Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

A copper-functionalized zirconium metal-organic framework for catalytic oxidative carboxylation of olefins and CO_2

Y B. N. Tran,[ab] Phuong T. K. Nguyen,*[ab] Vinh-Ai Dao,[c] and Van-Dung Le[d]

[a]Institute of Fundamental and Applied Sciences, Duy Tan University, Ho Chi Minh City 700000, Viet Nam

[b]Faculty of Natural Sciences, Duy Tan University, Da Nang, 550000, Viet Nam.

[c]Department of Physics, Faculty of Applied Sciences, HCMC University of Technology and Education, Ho Chi Minh City 700000, Vietnam

[d]Institute of Chemical Technology, Vietnam Academy of Science and Technology, Ho Chi Minh City 700000, Vietnam

*To whom correspondence should be addressed: Email, nguyentkieuphuong1@duytan.edu.vn.

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Section S1: Materials and Analytical Techniques

Chemicals and Materials

Copper (I) iodide (CuI, ≥ 99.5%), copper (II) chloride ($CuCl_2$, 97%), zirconium(IV) oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 99.5%), 1,8-diazabicylcloundec-7-ene (DBU, ≥ 99.0%), sodium hydroxide (NaOH, reagent grade, ≥ 98%), hydrochloric acid (HCl, 1 M), 4-methoxystyrene (≥97.5%), allylbenzene (98%), 1-allyl-4-methylbenzene (97%), *p*-methoxyallylbenzene (98%), 1-decene (≥97%), *tert*-butyl hydroperoxide solution (TBHP, 5.0 – 6.0 M in decane), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 98%), hydrogen peroxide solution (H_2O_2, 30% in water) and balloon (wall thickness 1 mil) were obtained from Sigma-Aldrich. Methyl-4-iodobenzoate (98%), bis(tripheny-phosphine)palladium(II) chloride ($PdCl_2(PPh_3)_2$, 98%), triethylamine (TEA, ≥99.5%), trimethylsilylacetylene (98%), dicobalt octacarbonyl ($Co_2(CO)_8$, 95%), anhydrous 1,4-dioxane (99.8%), anhydrous tetrahydrofuran (THF, 99.85%), anhydrous methanol (MeOH, 99.5%), *N,N*-dimethylformamide (DMF, 99.8%), benzoic acid (99.5 %), styrene (99.5%), 4-chlorostyrene (97%), cyclohexene (99%), aqueous tert-butyl hydroperoxide (TBHP, 70% solution in water), tetrabutylammonium bromide (nBu$_4$NBr, 99+%), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (DPIC, 97%), hexadecyltrimethylammonium bromide (HTAB, 99+%), 4-dimethylaminopyridine (DMAP, 99%), tetrabutylammonium chloride (nBu$_4$NCl, 95%), and N-bromosuccinimide (NBS, 99%) were purchased from Acros Organics. Anhydrous dichloromethane (DCM, ≥99.5%), ethyl acetate (EtOAc, ≥99.5%), diethyl ether (Et_2O, ≥99.7%), hexane (≥98.5%), anhydrous sodium sulfate (≥99%), ammonium chloride (99.998%), and glacial acetic acid (CH_3COOH, ≥99.85%) were obtained from Merck Chemical Co. Triethylamine and deionized water (ultrapure, 17.8 MΩ·cm resistivity, obtained from a Barnstead Easypure II system) were degassed with a stream of N_2 for 5 min prior to addition into the Sonogashira coupling reactions. Deuterated solvents, $CDCl_3$ and DMSO-d_6, were purchased from Cambridge Isotope Laboratories (Andover, MA). All other chemicals were used without further purification unless otherwise noted.

Analytical Techniques

Optical microscope images were collected on Nikon SMZ1000 Zoom Stereomicroscope. Elemental microanalyses (EA) were performed on a LECO CHNS-932 Analyzer. Thermal

gravimetric analysis (TGA) was performed on a TA Q500 thermal analysis system with the sample held in a platinum pan in a continuous airflow. Field-emission Scanning Electron Microscope (FE-SEM) was performed on an ultralow voltage imaging with Hitachi's S-4800 FE-SEM operating at an accelerating voltage of 1 kV. Energy dispersive X-ray analyzer (EDX) was conducted on a Horiba H-7593. For inductively coupled plasma analysis (ICP−MS), activated MOF sample (ca. 10 mg) was placed in 30 μL of DCl (20% in D_2O) and 570 μL of DMSO-d_6 and then sonicated for 10 min in order to fully digest the MOF and dissolve the linker constituents. X-ray fluorescence (XRF) analysis were carried out using a Bruker M4 Tornado model micro–fluorescence spectrometer.

An Agilent GC System 19091S-433 equipped with a mass selective detector Agilent 7890 (GC-MS) was used to confirm the products using a capillary HP-5MS 5% Phenyl Methyl Silox column (30 m × 250 μm × 0.25 μm). The temperature program for GC-MS analysis heated samples from 50 °C for 2 min; heated from 50 to 300 °C at 25 °C/min; held at 300 °C for 5 min. Inlet temperature was set at 250 °C and He was used as carrier gas with split flow 24.371 mL/min (split ratio 50 : 1). GC-FID analyses were performed using an Agilent GC System 123-0132 equipped with a flame ionization detector and a DB-1ms column (30 m × 320 μm × 0.25 μm). The temperature program for GC-FID analysis heated samples from 50 °C for 2 min; heated from 50 to 250 °C at 25 °C/min; held at 250 °C for 4 min. Inlet and detector temperature were set at 250 and 300 °C, respectively. N_2 was used as carrier gas with split flow 188.82 mL/min (split ratio 100 : 1). In back detector FID, H_2 and air flow were conducted with split flow of 30 mL/min and 400 mL/min, respectively. Biphenyl was used as internal standard to calculate the yield of reaction. Recycled MOF catalysts wer recovered by centrifugation and wash with DMF (3 × 3 mL), followed by MeOH (3 × 3 mL), and then dried under reduced pressure before reused in the next experiments under the same reaction condition.

Section S2: Characterizations of Zr-CPB and Zr-CPB-Cu

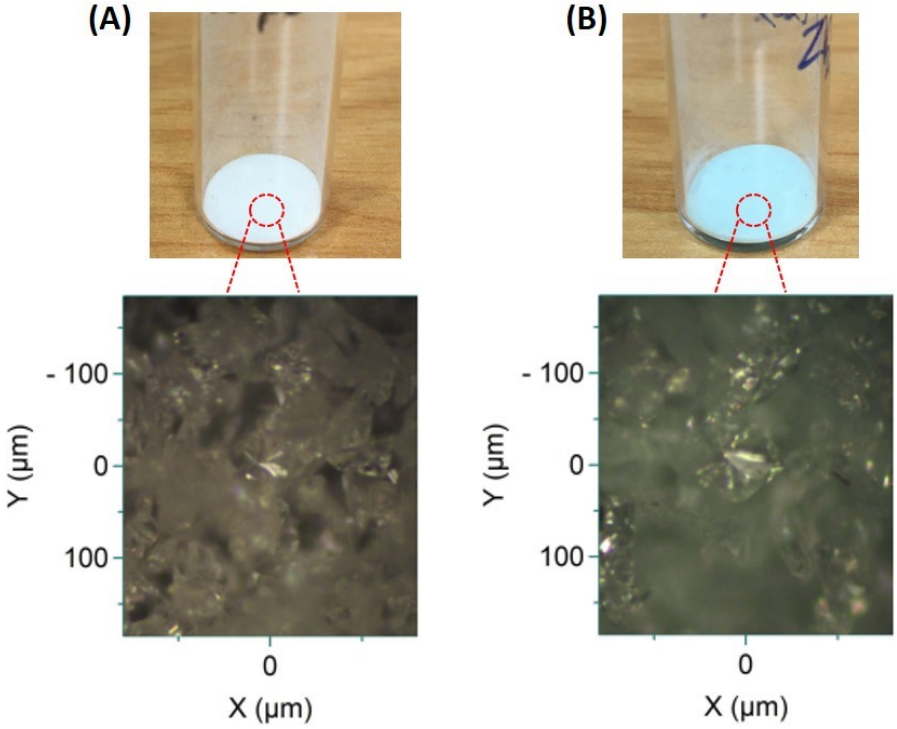


Figure S1. Optical microscope image of (A) Zr-CPB and (B) Zr-CPB-Cu crystals.

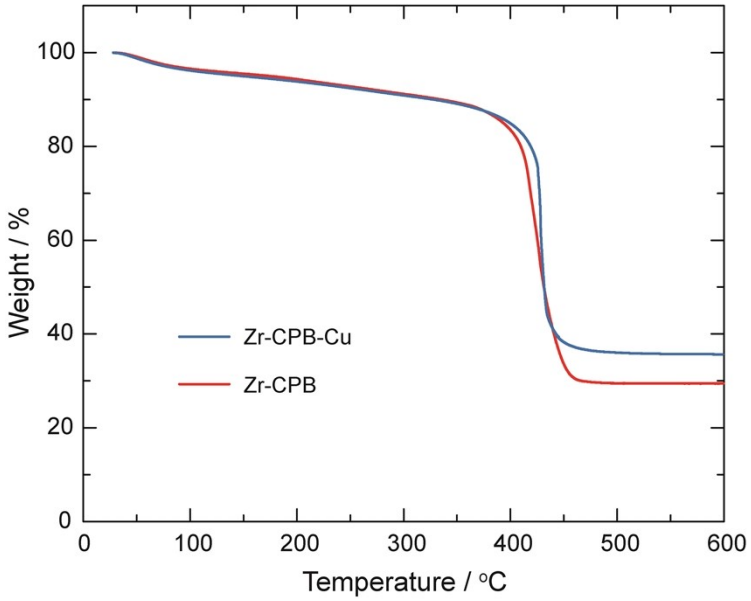


Figure S2. TGA traces of activated Zr-CPB (red) and Zr-CPB-Cu (blue) at a heating rate of 5 °C min^{-1} under air flow.

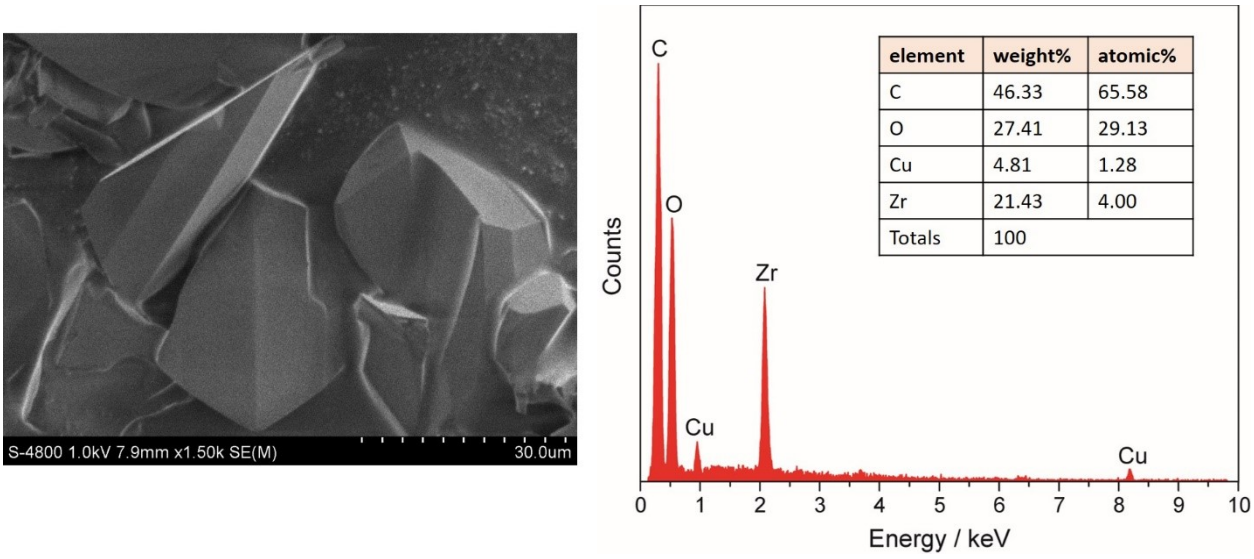


Figure S2. SEM-EDS analysis of Zr-CPB-Cu material.

Table S1. XRF compositional analysis of the activated Zr-CPB-Cu samples

Element	Chemical composition at.%		
	Zr-CPB	Zr-CPB-Cu	recycled Zr-CPB-Cu
Cu	-	4.68 ± 0.05	4.45 ± 0.10
Zr	21.47 ± 0.15	20.21 ± 0.12	20.10 ± 0.15

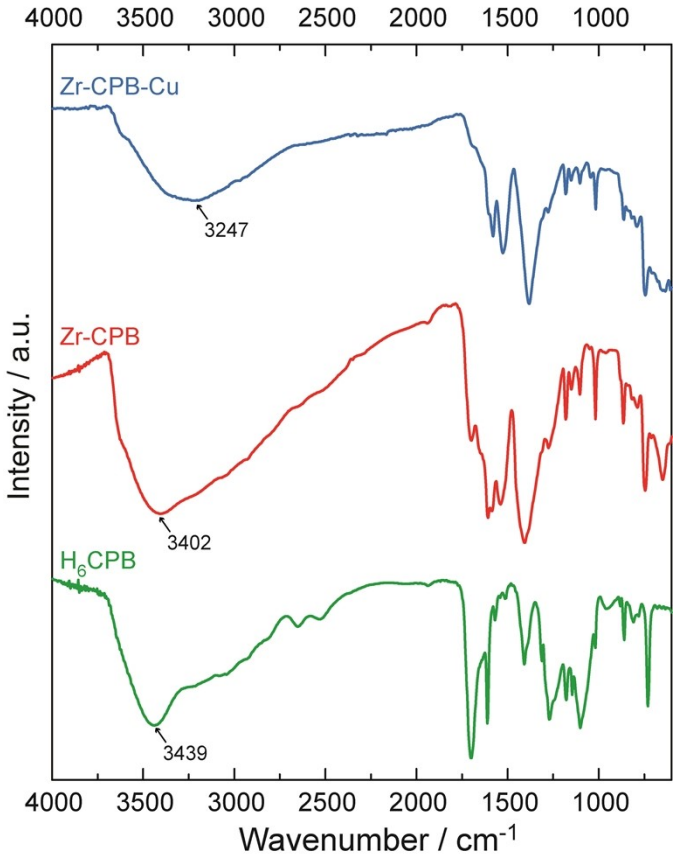


Figure S4. FT-IR spectra of H_6CPB (green), Zr-CPB (red), and Zr-CPB-Cu (blue)

Section S3. Powder X-Ray Diffraction, Structural Modelling and Refinement of Zr-CPB-Cu

The modeled Zr-CPB-Cu framework was built based on the Zr-CPB (MOF-893) by using Materials Studio 7.0 (Accelrys Software Inc.) software, in which atomic connectivity and monoclinic *C*2/*c* space group were retained. Geometry optimization was subsequently performed by using the universal force field implemented in the *Forcite* module, and the unit cell parameters were optimized until obtaining low energy convergence (10^{-4} kcal/mol). By using Reflex module, full profile pattern fitting Pawley refinement was evaluated on the experimental PXRD pattern and modeled structure in the 2θ range from 3.8 to 50°. A Pearson VII function was employed to define the peak profile. The unit cell parameters a, b, c, FWHM parameters U, V, W, profile parameters NA, NB, zero point, shift#1, and shift#2 were refined. The background coefficients were refined with 30th order polynomial. The refined unit cell parameters and fractional atomic coordinates for Zr-CPB were provided in Tables S1.

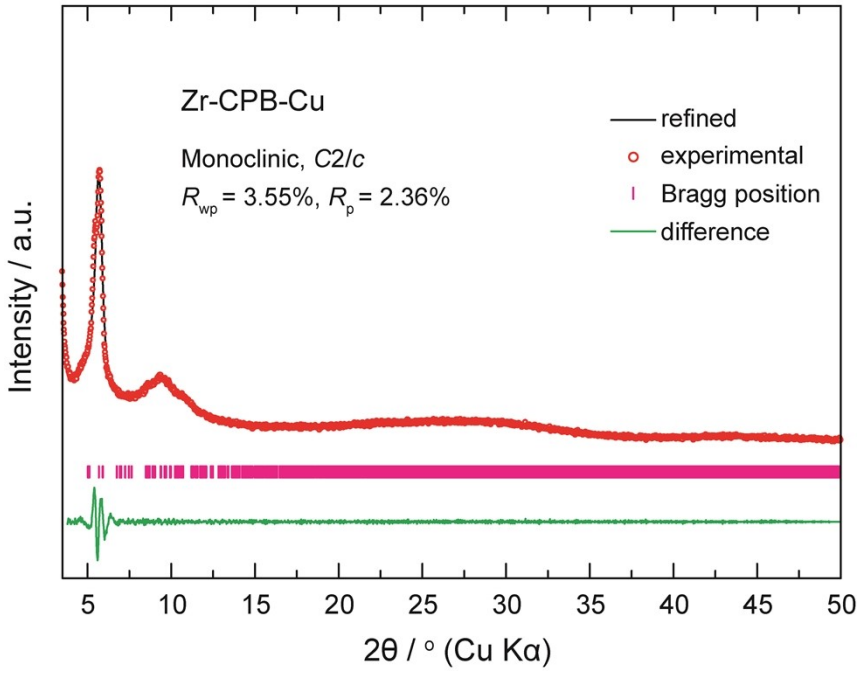


Figure S5. The Pawley refinement of Zr-CPB-Cu. Shown are the experimental (black), refined (red), and difference (green) patterns. The Bragg positions are marked as pink bars.

Table S2. Unit cell parameters and fractional atomic coordinates for the refined Zr-CPB-Cu.

Empirical formula, Space group		$C_{102}Zr_6Cu_2H_{72}O_{45}$, *C*2/*c*			
Refined unit cell		*a* = 24.5313 Å, *b* = 68.4490 Å, *c* = 19.4107 Å, α = γ = 90.0000°, β = 92.5973°.			
Pawley refinement		R_{wp} = 3.55%, R_{wp} (w/o background) = 3.04%, R_p = 2.36%			
Atom label	Atom type	*x*	*y*	*z*	Site Occupancy
Zr1	Zr	0.15333	0.35997	0.29194	1
Zr2	Zr	0.23753	0.35956	0.15867	1
Zr3	Zr	0.28868	0.34906	0.31446	1
Zr4	Zr	0.19099	0.40364	0.20243	1
Zr5	Zr	0.32584	0.39072	0.23069	1
Zr6	Zr	0.24423	0.39271	0.36151	1
O7	O	0.31353	0.37818	0.3268	1
O8	O	0.30906	0.36125	0.22103	1
O9	O	0.22287	0.36269	0.35858	1
O10	O	0.26098	0.40637	0.26764	1
O11	O	0.25785	0.38929	0.16227	1
O12	O	0.21965	0.3453	0.25107	1
O13	O	0.17493	0.39013	0.29826	1
O14	O	0.17033	0.37339	0.1955	1
O15	O	0.2462	0.32409	0.34731	1
O16	O	0.40569	0.38116	0.25985	1
O17	O	0.1933	0.43006	0.14599	1
O18	O	0.10244	0.40773	0.19841	1
O19	O	0.07158	0.37126	0.26647	1
O20	O	0.11443	0.33551	0.33453	1
O21	O	0.16884	0.33347	0.42839	1
O22	O	-0.1304	0.33592	0.27423	1
O23	O	-0.17604	0.34037	0.3734	1
O24	O	-0.2886	0.29032	0.69575	1
O25	O	-0.33189	0.27752	0.60551	1
O26	O	-0.22706	0.16826	0.64469	1
O27	O	-0.17845	0.17218	0.74668	1
O28	O	0.08692	0.14397	0.62395	1
O29	O	0.14194	0.16787	0.66083	1
O30	O	0.27573	0.22045	0.44931	1
O31	O	0.28336	0.2221	0.56204	1
O32	O	0.1825	0.39203	0.43202	1

O33	O	0.12854	0.36682	0.39254	1
O34	O	0.32166	0.40228	0.73916	1
O35	O	0.3173	0.37142	0.70945	1
O36	O	0.18151	0.40153	1.09516	1
O37	O	0.19637	0.36945	1.07077	1
O38	O	0.35417	0.416	0.18293	1
O39	O	0.30477	0.41369	0.08461	1
O40	O	0.64081	0.41196	0.20252	1
O41	O	0.69374	0.41214	0.10875	1
O42	O	0.82237	0.49327	-0.01541	1
O43	O	0.81734	0.50012	0.09435	1
O44	O	0.27935	0.38209	0.4541	1
O45	O	0.3102	0.35218	0.42093	1
O46	O	0.35964	0.3817	0.13724	1
O47	O	0.29601	0.36174	0.08391	1
O48	O	0.19334	0.42981	0.26076	1
O49	O	0.21144	0.42071	0.37297	1
C50	C	0.1297	0.32673	0.39044	1
C51	C	0.10099	0.30903	0.4127	1
C52	C	0.0697	0.29771	0.36526	1
H53	H	0.06657	0.30166	0.31126	1
C54	C	0.04162	0.28125	0.38749	1
H55	H	0.0173	0.27279	0.35038	1
C56	C	0.04291	0.27633	0.45774	1
C57	C	0.07548	0.28725	0.5047	1
H58	H	0.07672	0.28369	0.55913	1
C59	C	0.10466	0.30336	0.48233	1
H60	H	0.12862	0.31177	0.52001	1
C61	C	0.00509	0.26153	0.48464	1
C62	C	0.0255	0.24413	0.51519	1
C63	C	-0.01036	0.2316	0.54928	1
C64	C	-0.06431	0.23751	0.56023	1
C65	C	-0.08375	0.25542	0.53293	1
C66	C	-0.0505	0.26649	0.49002	1
C67	C	0.11688	0.23774	0.57376	1
H68	H	0.0995	0.2406	0.62307	1
C69	C	0.0844	0.23914	0.51257	1
C70	C	0.108	0.23568	0.44926	1
H71	H	0.08354	0.23671	0.40154	1
C72	C	0.16319	0.23067	0.44722	1
H73	H	0.18035	0.22805	0.39763	1

C74	C	0.19573	0.22901	0.50854	1
C75	C	0.17195	0.23265	0.57184	1
H76	H	0.1959	0.23159	0.61996	1
C77	C	0.25412	0.2236	0.50654	1
C78	C	0.00859	0.2122	0.57348	1
C79	C	0.02056	0.20896	0.64379	1
H80	H	0.01429	0.22041	0.68115	1
C81	C	0.04417	0.19138	0.66554	1
H82	H	0.05642	0.18951	0.71942	1
C83	C	0.0556	0.17687	0.61729	1
C84	C	0.03986	0.17952	0.54765	1
H85	H	0.04958	0.16862	0.50968	1
C86	C	0.01661	0.19721	0.52574	1
H87	H	0.00706	0.19956	0.47135	1
C88	C	0.09588	0.16192	0.63634	1
C89	C	-0.10194	0.22366	0.59283	1
C90	C	-0.10808	0.22348	0.66442	1
H91	H	-0.08784	0.23435	0.69704	1
C92	C	-0.13859	0.2087	0.69459	1
H93	H	-0.14235	0.20865	0.74996	1
C94	C	-0.16313	0.19394	0.65344	1
C95	C	-0.15754	0.19447	0.58173	1
H96	H	-0.17506	0.18313	0.54873	1
C97	C	-0.12667	0.20903	0.55205	1
H98	H	-0.11993	0.20838	0.49749	1
C99	C	-0.19193	0.17733	0.68406	1
C100	C	-0.13804	0.26947	0.62572	1
H101	H	-0.10202	0.26874	0.66002	1
C102	C	-0.13558	0.26358	0.55674	1
C103	C	-0.18212	0.26527	0.51259	1
H104	H	-0.18064	0.26112	0.45888	1
C105	C	-0.23135	0.27179	0.53832	1
H106	H	-0.26705	0.27279	0.50362	1
C107	C	-0.23457	0.27663	0.60849	1
C108	C	-0.18708	0.27587	0.65149	1
H109	H	-0.18809	0.27973	0.70553	1
C110	C	-0.28729	0.28188	0.63752	1
C111	C	-0.07316	0.28342	0.45105	1
C112	C	-0.08954	0.28123	0.38118	1
H113	H	-0.08782	0.26702	0.35677	1
C114	C	-0.10795	0.29733	0.34243	1

H115	H	-0.12204	0.29527	0.28927	1
C116	C	-0.11128	0.31571	0.37365	1
C117	C	-0.0951	0.31779	0.44383	1
H118	H	-0.09862	0.33174	0.46954	1
C119	C	-0.07556	0.3018	0.48204	1
H120	H	-0.06279	0.3037	0.53578	1
C121	C	-0.14021	0.33185	0.33789	1
C122	C	0.14152	0.38043	0.43643	1
C123	C	0.10694	0.38305	0.49636	1
C124	C	0.11	0.40053	0.53449	1
H125	H	0.13634	0.41236	0.51958	1
C126	C	0.07991	0.40286	0.59318	1
H127	H	0.08424	0.41619	0.62295	1
C128	C	0.04677	0.38767	0.61558	1
C129	C	0.04143	0.37055	0.57604	1
H130	H	0.01616	0.35865	0.59284	1
C131	C	0.07108	0.36829	0.51659	1
H132	H	0.06741	0.35473	0.48796	1
C133	C	0.02347	0.38877	0.68468	1
C134	C	0.05858	0.3889	0.74427	1
C135	C	0.03669	0.38905	0.81021	1
C136	C	0.07362	0.38877	0.87244	1
C137	C	0.10622	0.37235	0.88649	1
H138	H	0.10318	0.35963	0.85332	1
C139	C	0.1426	0.37215	0.9436	1
H140	H	0.16633	0.35903	0.95376	1
C141	C	0.14663	0.38832	0.98837	1
C142	C	0.11436	0.40491	0.97343	1
H143	H	0.11582	0.41747	1.00739	1
C144	C	0.07804	0.40511	0.9158	1
H145	H	0.05325	0.41794	0.90506	1
C146	C	0.17766	0.38648	1.05512	1
C147	C	0.23311	0.38768	0.72905	1
C148	C	0.20688	0.40456	0.75224	1
H149	H	0.23019	0.41741	0.76744	1
C150	C	0.15021	0.40498	0.75667	1
H151	H	0.13076	0.41809	0.77497	1
C152	C	0.11877	0.38857	0.73788	1
C153	C	0.14463	0.37174	0.71419	1
H154	H	0.12088	0.35892	0.69975	1
C155	C	0.20132	0.37128	0.70977	1

H156	H	0.22028	0.35809	0.69154	1
C157	C	0.29328	0.38711	0.7256	1
C158	C	0.30319	0.36565	0.46615	1
C159	C	0.32435	0.36189	0.53819	1
C160	C	0.19697	0.43327	0.32624	1
C161	C	0.18484	0.45354	0.34921	1
C162	C	0.34194	0.37081	0.08676	1
C163	C	0.37735	0.3686	0.02673	1
C164	C	0.34068	0.4223	0.12268	1
C165	C	0.36994	0.43906	0.09604	1
C166	C	0.38758	0.45402	0.14105	1
H167	H	0.37595	0.45409	0.19414	1
C168	C	0.42012	0.46903	0.11759	1
H169	H	0.43318	0.4806	0.15266	1
C170	C	0.43594	0.46906	0.04922	1
C171	C	0.41735	0.45442	0.00358	1
H172	H	0.42868	0.45459	-0.0497	1
C173	C	0.38414	0.4395	0.02684	1
H174	H	0.37104	0.42799	-0.00847	1
C175	C	0.46944	0.48516	0.02449	1
C176	C	0.52701	0.48365	0.02786	1
C177	C	0.55815	0.49936	0.00383	1
C178	C	0.55523	0.46569	0.05565	1
C179	C	0.55324	0.46078	0.12564	1
H180	H	0.52983	0.46958	0.15992	1
C181	C	0.58303	0.44489	0.15271	1
H182	H	0.58028	0.44154	0.20687	1
C183	C	0.61746	0.43396	0.11118	1
C184	C	0.6191	0.43878	0.04085	1
H185	H	0.64482	0.43063	0.00722	1
C186	C	0.58776	0.45431	0.01327	1
H187	H	0.58998	0.45781	-0.04094	1
C188	C	0.65277	0.41824	0.14234	1
C189	C	0.73331	0.49741	0.02766	1
C190	C	0.70709	0.49473	-0.03762	1
H191	H	0.73051	0.49215	-0.0827	1
C192	C	0.6502	0.49537	-0.04543	1
H193	H	0.63073	0.49312	-0.09599	1
C194	C	0.61863	0.49872	0.01178	1
C195	C	0.64449	0.50128	0.07702	1
H196	H	0.62052	0.5038	0.12169	1

C197	C	0.70136	0.50064	0.08495	1
H198	H	0.7203	0.50268	0.13592	1
C199	C	0.7936	0.49691	0.0359	1
Cu200	Cu	0.90118	0.62042	0.81347	1
H201	H	0.58565	0.6242	0.9665	1
H202	H	0.64607	0.62734	1.02209	1
H203	H	0.61348	0.35295	0.48059	1
H204	H	1.21477	0.46393	0.32588	1
H205	H	1.1908	0.45475	0.4063	1
H206	H	1.14365	0.45747	0.33273	1
Cu207	Cu	0.89753	0.60581	0.71924	1
H208	H	0.91598	0.59178	0.84969	1
H209	H	0.04762	0.3728	0.30576	1
H210	H	0.59152	0.63344	0.76076	1
H211	H	0.57054	0.61189	0.76751	1
H212	H	0.84614	0.56654	0.86179	1
H213	H	0.73327	0.68246	0.61405	1
H214	H	0.75208	0.68736	0.69005	1
O215	O	0.92463	0.59074	0.64752	1
O216	O	0.93719	0.62921	0.89522	1
H217	H	0.96838	0.63697	0.87965	1
H218	H	0.91265	0.63897	0.91477	1
H219	H	0.92826	0.57741	0.66702	1
H220	H	0.96268	0.59525	0.64329	1
H221	H	0.64695	0.62795	0.4473	1
H222	H	0.65671	0.65391	0.45917	1
H223	H	0.7114	0.63913	0.428	1

Section S4: Gas Adsorption Studies of Zr-MOFs

Gas selectivity calculated by Henry's Law

Virial-type equation was employed for estimation of Henry's constant:

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

Where P is pressure, N is the adsorbed amount, T is temperature, a_i and b_i are virial coefficient, and m and n are the number of virial coefficients required for adequate fitting of the isotherms. As a result, Henry's constant (K_H) at the temperature T can be calculated:

$$K_H = \exp(-b_0) \cdot \exp(-a_0/T)$$

The Henry's Law selectivity for gas component i over j is calculated:

$$S_{ij} = K_{Hi}/K_{Hj}$$

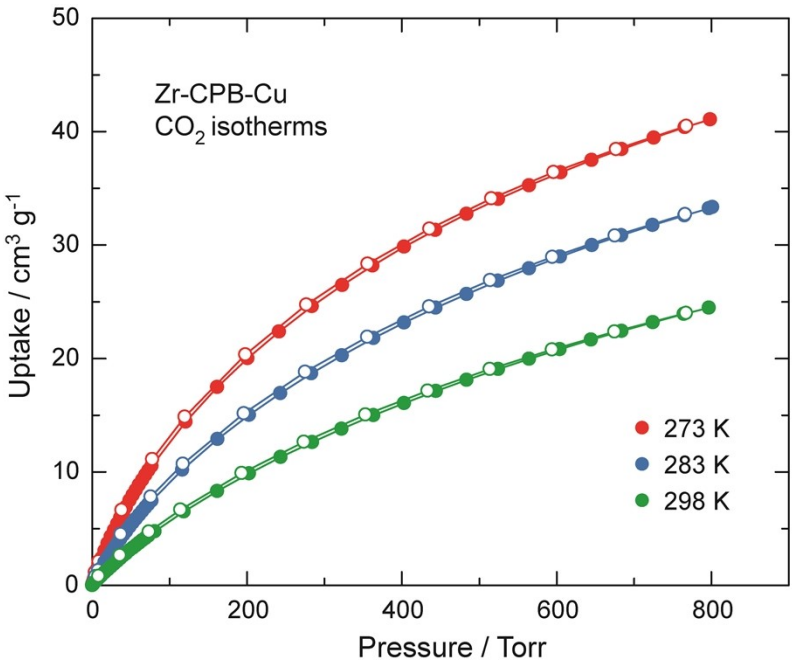


Figure S6. CO_2 isotherms for Zr-CPB-Cu at 273 (red), 283 (blue), and 298 K (green). Filled and open symbols represent adsorption and desorption branches, respectively. The connecting curves are guides for the eye.

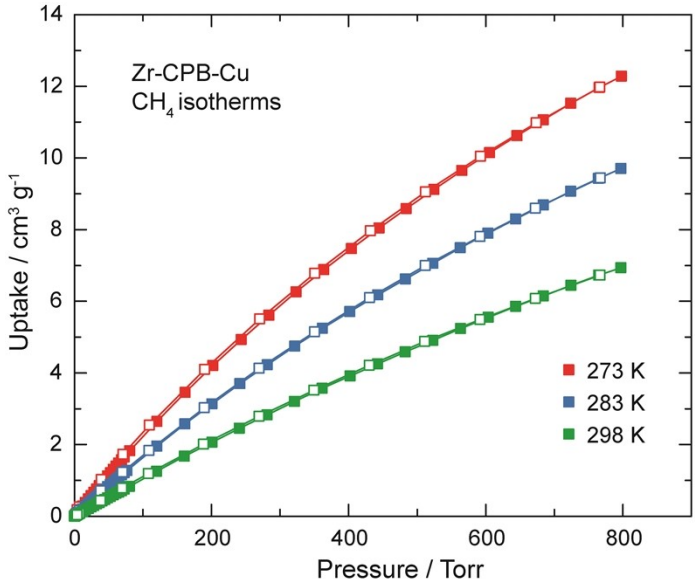


Figure S7. CH_4 isotherms for Zr-CPB-Cu at 273 (red), 283 (blue), and 298 K (green). Filled and open symbols represent adsorption and desorption branches, respectively. The connecting curves are guides for the eye.

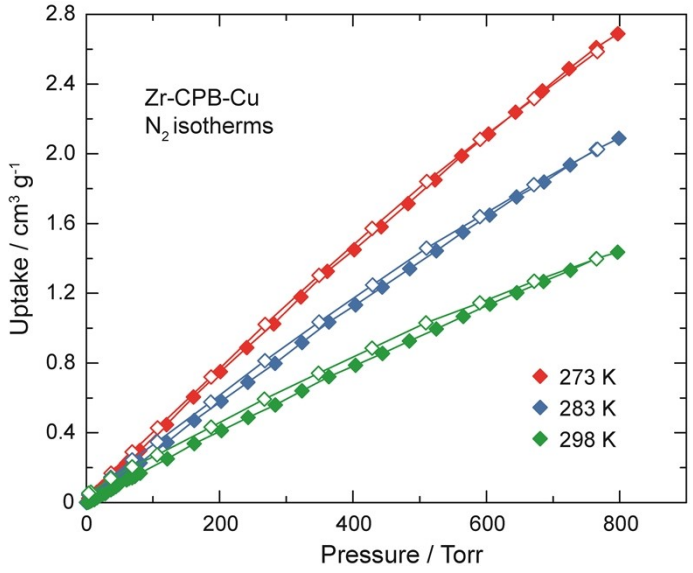


Figure S8. N_2 isotherms for Zr-CPB-Cu at 273 (red), 283 (blue), and 298 K (green). Filled and open symbols represent adsorption and desorption branches, respectively. The connecting curves are guides for the eye.

Section S5: Catalytic Oxidative Carboxylation Studies of Zr-MOFs

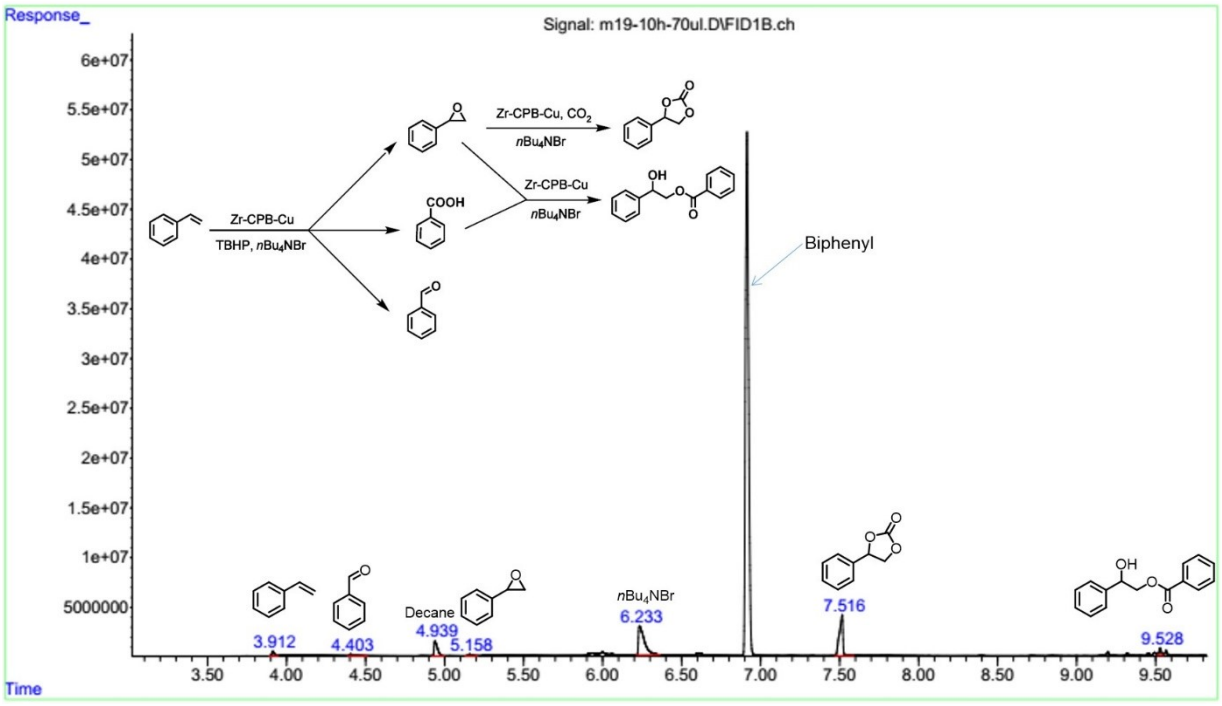
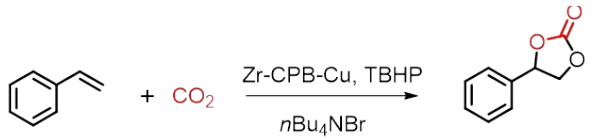


Figure S9. GC chart of the oxidative carboxylation reaction catalyzed by Zr-CPB-Cu after 12 h.

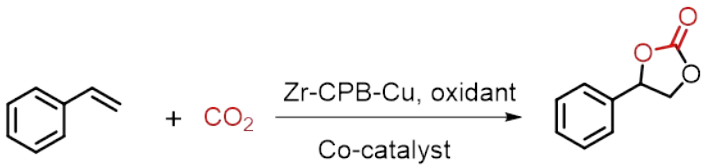
Table S3. Optimization of Zr-CPB-Cu amount for catalysis oxidative carboxylation of styrene and CO_2[a]



#	Amount/ mol %	Conversion/ %	Selectivity/ %	Yield/%	
				Styrene carbonate	Styrene oxide
1	0.1	87	93	81	5
2	0.2	97	95	92	0
3	0.3	95	87	82	0
4	0.4	93	73	68	0
5	No-MOF	87	45	39	10

[a]Reaction conditions: styrene (3.9 mmol), TBHP in decane (7.4 mmol), nBu$_4$NBr (8 mol %), CO_2 (balloon pressure), 80 °C, 12 h. The catalytic conversion of styrene, selectivity of styrene carbonate, and yield of products were quantified by GC-FID with the use of biphenyl as the internal standard.

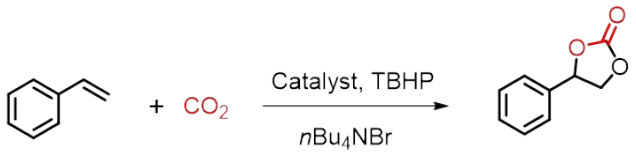
Table S4. Oxidative carboxylation reactions catalyzed by Zr-CPB-Cu with different oxidants and co-catalysts.[a]



#	Oxidant	Co-catalyst	Conversion/ %	Selectivity/ %	Yield/ %
1	TBHP in decane	*n*Bu_4NBr	97	95	92
2	TBHP in water		97	86	83
3	H_2O_2		70	62	43
4	NBS		56	85	48
5	TBHP in decane	*n*Bu_4NCl	94	70	66
6		HTAB	79	86	68
7		DPIC	64	62	40
8		DBU	78	74	58
9		DMAP	72	56	40

[a]Reaction conditions: styrene (3.9 mmol), styrene:oxidant (1:2), Zr-CPB-Cu (0.2 mol%), CO_2 (balloon pressure), 80 °C, 12 h, and co-catalyst (8 mol%). The catalytic conversion, selectivity, and yield were determined by GC-FID analysis using biphenyl as the internal standard. NBS: *N*-bromosuccinimide, *n*Bu_4NCl: tetrabutylammonium chloride, HTAB: hexadecyltrimethylammonium bromide, DPIC: 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene, and DMAP: 4-dimethylaminopyridine.

Table S5. Comparison of different catalysts for oxidative carboxylation of styrene and CO_2.[a]



#	Type	Catalyst	S_{BET}/ m^2 g^{-1}	CO_2 uptake/ cm^3 g^{-1}	Con. /%[c]	Sel. /%[c]	Yield / %
1		$ZrOCl_2 \cdot 8H_2O$	-	-	86	54	46
2		$CuCl_2$	-	-	82	45	37
3	Homo.	H_6CPB	-	-	78	50	39
4		H_6CPB + $ZrOCl_2 \cdot 8H_2O$ + $CuCl_2$	-	-	87	58	50
5	MOF	Cu-CPB[1]	300	58	65	74	48
6		HKUST-1[1]	1650	107	55	78	43
7		Zr-bpydc[1]	2110	33	88	65	57
8		ZIF-8[1]	1675	16	67	90	60

[a]Reaction conditions: styrene (3.9 mmol), catalyst (0.2 mol %, based on molecular weight), TBHP in decane (7.4 mmol), nBu$_4$NBr (8 mol %), CO_2 (balloon pressure), 80 °C, 12 h. The catalytic conversion (Con.) of styrene, selectivity (Sel.) of styrene carbonate, and yield of products were quantified by GC-FID analysis and the use of biphenyl as the internal standard.

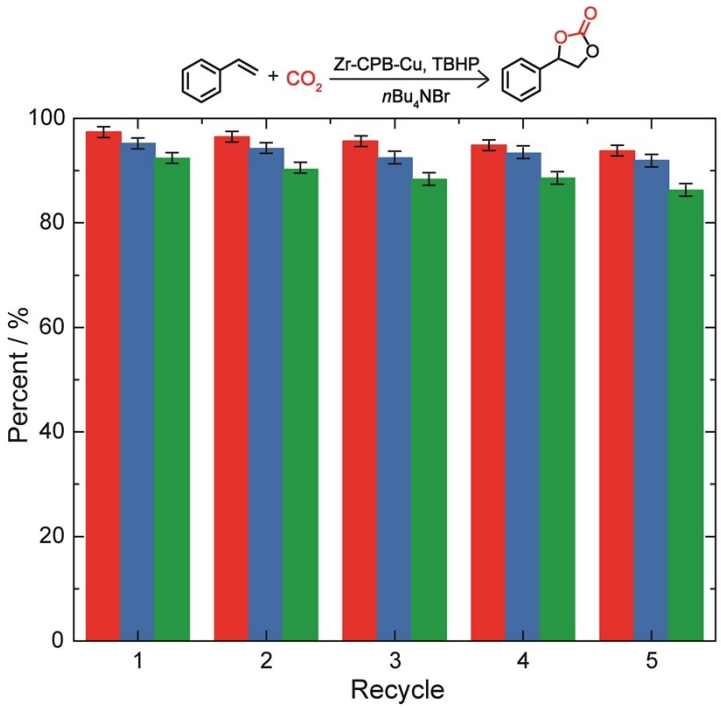


Figure S10. Recyclability of the Zr-CPB-Cu in the oxidative carboxylation of styrene and CO_2.

Styrene carbonate[2-5]

^{1}H NMR (500 MHz, DMSO) δ 7.42–7.48 (m, 5H), 5.85 (t, 1H, J = 7.5, 8.0 Hz), 4.87 (t, 1H, J = 8.0, 8.5 Hz), 4.40 (t, 1H, J = 8.0, 8.5 Hz) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 136.8, 129.8, 129.4, 127.1, 78.2, 71.3 ppm.

GC-MS (EI, 70 eV) *m*/*z*: 164 ([M]$^+$), 119, 105, 90.

4-chlorostyrene carbonate[2-6]

^{1}H NMR (400MHz, $CDCl_3$) δ 7.27 – 7.32 (2H, m), 7.42 – 7.44 (2H,m) 5.66 (ddt, 1H, J = 7.96, 7.96 Hz), 4.80 (dd, 1H, J = 8.43, 8.43 Hz), 4.31 (dd, 1H, J = 7.85, 7.89 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 135.8, 134.3, 129.5, 127.2, 77.2, 70.9 ppm.

GC-MS (EI, 70 V). *m*/*z* (70 eV): 201, 199, 139, 138, 127, 91, 90, 89.

4-methoxystyrene carbonate[4,5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (3H, s), 4.35 (1H, dd, J = 8.14, J = 8.17), 4.75 (1H, dd, J = 8.17, J = 8.17), 5.62 (1H, dd, J = 8.05, J = 8.11), 6.94 – 6.97 (2H, dd, m), 7.26-7.32 (2H, m) ppm.

^{13}C NMR (101MHz, $CDCl_3$) δ 55.4, 71.1, 78.1, 114.6, 127.4, 127.8, 154.9, 160.8 ppm.

GC-MS (EI, 70 V). m/z (70 eV): 195, 194, 151, 150, 121, 91, 63.

Allylbenzene carbonate[6,7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.15 (m, 5H), 5.07 – 4.85 (m, 1H), 4.54 – 4.38 (dd, 1H), 4.28 – 4.12 (dd, 1H), 3.28 – 3.12 (dd, 1H), 3.09 – 2.86 (dd, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 133.9, 129.4, 129.3, 129.0, 129.0, 127.6, 76.8, 68.5, 39.6 ppm.

GC-MS (EI, 70 V) *m*/*z*: 178, 105, 103, 92, 91, 77, 65, 51.

Allyltoluene carbonate[7,8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.07 (m, 5H), 4.97 – 4.85 (dd, 1H), 4.48 – 4.35 (dd, 1H), 4.24 – 4.12 (dd, 1H), 3.23 – 3.09 (dd, 1H), 3.00 – 2.86 (dd, 1H), 2.37-2.28 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 137.3, 130.3, 129.7, 129.7, 129.2, 129.2, 76.9, 68.4, 39.2, 21.1 ppm.

GC-MS (EI, 70 V) *m*/*z*: 192, 105, 91, 77, 65, 51.

4-allylanisole carbonate[7,8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 2H), 6.96 – 6.79 (m, 2H), 5.00 – 4.83 (dtd, 1H), 4.50 – 4.39 (dd, 1H), 4.24 – 4.13 (dd, 1H), 3.85 – 3.79 (s, 3H), 3.18 – 3.06 (dd, 1H), 3.02 – 2.87 (dd, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.1, 154.8, 130.4(2), 125.7, 114.4(2), 77.0, 68.4, 55.3, 38.70 ppm.

GC-MS (EI, 70 V). *m*/*z*: 208, 122, 121, 91, 91, 77, 65, 51.

Dec-1-ene carbonate[5,7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 – 4.64 (m, 1H), 4.59 – 4.46 (dd, 1H), 4.16 – 3.97 (dd, 1H), 1.90 – 1.75 (m, 1H), 1.75 – 1.60 (m, 1H), 1.55 – 1.16 (m, 12H), 1.02 – 0.74 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 77.1, 69.4, 33.90, 31.8, 29.3, 29.1, 29.1, 24.4, 22.6, 14.1 ppm.

GC-MS (EI, 70 V). *m*/*z* (70 eV): 201 ($[MH]^+$), 110, 96, 81, 67, 55.

***Cis*-Cyclohexene carbonate**[1,9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 – 4.63 (m, 2H), 1.90 – 1.80 (m, 4H), 1.61 – 1.53 (m, 2H), 1.42 – 1.35 (m, 2H) ppm

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.21, 73.7, 70.7, 19.2 ppm.

GC-MS (EI, 70 eV) *m*/*z*: 142 ($[M]^+$), 97, 83, 69, 55, 41, 27, 17.

Section S6: Post-Cycling Characterizations of Zr-CPB-Cu

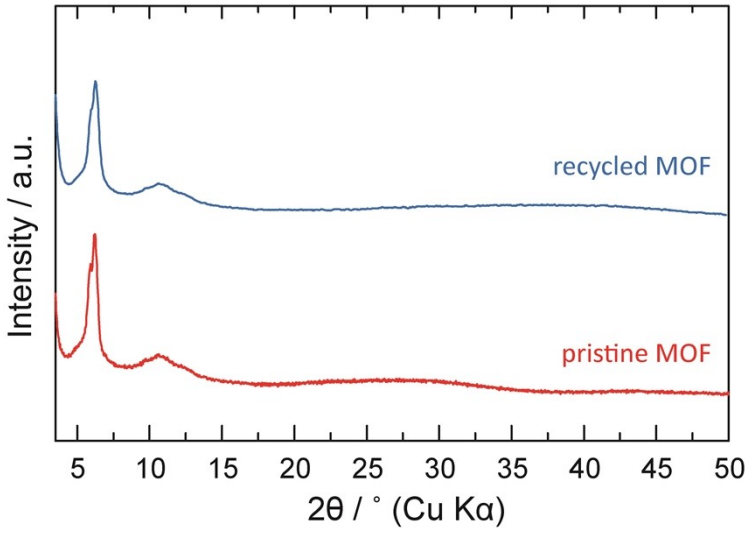


Figure S11. PXRD patterns of pristine (red) and recycled (blue) Zr-CPB-Cu catalyst.

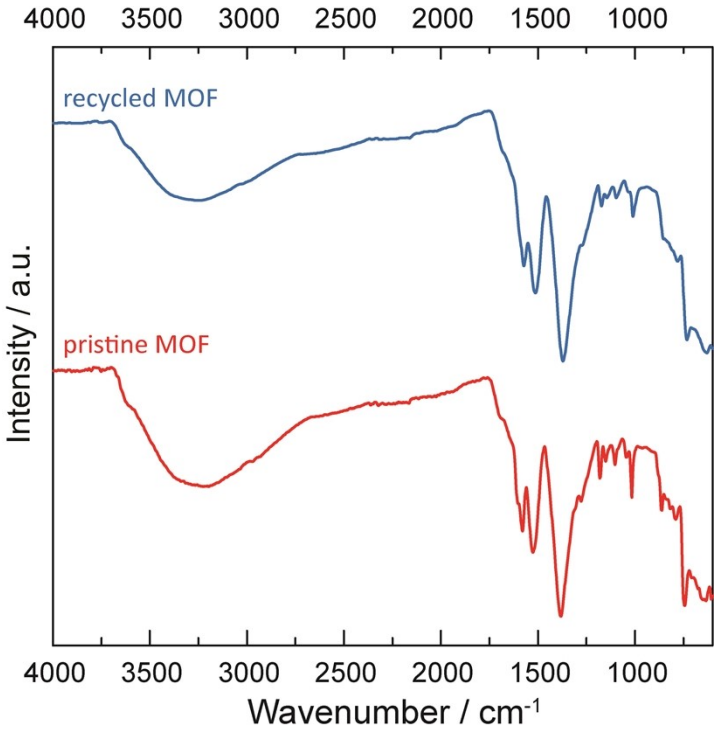


Figure S12. FTIR of pristine (red) and recycled (blue) Zr-CPB-Cu catalyst.

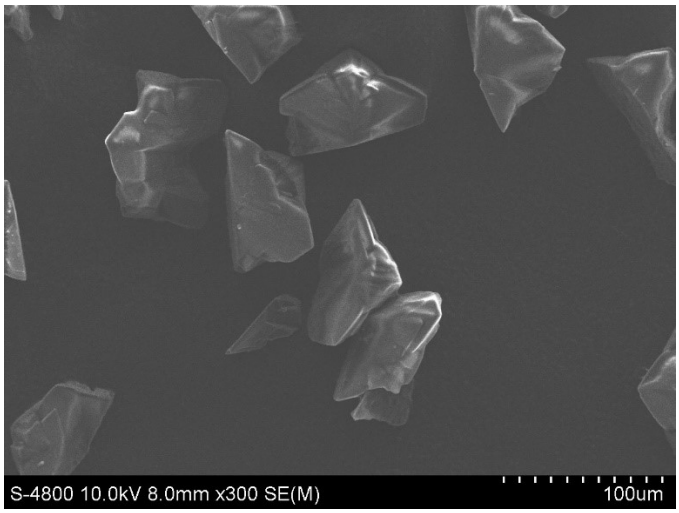


Figure S13. SEM image of the Zr-CPB-Cu after several catalytic reactions.

Section S6: References

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