

Electronic Supplementary Information

Effect of the allylic substituents on ring closing metathesis: The total synthesis of stagonolide B and 4-*epi*-stagonolide B

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Crystal Data for 2: Single crystals of the compound **2** were grown by slow evaporation a methanol solution of **2**. Colourless crystal of approximate size 0.14 x 0.05 x 0.02 mm, was used for data collection on *Bruker SMART APEX* CCD diffractometer using Mo-K α radiation with fine focus tube with 50kV and 30mA. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) was used for structure solution and full matrix least squares refinement on F². Hydrogen atoms were included in the refinement as per the riding model.

Table 1. Crystal data and structure refinement for 4-*epi*-stagonolide B.

| | |
|-----------------------------------|---|
| Empirical formula | C ₁₂ H ₂₀ O ₅ |
| Formula weight | 244.28 |
| Temperature | 295(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, C2 |
| Unit cell dimensions | a = 16.861(15) Å alpha = 90 deg. b = 4.981(4) Å beta = 112.087(14) deg. c = 16.109(14) Å gamma = 90 deg. |
| Volume | 1253.7(19) Å ³ |
| Z, Calculated density | 4, 1.294 Mg/m ³ |
| Absorption coefficient | 0.100 mm ⁻¹ |
| F(000) | 528 |
| Crystal size | 0.14 x 0.05 x 0.02 mm |
| Theta range for data collection | 1.36 to 25.00 deg. |
| Limiting indices | -20 ≤ h ≤ 19, -5 ≤ k ≤ 5, -15 ≤ l ≤ 19 |
| Reflections collected / unique | 5114 / 2177 [R(int) = 0.1106] |
| Completeness to theta | = 25.00 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9979 and 0.9864 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 2177 / 1 / 158 |
| Goodness-of-fit on F ² | 0.835 |
| Final R indices [I > 2σ(I)] | R1 = 0.0720, wR2 = 0.1554 |
| R indices (all data) | R1 = 0.1490, wR2 = 0.1731 |
| Absolute structure parameter | 5(3) |
| Largest diff. peak and hole | 0.277 and -0.275 e.Å ⁻³ |

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4-*epi*-stagonolide B. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | $U(\text{eq})$ |
|-------|---------|----------|---------|----------------|
| O(1) | 2588(2) | 6950(8) | 2109(3) | 38(1) |
| O(2) | 2028(3) | 11014(9) | 2140(4) | 60(2) |
| O(3) | 698(3) | 7078(8) | 4019(3) | 44(1) |
| O(4) | 3724(3) | 10129(8) | 4195(3) | 40(1) |
| O(5) | 4829(2) | 7019(8) | 3612(3) | 42(1) |
| C(1) | 1940(4) | 8615(16) | 2048(4) | 40(2) |
| C(2) | 1124(3) | 7182(13) | 1852(4) | 39(2) |
| C(3) | 715(4) | 7809(12) | 2533(4) | 42(2) |
| C(4) | 1188(4) | 6654(13) | 3467(4) | 38(2) |
| C(5) | 2070(4) | 7689(12) | 3863(4) | 38(2) |
| C(6) | 2751(4) | 6297(11) | 3892(4) | 36(2) |
| C(7) | 3634(4) | 7232(12) | 4079(4) | 39(2) |
| C(8) | 3928(3) | 6572(12) | 3335(4) | 34(2) |
| C(9) | 3460(4) | 7943(12) | 2434(4) | 37(2) |
| C(10) | 3813(4) | 7322(14) | 1735(4) | 45(2) |
| C(11) | 3381(5) | 8698(16) | 844(4) | 63(2) |
| C(12) | 3790(5) | 8050(20) | 172(5) | 95(3) |

Table 3. Bond lengths [\AA] and angles [deg] for 4-*epi*-stagonolide B.

| | |
|------------|----------|
| O(1)-C(1) | 1.346(8) |
| O(1)-C(9) | 1.450(7) |
| O(2)-C(1) | 1.207(8) |
| O(3)-C(4) | 1.439(6) |
| O(3)-H(3') | 0.8200 |
| O(4)-C(7) | 1.456(7) |
| O(4)-H(4') | 0.8200 |
| O(5)-C(8) | 1.431(6) |
| O(5)-H(5') | 0.8200 |
| C(1)-C(2) | 1.476(9) |
| C(2)-C(3) | 1.531(7) |
| C(2)-H(2A) | 0.9700 |
| C(2)-H(2B) | 0.9700 |
| C(3)-C(4) | 1.526(8) |
| C(3)-H(3A) | 0.9700 |

| | |
|------------------|-----------|
| C(3)-H(3B) | 0.9700 |
| C(4)-C(5) | 1.473(7) |
| C(4)-H(4) | 0.9800 |
| C(5)-C(6) | 1.328(7) |
| C(5)-H(5) | 0.9300 |
| C(6)-C(7) | 1.478(8) |
| C(6)-H(6) | 0.9300 |
| C(7)-C(8) | 1.496(8) |
| C(7)-H(7) | 0.9800 |
| C(8)-C(9) | 1.527(8) |
| C(8)-H(8) | 0.9800 |
| C(9)-C(10) | 1.490(8) |
| C(9)-H(9) | 0.9800 |
| C(10)-C(11) | 1.508(9) |
| C(10)-H(10A) | 0.9700 |
| C(10)-H(10B) | 0.9700 |
| C(11)-C(12) | 1.521(10) |
| C(11)-H(11A) | 0.9700 |
| C(11)-H(11B) | 0.9700 |
| C(12)-H(12A) | 0.9600 |
| C(12)-H(12B) | 0.9600 |
| C(12)-H(12C) | 0.9600 |
| | |
| C(1)-O(1)-C(9) | 120.1(5) |
| C(4)-O(3)-H(3') | 109.5 |
| C(7)-O(4)-H(4') | 109.5 |
| C(8)-O(5)-H(5') | 109.5 |
| O(2)-C(1)-O(1) | 122.8(6) |
| O(2)-C(1)-C(2) | 124.6(7) |
| O(1)-C(1)-C(2) | 112.6(6) |
| C(1)-C(2)-C(3) | 112.6(5) |
| C(1)-C(2)-H(2A) | 109.1 |
| C(3)-C(2)-H(2A) | 109.1 |
| C(1)-C(2)-H(2B) | 109.1 |
| C(3)-C(2)-H(2B) | 109.1 |
| H(2A)-C(2)-H(2B) | 107.8 |
| C(4)-C(3)-C(2) | 114.8(5) |
| C(4)-C(3)-H(3A) | 108.6 |
| C(2)-C(3)-H(3A) | 108.6 |
| C(4)-C(3)-H(3B) | 108.6 |
| C(2)-C(3)-H(3B) | 108.6 |
| H(3A)-C(3)-H(3B) | 107.5 |
| O(3)-C(4)-C(5) | 113.6(5) |
| O(3)-C(4)-C(3) | 110.2(5) |
| C(5)-C(4)-C(3) | 111.4(5) |

| | |
|---------------------|----------|
| O(3)-C(4)-H(4) | 107.1 |
| C(5)-C(4)-H(4) | 107.1 |
| C(3)-C(4)-H(4) | 107.1 |
| C(6)-C(5)-C(4) | 123.4(5) |
| C(6)-C(5)-H(5) | 118.3 |
| C(4)-C(5)-H(5) | 118.3 |
| C(5)-C(6)-C(7) | 129.3(5) |
| C(5)-C(6)-H(6) | 115.3 |
| C(7)-C(6)-H(6) | 115.3 |
| O(4)-C(7)-C(6) | 112.8(5) |
| O(4)-C(7)-C(8) | 105.6(5) |
| C(6)-C(7)-C(8) | 112.2(5) |
| O(4)-C(7)-H(7) | 108.7 |
| C(6)-C(7)-H(7) | 108.7 |
| C(8)-C(7)-H(7) | 108.7 |
| O(5)-C(8)-C(7) | 110.4(5) |
| O(5)-C(8)-C(9) | 109.6(5) |
| C(7)-C(8)-C(9) | 117.1(5) |
| O(5)-C(8)-H(8) | 106.4 |
| C(7)-C(8)-H(8) | 106.4 |
| C(9)-C(8)-H(8) | 106.4 |
| O(1)-C(9)-C(10) | 107.1(5) |
| O(1)-C(9)-C(8) | 106.4(5) |
| C(10)-C(9)-C(8) | 114.5(5) |
| O(1)-C(9)-H(9) | 109.5 |
| C(10)-C(9)-H(9) | 109.5 |
| C(8)-C(9)-H(9) | 109.5 |
| C(9)-C(10)-C(11) | 116.0(5) |
| C(9)-C(10)-H(10A) | 108.3 |
| C(11)-C(10)-H(10A) | 108.3 |
| C(9)-C(10)-H(10B) | 108.3 |
| C(11)-C(10)-H(10B) | 108.3 |
| H(10A)-C(10)-H(10B) | 107.4 |
| C(10)-C(11)-C(12) | 113.3(6) |
| C(10)-C(11)-H(11A) | 108.9 |
| C(12)-C(11)-H(11A) | 108.9 |
| C(10)-C(11)-H(11B) | 108.9 |
| C(12)-C(11)-H(11B) | 108.9 |
| H(11A)-C(11)-H(11B) | 107.7 |
| C(11)-C(12)-H(12A) | 109.5 |
| C(11)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(11)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |

Table 4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 4-*epi*-stagonolide B..
 The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U11 + \dots + 2 h k a^* b^* U12]$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|-------|--------|---------|--------|--------|-------|-------|
| O(1) | 36(2) | 27(2) | 48(2) | 1(2) | 11(2) | 8(2) |
| O(2) | 67(3) | 17(3) | 102(4) | 6(3) | 41(3) | 9(2) |
| O(3) | 49(3) | 32(3) | 62(3) | 8(3) | 32(2) | 5(3) |
| O(4) | 53(3) | 26(2) | 36(3) | 0(2) | 11(2) | -6(2) |
| O(5) | 33(2) | 29(2) | 62(3) | -6(3) | 17(2) | -1(2) |
| C(1) | 39(4) | 50(5) | 28(4) | 10(4) | 7(3) | 0(4) |
| C(2) | 42(4) | 30(4) | 43(4) | -13(4) | 13(3) | 6(4) |
| C(3) | 40(4) | 28(4) | 50(4) | 1(3) | 8(3) | 0(3) |
| C(4) | 50(4) | 27(4) | 42(4) | -4(3) | 24(3) | 4(3) |
| C(5) | 40(4) | 30(4) | 39(4) | -4(3) | 11(3) | -1(3) |
| C(6) | 42(4) | 15(3) | 47(4) | 5(3) | 14(3) | 4(3) |
| C(7) | 37(4) | 29(4) | 49(4) | 8(4) | 15(3) | 5(3) |
| C(8) | 36(4) | 20(3) | 47(4) | 3(3) | 17(3) | 4(3) |
| C(9) | 33(4) | 28(4) | 42(4) | -4(3) | 5(3) | 2(3) |
| C(10) | 42(4) | 47(5) | 49(4) | 4(4) | 19(3) | 7(4) |
| C(11) | 82(6) | 61(5) | 45(4) | 7(4) | 23(4) | -4(4) |
| C(12) | 100(7) | 142(10) | 57(5) | 13(6) | 47(5) | -6(6) |

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 4-*epi*-stagonolide B..

| | x | y | z | U(eq) |
|-------|------|-------|------|-------|
| H(3') | 616 | 8690 | 4052 | 66 |
| H(4') | 3913 | 10492 | 4730 | 60 |
| H(5') | 4937 | 8599 | 3752 | 62 |
| H(2A) | 1224 | 5265 | 1852 | 47 |
| H(2B) | 728 | 7678 | 1259 | 47 |
| H(3A) | 681 | 9743 | 2583 | 50 |

| | | | | |
|--------|------|-------|------|-----|
| H(3B) | 134 | 7117 | 2306 | 50 |
| H(4) | 1228 | 4709 | 3399 | 45 |
| H(5) | 2154 | 9408 | 4107 | 45 |
| H(6) | 2660 | 4470 | 3777 | 43 |
| H(7) | 4019 | 6363 | 4629 | 46 |
| H(8) | 3839 | 4639 | 3228 | 40 |
| H(9) | 3460 | 9890 | 2521 | 44 |
| H(10A) | 3778 | 5398 | 1636 | 54 |
| H(10B) | 4414 | 7808 | 1967 | 54 |
| H(11A) | 3400 | 10624 | 939 | 75 |
| H(11B) | 2784 | 8163 | 595 | 75 |
| H(12A) | 4402 | 8082 | 468 | 142 |
| H(12B) | 3616 | 9361 | -299 | 142 |
| H(12C) | 3611 | 6299 | -76 | 142 |

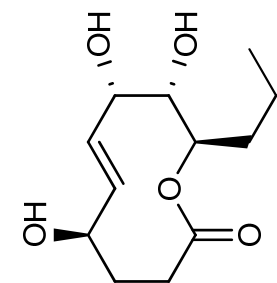
Table 6. Torsion angles [deg] for 4-*epi*-stagonolide B..

| | |
|------------------------|-----------|
| C(9)-O(1)-C(1)-O(2) | 10.0(9) |
| C(9)-O(1)-C(1)-C(2) | -170.3(5) |
| O(2)-C(1)-C(2)-C(3) | -54.6(9) |
| O(1)-C(1)-C(2)-C(3) | 125.7(6) |
| C(1)-C(2)-C(3)-C(4) | -69.8(8) |
| C(2)-C(3)-C(4)-O(3) | -173.0(5) |
| C(2)-C(3)-C(4)-C(5) | 59.9(7) |
| O(3)-C(4)-C(5)-C(6) | 133.4(6) |
| C(3)-C(4)-C(5)-C(6) | -101.5(7) |
| C(4)-C(5)-C(6)-C(7) | 165.2(6) |
| C(5)-C(6)-C(7)-O(4) | -3.9(9) |
| C(5)-C(6)-C(7)-C(8) | -123.0(7) |
| O(4)-C(7)-C(8)-O(5) | 68.2(6) |
| C(6)-C(7)-C(8)-O(5) | -168.6(5) |
| O(4)-C(7)-C(8)-C(9) | -58.1(6) |
| C(6)-C(7)-C(8)-C(9) | 65.1(7) |
| C(1)-O(1)-C(9)-C(10) | -124.5(5) |
| C(1)-O(1)-C(9)-C(8) | 112.5(5) |
| O(5)-C(8)-C(9)-O(1) | 168.2(4) |
| C(7)-C(8)-C(9)-O(1) | -65.0(6) |
| O(5)-C(8)-C(9)-C(10) | 50.1(7) |
| C(7)-C(8)-C(9)-C(10) | 176.8(5) |
| O(1)-C(9)-C(10)-C(11) | 63.8(7) |
| C(8)-C(9)-C(10)-C(11) | -178.5(5) |
| C(9)-C(10)-C(11)-C(12) | 178.1(6) |

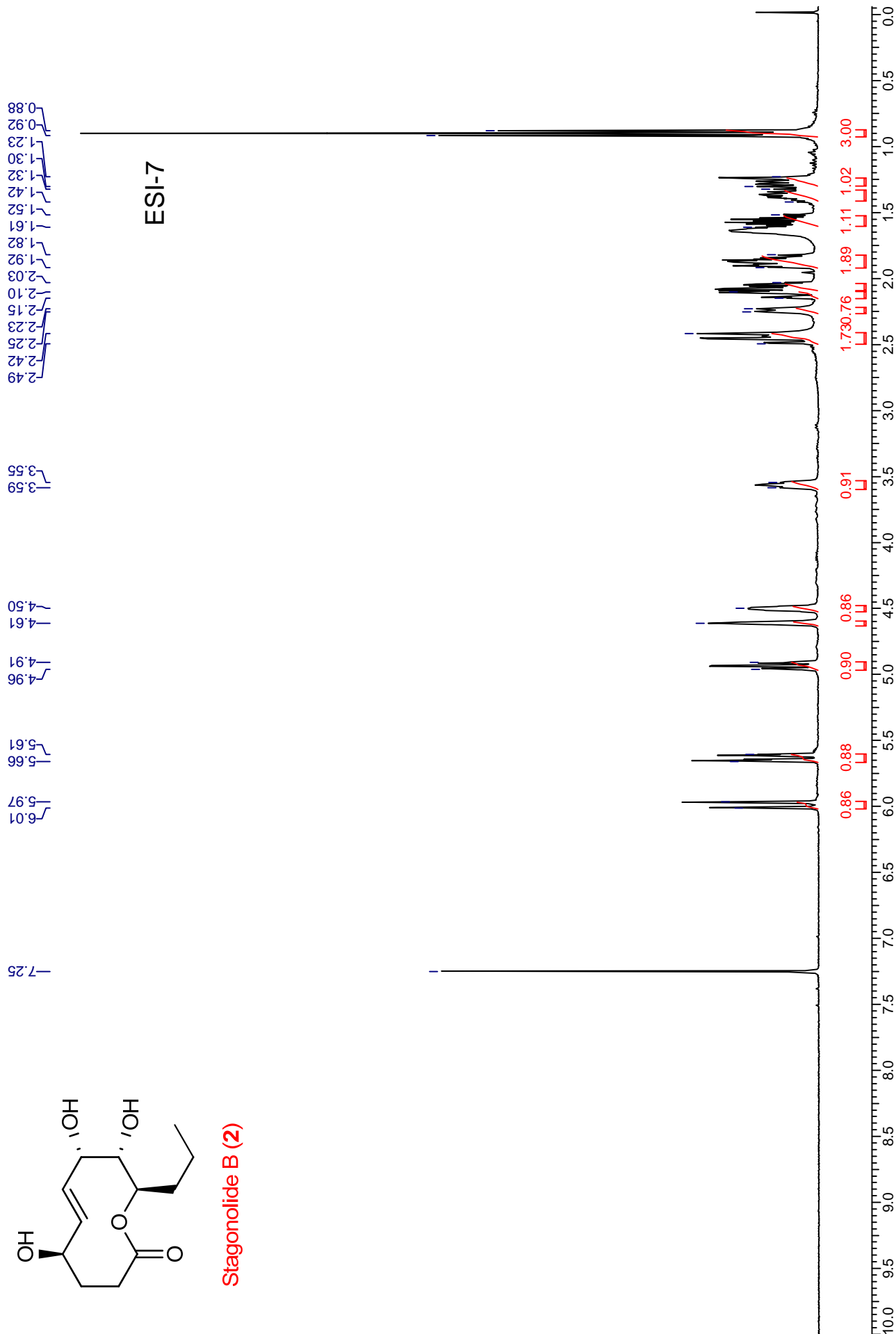
4 Aug 2009

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Chloroform-d

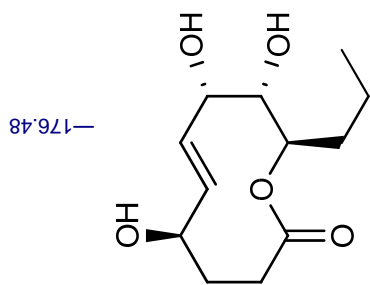


Stagonolide B (2)

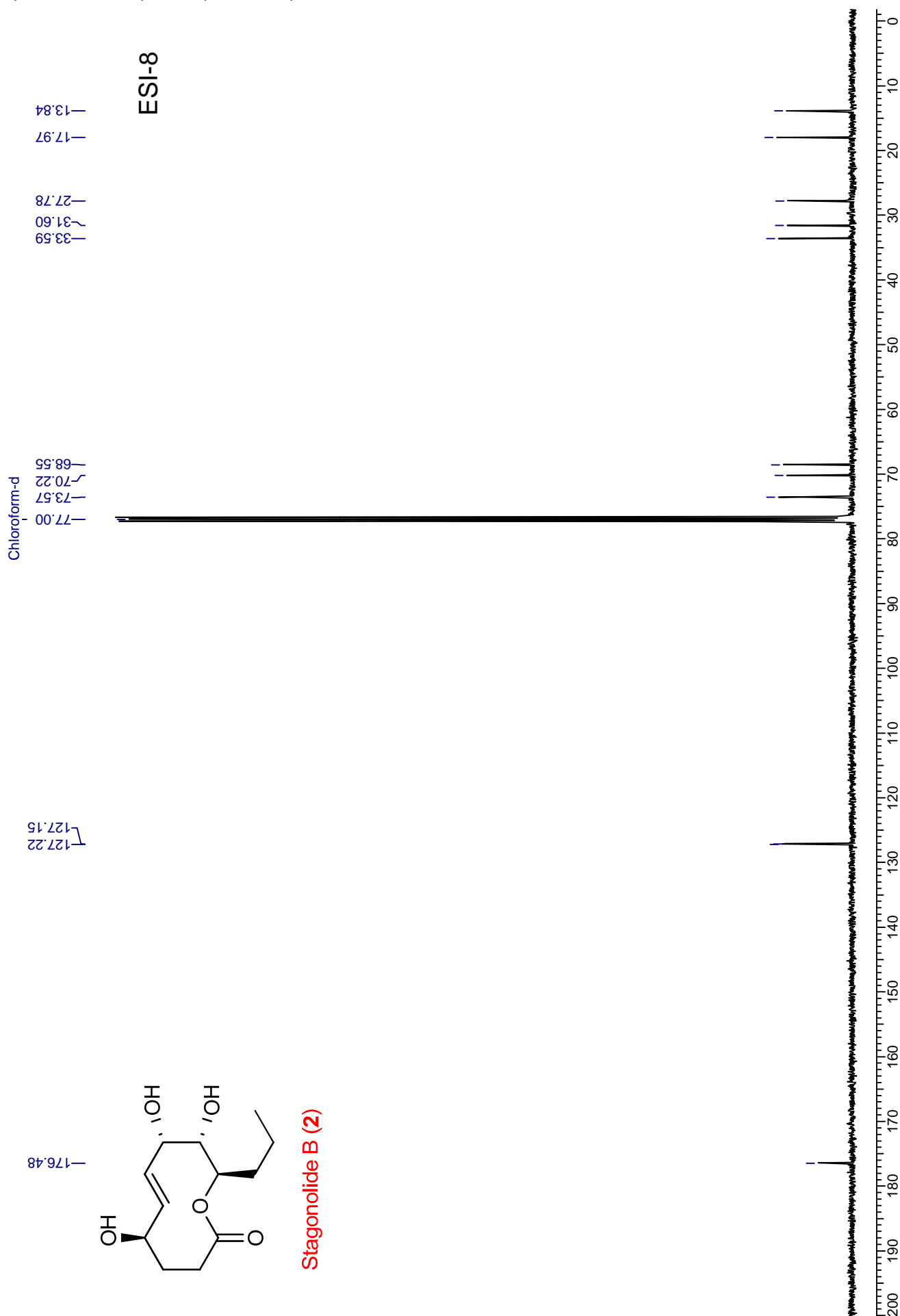


4 Aug 2009

| | | | | | | | |
|------------------------|--------|--------------|---------------------|------------------|----------|----------------------|-----------------|
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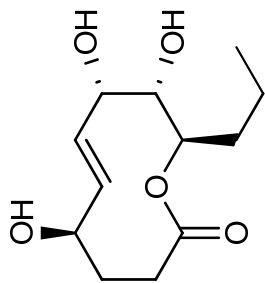


Stagonolide B (2)

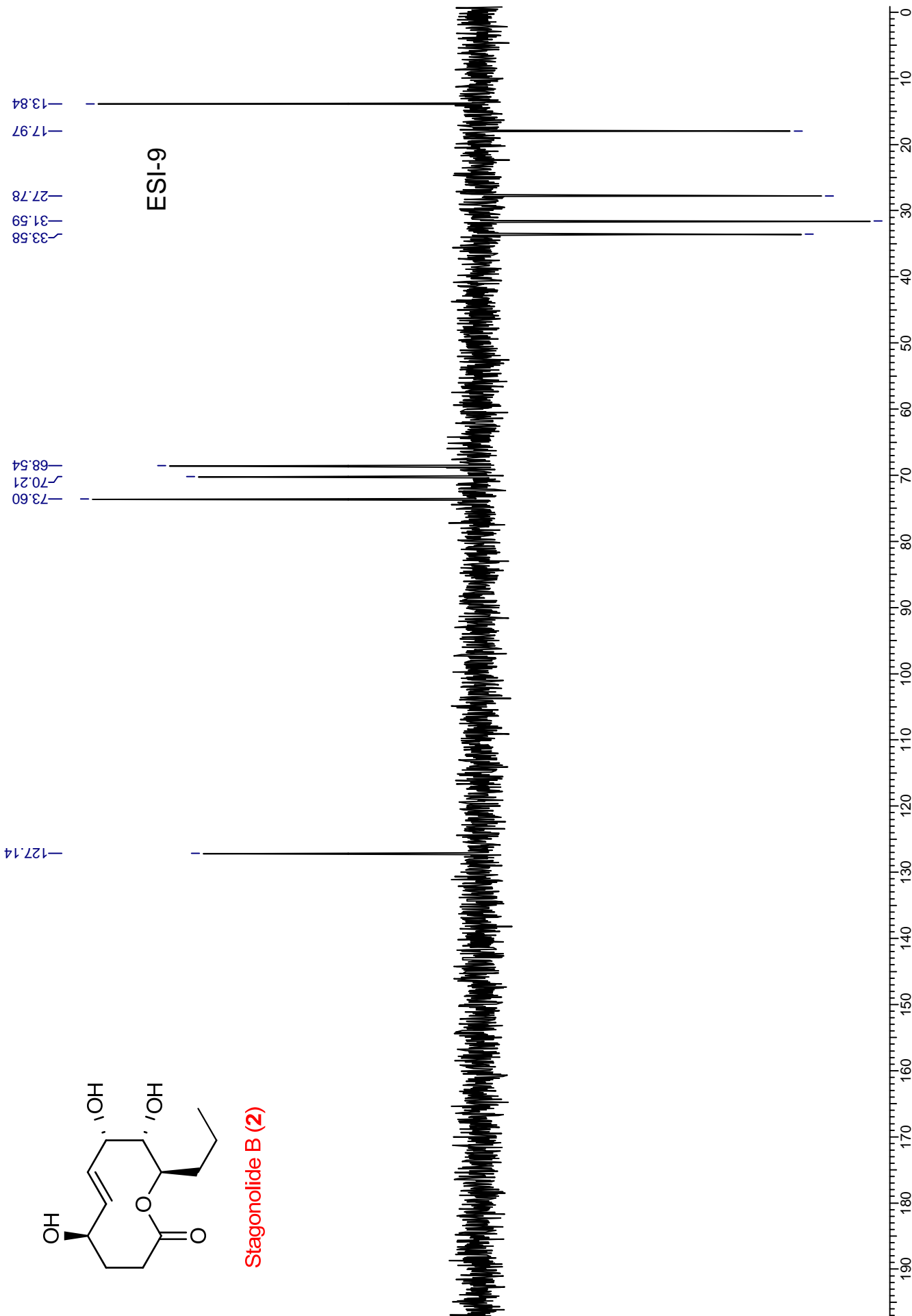


4 Aug 2009

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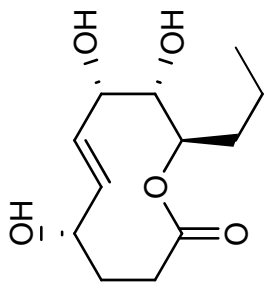


Stagonolide B (2)



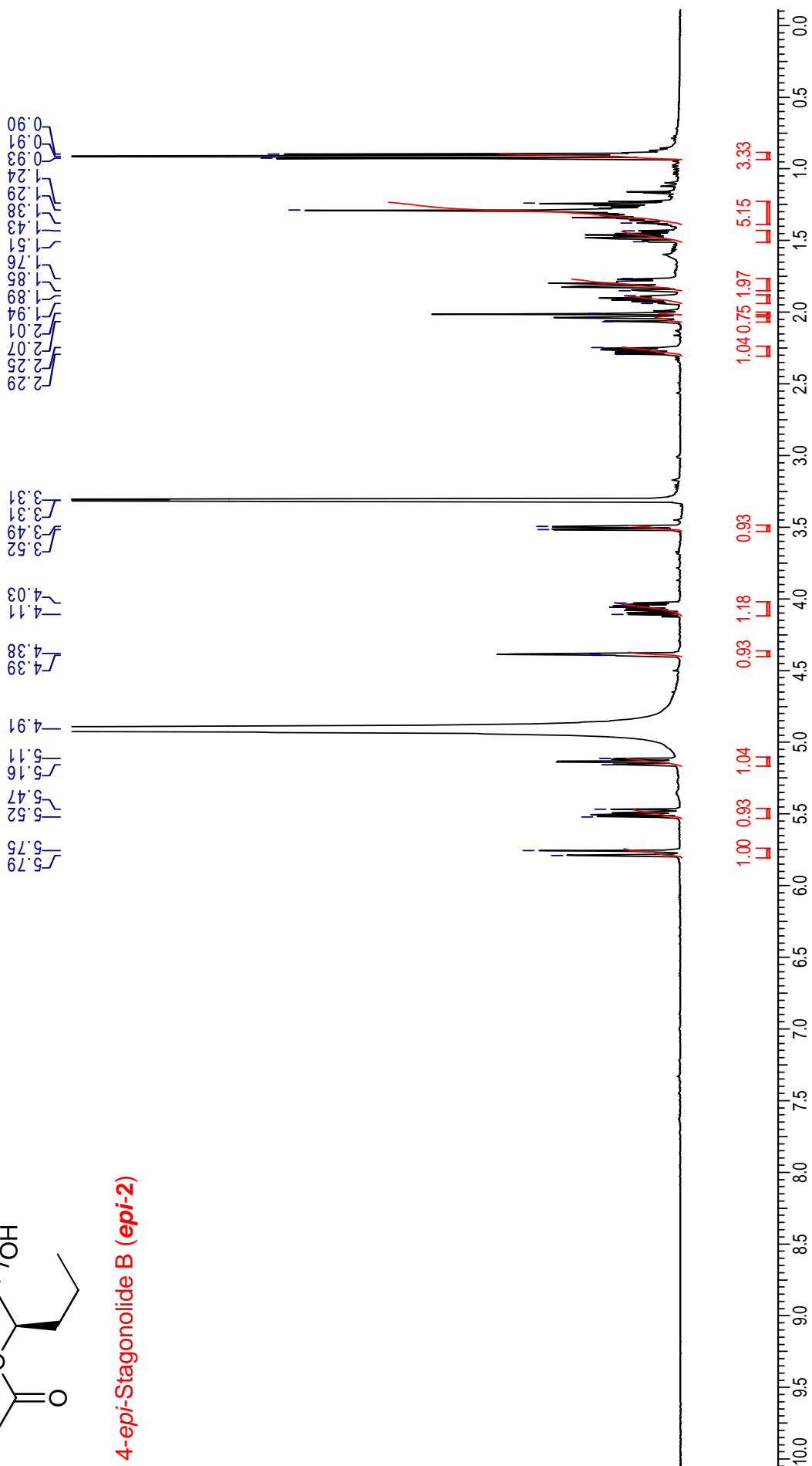
fdfsda
 M A MONDAL

| Acquisition Time (sec) | Comment | Date | Frequency (MHz) |
|------------------------|------------------------------|---------------------------|-----------------------------|
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| | Points Count: 32768 | | |

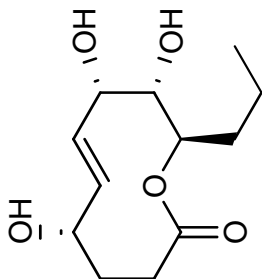


4-epi-Stagonolide B (*epi-2*)

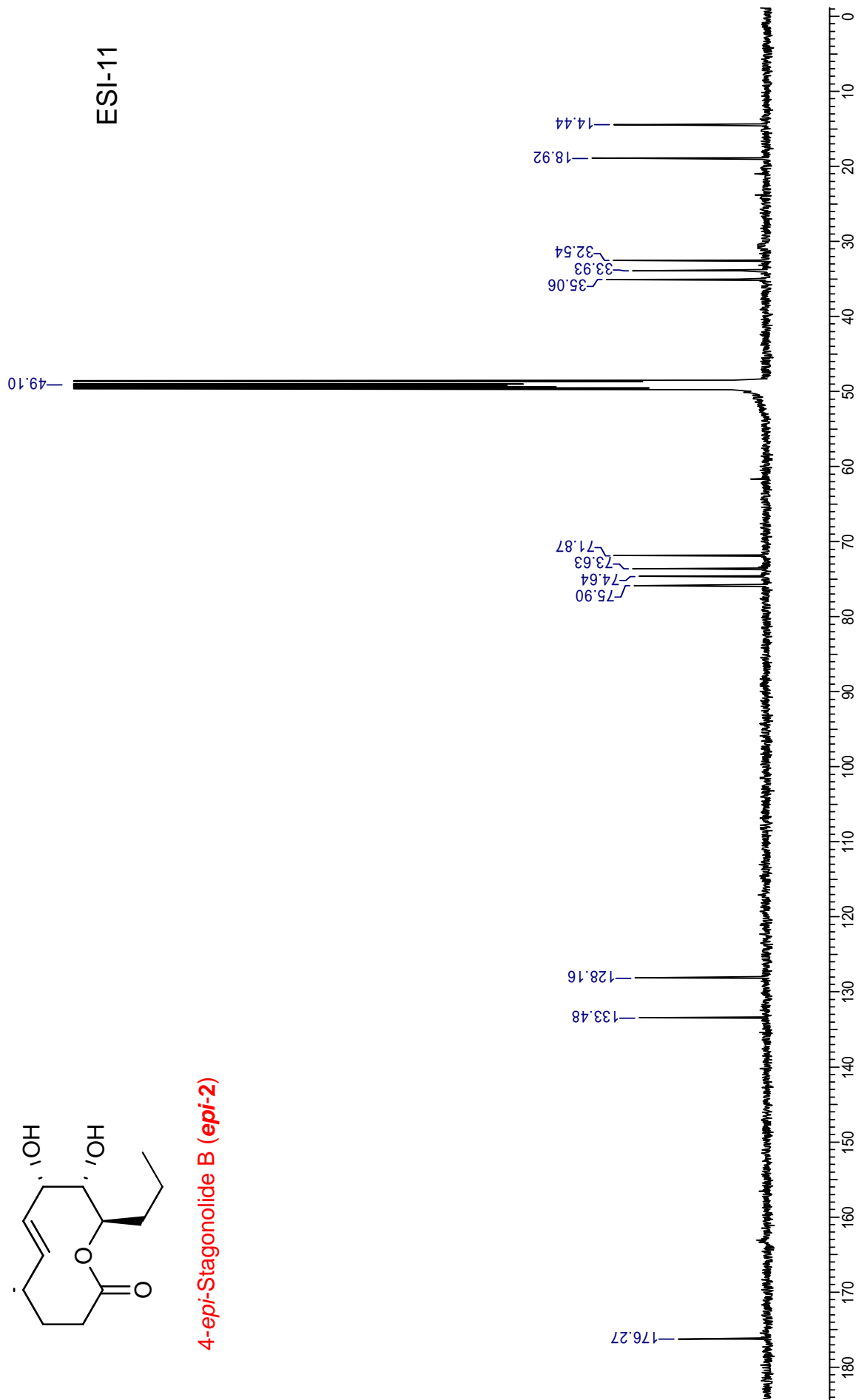
ESI-10



| | | | | | | | | | |
|------------------------|--------|------------------|---------------------|----------------------|--------|---------|-----------------|-----------------------|-------|
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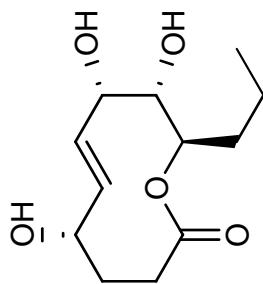


4-epi-Stagonolide B (epi-2)

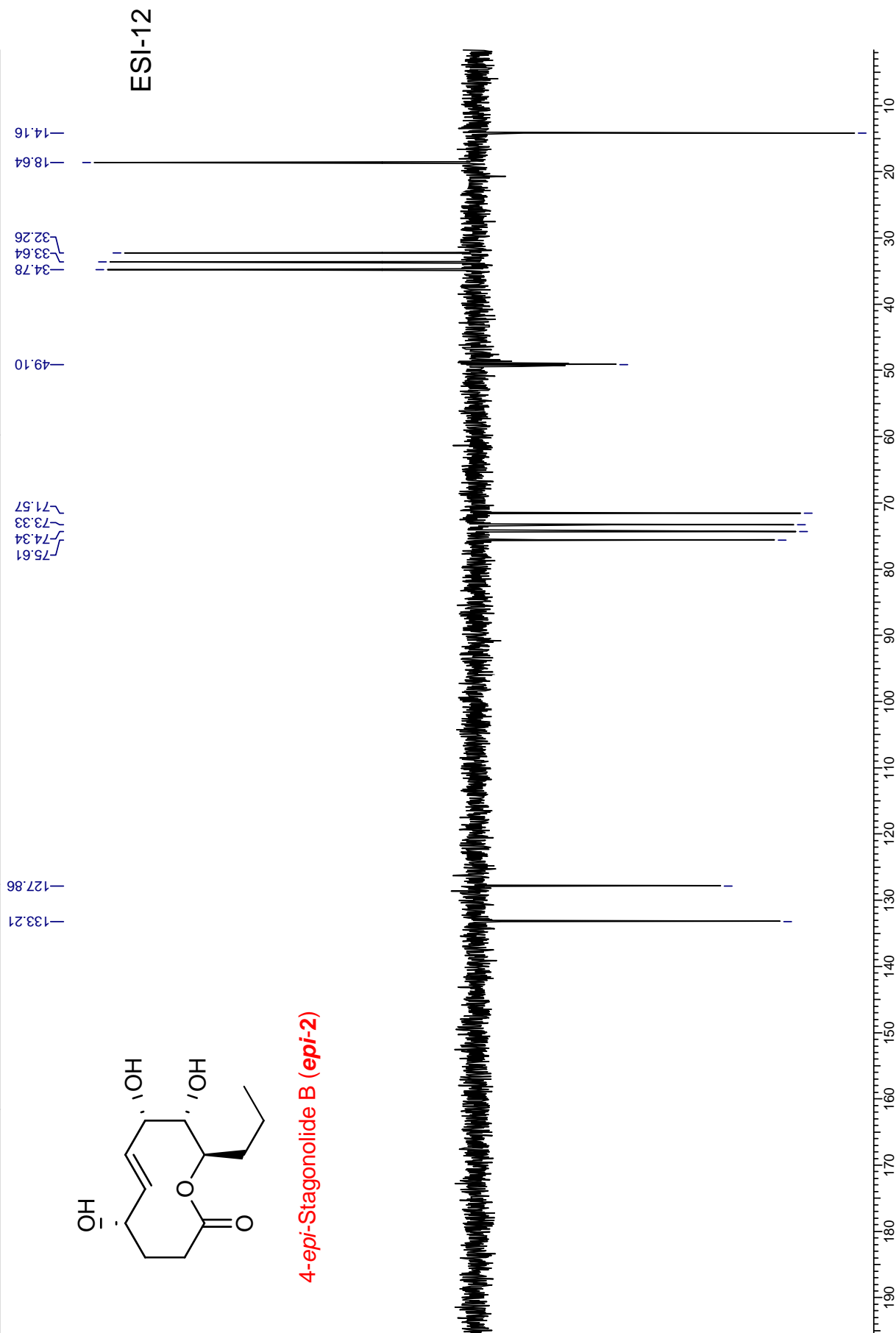


4 Aug 2009

| | | | | | | | |
|------------------------|--------|--------------|---------------------|------------------|----------|----------------------|-----------------|
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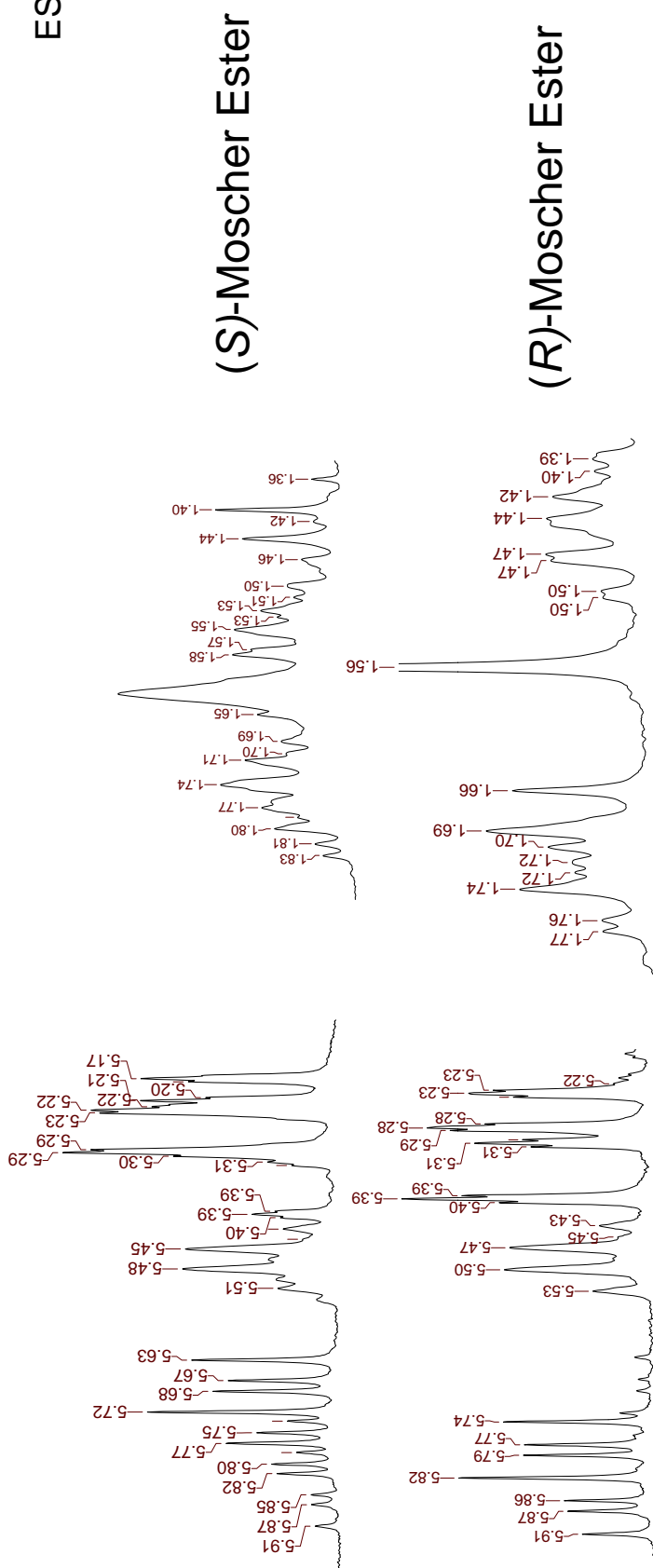


4-*epi*-Stagonolide B (*epi*-2)



Determination of the absolute stereochemistry of alcohol (*R*)-10

ESI-12



(*S*)-Moscher Ester

(*R*)-Moscher Ester

| | 1 | 2 | 3 | 4 | 5 |
|---|------|------|------|------|------|
| (<i>S</i>)-MTPA | 5.23 | 5.72 | 1.76 | 1.49 | 3.57 |
| (<i>R</i>)-MTPA | 5.31 | 5.82 | 1.71 | 1.41 | 3.54 |
| $\Delta\delta = (S\delta - \delta R) \times 1000$ | -80 | -100 | +50 | +80 | +30 |

