

[Supporting Information]

**Phenanthroline-Based Microporous Organic Polymer as a
Platform Immobilized Palladium Catalyst for Organic
Transformations**

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A. General information

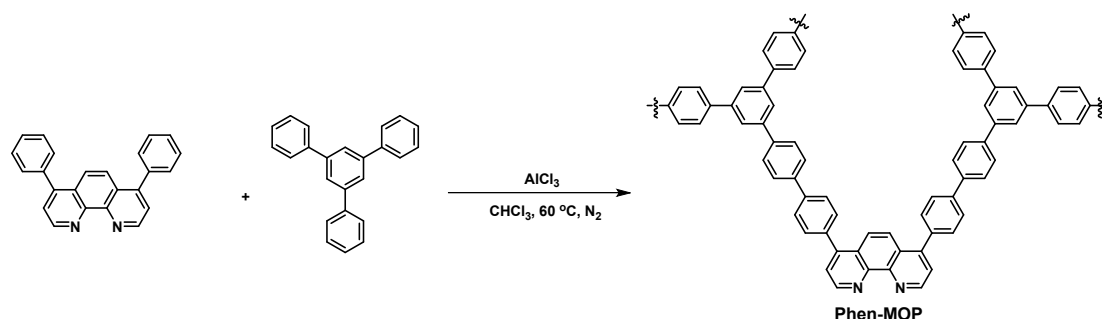
Chemicals and solvents were purchased from commercial suppliers. All equipment was thoroughly oven-dried. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash column chromatography (FCC) was carried out with silica gel (200–300 mesh). ^1H and ^{13}C liquid NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. The chemical shifts δ are given in ppm (parts per million) relative to tetramethylsilane (TMS) and the coupling constants J are given in Hz. All the spectra were recorded in CDCl_3 as solvent at room temperature. TMS served as the internal standard ($\delta = 0.00$ ppm) for ^1H NMR, while CDCl_3 as the internal standard ($\delta = 77.0$ ppm) for ^{13}C NMR. Elemental analysis was performed on an Elementar Analysensysteme GmbH VarioEL V3.00 elemental analyzer. N_2 adsorption and desorption isotherms were measured at 77 K using a Quantachrome autosorb IQ-2. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Solid-state NMR experiments were performed on a Bruker Avance II WB 400 MHz NMR spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 3 ms (ramp 100) and the recycle delay of 2 s on a 2.5 mm double resonance probe. Thermal properties of the synthesized materials were evaluated on a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument in the temperature range of 25 to 800 °C under nitrogen atmosphere with a heating rate of 10 °C/min. The Pd contents in polymer frameworks were determined by Agilent ICP-OES. Surface morphologies and microstructures of the synthesized materials were examined with a Hitachi S-4800 scanning electron microscope (SEM) and with a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained with an Thermo ESCALAB 250XI Scientific electron spectrometer using 150W Al $\text{K}\alpha$ radiation.

B. Materials and experimental procedures

Materials: 4,7-diphenyl-1,10-phenanthroline and 1, 3, 5-triphenylbenzene were received from J&K. Pd(OAc)₂ and Chloroform and anhydrous AlCl₃ were purchased from Energy Chemical (Shanghai, China) and used as received. All reagents were obtained from commercial suppliers and used without further purification. All catalytic reactions were performed in a 15 mL pressure tube.

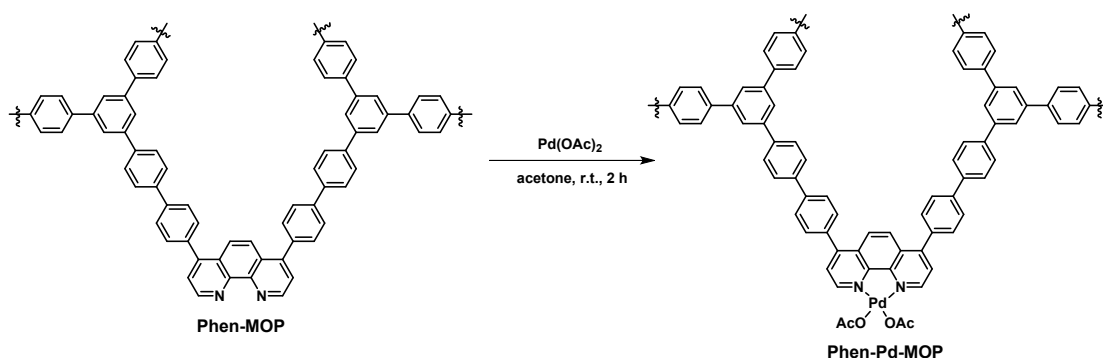
Experimental procedures:

1) Synthesis of **Phen-MOP** materials^[1]



Anhydrous AlCl₃ (665 mg, 5.0 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N₂ for 3 times. Next, 20 mL dried CHCl₃ was injected through a syringe and the mixture was heated to 60 °C for 30 min. Then 4,7-diphenyl-1,10-phenanthroline (166 mg, 0.5 mmol) and 1, 3, 5-triphenylbenzene (102 mg, 0.33 mmol) dissolved in 20 mL dried CHCl₃ were added into the system and the mixture kept stirring at 60 °C for 24 h. After the reaction completed, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 48 h. The polymer was dried at 80 °C under vacuum for 6 h to give a brown powder. Yield: 262 mg (98%). Elemental analysis (%) found: C 48.73, N 2.34, H 4.09.

2) Synthesis of **Phen-Pd-MOP** catalyst^[2]



Palladium acetate (45 mg, 0.2 mmol) was dissolved in 10 mL of acetone, and then **Phen-MOP** (100 mg, 0.08 mmol) was added. The mixture was kept stirring for 2 h at room temperature. After the reaction was complete, the resulting solid was filtered and washed thoroughly with acetone (10 mL $\times$ 5), distilled water (10 mL $\times$ 5) and MeOH (10 mL $\times$ 5), then dried at 80 °C under vacuum for 12 h to yield **Phen-Pd-MOP** as a brown powder (110 mg). The Pd content in **Phen-Pd-MOP** was 10.60 % as determined by ICP.

C. N₂ adsorption-desorption isotherms of **Phen-Pd-MOP** and the recycled **Phen-Pd-MOP**

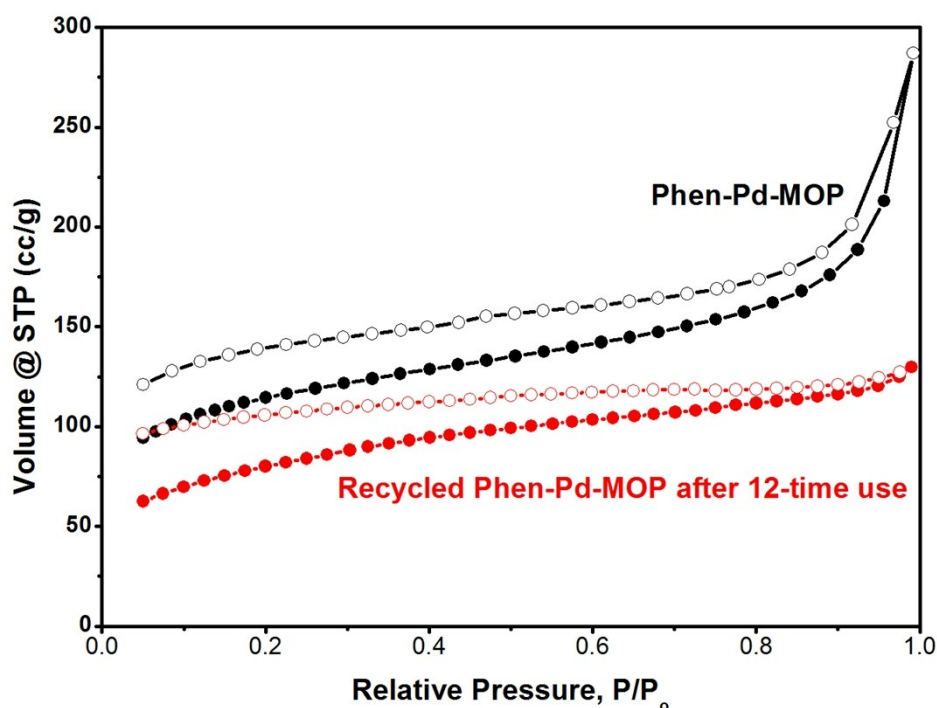


Fig. S1. N₂ adsorption-desorption isotherms of **Phen-Pd-MOP** and the recycled **Phen-Pd-MOP** after 12-time catalytic reactions. the BET surface area of **Phen-Pd-MOP** decrease to 403 m²/g, which is lower than **Phen-MOP** due to the Pd(OAc)₂ is handing in the nanopores volume. We also found that the BET surface area of **Phen-Pd-MOP** had decreased to 272 m²/g after the 12th recycled used, which could be due to the partial blocking of the polymeric nanopores by substrates and products.

D. N 1s XPS spectra for **Phen-MOP** and **Phen-Pd-MOP**

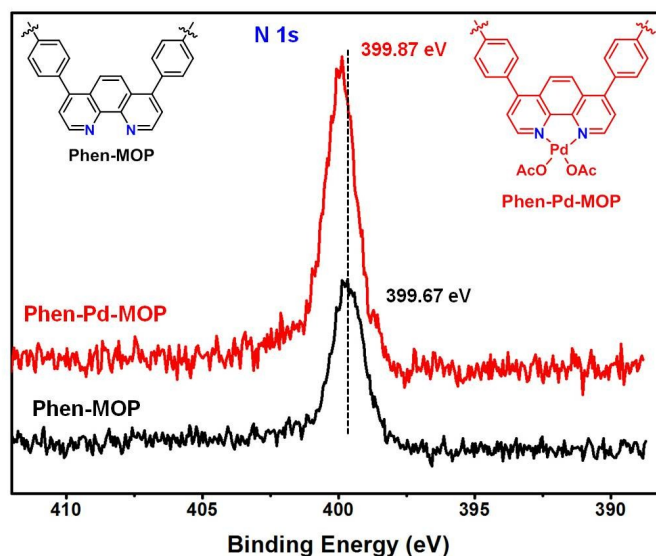


Fig. S2. N 1s XPS spectra for **Phen-MOP** and **Phen-Pd-MOP**

We also investigated the chemical states of N element in Phen-MOP and Phen-Pd-MOP frameworks by XPS spectrum. In comparison with Phen-MOP and Phen-Pd-MOP, the binding energy of N 1s in Phen-Pd-MOP was shifted from 399.67 to 399.87 eV, which further indicated that the Pd(OAc)₂ has strong coordinated with the *N,N*-bidentate ligand in Phen-MOP.

E. Powder X-Ray diffraction for **Phen-MOP**

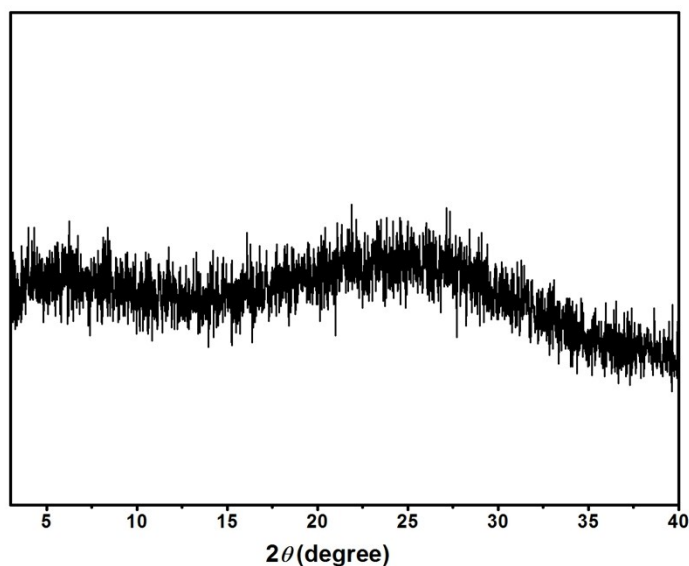
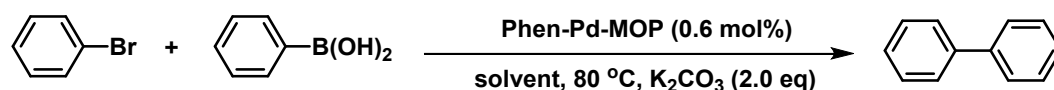


Figure S3. Powder X-ray diffraction pattern of **Phen-MOP**. No intensive diffraction peaks were observable.

F. Screening conditions for the Suzuki-Miyaura coupling reaction

Table S1. Screening conditions for the Suzuki-Miyaura coupling reaction.^[a]

Entry	Solvent	Time (h)	Yield (%) ^[b]	TON ^[e]
1	EtOAc	4	30	50
2	Toluene	4	55	92
3	H ₂ O	4	75	125
4	CH ₂ Cl ₂	4	60	100
5	THF	6	35	58
6	DMF	6	62	103
7	EtOH	1	95	158
8	MeOH	1	99	165
9	EtOH/ H ₂ O (1:1)	0.5	99	165
10 ^[c]	EtOH/ H ₂ O (1:1)	4	0	0
11 ^[d]	EtOH/ H ₂ O (1:1)	4	0	0

[a] General condition: phenylboronic acid (0.5 mmol), bromobenzene (0.75 mmol), K₂CO₃ (1.0 mmol), and **Phen-Pd-MOP** (0.6 mol%), solvent (1.0 mL), 80 °C.

[b] Isolated yield after silica gel column chromatography.

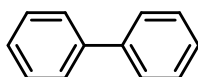
[c] In the absence of **Phen-Pd-MOP**.

[d] **Phen-MOP** as the catalyst.

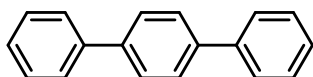
[e] TON = (moles of product)/(moles of Pd in the catalyst).

G. General procedure for the Suzuki-Miyaura coupling reaction^[3]

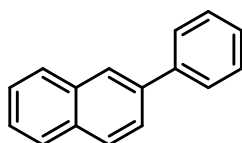
In a typical run of catalytic activity test of **Phen-Pd-MOP**, aryl halide (0.5 mmol), phenylboronic acid (91.5 mg, 0.75 mmol, 1.5 eq), K_2CO_3 (138 mg, 1.0 mmol, 2.0 eq), and **Phen-Pd-MOP** (3.0 mg, 0.6 mol%) were added to 1.0 mL of 1.0/1.0 EtOH-H₂O (v/v) mixture. The reaction mixture was stirred at 80 °C under ambient atmosphere. After the reaction was completed (monitored by TLC), the mixture was centrifuged and the solid was washed with EtOH (1 x 5 mL) and EtOAc (3 x 5 mL). The combined organic phase was washed with water to remove K_2CO_3 residue. After the evaporation of the solvent under vacuum, the residue was purified by flash column chromatography with petroleum ether or petroleum ether/EtOAc = 10:1 as the eluent.



Prepared according to the typical procedure with bromobenzene (or iodobenzene) and phenylboronic acid. The product was collected as clear oil after silica gel chromatography with petroleum ether (77.0 mg, 99%). ¹H NMR (400 MHz, CDCl₃): δ 7.65–7.58 (m, 4H), 7.46 (t, J = 7.6 Hz, 4H), 7.37 (t, J = 7.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 141.2, 128.7, 127.2, 127.1.

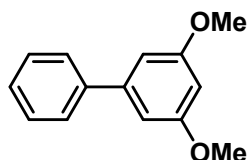


Prepared according to the typical procedure with 4-bromobiphenyl and phenylboronic acid. The product was collected as a white solid after silica gel chromatography with petroleum ether (109.8 mg, 95%). ¹H NMR (400 MHz, CDCl₃): δ 7.73–7.63 (m, 8H), 7.48 (t, J = 7.6 Hz, 4H), 7.38 (t, J = 7.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 140.7, 140.1, 128.8, 127.5, 127.3, 127.0.

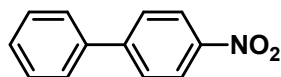


Prepared according to the typical procedure with 2-bromonaphthalene and

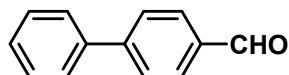
phenylboronic acid. The product was collected as a white solid after silica gel chromatography with petroleum ether (99.1 mg, 97%). ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, $J = 1.1$ Hz, 1H), 7.98–7.85 (m, 3H), 7.75 (tt, $J = 3.1, 1.9$ Hz, 3H), 7.55–7.46 (m, 4H), 7.42–7.38 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.1, 138.6, 133.7, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6.



Prepared according to the typical procedure with 1-bromo-3,5-dimethoxybenzene and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1 (101.1 mg, 94%). ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 7.5$ Hz, 2H), 7.49–7.41 (m, 2H), 7.36 (dd, $J = 15.4, 8.1$ Hz, 1H), 6.76 (d, $J = 2.2$ Hz, 2H), 6.50 (t, $J = 2.2$ Hz, 1H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.1, 143.5, 141.2, 128.7, 127.5, 127.2, 105.5, 99.3, 55.4.

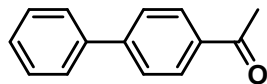


Prepared according to the typical procedure with *p*-nitrobromobenzene and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1 (92.8 mg, 93%). ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, $J = 8.8$ Hz, 2H), 7.75 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 7.4$ Hz, 2H), 7.54–7.37 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.6, 147.1, 138.8, 129.1, 128.9, 127.4, 124.1.

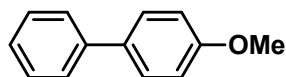


Prepared according to the typical procedure with 4-bromobenzaldehyde and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1 (83.6 mg, 92%). ^1H NMR (400 MHz, CDCl_3): δ 10.08 (s, 1H), 8.01–7.92 (m, 2H), 7.81–7.74 (m, 2H), 7.69–7.62 (m,

2H), 7.53–7.46 (m, 2H), 7.45–7.41 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 191.9, 147.2, 139.7, 135.2, 130.2, 129.0, 128.5, 127.9, 127.3.



Prepared according to the typical procedure with *p*-bromoacetophenones and phenylboronic acid. The product was collected as a pale yellow solid after silica gel chromatography with petroleum ether/EtOAc = 10:1 (95.0 mg, 97%). ^1H NMR (400 MHz, CDCl_3): δ 8.09–8.01 (m, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.67–7.61 (m, 2H), 7.49 (dd, J = 10.2, 4.7 Hz, 2H), 7.45–7.38 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.7, 145.8, 139.9, 135.8, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6.



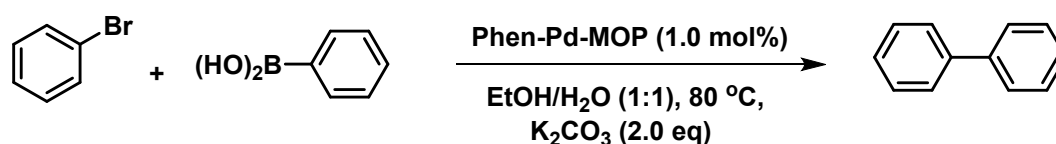
Prepared according to the typical procedure with 4-iodoanisole and phenylboronic acid. The product was collected as a white solid after silica gel chromatography with petroleum ether (90.2 mg, 98%). ^1H NMR (400 MHz, CDCl_3): δ 7.61–7.52 (m, 4H), 7.44 (dd, J = 10.4, 4.9 Hz, 2H), 7.37–7.28 (m, 1H), 7.06–6.94 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

H. Recyclability of **Phen-Pd-MOP** catalyst for the Suzuki-Miyaura

coupling reaction

The recycling experiment was performed by recovering the **Phen-Pd-MOP** catalyst using the centrifugation method. The recovered **Phen-Pd-MOP** catalyst was washed with EtOAc to remove the residual product and simply dried before reuse. We chose the Suzuki-Miyaura coupling reaction of bromobenzene to phenylboronic acid to investigate the recyclability of **Phen-Pd-MOP** catalyst, and the results are summarized in Table S2.

Table S2. Recycling of **Phen-Pd-MOP** catalyst for the Suzuki-Miyaura coupling reaction. ^[a]



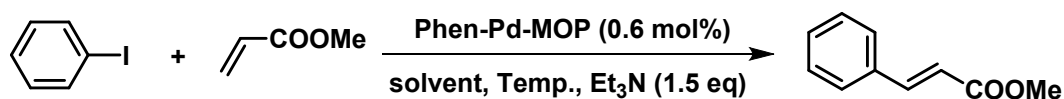
Cycle	Time (h)	Yield (%) ^[b]	Cycle	Time (h)	Yield (%) ^[b]
1	0.5	99	7	1	98
2	0.5	99	8	1	97
3	0.5	98	9	1	97
4	1	98	10	2	99
5	1	98	11	2	98
6	1	99	12	2	98

[a] General condition: phenylboronic acid (0.5 mmol), bromobenzene (0.75 mmol), K₂CO₃ (1.0 mmol), and **Phen-Pd-MOP** (0.005 mmol), EtOH/H₂O (0.5/0.5, 1.0 mL), 80 °C.

[b] Isolated yield after silica gel column chromatography.

I. Screening conditions for the Heck coupling reaction^[4]

Table S3. Screening conditions for the Heck coupling reaction of iodobenzene with methyl acrylate in the presence of **Phen-Pd-MOP**.^[a]



Entry	Solvent	Temp. (°C)	Time (h)	Yield (%) ^[b]	TON ^[e]
1	DMF	130	1	99	165
2	Toluene	130	3	55	92
3	THF	130	3	33	55
4	Acetone	130	3	80	133
5	H ₂ O	130	3	46	77
6	CH ₂ Cl ₂	130	3	40	67
7	EtOH	130	3	75	125
8	EtOAc	130	3.5	82	137
9	DMF/ H ₂ O	130	3	88	147
10	DMF	100	6	75	125
11 ^[c]	DMF	130	12	0	0
12 ^[d]	DMF	130	12	0	0

[a] General condition: iodobenzene (0.5 mmol), methyl acrylate (0.75 mmol), Et₃N (0.75 mmol), and **Phen-Pd-MOP** (0.6 mol%), solvent (1.0 mL), temperature.

[b] Isolated yield after silica gel column chromatography.

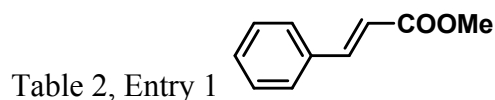
[c] In the absence of **Phen-Pd-MOP**.

[d] **Phen-MOP** as the catalyst.

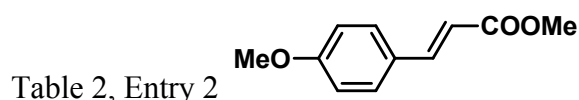
[e] TON = (moles of product)/(moles of Pd in the catalyst).

J. General procedure for the Heck coupling reaction

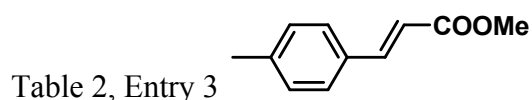
In a typical run of catalytic activity test of **Phen-Pd-MOP** for the Heck coupling reaction, aryl halides (0.5 mmol), methyl acrylate (64.5 mg, 0.75 mmol, 1.5 eq), Et₃N (0.75 mmol, 1.5 eq), and **Phen-Pd-MOP** (3.0 mg, 0.6 mol%) were added to 1.0 mL DMF. The reaction mixture was stirred at 130 °C under N₂ atmosphere. After the reaction was completed (monitored by TLC), the mixture was cooled down to room temperature, centrifuged and the **Phen-Pd-MOP** catalyst was washed with EtOAc (3 x 5 mL). The combined organic phase was washed with water and dried over anhydrous Na₂SO₄. After the evaporation of the solvent under vacuum, the residue was purified by flash column chromatography with petroleum ether/EtOAc (6:1 to 20:1) as the eluent.



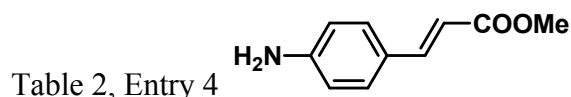
Prepared according to the typical procedure with iodobenzene and methyl acrylate. The product was collected as pale yellow oil after silica gel chromatography with petroleum ether/EtOAc = 20:1. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.55–7.53 (m, 2H), 7.40–7.39 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7.



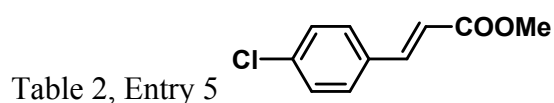
Prepared according to the typical procedure with 4-iodoanisole and methyl acrylate. The product was collected as white solid after silica gel chromatography with petroleum ether/EtOAc = 10:1. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 161.3, 144.4, 129.6, 127.0, 115.2, 114.2, 55.3, 51.5.



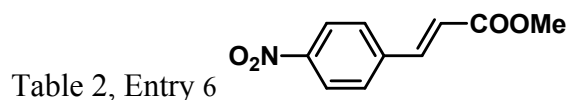
Prepared according to the typical procedure with 4-iodotoluene and methyl acrylate. The product was collected as white solid after silica gel chromatography with petroleum ether/EtOAc = 20:1. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.41 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 144.8, 140.7, 131.6, 129.6, 128.0, 116.7, 51.5, 21.4.



Prepared according to the typical procedure with 4-iodoaniline and methyl acrylate. The product was collected as yellow oil after silica gel chromatography with petroleum ether/EtOAc = 6:1. ^1H NMR (400 MHz, CDCl_3) δ 7.62–7.57 (m, 1H), 7.32–7.30 (m, 2H), 6.61 (dd, J = 10.8, 9.4 Hz, 2H), 6.22 (dt, J = 20.7, 10.3 Hz, 1H), 3.76 (d, J = 1.0 Hz, 3H), 2.93–2.86 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 162.5, 148.9, 145.1, 129.7, 114.6, 112.8, 51.3.



Prepared according to the typical procedure with 1-chloro-4-iodobenzene and methyl acrylate. The product was collected as white solid after silica gel chromatography with petroleum ether/EtOAc = 10:1. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 16.0 Hz, 1H), 7.45–7.43 (m, 2H), 7.36–7.34 (m, 2H), 6.40 (dd, J = 16.0, 0.9 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 143.3, 136.1, 132.8, 129.2, 129.1, 51.7.



Prepared according to the typical procedure with 1-iodo-4-nitrobenzene and methyl acrylate. The product was collected as yellow solid after silica gel chromatography with petroleum ether/EtOAc = 6:1. ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, J = 8.6 Hz, 2H), 7.74–7.66 (m, 3H), 6.56 (d, J = 16.1 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 141.9, 140.5, 128.6, 128.3, 124.3, 122.1, 52.0.

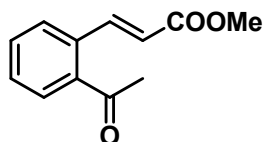


Table 2, Entry 7

Prepared according to the typical procedure with 1-(2-iodophenyl)ethanone and methyl acrylate. The product was collected as yellow oil after silica gel chromatography with petroleum ether/EtOAc = 6:1. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 15.9 Hz, 1H), 7.75 (td, J = 7.4, 1.3 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.51 – 7.45 (m, 2H), 6.29 (d, J = 15.9 Hz, 1H), 3.82 (s, 4H), 2.63 (s, 3H).

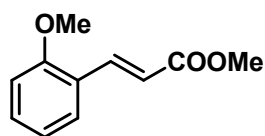


Table 2, Entry 8

Prepared according to the typical procedure with 2-iodoanisole and methyl acrylate. The product was collected as yellow oil after silica gel chromatography with petroleum ether/EtOAc = 10:1. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 16.2 Hz, 1H), 7.52 (dd, J = 7.7, 1.5 Hz, 1H), 7.38–7.34 (m, 1H), 7.29 – 6.91 (m, 2H), 6.54 (d, J = 16.2 Hz, 1H), 3.90 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 140.3, 131.5, 128.9, 123.4, 120.7, 118.3, 111.1, 55.5, 51.6.

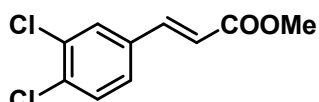


Table 2, Entry 9

Prepared according to the typical procedure with 1,2-dichloro-4-iodobenzene and methyl acrylate. The product was collected as white solid after silica gel chromatography with petroleum ether/EtOAc = 10:1. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 16.0 Hz, 1H), 7.38–7.36 (m, 3H), 6.43 (d, J = 16.0 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 141.7, 137.3, 135.5, 129.8, 126.2, 120.6, 51.9.

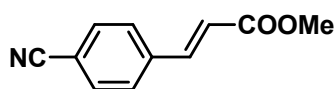


Table 2, Entry 11

Prepared according to the typical procedure with 4-iodobenzonitrile and methyl acrylate. The product was collected as yellow solid after silica gel chromatography with petroleum ether/EtOAc = 6:1. ^1H NMR (400 MHz, CDCl_3) δ 7.71–7.66 (m, 3H),

7.62 (d, $J = 8.3$ Hz, 2H), 6.53 (d, $J = 16.0$ Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 142.4, 138.7, 132.7, 128.4, 121.4, 113.4, 52.0.

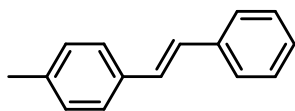


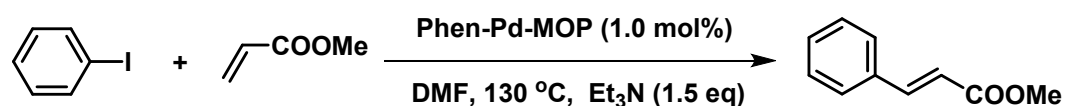
Table 2, Entry 13

Prepared according to the typical procedure with 4-iodotoluene and styrene. The product was collected as white solid after silica gel chromatography with petroleum ether. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.4$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.16 (d, $J = 7.9$ Hz, 2H), 7.07 (d, $J = 2.4$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 134.6, 129.4, 128.6, 127.7, 127.4, 126.4, 126.3, 21.2.

K. Recyclability of **Phen-Pd-MOP** catalyst for the Heck coupling reaction

The recycling experiment was performed by recovering the **Phen-Pd-MOP** catalyst using the centrifugation method. The recovered **Phen-Pd-MOP** catalyst was washed with EtOAc to remove the residual product and simply dried before reuse. We chose the Heck coupling reaction of iodobenzene to methyl acrylate to investigate the recyclability of **Phen-Pd-MOP** catalyst, and the results are summarized in Table S4.

Table S4. Recycling of **Phen-Pd-MOP** catalyst for the Heck coupling reaction. ^[a]



Cycle	Time (h)	Yield (%) ^[b]
1	1	99
2	1	98
3	1	98
4	2	99
5	2	97
6	2	98
7	4	98
8	4	98
9	4	97
10	4	97

[a] General condition: iodobenzene (0.5 mmol), methyl acrylate (0.75 mmol), Et₃N (0.75 mmol), and **Phen-Pd-MOP** (1.0 mol%), DMF (1.0 mL), 130 °C.

[b] Isolated yield after silica gel column chromatography.

References

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L. ^1H NMR and ^{13}C NMR spectra of the products

