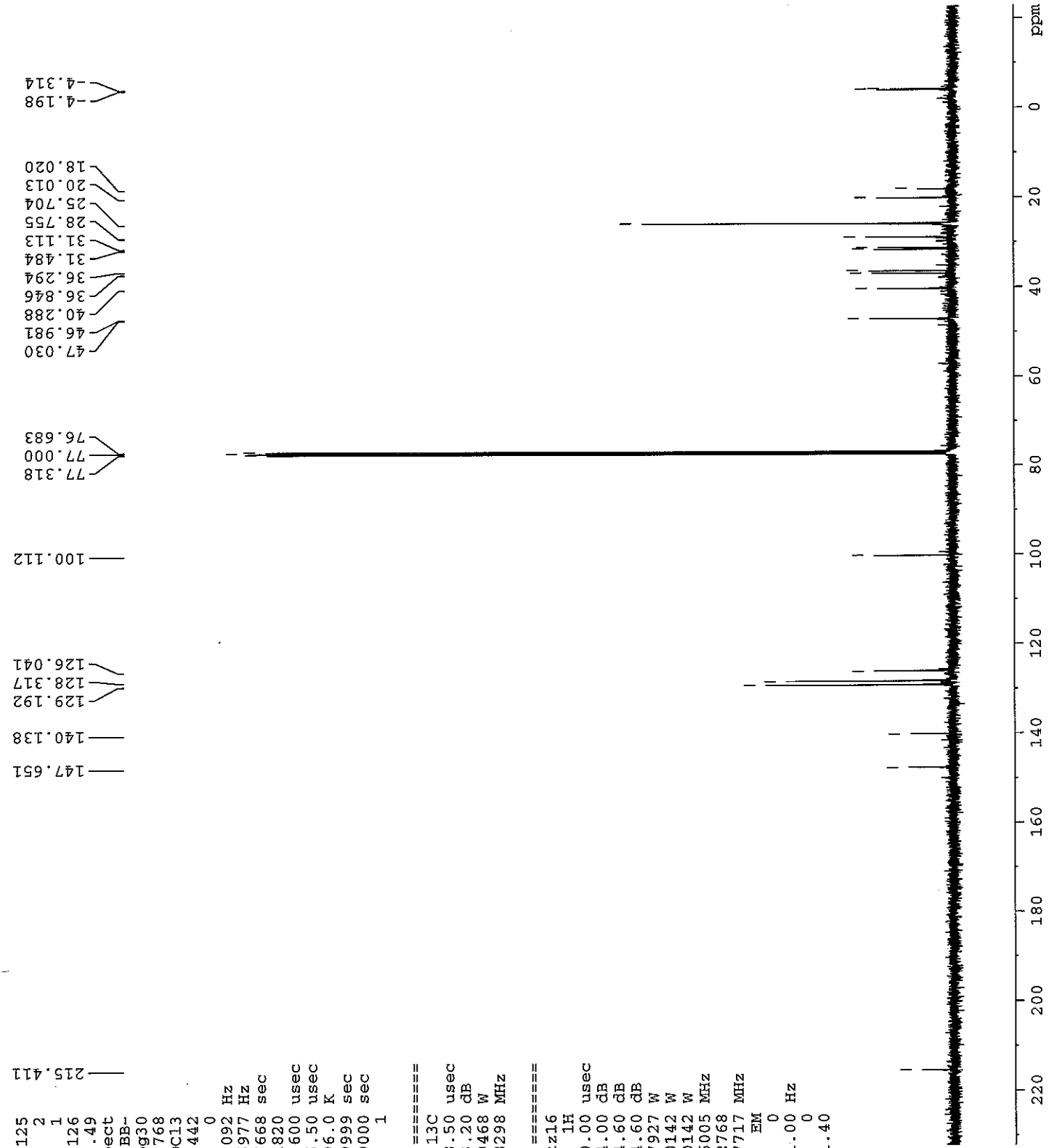



NAME PFD-III-125
EXPNO 1
PROCNO 1
Date_ 20110126
Time 21.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
TBSO
Ph
H
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm




```
NAME            PFD-III-125
EXPNO                     2
PROCNO                    1
Date_              20110126
Time                 21.49
INSTRUM              spect
PROBHD  5 mm PABBO BB-
PULPROG             zgpg30
TD                   32768
SOLVENT              CDC13
NS                     442
DS                       0
SWH              28409.092 Hz
FIDRES               0.866977 Hz
AQ                   0.576766 sec
RG                      1820
DW                     17.600 usec
DE                      6.50 usec
TE                     296.0 K
D1                   0.69999999 sec
D11                  0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                    3.20 dB
PL1W            49.53329468 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                    -4.00 dB
PL12                   14.60 dB
PL13                   14.60 dB
PL2W            26.94187927 W
PL12W            0.37190142 W
PL13W            0.37190142 W
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127717 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

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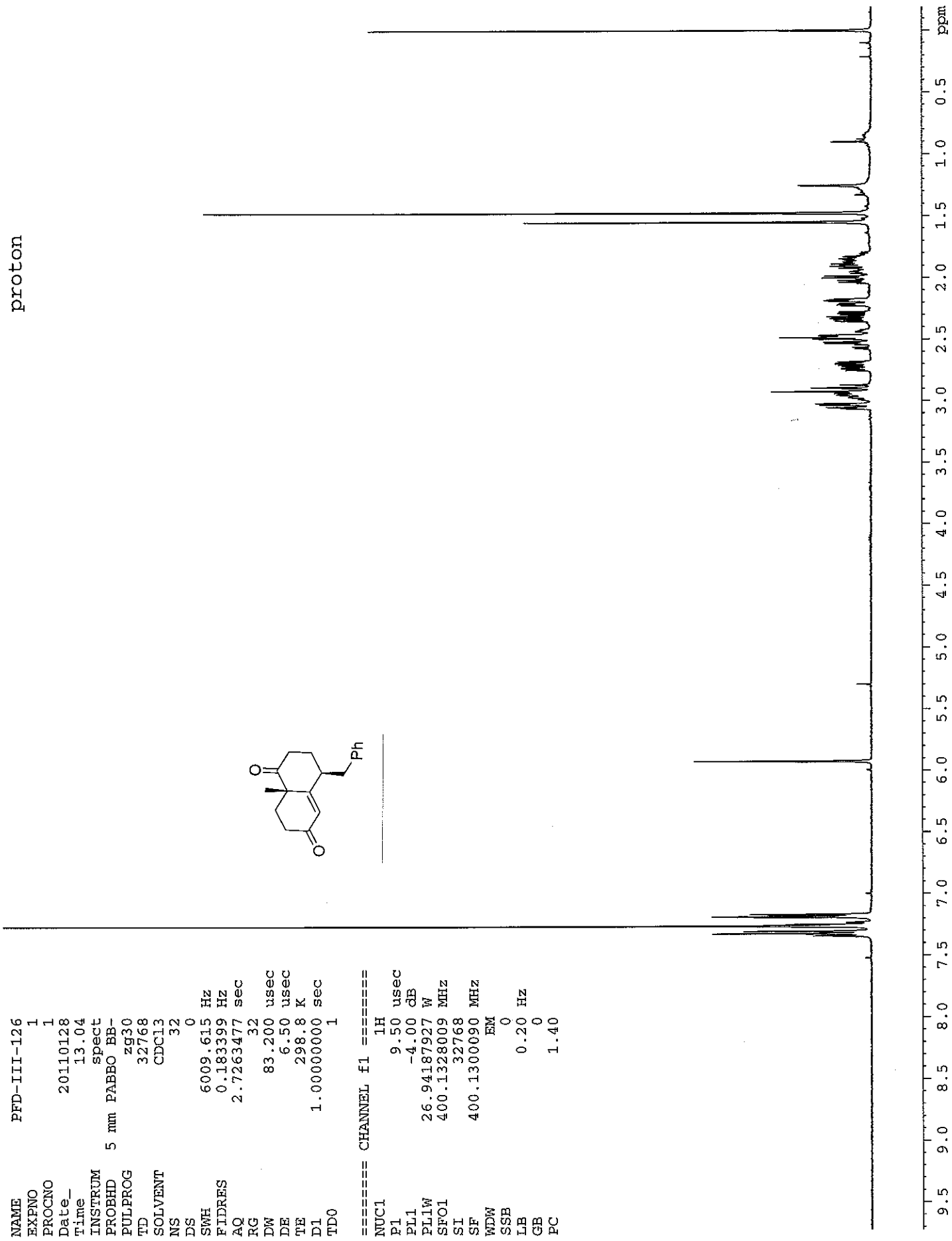

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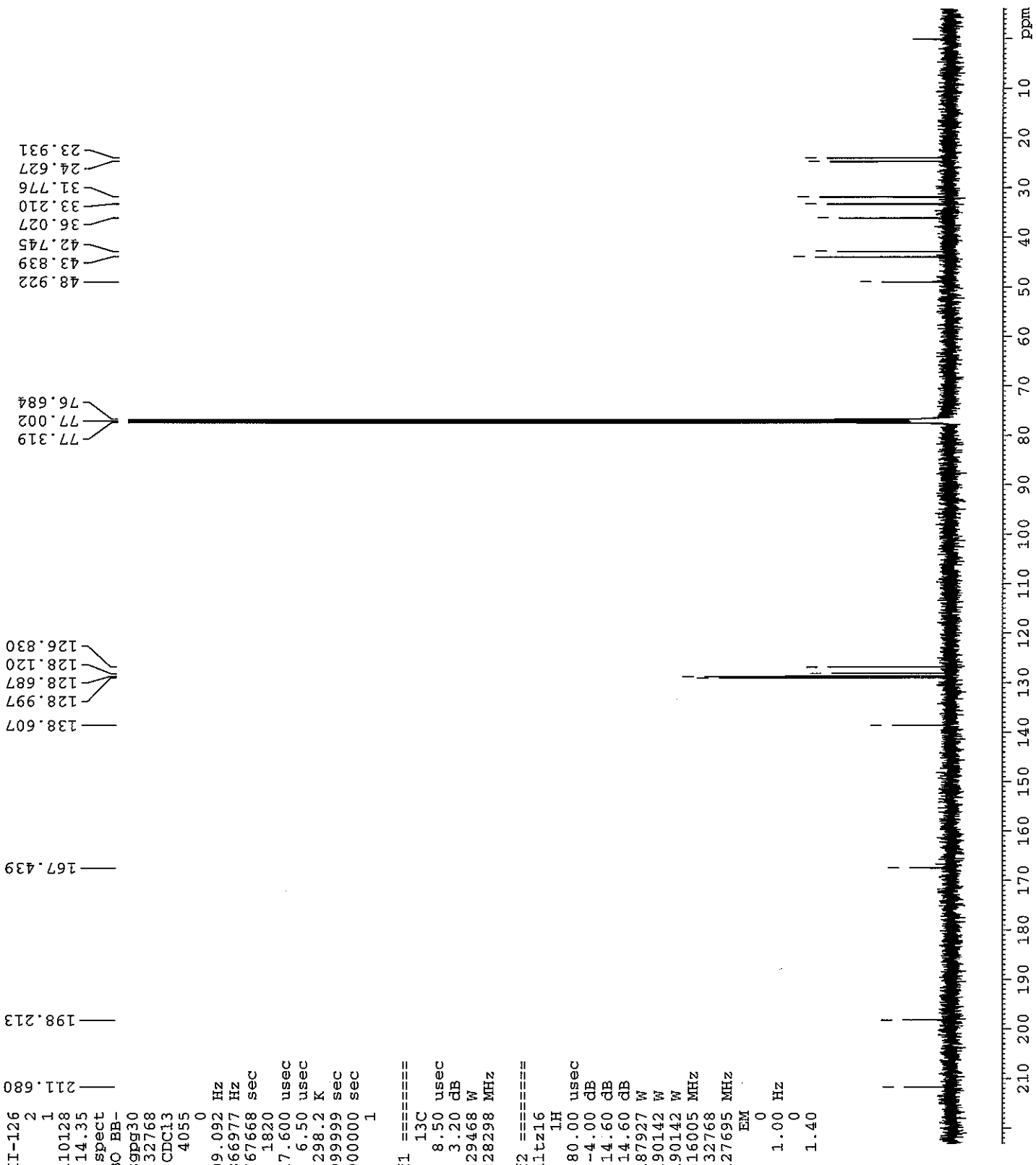


```
NAME                 PFD-III-126
EXPNO                          2
PROCNO                         1
Date_                   20110128
Time                       14.35
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                   zgpg30
TD                         32768
SOLVENT                   CDCl3
NS                          4055
DS                             0
SWH                    28409.092 Hz
FIDRES                     0.866977 Hz
AQ                         0.576766 sec
RG                          1820
DW                        17.600 usec
DE                         6.50 usec
TE                         298.2 K
D1                     0.69999999 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                          8.50 usec
PL1                         3.20 dB
PL1W                   49.53329468 W
SFO1                   100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                         1H
PCPD2                      80.00 usec
PL2                        -4.00 dB
PL12                       14.60 dB
PL13                       14.60 dB
PL2W                   26.94187927 W
PL12W                   0.37190142 W
PL13W                   0.37190142 W
SFO2                   400.1316005 MHz
SI                         32768
SF                     100.6127695 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

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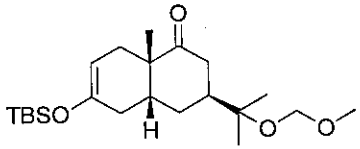
NAME	PFD-III-111-R2
EXPNO	1
PROCNO	1
Date_	20110126
Time	21.21
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	32
DW	83.200 usec
DE	6.50 usec
TE	295.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300091 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



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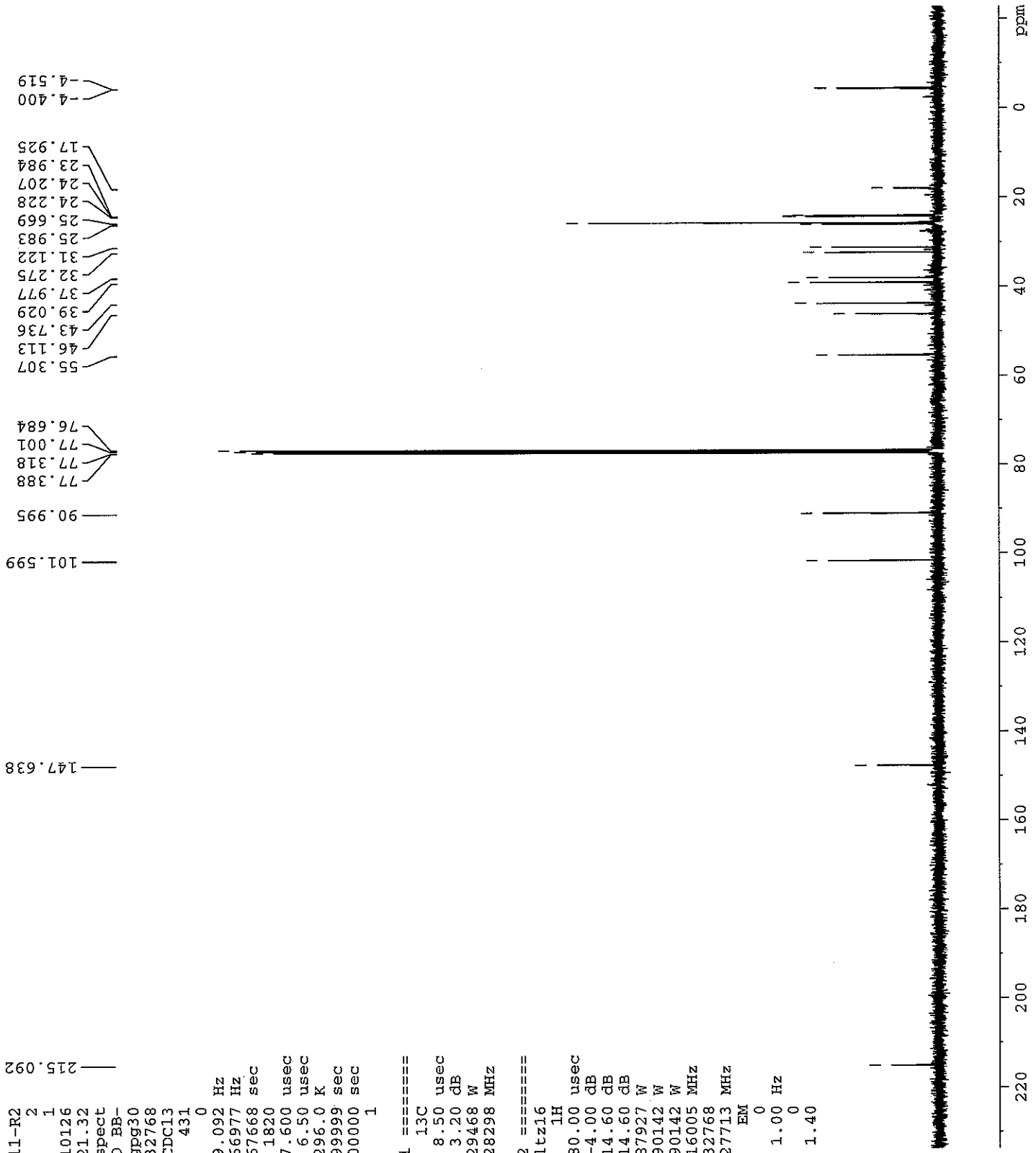
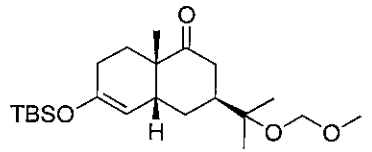



```
NAME          PFD-III-111-R2
EXPNO                      2
PROCNO                     1
Date_               20110126
Time                   21.32
INSTRUM                spect
PROBHD  5 mm PABBO BB-
PULPROG                zgpg30
TD                      32768
SOLVENT                CDC13
NS                       431
DS                         0
SWH                28409.092 Hz
FIDRES             0.866977 Hz
AQ                 0.5767668 sec
RG                      1820
DW                    17.600 usec
DE                     6.50 usec
TE                    296.0 K
D1                 0.69999999 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     8.50 usec
PL1                    3.20 dB
PL1W               49.53329468 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 80.00 usec
PL2                    -4.00 dB
PL12                   14.60 dB
PL13                   14.60 dB
PL2W               26.94187927 W
PL12W              0.37190142 W
PL13W              0.37190142 W
SFO2               400.1316005 MHz
SI                      32768
SF                 100.6127713 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                         0
PC                     1.40
```

NAME	PFD-III-111-R2
EXPNO	1
PROCNO	1
Date_	20110127
Time	14.13
INSTRUM	spect
PROBHD	5 mm PABBI 1H/
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	25
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	28.5
DW	83.200 usec
DE	6.50 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	7.25 usec
PL1	0.00 dB
PL1W	12.20776844 W
SFO1	399.9225995 MHz
SI	32768
SF	399.9200114 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



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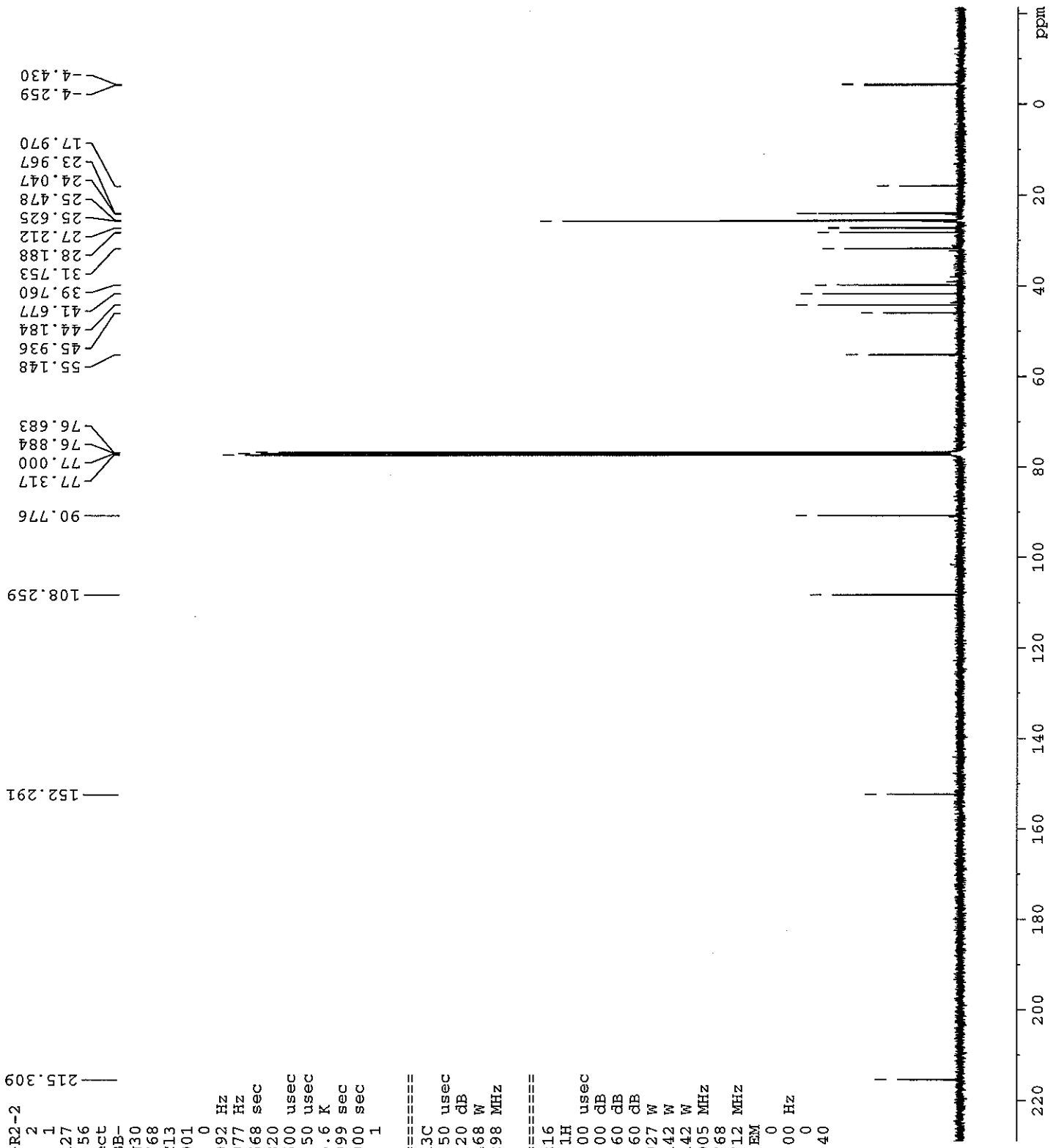


```
NAME                PFD-III-111-R2-2
EXPNO                             2
PROCNO                            1
Date_                      20110127
Time                          16.56
INSTRUM                       spect
PROBHD     5 mm PABBO BB-
PULPROG                    zgpg30
TD                          32768
SOLVENT                     CDCl3
NS                           1001
DS                              0
SWH                  28409.092 Hz
FIDRES                0.866977 Hz
AQ                    0.576766 sec
RG                          1820
DW                     17.600 usec
DE                      6.50 usec
TE                      295.6 K
D1                   0.69999999 sec
D11                  0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                         13C
P1                          8.50 usec
PL1                         3.20 dB
PL1W                 49.53329468 W
SFO1                 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                   80.00 usec
PL2                        -4.00 dB
PL12                       14.60 dB
PL13                       14.60 dB
PL2W                 26.94187927 W
PL12W                 0.37190142 W
PL13W                 0.37190142 W
SFO2                 400.1316005 MHz
SI                          32768
SF                   100.6127712 MHz
WDW                            EM
SSB                             0
LB                       1.00 Hz
GB                              0
PC                           1.40
```

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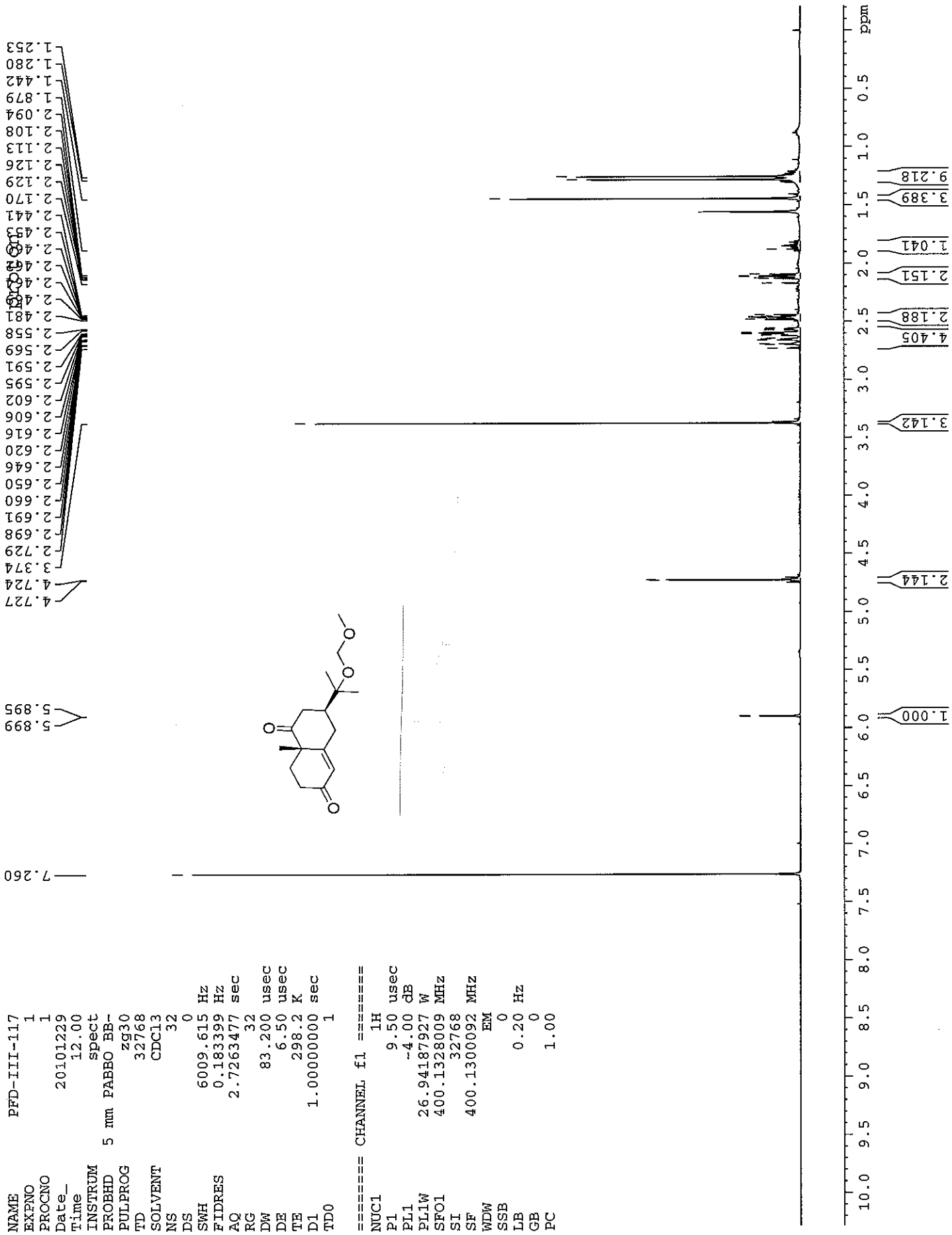
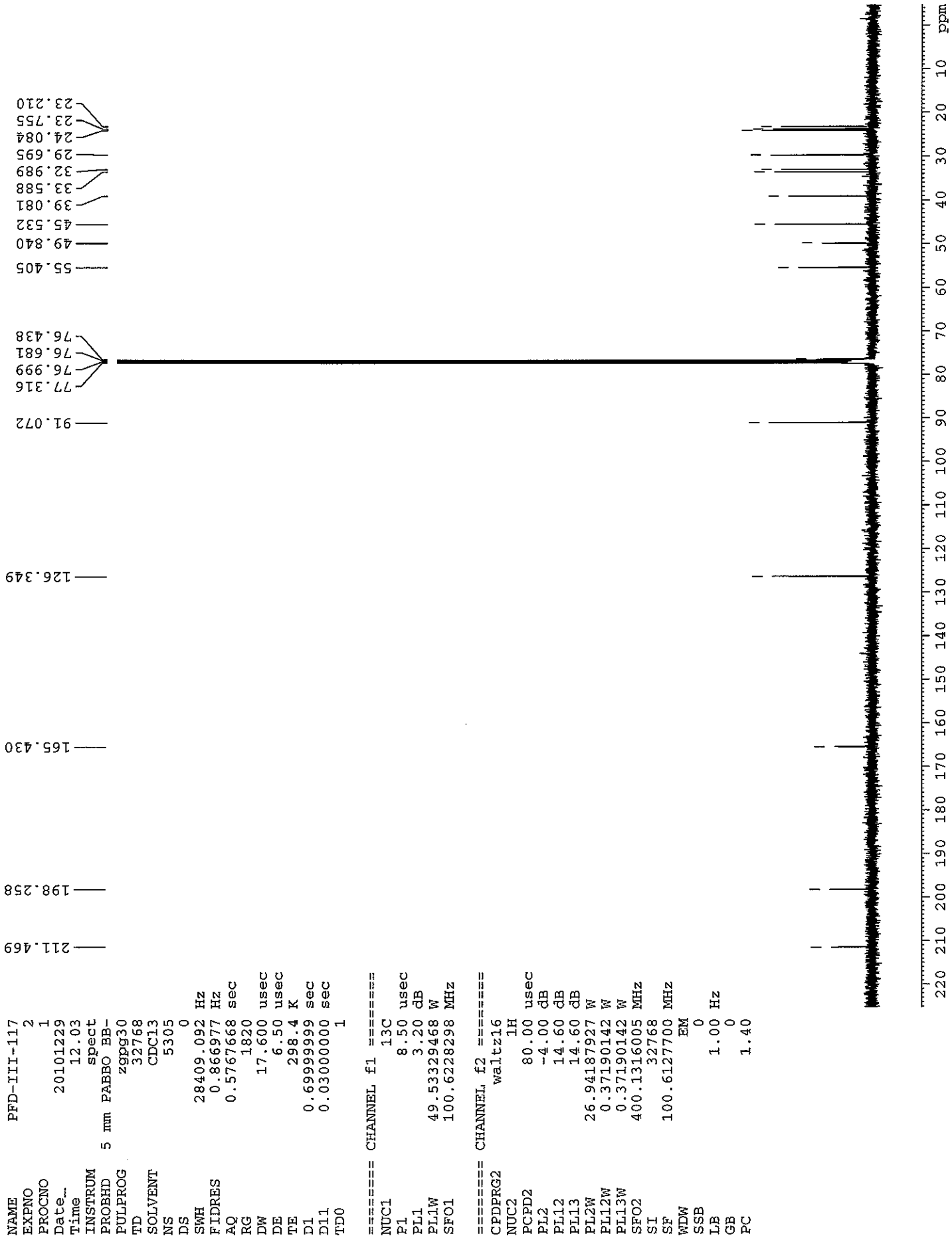
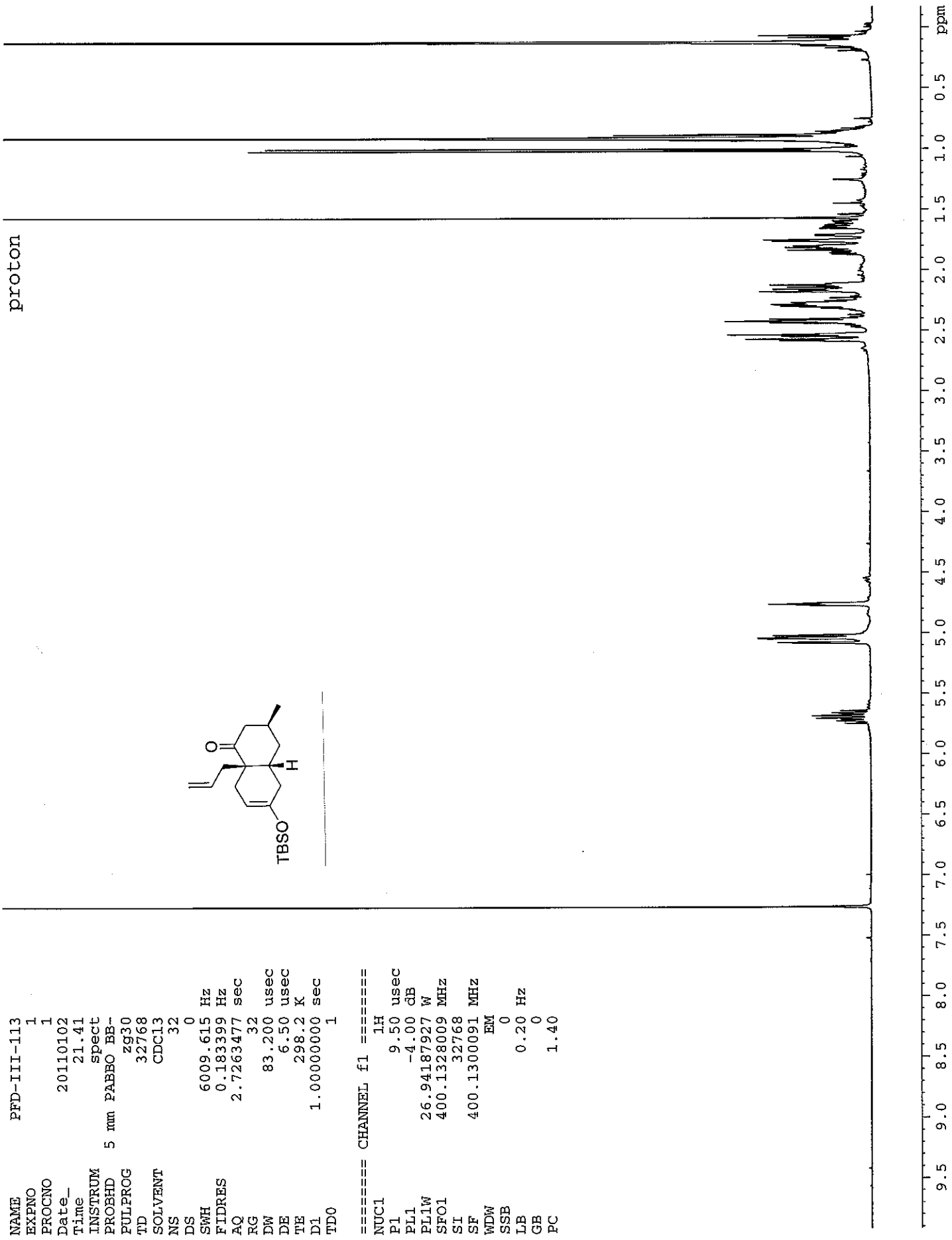





```
NAME                 PFD-III-117
EXPNO                          2
PROCNO                         1
Date_                20101229
Time                       12.03
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       32768
SOLVENT                  CDCl3
NS                            0
DS                         5305
SWH                28409.092 Hz
FIDRES              0.866977 Hz
AQ                  0.5767668 sec
RG                          1820
DW                        17.600 usec
DE                         6.50 usec
TE                       298.4 K
D1                  0.69999999 sec
D11                 0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                        13C
P1                         8.50 usec
PL1                        3.20 dB
PL1W               49.53329468 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                       -4.00 dB
PL12                      14.60 dB
PL13                      14.60 dB
PL2W               26.94187927 W
PL12W               0.37190142 W
PL13W               0.37190142 W
SFO2               400.1316005 MHz
SI                       32768
SF                 100.6127700 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```


proton
NAME PFD-III-113
EXPNO 1
PROCNO 1
Date_ 20110102
Time 21.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
O
H
TBSO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

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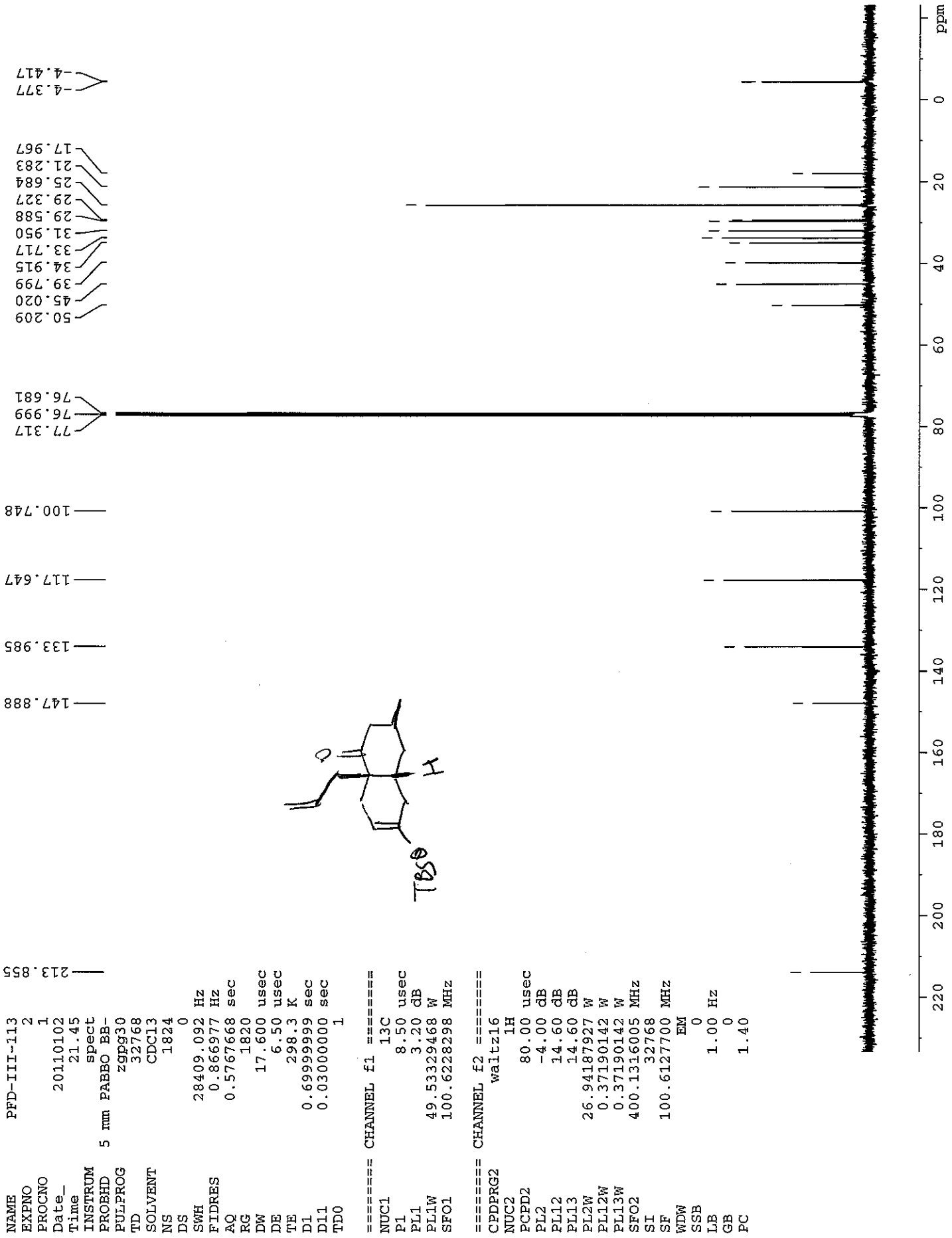



```
NAME                 PFD-III-113
EXPNO                          2
PROCNO                         1
Date_                   20110102
Time                       21.45
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                         32768
SOLVENT                  CDC13
NS                          1824
DS                             0
SWH                    28409.092 Hz
FIDRES                     0.866977 Hz
AQ                         0.5767668 sec
RG                          1820
DW                         17.600 usec
DE                          6.50 usec
TE                         298.3 K
D1                         0.69999999 sec
D11                        0.03000000 sec
TD0                            1

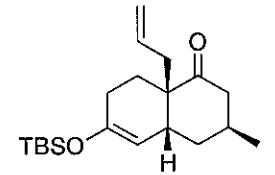
======== CHANNEL f1 ========
NUC1                         13C
P1                          8.50 usec
PL1                         3.20 dB
PL1W                   49.53329468 W
SFO1                   100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                         1H
PCPD2                      80.00 usec
PL2                        -4.00 dB
PL12                       14.60 dB
PL13                       14.60 dB
PL2W                   26.94187927 W
PL12W                   0.37190142 W
PL13W                   0.37190142 W
SFO2                   400.1316005 MHz
SI                         32768
SF                     100.6127700 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

NAME	PFD-III-113-R2
EXPNO	1
PROCNO	1
Date_	20110105
Time	20.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	32
DW	83.200 usec
DE	6.50 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

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

NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300090 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



proton

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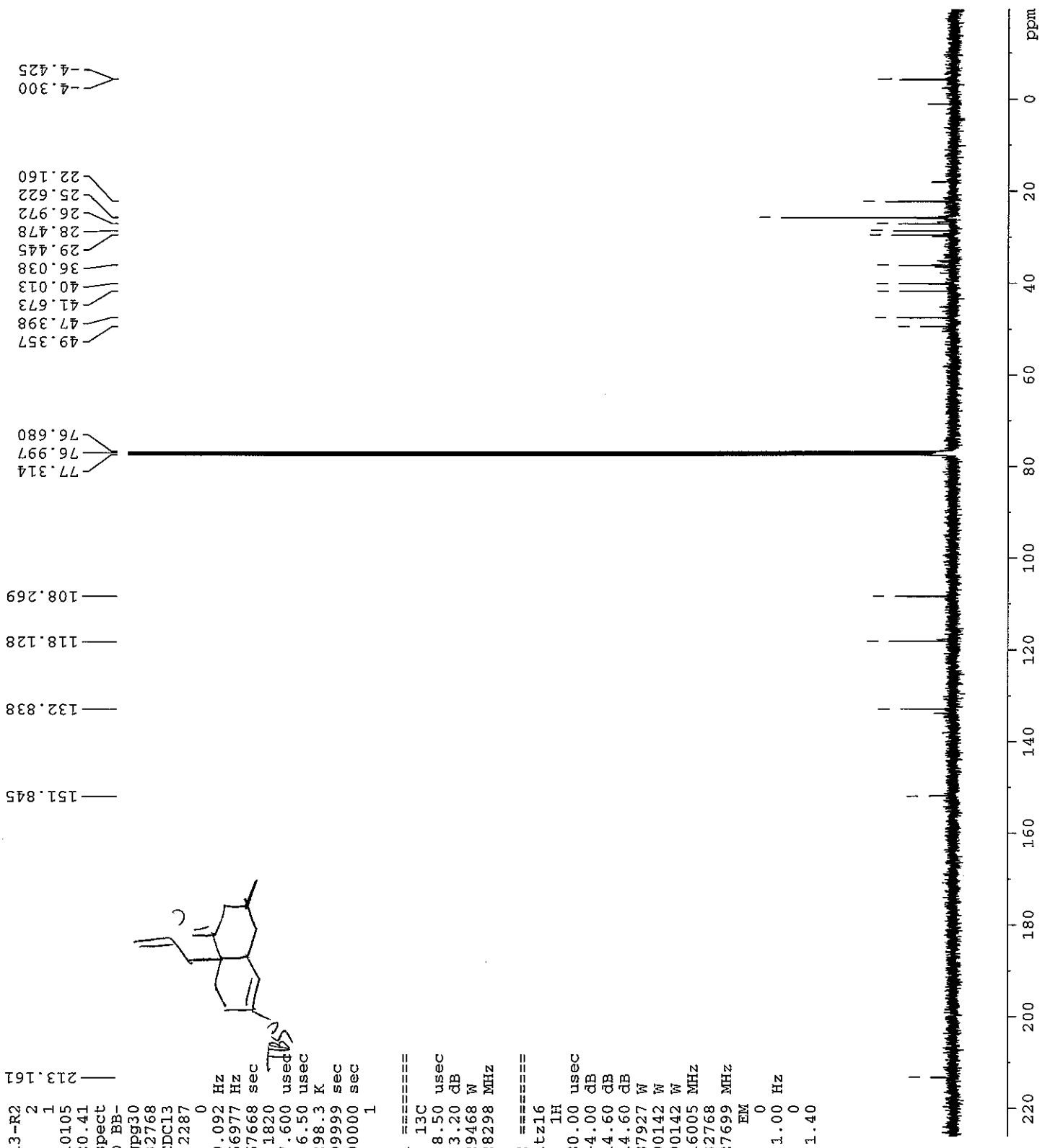


```
NAME          PFD-III-113-R2
EXPNO                      2
PROCNO                     1
Date_               20110105
Time                   20.41
INSTRUM                spect
PROBHD  5 mm PABBO BB-
PULPROG             zgpg30
TD                   32768
SOLVENT              CDC13
NS                    2287
DS                       0
SWH             28409.092 Hz
FIDRES              0.866977 Hz
AQ                0.5767668 sec
RG                     1820
DW                17.600 usec
DE                 6.50 usec
TE                   298.3 K
D1              0.69999999 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.50 usec
PL1                 3.20 dB
PL1W           49.53329468 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2              80.00 usec
PL2                -4.00 dB
PL12               14.60 dB
PL13               14.60 dB
PL2W           26.94187927 W
PL12W           0.37190142 W
PL13W           0.37190142 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127699 MHz
WDW                     EM
SSB                      0
LB                1.00 Hz
GB                       0
PC                    1.40
```

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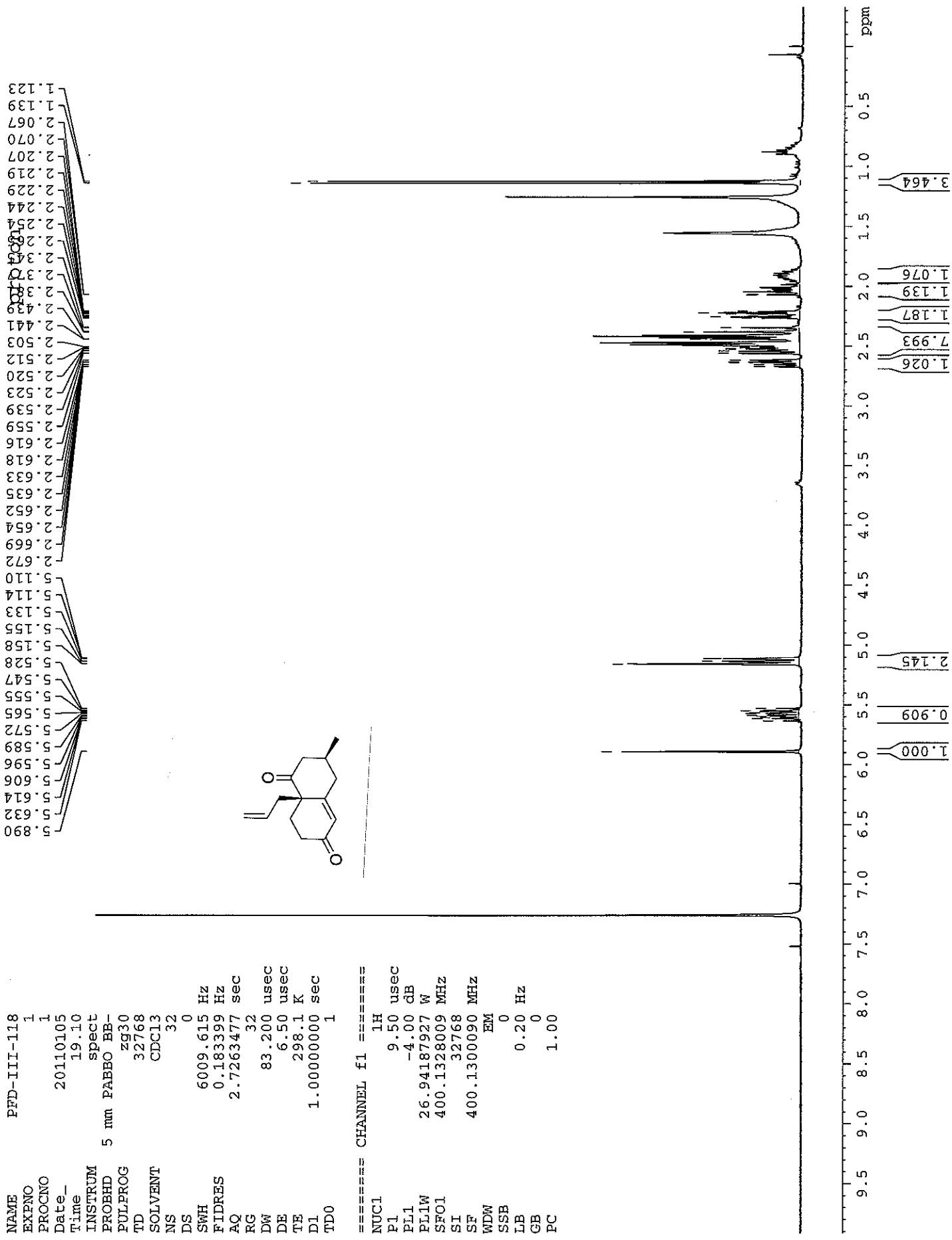

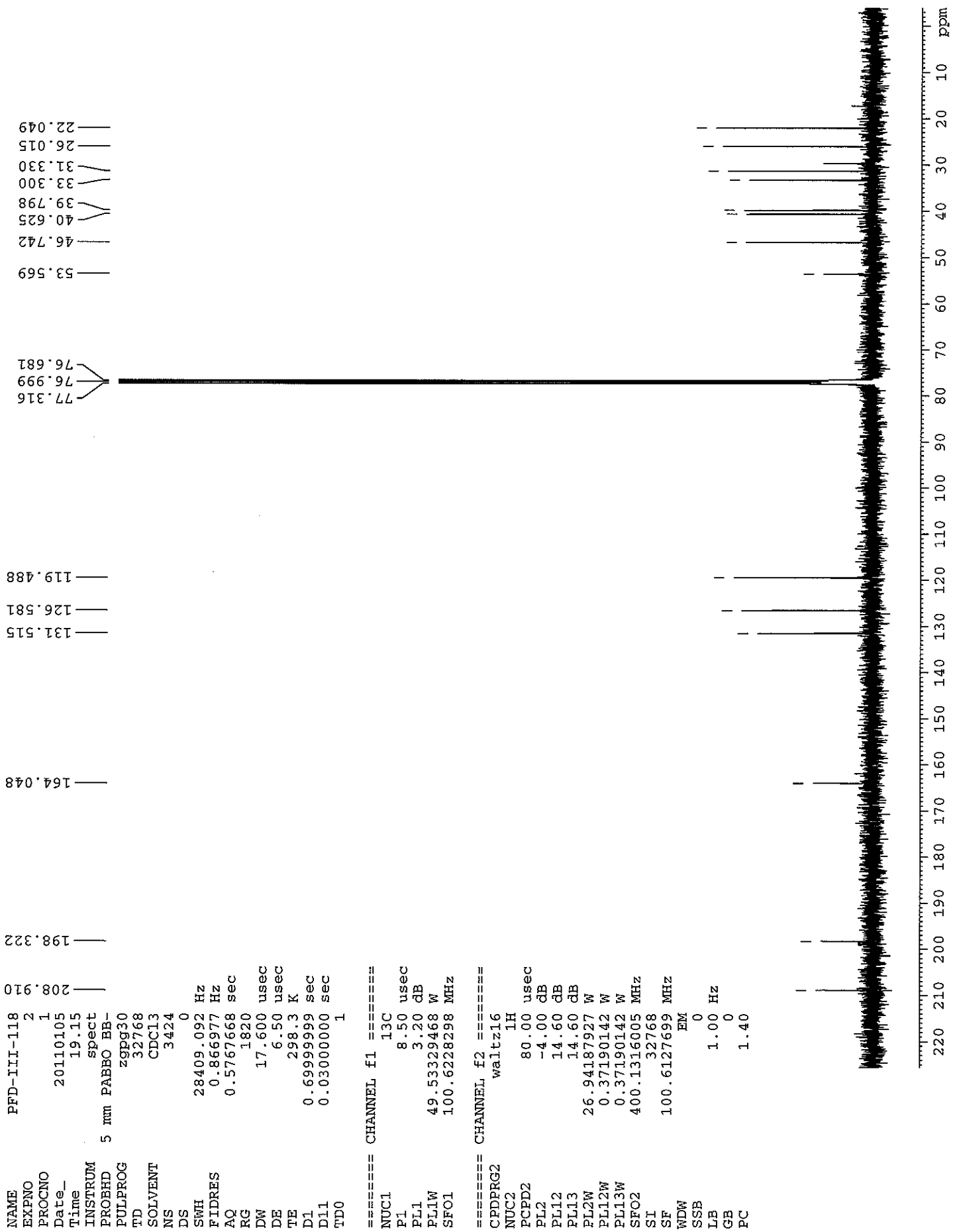
NAME PFD-III-118
EXPNO 2
PROCNO 1
Date_ 20110105
Time 19.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDC13
NS 3424
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 298.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127699 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
208.910
198.322
164.048
131.515
126.581
119.488
77.316
76.999
76.681
53.569
46.742
40.625
39.798
33.300
31.330
26.015
22.049
ppm

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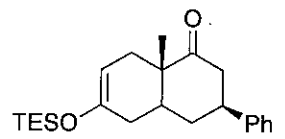
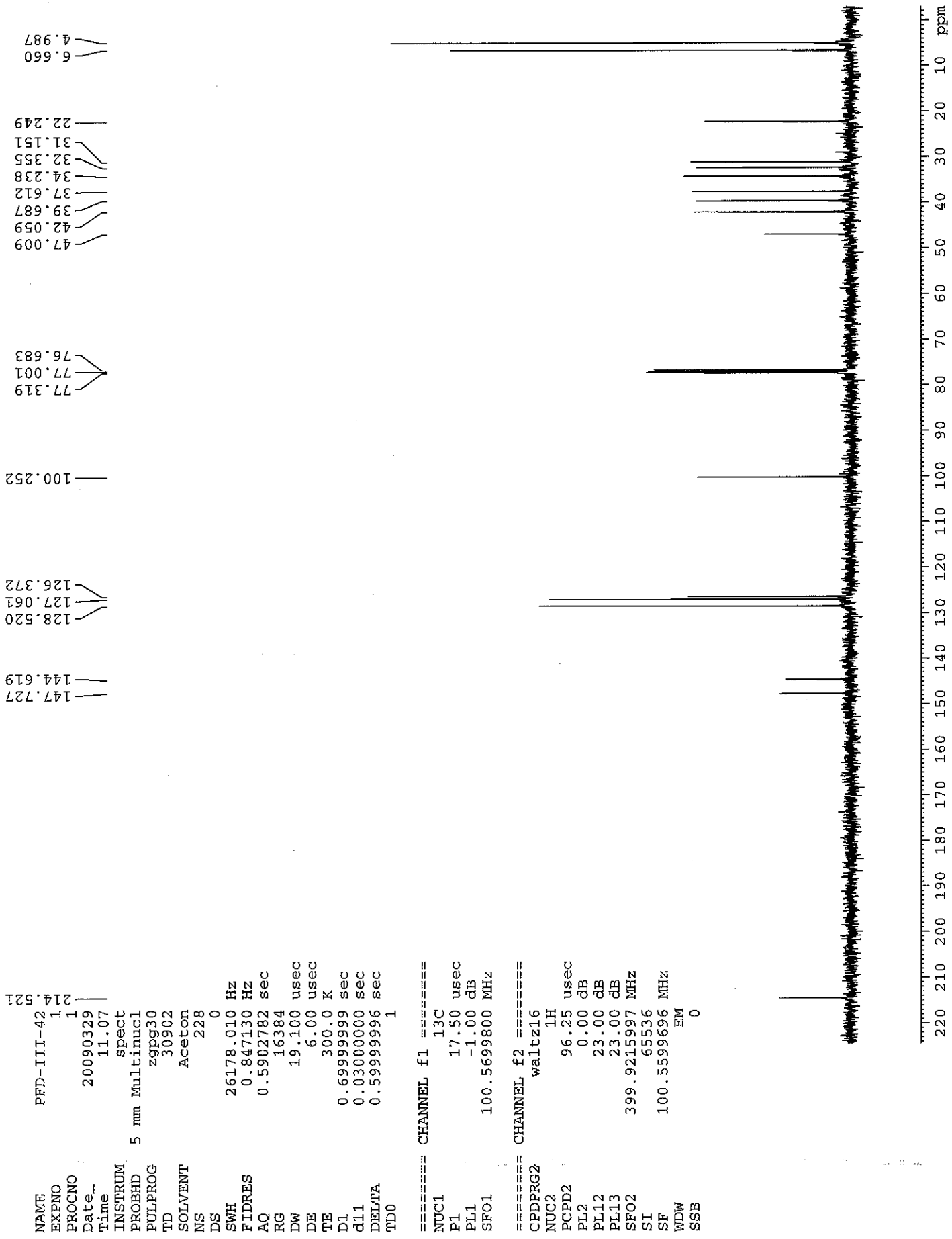
NAME	PFD-III-42
EXPNO	2
PROCNO	1
Date_	20090329
Time	11.01
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



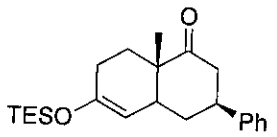



```
NAME            PFD-III-42
EXPNO                    1
PROCNO                   1
Date_             20090329
Time                 11.07
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG              zgpg30
TD                    30902
SOLVENT             Aceton
NS                       228
DS                         0
SWH                26178.010 Hz
FIDRES                0.847130 Hz
AQ                    0.5902782 sec
RG                        16384
DW                       19.100 usec
DE                        6.00 usec
TE                       300.0 K
D1                    0.69999999 sec
d11                   0.03000000 sec
DELTA                 0.59999996 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                        17.50 usec
PL1                       -1.00 dB
SFO1               100.5699800 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     96.25 usec
PL2                        0.00 dB
PL12                      23.00 dB
PL13                      23.00 dB
SFO2               399.9215997 MHz
SI                        65536
SF                 100.5599696 MHz
WDW                          EM
SSB                           0
```

NAME	PFD-III-43
EXPNO	1
PROCNO	1
Date_	20090330
Time	23.08
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200109 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



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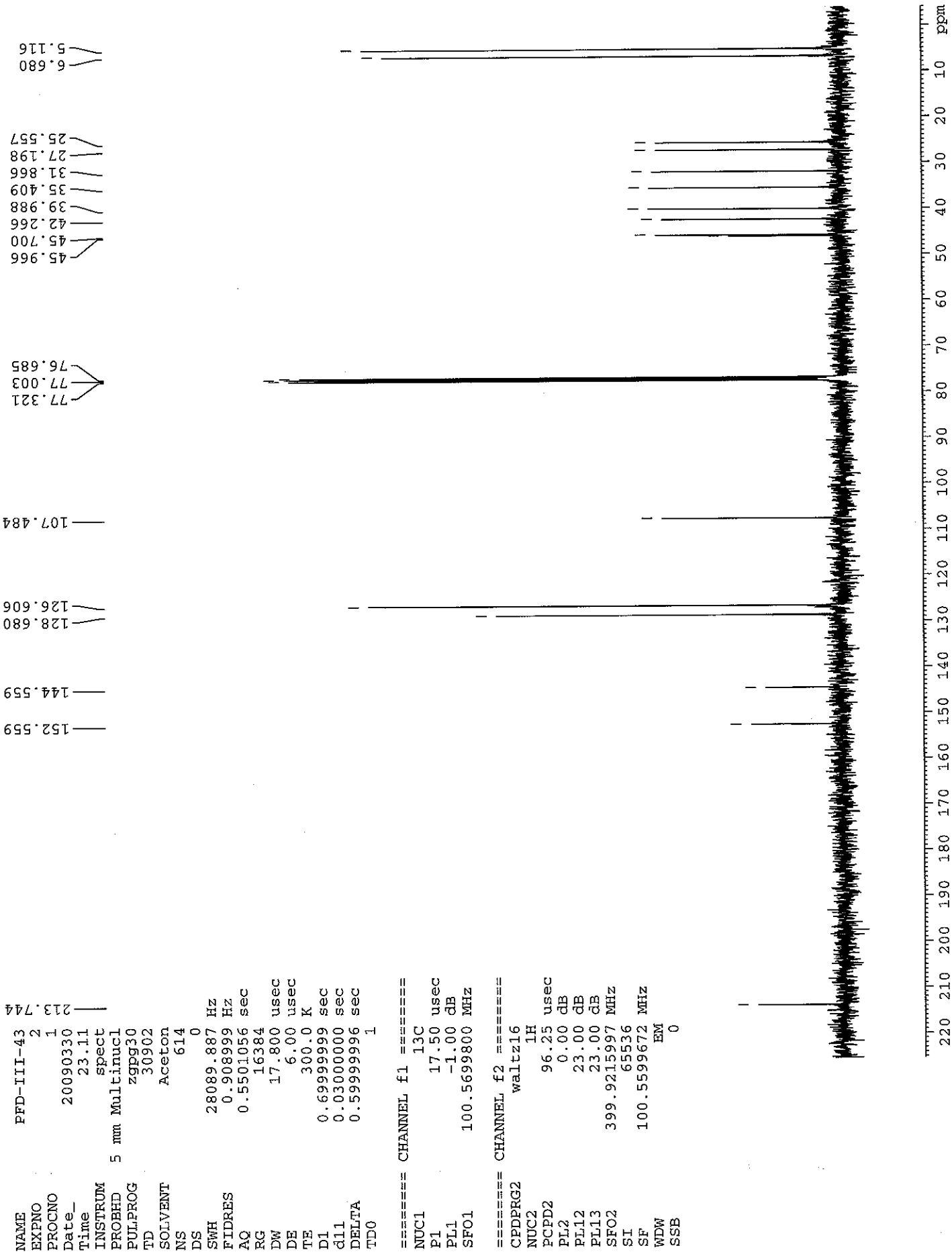

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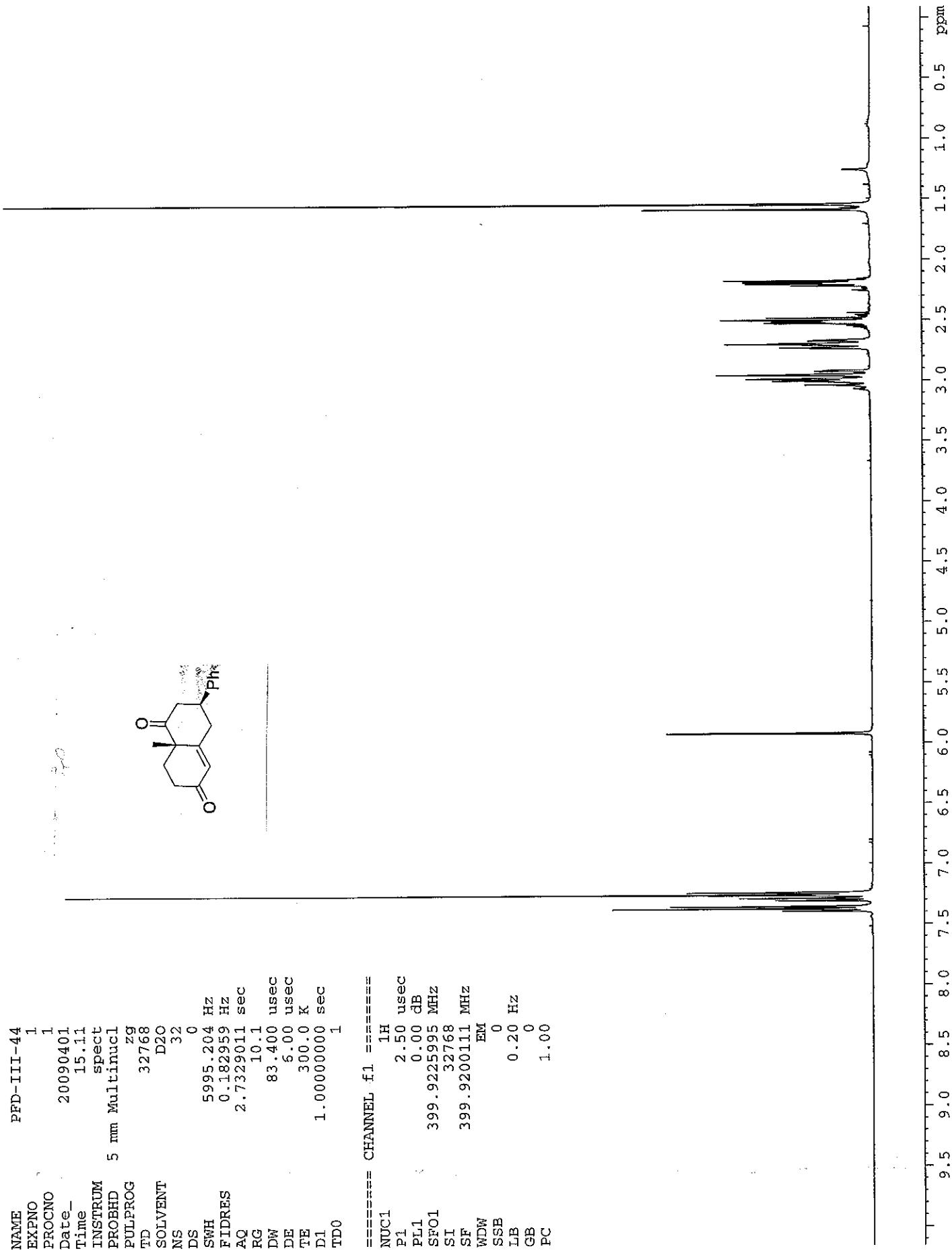
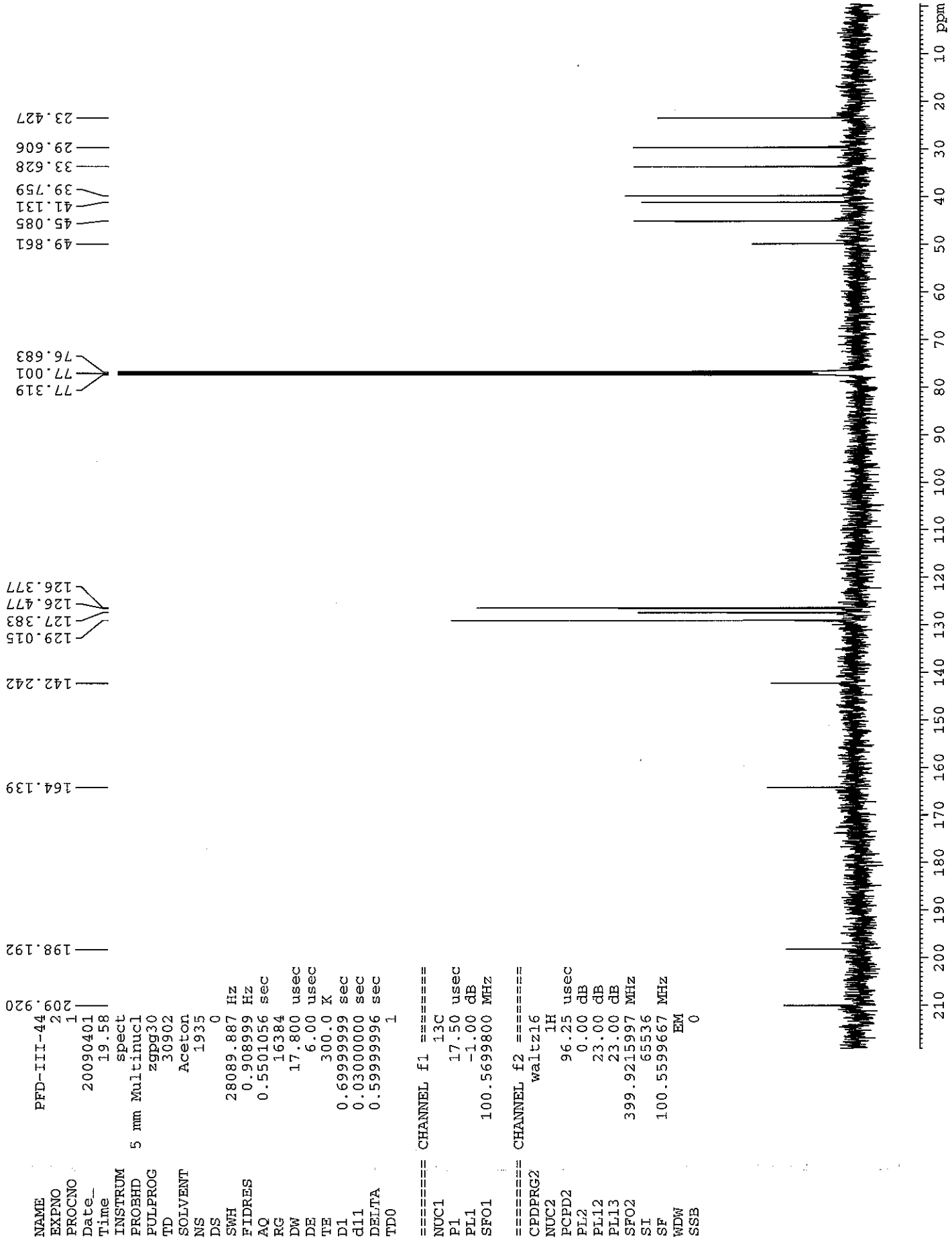


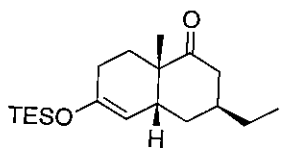


NAME	PFD-III-44
EXPNO	2
PROCNO	1
Date_	20090401
Time	19.58
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	30902
SOLVENT	Aceton
NS	1935
DS	0
SWH	28089.887 Hz
FIDRES	0.908999 Hz
AQ	0.5501056 sec
RG	16384
DW	17.800 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	17.50 usec
PL1	-1.00 dB
SFO1	100.5699800 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	96.25 usec
PL2	0.00 dB
PL12	23.00 dB
PL13	23.00 dB
SFO2	399.9215997 MHz
SI	65536
SF	100.5599667 MHz
WDW	EM
SSB	0

NAME	PFD-III-46
EXPNO	1
PROCNO	1
Date_	20090502
Time	17.23
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	19
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1

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

NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



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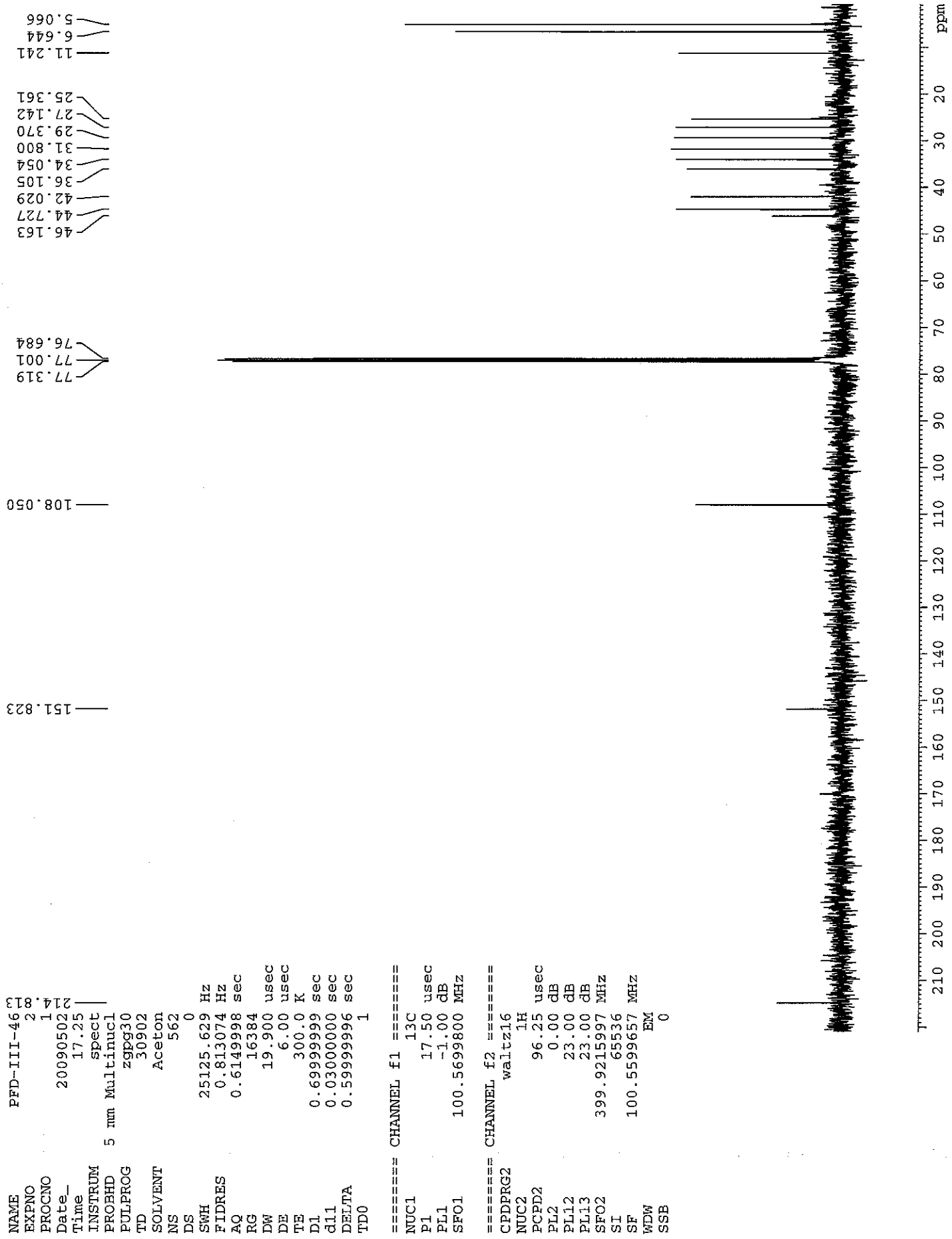
214.813
151.823
108.050
77.319
77.001
76.684
46.163
44.727
42.029
36.105
34.054
31.800
29.370
27.142
25.361
11.241
6.644
5.066
ppm
NAME PFD-III-46
EXPNO 2
PROCNO 1
Date_ 20090502
Time 17.25
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 562
DS 0
SWH 25125.629 Hz
FIDRES 0.813074 Hz
AQ 0.6149998 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599657 MHz
WDW EM
SSB 0

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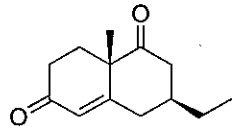
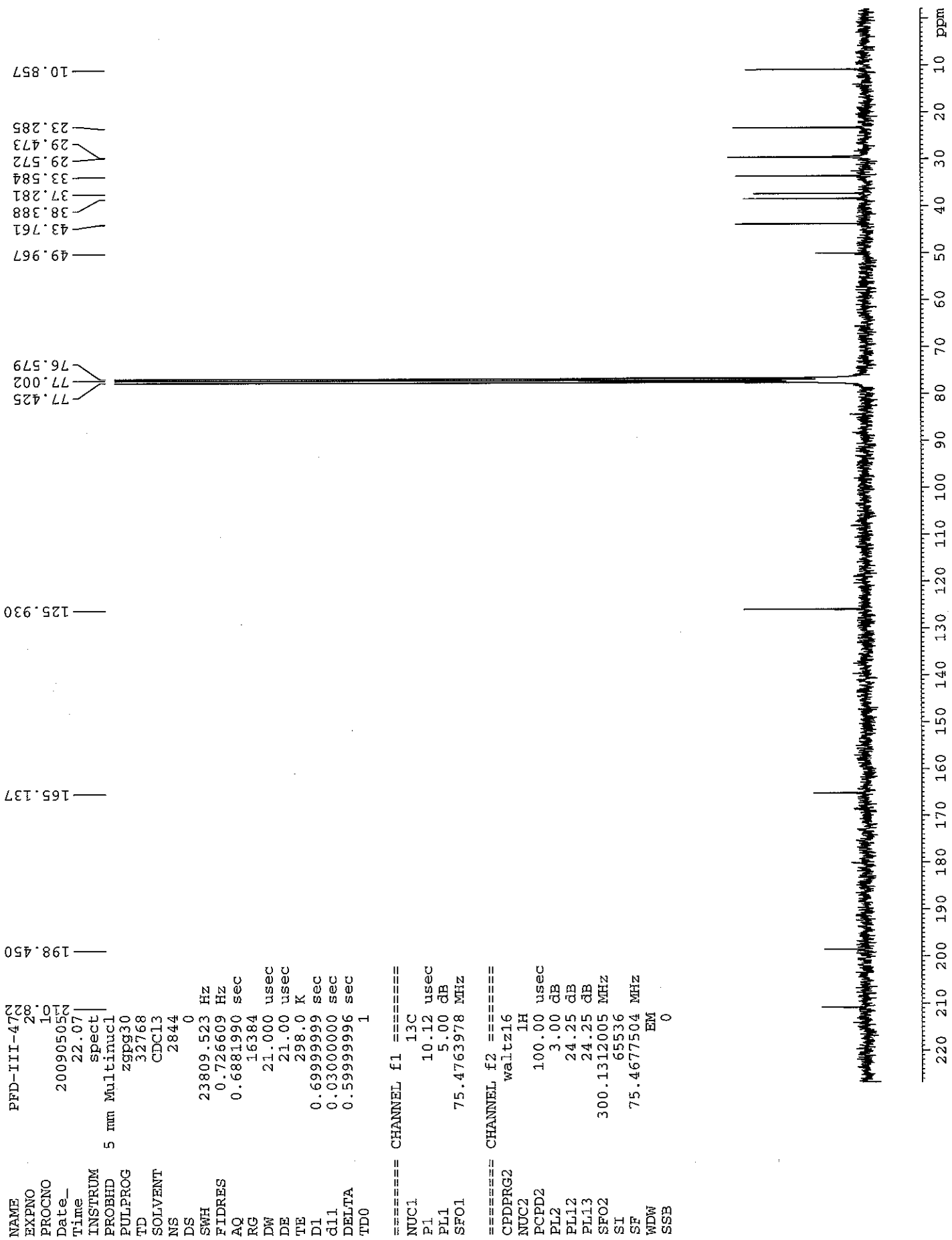
NAME	PFD-III-47
EXPNO	1
PROCNO	1
Date_	20090505
Time	16.12
INSTRUM	spect
PROBHD	5 mm TXI 13C Z
PULPROG	zg
TD	32768
SOLVENT	CDC13
NS	12
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	16
DW	83.200 usec
DE	5.50 usec
TE	300.0 K
D1	2.00000000 sec
TD0	1

======== CHANNEL f1 ========	
NUC1	1H
P1	3.00 usec
PL1	3.00 dB
SFO1	500.1325006 MHz
SI	16384
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00




10.857
23.285
29.473
29.572
33.584
37.281
38.388
43.761
49.967
76.579
77.002
77.425
125.930
165.137
198.450
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
NAME PFD-III-472
EXPNO 2
PROCNO 1
Date_ 20090505
Time 21.07.822
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2844
DS 0
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 0.6881990 sec
RG 16384
DW 21.000 usec
DE 21.00 usec
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.12 usec
PL1 5.00 dB
SFO1 75.4763978 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 24.25 dB
PL13 24.25 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677504 MHz
WDW EM
SSB 0

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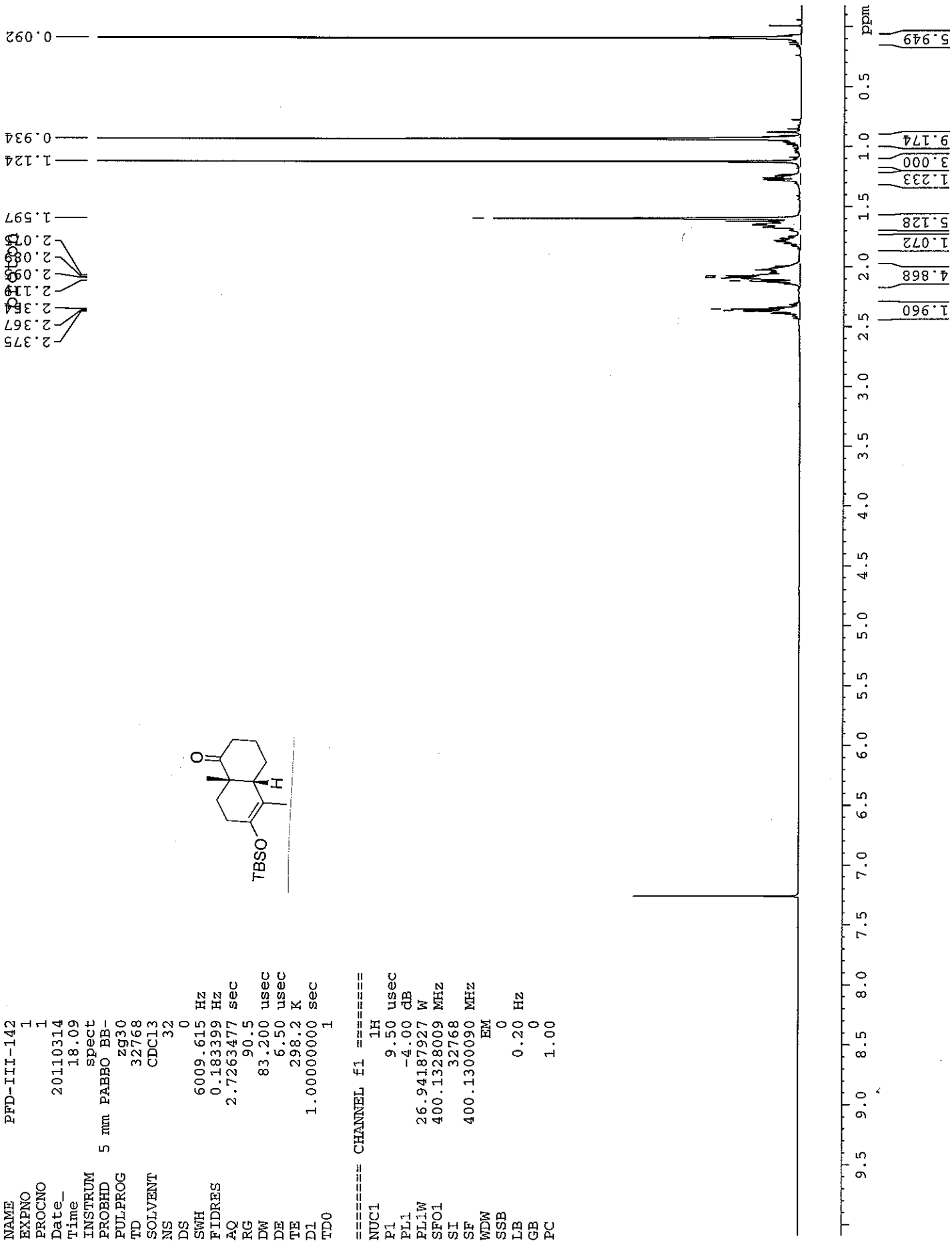
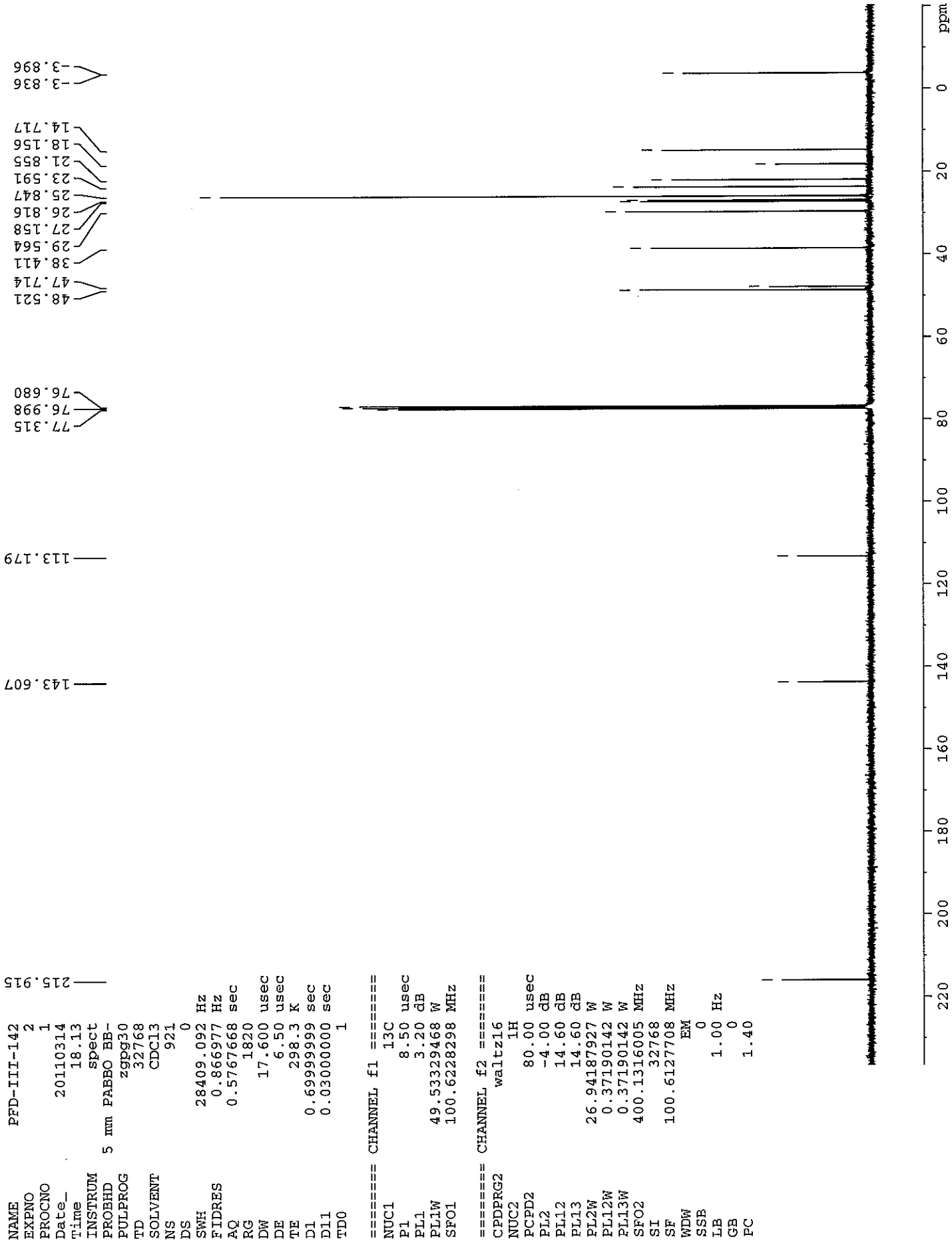



```
NAME            PFD-III-142
EXPNO                     1
PROCNO                    1
Date_              20110314
Time                  18.09
INSTRUM               spect
PROBHD  5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDC13
NS                       32
DS                        0
SWH                6009.615 Hz
FIDRES             0.183399 Hz
AQ                 2.7263477 sec
RG                      90.5
DW                     83.200 usec
DE                      6.50 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                       1

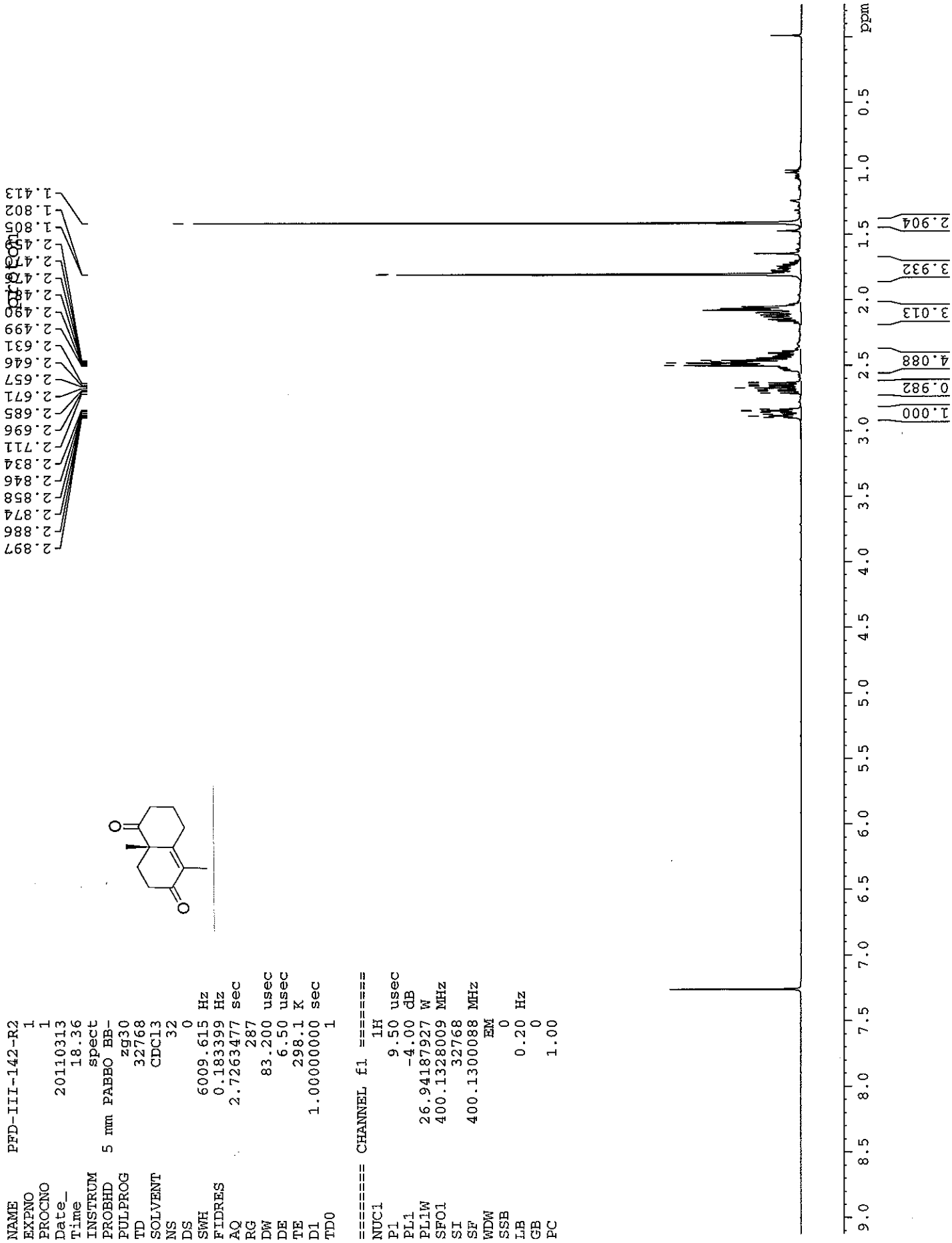
======== CHANNEL f1 ========
NUC1                      1H
P1                     9.50 usec
PL1                   -4.00 dB
PL1W               26.94187927 W
SFO1               400.1328009 MHz
SI                    32768
SF                 400.1300090 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      1.00
```




```
NAME                PFD-III-142
EXPNO                         2
PROCNO                        1
Date_                20110314
Time                    18.13
INSTRUM                 spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       32768
SOLVENT                  CDCl3
NS                         921
DS                           0
SWH                28409.092 Hz
FIDRES              0.866977 Hz
AQ                  0.5767668 sec
RG                        1820
DW                      17.600 usec
DE                       6.50 usec
TE                     298.3 K
D1                  0.69999999 sec
D11                 0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                       13C
P1                        8.50 usec
PL1                       3.20 dB
PL1W               49.53329468 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                      -4.00 dB
PL12                     14.60 dB
PL13                     14.60 dB
PL2W               26.94187927 W
PL12W               0.37190142 W
PL13W               0.37190142 W
SFO2               400.1316005 MHz
SI                       32768
SF                 100.6127708 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```


NAME PFD-III-142-R2
EXPNO 1
PROCNO 1
Date_ 20110313
Time 18.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 287
DW 83.200 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
2.897
2.886
2.874
2.858
2.846
2.834
2.711
2.696
2.685
2.671
2.657
2.646
2.631
2.499
2.490
2.478
2.473
2.453
1.805
1.802
1.413
2.904
3.932
3.013
4.088
0.982
1.000
ppm

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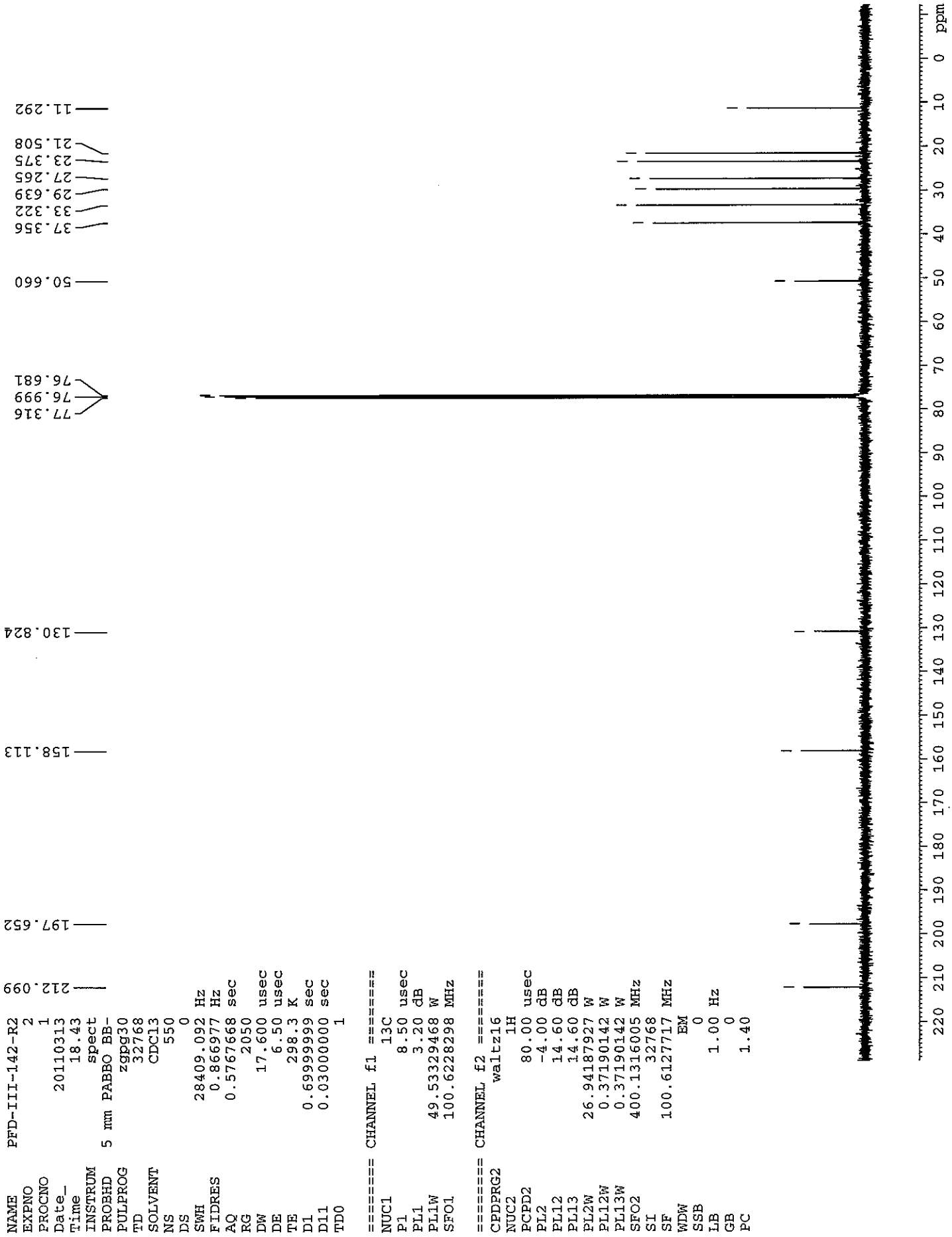



```
NAME                PFD-III-142-R2
EXPNO                            2
PROCNO                           1
Date_                     20110313
Time                         18.43
INSTRUM                      spect
PROBHD     5 mm PABBO BB-
PULPROG                   zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                           550
DS                             0
SWH                    28409.092 Hz
FIDRES                 0.866977 Hz
AQ                     0.5767668 sec
RG                          2050
DW                        17.600 usec
DE                         6.50 usec
TE                        298.3 K
D1                     0.69999999 sec
D11                    0.03000000 sec
TD0                              1

======== CHANNEL f1 ========
NUC1                          13C
P1                          8.50 usec
PL1                         3.20 dB
PL1W                   49.53329468 W
SFO1                   100.6228298 MHz

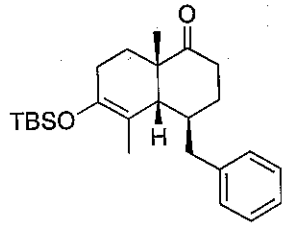
======== CHANNEL f2 ========
CPDPRG2                    waltz16
NUC2                           1H
PCPD2                      80.00 usec
PL2                        -4.00 dB
PL12                       14.60 dB
PL13                       14.60 dB
PL2W                   26.94187927 W
PL12W                   0.37190142 W
PL13W                   0.37190142 W
SFO2                   400.1316005 MHz
SI                         32768
SF                     100.6127717 MHz
WDW                            EM
SSB                             0
LB                          1.00 Hz
GB                              0
PC                          1.40
```

```
Current Data Parameters
NAME      PFD-III-143-R1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110409
Time               22.56
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                  71.8
DW                83.200 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PL1                -4.00 dB
PL1W        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.40
```



proton

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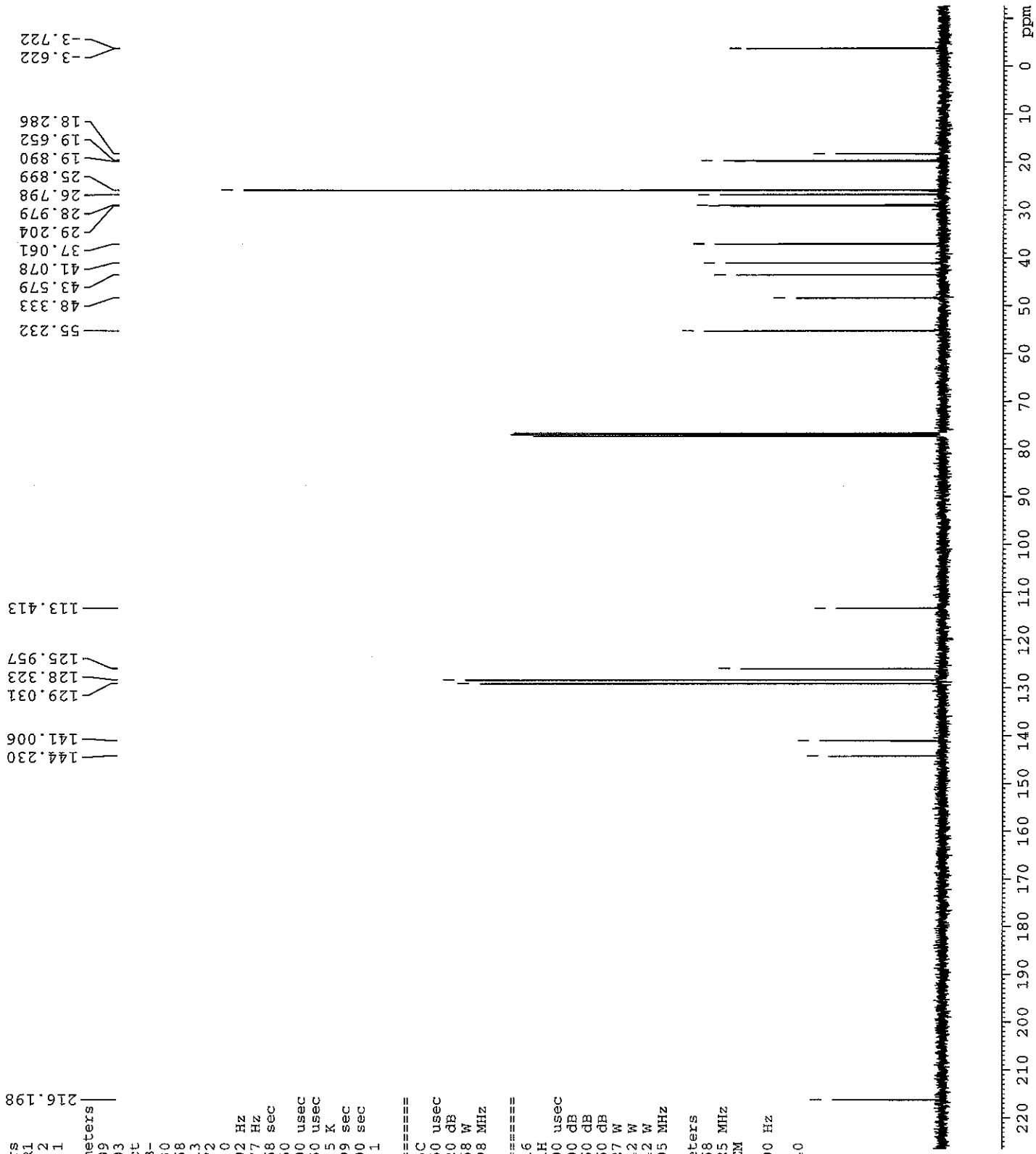


```
Current Data Parameters
NAME      PFD-III-143-R1
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_          20110409
Time              23.03
INSTRUM           spect
PROBHD  5 mm PABBO BB-
PULPROG         zgpg30
TD               32768
SOLVENT          CDCl3
NS                 172
DS                   0
SWH          28409.092 Hz
FIDRES           0.866977 Hz
AQ               0.5767668 sec
RG                2050
DW               17.600 usec
DE                6.50 usec
TE                298.5 K
D1           0.69999999 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                8.50 usec
PL1               3.20 dB
PL1W        49.53329468 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2          80.00 usec
PL2             -4.00 dB
PL12            14.60 dB
PL13            14.60 dB
PL2W        26.94187927 W
PL12W        0.37190142 W
PL13W        0.37190142 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI               32768
SF          100.6127725 MHz
WDW                EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

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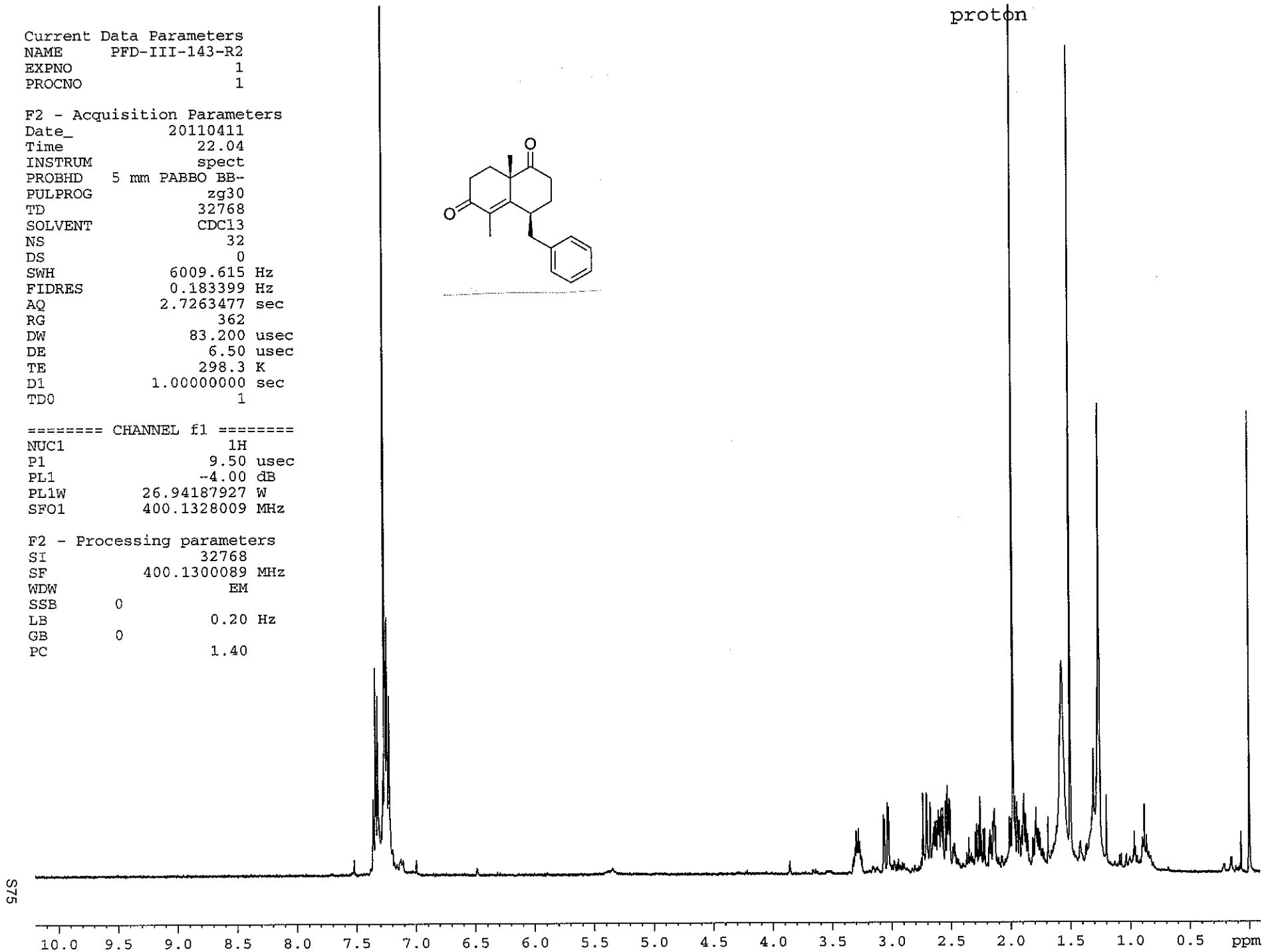

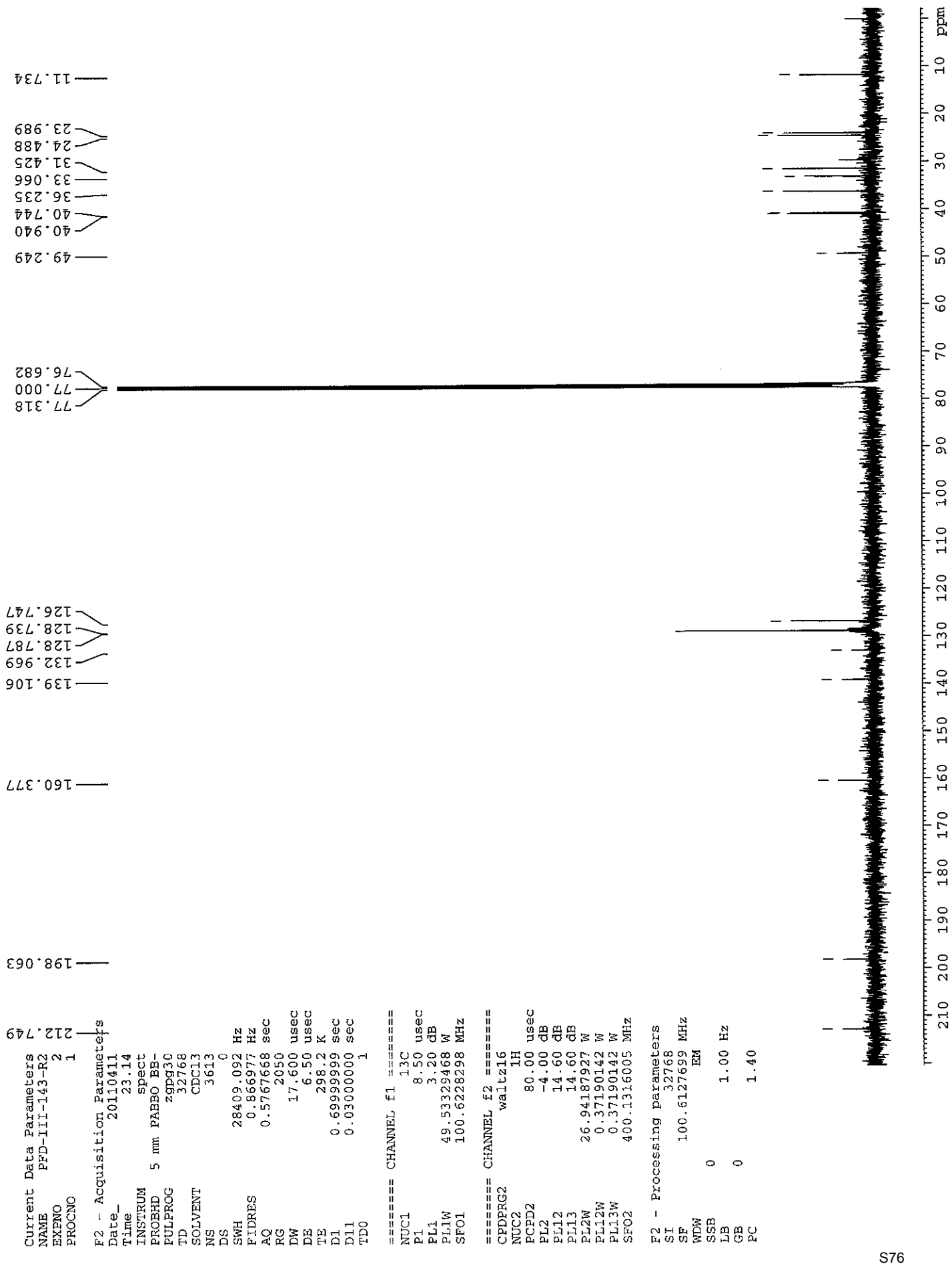
212.749
198.063
160.377
139.106
132.969
128.787
128.739
126.747
77.318
77.000
76.682
49.249
40.940
40.744
36.235
33.066
31.425
24.488
23.989
11.734
ppm
Current Data Parameters
NAME PFD-III-143-R2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110411
Time 23.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3613
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127699 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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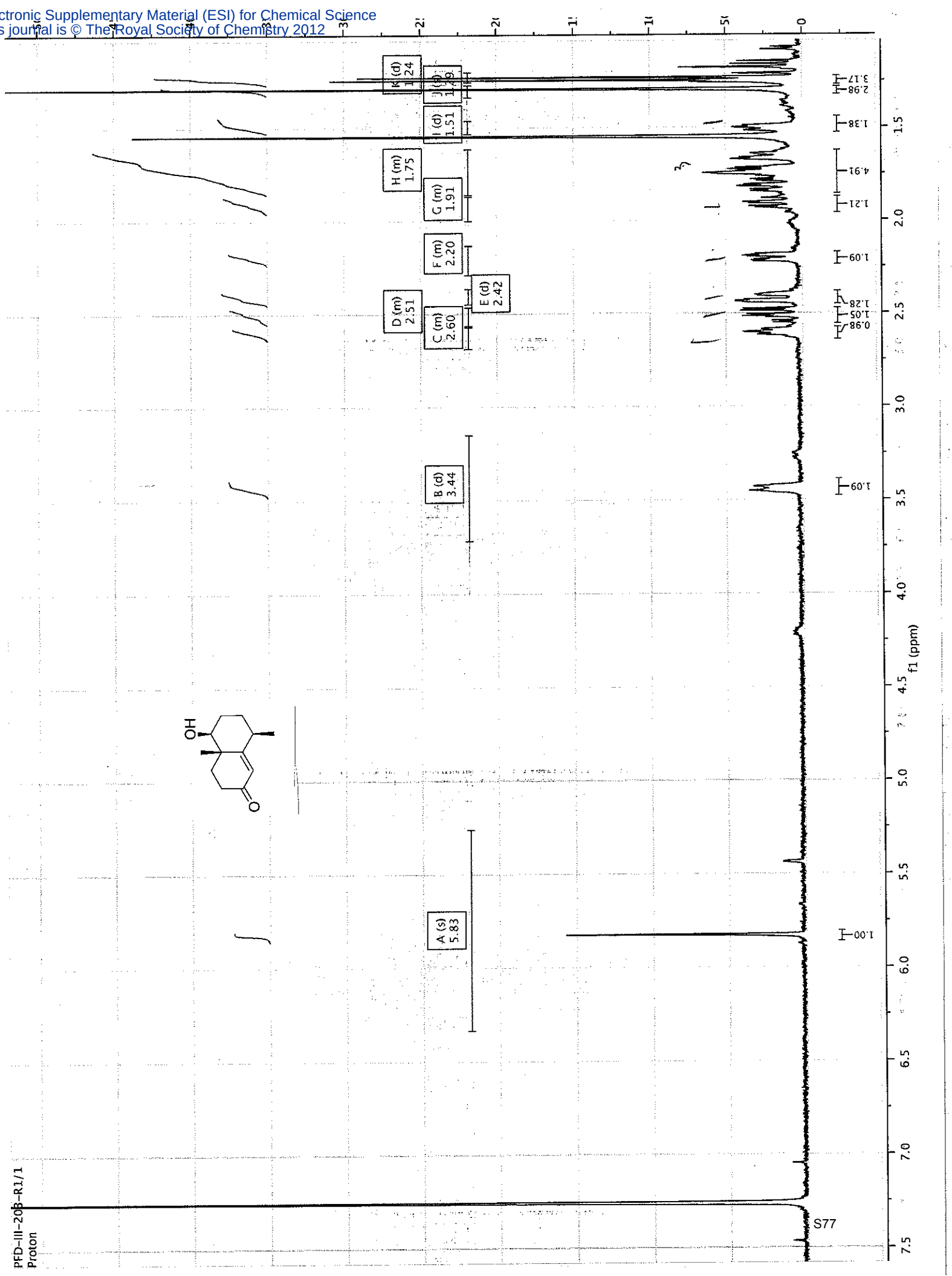

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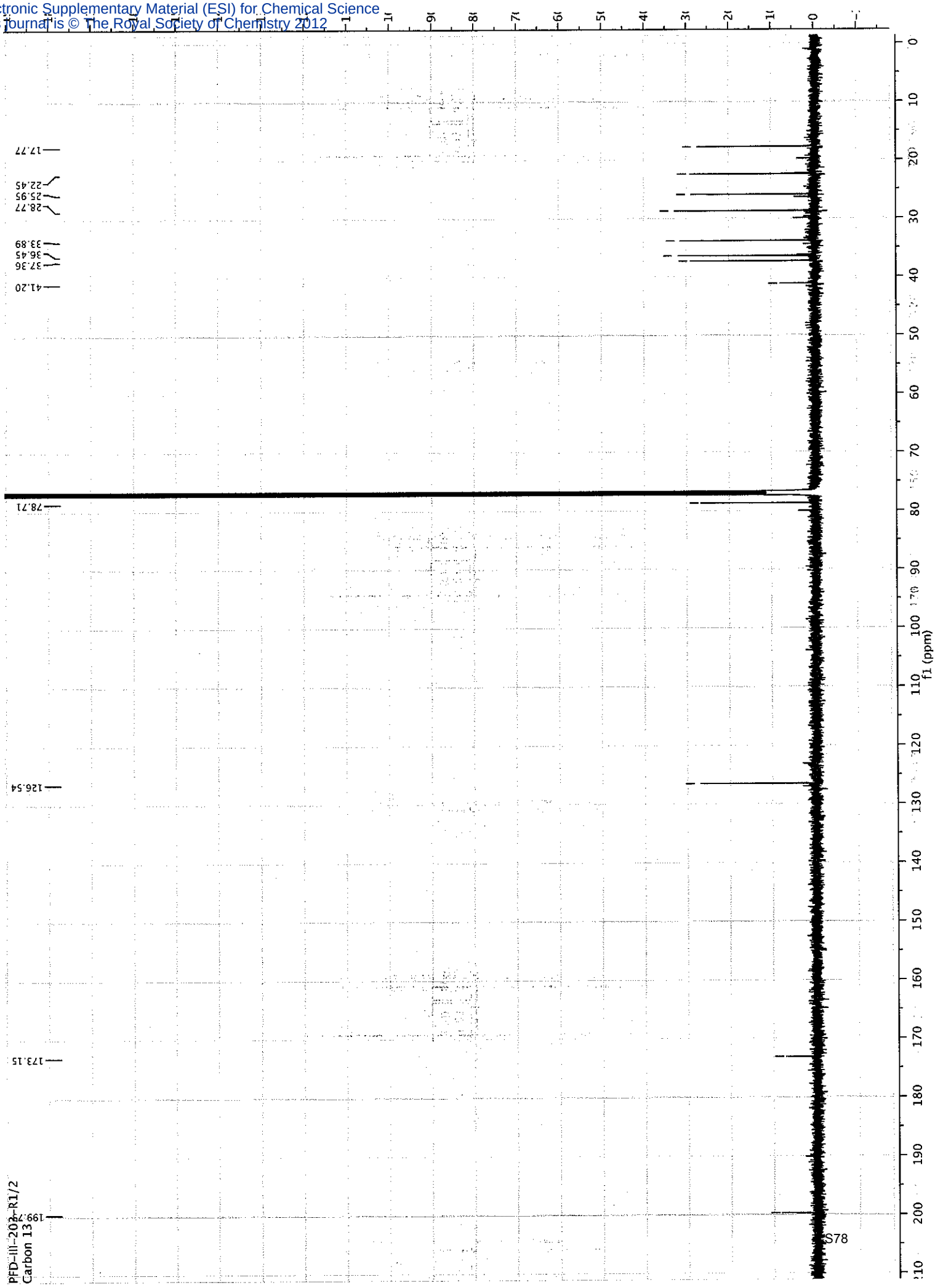

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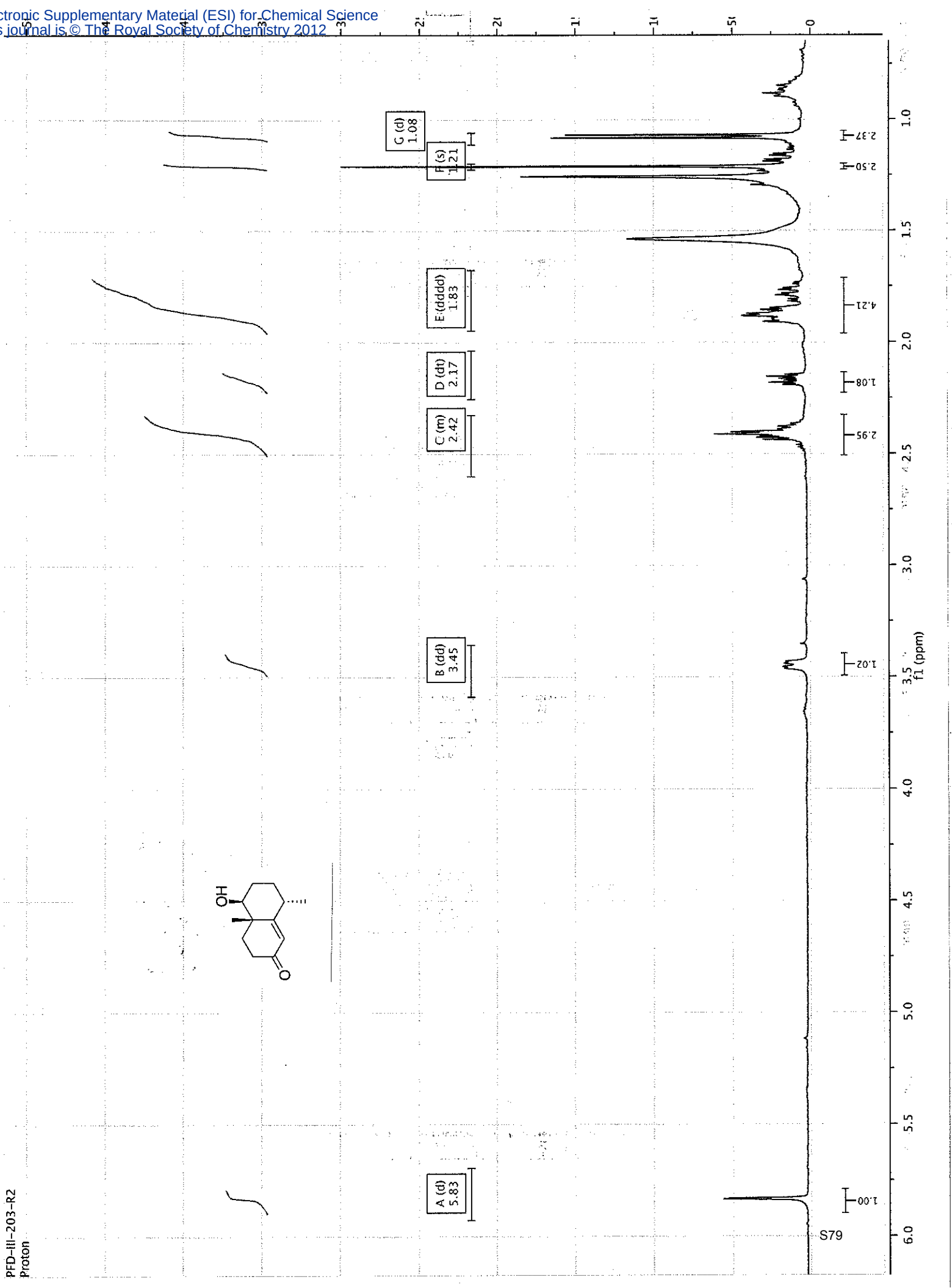

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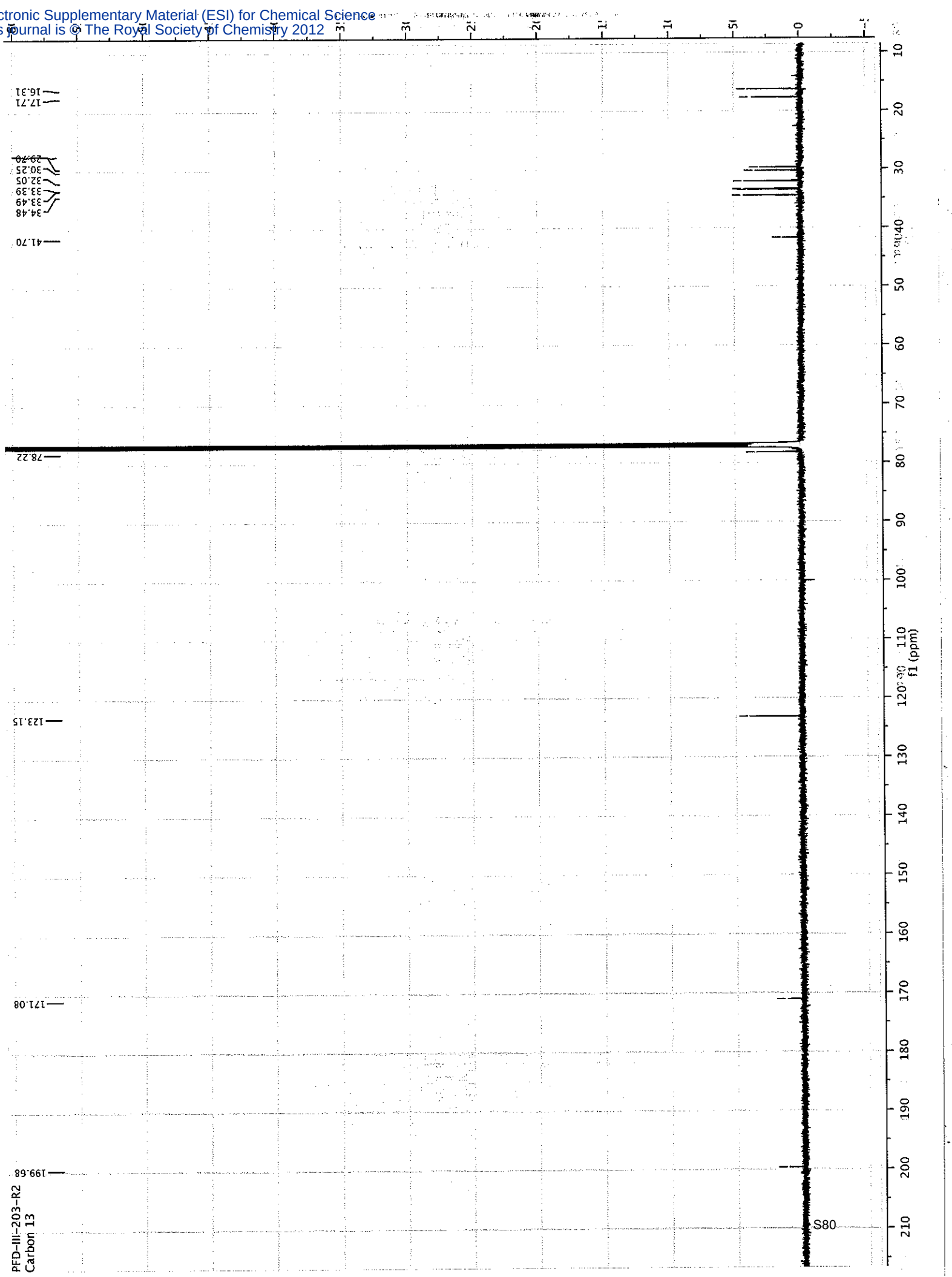

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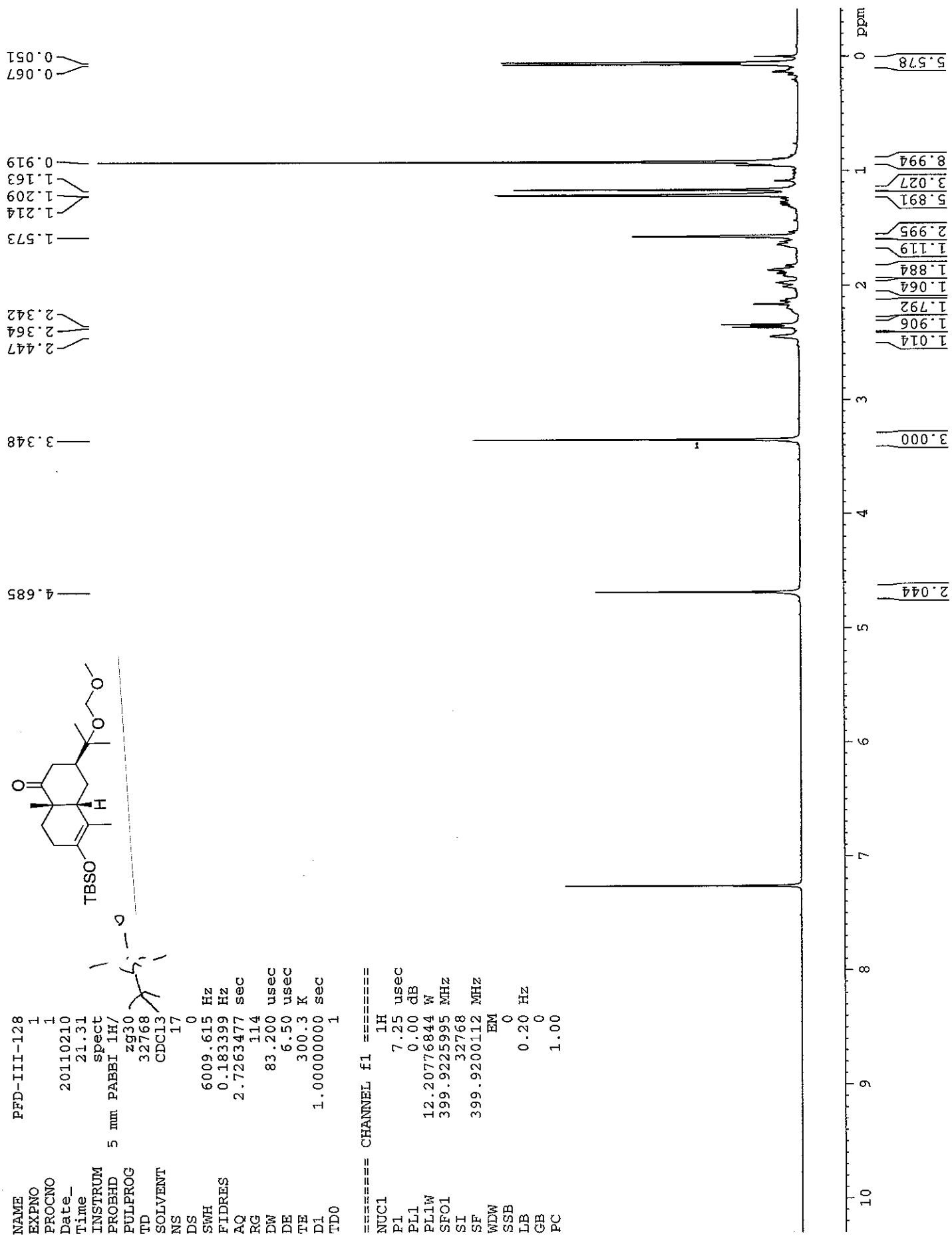

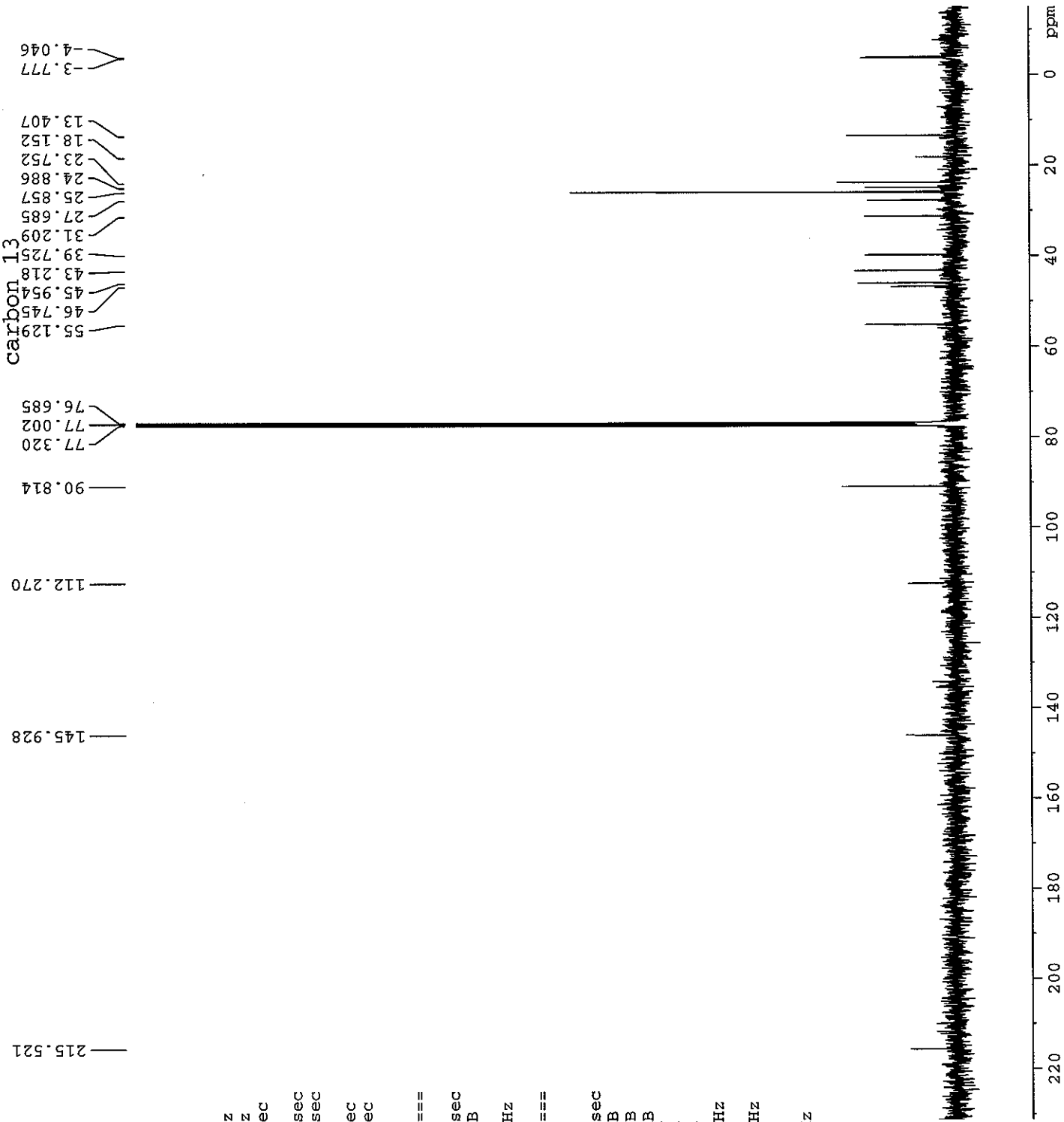


```
NAME                PFD-III-128
EXPNO                         2
PROCNO                        1
Date_              20110210
Time                      21.34
INSTRUM                   spect
PROBHD     5 mm PABBI 1H/
PULPROG                zgpg30
TD                         32768
SOLVENT                  CDCl3
NS                          128
DS                            0
SWH                28409.092 Hz
FIDRES             0.866977 Hz
AQ                 0.5767668 sec
RG                          181
DW                 17.600 usec
DE                    6.50 usec
TE                    300.3 K
D1                 0.69999999 sec
D11                0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                       13C
P1                      14.00 usec
PL1                     -4.60 dB
PL1W               94.90110779 W
SFO1               100.5710256 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                   90.00 usec
PL2                      0.00 dB
PL12                    21.88 dB
PL13                   120.00 dB
PL2W               12.20776844 W
PL12W               0.07918380 W
PL13W               0.00000000 W
SFO2               399.9215997 MHz
SI                         32768
SF                 100.5599652 MHz
WDW                          EM
SSB                           0
LB                     3.00 Hz
GB                            0
PC                         1.40
```

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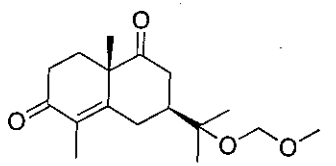
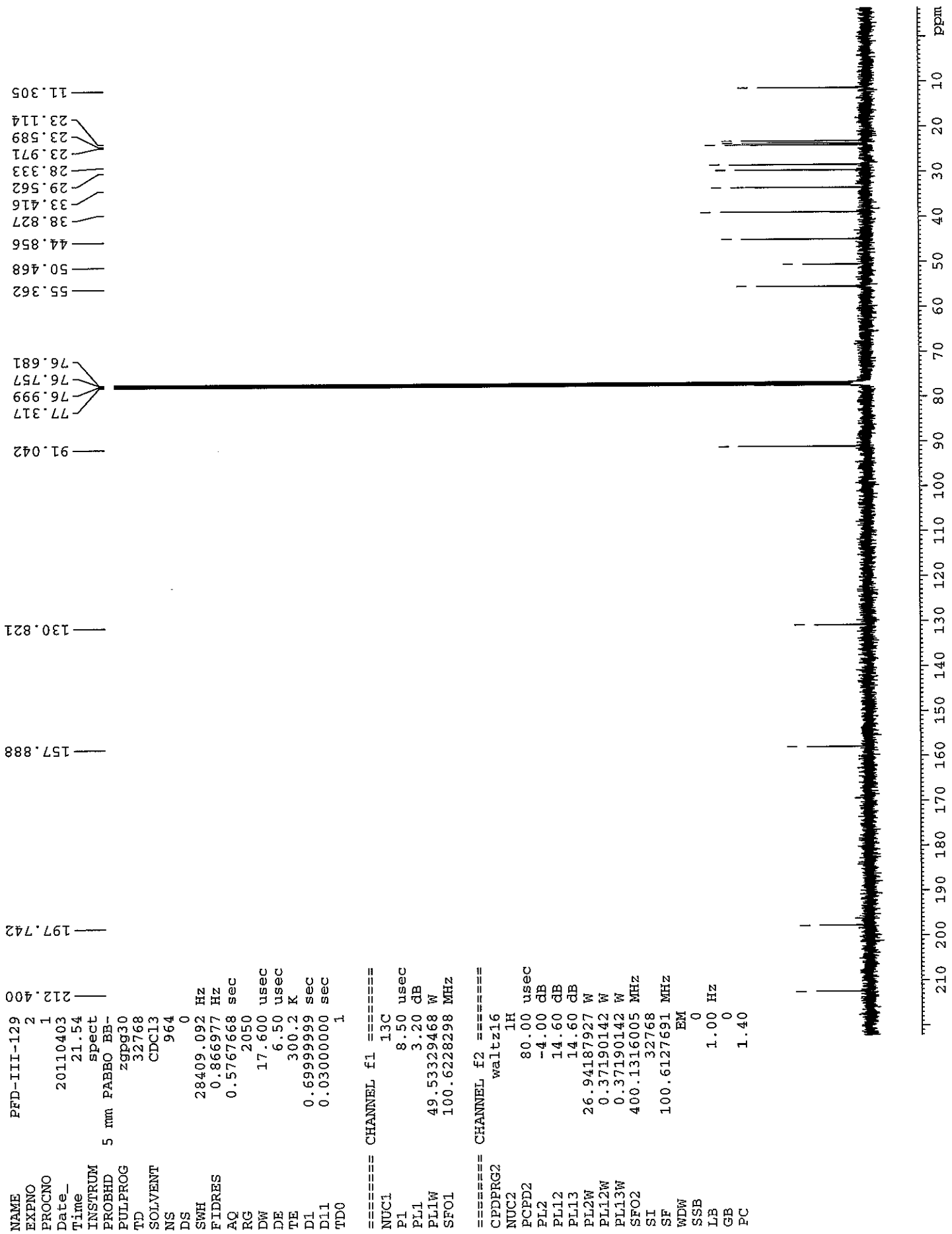
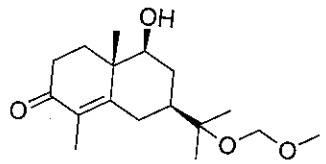
NAME	PFD-III-129
EXPNO	1
PROCNO	1
Date_	20110403
Time	21.47
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	512
DW	83.200 usec
DE	6.50 usec
TE	300.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300087 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00




NAME PFD-III-129
EXPNO 2
PROCNO 1
Date_ 20110403
Time 21.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 964
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
212.400
197.742
157.888
130.821
91.042
77.317
76.999
76.757
76.681
55.362
50.468
44.856
38.827
33.416
29.562
28.333
23.971
23.589
23.114
11.305
ppm

NAME	PFD-III-130
EXPNO	2
PROCNO	1
Date_	20110402
Time	20.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	5
DS	0
SWH	11160.714 Hz
FIDRES	0.340598 Hz
AQ	1.4680564 sec
RG	512
DW	44.800 usec
DE	6.50 usec
TE	300.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300087 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



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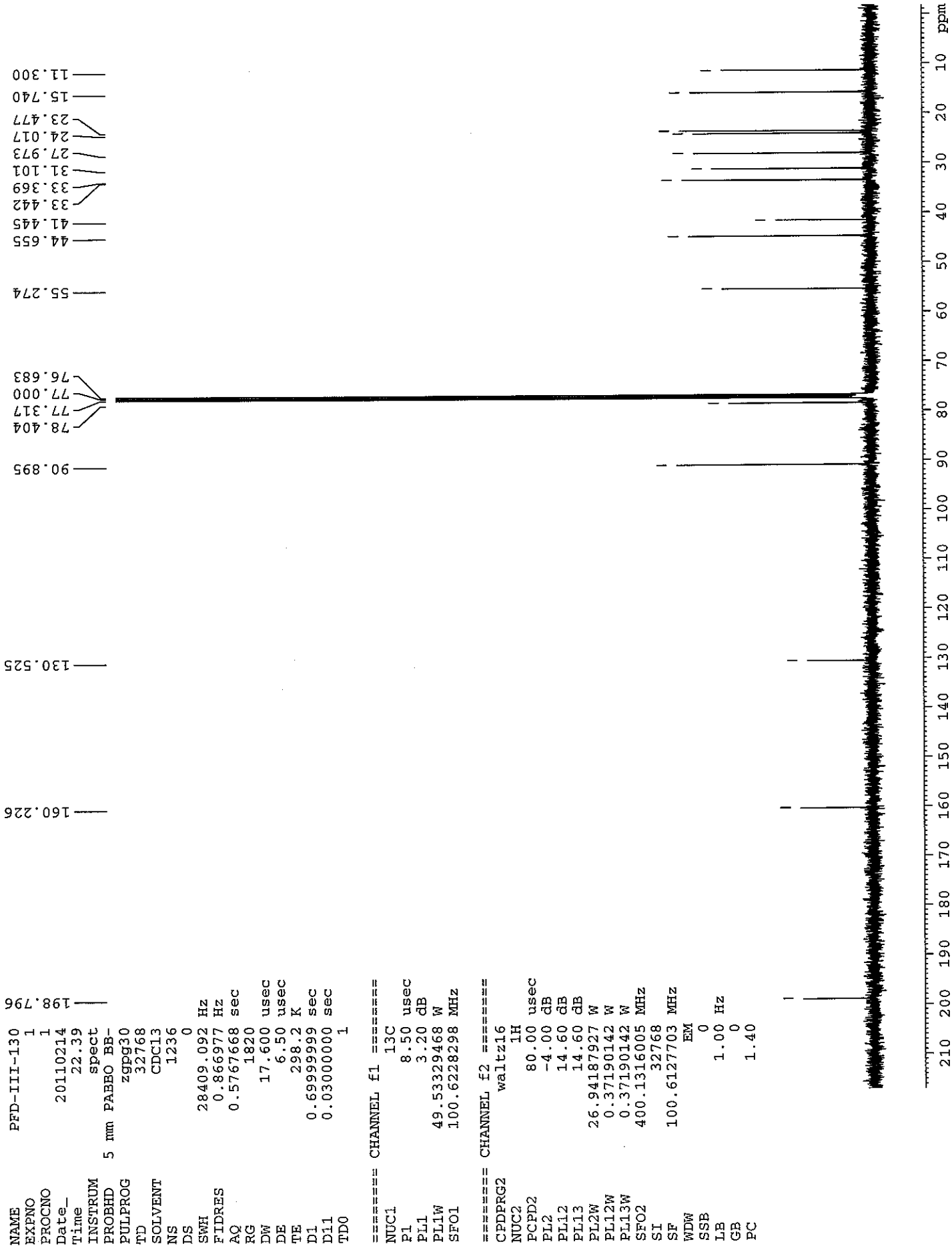

NAME	PFD-III-130
EXPNO	1
PROCNO	1
Date_	20110214
Time	22.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	1236
DS	0
SWH	28409.092 Hz
FIDRES	0.866977 Hz
AQ	0.5767668 sec
RG	1820
DW	17.600 usec
DE	6.50 usec
TE	298.2 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127703 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

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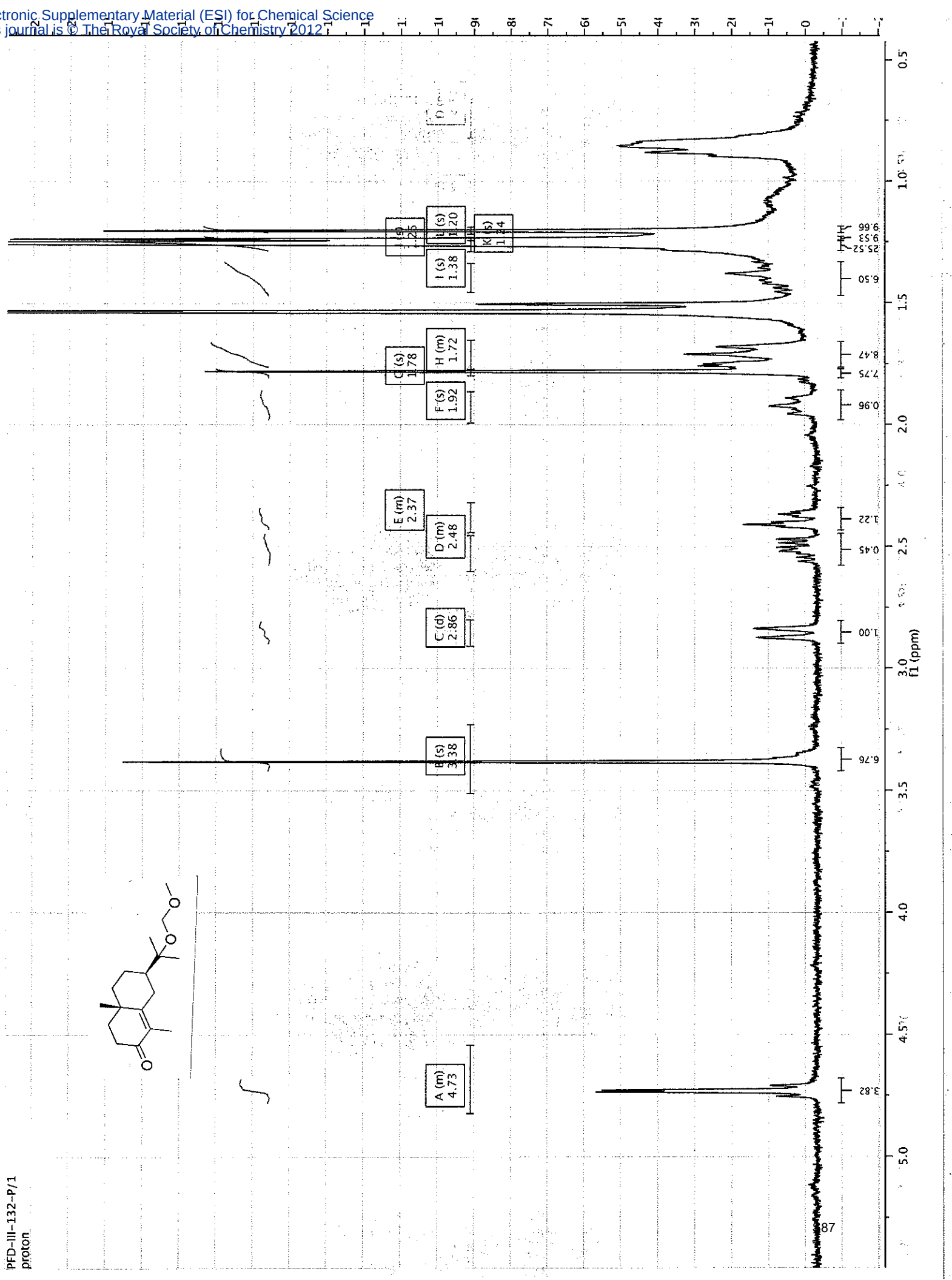

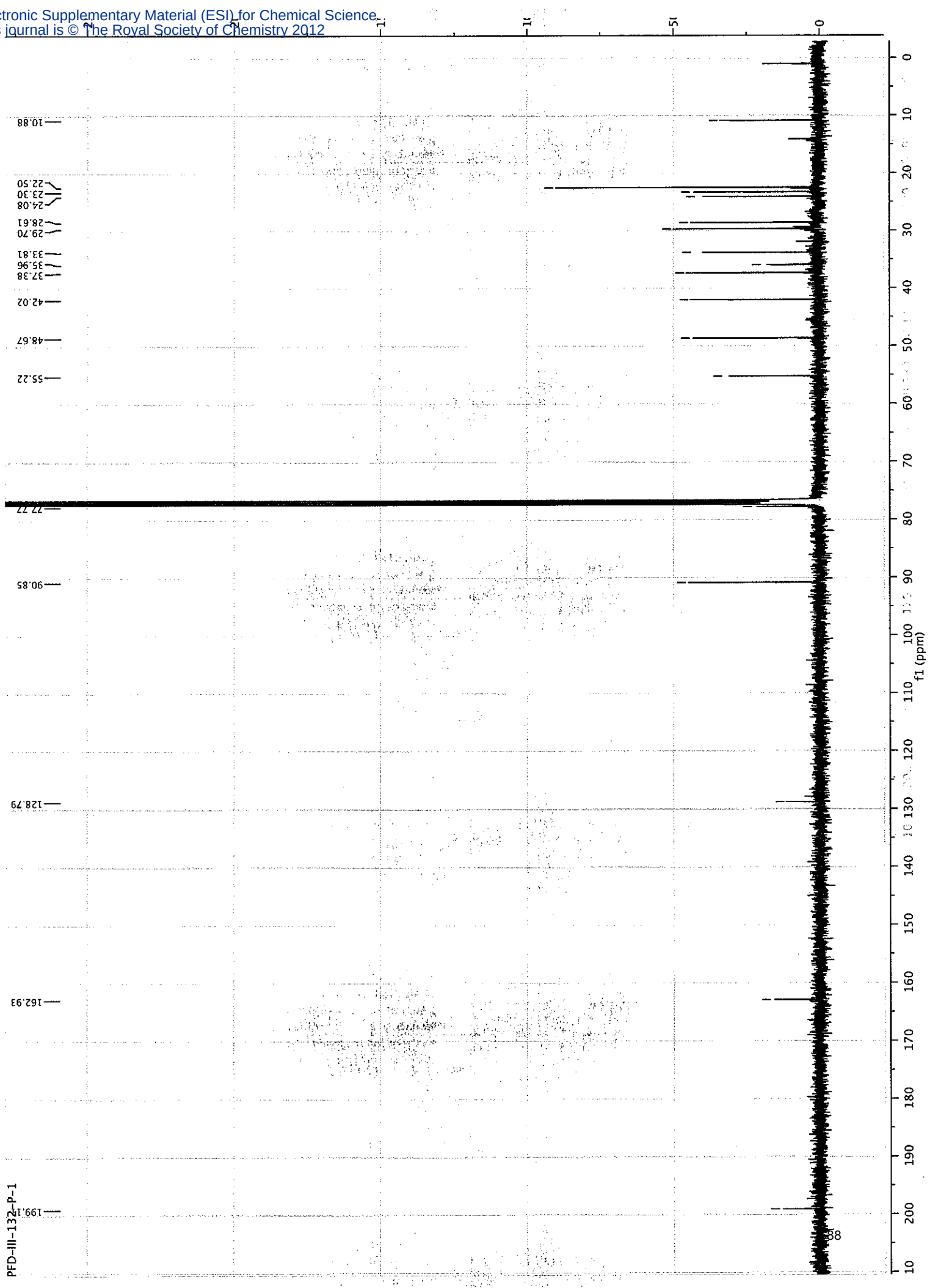
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22.50
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24.08
28.61
29.70
33.81
35.96
37.38
42.02
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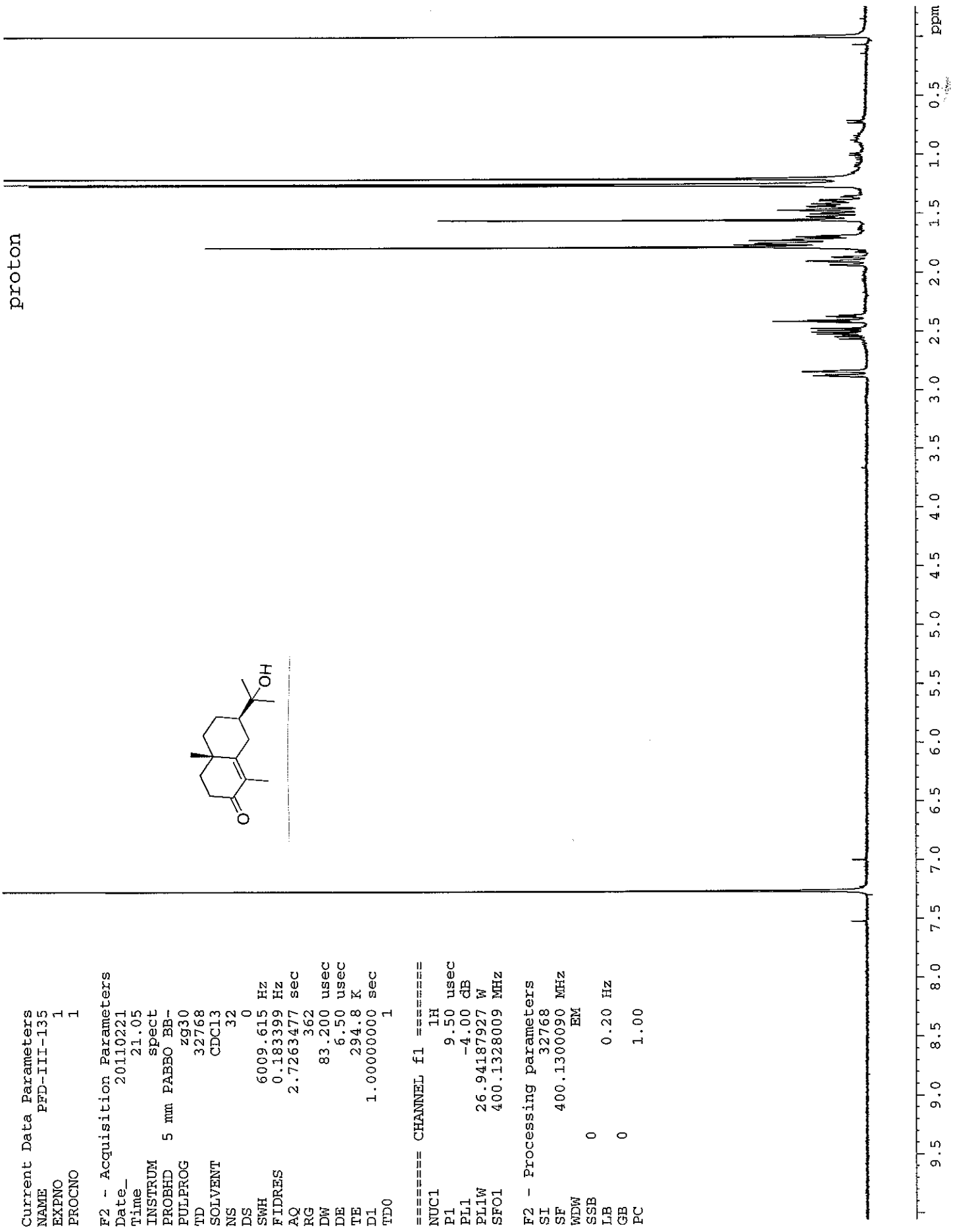
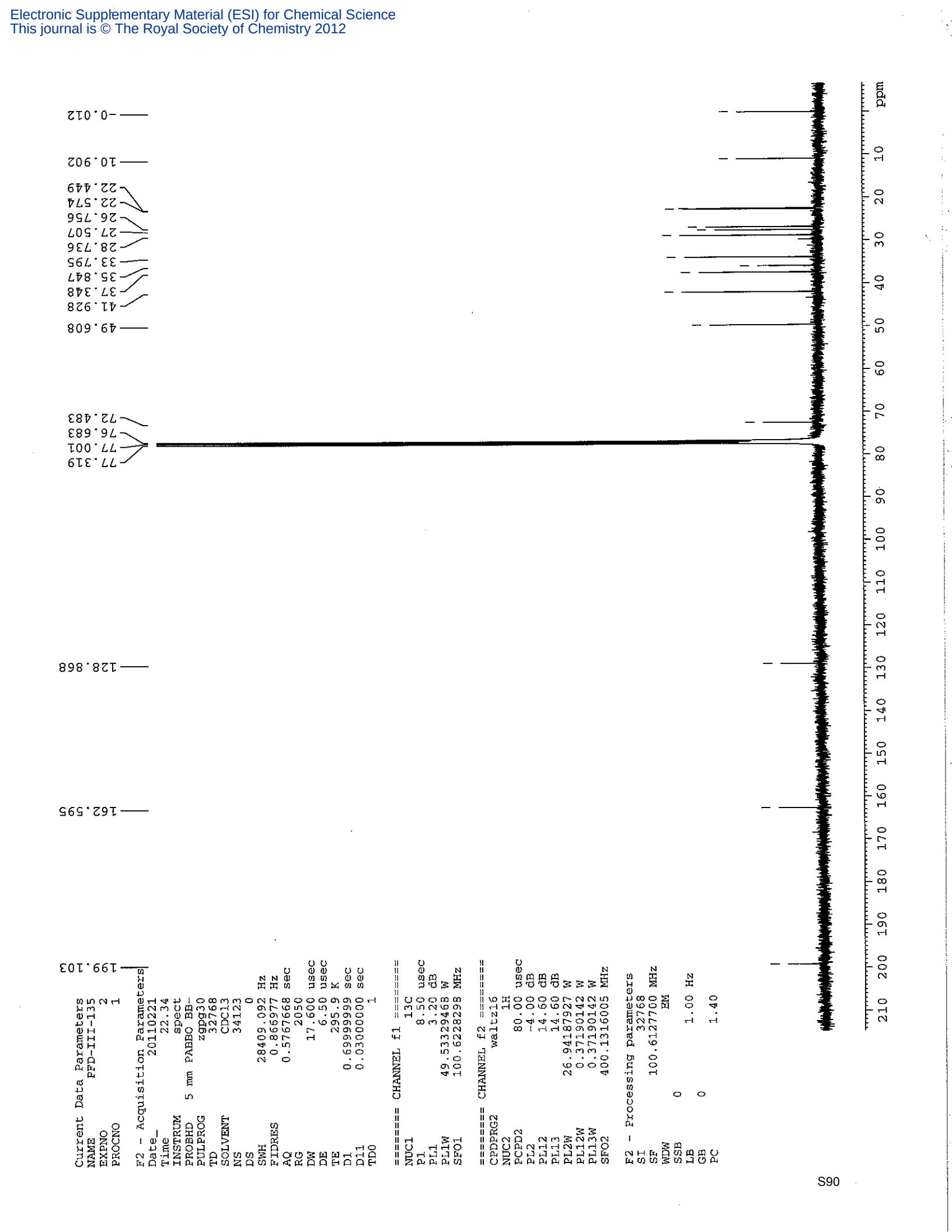
55.22
77.27
90.85
128.79
162.93
199.14
PFD-III-132-P-1
f1 (ppm)


proton
OH
O
Current Data Parameters
NAME PFD-III-135
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110221
Time 21.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 362
DW 83.200 usec
DE 6.50 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


Current Data Parameters
NAME PFD-III-135
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110221
Time 22.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 34123
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 295.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127760 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
199.103
162.595
128.868
77.319
77.001
76.683
72.483
49.608
41.928
37.348
35.847
33.795
28.736
27.507
26.756
22.574
22.449
10.902
-0.012
ppm

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```
Current Data Parameters
NAME         PFD-III-173
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110905
Time               17.06
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 40498
SOLVENT            CDCl3
NS                    43
DS                     0
SWH             7500.000 Hz
FIDRES          0.185194 Hz
AQ             2.6999166 sec
RG                  28.5
DW                66.667 usec
DE                  6.50 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PLW1         16.98200035 W
SFO1         500.1332508 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300131 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 4.00
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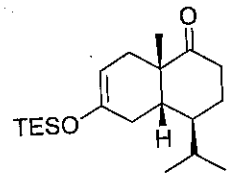

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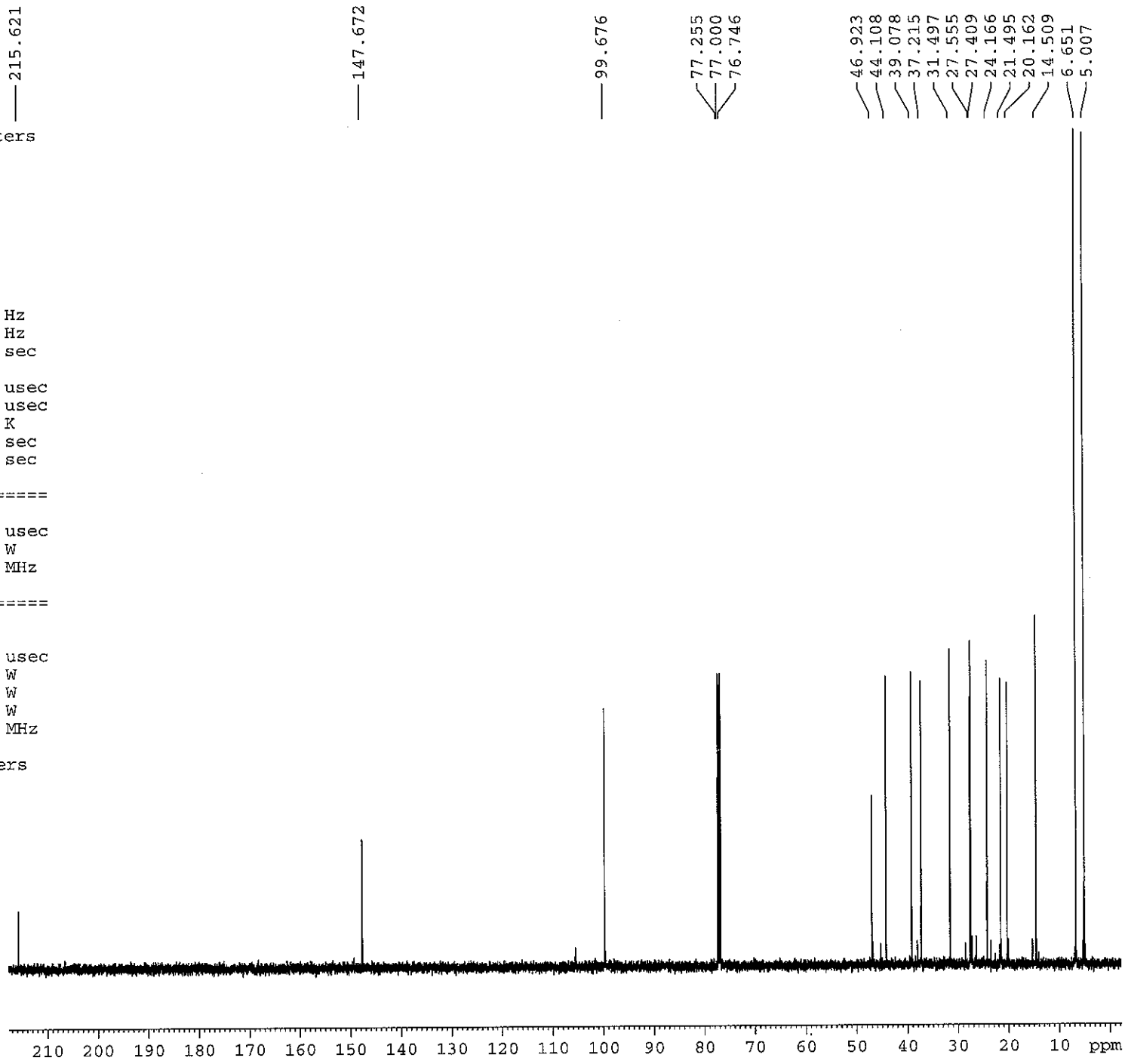
```
Current Data Parameters
NAME         PFD-III-173
EXPNO                  2
PROCNO                 1

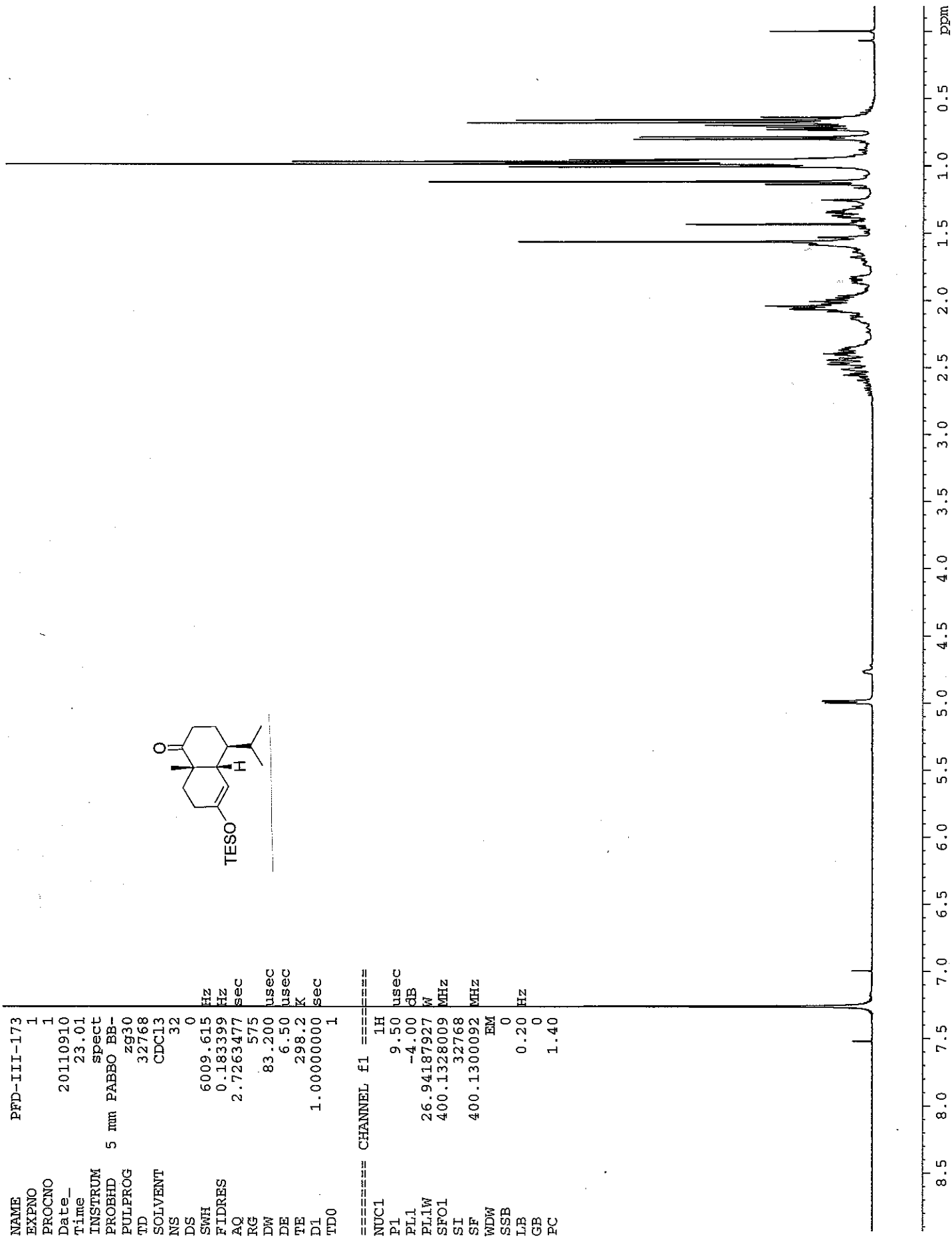
F2 - Acquisition Parameters
Date_           20110905
Time               17.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                41662
SOLVENT           CDCl3
NS                  117
DS                    0
SWH           29761.904 Hz
FIDRES         0.714366 Hz
AQ             0.6999716 sec
RG                  912
DW                16.800 usec
DE                 6.50 usec
TE                300.2 K
D1           1.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 9.13 usec
PLW1       123.02999878 W
SFO1        125.7703637 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            80.00 usec
PLW2        19.15500069 W
PLW12        0.43459001 W
PLW13        0.27814001 W
SFO2        500.1320005 MHz

F2 - Processing parameters
```




NAME PFD-III-173
EXPNO 1
PROCNO 1
Date_ 20110910
Time 23.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 575
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
O
H
TESO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

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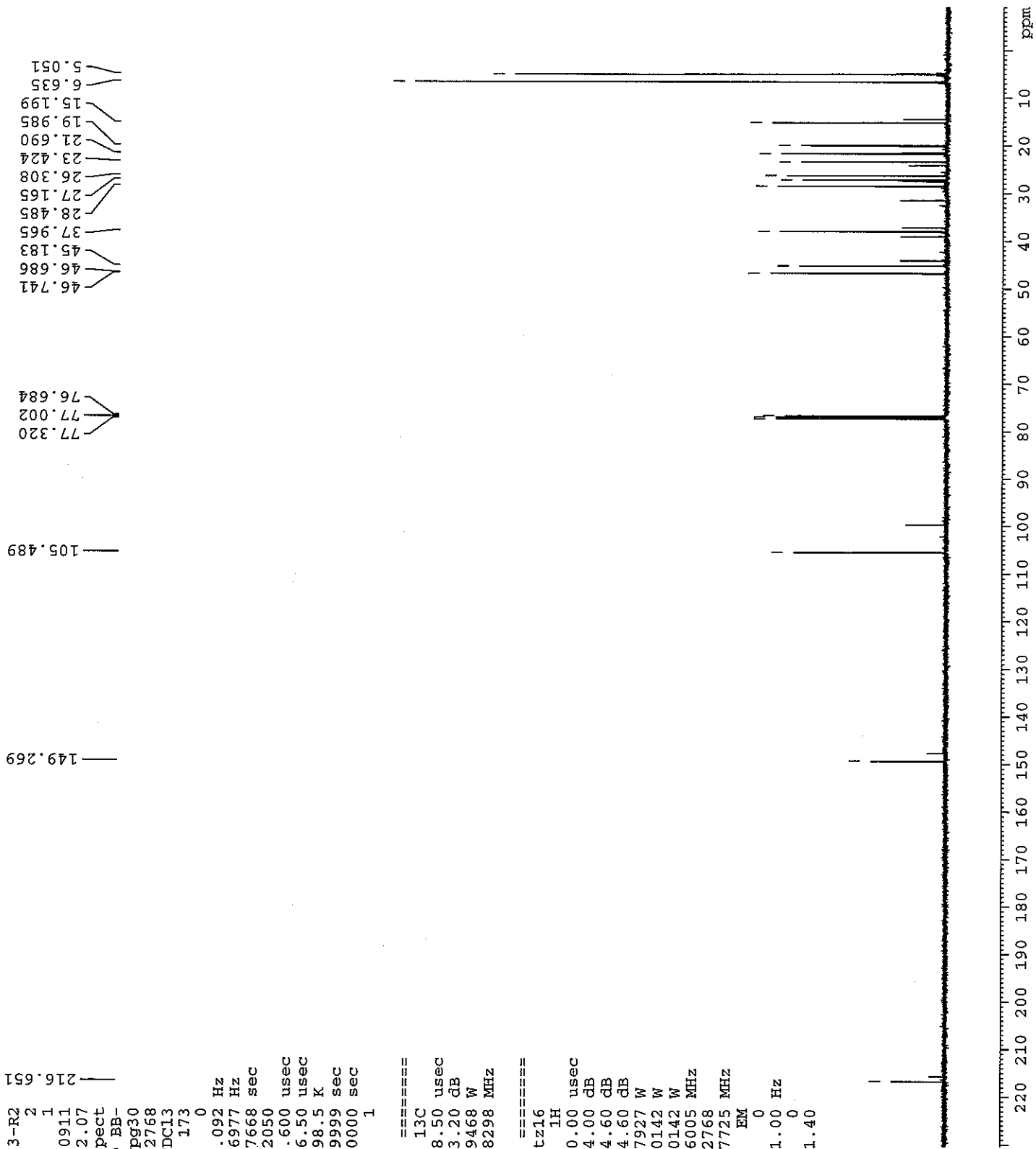


```
NAME                PFD-III-173-R2
EXPNO                            2
PROCNO                           1
Date_                     20110911
Time                         12.07
INSTRUM                      spect
PROBHD  5 mm PABBO BB-
PULPROG                    zgpg30
TD                          32768
SOLVENT                     CDCl3
NS                            173
DS                              0
SWH                     28409.092 Hz
FIDRES                  0.866977 Hz
AQ                      0.5767668 sec
RG                           2050
DW                         17.600 usec
DE                          6.50 usec
TE                         298.5 K
D1                      0.69999999 sec
D11                     0.03000000 sec
TD0                              1

======== CHANNEL f1 ========
NUC1                          13C
P1                          8.50 usec
PL1                         3.20 dB
PL1W                   49.53329468 W
SFO1                   100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                    waltz16
NUC2                            1H
PCPD2                      80.00 usec
PL2                        -4.00 dB
PL12                       14.60 dB
PL13                       14.60 dB
PL2W                   26.94187927 W
PL12W                   0.37190142 W
PL13W                   0.37190142 W
SFO2                   400.1316005 MHz
SI                          32768
SF                     100.6127725 MHz
WDW                            EM
SSB                             0
LB                          1.00 Hz
GB                              0
PC                          1.40
```

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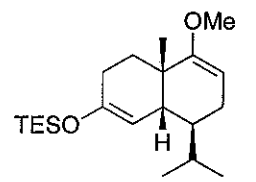
```
Current Data Parameters
NAME         PFD-III-176
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110913
Time               22.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 40498
SOLVENT            CDCl3
NS                    28
DS                     0
SWH             7500.000 Hz
FIDRES          0.185194 Hz
AQ             2.6999166 sec
RG                    36
DW                66.667 usec
DE                 6.50 usec
TE                299.9 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PLW1         16.98200035 W
SFO1         500.1332508 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300134 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.40
```



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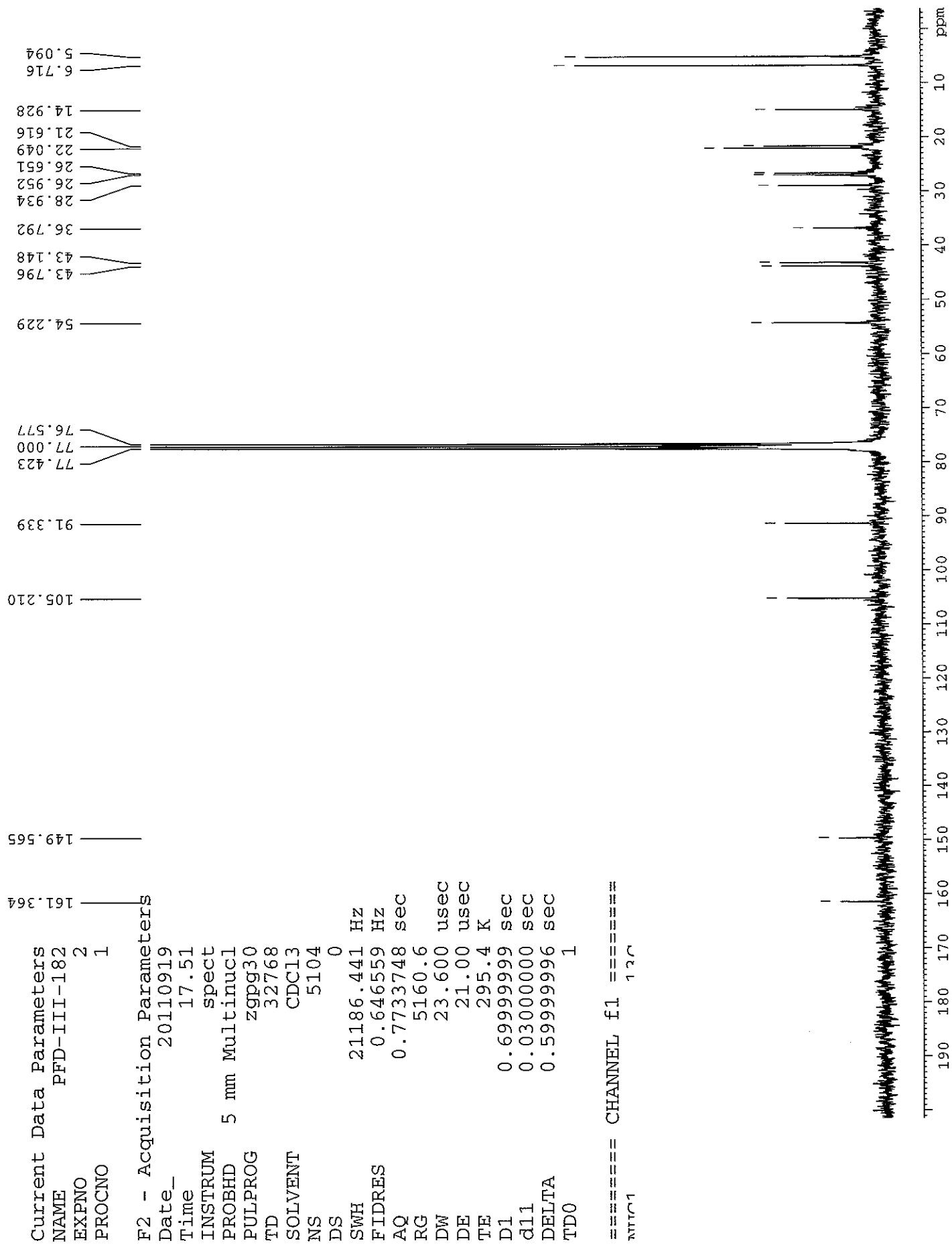

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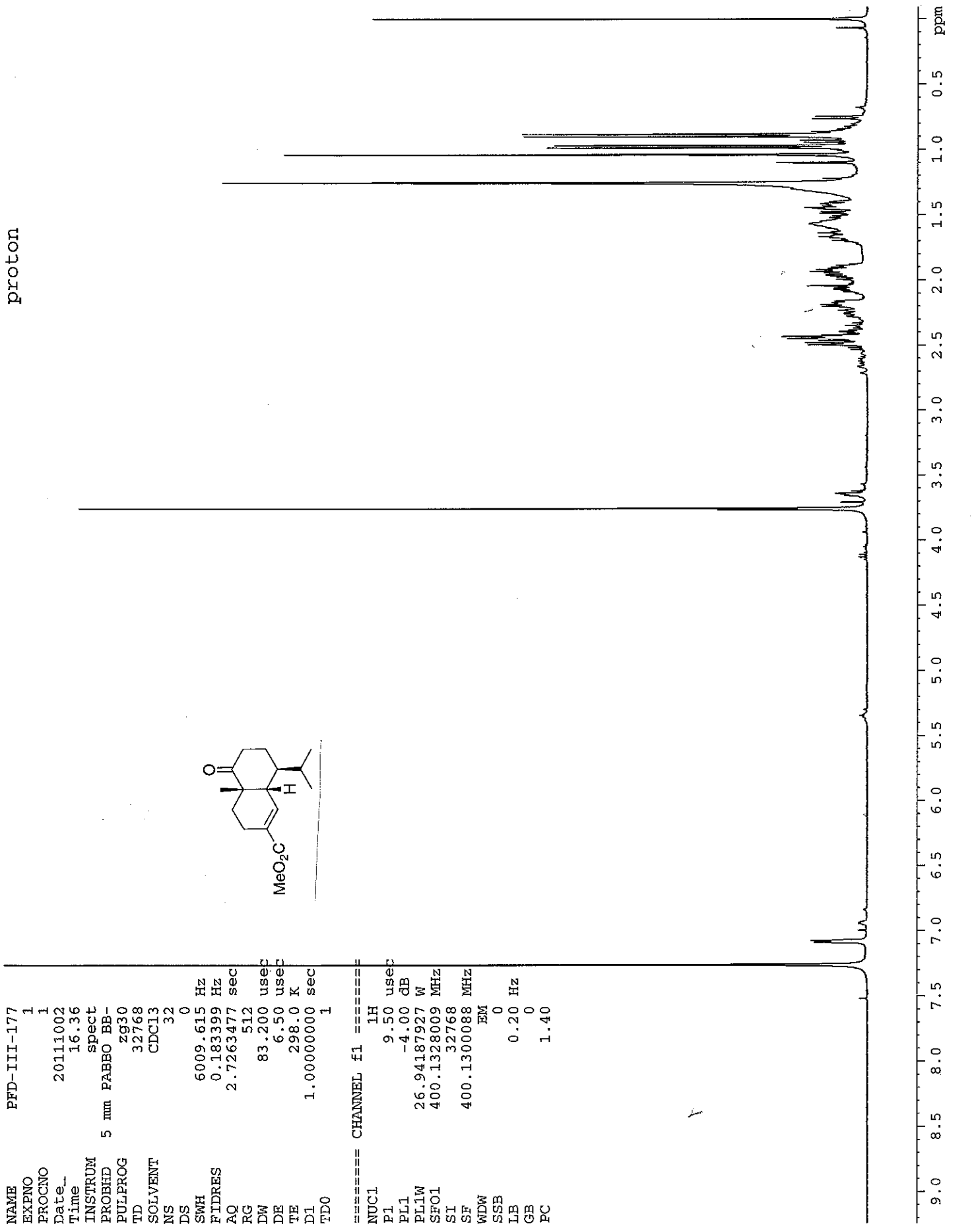
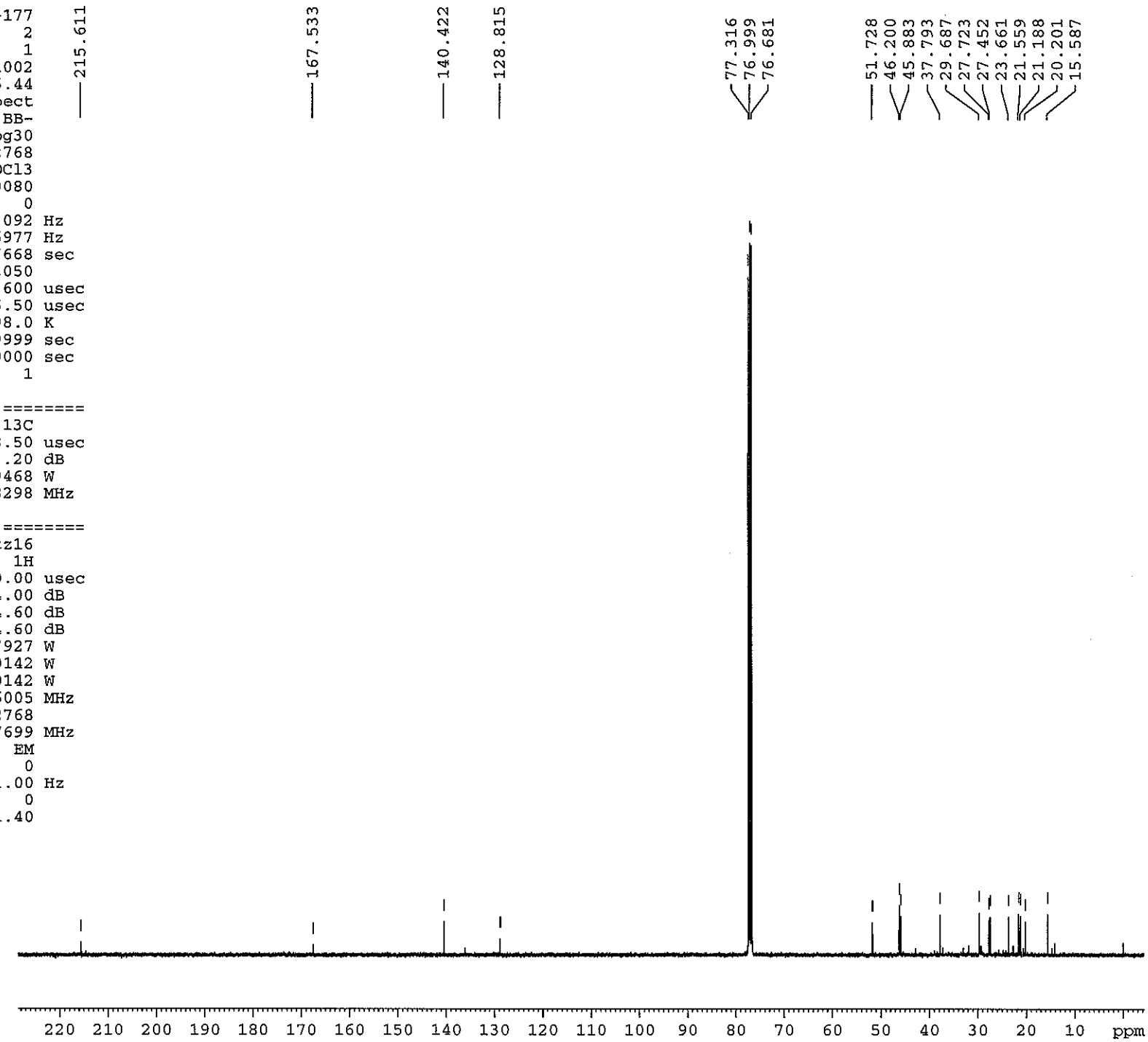


NAME	PFD-III-177
EXPNO	2
PROCNO	1
Date_	20111002
Time	16.44
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	10080
DS	0
SWH	28409.092 Hz
FIDRES	0.866977 Hz
AQ	0.5767668 sec
RG	2050
DW	17.600 usec
DE	6.50 usec
TE	298.0 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127699 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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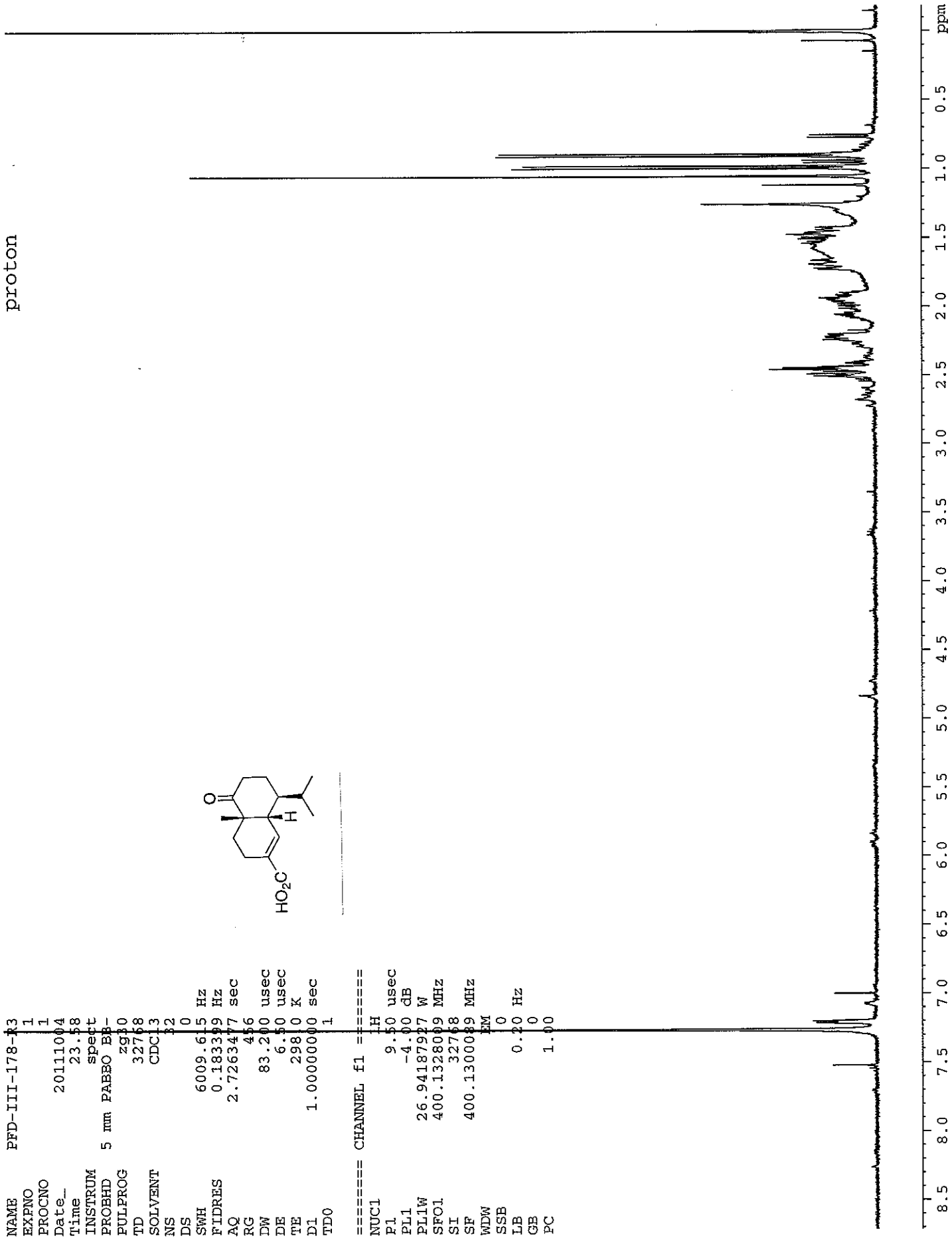

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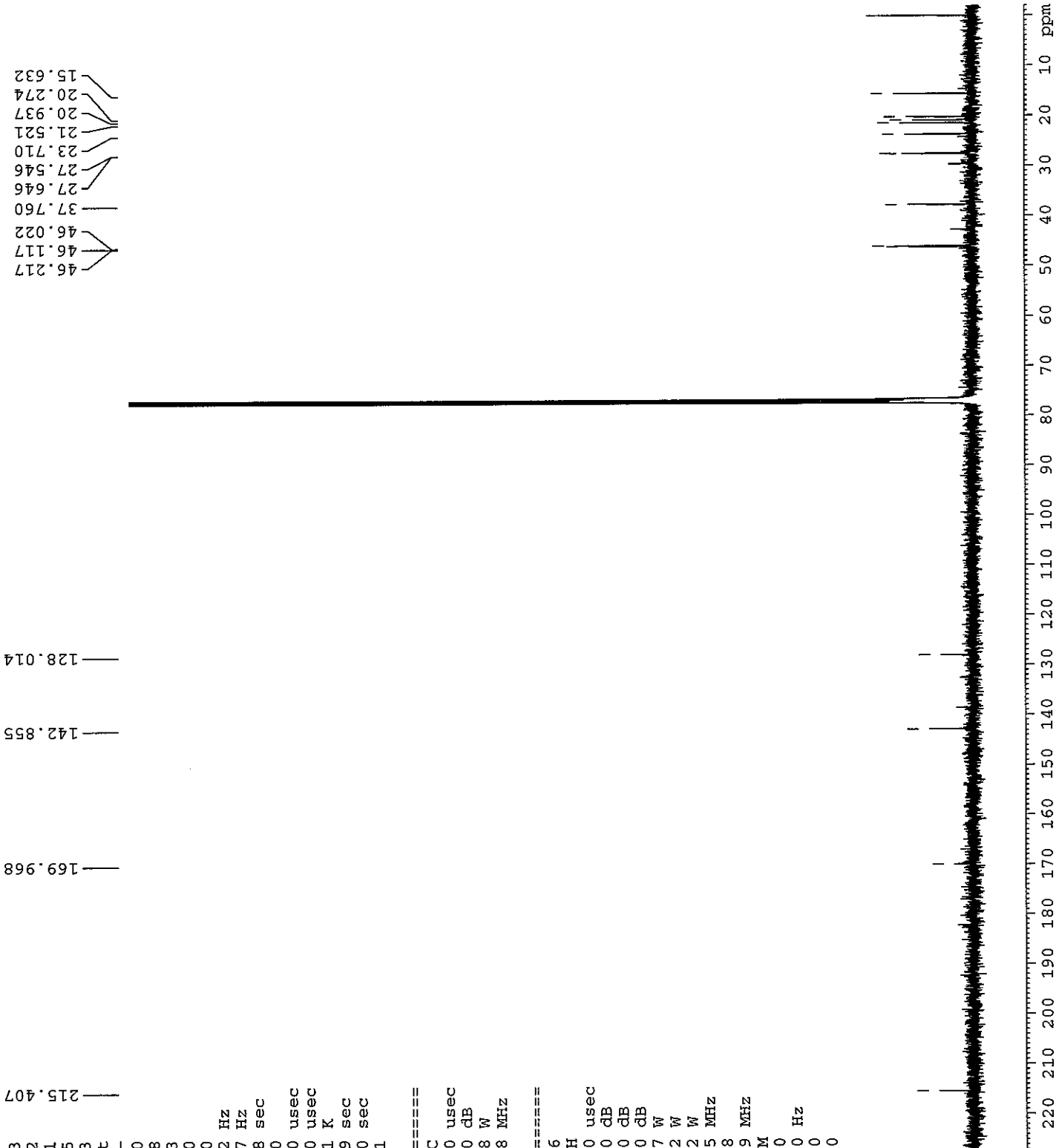


```
NAME          PFD-III-178-R3
EXPNO                  2
PROCNO                 1
Date_           20111005
Time                0.03
INSTRUM             spect
PROBHD  5 mm PABBO BB-
PULPROG            zgpg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH             28409.092 Hz
FIDRES              0.866977 Hz
AQ                0.5767668 sec
RG                   2050
DW                 17.600 usec
DE                  6.50 usec
TE                 298.1 K
D1                 0.69999999 sec
D11                0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                 3.20 dB
PL1W           49.53329468 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -4.00 dB
PL12               14.60 dB
PL13               14.60 dB
PL2W           26.94187927 W
PL12W           0.37190142 W
PL13W           0.37190142 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127699 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

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