

## Supporting Information

### Single-Site Palladium(II) Catalyst for Oxidative Heck Reaction: Catalytic Performance and Kinetic Investigations

Hui Duan,<sup>†</sup> Menghuan Li,<sup>†</sup> Guanghui Zhang,<sup>‡,§</sup> James R. Gallagher,<sup>§</sup> Zhiliang Huang,<sup>‡,§</sup> Yu Sun,<sup>‡</sup> Zhong Luo,<sup>†</sup> Hongzhong Chen,<sup>†</sup> Jeffrey T. Miller,<sup>§</sup> Ruqiang Zou,<sup>±</sup> Aiwen Lei,<sup>‡,\*</sup> Yanli Zhao<sup>†,¶\*</sup>

<sup>†</sup>Division of Chemistry and Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, 637371 Singapore

<sup>‡</sup>College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, China

<sup>§</sup>Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

<sup>±</sup> Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

<sup>¶</sup>School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore

E-mail: zhaoyanli@ntu.edu.sg, aiwenlei@whu.edu.cn

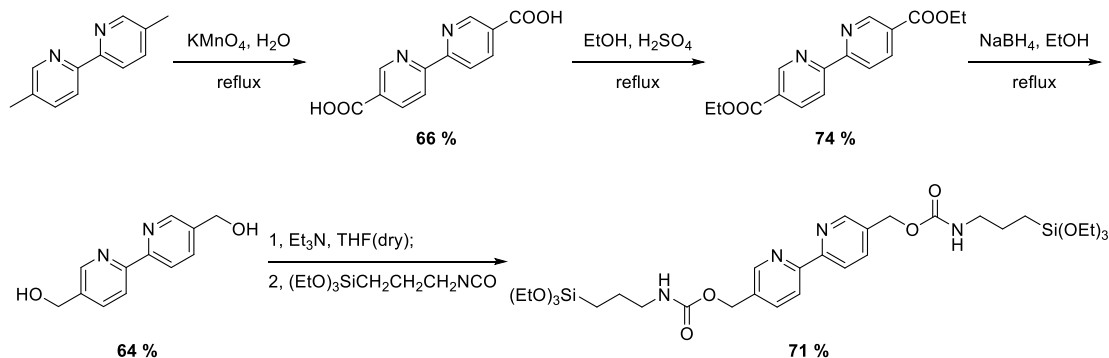
## Table of Contents

General information.....	3
Synthesis of 2,2'-bipyridine based organosilane precursor .....	3
Preparation of 2,2'-bipyridine functionalized MCM type PMOs.....	4
Passivation of silanol groups on sample PMOs-05-BiPy.....	5
Preparation of catalysts .....	5
Characterizations of the functionalized PMOs and the catalyst .....	7
TEM .....	7
Powder XRD .....	7
N <sub>2</sub> Adsorption/desorption isotherm .....	8
Contact angle of sample Si-PMOs-05-BiPy.....	10
FT-IR .....	10
TGA.....	11
Control experiments of the model reaction.....	12
Optimization of the ratio between two substrates.....	13
Plug Flow Reactor (PFR) set up of the model reaction.....	13
XAS data of fresh catalyst and recovered catalyst .....	12
Kinetic data of palladium catalyzed oxidative Heck reaction.....	17
NMR data of the products in Table 2 .....	19

## General information

All the chemicals were purchased from Sigma Aldrich and used as received. Non-aqueous THF, MeOH and DMSO were purchased from Sigma Aldrich and used directly. All non-aqueous reactions and manipulations were performed in a N<sub>2</sub> atmosphere using standard Schlenk techniques. All reactions were monitored by TLC and GC. NMR spectra were recorded on Bruker spectrometer at 300 MHz (<sup>1</sup>H NMR) and 75 MHz (<sup>13</sup>C NMR), or a Bruker spectrometer at 400 MHz (<sup>1</sup>H NMR) and 100 MHz (<sup>13</sup>C NMR). Tetramethylsilane (TMS) was used as an internal standard. All <sup>1</sup>H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants were reported in Hertz (Hz). FT-IR spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer with the sample powder diluted in KBr (1%). Typically, 4 scans with a resolution of 4 cm<sup>-1</sup> were collected for each sample. BET surface areas were obtained using a Micromeritics ASAP 2020M automated sorption analyzer. The transmission electron microscopy (TEM) images were obtained using a JEOL 2010. Powder X-ray diffraction (PXRD) measurements were performed on a SHIMADZU XRD-6000 Labx diffractometer at 40 kV and 30 mA using Cu Kα radiation (λ = 1.5418 Å). The palladium contents of catalysts were determined by ICP-MS (Agilent 7700).

## Synthesis of 2,2'-bipyridine based organosilane precursor



**Scheme S1.** Synthetic route of 2,2'-bipyridine based organosilane precursor.

[2,2'-Bipyridine]-5,5'-dicarboxylic acid:

To a stirred solution of potassium permanganate (4.38 g, 27.70 mmol) in water (60 mL), 5,5'-dimethyl-2,2'-bipyridine (0.79 g, 4.27 mmol) was added. The mixture was heated in an oil bath to reflux for 5 hours. Subsequently, the mixture was cooled down to room temperature followed by filtration. Then, the filtrate was washed by Et<sub>2</sub>O (100 mL) three times. After the pH value of the water phase was adjusted to 2, white floc solid appeared. The mixture was filtered and white solid was obtained. The solid was dried at 50 °C under vacuum overnight. [2,2'-Bipyridine]-5,5'-dicarboxylic acid (0.68 g, 2.80 mmol, 66 % yield) was obtained as a white solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400MHz): δ = 13.57 (br. s., 2 H), 9.20 (s, 2 H), 8.57 (d,

$J=8.3$  Hz, 2 H), 8.42 - 8.47 ppm (m, 2 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 101MHz):  $\delta$  = 166.5, 157.8, 150.8, 138.9, 127.6, 121.6 ppm.

Diethyl [2,2'-bipyridine]-5,5'-dicarboxylate:

[2,2'-Bipyridine]-5,5'-dicarboxylic acid (0.65 g, 2.65 mmol) was added to a mixture of ethanol (15 mL) and concentrated  $\text{H}_2\text{SO}_4$  (2 mL, 37.50 mmol). Then, the mixture was stirred and heated to reflux for 10 hours. The mixture was cooled down to room temperature and poured into ice water (100 mL). After the filtration, white solid was obtained. Needle diethyl [2,2'-bipyridine]-5,5'-dicarboxylate (0.59 g, 1.97 mmol, 74 % yield) was obtained after recrystallization by EtOH.  $^1\text{H}$  NMR (DMSO- $d_6$ , 400MHz):  $\delta$  = 9.22 (s, 2 H), 8.60 (d,  $J=8.3$  Hz, 2 H), 8.47 - 8.51 (m, 2 H), 4.40 (q,  $J=7.0$  Hz, 4 H), 1.37 ppm (t,  $J=7.2$  Hz, 6 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 101MHz):  $\delta$  = 164.9, 157.9, 150.5, 138.8, 126.9, 121.7, 61.8, 14.6 ppm.

[2,2'-Bipyridine]-5,5'-diylldimethanol:

To a solution of diethyl [2,2'-bipyridine]-5,5'-dicarboxylate (0.55 g, 1.83 mmol) in ethanol (55 mL),  $\text{NaBH}_4$  (1.52 g, 40.30 mmol) was added. The mixture was stirred and refluxed for 7 hours. After the solvent was removed by rotary evaporator, minimal  $\text{H}_2\text{O}$  was added to dissolve the solid. Then, the mixture was extracted with EtOAc (3 x 50 mL). After being dried by  $\text{Na}_2\text{SO}_4$ , the organic solvent was removed, and [2,2'-bipyridine]-5,5'-diylldimethanol (0.32 g, 1.17 mmol, 64 % yield) was obtained.  $^1\text{H}$  NMR (DMSO- $d_6$ , 400MHz):  $\delta$  = 8.61 (s, 2 H), 8.35 (d,  $J=8.3$  Hz, 2 H), 7.84 - 7.89 (m, 2 H), 5.38 (t,  $J=5.5$  Hz, 2 H), 4.60 ppm (d,  $J=5.0$  Hz, 4 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 101MHz):  $\delta$  = 154.5, 148.2, 138.4, 135.9, 120.3, 61.0 ppm.

[2,2'-bipyridine]-5,5'-diylbis(methylene) bis((3-(triethoxysilyl)propyl)carbamate):

Under the protection of  $\text{N}_2$ ,  $\text{Et}_3\text{N}$  (dry, 516  $\mu\text{L}$ , 3.70 mmol) was added to a solution of [2,2'-bipyridine]-5,5'-diylldimethanol (0.20 g, 0.93 mmol) in dry THF (9 mL). The mixture was stirred at room temperature overnight. Triethoxy(3-isocyanatopropyl)silane (460  $\mu\text{L}$ , 1.86 mmol) was added. After stirring for additional one day, the solvent and  $\text{Et}_3\text{N}$  were removed by rotary evaporator. The solid appeared after hexane (10 mL) was added to the mixture. [2,2'-bipyridine]-5,5'-diylbis(methylene) bis((3-(triethoxysilyl)propyl)carbamate) (0.47 g, 0.65 mmol, 71 % yield) was obtained by filtration.  $^1\text{H}$  NMR (DMSO- $d_6$ , 400MHz):  $\delta$  = 8.67 (s, 2 H), 8.38 (d,  $J=8.0$  Hz, 2 H), 7.88 - 7.95 (m, 2 H), 7.34 (t,  $J=5.6$  Hz, 2 H), 5.12 (s, 4 H), 3.73 (q,  $J=7.0$  Hz, 12 H), 2.98 (q,  $J=6.5$  Hz, 4 H), 1.46 (dt,  $J=15.5$ , 7.7 Hz, 4 H), 1.13 (t,  $J=6.9$  Hz, 18 H), 0.48 - 0.57 ppm (m, 4 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 101MHz):  $\delta$  = 156.4, 155.0, 149.3, 137.3, 133.8, 120.6, 63.1, 58.1, 43.5, 23.4, 18.7, 7.6 ppm

### Preparation of 2,2'-bipyridine functionalized MCM type PMOs

A gel was initially formed with EtOH (5.90 mL, 101 mmol),  $\text{H}_2\text{O}$  (20.75 mL, 1152 mmol),  $\text{NH}_4\text{OH}$  (6.05 mL, 81 mmol), tetraethyl orthosilicate (2 g, 9.60 mmol) and [2,2'-bipyridine]-5,5'-diylbis(methylene) bis((3-(triethoxysilyl)propyl)carbamate) (0.36 g, 0.51 mmol).

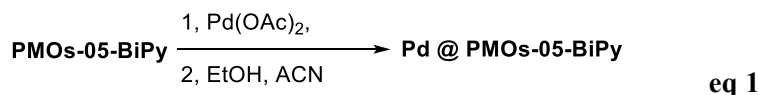
$N,N,N$ -Trimethylhexadecan-1-amonium bromide (0.44 g, 1.21 mmol) was dissolved in  $\text{H}_2\text{O}$  (20.75 mL, 1152 mmol), then  $\text{NH}_4\text{OH}$  (6.05 mL, 81 mmol) was added, and the mixture was heated to 40  $^\circ\text{C}$  with

stirring for 30 min. After the mixture was cooled down to room temperature, the premixed gel was slowly added in 30 min. The mixture was then stirred at room temperature for 120 min. After being heated to 90 °C and stirred for 4 days, solid was obtained and washed with H<sub>2</sub>O, which was dried under vacuum at 50 °C. The solid was added to a solution of 0.5 M HCl in EtOH, which was stirred for 2 hours. The sample was filtered and washed by EtOH to obtain PMOs-05-BiPy (0.90 g).

### Passivation of silanol groups on sample PMOs-05-BiPy

Under the protection of N<sub>2</sub>, PMOs-05-BiPy (500 mg) was decentralized in dry toluene (200 mL). Me<sub>3</sub>SiOEt (2.0 mL) was then added, and the mixture was stirred and refluxed for 2 days. After cooling down to room temperature, the sample was filtered and dried under vacuum for overnight. The passivated sample Si-PMOs-05-BiPy was obtained.

### Preparation of catalysts



#### Method A:

PMOs-05-BiPy (100 mg) was added to a 25 mL Schlenk tube, which was dried under vacuum at 90 °C overnight. After that, Pd(OAc)<sub>2</sub> (10 mg) was added under the protection of N<sub>2</sub>. Then, dry DMSO (2.5 mL) was added and the mixture was stirred at room temperature for 2 hours. Pd<sup>II</sup>@PMOs-05-BiPy was obtained after filtration and washing by plenty acetonitrile.

#### Method B:

PMOs-05-BiPy (100 mg) was added to a 25 mL Schlenk tube, which was dried under vacuum at 90 °C overnight. After that, Pd(OAc)<sub>2</sub> (10 mg) was added under the protection of N<sub>2</sub>. Then, dry DMSO (2.5 mL) was added and the mixture was stirred at 80 °C for overnight. The catalyst (Pd<sup>II</sup>@PMOs-05-BiPy) was obtained after filtration and washing by plenty acetonitrile.

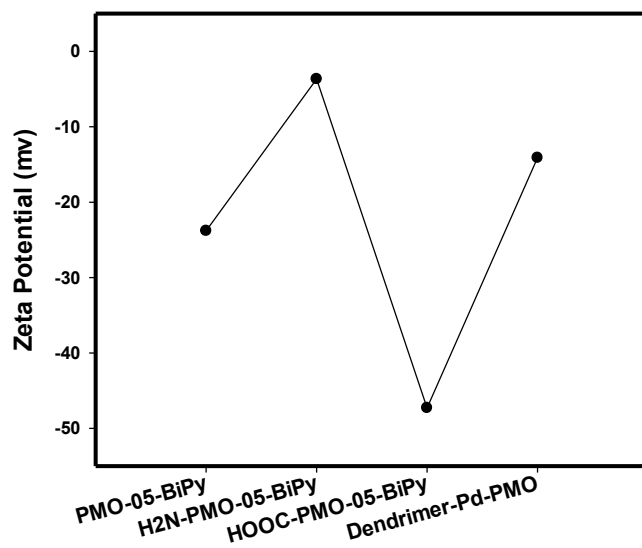
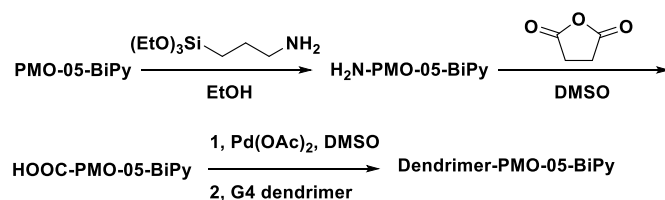
#### Method C:

PMOs-05-BiPy (100 mg) was added to a 25 mL Schlenk tube, which was dried under vacuum at 90 °C overnight. After that, Pd(OAc)<sub>2</sub> (10 mg) was added under the protection of N<sub>2</sub>. Then, dry EtOH (2.5 mL) was added and the mixture was stirred at room temperature for 3 hours. The catalyst (Pd<sup>II</sup>@PMOs-05-BiPy) was obtained after filtration and washing by plenty acetonitrile.

### Preparation of catalysts Pd''@PMOs

PMOs (100 mg) was added to a 25 mL Schlenk tube, which was dried under vacuum at 90 °C overnight. After that, Pd(OAc)<sub>2</sub> (10 mg) was added under the protection of N<sub>2</sub>. Then, dry DMSO (2.5 mL) was added and the mixture was stirred at room temperature for 2 hours. Pd''@PMOs (the color of this catalyst turned to gray during the drying process) was obtained after filtration and washed by acetonitrile.

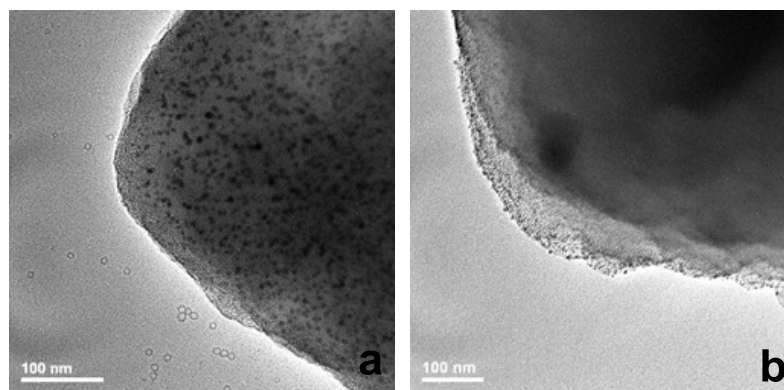
### Synthesis route of sample Dendrimer-Pd-PMO



**Figure S1.** Changes of zeta potential for each sample.

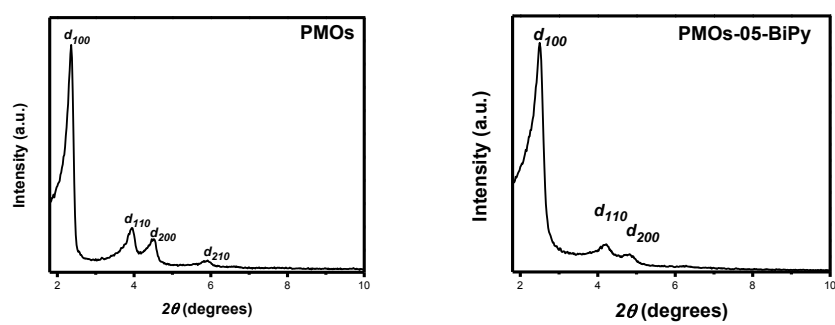
## Characterizations of the functionalized PMOs and the catalyst

### TEM



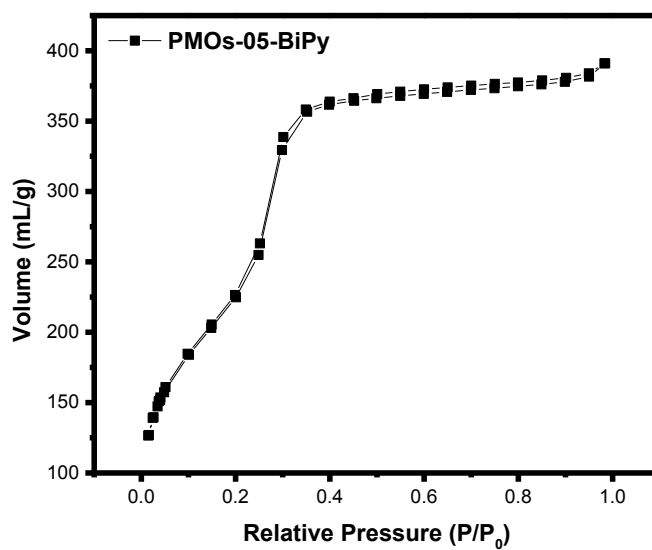
**Figure S2.** (a,b) TEM images of sample Pd''@PMOs.

### Powder XRD



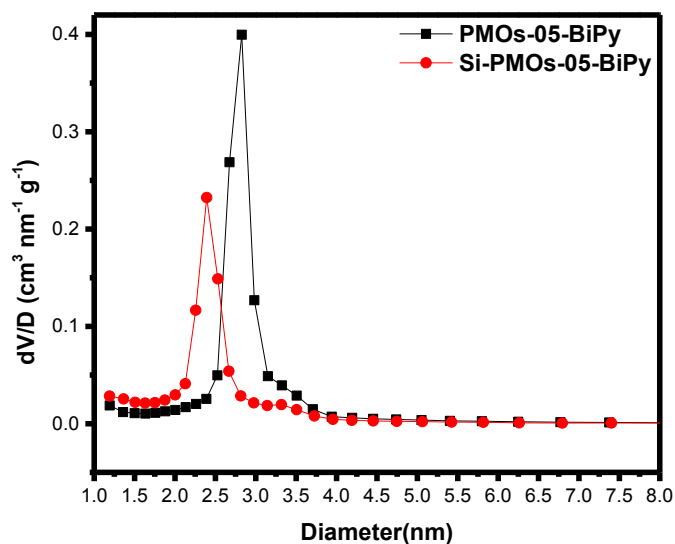
**Figure S3.** Powder XRD data of PMOs (without BiPy) and PMOs-05-BiPy.

*N<sub>2</sub> Adsorption/desorption isotherm*

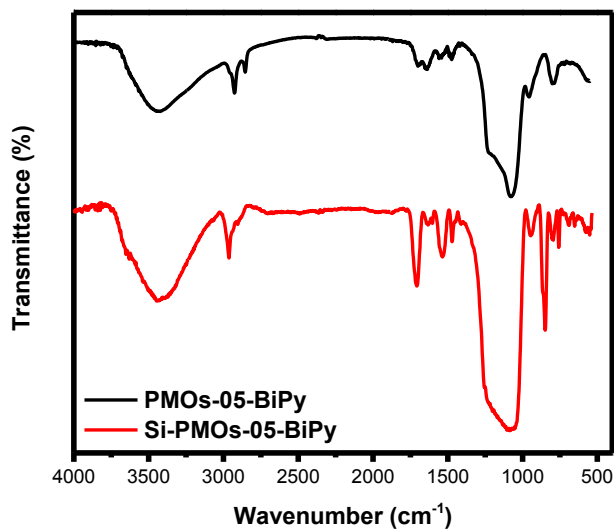


**Figure S4.** N<sub>2</sub> adsorption/desorption isotherm for PMOs-05-BiPy based on BJH method. The surface area is 817 m<sup>2</sup>/g, and the total pore volume is 0.6 mL/g.





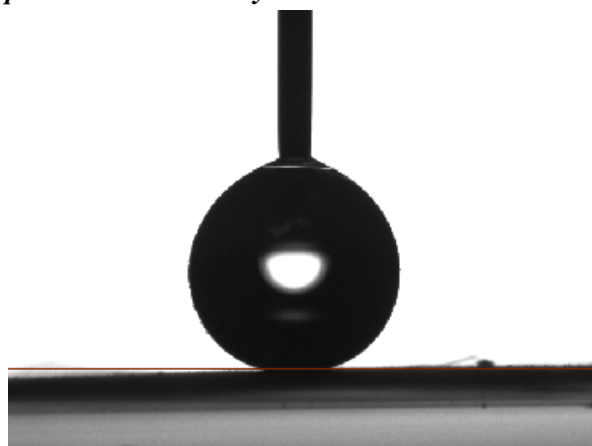
(a)



(b)

**Figure S5.** a) Pore diameters of sample PMOs-05-BiPy (2.9 nm) and passivated sample Si-PMOs-05-BiPy (2.4 nm); b) FT-IR spectra of samples PMOs-05-BiPy and passivated Si-PMOs-05-BiPy.

*Contact angle of sample Si-PMOs-05-BiPy*

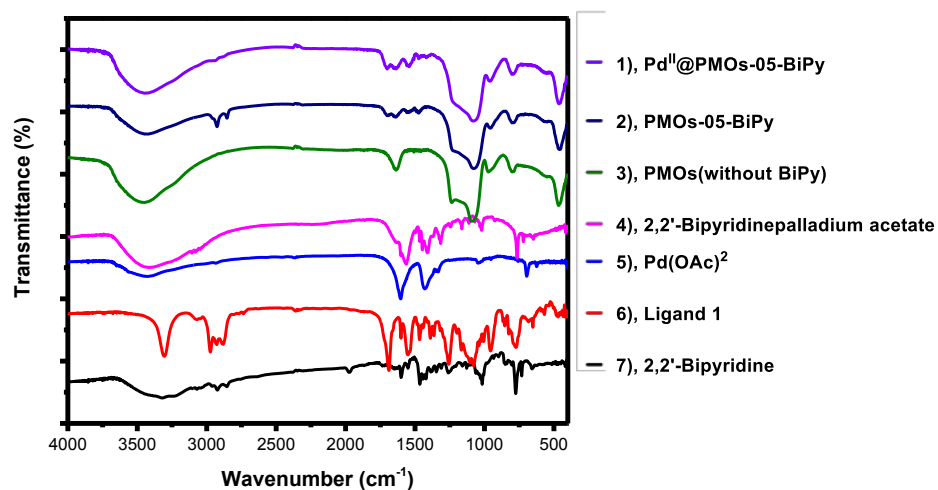


**Figure S6.** Contact angle of sample Si-PMOs-05-BiPy was test through sessile drop method.

**Table S1.** The contact angle of sample Si-PMOs-05-BiPy.

Time [s]	CA left [°]	CA right [°]	CA mean [°]	Volume [μL]	Baseline [mm]
0	164.7	164.7	164.7	3.71	0.65
0.99	163.8	163.9	163.9	3.76	0.65
2.99	165.9	166.0	166.0	3.75	0.63
3.99	163.2	163.2	163.2	3.76	0.67
			<b>164.4</b>		

*FT-IR*

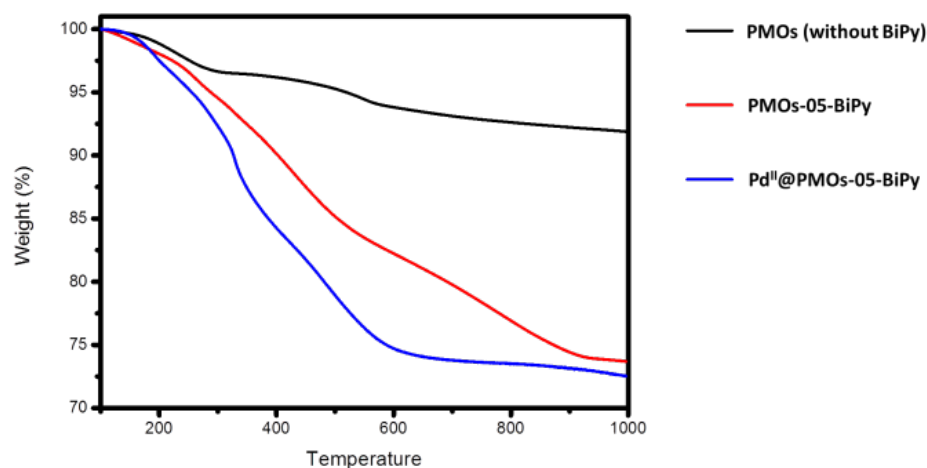


**Figure S7.** FT-IR spectra of Pd<sup>II</sup>@PMOs-05-BiPy, PMOs-05-BiPy, PMOs (without BiPy), 2,2'-bipyridine palladium acetate, Pd(OAc)<sub>2</sub>, ligand **1**, and 2,2'-bipyridine.

**Table S2.** Summary of the FT-IR data from Figure S7.

Samples	1	2	3	4	5	6	7
2926 $\text{cm}^{-1}$	None	<input checked="" type="checkbox"/>	None	None	None	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
1700 $\text{cm}^{-1}$	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	None	None	None	<input checked="" type="checkbox"/>	None
1550 $\text{cm}^{-1}$	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	None	<input checked="" type="checkbox"/>	None	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
1425~1411 $\text{cm}^{-1}$	<input checked="" type="checkbox"/>	None	None	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	None	None

### TGA



**Figure S8.** TGA data of PMOs (without BiPy), PMOs-05-BiPy and Pd<sup>II</sup>@PMOs-05-BiPy.

### General catalytic procedure

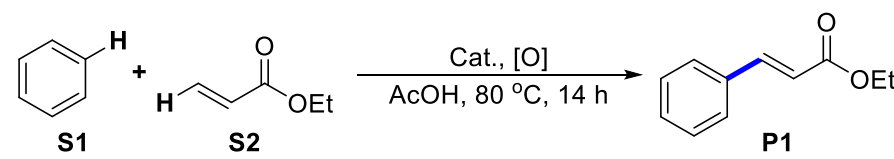
A Schlenk tube was charged with Pd<sup>II</sup>@PMOs-05-BiPy (20 mg), ethyl acrylate (53  $\mu\text{L}$ , 0.5 mmol) and AcOH (3.0 mL) under a N<sub>2</sub> atmosphere at room temperature, followed by the addition of benzene (1.8 mL, 20 mmol) and <sup>t</sup>BuOOH (76  $\mu\text{L}$ , 70 % solution in water, 1.1 eq). The resulting solution was stirred at 80 °C for 14 h, which was then filtered to remove the catalyst. The obtained filtrate was concentrated using rotary evaporator. To the residue was added water (10 mL), the mixture was extracted by diethyl ether (10 mL x 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, which was filtered and concentrated under reduced pressure. Finally, the residue was purified by flash chromatography (ethyl acetate : hexane = 1 : 100) to afford the desired product.

## Procedure for intermolecular kinetic isotope experiments

To a 10 mL vial were added Pd (II) (for Pd(OAc)<sub>2</sub>, 2.0 mg; for Pd<sup>II</sup>@PMOs-05-BiPy, 20 mg), ethyl acrylate (29  $\mu$ L, 0.28 mmol) and AcOH (1.5 mL), followed by the addition of benzene (0.5 mL, 5.6 mmol), *d*<sup>6</sup>-benzene (0.5 mL, 5.6 mmol) and *t*BuOOH (42  $\mu$ L, 70 % solution in water, 1.1 eq). The resulting solution was stirred at 80 °C for 10 h, which was then filtered to remove the catalyst. The obtained filtrate was concentrated using rotary evaporator. To the residue was added water (10 mL), the mixture was extracted by diethyl ether (10 mL x 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, which was filtered and concentrated under reduced pressure. Finally, the residue was purified by a fast flash to afford the crude product. Then analyze the crude product by <sup>1</sup>H NMR to obtain the *k*<sub>H</sub>/*k*<sub>D</sub>.

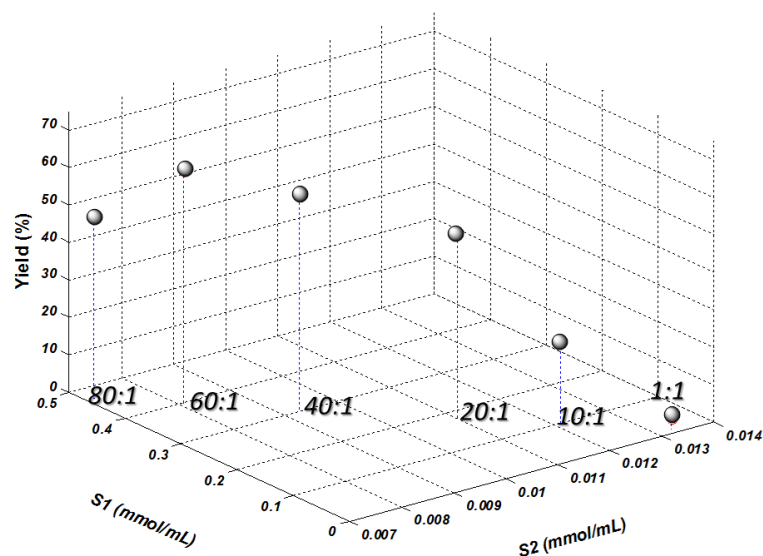
## Control experiments of the model reaction

**Table S3.** Control experiments of the model reaction.<sup>[a]</sup>

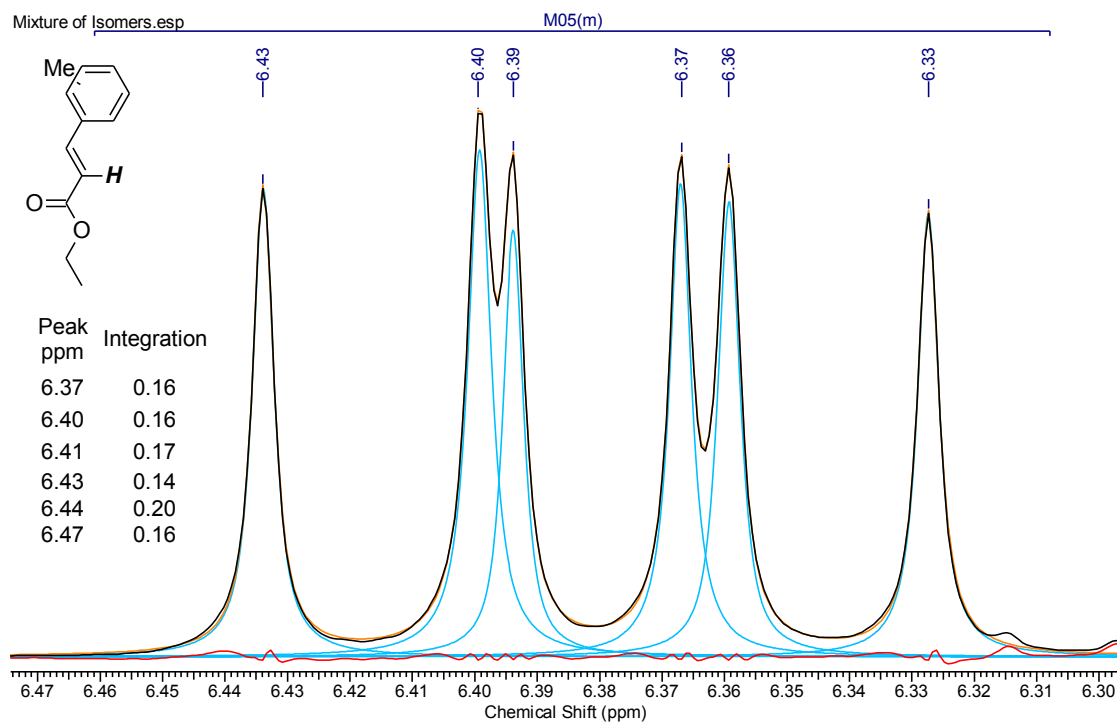
				
Entry	Cat.	[O]	Selectivity	Yield
1	Pd <sup>II</sup> @PMOs-05-BiPy	<i>t</i> -BuOOH <sup>[c]</sup>	98 %	58 %
2	Pd <sup>II</sup> @PMOs-05-BiPy	None	----	None
3	PMOs-05-BiPy	<i>t</i> -BuOOH <sup>[c]</sup>	----	None
4	None	<i>t</i> -BuOOH <sup>[c]</sup>	----	None
5	BiPy: Pd(OAc) <sub>2</sub> <sup>[b]</sup>	<i>t</i> -BuOOH <sup>[c]</sup>	----	Trace

[a] Reaction conditions: **S1** (20 mmol) and **S2** (0.5 mmol), AcOH as the solvent (4.0 mL), 80 °C, 14 h, and the conversions were determined by GC with dodecane as the internal standard, [b] 3.4 mg Bis(acetato-O)(2,2'-bipyridine-N,N')palladium (BiPy: Pd(OAc)<sub>2</sub>) used as the catalyst, [c] 1.1 equiv, 0.55 mmol, 70 % solution in water.

## Optimization of the ratio between two substrates



**Figure S9.** Optimization of the concentrations of two substrates. Reaction conditions: **S1** and **S2** (0.5 mmol), the ratio showed in picture is molar ratio of **S1** to **S2**, <sup>t</sup>BuOOH (70 % solution in water, 0.55 mmol), AcOH as the solvent (4.0 mL), 80 °C, 14 h, and the conversions were determined by GC with dodecane as the internal standard. All the selectivity is near or over 99 %.



**Figure S10.** NMR peak fitting for the mixture of P9 isomers.

## Plug Flow Reactor (PFR) set up of the model reaction

Conditions:

Syringe pump: Chemyx Syringe pump, F100; Tubing: PFA tubing 1/16 in x 0.020 in; T-mixer: PHENOMENEX, PEEK Tee, 0.020 in Thru-Hole; Reactor: empty column from PHENOMENEX, 1.0 mm ID x 1/8 in OD x 100 mm; 20 mg Pd<sup>II</sup>@PMOs-05-BiPy was filled; Method: the molar ratio of **S1** and **S2** was same to the batch reactor (40:1), 2.0 equiv. <sup>t</sup>BuOOH was used, flow rate was set to 2  $\mu$ L/min, and the temperature was set to 90 °C.

## XAS data of fresh catalyst and recovered catalyst

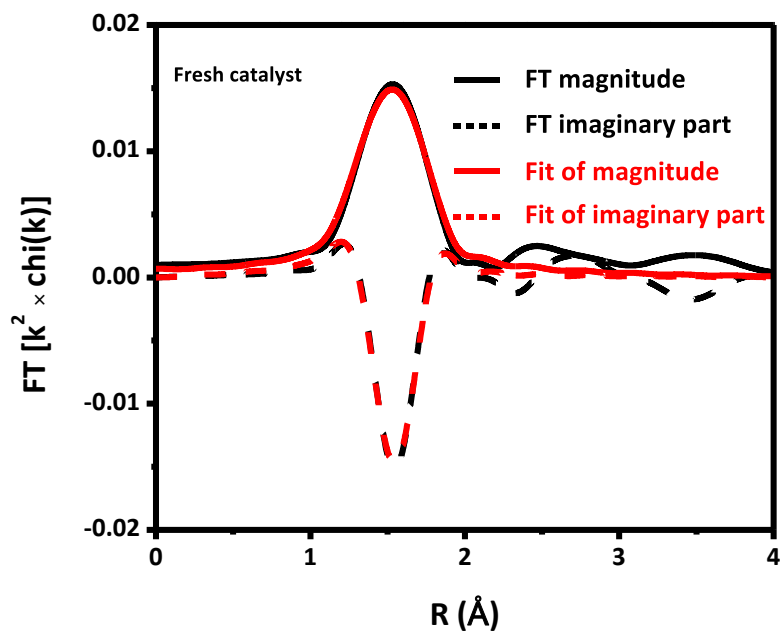
X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne national Laboratory. The data were collected in transmission quick scan mode. Insertion device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. The ionization chambers were optimized for the maximum current with linear response ( $\sim 10^{10}$  photons detected/sec) with 10 % absorption (35 % N<sub>2</sub> and 65 % Ar) in the incident ion chamber and 15 % absorption (100 % Ar) in the transmission detector. A Pd foil spectrum (edge energy 24350.0 eV) was acquired simultaneously with each measurement for energy calibration, and multiple scans were taken to ensure spectrum reproducibility.

All samples were grinded well with mortar and pestle, and then 80 mg of the sample was pressed into a cylindrical sample holder consisting of six wells with a radius of 2.0 mm, forming a self-supporting wafer. The sample holder was placed in a quartz tube (1-in. OD, 10-in. length) sealed with Kapton windows by two Ultra-Torr fittings and then used for transmission mode measurement.

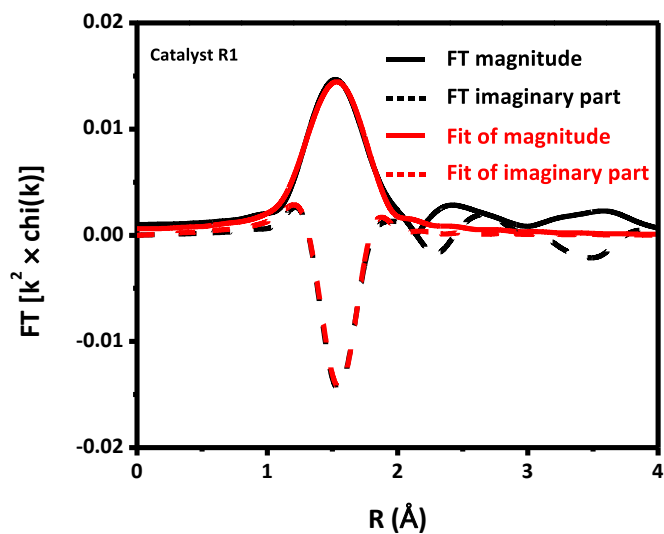
The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. Experimental phase shift and back scattering amplitude were used to fit the EXAFS data. Pd-O phase shift and back scattering amplitude were obtained from reference compound: Pd(OAc)<sub>2</sub> (4 Pd-O at 2.03 Å). Pd-O phase shift and back scattering amplitude were used to fit the Pd-O/N shell.

Background removal and normalization procedures were carried out using the Athena software package using standard methods. Standard procedures based on WinXAS 3.2 software were used to extract the extended X-ray absorption fine structure (EXAFS) data. Fourier filtering technique was used to remove the features below 1 Å in the R-space spectra. The coordination parameters were obtained by a least square fit in R-space of the nearest neighbor,  $k^2$ -weighted Fourier transform data.

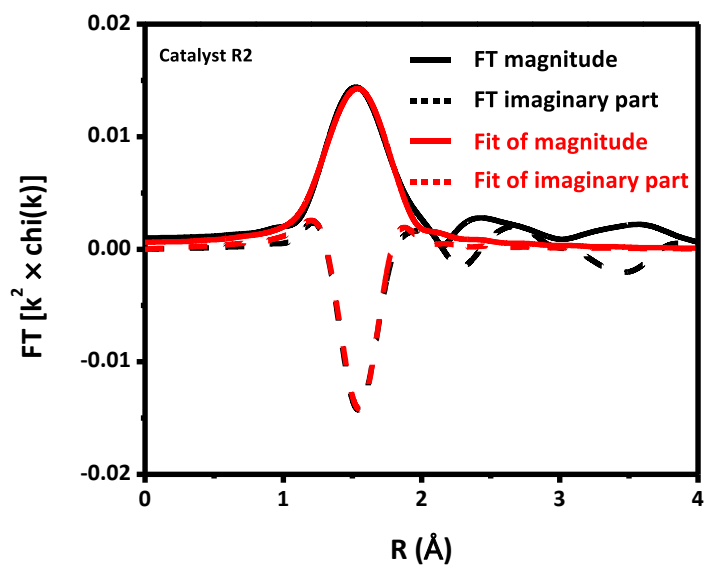
Catalyst R1 was recovered after the first use, Catalyst R2 was recovered after the second use, and Catalyst R3 was recovered after the third use.



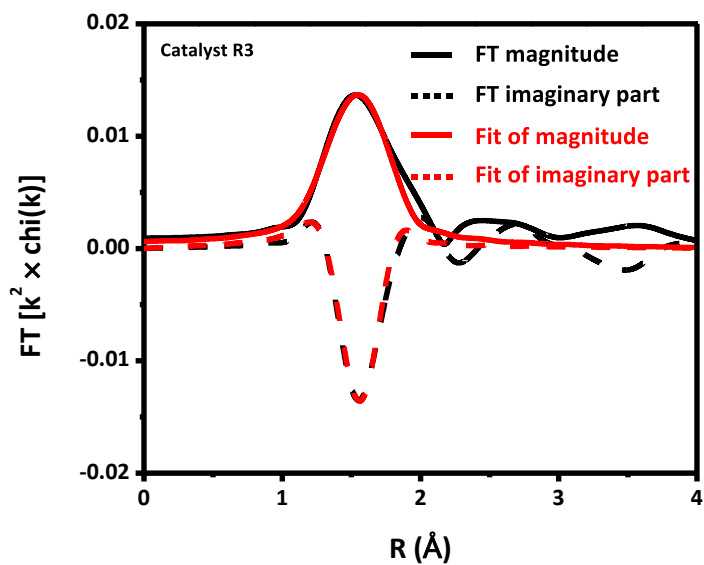
**Figure S11.** R-space EXAFS fitting results of the fresh Pd<sup>II</sup>@PMOs-05-BiPy catalyst. Fourier transform range: 3.08 Å<sup>-1</sup> – 12.72 Å<sup>-1</sup>; fitting range: 1.12 Å – 1.94 Å.



**Figure S12.** R-space EXAFS fitting results of recycled catalyst R1. Fourier transform range: 3.09 Å<sup>-1</sup> – 12.81 Å<sup>-1</sup>; fitting range: 1.10 Å – 1.93 Å.



**Figure S13.** R-space EXAFS fitting results of recycled catalyst R2. Fourier transform range:  $3.08 \text{ \AA}^{-1} - 12.96 \text{ \AA}^{-1}$ ; fitting range:  $1.13 \text{ \AA} - 1.91 \text{ \AA}$ .



**Figure S14.** R-space EXAFS fitting results of recycled catalyst R3. Fourier transform range:  $3.10 \text{ \AA}^{-1} - 13.06 \text{ \AA}^{-1}$ ; fitting range:  $1.12 \text{ \AA} - 1.97 \text{ \AA}$ .



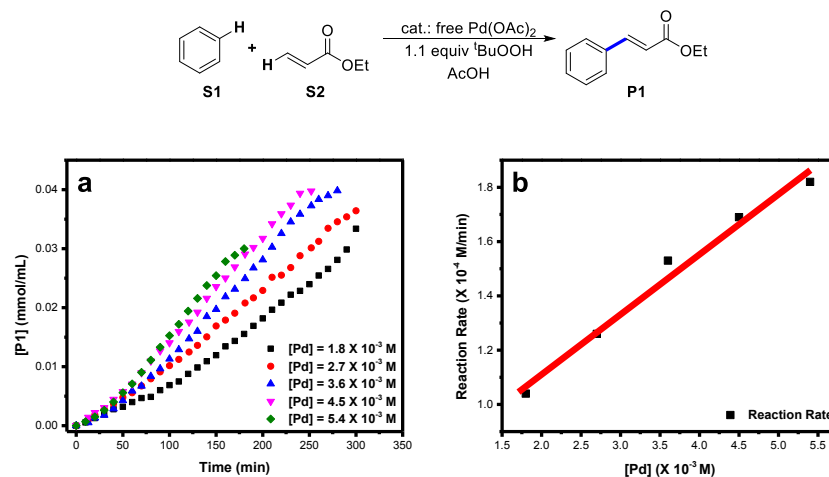
**Table S4.** Summary of the XANES and EXAFS fitting results of fresh catalyst and recycled catalysts.

Sample	Edge Energy (eV)	Oxidation State	Coordination Number	Bond Distance (Å)	$\sigma^2$	$\Delta E_0$
Fresh Catalyst	24353.8	II	4	2.03	0.0021	-0.415
Catalyst R1	24353.8	II	4	2.04	0.0026	-0.517
Catalyst R2	24353.8	II	4	2.04	0.0028	-0.161
Catalyst R3	24353.8	II	4	2.06	0.0030	0.976

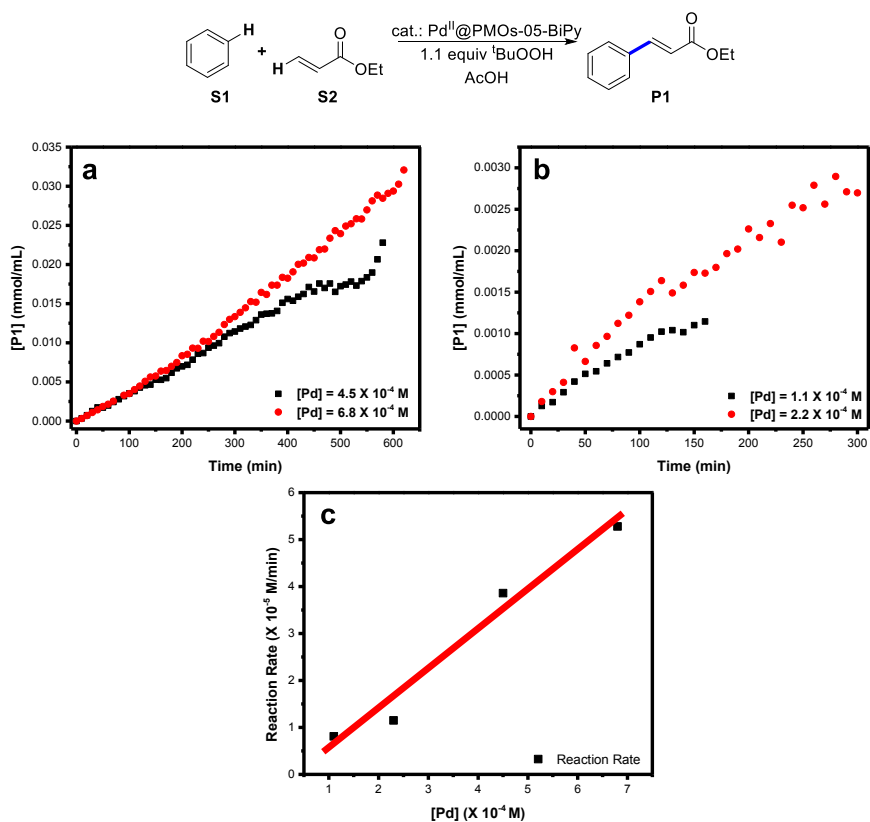
**Table S5.** Summary of the electronic and geometrical structures of the references.

	Edge Energy (eV)	Oxidation State	Coordination Number	Bond Distance (Å)	References
Pd foil	24350.0	0	12	2.74	<i>Physica Scripta</i> <b>2005</b> , T115, 749-752
Pd(OAc) <sub>2</sub>	24353.1	II	4	2.03	<i>Acta Cryst.</i> <b>2004</b> , C60, 449
PdO	24353.3	II	4	2.02	<i>Acta Cryst.</i> <b>1953</b> , 6, 661

**Kinetic data of palladium catalyzed oxidative Heck reaction**



**Figure S15.** Kinetic profiles of free Pd<sup>II</sup> in the model reaction when different palladium concentrations were employed and the linear relationship of rate vs palladium concentration. Reaction conditions: S1, 0.448 mmol, S2, 20.1 mmol, 85°C, 3.2 mL AcOH as the solution.

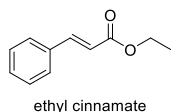


**Figure S16.** Kinetic profiles of Pd<sup>II</sup>@PMOs-05-BiPy in the model reaction when different palladium concentrations were employed and the linear relationship of rate vs palladium concentration. Reaction conditions: **S1**, 0.448 mmol, **S2**, 20.1 mmol, 85°C, 3.2 mL AcOH as the solution.

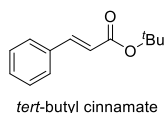
**Table S6.** Some KIE value of homogenous catalytic system.

Entry	[Pd]	[O]	k <sub>H</sub> /k <sub>D</sub>
1	Pd(OAc) <sub>2</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	4.4
2	Pd(OAc) <sub>2</sub>	<i>t</i> -BuOOH	4.5

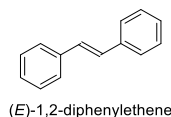
## NMR data of the products in Table 2



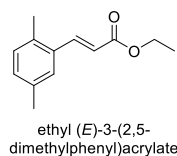
$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.70 (d,  $J$ =16.1 Hz, 1 H), 7.50 - 7.57 (m, 2 H), 7.34 - 7.43 (m, 3 H), 6.45 (d,  $J$ =15.8 Hz, 1 H), 4.28 (q,  $J$ =7.2 Hz, 2 H), 1.35 ppm (t,  $J$ =7.2 Hz, 3 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 167.0, 144.6, 134.5, 130.2, 128.9, 128.0, 118.3, 60.5, 14.3 ppm.



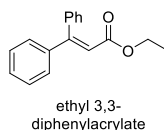
$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.62 (d,  $J$ =16.1 Hz, 1 H), 7.48 - 7.56 (m, 2 H), 7.34 - 7.43 (m, 3 H), 6.40 (d,  $J$ =16.1 Hz, 1 H), 1.56 ppm (s, 9 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 166.3, 143.6, 134.7, 130.0, 128.8, 128.0, 120.2, 80.5, 28.2 ppm.



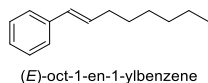
$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.55 (d,  $J$ =7.5 Hz, 4 H), 7.39 (t,  $J$ =7.7 Hz, 4 H), 7.25 - 7.33 (m, 2 H), 7.14 ppm (s, 2 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 137.4, 128.7, 127.6, 126.5 ppm.



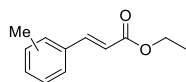
$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 8.00 (d,  $J$ =15.8 Hz, 1 H), 7.41 (s, 1 H), 7.13 (s, 2 H), 6.40 (d,  $J$ =15.8 Hz, 1 H), 4.31 (q,  $J$ =7.0 Hz, 2 H), 2.43 (s, 3 H), 2.36 (s, 3 H), 1.38 ppm (t,  $J$ =7.2 Hz, 3 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 167.2, 142.5, 135.7, 134.7, 133.2, 130.7, 127.0, 119.0, 60.5, 21.0, 19.3, 14.4 ppm.



$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.42 (d,  $J$ =1.8 Hz, 4 H), 7.33 - 7.39 (m, 6 H), 6.42 (s, 1 H), 4.10 (q,  $J$ =6.7 Hz, 2 H), 1.16 ppm (t,  $J$ =7.0 Hz, 3 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 166.1, 156.5, 140.9, 139.1, 129.4, 129.2, 128.4, 128.3, 128.1, 127.9, 117.5, 60.1, 14.0 ppm.

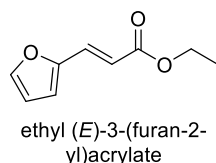


$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.34 - 7.39 (m, 2 H), 7.29 - 7.34 (m, 2 H), 7.18 - 7.24 (m, 1 H), 6.40 (d,  $J$ =15.9 Hz, 1 H), 6.20 - 6.31 (m, 1 H), 2.16 - 2.27 (m, 2 H), 1.44 - 1.53 (m, 2 H), 1.25 - 1.42 (m, 6 H), 0.87 - 0.95 ppm (m, 3 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 138.0, 131.3, 129.7, 128.5, 126.7, 125.9, 33.1, 31.8, 29.4, 28.9, 22.7, 14.1 ppm.

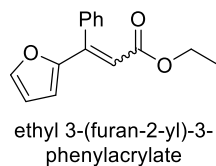


This sample is a **mixture of isomers**, and the molar ratio of *o*, *m* and *p* position products is 1.1, 1.0 to 1.2 with was determined both by GC and NMR peak fitting (Figure S10).

$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.97 (d,  $J$ =16.1 Hz, 0.32 H), 7.65 (d,  $J$ =16.1 Hz, 0.68 H), 7.53 (d,  $J$ =7.5 Hz, 0.30 H), 7.40 (d,  $J$ =8.0 Hz, 0.62 H), 7.33 - 7.36 (m, 0.27 H), 7.29 - 7.33 (m, 0.61 H), 7.22 - 7.28 (m, 0.62 H), 7.14 - 7.21 (m, 0.78 H), 6.31 - 6.46 (m, 1 H), 4.20 - 4.30 (m, 2 H), 2.42 (s, 0.95 H), 2.34 (s, 2.05 H), 1.28 - 1.36 ppm (m, 3 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 167.2, 167.0, 144.8, 144.6, 142.3, 140.6, 138.5, 137.6, 134.4, 133.4, 131.8, 131.1, 130.8, 130.0, 129.6, 128.8, 128.7, 128.1, 126.4, 126.3, 125.3, 119.3, 118.1, 117.2, 60.5, 60.4, 60.4, 21.4, 21.3, 19.8, 14.3 ppm.



$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.47 - 7.49 (m, 1 H), 7.43 (d,  $J$ =15.6 Hz, 1 H), 6.61 (d,  $J$ =3.3 Hz, 1 H), 6.44 - 6.49 (m, 1 H), 6.32 (d,  $J$ =15.8 Hz, 1 H), 4.25 (q,  $J$ =7.0 Hz, 2 H), 1.33 ppm (t,  $J$ =7.2 Hz, 3 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 167.0, 151.0, 144.7, 130.9, 116.0, 114.6, 112.2, 60.4, 14.3 ppm.



$^1\text{H}$  NMR (CHLOROFORM-*d*, 400MHz):  $\delta$  = 7.52 (s, 1 H), 7.38 - 7.44 (m, 3 H), 7.29 - 7.34 (m, 2 H), 6.54 (s, 1 H), 6.39 - 6.44 (m, 1 H), 6.11 (d,  $J$ =3.3 Hz, 1 H), 4.05 (q,  $J$ =7.0 Hz, 2 H), 1.12 ppm (t,  $J$ =7.0 Hz, 3 H).  $^{13}\text{C}$  NMR (CHLOROFORM-*d*, 101MHz):  $\delta$  = 166.1, 154.0, 144.5, 144.5, 136.4, 128.7, 128.2, 127.8, 115.0, 113.1, 112.2, 59.9, 14.0 ppm.