# Palladium-Metalated Porous Organic Polymers as Recyclable Catalysts for Chemoselective Decarbonylation of Aldehydes

Wen-Hao Li,<sup>†,§</sup> Cun-Yao Li,<sup>‡,§</sup> Li Yan,<sup>‡</sup> Hai-Tao Tang,<sup>\*,†</sup> Heng-Shan Wang<sup>†</sup> and Ying-Ming Pan<sup>\*,†</sup> Yun-Jie Ding<sup>\*,‡</sup>

<sup>†</sup>State Key Laboratory for the Chemistry and Molecular Engineering of Medicinal

Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China.

<sup>‡</sup>Dalian National Laboratory for Clean Energy, Collaborative Innovation Center of

Chemistry for Energy Materials, Dalian Institute of Chemical Physics, Chinese

Academy of Sciences, Dalian 116023, China.

panym@mailbox.gxnu.edu.cn;

httang@gxnu.edu.cn;

dyj@dicp.ac.cn

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#### **General Information**

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 °C petroleum ether (distillated prior to use) and analytical grade EtOAc (without further purification). <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a 400 MHz spectrometer. Chemical shifts were reported in ppm. <sup>1</sup>H NMR spectra were referenced to CDCl<sub>3</sub> (7.26 ppm), and <sup>13</sup>C-NMR spectra were referenced to CDCl<sub>3</sub> (77.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. HRMS spectra were recorded with Micromass OTOF2 Ouadrupole/Time -of-Flight Tandem mass spectrometer using electron spray ionization. The solid-state NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP/MAS probehead whose channel was tuned to 400.18 MHz. <sup>13</sup>C CP/MAS spectra were referenced to adamantane  $(C_{10}H_{16})$  standard (1.63 ppm). <sup>31</sup>P CP/MAS were referenced to adenosine diphosphate (ADP) (0.0 ppm). Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Ouantachrome Autosorb-1 system, and the samples were degassed for 10 h at 393K before the measurements were obtained. The specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The total pore volume at P/Po=0.995 and the pore size distribution curves were obtained from the desorption branches using the nonlocal density functional theory (NLDFT) method. Transmission electron microscopic (TEM) images were performed using a JEM-2100 with accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was performed using a HITACHI-4800. The X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific ESCALAB 250Xi with the Al K $\alpha$  irradiation at  $\theta$ =90° for X-ray sources, and the spectrometer binding energy was calibrated through the reference C 1s (284.9 eV). The samples were pressed to a tablet and were pasted on the sample stage using conducting resin and the pressure of the vacuum chamber was lower than 10-10 mbar when testing while a step size of 0.10 eV was employed. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449 F3), the sample was heated at the rate of 10 Kmin<sup>-1</sup> from room temperature up to 1073 K under a nitrogen atmosphere.

#### Preparation of POL-xantphos and Pd/POL-xantphos



9.9-Dimethylxanthene (s1, 5 g, 24 mmol), TMEDA (9 mL, 60 mmol) and THF (40 mL) was charged in a flask. Then *n*-BuLi (24 mL of 2.5 M solution in hexane, 60 mmol) was added dropwise at 0 °C, followed by stirring overnight at room temperature. 60 mmol of  $ClP(NEt_2)_2$  dissolved in 10 mL of Et<sub>2</sub>O was added dropwise at -78 °C and the afforded mixture was stirred at room temperature overnight. After removal of the precipitate and the solvent under vacuum, compound s3 (white powder) was afforded.



The obtained white powder s3 was dissolved in 250 mL of dry hexane, dry HCl gas was passed through the solution at room temperature for 0.5 h. Then the precipitate was removed, and the solvent was removed under vacuum. Thus compound s4 was afforded.



4.03 g of 4-bromostyrene (22 mmol) was dissolved in 40 ml of THF, *n*-BuLi (8.8 mL of 2.5 M solution in hexane, 22 mmol) was added dropwise at -78 °C, followed by stirring for 2 h at -78 °C. Then compound **s4** dissolved in 20 mL of THF was added dropwise in the mixture at -78 °C. After stirring for 2 h, the mixture was quenching with aq. NH<sub>4</sub>Cl, and extracted with ethyl acetate. The organic layer was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by silica gel chromatography (20:1 hexane/EtOAc) to give compound **s5** as the white solid. This compound is known and the spectroscopic data match previous reported (Ref. 11b in manuscript). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41- 7.38 (m, 2H), 7.27- 7.14 (m, 9H), 7.13- 7.07 (m, 7H), 6.95 (t, *J*<sub>1</sub>= 7.56 Hz, 2H), 6.69- 6.61 (dd, *J*<sub>1</sub>= 17.57 Hz, *J*<sub>2</sub>= 10.94 Hz, 4H), 6.59- 6.52 (m, 2H), 5.72 (d, *J* = 17.67 Hz, 4H), 5.22 (d, *J* = 11.04 Hz, 4H), 1.64 (s, 6H). <sup>31</sup>P NMR (161.8 MHz, CDCl<sub>3</sub>)  $\delta$  -18.5; HRMS (ESI): m/z calc. for C<sub>47</sub>H<sub>40</sub>OP<sub>2</sub> [M+H]<sup>+</sup>: 683.2627, found: 683.2628.



1.0 g of vinyl-functionalized xantphos monomer was dissolved in 10 mL of THF, followed by addition of 100 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 and denoted as POL-xantphos.



To a round-bottom flask was added POL-xantphos **s6** (0.5 g), THF (10 mL), and Pd(OAc)<sub>2</sub> (44 mg), the reaction mixture was stirred at room temperature for 5 h, the gray solid turned to yellow, the yellow solid was washed using MeOH, EtOAc, THF and MeCN 3 times, respectively, after filtration. Next, the yellow solid was reduced at 140 °C for 5 h under H<sub>2</sub> and cooled to room temperature to obtain **s7**.

#### General procedure for decarbonylation of aldehydes and recycling

#### studies

R-CHO 
$$\frac{Pd/POL-xantphos}{K_2CO_3}$$
 R-H

To a solution of aldehyde (0.6 mmol) in 1,4-dioxane or cyclohexane (2 mL),  $K_2CO_3$  (0.6 mmol) and palladium catalyst (2 mol%) were added and the mixture was stirred at 140-150 °C for 8 h in air. When the reaction was completed (monitored by GC-MS or TLC), the solution was filtered and washed with EtOAc and ether. The filtered solution was evaporated under vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product.



To study the recyclability of Pd/POL-xantphos, the decarbonylation of HMF **1a** was conducted under the same conditions as described above. After reaction, the catalyst was separated through centrifugation, *n*-dodecane was added to the supernatant liquid as an internal standard, and the mixture was filtered under vacuum, the yield was determined by GC and the catalyst was washed with EtOAc, and reused in a next run.



*o*-Bromobenzaldehyde **4g** (0.19 g, 1.0 mmol),  $K_2CO_3$  (1.0 mmol) and palladium catalyst (2 mol%) were added to 1,4-dioxane (2 mL) under air, and the reaction mixture was stirred at 100 °C for 8 h. Then, the temperature was raised to 140 °C and the mixture was stirred for 6 h. When the reaction was completed, the solution was filtered and washed with EtOAc and ether. The filtrate was evaporated under vacuum. The crude product was purified directly by silica gel column chromatography eluting with petroleum ether and ethyl acetate to afford the corresponding product **4h**.

#### Table S1. Optimization of the Pd/C.

CO <sub>3</sub> 140 °C, 8 h
Yield
41%
37%
46%
33%
29%

Reaction conditions: HMF **1a** (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (0.5 mmol), Pd/C catalyst (2 mol%), 1,4-dioxane (1.5 mL), 140 °C, 8 h, under air atmosphere, GC yield.

	HO	Pd catalyst, O <u>K<sub>2</sub>CO</u> 1,4-Dio:	Ligand <sub>3</sub> HO xane	Ľ)	
Entry	Catalyst	Ligand	Tempreture	Time	Yield (%)
1	Pd(OAc) <sub>2</sub>	Xantphos	80	8 h	0
2	Pd(OAc) <sub>2</sub>	Xantphos	100	8 h	0
3	Pd(OAc) <sub>2</sub>	Xantphos	120	8 h	19
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Xantphos	80	8 h	0
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Xantphos	100	8 h	0
6	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Xantphos	120	8 h	7
7	PdCl <sub>2</sub>	Xantphos	80	8 h	0
8	PdCl <sub>2</sub>	Xantphos	100	8 h	0
9	PdCl <sub>2</sub>	Xantphos	120	8 h	16
10	Pd/C	1	80	8 h	0 <sup>b</sup>
11	Pd/C	1	100	8 h	0 <sup>b</sup>
12	Pd/C	1	120	8 h	41 <sup>b</sup>
13	Pd/C	1	120	16 h	59 <sup>b</sup>

# Table S2. Optimization of the temperatures.

<sup>*a*</sup>Reaction conditions: HMF **1a** (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (0.5 mmol), catalyst (5 mol%), 1,4-dioxane (1.5 mL), GC yield. <sup>*b*</sup>Heterogeneous catalyst (2 mol%).

**Characterization of Polymers** 



Figure S1. TG curve of POL-xantphos.



Figure S2. Pore size distribution curves. POL-xantphos (left), fresh Pd/POL-xantphos

(middle), used Pd/POL-xantphos (right)



**Figure S3.** N<sub>2</sub> adsorption-desorption isotherms. Left: POL-xantphos, BET surface area: 561.0 m<sup>2</sup>/g, Total pore volume: 0.648 cm<sup>3</sup>/g. Middle: fresh Pd/POL-xantphos, BET surface area: 506.3 m<sup>2</sup>/g, Total pore volume: 0.596 cm<sup>3</sup>/g. Right: used Pd/POL-xantphos, BET surface area: 494.9 m<sup>2</sup>/g, Total pore volume: 0.6099 cm<sup>3</sup>/g.



Figure S4. TEM of POL-xantphos.



Figure S5. Scanning electron microscopy (SEM) of POL-xantphos.



**Figure S6.** Scanning electron microscopy (SEM) of fresh Pd/POL-xantphos (left). Scanning electron microscopy (SEM) of used Pd/POL-xantphos (right).



**Figure S7.** a) XPS spectra of POL-xantphos. b) XPS spectra of fresh Pd/POL-xantphos. c) XPS spectra of the Pd/POL-xantphos which was used 10 runs.

Two peaks at 342.3 eV and 337.0 eV for fresh Pd/POL-xantphos and two peaks at 341.9 eV and 336.6 eV for used Pd/POL-xantphos were assigned to  $3d_{3/2}$  and  $3d_{5/2}$  for Pd species. Compared to the Pd(OAc)<sub>2</sub> (343.8 and 338.6 eV)<sup>[1]</sup>, the Pd binding energy XPS was shifted negatively by 1.5 eV. Interestingly, the XPS spectra of P2p show that the fresh and used Pd/POL-dppm give the similary binding energy of 132.5 eV, compared with that of POL-xanphos (131.4 eV). These results demonstrate the coordination of Pd species with POL-xantphos.

[1]. Zhifeng Dai, et al. Chinese Journal of Catalysts. 2016, 36, 54-60.



The solid state <sup>13</sup>C NMR spectrum of polymeric ligand showed all aromatic group of carbons around 130.4 ppm, benzylic carbons around 43.4 ppm, aliphatic methyl groups at 34.2 ppm and methylene groups at 25.7 ppm.

**Figure S8.** a) The <sup>31</sup>P SSNMR of Pd/POL-xantphos. b) The <sup>31</sup>P of solid state nuclear magnetic resonance (SSNMR) of POL-xantphos. c) The <sup>13</sup>C SSNMR of POL-xantphos.



**Figure S9.** X-ray diffraction (XRD) of POL-xantphos (left), fresh Pd/POL-Xantphos (middle) and used Pd-POL-xantphos (right).

The XRD shows that all three samples are amorphous

### <sup>1</sup>H, <sup>13</sup>C NMR and GC-MS data of products

Furfuryl alcohol (1b)



Yield was determined by gas chromatography using n-dodecane as internal standard. GC yield 93 % GC-MS (m/z): 98.0  $[M]^+$ .

N,N-Dimethylaniline (3a)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22- 7.14 (m, 2H), 6.74- 6.61 (m, 3H), 2.88 (s, 3H), 2.87(s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.54, 129.05, 116.80, 112.76, 40.67. GC-MS (m/z): 121.1 [M]<sup>+</sup>.

tert-Butylbenzene (3b)



Yield was determined by gas chromatography using n-dodecane as internal standard. GC-MS (m/z): 134.2 [M]<sup>+</sup>.

Nitrobenzene (3c)



<sup>1</sup>H NMR (400 MHz, CDCl3) δ 8.22- 8.16 (m, 2H), 7.72- 7.65 (m, 1H), 7.56- 7.48 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.02, 134.51, 129.19, 123.30. GC-MS (m/z): 123.1 [M]<sup>+</sup>

Benzonitrile (3d)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61- 7.51 (m, 3H), 7.45- 7.37 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  132.50, 131.76, 128.83, 118.51, 112.02. GC-MS (m/z): 103.0 [M]<sup>+</sup>.

Anisole (3e)



Yield was determined by gas chromatography using n-dodecane as internal standard. GC-MS (m/z): 108.0  $[M]^+$ .

Benzoic acid (3f)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.33 (s, 1H), 8.34- 7.89 (m, 2H), 7.73- 7.29 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  172.60, 133.75, 130.17, 129.30, 128.41. GC-MS (m/z): 122.0[M]<sup>+</sup>.

Acetophenone (**3g**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93- 7.88 (m, 2H), 7.53- 7.47 (m, 1H), 7.43- 7.36 (m, 2H), 2.54 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.85, 136.85, 132.87, 128.33, 128.05, 26.34. GC-MS (m/z): 120.2 [M]<sup>+</sup>

Biphenyl (**3h-j and 3m**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55- 7.47 (m, 2H), 7.38- 7.38 (m, 2H), 7.29- 7.21 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.22, 128.72, 127.22, 127.14. GC-MS (m/z): 154.1 [M]<sup>+</sup>.

Styrene (3k)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43- 7.33 (m, 2H), 7.32- 7.24 (m, 2H), 7.23- 7.18 (m, 1H), 6.68 (dd, *J* = 17.65, 10.93 Hz, 1H), 5.71 (d, *J* = 17.62 Hz, 1H), 5.20 (d, *J* = 10.88 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.53, 136.85, 128.44, 127.71, 126.16, 113.65. GC–MS (m/z): 104.0 [M]<sup>+</sup>.

Phenylacetylene (31)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.54 (m, 2H), 7.41 – 7.34 (m, 3H), 3.15 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 132.05, 128.69, 128.23, 122.09, 83.60, 77.19. GC-MS (m/z): 102.1 [M]<sup>+</sup>.

Naphthalene (**3n**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91- 7.81 (m, 4H), 7.55- 7.44 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  133.44, 127.86, 125.80. GC-MS (m/z): 128.2 [M]<sup>+</sup>.

Anthracene (**30**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (s, 2H), 8.07- 7.96 (m, 4H), 7.52- 7.41 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 131.68, 128.15, 126.20, 125.33. GC–MS (m/z): 178.2 [M]<sup>+</sup>.

Pyrene (**3p**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25- 8.18 (m, 4H), 8.13- 8.07 (m, 4H), 8.06- 8.01 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 131.11, 127.34, 125.81, 124.90, 124.64. GC–MS (m/z): 202.1 [M]<sup>+</sup>.

Quinoline (**3q**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.94- 8.87 (m, 1H), 8.17- 8.08 (m, 2H), 7.84-7.76 (m, 1H), 7.74- 7.66 (m, 1H), 7.57- 7.48 (m, 1H), 7.40- 7.33 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.27, 148.15, 136.04, 129.41, 129.33, 128.22, 127.71, 126.49, 120.99. GC–MS (m/z): 129.1[M]<sup>+</sup>.

Indole (**3r**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (s, 1H), 7.61-7.70 (m, 1H), 7.42- 7.34 (m, 1H), 7.23-7.16 (m, 2H), 7.15- 7.08 (m, 1H), 6.60- 6.51 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.74, 127.82, 124.09, 121.95, 120.70, 119.78, 110.98, 102.59. GC–MS (m/z): 117.1 [M]<sup>+</sup>.

Isoquinoline (**3s**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.25 (s, 1H), 8.56- 8.48 (m, 1H), 8.00- 7.91 (m, 1H), 7.83-7.76 (m, 1H), 7.71 – 7.55 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.45, 142.92, 135.71, 130.27, 128.61, 127.55, 127.17, 126.39, 120.38. GC–MS (m/z): 129 [M]<sup>+</sup>.

2,3-Dihydro-7-azaindole (**3t**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.79- 7.70 (m, 1H), 7.22- 7.13 (m, 1H), 6.47- 6.37 (m, 1H), 4.92 (s, 1H), 3.53 (t, *J* = 8.4 Hz, 2H), 2.97 (t, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.64, 145.34, 131.15, 121.89, 112.85, 44.05, 27.51. GC–MS (m/z): 120.1 [M]<sup>+</sup>.

Thianaphthene (**3u**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91- 7.88 (m, 1H), 7.87- 7.82 (m, 1H), 7.48- 7.43 (m, 1H), 7.42 – 7.33 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.69, 139.56, 126.26, 124.17, 124.12, 123.81, 123.58, 122.45. GC–MS (m/z): 134.0 [M]<sup>+</sup>.

Oxole (**3v**)



Yield was determined by gas chromatography using n-dodecane as internal standard. GC yield 99 %.

Hendecane (3w)



Yield was determined by gas chromatography using n-dodecane as internal standard. GC-MS (m/z): 156.2  $[M]^+$ .

Furfuryl alcohol (4b)



Yield was determined by gas chromatography using n-dodecane as internal standard. GC-MS (m/z): 96.0  $[M]^+$ .

9-Fluorenone (4h)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70- 7.64 (m, 2H), 7.56- 7.45 (m, 4H), 7.35- 7.27 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.92, 144.44, 134.68, 134.16, 129.08, 124.33, 120.30. GC–MS (m/z): 180.1 [M]<sup>+</sup>.

# Copies of <sup>13</sup>C and <sup>1</sup>H NMR spectra for products

N,N-Dimethylaniline (3a)





Benzonitrile (3d)









Styrene (3k)



Phenylacetylene (31)



Naphthalene (3n)



Anthracene (30)



Pyrene (**3p**)



Quinoline (3q)



Indole (3r)





#### 2,3-Dihydro-7-azaindole (3t)



# Thianaphthene (3u)





