Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Palladium-carbon connected organometallic framework and its catalytic application

Ying Dong[a], Jing-Jing Jv[a], Xiao-Wei Wu[b], Jing-Lan Kan[a], Ting Lin[a], Yu-Bin Dong*[a]

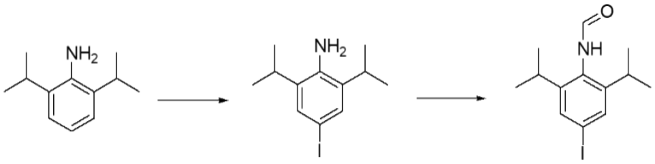
[a] College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, P. R. China. E-mail: yubindong@sdnu.edu.cn

[b] School of Chemical Engineering Nanjing University of Science and Technology Nanjing, Jiangsu 210094, P. R. China.

1. Materials and methods

All chemicals and solvents were at least of analytic grade and employed as received without further purification. The elemental analysis was conducted on a PerkinElmer Model 2400 analyzer. MS spectra were obtained by Bruker maxis ultra-high resolution-TOF MS system. NMR data were collected using an AM-400 spectrometer. The solid-state NMR spectra were obtained on Agilent 600 DD2 spectrometer. Infrared spectra were obtained in the 400-4000cm^{-1} range using a Bruker ALPHA FT-IR spectrometer. Powder X-ray diffraction (PXRD) measurements were performed at 293K on a D8 ADVANCE diffractometer (Cu Kα, λ = 1.5406Å). ICP analysis was performed on an IRIS InterpidII XSP and NU AttoM. XPS spectra were obtained from PHI Versaprobe II. Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min. HRTEM (High resolution transmission electron microscopy) analysis was performed on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope equipped with energy-dispersive X-ray detector (EDX). The elemental analysis was conducted on a PerkinElmer Model 2400 analyzer.

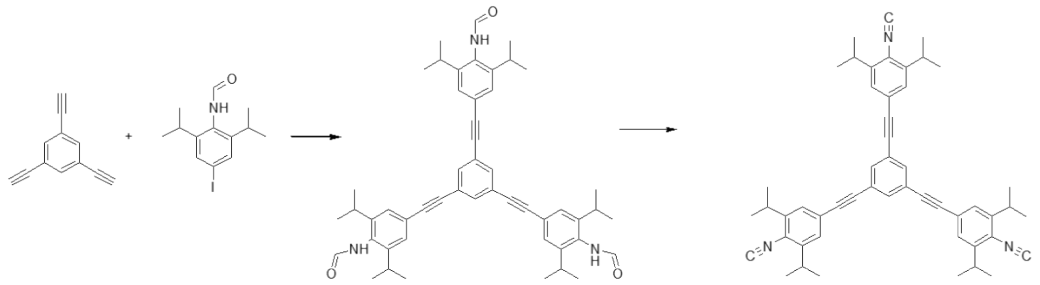
2. Synthesis and characterization of L and its precursors.



Synthesis of 4-iodo-2,6-diisopropylaniline.[1] A mixture of 2,6-diisopropylbenzenamine (2.54 g, 14.3 mmol) and I_2 (4.0 g, 15.7 mmol) was charged in 50 mL round-bottom flask. Then, 10 mL cyclohexane and 4 mL saturated Na_2CO_3 solution was added orderly. After stirring at room temperature for 12 h, the mixture was diluted with EtOAc (20 mL) and washed with saturated $Na_2S_2O_3$ (3 × 40 mL). The combined organic layer was dried with anhydrous $MgSO_4$. The crude product was purified by column chromatography (petroleum ether /EtOAc = 10/1) to give 4-iodo-2.6-diisopropylaniline as a deep brown oil (3.90 g, yield: 96%). ^{1}H NMR (400 MH$_Z$, $CDCl_3$) δ: 7.37 (s, 2H), 3.82 (s, 2H), 2.94 (m, 2H), 1.37 (d, *J* = 8.0 Hz, 12 H); ^{13}C NMR (400 MHz, $CDCl_3$), δ: 22.4 (4C), 28.0 (2C), 81.2 (1C), 131.8 (2C), 135.1 (2C), 140.2 (1C).; HRMS (ESI-TOF) calcd for $C_{12}H_{19}IN$ ([M+H]$^+$), *m/z* 304.0517; found, *m/z* 304.0592.; IR (KBr): 3486 (w), 3404 (w), 2961 (vs), 2870 (m), 1618 (s), 1570 (w), 1460 (s), 1438 (vs), 1384 (m), 1364 (m), 1350 (m), 1299 (w), 1250 (m), 1208 (m), 1125 (w), 1061 (w), 924 (w), 865 (m), 832 (w), 765 (w), 746 (w), 716 (w), 555 (w).

Synthesis of *N*-(4-iodo-2,6-diisopropylphenyl)formamide.[2] A mixture of formic acid (3.0 mL, 81.2 mmol) and acetic anhydride (3.0 mL, 31.8 mmol) was stirred at 55 °C for 3 h. After cooling to room temperature, 4-iodo-2,6-diisopropylaniline (4.48 g, 14.7 mmol) was gradually added using a water bath to keep the temperature below 39 °C. After cooling to room temperature and addition of anhydrous diethyl ether (10 mL), the mixture was stirred for additional 40 h at room temperature. Next, 10 % aqueous sodium carbonate was added to neutralize the mixture. The product was extracted by diethyl ether and the combined organic layer was dried with anhydrous $MgSO_4$. The crude product was purified by Al_2O_3 (petroleum ether /EtOAc = 20/1) to give white solid (4.48 g, yield: 92%). ^{1}H NMR (400 MH$_Z$, DMSO) δ: 9.55 (s, 1H), 8.35 (s, 1H), 7.52 (s, 2H), 3.30 (m, 2H), 1.15 (d, *J* = 8.0 Hz, 12H); ^{13}C NMR (400 MHz, DMSO) δ: 161.2 (1C), 149.0 (2C), 132.4 (2C), 131.9 (1C), 97.9 (1C), 28.5 (2C), 23.5 (4C).; HRMS (ESI-TOF) calcd for $C_{13}H_{18}INO$ ([M+Na]$^+$), *m/z* 354.0331, found 354.0371; IR

(KBr): 3174 (m), 2963 (s), 2864 (m), 2768 (w), 2161 (w), 2026 (w), 1599 (m), 1579 (m), 1463 (m), 1418 (m), 1386 (w), 1365. (w), 1345 (w), 1262 (m), 1172 (m), 1109 (w), 1074 (w), 1001 (m), 944 (w), 882 (m), 802 (w), 723 (w), 695 (w), 680 (w).



A L

Synthesis of N,N',N''-((benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(2,6-diisopropylbenzene-4,1-diyl))triformamide (A).[3] A mixture of 1,3,5-triethynylbenzene (0.150 g, 1.0 mmol), *N*-(4-iodo-2,6-diisopropylphenyl)formamide (0.994 g, 3.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.071 g, 0.1 mmol), copper(I) iodide (0.057 g, 0.3 mmol), diisopropylethylamine (DIPEA, 0.452 mL, 3 mmol) in 20 mL THF was charged in a 100 mL Schlenk flask. After stirred at 50 °C for 14 h, the precipitate was filtered and washed with CH_2Cl_2 to remove salts and redundant starting materials. The crude product was purified by Al_2O_3 (methanol/ CH_2Cl_2 = 200/1) to give **A** (0.494 g, yield: 64%). ^{1}H NMR (400 MH_Z, DMSO) δ: 9.57 (s, 3H), 8.35 (s, 3H), 7.83 (s, 3H), 7.41 (s, 6H), 3.09 (m, 6H), 1.17 (d, *J* = 8.0 Hz, 36H); ^{13}C NMR (400 MHz, DMSO), δ: 161.1 (3C), 147.0 (6c), 134.1 (3c), 130.0 (3c), 126.9 (6c), 124.4 (3c), 121.6 (3c), 91.8 (3c), 88.3 (3c), 28.6 (6c), 23.6 (12c); HRMS (ESI-TOF) calcd for $C_{51}H_{57}N_3O_3$ ($[M+Na]^+$), *m/z* 782.4298; found *m/z* 782.4269.; IR (KBr): 3173 (w), 2964 (s), 2864 (m), 2768.19 (w), 1664 (s), 1568 (m), 1537 (m), 1461 (m), 1408 (s), 1392 (s), 1362 (w), 1329 (m), 1281 (w), 1260 (w), 1233 (m), 1155 (w), 1039 (m), 941 (w), 892 (m), 868 (m), 808 (m), 741 (m), 615 (w), 521 (w), 401 (w).

Synthesis of 1,3,5-tris((4-isocyano-3,5-diisopropylphenyl)ethynyl)benzene L.[4] A mixture of **A** (0.076 g, 0.1 mmol), triethylamine (0.417 mL, 3 mmol) in 20 mL methylene chloride was cooled to 0 °C. $POCl_3$ (0.548 mL, 0.6 mmol) was slowly added by constant pressure drip funnel with stirring. The mixture was stirred for 1 h at 0 °C. Then, 10 % aqueous sodium carbonate was added and the solution of methylene chloride was washed several times with saturated sodium chloride solution. The product was purified by column on silica gel to afford colorless oil (0.635 g, yield: 90 %). ^{1}H NMR (400 MH_Z, $CDCl_3$) δ: 7.64 (s, 1H), 7.25 (s, 2H), 3.29 (m, 2H), 1.24 (d, *J* = 8.0 Hz, 12 H); ^{13}C NMR (400 MHz, $CDCl_3$), δ:170.4 (3c), 145.4 (6c), 134.4 (3c), 134.1 (3c), 126.8 (6c), 123.8 (3c), 123.7 (3c), 90.2 (3c), 89.1 (3c), 29.8 (6c), 22.5 (12c).; HRMS (ESI-TOF) calcd for $C_{51}H_{51}N_3$ ($[M+H]^+$), *m/z* 706.4161; found *m/z* 706.4158.; IR (KBr): 2964 (s), 2927 (s), 2872 (m), 2208.26(w), 2110 (s), 1599 (m), 1579 (m), 1463 (m), 1418 (m), 1386.18(w), 1365 (w), 1345 (w), 1262 (m), 1172 (w), 1109 (w), 1074 (w), 1001 (m), 944 (w), 882 (m), 802 (w), 761 (w), 723 (w), 695 (w), 668 (w), 541 (w).

3. Synthesis and characterization of Pd-OMF

Synthesis of Pd-OMF. In N_2, PdI_2 (54 mg, 0.15 mmol) and **L** (70 mg, 0.1 mmol) was suspended in 10 mL acetonitrile. The mixture was stirred for 3 days at 100 °C, then the solvent was removed in vacuum. The resulted solids were further treated by Soxhlet extraction with mixed solution of dichloromethane and acetone (100 mL : 100 mL) for 24 h, and then dried at 110 °C in vacuo to afford light yellow crystals (94 mg, yield: 76 %). IR (KBr): 2963 (s), 2928 (m), 2870 (m), 2181.94(s), 1660 (s),

1567 (w), 1533 (m), 1461 (m), 1408 (w), 1391 (m), 1362 (m), 1280 (w), 1259 (w), 1233 (m), 1154 (w), 1068 (w), 941 (w), 892 (w), 868 (m), 808 (m), 741 (m), 615 (w), 521 (w), 440 (w). Anal. Calcd for the desolvated sample $C_{51}H_{54}I_3N_3Pd_{1.5}$: C 49.03, H 4.36, N 3.36. Found: C 49.86, H 4.20, N 3.51. In addition, Pd and I content in **Pd-OMF** were respectively determined as 12.46 (calcd. 12.78 wt%) and 30.54 wt% (calcd. 30.47 wt%) based on ICP measurement.

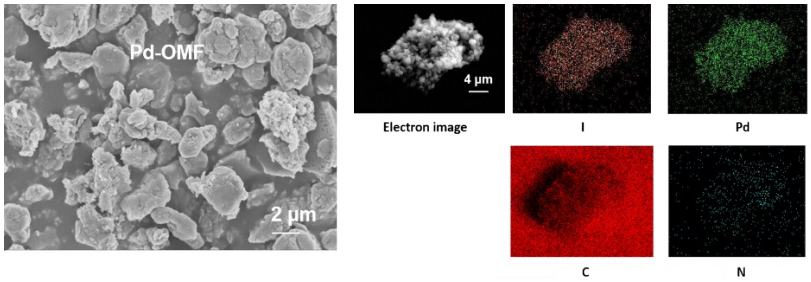


Fig. S1 Left: SEM image of **Pd-OMF**. Right: SEM-EDX spectrum of **Pd-OMF**.

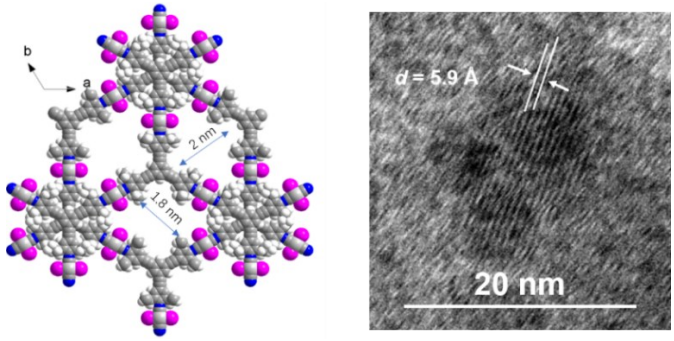


Fig. S2 Left: 2D layer of **Pd-OMF** with rhombic cavity. Right: TEM image of **Pd-OMF**.

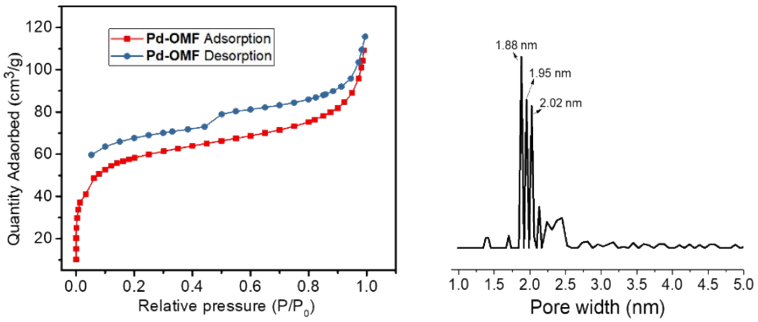


Fig. S3 Left: N_2 sorption isotherm of **Pd-OMF** at 77K. Right: the pore size distribution plot of **Pd-OMF**.

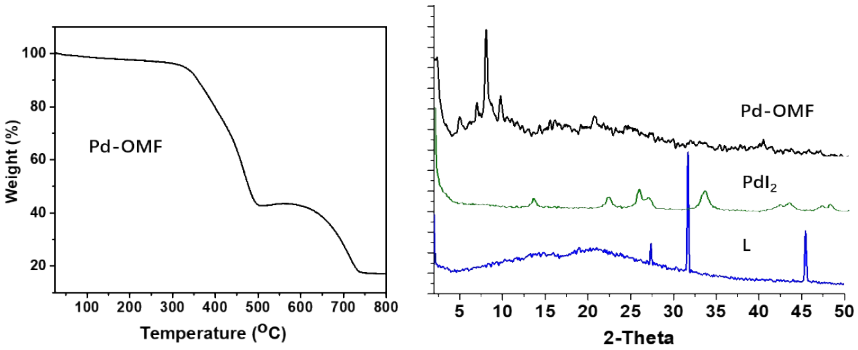


Fig. S4 Left: TGA trace of **Pd-OMF** (a negligible ca. 2% weight loss below 200 °C is associated with the loss of the encapsulated MeCN in the framework). Right: PXRD patterns of **Pd-OMF**, **L**, and **PdI_2**.

Table S1. Pd-OMF with *P*63/MMC mode

OMF: Space group: ***P63/MMC***			
a = b = 44.596 Å, c = 11.800 Å			
α = β = 90.0°, γ = 120.0°			
Atom	x	y	z
C1	0.15410	0.69445	-0.35715
C2	0.02755	0.82089	-0.35721
H3	0.16143	0.67405	-0.35973
H4	0.16455	0.71099	-0.43375
H5	0.12540	0.68171	-0.35965
H6	0.01475	0.79219	-0.35980
H7	0.04407	0.83132	-0.43387
H8	0.00718	0.82825	-0.35981
C9	0.26230	0.73770	-0.25000
C10	0.22591	0.77409	-0.25000
N11	0.20797	0.79203	-0.25000
C12	0.19298	0.80702	-0.25000
Pd13	0.16661	0.83339	-0.25000
C14	0.14025	0.85975	-0.25000
N15	0.12526	0.87474	-0.25000
C16	0.10732	0.89268	-0.25000
C17	0.07096	0.92904	-0.25000
C18	0.05234	0.94766	-0.25000
C19	0.28094	0.71906	-0.25000
C20	0.29655	0.70345	-0.25000
C21	0.31519	0.68481	-0.25000
C22	0.03674	0.96326	-0.25000
C23	0.01813	0.98187	-0.25000
C24	0.28037	0.77381	-0.25000
C25	0.26264	0.79252	-0.25000
C26	0.07057	0.87423	-0.25000
C27	0.05287	0.89295	-0.25000
I28	0.10640	0.77319	-0.25000
C29	0.16798	0.71671	-0.25000
C30	0.04983	0.83473	-0.25000
H31	0.30841	0.78738	-0.25000
H32	0.02482	0.87940	-0.25000
H33	0.15710	0.73429	-0.25000
H34	0.06739	0.82382	-0.25000
C35	0.35147	0.70294	-0.25000
H36	0.36551	0.73102	-0.25000
C37	0.03626	1.01813	-0.25000
H38	0.06435	1.03217	-0.25000

Table S2. Pd-OMF with *P*6/MMM mode.

OMF: Space group: ***P6/MMM***			
$a = b$ = 44.597 Å, c = 6.715 Å			
$\alpha = \beta$ = 90.0°, γ = 120.0°			
Atom	x	y	z
C1	0.48746	0.36111	0.81180
H2	0.49483	0.34074	0.80682
H3	0.49797	0.37777	0.67796
H4	0.45876	0.34837	0.80712
C5	0.59565	0.40435	1.00000
C6	0.55928	0.44072	1.00000
N7	0.54134	0.45866	1.00000
C8	0.52635	0.47365	1.00000
C9	0.38571	0.61429	1.00000
C10	0.62989	0.37011	1.00000
C11	0.64852	0.35148	1.00000
Pd12	0.50000	0.50000	1.00000
C13	0.61374	0.44046	1.00000
C14	0.59601	0.45917	1.00000
C15	0.50133	0.38334	1.00000
H16	0.64179	0.45403	1.00000
H17	0.49045	0.40093	1.00000
I18	0.43979	0.43979	1.00000
C19	0.6848	0.36961	1.00000
H20	0.69885	0.3977	1.00000
C1	0.48746	0.36111	0.81180
H2	0.49483	0.34074	0.80682
H3	0.49797	0.37777	0.67796
H4	0.45876	0.34837	0.80712
C5	0.59565	0.40435	1.00000
C6	0.55928	0.44072	1.00000
N7	0.54134	0.45866	1.00000
C8	0.52635	0.47365	1.00000
C9	0.38571	0.61429	1.00000
C10	0.62989	0.37011	1.00000
C11	0.64852	0.35148	1.00000
Pd12	0.50000	0.50000	1.00000
C13	0.61374	0.44046	1.00000
C14	0.59601	0.45917	1.00000
C15	0.50133	0.38334	1.00000
H16	0.64179	0.45403	1.00000
H17	0.49045	0.40093	1.00000
I18	0.43979	0.43979	1.00000

4. Product characterization and yield determination for the model Suzuki-Miyaura cross-coupling

reaction catalyzed by Pd-OMF (for Table 1)

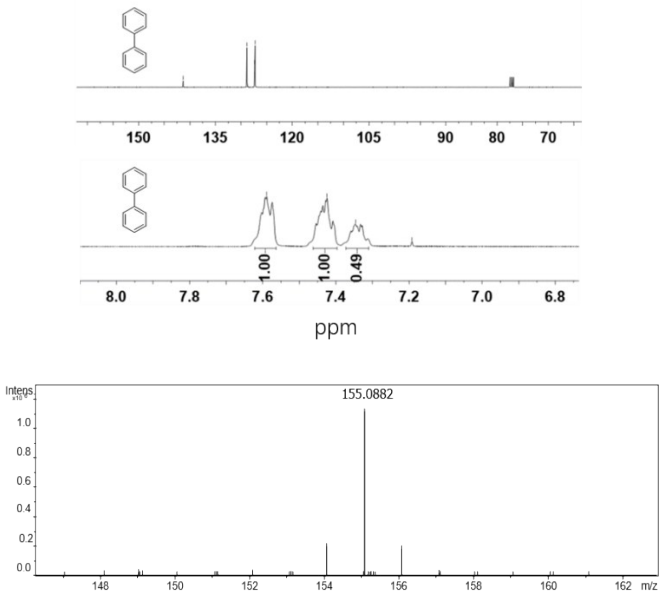
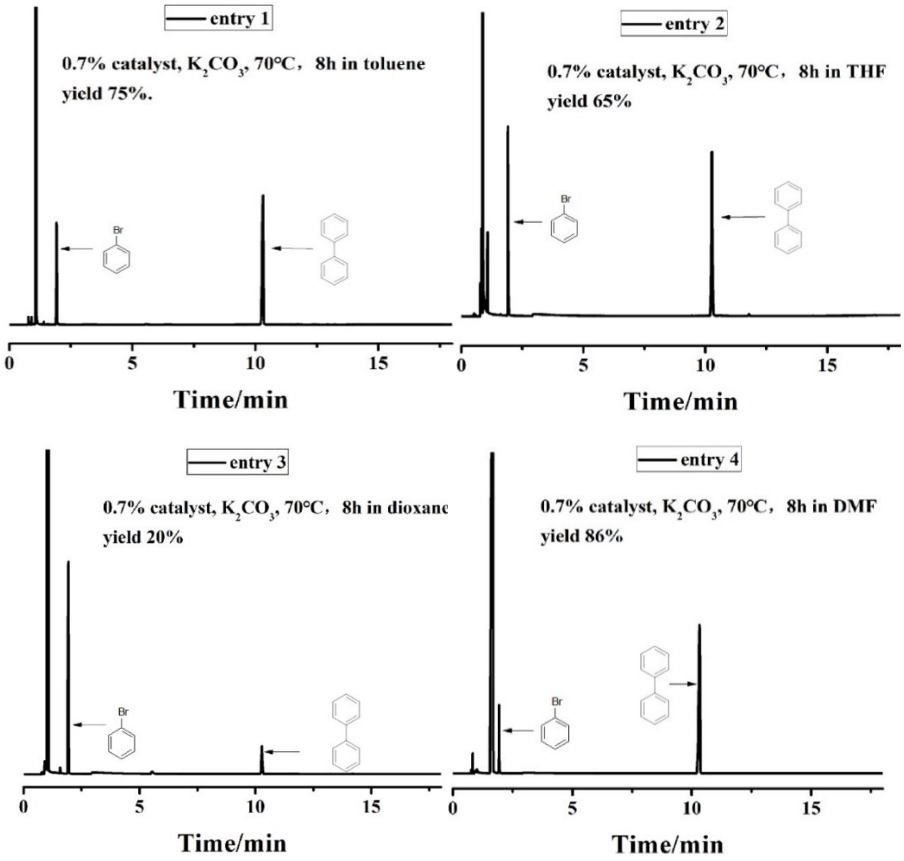
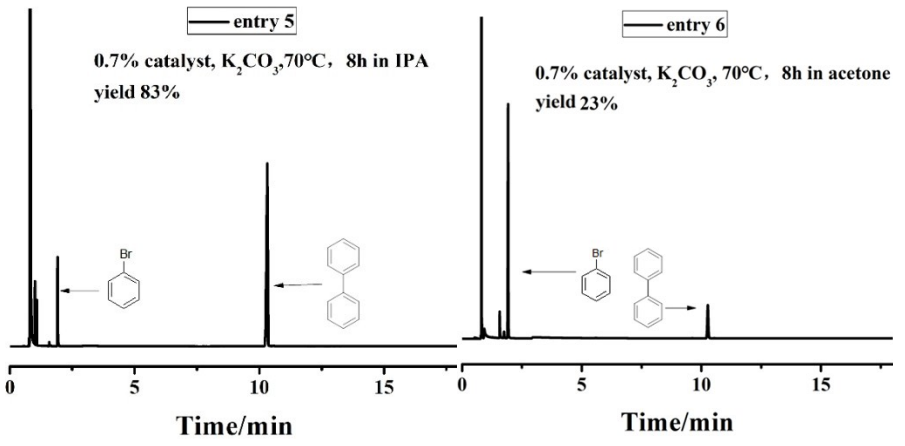
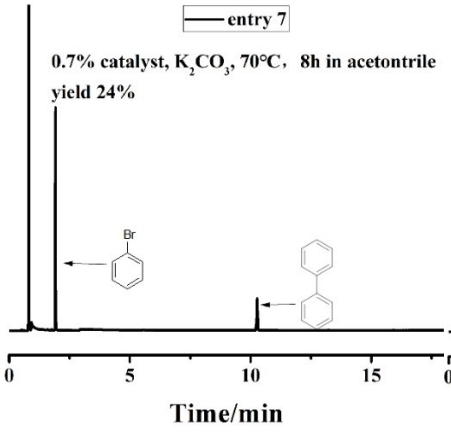


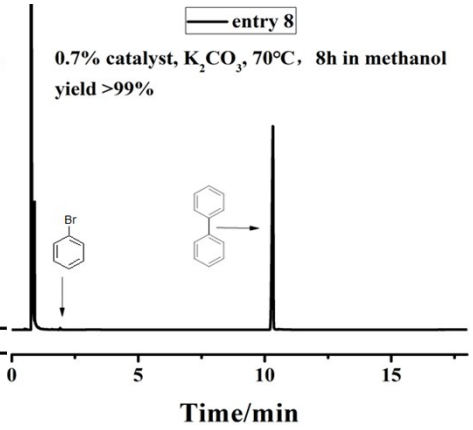
Fig. S5 NMR and MS spectra for the product generated from the model Suzuki-Miyaura cross-coupling reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64-7.66 (d, *J* = 8.0 Hz, 4H), 7.48-7.50 (m, 4H), 7.38-7.42 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 141.1 (2C), 128.8 (4C), 127.3 (2C), 127.2 (4C).; ESI-MS (ESI-MS: calcd for $C_{12}H_{10}$, 155.0855 ([M+H$^+$]); found: *m/z* 155.0882).

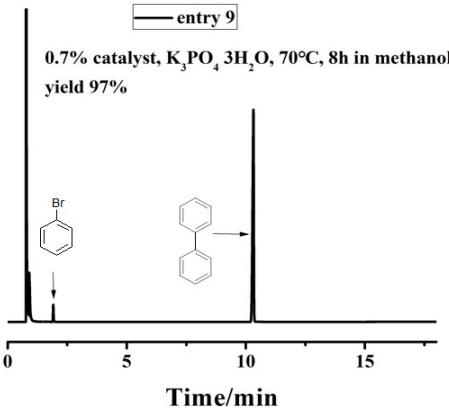


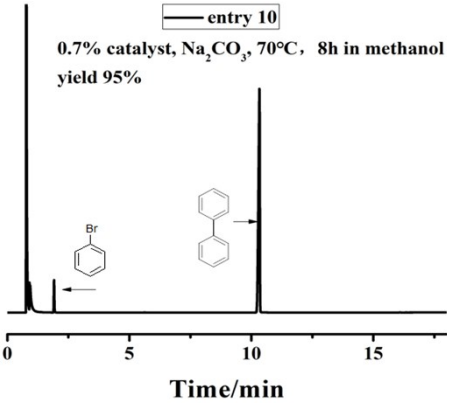

entry 5
0.7% catalyst, K_2CO_3,70℃，8h in IPA
yield 83%
Br
0
5
10
15
Time/min

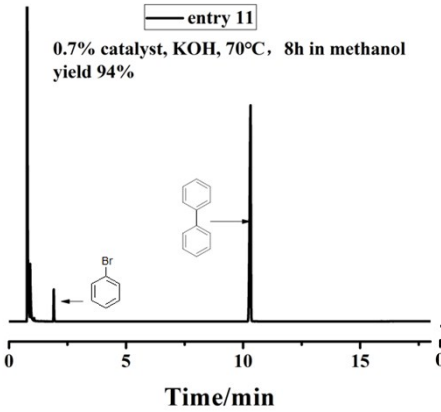
entry 6
0.7% catalyst, K_2CO_3, 70℃，8h in acetone
yield 23%
Br
0
5
10
15
Time/min

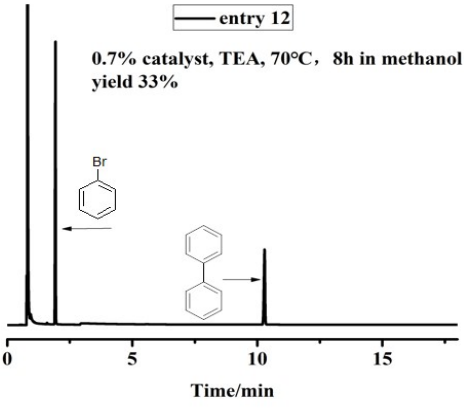

entry 7
0.7% catalyst, K_2CO_3, 70℃，8h in acetontrile
yield 24%
Br
0
5
10
15
Time/min


entry 8
0.7% catalyst, K_2CO_3, 70℃，8h in methanol
yield >99%
Br
0
5
10
15
Time/min


entry 9
0.7% catalyst, K_3PO_4 $3H_2O$, 70℃, 8h in methanol
yield 97%
Br
0
5
10
15
Time/min


entry 10
0.7% catalyst, Na_2CO_3, 70℃，8h in methanol
yield 95%
Br
0
5
10
15
Time/min


entry 11
0.7% catalyst, KOH, 70℃，8h in methanol
yield 94%
Br
0
5
10
15
Time/min


entry 12
0.7% catalyst, TEA, 70℃，8h in methanol
yield 33%
Br
0
5
10
15
Time/min

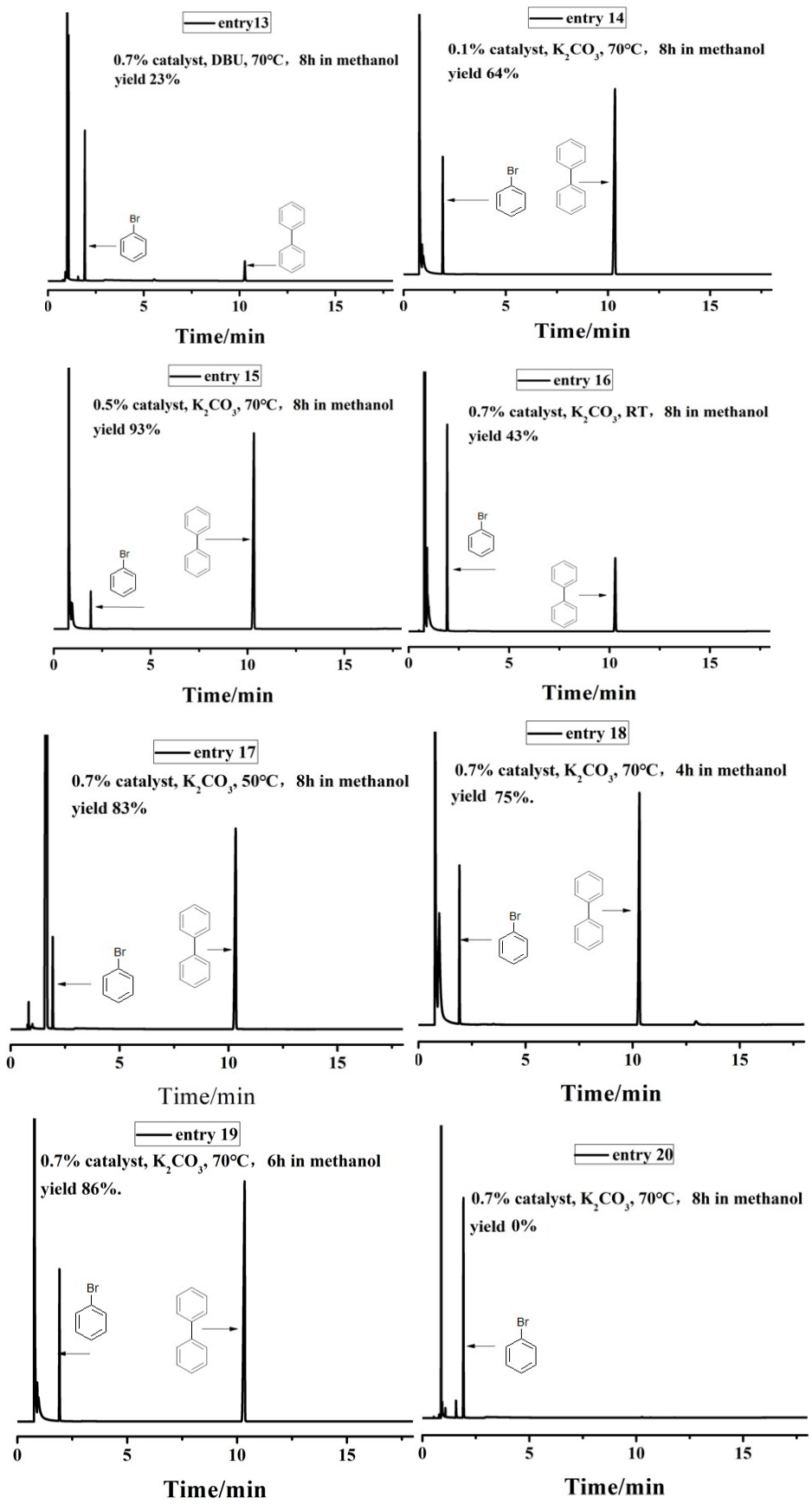


Fig. S6 GC analysis for the model Suzuki-Miyaura cross-coupling reaction catalyzed by **Pd-OMF** under different reaction conditions (for Table 1).

5. Recycle of Pd-OMF

After each catalytic run, the solid catalyst of **Pd-OMF** was recovered by centrifugation, washed with CH_3CN (3 × 2 mL), $CHCl_3$ (3 × 2 mL), and dried at 110°C for 24 h in vacuum, and then was reused for the next catalytic run under the same reaction conditions. After multiple catalytic runs, **Pd-OMF** was characterized by element analysis and ICP again. Anal. Calcd for the desolvated sample $C_{51}H_{54}I_3N_3Pd_{1.5}$: C 49.03, H 4.36, N 3.36. Found: C 49.52, H 4.45, N 3.44. Pd and I content in **Pd-OMF** were determined as 12.33 (calcd. 12.78 wt%) and 30.38 wt% (calcd. 30.47 wt%), respectively.

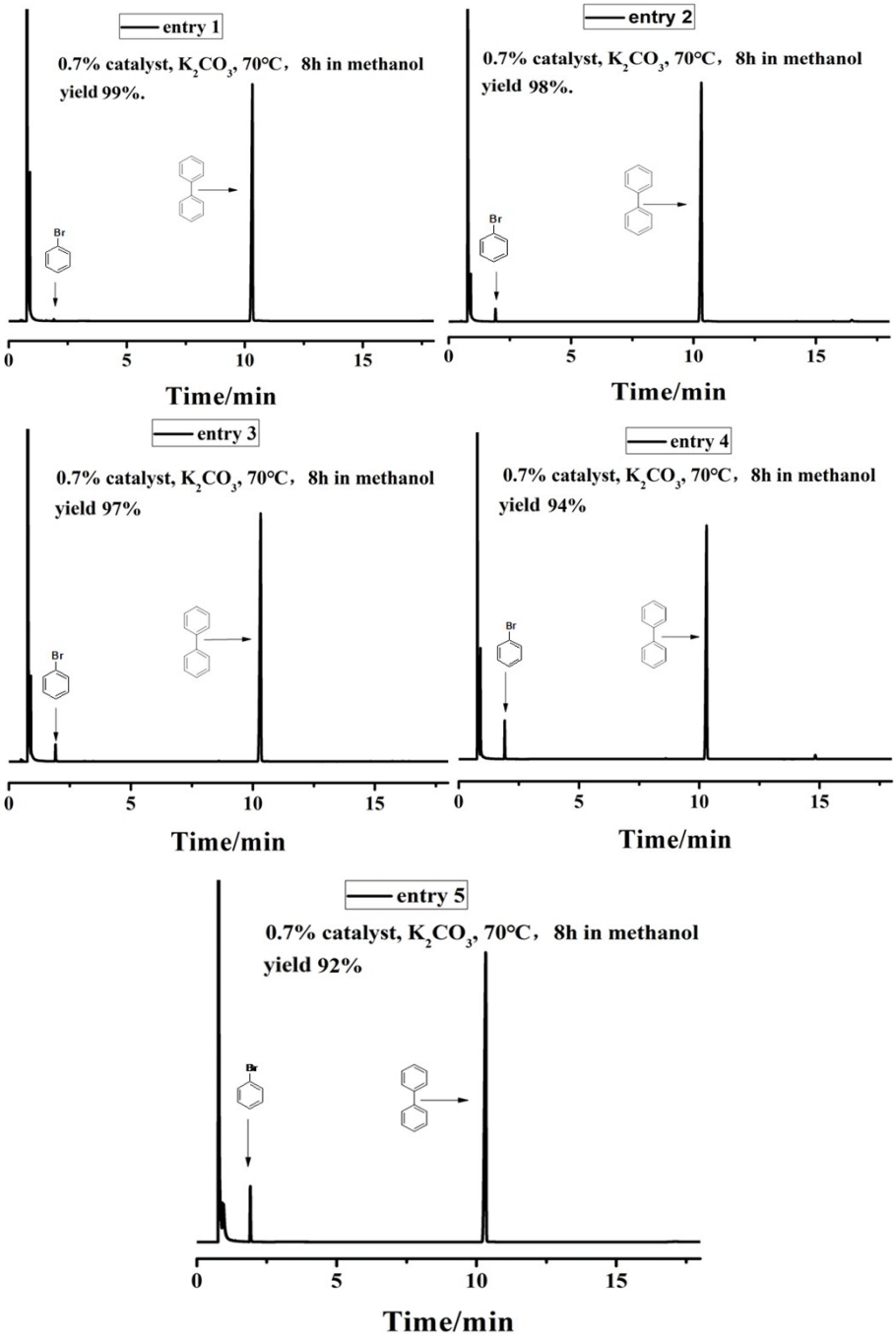


Fig. S7 GC analysis for the Suzuki cross-coupling reaction catalyzed by **Pd-OMF** for 5 catalytic runs.

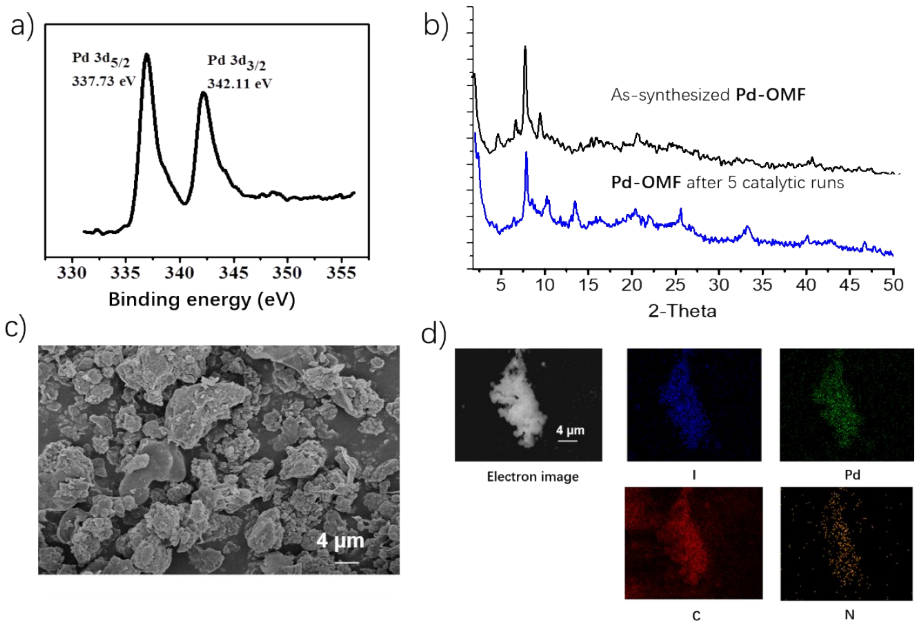
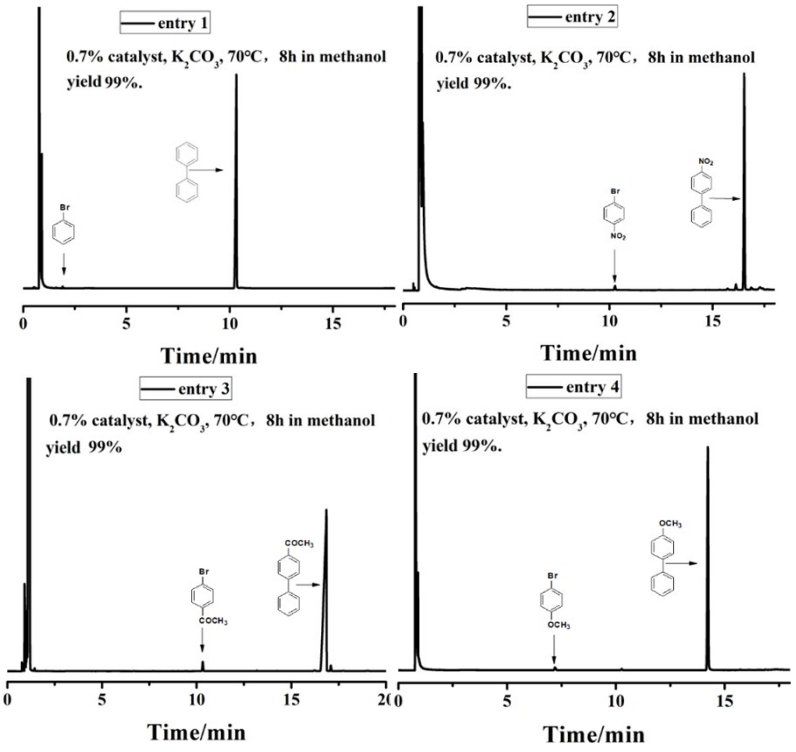


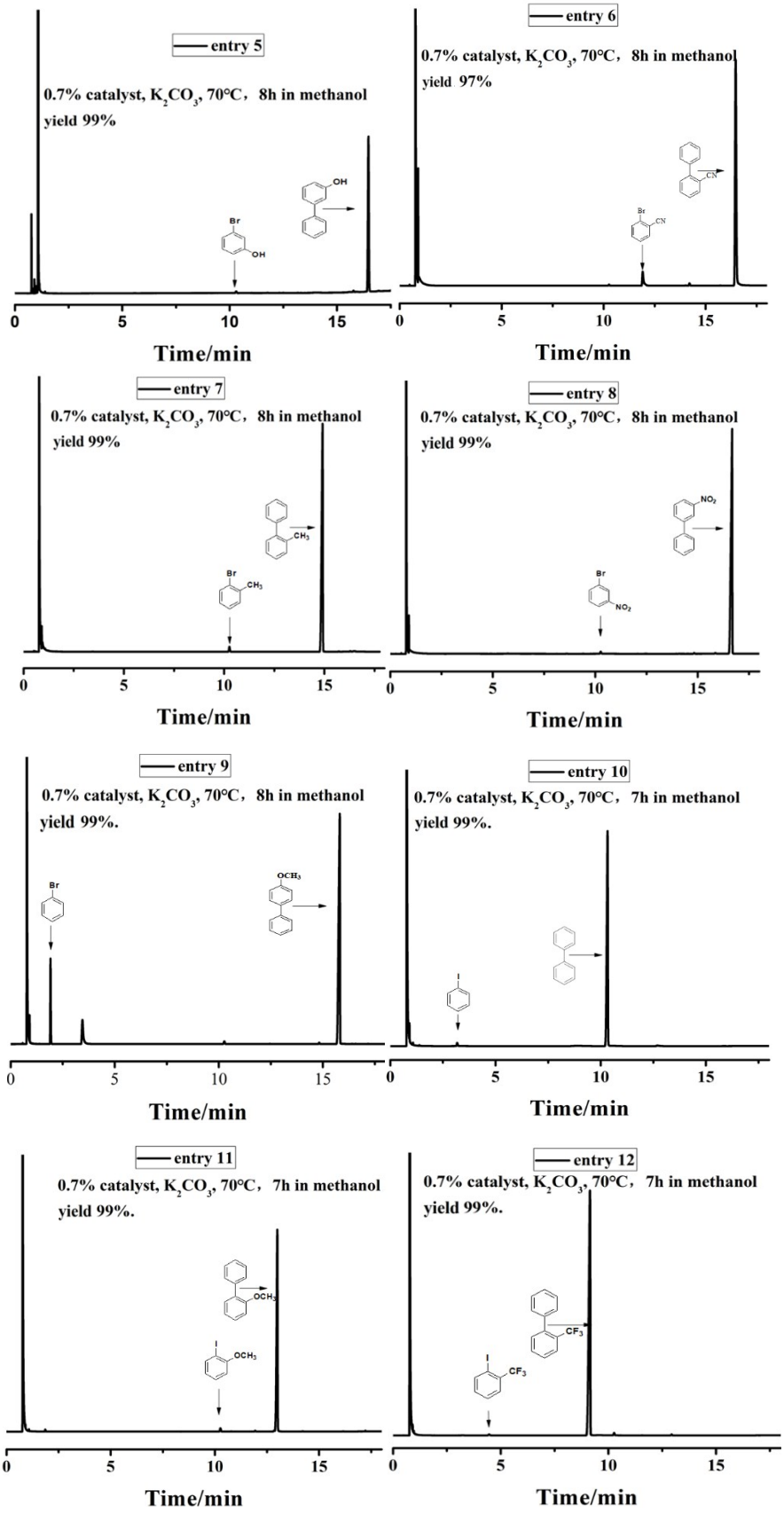
Fig. S8 XPS (a), PXRD (b), SEM (c), SEM-EDX (d) spectra of the **Pd-OMF** after five catalytic runs.

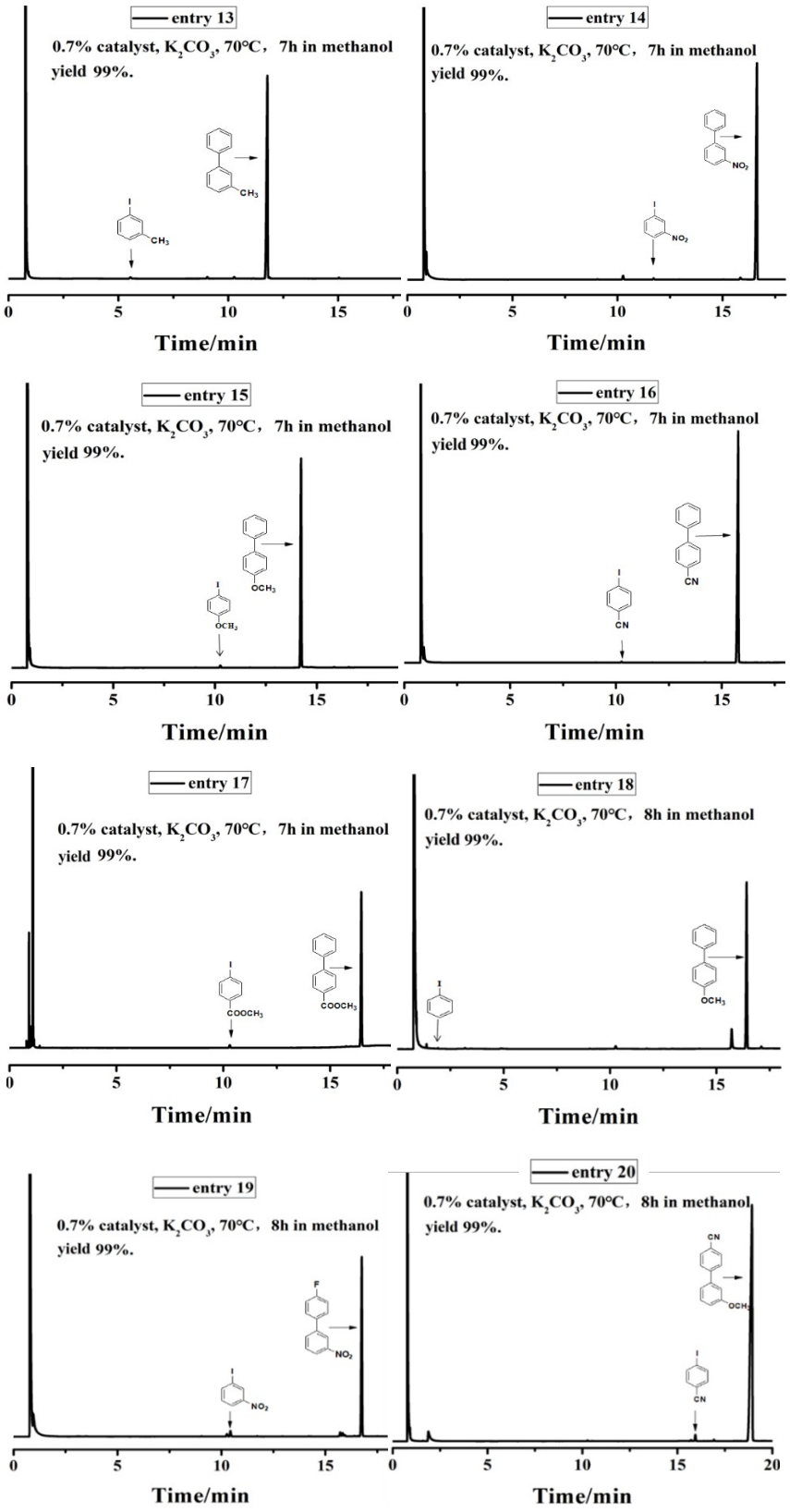
6. General catalytic procedure for the Pd-OMF promoted Suzuki-Miyaura cross-coupling reaction (for Table 2)

A mixture of halogeno-benzene (1.0 mmol), phenylboronic acid (1.1 mmol, 0.134 g), K_2CO_3 (2 mmol, 0.276 g) and **Pd-OMF** (6.6 mg, 0.7 mol% Pd equiv) in methanol (2 mL) was stirred at 70 °C for 7-8 h in N_2 to afford the corresponding products. Yield was determined by the GC.

7. GC results for the Pd-OMF promoted Suzuki-Miyaura cross-coupling reaction (for Table 2)




entry 5
0.7% catalyst, K2CO3, 70°C，8h in methanol
yield 99%
Time/min
entry 6
0.7% catalyst, K2CO3, 70°C，8h in methanol
yield 97%
Time/min
entry 7
0.7% catalyst, K2CO3, 70°C，8h in methanol
yield 99%
Time/min
entry 8
0.7% catalyst, K2CO3, 70°C，8h in methanol
yield 99%
Time/min
entry 9
0.7% catalyst, K2CO3, 70°C，8h in methanol
yield 99%.
Time/min
entry 10
0.7% catalyst, K2CO3, 70°C，7h in methanol
yield 99%.
Time/min
entry 11
0.7% catalyst, K2CO3, 70°C，7h in methanol
yield 99%.
Time/min
entry 12
0.7% catalyst, K2CO3, 70°C，7h in methanol
yield 99%.
Time/min


entry 13
0.7% catalyst, K2CO3, 70°C， 7h in methanol
yield 99%.
Time/min
entry 14
0.7% catalyst, K2CO3, 70°C， 7h in methanol
yield 99%.
Time/min
entry 15
0.7% catalyst, K2CO3, 70°C， 7h in methanol
yield 99%.
Time/min
entry 16
0.7% catalyst, K2CO3, 70°C， 7h in methanol
yield 99%.
Time/min
entry 17
0.7% catalyst, K2CO3, 70°C， 7h in methanol
yield 99%.
Time/min
entry 18
0.7% catalyst, K2CO3, 70°C， 8h in methanol
yield 99%.
Time/min
entry 19
0.7% catalyst, K2CO3, 70°C， 8h in methanol
yield 99%.
Time/min
entry 20
0.7% catalyst, K2CO3, 70°C， 8h in methanol
yield 99%.
Time/min

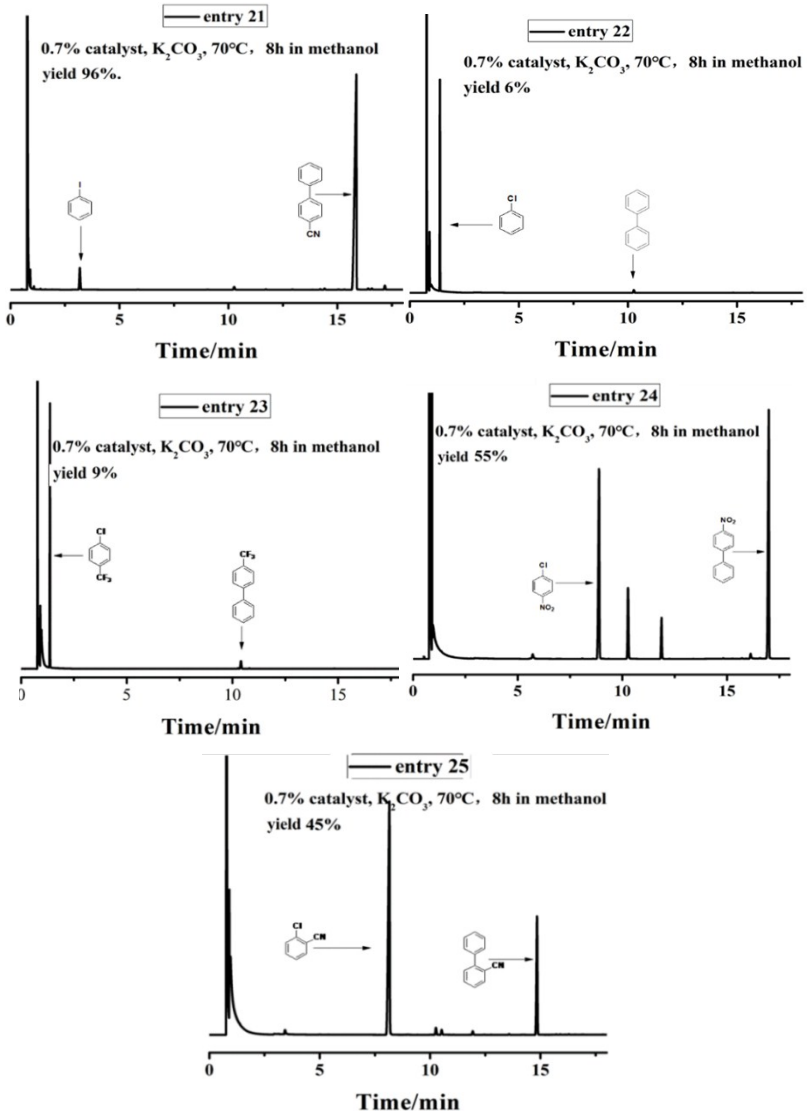


Fig. S9 GC results for the Suzuki-Miyaura cross-coupling reactions with various halogenobenzenes and phenylboronic acids catalyzed by **Pd-OMF** under given conditions (for Table 2).

8. Proposed mechanism

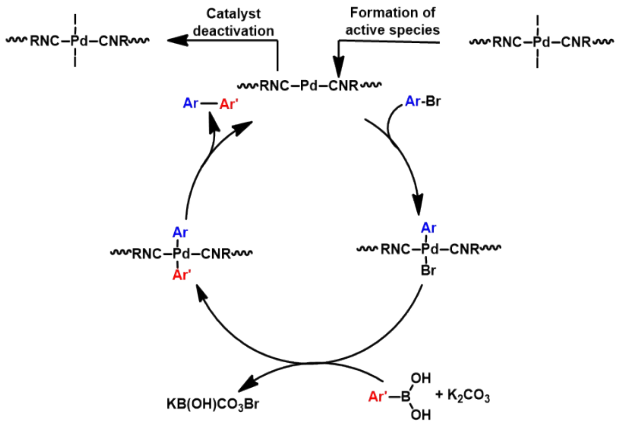


Fig. S10 Proposed mechanism for the model Suzuki-Miyaura cross-coupling reaction catalyzed by **Pd-OMF**.

9. Reference

(1) (a) Z.-L. Lu, A. Mayr, K.-K. Cheung, *Inorg. Chim. Acta.* 1999, **284**, 205-214. (b) Y.-B. Dong, L. Yang, K.-K. Cheung, A. Mayr, *J. Organomet. Chem.* 2000, **598**, 55–62.

(2) D. W. Price, S. M. Dirk, F. Maya, J. M. Tour, *Tetrahedron* 2003, **59**, 2497-2518.

(3) L. A. Büldt, X. W. Guo, A. Prescimone, O. S. A, Wenger, *Angew. Chem. Int. Ed*. 2016, **55**, 11247-11250.

(4) A. Mayr, L. F. Mao*, Inorg. Chem*. 1998, **37**, 5776-5780.