Supporting Information

Titanium-mediated Alkylative Cyclizations of 1,3-Diene-Tethered Esters

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Typical experimental procedure for the formation of **3a** and **4a**: A 3.0 M solution of methylmagnesium chloride (0.2 mL) in THF was added at 0 °C over a period of 5 min to a solution of Ti(O-*i*-Pr)$_4$ (0.16 mL, 0.55 mmol) in anhydrous THF (5 mL). After the mixture had been stirred for an additional 5 min, **1** (77 mg, 0.5 mmol) was added, followed by slow addition (over a period of 1 h) of a 2.0 M solution of cyclopentylmagnesium chloride (0.45 mL) in THF. The reaction mixture was then stirred for 10 min and quenched with addition of water (0.5 mL). The resulting mixture was stirred for an additional 1 h, dried over sodium sulfate, and filtered. The filter cake was washed with CH_2Cl_2 (10 mL), and the combined filtrates were concentrated under vacuum. Purification by column chromatography on silica gel afforded 38.5 mg (62%) of **3a** and 20.4 mg (21%) of **4a**.

Typical experimental procedure for the formation of **6**: A 3.0 M solution of methylmagnesium chloride (0.2 mL) in THF was added at 0 °C over a period of 5 min to a solution of Ti(O-*i*-Pr)$_4$ (0.16 mL, 0.55 mmol) in anhydrous THF (5 mL). After the mixture had been stirred for an additional 5 min, **2** (84 mg, 0.5 mmol) was added, followed by slow addition (over a period of 1 h) of a 2.0 M solution of cyclopentylmagnesium chloride (0.75 mL) in THF. The reaction mixture was then stirred for 10 min and quenched with addition of water (0.5 mL). The resulting mixture was stirred for an additional 1 h, dried over sodium sulfate, and filtered. The filter cake was washed with CH_2Cl_2 (10 mL), and the combined

filtrates were concentrated under vacuum. Purification by column chromatography on silica gel afforded 84.3 mg (81%) of **6**.

3a: IR (neat) 1739 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.72 (ddq, *J* = 10.8, 1.1, 6.8 Hz, 1H), 5.24 (ddq, *J* = 10.8, 8.6, 1.7 Hz, 1H), 3.11-3.03 (apparent q, 1H), 2.38~2.02 (m, 4H), 1.90~1.81 (m, 1H), 1.73~1.62 (m, 1H), 1.67 (dd, *J* = 6.8, 1.7 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 219.3, 128.2, 126.6, 48.4, 37.6, 30.8, 21.0, 13.4.

4a: IR (neat) 3325 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.51 (dt, *J* = 15.1, 6.8 Hz, 1H), 5.31 (dd, *J* = 15.1, 8.0 Hz, 1H), 3.84~3.78 (apparent q, 1H), 2.29~2.20 (apparent qn, 1H), 2.03~1.26 (m, 16H), 1.15~1.09 (m, 2H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 132.4, 130.9, 78.7, 52.0, 40.0, 39.0, 33.3, 32.2, 30.0, 25.1, 21.1.

3b: IR (neat) 1740 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.72 (ddt, *J* = 10.6, 1.0, 6.8 Hz, 1H), 5.24 (ddt, *J* = 10.6, 8.6, 1.7 Hz, 1H), 3.10~3.02 (apparent q, 1H), 2.33~2.02 (m, 4H), 1.89~1.85 (m, 1H), 1.73~1.63 (m, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 219.3, 128.1, 126.6, 48.4, 37.6, 30.8, 21.0, 13.3, 13.1, 12.9.

4b: IR (neat) 3345 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.51 (dt, *J* = 15.4, 6.8 Hz, 1H), 5.31 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.28~2.21 (apparent q, 1H), 2.02~1.25 (m, 16H), 1.14~1.09 (m, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 132.3, 130.9, 78.4, 78.2, 78.0, 51.9, 39.9, 39.0, 33.2, 32.2, 32.0, 31.8, 31.6, 30.0, 25.1, 25.0, 21.1.

5: IR (neat) 1711 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.62 (dq, *J* = 10.9, 6.6 Hz, 1H), 5.53 (ddq, *J* = 10.9, 8.5, 1.5 Hz, 1H), 3.32~3.25 (m, 1H), 2.48~2.42 (m, 1H), 2.35~2.27 (m, 1H), 2.05~2.00 (m, 2H), 1.91~1.65 (m, 4H), 1.58 (dd, *J* = 6.6, 1.5 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ ___.2, 127.5, 126.2, 49.0, 41.7, 34.5, 27.7, 24.3, 13.0.

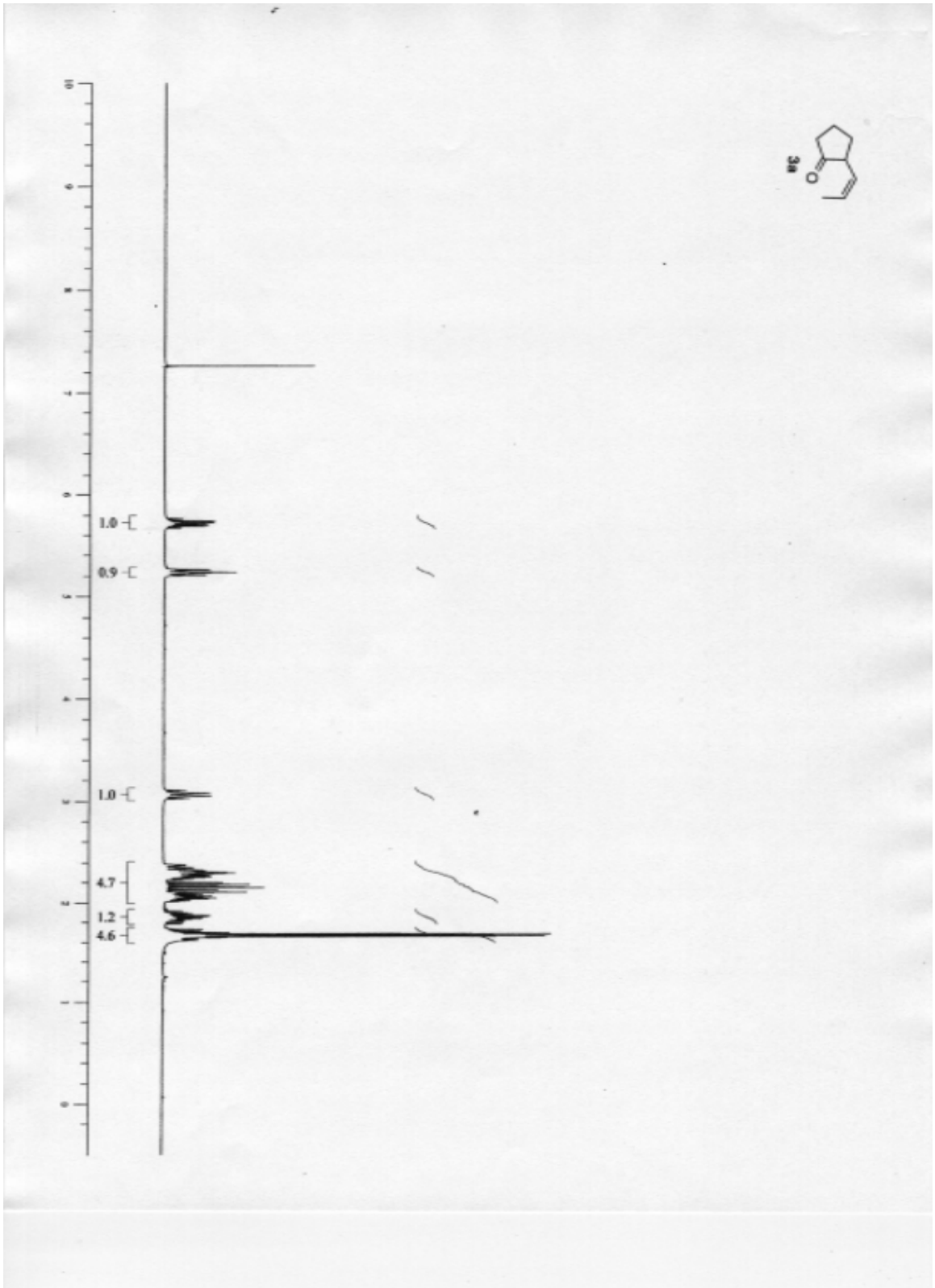
6a: IR (neat) 3390 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.58 (dt, *J* = 15.2, 7.0 Hz, 1H), 5.23 (dd, *J* = 15.2, 8.7 Hz, 1H), 3.17 (ddd, *J* = 9.9, 9.9, 4.0 Hz, 1H), 2.05~1.09

(m, 21H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 132.9, 132.5, 73.0, 50.3, 39.9, 39.0, 33.5, 32.2, 31.6, 25.3, 25.1, 24.8.

6b: IR (neat) 3397 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.58 (dt, 15.4, 6.7 Hz, 1H), 5.25 (ddt, *J* = 15.4, 8.7, 1.1 Hz, 1H), 3.18 (ddd, *J* = 9.8, 9.8, 4.1 Hz, 1H), 2.04~1.63 (m, 8H), 1.39 (tq, J = 7.4, 7.4 Hz, 2H), 1.30~1.16 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 133.3, 132.2, 73.0, 50.3, 34.7, 33.6, 31.6, 25.3, 24.8, 22.6, 13.6.

6c: IR (neat) 3407 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.63~5.52 (m, 1H), 5.22 (dd, *J* = 15.4, 8.7 Hz, 1H), 3.19~3.16 (m, 1H), 2.05~0.84 (m, 21H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 133.7, 133.2, 132.1, 131.9, 73.0, 50.3, 50.2, 39.7, 34.7, 33.6, 32.6, 31.6, 31.4, 29.2, 29.0, 25.3, 24.8, 22.5, 19.1, 14.0, 11.4.

6d: IR (neat) 3390 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.57 (dt, *J* = 15.4, 7.1 Hz, 1H), 5.23 (dd, *J* = 15.4, 8.9 Hz, 1H), 3.19 (ddd, *J* = 9.8, 9.8, 4.1 Hz, 1H), 2.04~1.59 (m, 8H), 1.34~1.17 (m, 5H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 133.2, 132.2, 73.0, 50.3, 42.0, 33.6, 31.6, 28.3, 25.3, 24.8, 22.3, 22.2.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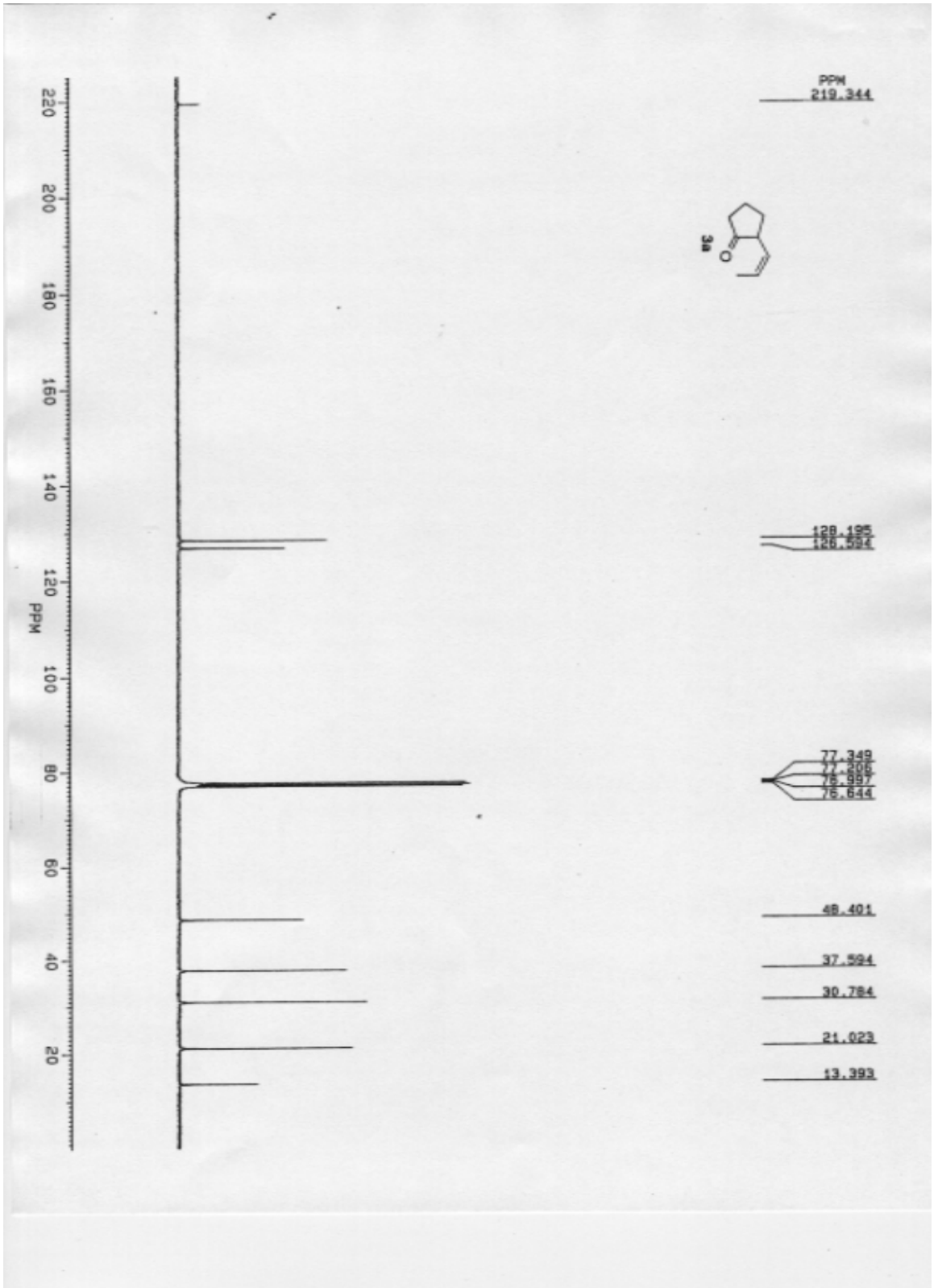
0.9
1.0
4.7
1.2
4.6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3a
O
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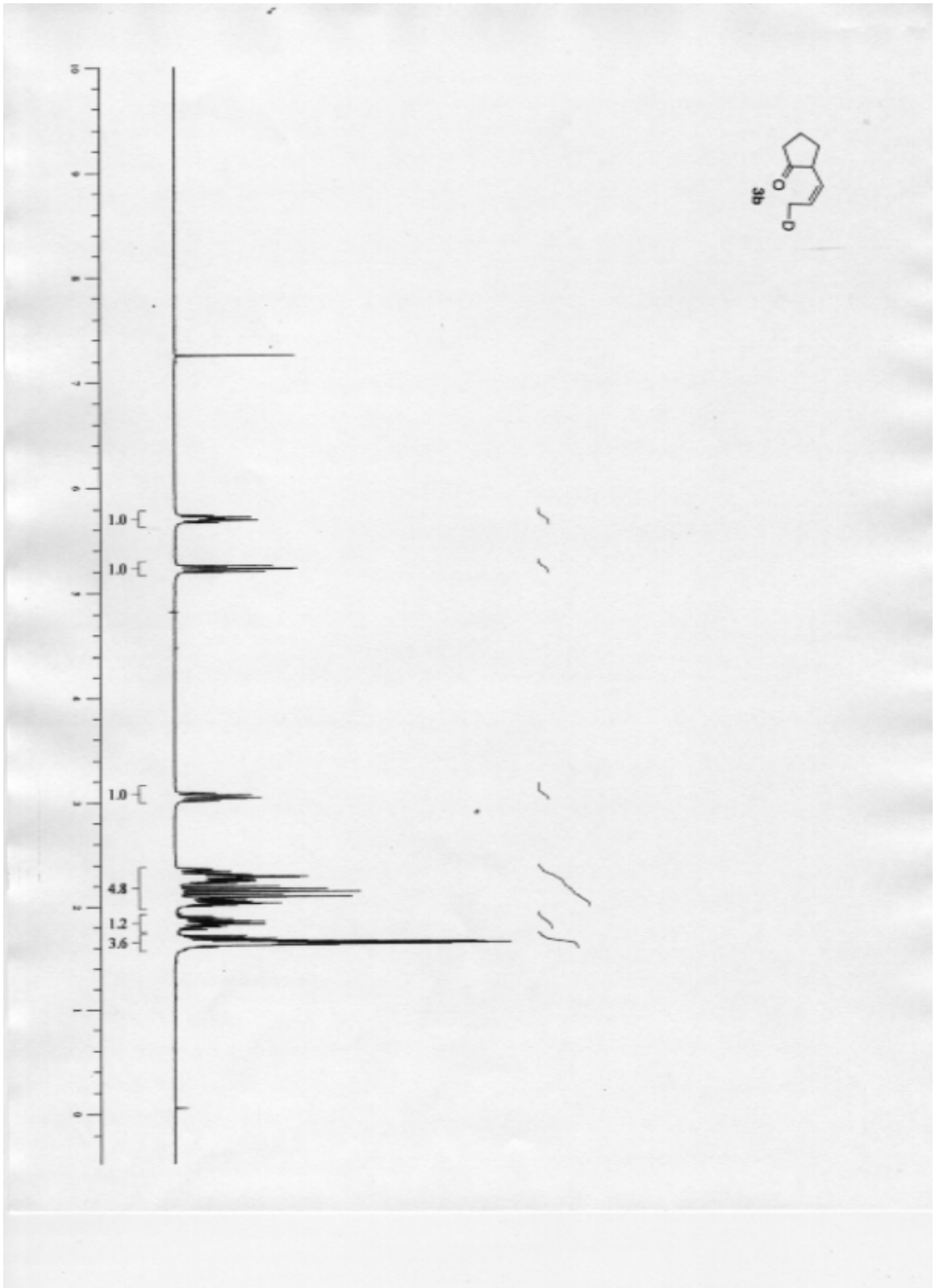
128.594
77.349
77.206
76.997
76.644
48.401
37.594
30.784
21.023
13.393
220
200
180
160
140
120
100
80
60
40
20
PPM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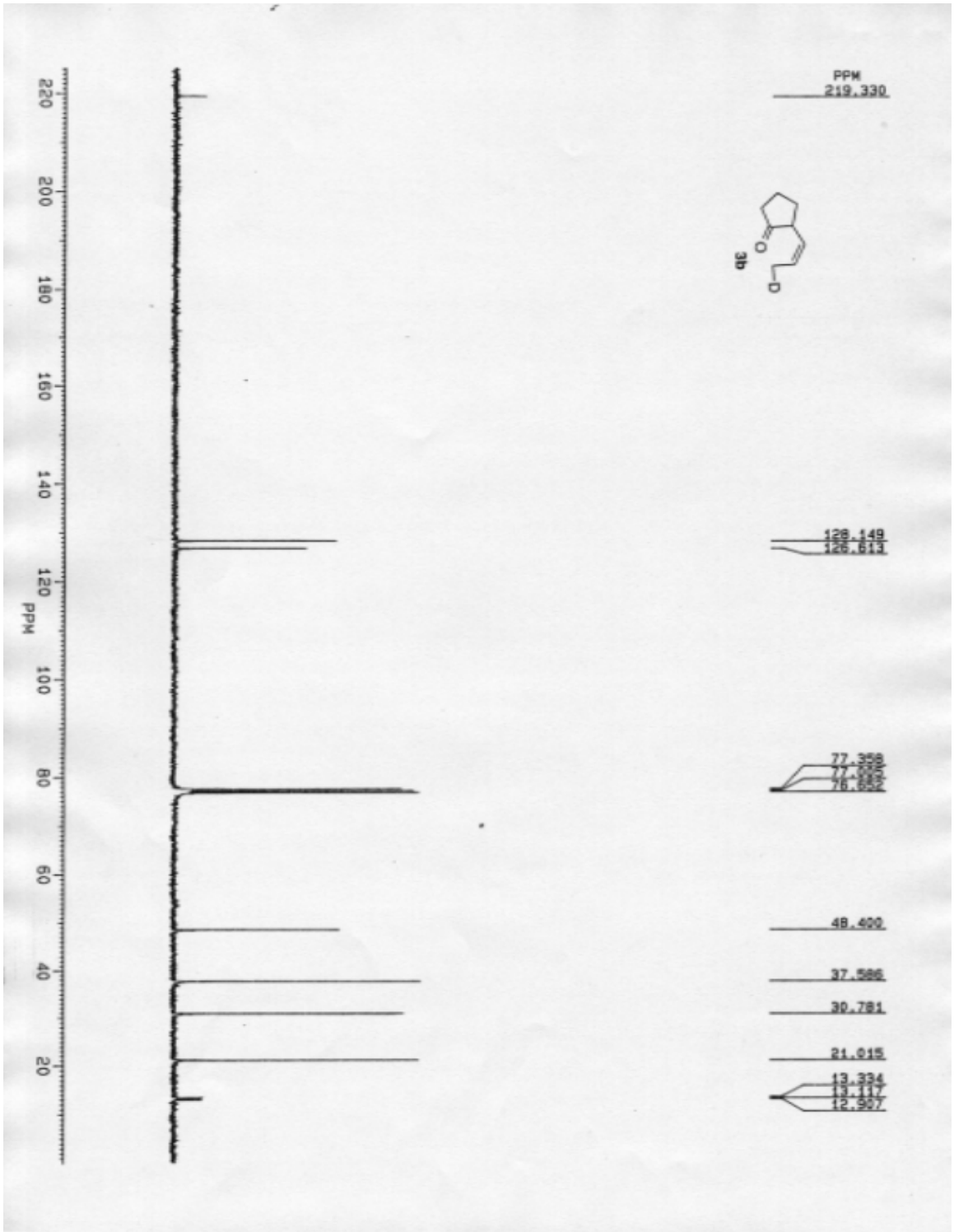
1.0
1.0
4.8
1.2
3.6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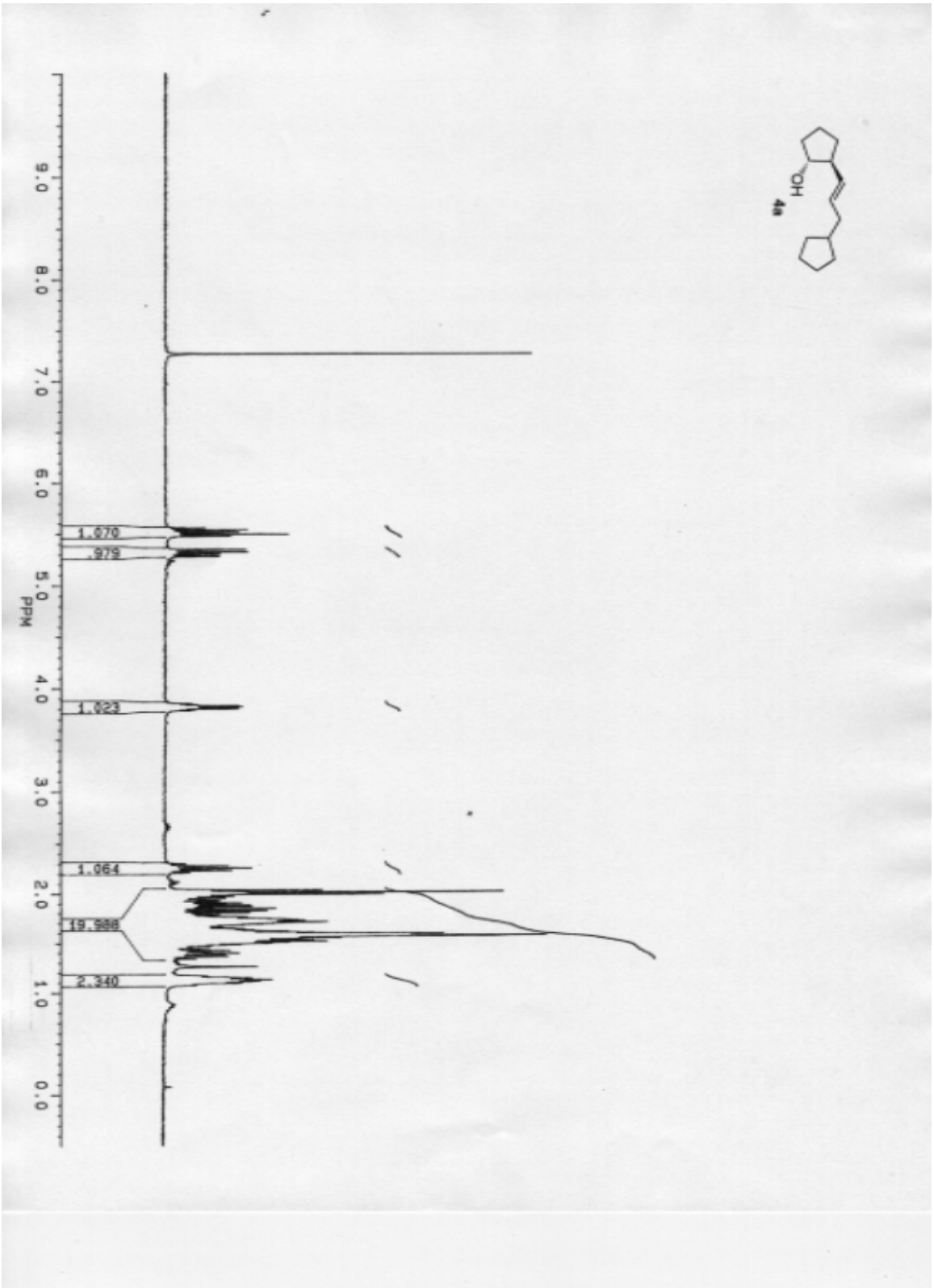
O
D
128.149
126.613
77.358
77.000
76.642
48.400
37.586
30.781
21.015
13.334
13.117
12.907
PPM
220
200
180
160
140
120
100
80
60
40
20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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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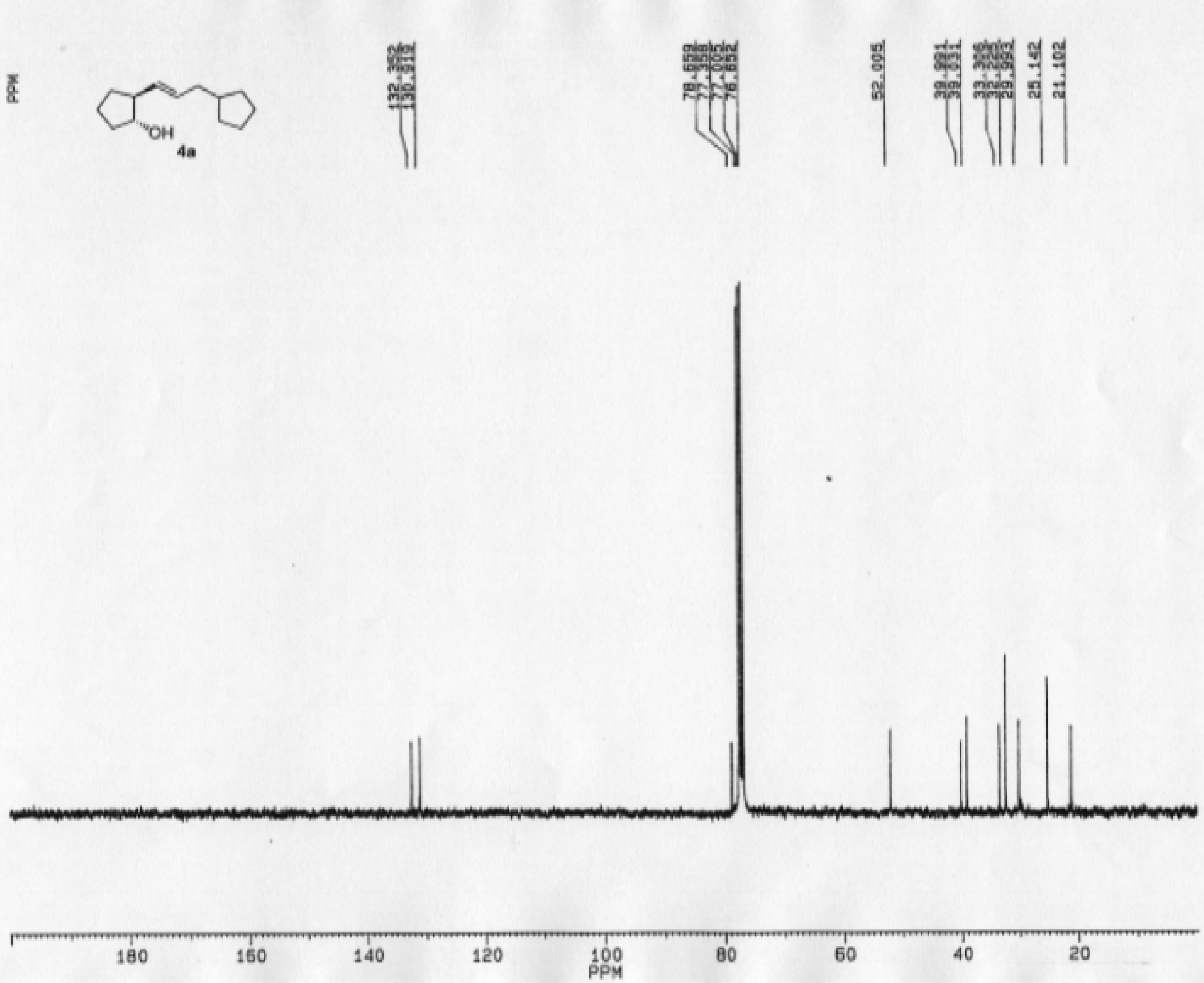
.979
1.023
1.064
19.988
2.340
OH
4a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78.659
77.005
76.652
52.005
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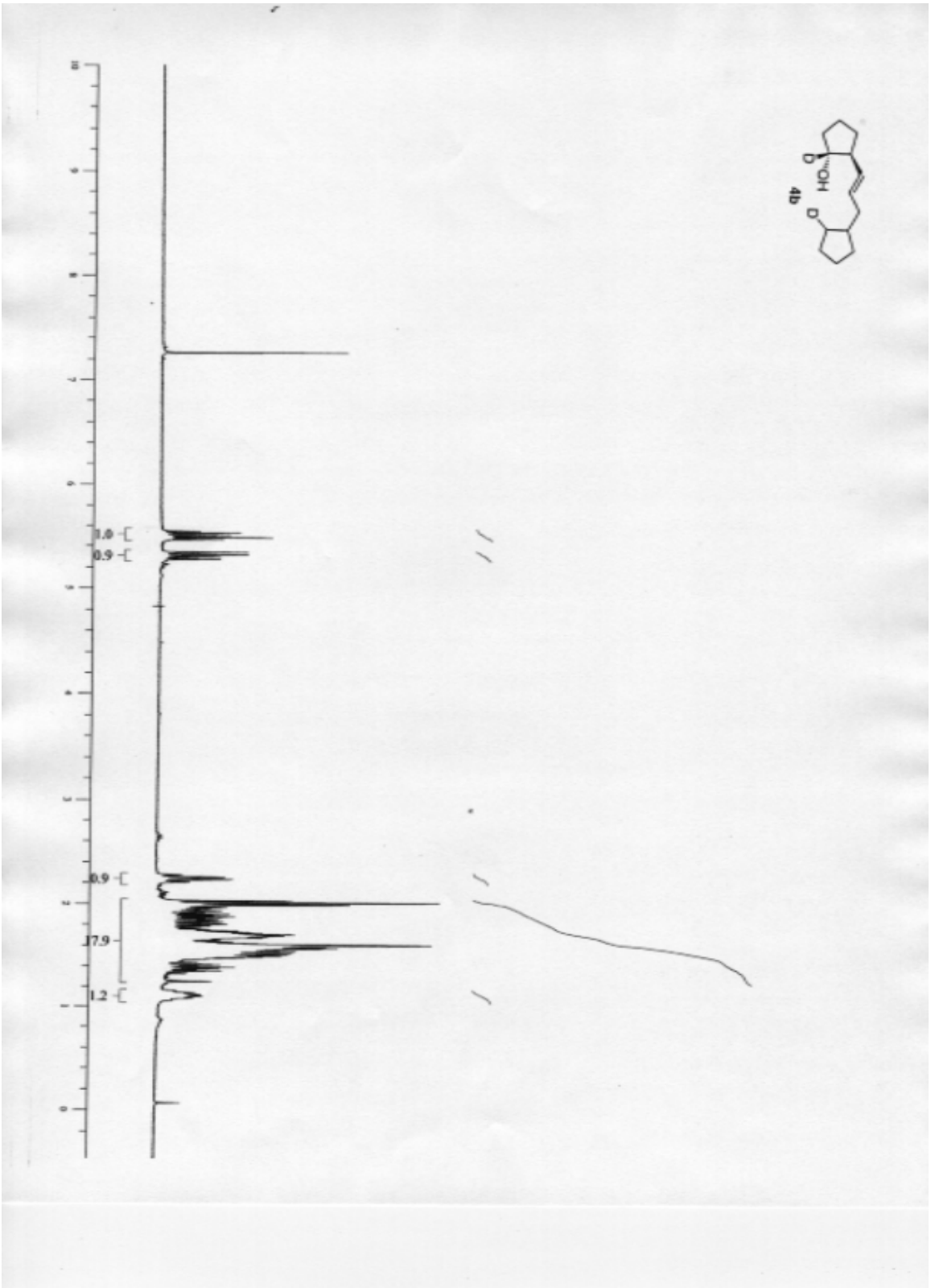
25.142
21.102
180
160
140
120
100
PPM
80
60
40
20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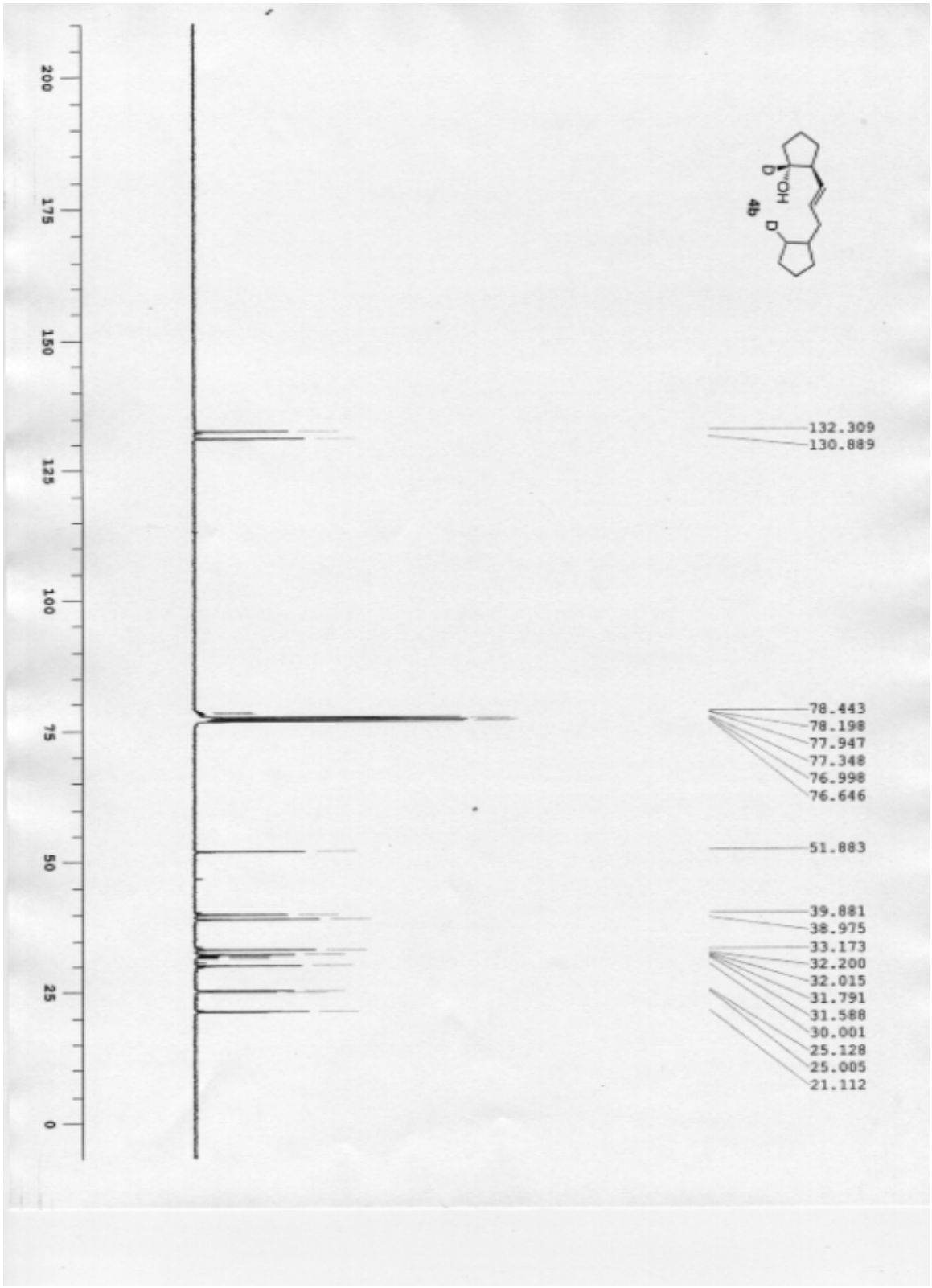
0.9
17.9
1.2
HO
O
O
4b


200
175
150
125
100
75
50
25
0
OH
D
D
4b
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78.443
78.198
77.947
77.348
76.998
76.646
51.883
39.881
38.975
33.173
32.200
32.015
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31.588
30.001
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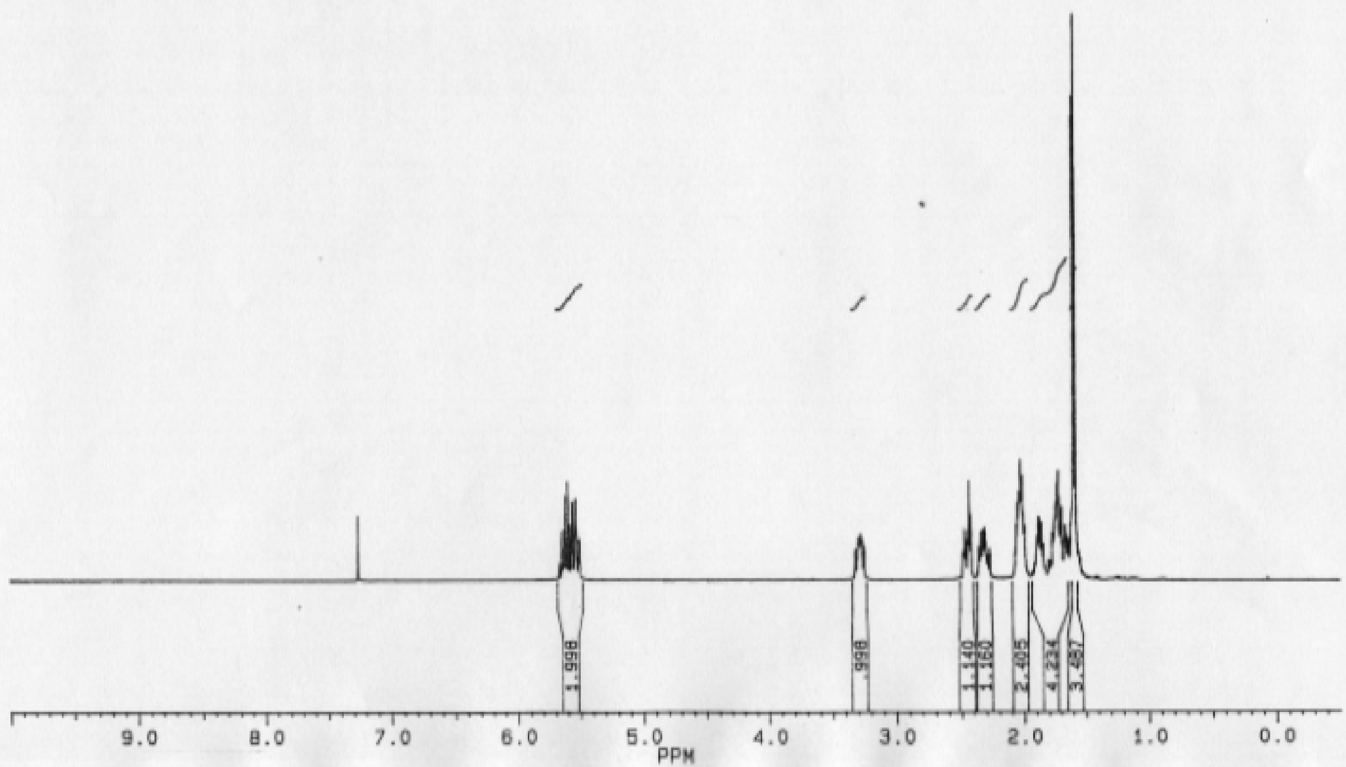
25.005
21.112

5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1.140
1.160
2.405
4.234
3.487
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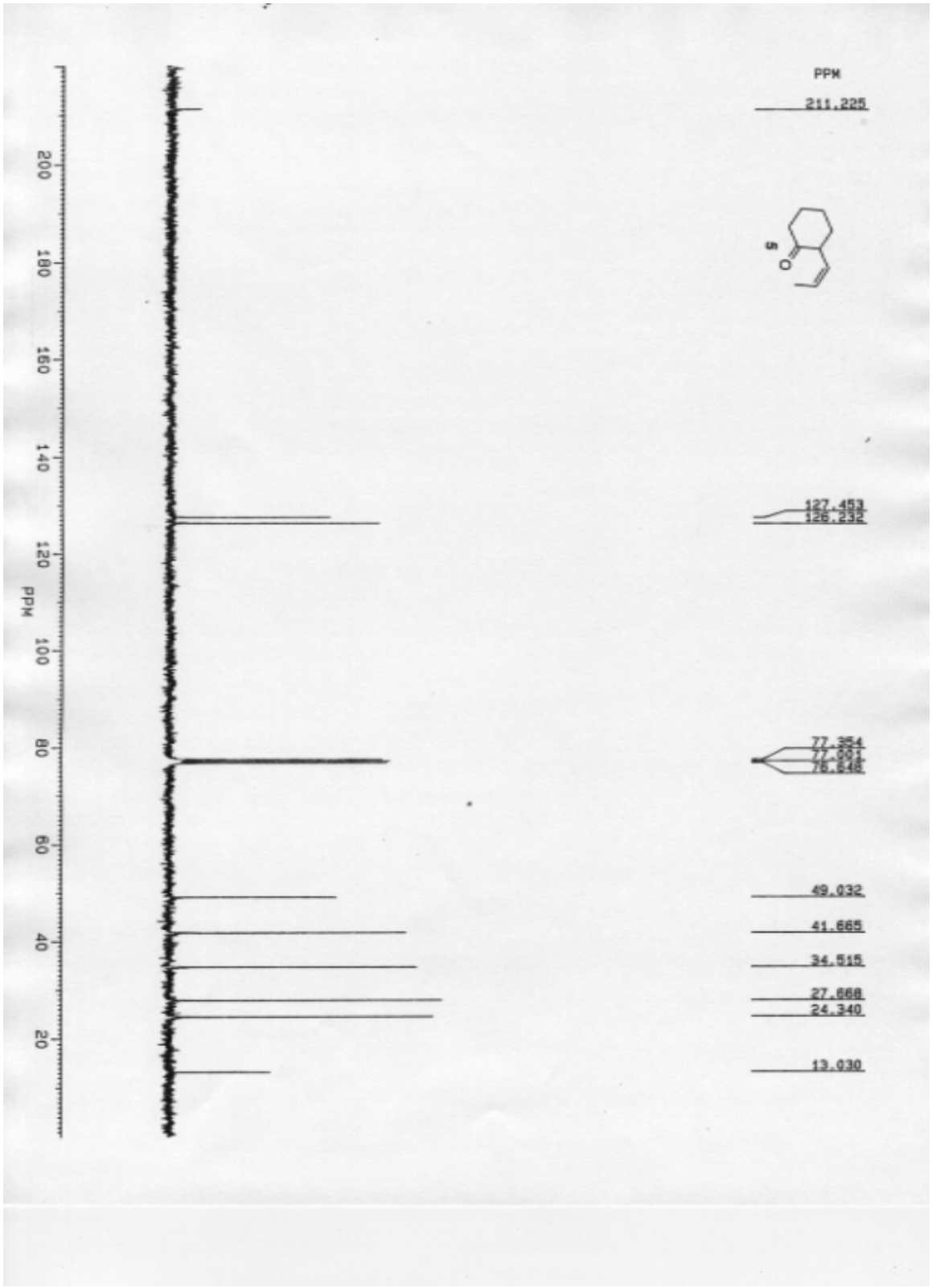
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM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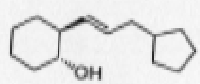
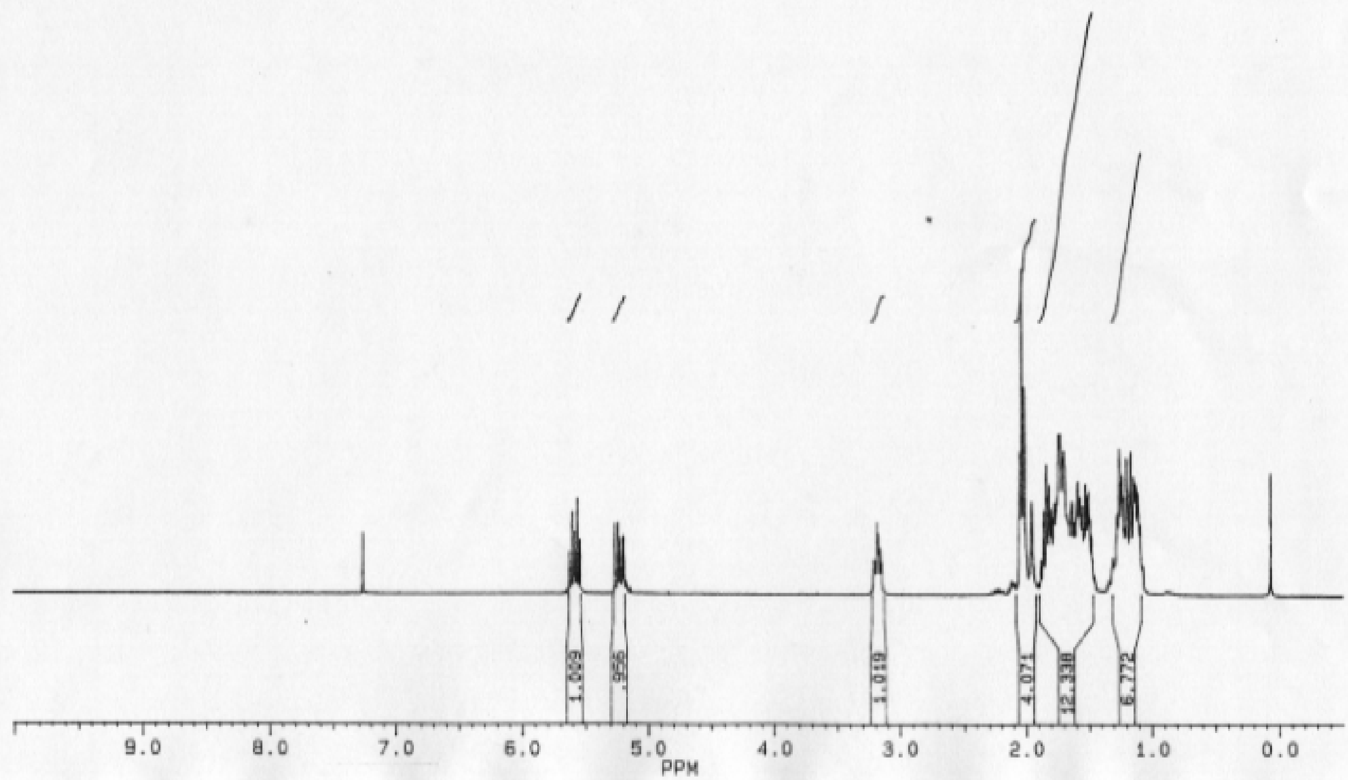
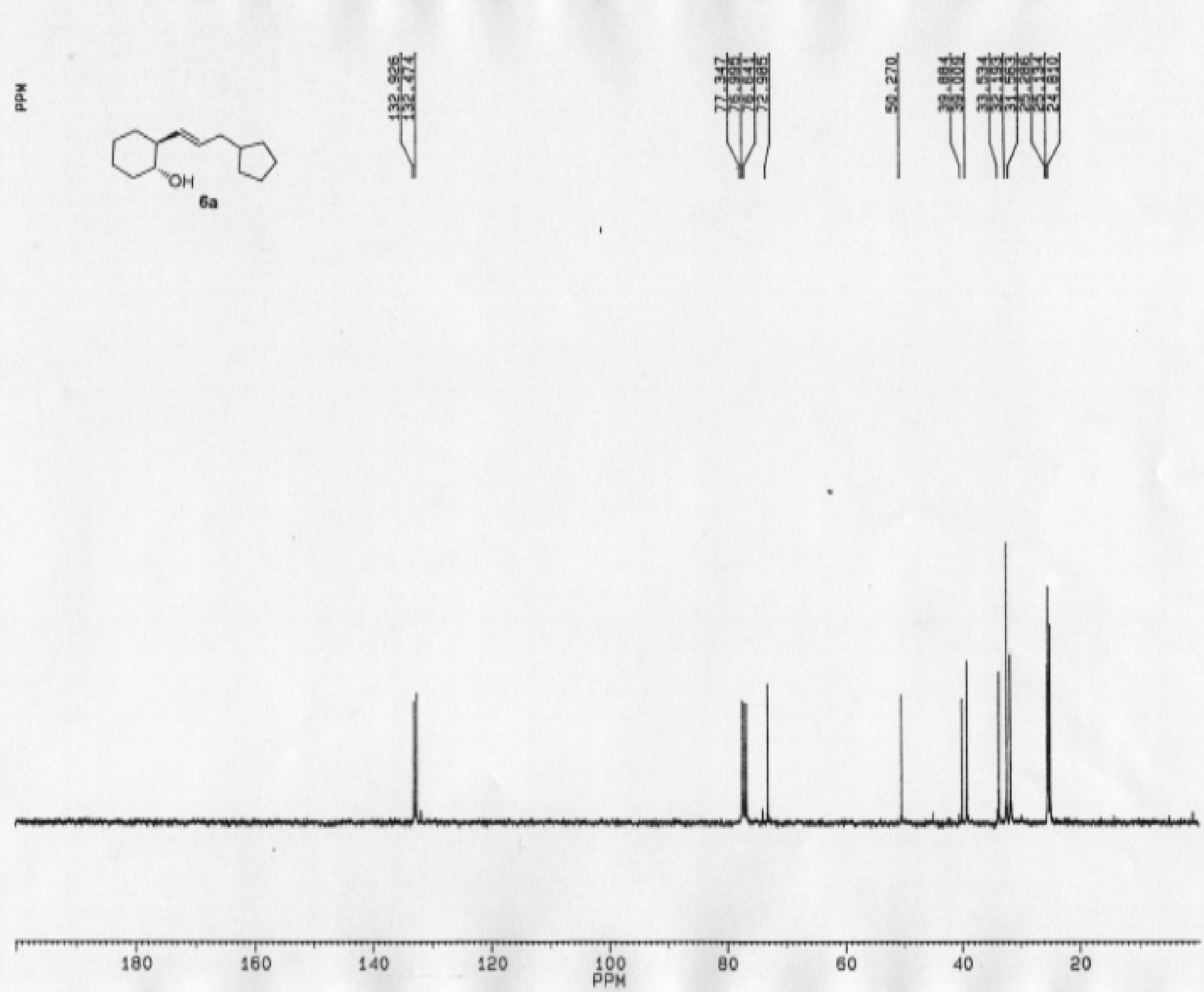
13.030
PPM
200
180
160
140
120
100
80
60
40
20
O



6a

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OH
6a
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77.347
76.641
72.985
50.270
39.009
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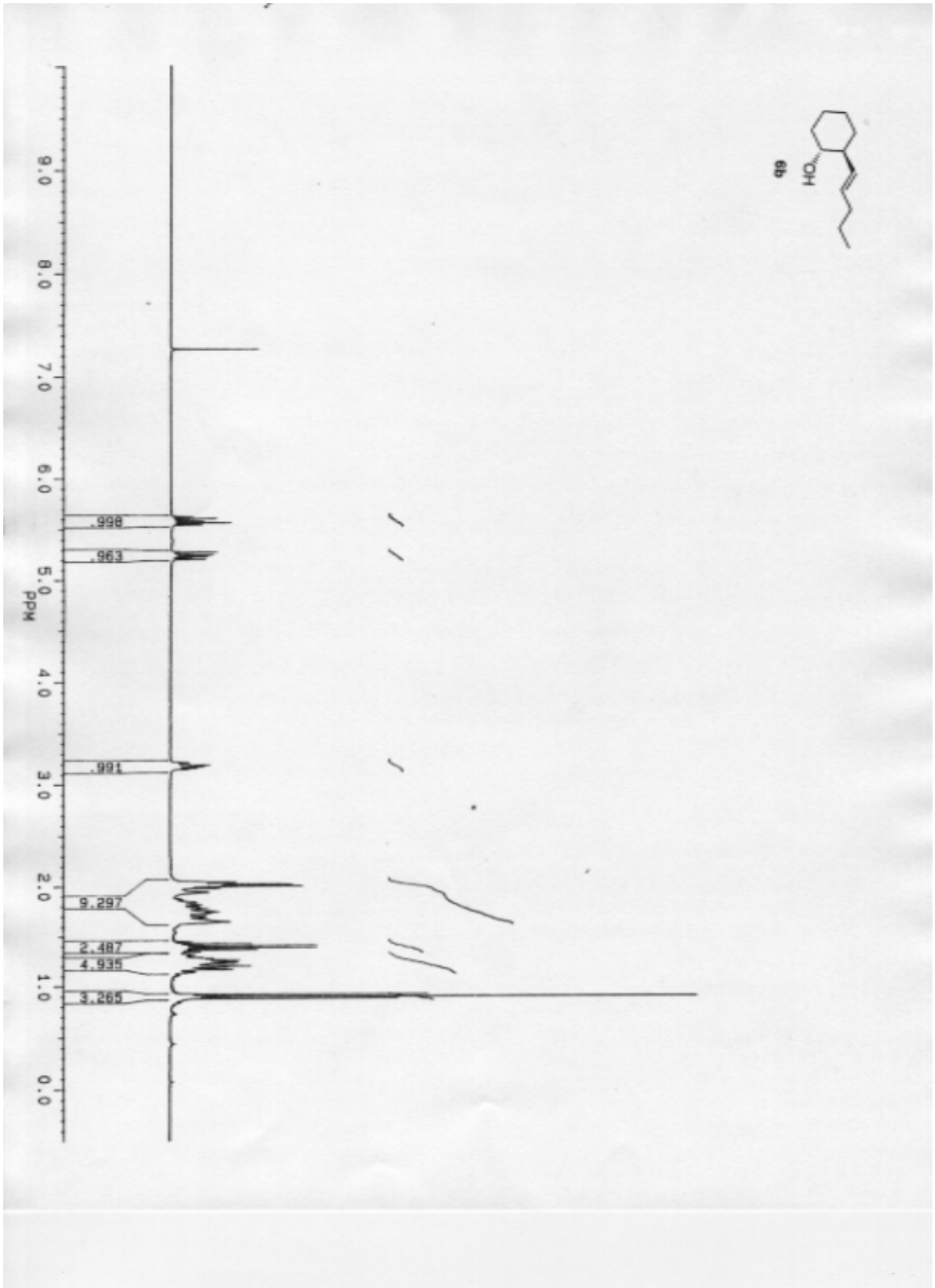
31.563
25.134
24.810
180
160
140
120
100
PPM
80
60
40
20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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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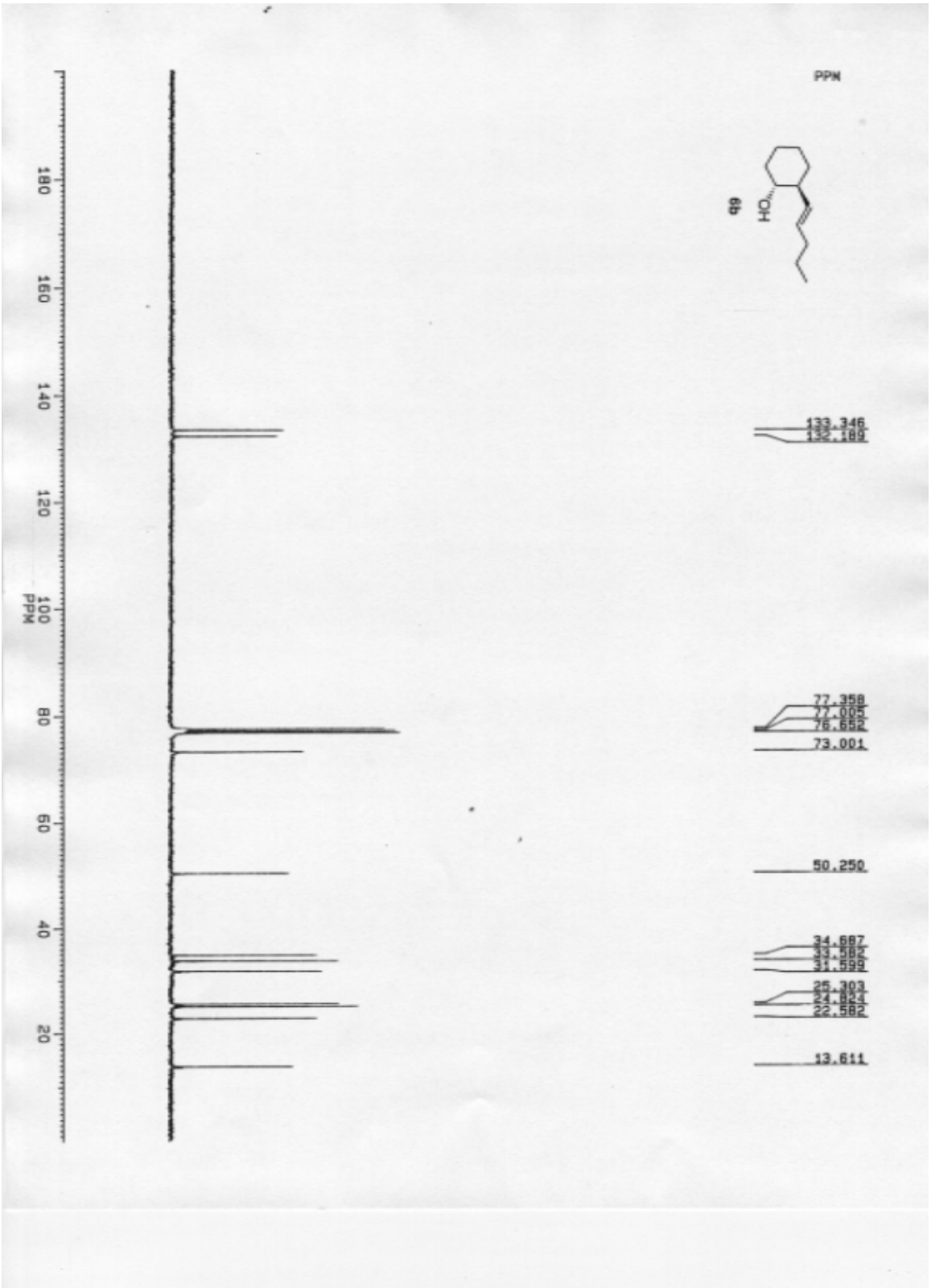
.991
9.297
2.487
4.935
3.265
OH
6b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69
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73.001
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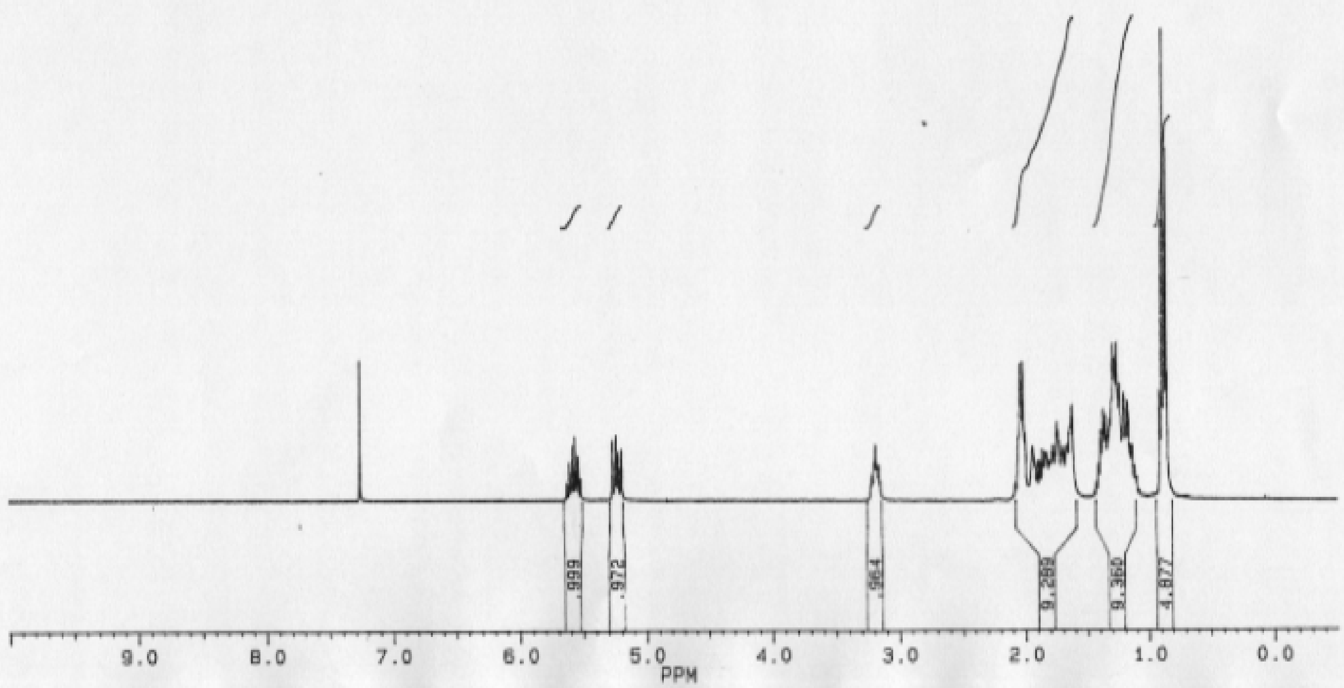
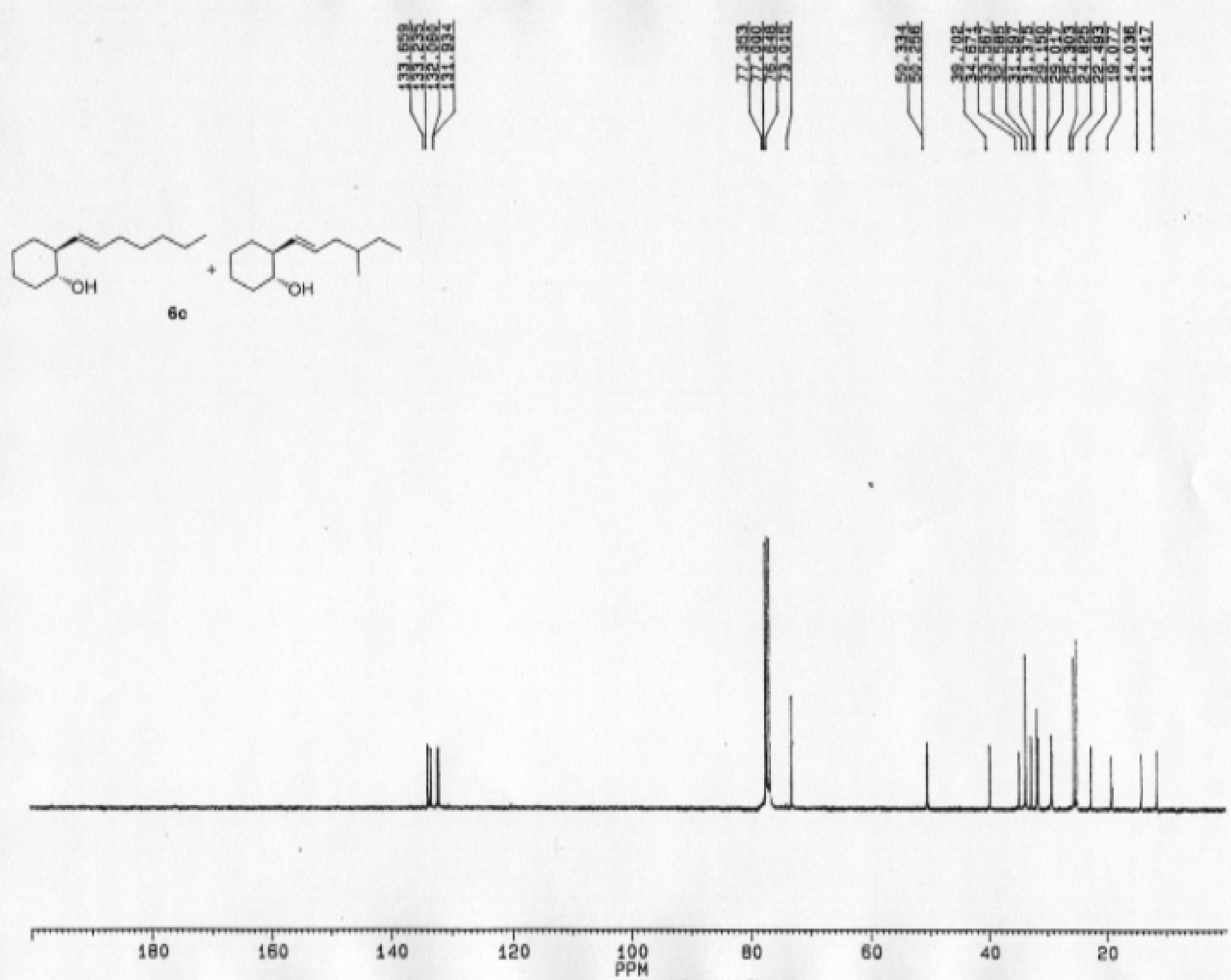
13.611
180
160
140
120
100
80
60
40
20
PPM

6c





6c
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77.000
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11.417
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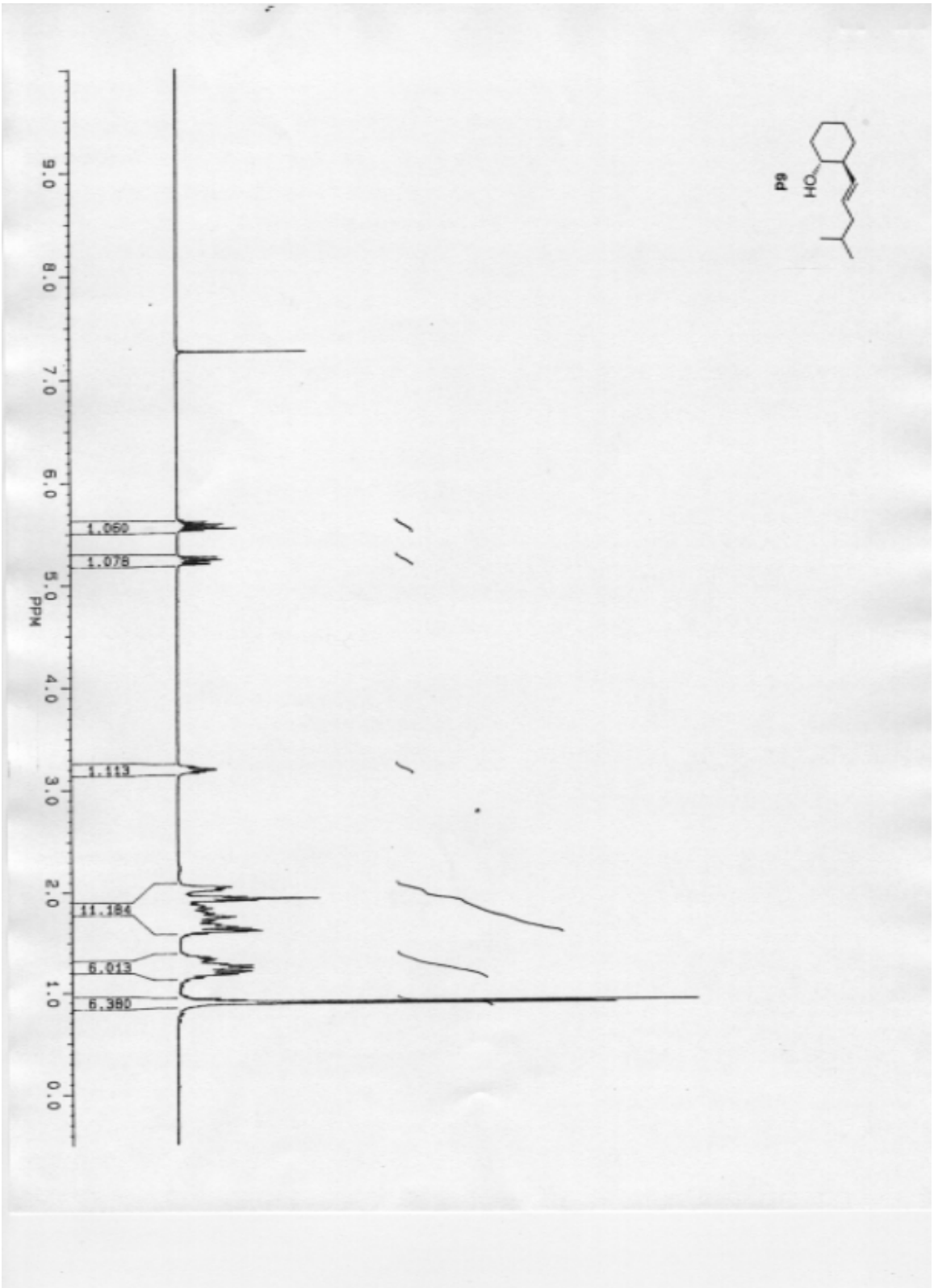
140
120
100
PPM
80
60
40
20


9d
HO
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
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PPM
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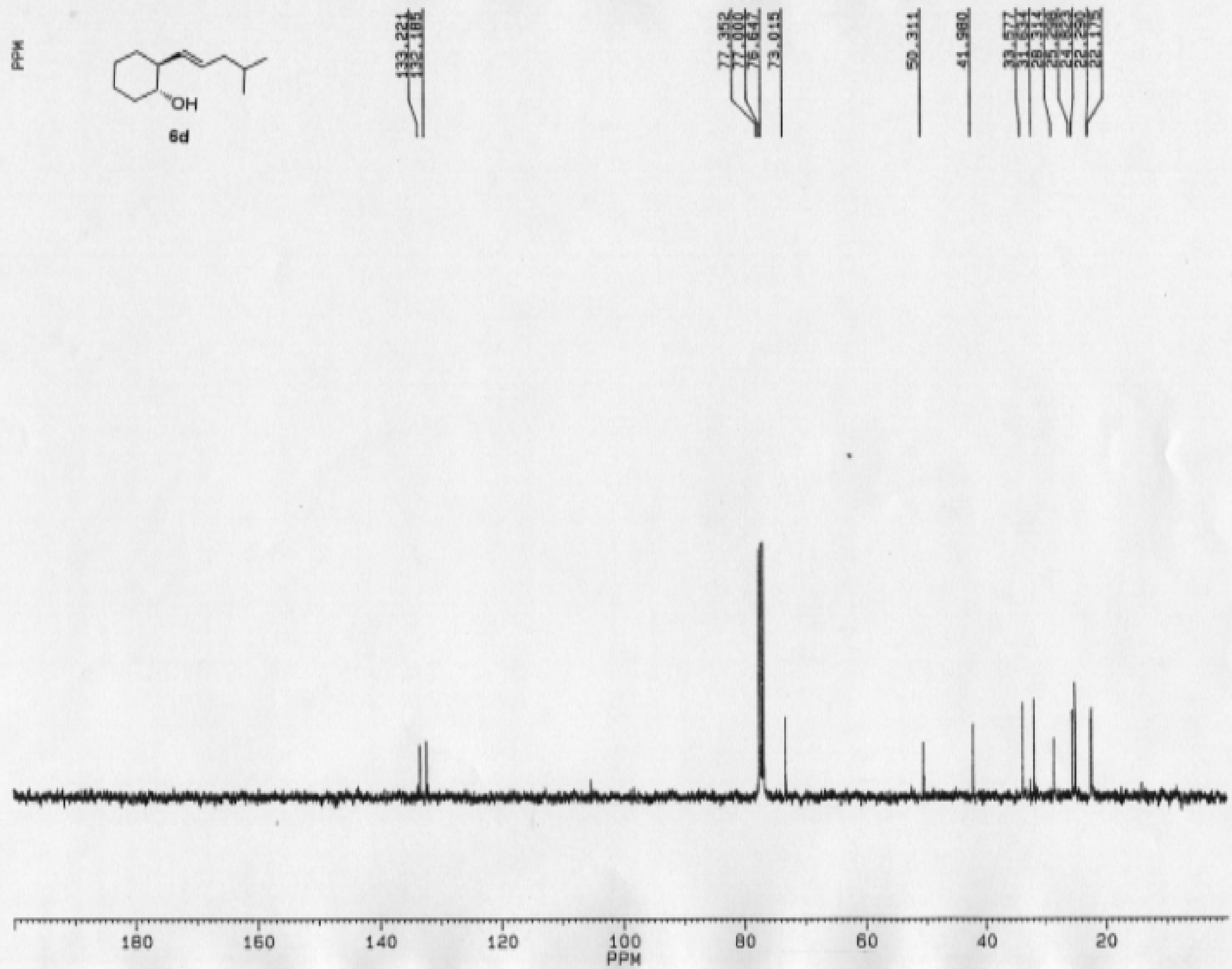
11.184
6.013
6.380


PPM
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6d
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76.647
73.015
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41.980
33.677
28.314
22.290
22.175
180
160
140
120
100
PPM
80
60
40
20