

# First Total Syntheses and Spectral Data Corrections of 11- $\alpha$ -Methoxycurvularin and 11- $\beta$ - Methoxycurvularin

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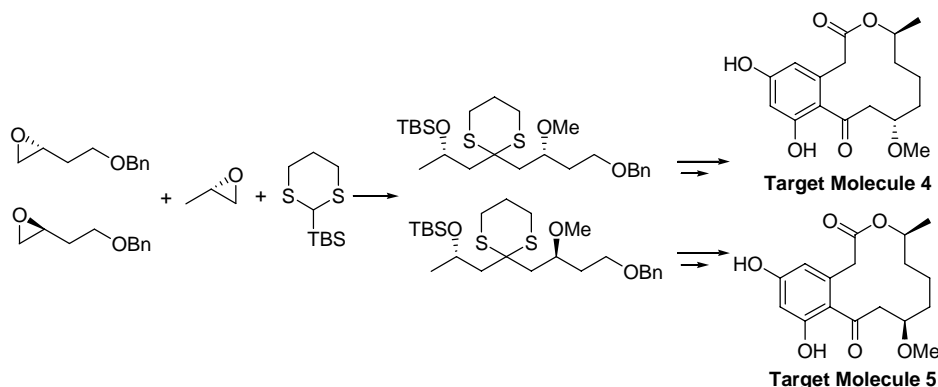
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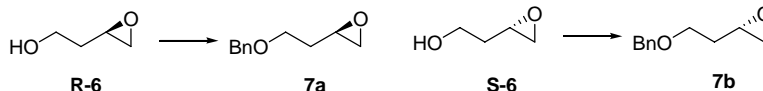
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## Experimental Procedures and Spectroscopic and Analytical Data of the Products

**Note:** 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.  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were recorded on a 300 MHz and a 400 MHz spectrometers. Chemical shifts are reported as  $\delta$  values relative to internal chloroform ( $\delta$  7.26 for  $^1\text{H}$  and 77.0 for  $^{13}\text{C}$ ).

### Syntheses of (R)-2-(2-(benzyloxy)ethyl)oxirane **7a** and (S)-2-(2-(benzyloxy)ethyl)oxirane **7b**

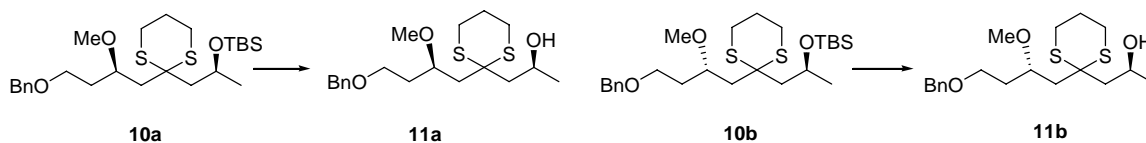


NaH (70%) (2.6 g, 75.7 mmol) was added to the solution of (R)-1,2-Epoxy-4-butanol **6** (3.33 g, 37.8 mmol) in THF (40 mL) at 0 °C, then  $\text{Bu}_4\text{N}^+\text{I}^-$  (10 mg) and BnBr (7.76 g, 45.36 mmol) was added. The solution was warmed to rt and stirred for 2h, quenched with saturated  $\text{NH}_4\text{Cl}$  solution and extracted with ether ( $3 \times 60$  mL), the combined organic solution were washed with brine ( $3 \times 15$  mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated in vacuo. The residue was purified by column chromatography (hexanes / EtOAc, 20:1) to give compound **7a** (6.69 g, 99.3%) as colorless oil:  $[\alpha]_{\text{D}}^{25} +16^\circ$  (C 2.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.39 (m, 5H), 4.54 (s, 2H), 3.64 (td,  $J = 11.1$  Hz, 9.6 Hz, 5.1 Hz, 3.9 Hz, 2H), 3.08 (m, 1H), 2.78 (t,  $J = 4.8$  Hz, 1H), 2.53 (t,  $J = 4.8$  Hz, 1H), 1.87-1.98 (m, 1H), 1.73-1.83 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 128.3, 127.5, 72.9, 66.9, 49.9, 46.9, 32.8; IR (KBr) 2922, 2860, 1103, 739,  $698\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_2$   $[\text{M}+\text{H}]^+$  179.1072 found 179.1070;

**7b** (9.2 g, 98.9%) was obtained from (S)-1,2-Epoxy-4-butanol **6** (4.6 g, 52.3 mmol) and BnBr (10.7 g, 62.8 mmol), by the same operation as the synthesis of **7a**:  $[\alpha]_{\text{D}}^{25} -15^\circ$  (c 2.13,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.39 (m, 5H), 4.54 (s, 2H), 3.63 (t,  $J = 6.9$  Hz, 2H), 3.07 (d,  $J = 2.4$  Hz, 1H), 2.78 (t,  $J = 4.8$  Hz, 1H), 2.52 (m, 1H), 1.92 (td,  $J = 19.8$  Hz, 6.0 Hz, 1H), 1.78 (td,  $J = 20.1$  Hz, 6.0 Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 128.3, 127.5, 72.9, 66.9, 49.9, 46.9, 32.8; IR (KBr) 2922,

2860, 1103, 739, 699  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_2$   $[\text{M}+\text{H}]^+$  179.1072 found 179.1069.

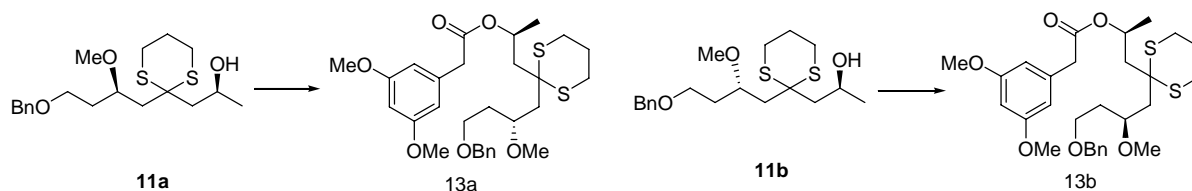
### Syntheses of compounds **11a** and **11b**



0.5 mL of hydrochloric acid (conc.) was added to a solution of **10a** (1.358 g, 2.8 mmol) in 50 mL of MeOH, and this mixture was stirred for 2 h at rt.  $\text{NaHCO}_3$  (500 mg, 6 mmol) was added. After stirring for 0.5 h, MeOH was removed in vacuo. The residue was dissolved in 150 mL of ether, washed with water ( $3 \times 10$  mL) and brine ( $2 \times 10$  mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated in vacuo. The residue was purified by column chromatography (hexanes / EtOAc, 4:1) to give compound **11a** (1.02 g, 99.2%) as colorless oil:  $[\alpha]_{\text{D}}^{25} -3^\circ$  (c 0.7,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.34 (m, 5H), 4.48 (t,  $J = 12.3$  Hz, 2H), 4.16 (t,  $J = 7.2$  Hz, 1H), 3.69 (dd,  $J = 11.7$  Hz, 4.8 Hz, 1H), 3.58 (d,  $J = 3.0$  Hz, 1H), 3.55 (dd,  $J = 7.2$  Hz, 4.8 Hz, 2H), 3.27 (s, 3H), 2.97 (ddd,  $J = 19.8$  Hz, 9.9 Hz, 3.3 Hz, 2H), 2.67-2.89 (m, 2H), 2.13 (d,  $J = 4.8$  Hz, 2H), 1.76-2.03 (m, 6H), 1.14 (d,  $J = 6.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 128.2, 127.5, 127.4, 75.1, 72.9, 66.5, 64.9, 56.0, 51.4, 46.3, 44.6, 34.0, 26.3, 25.9, 24.7, 23.4; IR (KBr) 3388, 2923, 1418, 1383, 1118  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{19}\text{H}_{30}\text{S}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  393.1534 found 393.1530;

**10b** (6.7 g, 13.8 mmol) was treated with 100 mL MeOH and 1 mL hydrochloric acid (conc.) by the same operation as the synthesis of **11a** to give **11b** (4.97 g, 97%) as colorless oil:  $[\alpha]_{\text{D}}^{25} +31^\circ$  (c 1.7,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.33 (m, 5H), 4.49 (dd,  $J = 13.5$  Hz, 11.7 Hz, 2H), 4.10-4.15 (m, 2H), 3.77 (ddd,  $J = 9.9$  Hz, 4.8 Hz, 1.8 Hz, 1H), 3.57 (t,  $J = 6.0$  Hz, 2H), 3.34 (s, 3H), 2.72 (dd,  $J = 12.0$  Hz, 6.0 Hz, 4H), 2.32 (dd,  $J = 15.0$  Hz, 9.0 Hz, 1H), 2.21 (dd,  $J = 15.0$  Hz, 1.8 Hz, 1H), 2.14 (dd,  $J = 15.0$  Hz, 9.0 Hz, 2H), 1.18-1.94 (m, 4H), 1.17 (d,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 128.3, 127.6, 127.5, 76.5, 73.1, 66.6, 63.7, 56.1, 51.4, 47.3, 42.7, 33.8, 26.0, 25.9, 25.1, 25.0; IR (KBr) 3436, 2929, 1420, 1369, 1113, 740  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{19}\text{H}_{30}\text{S}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  393.1534 found 393.1529.

## Syntheses of compounds **13a** and **13b**

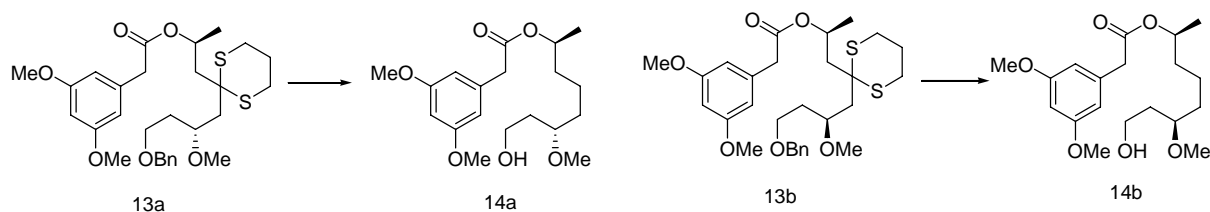


To a solution of **11a** (1.13 g, 3.05 mmol) and 3,5-dimethoxyphenylacetic acid **12** (718 mg, 3.66 mmol) in 30mL of anhydrous ether at rt was added DCC (755 mg, 3.66 mmol) and DMAP (37 mg, 0.3 mmol). After stirred for 3h at rt, the mixture was filtered. The ether solution was dissolved in 100mL of ether and washed with brine ( $3 \times 10$  mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated in vacuo. The residue was purified by column chromatography (hexanes / EtOAc, 10 : 1) to afford the title compound **13a** (1.64 g, 98.2%) as colorless oil:  $[\alpha]_{\text{D}}^{25} -25^\circ$  (c 1.2,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.34 (m, 5H), 6.42 (d,  $J = 2.4$  Hz, 2H), 6.33 (d,  $J = 2.4$  Hz, 1H), 5.29 (t,  $J = 6.3$  Hz, 1H), 4.49 (dd,  $J = 14.1$  Hz, 12.0 Hz, 2H), 3.71 (s, 6H), 3.68 (dd,  $J = 6.3$  Hz, 4.8 Hz, 1H), 3.57 (t,  $J = 4.8$  Hz, 2H), 3.50 (s, 2H), 3.27 (s, 3H), 2.63-2.73 (m, 4H), 2.41 (dd,  $J = 15.0$  Hz, 8.4 Hz, 1H), 2.01-2.19 (m, 3H), 1.78-1.91 (m, 4H), 1.20 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 160.5, 138.2, 136.1, 128.2, 127.6, 127.4, 107.3, 99.0, 75.8, 73.0, 68.7, 66.8, 55.9, 55.1, 51.2, 44.2, 43.0, 42.0, 33.8, 26.0, 24.9, 21.2; IR (KBr) 2933, 1731, 1598, 1458, 1295, 1204, 1155, 1066, 742  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{29}\text{H}_{40}\text{S}_2\text{O}_6$   $[\text{M}+\text{Na}]^+$  571.2164 found 571.2160.

**11b** (1.47 g, 13.4 mmol) was treated with 3,5-dimethoxyphenylacetic acid **12** (3.414 g, 17.4 mmol), DCC (3.584 g, 17.4 mmol) and DMAP (158 mg, 1.3 mmol) as described for the synthesis of **13a** to give **13b** (7.26 g, 98.6%) as colorless oil:  $[\alpha]_{\text{D}}^{25} -3^\circ$  (c 1.75,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.34 (m, 5H), 6.43 (s, 2H), 6.34 (s, 1H), 5.25 (t,  $J = 6.3$  Hz, 1H), 4.47 (d,  $J = 11.7$  Hz, 2H), 3.75 (s, 6H), 3.66 (dd,  $J = 10.5$  Hz, 4.8 Hz, 1H), 3.55 (t,  $J = 6.0$  Hz, 2H), 3.50 (s, 2H), 3.29 (s, 3H), 2.66-2.77 (m, 4H), 2.40 (dd,  $J = 15.3$  Hz, 7.8 Hz, 1H), 2.07 (d,  $J = 5.1$  Hz, 2H), 2.04 (d,  $J = 3.3$  Hz, 1H), 1.76-1.87 (m, 4H), 1.25 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 160.6, 138.3, 136.1, 128.2, 127.6, 127.4, 107.3, 99.0, 75.8, 72.9, 68.8, 66.8, 56.0, 55.2, 51.3, 45.2, 44.7, 41.9, 34.6, 26.3, 26.1, 24.7, 21.7; IR (KBr) 2932, 1731, 1598, 1458, 1295, 1204, 1155, 1065, 741  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{29}\text{H}_{40}\text{S}_2\text{O}_6$

$[M+Na]^+$  571.2164 found 571.2161.

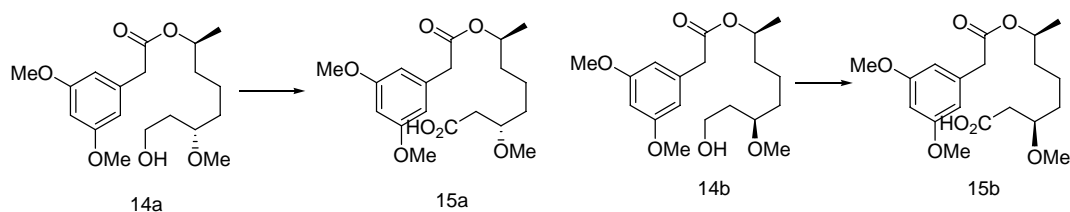
### Syntheses of compounds **14a** and **14b**



3 g of Raney Ni was added to a solution of **13a** (1.6 g, 2.9 mmol) in 30 mL of EtOH, the mixture was stirred for 4 h at 80 °C under H<sub>2</sub>, then cooled to rt and filtered. The EtOH solution was concentrated in vacuo and the residue was dissolved in 30 mL of EtOH, added 3 g of Raney Ni. The mixture was stirred for another 4 h at 80 °C under H<sub>2</sub>, cooled to rt and filtered, concentrated in vacuo. And the residue was purified by column chromatography (hexanes / EtOAc, 2 : 1) to give compound **14a** (0.78 g, 75.4%) as colorless oil:  $[\alpha]_D^{25} +25^\circ$  (c, 2.38, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.42 (s, 2H), 6.34 (s, 1H), 4.90 (dd,  $J$  = 12.3 Hz, 6.3 Hz, 1H), 3.76 (s, 6H), 3.69 (dd,  $J$  = 11.1 Hz, 5.4 Hz, 2H), 3.50 (s, 2H), 3.32 (dd,  $J$  = 17.7 Hz, 5.4 Hz, 1H), 3.30 (s, 3H), 2.62 (s, 1H), 1.37-1.67 (m, 6H), 1.27 (dd,  $J$  = 15.9 Hz, 7.2 Hz, 2H), 1.19 (d,  $J$  = 5.7 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  170.9, 160.7, 136.3, 107.2, 99.0, 80.5, 71.2, 60.7, 56.4, 55.2, 42.0, 35.9, 35.4, 32.6, 20.7, 19.9; IR (KBr) 3439, 2939, 1728, 1599, 1463, 1294, 1205, 1156, 1063, 837 cm<sup>-1</sup>; HRMS  $m/z$  calcd for C<sub>19</sub>H<sub>30</sub>O<sub>6</sub>  $[M+H]^+$  355.2121 found 355.2118.

**14b** (1.47 g, 76%) was obtained as colorless oil by treatment of **13b** (3.0 g, 5.47 mmol) with Raney Ni under H<sub>2</sub> by the same operation as the synthesis of **14a**:  $[\alpha]_D^{25} -5^\circ$  (c 1.15, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.42 (d,  $J$  = 2.4 Hz, 2H), 6.34 (t,  $J$  = 2.4 Hz, 1H), 4.90 (dd,  $J$  = 12.9 Hz, 6.3 Hz, 1H), 3.76 (s, 6H), 3.70 (dd,  $J$  = 11.1 Hz, 6.3 Hz, 2H), 3.50 (s, 2H), 3.32 (dd,  $J$  = 14.7 Hz, 6.0 Hz, 1H), 3.30 (s, 3H), 2.58 (s, 1H), 1.33-1.67 (m, 6H), 1.21-1.30 (m, 2H), 1.19 (d,  $J$  = 5.7 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  170.9, 160.7, 136.3, 107.2, 99.0, 80.5, 71.2, 60.8, 56.4, 55.2, 42.0, 35.9, 35.4, 32.6, 20.7, 19.9; IR (KBr) 3442, 2939, 1728, 1599, 1463, 1294, 1205, 1156, 1063, 837 cm<sup>-1</sup>; HRMS  $m/z$  calcd for C<sub>19</sub>H<sub>30</sub>O<sub>6</sub>  $[M+H]^+$  355.2121 found 355.2116.

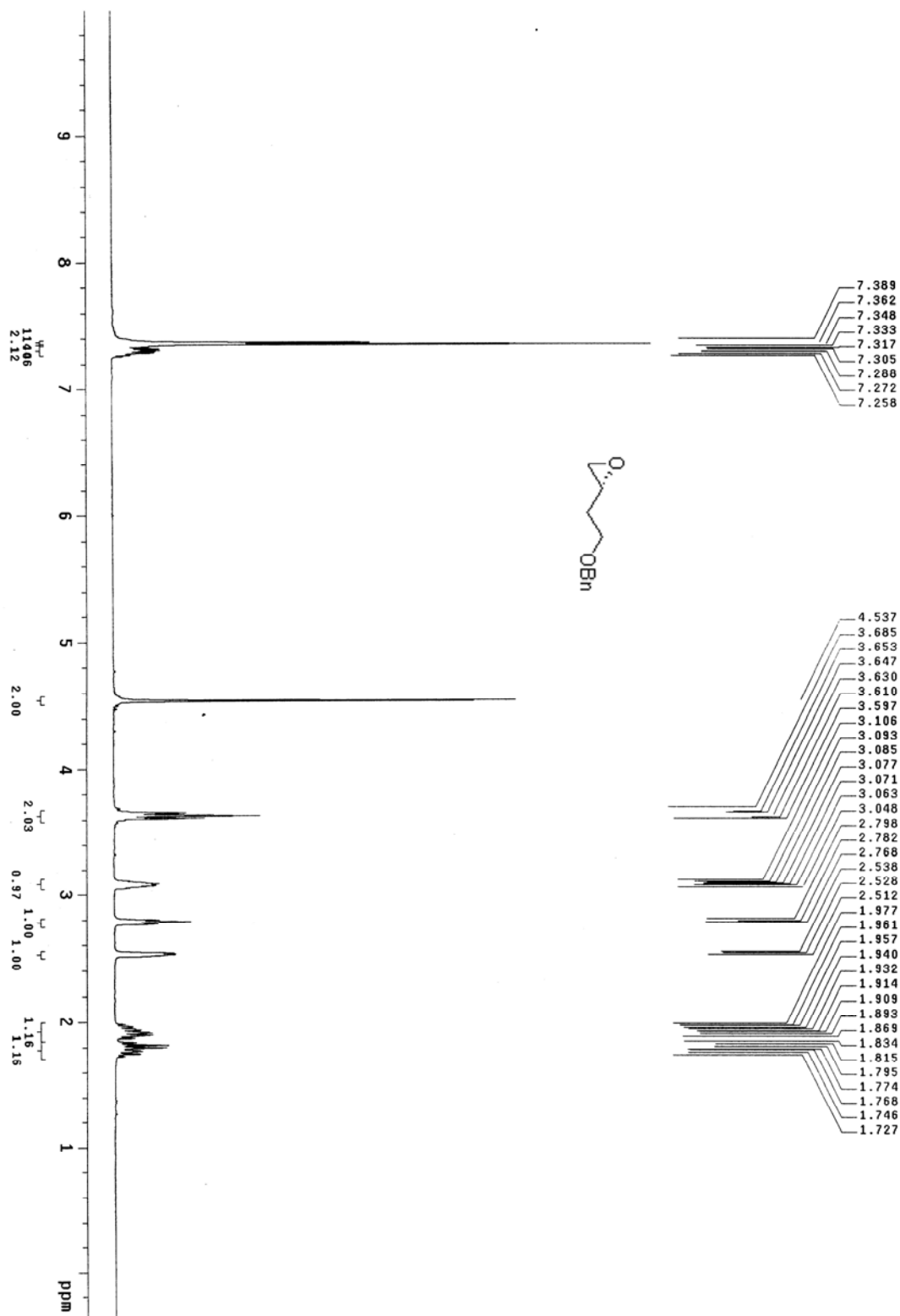
### Syntheses of compounds **15a** and **15b**

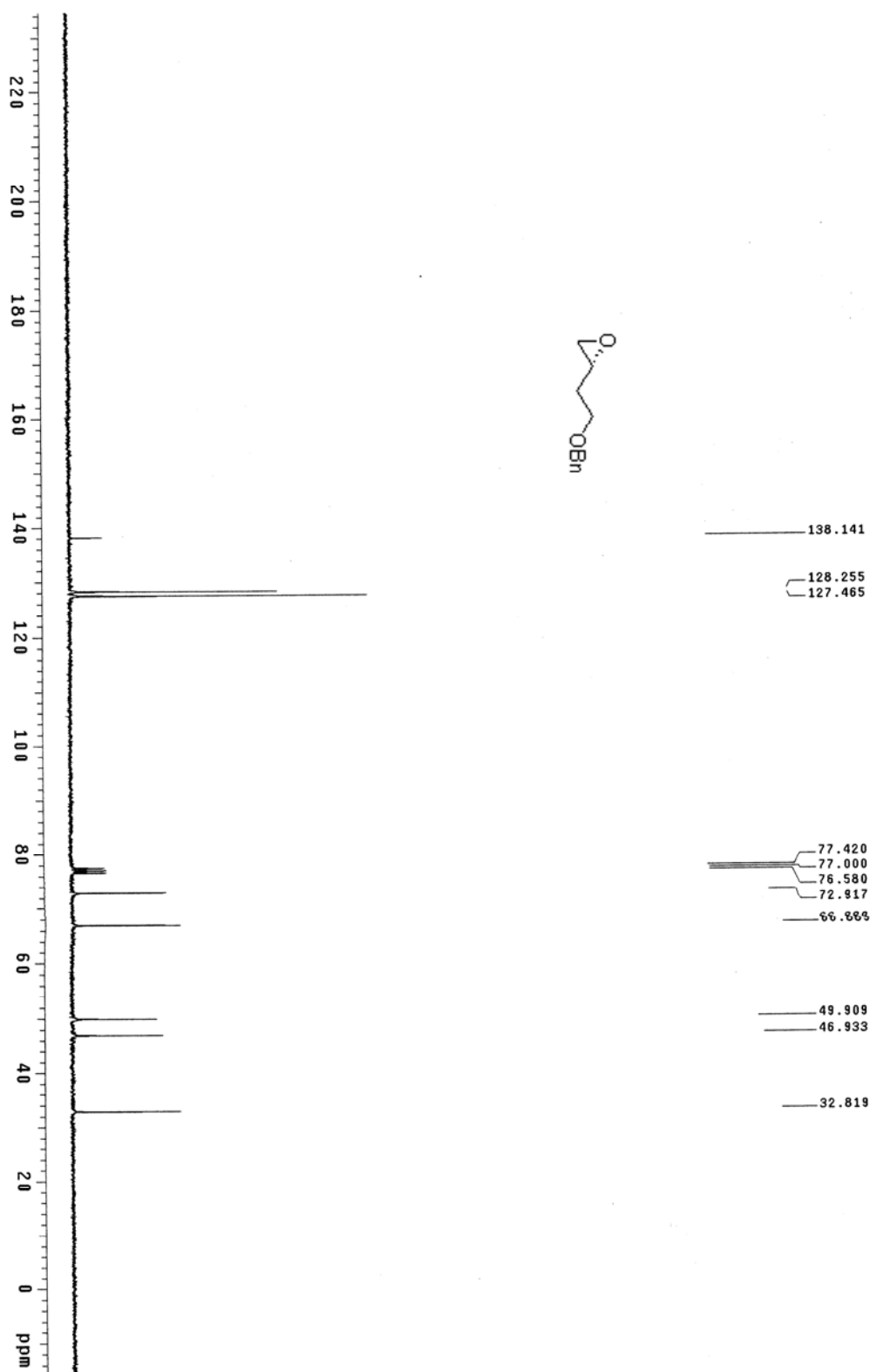


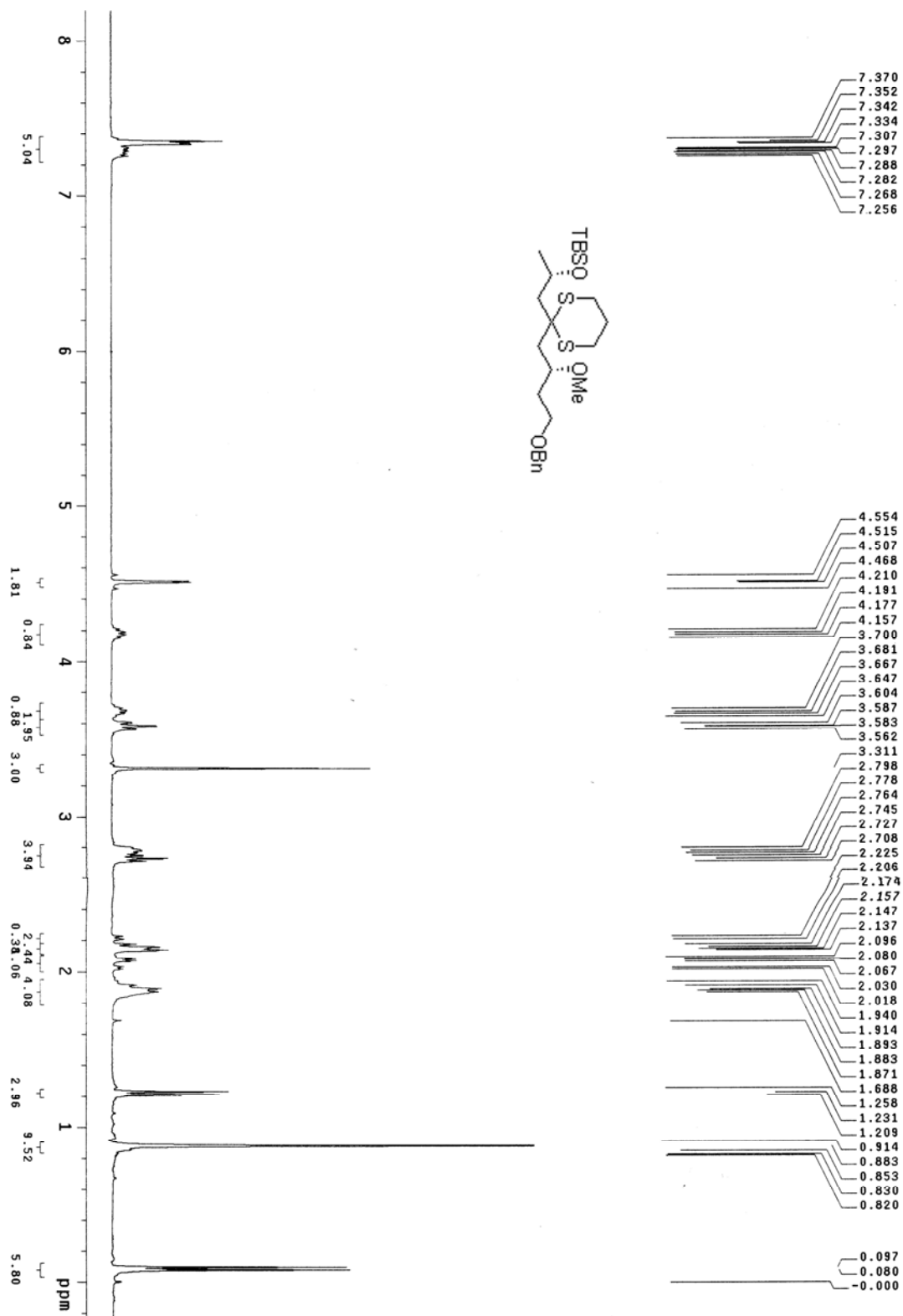
To a solution of **14a** (700 mg, 1.98 mmol) in acetone (50 mL) was added Jones reagent 2.8 mL at 0 °C and the mixture was stirred at the same temperature for 15 min. Isopropyl alcohol was added and the resulting mixture was filtered, concentrated in vacuo, the residue was dissolved in 150mL of EtOAc, washed with brine (3 × 15 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo. The residue was purified by column chromatography (hexanes / EtOAc / HOAc, 80:20:1) to afford the acid **15a** (634 mg, 86%) as colorless oil:  $[\alpha]_D^{25} +11^\circ$  (c 1.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.43 (d, *J* = 2.4 Hz, 2H), 6.36 (d, *J* = 2.4 Hz, 1H), 4.91 (dd, *J* = 12.3 Hz, 6.0 Hz, 1H), 3.77 (s, 6H), 3.58 (dd, *J* = 12.3 Hz, 6.0 Hz, 1H), 3.51 (s, 2H), 3.34 (s, 3H), 2.45 (ddd, *J* = 15.3 Hz, 6.9 Hz, 5.4 Hz, 2H), 1.38-1.64 (m, 4H), 1.25-1.36 (m, 2H), 1.20 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.8, 171.0, 167.1, 160.7, 136.3, 107.2, 99.0, 77.4, 71.2, 56.9, 55.2, 42.0, 38.9, 35.7, 33.3, 20.7, 19.8; IR (KBr) 2939, 1730, 1599, 1463, 1294, 1205, 1157, 1065, 835 cm<sup>-1</sup>; HRMS *m/z* calcd for C<sub>19</sub>H<sub>28</sub>O<sub>7</sub> [M+H]<sup>+</sup> 369.1913 found 369.1910.

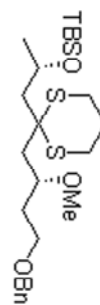
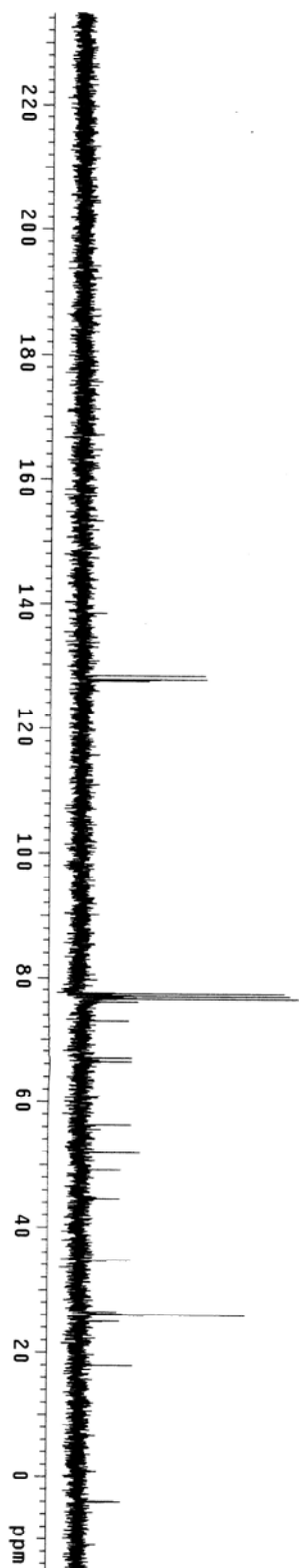
**15b** (1.267 g, 87%) was obtained as colorless oil by treatment of **14b** (1.4 g, 3.95 mmol) with 5mL of Jones reagent as the same operation for the synthesis of **15a**:  $[\alpha]_D^{25} +10^\circ$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.43 (s, 2H), 6.36 (s, 1H), 4.91 (dd, *J* = 12.3 Hz, 6.6 Hz, 1H), 3.77 (s, 6H), 3.57 (dd, *J* = 12.3 Hz, 5.7 Hz, 1H), 3.51 (s, 2H), 3.33 (s, 3H), 2.51 (dd, *J* = 15.9 Hz, 6.9 Hz, 1H), 2.40 (dd, *J* = 15.9 Hz, 4.8 Hz, 1H), 1.40-1.64 (m, 4H), 1.25-1.35 (m, 2H), 1.20 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.7, 171.0, 167.2, 160.7, 136.3, 107.2, 99.0, 77.4, 71.2, 56.9, 55.2, 42.0, 38.9, 35.7, 33.3, 20.8, 19.9; IR (KBr) 2937 1729, 1598, 1461, 1294, 1205, 1156, 1065, 835 cm<sup>-1</sup>; HRMS *m/z* calcd for C<sub>19</sub>H<sub>28</sub>O<sub>7</sub> [M+H]<sup>+</sup> 369.1913 found 369.1915.





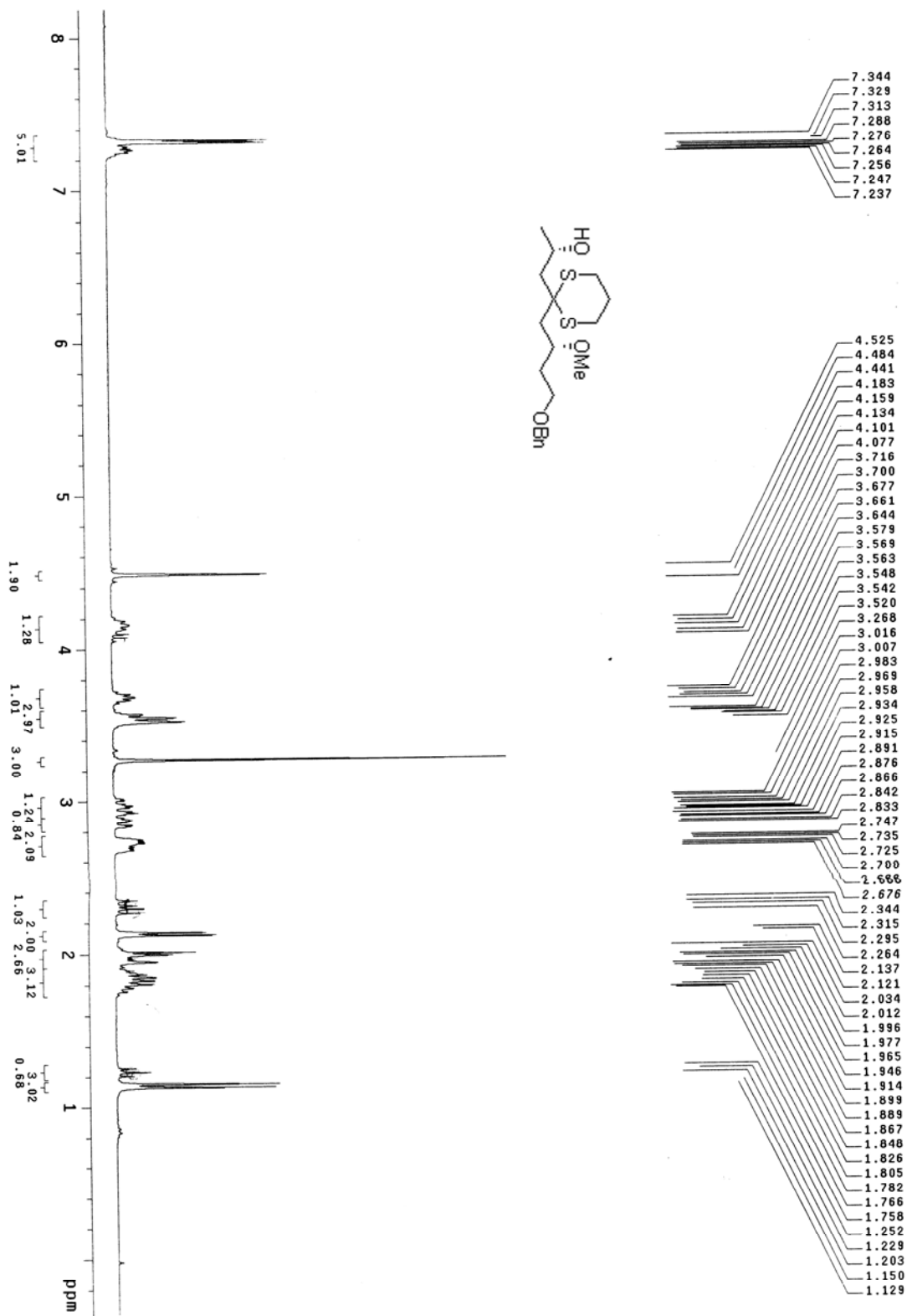


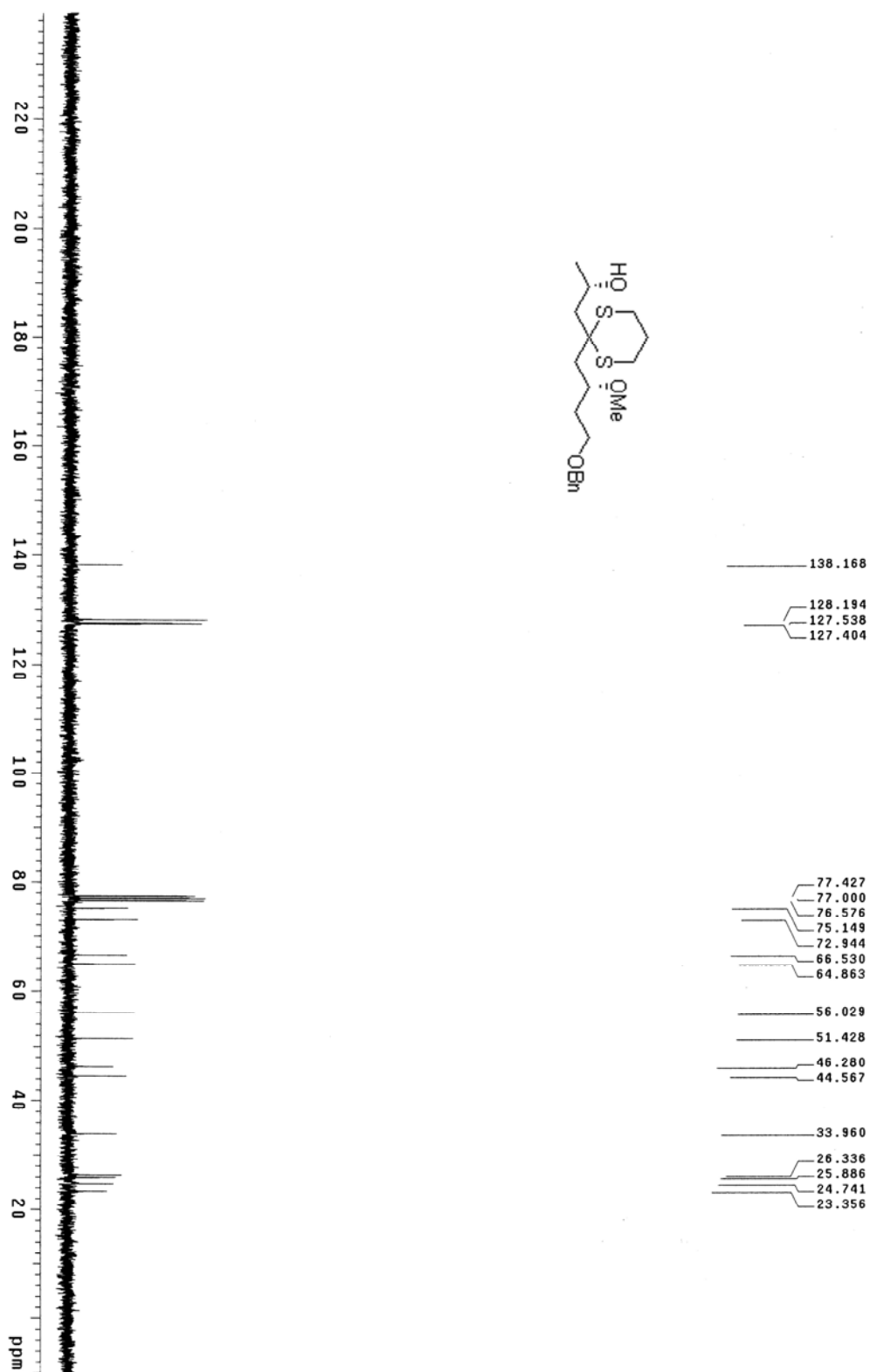


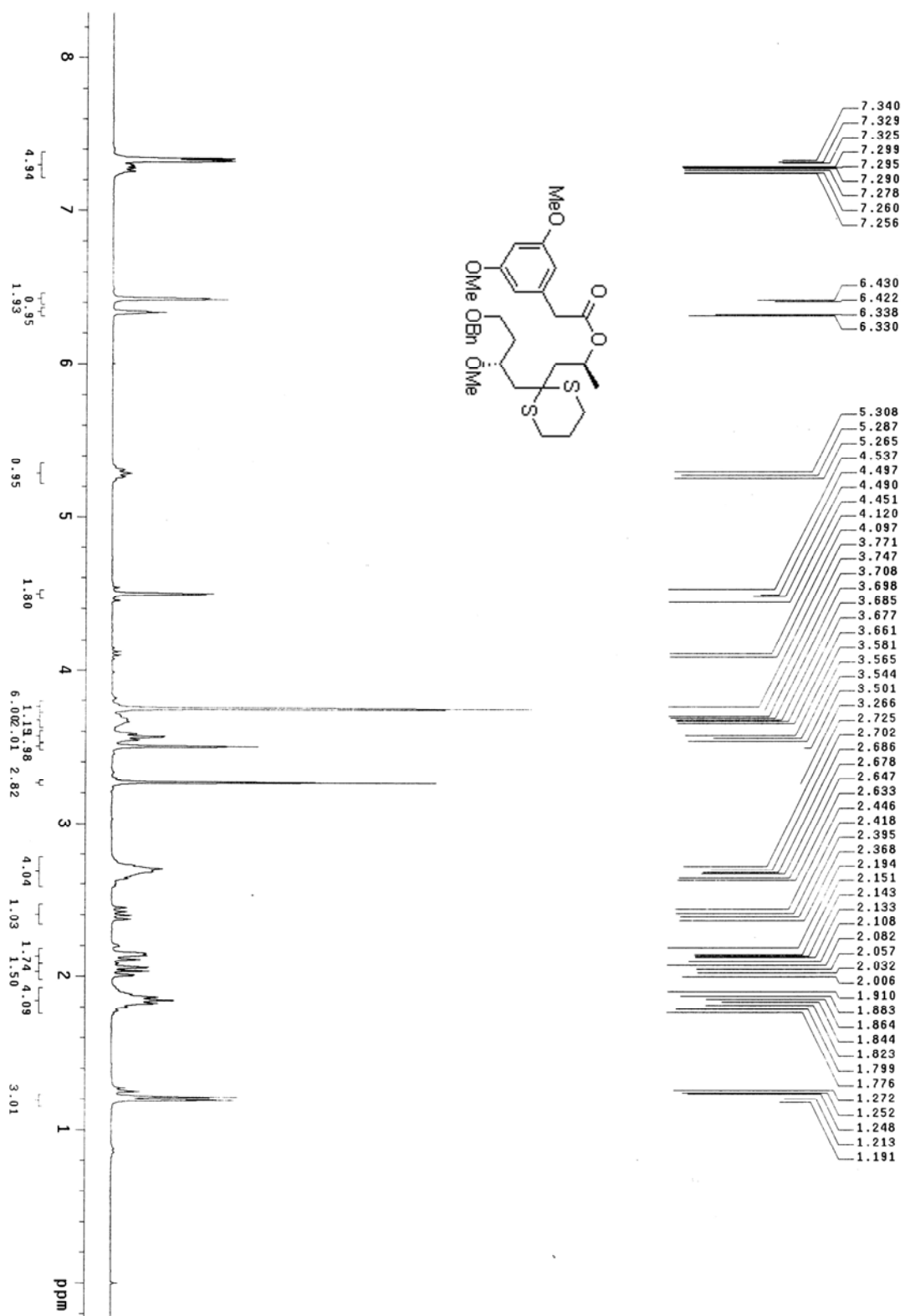


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127.652
127.465
77.420
76.996
76.573
76.038
73.016
66.896
66.290
56.274
51.905
49.161
44.579
34.647
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24.997
17.961
-3.971
-4.124

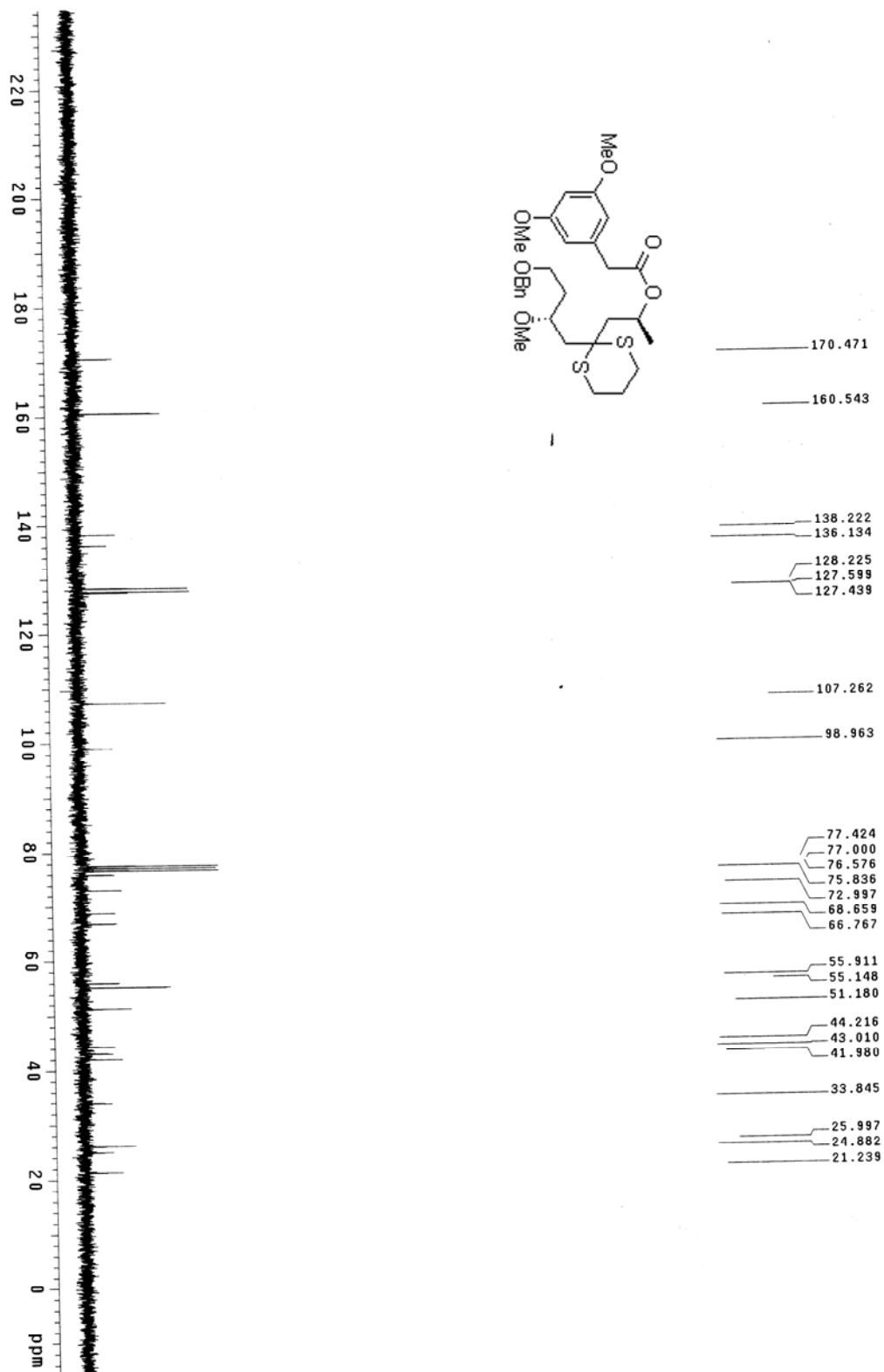


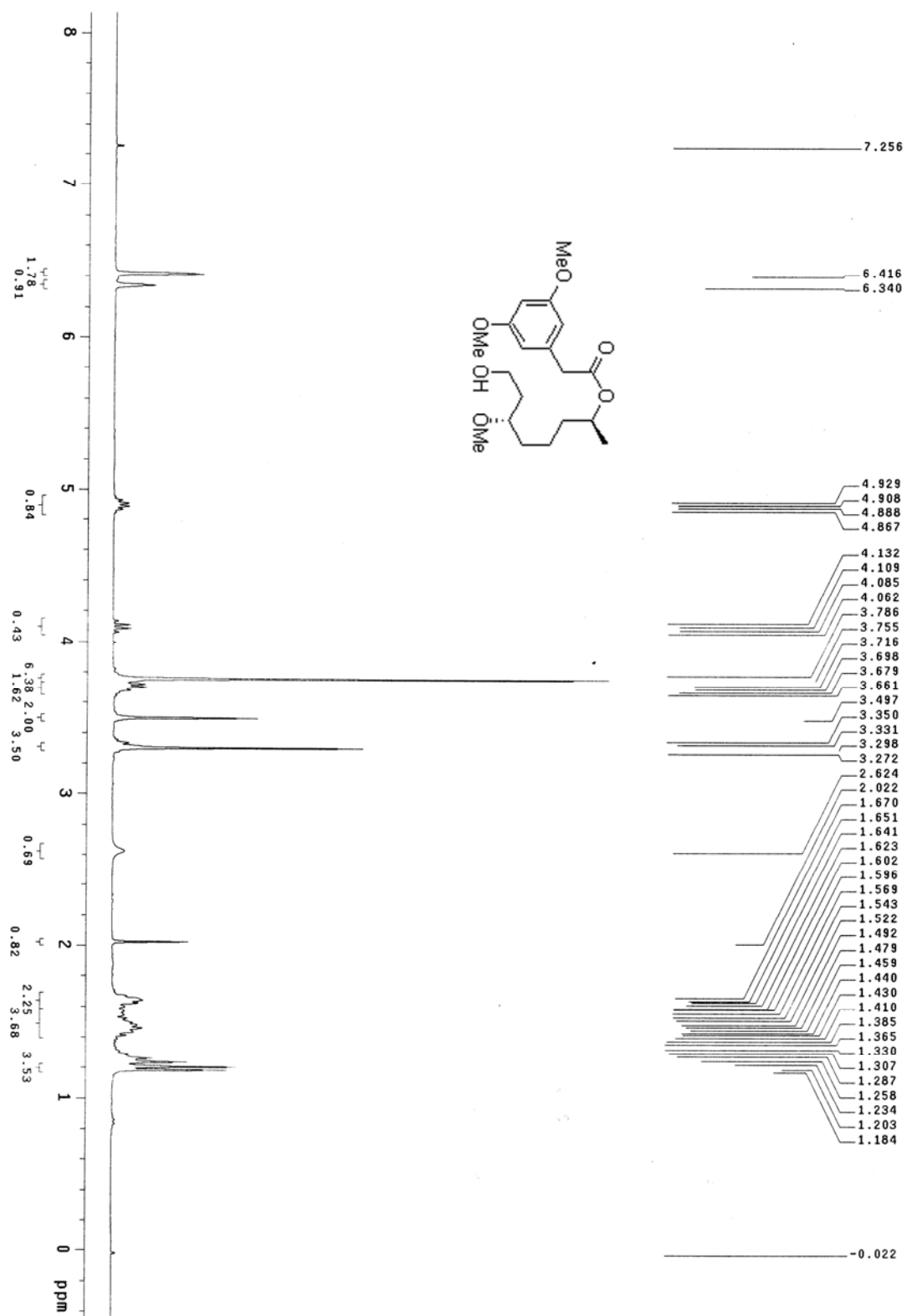


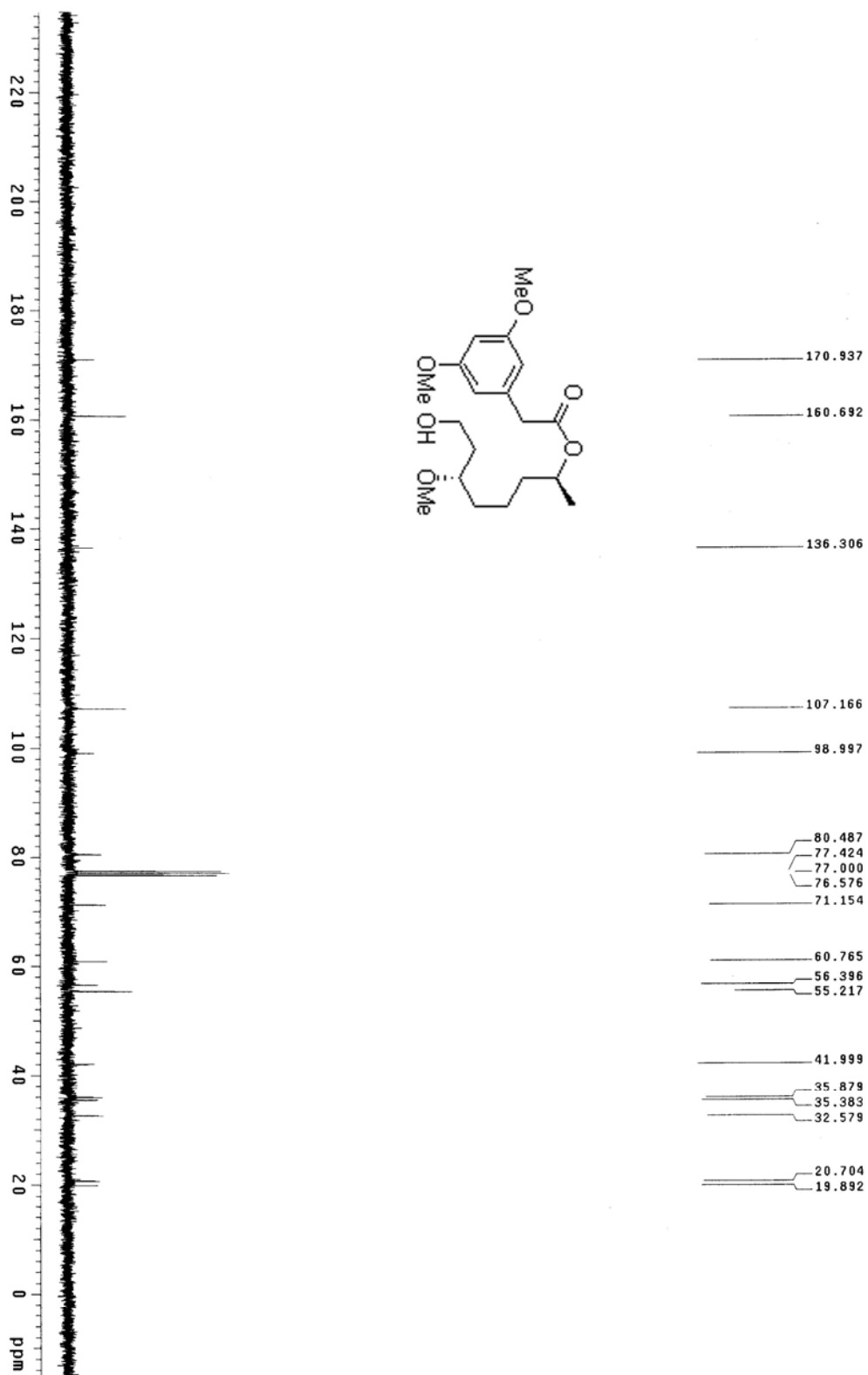


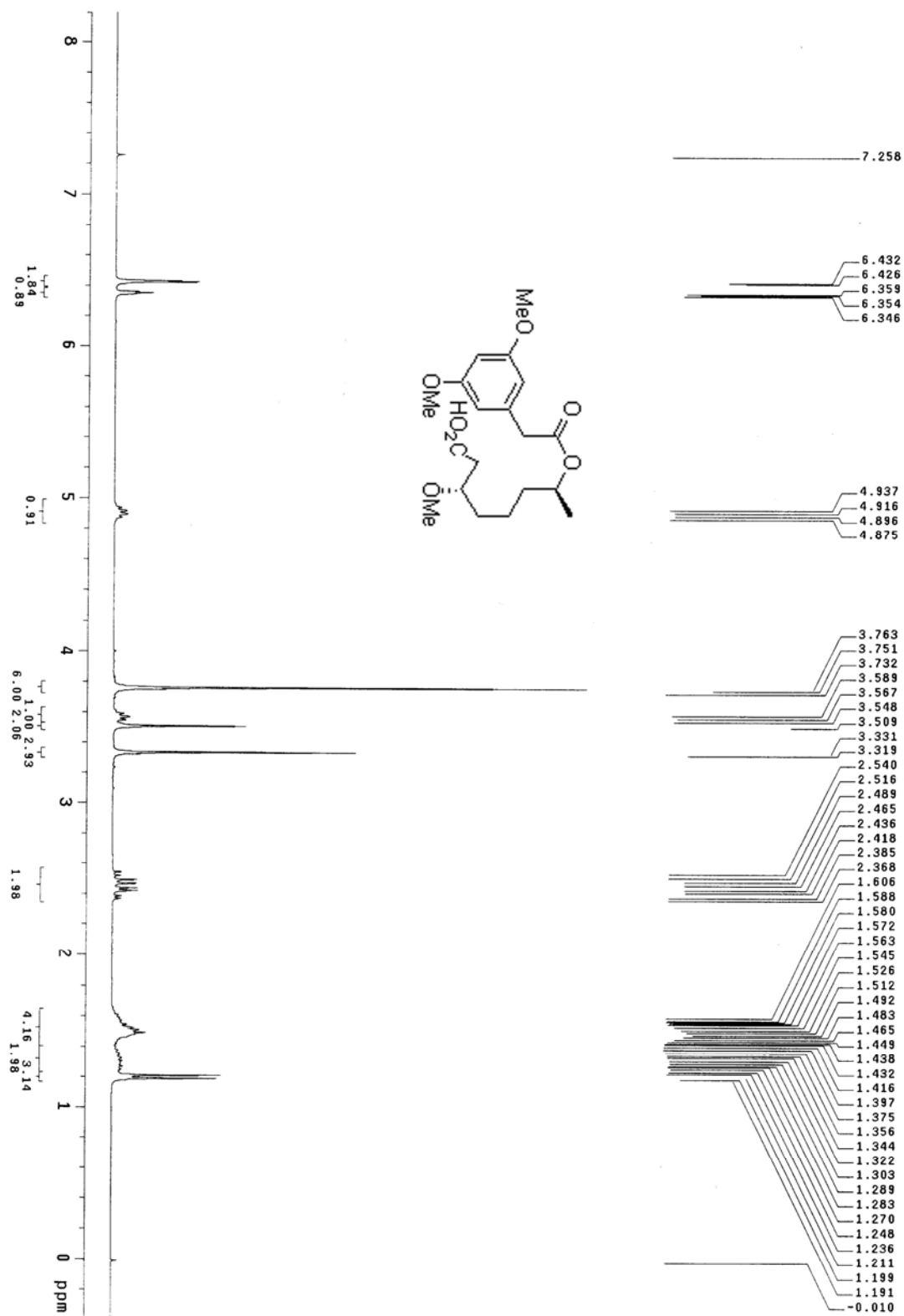


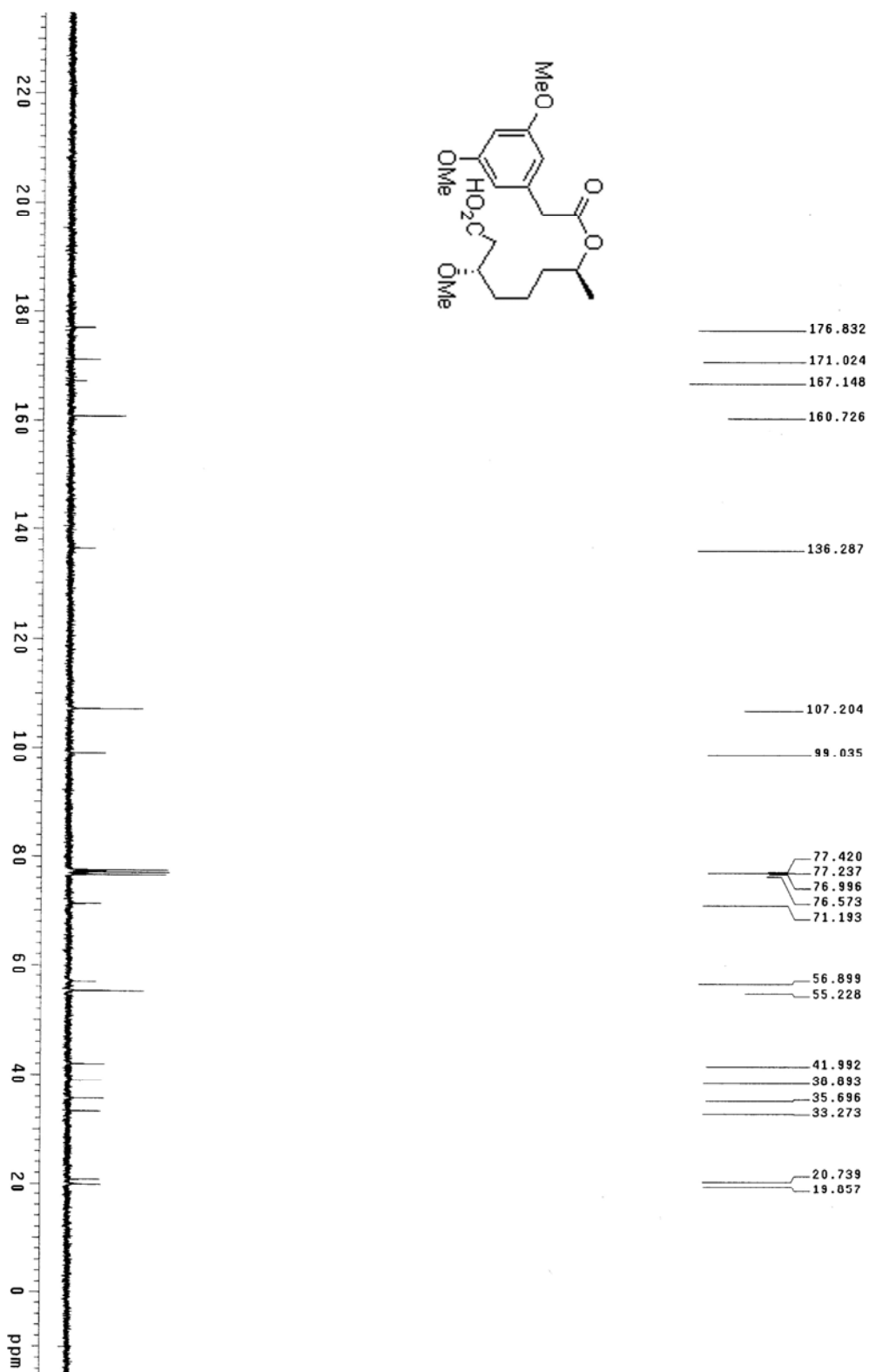


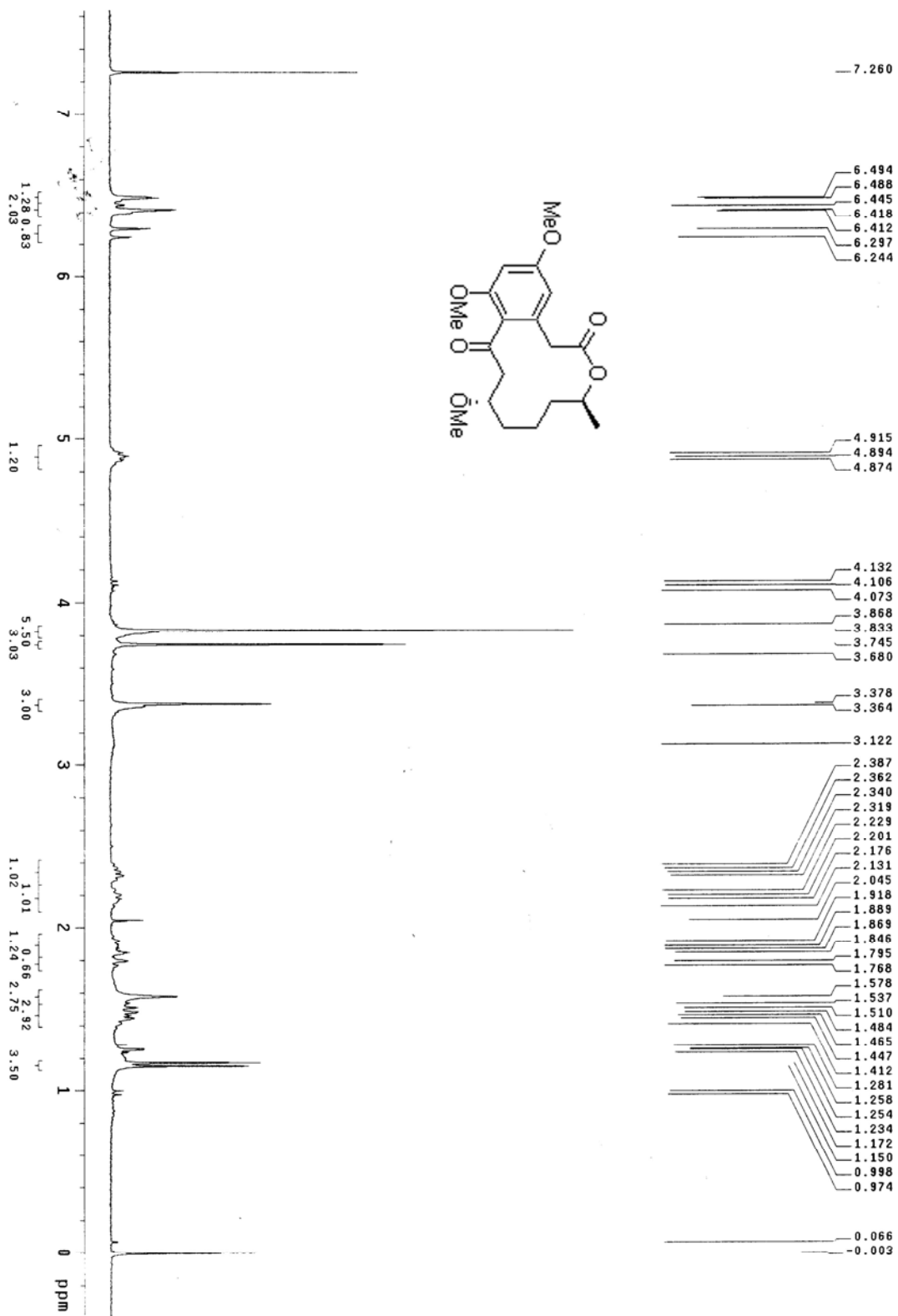


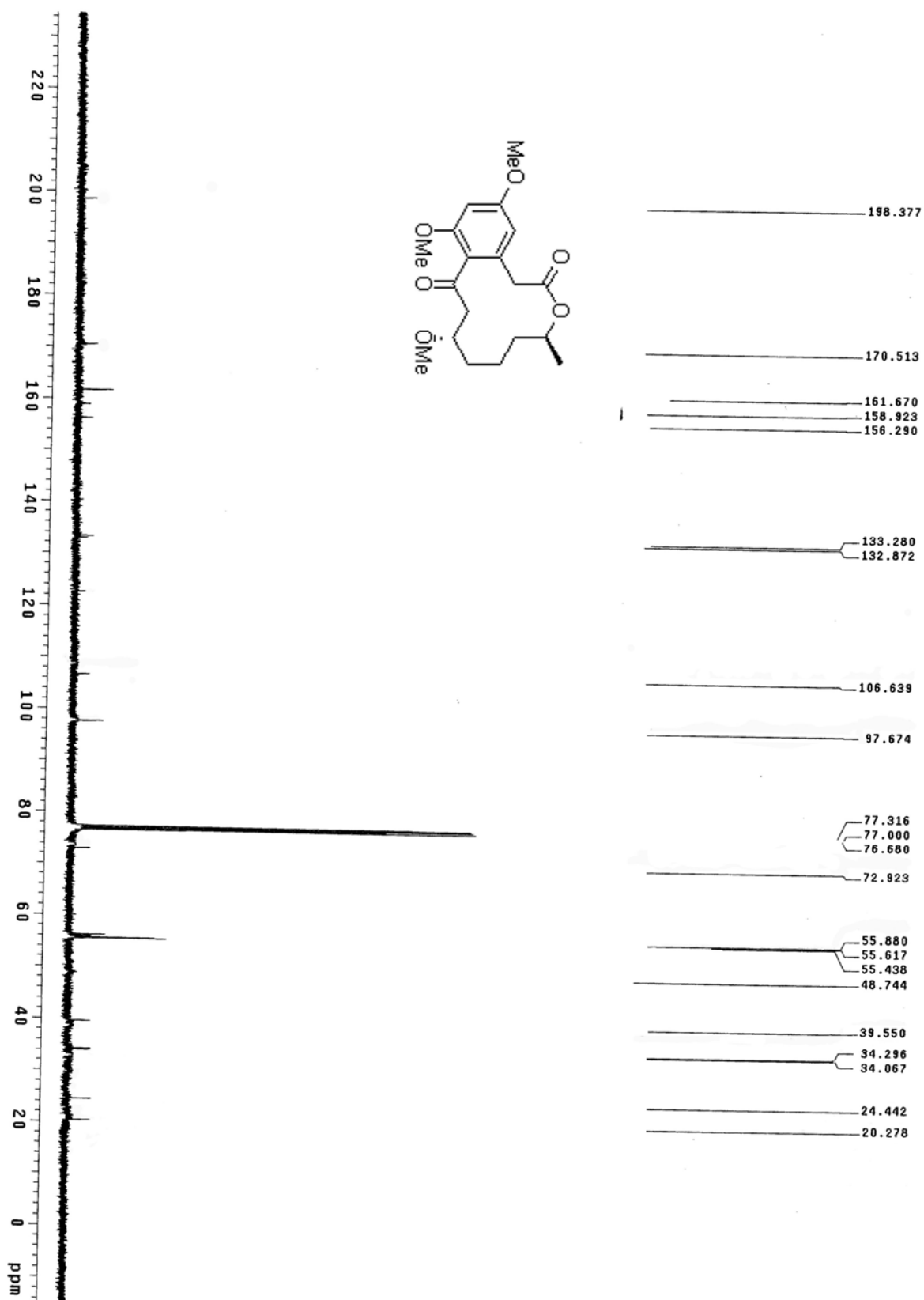


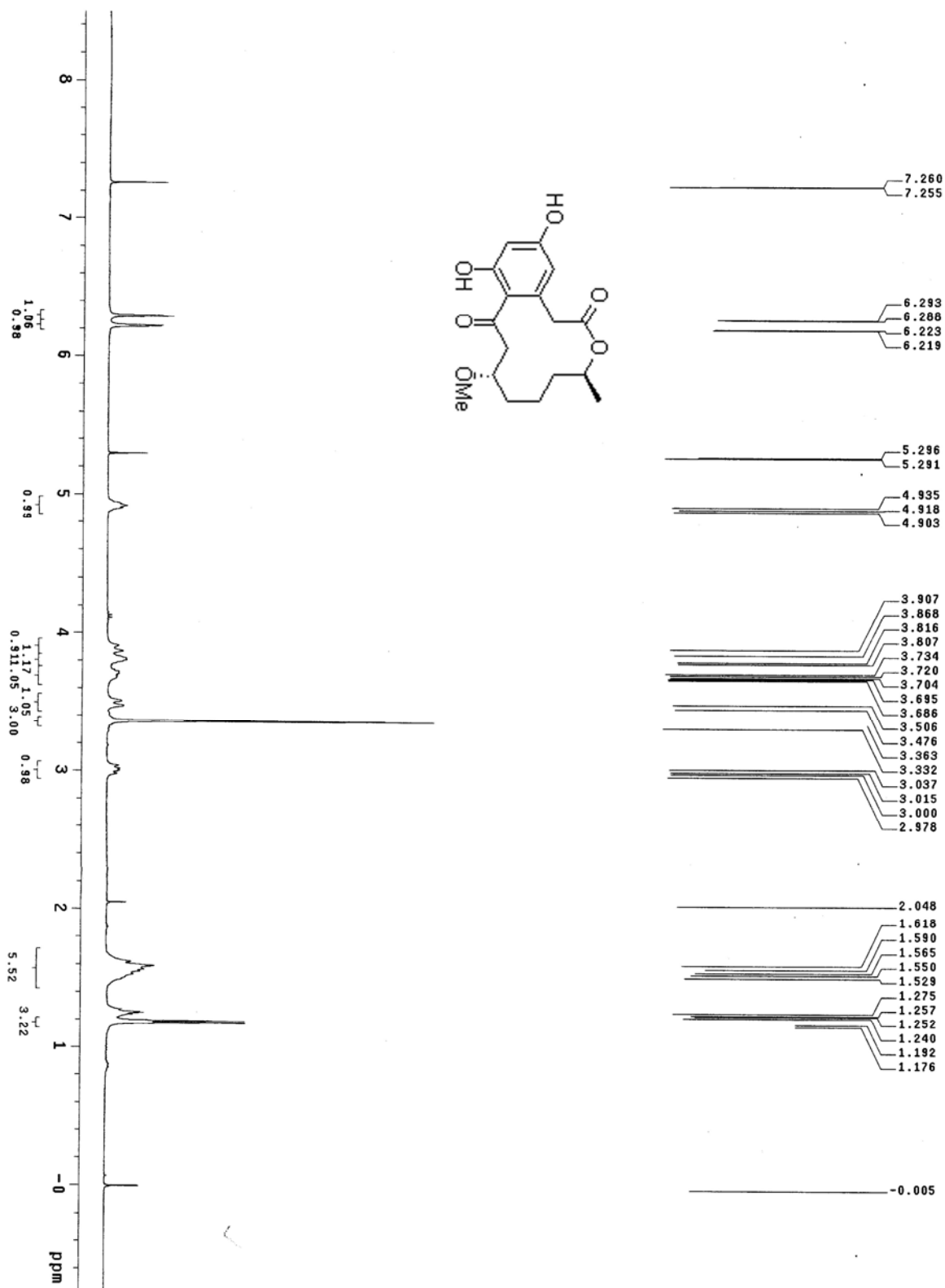




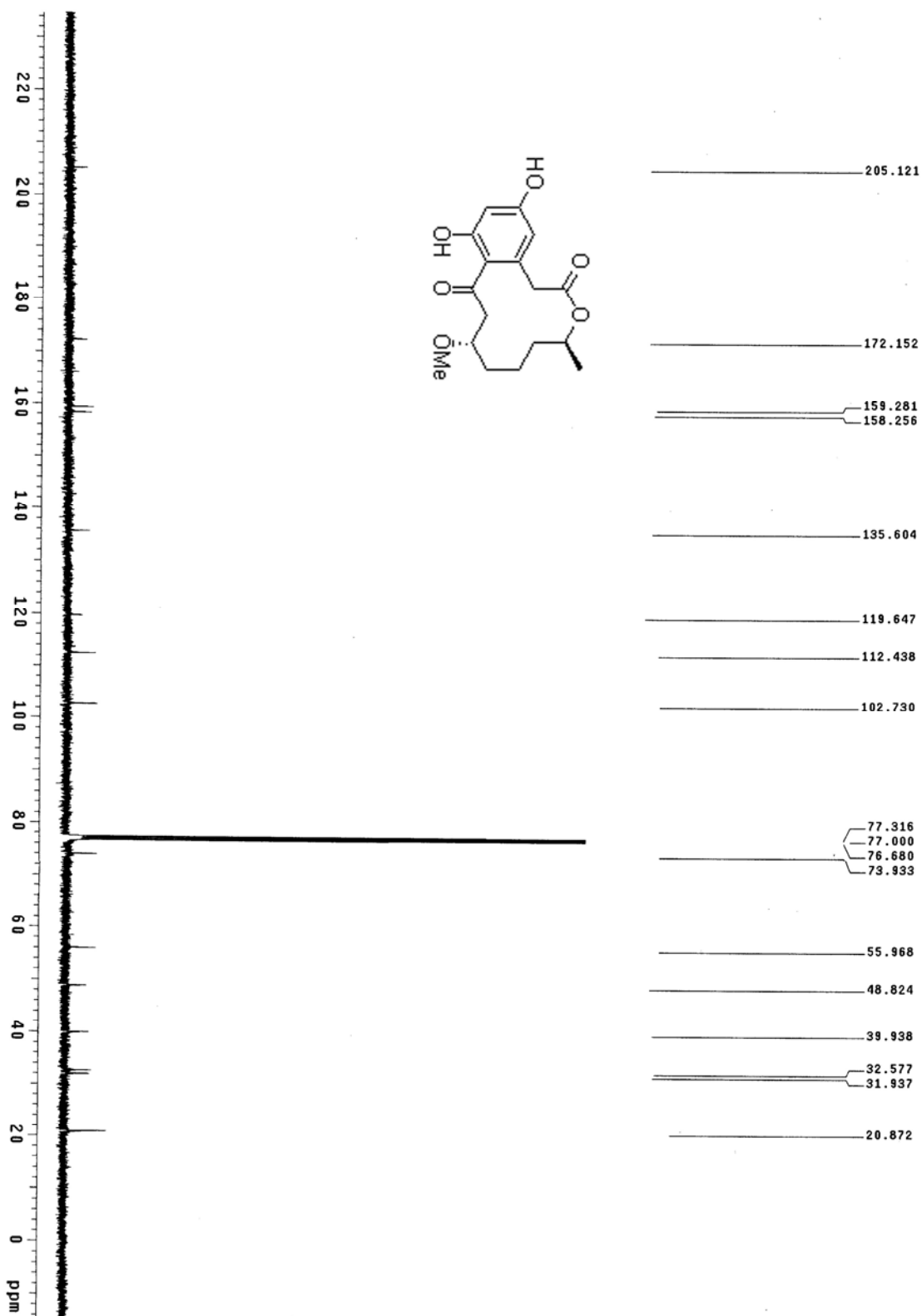


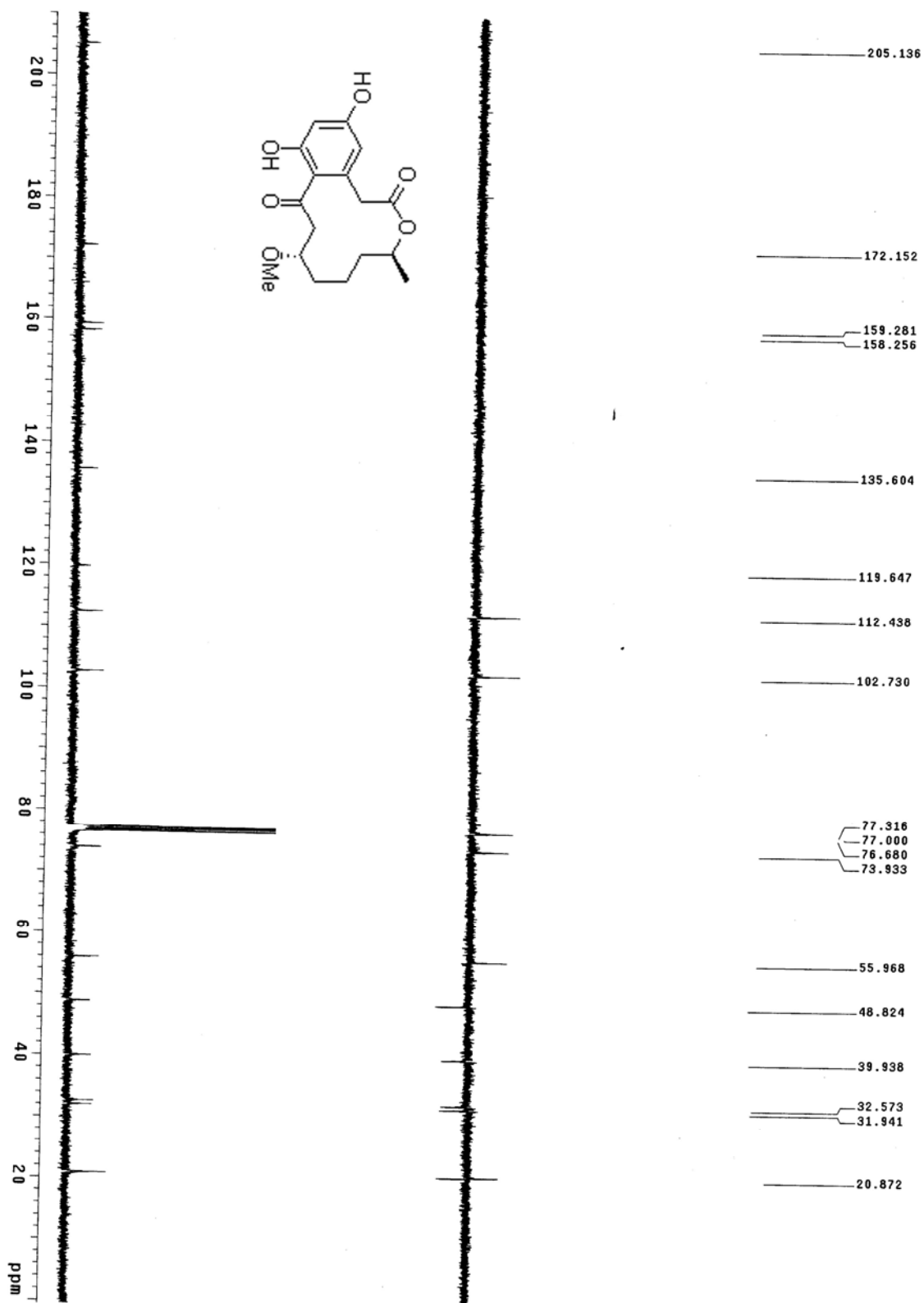


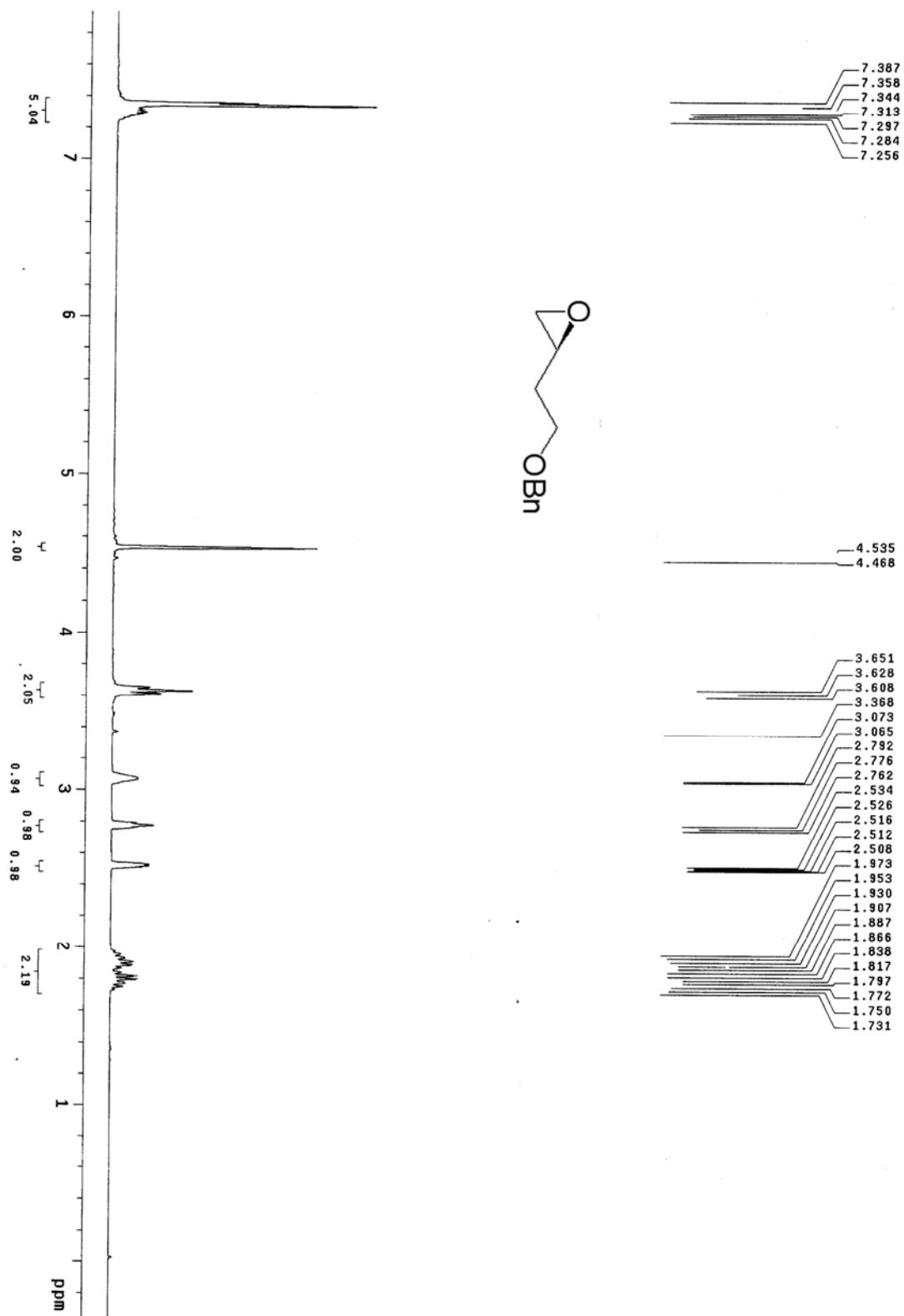


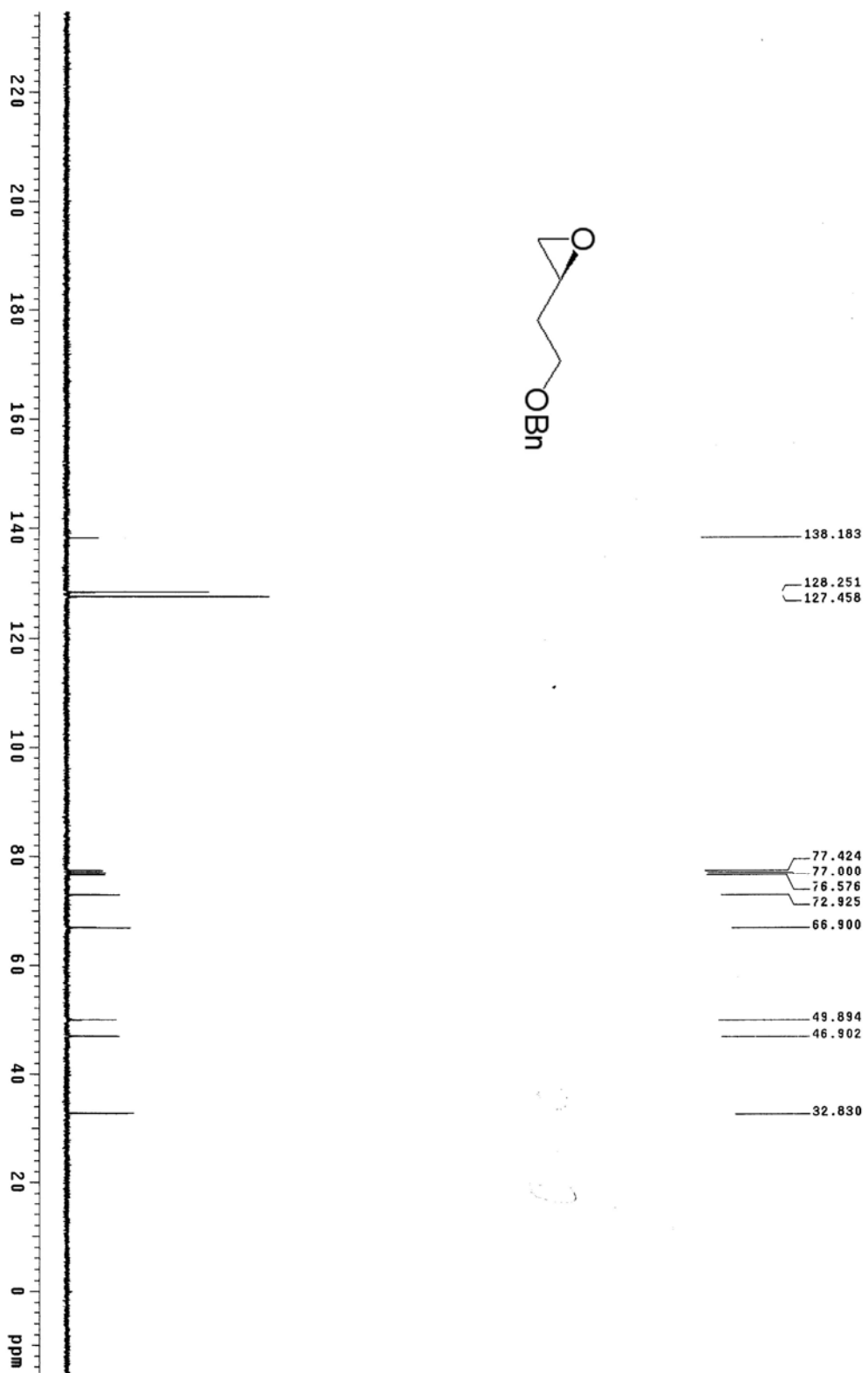




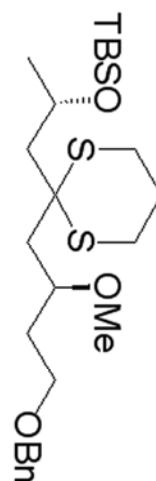
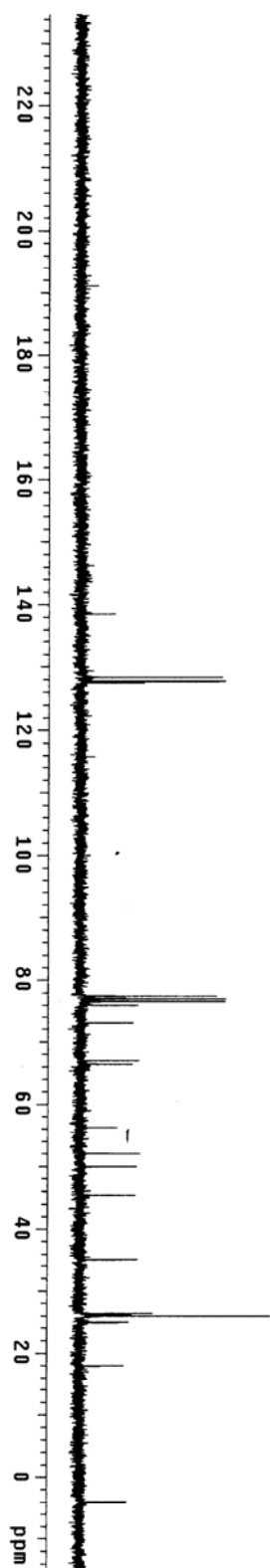












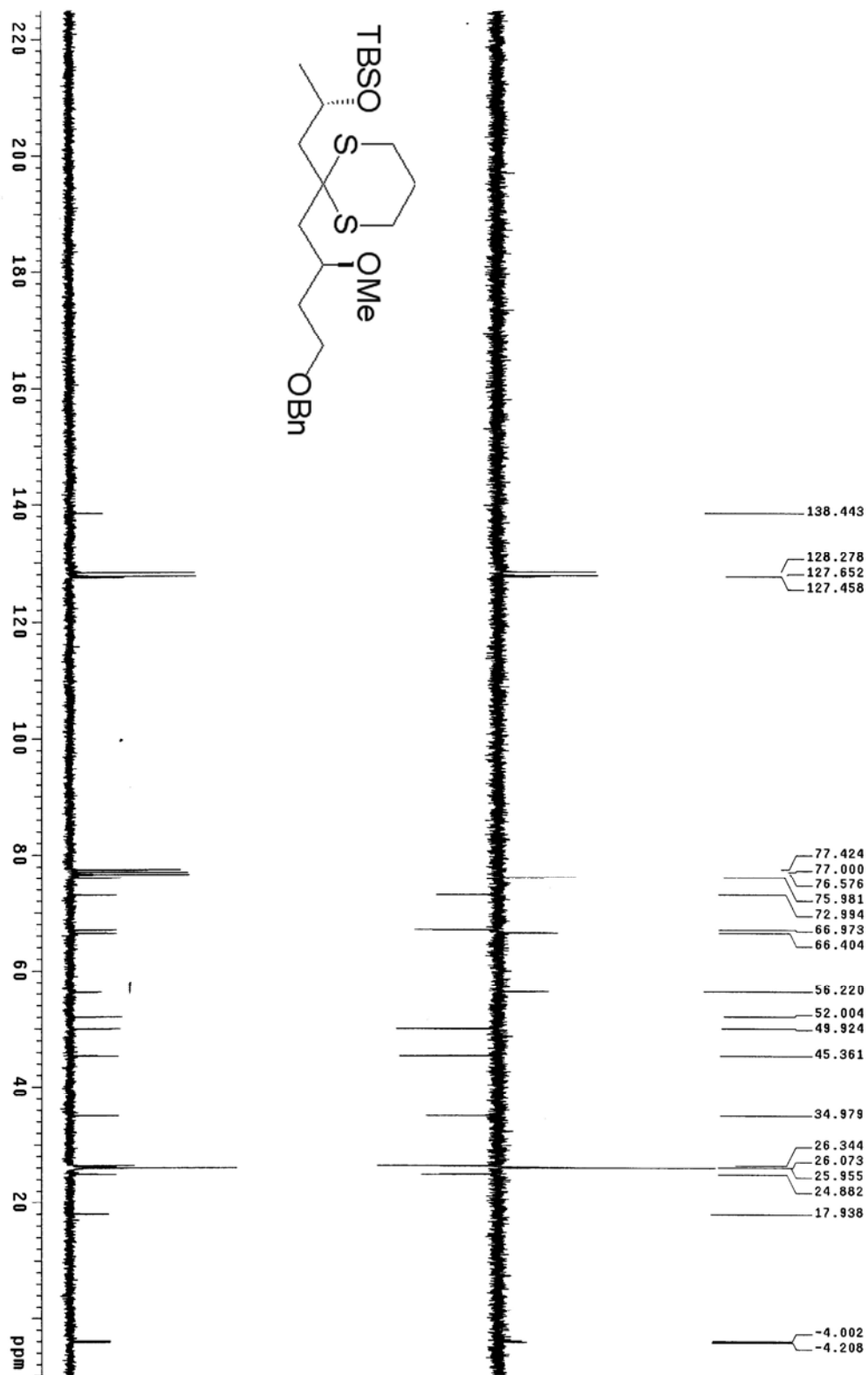
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127.458

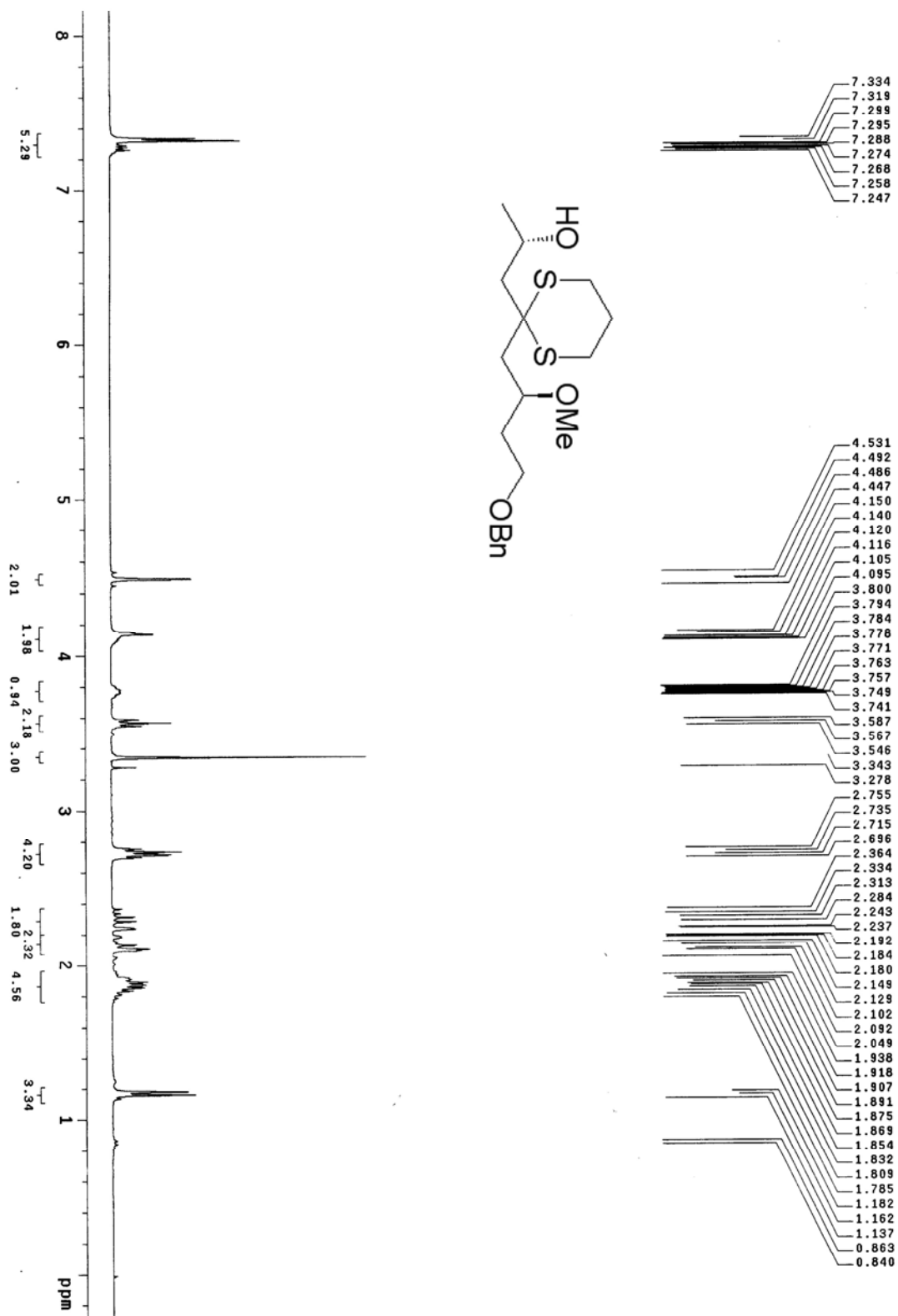
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66.404

56.220  
52.004  
49.924  
45.361

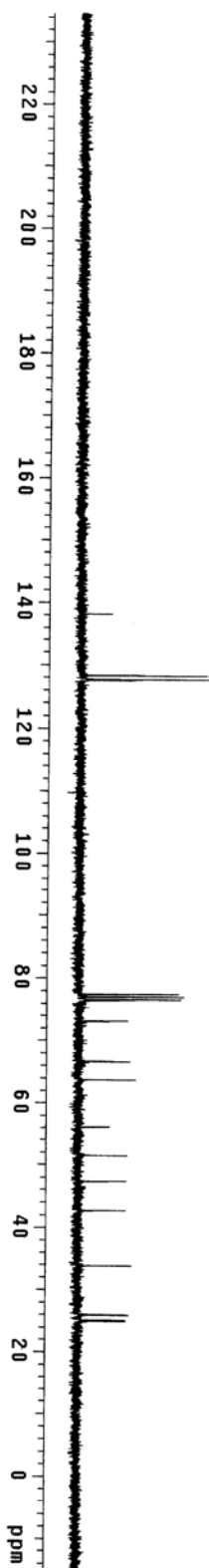
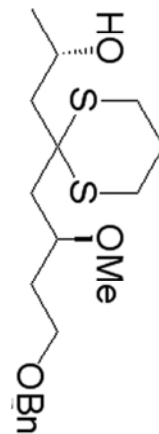
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17.938

-4.002  
-4.208







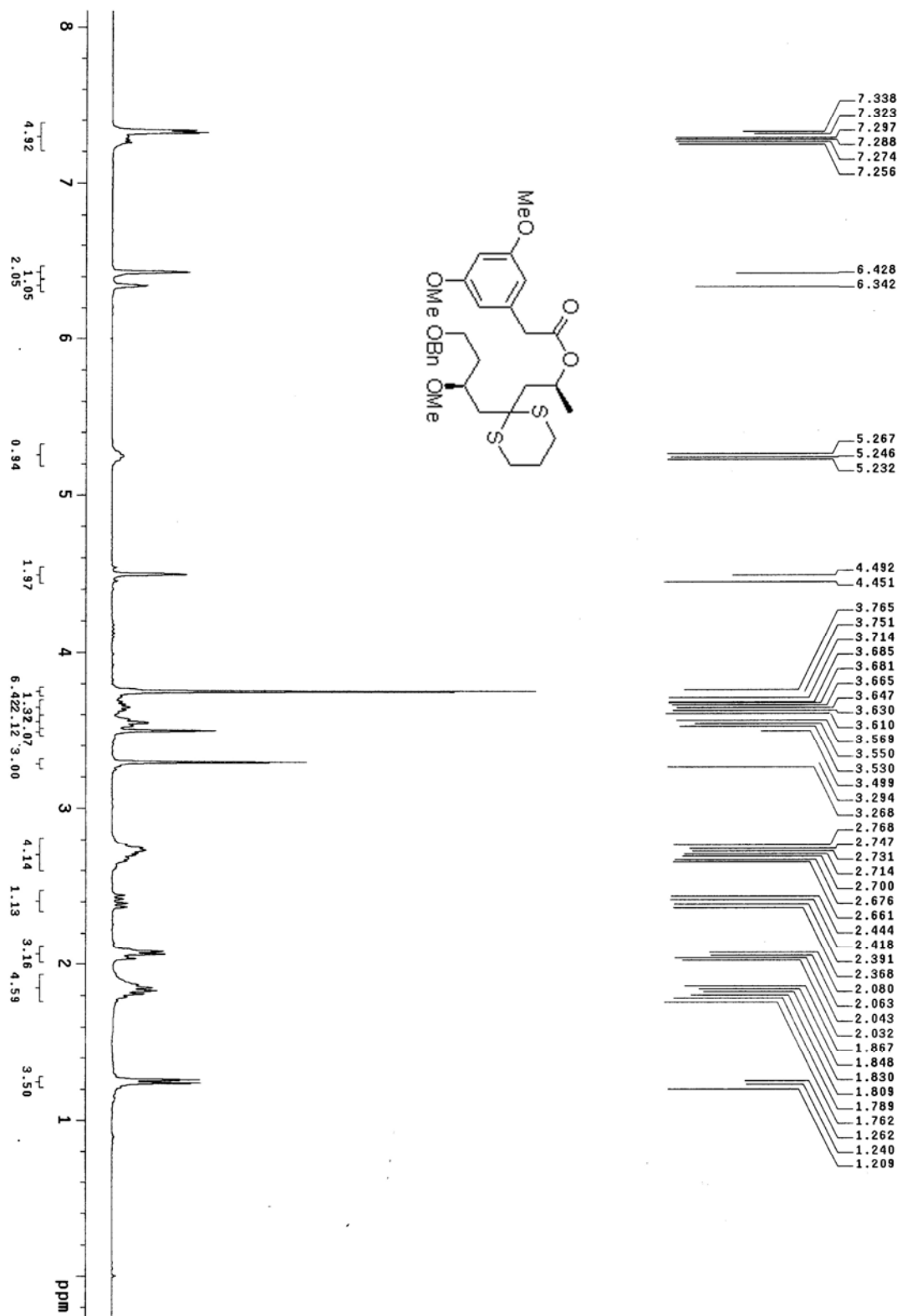


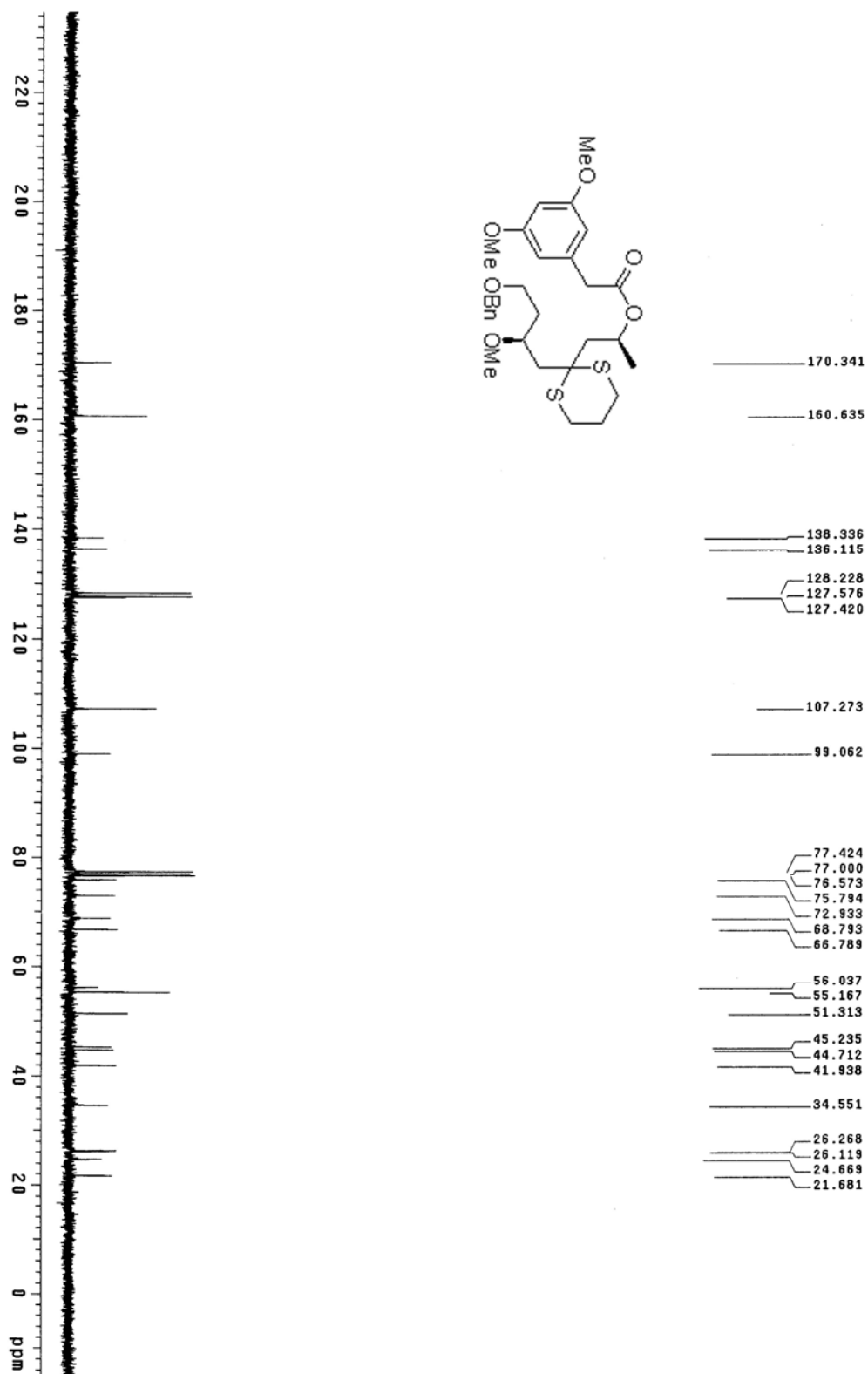
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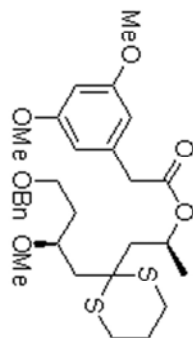
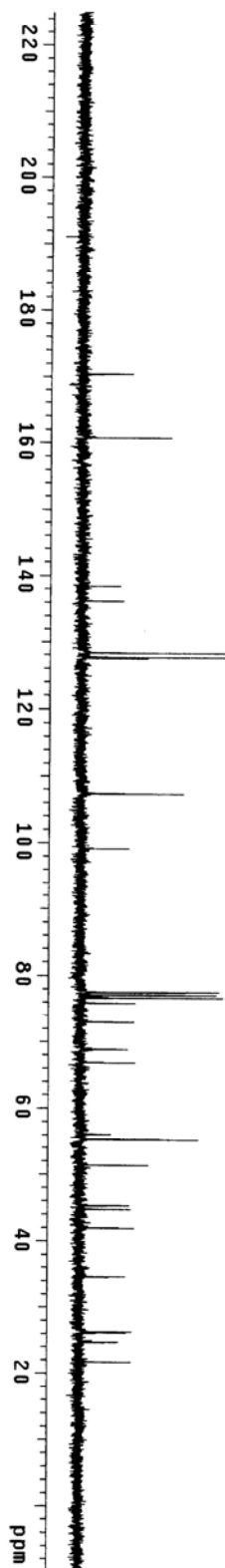
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63.703

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42.667

33.769  
25.981  
25.917  
25.096  
24.974







170.341
160.635
138.336
136.115
128.228
127.576
127.420
107.273
99.062
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77.000
76.573
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51.309
45.235
44.712
41.938
34.551
26.264
26.119
24.673
21.681

