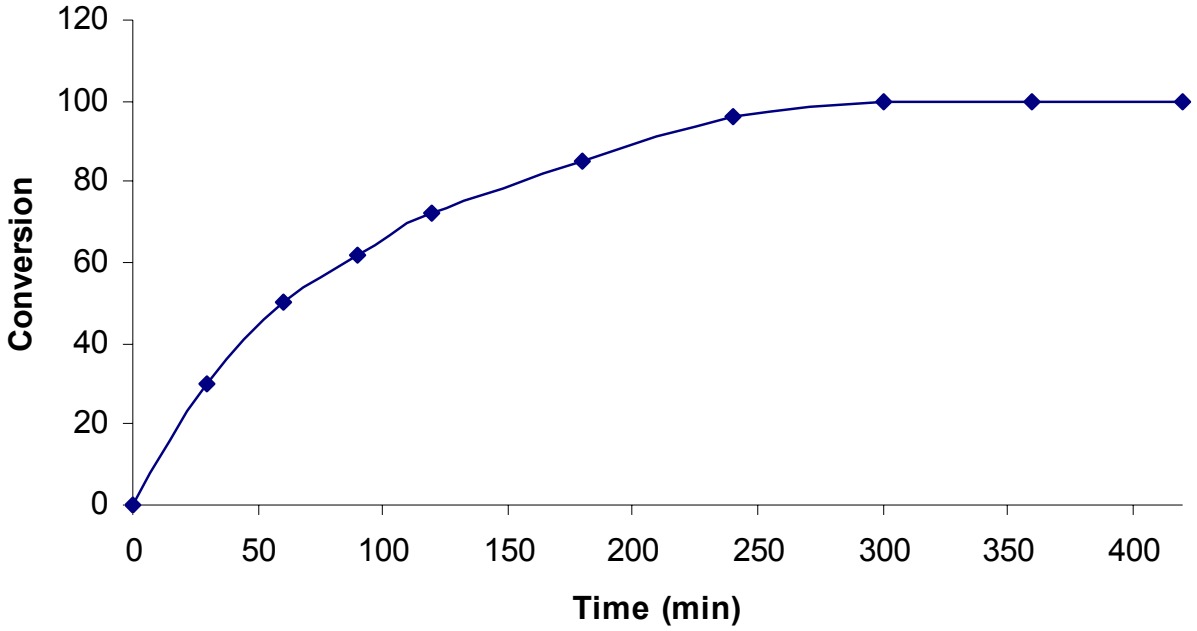
Electronic Supplementary Information for Dalton Transactions

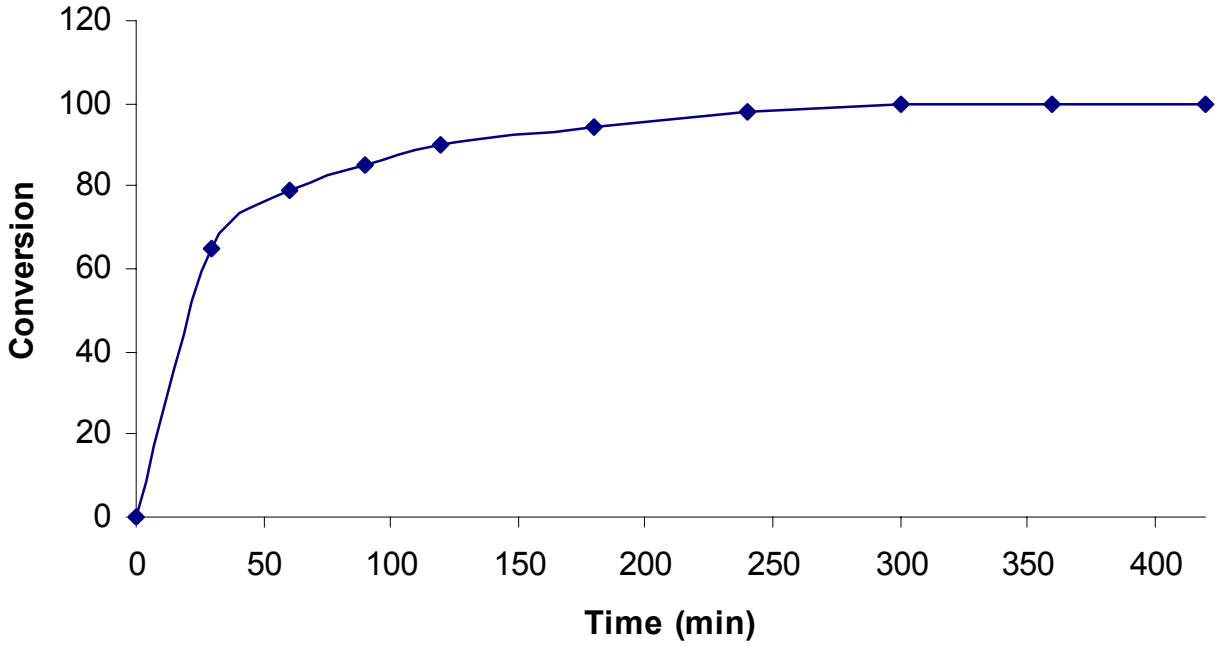
Supplementary Data

Manuscript: Expanded Ring and Functionalised Expanded Ring N-Heterocyclic Carbenes as Ligands in Catalysis

Authors: Abeer Binobaid, Manuel Iglesias, Dirk J. Beetstra, Benson Kariuki, Athanasia Dervisi*, Ian A. Fallis* and Kingsley J. Cavell*



(a) 1 bar H_2



(b) 3.5 bar H_2

Fig S1 Plots of conversion versus time for catalyst **22d**. For conditions see Table 3.

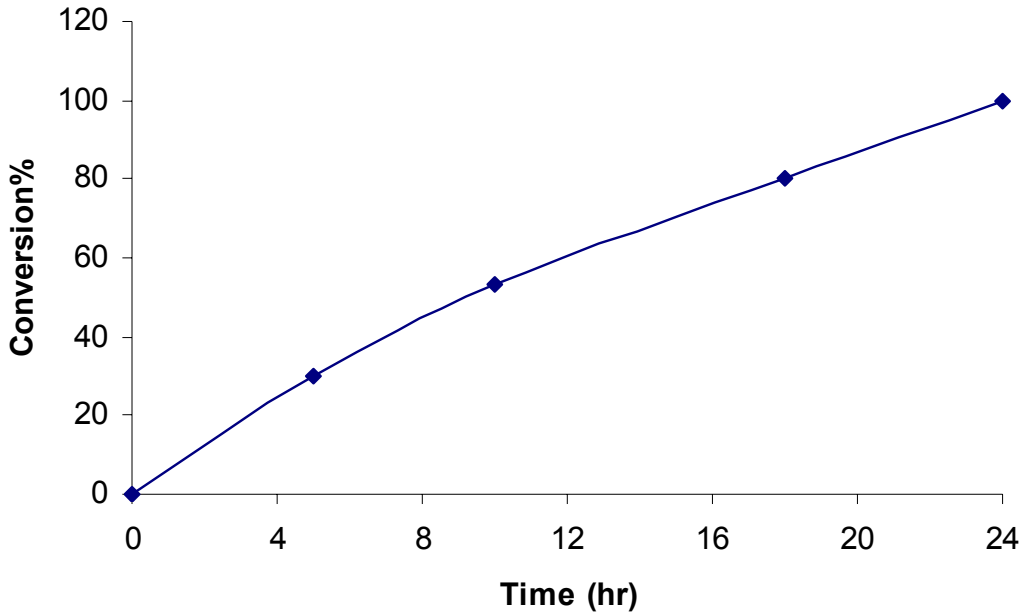


Fig S2 Plots of conversion versus time for catalyst **22d**. Conditions: Cyclooctene: 3.0 mmol; Catalyst: 0.01 mmol; EtOH: 5 ml; H_2: (3.5 bar). Determined by GC-MS.

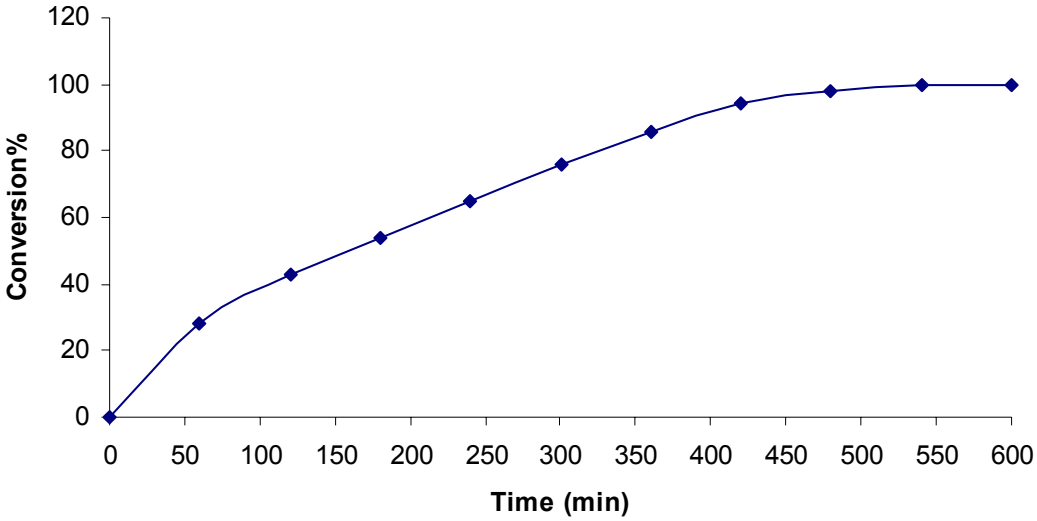


Fig S3 Plot of conversion versus time for catalyst **24b**. H_2: (1 atm). Determined by GC-MS. For other conditions see Table 3.

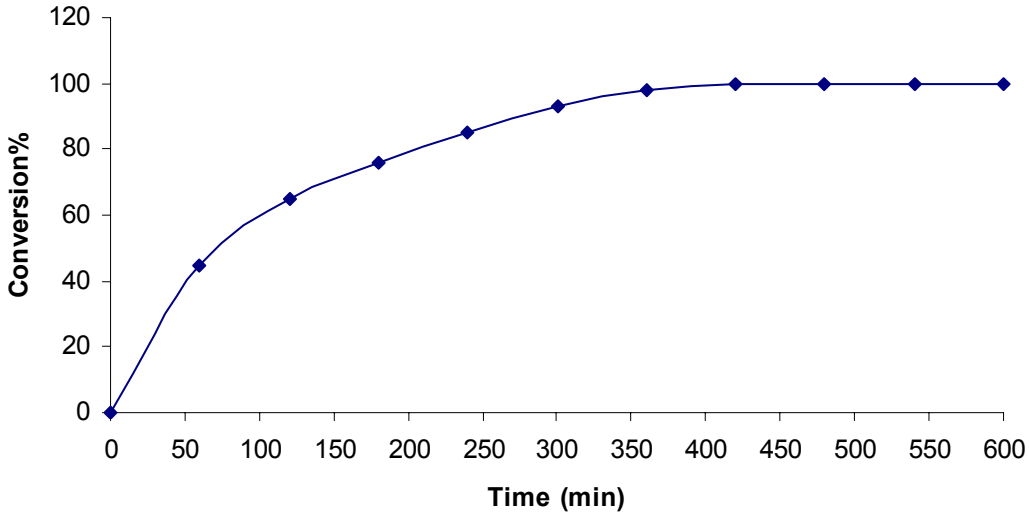


Fig S4 Plot of conversion versus time for catalyst **24b**. H_2: (3.5 atm). Determined by GC-MS. For other conditions see Table 3.

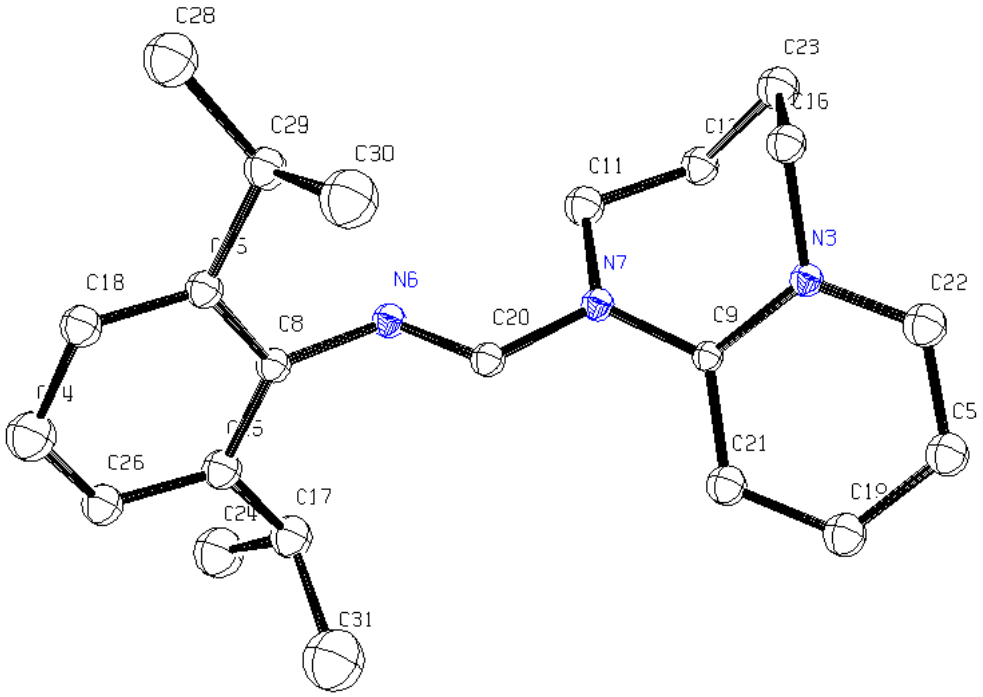


Fig S5 Structure of compound **15b** with alternative ring closure

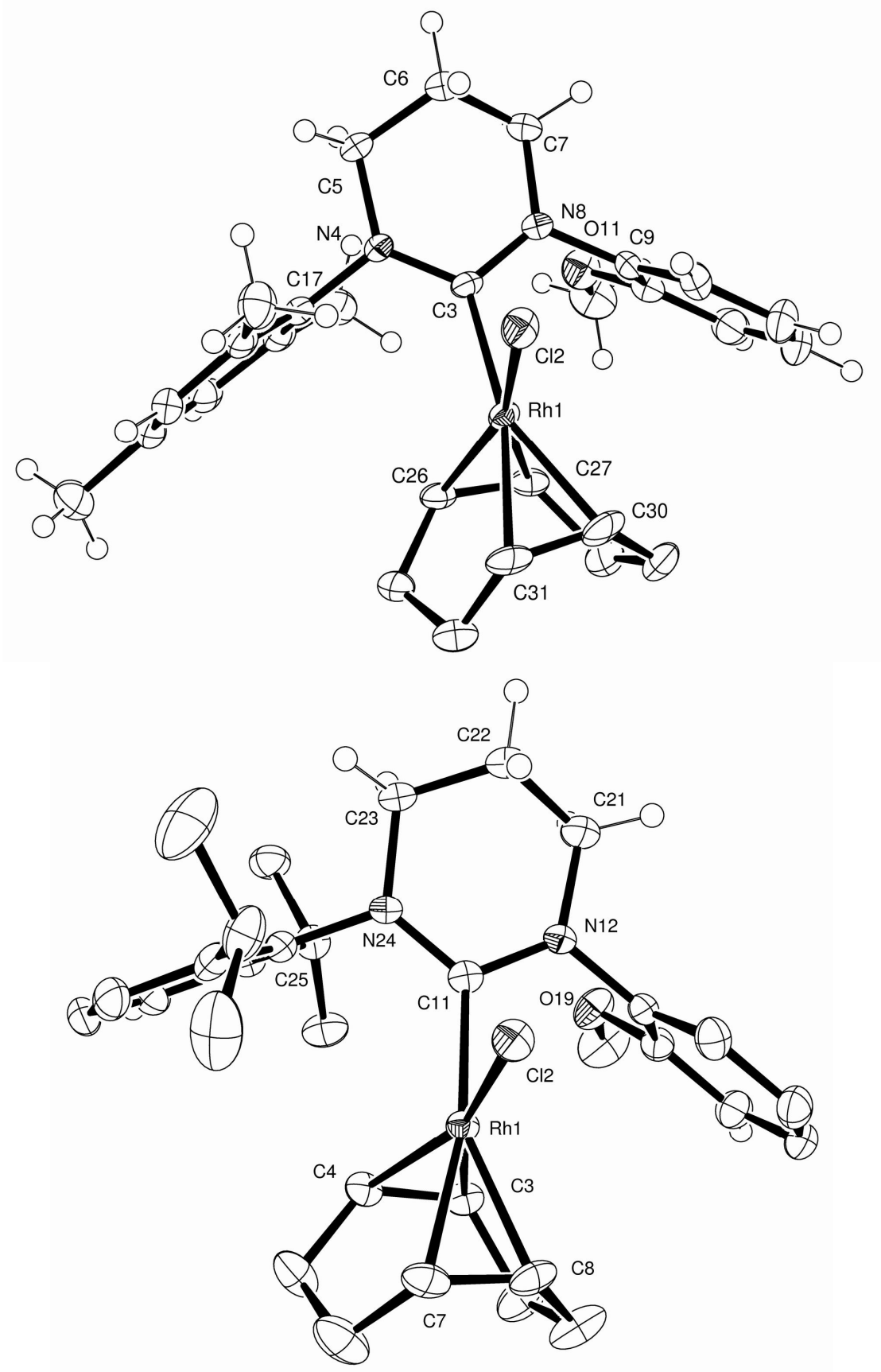
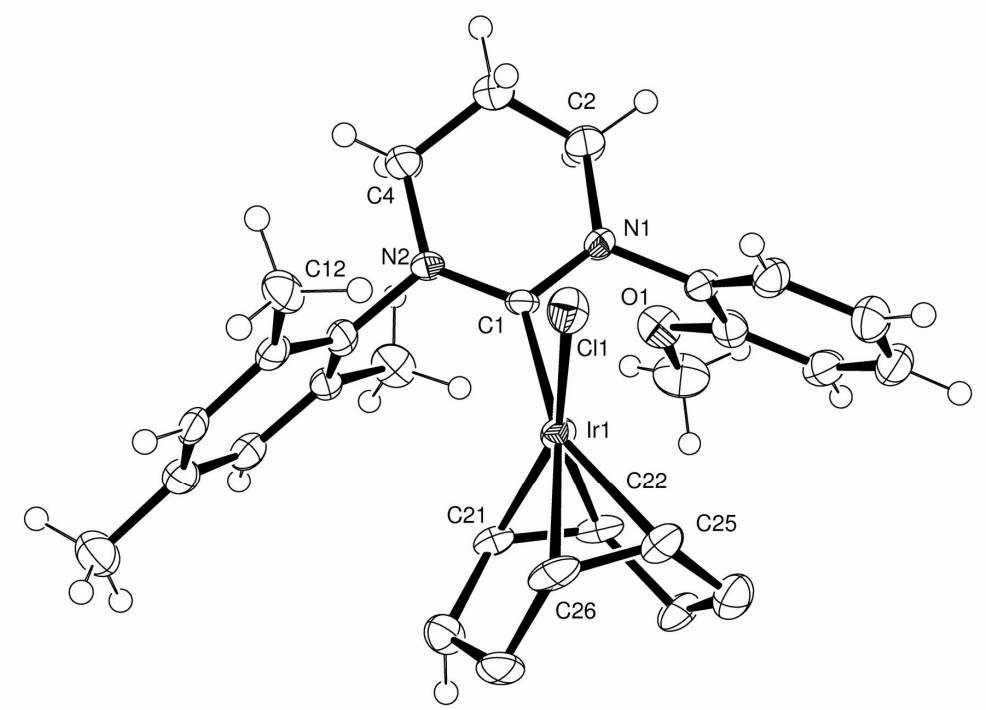


Fig S6 Displacement ellipsoid plots at 30% probability for **22a** and **22b**



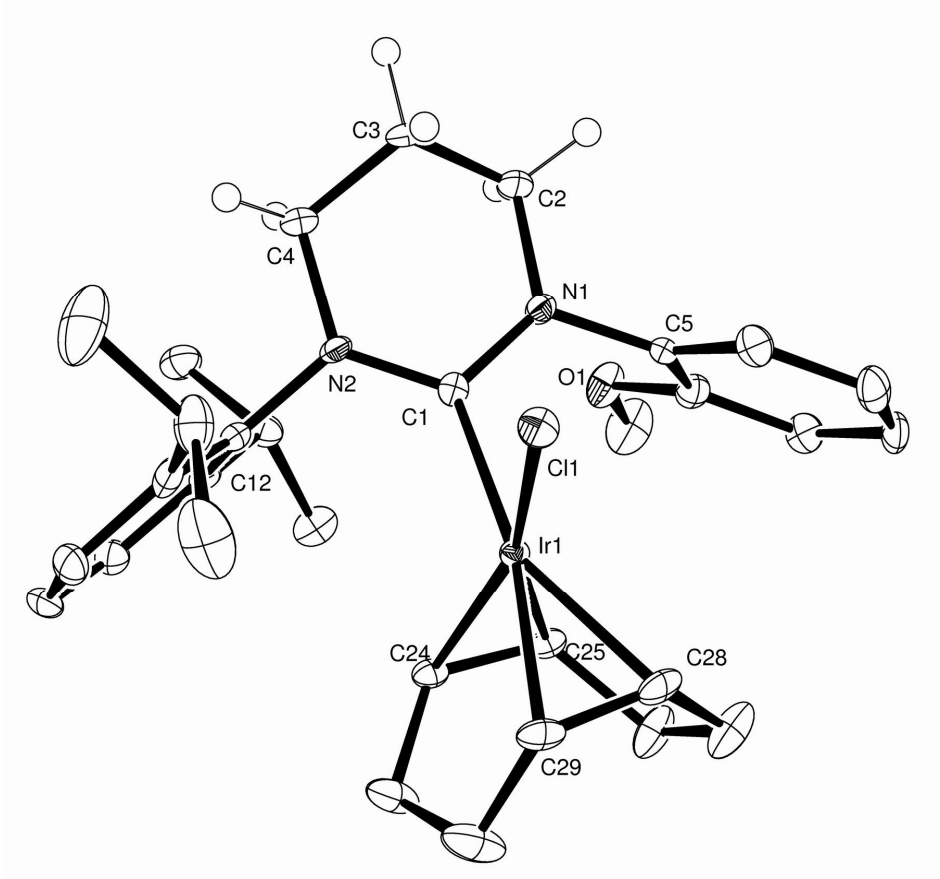


Fig S7 Displacement ellipsoid plots at 30% probability for **23a** and **23b**

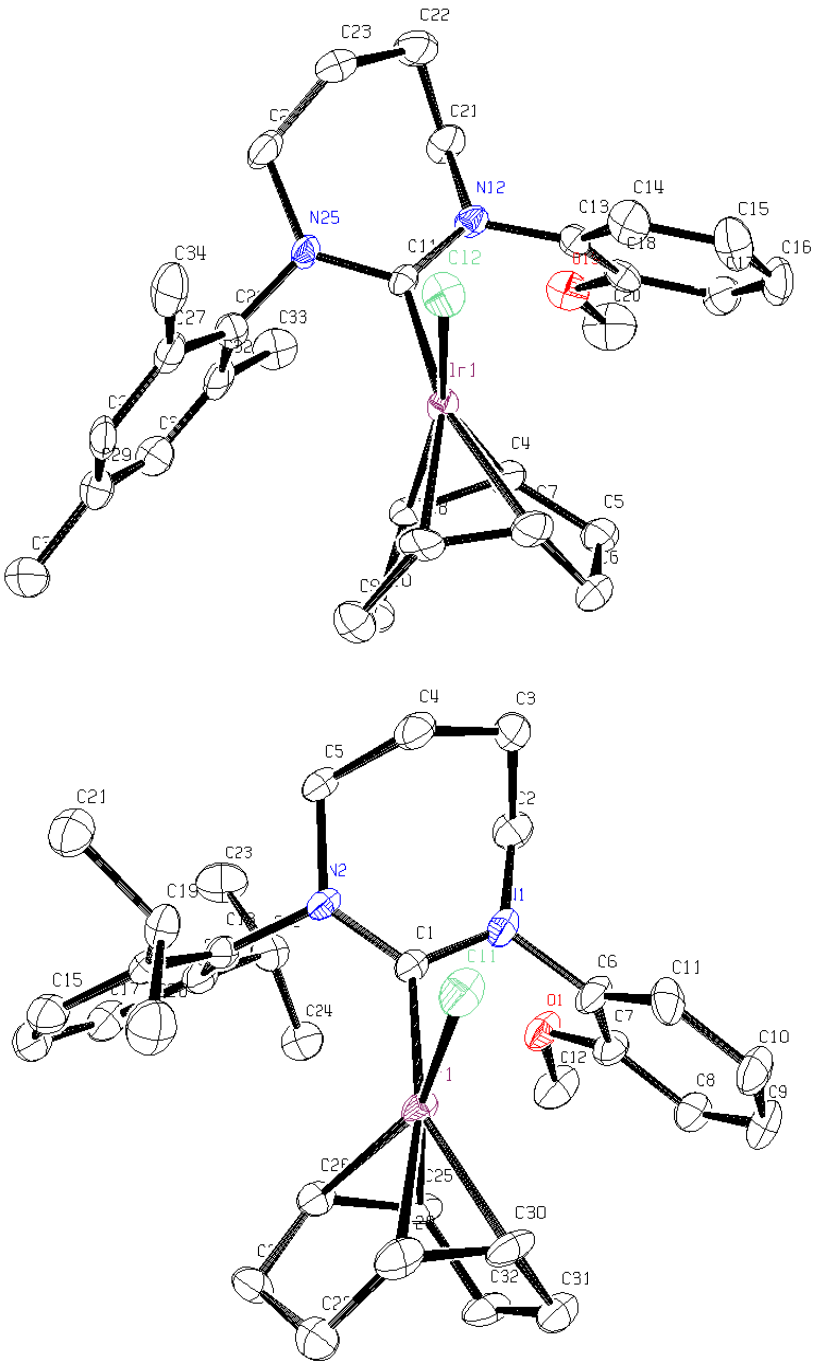


Fig S8 Displacement ellipsoid plots at 30% probability for **24a** and **24b**

Compound	**22a**	**22b**	**23a**	**23b**	**24a**	**24b**
Empirical	$C_{29}H_{38}Cl_3N$	$C_{31}H_{42}Cl_1N_2O_1R$	$C_{32}H_{44}ClIrN$	$C_{31}H_{42}ClIrN_2O$	$C_{33}H_{46}ClIrN$	$C_{32}H_{44}ClIrN_2O$

formula	$_2$ORh	h_1	$_2O_2$		$_2O_2$	
Formula weight	639.87	597.05	716.34	686.32	730.37	700.34
Temperature / K	150(2)	150 (2)	150(2)	150(2)	150(2)	150(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	P 2_1/n	P-1	P2_1/n	P-1	P2_1/c
a / Å	9.7164(2)	17.4487(3)	9.6970(5)	17.4350(3)	9.5131(2)	10.1870(2)
b/ Å	11.4614(4)	10.4263(2)	11.1510(6)	10.4170(2)	11.5515(2)	16.5340(3)
c / Å	13.2888(4)	17.7256(4)	13.9060(11)	17.6770(4)	14.2948(2)	19.4270(3)
α / °	86.629(2)	-	85.593(2)	-	80.8690(10)	-
β / °	78.935(2)	116.8549(9)	79.370(2)	116.7360(10)	82.8800(10)	118.7510(10)
γ / °	82.3150(10)	-	81.103(4)	-	82.0440(10)	-
V / Å^3	1438.50(7)	2876.96(10)	1458.28(16)	2867.26(10)	1527.65(5)	2868.73(9)
Z	2	4	2	4	2	4
σ (cal) / Mg/m^3	1.477	1.378	1.631	1.590	1.588	1.622
μ / mm^{-1}	0.897	0.712	4.701	4.776	4.489	4.775
Crystal size / mm^3	0.25x0.25x 0.25	0.20x0.20x0.08	0.15x0.15x0 .02	0.20x0.20x0.1 8	0.30x0.20x0 .10	0.38x0.08x0.0 5
Reflections collected	22407	47505	9737	10761	25944	46665
Independent reflections	6485	12657	6473	6537	6922	6540
R(int)	0.1097	0.075	0.0517	0.0268	0.0955	0.1803
Parameters	329	326	347	330	356	339
R1 [I>2σ(I)]	0.0417	0.0470	0.0481	0.0279	0.0401	0.0493
wR2 [I>2σ(I)]	0.0982	0.0874		0.0583	0.0940	0.1140

Electronic Supplementary Information for Dalton Transactions

Description of GC/MS method. Yields and substrate identities were determined by GC-MS analysis of reaction mixtures using an Agilent Technologies 6890N GC system with an Agilent Technologies 5973 inert MS detector with MSD. Column: Agilent 190915-433 capillary, 0.25 mm x 30 m x 0.25 μm. Capillary: 30 m x 250 μm x 0.25 μm nominal. Initial temperature at 50^{o}C, held for 4 minutes, ramp 5^{o}C/minute next 100^{o}C, ramp 10^{o}C/minute next 240^{o}C hold for 15 minutes. The temperature of the injector and the detector were held at 240^{o}C.