Total Synthesis of Bipinnatin J

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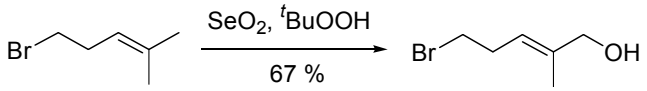
SUPPORTING INFORMATION

General

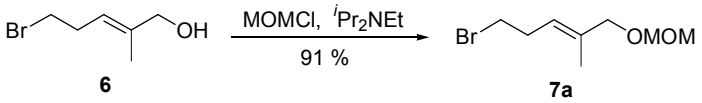
All reagents were commercially obtained (Aldrich, Acros) at the highest commercial quality and used without further purification. Air and moisture sensitive reagents were transferred via syringe or cannula. All moisture sensitive reactions were carried out in flame-dried glassware under an atmosphere of argon with freshly distilled solvents. The reactions were monitored by thin-layer chromatography carried out on 0.25mm Whatman silica gel plates using UV light as the visualizing agent. The NMR spectra were obtained on a Bruker DRX-400 (400 MHz) or a Bruker DRX-500 (500 MHz) spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad. Mass spectroscopic analyses were carried out at the facilities of The University of Chicago. IR spectra were recorded on a Nicolet Nexus 670 FT-IR and values are reported in cm^{-1} units.



5 **6**

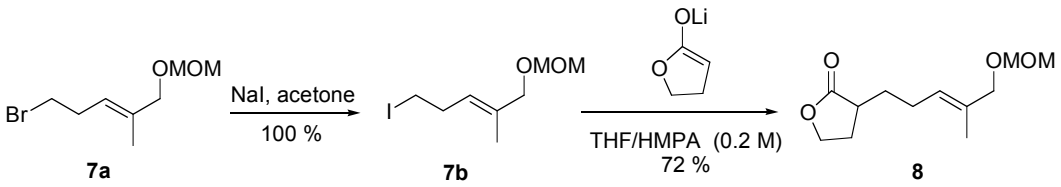
(*E*)-5-Bromo-2-methylpent-2-en-1-ol (**6**). Compound **6** was prepared by a modified literature procedure.[1] To a suspension of SeO_2 (0.832 g, 7.5 mmol, 0.5 equiv) in dry CH_2Cl_2 (20 mL) at 0 °C was added slowly anhydrous ^tBuOOH (5.0-6.0 M in decane, 5.45 mL, ~ 30.0 mmol, 2.0 equiv). The mixture was stirred at 0 °C for 5 min and the ice bath was removed. The resulting mixture was stirred at 25 °C for 30 min and was cooled to 0 °C. A solution of 5-bromo-2-methylpent-2-ene (2.45 g, 15.0 mmol) in dry CH_2Cl_2 (15 mL) was added slowly. The resulting suspension was then stirred at 25 °C for 12 h. The mixture was diluted with Et_2O (100 mL) and filtered to remove solid

compounds. The filtrate was washed with 10 % aq KOH (100 mL) and brine (100 mL). The organic solvent was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc 4:1) to afford 1.79 g of the indicated compound in a 67 % yield as a yellow oil with spectra identical to that reported in the literature.[1]



6 **7a**

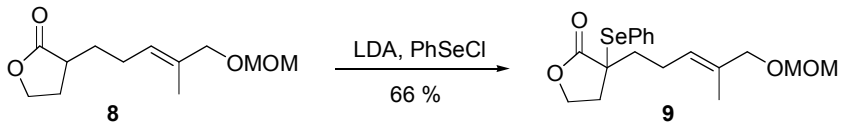
(*E*)-5-Bromo-2-(methoxymethoxy)pent-2-ene (7a). To a colorless solution of compound **6** (2.23 g, 12.45 mmol) in 20 mL dry CH_2Cl_2 at 0 ^{o}C under N_2 atmosphere was added $^{i}Pr_2NEt$ (2.38 mL, 13.69 mmol, 1.1 equiv) and MOMCl (1.41 mL, 18.67 mmol, 1.5 equiv). The resulting colorless mixture was then stirred at 25 ^{o}C for 3 h to reach completion. The reaction was diluted with Et_2O (100 mL) and washed with brine (2 x 100 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The yellow residue was chromatographed on silica gel (hexane/EtOAc 4:1) to afford 2.53 g of the indicated compound in a 91 % as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.58 (s, 3H), 2.64 (td, J = 7.0, 7.5 Hz, 2H), 3.38 (t, J = 7.0 Hz, 2H), 3.38 (s, 3H), 3.95 (s, 2H), 4.63 (s, 2H), 5.46 (qt, J = 1.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 31.3, 32.4, 55.3, 72.6, 95.4, 124.3, 134.9; IR (neat, cm^{-1}) 2986, 2931, 2883, 1461, 1440, 1151, 1049; MS calculated for $C_8H_{15}{}^{79}BrO_2$ (M^+ + H) 223.0, found 223.0.



7a **7b** **8**

(*E*)-3-(5-(Methoxymethoxy)-4-methylpent-3-enyl)dihydrofuran-2(3*H*)-one (8). To NaI (2.21 g, 14.76 mmol, 3.0 equiv) in a 6 dram vial was added a solution of compound **7a** (1.10 g, 4.92 mmol) in dry acetone (10 mL). The resulting mixture was stirred at 25 ^{o}C in the dark for 12 h to reach completion. The reaction was diluted with Et_2O (100 mL) and washed with brine (100 mL). The organic layer was dried over

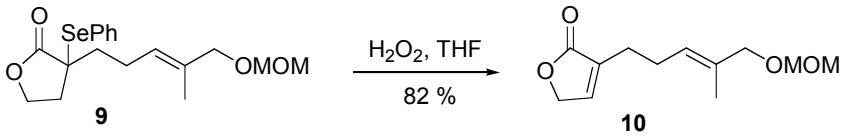
$MgSO_4$ and filtered. The solvent was removed under reduced pressure to afford 100 % yield of compound **7b**, which was used without further purification in next step. Compound **7b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.67 (s, 3H), 2.65 (td, *J* = 7.2, 7.6 Hz, 2H), 3.15 (t, *J* = 7.2 Hz, 2H), 3.38 (s, 3H), 3.94 (s, 2H), 4.64 (s, 2H), 5.41 (qt, *J* = 1.2, 7.6 Hz, 1H). To a solution of freshly prepared LDA (5.90 mmol, 1.2 equiv) in 15 mL THF at -78 ^{o}C under N_2 atmosphere was added γ-butyrolactone (0.473 mL, 6.15 mmol, 1.25 equiv). The resulting colorless solution was stirred at -78 ^{o}C for 15 min and HMPA (3.0 mL) was added slowly. Stirred at -78 ^{o}C for another 10 min and a solution of compound **7b** (4.92 mmol) in a mixed solvent of THF (5 mL) and HMPA (1.0 mL) was added through cannula. The resulting pale yellow solution was stirred at -78 ^{o}C for 1.5 h to reach completion. The reaction was diluted with Et_2O (100 mL) and washed with brine (100 mL). The organic solvent was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc 1:1) to afford 0.802 g of the indicated compound in a 72 % yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.49-1.56 (m, 1H), 1.67 (s, 3H), 1.91-2.00 (m, 2H), 2.13-2.24 (m, 2H), 2.36-2.42 (m, 1H), 2.49-2.54 (m, 1H), 3.37 (s, 3H), 3.93 (s, 2H), 4.18 (ddd, *J* = 6.5, 9.0, 9.5 Hz, 1H), 4.34 (ddd, *J* = 3.0, 8.5, 9.0 Hz, 1H), 4.61 (s, 2H), 5.43 (qt, *J* = 1.0, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 25.3, 28.7, 30.1, 38.6, 55.2, 66.4, 73.1, 95.4, 126.5, 133.2, 179.3; IR (neat, cm^{-1}) 2979, 2928, 1769; MS calculated for $C_{10}H_{15}O_2$ (M^+ - MOM) 167.1, found 167.1.



8 **9**

(*E*)-3-(5-(Methoxymethoxy)-4-methylpent-3-enyl)-3-(phenylselanyl)dihydrofuran-2(3*H*)-one (9). To a solution of freshly prepared LDA (5.81 mmol, 1.1 equiv) in 10 mL THF at -78 ^{o}C under N_2 atmosphere was added a solution of compound **8** (1.21 g, 5.28 mmol) in THF (8.0 mL). The resulting pale yellow solution was stirred at -78 ^{o}C for 30 min and HMPA (3.0 mL) was added slowly. After 5 min, a solution of PhSeCl (1.31 g, 6.86 mmol, 1.3 equiv) in THF (3.0 mL) was added into the reaction mixture. The reaction was stirred at -78 ^{o}C for 30 min to reach completion. The reaction was diluted with Et_2O (100 mL) and washed with brine (100 mL). The

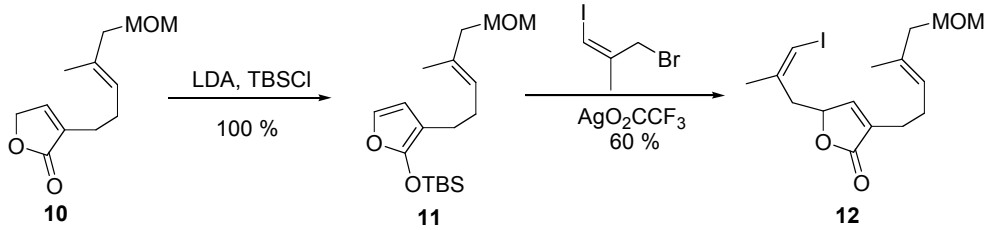
organic layer was dried over $MgSO_4$, filtered, concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc 1:1) to afford 1.34 g of the indicated compound in a 66 % yield as a yellow oil: ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.67 (s, 3H), 1.76 (ddd, *J* = 5.0, 11.0, 14.5, Hz, 1H), 1.93 (ddd, *J* = 5.0, 11.5, 14.0 Hz, 1H), 2.05-2.12 (m, 1H), 2.24 (ddd, *J* = 1.0, 6.0, 14.0 Hz, 1H), 2.36-2.46 (m, 2H), 3.36 (s, 3H), 3.91 (s, 2H), 4.22 (ddd, *J* = 6.0, 9.0, 10.5 Hz, 1H), 4.27 (ddd, *J* = 1.5, 9.0, 9.0 Hz, 1H), 4.61 (s, 2H), 5.39 (qt, *J* = 1.0, 7.5 Hz, 1H), 7.33 (dd, *J* = 7.0, 7.5 Hz, 2H), 7.42 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.63 (dd, *J* = 7.0, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 23.9, 34.6, 35.0, 48.9, 55.2, 65.0, 72.9, 95.4, 125.5, 126.3, 129.1, 129.9, 133.0, 137.8, 176.6; IR (neat, cm^{-1}) 3057, 2930, 1763; MS calculated for $C_{16}H_{19}O_2Se$ (M^+ - MOM) 323.0, found 323.0.



9 **10**

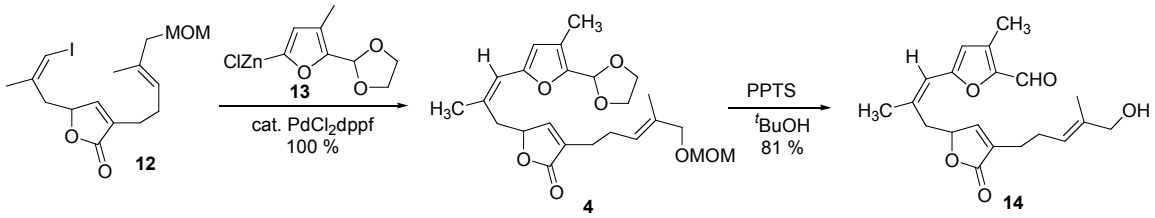
endo/exo 17:1

(*E*)-3-(5-(Methoxymethoxy)-4-methylpent-3-enyl)furan-2(5*H*)-one (10). To a yellow solution of compound **9** (1.30 g, 3.39 mmol) in 8 mL THF at 0 ^{o}C under N_2 atmosphere was added dropwise 30 % w/w aq. H_2O_2 (0.69 mL, 6.78 mmol, 2.0 equiv). The resulting yellow solution was stirred at 0 ^{o}C for 3 min. Removed the ice-water bath and the yellow solution was stirred at 25 ^{o}C for 2 min. The yellow color disappeared and a colorless solution was obtained. The reaction was stirred at 25 ^{o}C for another 10 min, diluted with Et_2O (100 mL), and washed with saturated aq $NaHCO_3$ (50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc 1:1) to afford 0.629 g of the indicated compound (endo/exo 17:1) in an 82 % yield as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.66 (s, 3H), 2.30-2.40 (m, 4H), 3.36 (s, 3H), 3.92 (s, 2H), 4.60 (s, 2H), 4.76 (d, *J* = 1.5 Hz, 1H), 476 (d, *J* = 2.0 Hz, 1H), 5.42 (qt, *J* = 1.0, 7.0 Hz, 1H), 7.11 (dd, *J* = 1.5, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 25.1, 25.4, 55.2, 70.1, 72.9, 95.3, 126.3, 133.3, 133.7, 144.5, 174.2; IR (neat, cm^{-1}) 2932, 2886, 2823, 1751, 1450, 1051; MS calculated for $C_{10}H_{13}O_2$ (M^+ - MOM) 165.1, found 165.1.



5-((*Z*)-3-Iodo-2-methylallyl)-3-((*E*)-6-methoxy-4-methylhex-3-enyl)furan-2(5*H*)-one (12). To a solution of freshly prepared LDA (2.81 mmol, 1.2 equiv) in THF (8.0 mL) at -78 ^{o}C under N_2 atmosphere was added a solution of compound **10** (0.530 g, 2.34 mmol) in THF (2.0 mL). The resulting pale yellow solution was stirred at -78 ^{o}C for 30 min and HMPA (3.0 mL) was added slowly. The reaction mixture was stirred at -78 ^{o}C for another 20 min and a solution of TBSCl (0.367 g, 2.43 mmol, 1.1 equiv) in THF (2.0 mL) was added dropwise. The reaction was then stirred at -78 ^{o}C for 20 min to reach completion. The reaction mixture was diluted with Et_2O (100 mL), and washed with 5 % aq NaCl (50 mL) and brine (50 mL). The organic layer was collected, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford compound **11** quantitatively, which was used in next step without further purification.

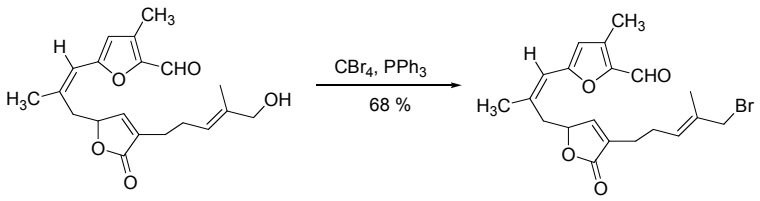
A solution of compound **11** (2.34 mmol) and 3-bromo-1-iodo-2-methylpropene[2] (0.79 g, 3.04 mmol, 1.3 equiv) in CH_2Cl_2 (10 mL) was added into a suspension of AgO_2CCF_3 (0.62 g, 2.81 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) at -40 ^{o}C. The resulting deep blue reaction mixture was stirred at -40 ^{o}C for 1 h and warmed slowly to 25 ^{o}C (approx. 3 h). The reaction was then diluted with Et_2O (100 mL) and filtered through Celite to remove silver salts. The filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc 2:1 and hexane/EtOAc 1:1) to afford 570 mg of the indicated compound in a 60 % yield as a yellow oil: ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.67 (s, 3H), 1.99 (d, J = 1.5 Hz, 3H), 2.30-2.40 (m, 4H), 2.54 (dd, J = 7.5, 13.5 Hz, 1H), 2.66 (dd, J = 6.0, 13.5 Hz, 1H), 3.37 (s, 3H), 3.92 (s, 2H), 4.61 (s, 2H), 5.05 (dd, J = 6.0, 7.5 Hz, 1H), 5.43 (dd, J= 5.5, 7.0 Hz, 1H), 6.12 (d, J = 1.0 Hz, 1H), 7.10 (d, J = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 24.8, 25.0, 25.4, 42.4, 55.2, 73.0, 78.5, 79.4, 95.3, 126.3, 133.3, 134.0, 142.4, 147.7, 173.3; IR (neat, cm^{-1}) 3063, 2924, 2822, 1758, 1438, 1051; MS calculated for $C_{14}H_{18}IO_2$ (M^+ - MOM) 345.0, found 345.0.



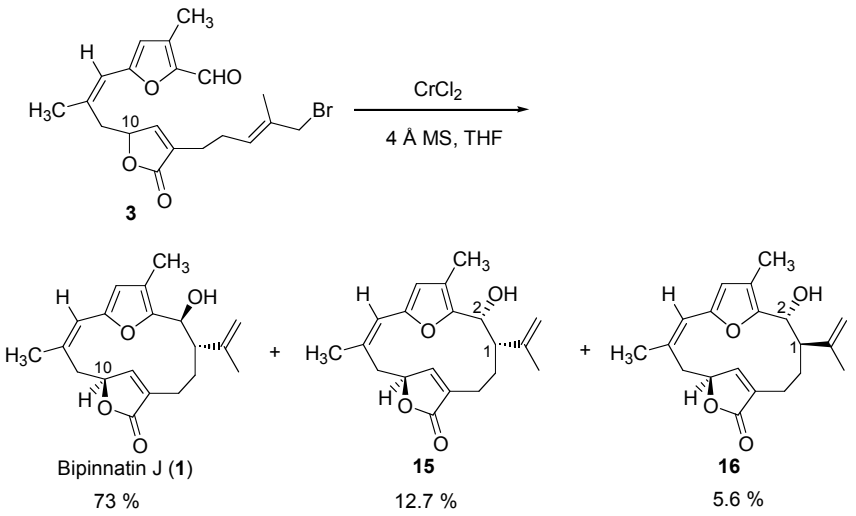
5-((*Z*)-3-(4-((*E*)-5-hydroxy-4-methylpent-3-enyl)-5-oxo-2,5-dihydrofuran-2-yl)-2-methylprop-1-enyl)-3-methylfuran-2-carbaldehyde (14). To a solution of dioxolane protected 3-methyl-2-furaldehyde[3] (0.484 g, 3.14 mmol, 3.3 equiv) in THF (8.0 mL) at -78 °C under N_2 atmosphere was added slowly a solution of ^{t}BuLi (1.7 M in pentane, 1.68 mL, 2.86 mmol, 3.0 equiv). The resulting brown solution was stirred at -78 °C for 15 min and a solution of $ZnCl_2$ (flame dry, 0.467 g, 3.42 mmol, 3.6 equiv) in THF (2.0 mL) was added dropwise. The resulting yellow clear solution was stirred at -78 °C for 30 min to generate the corresponding organozinc compound (approx. 2.86 mmol). The freshly prepared organozinc compound was added through cannula into a suspension of $PdCl_2$dppf (38.8 mg, 0.047 mmol, 0.05 equiv) and compound **12** (387 mg, 0.952 mmol) in THF (3.0 mL) at 0 °C. The resulting mixture was then stirred at 25 °C for 1 h to reach completion. The reaction was diluted with Et_2O (100 mL) and washed with brine (2 x 50 mL). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified on a short column (silica gel, hexane/EtOAc 2:1) to afford compound **4** in a quantitative yield. Compound **4** is not very stable on the silica gel and solvents and was used in the next step right away.

To a solution of compound **4** (0.378 g, 0.873 mmol) in ^{t}BuOH (30 mL) was added PPTS (1.32 g, 5.24 mmol, 6.0 equiv). The resulting colorless mixture was stirred at 25 °C for 10 min and was then refluxing under N_2 atmosphere in a 90 °C oil bath. After 8 h, the reaction was cooled to 25 °C, diluted with Et_2O (100 mL), and washed with brine (2 x 150 mL). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc 1:2) to afford 240 mg of the indicated compound in an 81 % yield as a yellow oil: ^{1}H NMR ($CDCl_3$, 400 Hz) δ 1.65 (s, 3H), 2.05 (d, J = 1.2 Hz, 3H), 2.13 (br s, 1H), 2.26-2.45 (m, 5H), 2.34 (s, 3H), 3.23 (d, J = 11.6 Hz, 1H), 3.99 (s, 2H), 5.11 (ddd, J = 1.6, 3.2, 8.4 Hz, 1H), 5.40 (qt, J = 1.2, 6.8 Hz, 1H), 6.17 (s, 1H), 6.18 (s, 1H), 7.33 (br s, 1H), 9.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.0, 13.7, 24.8, 25.3, 26.7, 38.3, 68.5, 81.6, 113.9,

115.3, 123.8, 133.4, 136.5 (br), 136.5, 141.9 (br), 175.6 (br), 147.4, 149.1, 157.0, 173.8; IR (neat, cm^{-1}) 3462 (br), 2922, 2856, 1751, 1662, 1499; MS calculated for $C_{20}H_{23}O_4$ (M^+ - OH) 327.2, found 327.1.



5-((*Z*)-3-(4-((*E*)-5-Bromo-4-methylpent-3-enyl)-5-oxo-2,5-dihydrofuran-2-yl)-2-methylprop-1-enyl)-3-methylfuran-2-carbaldehyde (3). To a yellow solution of compound **14** (230 mg, 0.667 mmol) in dry CH_2Cl_2 (20 mL) at 0 ^oC was added CBr_4 (0.228 g, 0.867 mmol, 1.3 equiv). The resulting mixture was stirred at 0 ^oC under N_2 atmosphere until CBr_4 was completely dissolved (approx. 3 min). Then PPh_3 (0.262 g, 1.00 mmol, 1.5 equiv) was added portionwise at 0 ^oC. After 5 min, the reaction was diluted with Et_2O (100 mL) and washed with brine (50 mL). The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 25 ^oC. The residue was chromatographed on silica gel (hexane/EtOAc 2:1) to afford 185 mg of the indicated compound in a 68 % yield as a colorless oil: ^1H NMR ($CDCl_3$, 500 Hz) δ 1.74 (s, 3H), 2.04 (d, J = 1.0 Hz, 3H), 2.29 (t, J = 7.0 Hz, 2H), 2.35 (s, 3H), 2.35-2.38 (m, 2H), 2.54 (dd, J = 8.0, 13.5 Hz, 1H), 3.18 (dd, J = 3.0, 13.5 Hz, 1H), 3.94 (s, 2H), 5.12-5.14 (m, 1H), 5.55 (t, J = 7.0 Hz, 1H), 6.18 (s, 1H), 6.18 (s, 1H), 7.26 (br s, 1H), 9.65 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.0, 14.6, 24.4, 25.8, 26.5, 38.0, 41.1, 81.0, 113.9, 115.6, 129.2, 132.9, 133.3, 135.7 (br), 140.9 (br), 147.3, 148.9, 156.5, 173.3, 175.5 (br); IR (neat, cm^{-1}) 2919, 2849, 1755, 1665, 1499; MS calculated for $C_{20}H_{23}{}^{81}BrO_4$ (M^+ + H) 409.1, found 409.1.



Bipinnatin J (1). To a suspension of 4 Å MS (activated powder, 2.0 g) and anhydrous $CrCl_2$ (1.09 g, 8.87 mmol, 20.6 equiv) in dry THF (290 mL) was added a solution of compound **3** (175 mg, 0.429 mmol) in dry THF (10 mL). The resulting green mixture was stirred at 25 ^{o}C for 16 h to reach completion. The reaction mixture was filtered through Celite to remove Molecular Sieves and chromium salts. The deep green solution was concentrated under reduced pressure. The residue was diluted with Et_2O (100 mL) and washed was brine (2 x 100 mL). The resulting pale yellow organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc 3:1) to afford 103 mg (73 % yield) of bipinnatin J, 17.9 mg (12.7 % yield) of compound **15**, and 8.0 mg (5.6 % yield) of compound **16**. Bipinnatin J[4]: mp 176-178 ^{o}C (white solid); ^{1}H NMR ($CDCl_3$, 400 Hz) δ 0.89 (ddd, *J* = 3.5, 13.8, 13.8 Hz, 1H), 1.66 (dddd, *J* = 3.3, 3.3, 10.6, 13.8 Hz, 1H), 1.79 (s, 3H), 1.88 (d, *J* = 2.8 Hz, OH, 1H), 1.99 (s, 3H), 2.04 (s, 3H), 2.05-2.12 (m, 1H), 2.36 (dd, *J* = 10.8, 10.8 Hz, 1H), 2.39 (ddd, *J* = 3.0, 14.4, 14.4 Hz, 1H), 2.72 (dd, *J* = 4.4, 11.8 Hz, 1H), 3.19 (dd, *J* = 11.6, 11.8 Hz, 1H), 4.50 (dd, *J* = 2.6, 10.9 Hz, 1H), 4.96-5.00 (m, 1H), 5.05 (s, 1H), 5.16 (s, 1H), 6.03 (s, 1H), 6.10 (s, 1H), 6.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.5, 17.5, 19.6, 25.8, 30.3, 39.7, 51.1, 64.9, 78.6, 113.8, 117.3, 118.7, 121.1, 129.0, 132.5, 142.1, 149.1, 151.0, 152.3, 174.3. The stereochemistry of compound **15** was determined by $J_{H1\text{-}H2}$ = 0 Hz (*cis*) and the comparison of its spectra to the known analogs.[5] Compound **15**: ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.28 (dddd, *J* = 1.1, 3.7, 13.8, 13.8 Hz, 1H), 1.84 (s, 3H), 1.86 (d, *J* = 3.6 Hz, OH, 1H), 1.99 (s, 3H), 1.96-2.05 (m, 1H), 2.12 (d, *J* = 1.1 Hz, 3H), 2.18-2.24 (m, 1H), 2.36 (d, *J* = 11.1 Hz, 1H), 2.38 (ddd, *J* = 3.0,

14.2, 14.2 Hz, 1H), 2.72 (dd, J = 4.5, 11.8 Hz, 1H), 3.00 (dd, J = 11.8, 11.8 Hz, 1H), 4.84 (s, 1H), 4.96 (s, 1H), 5.01-5.05 (m, 1H), 5.13 (dd, J = 1.2, 1.3 Hz, 1H), 6.01 (s, 1H), 6.08 (s, 1H), 7.03 (dd, J = 1.4, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.2, 19.9, 23.9, 25.5, 27.9, 39.9, 48.2, 70.4, 78.6, 112.4, 115.5, 117.5, 119.5, 128.0, 133.0, 143.9, 148.6, 149.6, 152.2, 174.6. The stereochemistry of compound **16** was determined by $J_{H^1\text{-}H^2}$ = 11.2 Hz (*trans*). Compound **16**: ^{1}H NMR ($CDCl_3$, 400 Hz) δ 1.11 (dd, J = 13.4, 13.4 Hz, 1H), 1.57-1.64 (m, 1H), 1.78 (br s, OH, 1H), 1.84 (s, 3H), 1.97 (d, J = 1.2 Hz, 3H), 1.99 (s, 3H), 2.08 (ddd, J = 1.8, 13.4, 13.4 Hz, 1H), 2.34-2.41 (m, 2H), 2.72 (dd, J = 10.1, 10.2 Hz, 1H), 3.66 (br dd, J = 10.3, 10.4 Hz, 1H), 4.46 (d, J = 11.2 Hz, 1H), 5.01 (s, 1H), 5.08-5.11 (m, 2H), 5.93 (s, 1H), 6.05 (d, J = 1.2 Hz, 1H), 7.16 (s, 1H).

References

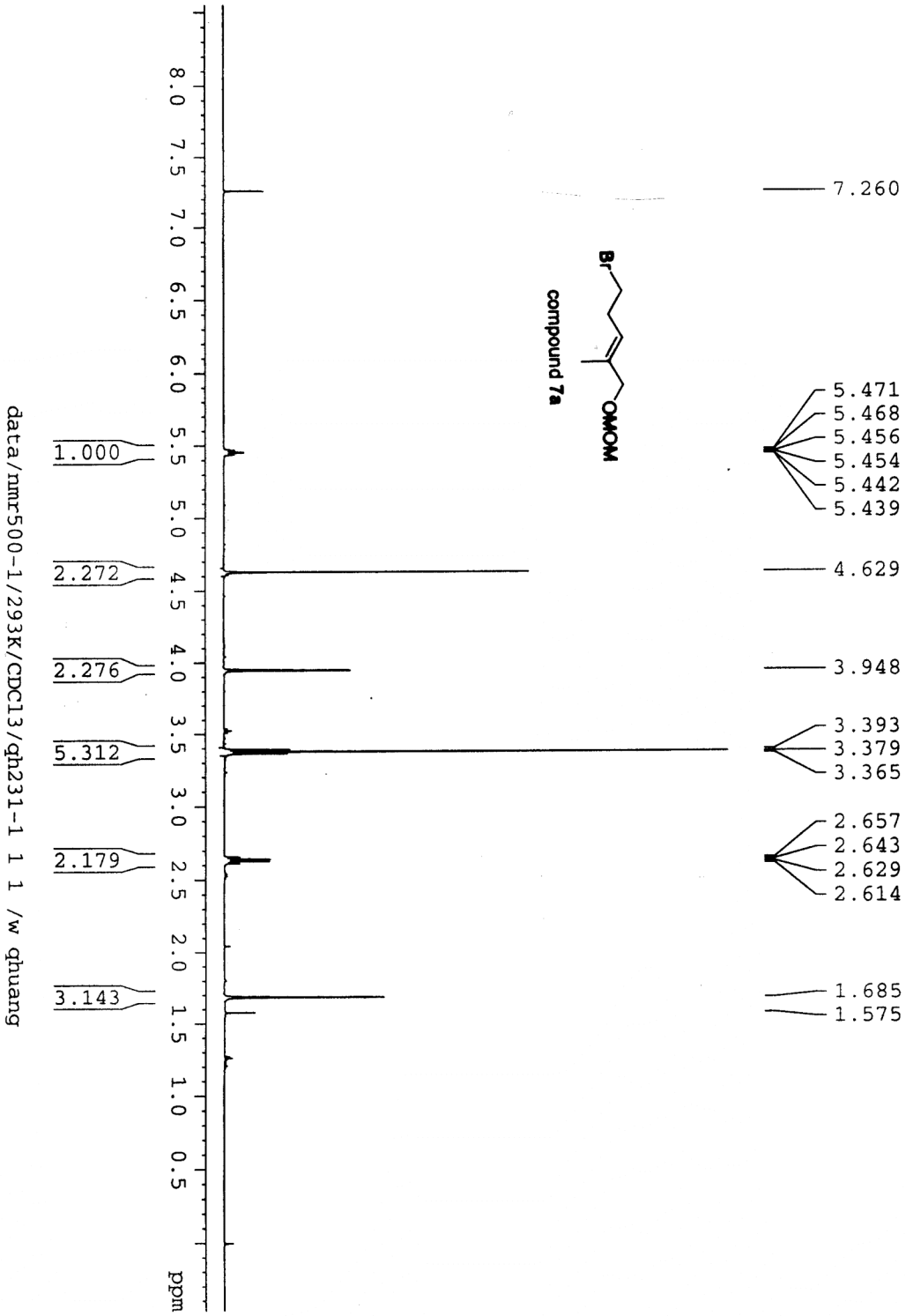
(1) Andresen, G.; Eriksen, A.; Dalhus, A. B.; Gundersen, L.-L.; Rise, F. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1662-1672.

(2) Larock, R. C.; Han, X. *J. Org. Chem.* **1999**, *64*, 1875-1887.

(3) Klein, L. L. *J. Org. Chem.* **1985,** *50*, 1770-1773.

(4) Rodríguez, A. D.; Shi, J.-G. *J. Org. Chem.* **1998**, *63*, 420-421.

(5) (a) Wright, A. E.; Burres, N. S.; Schulte, G. K. *Tetrahedron Lett*. **198**9, *30*, 3491-3494; (b) Rodríguez, A. D.; Shi, J.-G. *J. Org. Chem.* **1998**, *63*, 420-421; (c) Rodríguez, A. D.; Shi, J.-G.; Huang, S. D. *J. Nat. Prod.* **1999**, *62*, 1228-1237; (d) Rodríguez, A. D.; Shi, Y.-P. *J. Nat. Prod.* **2000**, *63*, 1548-1550.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3.379
3.365
2.657
2.643
2.629
2.614
1.685
1.575
1.000
2.272
2.276
5.312
2.179
3.143
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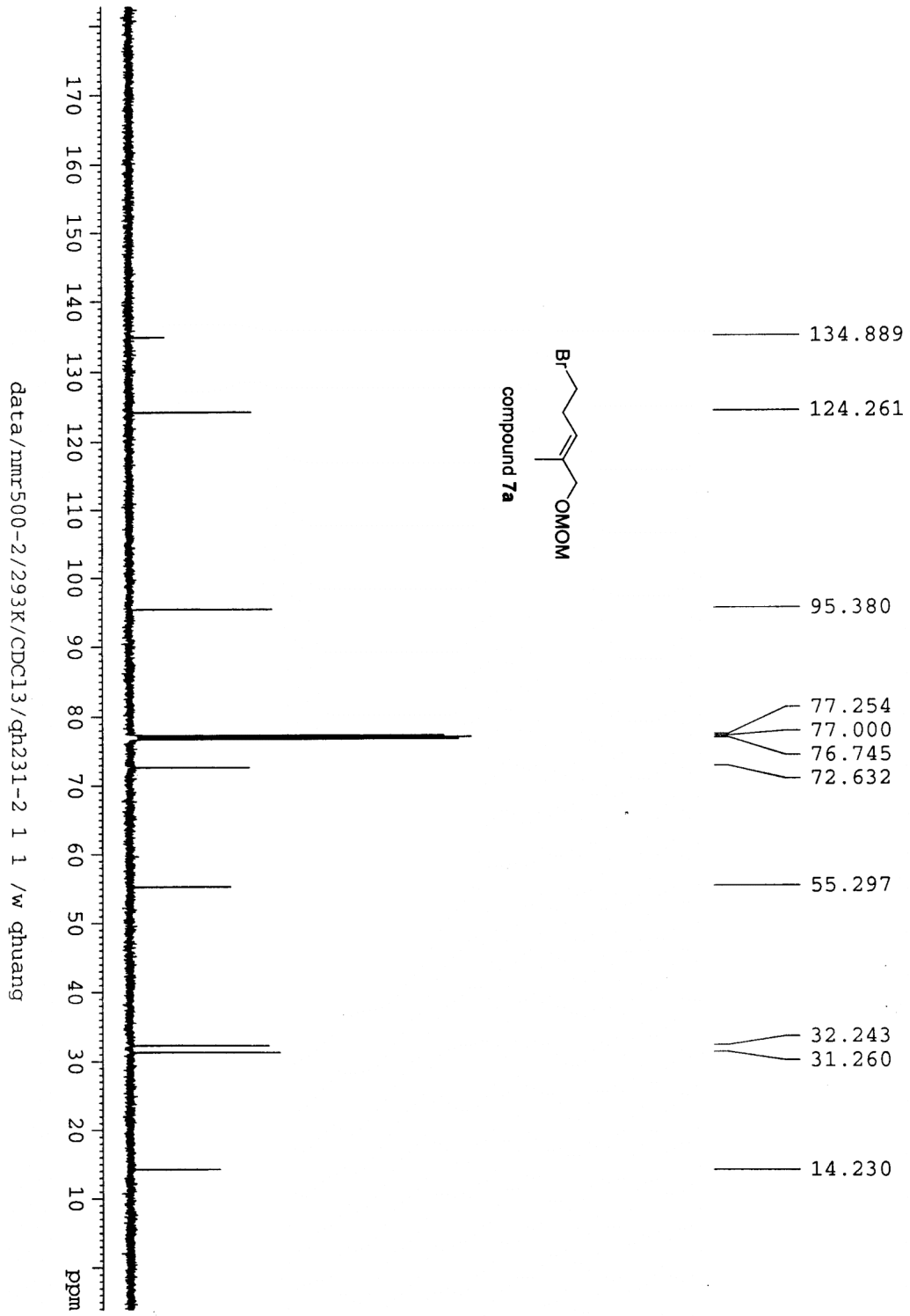
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77.000
76.745
72.632
55.297
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31.260
14.230
Br
OMOM
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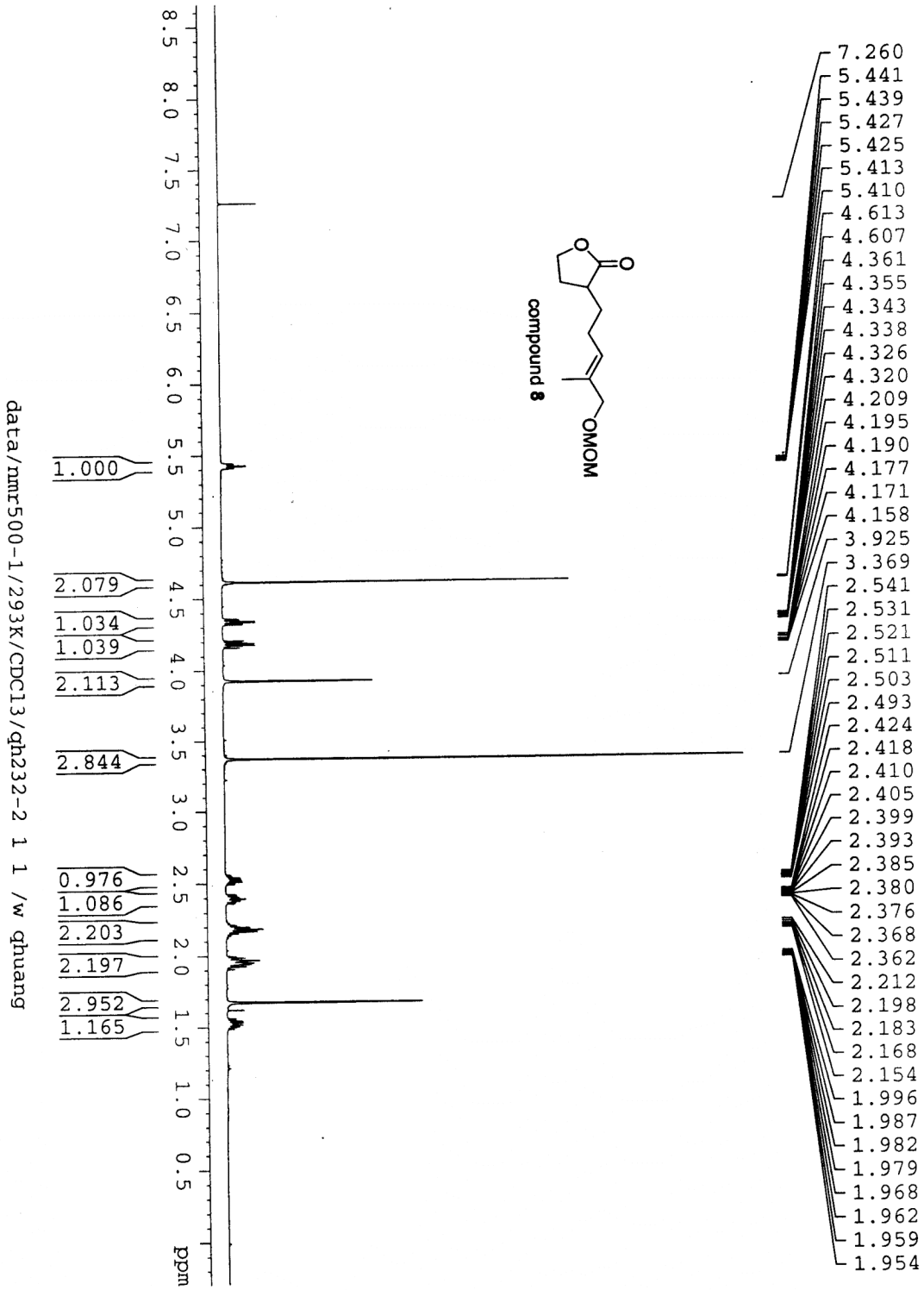
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4.355
4.343
4.338
4.326
4.320
4.209
4.195
4.190
4.177
4.171
4.158
3.925
3.369
2.541
2.531
2.521
2.511
2.503
2.493
2.424
2.418
2.410
2.405
2.399
2.393
2.385
2.380
2.376
2.368
2.362
2.212
2.198
2.183
2.168
2.154
1.996
1.987
1.982
1.979
1.968
1.962
1.959
1.954
1.000
2.079
1.034
1.039
2.113
2.844
0.976
1.086
2.203
2.197
2.952
1.165
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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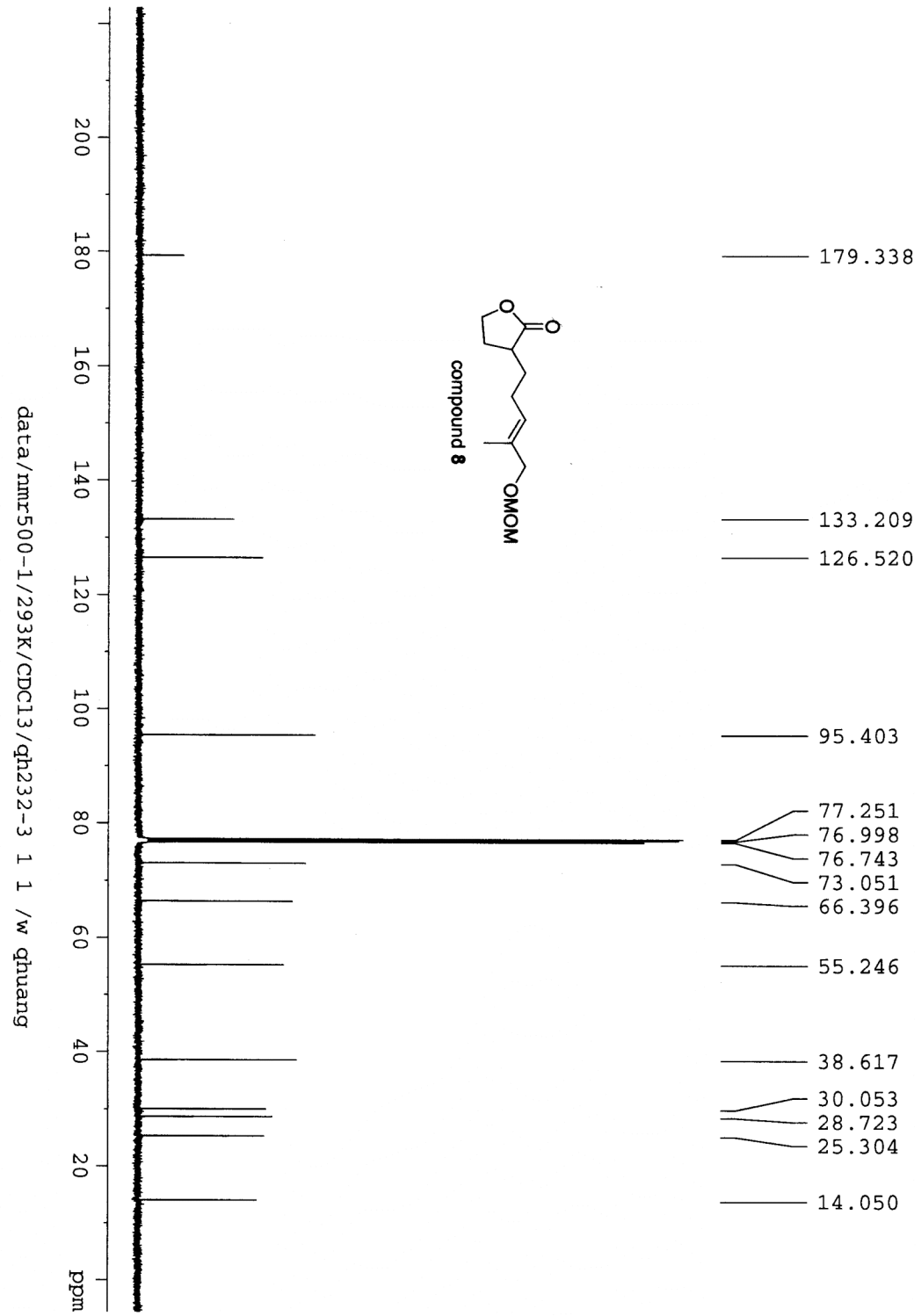
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60
40
20
ppm
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O
O
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76.743
73.051
66.396
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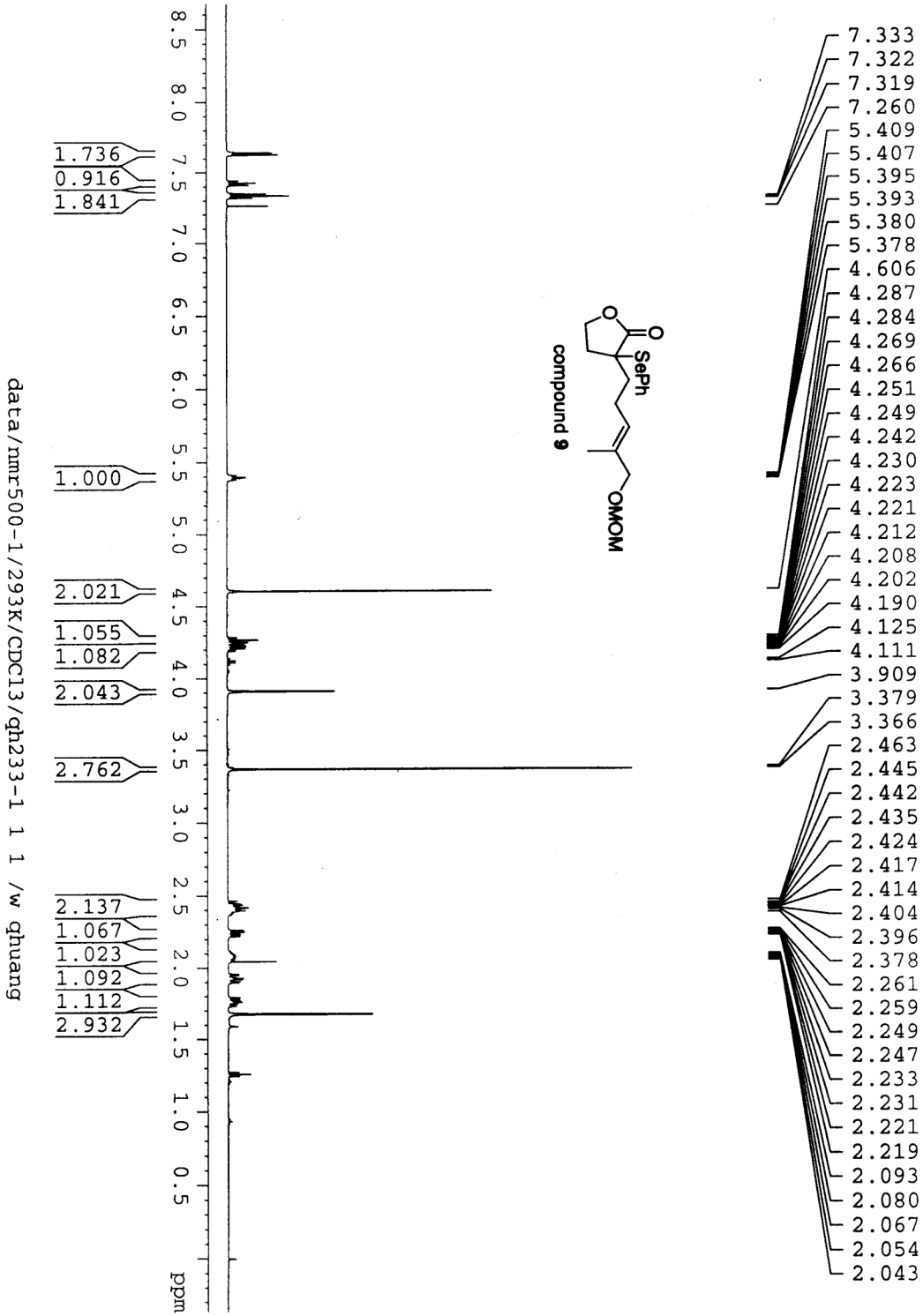
30.053
28.723
25.304
14.050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4.284
4.269
4.266
4.251
4.249
4.242
4.230
4.223
4.221
4.212
4.208
4.202
4.190
4.125
4.111
3.909
3.379
3.366
2.463
2.445
2.442
2.435
2.424
2.417
2.414
2.404
2.396
2.378
2.261
2.259
2.249
2.247
2.233
2.231
2.221
2.219
2.093
2.080
2.067
2.054
2.043
SePh
OMOM
compound 9
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1.841
1.000
2.021
1.055
1.082
2.043
2.762
2.137
1.067
1.023
1.092
1.112
2.932
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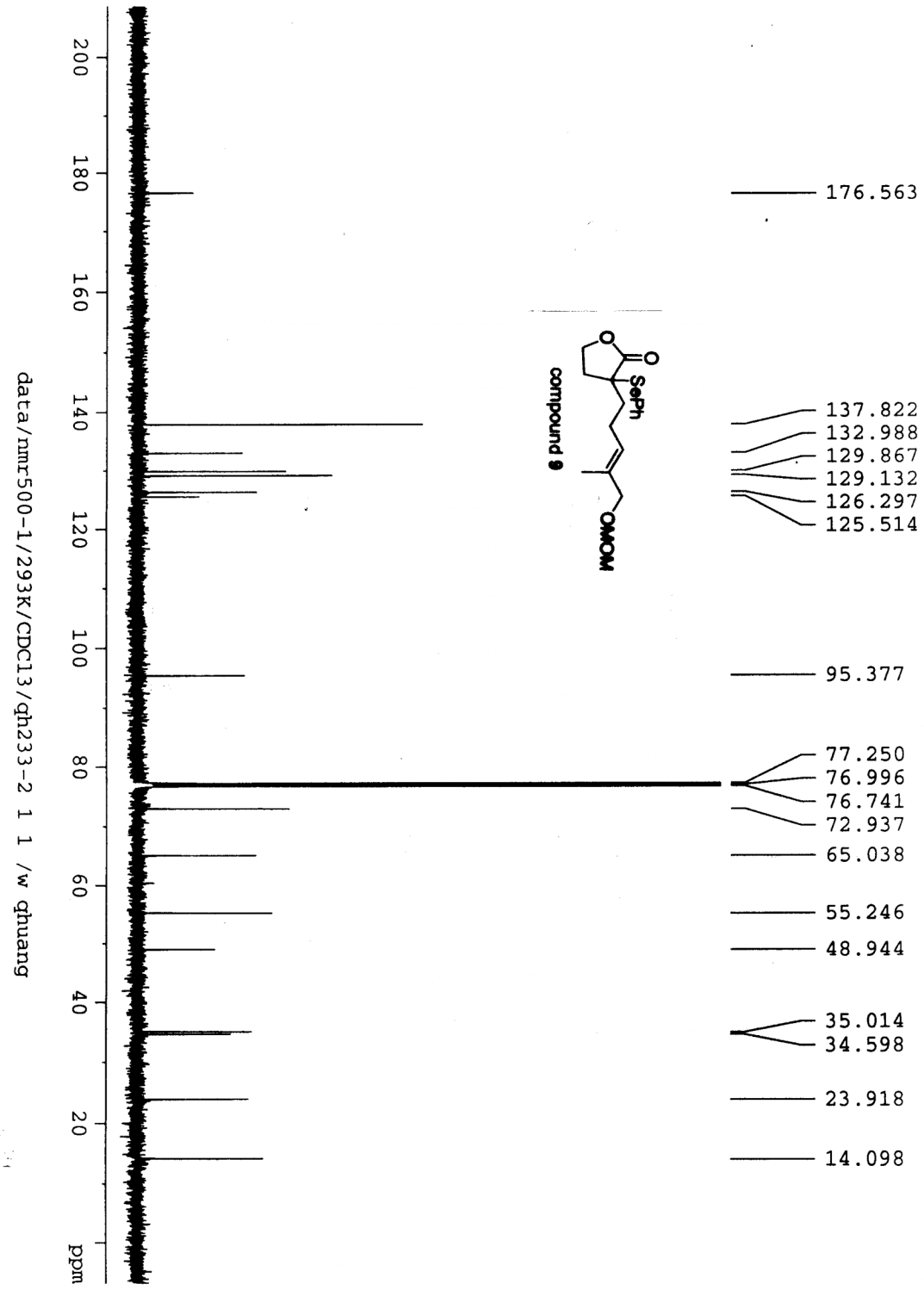
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200
180
160
140
120
100
80
60
40
20
ppm
compound 9
SePh
OMOM
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137.822
132.988
129.867
129.132
126.297
125.514
95.377
77.250
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76.741
72.937
65.038
55.246
48.944
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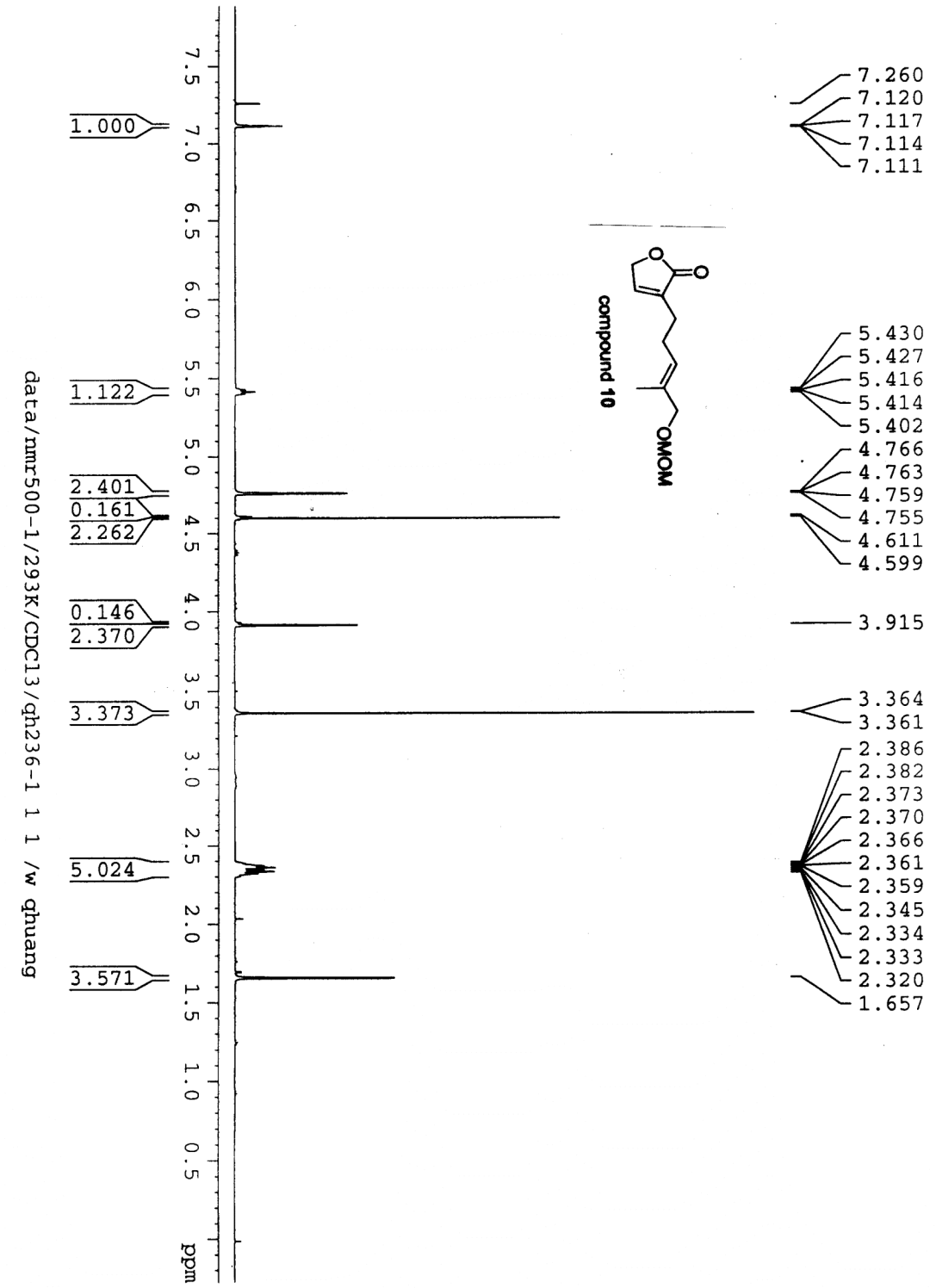
34.598
23.918
14.098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7.111
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5.427
5.416
5.414
5.402
4.766
4.763
4.759
4.755
4.611
4.599
3.915
3.364
3.361
2.386
2.382
2.373
2.370
2.366
2.361
2.359
2.345
2.334
2.333
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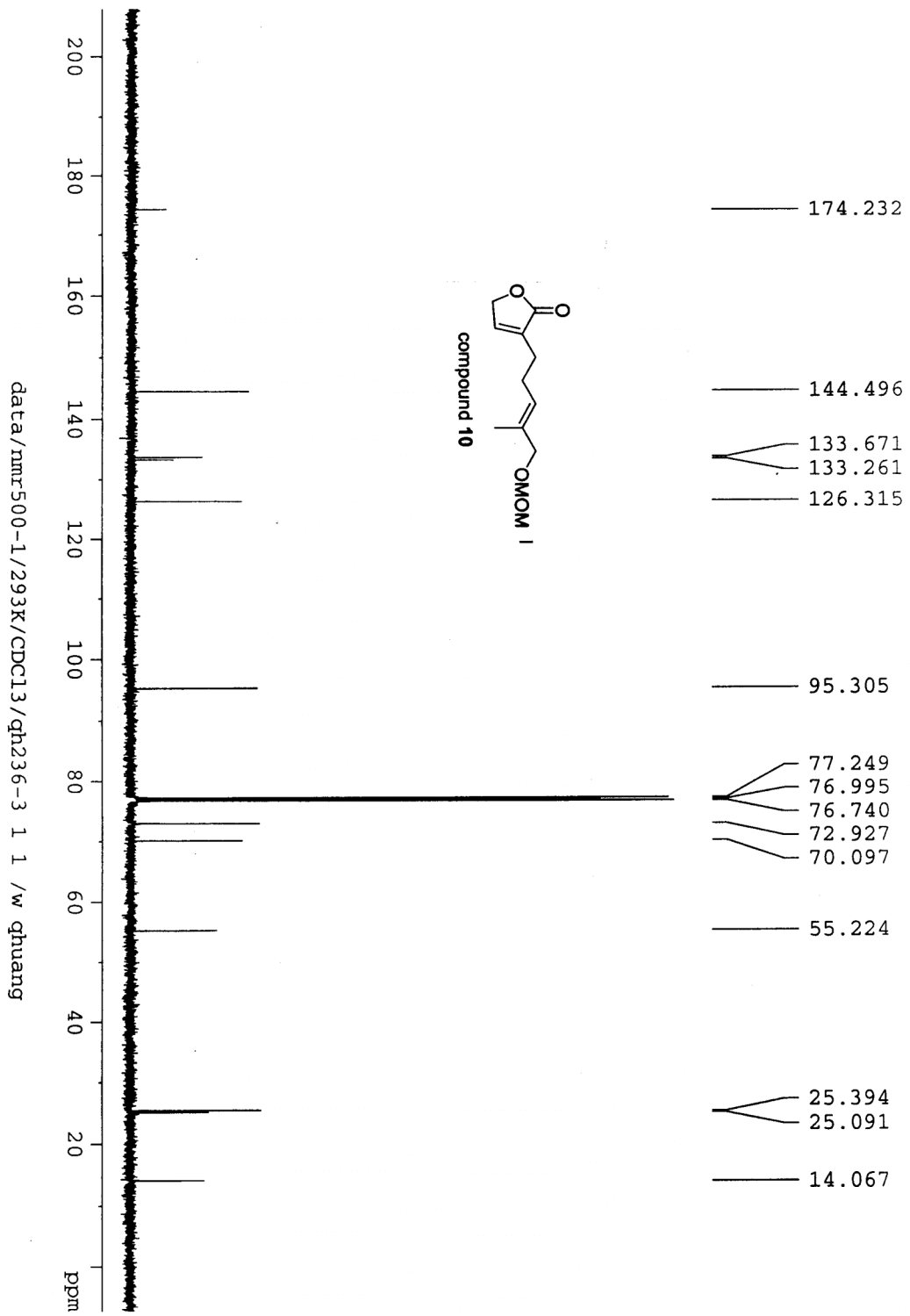
ppm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200
180
160
140
120
100
80
60
40
20
ppm
compound 10
OMOM I
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133.671
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76.995
76.740
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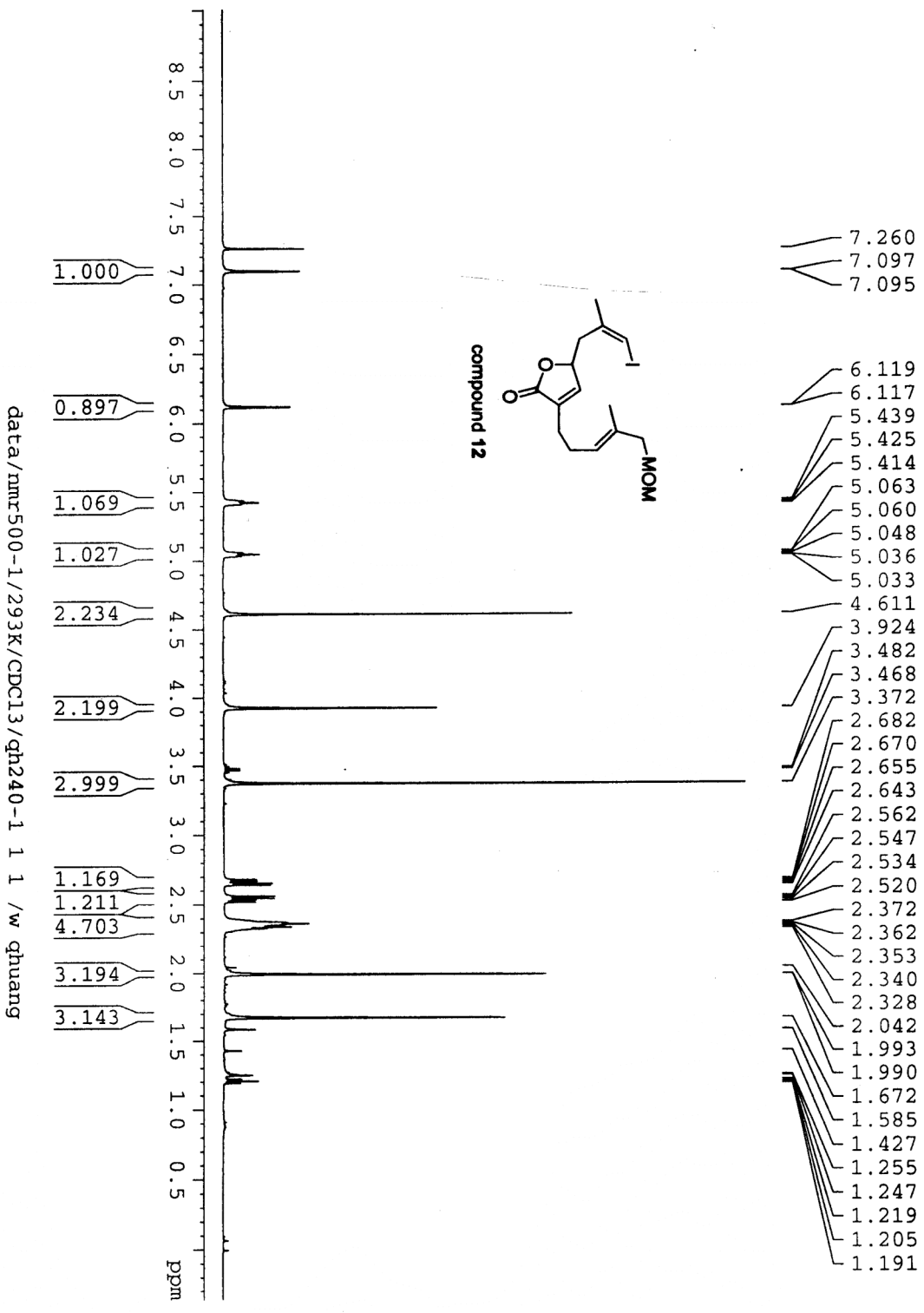
25.091
14.067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5.036
5.033
4.611
3.924
3.482
3.468
3.372
2.682
2.670
2.655
2.643
2.562
2.547
2.534
2.520
2.372
2.362
2.353
2.340
2.328
2.042
1.993
1.990
1.672
1.585
1.427
1.255
1.247
1.219
1.205
1.191
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0.897
1.069
1.027
2.234
2.199
2.999
1.169
1.211
4.703
3.194
3.143
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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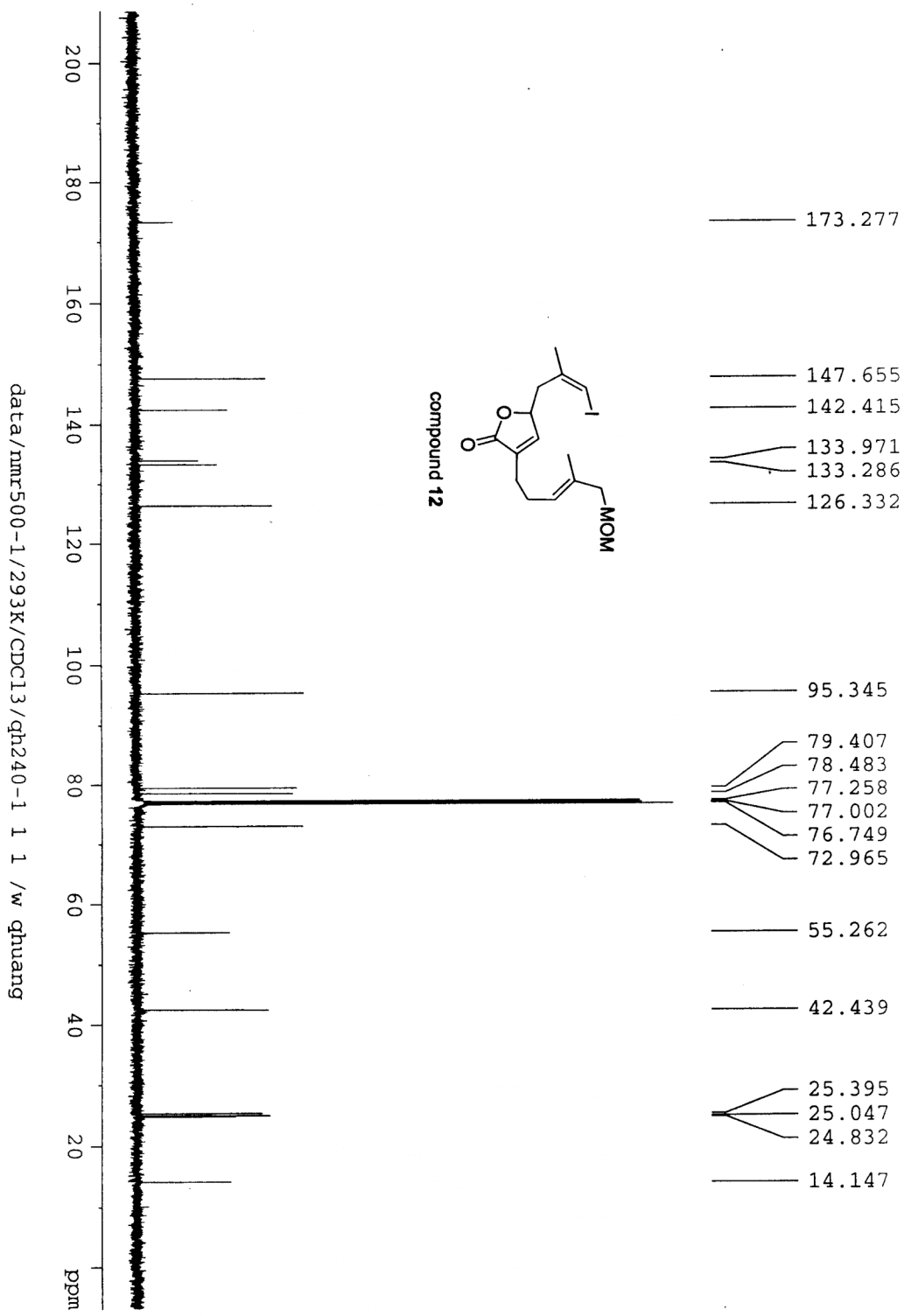
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180
160
140
120
100
80
60
40
20
ppm
compound 12
MOM
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133.971
133.286
126.332
95.345
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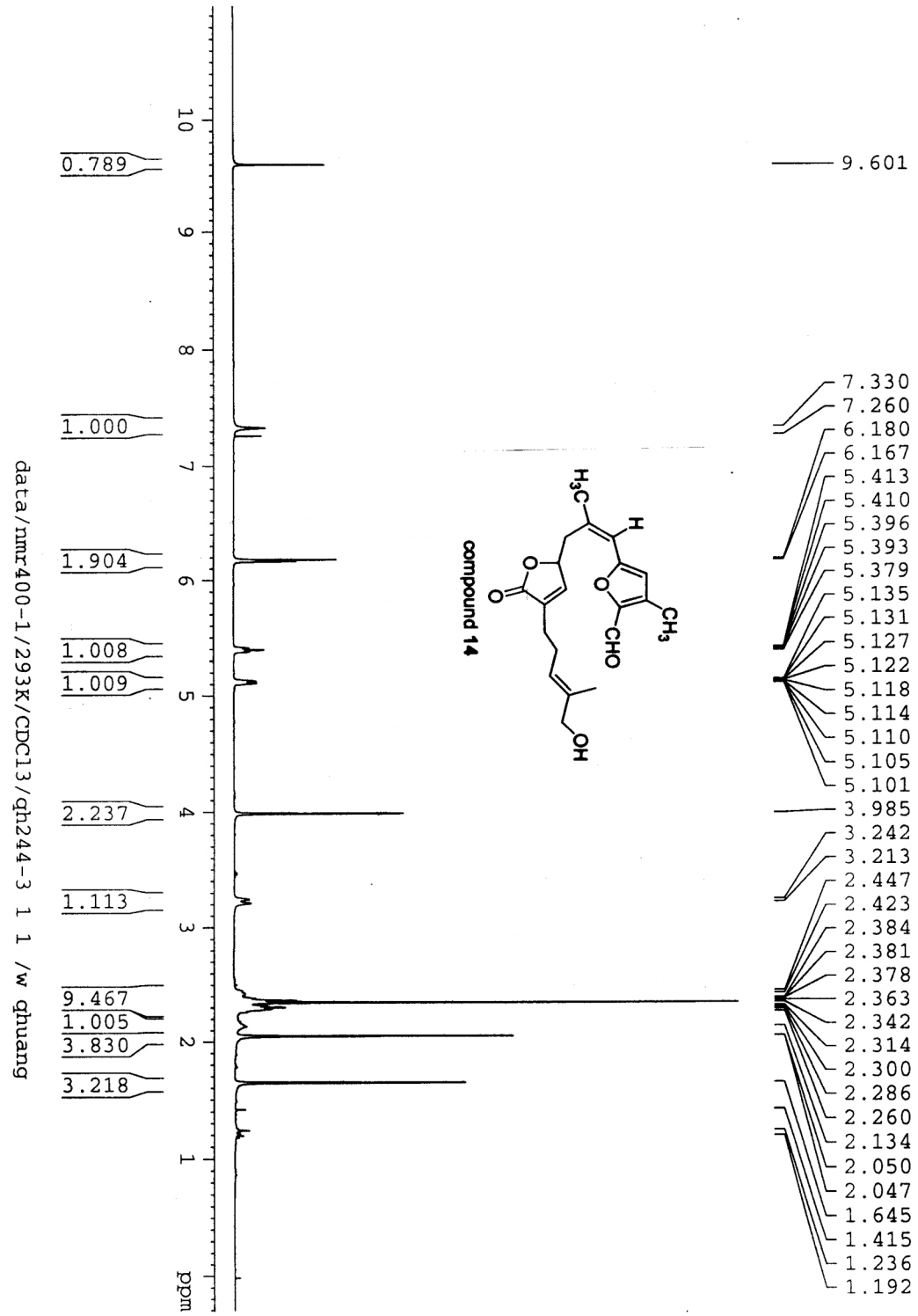
14.147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3.218
ppm
compound 14
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H
O
O
CHO
CH3
OH
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6.167
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5.410
5.396
5.393
5.379
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5.131
5.127
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5.118
5.114
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5.105
5.101
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2.384
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2.363
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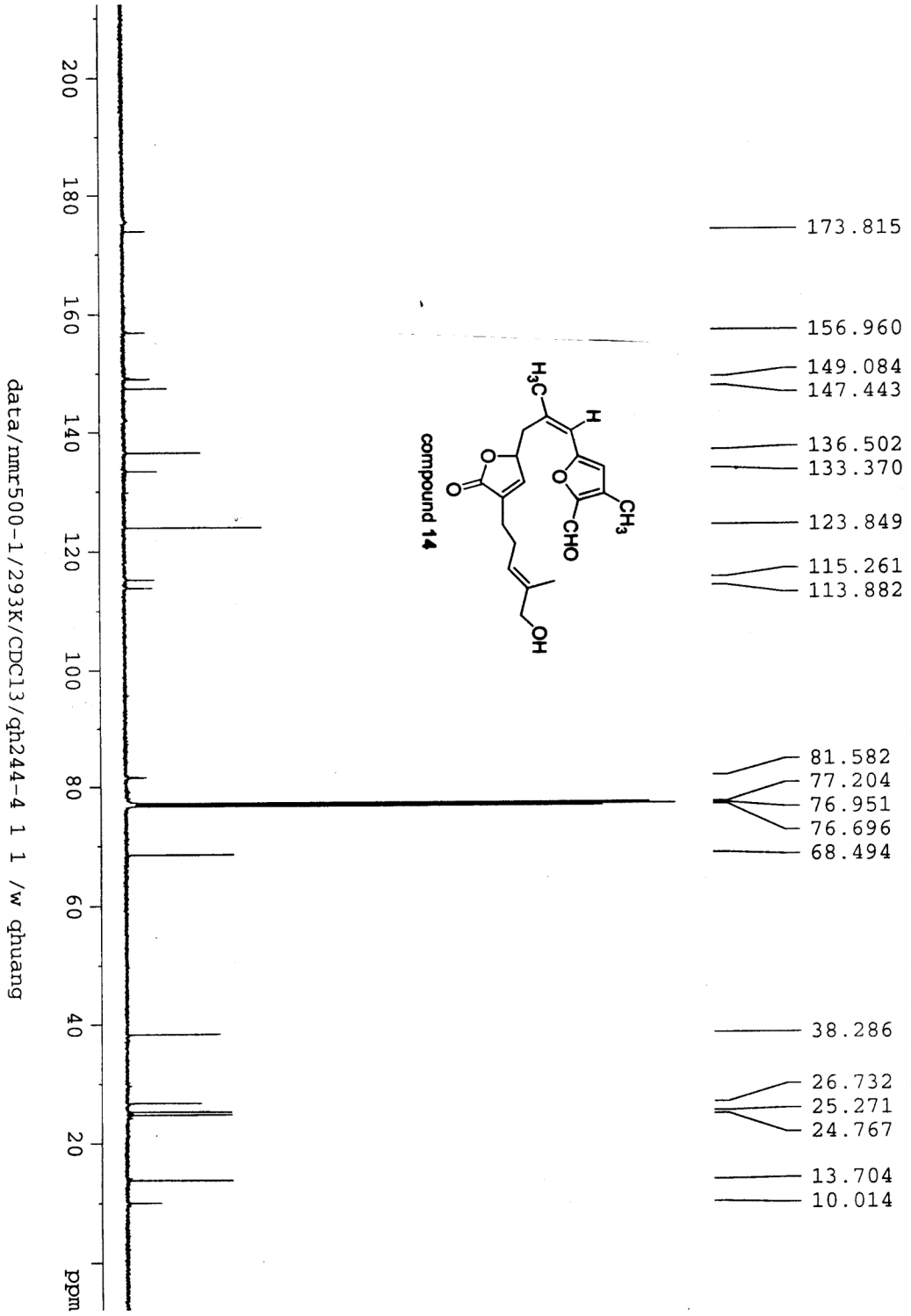
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120
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80
60
40
20
ppm
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H
O
O
O
CHO
CH_3
OH
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149.084
147.443
136.502
133.370
123.849
115.261
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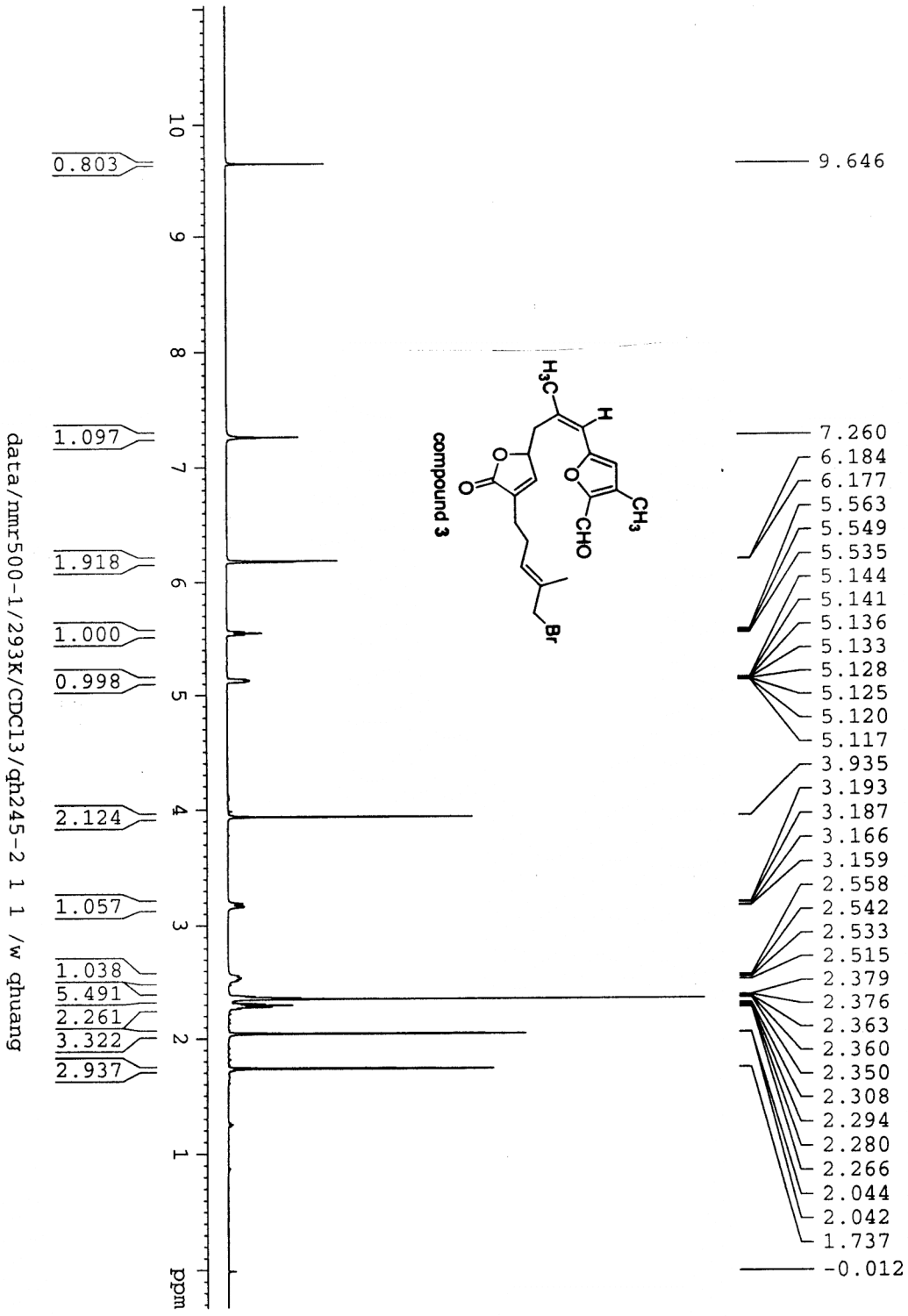
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2.937
ppm
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7.260
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6.177
5.563
5.549
5.535
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5.141
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5.133
5.128
5.125
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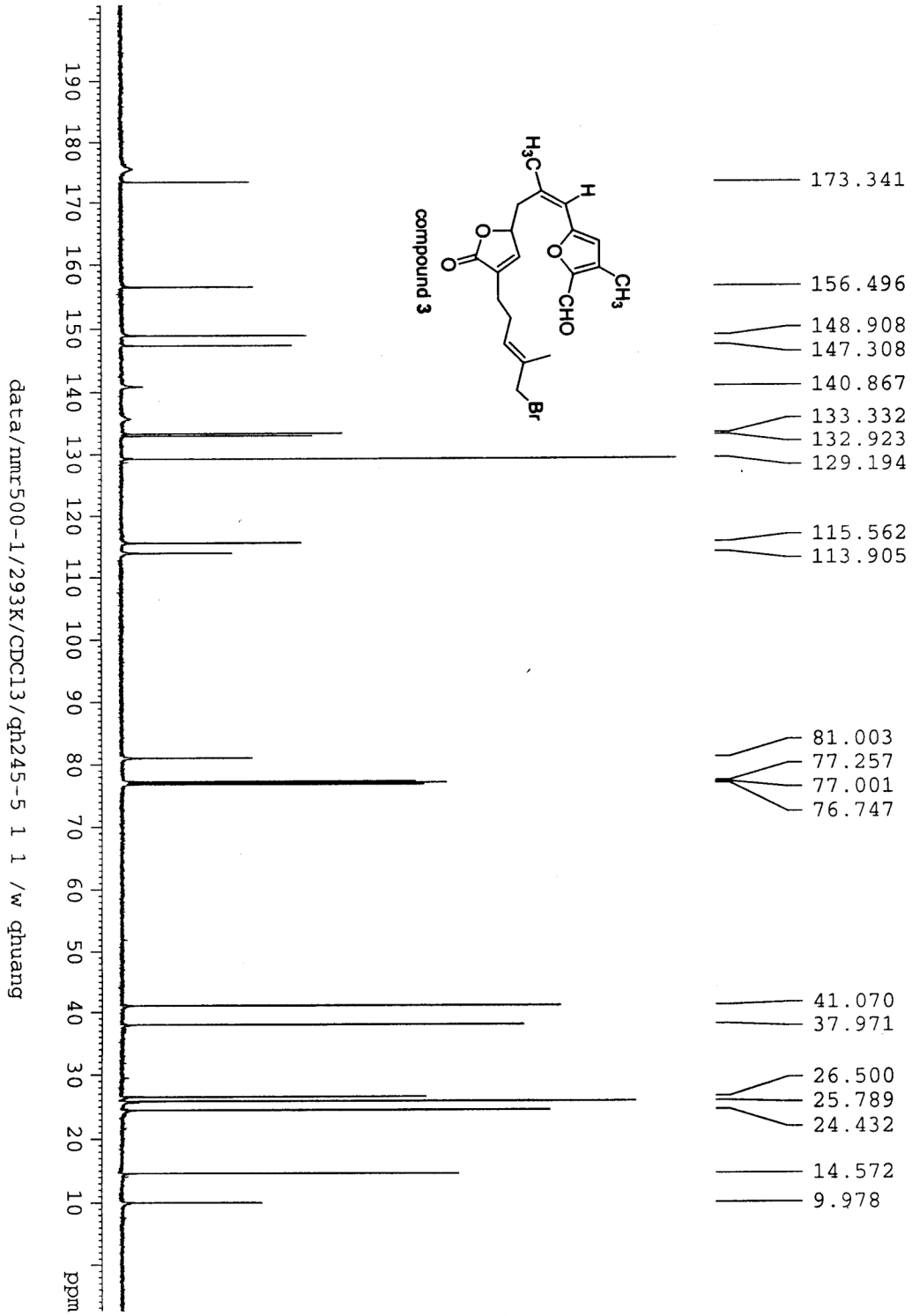
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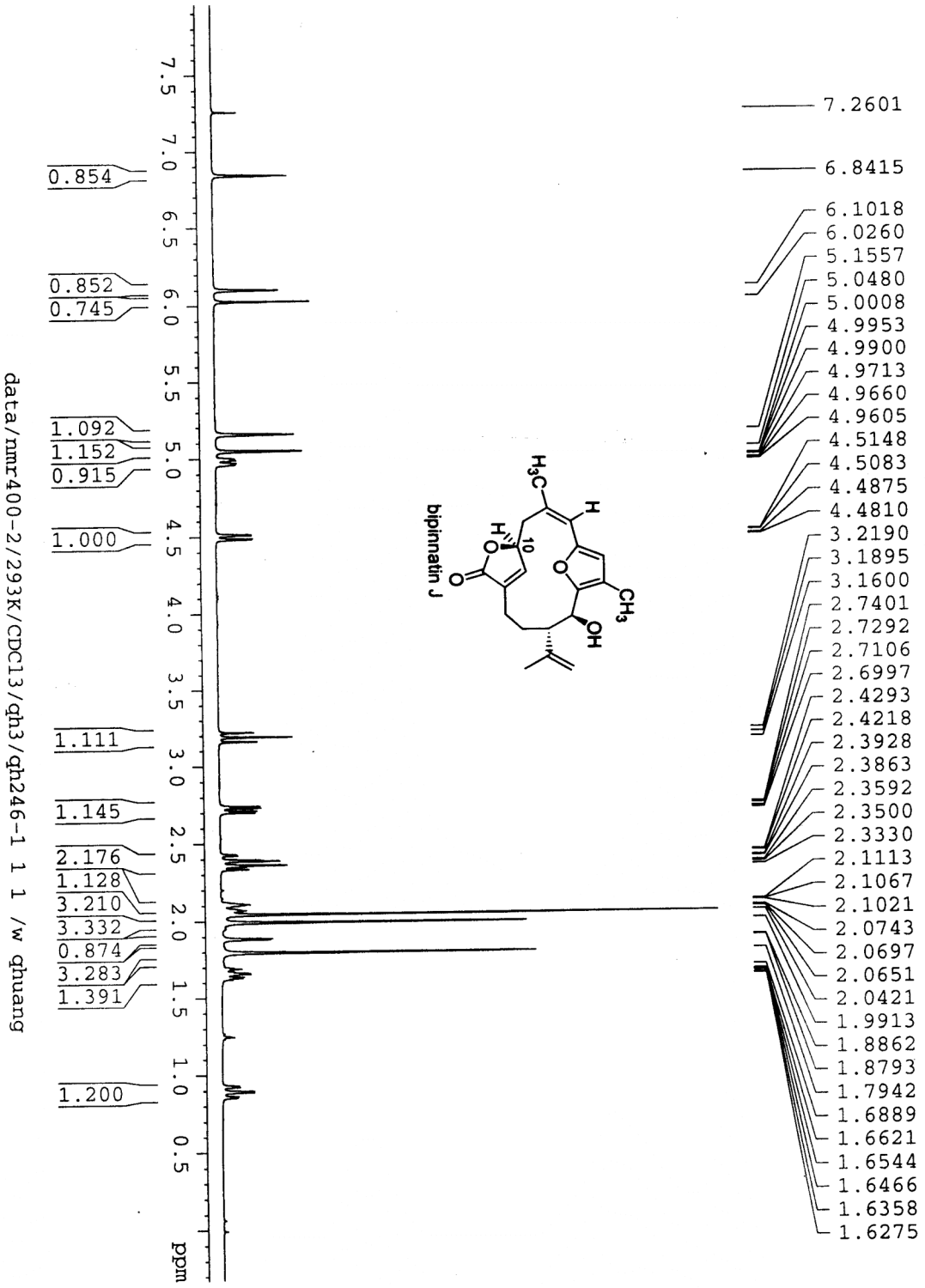
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4.9605
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4.5083
4.4875
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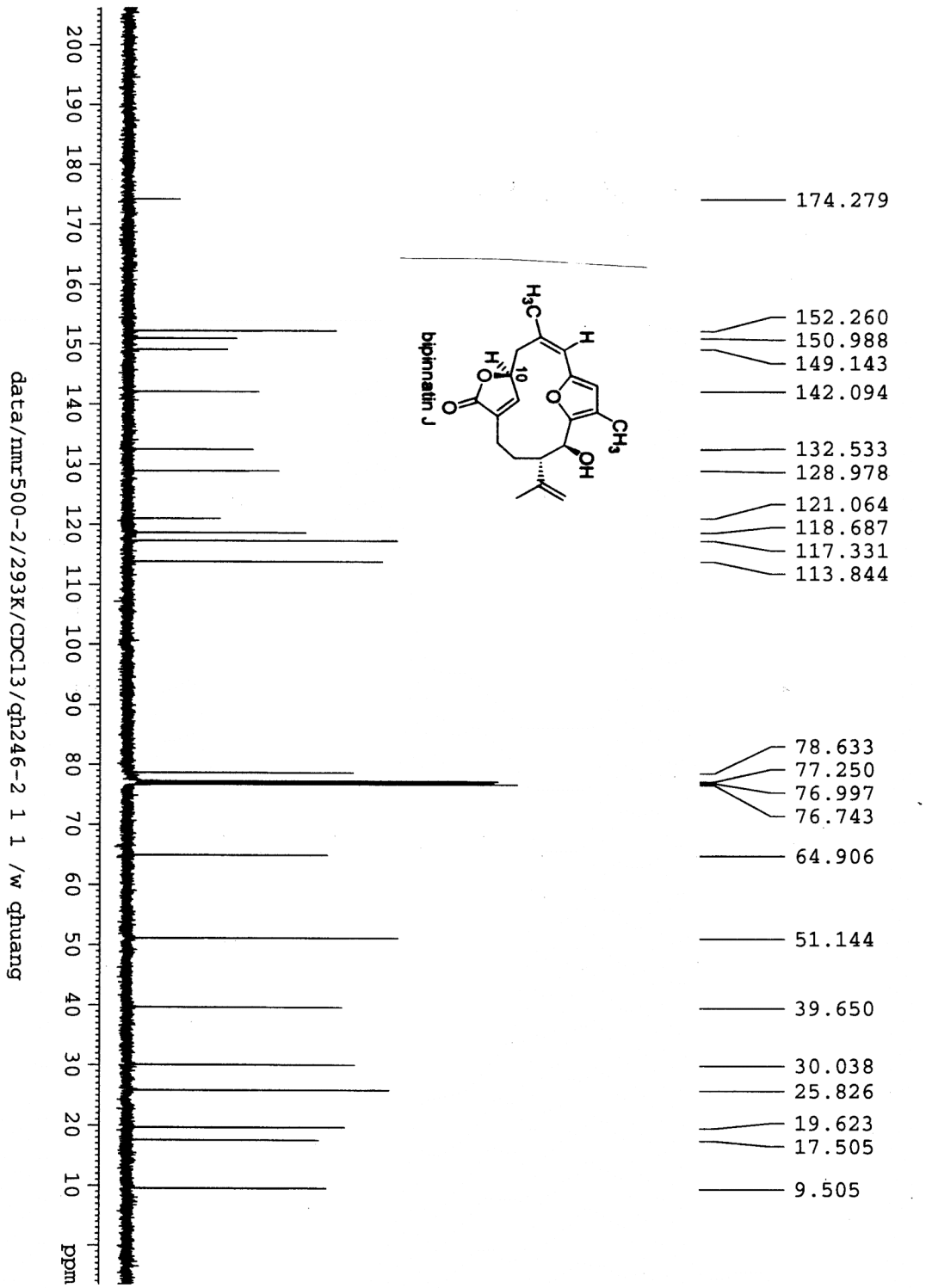
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76.997
76.743
64.906
51.144
39.650
30.038
25.826
19.623
17.505
9.505
bipinnatin J
data/nmr500-2/293K/CDCl3/qh246-2 1 1 /w qhuang
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm