Supporting Information

The First Asymmetric Total Syntheses and Determination of Absolute Configurations of Xestodecalactones B and C

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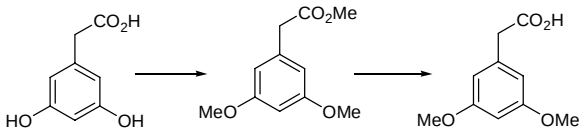
1. Experimental procedure and spectroscopic data

General Methods: Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). Optical rotations were measured on a precision automated polarimeter. Infrared spectra were recorded on a FT-IR spectrometer. ^{1}HNMR and ^{13}CNMR spectra were recorded on a 300 MHz and a 400 MHz spectrometers. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ^{1}H and 77.0 for ^{13}C).



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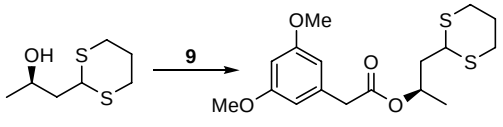
Methyl 3, 5-dimethoxyphenylacetate. Anhydrous potassium carbonate (62 g, 0.45 mol) was added to the solution of 3, 5-dihydroxyphenylacetate acid (15.2 g, 90 mmol) in acetone (300 mL) at rt, then dimethyl sulphate (32.7 mL, 0.36 mol) was added. The solution was refluxed for 12h, cooled to rt, filtered. The organic layers were concentrated *in vacuo*. The residue was purified by column chromatography (hexanes / EtOAc, 10:1) to afford methyl 3, 5-dimethoxyphenylacetate (17.108 g, 90%) as a pale yellow oil. ^{1}HNMR (300 MHz, $CDCl_3$) δ 6.43 (d, J = 2.4 Hz, 2H), 6.36 (t, J = 2.4 Hz, 1H), 3.77 (d, J =2.1 Hz, 6H), 3.68 (d, J = 2.1 Hz, 3H), 3.55 (s, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 171.7, 160.7, 135.9, 107.2, 99.0, 52.0, 41.3; IR (KBr) 3387, 2926, 1716, 1603, 1423, 1203, 1155, 1063 cm^{-1}.

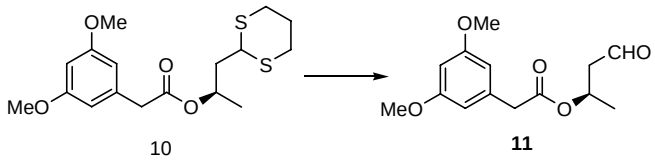
3,5-dimethoxyphenyl acetic acid (9). The solution of methyl 3,5-dimethoxyphenylacetate (17.0 g, 81 mmol) in 2 M KOH (81 mL) was refluxed for 0.5h,

and then cooled to room temperature. The solution was acidified with 2 M HCl to PH 1 and extracted with EtOAc (3 × 80 mL), the combined organic solutions were washed with brine, dried (Na_2SO_4) and concentrated in *vacuo*. The residue gave the 3,5-dimethoxyphenyl acetic acid **9** (14.92 g, 94%) as a white solid: mp 98-102 ^oC; ^{1}HNMR (300 MHz, $CDCl_3$) δ 11.77 (br, s, 1H), 6.46 (t, J = 2.4 Hz, 2H), 6.41 (t, J = 2.4 Hz 1H), 3.78 (s, 6H), 3.59 (s, 2H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 177.8, 160.7, 135.2, 107.4, 99.3, 55.2, 41.2; IR (KBr) 3388, 2923, 1702, 1605, 1205, 1154, 1064 cm^{-1}.

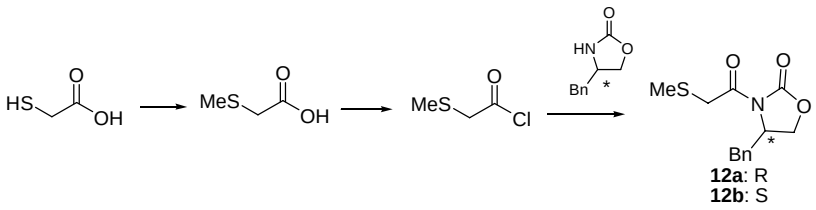


8 **10**

(R)-1-(1,3-dithian-2-yl) propan-2-yl 2-(3,5-dimethoxyphenyl) acetate (10). To a solution of (*R*)-DHP **8** (12.0 g, 67.3 mmol) and acid **9** (14.5 g, 74 mmol) in 100 mL of anhydrous Et_2O at rt was added DCC (15.244 g, 74 mmol) and DMAP (0.41 g, 3.4 mmol), after stirring for 3h at rt, the mixture was filtered, washed with brine, dried (Na_2SO_4) and concentrated in *vacuo*. The residue was purified by column chromatography (hexanes / EtOAc, 10:1) to afford the title compound **10** (23.24 g, 97%) as a colorless oil: $[\alpha]_D^{25}$ -25 (c 2.04, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 6.45 (t, J = 2.4 Hz, 2H), 6.36 (dd, J = 4.2 Hz, 2.4 Hz, 1H), 5.09-5.16 (m, 1H), 3.80-3.86 (m, 1H), 3.76 (dd, J = 6.6 Hz, 2.1 Hz, 6H), 3.52 (d, J = 2.1 Hz, 2H), 2.73-2.78 (m, 2H), 2.58-2.71 (m, 2H), 1.98-2.07 (m, 2H), 1.77-1.87 (m, 2H), 1.24 (td, J = 6.6 Hz, 2.1 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 170.5, 160.7, 136.3, 107.1, 99.1, 68.1, 55.2, 43.4, 42.1, 41.3, 30.2, 29.7, 25.7, 20.1; IR (KBr) 3387, 2926, 1733, 1599, 1461, 1155,1063 cm^{-1}; HRMS *m/z* calcd for $C_{17}H_{24}O_4S_2$ $[M+H]^+$ 357.1194; Found 357.1187.



(R)-1-formylpropan-2-yl 2-(3,5-dimethoxyphenyl)acetate (11). The solution of 1,3-dithiane derivative **10** (10.68 g, 30 mmol) in THF (30 mL) was added dropwise to a well stirred suspension of lead dioxide (28.68 g, 120 mmol) in 20% aqueous THF (105 mL), containing boron trifluoride etherate (31 mL, 180 mmol). The reaction was monitored by TLC and stirring of the mixture at room temperature was continued until all the dithiane derivative has disappeared. Ether (100 mL) was added and the precipitate was filtered. The filtrate was concentrated in *vacuo*. The residue was dissolved in 200 mL of ether, washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash chromatography through a silica gel (hexanes / EtOAc, 10:1) to afford the title compound **11** (6.86 g, 86%) as a colorless oil: $[\alpha]_D^{25}$ -8 (c 1.1, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 9.69 (t, J = 1.5 Hz, 1H), 6.41 (d, J = 2.4 Hz, 2H), 6.37 (d, J = 2.4 Hz, 1H), 5.38 (dd, J = 12.3 Hz, 6.0 Hz, 1H), 3.79 (d, J = 6.0 Hz, 6H), 3.52 (s, 2H), 2.73 (ddd, J = 13.5 Hz, 6.0 Hz, 2.4 Hz, 1H), 2.58 (ddd, J = 13.5 Hz, 6.0 Hz, 2.4 Hz, 1H), 1.32 (d, J = 6.0 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 199.3, 170.6, 160.7, 135.8, 107.1, 99.1, 66.4, 55.3, 49.4, 41.6, 20.0; IR (KBr) 2940, 2840, 1730, 1597, 1464, 1205, 1157, 1065, 974, 838 cm^{-1}; HRMS *m/z* calcd for $C_{14}H_{18}O_5$ $[M+H]^+$ 267.1232; Found 267.1228.

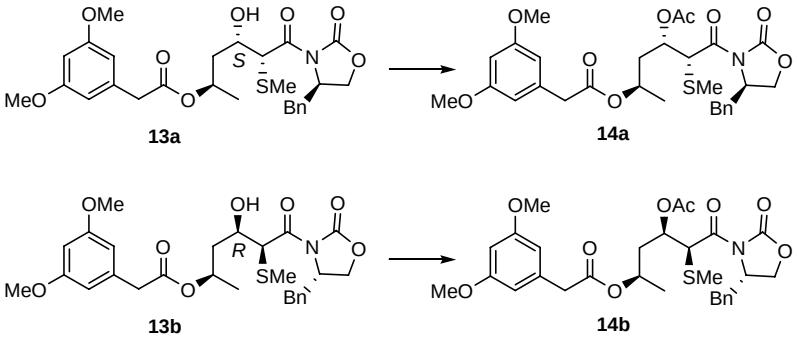


2-(methylthio)acetic acid. 2M NaOH (200 mL) was added to a suspension of 2-mercaptoacetic acid (9.2 g, 100 mmol) in 40 mL of EtOH at 0 ^{o}C, after stirring for 15min,

MeI (7.5 mL, 120 mmol) was added, the stirring was continued for 1h at 0 ^{o}C, then EtOH was removed under reduced pressure. The solution was acidified with 2M HCl and extract with EtOAc (3×150 mL), washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was distilled at 5 mmHg (76-78 ^{o}C) to afford 2-(methylthio)acetic acid (9.5g, 89%) as a colorless oil: ^{1}HNMR (300 MHz, $CDCl_3$) δ 12.04 (s, 1H), 3.17 (t, J = 3.0 Hz, 2H), 2.18 (t, J = 4.2 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 176.9, 35.3, 16.1; IR (KBr) 3170, 1710, 1426, 1295, 1142 cm^{-1}.

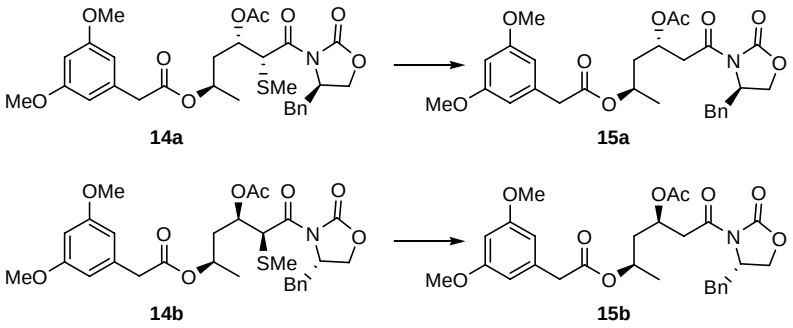
(R)-4-benzyl-3-(2-(methylthio)acetyl)oxazolidin-2-one 12a and (S)-12b. In a round bottom flask with a reflux condenser was placed 2-(methylthio)acetic acid (9.0 g, 84.9 mmol) and oxayl chloride (18.5 mL, 0.212 mol) in 50 mL of benzene. After once starting, the reaction proceeded spontaneously for 30min. The mixture was refluxed for 2h. The reaction mixture was then distilled under atmospheric pressure till the excess of oxalyl chloride and benzene were collected and then generally under diminished pressure (20 mmHg) to obtain 2-(methylthio)acetic acid chloride (9.5 g, 90%) as a colorless oil. To a solution of the (R)-oxazolidinone (3.54 g, 20 mmol) in anhydrous THF (60 mL) at -78 ^{o}C under Ar was added 8.06 mL (20 mmol) of n-BuLi (2.48 M in hexanes). After 15min, the freshly distilled 2-(methylthio)acetic acid chloride (2.74 g, 22 mmol) was added. The mixture was stirred at -78 ^{o}C for 30min and at 0 ^{o}C for 15min. The reaction was quenched with excess saturated aqueous ammonium chloride, and the resultant slurry was concentrated in *vacuo*. The residue was diluted with ether (100 mL) and washed successively with saturated aqueous sodium bicarbonate and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel to afford the desired (*R*)-oxazolidone **12a** (4.91 g, 92%) as a colorless oil. $[\alpha]_D^{25}$ +51 (c 1.34, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 7.25-7.34 (m,

3H), 7.21 (d, *J* = 6.9 Hz, 2H), 4.68 (td, *J* = 9.3 Hz, 3.9 Hz, 1H), 4.14-4.24 (m, 2H), 3.81 (dd, *J* = 27.6 Hz, 13.5 Hz, 2H), 3.28 (dd, *J* = 13.5 Hz, 3.3 Hz, 1H), 2.79 (dd, *J* = 13.5 Hz, 9.3 Hz, 1H), 2.19 (s, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 168.6, 153.0, 134.9, 129.3, 128.8, 127.2, 66.1, 55.0, 37.5, 36.4, 15.7; IR (KBr) 2920, 1780, 1692, 1317, 1211, 1105, 1000, 743, 705 cm^{-1}; HRMS *m/z* calcd for $C_{13}H_{15}NO_3S$ $[M+H]^+$ 266.0851; Found 266.0847; (*S*)-oxazolidone **12b** (4.85 g, 91%) was obtained from (*S*)- oxazolidinone (3.54 g, 20 mmol) and 2-(methylthio)acetic acid chloride (2.74 g, 22 mmol) by the same operation as the synthesis of **12a**. $[\alpha]_D^{25}$ -63 (c 2.0, $CHCl_3$); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.19-7.32 (m, 5H), 4.64-4.68 (m, 1H), 4.13-4.22 (m, 2H), 3.78 (ddd, *J* = 36.0 Hz, 14.4 Hz, 1.2 Hz, 2H), 3.26 (dd, *J* = 13.6 Hz, 3.2 Hz, 1H), 2.78 (dd, *J* = 13.6 Hz, 9.6 Hz, 1H), 2.17 (d, *J* = 2.4 Hz, 3H), 1.17 (dd, *J* = 4.4 Hz, 2.4 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 168.6, 153.0, 134.9, 129.2, 128.7, 127.1, 66.0, 54.9, 37.4, 36.4, 15.7; IR (KBr) 2920, 1780, 1693, 1356, 1317, 1211, 1105, 1000, 742, 704 cm^{-1}; HRMS *m/z* calcd for $C_{13}H_{15}NO_3S$ $[M+H]^+$ 266.0851; Found 266.0855.



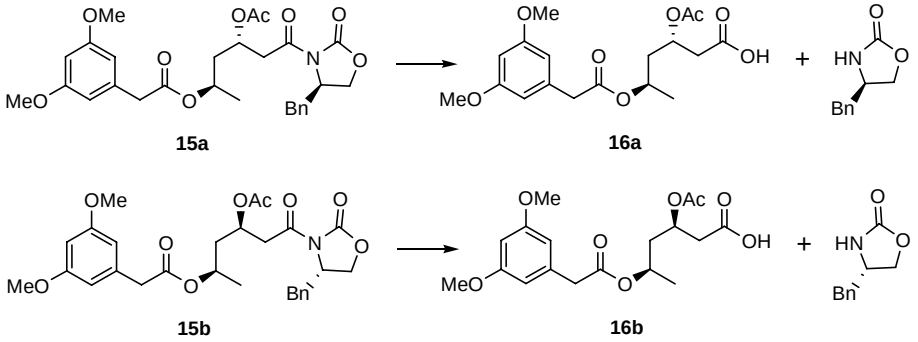
Compounds 14a and 14b. 1 mL of pyridine was added to the solution of **13a** (5.31 g, 10 mmol) in 15 mL of Ac_2O. After stirring at rt for 5h, the mixture was slowly added to the saturate aqueous $NaHCO_3$, extracted with ether (4 × 50 mL). The organic layer was washed with 20 mL $NaHCO_3$, 20 mL 1 M HCl, 20 mL brine, dried over Na_2SO_4, and

concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (hexanes / EtOAc, 4:1) to afford the title compound **14a** (5.50 g, 96%) and it's diastereomer (229 mg) produced from the aodol reaction as colorless oil. The diastereoselectivity of the aldol addition was 96 : 4. $[\alpha]_D^{25}$ +36 (c 2.17, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 7.22-7.36 (m, 5H), 6.40 (d, J = 2.1 Hz, 2H), 6.34 (d, J = 2.4 Hz, 1H), 5.47 (td, J = 7.8 Hz, 3.6 Hz, 1H), 4.91-4.97 (m, 1H), 4.64-4.70 (m, 1H), 4.10-4.21 (m, 2H), 3.75 (s, 6H), 3.50 (s, 2H), 3.23 (dd, J = 13.5 Hz, 3.6 Hz,1H), 2.76 (dd, J = 13.5 Hz, 9.9 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 1.96-2.03 (m, 2H), 1.87-1.93 (m, 1H), 1.26 (dd, J = 9.9 Hz, 6.3 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 167.9, 160.7, 152.9,136.0, 134.9, 129.4, 128.9, 127.3, 107.3, 99.0, 68.4, 67.2, 66.0, 55.2, 55.0, 47.6, 41.5, 38.3, 37.7, 20.9, 18.9, 12.7; IR (KBr) 3397, 2923, 1777, 1738, 1685, 1598, 1366, 1206, 1155, 1063 cm^{-1}; HRMS *m/z* calcd for $C_{29}H_{35}NO_9S$ $[M+Na]^+$ 596.1930; Found 596.1925; Protected **13b** (5.31 g, 10 mmol) with 15 mL Ac_2O and 1 mL pyridine affording **14b** (5.58 g, 97%) and it's diastereomer (173 mg). The diastereoselectivity of the aldol addition was 97 : 3. $[\alpha]_D^{25}$ -37 (c 2.45, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 7.22-7.34 (m, 5H), 6.44 (d, J = 2.1 Hz, 2H), 6.34 (d, J = 2.4 Hz, 1H), 5.44-5.50 (m, 1H), 4.94-4.98 (m, 1H), 4.84 (dd, J = 7.2 Hz, 2.4 Hz, 1H), 4.71 (br, t, J = 7.2 Hz, 1H), 4.12-4.22 (m, 2H), 3.73 (dd, J = 6.6 Hz, 3.6 Hz, 6H), 3.54 (s, 2H), 3.25 (d, J = 13.5 Hz, 1H), 2.76 (dd, J = 13.5 Hz, 9.9 Hz, 1H), 2.12 (d, J = 3.6 Hz, 3H), 2.07 (t, J = 3.6 Hz, 3H), 1.82-1.94 (m, 2H), 1.21 (dd, J = 6.6 Hz, 2.4 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 170.8, 169.9, 168.0, 152.7, 136.0, 134.8, 129.3, 128.8, 127.2, 107.2, 99.1, 67.0, 66.4, 65.9, 55.1, 54.9, 48.3, 41.4, 38.5, 37.4, 20.6, 20.1, 13.0; IR (KBr) 3366, 2929, 1777, 1740, 1689, 1599, 1459, 1365, 1231, 1206, 1153, 1100 cm^{-1}; HRMS *m/z* calcd for $C_{29}H_{35}NO_9S$ $[M+Na]^+$ 596.1930; Found 596.1928.



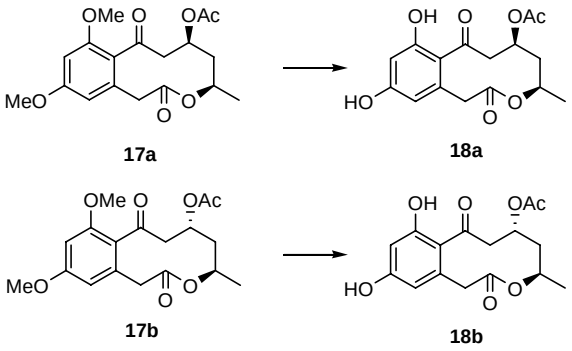
Compounds 15a and 15b. *n*-Bu_3SnH (9.4 mL, 34.9 mmol, 4eq) and AIBN (148 mg, 0.9 mmol, 0.1eq) were added to the solution of **14a** (5.0 g, 8.73 mmol) in anhydrous benzene (80 mL) under Ar. The solution was warmed to 80 ^oC and stirred for 45min. The mixture was allowed to cool to rt, and the solvent was evaporated in *vacuo*. Flash chromatography on silica gel (hexanes / EtOAc, 4:1) afforded **15a** (4.374 g, 95%) as a colorless oil. $[\alpha]_D^{25}$ +56 (c 2.0, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 7.21-7.36 (m, 3H), 7.19 (d, J = 6.6 Hz, 2H), 6.43 (d, J = 2.4 Hz, 2H), 6.34 (t, J = 2.4 Hz, 1H), 5.35 (td, J = 8.4 Hz, 3.9 Hz, 1H), 5.00-5.04 (m, 1H), 4.57-4.63 (m, 1H), 4.13-4.26 (m, 2H), 3.77 (d, J = 1.2 Hz, 6H), 3.55 (s, 2H), 3.21-3.33 (m, 2H), 3.05 (dd, J = 15.6 Hz, 8.1 Hz, 1H), 2.75 (dd, J = 13.2 Hz, 10.2 Hz, 1H), 2.01 (d, J = 1.8 Hz, 3H), 1.93 (dd, J = 9.9 Hz, 4.2 Hz, 1H), 1.82 (dd, J = 9.9 Hz, 4.2 Hz, 1H), 1.23 (d, J = 6.6 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 170.9, 170.4, 169.6, 160.6, 153.5, 136.1, 135.1, 129.4, 128.9, 127.3, 107.1, 99.2, 67.3, 66.6, 66.2, 55.2, 55.1, 41.6, 40.9, 40.5, 37.7, 20.9, 20.3; IR (KBr) 3543, 2938, 1783, 1736, 1598, 1460, 1391, 1294, 1236, 1155, 1063 cm^{-1}; HRMS *m/z* calcd for $C_{28}H_{33}NO_9$ $[M+Na]^+$ 550.2053; Found 550.2050; Treatment of 5.3 g (9.25 mmol) **14b** with n-Bu_3SnH (9.9 mL, 37.0 mmol, 4eq) and AIBN (148 mg, 0.9 mmol, 0.1eq) as described for the synthesis of **15a** afforded **15b** (4.69 g, 96%) as a colorless oil. $[\alpha]_D^{25}$ -60 (c 2.0, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 7.26-7.35 (m, 3H), 7.20 (d, J = 1.8 Hz, 2H), 6.43 (d, J = 2.1 Hz, 2H), 6.34 (t, J = 2.4 Hz, 1H), 5.32-5.38 (m, 1H), 5.02 (td, J = 6.0 Hz, 3.6

Hz, 1H), 4.57-4.63 (m, 1H), 4.22 (t, J = 8.4 Hz, 1H), 4.14 (dd, J = 8.4 Hz, 3.0 Hz, 1H), 3.76 (s, 6H), 3.52 (s, 2H), 3.22-3.29 (m, 2H), 3.05 (dd, J = 8.8 Hz, 6.6 Hz, 1H), 2.76 (dd, J = 13.5 Hz, 8.8 Hz, 1H), 2.00 (s, 3H), 1.91-1.99 (m, 1H), 1.79-1.87 (m, 1H), 1.24 (d, J = 6.6 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 169.5, 160.7, 153.4, 136.1, 135.1, 129.3, 128.8, 127.2, 107.2, 99.3, 67.3, 66.6, 66.2, 55.2, 55.1, 41.6, 40.9, 40.5, 37.7, 20.8, 20.2; IR (KBr) 3394, 2930, 1781, 1736, 1701, 1599, 1459, 1390, 1233, 1204, 1153, 1063 cm^{-1}; HRMS *m/z* calcd for $C_{28}H_{33}NO_9$ $[M+Na]^+$ 550.2053; Found 550.2048.



Compounds 16a and 16b. A solution of 2.16 g (4.08 mmol) **15a** in 45 mL of THF (stabilized with 0.025% BHT) and 12.6 mL of water, stirred at 0 ^{o}C under Ar, was treated with 3.7 mL (32.64 mmol, 8.0eq) of 31% H_2O_2 followed by 344 mg (8.16 mmol, 2.0eq) of LiOH. The resulting mixture was stirred at 0 ^{o}C for 15min, and treated with a solution of 10.3 g (40.8 mmol, 10eq) of Na_2SO_3 in 40 mL of H_2O followed by 48 mL of 0.5 M $NaHCO_3$. The THF was evaporated in *vacuo*. The aqueous residue was diluted to 100 mL with H_2O and extracted with four 60 mL portions of CH_2Cl_2. The CH_2Cl_2 extracts were combined, dried (Na_2SO_4) and evaporated in *vacuo* to yield 611 mg of (*R*)-oxazolidinone as a white solid. Recovery of oxazolidinone was 85%. The aqueous phase was acidified to PH 1-2 with 5 M HCl and extracted with four 75 mL portions of EtOAc. The extracts were combined, dried (Na_2SO_4) and evaporated in *vacuo*. The residue was purified by flash chromatography on silica gel (hexanes / EtOAc / AcOH, 40:10:1) to afford (1.367 g,

91%) of **16a** as a colorless oil. $[\alpha]_D^{25}$ -4 (c 2.0, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$) δ 6.42 (d, J = 1.8 Hz, 2H), 6.35 (d, J = 2.4 Hz, 1H), 5.18-5.27 (m, 1H), 4.94-5.01 (m, 1H), 3.73 (t, J = 11.7 Hz, 6H), 3.54 (s, 2H), 2.57 (ddd, J = 6.9 Hz, 6.0 Hz, 2H), 2.01 (s, 3H), 1.79-1.94 (m, 2H), 1.22 (d, J = 6.0 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 175.3, 171.0, 170.4, 160.7, 136.0, 107.2, 99.2, 67.4, 66,6, 63.5, 55.3, 41.6, 40.1, 39.1, 20.9, 20.3; IR (KBr) 3246, 2938, 1737, 1599, 1463, 1239, 1205, 1155, 1064 cm^{-1}; HRMS *m/z* calcd for $C_{18}H_{24}O_8$ $[M+H]^+$ 369.1549; Found 369.1545; 1.258 g (84%) of **16b** was obtained as a colorless oil by treating **15b** (2.16 g, 4.08 mmol) with 3.7 mL (32.64 mmol, 8.0eq) of 31% H_2O_2 and 344 mg (8.16 mmol, 2.0eq) of LiOH workup as the synthesis of **16a**. $[\alpha]_D^{25}$ -27 (c 2.0, $CHCl_3$); ^{1}HNMR (300MHz, $CDCl_3$) δ 8.99 (br, s, 1H), 6.41 (d, J = 2.1 Hz, 2H), 6,34 (d, J = 2.1 Hz, 1H), 5.17-5.26 (m, 1H), 5.92-5.01 (m, 1H), 3.77 (dd, J = 6.9 Hz, 1.2 Hz, 6H), 3.52 (s, 2H), 2.57 (ddd, J = 6.9 Hz, 5.7 Hz, 2H), 2.07 (s, 3H), 1.82-1.96 (m, 2H), 1.21 (d, J = 6.3 Hz, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 175.3, 170.9, 170.3, 160.7, 136.0, 107.2, 99.3, 67.3, 66.6, 55.2, 41.6, 40.0, 39.0, 20.8, 20.2; IR (KBr) 3215, 2938, 1739, 1600, 1464, 1432, 1294, 1238, 1205, 1154, 1064 cm^{-1}; HRMS *m/z* calcd for $C_{18}H_{24}O_8$ $[M+H]^+$ 369.1549; Found 369.1553.

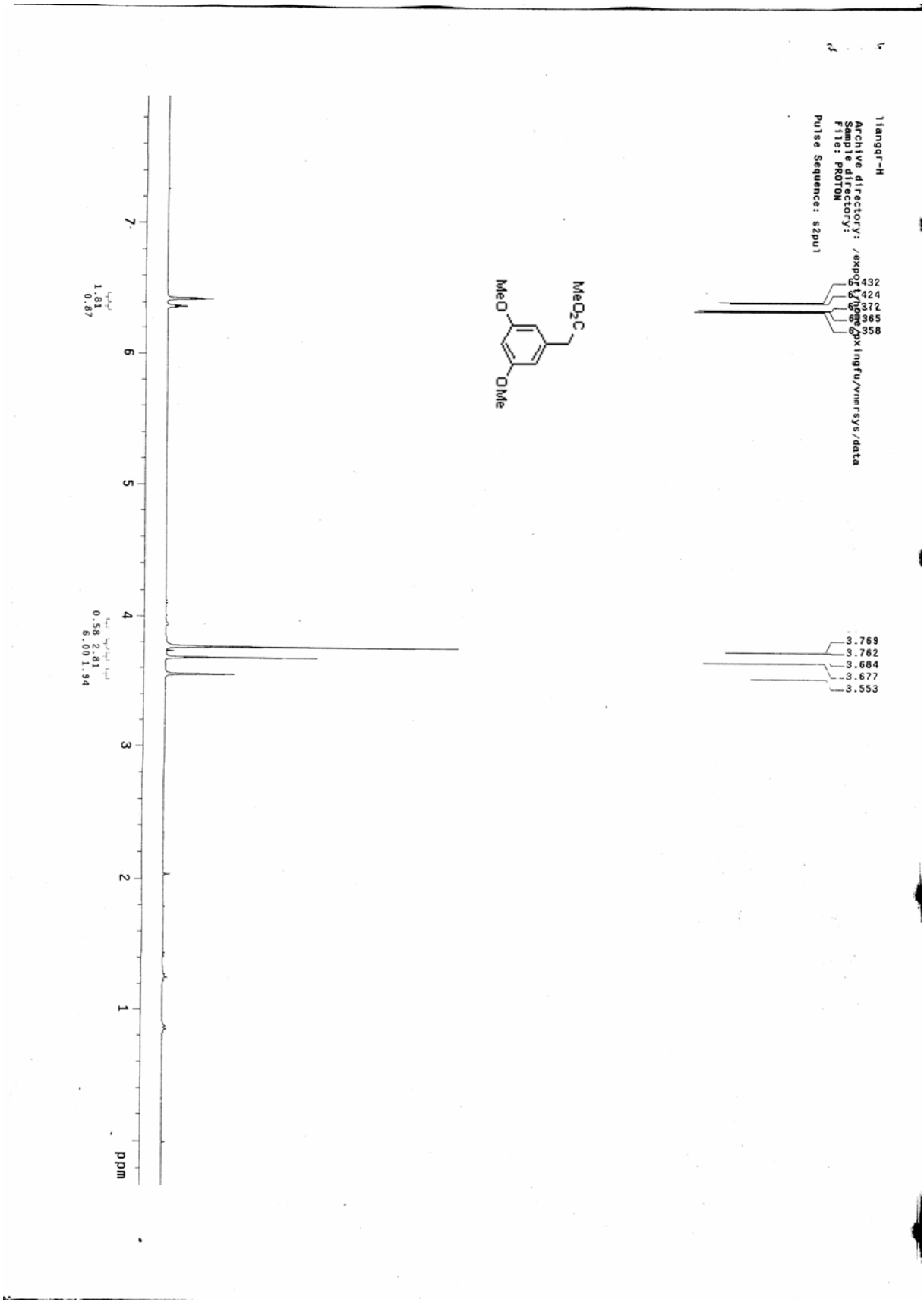


17a **18a**

17b **18b**

Compounds 18a and 18b. Iodine (1.646 g, 6.48 mmol) was added to a mixture of aluminum (234 mg, 8.68 mmol) in dry benzene. The mixture was refluxed for 1h, cooled

to room temperature, n-$Bu_4N^+I^-$ (10 mg, 0.028 mmol) and **17a** (76 mg, 0.216 mmol) in dry benzene (8 mL) were added. The mixture was stirred for 45min at rt and quenched with water. After acidification with 2M HCl the mixture was extracted with EtOAc (3×50 mL). The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (hexanes / EtOAc, 1:1) to afford the title compound **18a** (66 mg, 95%) as a white solid. mp 156-160 ^oC; $[\alpha]_D^{25}$ +14 (c 0.5, CH_3OH); ^{1}HNMR (400 MHz, Me_2CO-d_6) δ 9.03 (br, s, 1H), 8.74 (br, s, 1H), 6.38 (d, J = 2.4 Hz, 1H), 6.28 (d, J = 3.2 Hz, 1H), 5.22-5.29 (m, 1H), 4.91-4.97 (m, 1H), 3.77 (d, J = 22.8 Hz, 1H), 3.47 (dd, J = 22.8 Hz, 4.0 Hz, 1H), 3.59 (d, J = 22.8 Hz, 1H), 3.06 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 2.04-2.14 (m, 1H), 1.98 (s, 3H), 1.88-1.95 (m, 1H), 1.23 (dd, J = 8.4 Hz, 1.6 Hz, 3H); ^{13}CNMR (100 MHz, Me_2CO-d_6) δ 203.2, 170.2, 169.5, 160.0, 157.4, 136.7, 121.6, 111.0, 110.6, 102.2, 69.1, 68.4, 49.3, 40.9, 39.5, 21.1, 19.8; IR (KBr) 3336, 1735, 1611, 1465, 1367, 1259, 1162, 1046, 846 cm^{-1}; HRMS *m/z* calcd for $C_{16}H_{18}O_7$ $[M+H]^+$ 323.1131; Found 323.1128; **18b** (79 mg, 96%) was obtained as a pale yellow solid from **17b** (90 mg) as described for the synthesis of **18a**. mp 163-165 ^oC; $[\alpha]_D^{25}$ +25 (c 0.65, CH_3OH); ^{1}HNMR (400 MHz, Me_2CO-d_6) δ 9.11 (s, 1H), 8.83 (s, 1H), 6.48 (d, J = 2.0 Hz, 1H), 6.33 (s, 1H), 5.30 (t, J = 9.6 Hz, 1H), 4.95 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 4.06 (d, J = 15.2 Hz, 1H), 3.43 (dd, J = 15.2 Hz, 11.2 Hz, 1H), 3.04 (d, J = 6.4 Hz, 2H), 2.10-2.12 (m, 1H), 2.06 (s, 3H), 1.94-2.02 (m, 1H), 1.22 (d, J = 6.4 Hz, 3H); ^{13}CNMR (75MHz, Me_2CO-d_6) δ 203.6, 170.1, 169.4, 160.4, 157.9, 136.1, 122.6, 110.7, 102.4, 72.3, 71.4, 52.4, 43.8, 40.5, 21.2, 21.0; IR (KBr) 3343, 2933, 1732, 1706, 1591, 1466, 1366, 1244, 1160, 1061, 955, 854 cm^{-1}; HRMS *m/z* calcd for $C_{16}H_{18}O_7$ $[M+H]^+$ 323.1131; Found 323.1134.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6.358
3.769
3.762
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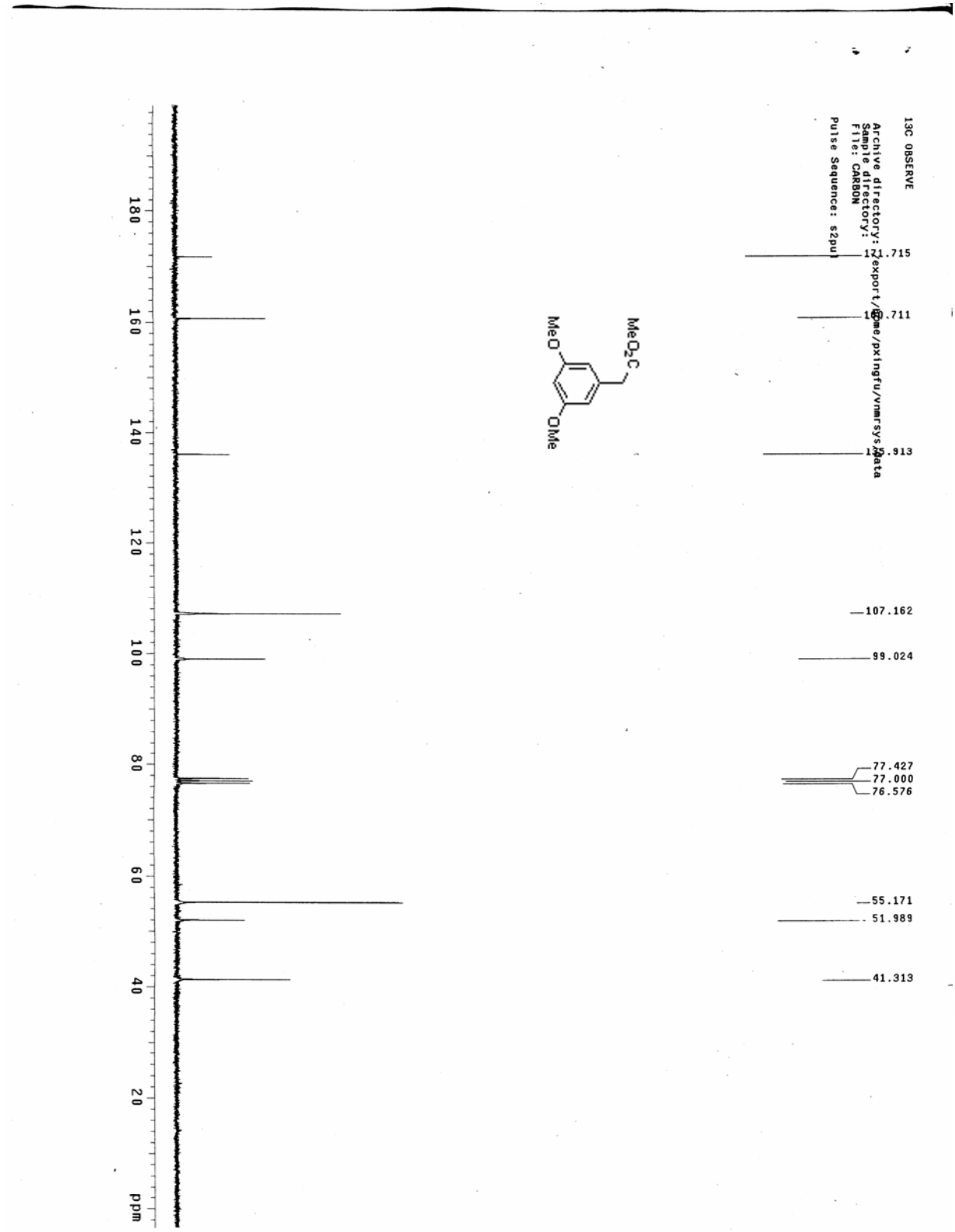
3.553
MeO2C
MeO
OMe
1.81
0.87
0.58 2.81
6.00 1.94
ppm


13C OBSERVE
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77.000
76.576
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OMe
MeO2C
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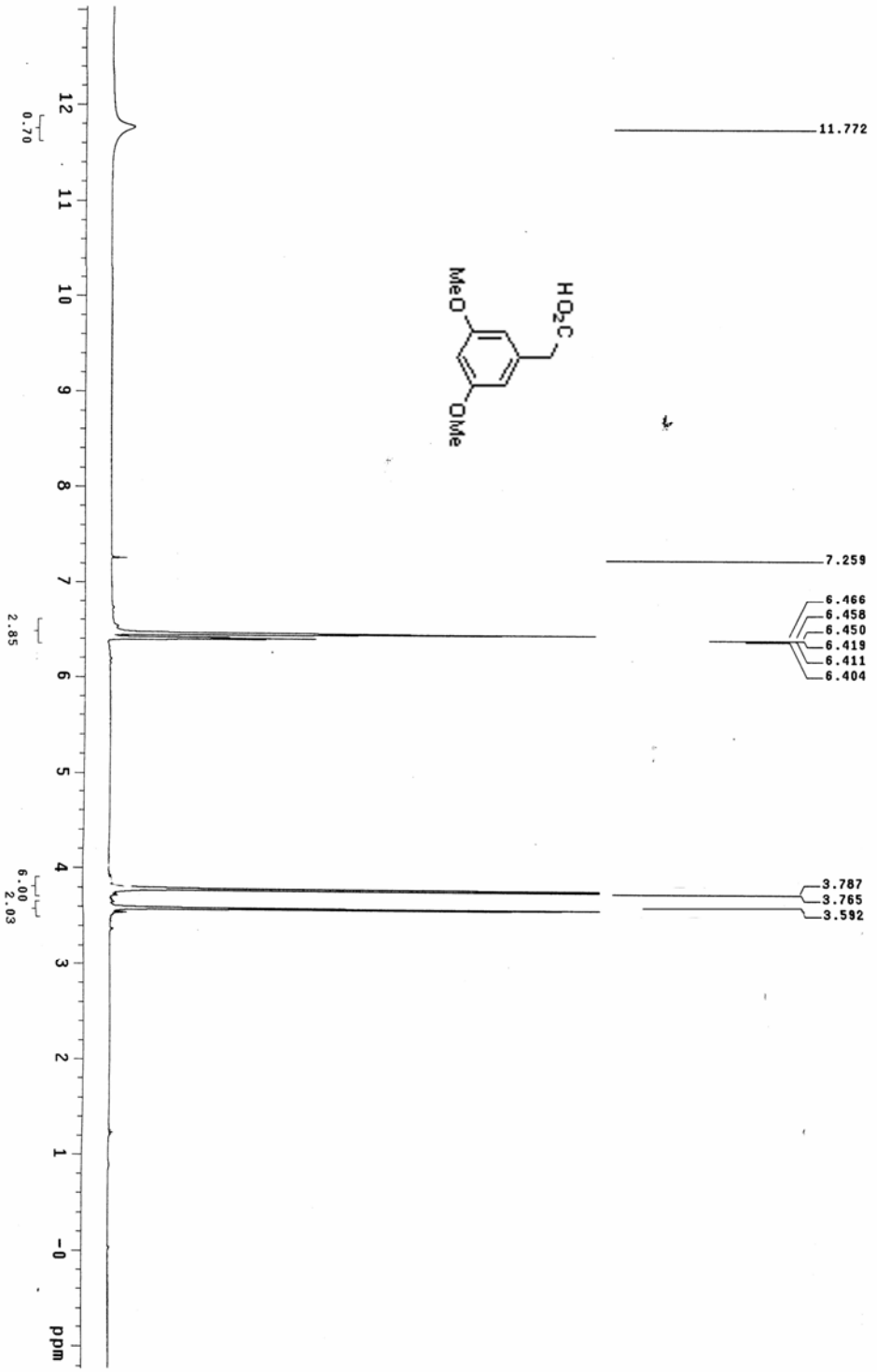
160
140
120
100
80
60
40
20
ppm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6.450
6.419
6.411
6.404
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3.765
3.592
MeO
OMe
HO2C
0.70
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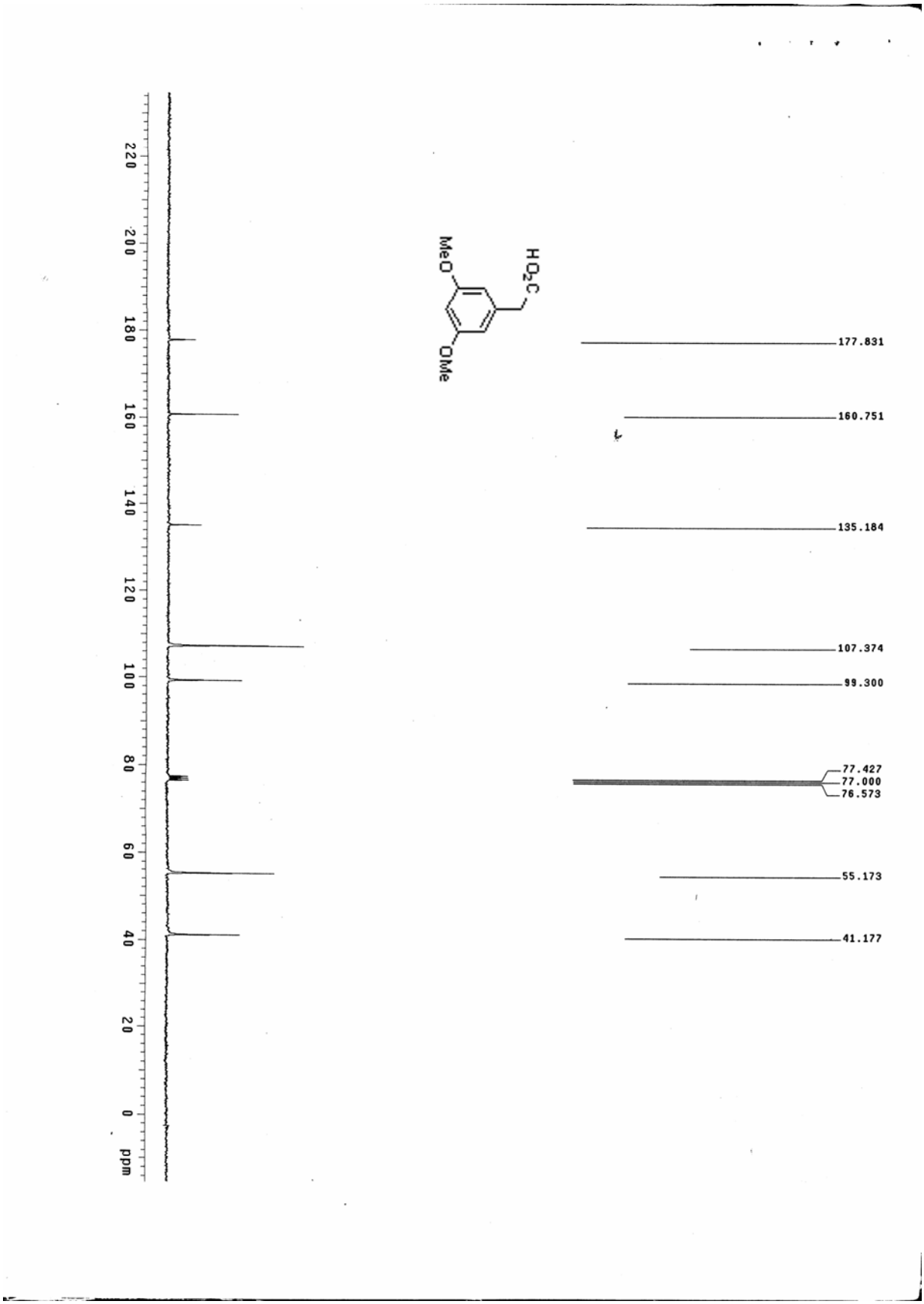
6.00
2.03
ppm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HO2C
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120
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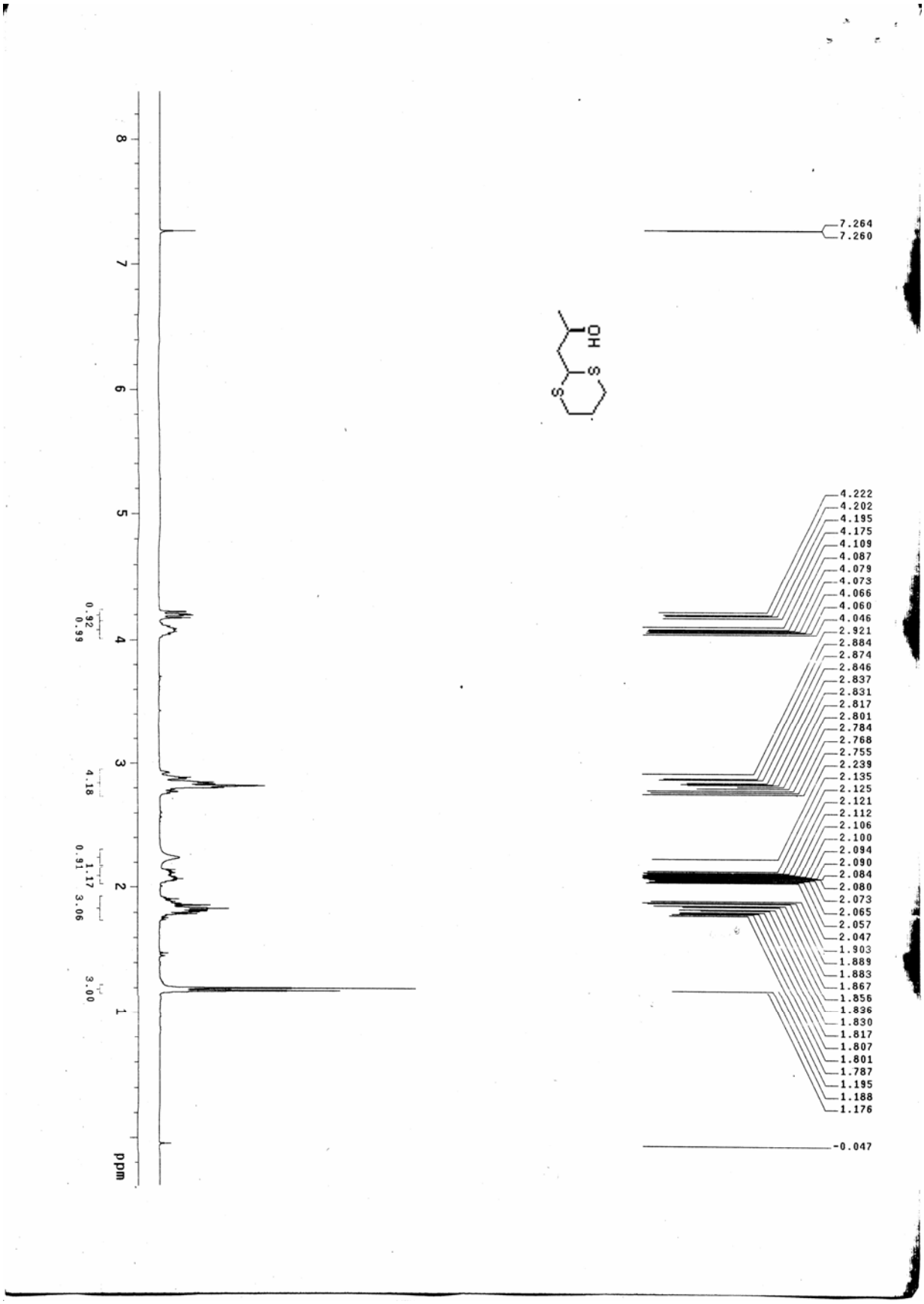
80
60
40
20
0
ppm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4.222
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4.175
4.109
4.087
4.079
4.073
4.066
4.060
4.046
2.921
2.884
2.874
2.846
2.837
2.831
2.817
2.801
2.784
2.768
2.755
2.239
2.135
2.125
2.121
2.112
2.106
2.100
2.094
2.090
2.084
2.080
2.073
2.065
2.057
2.047
1.903
1.889
1.883
1.867
1.856
1.836
1.830
1.817
1.807
1.801
1.787
1.195
1.188
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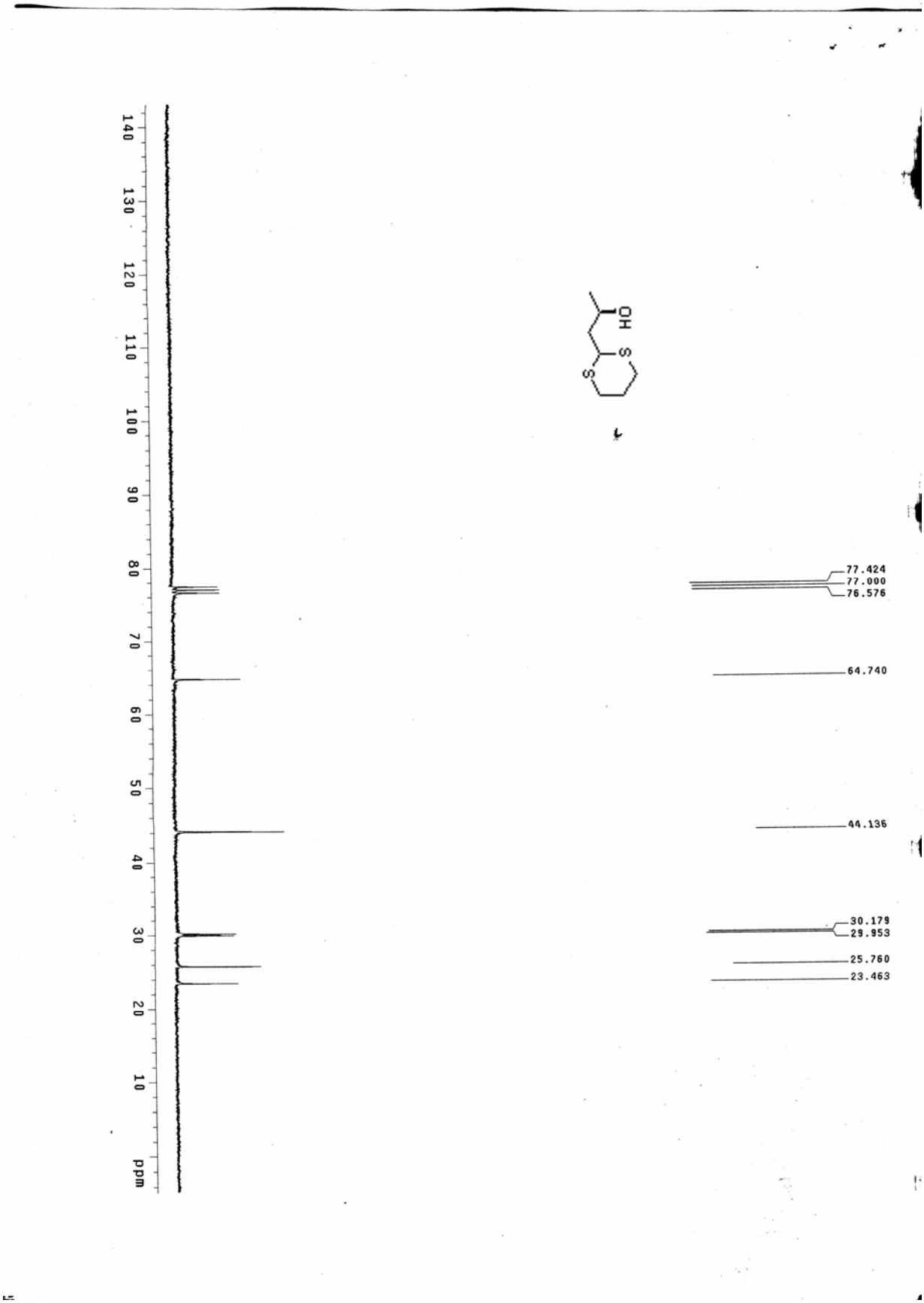
3.00
ppm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S
S
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130
120
110
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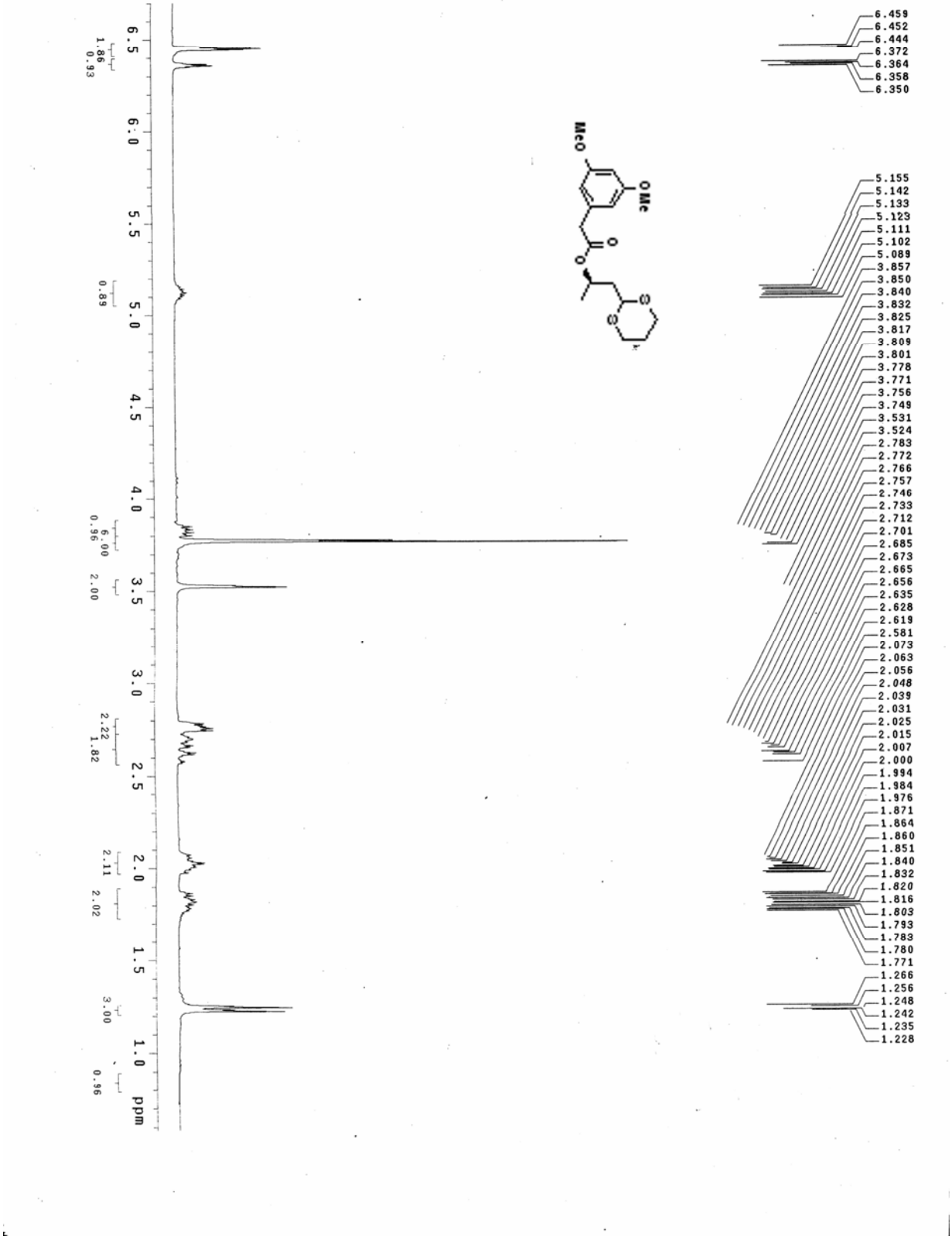
90
80
70
60
50
40
30
20
10
ppm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6.358
6.350
5.155
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5.133
5.123
5.111
5.102
5.089
3.857
3.850
3.840
3.832
3.825
3.817
3.809
3.801
3.778
3.771
3.756
3.749
3.531
3.524
2.783
2.772
2.766
2.757
2.746
2.733
2.712
2.701
2.685
2.673
2.665
2.656
2.635
2.628
2.619
2.581
2.073
2.063
2.056
2.048
2.039
2.031
2.025
2.015
2.007
2.000
1.994
1.984
1.976
1.871
1.864
1.860
1.851
1.840
1.832
1.820
1.816
1.803
1.793
1.783
1.780
1.771
1.266
1.256
1.248
1.242
1.235
1.228
MeO
OMe
O
O
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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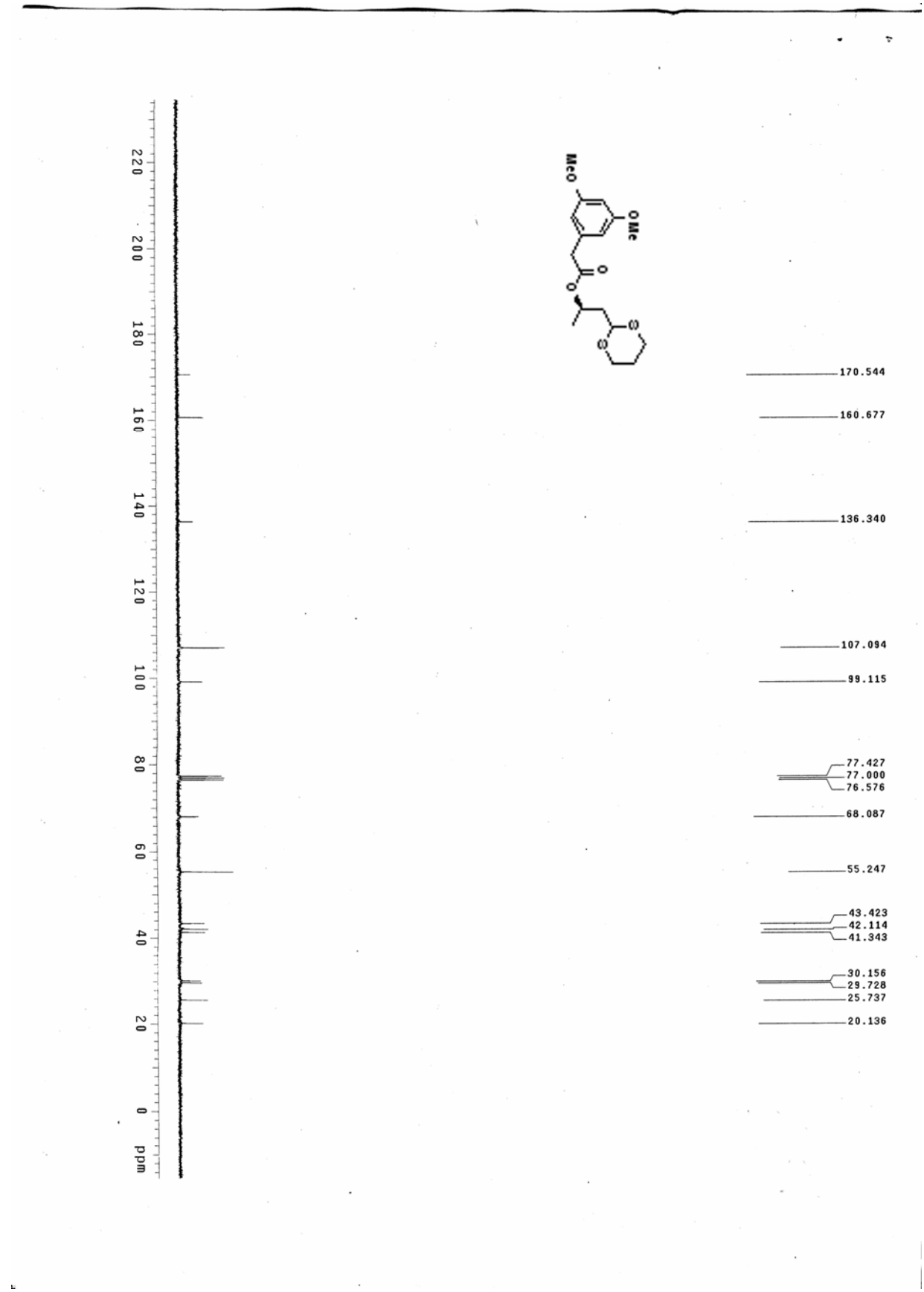
3.00
0.96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OMe
O
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm
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160.677
136.340
107.094
99.115
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77.000
76.576
68.087
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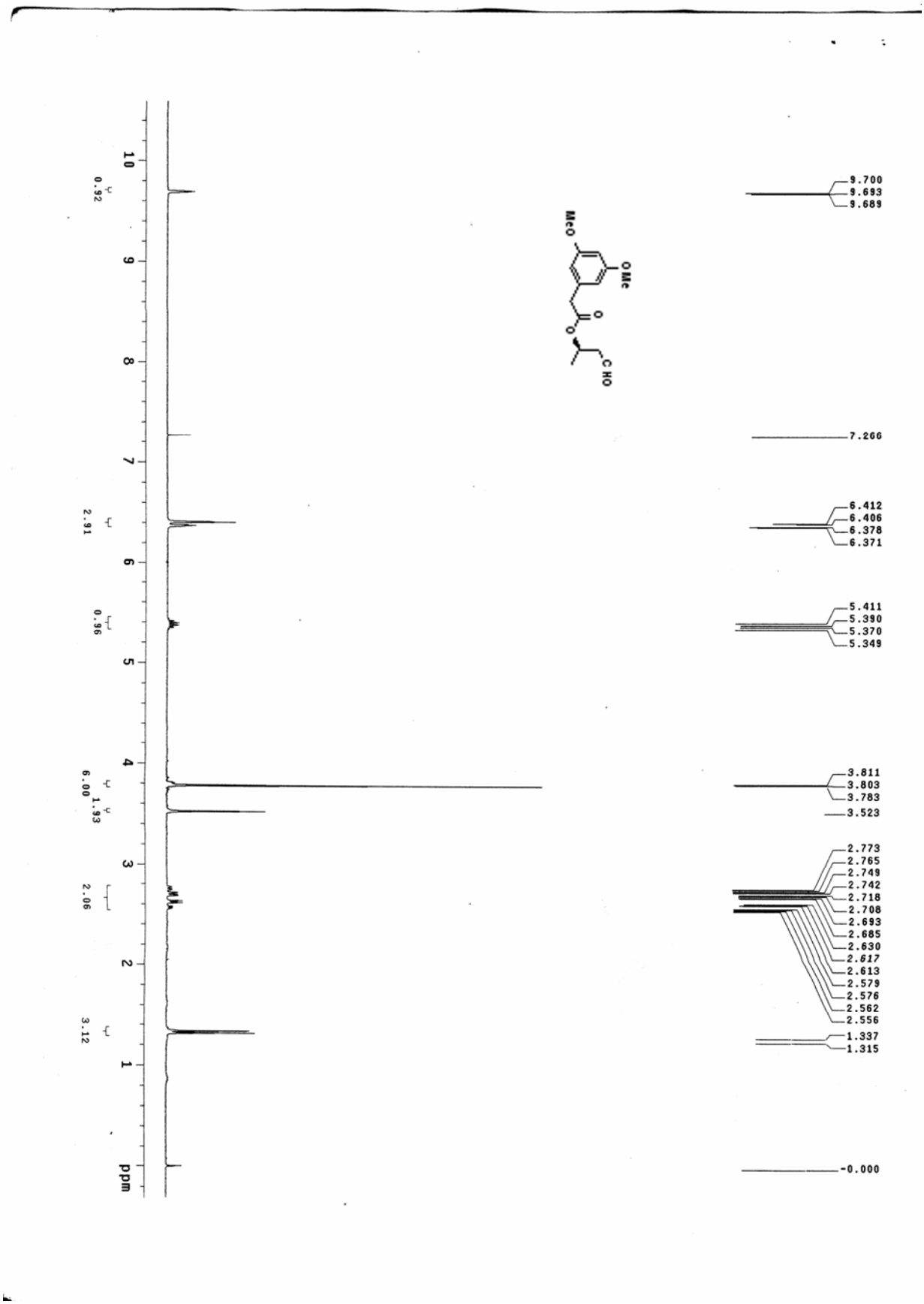
41.343
30.156
29.728
25.737
20.136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3.811
3.803
3.783
3.523
2.773
2.765
2.749
2.742
2.718
2.708
2.693
2.685
2.630
2.617
2.613
2.579
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2.562
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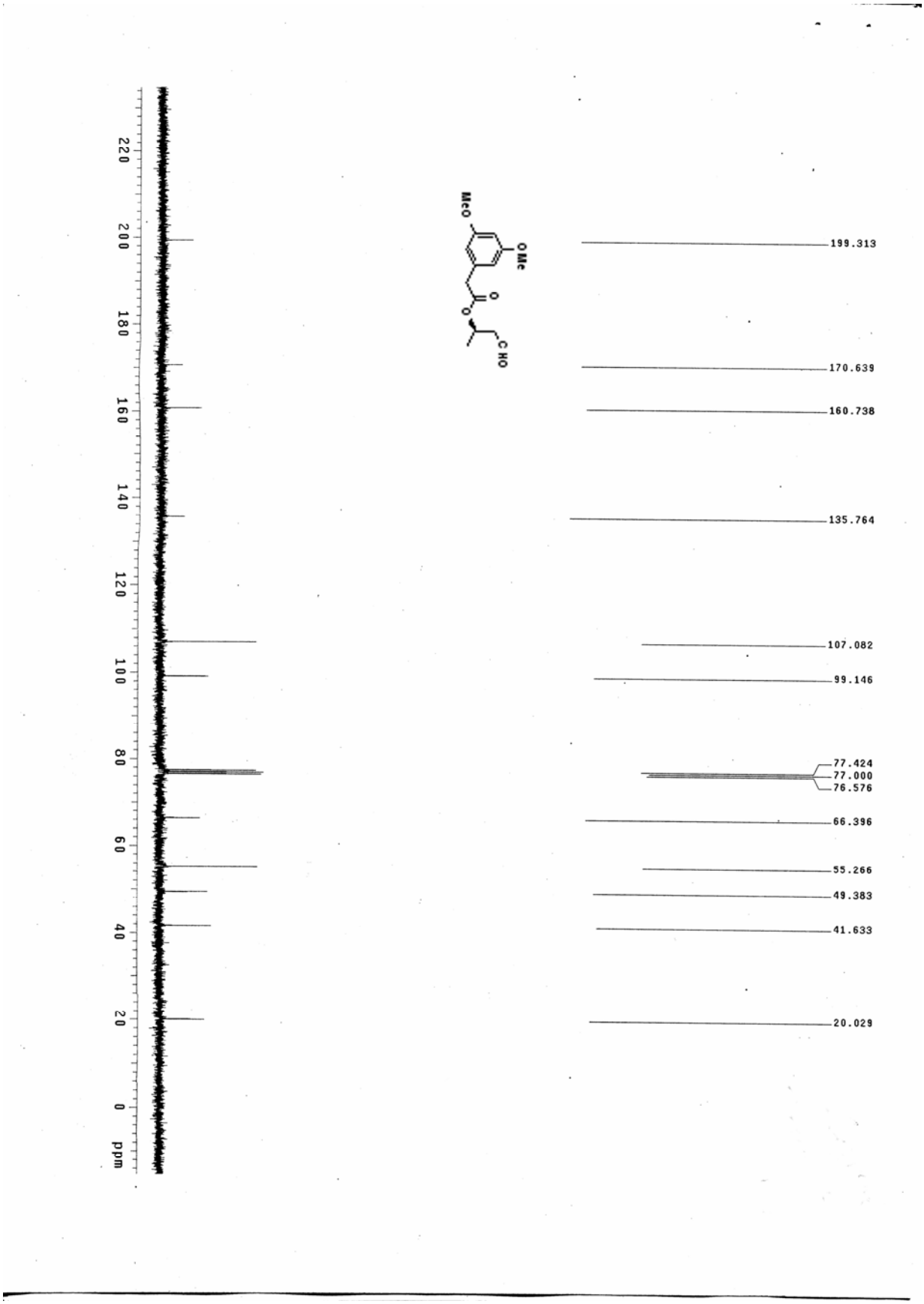
OMe
O
O
CHO
ppm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99.146
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66.396
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120
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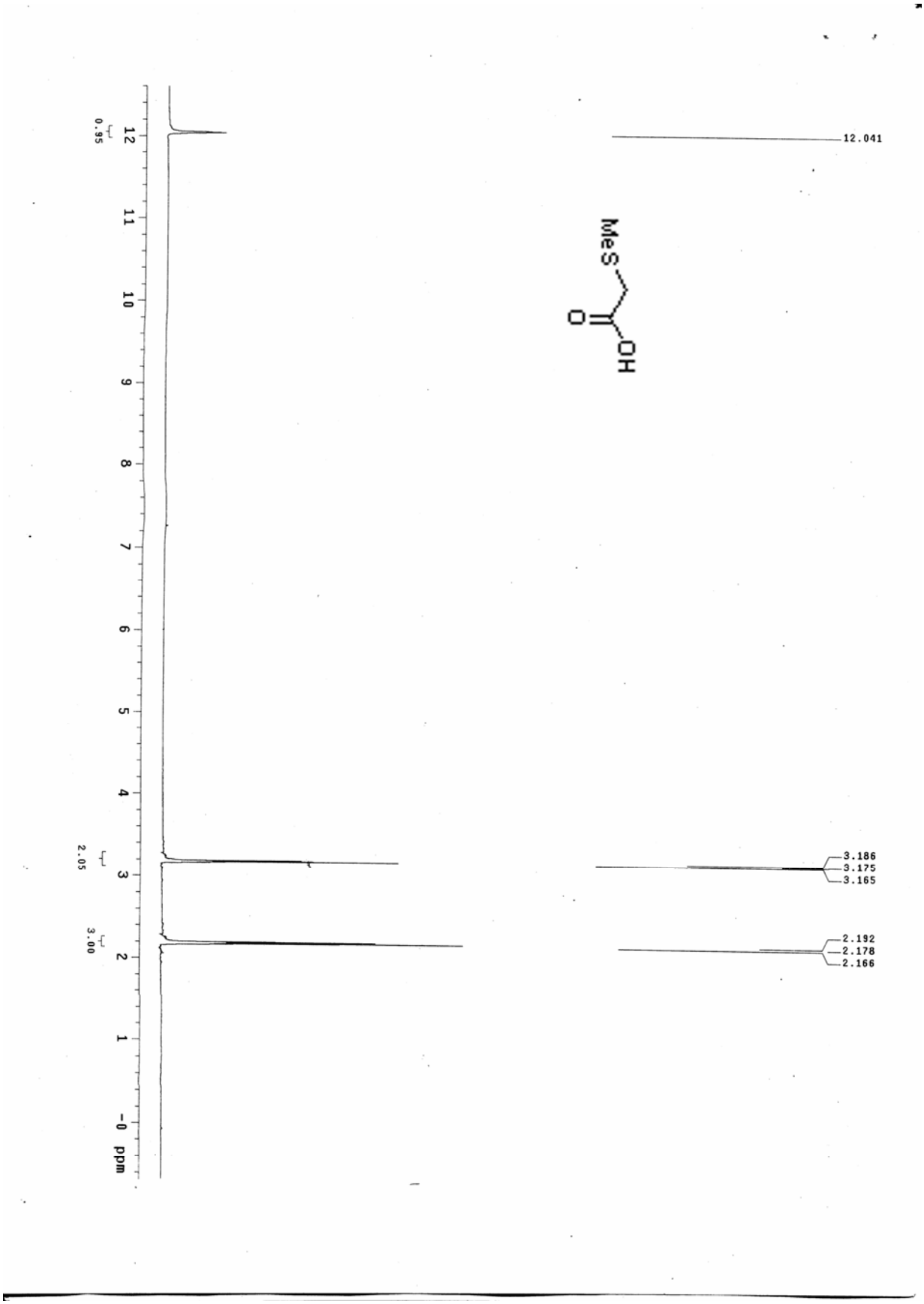
80
60
40
20
0
ppm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2.178
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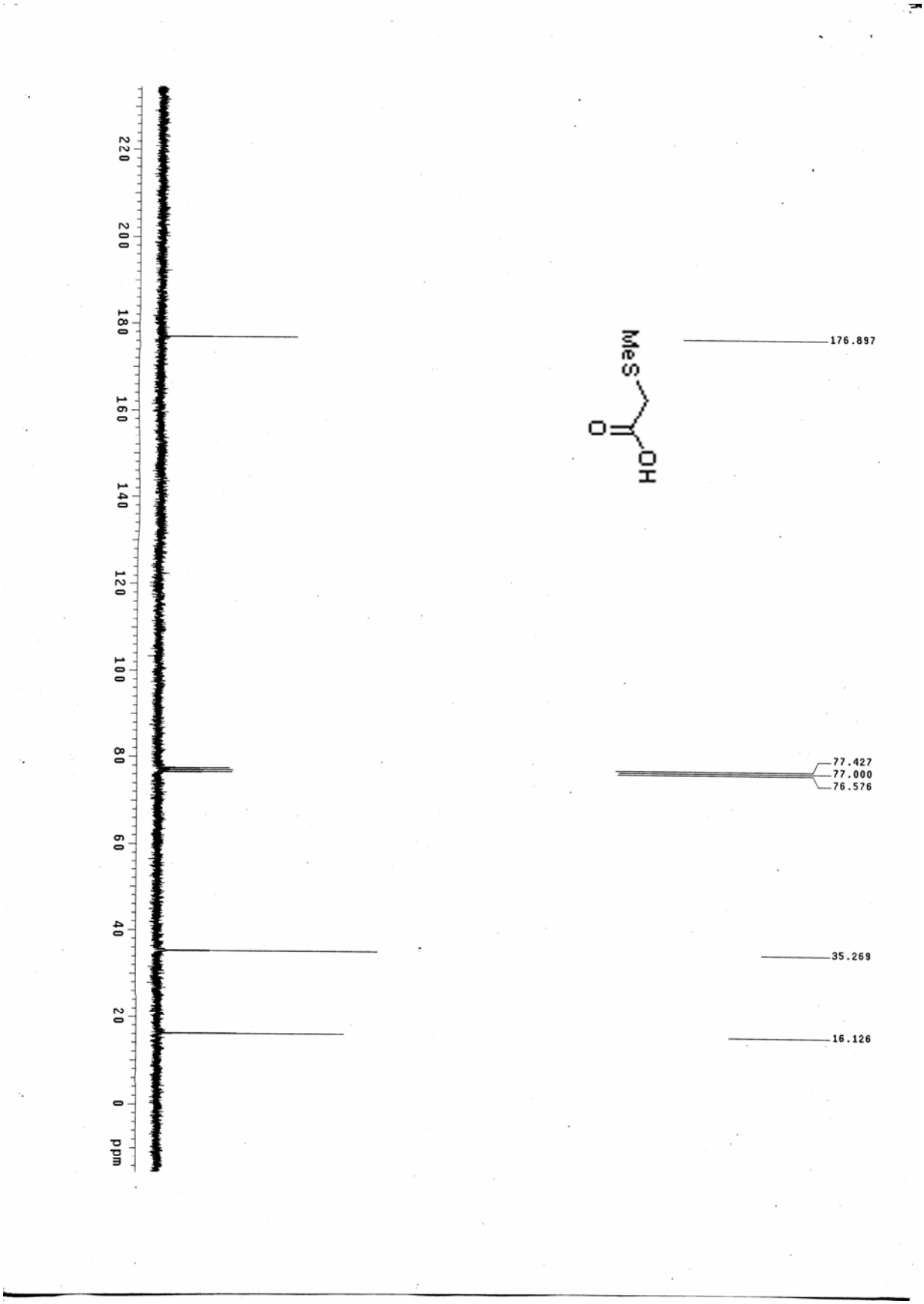
3.00
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm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120
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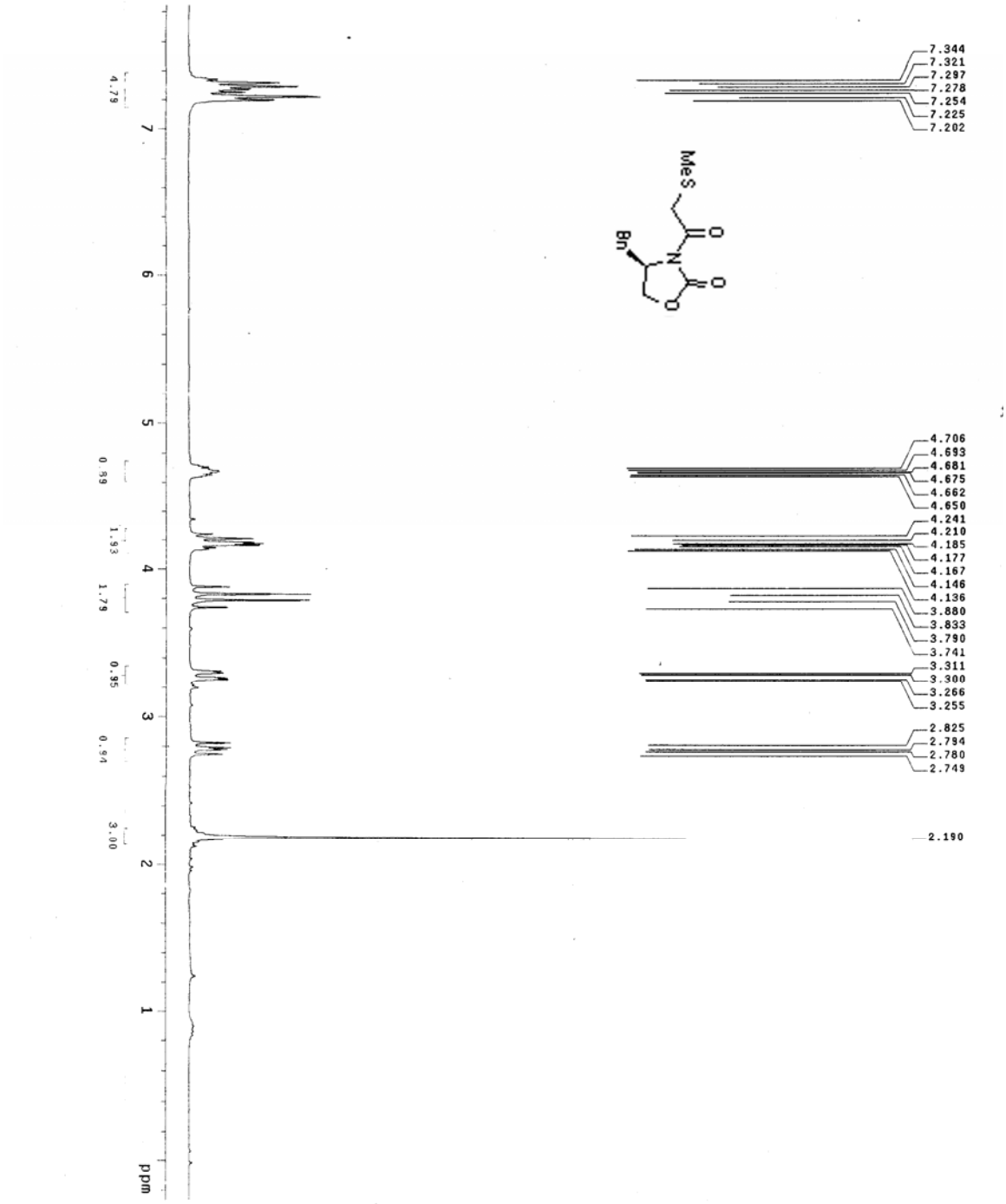
60
40
20
0
ppm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7.254
7.225
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N
O
O
O
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4.693
4.681
4.675
4.662
4.650
4.241
4.210
4.185
4.177
4.167
4.146
4.136
3.880
3.833
3.790
3.741
3.311
3.300
3.266
3.255
2.825
2.794
2.780
2.749
2.190
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1.79
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3.00
7
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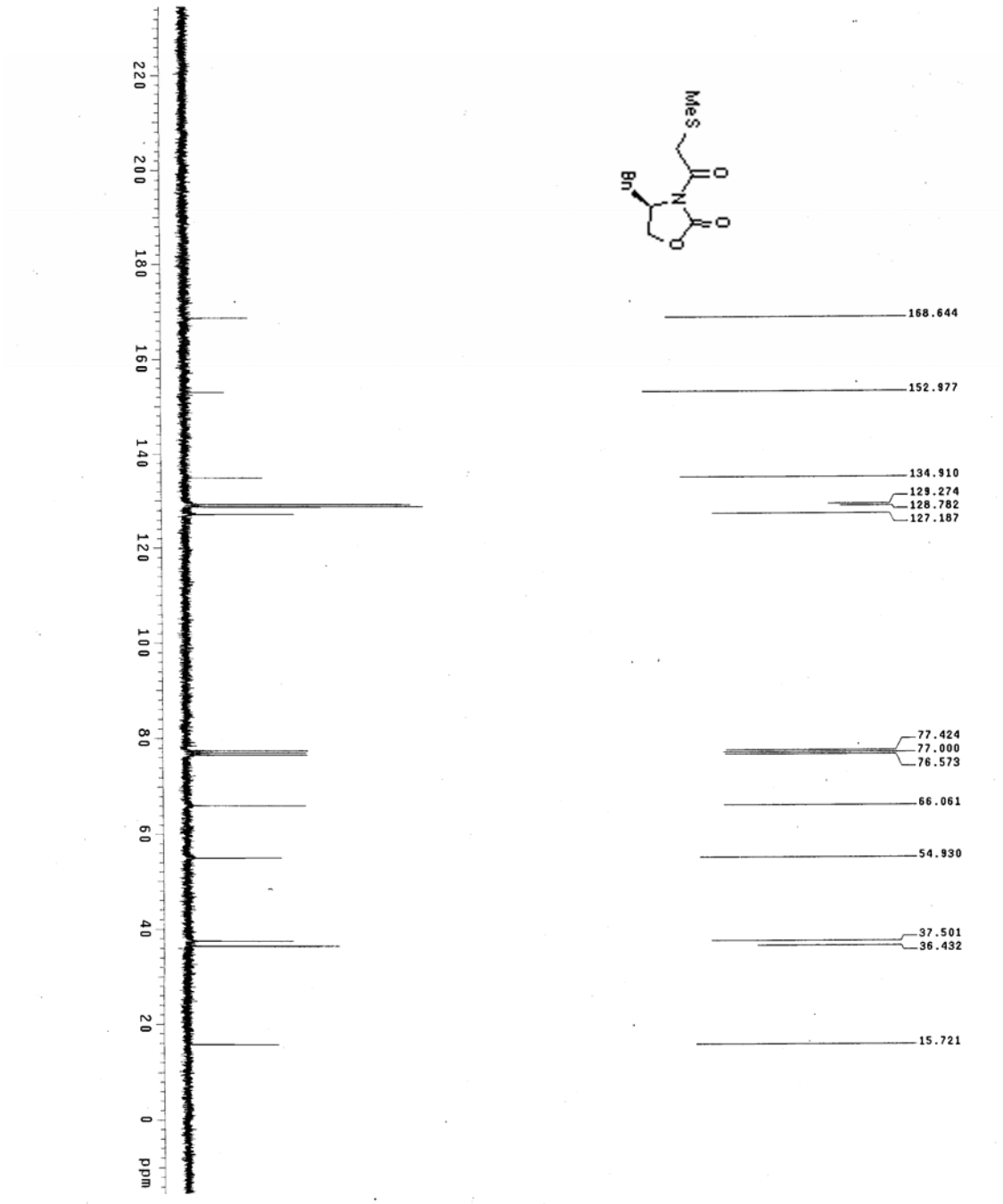
4
3
2
1
ppm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120
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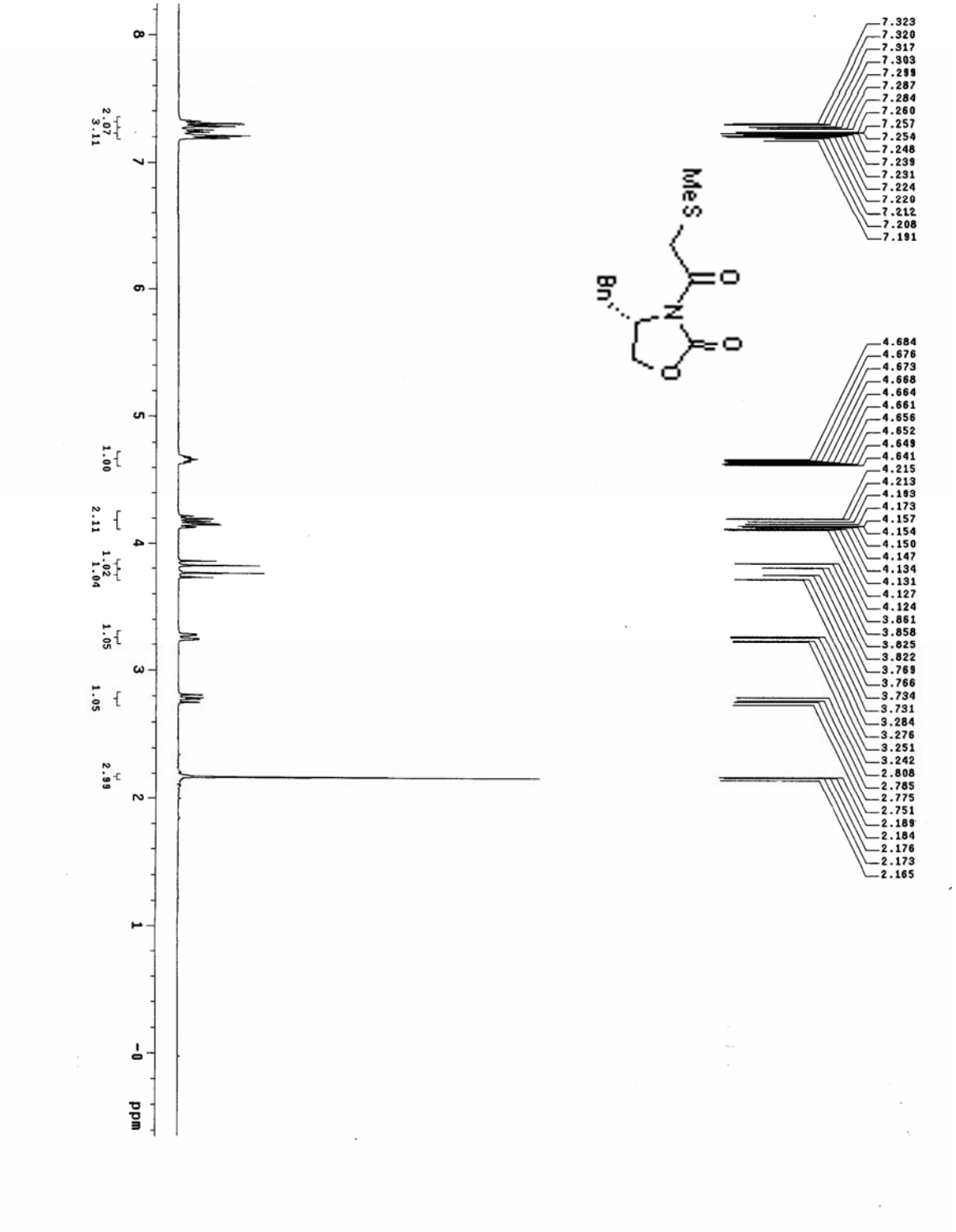
60
40
20
0
ppm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7.257
7.254
7.248
7.239
7.231
7.224
7.220
7.212
7.208
7.191
4.684
4.676
4.673
4.668
4.664
4.661
4.656
4.652
4.649
4.641
4.215
4.213
4.183
4.173
4.157
4.154
4.150
4.147
4.134
4.131
4.127
4.124
3.861
3.858
3.825
3.822
3.769
3.766
3.734
3.731
3.284
3.276
3.251
3.242
2.808
2.785
2.775
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2.189
2.184
2.176
2.173
2.165
2.07
3.11
1.00
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1.05
1.05
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6
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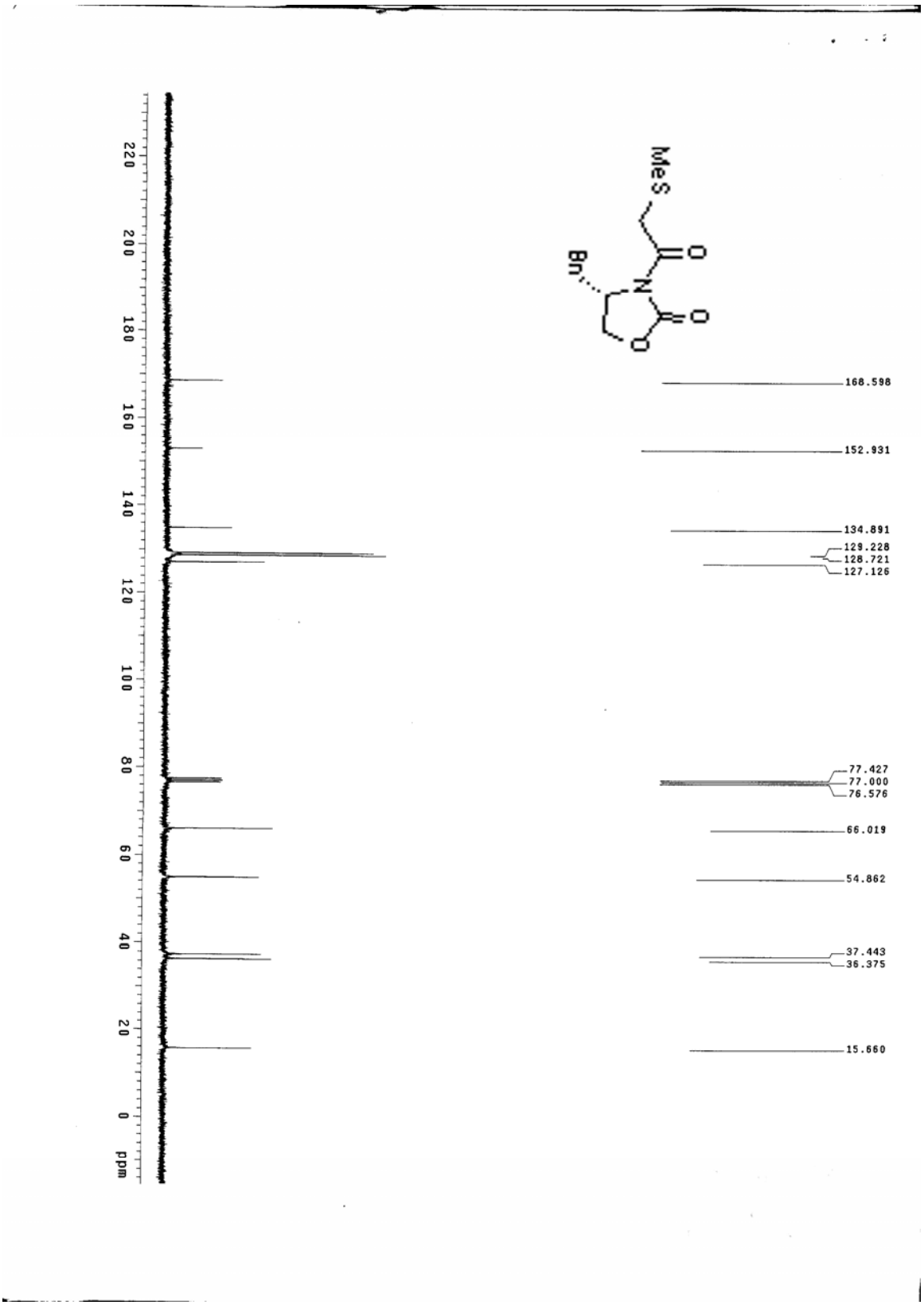
ppm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66.019
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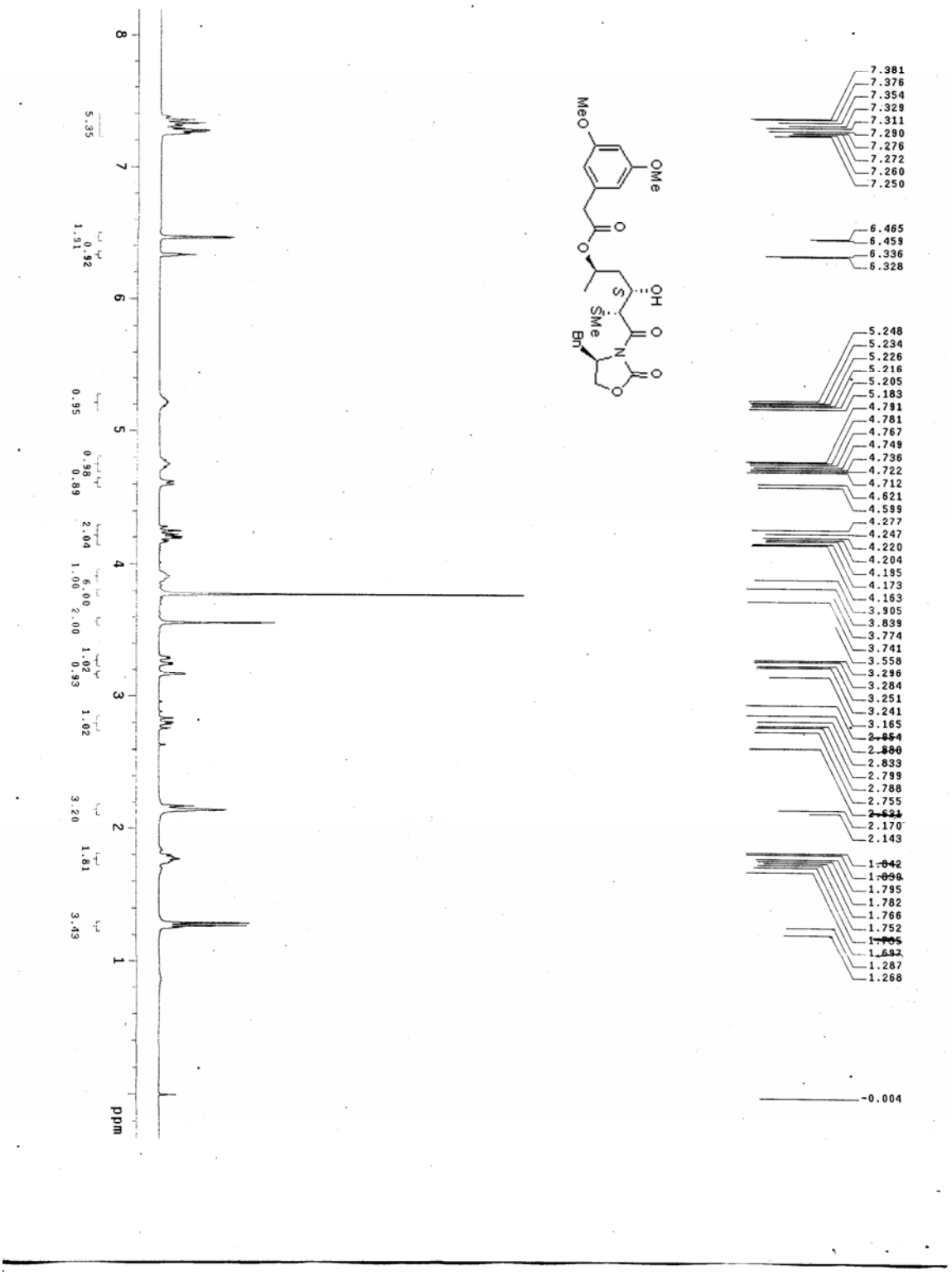
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7.250
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6.459
6.336
6.328
5.248
5.234
5.226
5.216
5.205
5.183
4.791
4.781
4.767
4.749
4.736
4.722
4.712
4.621
4.599
4.277
4.247
4.220
4.204
4.195
4.173
4.163
3.905
3.839
3.774
3.741
3.558
3.296
3.284
3.251
3.241
3.165
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2.880
2.833
2.799
2.788
2.755
2.631
2.170
2.143
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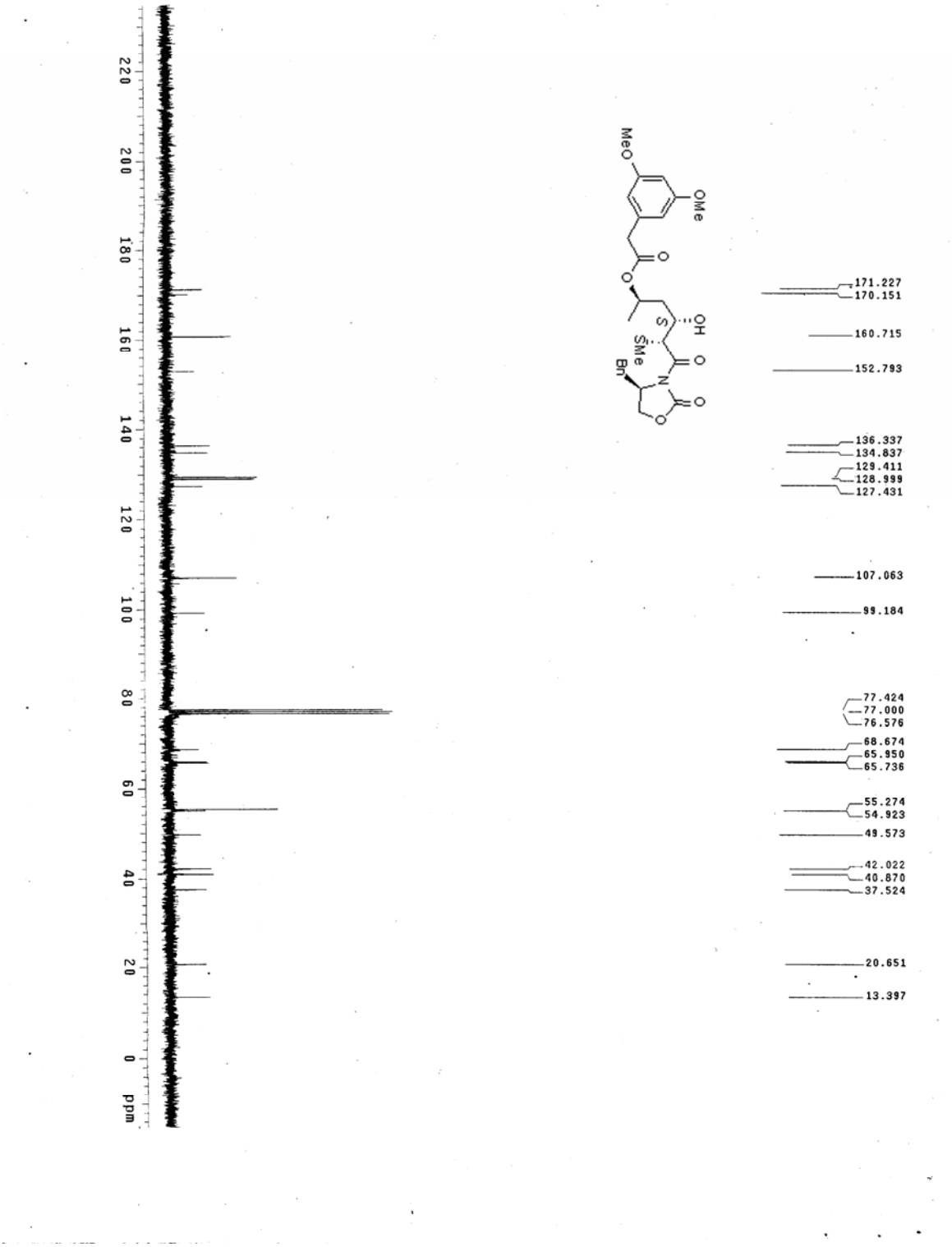
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OMe
OH
SMe
Bn
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170.151
160.715
152.793
136.337
134.837
129.411
128.999
127.431
107.063
99.184
77.424
77.000
76.576
68.674
65.950
65.736
55.274
54.923
49.573
42.022
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13.397
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200
180
160
140
120
100
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60
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20
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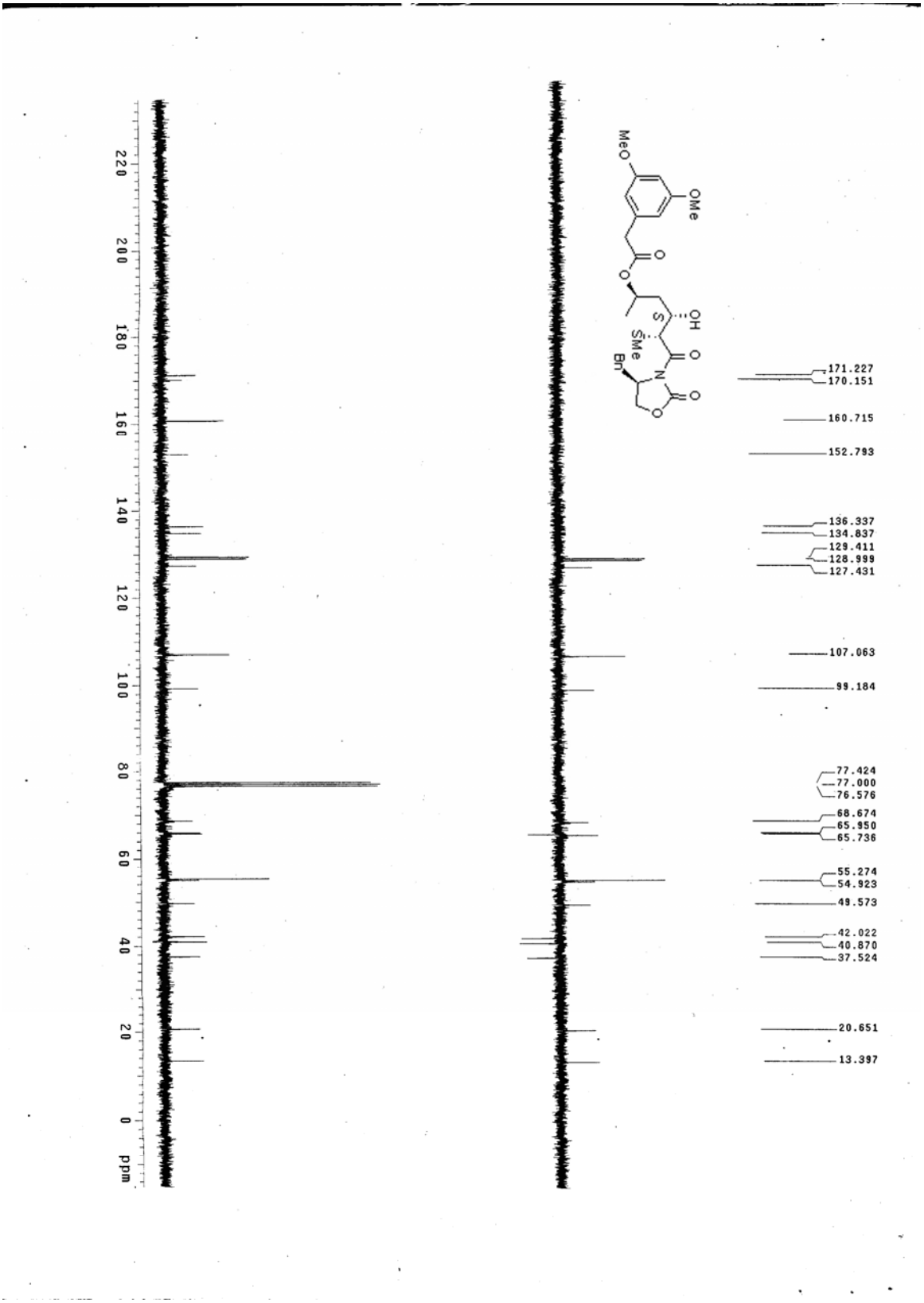
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OMe
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O
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SiMe
Bn
N
O
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171.227
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152.793
136.337
134.837
129.411
128.999
127.431
107.063
99.184
77.424
77.000
76.576
68.674
65.950
65.736
55.274
54.923
49.573
42.022
40.870
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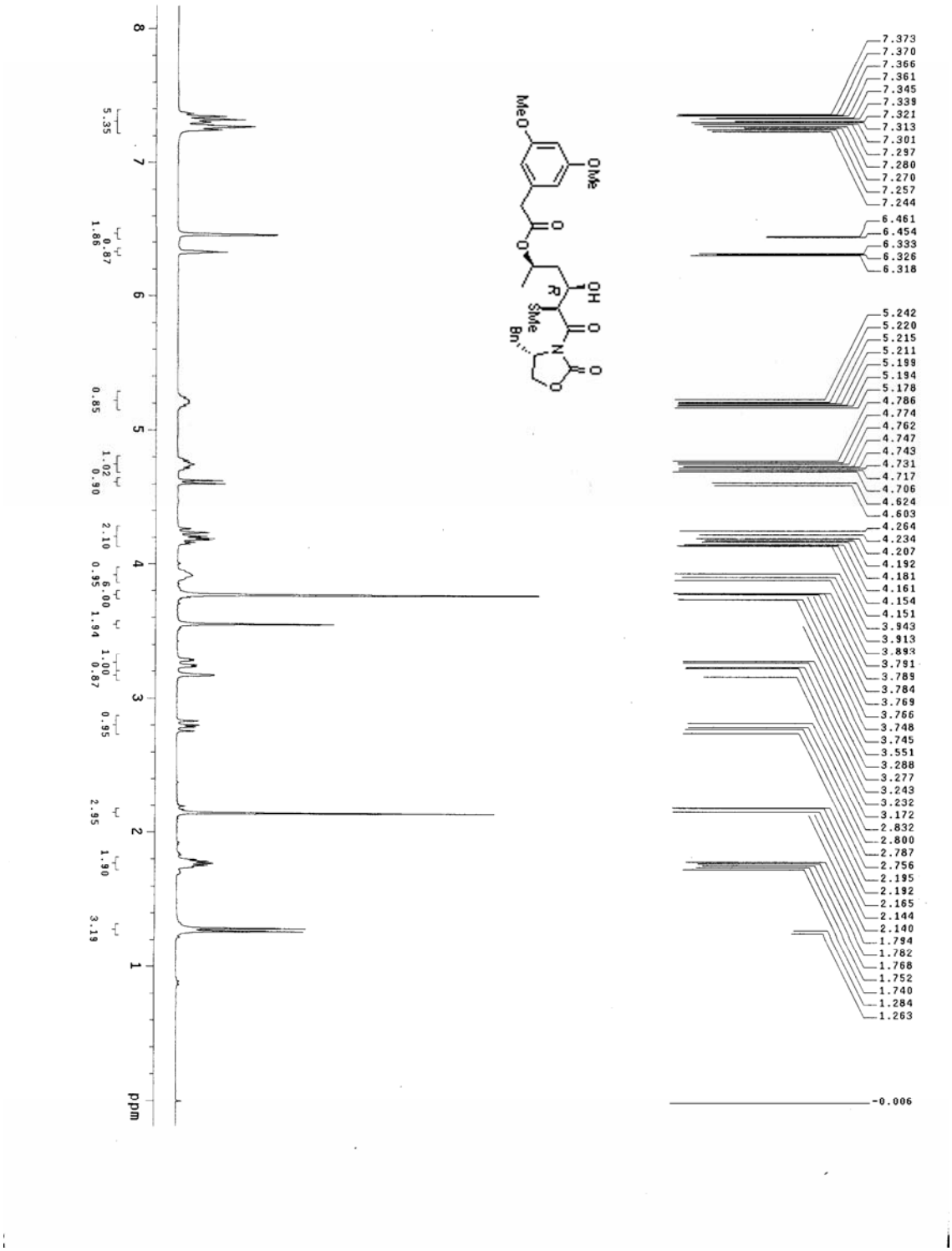
13.397
220
200
180
160
140
120
100
80
60
40
20
0
ppm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OMe
OH
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O
O
N
O
R
SiMe
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7.339
7.321
7.313
7.301
7.297
7.280
7.270
7.257
7.244
6.461
6.454
6.333
6.326
6.318
5.242
5.220
5.215
5.211
5.199
5.194
5.178
4.786
4.774
4.762
4.747
4.743
4.731
4.717
4.706
4.624
4.603
4.264
4.234
4.207
4.192
4.181
4.161
4.154
4.151
3.943
3.913
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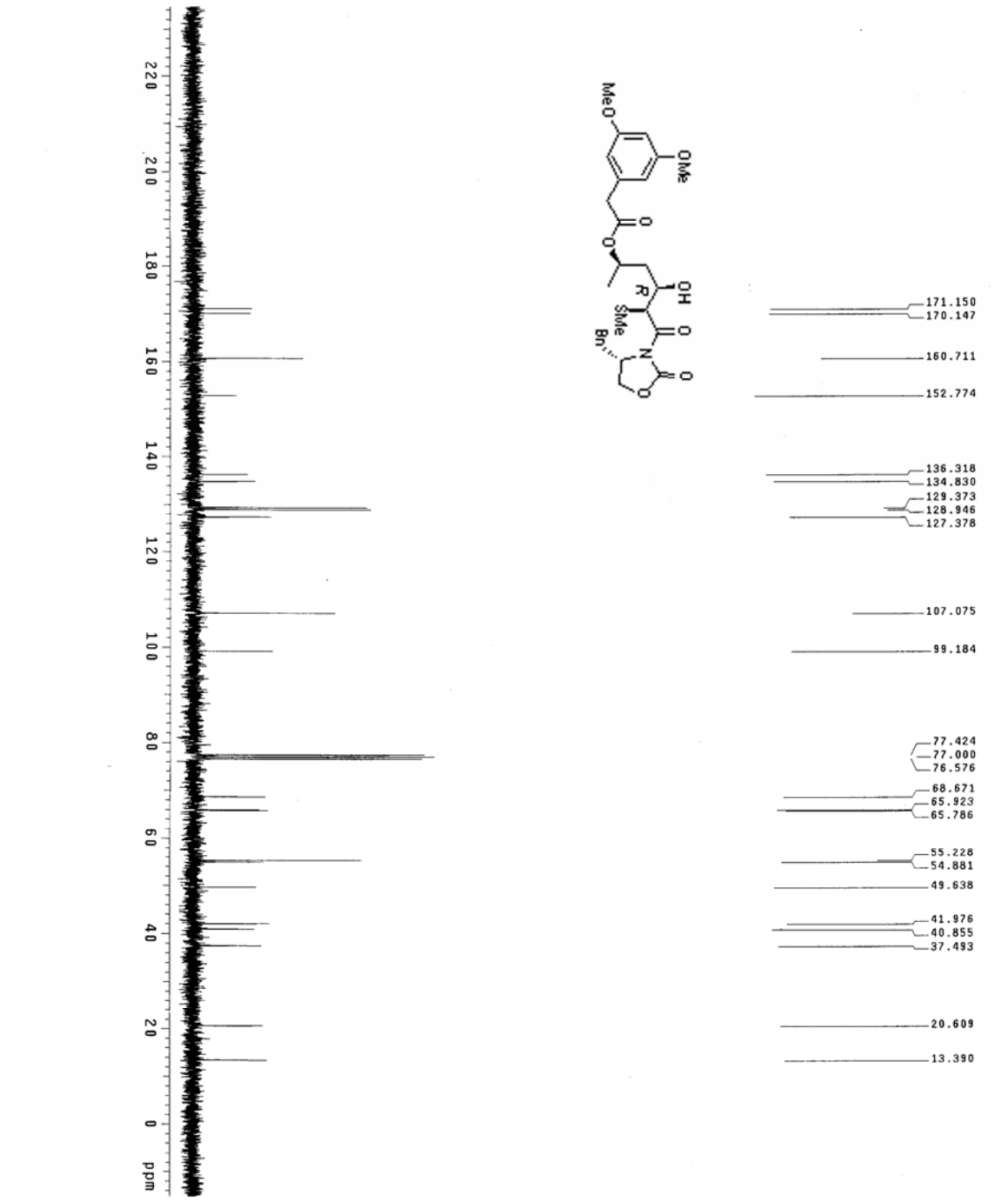
3.791
3.789
3.784
3.769
3.766
3.748
3.745
3.551
3.288
3.277
3.243
3.232
3.172
2.832
2.800
2.787
2.756
2.195
2.192
2.165
2.144
2.140
1.794
1.782
1.768
1.752
1.740
1.284
1.263
-0.006
5.35
0.87
1.86
0.85
1.02
0.90
2.10
0.95
6.00
1.94
1.00
0.87
0.95
2.95
1.90
3.19
8
7
6
5
4
3
2
1
ppm


MeO
OMe
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O
R
OH
O
SMe
Bn
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O
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76.576
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54.881
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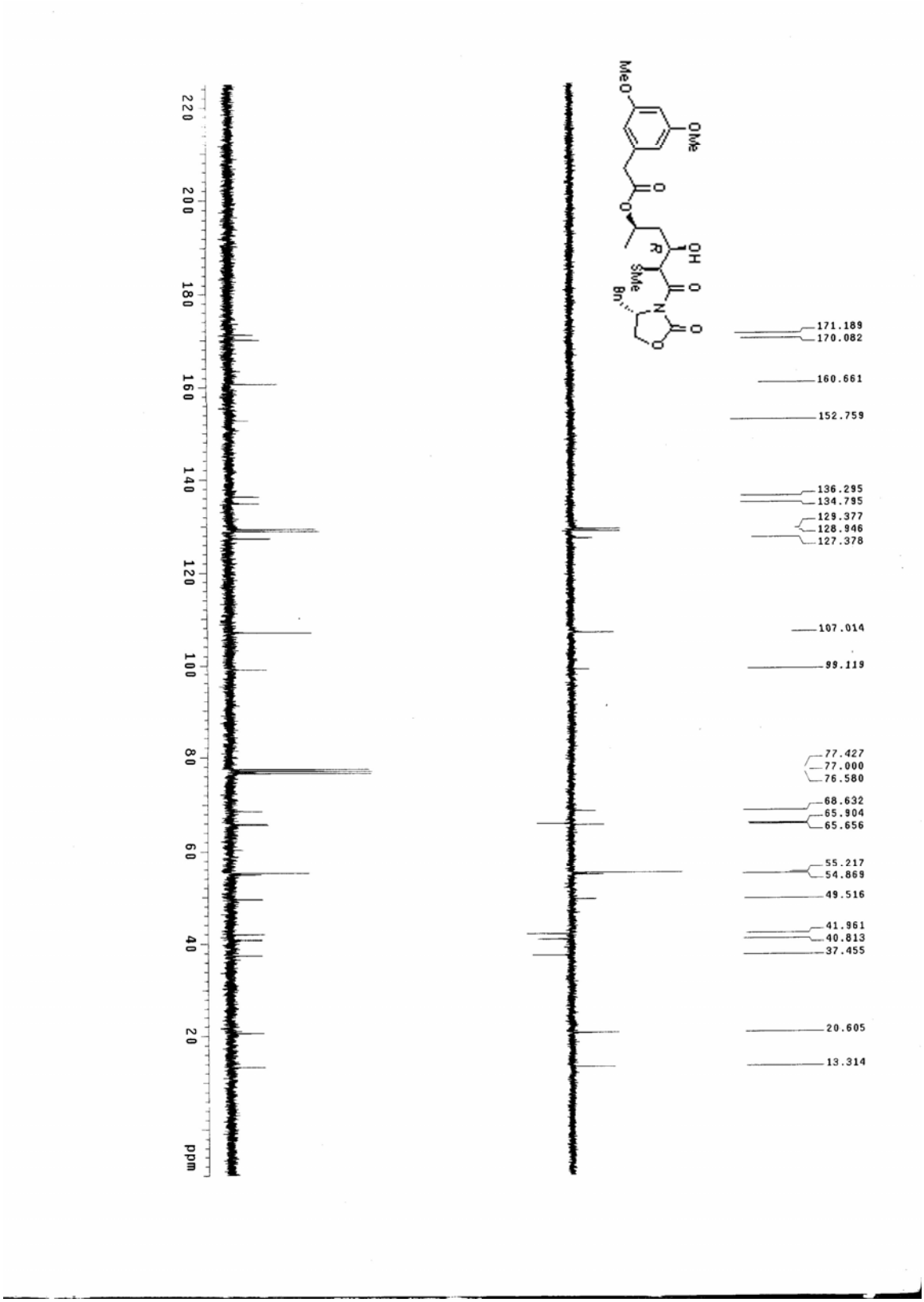
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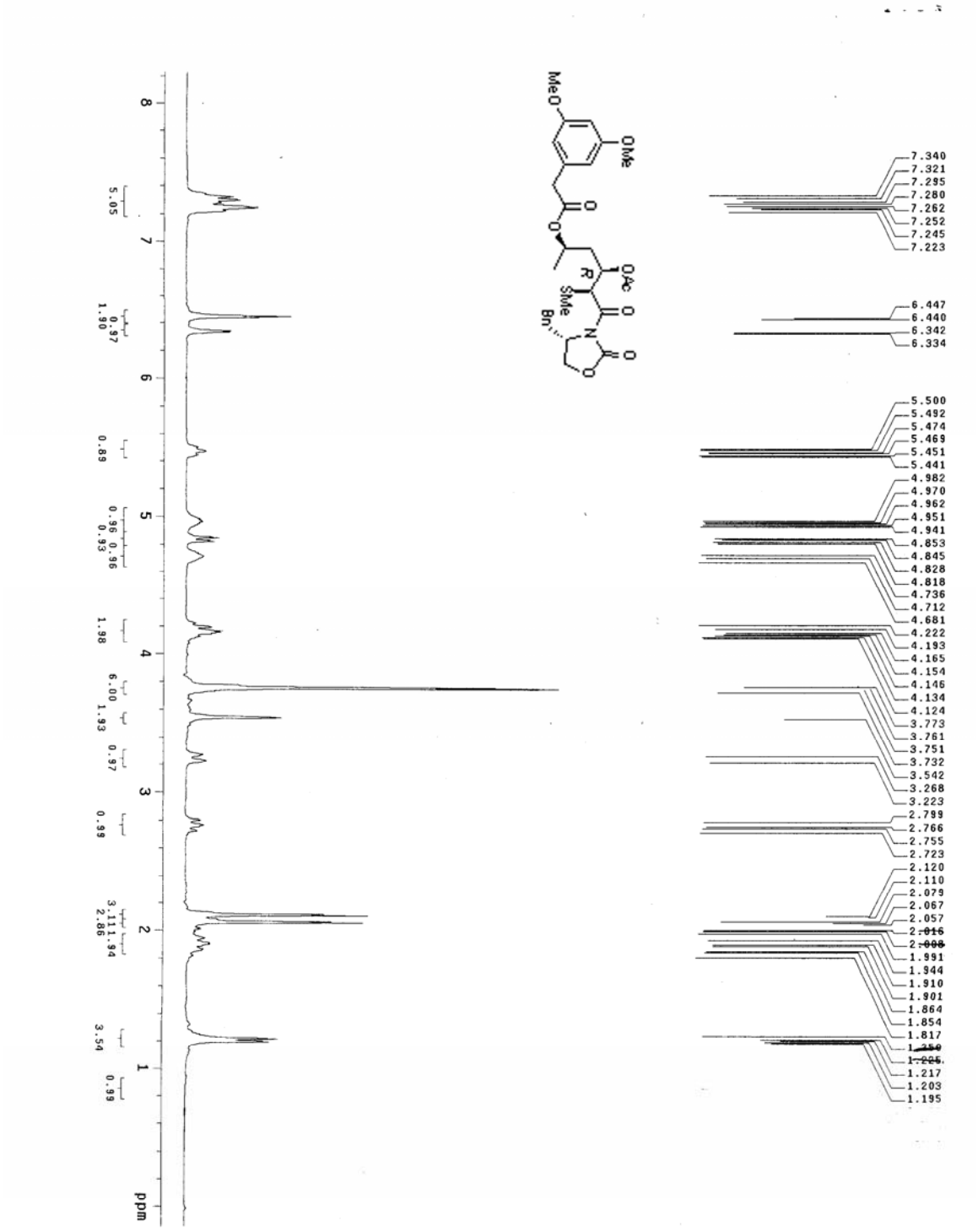
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6.342
6.334
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5.469
5.451
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4.941
4.853
4.845
4.828
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4.681
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4.193
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2.057
2.016
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1.225
1.217
1.203
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1.93
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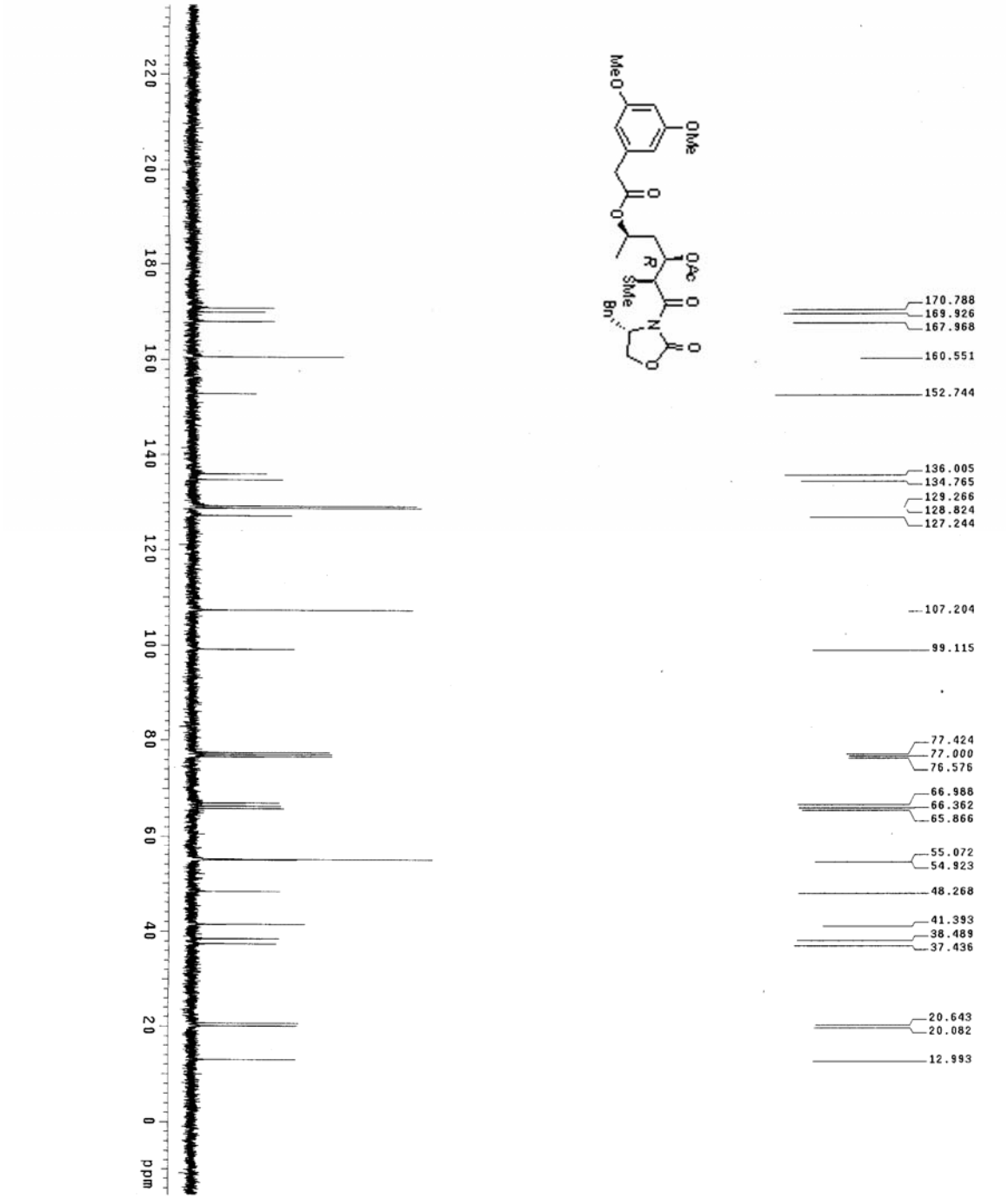
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65.866
55.072
54.923
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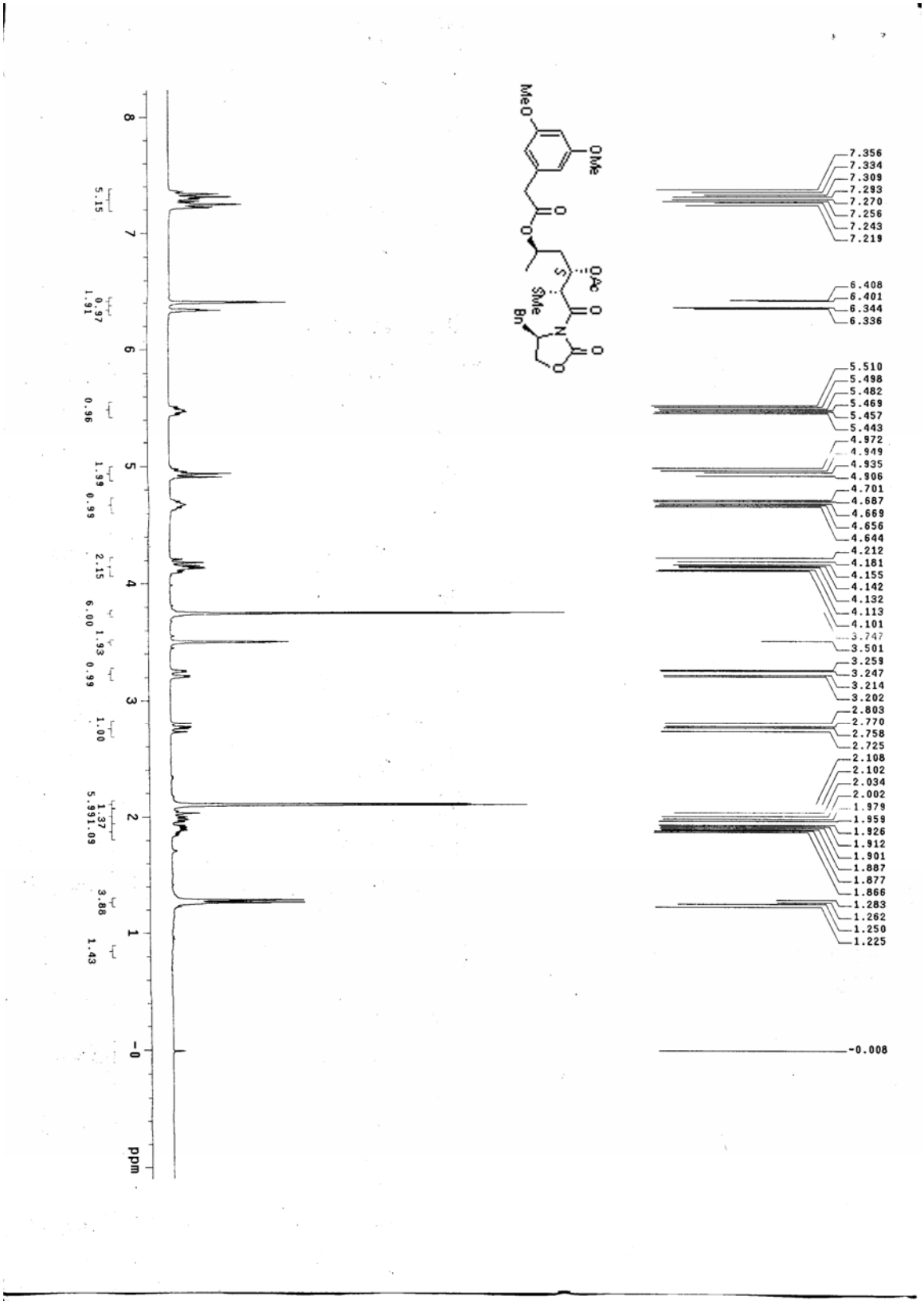
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4.644
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4.142
4.132
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3.501
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3.214
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2.102
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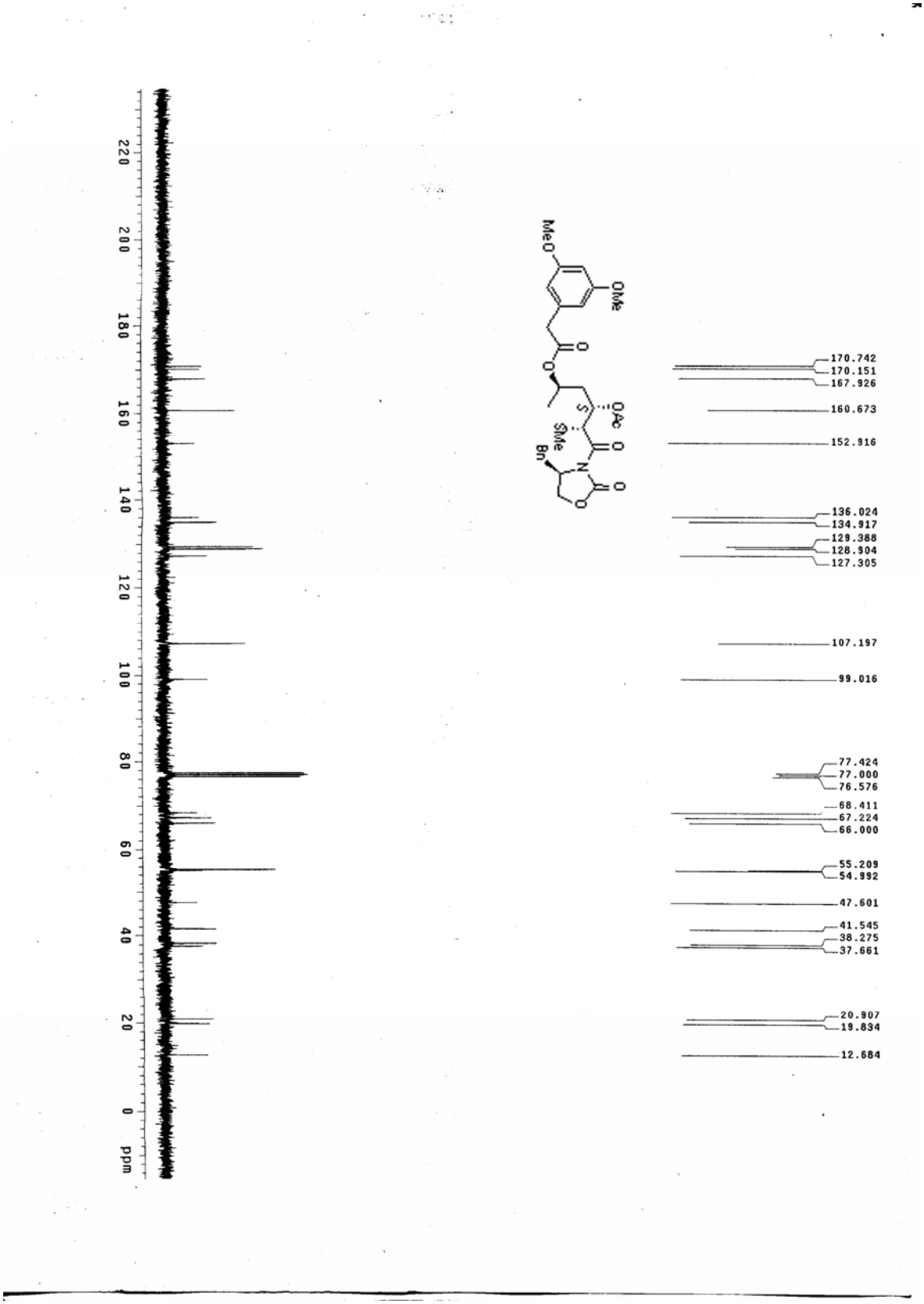
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67.224
66.000
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54.992
47.601
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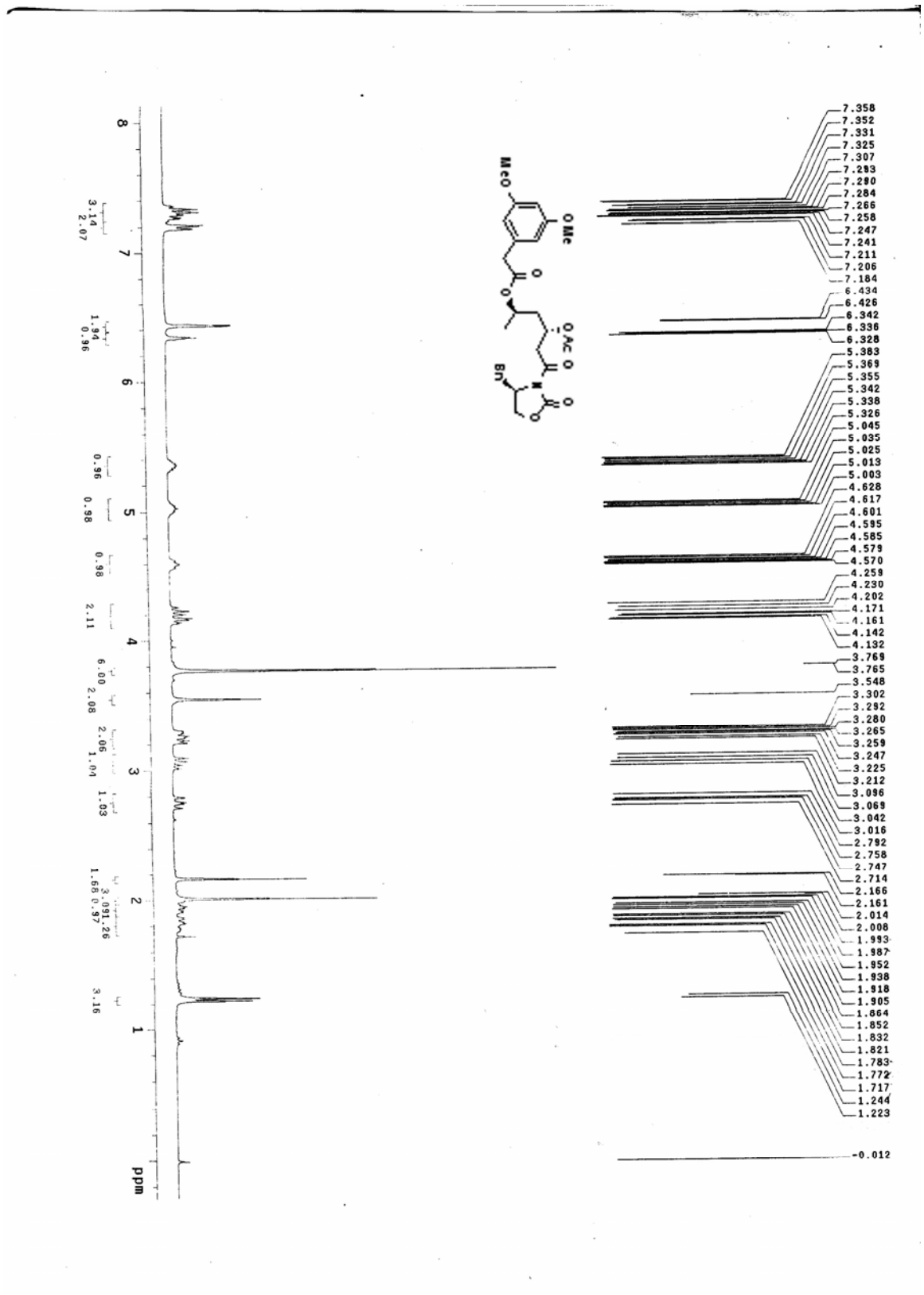
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OAc
O
Bn
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7.290
7.284
7.266
7.258
7.247
7.241
7.211
7.206
7.184
6.434
6.426
6.342
6.336
6.328
5.383
5.369
5.355
5.342
5.338
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4.595
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4.161
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3.259
3.247
3.225
3.212
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3.042
3.016
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2.758
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2.714
2.166
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1.938
1.918
1.905
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1.821
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1.772
1.717
1.244
1.223
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0.96
0.98
0.98
2.11
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2.08
2.06
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1.03
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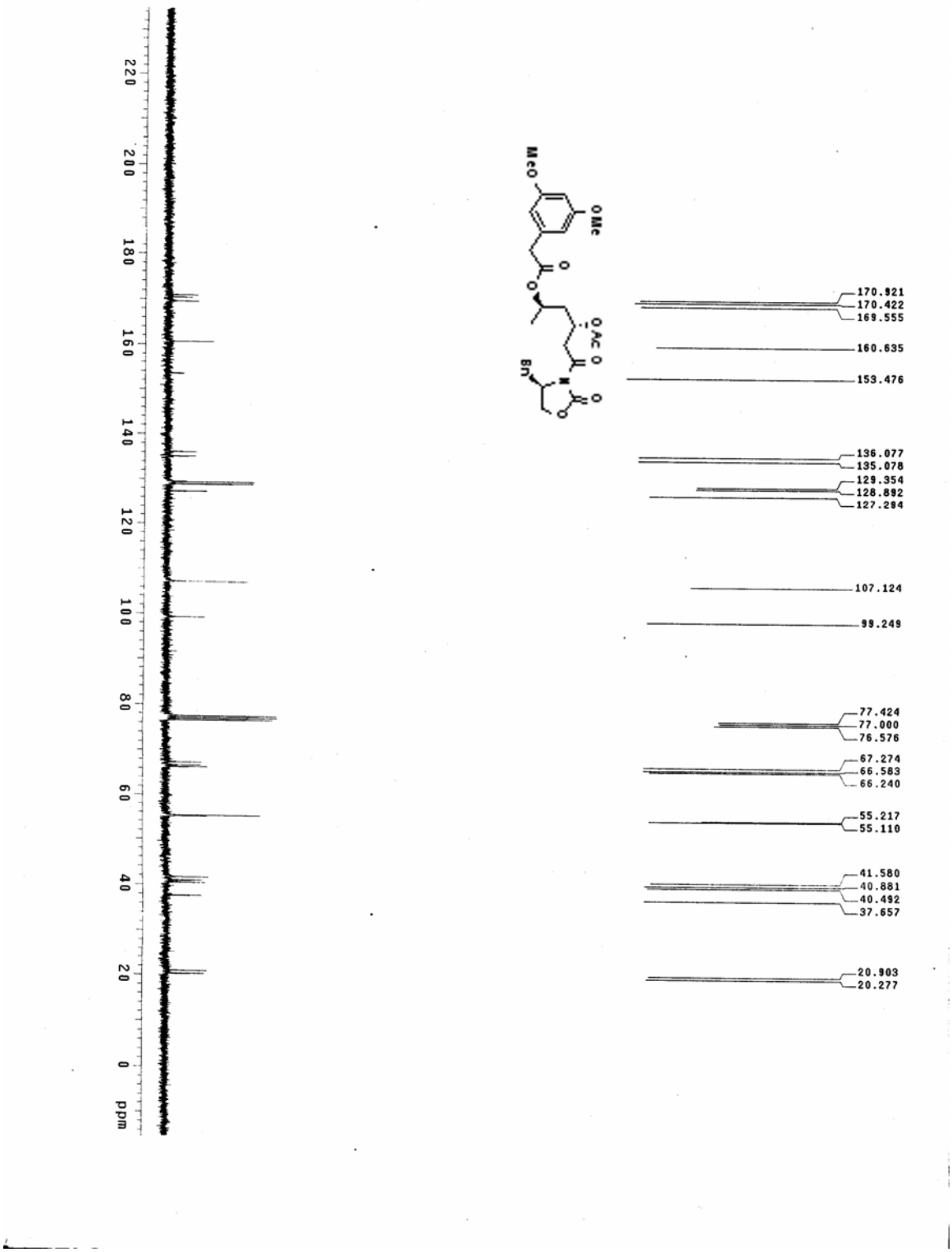
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OAc
O
O
Bn
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O
O
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107.124
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77.000
76.576
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66.240
55.217
55.110
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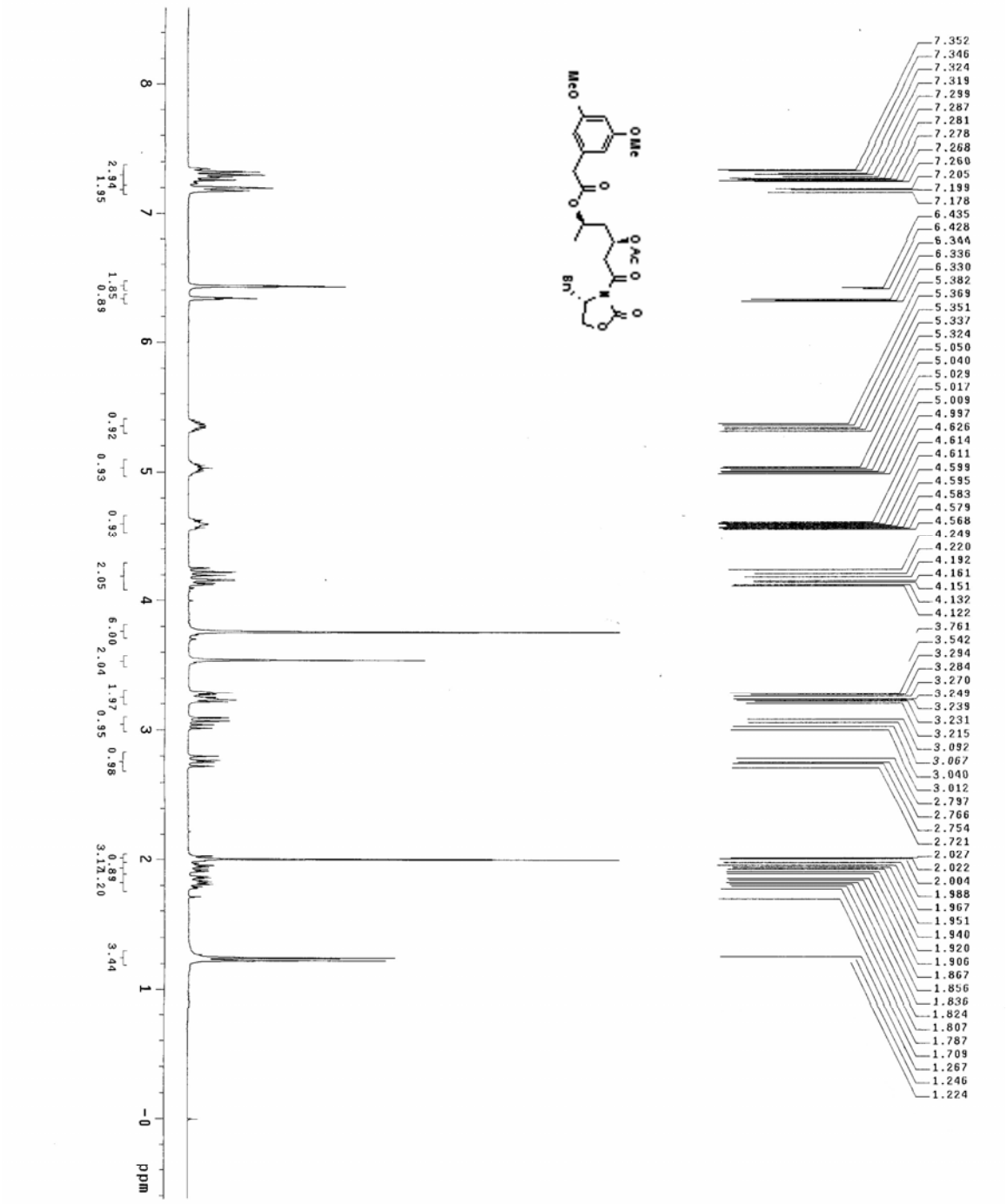
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4.599
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2.027
2.022
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1.940
1.920
1.906
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1.836
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0.92
0.93
0.93
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2.04
1.97
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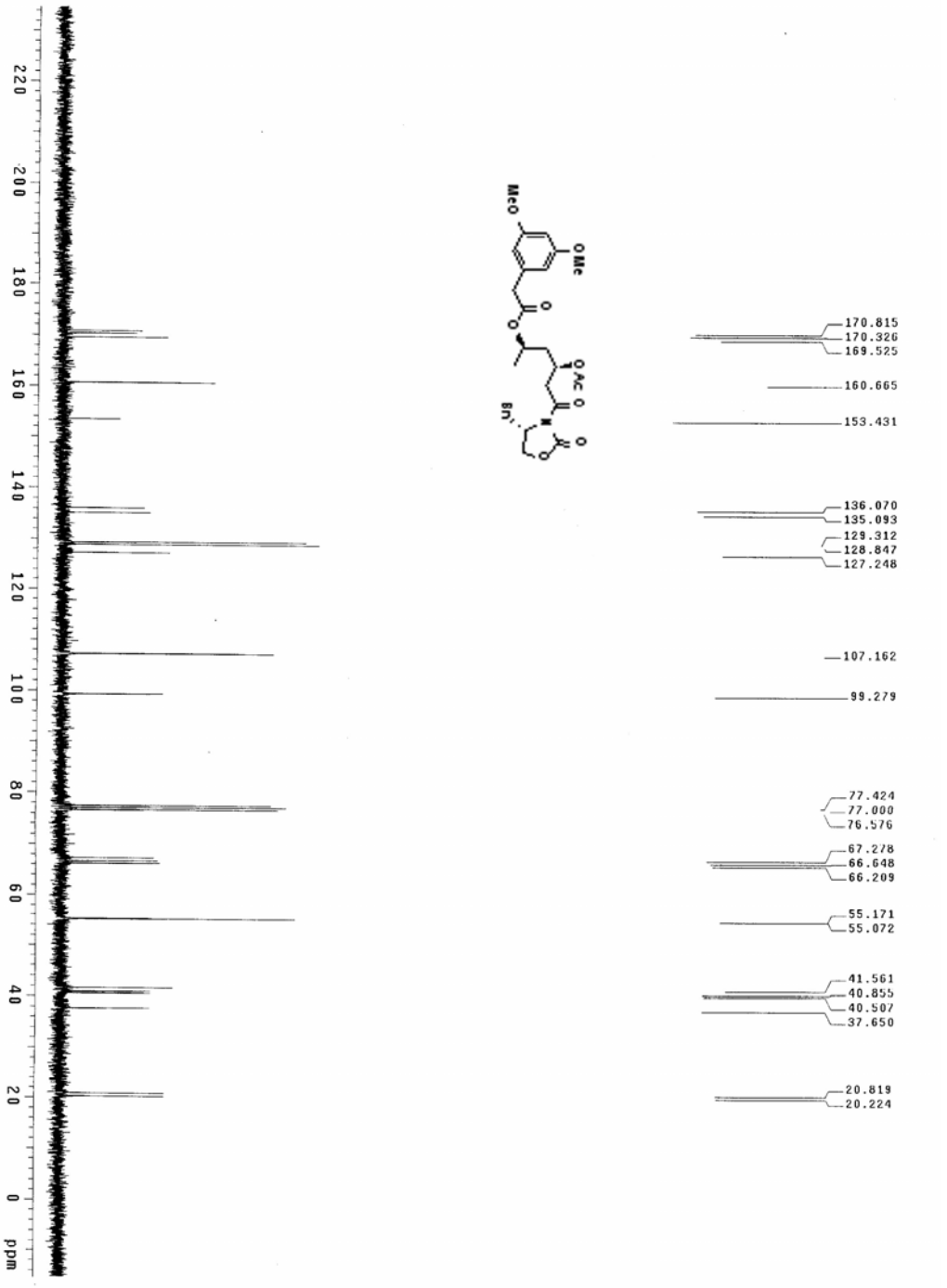
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200
180
160
140
120
100
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60
40
20
0
ppm
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OAc
Bn
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135.093
129.312
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99.279
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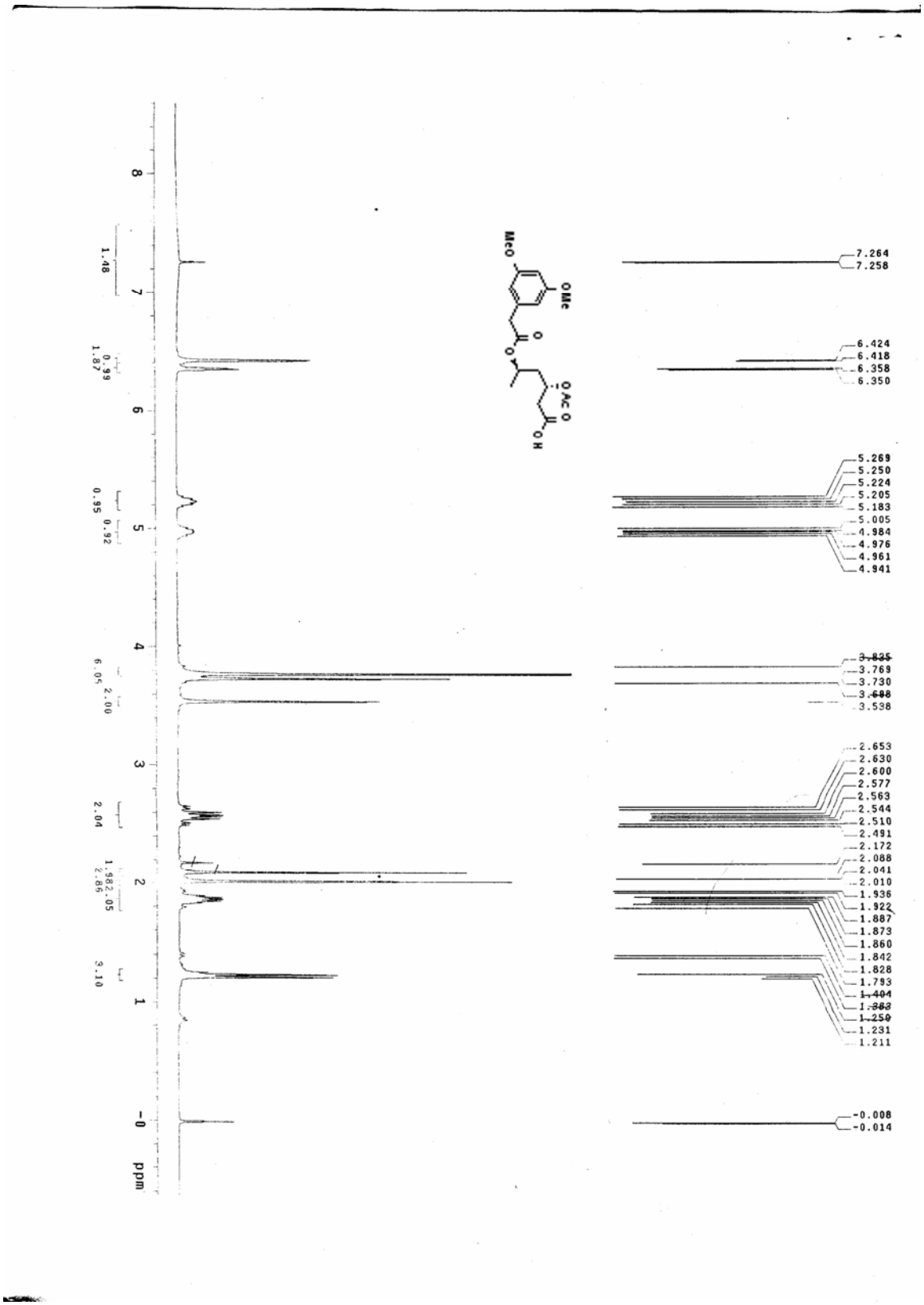
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O
OAc
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OH
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5.250
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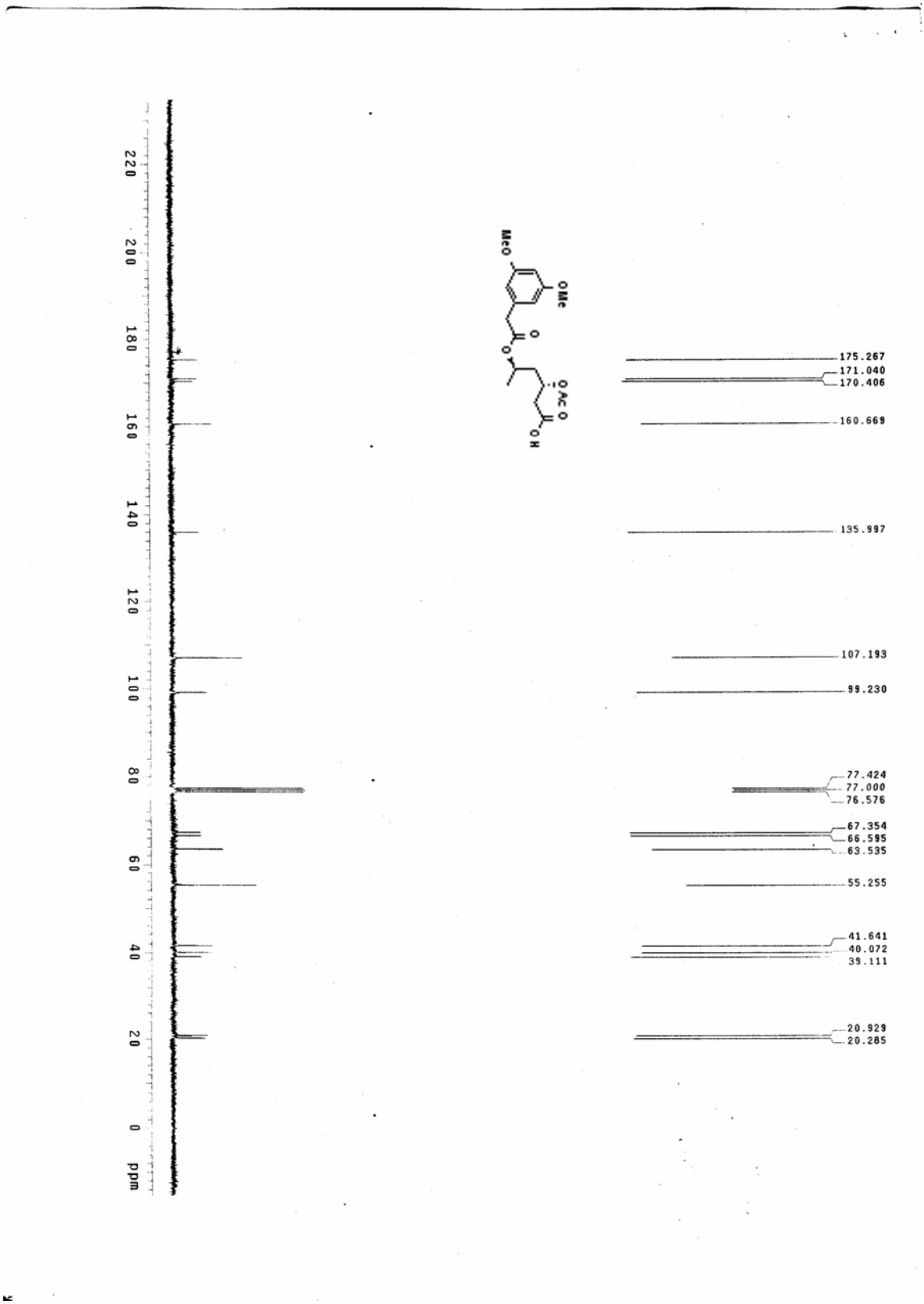
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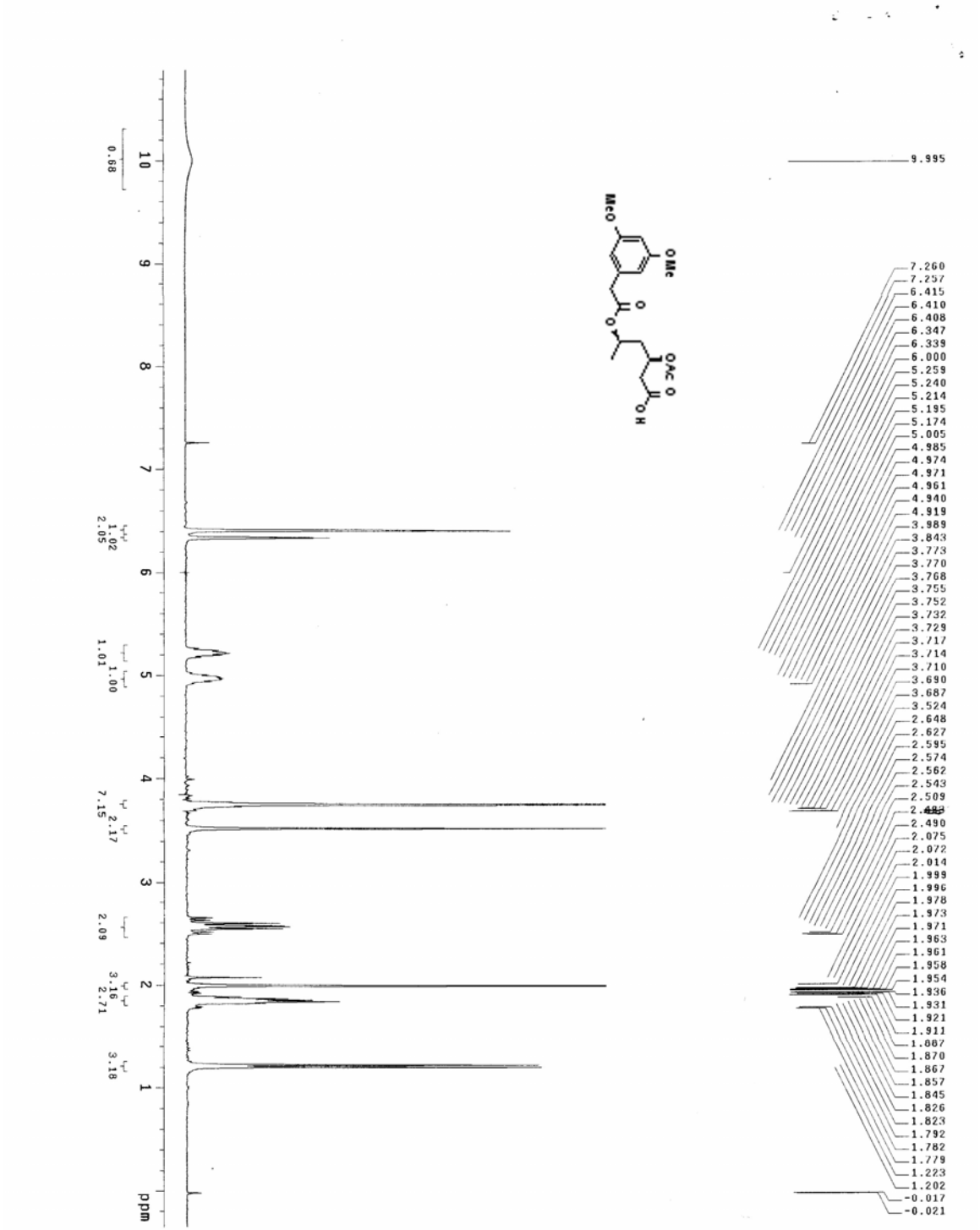
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3.729
3.717
3.714
3.710
3.690
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2.627
2.595
2.574
2.562
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OAc
O
OH
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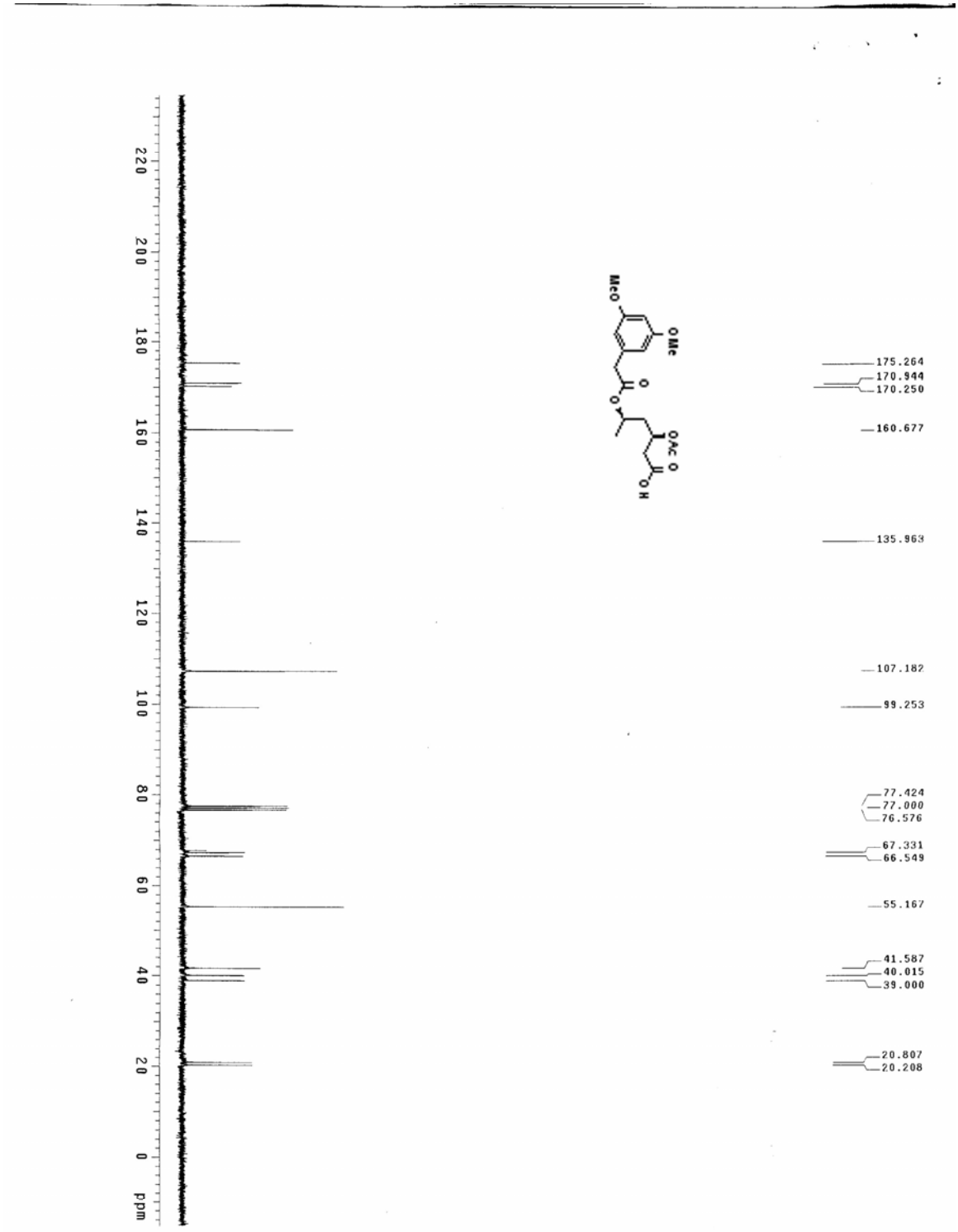
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76.576
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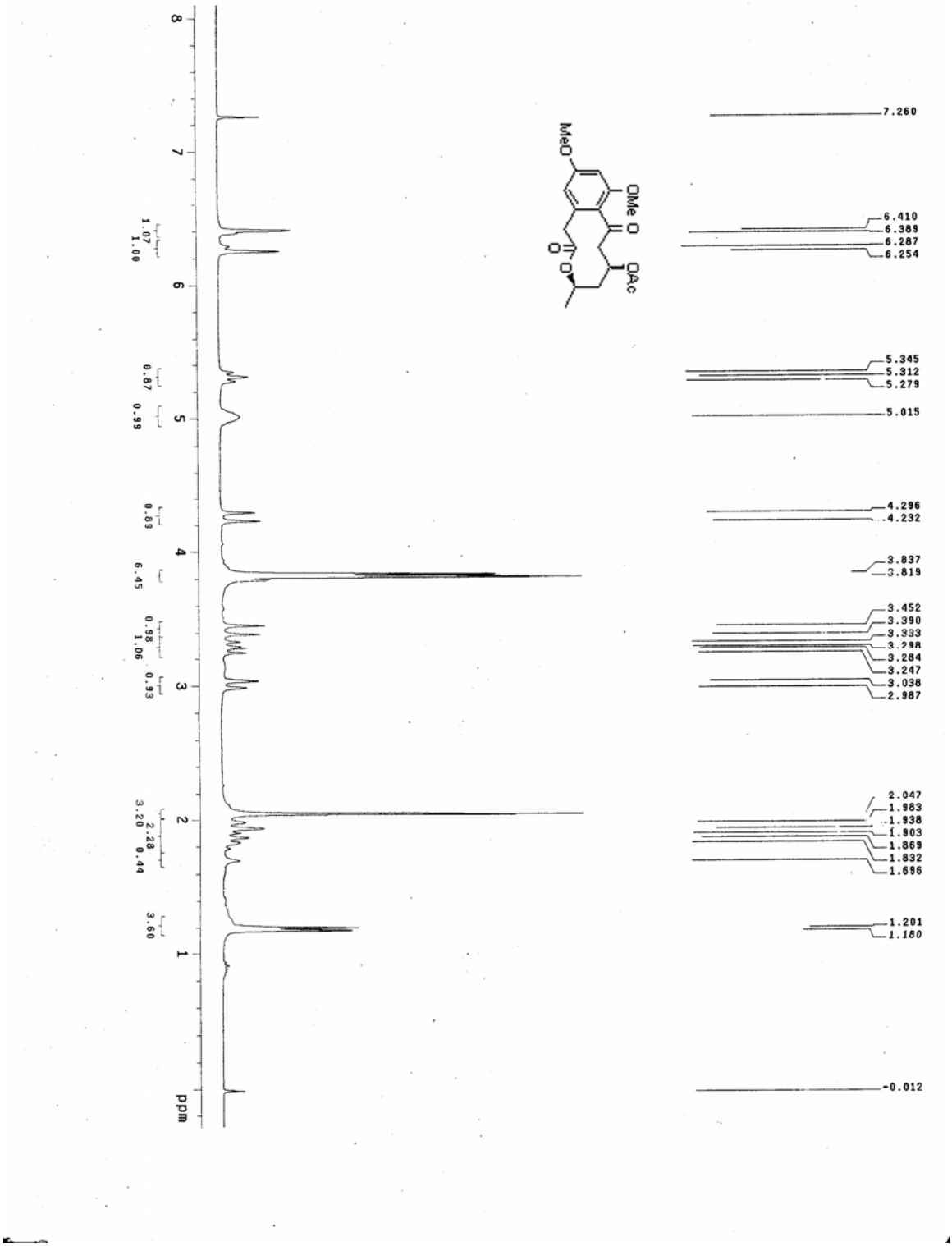
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4.232
3.837
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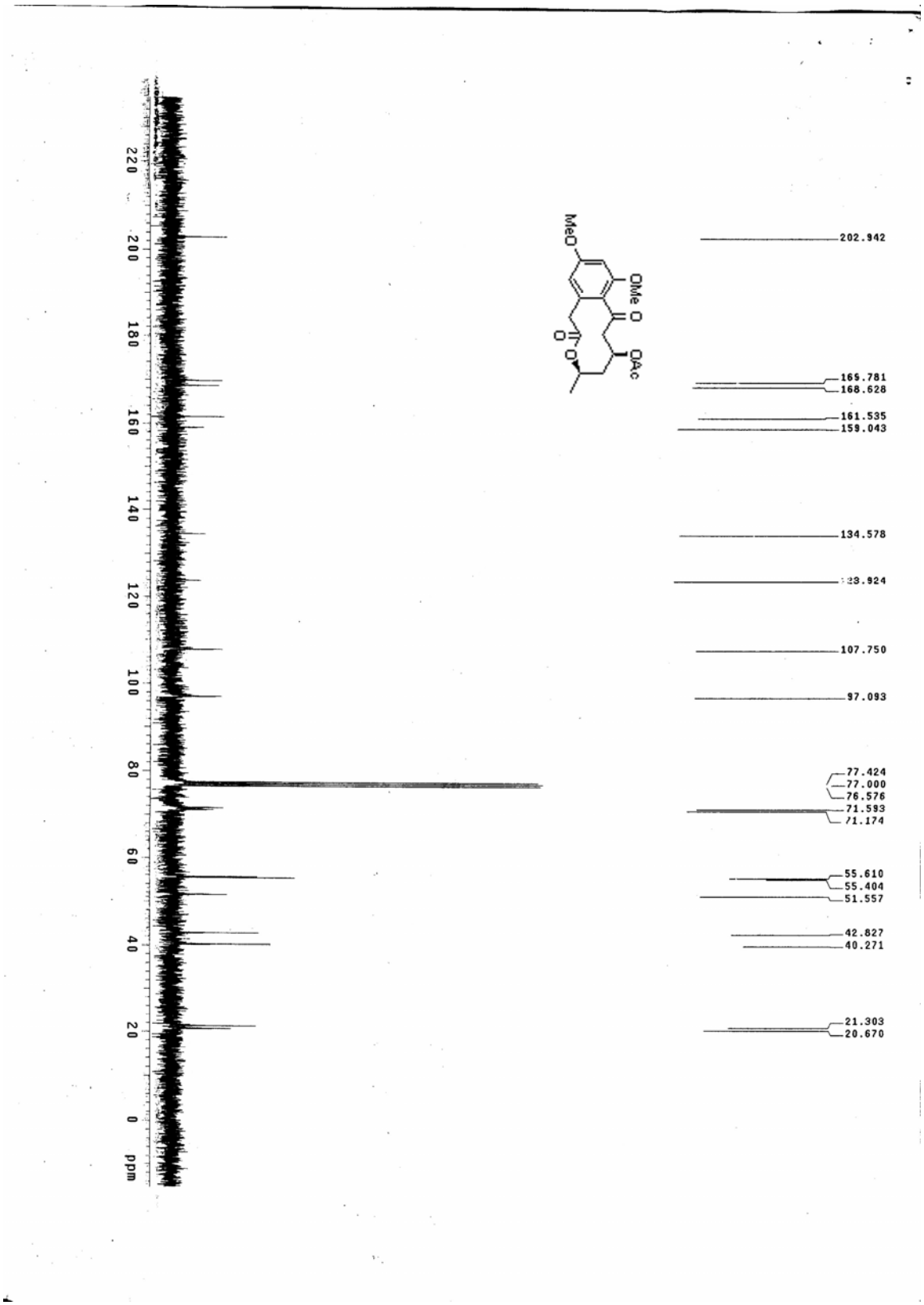
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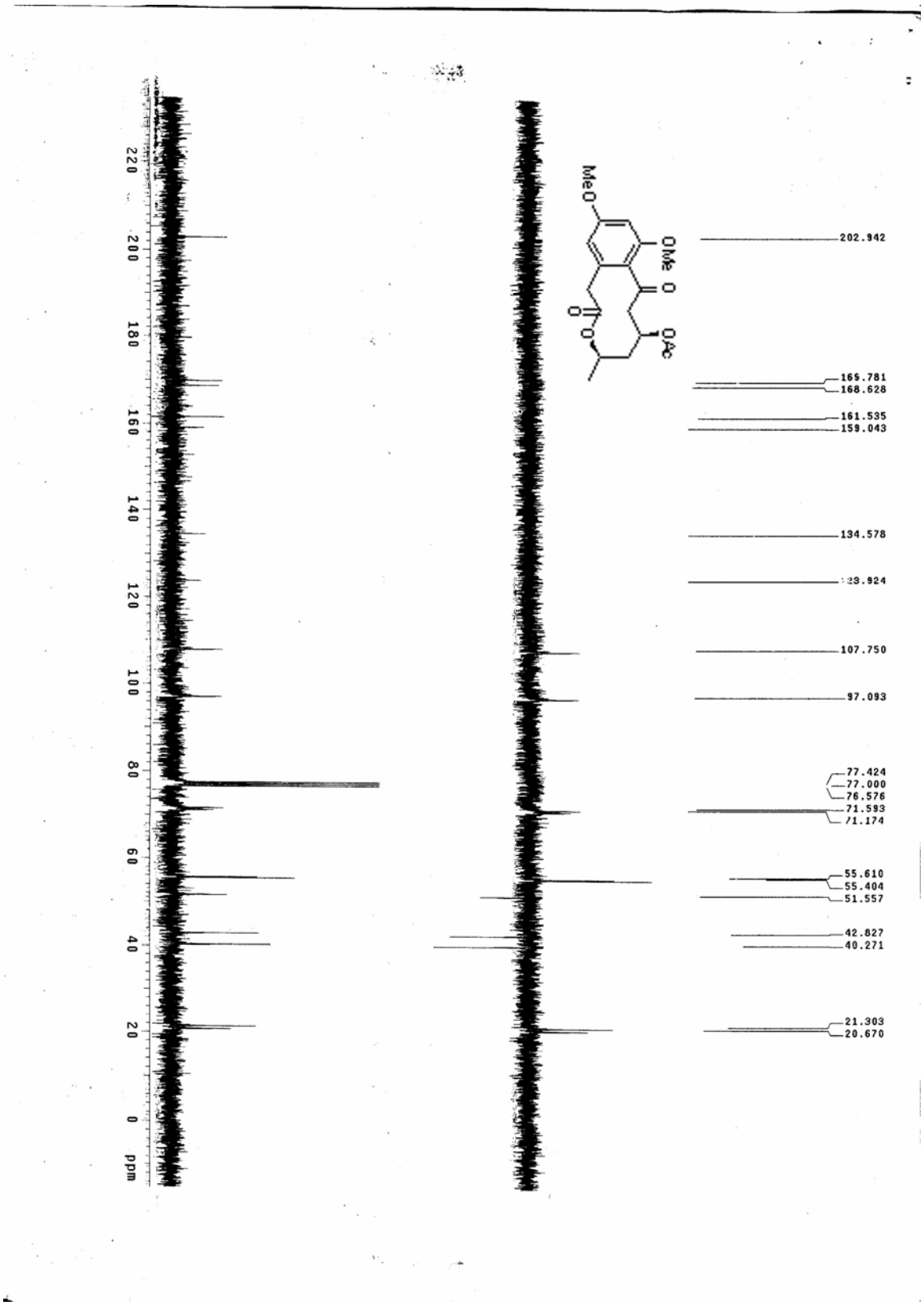
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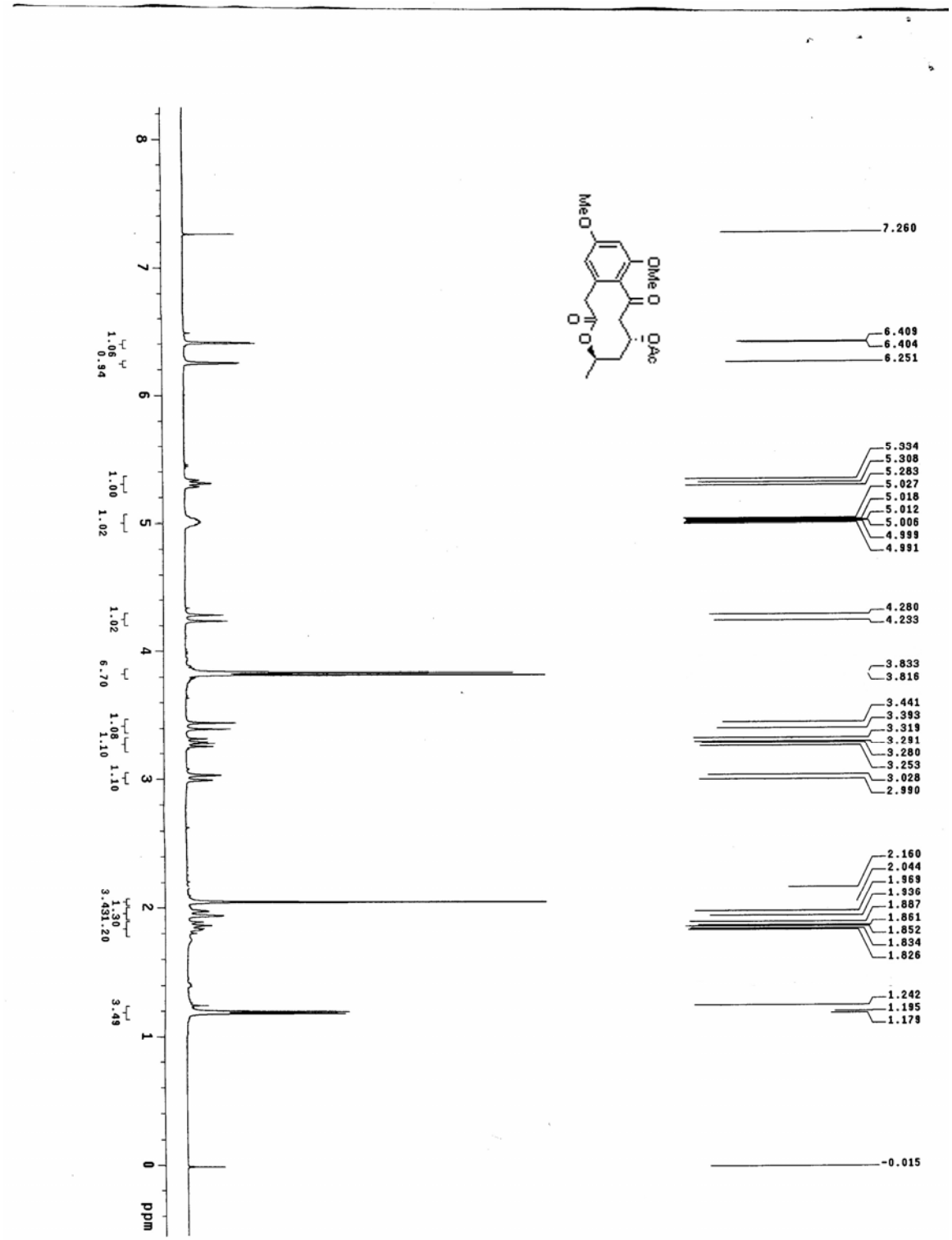
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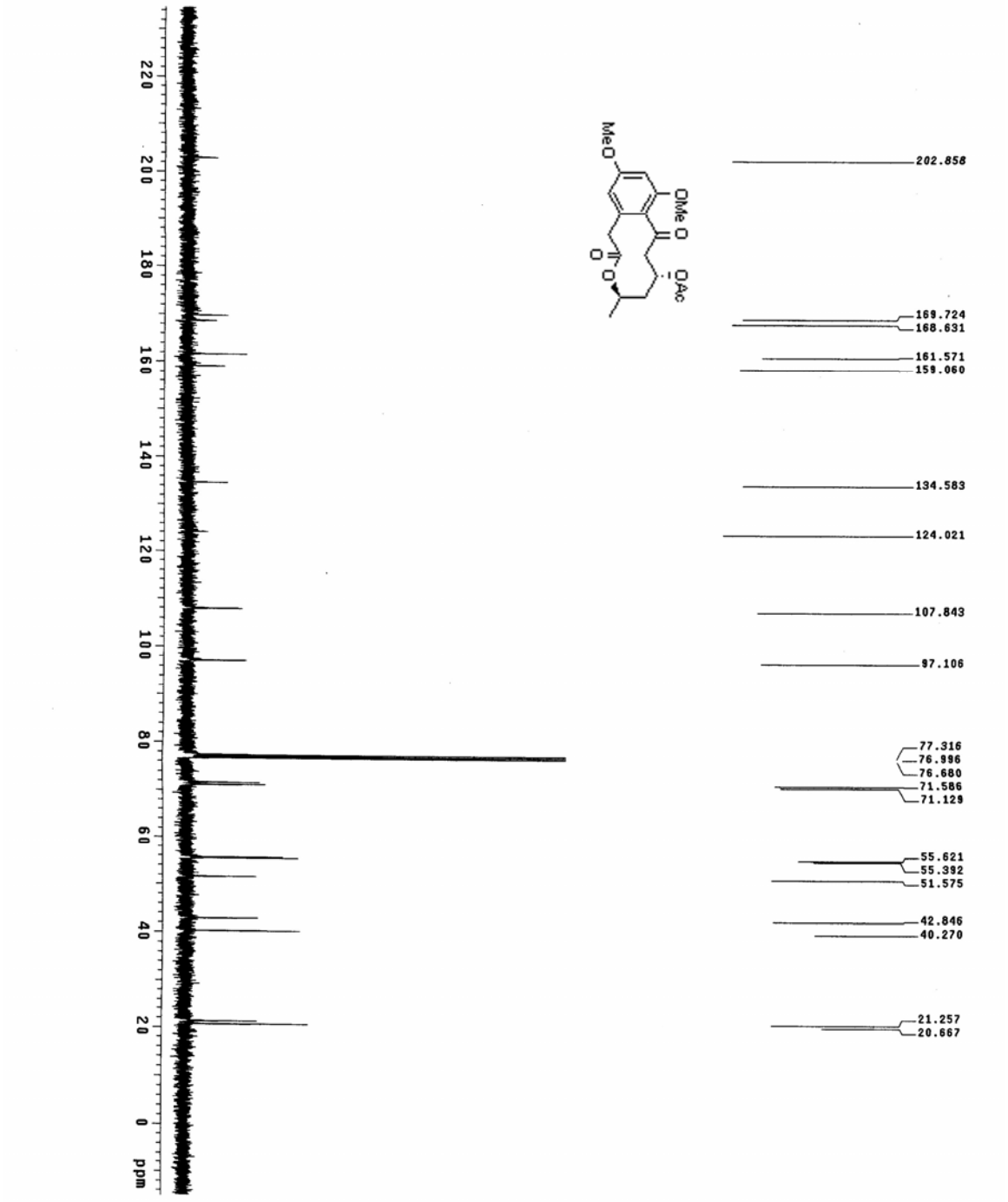
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71.129
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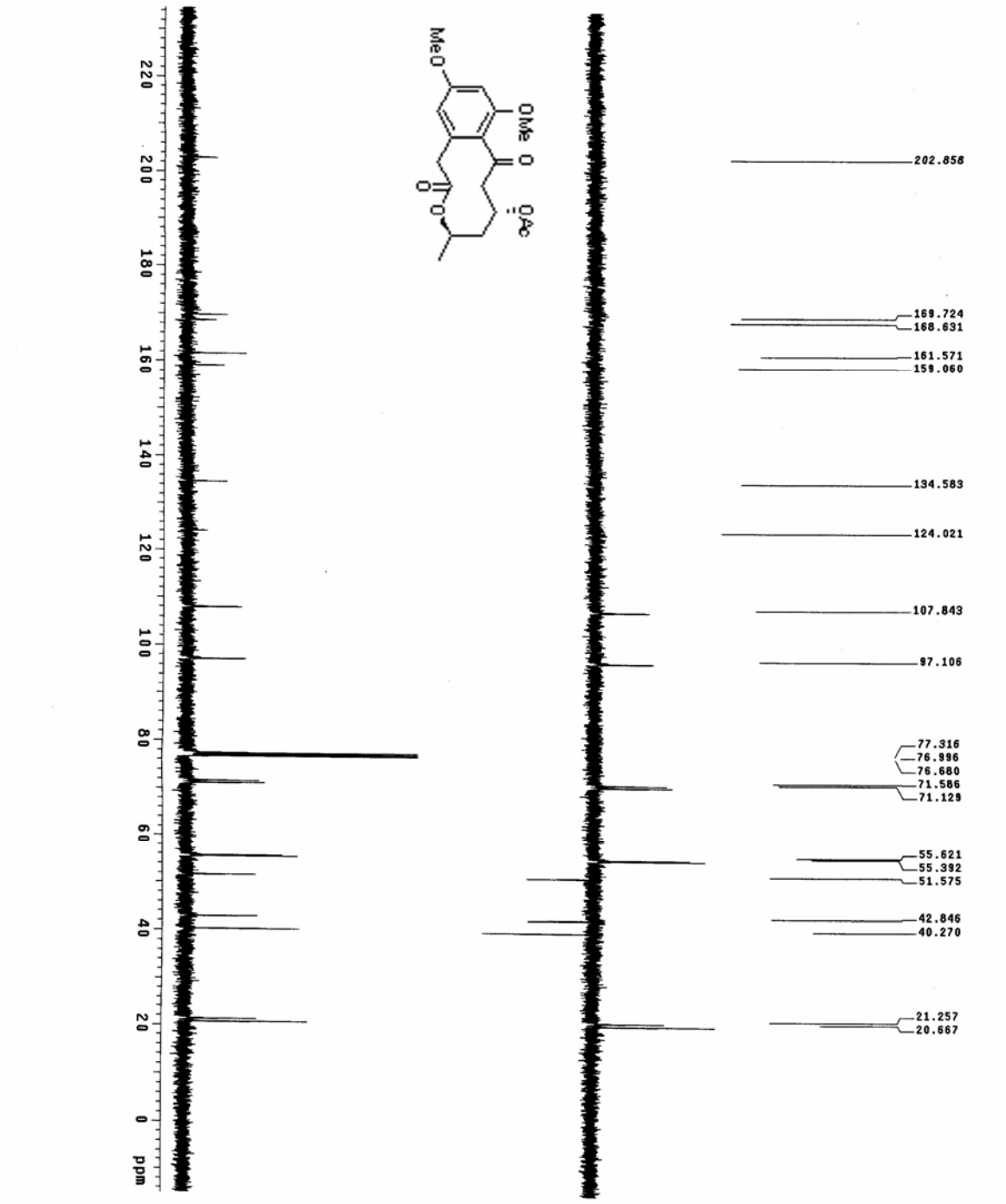
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0
ppm
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169.724
168.631
161.571
159.060
134.583
124.021
107.843
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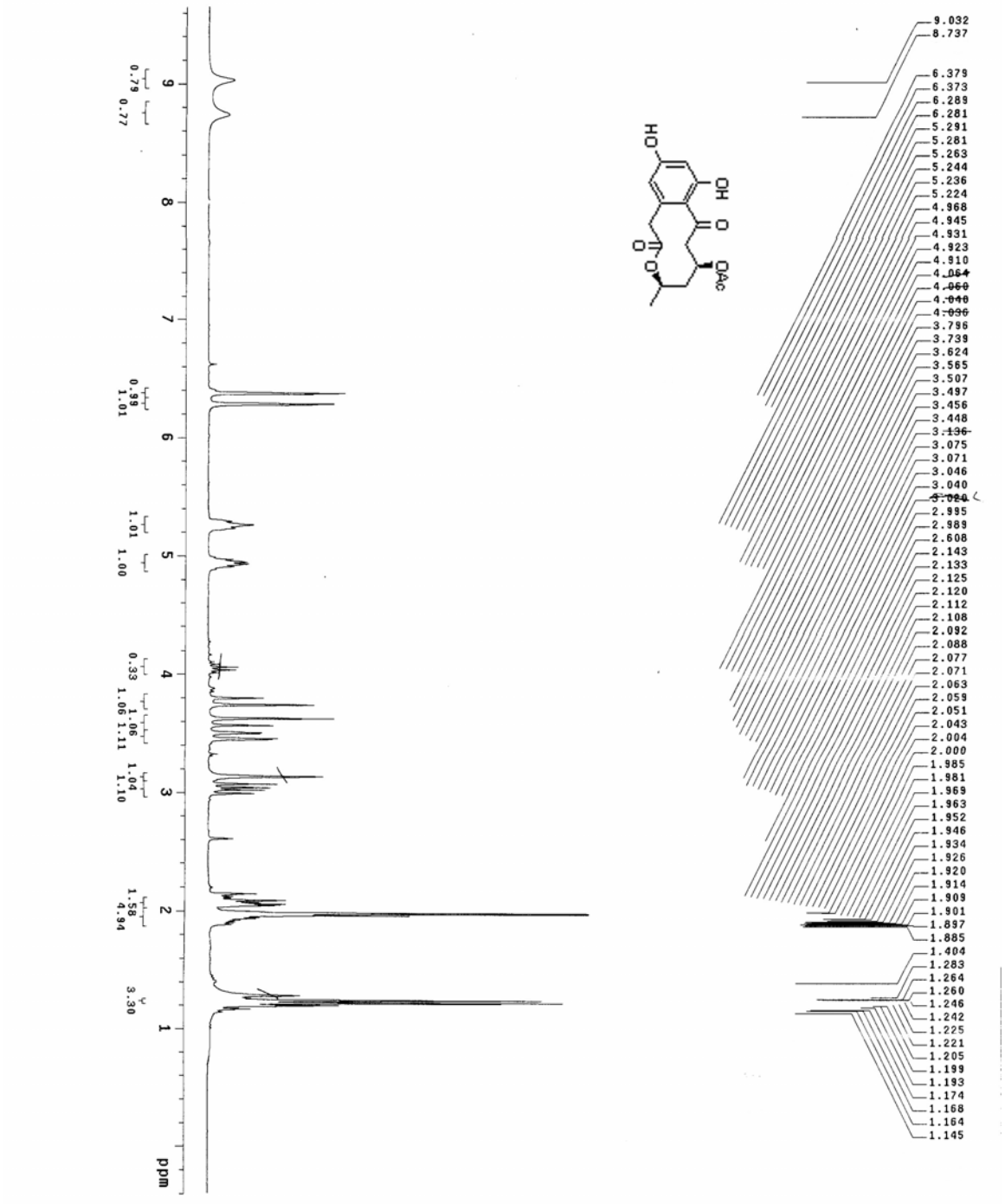
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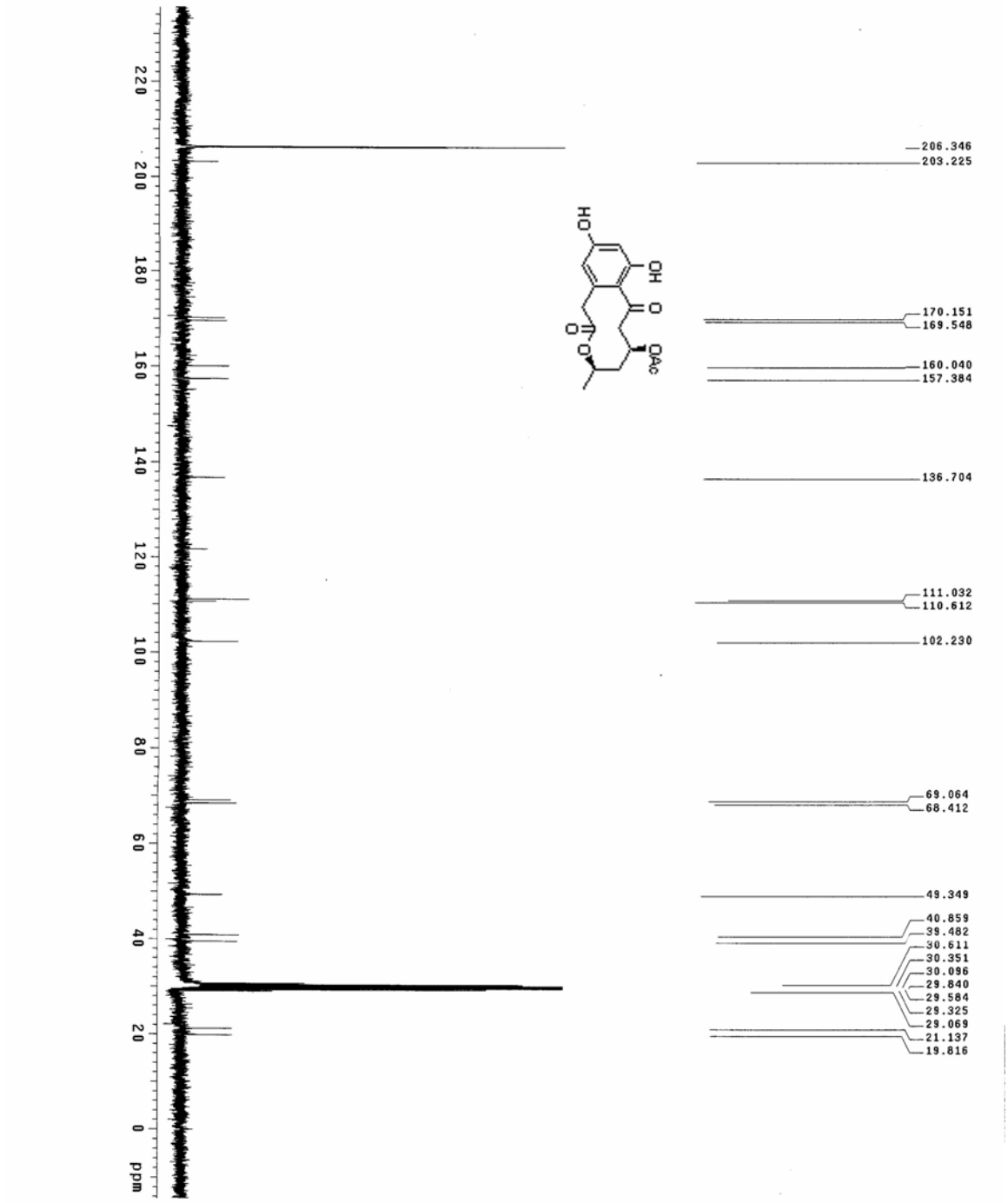
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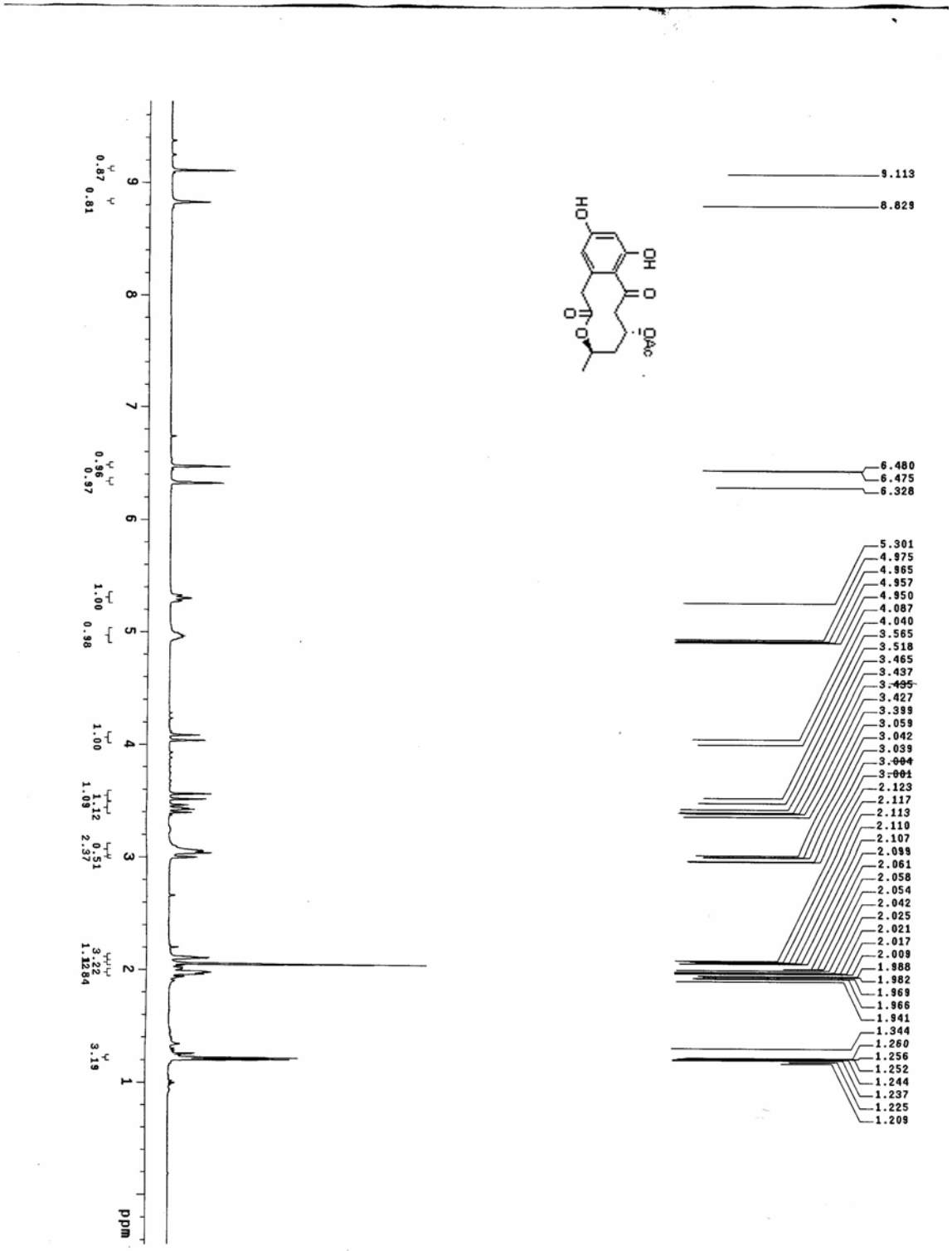
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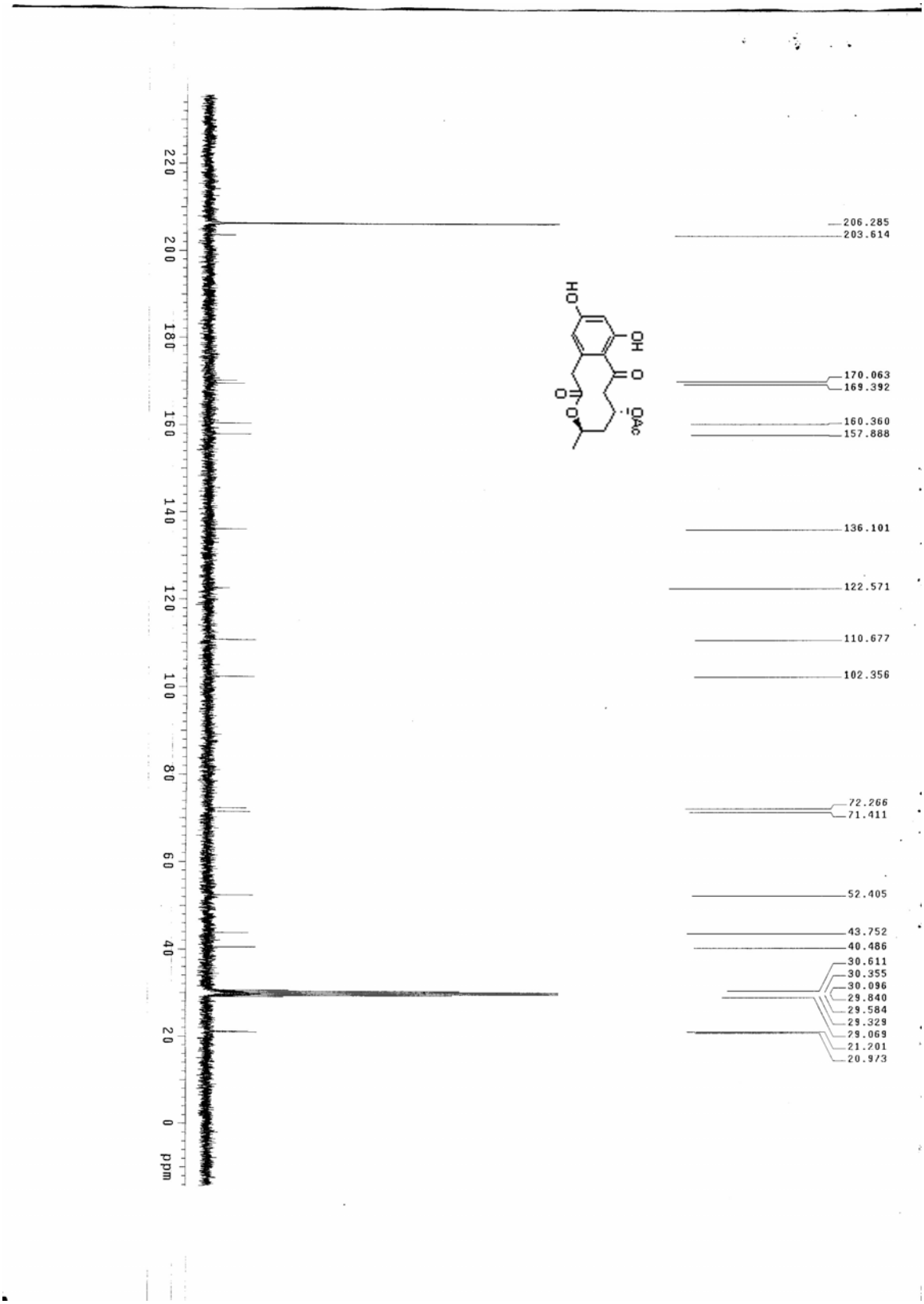
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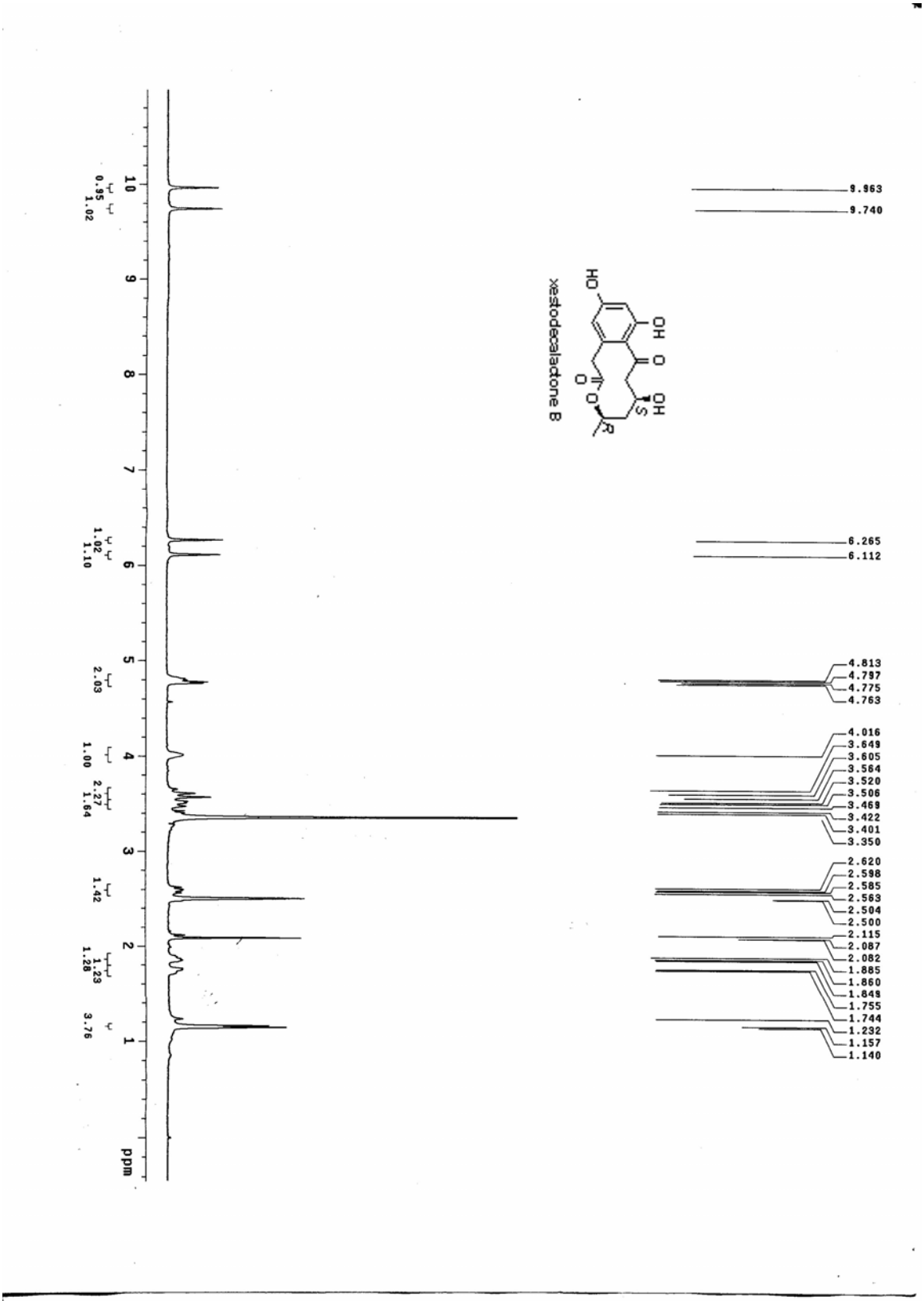
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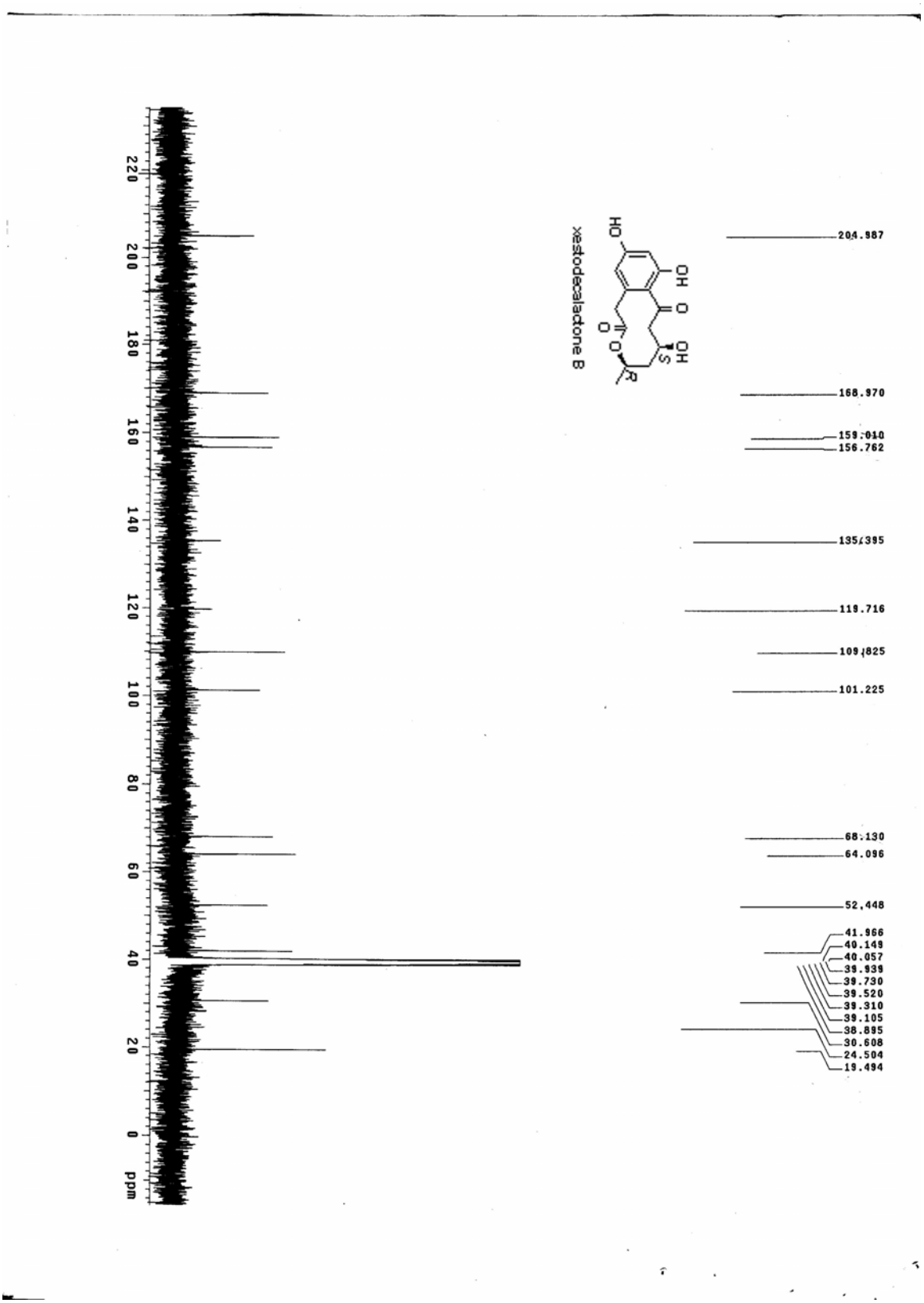
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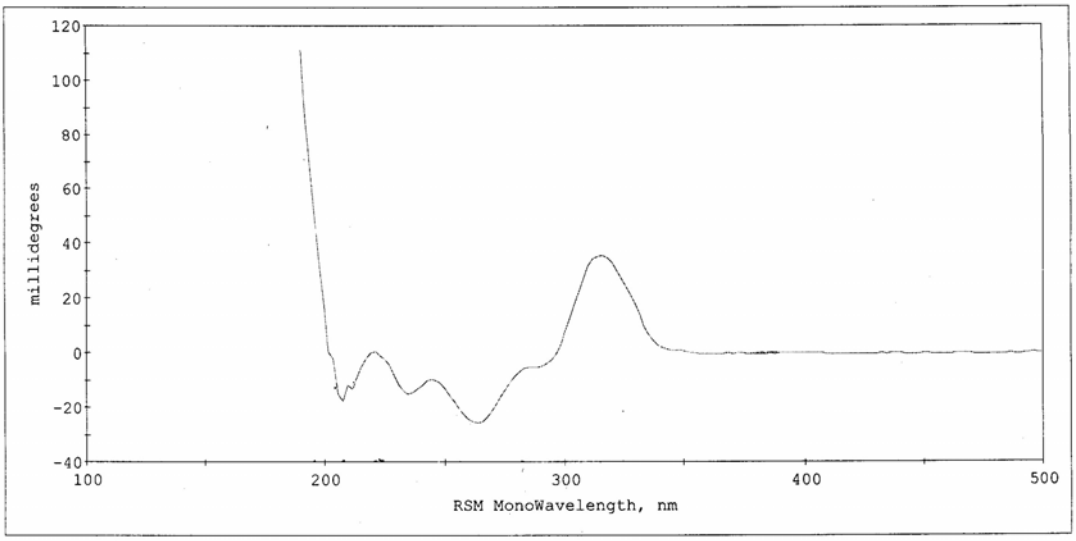

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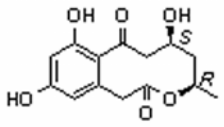

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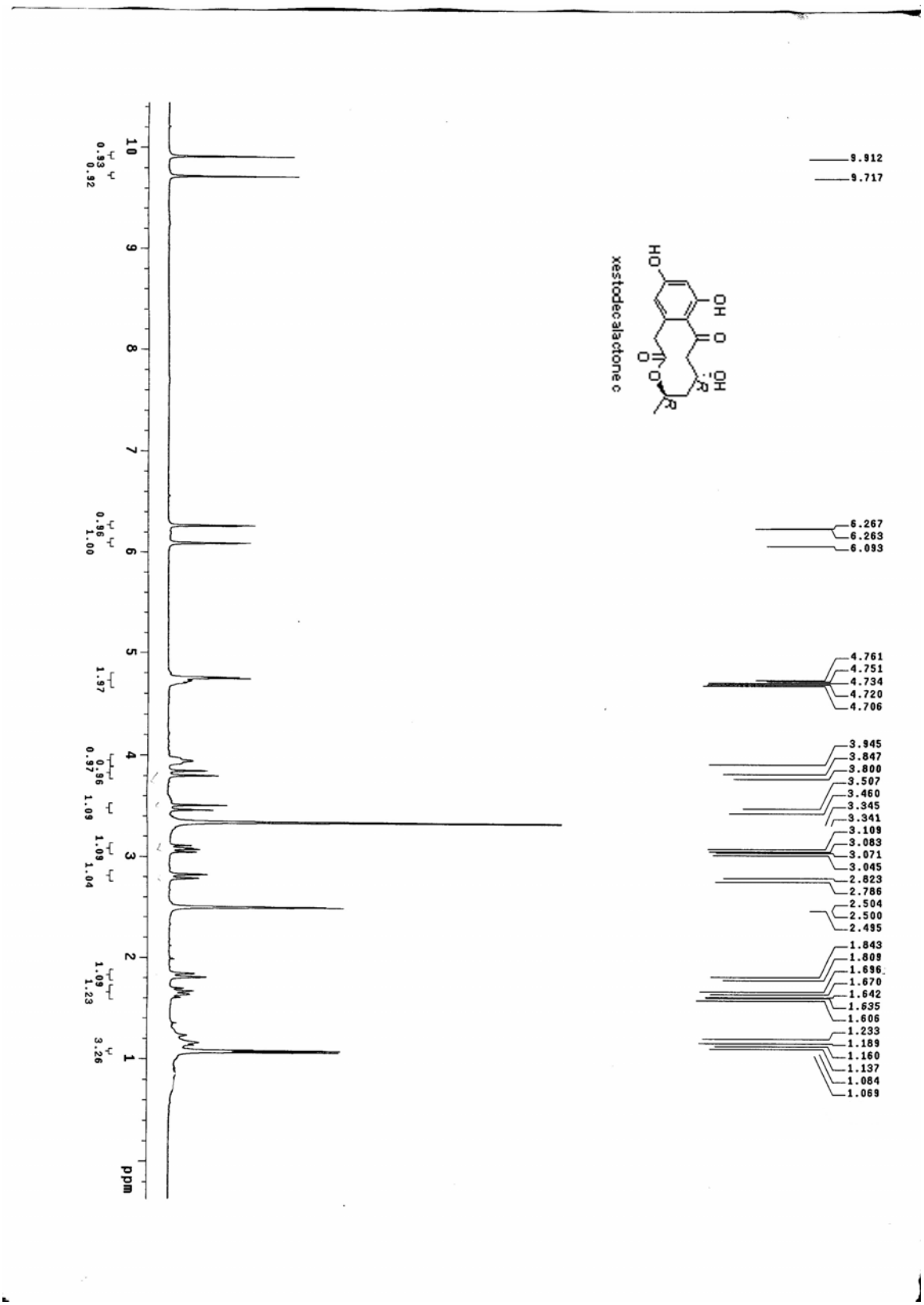
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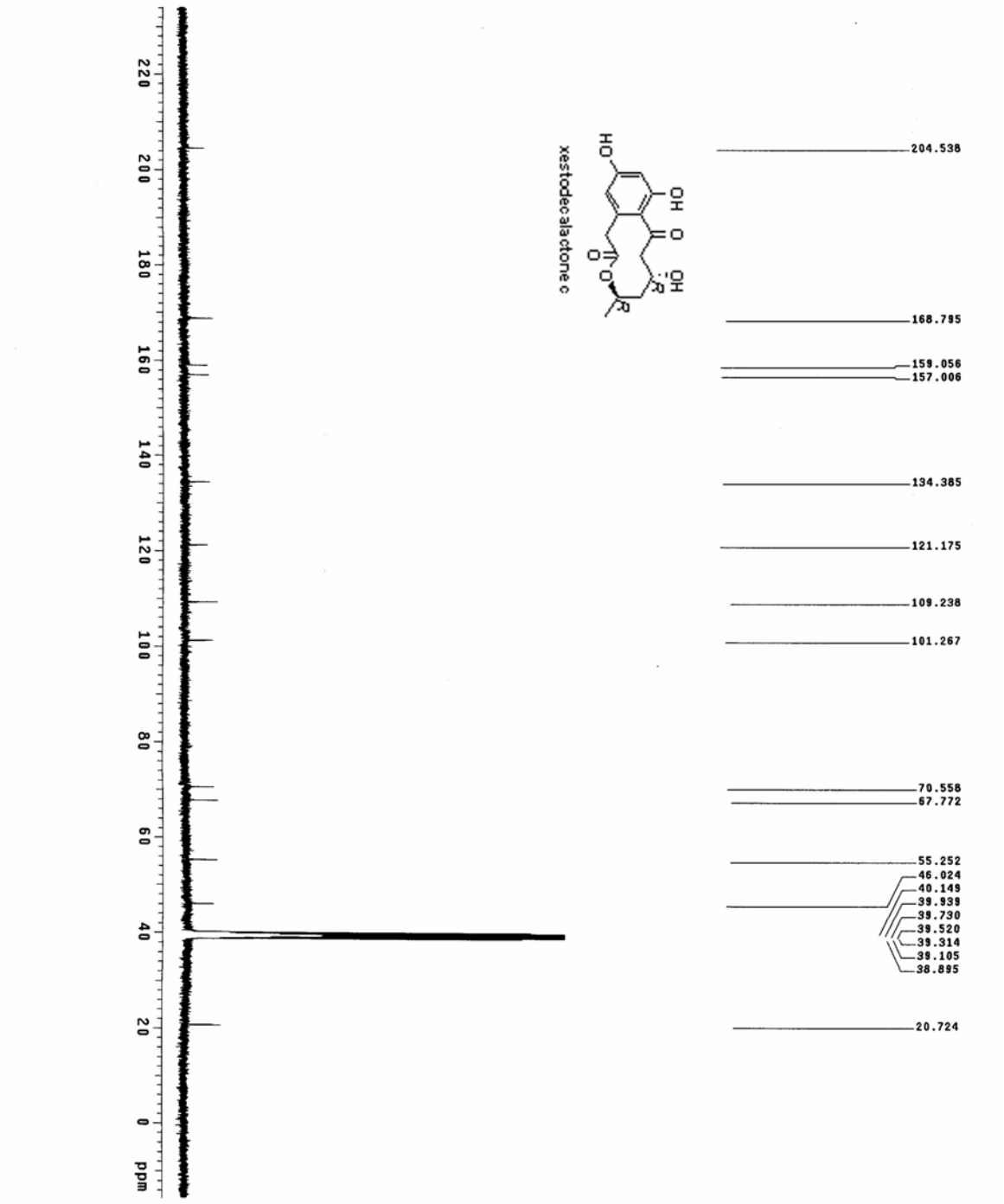
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39.520
39.314
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200
180
160
140
120
100
80
60
40
20
0
ppm


xestodecalactone C
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159.056
157.006
134.385
121.175
109.238
101.267
70.558
67.772
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2-Subtract-Smooth-Smooth-Smooth

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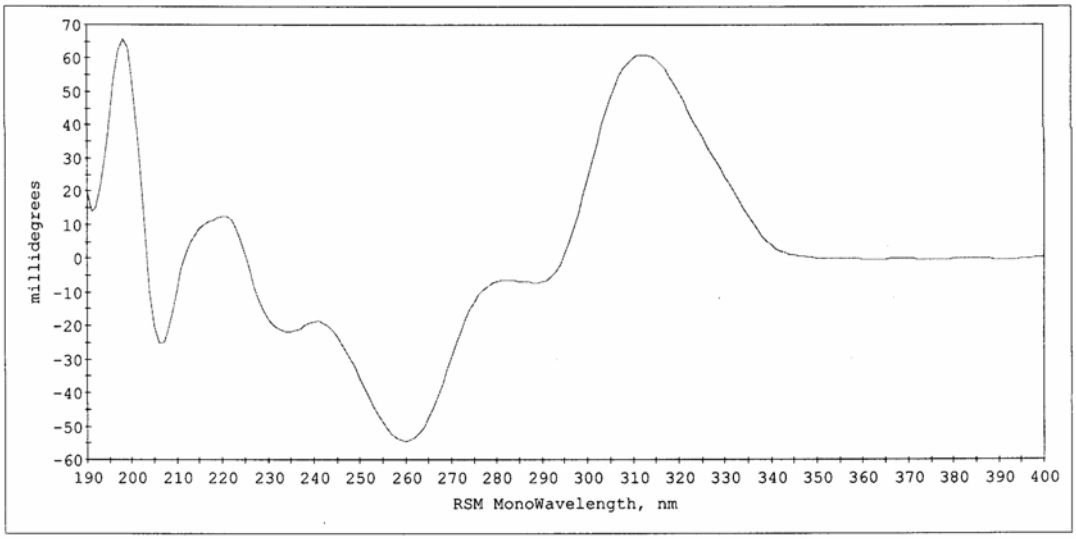

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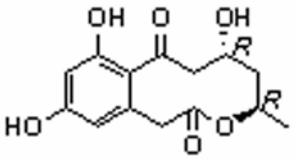

xestodecalactone c

Table 1: Comparison of the ^{1}HNMR data of the natural product xestodecalactone **B** from isolation with the synthetic compound (400 M, DMSO-*d*6)

	natural xestodecalactone **B**		synthetic xestodecalactone **B**	
^{1}H	δ	J (Hz)	δ	J (Hz)
2	6.27	d, 2.2	6.27	s
4	6.11	d, 2.2	6.11	s
8α	3.48	bdd, 2.6, 14.5	3.48	t, 14.8
8β	2.60	dd, 9.5, 14.4	2.59	dd, 8.8, 14.8
9	4.02	m	4.02	s
10α	1.73	ddd, 3.2, 6.9, 14.6	1.74	d, 4.4
10β	1.87	ddd, 4.0, 7.3, 14.6	1.86	d, 4.4
11	4.81	ddq, 4.3, 6.4, 6.4	4.81	d, 6.4
13α	3.53	d, 17.3	3.54	d, 14.8
13β	3.63	d, 17.3	3.63	d, 14.8
14	1.15	d, 6.4	1.15	d, 6.8
Ar-OH	~9.8		9.96	s
	~9.8		9.74	s
9-OH	not detected		4.77	d, 4.8

Table 2: Comparison of the ^{1}HNMR data of the natural product xestodecalactone **C** from isolation with the synthetic compound (400 M, DMSO-*d*6)

	natural xestodecalactone **C**		synthetic xestodecalactone **C**	
^{1}H	δ	J (Hz)	δ	J (Hz)
2	6.27	d, 2.1	6.27	d, 1.6
4	6.10	d, 2.1	6.09	s
8α	3.08	dd, 10.4, 15.1	3.08	dd, 10.4, 14.8
8β	2.81	bd, 15.1	2.81	d, 14.8
9	3.95	bt, 10.0	3.95	bs
10α	1.65	ddd, 9.8, 11.4, 14.5	1.64	dd, 11.2, 14.8
10β	1.83	bd, 14.5	1.83	d, 13.6
11	4.70	ddq, 2.5, 11.4, 6.2	4.72	dd, 5.6, 11.2
13α	3.48	d, 18.7	3.48	d, 18.8
13β	3.82	d, 19.0	3.82	d, 18.8
14	1.08	d, 6.2	1.08	d, 6.0
Ar-OH	9.98	s	9.91	s
	9.87	s	9.72	s
9-OH	4.83	d, 2.9	4.76	d, 4.0

Table 3: Comparison of the ^{13}CNMR data of the natural products xestodecalactones **B** and **C** from isolation with the synthetic compounds (100 M, DMSO-*d*6)

carbon	natural xesto-decalactone **B**	synthetic xest-odecalactone **B**	natural xestod ecalactone **C**	synthetic xes-todecalactone**C**
1	156.84	156.8	157.08	157.0
2	101.22	101.2	101.26	101.3
3	159.07	159.0	159.11	159.1
4	109.85	109.8	109.25	109.2
5	135.48	135.4	134.43	134.4
6	119.67	119.7	121.15	121.2
7	205.04	205.0	204.60	204.5
8	52.48	52.5	55.29	55.3
9	64.13	64.1	67.82	67.8
10	41.98	42.0	46.03	46.0
11	68.18	68.1	70.60	70.6
12	169.18	169.0	168.85	168.8
13	37.83	30.6	38.66	38.9
14	19.53	19.5	20.77	20.7