Supporting Information

Polar functional groups anchored 2D MOF template for stabilization of Pd(0) nps towards catalytic C-C coupling reaction

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Experimental Section

Materials and methods.

$Cu(NO_3)_2 \cdot 3H_2O$, 1,2-bis(4-ypridyl)ethane, 1,2,3-benzenetricarboxylate were purchased from Sigma Aldrich Chemical Co. and used as received. All substrates used for catalysis were obtained from commercial chemical suppliers such as Spectrochem and used without further purification.

Characterization Techniques

Suitable single crystals of **1** were mounted on a thin glass fiber with commercially available super glue. X-ray single crystal structural data were collected on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray 12 source with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. Powder X-ray diffraction (PXRD) measurements of all compounds were recorded on Bruker D8 Discover instrument using Cu-Kα radiation. Thermogravimetric analysis (TGA) was carried out (Mettler Toledo) in nitrogen atmosphere in the temperature range 30 – 500 °C (heating rate = 5 °C min^{-1}). Elemental analysis was carried out using a Thermo Scientific Flash 2000 CHN analyzer. Adsorption Measurements of N_2 (77K) and CO_2 (195 K) studies were carried out using QUANTACHROME QUADRASORB *SI* and AUTOSORB *IQ2* instrument. The adsorbent samples were degassed at 140 °C for 12 h under a high vacuum (10-1 Pa) prior to measurements and adsorption isotherms were measured, all the operations were computer-controlled and automatic. For TEM measurements JEOL JEM 3010 instrument operating at an accelerating voltage of 300 kV was used and the samples were prepared by dispersing in ethanol by sonication before drop casting on a carbon-coated copper grid. Inductively coupled plasma-optical emission spectral (ICP-OES) analyses were performed using Perkin Elmer OPTIMA 7000 spectrometer. 1H-NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard at ambient temperature on a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer.

Synthesis of $\{[Cu\ (1,\ 2,\ 3\text{-btc})(bpe)\cdot(H_2O)]\cdot H_2O\}_n$ (1)

$Cu(NO_3)_2.3H_2O$ (1 mmol, 0.242 g) was dissolved in distilled water (50 mL). Sodium 1,2,3-benzenetricarboxylate ($Na_3$1.2,3-btc; 0.5 mmol, 0.138 g) and 4,4'-bipyridylethane (bpe; 0.5 mmol, 0.092 g) were dissolved in water and methanol in the ratio of 7:3 respectively and the resultant mixture (24 mL) was sonicated for 15 min to obtain a homogeneous solution. A solution mixture of $Na_3$1.2,3-btc and bpe (2 mL) was slowly and carefully layered on top of the solution of $Cu(NO_3)_2.3H_2O$ solution (2 mL) using a buffer solution of water and methanol (3:7, 2 mL) in a crystal tube, which was sealed and left undisturbed at room temperature. Deep blue block single crystals were grown at the junction of the two different solvents after one month. The crystals were separated and washed with water and methanol, and subsequently subjected to X-ray diffraction. A bulk amount of the compound was synthesized by direct mixing of the corresponding ligands solution with a water solution of Cu(II). Yield: 88%; IR (KBr): v=1721 (C=O), 1115 (C-O), 3604 (OH), 1548 cm^{-1} (Ar C=C); Anal. Calcd. For (**1**), $C_{21}H_{15}CuN_2O_8$: C, 51.80; H, 3.11; N, 5.75. Found: C, 50.98; H, 3.13; N, 5.54.

Preparation of Pd(0)@1a Composite

Desolvated framework of **1** i.e. **1a** (0.005 g, 0.01 mmol) was dispersed in ethanol (1 mL) by sonication for 5 min. To this suspension, a solution of K_2PdCl_4 (500 µL) [prepared by stirring the mixture of $PdCl_2$ (0.005g), KCl and H_2O (5 mL) for 10 h] was added and followed by the addition of $NaBH_4$ (10^{-4} M). The mixture was then washed thoroughly with ethanol, centrifuged and dried in an oven at 120 °C. The composite has been characterized by PXRD, TEM, EDAX, XPS and ICP-OES analyses.

General Procedure for Catalytic Reaction Using Pd(0)@1a

In a dried schlenk tube, aryl halide (1 eq), aryl boronic acid (1 eq), Cs_2CO_3 (1.5 eq) was added followed by the addition of THF (5 mL). The reaction mixture is degassed and purged with nitrogen followed by addition of **Pd(0)@1a** (1.5 mg) and stirred for 24 hrs at 60 °C and cooled to room temperature. The reaction mixture is filtered to separate the catalyst and dried under reduced pressure. The crude mixture is extracted with DCM and dried over anhydrous sodium sulphate ($Na_2SO_{4)}$ and analyzed using ^{1}H-NMR spectroscopy.

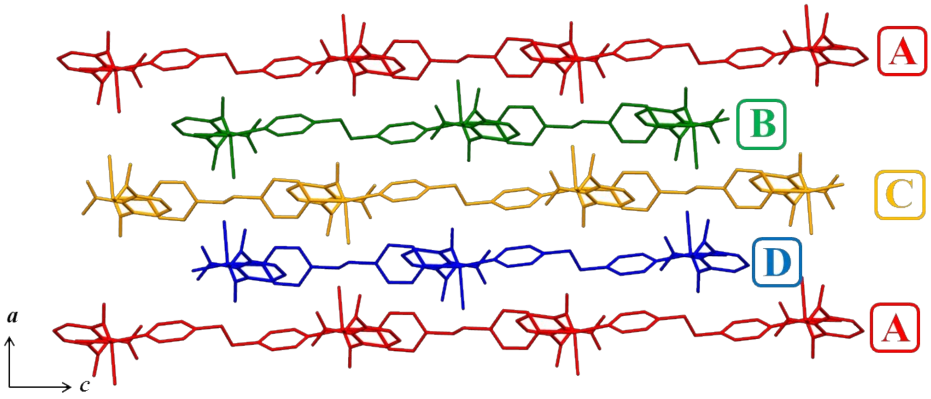


Fig. S1 ABCD…ABCD packing in **1**.

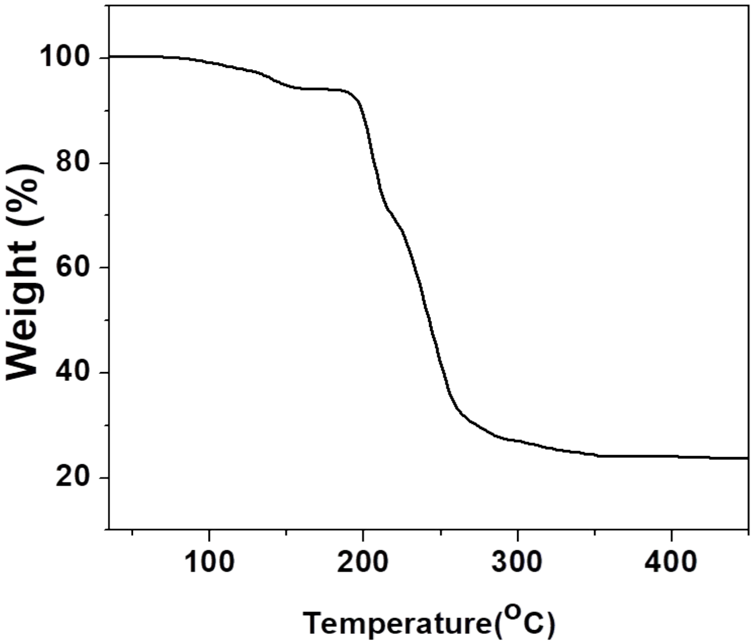


Fig. S2 TGA of assynthesized **1** under N_2 atmosphere in the range of 30-500 °C with a heating rate of 5 °C/min.

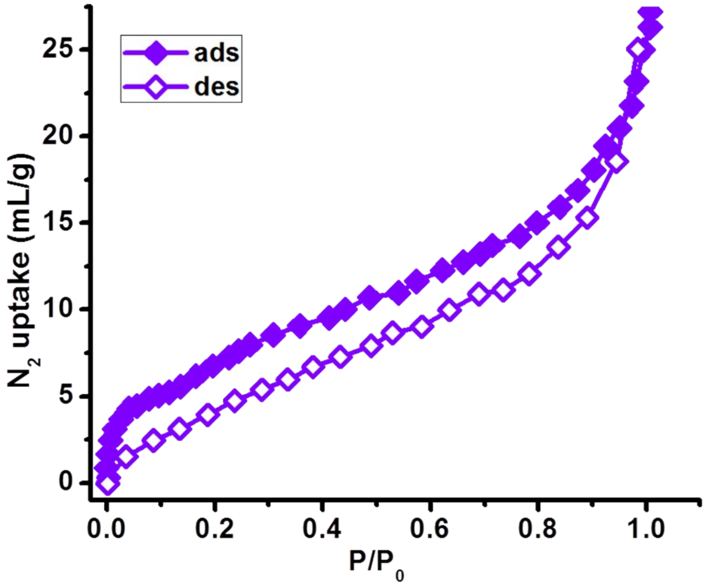


Fig. S3 N$_2$ adsorption isotherm of **1a**; adsorption (filled symbols) and desorption (open symbols) at 77 K.

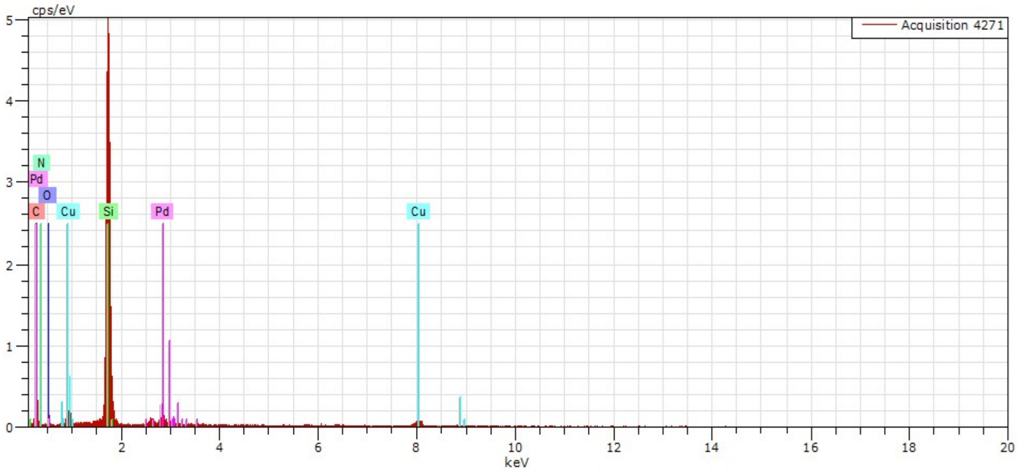
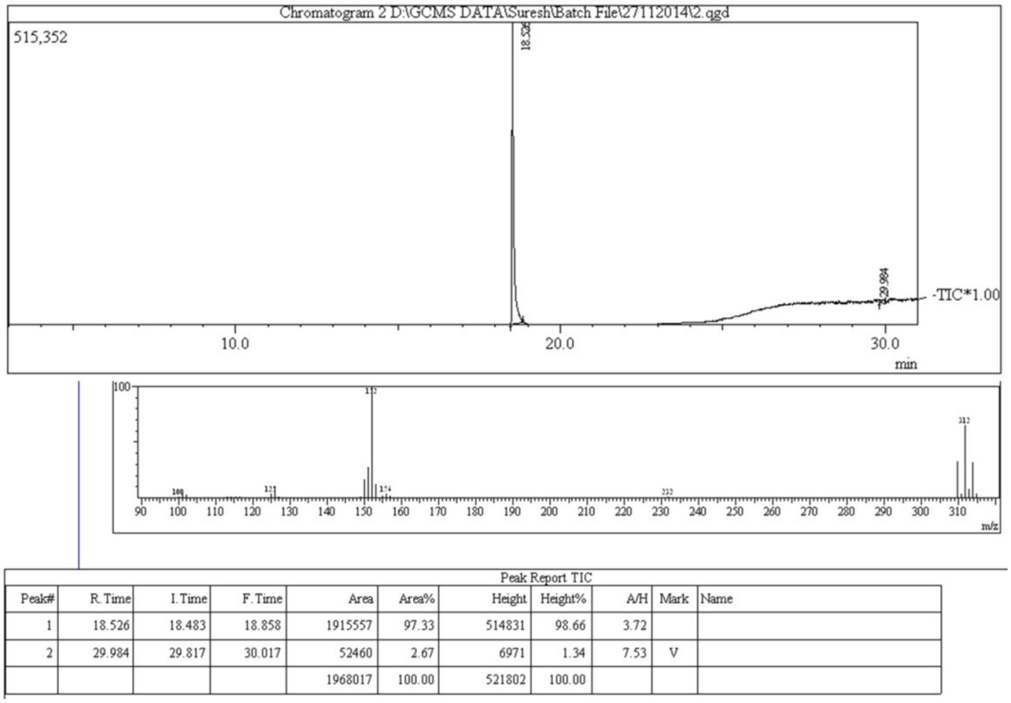


Fig. S4 EDAX of **Pd(0)@1a** showing the presence of both 'Pd' and 'Cu' in the composite.



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	18.526	18.483	18.858	1915557	97.33	514831	98.66	3.72		
2	29.984	29.817	30.017	52460	2.67	6971	1.34	7.53	V	
				1968017	100.00	521802	100.00			

Fig. S5 GC-MS of the catalytic reaction of a phenylboronic acid and iodobenzene showing near complete conversion within 24 hrs.

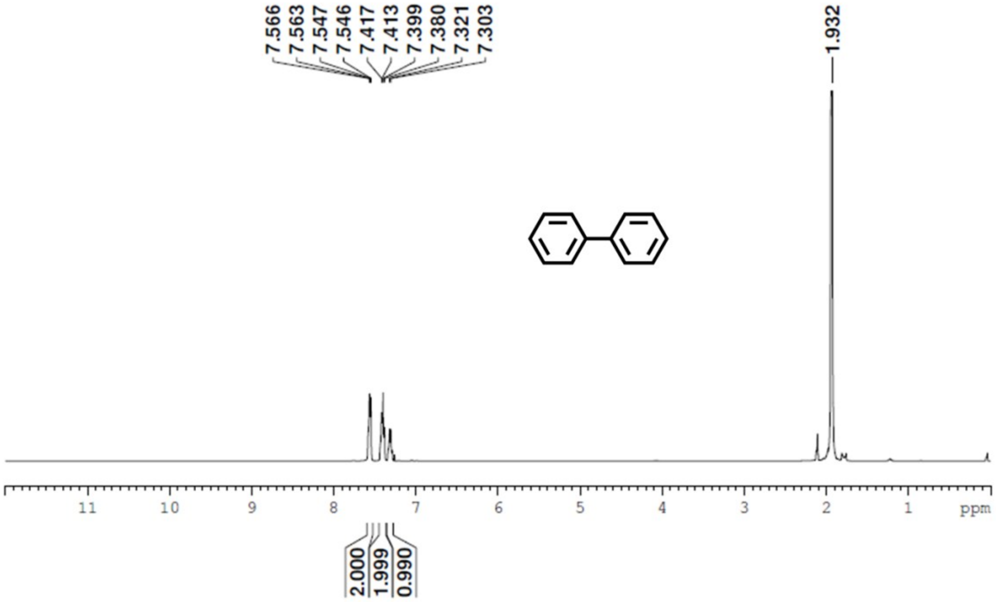


Fig. S6 ^{1}H-NMR spectra of biphenyl in $CDCl_3$.

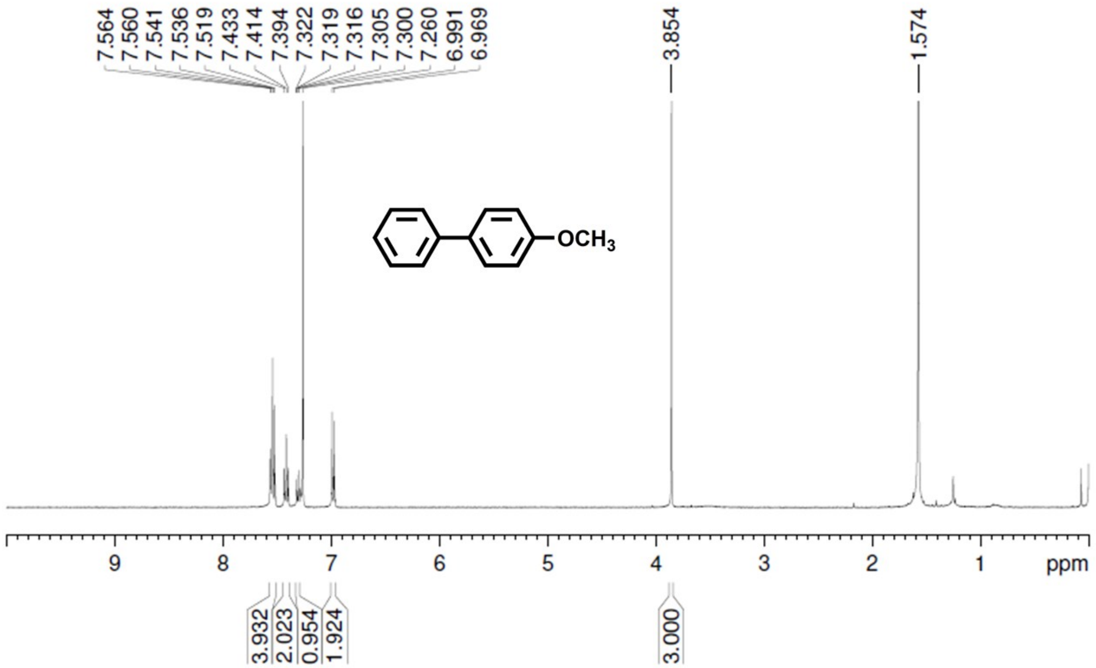


Fig. S7 ^{1}H-NMR spectra of 4-methoxybiphenyl in $CDCl_3$.

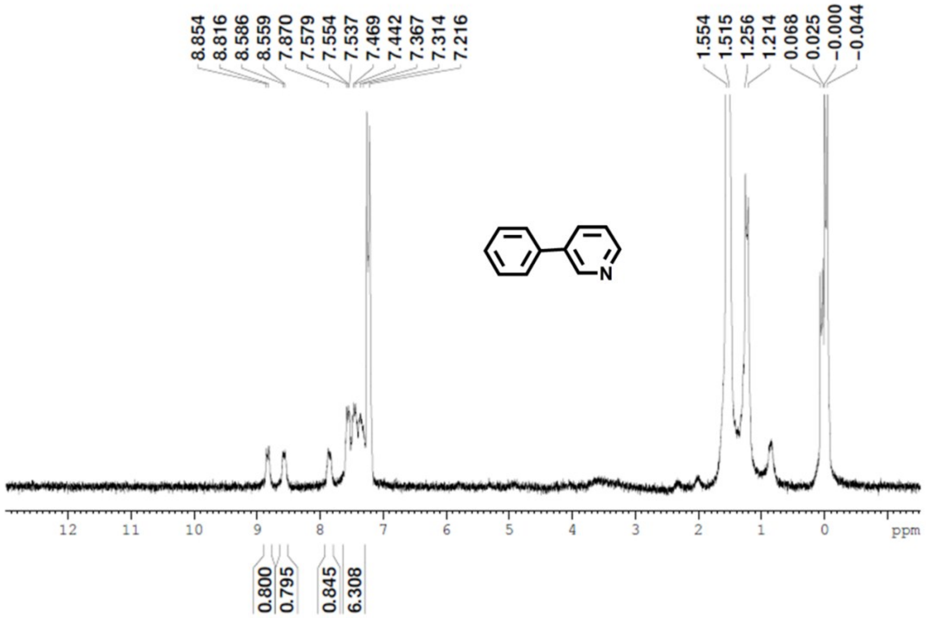


Fig. S8 ^{1}H-NMR spectra of 3-phenylpyridine in $CDCl_3$.

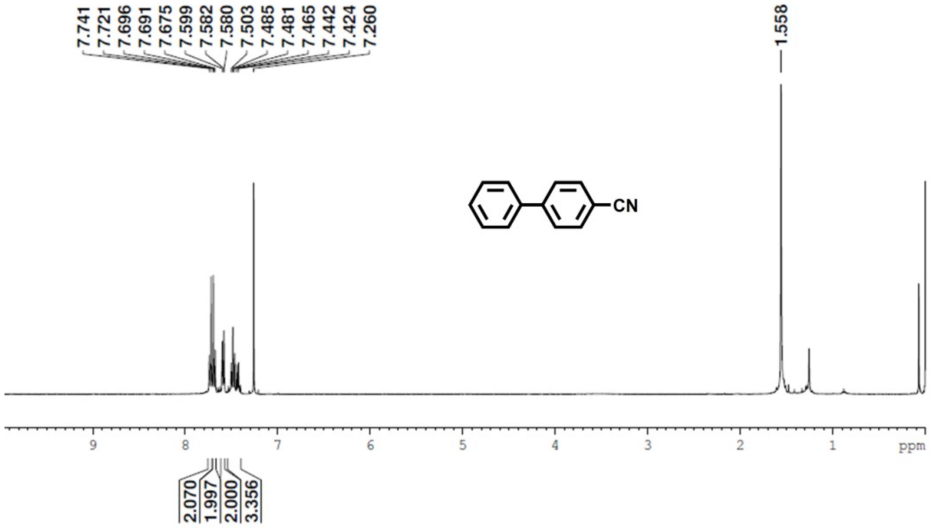


Fig. S9 ^{1}H-NMR spectra of 4-phenylcyanobenzene in $CDCl_3$.

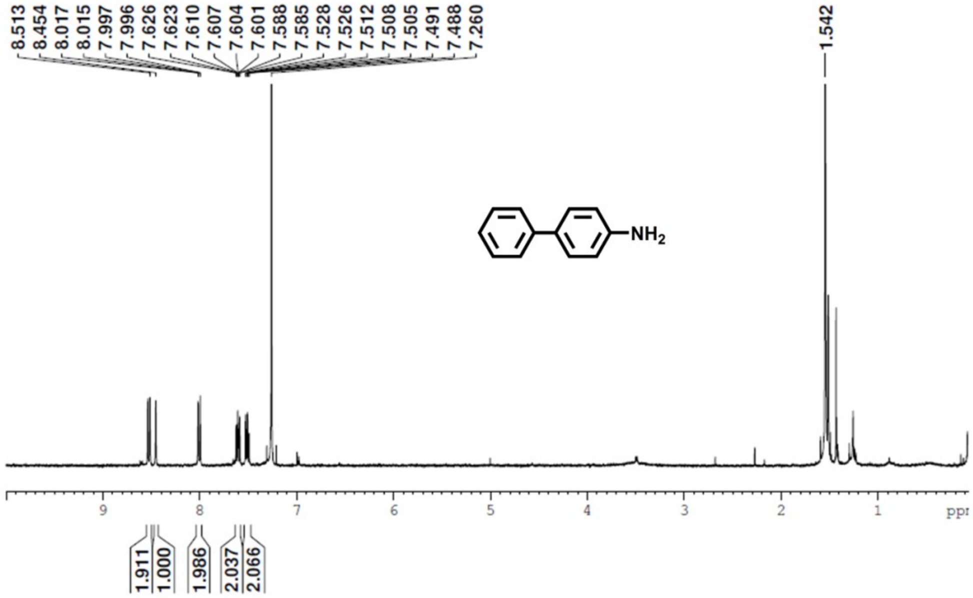


Fig. S10 ^{1}H-NMR spectra of 4-phenylaniline in $CDCl_3$.

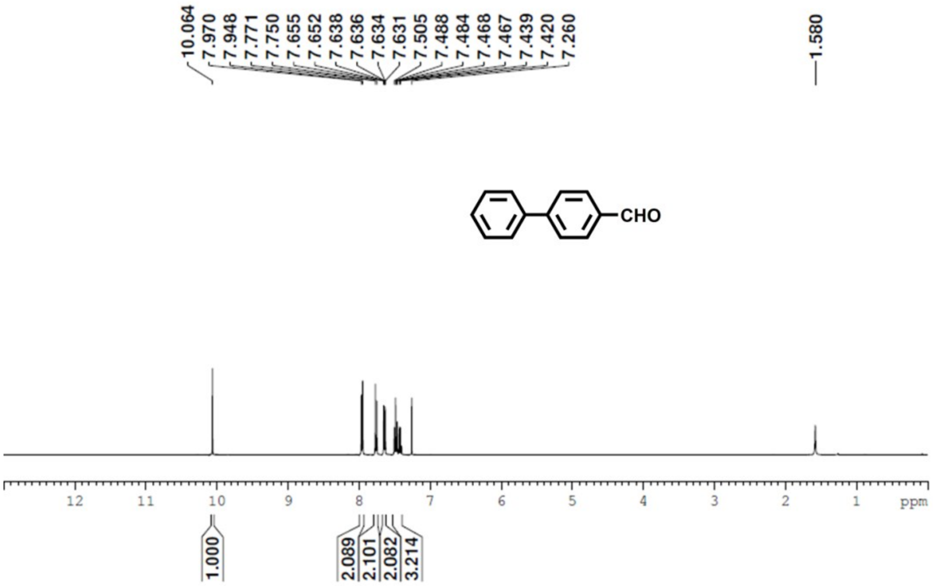


Fig. S11 ^{1}H-NMR spectra of biphenylcaboxyaldehyde in $CDCl_3$.

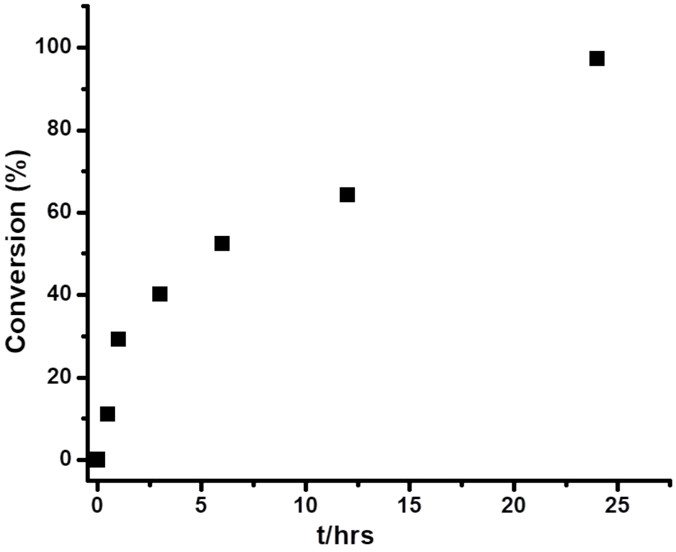


Fig. S12 Time dependent conversion of iodobenzene to biphenyl using **Pd(0)@1a** catalyst.

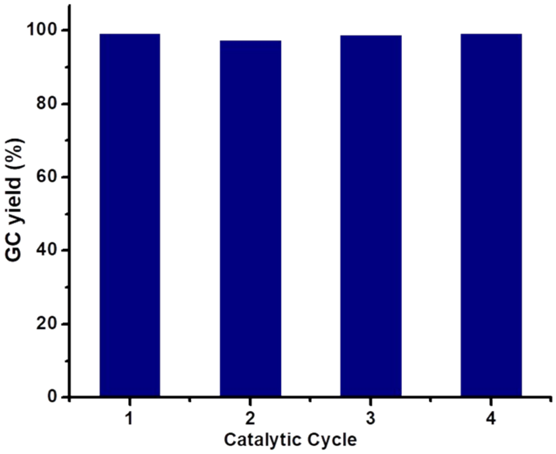


Fig. S13 Catalytic performance of **Pd(0)@1a** upto four catalytic cycles showing excellent recyclability of the catalyst.

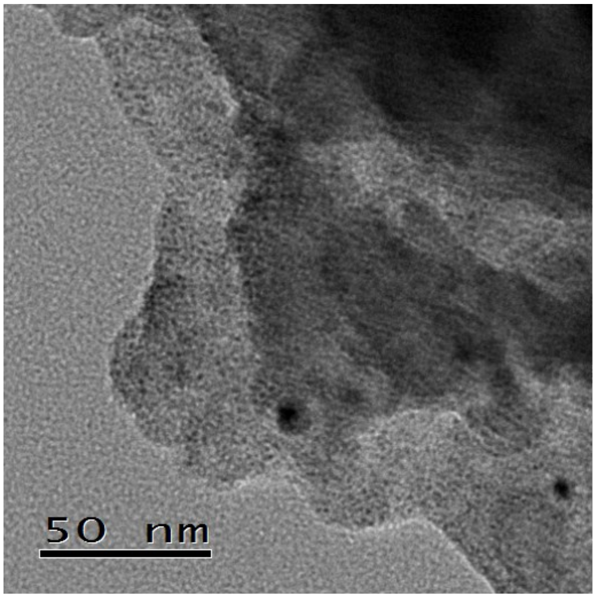


Fig. S14 TEM images of **Pd(0)@1a** after four catalytic cycles.

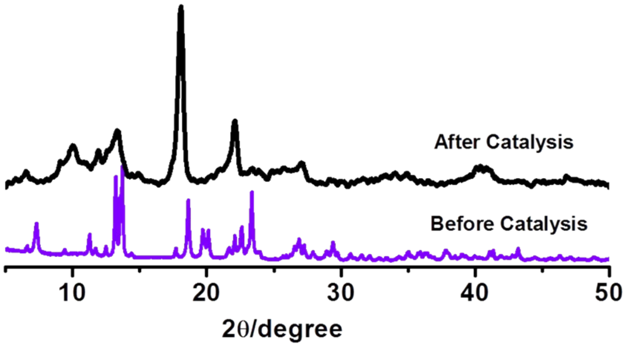


Fig. S15 PXRD pattern of **Pd(0)@1a** before (blue) and after four catalytic cycles (black).

Table 1. Crystal data and structure refinement parameters for 1.

Identification code	**1**
Empirical formula	$C_{21}H_{20}N_2O_8Cu$
Formula weight	491.93
Temperature/K	298.15
Crystal system	triclinic
Space group	P-1
a/Å	7.9154(17)
b/Å	10.025(2)
c/Å	13.447(3)
α/°	88.038(9)
β/°	89.073(9)
γ/°	70.501(7)
Volume/Å^3	1005.2(4)
Z	2
ρ_{calc}g/cm^3	1.625
μ/mm^{-1}	1.141
F(000)	506.0
Crystal size/mm^3	0.011 × 0.008 × 0.006
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.46 to 50
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-13 \le l \le 15$
Reflections collected	11386
Independent reflections	3456 [R_{int} = 0.1244, R_{sigma} = 0.2247]
Data/restraints/parameters	3456/12/289
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0882, wR_2 = 0.2229
Final R indexes [all data]	R_1 = 0.1859, wR_2 = 0.2861
Largest diff. peak/hole / e Å^{-3}	1.23/-1.28
Identification code	**1**
Empirical formula	$C_{21}H_{20}CuN_2O_8$
Formula weight	491.93
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.9154(17)
b/Å	10.025(2)
c/Å	13.447(3)
α/°	88.038(9)
β/°	89.073(9)
γ/°	70.501(7)
Volume/Å^3	1005.2(4)
Z	2

ρ_{calc}g/cm^3	1.625
μ/mm^{-1}	1.141
F(000)	506.0
Radiation	MoKα (λ = 0.71073)
2Theta range for data collection/°	3.04 to 50.08
Index ranges	$-9 \leq h \leq 6$, $-11 \leq k \leq 11$, $-13 \leq l \leq 15$
Reflections collected	10928
Independent reflections	3371 [R_{int} = 0.1093, R_{sigma} = 0.1220]
Data/restraints/parameters	3371/0/294
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0915, wR_2 = 0.2394

Table 2. Bond Lengths for 1

Atom	Atom	Length/Å
Cu01	O2	1.933(6)
Cu01	O3^1	1.951(6)
Cu01	N1	2.008(7)
Cu01	N2	1.988(8)
Cu01	O1W	2.381(7)
O3	Cu01^2	1.951(6)

Table 3. Bond Angles for 1

Atom	Atom	Atom	Angle/°
O2	Cu01	O3^1	174.6(2)
O2	Cu01	N1	86.7(3)
O2	Cu01	N2	94.0(3)
O2	Cu01	O1W	90.6(2)
O3^1	Cu01	N1	88.2(3)
O3^1	Cu01	N2	90.6(3)
O3^1	Cu01	O1W	91.5(2)
N1	Cu01	O1W	95.6(3)
N2	Cu01	N1	166.7(3)
N2	Cu01	O1W	97.6(3)
C1	O2	Cu01	115.0(6)
C8	O3	Cu01^2	126.0(6)
C10	N1	Cu01	120.5(6)
C10	N1	C14	118.3(8)
C14	N1	Cu01	121.0(7)
C20	N2	Cu01	123.3(6)
C19	N2	Cu01	121.5(7)

Table 4. Comparison of catalytic performance of various Pd@MOFs towards different organic transformations.

S.No	Pd@MOF	Pd(0) nps loading (wt%)	Catalytic reaction	Time (hr)	Yield (%)
1[S1]	Pd@MIL-101Cr-NH_2	8	Suzuki-Miyura coupling	6	>99
2[S2]	Pd(0)@1a (This work)	3.2	Suzuki coupling	24	95
3[S3]	Pd/MIL-101	3	One pot indole synthesis	15	93
4[S4]	Pd/APS-MIL-101	0.93	Heck coupling	1	>95
5[S4]	Pd/ED-MIL-101	0.95	Heck coupling	1	>90
6[S5]	Pd@MOF-3	26.9	Heck coupling	24	99

References.

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S2 *Present work*

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