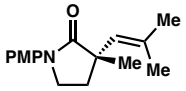
# *APPENDIX 4*

*X-Ray Crystallographic Reports Relevant to Chapter 2: Formation of All-Carbon Quaternary Centers via Enantioselective Pd-Catalyzed α-Vinylation of γ-Lactams*

## A4.1 GENERAL EXPERIMENTAL

X-ray crystallographic analysis was obtained from the Caltech X-Ray Crystallography Facility using a Bruker D8 Venture Kappa Duo Photon 100 CMOS diffractometer.

## A4.2 X-RAY CRYSTAL STRUCTURE ANALYSIS OF PRODUCT 130




***130***

Vinylated lactam **130** was recrystallized from slow evaporation in hexanes at 23 °C to provide crystals suitable for X-ray analysis.

***Figure A4.1*** *X-ray crystal structure of lactam* ***130***.

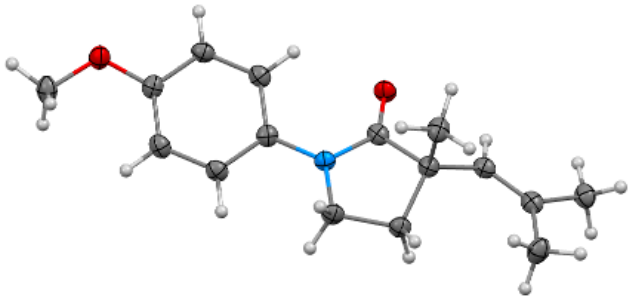


***Table A4.1.*** *Crystal data and structure refinement for lactam* ***130****.*

| | | |
|---|---|---|
| Identification code | V24190 | |
| Empirical formula | C16 H21 N O2 | |
| Formula weight | 259.34 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | a = 7.3874(10) Å | a= 90°. |
| | b = 9.1155(13) Å | b= 90°. |
| | c = 20.860(3) Å | g = 90°. |
| Volume | 1404.7(3) Å3 | |
| Z | 4 | |
| Density (calculated) | 1.226 Mg/m3 | |
| Absorption coefficient | 0.636 mm-1 | |
| F(000) | 560 | |
| Crystal size | 0.150 x 0.100 x 0.005 mm3 | |
| Theta range for data collection | 4.239 to 74.536°. | |
| Index ranges | -9<=h<=9, -11<=k<=10, -26<=l<=26 | |
| Reflections collected | 21524 | |
| Independent reflections | 2879 [R(int) = 0.1102] | |
| Completeness to theta = 67.679° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7538 and 0.6287 | |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 2879 / 0 / 176 |
| Goodness-of-fit on F2 | 1.062 |
| Final R indices [I>2sigma(I)] | R1 = 0.0436, wR2 = 0.0947 |
| R indices (all data) | R1 = 0.0574, wR2 = 0.1004 |
| Absolute structure parameter | 0.0(3) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.173 and -0.182 e.Å-3 |

***Table A4.2*** *Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for* ***130****. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.*

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4790(4) | 5751(3) | 3452(1) | 21(1) |
| O(1) | 4177(3) | 6906(2) | 3656(1) | 26(1) |
| C(2) | 6222(4) | 4815(3) | 3796(1) | 21(1) |
| C(5) | 5146(4) | 3885(3) | 4282(1) | 28(1) |
| C(6) | 7569(4) | 5786(3) | 4137(1) | 22(1) |
| C(7) | 9203(4) | 5434(3) | 4356(1) | 24(1) |
| C(8) | 10344(4) | 6545(3) | 4705(1) | 27(1) |
| C(9) | 10082(4) | 3964(3) | 4275(2) | 32(1) |
| C(3) | 6944(4) | 3841(3) | 3251(1) | 24(1) |
| C(4) | 5384(4) | 3742(3) | 2771(1) | 25(1) |
| N(1) | 4290(3) | 5050(2) | 2897(1) | 21(1) |
| C(10) | 2709(4) | 5361(3) | 2530(1) | 21(1) |
| C(11) | 2486(4) | 4690(3) | 1933(1) | 24(1) |
| C(12) | 900(4) | 4883(3) | 1582(1) | 25(1) |
| C(13) | -480(4) | 5762(3) | 1821(1) | 23(1) |
| O(2) | -2108(3) | 6022(2) | 1528(1) | 28(1) |
| C(16) | -2465(5) | 5246(3) | 947(1) | 31(1) |
| C(14) | -238(4) | 6463(3) | 2410(1) | 25(1) |
| C(15) | 1327(4) | 6257(3) | 2761(1) | 24(1) |

***Table A4.3*** *Bond lengths [Å] and angles [°] for* ***130****.*

| | |
|---|---|
| C(1)-O(1) | 1.222(3) |
| C(1)-N(1) | 1.373(3) |
| C(1)-C(2) | 1.538(4) |
| C(2)-C(6) | 1.509(4) |
| C(2)-C(3) | 1.538(4) |
| C(2)-C(5) | 1.542(4) |
| C(5)-H(5A) | 0.9800 |
| C(5)-H(5B) | 0.9800 |
| C(5)-H(5C) | 0.9800 |
| C(6)-C(7) | 1.329(4) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(9) | 1.499(4) |
| C(7)-C(8) | 1.506(4) |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| C(3)-C(4) | 1.529(4) |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |

| | |
|---|---|
| C(4)-N(1) | 1.464(4) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| N(1)-C(10) | 1.425(4) |
| C(10)-C(15) | 1.394(4) |
| C(10)-C(11) | 1.396(4) |
| C(11)-C(12) | 1.393(4) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(13) | 1.389(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-O(2) | 1.370(4) |
| C(13)-C(14) | 1.397(4) |
| O(2)-C(16) | 1.427(3) |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(14)-C(15) | 1.381(4) |
| C(14)-H(14) | 0.9500 |
| C(15)-H(15) | 0.9500 |
| O(1)-C(1)-N(1) | 126.5(3) |
| O(1)-C(1)-C(2) | 124.8(2) |
| N(1)-C(1)-C(2) | 108.7(2) |
| C(6)-C(2)-C(1) | 110.3(2) |

| | |
|---|---|
| C(6)-C(2)-C(3) | 117.3(2) |
| C(1)-C(2)-C(3) | 102.3(2) |
| C(6)-C(2)-C(5) | 110.6(2) |
| C(1)-C(2)-C(5) | 104.9(2) |
| C(3)-C(2)-C(5) | 110.3(2) |
| C(2)-C(5)-H(5A) | 109.5 |
| C(2)-C(5)-H(5B) | 109.5 |
| H(5A)-C(5)-H(5B) | 109.5 |
| C(2)-C(5)-H(5C) | 109.5 |
| H(5A)-C(5)-H(5C) | 109.5 |
| H(5B)-C(5)-H(5C) | 109.5 |
| C(7)-C(6)-C(2) | 128.2(2) |
| C(7)-C(6)-H(6) | 115.9 |
| C(2)-C(6)-H(6) | 115.9 |
| C(6)-C(7)-C(9) | 124.8(3) |
| C(6)-C(7)-C(8) | 120.8(3) |
| C(9)-C(7)-C(8) | 114.4(3) |
| C(7)-C(8)-H(8A) | 109.5 |
| C(7)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(7)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |

| | |
|---|---|
| C(7)-C(9)-H(9A) | 109.5 |
| C(7)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| C(7)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(4)-C(3)-C(2) | 104.8(2) |
| C(4)-C(3)-H(3A) | 110.8 |
| C(2)-C(3)-H(3A) | 110.8 |
| C(4)-C(3)-H(3B) | 110.8 |
| C(2)-C(3)-H(3B) | 110.8 |
| H(3A)-C(3)-H(3B) | 108.9 |
| N(1)-C(4)-C(3) | 104.5(2) |
| N(1)-C(4)-H(4A) | 110.8 |
| C(3)-C(4)-H(4A) | 110.8 |
| N(1)-C(4)-H(4B) | 110.8 |
| C(3)-C(4)-H(4B) | 110.8 |
| H(4A)-C(4)-H(4B) | 108.9 |
| C(1)-N(1)-C(10) | 125.6(2) |
| C(1)-N(1)-C(4) | 112.4(2) |
| C(10)-N(1)-C(4) | 121.2(2) |
| C(15)-C(10)-C(11) | 118.6(3) |
| C(15)-C(10)-N(1) | 122.1(2) |

| | |
|---|---|
| C(11)-C(10)-N(1) | 119.3(2) |
| C(12)-C(11)-C(10) | 120.9(3) |
| C(12)-C(11)-H(11) | 119.6 |
| C(10)-C(11)-H(11) | 119.6 |
| C(13)-C(12)-C(11) | 120.1(3) |
| C(13)-C(12)-H(12) | 120.0 |
| C(11)-C(12)-H(12) | 120.0 |
| O(2)-C(13)-C(12) | 125.7(2) |
| O(2)-C(13)-C(14) | 115.2(2) |
| C(12)-C(13)-C(14) | 119.1(3) |
| C(13)-O(2)-C(16) | 117.1(2) |
| O(2)-C(16)-H(16A) | 109.5 |
| O(2)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| O(2)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(15)-C(14)-C(13) | 120.7(3) |
| C(15)-C(14)-H(14) | 119.7 |
| C(13)-C(14)-H(14) | 119.7 |
| C(14)-C(15)-C(10) | 120.7(3) |
| C(14)-C(15)-H(15) | 119.6 |
| C(10)-C(15)-H(15) | 119.6 |

Symmetry transformations used to generate equivalent atoms:

***Table A4.4*** *Anisotropic displacement parameters ($Å^2$ x $10^3$) for* ***130****. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.*

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 25(1) | 17(1) | 22(1) | 1(1) | 2(1) | -4(1) |
| O(1) | 30(1) | 19(1) | 27(1) | -4(1) | -3(1) | 4(1) |
| C(2) | 23(1) | 18(1) | 24(1) | 1(1) | -1(1) | -1(1) |
| C(5) | 27(2) | 28(1) | 28(1) | 6(1) | -2(1) | -4(1) |
| C(6) | 26(1) | 16(1) | 24(1) | -1(1) | 2(1) | -2(1) |
| C(7) | 27(2) | 22(1) | 23(1) | 1(1) | 2(1) | -5(1) |
| C(8) | 29(1) | 25(1) | 28(1) | -2(1) | -2(1) | -5(1) |
| C(9) | 30(2) | 25(1) | 40(2) | 0(1) | -8(1) | 3(1) |
| C(3) | 25(1) | 18(1) | 28(1) | -2(1) | -2(1) | 3(1) |
| C(4) | 26(1) | 18(1) | 30(1) | -3(1) | -1(1) | 4(1) |
| N(1) | 24(1) | 16(1) | 23(1) | 0(1) | -1(1) | 2(1) |
| C(10) | 25(1) | 15(1) | 23(1) | 3(1) | 0(1) | -1(1) |
| C(11) | 29(1) | 17(1) | 25(1) | -1(1) | 0(1) | 2(1) |
| C(12) | 33(2) | 18(1) | 24(1) | -1(1) | -2(1) | -1(1) |
| C(13) | 24(1) | 17(1) | 27(1) | 3(1) | -3(1) | -1(1) |
| O(2) | 29(1) | 26(1) | 29(1) | -3(1) | -6(1) | 2(1) |
| C(16) | 37(2) | 24(1) | 31(1) | -2(1) | -10(1) | -2(1) |
| C(14) | 28(2) | 20(1) | 26(1) | -1(1) | 3(1) | 1(1) |
| C(15) | 29(2) | 18(1) | 24(1) | -1(1) | 0(1) | -1(1) |

***Table A4.5*** *Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for* ***130***.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5A) | 5974 | 3226 | 4510 | 42 |
| H(5B) | 4233 | 3304 | 4055 | 42 |
| H(5C) | 4546 | 4534 | 4591 | 42 |
| H(6) | 7202 | 6773 | 4203 | 27 |
| H(8A) | 9672 | 7468 | 4744 | 41 |
| H(8B) | 11465 | 6717 | 4466 | 41 |
| H(8C) | 10637 | 6174 | 5134 | 41 |
| H(9A) | 9147 | 3206 | 4240 | 47 |
| H(9B) | 10851 | 3759 | 4648 | 47 |
| H(9C) | 10824 | 3966 | 3886 | 47 |
| H(3A) | 8025 | 4289 | 3050 | 28 |
| H(3B) | 7271 | 2855 | 3414 | 28 |
| H(4A) | 5844 | 3745 | 2326 | 29 |
| H(4B) | 4667 | 2839 | 2841 | 29 |
| H(11) | 3427 | 4093 | 1765 | 29 |
| H(12) | 761 | 4413 | 1179 | 30 |
| H(16A) | -1567 | 5522 | 623 | 46 |
| H(16B) | -3679 | 5496 | 793 | 46 |
| H(16C) | -2394 | 4189 | 1027 | 46 |

| | | | | |
|---|---|---|---|---|
| H(14) | -1161 | 7088 | 2572 | 30 |
| H(15) | 1463 | 6731 | 3163 | 29 |

***Table A4.6*** *Torsion angles [°] for* ***130***.

| | |
|---|---|
| O(1)-C(1)-C(2)-C(6) | -36.0(4) |
| N(1)-C(1)-C(2)-C(6) | 146.0(2) |
| O(1)-C(1)-C(2)-C(3) | -161.5(3) |
| N(1)-C(1)-C(2)-C(3) | 20.4(3) |
| O(1)-C(1)-C(2)-C(5) | 83.2(3) |
| N(1)-C(1)-C(2)-C(5) | -94.8(3) |
| C(1)-C(2)-C(6)-C(7) | -162.8(3) |
| C(3)-C(2)-C(6)-C(7) | -46.2(4) |
| C(5)-C(2)-C(6)-C(7) | 81.6(4) |
| C(2)-C(6)-C(7)-C(9) | 3.0(5) |
| C(2)-C(6)-C(7)-C(8) | -178.0(3) |
| C(6)-C(2)-C(3)-C(4) | -147.2(2) |
| C(1)-C(2)-C(3)-C(4) | -26.3(3) |
| C(5)-C(2)-C(3)-C(4) | 84.9(3) |
| C(2)-C(3)-C(4)-N(1) | 23.5(3) |
| O(1)-C(1)-N(1)-C(10) | -14.5(4) |
| C(2)-C(1)-N(1)-C(10) | 163.5(2) |
| O(1)-C(1)-N(1)-C(4) | 175.9(3) |
| C(2)-C(1)-N(1)-C(4) | -6.1(3) |
| C(3)-C(4)-N(1)-C(1) | -11.2(3) |
| C(3)-C(4)-N(1)-C(10) | 178.7(2) |
| C(1)-N(1)-C(10)-C(15) | -11.4(4) |

| | |
|---|---|
| C(4)-N(1)-C(10)-C(15) | 157.3(2) |
| C(1)-N(1)-C(10)-C(11) | 172.0(2) |
| C(4)-N(1)-C(10)-C(11) | -19.3(4) |
| C(15)-C(10)-C(11)-C(12) | -1.4(4) |
| N(1)-C(10)-C(11)-C(12) | 175.3(3) |
| C(10)-C(11)-C(12)-C(13) | 0.5(4) |
| C(11)-C(12)-C(13)-O(2) | -179.0(3) |
| C(11)-C(12)-C(13)-C(14) | 1.0(4) |
| C(12)-C(13)-O(2)-C(16) | 4.4(4) |
| C(14)-C(13)-O(2)-C(16) | -175.7(2) |
| O(2)-C(13)-C(14)-C(15) | 178.3(3) |
| C(12)-C(13)-C(14)-C(15) | -1.7(4) |
| C(13)-C(14)-C(15)-C(10) | 0.9(4) |
| C(11)-C(10)-C(15)-C(14) | 0.7(4) |
| N(1)-C(10)-C(15)-C(14) | -175.9(3) |

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Symmetry transformations used to generate equivalent atoms: