Supporting Information for

Electrochemical Annulation of Five-Membered Rings Through Dearomatization of Furans and Thiophenes

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General Experimental

All reactions were carried out in flame-dried glassware under an atmosphere of argon unless otherwise noted. Tetrahydrofuran was freshly distilled from Na/benzophenone. Mixtures of TMSCl and Et_3N refer to the supernatant liquid from a centrifuged 1:1 v:v solution made in a flame dried distillation receiver under argon. These solutions can be kept up to 3 days in a -20^oC freezer. Commercially available enones *must be* distilled prior to use and kept in a freezer under an atmosphere of argon. Copper (I) iodide was either purchased at 99.99% purity (Aldrich) or purified by Soxhalet extraction with CH_2Cl_2. Electrolysis reactions were carried out as previously reported (see ref. 2) with alternating stainless steel cathodes and carbon anodes. No attempts were made to exclude air or water from these reactions. NMR spectra were obtained either on a Bruker 300 or a Varian Inova 500. Elemental analyses were performed by Atlantic Microlab, Inc. and high-resolution mass spectra were obtained from the Washington University Resource for Biomedical and Bio-organic Mass Spectrometry.

General cuprate procedure:

A solution of 2-(2-furyl)-ethyl bromide (**2b**) (1.0g, 5.7 mmol) in THF (5.5 mL) was purged with argon for 10 min. This solution was then added to a flask containing Mg turnings (0.137 g, 5.7 mmol). After 2.5 h the majority of the Mg had dissolved and a clear dark solution had formed. The solution was cooled to 0^0C and CuI (0.165 g, 0.87mmol) was added. After stirring for 5 min the turbid black solution was cooled to -78^0C. A mixture of TMSCl:Et_3N (5.5 mL) was added, followed by N,N,N,N-tetramethylethylenediamine (0.90mL, 5.5 mmol). Next, the addition of the enone (4.5 mmol) produced a bright yellow solution. The mixture was allowed to warm to ambient temperature over 5 h and then placed in the refrigerator overnight. The black mixture was then poured into an ice-cold mixture of pentane (100 mL) and saturated aqueous NH_4Cl (50 mL). The pentane layer was separated and washed with $NaHCO_3$, then brine, and dried over Na_2SO_4. Removal of solvent provided the crude enolether as a pale yellow oil.

General electrolysis procedure

A 50-mL beaker was charged with the crude enolether (0.69 mmol) and 34.5 mL of an electrolyte solution (4:1 CH_3CN:2-propanol, 0.1M $LiClO_4$, and 0.08M 2,6-lutidine) and stirred until homogeneous. An electrode system consisting of alternating plates of carbon (anode) and steel (cathode) was inserted and charged with a constant current of 22.0 mA (current density = $1mA/cm^2$). The reaction was monitored by TLC every 30 minutes until complete. Once complete, the volatiles were removed under vacuum, and the crude material was dissolved in ether (40 mL) and washed with 1 M HCl (15 mL). The aqueous phase was extracted with Et_2O (2x25 mL), and the combined organic phases were washed with water, $NaHCO_3$, brine and dried over Na_2SO_4. The crude material was concentrated *in vaccuo* and chromatographed *through degassed silica gel* to provide the desired compounds. Typical amounts of charged passed ranged from 2.1-2.3 F/mol.

In order to isolate spirocyclic ketals, the crude product after electrolysis was concentrated, then taken up in ether and washed with water (3x20 mL). The combined aqueous layers were extracted with ether (2x20 mL) and the combined organic layers were washed with $NaHCO_3$ (20 mL) and brine (20 mL) and dried over Na_2SO_4. The crude material was concentrated *in vaccuo* and chromatographed (10:1 hexanes: ethyl acetate) *through degassed silica gel* to provide the desired compounds as viscous oils. Reported ratios are isolated ratios after column chromatography and all coincide with ratios obtained from GC/MS analysis.

General procedure for oxidations with Fetizon's reagent (Ag_2CO_3/Celite)

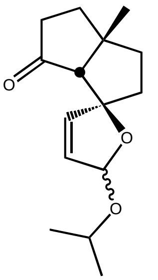
Hydrolysis of spirocyclic ketals was first accomplished by dissolving 50mg of **14a** in 3 mL of ether followed by addition to 5 mL of 1M HCl with vigorous stirring. The hydrolysis was monitored by

TLC until complete consumption of starting material was achieved (typical reaction times depended on isomer but ranged from 2 hours to 8 hours). Once complete, the aqueous layer was extracted twice with ethyl acetate (10 mL) and the combined organic layers were washed with $NaHCO_3$ (10 mL) and brine (10 mL) and dried over Na_2SO_4. After concentration, the crude lactols, isolated as yellowish solids, were taken forward without the benefit of further purification.

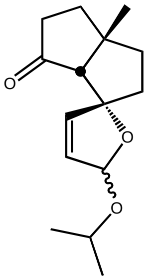
The crude lactol mixtures were first dissolved in 4 mL of degassed benzene and 200 mg of Fetizon's reagent (Ag_2CO_3/Celtie, Aldrich) was added. The mixture was refluxed under argon until black. The reaction was checked by TLC until complete, but was generally finished once the color changed. The crude reaction mixture was diluted with 5 mL of ether and filtered through a 3 inch plug of celite and silica gel. The plug was washed with an additional 25 mL of ether and the combined organics concentrated to provide either **16** or **17** as white solids (79% and 80%, respectively) that were fully characterized without purification.

General ozonlysis procedure

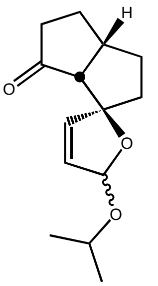
A crude mixture of lactols (from hydrolysis of **15a**) were dissolved in CH_2Cl_2 and cooled to -78^oC. Ozone was passed until a blue color persisted (typical reaction time 2-5 minutes). The solution was purged with nitrogen for 10 minutes and 0.5 mL of Me_2S was added. The reaction was stirred at -78^oC for 30 minutes and allowed to warm to ambient temperature. The reaction continued to stir for 4 hours and concentrated *in vaccuo*. Chromatography provided **18** as a colorless oil.



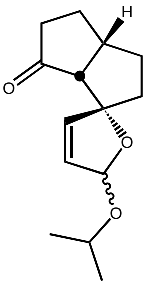
5`-isopropoxy-1-methyl-spiro[2`-oxo-bicyclo[3.3.0]octan-6-one-*R-4,2`-cyclopent-3`-ene] (15a)** Isolated as a colorless oil. IR (neat) ν_{max} 3088, 2970, 2877, 1734, 1455, 1372cm^{-1}; ^{1}H NMR (500 MHz) δ (mixture) 6.23 (dd, *J*=5.9 Hz, 1.2 Hz,1H), 6.18 (dd, *J*=5.9 Hz, 1.0 Hz, 1H), 5.83-5.85 (m, 1H), 5.79-5.81 (m, 1H), 3.94 (septet, *J*=6.1 Hz, 1H), 3.93 (septet, *J*=6.1 Hz, 1H), 2.26-2.42 (m, 2H), 2.21 (s, 1H), 1.96-2.10 (m, 2H), 1.82-1.94 (m, 2H), 1.71-1.80 (m, 2H), 1.41 (s, 3H), 1.40 (s, 3H), 1.23 (d, *J*=6.1 Hz, 3H), 1.20 (d, *J*=6.3 Hz, 3H), 1.17 (d, *J*=6.3 Hz, 3H), 1.16 (d, *J*=6.1 Hz, 3H); ^{13}C NMR (125 MHz) δ (major isomer) 218.0, 136.7, 128.2, 107.2, 100.0, 70.8, 67.1, 48.4, 41.2, 40.1, 39.8, 35.3, 28.2, 24.0, 22.9; EI-HRMS *m/z* calculated for $C_{15}H_{22}O_3$ (M^+): 250.1569, found: 250.1571.



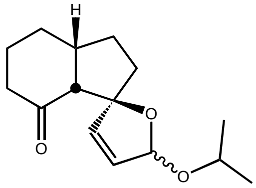
5`-isopropoxy-1-methyl-spiro[2`-oxo-bicyclo[3.3.0]octan-6-one-*S-4,2`-cyclopent-3`-ene] (15b)** Isolated as a colorless oil. IR (neat) ν_{max} 3088, 2970, 2877, 1734, 1455, 1372cm^{-1}; ^{1}H NMR (500 MHz) δ 6.206 (dd, *J*=5.9 Hz, 1.2 Hz,1H), 5.82 (dd, *J*=5.6 Hz, 1.2 Hz, 1H), 5.70 (dd, *J*=5.6 Hz, 1.2 Hz, 1H), 3.87 (septet, *J*=6.1 Hz, 1H), 2.55 (ddd, *J*= 17.8 Hz, 9.0 Hz, 0.98 Hz, 1H), 2.22-2.28 (m, 1H), 2.19 (s, 1H), 2.06-2.12 (m, 2H), 1.95-2.04 (m, 2H), 1.71-1.78 (m, 2H), 1.25 (d, *J*=6.6 Hz, 3H), 1.20 (s, 3H), 1.14 (d, *J*=6.1 Hz, 3H); ^{13}C NMR (125 MHz) δ 217.9, 136.6, 128.1, 107.1, 100.0, 71.1, 67.0, 48.4, 41.2, 40.0, 39.8, 35.3, 24.0, 22.9, 22.6; EI-HRMS *m/z* calculated for $C_{15}H_{22}O_3$ (M^+): 250.1569, found: 250.1580.



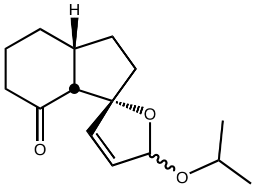
(1*S)-5`-isopropoxy-spiro[2`-oxo-bicyclo[3.3.0]octan-6-one-*R**-4,2`-cyclopent-3`-ene] (16a)** Isolated as a colorless oil (mixture). IR (neat) υ_{max} (cm^{-1}) 3090, 2967, 2877, 1732, 1627, 1455; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.28 (dd, *J*= 5.8 Hz, 1.0 Hz, 1H), 6.24 (dd, *J*= 5.8 Hz, 1.0 Hz, 1H), 5.86 (dd, *J*= 5.8 Hz, 1.0 Hz, 1H), 5.83 (dd, *J*= 5.9 Hz, 1.3 Hz, 1H), 5.78-580 (m, 2H), 3.92 (partial septet, *J*=6.4 Hz, 2H), 3.08-3.14 (m, 2H), 2.70, (d, *J*= 8.0 Hz, 1H), 2.57 (d, *J*= 8.5 Hz, 1H), 2.30-2.40 (m, 2H), 2.23-2.28 (m, 2H), 2.06-2.14 (m, 1H), 1.84 (ddt, *J*= 13.4 Hz, 7.3 Hz, 1.9 Hz, 1H), 1.70-1.80 (m, 4H), 1.64-1.69 (m, 4H), 1.55-1.64 (m, 2H), 1.22 (d, *J*= 6.3 Hz, 3H), 1.20 (d, *J*= 6.3 Hz, 3H), 1.16 (d, *J*=6.1 Hz, 3H), 1.15 (d, *J*=6.1 Hz, 3H); ^{13}C NMR (125 MHz) δ 219.0 218.4, 135.3, 138.0, 127.5, 127.4, 106.5, 106.1, 98.9, 98.6, 70.6, 70.0, 64.8, 63.4, 40.2, 40.1, 39.9, 39.0, 38.7, 38.3, 31.9, 31.8, 27.9, 27.8, 24.2, 24.1, 22.9, 22.8; HRMS m/z calculated for $C_{14}H_{20}O_3$: 236.1412, found: 236.1410.



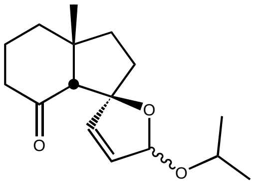
(1*S)-5`-isopropoxy-spiro[2`-oxo-bicyclo[3.3.0]octan-6-one-*S**-4,2`-cyclopent-3`-ene] (16b)** Isolated as a colorless oil (one isomer). IR (neat) υ$_{max}$ (cm^{-1}) 3090, 2967, 2877, 1732, 1627, 1455; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.07 (dd, *J*= 5.6 Hz, 1.2 Hz, 1H), 5.85 (dd, *J*= 5.6 Hz, 1.2 Hz, 1H), 5.72 (m, 1H), 3.89 (septet, *J*=6.1 Hz, 1H), 2.85-2.94 (m, 1H), 2.61, (d, *J*= 9.8 Hz, 1H), 2.45-2.54 (m, 1H), 2.06-2.20 (m, 3H), 1.95-1.94 (m, 1H), 1.84-1.91 (m, 3H), 1.22 (d, *J*= 6.4 Hz, 3H), 1.16 (d, *J*=6.1 Hz, 3H); ^{13}C NMR (125 MHz) δ 218.4, 136.4, 128.4, 107.2, 99.3, 70.8, 59.3, 42.4, 41.6, 39.7, 32.5, 27.8, 24.0, 22.9; HRMS m/z calculated for $C_{14}H_{20}O_3$: 236.1412, found:236.1405.



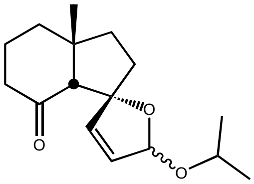
(1*S)-5`-isopropoxy-spiro[2`-oxo-bicyclo[4.3.0]nonan-6-one-*R**-4,2`-cyclopent-3`-ene] (17a)** Isolated as a pale-yellow oil mixture, which solidified in a -20°C freezer. IR (neat) υ$_{max}$ (cm^{-1}) 3077, 2936, 2866, 1692, 1616, 1566, 1450; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.78 (dd, *J*= 5.9 Hz, 1.0 Hz, 1H), 6.57 (dd, *J*= 6.1 Hz, 1.4 Hz, 1H), 5.72-5.74 (m, 3H), 5.71 (m, 1H), 3.93 (septet, *J*= 6.1 Hz, 1H), 3.92 (septet, *J*= 6.1 Hz, 1H), 3.09-3.16 (m, 1H), 2.90-2,98 (m, 1H), 2.83 (d, *J*= 7.3 Hz, 1H), 2.75 (d, *J*= 7.8 Hz, 1H), 2.36-2.45 (m, 2H), 2.12-2.23 (m, 2H), 2.06-2.10 (m, 2H), 1.81-1.98 (m, 6H), 1.54-1.71 (m, 4H), 1.41-1.52 (m, 4H), 1.24 (d, *J*= 6.1 Hz, 3H), 1.21 (d, *J*= 6.1 Hz, 3H), 1.16 (d, *J*= 6.1 Hz, 3H), 1.15 (d, *J*= 6.1 Hz, 3H); ^{13}C NMR (125 MHz) δ 212.1, 212.0, 137.4, 136.5, 127.0, 126.4, 105.7, 105.6, 98.2, 97.6, 70.7, 70.3, 66.2, 63.8, 43.2, 42.1, 37.4, 35.1, 27.9, 27.3, 26.6, 26.5, 24.8, 24.6, 24.5, 24.2, 24.1, 24.0, 22.8, 22.7; HRMS m/z calculated for $C_{15}H_{22}O_3$: 250.1569, found: 250.1580.



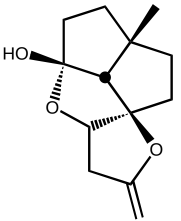
(1*S)-5`-isopropoxy-spiro[2`-oxo-bicyclo[4.3.0]nonan-6-one-*S**-4,2`-cyclopent-3`-ene] (17b)** Isolated as a colorless oil, which solidified in a -20°C freezer. IR (neat) υ$_{max}$ (cm^{-1}) 3077, 2936, 2866, 1692, 1616, 1566, 1450; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.05 (dd, *J*= 5.9 Hz, 1.0 Hz, 1H), 5.76 (dd, *J*= 5.9 Hz, 1.0 Hz, 1H), 5.64 (s, 1H), 3.89 (septet, *J*= 6.1 Hz, 1H), 2.59 (d, *J*= 8.8 Hz, 1H), 2.45-2.52 (m, 1H), 2.28-2.40 (m, 2H), 1.90-2.05 (m, 4H), 1.75-1.86 (m, 3H), 1.57-1.65 (m, 1H), 1.24 (d, *J*= 6.4 Hz, 3H), 1.16 (d, *J*= 6.1 Hz, 3H); ^{13}C NMR (125 MHz) δ 212.1, 137.3, 127.3, 107.2, 100.0, 70.8, 60.0, 41.5, 39.2, 31.3, 29.6, 26.6, 24.1, 23.6, 22.9; HRMS m/z calculated for $C_{15}H_{22}O_3$: 250.1569, found: 250.1577.



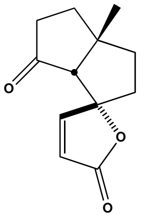
5`-isopropoxy-(*S\**)-1-methyl-spiro[2`-oxo-bicyclo[4.3.0]nonan-6-one-(*S)-4,2`-cyclopent-3`-ene] (18a)** Isolated as a colorless oil, which solidified in a -20^{o}C freezer. IR (neat) υ_{max} 3089, 2960, 2866, 1700, 1622, 1461cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (dd, *J*= 5.9 Hz, 1.2 Hz, 1H), 5.75 (dd, *J*= 5.9 Hz, 1.2 Hz, 1H), 5.62 (m, 1H), 3.89 (septet, *J*= 6.3 Hz, 1H), 2.44 (ddd, *J*= 16.1 Hz, 13.1 Hz, 6.4 Hz, 1H), 2.28 (s, 1H), 2.20-2.25 (m, 1H), 1.95-2.05 (m, 4H), 1.85-1.90 (m, 1H), 1.75-1.81 (m, 1H), 1.55-1.60 (m, 1H), 1.46-1.50 (m, 1H), 1.24 (d, 6.1 Hz, 3H), 1.16 (d, *J*= 6.1 Hz, 3H), 1.10 (s, 3H); ^{13}C NMR (125 MHz) δ 212.4, 137.5, 127.1, 107.1, 100.7, 70.9, 67.4, 44.4, 41.0, 40.0, 39.1, 35.2, 28.8, 24.1, 22.9, 21.0; HRMS m/z calculated for $C_{16}H_{24}O_3$: 264.1725, found: 264.1731.



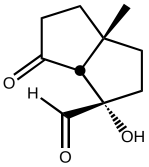
5`-isopropoxy-(*S\**)-1-methyl-spiro[2`-oxo-bicyclo[4.3.0]nonan-6-one-(*S)-4,2`-cyclopent-3`-ene] (18b)** Isolated as a pale-yellow oil mixture, which solidified in a -20^{o}C freezer. IR (neat) υ_{max} 3089, 2960, 2866, 1700, 1622, 1461cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (major) 6.15 (dd, *J*= 5.9 Hz, 1.2 Hz, 1H), 5.81 (m, 1H), 5.78 (dd, *J*= 5.9 Hz, 1.2 Hz, 1H), 3.97 (septet, *J*= 6.1 Hz, 1H), 2.71 (s, 1H), 2.60 (ddd, *J*= 16.1 Hz, 11.7 Hz, 6.6 Hz, 1H), 2.31-2.37 (m, 1H), 2.04-2.16 (m, 2H), 1.90-2.01 (m, 2H), 1.75-1.86 (m, 1H), 1.60-1.72 (m, 2H), 1.48-1.54 (m, 1H), 1.24 (d, *J*= 6.3 Hz, 3H), 1.20 (s, 3H), 1.17 d, *J*= 6.3 Hz, 3H); ^{13}C NMR (125 MHz) δ 212.1, 135.6, 127.9, 105.7, 99.6, 70.6, 68.5, 44.6, 40.5, 39.4, 38.9, 34.3, 28.2, 24.1, 22.7, 21.4; HRMS m/z calculated for $C_{16}H_{24}O_3$: 264.1725, found: 264.1732.



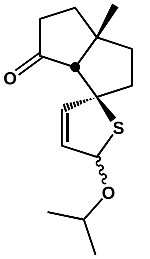
Hydrate (16) Isolated as a white solid (m.p.124.5-125.1 ^{o}C). IR (CCl_4): 3409, 2951, 2867, 2380, 1775cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.43 (dd, *J*=6.8, 2.4 Hz, 1H), 3.89 (s, 1H), 2.90 (dd, *J*=18.5, 2.4 Hz, 1H), 2.82 (dd, *J*= 18.8, 6.8 Hz, 1H), 2.48 (s, 1H), 2.22 (ddd, *J*=24.4, 8.3, 2.6 Hz, 1H), 2.03 (m, 2H), 1.94 (ddd, *J*=13.4, 61, 3.4 Hz, 1H), 1.60-1.80, (m, 4H), 1.27 (s, 3H); ^{13}C NMR (125 MHz) δ175.7, 119.1, 102.6, 81.6, 70.0, 49.8, 38.0, 37.9, 37.2, 36.7, 34.9, 27.6; Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19; O, 28.54. Found: C, 64.05; H, 7.23; O, 28.26.



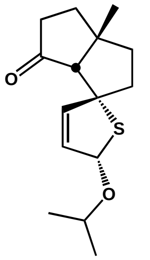
1-methyl-spiro[2`-oxo-bicyclo[3.3.0]octan-6-one-*S*\*-4,2`-cyclopent-3`-ene-5`-one] (17) Isolated as a white solid (m.p 134.1-135.1 °C). IR (CCl_4): 2952, 2866, 1761, 1737. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J*=5.6Hz, 1H), 6.12 (d, *J*=5.6Hz, 1H), 2.60 (ddd, *J*=18.3Hz, 9.0Hz, 6.6Hz, 1H), 2.45 (s, 3H), 2.31-2.38 (m, 1H), 2.16 -2.28 (m, 3H), 1.85-1.96 (m, 1H), 1.93-2.02 (m, 2H), 1.31 (s, 1H); ^{13}C NMR (125 MHz) δ 214.3, 171.6, 157.1, 122.0, 96.9, 65.3, 48.9, 39.9, 39.7, 38.9, 35.6, 28.3. Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; O, 23.27. Found: C, 69.65; H, 6.84; O, 23.29.



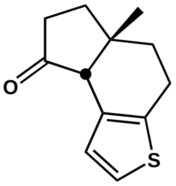
1-hydroxy-3a-methyl-6-oxo-octahydro-pentalene-1-carbaldehyde (18) Isolated as a colorless oil. IR (neat) ν_{max} 3399, 2944, 2870, 1751, 1715, 1642cm^{-1}; ^{1}H NMR (500 MHz) δ 9.53 (s, 1H), 3.60 (s, 1H), 2.47-2.53 (m, 2H), 2.35-2.42 (m, 1H), 2.06-2.20 (m, 3H), 1.80-1.90 (m, 3H), 1.30 (s, 3H); ^{13}C NMR (125 MHz) δ 217.9, 200.3, 87.4, 64.6, 49.1, 40.0, 39.0, 36.9, 34.8, 27.5; EI-HRMS *m/z* calculated for $C_{10}H_{14}O_3$ (M^+): 182.0943, found: 182.0951.



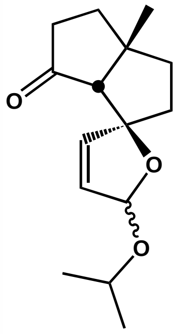
5`-isopropoxy-(*S*\*)-1-methyl-spiro[2`-thia-bicyclo[3.3.0]octan-6-one-(*R)-4,2`-cyclopent-3`-ene] (21)** Isolated as a pale yellow oil. IR (neat) υ_{max}: 3054, 2944, 2859, 1732, 1452; ^{1}H NMR (500 MHz, $CDCl_3$) δ (mixture) 6.13 (dd, *J*= 1.2 Hz, 0.9 Hz, 1H), 6.08 (dd, *J*= 1.2 Hz, 0.9 Hz, 1H), 6.04 (d, *J*= 6.3 Hz, 1H), 6.02 (d, *J*= 6.3 Hz, 1H), 5.89 (ddd, *J*= 6.3 Hz, 2.4 Hz, 0.9 Hz, 1H), 5.86 (ddd, *J*= 6.2 Hz, 2.4 Hz, 0.9 Hz, 1H), 3.78 (septet, *J*= 6.3 Hz, 1H), 3.75 (septet, *J*= 6.1 Hz, 1H), 2.59 (s, 1H), 2.41 (s, 1H), 2.25-2.35 (m, 4H), 1.95-2.05 (m, 4H), 1.86-1.93 (m, 4H), 1.75-1.83 (m, 4H), 1.39 (s, 3H), 1.37 (s, 3H), 1.15-1.20 (m, 12H); ^{13}C NMR (125 MHz) δ (mixture) 21.6, 21.7, 23.1, 23.5, 27.8, 28.7, 36.4, 36.6, 40.0, 40.2, 41.1, 41.3, 44.6, 45.2, 48.1, 48.4, 68.3, 69.3, 70.3, 70.9, 72.3, 72.6, 91.9, 92.0, 130.1, 130.6, 139.3, 140. 2, 215.4, 217.2; EI-HRMS *m/z* calculated for $C_{15}H_{22}O_2S$ (M^+): 266.1341, found: 266.1334.

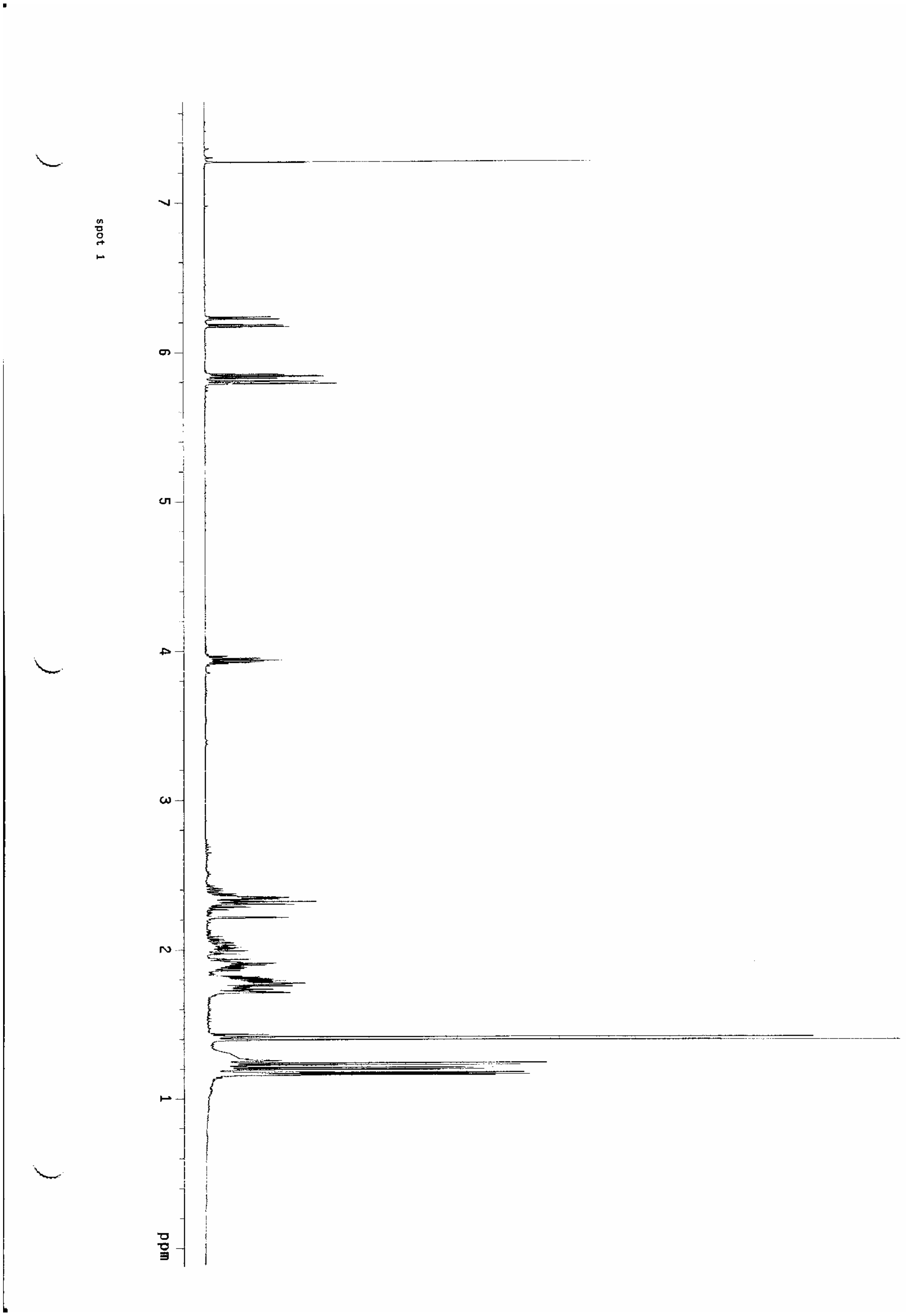


5`-isopropoxy-(*S**)-1-methyl-spiro[2`-thia-bicyclo[3.3.0]octan-6-one-(*S)-4,2`-cyclopent-3`-ene] (22)** Isolated as a pale yellow oil. IR (neat) υ$_{max}$: ^{1}H NMR (500 MHz, CDCl$_3$) δ (mixture) 6.09 (dd, *J*= 1.2 Hz, 0.9 Hz, 1H), 6.07, (dd, *J*= 1.2 Hz, 0.9 Hz, 1H), 5.95-6.02 (m, 2H), 5.81-5.89 (m, 2H), 3.70 (septet, *J*= 6.1 Hz, 1H), 3.45 (septet, *J*= 6.1 Hz, 1H), 2.42-2.52 (m, 4H), 2.20-2.32 (m, 4H), 1.94-2.02 (m, 4H), 1.78-1.88 (m, 4H), 1.23 (s, 3H), 1.19 (d, *J*= 6.1 Hz, 3H), 1.13 (s, 3H), 1.09 (d, *J*=6.1 Hz, 3H); ^{13}C NMR (125 MHz) δ (mixture) 21.9, 22.1, 23.3, 23.6, 27.1, 28.9, 36.5, 36.6, 41.0, 41.2, 42.1, 42.4, 44.3, 45.2, 48.5, 48.6, 68.5, 69.4, 70.8, 70.9, 72.1, 72.7, 92.0, 92.3, 130.2, 130.5, 139.7, 140. 2, 215.3, 217.8; EI-HRMS *m/z* calculated for $C_{15}H_{22}O_2S$ (M^+): 266.1341, found: 266.1340.



5a-methyl-4,5,5a,6,7,8a-hexahydro-3-thia-*as*-indacen-8-one (23) Isolated as a white solid (m.p. 61.2-61.7°C). ^{1}H NMR (500 MHz, toluene-d_8) δ 7.28 (d, *J*=1.7 Hz, 1H), 6.18 (d, *J*= 1.7 Hz, 1H), 3.37 (s, 1H), 2.49-2.55 (m, 1H), 2.43 (ddd, *J*= 8.7Hz, 2.7Hz, 1.0Hz, 1H), 2.41 (dd, *J*=10.6Hz, 8.4Hz, 1H), 2.31-2.36 (m, 1H), 1.84-1.99 (m, 2H), 1.70-1.72 (m, 4H), 1.27 (s, 3H); ^{13}C NMR (125 MHz) δ 21.8, 25.1, 31.5, 33.1, 35.2, 38.2, 56.2, 122.3, 128.3, 130.6, 134.7 215.3; Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; O, 7.76; S, 15.54. Found: C, 69.85; H, 6.77; O, 7.53; S, 15.37.

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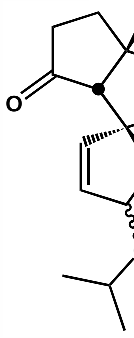
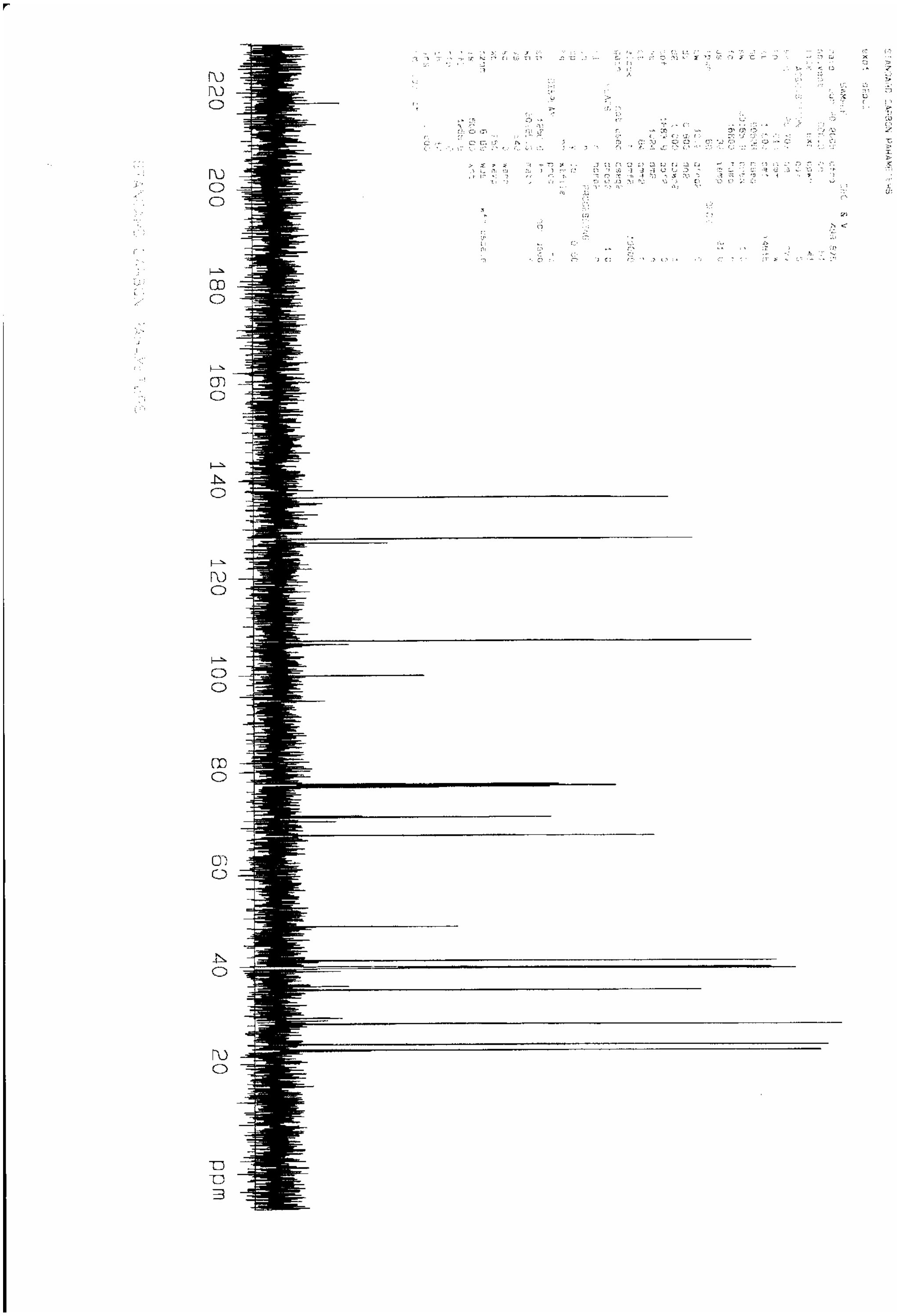
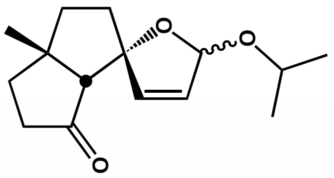
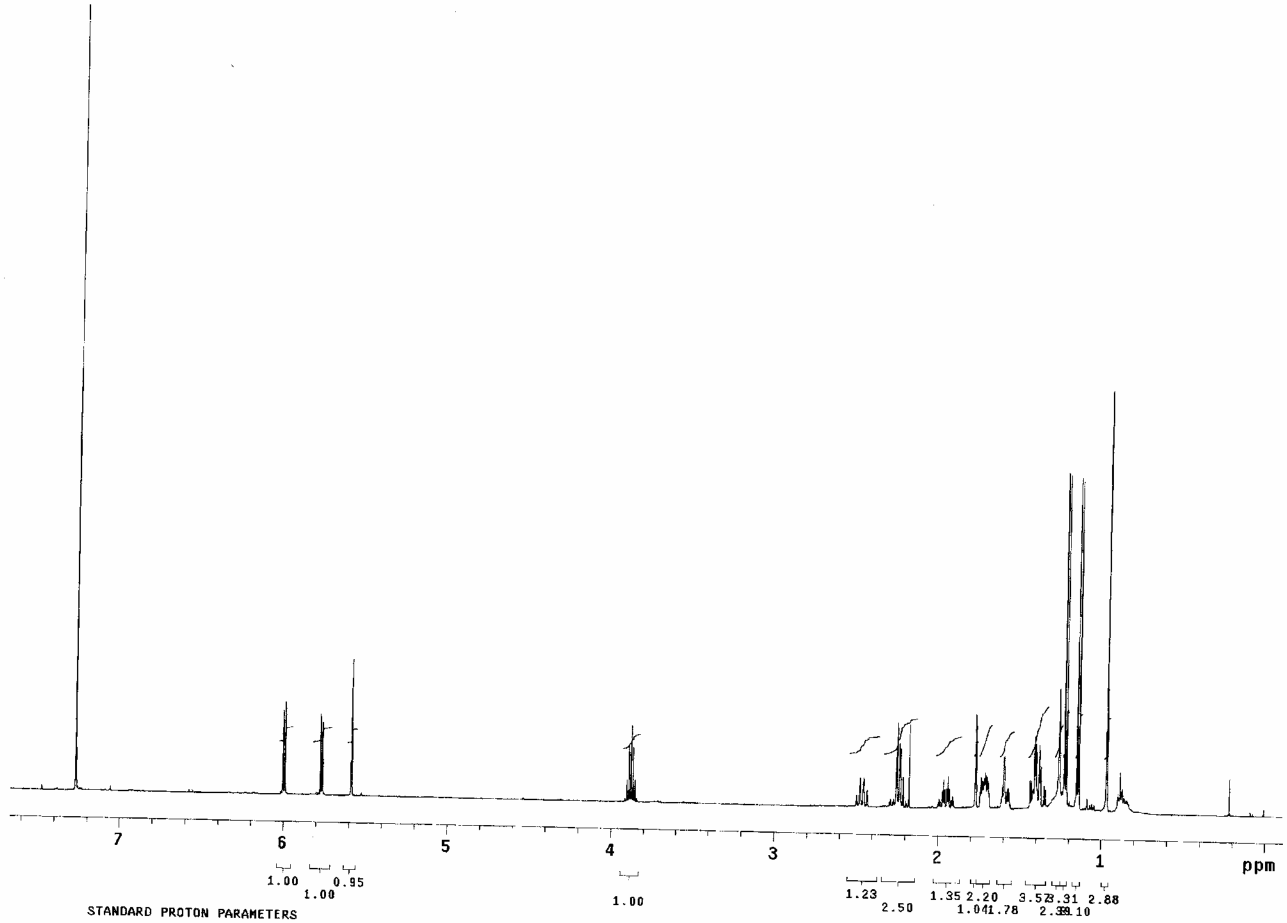
7
6
5
4
3
2
1
ppm





220
200
180
160
140
120
100
80
60
40
20
ppm
STANDARD CARBON PARAMETERS

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6
5
4
3
2
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2.20
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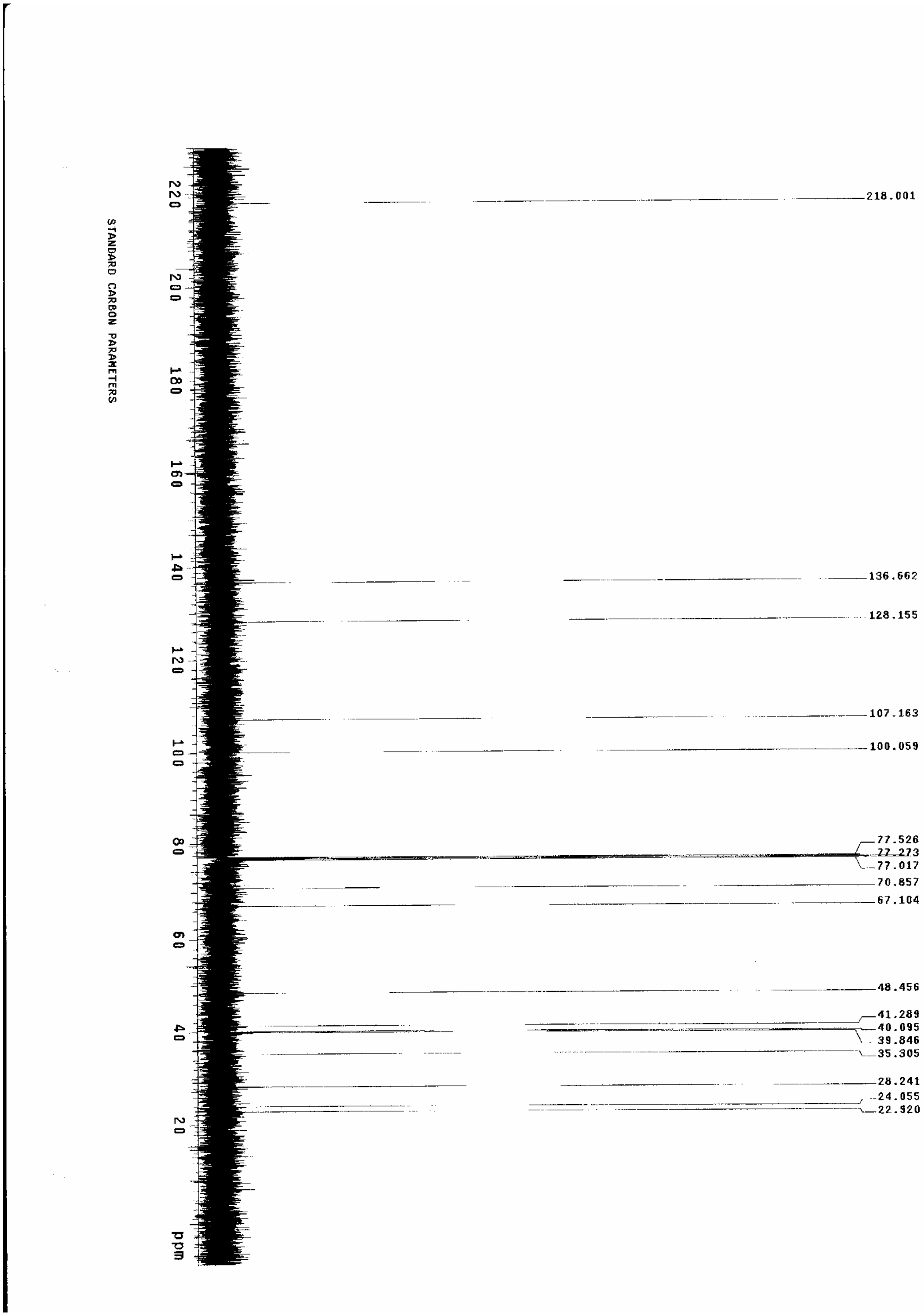
3.57
2.33
3.31
3.10
2.88
STANDARD PROTON PARAMETERS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180
160
140
120
100
80
60
40
20
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107.163
100.059
77.526
77.273
77.017
70.857
67.104
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41.289
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39.846
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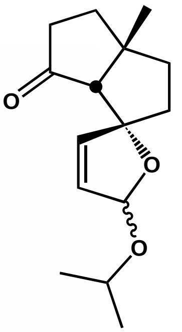
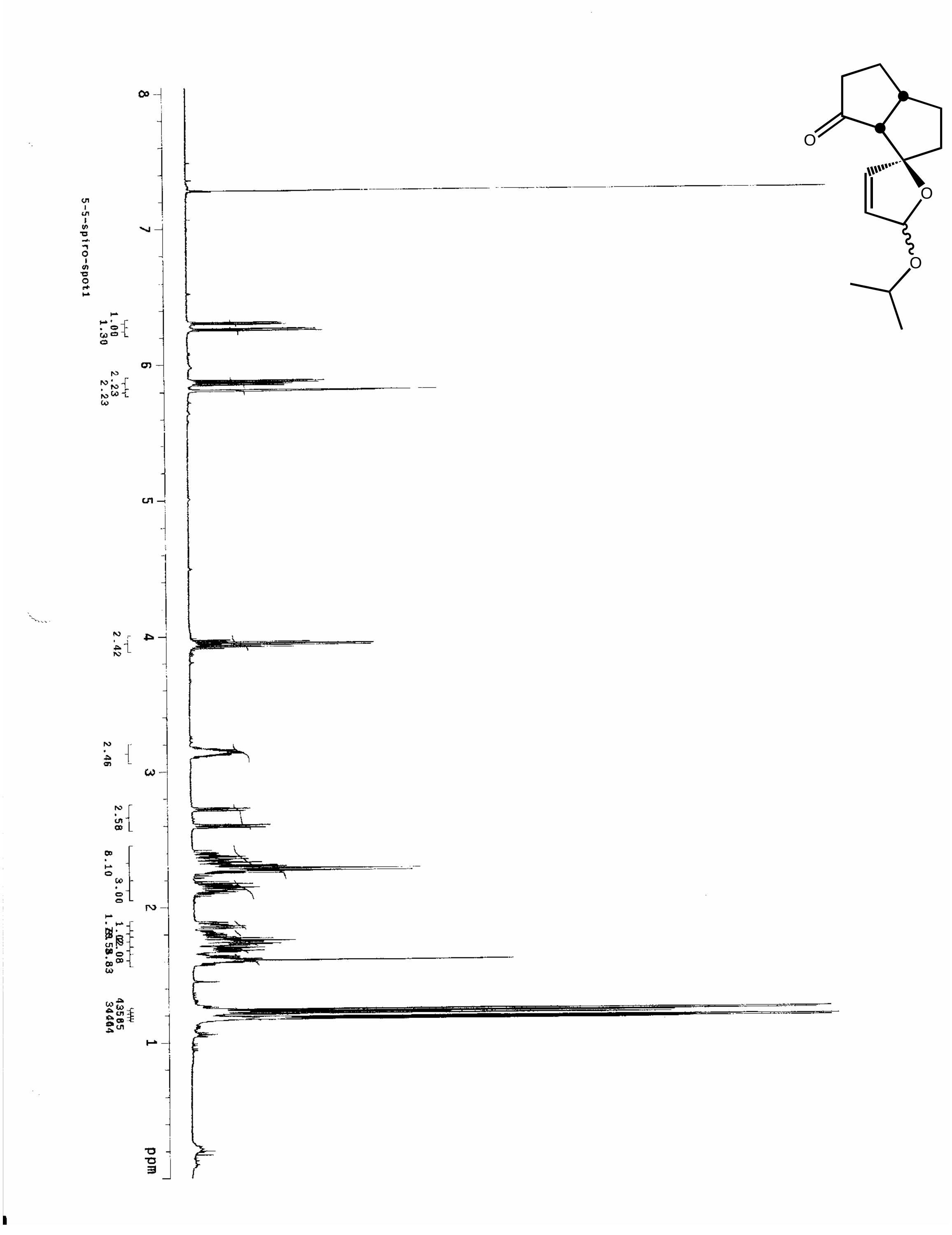
24.055
22.920


O
O
O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O
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2.46
2.58
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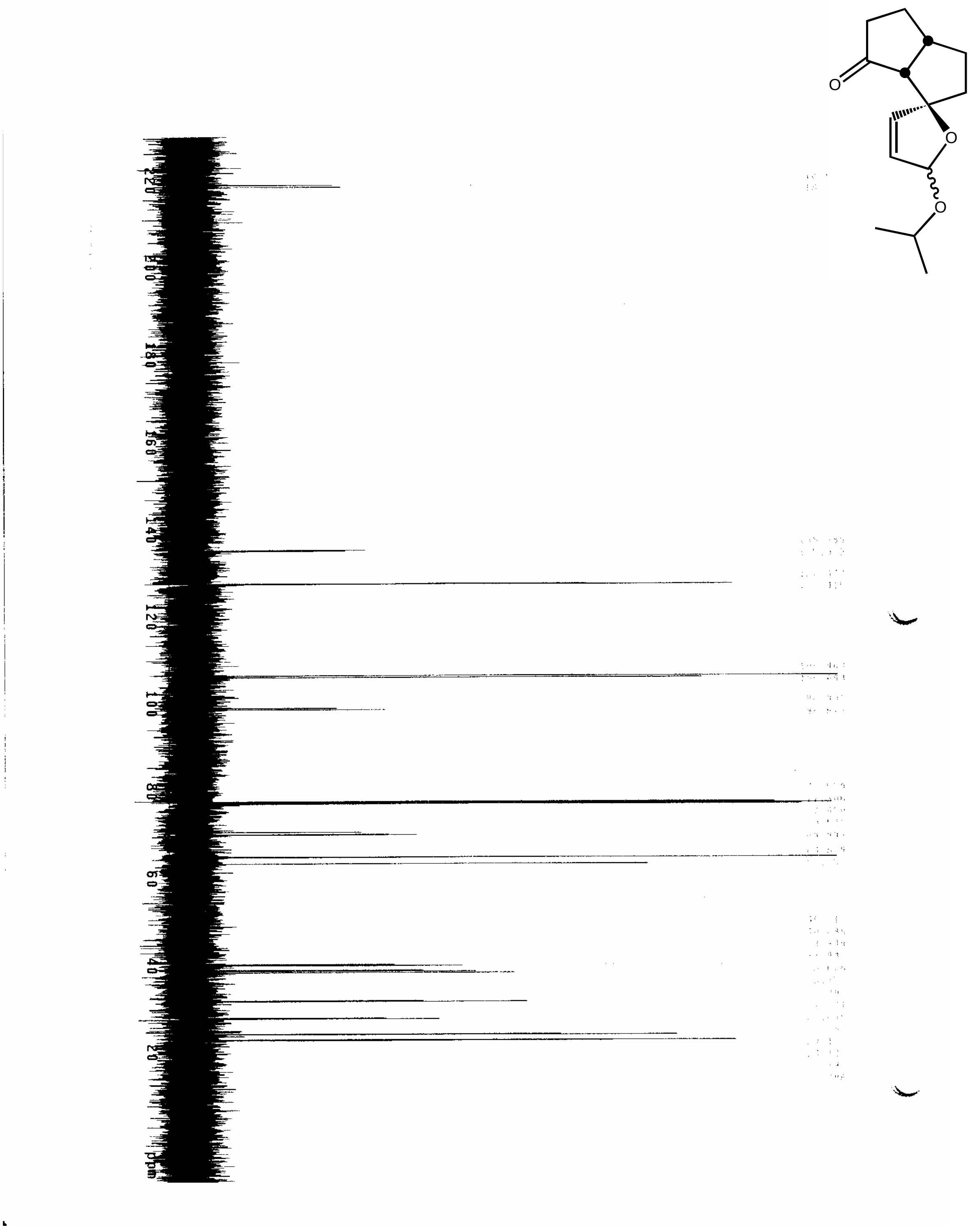
3.00
8
7
6
5
4
3
2
1
ppm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180
160
140
120
100
80
60
40
20
ppm
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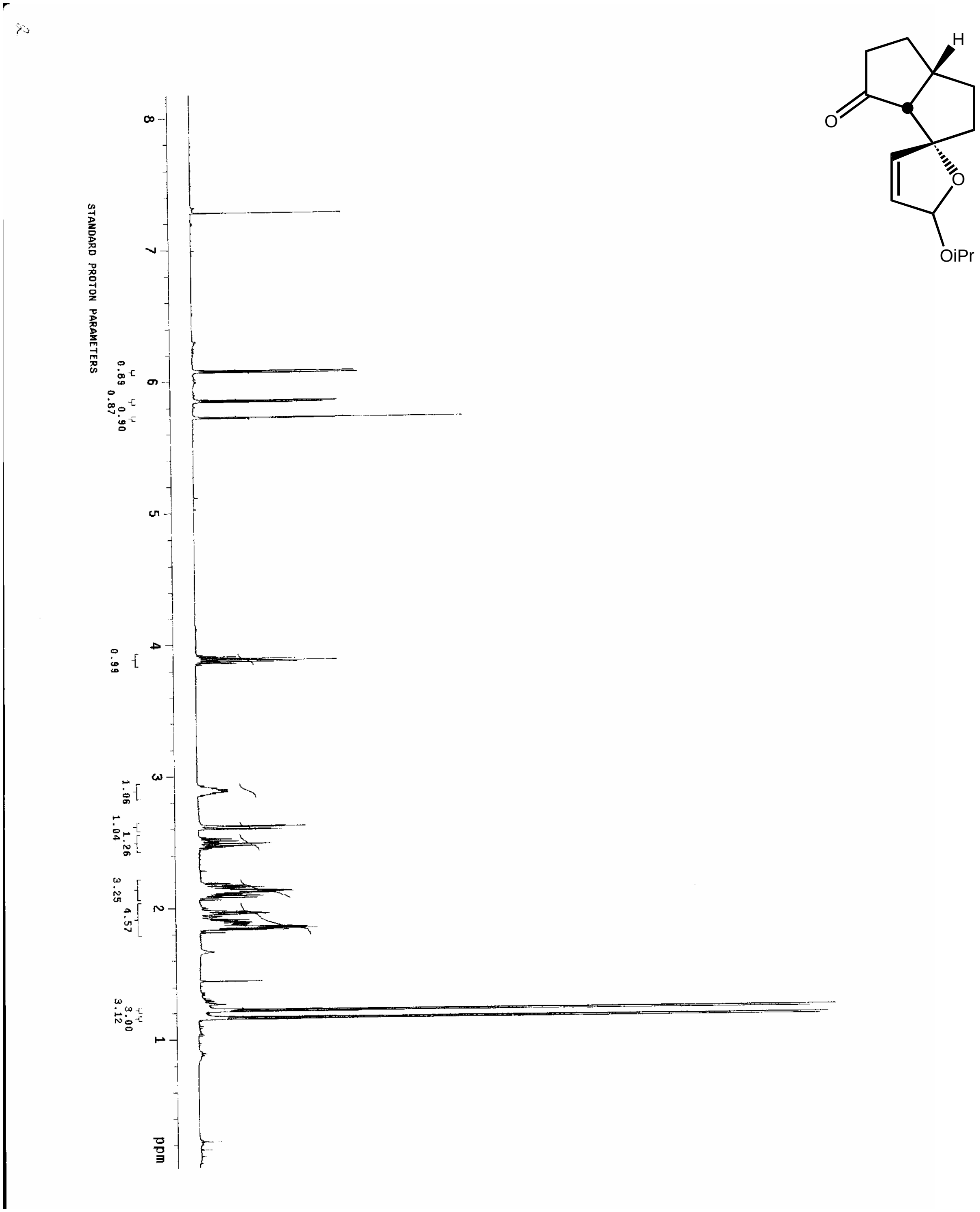
O
O


H
O
O
OiPr
STANDARD PROTON PARAMETERS
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7
6
5
4
3
2
1
ppm
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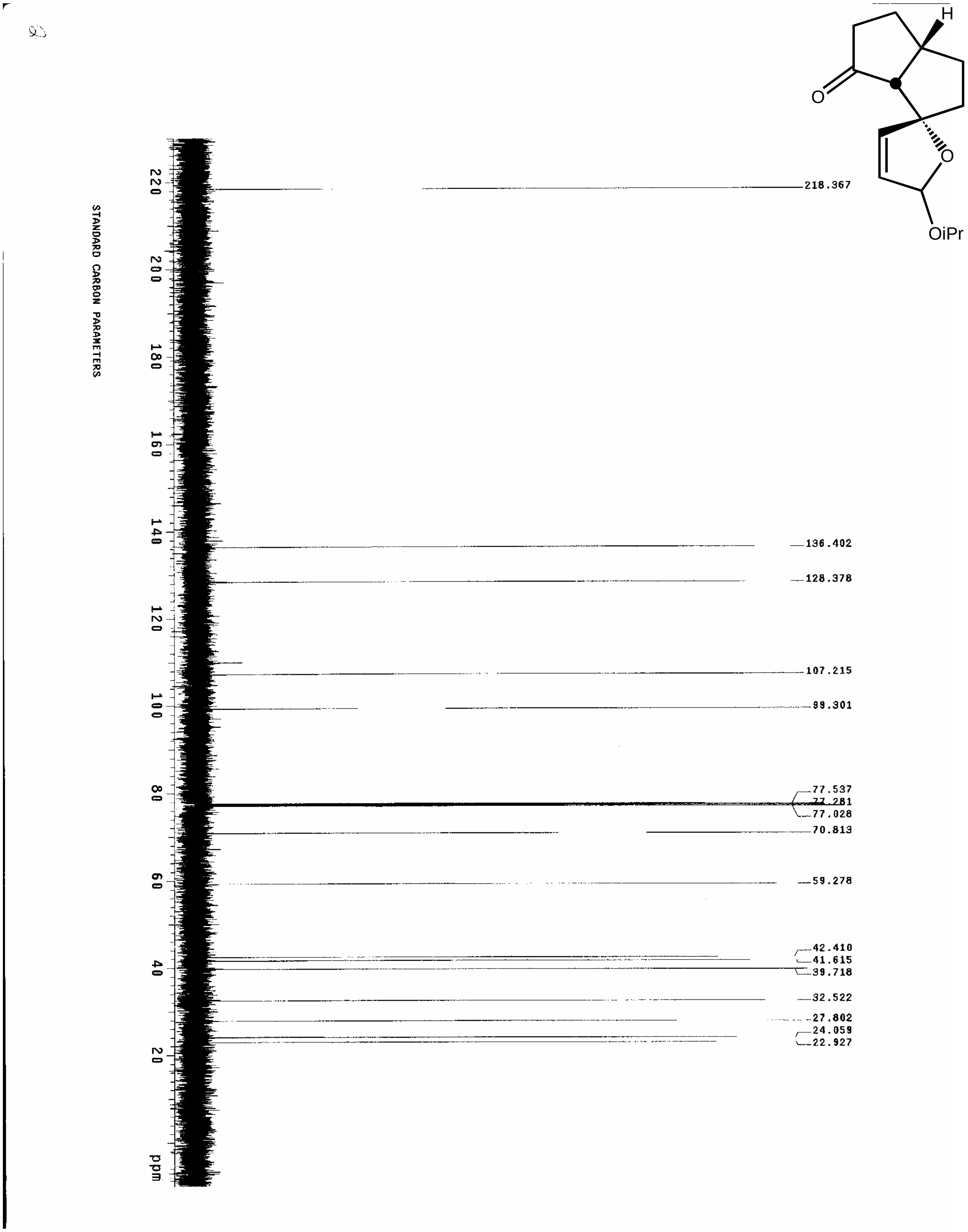
0.90
0.99
1.06
1.04
1.26
3.25
4.57
3.00
3.12



O
H
O
OiPr
STANDARD CARBON PARAMETERS
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160
140
120
100
80
60
40
20
ppm
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128.378
107.215
99.301
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77.281
77.028
70.813
59.278
42.410
41.615
39.718
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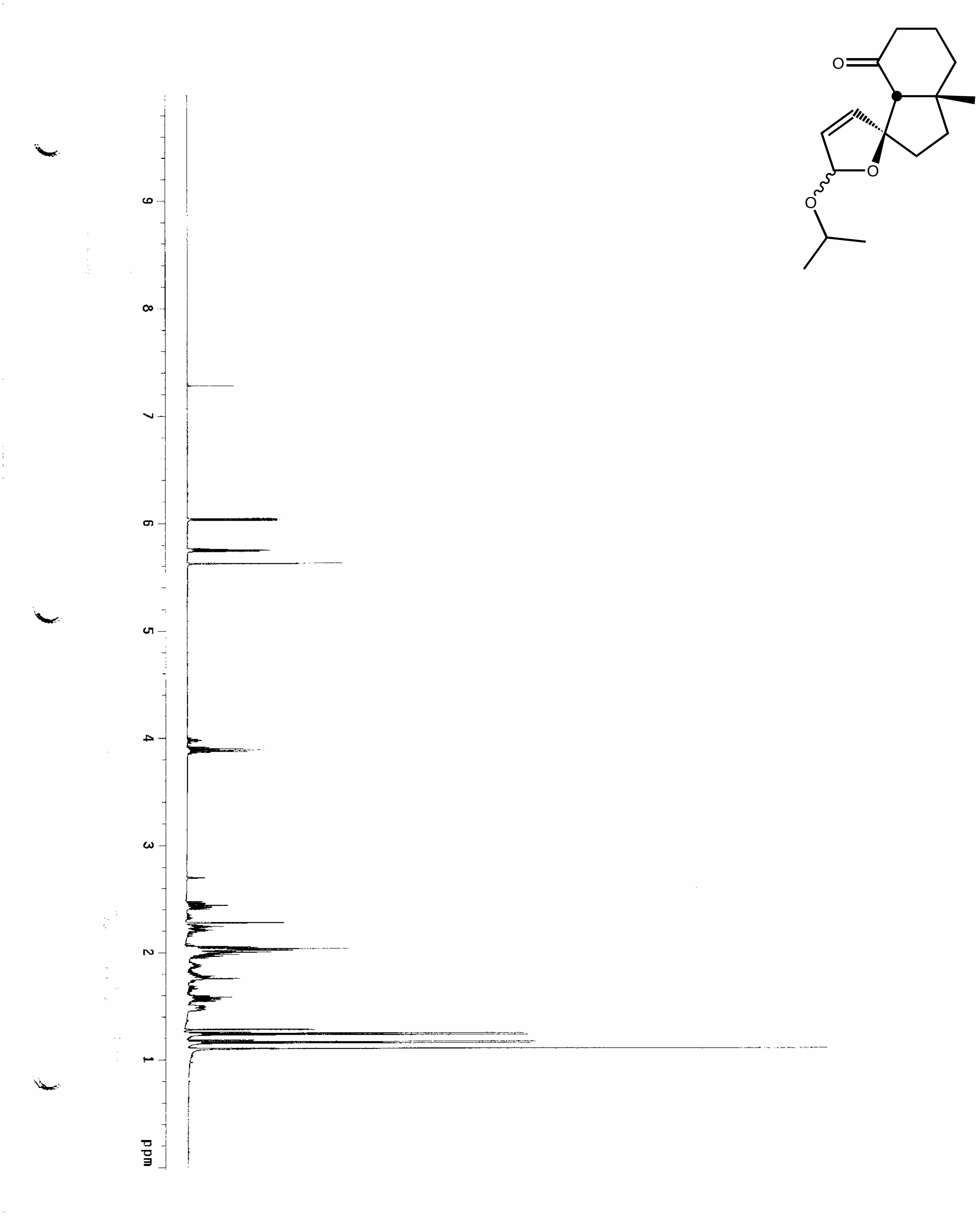
27.802
24.059
22.927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O
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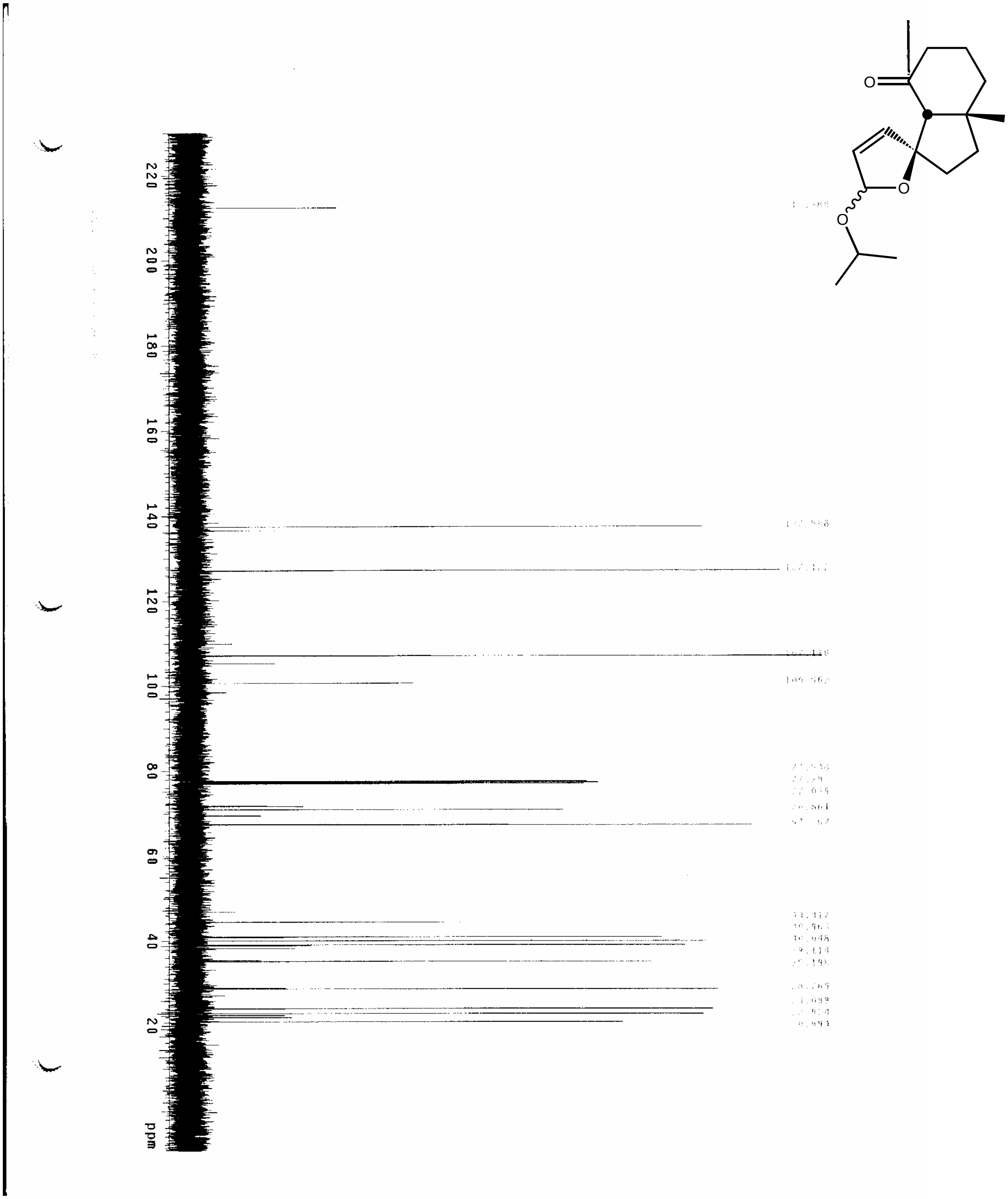
8
7
6
5
4
3
2
1
ppm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O
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120
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80
60
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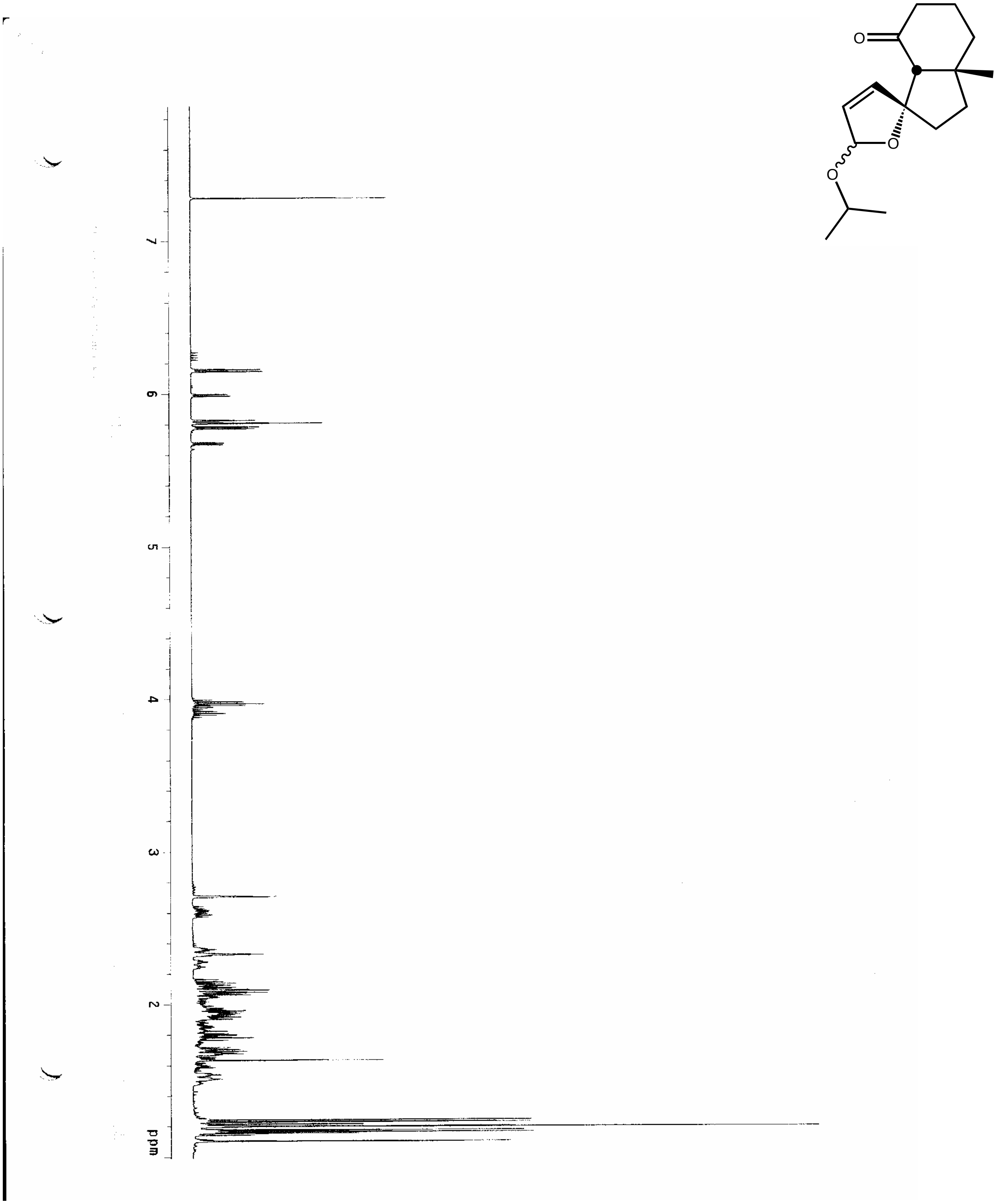
20
ppm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O
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6
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4
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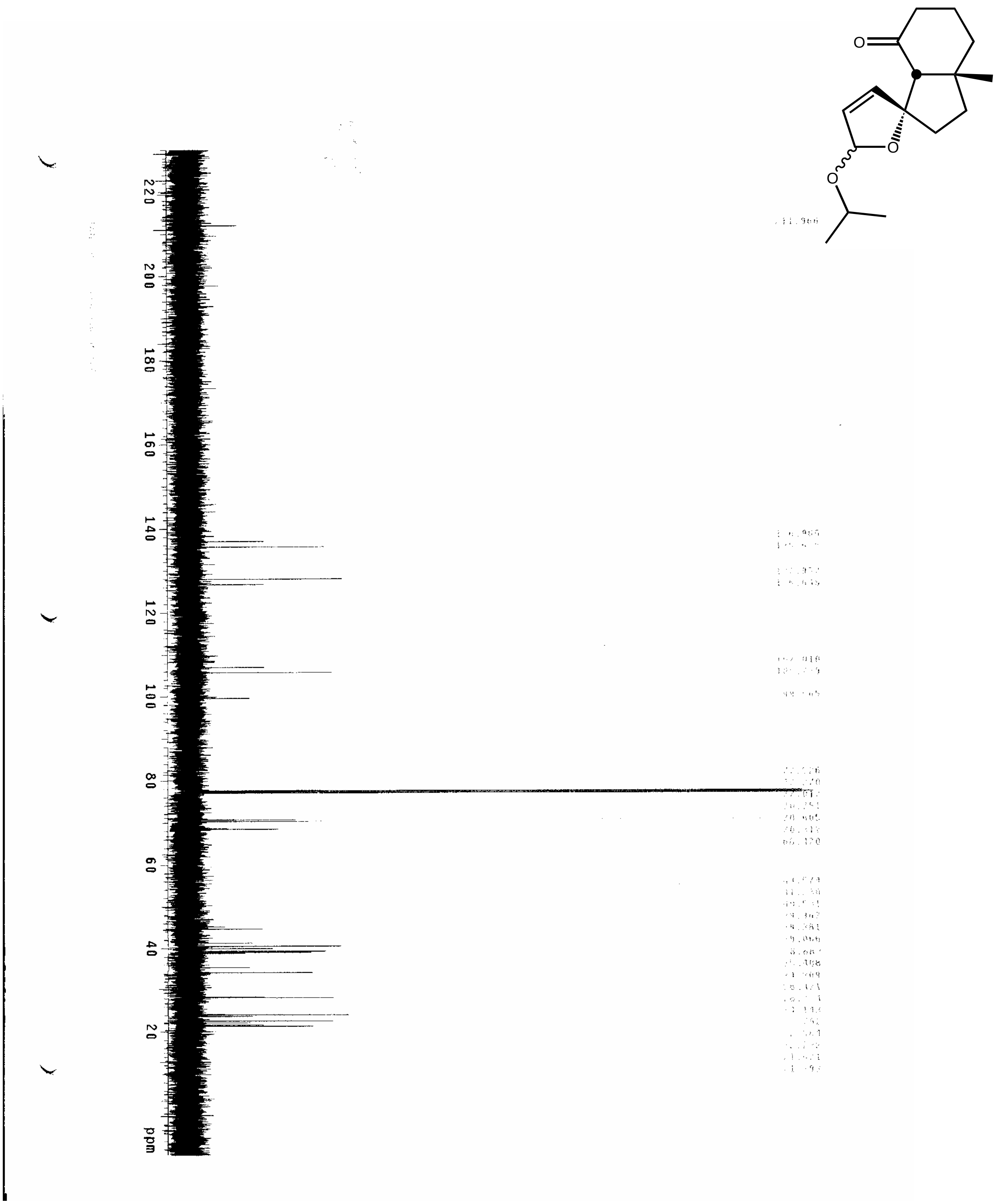
ppm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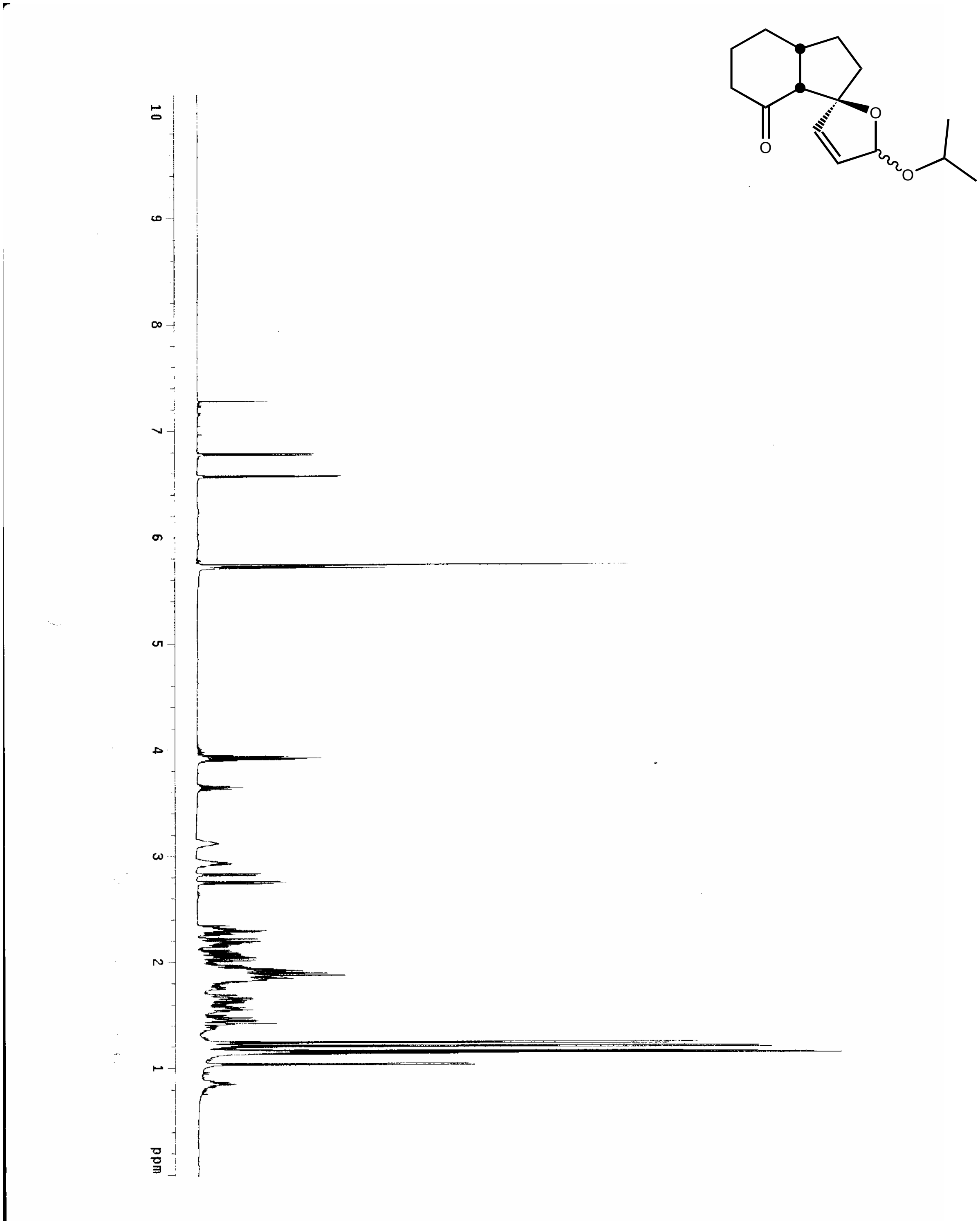
66.170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9
8
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6
5
4
3
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ppm
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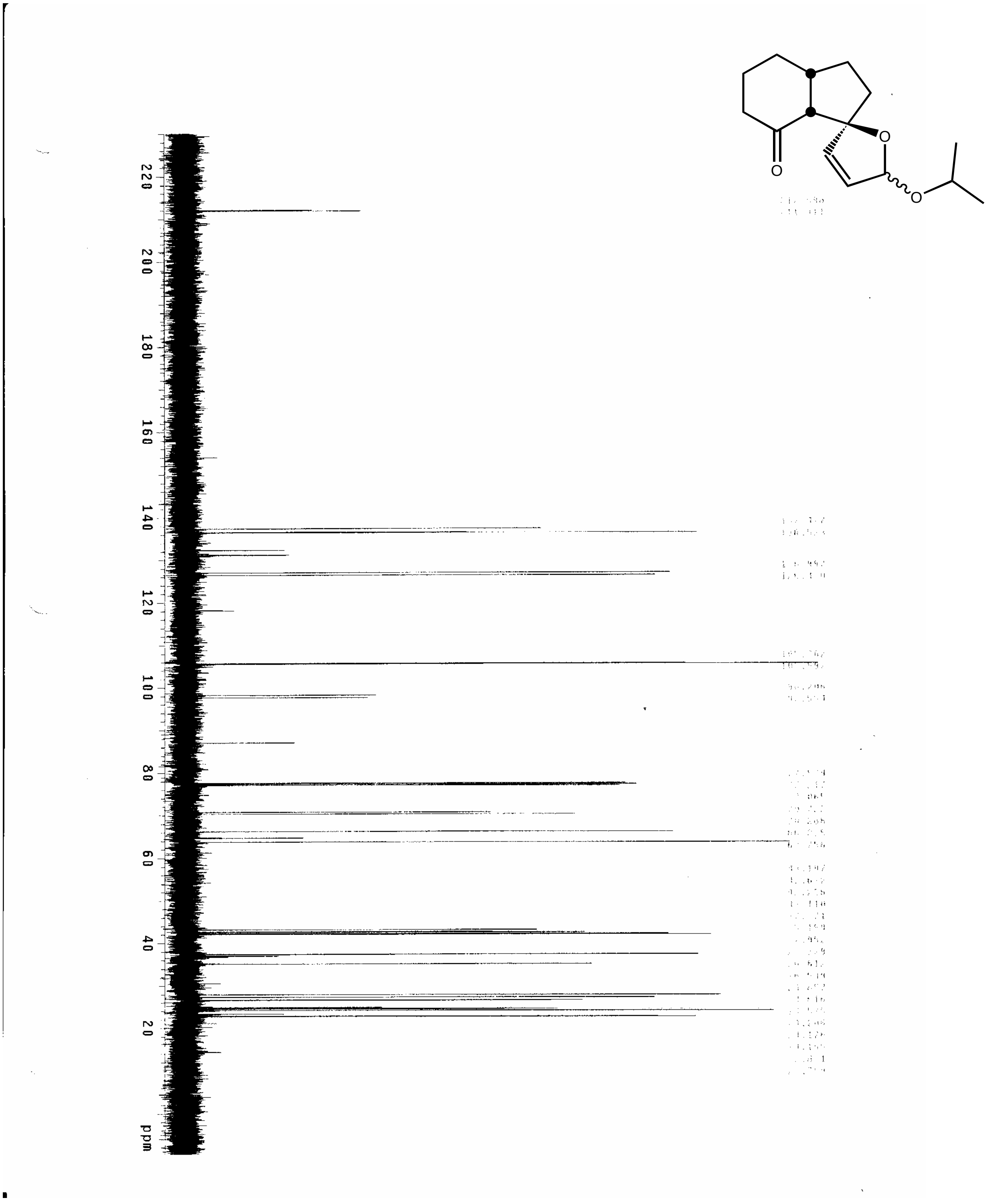
O
O


O
O
O
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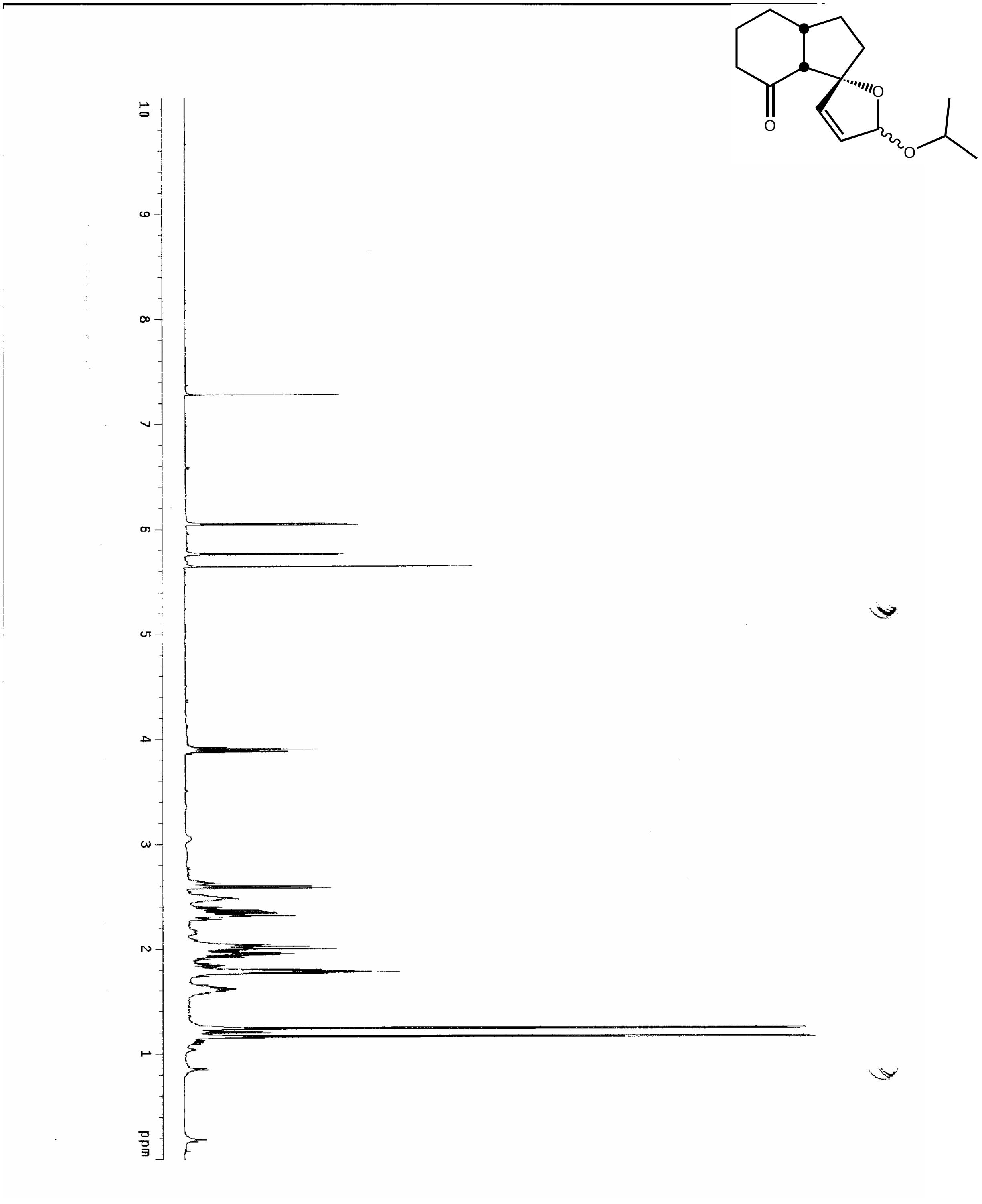
80
60
40
20
ppm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O
O
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9
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7
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5
4
3
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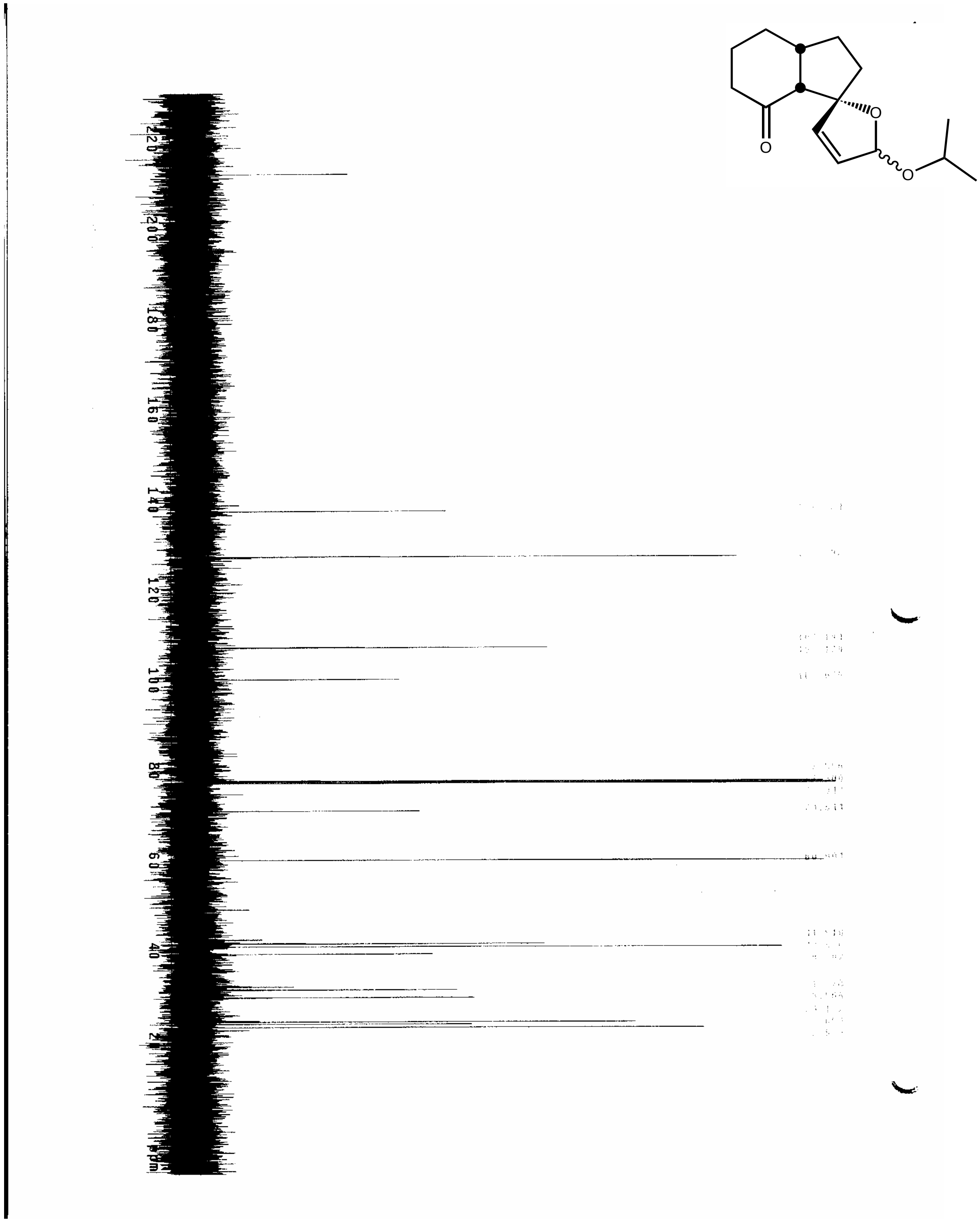
1
ppm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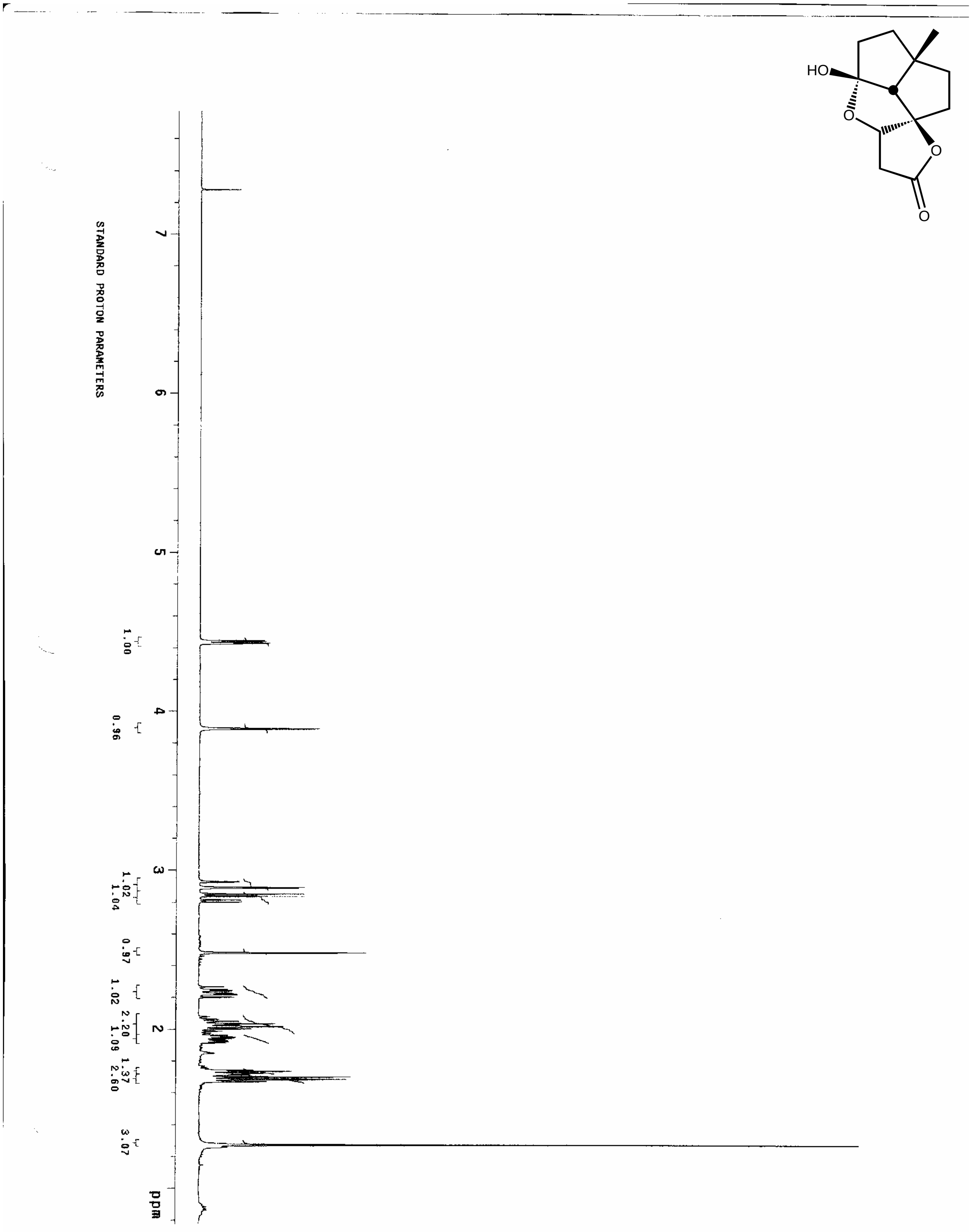
160
140
120
100
80
60
40
20
ppm
O
O
O


HO
O
O
O
STANDARD PROTON PARAMETERS
7
6
5
4
3
2
ppm
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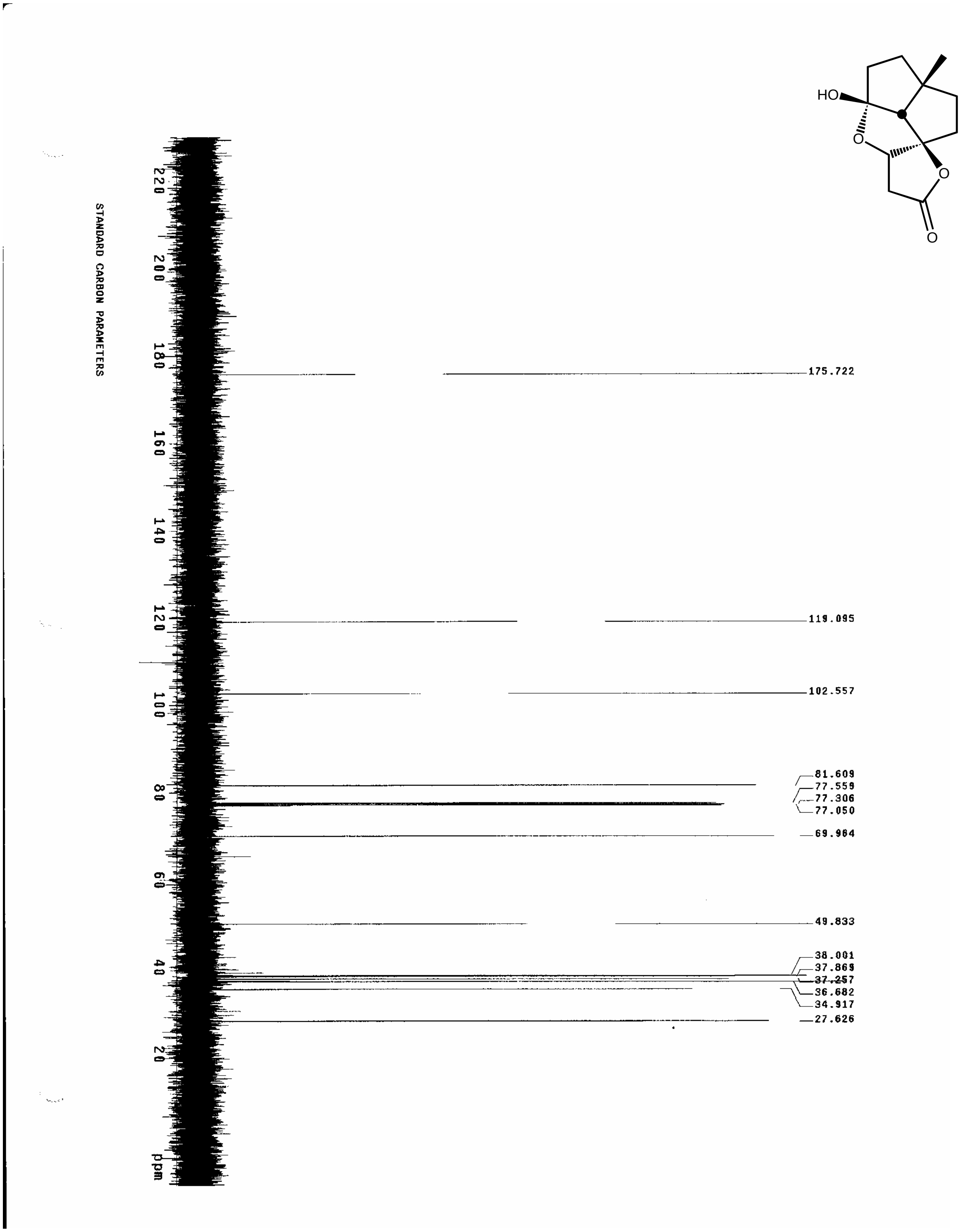
1.02
1.04
0.97
1.02
2.20
1.09
1.37
2.60
3.07


HO
O
O
O
STANDARD CARBON PARAMETERS
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200
180
160
140
120
100
80
60
40
20
ppm
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119.095
102.557
81.609
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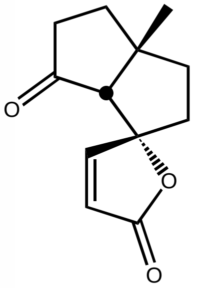
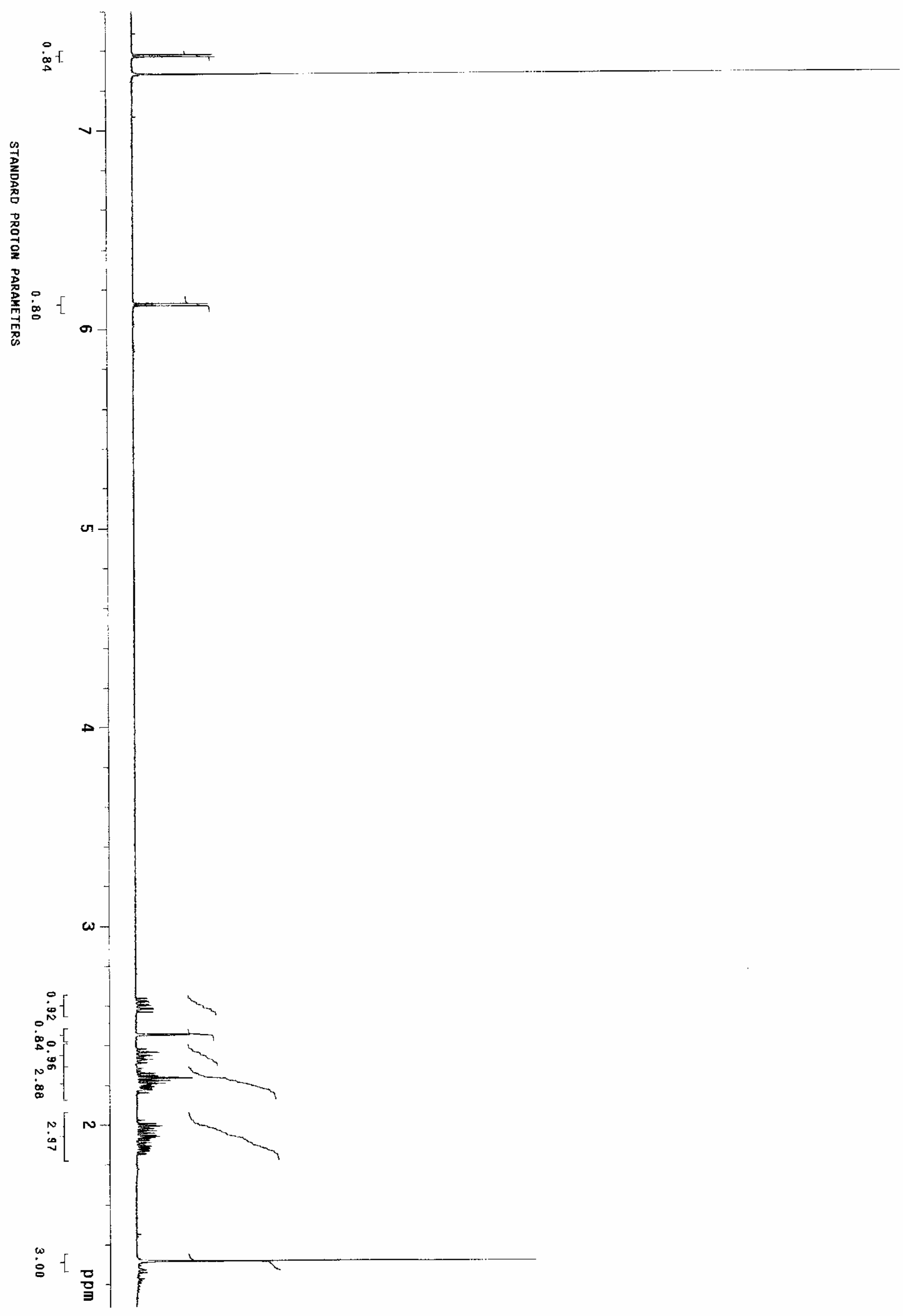
77.050
69.964
49.833
38.001
37.869
37.257
36.682
34.917
27.626


O
O
O


0.84
0.80
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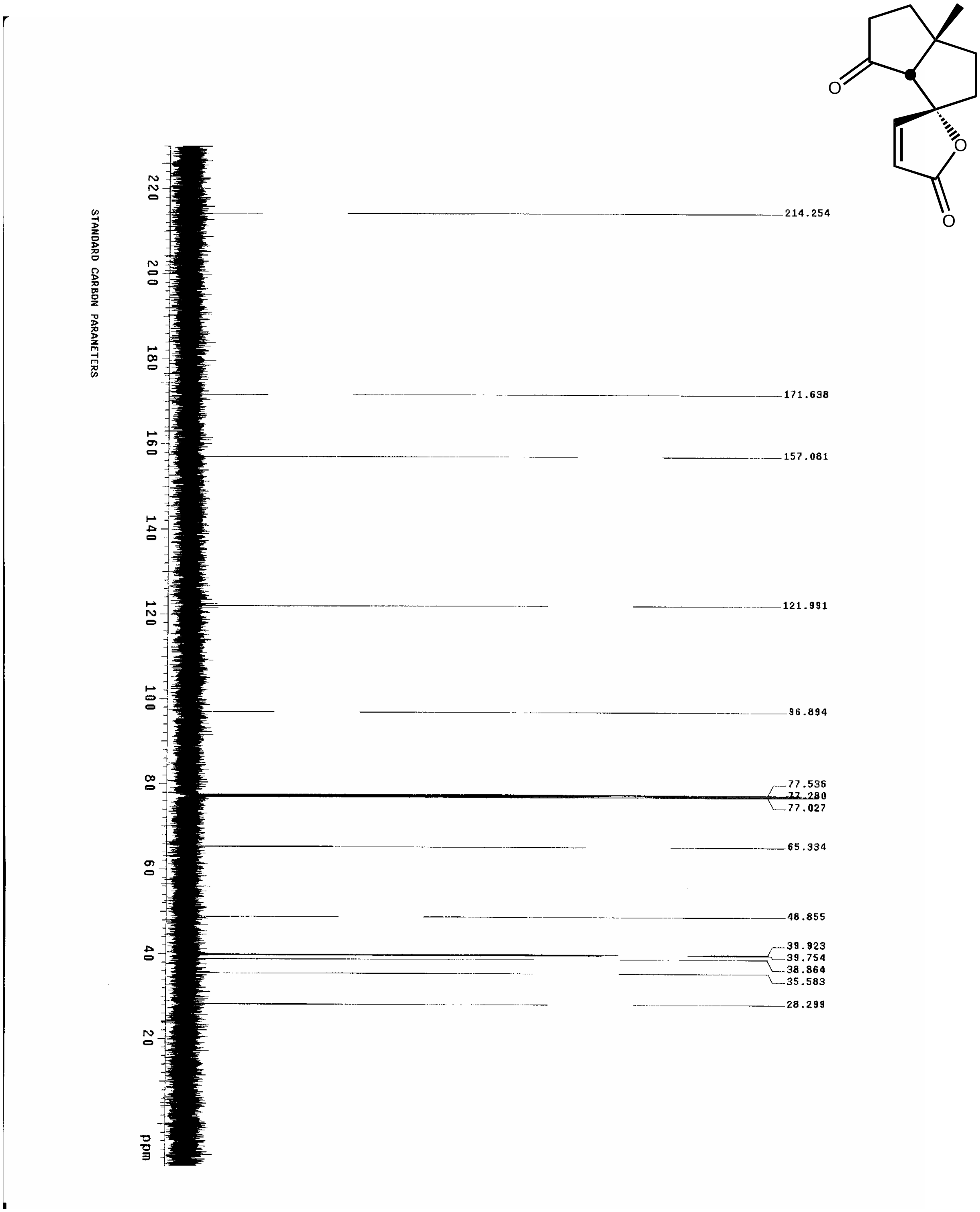
0.96
2.88
2.97
3.00
7
6
5
4
3
2
ppm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121.991
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77.536
77.280
77.027
65.334
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39.923
39.754
38.864
35.583
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200
180
160
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120
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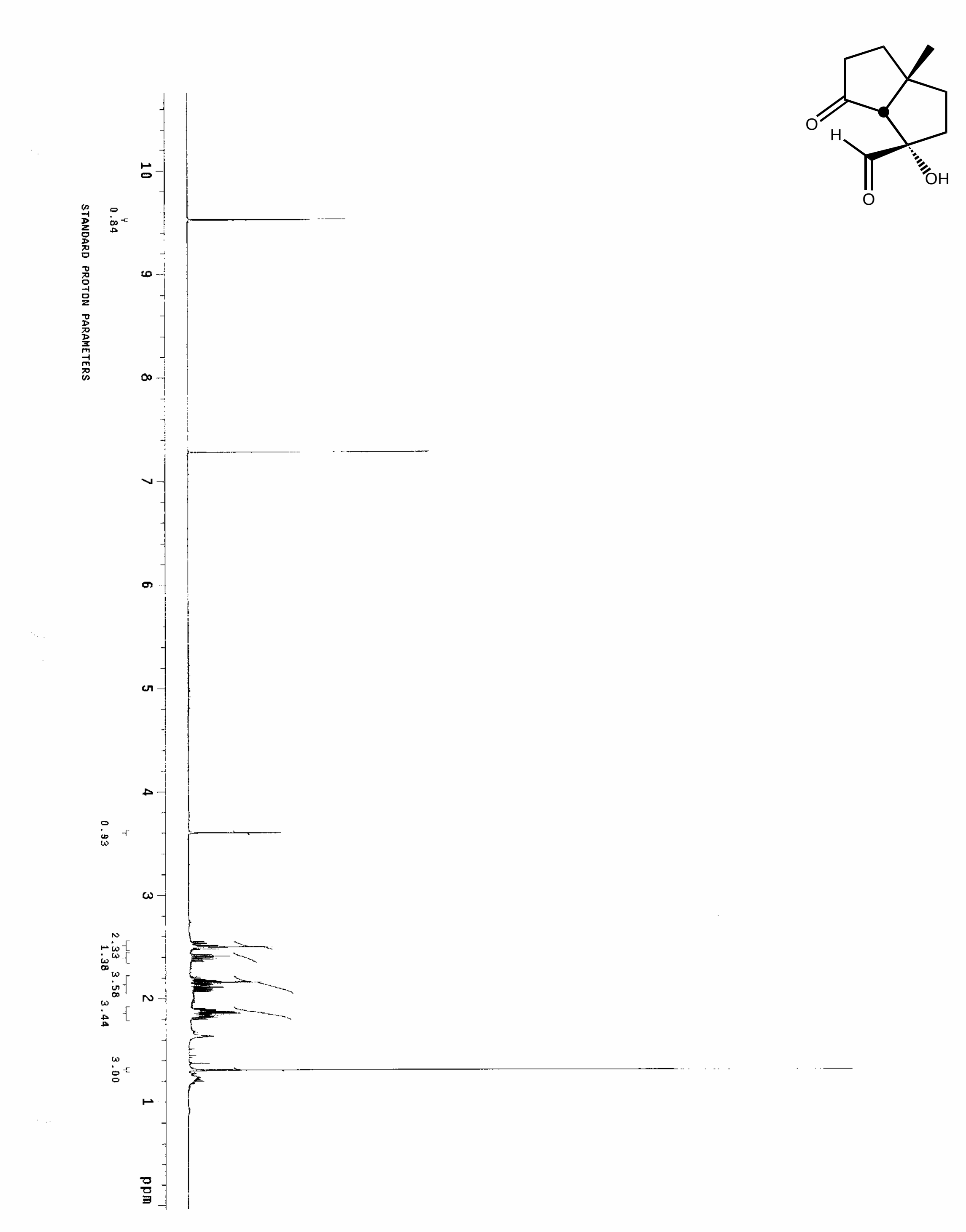
80
60
40
20
ppm
O
O
O



O
H
OH
O
10
9
8
7
6
5
4
3
2
1
ppm
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3.58
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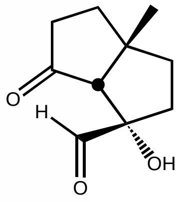
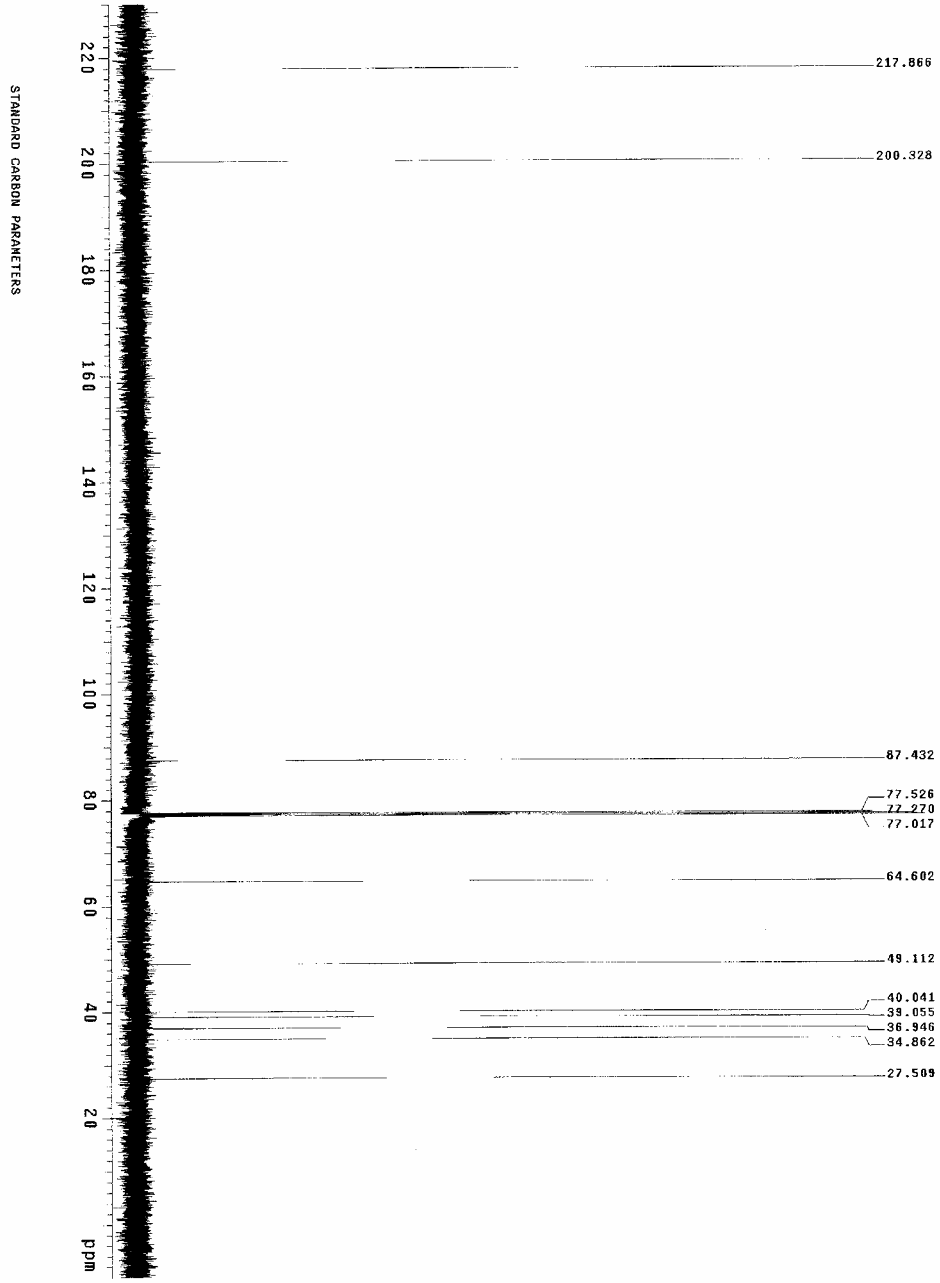
STANDARD PROTON PARAMETERS


O
H
OH
O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180
160
140
120
100
80
60
40
20
ppm
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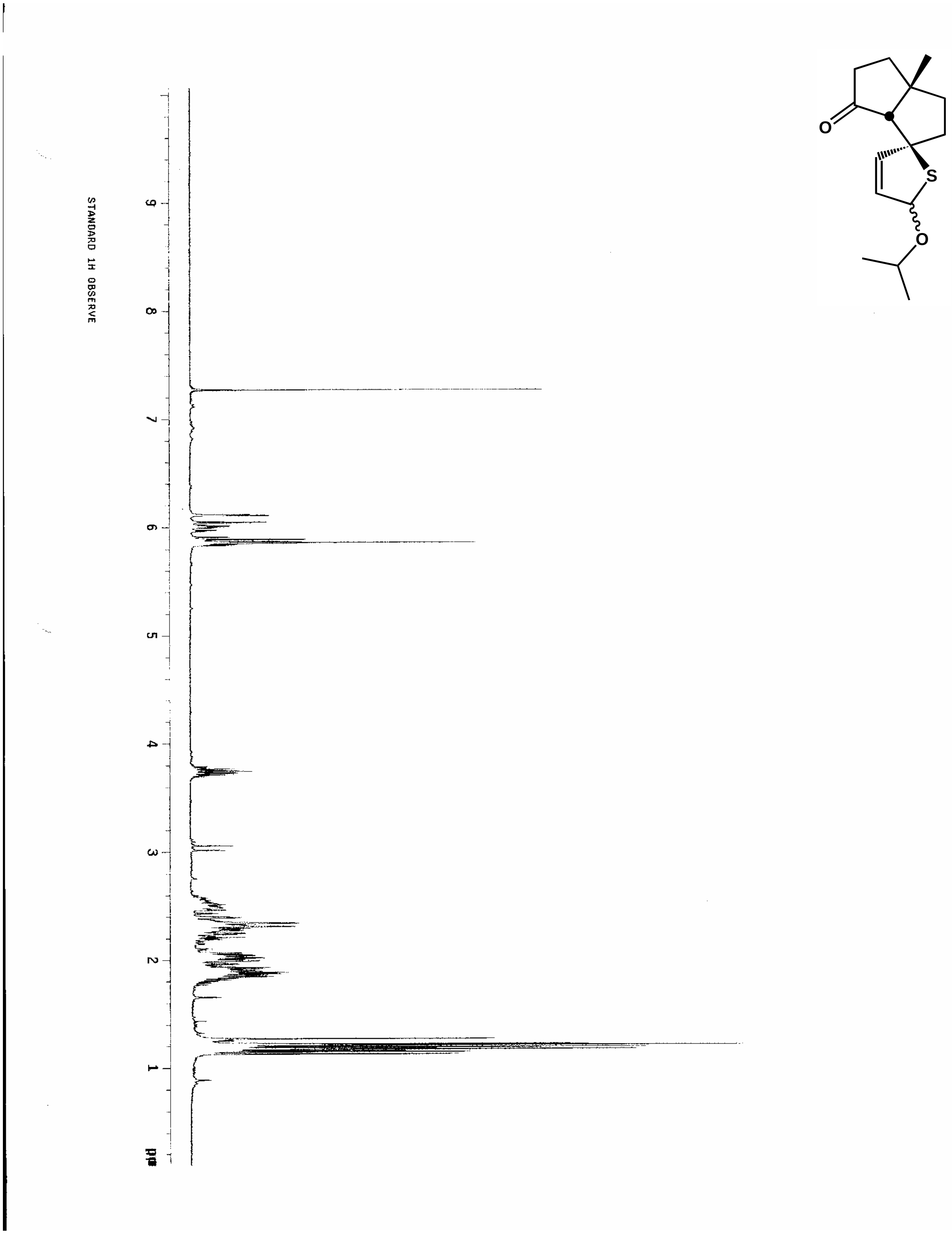
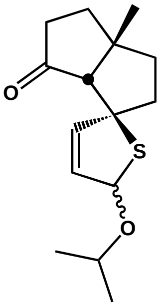
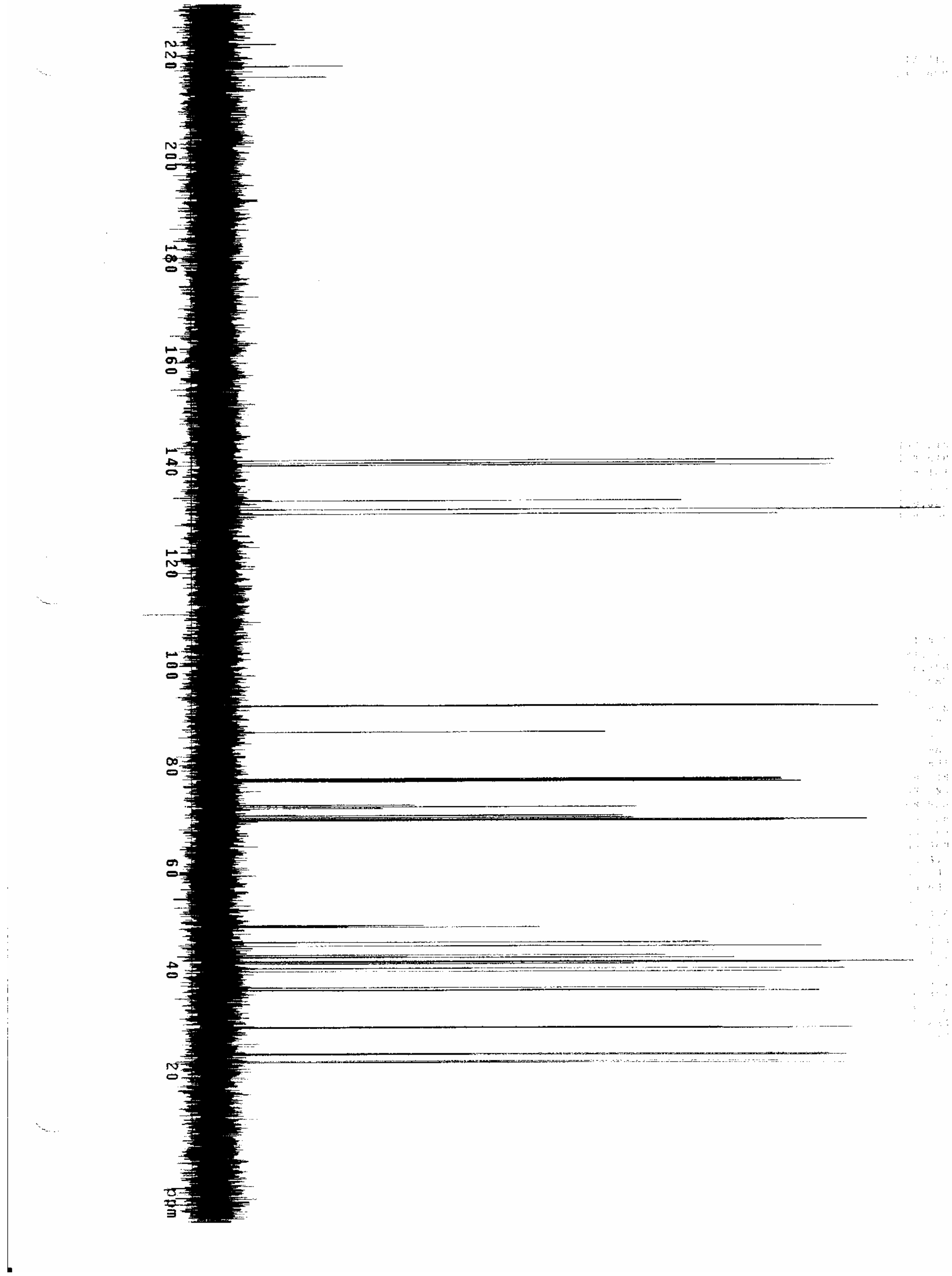
36.946
34.862
27.509


STANDARD 1H OBSERVE
9
8
7
6
5
4
3
2
1
ppm
O
S
O


O
S
O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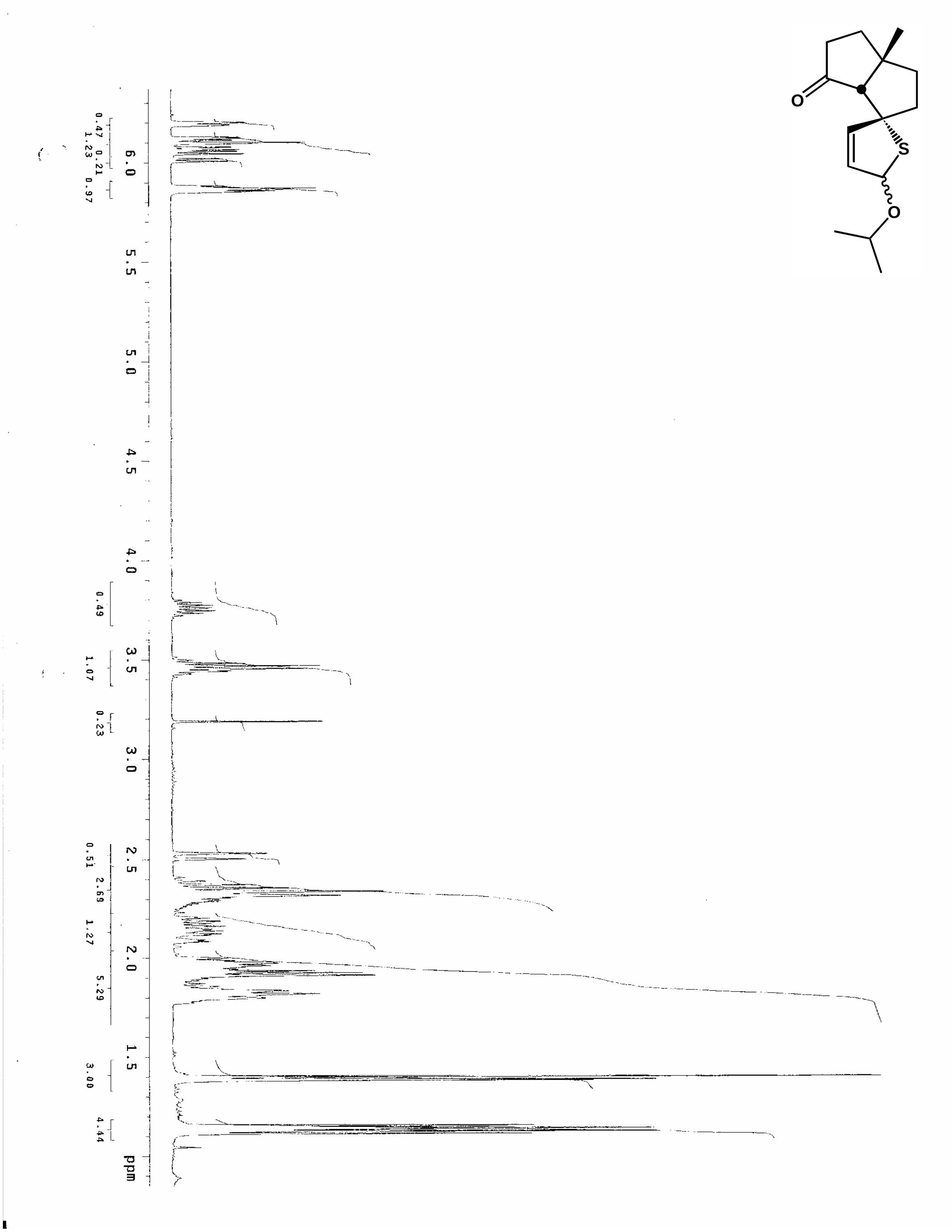
200
180
160
140
120
100
80
60
40
20
ppm


O
S
O
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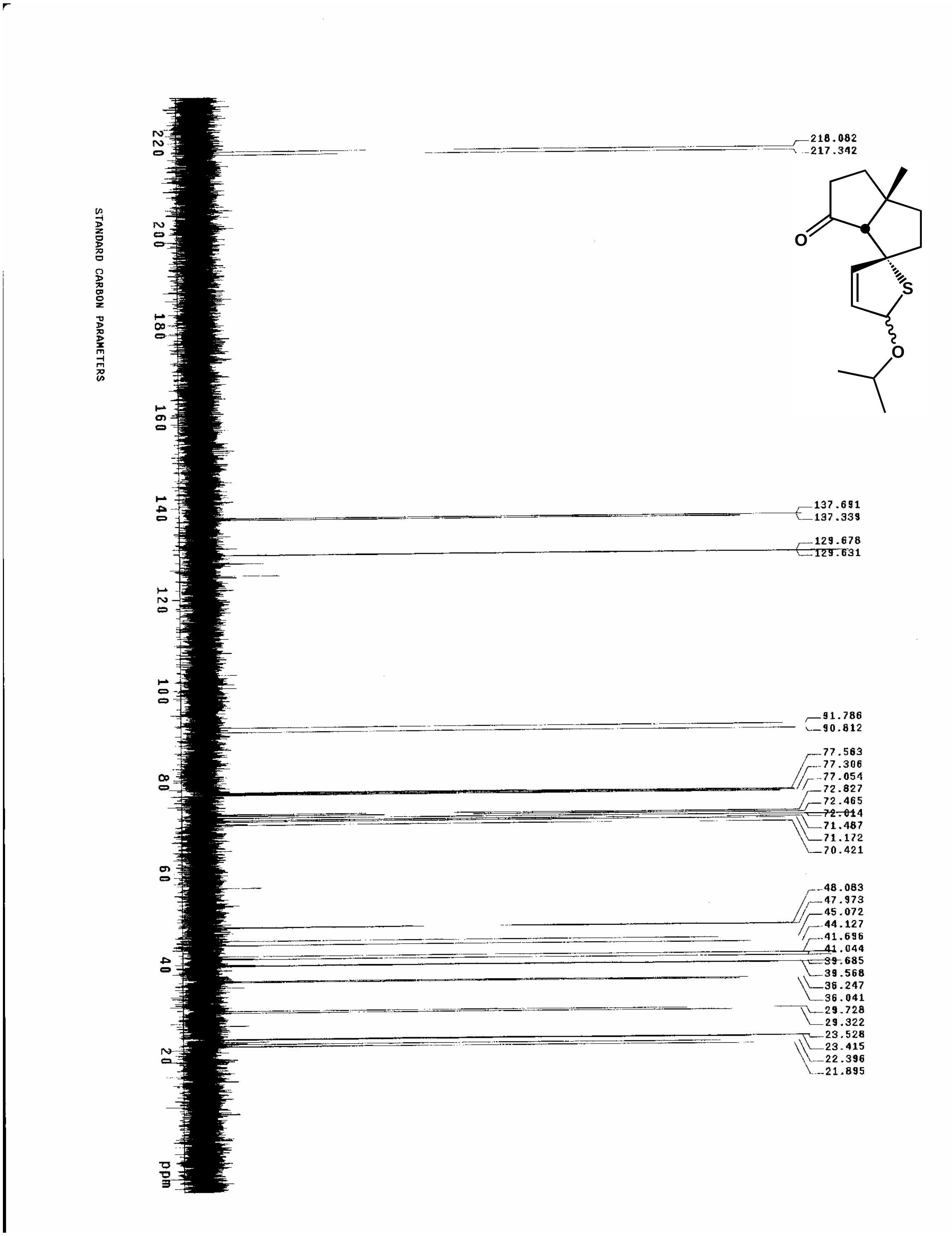
1.23
0.97
6.0
5.5
5.0
4.5
4.0
0.49
3.5
1.07
0.23
3.0
2.5
0.51
2.69
1.27
2.0
5.29
1.5
3.00
4.44
ppm


STANDARD CARBON PARAMETERS
220
200
180
160
140
120
100
80
60
40
20
ppm
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217.342
O
S
O
137.691
137.339
129.678
129.631
91.786
90.812
77.563
77.306
77.054
72.827
72.465
72.014
71.487
71.172
70.421
48.083
47.973
45.072
44.127
41.696
41.044
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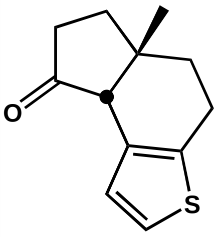
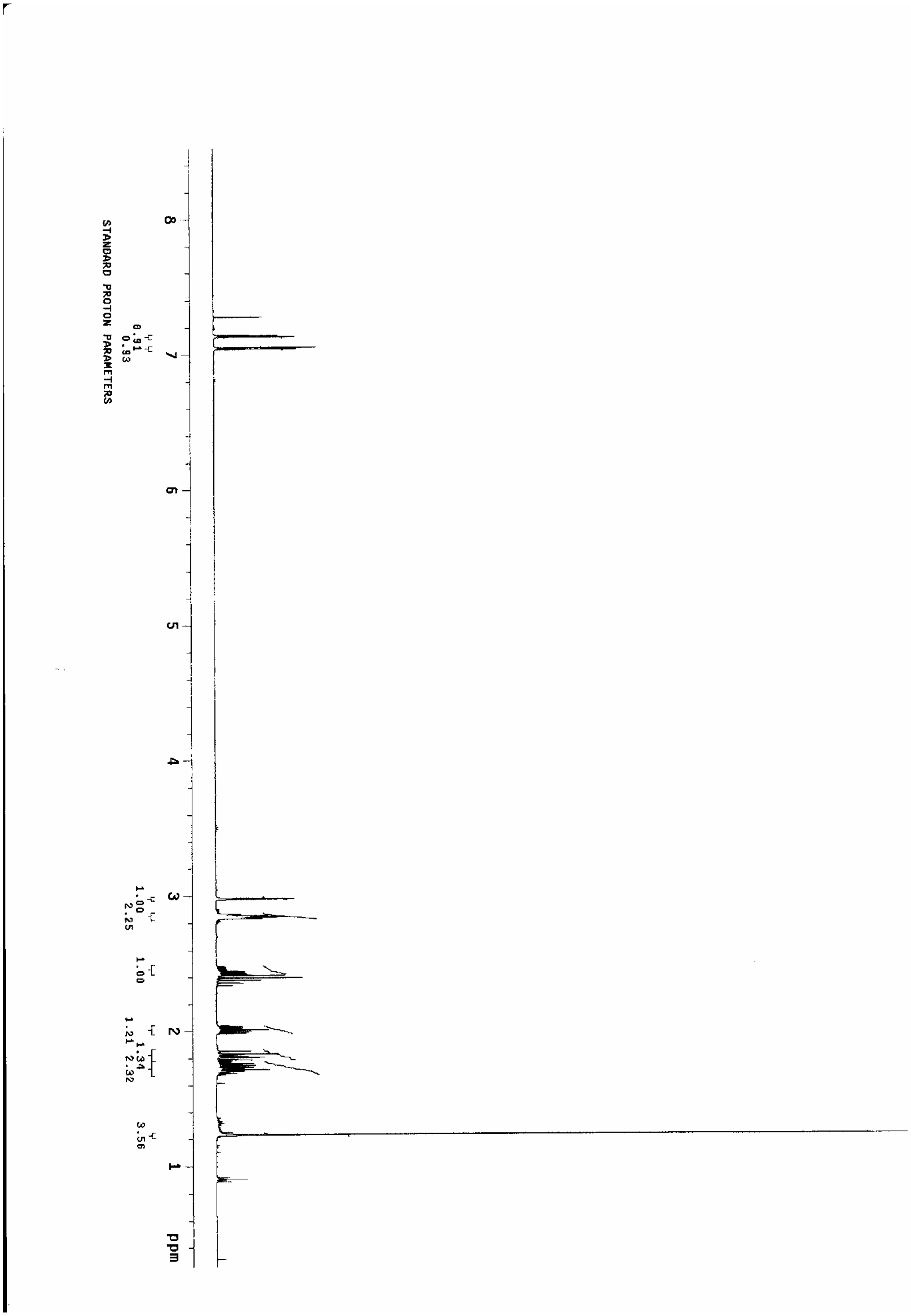
21.895


O
S


8
7
6
5
4
3
2
1
ppm
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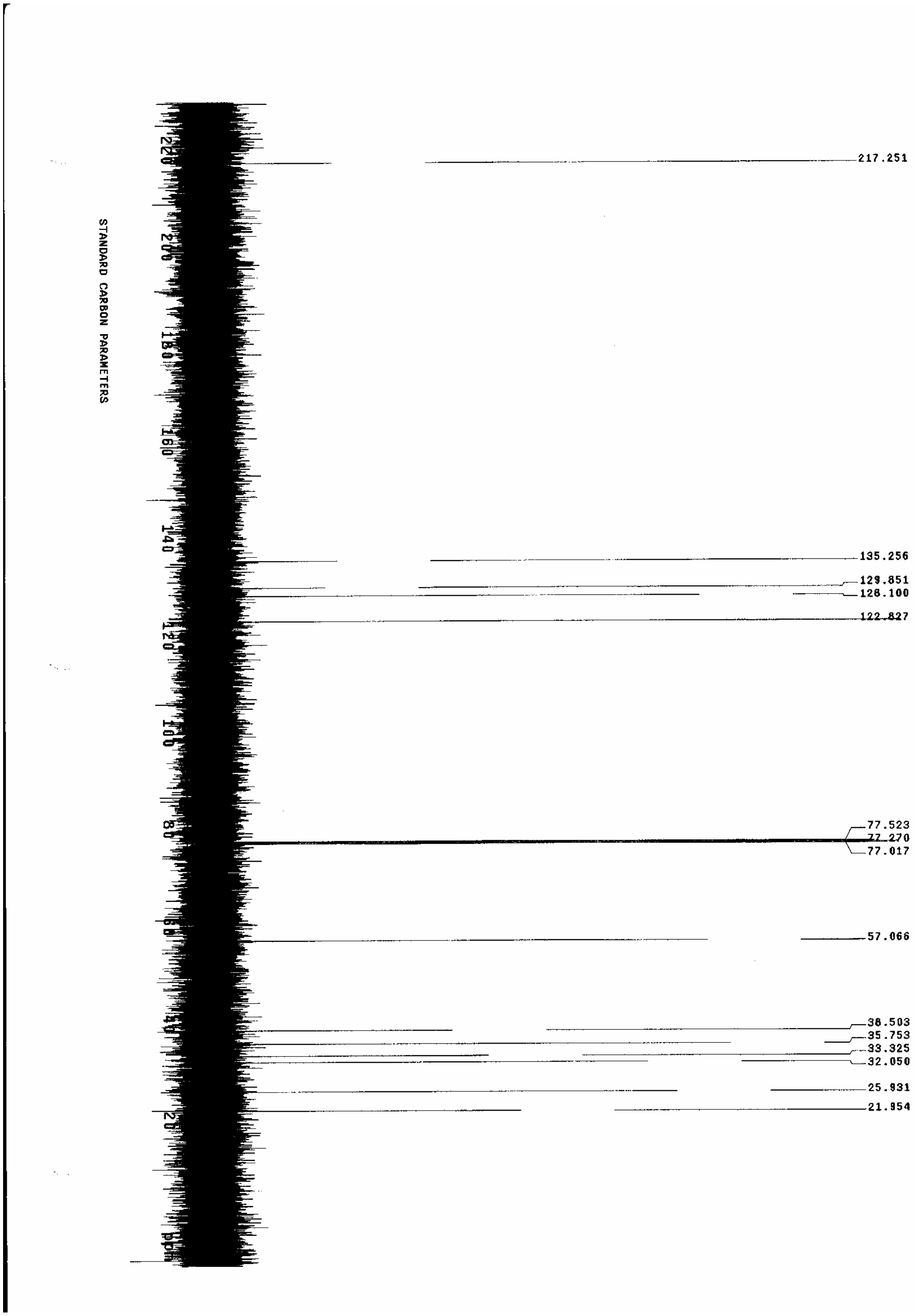
1.00
1.21
1.34
2.32
3.56
STANDARD PROTON PARAMETERS


STANDARD CARBON PARAMETERS
220
200
180
160
140
120
100
80
60
40
20
ppm
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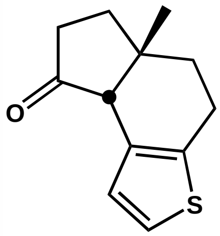
129.851
128.100
122.827
77.523
77.270
77.017
57.066
38.503
35.753
33.325
32.050
25.831
21.954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