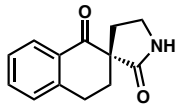
APPENDIX 6

X-Ray Crystallographic Reports Relevant to Chapter 2: An Enantioselective Spirocyclization of Pd-Enolates and Isocyanates

A6.1 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.

A6.2 X-RAY CRYSTAL STRUCTURE ANALYSIS OF PRODUCT 167



167

Compound **167** was crystallized from a mixture of dichloromethane and pentane at 23 °C to provide crystals suitable for X-ray analysis.

Figure A6.1 *X-ray crystal structure of spirocycle* ***167****.*

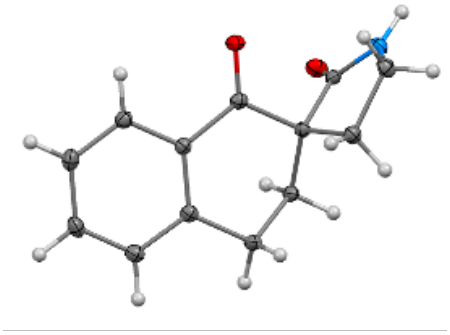


Table A6.1. *Crystal data and structure refinement for spirocycle* ***167****.*

Empirical formula	C13 H13 N O2	
Formula weight	215.24	
Temperature	101(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.9799(8) Å	a= 90°.
	b = 6.1366(5) Å	b= 105.205(7)°.
	c = 12.9790(12) Å	g = 90°.
Volume	536.47(9) Å3	
Z	2	
Density (calculated)	1.332 Mg/m3	
Absorption coefficient	0.730 mm-1	
F(000)	228	
Crystal size	0.200 x 0.200 x 0.100 mm3	
Theta range for data collection	3.529 to 74.548°.	
Index ranges	-8<=h<=8, -7<=k<=7, -15<=l<=16	
Reflections collected	11830	
Independent reflections	2157 [R(int) = 0.0460]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6123	
Refinement method	Full-matrix least-squares on F2	

Data / restraints / parameters	2157 / 2 / 148
Goodness-of-fit on F2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0740
R indices (all data)	R1 = 0.0294, wR2 = 0.0744
Absolute structure parameter	-0.05(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.161 and -0.205 e.Å-3

Table A6.2 *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for* ***167****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
N(1)	1891(2)	7872(2)	5903(1)	14(1)
C(1)	2707(2)	5936(3)	5824(1)	12(1)
O(1)	1974(2)	4411(2)	5235(1)	17(1)
C(2)	4792(2)	5877(3)	6599(1)	11(1)
C(3)	5210(2)	8322(3)	6870(1)	14(1)
C(4)	3131(2)	9317(3)	6693(1)	16(1)
C(5)	4621(2)	4699(3)	7611(1)	12(1)
O(2)	3133(2)	4913(2)	7929(1)	18(1)
C(6)	6324(2)	3348(3)	8200(1)	12(1)
C(7)	6133(3)	2167(3)	9098(1)	14(1)
C(8)	7667(3)	855(3)	9653(1)	17(1)
C(9)	9402(3)	700(3)	9313(1)	17(1)
C(10)	9604(2)	1876(3)	8432(1)	15(1)
C(11)	8077(2)	3216(3)	7865(1)	13(1)
C(12)	8296(2)	4492(3)	6908(1)	14(1)
C(13)	6290(2)	4788(3)	6095(1)	13(1)

Table A6.3 *Bond lengths [Å] and angles [°] for* ***167****.*

N(1)-C(1)	1.333(2)
N(1)-C(4)	1.457(2)
N(1)-H(1N)	0.886(18)
C(1)-O(1)	1.231(2)
C(1)-C(2)	1.537(2)
C(2)-C(13)	1.525(2)
C(2)-C(5)	1.532(2)
C(2)-C(3)	1.551(2)
C(3)-C(4)	1.535(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-O(2)	1.221(2)
C(5)-C(6)	1.486(2)
C(6)-C(11)	1.405(2)
C(6)-C(7)	1.408(2)
C(7)-C(8)	1.382(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.396(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.390(3)

C(9)-H(9)	0.9500
C(10)-C(11)	1.394(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.509(2)
C(12)-C(13)	1.527(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(1)-N(1)-C(4)	114.20(14)
C(1)-N(1)-H(1N)	123.6(16)
C(4)-N(1)-H(1N)	122.0(16)
O(1)-C(1)-N(1)	127.51(15)
O(1)-C(1)-C(2)	123.79(15)
N(1)-C(1)-C(2)	108.71(14)
C(13)-C(2)-C(5)	112.16(14)
C(13)-C(2)-C(1)	111.58(13)
C(5)-C(2)-C(1)	107.40(12)
C(13)-C(2)-C(3)	114.31(13)
C(5)-C(2)-C(3)	108.32(13)
C(1)-C(2)-C(3)	102.44(13)
C(4)-C(3)-C(2)	103.69(13)
C(4)-C(3)-H(3A)	111.0

C(2)-C(3)-H(3A)	111.0
C(4)-C(3)-H(3B)	111.0
C(2)-C(3)-H(3B)	111.0
H(3A)-C(3)-H(3B)	109.0
N(1)-C(4)-C(3)	103.11(13)
N(1)-C(4)-H(4A)	111.1
C(3)-C(4)-H(4A)	111.1
N(1)-C(4)-H(4B)	111.1
C(3)-C(4)-H(4B)	111.1
H(4A)-C(4)-H(4B)	109.1
O(2)-C(5)-C(6)	121.53(14)
O(2)-C(5)-C(2)	120.25(14)
C(6)-C(5)-C(2)	118.21(13)
C(11)-C(6)-C(7)	120.39(15)
C(11)-C(6)-C(5)	121.15(14)
C(7)-C(6)-C(5)	118.45(14)
C(8)-C(7)-C(6)	120.23(15)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	119.46(16)
C(7)-C(8)-H(8)	120.3
C(9)-C(8)-H(8)	120.3
C(10)-C(9)-C(8)	120.54(16)

C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7
C(9)-C(10)-C(11)	120.83(15)
C(9)-C(10)-H(10)	119.6
C(11)-C(10)-H(10)	119.6
C(10)-C(11)-C(6)	118.54(15)
C(10)-C(11)-C(12)	120.84(14)
C(6)-C(11)-C(12)	120.62(14)
C(11)-C(12)-C(13)	110.96(13)
C(11)-C(12)-H(12A)	109.4
C(13)-C(12)-H(12A)	109.4
C(11)-C(12)-H(12B)	109.4
C(13)-C(12)-H(12B)	109.4
H(12A)-C(12)-H(12B)	108.0
C(2)-C(13)-C(12)	111.33(13)
C(2)-C(13)-H(13A)	109.4
C(12)-C(13)-H(13A)	109.4
C(2)-C(13)-H(13B)	109.4
C(12)-C(13)-H(13B)	109.4
H(13A)-C(13)-H(13B)	108.0

Symmetry transformations used to generate equivalent atoms:

Table A6.4 *Anisotropic displacement parameters ($Å^2$ x 10^3) for* ***167****. 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
N(1)	11(1)	14(1)	17(1)	2(1)	2(1)	3(1)
C(1)	10(1)	14(1)	12(1)	1(1)	4(1)	-1(1)
O(1)	13(1)	17(1)	19(1)	-4(1)	1(1)	-2(1)
C(2)	10(1)	11(1)	12(1)	0(1)	1(1)	0(1)
C(3)	13(1)	12(1)	17(1)	-1(1)	2(1)	-1(1)
C(4)	17(1)	12(1)	19(1)	-2(1)	3(1)	2(1)
C(5)	11(1)	12(1)	13(1)	-2(1)	2(1)	-2(1)
O(2)	14(1)	24(1)	20(1)	6(1)	8(1)	4(1)
C(6)	12(1)	11(1)	13(1)	-1(1)	2(1)	-1(1)
C(7)	15(1)	14(1)	16(1)	1(1)	5(1)	-1(1)
C(8)	20(1)	14(1)	15(1)	3(1)	2(1)	-2(1)
C(9)	16(1)	13(1)	19(1)	1(1)	-1(1)	2(1)
C(10)	13(1)	14(1)	18(1)	-2(1)	3(1)	1(1)
C(11)	12(1)	12(1)	13(1)	-2(1)	2(1)	-2(1)
C(12)	11(1)	17(1)	16(1)	3(1)	5(1)	1(1)
C(13)	11(1)	14(1)	13(1)	0(1)	3(1)	1(1)

Table A6.5 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for* ***167****.*

	x	y	z	U(eq)
H(1N)	660(30)	8230(40)	5550(16)	17
H(3A)	5996	8511	7619	17
H(3B)	5935	8996	6390	17
H(4A)	2705	9325	7362	20
H(4B)	3093	10826	6417	20
H(7)	4946	2272	9322	17
H(8)	7543	64	10262	20
H(9)	10452	-216	9687	20
H(10)	10797	1765	8214	18
H(12A)	9214	3715	6568	17
H(12B)	8876	5939	7143	17
H(13A)	6464	5690	5494	15
H(13B)	5775	3347	5807	15

Table A6.6 *Torsion angles [°] for* ***167****.*

C(4)-N(1)-C(1)-O(1)	178.91(16)
C(4)-N(1)-C(1)-C(2)	-1.57(19)
O(1)-C(1)-C(2)-C(13)	41.0(2)
N(1)-C(1)-C(2)-C(13)	-138.59(14)
O(1)-C(1)-C(2)-C(5)	-82.34(19)
N(1)-C(1)-C(2)-C(5)	98.11(16)
O(1)-C(1)-C(2)-C(3)	163.67(15)
N(1)-C(1)-C(2)-C(3)	-15.87(17)
C(13)-C(2)-C(3)-C(4)	146.75(14)
C(5)-C(2)-C(3)-C(4)	-87.42(14)
C(1)-C(2)-C(3)-C(4)	25.89(16)
C(1)-N(1)-C(4)-C(3)	18.53(19)
C(2)-C(3)-C(4)-N(1)	-26.88(16)
C(13)-C(2)-C(5)-O(2)	-157.93(15)
C(1)-C(2)-C(5)-O(2)	-35.0(2)
C(3)-C(2)-C(5)-O(2)	74.98(18)
C(13)-C(2)-C(5)-C(6)	23.5(2)
C(1)-C(2)-C(5)-C(6)	146.42(15)
C(3)-C(2)-C(5)-C(6)	-103.61(16)
O(2)-C(5)-C(6)-C(11)	-176.14(16)
C(2)-C(5)-C(6)-C(11)	2.4(2)
O(2)-C(5)-C(6)-C(7)	4.9(2)

C(2)-C(5)-C(6)-C(7)	-176.55(15)
C(11)-C(6)-C(7)-C(8)	-0.4(2)
C(5)-C(6)-C(7)-C(8)	178.63(15)
C(6)-C(7)-C(8)-C(9)	-0.4(3)
C(7)-C(8)-C(9)-C(10)	0.9(3)
C(8)-C(9)-C(10)-C(11)	-0.6(3)
C(9)-C(10)-C(11)-C(6)	-0.2(2)
C(9)-C(10)-C(11)-C(12)	-179.98(16)
C(7)-C(6)-C(11)-C(10)	0.7(2)
C(5)-C(6)-C(11)-C(10)	-178.30(15)
C(7)-C(6)-C(11)-C(12)	-179.55(15)
C(5)-C(6)-C(11)-C(12)	1.5(2)
C(10)-C(11)-C(12)-C(13)	149.00(15)
C(6)-C(11)-C(12)-C(13)	-30.8(2)
C(5)-C(2)-C(13)-C(12)	-52.74(18)
C(1)-C(2)-C(13)-C(12)	-173.29(14)
C(3)-C(2)-C(13)-C(12)	71.06(18)
C(11)-C(12)-C(13)-C(2)	56.21(19)

Symmetry transformations used to generate equivalent atoms:

Table A6.7 *Hydrogen bonds for* ***167*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.886(18)	1.994(19)	2.8742(18)	173(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y+1/2,-z+1