Electronic Supplementary Information

Zr-hydroxamate metal-organic framework with intrinsic chelating sites for postsynthetic Pd metalation and Suzuki-Miyaura catalysis

Zhen-Wu Shao,[a] Chaozhi Xiong,[a] Jiajie Yang,[a] Zhewei Mei,[a] Li Xiong,[a] Wenjing Wu,[a] and Chong Liu[a]*

a. School of Chemical Engineering, Sichuan University, Chengdu, 610065, China

E-mail: liuchong@scu.edu.cn

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1. General procedures

All purchased chemicals were used without further purification except where otherwise noted. Ultrapure water was obtained from a Millipak® Express 40 system (Merk-Millipore, Darmstadt, Germany).

Single-crystal X-ray diffraction (SC-XRD) data for SUM-1-pz were collected on a Bruker D8 Venture single-crystal X-ray diffractometer (Ga Kα radiation, λ = 1.34139 Å) at 193 K.

Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku MiniFlex600 at 40 kV, 40 mA for Cu Kα, (λ = 1.54178 Å) with a scan speed of 10°/min from 3° to 30° at a step size of 0.01°. The simulated powder pattern was obtained using Materials Studio based on the crystal structure of the corresponding MOF.

Optical microscopic images were obtained using a Ruihong BM-500T microscope.

^{1}H NMR spectra were collected on a JNM-ECZ400S/L1 (400 MHz) spectrometer (JEOL Ltd., Tokyo, Japan).

N_2 adsorption–desorption isotherms were collected on a BELSORP MAX system (MicrotracBEL, Japan). Pore size distribution was estimated using the non-local density functional theory (NLDFT) for the adsorption data points using a cylindrical pore metal oxide model.

Thermogravimetric analysis (TGA) was carried out on a TA Discovery SDT 650 simultaneous thermal analyzer from room temperature to 600 ℃ at a heating rate of 10 ℃/min in a N_2 flow of 100 mL/min.

Scanning electron microscopy (SEM) images were obtained using a ZEISS Gemini 300 with accelerating voltages of 0.02–30 kV. Oxford energy-dispersive X-ray spectroscopy (EDX) and Inca software were used to acquire elemental mapping of the crystal surfaces.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha equipped with Al Kα irradiation.

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed on an Agilent 7700(MS).

X-ray absorption near edge structure (XANES) and X-ray absorption fine structure

(XAFS) were performed on the XAFS station of the 1W1B beam line of the Beijing Synchrotron Radiation Facility (BSRF) using transmission mode. Extended X-ray Absorption Fine Structure (EXAFS) data were collected through a fixed-exit double-crystal Si (111) monochromator. The Pd K-edge spectra were processed following the conventional procedure using the IFEFFIT package.

2. Syntheses of PZDH, SUM-1-pz and SUM-1-pz-Pd

2.1 Synthesis of dimethyl 2,5-pyrazinedicarboxylate

Dimethyl 2,5-pyrazinedicarboxylate was synthesized according to the procedure reported by Correia et al with minor modification[1]: 2,5-pyrazinedicarboxylic acid (3.36 g, 20.0 mmol) was dissolved in 60 mL MeOH. Then, 1.5 mL HCl (37%) was added and the mixture was refluxed for 24 h. Afterwards, solvent was evaporated and the residue was dissolved in 100 mL of saturated $NaHCO_3$ aqueous solution. This aqueous phase was extracted with DCM (3 × 100 mL). The DCM phase was then dried over Na_2SO_4 and the final product was collected by filtration and concentration (yield: 2.46 g, 62.5%). The product was used directly in the next step. ^1H NMR (400 MHz, $CDCl_3$): 9.39 (s, 2 H, H_{pz}), 4.07 (s, 6 H, CH_3), shown in Fig. S1.

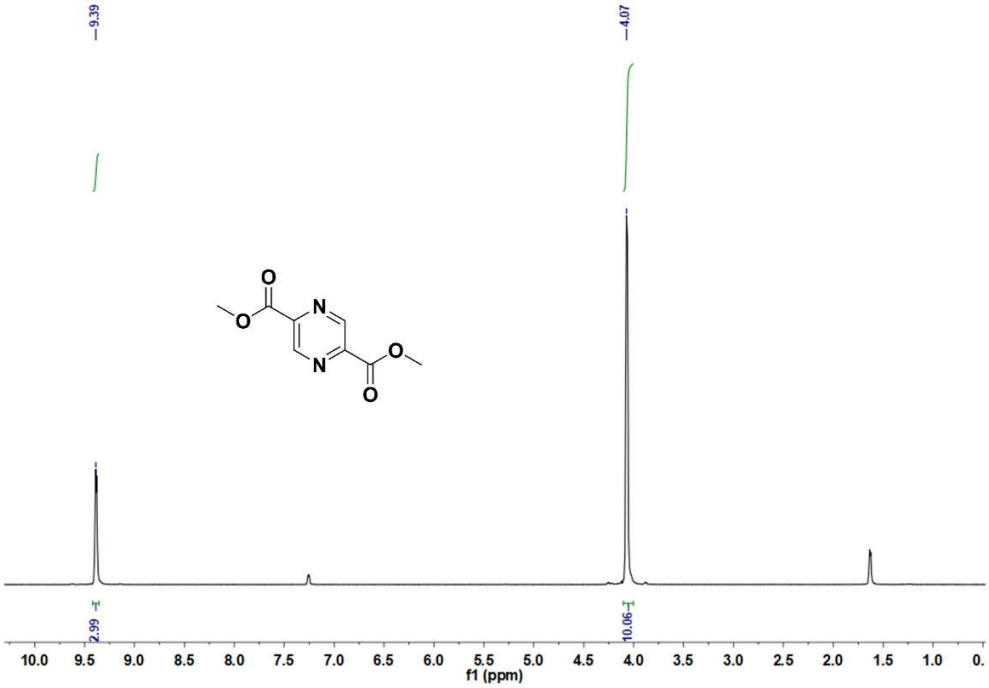

Fig. S1 ^1H NMR spectrum of dimethyl 2,5-pyrazinedicarboxylate in $CDCl_3$.

2.2 Synthesis of pyrazine-2,5-dihyroxamic acid (PZDH)

PZDH was synthesized according to the procedure reported by Carlos et al with minor modification[2]: hydroxylamine hydrochloride (2.52 g, 36 mmol) was mixed with sodium hydroxide (2.88 g, 72 mmol) in deionized water (18 mL). The aqueous solution

was then added to a suspension of dimethyl 2,5-pyrazinedicarboxylate (2.35 g, 12 mmol) in methanol (20 mL). The resulting mixture was stirred for 72 h at 40 ℃ before cooling down to room temperature and subsequently acidified to pH 5.5 with a solution of 30% acetic acid. The faint yellow solids were collected by filtration and washed successively with deionized H_2O (3 × 30 mL). The final product PZDH was dried in air overnight (yield: 1.8 g, 76%). ^{1}H NMR (400 MHz, DMSO-d_6): 11.76 (brs, 2H), 9.34 (brs, 2H), 9.05(s, 4H), shown in Fig. S2.

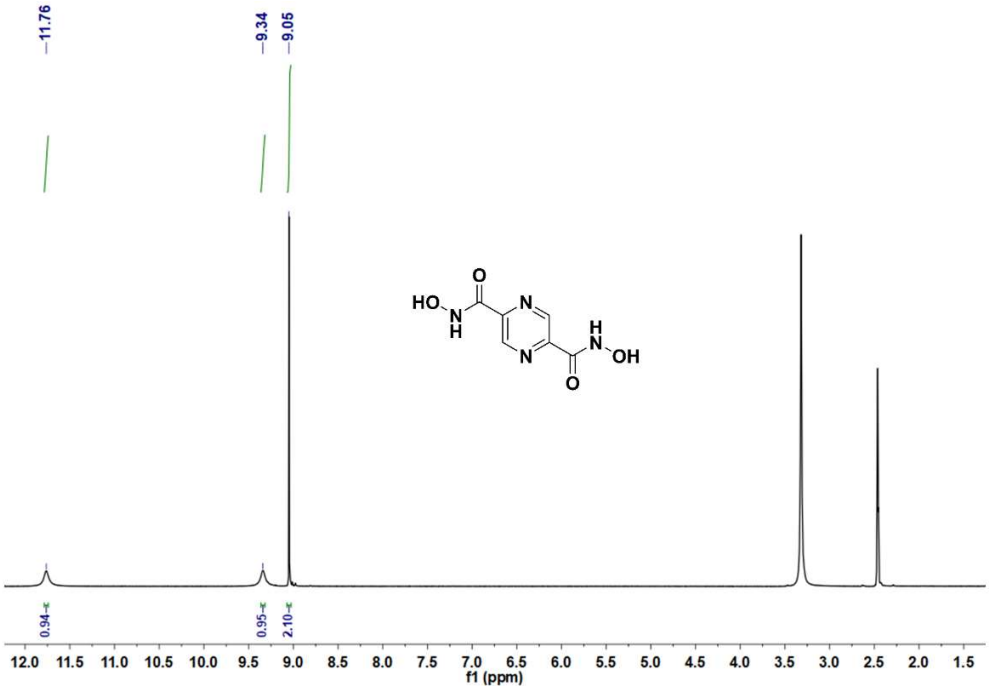

Fig. S2 ^{1}H NMR spectrum of PZDH in DMSO-d_6.

2.3 Synthesis of SUM-1-pz

Ultrasonic dissolve PZDH (5.9 mg, 0.030 mmol) and $ZrCl_4$ (1.17 mg, 0.005 mmol) in 1 mL DMF in a 4 mL glass bottle. Then add 250 μL HCl and keep the mixture at 90 °C for 72 h. After cooling to room temperature, collect the single crystals. Before drying in the air, wash the crystals with dry DMF (3 × 20 mL) and then with acetone (3 × 20 mL).

Fig. S3 Optical microscopic image of SUM-1-pz crystals.

2.4 Syntheses of SUM-1-pz-Pd and SUM-1-pz-Pd-2

4.8 mg SUM-1-pz and 10.4 mg $PdCl_2(CH_3CN)_2$ were mixed in a 4 mL glass vial with 1 mL acetonitrile and stirred at room temperature for 2 h. The mixture was filtered, washed with acetonitrile (3 × 20 mL), and dried in vacuo at room temperature. The product is named SUM-1-pz-Pd and characterized in Section 4.

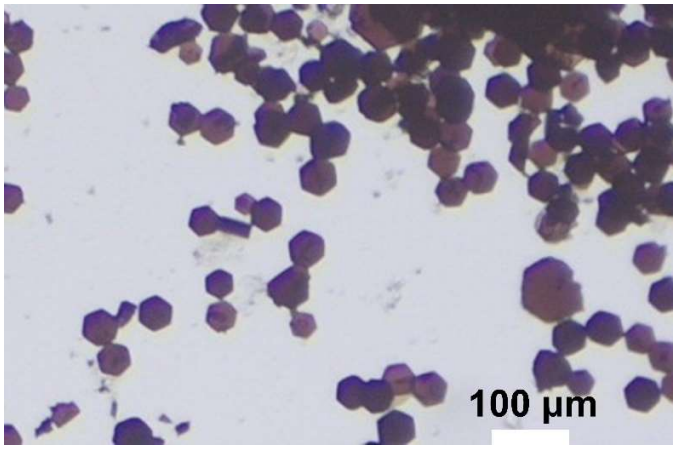

Fig. S4 Optical microscopic image of SUM-1-pz-Pd crystals.

For a lower Pd loading, 4.8 mg SUM-1-pz and 1.0 mg $PdCl_2(CH_3CN)_2$ were mixed in a 4 mL glass vial with 1 mL acetonitrile and stirred at room temperature for 2 h. The mixture was filtered, washed with acetonitrile (3 × 20 mL), and dried in vacuo at room temperature. The product is named SUM-1-pz-Pd-2 and characterized in Section 4.

3. Crystal structure of SUM-1-pz

Table S1 Crystal data and structure refinement details for SUM-1-pz

CCDC deposition number	2374114
Compound name	SUM-1-pz
Formula	$C_{33}H_{57}N_{15}O_{15}Zr$
Formula weight	995.136
Temperature/K	193.15
Crystal system	hexagonal
Space group	*P6/mcc*
a/Å	22.8945(4)
b/Å	22.8945(4)
c/Å	16.5284(5)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	7502.8(3)
Z	6
ρ_{calc} g/cm^3	1.321
μ/mm-1	1.611
F(000)	3126.4
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
Theta range for data collection /°	3.88 to 120.76
Index ranges	-27 ≤ h ≤ 29, -28 ≤ k ≤ 26, -19 ≤ l ≤ 21
Reflections collected	55736
Independent reflections	2947 [R_{int} = 0.0735, R_{sigma} = 0.0274]
Data / restraints / parameters	2947/24/67
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1493
R indices (all data)	R_1 = 0.0541, wR_2 = 0.1567
Largest diff. peak and hole /e Å^{-3}	0.60/-0.71

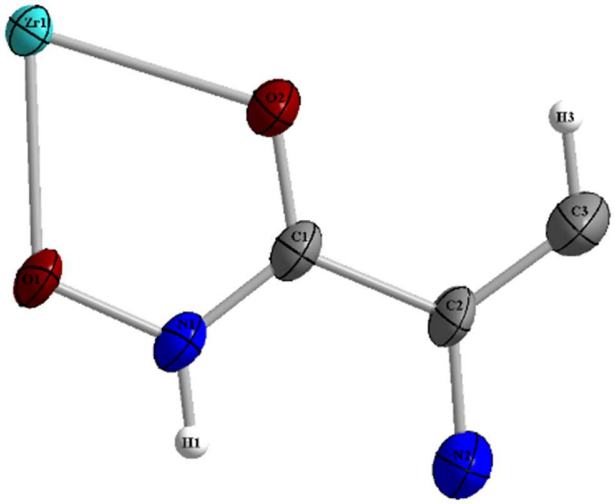

Fig. S5 ORTEP diagram of the asymmetric unit of SUM-1-pz (50% probability factor for the thermal ellipsoids), generated in Diamond 3.2k.

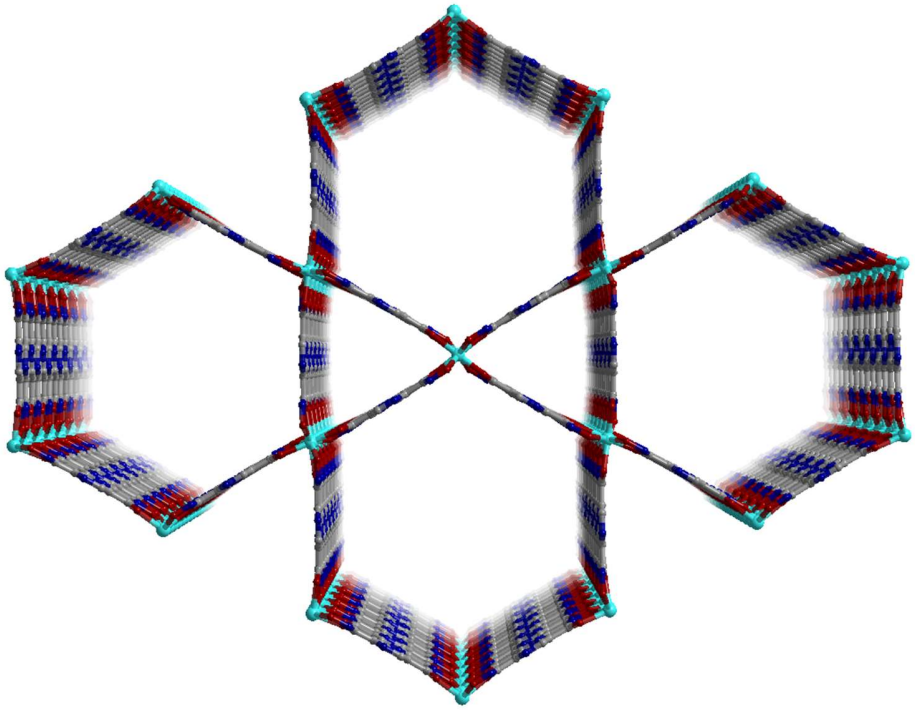

Fig. S6 Crystal structure of SUM-1-pz, in packed mode, viewed along the *c* axis. Zr: aqua spheres; C: gray spheres; N: blue spheres; O: red spheres; H: omitted for clarity.

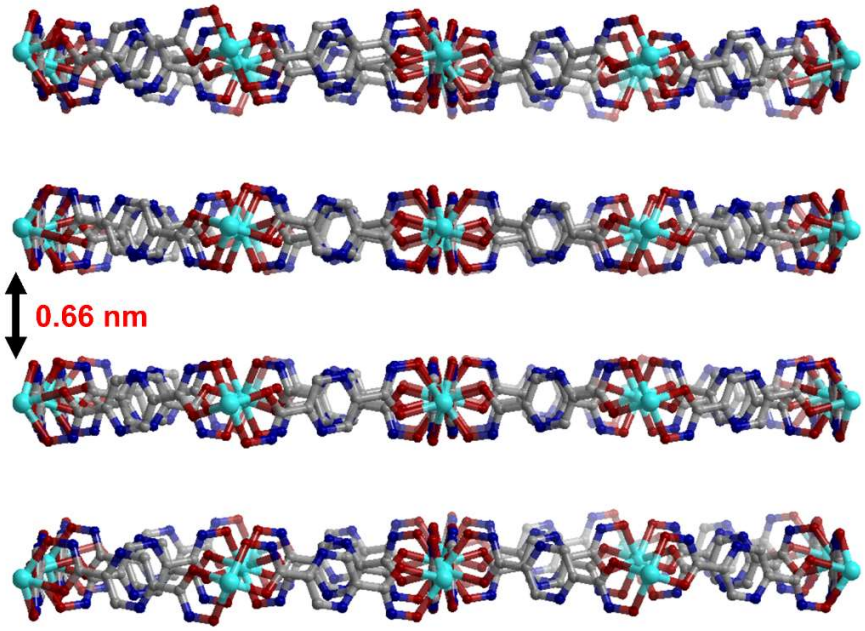

Fig. S7 Crystal structure of SUM-1-pz, in packed mode, viewed along the *a* axis. Zr: aqua spheres; C: gray spheres; N: blue spheres; O: red spheres; H: omitted for clarity.

4. Characterization of SUM-1-pz and metalated products

4.1 Stability of SUM-1-pz in aqueous solutions with varied pH

For SUM-1-pz, as-synthesized MOFs were washed with dry DMF (3×), then washed (3×) and soaked for 24 hours in aqueous solutions with corresponding pH values. Solutions with different pH were obtained by adding HCl or NaOH to deionized water. After 24 hours, the samples were examined with PXRD.

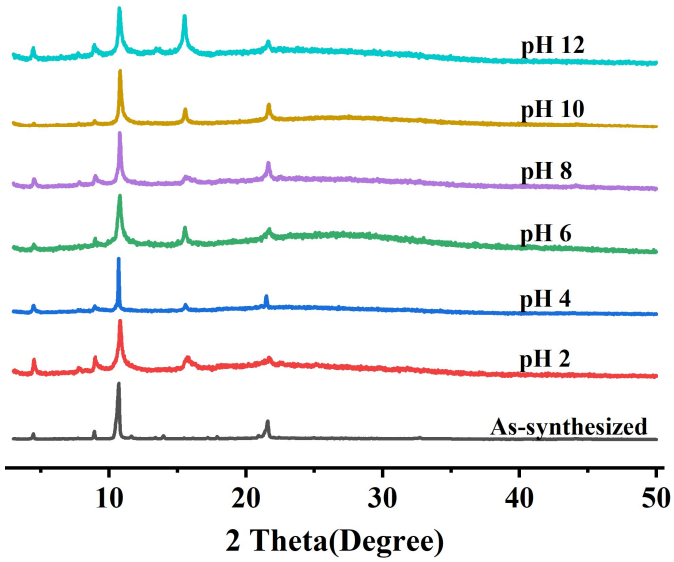

Fig. S8 PXRD patterns of SUM-1-pz after soaking in aqueous solutions of indicated pH values for 24 hours, comparing to that of an as-synthesized sample (black).

4.2 Stability of SUM-1-pz in various organic solvents

For SUM-1-pz, as-synthesized MOFs were washed with dry DMF (3×), then washed (3×) and soaked for 24 hours in various organic solvents. After 24 hours, the samples were examined with PXRD.

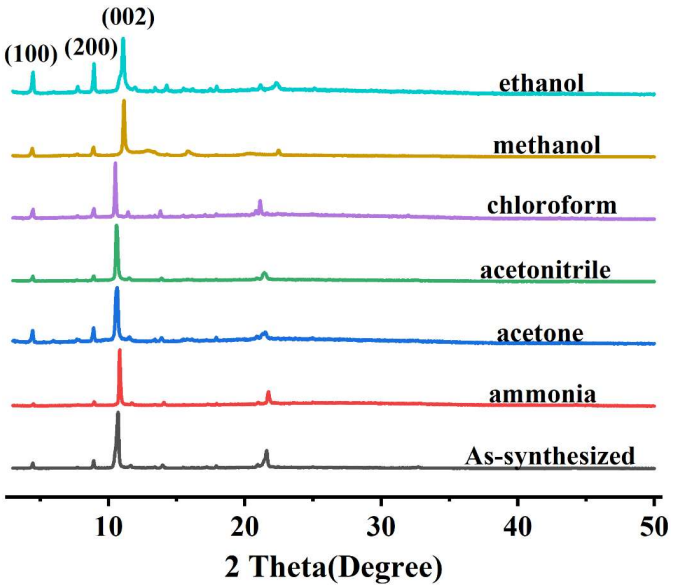

Fig. S9 PXRD patterns of SUM-1-pz after soaking in various organic solvents for 24 hours, comparing to that of an as-synthesized sample (black).

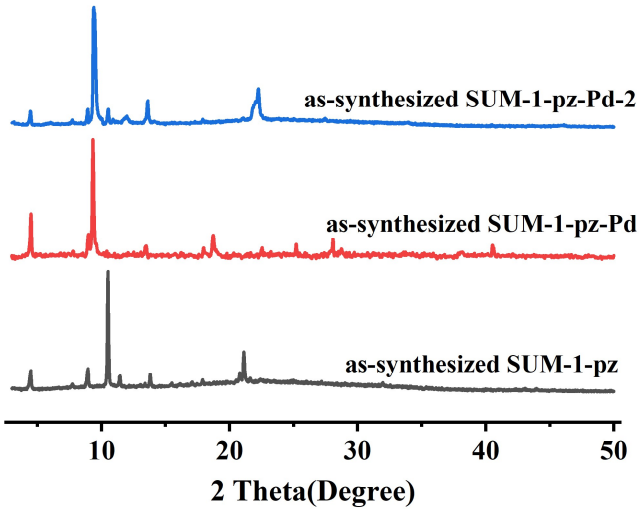

Fig. S10 PXRD patterns of metalated MOFs with different Pd loadings: SUM-1-pz-Pd (red) and SUM-1-pz-Pd-2 (blue), comparing with that of SUM-1-pz (black).

4.3 ICP-MS results of SUM-1-pz-Pd and SUM-1-pz-Pd-2

For ICP-MS, SUM-1-pz-Pd or SUM-1-pz-Pd-2 was washed with dry DMF (3×) and acetone (3×) before digested in HCl/HNO_3 (v/v 1:1) at 100 °C.

Table S2 ICP-MS of SUM-1-pz-Pd

Sample volume（mL）	Constant volume (mL)	Test Elements	concentration（mg/L）	Dilution ratio (f)	Original sample concentration (mg/L)
1	10	Pd	1.944	10	19.44
1	10	Zr	2.243	10	22.43

Table S3 ICP-MS of SUM-1-pz-Pd-2

Sample volume（μL）	Constant volume (mL)	Test Elements	concentration（μg/L）	Dilution ratio (f)	Original sample concentration (mg/L)
25	25	Pd	6.057	1000	6.057
25	25	Zr	64.96	1000	64.96

Table S4 Summary of Pd loading and catalytic yields in various MOF-based catalysts

Catalyst	Pd (wt%)	Yield (%[a])	Ref.
Pd:$[Cu_2L_2(MeOH)_2]_4NO_3·4H_2O$	11	93	3
Pd–$ZnLCl_2·8H_2O$	7.8	96	4
IRMOF-3-PI-Pd	2.6	100[b]	5
UiO-67-Pdbpydc$_{0.5}$/bpdc$_{0.5}$	12	/	6
Pd^{2+}@UiO-67	1.1	88	7
Pd^{2+}/AZC	0.5	/	8
MIL-53-NH_2(Al)–Mal–Pd	2.1~2.4	/	9
Pd-CP1	7.84	/	10
Pd/MIL-101(Cr)	0.56	/	11
MIL-53(Al)-NH_2	0.97	/	11
SUM-1-pz-Pd	**14**	>99	**This work**

[a] Isolated yield based on aryl bromide to generate 4-methylbiphenyl
[b] The product was biphenyl

4.4 SEM of SUM-1-pz and SUM-1-pz-Pd

Corresponding MOF samples were washed with DMF (3×) and DCM (3×), dried at 100 ºC overnight before imaging.

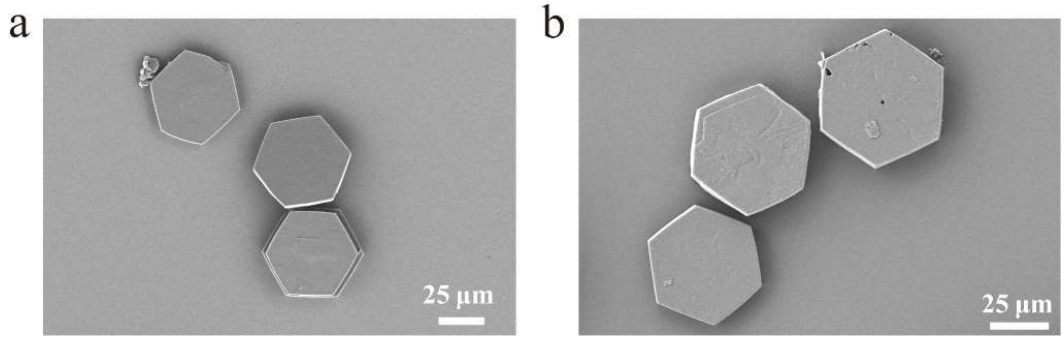

Fig. S11 SEM images of (a) SUM-1-pz and (b) SUM-1-pz-Pd.

4.5 EDX of SUM-1-pz-Pd

SUM-1-pz-Pd was washed with DMF (3×) and DCM (3×), dried at 100 ºC overnight before analysis.

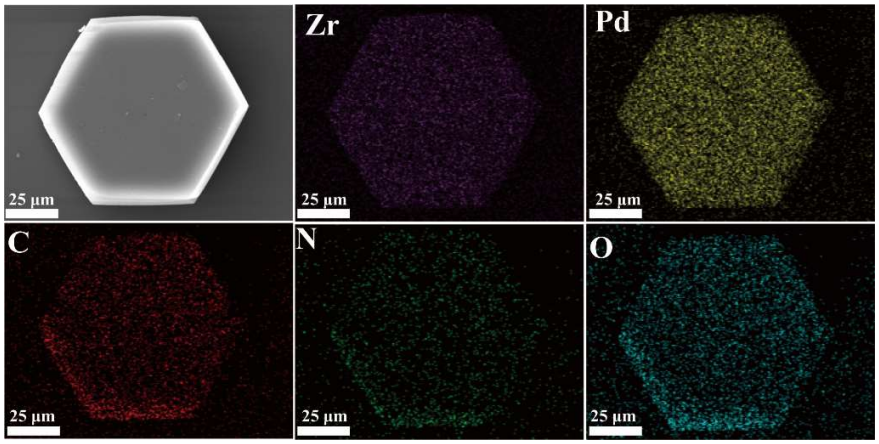

Fig. S12 EDX elemental mapping of SUM-1-pz-Pd.

4.6 EDX of SUM-1-Pd

SUM-1 was prepared according to our original report[12] and treated under the metalation condition described in section 2.4, then washed with DMF (3×) and DCM (3×), dried at 100 ºC overnight before analysis.

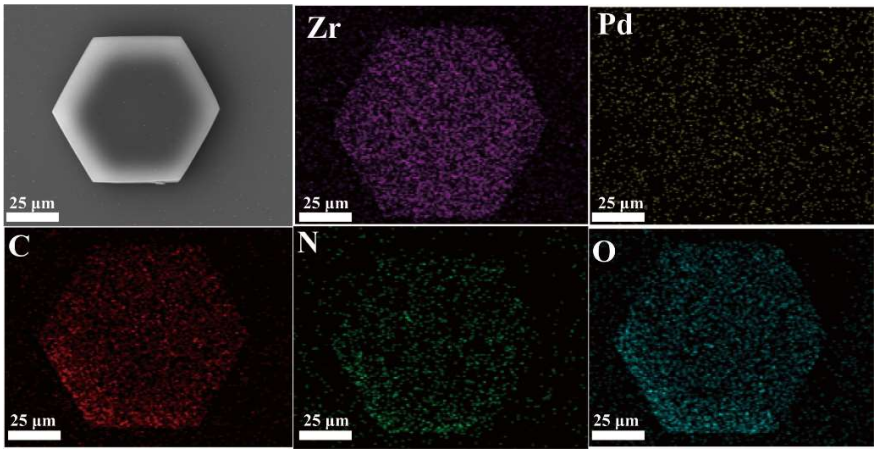

Fig. S13 EDX elemental mapping of SUM-1-Pd

4.7 N_2 sorption of SUM-1-pz and SUM-1-pz-Pd

The same activation procedure was performed on both SUM-1-pz and SUM-1-pz-Pd: as-synthesized MOFs were washed with dry DMF (3×) and exchanged with acetone (3×) for 72 h, followed by activation at 100 ºC for 12 h on the degas station of BELSORP MAX. After N_2 adsorption-desorption isotherms (Fig. S14-S15) were acquired at 77 K, pore size distribution was estimated by applying the non-local density functional theory (NLDFT) on the adsorption data points using a cylindrical pore metal oxide model, as shown in Fig. S16-S17.

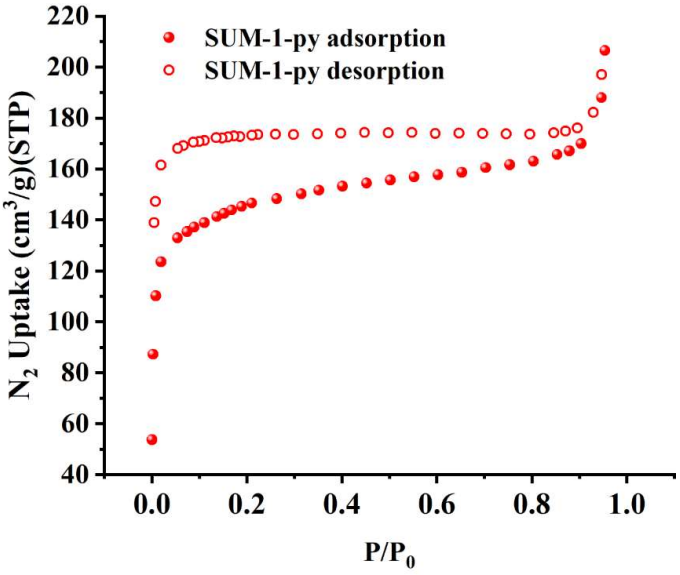

Fig. S14 N_2 adsorption-desorption isotherms of SUM-1-pz at 77 K.

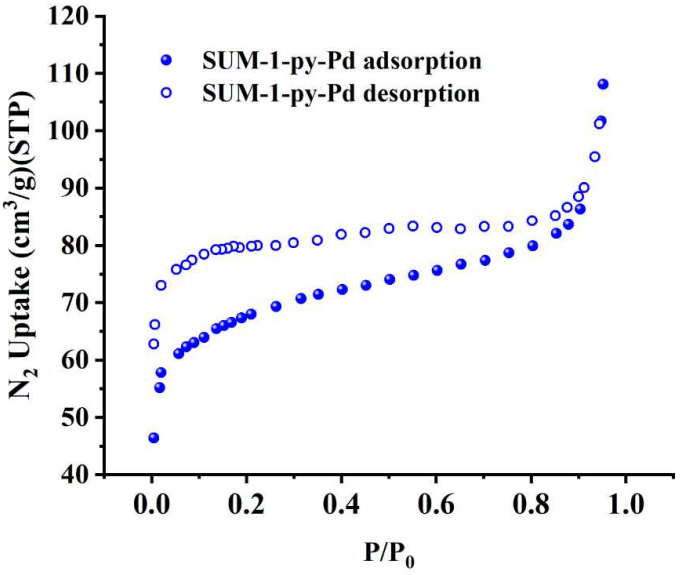

Fig. S15 N_2 adsorption-desorption isotherms of SUM-1-pz-Pd at 77 K.

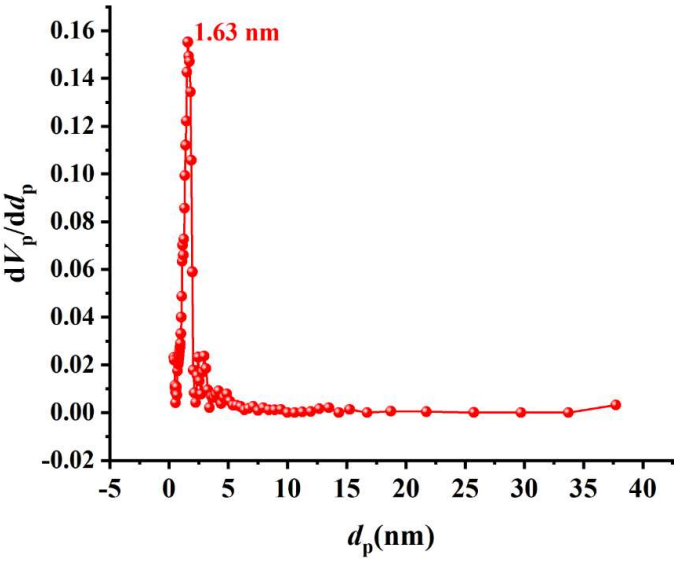

Fig. S16 Pore size distribution plot of SUM-1-pz.

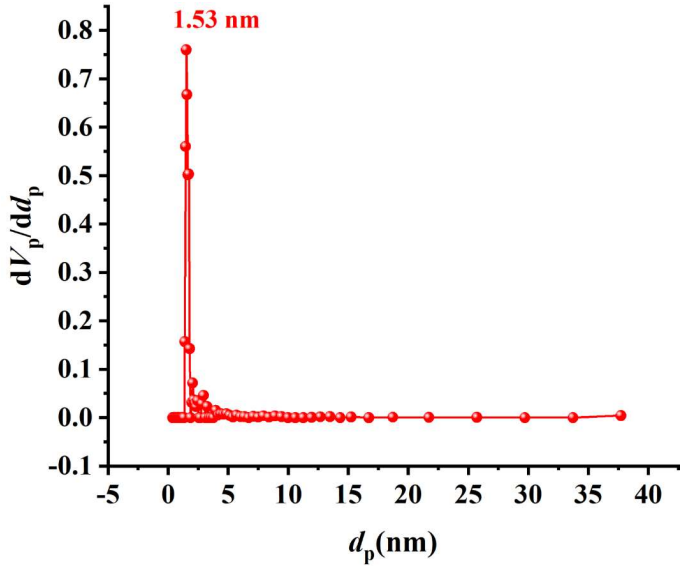

Fig. S17 Pore size distribution plot of SUM-1-pz-Pd.

4.8 Thermogravimetric analysis (TGA) of SUM-1-pz and SUM-1-pz-Pd

For TGA, the as-synthesized MOF crystals were washed with dry DMF (3×), DCM (3×) and dried with N_2 until they became free-flowing solids, and then loaded into a ceramic pan for analysis.

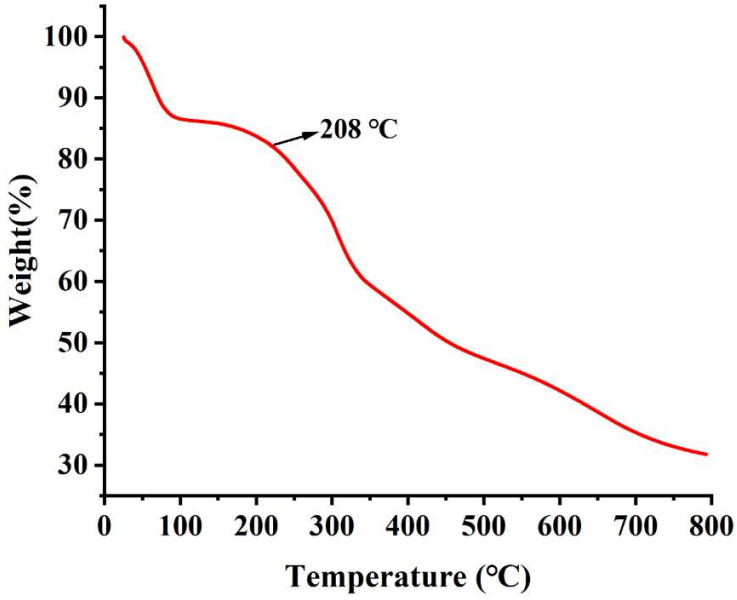

Fig. S18 TGA profile of SUM-1-pz.

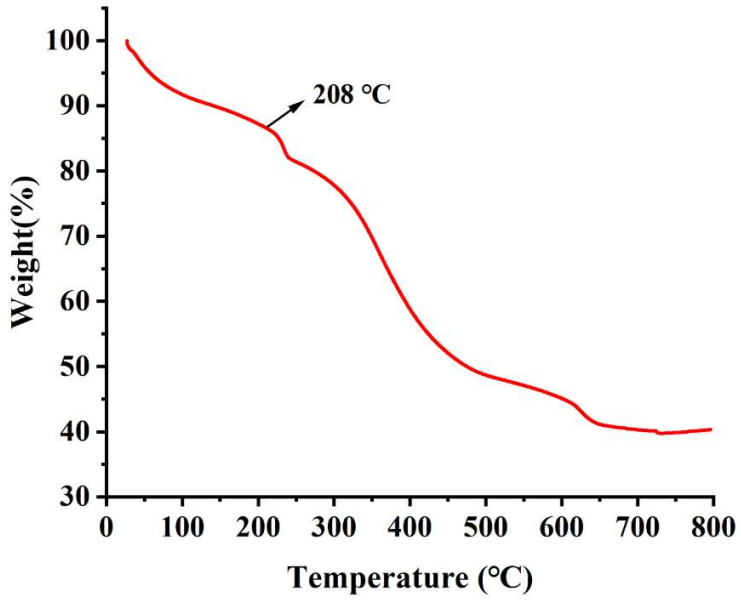

Fig. S19 TGA profile of SUM-1-pz-Pd.

4.9 XPS of $PdCl_2(CH_3CN)_2$, SUM-1-pz, and SUM-1-pz-Pd

As-synthesized MOF samples were washed with DMF (3×) and DCM (3×), dried at 100 ºC overnight before XPS. $PdCl_2(CH_3CN)_2$ was directly tested.

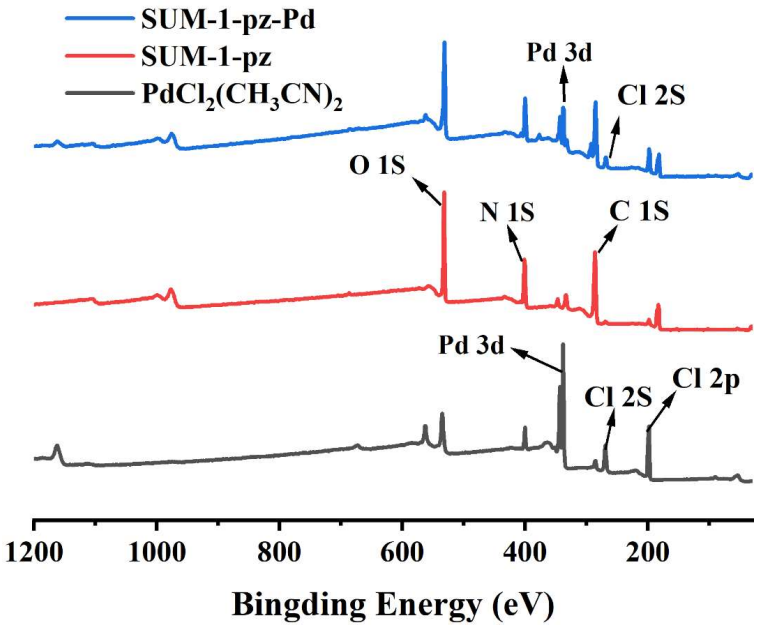

Fig. S20 XPS survey of $PdCl_2(CH_3CN)_2$ (black), SUM-1-pz (red) and SUM-1-pz-Pd (blue).

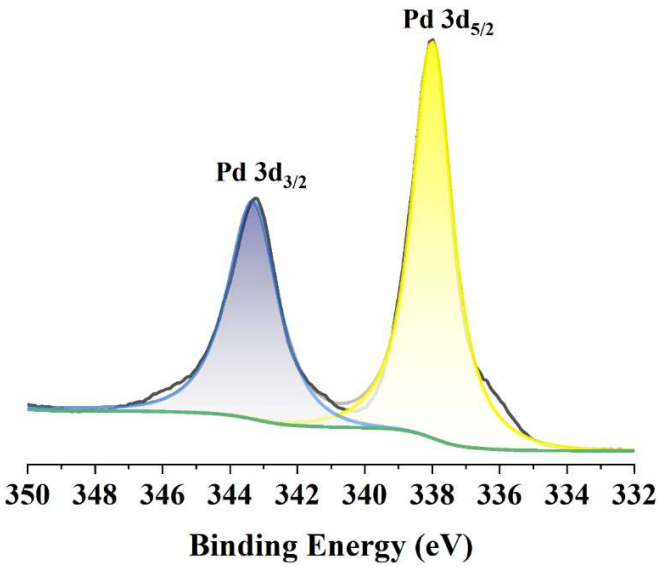

Fig. S21 Pd 3d high-resolution XPS spectrum of $PdCl_2(CH_3CN)_2$.

4.10 XAFS of SUM-1-pz-Pd

SUM-1-pz-Pd crystals were washed with DMF (3×) and DCM (3×), dried at 100 ºC overnight before XAFS.

Table S5 EXAFS fitting parameters at the Pd K-edge for SUM-1-pz-Pd (S_0^2 = 915)

Sample	Shell	CN[a]	R(Å)[b]	σ^2 (Å^2·10^{-3})[c]	ΔE_0 (eV)[d]	R factor (%)
SUM-1-pz-Pd	Pd-N	2.05±0.75	2.24±0.03	0.019±0.003	6.95± 2.54	1.09
	Pd-Cl	1.83±0.59	2.35±0.05	0.009±0.001		

[a] CN = coordination number;

[b] R = distance between absorber and backscatter atoms;

[c] σ^2 = Debye-Waller factor to account for both thermal and structural disorders;

[d] ΔE_0 = inner potential correction;

R factor indicates the goodness of the fit. Fitting range: 2.0 < k (/Å) < 10.0 and 1.0 < R (Å)< 3.0 (SUM-1-pz-Pd).

5. Suzuki-Miyaura cross-coupling reactions

5.1 Catalytic experiments

Aryl bromide (1 mmol) and phenylboronic acid (1.1 mmol) were dissolved in 0.5 mL of ethanol. With continuous stirring, a solution of K_2CO_3 (1 mmol) in water (0.5 mL) was added. SUM-1-pz-Pd (2 mg) was added last to the reaction mixture at room temperature or at 80 ºC (Table 1 of the main text). At the end of the catalytic reaction, the MOF catalyst was collected by centrifugation. The supernatant was extracted with dichloromethane (4 × 15 mL). The combined organic phase was successively washed with water and brine, before dried over Na_2SO_4. The crude product was obtained from filtration and concentration in vacuo, before purified by column chromatography using a mixture of n-hexane and ethyl acetate as eluent. The isolated Suzuki-Miyaura product was weighed to calculate the yield and analysed using ^{1}H NMR (Fig. S22-S28). All the products were known compounds and have been previously reported in the literature. Therefore, the ^{1}H NMR spectra of the products in the present work were compared to references to confirm the consistency.

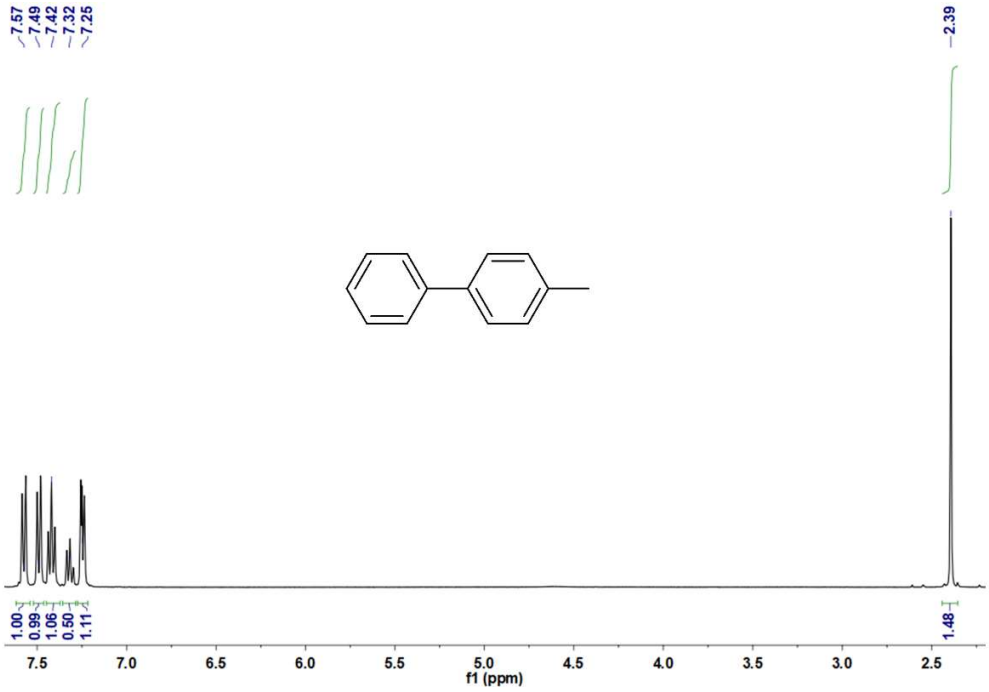

Fig. S22 ^{1}H NMR spectrum of 4-methyl biphenyl in $CDCl_3$.

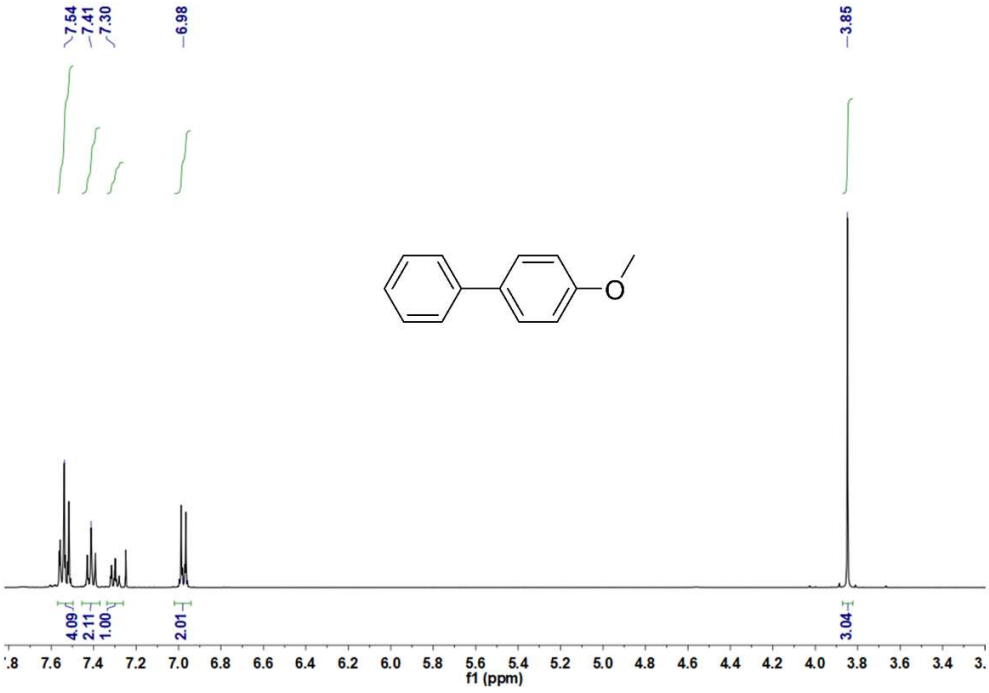

Fig. S23 ^{1}H NMR spectrum of 4-methoxy biphenyl in $CDCl_3$.

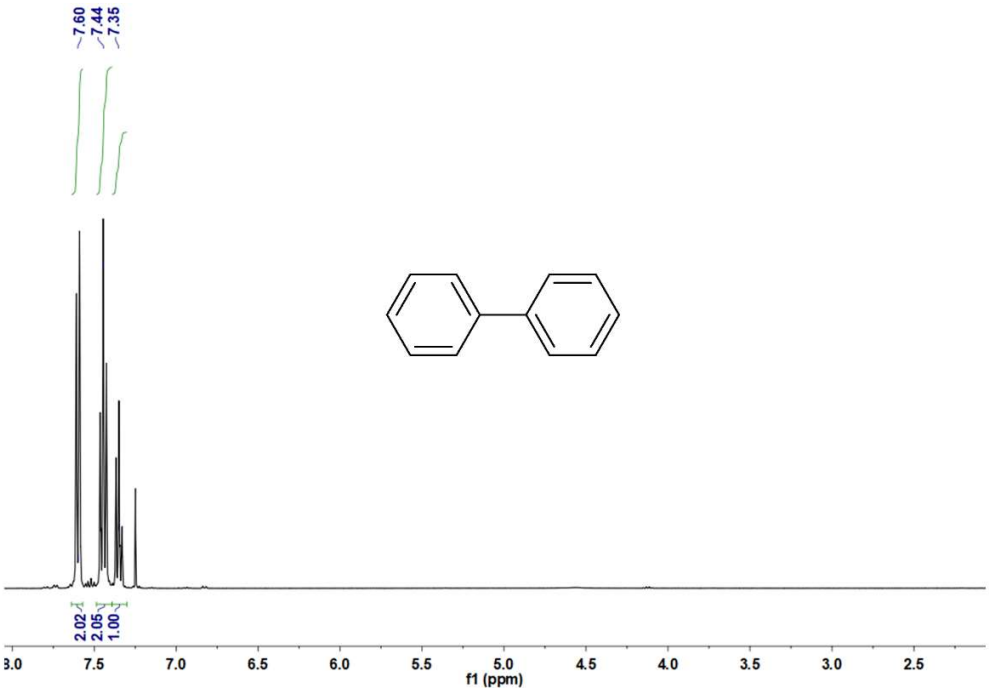

Fig. S24 ^{1}H NMR spectrum of biphenyl in $CDCl_3$.

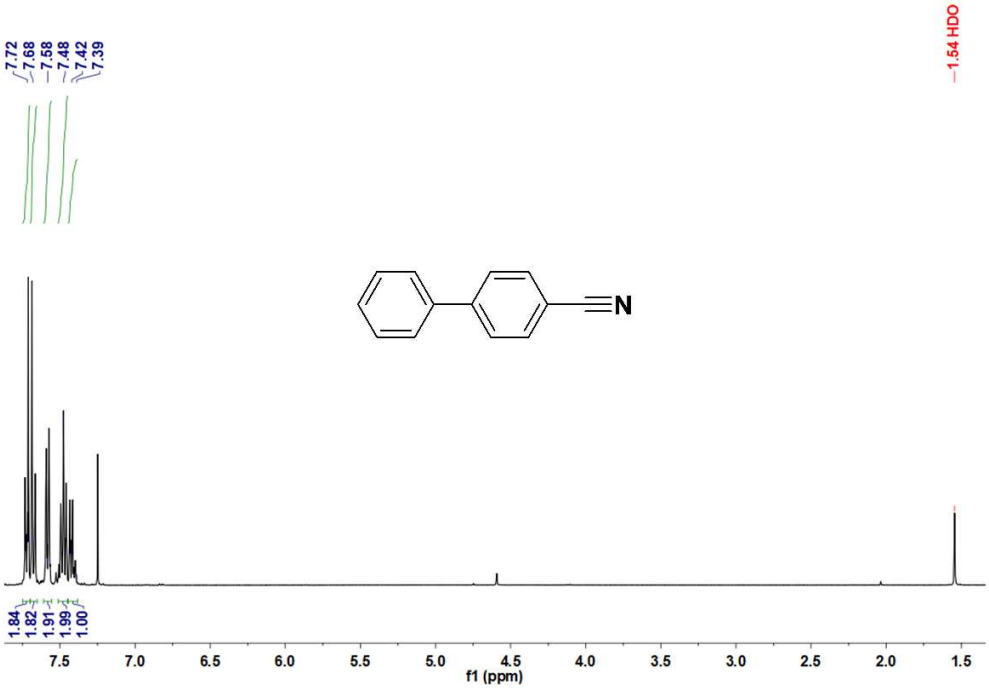

Fig. S25 ^{1}H NMR spectrum of 4-cyano biphenyl in $CDCl_3$.

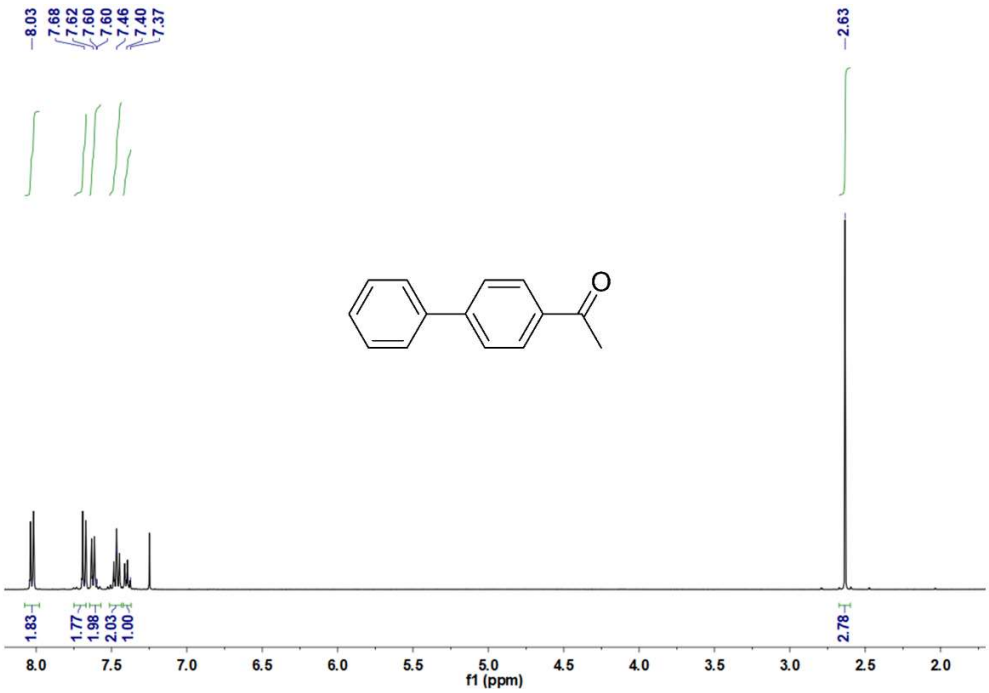

Fig. S26 ^{1}H NMR spectrum of 4-acetyl biphenyl in $CDCl_3$.

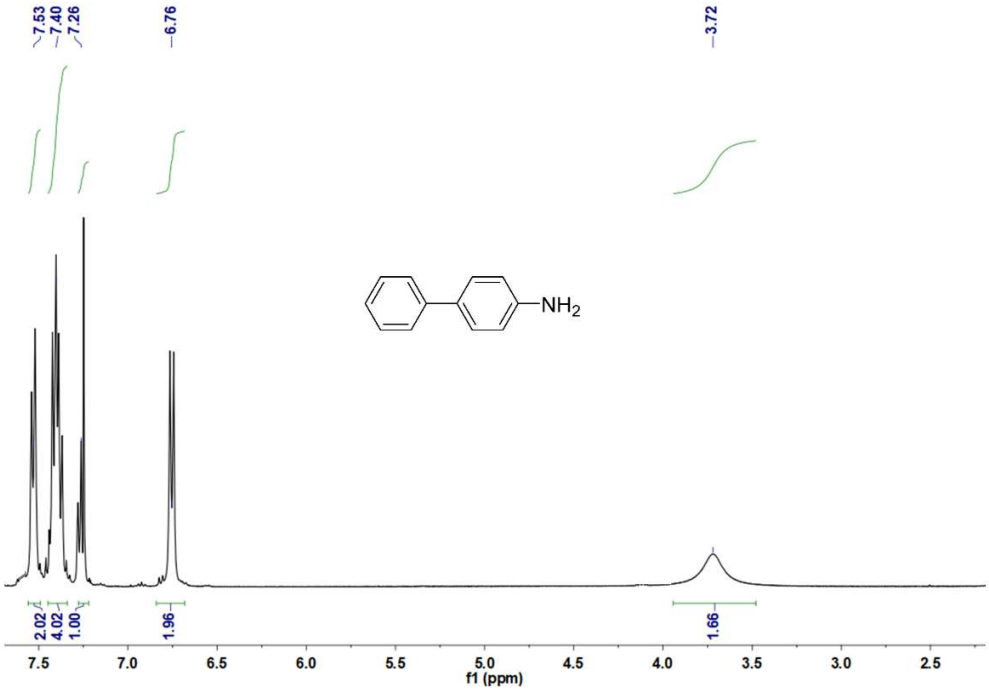

Fig. S27 ^{1}H NMR spectrum of 4-phenyl aniline in $CDCl_3$.

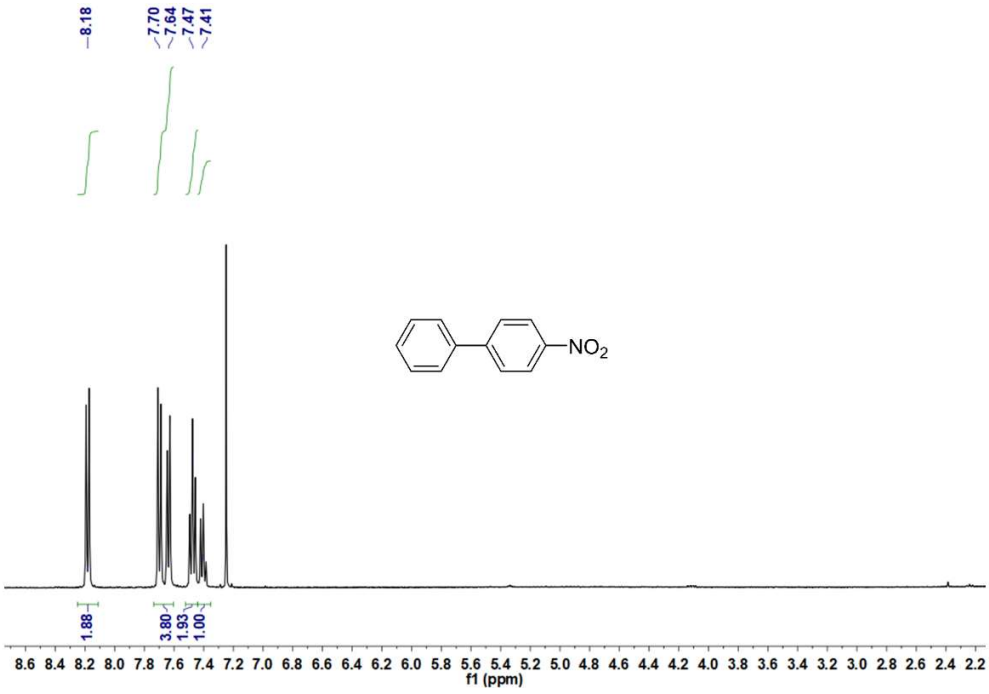

Fig. S28 ^{1}H NMR spectrum of 4-nitro biphenyl in $CDCl_3$.

To assess the catalytic performance of a lowered Pd loading, SUM-1-pz-Pd-2 was used to replace SUM-1-pz-Pd in the protocol described in the beginning of this section.

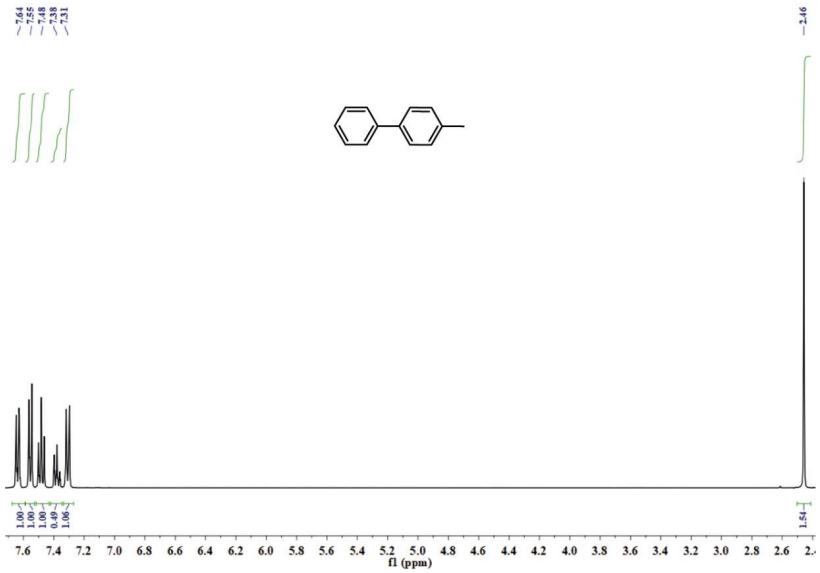

Fig. S29 ^{1}H NMR spectrum of 4-methylbiphenyl (catalyzed by SUM-1-pz-Pd-2) in $CDCl_3$.

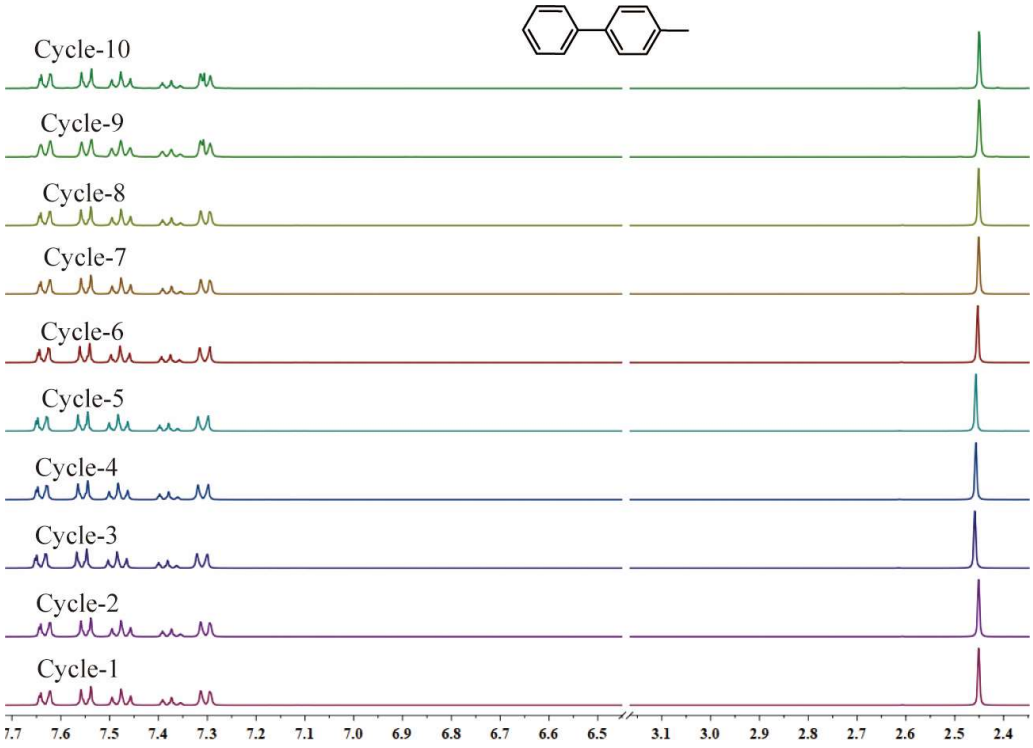

Fig. S30 ^{1}H NMR spectra of the catalytic product 4-methylbiphenyl in $CDCl_3$ after 1-10 cycles, using SUM-1-pz-Pd as the catalyst.

5.2 Suzuki-Miyaura catalytic cycling stability

To determine the recyclability, the catalyst (SUM-1-pz-Pd) was recovered after each run of reaction through centrifugation and decantation of the clear supernatant. The recovered catalyst was washed thoroughly with deionized water and ethanol, followed by vacuum drying at 80 ℃ overnight. Then, the catalyst was reused with a fresh charge of reactant for a subsequent cycle under the identical reaction condition.

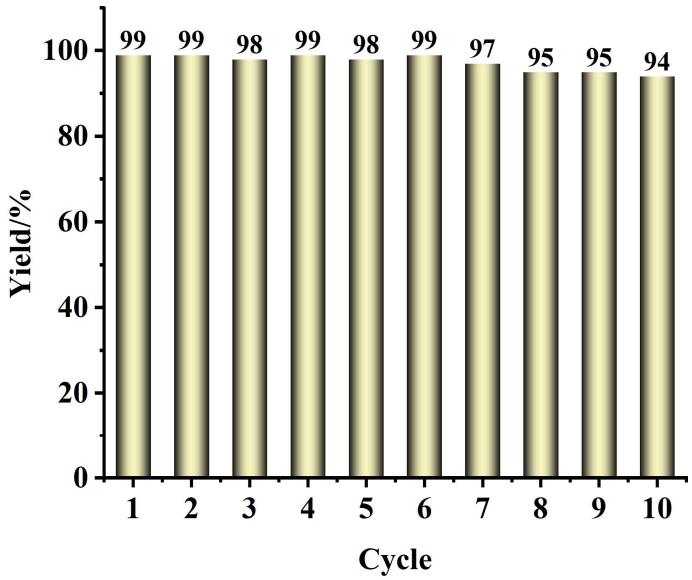

Fig. S31 Catalytic cycling stability of SUM-1-pz-Pd.

Table S6 ICP-MS analysis of Pd in the supernatant after catalytic reaction

Sample volume (mL)	Constant volume (mL)	Test Element	concentration (mg/L)	Dilution ratio (f)	Original sample concentration (mg/L)
1	10	Pd	0.0265	10	0.2649

Table S7 ICP-MS analysis of SUM-1-pz-Pd after 10 catalytic cycles

Sample volume (μL)	Constant volume (mL)	Test Elements	concentration (μg/L)	Dilution ratio (f)	Original sample concentration (mg/L)
25	25	Pd	68.93	1000	68.93
25	25	Zr	82.15	1000	82.15

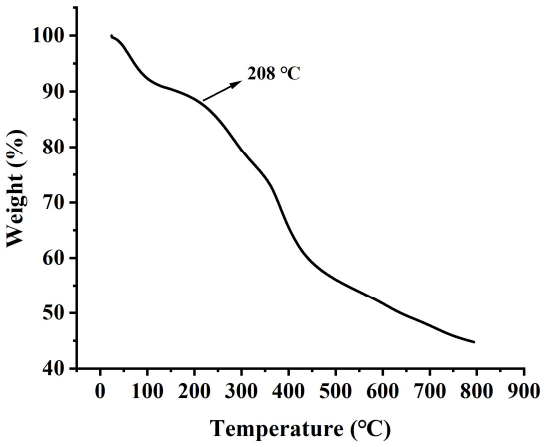

Fig. S32 TGA profile of SUM-1-pz-Pd after catalysis.

5.3 Mechanistic calculation of Suzuki-Miyaura catalysis

Kohn–Sham density functional theory (DFT)[13] calculations were performed using the Gaussian 16 program.[14] In this work, the hybrid functional B3LYP[15] was used for geometry optimization and harmonic frequency calculations on the mononuclear and dinuclear species of SUM-1-pz/SUM-1-pz-Pd system in the gas phase. The calculated vibrational frequencies are positive confirming that the fully optimized structures were stationary points on the potential energy surface, and the corresponding thermochemistry corrections to the free energy were obtained. A mixed basis sets of SDD[16] and 6-311++G**[17] were considered for the Pd atom and all other atoms, respectively. Grimme's dispersion correction D3(BJ) was also included to consider the non-covalent interactions during optimizations.[18]

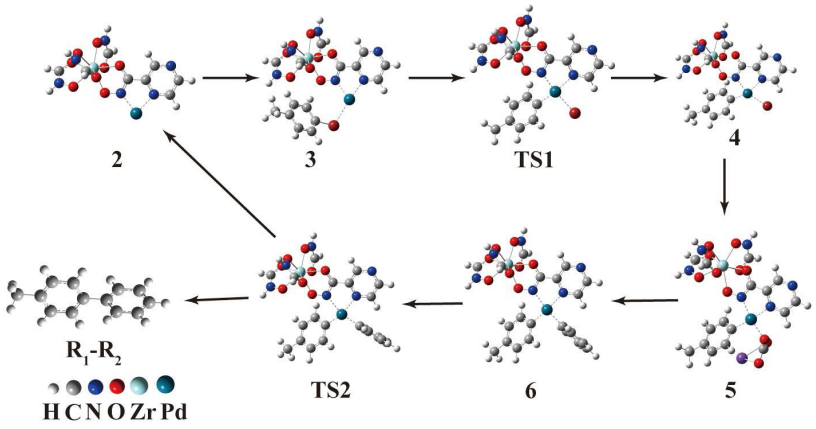

Fig. S33 Molecular models used in the catalytic process, after DFT/B3LYP optimization.

Table S8 Cartesian coordinates (in Å) of DFT/B3LYP optimized geometry for all molecular models involved in the catalytic reactions

2				**R_1-Br**			
O	-1.05610000	0.51229800	-2.16284500	C	0.36090100	1.21415300	-0.00425600
O	-2.25933800	2.20976000	-0.53289700	C	1.75643200	1.20107800	-0.01035100
N	-1.83631200	2.57528500	-1.76658000	C	2.47609000	0.00018500	-0.01021000
H	-2.03698900	3.52998600	-2.03844600	C	1.75643300	-1.20087600	-0.01035800
C	-1.25149300	1.69641200	-2.55197600	C	0.36103900	-1.21401000	-0.00425000
O	-1.10050500	-0.34374800	2.17135400	C	-0.31649400	0.00010800	-0.00024300
O	-3.28432400	0.82821600	1.40628100	H	-0.18405700	2.15127000	-0.00674800
N	-3.15970200	0.34971900	2.66800400	H	2.29218000	2.14697800	-0.01701800
H	-3.90725600	0.58323500	3.31017300	H	2.29225600	-2.14675400	-0.01705500
C	-2.01541500	-0.20109200	3.02177200	H	-0.18394500	-2.15111400	-0.00673400
N	4.05237000	2.82732500	0.73659800	Br	-2.27555300	-0.00005800	0.00308800
C	5.07193200	1.97640600	0.55242700	C	3.98514200	-0.00015400	0.01549200
C	4.86551900	0.63479200	0.23556400	H	4.36294500	-0.01353200	1.04642700
H	5.69264900	-0.05229300	0.08849200	H	4.39387700	-0.88002100	-0.49227300
O	0.18512800	1.22161200	0.29428000	H	4.39385800	0.89232100	-0.46962100
O	-0.12167600	-1.29523400	-0.28022900				
N	1.10819500	-0.81435400	-0.16375300				
N	3.62964800	0.14169200	0.09973400				
C	2.58176400	0.98391600	0.28041500				
C	1.21985200	0.46423800	0.13655100				
C	2.82378900	2.33145300	0.60194800				
H	1.97827600	2.99595600	0.74833800				
O	-3.60600600	-0.09811100	-1.36386700				
O	-2.63536500	-1.81408400	0.31684100				
N	-3.85331100	-2.00650900	-0.24154300				
H	-4.29633400	-2.89811800	-0.05490500				
C	-4.28818300	-1.12729700	-1.12107900				
Zr	-1.75804200	0.16482600	0.00965200				
H	6.07873400	2.37083400	0.65985000				
H	-0.94601200	2.04535700	-3.54315100				
H	-5.24540100	-1.33267500	-1.60931600				
H	-1.91136600	-0.51902600	4.06350400				
Pd	2.87626200	-1.85102200	-0.37093300				

3				TS1			
O	-2.72486900	0.96720300	-2.08224600	O	1.85323200	-0.08401100	-2.05221900
O	-4.20562300	1.07117900	0.09632500	O	3.89006900	-1.50365800	-1.22851800
N	-4.46044000	1.85304500	-0.97887700	N	3.48566600	-1.53424600	-2.52144300
H	-5.26463200	2.46401500	-0.90289300	H	4.02775100	-2.12512100	-3.14046100
C	-3.70454300	1.76398500	-2.05142900	C	2.45498200	-0.81011000	-2.89543000
O	-0.94808000	-0.66193800	1.64665500	O	2.25566900	-0.55215800	2.19939100
O	-3.52090300	-0.99340300	1.55458200	O	4.58894500	-0.61920500	1.11037800
N	-2.78910000	-1.51001000	2.57142300	N	4.46245100	-0.65088500	2.46030700
H	-3.31482100	-1.92046700	3.33369100	H	5.31645100	-0.79873200	2.98457600
C	-1.48983200	-1.28313400	2.59337900	C	3.24867500	-0.64884600	2.97014100
N	0.52342100	5.14466500	1.98458700	N	-1.46138900	-5.09070900	0.01536200
C	1.83940300	5.16083700	1.72929100	C	-2.73203600	-4.67508800	0.04114000
C	2.46750900	4.14096500	1.01651700	C	-3.08255200	-3.31946800	0.07845400
H	3.53446400	4.15068500	0.81996500	H	-4.10888600	-2.96468000	0.09016900
O	-1.59508800	1.79263500	0.52300800	O	1.40562600	-1.96962900	0.04253800
O	-0.37998600	0.04242100	-0.92377500	O	0.62896600	0.46138100	0.23816200
N	0.33471500	1.07611100	-0.47182000	N	-0.29887100	-0.42904200	0.17096300
N	1.77123500	3.09888500	0.54684600	N	-2.13436600	-2.38463400	0.09336600
C	0.43565100	3.06820800	0.78273200	C	-0.84585400	-2.78393500	0.06965900
C	-0.33187300	1.93501600	0.26582200	C	0.17541600	-1.72430300	0.09256200
C	-0.16546800	4.10543400	1.51504700	C	-0.51949500	-4.14173400	0.02933700
H	-1.23229600	4.06179100	1.71011500	H	0.52057000	-4.45309800	0.00970800
O	-4.07694300	-1.30836700	-1.31019900	O	4.09701500	1.27620200	-1.22630200
O	-1.74365500	-2.18253200	-0.59680500	O	2.83034900	1.83516500	0.92591300
N	-2.66685000	-3.02444600	-1.12473100	N	3.58790300	2.78031500	0.32624800
H	-2.34362000	-3.95719600	-1.35167300	H	3.54343800	3.70998000	0.72663400
C	-3.82399400	-2.52060500	-1.51086100	C	4.20604200	2.45553900	-0.78772400
Zr	-2.41842000	-0.15595900	-0.11182500	Zr	2.80694700	-0.12323500	0.02649400
H	2.41131300	6.00490600	2.10518400	H	-3.50304900	-5.44088300	0.03006100
H	-3.96133700	2.40853900	-2.89695600	H	2.14878000	-0.86569900	-3.94255000
H	-4.53079100	-3.20432900	-1.99191900	H	4.79628800	3.22198200	-1.29413600
H	-0.92807200	-1.66379600	3.45240300	H	3.14673700	-0.73466500	4.05420700
Pd	2.43816300	1.35476900	-0.49551300	Pd	-2.31047700	-0.18733100	0.07509600
C	1.90434400	-4.10898100	1.38170100	C	-1.90571800	4.60897400	-0.07753800
C	3.28531300	-3.94763800	1.19771000	C	-2.72651500	3.99971600	0.87585400
C	3.79159600	-2.96820600	0.34156400	C	-2.88525900	2.61023700	0.91938800

C	2.87630000	-2.15970400	-0.31967600	C	-2.20082000	1.80041300	0.01127000
C	1.50537300	-2.26810600	-0.17380100	C	-1.37243800	2.39614300	-0.94762900
C	1.03355000	-3.26019400	0.69096300	C	-1.23583500	3.78441200	-0.99139900
H	3.98032800	-4.59171800	1.73085700	H	-3.26595300	4.61836300	1.59039700
H	4.85994400	-2.84148200	0.20626400	H	-3.55292300	2.17041500	1.65256500
H	0.80609400	-1.59844900	-0.66668900	H	-0.81826800	1.78616600	-1.65481200
H	-0.04236500	-3.34162400	0.81045000	H	-0.59572500	4.23262000	-1.75003100
C	1.37275100	-5.18974800	2.29226800	C	-1.74423600	6.11007800	-0.12868500
H	1.36991000	-6.16611500	1.79009600	H	-2.01171300	6.51031700	-1.11471200
H	1.98468300	-5.29258700	3.19517800	H	-2.37945100	6.60362000	0.61394600
H	0.34398800	-4.97723700	2.60048500	H	-0.70729400	6.41234800	0.06929100
Br	3.58578100	-0.76314400	-1.54679100	Br	-4.78421600	-0.16847900	-0.08239400
4				**5**			
O	-1.84925900	-0.08048200	2.05102500	O	1.92131400	0.04571300	-2.14409600
O	-3.89271500	-1.49434300	1.23441000	O	4.32836100	-0.69060500	-1.35681300
N	-3.48677600	-1.52265400	2.52695400	N	3.83130800	-1.04413900	-2.56621800
H	-4.03034600	-2.10958000	3.14840900	H	4.44939200	-1.58676100	-3.15722900
C	-2.45261900	-0.80155800	2.89726300	C	2.62920000	-0.64885700	-2.92537000
O	-2.25926200	-0.55788700	-2.19881600	O	2.86768400	-0.01594200	2.14342200
O	-4.59110200	-0.61961100	-1.10609400	O	4.92109300	0.72242100	0.75301300
N	-4.46664500	-0.65384200	-2.45615800	N	4.95745400	0.75402500	2.10708600
H	-5.32161200	-0.80150900	-2.97889300	H	5.85586500	0.96185500	2.52607500
C	-3.25362600	-0.65457000	-2.96781700	C	3.90146900	0.33011500	2.77184100
N	1.45783300	-5.09268900	-0.00828900	N	0.19894100	-5.45242600	0.23065500
C	2.72863000	-4.67773600	-0.03641300	C	-1.13636000	-5.37913800	0.30552100
C	3.07972700	-3.32233500	-0.07668500	C	-1.81494500	-4.15872300	0.36475200
H	4.10622700	-2.96808700	-0.09027900	H	-2.89560600	-4.07159500	0.41446100
O	-1.40788600	-1.96994700	-0.03910500	O	2.17977900	-1.68752700	0.08519800
O	-0.62932100	0.46013700	-0.24142000	O	0.79802800	0.46820200	0.30662600
N	0.29768700	-0.43083300	-0.17124900	N	0.14295500	-0.68123300	0.36036400
N	2.13198200	-2.38709400	-0.09223300	N	-1.12935100	-3.01663600	0.35031000
C	0.84326800	-2.78573400	-0.06615500	C	0.21706100	-3.06150300	0.27271400
C	-0.17754600	-1.72561700	-0.09017200	C	0.91479500	-1.77066100	0.23963400
C	0.51635000	-4.14328700	-0.02287700	C	0.87053400	-4.29814000	0.21261800
H	-0.52383100	-4.45414100	-0.00136900	H	1.95373200	-4.33350100	0.14944900
O	-4.08588600	1.28836500	1.22489400	O	3.71673300	2.04751300	-1.56429400

O	-2.83001000	1.83226400	-0.93713000
N	-3.57818900	2.78398000	-0.33624700
H	-3.53027200	3.71207300	-0.73992000
C	-4.19123400	2.46680200	0.78262600
Zr	-2.80719200	-0.12143200	-0.02653400
H	3.49930200	-5.44386700	-0.02488000
H	-2.14513900	-0.85522400	3.94412100
H	-4.77423900	3.23819400	1.28985300
H	-3.15351200	-0.74267000	-4.05187100
Pd	2.30893100	-0.18980800	-0.07541300
C	2.19929100	1.79776400	-0.00885300
C	1.37338900	2.39216200	0.94976800
C	2.87910800	2.60875000	-0.92274100
C	1.23382100	3.78247300	0.99096300
H	0.81795800	1.78289100	1.65655500
C	2.71779300	3.99574600	-0.88204500
H	3.54067900	2.16742800	-1.66058900
C	1.90014000	4.60582700	0.07698000
H	0.59238300	4.23100200	1.74788100
H	3.25031400	4.61379000	-1.60271400
C	1.76968400	6.10936300	0.13947400
H	2.63951800	6.56735800	0.62938300
H	1.69708400	6.54905900	-0.86213800
H	0.88148000	6.41045600	0.70572700
Br	4.78303100	-0.16980200	0.07713200

O	2.53265200	2.41007000	0.70753000
N	3.14622600	3.43854300	0.07891200
H	3.02740400	4.35417100	0.49563600
C	3.70500500	3.21548700	-1.09249400
Zr	2.94785600	0.42944400	-0.11091300
H	-1.68493000	-6.31709200	0.31532600
H	2.28156300	-0.95195700	-3.91721000
H	4.14483100	4.06944400	-1.61528900
H	3.96870100	0.29766800	3.86279700
Pd	-1.84140900	-0.98618600	0.41104200
C	-2.30746100	0.95846500	0.50432600
C	-1.71291300	1.89346600	-0.35916900
C	-3.27422100	1.41434800	1.41436500
C	-2.09353000	3.24000800	-0.32582100
H	-0.93290000	1.57717400	-1.04357200
C	-3.63166000	2.77048500	1.46348300
H	-3.77458000	0.71206800	2.07347800
C	-3.04951200	3.70643000	0.59421600
H	-1.61688400	3.94642800	-1.00434800
H	-4.36773600	3.10280200	2.19438200
C	-3.39471200	5.17583700	0.68206200
H	-4.40609600	5.33200300	1.07453200
H	-2.70516700	5.70350100	1.35414300
H	-3.32710500	5.66797200	-0.29532100
O	-3.74086900	-1.61218300	0.30213900
C	-4.62171400	-0.91084000	-0.42759200
O	-4.36804500	-0.74874900	-1.65466900
O	-5.61811700	-0.43013500	0.17373300
K	-5.19619700	1.72656900	-1.36901700

K_2CO_3

C	-0.00017400	0.80896800	0.00027100
O	-1.12733800	1.42636500	0.00044700
O	1.12675900	1.42669300	-0.00061900
O	-0.00003500	-0.53935800	0.00081700
K	2.51396800	-0.61474300	-0.00007800
K	-2.51365400	-0.61491000	-0.00027900

KBr

Br	0.00000000	0.00000000	1.05436300
K	0.00000000	0.00000000	-1.94224800

R_2-B(OH)$_2$				K_2CO_3-KCO_3- B(OH)$_2$			
C	0.54950200	-1.20508900	-0.00007100	B	-0.45985200	-0.88308000	0.74850100
C	1.94333000	-1.20894800	-0.00005400	O	-0.99584200	0.34895200	1.34544200
C	2.64237900	-0.00006100	0.00000300	H	-0.23634800	0.68189600	1.88617000
C	1.94343500	1.20889800	0.00005500	O	-1.22094700	-2.07185100	1.13822600
C	0.54961500	1.20517200	0.00007700	H	-0.96441100	-2.27157200	2.04957000
C	-0.17307100	0.00008200	0.00000200	O	0.97284700	-1.06276900	1.05749900
H	0.00631000	-2.14576400	-0.00011200	O	-0.68672800	-0.86407800	-0.76979600
H	2.48582000	-2.15071700	-0.00010000	C	-0.59353100	0.35095000	-1.42178000
H	3.72938200	-0.00009500	-0.00001400	C	1.86967800	-0.00958900	1.24275300
H	2.48602500	2.15060900	0.00009100	O	3.00330100	-0.18703800	0.75559400
H	0.00650800	2.14590300	0.00012400	O	-1.63598700	1.05790000	-1.48788100
B	-1.73188600	0.00002200	-0.00001400	O	0.55391900	0.67449100	-1.85380200
O	-2.38076900	-1.21276200	0.00012800	O	1.44093000	1.02442600	1.85395500
H	-3.34617600	-1.15385000	0.00013200	K	-3.17272900	-0.41506800	0.10646500
O	-2.38089100	1.21273900	-0.00013600	K	0.36657000	2.56205100	0.01143100
H	-3.34629300	1.15367000	-0.00005500	K	1.98464300	-1.48400100	-1.32410500
6				**TS2**			
O	-2.0882590	0.0704890	2.0527200	O	-2.0823570	0.0662180	2.0522030
O	-4.1442300	-1.3874700	1.3441260	O	-4.1426730	-1.3871920	1.3472100
N	-3.6987840	-1.3688490	2.6233020	N	-3.6945650	-1.3700810	2.6255240
H	-4.2167680	-1.9397560	3.2804930	H	-4.2123590	-1.9402510	3.2834950
C	-2.6608310	-0.6273390	2.9389490	C	-2.6544290	-0.6308060	2.9392940
O	-2.5991350	-0.5526870	-2.1735520	O	-2.6026370	-0.5544780	-2.1733630
O	-4.9017890	-0.5904060	-1.0155110	O	-4.9029880	-0.5918520	-1.0104000
N	-4.8122260	-0.6743560	-2.3662410	N	-4.8163150	-0.6738570	-2.3614570
H	-5.6793680	-0.8461970	-2.8606270	H	-5.6845480	-0.8448390	-2.8542200
C	-3.6130290	-0.6844540	-2.9100470	C	-3.6182380	-0.6844570	-2.9077820
N	1.0759700	-5.0742500	0.1010960	N	1.0782380	-5.0744640	0.0977800
C	2.3557280	-4.6925570	0.0242900	C	2.3578150	-4.6921970	0.0208640
C	2.7380510	-3.3522180	-0.0945200	C	2.7395110	-3.3516640	-0.0977810
H	3.7748210	-3.0365090	-0.1519070	H	3.7761390	-3.0354640	-0.1551000
O	-1.7187010	-1.9112850	0.0143950	O	-1.7178680	-1.9126790	0.0128720
O	-0.9145070	0.4979460	-0.2919270	O	-0.9146900	0.4969810	-0.2943120
N	0.0067880	-0.4035520	-0.2422670	N	0.0068980	-0.4042860	-0.2450930
N	1.8183330	-2.3864340	-0.1398960	N	1.8193550	-2.3862980	-0.1429260

C	0.5199290	-2.7536890	-0.0582720	C	0.5211170	-2.7541250	-0.0611220
C	-0.4856800	-1.6792070	-0.0923000	C	-0.4850100	-1.6800780	-0.0946380
C	0.1620980	-4.0996320	0.0606870	C	0.1639190	-4.1002490	0.0576970
H	-0.8854580	-4.3783950	0.1231950	H	-0.8834990	-4.3794960	0.1203490
O	-4.3701710	1.3806690	1.2378390	O	-4.3608310	1.3829760	1.2423190
O	-3.1247450	1.8753690	-0.9449540	O	-3.1275690	1.8722690	-0.9485400
N	-3.8749600	2.8380930	-0.3637200	N	-3.8730700	2.8369610	-0.3646020
H	-3.8326810	3.7562990	-0.7898340	H	-3.8322240	3.7543810	-0.7925610
C	-4.4810290	2.5462210	0.7663440	C	-4.4730270	2.5479070	0.7693790
Zr	-3.0913400	-0.0589190	0.0047670	Zr	-3.0904730	-0.0602260	0.0059590
H	3.1084800	-5.4757600	0.0606800	H	3.1109230	-5.4750680	0.0570520
H	-2.3229250	-0.6438800	3.9777050	H	-2.3143810	-0.6485080	3.9773420
H	-5.0640550	3.3292790	1.2559970	H	-5.0522850	3.3324770	1.2610400
H	-3.5424610	-0.8103710	-3.9929120	H	-3.5501440	-0.8092190	-3.9909450
Pd	2.1107760	-0.2124180	-0.1819210	Pd	2.1105190	-0.2120030	-0.1839180
C	4.1068940	-0.2532340	0.0320880	C	6.1540430	0.0973810	1.3169820
C	4.8852660	-0.8828670	-0.9582820	C	6.9104420	-0.5344600	0.3268580
C	4.7751760	0.2420280	1.1649210	C	6.2721440	-1.0177080	-0.8158820
C	6.2709780	-1.0215660	-0.8188290	C	4.8864660	-0.8802390	-0.9569130
H	4.4097930	-1.2605000	-1.8625060	C	4.1064120	-0.2513290	0.0325980
C	6.1563160	0.0937240	1.3141090	C	4.7729420	0.2444450	1.1662380
H	4.2091160	0.7593160	1.9341580	H	6.6433210	0.4864590	2.2073430
C	6.9110200	-0.5388360	0.3231580	H	7.9859890	-0.6417550	0.4417440
H	6.8481820	-1.5035660	-1.6053190	H	6.8506780	-1.4991580	-1.6017310
H	6.6469540	0.4824110	2.2038940	H	4.4123820	-1.2582240	-1.8617240
H	7.9866040	-0.6470700	0.4368100	H	4.2055310	0.7611870	1.9348470
C	2.2058200	1.7883210	-0.1287960	C	2.2032760	1.7887430	-0.1290580
C	3.0824250	2.5562740	-0.9119060	C	1.3057950	2.4710290	0.7060700
C	1.3081020	2.4725220	0.7054830	C	3.0811930	2.5585040	-0.9099260
C	3.0444540	3.9513430	-0.8775060	C	1.2865120	3.8684380	0.7542390
H	3.8045740	2.0636220	-1.5556600	H	0.5979960	1.9182490	1.3173360
C	1.2886800	3.8694600	0.7511200	C	3.0434700	3.9529490	-0.8729160
H	0.5986990	1.9207040	1.3157470	H	3.8057720	2.0668060	-1.5516750
C	2.1531900	4.6331760	-0.0399440	C	2.1497320	4.6334830	-0.0359320
H	3.7294510	4.5203050	-1.5045700	H	0.5837140	4.3708040	1.4177360
H	0.5843920	4.3730150	1.4122390	H	3.7310200	4.5228800	-1.4964210
C	2.1487460	6.1422280	0.0253050	C	2.1324060	6.1430520	0.0146860

H	1.2244420	6.5197520	0.4764600	H	1.3364680	6.5099960	0.6717340
H	2.9849080	6.5227060	0.6279500	H	3.0825550	6.5455620	0.3897860
H	2.2438390	6.5888200	-0.9716440	H	1.9721520	6.5789050	-0.9797920

R_1-R_2

C	3.32682700	-1.14508500	-0.38470700
C	1.93356700	-1.14282000	-0.38359600
C	1.21405000	0.00031000	0.00010000
C	1.93680600	1.14207100	0.38163800
C	3.33009200	1.14181600	0.37823500
C	4.03198000	-0.00224400	-0.00438200
H	3.86295000	-2.03864300	-0.69264600
H	1.39289400	-2.02707000	-0.70807900
H	1.39888500	2.02724100	0.70813000
H	3.86879300	2.03437900	0.68455500
H	5.11827200	-0.00321500	-0.00610500
C	-0.26729000	0.00118500	0.00180700
C	-0.99271100	1.14034300	-0.37893300
C	-0.99268100	-1.13624600	0.38861100
C	-2.38479400	1.13967500	-0.37287800
H	-0.45891900	2.02854600	-0.70427800
C	-2.38457200	-1.13259400	0.39193200
H	-0.45851300	-2.02216000	0.71952300
C	-3.10775000	0.00334700	0.00872100
H	-2.92086200	2.03552600	-0.67763400
H	-2.92043400	-2.02456300	0.70827900
C	-4.61630700	-0.00605100	-0.01719600
H	-4.99496300	-0.35574800	-0.98694400
H	-5.02545300	-0.67221200	0.74971600
H	-5.02595500	0.99568500	0.14936900

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