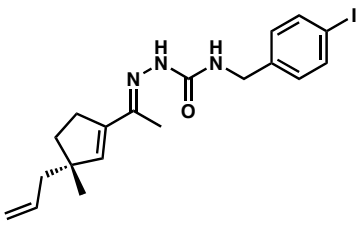
APPENDIX 3

X-Ray Crystallography Reports Relevant to Chapter 2:

Palladium-Catalyzed Asymmetric Alkylation in the Synthesis of

Cyclopentanoid and Cycloheptanoid Core Structures

A3.1 CRYSTAL STRUCTURE ANALYSIS OF 81

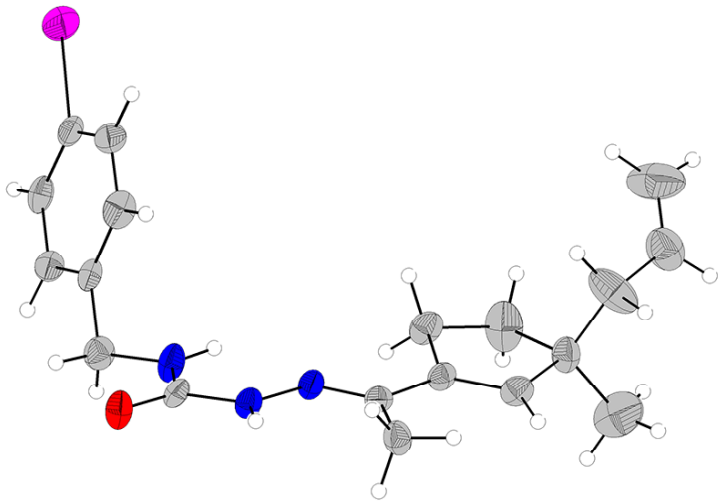


Compound **81**

(AYH02) (CCDC 686849)

Contents

*Figure A3.1. Semicarbazone **81** is shown with 50% probability ellipsoids.*



*CCDC 686849 (**81**) contains the supplementary crystallographic data for this appendix. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.*

*Table A3.1. Crystal data and structure refinement for semicarbazone **81** (CCDC 686849).*

Empirical formula	$C_{19}H_{24}N_3OI$
Formula weight	437.31
Crystallization solvent	Dichloromethane/pentane
Crystal habit	Needle
Crystal size	0.28 x 0.11 x 0.07 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 9911 reflections used in lattice determination	2.57 to 28.78°
Unit cell dimensions	a = 17.160(4) Å b = 5.5921(14) Å β = 90.689(6)° c = 19.984(5) Å
Volume	1917.6(8) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.515 Mg/m^3
F(000)	880
Data collection program	Bruker APEX2 v2.1-0
θ range for data collection	1.55 to 29.84°
Completeness to θ = 29.84°	88.9 %
Index ranges	$-23 \le h \le 23, -7 \le k \le 7, -26 \le l \le 25$
Data collection scan type	ω scans; 16 settings
Data reduction program	Bruker SAINT-Plus v7.34A
Reflections collected	8962
Independent reflections	8962 [R_{int} = 0.0000]
Absorption coefficient	1.680 mm^{-1}
Absorption correction	Semi-empirical from equivalents (TWNABS)
Max. and min. transmission	0.7460 and 0.5010

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8962 / 1 / 437
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.609
Final R indices [I>2σ(I), 7203 reflections]	R1 = 0.0409, *w*R2 = 0.0481
R indices (all data)	R1 = 0.0619, *w*R2 = 0.0493
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	0.003(11)
Largest diff. peak and hole	0.807 and –0.967 e.Å^{-3}

Special Refinement Details

The structure was refined as a single component, although the crystals were twins, using an HKLF4 format reflection file prepared with TWINABS (see below). The two orientations were separated using CELL_NOW as follows.

Rotated from first domain by 178.9 degrees about reciprocal axis –0.032 1.000 0.104 and real axis –0.001 1.000 0.007. Twin law to convert hkl from first to this domain (SHELXL TWIN matrix):

-1.000 -0.065 0.016

-0.003 0.998 0.014

-0.022 0.207 -0.999

From Saint integration; Twin Law, Sample 1 of 1 transforms h1.1(1)->h1.2(2)

-0.99897 -0.07583 0.01646

-0.00750 0.99693 0.01538

-0.02464 0.19596 -0.99910

Twinabs;

PART 1 - Refinement of parameters to model systematic errors

18757 data (4443 unique) involve domain 1 only, mean I/sigma 13.7

18551 data (4364 unique) involve domain 2 only, mean I/sigma 7.1

10342 data (4106 unique) involve 2 domains, mean I/sigma 19.2

HKLF 4 dataset constructed from all observations involving domains 1..2

8970 Corrected reflections written to file twin4.hkl

Reflections merged according to point-group 2

Minimum and maximum apparent transmission: 0.501007 0.745969

Additional spherical absorption correction applied with mu*r = 0.2000

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100 K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Figure A3.2. Semicarbazone **81** (CCDC 686849).*

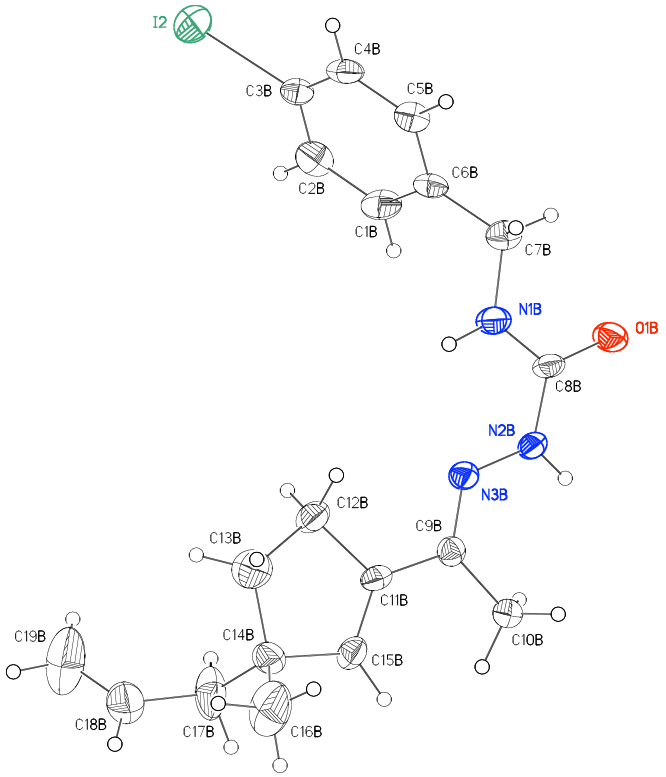


*Table A3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for semicarbazone **81** (CCDC 686849). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
I(1)	9525(1)	8297(1)	6590(1)	36(1)
O(1A)	7955(1)	941(3)	3051(1)	30(1)
N(1A)	7500(2)	3872(4)	3727(1)	30(1)
N(2A)	6670(2)	1070(4)	3270(1)	28(1)
N(3A)	6059(2)	2296(4)	3562(1)	28(1)
C(1A)	8489(2)	4383(5)	4938(2)	26(1)
C(2A)	8786(2)	5006(6)	5555(2)	27(1)
C(3A)	9158(2)	7186(5)	5637(2)	24(1)
C(4A)	9240(2)	8700(6)	5094(2)	23(1)
C(5A)	8934(2)	8049(6)	4481(2)	24(1)
C(6A)	8541(2)	5886(5)	4389(2)	21(1)
C(7A)	8214(2)	5251(6)	3716(2)	29(1)
C(8A)	7411(2)	1915(5)	3335(2)	24(1)
C(9A)	5356(2)	1676(5)	3411(2)	25(1)
C(10A)	5153(2)	-221(5)	2912(2)	34(1)

Table A3.2 (cont.)

C(11A)	4738(2)	3016(6)	3736(2)	25(1)
C(12A)	4902(2)	5012(5)	4229(2)	30(1)
C(13A)	4096(2)	6199(5)	4302(2)	34(1)
C(14A)	3501(2)	4222(5)	4130(2)	33(1)
C(15A)	3985(2)	2625(5)	3693(2)	32(1)
C(16A)	3271(2)	2838(6)	4771(2)	47(1)
C(17A)	2751(2)	5160(6)	3793(2)	36(1)
C(18A)	2864(2)	6198(6)	3116(2)	39(1)
C(19A)	2612(2)	8233(8)	2900(2)	51(1)
I(2)	5760(1)	351(1)	-1541(1)	52(1)
O(1B)	6661(1)	7118(3)	2275(1)	34(1)
N(1B)	7173(2)	4167(4)	1625(1)	34(1)
N(2B)	7955(2)	7040(4)	2098(1)	27(1)
N(3B)	8578(2)	5882(4)	1807(1)	26(1)
C(1B)	6496(2)	3858(5)	289(2)	33(1)
C(2B)	6341(2)	3322(8)	-374(2)	35(1)
C(3B)	5958(2)	1240(6)	-534(2)	29(1)
C(4B)	5742(2)	-303(6)	-40(2)	31(1)
C(5B)	5895(2)	235(6)	618(2)	28(1)
C(6B)	6287(2)	2329(5)	795(2)	26(1)
C(7B)	6454(2)	2863(6)	1519(2)	32(1)
C(8B)	7233(2)	6143(5)	2016(2)	25(1)
C(9B)	9266(2)	6619(5)	1925(2)	24(1)
C(10B)	9471(2)	8670(6)	2382(2)	33(1)
C(11B)	9892(2)	5325(6)	1586(2)	25(1)
C(12B)	9704(2)	3469(7)	1051(2)	34(1)
C(13B)	10499(2)	2401(6)	903(2)	54(1)
C(14B)	11131(2)	4019(5)	1204(2)	33(1)
C(15B)	10659(2)	5558(6)	1666(2)	30(1)
C(16B)	11736(3)	2543(7)	1600(2)	67(2)
C(17B)	11522(2)	5571(7)	690(2)	58(1)
C(18B)	12017(3)	4302(6)	194(2)	52(1)
C(19B)	11859(3)	3982(7)	-416(2)	77(2)

*Table A3.3. Bond lengths [Å] and angles [°] for semicarbazone **81** (CCDC 686849).*

I(1)-C(3A)	2.092(3)		
O(1A)-C(8A)	1.226(4)	C(8A)-N(1A)-C(7A)	120.7(3)
N(1A)-C(8A)	1.354(4)	C(8A)-N(2A)-N(3A)	119.8(3)
N(1A)-C(7A)	1.449(4)	C(9A)-N(3A)-N(2A)	118.6(3)
N(2A)-C(8A)	1.361(4)	C(2A)-C(1A)-C(6A)	122.1(3)
N(2A)-N(3A)	1.388(3)	C(1A)-C(2A)-C(3A)	119.6(3)
N(3A)-C(9A)	1.289(4)	C(2A)-C(3A)-C(4A)	119.8(3)
C(1A)-C(2A)	1.375(5)	C(2A)-C(3A)-I(1)	120.1(2)
C(1A)-C(6A)	1.386(4)	C(4A)-C(3A)-I(1)	119.9(2)
C(2A)-C(3A)	1.385(4)	C(5A)-C(4A)-C(3A)	119.7(3)
C(3A)-C(4A)	1.384(4)	C(4A)-C(5A)-C(6A)	121.7(3)
C(4A)-C(5A)	1.376(4)	C(1A)-C(6A)-C(5A)	117.2(3)
C(5A)-C(6A)	1.397(5)	C(1A)-C(6A)-C(7A)	122.8(3)
C(6A)-C(7A)	1.494(4)	C(5A)-C(6A)-C(7A)	120.1(3)
C(9A)-C(11A)	1.457(4)	N(1A)-C(7A)-C(6A)	115.0(3)
C(9A)-C(10A)	1.494(4)	O(1A)-C(8A)-N(1A)	123.1(3)
C(11A)-C(15A)	1.312(4)	O(1A)-C(8A)-N(2A)	121.2(3)
C(11A)-C(12A)	1.514(5)	N(1A)-C(8A)-N(2A)	115.8(3)
C(12A)-C(13A)	1.542(4)	N(3A)-C(9A)-C(11A)	116.2(3)
C(13A)-C(14A)	1.542(5)	N(3A)-C(9A)-C(10A)	123.9(3)
C(14A)-C(15A)	1.505(4)	C(11A)-C(9A)-C(10A)	119.8(3)
C(14A)-C(17A)	1.538(5)	C(15A)-C(11A)-C(9A)	127.4(3)
C(14A)-C(16A)	1.552(5)	C(15A)-C(11A)-C(12A)	109.9(3)
C(17A)-C(18A)	1.487(5)	C(9A)-C(11A)-C(12A)	122.6(3)
C(18A)-C(19A)	1.290(5)	C(11A)-C(12A)-C(13A)	102.6(3)
I(2)-C(3B)	2.096(3)	C(12A)-C(13A)-C(14A)	105.2(2)
O(1B)-C(8B)	1.242(4)	C(15A)-C(14A)-C(17A)	114.4(3)
N(1B)-C(8B)	1.356(4)	C(15A)-C(14A)-C(13A)	100.7(3)
N(1B)-C(7B)	1.447(4)	C(17A)-C(14A)-C(13A)	113.7(3)
N(2B)-C(8B)	1.346(4)	C(15A)-C(14A)-C(16A)	109.3(3)
N(2B)-N(3B)	1.383(3)	C(17A)-C(14A)-C(16A)	108.2(3)
N(3B)-C(9B)	1.270(4)	C(13A)-C(14A)-C(16A)	110.3(3)
C(1B)-C(6B)	1.376(4)	C(11A)-C(15A)-C(14A)	114.4(3)
C(1B)-C(2B)	1.380(5)	C(18A)-C(17A)-C(14A)	114.4(3)
C(2B)-C(3B)	1.373(5)	C(19A)-C(18A)-C(17A)	127.0(3)
C(3B)-C(4B)	1.366(4)	C(8B)-N(1B)-C(7B)	123.6(3)
C(4B)-C(5B)	1.372(4)	C(8B)-N(2B)-N(3B)	119.3(3)
C(5B)-C(6B)	1.394(5)	C(9B)-N(3B)-N(2B)	119.4(3)
C(6B)-C(7B)	1.501(5)	C(6B)-C(1B)-C(2B)	121.4(3)
C(9B)-C(11B)	1.467(4)	C(3B)-C(2B)-C(1B)	119.6(3)
C(9B)-C(10B)	1.504(4)	C(4B)-C(3B)-C(2B)	120.0(3)
C(11B)-C(15B)	1.330(4)	C(4B)-C(3B)-I(2)	120.1(3)
C(11B)-C(12B)	1.522(4)	C(2B)-C(3B)-I(2)	119.8(2)
C(12B)-C(13B)	1.521(5)	C(3B)-C(4B)-C(5B)	120.3(3)
C(13B)-C(14B)	1.530(5)	C(4B)-C(5B)-C(6B)	120.9(3)
C(14B)-C(15B)	1.505(4)	C(1B)-C(6B)-C(5B)	117.7(3)
C(14B)-C(17B)	1.509(5)	C(1B)-C(6B)-C(7B)	122.4(3)
C(14B)-C(16B)	1.537(6)	C(5B)-C(6B)-C(7B)	119.8(3)
C(17B)-C(18B)	1.493(5)	N(1B)-C(7B)-C(6B)	113.3(3)
C(18B)-C(19B)	1.260(5)	O(1B)-C(8B)-N(2B)	121.1(3)

Table A3.3 (cont.)

O(1B)-C(8B)-N(1B)	123.0(3)	C(12B)-C(13B)-C(14B)	108.9(3)
N(2B)-C(8B)-N(1B)	115.9(3)	C(15B)-C(14B)-C(17B)	109.6(3)
N(3B)-C(9B)-C(11B)	116.0(3)	C(15B)-C(14B)-C(13B)	101.3(3)
N(3B)-C(9B)-C(10B)	124.7(3)	C(17B)-C(14B)-C(13B)	112.9(3)
C(11B)-C(9B)-C(10B)	119.3(3)	C(15B)-C(14B)-C(16B)	110.9(3)
C(15B)-C(11B)-C(9B)	128.7(3)	C(17B)-C(14B)-C(16B)	110.8(3)
C(15B)-C(11B)-C(12B)	110.6(3)	C(13B)-C(14B)-C(16B)	110.9(3)
C(9B)-C(11B)-C(12B)	120.7(3)	C(11B)-C(15B)-C(14B)	114.2(3)
C(13B)-C(12B)-C(11B)	102.9(3)	C(18B)-C(17B)-C(14B)	116.1(3)
		C(19B)-C(18B)-C(17B)	126.3(5)

Table A3.4. Anisotropic displacement parameters ($Å^2$ x 10^4) for semicarbazone ***81*** *(CCDC 686849). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	340(2)	433(1)	310(1)	1(1)	-116(1)	-2(1)
O(1A)	177(14)	294(13)	431(15)	-131(10)	-15(11)	35(10)
N(1A)	166(17)	377(19)	352(17)	-168(12)	3(13)	-6(12)
N(2A)	150(17)	315(15)	378(18)	-133(12)	-22(13)	22(12)
N(3A)	186(19)	310(15)	328(18)	-35(12)	-35(15)	38(13)
C(1A)	190(20)	176(16)	420(20)	13(15)	-22(18)	9(13)
C(2A)	250(20)	237(18)	320(20)	88(15)	-7(16)	-4(16)
C(3A)	170(20)	261(17)	270(20)	-18(14)	-7(16)	69(14)
C(4A)	180(20)	200(20)	310(20)	-23(14)	-29(15)	-13(14)
C(5A)	240(20)	201(19)	275(19)	26(16)	5(15)	34(16)
C(6A)	171(19)	195(18)	269(19)	-26(14)	-8(15)	64(14)
C(7A)	260(20)	280(18)	330(20)	-40(17)	-16(16)	-38(18)
C(8A)	200(20)	257(18)	260(20)	-33(14)	-61(17)	19(16)
C(9A)	200(20)	231(17)	330(20)	-9(14)	-9(18)	-26(15)
C(10A)	200(20)	410(20)	430(20)	-69(17)	3(18)	-44(17)
C(11A)	190(20)	240(20)	330(20)	21(16)	-31(15)	-26(17)
C(12A)	250(20)	283(18)	360(20)	-23(16)	-60(16)	-30(16)
C(13A)	260(20)	305(19)	440(20)	-99(15)	-50(18)	42(16)
C(14A)	190(20)	305(19)	490(30)	-7(15)	9(19)	19(15)
C(15A)	260(20)	240(20)	460(20)	-48(14)	-26(19)	-18(15)
C(16A)	360(30)	500(30)	540(30)	114(18)	30(20)	88(19)
C(17A)	250(20)	390(20)	450(20)	-34(18)	9(18)	40(20)
C(18A)	270(20)	480(20)	420(30)	-75(18)	-70(20)	77(18)
C(19A)	410(30)	600(20)	510(20)	40(20)	-88(19)	120(30)
I(2)	431(2)	791(2)	333(2)	-69(1)	-57(1)	-30(2)
O(1B)	227(16)	346(12)	447(16)	-105(10)	2(13)	9(11)
N(1B)	220(19)	350(17)	440(20)	-151(12)	-38(16)	9(12)
N(2B)	230(20)	301(15)	272(17)	-106(12)	-29(14)	3(13)
N(3B)	208(18)	309(16)	277(16)	-57(12)	-23(14)	26(14)
C(1B)	340(30)	190(20)	470(30)	-9(15)	-50(20)	-62(15)
C(2B)	310(20)	404(19)	350(20)	130(20)	-22(16)	20(20)
C(3B)	190(20)	370(20)	310(20)	-17(16)	-51(17)	17(16)
C(4B)	200(20)	270(20)	450(30)	-58(16)	-50(18)	-39(15)
C(5B)	270(20)	236(18)	340(20)	71(16)	-20(16)	-10(17)
C(6B)	170(20)	246(18)	350(20)	8(15)	-46(17)	-2(14)
C(7B)	300(20)	310(20)	360(20)	-12(15)	-23(17)	-59(16)
C(8B)	200(20)	282(19)	270(20)	-34(14)	-76(16)	-6(16)
C(9B)	250(20)	257(18)	220(20)	11(14)	2(17)	11(16)
C(10B)	260(20)	400(20)	330(20)	-104(16)	37(16)	-60(18)
C(11B)	250(20)	241(17)	253(19)	-25(16)	-45(15)	-52(18)
C(12B)	340(20)	341(18)	330(20)	-105(19)	-60(16)	10(20)
C(13B)	450(30)	450(20)	730(30)	-310(20)	70(30)	-4(19)
C(14B)	250(20)	350(20)	390(20)	-54(15)	20(19)	25(15)

Table A3.4 (cont.)

C(15B)	340(20)	290(18)	266(19)	-75(16)	-25(16)	33(18)
C(16B)	720(40)	680(30)	610(30)	-170(20)	-50(30)	380(30)
C(17B)	840(30)	400(20)	510(30)	-150(20)	330(20)	-90(20)
C(18B)	500(30)	540(30)	520(30)	-104(19)	110(30)	-49(19)
C(19B)	1060(50)	830(40)	420(30)	40(20)	60(30)	500(30)

*Table A3.5. Hydrogen bonds for semicarbazone **81** (CCDC 686849) [Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2A)-H(2A)...O(1B)#1	0.88	2.13	2.972(3)	159.7
N(2B)-H(2B)...O(1A)#2	0.88	2.04	2.895(3)	163.1

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z
#2 x,y+1,z