Supporting information for:

Synthesis and Orthogonal Heteroarylation of Oxazolo[5',4':4,5]pyrano[1,3-*b*]pyridine by Intra- and Intermolecular Pd-Catalyzed Direct C–H Functionalization

Laure Théveau,[a] Cédric Schneider,[a] Olivier Querolle,[b] Lieven Meerpoel,[b] Vincent Levacher,[a] Christophe Hoarau[a]*

[a]*Normandie Univ, COBRA, UMR 6014 et FR 3038, Univ Rouen ; INSA Rouen, CNRS, IRCOF 1 rue Tesnière 76 821 Mont-Saint-Aignan Cedex, France*
[b]*Janssen Research & Development, Division of Janssen-Cilag S. A. Chaussée du Vexin,, BP 615, 27106 Val de Reuil Cedex, France*

E-mail: christophe.hoarau@insa-rouen.fr

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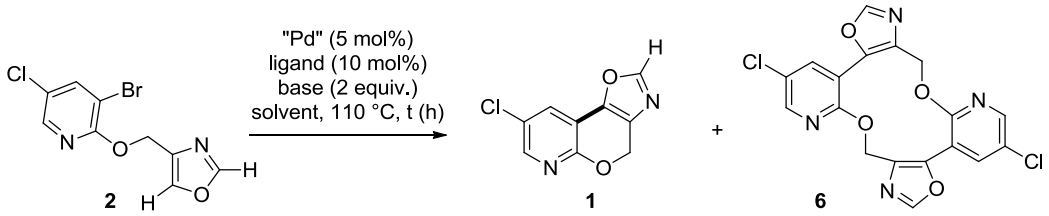
General information

Commercially available reagents were used throughout without further purification. Reactions were routinely carried out under an N_2 atmosphere using oven or flame-dried glassware. Melting points were determined on a hot stage melting point apparatus and are uncorrected. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded using a 300 spectrometer operating at 300 MHz (^{1}H frequency, corresponding ^{13}C and ^{19}F frequencies are 75 and 282 MHz). The chemical shifts are calibrated to residual proton and carbon resonance of $CDCl_3$ (^{1}H 7.26 and ^{13}C 77.16 ppm) or DMSO (^{1}H 2.52 and ^{13}C 39.5 ppm). In the ^{13}C NMR spectra, signals corresponding to C, CH, CH_2, or CH_3 groups are assigned from DEPT. The obtained signal multiplicities were distinguished with the common abbreviations s (singlet), d (doublet), t (triplet), q (quartet), bs (broad singlet), hep (heptet), sex (sextet) and the combinations thereof. IR spectra were recorded on a FT-IR intrument. Low resolution mass spectra analyses were performed with spectrometer in chemical ionisation. High Resolution Mass spectra (HRMS) were performed under ESI conditions with a micro Q-TOF detector. All reactions were monitored by thin-layer chromatography with silica gel 60 F_{254} pre-coated aluminium plates (0.25 mm). Flash chromatography was performed with the indicated solvents using silica gel 60 (35-70 µm mesh).

Experimental section

Synthesis of 8-Chloro-4*H*-oxazolo[5',4':4,5]pyrano[2,3-*b*]pyridine 1:

a) Optimization:



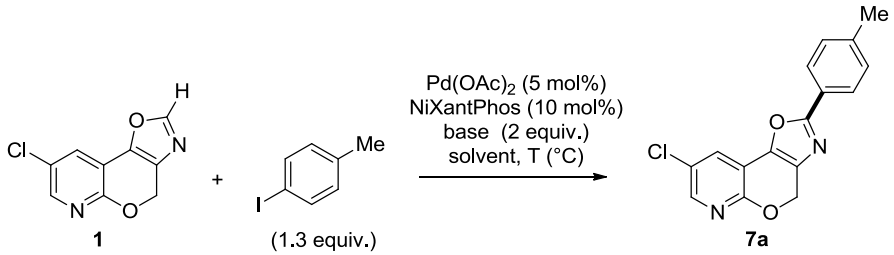
Entry	[Pd] source	Solvent	Base	T (°C)	t (h)	Yield (%)	Ratio **1**:**6**
1	$PdCl_2(PPh_3)_2$	DMAc	K_2CO_3	110	1	38	8:2
2	$PdCl_2(PPh_3)_2$	DMAc	nBu$_4$OAc	110	1	36	8:2
3	$PdCl_2(PPh_3)_2$	DMAc	KOAc	110	1	62	8:2
4	$Pd(OAc)_2$	DMAc	KOAc	110	1	24	8:2

5	$Pd(OAc)_2/PCy_3HBF_4$	DMAc	KOAc	110	1	48	8:2
6	$Pd(OAc)_2/P(tBu)_3HBF_4$	DMAc	KOAc	110	12	--	--
7	$PdCl_2(dppf)•CH_2Cl_2$	DMAc	KOAc	110	1	65	8:2
8	$PdCl_2(dppf)•CH_2Cl_2$	DMAc	K_2CO_3	110	1	55	8:2
9	$PdCl_2(dppf)•CH_2Cl_2$	DMAc	nBu_4OAc	110	1	52	8:2
10	$PdCl_2(dppf)•CH_2Cl_2$	DMAc	KOAc	90	1	51	8:2
11	$PdCl_2(dppf)•CH_2Cl_2$	DMAc	KOAc	70	12	--	--
12[d]	$PdCl_2(dppf)•CH_2Cl_2$	DMAc	KOAc	110	1	75	9:1
13[e]	*$PdCl_2(dppf)•CH_2Cl_2$*	*DMAc*	*KOAc*	*110*	*1*	*80, 72[f]*	*100*

Pd-catalyzed C–H heteroarylation of compound 1 with various heteroaryl iodides:

a) Optimization:

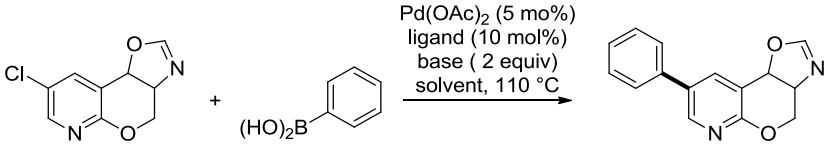
- Screening of bases, solvents and temperature



Entry	Base	Solvent	T (°C)	t (h)	Yield (%)
1	*t*BuONa	THF	60	2	82
2	*t*BuOLi	THF	60	2	50
3	*t*BuOK	THF	60	2	-
4	*t*BuONa	THF	r.t.	12	71
5	*t*BuONa	1,4-Dioxane	r.t.	12	10
6	*t*BuONa	Toluene	r.t.	12	Trace
7	*tBuONa*	*DME*	*r.t.*	*12*	*87*

Suzuki Miyaura cross-coupling at the C-8 position with aryl boronic acids:

a) *Optimization:*



Entry	Ligand	Base	Solvent	Yield (%)
1	SPhos	K_3PO_4	Toluene	20
2	SPhos	Cs_2CO_3	Toluene	0
3	CyJohnPhos	K_3PO_4	Toluene	0
4	XPhos	K_3PO_4	Toluene	25
5	XPhos	K_3PO_4	1,4-dioxane	64
6	XPhos	K_3PO_4	1,4-dioxane/H_2O	70

Table 3

Cristallographic data

DATA COLLECTION

The crystal structure of **1**, [$C_9H_5ClN_2O_2$], has been determined from single crystal X-Ray diffraction. The chosen crystal was stuck on a glass fibre, glued and mounted on the full three-circle goniometer of a Bruker SMART APEX diffractometer with a CCD area detector. three sets of exposures (a total of 1800 frames) were recorded, corresponding to three ω scans (steps of 0.3°), for four different values of ϕ. The details of data collection are given in annexe 1.

The cell parameters and the orientation matrix of the crystal were preliminary determined by using SMART Software[1]. Data integration and global cell refinement were performed with SAINT Software[2]. Intensities were corrected for Lorentz, polarisation, decay and absorption effects (SAINT and SADABS Softwares) and reduced to F_O^2. The program package WinGX[3] was used for space group determination, structure solution and refinement.

DATA REFINEMENT

The standard space group *P*-1 (n°2) was determined from systematic extinctions and relative F_O^2 of equivalent reflections. The structure was solved by direct methods[4]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located from subsequent difference Fourier syntheses and placed with geometrical constraints (SHELXL[5]). The final cycle of full-matrix least-square refinement on F^2 was based on 1664 observed reflections and 127 variable parameters and converged with unweighted and weighted agreement factors of:

R1 = 0.0488, wR2 = 0.1415 for 1331 reflections with I>2σI and R1 = 0.0590, wR2 = 0.1483 for all data.

The refinement data are given in annexe 1 table 2

CRYSTALLOGRAPHIC DATA AND STRUCTURAL DESCRIPTION

Crystallographic data

The crystal data are collected in Table 1. The full crystallographic parameters (atomic coordinates, bond length, angles and anisotropic displacements) are reported in annexe 2.

Table 1: Crystal data

Chemical Formula	C9H5ClN2O2
Molecular Weight / *g.mol*$^{-1}$	208.6
Crystal System	Triclinic
Space Group	*P*-1
Z , Z' (asymmetric units per unit cell)	2,1
a / *Å*	6.6155(11)
b / *Å*	7.0220(12)
c / *Å*	9.6435(17)
α /°	82.132(3)
β / °	76.879(3)
γ /°	71.863(3)
V / *Å*^{3}	413.5(1)
d_{calc} / *g.cm*$^{-3}$	1.675
F(000) / *e*$^{-}$	212
Absorption coefficient μ (MoKα_1) / *mm*$^{-1}$	0.430

Structural description

The asymmetric unit is composed of one molecule of C9H5N2O2Cl (Figure 1).

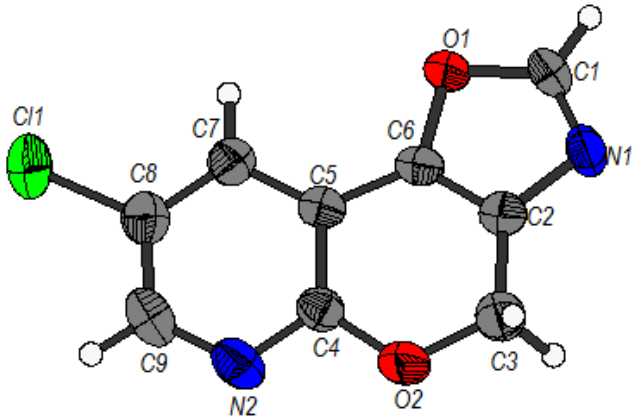


Figure 1: Asymmetric unit in thermal elliposoidal representation with atom labels

Between aromatic parts of adjacent molecules, along b, the distance is at circa 3.6Å (figure2). These ππ interactions lead to rows along. b. These rows are stacked in the two other directions by means of weak Van der waals interactions (figure3).

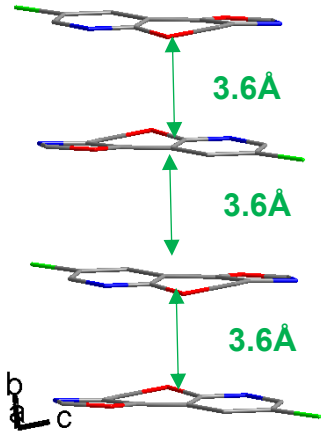


Figure 2: along b, the molecules are spaced at 3.6Å

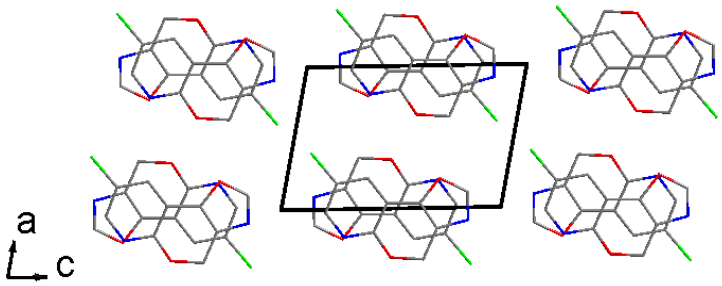


Figure 3: Projection along b.

Sofwares :

(1)- SMART for WNT/2000 V5.622 (2001), Smart software reference manual, Bruker Advanced X Ray Solutions, Inc., Madison, Wisconsin, USA.

(2)- SAINT+ V6.02 (1999), Saint software reference manual, Bruker Advanced X Ray Solutions, Inc., Madison, Wisconsin, USA.

(3)-WinGX: Version 1.70.01: An integrated system of Windows Programs for the solution, refinement and analysis of Single Crystal X-Ray Diffraction Data, By LouisJ. Farrugia, Dept. of chemistry, University of Glasgow.

L. J. Farrugia (1999) J. Appl. Cryst. 32, 837-838.

(4)-include in WinGX suite : SIR 92: A. Altomare, G. Cascarano, & A. Gualardi (1993) J. Appl. Cryst. 26, 343-350; SHELXS-97: Sheldrick, G. M., (1990) Acta cryst, A46, 467.

(5)-include in WinGX suite: SHELXL-97 – a program for crystal structure refinement, G. M. .Sheldrick, University of Goettingen, Germany, 1997, release 97-2.

(6)-PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germany.

ANNEXE 1 :

- Table 1 : DATA COLLECTION FOR C9 H5 Cl N2 O2

Date	11/10/13
Temperature / *K*	RT
Radiation	Mo-Kα_1 (λ = 0.71073Å)
Monochromator	Graphite
Collimator / *mm*	0.5
Generator set	50 kV 40mA
Crystal-detector distance / *mm*	60
Detector 2θ angle / °	-28
ω oscillations / °	-0.3
ω scan 1	χ = 54.7°, ϕ = 0°, -28° ≤ ω ≤ -208°
ω scan 2	χ = 54.7°, ϕ = 120°, -28° ≤ ω ≤ -208°
ω scan 3	χ = 54.7°, ϕ = 240°, -28° ≤ ω ≤ -208°
Time exposure / *s*	20
Total number of reflections	3312
Unique reflections [F_o > 4.0 $\sigma(F_o)$]	1664 / 1331
θ range / °	2.17 to 26.42
hkl range	-8≤h≤8; -8≤k≤8, -11≤l≤11
$R_{int} = \Sigma[\|F_O^2 - F_O^2(mean)\|]$ /	0.0148

$\Sigma[F_O^2]$	
Completeness to θ = 26.40 / %	98.4

- Table 2 : REFINEMENT DATA FOR C9 H5 Cl N2 O2

Number of reflections (n) (with $F_O > 4.0\ \sigma(F_O)$)	1664 / 1331
Number of refined parameters (p) / restraints	127 / 0
Reflection / parameter ratio	
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1415
R indices (all data)	R1 = 0.0590, wR2 = 0.1483
Goodness of Fit indicator (Restrained GooF)	1.070
Maximum peak in Final Difference Map / e^- $Å^{-3}$	0.421
Maximum hole in Final Difference Map / e^- $Å^{-3}$	-0.155

$R_1 = \Sigma\ (||F_O|-|F_C||)\ /\ \Sigma\ |F_O|$

$wR_2 = [\ \Sigma\ [\ w\ (F_O^2 - F_C^2)^2\ ]\ /\ \Sigma\ [\ w\ (F_O^2)^2\ ]\ ]^{1/2}$

$GooF = [\Sigma\ [\ w\ (F_O^2 - F_C^2)^2\ ]\ /\ (n - p)\ ]^{1/2}$

ANNEXE 2 : CRYSTALLOGRAPHIC DATA

Table 1a: Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
C(1)	1103(4)	1225(4)	8358(2)	49(1)
C(2)	-1436(4)	2133(3)	7262(2)	39(1)
C(3)	-3591(4)	2732(4)	6898(3)	49(1)
C(4)	-1635(3)	2828(3)	4407(2)	37(1)
C(5)	407(3)	2453(3)	4774(2)	36(1)
C(6)	358(3)	2023(3)	6280(2)	37(1)
C(7)	2160(4)	2493(3)	3694(2)	42(1)
C(8)	1803(4)	2900(4)	2322(3)	46(1)
C(9)	-240(5)	3263(4)	2056(3)	52(1)
Cl(1)	3952(1)	2921(1)	908(1)	68(1)
N(1)	-881(3)	1604(3)	8610(2)	44(1)
N(2)	-1968(3)	3220(3)	3095(2)	50(1)
O(1)	2093(2)	1424(3)	6956(2)	45(1)
O(2)	-3433(3)	2709(3)	5386(2)	55(1)

Table 1b: Hydrogen coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)

H(1)	1896	823	9083	59
H(3A)	-4395	1820	7406	59
H(3B)	-4380	4073	7195	59
H(7)	3537	2253	3886	51
H(9)	-436	3550	1117	62

Table 2: Bond lengths (Å)

C(1)-N(1)	1.228(3)
C(1)-O(1)	1.370(3)
C(1)-H(1)	0.93
C(2)-C(6)	1.329(3)
C(2)-N(1)	1.401(3)
C(2)-C(3)	1.465(3)
C(3)-O(2)	1.440(3)
C(3)-H(3A)	0.97
C(3)-H(3B)	0.97
C(4)-N(2)	1.311(3)
C(4)-O(2)	1.358(3)
C(4)-C(5)	1.411(3)
C(5)-C(7)	1.377(3)
C(5)-C(6)	1.437(3)
C(6)-O(1)	1.373(3)
C(7)-C(8)	1.372(3)
C(7)-H(7)	0.93
C(8)-C(9)	1.372(4)
C(8)-Cl(1)	1.735(3)
C(9)-N(2)	1.344(3)

C(9)-H(9)	0.93

Table 3: Angles (°)

N(1)-C(1)-O(1)	116.8(2)	C(4)-C(5)-C(6)	113.29(19)
N(1)-C(1)-H(1)	121.6	C(2)-C(6)-O(1)	108.21(19)
O(1)-C(1)-H(1)	121.6	C(2)-C(6)-C(5)	124.4(2)
C(6)-C(2)-N(1)	109.0(2)	O(1)-C(6)-C(5)	127.35(19)
C(6)-C(2)-C(3)	122.3(2)	C(8)-C(7)-C(5)	117.6(2)
N(1)-C(2)-C(3)	128.6(2)	C(8)-C(7)-H(7)	121.2
O(2)-C(3)-C(2)	111.06(19)	C(5)-C(7)-H(7)	121.2
O(2)-C(3)-H(3A)	109.4	C(7)-C(8)-C(9)	120.5(2)
C(2)-C(3)-H(3A)	109.4	C(7)-C(8)-Cl(1)	119.9(2)
O(2)-C(3)-H(3B)	109.4	C(9)-C(8)-Cl(1)	119.5(2)
C(2)-C(3)-H(3B)	109.4	N(2)-C(9)-C(8)	122.7(2)
H(3A)-C(3)-H(3B)	108	N(2)-C(9)-H(9)	118.6
N(2)-C(4)-O(2)	113.39(19)	C(8)-C(9)-H(9)	118.6
N(2)-C(4)-C(5)	123.9(2)	C(1)-N(1)-C(2)	103.96(19)
O(2)-C(4)-C(5)	122.6(2)	C(4)-N(2)-C(9)	117.0(2)
C(7)-C(5)-C(4)	118.3(2)	C(1)-O(1)-C(6)	101.97(17)
C(7)-C(5)-C(6)	128.4(2)	C(4)-O(2)-C(3)	123.00(18)

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

	U11	U22	U33	U23	U13	U12
C(1)	55(2)	66(2)	31(1)	5(1)	-17(1)	-23(1)
C(2)	39(1)	37(1)	42(1)	-3(1)	-10(1)	-10(1)
C(3)	42(1)	59(2)	45(1)	-3(1)	-9(1)	-11(1)

C(4)	35(1)	36(1)	40(1)	-4(1)	-11(1)	-5(1)
C(5)	38(1)	31(1)	40(1)	-3(1)	-11(1)	-9(1)
C(6)	35(1)	37(1)	43(1)	-1(1)	-15(1)	-11(1)
C(7)	42(1)	43(1)	43(1)	-2(1)	-8(1)	-14(1)
C(8)	53(1)	41(1)	43(1)	-6(1)	-5(1)	-12(1)
C(9)	67(2)	48(2)	38(1)	-4(1)	-17(1)	-8(1)
Cl(1)	75(1)	89(1)	37(1)	-4(1)	2(1)	-30(1)
N(1)	50(1)	52(1)	28(1)	1(1)	-9(1)	-13(1)
N(2)	50(1)	52(1)	44(1)	-5(1)	-20(1)	-3(1)
O(1)	35(1)	64(1)	38(1)	2(1)	-14(1)	-16(1)
O(2)	35(1)	83(1)	48(1)	-4(1)	-15(1)	-15(1)

Table 5: Torsion angles (°)

C(6)-C(2)-C(3)-O(2)	13.4(3)	C(5)-C(7)-C(8)-C(9)	0.4(4)
N(1)-C(2)-C(3)-O(2)	-166.8(2)	C(5)-C(7)-C(8)-Cl(1)	-178.64(16)
N(2)-C(4)-C(5)-C(7)	-0.2(3)	C(7)-C(8)-C(9)-N(2)	-0.8(4)
O(2)-C(4)-C(5)-C(7)	176.1(2)	Cl(1)-C(8)-C(9)-N(2)	178.26(19)
N(2)-C(4)-C(5)-C(6)	-178.8(2)	O(1)-C(1)-N(1)-C(2)	0.2(3)
O(2)-C(4)-C(5)-C(6)	-2.5(3)	C(6)-C(2)-N(1)-C(1)	-0.3(3)
N(1)-C(2)-C(6)-O(1)	0.2(3)	C(3)-C(2)-N(1)-C(1)	179.9(2)
C(3)-C(2)-C(6)-O(1)	-180.0(2)	O(2)-C(4)-N(2)-C(9)	-176.77(19)
N(1)-C(2)-C(6)-C(5)	179.65(19)	C(5)-C(4)-N(2)-C(9)	-0.1(3)
C(3)-C(2)-C(6)-C(5)	-0.5(4)	C(8)-C(9)-N(2)-C(4)	0.6(4)
C(7)-C(5)-C(6)-C(2)	175.9(2)	N(1)-C(1)-O(1)-C(6)	-0.1(3)
C(4)-C(5)-C(6)-C(2)	-5.7(3)	C(2)-C(6)-O(1)-C(1)	0.0(2)
C(7)-C(5)-C(6)-O(1)	-4.8(4)	C(5)-C(6)-O(1)-C(1)	-179.5(2)

C(4)-C(5)-C(6)-O(1)	173.7(2)	N(2)-C(4)-O(2)-C(3)	-166.0(2)
C(4)-C(5)-C(7)-C(8)	0.1(3)	C(5)-C(4)-O(2)-C(3)	17.3(3)
C(6)-C(5)-C(7)-C(8)	178.5(2)	C(2)-C(3)-O(2)-C(4)	-21.6(3)

Table 6: Calculated reflections from PowderCell*

h	k	l	2θ/°	d/Å	I/rel.	|F(hkl)|
0	0	1	9.43	9.37	36.25	21.07
1	0	0	14.36	6.17	43.89	35.46
1	0	1	15.57	5.69	36.13	34.95
1	1	0	16.51	5.37	4.77	13.48
0	0	2	18.93	4.68	9.56	21.97
-1	-1	1	20.85	4.26	18.87	34.12
1	0	2	21.44	4.14	22.76	38.57
1	1	2	22.14	4.01	18.72	36.16
1	-1	0	22.30	3.98	5.29	19.37
0	1	2	22.40	3.97	9.81	26.49
1	-1	1	23.51	3.78	10.64	29.02
-1	1	1	25.00	3.56	8.60	27.83
1	2	0	26.46	3.37	6.48	25.65
1	2	1	26.47	3.37	80.37	90.34
0	2	0	26.77	3.33	100.00	101.98
2	1	1	27.47	3.24	8.91	31.29
0	2	1	27.78	3.21	48.77	74.07
-1	-1	2	27.98	3.19	5.37	24.76
1	-1	2	28.15	3.17	5.38	24.96
2	0	1	28.64	3.11	15.53	43.18
0	-2	1	29.09	3.07	7.50	30.52

1	0	3	29.40	3.04	5.95	27.49
1	2	2	29.76	3.00	4.83	25.10

Source: Cu-$K_{\alpha 1}$ (λ = 1.540598 Å)

Condition on reflections: I ≥ 2

Range (2θ): From 3° to 30°

*PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germany.

DATA COLLECTION

The crystal structure of **6**, $[C_9H_5ClN_2O_2]_2$, has been determined from single crystal X-Ray diffraction. The chosen crystal was stuck on a glass fibre, glued and mounted on the full three-circle goniometer of a Bruker SMART APEX diffractometer with a CCD area detector. **Three** sets of exposures (a total of **1800** frames) were recorded, corresponding to **three** ω scans (steps of 0.3°), for four different values of ϕ. The details of data collection are given in annexe 1.

The cell parameters and the orientation matrix of the crystal were preliminary determined by using SMART Software[1]. Data integration and global cell refinement were performed with SAINT Software[2]. Intensities were corrected for Lorentz, polarisation, decay and absorption effects (SAINT and SADABS Softwares) and reduced to F_O^2. The program package WinGX[3] was used for space group determination, structure solution and refinement.

DATA REFINEMENT

The standard space group *P*-1 (n°2) was determined from systematic extinctions and relative F_O^2 of equivalent reflections. The structure was solved by direct methods[4]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located from subsequent difference Fourier syntheses and placed with geometrical constraints (SHELXL[5]). The final cycle of full-matrix least-square refinement on F^2 was based on 1668 observed reflections and 128 variable parameters and converged with unweighted and weighted agreement factors of:

R1 = 0.0346, wR2 = 0.0890 for 1492 reflections with $I>2\sigma I$ and R1 = 0.0387, wR2 = 0.0917 for all data.

The refinement data are given in annexe 1 table 2

CRYSTALLOGRAPHIC DATA AND STRUCTURAL DESCRIPTION

Crystallographic data

The crystal data are collected in Table 1. The full crystallographic parameters (atomic coordinates, bond length, angles and anisotropic displacements) are reported in annexe 2.

Table 1: Crystal data

Chemical Formula	$[C_9H_5ClN_2O_2]_2$

Molecular Weight / $g.mol^{-1}$	417.2
Crystal System	Triclinic
Space Group	*P*-1
Z , Z' (asymmetric units per unit cell)	1, 0.5
a / *Å*	4.6985(7)
b / *Å*	9.6719(14)
c / *Å*	9.8461(14)
	111.248(2)
β / °	92.409(2)
	91.899(2)
V / $Å^3$	416.09
d_{calc} / $g.cm^{-3}$	1.665
F(000) / e^-	212
Absorption coefficient μ (MoKα_1) / mm^{-1}	0.427

Structural description

The asymmetric unit is composed of one half of the compound CS874 (Figure 1). The other part of the molecule is generated by the inversion centre.

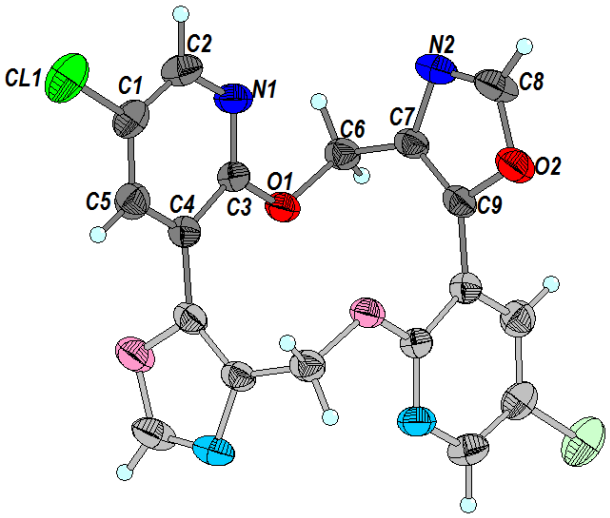


Figure 1: The full molecule of CS874. In light colour the part generated by the inversion centre.

Sofwares :

(1)- SMART for WNT/2000 V5.622 (2001), Smart software reference manual, Bruker Advanced X Ray Solutions, Inc., Madison, Wisconsin, USA.

(2)- SAINT+ V6.02 (1999), Saint software reference manual, Bruker Advanced X Ray Solutions, Inc., Madison, Wisconsin, USA.

(3)-WinGX: Version 1.70.01: An integrated system of Windows Programs for the solution, refinement and analysis of Single Crystal X-Ray Diffraction Data, By LouisJ. Farrugia, Dept. of chemistry, University of Glasgow.

L. J. Farrugia (1999) J. Appl. Cryst. 32, 837-838.

(4)-include in WinGX suite : SIR 92: A. Altomare, G. Cascarano, & A. Gualardi (1993) J. Appl. Cryst. 26, 343-350; SHELXS-97: Sheldrick, G. M., (1990) Acta cryst, A46, 467.

(5)-include in WinGX suite: SHELXL-97 – a program for crystal structure refinement, G. M. .Sheldrick, University of Goettingen, Germany, 1997, release 97-2.

(6)-PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germany.

ANNEXE 1 :

- Table 1 : DATA COLLECTION FOR CS874

Date	22/01/2015
Temperature / *K*	RT
Radiation	Mo-Kα_1 (λ = 0.71073Å)
Monochromator	Graphite
Collimator / *mm*	0.5
Generator set	50 kV 40mA
Crystal-detector distance / *mm*	60
Detector 2θ angle / °	-28
ω oscillations / °	-0.3
ω scan 1	χ = 54.7°, ϕ = 0°, -28° ≤ ω ≤ -208°
ω scan 2	χ = 54.7°, ϕ = 120°, -28° ≤ ω ≤ -208°
ω scan 3	χ = 54.7°, ϕ = 240°, -28° ≤ ω ≤ -208°
Time exposure / *s*	20
Total number of reflections	3322
Unique reflections [F_o > 4.0 $\sigma(F_o)$]	1668 /1492
θ range / °	2.22 to 26.33
hkl range	-5≤h≤5 ; -11≤k≤12 ; -11≤l≤12
R_{int} = $\Sigma[\|F_O^2 - F_O^2(mean)\|] / \Sigma[F_O^2]$	0.0119
Completeness to θ = 26.40 / %	98.8

- Table 2 : REFINEMENT DATA FOR CS874

Number of reflections (n) (with $F_O > 4.0\ \sigma(F_O)$)	1668 / 1492
Number of refined parameters (p) / restraints	128 / 0
Reflection / parameter ratio	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0890
R indices (all data)	R1 = 0.0387, wR2 = 0.0917
Goodness of Fit indicator (Restrained GooF)	1.048
Maximum peak in Final Difference Map / $e^{-}Å^{-3}$	0.246
Maximum hole in Final Difference Map / $e^{-}Å^{-3}$	-0.254

$R_1 = \Sigma\ (||F_O|-|F_C||)\ /\ \Sigma\ |F_O|$

$wR_2 = [\ \Sigma\ [\ w\ (F_O^2 - F_C^2)^{\ 2}]\ /\ \Sigma\ [\ w\ (F_O^2)^2\ ]\ ]^{1/2}$

$GooF = [\Sigma\ [\ w\ (F_O^2 - F_C^2)^{\ 2}]\ /\ (n - p)\ ]^{1/2}$

ANNEXE 2 : CRYSTALLOGRAPHIC DATA

Table 1a: Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
C(1)	1451(4)	7504(2)	2547(2)	38(1)
C(2)	2952(4)	8445(2)	3770(2)	41(1)
C(3)	5410(3)	6552(2)	4016(2)	30(1)
C(4)	3952(4)	5497(2)	2783(2)	32(1)
C(5)	1934(4)	6008(2)	2049(2)	38(1)
C(6)	8637(4)	7054(2)	6106(2)	33(1)
C(7)	6638(3)	7193(2)	7278(2)	31(1)
C(8)	3963(4)	8181(2)	8996(2)	47(1)

C(9)	4426(4)	3902(2)	2325(2)	33(1)
Cl(1)	-1088(1)	8191(1)	1661(1)	56(1)
N(1)	4916(3)	7975(2)	4508(2)	38(1)
N(2)	5581(3)	8535(2)	8150(2)	41(1)
O(1)	7451(2)	6049(1)	4700(1)	34(1)
O(2)	3792(3)	6718(1)	8792(1)	43(1)

Table 1b: Hydrogen coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
H(2)	2596	9450	4104	50
H(5)	908	5352	1227	46
H(6A)	9040	8025	6059	40
H(6B)	10420	6690	6341	40
H(8)	2971	8879	9703	56

Table 2: Bond lengths (Å)

C(1)-C(2)	1.366(3)
C(1)-C(5)	1.379(3)
C(1)-Cl(1)	1.7351(17)
C(2)-N(1)	1.340(2)
C(3)-N(1)	1.316(2)
C(3)-O(1)	1.3504(19)
C(3)-C(4)	1.403(2)
C(4)-C(5)	1.378(2)
C(4)-C(9)	1.470(2)

C(6)-O(1)	1.4477(19)
C(6)-C(7)	1.489(2)
C(7)-C(9)#1	1.343(2)
C(7)-N(2)	1.393(2)
C(8)-N(2)	1.278(2)
C(8)-O(2)	1.354(2)
C(9)-C(7)#1	1.343(2)
C(9)-O(2)#1	1.379(2)
O(2)-C(9)#1	1.379(2)
C(1)-C(2)	1.366(3)
C(1)-C(5)	1.379(3)
C(1)-Cl(1)	1.7351(17)
C(2)-N(1)	1.340(2)
C(3)-N(1)	1.316(2)

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

Table 3: Angles (°)

C(2)-C(1)-C(5)	119.33(16)
C(2)-C(1)-Cl(1)	119.95(14)
C(5)-C(1)-Cl(1)	120.71(14)
N(1)-C(2)-C(1)	122.58(16)
N(1)-C(3)-O(1)	119.56(14)
N(1)-C(3)-C(4)	123.67(15)
O(1)-C(3)-C(4)	116.76(13)
C(5)-C(4)-C(3)	117.14(15)
C(5)-C(4)-C(9)	120.75(14)
C(3)-C(4)-C(9)	122.04(15)
C(4)-C(5)-C(1)	119.29(16)

O(1)-C(6)-C(7)	111.38(13)
C(9)#1-C(7)-N(2)	109.15(15)
C(9)#1-C(7)-C(6)	127.26(14)
N(2)-C(7)-C(6)	123.59(15)
N(2)-C(8)-O(2)	115.30(16)
C(7)#1-C(9)-O(2)#1	107.88(14)
C(7)#1-C(9)-C(4)	133.52(15)
O(2)#1-C(9)-C(4)	118.52(14)
C(3)-N(1)-C(2)	117.97(15)
C(8)-N(2)-C(7)	104.16(15)
C(3)-O(1)-C(6)	117.67(12)
C(8)-O(2)-C(9)#1	103.50(14)

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

	U11	U22	U33	U23	U13	U12
C(1)	33(1)	43(1)	44(1)	24(1)	1(1)	3(1)
C(2)	44(1)	30(1)	51(1)	17(1)	2(1)	7(1)
C(3)	34(1)	26(1)	31(1)	10(1)	3(1)	2(1)
C(4)	37(1)	28(1)	30(1)	10(1)	2(1)	-1(1)
C(5)	40(1)	39(1)	35(1)	14(1)	-3(1)	-4(1)
C(6)	34(1)	29(1)	34(1)	9(1)	-4(1)	-1(1)
C(7)	34(1)	25(1)	30(1)	4(1)	-6(1)	0(1)
C(8)	53(1)	31(1)	45(1)	-2(1)	9(1)	4(1)
C(9)	36(1)	30(1)	27(1)	4(1)	-1(1)	1(1)
Cl(1)	43(1)	71(1)	70(1)	45(1)	-3(1)	10(1)
N(1)	45(1)	26(1)	40(1)	9(1)	-2(1)	4(1)
N(2)	47(1)	26(1)	42(1)	2(1)	1(1)	3(1)

O(1)	40(1)	26(1)	31(1)	6(1)	-2(1)	5(1)
O(2)	50(1)	35(1)	37(1)	4(1)	10(1)	1(1)

Table 5: Torsion angles (°)

C(5)-C(1)-C(2)-N(1)	0.7(3)
Cl(1)-C(1)-C(2)-N(1)	179.32(14)
N(1)-C(3)-C(4)-C(5)	1.1(2)
O(1)-C(3)-C(4)-C(5)	-177.85(14)
N(1)-C(3)-C(4)-C(9)	-175.77(16)
O(1)-C(3)-C(4)-C(9)	5.2(2)
C(3)-C(4)-C(5)-C(1)	0.1(2)
C(9)-C(4)-C(5)-C(1)	177.07(15)
C(2)-C(1)-C(5)-C(4)	-1.0(3)
Cl(1)-C(1)-C(5)-C(4)	-179.59(13)
O(1)-C(6)-C(7)-C(9)#1	58.9(2)
O(1)-C(6)-C(7)-N(2)	-121.40(16)
C(5)-C(4)-C(9)-C(7)#1	-92.6(2)
C(3)-C(4)-C(9)-C(7)#1	84.2(2)
C(5)-C(4)-C(9)-O(2)#1	83.7(2)
C(3)-C(4)-C(9)-O(2)#1	-99.49(18)
O(1)-C(3)-N(1)-C(2)	177.51(15)
C(4)-C(3)-N(1)-C(2)	-1.4(3)
C(1)-C(2)-N(1)-C(3)	0.5(3)
O(2)-C(8)-N(2)-C(7)	-0.1(2)
C(9)#1-C(7)-N(2)-C(8)	-0.47(19)
C(6)-C(7)-N(2)-C(8)	179.75(16)
N(1)-C(3)-O(1)-C(6)	11.4(2)
C(4)-C(3)-O(1)-C(6)	-169.58(14)
C(7)-C(6)-O(1)-C(3)	76.11(17)
N(2)-C(8)-O(2)-C(9)#1	0.6(2)

Table 6: Calculated reflections from PowderCell*

h	k	l	2θ/°	d/Å	I/rel.	|F(hkl)|
0	0	1	9.65	9.16	17.90	12.64
0	1	0	9.82	9.00	52.11	21.95
0	-1	1	10.98	8.05	2.45	5.32
0	1	1	16.11	5.50	28.65	26.90
0	-1	2	18.24	4.86	16.33	23.06
0	-2	1	18.51	4.79	6.93	15.26
1	0	0	18.92	4.69	32.13	33.59
0	0	2	19.36	4.58	30.97	33.78
0	2	0	19.71	4.50	98.55	61.37
-1	0	1	20.76	4.28	20.51	29.54
1	-1	0	20.89	4.25	11.92	22.67
1	0	1	21.77	4.08	2.04	9.78
-1	-1	1	21.88	4.06	23.56	33.44
1	-1	1	21.96	4.04	22.15	32.55
0	2	1	25.00	3.56	2.40	12.26
1	1	1	25.76	3.46	47.90	56.58
-1	-1	2	25.94	3.43	100.00	82.34
1	-2	1	26.25	3.39	2.22	12.43
-1	0	2	26.38	3.38	19.86	37.35
1	-1	2	26.84	3.32	40.14	54.08
-1	-2	1	26.92	3.31	29.23	46.30
0	-3	1	27.68	3.22	5.80	21.24
1	0	2	27.99	3.19	8.05	25.33
0	-3	2	29.01	3.08	8.19	26.53
-1	-2	2	29.15	3.06	42.44	60.70
0	0	3	29.22	3.05	23.05	44.86
1	-2	2	29.28	3.05	16.66	38.22
0	3	0	29.75	3.00	3.72	18.36

Source: Cu-$K_{\alpha 1}$ (λ = 1.540598 Å)

Condition on reflections: I ≥ 2

Range (2θ): From 3° to 30°

*PowderCell for Windows (version 2.4) by Kraus W. & Nolze G., Federal institute for materials Research and testing, Rudower Chausse 5, 12489 Berlin Germa