07-02-01

*Supporting Information for:*

# Stereocontrolled Construction of Tetrahydrofurans and γ-Butyrolactones Using Organomolybdenum Chemistry

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**General Procedures.** All reactions were performed under argon atmosphere, in freshly distilled (under nitrogen) solvents. All reagents used are commercially available. Analytical thin-layer chromatography was performed on aluminum plates precoated with Merck $F_{254}$ silica gel. Visualization was done either with UV light or with phosphomolybdic acid (solution in EtOH) for molybdenum complexes, and with vanillin for organic products **11** and **12**. Flash-chromatography was performed with hexanes-ethyl acetate or hexanes-diethyl ether mixtures on silica gel with mesh 170-400, under nitrogen pressure. NMR spectra were recorded on a Varian Gemini 300 (300 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. Mass spectra were recorded in-house using a Kratos MS25A instrument. IR spectra were recorded on a Nicolet Impact 400 spectrometer. The melting points were measured on a Thomas Hoover apparatus and are uncorrected.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(1,2,3)-(±)-(2*R*,3*R*)-5-ethoxycarbonyl-2-methyl-2,4*E*-pentadien-1-yl]molybdenum (2).** To a solution of triethylphosphonoacetate (246.6 mg, 1.1 mmol, 1.1 equiv.) in THF (2 mL), 0.86 mL of a 1.4 M solution of BuLi in hexane was added dropwise at -78 °C. After 1 h of stirring, aldehyde **1** (448 mg, 1 mmol) in THF (4 mL) was added dropwise, and the reaction mixture was stirred at -78 °C for an additional 4 h. The reaction was quenched at room temperature with a saturated solution of $NH_4Cl$ (3 mL). The organic layer was separated, diluted with diethyl ether (20 mL), washed with brine (3 x 2 mL) and with water (2 mL), and dried over $Na_2SO_4$. The solvent was then removed under reduced pressure, and the crude product was purified by flash-chromatography (hexanes/EtOAc 4:1) to give **2** as a dark-red solid (479-493 mg, 92-95% yield): m.p. 165-167 °C dec; $^1$H NMR (300 MHz, CDCl3) $\delta$ (ppm) 8.04 (s, br, 3H), 7.64 (dd, $J$ = 15.3, 11.9 Hz, 1H), 7.54 (s, br, 3H), 6.23 (d, $J$ = 15.3 Hz, 1H), 6.19 (dd, $J$ = 2.2 Hz, 3H), 4.31, 4.23 (dq, AB system, $J$ = 10.8, 7.1 Hz, 2H), 3.68 (d, $J$ = 2.1 Hz, 1H), 2.20 (d, $J$ = 11.9 Hz, 1H), 1.79 (s, 3H), 1.53 (s, br, 1H), 1.34 (d, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl3) $\delta$ (ppm) 228.9, 228.4, 166.8, 147.7, 145.1, 135.8, 119.5, 105.3, 87.1, 74.0, 57.7, 15.3, 14.2; TLC Rf 0.27 (hexanes/EtOAc 4:1); IR (KBr, cm$^{-1}$) 2498, 1941, 1869, 1711, 1626, 1259; HRMS(EI) M$^+$ calcd. for $C_{20}H_{23}O_4N_6MoB$ ($^{98}$Mo) 520.0935, found 520.0956.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*)-6-hydroxy-2-methyl-2,4*E*-hexadien-1-yl]molybdenum (3).** A 1 M solution of diisobutylaluminum hydride in hexane (0.625 mL, 0.625 mmol, 2.4 equiv) was added dropwise to a solution of **2** (136 mg, 0.26 mmol) in THF (1.5 mL), at -78 °C. The reaction was quenched with methanol (0.2 mL) after 45 min at -78 °C, the solution was allowed to warm to room temperature and filtered, and the precipitate was washed with ethyl acetate. After drying over $Na_2SO_4$, the solution was concentrated under reduced pressure, and the crude product was purified by flash-chromatography (hexanes/EtOAc 7:3) to give **4** as an orange solid (122.5 mg, 98% yield): m.p. 155-157 °C dec; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ (ppm) 8.05 (s, br, 3H), 7.18 (s, br, 3H), 6.49 (dddd, $J$ = 15.4, 11.4, 1.7 Hz, 1H), 6.10 (ddd, $J$ = 15.4, 5.0 Hz, 1H), 5.75 (s, br, 3H), 3.88 (unresoved AB, br, 2H), 3.40 (d, $J$ = 2.1 Hz, 1H), 2.46 (d, $J$ = 11.4 Hz, 1H), 1.55 (s, 3H), 1.40 (d, $J$ = 2.08 Hz, 1H) 0.74 (s, br, 1H); $^{13}$C NMR (75 MHz, $C_6D_6$) $\delta$ (ppm) 230.0, 229.7, 145.5, 135.6, 133.1, 129.8, 105.5, 83.6, 80.9, 62.9, 57.2, 15.4; TLC Rf 0.22 (hexanes/EtOAc 2:1); IR (NaCl, cm$^{-1}$) 3418, 2492, 1936, 1852; HRMS(EI) M$^+$ calcd. for $C_{18}H_{21}O_3N_6MoB$ ($^{98}$Mo) 478.0828, calc [M-2CO]$^+$ 422.0929, found 422.0922.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*,4*R*,5*S*)-4,5,6-trihydroxy-2-methyl-2-hexen-1-yl]molybdenum (4).** A solution of $OsO_4$ (150 mg, 0.59 mmol, 1.1 equiv) in THF (7.5 mL) was added to a solution of **3** (255 mg, 0.536 mmol) and pyridine (0.65 mL, 15 equiv) in THF (4 mL), at 0 °C. After 4 h of stirring, the reaction mixture was diluted with methanol (15 mL), and $H_2S$ was bubbled through for 2 min at the same temperature, when a black precipitate was formed. The reaction mixture was allowed to warm to room temperature, and then it was filtered through Celite, and the precipitate was washed with ethyl acetate. The filtrate was concentrated under reduced pressure, and the crude product was purified by flash-chromatography (hexanes/EtOAc 1:3) to give **4** as a yellow solid (237 mg, 87% yield): m.p. 98-100 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm) 8.03 (s, br, 3H), 7.56 (d, $J$ = 2.2 Hz, 3H), 6.21 (dd, $J$ = 2.2 Hz, 3H), 4.71 (d, $J$ = 9.9 Hz, 1H), 4.43 (dd, $J$ = 5.7 Hz, 1H), 3.97, 3.94 (dd, AB system, $J$ = 11.2, 5.7 Hz, 2H), 3.78 (s, br, 1H), 2.00 (d, $J$ = 9.9 Hz, 1H), 1.82 (s, 3H), 1.68 (s, br, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ (ppm) 231.2, 230.5, 145.0, 135.8, 105.5, 89.1, 76.2, 72.3, 70.6, 64.6, 62.9, 15.9; TLC Rf 0.35 (hexanes/ EtOAc 1:4); IR (NaCl, cm$^{-1}$) 3407, 2933, 2490, 1939, 1849; HRMS(FAB) M$^+$ calcd. for $C_{18}H_{23}O_5N_6MoB$ ($^{98}$Mo) 512.0881, found 512.0883.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*,5*R*)-5,6-dihydroxy-2-methyl-2-hexen-1-yl]molybdenum (5) and dicarbonyl[hydridotris(1-pyrazolyl) borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*)-6-hydroxy-2-methyl-2-hexen-1-yl]molybdenum (6).** A 1 M solution of $BH_3$ in THF (1 mL, 1 mmol, 10 equiv) was added dropwise to a solution of **4** (50 mg, 0.105 mmol) in THF (0.5 mL), at -8 - 0 °C. After 1 h, water was added via syringe to destroy the excess of borane, and then 3M NaOH (0.35 mL, 1.05 mmol, 10 equiv) and 30 wt % $H_2O_2$ (36 mg, 0.315 mmol, 3 equiv) were added and the reaction mixture was stirred at room temperature for 1 h. The aqueous layer was saturated with $K_2CO_3$, and the organic layer was extracted with ethyl acetate, washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The crude material was separated by flash-chromatography (hexanes/EtOAc 3:2) to give **5** (31 mg, 60%) and **6** (13 mg, 26%). **5**: Yellow solid; m.p. 114-116 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm) 8.06 (s, br, 3H), 7.54 (d, *J* = 2.1 Hz, 3H), 6.19 (dd, *J* = 2.1 Hz, 3H), 4.05 (dddd, *J* = 7.1, 6.4, 3.2 Hz, 1H), 3.87 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.70 (dd, *J* = 11.0, 7.1 Hz, 1H), 3.58 (d, *J* = 1.6 Hz, 1H), 2.65 (dd, *J* = 6.4 Hz, 2H), 1.66 (s, 3H), 1.59 (dd, *J* = 7.1 Hz, 1H), 1.42 (d, *J* = 1.6 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ (ppm) 229.8, 228.4, 144.8, 135.7, 105.3, 84.1, 76.7, 73.6, 66.3, 59.1, 34.4, 15.1; TLC Rf 0.16 (hexanes/EtOAc 1:1); IR (NaCl, $cm^{-1}$) 3349, 2927, 2487, 1933, 1842; HRMS(FAB) $M^+$ calcd. for $C_{18}H_{23}O_4N_6MoB$ ($^{98}$Mo) 496.0934, found 496.0969. **6**: Yellow solid; m.p. 68-70 °C dec; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 8.08 (d, *J* = 2.1 Hz, 3H), 7.54 (d, *J* = 2.1 Hz, 3H), 6.19 (dd, *J* = 2.1 Hz, 3H), 3.84 (t, *J* = 6.7 Hz, 2H), 3.53 (d, *J* = 1.9 Hz, 1H), 2.44-2.61 (m, 2H), 1.96 (t, *J* = 6.7 Hz, 1H), 1.66 (dd, *J* = 9.4, 5.0 Hz, 1H), 1.61 (s, 3H), 1.33 (d, *J* = 1.9 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 229.6, 228.9, 144.9, 135.7, 105.2, 82.8, 81.7, 62.4, 58.4, 34.7, 27.1, 14.6; TLC Rf 0.3 (hexanes/EtOAc 3:2); IR (NaCl, $cm^{-1}$) 3399, 2921, 2491, 1934, 1837; HRMS(FAB) $M^+$ calcd. for $C_{18}H_{23}O_3N_6MoB$ ($^{98}$Mo) 480.0978, found 480.0972.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*)-5-methoxycarbonyl-2-methyl-2,4*Z*-pentadien-1-yl]molybdenum (7) and dicarbonyl[hydridotris(1-pyrazolyl)borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*)-5-methoxycarbonyl-2-methyl-2,4*E*-pentadien-1-yl]molybdenum (8).** To a solution of bis(2,2,2-trifluoroethyl)(methoxycarbonylmethyl)phosphonate (88 mg, 2.6 mmol, 1.05 equiv.) and [18]-crown-6 (330 mg, 1.25 mmol, 5 equiv) in THF (2 mL), was added a 0.5 M solution of KHMDS in hexane

(0.55 mL, 0.275 mmol, 1.1 equiv), at -78 °C. After 1 h of stirring, aldehyde **1** (112 mg, 0.25 mmol) in THF (3 mL) was added dropwise, and the reaction mixture was stirred at -78 °C for an additional 2 h. The reaction was quenched at room temperature with a saturated solution of $NH_4Cl$ (3 mL). The organic layer was separated, diluted with diethyl ether (20 mL), washed with brine (3 x 2 mL) and with water (2 mL), and dried over $Na_2SO_4$. The solvent was then removed under reduced pressure, and the crude material was purified by flash-chromatography (hexanes/EtOAc 4:1) to give a mixture of **7** and **8** in a 7:3 ratio (121-125 mg, 96-99% total yield) as a thick red oil. **7** and **8** were separated by multiple elution preparative TLC (hexanes/EtOAc 4:1). **7**: Dark-red solid: m.p. 72-74 °C dec; $^1H$ NMR (200 MHz, $C_6D_6$) $\delta$ (ppm) 7.90 (d, $J$ = 2.1 Hz, 3H), 7.16 (overlapped on the solvent peak, 3H), 6.58 (dd, $J$ = 11.9 Hz, 1H) 6.03 (d, $J$ = 11.9 Hz, 1H), 5.69 (dd, $J$ = 2.1 Hz, 3H), 4.38 (d, $J$ = 11.9 Hz, 1H), 3.47 (s, 3H), 3.36 (d, $J$ = 2.2 Hz, 1H), 1.62 (d, $J$ = 2.2 Hz, 1H), 1.50 (s, 3H); $^{13}C$ NMR (50 MHz, $C_6D_6$) $\delta$ (ppm) 230.3, 228.8, 166.9, 147.7, 145.5, 135.7, 117.9, 105.6, 89.3, 70.7, 57.5, 50.7, 15.3; TLC Rf 0.26 (hexanes/EtOAc 4:1); IR (NaCl, $cm^{-1}$) 2488, 1945, 1859, 1719, 1621; HRMS(EI) $M^+$ calcd. for $C_{19}H_{21}O_4N_6MoB$ ($^{98}Mo$) 506.0778, found 506.0768. **8**: Dark-red solid: m.p. 168-170 °C dec; $^1H$ NMR (200 MHz, $C_6D_6$) $\delta$ (ppm) 7.95 (s, br, 3H), 7.91 (dd, $J$ = 15.2, 11.9 Hz, 1H) 7.11 (d, $J$ = 2.2 Hz, 3H), 6.46 (d, $J$ = 15.2 Hz, 1H), 5.73 (dd, $J$ = 2.2 Hz, 3H), 3.48 (s, 3H), 3.36 (d, $J$ = 2.1 Hz, 1H), 2.05 (d, $J$ = 11.9 Hz, 1H), 1.48 (s, 3H) 1.38 (d, $J$ = 2.1 Hz, 1H); $^{13}C$ NMR (50 MHz, $C_6D_6$) $\delta$ (ppm) 229.2, 229.0, 167.1, 148.2, 145.5, 135.7, 119.6, 105.7, 87.3, 74.0, 57.9, 51.0, 14.9; TLC Rf 0.26 (hexanes/EtOAc 4:1); IR (NaCl, $cm^{-1}$) 2485, 1943, 1858, 1714, 1659; HRMS(EI) $M^+$ calcd. for $C_{19}H_{21}O_4N_6MoB$ ($^{98}Mo$) 506.0778, found 506.0778.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*)-6-hydroxy-2-methyl-2,4*Z*-hexadien-1-yl]molybdenum (9).** A 1 M solution of diisobutylaluminum hydride in hexane (0.132 mL, 0.132 mmol, 3 equiv) was added dropwise to a solution of

**7** (22 mg, 0.044 mmol) in THF (0.15 mL), at -78 °C. The reaction was quenched with methanol (0.15 mL) after 1.5 h at -78 °C, the solution was allowed to warm to room temperature and filtered, and the precipitate was washed with ethyl acetate. After drying over $Na_2SO_4$, the solution was concentrated under reduced pressure, and the crude product was purified by flash-chromatography (hexanes/EtOAc 3:2) to give **9** as an orange solid (20 mg, 96% yield): m.p. 80-82 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm) 8.12 (s, br, 3H), 7.54 (s, br, 3H), 6.29 (dd, $J$ = 11.4 Hz, 1H), 6.20 (ddd, $J$ = 11.4, 6.8 Hz, 1H), 6.18 (dd, $J$ = 2.2 Hz, 3H), 4.50, 4.38 (dd, AB system, $J$ = 13.1, 6.8 Hz, 2H), 3.62 (d, $J$ = 2.3 Hz, 1H), 2.77 (d, $J$ = 11.4 Hz, 1H), 1.68 (s, 3H), 1.43 (d, $J$ = 2.3 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ (ppm) 230.8, 229.2, 145.0, 135.9, 132.0, 131.1, 105.2, 85.0, 75.4, 58.2, 57.0, 15.3; TLC Rf 0.57 (hexanes/EtOAc 1:1); IR (NaCl, cm$^{-1}$) 3392, 2487, 1936, 1879; HRMS(EI) M$^+$ calcd. for $C_{18}H_{21}O_3N_6MoB$ ($^{98}$Mo) 478.0828, found 478.0829.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][*η*-(1,2,3)-(±)-(2*R*,3*R*,5*S*)-5,6-dihydroxy-2-methyl-2-hexen-1-yl]molybdenum** **(10).** A 1 M solution of $BH_3$ in THF (1 mL, 1 mmol, 10 equiv) was added dropwise to a solution of **9** (50 mg, 0.105 mmol) in THF (0.5 mL), at -30 °C. After 2.5 h, water was added via syringe to destroy the excess of borane, and then NaOH 3 M (0.35 mL, 1.05 mmol, 10 equiv) and 30 wt % $H_2O_2$ (36 mg, 0.315 mmol, 3 equiv) were added and the reaction mixture was stirred at room temperature for 1 h. The aqueous layer was saturated with $K_2CO_3$, and the organic layer was extracted with ethyl acetate, washed with brine, dried over $Na_2SO_4$, and concentrated under low pressure. The crude material was separated by flash-chromatography (hexanes/EtOAc 3:2) to give **6** (23 mg, 46%), and **10** (24 mg, 46%). **10**: Yellow solid; m.p. 108-110 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm) 8.09 (s, br, 3H), 7.54 (d, $J$ = 2.1 Hz, 3H), 6.19 (dd, $J$ = 2.1 Hz, 3H), 4.04 (m, unresolved, 1H), 3.89 (dd, $J$ = 11.0, 3.0 Hz, 1H), 3.67 (dd, $J$ = 11.0, 7.1 Hz, 1H), 3.55 (d, $J$ = 1.8 Hz, 1H), 2,72 (ddd, $J$ = 13.6, 7.1, 3.6 Hz, 1H), 2.59

(ddd, *J* = 13.6, 10.4, 6.0 Hz, 1H), 1.67 (dd, *J* = 10.4, 3.6 Hz, 1H), 1.61 (s, 3H), 1.38 (s, br, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ (ppm) 229.8, 228.4, 144.9, 135.6, 105.2, 83.4, 76.0, 75.9, 66.4, 58.4, 34.4, 15.1; TLC Rf 0.16 (hexanes/EtOAc 1:1); IR (NaCl, cm$^{-1}$) 3367, 2920, 2496, 1932, 1840; HRMS(FAB) M$^+$ calcd. for $C_{18}H_{23}O_4N_6MoB$ ($^{98}$Mo) 496.0934, found 496.0924.

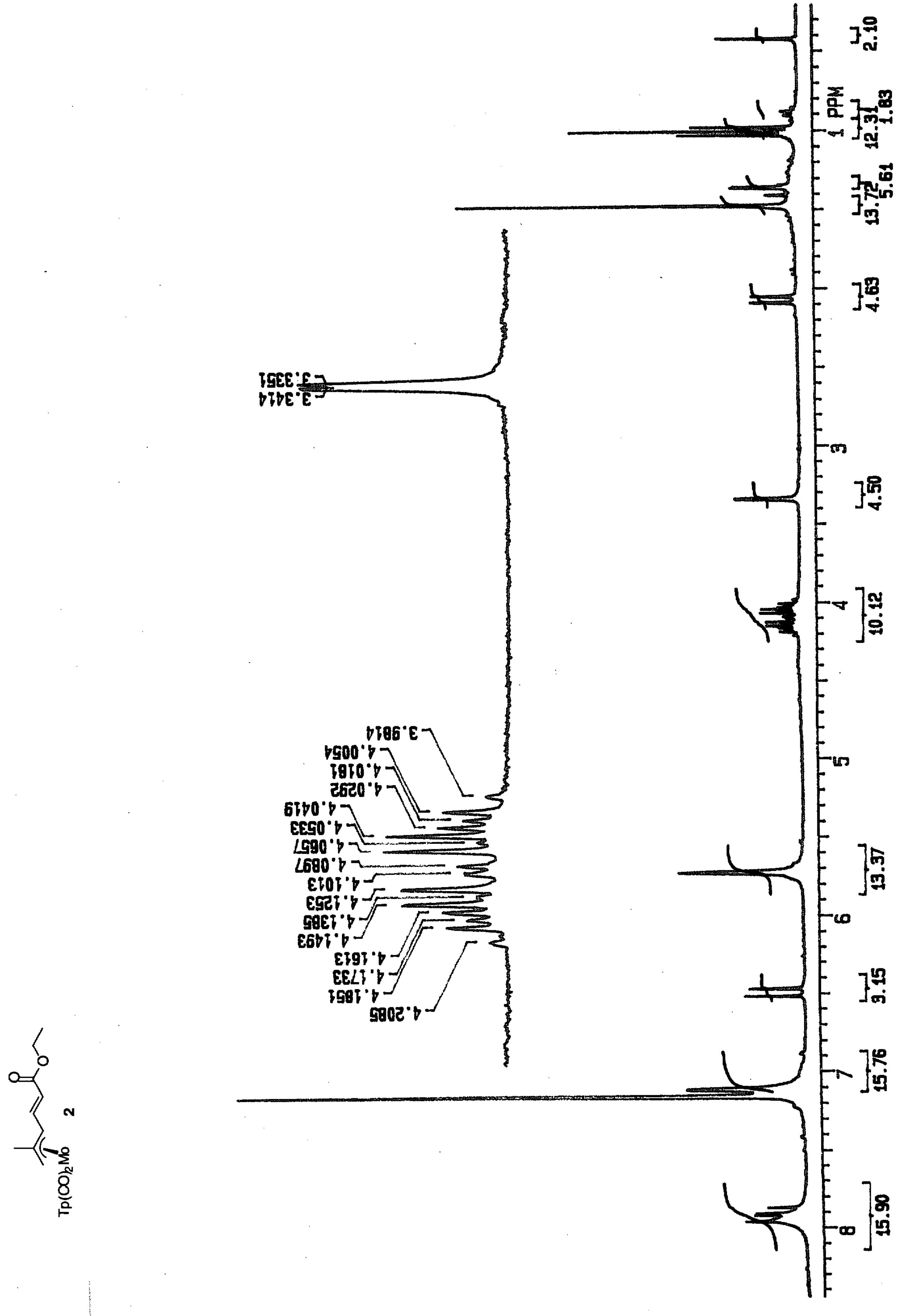
**(±)-(2*R*,3*S*,4*S*)-2-isopropenyltetrahydro-3,4-furandiol (11).** $NOBF_4$ (36 mg, 0.306 mmol, 1.2 equiv) was added to a solution of **4** (130 mg, 0.255 mmol) in acetonitrile (3 mL) at 0 °C, and the reaction mixture was stirred for 10 min. A change in color from yellow to green was observed. Anhydrous $Na_2CO_3$ (65 mg) was added to the reaction, and stirring was continued for 2 h at 0 °C, and for additional 3 h at room temperature, while exposed to air. The solvent was evaporated, and the crude product subjected directly to flash-chromatography purification ($Et_2O$) to give **11** as a colorless oil (18 mg, 49%): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 5.27 (m, 1H), 5.14 (m, 1H), 4.54 (s, br, 1H), 4.38 (d, br, *J* = 4.2 Hz, 1H), 4.25 (dd, *J* = 9.9, 4.2 Hz, 1H), 4.00 (d, *J* = 2.9 Hz, 1H), 3.77 (dd, *J* = 9.9, 1.2 Hz, 1H), 1.85 (s, br, 1H), 1.77 (s, br, 3H), 1.72 (s, br, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 140.1, 113.4, 83.4, 77.2, 75.9, 74.1, 20.1; TLC Rf 0.29 ($Et_2O$); IR (NaCl, cm$^{-1}$) 3200-3600, 1659; HRMS(FAB) [M+H]$^+$ calcd. for $C_7H_{12}O_3$ 145.0866, found 145.0855.

**(±)-(3*R*,5*S*)-5-isopropenyltetrahydro-3-furanol (12).** $NOBF_4$ (57 mg, 0.486 mmol, 1.2 equiv) was added to a solution of **5** (200 mg, 0.405 mmol) in acetonitrile (5 mL) at 0 °C, and the reaction mixture was stirred for 10 min. A change in color from yellow to green was observed. Anhydrous $Na_2CO_3$ (100 mg) was added to the reaction, and stirring was continued for 2 h at 0 °C, and for additional 3 h at room temperature, while exposed to air. The solvent was evaporated, and the crude product subjected directly to flash-chromatography purification (hexanes/$Et_2O$ 1:3) to give **12** as a colorless oil (35 mg, 68%):$^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 5.00 (m, 1H), 4.81 (m, 1H), 4.55 (dd, *J* =

10.0, 6.0, 1H), 4.51 (m, 1H), 4.03 (dd, $J$ = 9.8, 4.1 Hz, 1H), 3.79 (ddd, $J$ = 9.8, 1.4, 1.4 Hz, 1H), 2.17 (s, br, 1H), 2.05 (dddd, $J$ = 13.3, 6, 1.3, 1.3 Hz, 1H), 1.81 (ddd, $J$ = 13.3, 10, 5.2 Hz, 1H), 1.70 (s, br, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 145.0, 110.5, 80.9, 75.9, 72.7, 40.5, 17.7; TLC Rf 0.27 (hexanes/$Et_2O$ 1:3); IR (NaCl, cm$^{-1}$) 3200-3600, 1658; HRMS(EI) M$^+$ calcd. for $C_7H_{12}O_3$ 128.0837, found 128.0831.

**Dicarbonyl[hydridotris(1-pyrazolyl)borato][$\eta$-(1,2,3)-(±)-(2*R*,3*R*,4*R*,5*R*)-5-ethoxycarbonyl-4,5-dihydroxy-2-methyl-2-penten-1-yl]molybdenum (13).** A solution of $OsO_4$ (14 mg, 0.055 mmol, 1.08 equiv) in THF (0.72 mL) was added to a solution of **2** (26.5 mg, 0.051 mmol) and TMEDA (6.5 mg, 0.055 mmol, 1.08 equiv) in methylene chloride (1.3 mL), at -78 °C. After 1.5 h of stirring, the reaction mixture was diluted with methanol, and $H_2S$ was bubbled through for 2 min at the same temperature, when a black precipitate was formed. The reaction mixture was allowed to warm to room temperature, then it was filtered through Celite, and the precipitate was washed with ethyl acetate. The combined filtrate and washings were evaporated, and the crude product was purified by flash-chromatography (45% EtOAc in hexanes) to give **13** as a yellow solid (26.5 mg, 94% yield): m.p. 123-125 °C dec; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ (ppm) 8.02 (s, br, 3H), 7.21 (d, $J$ = 1.9 Hz, 3H), 5.78 (dd, $J$ = 1.9 Hz, 3H), 5.14 (dd, $J$ = 10.7 Hz, 1H), 4.91 (d, $J$ = 4.2 Hz, 1H) 3.90, 3.86 (dq, AB system, $J$ = 10.7, 7.1 Hz, 2H), 3.51 (s, br, 1H), 3.21 (d, $J$ = 4.2 Hz, 1H), 2.40 (d, $J$ = 10.7 Hz, 1H), 2.21 (d, $J$ = 9.9 Hz, 1H), 1.77 (s, 3H), 1.54 (s, br, 1H), 0.83 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $C_6D_6$) $\delta$ (ppm) 230.1, 230.0, 173.3, 145.7, 135.7, 105.7, 75.4, 72.7, 71.4, 61.9, 15.9, 13.7; TLC Rf 0.34 (45% EtOAc in hexanes); IR (NaCl, cm$^{-1}$) 3476, 2923, 2499, 1941, 1855, 1738, 1670; HRMS(FAB) M$^+$ calcd. for $C_{20}H_{25}O_6N_6MoB$ ($^{98}$Mo) 554.0990, [M+Na]$^+$ calcd 577.0887, found 577.0892.

**(±)-(3*R*,4*S*,5*R*)-5-isopropenyl-3,4-dihydroxytetrahydro-2-furanone (15).** Diol ester **13** (100 mg, 0.181 mmol) was stirred with KOH (41 mg, 0,725 mmol, 4 equiv) in a water (1 mL) MeOH (3 mL) mixture for 6 h at room temperature. Then the reaction mixture was cooled to 0 °C, EtOAc was added (10 mL) and the solution was neutralized with 10% HCl to a pH 3. The organic layer was separated, and the aqueous layer was extracted with EtOAc (10 mL). $Et_3N$ was added to the combined organic phase, to a pH 7-8. After drying over $Na_2SO_4$, the solvent was evaporated, providing crude acid **14**, as a triethylammonium salt in quantitative yield. After drying under vacuum overnight, **14** was subjected to demetalation without purification. $NOBF_4$ (25 mg, 0.211 mmol, 1.3 equiv) was added to a solution of **14** (85 mg, 0.162 mmol) in acetonitrile (2 mL) at 0 °C, and the reaction mixture was stirred for 10 min. A change in color from yellow to green was observed. Dry $Et_3N$ (0.034 mL, 1.5 equiv) was added to the reaction, and stirring was continued for 1 h at 0 °C, and for additional 2 h at room temperature, while exposed to air, when the color turned brown. The solvent was evaporated, and the crude product was subjected directly to flash-chromatography purification (hexanes/EtOAc 1:2) to give **15** as a colorless oil (17 mg, 64% for two steps, from **13**): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 5.21 (m, 1H), 5.18 (m, 1H), 5.09 (d, $J$ = 5.3 Hz, 1H), 4.38-4.50 (2H), 1.83 (s, br, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 175.2, 137.9, 115.7, 83.25, 73.35, 73.25, 19.17; TLC Rf 0.29 (hexanes/EtOAc 1:2); IR (NaCl, cm$^{-1}$) 3200-3600, 1775, 1651; HRMS(FAB) $[M+H]^+$ calcd. for $C_7H_{12}O_3$ 159.0659, found 159.0665.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4.0657
4.0897
4.1013
4.1253
4.1385
4.1493
4.1613
4.1733
4.1851
4.2085
PPM
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3
4
5
6
7
8
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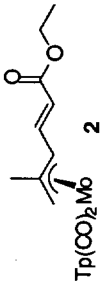
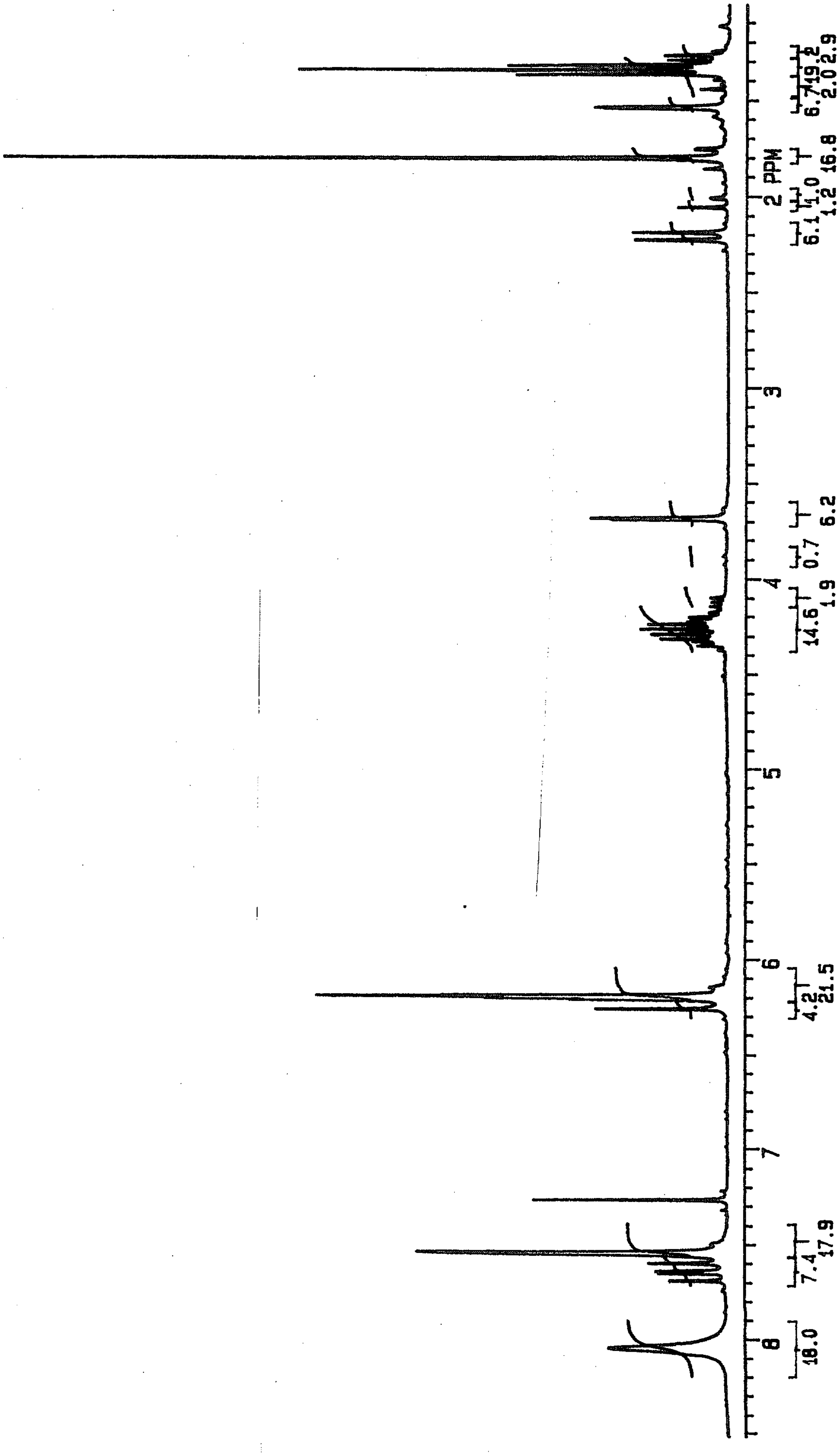
13.37
3.15
15.76
15.90


O
O
Tp(CO)₂Mo

2


8
7
6
5
4
3
2 PPM
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7.4
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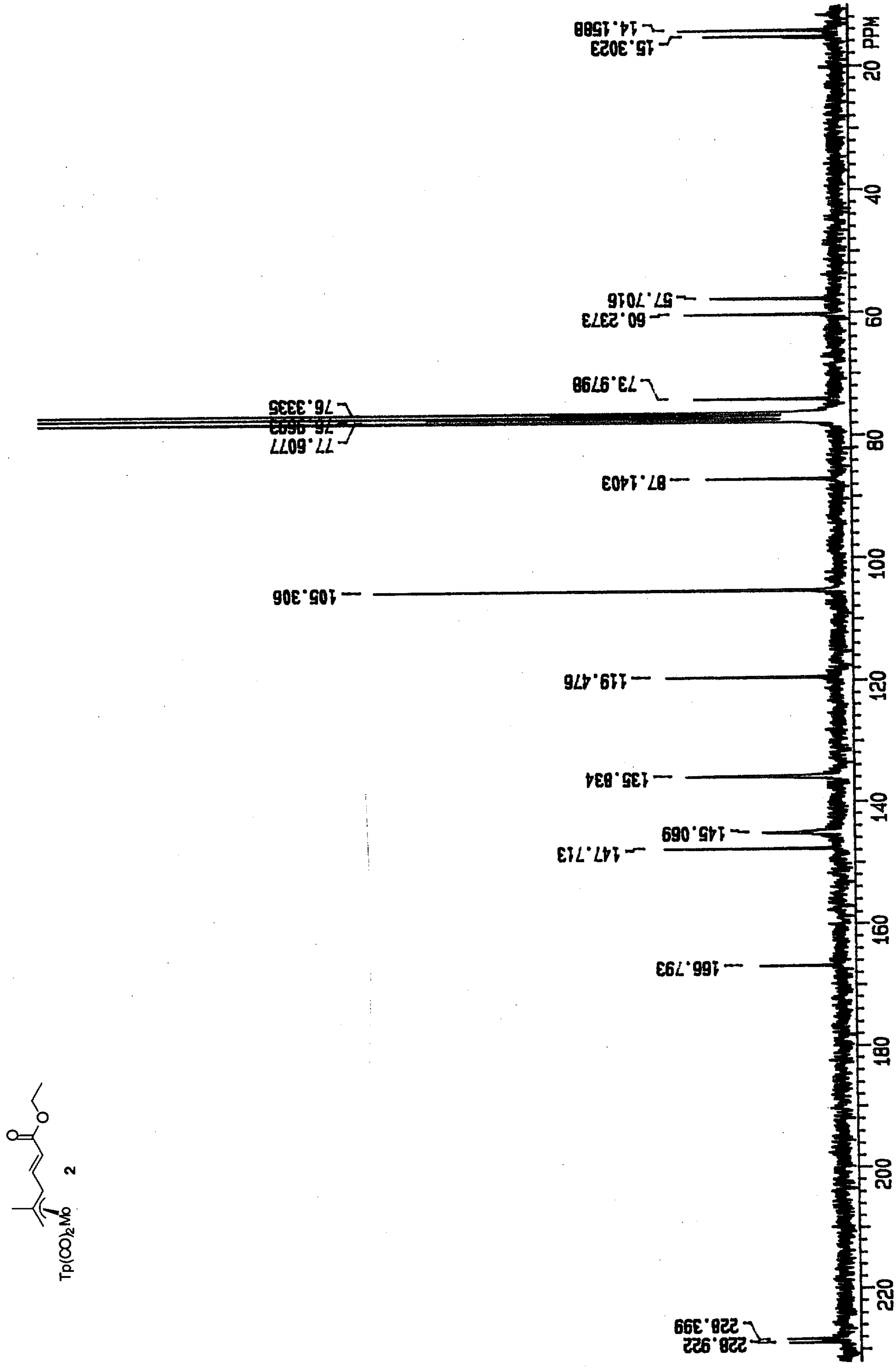
4.2
21.5
14.6
1.9
0.7
6.2
6.1
1.2
1.0
16.8
6.7
19.2
2.0
2.9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73.9798
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119.476
135.834
145.069
147.713
166.793
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PPM
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40
60
80
100
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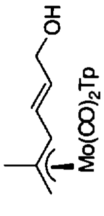
140
160
180
200
220
Tp(CO)2Mo

2



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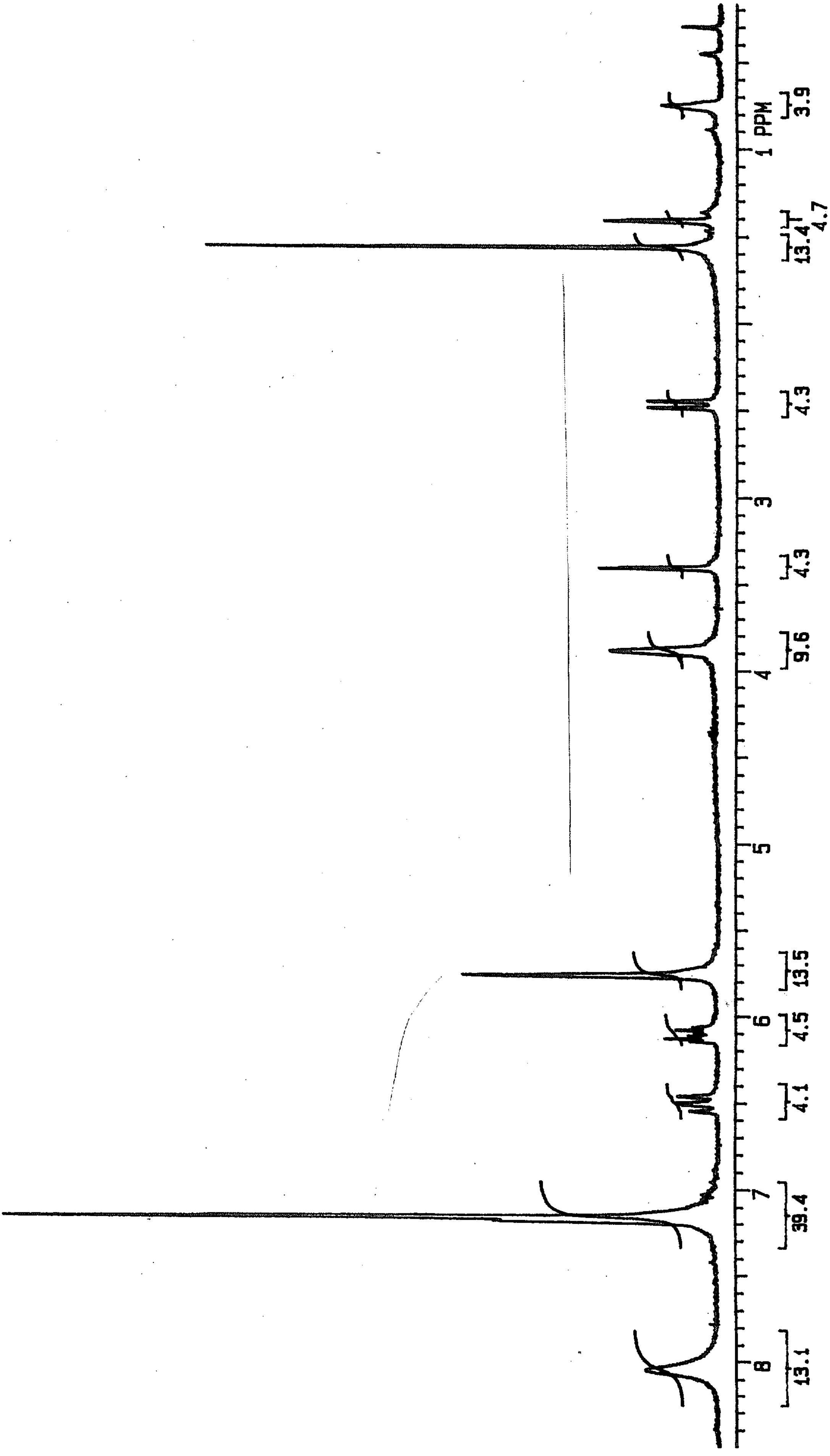

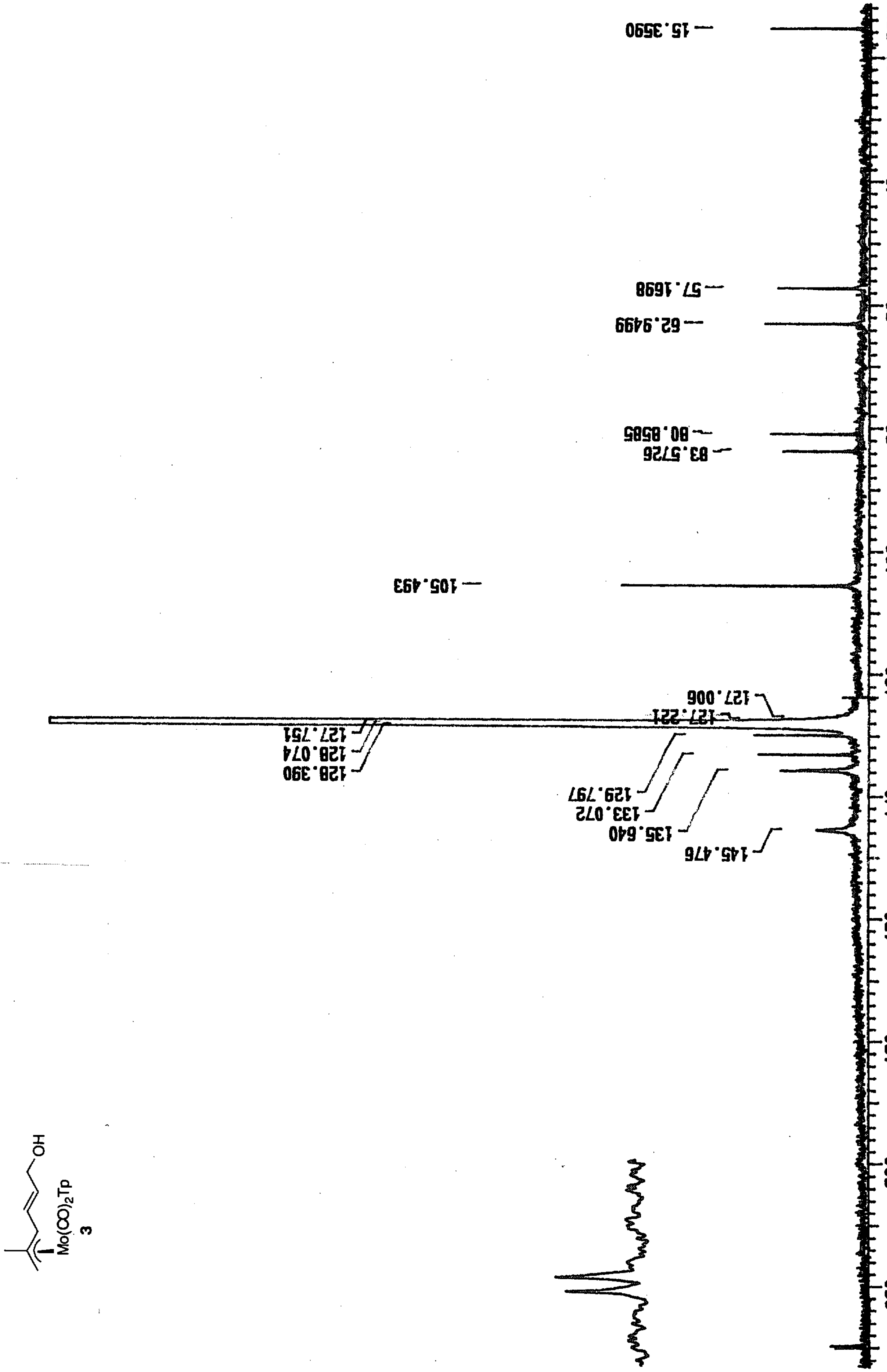
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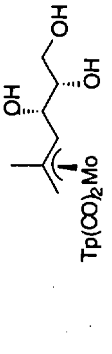
129.797
133.072
135.640
145.476
PPM
20
40
60
80
100
120
140
160
180
200
220
OH
Mo(CO)$_2$Tp
3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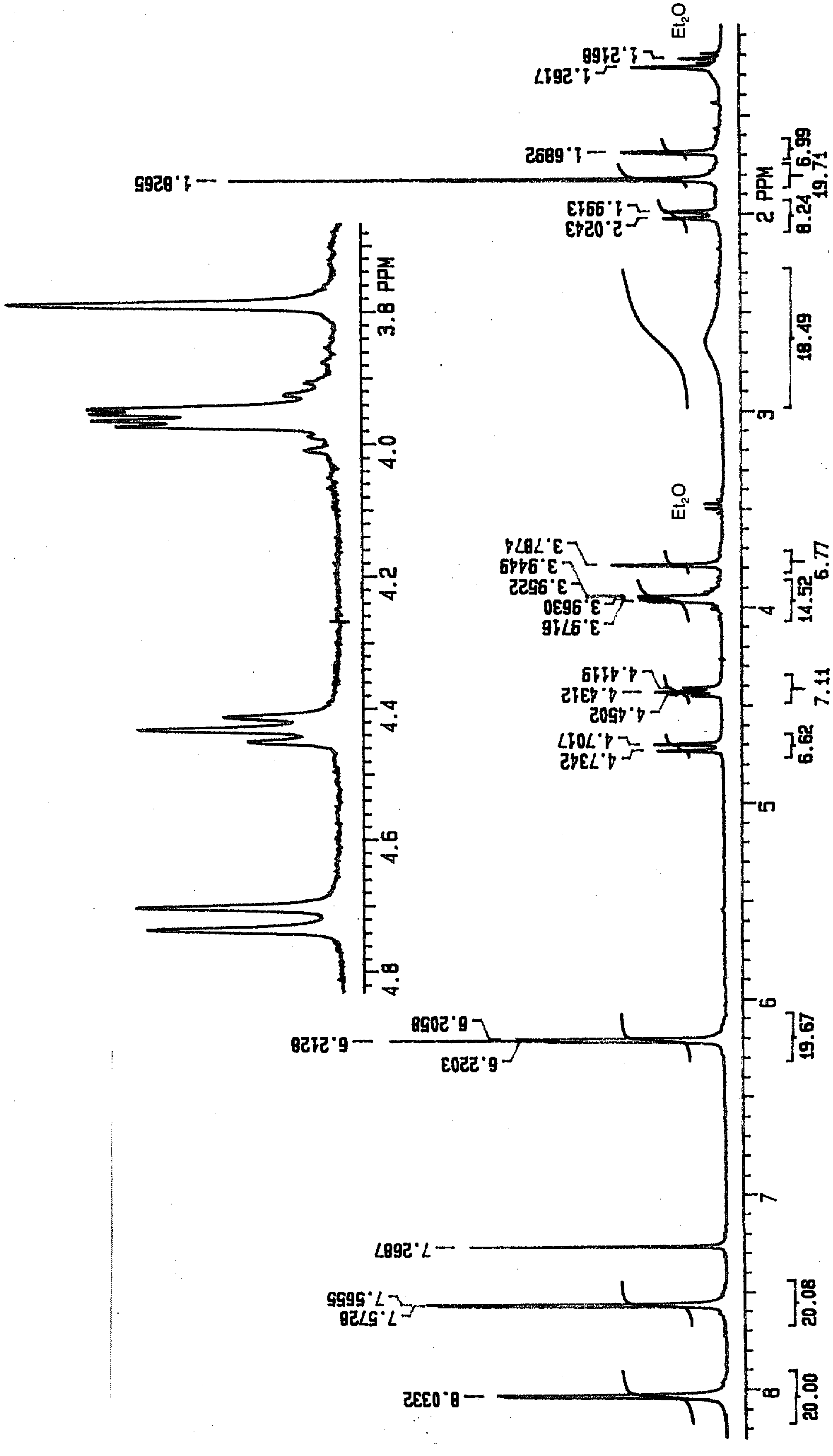
OH
OH
OH

4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Et$_2$O
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3.9630
3.9716
4.4119
4.4312
4.4502
4.7017
4.7342
6.2058
6.2128
6.2203
7.2687
7.5655
7.5728
8.0332
2 PPM
3
4
5
6
7
8
6.99
19.71
8.24
18.49
6.77
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20.08
20.00
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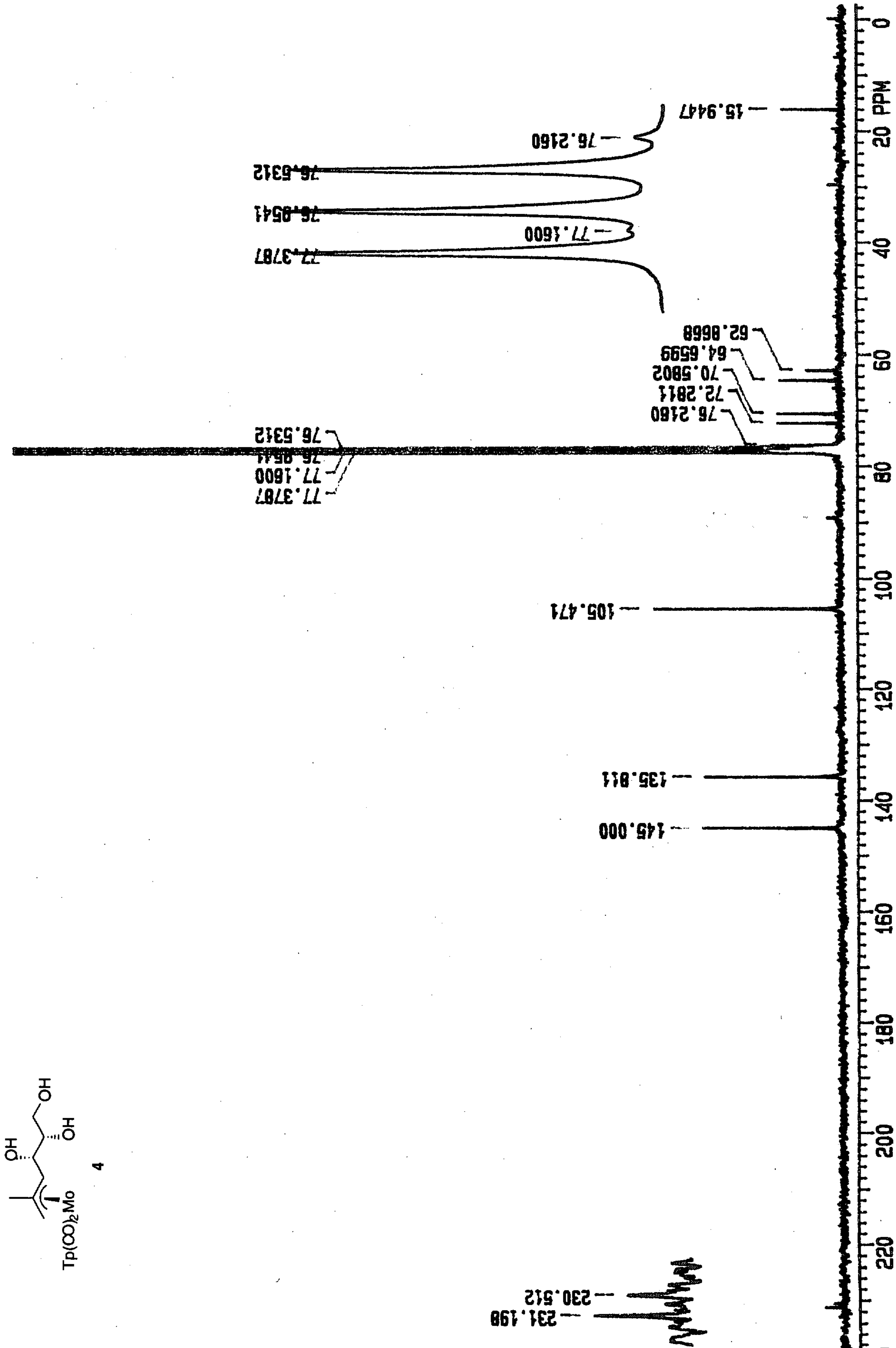
4.6
4.8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76.5312
76.8541
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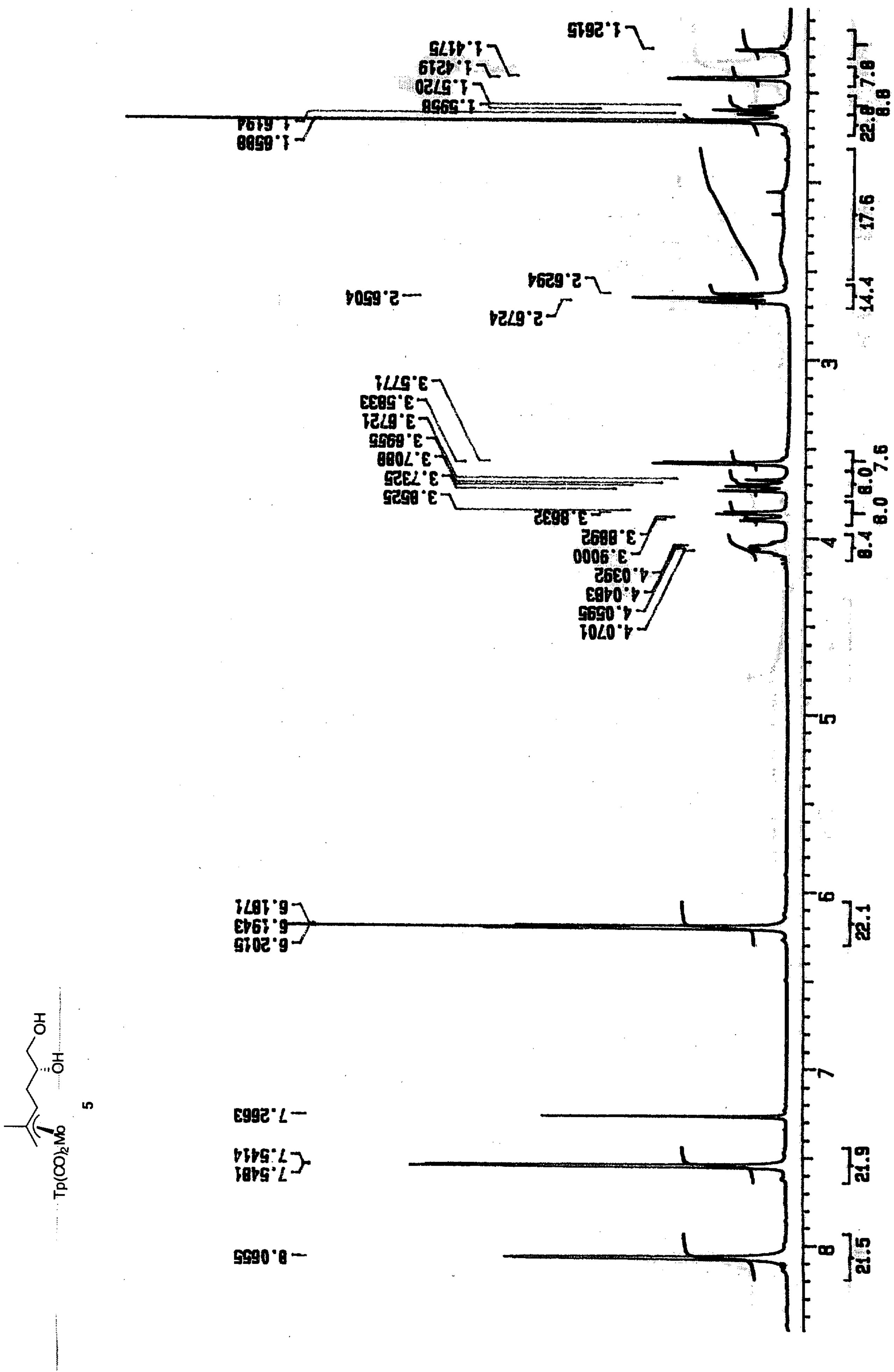
OH
OH
OH
4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3.5833
3.6721
3.6955
3.7088
3.7325
3.8525
3.8632
3.8892
3.9000
4.0392
4.0483
4.0595
4.0701
6.1871
6.1943
6.2015
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7.5481
8.0655
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8.8
22.8
17.6
14.4
7.6
6.0
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22.1
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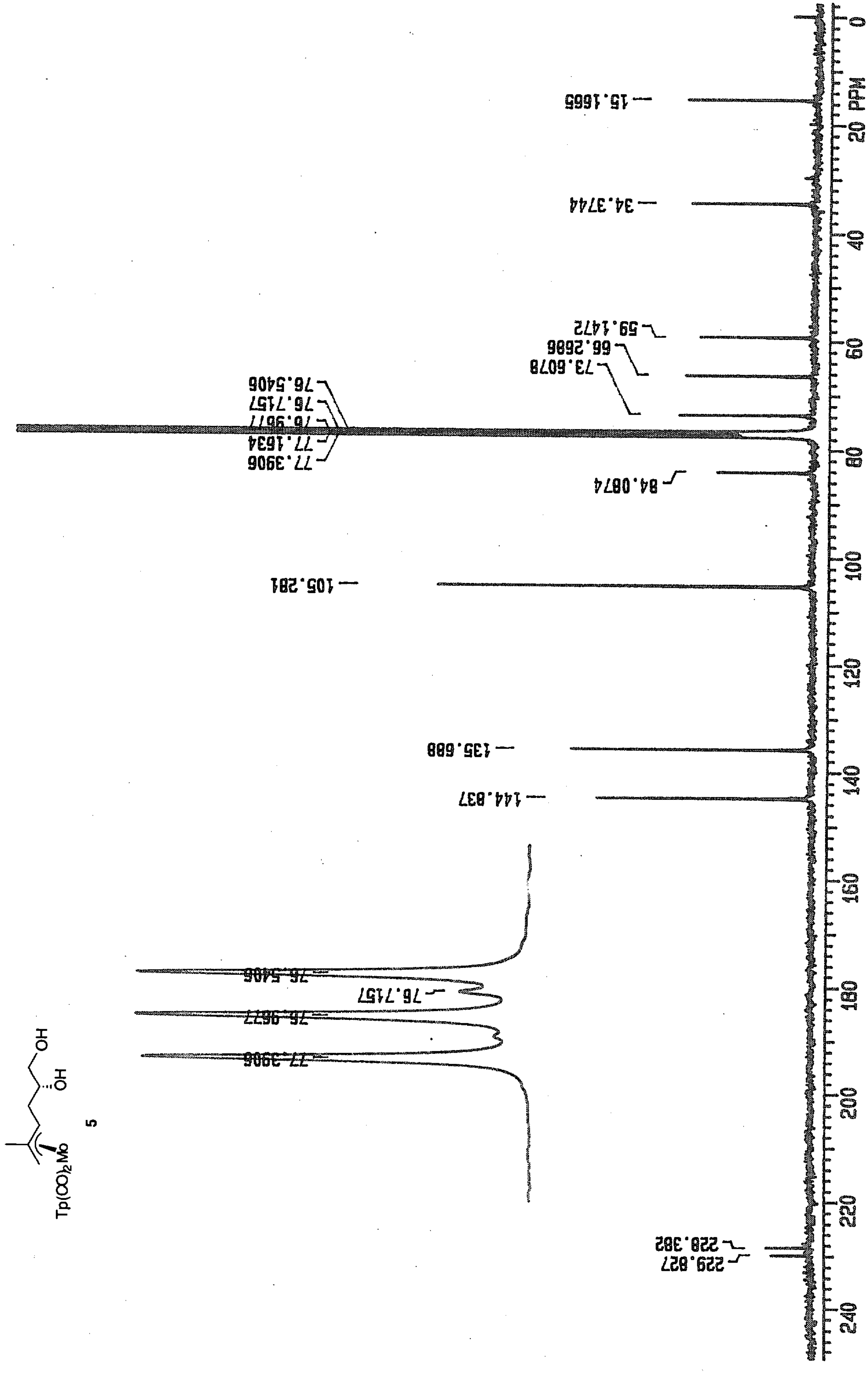
6
7
8
Tp(CO)2Mo
OH
OH

5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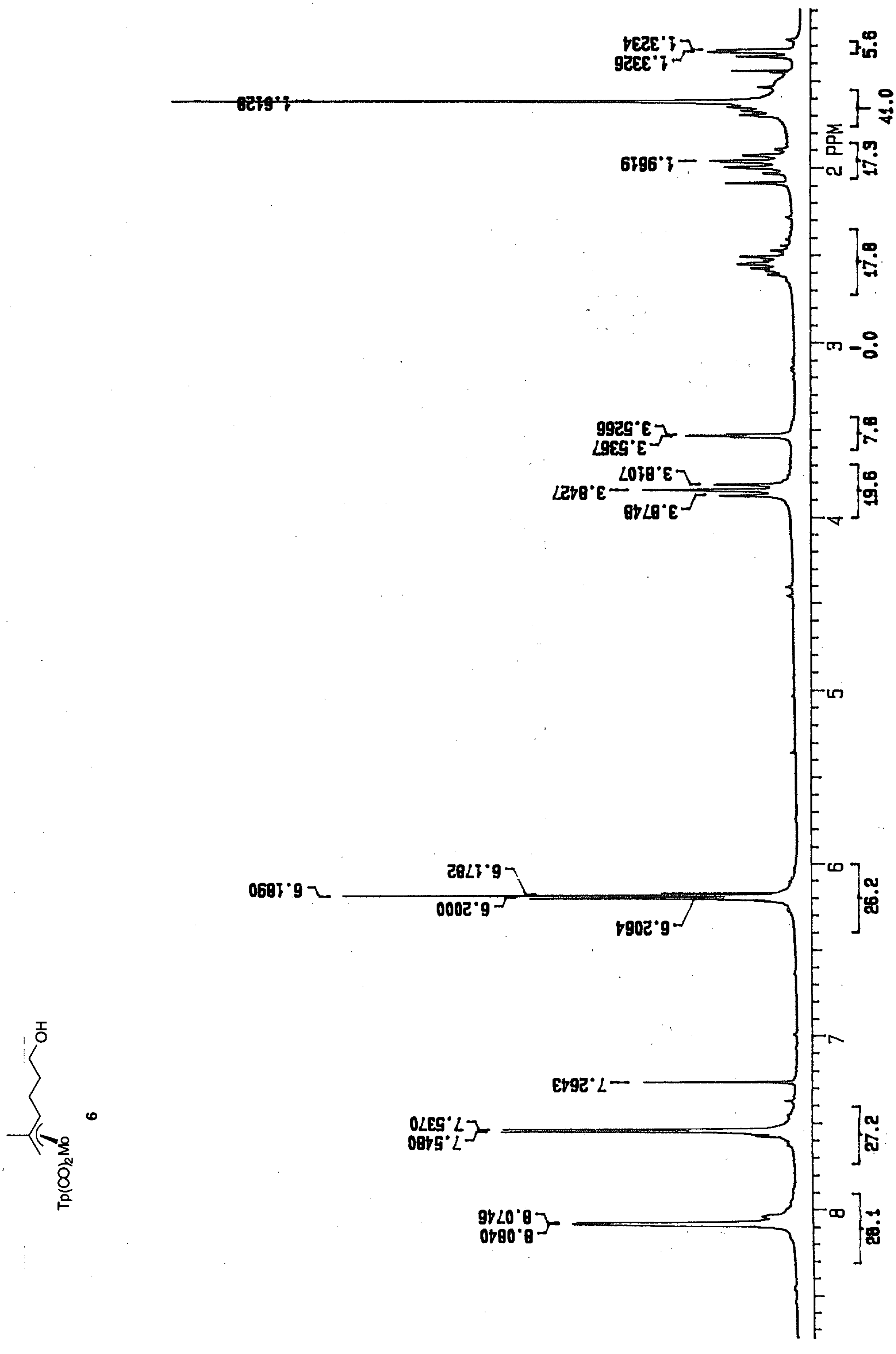
Tp(CO)2Mo
OH
OH

5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6.2000
6.2064
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7.5370
7.5480
8.0746
8.0840
2 PPM
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4
5
6
7
8
5.8
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17.8
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7.8
19.6
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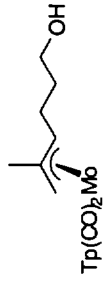
27.2
28.1
Tp(CO)$_2$Mo
OH
6



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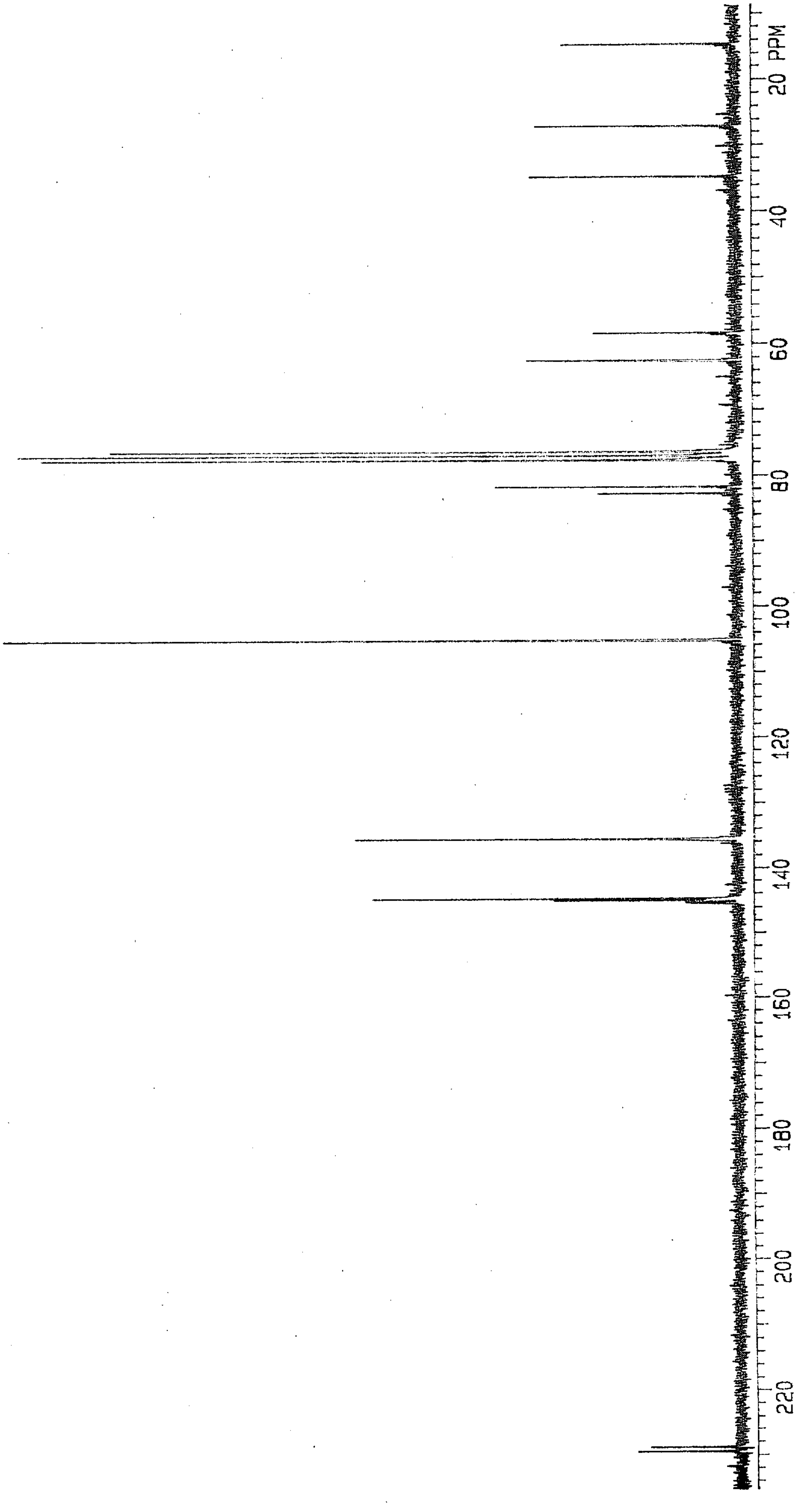

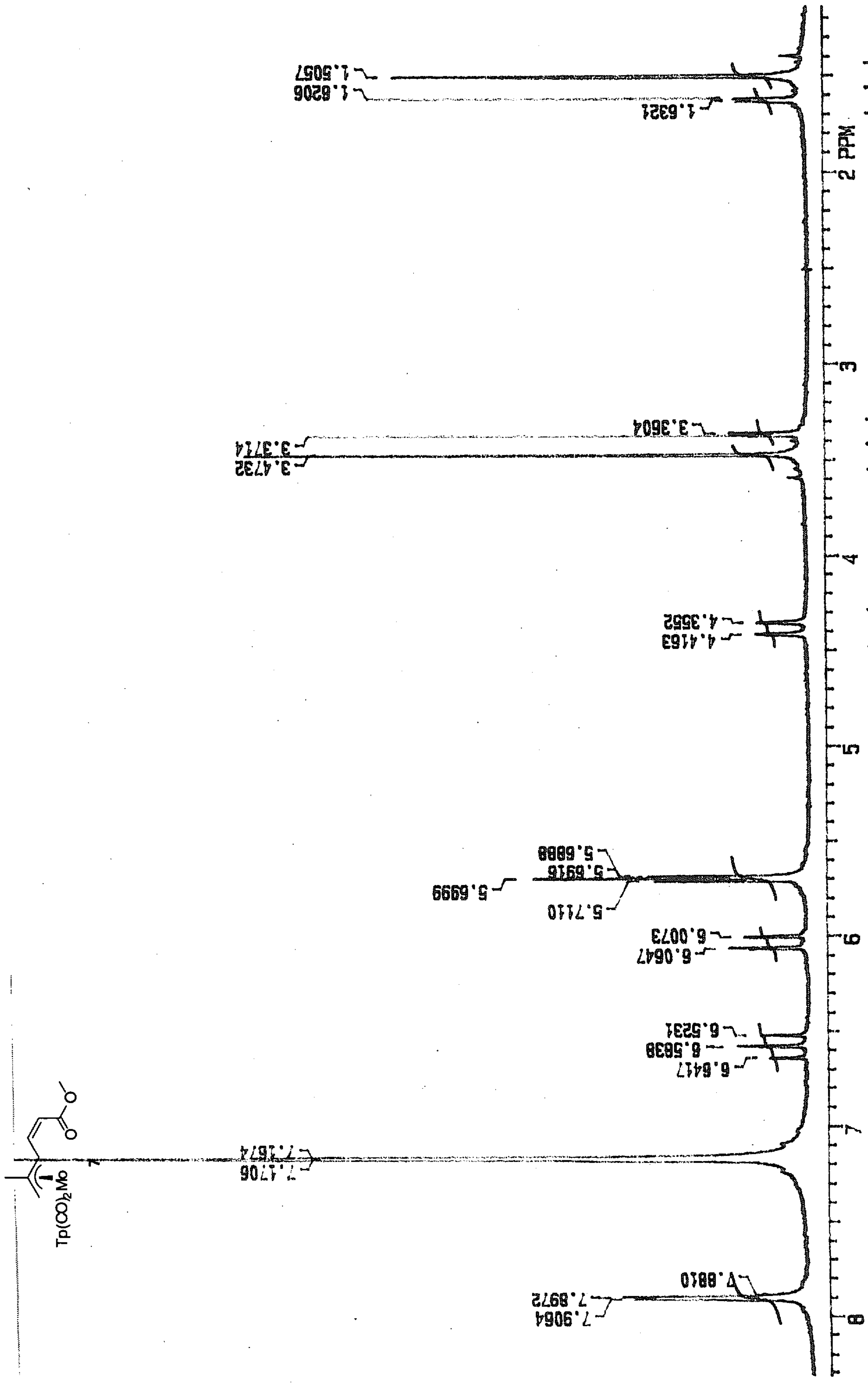
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5.6999
5.7110
6.0073
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6.5838
6.6417
7.1674
7.1706
7.8810
7.8972
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3
4
5
6
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4.75
4.36
12.92
4.70
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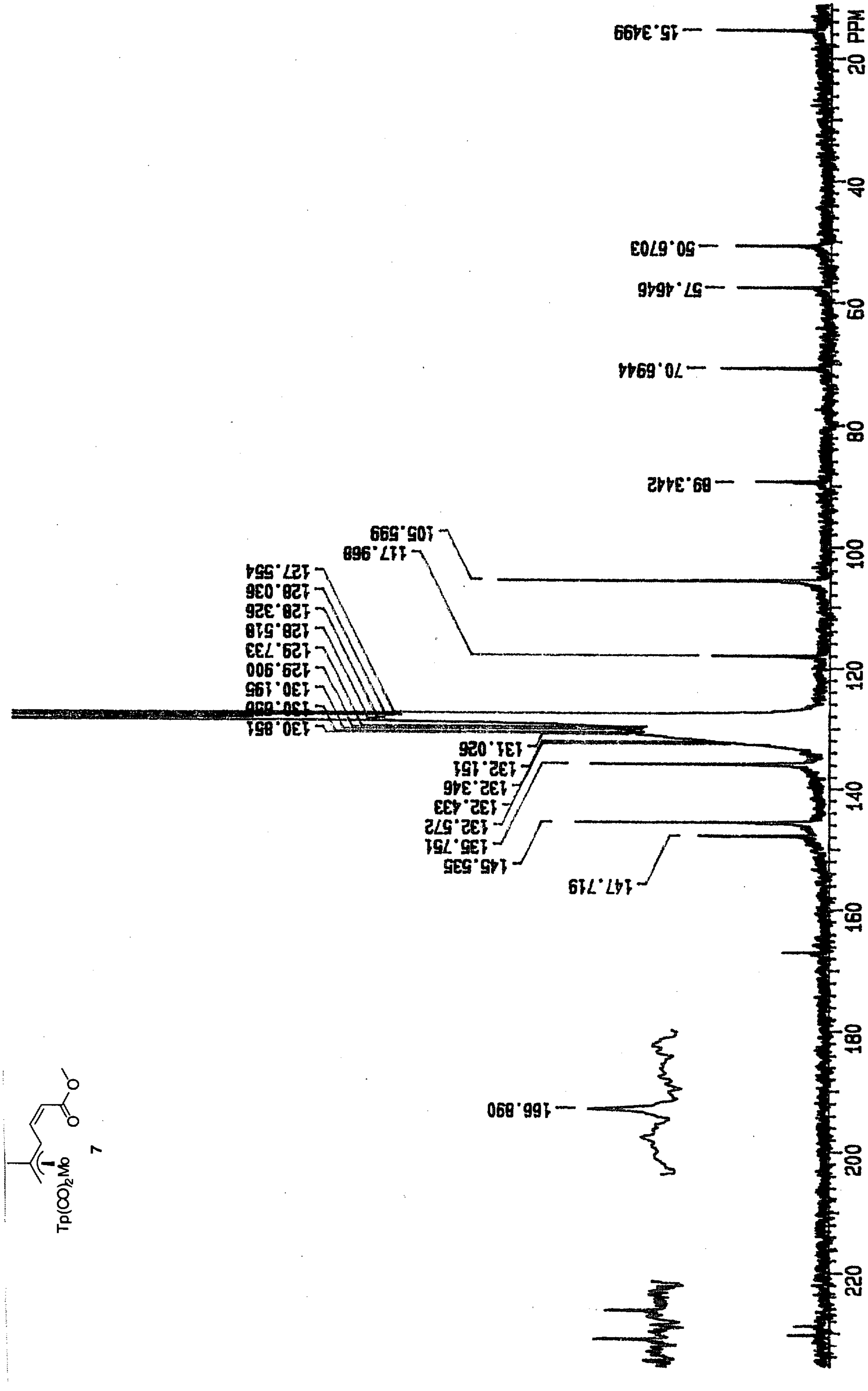
14.25
$Tp(CO)_2Mo$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130.195
130.851
131.026
132.151
132.346
132.433
132.572
135.751
145.535
147.719
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Tp(CO)$_2$Mo
PPM
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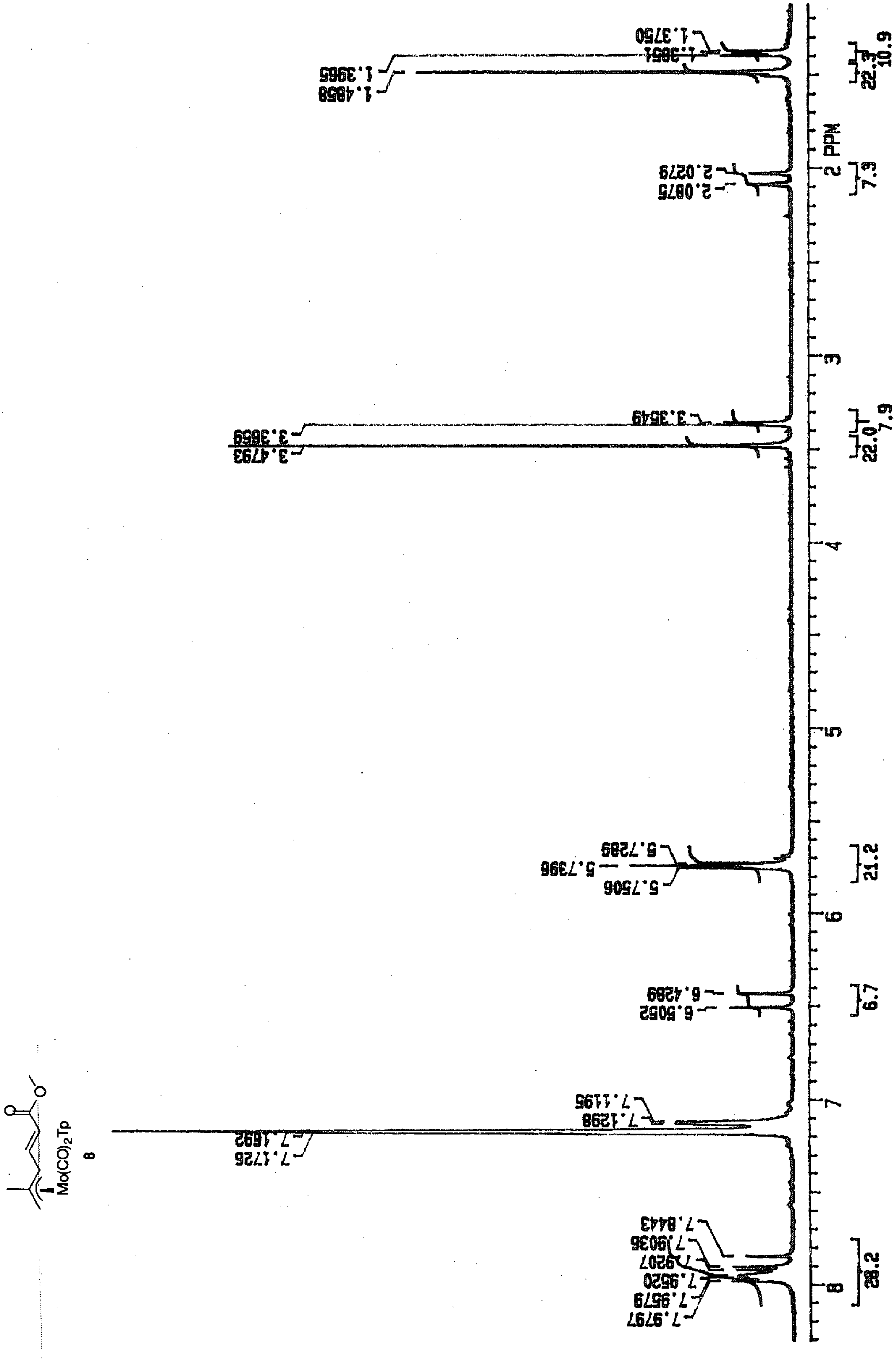
40
60
80
100
120
140
160
180
200
220

7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5.7396
5.7506
6.4289
6.5052
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7.1692
7.1726
7.8443
7.9036
7.9207
7.9520
7.9579
7.9797
2 PPM
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7
8
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7.9
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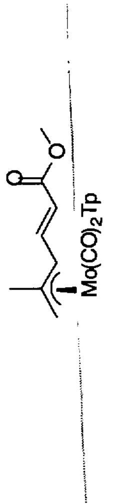
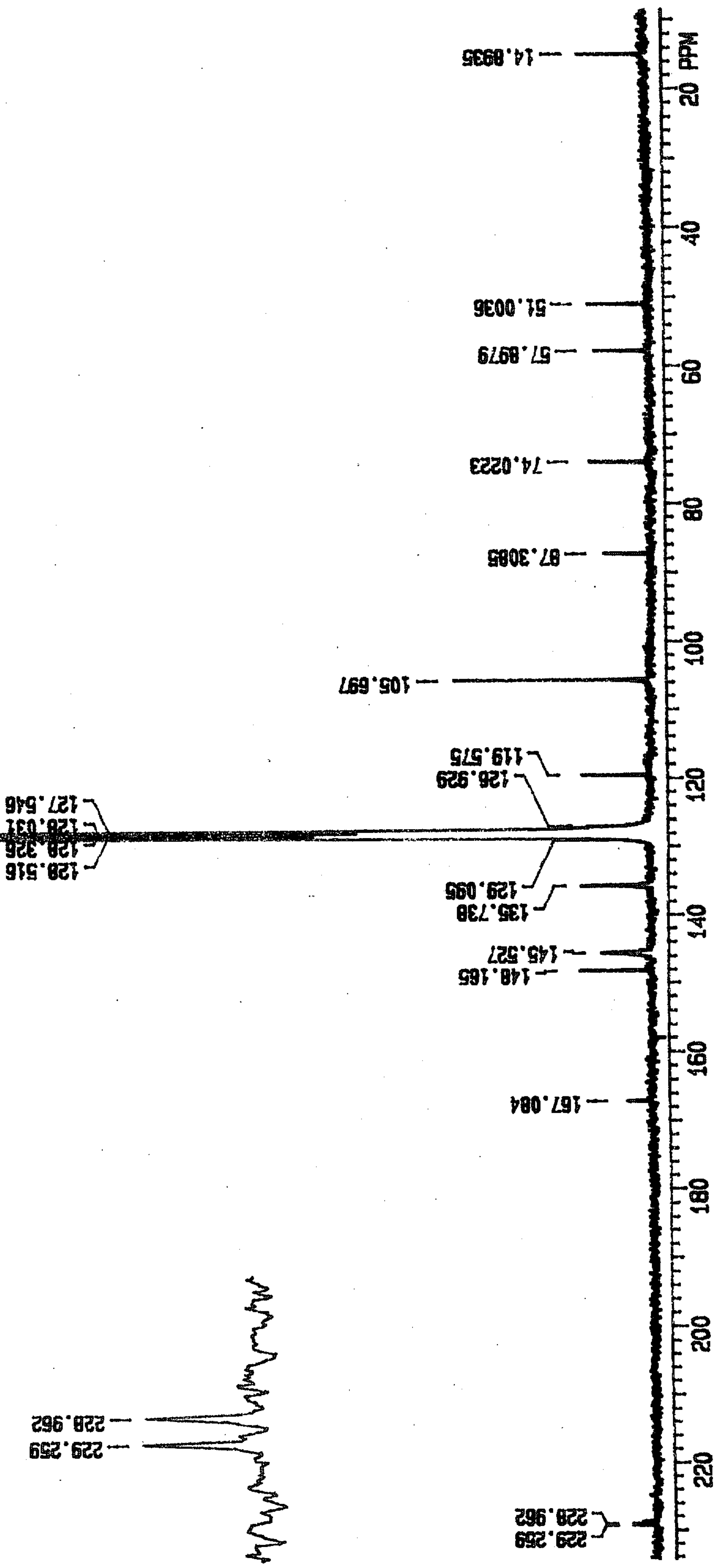
7.9
21.2
6.7
28.2

8


Mo(CO)$_2$Tp

8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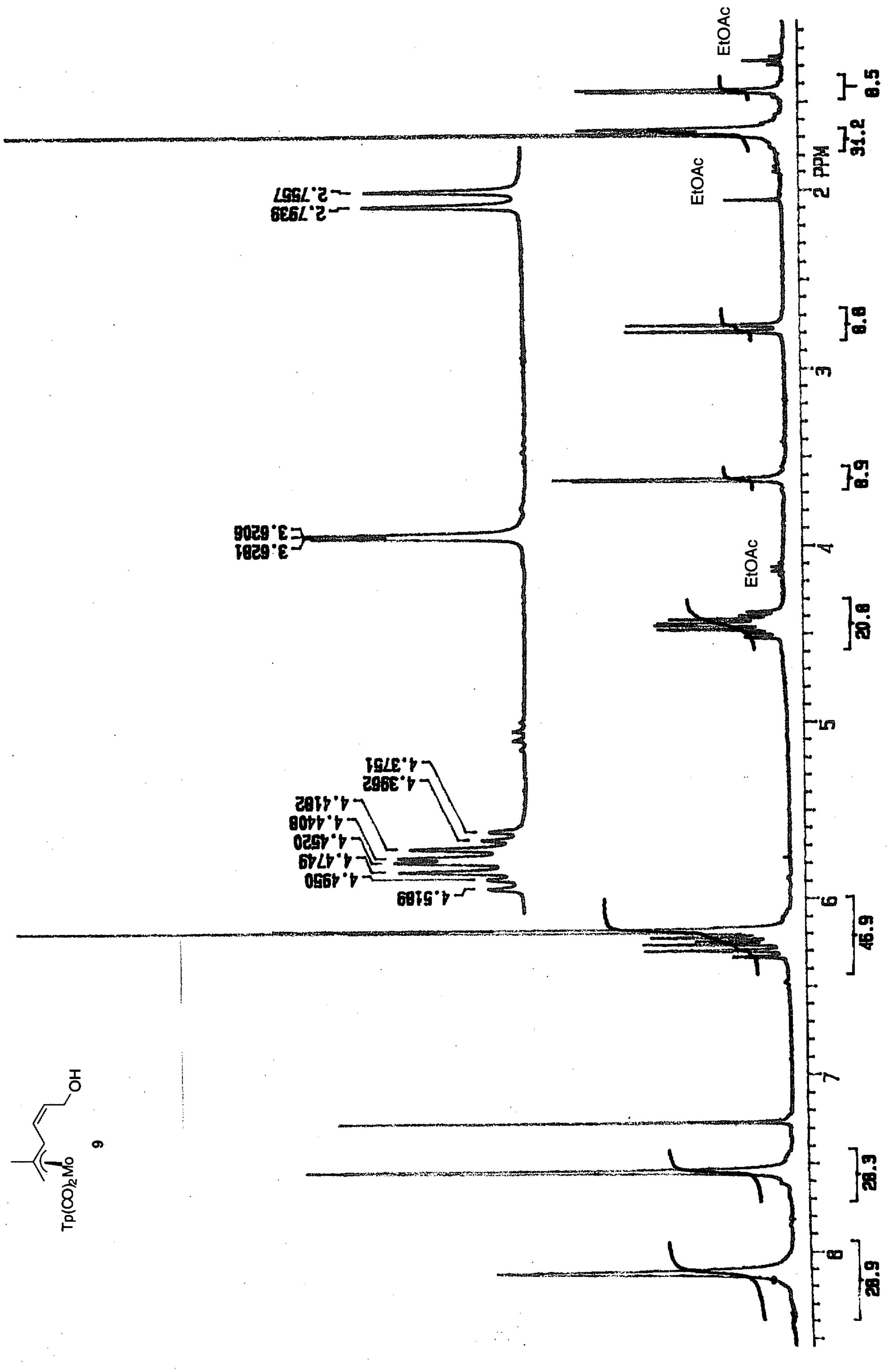
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EtOAc
EtOAc
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7
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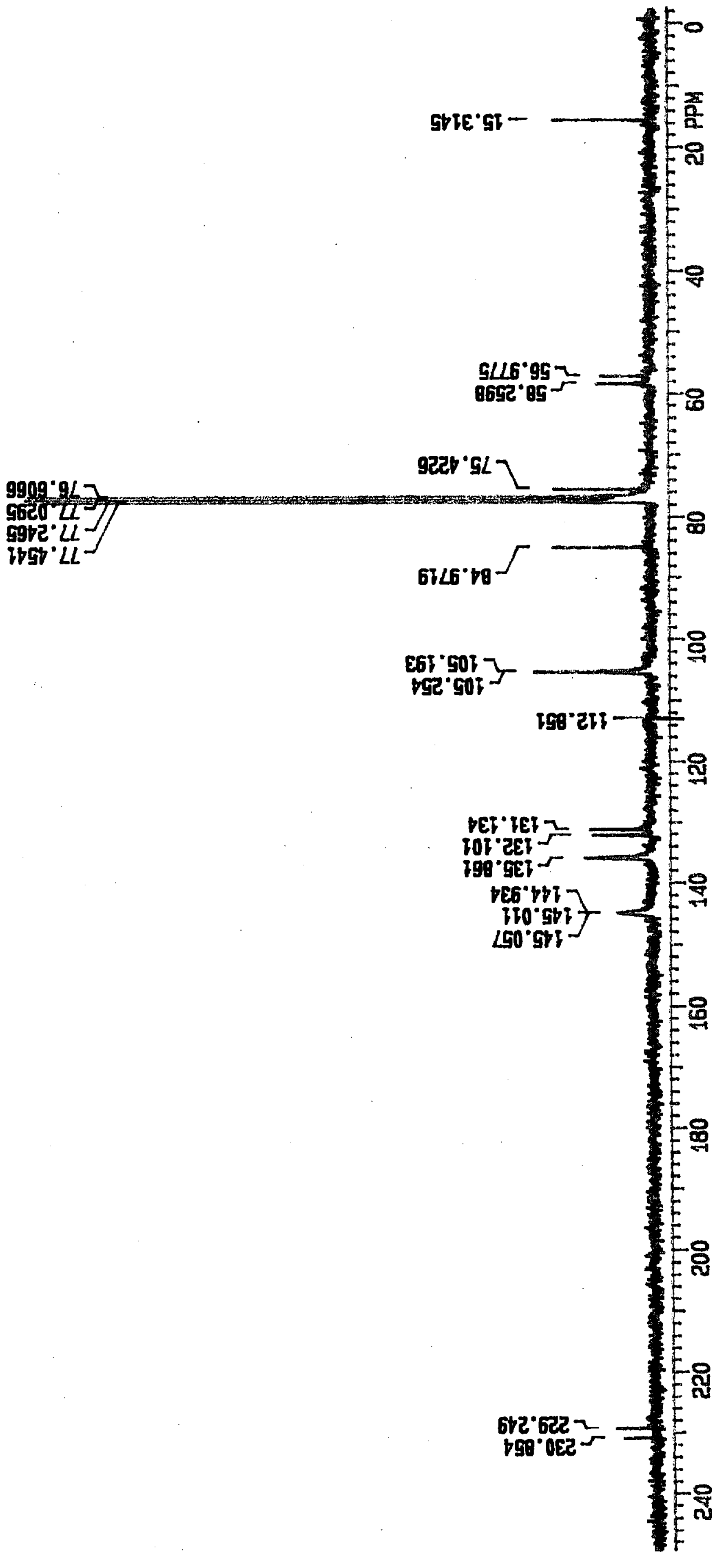
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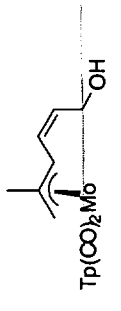
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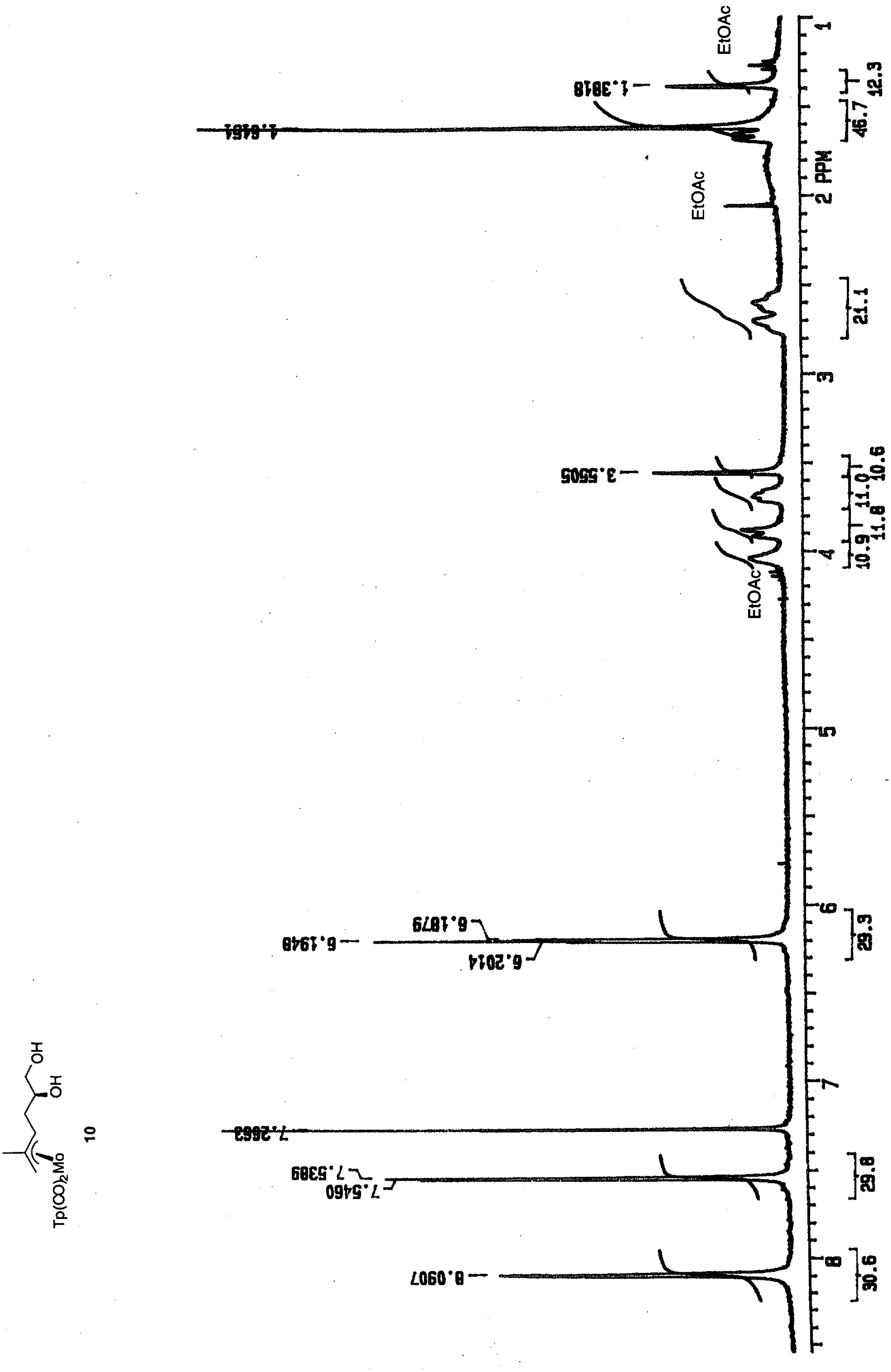
9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21.1
10.6
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29.8
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1
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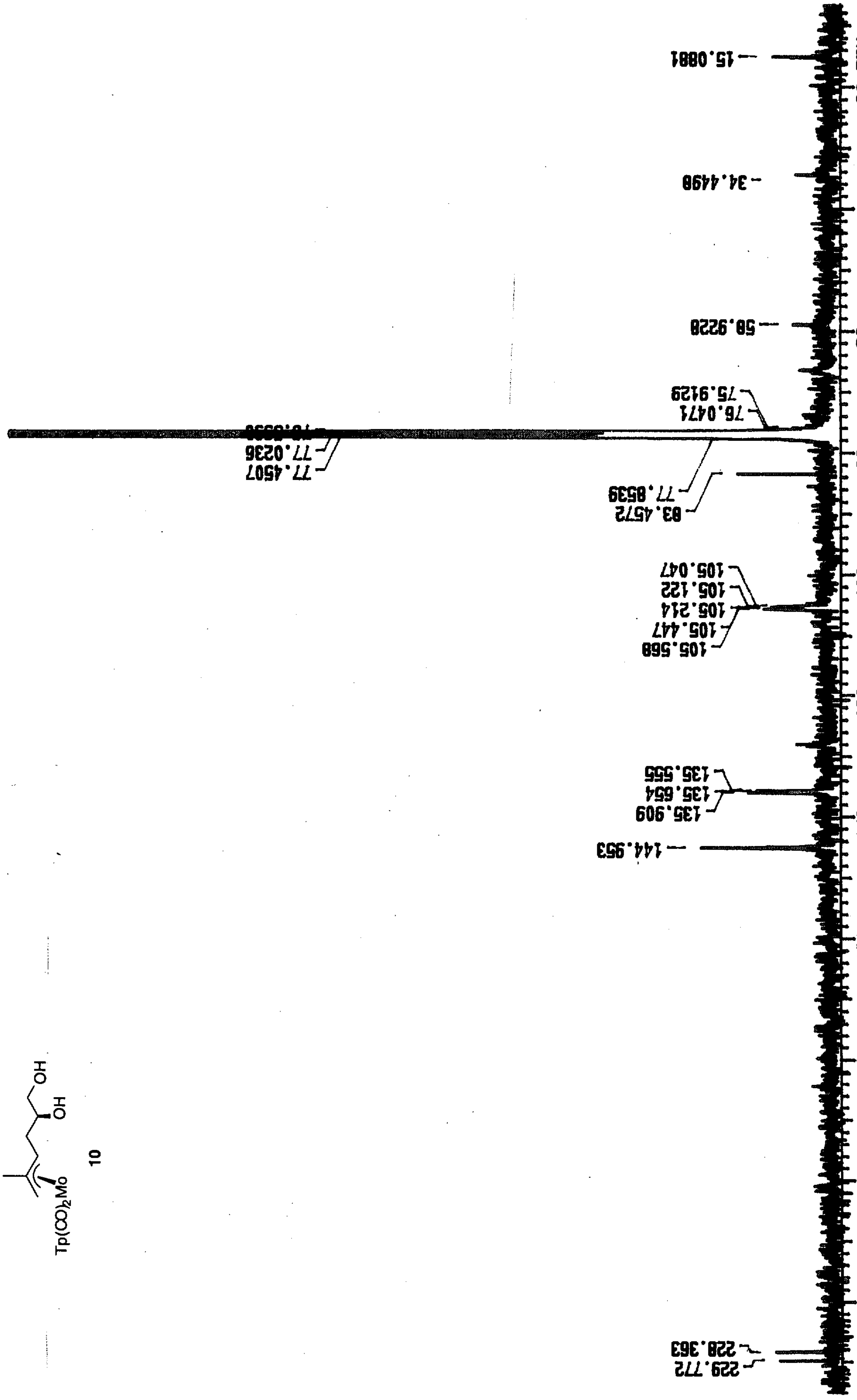
5
6
7
8

10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135.909
144.953
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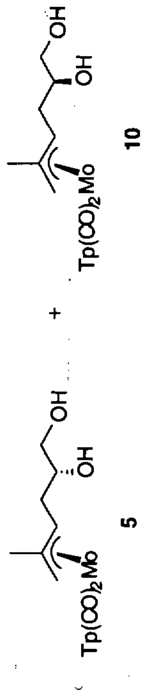
20 PPM
60
80
100
120
140
160
180
200
220
Tp(CO)₂Mo
OH
HO

10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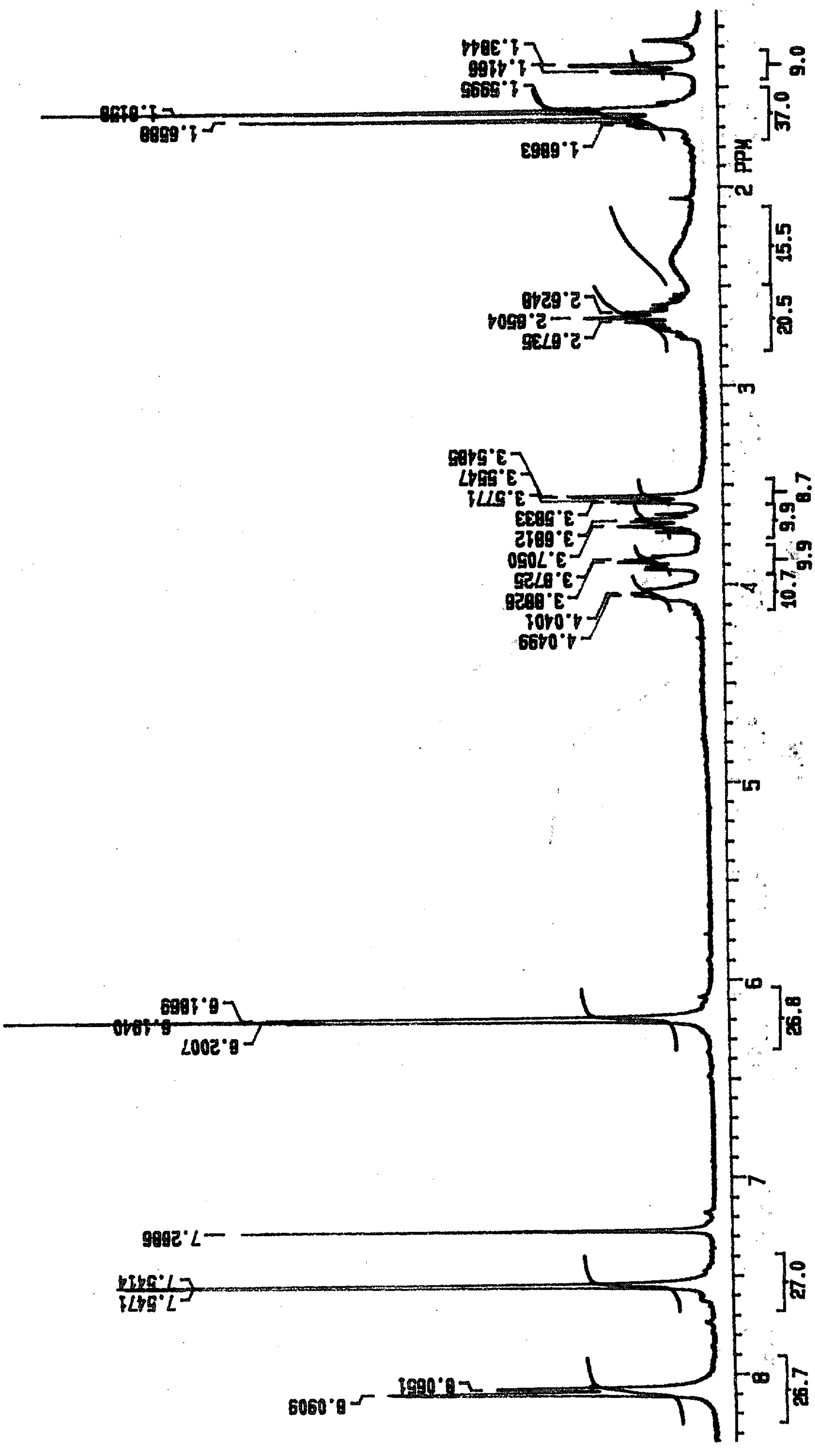
OH
OH
Tp(CO)2Mo
OH
OH
+

5

10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3.5547
3.5771
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PPM
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6
7
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9.9
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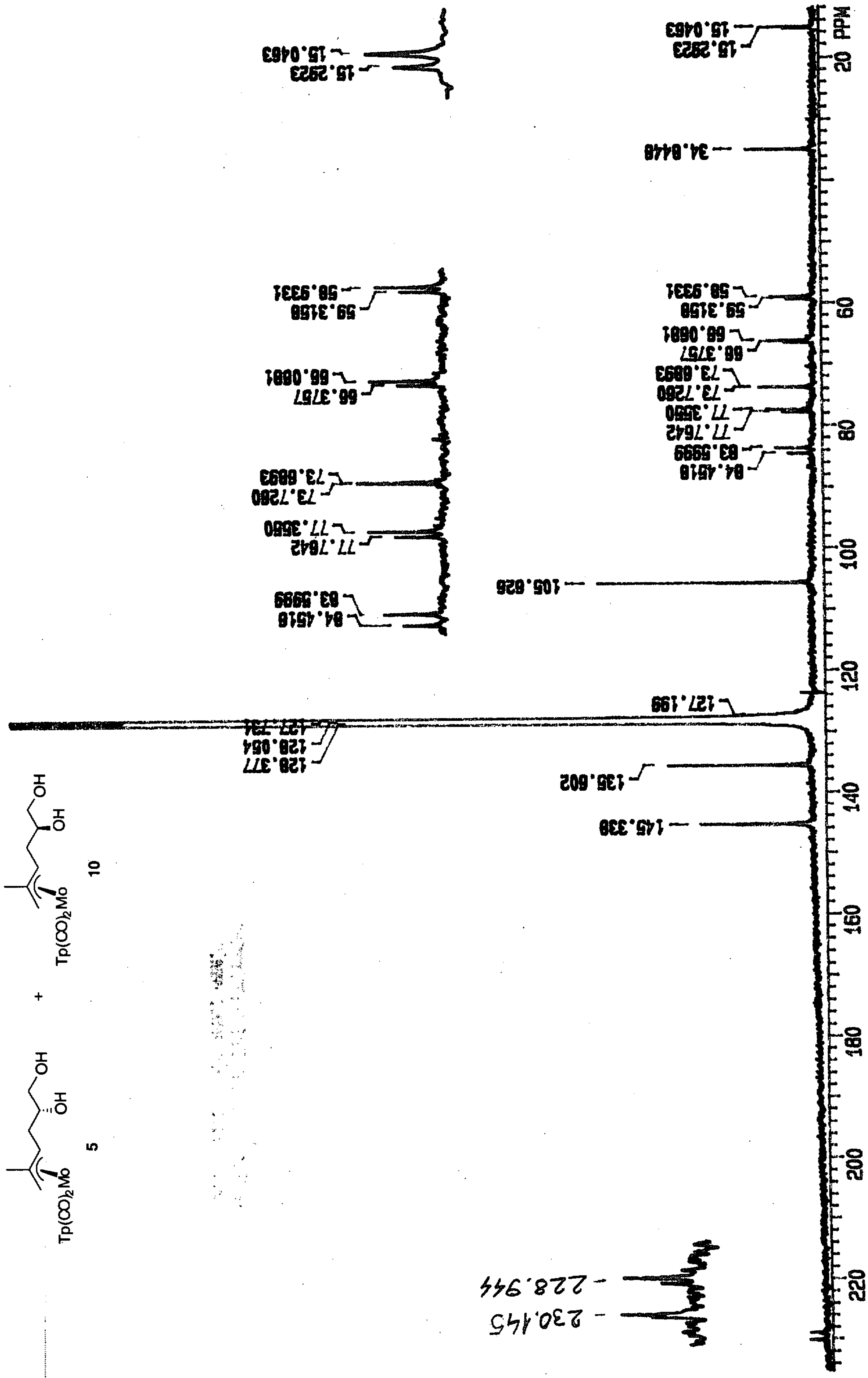
26.7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OH
5
+
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OH
OH
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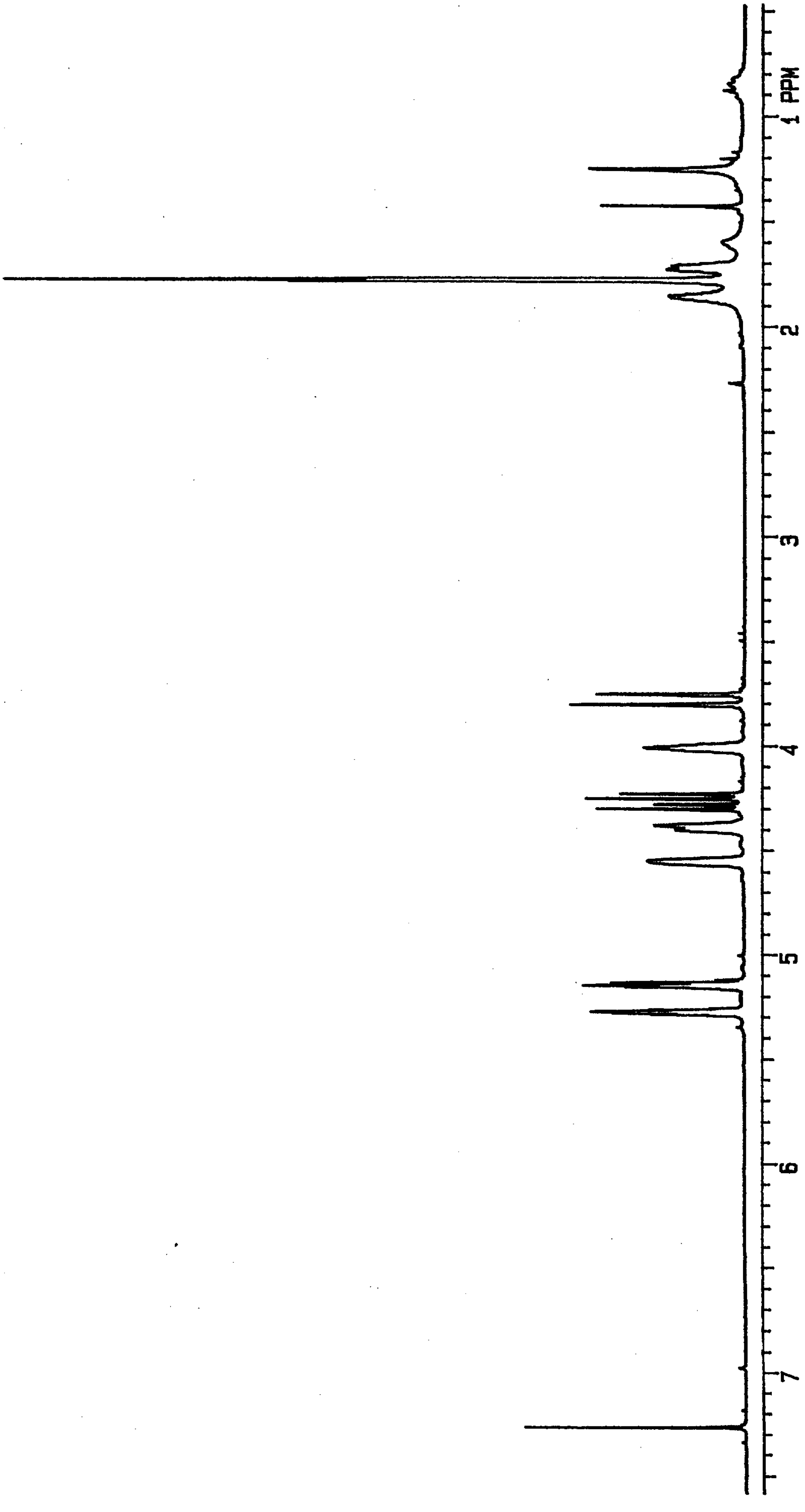
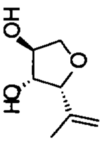
PPM
20
60
80
100
120
140
160
180
200
220





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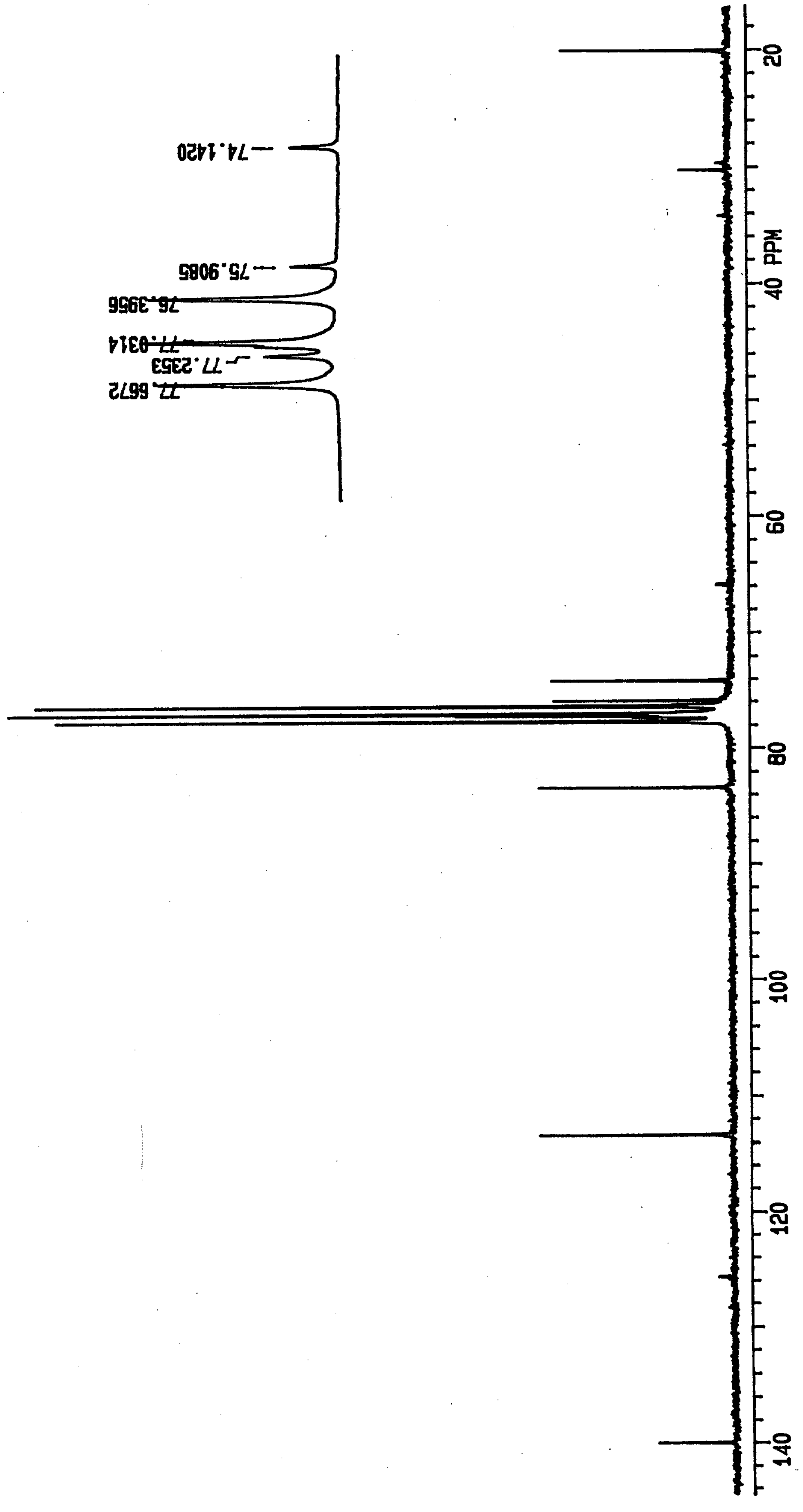
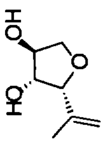
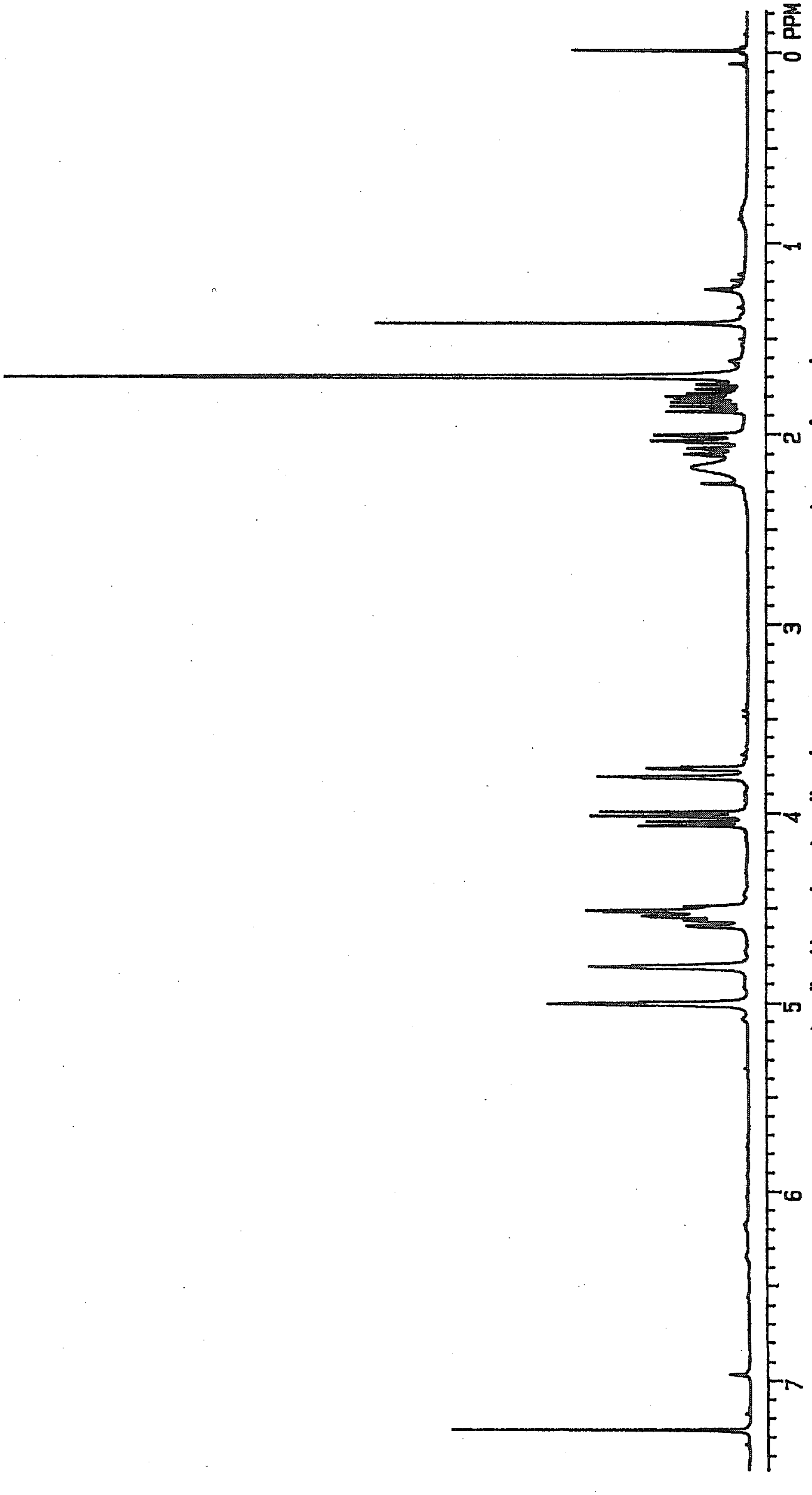
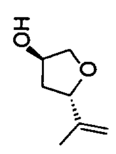

74.1420
75.9085
76.3956
77.0314
77.2353
77.6672
20
40 PPM
60
80
100
120
140


OH
HO
O

11





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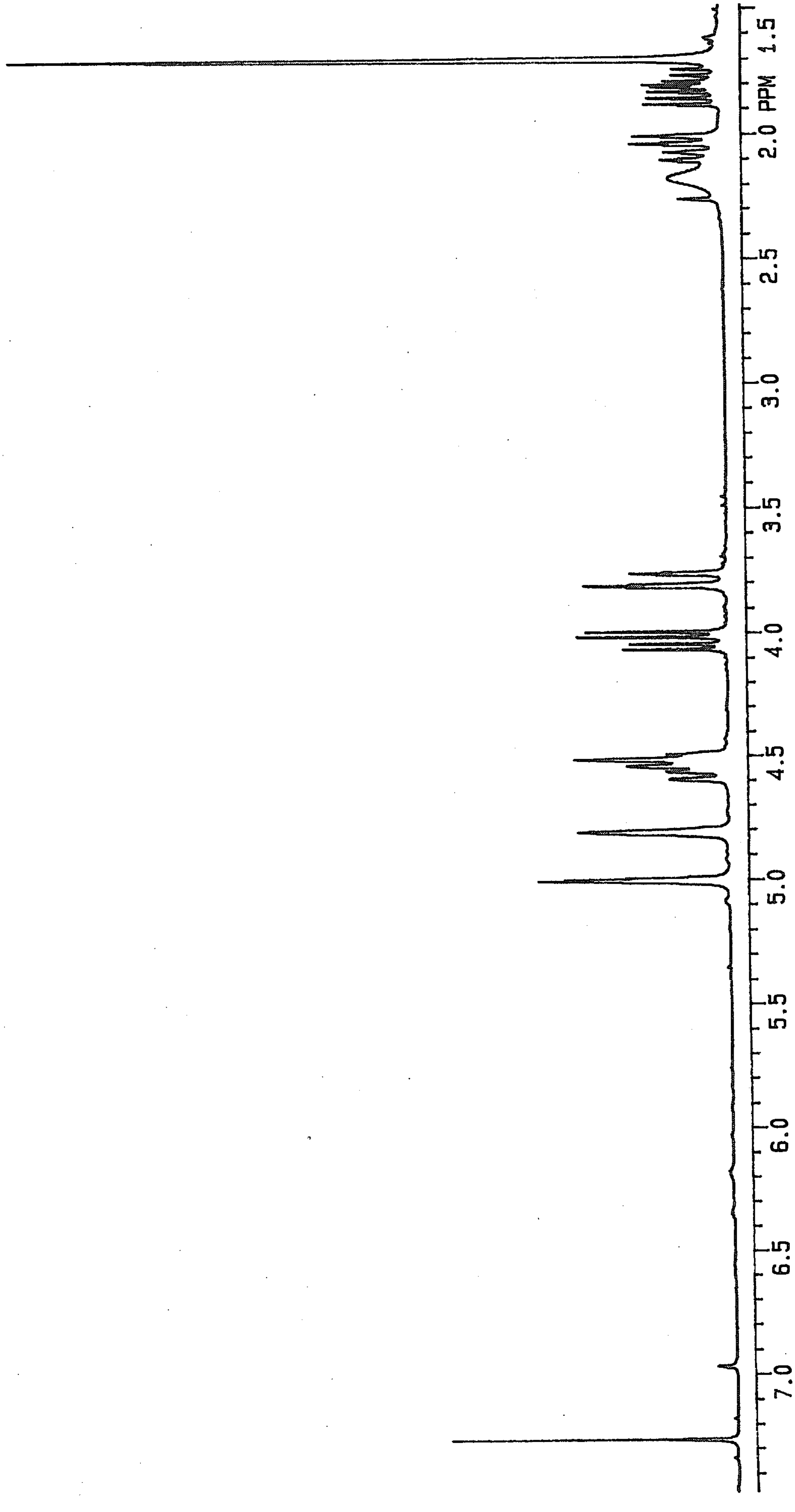

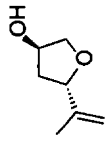

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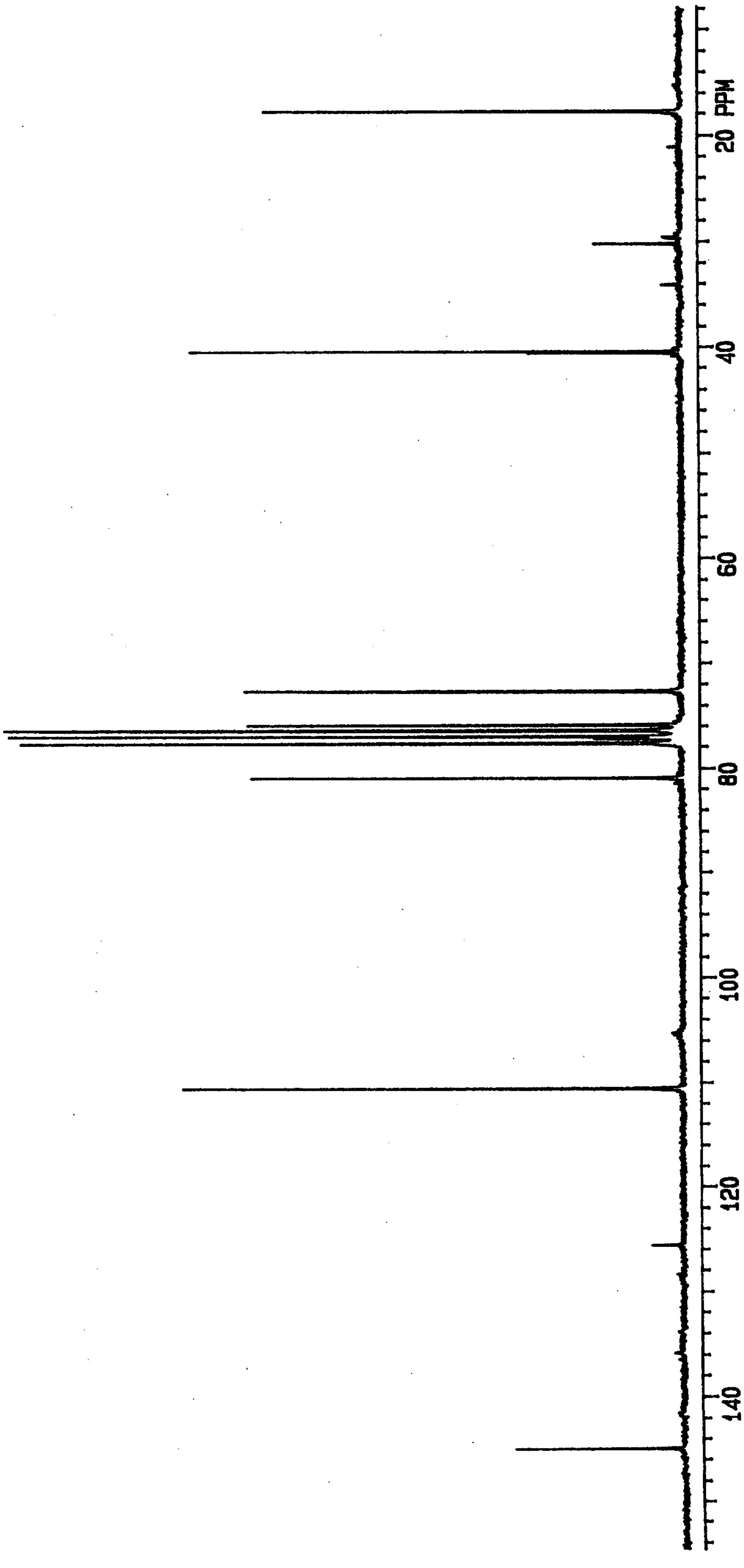
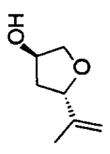
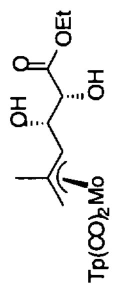
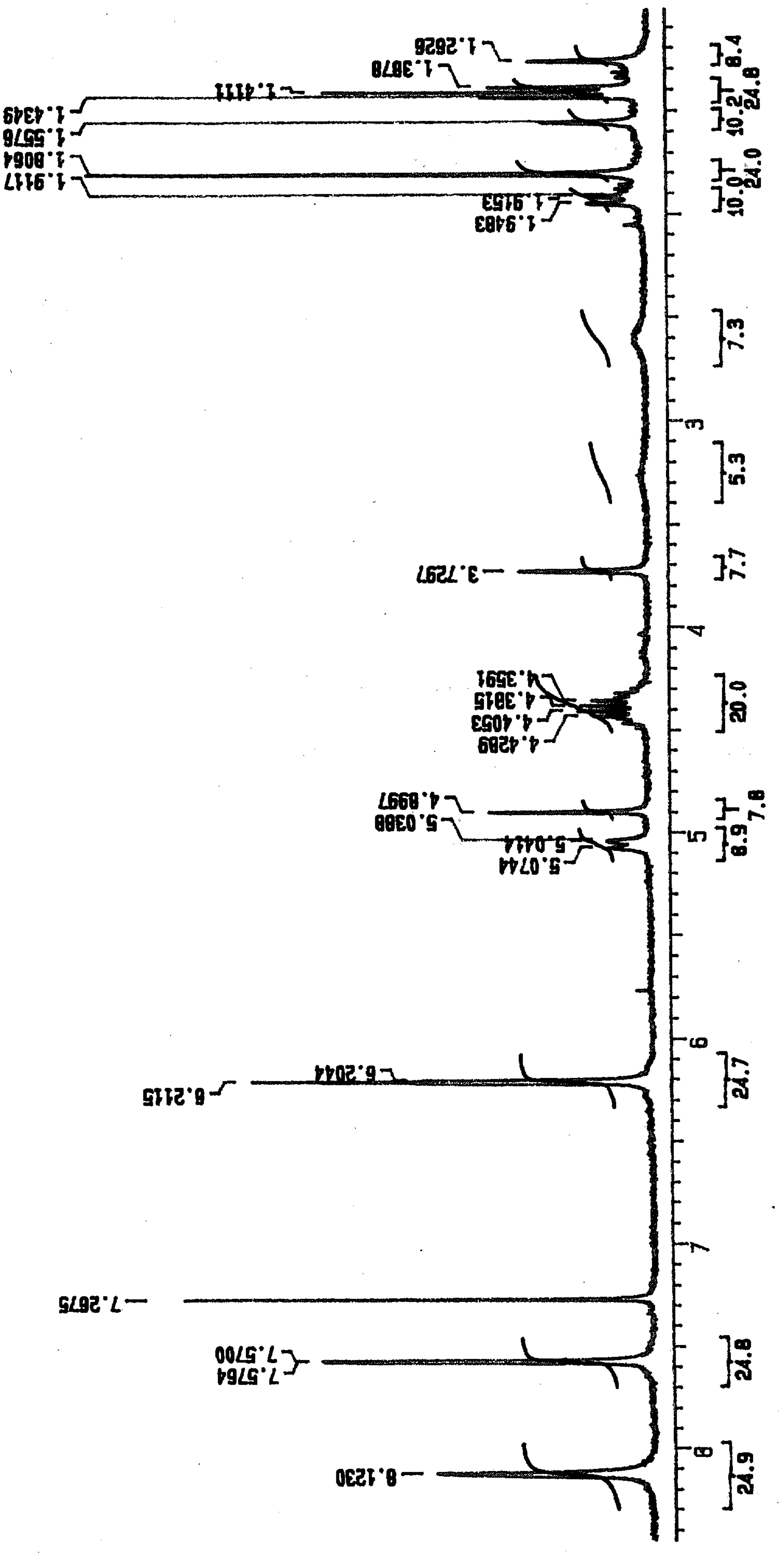


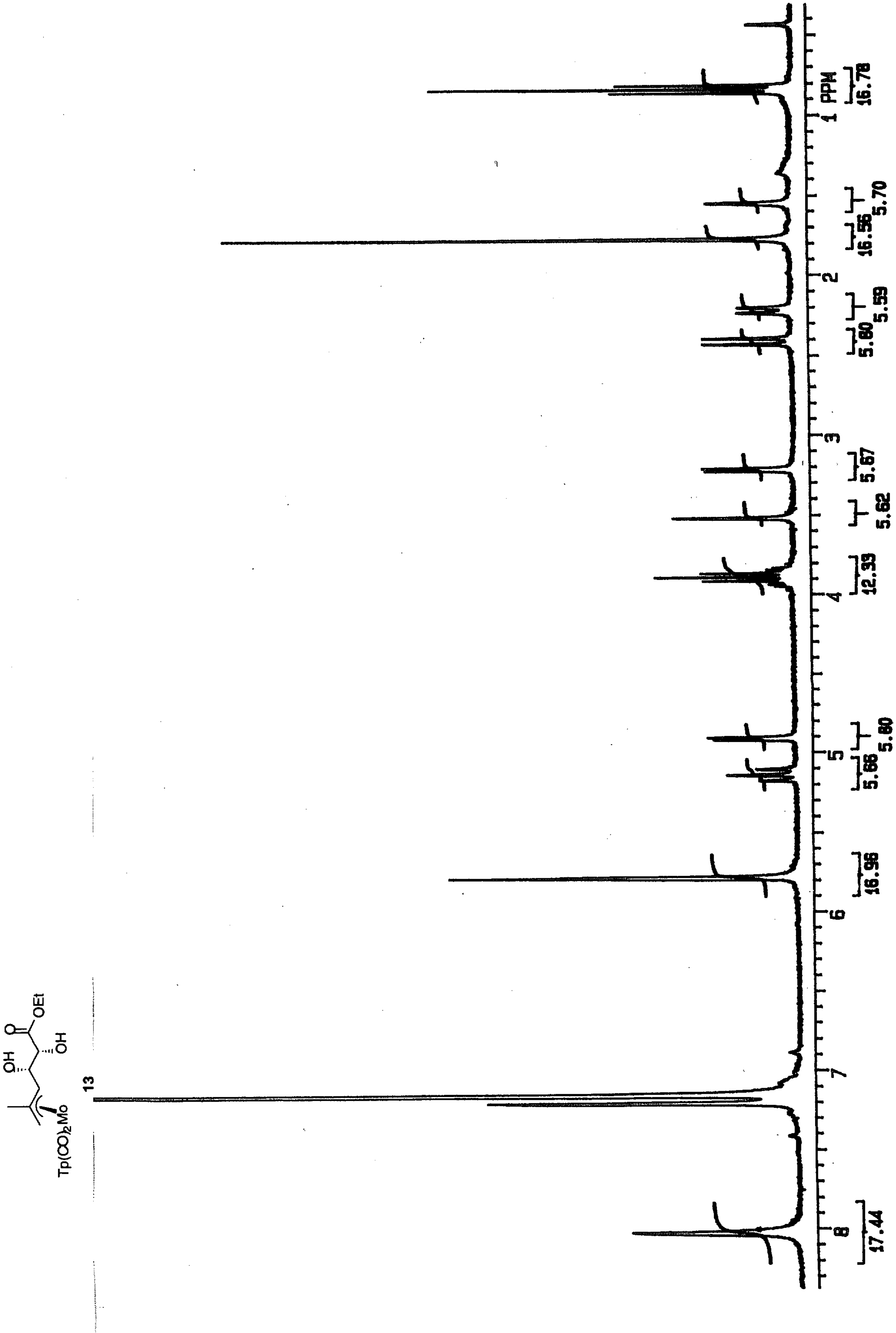


12


Tp(CO)$_2$Mo
OH
OH
O
OEt

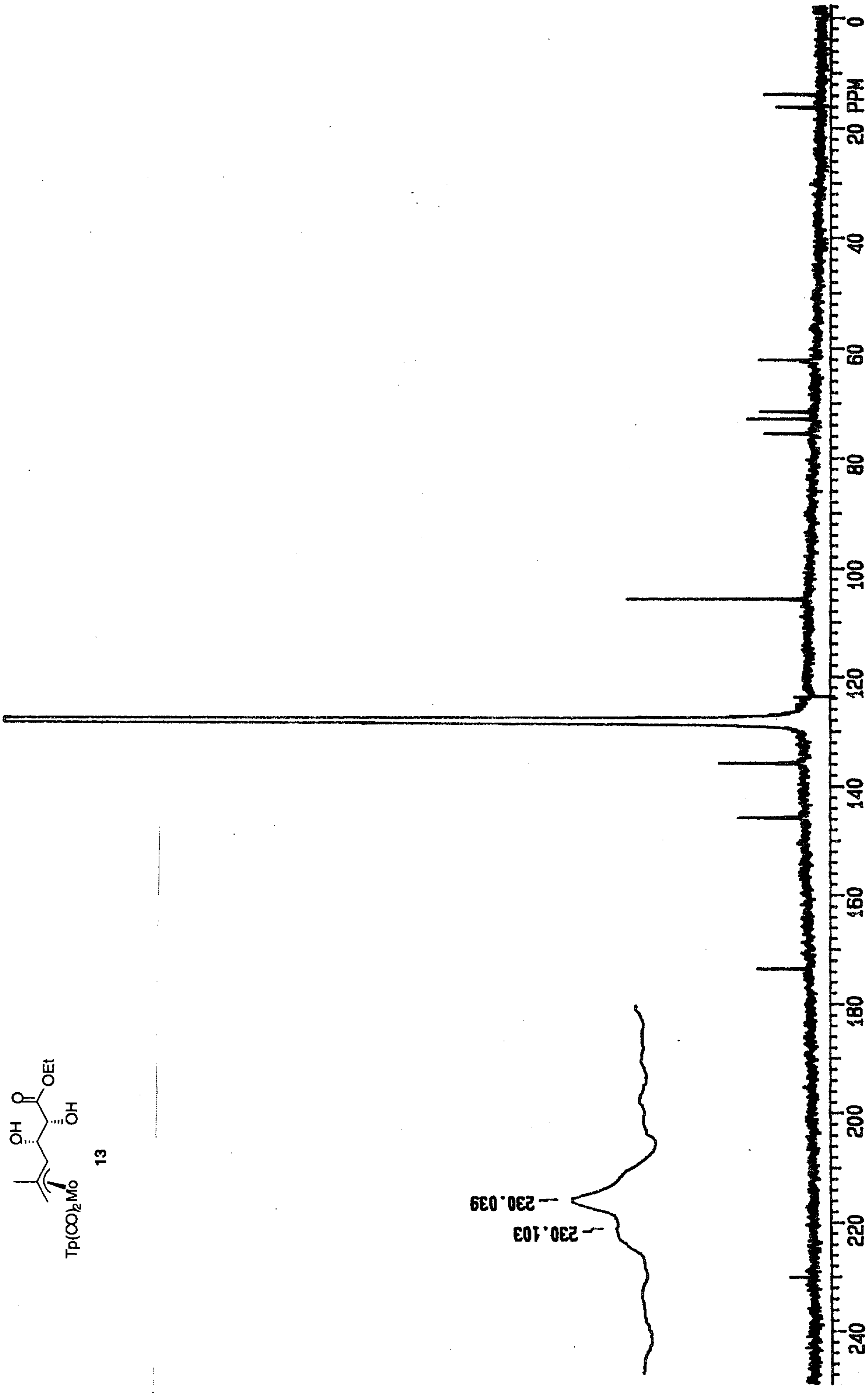
13


1.2626
1.3878
1.4111
1.4349
1.5578
1.8064
1.9117
1.9153
1.9483
3.7297
4.3591
4.3815
4.4053
4.4289
4.8997
5.0388
5.0414
5.0744
6.2044
6.2115
7.2675
7.5700
7.5764
8.1230
8.4
24.8
10.2
24.0
10.0
7.3
5.3
7.7
20.0
8.9
7.8
24.7
24.8
24.9
3
4
5
6
7
8

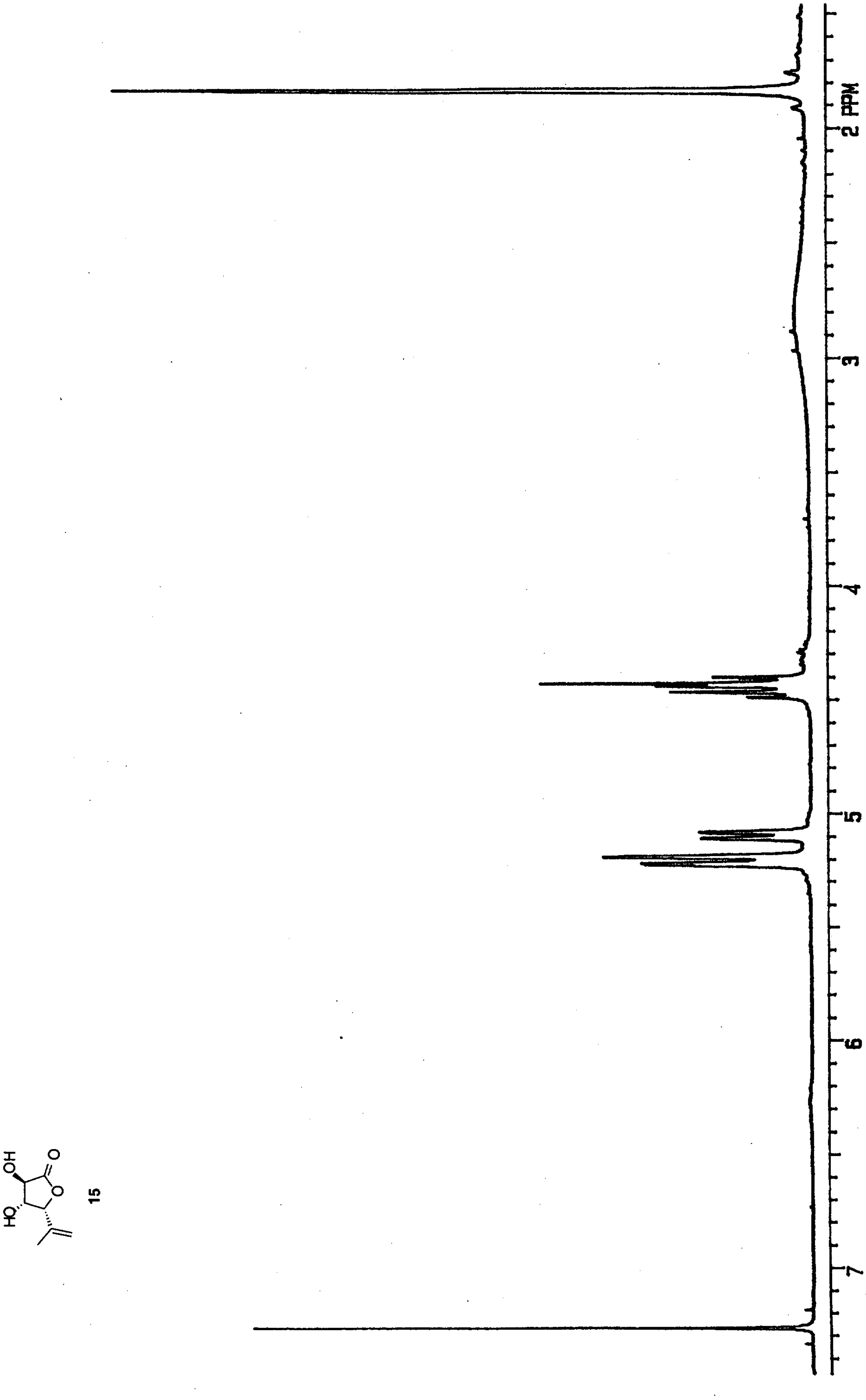


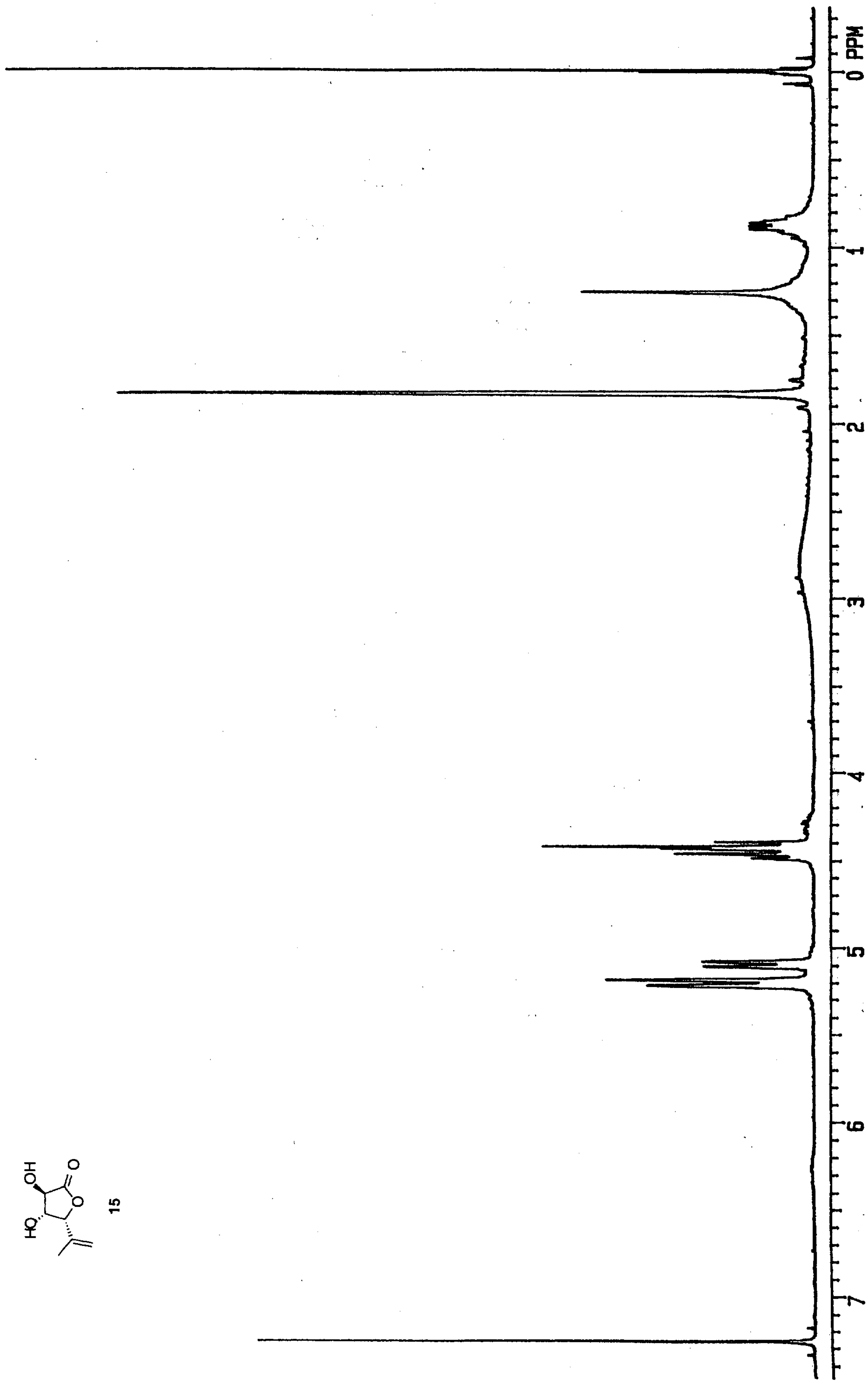
13

Tp(CO)2Mo
OH
OH
OEt
O
PPM
1
2
3
4
5
6
7
8
16.78
5.70
16.56
5.59
5.60
5.67
5.62
12.33
5.80
5.66
16.96
17.44


Tp(CO)$_2$Mo
OH
OH
O
OEt
230.039
230.103
PPM
0
20
40
60
80
100
120
140
160
180
200
220
240

13


2 PPM
3
4
5
6
7
HO
OH
O
O
15



15