SUPPORTING INFORMATION

A 4+3 Cycloaddition Approach to the Synthesis of Spatol. A Formal Total Synthesis of Racmic Spatol

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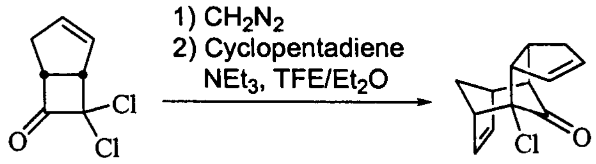
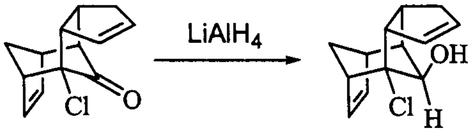
General Procedures.

Melting points were determined using a Fisher-Johns Hot Stage melting point apparatus and were uncorrected. ^1H NMR spectra were recorded on a Brüker AMX-250 or Brüker AMX-500 at 250 and 500 MHz respectively as $CDCl_3$ solutions with tetramethylsilane (0.05% by volume) as the internal reference. ^{13}C NMR spectra were obtained on the same instruments at 62.9 or 125.8 MHz with $CDCl_3$ ($\delta = 77$ ppm) as the internal reference. The NMR data for compound **12** and **13** were reported as a mixture of two C1-epimers. The major isomer was determined by peak's intensity. Elemental analyses were performed by MHW Laboratories in Phoenix, AZ.

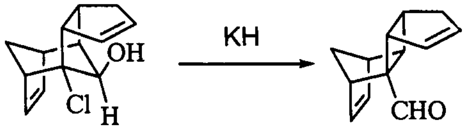
THF and diethyl ether were purchased from Aldrich chemical company and were distilled over sodium-benzophenone. Trifluoroethanol was purchased from Halocarbon Products Corp., and distilled over anhydrous $CaSO_4$. Triethylamine was purchased from Fisher Scientific Company and distilled over CaH_2. Dicyclopentadiene, Diazald®, $LiAlH_4$, KH, $NaClO_2$, resorcinol, *t*-BuOH, I_2, acetonitrile, Bu_3SnH, AIBN, benzene, $Na_2CrO_4.4H_2O$, acetic acid, acetic anhydride, 10% Pd(C), DIBAL-H, hydrazine hydrate, KOH, and PCC were purchased from Aldrich chemical company.



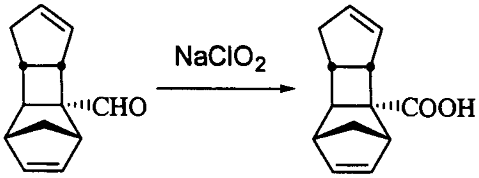
To a cool solution (0°C) of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one (10.2 g, 57.6 mmol) in Et_2O (100 mL) was added a solution of CH_2N_2, which was previously prepared by addition of Diazald® solution (15 g in 135 mL of Et_2O) to a mixture of 95% EtOH (30 mL), water (24 mL), and KOH (15 g) at 70°C. The yellow solution was stirred at 0 °C for 2 hours, concentrated under reduced pressure, and dissolved in 1:1 mixture of Et_2O and trifluoroethanol (800 mL). The solution was cooled in an IPA/dry ice bath, cyclopentadiene (50 mL, 576.10 mmol) and triethylamine (24 mL, 172.85 mmol) were added, and the reaction was stirred for 3 hours while it was allowed to warm to room temperature. The brownish solution was concentrated on rotavap until the volume decreased by half and poured into a 1-L separatory funnel with 500 mL of water. The organic phase was separated, and the aqueous layer was further extracted with Et_2O (200 mL) two times. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was then purified by flash chromatography (20:1, hexanes/EtOAc) on silica gel to yield 0.64 g (5%) of minor product and 8.77 g (69%) of major product as colorless solid. Only the major isomer was characterized: mp. 79-81 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 6.28-6.23 (m, 2H), 5.76-5.71 (m, 1H), 5.61-5.57 (m, 1H), 3.43-3.40 (m, 1H), 3.07-3.06 (m, 1H), 2.92-2.69 (m, 3H), 2.41 (d, J = 6.3 Hz, 1H), 2.33 (d, J = 11.5 Hz, 1H), 2.17-2.07 (m, 1H), 1.72 (dt, J = 3.6, 11.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 203.9, 138.6, 135.6, 133.0, 128.6, 79.2, 55.2, 55.1, 54.8, 44.2, 40.2, 39.6, 39.1; IR (Nujol) 1789, 1466, 727 cm^{-1}; Anal. Calcd for $C_{13}H_{13}ClO$: C, 70.75; H, 5.94. Found: C, 70.81; H, 6.00.



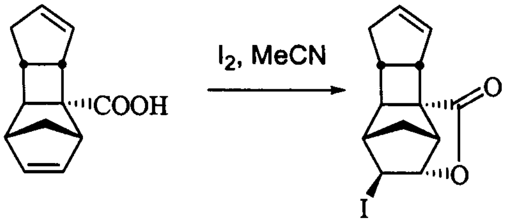
A solution of ketone (3.5 g, 15.86 mmol) in Et_2O (160 mL) was cooled in an ice-bath and $LiAlH_4$ (1.2 g, 31.71 mmol) was added portionwise with stirring. The mixture was stirred for 1 hour and the reaction was quenched by slow addition of water. The white precipitate was filtered off, and the filtrate concentrated under reduced pressure. The residue was purified by flash chromatography (10:1, hexane: EtOAc) on silica gel to afford the product as a white solid (3.4 g, 97%): mp. 63-64 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 6.60-6.54 (m, 2H), 5.90-5.85 (m, 1H), 5.78-5.73 (m, 1H), 3.63 (dd, finely split, J = 2.9, 11.8 Hz, 1H), 3.28-3.24 (m, 1H), 3.13 (d, J = 11.8 Hz, 1H), 2.87 (s, br, 1H), 2.75 (dd, finely split, J = 11.8, 18.9 Hz, 1H), 2.64 (s, br 1H), 2.58-2.49 (m, 1H), 2.29 (d, J = 10.9 Hz, 1H), 2.16 (t, J = 4.5 Hz, 1H), 2.10-1.98 (m, 1H), 1.70 (dt, J = 3.6, 7.1 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 141.6, 138.3, 134.8, 130.9, 77.9, 75.9, 59.1, 52.9, 47.0, 43.8, 42.3, 41.0, 40.6; IR ($CHCl_3$) 3375, 2930, 2859, 1462, 1083 cm^{-1}; Anal. Calcd for $C_{13}H_{15}ClO$: C, 70.11; H, 6.79. Found: C, 70.33; H, 6.88.



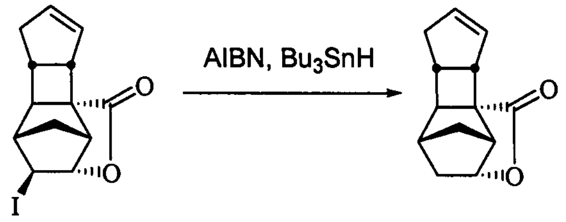
To a 250 mL round-bottomed flask was placed 30% KH in mineral oil (4.0 g, 29.86 mmol). After the mineral oil was removed by washing with dry THF, 290 mL of freshly distilled THF was added and the suspension was cooled to 0°C. A solution of chloro-alcohol (1.33 g, 5.97 mmol) in THF (10 mL) was added slowly. The mixture was allowed to warm to room temperature and stirred for 3 hours. The reaction was quenched by slow addition of water (100 mL). The organic layer was separated, and the aqueous phase was extracted with Et_2O (100 mL x 2). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude product was purified by flash chromatography on silica gel (10:1, hexane: EtOAc) to afford the product as colorless oil (1.04 g, 94%). Since this compound was unstable, only NMR data were obtained: ^1H NMR (250 MHz, $CDCl_3$) δ 9.51 (s, 1H), 6.05 (dd, J = 3.2, 5.7 Hz, 1H), 5.95 (dd, J = 2.9, 5.7, 1H), 5.86-5.81 (m, 1H), 5.70-5.65 (m, 1H), 3.12-3.07 (m, 1H), 3.00-2.97 (m, 1H), 2.85-2.82 (m, 1H), 2.71 (dd, finely split, J = 9.5, 17.5 Hz, 1H), 2.38-2.20 (m 2H), 2.06-2.03 (m, 1H), 1.96 (d, J = 9.2 Hz, 1H), 1.45 (dd, finely split, J = 1.6, 9.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 205.2, 135.9, 134.5, 133.3, 128.7, 65.9, 49.7, 46.8, 45.4, 45.3, 42.8, 39.9, 35.5.



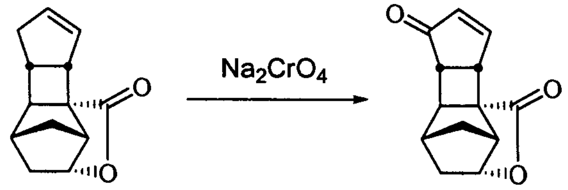
To a solution of aldehyde (1.00 g, 5.37 mmol) in *t*-butanol (13 mL) was added pH 3.98 acetate buffer (10 mL), resorcinol (0.77 g, 6.98 mmol), and a solution of $NaClO_2$ (0.61 g, 6.71 mmol) in water (2 mL). The mixture was stirred at room temperature for 90 minutes then poured into a separatory funnel. The mixture was extracted with Et_2O, and the organic phase washed with water and brine, dried over $MgSO_4$, filtered, and evaporated. Crude product was purified by flash chromatography on silica gel (4:1, hexanes: EtOAc) to give the product as a white solid (0.96 g, 88%): mp. 138-139 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 11.34 (s, br, 1H), 6.13 (dd, J = 3.0, 5.7 Hz, 1H), 5.97 (dd, J = 2.8, 5.7 Hz, 1H), 5.91-5.87 (m, 1H), 5.66-5.60 (m, 1H), 3.10-3.04 (m, 1H), 2.98 (d, J = 1.3 Hz, 1H), 2.82-2.79 (m, 1H), 2.67 (dd, finely split, J = 9.5, 17.2 Hz, 1H), 2.33 (ddq, J = 2.3, 3.2, 17.2 Hz, 1H), 2.14 (ddt, J = 2.6, 6.9, 9.6 Hz, 1H), 1.95-1.92 (m, 2H), 1.43 (dd, finely split, J = 1.6, 9.4, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 180.0, 137.0, 134.3, 133.8, 128.6, 59.4, 49.9, 46.9, 46.8, 45.3, 42.8, 40.3, 34.9; IR (Nujol) 3289, 1695, 1453, 1313, 1250 cm^{-1}; Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.19; H, 6.98.



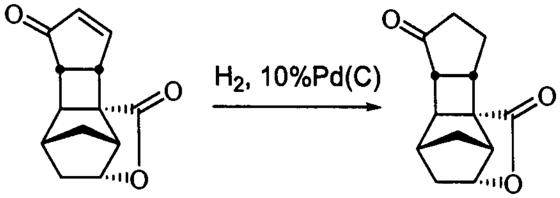
A solution of carboxylic acid (0.81 g, 4.00 mmol) in acetonitrile (20 mL) was mechanically stirred at 0°C and iodine (3.05 g, 12.01 mmol) was added in one portion. The reaction was protected from light, stirred at 0°C for 24 hours, then a saturated solution of $NaHCO_3$ in water was added. The layers were separated and the aqueous phase was extracted with Et_2O (25 mL x 3). The combined organic phases were washed with a saturated solution of $Na_2S_2O_3$ in water (50 mL), dried over $MgSO_4$, filtered, and evaporated. Crude product was purified by flash chromatography on silica gel (10:1, hexanes: EtOAc) to give the product as a white solid (0.98 g, 75%): mp. 127-129 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.15-6.10 (m, 1H), 5.90-5.85 (m, 1H), 4.94 (d, J = 5.0 Hz, 1H), 3.65 (s, 1H), 3.16-3.10 (m, 1H), 2.69 (s, 1H), 2.67-2.58 (m, 1H), 2.55-2.47 (m, 1H), 2.43-2.40 (m, 3H), 2.30 (dd, finely split, J = 2.3, 16.7 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 175.2, 131.1, 129.4, 85.7, 55.1, 49.9, 49.5, 48.9, 46.2, 40.1, 35.8, 33.1, 28.4; IR (Nujol) 1777, 1469, 1373, 989 cm^{-1}; Anal. Calcd for $C_{13}H_{13}IO_2$: C, 47.58; H, 3.99. Found: C, 47.65; H, 4.17.



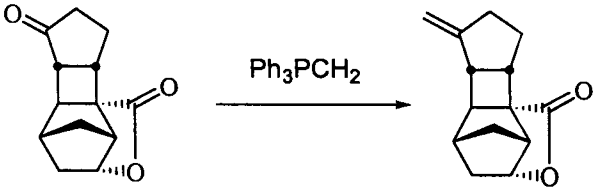
To a solution of iodolactone (0.7 g, 2.13 mmol) in benzene (21 mL) was added *n*-Bu_3SnH (0.7 mL, 2.60 mmol) and AIBN (0.04 g, 0.21 mmol). The mixture was heated under reflux for 3 hours, and the volatile compounds were removed by rotary evaporator. The crude product was purified by flash chromatography on silica gel (4:1, hexanes: EtOAc) to give the product as a white solid (0.38 g, 88%): mp. 77-78 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.19-6.14 (m, 1H), 5.89-5.85 (m, 1H), 4.58 (dd, J = 5.0, 8.1, 1H), 3.14-3.07 (m, 2H), 2.63 (ddq, J = 2.0, 8.5, 16.9, 1H), 2.48-2.31 (m, 3H), 2.28-2.19 (m, 2H), 1.77-1.61 (m, 2H), 1.30 (dd, J = 3.4, 14.0, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 177.4, 131.0, 130.0, 77.2, 56.0, 51.9, 49.0, 46.6, 40.2, 39.1, 36.4, 35.5, 33.7; IR (Nujol) 1777, 1469, 1343, 1050 cm^{-1}; Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.19; H, 6.98.



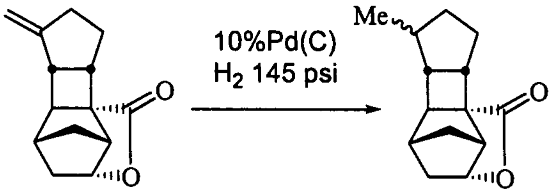
To a 50 mL round-bottomed flask was added alkene (0.2 g, 0.99 mmol), acetic acid (6 mL), acetic anhydride (3 mL), and Na_2CrO_4 (0.53 g, 2.97 mmol). The mixture was stirred at 60 °C for 6 hours, and then diluted with water and EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Crude product was purified by flash chromatography on silica gel (1:1, hexanes: EtOAc) to afford the product as a colorless crystal (0.11 g, 55%): mp. 143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, J = 3.0, 5.5 Hz, 1H), 6.46 (d, J = 5.6 Hz, 1H), 4.71 (dd, J = 5.0, 8.0 Hz, 1H), 3.27-3.25 (m, 2H), 2.62-2.59 (m, 2H), 2.52-2.51 (m, 1H), 2.13 (d, J = 11.9 Hz, 1H), 1.91-1.76 (m, 2H), 1.39 (dd, J = 3.2, 14.3 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 208.7, 176.0, 163.8, 136.5, 78.0, 50.5, 50.4, 49.3, 43.6, 41.2, 39.3, 36.5, 33.2; IR ($CHCl_3$) 3022, 2970, 1767, 1737, 1350, 1219, 1104, 1065, 997 cm^{-1}; Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.08; H, 5.58



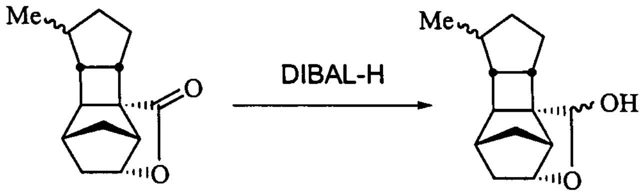
To a solution of enone (0.15 g, 0.69 mmol) in EtOAc (3 mL) was added 10% Pd on carbon (0.01 g) and the reaction flask was capped with a rubber septum. The mixture was stirred under H_2-atmosphere (balloon) for 5 hours, filtered, and concentrated under reduced pressure. Crude product was purified by flash chromatography on silica gel (1:1, hexanes: EtOAc) to give the product as a white solid (0.145 g, 97%): mp. 102-104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.62 (dd, J = 5.0, 8.1 Hz, 1H), 3.10-3.03 (m, 2H), 2.96-2.82 (m, 1H), 2.73 (t, J = 7.7 Hz, 1H), 2.48 (d, 2.2 Hz, 1H), 2.40-2.26 (m, 3H), 2.08-2.03 (m, 1H), 2.01-1.86 (m, 1H), 1.81-1.71 (m, 2H), 1.40 (dd, J = 3.3, 14.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 219.3, 176.6, 77.0, 50.5, 50.0, 45.4, 45.3, 39.2, 37.1, 36.8, 35.6, 33.2, 21.7; IR (Nujol) 1761, 1731, 1449, 1374, 1344 cm^{-1}; Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.70; H, 6.63.



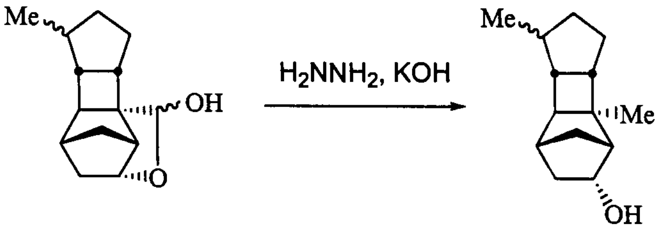
A suspension of triphenymethylphosphonium iodide (1.48 g, 3.66 mmol) in THF (16 mL) was cooled in an ice-bath for 5 minutes, and then a 2.5 M solution of BuLi in hexane (1.1 mL, 2.75 mmol) was added dropwise and the mixture was stirred for 20 minutes. A solution of ketone (0.4 g, 1.83 mmol) in THF (2 mL) was added via a syringe and the mixture was stirred at room temperature for 3 hours. The reaction was quenched by addition of methanol. Volatile compounds were removed under reduced pressure. Crude product was purified by flash chromatography on silica gel (4:1, hexane: EtOAc) to afford the product as colorless oil (0.30 g, 77%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.80 (s, 1H), 4.71 (s, 1H), 4.56 (dd, J = 5.0, 8.0 Hz, 1H), 3.01 (d, J = 5.0 Hz, 1H), 2.88-2.70, (m, 2H), 2.59-2.55 (m, 2H), 2.47-2.31 (m, 2H), 2.23 (s, 1H), 2.17-2.12 (m, 1H), 1.75-1.64 (m, 2H), 1.62-1.43 (m, 1H), 1.35 (dd, J = 3.3, 14.3 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 177.1, 155.3, 105.0, 76.9, 54.4, 50.0, 44.7, 44.3, 39.7, 39.1, 36.7, 33.4, 33.3, 26.2; IR ($CHCl_3$) 3021, 2963, 2915, 1766, 1350, 1012 cm^{-1}; Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.65; H, 7.65.



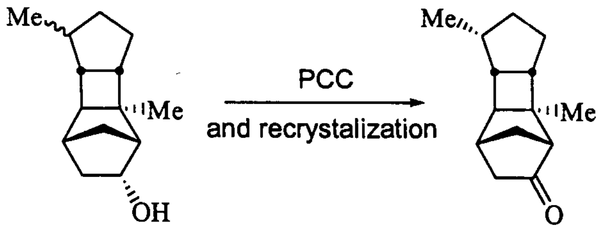
To a solution of alkene (0.05 g, 0.23 mmol) in ethyl acetate (2 mL) was added 10% Pd on C (10 %wt) and the reaction vessel was connected to a medium pressure hydrogenation manifold. The system was flushed with hydrogen gas for a few minutes and pressurized to 145 psi. The mixture was megnetically stirred under H_2-atmosphere for 6 hours, filtered, and concentrated under reduced pressure. The ratio of two epimers was determined by integration of the $-CH_3$ signals (0.94 and 0.77 ppm). Crude product was purified by flash chromatography on silica gel (1:1, hexanes: EtOAc) to give the product as a white solid (0.05 g, 99%): mp. 76-80 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.55-4.48 (m, 1H), 2.97-2.95 (m, 1H), 2.74-2.61 (m, 1H), 2.47-2.41 (m, 1H), 2.28-2.26 (m, 1H), 2.20-2.03 (m, 3H), 1.93-1.26 (m, 7H), 0.94 (major) and 0.77 (minor) (d, J = 6.45 (major) and 7.16 (minor) Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 177.2, 177.1, 76.8, 53.3, 49.8, 46.7, 46.6, 43.7, 43.4, 39.7, 39.4, 39.2, 39.12, 39.07, 37.2, 36.7, 36.6, 33.8, 33.5, 33.4, 33.1, 26.5, 23.5, 20.1, 12.8; IR (CH_2Cl_2) 3057, 2959, 2872, 1761, 1260 cm^{-1}; Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.91; H, 8.38.



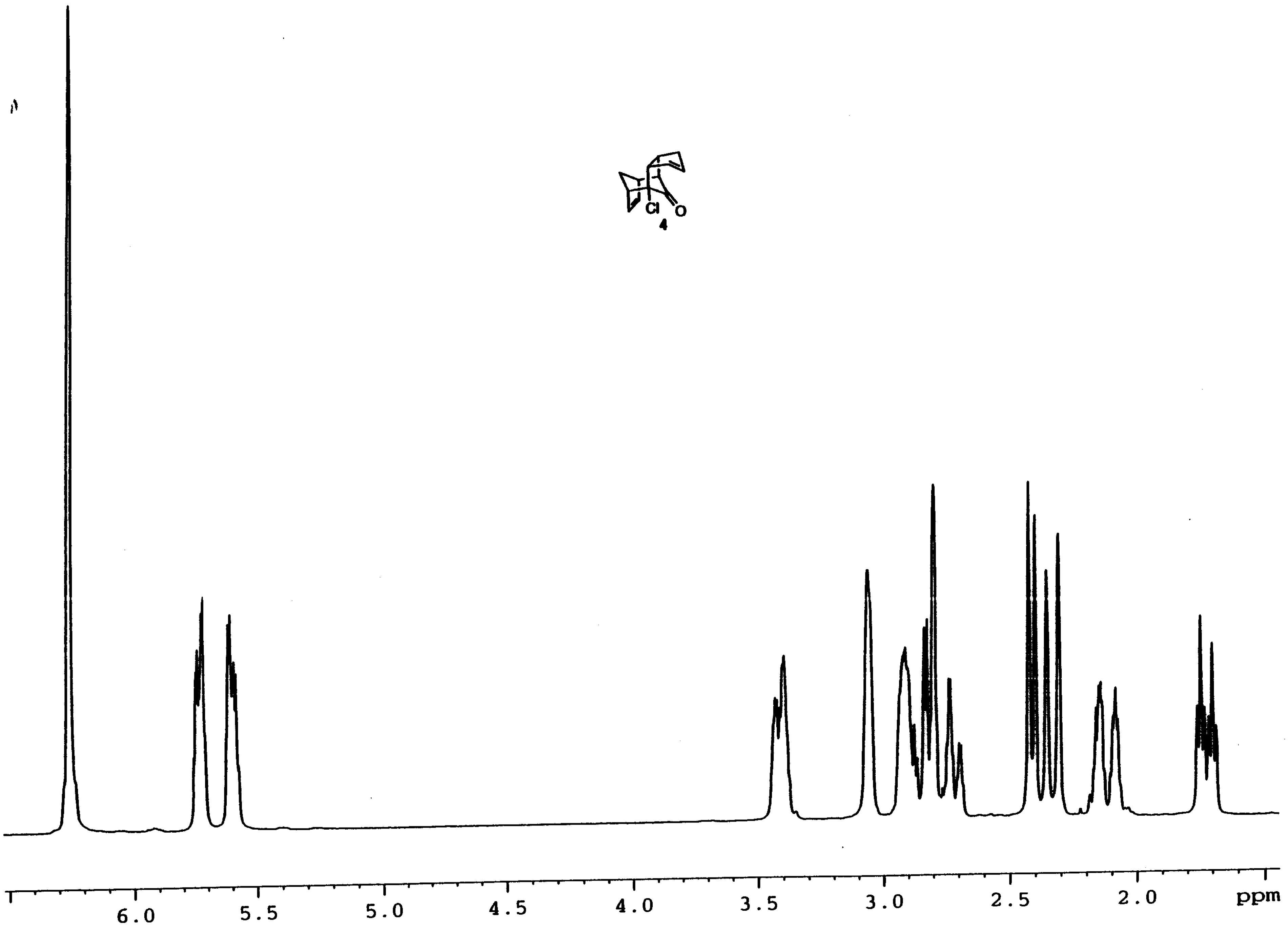
A solution of lactone (0.31 g, 1.40 mmol) in toluene (14 mL) was cooled to –78 °C, and a 1M solution of DIBAL-H in toluene (1.4 mL, 1.42 mmol) was slowly added. The mixture was stirred for 1 hour, and the reaction was quenched with water and extracted with Et_2O. The organic phase was dried over $MgSO_4$, filtered, and concentrated. Crude product was purified by flash chromatography on silica gel (2:1, hexanes: EtOAc) to give two inseparable diastereomeric products as a white solid (0.296 g, 96%): mp. 110-115 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.21 (minor) and 5.15 (major) (d, J = 7.0 (minor) and 4.4 (major) Hz, 1H), 4.38-4.32 (m, 1H), 3.29-3.26 (m, 1H), 2.68 (d, J = 5.1 Hz, 1H), 2.51-2.42 (m, 1H), 2.07-1.26 (m, 11H), 1.11 (major) and 1.02 (minor) (dd, J = 3.2, 13.0 (major) and 3.3, 10.5 (minor) Hz, 1H), 0.95 (major) and 0.78 (minor) (d, J = 6.4 (major) and 7.0 (minor) Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 98.8, 98.4, 78.2, 52.0, 49.2, 46.1, 46.0, 43.2, 42.4, 39.8, 39.6, 39.5, 38.9, 37.6, 37.5, 33.9, 33.0, 32.8, 28.4, 25.6, 20.1, 13.1; IR ($CHCl_3$) 3409, 2955, 2938, 2669, 1219, 1108, 972 cm^{-1}; Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.48; H, 9.37.



To a solution of lactol (0.24 g, 1.10 mmol) in diethylene glycol (22 mL) was added hydrazine hydrate (83 mg, 1.65 mmol), and KOH (0.56 g, 9.90 mmol). The mixture was heated in a silicon oil bath at 200°C for 2 hours, allowed to cool to room temperature, diluted with water (25 mL), and extracted with ether (20 mL x 3). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude product was purified by flash chromatography on silica gel (4:1, hexane: EtOAc) to afford the product as colorless crystals (0.18 g, 82%): mp. 106-110°C; ^1H NMR (250 MHz, $CDCl_3$) δ 4.32-4.25 (m, 1H), 2.15-1.32 (m, 14H), 1.26 (minor) and 1.23 (major) (s, 3H), 0.94 (major) and 0.79 (minor) (d, J = 6.2 (major) and 6.9 (minor) Hz, 3H), 0.79-0.73 (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 76.23, 76.16, 53.1, 50.0, 48.7, 46.13, 46.07, 45.5, 45.1, 41.2, 41.1, 40.9, 40.7, 39.0, 36.3, 35.7, 35.3, 35.1, 34.9, 33.2, 33.1, 28.1, 25.4, 21.5, 16.9, 15.8, 14.0; IR (Nujol) 3276, 1467, 1373 cm^{-1}; Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.35; H, 10.66.



To a solution of alcohol (0.1 g, 0.49 mmol) in CH_2Cl_2 (5 mL) was added PCC (0.24 g, 0.98 mmol) and stirred at room temperature for 18 hours. The reaction was diluted with Et_2O (20 mL) and filtered through a plug of Celite. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel. The product was obtained as a white solid (94 mg, 94%). The mixture of two epimers was dissolved in a minimum amount of pentane and cooled in an IPA/dry ice bath. The resulting crystals were separated from the solution by cold filtration. The product was obtained as colorless crystals (62 mg, 62%): mp. 52-54 °C (lit. 53-55°C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (dd, J = 4.1, 10.9 Hz, 1H), 2.29 (s, 1H), 2.19 (t, J = 7.3 Hz, 1H), 2.13 (s, 1H), 2.03 (dt, J = 4.5 12.0 Hz, 2H), 1.93-1.87 (m, 1H), 1.82-1.77 (m, 1H), 1.74-1.59 (m, 4H), 1.57-1.49 (m, 1H), 1.38-1.33 (m, 1H), 0.99 (d, J = 6.6 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 216.3, 59.1, 45.1, 43.2, 42.9, 42.4, 39.1, 39.0, 36.7, 35.1, 33.0, 28.3, 16.3, 13.8; IR (CH_2Cl_2) 2981, 2871, 1747, 1451, 1390, 1127 cm^{-1}; Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.40; H, 9.95.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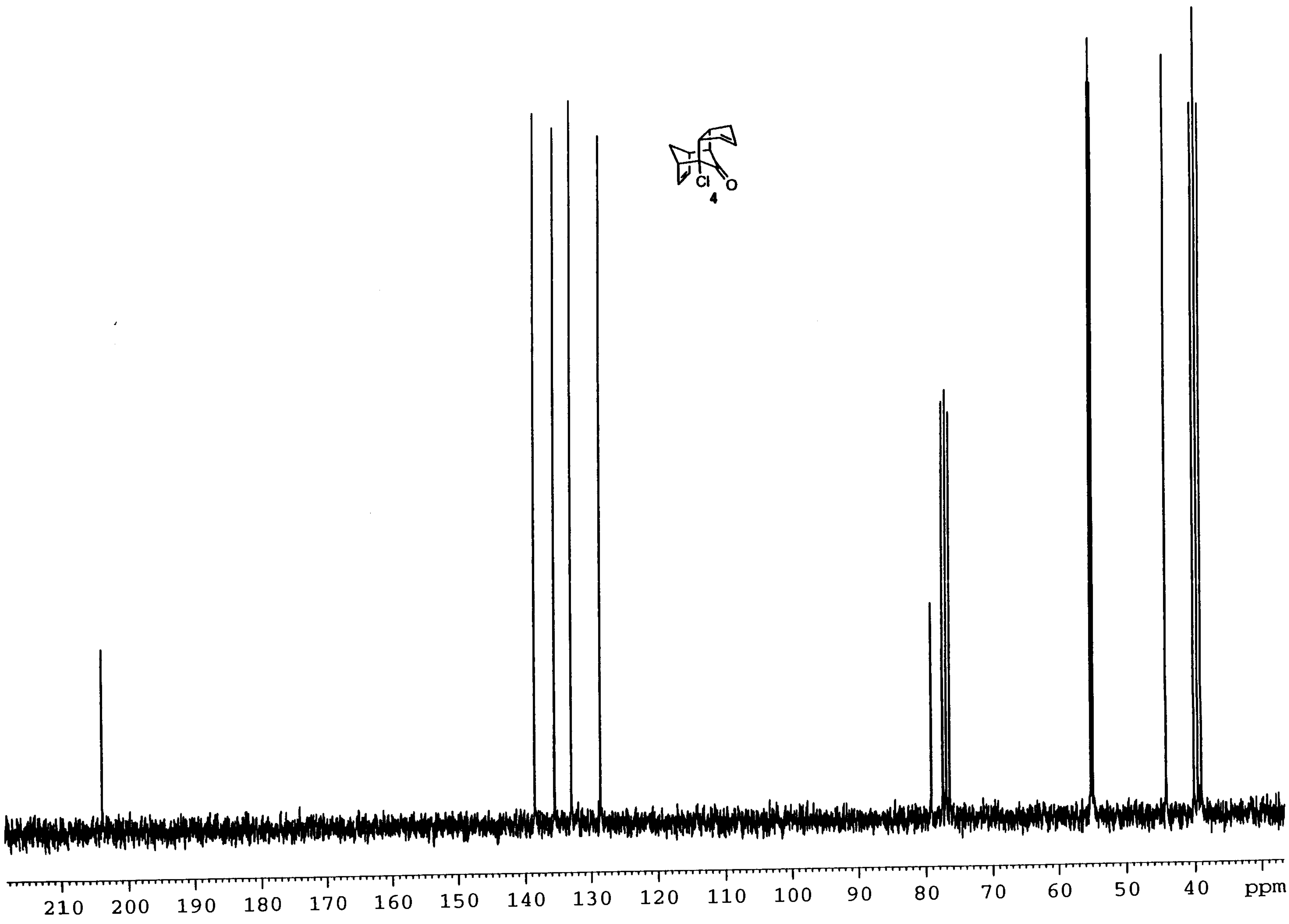

4

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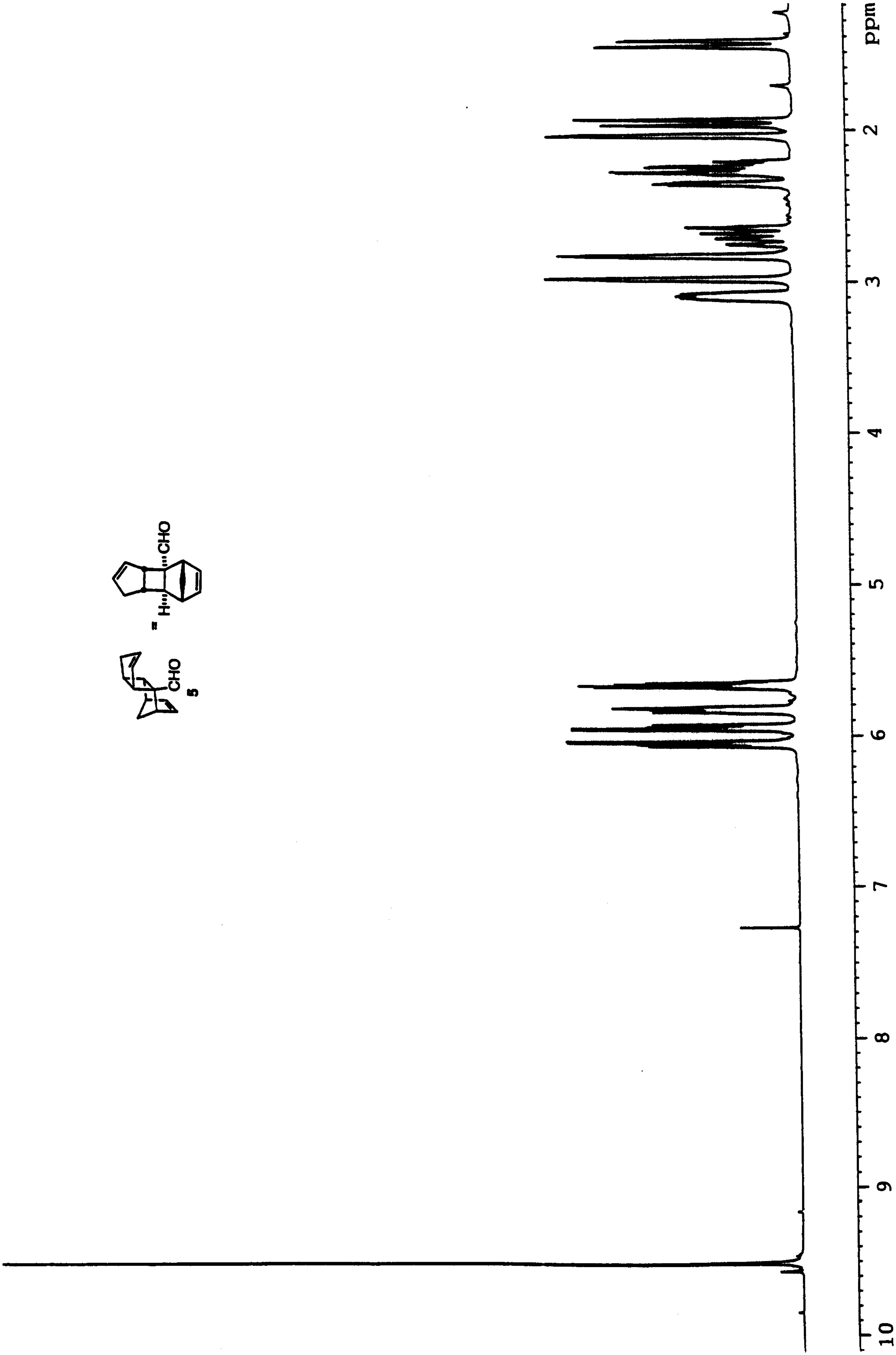
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8
9
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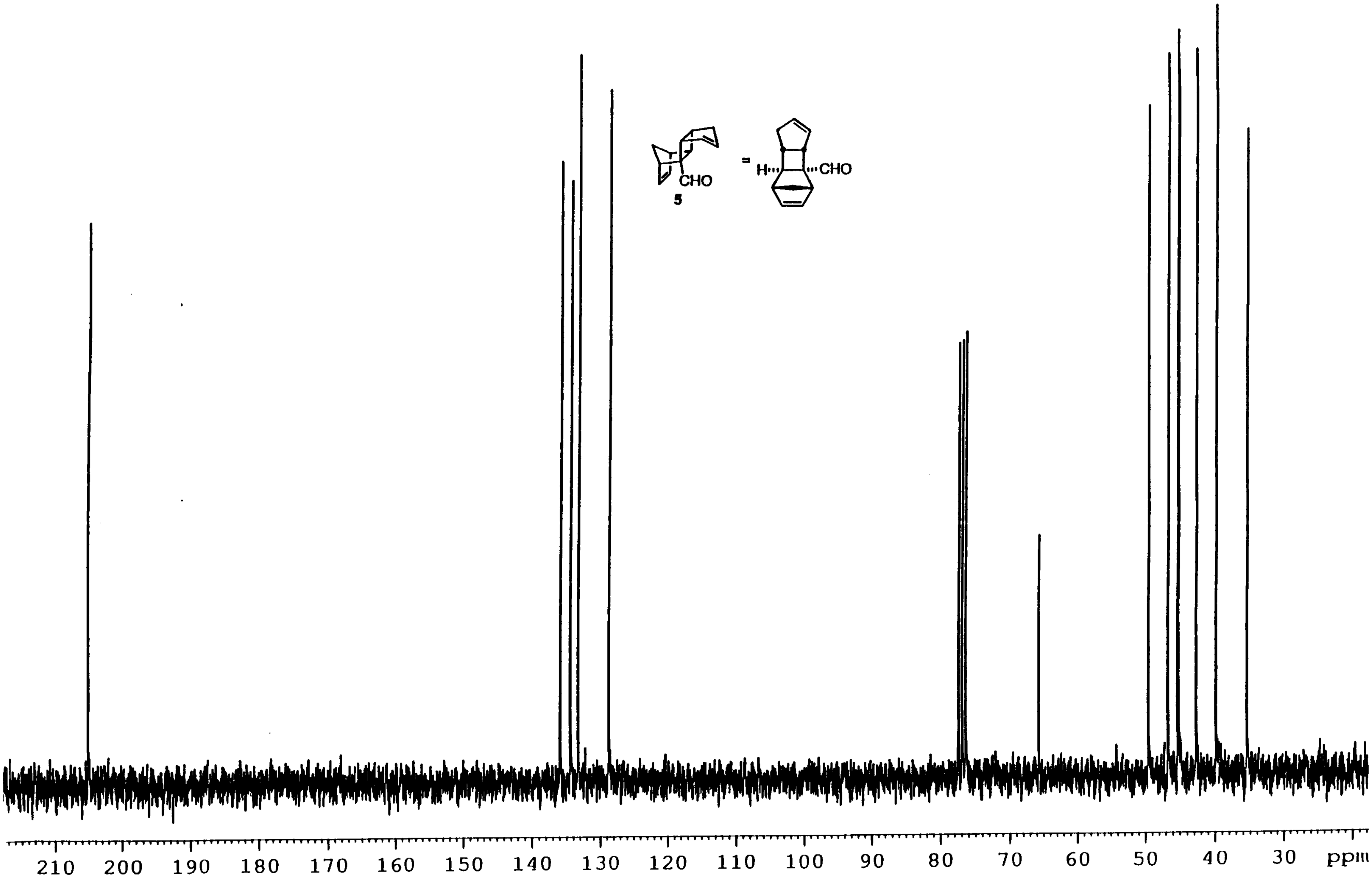
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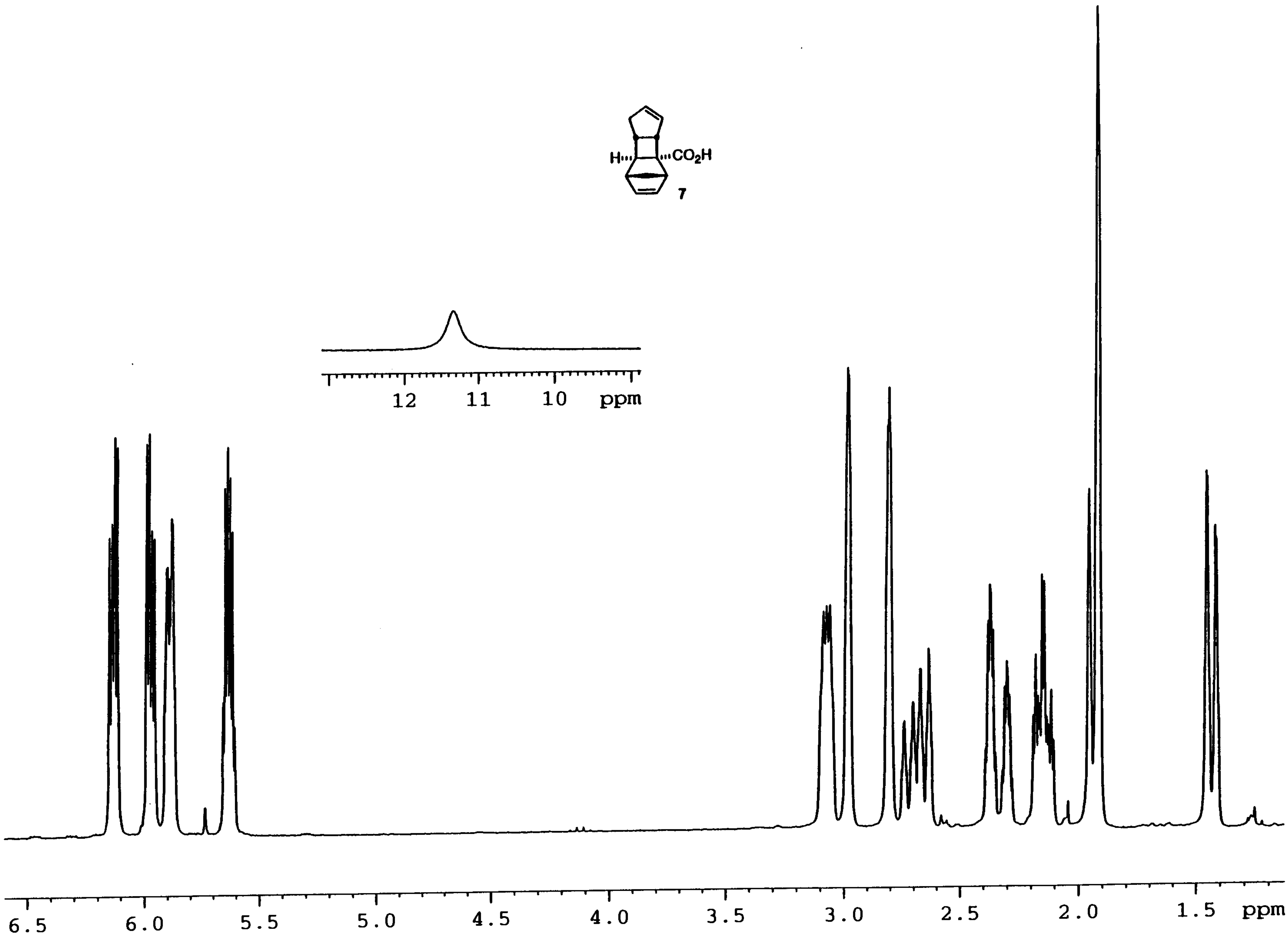
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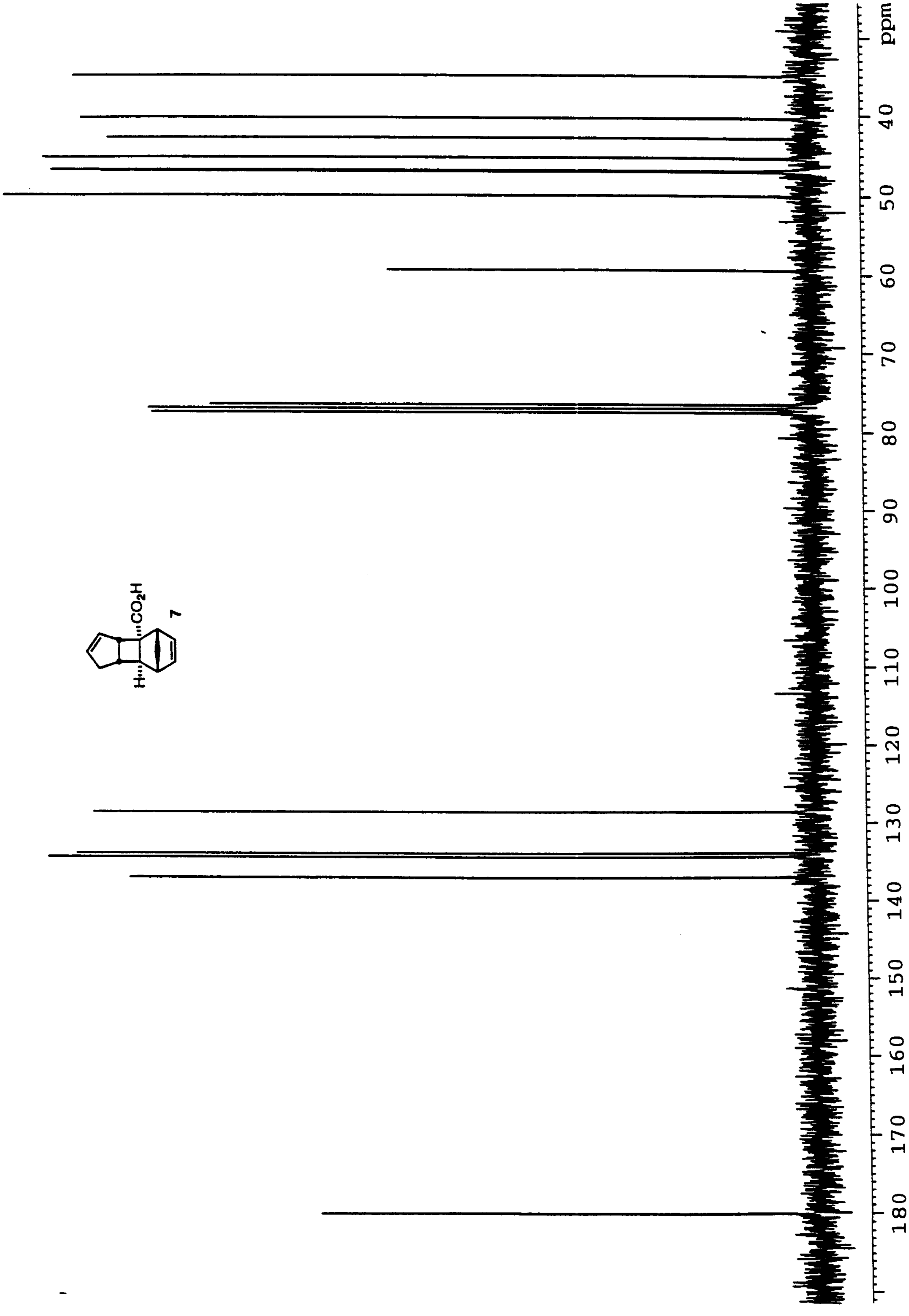

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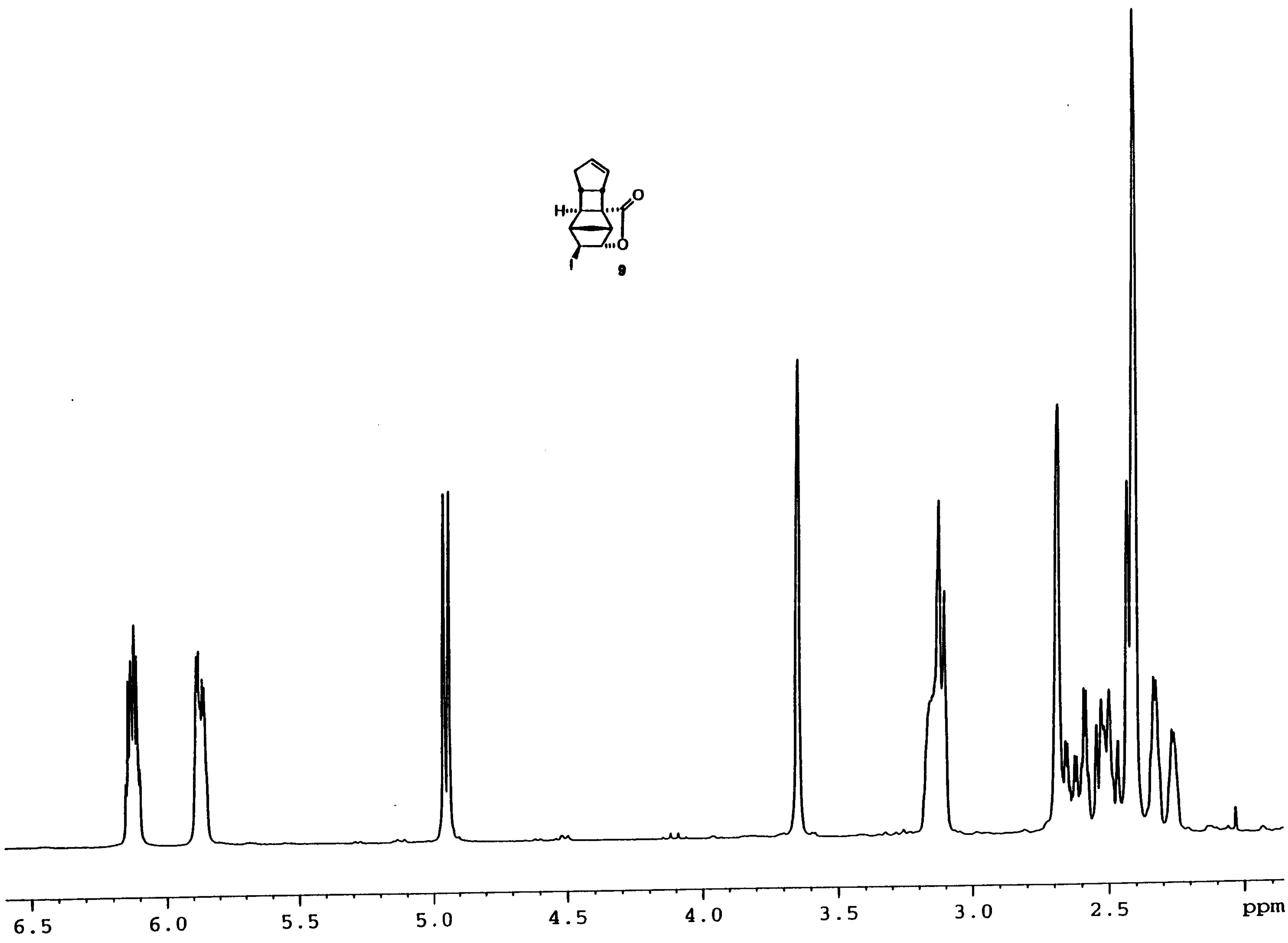
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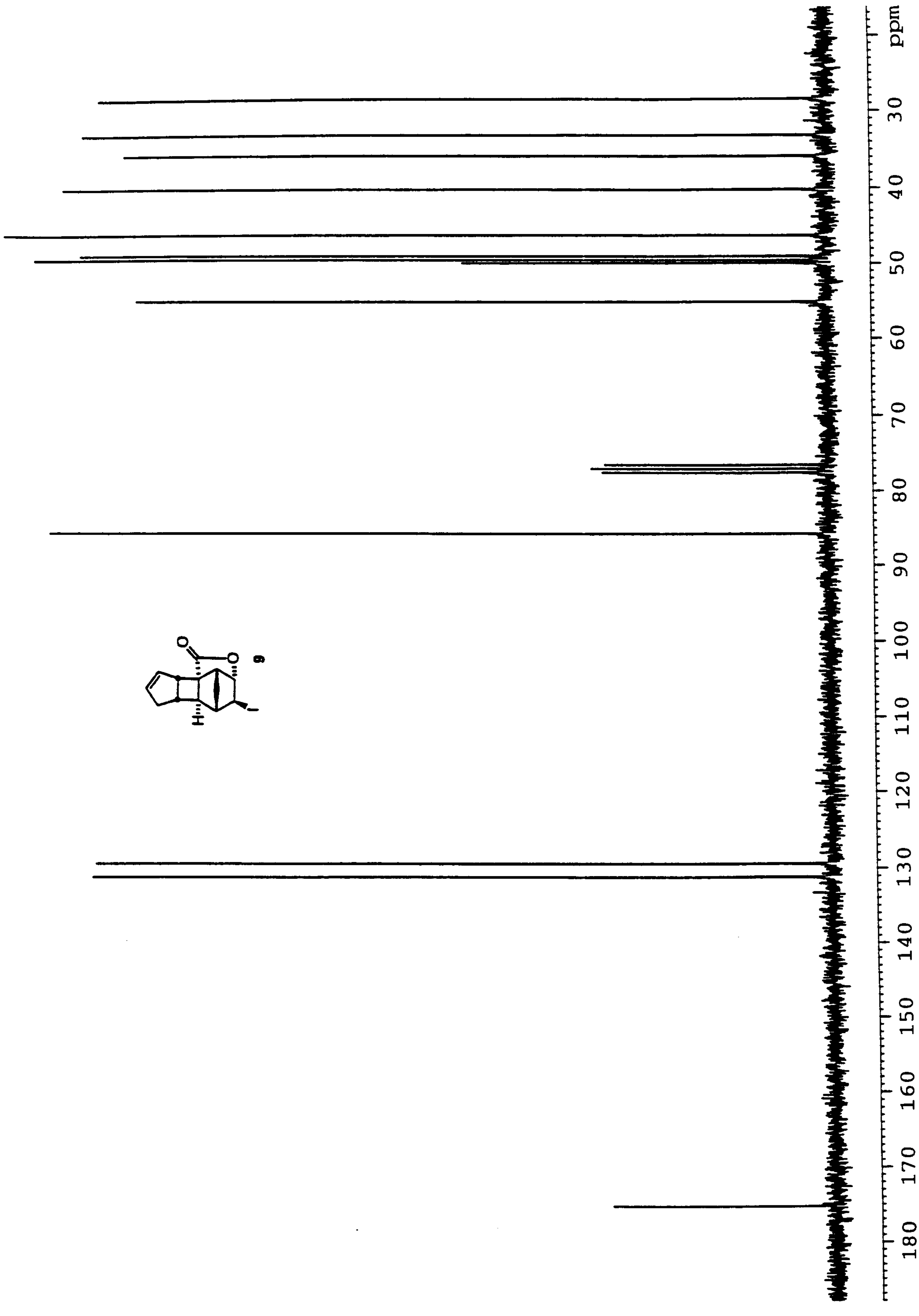

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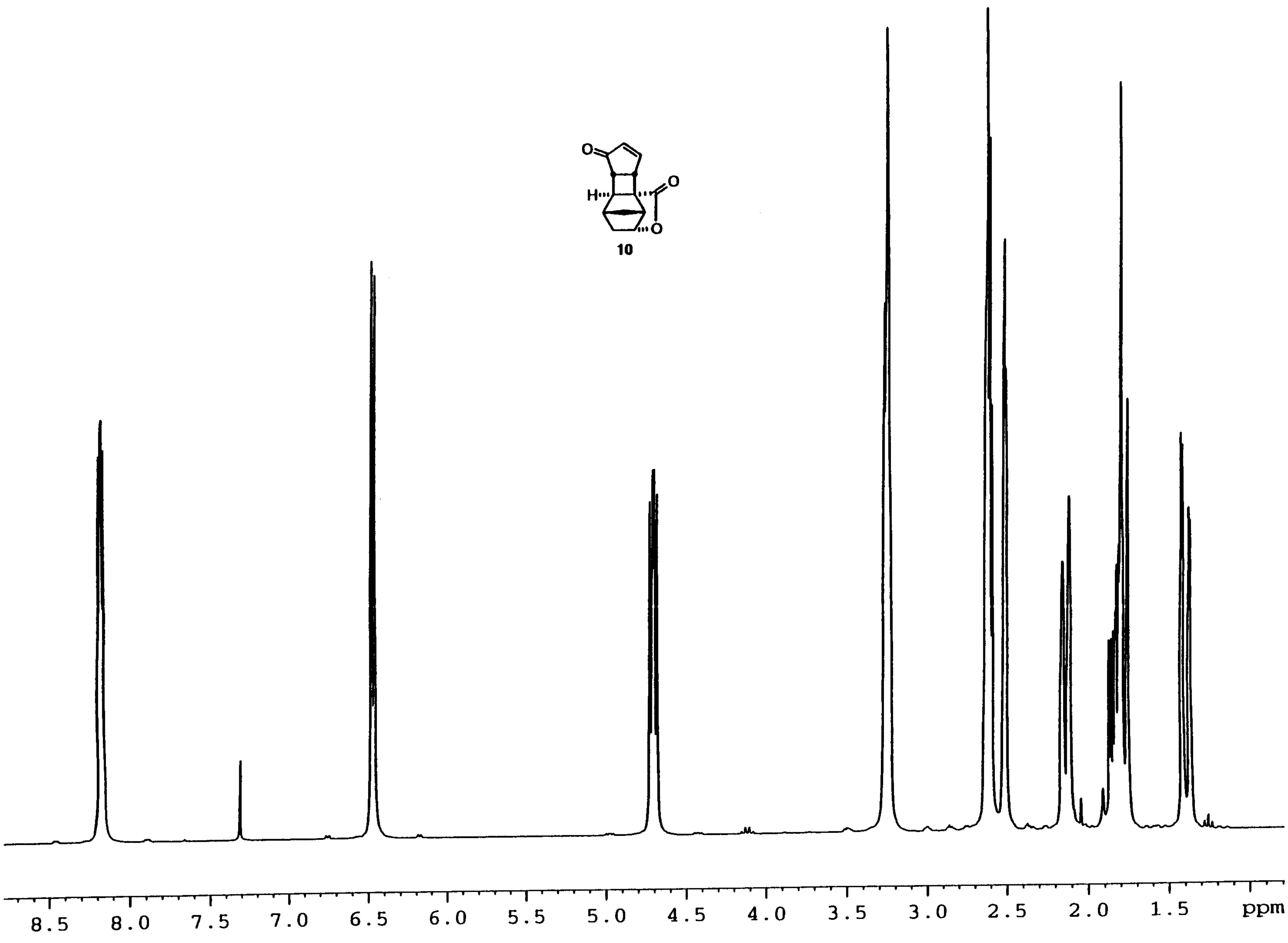
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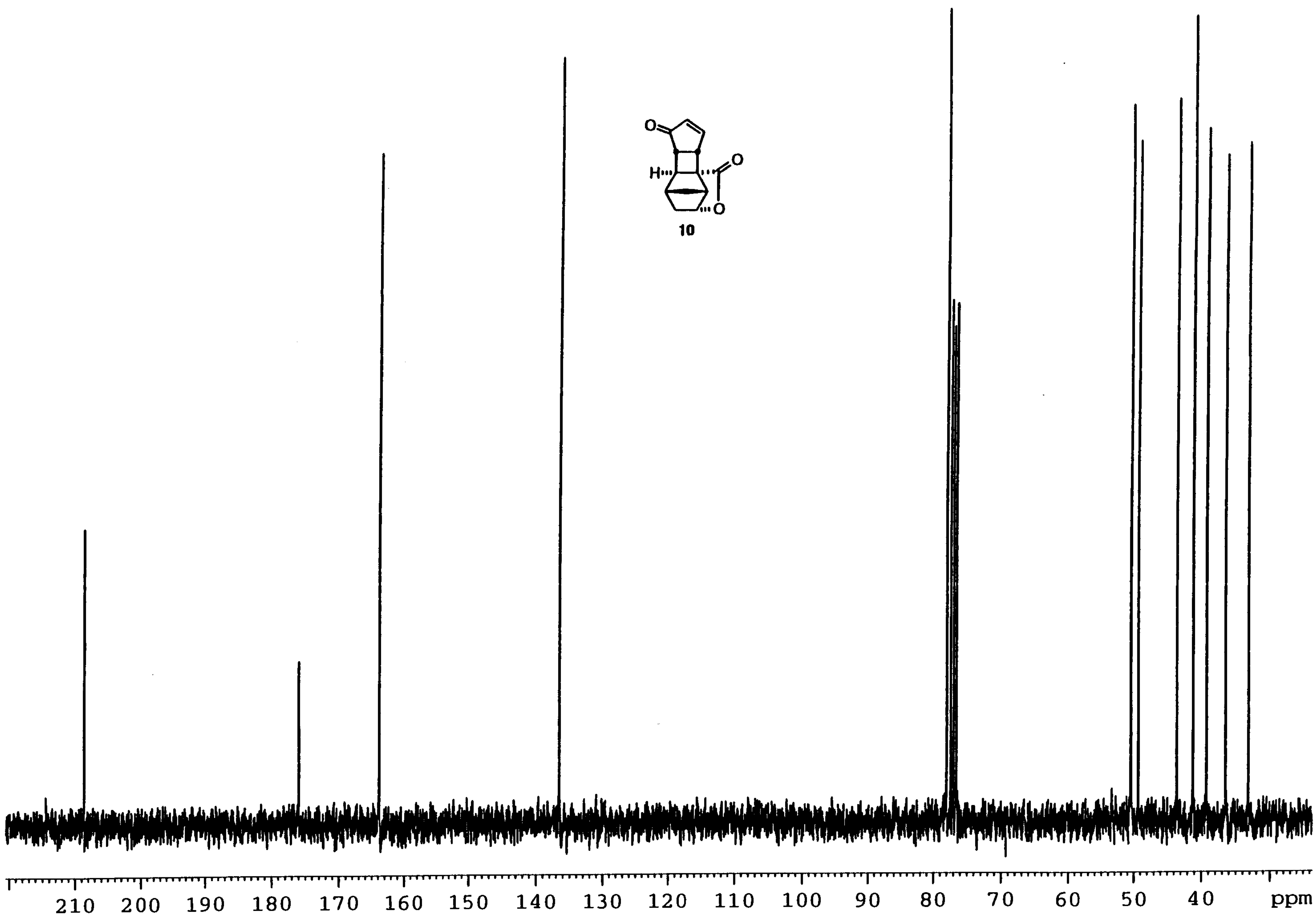
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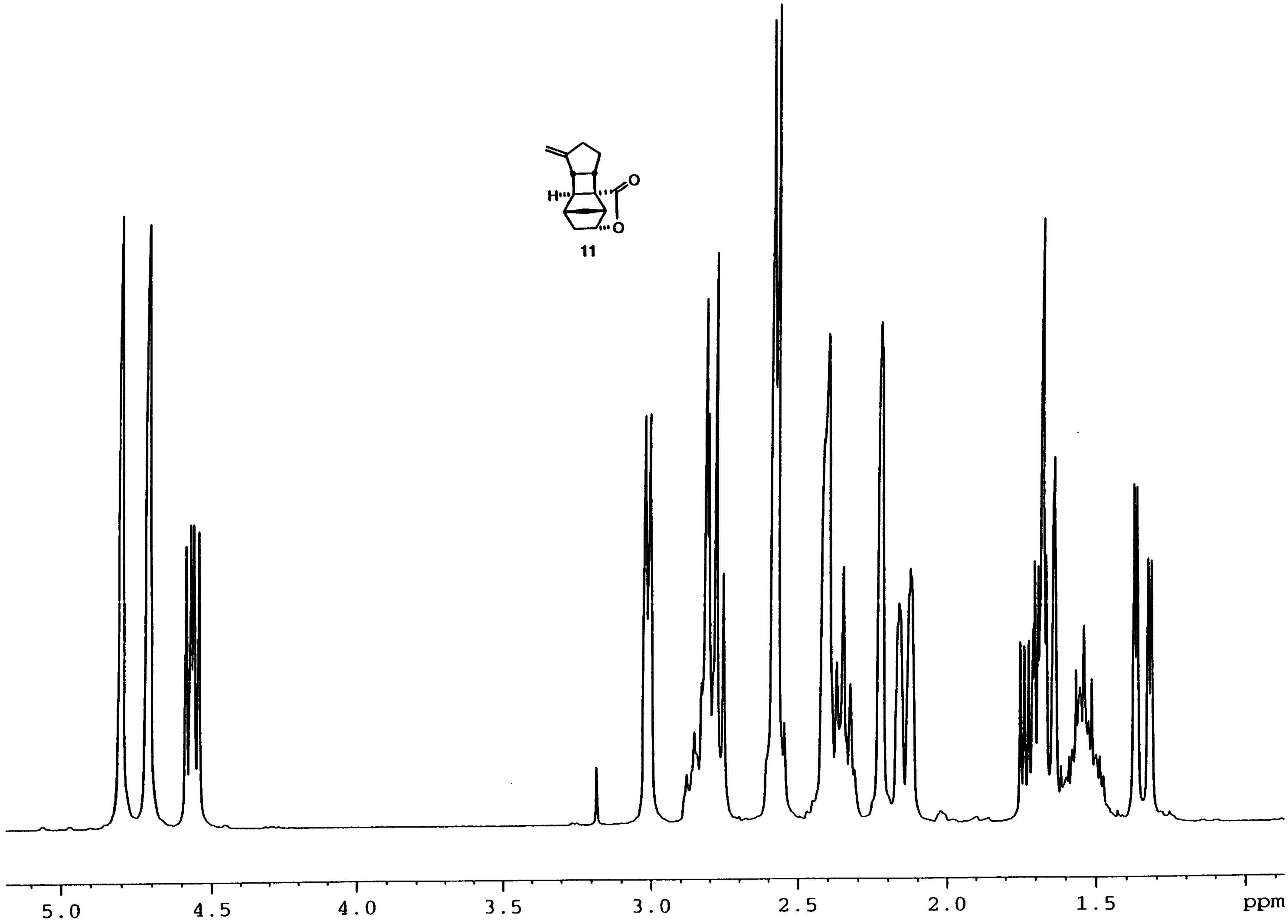
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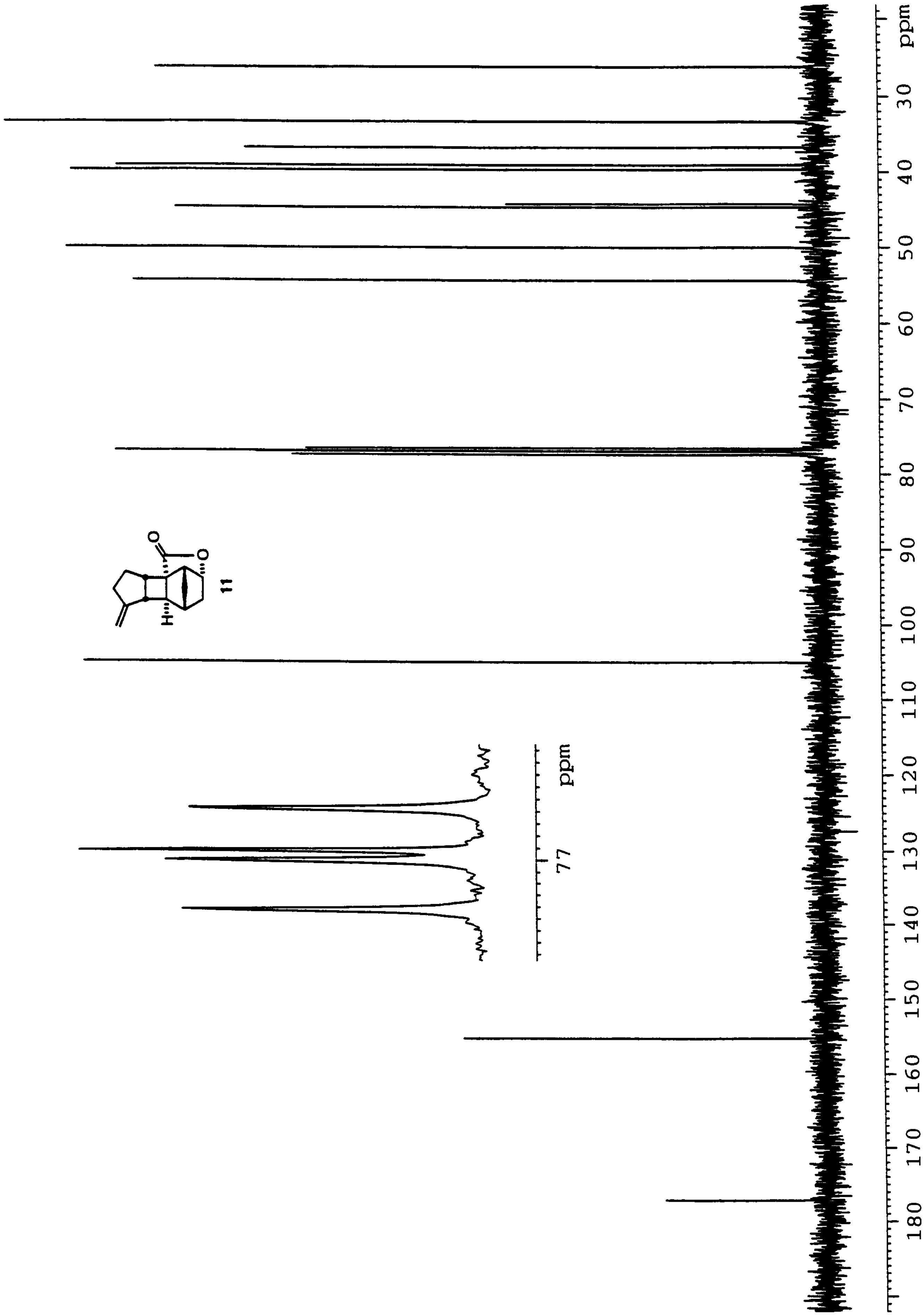
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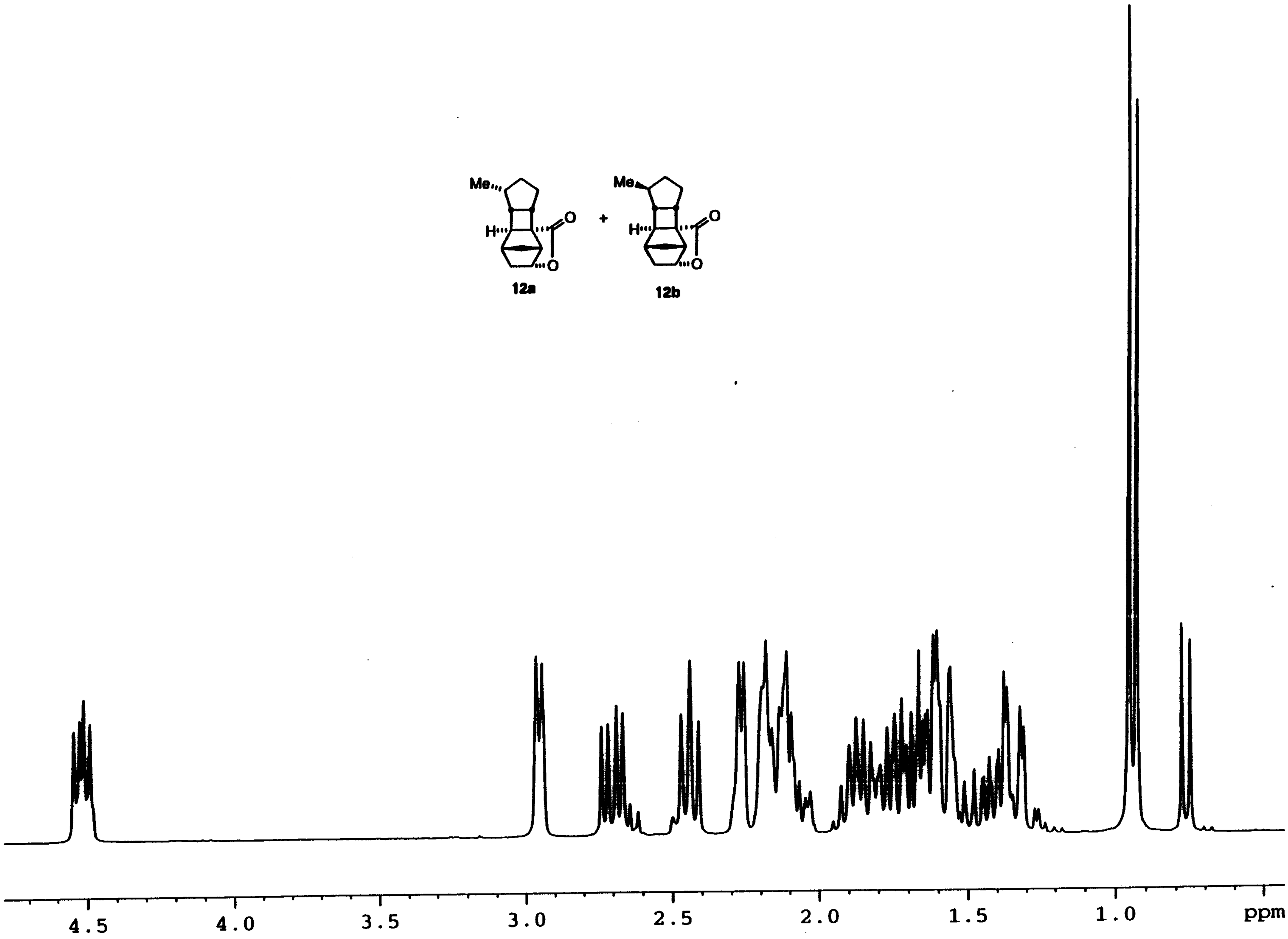
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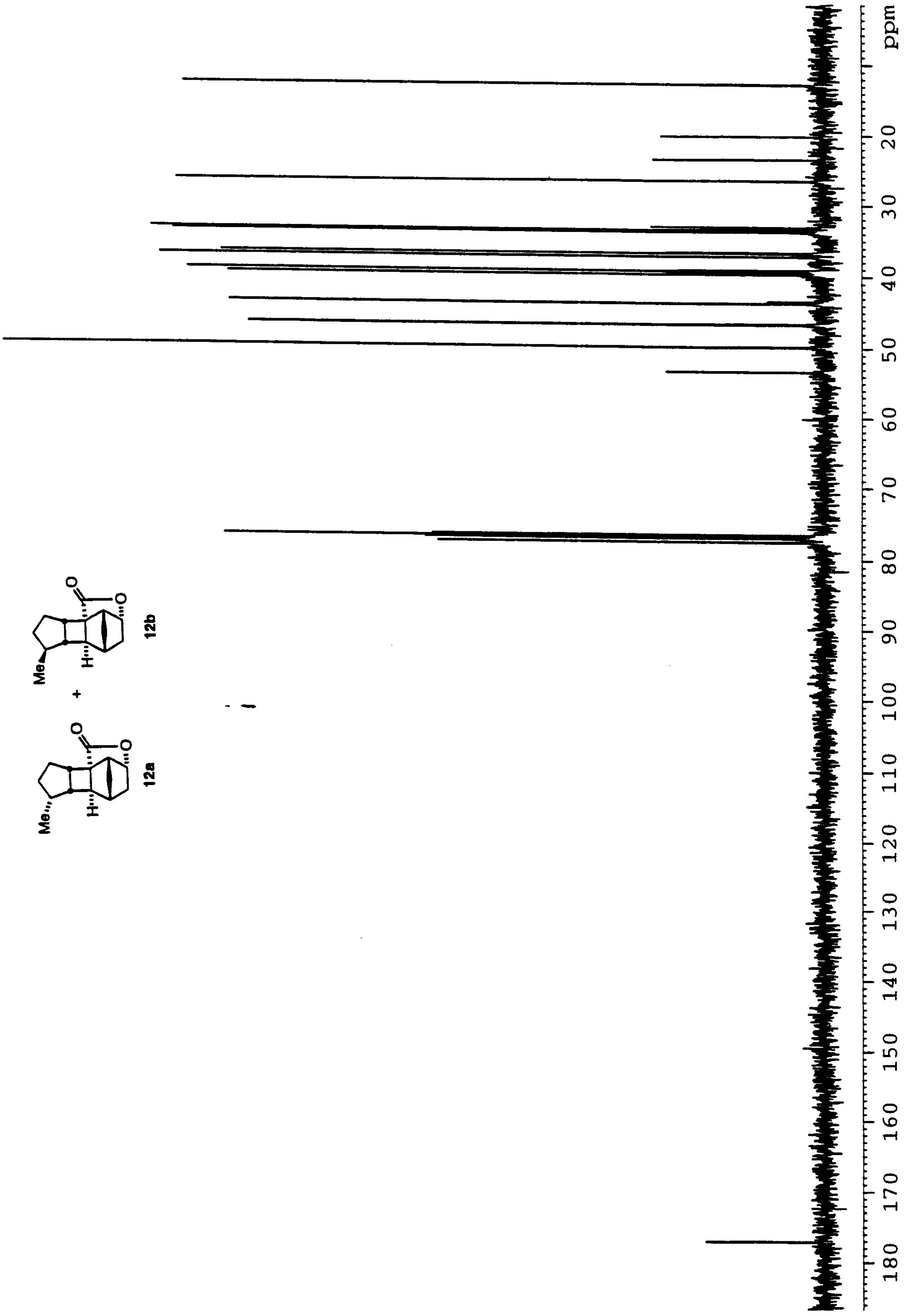
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O
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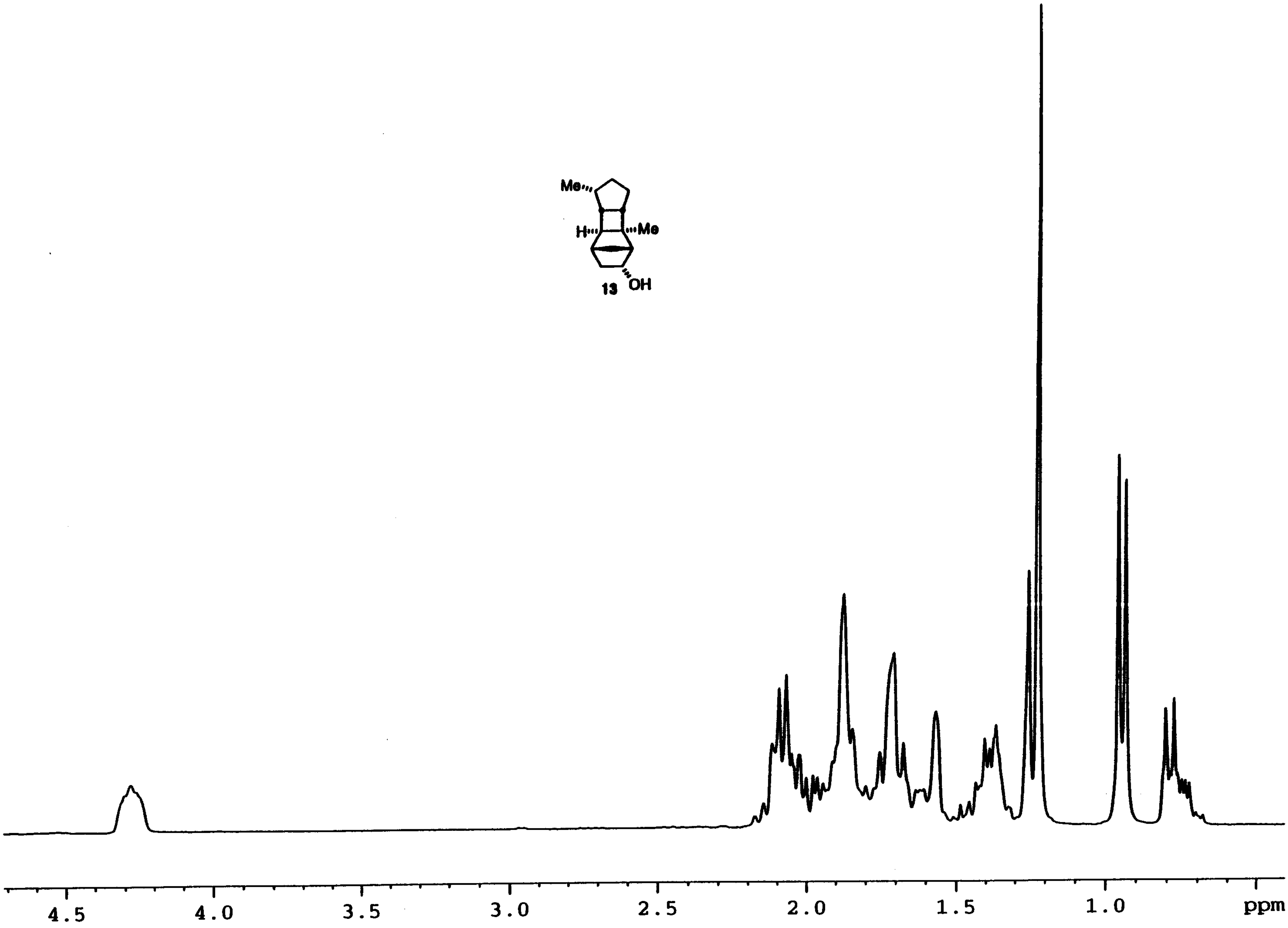
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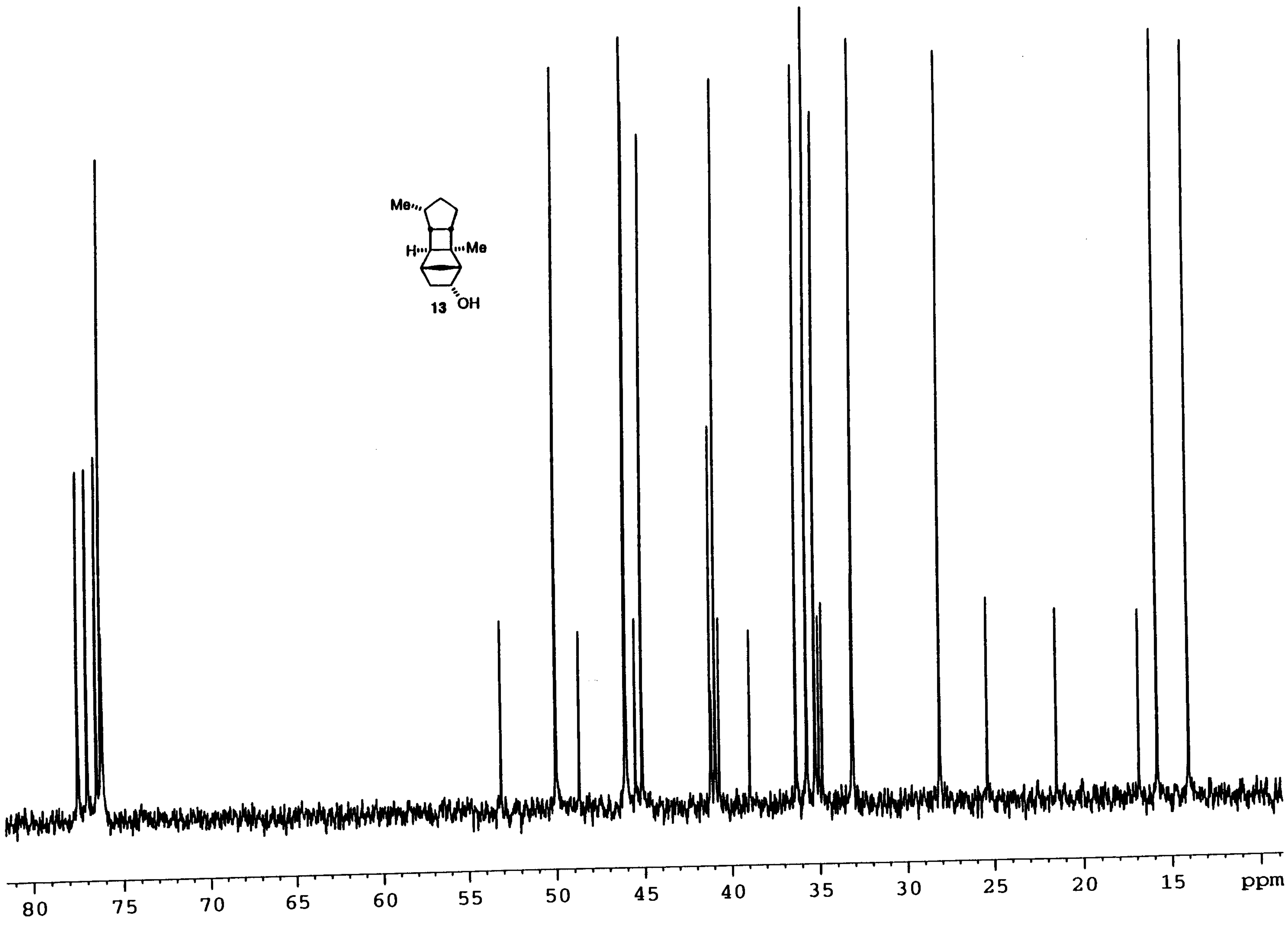
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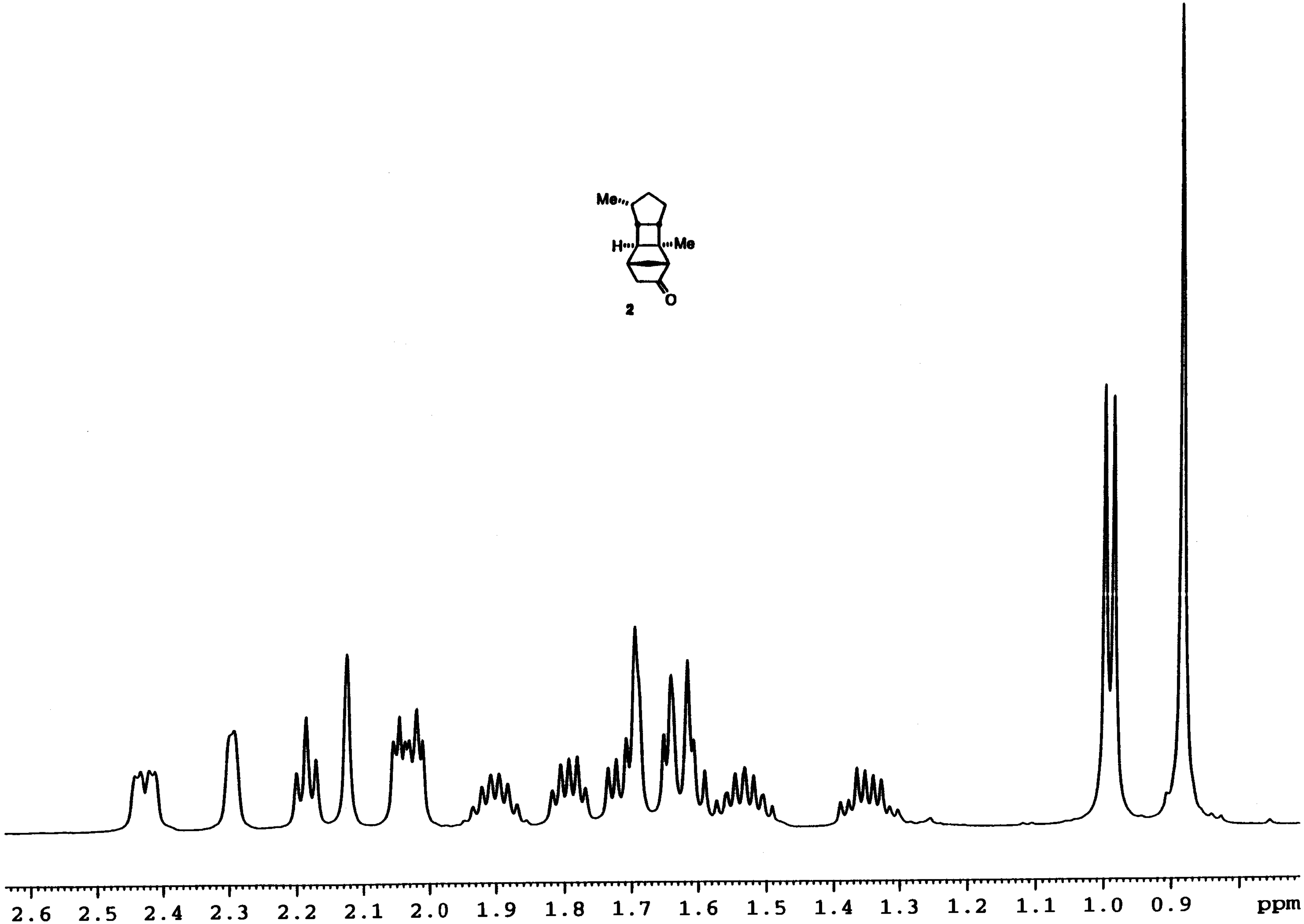

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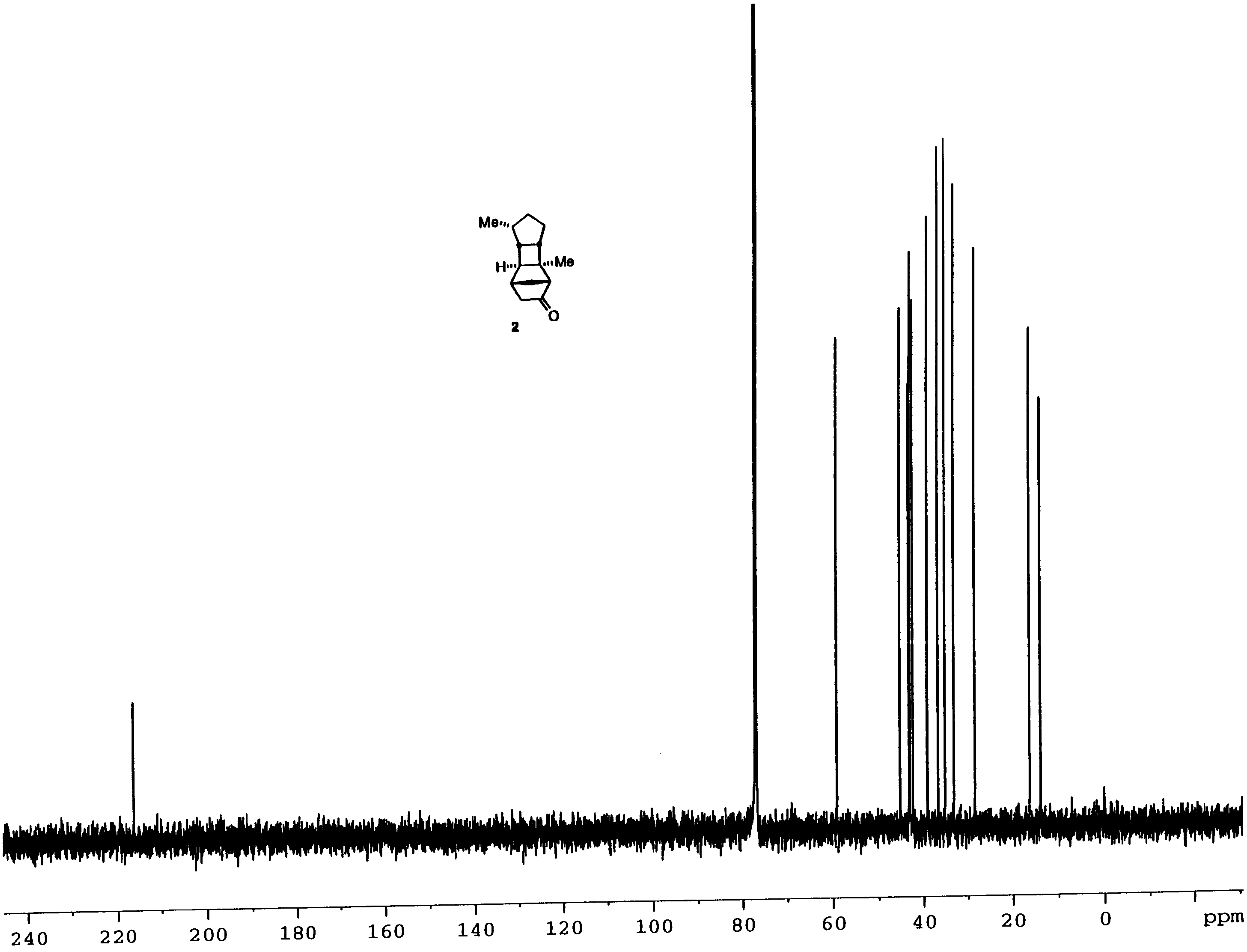

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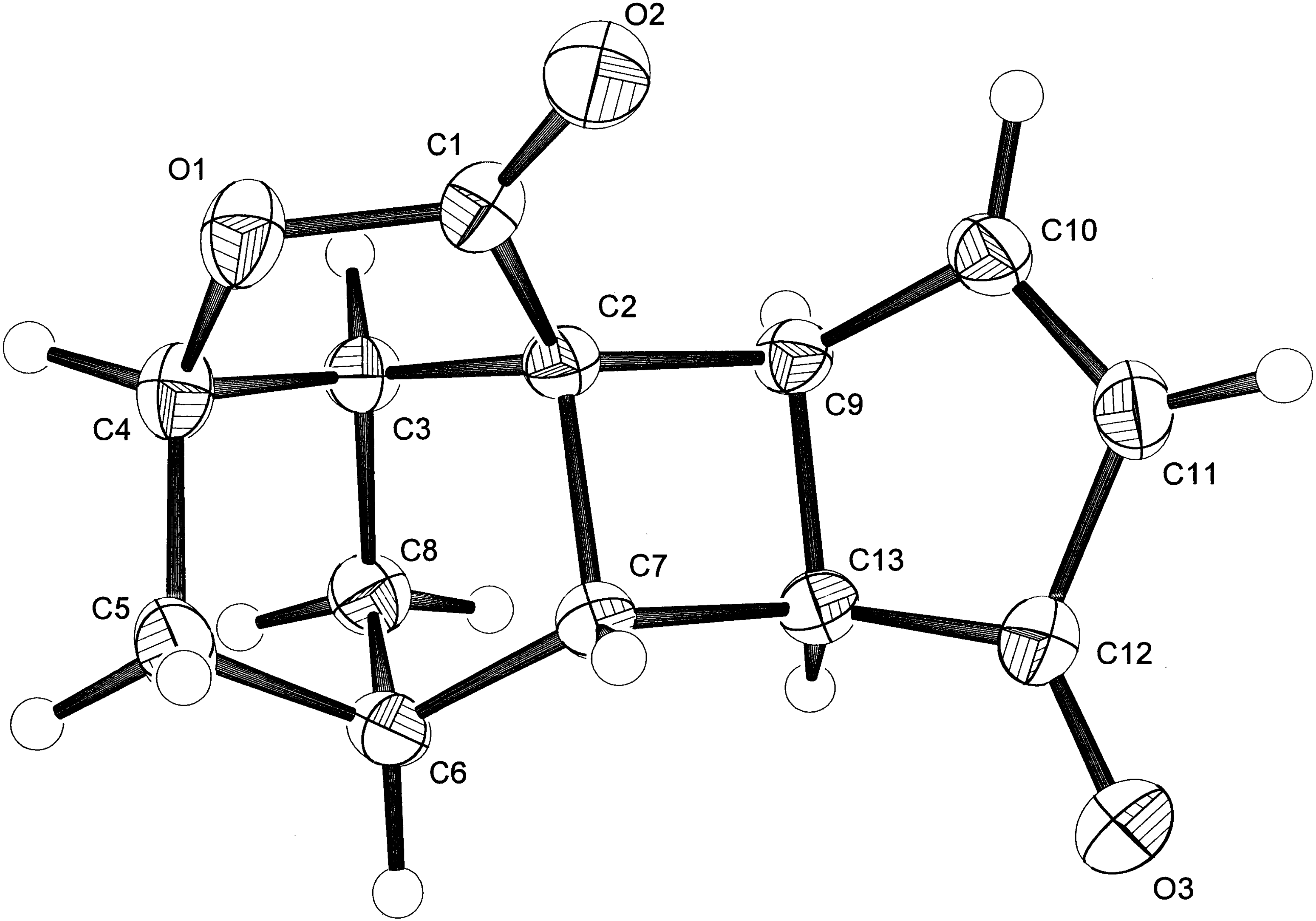
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C10
C2
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C4
C3
C11
C8
C7
C13
C5
C12
C6
O3

Table 1. Crystal data and structure refinement for prxi25a.

Identification code	PR-XI-25-A1
Empirical formula	C13 H12 O3
Formula weight	216.23
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 8.1348(4) A alpha = 90 deg. b = 12.0317(5) A beta = 90 deg. c = 20.4322(9) A gamma = 90 deg.
Volume	1999.81(16) A^3
Z, Calculated density	8, 1.436 Mg/m^3
Absorption coefficient	0.102 mm^-1
F(000)	912
Crystal size	0.50 x 0.40 x 0.40 mm
Theta range for data collection	1.99 to 27.11 deg.
Limiting indices	-10<=h<=6, -14<=k<=15, -26<=l<=26
Reflections collected / unique	11475 / 2213 [R(int) = 0.0274]
Completeness to theta = 27.11	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.80
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2213 / 0 / 145
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1058
R indices (all data)	R1 = 0.0472, wR2 = 0.1118
Largest diff. peak and hole	0.320 and -0.185 e.A^-3

Table 3. Bond lengths [A] and angles [deg] for prxi25a.

O(1)-C(1)	1.3643(16)
O(1)-C(4)	1.4696(16)
O(2)-C(1)	1.2004(16)
O(3)-C(12)	1.2163(18)
C(1)-C(2)	1.5027(17)
C(2)-C(3)	1.5341(17)
C(2)-C(9)	1.5419(17)
C(2)-C(7)	1.5866(17)
C(3)-C(8)	1.5298(18)
C(3)-C(4)	1.5316(18)
C(4)-C(5)	1.543(2)
C(5)-C(6)	1.5482(19)
C(6)-C(7)	1.5299(17)
C(6)-C(8)	1.5373(19)
C(7)-C(13)	1.5671(18)
C(9)-C(10)	1.4969(18)
C(9)-C(13)	1.5511(17)
C(10)-C(11)	1.335(2)
C(11)-C(12)	1.471(2)
C(12)-C(13)	1.5156(18)

C(1)-O(1)-C(4)	108.81(9)
O(2)-C(1)-O(1)	121.67(12)
O(2)-C(1)-C(2)	130.72(12)
O(1)-C(1)-C(2)	107.55(10)
C(1)-C(2)-C(3)	103.73(10)
C(1)-C(2)-C(9)	125.27(11)
C(3)-C(2)-C(9)	118.67(10)
C(1)-C(2)-C(7)	114.02(10)
C(3)-C(2)-C(7)	102.15(9)
C(9)-C(2)-C(7)	90.23(9)
C(8)-C(3)-C(4)	103.99(11)
C(8)-C(3)-C(2)	105.67(10)
C(4)-C(3)-C(2)	96.82(10)
O(1)-C(4)-C(3)	105.33(10)
O(1)-C(4)-C(5)	112.68(11)
C(3)-C(4)-C(5)	103.59(11)
C(4)-C(5)-C(6)	103.22(11)
C(7)-C(6)-C(8)	102.50(10)
C(7)-C(6)-C(5)	105.78(11)
C(8)-C(6)-C(5)	100.62(10)
C(6)-C(7)-C(13)	119.92(11)
C(6)-C(7)-C(2)	103.17(9)
C(13)-C(7)-C(2)	88.15(9)
C(3)-C(8)-C(6)	95.23(10)
C(10)-C(9)-C(2)	116.84(10)
C(10)-C(9)-C(13)	103.62(10)
C(2)-C(9)-C(13)	90.35(9)
C(11)-C(10)-C(9)	113.21(12)
C(10)-C(11)-C(12)	110.43(12)
O(3)-C(12)-C(11)	126.92(14)
O(3)-C(12)-C(13)	125.72(13)
C(11)-C(12)-C(13)	107.30(11)

C(12)-C(13)-C(9)	105.35(10)
C(12)-C(13)-C(7)	113.22(11)
C(9)-C(13)-C(7)	90.62(9)

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [deg] for prxi25a.

C(4)-O(1)-C(1)-O(2)	179.32(13)
C(4)-O(1)-C(1)-C(2)	-3.22(14)
O(2)-C(1)-C(2)-C(3)	-154.35(15)
O(1)-C(1)-C(2)-C(3)	28.50(13)
O(2)-C(1)-C(2)-C(9)	-13.3(2)
O(1)-C(1)-C(2)-C(9)	169.56(11)
O(2)-C(1)-C(2)-C(7)	95.40(17)
O(1)-C(1)-C(2)-C(7)	-81.75(12)
C(1)-C(2)-C(3)-C(8)	-146.15(11)
C(9)-C(2)-C(3)-C(8)	69.65(14)
C(7)-C(2)-C(3)-C(8)	-27.39(12)
C(1)-C(2)-C(3)-C(4)	-39.51(12)
C(9)-C(2)-C(3)-C(4)	176.29(11)
C(7)-C(2)-C(3)-C(4)	79.25(11)
C(1)-O(1)-C(4)-C(3)	-23.46(14)
C(1)-O(1)-C(4)-C(5)	88.79(13)
C(8)-C(3)-C(4)-O(1)	146.27(10)
C(2)-C(3)-C(4)-O(1)	38.21(12)
C(8)-C(3)-C(4)-C(5)	27.75(12)
C(2)-C(3)-C(4)-C(5)	-80.31(11)
O(1)-C(4)-C(5)-C(6)	-105.85(12)
C(3)-C(4)-C(5)-C(6)	7.46(12)
C(4)-C(5)-C(6)-C(7)	66.66(12)
C(4)-C(5)-C(6)-C(8)	-39.71(12)
C(8)-C(6)-C(7)-C(13)	-56.95(14)
C(5)-C(6)-C(7)-C(13)	-161.95(11)
C(8)-C(6)-C(7)-C(2)	38.58(12)
C(5)-C(6)-C(7)-C(2)	-66.42(12)
C(1)-C(2)-C(7)-C(6)	104.26(12)
C(3)-C(2)-C(7)-C(6)	-6.94(12)
C(9)-C(2)-C(7)-C(6)	-126.40(10)
C(1)-C(2)-C(7)-C(13)	-135.40(11)
C(3)-C(2)-C(7)-C(13)	113.39(10)
C(9)-C(2)-C(7)-C(13)	-6.06(9)
C(4)-C(3)-C(8)-C(6)	-51.32(11)
C(2)-C(3)-C(8)-C(6)	50.03(12)
C(7)-C(6)-C(8)-C(3)	-53.80(12)
C(5)-C(6)-C(8)-C(3)	55.16(11)
C(1)-C(2)-C(9)-C(10)	20.72(18)
C(3)-C(2)-C(9)-C(10)	156.62(11)
C(7)-C(2)-C(9)-C(10)	-99.36(12)
C(1)-C(2)-C(9)-C(13)	126.21(12)
C(3)-C(2)-C(9)-C(13)	-97.89(12)
C(7)-C(2)-C(9)-C(13)	6.12(9)
C(2)-C(9)-C(10)-C(11)	100.35(14)
C(13)-C(9)-C(10)-C(11)	2.90(15)
C(9)-C(10)-C(11)-C(12)	-1.80(17)
C(10)-C(11)-C(12)-O(3)	-177.44(16)
C(10)-C(11)-C(12)-C(13)	-0.14(16)
O(3)-C(12)-C(13)-C(9)	179.21(15)
C(11)-C(12)-C(13)-C(9)	1.88(14)
O(3)-C(12)-C(13)-C(7)	81.74(18)
C(11)-C(12)-C(13)-C(7)	-95.59(13)

C(10)-C(9)-C(13)-C(12)	-2.74(13)
C(2)-C(9)-C(13)-C(12)	-120.52(11)
C(10)-C(9)-C(13)-C(7)	111.58(10)
C(2)-C(9)-C(13)-C(7)	-6.20(9)
C(6)-C(7)-C(13)-C(12)	-142.80(12)
C(2)-C(7)-C(13)-C(12)	113.05(11)
C(6)-C(7)-C(13)-C(9)	110.17(12)
C(2)-C(7)-C(13)-C(9)	6.03(9)

Symmetry transformations used to generate equivalent atoms: