Supporting Information for

Porphyrin porous organic polymer with bicatalytic sites for highly efficient one-pot tandem catalysis

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1. General Information

All reagents and solvents were reagent grade, purchased from commercial sources and used without further purification. FT-IR spectra were collected on an ABB Bomem FTLA 2000-104 spectrometer with KBr pellets in the 400-4000 cm⁻¹ region. Solution nuclear magnetic resonance (NMR) spectra were recorded on an AVANCE III (400 MHz) instrument at 298 K using standard Bruker software, and chemical shifts were reported in parts per milion (ppm) downfield from tetramethylsilane. Solid-state ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR measurement was performed with a Bruker AVANCE III 500 spectrometer. UV-Vis absorbance spectra were collected on a UV-3600 Plus UV-VIS-NIR spectrophotometer. Scanning Electron Microscopy (SEM, HitachiS-4800) accompanied by Energy dispersive X-ray spectrometry (EDX, accelerated voltage: 20 kV) was used to study the morphology and element distribution of the samples. Transmission electron microscopy (TEM) images were obtained on a JEOL model JEM-2100 microscope. The X-ray photoelectron spectra (XPS) were carried out by Multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI), from which can analyze the composition of elements. The nitrogen sorption isotherms and pore-size distribution curves were measured at the temperature of liquid nitrogen (77 K) by using an automatic volumetric adsorption equipment (Mircomeritics, ASAP2010). Thermal gravimetric analysis (TGA) measurement was performed on a TGA/1100SF thermo grabinetric analyzer. Powder X-ray diffraction (PXRD) dates were collected on a D8 Advance Xray diffractometer (Bruker AXS Germany) with Cu Ka radiation at 40 kV 200 mA with scanning rate of $2^{\circ} \cdot \min^{-1} (2\theta)$ at room temperature. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m \times 0.25 mm, Hewlett-Packard) with dodecane as an internal standard. GC-MS analysis was conducted on a Shimadzu GC-MS-QP2010 instrument equipped with a Restec-5HT column (30 m \times 0.25 mm, Hewlett-Packard).

2. Catalytic reactions

The reactions were carried out in a three-necked flask reactor (5 mL). Heteroarene boronic acid (2 mmol), aryl bromide (2 mmol) were dissolved in 5 mL of DMAc, K_2CO_3 (2 mmol) as the base, and then the mixture was stirred at 130 °C for 12 h under aerobic environment with 0.005 mmol of catalyst. The samples of the reaction mixture were analyzed by GC-MS using a Restec-5HT capillary column and a flame ionization detector (FID). To ensure the accuracy of the data, yield is the average of two parallel reactions. After the completion of the reaction, the bifunctionalized catalyst material was separated by filtration and washed with toluene, THF, and Et₂O, and then was reused for the above one-pot tandem reaction.

To verify that the Pd-porphyrin sites in **PPOP-1(Pd)** only catalyzes the Suzuki coupling reaction, and the Pd-imine center only catalyzes C-H activation. Two catalysts with one type of catalytic sites PPOP-1(Pd_{0.5}) and PPOP-1(Zn_{0.5}Pd_{0.5}) were designed for control experiments. PPOP-1(Pd_{0.5}) containing only Pd-porphyrin catalytic site was synthesized by reacting of metal palladium porphyrin with acenaphthenequinone. **PPOP-1**($Zn_{0.5}Pd_{0.5}$) containing only Pd-imine site was catalytic constructed by reacting of inactive zinc porphyrin with acenaphthenequinone, and subsequently post-modifying with PdCl₂ to form Pd-imine one type of catalytic centers. In addition, two homogeneous catalysts TPP(Pd) and ANB(Pd) were synthesized to compare the catalytic performance with the heterogeneous catalyst PPOP-1(Pd).

3. Synthesis of PPOP-1(Pd) with bicatalytic sites

3.1 Synthesis of 5, 10, 15, 20-tetra(4-aminophenyl)porphyrin (TAPP)



This compound was prepared by the method described in the literature with slight modifications.^[S1] To a 100 mL round bottom flask equipped with a stir bar and condenser was added the 4-nitrobenzaldehyde (11 g, 0.073 mol) and acetic anhydride (12 mL, 0.127 mol) under a nitrogen atmosphere. The solids were dissolved in 50 mL of propanoic acid. The solution was then refluxed, to which pyrrole (5 mL, 0.172 mol) was added slowly. After refluxing for 4 h, the resulting mixture was cooled to give a precipitate which was collected by filtration, washed with H₂O and methanol, and dried under vacuum. The resulting powder was dissolved in pyridine (25 mL) which was refluxed for 1.5 h. The reaction mixture was then cooled. The precipitate was collected by filtration and washed with acetone to give 5, 10, 15, 20-tetrakis (4nitrophenyl) porphyrin as purple microcrystals with a yield of 17%. The product (2.5 g) was dissolved in concentrated HCl (20 mL), to which was added SnCl₂ (7.0 g, 29 mmol), and concentrated HCl (65 mL) dropwise. The resulting mixture was stirred at room temperature for 2.5 h, then stirred at 80 °C for 0.5 h, and chilled to 0 °C. Gray solid was obtained via vacuum filtration, followed by de-acidification with aqueous ammonia. Finally, the raw product was purified by soxhlet extraction with chloroform to gain violet TAPP with a yield of 37%. FT-IR: v_{max} 3444, 1622, 1514, 1384, 1180, 1128, 1043, 804 and 692 cm⁻¹. ¹H NMR (400 MHz, DMSO, δ ppm): 8.89 (s, 8H), 7.85 (d, 8H), 7.00 (d, 8H), 5.57 (s, 8H), -2.73 (s, 2H). ¹³C NMR (101 MHz, DMSO, δ ppm): 148.98, 135.92, 129.20, 121.04, 112.98. MS (EI) m/z: 675.3 M⁺.

3.2 Synthesis of PPOP-1



A Pyrex glass tube was charged with TAPP (33.7 mg, 0.05 mmol), acenaphthequinone (18.2 mg, 0.1 mmol), 4 mL of toluene, and 0.2 mL of 3 M aqueous acetic acid. This mixture was sonicated for 10 minutes in order to get a uniform dispersion. After being degassed by freeze-pump-thaw technique three times, the tube was sealed. The tube was then placed in an oven at 120 °C for 72 h to obtain a brown precipitate. The resulting precipitate was filtered, washed with anhydrous tetrahydrofuran and extracted by Soxhlet extractor for 24 h. The solid was dried at 80 °C under vacuum for 12 h to gain **PPOP-1** with a yield of 74%. FT-IR (powder): v_{max} 3438, 1722, 1604 1515, 1384, 1180, 1114, 1039, 802 and 690 cm⁻¹. ¹³C CP/MAS: 148.71, 135.95, 128.87, 120.88, 112.63.

3.3 Synthesis of PPOP-1(Pd)



In a typical synthesis of PPOP-1(Pd), the pre-synthesized **PPOP-1** (55 mg) and the PdCl₂ (177 mg) were dispersed in 15 mL of MeOH. The mixture was refluxed for 12 h under a nitrogen atmosphere. After cooling down to room temperature, powder was obtained by centrifuging. The resulting precipitate was washed with DMF and anhydrous THF and dried at 80 °C under vacuum for 12 h to gain the **PPOP-1(Pd)** with a yield of 80%. FT-IR (powder): v_{max} 3436, 1717, 1606 1521, 1382, 1181, 1112, 1042, 801 and 690 cm⁻¹. ¹³C CP/MAS: 148.41, 135.74, 128.62, 120.57, 112.21.

4. Synthesis of PPOP-1(Pd_{0.5}) with only Pd-porphyrin catalytic sites
4.1 Synthesis of palladium(II) 5, 10, 15, 20-tetra(4-aminophenyl)porphyrin (Pd-TAPP)



Pd-TAPP was synthesized by a modified method from the literature.^[S2] TAPP (100 mg, 0.148 mmol, 1 eq.) and excess palladium chloride (131 mg, 0.74 mmol, 5 eq.) were refluxed in DMF at 150 °C under N₂ for 3 h. After the mixture was cooled to room temperature, Pd-TAPP was washed with water (3×15 mL) and filtered and evaporated. Finally, the obtained product was dried under vacuum at 80 °C for 12 hours to gain dark purple Pd-TAPP with a yield of 67.2%. FT-IR: v_{max} 3440, 1625, 1517, 1370, 1180, 1140, 1035, 802 and 675 cm⁻¹. ¹H-NMR (DMSO, 400MHz): 8.78 (s, 8H), 7.64 (d, 8H), 6.92 (d, 8H) 5.52 (s, 8H). ¹³C NMR (101 MHz, DMSO, δ ppm): 148.37, 135.75, 129.64, 121.72, 112.51. MS (EI) m/z: 778.2 M⁺.

4.2 Synthesis of PPOP-1(Pd_{0.5})



The synthesis process is the same as the synthesis of **PPOP-1**. Pd-TAPP (38.9 mg, 0.05 mmol) was reacted with acenaphthequinone (18.2 mg, 0.1 mmol) in the presence of aqueous acetic acid (3 M) catalysis. The resulting dark brown precipitate was filtered, washed with anhydrous tetrahydrofuran and extracted by Soxhlet extractor for 24 h. The solid was dried at 80 °C under vacuum for 12 h yield **PPOP-1(Pd_{0.5})** with a yield of 78.4%. FT-IR (powder): v_{max} 3438, 1717, 1602 1521, 1379, 1180, 1117, 1045, 802 and 695 cm⁻¹. ¹³C CP/MAS: 148.72, 135.83, 128.52, 120.37, 112.77.

5. Synthesis of PPOP-1(Zn_{0.5}Pd_{0.5}) with only Pd-imine catalytic sites 5.1 Synthesis of zinc(II) 5, 10, 15, 20-tetra(4-aminophenyl)porphyrin (Zn-TAPP)



Zn-TAPP was synthesized by a modified literature method. ^[S3] TAPP (100 mg, 0.148 mmol, 1 eq.) was dissolved in a 1:3 mixture of DMF and CHCl₃ (60 mL total). Then a solution of zinc (II) acetate dihydrate (130 mg, 0.593 mmol, 4 eq.) in MeOH (10 mL) was added. The resulting mixture was heated under reflux for 24 hours. After cooling down, the mixture was washed with water (3×15 mL) and filtered and evaporated. Finally, the obtained product was dried under vacuum at 80 °C for 12 hours to gain dark purple Zn-TAPP with a yield of 85.4%. FT-IR: v_{max} 3442, 1627, 1518, 1375, 1179, 1131, 1040, 799 and 689 cm⁻¹. ¹H-NMR (DMSO, 400MHz): 8.84 (s, 8H), 7.81 (d, 8H), 6.97 (d, 8H), 5.44 (s, 8H). ¹³C NMR (101 MHz, DMSO, δ ppm): 148.75, 135.37, 129.81, 121.44, 112.49. MS (EI) m/z: 736.2 M⁺.

5.2 Synthesis of PPOP-1(Zn_{0.5})



The synthesis process is the same as the synthesis of **PPOP-1**. Zn-TAPP (36.8 mg, 0.05 mmol) was reacted with acenaphthequinone (18.2 mg, 0.1 mmol) in the presence of aqueous acetic acid (3 M) catalysis. The resulting dark brown precipitate was filtered, washed with anhydrous tetrahydrofuran and extracted by Soxhlet extractor for 24 h. The solid was dried at 80 °C under vacuum for 12 h yield **PPOP-1(Zn_{0.5})** with a yield of 72.4%. FT-IR (powder): v_{max} 3441, 1722, 1607 1517, 1383, 1177, 1124, 1057, 804 and 693 cm⁻¹. ¹³C CP/MAS: 148.67, 135.92, 128.54, 120.38, 112.77.

5.3 Synthesis of PPOP-1(Zn_{0.5}Pd_{0.5})



For control experiments, the catalyst was synthesized by loading palladium (II) on **PPOP-1(Zn_{0.5})**. The pre-synthesized **PPOP-1(Zn_{0.5})** (85 mg) and the PdCl₂ (88.5 mg) were dispersed in 15 mL of MeOH. The mixture was refluxed for 12 h under a nitrogen atmosphere. After cooling down to room temperature, powder was obtained by centrifuging. The resulting precipitate was washed with DMF and anhydrous THF and dried at 80 °C under vacuum for 12 h to yield the **PPOP-1(Zn_{0.5}Pd_{0.5})** with a yield of 84.2%. FT-IR (powder): v_{max} 3437, 1715, 1608 1522, 1380, 1176, 1124, 1031, 800 and 691 cm⁻¹. ¹³C CP/MAS: 148.54, 135.88, 128.47, 120.22, 112.67.

6. Synthesis of homogeneous catalytic compounds

6.1 Synthesis of palladium (II) meso-tetraphenylporphyrine (TPP(Pd))



The compound was synthesized by loading palladium(II) on meso-tetraphenylporphyrine (TPP). TPP was purchased from a commercial source. TPP (70 mg, 0.065 mmol) were dissolved in anhydrous benzonitrile (30 mL), then PdCl₂ (23 mg, 0.13 mmol) was added, and refluxed for 3 h under argon atmosphere. After removal of the solvents under reduced pressure, CH₂Cl₂ (50 mL) was added and the mixture was washed with water (3 × 50 mL). The organic layer was dried over MgSO₄, filtered, concentrated, and the residue was purified by column chromatography on a silica gel (CH₂Cl₂/hexane, 4:3 v/v) to obtain an orange solid **TPP(Pd)** with a yield of 93%. ¹H NMR (400 MHz, CDCl₃): 8.81 (s, 8H), 8.16 (d, 8H), 7.71–7.79 (m, 12H). ¹³C NMR (101 MHz, DMSO, δ ppm): δ 148.8, 141.8, 141.1, 131.2, 129.4, 123.0, 121.1, 35.2, 31.9. MS (EI) m/z: 719.2 M⁺.

6.2 Synthesis of palladium(II) [N, N'-1,2-acenaphthylenediylid enebis(benzenamine)]dichloro (ANB(Pd))



N, N'-1,2-acenaphthylenediylidenebis(benzenamine) (ANB) was purchased from a commercial source. Under the argon atmosphere, PdCl₂ (39.0 mg, 0.22 mmol) was added to a solution of ABN (66.4 mg, 0.20 mmol) in CH₃CN (20 mL). The reaction mixture was stirred at room temperature for 3 h and then concentrated to half of the volume under reduced pressure. Upon the addition of diethyl ether, a red-orange solid precipitate was formed. The precipitate was filtered off, washed with hexane, diethyl ether and dried in vacuum to gain **ANB(Pd)** with a yield of 86%. ¹H NMR (400 MHz, CDCl₃): 8.10 (d, 2H), 7.57 (t, 4H), 7.51 (t, 2H), 7.47 (dd, 2H), 7.40 (m, 4H), 6.79 (d, 2H), ¹³C NMR (101 MHz, DMSO, δ ppm): 175.3, 147.5, 145.1, 132.6, 131.6, 129.7, 129.2, 129.1, 126.3, 125.0, 122.7. MS (EI) m/z: 524.0 M⁺.

7. Characterization



Fig. S1 ¹H NMR spectrum of 5, 10, 15, 20-tetra (4-aminophenyl) porphyrin (TAPP).



Fig. S2 ¹³C NMR spectrum of 5, 10, 15, 20-tetra (4-aminophenyl) porphyrin (TAPP).



Fig. S3 Solid UV-vis spectra of the PPOP-1 before and after palladium loading.

Solid UV-vis spectra of the **PPOP-1** before loading palladium can observe the characteristic absorption peak (Soret band) of porphyrin at 418 nm and the four Q-band absorption peaks. However, when **PPOP-1** is loaded with palladium, the absorption peaks of the four Q bands are reduced to two, from which it can be inferred that the porphyrin sites are occupied by palladium(II).



Fig. S4 Energy dispersive X-ray spectroscopy (EDX) spectrum of PPOP-1(Pd).



Fig. S5 (a) SEM and (b) TEM images of PPOP-1.



Fig. S6 TGA curve of PPOP-1(Pd).



Fig. S7 FT-IR spectra of PPOP-1(Pd) in different solvents after stirring for 3 days.



Fig. S8 FT-IR spectra of **PPOP-1(Pd)** after treatment for 3 days in HCl (6 M) solutions and NaOH (6 M) solutions.



Fig. S9 ¹H NMR spectrum of Zinc(II) 5, 10, 15, 20-tetra (4-aminophenyl) porphyrin (Zn-TAPP). The hydrogen in the middle of the porphyrin was replaced by zinc(II).



Fig. S10 ¹H NMR spectrum of Palladium (II) 5, 10, 15, 20-tetra (4-aminophenyl) porphyrin (Pd-TAPP). The hydrogen in the middle of the porphyrin was replaced by palladium (II), resulting in the disappearance of the corresponding peak (-2.63 ppm) in ¹H NMR.



Fig. S11 Infrared spectra of PPOP-1(Zn_{0.5}) (blue) and PPOP-1(Pd_{0.5}) (red).



Fig. S12 ¹³C CP/MAS NMR spectra of PPOP-1($Zn_{0.5}$) (blue) and PPOP-1($Pd_{0.5}$) (red).



Fig. S13 XPS spectra of PPOP-1(Pd_{0.5}) (a) and PPOP-1(Zn_{0.5}, Pd_{0.5}) (b).

The XPS survey spectrum of **PPOP-1(Pd**_{0.5}) (Fig. S13a) clearly shows the presence of palladium, carbon, oxygen, and nitrogen. The XPS survey spectrum of **PPOP-1(Zn**_{0.5}, **Pd**_{0.5}) (Fig. S13b) shows the presence of palladium, zinc, carbon, oxygen, and nitrogen.



Fig. S14 Kinetics of the tandem reaction between 2-thiopheneboronic acid and bromobenzene.

The kinetic study showed that the completion of the reaction occurred within 12 h. It was understood from the control experiments that this tandem reaction proceeded through two sequential steps: (1) Pd(II)-porphyrin units give Suzuki coupling catalysis while α -diimine palladium active sites favor direct C-H bond arylation of heteroarenes. The two reactions take place simultaneously, yielding two intermediates; (2) the intermediates further react with bromobenzene through the catalysts to give the final products.



Fig. S15 Yield of catalytic recyclability studies for the coupling bromobenzene and 2thiopheneboronic acid by **PPOP-1(Pd)**.



Fig. S16 TEM image of the PPOP-1(Pd) after 5 cycles.

8. Analysis of the tandem catalytic reactions

Table S1. Control experiment: catalytic activity test of **PPOP-1**($Zn_{0.5}Pd_{0.5}$) in the tandem catalysis of C-H arylation and Suzuki coupling reactions^a



K,CO	, DMAc
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Entry	v	Ar-Br	Conversion (%)	Yield 9	% ^b
	X		1	2(a)/2(b)	3
1	S	⟨Br	96	0/96	0
2	S	H ₂ N-	96	1/95	0
3	S	HO-	96	0/96	0
4	S	H ₃ C-	94	1/93	0
5	0	⟨Br	91	1/89	0
6	0	H₂N-∕_>Br	91	0/91	0
7	Ο	HO-	92	1/91	0
8	0	H ₃ C-	90	0/90	0

^aCatalyst **PPOP-1(Zn_{0.5}Pd_{0.5})** (0.005 mmol), heteroarene boronic acid (2 mmol), aryl bromide (4.5 mmol), K₂CO₃ (2 mmol) and DMAc (5 mL), in an aerobic environment were stirred 130 °C for 12 h; ^bYield [%] was determined by GC-MS using an internal standard and the yields are given in average over two parallel reactions.

Table S2. Control experiment: catalytic activity test of **PPOP-1(Pd**_{0.5}) in the tandem catalysis of C-H arylation and Suzuki coupling reactions^a



Entry	x		Conversion (%)	Yield % ^b		
		Ar-Br	1	2(a)/2(b)	3	
1	S	<u>ಎಂದ್ರೆ ಕೌರ್ಣರ್ ಮಾಗಿದೆ ನಾಲಕಿ</u>	100	92/5	3	
2	S		100	93/5	2	
3	S		96	91/4	1	
4	S		98	92/5	1	
5	0	Sandaga Patrimitian (1998) (19	94	92/1	1	
6	0		94	93/1	0	
7	0		90	90/0	0	
8	0		93	91/1	1	

^aCatalyst **PPOP-1(Pd_{0.5})** (0.005 mmol), heteroarene boronic acid (2 mmol), aryl bromide (4.5 mmol), K_2CO_3 (2 mmol) and DMAc (5 mL), in an aerobic environment were stirred 130 °C for 12 h; ^bYield [%] was determined by GC-MS using an internal standard and the yields are given in average over two parallel reactions.

Table S3. Comparative experiment: catalytic activity test of **TPP(Pd)** in the tandem catalysis of C-H arylation and Suzuki coupling reactions^a



K₂CO₃, DMAc

Entry	v	A., D.,	Conversion (%)	Yield % ^b		
	X	Ar-Br	1	2(a)/2(b)	3	
1	S	Configuration and the second	100	97/1	2	
2	S		100	96/2	2	
3	S		97	95/3	1	
4	S		98	96/2	1	
5	0	200322*560*0584028	95	93/1	1	
6	0		94	92/2	0	
7	0		92	91/1	0	
8	0		93	92/0	1	

^aCatalyst **TPP(Pd)** (0.005 mmol), heteroarene boronic acid (2 mmol), aryl bromide (4.5 mmol), K_2CO_3 (2 mmol) and DMAc (5 mL), in an aerobic environment were stirred 130 °C for 12 h; ^bYield [%] was determined by GC-MS using an internal standard and the yields are given in average over two parallel reactions.

Table S4. Comparative experiment: catalytic activity test of **ANB(Pd)** in the tandem catalysis of C-H arylation and Suzuki coupling reactions^a



Entry	v	A+ D+	Conversion (%)	Yield % ^b		
	^	AI-DI	1	2(a)/2(b)	3	
1	S		98	1/95	1	
2	S		97	1/95	1	
3	S		97	0/97	0	
4	S		94	0/94	0	
5	0	and a second	93	1/92	0	
6	0		93	0/93	0	
7	0		91	1/90	0	
8	0		92	0/92	0	

^aCatalyst **ANB(Pd)** (0.005 mmol), heteroarene boronic acid (2 mmol), aryl bromide (4.5 mmol), K_2CO_3 (2 mmol) and DMAc (5 mL), in an aerobic environment were stirred 130 °C for 12 h; ^bYield [%] was determined by GC-MS using an internal standard and the yields are given in average over two parallel reactions.

Table S5. Comparative experiment: catalytic activity test of **TPP(Pd)**:**ANB(Pd)**=1:1 in the tandem catalysis of C-H arylation and Suzuki coupling reactions^a



Frature -	v	A., D.,	Conversion (%)	Yield % ^b	
Entry	~	Ar-br	1	3	
1	S		100	97	
2	S		100	96	
3	S		97	93	
4	S		98	93	
5	0		95	82	
6	0		94	73	
7	0		92	64	
8	0		93	58	

^aCatalyst **TPP(Pd)**:**ANB(Pd)**=1:1 (Total 0.005 mmol), heteroarene boronic acid (2 mmol), aryl bromide (4.5 mmol), K_2CO_3 (2 mmol) and DMAc (5 mL), in an aerobic environment were stirred 130 °C for 12 h; ^bYield [%] was determined by GC-MS using an internal standard and the yields are given in average over two parallel reactions.

Table S6. Comparison of the C-H arylation and Suzuki coupling reaction catalyzed by previously reported heterogeneous palladium catalysts^{*a*} and homogeneous α -diimine palladium catalysts.^{*b*}

No	Name of Catalyst	Substrate	Time	Yield	Ref.
1	Pd/COF-LZU1 ^a	bromobenzene	3 h	97%	4
2	Pd@PPPP-2 ^a	bromobenzene	3 h	94%	5
3	Pd(OAc) ₂ @COF-300 ^a	bromobenzene	0.3 h	80%	6
4	Pd/H ₂ P-Bph-COF ^a	p-nitrobroMobenzene	1.5 h	97%	7
5	PPOP-1(Pd)	2-thiopheneboronic acid	12 h	97%	This work
6	$Pd(phen)_2(PF6)_2^b$	thiophene	18 h	80%	8
7	bis(alkoxo)palladium ^b	2-methylthiophene	24 h	82 %	9
8	$Pd(OAc)_2/1, 10$ -phenanthroline ^b	pyridine	48 h	79 %	10
9	α -diimine palladium complexes (C3) ^b	thianaphthene	12 h	97 %	11

^{*a*}Reaction conditions: heterogeneous Pd-porphyrin catalyst, phenylboronic acid in p-xylene or similar solvent. ^{*b*}Reaction conditions: homogeneous palladium catalysts, aryl halide in similar solvent.

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