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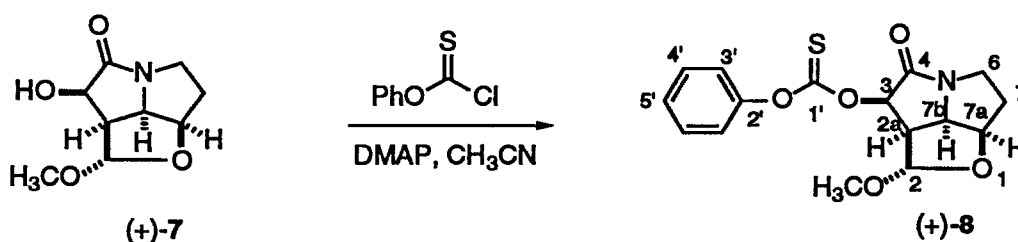
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## Tandem [4+2]/[3+2] Cycloadditions of Nitroalkenes. 13. Synthesis of (-)-Platynecine

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Supporting Information

**(2*S*,2*aR*,3*R*,7*aR*,7*bR*)-Hexahydro-2-methoxy-3-[(phenoxythiocarbonyl)-oxy]-furo[2,3,4-*gh*]-pyrrolizin-4[2*H*]-one (+)-8.**



### Analytical data for (+)-8

**M.W.** 335.38

**mp:** 140-141° C (Hexane/EtOAc)

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

7.45-7.40 (m, 2 H, HC(4')), 7.32-7.29 (m, 1 H, HC(5')), 7.17-7.14 (m, 2 H, HC(3')), 6.28 (d, *J* = 8.3, 1 H, HC(3)), 5.12 (s, 1 H, HC(2)), 4.68 (dd, *J* = 3.7, 3.7, 1 H, HC(7a)), 4.22 (dd, *J* = 5.6, 3.2, 1 H, HC(7b)), 4.04 (ddd, *J* = 13.8, 9.0, 6.8, 1 H, H<sub>a</sub>C(6)), 3.44 (dd, *J* = 8.3, 5.6, 1 H, HC(2a)), 3.34 (s, 3 H, H<sub>3</sub>C(8)), 3.12 (ddd, *J* = 15.4, 10.9, 4.5, 1 H, H<sub>b</sub>C(6)), 2.29-2.13 (m, 2 H, H<sub>2</sub>C(7)).

**<sup>13</sup>C NMR:** (100.6 MHz, CDCl<sub>3</sub>)

194.10 (C(1')), 170.52 (C(4)), 153.43 (C(2')), 129.56 (C(4')), 126.73 (C(5')), 121.67 (C(3')), 105.77 (C(2)), 81.67 (C(3)), 79.73 (C(7a)), 66.30 (C(7b)), 54.90 (C(8)), 49.62 (C(2a)), 42.99 (C(6)), 29.59 (C(7)).

**IR:** (CCl<sub>4</sub>)

2957 (m), 2928 (m), 2873 (w), 2858 (w), 1737 (s), 1491 (m), 1392 (w), 1336 (w), 1300 (m), 1282 (s), 1258 (m), 1245 (m), 1218 (s), 1209 (s), 1199 (s), 1118 (m), 1104 (m), 1080 (m), 1037 (w), 1024 (w), 1013 (m).

**MS:** (FAB)

336 (M<sup>+</sup>1, 93), 306 (35), 305 (56), 304 (89), 183 (56), 182 (30), 155 (32), 152 (41), 135 (48), 122 (100), 121 (31), 119 (69), 103 (58).

**TLC:** R<sub>f</sub> 0.33 (EtOAc/hexane, 2/1), [KMnO<sub>4</sub>]

**Rotation:**  $[\alpha]_D^{23} = +47.3$  (c = 0.90, CHCl<sub>3</sub>)

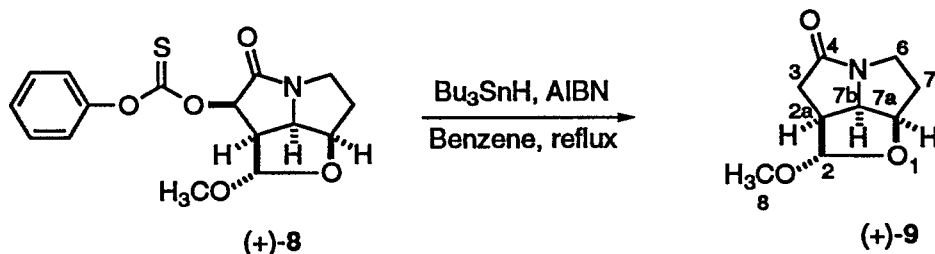
**HPLC:** Column: Regis, (R,R)-Whelko-01 (hexane/EtOAc, 70/30), 0.5 mL/min) t<sub>R</sub> (+)-8 19.0 min (98.6%); t<sub>R</sub> (-)-8 23.1 min (1.4%); 97% ee.

**Analysis:** (C<sub>16</sub>H<sub>17</sub>NO<sub>5</sub>S)

Calcd: C, 57.30; H, 5.11; N, 4.18; S, 9.56.

Found: C, 57.23; H, 5.04; N, 4.25; S, 9.31.

**(2S,2aS,7aR,7bR)-Hexahydro-2-methoxy-furo[2,3,4-gh]-pyrrolizin-4[2H]-one (+)-(-9).**



**Analytical data for (+)-9**

**M.W.** 183.21

**mp:** 94 -95° C (hexane/EtOAc)

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

4.74 (s, 1 H, HC(2)), 4.53 (dd, J = 4.6, 3.4, 1 H, HC(7a)), 4.29 (dd, J = 4.7, 3.4, 1 H, HC(7b)), 3.99-3.92 (m, 1 H, H<sub>2</sub>C(6)), 3.28 (s, 3 H, H<sub>3</sub>C(8)),

3.04 - 2.97 (m, 1H, H<sub>b</sub>C(6)), 2.92 (dd,  $J = 9.3, 7.8$ , H<sub>a</sub>C(3)), 2.82 (dd,  $J = 9.5, 6.2$ , 1 H, HC(2a)), 2.36 (d,  $J = 16.8$ , 1 H, H<sub>b</sub>C(3)), 2.24-2.12 (m, 2 H, H<sub>2</sub>C(7)).

**<sup>13</sup>C NMR:** (100.6 MHz, CDCl<sub>3</sub>)

177.28 (C(4)), 112.71 (C(2)), 81.20 (C(7a)), 70.19 (C(7b)), 54.36 (C(8)), 44.14 (C(2a)), 43.13 (C(6)), 37.57 (C(3)), 31.53 (C(7)).

**IR:** (CHCl<sub>3</sub>)

3028 (w), 3023(w), 3018 (m), 3013 (m), 3010 (m), 2957 (m), 2937 (w), 2914 (w), 1691 (s), 1400 (w), 1338 (w), 1289 (w), 1251 (w), 1234 (m), 1194 (m), 1104 (m), 1090 (m), 1061 (s), 1000 (s).

**MS:** (FAB)

184 (M<sup>+</sup>+H, 100), 152 (8), 119 (15).

**TLC:** R<sub>f</sub> 0.16 (EtOAc), [Anisaldehyde]

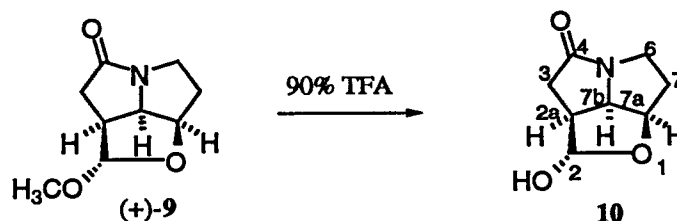
**Rotation:**  $[\alpha]_D^{22} = +146.3$  (c = 0.93, CHCl<sub>3</sub>)

**Analysis:** (C<sub>9</sub>H<sub>13</sub>NO<sub>3</sub>)

Calcd: C, 59.00 ; H, 7.15; N, 7.65.

Found: C, 58.86; H, 7.13; N, 7.66.

**(2a*S*,7a*R*,7b*R*)-Hexahydro-2-hydroxy-furo[2,3,4-*gh*]-pyrrolizin-4[2*H*]-one (10).**



**Analytical data for 10**

**M.W.** 169.18

**<sup>1</sup>H NMR:** (500 MHz, CD<sub>3</sub>OD)

5.37 (s, 1 H, HC(2)), 4.69 (dd,  $J = 4.9, 3.5$ , 1 H, HC(7a)), 4.43 (dd,  $J = 6.1, 3.4$ , 1 H, HC(7b)), 3.84 (ddd,  $J = 11.6, 9.2, 5.5$ , 1 H, H<sub>a</sub>C(6)), 3.06-2.98 (m, 2 H, H<sub>b</sub>C(6), H<sub>a</sub>C(3)), 2.82 (dd,  $J = 8.8, 6.2$ , 1 H, HC(2a)), 2.36 (d,  $J = 17.1$ , 1 H, H<sub>b</sub>C(3)), 2.29-2.22 (m, 1 H, H<sub>a</sub>C(7)) 2.11 (ddd,  $J = 14.4, 9.2, 5.1$ , 1 H, H<sub>b</sub>C(7)).

**<sup>13</sup>C NMR:** (125 MHz, CD<sub>3</sub>OD)

180.12 (C(4)), 107.59 (C(2)), 82.16 (C(7a)), 72.10 (C(7b)), 46.39 (C(2a)), 43.85 (C(6)), 38.77 (C(3)), 32.18 (C(7)).

**IR:** (CHCl<sub>3</sub>)

3040 (w), 3031 (m), 3025 (w), 1690 (s), 1411 (w), 1227 (m), 1219 (w), 1212 (w), 1200 (m).

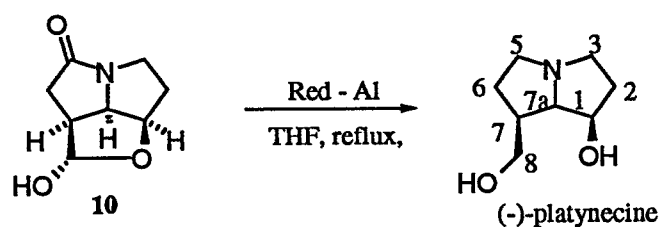
**MS:** (FAB)

170 (M<sup>+</sup>+1, 78), 155 (60), 152 (23), 135 (40), 119 (100), 103 (47).

**HRMS:** (FAB) Calcd for C<sub>8</sub>H<sub>12</sub>NO<sub>3</sub>, 170.081718. Found, 170.081800

**TLC:** R<sub>f</sub> 0.34 (10/1 CHCl<sub>3</sub>, CH<sub>3</sub>OH), [KMnO<sub>4</sub>]

**(-)-Platynecine (4).**



**Analytical data for (-)-4**

**M.W.** 157.2

**mp:** 145 -146° C (acetone)

**<sup>1</sup>H NMR:** (500 MHz, CD<sub>3</sub>OD)

4.23-4.22 (m, 1 H, HC(1)), 3.93 (d,  $J = 5.5$ , 2 H, H<sub>2</sub>C(8)), 3.24 (dd,  $J = 8.0$ , 3.2, 1 H, HC(7a)), 3.21-3.17 (m, 1 H, H<sub>a</sub>C(3)), 3.10-3.05 (m, 1 H, H<sub>a</sub>C(5)), 2.86-2.80 (m, 1 H, H<sub>b</sub>C(3)), 2.78-2.74 (m, 1 H, H<sub>b</sub>C(5)) 2.47-2.39 (m, 1 H, HC(7)), 2.02-1.94 (m, 1 H, H<sub>a</sub>C(6)), 1.90-1.82 (m, 2 H, H<sub>2</sub>C(2)), 1.74-1.68 (m, 1H, H<sub>b</sub>C(6)).

**<sup>13</sup>C NMR:** (125 MHz, CD<sub>3</sub>OD)

73.15 (C(1)), 72.62 (C(7a)), 61.73 (C(8)), 56.58 (C(5)), 54.81 (C(3)), 45.08 (C(7)), 37.33 (C(2)), 28.87 (C(6)).

**IR:** (CHCl<sub>3</sub>)

3329 (br), 3026 (s), 3021 (s), 3005 (s), 2972 (s), 2943 (s), 2882 (s), 1442 (w), 1351 (w), 1227 (m), 1216 (m), 1168 (w), 1124 (m), 1050 (w), 1011 (m).

**MS:** (FAB)

158 (M<sup>++</sup> 1, 100), 155 (30), 135 (20), 119 (52) 103 (24).

**TLC:** R<sub>f</sub> 0.09 (10/5/1, CHCl<sub>3</sub>, CH<sub>3</sub>OH, NH<sub>4</sub>OH), [KMnO<sub>4</sub>]

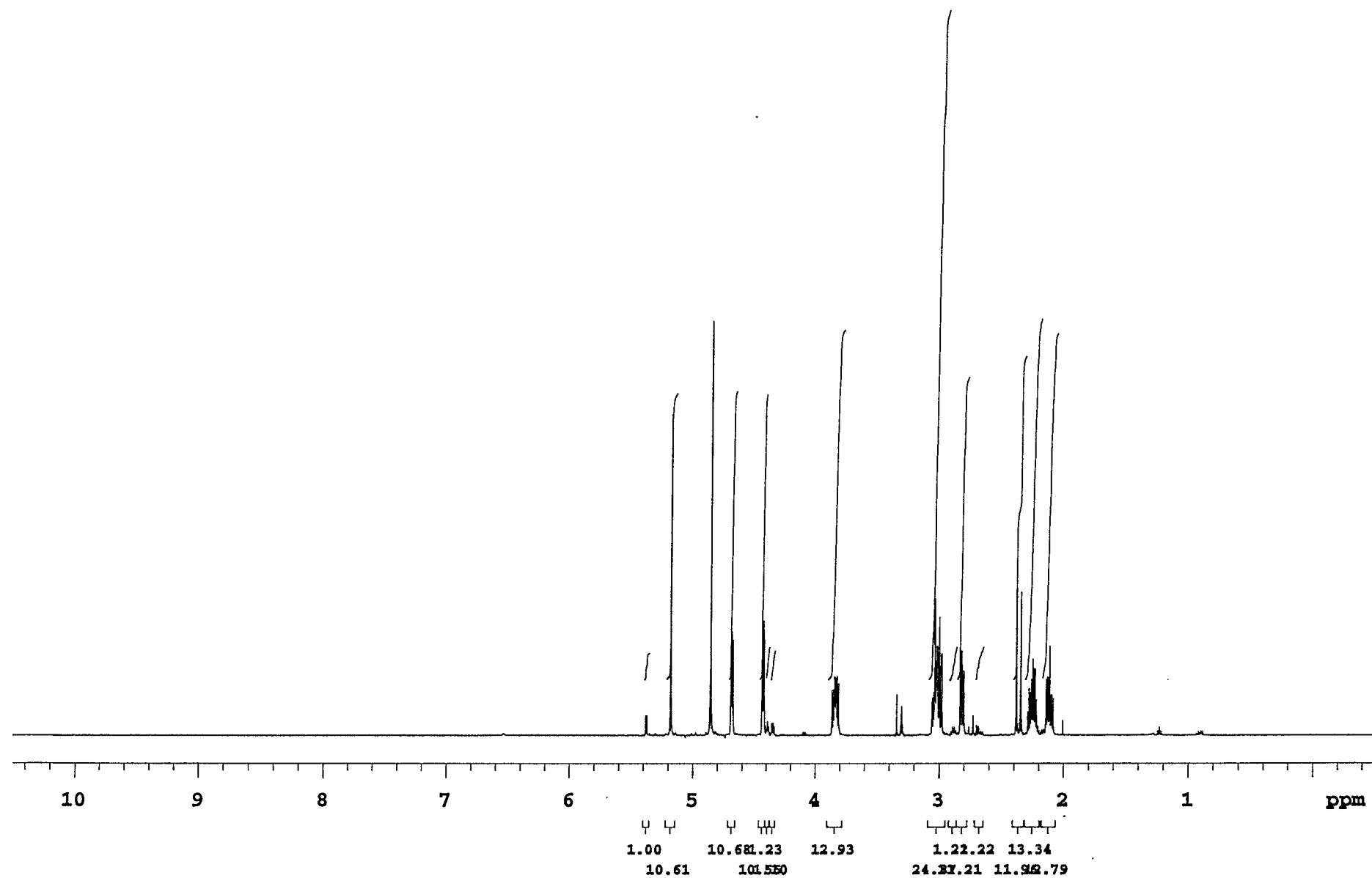
**Rotation:**  $[\alpha]_D^{22} = -61.5$  (c = 1.0, CHCl<sub>3</sub>)

**Analysis:** (C<sub>8</sub>H<sub>15</sub>NO<sub>2</sub>)

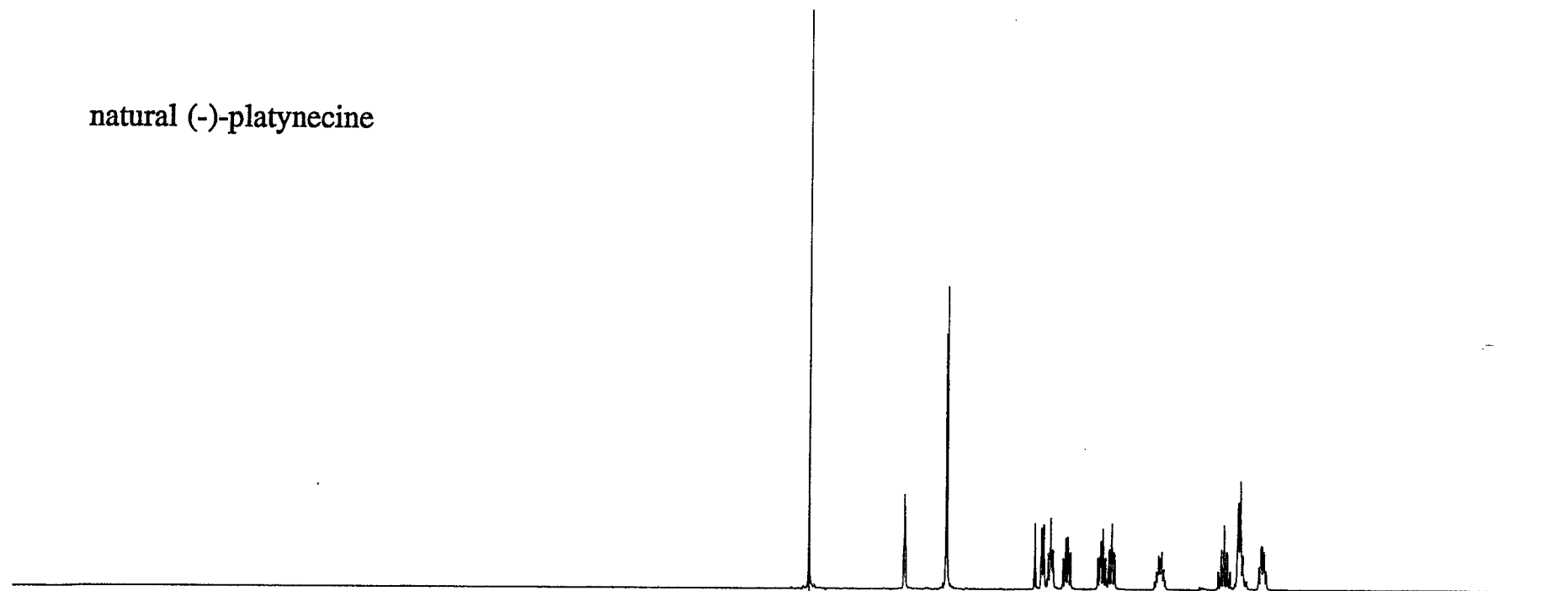
Calcd: C, 61.12 ; H, 9.62; N, 8.91.

Found: C, 61.12 ; H, 9.63; N, 8.71.

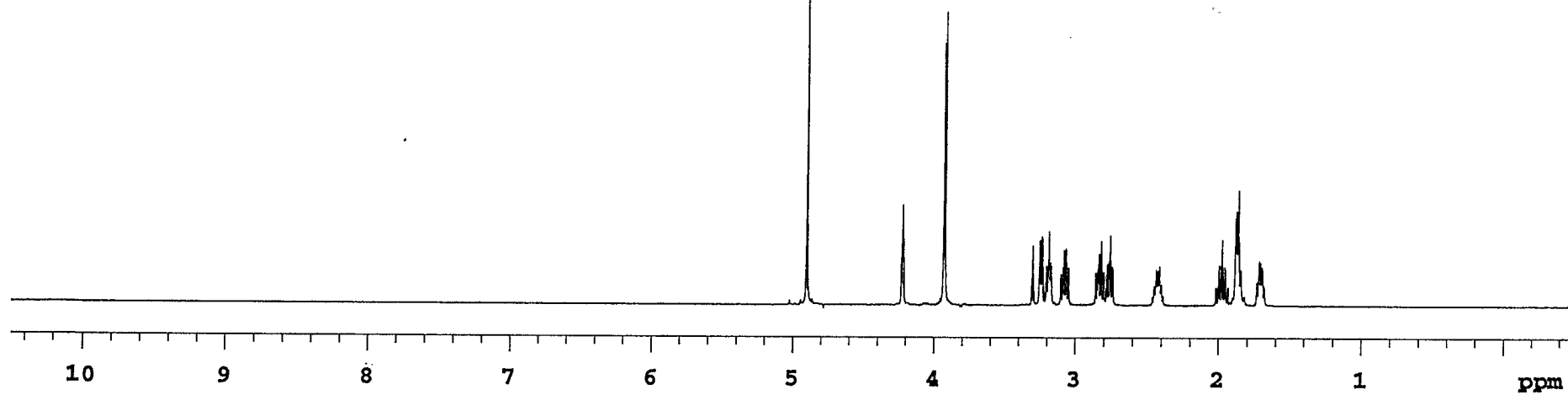
(2a*S*,7a*R*,7b*R*)-Hexahydro-2-hydroxy-furo[2,3,4-*gh*]-pyrrolizin-4[2*H*]-one (10)



natural (-)-platynecine



synthetic (-)-platynecine



10

9

8

7

6

5

4

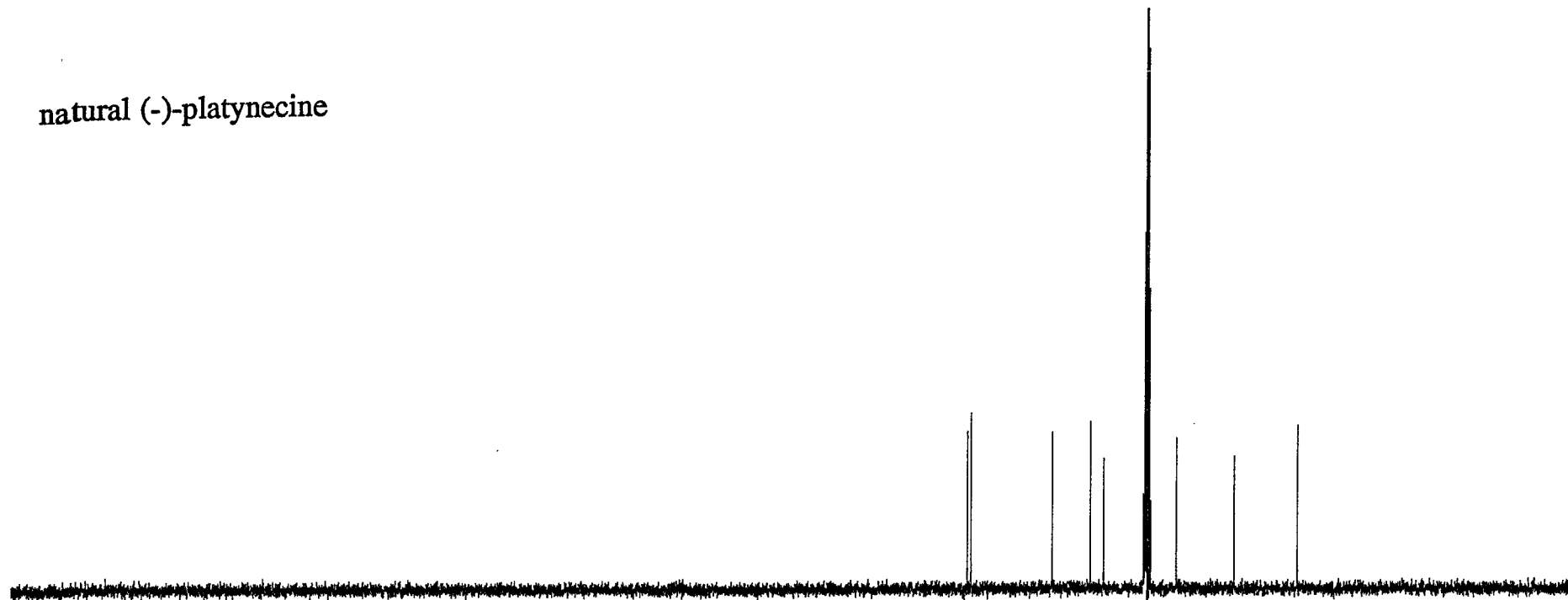
3

2

1

ppm

natural (-)-platynecine



synthetic (-)-platynecine

