Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Hydrogen generation from formic acid decomposition on a highly efficient iridium catalyst bearing diaminoglyoxime ligand

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General: ^{1}H NMR and ^{13}C NMR spectra were recorded on a BrukerAvance 400 NMR spectrometer. Chemical shifts are given in ppm and spin-spin coupling constants, *J*, are given in Hz. Column chromatography was performed on silica gel (200-300 mesh). GC analysis results was obtained with Techcomp GC7890Ⅱ equipped with a TCD and a FID. The pH values were measured on a ZDJ-400DH multi-function titrator with a glass electrode after calibration to standard buffer solutions. The residual concentration of formic acid was measured by SHINEHA CIC-100 ion chromatograph with Shodex IC SI-52 4E column using Na_2CO_3 solution (3.6 mM) as the eluent. HRMS data were recorded on a Finnigan MAT 95 system. Formic acid (98%) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. $[IrCp^*Cl_2]_2$(98%) was purchased from J&K. Sodium formate was purchased from Sinopharm Chemical Reagent Co. Ltd. Ligands **L1**[1], **L2**[1], **L4**[1,2], **L5**[3], **L6**[4] were known compounds and synthesized according to literature procedures. **L3** was purchased from J&K Company. **L7** and **L8** were new compounds and synthesized according to the procedure of **L6**[4].

Characterization of ligands:

L1(Glyoxime), white solid;^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 7.72 (s, 2H), 11.61 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO): δ (ppm) = 145.9.

L2(Dichloroglyoxime), white solid; ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 13.11 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO): δ (ppm) = 131.2.

L4 (Diaminoglyoxime), white solid; ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.75 (s, 2H), 5.16 (s, 4H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): δ (ppm) = 145.8

L5 (Di-iso-propylamineglyoxime), slightly yellow solid; ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.61 (s, 2H), 5.37 (d, 2H, *J* = 12 Hz), 3.32-3.43 (m, 2H), 1.04-1.06 (m, 12 H); ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO): δ (ppm) = 147.3, 44.7, 24.8.

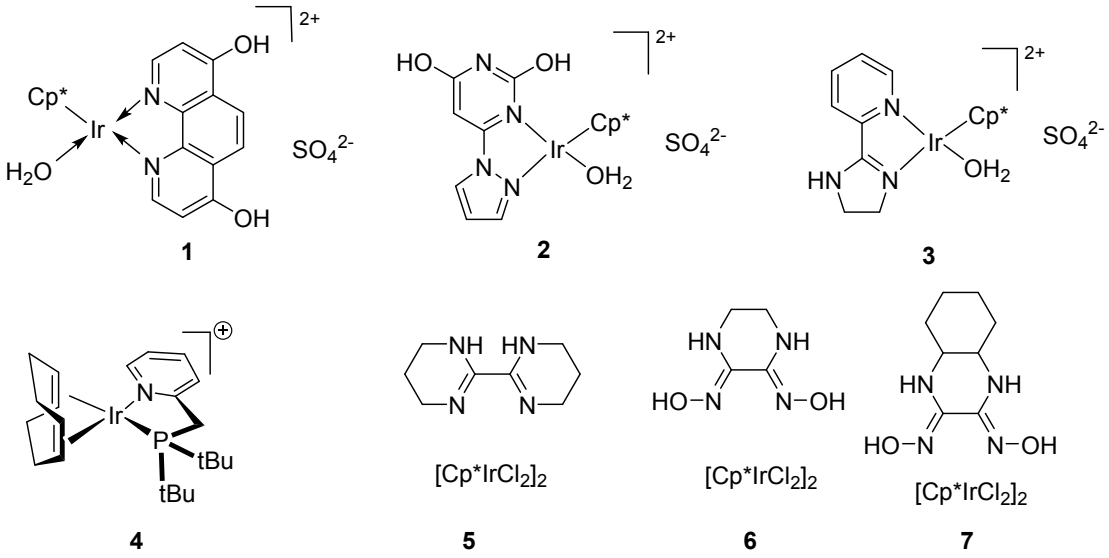
L6 (2,3-Piperazinedione dioximes), white solid; ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.47 (s, 2H), 6.29 (s, 2H), 3.10 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO): δ (ppm) = 144.3, 40.6;

L7 (5-Methyl-Piperazine-2,3-dione dioximes), white solid; ^{1}H NMR (400 MHz, d_6-

DMSO): δ (ppm) = 1H NMR (400 MHz, DMSO) δ 9.59 (s, 1H), 9.51 (s, 1H), 6.29 (s, 1H), 6.02 (s, 1H), 3.40-3.35 (m, 1H), 3.20-3.15 (m, 1H), 2.79 (ddd, *J* = 11.6, 8.4, 2.4 Hz, 1H), 1.09 (d, *J* = 6.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, d_6-DMSO): δ (ppm) = 143.89, 143.88, 45.7, 45.2, 19.3; HRMS: calcd. for$C_5H_{11}N_4O_2$ $[M+H]^+$, 159.0882, Found 159.0889.

L8 (Octahydroquinoxaline-2,3-dione dioxime), white solid; ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) = 9.65 (s, 2H), 5.92 (s, 2H), 2.78-2.76 (m, 2H), 1.98 (d, *J* = 12.4 Hz, 2H), 1.64 (d, *J* = 8.4 Hz, 2H), 1.27-1.11 (m, 4H); ^{13}C {^{1}H} NMR (100 MHz, d_6-DMSO): δ (ppm) = 144.2, 55.7, 30.1, 24.0; HRMS: calcd. for $C_8H_{15}N_4O_2$ $[M+H]^+$, 199.1195, Found 199.1211.

Scheme S1 Selected homogeneous catalysts for large amount of formic acid dehydrogenation in water or without solvents



1 2 3 4 5 6 7

Catalyst	Solvent	Additives	T (°C)	Time (h)	TON (×10⁴)	Average rate (h^{-1})	Ref.
1	H_2O	None	60	2600	500	1923	(5)
2	H_2O	None	60	580	205	3534	(6)
3	H_2O	None	50	363	200	5510	(7)
4	None	SF	90	2880	216	750	(8)
5	H_2O	None	80	14	240	171000	(9)
6 or 7	H_2O	None	90	12.5	**220**	**176000**	This work
7	H_2O	None	90	60	**390**	**65000**	This work
6	H_2O	None	70	45	**220**	**48889**	This work
6	H_2O	None	70	175	**502**	**28686**	This work

6	H_2O	None	25	380	**40**	**0.105**	This work

References:

(1) (a) N. Fischer, T. M. Klapötke, M. Reymann, J. Stierstorfer, *Eur. J. Inorg. Chem*. **2013**, 2167-2180; (b) P. L. van der Peet, T. U. Connell, C. Gunawan, J. M. White, P. S. Donnelly, S. J. Williams, *J. Org. Chem*. **2013**, *78*, 7298-7304.

(2) A. K. Zelenin, M. L. Trudell, *J. Heterocyclic Chem.***1997**, *34*, 1057-1060.

(3) (a) V. G. Andrianov, A. V. Eremeev, *Zhurnal Organicheskoi Khimii*, **1991**, *27*, 112-116; (b) G. Gümüs, V. Ahsen, C. Lebrun, D. Luneau, J. Pécaut, *New. J. Chem.***2004**, *28*, 177-179.

(4) R. L. Willer, *J. Org. Chem.* **1985**, *50*, 5123-5127.

(5) M. Iguchi, Y. Himeda, Y. Manaka, H. Kawanami, *ChemSusChem***2016**, *9*, 2749-2753.

(6) W.-H. Wang, M. Z. Ertem, S. Xu, N. Onishi, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, *ACS Catal.***2015**, *5*, 5496-5504.

(7) N. Onishi, M. Z. Ertem, S. Xu, A. Tsurusaki, Y. Manaka, J. T. Muckerman, E. Fujita, Y. Himeda, *Catal. Sci. Technol.*, **2016**, *6*, 988-992.

(8) J. J. A. Celaje, Z. Lu, E. A. Kedzie, N. J. Terrile, J. N. Lo, T. J. Williams, *Nat. Commun*. **2016**, 11308

(9) Z. Wang, S.-M. Lu, J. Li, J. Wang, C. Li, *Chem. Eur. J.*, **2015**, 21, 12592-12595.

Reaction conditions optimization

Table S1 pH dependence of the FA dehydrogenation with **Ir-L7**

Entry	**pH**	**TOF (h^{-1})**
1	0.71	1625[a]
2	1.10	5938[a]
3	1.31	8750
4	1.59	13750
5	1.78	33750
6	1.95	33750
7	2.26	32500
8	2.52	28750
9	2.68	26250
10	3.06	22500
11	3.30	20000
12	3.51	15000
13	3.69	12500
14	4.10	7500
15	4.74	1875
16	8.01	0

General reaction conditions: complex **Ir-L7** (1.0 μmol), 60 °C, FA/HCO_2Na (1.0 M of FA and HCOONa, 10.0 mL) or FA/CH_3SO_3H (FA, 1.0 M, 10.0 mL); TOF was calculated based on the conversion in the first 3 minutes. [a:] TOF was calculated based on the conversion in the first 8 minutes.

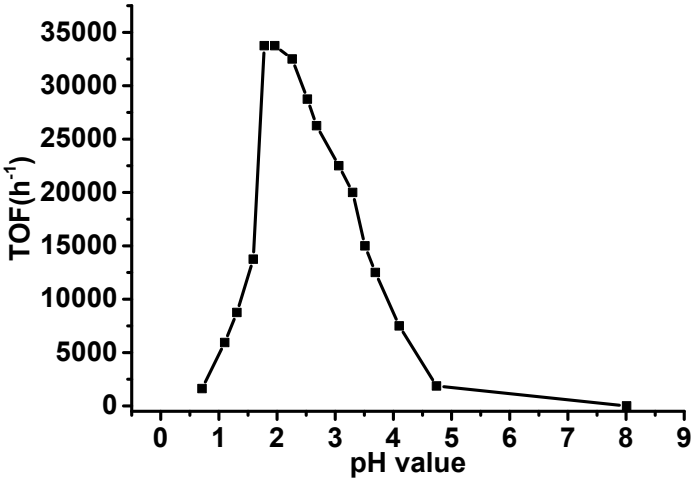


Fig. S1 pH dependence of the reaction initial TOF. Reaction conditions: complex **Ir-L7** (1.0 μmol), 60 °C, FA/HCO_2Na (1.0 M, 10.0 mL) or FA/CH_3SO_3H (FA, 1.0 M, 10.0 mL)

Table S2 Temperature dependence of the FA dehydrogenation with **Ir-L7**

Entry	**Temp. (°C)**	**TOF (h^{-1})**
1	30	2500[a]
2	40	6875
3	50	16250
4	60	33750
5	70	65000
6	80	116250
7	90	213750

General reaction conditions: **Ir-L7** (1.0 μmol); FA (1.0 M, 10.0 mL), TOF was calculated based on the conversion in the first 3 minutes. [a:] TOF was calculated based on the conversion in the first 5 minutes.

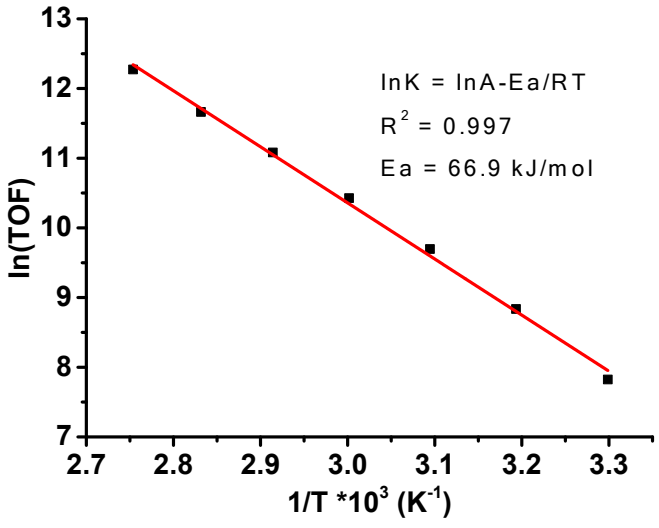


Fig. S2 Temperature dependence of the reaction initial TOF. Reaction conditions: **Ir-L7** (1.0 μmol), 30-90 °C, FA (1.0 M, 10.0 mL).

Table S3 Catalyst concentration dependence of the FA dehydrogenation with **Ir-L7**

Entry	Catalyst concentration(μM)	TOF (h^{-1})
1	25	32500
2	50	35000
3	100	33750
4	200	30000

General reaction conditions: **Ir-L7** (0.25-2.0 μmol); FA (1.0 M, 10.0 mL), 60 °C; TOF was calculated based on the conversion in the first 3 minutes.

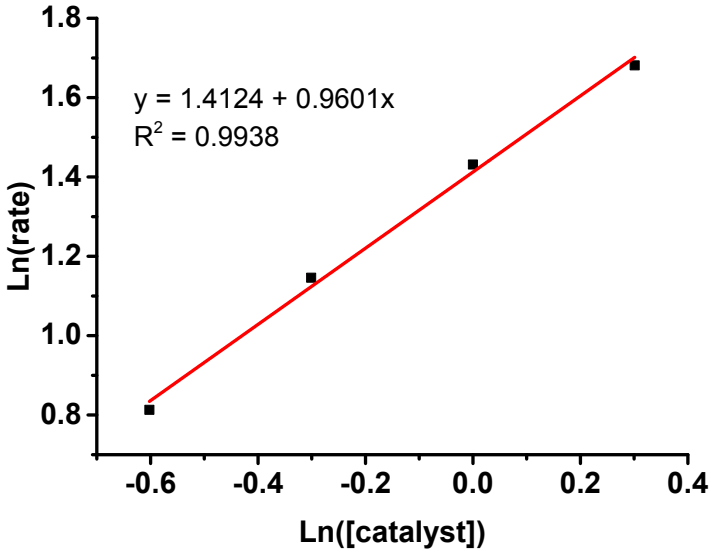


Fig. S3 Catalyst concentration dependence of the reaction initial TOF, Reaction conditions: complex **Ir-L7** (25-200 μM), 60 °C, FA (1.0 M, 10.0 mL).

Table S4 FA concentration dependence of the FA dehydrogenation with **Ir-L7**

Entry	FA (M)	Time (min)	Initial TOF (h^{-1})	Average rate (h^{-1})	Residual FA (mmol)	TON
1	0. 5	19	27500	15729	0.019	4981
2	1.0	28	33750	21388	0.019	9981
3	2.0	45	36250	26661	0.004	19996
4	4.0	75	37500	31995	0.006	39994
5	6.0	125	31250	28795	0.010	59990
6	8.0	164	28750	29265	0.008	79992
7	10.0	320	17500	18747	0.016	99984
8	12.0	385	13750	18699	0.015	119985
9	20.0	420	1875	2500	182.5	17500

General reaction conditions: complex **Ir-L7** (1.0 μmol); FA (0.5-20.0 M, 10.0 mL), 60 °C; TOF was

calculated based on the conversion in the first 3 minutes.

Table S5 The stabilities and efficiencies of the different iridium catalysts for different amount FA dehydrogenation at 90 °C

Entry	Cat.	FA (mol)	React. time (h)	TON($\times10^4$)	Average rate ($\times10^4$, h^{-1})
1	**Ir/L4**	0.9	9.25	90	9.7
2		1.8	44.0	81	1.8
3	**Ir/L6**	0.9	5.8	90	15.5
4		1.8	18.0	180	10.0
5		2.2	21.0	220	10.5
6	**Ir/L7**	0.9	5.25	90	17.1
7		1.8	13.5	180	13.3
8		2.2	22.5	220	9.8
9	**Ir/L8**	0.9	5.5	90	16.3
10		1.8	13.5	180	13.3
11		2.2	17.5	220	12.6
12	**Ir-L7**	0.9	6.0	90	15.0
13		1.8	15.0	180	12.0
14		2.2	21.0	220	10.5
15	**Ir-L8**	0.9	5.8	90	15.5
16		1.8	16.0	180	11.2
17		2.2	20.5	220	10.7

General reaction conditions: iridium complex: (1.0 μmol); for in situ catalyst: $[IrCp^*Cl_2]_2$ (0.5 μmol), **L**/Ir = 1.2, FA (10.0 M), 90 °C; The residual FA amount was measured by ion chromatograph and all the reactions have 99.9% conversion except entry 2;

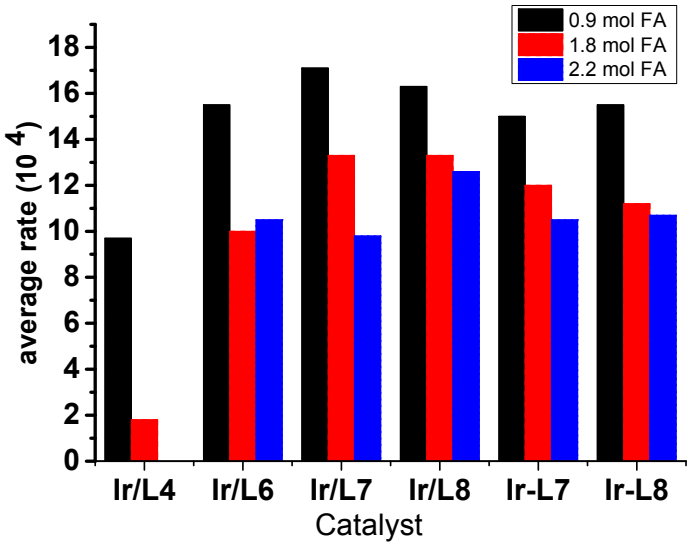


Fig. S4 The catalytic efficiencies comparison of different iridium catalysts for different amount FA dehydrogenation. General reaction conditions: iridium complex: (1.0 μmol); for in situ catalyst:

$[IrCp^*Cl_2]_2$ (0.5 μmol), **L**/Ir = 1.2, FA (10.0 M), 90 °C;

Table S6 The effect of the **L**/Ir ratio on FA dehydrogenation at 90 °C

Entry	Cat.	L/Ir	Time(h)	Average rate ($\times 10^4$, h^{-1})
1	**Ir/L6**	2.0	15.0	14.7
2	**Ir/L6**	4.4	12.5	17.6
3	**Ir/L6**	7.0	13.5	16.3
4	**Ir/L8**	2.0	14.5	15.2
5	**Ir/L8**	4.4	12.5	17.6
6	**Ir/L8**	7.0	12.5	17.6

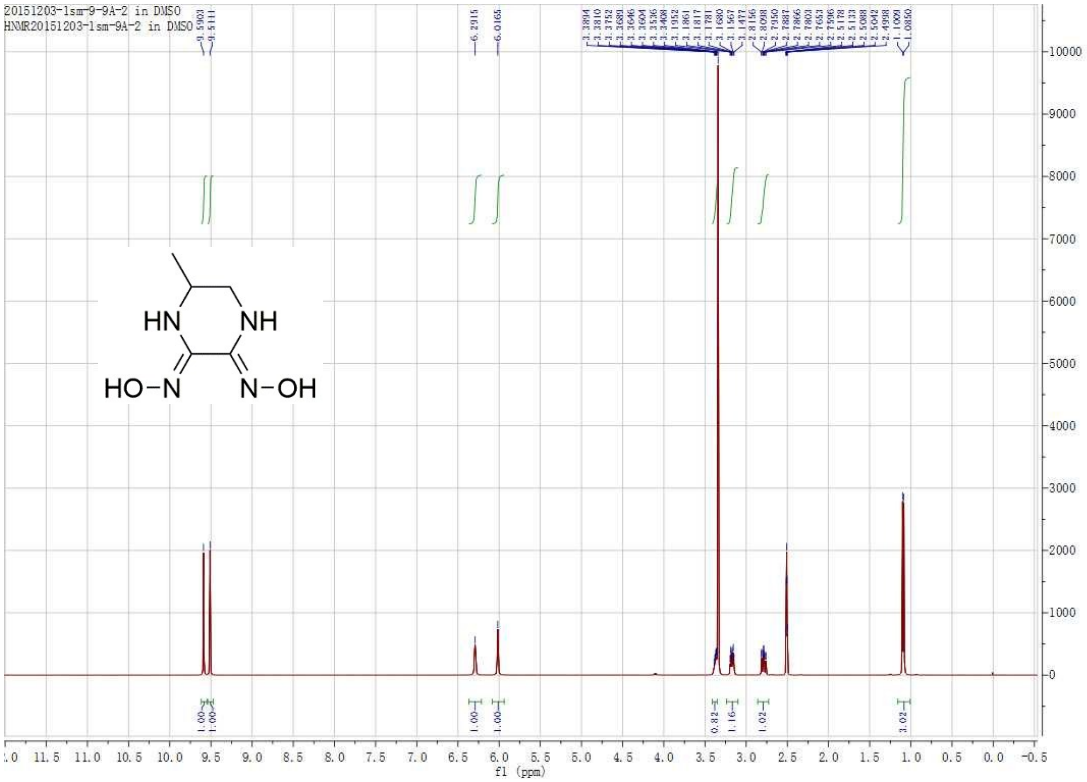
[a:] General reaction conditions: iridium complex: (1.0 μmol); for in situ catalyst: $[IrCp^*Cl_2]_2$ (0.5 μmol), FA (10.0 M, 220 mL), 90 °C; The residual FA amount was measured by ion chromatograph and all the reactions have 99.9% conversion.

Table S7 FA concentration dependence of the FA dehydrogenation with **Ir/L6** at 25 °C

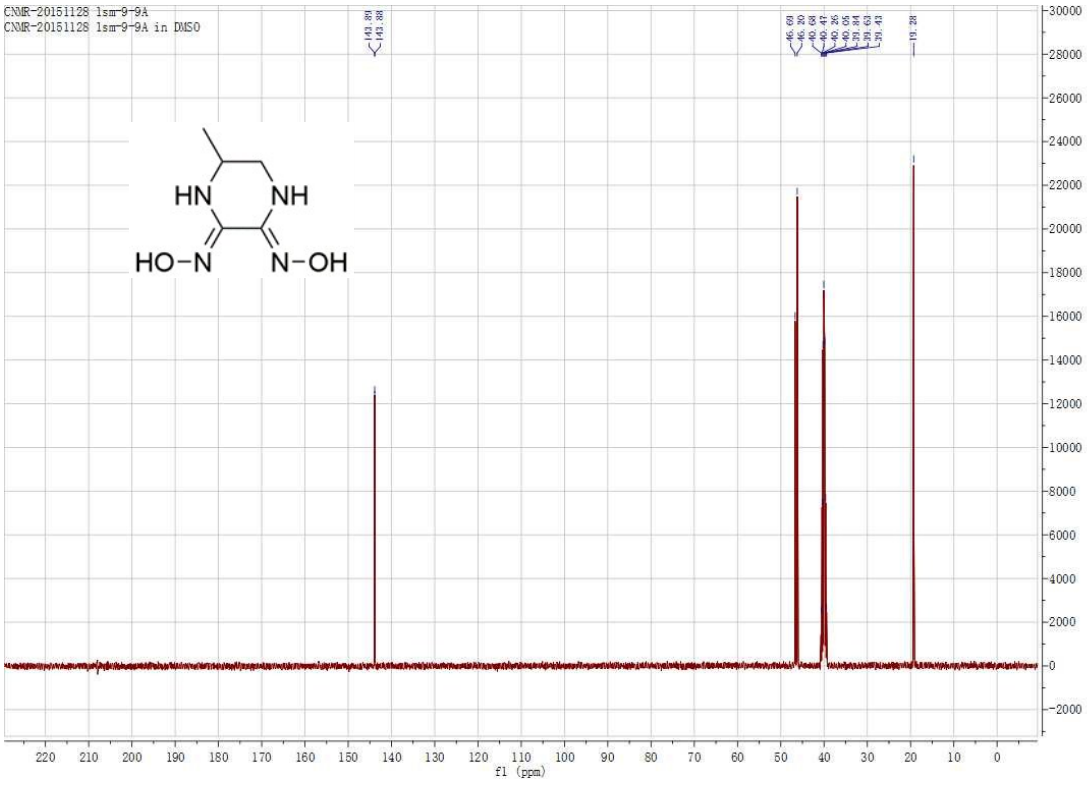
Entry	FA (M)	Time (h)	Initial TOF (h^{-1})	TON
1	0. 5	6.5	1000	5000
2	1.0	9.5	1375	10000
3	2.0	16	1417	20000
4	4.0	30	1375	40000
5	6.0	46	1292	59990
6	10.0	98	708	99857
7	12.0	134	500	119966

General reaction conditions: in situ form catalyst from $[IrCp^*Cl_2]_2$ (0.5 μmol) and **L6** (1.2 μmol); FA (0.5-12.0 M, 10.0 mL), 25 °C; TOF was calculated based on the conversion in the first 30 minutes.

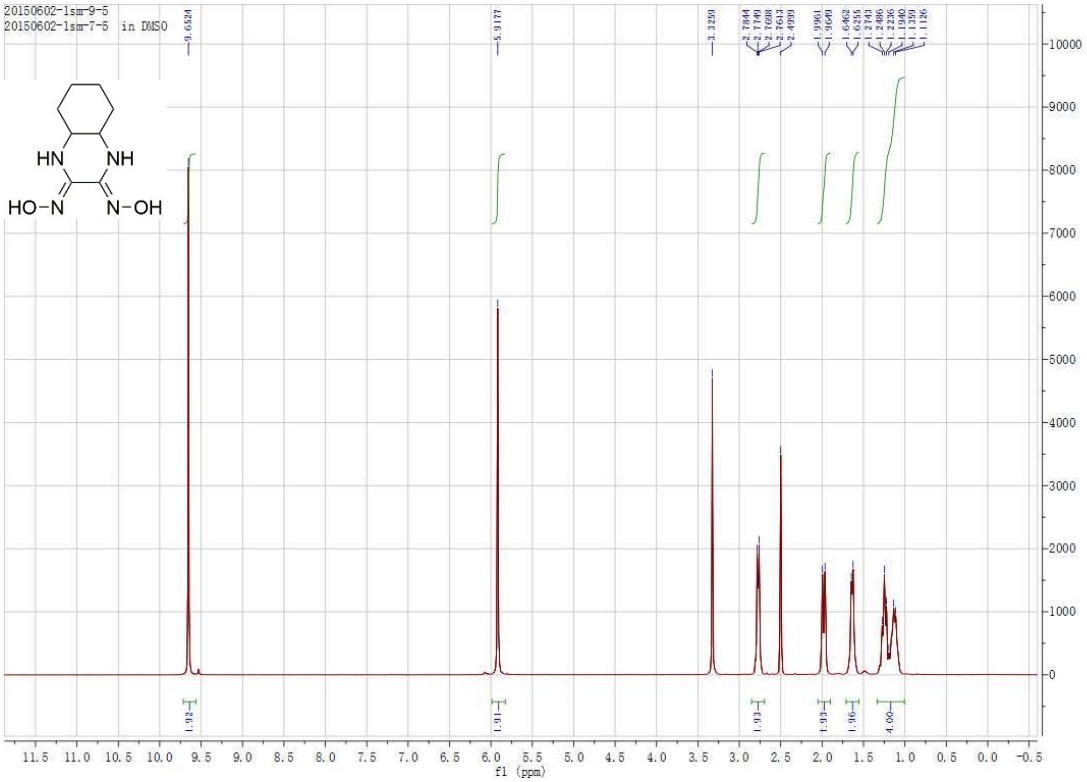
^{1}H NMR spectra of ligand **L7** in DMSO-D6



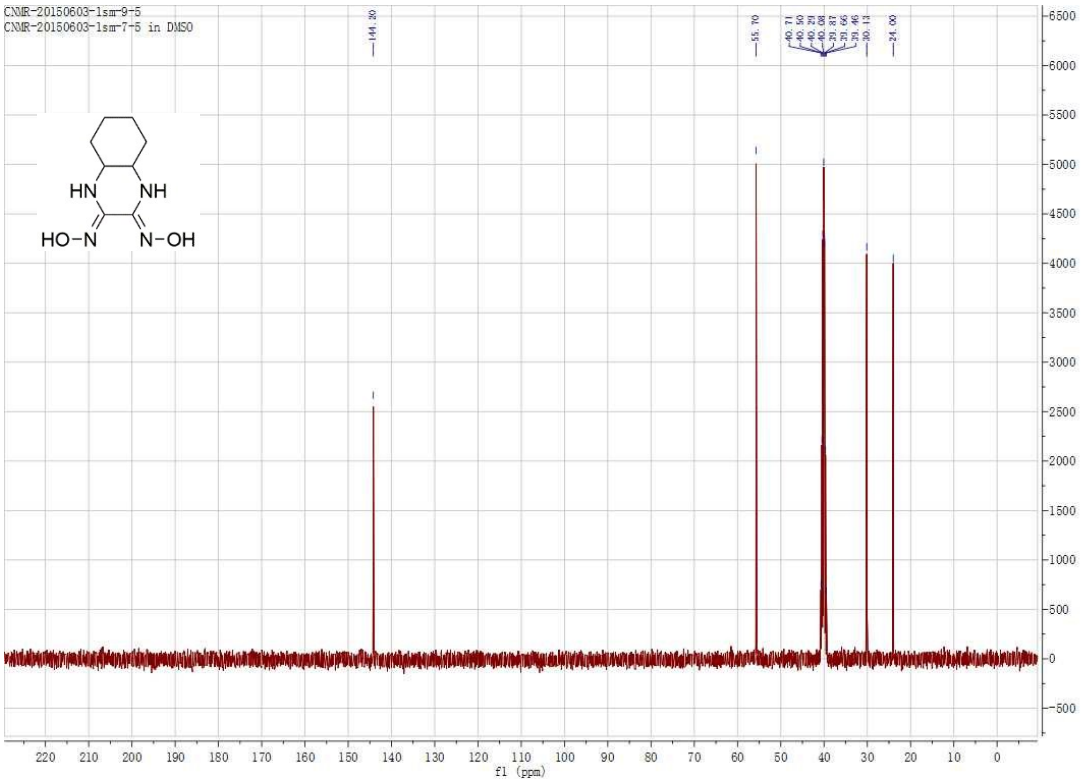
^{13}C NMR spectra of ligand **L7** in DMSO-D6



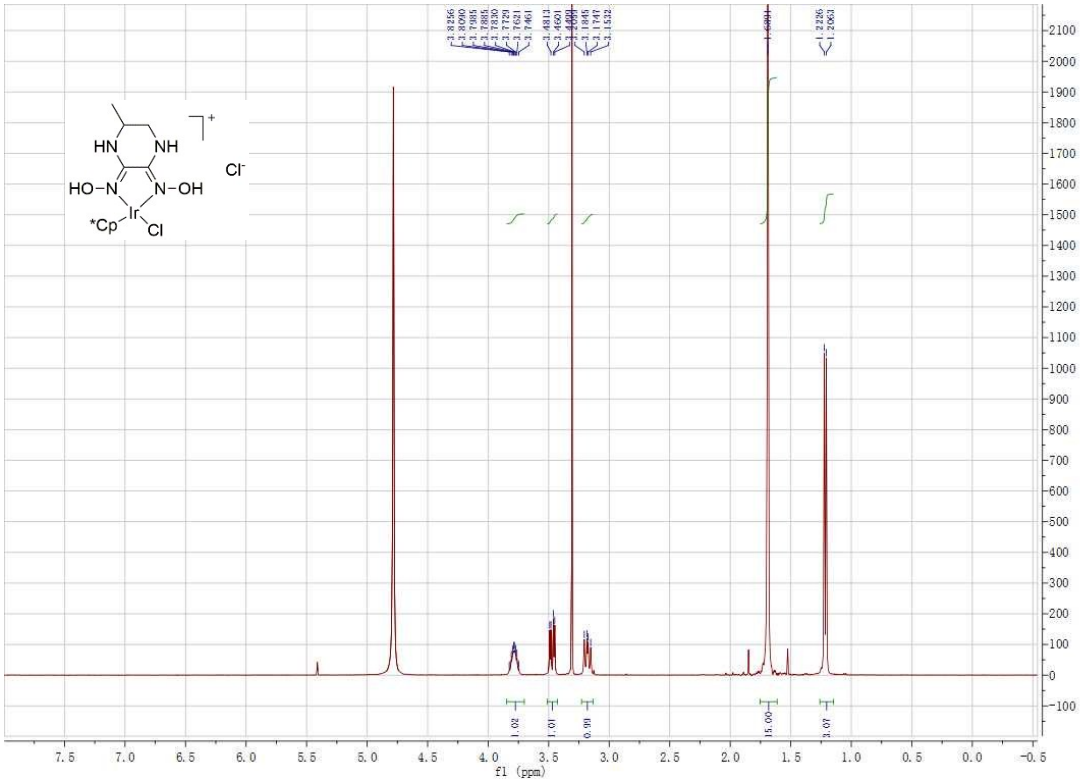
^{1}H NMR spectra of ligand **L8** in DMSO-D6



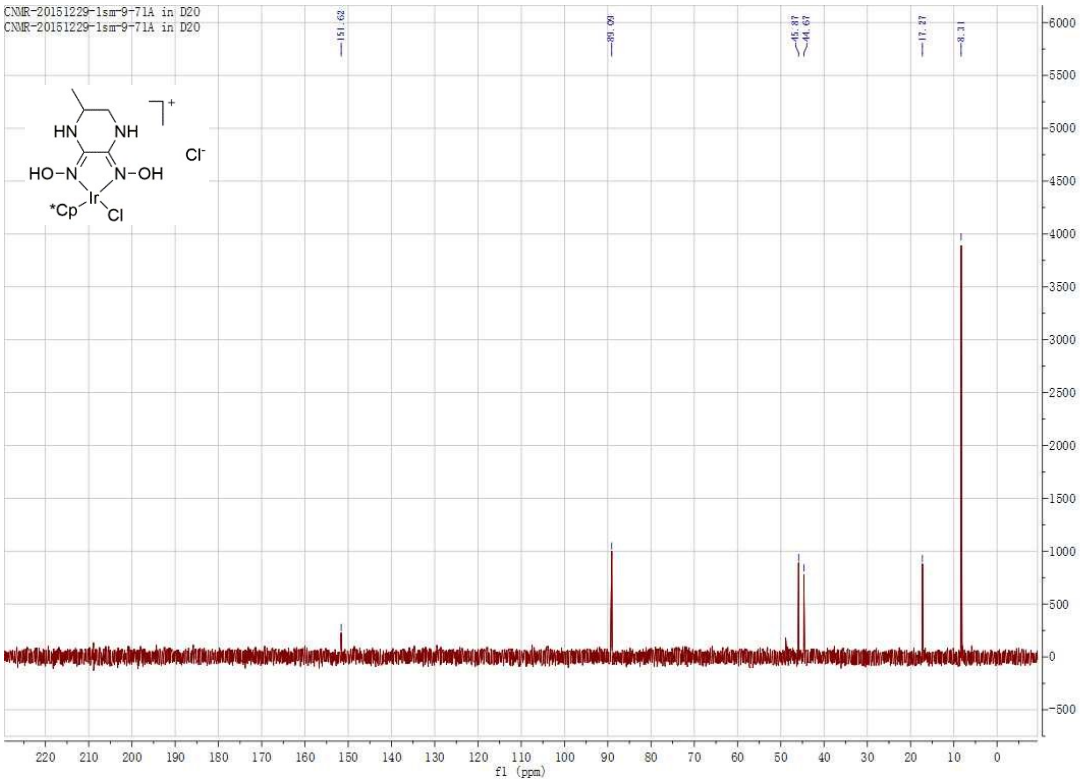
^{13}C NMR spectra of ligand **L8** in DMSO-D6



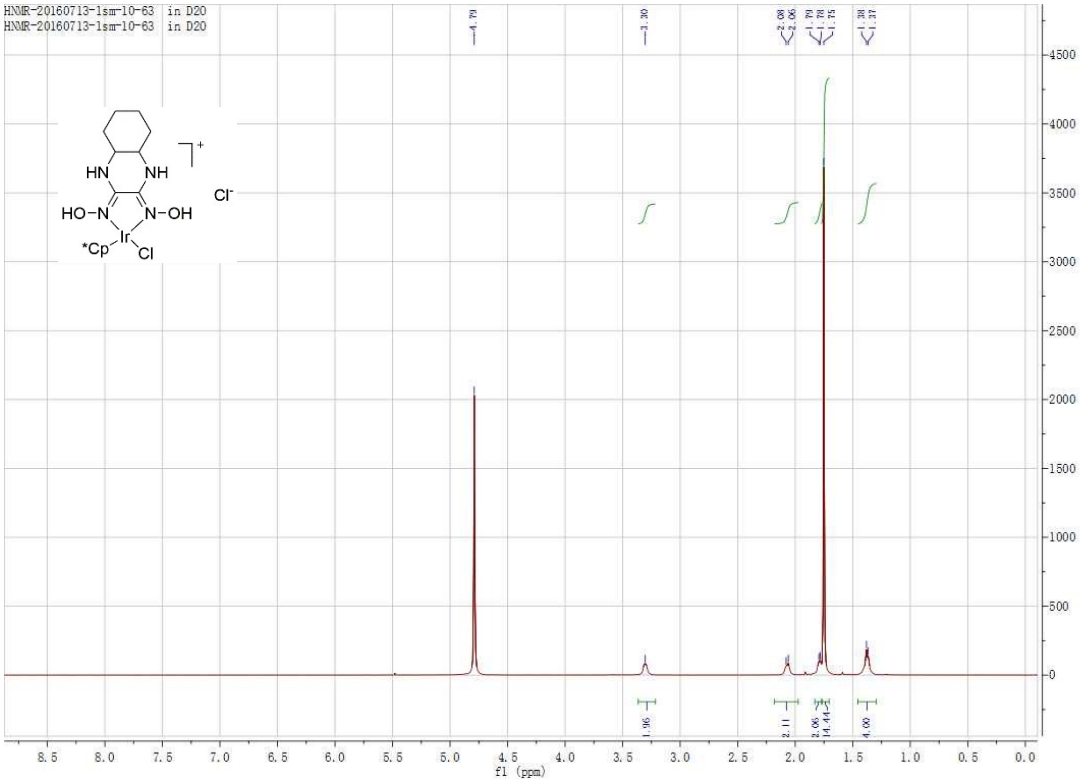
^{1}H NMR spectra of **Ir-L7** in D_2O, some solvent MeOH remained.



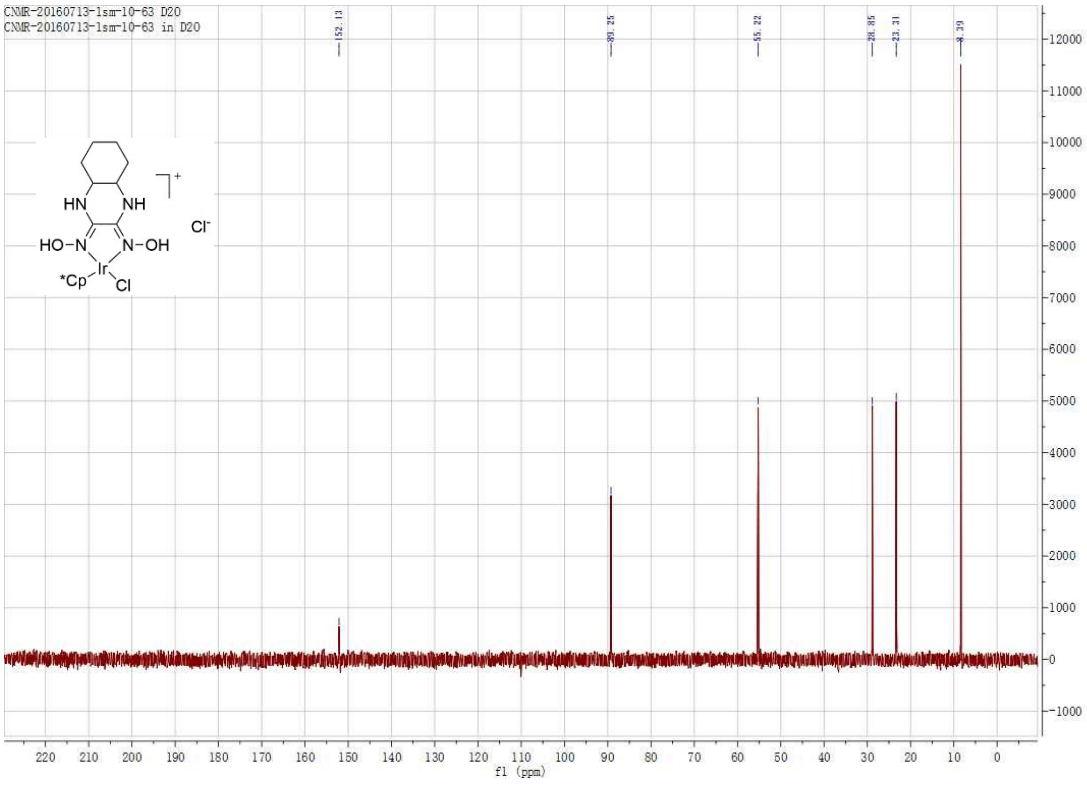
^{13}C NMR spectra of **Ir-L7** in D_2O, some solvent MeOH remained.



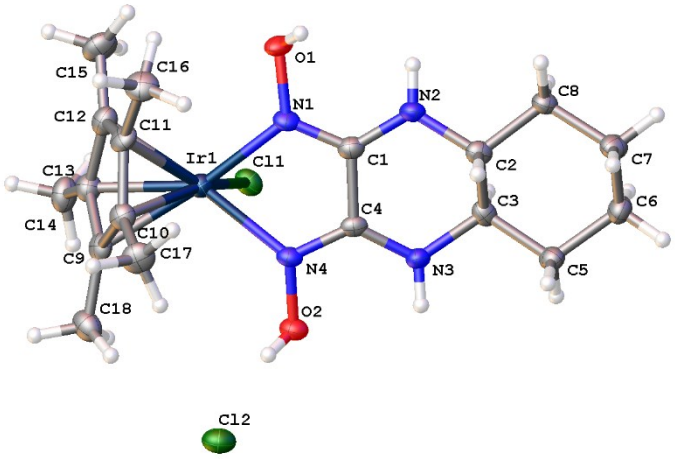
^{1}H NMR spectra of **Ir-L8** in D_2O.



^{13}C NMR spectra of **Ir-L8** in D_2O



Crystal structure of[Cp*Ir(L8)(Cl)][Cl]:



CCDC 1532094 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for mo_dm16457_0m.

Identification code	mo_dm16457_0m	
Empirical formula	C18 H29 Cl2 Ir N4 O2	
Formula weight	596.57	
Temperature	130 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1521(12) Å	□= 88.195(2)°.
	b = 9.6810(12) Å	□= 86.069(2)°.
	c = 11.7658(15) Å	□ = 89.089(2)°.
Volume	1039.4(2) Å^3	
Z	2	
Density (calculated)	1.906 Mg/m^3	
Absorption coefficient	6.701 mm^{-1}	
F(000)	584	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.736 to 27.531°.	
Index ranges	-9<=h<=11, -12<=k<=12, -15<=l<=15	
Reflections collected	8434	
Independent reflections	4763 [R(int) = 0.0325]	

Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5408
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4763 / 0 / 249
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0818
R indices (all data)	R1 = 0.0506, wR2 = 0.0883
Extinction coefficient	n/a
Largest diff. peak and hole	2.879 and -3.180 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_dm16457_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	6195(1)	7155(1)	7512(1)	20(1)
Cl(1)	6222(2)	9635(1)	7582(1)	24(1)
O(1)	9487(4)	7023(4)	6993(3)	26(1)
O(2)	4234(4)	8072(4)	5515(3)	25(1)
N(1)	8137(5)	7299(5)	6539(4)	21(1)
N(2)	9317(5)	7939(5)	4763(4)	23(1)
N(3)	6532(5)	8706(5)	4111(4)	21(1)
N(4)	5608(5)	7595(5)	5829(4)	20(1)
C(1)	8136(6)	7728(6)	5483(5)	22(1)
C(2)	9106(6)	8256(6)	3564(5)	22(1)
C(3)	7852(6)	9281(6)	3480(5)	23(1)
C(4)	6665(6)	8040(5)	5104(5)	19(1)
C(5)	7576(6)	9602(6)	2245(5)	24(1)
C(6)	8981(7)	10122(7)	1588(5)	28(1)
C(7)	10267(7)	9154(7)	1718(5)	27(1)
C(8)	10499(6)	8860(6)	2978(5)	22(1)
C(9)	4339(7)	6188(6)	8474(5)	23(1)
C(10)	5293(7)	5146(6)	7942(5)	24(1)
C(11)	6707(7)	5244(6)	8389(5)	25(1)
C(12)	6651(7)	6386(6)	9174(5)	26(1)
C(13)	5182(7)	6930(6)	9243(5)	25(1)
C(14)	4621(8)	8077(7)	9978(5)	32(1)
C(15)	7873(8)	6880(7)	9829(6)	35(2)
C(16)	8005(7)	4353(6)	8094(6)	33(1)
C(17)	4873(8)	4099(6)	7110(6)	33(1)
C(18)	2738(7)	6386(7)	8316(6)	33(1)
Cl(2)	1930(2)	5823(2)	5359(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for mo_dm16457_0m.

Ir(1)-Cl(1)	2.4054(14)
Ir(1)-N(1)	2.052(5)
Ir(1)-N(4)	2.116(5)
Ir(1)-C(9)	2.182(6)
Ir(1)-C(10)	2.157(5)
Ir(1)-C(11)	2.151(6)
Ir(1)-C(12)	2.135(6)
Ir(1)-C(13)	2.185(6)
O(1)-H(1)	0.8193
O(1)-N(1)	1.398(6)
O(2)-H(2)	0.8202
O(2)-N(4)	1.402(6)
N(1)-C(1)	1.297(7)
N(2)-H(2A)	0.8609
N(2)-C(1)	1.341(7)
N(2)-C(2)	1.459(7)
N(3)-H(3)	0.8604
N(3)-C(3)	1.481(7)
N(3)-C(4)	1.329(7)
N(4)-C(4)	1.313(7)
C(1)-C(4)	1.472(8)
C(2)-H(2B)	1.0000
C(2)-C(3)	1.511(8)
C(2)-C(8)	1.524(8)
C(3)-H(3A)	1.0000
C(3)-C(5)	1.513(8)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(5)-C(6)	1.538(8)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-C(7)	1.506(9)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(7)-C(8)	1.528(8)
C(8)-H(8A)	0.9900

C(8)-H(8B)	0.9900
C(9)-C(10)	1.452(8)
C(9)-C(13)	1.445(8)
C(9)-C(18)	1.498(9)
C(10)-C(11)	1.436(8)
C(10)-C(17)	1.503(8)
C(11)-C(12)	1.461(8)
C(11)-C(16)	1.485(9)
C(12)-C(13)	1.434(9)
C(12)-C(15)	1.495(8)
C(13)-C(14)	1.492(8)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800

N(1)-Ir(1)-Cl(1)	86.82(14)
N(1)-Ir(1)-N(4)	74.49(18)
N(1)-Ir(1)-C(9)	158.5(2)
N(1)-Ir(1)-C(10)	119.4(2)
N(1)-Ir(1)-C(11)	96.5(2)
N(1)-Ir(1)-C(12)	108.4(2)
N(1)-Ir(1)-C(13)	145.2(2)
N(4)-Ir(1)-Cl(1)	82.41(13)
N(4)-Ir(1)-C(9)	108.5(2)
N(4)-Ir(1)-C(10)	104.64(19)
N(4)-Ir(1)-C(11)	131.8(2)

N(4)-Ir(1)-C(12)	170.73(19)
N(4)-Ir(1)-C(13)	140.0(2)
C(9)-Ir(1)-Cl(1)	114.62(16)
C(9)-Ir(1)-C(13)	38.6(2)
C(10)-Ir(1)-Cl(1)	153.72(17)
C(10)-Ir(1)-C(9)	39.1(2)
C(10)-Ir(1)-C(13)	65.2(2)
C(11)-Ir(1)-Cl(1)	145.27(16)
C(11)-Ir(1)-C(9)	65.2(2)
C(11)-Ir(1)-C(10)	38.9(2)
C(11)-Ir(1)-C(13)	65.2(2)
C(12)-Ir(1)-Cl(1)	106.40(16)
C(12)-Ir(1)-C(9)	65.5(2)
C(12)-Ir(1)-C(10)	66.2(2)
C(12)-Ir(1)-C(11)	39.9(2)
C(12)-Ir(1)-C(13)	38.8(2)
C(13)-Ir(1)-Cl(1)	92.86(16)
N(1)-O(1)-H(1)	109.4
N(4)-O(2)-H(2)	109.5
O(1)-N(1)-Ir(1)	122.0(3)
C(1)-N(1)-Ir(1)	119.7(4)
C(1)-N(1)-O(1)	118.1(5)
C(1)-N(2)-H(2A)	120.5
C(1)-N(2)-C(2)	118.9(5)
C(2)-N(2)-H(2A)	120.6
C(3)-N(3)-H(3)	120.2
C(4)-N(3)-H(3)	120.4
C(4)-N(3)-C(3)	119.4(5)
O(2)-N(4)-Ir(1)	126.0(3)
C(4)-N(4)-Ir(1)	116.0(4)
C(4)-N(4)-O(2)	111.4(4)
N(1)-C(1)-N(2)	126.5(5)
N(1)-C(1)-C(4)	113.7(5)
N(2)-C(1)-C(4)	119.8(5)
N(2)-C(2)-H(2B)	109.2
N(2)-C(2)-C(3)	109.2(5)
N(2)-C(2)-C(8)	110.1(5)
C(3)-C(2)-H(2B)	109.2

C(3)-C(2)-C(8)	109.8(5)
C(8)-C(2)-H(2B)	109.2
N(3)-C(3)-C(2)	108.9(5)
N(3)-C(3)-H(3A)	108.7
N(3)-C(3)-C(5)	111.2(5)
C(2)-C(3)-H(3A)	108.7
C(2)-C(3)-C(5)	110.6(5)
C(5)-C(3)-H(3A)	108.7
N(3)-C(4)-C(1)	119.3(5)
N(4)-C(4)-N(3)	127.5(5)
N(4)-C(4)-C(1)	113.2(5)
C(3)-C(5)-H(5A)	109.6
C(3)-C(5)-H(5B)	109.6
C(3)-C(5)-C(6)	110.5(5)
H(5A)-C(5)-H(5B)	108.1
C(6)-C(5)-H(5A)	109.6
C(6)-C(5)-H(5B)	109.6
C(5)-C(6)-H(6A)	109.1
C(5)-C(6)-H(6B)	109.1
H(6A)-C(6)-H(6B)	107.8
C(7)-C(6)-C(5)	112.6(5)
C(7)-C(6)-H(6A)	109.1
C(7)-C(6)-H(6B)	109.1
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
C(6)-C(7)-C(8)	110.7(5)
H(7A)-C(7)-H(7B)	108.1
C(8)-C(7)-H(7A)	109.5
C(8)-C(7)-H(7B)	109.5
C(2)-C(8)-C(7)	109.3(5)
C(2)-C(8)-H(8A)	109.8
C(2)-C(8)-H(8B)	109.8
C(7)-C(8)-H(8A)	109.8
C(7)-C(8)-H(8B)	109.8
H(8A)-C(8)-H(8B)	108.3
C(10)-C(9)-Ir(1)	69.5(3)
C(10)-C(9)-C(18)	125.9(5)
C(13)-C(9)-Ir(1)	70.8(3)

C(13)-C(9)-C(10)	107.8(5)
C(13)-C(9)-C(18)	126.1(6)
C(18)-C(9)-Ir(1)	128.5(4)
C(9)-C(10)-Ir(1)	71.4(3)
C(9)-C(10)-C(17)	126.6(6)
C(11)-C(10)-Ir(1)	70.3(3)
C(11)-C(10)-C(9)	108.0(5)
C(11)-C(10)-C(17)	125.4(6)
C(17)-C(10)-Ir(1)	126.0(4)
C(10)-C(11)-Ir(1)	70.8(3)
C(10)-C(11)-C(12)	108.0(5)
C(10)-C(11)-C(16)	126.0(5)
C(12)-C(11)-Ir(1)	69.5(3)
C(12)-C(11)-C(16)	126.0(6)
C(16)-C(11)-Ir(1)	124.7(4)
C(11)-C(12)-Ir(1)	70.7(3)
C(11)-C(12)-C(15)	126.9(6)
C(13)-C(12)-Ir(1)	72.5(3)
C(13)-C(12)-C(11)	107.7(5)
C(13)-C(12)-C(15)	125.4(6)
C(15)-C(12)-Ir(1)	124.2(4)
C(9)-C(13)-Ir(1)	70.6(3)
C(9)-C(13)-C(14)	125.7(6)
C(12)-C(13)-Ir(1)	68.8(3)
C(12)-C(13)-C(9)	108.5(5)
C(12)-C(13)-C(14)	125.8(6)
C(14)-C(13)-Ir(1)	126.1(4)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
C(11)-C(16)-H(16A)	109.5
C(11)-C(16)-H(16B)	109.5
C(11)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(10)-C(17)-H(17A)	109.5
C(10)-C(17)-H(17B)	109.5
C(10)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(9)-C(18)-H(18A)	109.5
C(9)-C(18)-H(18B)	109.5
C(9)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_dm16457_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	22(1)	16(1)	21(1)	-3(1)	-2(1)	1(1)
Cl(1)	24(1)	17(1)	32(1)	-4(1)	2(1)	-2(1)
O(1)	18(2)	34(2)	25(2)	-1(2)	-6(2)	7(2)
O(2)	18(2)	27(2)	31(2)	-1(2)	-3(2)	2(2)
N(1)	15(2)	21(2)	27(2)	-3(2)	-2(2)	5(2)
N(2)	16(2)	27(2)	26(2)	0(2)	-5(2)	-1(2)
N(3)	18(2)	26(2)	21(2)	1(2)	-4(2)	0(2)
N(4)	15(2)	19(2)	26(2)	-2(2)	-3(2)	2(2)
C(1)	21(3)	19(3)	26(3)	-3(2)	-5(2)	2(2)
C(2)	21(3)	21(3)	23(3)	-6(2)	-2(2)	0(2)
C(3)	23(3)	21(3)	24(3)	-5(2)	1(2)	-3(2)
C(4)	20(3)	15(2)	24(3)	-6(2)	-6(2)	1(2)
C(5)	22(3)	22(3)	27(3)	3(2)	-4(2)	0(2)
C(6)	30(4)	30(3)	24(3)	4(2)	-2(2)	1(3)
C(7)	22(3)	31(3)	28(3)	-3(2)	0(2)	4(2)
C(8)	17(3)	25(3)	25(3)	-2(2)	-1(2)	0(2)
C(9)	30(3)	15(3)	25(3)	4(2)	-1(2)	0(2)
C(10)	28(3)	15(3)	28(3)	-1(2)	-2(2)	-1(2)
C(11)	30(3)	17(3)	27(3)	4(2)	-7(2)	3(2)
C(12)	34(4)	20(3)	24(3)	-1(2)	-3(2)	-2(2)
C(13)	30(3)	21(3)	24(3)	-1(2)	1(2)	3(2)
C(14)	46(4)	25(3)	26(3)	-1(2)	3(3)	1(3)
C(15)	43(4)	29(3)	34(3)	-7(3)	-15(3)	-2(3)
C(16)	34(4)	21(3)	44(4)	-4(3)	-4(3)	8(3)
C(17)	40(4)	21(3)	38(3)	-8(3)	-7(3)	-3(3)
C(18)	30(4)	24(3)	43(4)	4(3)	3(3)	-1(3)
Cl(2)	24(1)	30(1)	40(1)	-5(1)	-6(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_dm16457_0m.

	x	y	z	U(eq)
H(1)	9996	6547	6554	31
H(2)	3652	7434	5574	30
H(2A)	10184	7889	5004	27
H(3)	5688	8802	3836	26
H(2B)	8863	7388	3182	26
H(3A)	8116	10155	3842	27
H(5A)	6794	10317	2203	28
H(5B)	7240	8760	1891	28
H(6A)	8803	10234	769	33
H(6B)	9221	11040	1866	33
H(7A)	11160	9572	1339	32
H(7B)	10092	8276	1344	32
H(8A)	11325	8199	3051	27
H(8B)	10741	9726	3344	27
H(14A)	5359	8801	9969	49
H(14B)	4418	7721	10761	49
H(14C)	3718	8463	9688	49
H(15A)	8812	6562	9470	52
H(15B)	7760	6508	10614	52
H(15C)	7850	7892	9833	52
H(16A)	8083	4210	7271	49
H(16B)	7898	3459	8502	49
H(16C)	8891	4803	8313	49
H(17A)	4132	4503	6631	49
H(17B)	4473	3283	7527	49
H(17C)	5740	3829	6628	49
H(18A)	2506	7376	8252	50
H(18B)	2167	5974	8972	50
H(18C)	2493	5937	7620	50

Table 6. Torsion angles [°] for mo_dm16457_0m.

Ir(1)-N(1)-C(1)-N(2)	176.5(4)
Ir(1)-N(1)-C(1)-C(4)	-1.3(6)
Ir(1)-N(4)-C(4)-N(3)	-161.5(4)
Ir(1)-N(4)-C(4)-C(1)	18.8(6)
Ir(1)-C(9)-C(10)-C(11)	61.1(4)
Ir(1)-C(9)-C(10)-C(17)	-121.5(6)
Ir(1)-C(9)-C(13)-C(12)	-58.5(4)
Ir(1)-C(9)-C(13)-C(14)	121.0(6)
Ir(1)-C(10)-C(11)-C(12)	59.8(4)
Ir(1)-C(10)-C(11)-C(16)	-119.4(6)
Ir(1)-C(11)-C(12)-C(13)	63.5(4)
Ir(1)-C(11)-C(12)-C(15)	-118.7(6)
Ir(1)-C(12)-C(13)-C(9)	59.6(4)
Ir(1)-C(12)-C(13)-C(14)	-119.9(6)
O(1)-N(1)-C(1)-N(2)	0.1(8)
O(1)-N(1)-C(1)-C(4)	-177.7(4)
O(2)-N(4)-C(4)-N(3)	-8.3(7)
O(2)-N(4)-C(4)-C(1)	172.0(4)
N(1)-C(1)-C(4)-N(3)	168.6(5)
N(1)-C(1)-C(4)-N(4)	-11.7(7)
N(2)-C(1)-C(4)-N(3)	-9.3(8)
N(2)-C(1)-C(4)-N(4)	170.4(5)
N(2)-C(2)-C(3)-N(3)	-56.0(6)
N(2)-C(2)-C(3)-C(5)	-178.4(4)
N(2)-C(2)-C(8)-C(7)	178.7(5)
N(3)-C(3)-C(5)-C(6)	-176.8(5)
C(1)-N(2)-C(2)-C(3)	43.0(7)
C(1)-N(2)-C(2)-C(8)	163.6(5)
C(2)-N(2)-C(1)-N(1)	172.3(5)
C(2)-N(2)-C(1)-C(4)	-10.1(8)
C(2)-C(3)-C(5)-C(6)	-55.8(6)
C(3)-N(3)-C(4)-N(4)	172.2(5)
C(3)-N(3)-C(4)-C(1)	-8.1(7)
C(3)-C(2)-C(8)-C(7)	-61.0(6)
C(3)-C(5)-C(6)-C(7)	53.0(7)
C(4)-N(3)-C(3)-C(2)	40.7(6)

C(4)-N(3)-C(3)-C(5)	162.8(5)
C(5)-C(6)-C(7)-C(8)	-54.1(7)
C(6)-C(7)-C(8)-C(2)	57.6(6)
C(8)-C(2)-C(3)-N(3)	-176.8(4)
C(8)-C(2)-C(3)-C(5)	60.8(6)
C(9)-C(10)-C(11)-Ir(1)	-61.8(4)
C(9)-C(10)-C(11)-C(12)	-2.0(6)
C(9)-C(10)-C(11)-C(16)	178.8(6)
C(10)-C(9)-C(13)-Ir(1)	59.9(4)
C(10)-C(9)-C(13)-C(12)	1.4(6)
C(10)-C(9)-C(13)-C(14)	-179.1(5)
C(10)-C(11)-C(12)-Ir(1)	-60.6(4)
C(10)-C(11)-C(12)-C(13)	2.9(6)
C(10)-C(11)-C(12)-C(15)	-179.3(6)
C(11)-C(12)-C(13)-Ir(1)	-62.3(4)
C(11)-C(12)-C(13)-C(9)	-2.7(6)
C(11)-C(12)-C(13)-C(14)	177.8(5)
C(13)-C(9)-C(10)-Ir(1)	-60.7(4)
C(13)-C(9)-C(10)-C(11)	0.4(6)
C(13)-C(9)-C(10)-C(17)	177.8(6)
C(15)-C(12)-C(13)-Ir(1)	119.9(6)
C(15)-C(12)-C(13)-C(9)	179.5(6)
C(15)-C(12)-C(13)-C(14)	0.0(10)
C(16)-C(11)-C(12)-Ir(1)	118.6(6)
C(16)-C(11)-C(12)-C(13)	-177.9(6)
C(16)-C(11)-C(12)-C(15)	-0.1(10)
C(17)-C(10)-C(11)-Ir(1)	120.7(6)
C(17)-C(10)-C(11)-C(12)	-179.5(5)
C(17)-C(10)-C(11)-C(16)	1.3(10)
C(18)-C(9)-C(10)-Ir(1)	123.4(6)
C(18)-C(9)-C(10)-C(11)	-175.5(5)
C(18)-C(9)-C(10)-C(17)	2.0(9)
C(18)-C(9)-C(13)-Ir(1)	-124.2(6)
C(18)-C(9)-C(13)-C(12)	177.3(5)
C(18)-C(9)-C(13)-C(14)	-3.2(9)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_dm16457_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)