Supplementary Information (SI) for Catalysis Science & Technology.

Supplementary Information

Title：Boosted Hydroformylation of High-Carbon Olefins with Optimized n/i Ratio via Monodisperse Rhodium Catalysts Supported on Copolymerized Porous Organic Ligands

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1 General Experimental

1.1 Chemicals and Materials

All solvents were purified according to standard laboratory protocols. Unless otherwise specified, all other reagents were of analytical grade and used as received without further purification. Linear α-olefins, including 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, and 1-undecene, were purchased from Shanghai Macklin Biochemical Co., Ltd. Syngas was supplied by Dalian Kena Science and Technology Co., Ltd. Magnesium powder and azobisisobutyronitrile (AIBN) were obtained from Sigma-Aldrich. Phosphorus trichloride (PCl_3) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was distilled over sodium/benzophenone under an argon (Ar) atmosphere to ensure anhydrous and oxygen-free conditions. Similarly, PCl_3 was subjected to distillation under an Ar atmosphere prior to use to remove potential impurities and avoid hydrolysis or oxidation.

1.2 Catalyst Characterization

Nitrogen sorption isotherms were acquired using a Quantachrome Autosorb-1 adsorption analyzer at 77 K (liquid nitrogen temperature). Scanning electron microscopy (SEM) characterization was carried out on a JSM-7800F microscope, operating with an accelerating voltage in the range of 0.01–30 kV. Transmission electron microscopy (TEM) images were recorded using a JEM-2100 microscope under an acceleration voltage of 200 kV. Thermogravimetric analysis (TGA) was performed on a STA449F5-Thermostar thermal analyzer to evaluate thermal stability.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were captured using a JEM-ARM200F STEM/TEM instrument for elemental distribution analysis. Solid-state ^{13}C magic-angle spinning (MAS) NMR and ^{31}P MAS NMR spectra were collected on a Bruker AVANCE 600 AV spectrometer to elucidate the local chemical environment of carbon and phosphorus species. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a ThermoScientific ESCALAB 250Xi system with Al Kα radiation as the X-ray source (θ = 90°). The binding energy scale of the spectrometer was calibrated against the C 1s reference peak at 284.8 eV to ensure data accuracy.

Gas chromatography was detected by Agilent 7890B gas chromatography (GC) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID).

Inductively coupled plasma optical emissi on spectrometry (ICP−OES) was employed for elemental composition quantification using a PerkinElmer Optima 7300 DV instrument.

In situ diffuse reflection infrared Fourier transform spectroscopy (*in situ* DRIFTS) measurements were performed on a Bruker VERTEX 80 V Fourier transform infrared spectrometer, covering the wavenumber range of 4000–800 cm^{-1}. The spectrometer was equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and a high-temperature reaction cell fitted with ZnSe windows, ensuring reliable acquisition of in situ spectral information under reaction-relevant conditions.

Rh K-edge X-ray absorption fine structure (XAFS) spectra of the as-prepared samples were collected at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics (SINAP), Chinese Academy of Sciences (Shanghai, China). A Si (311) crystal monochromator was employed for monochromatization of the X-ray beam. The storage ring of SSRF operated at an energy of 3.5 GeV with an injection current of 200 mA. Notably, the X-ray absorption spectra were recorded in transmission mode, while the spectra of all prepared catalysts were acquired in fluorescence mode to enhance detection sensitivity for low Rh loading samples. The raw XAFS data were processed using the IFEFFIT software package: energy calibration was conducted with reference to the first inflection point at 23220 eV, followed by background subtraction and normalization to eliminate spectral artifacts. For extended X-ray absorption fine structure (EXAFS) analysis, Fourier transformation was applied to the k^3-weighted EXAFS oscillations. In the subsequent curve-fitting procedure, the structural parameters for Co–C, Co–P, and Co–S coordination paths were derived from ab initio multiple scattering calculations using the FFEF6 code, ensuring the reliability of the structural fitting results.

1.3 Synthesis of monomers, CPOL and metalation

1.3.1 Synthesis of 3v-PPh_3 Monomer.

All following manipulations were carried out under an inert argon atmosphere using standard Schlenk techniques. A 100 mL three-necked round-bottom flask equipped with a magnetic stir bar was charged with magnesium powder (0.5 g, 20 mmol, 1.0 equiv) and anhydrous diethyl ether (10 mL). The resulting suspension was stirred vigorously in an ice-water bath for 2 h to ensure complete activation of magnesium.Subsequently, a solution of 4-bromostyrene (4 g, 22 mmol, 1.1 equiv) in anhydrous diethyl ether (10 mL, denoted as Solution 1) was slowly added dropwise to the flask via a syringe, followed by continuous stirring for 2 h under ice-water bath conditions. Afterward, a solution of phosphorus trichloride (PCl_3, 2 g, 20 mmol, 1 equiv) in anhydrous diethyl ether (10 mL, denoted as Solution 2) was added dropwise in a similar manner, and the reaction mixture was further stirred for another 2 h while maintaining the low-temperature environment.

Deionized water (10 mL) was then added cautiously to quench the reaction, and the mixture was stirred for an additional 0.5 h at room temperature to ensure complete hydrolysis of residual reactive intermediates. The resulting mixture was extracted with anhydrous diethyl ether (90 mL, 3 × 30 mL portions) to isolate the organic phase. The combined organic extracts were filtered through a pad of anhydrous sodium sulfate to remove residual moisture, and the solvent was evaporated under reduced pressure using a rotary evaporator to afford a crude product.The crude product was purified by silica gel column chromatography using a mixed eluent of ethyl acetate (EtOAc)/petroleum ether (v/v = 5:95). The fractions containing the target compound were collected and concentrated under reduced pressure, and the resulting residue was recrystallized from n-hexane to afford 1.24g of monomer 3v-PPh_3 as a white crystalline solid, corresponding to an overall yield of 55% [1].

1.3.2 Synthesis of 4v-Xano Monomer.

All following manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. A 250 mL three-necked round-bottom flask equipped with a magnetic stir bar, a pressure-equalizing dropping funnel, and a reflux condenser (topped with an argon inlet) was charged with diethylamine ($HNEt_2$, 20.7 mL) and anhydrous n-hexane (100 mL). The resulting mixture was stirred vigorously in an ice-water bath until $HNEt_2$ was completely dissolved to form a homogeneous solution. Subsequently, a solution of phosphorus trichloride (PCl_3, 4.4 mL) in anhydrous n-hexane (10 mL) was added dropwise via the dropping funnel to the above mixture over a period of 30 minutes, while maintaining the reaction temperature strictly at 0 °C by adjusting the rate of addition and cooling bath intensity. After the completion of PCl_3 addition, the reaction mixture was stirred continuously at 0 °C for an additional 30 minutes to ensure thorough mixing and preliminary reaction of the reactants. The cooling bath was then removed, and the reaction system was heated to reflux at 70 °C (oil bath temperature) for 48 hours to drive the reaction to completion. Upon finishing the reflux period, the reaction mixture was allowed to cool naturally to room temperature under argon protection.

The resulting suspension was filtered under an argon atmosphere using a pre-dried glass frit to separate the insoluble by-products. The collected solid residue was washed twice with anhydrous n-hexane (20 mL each time) to recover any adsorbed target product, and the washings were combined with the filtrate. The combined organic solution was concentrated using rotary evaporation to remove solvent, affording bis(diethylamino)chlorophosphine [$ClP(NEt_2)_2$] as a white solid. It was used directly for the next reaction without further processing.

All following manipulations were carried out under an inert argon atmosphere using standard Schlenk techniques. A 250 mL three-necked round-bottom flask, equipped with a magnetic stir bar, a pressure-equalizing dropping funnel, and a gas inlet adapter, was charged with 9,9-dimethylxanthene (5.0 g, 24 mmol), N,N,N′,N′-tetramethylethylenediamine (TMEDA, 9.0 mL, 60 mmol), and anhydrous diethyl ether (40 mL). The resulting mixture was stirred at ambient temperature until a homogeneous solution was formed, then cooled to 0 °C using an ice-water bath. n-Butyllithium (n-BuLi, 2.5 M in hexane, 24 mL, 60 mmol) was added dropwise via the dropping funnel over a period of 30 minutes, maintaining the internal temperature strictly at 0 ^{o}C. After complete addition, the reaction mixture was stirred at 0 ^{o}C for an additional 30 minutes.

Subsequently, the cooling bath was removed, and the system was allowed to warm slowly to room temperature (rt, ~25 ^{O}C) with continuous stirring for 24 hours to drive the deprotonation to completion.

Thereafter, the reaction flask was transferred to a dry ice-acetone bath (-78 ^{O}C) and equilibrated at this temperature for 15 minutes. A pre-prepared solution of bis(diethylamino)chlorophosphine ($ClP(NEt_2)_2$, 60 mmol) in anhydrous diethyl ether (10 mL) was added dropwise to the lithiated species over 20 minutes, and the resulting mixture was stirred overnight (12-16 hours) while gradually warming to room temperature.

Upon completion of the reaction (monitored by thin-layer chromatography, TLC), the mixture was filtered under argon atmosphere through a pad of celite. The filter cake was rinsed twice with anhydrous diethyl ether (2 × 15 mL), and the combined filtrates were concentrated using rotary evaporation to afford a crude solid. The crude solid was redissolved in anhydrous n-hexane (100 mL), and dry hydrogen chloride (HCl) gas was bubbled through the solution for 30 minutes. The HCl gas was generated in situ by dropwise addition of concentrated sulfuric acid (50 mL) to concentrated hydrochloric acid (25 mL) using a sulfuric acid drying train.The resulting mixture was again filtered under argon atmosphere, and the collected solid was washed twice with anhydrous n-hexane (2 × 20 mL). Final concentration via rotary evaporation afforded compound D as a white solid. D was used directly for the next reaction without further processing.

Under an argon atmosphere, a 250 mL three-necked round-bottom flask was charged with 4-vinylphenol (5.36 g), 4-dimethylaminopyridine (DMAP, 0.27 g), triethylamine (NEt_3, 15 mL), and anhydrous tetrahydrofuran (THF, 50 mL). The resulting mixture was stirred at ambient temperature until a homogeneous solution was formed. Subsequently, a solution of compound D (10 mmol) in anhydrous THF (10 mL) was added dropwise to the reaction system via a dropping funnel, and the mixture was continuously stirred for 4 hours to ensure complete conversion.

Upon completion of the reaction (monitored by thin-layer chromatography, TLC), THF was removed under reduced pressure using a rotary evaporator. The residual oil was dissolved in toluene, and the resulting solution was filtered through a pad of celite. The filtrate was concentrated under reduced pressure to afford a crude product. The crude product was further purified by silica gel column chromatography using a mixed eluent of ethyl acetate (EtOAc) and petroleum ether (v/v = 5:95). The synthesis route of B, C and D were according to our previous works [2]. The collected fractions containing the target compound were combined and concentrated, followed by recrystallization from n-hexane. Finally, a white crystalline solid (0.92g of 4v-Xano monomer) was obtained with high purity, and its structure was confirmed by ^{1}H NMR and ^{13}C NMR and HRMS(m/z, $[M+H]^+$ calc. for $C_{47}H_{41}P_2O_5^+$, 747.2424; found, 747.2452). The total yield of 4v-Xano was 5.1 %.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 7.4 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.32 (dd, J = 9.0, 2.0 Hz, 1H), 7.21 (m, 8H), 7.14 – 7.06 (m, 1H), 7.00 (d, J = 8.5 Hz, 8H), 6.61 (m, 4H), 5.59 (d, J = 17.6 Hz, 4H), 5.14 (d, J = 10.9 Hz, 4H), 1.64 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.22, 155.20, 155.17, 152.29, 152.18, 152.07, 136.29, 132.99, 130.29, 129.12, 128.61, 127.70, 127.51, 127.34, 123.94, 120.28, 120.23, 120.18, 115.50, 112.73, 34.26, 32.06. ^{31}P NMR (162 MHz, Chloroform-d) δ 149.75.

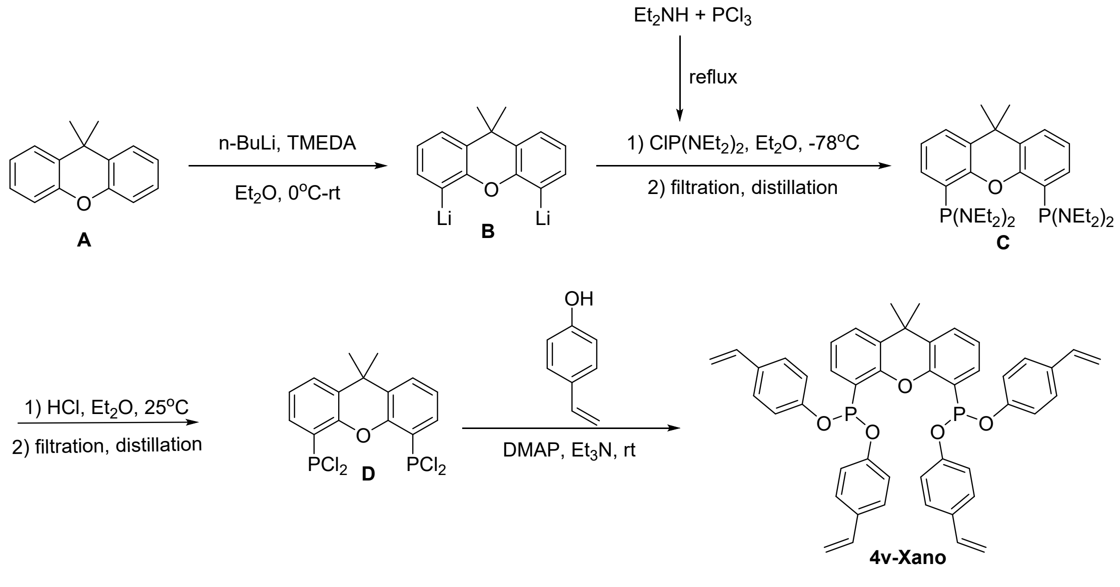

Figure S1 Typical synthesis procedure of 4v-Xano monomer

References:

[1] a) Q. Sun, M. Jiang, Z. Shen, et al. Chem. Commun., 2014, 50, 11844; b) M. Jiang M., L. Yan, Y. Ding, et al. J. Mol. Catal. A: Chem., 2015, 404, 211; c) Y. B. Zhou, C. Y. Li, M. Lin, et al. Adv. Syn. & Catal., 2015, 357, 2503; d) C. Li, L. Yan, L. Lu, et al. Green Chem., 2016, 18, 2995.

[2] C. Li, K. Sun, W. Wang, et al. J. Catal., 2017, 353(353): 123-132.

1.3.3 Synthesis of CPOL-Xano&10PPh_3.

All manipulations were performed under an inert argon atmosphere. Typically, 2.0 g of 3v-PPh_3 and 0.2 g of 4v-Xano were accurately weighed and dissolved in 20 mL of anhydrous tetrahydrofuran (THF, ≥99.9%, dried over molecular sieves 4Å prior to use) in a flame-dried Schlenk flask. Subsequently, 50 mg of 2,2'-azobis(isobutyronitrile) (AIBN, recrystallized from methanol to remove impurities) was added as the free-radical initiator. The mixture was magnetically stirred at room temperature until complete dissolution of all components was achieved, ensuring homogeneous dispersion of monomers and initiator.

The homogeneous solution was then transferred via an Ar-purged syringe into a 100 mL stainless-steel autoclave equipped with a Teflon liner. The autoclave was sealed tightly, purged with Ar three times to eliminate residual air, and subsequently placed in a preheated oven maintained at 100 ± 1 °C for a controlled polymerization duration of 24 h. After the polymerization was completed, the autoclave was allowed to cool down naturally to room temperature. The resulting CPOL was retrieved, subjected to Soxhlet extraction with anhydrous THF for 8 h to remove unreacted monomers, oligomers, and residual initiator, and then dried under vacuum at 60 °C for 6 h until a constant weight was achieved. The purified CPOL was collected and stored in a desiccator for subsequent characterization.

CPOL with different mass ratios of 4v-Xano to 3v-PPh_3 were prepared following the identical procedure described above, except for adjusting the mass ratio of the two monomers.

1.3.4 Preparation of Rh/CPOL-Xano&10PPh_3.

The Rh/CPOL catalyst was fabricated via a facile solution impregnation method under an inert atmosphere, as detailed below. Typically, rhodium acetylacetonate dicarbonyl [$Rh(CO)_2acac$, 0.0074 g] was dissolved in 30 mL of anhydrous tetrahydrofuran (THF) in a 50 mL three-necked round-bottom flask purged with argon. The mixture was stirred vigorously for 20 minutes to afford a homogeneous yellowish solution. Subsequently, 2.0 g of CPOL support was added to the above solution under a continuous argon flow. The resulting suspension was stirred magnetically at room temperature for 24 h under argon atmosphere to facilitate the sufficient anchoring of rhodium species onto the CPOL support. Afterwards, the solid product was isolated by vacuum filtration, followed by thorough washing with 30 mL of anhydrous THF. The fresh Rh/CPOL catalyst was finally dried under vacuum at 60 °C for 12 h to remove residual solvent.

1.4 Catalytic performance evaluation

The hydroformylation of 1-octene was carried out in a 50 mL stainless-steel autoclave equipped with a magnetic stir bar for homogeneous mixing. The reaction system was assembled by sequentially adding 5.0 g of toluene (as the solvent), 0.0686 g of Rh/CPOL catalyst (rhodium loading: 0.15 wt%), and 0.5611 g of 1-octene, corresponding to a substrate-to-catalyst molar ratio (S/C) of 5000. Subsequently, the autoclave was sealed and purged with syngas ($CO:H_2$= 1:1, v/v) for three cycles to completely eliminate air from the reactor. After purging, the autoclave was pressurized with the same syngas to an initial pressure of 1.0 MPa. The reaction was initiated by heating the autoclave to 373 K (100 °C) in a temperature-controlled oil bath, and maintained at this temperature for 5 h under constant stirring at 200 r/min.

Upon completion of the reaction, the autoclave was cooled to ambient temperature naturally, and the residual pressure was carefully released under atmospheric conditions. The reaction mixture was then subjected to centrifugation. The qualitative and quantitative analyses of the reaction products were performed using an Agilent 7890B gas chromatograph (GC) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). n-Butanol was employed as the internal standard to ensure accurate quantification of 1-octene conversion, aldehyde selectivity, and n/i ratio.

TON was calculated using following equation:

$$\mathrm{TON} = \frac{\mathrm{N(1\text{-}octene)}}{\mathrm{N(Rh)}} \times \mathrm{conversion}$$

Where, N(1-octene) is the amount of 1-octene, N(Rh) is the amount of rhodium, conversion is the conversion rate of 1-octene.

Or: TON =TOF×Time for continuous reaction.

For the recycling evaluation, upon completion of the reaction, the autoclave was cooled to room temperature and carefully opened inside a nitrogen-filled glove box. The catalyst was recovered via centrifugation and subsequently reused directly in the next run without further purification.

2. Hydroformylation of 1-octene

Table S1. Hydroformylation of 1-octene using different catalysts [a,b]

temp.	conv. (%)	Alkane sel. (%)	iso-alkene sel. (%)	Aldehydes sel. (%)	n/i ratio	TON
80℃	35.3	1.8	7.7	90.5	8.4	1765
100℃	93.3	1.6	11.2	87.2	11.0	4665
120℃	85.2	3.1	23.0	74.0	10.5	4260
140℃	96.2	6.8	37.5	55.7	9.0	4810

[a] Reaction conditions: 0.5611g 1-octene (5.0 mmol), 0.0686 g catalyst (Rh loading of 0.15 wt%), S/C = 5000, CO:H_2 = 1:1 (1.0 MPa initial pressure), 5.0g toluene, 100 °C for 5h

[b] gas chromatography: Agilent 7890B gas chromatography with an HP-5 column, using an FID detector and 1,4-dioxane as an internal standard

Table S2. Hydroformylation of 1-octene using different pressure [a, b]

press	conv. (%)	alkane sel. (%)	iso-alkene sel. (%)	aldehydes sel. (%)	n/i ratio	TON
0.5MPa	65.0	2.3	22.7	75.0	12.2	3250
1.0MPa	93.3	1.6	11.2	87.2	11.0	4665
1.5MPa	75.4	1.4	8.3	90.3	8.3	3770
2.0MPa	65.1	1.4	6.0	92.6	7.2	3255

[a] Reaction conditions: 0.5611g 1-octene (5.0 mmol), 0.0686 g catalyst (Rh loading of 0.15 wt%), S/C = 5000, CO:H_2 = 1:1, 5.0g toluene, 100 °C for 5h

[b] gas chromatography: Agilent 7890B gas chromatography with an HP-5 column, using an FID detector and 1,4-dioxane as an internal standard

3. Hydroformylation of propene in a fixed-bed reactor

The hydroformylation of propene was carried out in a continuous-flow fixed-bed reactor. The reactor had a length of 40 cm and an inner diameter of 9 mm. In a typical run, the bottom of the reactor was filled with 12 mL of quartz sand, followed by a small plug of silica wool (< 1 mL) and 0.3 g of Rh/CPOL-1xano&10PPh$_3$ catalyst (ca. 1.2 mL). Then, another small plug of silica wool (< 1 mL) was added, and the upper part of the reactor was filled with an additional 12 mL of quartz sand. In this way, the catalyst bed was positioned in the middle of the reactor. The reactor was heated by a tube furnace, and the temperature was monitored by a thermocouple inserted into the thermocouple well located between the sample ports. The effluent passed through a condenser filled with 150 mL of deionized water (introduced into the condenser by a pump). The products were trapped by dissolution in the water. The sampling valve was opened to withdraw the aqueous sample, and the aqueous solution containing the products was analysed off-line. After sampling, 150 mL of fresh deionized water was pumped into the condenser again to capture the linear and branched butanal (n-butanal and isobutanal).

The aqueous solutions were analysed using an Agilent 7890A gas chromatograph equipped with an HP-5 column (30 m × 0.32 mm i.d.). The column temperature was initially held at 40 °C for 5 min, then increased to 100 °C at 5 °C min^{-1}, held at 100 °C for 2 min, and finally raised to 175 °C at 10 °C min^{-1}. Helium was used as the carrier gas and the column head pressure was maintained at 4 psi. The injector temperature was 250 °C (inlet pressure 4 psi, split ratio 50:1). The flame ionization detector (FID) was held at 220 °C, with hydrogen and air flows of 30- and 300-mL min^{-1}, respectively. Ethanol was employed as an internal standard, and the GC was calibrated with known amounts of linear and branched butanal.

The tail gas was analysed on-line using another Agilent 7890A gas chromatograph equipped with a Porapak-QS column (3 m × 3 mm i.d.). The column temperature was held at 40 °C for 5 min and then increased to 150 °C at 5 °C min^{-1}. Helium was used as the carrier gas at a column flow rate of 22 mL min^{-1}. The injection port was maintained at 120 °C with a total helium flow of 25 mL min⁻¹. The thermal conductivity detector (TCD) was operated at 250 °C with a reference gas flow of 30 mL min⁻¹. The GC was calibrated using known amounts of H_2, CO, propene, and propane, and the results were calculated by the normalization method. A simplified flow chart of the hydroformylation setup is shown in Scheme 1.

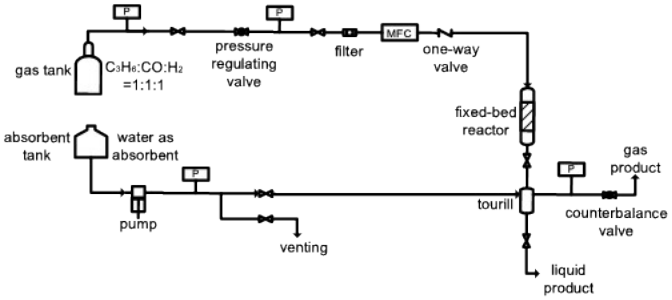

Figure S2 The simple flow chart of the hydroformylation equipment（reaction conditions: T =120 °C, P = 1.0 MPa (C_3H_6 : CO : H_2 = 1 : 1 : 1), GHSV = 1500 h⁻¹）.

4. SEM and TEM images of catalyst

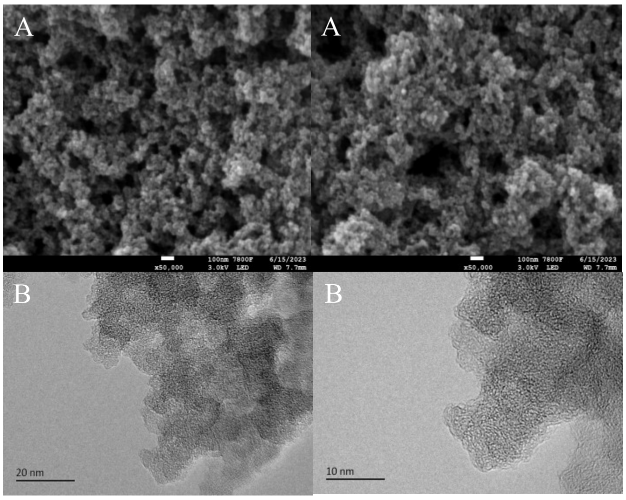

Figure S3 (A) SEM and (B) TEM images of CPOL-1Xano&10PPh3

5. NMR Spectra of 4v-Xano monomer

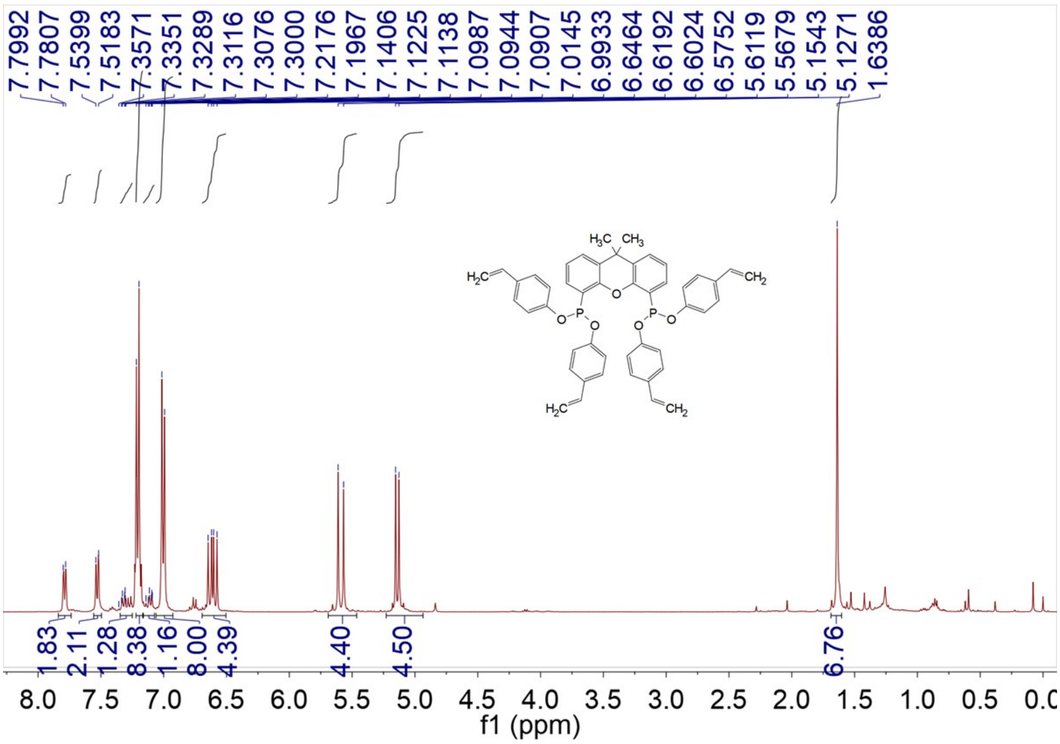

Figure S4 ^{1}H NMR of 4v-Xano monomer

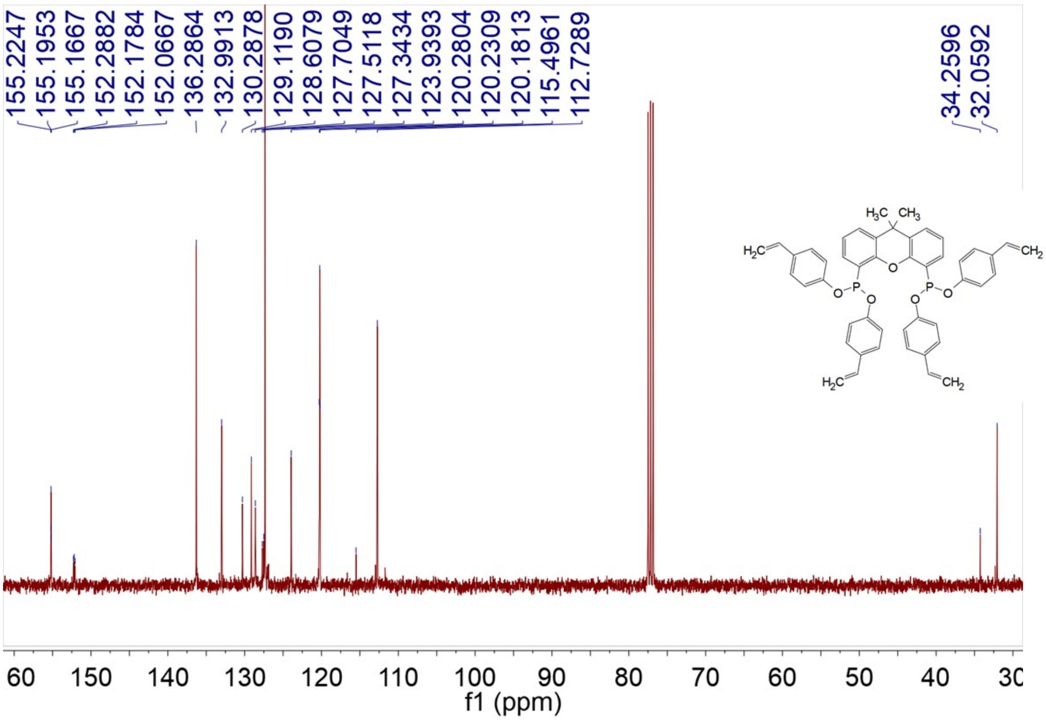

Figure S5 ^{13}C NMR of 4v-Xano monomer

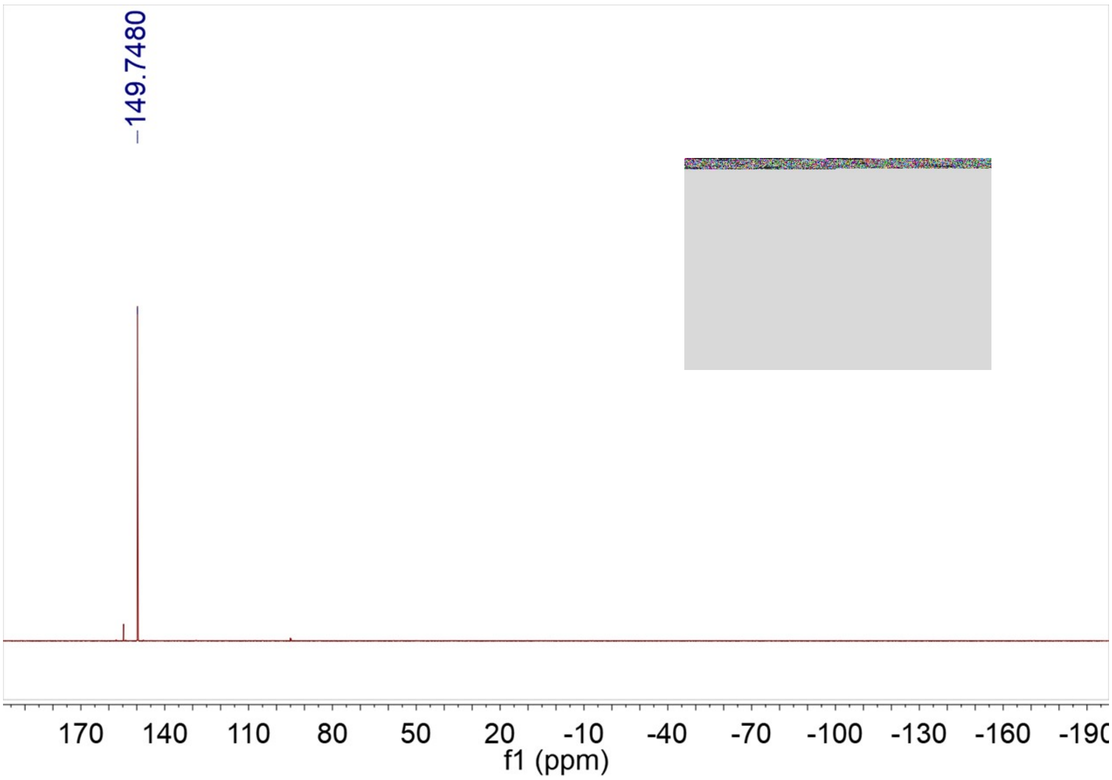

Figure S6 ^{31}P NMR of 4v-Xano monomer

6. Rh concentration of fresh and spend catalysts

Table S3. Rh concentration of fresh and spend catalysts

Sample	Rh content(wt.%)
Rh/CPOL-1Xano&10PPh$_3$ (fresh sample)	0.144 %
Rh/CPOL-1Xano&10PPh$_3$ (spend sample, 6 runs)	0.142 %

7. Textural Parameters of POLs, CPOLs, Rh/POLs and Rh/CPOLs

Table S4. Textural Parameters of POLs and CPOLs

Polymers	Pore volume (cm^3/g)	BET surface area (m^2/g)	Micropore (%)
CPOL-Xano/20PPh$_3$	1.690	949.3	24.5
CPOL-Xano/10PPh$_3$	2.576	1455.3	24.9

CPOL-Xano/5PPh$_3$	1.985	1144.7	25.6
POL-Xano	0.246	247.7	39.9

Table S5. Textural Parameters of Rh/POLs and Rh/CPOLs

Catalysts	Pore volume (cm^3/g)	BET surface area (m^2/g)	Micropore (%)
Rh/CPOL-Xano/20PPh$_3$	1.390	873.9	27.5
Rh/CPOL-Xano/10PPh$_3$	1.907	1334.4	25.5
Rh/CPOL-Xano/5PPh$_3$	1.543	914.2	24.4
Rh/POL-Xano	0.212	213.3	39.1