Porous Organic Ligands (POLs) for Synthesizing Highly Efficient Heterogeneous Catalysts

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Materials. Solvents were purified according to standard laboratory methods. THF was distilled over sodium/benzophenone. Toluene and acetonitrile were distilled over calcium hydride. 4-bromostyrene, magnesium powder, acetyl bromide, PBr_3, 4-Vinylphenylboronic acid, 3-*tert*-butylphenol, $SnCl_4$, tributylamine, paraformaldehyde, Br_2, cyclohexane diamine, PPh_3, $PdCl_2$, $Pd(OAc)_2$, $RhCl_3\cdot 3H_2O$, 2,2'-biyridine (bpy), benzeneboronic acid, aryl halide, ketones, 1-octene, and 2-octene were purchased from Aladdin Company, Co. Ltd. Fuming H_2SO_4, fuming HNO_3, azobisisobutyronitrile (AIBN), and PCl_3 were obtained from Tianjin Guangfu Chemical Reagent. $Pd(PPh_3)_4$, $RhH(CO)(PPh_3)_3$, $Rh(CO)_2(acac)$ was synthesized according to the literature.

Synthesis of POL-PPh₃. POP-PPh_3 was synthesized from polymerization of trivinyl-functionalized PPh_3 (3V-PPh_3) under solvothermal conditions. As a typical run, 1.0 g of 3V-PPh_3 was dissolved in 10 mL of THF, followed by the addition of 25 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of THF under vacuum, a solid monolith was obtained.

3V-PPh_3 was synthesized from the reaction between PCl_3 (33 mmol in 30 mL of THF) and (4-vinylphenyl)magnesium bromide solution (100 mmol). After the reaction, 50 mL of saturated NH_4Cl aqueous was added. The organic phase was extracted with excessive of ethyl acetate, which was dried with $MgSO_4$. After filtering and purifying by silica gel chromatography (5% EtOAc/Petroleum ether), 3V-PPh_3 was obtained. ^1H NMR (400 MHz, DMSO-d6, 298K, TMS): δ 7.48 (d, 6H, *J*=7.6Hz), 7.22 (t, 6H, *J*=7.6Hz), 6.69-6.76 (m, 3H), 5.85 (d, 2H, *J*=18 Hz), 5.30 (d, 2H, *J*=10.8Hz) ppm. ^{13}C NMR (100 MHz, DMSO-d6) δ 115.76, 126.79, 126.86, 133.76, 133.95, 136.41, 136.55, 138.08 ppm. ^{31}P NMR (162 MHz): δ -7.94 (s, 1P) ppm.

Synthesis of nonporous polymerized PPh₃ (NOL-PPh₃). As a typical run, 1.0 g of 3V-PPh_3 was dissolved in 10 mL of acetic ether, followed by the addition of 25 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. The polymer was obtained after evaporation of acetic ether under vacuum.

Synthesis of porous polymers with different P concentrations (POPs-PPh₃). A family of porous polymers with different P concentrations were prepared from solvothermal copolymerization of divinylbenzene with 3V-PPh_3 in different ratios. As a typical run, 0.068g of 3V-PPh_3 and 0.932g of divinybenzene were dissolved in 10 mL of THF, followed by addition of 25 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of solvent, a white solid product was obtained and the P concentration in the polymer was 0.2 mmol/g.

Synthesis of M/POL-PPh$_3$. As a typical run for supporting metal species, 1 g of POL-PPh$_3$ was swelled in 40 mL of toluene for 30 min, followed by the addition of 0.052 g of Rh(CO)$_2$(acac). After stirring at room temperature under N_2 atmosphere for 24 h, the Rh(CO)$_2$(acac)/POL-PPh$_3$ was obtained after filtering, washing with excessive of toluene, and drying at 50 °C under vacuum. The metal loading was determined by inductively coupled plasma (ICP) analysis.

Synthesis of POL-bpy. POL-bpy was synthesized from polymerization of 4,4'-bis-(4-vinyl-phenyl)-2,2'-bipyridine (2V-bpy) under solvothermal conditions. As a typical run, 0.5 g of 2V-bpy was dissolved in 20 mL of THF, followed by the addition of 15 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of THF, a solid monolith was obtained, which was denoted as POL-bpy.

2V-bpy was synthesized from 2,2'-bipyridine. At first, 2,2'-bipyridine was oxidized to 2,2'-bipyridine N,N'-dioxide [^{1}H NMR, 400MHz, DMSO-d6, 298K, TMS: δ 8.32 (d, 2H, *J*=6Hz), 7.59-7.62(m, 2H), 7.47-7.51 (d, 2H), 7.39 (d, 1H, *J*=7.6Hz) ppm], which was treated with the mixture of fuming H_2SO_4 and fuming HNO_3 under stirring to form 4,4'-dinitro-2,2'-bipyridine N,N'-dioxide [^{1}H NMR, 400MHz, DMSO-d6, 298K, TMS: δ 8.67 (d, 2H, *J*=3.6Hz), 8.57 (d, 2H, *J*=6.8Hz), 8.34-8.37 (m, 2H) ppm]. After reaction with acetyl bromide, 4,4'-dibromo-2,2'-bipyridine N,N'-dioxide was obtained,[1] which was reacted with PBr_3 to form 4,4'-bromo-2,2'-bipyridine [^{1}H NMR, 400MHz, $CDCl_3$, 298K, TMS: δ 8.59 (d, 2H, *J*=1.2Hz), 8.47 (d, 2H, *J*=5.2Hz), 7.49-7.50 (m, 2H) ppm]. Finally, after the reaction of 4,4'-bromo-2,2'-bipyridine with 4-vinylphenylboronic acid, 2V-bpy was obtained. ^{1}H NMR (400MHz, $CDCl_3$, 298K, TMS): δ 8.73-8.75 (m, 4H), 7.77 (d, 2H, *J*=8Hz), 7.54-7.57 (m, 6H), 6.75-6.82 (m, 2H), 5.85 (d, 2H, *J*=18Hz), 5.34 (d, 2H, *J*=10.8Hz) ppm. ^{13}C NMR (100MHz, $CDCl_3$) 156.51, 149.55, 148.72, 138.3, 137.35, 136.06, 127.21, 126.77, 121.33, 118.84, 114.82 ppm.

Synthesis of CuBr$_2$/POL-bpy. POL-bpy (0.5 g) and $CuBr_2$ (0.104 g) was added in 50mL of acetone and the mixture was striied at room temperature overnight. After that the mixture was filtrated, washed and then dried at 50 °C under vacuum. The obtained powder was denoted as $CuBr_2$/POL-bpy.

Synthesis of Eu(DBM)$_3$/POL-bpy. As a typical run, Eu(DBM)$_3$·2H_2O (0.2 g) and POL-bpy (0.085 g) was added in 20 mL of ethanol and stirred under refluxing for 12 h. The product was obtained after filtering, washing excessively with acetone and drying under vacuum.

Synthesis of POL-salen. POL-salen was synthesized from bivinyl-functionalized salen monomer (2V-salen) under solvothermal conditions. As a typical run, 0.5 g of

2V-salen was dissolved in 5 mL of DMF, followed by addition of 10 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of solvent, a yellow solid product was obtained.

2V-salen was synthesized from 3-*tert*-butylphenol. At first, the reaction of 3-*tert*-butylphenol with paraformaldehyde formed 3-*tert*-butyl-2-hydroxybenzaldehyde [^{1}H NMR, 400MHz, $CDCl_3$, 298K, TMS: δ 11.84 (s, 1H), 9.89 (s, 1H), 7.56 (d, 1H, *J*=7.6Hz), 7.42 (d, 1H, *J*=7.6Hz), 6.98 (t, 1H, *J*=7.6Hz), 1.46 (s, 9H) ppm],[2] followed by reacting with Br_2 to form 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde [^{1}H NMR, 400MHz, $CDCl_3$, 298K, TMS: δ 11.80 (s, 1H), 9.96 (s, 1H), 7.77 (d, 1H, *J*=2Hz), 7.61 (d, 1H, *J*=2.4Hz), 7.48-7.54 (m, 4H), 6.73-6.80 (m, 1H), 5.80 (d, 1H, *J*=17.6Hz), 5.29 (d, 1H, *J*=10.8Hz) ppm].[3] After reaction with 4-vinylphenylboronic acid, 5-*tert*-butyl-4-hydroxy-4'-vinyl-biphenyl-3-carbaldehyde was obtained [^{1}H NMR, 400MHz, $CDCl_3$, 298K, TMS: δ 8.73-8.75 (m, 4H), 7.77 (d, 2H, *J*=8Hz), 7.54-7.57 (m, 6H), 6.75-6.82 (m, 2H), 5.85 (d, 2H, *J*=18Hz), 5.34 (d, 2H, *J*=10.8Hz), 1.43 (s, 9H) ppm],[4] which reacted with (*R, R*)-cyclohexane diamine to produce 2V-salen monomer. ^{1}H NMR, 400MHz, $CDCl_3$, 298K, TMS: δ 14.04 (s, 2H), 8.38 (s, 2H), 7.63-7.24 (m, 12H), 6.73-6.81 (m, 2H), 5.80 (d, 2H, *J*=17.2Hz), 5.28 (d, 2H, *J*=11.2Hz), 3.40 (t, 2H, *J*=4.6Hz), 1.47-2.07 (m, 8H), 1.44 (s, 9H) ppm. ^{13}C NMR (100MHz, $CDCl_3$) 166.37, 160.68, 141.10, 138.22, 137.12, 136.44, 131.02, 128.89, 128.66, 127.32, 127.21, 119.34, 114.14 ppm.

Synthesis of Mn^{III}/POL-salen: POL-salen (0.5 g) and $Mn(OAc)_2 \cdot 4H_2O$ (0.045 g, 3.0 equiv) was added in 150 mL of ethanol under N_2 and the mixture was refluxed at 80 °C overnight. After cooling to room temperature, LiCl (0.023 g) was added and a gentle stream of air was introduced to the mixture under stirring for 12 h. The mixture was filtrated, washed with excessive of ethanol and water, and then dried at 50 °C under vacuum. The obtained brown product was denoted as Mn^{III}/POL-salen.

Characterizations. Nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2020M and Tristar system. The samples were outgassed for 10 h at 100 °C before the measurements. ICP analysis was measured with a Perkin-Elmer plasma 40 emission spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS at δ=0 ppm, and J values are given in Hz. ^{13}C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS), and ^{31}P (161.8 MHz) MAS solid-state NMR experiments were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. The ^{31}P NMR chemical shifts were referenced to the 85% H_3PO_4. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα irradiation at θ=90° for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV. Scanning electron microscopy (SEM) was performed using a Hitachi SU 1510. Transmission electron microscope (TEM) images were performed using a Hitachi HT-7700 and Titan ChemiSTEM. The fluorescence excitation and emission spectra were recorded on a Hitachi HT-7000 spectrophotometer at the liquid nitrogen temperature (77 K) equipped with a 450 W Xenon lamp as an excitation source.

Catalyst tests.

Hydroformylation of octene. As a typical run, a desired amount of Rh catalyst, octene (3.0 g), and toluene (6.0 g) were added into a stainless steel autoclave (30 mL). After sealing and purging with syngas ($CO/H_2 = 1:1$) for 3 times, the pressure of syngas was adjusted to desired value and the autoclave was heated to 90 °C (2 °C/min), stirring at 90 °C for 4 h. During the reaction, the syngas was filled up from a reservoir to maintain the pressure. After the reaction, the catalyst was taken out from the system by centrifugation and analyzed by gas chromatography (Agilent 6890 gas chromatography equipped with a flame ionization detector and a SE-54 capillary column).

For recycling the catalyst, the catalyst was separated by centrifugation, washing with degassed toluene under N_2 atmosphere, which was used directly for the next run.

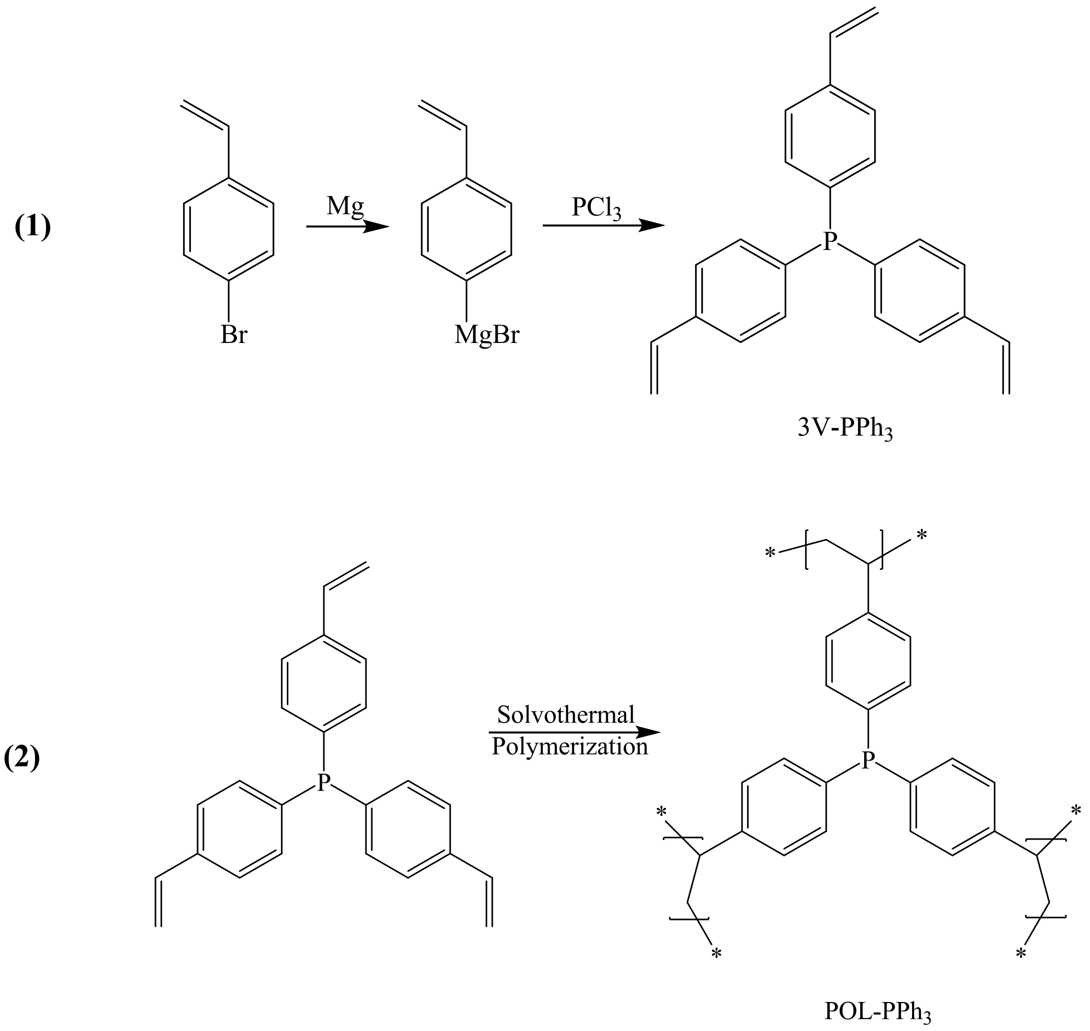
Hydroformylation of styrene. As a typical run, Rh catalyst (2.5 μmol), styrene (0.52 g), and toluene (10 g) were added into a stainless steel autoclave (100 mL). After sealing and purging with syngas ($CO/H_2 = 1:1$) for 3 times, the pressure of syngas was adjusted to desired value and the autoclave was put into a preheated oil bath, stirring at 80 °C for 12 h. After the reaction, the catalyst was taken out from the system by centrifugation and analyzed by gas chromatography (GC-1690 Kexiao Co., flame ionization detector).

Aerobic oxidation of primary alcohols to aldehydes. These reactions were carried out according to the literature.[5]

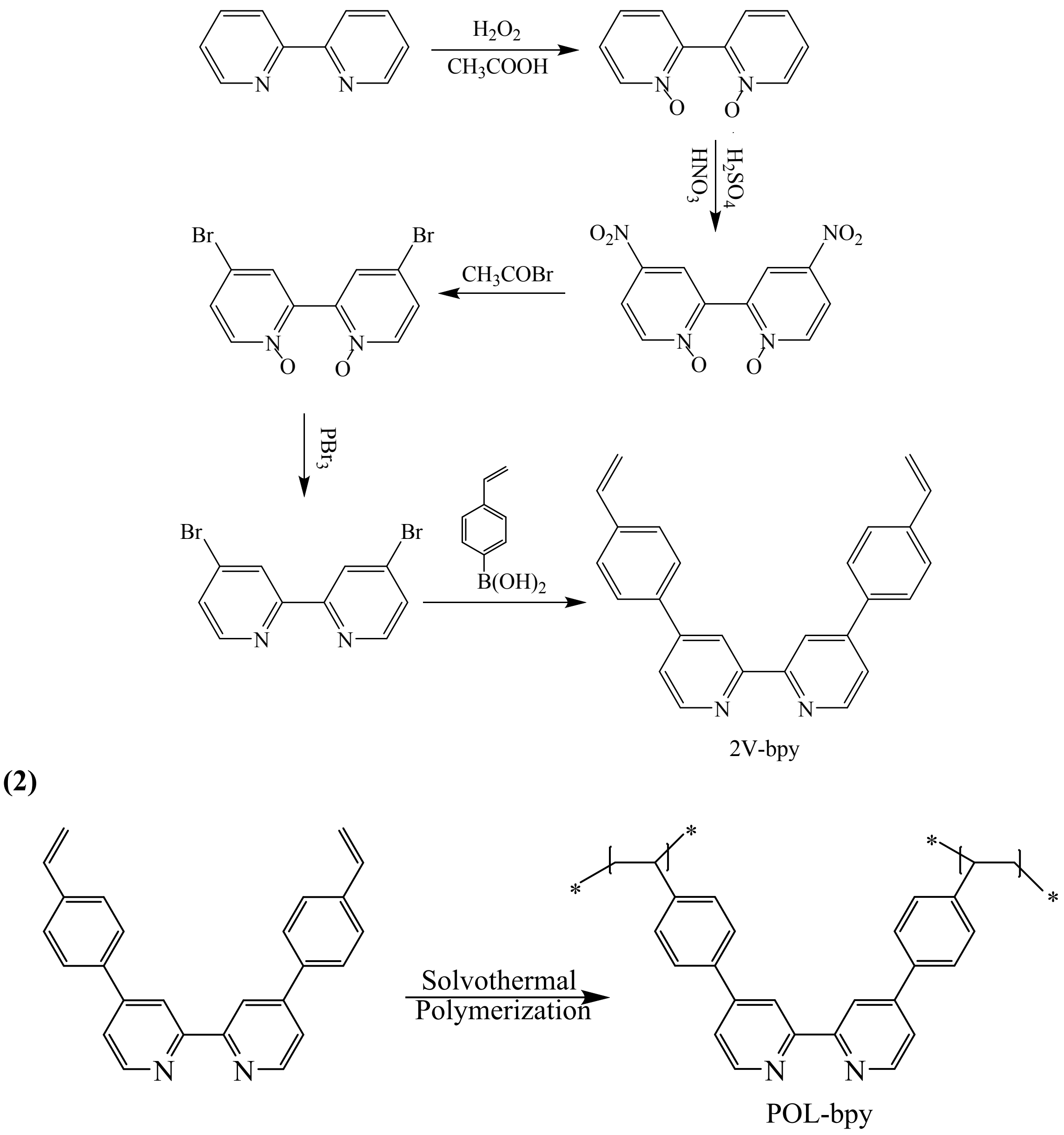
Enantioselective epoxidation of styrene: Enantioselective epoxidation reactions were carried out using homogeneous Mn^{III}(Salen) complex and heterogeneous Mn^{III}/POL-Salen as catalysts (4.0 mol%) with styrene (1 mmol) as substrates in 4 mL of dichloromethane in the presence of PyNO (0.5 mmol) as an axial base with aqueous buffered 2 mmol NaOCl (0.5 M, pH=11.3) as an oxidant. The NaOCl was added in four equal portions at 0 °C and reaction for 6 h. After completion of the reaction, Mn^{III}/POL-Salen catalyst was separated by centrifugation (filtered through a plug of silica for homogeneous Mn^{III}(Salen) complex). The liquid was analyzed by GC on a Supelco γ-DEX 225 capillary column.

For recycling the catalyst, the catalyst was separated by centrifugation, washed with dichloromethane, and then another portion of styrene (1.0 mmol), PyNO (0.5 mmol), dichloromethane (4.0 mL) and NaOCl (2.0 mmol) were added. The reactions were conducted at 0 °C for 6 h.

Supporting Schemes

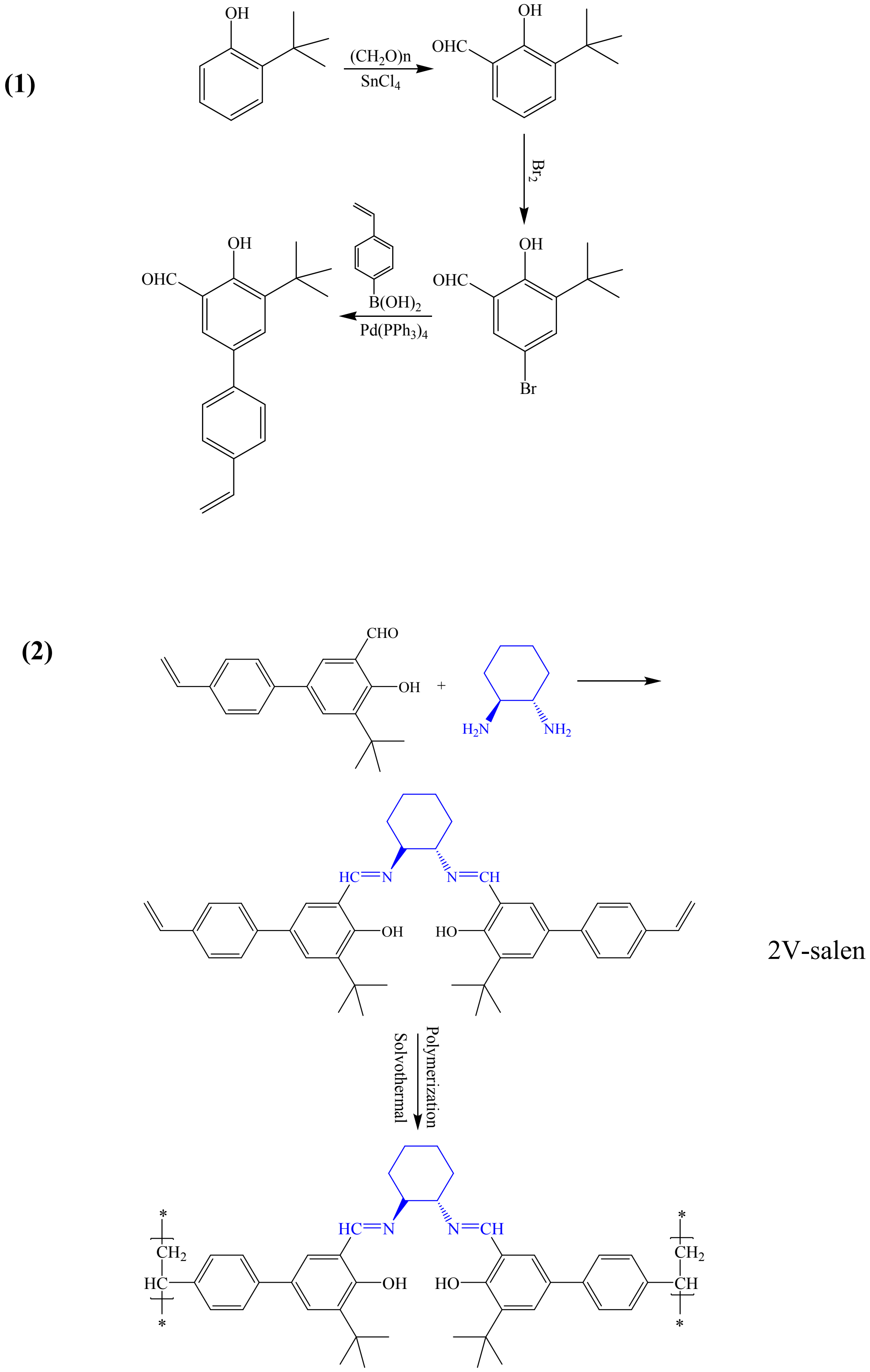


Scheme S1. Synthesis of POL-PPh$_3$.



Scheme S2. Synthesis of POL-bpy.

(1)



Scheme S3. Synthesis of POL-salen.

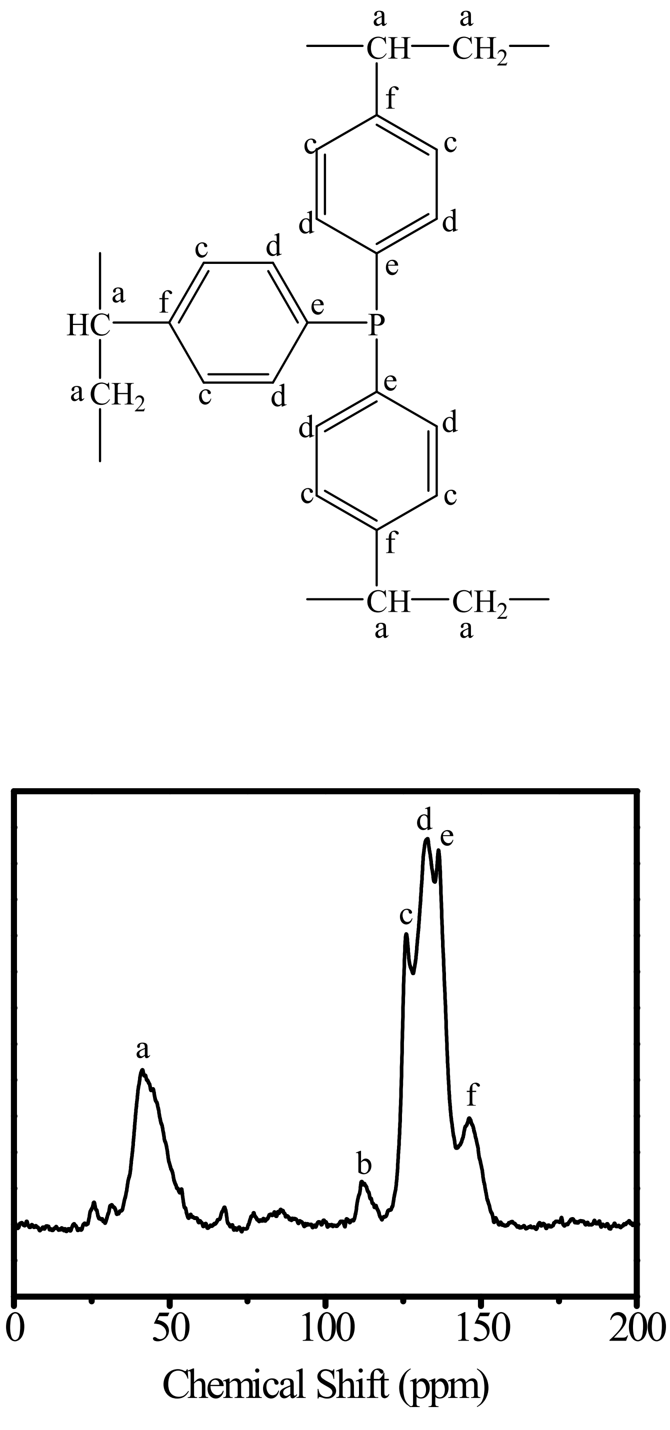


Figure S1. ^{13}C MAS NMR spectrum of POL-PPh_3.

The peak at b is assigned to unpolymerized vinyl groups. Because this peak is very small, it is indicated that the sample has high degree of polymerization.

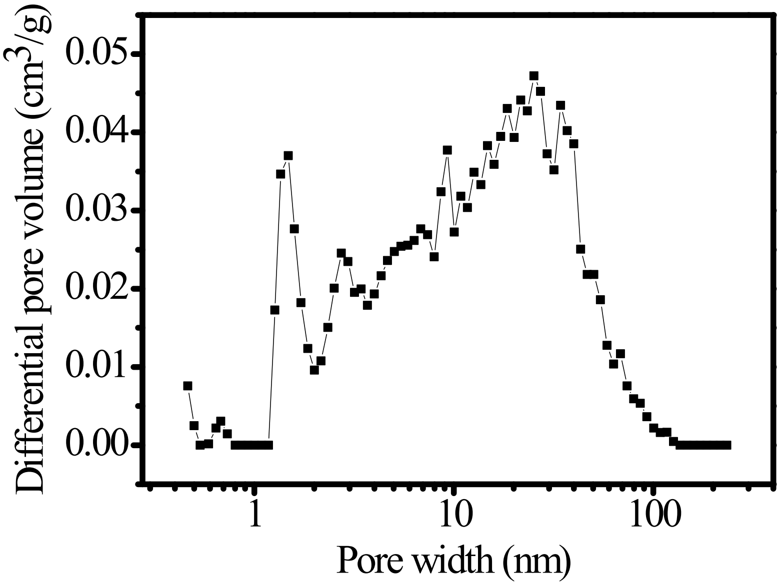


Figure S2. Pore size distribution of POL-PPh_3 calculated from non-local density functional theory (NLDFT).

This figure shows that the sample has hierarchical porosity.

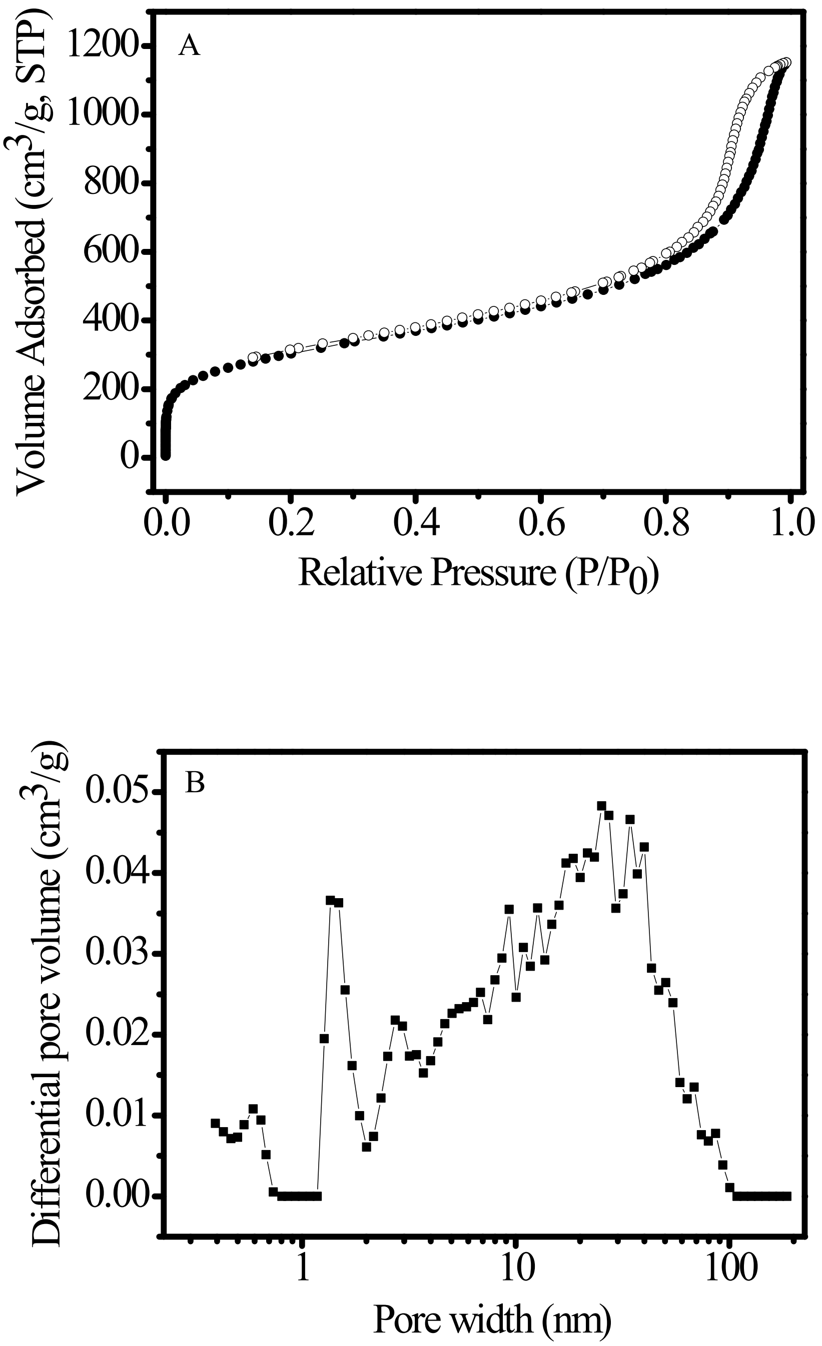


Figure S3. (A) Nitrogen sorption isotherms, (B) pore size distribution of POL-PPh_3 treated in boiling water for 240 h. Pore size distribution is calculated from non-local density functional theory (NLDFT).

These results indicate that the sample has superior hydrothermal stability. In contrast, most of MOFs catalysts are normally sensitive to water.

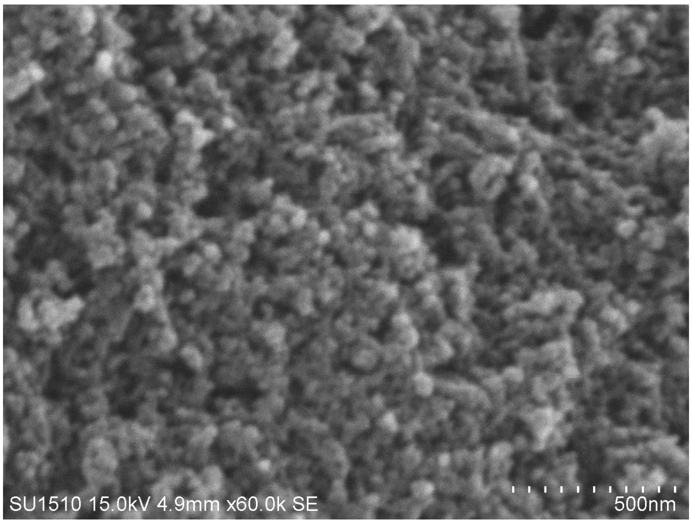


Figure S4. SEM image of POL-PPh_3 treated in boiling water for 240 h.

This figure indicates the superior hydrothermal stability of the hierarchical porosity.

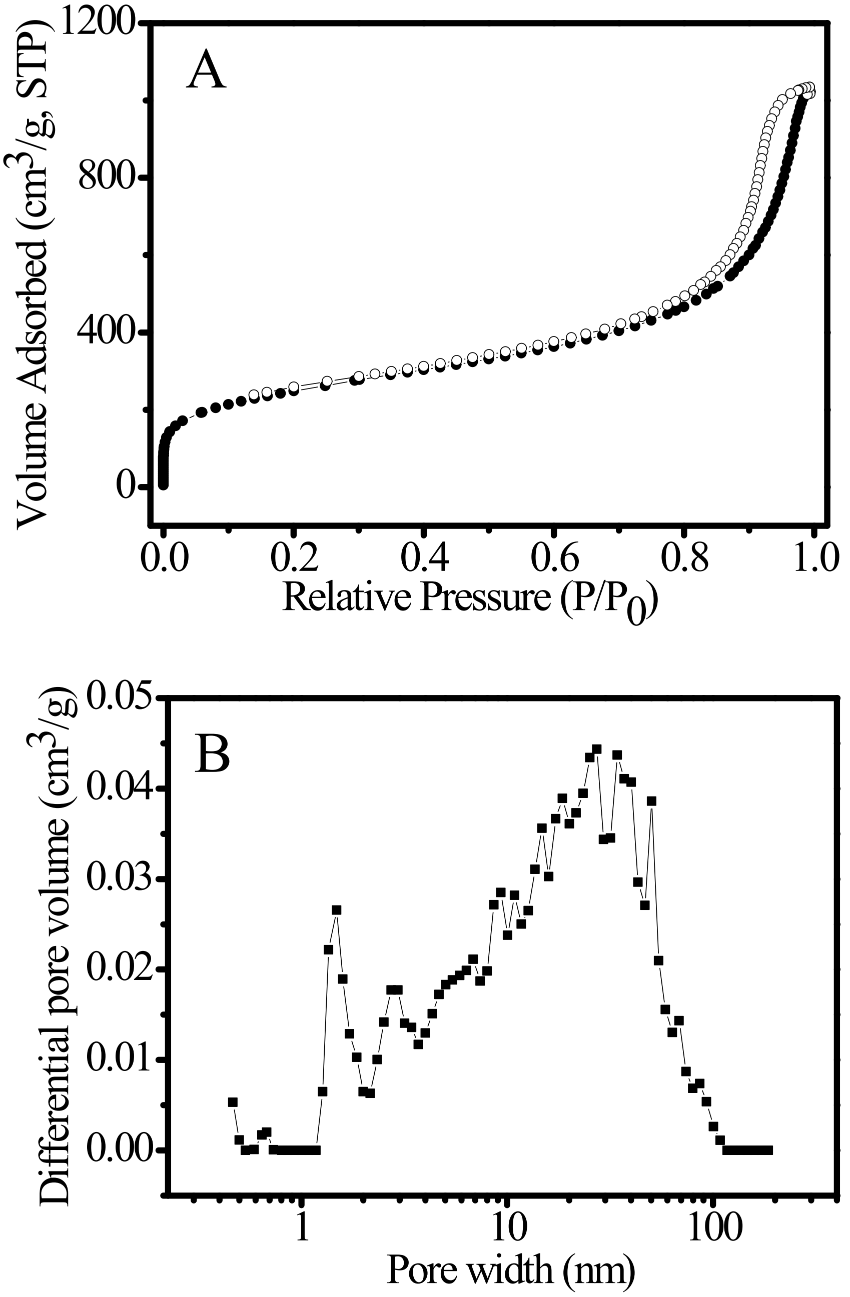


Figure S5. (A) Nitrogen sorption isotherms, (B) Pore size distribution of $Rh(CO)_2(acac)$/POL-PPh_3. Pore size distribution is calculated from non-local density functional theory (NLDFT), Rh loading at 2.0 wt.%.

This figure indicates the hierarchical porosity in the sample.

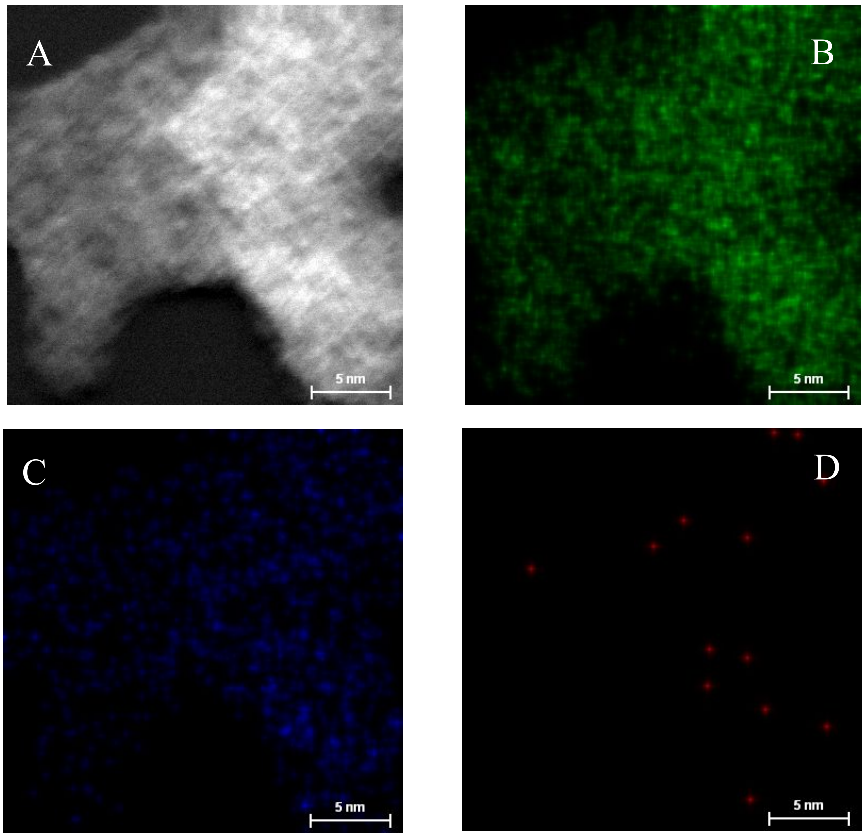


Figure S6. (A) HAADF-STEM image, (B) C, (C) P, and (D) Rh EDX mappings of $Rh(CO)_2(acac)/POL\text{-}PPh_3$.

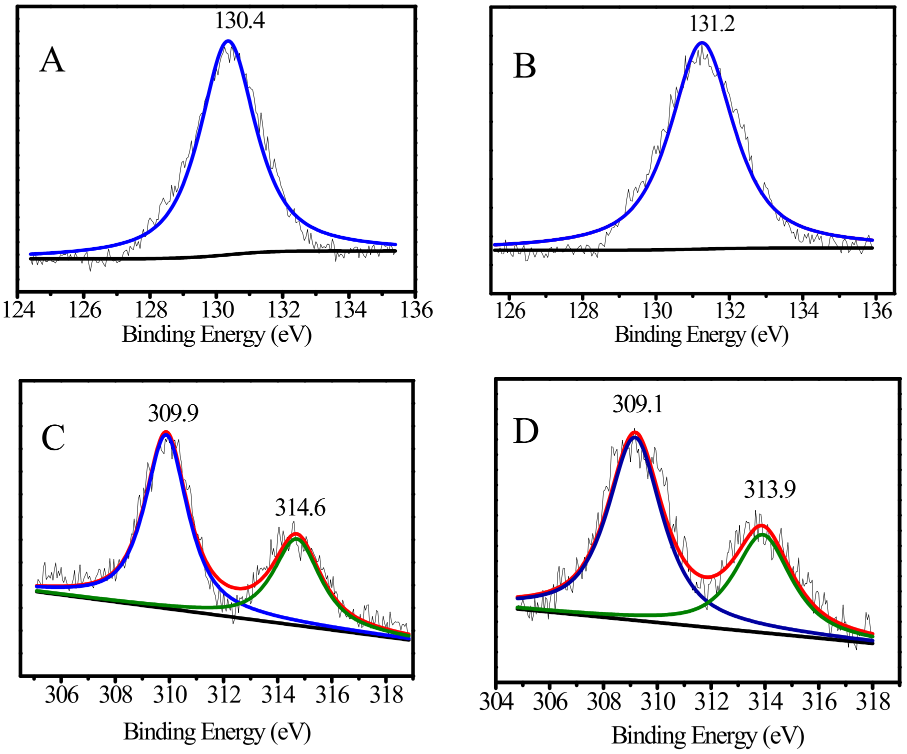
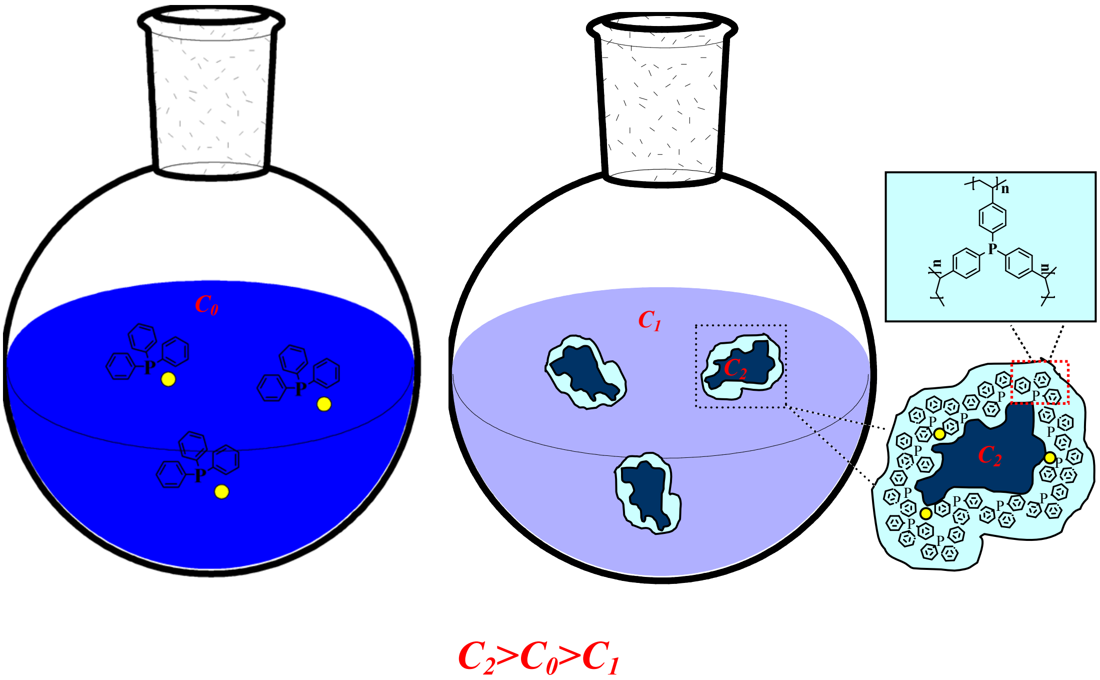


Figure S7. P2p XPS spectra of (A) POL-PPh_3 and (B) $Rh(CO)_2(acac)$/POL-PPh_3 samples; Rh3d XPS spectra of (C) $Rh(CO)_2(acac)$ and (D) $Rh(CO)_2(acac)$/POL-PPh_3 samples.



(A) Reactants and organic ligands in homogeneous catalytic system

(B) Concentration of reactants in M/POLs catalytic system

● Metal species

Figure S8. Proposed scheme for the reactants and ligands in homogeneous and heterogeneous M/POLs systems.

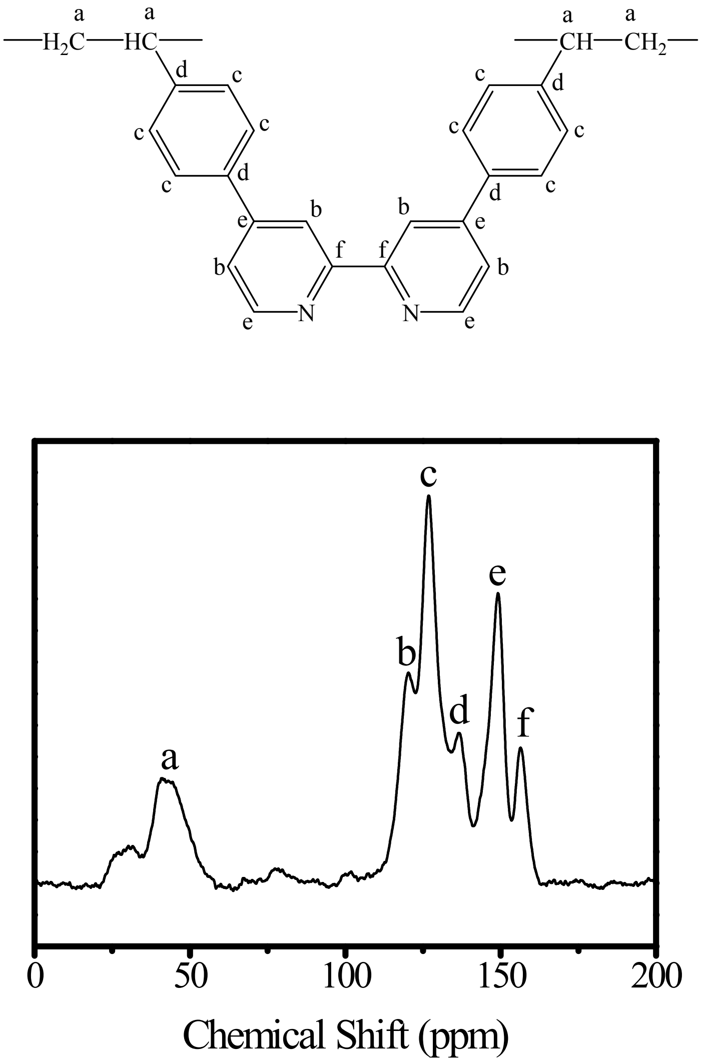


Figure S9. ^{13}C MAS NMR spectrum of POL-bpy.

This figure indicates the successful synthesis of POL-bpy.

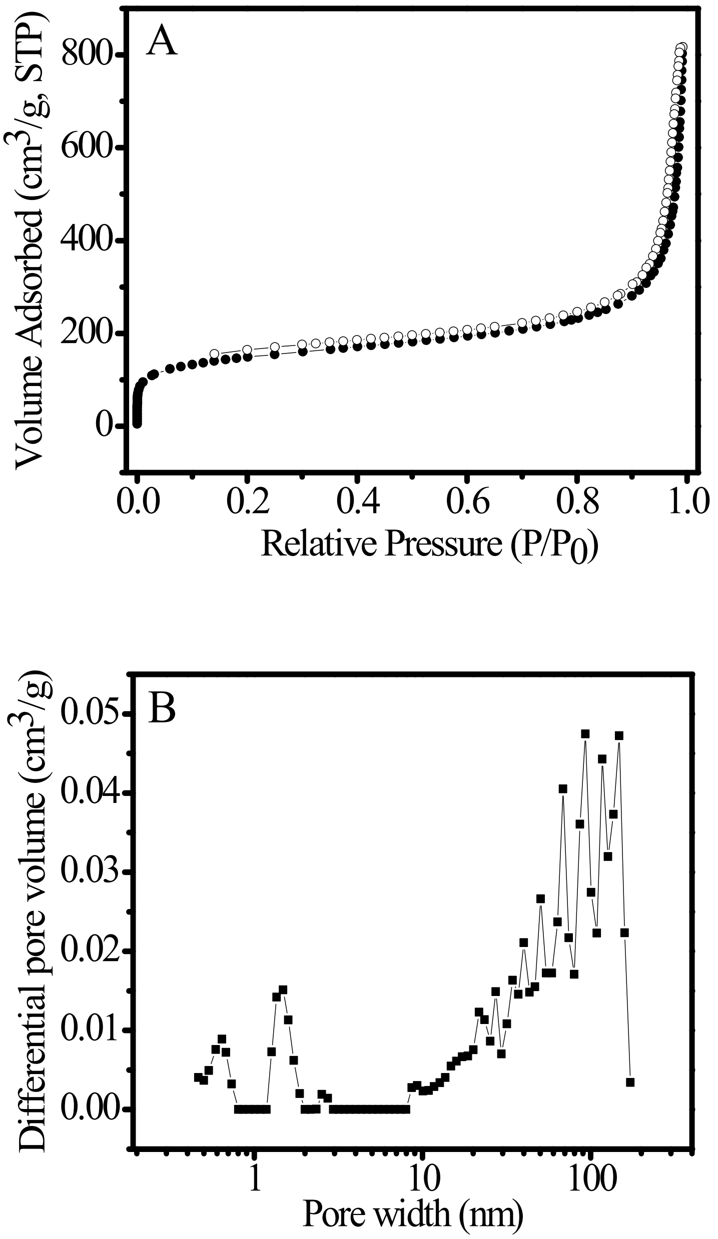


Figure S10. (A) Nitrogen sorption isotherms and (B) pore size distribution of POL-bpy. Pore size distribution is calculated from non-local density functional theory (NLDFT).

These figures indicate the hierarchical porosity of POL-bpy.

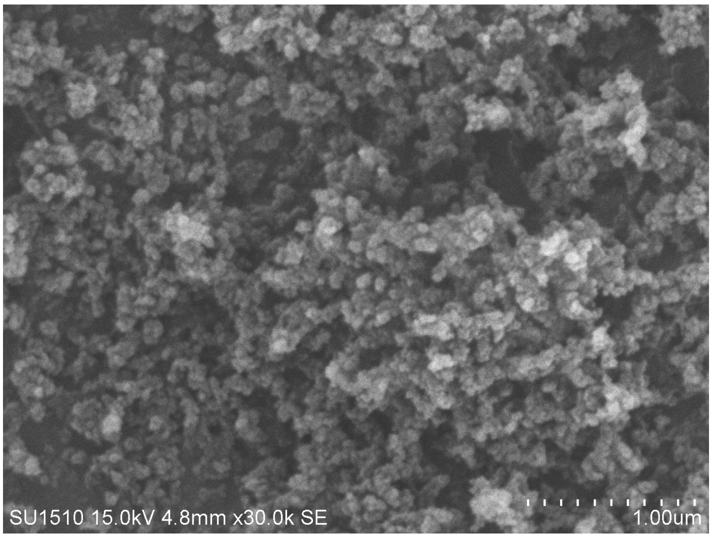


Figure S11. SEM image of POL-bpy.

This figure confirms the hierarchical porosity of POL-bpy.

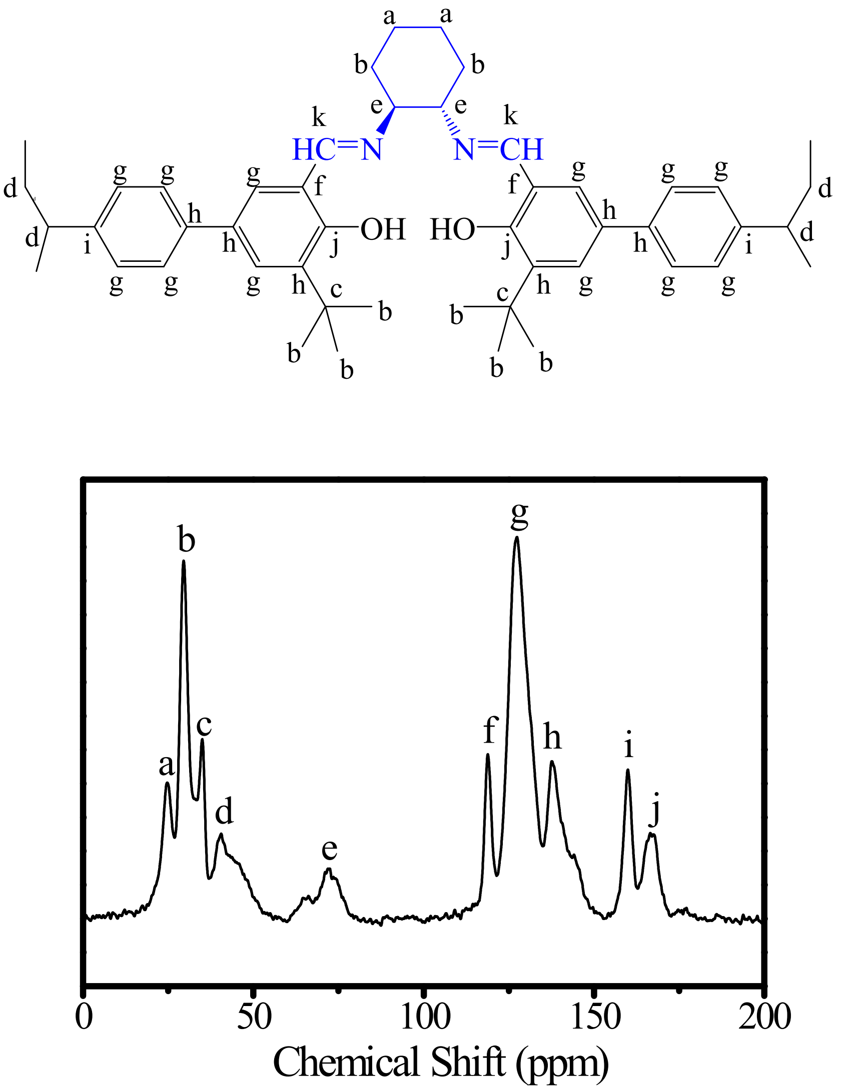


Figure S12. ^{13}C MAS NMR spectrum of POL-salen.

This figure indicates the successful synthesis of POL-salen.

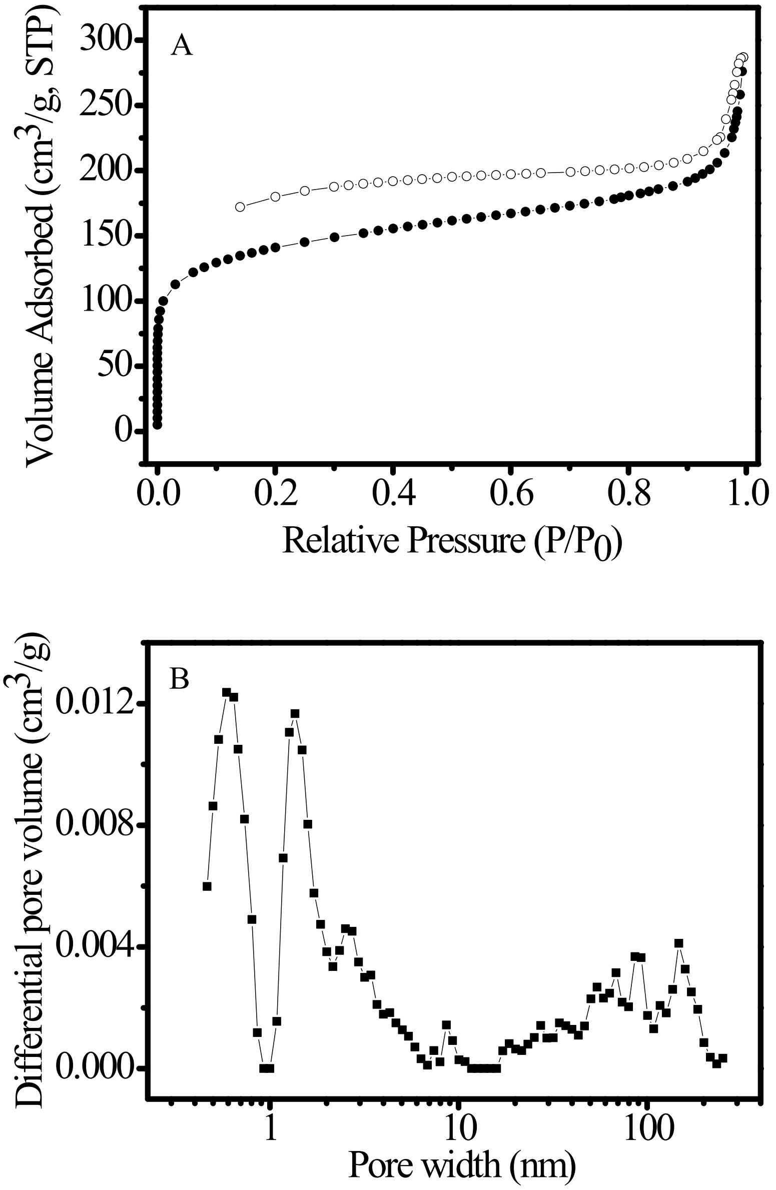


Figure S13. (A) Nitrogen sorption isotherms and (B) pore size distribution of POL-salen. Pore size distribution is calculated from non-local density functional theory (NLDFT).

These figures indicate the hierarchical porosity of POL-salen.

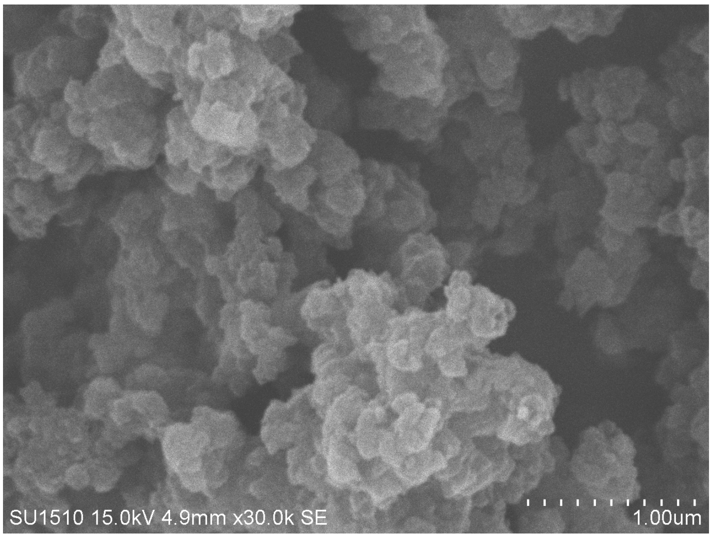


Figure S14. SEM image of POL-salen

This figure indicates the hierarchical porosity of POL-salen.

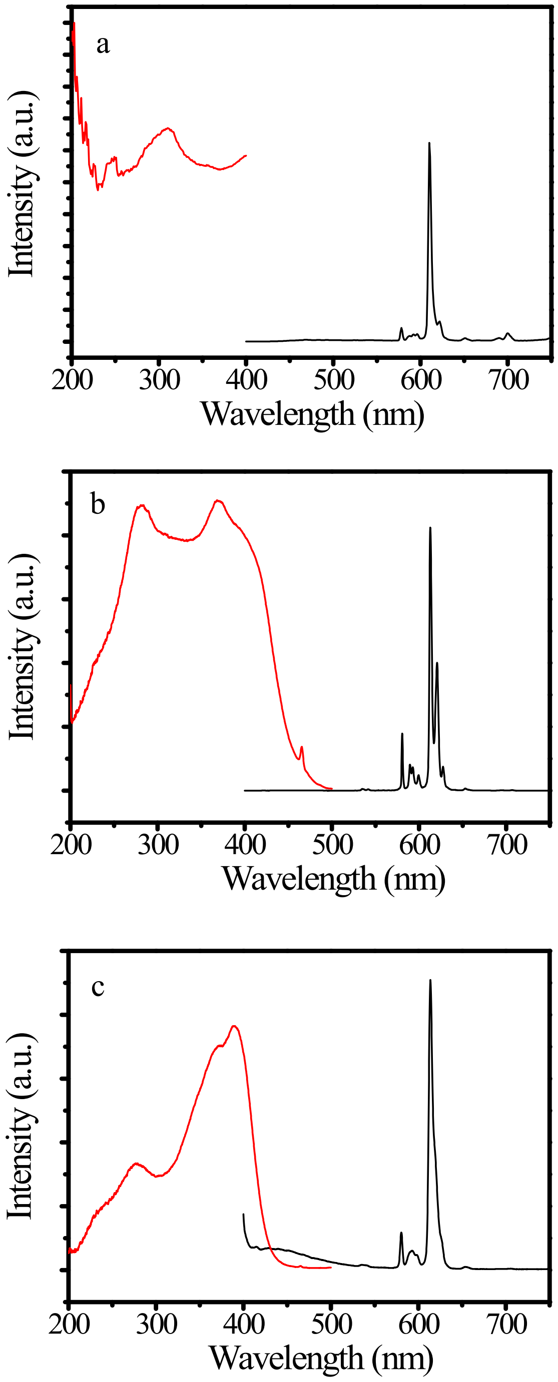
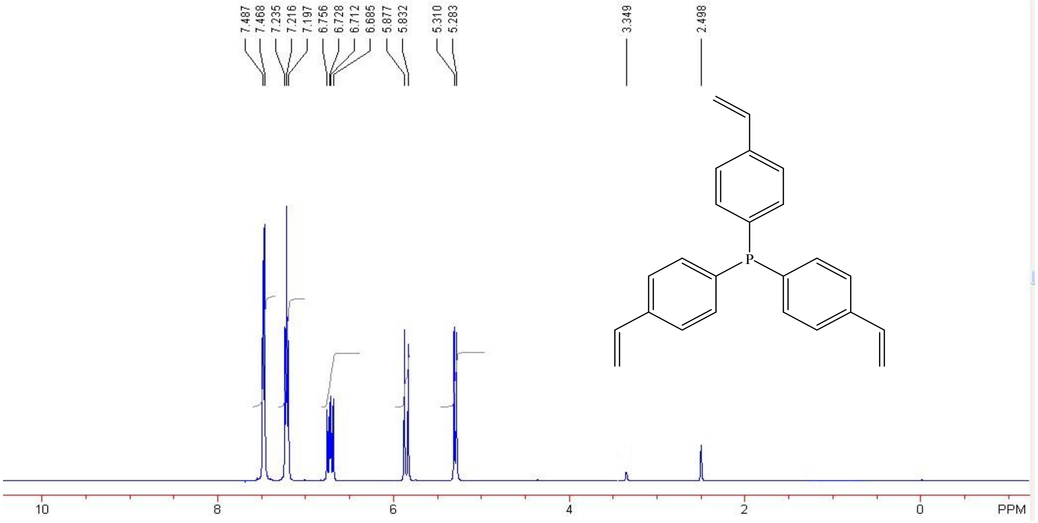


Figure S15. Excitation (red) and emission spectra (black) of (a) $Eu(DBM)_3 \cdot 2H_2O$ (λ_{ex}=309 nm), (b) $Eu(DBM)_3$bpy (λ_{ex}=370 nm), and (c) $Eu(DBM)_3$/POL-bpy (λ_{ex}=390 nm). All the excitation spectra were obtained by monitoring the emission wavelength of the Eu^{3+} ions at 612 nm.

These results indicate that the Eu(DBM)$_3$/POL-bpy is an outstanding fluorescent materials.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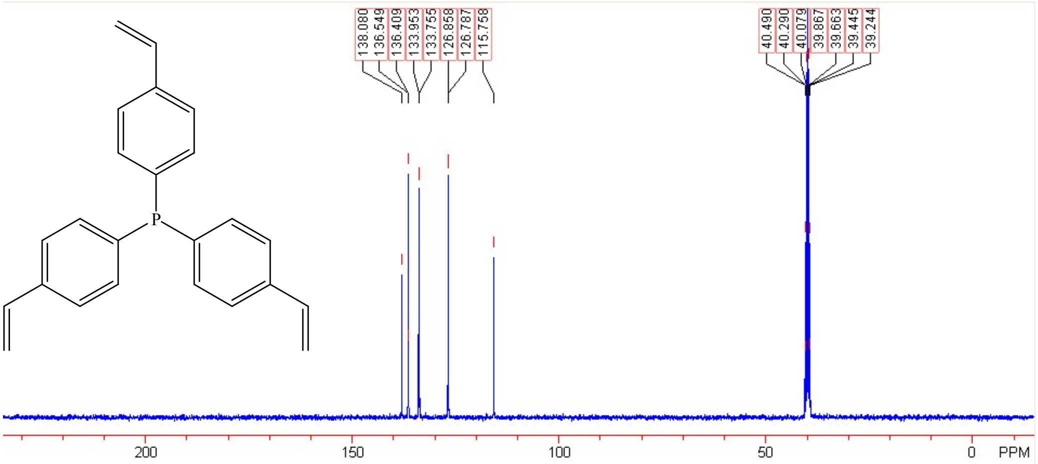
PPM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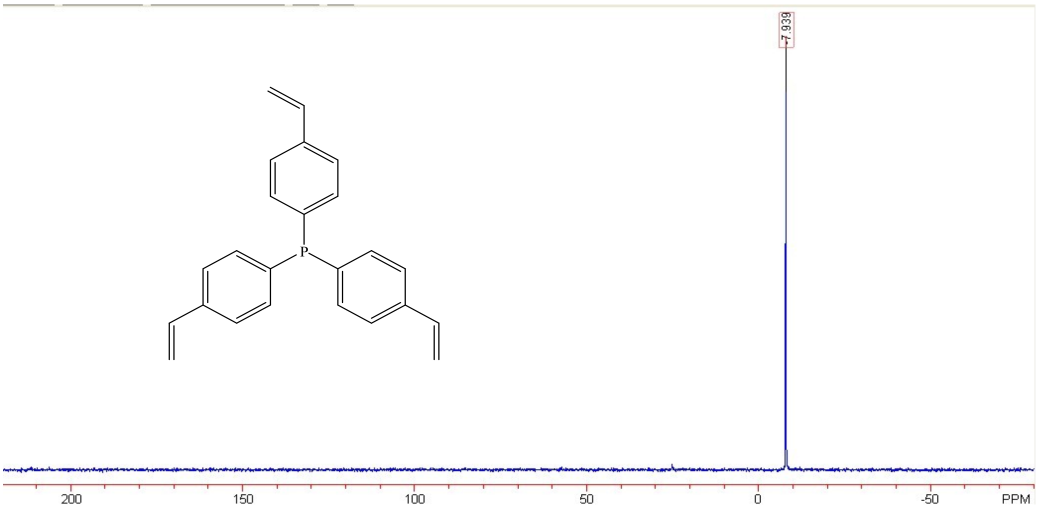
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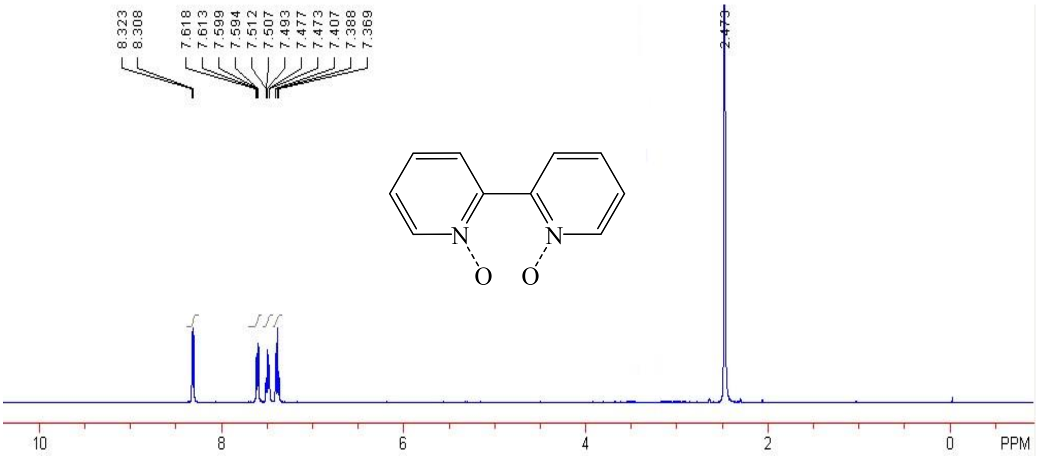
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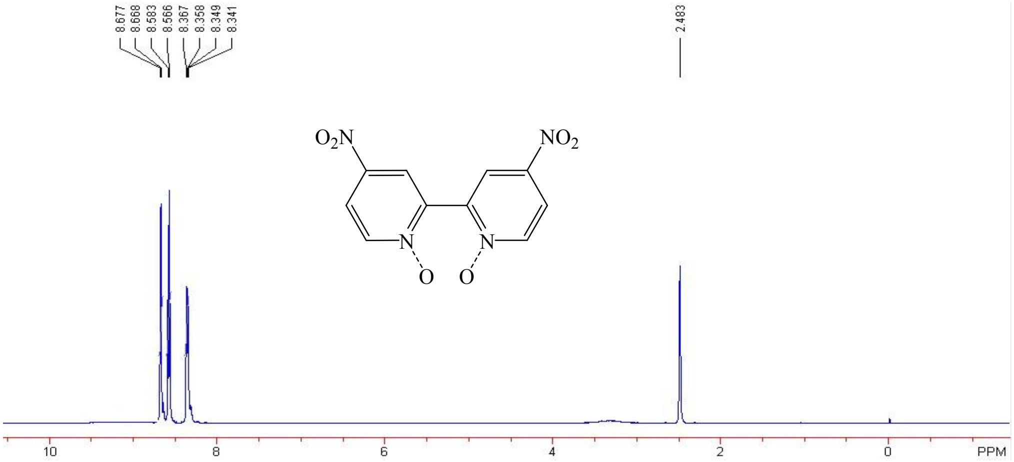
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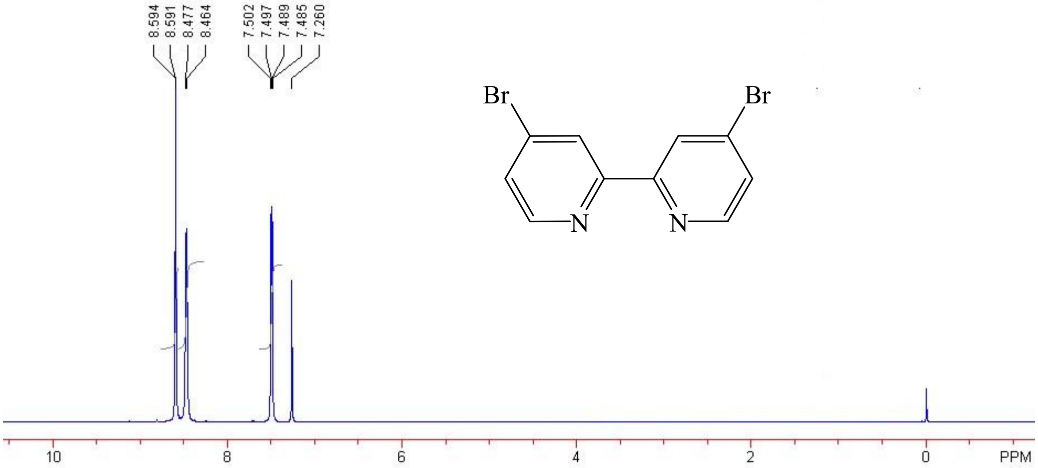
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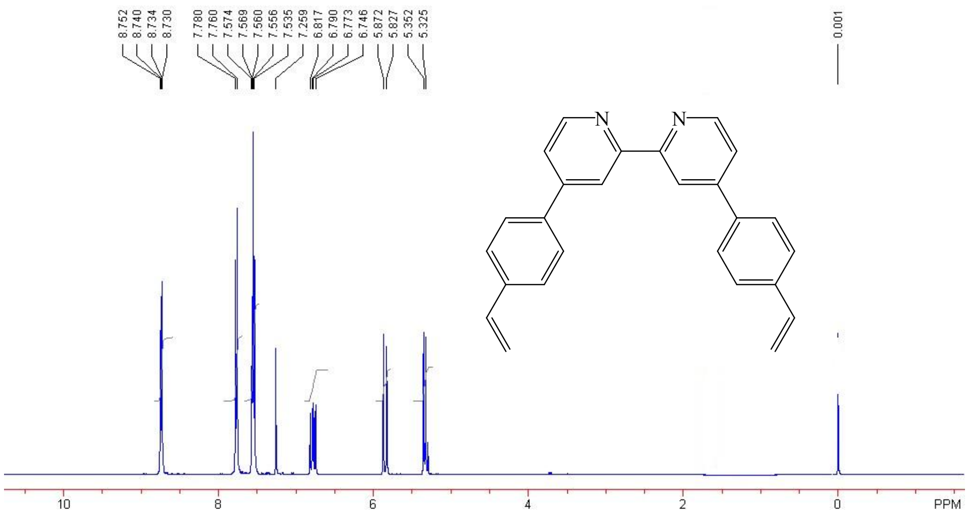
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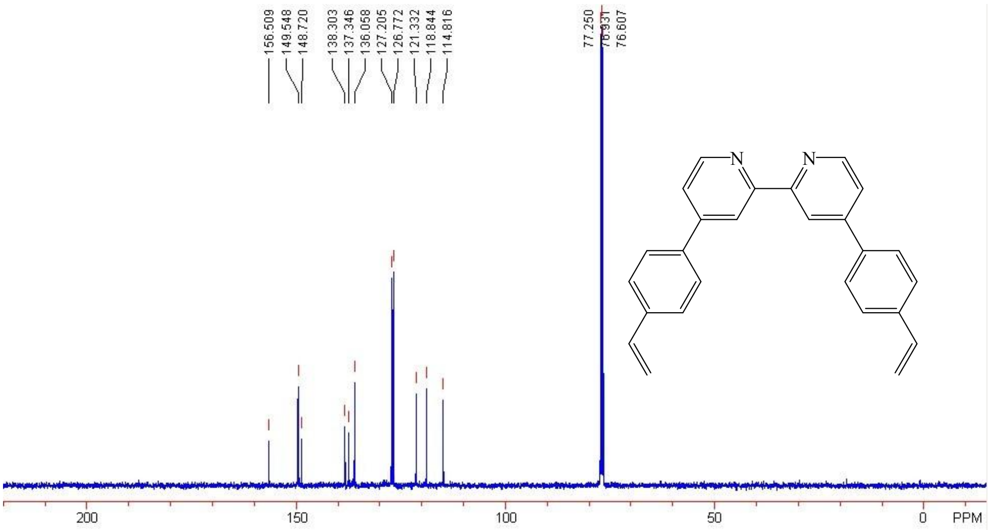
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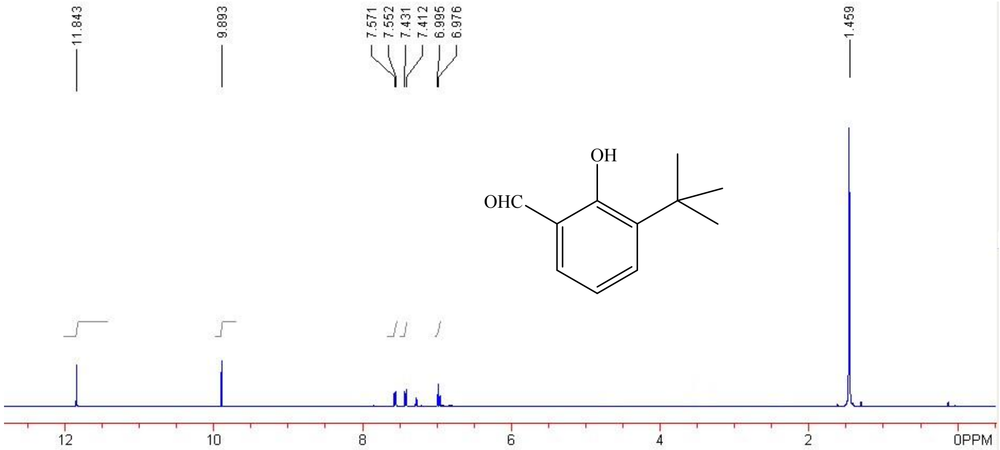
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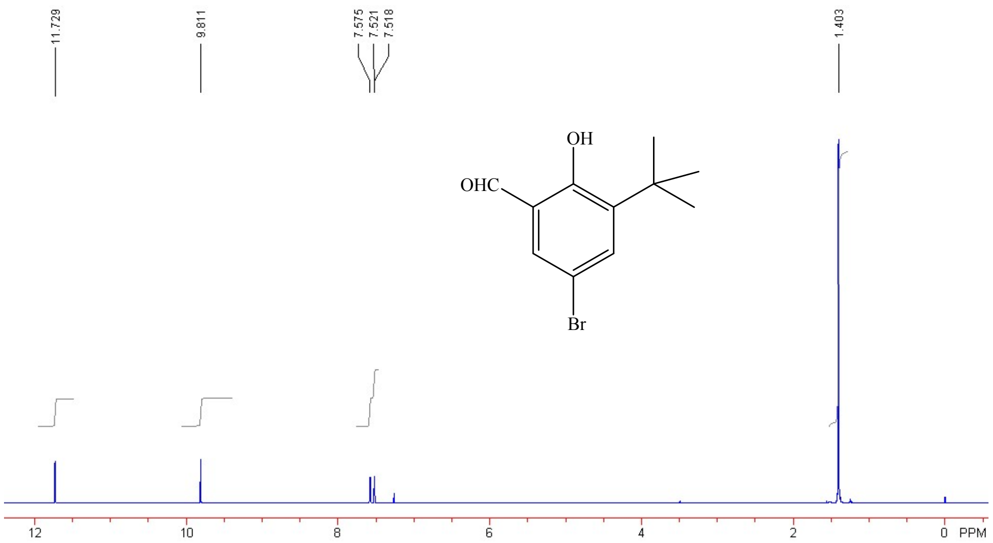
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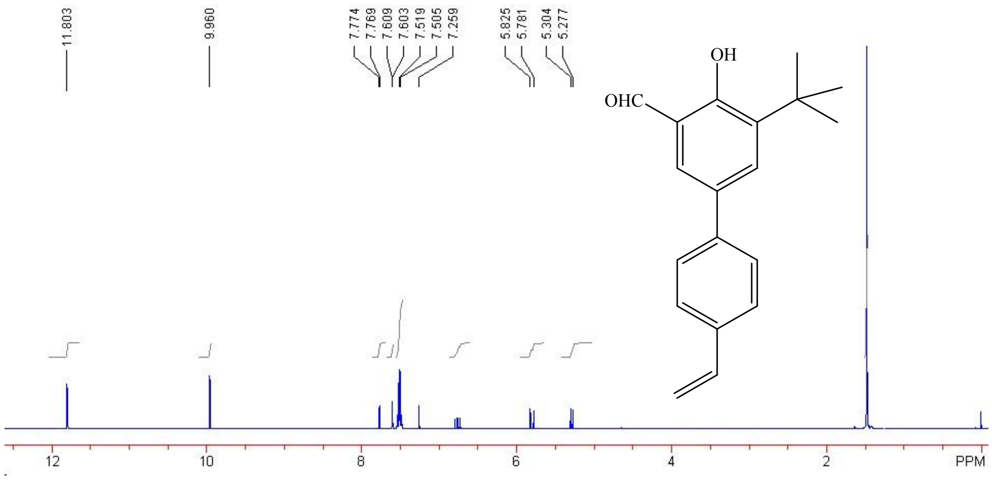
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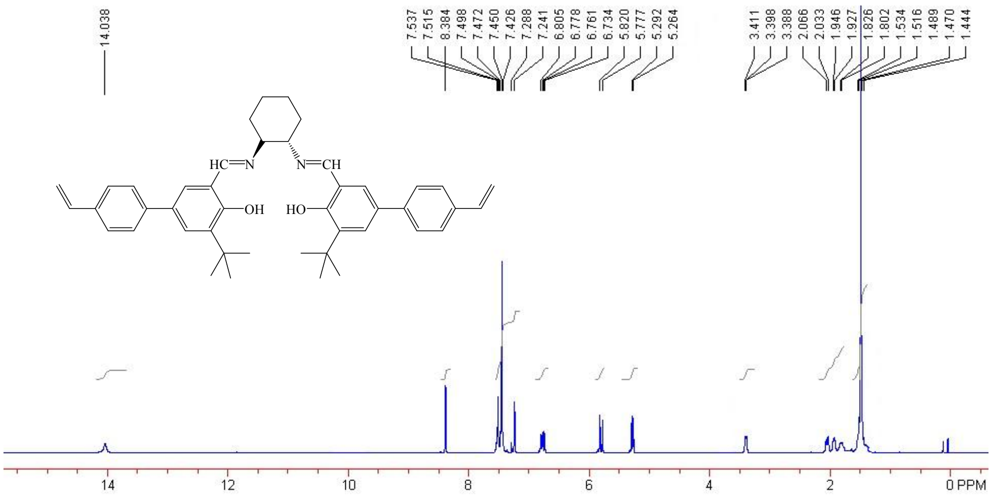
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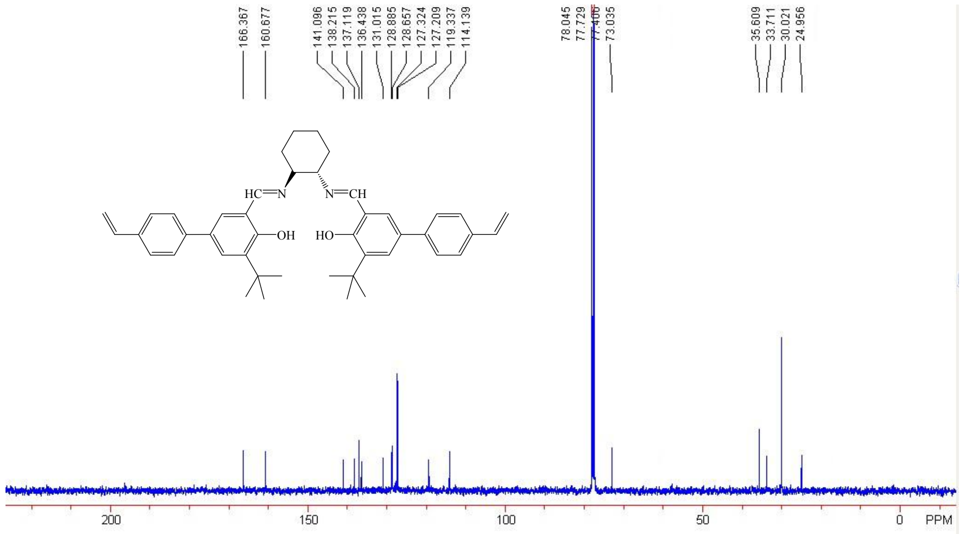


Figure S16. NMR spectra of organic compounds.

These results confirm the successful synthesis of the organic compounds.

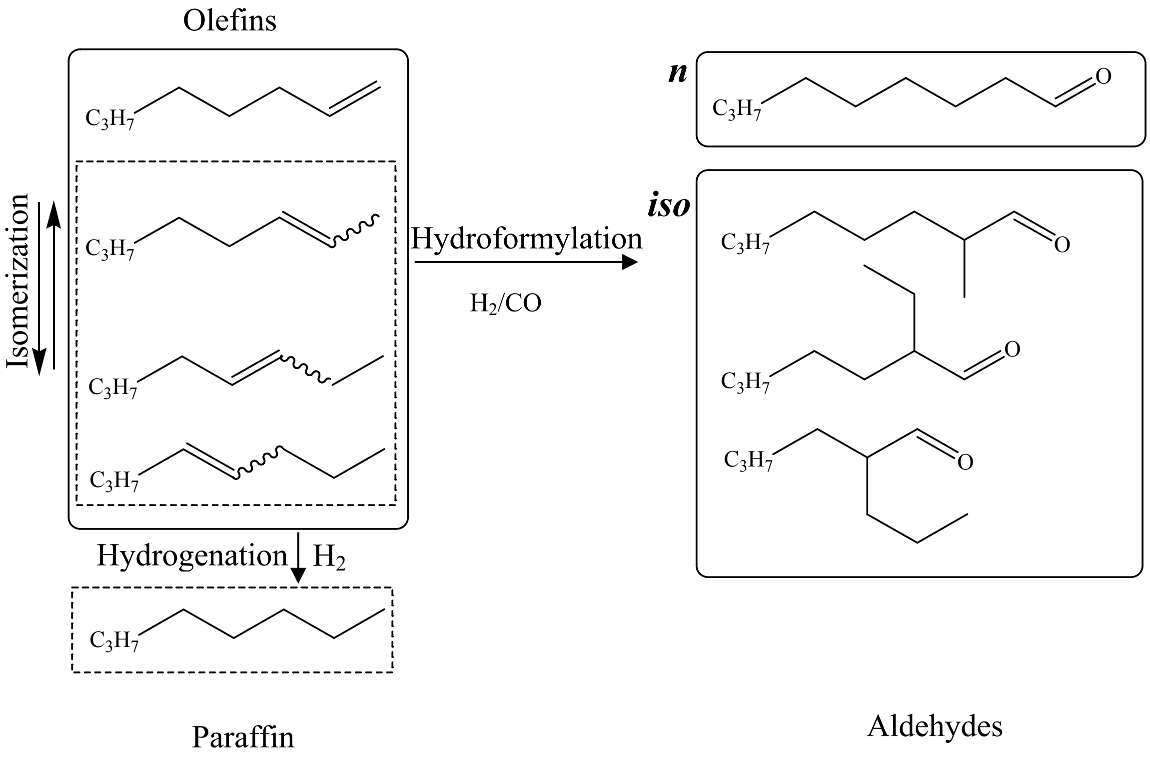
Supporting Tables

Table S1. Textural parameters for POL-PPh_3 treated in boiling water and M/POL-PPh_3.

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
POL-PPh_3 [a]	1091	1.73
$Rh(CO)_2(acac)$/POL-PPh_3	1032	1.69

[a] POL-PPh_3 treated in boiling water for 240 h.

Table S2. Catalytic performance of hydroformylation of octene over various catalysts.[a]



Entry	Catalyst	Type of PPh$_3$ [b]	Conv. (%) [c]	Paraffin (%) [c]	Iso-olefins (%) [c]	Aldehydes (%) [c]
1	$Rh(CH_3COO)_2$	--	98.1	10.2	47.6	42.2 (0.6)
2	$RhH(CO)(PPh_3)_3$	PPh_3	99.4	0.7	0.9	98.4 (2.01)
3	$Rh(CO)_2(acac)$	PPh_3	98.9	0.2	2.6	97.2 (0.66)
4	$Rh(CH_3COO)_2$	PPh_3	98.6	4.1	11.9	84.0 (0.79)
5	$RhH(CO)(PPh_3)_3$	POL-PPh_3	99.4	0.6	3.0	96.4 (1.64)
6	$Rh(CO)_2(acac)$	POL-PPh_3	99.1	1.3	10.5	88.2 (0.71)
7	$Rh(CH_3COO)_2$	POL-PPh_3	98.3	6.7	21.0	72.3 (0.83)

8	Rh(CH$_3$COO)$_2$/POL-PPh$_3$	--	97.0	8.0	25.4	66.6 (0.89)
9 [d]	RhH(CO)(PPh$_3$)$_3$/ POL-PPh$_3$	--	99.1	3.9	16.3	79.8 (0.69)
10 [e]	RhH(CO)(PPh$_3$)$_3$/ POL-PPh$_3$	--	99.4	1.3	6.1	92.6 (0.82)
11 [f]	RhH(CO)(PPh$_3$)$_3$	--	90.4	4.8	9.5	85.7
12 [f]	RhH(CO)(PPh$_3$)$_3$/ POL-PPh$_3$	--	89.7	3.3	8.9	87.8

[a] Reaction conditions: syngas (CO/H$_2$ =1:1) (2.0 MPa), 1-octene (3.0 g), S/C=6000, toluene (6.0 g), 90 °C, 4 h.

[b] 10 mg was added.

[c] Determined by GC on SE-54 capillary column (linear/branched selectivity).

[d] S/C=10000.

[e] Reuse.

[f] 2-octene was used as substrate, S/C=3000.

Table S3. Recycling tests of $RhH(CO)(PPh_3)_3$/POL-PPh_3 in the hydroformylation of 1-octene.[a]

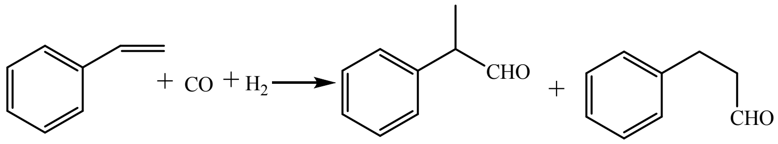
Entry	Conv.(%) [b]	Paraffin (%) [b]	Iso-olefins (%) [b]	Aldehydes (%) [b]
0	99.4	1.5	6.4	92.1 (0.87)
1	99.4	1.3	6.1	92.6 (0.82)
2	99.4	1.4	6.3	92.2 (0.78)
3	99.6	1.0	5.3	93.7 (0.86)
4	99.4	2.2	9.3	88.5 (0.92)
5	99.4	1.9	8.3	89.9 (0.85)
6	99.4	1.7	8.1	90.2 (0.87)

[a] Reaction conditions: syngas (CO/H_2 = 1:1) (2.0 MPa), 1-octene (3.0 g), S/C=6000, toluene (6.0 g), 90 °C, 4 h.

[b] Determined by GC on SE-54 capillary column (linear/branched selectivities).

This table indicates the excellent recyclability of $PdCl_2(PPh_3)_2$/POL-PPh_3 in hydroformylation of 1-octene.

Table S4. Catalytic data in styrene hydroformation over Rh/POL-PPh_3 and Rh/NOL-PPh_3.[a]



Run	Catalyst	Conv. (%)	Aldehyde Select. (%) [c]	Yield (%)
1	Rh(CO)$_2$(acac)/POL-PPh$_3$	>99.5	>99.5 (78.7)	>99.5
2	Rh(CO)$_2$(acac)/NOL-PPh$_3$[b]	48.2	>93.4 (42.3)	20.3

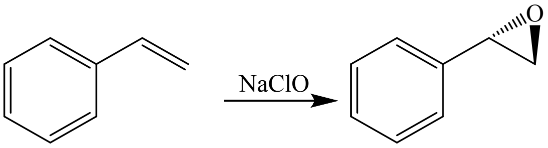
[a] Reaction conditions: CO/H_2 = 1:1 (1.0 MPa), styrene (0.52 g), S/C at 2000 (molar ratio of substrate to catalyst), toluene (10.0 g), 80 °C for 12 h, Rh loading at 2.0 wt.%; [b] The sample surface area less than 1 m^2/g; [c] Catalytic selectivity in parentheses was 2-phenyl propionaldehyde selectivity in the products

Table S5. Recycling tests of $CuBr_2$/POL-bpy in oxidation of benzyl alcohol.[a]

Entry	Yield (%)
0	94.2
1	94.4
2	93.1
3	92.8
4	91.9
5	92.2

[a] Reaction conditions: benzyl alcohol (1.0 mmol), $CuBr_2$/POL-bpy (5.0 mol%), TEMPO (5.0 mol%), KOH (10 mol%), CH_3CN (2.0 mL), H_2O (1.0 mL), 1 atm of air, RT, 6 h.

Table S6. Asymmetric epoxidation of styrene over homogeneous Mn^{III}(Salen) complex and heterogeneous Mn^{III}/POL-Salen catalysts.[a]



Entry	Catalyst	Conv.(%) [e]	Select.(%) [e]	ee.(%) [e]
1 [b]	Mn^{III}/salen	>99.5	>99.5	40.8
2 [c]	Mn^{III}/POL-salen	>99.5	>99.5	41.7
3 [d]	Mn^{III}/POL-salen	>99.5	>99.5	41.1

[a] Reaction conditions: styrene (1.0 mmol), PyNO (0.5 mmol), CH_2Cl_2 (4.0 mL), NaClO (2.0 mmol, 0.5 M, PH=11.5), 0 °C, 6 h; [b] 4.0 mol% was used; [c] Mn loading at 2.0 wt.% and 4.0 mol% was used; [d] Recylces for 6 times; [e] Determined by GC on a Supelco γ-DEX 225 capillary column.

Table S7. Recycling tests of Mn^{III}/POL-Salen in asymmetric epoxidation of styrene.[a]

Entry	Conv. (%)[b]	Select. (%) [b]	ee (%) [b]
0	>99.5	>99.5	41.7
1	>99.5	>99.5	41.7
2	>99.5	>99.5	41.3
3	>99.5	>99.5	40.8
4	98.3	>99.5	41.1
5	99.1	>99.5	40.4
6	97.6	>99.5	41.1

[a] Reaction conditions: styrene (1.0 mmol), PyNO (0.5 mmol), CH_2Cl_2 (4.0 mL), NaClO (2.0 mmol, 0.5 M, pH=11.5), 0 °C, 6 h, catalyst (4.0 mol%).

[b] Determined by GC on a Supelco γ-DEX 225 capillary column.

Supporting References:

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2. M. Cavazzini, A. Manfredi, F. Montanari, S. Quici, G. Pozzi, *Eur. J. Org. Chem.*, 2001, 4639.
3. Y. -L. Wong, L. H. Tong, J. R. Dilworth, D. K. P. Ng, H. K. Lee, *Dalton Trans.*, 2010, **39**, 4602.
4. H. Sellner, J. K. Karjalainen, D. Seebach, *Chem. Eur. J.*, 2001, **13**, 2873.
5. P. Gamez, I. W. C. E. Arends, J. Reedijk, R. A. Sheldon, *Chem. Commun.*, 2003, 2414.