

Supporting information for

**Highly Efficient Catalyst for CO₂ Hydrogenation to Formic Acid
in Water Catalyzed by Hydrophobic Porous Polymers
Containing Stable Metal-Hydride**

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Table of Contents

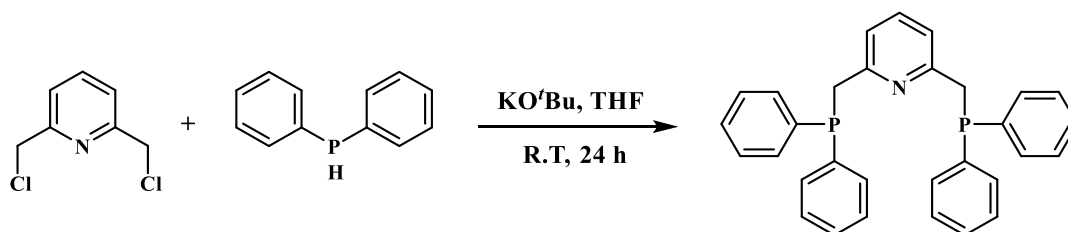
1. General information
2. Experimental methods
3. Previous work of CO₂ hydrogenation to formic acid
4. High resolution mass spectra
5. Detailed configurations for theoretical calculation
6. Adsorption capacity of CO₂
7. ¹³C solid-state NMR analysis of catalysts
8. NMR spectra of PNP and PNP-Ir
9. Elemental distribution of p-PNP-Ir (2a)
10. FT-IR spectra of the p-PNP-Ir (2e)
11. XPS spectra of p-PNP-Ir (2a)
12. Reaction data of Hydrogenation of CO₂ to formic acid
13. References

1. General information

The manipulations which are sensitive to moisture or air were performed in a nitrogen-filled glove box (JMS-1X) or using standard Schlenk techniques unless stated otherwise. NMR spectra were recorded on a Bruker AV 500 (or Bruker AV 400) spectrometer. The NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts are given in ppm and referenced to SiMe₄ (¹H, ¹³C). H₂ (99.999 vt.%) and CO₂ (99.99 vt.%) were purchased from Nanjing Tianze Gas Center, Nanjing. Part of the solvent used for catalyst synthesis is distilled after drying with an appropriate desiccant. Commercially available reagents were purchased from TCI Chemical. NMR spectra were recorded on a Bruker AV 400 spectrometer. Ir element content analysis was conducted on agilent ICP-OES730. Fourier transform infrared spectroscopy (FT-IR) spectra were collected using Bruker Tenson-27 FT-IR spectrometer. Solid-state nuclear magnetic resonance measurements were carried out using a Bruker AVIII NMR spectrometer (400 MHz) MHz). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) elemental analysis were conducted by ZEISS Gemini SEM 300. Thermogravimetric analysis (TGA) was performed under N₂ on a TGA Q 500, V20.13 with a balance gas flow of 10 mL/min and a sample gas flow of 25 mL/min. X-ray photoelectron spectroscopy (XPS) analysis was performed by PHI 5000 Versa Probe (ULVAC-PHI, JPN). Surface parameters were determined by using BET adsorption models, and pore size distributions were determined using the NLDFT model equipped in the instruments.

2. Experimental Methods

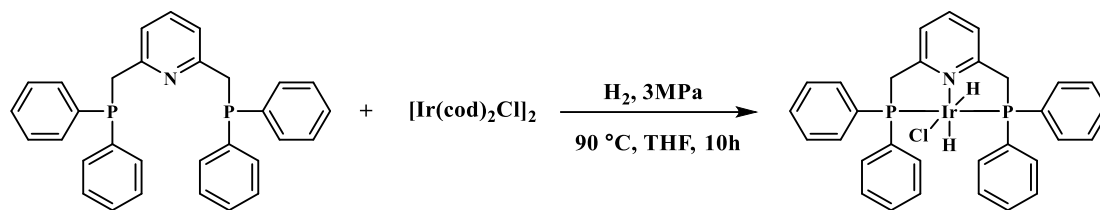
2.1. Synthesis and characterization of PNP-Ir catalysts



Synthesis of PNP-Ph:

Potassium tert-butoxide (3.37 g, 30 mmol, 4.0 eq.) was added to a solution of the diphenylphosphane (2.61 mL, 2.79 g, 15 mmol, 2.0 eq.) in 75 ml of dry THF. The reaction mixture was cooled to 0 °C and 2,6-bis(chloro- methyl)pyridine (1.32 g, 7.5 mmol, 1.0 eq.) was added. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed in vacuo and the remaining solid was dissolved in dichloromethane (100 mL) and water (100 ml). The organic layer was separated and the water layer was further extracted with dichloromethane (2 x 100 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by crystallization from chloroform/acetone giving the desired air-stable product (2.67 g, 75% yield) as a white solid.

Characterization of PNP-Ph: ¹H NMR (400 MHz, Chloroform-*d*) = 7.44 – 7.40 (m, 8H), 7.29 – 7.28 (m, 12H), 7.20 (t, J = 7.8 Hz, 1H), 6.71 (d, J = 7.5 Hz, 2H), 3.58 (s, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ = 157.61 (d, J = 7.7 Hz), 138.53 (d, J = 15.2 Hz), 136.11, 133.04, 132.86, 128.58, 128.36, 128.29, 120.94 (d, J = 5.8 Hz), 38.67 (d, J = 16.5 Hz). ³¹P NMR (162 MHz, Chloroform-*d*) δ = -10.90 (s, 2P)

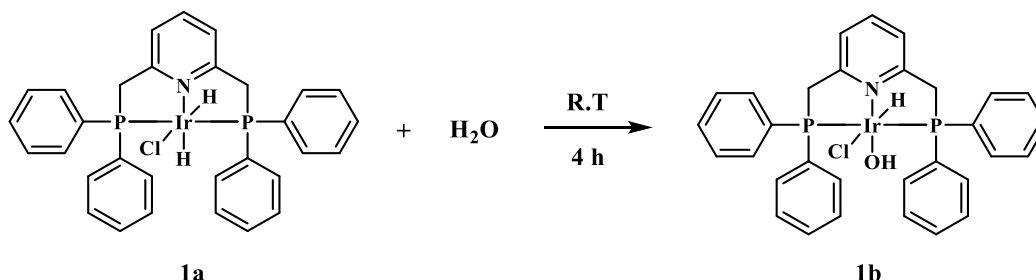


Synthesis of PNP-Ph-Ir:

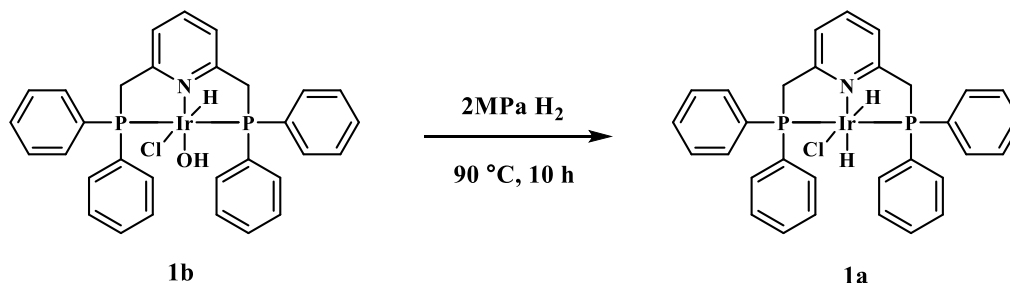
To a 50 mL stainless reaction still, $[\text{Ir}(\text{cod})_2\text{Cl}]_2$ (100 mg, 150 μmol), PNP-Ph (212 mg, 450 μmol), and THF (20 mL) were charged under argon atmosphere. The mixture was pressurized by hydrogen (3 MPa) and stirred at 90 °C for 10 h. The solvent was removed in vacuo and the resulting residue was washed with hexane. The volatiles were removed under vacuum and the products were isolated by flash chromatography on silica gel (eluent: ethyl acetate). The result is a solid white powder of PNP-Ph-Ir 1a (70 mg, 64% yield).

Characterization of PNP-Ph-Ir: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.49 (m, 9H), 7.45 – 7.04 (m, 14H), 4.61 (dt, J = 16.7, 4.8 Hz, 2H), 4.14 (dt, J = 16.7, 4.8 Hz, 2H), -18.31 (td, J = 13.5, 7.3 Hz, 1H), -21.52 (td, J = 16.4, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.78, 136.26, 133.63, 132.84, 131.18, 130.23, 128.27, 120.30, 48.13, 29.70. ^{31}P NMR (162 MHz, Chloroform-*d*) δ = 22.35 (s, 2P). ESI-MS of $[\text{M}_1-\text{Cl}]^+$, $(\text{C}_{31}\text{H}_{29}\text{IrNP}_2)^+$, cal.: 670.1399, found: 670.1392.

2.2. Transformation process between 1a and 1b



100 mg 1a, 5 mL CHCl_3 and 50mg water were added to the screw bottle. The mixture was stirred at room temperature for 4 h and the solvent was removed under vacuum to obtain a yellow powder 1b (97% yield).



To a 50 mL stainless reaction still, 80 mg 1b, and dry THF (10 mL) were charged under argon atmosphere. The mixture was pressurized by hydrogen (2 MPa) and stirred at 90 °C for 10 h. The solvent was removed in vacuo and the resulting residue was washed with hexane. The result is a solid white powder of 1a (90% yield).

2.3 Synthesis of p-PNP-Ir 2a~2e

Synthesis of p-PNP-Ir 2a. PNP-Ph-Ir complex 1a (0.1 mmol, 70 mg), benzene (0.1 mmol, 8 mg) was dissolved in 5 mL of 1,2-dichloroethane. After stirring for several minutes, anhydrous FeCl₃ (2.0 mmol, 324 mg) and formaldehyde dimethyl acetal (FDA) (2.0 mmol, 152 mg) were added. The resulting mixture was heated to 85 °C and stirred for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was washed by methanol, distilled water, dichloromethane, and acetone successively. Further purification of the polymer was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 60 °C to give a dark brown powder and denoted as p-PNP-Ir 2a (yield: 58%).

Synthesis of p-PNP-Ir 2b. PNP-Ph-Ir complex 1a (0.1 mmol, 70 mg), benzene (0.5 mmol, 39 mg) were dissolved in 5 mL of 1,2-dichloroethane. After stirring for several minutes, anhydrous FeCl₃ (2.0 mmol, 324 mg) and formaldehyde dimethyl acetal (FDA) (2.0 mmol, 152 mg) were added. The resulting mixture was heated to 85 °C and stirred for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was washed by methanol, distilled water, dichloromethane, and acetone successively. Further purification of the polymer was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 60 °C to give a dark brown powder and denoted as p-PNP-Ir 2b (yield: 63%).

Synthesis of p-PNP-Ir 2c. PNP-Ph-Ir complex 1a (0.1 mmol, 70 mg), benzene (1.0 mmol, 78 mg) were dissolved in 5 mL of 1,2-dichloroethane. After stirring for several minutes, anhydrous FeCl₃ (2.0 mmol, 324 mg) and formaldehyde dimethyl acetal (FDA) (2.0 mmol, 152 mg) were added. The resulting mixture was heated to 85 °C and stirred for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was washed by methanol, distilled water, dichloromethane, and acetone successively. Further purification of the polymer was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 60 °C to give a dark brown powder and denoted as p-PNP-Ir 2c (yield: 77%).

Synthesis of p-PNP-Ir 2d. PNP-Ph-Ir complex 1a (0.1 mmol, 70 mg), benzene (5.0 mmol, 390 mg) were dissolved in 5 mL of 1,2-dichloroethane. After stirring for several minutes, anhydrous FeCl₃ (2.0 mmol, 324 mg) and formaldehyde dimethyl acetal (FDA) (2.0 mmol, 152 mg) were added. The resulting mixture was heated to 85 °C and stirred for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was washed by methanol, distilled water, dichloromethane, and acetone successively. Further purification of the polymer was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 60 °C to give a dark brown powder and denoted as p-PNP-Ir 2d (yield: 82%).

Synthesis of p-PNP-Ir 2e. PNP-Ph-Ir complex 1a (0.1 mmol, 70 mg), benzene (10 mmol, 780 mg) were dissolved in 5 mL of 1,2-dichloroethane. After stirring for several minutes, anhydrous FeCl₃ (2.0 mmol, 324 mg) and formaldehyde dimethyl acetal (FDA) (2.0 mmol, 152 mg) were added. The resulting mixture was heated to 85 °C and stirred for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was washed by methanol, distilled water, dichloromethane, and acetone successively. Further purification of the polymer was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 60 °C to give a dark brown powder and denoted as p-PNP-Ir 2e (yield: 89%).

2.4 The preparation of solution for ICP-AES test

The accurately weighed p-PNP-Ir was added into a 20 mL sealed tube equipped with a magnetic

stirring bar, then 2 mL concentrated HNO₃ and 2 mL concentrated HCl were added into the tube. The tube was added into an oil bath and heated to 100 °C for 12 h, then the mixture was cooling to room temperature and transferred into a round-bottom flask and diluted with deionized water. The solution was used for further ICP-AES test.

2.5 Typical procedure for the hydrogenation of CO₂ with H₂

The catalyst PNP-Ph-Ir (0.01 or 0.001 μmol) [solution of THF(4×10⁻⁴ mol/L or 4×10⁻⁵ mol/L)], 5 mL H₂O and 5 mmol base were added into the 50 mL high pressure reaction kettle. Then, 20 bar CO₂ and 50 bar H₂ were introduced at room temperature and reacted at 120°C for 12 or 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. Isopropanol was added into the reaction kettle as internal standard, and 100μL reaction solution was taken out and mixed with 400μL D₂O for ¹H NMR analysis to determine the amount of formate.

The catalyst p-PNP-Ir 2a-2e 2mg, 5 mL H₂O and 5 mmol base were added into the 50 mL high pressure reaction kettle. Then, 20 bar CO₂ and 50 bar H₂ were introduced at room temperature and reacted at 120°C or 150°C for 12 or 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. Isopropanol was added into the reaction kettle as internal standard, and 100μL reaction solution was taken out and mixed with 400μL D₂O for ¹H NMR analysis to determine the amount of formate.

2.6 Catalyst recycling for the hydrogenation of CO₂ with H₂

The catalyst p-PNP-Ir 2e 5 mg, 5 mL H₂O and 5 mmol DBU were added into the 50 mL high pressure reaction kettle. Then, 20 bar CO₂ and 50 bar H₂ were introduced at room temperature and reacted at 150°C for 12 or 24 h. After the reaction, the residual gases were released carefully. The catalyst was recovered by simple centrifugation and decantation. After that, the catalyst was transferred back into the autoclave, which was recharged with, 5 mL H₂O, 5 mmol DBU, CO₂ (20 bar) and H₂ (50 bar) for the next run. Isopropanol was added into the reaction solution as internal standard, and 100μL reaction solution was taken out and mixed with 400μL D₂O for ¹H NMR analysis to determine the amount of formate.

2.7 Theoretical calculation method

All the structures were fully optimized with the B3LYP method based on DFT including the dispersion corrections using the Empirical Dispersion = GD3BJ keyword. The LANL2DZ basis set was used for Ir atom, and the 6-31+g(d) basis set was used to optimize the other atoms [abbr.: B3LYP/6-31+g(d)/LANL2DZ]. Energy calculations and Zero-point energy (ZPE) correction have been done by using the same level of theory. The computed stationary points have been characterized as minima or transition states by diagonalizing the Hessian matrix and analyzing the vibrational normal modes. In this way, if the imaginary frequency is not displayed, the stationary point can be classified as minima, and if only one imaginary frequency is obtained, the stationary point can be classified as a transition state (TS). The particular nature of the transition states has been determined by analyzing the motion described by the eigenvector associated with the imaginary frequency. All calculations were performed with the Gaussian 09 programs.^[1]

3. Previous work of CO₂ hydrogenation to formic acid

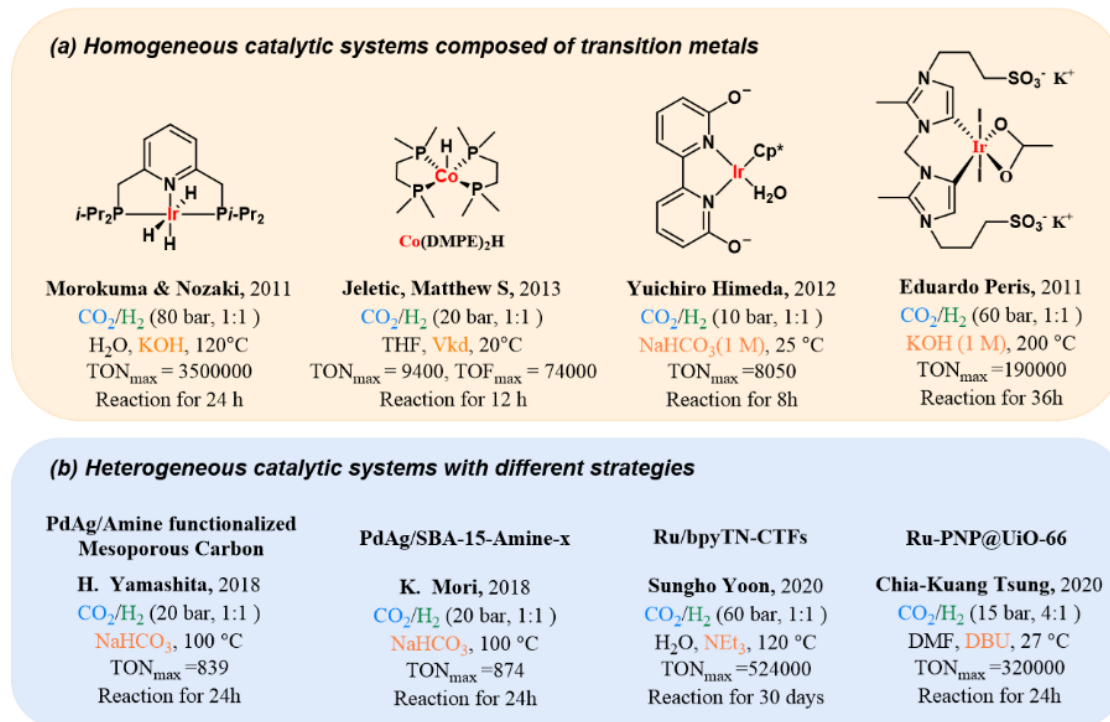
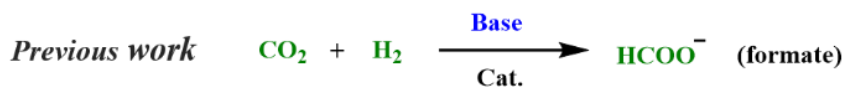


Figure S1. CO₂ hydrogenation to formic acid with diverse catalysts

4. High resolution mass spectra (ESI-MS)

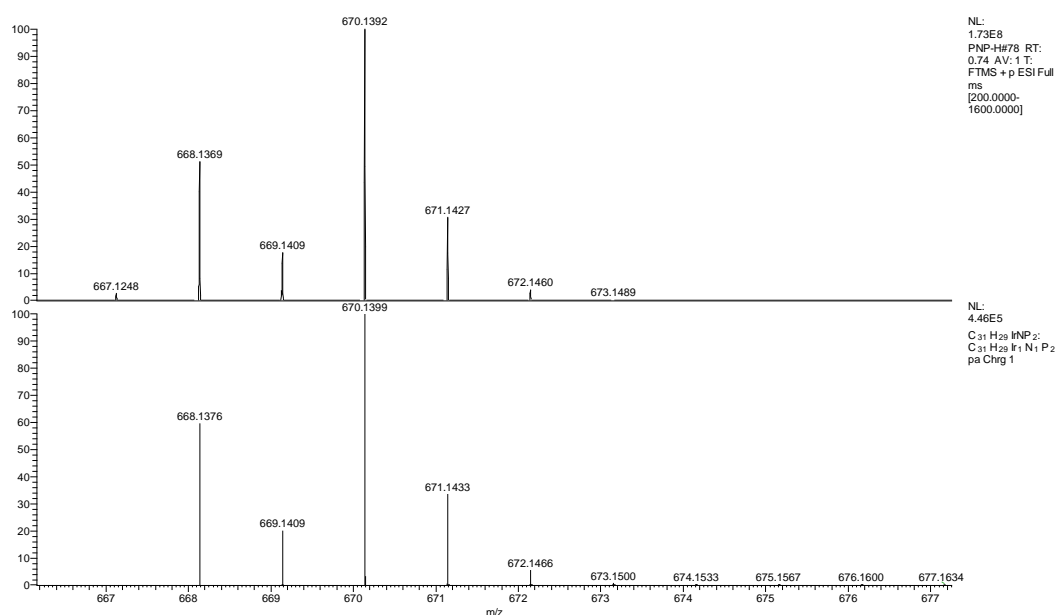


Figure S2. High resolution mass spectra of 1a at m/z [M₁-Cl]⁺. above: found values; below: calculated values

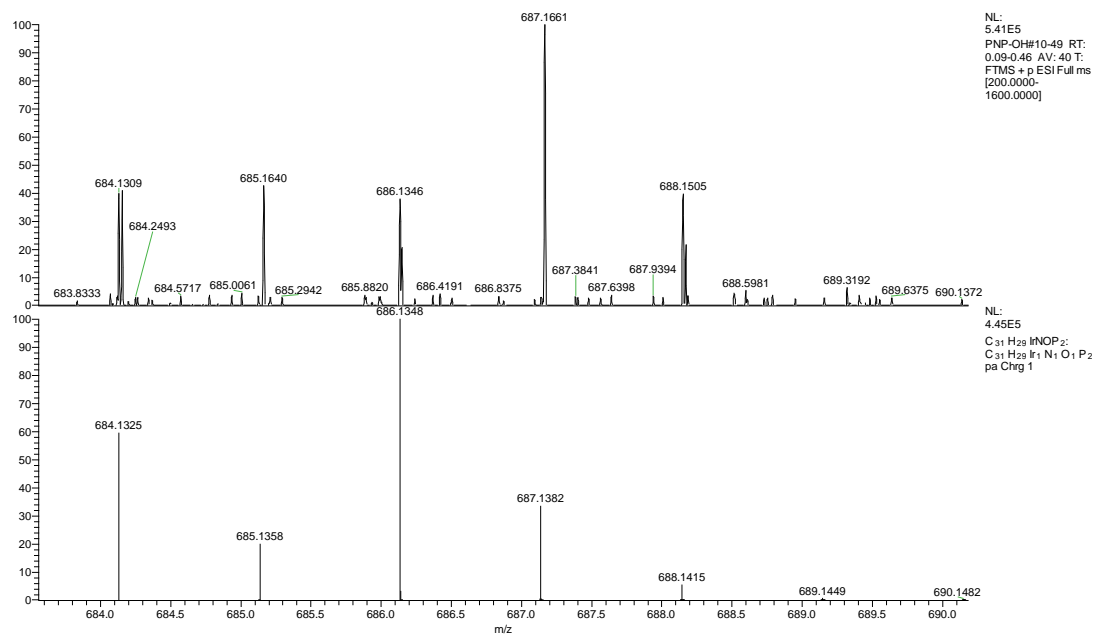


Figure S3. High resolution mass spectra of 1b at m/z $[M_2-Cl]^+$. above: found values; below: calculated values

5. Detailed configurations for theoretical calculation

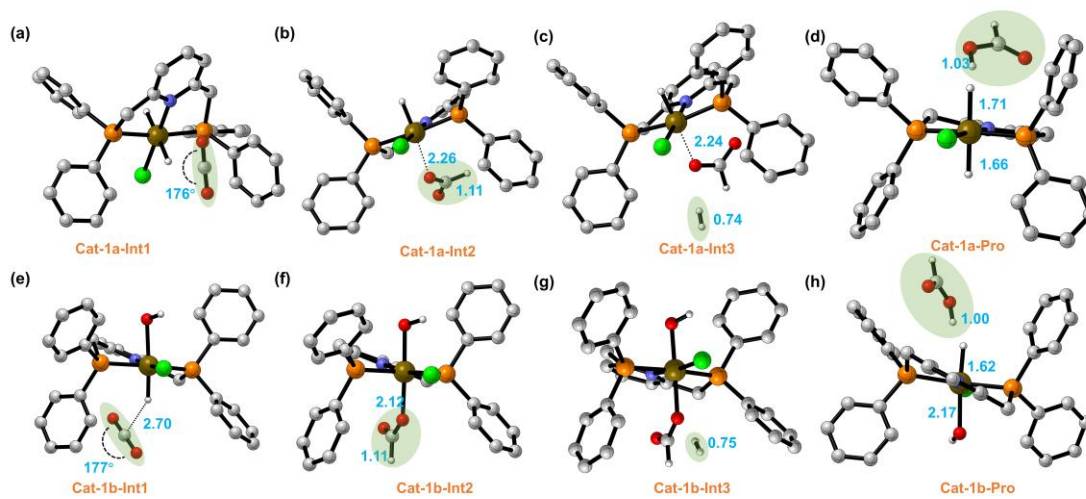


Figure S4. The optimized structures

6. Adsorption capacity of CO₂

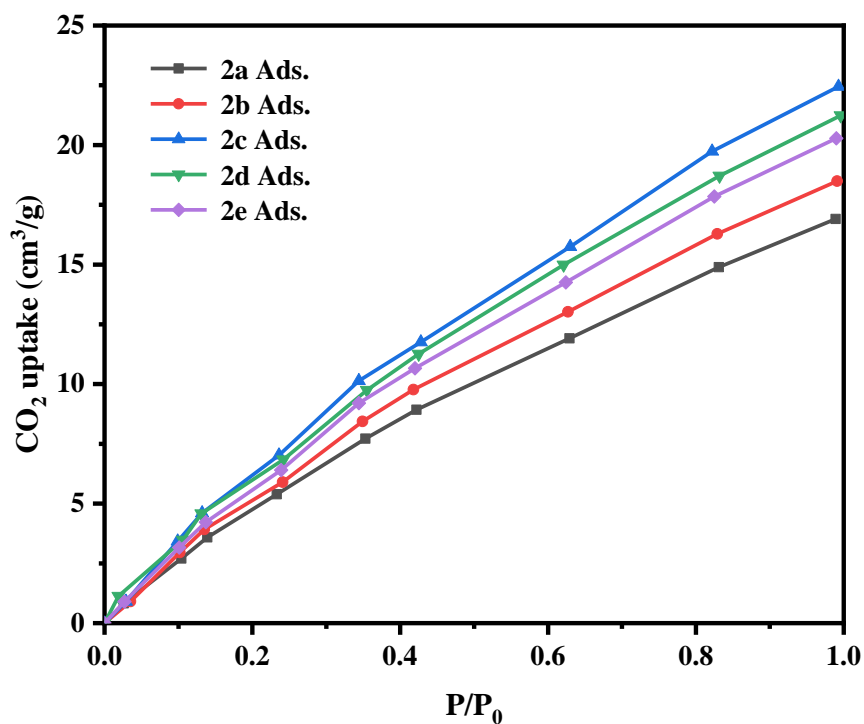


Figure S5. the adsorption capacity of CO₂ by p-PNP-Ir

7. Solid state ¹³C NMR analysis of catalysts.

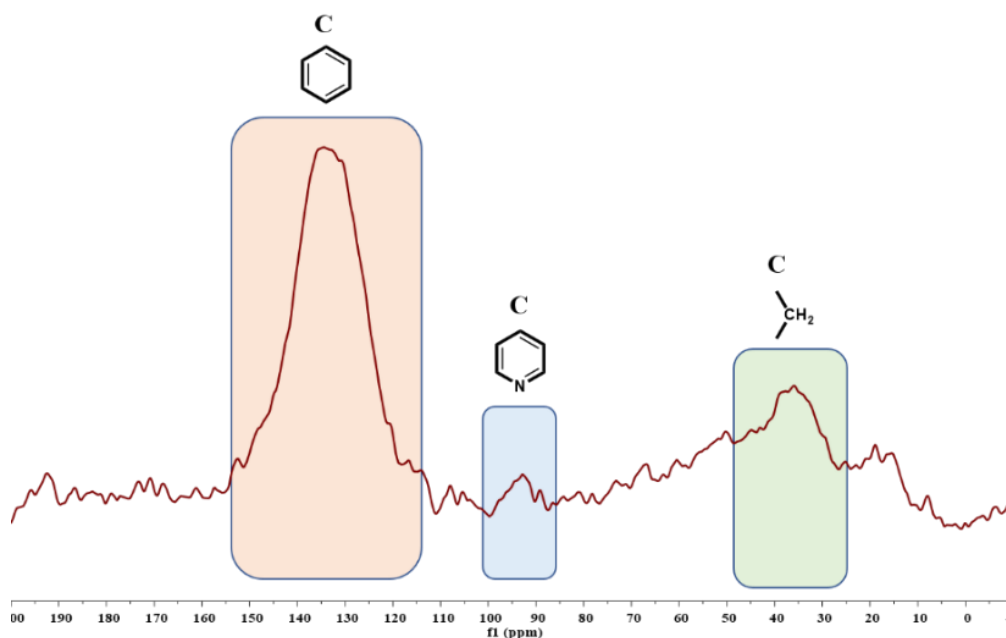


Figure S6. Solid-state ¹³C NMR spectra of p-PNP-Ir 2a

8. NMR spectra of PNP and PNP-Ir

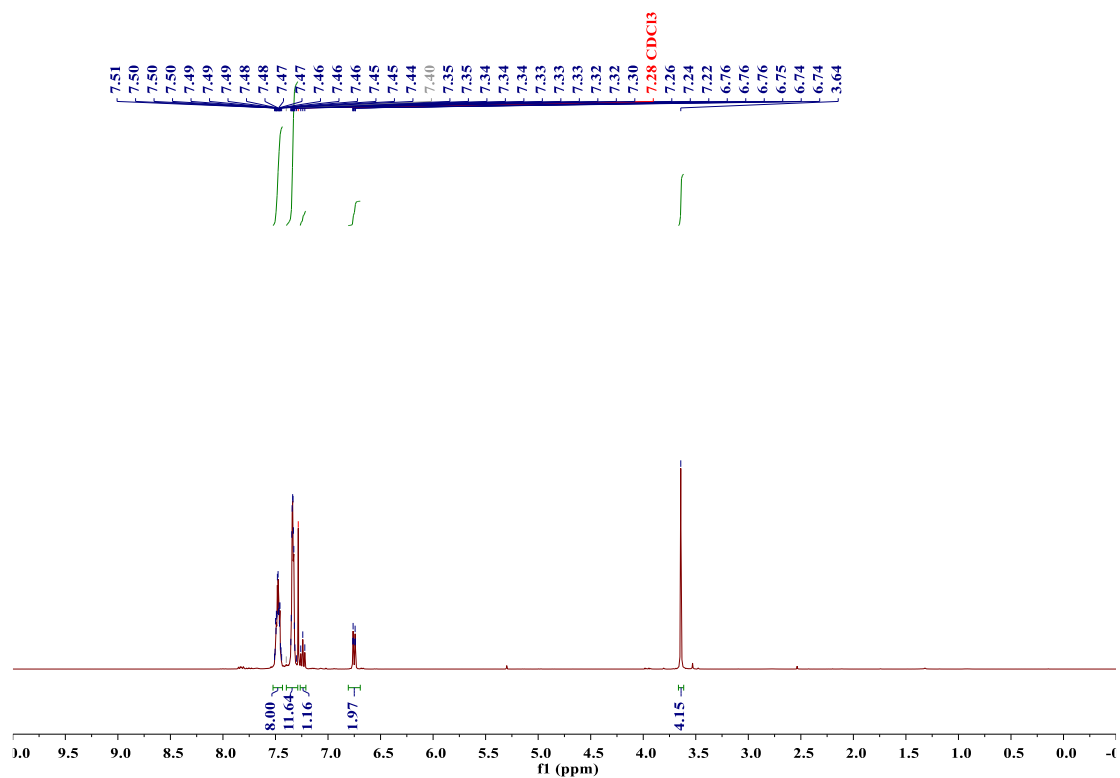


Figure S7. ¹H NMR of PNP

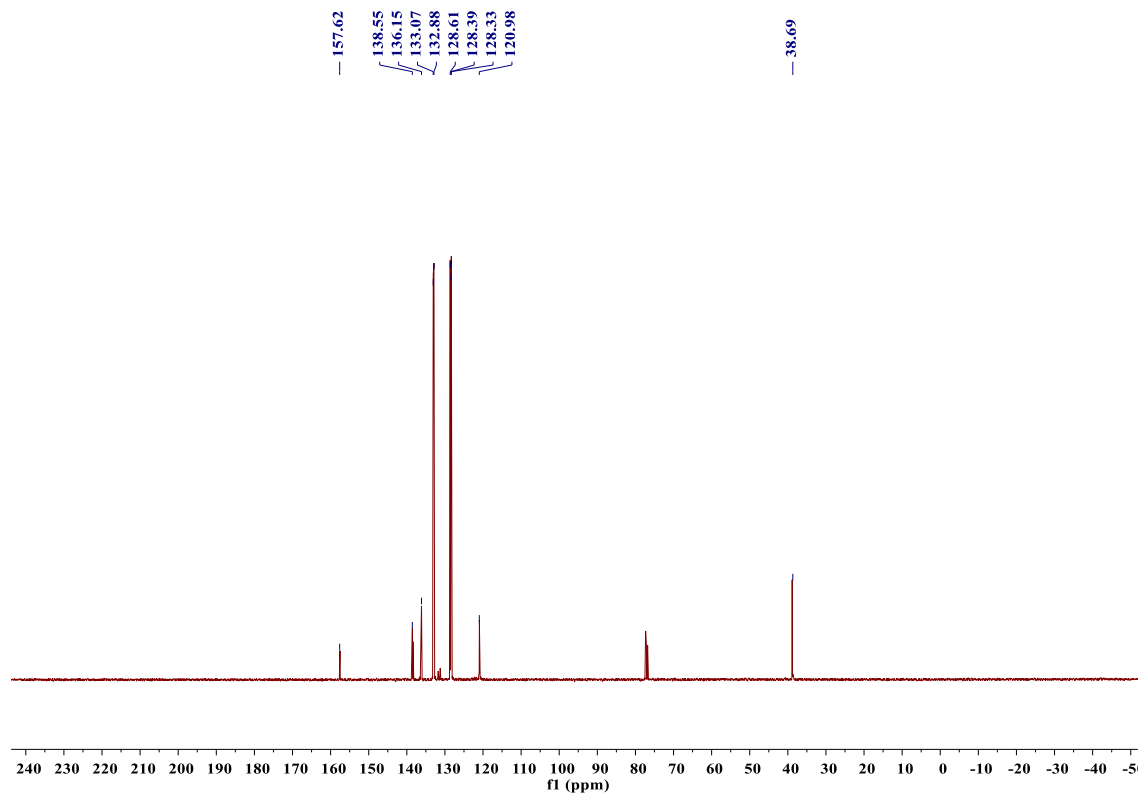


Figure S8. ¹³C NMR of PNP

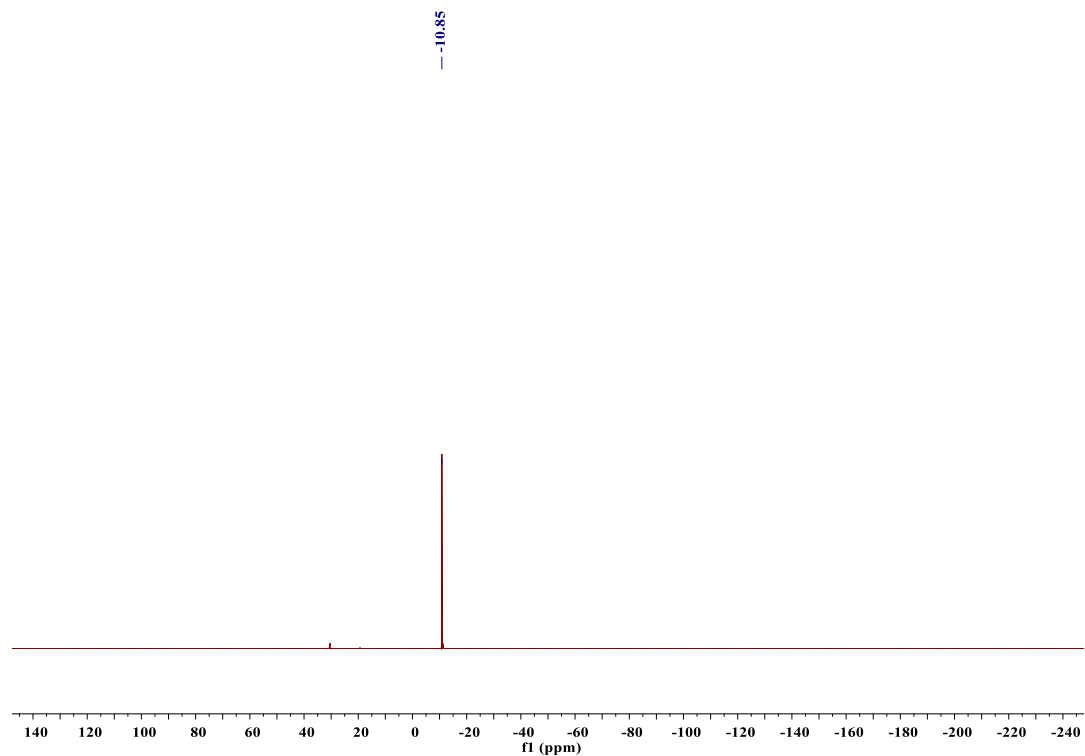


Figure S9. ³¹P NMR spectra of PNP

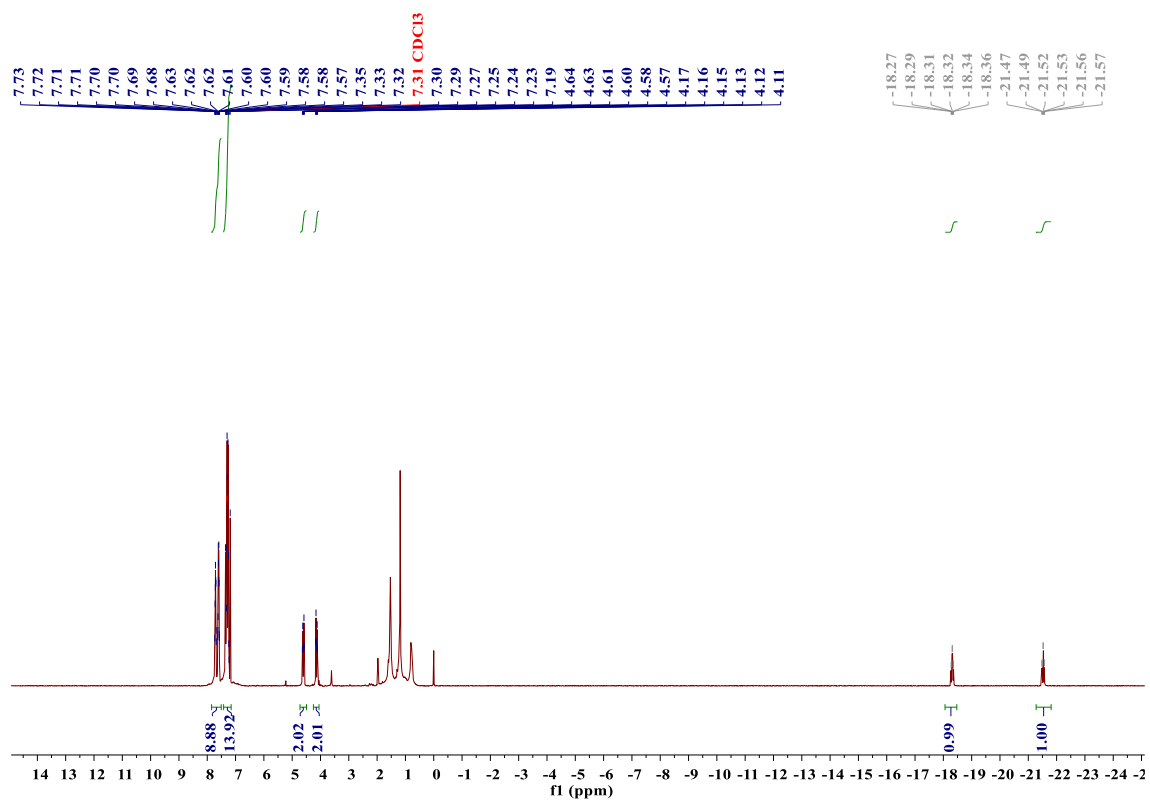


Figure S10. ¹H NMR of PNP-Ir 1a

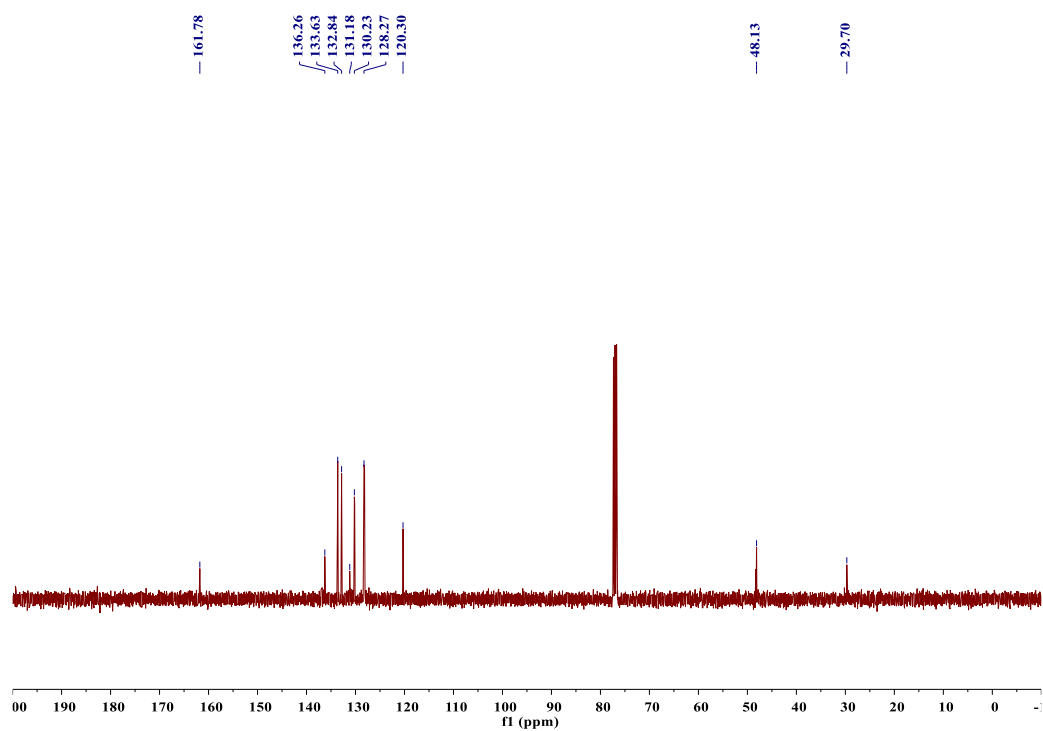


Figure S11. ^{13}C NMR of PNP-Ir 1a

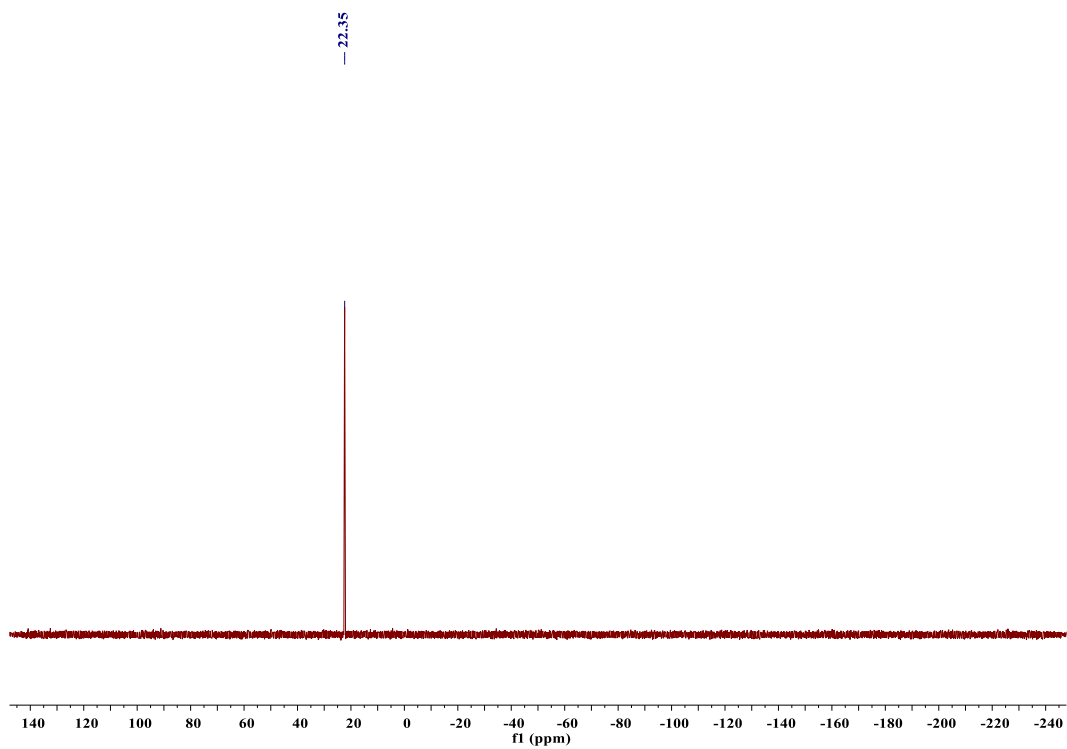
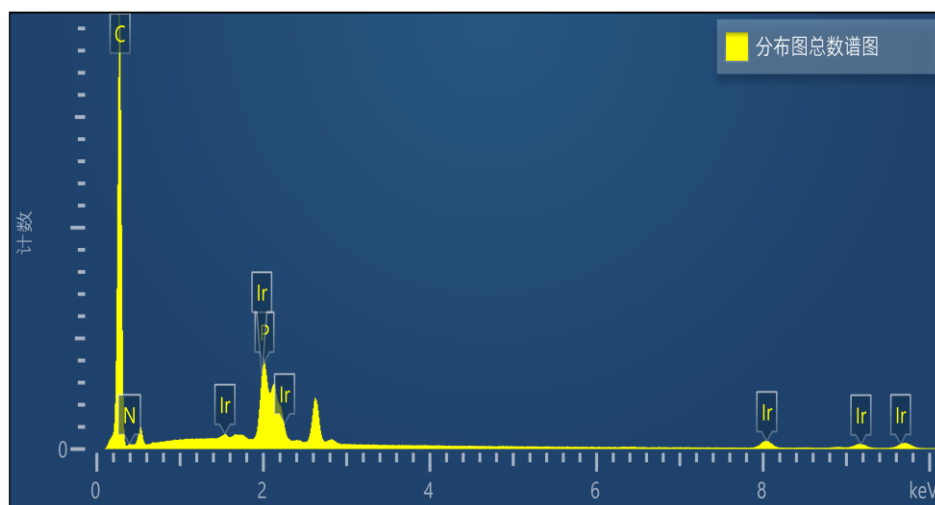


Figure S12. ^{31}P NMR of PNP-Ir 1a

9. Elemental distribution of p-PNP-Ir 2a



Distribution diagram Total spectrum diagram		
Element	Wt%	At%
C	86.52	95.20
N	3.63	3.42
P	1.96	0.84
Ir	7.89	0.54
Total amount:	100.00	100.00

Figure S13. Element analysis of p-PNP-Ir 2a by EDS-mapping.

10. FT-IR spectra of the p-PNP-Ir (2e)

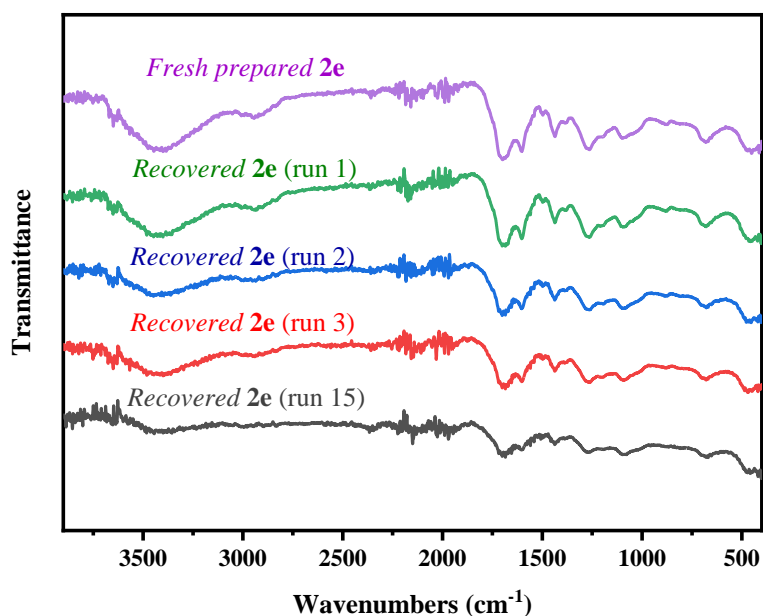


Figure S14. Fourier-transform infrared (FT-IR) spectra of the fresh prepared p-PNP-Ir 2e (purple line), the recovered 2e hydrogenation of CO₂ to HCOOH after the 1st run (green line), the 2nd (blue line), the 3rd (red cyan) and the 15th (gray cyan) run.

11. XPS spectra of p-PNP-Ir (2a)

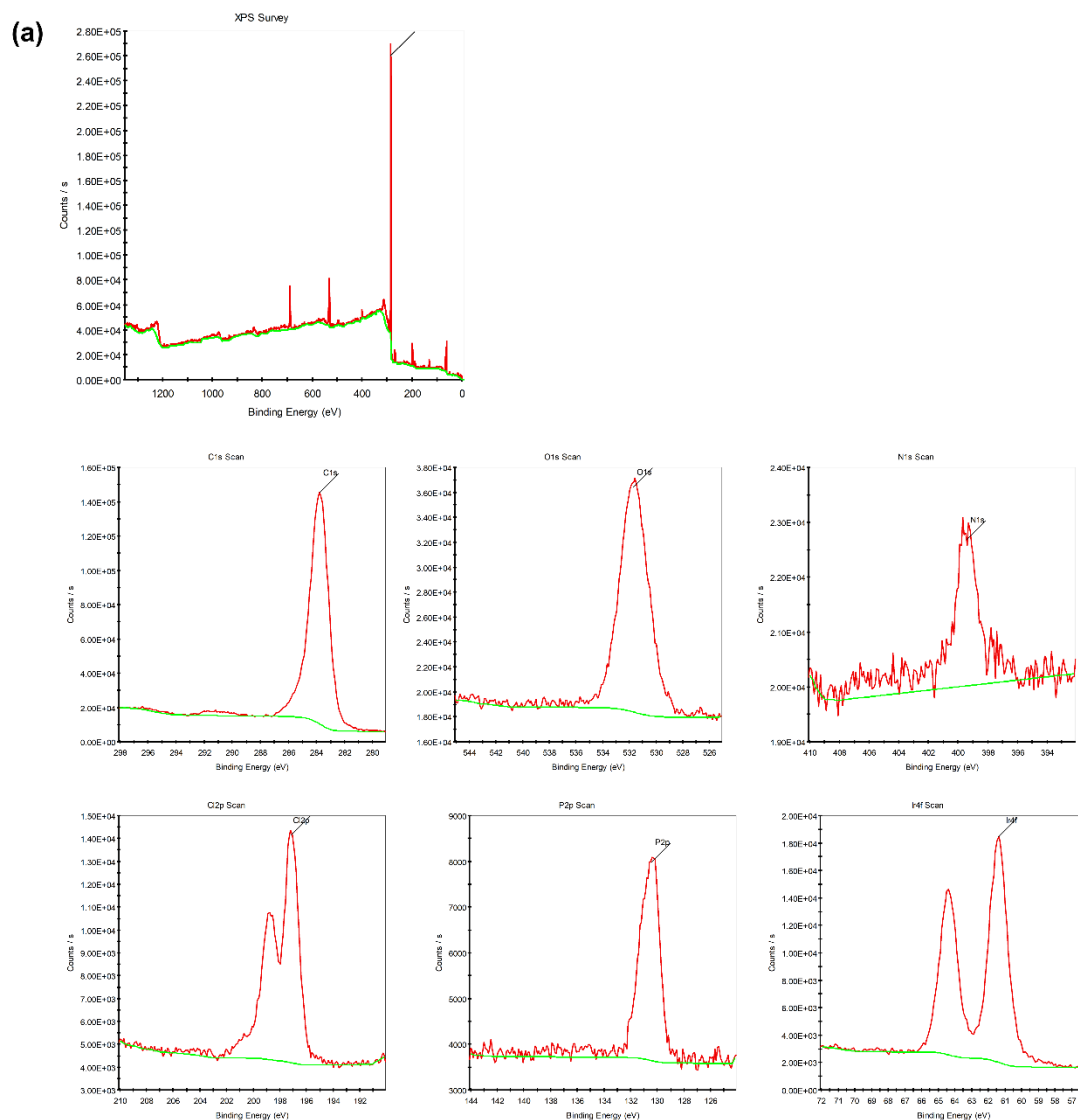


Figure S15. X-ray photoelectron spectroscopy (XPS): (a) Survey spectrum of p-PNP-Ir 2a;

(b) Content analysis of p-PNP-Ir 2a

12. Reaction data of Hydrogenation of CO₂ to formic acid

Table S1. Hydrogenation of CO₂ to formic acid under other different conditions.

Entry ^[a]	Cat.	Cat-loading (μmol) ^[b]	Time (h)	Base	T (°C)	TON	Base usage
1	PNP-Ir (1a)	0.01	12	DBN	150	37,100	7.4%
2	PNP-Ir (1a)	0.01	12	TEA	150	14,300	2.9%
3	PNP-Ir (1a)	0.01	12	KOH	150	80,400	16.1%
4	PNP-Ir (1a)	0.01	12	KHCO ₃	150	37,600	7.5%
5	PNP-Ir (1a)	0.002	12	KOH	150	173,100	6.9%
6	p-PNP-Ir (2a)	1.211	12	DBU	150	2,000	49.5%
7	p-PNP-Ir (2b)	0.134	12	DBU	150	17,100	45.9%
8	p-PNP-Ir (2c)	0.039	12	DBU	150	54,900	42.9%
9	p-PNP-Ir (2d)	0.014	12	DBU	150	129,200	36.2%
10	p-PNP-Ir (2e)	0.002	12	DBN	150	265,100	10.6%
11	p-PNP-Ir (2e)	0.002	12	TEA	150	57,900	2.4%
12	p-PNP-Ir (2e)	0.002	24	KOH	150	813,000	32.5%
13	p-PNP-Ir (2e)	0.002	12	KHCO ₃	150	75,300	3.0%
14	p-PNP-Ir (2e)	0.002	12	K ₂ CO ₃	150	519,100	20.8%

[a] Standard conditions: Cat: 2 mg, Solvent: H₂O (5 mL), Base (DBU, 5 mmol), CO₂:H₂ (20:50 bar). The amount of formate and TON was determined by ¹H NMR with isopropanol as the internal standard; [b] Ir content for p-PNP-Ir 2a-2e.

Table S2. Hydrogenation of CO₂ to formic acid in different solvents.

Entry	Cat.	Solvent	Time (h)	P _{H₂+CO₂} (bar)	T (°C)	TON
1		THF	12	70	150	38300
2	p-PNP-Ir	dioxane	12	70	150	24600
3	(2e)	MeCN	12	70	150	21800
4		H ₂ O	12	70	150	585400

Reaction condition: 0.01 μmol cat. Solvent: H₂O (5 mL). KOH (5 mmol). CO₂:H₂ (bar) (20:50). 150°C.

13 References

[1] M. J. Frisch, et al., GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA, 2009.