# Supporting Information

# Post-Synthetic Metalation of Robust Hydrogen-Bonded Organic Framework for Heterogeneous Catalysis

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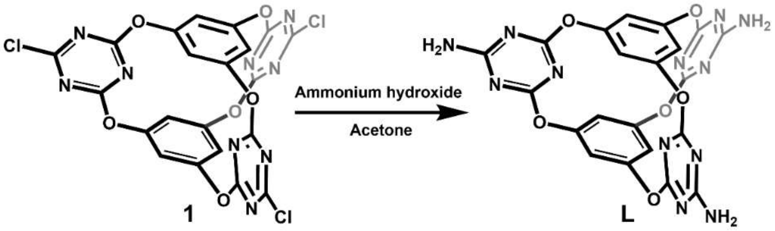
## Caption of Content

## Experimental Section.

**General information.** All chemicals were obtained from commercial sources and used without further purification. **1** was prepared according to the published procedure.[S1]



**Scheme S1**. Schematic synthesis of the building block (**L**) for the assembly of HOF-19.

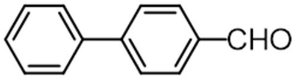
**Synthesis of L and HOF-19.** To a solution of **1** (585 mg, 1.00 mmol) in acetone (30 mL), ammonium hydroxide (250 μL, 28%) was added, Scheme S1. The resulting mixture was stirred over night at room temperature. The white solid was obtained by filtration and washing with acetone (10 mL × 3) and water (10 mL × 3). The product **L** was dried at room temperature and obtained with the yield of 72% (370 mg). $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ (ppm) 7.77 (s, 6H), 6.70 (s, 6H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ (ppm) 172.02, 170.02, 152.72, 114.96. Anal. Calcd for $C_{21}H_{12}N_{12}O_6 \cdot H_2O$: C 46.16; H 2.58; N 30.76. Found: C 46.11; H 2.51; N 30.81. The single crystals of HOF-19 were obtained by the slow evaporation of formic acid solution containing **L**, and bulk material of this HOF was prepared by the slow diffusion of acetone into formic acid solution in a yield of 50%.

**Synthesis of HOF-19⊃Pd(II) and regeneration of HOF-based catalyst.** HOF-19a (53.0 mg) was immersed in an acetone solution (10 mL) containing palladium acetate (22.4 mg, 0.100 mmol) for 12.0 hours at room temperature. The resulting solid was isolated by centrifugation and washed with acetone and water for three times, and dried under vacuum at room temperature for 6.0 hours to yield HOF-19⊃Pd(II) (68.0 mg) as a brown powder. The Pd content in HOF-19⊃Pd(II) is 3.8 wt% as determined by ICP.

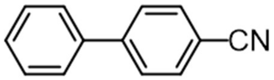
The deactivated catalyst was obtained after the continuous coupling reaction of phenylboronic acid (1.83 g × 5) and 4-bromobenzonitrile (2.02 g × 5) in the presence of $K_2CO_3$ (2.76 g) with the help of HOF-19⊃Pd(II) (150 mg) in *p*-xylene (40 mL) for 20.0 hours. The catalyst was separated by centrifugation and washed by *p*-xylene (20 mL × 3), water (20 mL × 3), and acetone (20 mL × 3), which was dried at room temperature and obtained in a yield of *ca*. 89% (134 mg). The regenerated HOF-based catalyst was obtained by the same synthesis method of HOF-19 bulk material, by diffusing acetone into a formic acid solution (10 mL) of the deactivated species (134 mg). After five days, the regenerated species was collected by filtration and dried at room temperature, which was obtained in a yield of 41% (55.1 mg).

**Catalytic activity test of HOF-19⊃Pd(II).** In a typical run of catalytic activity test, aryl halide (1.00 mmol), phenylboronic acid (183 mg, 1.50 mmol), $K_2CO_3$ (276 mg, 2.00 mmol), and HOF-19⊃Pd(II) (7.5 mg, 0.260 mmol%) were added to *p*-xylene (4 mL), which were stirred at 150ºC at $N_2$ atmosphere and monitored by thin-layer chromatography (TLC). After the reaction completed, the mixture was centrifugated, and the organic phase was separated. The solid was washed with dichloromethane (3 × 5 mL). The organic phases were combined and washed with water (20 mL) to remove $K_2CO_3$ residue. The combined organic phase was then evaporated under vacuum to give the crude product. The crude product was further purified by column chromatography over silica gel to obtain the target product.

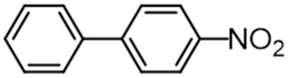
In the recycle test, the reaction of 4-bromobenzonitrile (182 mg, 1.00 mmol) with phenylboronic acid (183 mg, 1.50 mmol) in presence of $K_2CO_3$ (276 mg, 2.00 mmol), HOF-19$\supset$Pd(II) (15.0 mg, 0.520 mmol%), and *p*-xylene (4 mL) was carried out. After each cycle, the catalyst was separated by centrifugation and washed by *p*-xylene (3 mL × 3), which was used directly in the next cycle of reaction.



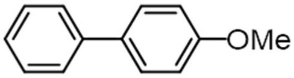
Prepared according to the aforementioned procedure with 4-bromobenzaldehyde as starting material. The product was collected as a white solid with a yield of 97% (177 mg) after silica gel chromatography (dichloromethane:*n*-hexane = 1:2). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 10.01 (s, 1H), 7.97 (d, $J$ = 8.0 Hz, 2H), 7.77 (d, $J$ = 8.0 Hz 2H), 7.66 (d, $J$ = 8.0 Hz, 2H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 1H).



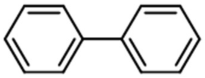
Prepared according to the aforementioned procedure with 4-bromobenzonitrile as starting material. The product was collected as white solid with a yield of 97% (174 mg) after silica gel chromatography (dichloromethane:petroleum ether = 2:3). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.74-7.68 (m, 4H), 7.60 (d, $J$ = 8.0 Hz, 2H), 7.51 (m, 3H).



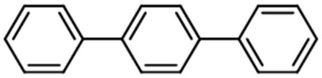
Prepared according to the aforementioned procedure with 1-bromo-4-nitrobenzene as starting material. The product was collected as a pale yellow solid with a yield of 97% (193 mg) after silica gel chromatography (dichloromethane:*n*-hexane = 1:2). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.32 (d, $J$ = 8.0 Hz, 2H), 7.76 (d, $J$ = 8.0 Hz, 2H), 7.64 (d, $J$ = 8.0 Hz, 2H), 7.52-7.43 (m, 3H).



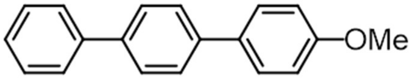
Prepared according to the aforementioned procedure with 4-bromoanisole (or 4-iodoanisole) as starting material. The product was collected as a white solid with a yield of 96% (177 mg) from 4-bromoanisole as stating material and 97% (179 mg) from 4-iodoanisole as stating material after silica gel chromatography (dichloromethane:*n*-hexane = 1:3). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.56-7.52 (m, 4H), 7.44 (t, $J$ = 8.0 Hz, 2H), 7.32-7.29 (m, 1H), 6.99 (d, $J$ = 8.0 Hz, 2H), 3.86 (s, 3H).



Prepared according to the aforementioned procedure with 4-bromobenzene as starting material. The product was collected as colorless oil with a yield of 98% (151 mg) after silica gel chromatography (petroleum ether). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.61 (d, $J$ = 8.0 Hz, 4H), 7.46 (t, $J$ = 8.0 Hz, 4H), 7.37 (t, $J$ = 8.0 Hz, 2H).



Prepared according to the aforementioned procedure with 4-bromobiphenyl as starting material. The product was collected as a white solid with a yield of 19% (43.7 mg) after silica gel chromatography (dichloromethane:*n*-hexane = 1:9). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.69 (s, 4H), 7.66-7.64 (m, 4H), 7.49 (t, $J$ = 7.6 Hz, 4H), 7.39 (t, $J$ = 7.6 Hz, 2H).



Prepared according to the aforementioned procedure with 4-bromo-4'-methoxybiphenyl as starting material. The product was collected as a white solid with a yield of 13% (33.8 mg) after silica gel chromatography (dichloromethane:*n*-hexane = 1:4). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.67-7.58 (m, 8H), 7.51-7.44 (m, 2H), 7.40 (t, $J$ = 7.6 Hz, 1H), 7.00 (d, $J$ = 8.8 Hz, 2H), 3.87 (s, 3H).

**Physical characterization.** NMR spectra were recorded on a Bruker DPX 400 spectrometer ($^1$H: 400 MHz, $^{13}$C: 100 MHz) in $CDCl_3$ and DMSO-$d_6$. $^1$H NMR spectra were referenced internally using the residual solvent resonances ($\delta$ = 7.26 ppm for

$CDCl_3$ and $\delta$ = 2.50 ppm for DMSO-$d_6$) relative to $SiMe_4$. $^{13}C$ NMR spectrum was referenced internally by using the solvent resonance ($\delta$ = 39.52 ppm for DMSO-$d_6$). Elemental analysis was performed on an Elementar Vavio El III. Powder X-ray diffraction (PXRD) data were collected with a TTR III multi-function X-ray diffractometer operated at 40 kV and 300 mA with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) data were conducted on an ESCALAB 250Xi system. Al Kα X-ray (6 mA × 12 KV) was utilized as the irradiation source. All measurements were performed in the CAE mode with the reference of C 1s (284.8 eV). The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 PLUS HD88 system. The samples were degassed at room temperature for 24.0 hours before the measurement. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer instrument over the temperature range of 25 to 800°C under nitrogen atmosphere with a heating rate of 10°C/min. The Pd content of the HOF-19⊃Pd(II) sample was determined by inductively coupled plasma (ICP) analysis with an Agilent 7700X ICP-MS instrument. Energy dispersive spectroscopy (EDS) mapping images were collected by transmission electron microscopy (JEM-2100F) at an operation voltage of 200 kV. Scanning electron microscopy (SEM) images were performed on a HITACHI SU8010 microscope operated at an accelerating voltage of 3.0 KV.

**Single crystal crystallography.** Crystallographical data of HOF-19 was collected on a diffractometer of SuperNova, Dual, Cu at home/near, AtlasS2 with Cu *Kα* radiation (λ = 1.54184 Å) at 200.00 K. The structure was solved by the direct method (SHELXS-2014) and refined by full-matrix least-squares (SHELXL-2014) on $F^2$.[S2] Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Because there are seriously disordered solvent molecules in the HOF-19 pores, 'SQUEEZE' command was employed. CCDC 1900772 for HOF-19 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Theoretical simulation.** For the purpose of theoretically determining the molecular sizes of selected reaction substrates, density functional theory (DFT) calculations were carried out on the basis of B97XD/BS1[S3] using Gaussian 09 D.01 software package.[S4] The BSI represents a mix basis sets where 6-311G(d)[S5] for C, H, O, and N atoms and LanL2DZ[S6] for Br atom.

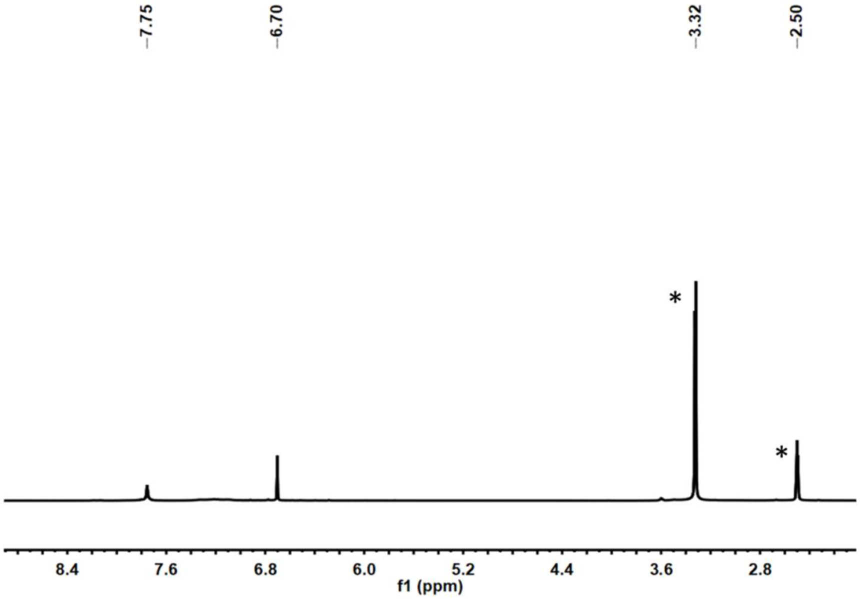


**Figure S1.** $^{1}$H NMR spectrum of **L** in DMSO-$d_6$. * denotes the solvent impurity in DMSO-$d_6$.

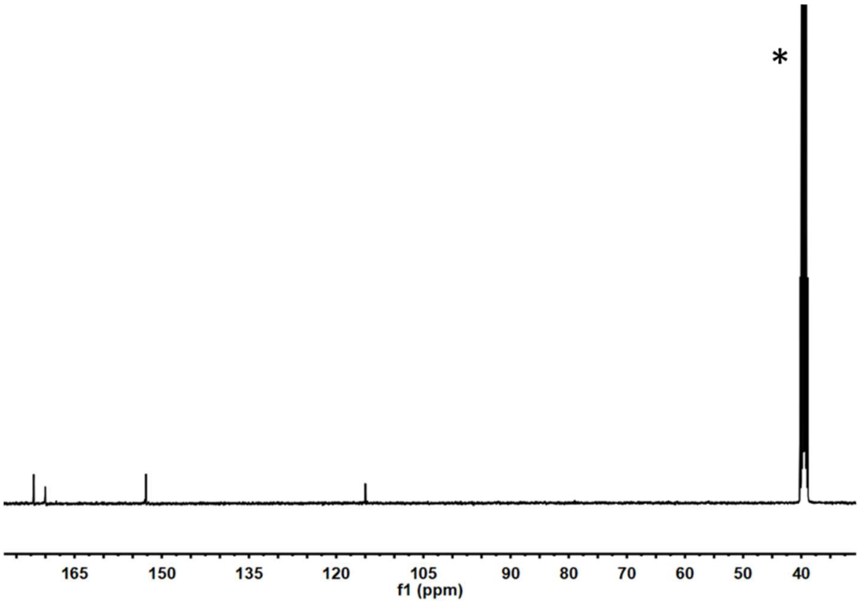


**Figure S2.** $^{13}$C NMR spectrum of **L** in DMSO-$d_6$. * denotes the solvent impurity in DMSO-$d_6$.

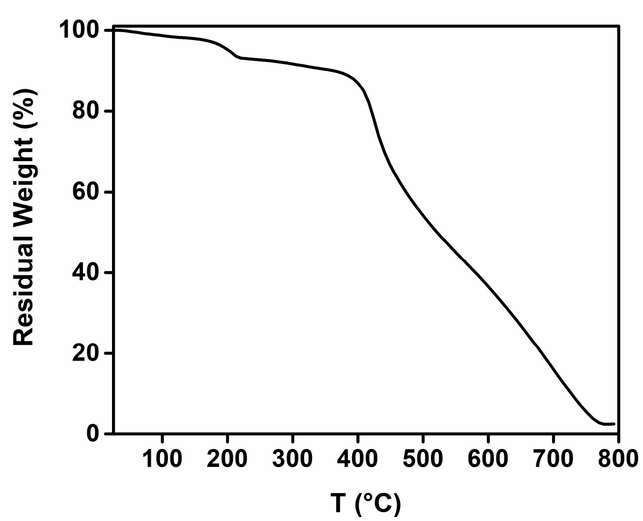


**Figure S3.** TGA curve of as-synthesized HOF-19 in the range of 25 to 800°C.

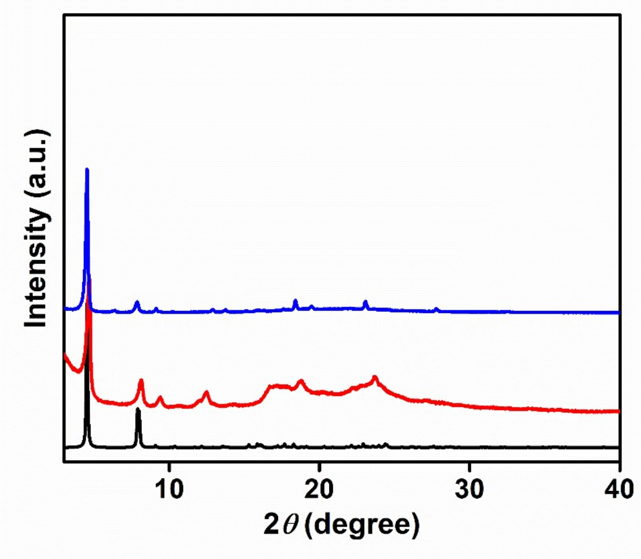


**Figure S4.** PXRD profiles of as-synthesized HOF-19 (red) and HOF-19a (blue) in comparison with a simulated powder pattern based on the single-crystal structure of HOF-19 without the solvent molecules included (black).

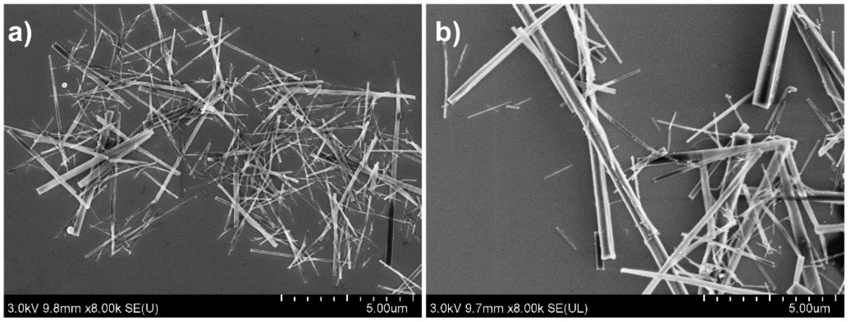


**Figure S5.** SEM photos of (a) activated HOF-19a and (b) HOF-19⊃Pd(II).

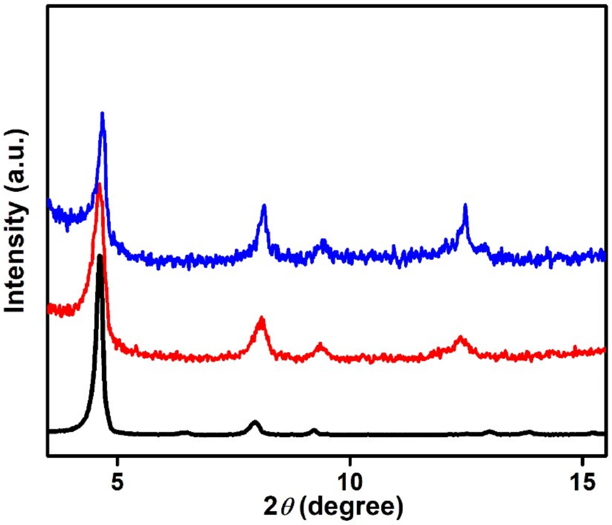


**Figure S6.** PXRD profiles of HOF-19a (black), HOF-19⊃Pd(II) (red), and HOF-19⊃Pd(II) after four cycles of reaction (blue).

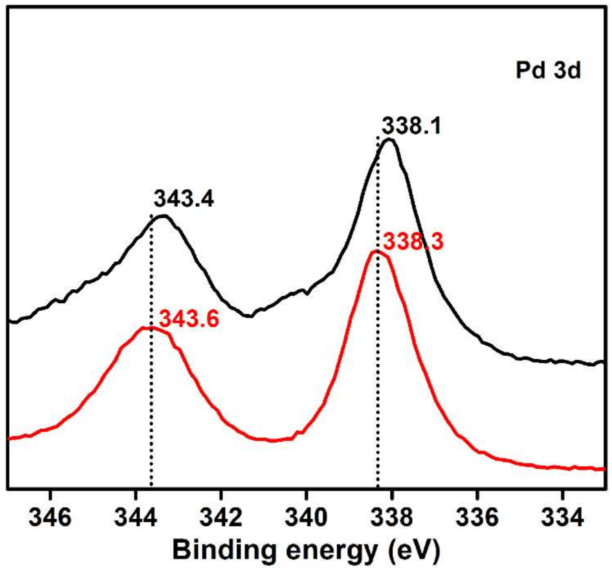


**Figure S7.** XPS spectra of HOF-19⊃Pd(II) (black) and $Pd(OAc)_2$ (red).

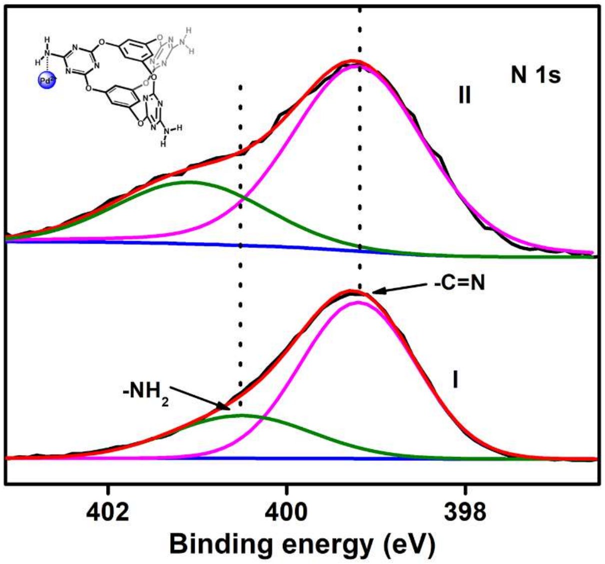


**Figure S8.** XPS deconvolution of HOF-19 (I) and HOF-19⊃Pd(II) (II) and possible amino binding site to complex with palladium ion (insert). Experimental spectra (black); background spectra (blue); Voigt curves (green and pink); simulated spectra comprising the sum of the Voigt curves (red).

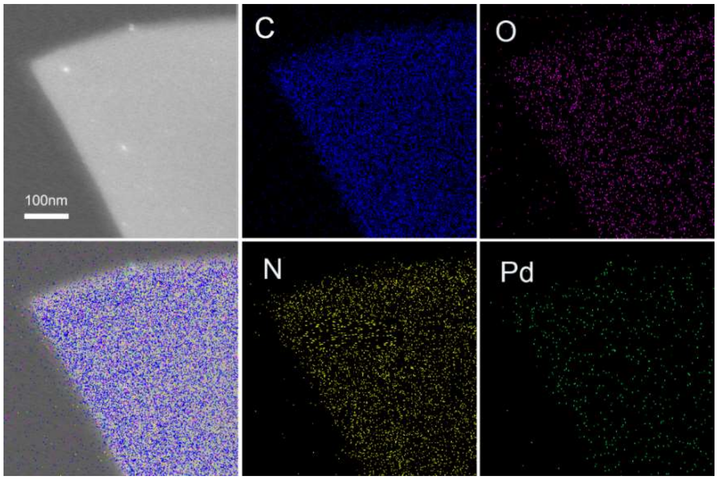


**Figure S9.** EDS mapping of HOF-19⊃Pd(II).

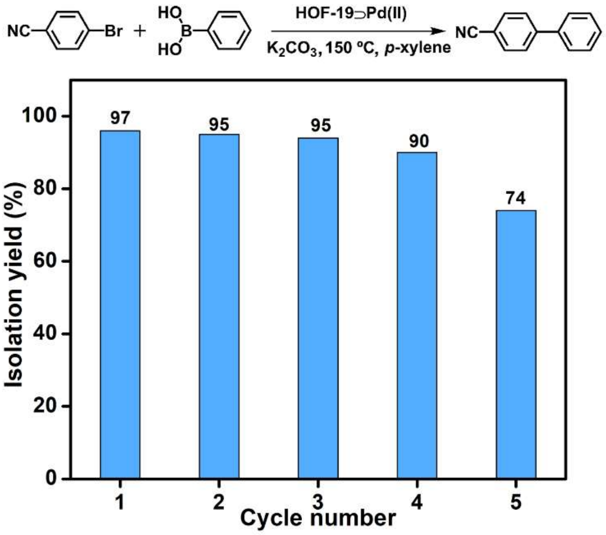


**Figure S10.** Recycle test of HOF-19⊃Pd(II) in the Suzuki-Miyaura coupling reaction of 4-bromobenzonitrile and phenylboronic acid (The reaction conditions: 4-bromobenzonitrile (1.00 mmol), phenylboronic acid (1.50 mmol), $K_2CO_3$ (2.00 mmol), and HOF-19⊃Pd(II) (15.0 mg), *p*-xylene (4 mL), 150°C, 2.0 hours).

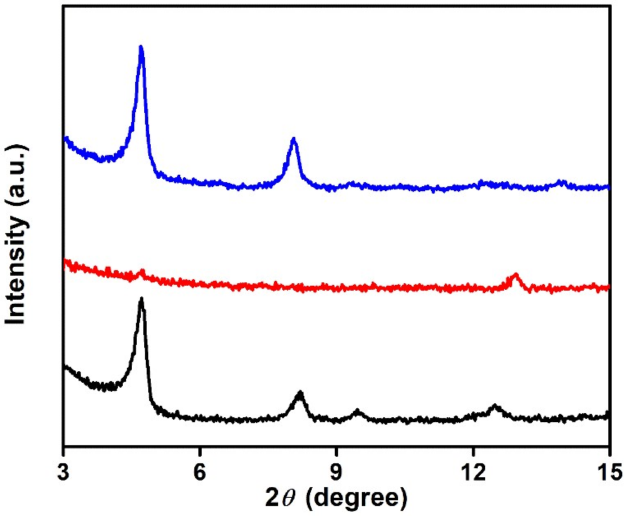


**Figure S11.** PXRD profiles of regenerated HOF-19⊃Pd(II) (blue) and deactivated HOF-19⊃Pd(II) (red) in comparison with that of as synthesized HOF-19⊃Pd(II) (black).

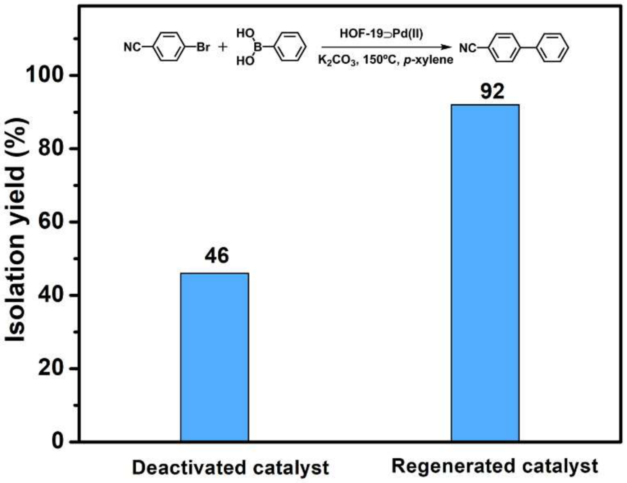


**Figure S12**. Catalytic performance of deactivated HOF-19⊃Pd(II) (7.5 mg) and regenerated species (7.5 mg) in the Suzuki-Miyaura coupling reaction of 4-bromobenzonitrile (1.00 mmol) with phenylboronic acid (1.50 mmol) in the presence of $K_2CO_3$ (2.00 mmol) in p-xylene (4 mL) at 150°C in 3.0 hours.

**Table S1.** Crystallographic and refinement parameters for HOF-19.

| crystal data | HOF-19 |
|---|---|
| system | monoclinic |
| space group | $C2/m$ |
| MF | $C_{21}H_{12}N_{12}O_6$ |
| FW | 528.43 |
| $a$ /Å | 23.0932(15) |
| $b$ /Å | 8.0164(4) |
| $c$ /Å | 20.0514(18) |
| $\alpha$ /° | 90 |
| $\beta$ /° | 105.212(8) |
| $\gamma$ /° | 90 |
| volume /Å$^3$ | 3581.9(5) |
| Z | 4 |
| density /g/cm$^3$ | 0.98 |
| solvent-accessible void space /%[S7] | 47 |
| theoretical pore volume /cm$^3$/g | 0.48 |
| refinement parameters | $R_1 = 0.0740$[a], $wR_2 = 0.2254$[b] |

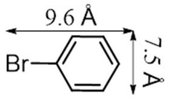
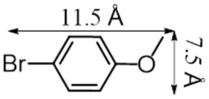
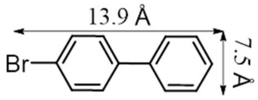
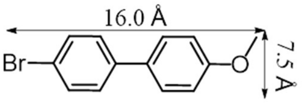
[a] $R_1 = \Sigma|F_o\text{-}|F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2\text{-}F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

**Table S2**. Hydrogen bonding interaction in the crystal structure of HOF-19.

| D-H···A | distance(H···A) /Å | distance (D···A) /Å | angle(DHA) /º |
|---|---|---|---|
| N(1)-H(1B)...N(8)#2 | 2.25 | 3.060(3) | 158.2 |
| N(1)-H(1A)...N(8)#3 | 2.24 | 3.060(3) | 158.7 |
| N(2)-H(2B)...N(6)#4 | 2.21 | 3.065(3) | 170.4 |
| N(2)-H(2A)...N(6)#5 | 2.21 | 3.065(3) | 170.4 |
| N(3)-H(3B)...N(4)#6 | 2.25 | 3.061(3) | 158.2 |
| N(3)-H(3A)...N(4)#7 | 2.25 | 3.061(3) | 158.5 |
| N(1)-H(1B)...N(8)#2 | 2.25 | 3.060(3) | 158.2 |
| N(1)-H(1A)...N(8)#3 | 2.24 | 3.060(3) | 158.7 |
| N(2)-H(2B)...N(6)#4 | 2.21 | 3.065(3) | 170.4 |
| N(2)-H(2A)...N(6)#5 | 2.21 | 3.065(3) | 170.4 |
| N(3)-H(3B)...N(4)#6 | 2.25 | 3.061(3) | 158.2 |
| N(3)-H(3A)...N(4)#7 | 2.25 | 3.061(3) | 158.5 |

[a] Symmetric code for HOF-19: #1 x, -y+1, z; #2 x-1/2, y+1/2, z; #3 x-1/2, -y+1/2, z; #4 -x+1/2, y+1/2, -z+1; #5 -x+1/2, -y+1/2, -z+1; #6 x+1/2, -y+1/2, z; #7 x+1/2, y+1/2, z.

**Table S3**. Comparison of molecular sizes of bromobenzene (entry 1), 1-bromo-4-methoxybenzene (entry 2), 4-bromo-1,1'-biphenyl (entry 3), and 4-bromo-4'-methoxy-1,1'-biphenyl (entry 4).

| Entry | Molecular size | Entry | Molecular size |
|---|---|---|---|
| 1 |  | 2 |  |
| 3 |  | 4 |  |

**Reference:**

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(S4) Frisch, M. J., etal., Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford CT, **2010**.

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