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Solid-Phase Synthesis of Diverse E- and F-Series Prostaglandins

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Supplementary Material

General

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Tetrakis(triphenylphosphine)palladium was prepared according to the literature procedure.[1] 3-buten-1-ol methyl ether was prepared according to the method of Brown and coworkers.[2] (S)-1-Octyn-3-ol was purchased from Aldrich and protected with triethylsilyl chloride under standard conditions. The alkyne 4,4-dimethyl-1-octyn-3-ol was prepared according the the literature procedure and protected with triethylsilyl chloride under standard conditions.[3] Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium/benzophenone immediately before use. Pyridine and dichloromethane were distilled under N_2 from sodium hydride, and toluene was distilled from sodium. All reactions were run under a blanket of dry nitrogen using standard techniques unless stated otherwise. Organic layers were dried over anhydrous magnesium sulfate unless stated otherwise. Flash column chromatography was carried out using Merck 60 230-400 mesh silica gel. Thin layer chromatography (tlc) analyses were performed with Merck Kieselgel 60 F_{254} plates and visualized using *p*-anisaldehyde staining. ^1H NMR spectra were obtained with a Bruker AMX-300, AMX-400, AM-400 or AM-500 FT spectrometer. Proton-decoupled ^{13}C spectra were obtained with the same instruments with a line broadening of 1.5 Hz. Chemical shifts are reported in ppm, and coupling constants are reported in Hertz. Unless otherwise noted, spectra were obtained in $CDCl_3$ with residual $CHCl_3$ as an internal standard at 7.26 ppm; spectra obtained in d_6-DMSO were referenced to the residual DMSO at 2.49 ppm. Elemental analyses were performed by M-H-W Labs, Phoenix, AZ, or by the University of California, Berkeley, Department of Chemistry Microanalytical Laboratory. Polystyrene SX-1 beads (200-400 mesh) were obtained from Bio-Rad. Most simple resin reactions at rt were carried out in fritted cartridges (Applied Separations). It was not necessary to use distilled solvents for rinsing of resin, and in the rinsing procedure a sufficient amount of solvent was added to slurry the beads followed by agitation for approximately 30 seconds, followed by draining the solvent. A filtration cannula (Pharmacia, Uppsala, Sweden) is useful for filtration of resins in round-bottom flasks.

Cis-(4(R)-tert-Butyldimethylsilyl)-2-bromo-cyclopentene-1,4-diol[4] 4-(R)-tert-butylsilyloxy-2-cyclopentenone (6.0 g, 28 mmol) was dissolved in 90 mL of CH_2Cl_2 in a 250 mL round-bottomed flask and chilled in an ice bath. Bromine (1.60 mL, 31.1 mmol) dissolved in 30 mL of CH_2Cl_2 was added dropwise at a slightly slower rate than the rate at which it reacts. After TLC eluting in 1:4 ethyl acetate/hexanes indicated conplete reaction, 4.5 g (45 mmol) of triethylamine dissolved in 30 mL of CH_2Cl_2 was added and the reaction was allowed to warm to rt over 1 h. The reaction solution was then extracted with a 1.0 M sodium bisulfate solution (3 x 50 mL), a saturated $NaHCO_3$ solution (3 x 50 mL) and brine (1 x 50 mL). The aqueous layers were back-extracted with CH_2Cl_2 (2 x 10

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(1) Coulson, D. R.; Satek, L. C.; Grim S. O. *Inorg. Syn.*, **1972**, 121-124.
(2) Brown, H. C.; G. J. Lynch. *J. Org. Chem.*, **1981**, *46*, 531-538.
(3) Bernady, K. F.; Floyd, M., Jr.; Poletto, J. F.; Schaub, R. E.; Weiss, M. J. U. S. Pat. 4 123 456, 1978.
(4) Nakazawa, M.; Sakamoto, Y.; Takahashi, T.; Tomooka, K.; Ishikawa, K.; Nakai, T. *Tetrahedron Lett.* **1993**, *34*, 5923-5926.

mL) and the combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The crude α-bromoenone was then dissolved in 200 mL of methanol and chilled to -78 °C. A solution was then prepared by dissolving 6.9 g (28 mmol) of anhydrous $CeCl_3$ in 80 mL of methanol with heating. The $CeCl_3$ solution was added to the chilled α-bromoenone solution and the temperature was allowed to return to -78 °C, at which time 1.1 g (29 mmol) of $NaBH_4$ was added. The reaction was monitored by tlc, and when complete (10 min or less) 50 mL of a saturated NH_4Cl solution was added slowly. The solution was diluted with 50 mL of water, and extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were washed with a saturated $NaHCO_3$ solution (1 x 25 mL) and brine (1 x 25 mL). The combined aqueous layers were back extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic layers were dried and concentrated to a brown-red oil. Chromatography eluting with 9:1 hexanes/ethyl acetate provided 7.26 g (88%) of product as a colorless oil. On storage at -20 °C for several days the product crystallized. A small crystal was saved as a seed and used to initiate crystallization of the rest of the product from pentane at -20 °C. White crystals (5.14 g, 62%) were obtained and found to be one diastereomer by ^1H and ^{13}C NMR spectroscopy. mp 44-45°C. IR: 3378, 2926, 1620, 1256, 1033 cm^{-1}. ^1H NMR (500 MHz) δ 0.071 (s, 3H), 0.072 (s, 3H), 0.87 (s, 9H), 1.70 (dt, 1H, J = 13.5, 4.8), 2.03 (d, 1H, J = 7.3), 2.78 (dt, 1H, J = 13.5, 7.2), 4.46 (m, 1H), 4.60 (m, 1H), 6.03 (d, 1H, J = 1.1). ^{13}C NMR (125 MHz) δ –4.7, 18.0, 25.8, 43.6, 73.4, 76.8, 129.4, 136.5.

Compound 2. In a round-bottomed flask 9.6 g (33 mmol) of (4(R)-tert-butyldimethylsilyl)-2-bromo-cyclopentene-1,4-diol (8:1 cis/trans) was dissolved in 66 mL of pyridine and 0.4 g (3.3 mmol) of 4-*N*,*N*-dimethylaminopyridine was added, followed by 18.4 g (49.9 mmol) of 4,4',4''-trimethoxytrityl chloride. The reaction mixture was stirred at 50 °C until tlc indicated complete reaction (approx. 1 h). The reaction solution was diluted with 200 mL of CH_2Cl_2 and extracted with a 1 M citric acid solution (3 x 50 mL), a saturated $NaHCO_3$ solution (3 x 50 mL), and brine (1 x 25 mL). The aqueous layers were separately back-extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The product was purified by chromatorgaphy eluting with 4:1 ethyl acetate/hexanes to afford 20.2 g (98%) of the title compound as a white foam. IR: 3394, 2955, 1608, 1508, 1251, 1176, 1038, 830 cm^{-1}. ^1H NMR (400 MHz) δ -0.20 (s, 3H), 0.15 (s, 3H), 0.86 (s, 9H), 1.71 (m, 1H), 2.17 (m, 1H), 3.82 (s, 9H), 4.24 (t, 1H, J = 6.3), 4.46 (dt, 1H, J = 1.7, 6.1), 6.07 (t, 1H, J = 1.7), 6.84 (d, 6H, J = 8.9), 7.46 (d, 6H, J = 8.9). ^{13}C NMR (100 MHz) δ -4.7, -4.6, 18.0, 25.7, 43.5, 55.1, 73.5, 76.7, 86.2, 112.9, 127.7, 130.4, 137.1, 137.2, 158.5. Anal. Calcd. for $C_{33}H_{41}O_5SiBr$: C, 63.35; H, 6.61. Found: C, 63.23; H, 6.67.

Compound 3. Compound **2** (20.2 g, 32.3 mmol) was dissolved in 50 mL of THF and 50 mL of a 1 M solution of TBAF in THF was added. The reaction solution was stirred at rt until tlc indicated completion, and then 100 mL of diethyl ether was added and the reaction solution was extracted with water (3 x 25 mL) and brine (1 x 25 mL). The aqueous layers were back-extracted with CH_2Cl_2 (2x 10 mL) and the combined organic layers were dried over Na_2SO_4. Chromatography eluting with 9:1 hexanes/ethyl acetate affords 15.4 g (94%) of the title compound as a white foamy solid. IR: 3388, 1607, 1507, 1249, 1176, 1033, 830 cm^{-1}. ^1H NMR (300 MHz) δ 1.0 (m, 1H), 1.64 (s, 1H, OH) 1.75 (dt, 1H, J = 7.0, 7.0) 3.79 (s, 9H), 4.25 (s, br, 1H), 4.50 (t, 1H, J = 5.6) 6.16 (s, 1H), 6.82 (d, 6H, J = 8.9), 7.47 (d, 6H, J = 8.9). ^{13}C NMR (75 MHz) δ 42.9, 55.1, 73.4, 77.5, 86.5, 113.0, 129.1, 130.3, 136.9, 137.2, 158.4. Anal. calcd. for $C_{27}H_{27}O_5Br$: C, 63.41; H, 5.32. Found: C, 63.14; H, 5.54.

Compound 5. A round-bottomed flask was charged with 20 mL of THF, and the solvent was chilled to -78 C. To the flask was added 13.2 mL of a 1.5 M solution of *tert*-butyllithium (19.8 mmol) in pentane. A solution of 5.9 g (9.4 mmol) of compound **2** (8:1 cis/trans) dissolved in 20 mL of THF was then added dropwise via syringe pump. After the addition was complete, 0.84 g (9.4 mmol) of copper cyanide was added and the solution was warmed to -40 °C for 15 min, at which time the solution became

homogeneous. The reaction solution was re-chilled to -78 °C and a solution of 2.0 g (10 mmol) of (Z)-1,3-dibromo-1-propene dissolved in 10 mL of THF was added dropwise via syringe pump. The reaction solution was stirred for 1 h at -78 °C and then the cooling bath was removed and the reaction solution was allowed to warm to -20 °C. The reaction was quenched by the addition of 30 mL of a saturated NH_4Cl solution, and 50 mL of diethyl ether was added. The aqueous layer was separated, and the organic layer was washed with 30 mL of a saturated NH_4Cl solution and 30 mL of brine. The combined aqueous layers were back-extracted with ether (2 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Chromatography eluting with a gradient of 9:1 hexanes/ethyl acetate increasing to 4:1 hexanes/ethyl acetate afforded 3.2 g (51%) of a white foamy solid. The solid (3.00 g, 4.44 mmol) was then dissolved in 10 mL of THF and treated with 11 mL of a 1 M solution of TBAF in THF (11 mmol). The reaction mixture was stirred at rt until tlc indicated completion (approx. 4 h) and then 20 mL of ether was added and the reaction solution was extracted with water (3 x 10 mL) and brine (1 x 10 mL). The combined aqueous layers were back-extracted with ether (2 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Chromatography eluting with a gradient of 19:1 hexanes/ethyl acetate increasing to 9:1 hexanes/ethyl acetate afforded 1.8 g (73%) of the title compound as a white foam. IR: 3406, 2835, 1607, 1507, 1249, 1176, 1035, 829 cm^{-1}. ^1H NMR (500 MHz) δ 1.25 (m, 1H), 1.58 (s, 1H, OH) 1.98 (m, 1H), 2.73 (dd, 1H, J = 17.6, 6.7), 3.14 (dd, 1H, J = 17.7, 6.3), 3.79 (s, 9H), 4.33 (s, br, 1H), 4.38 (t, 1H, J = 6.0), 5.57 (s, 1H), 6.18 (dt, 1H, J = 7.0, 7.0), 6.25 (d, 1H, J = 7.0), 6.83 (d, 6H, J = 8.9), 7.39 (d, 6H, J = 8.9). ^{13}C NMR (125 MHz) δ 29.4, 44.1, 55.2, 73.8, 77.2, 86.3, 109.0, 113.0, 130.2, 130.3, 131.9, 137.4, 146.3, 158.4. Anal. Calcd. for $C_{30}H_{31}O_5Br$: C, 65.34; H, 5.67. Found: C, 65.29; H, 5.77.

Sodium 1-(benzenesulfonamido)-6-heptenoate. In a 500 mL round-bottomed flask 6-heptenioc acid[5] (5.25 g, 41.0 mmol) was dissolved in 160 mL of THF and the solution was chilled to -15 °C. *N*-methylmorpholine (3.93 g, 38.9 mmol) was added, followed by isobutyl chloroformate (5.32 g, 38.9 mmol) at a dropwise rate over 15 min. When the addition was complete, a portion of *N,N*-dimethylaminopyridine (0.24 g, 2.0 mmol) was added, followed by a solution of benzenesulfonamide (6.13 g, 38.9 mmol) and *N*-methylmorpholine (3.93 g, 38.9 mmol) dissolved in 40 mL of DMF. The cooling bath was removed, and the solution was stirred for 2 h. The reaction mixture was poured into 40 mL of a 1 M $NaHSO_4$ solution in a separatory funnel and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were extracted once with 20 mL of a saturated $NaHCO_3$ solution and once with 20 mL of brine. The aqueous layers were back-extracted with 10 mL of ethyl acetate and the conbined organic layers wre dried and concentrated in vacuo. Chromatography eluting with 3:1:1 hexanes/ethyl acetate/CH_2Cl_2 removes unreacted benzenesulfonamide. Bulb to bulb distillation at 0.05 torr provides unreacted carboxylic acid (1.5 g, 29%, b.p. 80-100 °C, uncorrected) followed by 7.00 g (67%) of 1-benzenesulfonamido-6-heptenoic acid, b.p. 120-140 °C. The purified *N*-acylsulfonamide (7.00 g, 26.2 mmol) is dissolved in 100 mL of CH_3OH, and 0.500 g (21.8 mmol) of sodium is added in small pieces. After the metal has completely dissolved, the solvent is removed in vacuo to yield a white powder. Trituration with dry toluene until no more sulfonamide is visible by tlc gives 6.22 g (82%) of the analytically pure sodium salt. IR (KBr): 2929, 1602, 1446, 1377, 1233, 1136, 1093, 853 cm^{-1}. ^1H NMR (400 MHz, DMSO) δ 1.19 (quint, 2H, J = 7.5), 1.38 (quint, 2H, J = 7.5), 1.90 (q, 2H, J = 6.9), 2.06 (t, 2H, J = 7.3), 4.8-5.0 (m, 2H), 5.71-5.82 (m, 1H), 7.56 (t, 2H, J = 7.4), 7.67 (t, 1H, J = 7.4), 8.08 (d, 2H, J = 7.9) ^{13}C NMR (100 MHz, DMSO) δ 29.5, 32.8, 38.0,

(5) Although 6-heptenoic acid is commercially available from Aldrich, it is relatively expensive (~$45/g). It can easily be prepared from 7-octene-1,2-diol ($1.50/g) by sodium periodate cleavage followed by Jones oxidation and distillation in 70% overall yield.

42.2, 119.8, 132.0, 133.5, 136.9, 143.7, 147.8, 180.0. Anal. Calcd. For $C_{13}H_{16}NNaO_3S$: C, 53.97; H, 5.57; N, 4.84. Found: C, 54.00; H, 5.60; N, 4.90.

Bromopolystyrene (1.0 mmol/g): 30 g of Bio-Rad SX-1 beads are placed in a 500 mL round-bottomed flask and solvated in 300 mL of dry CCl_4. Thallium(III) acetate (1.00 g, 2.62 mmol) was added and the flask was covered with aluminum foil and the reaction mixture was stirred 30 min at rt. **CAUTION: Thallium acetate is a known poison. Handle only using proper safety precautions in a well ventilated hood.** The flask was placed on a heating mantle and 5.75 g (36 mmol) of bromine was added via syringe. The slurry was heated to reflux, and stirred at that temperature for 1.5 h. The slurry typically loses the red-brown color of bromine after about 10 min at reflux, and remains a dark reddish-brown until workup. The slurry was then allowed to cool to rt, and the beads were isolated by filtration on a coarse 600 mL glass fritted funnel. The beads were then washed with 1:1 acetone/water (3x), acetone (3x), benzene (3x) and methanol (3x) and dried in vacuo to yield 35.5 g (99%) of dry beads.

Chlorodibutylsilyl-derived polystyrene: Bromopolystyrene beads (10 g, 1.0 mmol/g, 20 mmol) were placed in a flask with a sidearm separated by a course filter. The beads were solvated in 100 mL of dry toluene, and 20 ml of 2.5 M n-BuLi in hexanes was added. The slurry was heated to 60 °C for 3 h and then allowed to cool to rt. The reaction solvent was drained through the sidearm, and the beads were washed with dry toluene (3x) and dry THF (3-5x, until the solvent drained was no longer bright yellow). The last portion of THF was removed, and the flask was placed in a bath at -20 °C. Enough dry THF to slurry the beads (approx. 30 mL) was added, followed by dichlorodibutylsilane (8.53 g, 0.0400 mol) distilled from sodium carbonate. The cooling bath was removed, and the reaction mixture was stirred for 2 h. The beads were then washed with distilled THF (3x), and distilled ether (3x) and dried with a stream of dry nitrogen. The chlorodibutylsilyl-derivatized beads are very sensitive to any moisture. For this reason, the loading step is typically performed without fully drying the beads or removing them from the nitrogen atmosphere.

Loading dibutylsilyl-derived polystyrene beads: Chlorodibutylsilyl-derivatized beads (7.0 g, 7.0 mmol) prepared above were swollen in 70 mL of dry CH_2Cl_2. Imidazole (1.42 g, 21.0 mmol) was added followed by 1.8 g (3.3 mmol) of compound **5**. The slurry was stirred at rt for 2 h, and then methanol (7 mL) was added and the slurry was stirred an additional 15 min. The solvents were then removed by filtration and the beads were washed with DMF/water 1:1 (3 x), DMF (3x), CH_2Cl_2 (3x), and ether (3x) and dried first by flushing with N_2 and then in vacuo (0.05 torr). TMT quantitation ($\varepsilon_{484} = 87\ 100$) gives a loading level of 0.35 mmol/g of beads, and 7.42 g of beads are recovered (80% loading efficiency). The alcohol **3** was loaded in an identical manner.

TMT Quantitation

The procedure is very similar to the DMT quantitation, described by Caruthers and coworkers, *Meth. Enzymol.* **1987**, *154*, 287-313. A 5 - 10 mg portion of resin **3** or **5** is weighed into a 10.0 mL volumetric flask. The TMT cation is released by addition of 10.0 mL of 3% trichloroacetic acid in CH_2Cl_2. The bright orange solution (100 mL) is diluted to 4.0 mL with a 0.1 M solution of *p*-toluenesulfonic acid monohydrate in acetonitrile, and the resulting solution is analyzed spectrophotometrically at 484 nm. The resin loading is calculated by the following equation:

$$\text{Loading (mmol/g)} = \frac{\text{Absorbance}}{217.75 \times (\text{amount of resin in grams})}.$$

The extinction coefficient of the TMT cation was determined by a 5-point titration curve collecting two repetitions per point with a 0.1 M solution of *p*-toluenesulfonic acid monohydrate in acetonitrile, and was determined to be 87,100 at 484 nm with a R value of 0.9999.

Solid-phase synthesis of prostaglandins. TMT Cleavage. Polystyrene beads (1.0 g, 0.46 mmol/g) loaded with the core **3** or **5** are placed in a fritted syringe and

solvated in 10 mL of CH_2Cl_2. The solvent is removed, and 10 mL of a 1 M solution of formic acid in CH_2Cl_2 is added. The solution is removed after 1.0 min and the beads are quickly rinsed with CH_2Cl_2 (3 x 10 mL). This procedure is repeated 4 times for a total HCOOH contact time of 5 min. After the last subjection the beads are rinsed with DMF (3x), CH_2Cl_2 (3x), and then THF (3x) and taken directly to the next step.

Suzuki-Miyuara coupling. An alkene (2.5 mmol) is dissolved in 10 mL of THF and treated with 0.28 g (2.3 mmol) of 9-BBN. The reaction solution is stirred for 6 h at rt. Separately, 1 g of resin **7** or **11** (0.46 mmol/g, 0.46 mmol) is placed in a 50 mL round-bottomed flask. The solution of the hydroborated alkene is added via cannula. A 2.5 mL portion of 2 M Na_2CO_3 is then degassed by bubbling nitrogen through the solution for 10 min, and then the degassed solution is added to the solvated beads. The flask is then charged with 75 mg of $Pd(PPh_3)_4$ (0.065 mmol) and a condenser is placed on the flask. The solution is heated to reflux and stirred at that temperature for 12 h. The slurry is allowed to cool, and then the beads are washed with DMF/water (3x), DMF (3x), CH_2Cl_2 (3x), and ether (3x) and dried *in vacuo*.

Oxidation. Support-bound alcohol beads from above (1.0 g, 0.46 mmol/g, 0.46 mmol) are placed in a 50 mL round-bottomed flask and solvated in 10 mL of CH_2Cl_2. A 0.6 g (1.41 mmol) portion of Dess-Martin periodinane is then added and a condenser is placed on the flask. The slurry is heated to reflux for 2 h, and then allowed to cool to rt. The beads are then washed with DMF (3x), CH_2Cl_2 (3x), and ether (3x) and dried *in vacuo*.

Cuprate addition: A solution of 1.00 mmol of an 1-alkyne in 5 mL of THF is treated with 0.257 g (1.00 mmol) of Cp_2ZrHCl. After 20 min at rt, the homogeneous solution is chilled to -78 °C and treated with 2.0 mmol of a 1.4 M solution of methyllithium in diethyl ether. After 15 min copper (I) cyanide (89.6 mg, 1.00 mmol) is added, followed by an additional 1.0 mmol of 1.4 M methyllithium in ether. The solution is warmed to -20 °C for 15 min, at which time it again becomes homogeneous, and then the solution is rechilled to -78 °C. In a separate flask, support-bound enone beads **8** or **12** from above (0.40 g, 0.50 mmol/g, 0.20 mmol) are solvated in 3 mL of THF. The slurry is chilled to -78 °C and the chilled cuprate solution is added to the beads by teflon cannula. The reaction slurry is stirred at -78 °C for 30 min and then warmed to -20 °C for 15 min to ensure complete reaction. The solution is then re-chilled to -78 °C and the reaction is quenched by the addition of 10 mL of a chilled (-78 °C) 10% solution of acetic acid in THF. The solution is removed and the beads are rinsed with 1:1 DMF/water (3x), DMF (3x), CH_2Cl_2, and ether (3x).

Optional Reduction: Resin (0.40 g, 0.46 mmol/g, 0.18 mmol) is swollen in 4.0 mL of THF. The slurry is chilled to -78 °C and 1.0 mL of a 1 M solution of L-selectride in THF is added. The slurry is stirred at -78 °C for 1 h and then quenched with 10 mL of a prechilled 10% solution of acetic acid in THF. The solution is removed and the beads are rinsed with 1:1 DMF/water (3x), DMF (3x), CH_2Cl_2, and ether (3x).

Activation of *N*-acylculfonamide resin: Resin (0.40 g, 0.46 mmol/g, 0.18 mmol) is solvated in 4 mL of dry *N*-methylpyrrolidone. Bromoacetonitrile is run through a plug of activated basic alumina, and then 0.48 g (4.0 mmol) of bromoacetonitrile is added to the resin slurry with slow stirring. Diisopropylethylamine (0.26 g, 2 mmol) is then added, and the reaction slurry is slowly stirred for 6 h. The solution is removed and the beads are rinsed with NMP (3x), CH_2Cl_2, and ether (3x).

Displacement of the activated sulfonamide: The resin (0.20 g, 0.45 mmol/g, 0.090 mmol) is solvated in 2.0 mL of dry NMP. **For amines:** 2.0 mmol of an amine is added and the slurry is stirred for 15 min at rt. The solution is removed and the beads are rinsed with DMF (3x), CH_2Cl_2, and ether (3x). **For alcohols:** 4.0 mmol of an alcohol and 33 mg (0.27 mmol) of *N,N*-dimethylaminopyridine are added. The reaction slurry is heated to 50 °C and stirred for 6 h (methanol and ethanol) or 8 h (isopropanol). The solution is removed and the beads are rinsed with DMF (3x), CH_2Cl_2, and ether (3x).

Cleavage: Beads (0.20 g, 0.45 mmol/g, 0.090 mmol) are swollen in THF in a disposable glass vial. HF/pyridine solution (17.5% HF, 0.5 mL) is added, and the slurry

is stirred at rt for 2 h. The beads are separated from the solution and washed with 2 additional 1 mL portions of THF. The combined THF layers are diluted with 5 mL of ethyl acetate and the organic layer is washed with a saturated bicarbonate solution (2 x 5 mL) and brine (1 x 5 mL). The combined aqueous layers are back-extracted with 3 x 2 mL of ethyl acetate, and the combined organic layers are dried and concentrated. Chromatography eluting with a gradient of 3:2 ethyl acetate/hexanes increasing to 4:1 ethyl acetate/hexanes provides the E series prostaglandins and chromatography eluting with a gradient of 4:1 ethylacetate/hexanes increasing to pure ethyl acetate provides the F series prostaglandins.

Physical properties of prostaglandins in table 1.

For most of the prostaglandins isolated, the alcohol OH peaks were very broad or rapidly exchanged with water in the solvent, and are not reported except where noted in entry 10.

Entry 1. IR: 3386, 2930, 1744, 1120, 1078 cm^{-1}. ^1H NMR (300 MHz) δ 0.88 (t, 3H, J = 6.8), 1.20-1.45 (m, 7H), 1.45-1.61 (m, 4H), 2.01 (q, 2H, J = 7.3), 2.07 (dt, 1H, J = 11.6, 5.8), 2.19 (dd, 1H, J = 18.5, 9.9), 2.30-2.42 (m, 4H), 2.73 (ddd, 1H, J = 19.6, 7.4, 1.2), 3.31 (s, 3H), 3.36 (t, 2H, J = 6.4), 4.00-4.10 (m, 2H), 5.22-5.32 (m, 1H), 5.36-5.47 (m, 1H), 5.56 (dd, 1H, J = 15.2, 8.2), 5.63 (dd, 1H, J = 15.2, 7.5). ^{13}C NMR (100 MHz) δ 14.0, 22.6, 25.0, 25.2, 26.0, 27.1, 29.2, 31.7, 37.3, 46.1, 53.7, 54.6, 58.5, 72.0, 72.7, 73.0, 125.6, 131.4, 131.9, 136.9, 214.2. HRMS (FAB, m-nitrobenzyl alcohol + LiCl) calcd. for $C_{21}H_{36}O_4Li$ (M+Li) 359.277364, found 359.277100. Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.55; H, 10.29. Found: C, 71.45; H, 10.08.

Entry 2. IR 3374, 2228, 2857, 1743, 1077, 1154, 968 cm^{-1}. ^1H NMR (500 MHz) δ 0.87 (t, 3H, J = 6.8), 0.88 (t, 3H, J = 6.9), 1.20-1.35 (m, 14H), 1.45-1.52 (m, 1H), 1.52-1.60 (m, 1H), 1.97 (q, 2H, J = 7.1), 2.08 (dt, 1H, J = 12.2, 5.4), 2.18 (dd, 1H, J = 10.0, 10.0), 2.33 (t, 2H, J = 6.4), 2.38 (m, 1H), 2.72 (dd, 1H, J = 18.2, 7.2), 4.03 (q, 1H, J = 8.8), 4.08 (q, 1H, J = 6.9), 5.20-5.27 (m, 1H), 5.39-5.44 (m, 1H), 5.51 (dd, 1H, J = 15.2, 8.8), 5.62 (dd, 1H, J = 15.2, 7.7). ^{13}C NMR (125 MHz) δ 14.0, 14.1, 22.6, 22.6, 24.9, 25.2, 27.4, 29.0, 29.5, 31.7, 31.8, 37.3, 46.1, 53.8, 54.7, 71.9, 73.3, 125.0, 132.1, 132.4, 136.8, 214.2. Anal. Calcd. for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93. Found: C, 75.44; H, 10.70.

Entry 3. This compound was isolated as an approximate 1:1 mixture of diastereomers at the C_{15} hydroxyl group. IR: 3438, 2932, 2862, 1743, 1118, 1082 cm^{-1}. ^1H NMR (400 MHz) δ 0.76 (m, 18H), 1.15-1.40 (m, 14H), 1.50-1.60 (m, 4H), 1.90-2.25 (m, 10H), 2.35-2.24 (m, 6H), 2.70 (t, 1H, J = 6.6), 2.74 (t, 1H, J = 6.6), 3.30 (s, 3H), 3.31 (s, 3H), 3.35 (m, 2H), 3.36 (m, 2H), 3.74 (d, 1H, J = 7.8), 3.84 (d, 1H, J = 6.7), 4.03 (q, 1H, J = 7.8), 4.06 (q, 1H, J = 7.5), 5.24-5.54 (m, 2H), 5.36-5.46 (m, 2H), 5.57 (dd, 1H, J = 15.2, 9.0), 5.60 (dd, 1H, J = 15.2, 9.0), 5.71 (dd, 1H, J = 15.2, 6.8), 5.73 (dd, 1H, J = 15.2, 6.8). ^{13}C NMR (100 HMz) δ 14.1, 22.7, 22.8, 23.0, 23.7, 25.0, 25.1, 25.9, 26.0, 27.1, 29.2, 29.2, 37.1, 37.4, 38.6, 38.7, 46.2, 46.4, 53.3, 53.8, 54.6, 54.7, 58.5, 72.0, 72.2, 72.7, 72.7, 79.0, 79.9, 125.6, 125.6, 131.1, 131.9, 132.0, 133.5, 133.8, 214.3. HRMS (FAB, m-nitrobenzyl alcohol + LiCl) calcd. for $C_{23}H_{40}O_4Li$ (M+Li) 387.308665, found 387.308500.

Entry 4. IR: 3375, 2929, 2858, 1457, 1120, 969 cm^{-1}. ^1H NMR (500 MHz) δ 0.88 (t, 3H, J = 6.6), 1.23-1.53 (m, 9H), 1.53-1.66 (m, 4H), 1.71 (dd, 1H, 14.7, 3.0), 2.23-2.28 (m, 3H), 2.20-2.30 (m, 3H), 3.32 (s, 3H), 3.37 (t, 2H, J = 6.5H), 3.90 (m, br, 1H), 4.04 (q, 1H, J = 7.0), 4.15 (m, br, 1H), 5.38-5.42 (m, 2H), 5.45 (dd, 1H, J = 15.2, 7.4), 5.54 (dd, 1H, 15.2, 7.4). ^{13}C NMR (125 MHz) δ 14.0, 22.6, 25.2, 25.5, 26.1, 27.0, 29.1, 31.7, 37.2, 42.8, 50.1, 55.7, 58.5, 72.7, 72.7, 73.1, 77.7, 128.2, 130.6, 132.9, 135.4. HRMS (FAB, m-nitrobenzyl alcohol) calcd. for $C_{21}H_{39}O_4$ (M+H) 355.284835, found 355.284710. Anal. Calcd. for $C_{21}H_{38}O_4$: C, 71.14; H, 10.80. Found: C, 71.01; H, 10.59.

Entry 5. IR: 3367, 2925, 2856, 1738, 1075 cm^{-1}. ^1H NMR 500 (MHz) δ 0.85 (t, 3H, J = 7.1), 0.87 (t, 3H, J = 6.6), 1.14-1.35 (m, 13H), 1.35-1.52 (m, 2H), 1.52-1.66 (m, 2H), 1.97 (dt, 1H, J = 12.1, 6.0), 2.20 (dd, 1H, J = 18.3, 10.0), 2.31 (dt, 1H, J = 12.1,

8.9), 2.70 (dd, 1H, J = 18.4, 7.4), 2.92 (s, br, 1H), 4.00 (q, 1H, J = 8.6), 4.07 (q, 1H, J = 7.1), 5.51 (dd, 1H, J = 15.2, 8.9), 5.62 (dd, 1H, J = 15.2, 7.8). ^{13}C NMR (125 MHz) δ 14.0, 14.0, 22.6, 25.1, 26.8, 27.8, 29.4, 29.7, 31.6, 31.6, 37.2, 45.8, 54.6, 55.0, 71.8, 73.3, 132.5, 136.6, 214.8. HRMS (FAB, m-nitrobenzyl alcohol + LiCl) calcd. for $C_{19}H_{34}O_3Li$ (M+Li) 317.266800, found 317.266370.

Entry 6. IR: 3354, 2927, 2856, 1458, 1339, 1078, 971, 750 cm^{-1}. ^1H NMR (500 MHz) δ 0.87 (t, 3H, J = 6.7), 0.88 (t, 3H, J = 6.8), 1.20-1.60 (m, 18H), 2.18 (dd, 1H, J = 14.7, 3.1), 2.20-2.30 (m, 2H), 2.55-2.65 (m, 1H), 3.96 (s, br, 1H), 4.09 (q, 1H, J = 6.9), 4.22 (s, br, 1H), 5.51 (dd, 1H, J = 15.2, 8.9), 5.58 (dd, 1H, J = 15.2, 7.6). ^{13}C NMR (100 MHz) δ 14.0, 14.0, 22.6, 22.6, 25.1, 28.0, 28.1, 29.6, 31.7, 31.8, 37.3, 43.0, 50.6, 56.3, 72.6, 73.6, 78.6, 132.3, 134.4. Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.03; H, 11.61. Found: C, 72.82; H, 11.99.

Entry 7. IR: 3374, 2931, 2858, 1735, 1450, 1345, 1170, 1087 cm^{-1}. ^1H NMR (500 MHz) δ 0.86 (t, 3H, J = 6.8), 1.15-1.40 (m, 11H), 1.50-1.65 (m, 6H), 1.97-2.05 (m, 1H), 2.17-2.30 (m, 4H), 2.32-3.41 (m, 1H), 2.72 (dd, 1H, J = 18.6, 7.3), 4.00-4.15 (m, 2H), 5.55 (dd, 1H, J = 15.2, 8.7), 5.65 (dd, 1H, J = 15.2, 7.1), 7.52 (t, 2H, J = 7.6), 7.62 (t, 1H, J = 7.4), 8.03 (d, 2H, J = 8.6). ^{13}C NMR (125 MHz) δ 14.0, 22.6, 24.1, 25.1, 26.1, 27.2, 28.3, 28.8, 31.6, 36.2, 37.1, 46.0, 54.3, 54.4, 71.8, 73.0, 128.1, 128.9, 131.6, 133.8, 136.7, 138.8, 171.8, 215.7. Anal. Calcd. for $C_{26}H_{39}NO_6S$: C, 63.26; H, 7.96; N, 2.84. Found: C, 63.01; H, 7.81; N, 2.83.

Entry 8. IR: 3351, 2932, 2858, 1739, 1652, 1545, 1078 cm^{-1}. ^1H NMR δ (300 MHz) 0.87 (t, 3H, J = 16.1), 1.15-1.65 (m, 17H), 1.96 (dt, 2H, J = 12.0, 6.0), 2.13-2.25 (m, 3H), 2.27-2.39 (m, 1H), 2.69 (dd, 1H, J = 17.7, 7.1), 4.00 (q, 1H, J = 8.3), 4.05-4.10 (m, 1H), 4.41 (d, 2H, J = 5.7), 5.54 (dd, 1H, J = 15.2, 8.5), 5.63 (dd, 1H, J = 15.2, 7.1), 5.90 (s, br, 1H), 7.20-7.40 (m, 5H). ^{13}C NMR (125 MHz) δ 14.0, 22.6, 25.1, 25.4, 26.3, 27.5, 28.8, 29.1, 31.7, 36.6, 37.2, 43.6, 45.9, 54.3, 54.6, 71.8, 71.8, 127.5, 127.8, 128.7, 131.5, 136.9, 138.2, 173.1, 215.0. Anal. Calcd. for $C_{27}H_{41}NO_4$: C, 73.10; H, 9.32; N, 3.16. Found: C, 73.34, H, 9.12; N, 3.34.

Entry 9. IR : 3396, 2930, 2857, 1738, 1464, 1161 cm^{-1}. ^1H NMR (500 MHz) δ 0.88 (t, 3H, J = 6.8), 1.24 (t, 3H, J = 14.6), 1.23-1.38 (m, 11H), 1.42-1.63 (m, 6H), 1.97 (dt, 1H, J = 12.0, 6.0), 2.20 (dd, 1H, J = 18.5, 9.9), 2.26 (t, 2H, J = 7.5), 2.32 (dt, 1H, J = 12.1, 9.0), 2.70 (m, 2H), 3.66 (s, br, 1H), 4.02 (q, 1H, J = 8.8), 4.50 (q, 2H, J = 7.1), 5.54 (dd, 1H, J = 15.2, 8.9), 5.64 (dd, 1H, J = 15.2, 7.3). ^{13}C NMR (100 MHz) δ 13.9, 14.2, 22.5, 24.8, 25.1, 26.5, 27.6, 28.8, 29.3, 31.6, 34.2, 37.2, 45.8, 54.4, 54.8, 60.2, 71.8, 73.0, 131.9, 136.7, 173.8, 214.6. Anal. Calcd. for $C_{22}H_{38}O_5$: C, 69.07; H, 10.01. Found, C, 69.37; H, 9.74.

Entry 10. IR: 3371, 2929.5, 2857, 1739, 1169.9 cm^{-1}. ^1H NMR (500 MHz) δ 0.88 (t, 3H, J = 6.7), 1.20-1.50 (m, 14H), 1.52-1.65 (m, 4H), 1.73 (dd, 1H, J = 14.8, 3.0), 1.88 (s, br, 1H), 2.16-2.21 (m, 2H), 2.29 (t, 2H, J = 7.5), 2.34 (s, br, 1H (OH)), 2.45 (s, br, 1H, OH)), 3.20 (s, br, 1H (OH)), 3.66 (s, 3H), 3.92 (s, br 1H), 4.04 (q, 1H, J = 6.7), 4.16 (s, br, 1H), 4.55 (dd, 1H, J = 15.2, 8.9), 5.52 (dd, 1H, J = 15.2, 7.2). ^{13}C NMR (125 MHz) δ 14.0, 22.6, 24.8, 25.2, 27.6, 27.7, 29.0, 29.5, 31.7, 34.0, 37.2, 42.9, 50.1, 51.5, 56.2, 73.0, 73.2, 78.0, 133.2, 135.0, 174.4. HRMS (FAB, m-nitrobenzyl alcohol + LiCl) calcd. for $C_{21}H_{38}O_5Li$ (M+Li) 377.287929, found 377.287210.

Entry 11. IR: 3363, 2431, 2857, 1733, 1467, 1109 cm^{-1}. ^1H NMR (500 MHz) δ 0.88 (t, 3H, J = 6.9), 1.20 (d, 6H, J = 6.2), 1.23-1.34 (m, 11H), 1.34-1.5 (m, 4H), 1.5-1.64 (m, 4H), 1.72 (dd, 1H, J = 14.9, 3.3), 2.17-2.25 (m, 2H), 2.24 (t, 2H, J = 7.5), 3.87-3.92 (m, 1H), 4.03 (q, 1H, J = 6.8), 4.15 (m, 1H), 4.98 (septet, 1H, J = 6.3), 5.44 (dd, 1H, J = 15.2, 9.0), 5.51 (dd, 1H, J = 15.2, 7.4). ^{13}C NMR (125 MHz) δ 14.0, 21.8, 22.6, 24.8, 25.2, 27.6, 27.8, 28.9, 29.5, 31.7, 34.6, 37.2, 42.9, 50.1, 56.2, 67.4, 73.0, 73.2, 78.1, 133.2, 135.0, 173.5. HRMS (FAB, m-nitrobenzyl alcohol + LiCl) calcd. for $C_{23}H_{42}O_5Li$ (M+Li) 405.319229, found 405.319650.

Proton Starting Parameters, 10/06/92 RN rev.5/9/94.

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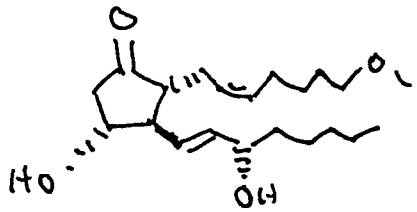

VI-83

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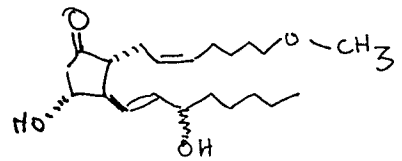

VI-83

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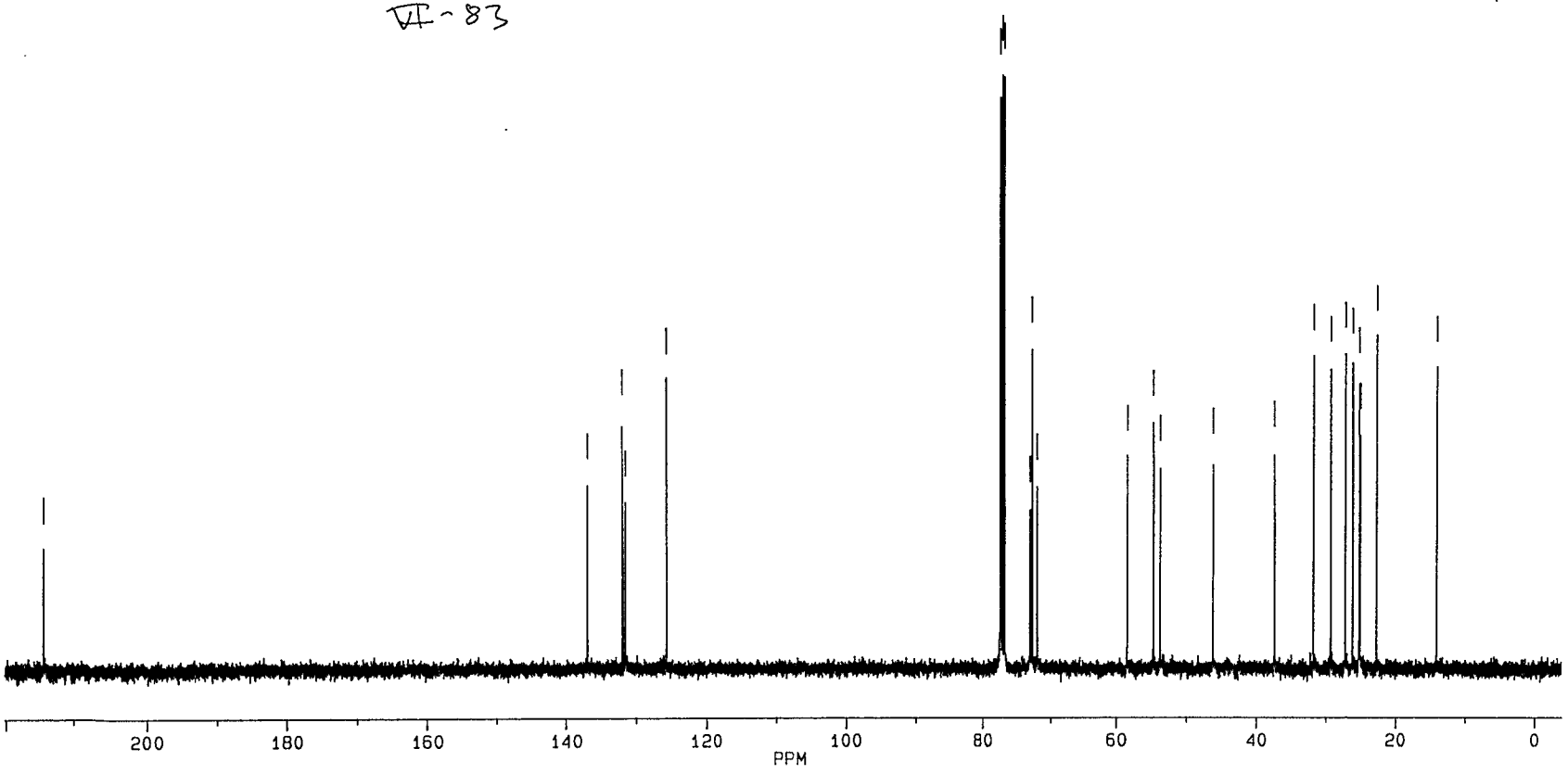

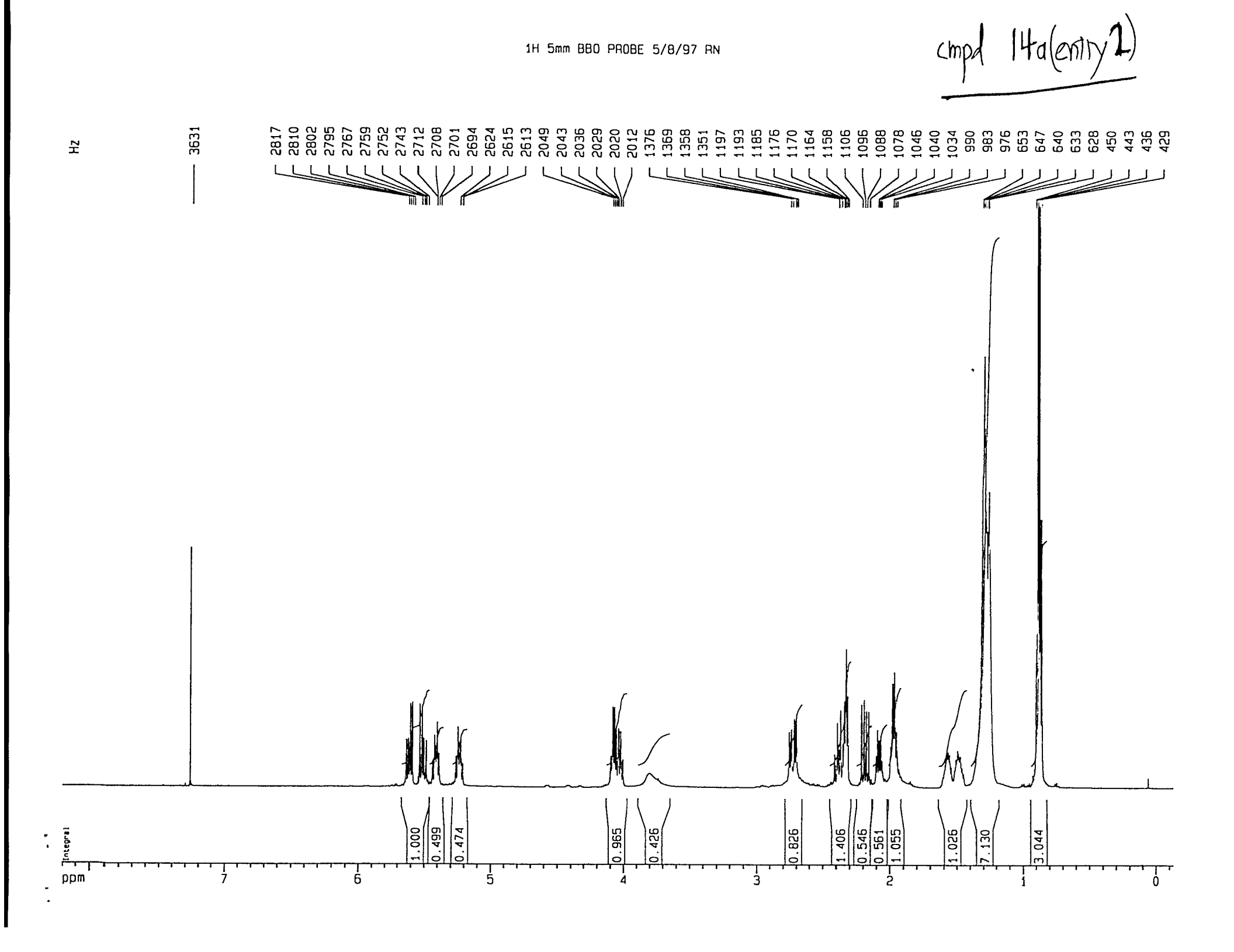
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cmpl 14a (entry 2)

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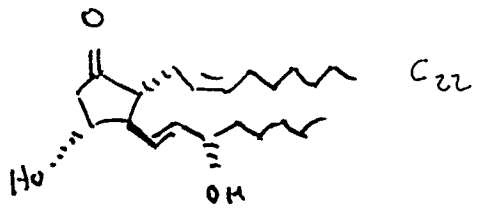

C_{22}

Carbon Basic Parameters. Aug 4 92 RN

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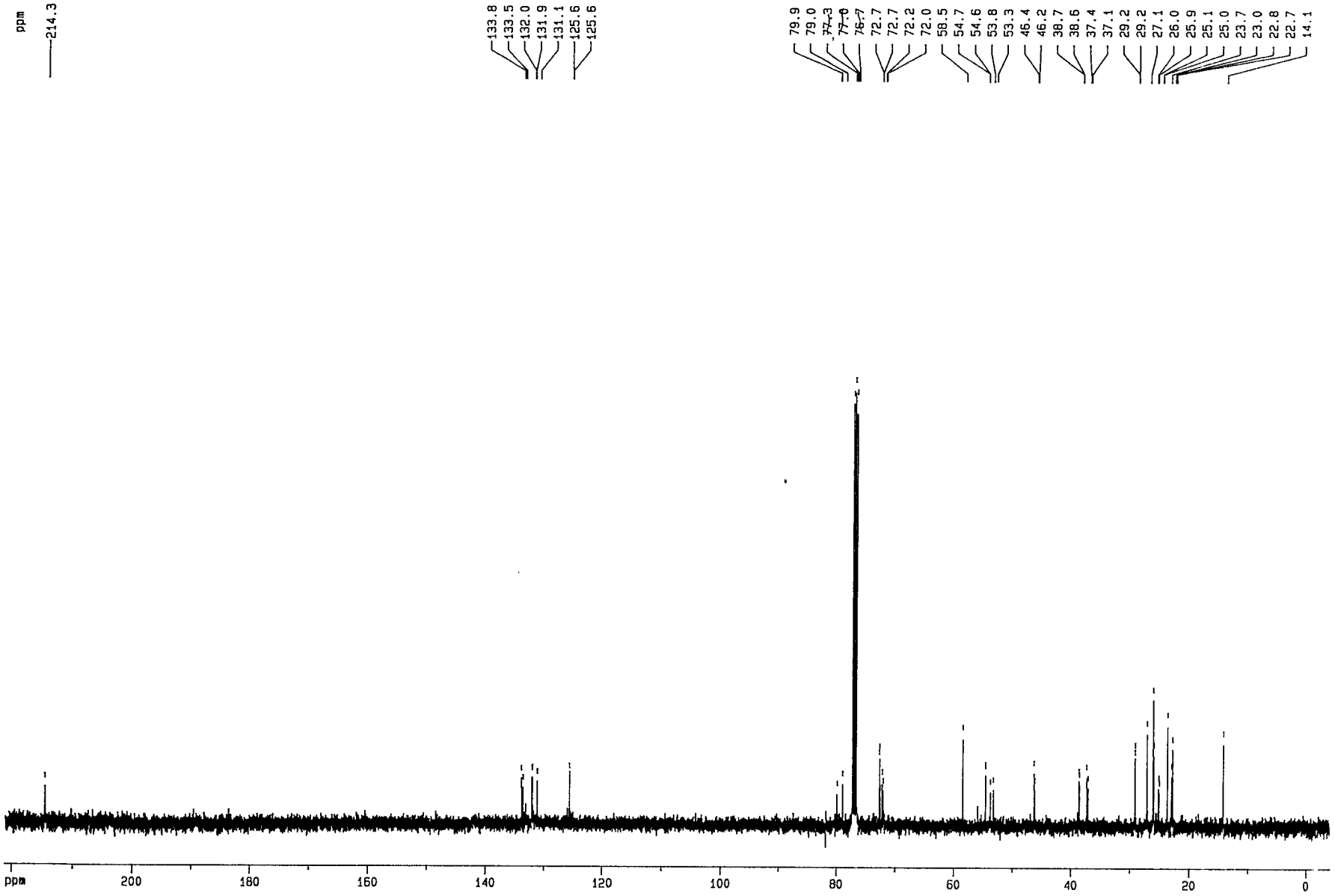

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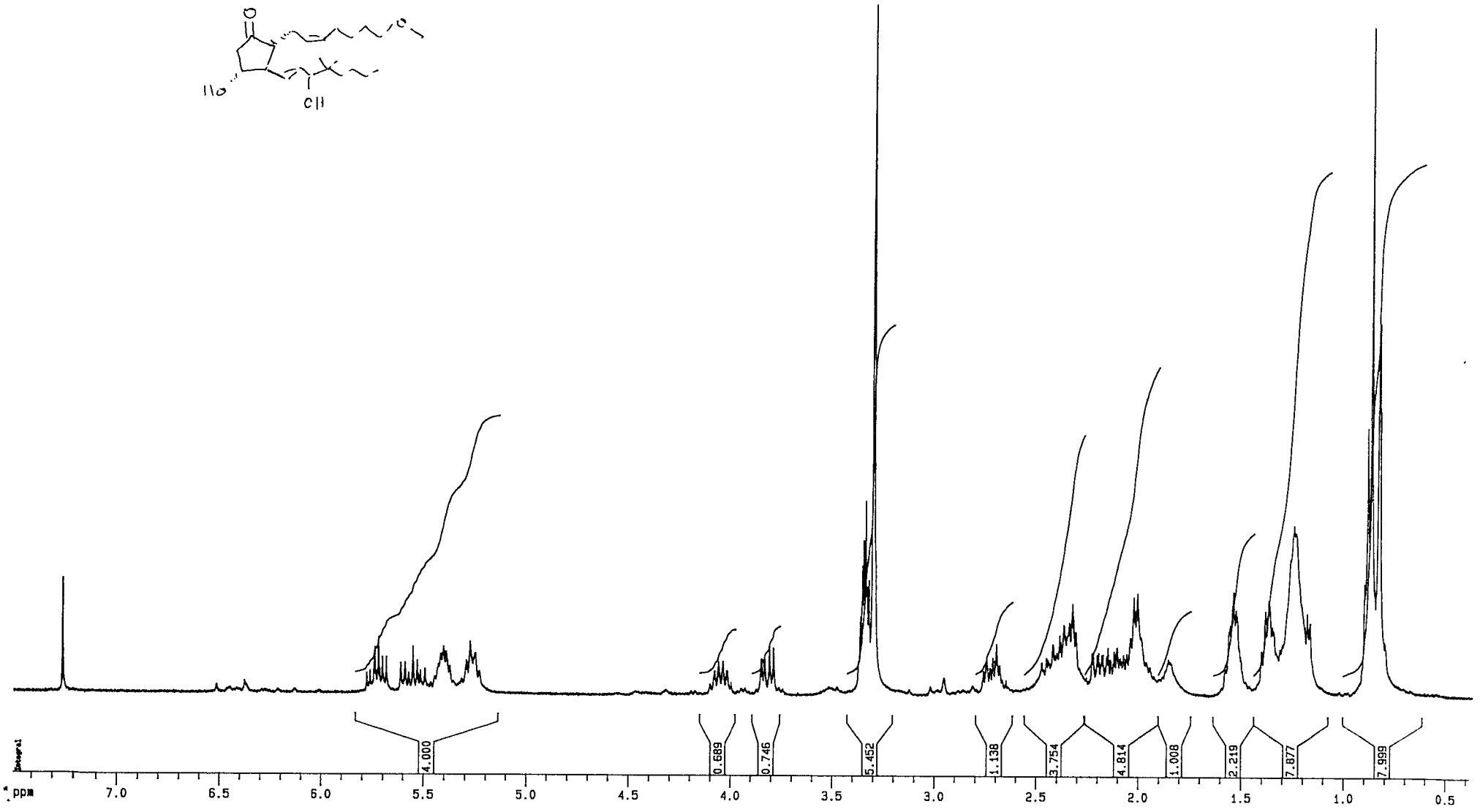

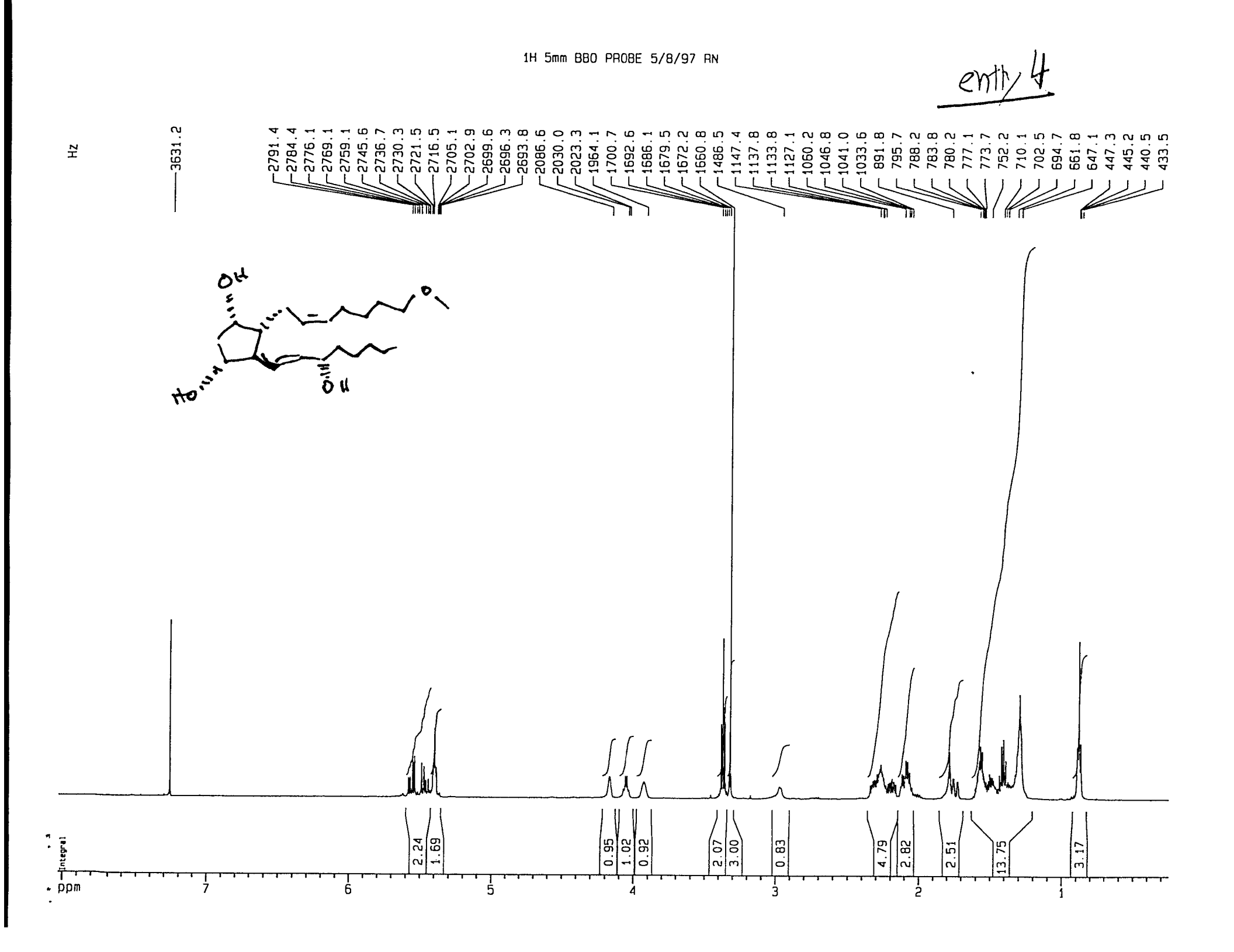
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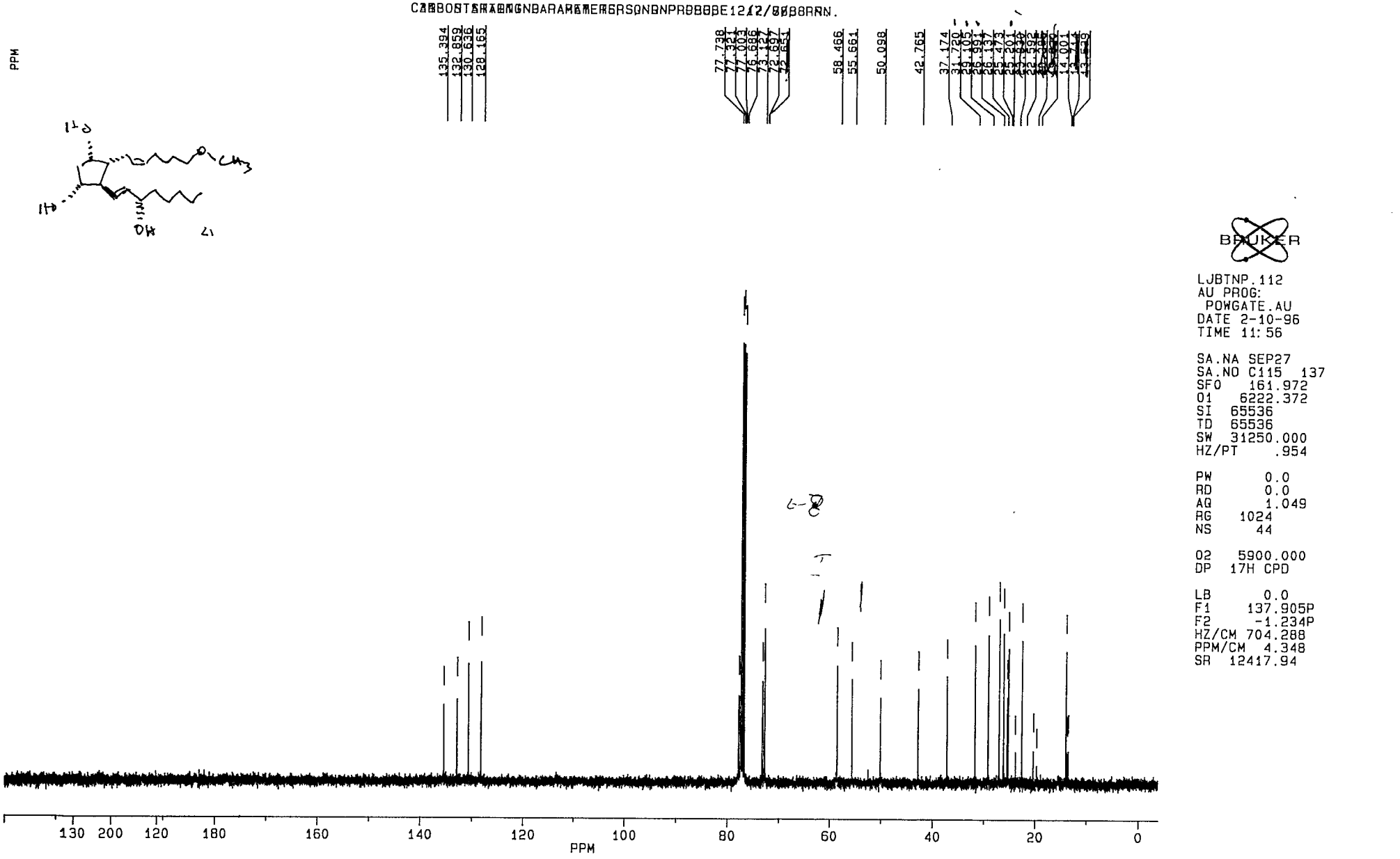
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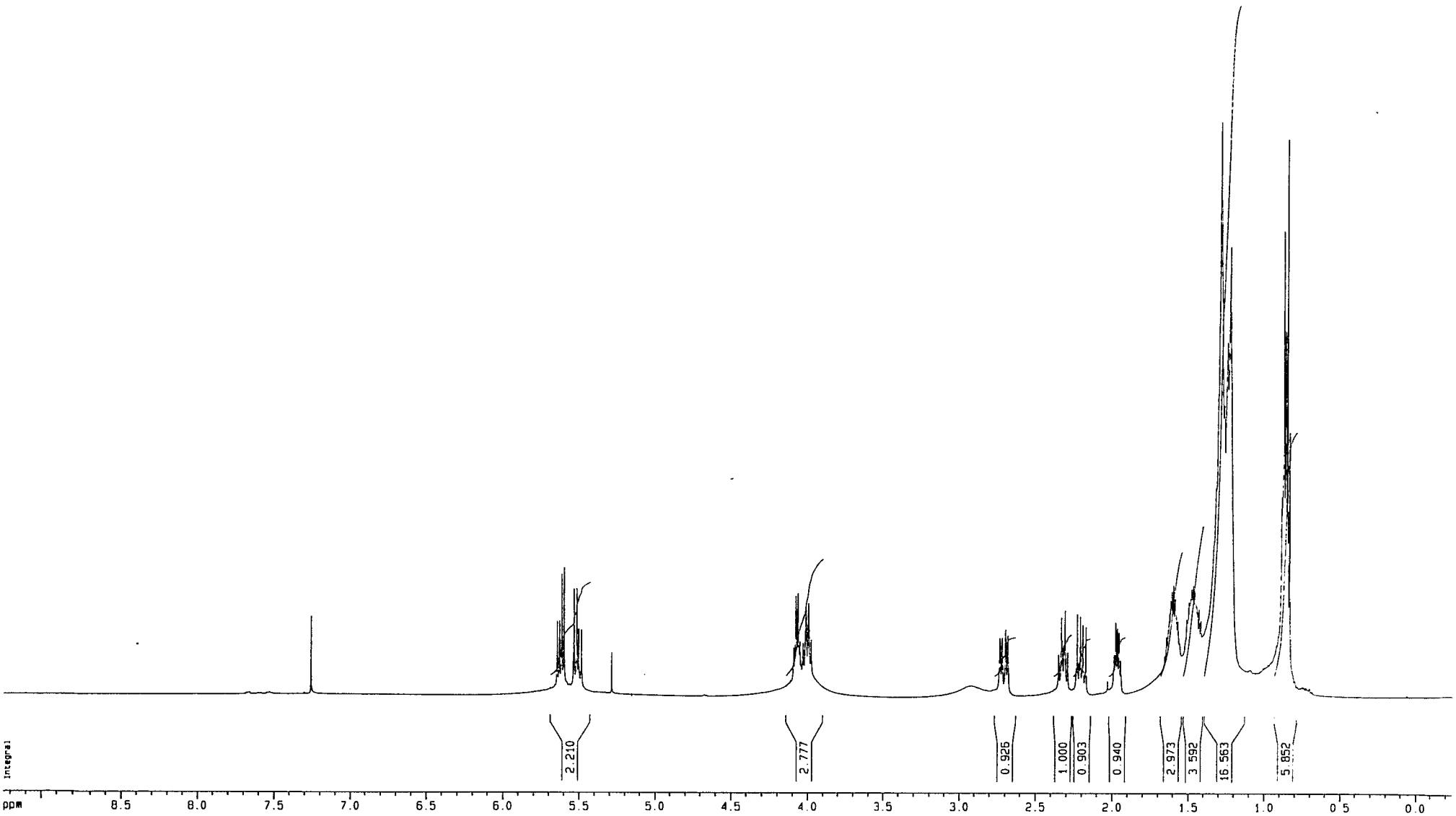
PROTON, C-H INVERSE PROBE, 3/11/91



CARBON. H-C INVERSE PROBE 3/11/91

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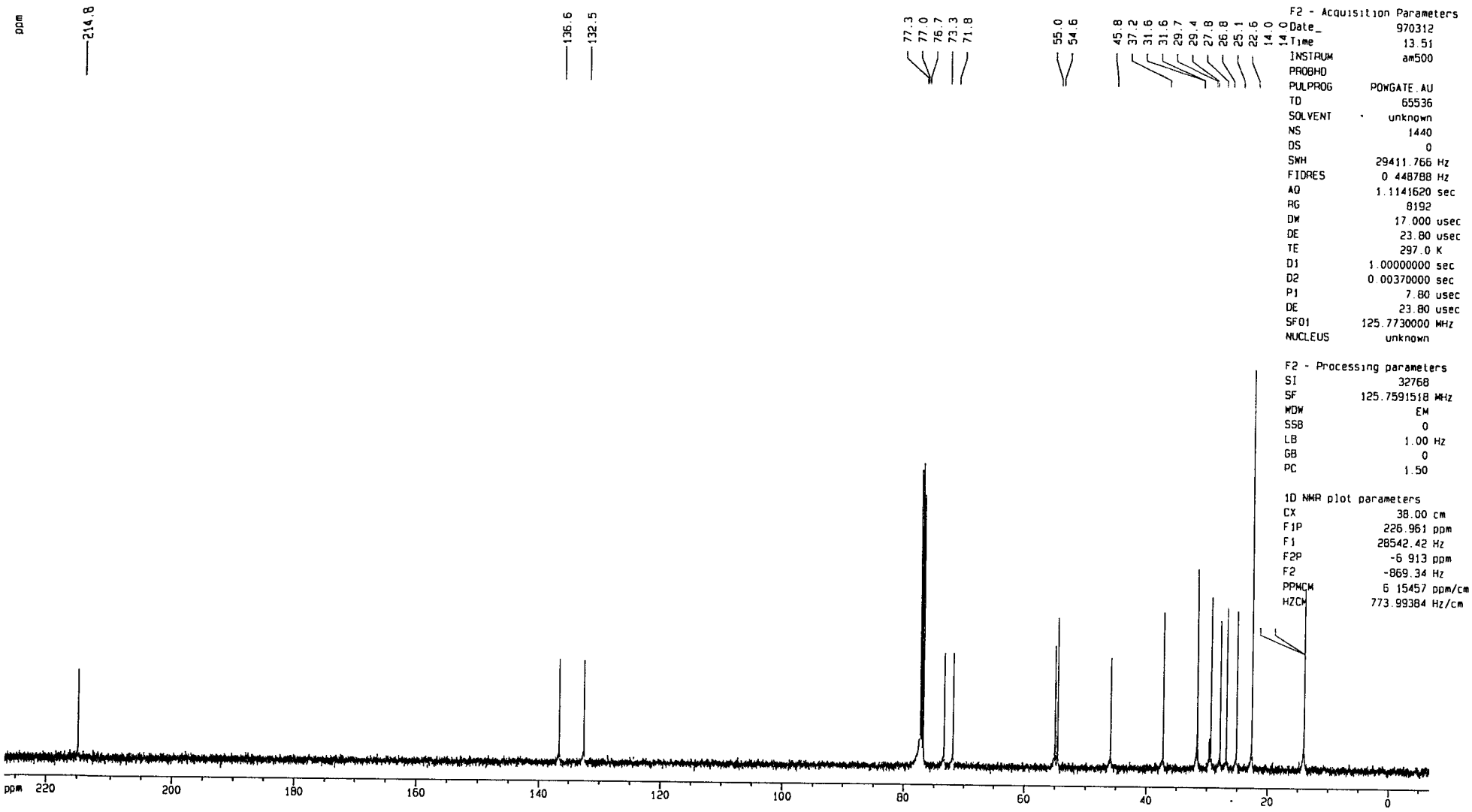

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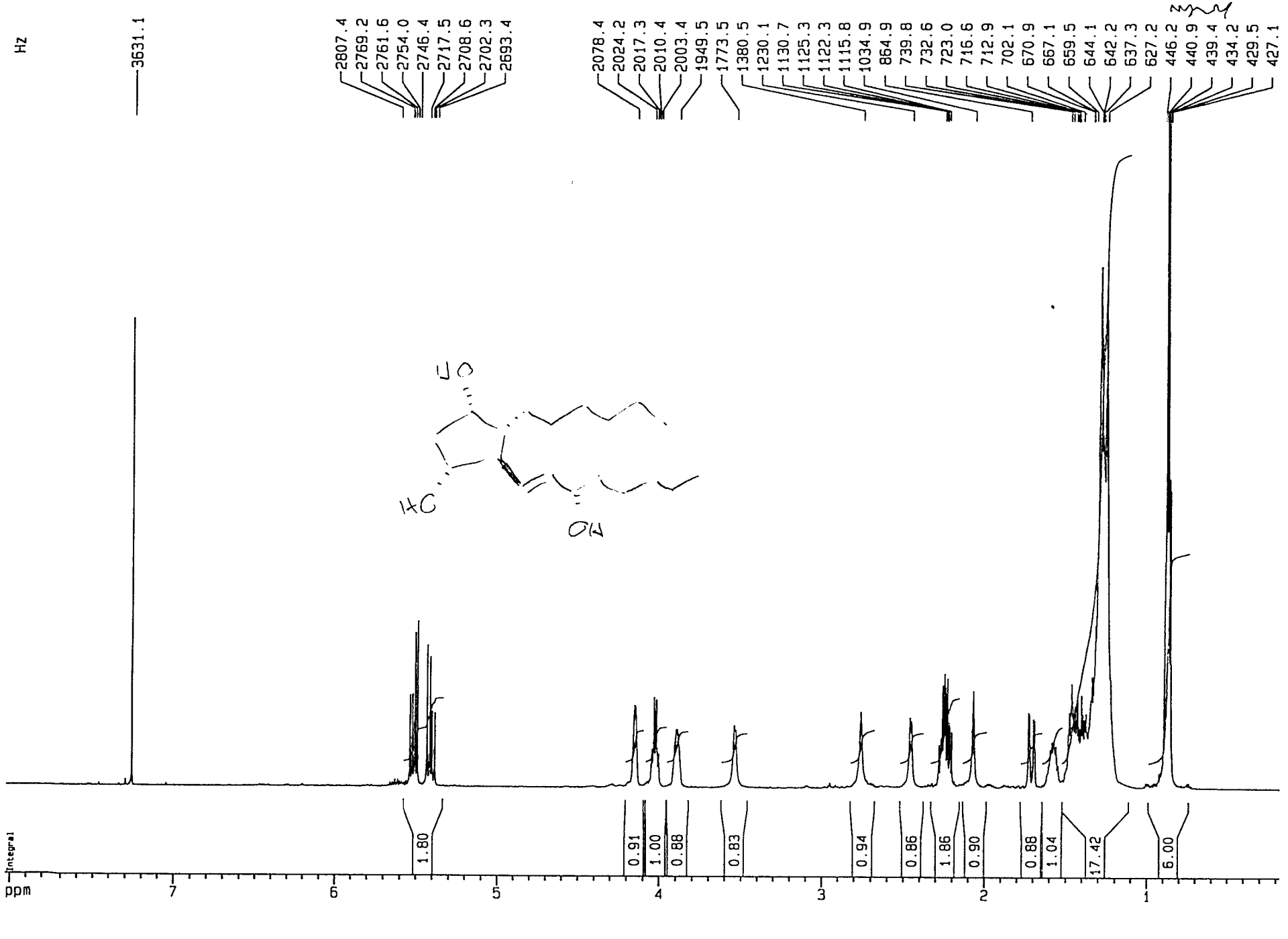
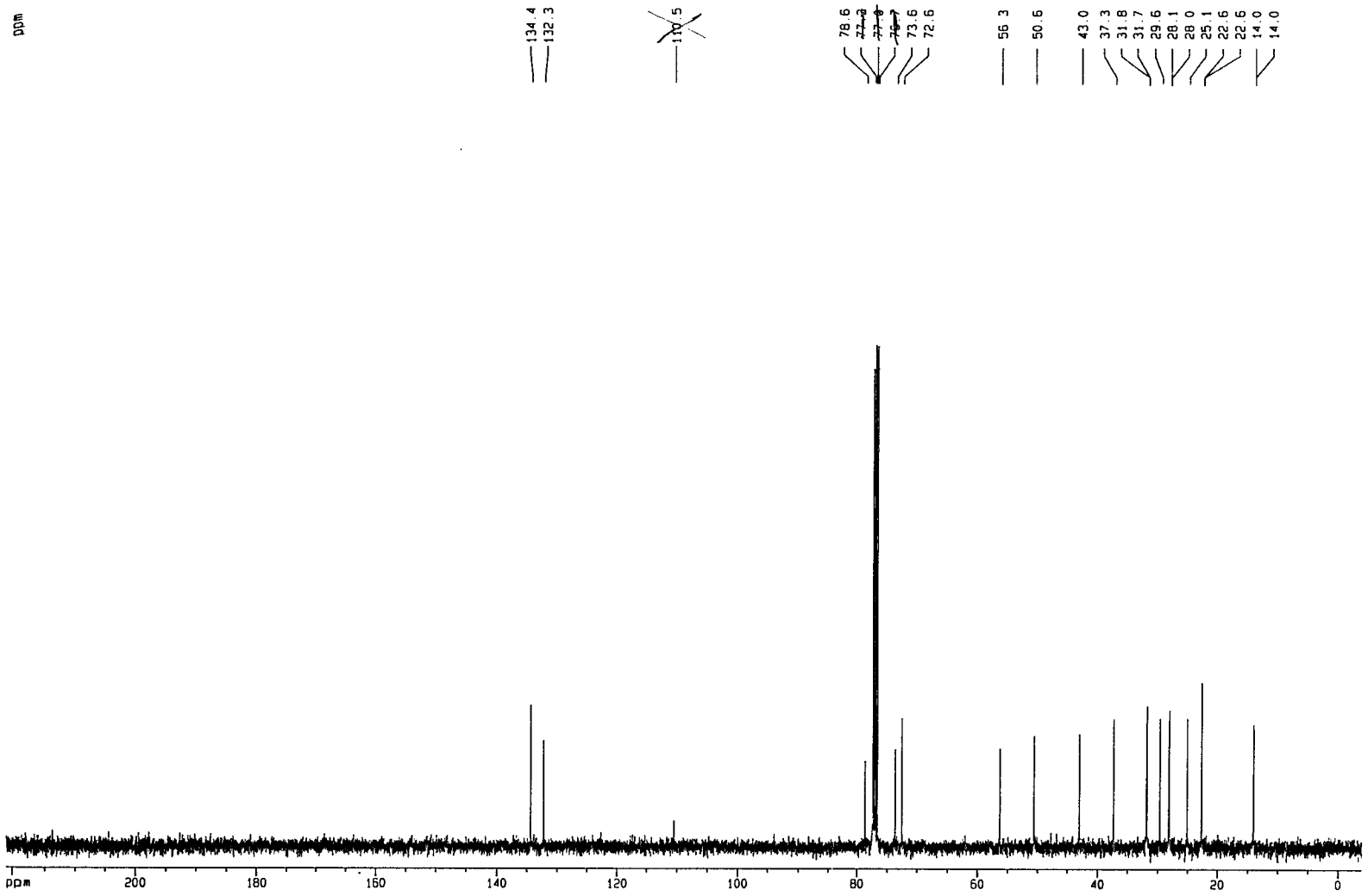
(entry 6)

1H 5mm BBO PROBE 5/8/97 RN



entry 6

CARBON STARTING PARAMETERS, QNP PROBE 12/7/88 RN.



Data Set

NAME	PGFC6
EXPNO	1
PROCNO	1
USER	drew

F2 - Acquisition Parameters

Date_	970527
Time	10.15
INSTRUM	am400
PROBHD	
PULPROG	POWGATE.AU
TD	65536
SOLVENT	unknown
NS	1135
DS	0
SWH	25000.000 Hz
AQ	1.3107700 sec
RG	1
TE	297.0 K
D1	0.10000000 sec
D2	0.00356000 sec
P1	12.00 usec
SFO1	100.6249899 MHz

F2 - Processing parameters

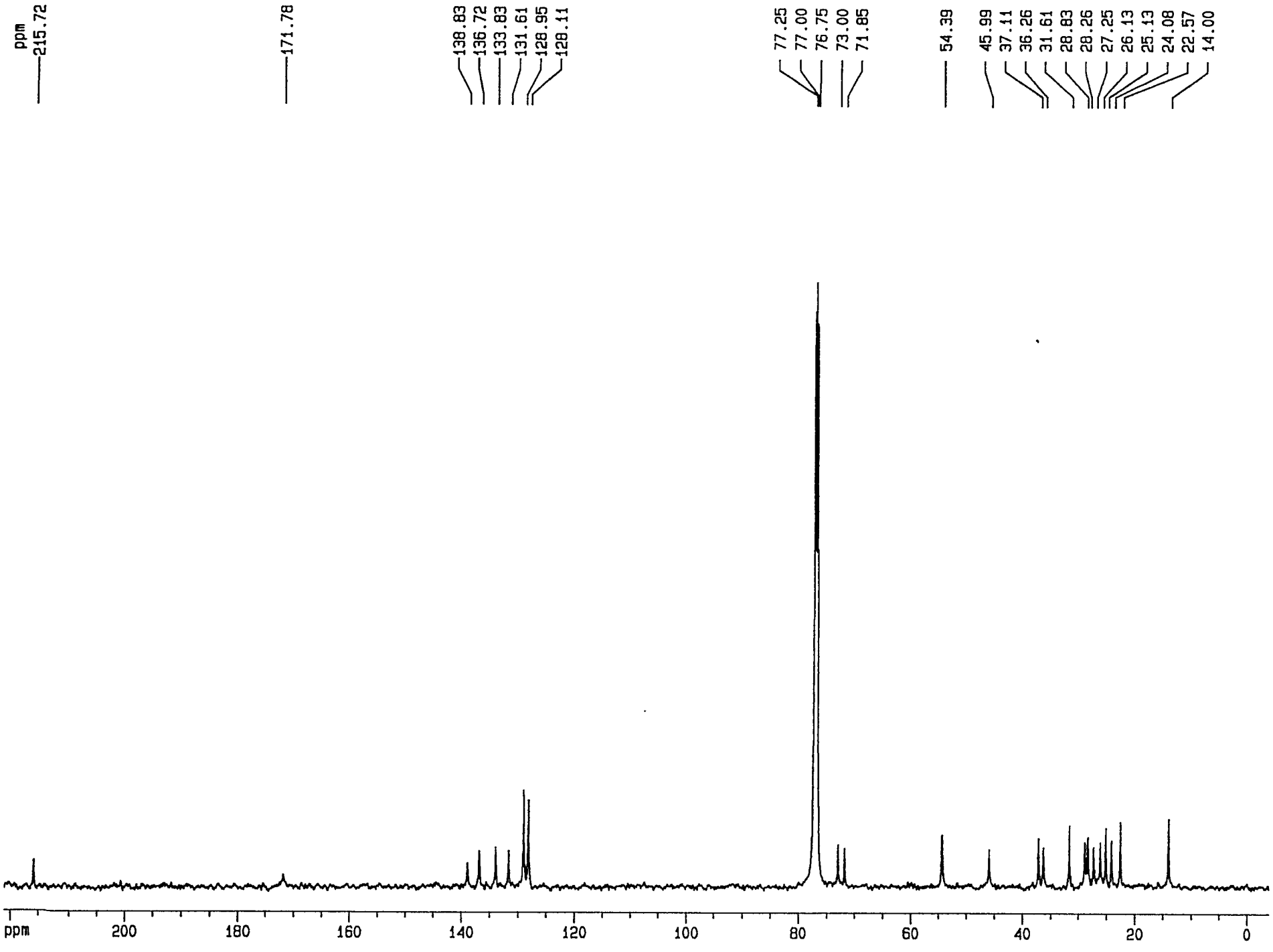
SI	32768
SF	100.6138728 MHz
WDW	EM
SSB	0
LB	0.75 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	32.14 cm
F1P	221.000 ppm
F1	22235.67 Hz
F2P	-4.000 ppm
F2	-402.46 Hz
PPMCM	7.00000 ppm/cm
HZCM	704.29718 Hz/cm

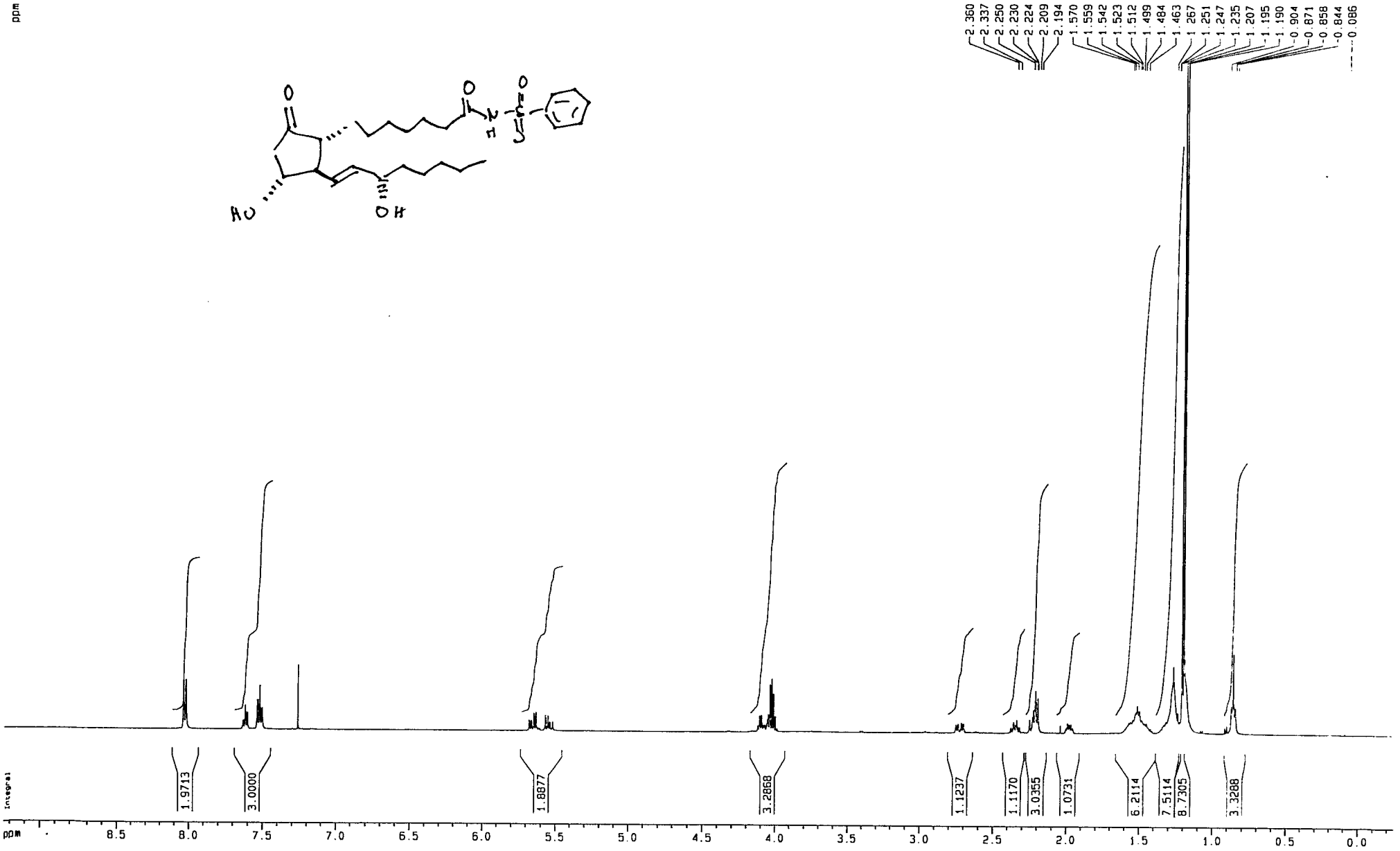
cmpd 18q (entry 7)

13C 5mm BB PROBE 5/9/97 AN



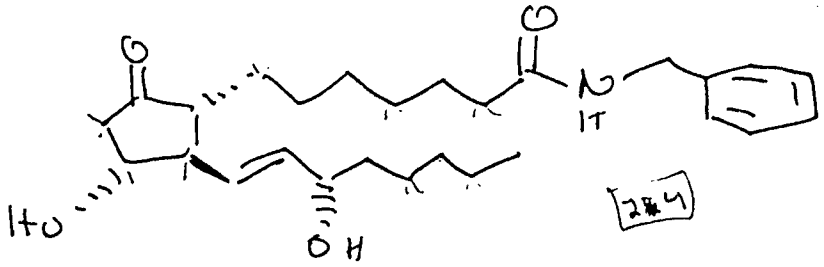
1H 5mm BBO PROBE 5/8/97 RN

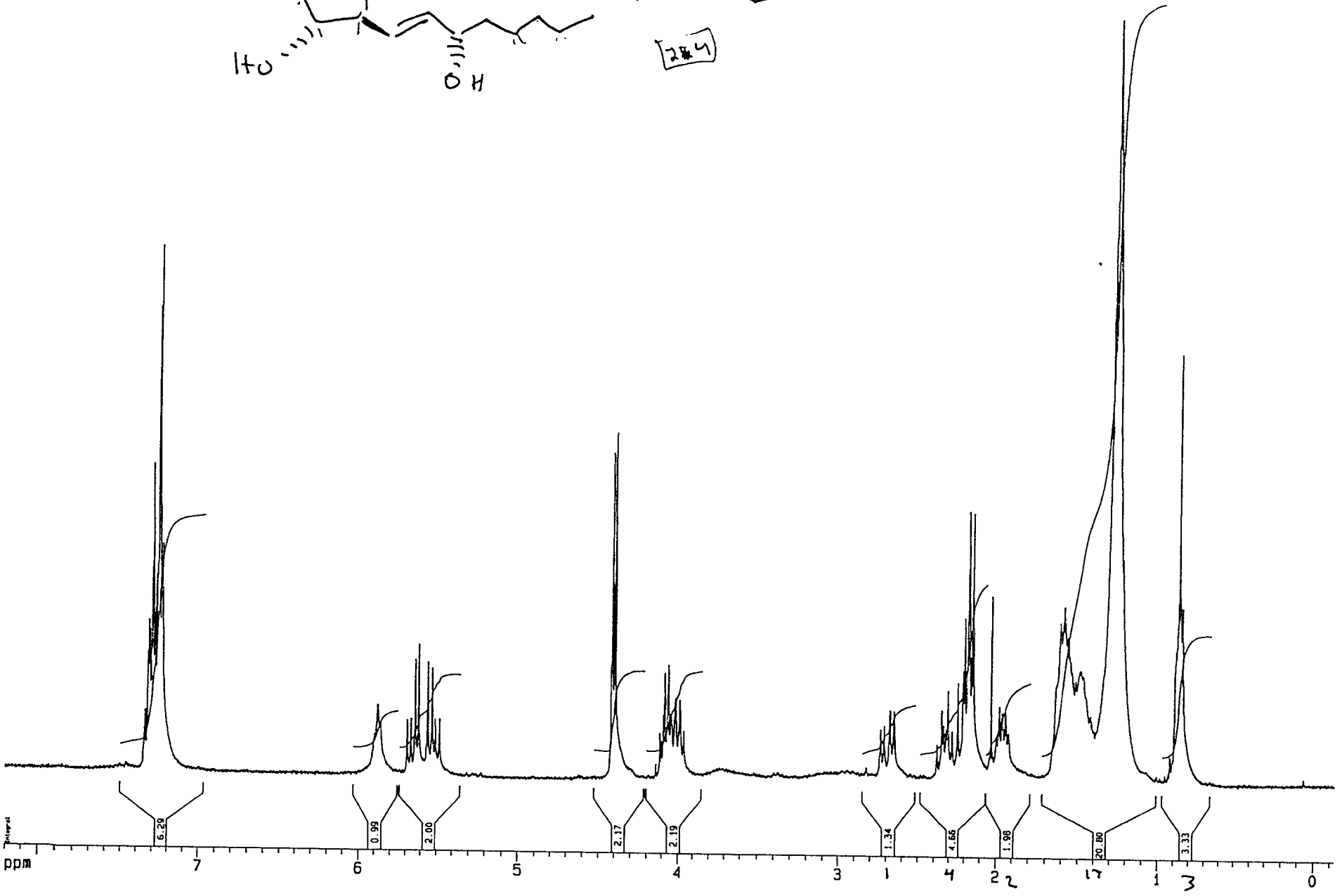
cmpd 18a (entry 7)



Proton Starting Parameters. 10/06/92 RN rev.5/9/94.

entry 8





entry 8

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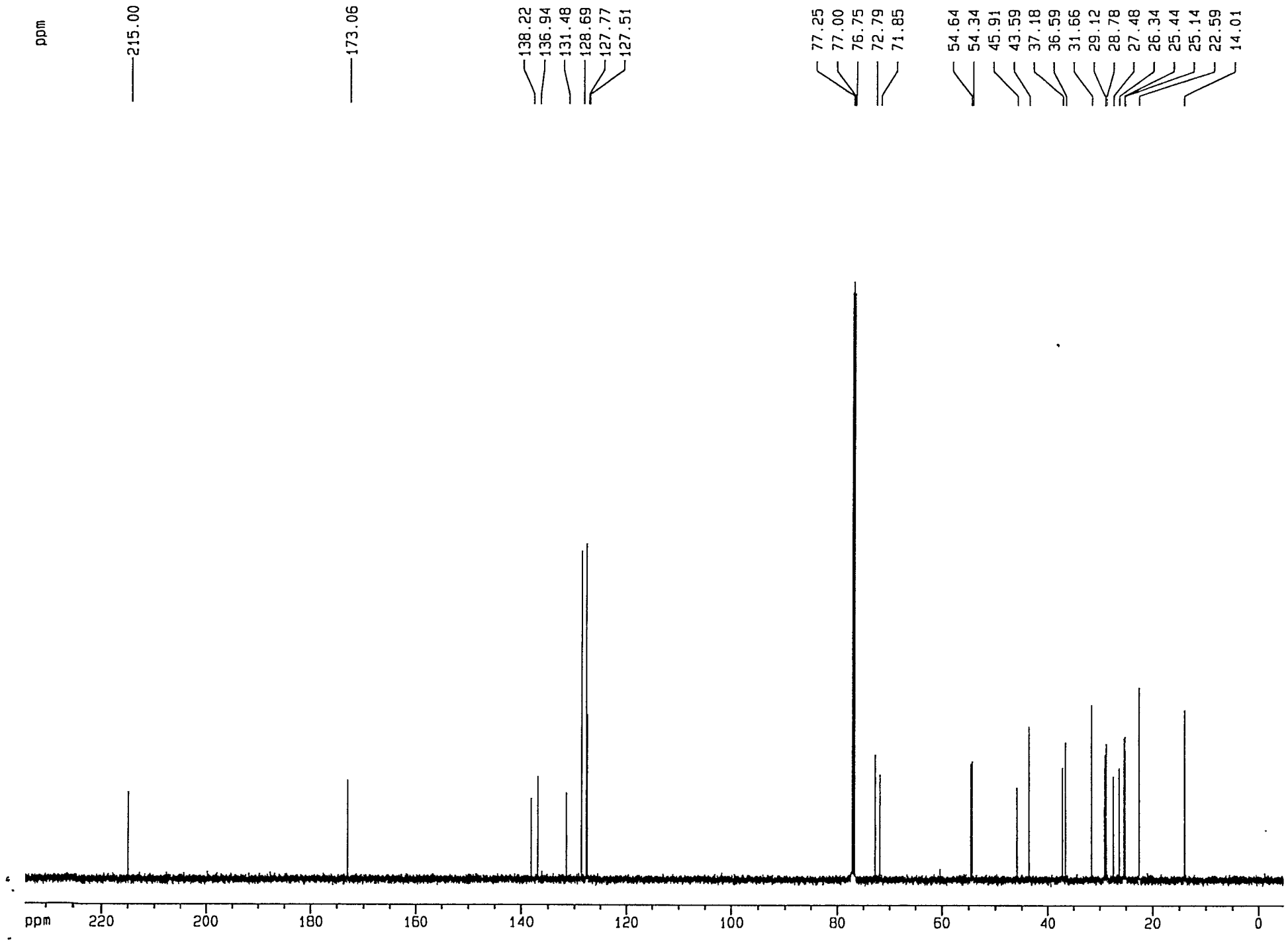
#	ADDRESS	FREQUENCY [Hz]	FREQUENCY [PPM]	INTENSITY
1	4358.4	2205.143	7.3472	1.12
2	4381.4	2200.048	7.3302	2.22
3	4389.5	2198.261	7.3243	2.82
4	4408.0	2194.176	7.3107	1.95
5	4420.9	2191.315	7.3011	5.74
6	4449.1	2185.087	7.2804	3.63
7	4468.6	2180.761	7.2660	8.79
8	4479.8	2178.297	7.2578	10.01
9	4503.2	2173.121	7.2405	4.23
10	6342.3	1766.403	5.8854	1.27
11	6601.1	1709.177	5.6947	1.00
12	6633.0	1702.122	5.6712	1.02
13	6670.2	1693.900	5.6438	2.13
14	6702.0	1686.868	5.6204	2.40
15	6778.1	1670.044	5.5643	2.08
16	6816.7	1661.500	5.5359	1.96
17	6847.3	1654.728	5.5133	1.01
18	6885.5	1646.281	5.4852	1.01
19	8328.1	1327.268	4.4223	6.05
20	8353.7	1321.606	4.4034	6.44
21	8738.9	1236.423	4.1196	0.80
22	8751.4	1233.654	4.1104	0.66
23	8771.6	1229.198	4.0955	1.16
24	8781.7	1226.961	4.0881	1.92
25	8812.5	1220.150	4.0654	2.08
26	8834.1	1215.374	4.0494	1.14
27	8874.6	1206.411	4.0196	1.45
28	8912.5	1198.044	3.9917	1.43
29	8950.2	1189.706	3.9639	0.85
30	10610.7	822.489	2.7404	0.92
31	10644.8	814.950	2.7153	0.99
32	10694.0	804.068	2.6790	1.28
33	10725.0	797.211	2.6562	1.28
34	11098.8	714.554	2.3808	0.66
35	11137.6	705.978	2.3522	1.30
36	11153.7	702.415	2.3403	1.02
37	11192.1	693.912	2.3120	1.66
38	11231.3	685.258	2.2832	0.91
39	11282.3	673.969	2.2456	1.81
40	11327.1	664.069	2.2126	2.04
41	11340.8	661.030	2.2025	3.02
42	11373.4	653.821	2.1784	5.04
43	11409.5	645.836	2.1518	5.02
44	11570.7	610.206	2.0331	3.51
45	11638.2	595.259	1.9833	1.38
46	11666.8	588.944	1.9623	1.26
47	11693.9	582.941	1.9423	1.27
48	12142.7	483.712	1.6117	2.95
49	12176.5	476.230	1.5867	3.27
50	12313.5	445.923	1.4858	2.07
51	12598.0	383.012	1.2761	14.40
52	12635.7	374.687	1.2484	8.99
53	12667.3	367.687	1.2251	4.16
54	13076.9	277.122	0.9233	0.47
55	13149.8	260.982	0.8696	8.08
56	13179.9	254.332	0.8474	3.25

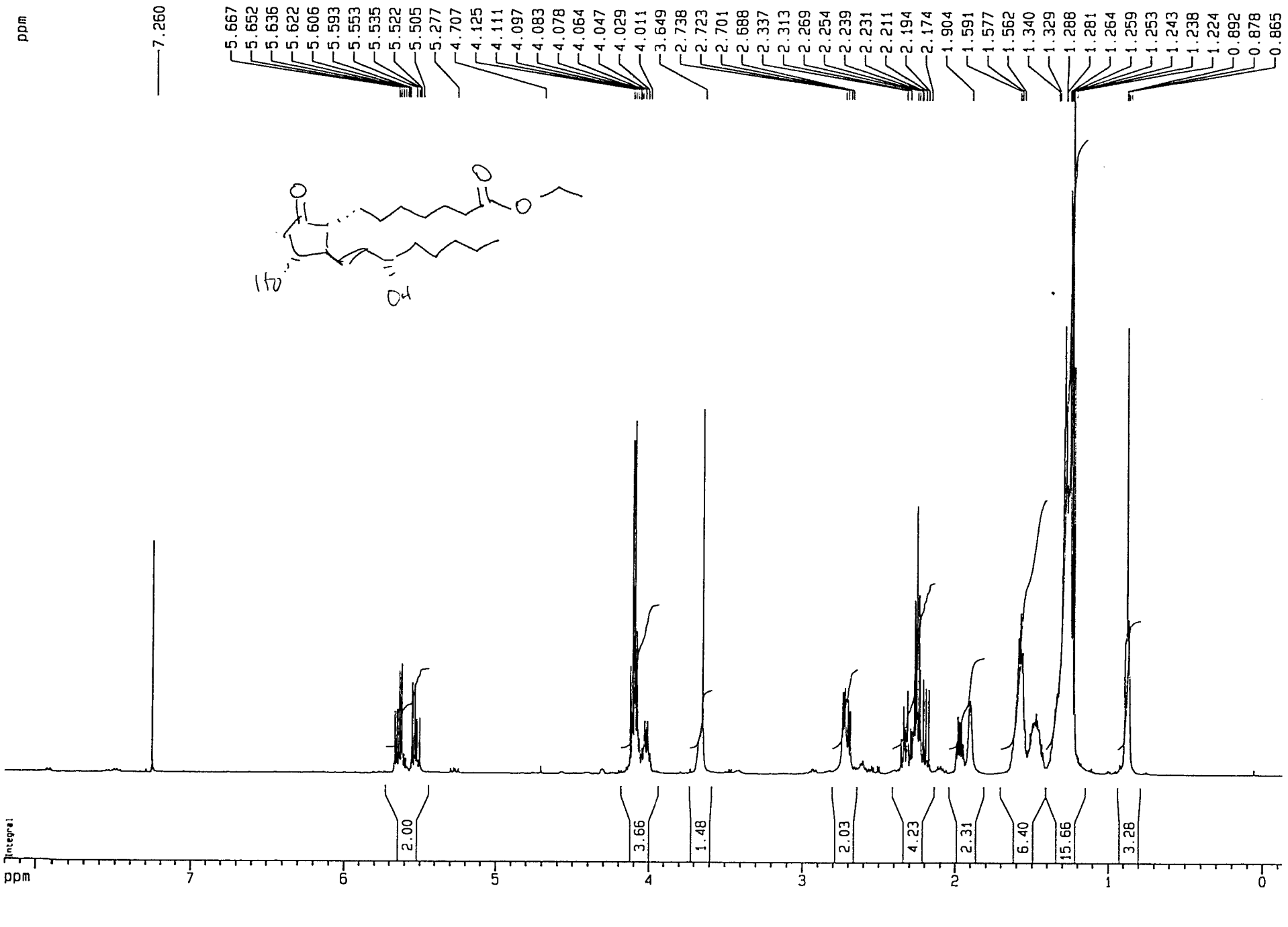
entry 8

13C 5mm BB PROBE 5/9/97 AN



1H 5mm BBO PROBE 5/8/97 AN

entry 9



entry 9

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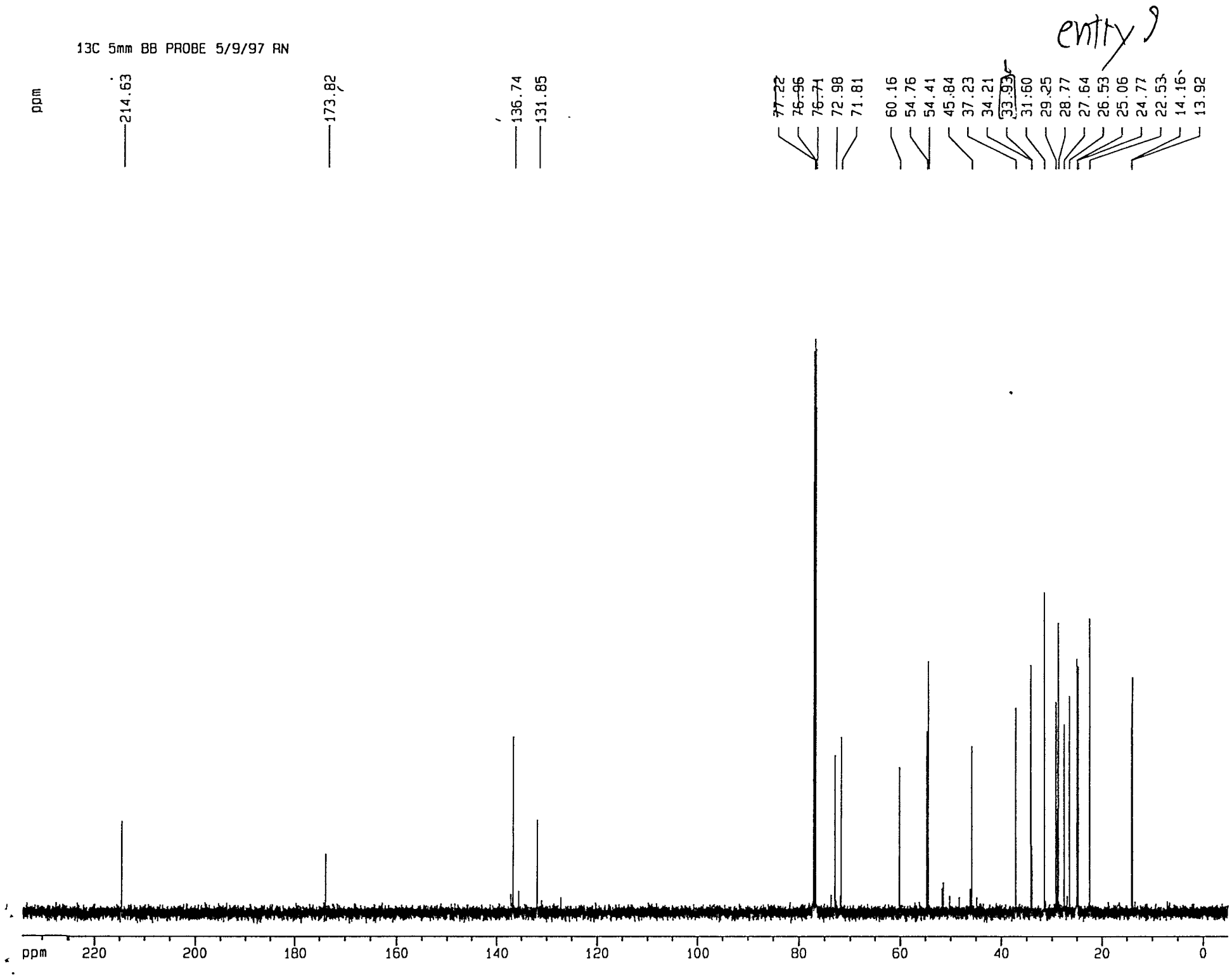
#	ADDRESS	FREQUENCY [Hz]	FREQUENCY [PPM]	INTENSITY
1	37847.1	1369.274	2.7378	0.86
2	37896.1	1361.792	2.7229	0.90
3	37967.7	1350.865	2.7010	0.78
4	38010.1	1344.401	2.6881	0.66
5	38275.9	1303.841	2.6070	0.14
6	38467.6	1274.593	2.5485	0.09
7	38506.9	1268.590	2.5365	0.07
8	38593.8	1255.330	2.5100	0.09
9	38632.5	1249.426	2.4982	0.08
10	39102.4	1177.737	2.3549	0.38
11	39159.9	1168.957	2.3373	0.71
12	39181.1	1165.716	2.3308	0.48
13	39218.3	1160.045	2.3195	0.46
14	39239.0	1156.892	2.3132	0.87
15	39297.3	1147.997	2.2954	0.48
16	39326.1	1143.601	2.2866	0.45
17	39383.8	1134.794	2.2690	1.81
18	39432.9	1127.293	2.2540	2.80
19	39482.8	1119.684	2.2388	1.86
20	39509.8	1115.562	2.2305	1.09
21	39574.6	1105.679	2.2108	0.99
22	39630.9	1097.092	2.1936	0.89
23	39695.5	1087.227	2.1739	0.89
24	39948.3	1048.662	2.0968	0.09
25	40284.4	997.369	1.9942	0.29
26	40320.7	991.836	1.9832	0.61
27	40360.0	985.837	1.9712	0.55
28	40399.6	979.796	1.9591	0.54
29	40438.2	973.899	1.9473	0.32
30	40581.3	952.070	1.9036	0.77
31	41606.6	795.616	1.5908	1.42
32	41652.8	788.565	1.5767	1.68
33	41702.3	781.023	1.5616	1.28
34	41749.7	773.789	1.5472	0.57
35	41855.9	757.584	1.5148	0.43
36	41900.3	750.810	1.5012	0.54
37	41920.4	747.736	1.4951	0.55
38	41964.7	740.977	1.4816	0.58
39	41987.6	737.483	1.4746	0.64
40	42017.7	732.887	1.4654	0.57
41	42076.1	723.977	1.4476	0.38
42	42110.5	718.731	1.4371	0.32
43	42147.1	713.152	1.4259	0.23
44	42428.8	670.159	1.3400	0.85
45	42464.5	664.710	1.3291	0.92
46	42599.4	644.129	1.2879	4.68
47	42620.6	640.892	1.2815	3.69
48	42677.7	632.189	1.2640	2.97
49	42695.4	629.478	1.2586	3.21
50	42715.2	626.466	1.2526	6.11
51	42746.8	621.636	1.2429	1.49
52	42762.0	619.317	1.2383	9.00
53	42808.8	612.171	1.2240	4.26
54	42904.6	597.561	1.1948	0.19
55	43897.7	446.020	0.8918	1.39
56	43942.2	439.229	0.8782	4.67


entry 9
13C 5mm BB PROBE 5/9/97 RN
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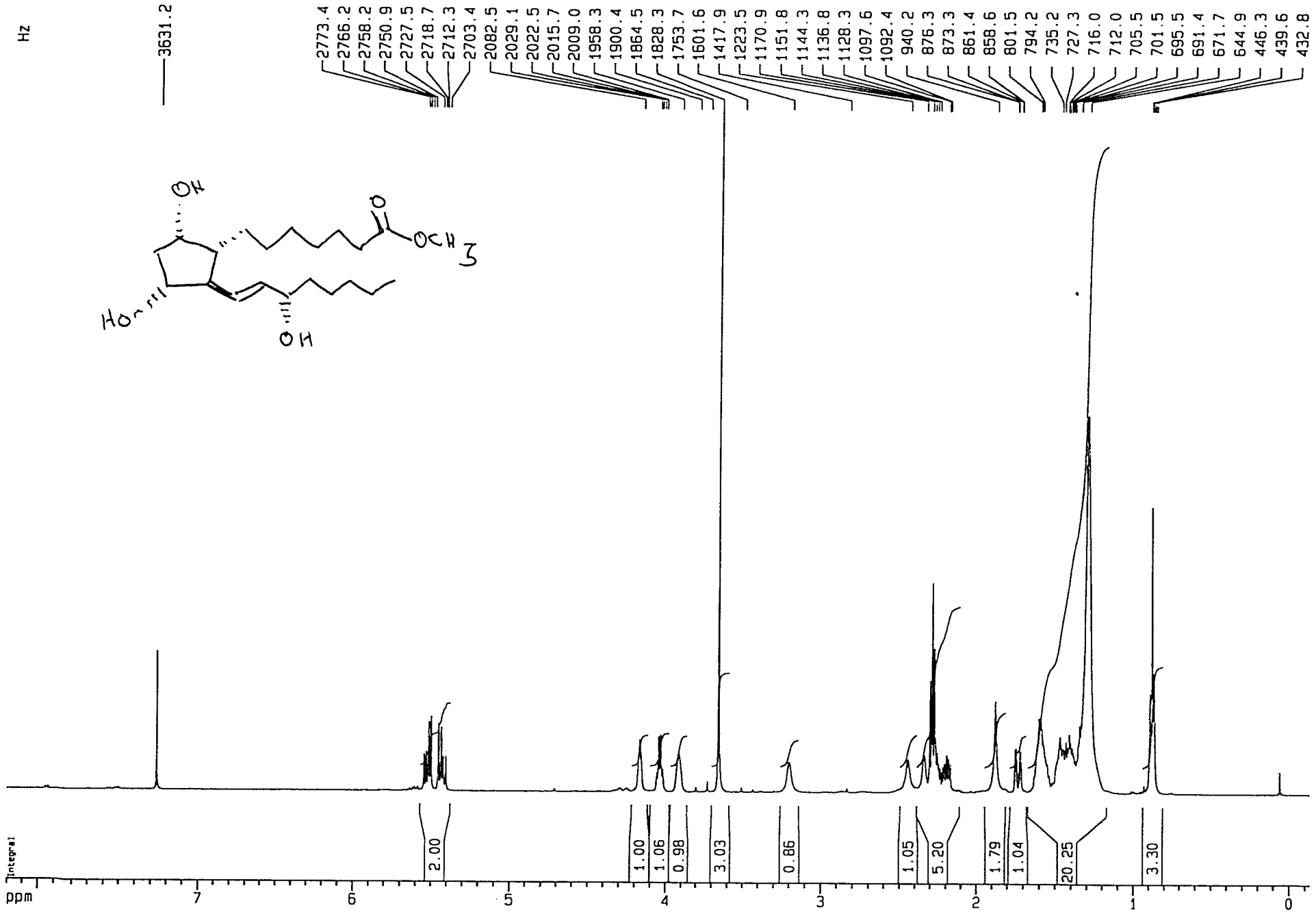
173.82
136.74
131.85
77.22
76.96
76.71
72.98
71.81
60.16
54.76
54.41
45.84
37.23
34.21
33.93
31.60
29.25
28.77
27.64
26.53
25.06
24.77
22.53
14.16
13.92
ppm
220
200
180
160
140
120
100
80
60
40
20
0

1H 5mm BBO PROBE 5/8/97 RN

entry 18



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#	ADDRESS	FREQUENCY [Hz]	[PPM]	INTENSITY
1	23023.5	3631.173	7.2605	1.42
2	28644.8	2773.431	5.5454	0.38
3	28692.2	2766.194	5.5309	0.40
4	28744.6	2758.209	5.5150	0.71
5	28792.3	2750.925	5.5004	0.76
6	28945.6	2727.541	5.4537	0.69
7	29003.7	2718.662	5.4359	0.65
8	29045.3	2712.322	5.4232	0.35
9	29103.5	2703.445	5.4055	0.35
10	33173.1	2082.468	4.1639	0.54
11	33522.6	2029.137	4.0572	0.20
12	33566.1	2022.505	4.0440	0.57
13	33610.9	2015.659	4.0303	0.58
14	33654.9	2008.955	4.0169	0.23
15	33986.9	1958.287	3.9156	0.39
16	34366.3	1900.403	3.7998	0.05
17	34601.9	1864.456	3.7279	0.11
18	34838.7	1828.314	3.6557	9.00
19	35327.5	1753.729	3.5065	0.05
20	36324.2	1601.642	3.2025	0.31
21	37528.1	1417.947	2.8352	0.04
22	38802.2	1223.530	2.4464	0.35
23	39147.0	1170.924	2.3412	0.39
24	39272.5	1151.773	2.3029	1.16
25	39321.4	1144.312	2.2880	2.15
26	39370.5	1136.815	2.2730	1.48
27	39426.4	1128.294	2.2560	0.41
28	39453.6	1124.141	2.2477	0.30
29	39489.8	1118.616	2.2367	0.26
30	39531.1	1112.313	2.2240	0.27
31	39564.4	1107.234	2.2139	0.30
32	39582.6	1104.457	2.2083	0.30
33	39627.7	1097.573	2.1946	0.39
34	39661.8	1092.380	2.1842	0.35
35	39679.7	1089.647	2.1787	0.35
36	39712.9	1084.577	2.1686	0.30
37	40659.4	940.152	1.8798	0.94
38	41078.0	876.277	1.7521	0.45
39	41097.6	873.294	1.7461	0.46
40	41175.3	861.431	1.7224	0.42
41	41193.6	858.638	1.7168	0.43
42	41568.4	801.453	1.6025	0.77
43	41616.1	794.170	1.5879	0.74
44	42002.8	735.160	1.4699	0.58
45	42054.1	727.330	1.4543	0.46
46	42128.6	715.963	1.4316	0.53
47	42154.8	711.968	1.4236	0.47
48	42197.3	705.481	1.4106	0.61
49	42223.5	701.483	1.4026	0.53
50	42262.5	695.543	1.3907	0.47
51	42289.5	691.416	1.3825	0.42
52	42418.6	671.717	1.3431	0.69
53	42594.1	644.943	1.2896	3.86
54	43776.0	464.593	0.9289	0.08
55	43895.9	446.307	0.8924	1.02
56	43939.7	439.613	0.8790	2.94

entry 10

13C 5mm BB PROBE 5/9/97 RN

entry 10

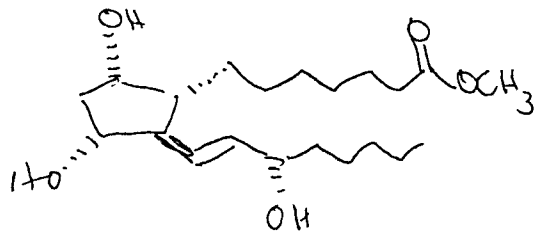
ppm

174.35

135.00
133.19

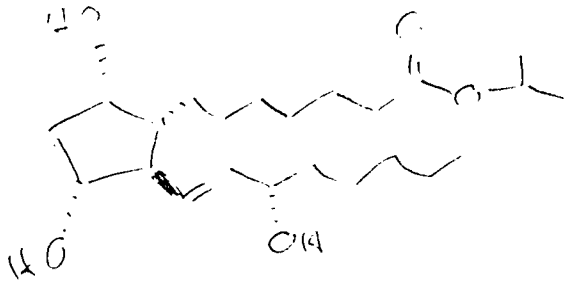
78.04
~~77.25~~
77.00
~~76.75~~
73.15
73.00

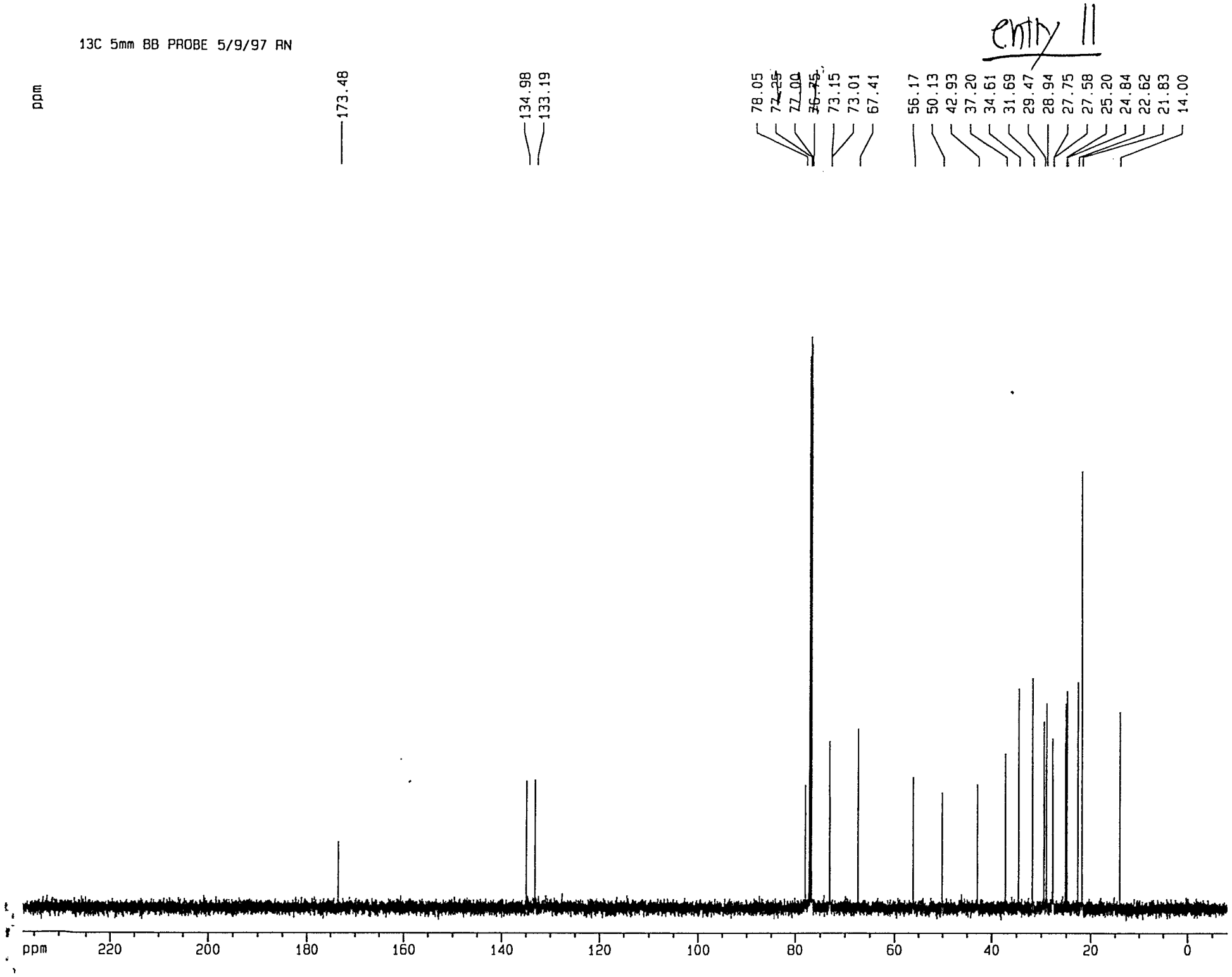
56.15
51.46
50.11
42.94
37.20
33.99
31.69
29.45
28.96
27.74
27.58
25.20
24.77
22.62
13.99



1H 5mm BBO PROBE 5/8/97 RN

entry 11




13C 5mm BB PROBE 5/9/97 RN
entry 11
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133.19
78.05
77.25
77.00
36.75
73.15
73.01
67.41
56.17
50.13
42.93
37.20
34.61
31.69
29.47
28.94
27.75
27.58
25.20
24.84
22.62
21.83
14.00
ppm
220
200
180
160
140
120
100
80
60
40
20
0