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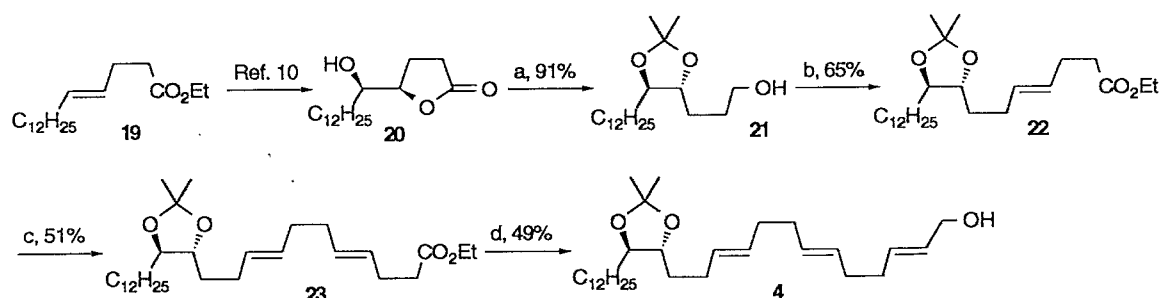
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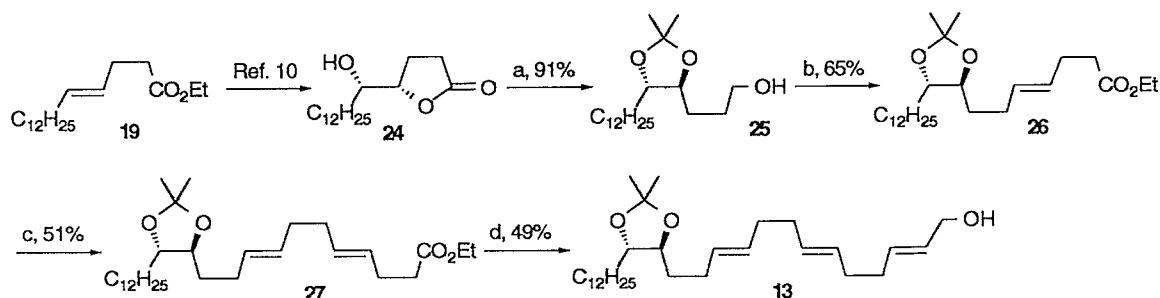
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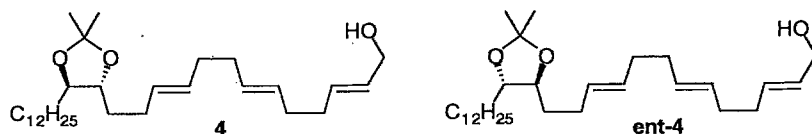
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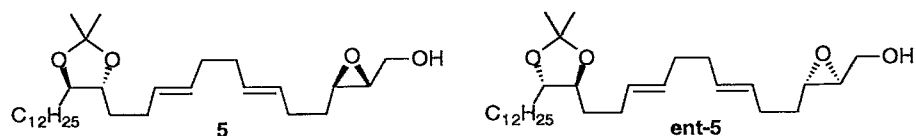
Scheme 1: Key: a) i. LAH, ether-THF, 0 °C-reflux, 2 h, ii. (MeO)₂CMe₂, acetone, TsOH, rt, 0.5 h; b) i. PCC, celite, CH₂Cl₂, rt, 2 h, ii. vinylmagnesium bromide, THF, -20 °C, 0.5 h, iii. (EtO)₃CMe, propionic acid, xylene, reflux, 2 h; c) i. LAH, ether, 0 °C-rt, 2 h, ii. step b; d) i. DIBAL-H, toluene, -78 °C, 2 h then (EtO)₂P(O)CHNaCO₂Et, THF, -78 °C-rt, 16 h, ii. DIBAL-H, THF, -78 °C, 2 h.



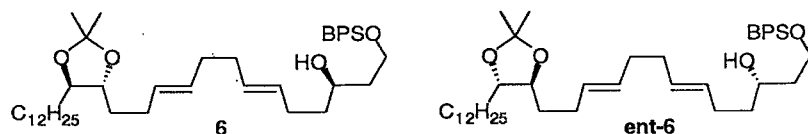
Scheme 2: Key: a) i. LAH, ether-THF, 0 °C-reflux, 2 h, ii. (MeO)₂CMe₂, acetone, TsOH, rt, 0.5 h; b) i. PCC, celite, CH₂Cl₂, rt, 2 h, ii. vinylmagnesium bromide, THF, -20 °C, 0.5 h, iii. (EtO)₃CMe, propionic acid, xylene, reflux, 2 h; c) i. LAH, ether, 0 °C-rt, 2 h, ii. step b; d) i. DIBAL-H, toluene, -78 °C, 2 h then (EtO)₂P(O)CHNaCO₂Et, THF, -78 °C-rt, 16 h, ii. DIBAL-H, THF, -78 °C, 2 h.

Compound 4 and ent-4:

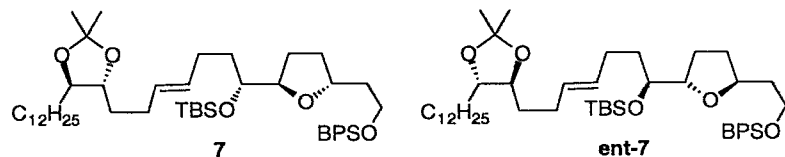
¹H NMR: δ 5.64 (m, 2 H), 5.40 (m, 4 H), 4.07 (d, J = 4.9 Hz, 2 H), 3.58 (m, 2 H), 2.25-2.00 (m, 10 H), 1.60-1.20 (m and br s, 24 H), 1.36 (s, 6 H), 0.86 (t, J = 7.1 Hz, 3 H). ¹³C NMR: δ 132.7, 130.3, 129.7, 129.2, 80.9, 80.3, 63.8, 33.0, 32.9, 32.6, 32.2, 32.1, 31.9, 29.8, 29.6, 29.6, 29.5, 29.4, 29.0, 27.3, 26.2, 22.7, 14.1. MS analysis (C₃₀H₅₄O₃ = 462) found 462 (M⁺), 485 (MNa⁺).

Compound 5 and ent-5:

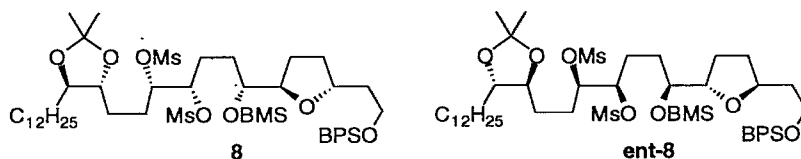
¹H NMR: δ 5.41 (m, 4 H), 3.89 (ddd, J = 12.5, 5.4, 2.4 Hz, 1 H), 3.62 (m, 3 H), 2.95 (m, 1 H), 2.91 (m, 1 H), 2.22-2.00 (m, 8 H), 1.76 (m, 1 H), 1.68-1.20 (m and br s, 26 H), 1.36 (s, 6 H), 0.86 (t, J = 7.1 Hz, 3 H). ¹³C NMR: δ 130.8, 130.2, 129.7, 129.0, 107.8, 80.9, 80.3, 61.6, 58.4, 55.4, 32.9, 32.8, 32.5, 31.9, 31.5, 29.8, 29.6, 29.6, 29.5, 29.3, 29.0, 28.9, 27.3, 26.1, 22.7, 14.1. MS analysis (C₃₀H₅₄O₄ = 478) found 478 (M⁺), 501 (MNa⁺).

Compound 6 and ent-6:

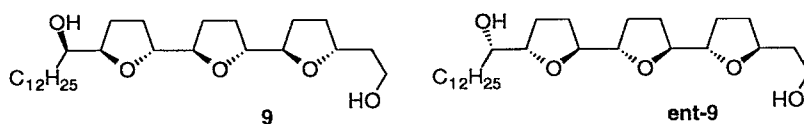
¹H NMR: δ 7.67 (m, 4H), 7.43 (m, 6H), 5.42 (m, 4 H), 3.85 (m, 3H), 3.59 (m, 2 H), 3.22 (d, J = 2.4 Hz, 1H), 2.20-2.00 (m, 8 H), 1.75-1.20 (m and br s, 28 H), 1.37 (s, 6 H), 1.03 (s, 9 H), 0.87 (t, J = 7.0 Hz, 3 H). ¹³C NMR: δ 135.5, 133.0, 130.3, 130.1, 129.8, 129.6, 127.7, 107.7, 80.9, 80.3, 71.2, 63.5, 38.3, 37.3, 33.0, 32.9, 32.7, 31.9, 29.8, 29.6, 29.5, 29.3, 29.0, 28.7, 27.3, 26.2, 22.7, 19.0, 14.1. MS analysis (ESI, C₄₆H₇₄O₄Si = 719) found 720 (MH⁺), 742 (MNa⁺).

Compound 7 and ent-7:

¹H NMR: δ 7.66 (m, 4 H), 7.39 (m, 6 H), 5.42 (m, 2 H), 4.09 (m, 1 H), 4.04 (m, 1 H), 3.86 (q, J = 8.0 Hz, 1 H), 3.73 (m, 2 H), 3.57 (m, 3 H), 2.20-1.20 (m and br s, 36 H), 1.37 (s, 6 H), 1.03 (s, 9 H), 0.87 (t, J = 7.0 Hz, 3 H), 0.86 (s, 9 H), 0.02 (s, 6 H). ¹³C NMR: δ 135.5, 130.8, 129.5, 127.6, 81.2, 80.9, 80.4, 76.4, 74.6, 61.5, 38.7, 33.0, 32.9, 32.6, 32.5, 31.9, 29.8, 29.6, 29.5, 29.3, 29.1, 28.8, 27.6, 27.3, 26.8, 26.2, 26.0, 22.7, 14.1, -4.2, -4.7.

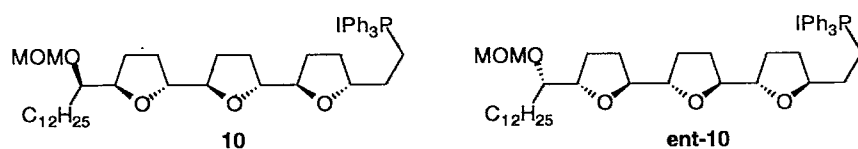
Compound 8 and ent-8:

^1H NMR: δ 7.65 (m, 4 H), 7.38 (m, 6 H), 4.85 (m, 1 H), 4.77 (m, 1 H), 4.01 (m, 1 H), 3.84 (q, $J = 7.0$ Hz, 1 H), 3.73 (t, $J = 6.4$ Hz, 2 H), 3.56 (m, 3 H), 3.08 (s, 3 H), 3.04 (s, 3 H), 2.10-1.20 (m and br s, 36 H), 1.35 (s, 6 H), 1.03 (s, 9 H), 0.87 (t, $J = 6.6$ Hz, 3 H), 0.85 (s, 9 H), 0.03 (s, 3 H), 0.02 (s, 3 H). ^{13}C NMR: δ 135.5, 129.5, 127.6, 108.0, 81.5, 81.2, 80.9, 80.8, 80.4, 76.5, 61.5, 38.9, 38.8, 38.7, 32.7, 32.5, 31.9, 29.6, 29.5, 29.3, 28.1, 27.8, 27.6, 27.3, 27.2, 26.8, 26.1, 26.0, 22.7, 14.1, -4.2, -4.7. MS analysis (ESI, $\text{C}_{54}\text{H}_{94}\text{O}_{11}\text{S}_2\text{Si}_2 = 1038$) found 1061 (MNa^+).

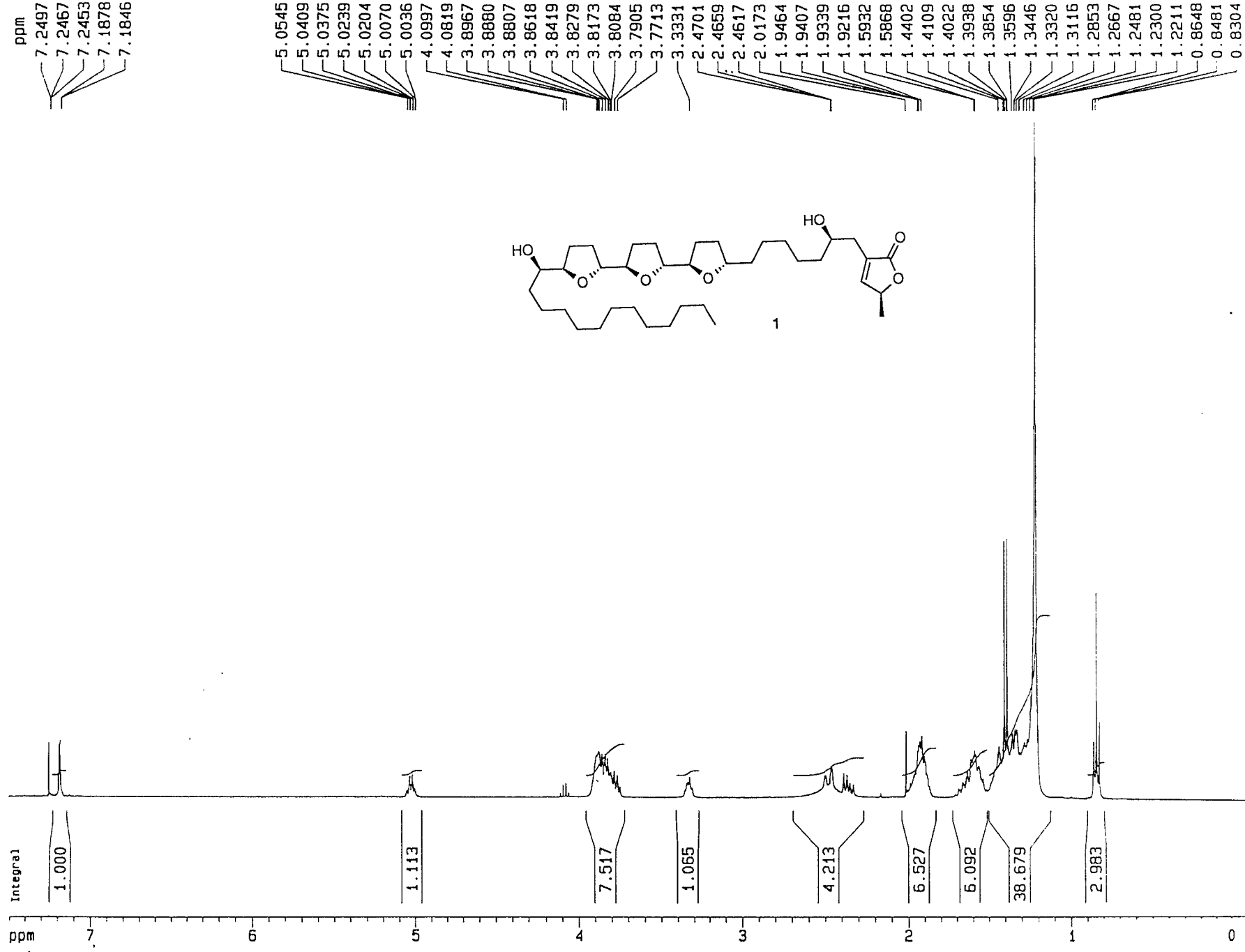
Compound 9 and ent-9:

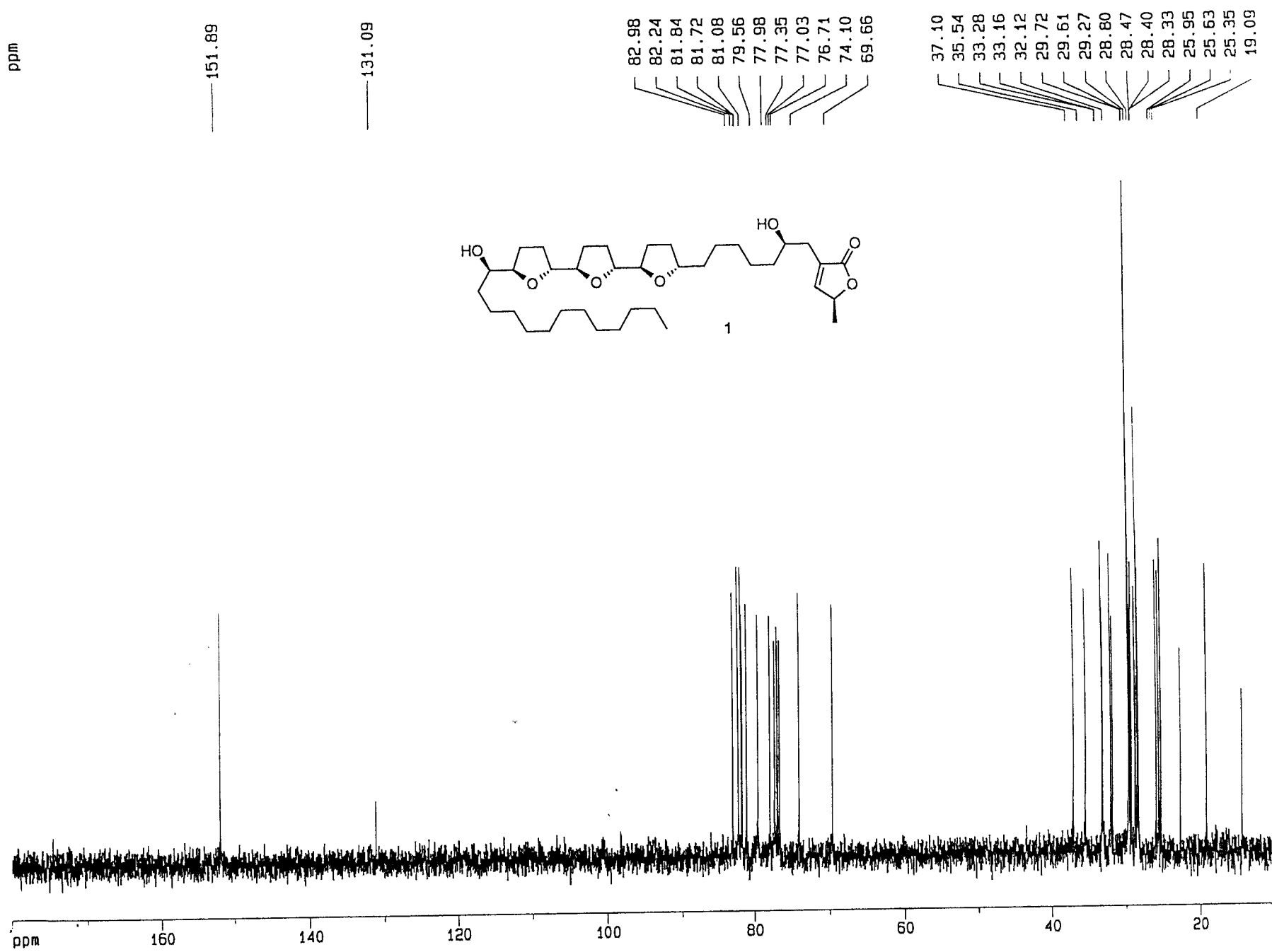
^1H NMR: δ 4.10 (m, 1 H), 3.94-3.74 (m, 7 H), 3.33 (m, 1 H), 2.61 (br s, 1 H), 2.10-1.15 (m and br s, 37 H), 0.84 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR: δ 83.2, 83.0, 82.0, 81.7, 81.6, 81.5, 81.3, 79.5, 74.1, 61.5, 60.4, 37.3, 33.3, 32.4, 31.9, 29.7, 29.6, 29.4, 28.8, 28.5, 28.4, 28.2, 28.0, 25.6, 22.7, 14.2, 14.1. MS analysis ($\text{C}_{27}\text{H}_{50}\text{O}_5 = 454$) found 455 (MH^+).

Compound 10 and ent-10:

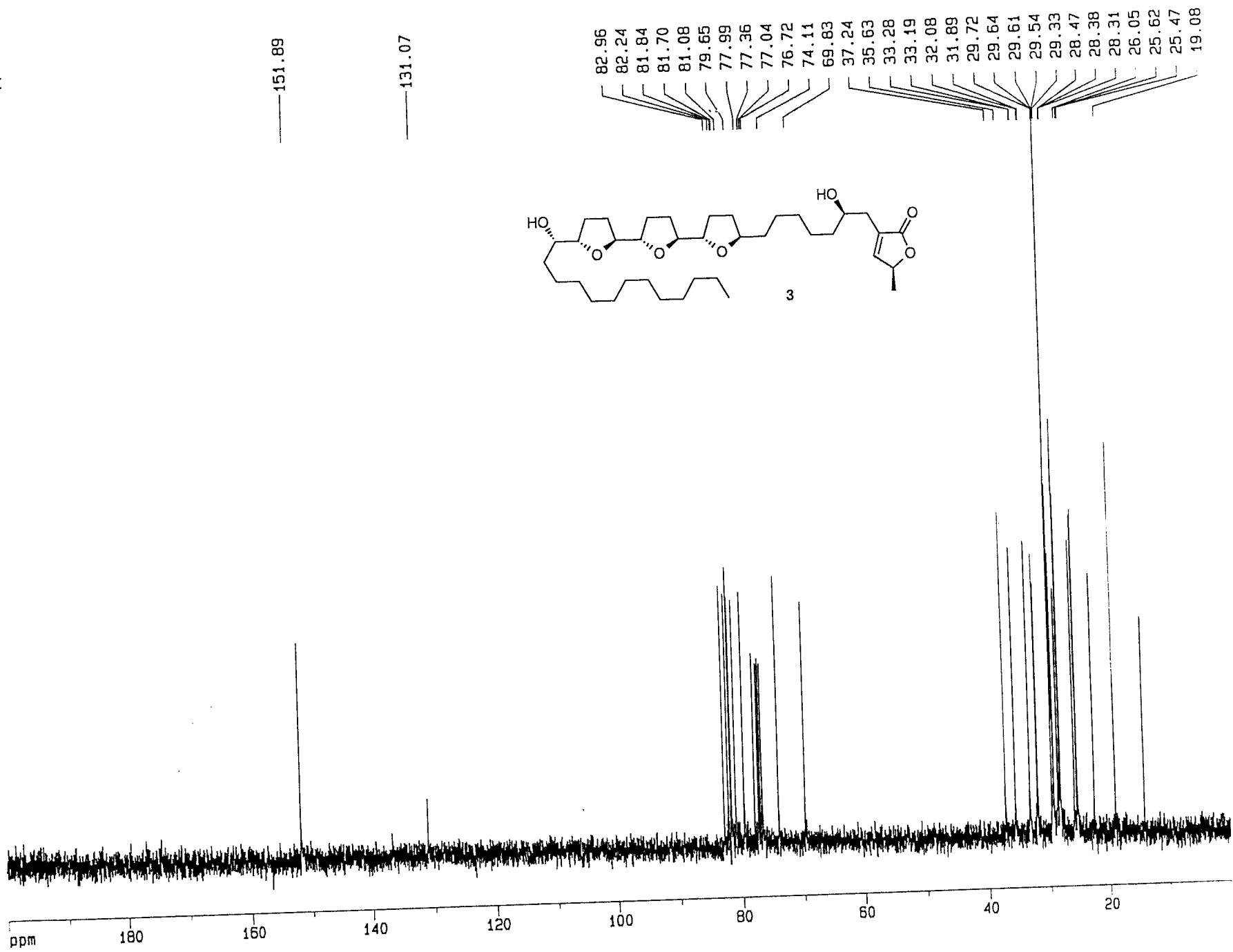


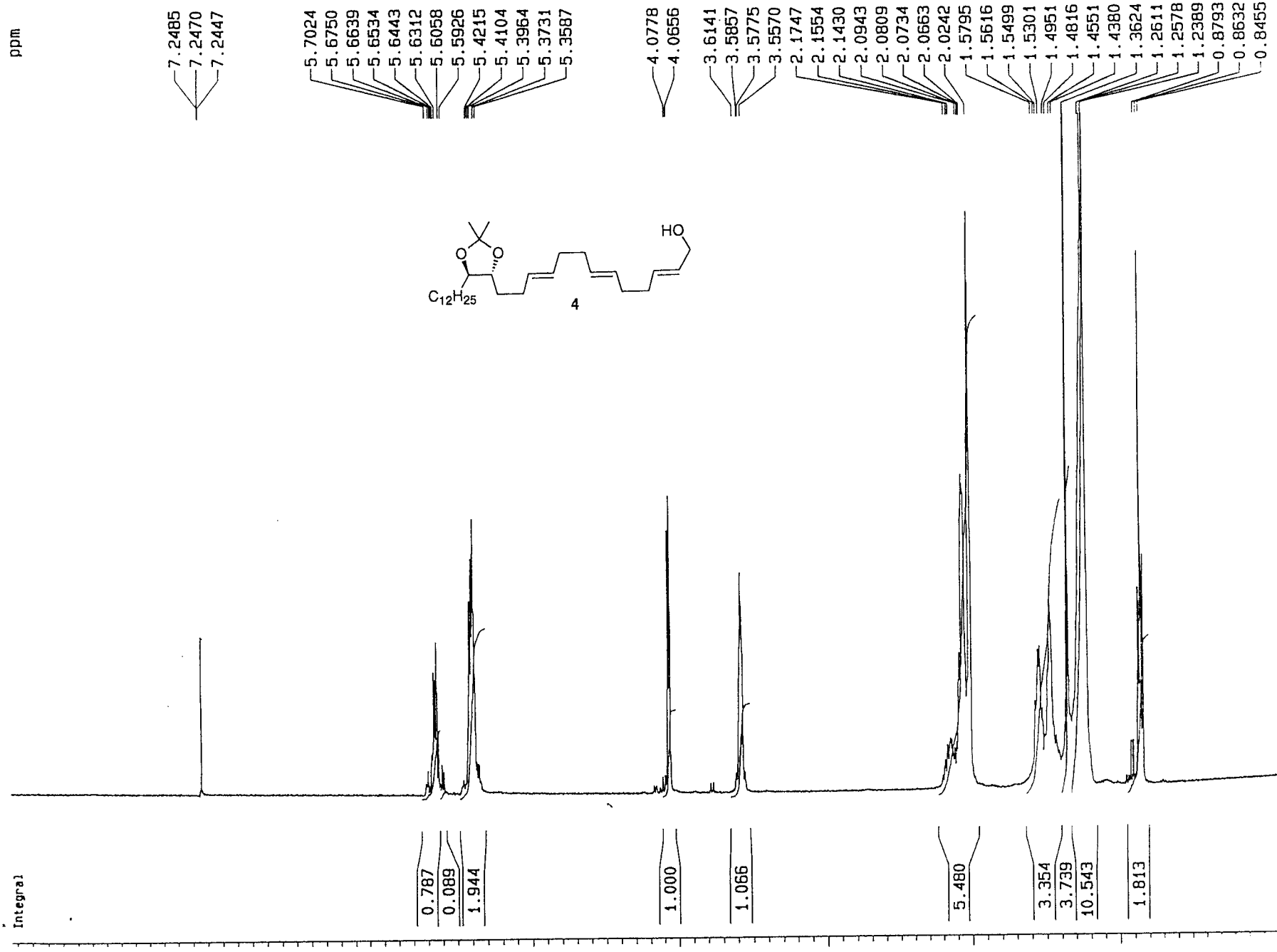
^1H NMR: δ 7.81 (m, 9 H), 7.70 (m, 6 H), 4.79 (d, $J = 6.8$ Hz, 1 H), 4.63 (d, $J = 6.8$ Hz, 1 H), 4.24 (m, 1 H), 3.99 (m, 1 H), 3.96-3.62 (m, 6 H), 3.45 (m, 1 H), 3.35 (s, 3 H), 2.22-1.15 (m and br s, 38 H), 0.86 (t, $J = 7.1$ Hz, 3 H). MS analysis ($\text{C}_{47}\text{H}_{69}\text{O}_5\text{PI} = 870$) found 743 (MH-I^+).

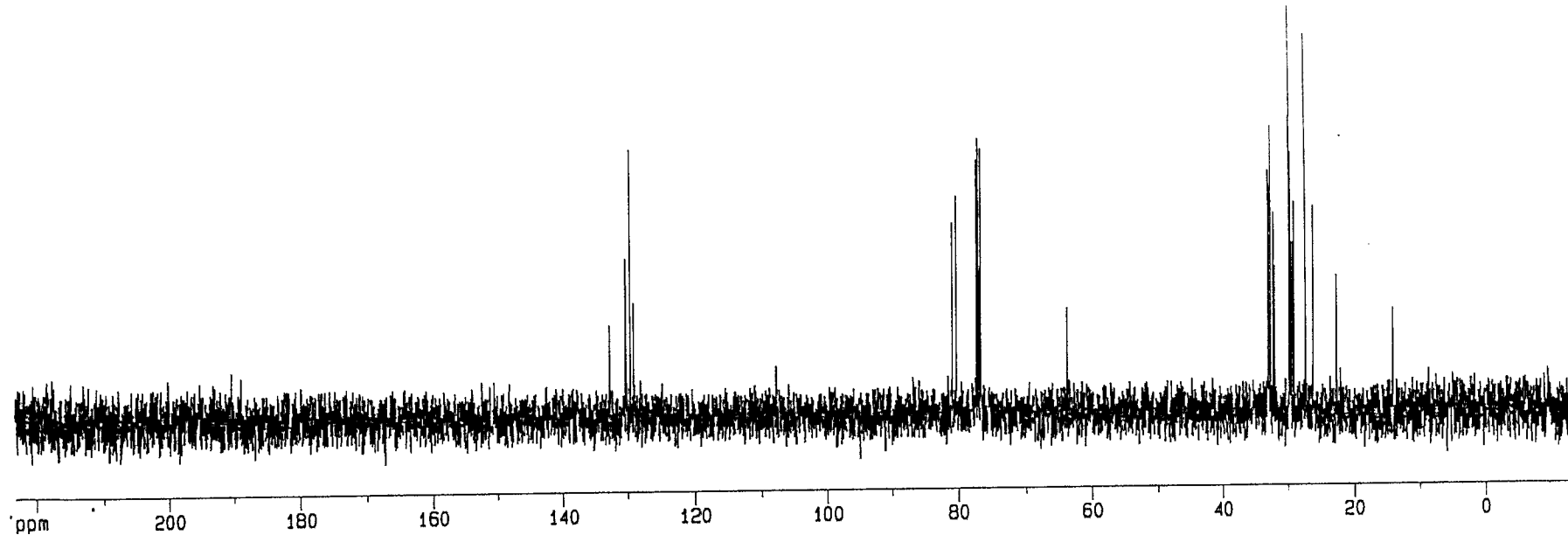




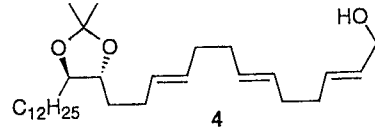
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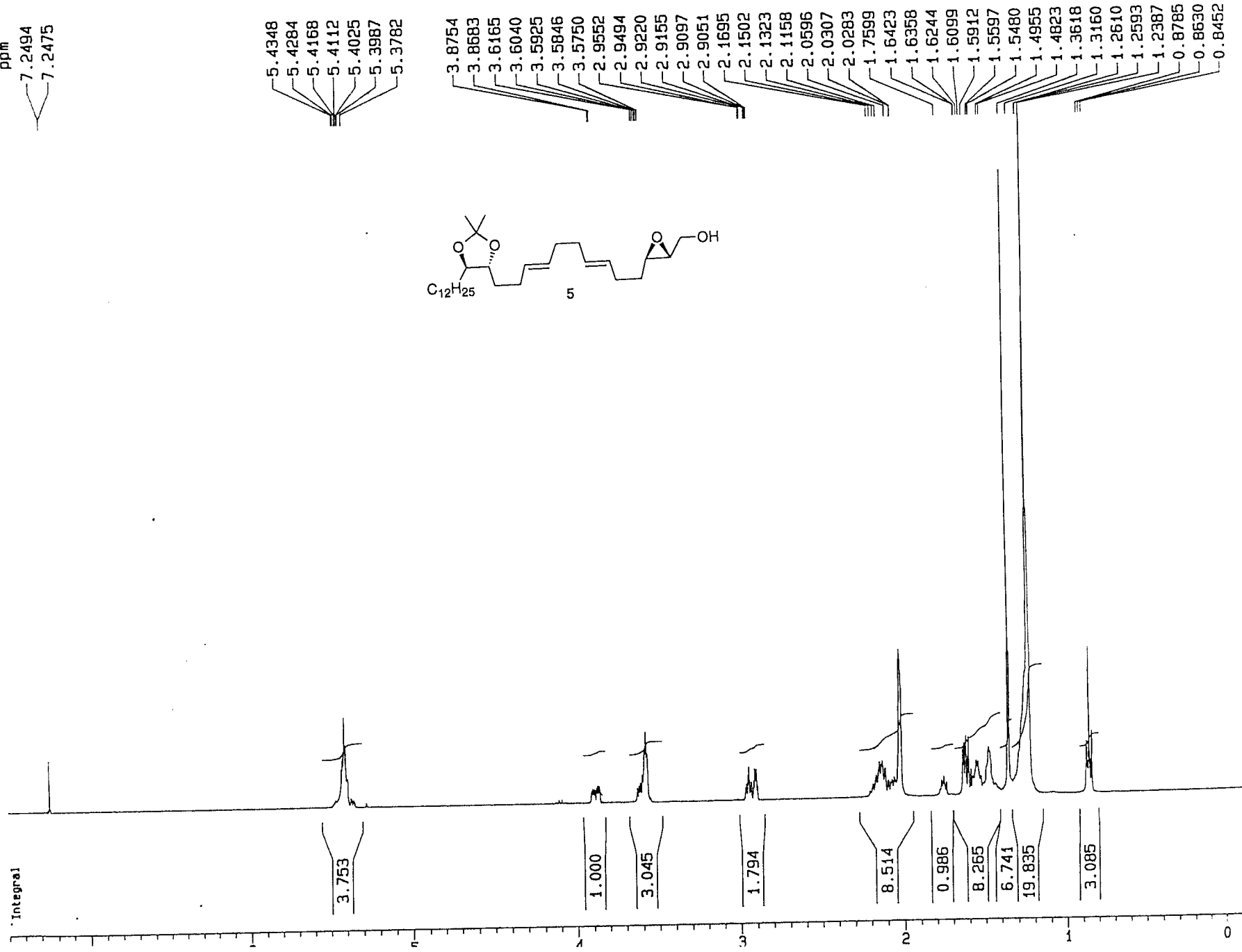


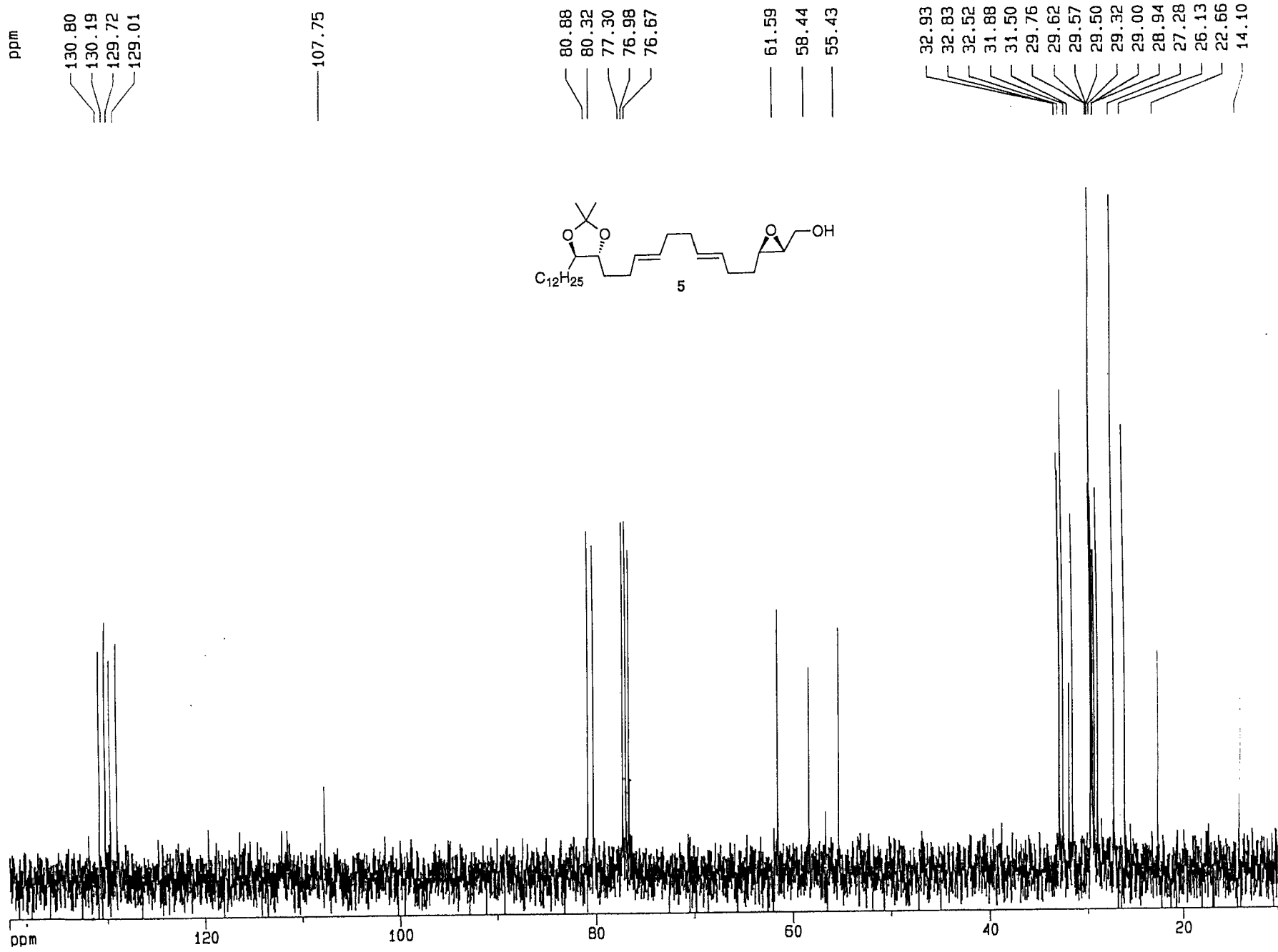
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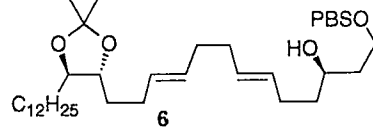




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5.404
5.287

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Integral

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4.15

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1.00

9.77

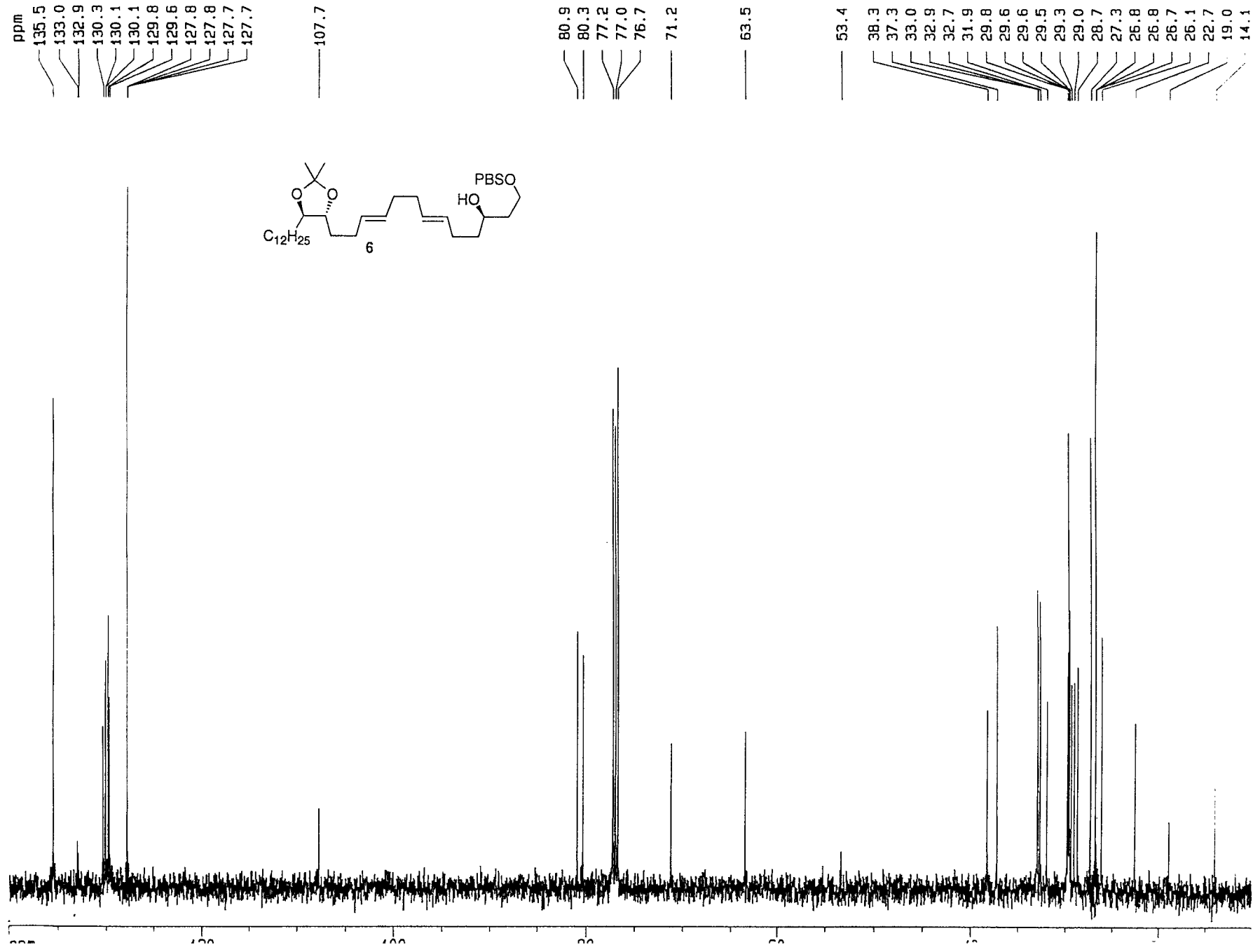
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23.51

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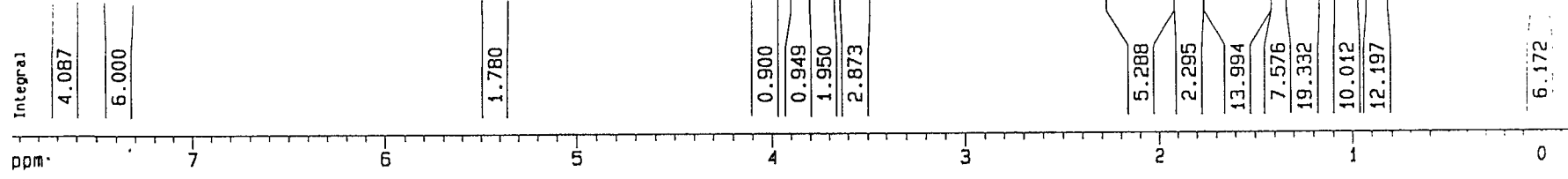
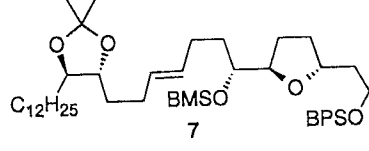
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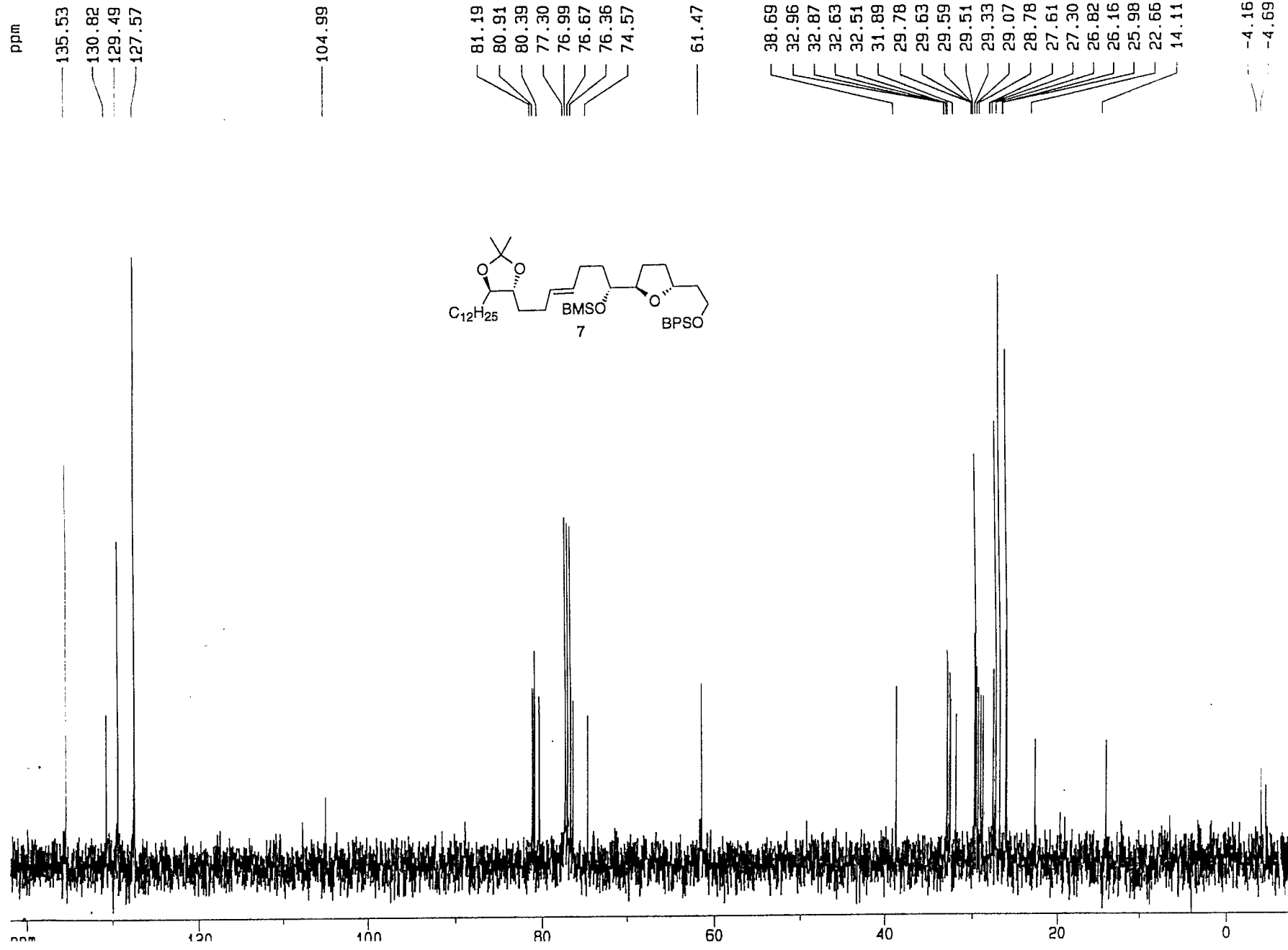


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5.408

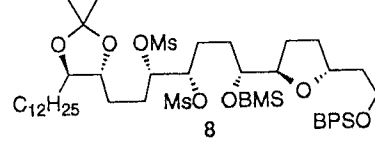
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0.858
0.028





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7.2480

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0.0208



Integral

4.000

5.702

0.855

0.827

0.867

0.870

2.008

2.849

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2.962

3.338

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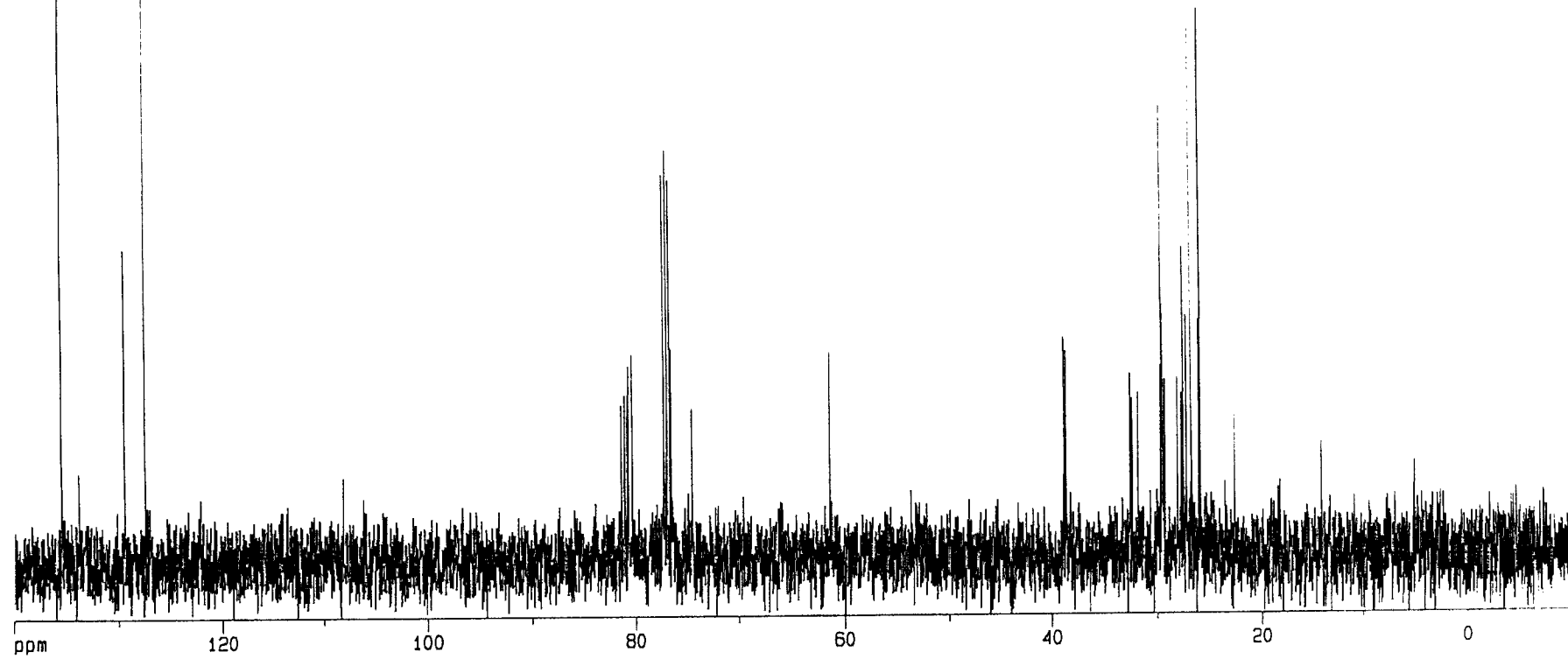
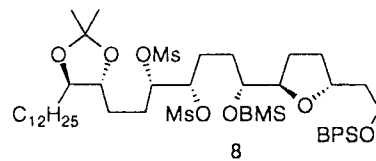
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 --- 127.58

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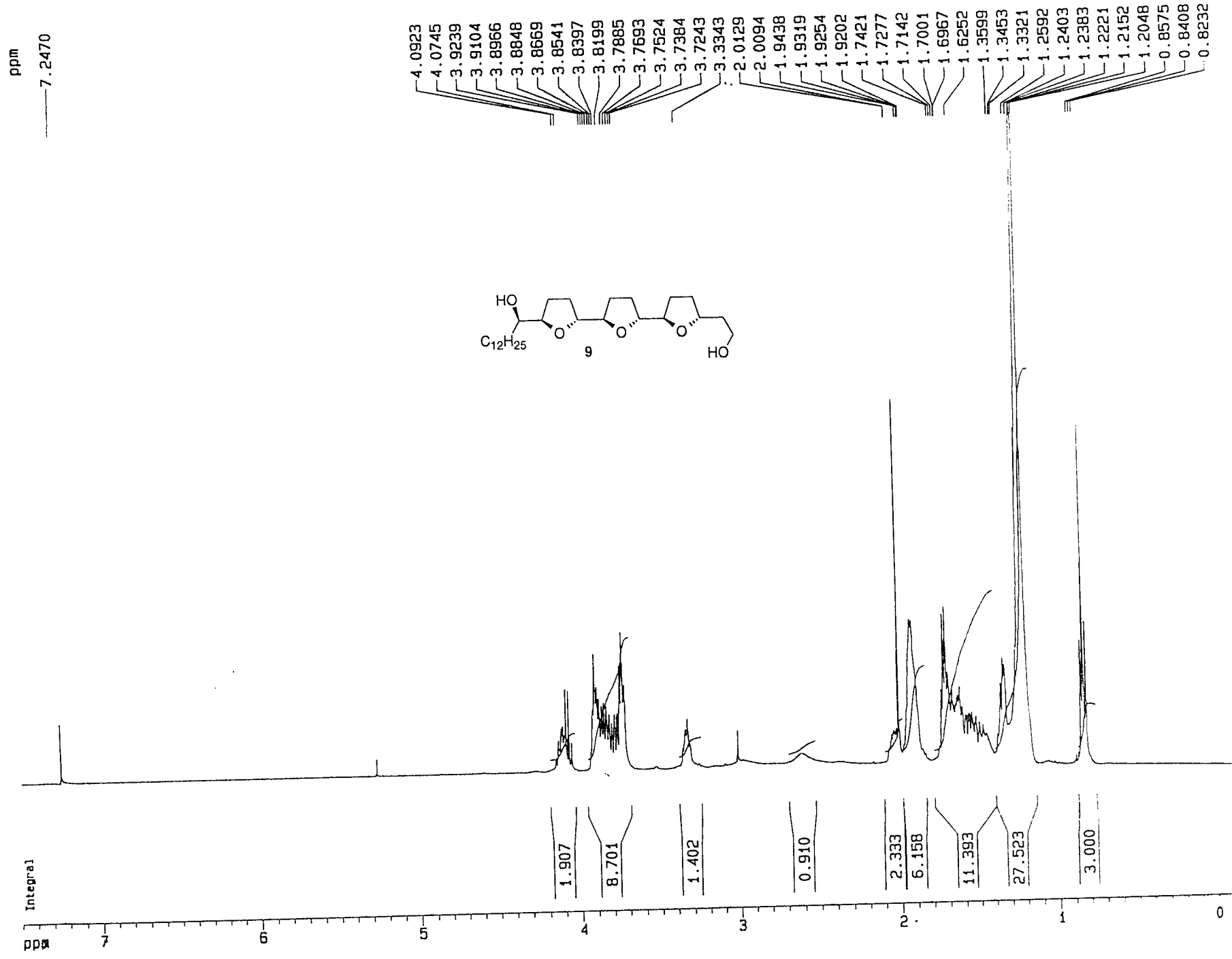
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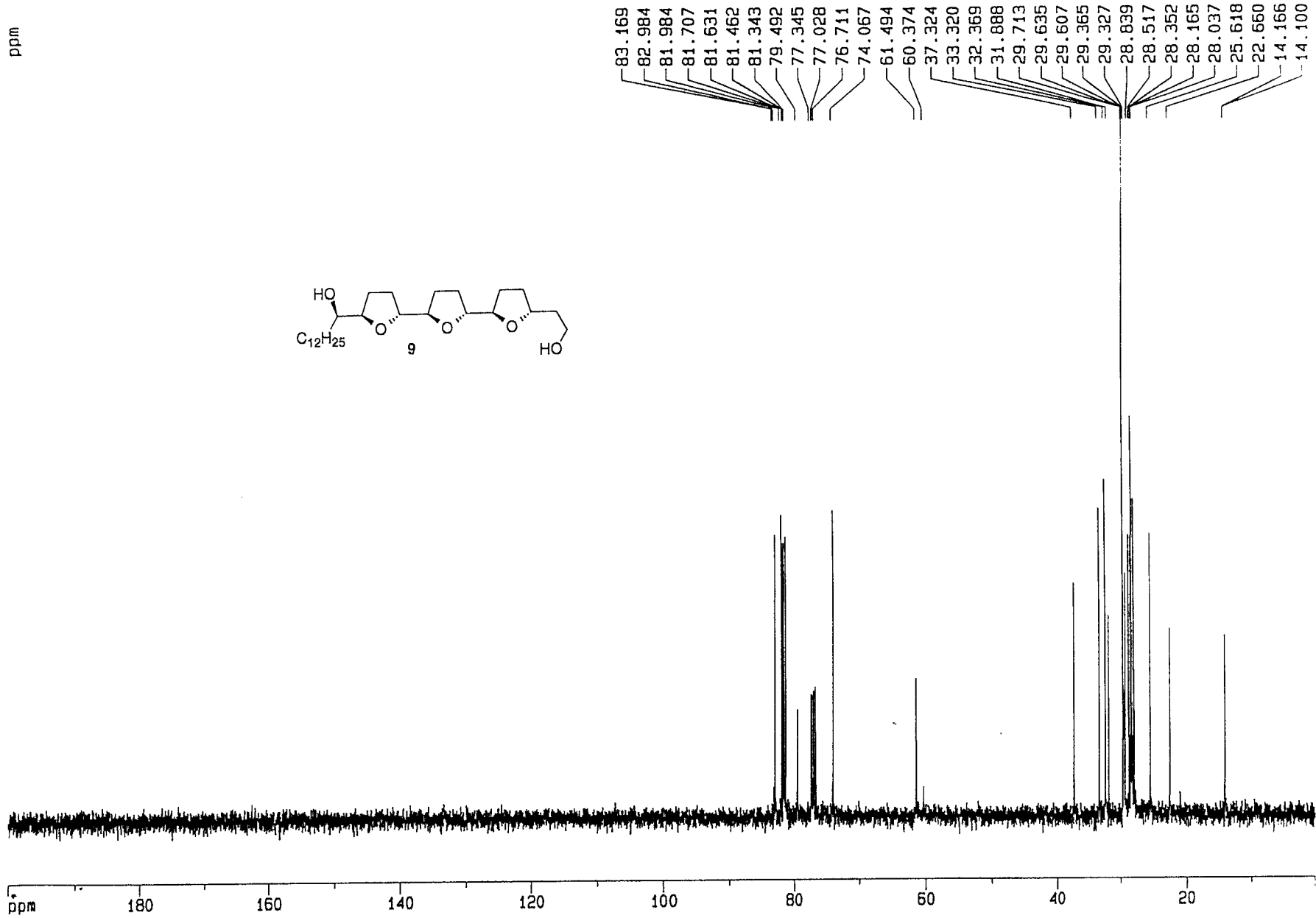
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-4.24
 -4.72



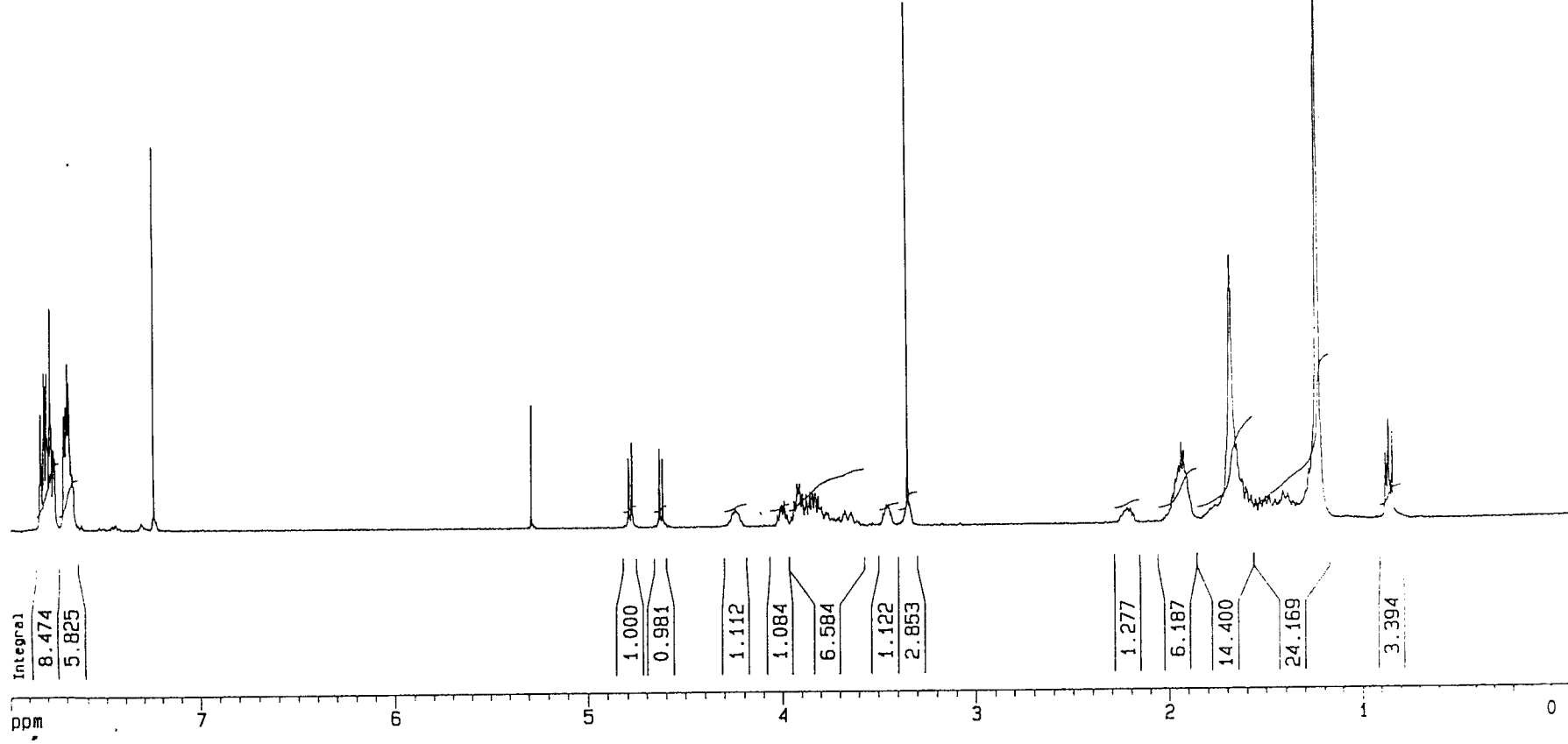
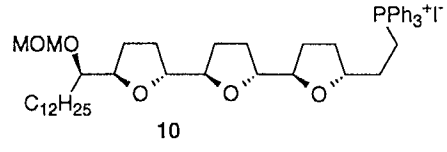
S20

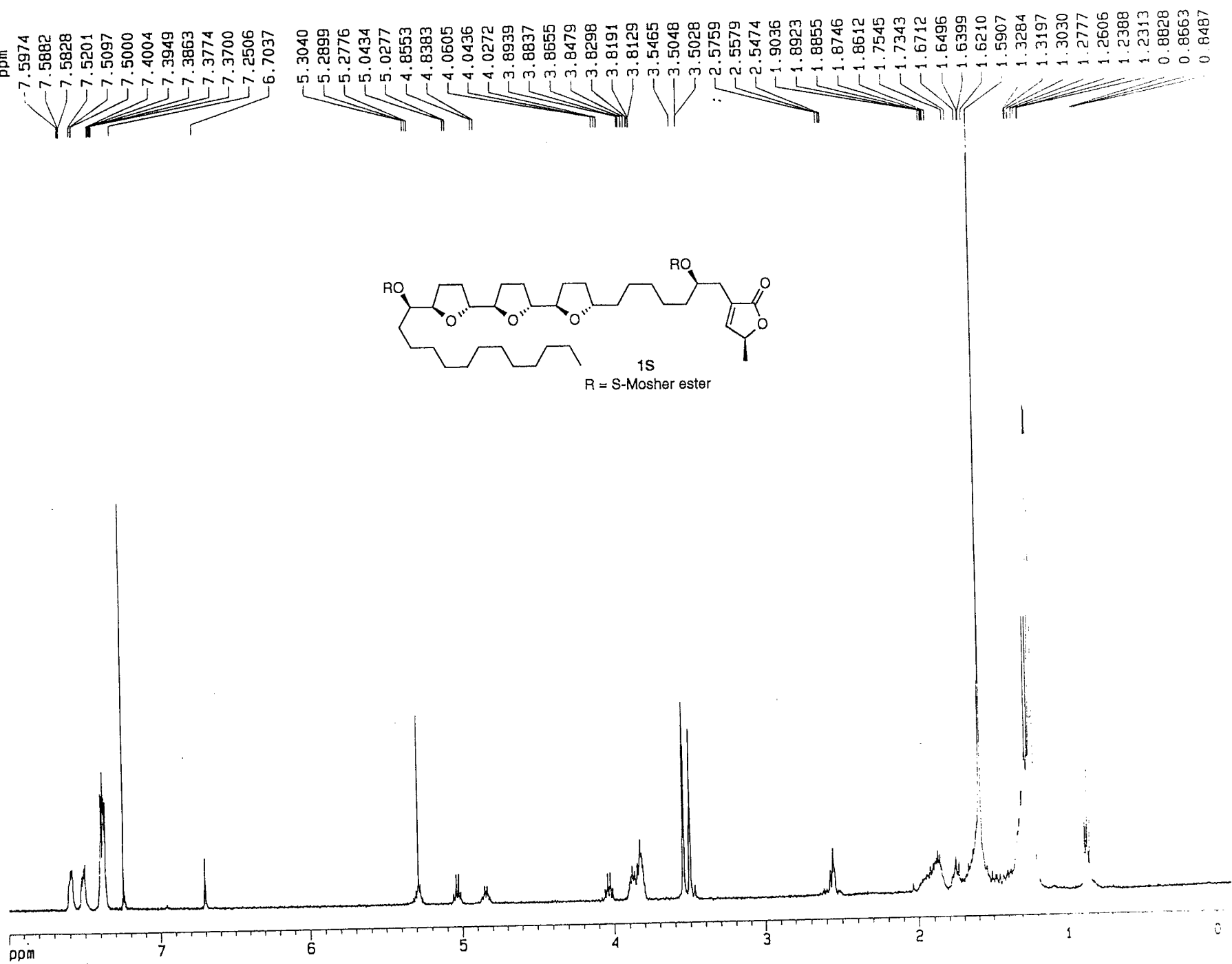




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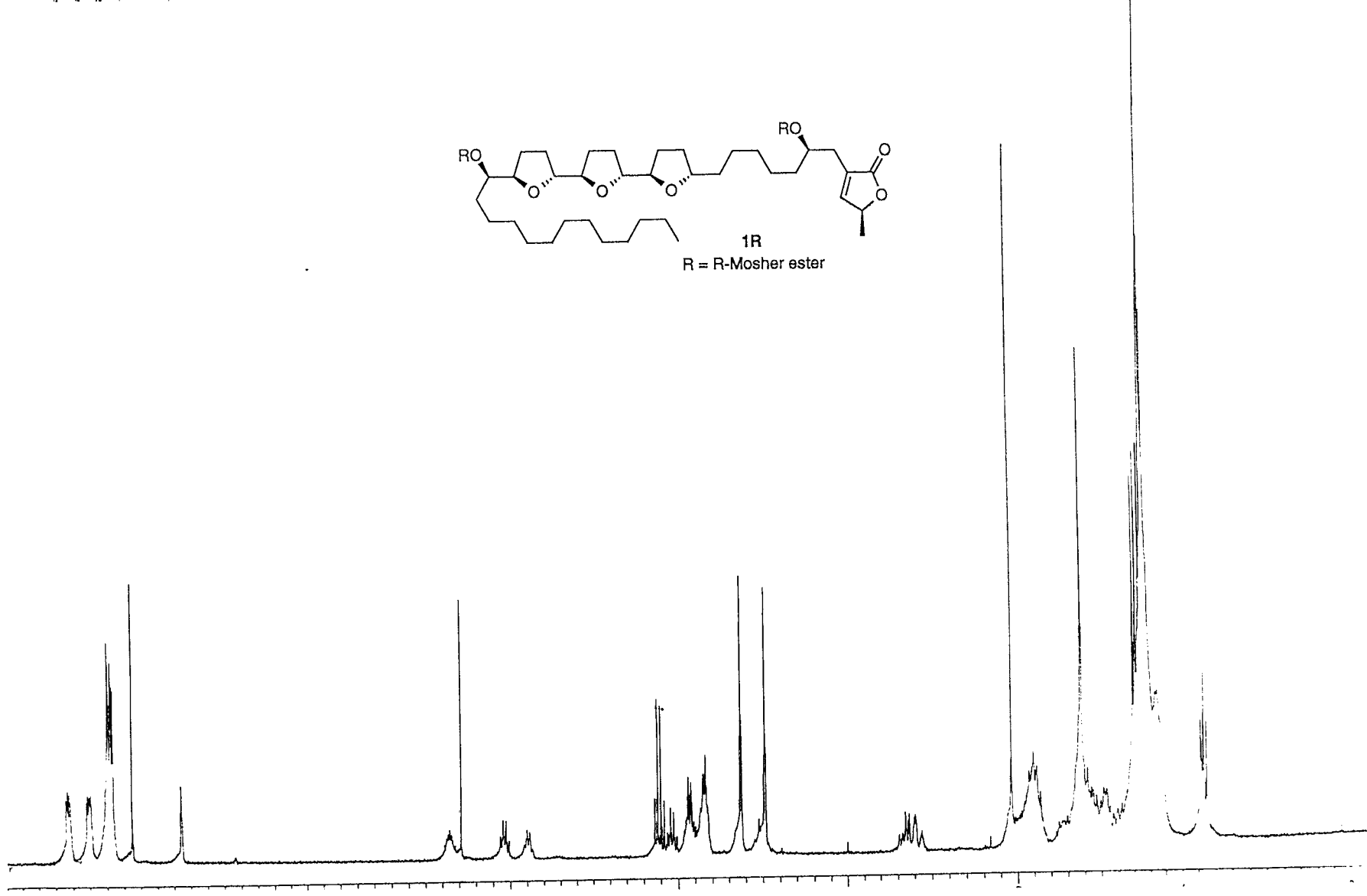
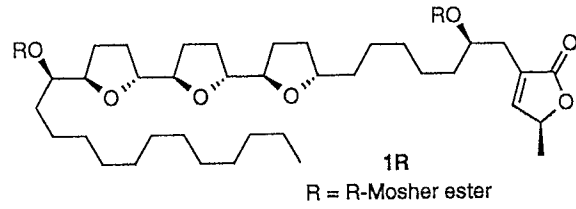


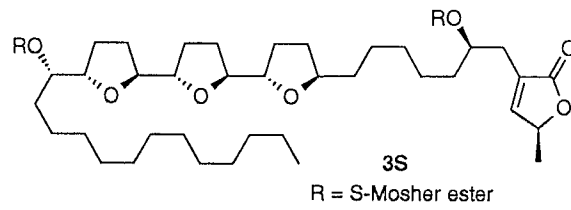
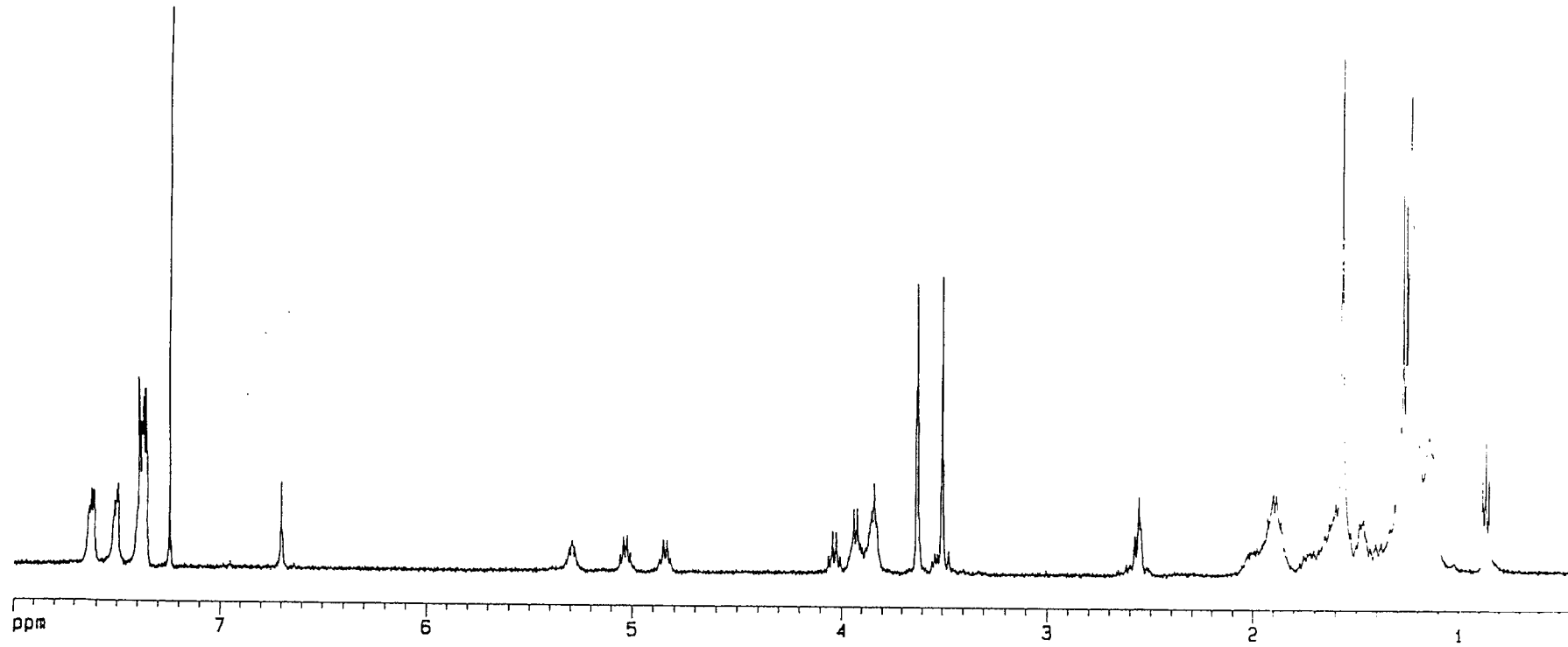
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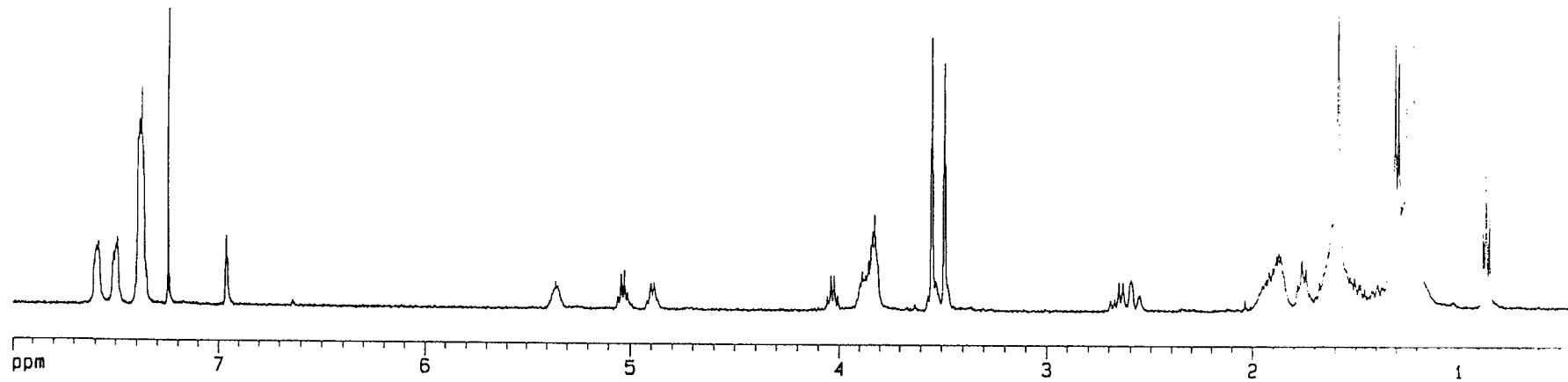
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6.956

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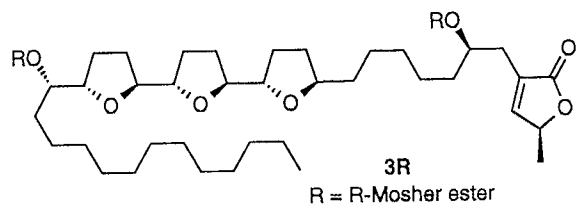




ppm

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1.5082
1.3092
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1.2759
1.2311
0.8826
0.8663
0.8488



Partial ^1H NMR spectra of R and S Mosher esters of synthetic 1 and 3 (400 MHz), natural 1 (500 MHz) and authentic 3 (500 MHz)

