Stereospecific Solid-State Cyclodimerization of Bis(*trans*-2-butenoato)calcium and Triaquabis(*trans*-2-butenoato)magnesium

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Supporting Information

General methods and Instrumentation. Melting points were determined on a Laboratory Devices Mel-Temp apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer 1650 FT-IR Spectrophotometer and are reported in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian XL-300 (300 MHz), Varian Unity Inova-400 (400 MHz) or Varian Unity Inova-600 (600MHz) spectrometer. NOESY and GCOSY experiments were recorded on a Varian Unity Inova-400 (400 MHz) or -600 (600MHz) spectrometer. Chemical shifts are given in ppm upfield from TMS (δ). NMR spectra in D_2O were referenced to HDO or acetone at δ 4.79 and δ 2.08, respectively. NMR spectra in DMSO-d_6 were referenced to residual solvent at δ 2.50. ^{13}C NMR multiplicities were assigned by APT experiments. The following abbreviations are used to indicate signal multiplicity (NMR) or spectral characteristics (IR): s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplet; dq, doublet of quartet; ddd, doublet of doublet of doublets; ddt, doublet of doublet of triplets; m, multiplet; br, broad; sh, shoulder. A Gammacell 220 Irradiator (Atomic Energy of Canada, Ltd.) equipped with a ^{60}Co source, was used for some γ-irradiation experiments. The nominal activity of the source at the times of the experiments varied from 219 – 286 Gy/h. The facility at the Radiation Laboratory, University of Massachusetts Lowell with nominal activity of 20 kGy/h was used for other experiments. Gas chromatography was carried out on a Perkin-Elmer 8310 capillary gas chromatograph using a silica-bonded column (HELIFLEX RSL-150, 30 m × 0.25 mm) under the following conditions: 60 - 150 ºC, 10 ºC/min, 5 min isothermal; 150 - 190 ºC, 20 ºC/min, 8 min isothermal; detector temperature 280 ºC, injection temperature 240 ºC. The liquid phase is a non-polar polydimethylsiloxane that is similar to SE-30, OV-1, or ALLTECH AT-1. GC/MS data were obtained on a Hewlett-Packard 5890 Gas Chromatograph with a Hewlett-Packard Mass Spectrometer Detector using a capillary column (CP-SIL 19, 30 m × 0.32 m) under the following conditions: 50 – 250 ºC, 5 ºC/min, 2 min isothermal; detector temperature 280 ºC, injection temperature 240 ºC. Diazomethane was prepared by adding *N*-nitroso-*N*-methylurea to a mixture of 40% by weight aqueous KOH solution and ether.[s1] All purchased starting materials were used without further purification.

Bis(*trans*-2-butenoato)calcium (4). Calcium carbonate (2.39 g, 23.9 mmol) was added to a solution of *trans*-2-butenoic acid (4.12 g, 47.8 mmol) in 50 mL of H_2O at 25 ºC. This suspension was stirred for 7 h during which time most of the calcium carbonate dissolved. The pale yellow solution was filtered by gravity to remove unreacted calcium carbonate and allowed to evaporate for 7-8 d until it appeared to be dry. The solid residue was washed three times with 50 mL portions of acetone to remove excess *trans*-2-butenoic acid and to expedite the drying process. The solid residue was further dried in a desiccator over anhydrous calcium sulfate to give 4.46 g (89%) of **4** as a colorless solid that was used for all γ-irradiation experiments: ^{1}H NMR (D_2O) 6.55 (dq, 1, J = 15.5, 6.8), 5.70 (dq, 1, J = 15.5, 1.7), 1.67 (dd, 1, J = 6.8, 1.7); ^{13}C NMR (D_2O) 170.1 (C), 135.1 (CH), 120.7 (CH), 10.55 (CH_3); IR (KBr) 2962, 1665, 1579, 1445.

Single Crystals of Bis(*trans*-2-butenoato)calcium (4). For the original determination, which yielded poor quality crystals,[10] crystals were prepared by addition of calcium carbonate (0.301 g, 3.00 mmol) to *trans*-2-butenoic acid (0.498 g, 5.78 mmol) in 50 mL of H_2O at 25 ºC. The suspension was stirred for 0.5 h and filter by gravity. The pale yellow filtrate was transferred to a 90 mm × 50 mm Pyrex crystallizing dish that was then covered with Parafilm. Twenty to thirty holes were created with a needle in order to ensure slow evaporation. After five days, thin needle-like colorless crystals formed on the bottom of the dish. The crystals were washed three times with 25 mL portions of diethyl ether and further dried in a desiccator for two to three days.

For the improved preparation, using the methodology suggested by Doxsee,[24] calcium hydroxide (0.741 g, 0.01 mol) was added to *trans*-2-butenoic acid (1.722 g, 0.02 mol) in 20 mL of H_2O. The solution was stirred for 30 min and 20 mL of pyridine was transferred slowly to the clear solution and the resulting yellow solution was placed in the hood to allow slow evaporation. After 5 days, long column shape crystals were produced in 92% yield.

γ-Irradiation of Bis(*trans*-2-butenoato)calcium (4). A sample of **4** (1.0 g, 4.76 mmol) was γ-irradiated in a loosely capped vial at 25 ºC for 24 h (7 kGy), and then heated at 60 ºC for 24 h. This γ-irradiation/heating cycle was then repeated to give material that was analyzed as described below.

An NMR sample was prepared by suspending a portion in 20 drops of D_2O and adding 3 drops of 38% DCl in D_2O to give a homogeneous solution. Analysis of the ^{1}H NMR spectrum indicated the solution contained a 95.4:4.6 mixture of *trans*-2-butenoic acid and *cis trans*-nepetic acid (**5b**) and traces of other compounds: ^{1}H NMR (D_2O) δ 7.03 (dq, 0.954 × 1, *J* = 15.6, 6.9), 5.86 (dq, 0.954 × 1, *J* = 15.6, 1.7), 3.24 (ddd, 0.046 × 1, *J* = 9.2, 8.5, 8.1, **5b**), 2.70 (dd, 0.046 × 1, *J* = 9.1, 8.1, **5b**), 1.86 (dd, 0.954 × 3, *J* = 6.9, 1.7), 1.05 (d, 0.046 × 3, *J* = 6.7**, 5b**). The yield of **5b** is 8.8% because two molecules of **4** are converted to one molecule of **5b**.

A second portion (205 mg) of irradiated and heated material was dissolved in 10 mL of 1 M HCl. The resulting solution was extracted five times with 10 mL portions of ether. The combined ether layers were treated with 15-17 mL of ethereal diazomethane, dried ($MgSO_4$), filtered, and diluted with an equal amount of ether for GC analysis. Five peaks were observed at 1.5 (89.9%, methyl *trans*-2-butenoate), 16.2 (0.3%), 17.1 (7.6%, dimethyl *cis*,*trans*-nepetate, **5c**), 17.2 (0.6%), and 34.4 (1.6%) min.

The percent conversion by GC analysis was determined to be 7.5% as follows. GC analysis of a 12:1 molar mixture of methyl *trans*-2-butenoate and authentic **5c** showed two peaks at 1.5 (86.1%) and 17.1 (13.9%) min, respectively. The 12:1 molar ratio of gives an observed response ratio is 6.2:1.Therefor the peak area for methyl *trans*-2-butenoate must be multiplied by 1.93 to adjust for the less intense response to the FID. The observed peak ratios in the previous paragraph for methyl *trans*-2-butenoate (89.9%) and **5c** (7.6%) after multiplication of the 89.9% for methyl *trans*-2-butenoate by 1.93 and normalization to 100% (this neglects minor products) gives molar ratios of methyl *trans*-2-butenoate (96.1%) and **5c** (3.9%). Because two molecules of monomer are converted one molecule of **5c,** the yield of **5c** is calculated to be 7.5%, which corresponds well with the 8.8% yield calculated by analysis of the NMR spectrum of *trans*-2-butenoic acid and **5b**.

A third portion (202 mg) of irradiated and heated material was added to 10 mL of H_2O. The mixture was stirred vigorously for 45 min to dissolve unreacted **4** and filtered. The insoluble residue was dried at 25 ºC for 3 d to provide 10.5 mg (5.2%) of almost pure **5a**. This was dissolved in 1.5 mL of D_2O and 3 drops of 38% DCl in D_2O to give a solution of **5b** and $CaCl_2$ in D_2O: ^{1}H NMR (D_2O) 3.25 (ddd, 1, *J* = 9.2, 8.5, 8.1), 2.69 (dd, 1, *J* = 9.1, 8.1), 2.34-2.24 (m, 1), 2.06-2.02 (m, 1), 2.01-1.91 (m, 1), 1.91-1.81 (m, 1), 1.31-1.21 (m, 1), 1.05 (d, 3, *J* = 6.7); ^{13}C NMR (D_2O) δ 178.9 (C), 178.5 (C), 53.8 (CH), 46.9 (CH), 37.8 (CH), 33.0 (CH_2), 28.2 (CH_2), 19.3 (CH_3). The spectral data are identical to those of an authentic sample of **5b**.[12,13] The ^{1}H NMR spectrum of a mixture of synthetic and authentic **5b** showed the presence of only a single compound.

The filtrate after removal of most of poorly soluble **5a** was acidified with 5 mL of 1 M HCl and extracted five times with 10 mL portions of ether. The ethereal extracts were treated with 4-5 mL of ethereal diazomethane, dried ($MgSO_4$), filtered, and diluted with an equal amount of ether for GC analysis, which gave five peaks at 1.5 (96.5%), 16.2 (0.4%), 17.1 (0.9%, **5c**), 17.2 (0.4%), and 34.4 (1.8%) min. GC/MS on a medium polarity column showed five peaks at 7.92 (79%, methyl *trans*-2-butenoate), 26.27 (1.9%), 27.47 (2.5%), 27.83 (5.0%, dimethyl *cis*,*trans*-nepetate, **5c**), and 35.85 (11.5%) min. On this column, **5c** eluted fourth rather than third as on the less polar column used for GC analysis. The GC/MS shows more trimer and less monomer than regular GC with a flame ionization detector due to different detector sensitivities.

Methyl *trans*-2-butenoate: t_r = 7.92 min; GC/MS (*m/z*) 100 (M^+, 18), 85 (M^+-CH_3, 20), 69 (M^+-OCH_3, 100), 41 (52), 39 (36).

First unknown dimer: t_r = 26.27 min; GC/MS (*m/z*) 169 (M^+-OCH_3, 18), 168 (23), 140 (30), 127 (30), 126 (18), 104 (21), 100 (45), 99 (67), 81 (34), 69 (42), 59(100).

Second unknown dimer: t_r = 27.47 min; GC/MS (*m/z*) 185 (M^+-CH_3, 5), 169 (M^+-OCH_3, 23), 157 (33), 142 (14), 141 (25), 127 (100), 104 (19), 100 (57), 99(60), 97 (44), 81 (49), 69 (90), 59 (88), 41 (95), 39 (51).

Dimethyl *cis*,*trans*-nepetate (**5c**): t_r = 27.83 min; GC/MS (*m/z*) 169 (M^+-OCH_3, 20), 145 (10), 140 (23), 113 (29), 109 (11), 81 (100).

Unknown trimer: t_r = 35.85 min; GC/MS (*m/z*) 270 (M^+-CH_3OH, 9), 237 (9), 236 (18), 229 (13), 209 (16), 208 (19), 177 (25), 176 (26), 169 (26), 142 (66), 135 (19), 128 (29), 114 (100), 95 (61), 69 (72), 59 (94).

A sample of 40.8 mg of water-insoluble **5a** obtained by the above procedure was dissolved in 5 mL of 1 M HCl, which was extracted five times with 10 mL portions of ether. The combined ethereal extracts were treated with 2-3 mL of ethereal diazomethane, dried ($MgSO_4$), filtered, and concentrated to give 23 mg of dimethyl *cis*,*trans*-nepetate (**5c**) containing a trace of methyl *trans*-2-butenoate: ^{1}H NMR ($CDCl_3$) 3.70 (s, 3), 3.65 (s, 3), 3.15 (ddd, 1, *J* = 9.0, 8.6, 7.6), 2.60 (dd, 1, *J* = 8.8, 8.6), 2.45-2.35 (m, 1), 2.10-1.80 (m, 3), 1.30-1.20 (m, 1), 1.10 (d, 3, *J* = 6.6). Only a single peak at 17.1 min (dimethyl *cis*,*trans*-nepetate, **5c)** was observed in the GC. An authentic sample of **5b** was converted analogously to **5c**. The ^{1}H NMR spectrum and GC are identical to those of synthetic **5c**.

Assignment of the ^{1}H NMR Spectrum of Authentic *cis,trans*-Nepetic Acid (5b):[12,13] ^{1}H NMR (D_2O) 3.25 (ddd, 1, *J* = 8.1, 8.5, 8.8, $H_{1\alpha}$), 2.69 (dd, 1, *J* = 8.5, 9.2, $H_{2\alpha}$), 2.24-2.34 (m, 1, $H_{3\beta}$), 2.02-2.06 (m, 1, $H_{5\alpha}$), 1.91-2.01 (m, 1, $H_{4\beta}$), 1.84-1.91 (m, 1, $H_{5\beta}$), 1.21-1.31 (m, 1, $H_{4\alpha}$), 1.05 (d, 3, *J* = 6.7). Irradiation of the peak at δ 1.05 showed NOEs to the peaks at δ 1.21-1.31, 2.24-2.34, 2.69 and 3.25 (small). Irradiation of the peak at δ 1.21-1.31 showed NOEs to the peaks at δ 1.10, 1.91-2.01, 2.02-2.06, 2.24-2.34 (small), 2.69 and 3.25. Irradiation of the peak at δ 2.02-2.06 showed NOEs to the peaks at δ 1.21-1.31, 2.69 (small) and 3.29. Irradiation of the peak at δ 2.24-2.34 showed NOEs to the peaks at δ 1.10, 1.84-1.91 (small), 2.02-2.06 and 2.69. Irradiation of the peak at δ 2.69 showed NOEs to the peaks at δ 1.10, 1.21-1.31 (small), 2.02-2.06 (small), 2.24-2.34 and 3.25. Irradiation of the peak at δ 3.25 showed NOEs to the peaks at δ 1.10 (small), 1.21-1.31 (small), 1.84-1.91 (small), 2.02-2.06 and 2.69. This data is presented in Table S1.

Preparation of Aqueous Magnesium *trans*-2-butenoate. A stock solution was prepared using a 100 mL three-necked round-bottomed flask equipped with a thermometer, a condenser and a stopper. The flask was charged with 30 mL of water and maintained at 75 ºC using a heating mantle. *trans*-2-Butenoic acid (5.319 g, 61.8 mmol) was added slowly to the flask.

$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ (3.000 g, 6.178 mmol) was added in several portions. Each time that the bubbling subsided, a new portion was added. After the addition was complete, the solution was stirred for 1 h at 75 ºC. The solution was filtered through a preheated funnel (~75 ºC) into a preheated flask.

Preparation of Hexaaquamagnesium *trans*-2-Butenoate Dihydrate (9). The aqueous stock solution (1 mL) was placed in a Pyrex culture tube (18 × 150 mm). An organic solvent (5 or 10 mL of ethyl acetate, cyclohexane, hexanes, ethyl ether or benzene) was layered carefully with a syringe on the top of the aqueous solution and the tube was capped tightly. After 1-2 d, prismatic crystals of **9** were formed. In optimal cases, 81 mg (23%) for ethyl acetate, 37 mg (11%) for ethyl ether, and 28 mg (8%) for hexanes were obtained from the 1:10 mixtures of aqueous stock solution and organic solvent. The ^{1}H and ^{13}C-NMR spectra are identical to those obtained for compound **11**.

Addition of either 5 or 10 mL of acetone or acetonitrile to the 1 mL of aqueous stock solution resulted in the formation of **9**, **11**, or a mixture of both as could be determined by visual inspection of the crystals. Although the use of these solvents did not lead exclusively to **9**, the yields of crystalline material were much higher than with other organic solvents (276 mg with 5 mL of acetonitrile and 201 mg with 5 mL of acetone).

Preparation of triaquabis(*trans*-2-butenoato)magnesium (11). To 5 mL of the above stock solution (at 25-35 ºC), DMF (5 or 10 mL) was added and the solution was stirred for 30 min. The solution was allowed to evaporate slowly. Not all the trials were successful; in optimal cases, after 2-3 d, platelike crystals of **11** appeared. Crystals obtained from the 1:1 mixture of aqueous stock solution and DMF were of higher quality. 543 mg (43%) of **9** was obtained from the 1:2 mixture of mixture of aqueous stock solution and DMF: ^{1}H NMR (D_2O) 6.65 (dq, 1, J = 15.3, 6.7), 5.83 (dq, 1, J = 15.3, 1.8), 1.80 (dd, 3, J = 6.7, 1.8); ^{13}C NMR (D_2O) 177.0 (C), 142.4 (CH), 128.2 (CH), 17.9 (CH_3). Crystalline **11** was also be obtained by diffusion with acetone or acetonitrile as described above for the preparation of **9**.

γ-Irradiation of Triaquabis(*trans*-2-butenoato)magnesium (11). Samples of **11** were placed in loosely capped vials and exposed to γ-rays for 2, 4, 8, 16, 32, 64 and 128 d. All irradiated samples of **11** were completely soluble in water. NMR samples were prepared by dissolution of ca. 5 mg of irradiated **11** in 1.5 mL of D_2O to give a homogeneous solution. The percent conversion to magnesium *trans,trans*-nepetate (**15a**) was determined by integrating the methyl doublet of **15a** and either the methyl doublet of unreacted **11** (for high conversion) or the ^{13}C satellite (0.5%) of the methyl doublet of **11** (for low conversion). The conversion to **15a** was 0.3% (2 d), 0.8% (4 d), 2% (8 d), 12% (16 d), 19% (32 d), 27% (64 d) and 43% (128 d). The major dimer (about 63% of the product mixture, although selectivity decreased between 64 and 128 d) was accompanied by several unidentified minor products). Neither **10** nor the magnesium salt of **5b** were formed. The ^1H NMR spectrum of the sample irradiated for 128 d in D_2O showed product methyl doublets in the indicated percentage at δ 0.82 (J = 7.3, 5%), 0.86 (J = 7, 4.5%), 0.87 (J = 7, 4.5%), 0.97 (J = 6.7, 3%), 1.022 (J = 6.1, 63%, **15a**), 1.086 (J = 6.4, 8%), 1.349 (J = 4.9, 12.5%). The ^1H NMR spectral peaks for **15a** in this sample are identical to those of a pure sample prepared by reaction of authentic **15b** with $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ (see below). Doping this sample with calcium *cis,trans* nepetate (**5a**) showed the presence of two different dimers. Doping with an authentic sample of *trans,trans* nepetic acid (**15b**) increased the peaks of the major synthetic dimer without introducing any new peaks thereby establishing the structure of the major synthetic dimer.

Assignment of the ^1H NMR Spectrum of Magnesium *trans,trans*-Nepetate (15a). An authentic sample of *trans,trans*-nepetic acid (**15b**)[12,13] (10 mg, 0.06 mmol) was dissolved in 1 mL of water and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ **(**1.00 mg, 0.002 mmol) was added. The reaction mixture was heated at reflux for 10 minutes and concentrated under reduced pressure to give a white solid. The solid was washed with acetone twice to remove any excess acid, dried, and collected to give 7 mg (57%) of **15a** as a white solid: ^1H NMR (D_2O) 2.83 (ddd, 1, J = 8, 9.9, 9.9, $H_{1\beta}$), 2.30 (dd, 1, J = 9.9, 9.7, $H_{2\alpha}$), 1.92-2.05 (m, 2, $H_{3\beta5\beta}$), 1.81-1.88 (m, 1, $H_{4\beta}$), 1.68-1.76 (m, 1, $H_{5\alpha}$), 1.29 (ddd, 1, J = 9.1, 11.6, 12.2, $H_{4\alpha}$), 1.02 (d, 3, J = 6.7). Irradiation of the peak at δ 1.02 showed NOEs to the peaks at δ 1.29, 1.81-1.88 (small), 1.92-2.05, 2.30. Irradiation of the peak at δ 1.29 showed NOEs to the peaks at δ 1.02, 1.81-1.88, 1.92-2.05, 2.30 (small). Irradiation of the peak at δ 1.68-1.76 showed NOEs to the peaks at δ 1.29 (small), 1.81-1.88 (small) and 1.92-2.05, 2.30 (small), and 2.83 (small). Irradiation of the peak at δ 1.81-1.88 showed NOEs to the peaks at δ 1.02 (small), 1.29 and 1.68-1.76 (small). Irradiation of the peak at δ 1.92-2.05 showed NOEs to the peaks at δ 1.02, 1.29 (small), 1.68-1.76 and 2.83. Irradiation of the peak at δ 2.30 showed NOEs to the peaks at δ 1.02, 1.29, 1.68-1.76 (small), 1.81-1.88 (small), 1.92-2.05 and 2.83 (small). Irradiation of the peak at δ 2.83 showed NOEs to the peaks at δ 1.92-2.05 and 2.30. This data is presented in Table S2.

Data for authentic **15b**: ^{1}H NMR (D_2O) δ 3.15 (ddd, 1, *J* = 9.6, 9, 9), 2.57 (dd, 1, *J* = 9.6, 9.6), 2.2-2.1 (m , 1), 2.1-2.02 (m, 1), 2.00-1.85 (m, 1), 1.45-1.35 (m, 1), 1.11 (d, 3, *J* = 6.4).

tert**-Butyl 3-Hydroxybutanoate-*3-d* (23)**. Sodium borodeuteride (1.32 g, 32 mmol) was added to a cooled solution of *tert*-butyl acetoacetate (10 g, 63 mmol, **22**) in 35 mL of ethanol at 0 ºC. The resulting mixture was stirred at 0 ºC for 1 h and warmed to room temperature. The mixture was then concentrated under reduced pressure, dissolved in water and acidified with concentrated hydrochloric acid (2 mL) until the pH reached 4. The aqueous layer was extracted with 3 × 30 mL of methylene chloride and the organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure to give a light yellow oil. Bulb-to-bulb distillation (55 ºC, 0.03 torr) afforded 7.2 g (71%) of **23** as a colorless oil: ^{1}H NMR ($CDCl_3$) 2.40 (d, 1, *J* = 16.5), 2.33 (d, 1, *J* = 16.5), 1.46 (s, 9), 1.20 (s, 3).

tert**-Butyl 3-Methanesulfonyloxybutanoate-*3-d* (24).** Triethylamine (6.6 g, 65 mmol) was added to a stirred solution of **23** (7.2 g, 43 mmol) in 35 mL of methylene chloride. The reaction mixture was stirred at room temperature for 10 min, cooled to 0 ºC, and methanesulfonyl chloride (4.9 g, 43 mmol) was added dropwise over 20 minutes. The mixture was stirred at 0 ºC for 1 h, warmed to room temperature, and carefully poured into 1 M $NaHCO_3$ solution (30 mL). The aqueous and organic layers were separated, and the aqueous layer was extracted with 3 × 30 mL of methylene chloride. The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure to give an orange oil. Bulb-to-bulb distillation (70 ºC, 0.5 torr) afforded 9.6 g (82%) of **24** as a light yellow oil: ^{1}H NMR ($CDCl_3$) 3.04 (s, 3), 2.67 (d, 1, *J* = 16.5), 2.47 (d, 1, *J* = 16.5), 1.48 (s, 3), 1.46 (s, 9).

***tert*-Butyl *trans*-2-Butenoate-*3-d* (25).** 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (10.1 g, 66 mmol) was added dropwise to a solution of **24** (9.0 g, 33 mmol) in 40 mL of methylene chloride. The reaction mixture was stirred at room temperature for 24 h, and treated with a 1 M solution of acetic acid (25 mL). The aqueous and organic layers were separated, and the aqueous layer was extracted with 3 × 30 mL of methylene chloride. The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure to give a yellow oil. Purification using bulb-to-bulb distillation (50 ºC, 0.5 torr) afforded 3.8 g (81%) of **25** as a colorless oil: ^{1}H NMR ($CDCl_3$) 5.75 (br s, 1), 1.84 (s, 3), 1.48 (s, 9).

***trans*-2-Butenoic-*3-d* Acid (26).** Ester **25** (2.00 g, 14 mmol) was dissolved in 30 mL of distilled benzene and *p*-toluenesulfonic acid (0.27 g, 1.4 mmol) was added. The reaction mixture was heated for 1 h at reflux in a flask fitted with a Dean-Stark trap and condenser. The reaction mixture was then cooled to room temperature and concentrated under reduced pressure to give a mixture of *trans*-2-butenoic-*3-d* acid (**26**) and *p*-toluenesulfonic acid as a light yellow solid. The solid was purified by filtration through 25 g of silica gel column (7:3 hexane/ethyl acetate) to give 0.95 g (78%) of **26** as a white solid: ^{1}H NMR ($CDCl_3$) 5.87 (br s, 1), 1.94 (s, 3). Deuterium incorporation was determined to be 98-99% by integration of the residual peak for the C_3-H group at δ 7.11.

Bis(*trans*-2-butenoato-3-*d*)calcium (19). Acid **26** (200 mg, 2.2 mmol) was dissolved in 20 mL of water, and calcium carbonate (110 mg, 1.1 mmol) was added in small portions. The reaction mixture was stirred at room temperature until all evolution of CO_2 ceased. Excess calcium carbonate was removed by gravity filtration and the filtrate was concentrated under reduced pressure to give a colorless solid. The solid was washed several times with acetone to remove any excess acid, dried and collected to give 136 mg (98%) of **19** as a colorless solid: mp > 220 ºC.

Triaquabis(*trans*-2-butenoato-3-*d*)magnesium (27). Acid **26** (200 mg, 2.2 mmol) was dissolved in 20 mL of water, warmed to 80 ºC, and $(MgCO_3)_4.Mg(OH)_2.5H_2O$ (107 mg, 0.22 mmol) was added in small portions. Once the addition was complete, the reaction mixture was heated at 80 ºC for 1 h, cooled to room temperature and excess $(MgCO_3)_4.Mg(OH)_2.5H_2O$ was removed by gravity filtration. The filtrate was concentrated under reduced pressure to give a colorless solid. The solid was washed several times with acetone to remove any excess acid, dried, and collected to give 109 mg (90%) of **27** as a colorless solid; mp > 220 ºC. This simple procedure was investigated because the supply of deuterated acid **26** was limited. Fortunately it gave only **27**, the deuterium analogue of **11**, free of the deuterium analogue of **9** as determined by the absence of the deuterium analogue of **10** in the product mixture.

γ-Irradiation of Bis(*trans*-2-butenoato-3-*d*)calcium (19) Under Nitrogen. Salt **19** (100 mg, 0.78 mmol) was placed in a 3 mm inside diameter glass tube and packed tightly using a glass rod. A septum was placed at the rim of the glass tube and the sample was evacuated for 3 min. The sample was then placed under nitrogen for 3 min and sealed using an air/gas flame and subjected to γ-rays (500 kGy, 25 h at the Radiation Laboratory, University of Massachusetts Lowell). Water (1.5 mL) was then added to the solid. Some of the solid did not dissolve. The solution was filtered and the residue was dried to give 26 mg (24.3%) of calcium *cis,trans*-nepetate-*3,5*-d_2 (**21a**) as a white solid containing about 5% of unreacted **19**. The NMR sample of the free acid **21b** was prepared by suspending 10 mg of calcium salt **21a** in 1 mL of D_2O and adding 2 drops of DCl (20 wt% solution in D_2O) to give a homogeneous solution of **21b**: ^1H NMR (D_2O/DCl, zeroed from residual acetone peak at δ 2.08) 3.28 (dd, 1, $J = 8.5, 9.2$), 2.72 (d, 1, $J = 9.2$), 2.02 (ddd, 1, $J = 8.5, 8.5, 3.7$), 1.95 (dd, 1, $J = 3.7, 12.8$), 1.27 (dd, 1, $J = 8.5, 12.8$), 1.06 (s, 3). This data is presented in Table S3.

γ-Irradiation of Triaquabis(*trans*-2-butenoato-3-*d*)magnesium (27) Under Nitrogen. Salt **27** (100 mg, 0.91 mmol) was placed in a 3 mm inside diameter glass tube and packed tightly using a glass rod. A septum was placed at the rim of the glass tube and the sample was evacuated for 3 min. The sample was then placed under nitrogen for 3 min and sealed using an air/gas flame and subjected to γ-rays (500 kGy, 25 h at the Radiation Laboratory, University of

Massachusetts Lowell). The NMR sample was prepared by dissolving 10 mg of the product in 1 mL of D_2O. Analysis of the sample revealed that the product consisted of salt **28a** (65%) and unreacted **27**: ^{1}H NMR (D_2O) 2.80 (dd, 1, J = 7.9, 9.8), 2.27 (d, 1, J = 9.8), 1.82 (dd, J = 4.5, 12.2), 1.66-1.72 (m, 1), 1.26 (dd, 1, J = 9.1, 12.2), 0.99 (s, 3). This data is presented in Table S4.

X-Ray data collection, solution, and refinement for 4 and 11. Data collection was carried out at room temperature (low temperature apparatus was not available) on a CAD-4 Turbo diffractometer equipped with MoKα radiation;[25] completeness values for the two structures were 99.5 and 99.7%, respectively. The structures were solved by direct methods (SIR92).[26] From the lack of systematic absences, the observed metric constants and intensity statistics, space groups $P2/c$ and $P2_1/c$, respectively, were chosen initially; subsequent solution and refinement confirmed the correctness of the choices. Full-matrix least squares refinement was carried out using the Oxford University *Crystals for Windows* system.[27] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; minor component disordered atoms were refined using isotropic displacement parameters. After preliminary location on electron density difference maps, hydrogen atoms were first regularized with the use of restraints and subsequently allowed to ride on the corresponding C and/or O atoms.

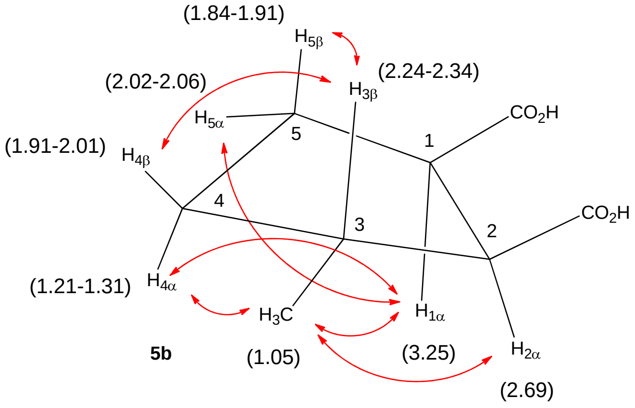
Compound **4** exhibited significant disorder of the *trans*-2-butenoate moiety (C atoms numbered 2/3/4 and 21/31/41), which was resolved successfully. The disorder was described with a constraint that the occupancies of the major and minor components sum to 1.0; the major component occupancy refined to 0.952(5). Distance, angle and vibrational restraints were applied to the atoms of the minor component. The final least-squares refinement converged to $R_1 = 0.0333$; $wR_2 = 0.0420$ ($I > 1.96\sigma(I)$, 1246 data) and $R_1 = 0.0455$; $wR_2 = 0.0594$ (F, all 1462 data, 74 parameters). For compound **11**, only very thin, weakly-diffracting crystals could be obtained. Nonetheless, a satisfactory structure analysis could be easily realized, as the material was well-ordered. The final least-squares refinement converged to $R_1 = 0.0478$; $wR_2 = 0.0351$ ($I > 1.96\sigma(I)$, 1154 data) and $R_1 = 0.1648$; $wR_2 = 0.0855$ (F, all 2490 data, 145 parameters). The final CIF files are available as supporting material; we note that the CheckCIF routine produced one alert B item for each structure, related to disorder of the butenoate moiety in **4** and to the overdetermination ratio of 7.96 in **11**. Accordingly, the CIF file contains validation reply form items which explain these issues in detail.

References

S1. F. Arndt, *Org. Syn., Coll. Vol. II*, 165 (see note 3).

Table S1. Chemical Shifts and COSY Cross Peaks and NOESY Data for **5b**.

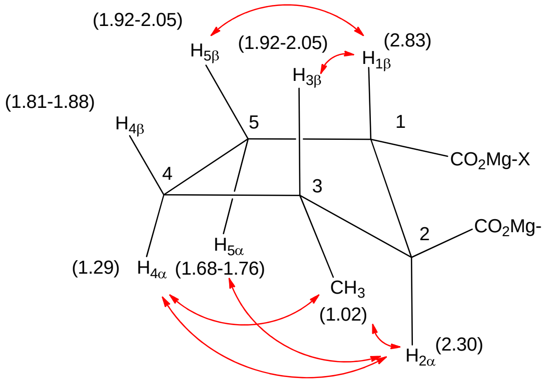
Hydrogen #, Chemical Shift (ppm), Splitting Pattern	COSY Cross peaks	1D NOESY peaks
$H_{1\alpha}$, 3.25 (dd, 1, *J* = 8.5, 8.8)	2.69, 2.02-2.06	1.05 (w), 1.21-1.31 (w), 1.84-1.91 (w), 2.02-2.06, 2.69
$H_{2\alpha}$, 2.69 (dd, 1, *J* = 8.5, 9.2)	3.25, 2.24-2.34	1.05, 1.21-1.31 (w), 2.02-2.06 (w), 2.24-2.34, 3.25
$H_{3\beta}$, 2.24-2.34 (m, 1)	2.69, 1.05, 1.91-2.01	1.05, 1.84-1.91 (w), 1.91-2.01, 2.69,
$H_{4\alpha}$, 1.21-1.31 (m, 1)	2.24-2.34, 2.02-2.06, 1.91-2.01, 1.84-1.91	1.05, 2.02-2.06, 2.24-2.34 (w), 2.69, 3.25,
$H_{4\beta}$, 1.91-2.01 (m, 1)	2.24-2.34, 1.21-1.31, 1.84-1.91, 2.02-2.06	-----
$H_{5\alpha}$, 2.02-2.06 (m, 1)	3.25, 1.21-1.31, 1.84-1.91	1.21-1.31, 2.69 (w), 3.25
$H_{5\beta}$, 1.84-1.91 (m, 1)	3.25, 1.21-1.31, 2.02-2.06-1.91-2.01	-----
Me, 1.05 (d, 3, *J* = 6.7)	2.24-2.34	1.21-1.31, 2.24-2.34, 2.69, 3.25



5b

Table S2. Chemical Shifts and COSY Cross Peaks and NOESY Data for **15a**

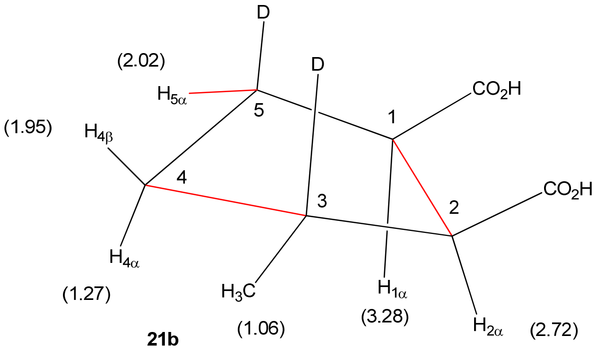
Hydrogen #, Chemical Shift (ppm), Splitting Pattern	COSY Cross peaks	1D NOESY peaks
$H_{1\beta}$, 2.83 (ddd, 1, J = 8, 9.9, 9.9)	1.68-1.76, 1.81-1.88, 2.30	1.92-2.05, 2.30
$H_{2\alpha}$, 2.30 (dd, 1, J = 9.9, 9.7)	1.92-2.05, 2.83	1.02, 1.29, 1.68-1.76 (w), 1.81-1.88 (w), 1.92-2.05, 2.83 (w)
$H_{3\beta}$, 1.92-2.05 (m, 1)	1.02, 1.29, 1.81-1.88, 2.30	1.02, 1.29 (w), 1.68-1.76, 2.83
$H_{4\alpha}$, 1.29 (ddd, 1, J = 9.1, 11.6, 12.2)	1.81-1.88, 1.92-2.05, 1.68-1.76	1.02, 1.81-1.88, 1.92-2.05, 2.30 (w)
$H_{4\beta}$, 1.81-1.88 (m, 1)	1.29, 1.68-1.76, 1.92-2.05	1.02 (w), 1.29, 1.68-1.76 (w)
$H_{5\alpha}$, 1.68-1.76 (m, 1)	1.29, 1.81-1.88, 1.92-2.05, 2.83	1.29 (w), 1.81-1.88 (w), 1.92-2.05, 2.30 (w), 2.83 (w)
$H_{5\beta}$, 1.92-2.05 (m, 1)	1.29, 1.68-1.76, 1.81-1.88, 2.83	1.02, 1.29 (w), 1.68-1.76, 2.83
Me, 1.02 (d, 3, J = 6.7)	1.92-2.05	1.29, 1.81-1.88 (w), 1.92-2.05, 2.30



15a

Table **S3**. Chemical Shifts and Splitting Patterns for **21b**

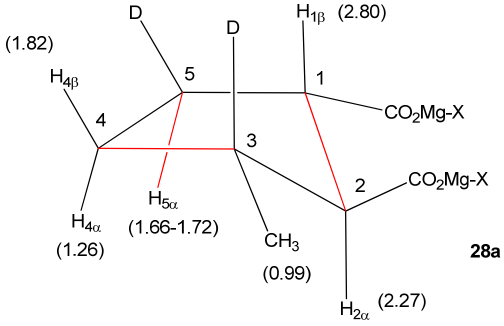
Hydrogen	Chemical shift (ppm)	Splitting pattern
$H_{2\alpha}$	3.28	(dd, 1, *J* = 8.5, 9.2)
$H_{1\alpha}$	2.72	(d, *1*, J = 9.2)
$H_{4\alpha}$	1.27	(dd, 1, *J* = 8.5, 12.8)
$H_{4\beta}$	1.95	(dd, 1, *J* = 3.7, 12.8)
$H_{5\alpha}$	2.02	(ddd, 1, *J* = 8.5, 8.5, 3.7)
Me	1.06	(s, 3)



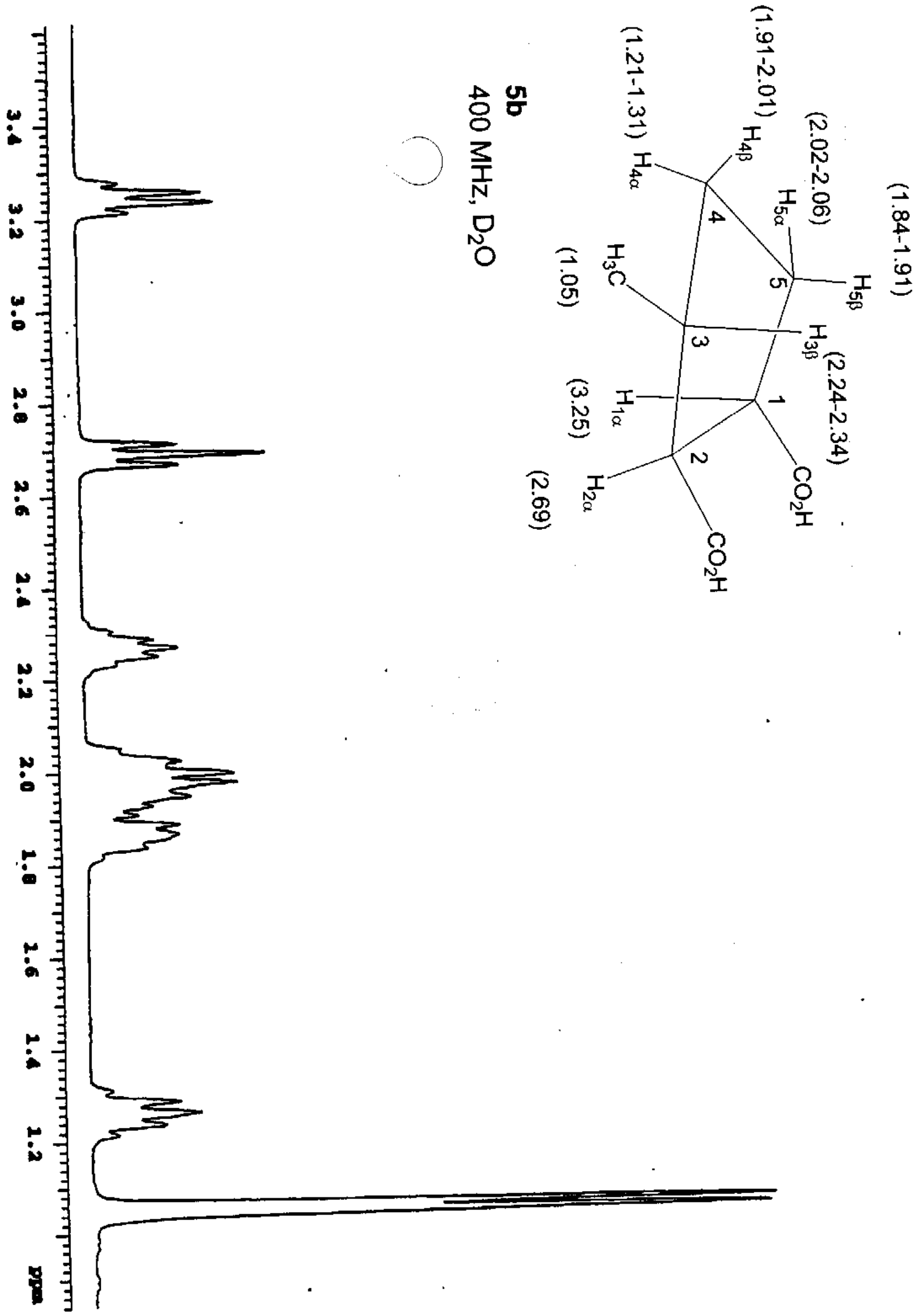
21b

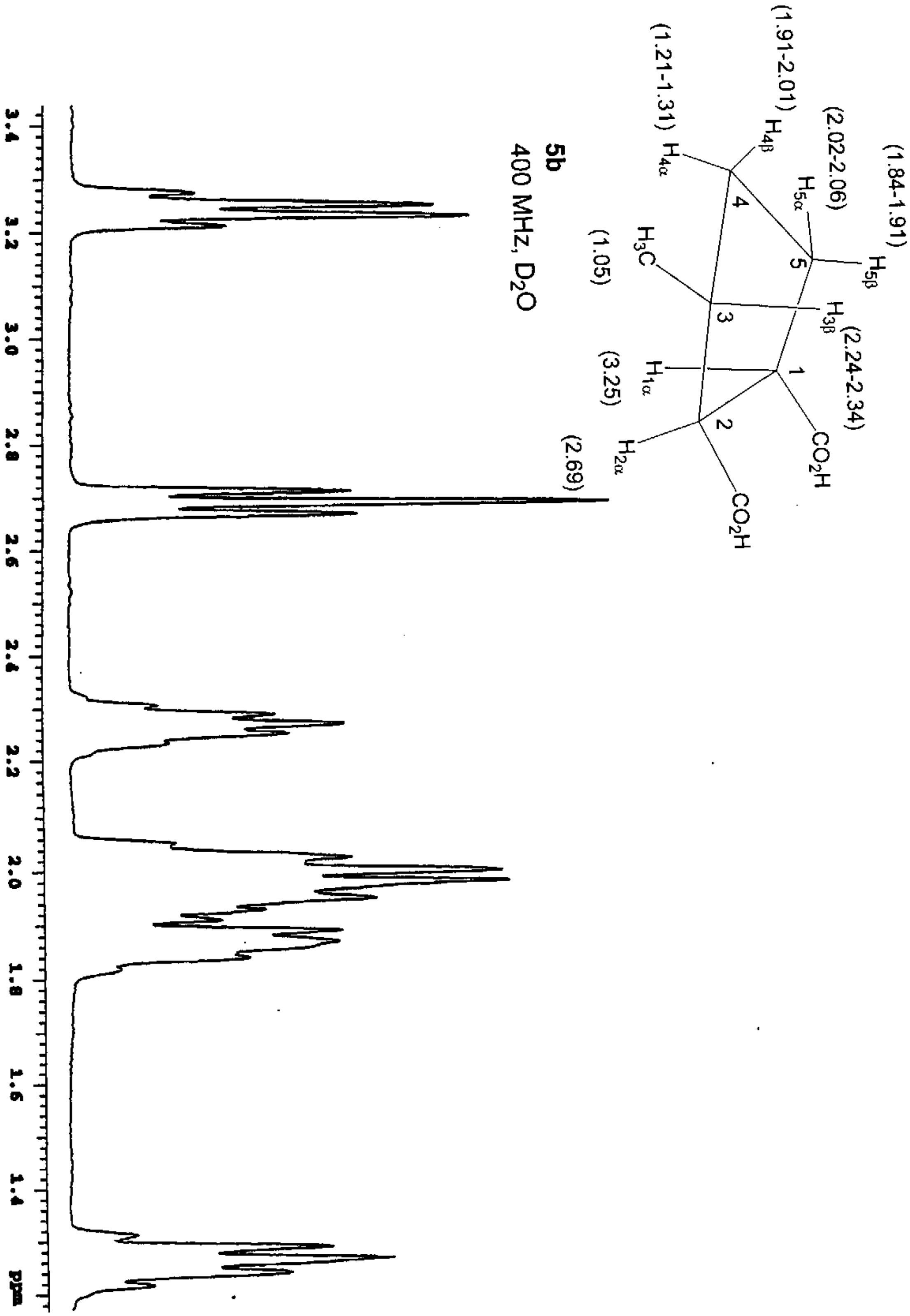
Table S4. Chemical Shifts and Splitting Patterns for **28a**

Hydrogen	Chemical shift (ppm)	Splitting pattern
$H_{1\beta}$	2.80	(dd, 1, *J* = 7.9, 9.8)
$H_{2\alpha}$	2.27	(d, 1, *J* = 9.8)
$H_{4\alpha}$	1.26	(dd, 1, *J* = 9.1, 12.2)
$H_{4\beta}$	1.82	(dd, 1, *J* = 4.5, 12.2)
$H_{5\alpha}$	1.66-1.72	(m, 1)
Me	0.99	(s, 3)



28a


5b
400 MHz, D2O
(1.84-1.91)
$H_{5\beta}$
(2.02-2.06)
$H_{5\alpha}$
(1.91-2.01)
$H_{4\beta}$
(1.21-1.31)
$H_{4\alpha}$
H_3C
(1.05)
$H_{3\beta}$
(2.24-2.34)
$H_{1\alpha}$
(3.25)
$H_{2\alpha}$
(2.69)
CO_2H
CO_2H
1
2
3
4
5
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm


5b

400 MHz, D_2O

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 Temp. 25.0 C / 298.1 K
INOVA-600  "meiboom"

PULSE SEQUENCE: gCOSY
 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width    8000.0 Hz
 2D Width 8000.0 Hz
 Single scan
 128 increments
OBSERVE   H1, 599.6964750 MHz
DATA PROCESSING
 Sq. sine bell 0.064 sec
F1 DATA PROCESSING
 Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
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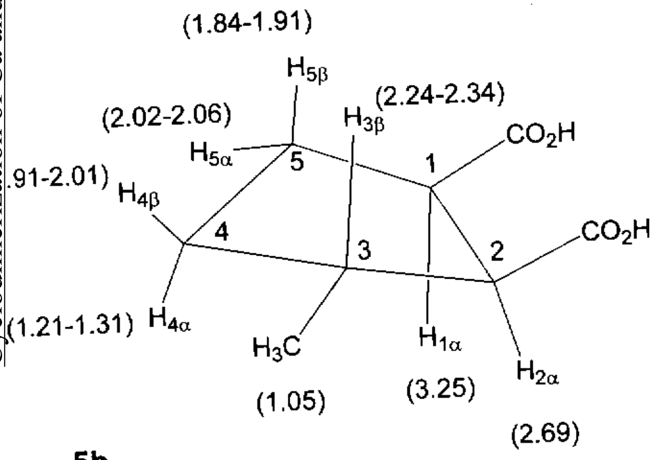
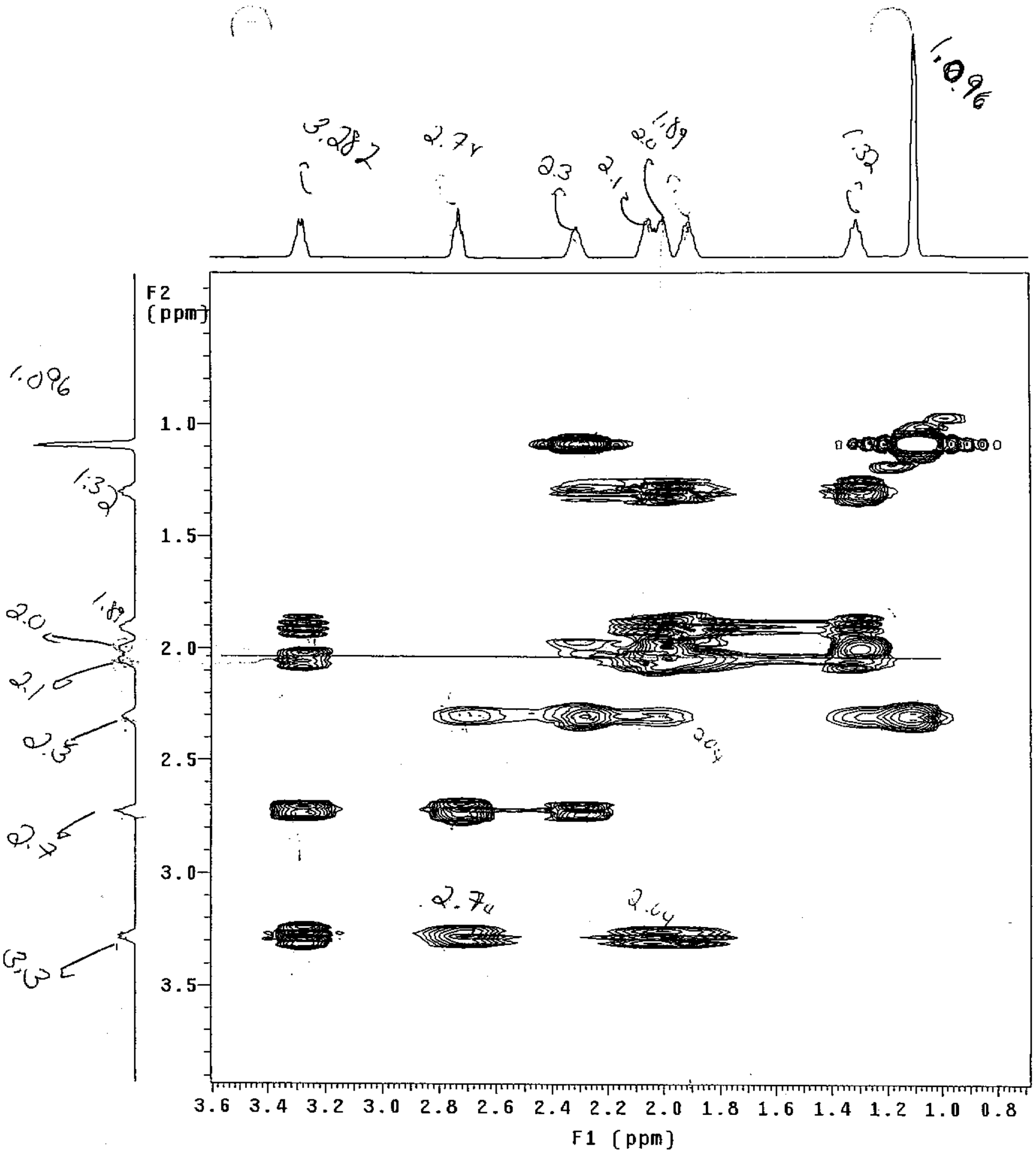
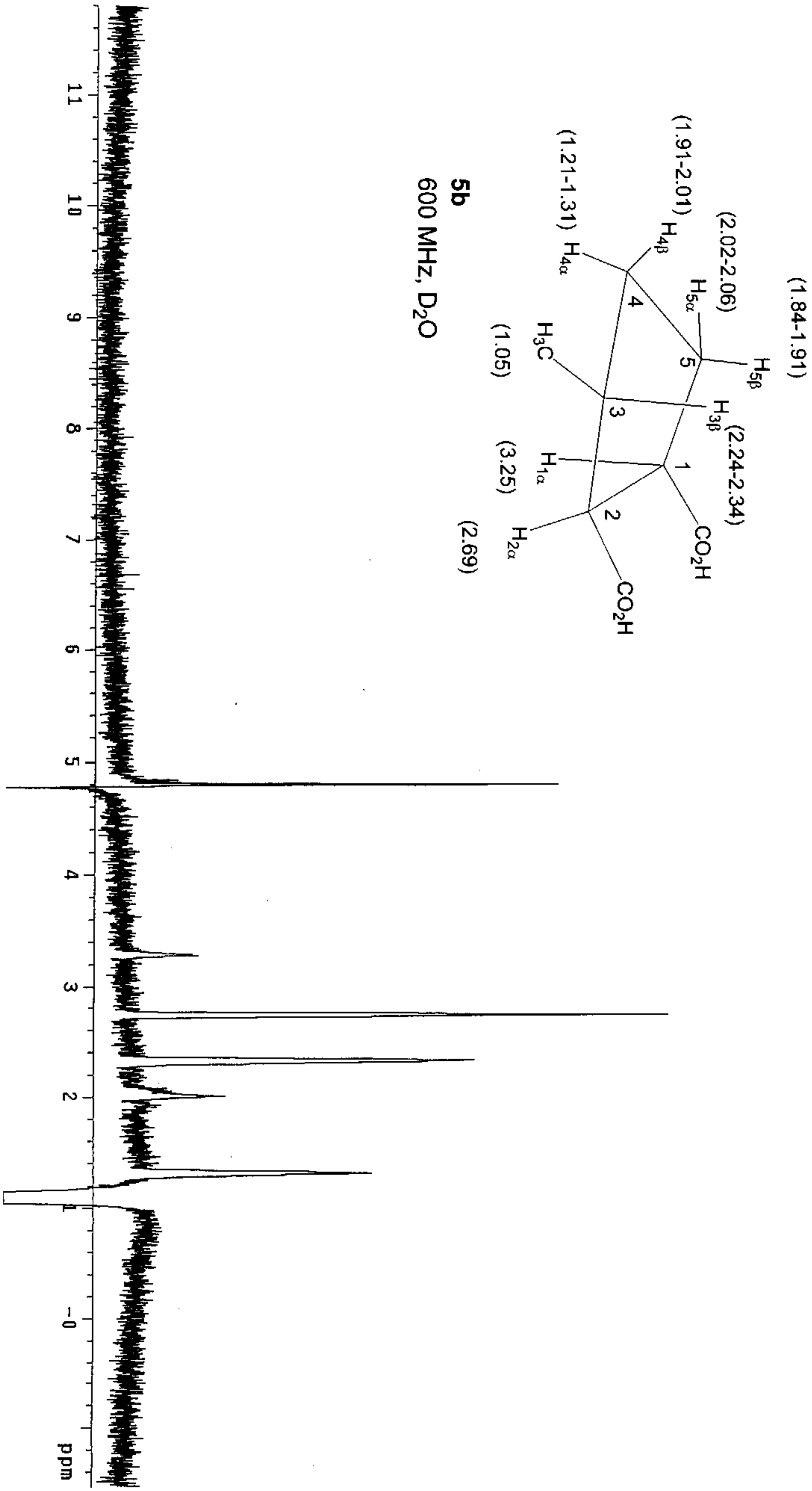
G-COSY



5b

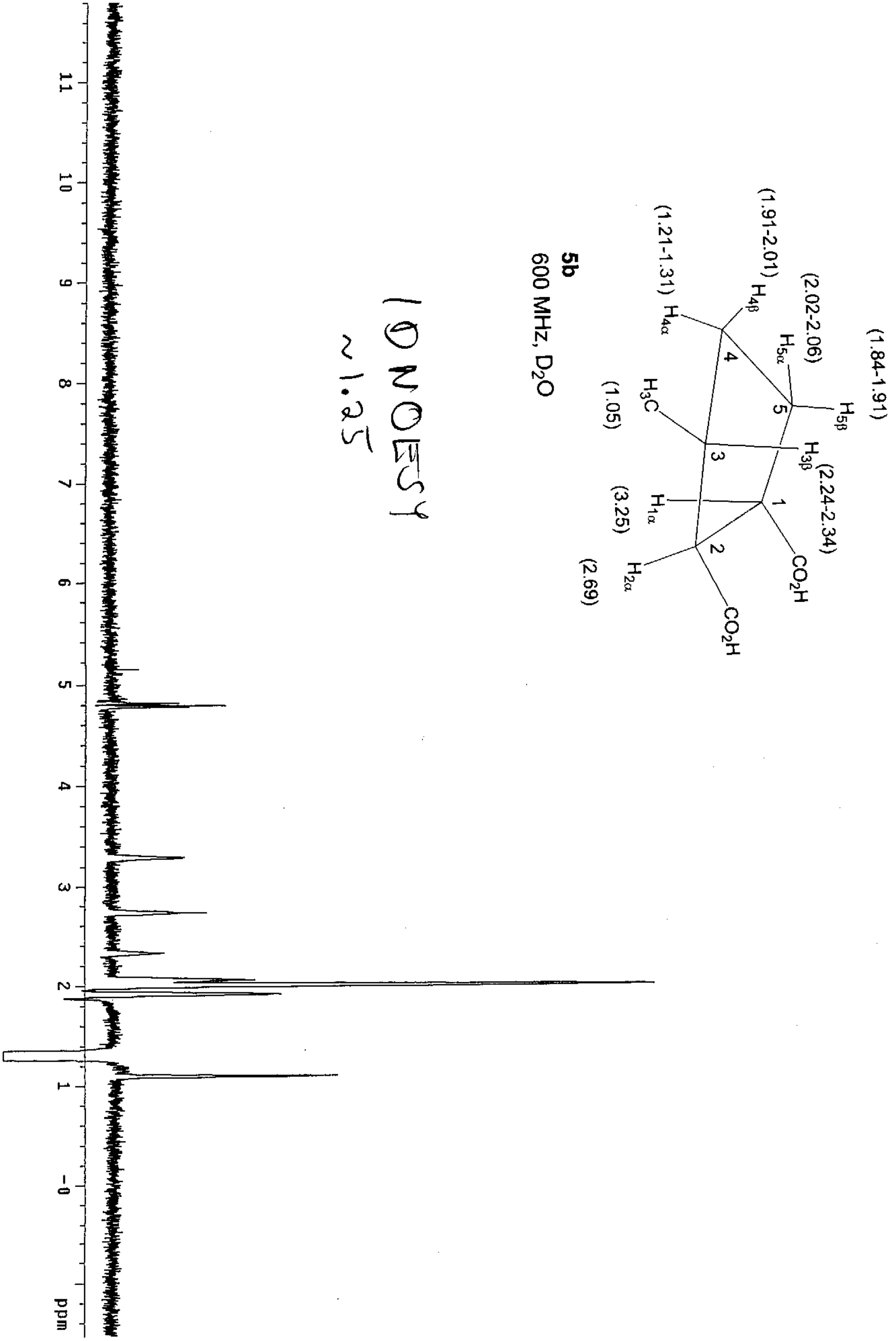
600 MHz, D_2O





5b
600 MHz, D_2O

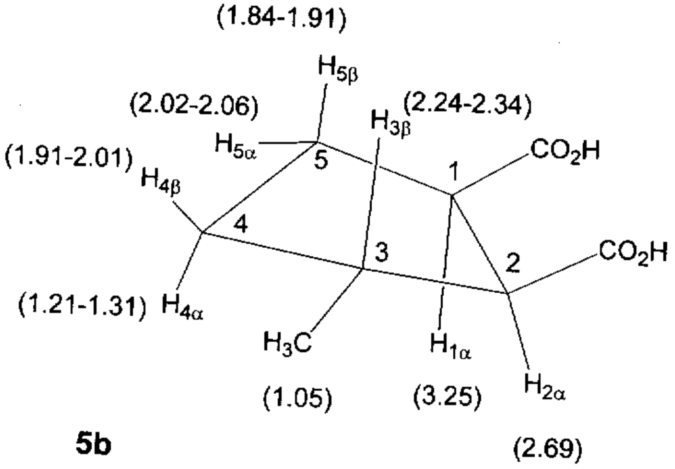
1D NOESY
δ1.05



5b
600 MHz, D_2O

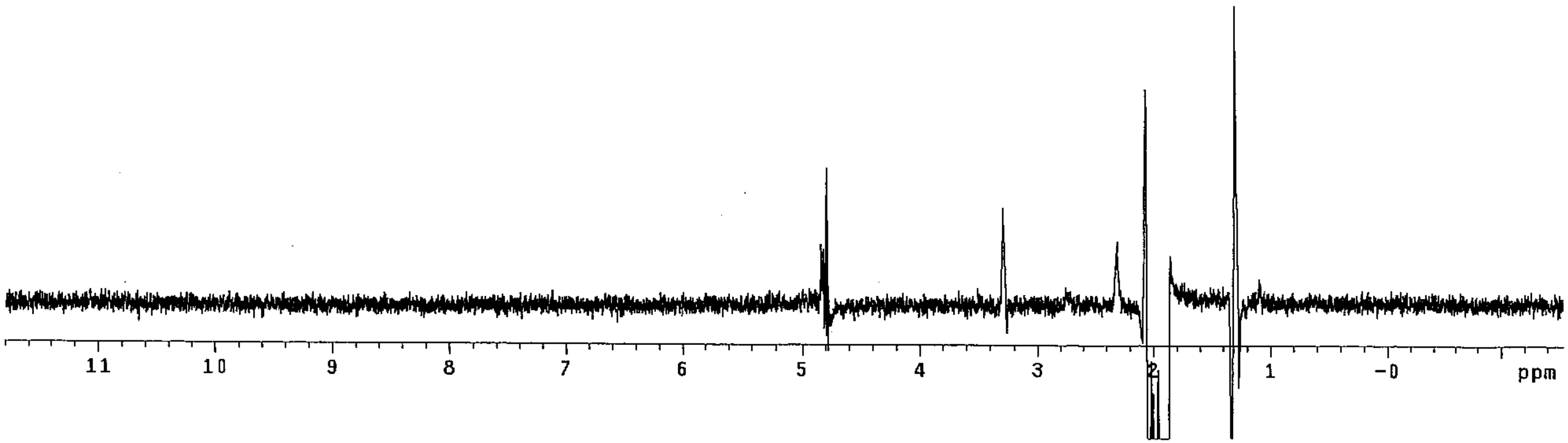
1D NOESY
~1.25

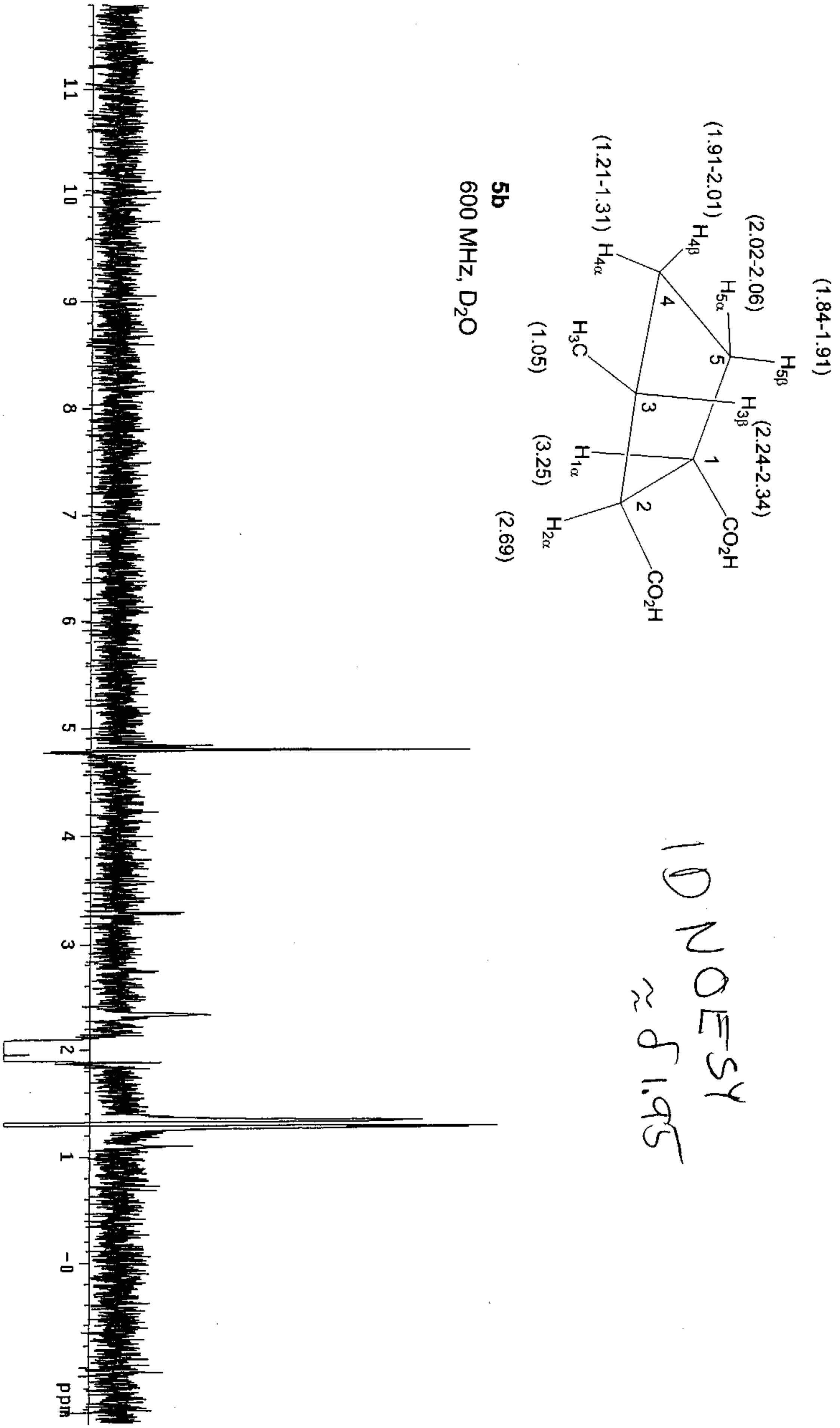
1D NOESY ≈ δ1.85



5b

600 MHz, D_2O

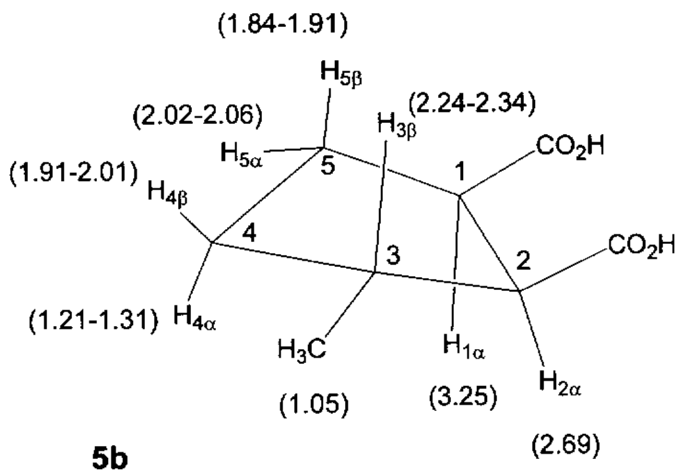




5b

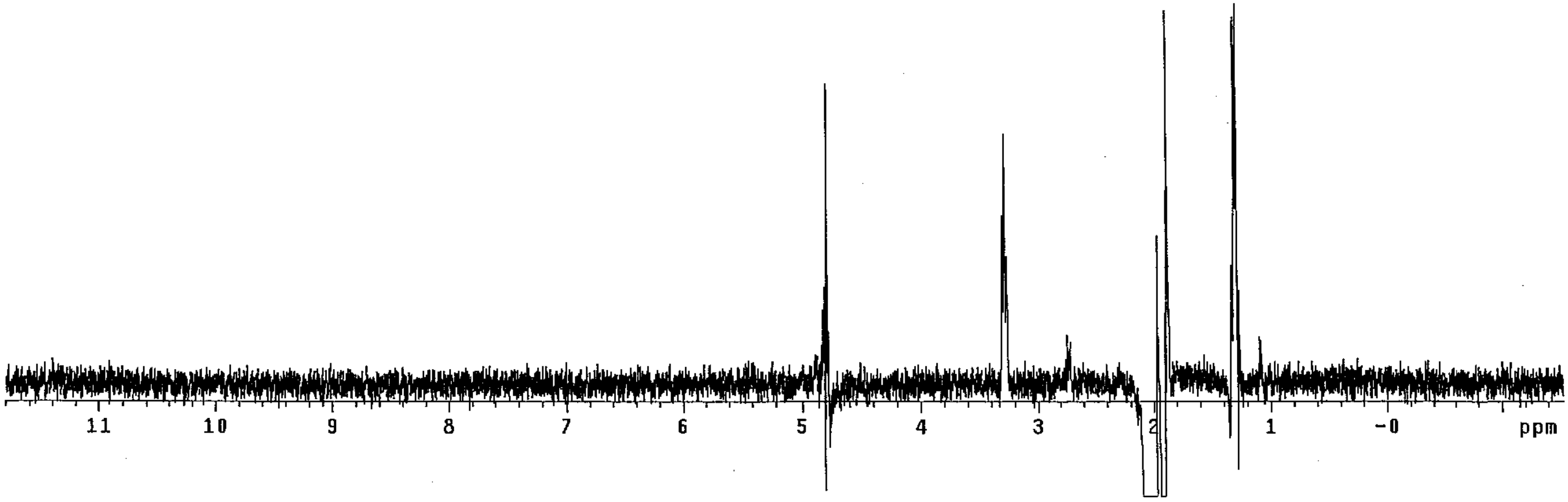
600 MHz, D_2O

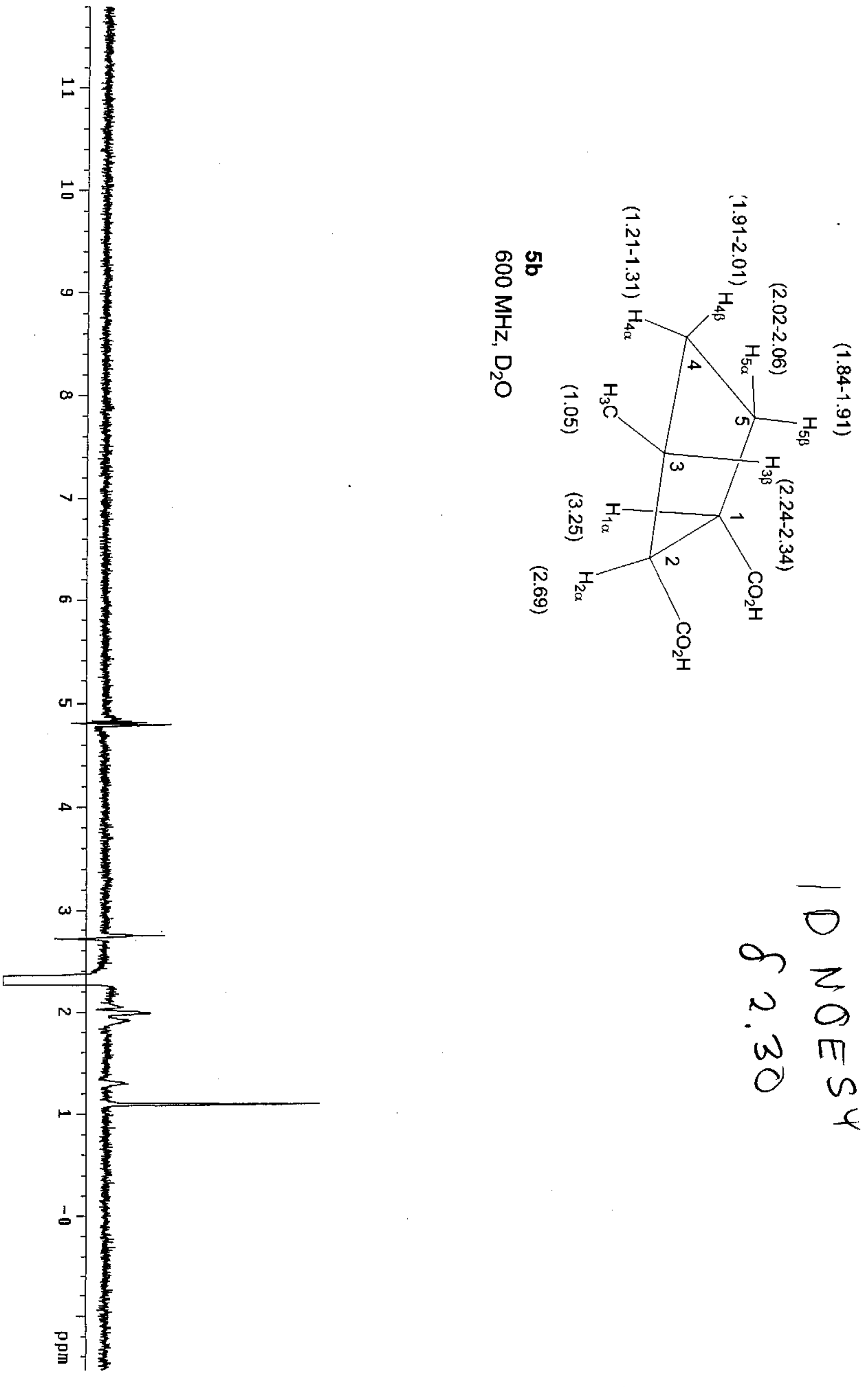
1D NOESY
≈ δ1.95



5b
600 MHz, D_2O

1D NOESY
~δ 2.05

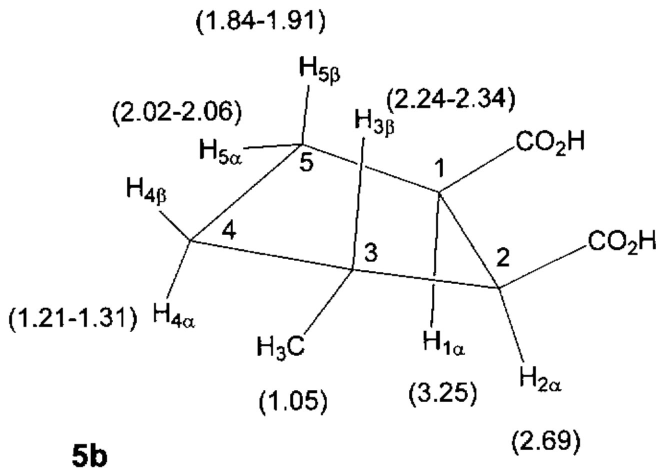




5b

600 MHz, D_2O

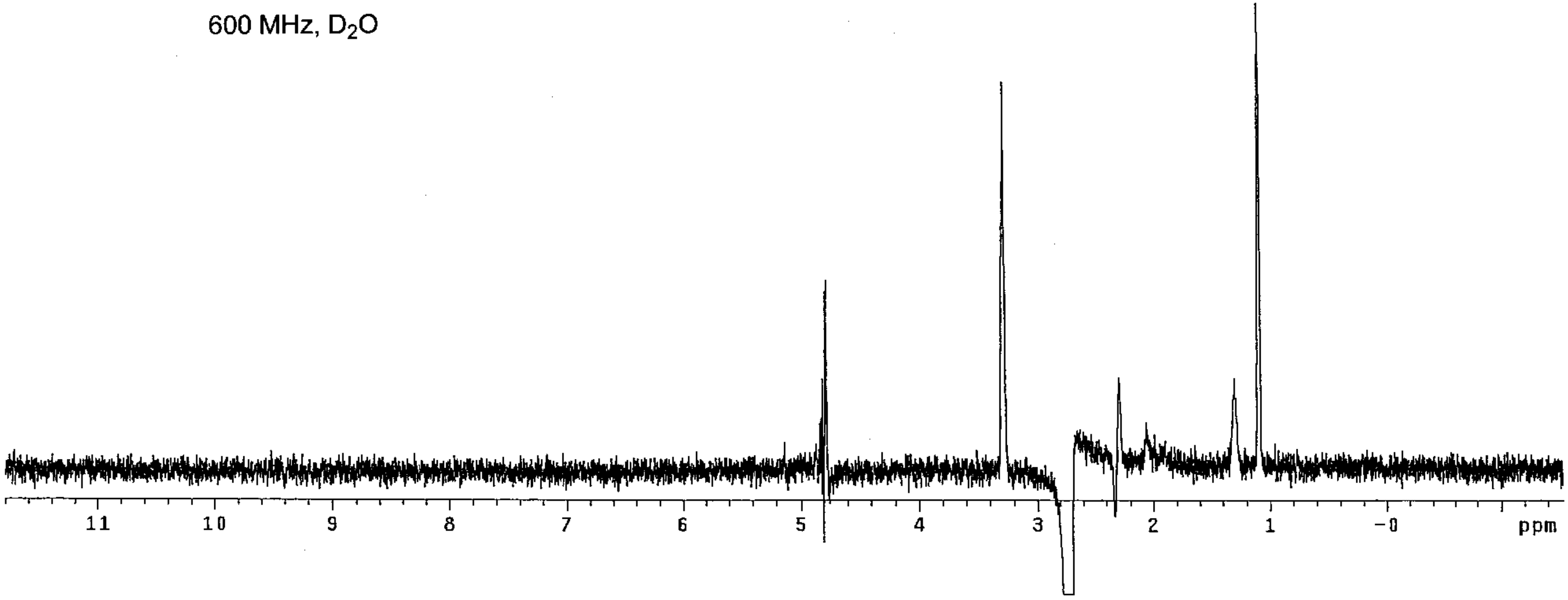
1D NOESY
δ 2.30

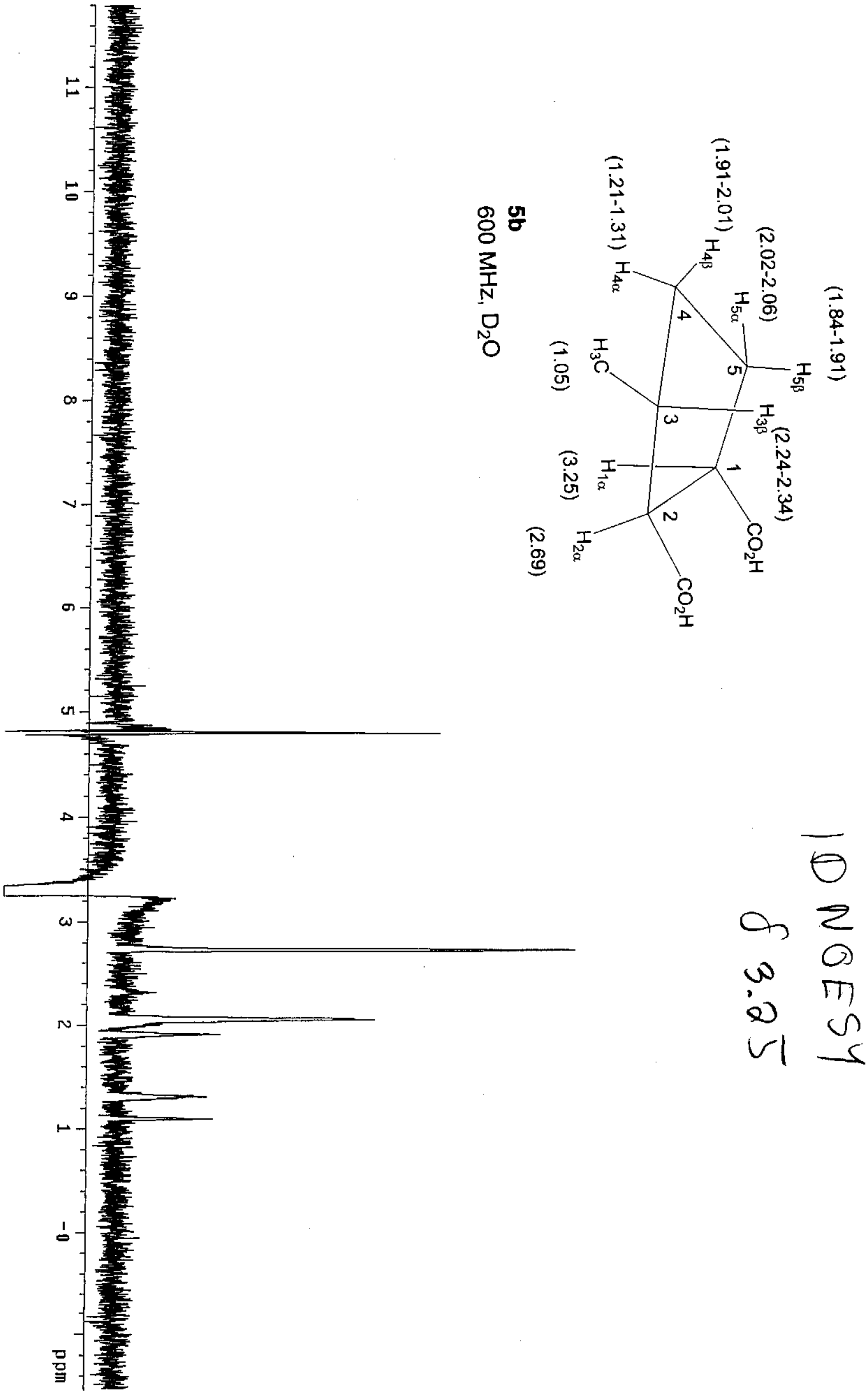


5b

600 MHz, D_2O

1DNOESY
δ2.69



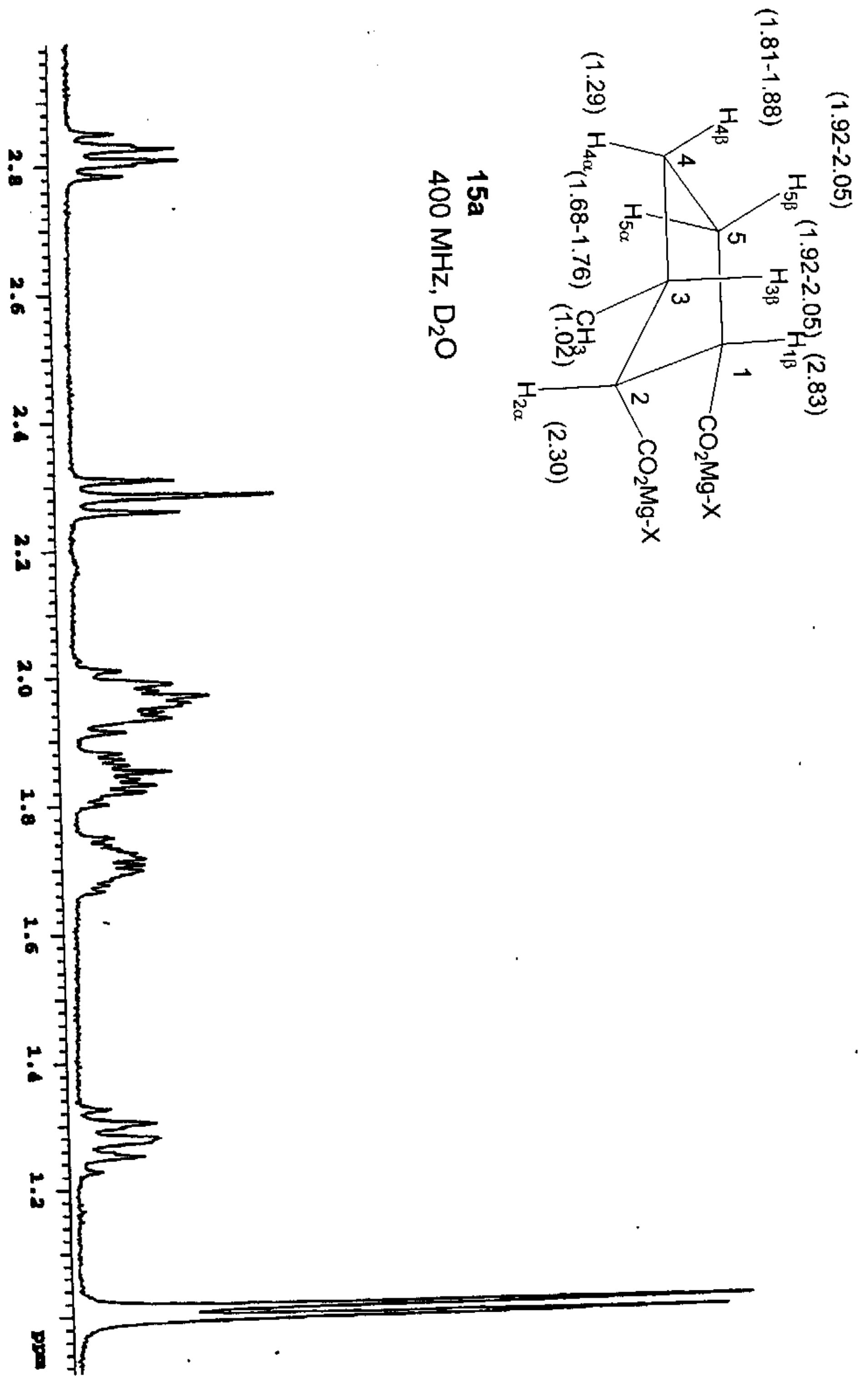


5b

600 MHz, D_2O

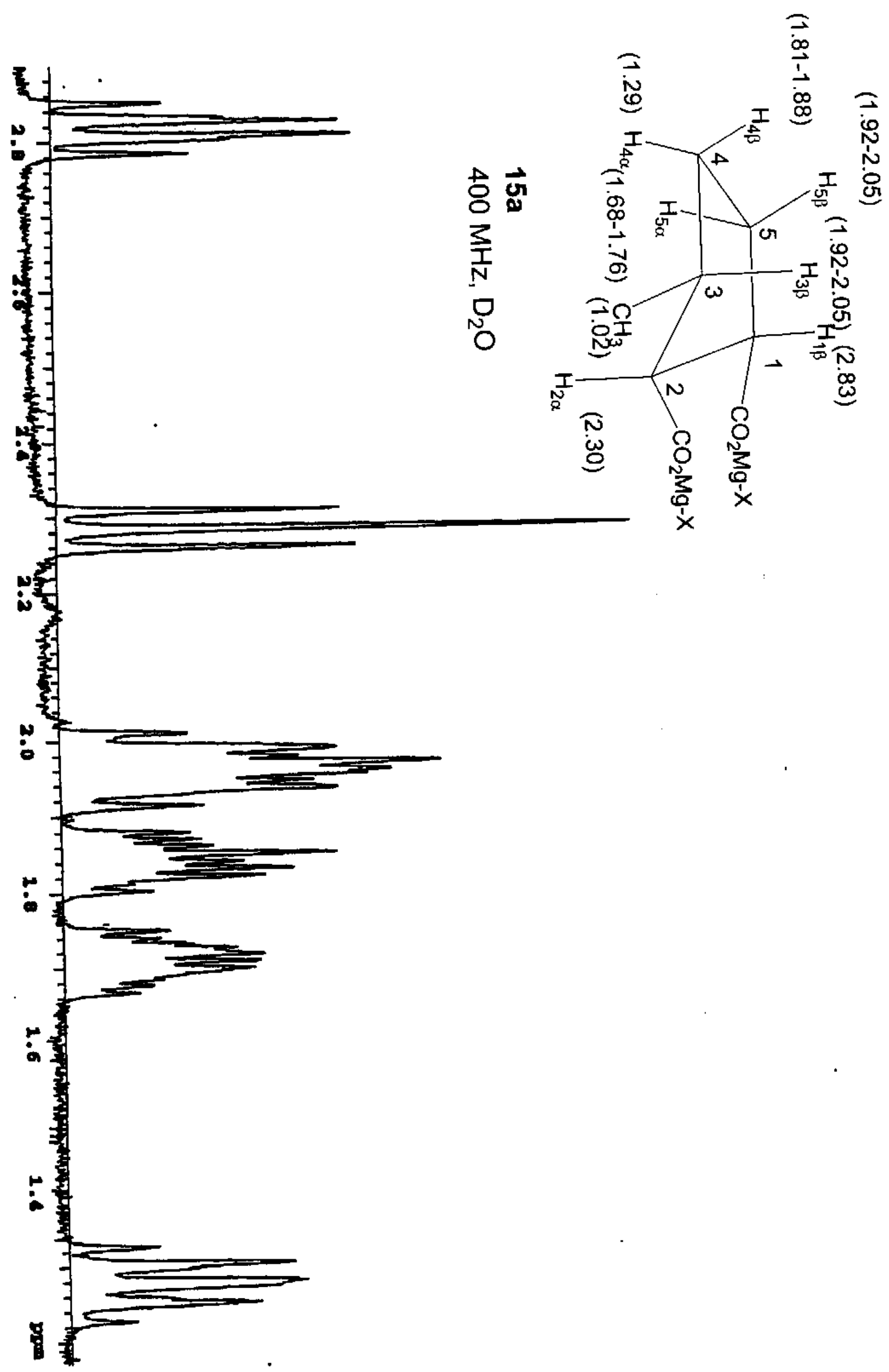
1D NOESY

δ 3.25



15a

400 MHz, D_2O



15a

400 MHz, D_2O

```
magnesi   c,t-nepetate cosy

Pulse Sequence: gCOSY

 Solvent: D2O
 Ambient temperature
File: mgttnepeticcosy
INOVA-400  "fid"

PULSE SEQUENCE: gCOSY
 Relax. delay 1.000 sec
 Acq. time 0.205 sec
 Width     5000.0 Hz
 2D Width 5000.0 Hz
 Single scan
 128 increments
OBSERVE   H1, 399.7542101 MHz
DATA PROCESSING
 Sq. sine bell 0.102 sec
F1 DATA PROCESSING
 Sq. sine bell 0.026 sec
FT size 2048 x 2048
Total time 2 min, 56 sec
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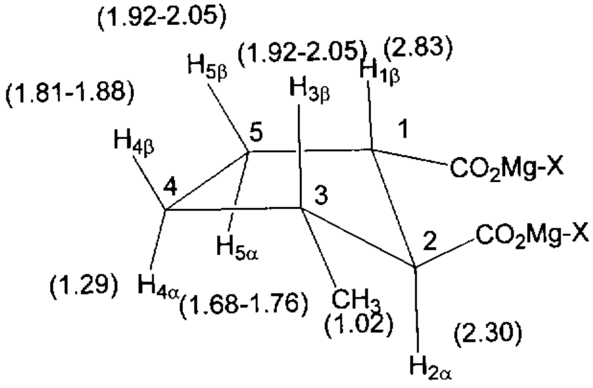
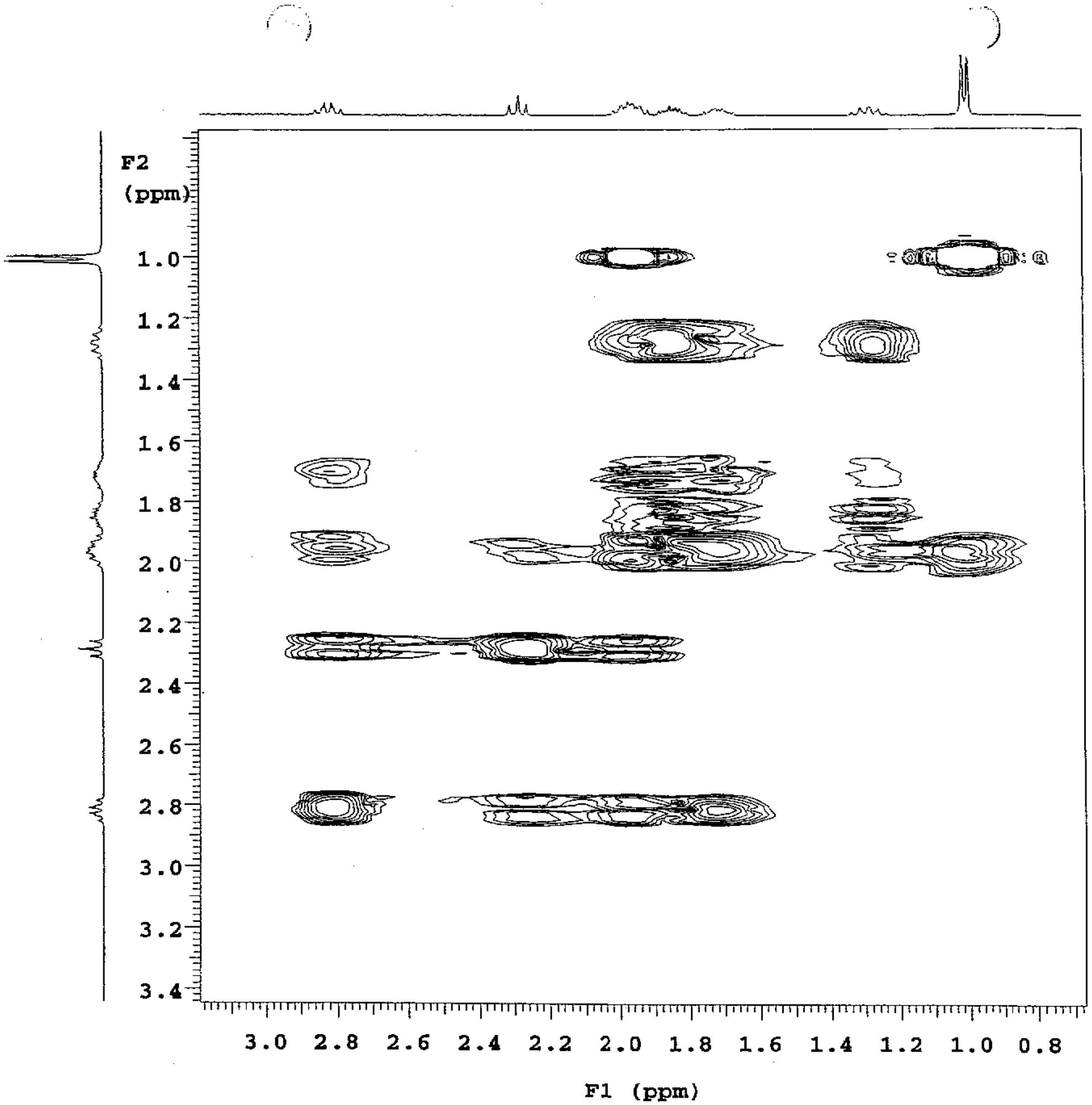


15a

400 MHz, D$_2$O



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  3       902.126  2.257     69.5
  4       792.860  1.983     47.9
  5       786.145  1.967     36.9
  6       739.142  1.849     15.8
  7       605.459  1.515     -7.3
  8       519.999  1.301     29.5
  9       508.401  1.272     28.9
 10       499.245  1.249     28.3
 11       403.408  1.009  -11179.5
 12       397.303  0.994  -11012.7
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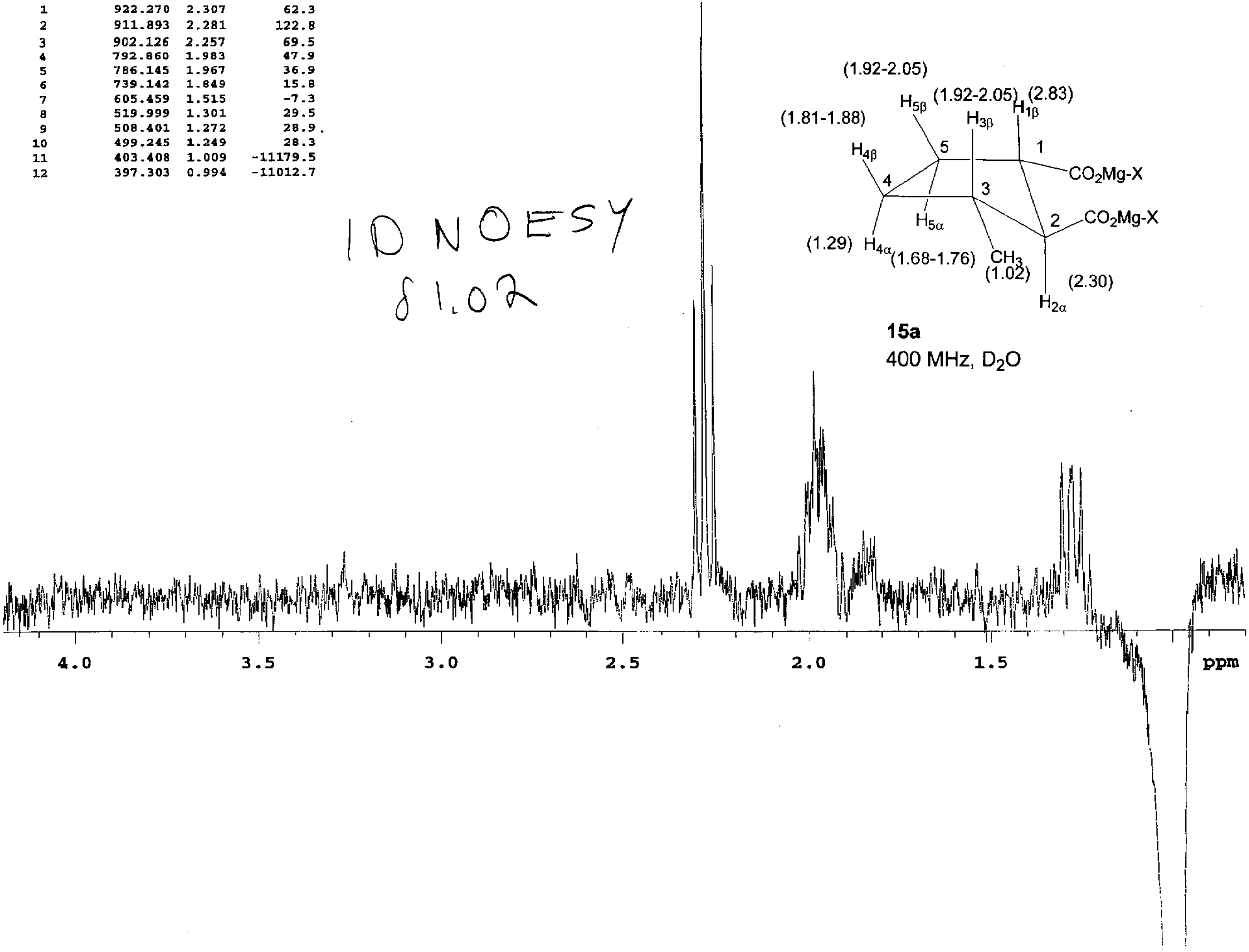
1D NOESY
δ 1.02



15a

400 MHz, D_2O

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  2      1131.036  2.829       13.6
  3      1089.527  2.725       -8.2
  4       921.659  2.306       26.3
  5       911.893  2.281       55.1
  6       902.126  2.257       25.6
  7       821.550  2.055       -6.3
  8       802.626  2.008       29.5
  9       795.912  1.991       19.1
 10       792.249  1.982       20.9
 11       787.366  1.970       -9.4
 12       785.534  1.965       15.3
 13       781.261  1.954      -13.8
 14       779.430  1.950        7.7
 15       776.988  1.944      -18.2
 16       773.326  1.935       19.1
 17       771.495  1.930      -10.8
 18       762.949  1.909       25.4
 19       750.740  1.878       92.3
 20       746.467  1.867       65.5
 21       743.415  1.860      125.8
 22       739.142  1.849      116.7
 23       734.869  1.838       88.8
 24       731.206  1.829       84.1
 25       726.934  1.818      111.4
 26       719.608  1.800       52.7
 27       698.854  1.748       32.6
 28       691.529  1.730       31.3
 29       689.087  1.724      -10.6
 30       687.256  1.719       21.8
 31       682.372  1.707       -5.9
 32       675.658  1.690       13.1
 33       529.155  1.324     -557.7
 34       519.999  1.301    -1314.3
 35       510.232  1.276    -1387.8
 36       507.791  1.270    -1327.2
 37       498.634  1.247    -1207.3
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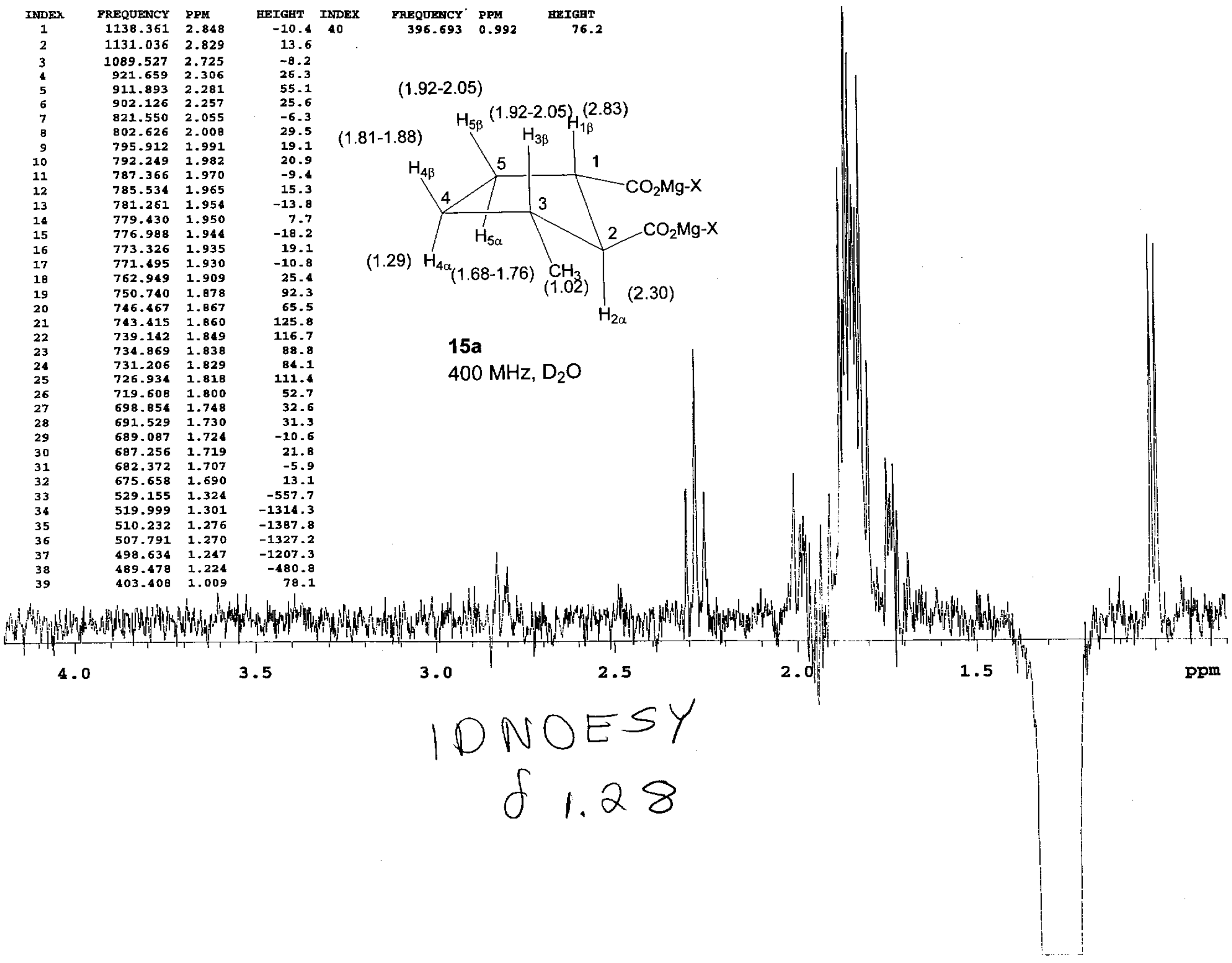

15a

400 MHz, D_2O

1D NOESY

δ 1.28

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  3       1119.438  2.800       20.2
  4       1112.112  2.782       -9.2
  5        912.503  2.283       28.9
  6        902.736  2.258       16.0
  7        861.838  2.156       -8.0
  8        802.626  2.008       62.2
  9        794.080  1.986      125.5
 10        784.924  1.964      125.0
 11        776.378  1.942       68.6
 12        761.728  1.905       -5.8
 13        751.351  1.880       12.9
 14        749.519  1.875      -22.4
 15        744.636  1.863       19.8
 16        742.194  1.857      -22.1
 17        738.532  1.847       30.8
 18        734.869  1.838      -45.3
 19        731.206  1.829       51.6
 20        727.544  1.820      -86.3
 21        723.881  1.811       32.7
 22        719.608  1.800      -61.7
 23        698.854  1.748     -549.6
 24        694.581  1.738     -569.3
 25        691.529  1.730     -665.1
 26        689.087  1.724     -821.4
 27        685.425  1.715    -1084.0
 28        681.762  1.705    -1115.0
 29        678.099  1.696    -1069.9
 30        672.606  1.683     -605.0
 31        669.553  1.675     -579.0
 32        665.280  1.664     -490.4
 33        538.922  1.348        5.2
 34        529.155  1.324      -22.7
 35        519.999  1.301       19.5
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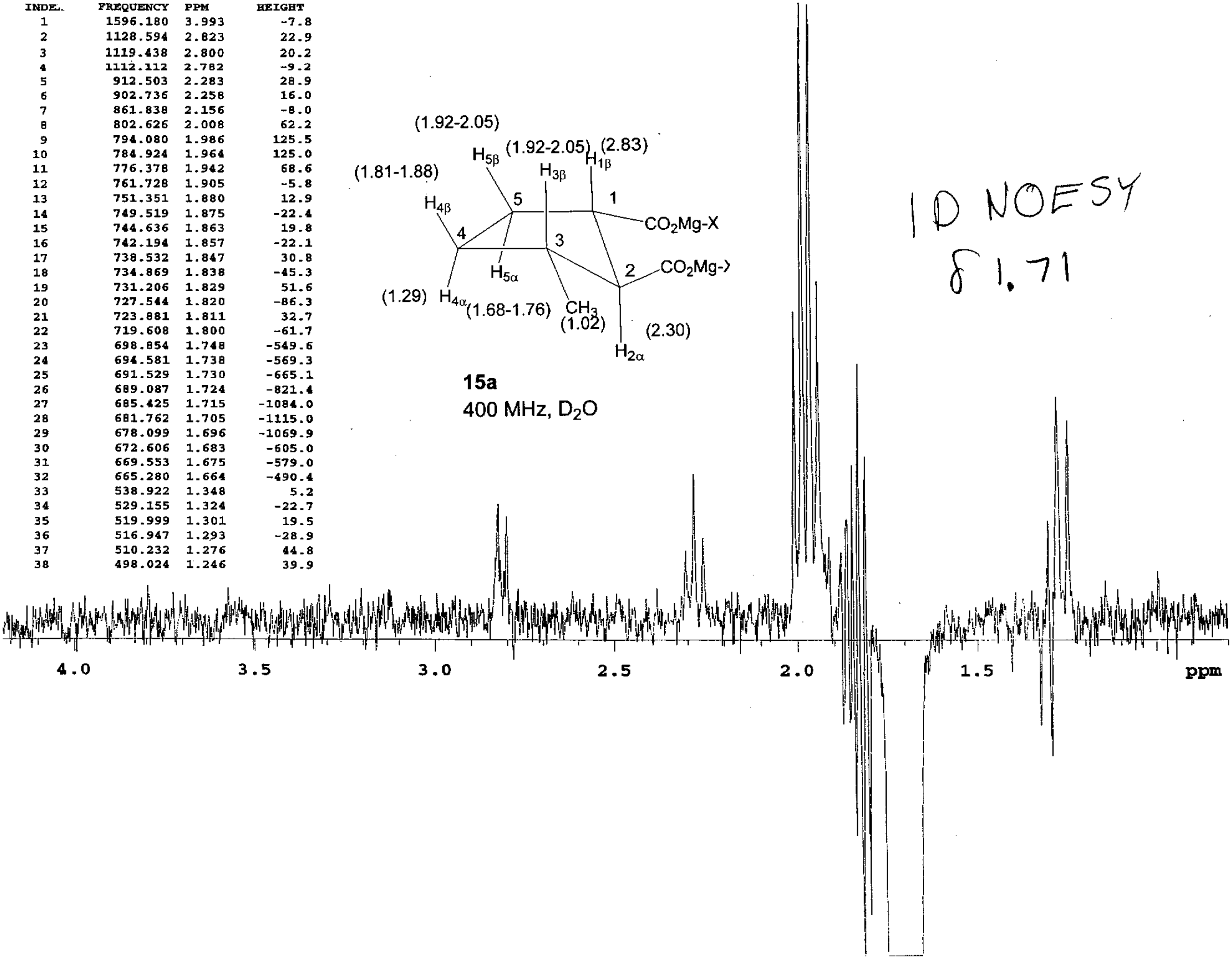


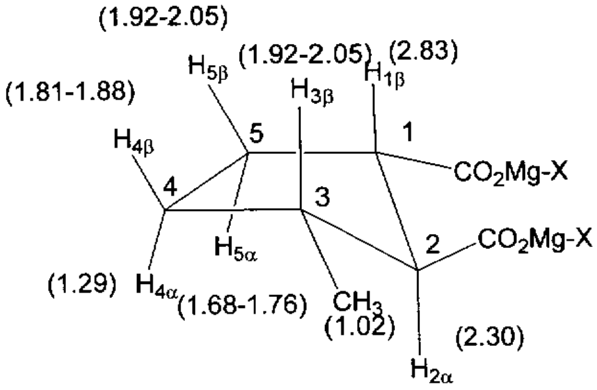
15a

400 MHz, D_2O

1D NOESY

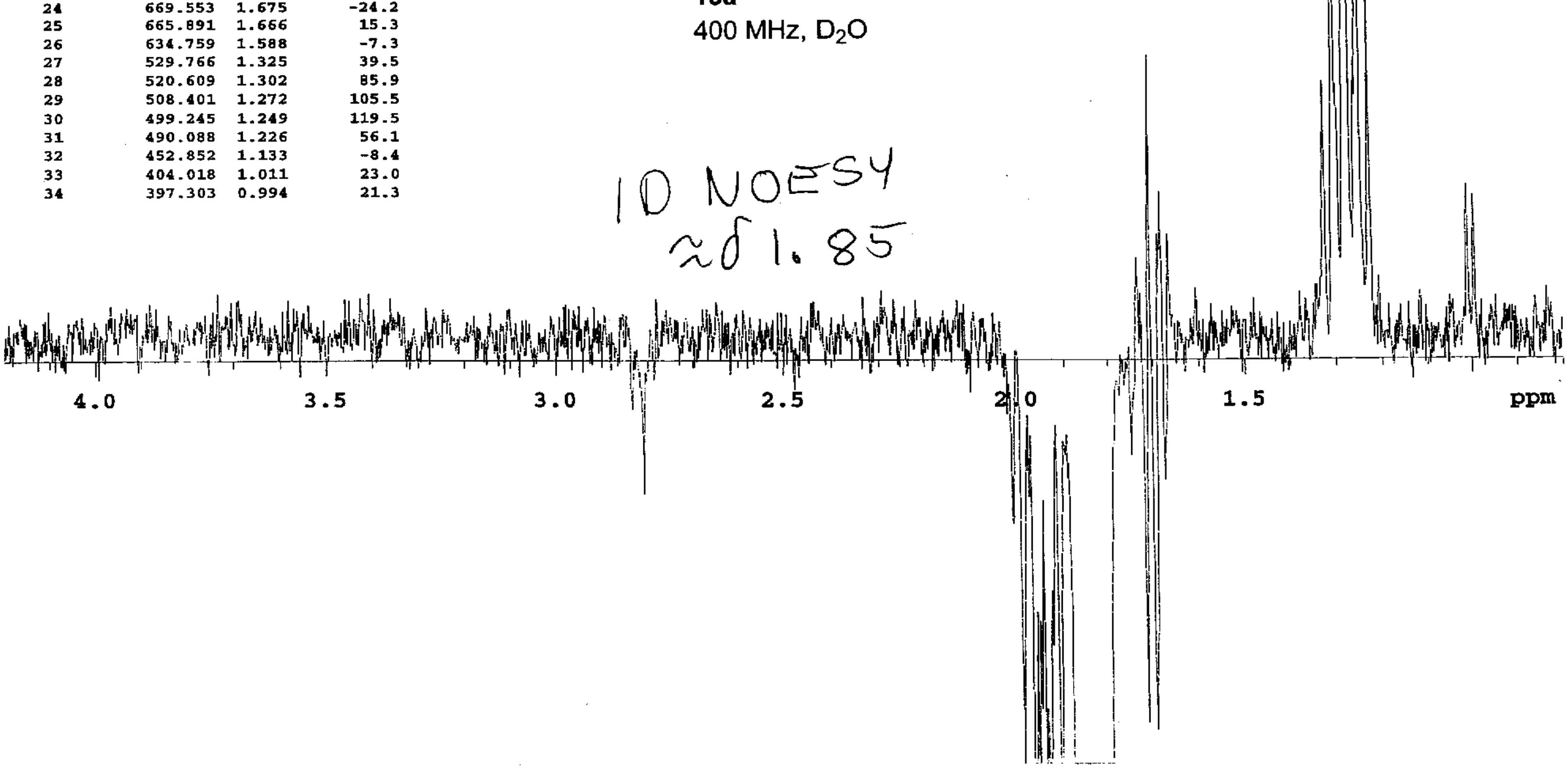
δ 1.71

INDEX	FREQUENCY	PPM	HEIGHT
1	1122.490	2.808	-26.3
2	803.237	2.009	-31.2
3	795.301	1.989	-72.9
4	786.145	1.967	-109.0
5	782.482	1.957	-75.7
6	776.378	1.942	-80.5
7	773.936	1.936	-122.5
8	764.169	1.912	-114.9
9	751.351	1.880	-424.1
10	747.078	1.869	-469.4
11	743.415	1.860	-595.0
12	739.752	1.851	-978.9
13	735.479	1.840	-621.7
14	731.817	1.831	-908.0
15	727.544	1.820	-763.8
16	724.492	1.812	-326.6
17	720.219	1.802	-343.7
18	698.854	1.748	-20.2
19	693.360	1.734	11.4
20	686.035	1.716	-63.6
21	682.372	1.707	44.0
22	678.710	1.698	-64.6
23	672.606	1.683	22.1
24	669.553	1.675	-24.2
25	665.891	1.666	15.3
26	634.759	1.588	-7.3
27	529.766	1.325	39.5
28	520.609	1.302	85.9
29	508.401	1.272	105.5
30	499.245	1.249	119.5
31	490.088	1.226	56.1
32	452.852	1.133	-8.4
33	404.018	1.011	23.0
34	397.303	0.994	21.3



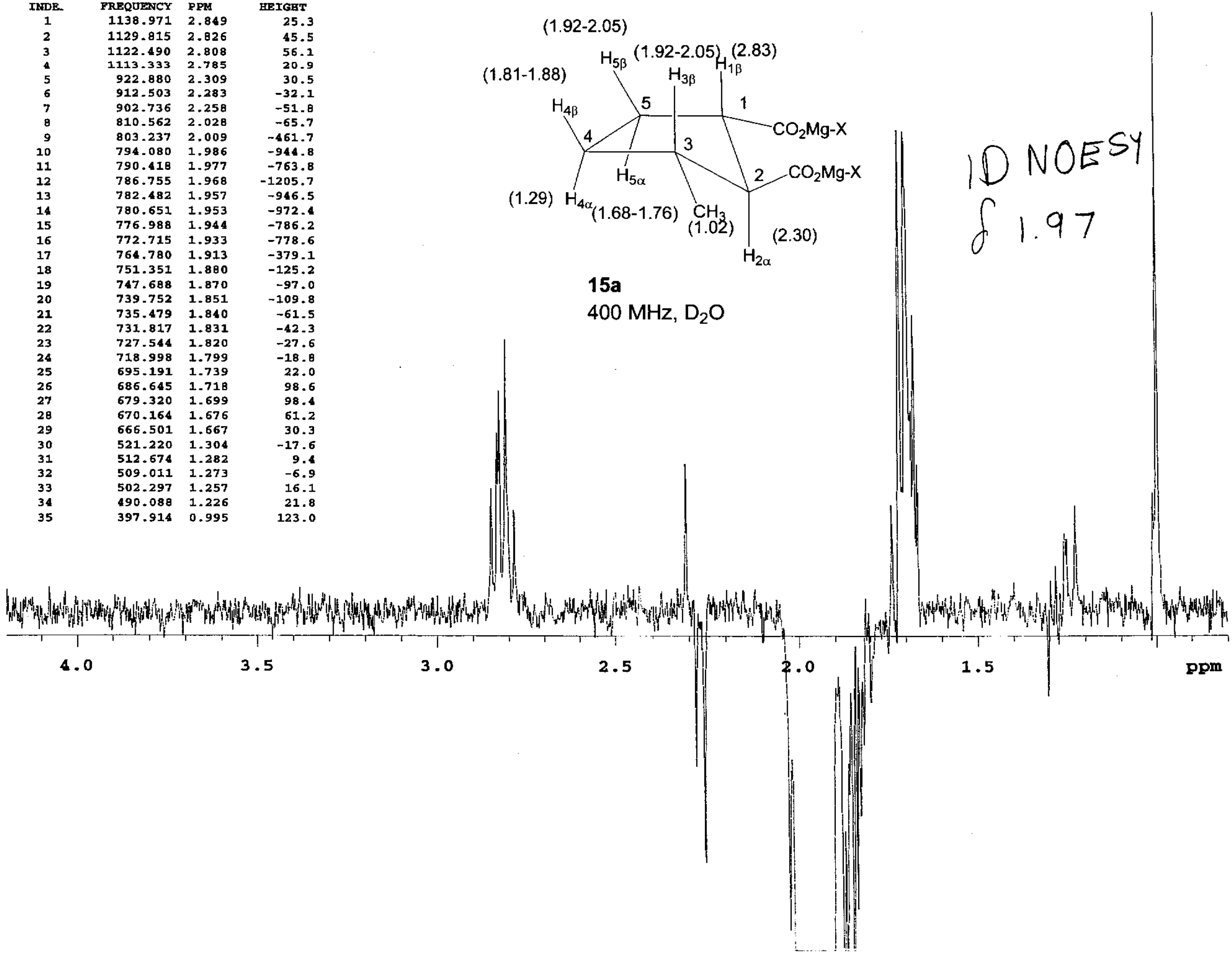
15a

400 MHz, D_2O



1D NOESY

≈δ 1.85

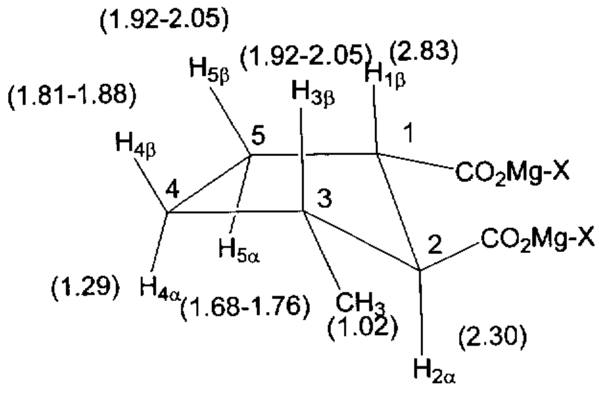


15a
400 MHz, D_2O

1D NOESY
δ 1.97

```
INDE.   FREQUENCY   PPM      HEIGHT
  1      1138.971  2.849       25.3
  2      1129.815  2.826       45.5
  3      1122.490  2.808       56.1
  4      1113.333  2.785       20.9
  5       922.880  2.309       30.5
  6       912.503  2.283      -32.1
  7       902.736  2.258      -51.8
  8       810.562  2.028      -65.7
  9       803.237  2.009     -461.7
 10       794.080  1.986     -944.8
 11       790.418  1.977     -763.8
 12       786.755  1.968    -1205.7
 13       782.482  1.957     -946.5
 14       780.651  1.953     -972.4
 15       776.988  1.944     -786.2
 16       772.715  1.933     -778.6
 17       764.780  1.913     -379.1
 18       751.351  1.880     -125.2
 19       747.688  1.870      -97.0
 20       739.752  1.851     -109.8
 21       735.479  1.840      -61.5
 22       731.817  1.831      -42.3
 23       727.544  1.820      -27.6
 24       718.998  1.799      -18.8
 25       695.191  1.739       22.0
 26       686.645  1.718       98.6
 27       679.320  1.699       98.4
 28       670.164  1.676       61.2
 29       666.501  1.667       30.3
 30       521.220  1.304      -17.6
 31       512.674  1.282        9.4
 32       509.011  1.273       -6.9
 33       502.297  1.257       16.1
 34       490.088  1.226       21.8
 35       397.914  0.995      123.0
```

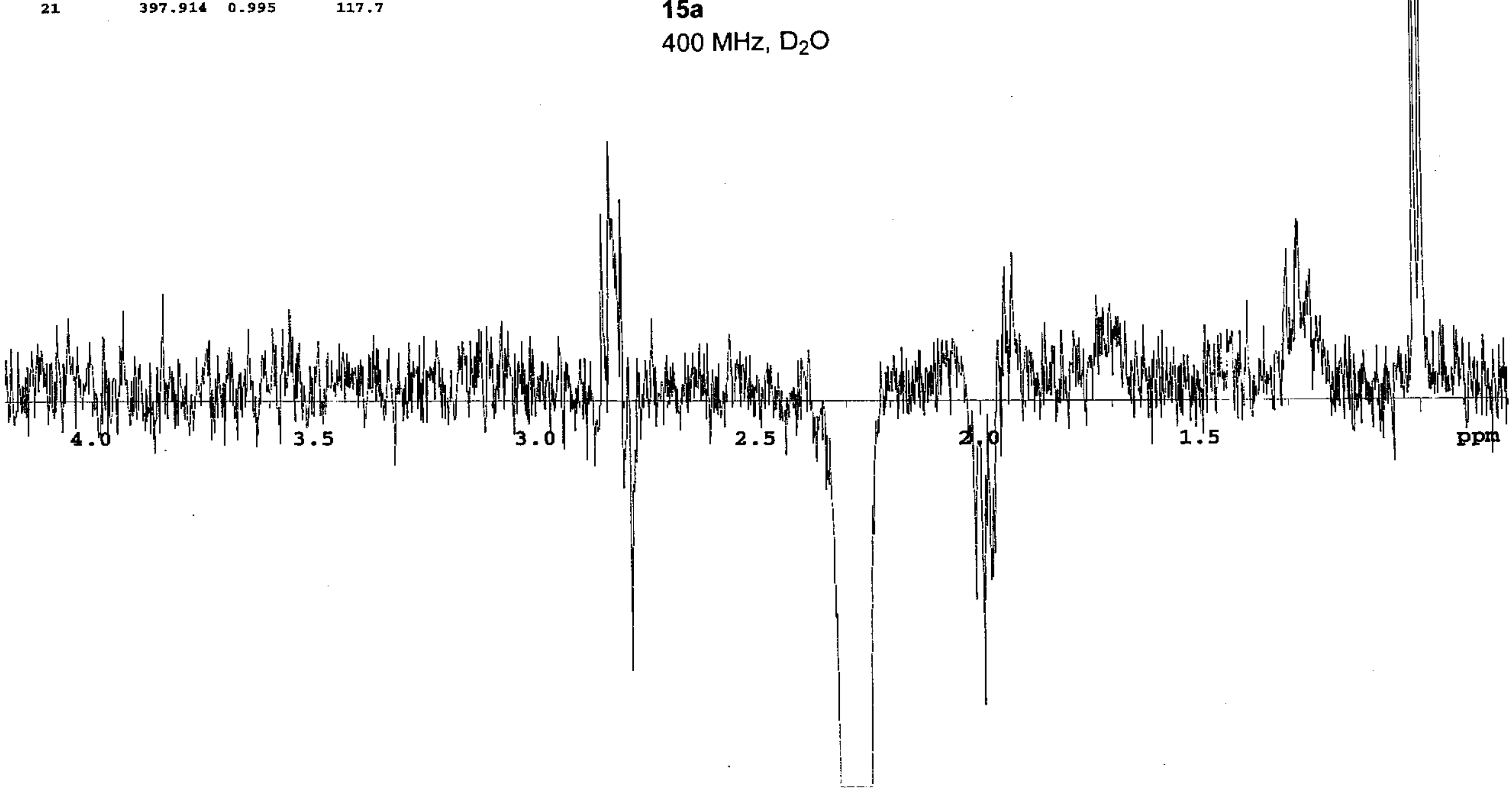
INDEX	FREQUENCY	PPM	HEIGHT
1	1534.527	3.839	13.1
2	1145.686	2.866	-16.0
3	1138.971	2.849	26.2
4	1134.088	2.837	-7.1
5	1132.256	2.832	38.6
6	1121.879	2.806	28.8
7	1112.723	2.784	-50.1
8	1093.189	2.735	8.8
9	922.880	2.309	-3014.9
10	913.113	2.284	-5615.9
11	903.347	2.260	-3111.8
12	836.200	2.092	5.4
13	803.847	2.011	-38.6
14	797.133	1.994	-56.2
15	790.418	1.977	-35.2
16	770.274	1.927	19.8
17	643.305	1.609	-12.5
18	510.232	1.276	25.2
19	424.773	1.063	-15.5
20	404.629	1.012	121.3
21	397.914	0.995	117.7



15a

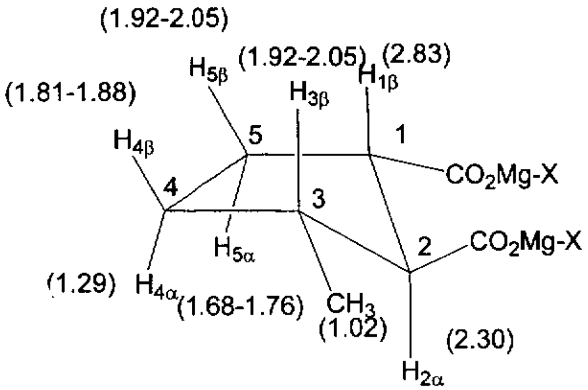
400 MHz, D_2O

1D NOESY
δ2.30

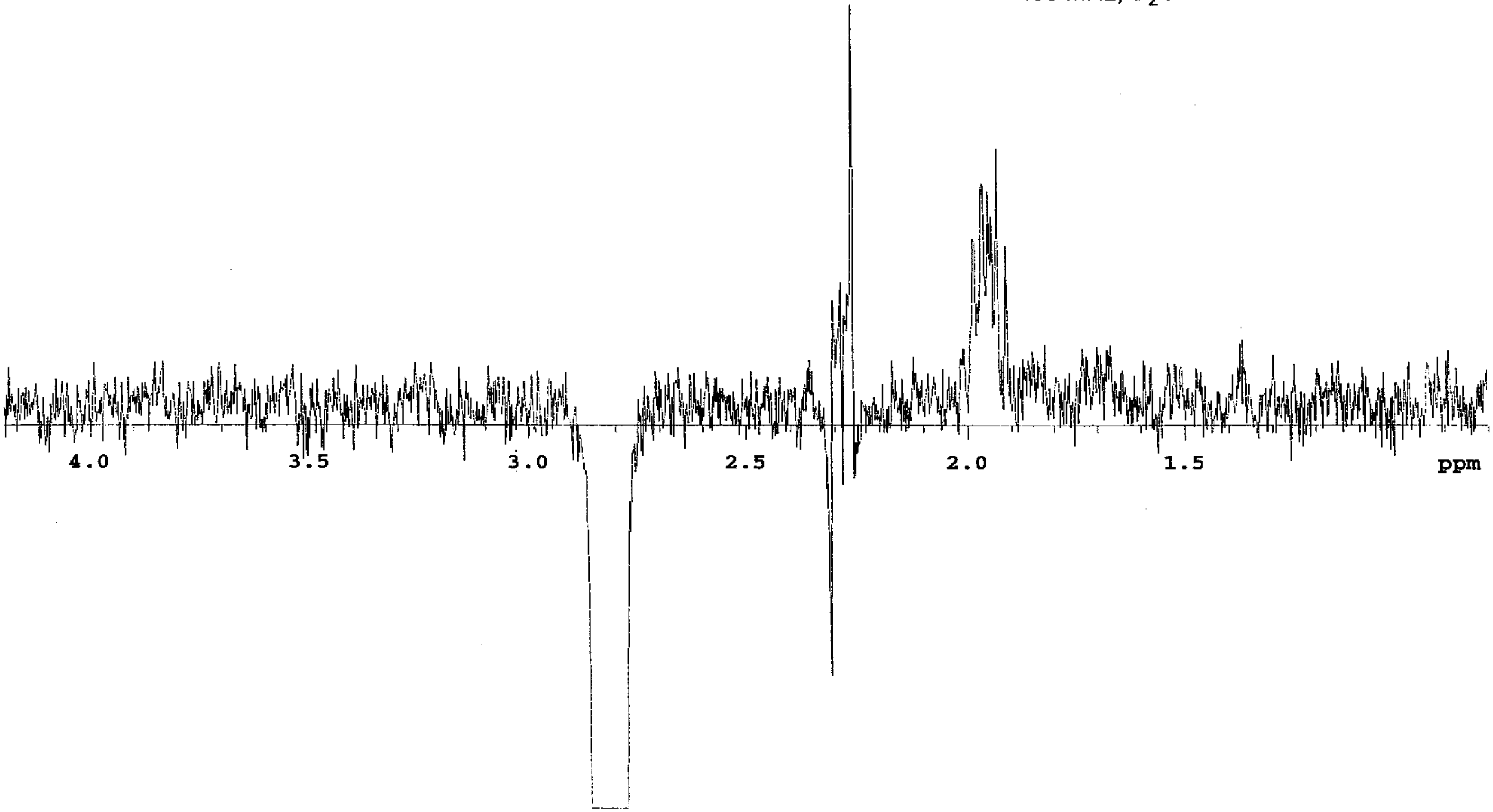


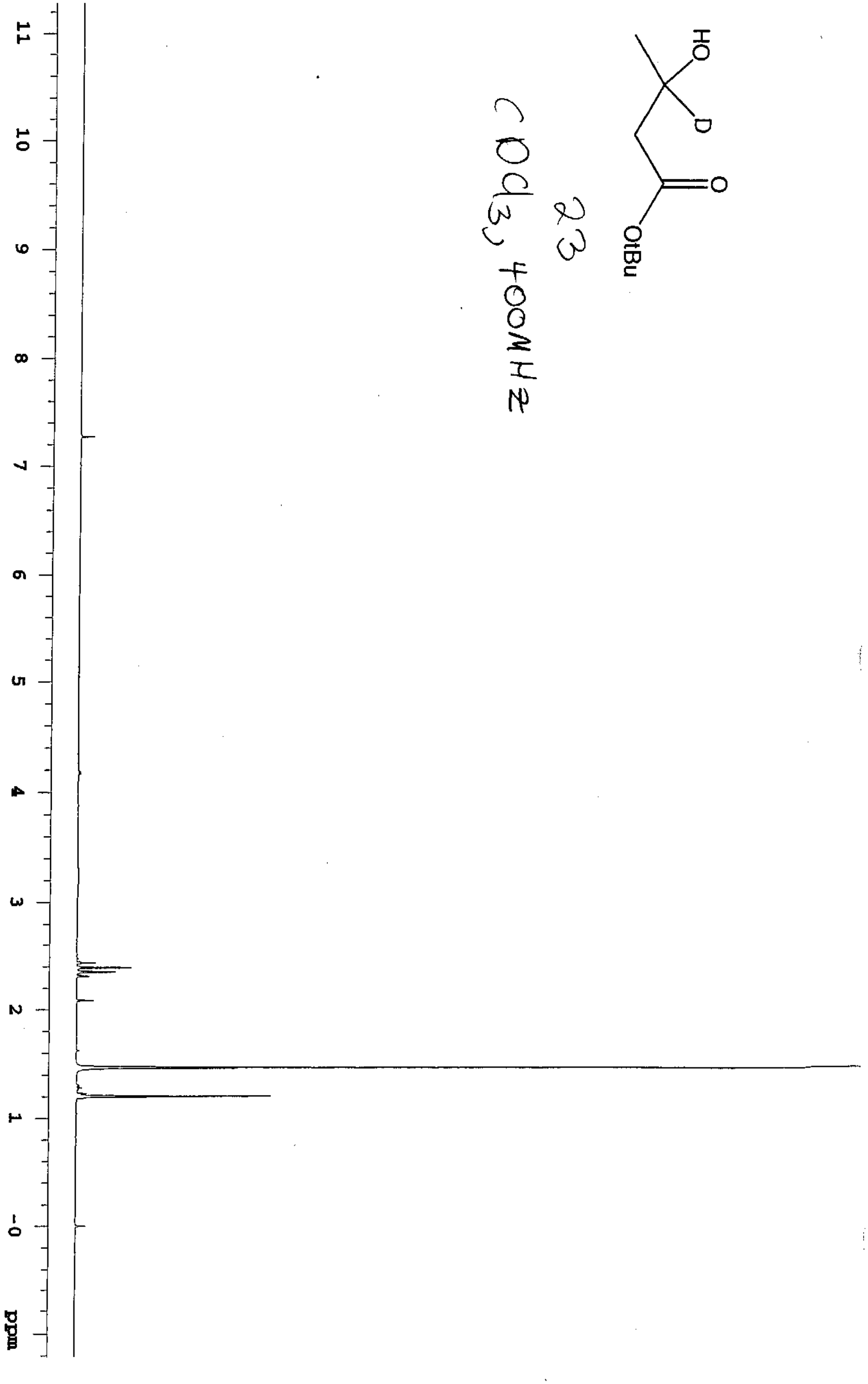
INDEX	FREQUENCY	PPM	HEIGHT
1	1532.696	3.834	5.9
2	1138.971	2.849	-1013.3
3	1132.256	2.832	-1321.8
4	1129.815	2.826	-2198.7
5	1122.490	2.808	-2319.7
6	1120.048	2.802	-1406.7
7	1112.723	2.784	-1146.5
8	941.804	2.356	6.1
9	922.880	2.309	-47.4
10	913.724	2.286	19.4
11	912.503	2.283	-15.2
12	903.347	2.260	66.3
13	901.515	2.255	-14.1
14	786.145	1.967	36.2
15	772.715	1.933	42.0
16	764.169	1.912	25.6
17	502.907	1.258	-11.1

1D NOESY
~δ 2.83



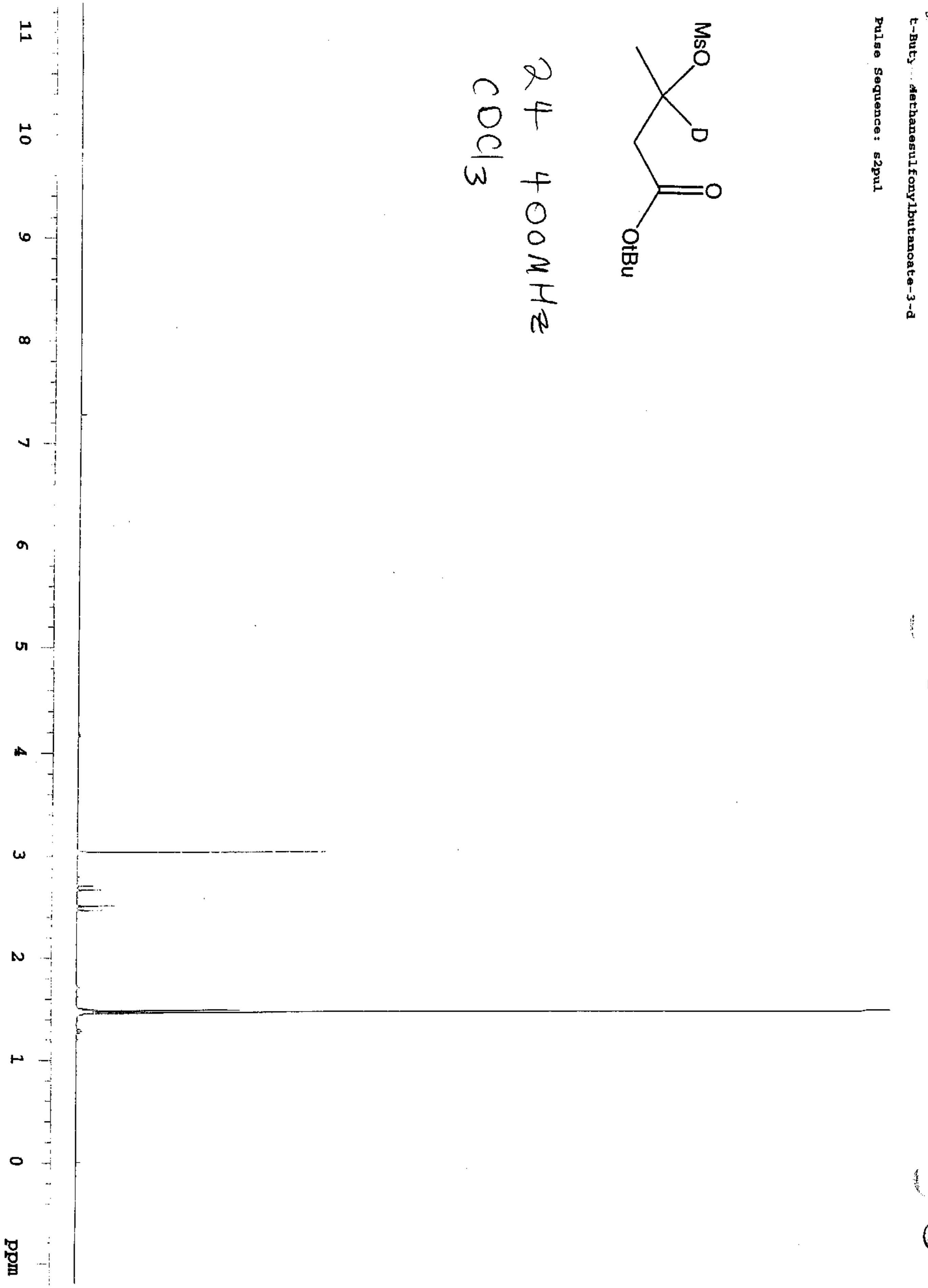
15a
400 MHz, D_2O





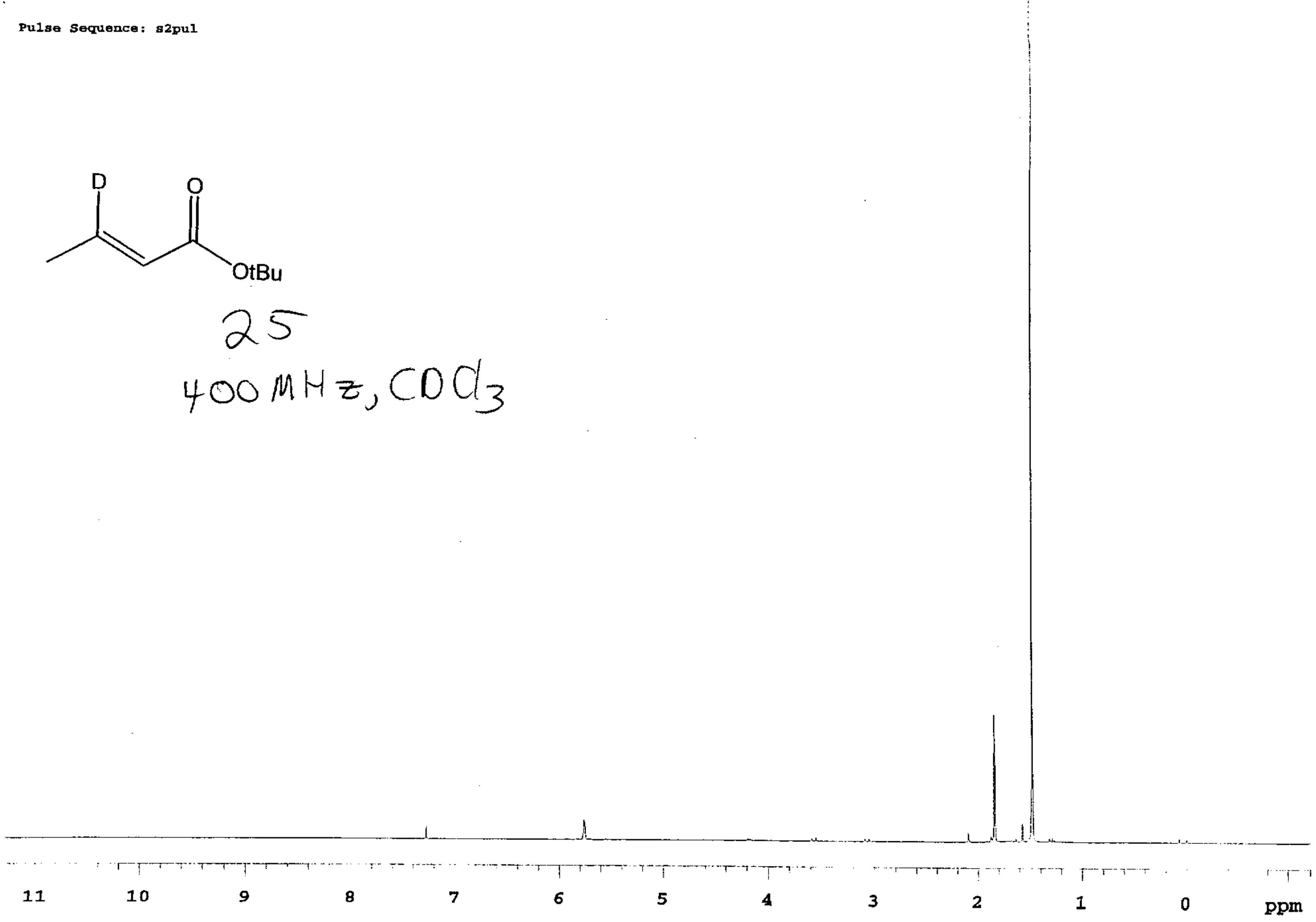
23

$CDCl_3$, 400MHz


t-Buty Methanesulfonylbutanoate-3-d
Pulse Sequence: s2pul
MsO
D
O
OtBu
24 400MHz
CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm

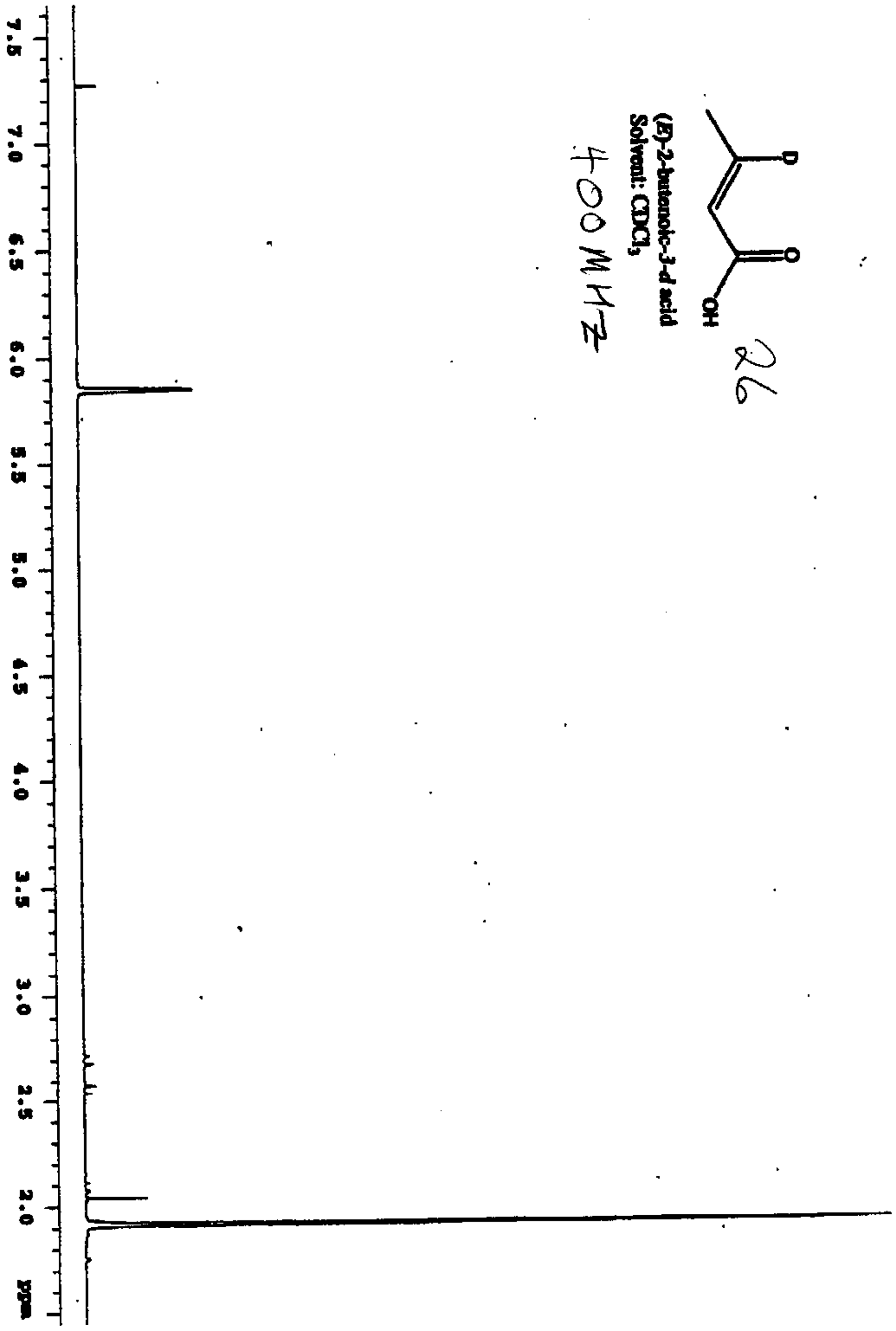
t-Butyl (E)-2-Butenoate-3-d

Pulse Sequence: s2pul



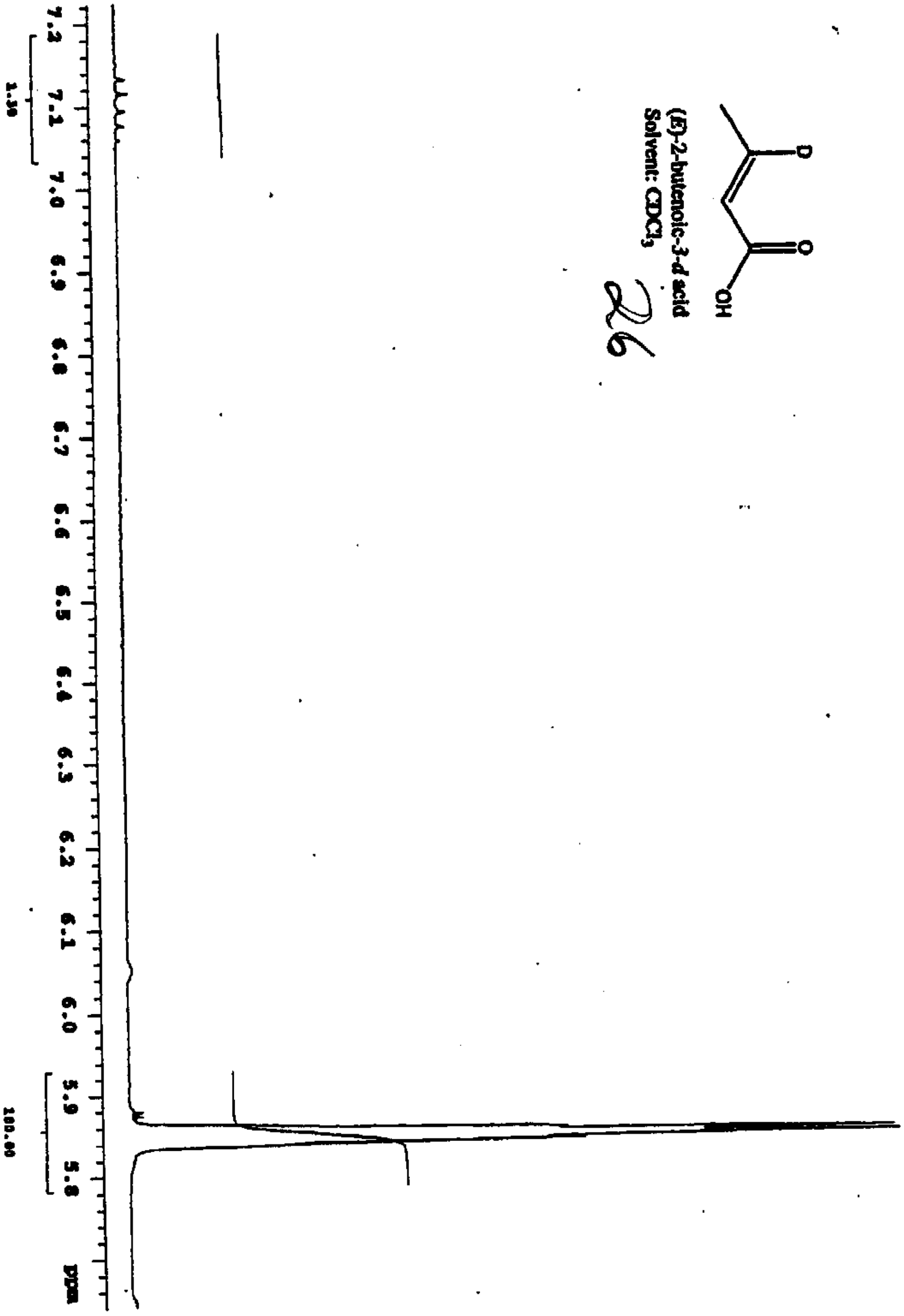
25

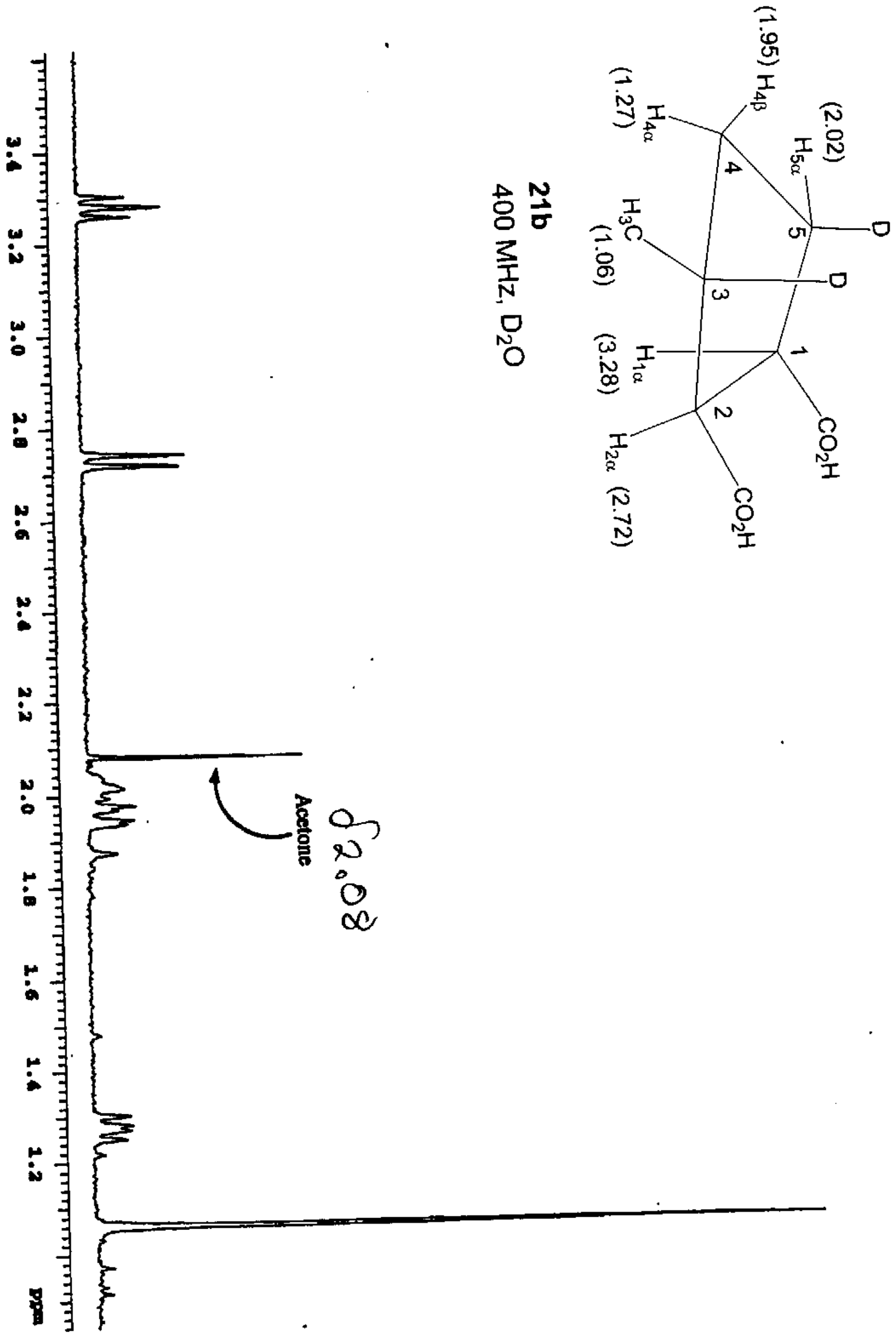
400 MHz, $CDCl_3$



26

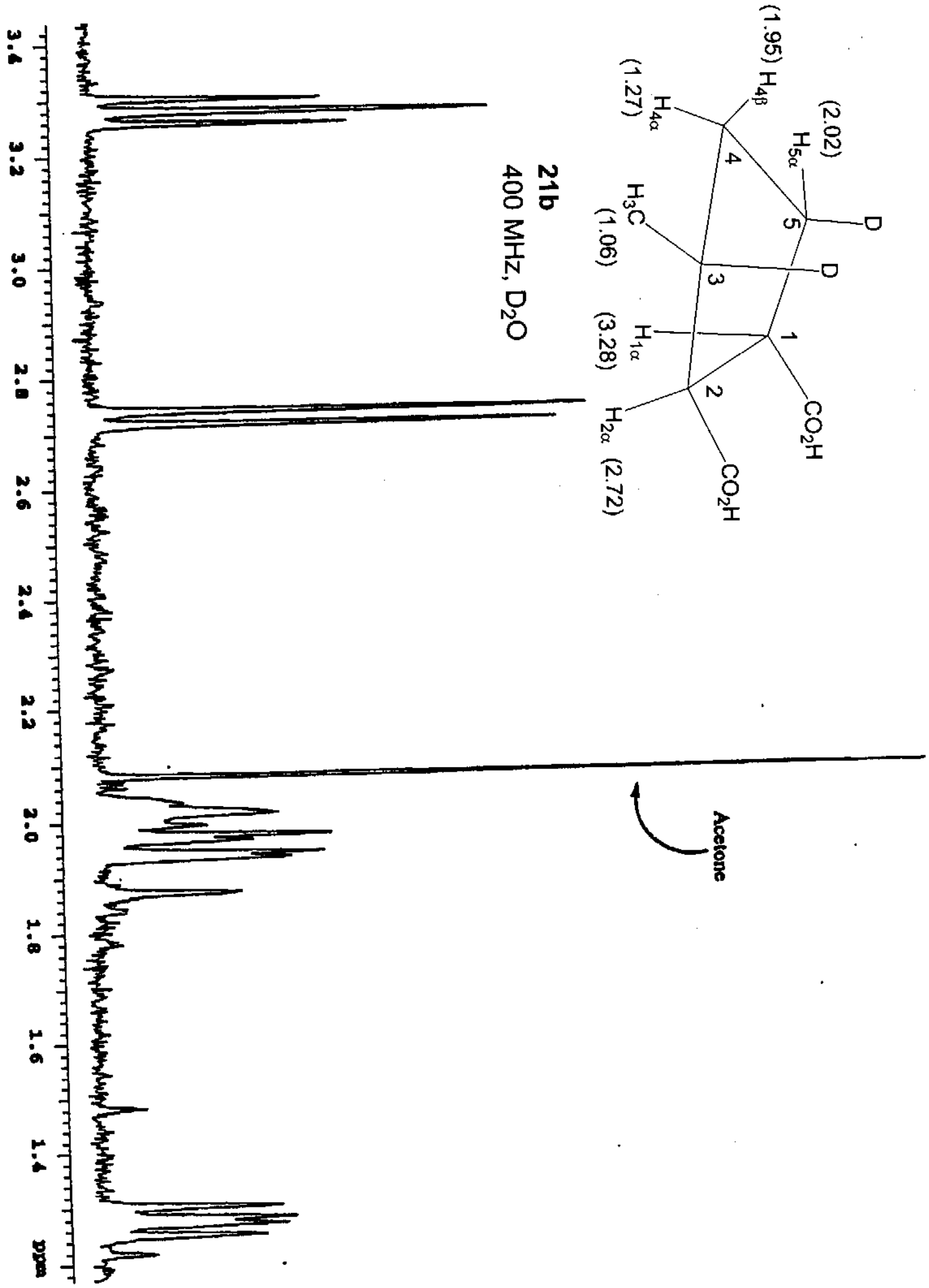
D
O
OH
(E)-2-butenoic-3-d acid
Solvent: $CDCl_3$
400 MHz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


D
O
OH
(E)-2-butenoic-3-d acid
Solvent: CDCl$_3$
26
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
ppm
1.39
100.00

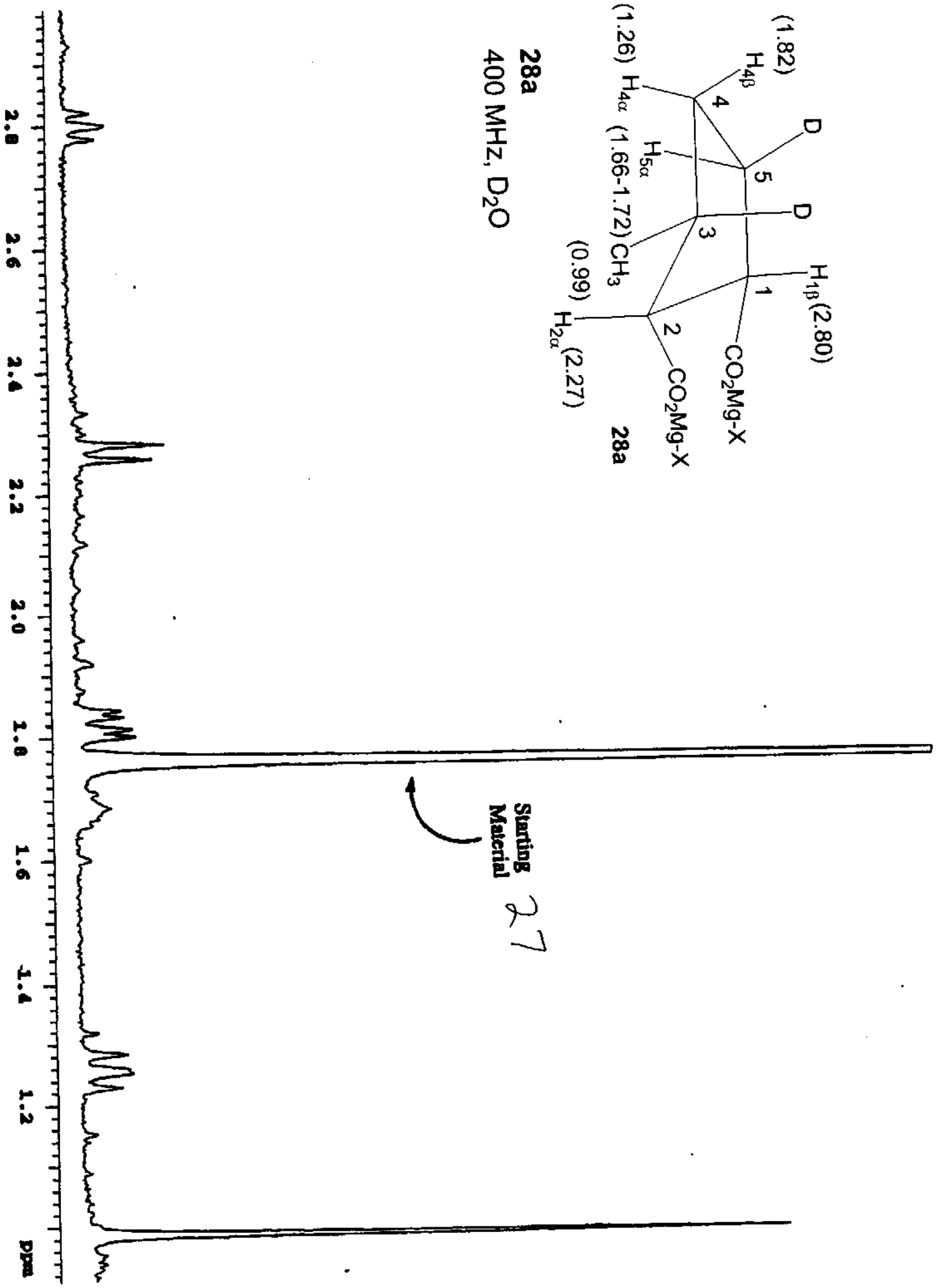


21b

400 MHz, D_2O


21b

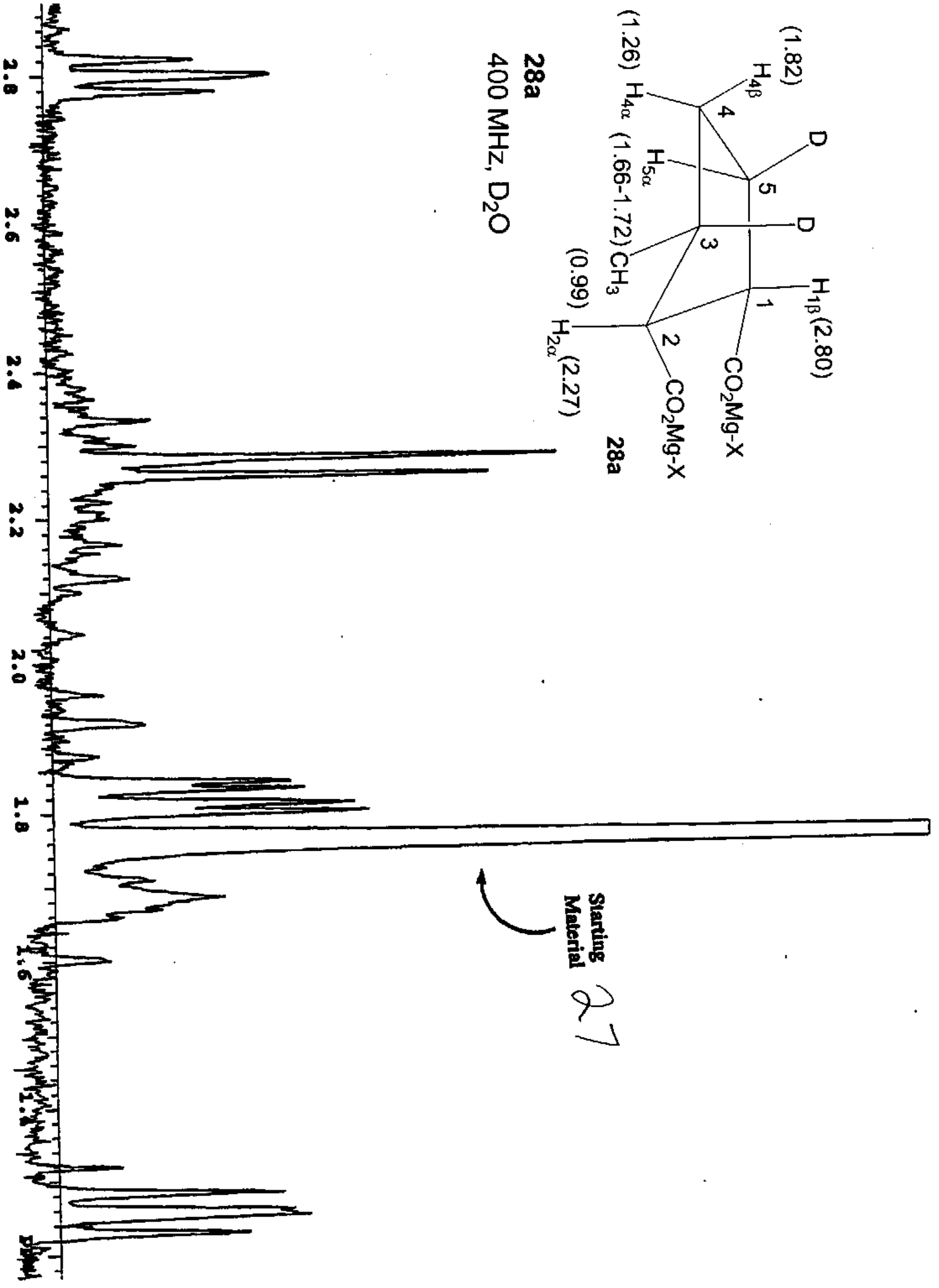
400 MHz, D_2O



28a

400 MHz, D_2O

27


D
D
5
4
3
2
1
(1.82) H4β
(1.26) H4α
H5α (1.66-1.72)
CH3 (0.99)
H2α (2.27)
H1β (2.80)
CO2Mg-X
CO2Mg-X
28a
28a
400 MHz, D2O
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
Starting Material
27