Supporting Information

Alternative energy input for transfer hydrogenation using NHC-iridium based catalysts in glycerol as hydrogen donor and solvent

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1.- General Procedures

All manipulations were carried out under nitrogen using standard Schlenk techniques and high vacuum, unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN). All other reagents were used as received from commercial suppliers. Glycerol was used as received form Sigma-Aldrich (ref. G9012, >99%). The products were identified by GCMS-QP2010 (Shimadzu) gas chromatograph/mass spectrometer equipped with a Teknokroma (TRB-5MS, 30 m 0.25 mm x 0.25 mm) column, and the spectra obtained were compared with the standard spectra. The yields, conversion and product selectivity were determined by a GC-2010 (Shimadzu) gas chromatograph equipped with a FID and a Teknokroma (TRB-5MS, 30 m0.25 mm 0.25 mm) column. NMR spectra were recorded on Varian spectrometers operating at 300 or 500 MHz (^{1}H NMR) and 75 and 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in ppm and *J* in hertz). NMR spectra were recorded at room temperature with the appropriate deuterated solvent ($CDCl_3$, CD_3OD or d6-DMSO). The identity of analytically pure samples of the saturated alcohols was assessed by comparison of their ^{1}H NMR data previously described in the literature and by their fragmentation in GC/MS. Microwave-assisted reactions were performed in sealed vessels with a Biotage Initiator 60 EXP® instrument. The temperature was measured with an IR sensor on the outer surface of the reaction vial. Open vessel sonochemical reactions were performed in probe systems (VCX-400 Sonics Materials Vibracell, USA) equipped with an immersion horn made from titanium alloy. The working frequency was 20 KHz, using 40% amplitude. Analytical high performance liquid chromatography (HPLC) was performed on a Waters Millenium 717 equipped with Autosampler, with a variable wavelength diode detector using a CHROMOLITH RP18 column (50 x 4,6 mm), flow 5 mL/min, linear gradient CH_3CN in water 0-100% (+ 0.1% TFA) in 4.5 min. Transmission Electron Microscopy (TEM) micrographs were recorded on a JEOL 1200EX2 (Made in Tokyo, Japan – 1990) at an operating voltage of 100 kV. The particles were dispersed in ethanol (microwave experiments) or in water (ultrasound experiments) by ultrasonication during 30 minutes, loaded on a carbon-coated copper grids (300 Mesh), and then allowed to dry at romm temperature before recording the micrographs.

2.- Catalytic studies. General procedures.

General method for TH in an oil-bath. In a typical experiment of transfer hydrogenation using glycerol as hydrogen donor a capped vessel containing a stirrer bar was charged with the substrate (0.5 mmol), potassium hydroxide (0.5 mmol), anisole as internal reference (0.5 mmol), catalyst (2.5 %) in 0.8 mL of glycerol. The solution was heated to 80 - 120 ºC for the appropriate time. During the reaction monitoring, yields and conversions were determined by GC chromatography. Products and intermediates were characterized by GC/MS. Isolated products were characterized by ^{1}H NMR and ^{13}C NMR after column chromatography purification using mixtures of n-hexanes/ethylacetate.

General method for TH under microwave irradiation. In a typical experiment, a mixture of substrate (0.5 mmol), catalyst (2.5 mol %) and finely powdered KOH (0.028 g, 0.5 mmol) in glycerol (0.4 mL) was heated under microwave irradiation at 120°C for 1 hour, in a sealed reactor. After cooling, a mixture 2:1 *v/v* of Et_2O/CH_2Cl_2 (3 mL) was added to the crude and left under stirring, at room temperature for 5 minutes. The supernatant is recovered and the operation is repeated three times. The organic phase is dried on Mg_2SO_4, filtered and evaporated under reduced pressure to afford the reduced product as a pure compound. Product conversion was determined by HPLC; yield was determined by GC/MS.

General method for TH under sonication. In a typical experiment, a mixture of substrate (0.5 mmol), catalyst (2.5 mol %) and finely powdered KOH (0.028 g, 0.5 mmol) in glycerol (0.4 mL) was placed in a Pirex glass reactor and clamped to a vertical support on a magnetic stirrer. The vessel was hold in place such that the tip of the horn was immersed in the reaction mixture to a depth of 1.0 cm and the glass part did not touch the sonochemical probe. The reaction was sonicated at 98°C continously during the indicated time (Table 3), with 40% Amplitude, while keeping vigorous magnetic stirring. At the end of the reaction, a mixture 2:1 *v/v* of Et_2O/CH_2Cl_2 (3 mL) was added to the crude and left under stirring, at room temperature for 5 minutes. The supernatant is recovered and the operation is repeated three times. The organic phase is dried on Mg_2SO_4, filtered and evaporated under reduced pressure to afford the reduced product as a pure compound. Product conversion was determined by HPLC; yield was determined by GC/MS.

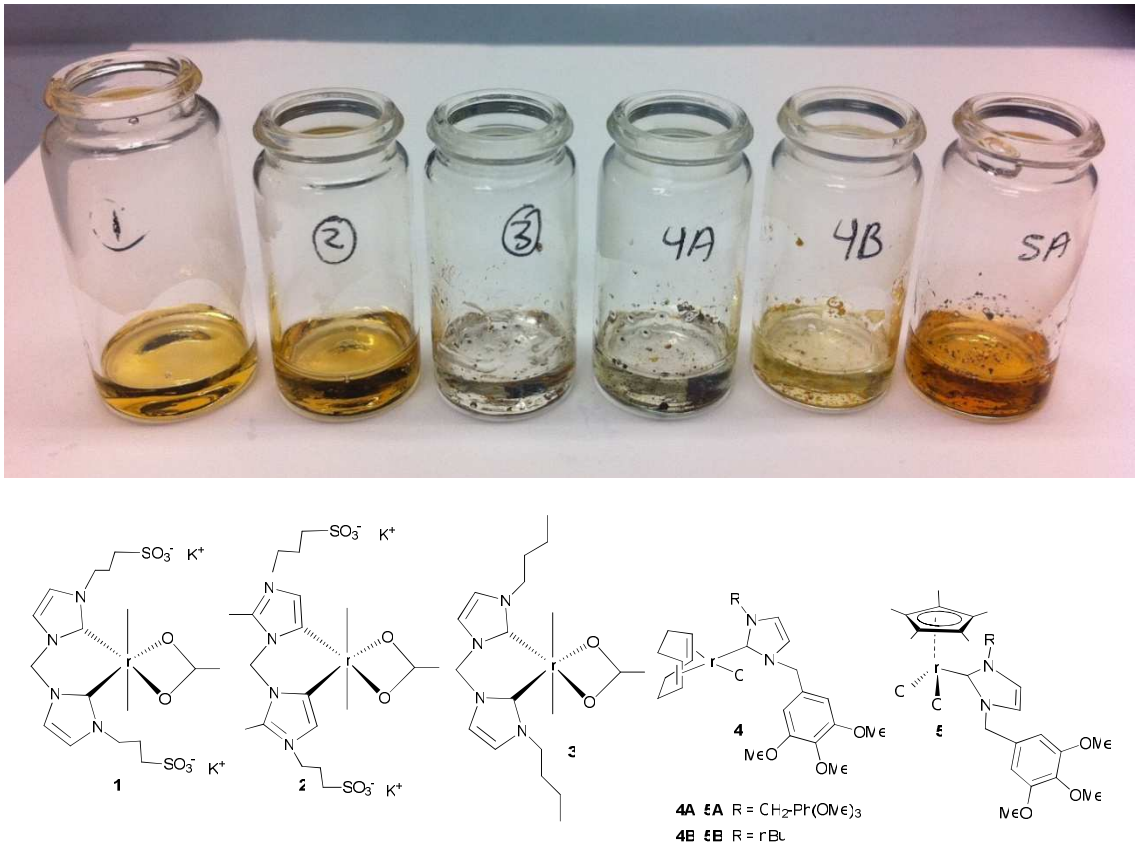

Figure 1. Solubility tests of catalysts **1**-**5** in glycerol, 0.005 mmol/mL at room temperature. Catalyst **1** and **2** are completely soluble, **3** is insoluble, and **4A/B** and **5A** are partially soluble.

Figure 2. Equipment for ultrasound experiments

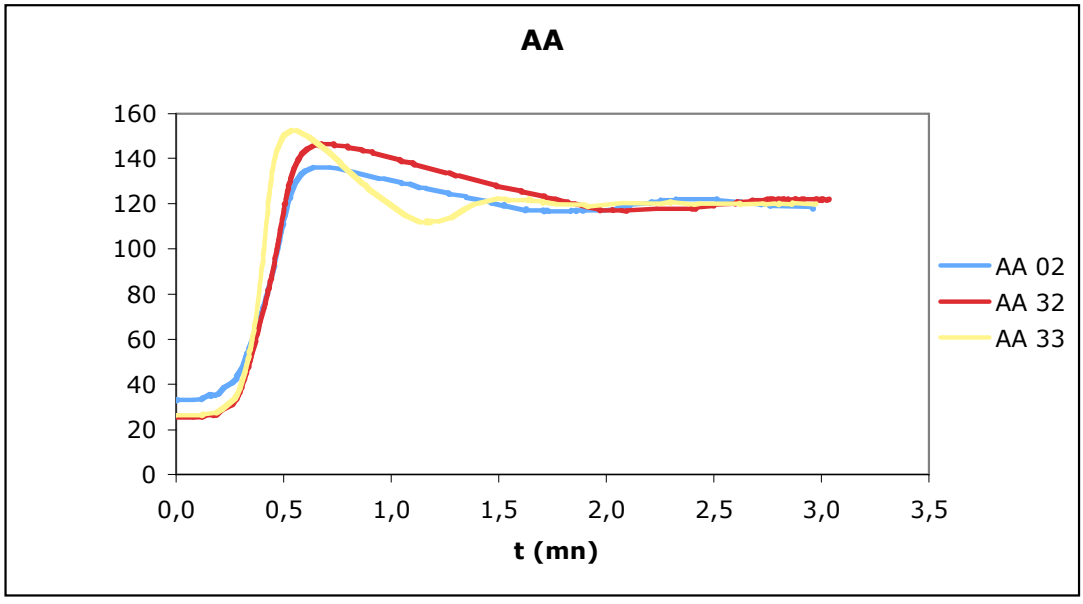

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Figure 3. Study of the rise of the temperature as a function of the heating mode under microwave activation. *Legend*: AA02 - starting heating power set off (Table 2, entry 3); AA32 - starting heating power set at its maximum level (400 W) (Table 2, entry 5); AA33 : simultaneous cooling system, with starting heating power off (Table 2, entry 4).

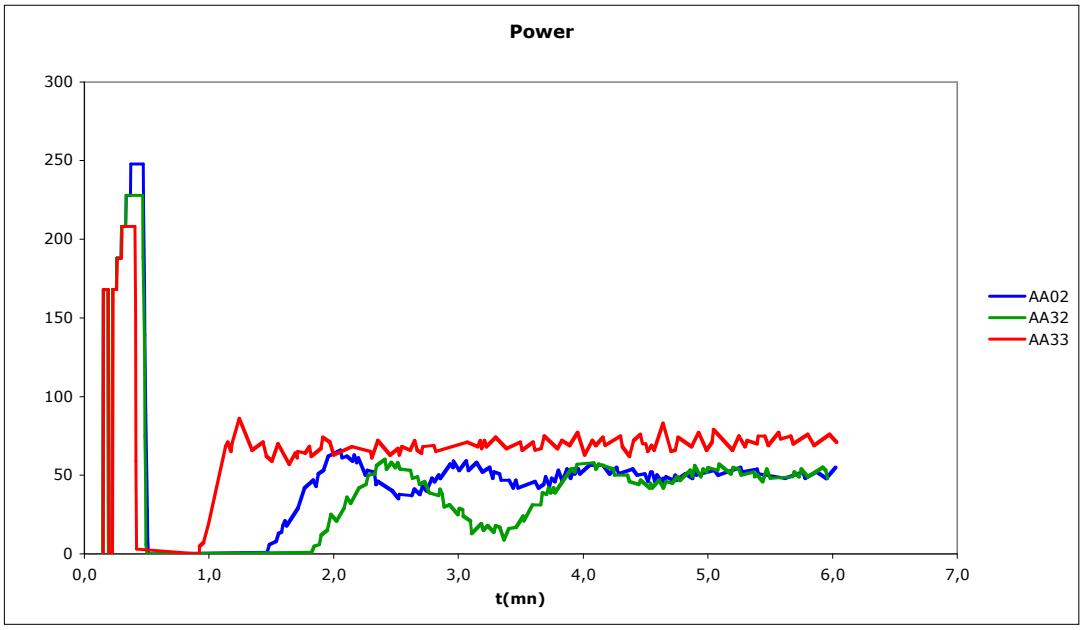
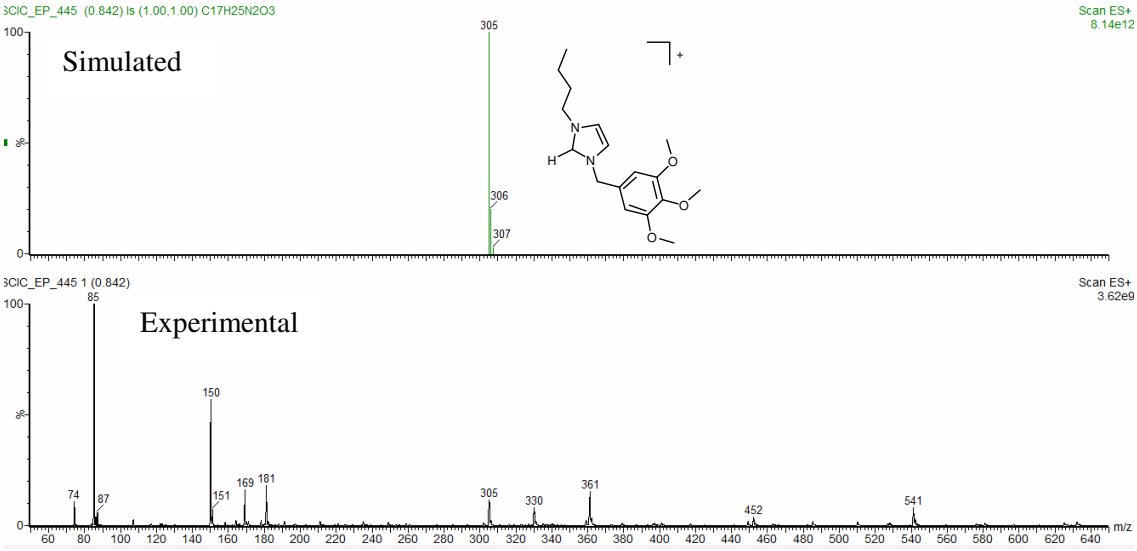


Figure 4. Study of the rise of the Power as a function of the heating mode under microwave activation. *Legend*: AA02 - starting heating power set off (Table 2, entry 3); AA32 - starting heating power set at its maximum level (400 W) (Table 2, entry 5); AA33 : simultaneous cooling system, with starting heating power off (Table 2, entry 4).

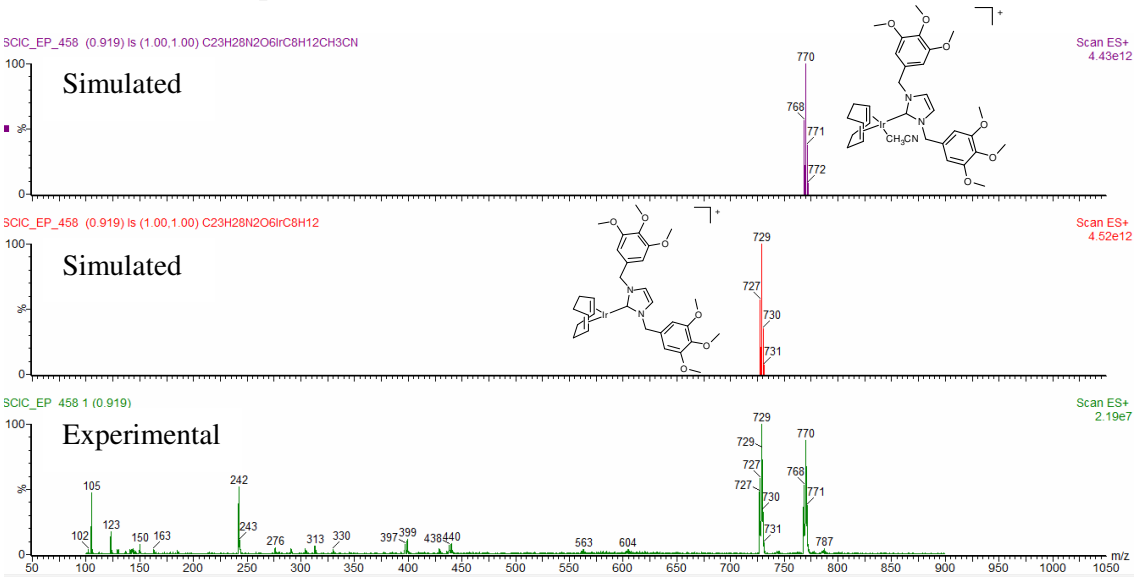
3.- Electrospray Mass Ionization Mass Spectroscopy (ESIMS)

Electrospray mass spectra were recorded on a Micromass Quatro LC instrument using acetonitrile. Nitrogen was employed as drying and nebulising gas.

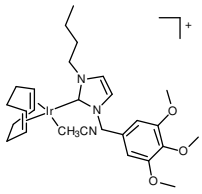
3.1- ESIMS of compound A

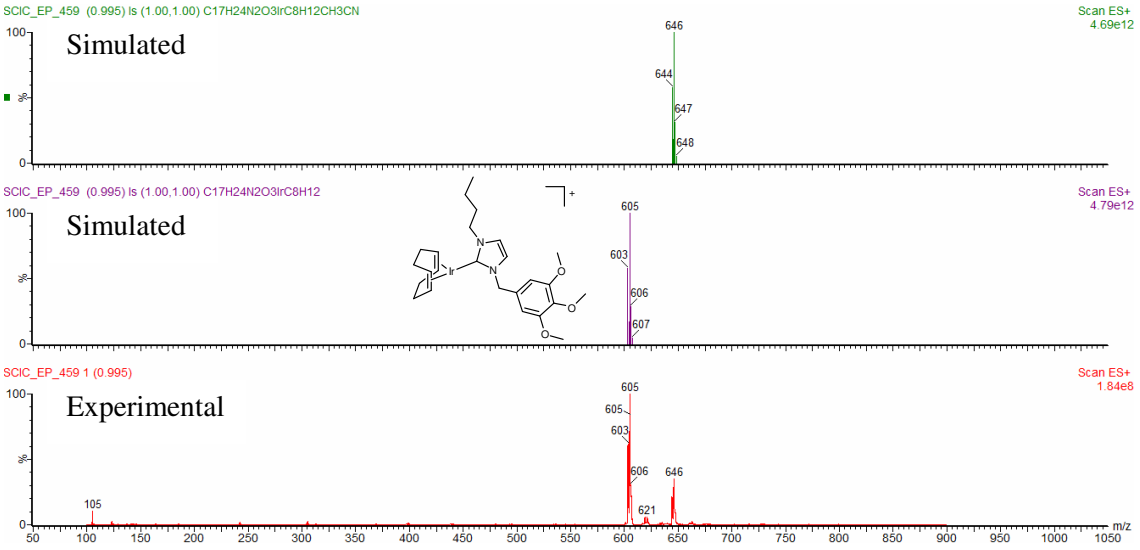


3.2- - ESIMS of compound 4A

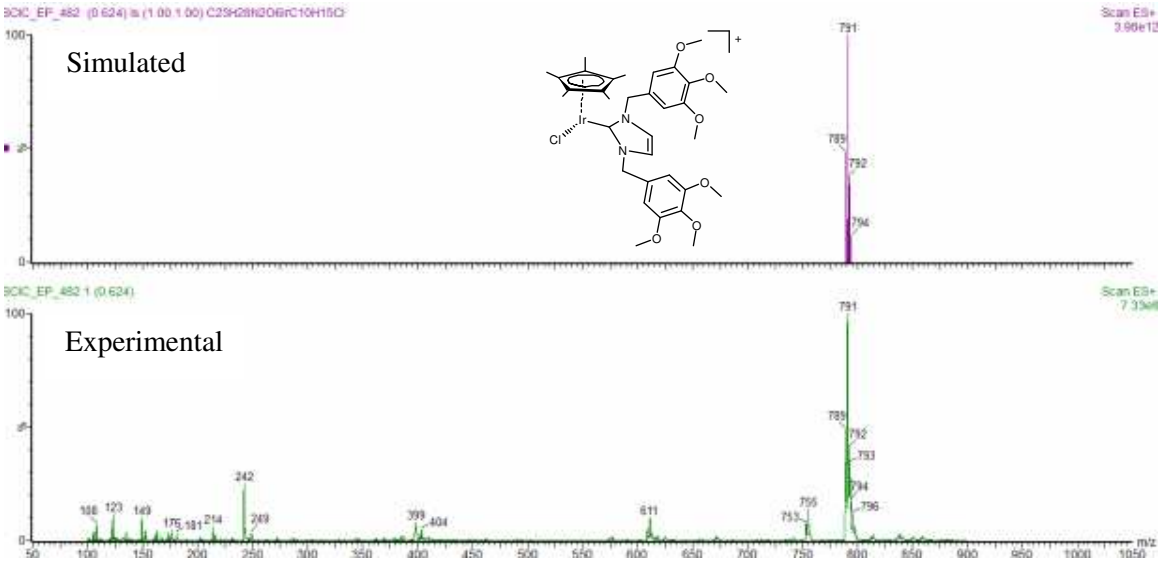


3.3- - ESIMS of compound 4B

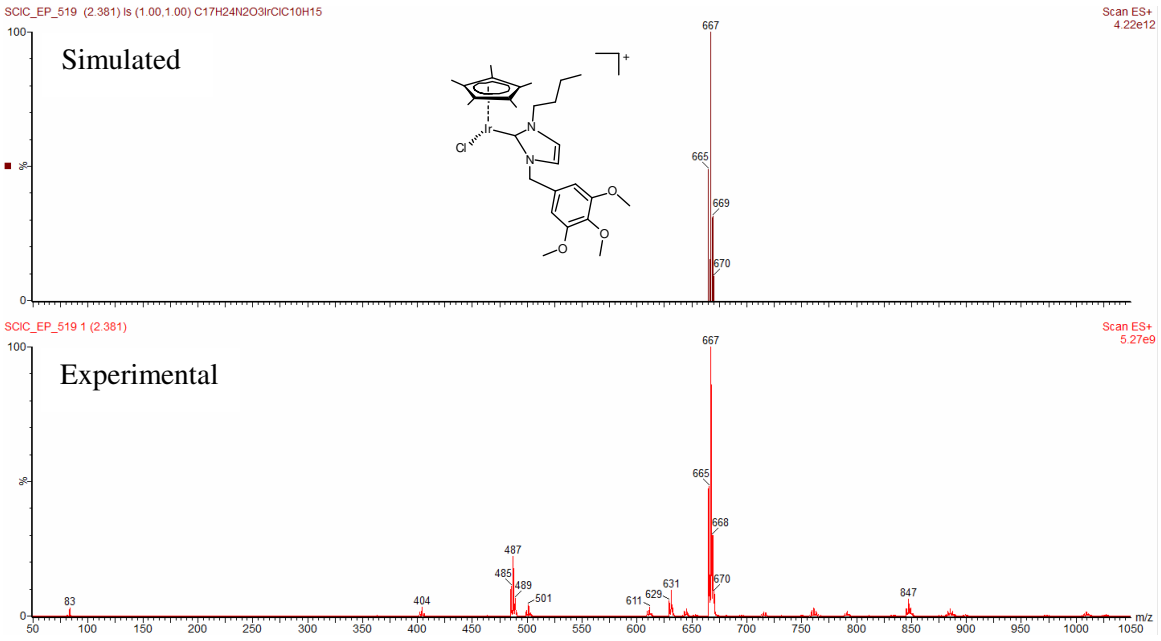




3.4- - ESIMS of compound 5A



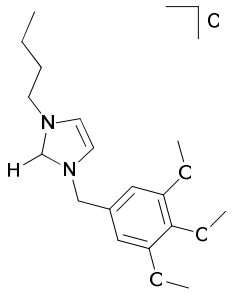
3.5- - ESIMS of compound 5B



4.- High Resolution Mass Spectroscopy (HRMS)

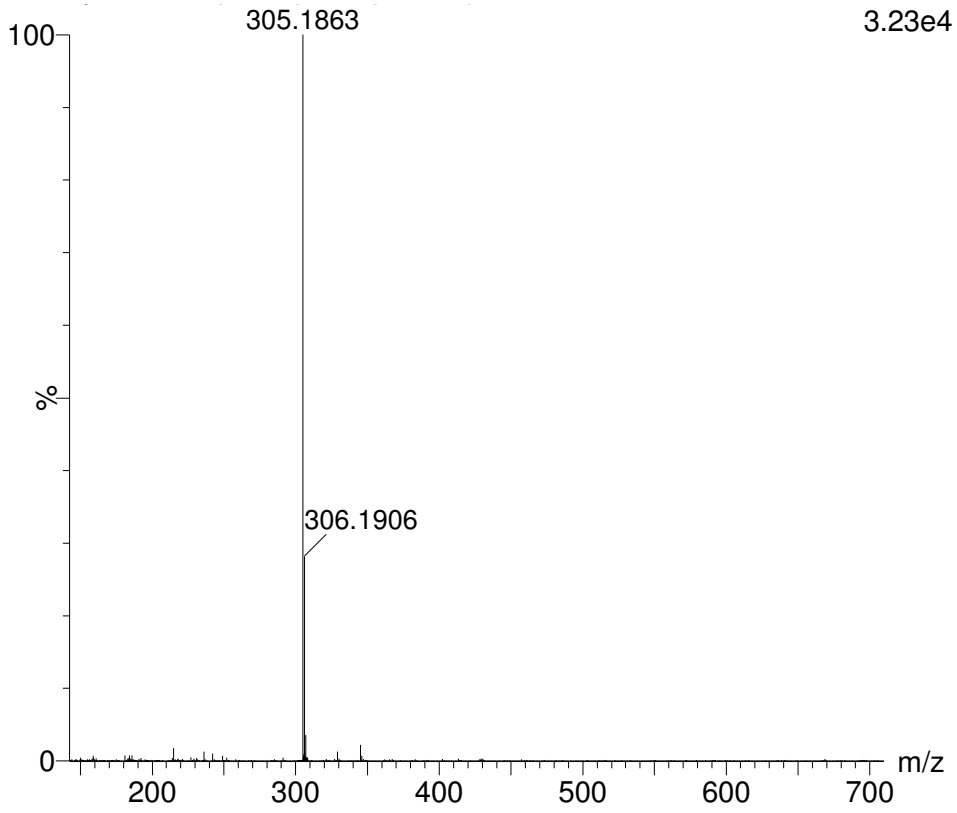
A QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used. The drying gas as well as nebulizing gas was nitrogen at a flow of 400L/h and 80 L/h respectively. The temperature of the source block was set to 120 ºC and the desolvation temperature to 150ºC. A capillary voltage of 3.5 KV was used in the positive scan mode and the cone voltage was set to 30V. Mass calibration was performed using a solution of sodium iodide in isopropanol:water (50:50) from m/z 150 to 1000 a.m.u. Sample solutions (aprox. $1x10^{-4}$ M) were infused via syringe pump directly connected to the interface at a flow of 10 µl/min. A 1 µg/mL solution of 3,5-diiodo-L-tyrosine was used as lock mass.

4.1- HRMS of compound A



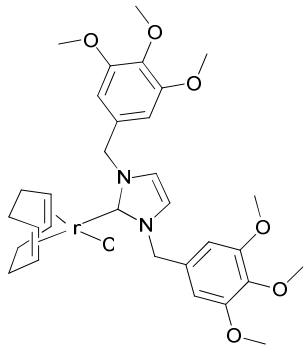
MW = 340.85 g/mol

Fragment: 305.1863 $[M - Cl]^+$



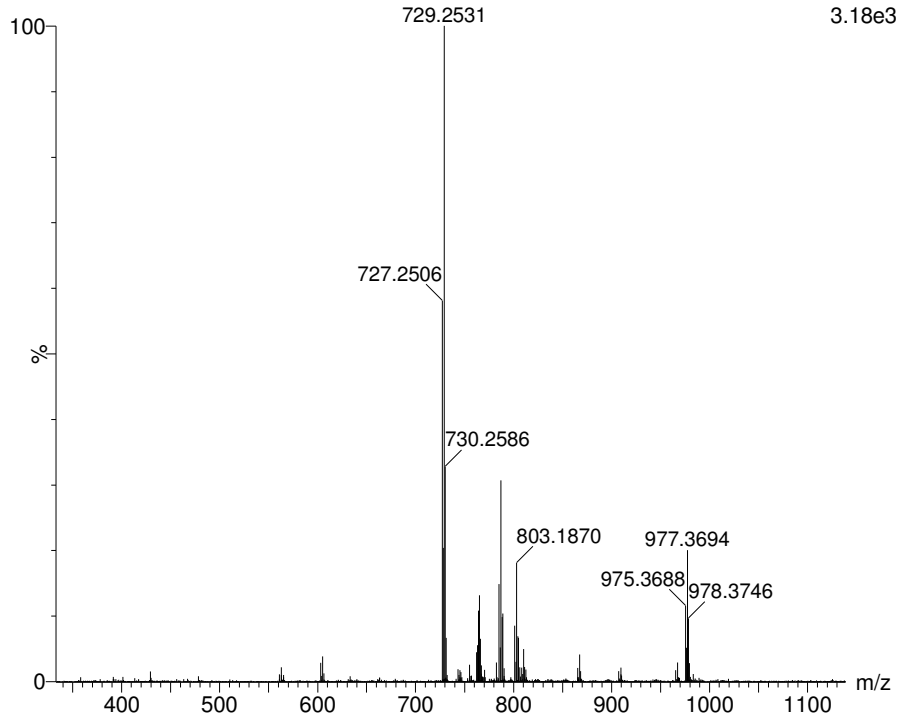
Peak (m/z)	Experimental mass	Theoretical mass	Relative error (ppm)
305.18	305.1863	305.1865	0.7

4.2- HRMS of compound 4A

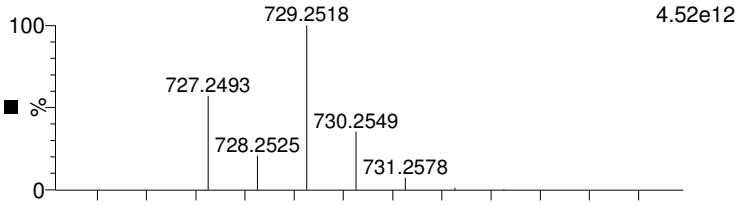


MW = 764.3326 g/mol

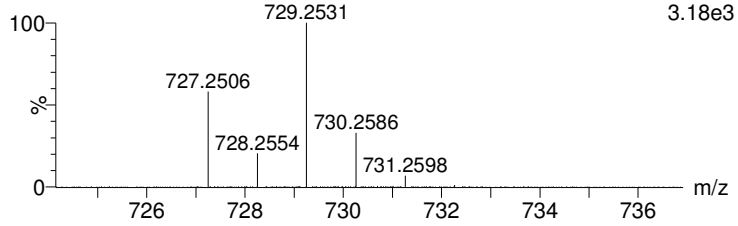
Fragment: 729.2531 $[M - Cl]^+$



Theoretical mass



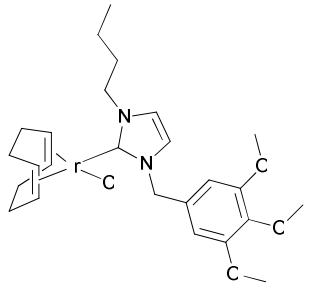
Experimental mass



Peak (m/z)	Experimental mass	Theoretical mass	Relative error (ppm)

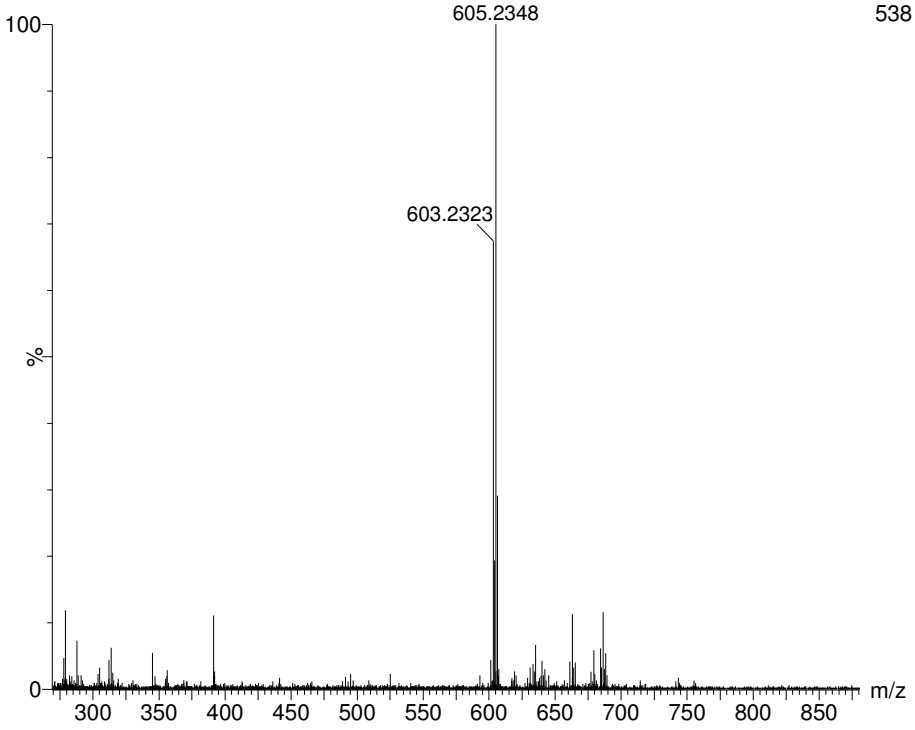
729.2	729.2531	729.2518	1.7

4.3- HRMS of compound 4B

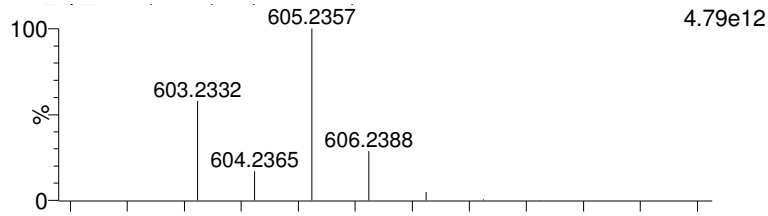


MW = 640.2378 g/mol

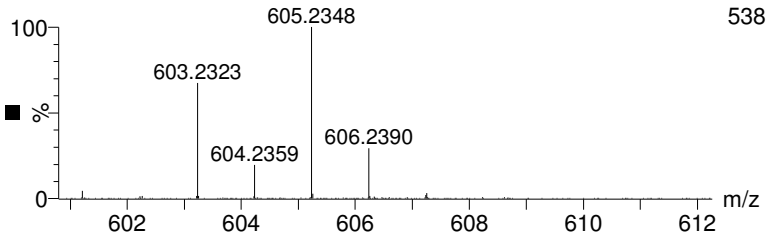
Fragment: 605.2348 $[M - Cl]^+$



Theoretical mass

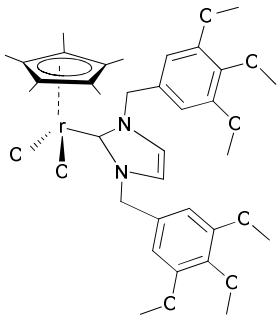


Experimental mass



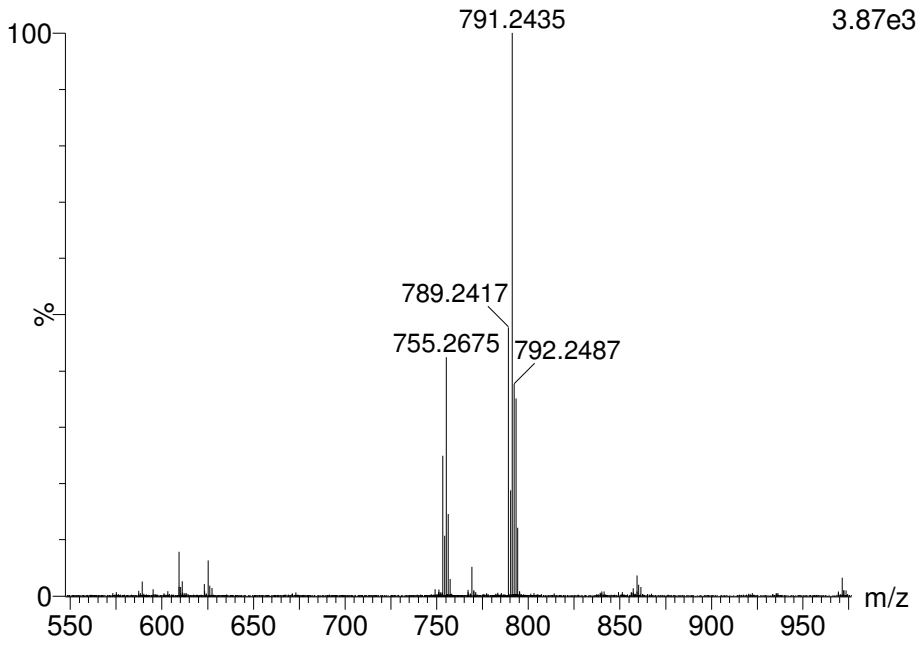
Peak (m/z)	Experimental mass	Theoretical mass	Relative error (ppm)
605.2	605.2348	605.2357	1.0

4.4- HRMS of compound 5A

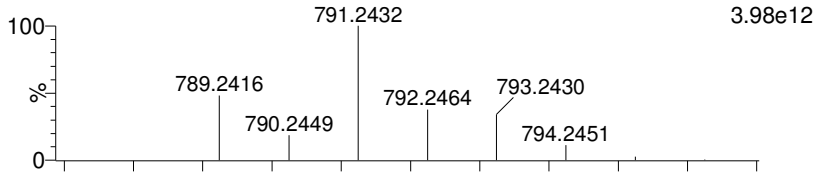


MW = 826.8312 g/mol

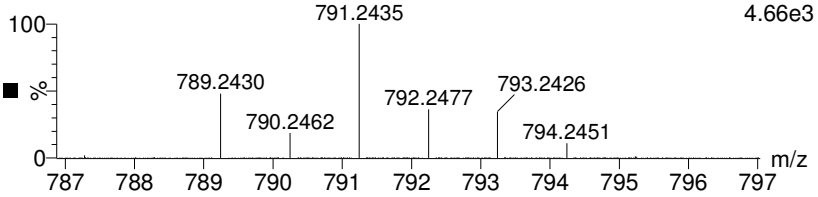
Fragment: 791.2435 $[M\text{-}Cl]^+$



Theoretical mass

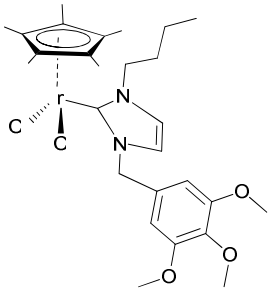


Experimental mass



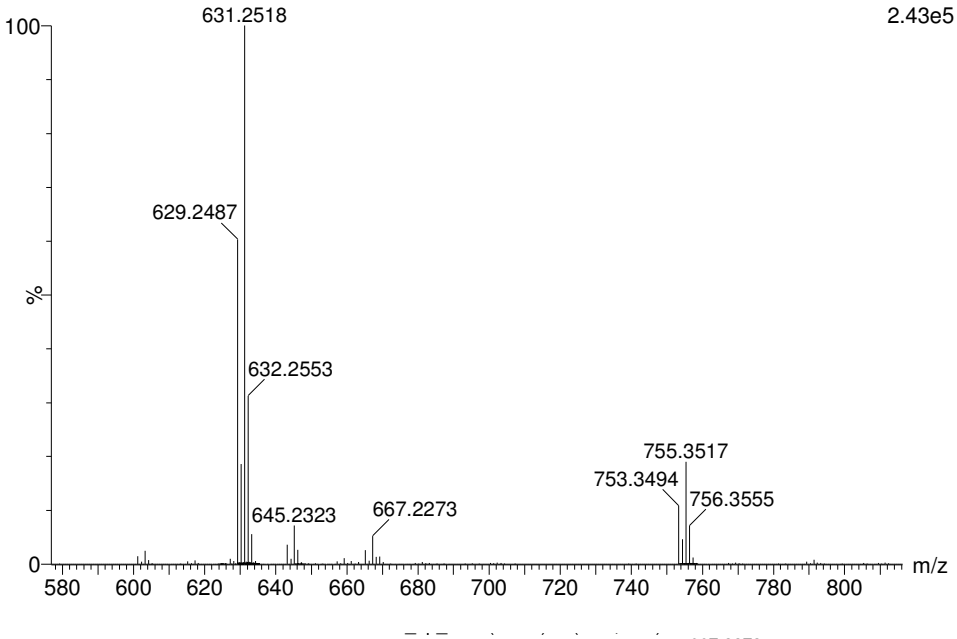
Peak (m/z)	Experimental mass	Theoretical mass	Relative error (ppm)
791.2435	791.2435	791.2432	0.3

4.5- HRMS of compound 5B

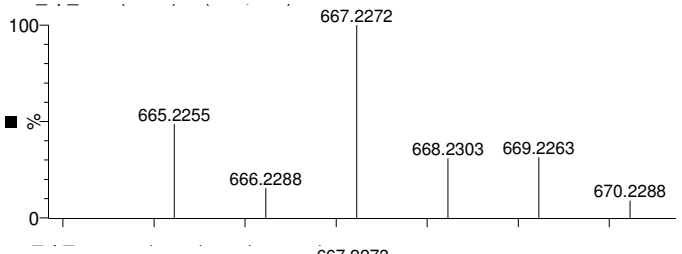


MW = 702.74 g/mol

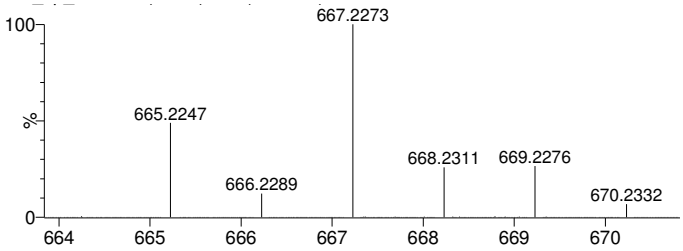
Fragment: 667.2 $[M - Cl]^+$



Theoretical mass



Experimental mass

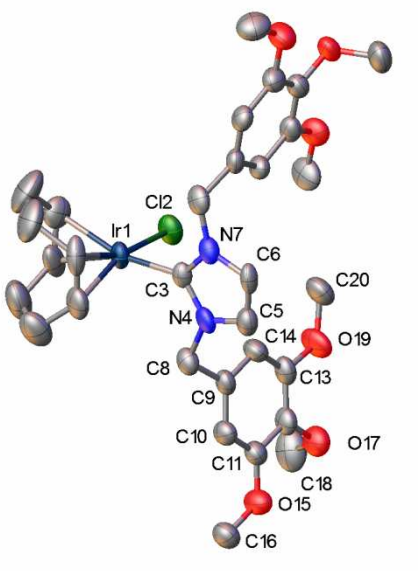


Peak (m/z)	Experimental mass	Theoretical mass	Relative error

			(ppm)
667.2	667.2273	667.2272	0.2

5.- X-Ray Diffraction Studies

Crystallographic data and structure refinement for complexes **4A**, **4B** and **5A**.



Molecular diagram of complex **4A** (Code str1215). Ellipsoids at 50% probability level. Hydrogens omitted for clarity. Selected bond lengths [Å] and angles [º]: Ir(1) - C(3) 2.015(8), Ir(1) - Cl(2) 2.372(2), Ir(1) – C(35) 2.094(9), C(3) - N(4) 1.366(11), N(4) - C(8) 1.462(11), C(3) - Ir(1) - Cl(2) 89.4(2), C(3) - N(4) - C(8) 124.1(8), C(11) - O(15) - C(16) 117.1(7). α = 85.8º (α = angle form between the iridium coordination plane and the azole ring plane.

Table 1 Crystal data and structure refinement for **4A** (str1215)

Identification code	str1215
Empirical formula	$C_{31}H_{40}N_2O_6ClIr$
Formula weight	764.30
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9905(10)
b/Å	22.494(3)
c/Å	13.6491(15)
α/°	90.00
β/°	97.129(3)
γ/°	90.00
Volume/Å^3	3043.6(6)

Z	4
ρ_{calc}mg/mm^3	1.668
m/mm^{-1}	4.520
F(000)	1528.0
Crystal size/mm^3	0.18 × 0.15 × 0.11
2Θ range for data collection	3.52 to 55°
Index ranges	$-12 \leq h \leq 10$, $-27 \leq k \leq 29$, $-15 \leq l \leq 17$
Reflections collected	20195
Independent reflections	6984[R(int) = 0.0662]
Data/restraints/parameters	6984/0/376
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1275
Final R indexes [all data]	R_1 = 0.1140, wR_2 = 0.1570
Largest diff. peak/hole / e Å^{-3}	4.13/-1.21

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4A** (str1215). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ir1	1974.8(3)	3683.87(16)	2916.8(3)	43.04(14)
Cl2	552(2)	3648.1(11)	1391.6(17)	55.4(6)
C3	329(8)	3691(4)	3632(5)	37.0(18)
N7	-308(7)	3250(3)	4052(5)	42.7(17)
O32	-1911(7)	680(3)	3013(6)	68(2)
N4	-375(7)	4188(3)	3831(5)	44.6(18)
O30	-3332(6)	1160(3)	1391(5)	57.7(18)
C6	-1399(8)	3459(5)	4480(6)	46(2)
O28	-3150(7)	2320(3)	998(5)	61.8(19)
C5	-1444(9)	4041(5)	4339(7)	53(2)
O19	-3625(7)	5039(3)	804(5)	75(2)
C21	65(9)	2637(4)	4000(7)	51(2)
C22	-889(8)	2249(4)	3334(7)	43(2)
O17	-3791(7)	6190(3)	1211(6)	68(2)
O15	-2231(7)	6695(3)	2684(5)	64.6(19)
C27	-975(8)	1653(4)	3545(7)	47(2)
C26	-1796(10)	1274(4)	2886(8)	52(2)
C25	-2517(9)	1519(4)	2037(7)	49(2)
C24	-2417(9)	2120(4)	1851(6)	47(2)
C23	-1613(8)	2497(4)	2475(7)	45(2)
C33	-1066(12)	410(5)	3808(9)	76(3)
C31	-4684(11)	1150(5)	1606(10)	80(4)
C29	-3022(10)	2924(5)	728(8)	71(3)
C8	3(9)	4792(4)	3580(7)	49(2)
C9	-1098(8)	5146(4)	2994(6)	44(2)

C14	-1901(9)	4883(4)	2217(7)	54(2)
C13	-2788(9)	5240(5)	1611(7)	51(2)
C12	-2889(9)	5841(4)	1788(7)	52(2)
C11	-2085(9)	6099(4)	2582(7)	47(2)
C10	-1174(9)	5745(4)	3186(7)	50(2)
C20	-3636(11)	4421(5)	610(9)	74(3)
C18	-3192(13)	6509(6)	470(9)	91(4)
C16	-1385(10)	6977(4)	3464(8)	63(3)
C34	3251(9)	3447(6)	4204(7)	67(3)
C35	3111(10)	4058(6)	4157(7)	65(3)
C36	4154(13)	4505(6)	3857(9)	88(4)
C37	4591(12)	4382(7)	2897(10)	100(5)
C38	3672(10)	3997(6)	2220(8)	68(3)
C39	3692(11)	3374(6)	2241(8)	64(3)
C40	4581(14)	2991(7)	2921(12)	114(5)
C41	4527(12)	3112(7)	3975(11)	96(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4A** (str1215). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Ir1	28.32(18)	61.0(3)	37.7(2)	-1.99(19)	-4.37(12)	-4.05(17)
Cl2	48.0(13)	76.4(17)	38.0(12)	-2.5(12)	-9.3(10)	-7.8(12)
C3	31(4)	56(5)	23(4)	-2(4)	-2(3)	-3(4)
N7	34(4)	55(5)	37(4)	8(3)	-6(3)	-4(3)
O32	63(5)	53(5)	83(6)	2(4)	-5(4)	-6(4)
N4	32(4)	55(5)	43(4)	-2(4)	-11(3)	-12(3)
O30	44(4)	61(4)	67(5)	-24(3)	2(3)	-12(3)
C6	26(4)	78(7)	36(5)	1(4)	5(4)	-9(4)
O28	62(4)	69(5)	48(4)	-9(3)	-17(3)	2(3)
C5	36(5)	70(7)	50(6)	-7(5)	0(4)	-3(5)
O19	73(5)	71(5)	71(5)	-13(4)	-35(4)	-10(4)
C21	38(5)	68(7)	43(5)	7(5)	-14(4)	-2(4)
C22	27(4)	54(6)	48(5)	-4(4)	3(4)	-1(4)
O17	55(4)	73(5)	69(5)	-1(4)	-17(4)	3(3)
O15	61(4)	54(5)	73(5)	-8(4)	-16(4)	6(3)
C27	35(5)	55(6)	48(6)	0(5)	-6(4)	8(4)
C26	44(5)	48(6)	65(6)	0(5)	10(5)	-3(4)
C25	41(5)	53(6)	53(6)	-12(5)	3(4)	-5(4)
C24	37(5)	63(7)	39(5)	-11(4)	-3(4)	0(4)
C23	34(5)	46(5)	53(6)	-2(4)	-8(4)	2(4)
C33	92(9)	55(7)	82(9)	11(6)	10(7)	10(6)
C31	46(6)	96(9)	94(9)	-27(7)	-2(6)	-12(6)
C29	64(7)	79(8)	61(7)	11(6)	-30(6)	0(6)

C8	40(5)	56(6)	47(6)	5(4)	-9(4)	-5(4)
C9	33(5)	55(6)	43(5)	-6(4)	-3(4)	-6(4)
C14	50(5)	42(5)	66(7)	-8(5)	-6(5)	-6(4)
C13	38(5)	68(7)	46(6)	-4(5)	-7(4)	-8(4)
C12	37(5)	62(7)	53(6)	1(5)	-13(4)	0(4)
C11	42(5)	46(5)	52(6)	-3(4)	0(4)	-5(4)
C10	43(5)	52(6)	50(6)	-7(4)	-11(4)	-1(4)
C20	65(7)	69(8)	81(8)	-20(6)	-12(6)	-18(6)
C18	74(8)	136(12)	59(8)	25(8)	-14(7)	-3(8)
C16	60(6)	59(7)	66(7)	-12(5)	-5(5)	-7(5)
C34	30(5)	123(10)	47(6)	23(6)	1(4)	-8(6)
C35	40(5)	92(9)	57(7)	-10(6)	-12(5)	-8(6)
C36	87(9)	108(10)	67(8)	-24(7)	2(7)	-31(8)
C37	59(8)	136(13)	103(11)	-21(9)	9(8)	-34(8)
C38	45(6)	104(9)	61(7)	-30(7)	23(5)	-26(6)
C39	60(7)	81(8)	54(7)	7(6)	22(5)	0(6)
C40	74(9)	150(14)	119(13)	11(11)	19(9)	59(9)
C41	50(7)	140(13)	96(11)	25(9)	-5(7)	30(7)

Table 4 Bond Lengths for **4A** (str1215).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ir1	Cl2	2.372(2)	O17	C12	1.369(11)
Ir1	C3	2.015(8)	O17	C18	1.430(14)
Ir1	C34	2.107(10)	O15	C11	1.356(11)
Ir1	C35	2.094(9)	O15	C16	1.423(11)
Ir1	C38	2.162(9)	C27	C26	1.422(13)
Ir1	C39	2.162(10)	C26	C25	1.399(14)
C3	N7	1.344(10)	C25	C24	1.380(13)
C3	N4	1.366(11)	C24	C23	1.386(12)
N7	C6	1.381(11)	C8	C9	1.505(12)
N7	C21	1.433(11)	C9	C14	1.381(12)
O32	C26	1.354(10)	C9	C10	1.378(12)
O32	C33	1.426(12)	C14	C13	1.390(13)
N4	C5	1.384(11)	C13	C12	1.379(13)
N4	C8	1.462(11)	C12	C11	1.394(12)
O30	C25	1.383(11)	C11	C10	1.398(12)
O30	C31	1.417(12)	C34	C35	1.380(17)
C6	C5	1.323(14)	C34	C41	1.545(16)
O28	C24	1.372(10)	C35	C36	1.541(15)
O28	C29	1.419(12)	C36	C37	1.458(16)
O19	C13	1.375(10)	C37	C38	1.496(15)
O19	C20	1.415(12)	C38	C39	1.401(16)
C21	C22	1.510(12)	C39	C40	1.480(16)

C22	C27	1.378(13)	C40	C41	1.472(18)
C22	C23	1.413(12)			

Table 5 Bond Angles for **4A** (str1215).

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C3	Ir1	Cl2	89.4(2)	C25	C26	C27	119.1(9)
C3	Ir1	C34	92.5(3)	O30	C25	C26	120.0(9)
C3	Ir1	C35	89.9(4)	C24	C25	O30	120.3(9)
C3	Ir1	C38	160.5(4)	C24	C25	C26	119.7(9)
C3	Ir1	C39	161.5(4)	O28	C24	C25	115.7(8)
C34	Ir1	Cl2	163.3(4)	O28	C24	C23	121.9(9)
C34	Ir1	C38	91.3(4)	C25	C24	C23	122.4(9)
C34	Ir1	C39	81.0(4)	C24	C23	C22	117.8(9)
C35	Ir1	Cl2	158.3(4)	N4	C8	C9	115.0(7)
C35	Ir1	C34	38.4(5)	C14	C9	C8	119.9(8)
C35	Ir1	C38	81.3(4)	C10	C9	C8	118.0(8)
C35	Ir1	C39	95.5(4)	C10	C9	C14	121.7(8)
C38	Ir1	Cl2	92.4(3)	C9	C14	C13	118.4(9)
C38	Ir1	C39	37.8(4)	O19	C13	C14	124.5(9)
C39	Ir1	Cl2	92.0(3)	O19	C13	C12	114.3(8)
N7	C3	Ir1	131.2(7)	C12	C13	C14	121.2(8)
N7	C3	N4	103.7(7)	O17	C12	C13	121.3(8)
N4	C3	Ir1	125.1(6)	O17	C12	C11	118.9(9)
C3	N7	C6	111.7(8)	C13	C12	C11	119.8(9)
C3	N7	C21	123.3(8)	O15	C11	C12	115.6(8)
C6	N7	C21	124.8(8)	O15	C11	C10	124.9(8)
C26	O32	C33	117.8(8)	C12	C11	C10	119.5(9)
C3	N4	C5	110.5(7)	C9	C10	C11	119.4(8)
C3	N4	C8	124.1(8)	C35	C34	Ir1	70.3(6)
C5	N4	C8	125.3(8)	C35	C34	C41	123.8(10)
C25	O30	C31	112.2(7)	C41	C34	Ir1	112.5(8)
C5	C6	N7	106.8(8)	C34	C35	Ir1	71.3(6)
C24	O28	C29	118.6(7)	C34	C35	C36	126.4(10)
C6	C5	N4	107.2(8)	C36	C35	Ir1	111.4(7)
C13	O19	C20	117.6(8)	C37	C36	C35	113.7(10)
N7	C21	C22	115.9(7)	C36	C37	C38	115.9(10)
C27	C22	C21	119.2(8)	C37	C38	Ir1	111.8(7)
C27	C22	C23	121.2(8)	C39	C38	Ir1	71.1(6)
C23	C22	C21	119.5(8)	C39	C38	C37	124.1(12)
C12	O17	C18	113.1(9)	C38	C39	Ir1	71.1(6)
C11	O15	C16	117.1(7)	C38	C39	C40	126.9(12)

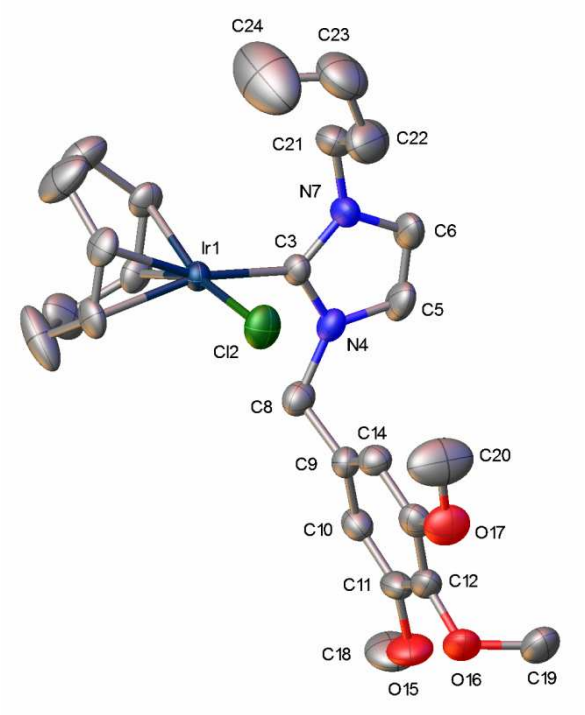
C22	C27	C26	119.8(9)	C40	C39	Ir1	111.5(7)
O32	C26	C27	124.1(9)	C41	C40	C39	114.4(11)
O32	C26	C25	116.8(9)	C40	C41	C34	114.8(10)

Single crystals of $C_{31}H_{40}N_2O_6ClIr$ [str1215] were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Data collection was performed on a SuperNova dual source equipped with a CCD Atlas detector diffractometer (Agilent Technologies). The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. SHELXS-97 (Sheldrick, 1990)
3. SHELXL, G.M. Sheldrick, Acta Cryst. 2008. A64, 112-122

Crystal structure determination of [str1215]

Crystal Data. $C_{31}H_{40}N_2O_6ClIr$, M =764.30, monoclinic, a = 9.9905(10) Å, b = 22.494(3) Å, c = 13.6491(15) Å, β = 97.129(3)°, V = 3043.6(6) Å^3, T = 293(2), space group $P2_1/c$ (no. 14), Z = 4, μ(Mo Kα) = 4.520, 20195 reflections measured, 6984 unique (R_{int} = 0.0662) which were used in all calculations. The final wR_2 was 0.1570 (all data) and R_1 was 0.0574 (>2sigma(I)).



Molecular diagram of complex **4B** (Code str1262). Ellipsoids at 50% probability level. Hydrogens omitted for clarity. Selected bond lengths [Å] and angles [º]: Ir(1) - C(3) 2.031(3), Ir(1) - Cl(2) 2.3581(9), Ir(1) – C(25) 2.166(3), C(3) - N(4) 1.357(4), N(4) - C(8) 1.460(5), C(3) - Ir(1) - Cl(2) 88.22(9), C(3) - N(4) - C(8) 124.2(3), C(12) - O(16) - C(19) 114.0(3). α = 86.0º (α = angle form between the iridium coordination plane and the azole ring plane.

Table 1 Crystal data and structure refinement for **4B** (str1262)

Identification code	str1262
Empirical formula	$C_{25}H_{36}ClIrN_2O_3$
Formula weight	640.21
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.0092(4)
b/Å	7.85644(12)
c/Å	14.5126(2)
α/°	90.00
β/°	104.1763(16)
γ/°	90.00
Volume/Å^3	2543.55(7)
Z	4
ρ_{calc}mg/mm^3	1.672

m/mm^{-1}	5.382
F(000)	1272.0
Crystal size/mm^3	0.1 × 0.08 × 0.07
2Θ range for data collection	5.62 to 58.96°
Index ranges	-30 ≤ h ≤ 30, -10 ≤ k ≤ 10, -18 ≤ l ≤ 19
Reflections collected	35349
Independent reflections	6443[R(int) = 0.0392]
Data/restraints/parameters	6443/0/293
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0268, wR_2 = 0.0546
Final R indexes [all data]	R_1 = 0.0359, wR_2 = 0.0592
Largest diff. peak/hole / e Å^{-3}	0.81/-0.91

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4B** (str1262). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ir1	1568.93(5)	3220.98(15)	2109.22(8)	28.63(5)
Cl2	2213.2(5)	2125.3(13)	3502.8(6)	50.4(2)
O15	4352.8(15)	-1408(4)	683(2)	67.8(9)
O16	4719.8(14)	-1756(3)	2574(2)	60.4(8)
O17	4214.7(14)	-58(4)	3741.4(19)	60.6(8)
N4	2704.2(12)	4067(4)	1477(2)	37.0(6)
N7	2433.3(13)	6205(4)	2185(2)	41.2(7)
C3	2271.0(14)	4603(4)	1897(2)	32.0(7)
C5	3128.1(17)	5334(5)	1512(3)	51.2(10)
C6	2960.3(18)	6651(5)	1955(3)	53.9(11)
C8	2708.7(16)	2402(5)	1032(2)	41.7(8)
C9	3264.1(15)	1368(4)	1448(2)	35.8(7)
C10	3553.8(16)	534(4)	843(3)	40.1(8)
C11	4043.9(17)	-498(5)	1217(3)	45.1(9)
C12	4254.0(16)	-670(4)	2192(3)	43.8(9)
C13	3967.8(17)	198(4)	2797(3)	40.8(8)
C14	3471.9(16)	1203(4)	2426(2)	38.1(7)
C18	4220(3)	-1109(7)	-304(4)	84.1(17)
C19	5291.3(19)	-980(6)	2768(4)	64.8(12)
C20	3959(3)	825(9)	4389(3)	99(2)
C21	2118(2)	7259(5)	2744(3)	53.6(10)
C22	2364(2)	7030(7)	3818(4)	76.5(15)
C23	1961(3)	7783(8)	4407(4)	92.5(18)
C24	1418(4)	6933(11)	4313(6)	161(4)

C25	942.3(16)	1155(5)	2088(3)	42.1(8)
C26	781.6(16)	2494(5)	2585(3)	41.7(8)
C27	270(2)	3680(7)	2207(4)	83.6(17)
C28	338(2)	4830(6)	1436(3)	63.2(12)
C29	934.2(16)	4741(5)	1178(2)	40.5(8)
C30	1108.5(16)	3370(5)	675(2)	41.1(8)
C31	722(2)	1832(6)	341(3)	67.5(14)
C32	627(3)	699(7)	1081(3)	88(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4B** (str1262).The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
Ir1	26.35(7)	29.36(7)	29.83(7)	0.35(5)	6.20(5)	-2.78(5)
Cl2	45.4(6)	63.4(6)	37.6(4)	11.0(4)	0.9(4)	-1.7(4)
O15	64(2)	61.6(19)	84(2)	-23.6(17)	30.9(18)	13.9(16)
O16	46.9(18)	30.5(14)	100(2)	5.8(14)	10.3(16)	7.5(12)
O17	67(2)	58.8(18)	52.3(16)	13.3(14)	6.2(14)	13.7(15)
N4	26.5(15)	38.1(16)	46.6(16)	5.9(13)	9.5(12)	0.6(12)
N7	33.9(16)	28.0(14)	62.6(19)	-0.6(14)	13.2(14)	-4.0(12)
C3	27.9(16)	28.6(16)	40.2(17)	5.3(13)	9.7(13)	-3.6(13)
C5	30(2)	50(2)	77(3)	11(2)	19.6(18)	-4.6(17)
C6	37(2)	35(2)	90(3)	9(2)	16(2)	-8.3(16)
C8	35(2)	50(2)	38.7(18)	-3.6(16)	5.7(15)	2.9(17)
C9	28.4(18)	34.2(17)	44.1(18)	-3.3(14)	7.6(14)	-2.8(14)
C10	40(2)	36.8(19)	45.5(19)	-8.1(15)	14.8(16)	-6.6(15)
C11	40(2)	32.3(18)	68(2)	-14.5(17)	22.1(18)	-2.7(15)
C12	35(2)	26.5(17)	69(2)	1.5(16)	11.0(17)	0.2(14)
C13	43(2)	30.9(17)	47.2(19)	4.2(15)	7.6(16)	-3.6(15)
C14	38(2)	35.8(18)	42.7(19)	-1.0(15)	14.5(15)	1.7(15)
C18	94(4)	84(4)	88(4)	-36(3)	49(3)	7(3)
C19	44(3)	50(2)	96(3)	7(2)	9(2)	11(2)
C20	128(6)	115(5)	47(3)	0(3)	9(3)	45(4)
C21	50(2)	35(2)	75(3)	-10.7(19)	14(2)	0.0(18)
C22	67(3)	82(4)	72(3)	-25(3)	0(3)	5(3)
C23	119(6)	75(4)	82(4)	-16(3)	21(4)	-3(4)
C24	201(10)	166(8)	158(8)	-51(6)	123(8)	-78(7)
C25	40(2)	40.9(19)	47(2)	0.7(16)	15.5(16)	-20.2(16)
C26	32.7(19)	53(2)	44.8(19)	7.1(17)	20.4(15)	-6.0(17)
C27	52(3)	93(4)	120(5)	39(3)	48(3)	21(3)
C28	50(3)	77(3)	65(3)	11(2)	18(2)	26(2)
C29	34.7(19)	43(2)	39.5(18)	12.2(15)	0.8(14)	6.3(15)
C30	31.5(19)	58(2)	30.2(16)	5.4(15)	0.6(14)	1.4(16)
C31	76(3)	65(3)	46(2)	-8(2)	-14(2)	-5(2)

C32	113(5)	102(4)	56(3)	-30(3)	32(3)	-76(4)

Table 4 Bond Lengths for **4B** (str1262).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ir1	Cl2	2.3581(9)	C8	C9	1.510(5)
Ir1	C3	2.031(3)	C9	C10	1.390(5)
Ir1	C25	2.166(3)	C9	C14	1.389(5)
Ir1	C26	2.167(3)	C10	C11	1.387(5)
Ir1	C29	2.102(3)	C11	C12	1.385(5)
Ir1	C30	2.095(3)	C12	C13	1.398(5)
O15	C11	1.373(4)	C13	C14	1.384(5)
O15	C18	1.410(6)	C21	C22	1.533(6)
O16	C12	1.376(4)	C22	C23	1.526(8)
O16	C19	1.414(5)	C23	C24	1.393(10)
O17	C13	1.364(4)	C25	C26	1.377(5)
O17	C20	1.408(6)	C25	C32	1.506(5)
N4	C3	1.357(4)	C26	C27	1.496(6)
N4	C5	1.386(5)	C27	C28	1.476(6)
N4	C8	1.460(5)	C28	C29	1.509(5)
N7	C3	1.350(4)	C29	C30	1.413(5)
N7	C6	1.379(5)	C30	C31	1.508(6)
N7	C21	1.469(5)	C31	C32	1.452(6)
C5	C6	1.325(6)			

Table 5 Bond Angles for **4B** (str1262).

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C3	Ir1	Cl2	88.22(9)	C14	C9	C10	120.2(3)
C3	Ir1	C25	161.70(14)	C11	C10	C9	119.9(3)
C3	Ir1	C26	161.24(14)	O15	C11	C10	124.5(4)
C3	Ir1	C29	92.97(13)	O15	C11	C12	115.2(4)
C3	Ir1	C30	92.68(14)	C12	C11	C10	120.3(3)
C25	Ir1	Cl2	90.88(11)	O16	C12	C11	121.0(3)
C25	Ir1	C26	37.05(14)	O16	C12	C13	119.3(4)
C26	Ir1	Cl2	91.69(10)	C11	C12	C13	119.6(3)
C29	Ir1	Cl2	161.94(10)	O17	C13	C12	114.5(3)
C29	Ir1	C25	93.51(15)	O17	C13	C14	125.1(3)
C29	Ir1	C26	81.45(14)	C14	C13	C12	120.3(3)
C30	Ir1	Cl2	158.64(11)	C13	C14	C9	119.7(3)
C30	Ir1	C25	81.64(14)	N7	C21	C22	112.7(4)
C30	Ir1	C26	94.16(14)	C23	C22	C21	113.6(5)
C30	Ir1	C29	39.34(14)	C24	C23	C22	114.4(5)

C11	O15	C18	118.2(4)	C26	C25	Ir1	71.5(2)
C12	O16	C19	114.0(3)	C26	C25	C32	124.2(4)
C13	O17	C20	117.3(3)	C32	C25	Ir1	110.7(3)
C3	N4	C5	110.4(3)	C25	C26	Ir1	71.43(19)
C3	N4	C8	124.2(3)	C25	C26	C27	124.9(4)
C5	N4	C8	125.4(3)	C27	C26	Ir1	111.3(3)
C3	N7	C6	110.8(3)	C28	C27	C26	116.1(4)
C3	N7	C21	124.0(3)	C27	C28	C29	115.6(3)
C6	N7	C21	125.0(3)	C28	C29	Ir1	113.4(2)
N4	C3	Ir1	127.0(2)	C30	C29	Ir1	70.03(19)
N7	C3	Ir1	128.4(2)	C30	C29	C28	123.6(4)
N7	C3	N4	104.5(3)	C29	C30	Ir1	70.62(19)
C6	C5	N4	107.0(3)	C29	C30	C31	123.9(4)
C5	C6	N7	107.3(3)	C31	C30	Ir1	112.9(3)
N4	C8	C9	113.7(3)	C32	C31	C30	115.9(3)
C10	C9	C8	119.4(3)	C31	C32	C25	116.6(4)
C14	C9	C8	120.3(3)				

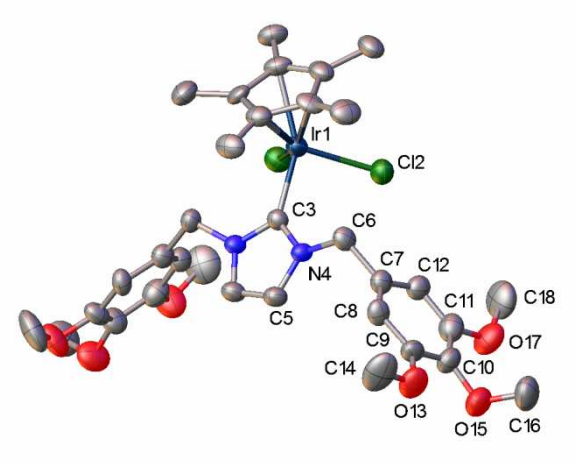
Experimental

Single crystals of $C_{25}H_{36}ClIrN_2O_3$ [str1262] were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Data collection was performed on a SuperNova dual source equipped with a CCD Atlas detector diffractometer (Agilent Technologies). The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. SHELXS-97 (Sheldrick, 1990)
3. SHELXL, G.M. Sheldrick, Acta Cryst. 2008. A64, 112-122

Crystal structure determination of [str1262]

Crystal Data. $C_{25}H_{36}ClIrN_2O_3$, M =640.21, monoclinic, a = 23.0092(4) Å, b = 7.85644(12) Å, c = 14.5126(2) Å, β = 104.1763(16)°, V = 2543.55(7) Å^3, T = 293(2), space group $P2_1/c$ (no. 14), Z = 4, μ(Mo Kα) = 5.382, 35349 reflections measured, 6443 unique (R_{int} = 0.0392) which were used in all calculations. The final wR_2 was 0.0592 (all data) and R_1 was 0.0268 (>2sigma(I)).



Molecular diagram of complex **5A** (str1232). Ellipsoids at 50% probability level. Hydrogens omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1) - C(3) 2.061(11), Ir(1) - Cl(2) 2.428(2), Ir(1) – Cp(cent) 1.979, C(3) - N(4) 1.356(9), N(4) - C(5) 1.384(10), C(3) - Ir(1) - Cl(2) 90.8(2), C(3) - N(4) - C(5) 111.5(7), C(3) - N(4) - C(6) 124.5(7).

Table 1 Crystal data and structure refinement for **5A** (str1232)

Identification code	str1232
Empirical formula	$C_{33}H_{43}Cl_2IrN_2O_6$
Formula weight	826.79
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	7.8446(9)
b/Å	28.210(2)
c/Å	8.2365(10)
α/°	90.00
β/°	114.610(14)
γ/°	90.00
Volume/Å^3	1657.1(3)
Z	2
ρ_{calc}mg/mm^3	1.657
m/mm^{-1}	4.236
F(000)	828.0
Crystal size/mm^3	0.11 × 0.09 × 0.08

2Θ range for data collection	5.62 to 55°
Index ranges	$-9 \leq h \leq 10$, $-36 \leq k \leq 36$, $-10 \leq l \leq 10$
Reflections collected	14723
Independent reflections	3811[R(int) = 0.1048]
Data/restraints/parameters	3811/0/211
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	$R_1 = 0.0654$, $wR_2 = 0.1155$
Final R indexes [all data]	$R_1 = 0.1048$, $wR_2 = 0.1302$
Largest diff. peak/hole / e $Å^{-3}$	2.88/-1.23

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5A** (str1232). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ir1	3602.6(7)	2500	9613.0(6)	36.81(18)
N4	1883(9)	2878(2)	5747(9)	36.2(16)
C21	5826(12)	2746(3)	12149(12)	47(2)
C20	6151(11)	2907(3)	10625(11)	43(2)
C19	6363(16)	2500	9737(17)	47(3)
C23	6490(13)	3413(3)	10303(13)	62(3)
C22	6852(17)	2500	8143(17)	54(3)
C3	2313(15)	2500	6862(15)	35(3)
C5	1184(11)	2738(3)	3978(12)	43(2)
C6	2494(12)	3372(3)	6322(12)	43(2)
C7	1091(12)	3741(3)	5175(12)	44(2)
C8	1299(13)	3957(3)	3787(12)	44(2)
C12	-377(12)	3852(3)	5631(12)	47(2)
C9	12(14)	4292(3)	2775(12)	50(2)
C10	-1549(13)	4399(3)	3111(13)	52(2)
C11	-1699(13)	4178(3)	4562(15)	57(3)
C18	-3215(17)	4195(4)	6530(18)	89(4)
C14	1781(18)	4469(4)	1096(18)	94(4)
O17	-3266(10)	4310(3)	4831(11)	74(2)
O13	127(11)	4536(2)	1392(10)	72(2)
O15	-2928(11)	4688(2)	1981(10)	76(2)
C16	-2961(18)	5136(3)	2595(17)	85(4)
C24	5586(13)	3058(3)	13523(12)	54(2)
Cl2	1414(3)	1908.2(8)	9739(3)	50.1(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5A** (str1232). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ir1	39.7(3)	35.1(2)	33.6(3)	0	13.3(2)	0
N4	37(4)	33(3)	31(4)	1(3)	6(3)	1(3)
C21	38(5)	60(5)	36(5)	-11(4)	7(4)	-3(4)
C20	34(5)	52(5)	36(5)	-10(4)	8(4)	-22(4)
C19	37(7)	58(8)	38(8)	0	9(6)	0
C23	54(6)	57(6)	60(7)	-5(5)	9(5)	-17(5)
C22	41(7)	81(9)	45(9)	0	24(7)	0
C3	38(6)	36(6)	32(7)	0	15(6)	0
C5	47(5)	44(4)	31(5)	2(4)	9(4)	2(4)
C6	52(5)	32(4)	43(5)	-1(4)	19(5)	-6(4)
C7	51(6)	34(4)	46(6)	-1(4)	18(5)	0(4)
C8	59(6)	31(4)	49(6)	4(4)	30(5)	-1(4)
C12	51(6)	36(4)	49(6)	3(4)	17(5)	0(4)
C9	66(6)	39(5)	35(6)	6(4)	13(5)	10(4)
C10	54(6)	42(5)	56(7)	9(5)	18(5)	12(4)
C11	51(6)	51(5)	70(7)	-6(5)	25(6)	-1(5)
C18	81(9)	103(9)	109(11)	-1(8)	64(9)	16(7)
C14	122(11)	84(8)	103(10)	53(7)	75(10)	29(8)
O17	59(4)	81(5)	87(6)	18(4)	35(4)	19(4)
O13	99(6)	56(4)	66(5)	27(4)	41(5)	21(4)
O15	89(5)	52(4)	73(5)	7(4)	20(5)	24(4)
C16	115(10)	53(6)	90(9)	3(6)	45(8)	25(6)
C24	49(6)	64(6)	41(6)	-16(5)	10(5)	-4(5)
Cl2	53.8(14)	49.4(12)	48.6(14)	1.1(10)	22.7(12)	-5.9(10)

Table 4 Bond Lengths **5A** (str1232).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ir1	C21	2.203(9)	C19	C22	1.513(16)
Ir1	$C21^1$	2.203(9)	C3	$N4^1$	1.356(9)
Ir1	C20	2.150(7)	C5	$C5^1$	1.343(16)
Ir1	$C20^1$	2.150(7)	C6	C7	1.524(11)
Ir1	C19	2.125(11)	C7	C8	1.364(11)
Ir1	C3	2.061(11)	C7	C12	1.387(11)
Ir1	$Cl2^1$	2.428(2)	C8	C9	1.381(12)
Ir1	Cl2	2.428(2)	C12	C11	1.391(13)
N4	C3	1.356(9)	C9	C10	1.396(13)
N4	C5	1.384(10)	C9	O13	1.366(10)
N4	C6	1.484(9)	C10	C11	1.396(13)
C21	$C21^1$	1.390(17)	C10	O15	1.364(11)
C21	C20	1.453(11)	C11	O17	1.388(11)

C21	C24	1.505(11)	C18	O17	1.420(13)
C20	C19	1.408(11)	C14	O13	1.429(11)
C20	C23	1.496(12)	O15	C16	1.365(11)
C19	C20[1]	1.408(11)			

[1]+X,1/2-Y,+Z

Table 5 Bond Angles for **5A** (str1232).

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C21	Ir1	C21[1]	36.8(5)	C24	C21	Ir1	126.8(6)
C21[1]	Ir1	Cl2	92.1(2)	C21	C20	Ir1	72.5(4)
C21	Ir1	Cl2	118.1(2)	C21	C20	C23	124.0(8)
C21	Ir1	Cl2[1]	92.1(2)	C19	C20	Ir1	69.8(6)
C21[1]	Ir1	Cl2[1]	118.1(2)	C19	C20	C21	107.2(8)
C20	Ir1	C21[1]	63.9(3)	C19	C20	C23	128.2(8)
C20	Ir1	C21	39.0(3)	C23	C20	Ir1	130.3(6)
C20[1]	Ir1	C21	63.9(3)	C20	C19	Ir1	71.7(5)
C20[1]	Ir1	C21[1]	39.0(3)	C20[1]	C19	Ir1	71.7(5)
C20[1]	Ir1	C20	64.6(5)	C20[1]	C19	C20	109.3(11)
C20	Ir1	Cl2[1]	100.1(2)	C20[1]	C19	C22	125.3(5)
C20[1]	Ir1	Cl2[1]	155.6(2)	C20	C19	C22	125.3(5)
C20[1]	Ir1	Cl2	100.1(2)	C22	C19	Ir1	125.4(9)
C20	Ir1	Cl2	155.6(2)	N4[1]	C3	Ir1	127.9(5)
C19	Ir1	C21[1]	64.3(4)	N4	C3	Ir1	127.9(5)
C19	Ir1	C21	64.3(4)	N4	C3	N4[1]	103.8(9)
C19	Ir1	C20	38.5(3)	C5[1]	C5	N4	106.6(4)
C19	Ir1	C20[1]	38.5(3)	N4	C6	C7	112.9(7)
C19	Ir1	Cl2[1]	136.27(6)	C8	C7	C6	121.1(7)
C19	Ir1	Cl2	136.28(6)	C8	C7	C12	121.9(8)
C3	Ir1	C21	151.0(3)	C12	C7	C6	117.0(8)
C3	Ir1	C21[1]	151.0(3)	C7	C8	C9	119.9(8)
C3	Ir1	C20	112.2(3)	C7	C12	C11	117.5(8)
C3	Ir1	C20[1]	112.2(3)	C8	C9	C10	120.7(8)
C3	Ir1	C19	94.4(4)	O13	C9	C8	124.3(8)
C3	Ir1	Cl2[1]	90.8(2)	O13	C9	C10	115.0(8)
C3	Ir1	Cl2	90.8(2)	C9	C10	C11	117.8(8)
Cl2	Ir1	Cl2[1]	86.88(10)	O15	C10	C9	120.4(9)
C3	N4	C5	111.5(7)	O15	C10	C11	121.7(8)
C3	N4	C6	124.5(7)	C12	C11	C10	122.1(8)
C5	N4	C6	122.5(6)	O17	C11	C12	123.5(9)
C21[1]	C21	Ir1	71.6(2)	O17	C11	C10	114.4(9)
C21[1]	C21	C20	108.2(5)	C11	O17	C18	115.6(8)
C21[1]	C21	C24	125.7(5)	C9	O13	C14	117.1(8)

C20	C21	Ir1	68.5(5)	C10	O15	C16	115.6(9)
C20	C21	C24	126.1(8)				

[1]+X,1/2-Y,+Z

Experimental

Single crystals of $C_{33}H_{43}Cl_2IrN_2O_6$ **5A** (str1232) were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Data collection was performed on a SuperNova dual source equipped with a CCD Atlas detector diffractometer (Agilent Technologies). The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. SHELXS-97 (Sheldrick, 1990)
3. SHELXL, G.M. Sheldrick, Acta Cryst. 2008. A64, 112-122

Crystal structure determination of [str1232]

Crystal Data. $C_{33}H_{43}Cl_2IrN_2O_6$, M =826.79, monoclinic, a = 7.8446(9) Å, b = 28.210(2) Å, c = 8.2365(10) Å, β = 114.610(14)°, V = 1657.1(3) Å^3, T = 293(2), space group $P2_1/m$ (no. 11), Z = 2, μ(Mo Kα) = 4.236, 14723 reflections measured, 3811 unique (R_{int} = 0.1048) which were used in all calculations. The final wR_2 was 0.1302 (all data) and R_1 was 0.0654 (>2sigma(I)).