Supporting information

1. General

All materials were purchased from commercial suppliers and used without any purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on the Bruker 400M spectrometers using tetramethylsilane as an internal standard. ESI-MS was performed using Bruker ultrafleXtreme MALDI TOF/TOF. pH values were measured on OHAUS ST3100 pH meter with a glass electrode after calibration with standard buffer solutions. GC analysis results were obtained with agilent 7890B equipped with a TCD and a FID.

2. Synthesis and characterization of the ligands and catalysts

$[Cp^*Ir(H_2O)_3]SO_4$ was synthesized according to the procedure reported.[1] $[Cp^*IrCl_2]_2$ (405.6 mg, 0.509 mmol) and Ag_2SO_4 (314.5 mg, 1.009 mmol) was mixed in 50 mL deionized water in a bottle under N_2 atmosphere. The solution was stirred at 40 °C for 9 h. Afterwards, the insoluble compounds was filtered. The yellow solid (449.9 mg, 93%) was obtained after removal of the solvent.

***N*-(Methylsulfonyl)-2-pyridinecarboxamide (L1)** was synthesized according to the procedure reported by Cohen et al.[2] Picolinic acid (0.31 g, 2.5 mmol) was dissolved in CH_2Cl_2 (50 mL). Then methanesulfonamide (0.24 g, 2.5 mmol), 4-(dimethylamino)pyridine (0.31 g, 2.5 mmol) and *N*,*N*- dicyclohexylcarbodiimide (0.52 g, 2.5 mmol) were added. The solution was stirred for 18 h at ambient temperature. The formed insoluble solid was filtered and the filtrate was washed with saturated sodium bicarbonate solution. The aqueous layer was washed with ether (2× 20 mL). The pH of the solution was adjusted to 1.0 with 6 M HCl. Then the solution was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$. The product was obtained as a white solid. Yield: 0.13 g (0.7 mmol, 26 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.71 (s, 1H), 8.72 (dt, J = 4.8, 1.3 Hz, 1H), 8.13 – 8.04 (m, 2H), 7.73 (ddd, J = 6.9, 4.7, 2.3 Hz, 1H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.61, 149.31, 148.35, 138.81, 128.63, 123.66, 41.60. ESI-MS calculated for $[C_7H_7N_2O_3S]^-$ 199.02, found m/z 199.02 $[M-H]^-$.

***N*-(Phenylsulfonyl)-2-pyridinecarboxamide (L2)** was synthesized according to the

procedure described for **L1** using benzenesulfonamide (0.39 g, 2.5 mmol) instead of methanesulfonamide. The product was a white solid 0.13 g (0.5 mmol, 21 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.41 (s, 1H), 8.71 (d, J = 4.8 Hz, 1H), 8.12 – 8.00 (m, 3H), 7.97 (d, J = 7.7 Hz, 1H), 7.79 – 7.69 (m, 1H), 7.70 (d, J = 5.0 Hz, 1H), 7.67 – 7.53 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.89, 149.12, 148.28, 139.92, 138.98, 134.18, 132.25, 129.55, 129.40, 128.63, 128.17, 126.04, 123.76. ESI-MS calculated for $[C_{12}H_{11}N_2O_3S]^+$ 263.04, found m/z 263.04 $[M+H]^+$.

***N*-(2-Pyridinylmethyl)benzamide (L3)** was synthesized according to the procedure reported by Gooben et al.[3] 2-(aminomethyl)-pyridine (10.0 mmol, 1.04 mL) and triethylamine (4.15 g, 39.0 mmol) were dissolved in 50 mL CH_2Cl_2 . Benzoyl chloride (11.0 mmol, 1.29 mL) was added to the mixture. The reaction mixture was stirred overnight. Then the mixture was washed by aqueous 1 N HCl (20 mL), a saturated aqueous solution of sodium bicarbonate (30 mL) and brine (50 mL). The mixture was dried over $MgSO_4$ and the solvent was removed in vacuo. The crude residue was purified by flash column chromatography (SiO_2, ethyl acetate: hexane =1:1). The product was obtained as a colorless solid 1.06 g (5.0 mmol, 50%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (ddd, J = 5.0, 1.8, 1.0 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.73 – 7.63 (m, 2H), 7.54 – 7.46 (m, 1H), 7.48 – 7.39 (m, 2H), 7.32 (dt, J = 7.9, 1.0 Hz, 1H), 7.21 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 4.75 (d, J = 4.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.43, 156.32, 149.02, 136.86, 134.39, 131.50, 128.55, 127.12, 122.45, 122.22, 44.77. ESI-MS calculated for $[C_{13}H_{13}N_2O]^+$ 213.10, found m/z 213.10 $[M+H]^+$.

***N*-Phenylpicolinamide (L4)** was purchased from Pide pharmce. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.64 (s, 1H), 8.76 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H), 8.19 (dt, J = 7.8, 1.1 Hz, 1H), 8.08 (td, J = 7.7, 1.7 Hz, 1H), 8.00 – 7.89 (m, 2H), 7.69 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.14 (tt, J = 7.4, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.45, 149.90, 148.39, 138.36, 138.10, 128.68, 126.88, 123.92, 122.37, 120.25. ESI-MS(+) calculated for $[C_{12}H_{11}N_2O]^+$ 199.08, found 199.09.

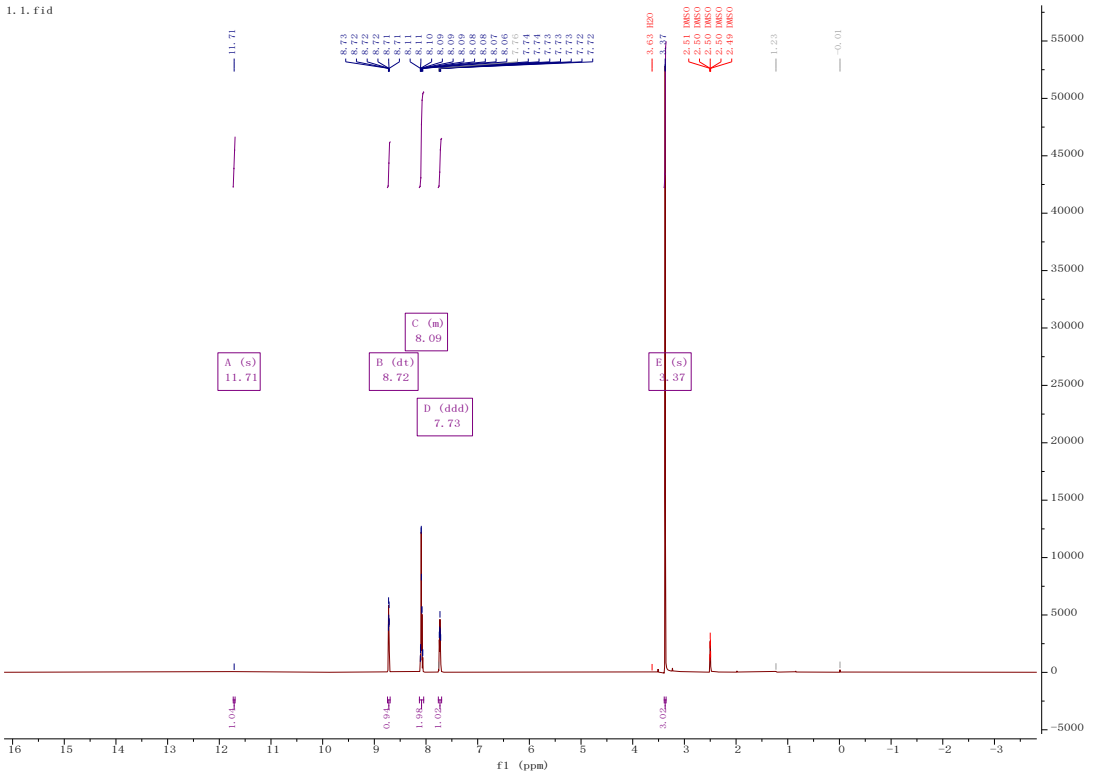

Figure S1 ^{1}H NMR spectra of **L1**

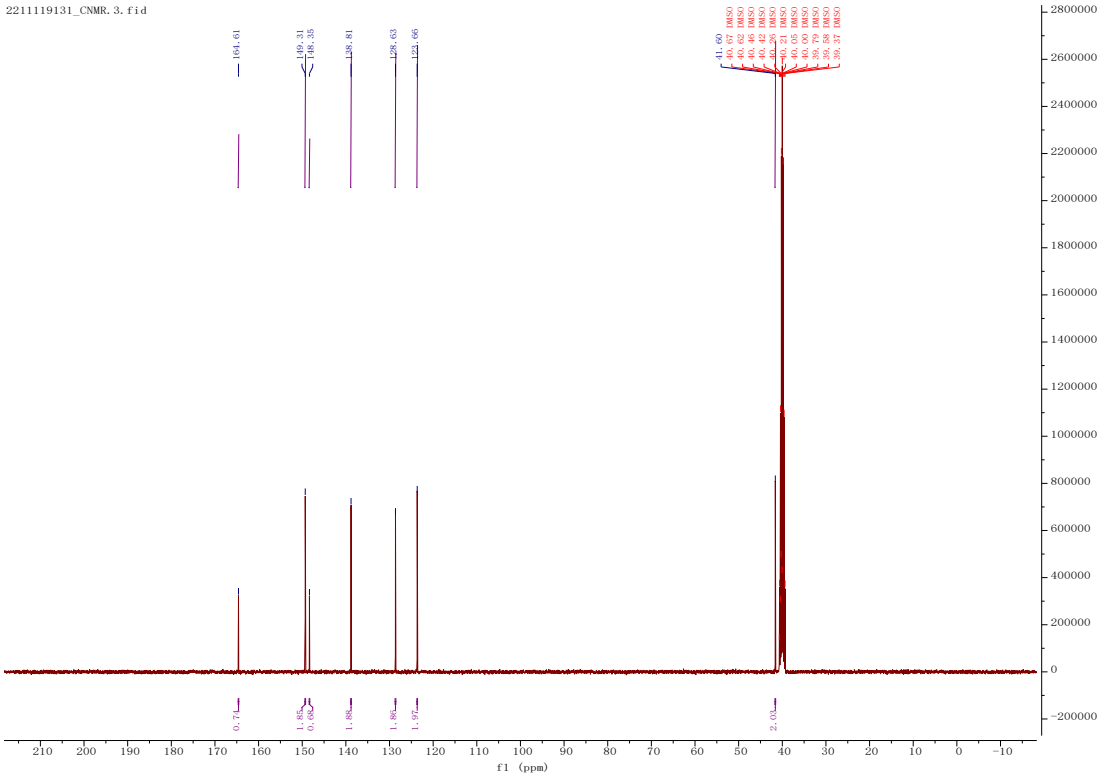

Figure S2 ^{13}C NMR spectra of **L1**

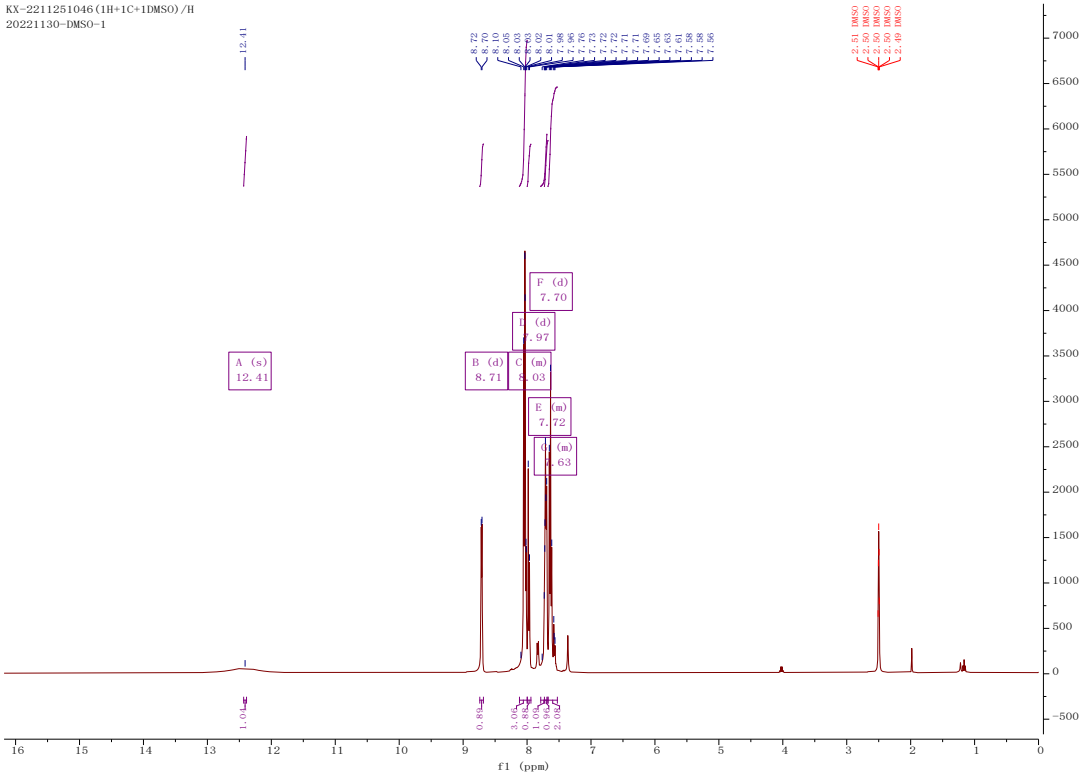

Figure S3 ^{1}H NMR spectra of **L2**

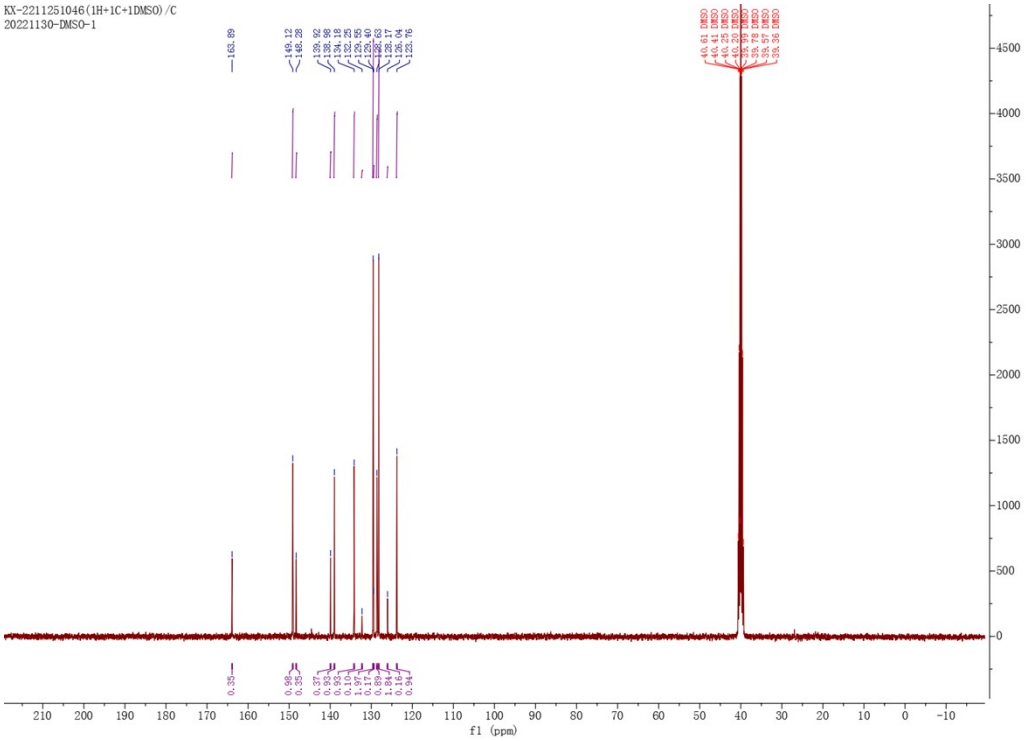

Figure S4 ^{13}C NMR spectra of **L2**

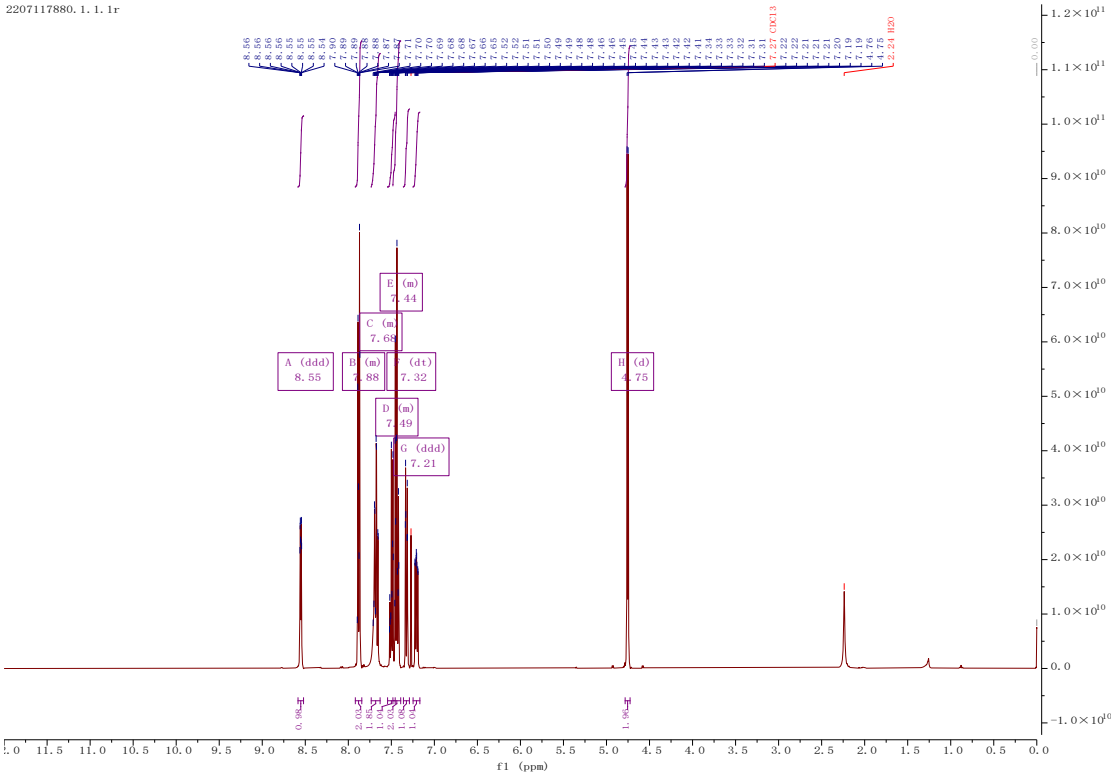

Figure S5 ^{1}H NMR spectra of **L3**

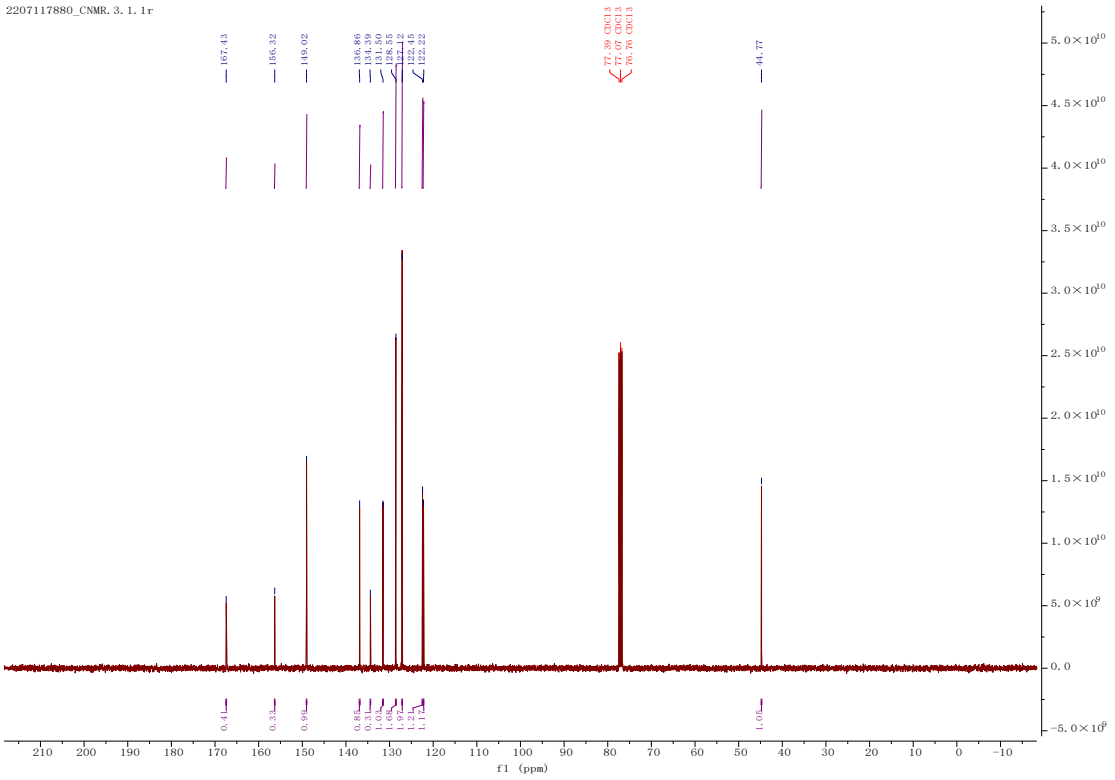

Figure S6 ^{13}C NMR spectra of **L3**

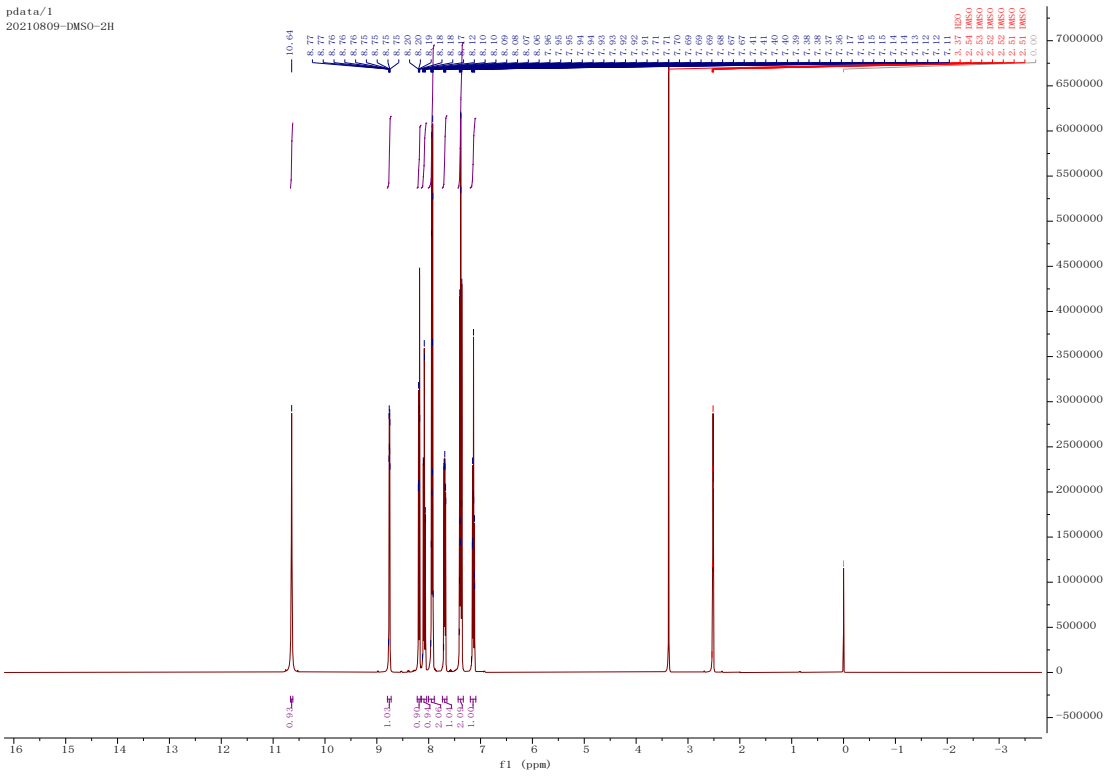

Figure S 7 ^{1}H NMR spectra of **L4**

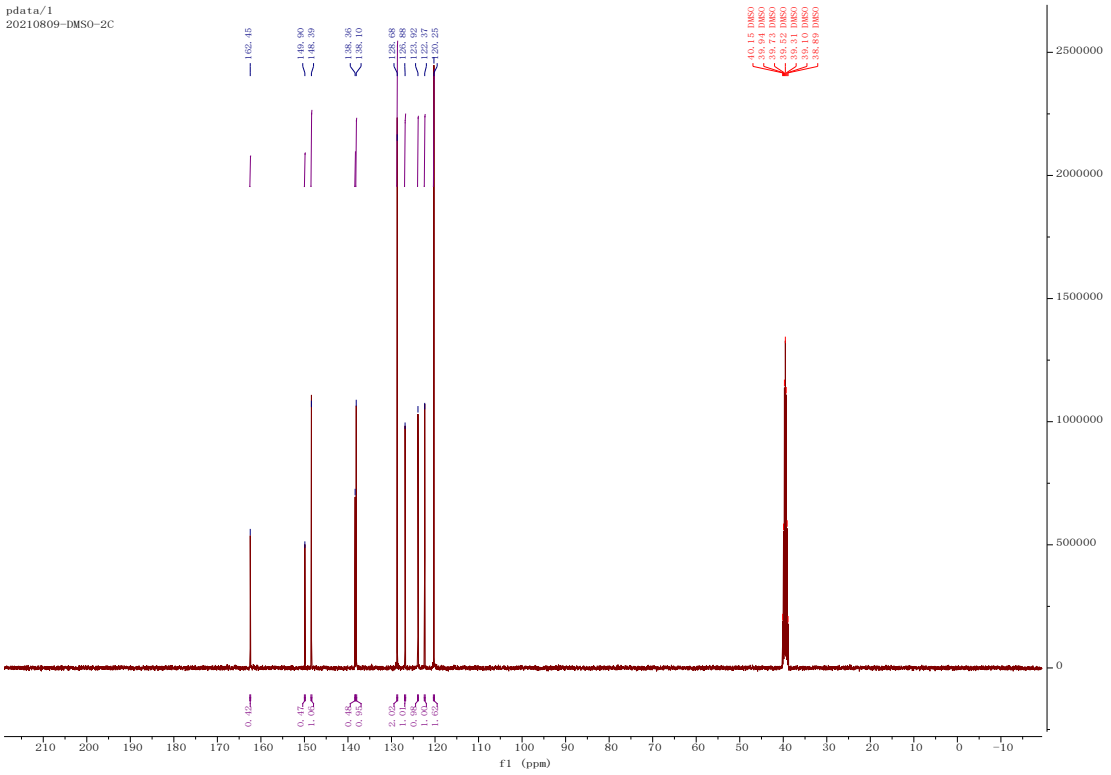

Figure S 8 ^{13}C NMR spectra of **L4**

In-situ catalysts solution used in "catalyst screening" were in-situ synthesized by stirring $[Cp^*Ir(H_2o)_3]SO_4$ and equivalent corresponding ligands (**L1**-**L3** and **L4**) in water in the air overnight.

Preparation of **C1** complex. **L1** (120 mg, 0.60 mmol) and $[Cp^*Ir(H_2O)_3]SO_4$ (287 mg, 0.60 mmol) was mixed in 30 mL deionized water. The resulting mixture was stirred overnight. Afterwards the water was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/MeOH/ether to generated pale yellow power as the product. Yield: 239 mg (62%). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 8.95 (d, J = 5.6 Hz, 1H), 8.45 (t, J = 7.7 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.06 (t, J = 6.6 Hz, 1H), 3.42 (s, 3H), 1.67 (s, 15H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ 169.90, 152.92, 151.34, 142.20, 131.77, 128.19, 96.05, 41.93, 8.76. IR (KBr pellet, cm^{-1}): 3441(m), 2966(w), 2915(w), 1645(s), 1604(m), 1315(s), 1288(m), 1189(m), 1144(s), 1034(w), 920(m), 831(w), 762(w), 542(m), 523(w). Elemental analysis calcd (%) for $C_{17}H_{25}IrN_2O_8S_2$: C 31.82, H 3.93, N 4.37; found C 31.59, H 4.07, N 4.20. ESI-MS calculated for $[C_{17}H_{22}IrN_2O_3S]^+$ 527.098, found m/z 527.0972 $[M\text{-}HSO_4\text{-}H_2O]^+$.

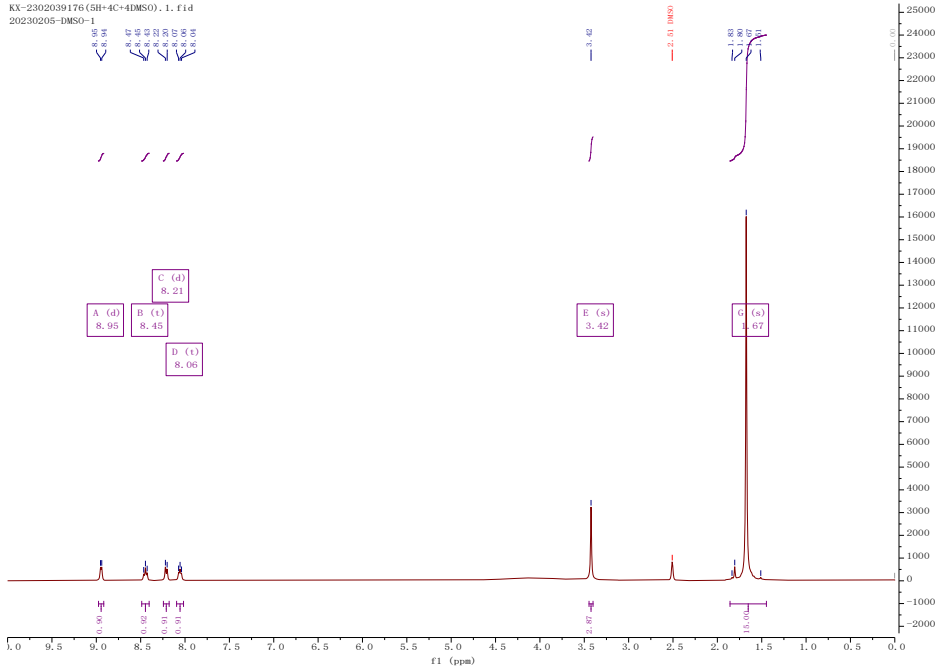

Figure S9 ^{1}H NMR spectra of **C1**

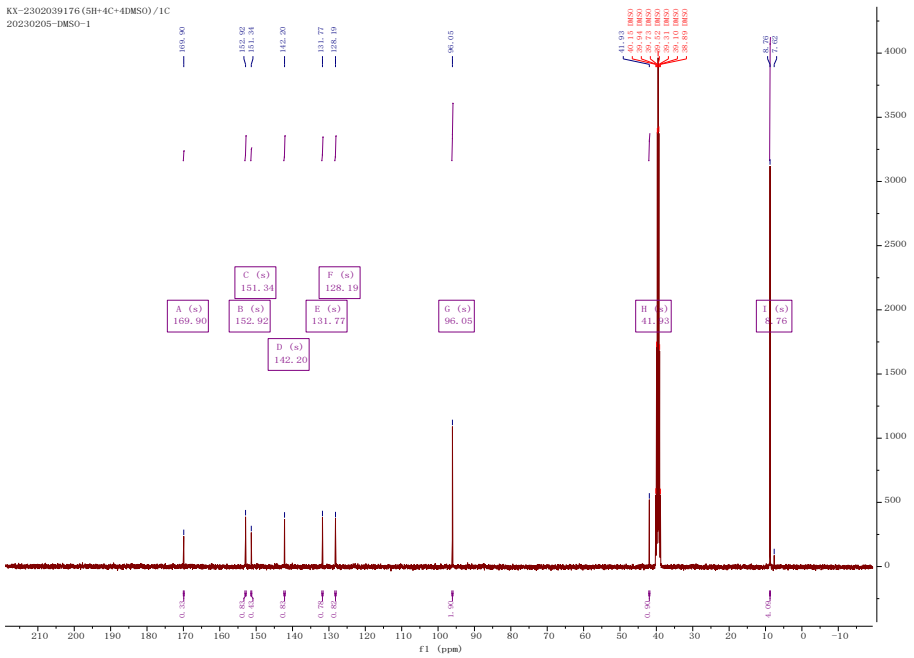

Figure S10 ^{13}C NMR spectra of **C1**

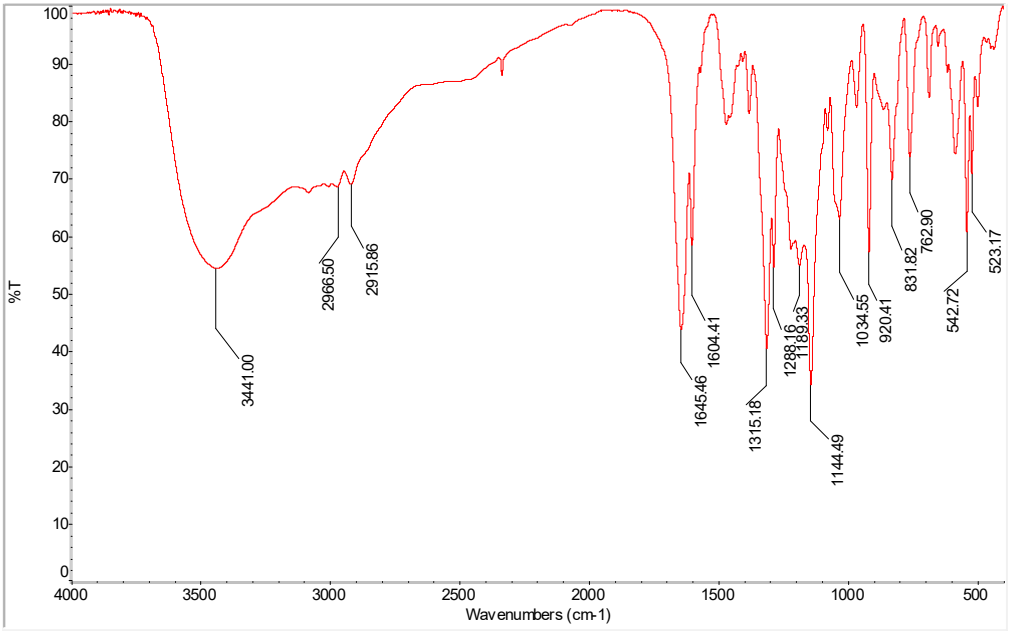

Figure S 11 IR spectra of **C1**

Preparation of **C2** complex. **L2** (157 mg, 0.60 mmol) and [Cp*Ir(H_2O)$_3$]SO_4 (287 mg, 0.60 mmol) was mixed in 30 mL MeOH. The resulting mixture was stirred overnight. Afterwards the solvent was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2 to generated pale yellow power as the product. Yield: 240 mg (57%). ^{1}H NMR (400 MHz, Methanol-d_4) δ 9.10 (d, J = 5.5 Hz, 1H), 8.23 (td, J = 7.8, 1.4 Hz, 1H), 8.01 – 7.90 (m, 4H), 7.61 – 7.44 (m, 3H), 1.72 (s, 15H). ^{13}C NMR

(101 MHz, Methanol-d_4) δ 152.17, 141.21, 140.69, 132.38, 130.54, 128.26, 127.97, 126.49, 125.69, 88.48, 8.33. IR (KBr pellet, cm^{-1}): 3423(m), 2963(m), 2923(m), 1655(m), 1604(w), 1447(w), 1384(w), 1320(m), 1280(m), 1261(m), 1152(s), 1085(m), 1030(m), 923(w), 834(m), 804(m), 760(w), 720(w), 688(w). Elemental analysis calcd (%) for $C_{22}H_{27}IrN_2O_8S_2$: C 37.54, H 3.87, N 3.98; found C 37.40, H 3.96, N 3.89. ESI-MS calculated for $[C_{22}H_{24}IrN_2O_3S]^+$ 589.114, found m/z 589.1146 $[M\text{-}HSO_4\text{-}H_2O]^+$.

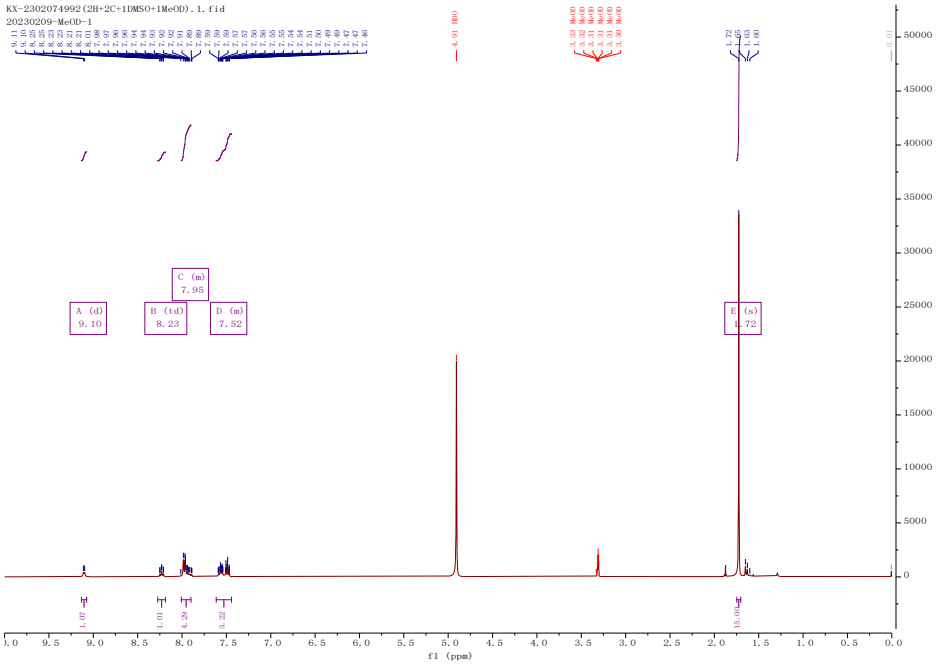

Figure S 12 ^{1}H NMR spectra of **C2**

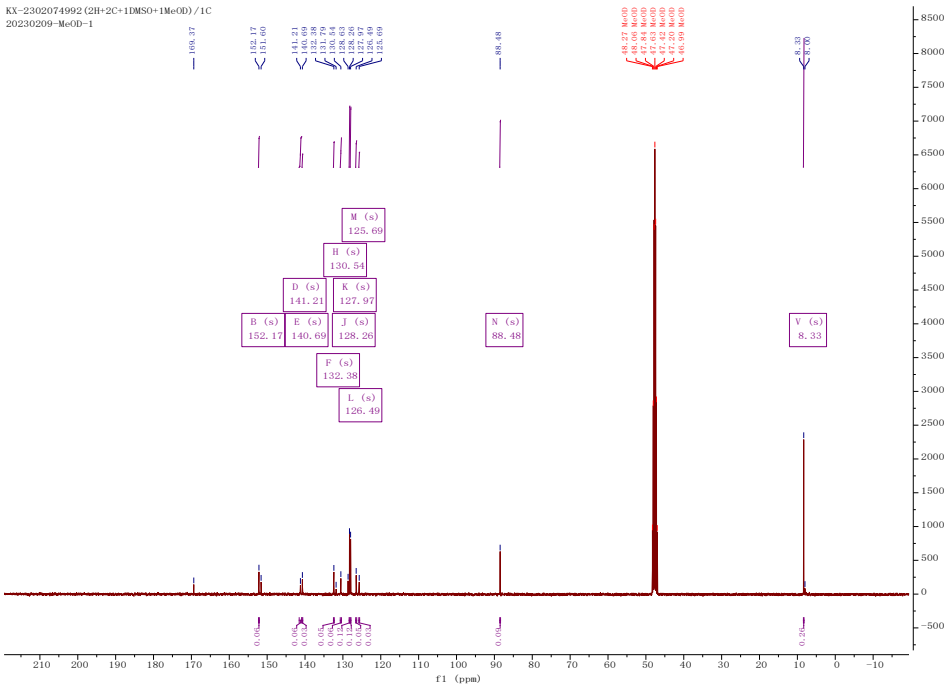

Figure S 13 ^{13}C NMR spectra of **C2**

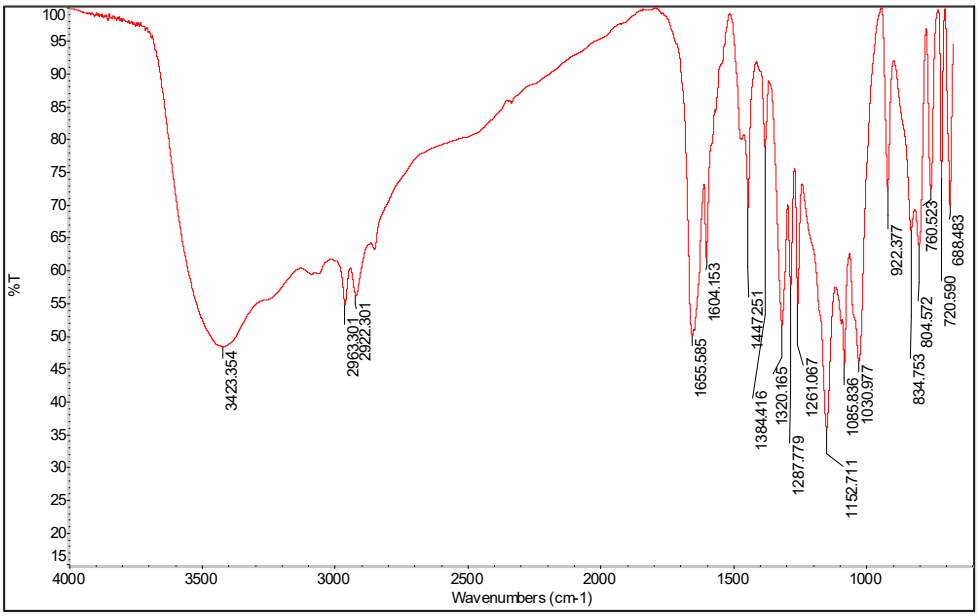

Figure S 14 IR spectra of **C2**

Preparation of **C3** complex. **L3** (127 mg, 0.60 mmol) and $[Cp^*Ir(H_2O)_3]SO_4$ (287 mg, 0.60 mmol) was mixed in 30 mL MeOH. The resulting mixture was stirred overnight. Afterwards the solvent was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/ether to generated pale yellow power as the product. Yield: 231 mg (59%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63 (dd, J = 6.0, 1.5 Hz, 1H), 8.13 (td, J = 7.7, 1.5 Hz, 1H), 7.83 – 7.73 (m, 1H), 7.65 – 7.52 (m, 1H), 7.52 – 7.39 (m, 5H), 7.43 – 7.25 (m, 1H), 5.10 (s, 1H), 4.98 (s, 1H), 1.75 (s, 15H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.37, 165.37, 151.87, 140.78, 138.99, 128.37, 127.32, 126.54, 125.93, 122.41, 94.16, 61.88, 44.81, 8.50. IR (KBr pellet, cm^{-1}): 3428(m), 2915(w), 1720(m), 1648(w), 1579(m), 1548(w), 1437(w), 1383(w), 1288(w), 1268(w), 1115(s), 1053(w), 940(w), 851(w), 770(w), 742(w), 618(m). Elemental analysis calcd (%) for $C_{23}H_{29}IrN_2O_6S$: C 42.26, H 4.47, N 4.28; found C 42.15, H 4.60, N 4.19. ESI-MS calculated for $[C_{23}H_{26}IrN_2O]^+$ 539.167, found m/z 539.1665 $[M\text{-}HSO_4\text{-}H_2O]^+$.

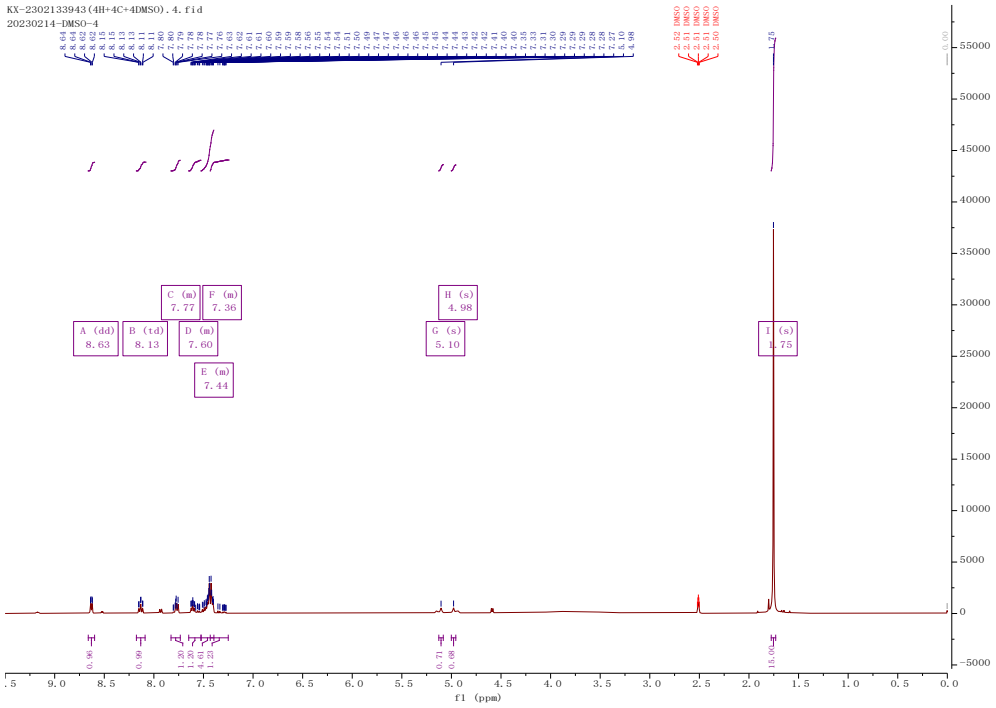

Figure S 15 ^{1}H NMR spectra of **C3**

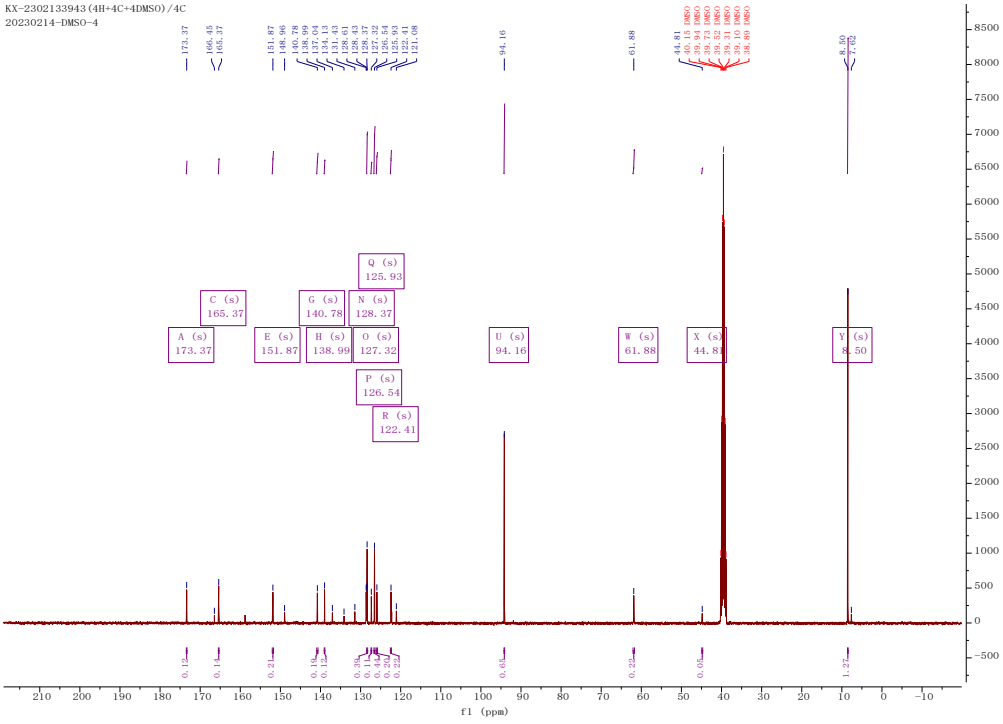

Figure S 16 ^{13}C NMR spectra of **C3**

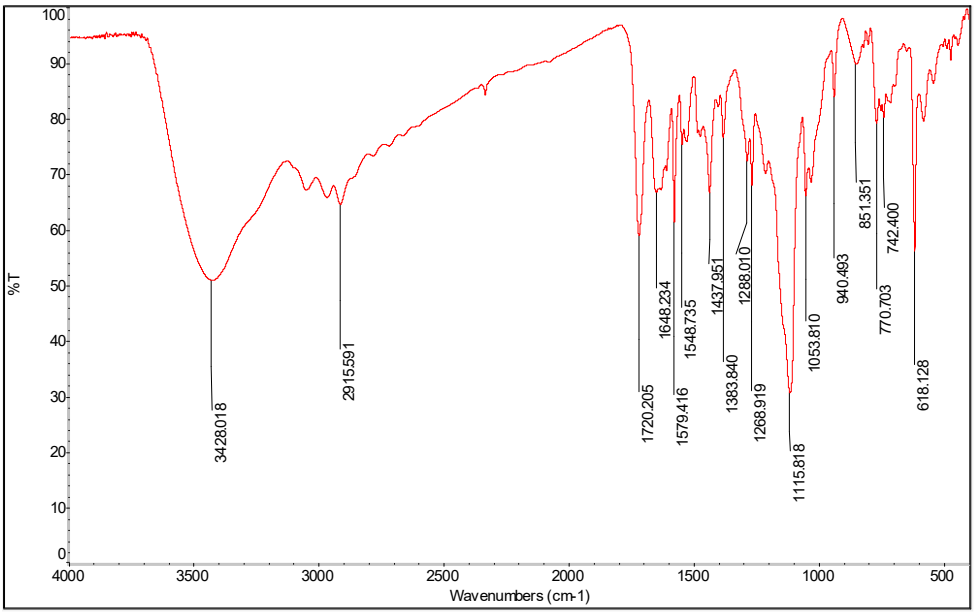

Figure S 17 IR spectra of **C3**

3. Calculation of TOF and TON

TON was calculated by equation 1. No blank reaction was observed without catalyst. The water vapor and formation of CO (GC test shows no CO in formic acid decomposition gas) was neglected.

$$TON = \frac{\frac{v_{total}}{2 * V_{m,20\,°C}}}{n_{cat}} \qquad (1)$$

$V_{m,H_2,20\,°C}$ was calculated using van der Waals equation 2:

$$V_{m,H_2,20\,°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.16\ L \cdot mol^{-1} \approx 24\ L \cdot mol^{-1} \qquad (2)$$

R: 8.3145 m^3 Pa mol^{-1} K^{-1}

T: 298.15 K

p: 101325 Pa

a: $2.49 \cdot 10^{-10}$ Pa·m^3·mol^{-2}

b: $26.7 \cdot 10^{-6}$ m^3·mol^{-1}

$V_{m,CO_2,20\,°C}$ was calculated using van der Waals equation 3:

$$V_{m,CO_2,20\,°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.10\ L \cdot mol^{-1} \approx 24\ L \cdot mol^{-1} \quad (3)$$

R: 8.3145 m^3 Pa mol^{-1} K^{-1}

T: 298.15 K

p: 101325 Pa

a: $36.5 \cdot 10^{-10} \cdot Pa \cdot m^3 \cdot mol^{-2}$

b: $42.7 \cdot 10^{-6}$ $m^3 \cdot mol^{-1}$

The TOF was calculated is based on TON calculation.

For example, at 80 °C, using 1μmol complex **3** in 0.9 M aqueous solution of FA , 30 mL gas was generated in the first 2 min, so

$$TOF = \frac{\frac{30}{2 * 24 * 1000}}{0.000001} \times \frac{60}{2} = 18,750\ h^{-1} \quad (4)$$

4. General procedure for the catalytic FADH

The reaction bottle was charged with 9.0 mL of prepared aqueous FA/SF solution in air and sealed. Afterwards, the reaction bottle was heated at given temperature (e.g. 80 °C) in a water bath till the required temperature was attained. Then, 1.0 mL of aqueous catalyst solution was injected in the reaction bottle through a rubber and the timing started immediately. The side branch was connected to the atmospheric gas burette. The volume of the gas generated was recorded. Since the reaction solution consisted of 9.0 mL FA /SF solution and 1 mL catalysts solution, all concentrations of the substrates (e.g. FA, catalyst.) in the reaction solution were converted into the actual concentrations.

KIE experiment

The HCOOH/H_2O, HCOOH/D_2O, DCOOD/H_2O and DCOOD/D_2O solutions were prepared using different combinations of reagents and deuterated reagents. Catalysts used in KIE experiment were in-situ synthesized by stirring $[Cp^*Ir(H_2O)_3]SO_4$ and equivalent corresponding ligands in methanol overnight. Afterwards, the methanol was removed under reduced pressure and water or D_2O was added to prepare the catalyst solution. Since the reaction solution consisted of 9.0 mL HCOOH/DCOOD solution

and 1.0 mL catalyst solution, the concentration of HCOOH/DCOOD in the reaction are converted to 0.9 times of the configured solution. The catalytic dehydrogenation of FA was carried according to the procedure aforementioned.

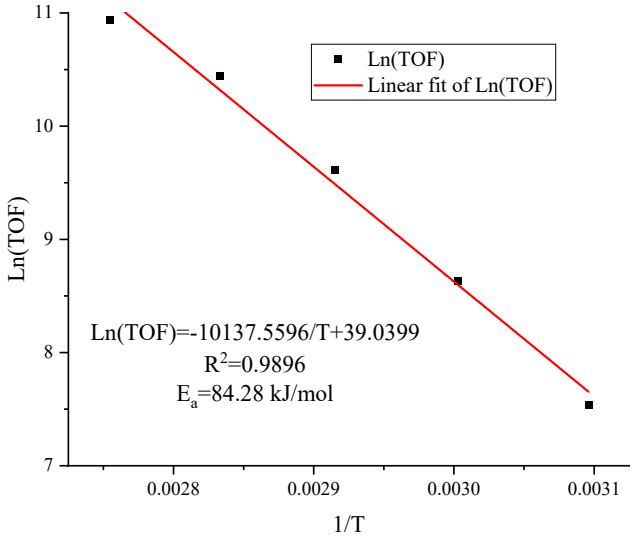

Figure S 18 Arrhenius plot of initial TOF value for aqueous FADH using **C1**.

(V= 10 mL, c (FA)= 0.9 M, c (Ir)= 0.1 mmol/L.)

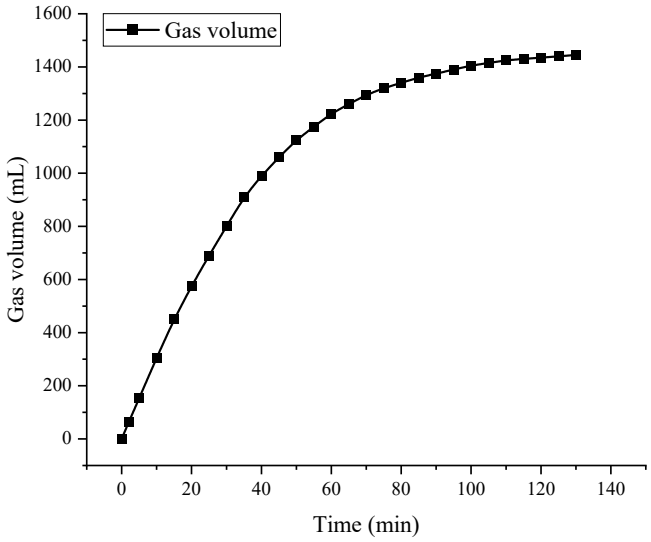

Figure S 19 FADH catalyzed by **C1** under optimized conditions

(T= 80 °C, V= 10 mL, c(FA)+c(SF)= 3.6 M, FA: SF=9:1, c(cata)= 0.02 mmol/L.)

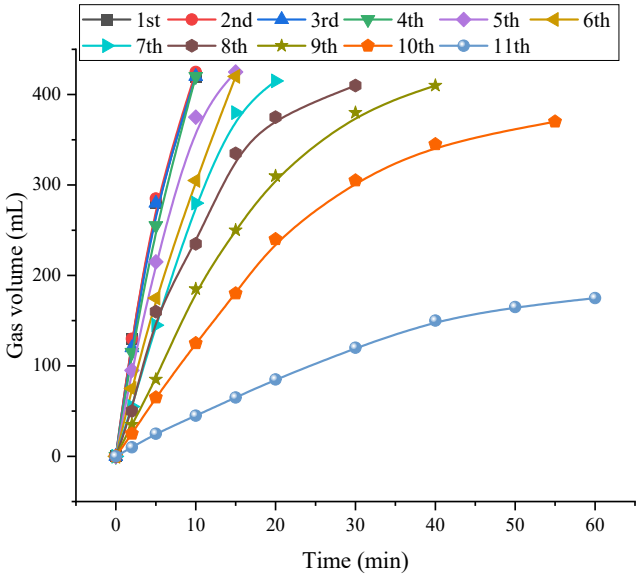

Figure S 20 Repeated use of the same solution of in-situ generated catalyst from $[Cp^*Ir(H_2O)_3]SO_4$ and **L4**

(Reaction conditions: T= 80 °C, V= 10 mL, c(FA)= 0.9 M, c(cata)= 0.1 mmol/L, FA addition=0.9 mmol per cycle)

5. Gas composition analysis:

The gas generated by different catalysts were analyzed by a GC with a TCD and a FID detector. The products of FA decomposition were confirmed to be H_2 and CO_2 with no detectable level CO. Besides, the air in the reaction bottle were also collected and detected. The detection limit of CO is 10 ppm.

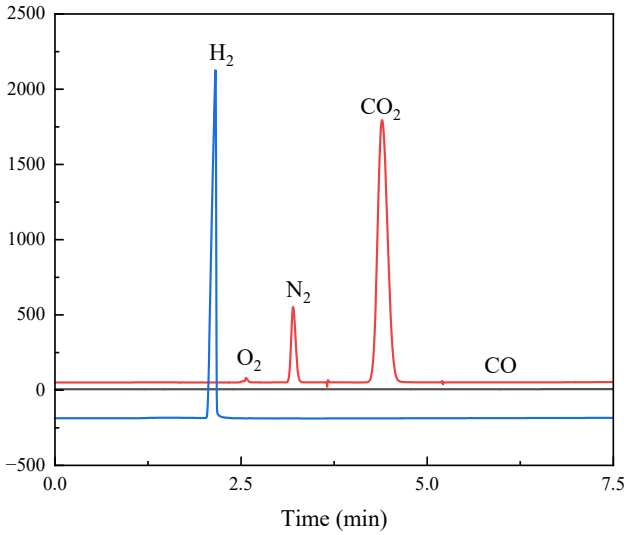

Figure S 21 GC of gas produced using **C1**

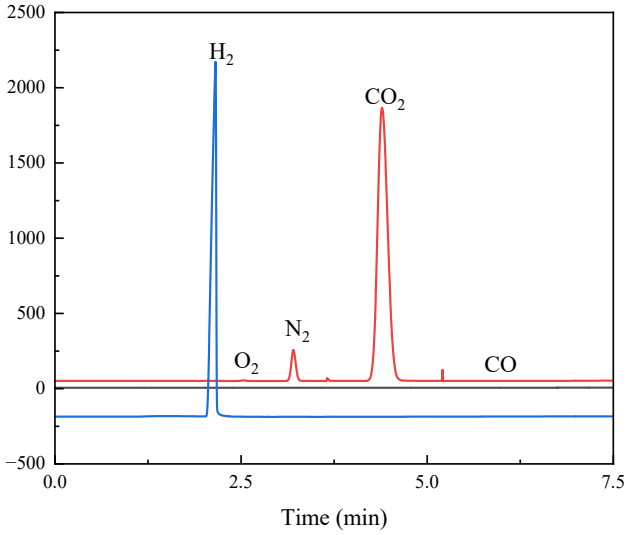

Figure S 22 GC of gas produced using **C2**

6. NMR analysis of Ir-H species

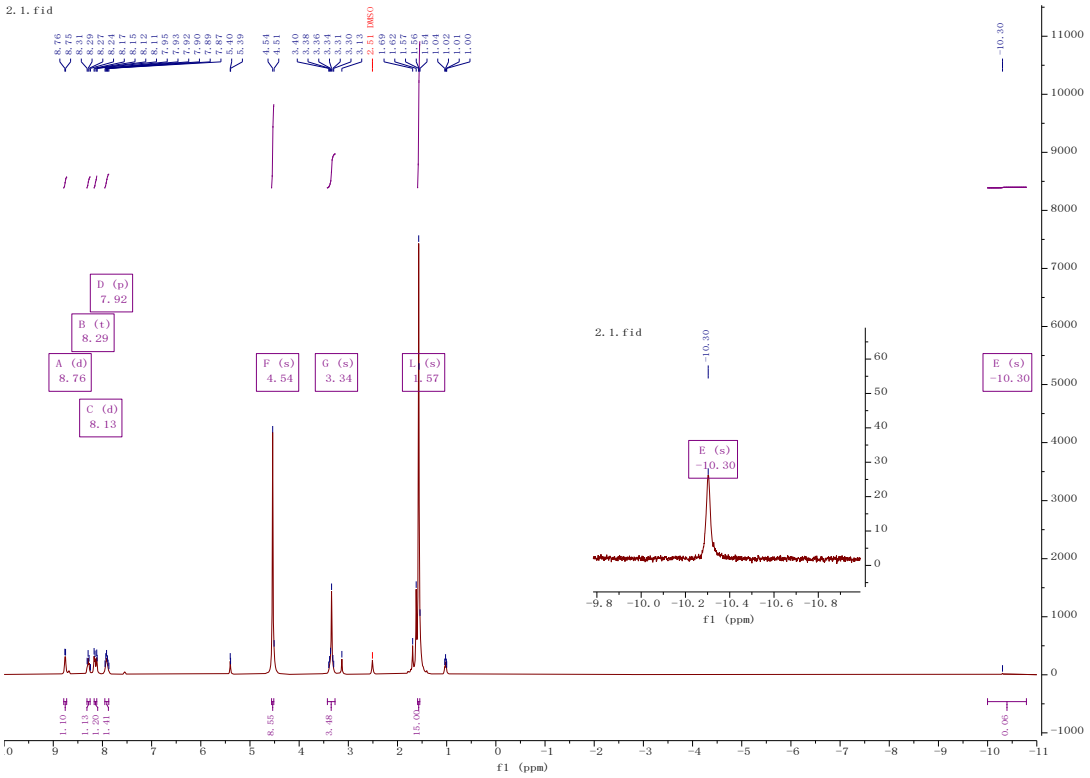

Figure S23 ^{1}H NMR spectra of Ir-H specie produced by the reactions of **C1** with SF in the mixed solvents of DMSO-d_6 and D_2O (v:v=5:5) under air.

References

1 S. Ogo, N. Makihara and Y. Watanabe, *Organometallics*, 1999, **18**, 5470-5474.

2 B.L. Dick and S.M. Cohen, *Inorg. Chem.*, 2018, **57**, 9538-9543.

3 D. Katayev, K.F. Pfister, T. Wendling and L.J. Gooßen, *Chemistry : a European journal*, 2014, **20**, 9902-9905.