APPENDIX 2

X-Ray Crystallography Reports Relevant to Chapter 2:

Enantioselective Synthesis of Pyrroloindolines by a Formal (3 + 2)

Cycloaddition[†]

[†] The work disclosed in this appendix for the x-ray crystallographic analysis of **100c** and **106g** was completed entirely by Larry Henling and Dr. Michael Day in the Caltech X-ray crystallography lab.

A2.1 CRYSTAL STRUCTURE ANALYSIS OF PYROLLOINDOLINE 106g

*Figure A2.1. Pyrroloindoline **106g** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 787164.*

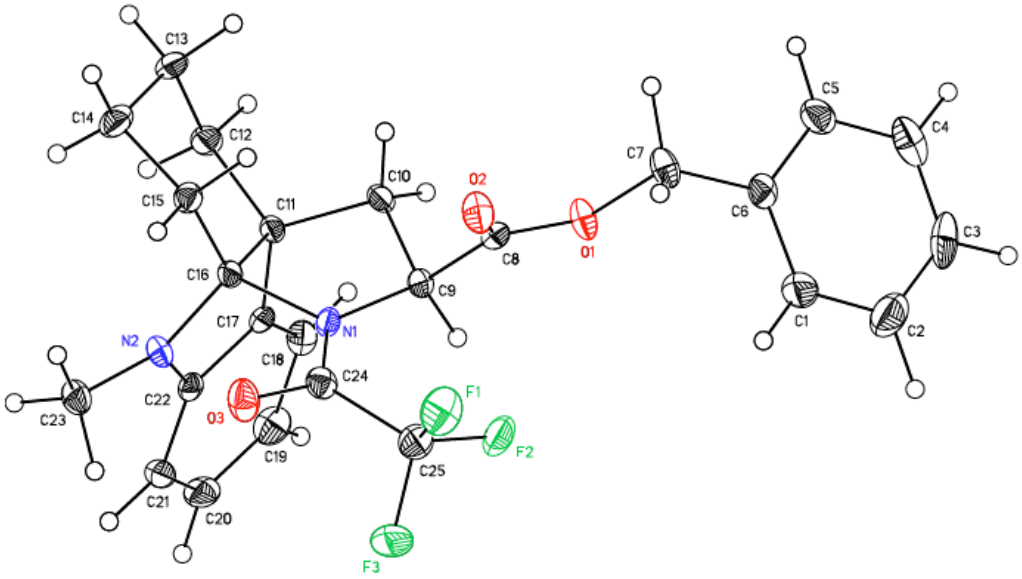

Table A2.1. Crystal data and structure refinement for pyrroloindoline ***106g*** *(CCDC 787164).*

Empirical formula	$C_{25}H_{25}F_3N_2O_3$
Formula weight	458.47
Crystallization Solvent	Hexanes/ethyl acetate
Crystal Habit	Plate
Crystal size	0.23 x 0.19 x 0.02 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 5569 reflections used in lattice determination	2.19 to 24.93°	
Unit cell dimensions	a = 9.8089(6) Å b = 8.4633(5) Å c = 13.9252(9) Å	α= 90° β= 108.657(3)° γ = 90°
Volume	1095.26(12) $Å^3$	
Z	2	
Crystal system	Monoclinic	
Space group	P 2_1	
Density (calculated)	1.390 Mg/m^3	
F(000)	480	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	2.19 to 30.52°	
Completeness to θ = 30.52°	91.3 %	
Index ranges	$-13 \le h \le 13, -11 \le k \le 11, -19 \le l \le 19$	
Data collection scan type	ω scans; 8 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	20200	
Independent reflections	5883 [R_{int}= 0.0461]	
Absorption coefficient	0.109 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9978 and 0.9755	

Table A2.1 (continued)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	5883 / 1 / 398
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.140
Final R indices [I>2σ(I), 4601 reflections]	R1 = 0.0393, *w*R2 = 0.0443
R indices (all data)	R1 = 0.0561, *w*R2 = 0.0463
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure determination	Unknown
Absolute structure parameter	0.1(4)
Largest diff. peak and hole	0.245 and -0.273 e.Å^{-3}

Special Refinement Details

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

It is not possible to reliably determine the absolute configuration of this molecule due to the lack of atoms with sufficient anomalous scattering.

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.

Table A2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for pyrroloindoline ***106g*** *(CCDC 787164). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
F(1)	3918(1)	4664(1)	10172(1)	32(1)
F(2)	3607(1)	4695(1)	8564(1)	27(1)
F(3)	3993(1)	2504(1)	9381(1)	33(1)
O(1)	1918(1)	7940(1)	7621(1)	20(1)
O(2)	1842(1)	7188(1)	9164(1)	22(1)
O(3)	1481(1)	2670(1)	9761(1)	25(1)
N(1)	684(1)	4212(1)	8351(1)	14(1)
N(2)	-1102(1)	2048(2)	7926(1)	14(1)
C(1)	4492(2)	9288(2)	7202(1)	28(1)
C(2)	5169(2)	9805(2)	6533(2)	35(1)
C(3)	4687(2)	11150(2)	5965(2)	32(1)
C(4)	3526(2)	11960(2)	6066(1)	31(1)
C(5)	2821(2)	11417(2)	6732(1)	25(1)
C(6)	3305(2)	10072(2)	7304(1)	18(1)
C(7)	2596(2)	9456(2)	8032(1)	22(1)
C(8)	1606(2)	6946(2)	8279(1)	16(1)
C(9)	838(2)	5515(2)	7694(1)	14(1)
C(10)	-729(2)	5990(2)	7108(1)	15(1)
C(11)	-1598(2)	4502(2)	7091(1)	13(1)
C(12)	-3220(2)	4815(2)	6864(1)	18(1)
C(13)	-3617(2)	5480(2)	7758(1)	21(1)
C(14)	-3057(2)	4415(2)	8680(1)	21(1)
C(15)	-1419(2)	4324(2)	8991(1)	16(1)
C(16)	-899(2)	3723(2)	8148(1)	13(1)
C(17)	-1397(2)	3220(2)	6391(1)	13(1)
C(18)	-1534(2)	3247(2)	5377(1)	19(1)
C(19)	-1410(2)	1830(2)	4889(1)	23(1)
C(20)	-1171(2)	419(2)	5432(1)	22(1)
C(21)	-1052(2)	377(2)	6453(1)	18(1)
C(22)	-1167(2)	1787(2)	6929(1)	14(1)
C(23)	-1076(2)	774(2)	8626(1)	19(1)
C(24)	1708(2)	3572(2)	9147(1)	17(1)
C(25)	3315(2)	3892(2)	9305(1)	22(1)

*Table A2.3. Bond lengths [Å] and angles [°] for pyrroloindoline **106g** (CCDC 787164).*

F(1)-C(25)	1.3329(18)	C(18)-H(18)	0.935(15)
F(2)-C(25)	1.3403(19)	C(19)-C(20)	1.393(2)
F(3)-C(25)	1.3374(18)	C(19)-H(19)	0.969(15)
O(1)-C(8)	1.3487(18)	C(20)-C(21)	1.389(2)
O(1)-C(7)	1.4743(19)	C(20)-H(20)	0.965(15)
O(2)-C(8)	1.1966(17)	C(21)-C(22)	1.387(2)
O(3)-C(24)	1.2187(19)	C(21)-H(21)	0.994(15)
N(1)-C(24)	1.3487(18)	C(23)-H(23A)	1.054(15)
N(1)-C(9)	1.4715(19)	C(23)-H(23B)	0.989(15)
N(1)-C(16)	1.5426(18)	C(23)-H(23C)	1.010(14)
N(2)-C(22)	1.3868(18)	C(24)-C(25)	1.544(2)
N(2)-C(23)	1.4491(19)		
N(2)-C(16)	1.4507(18)	C(8)-O(1)-C(7)	116.90(12)
C(1)-C(2)	1.377(3)	C(24)-N(1)-C(9)	127.88(13)
C(1)-C(6)	1.387(2)	C(24)-N(1)-C(16)	118.98(12)
C(1)-H(1)	0.945(17)	C(9)-N(1)-C(16)	112.63(11)
C(2)-C(3)	1.380(3)	C(22)-N(2)-C(23)	122.70(14)
C(2)-H(2)	1.029(19)	C(22)-N(2)-C(16)	109.17(13)
C(3)-C(4)	1.374(3)	C(23)-N(2)-C(16)	127.76(14)
C(3)-H(3)	0.968(16)	C(2)-C(1)-C(6)	121.29(18)
C(4)-C(5)	1.401(2)	C(2)-C(1)-H(1)	119.9(10)
C(4)-H(4)	0.946(18)	C(6)-C(1)-H(1)	118.8(11)
C(5)-C(6)	1.383(2)	C(1)-C(2)-C(3)	119.92(19)
C(5)-H(5)	0.969(14)	C(1)-C(2)-H(2)	121.2(11)
C(6)-C(7)	1.494(2)	C(3)-C(2)-H(2)	118.8(11)
C(7)-H(7A)	1.088(16)	C(4)-C(3)-C(2)	119.75(18)
C(7)-H(7B)	0.972(14)	C(4)-C(3)-H(3)	118.6(10)
C(8)-C(9)	1.518(2)	C(2)-C(3)-H(3)	121.6(10)
C(9)-C(10)	1.545(2)	C(3)-C(4)-C(5)	120.33(18)
C(9)-H(9)	1.013(13)	C(3)-C(4)-H(4)	118.3(11)
C(10)-C(11)	1.517(2)	C(5)-C(4)-H(4)	121.3(11)
C(10)-H(10A)	1.001(13)	C(6)-C(5)-C(4)	119.98(18)
C(10)-H(10B)	0.990(14)	C(6)-C(5)-H(5)	121.8(9)
C(11)-C(17)	1.513(2)	C(4)-C(5)-H(5)	118.2(9)
C(11)-C(12)	1.543(2)	C(5)-C(6)-C(1)	118.71(17)
C(11)-C(16)	1.557(2)	C(5)-C(6)-C(7)	121.90(16)
C(12)-C(13)	1.525(2)	C(1)-C(6)-C(7)	119.38(15)
C(12)-H(12A)	0.954(15)	O(1)-C(7)-C(6)	106.95(13)
C(12)-H(12B)	1.045(15)	O(1)-C(7)-H(7A)	111.0(9)
C(13)-C(14)	1.521(2)	C(6)-C(7)-H(7A)	111.9(9)
C(13)-H(13A)	1.068(16)	O(1)-C(7)-H(7B)	105.6(9)
C(13)-H(13B)	0.952(14)	C(6)-C(7)-H(7B)	115.4(9)
C(14)-C(15)	1.526(2)	H(7A)-C(7)-H(7B)	105.8(12)
C(14)-H(14A)	0.955(14)	O(2)-C(8)-O(1)	125.53(15)
C(14)-H(14B)	0.953(14)	O(2)-C(8)-C(9)	126.07(15)
C(15)-C(16)	1.510(2)	O(1)-C(8)-C(9)	108.32(13)
C(15)-H(15A)	0.950(14)	N(1)-C(9)-C(8)	113.32(12)
C(15)-H(15B)	1.009(16)	N(1)-C(9)-C(10)	103.92(12)
C(17)-C(18)	1.375(2)	C(8)-C(9)-C(10)	108.33(12)
C(17)-C(22)	1.404(2)	N(1)-C(9)-H(9)	112.3(8)
C(18)-C(19)	1.404(2)	C(8)-C(9)-H(9)	108.3(8)

Table A2.3 (continued)

C(10)-C(9)-H(9)	110.5(7)	N(2)-C(16)-N(1)	111.25(12)
C(11)-C(10)-C(9)	104.52(12)	C(15)-C(16)-N(1)	109.73(12)
C(11)-C(10)-H(10A)	114.5(7)	N(2)-C(16)-C(11)	102.90(12)
C(9)-C(10)-H(10A)	110.4(7)	C(15)-C(16)-C(11)	115.86(13)
C(11)-C(10)-H(10B)	112.1(8)	N(1)-C(16)-C(11)	99.95(11)
C(9)-C(10)-H(10B)	109.6(7)	C(18)-C(17)-C(22)	120.54(15)
H(10A)-C(10)-H(10B)	105.7(10)	C(18)-C(17)-C(11)	131.23(15)
C(17)-C(11)-C(10)	114.67(13)	C(22)-C(17)-C(11)	107.92(14)
C(17)-C(11)-C(12)	109.24(12)	C(17)-C(18)-C(19)	119.20(16)
C(10)-C(11)-C(12)	113.47(13)	C(17)-C(18)-H(18)	121.0(10)
C(17)-C(11)-C(16)	101.33(12)	C(19)-C(18)-H(18)	119.7(9)
C(10)-C(11)-C(16)	105.18(12)	C(20)-C(19)-C(18)	119.67(16)
C(12)-C(11)-C(16)	112.29(13)	C(20)-C(19)-H(19)	122.6(10)
C(13)-C(12)-C(11)	114.34(13)	C(18)-C(19)-H(19)	117.7(10)
C(13)-C(12)-H(12A)	107.5(10)	C(21)-C(20)-C(19)	121.50(17)
C(11)-C(12)-H(12A)	107.9(9)	C(21)-C(20)-H(20)	118.3(9)
C(13)-C(12)-H(12B)	111.6(8)	C(19)-C(20)-H(20)	120.2(9)
C(11)-C(12)-H(12B)	108.0(8)	C(22)-C(21)-C(20)	118.26(16)
H(12A)-C(12)-H(12B)	107.2(11)	C(22)-C(21)-H(21)	121.5(9)
C(14)-C(13)-C(12)	110.66(15)	C(20)-C(21)-H(21)	120.2(9)
C(14)-C(13)-H(13A)	108.2(8)	N(2)-C(22)-C(21)	129.06(15)
C(12)-C(13)-H(13A)	112.9(9)	N(2)-C(22)-C(17)	110.12(14)
C(14)-C(13)-H(13B)	110.4(9)	C(21)-C(22)-C(17)	120.82(14)
C(12)-C(13)-H(13B)	110.4(9)	N(2)-C(23)-H(23A)	111.7(9)
H(13A)-C(13)-H(13B)	104.1(12)	N(2)-C(23)-H(23B)	111.3(9)
C(13)-C(14)-C(15)	109.41(14)	H(23A)-C(23)-H(23B)	108.3(11)
C(13)-C(14)-H(14A)	109.4(9)	N(2)-C(23)-H(23C)	110.2(8)
C(15)-C(14)-H(14A)	111.8(8)	H(23A)-C(23)-H(23C)	107.9(12)
C(13)-C(14)-H(14B)	110.8(9)	H(23B)-C(23)-H(23C)	107.3(12)
C(15)-C(14)-H(14B)	109.7(8)	O(3)-C(24)-N(1)	124.92(15)
H(14A)-C(14)-H(14B)	105.7(12)	O(3)-C(24)-C(25)	114.67(14)
C(16)-C(15)-C(14)	112.55(13)	N(1)-C(24)-C(25)	120.33(14)
C(16)-C(15)-H(15A)	110.5(9)	F(1)-C(25)-F(3)	107.01(13)
C(14)-C(15)-H(15A)	112.1(8)	F(1)-C(25)-F(2)	107.80(13)
C(16)-C(15)-H(15B)	108.1(9)	F(3)-C(25)-F(2)	106.44(14)
C(14)-C(15)-H(15B)	107.2(8)	F(1)-C(25)-C(24)	110.64(14)
H(15A)-C(15)-H(15B)	106.1(11)	F(3)-C(25)-C(24)	108.48(13)
N(2)-C(16)-C(15)	115.92(14)	F(2)-C(25)-C(24)	116.05(13)

Table A2.4. Anisotropic displacement parameters ($Å^2$x 10^4) for pyrroloindoline ***106g*** *(CCDC 787164). 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}
F(1)	210(5)	405(7)	277(6)	-65(5)	-6(4)	-86(5)
F(2)	160(5)	341(6)	323(6)	69(5)	108(4)	-5(5)
F(3)	213(6)	254(6)	502(7)	52(5)	91(5)	83(5)
O(1)	264(7)	161(6)	174(6)	-7(5)	60(5)	-94(5)
O(2)	303(7)	209(7)	174(6)	-42(5)	108(5)	-79(5)
O(3)	193(6)	262(7)	244(7)	90(6)	17(5)	-38(5)
N(1)	107(7)	148(7)	153(7)	23(6)	45(5)	-12(6)
N(2)	187(7)	114(7)	132(7)	12(6)	51(6)	-22(6)
C(1)	209(10)	220(10)	396(12)	34(10)	81(9)	15(9)
C(2)	232(11)	385(12)	455(13)	-89(11)	156(9)	-69(10)
C(3)	311(12)	403(13)	251(11)	-71(9)	108(9)	-241(10)
C(4)	362(12)	230(11)	267(11)	65(10)	12(9)	-97(10)
C(5)	209(10)	169(9)	342(11)	-11(8)	39(9)	-20(8)
C(6)	151(9)	168(9)	190(9)	-37(7)	18(7)	-58(7)
C(7)	257(10)	155(9)	236(10)	-40(8)	53(8)	-94(8)
C(8)	122(8)	159(9)	202(9)	-4(8)	64(7)	8(7)
C(9)	149(9)	130(8)	134(8)	17(7)	51(7)	-6(7)
C(10)	160(9)	100(8)	179(9)	12(7)	43(7)	-1(7)
C(11)	125(8)	108(8)	149(8)	4(7)	37(6)	-11(7)
C(12)	135(9)	164(9)	222(9)	6(8)	27(7)	9(8)
C(13)	127(9)	189(9)	315(10)	-24(9)	93(8)	20(8)
C(14)	182(10)	250(10)	242(10)	-46(9)	120(8)	-1(8)
C(15)	164(9)	166(9)	162(8)	-8(8)	68(7)	-12(7)
C(16)	104(8)	115(8)	170(8)	8(7)	31(7)	-9(7)
C(17)	83(8)	144(8)	174(8)	-2(7)	42(7)	-2(6)
C(18)	173(9)	207(10)	186(9)	24(8)	51(7)	-16(8)
C(19)	249(10)	297(11)	173(9)	-38(9)	93(8)	-11(8)
C(20)	208(9)	197(9)	256(10)	-91(9)	96(8)	-6(8)
C(21)	161(9)	136(8)	236(10)	-1(8)	58(7)	8(7)
C(22)	89(8)	146(8)	172(8)	-22(8)	37(7)	-24(7)
C(23)	235(10)	170(10)	177(9)	34(8)	81(8)	-14(8)
C(24)	173(9)	160(9)	175(9)	-21(8)	39(7)	-19(7)
C(25)	180(10)	232(10)	248(10)	11(8)	48(8)	1(8)

Table A2.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for pyrroloindoline ***106g*** *(CCDC 787164).*

	x	y	z	U_{iso}
H(1)	4843(17)	8390(20)	7608(13)	38(6)
H(2)	6021(19)	9190(20)	6434(14)	55(7)
H(3)	5155(16)	11553(18)	5500(11)	26(5)
H(4)	3201(18)	12870(20)	5659(13)	51(6)
H(5)	2013(15)	12023(17)	6791(10)	19(5)
H(7A)	1806(16)	10280(20)	8136(12)	37(5)
H(7B)	3239(14)	9221(18)	8708(11)	20(5)
H(9)	1360(13)	5177(17)	7207(10)	10(4)
H(10A)	-798(13)	6411(15)	6422(9)	3(4)
H(10B)	-1028(13)	6869(17)	7465(10)	13(4)
H(12A)	-3714(15)	3834(17)	6680(11)	15(4)
H(12B)	-3564(14)	5555(17)	6232(11)	21(4)
H(13A)	-3204(16)	6640(20)	7967(11)	35(5)
H(13B)	-4632(15)	5603(18)	7581(11)	23(5)
H(14A)	-3490(14)	3396(17)	8527(10)	10(4)
H(14B)	-3337(14)	4805(17)	9231(11)	13(4)
H(15A)	-1022(14)	3712(18)	9588(11)	13(4)
H(15B)	-1040(15)	5431(19)	9167(11)	22(4)
H(18)	-1721(14)	4191(18)	5008(11)	19(5)
H(19)	-1521(15)	1876(19)	4172(11)	24(4)
H(20)	-1059(14)	-557(18)	5107(11)	14(4)
H(21)	-902(14)	-646(18)	6824(11)	20(4)
H(23A)	-103(16)	136(19)	8815(12)	40(5)
H(23B)	-1203(13)	1175(17)	9259(12)	11(4)
H(23C)	-1889(14)	10(18)	8313(11)	21(5)

A2.2 CRYSTAL STRUCTURE ANALYSIS OF PYRROLOINDOLINE 100c

*Figure 2.2. Pyrroloindoline **100c** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 788553.*

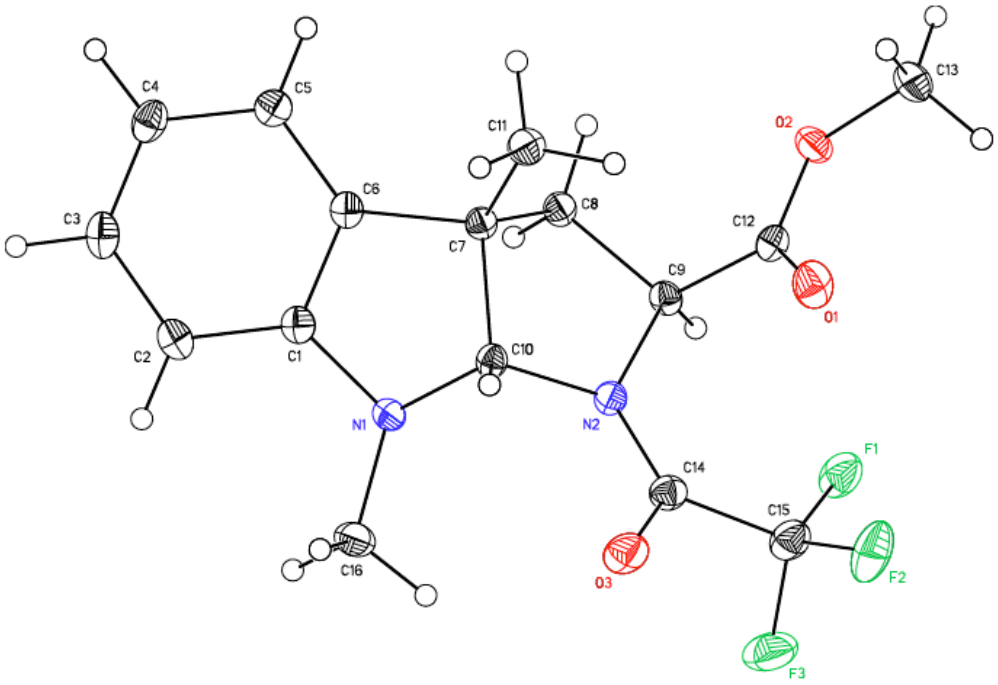

*Table A2.6. Crystal data and structure refinement for pyrroloindoline **100c** (CCDC 788553).*

Empirical formula	$C_{16}H_{17}F_3N_2O_3$
Formula weight	342.32
Crystallization Solvent	Chloroform
Crystal Habit	Block
Crystal size	0.31 x 0.30 x 0.28 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9932 reflections used in lattice determination	3.07 to 36.76°	
Unit cell dimensions	a = 13.9506(5) Å b = 7.2073(2) Å c = 16.3208(5) Å	α= 90° β= 107.9900(10)° γ = 90°
Volume	1560.77(9) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P $2_1/c$	
Density (calculated)	1.457 Mg/m^3	
F(000)	712	
Data collection program	Bruker SMART v5.630	
θ range for data collection	1.53 to 37.55°	
Completeness to θ = 37.55°	88.2 %	
Index ranges	$-22 \le h \le 22, -11 \le k \le 12, -26 \le l \le 26$	
Data collection scan type	ω scans at 7 settings	
Data reduction program	Bruker SAINT v6.45A	
Reflections collected	35665	
Independent reflections	7261 [R_{int}= 0.0549]	
Absorption coefficient	0.125 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9660 and 0.9624	

Table A2.6 (continued)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7261 / 0 / 285
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.940
Final R indices [I>2σ(I), 4934 reflections]	R1 = 0.0469, *w*R2 = 0.0737
R indices (all data)	R1 = 0.0757, *w*R2 = 0.0765
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.427 and -0.429 e.Å^{-3}

Special Refinement Details

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

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.

Table A2.7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pyrroloindoline ***100c*** *(CCDC 788553). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
F(1)	7030(1)	5654(1)	4071(1)	26(1)
F(2)	5844(1)	4727(1)	4558(1)	34(1)
F(3)	7372(1)	4868(1)	5397(1)	32(1)
O(1)	5686(1)	3285(1)	2789(1)	23(1)
O(2)	6430(1)	4211(1)	1815(1)	19(1)
O(3)	6740(1)	1296(1)	4926(1)	23(1)
N(1)	8666(1)	-681(1)	4302(1)	15(1)
N(2)	7456(1)	1872(1)	3869(1)	14(1)
C(1)	9002(1)	-1980(1)	3811(1)	15(1)
C(2)	9801(1)	-3225(1)	4089(1)	19(1)
C(3)	10002(1)	-4371(1)	3469(1)	20(1)
C(4)	9425(1)	-4302(1)	2610(1)	18(1)
C(5)	8620(1)	-3049(1)	2340(1)	16(1)
C(6)	8421(1)	-1888(1)	2943(1)	14(1)
C(7)	7622(1)	-411(1)	2841(1)	13(1)
C(8)	7975(1)	1517(1)	2628(1)	14(1)
C(9)	7490(1)	2906(1)	3095(1)	14(1)
C(10)	7643(1)	-124(1)	3784(1)	13(1)
C(11)	6586(1)	-959(1)	2246(1)	18(1)
C(12)	6424(1)	3475(1)	2559(1)	15(1)
C(13)	5449(1)	4754(2)	1236(1)	24(1)
C(14)	6975(1)	2367(1)	4443(1)	16(1)
C(15)	6795(1)	4432(1)	4596(1)	21(1)
C(16)	8848(1)	-1024(1)	5219(1)	20(1)

*Table A2.8. Bond lengths [Å] and angles [°] for pyrroloindoline **100c** (CCDC 788553).*

F(1)-C(15)	1.3386(10)	C(2)-C(1)-N(1)	128.22(8)
F(2)-C(15)	1.3259(11)	C(6)-C(1)-N(1)	110.78(7)
F(3)-C(15)	1.3442(11)	C(1)-C(2)-C(3)	117.64(9)
O(1)-C(12)	1.2063(10)	C(1)-C(2)-H(2)	121.0(6)
O(2)-C(12)	1.3275(10)	C(3)-C(2)-H(2)	121.3(6)
O(2)-C(13)	1.4557(11)	C(4)-C(3)-C(2)	121.76(9)
O(3)-C(14)	1.2180(10)	C(4)-C(3)-H(3)	121.1(6)
N(1)-C(1)	1.4053(11)	C(2)-C(3)-H(3)	117.2(6)
N(1)-C(16)	1.4596(11)	C(3)-C(4)-C(5)	120.00(9)
N(1)-C(10)	1.4714(11)	C(3)-C(4)-H(4)	119.5(6)
N(2)-C(14)	1.3578(10)	C(5)-C(4)-H(4)	120.5(6)
N(2)-C(10)	1.4767(11)	C(6)-C(5)-C(4)	118.94(8)
N(2)-C(9)	1.4803(10)	C(6)-C(5)-H(5)	120.8(6)
C(1)-C(2)	1.3925(12)	C(4)-C(5)-H(5)	120.2(6)
C(1)-C(6)	1.4000(12)	C(5)-C(6)-C(1)	120.66(8)
C(2)-C(3)	1.3987(13)	C(5)-C(6)-C(7)	130.64(8)
C(2)-H(2)	0.967(11)	C(1)-C(6)-C(7)	108.71(7)
C(3)-C(4)	1.3852(14)	C(6)-C(7)-C(11)	114.12(7)
C(3)-H(3)	0.983(11)	C(6)-C(7)-C(10)	101.47(6)
C(4)-C(5)	1.4010(13)	C(11)-C(7)-C(10)	113.12(7)
C(4)-H(4)	0.987(11)	C(6)-C(7)-C(8)	112.45(7)
C(5)-C(6)	1.3827(12)	C(11)-C(7)-C(8)	113.18(7)
C(5)-H(5)	0.981(10)	C(10)-C(7)-C(8)	101.18(6)
C(6)-C(7)	1.5128(11)	C(9)-C(8)-C(7)	104.77(7)
C(7)-C(11)	1.5244(12)	C(9)-C(8)-H(8A)	107.3(5)
C(7)-C(10)	1.5431(12)	C(7)-C(8)-H(8A)	109.5(5)
C(7)-C(8)	1.5486(12)	C(9)-C(8)-H(8B)	113.3(5)
C(8)-C(9)	1.5351(12)	C(7)-C(8)-H(8B)	112.1(5)
C(8)-H(8A)	0.983(9)	H(8A)-C(8)-H(8B)	109.7(7)
C(8)-H(8B)	0.978(10)	N(2)-C(9)-C(12)	109.94(7)
C(9)-C(12)	1.5300(12)	N(2)-C(9)-C(8)	103.30(6)
C(9)-H(9)	0.988(10)	C(12)-C(9)-C(8)	113.04(7)
C(10)-H(10)	0.995(10)	N(2)-C(9)-H(9)	110.8(5)
C(11)-H(11A)	0.965(10)	C(12)-C(9)-H(9)	109.1(6)
C(11)-H(11B)	1.003(11)	C(8)-C(9)-H(9)	110.5(5)
C(11)-H(11C)	0.999(10)	N(1)-C(10)-N(2)	112.31(7)
C(13)-H(13A)	0.977(13)	N(1)-C(10)-C(7)	104.68(6)
C(13)-H(13B)	0.981(13)	N(2)-C(10)-C(7)	105.96(6)
C(13)-H(13C)	0.993(10)	N(1)-C(10)-H(10)	111.1(6)
C(14)-C(15)	1.5425(13)	N(2)-C(10)-H(10)	108.2(6)
C(16)-H(16A)	0.981(11)	C(7)-C(10)-H(10)	114.6(6)
C(16)-H(16B)	0.995(11)	C(7)-C(11)-H(11A)	110.1(6)
C(16)-H(16C)	1.032(11)	C(7)-C(11)-H(11B)	112.0(6)
		H(11A)-C(11)-H(11B)	109.4(8)
C(12)-O(2)-C(13)	115.50(7)	C(7)-C(11)-H(11C)	109.9(6)
C(1)-N(1)-C(16)	119.27(7)	H(11A)-C(11)-H(11C)	109.3(8)
C(1)-N(1)-C(10)	106.79(6)	H(11B)-C(11)-H(11C)	106.0(8)
C(16)-N(1)-C(10)	117.85(7)	O(1)-C(12)-O(2)	125.21(8)
C(14)-N(2)-C(10)	117.43(7)	O(1)-C(12)-C(9)	124.32(8)
C(14)-N(2)-C(9)	127.57(7)	O(2)-C(12)-C(9)	110.47(7)
C(10)-N(2)-C(9)	110.89(6)	O(2)-C(13)-H(13A)	110.9(7)
C(2)-C(1)-C(6)	120.99(8)	O(2)-C(13)-H(13B)	104.4(7)

H(13A)-C(13)-H(13B)	111.2(10)	F(2)-C(15)-C(14)	110.93(7)
O(2)-C(13)-H(13C)	109.8(6)	F(1)-C(15)-C(14)	116.56(7)
H(13A)-C(13)-H(13C)	108.9(9)	F(3)-C(15)-C(14)	107.73(7)
H(13B)-C(13)-H(13C)	111.6(9)	N(1)-C(16)-H(16A)	113.7(6)
O(3)-C(14)-N(2)	124.68(8)	N(1)-C(16)-H(16B)	111.6(6)
O(3)-C(14)-C(15)	114.65(8)	H(16A)-C(16)-H(16B)	106.5(9)
N(2)-C(14)-C(15)	120.31(8)	N(1)-C(16)-H(16C)	109.4(6)
F(2)-C(15)-F(1)	107.73(7)	H(16A)-C(16)-H(16C)	109.0(9)
F(2)-C(15)-F(3)	107.33(7)	H(16B)-C(16)-H(16C)	106.3(8)
F(1)-C(15)-F(3)	106.10(7)		

Table A2.9. Anisotropic displacement parameters ($Å^2x\ 10^4$) for pyrroloindoline ***100c*** *(CCDC 788553). 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}
F(1)	397(4)	154(3)	284(3)	2(2)	184(3)	4(2)
F(2)	300(3)	299(3)	515(4)	-18(3)	244(3)	84(3)
F(3)	471(4)	268(3)	219(3)	-85(2)	112(3)	-48(3)
O(1)	161(3)	278(4)	279(4)	49(3)	99(3)	37(3)
O(2)	172(3)	254(3)	144(3)	40(3)	36(2)	56(3)
O(3)	311(4)	215(3)	224(4)	15(3)	169(3)	-8(3)
N(1)	153(4)	168(3)	124(4)	14(3)	38(3)	26(3)
N(2)	160(3)	125(3)	145(4)	17(3)	73(3)	6(3)
C(1)	144(4)	129(4)	173(4)	14(3)	58(3)	-15(3)
C(2)	166(4)	189(4)	191(5)	35(4)	37(4)	16(3)
C(3)	165(4)	164(4)	273(5)	33(4)	83(4)	31(4)
C(4)	187(4)	152(4)	244(5)	2(4)	123(4)	4(3)
C(5)	163(4)	159(4)	173(4)	12(3)	79(4)	-18(3)
C(6)	126(4)	127(4)	168(4)	18(3)	64(3)	-10(3)
C(7)	123(4)	136(4)	135(4)	9(3)	51(3)	5(3)
C(8)	135(4)	160(4)	149(4)	18(3)	62(3)	16(3)
C(9)	141(4)	135(4)	142(4)	32(3)	60(3)	2(3)
C(10)	138(4)	119(4)	153(4)	8(3)	59(3)	3(3)
C(11)	145(4)	200(5)	173(5)	-17(4)	40(3)	-2(4)
C(12)	166(4)	124(4)	174(4)	-13(3)	59(3)	5(3)
C(13)	189(5)	314(6)	181(5)	4(4)	-9(4)	86(4)
C(14)	157(4)	184(4)	157(4)	-8(3)	55(3)	-4(3)
C(15)	236(5)	199(5)	217(5)	-8(4)	119(4)	2(4)
C(16)	227(5)	211(5)	140(4)	12(4)	38(4)	0(4)

Table A2.10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for pyrroloindoline ***100c*** *(CCDC 788553).*

	x	y	z	U_{iso}
H(2)	10204(8)	-3288(14)	4688(7)	29(3)
H(3)	10564(8)	-5250(15)	3671(7)	31(3)
H(4)	9580(8)	-5150(15)	2193(7)	25(3)
H(5)	8186(7)	-3046(13)	1739(6)	18(2)
H(8A)	8709(7)	1622(12)	2888(6)	13(2)
H(8B)	7792(7)	1733(12)	2008(6)	14(2)
H(9)	7912(7)	4029(14)	3258(6)	18(2)
H(10)	7123(7)	-838(13)	3953(6)	21(3)
H(11A)	6614(7)	-1149(14)	1668(7)	23(3)
H(11B)	6061(8)	-1(16)	2237(7)	30(3)
H(11C)	6357(7)	-2128(15)	2457(6)	25(3)
H(13A)	5013(9)	3673(18)	1051(8)	44(3)
H(13B)	5601(9)	5341(17)	748(8)	43(3)
H(13C)	5121(8)	5635(14)	1533(6)	23(3)
H(16A)	8501(8)	-2125(16)	5340(7)	36(3)
H(16B)	8625(7)	39(15)	5504(7)	25(3)
H(16C)	9612(8)	-1168(14)	5520(7)	27(3)