A Visible-Light-Driven Transfer Hydrogenation on CdS Nanoparticles Combined with Iridium Complexes

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Supplementary Information

Experimental Section

General: $[(Cp^*IrCl_2)_2]$ and $[Cp^*RhCl_2)_2]$ were obtained from Sigma-Aldrich company. Dihydroxy-2,2'-bipyridine was synthesized according to literature[1]. CdS was prepared as reported previously[2]. Complex $[Cp^*Rh(bipy)(H_2O)]^{2+3}$ and iridium complex **1-4** [4]were synthesized according to literature. The solution pH value was adjusted by dilute aqueous H_2SO_4 or NaOH. All other reagents were used without purification as commercially available.

Typical procedure for the photocatalytic reduction of cyclohexanone: 20 μL aqueous solution of complex **1** (2 μmol) and CdS powder (10 mg) were introduced in 5 mL degassed aqueous solution (containing 1 mL lactic acid). After ultrasonic pretreatment for 5 min, cyclohexanone (0.2 mL, 2 mmol) was added to the resulting solution. The reaction solution was irradiated with Xe lamp equipped with a cut-off filter ($\lambda > 400$ nm). After reaction, the products were extracted by ethyl acetate, and analyzed by an Agilent 6890N GC equipped with HP 19091G-B213 (30 m × 0.32 mm × 0.25 μm) column. The experiments involving H_2 evolution were carried out in a Pyrex reaction cell (250 mL) connected to a closed gas circulation and evacuation system. The amount of H_2 produced was analyzed using an online gas chromatography.

Electrochemical analysis: CdS/FTO was prepared according to the literature method[5]. A three-electrode system was used to obtain linear voltammetry; CdS/FTO (working,

1.0 cm×1.5 cm), Ag/AgCl (reference, 0.197 V versus normal hydrogen electrode), and a platinum wire (counter) were connected to a multichannel potentiostat/galvanostat (CHI760C, Shanghai Chenhua Co., China) with a 50 mVs^{-1} scan rate.

Table S1: Examination of the reduction of cyclohexanone under different conditions[a]

Catalyst	Irradiation[b] (λ > 400 nm)	T (^{o} C)	TON for cyclohexanone
1	No	40	-
1	Yes	40	-
CdS	Yes	40	-
Ir/CdS[c]	Yes	40	-
H_2IrCl_6/CdS	Yes	40	-
1/CdS	No	40	-
1/CdS	Yes	40	100
1/CdS	Yes	20	40

[a] Reactions conditions: 10 mg CdS, 2μmol complex **1**, substrate/**1** = 1000, 5 mL H_2O water (containing 1 mL lactic acid) under Ar. Reaction is 1 h. [b] Xe lamp. [c]Loading with 0.4 wt % iridium

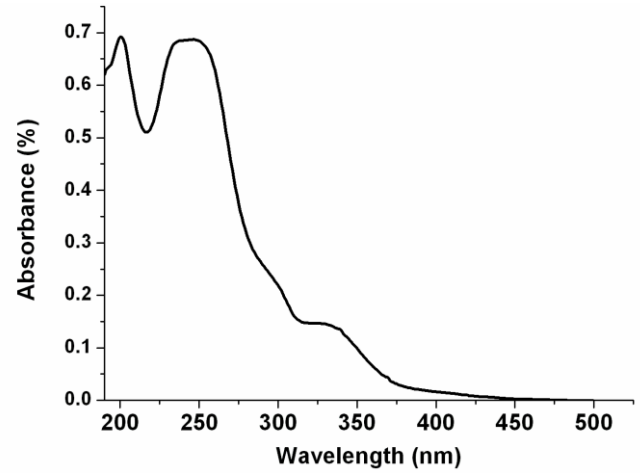

Fig. S1 The UV-vis spectra of complex **1**

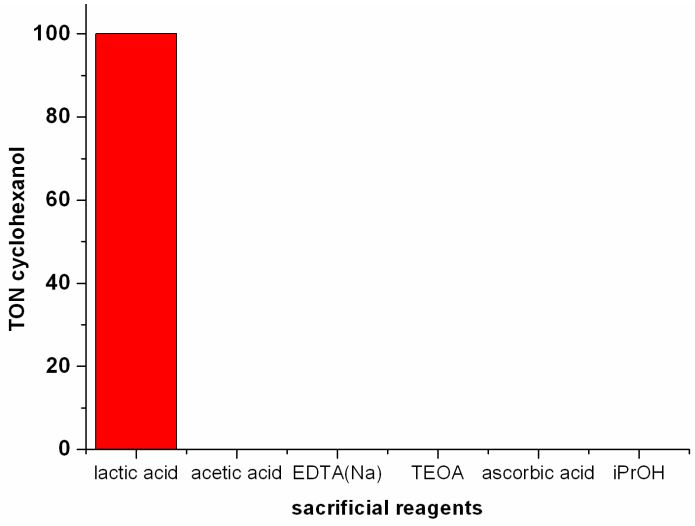

Fig. S2 Screen of different sacrificial reagents for coupling system of CdS and complex **1** under visible light irradiation. See Table S1 for conditions

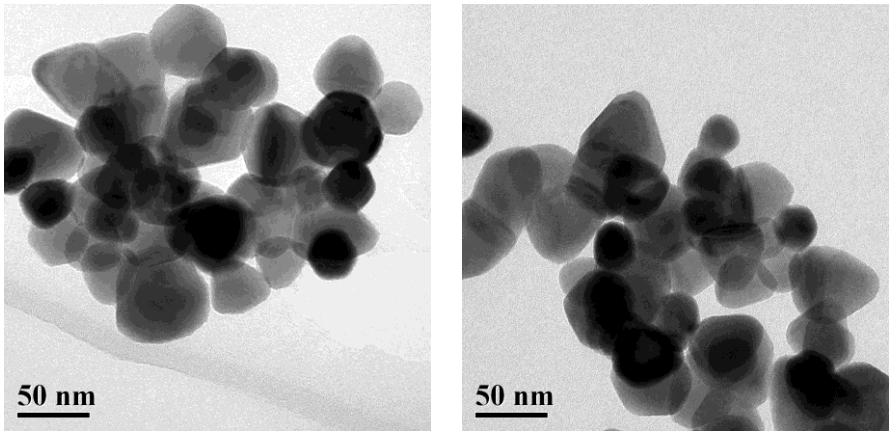

Fig. S3 TEM image of CdS powder before reaction (left) and after reaction (right)

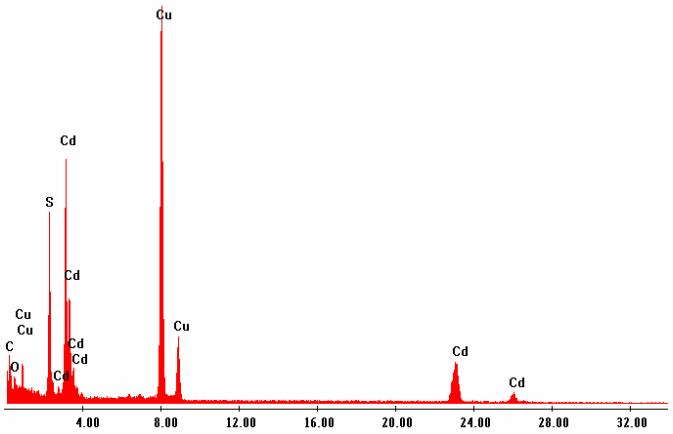

Fig. S4 The EDX analysis of used CdS sample

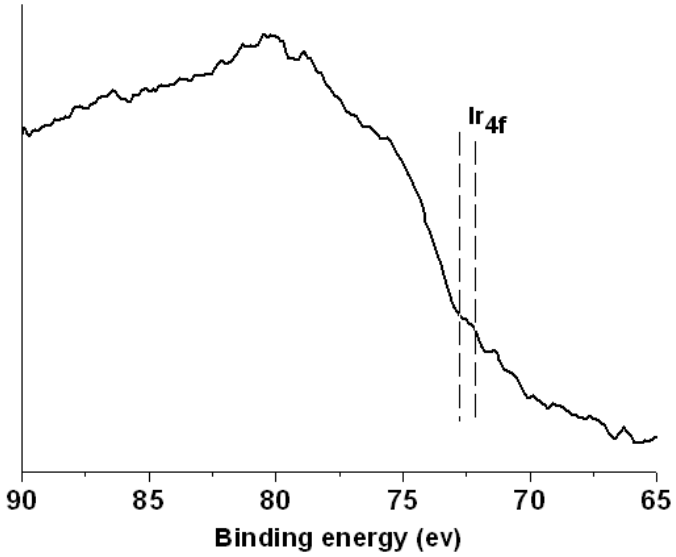

Fig. S5 The XPS analysis of used CdS sample

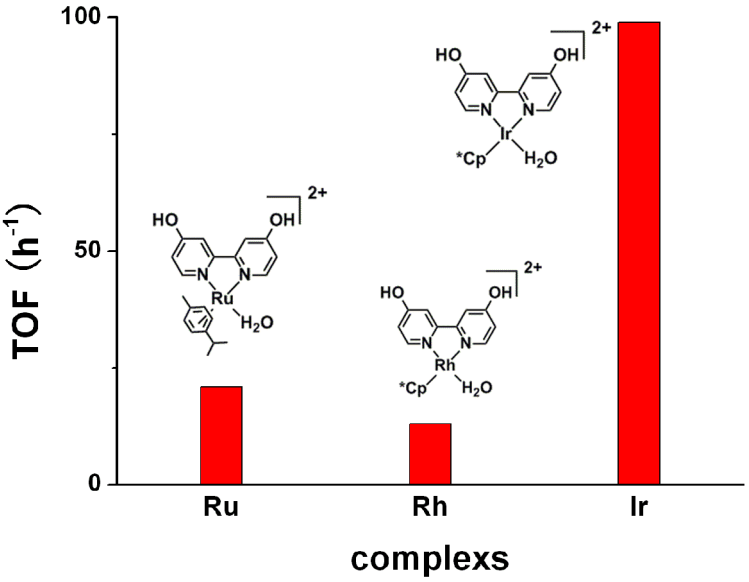

Fig. S6 Comparison of activities ruthenium, rhodium and iridium complexes coupling with CdS under visible light irradiation. See Table S1 for conditions.

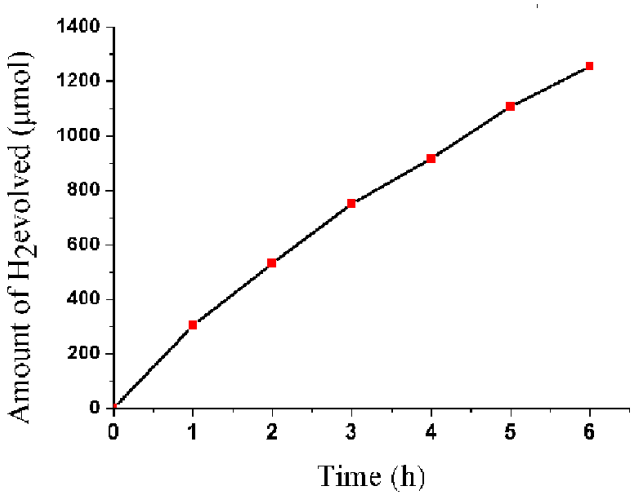

Fig. S7 The evolution of H_2 as a function of time under the visible light irradiation ($\lambda > 400$ nm). Conditions: 10 μ mol complex **1** and 100 mg CdS in 100 mL H_2O (containing 10 mL lactic acid).

Table S2. Comparison of H_2 and cyclohexanol generated with different conditions[a]

Catalyst	Substrate	TON	
		H_2	cyclohexanol
Complex **1** + CdS	--	681	--
Complex **1** + CdS	cyclohexanone	<10	361

[a] Reaction were performed in 100 mL H_2O (containing 10 mL lactic acid) at 40 ^oC in 6 h. CdS is 100 mg and complex **1** is 10 μ mol.

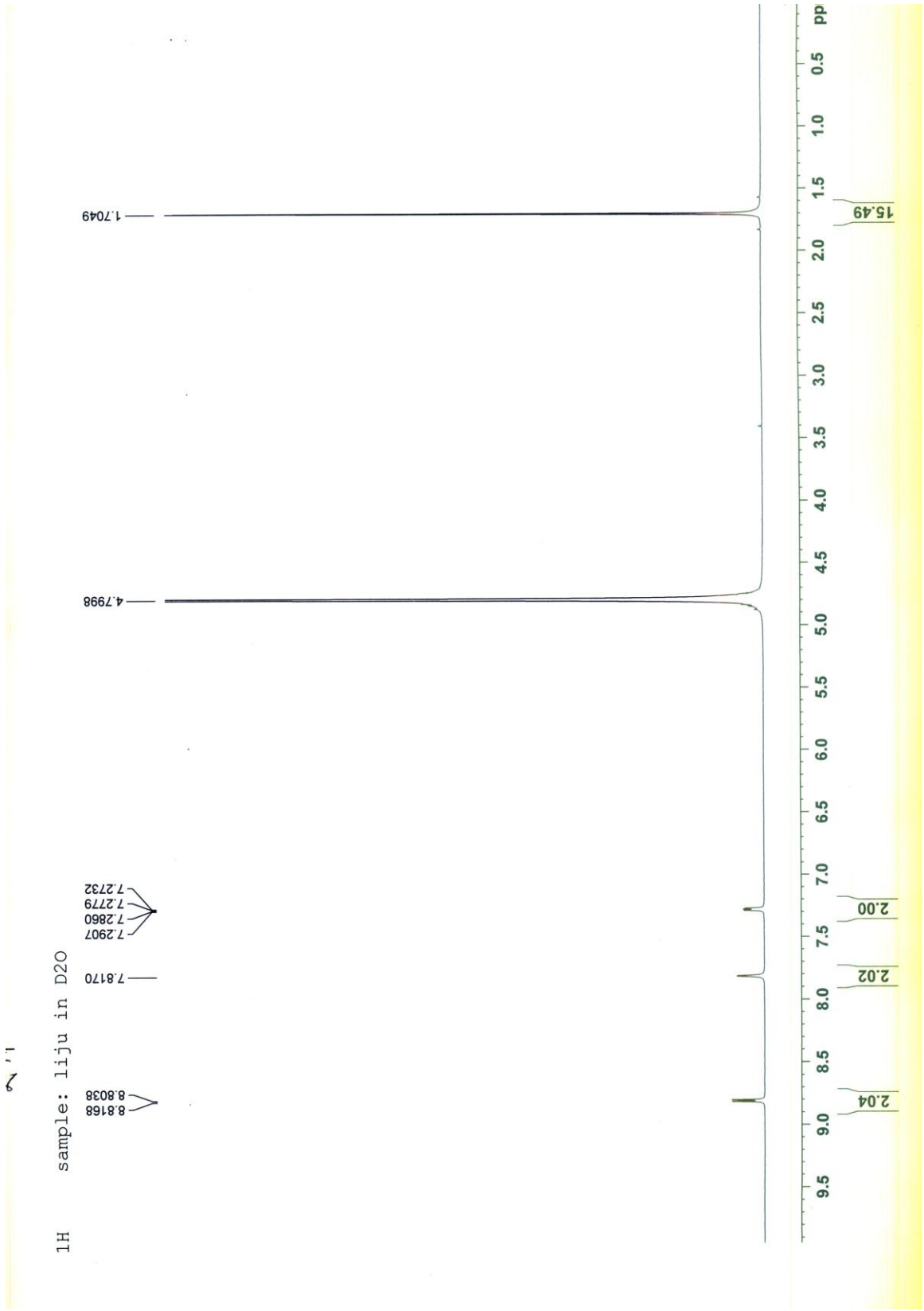

Fig. S8 The ^{1}H NMR of complex **1**

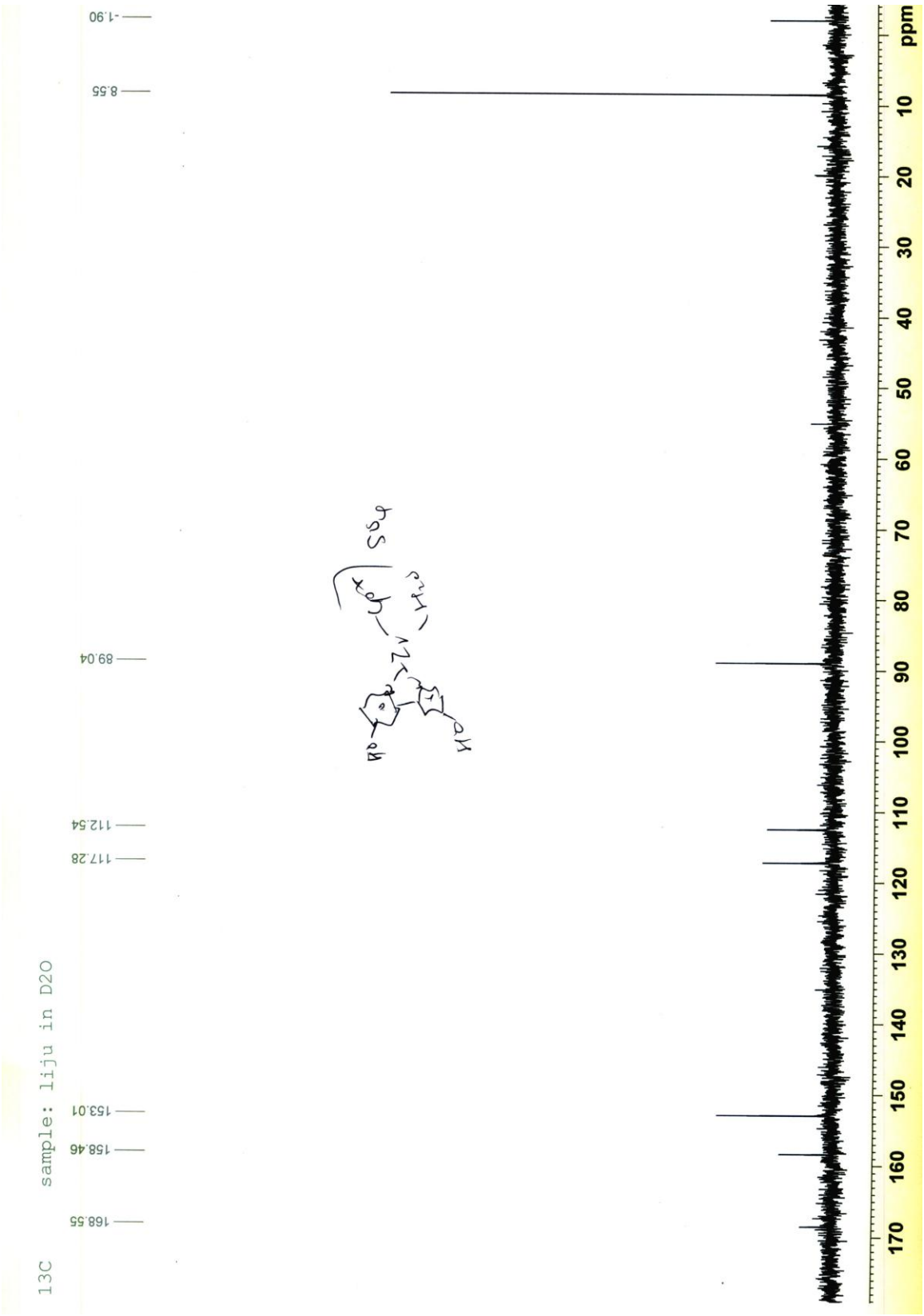

Fig. S9 The ^{13}C NMR of complex **1**

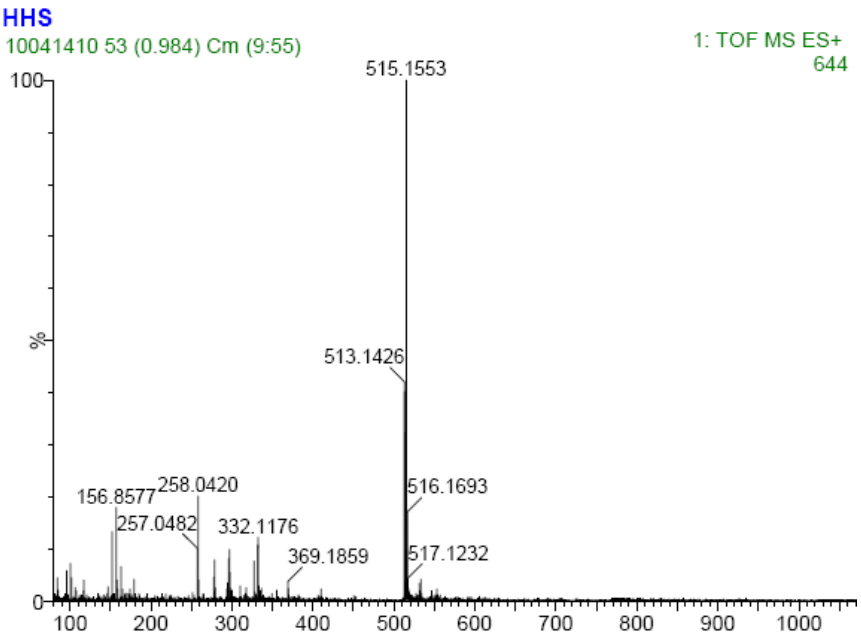

Fig. S10 The HRMS of iridium complex **1**

References

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3. F. Hollmann, B. Witholt and A. Schmid, *J. Mol. Catal., B: Enzym*, 2002, **19**, 167-176.

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