

Supporting Information

The effect of the position of cross-linkers on the structure and microenvironment of PPh₃ moiety in porous organic polymers

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1. Experimental Procedures

1.1 Characterizations

Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Quantachrome Autosorb-1 system. The samples were degassed for 12 h at 393 K before test. The specific surface areas were calculated from the adsorption data using Brunauer–Emmett–Teller (BET) methods. The pore size distribution curves were obtained from the adsorption branches using the non-local density functional theory (NLDFT) method.

Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449 F3), the samples were heated at a rate of 10 K min⁻¹ from 313 K to 973 K under a nitrogen atmosphere.

Transmission electron microscopy (TEM) was performed using a JEM-2100 with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was performed using a JSM-7800 F.

Solid-state ³¹P MAS NMR experiments were recorded on a VARIAN Infinity plus spectrometer equipped with a 2.5 mm probe at a frequency of 161.8 MHz. The experiments were recorded under a magic angle spinning rate of 10 kHz and a delay of 3.0 s. Solid-state ³¹P NMR chemical shifts were referenced to 85% H₃PO₄. ¹³C MAS NMR spectra were obtained under a magic angle spinning rate of 6 kHz.

XPS was conducted using a Thermo Scientific instrument and the spectrometer binding energy was calibrated through the reference C 1s (284.6 eV).

The FT-IR facility for characterizing the catalytic performance of Rh/3vPPh₃-POLs in hydroformylation reactions consisted of an in-situ cell. The gaseous feeds, recirculating cooling water system, temperature controller and vacuum pump were connected to the in-situ cell. In situ FT-IR spectra were collected on a Fourier transform infrared spectrometer (Thermo Scientific Nicolet iS50) equipped with an in-situ cell accessory for testing all the samples. The MCT/A was used as detector. All spectra were collected with a resolution of 4 cm⁻¹ and accumulation of 32 scans. The ZnSe windows were installed in separate stainless-steel housings. As a typical run, the sample (About 10 mg) was pressed into sample vessel (diameter: 13 mm) and then loaded into the in-situ cell. Then the in-situ cell was sealed and purged with nitrogen for 30 min. Later, switch on the recirculating cooling water supply and regulate the temperature controller to 383 K. The

background spectrum was collected after heat to 383 K for 60 min in a flow of N₂. Subsequently, a syngas (CO/H₂ = 1:1, 0.1 MPa) was purged into the in-situ cell for 60 min. After 60 min of adsorption, the cell was purged under N₂. The real-time FTIR spectrum data was collected every 5 min until the spectrogram was unchanged.

Rh K-edge X-ray absorption fine structure (EXAFS and XANES) spectra of the prepared samples were obtained at the BL14W1 beamline of SSRF, SINAP (Shanghai, China) with the use of a Si (311) crystal monochromator. The storage ring was operated at 3.5 GeV with injection currents of 200 mA. Pd foil was used as standard sample, and the X-ray absorption spectra were measured in the transmission mode. All spectra of the prepared Rh/3vPPh₃-POLs were tested in the fluorescence mode. The raw data were energy-calibrated at 23220 eV, first inflection point, background-corrected, and normalized using the IFEFFIT software. Fourier transformation of the EXAFS data was applied to the k^3 -weighted functions. For the curve-fitting analysis, Rh-C and Rh-P path parameters were obtained from the ab initio multiple scattering codes FFEF6.

Inductively coupled plasma (ICP) was measured on an ICPS-8100 apparatus.

2. Supporting Tables

Table S1 Hydroformylation of 1-octene using different samples

Samples	Conversion (%)	Aldehydes selectivity (%)	Iso-alkenes selectivity (%)	Alkane selectivity (%)	l/b ratio
Rh(CO) ₂ (acac) ^{a)}	99	8.5	74.7	16.8	0.6
Rh- <i>p</i> -3vPPh ₃ ^{b)}	99	89.0	9.7	1.3	2.9
Rh- <i>m</i> -3vPPh ₃ ^{c)}	98	93.1	6.2	0.7	4.0
Rh- <i>o</i> -3vPPh ₃ ^{d)}	99	92.8	6.9	0.3	4.9
Rh/ <i>p</i> -3vPPh ₃ -POL	98	65.5	21.7	12.8	3.0
Rh/ <i>m</i> -3vPPh ₃ -POL	99	88.6	10.4	1.0	10.1
Rh/ <i>o</i> -3vPPh ₃ -POL	99	47.1	49.8	3.1	2.3

Reaction conditions: 0.060 g catalyst (Rh loading at 0.25 %), S/C=6000, toluene (5.0 g), 383 K, 1 MPa for 12 h. Syngas: CO:H₂=1:1. ^{a)} 0.95 mg Rh(CO)₂(acac); ^{b)} 0.95 mg Rh(CO)₂(acac)+59.62 mg of *p*-3vPPh₃, ^{c)} 0.95 mg Rh(CO)₂(acac)+59.62 mg of *m*-3vPPh₃, S/C=6000. ^{d)} 0.95 mg Rh(CO)₂(acac)+59.62 mg of *o*-3vPPh₃, S/C=6000.

Table S2 The influence of syngas pressure on hydroformylation of 1-octene by Rh/*m*-3vPPh₃-POL

Pressure (MPa)	Conversion (%)	Aldehydes selectivity (%)	Iso-alkenes selectivity (%)	Alkane selectivity (%)	l/b ratio
0.5	92	83.2	13.7	3.1	15.7
1.0	99	88.6	10.4	1.0	10.1
1.5	95	89.5	7.6	2.9	10.0
2.0	94	90.9	6.7	2.4	8.1

Reaction conditions: 0.060 g Rh/*m*-3vPPh₃-POL catalyst (Rh loading at 0.25%), S/C=6000, toluene (5.0 g), 383 K for 12 h. Syngas: CO:H₂=1:1.

Table S3 The influence of temperature on hydroformylation of 1-octene by Rh/*m*-3vPPh₃-POL catalyst

Temperature (K)	Conversion (%)	Aldehydes selectivity (%)	Iso-alkenes selectivity (%)	Alkane selectivity (%)	l/b ratio
373	78	92.5	5.3	2.2	9.0
383	99	88.6	10.4	1.0	10.1
393	97	82.8	13.6	3.6	13.3
403	98	71.7	22.1	6.2	11.5

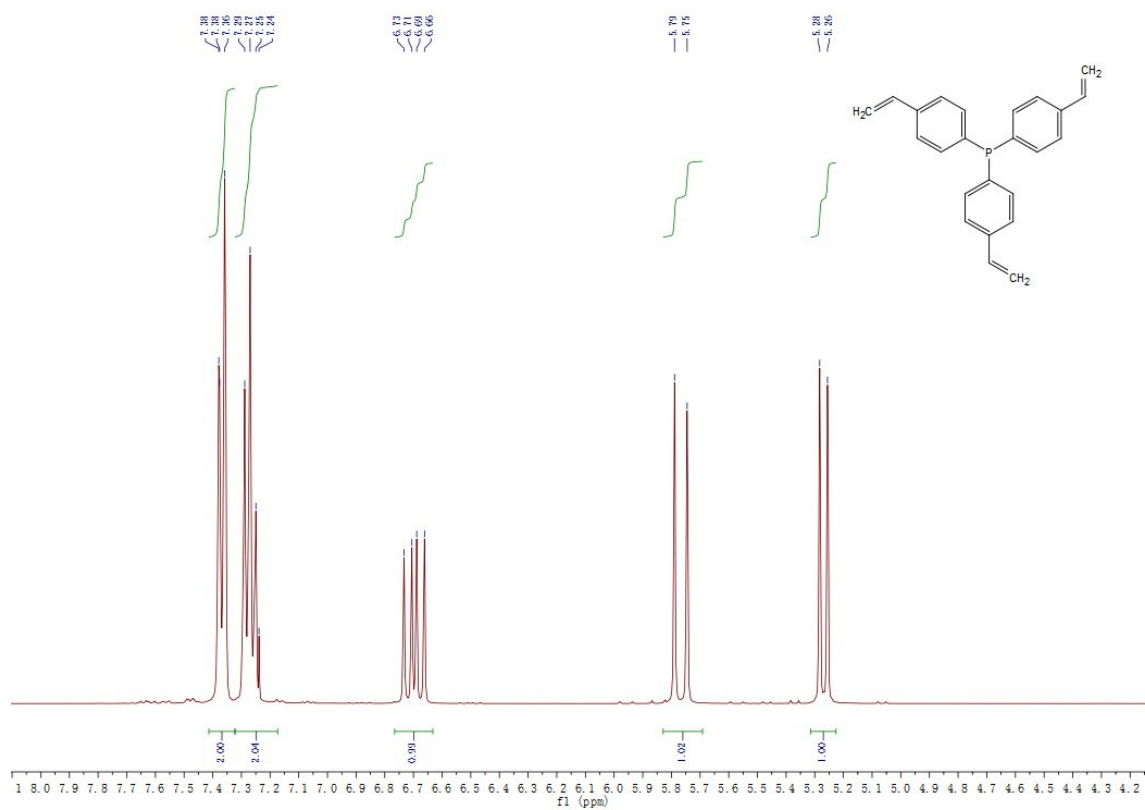
Reaction conditions: 0.060 g Rh/*m*-3vPPh₃-POL catalyst (Rh loading at 0.25%), S/C=6000, toluene (5.0 g), 1MPa for 12 h. Syngas: CO:H₂=1:1.

Table S4 Turnover frequency (TOF) of Rh/*m*-3vPPh₃-POL

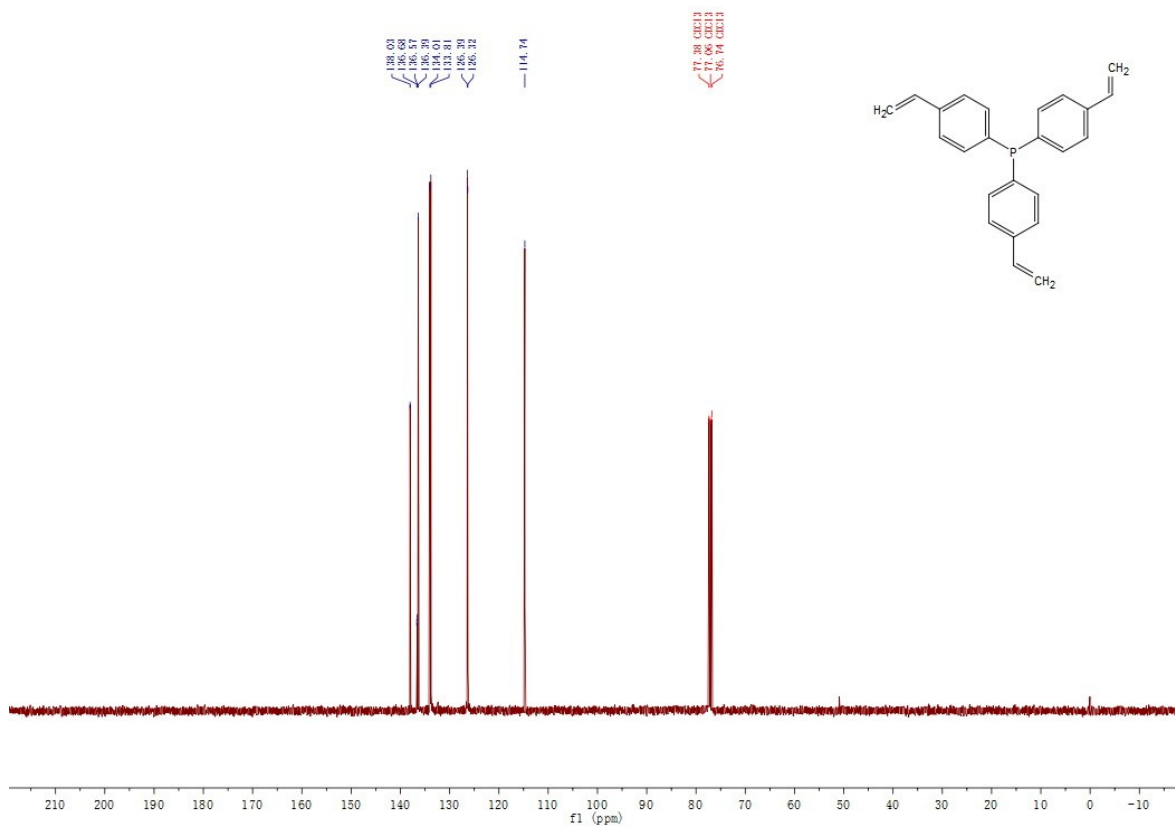
Conversion (%)	Aldehydes selectivity (%)	iso-alkenes selectivity (%)	Alkane selectivity (%)	l/b	TOF (h ⁻¹)
24	87.4	4.1	8.5	13.3	2221.6

Reaction conditions: 0.060 g catalyst (Rh loading at 0.25 %), S/C=6000, toluene (5.0 g), 383 K, 1 MPa for 40 min. Syngas: CO:H₂=1:1.

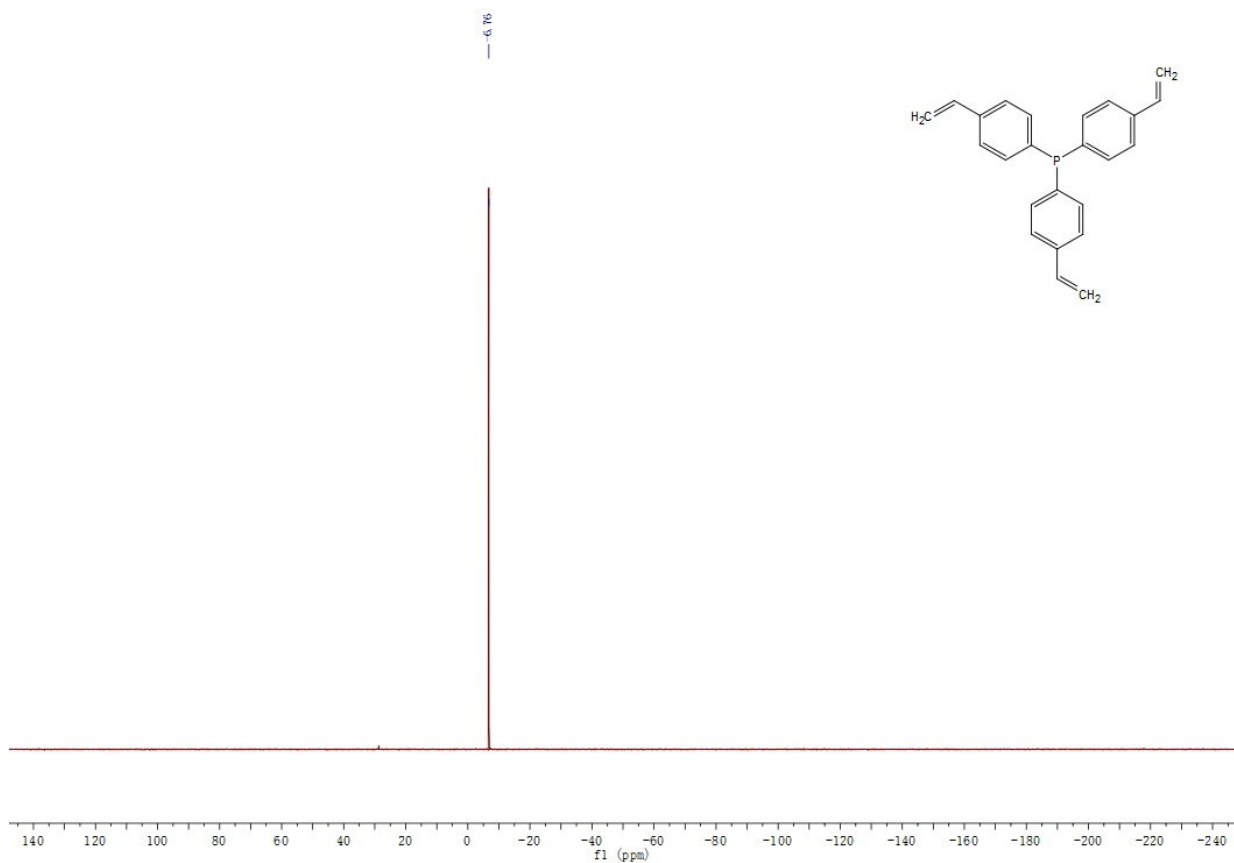
3. Supporting Figures



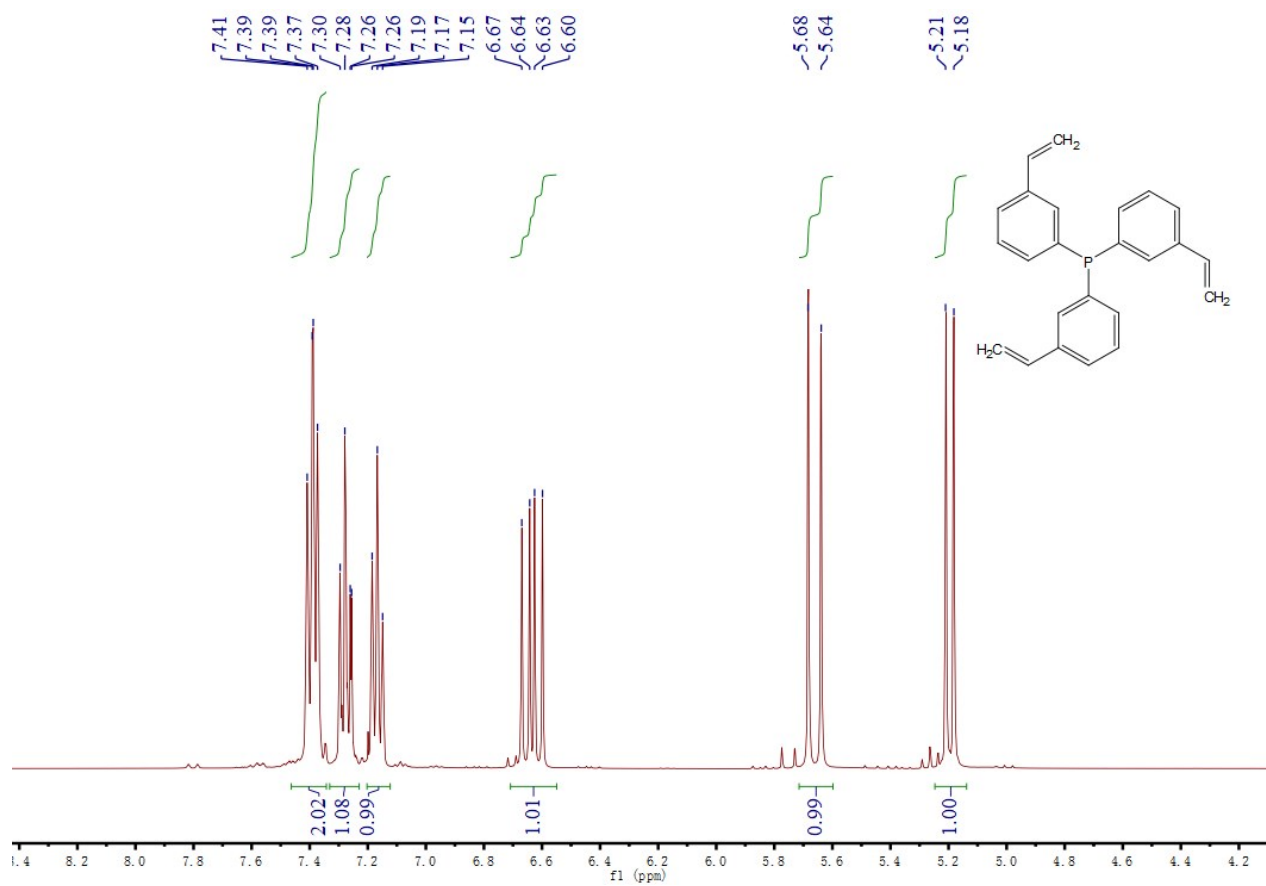
¹H NMR spectrum of *p*-3vPPH₃



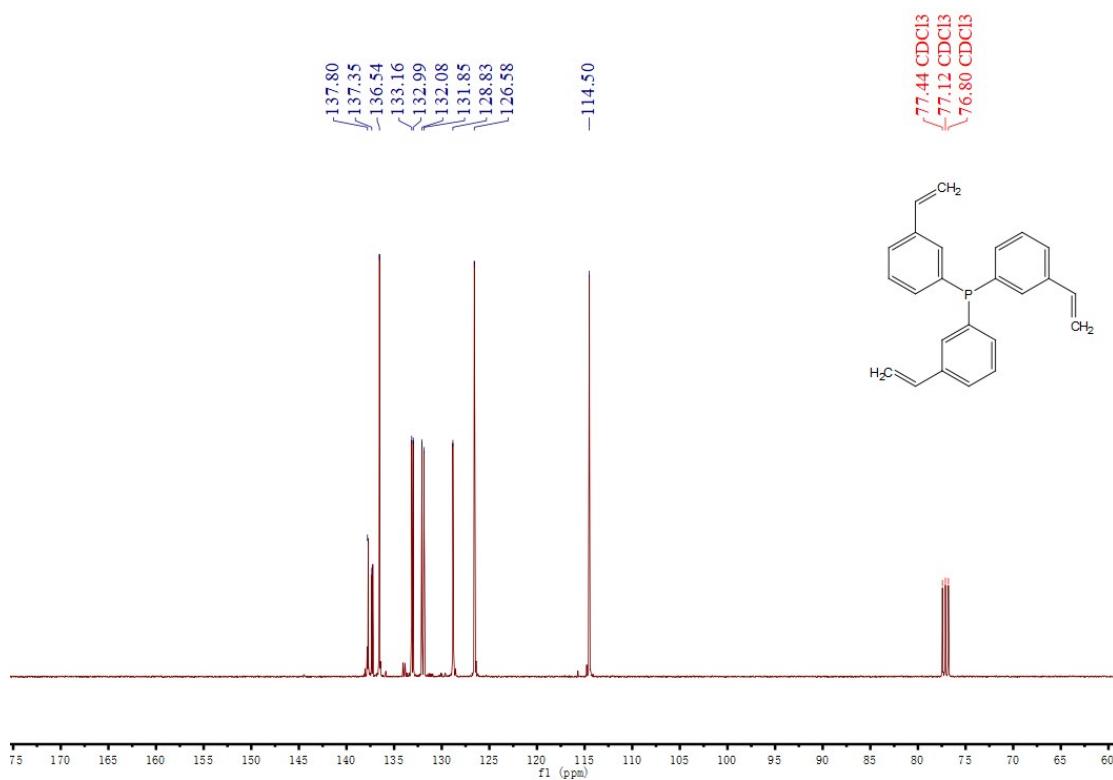
¹³C NMR spectrum of *p*-3vPPH₃



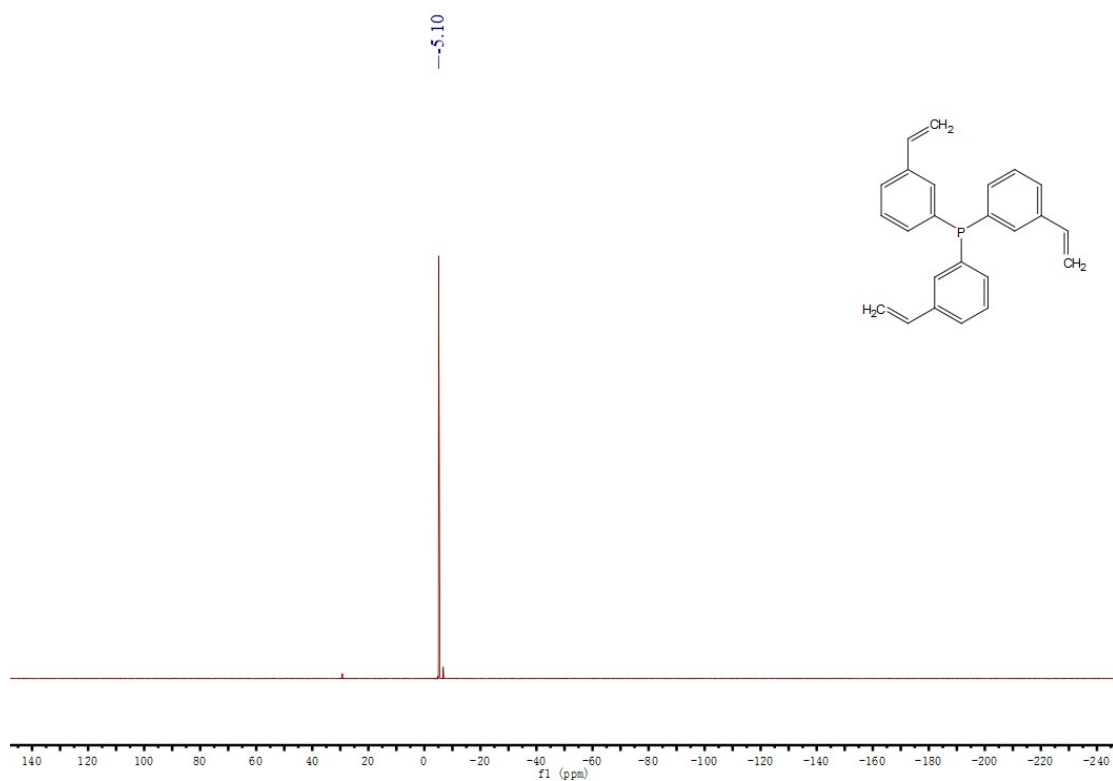
³¹P NMR spectrum of *p*-3vPPh₃



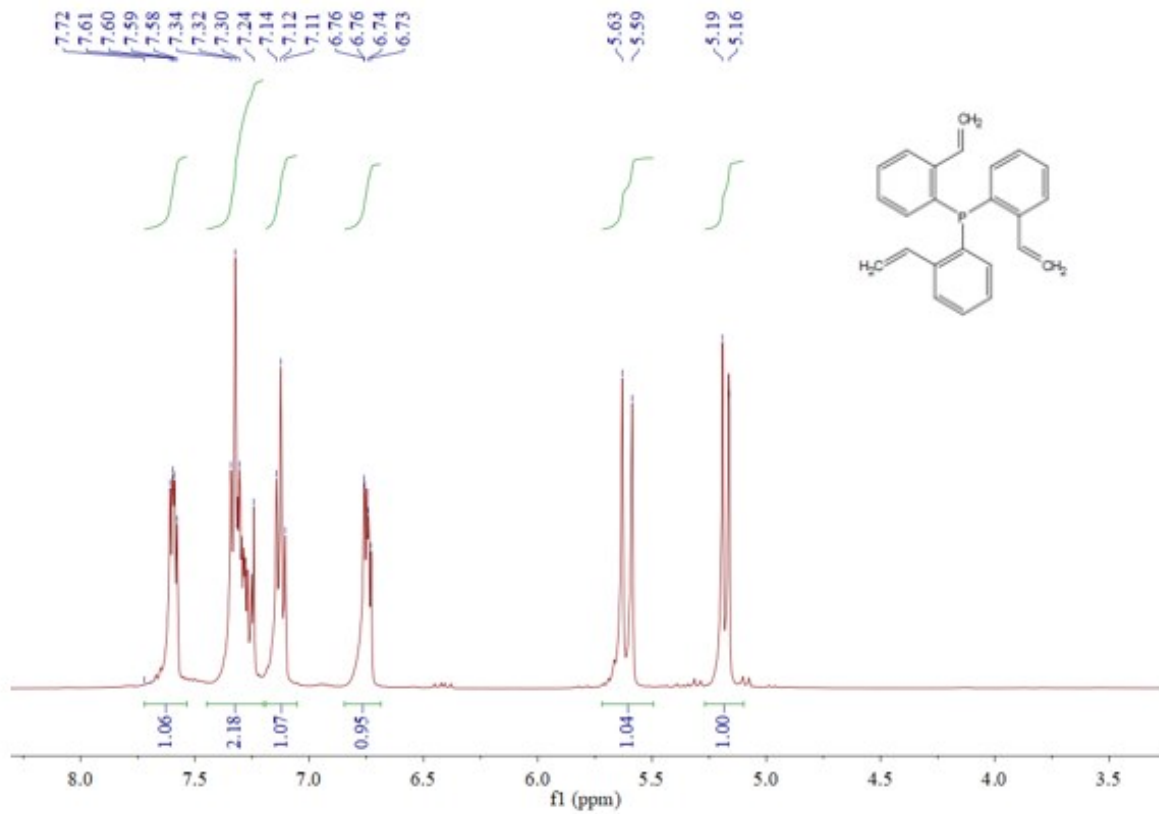
¹H NMR spectrum of *m*-3vPPh₃



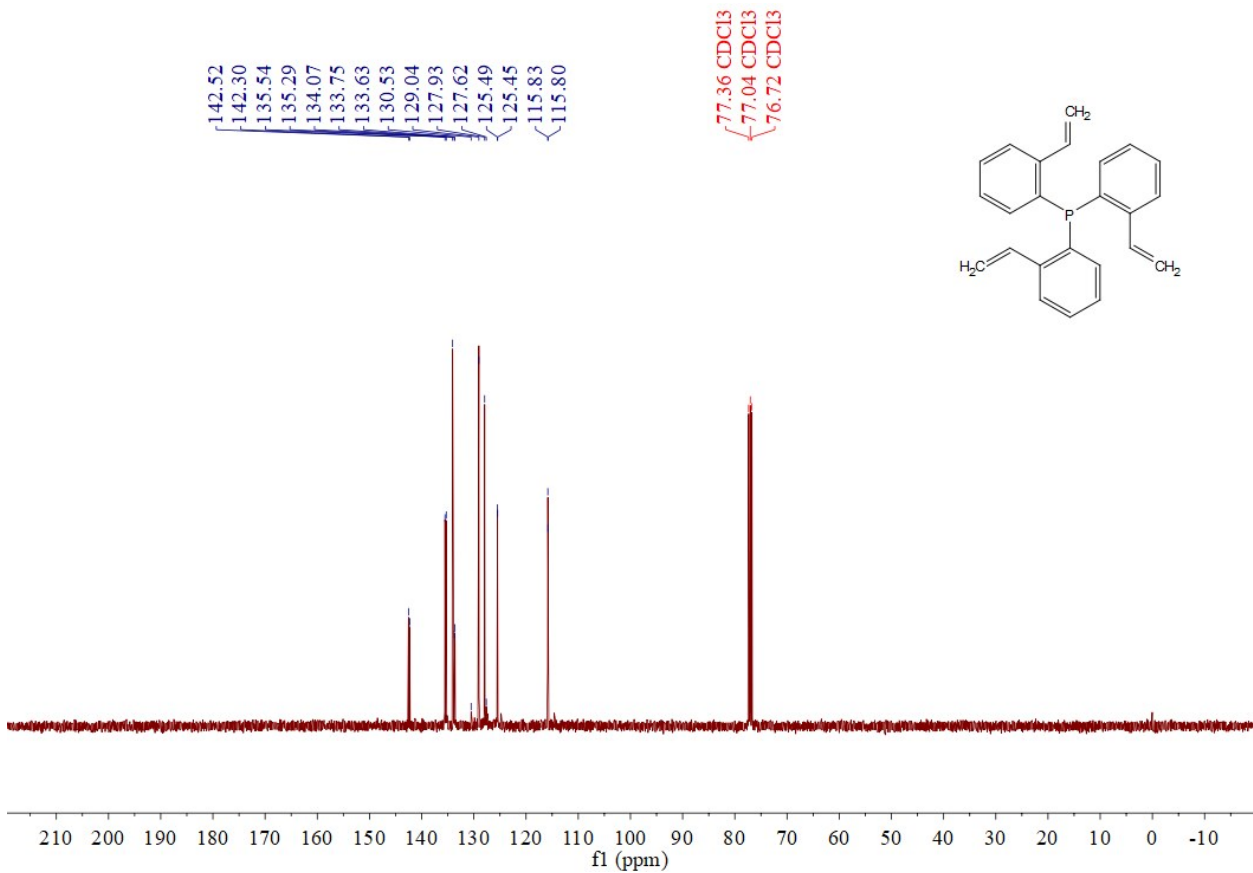
¹³C NMR spectrum of *m*-3vPPh₃



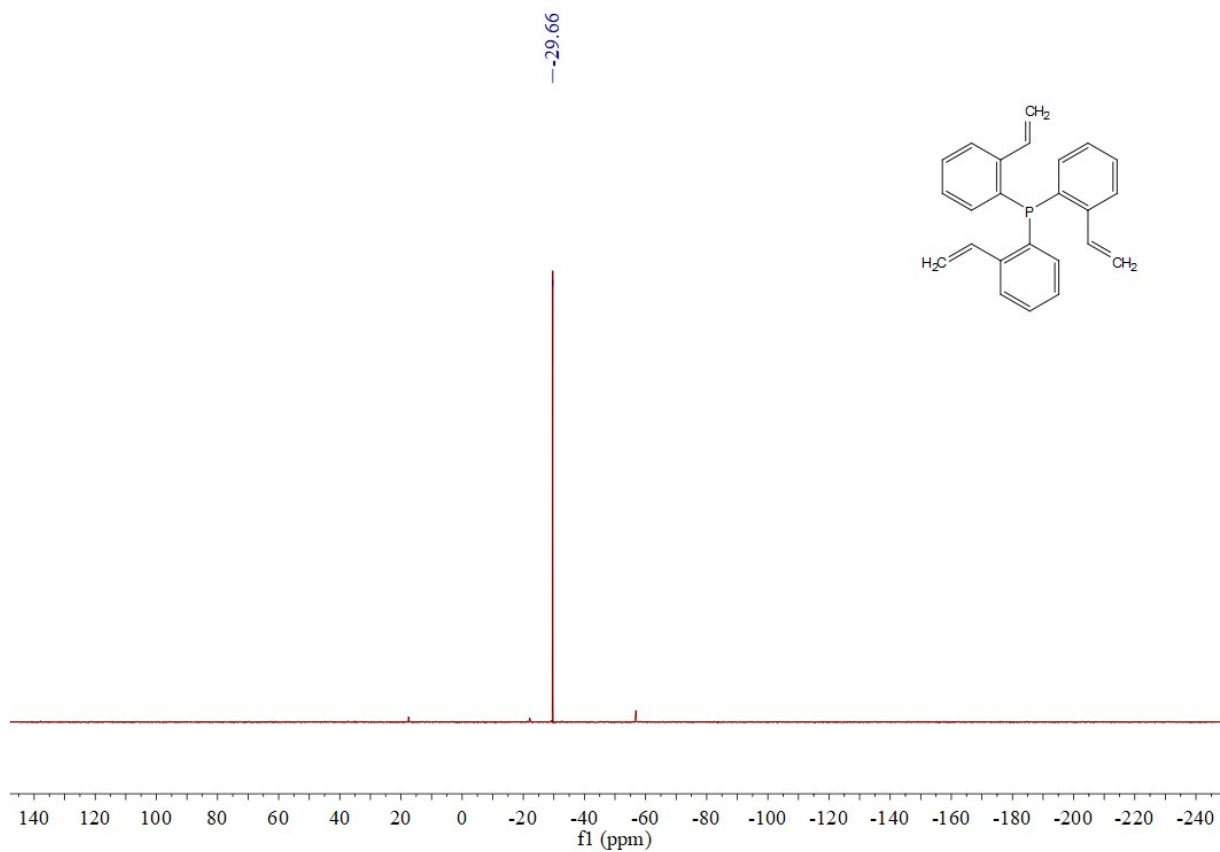
³¹P NMR spectrum of *m*-3vPPh₃



¹H NMR spectrum of *o*-3vPPh₃



¹³C NMR spectrum of *o*-3vPPh₃



^{31}P NMR spectrum of *o*-3vPPh₃

Fig. S1 NMR spectra of *p*-3vPPh₃, *m*-3vPPh₃ and *o*-3vPPh₃

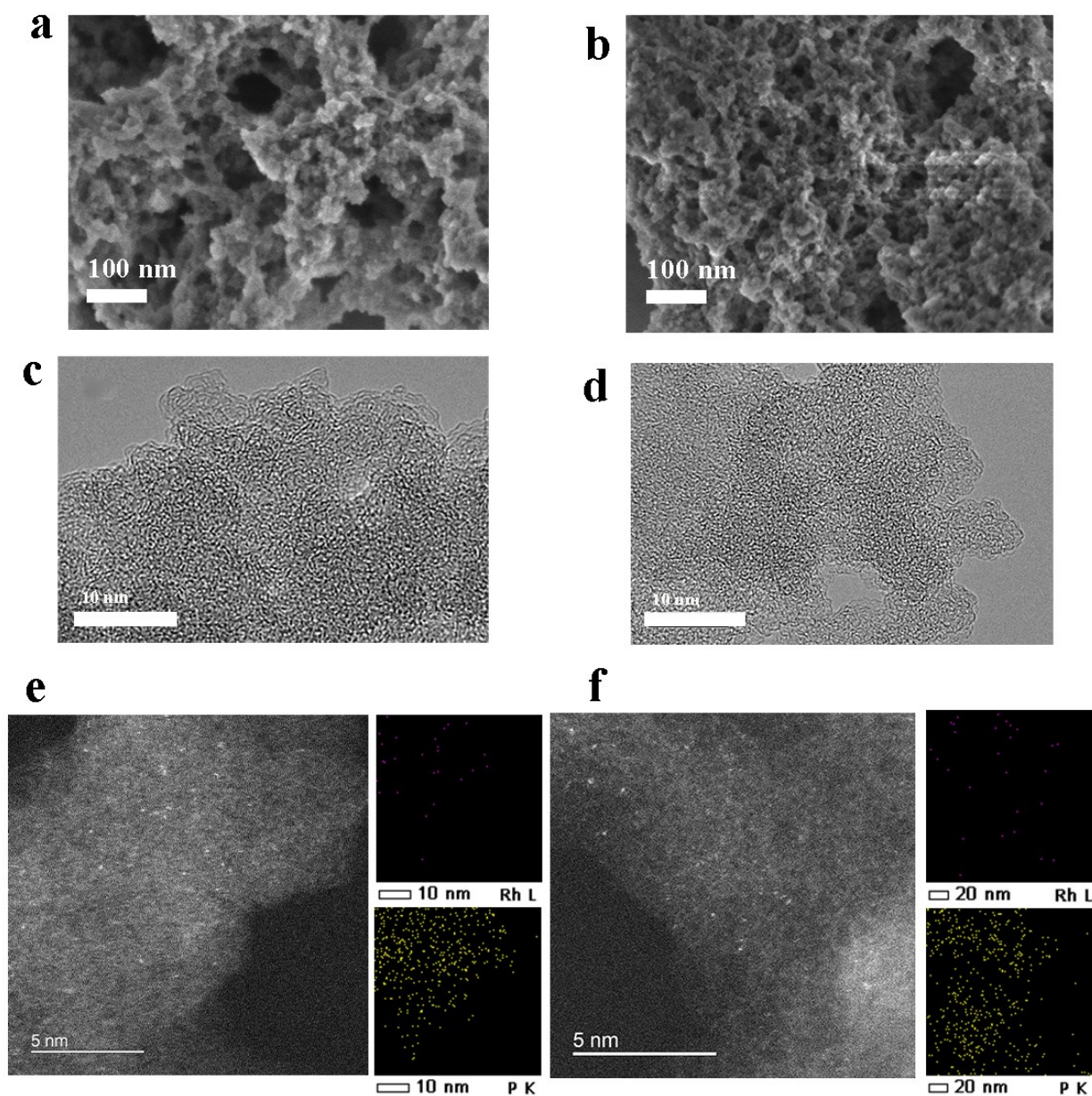


Fig. S2 (a) The SEM image of Rh/*m*-3vPPh₃-POL; (b) The SEM image of used Rh/*m*-3vPPh₃-POL; (c) The TEM image of Rh/*m*-3vPPh₃-POL; (d) The TEM image of used Rh/*m*-3vPPh₃-POL; (e) The HADDF-STEM and HADDF-EDS element maps images of Rh/*m*-3vPPh₃-POL; (f) The HADDF-STEM and HADDF-EDS element maps images of used Rh/*m*-3vPPh₃-POL.

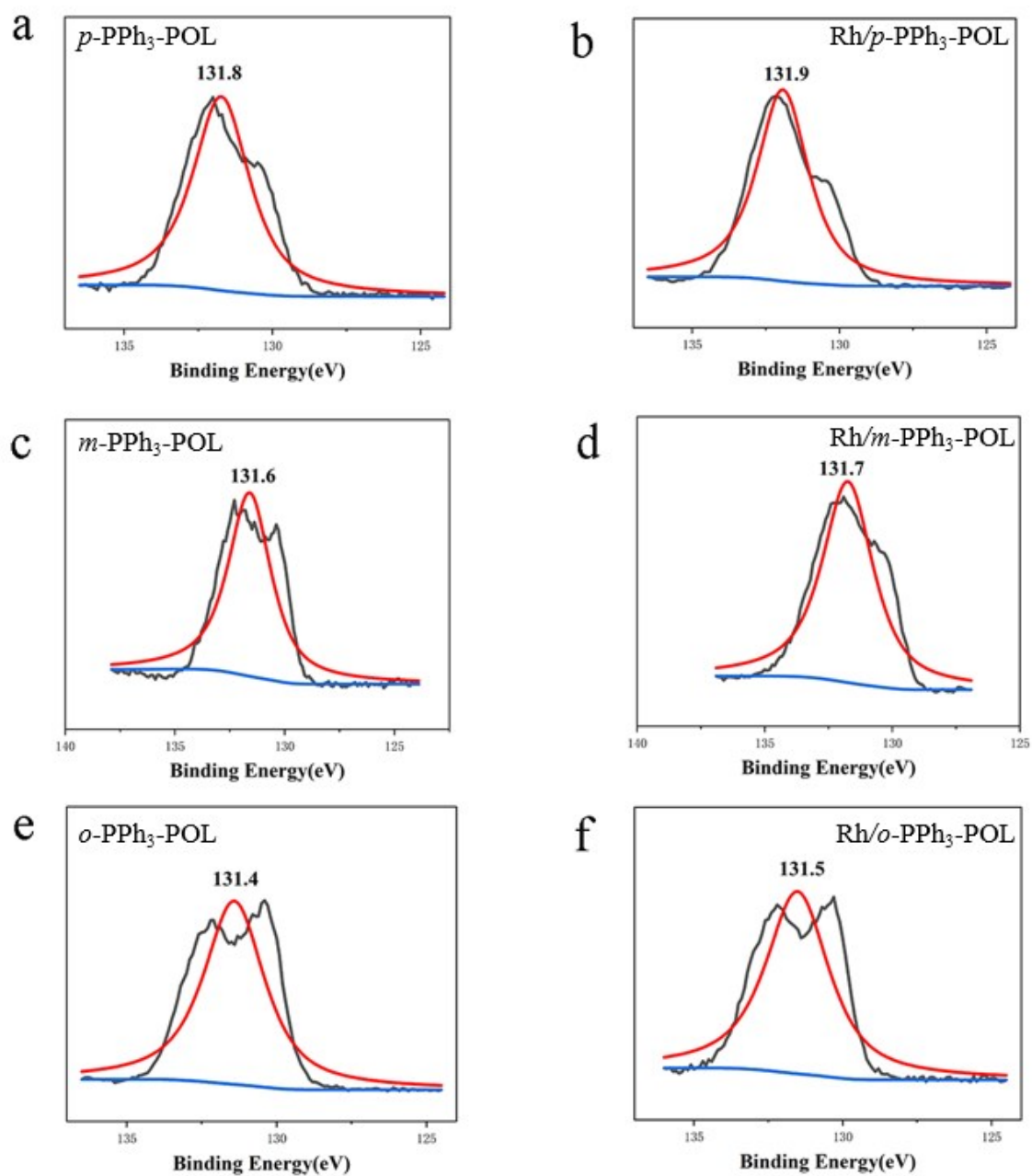
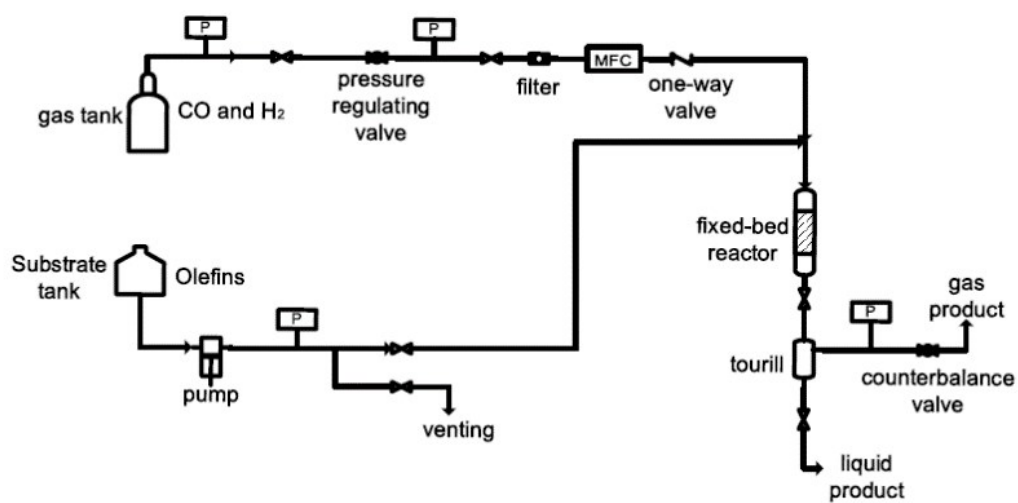


Fig. S3 The P2p XPS spectra of PPh₃-POLs and corresponding Rh/PPh₃-POLs. (a) *p*-3vPPh₃-POL, (b) 0.25wt% Rh/*p*-3vPPh₃-POL, (c) *m*-3vPPh₃-POL, (d) 0.25wt% Rh/*m*-3vPPh₃-POL, (e) *o*-3vPPh₃-POL, (f) 0.25wt% Rh/*o*-3vPPh₃-POL.

4. Supporting Scheme



Scheme S1 Flow chart of hydroformylation of 1-octene in a fixed-bed reactor.