

A New Layered Metal-Organic Framework as Promising Heterogeneous Catalyst for Olefin Epoxidation Reactions

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Supporting Information

I. General Information and Synthesis

Reagents and Materials. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.7%), 4,4'-oxydibenzoic acid (H_2oba) (Sigma Aldrich, 99%), triethylamine (TEA) (Sigma Aldrich, 99.9%), acetonitrile (Sigma Aldrich, 99.8%), dimethyl sulfoxide (DMSO) (Alfa Aesar, 99.9%), methanol (Fisher Scientific, 99.9%), toluene (Acros, 99%), Styrene (Sigma Aldrich, 99%), 4-chlorostyrene (Sigma Aldrich, 99%), 4-tertbutylstyrene (Sigma Aldrich, 93%), ethyl cinnamate (Sigma Aldrich, 99%), trans-stilbene (Sigma Aldrich, 99%), tertbutyl hydroperoxide (TBHP) (Sigma Aldrich, 5.5M in decane) and chlorobenzene (Fisher Scientific, 99%). All chemicals were used as received without further purification unless stated otherwise.

Instruments and Methods: Thermogravimetric profiles were collected on a TA Q50 Thermogravimetric Analyzer with a temperature ramp of 10 °C/min from room temperature to 600 °C under nitrogen gas flow. Powder X-ray diffraction patterns were recorded on a Rigaku Ultima IV X-Ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Graphite monochromator was used and the generator power settings were set to 40 kV and 44 mA. Data were collected between a 2θ of 3-50° with a step size of 0.02° and a scanning speed of 4.0 deg/min.

The catalytic reactions were probed by withdrawing reaction mixture aliquots at selected time intervals. The reaction analysis was performed by gas chromatography using an Agilent 6850 gas chromatograph (GC) equipped with an HP-1 column (1% dimethyl polysiloxane, 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness) and a flame ionization detector (FID).

The GC measurements were calibrated using chlorobenzene as an internal standard to obtain reactant conversion, product selectivity and reaction yield. The products were further confirmed by an HP gas chromatograph-mass spectrometer (GC-MS, HP-5972) containing an HP-5 MS 50 m \times 0.200 mm \times 0.33 μm capillary column.

Synthesis of $[\text{Co}(\text{Hoba})_2 \cdot 2\text{H}_2\text{O}](\mathbf{1})$ and $[\text{Co}(\text{Hoba})_2](\mathbf{1}')$: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.4 mmol) and H_2oba (0.8 mmol) were mixed in 10 mL of distilled water, two drops of TEA were added in to the solution to adjust the pH value to ~ 7.00 . The solution was then heated at 120 °C for 3 days, followed by cooling at a rate of 0.1 °C/min to room temperature. The pink plate-like crystals of **1** (0.1452 g, 0.24 mmol, 60 % yield based on cobalt) were collected. **1'** was obtained by heating **1** at 150 °C under vacuum for 2 hours, which resulted in a color change of the sample from pink to purple, indicating the transformation of **1** to **1'**. **1** can be easily regenerated by immersing **1'** in water and stirring overnight at room temperature.

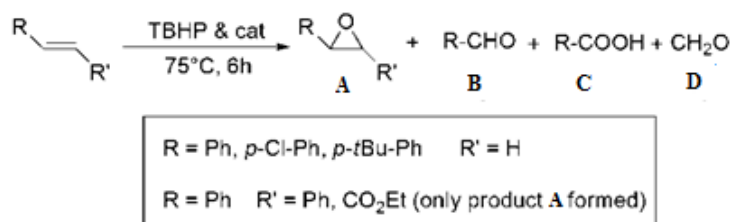
II. Structure Characterization and Analysis

The coordination around Co(II) in compound **1** is shown in Figure S1. The PXRD patterns of the as-made sample (**1**), water-free sample (**1'**) and water-regenerated sample are shown in Figure S2 along with a simulated pattern from single crystal data. As indicated by the sharp PXRD peaks, **1'** remains highly crystalline with (001), (002), (003), (004) and (005) peaks shifted slightly to lower angles (Figure S3). These peaks all correlate to the *c* direction in the crystal structure and the shifts suggest a unit cell expansion in the *c* direction. This is most likely due to the hydrogen bond breaking upon removal of coordinated water molecules in **1** (Figure S4).

Thermogravimetric analysis (Figure S5) shows a perfect match of 6.0% weight loss (designated to coordinated water molecules) compared with the theoretical value (5.9%) calculated from single crystal structure.

The PXRD patterns of **1'** before and after catalytic reactions in acetonitrile solvent and under solvent-free conditions are shown in Figures S6 and S7, respectively. Clearly the structure is retained after 4 cycles of reactions. Small structure changes of the framework are possible during the catalytic reactions since the oxidation state of Co may vary from Co(II) to Co(III) and then back to Co(II) (see Scheme 2). However, the PXRD analysis shows that the structure remains nearly the same after multiple cycles of

catalytic reactions (see Figures S6-S8). This may simply suggest that the layered framework of **1'** is sufficiently flexible so that it can be readily and rapidly restored from any possible changes occurred during the reactions.



Scheme S1. “Solvent-free”⁴ epoxidation of olefins catalyzed by **1'**.

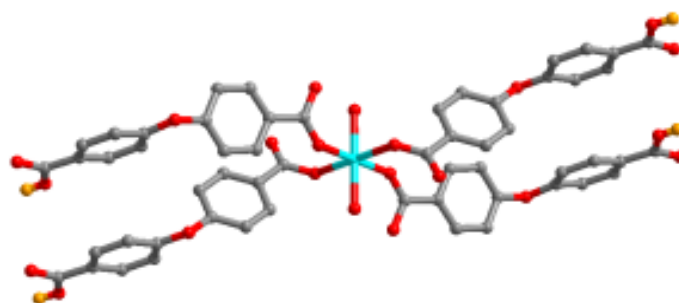


Figure S1. The primary building unit (PBU) in **1** and the coordination around Co(II).

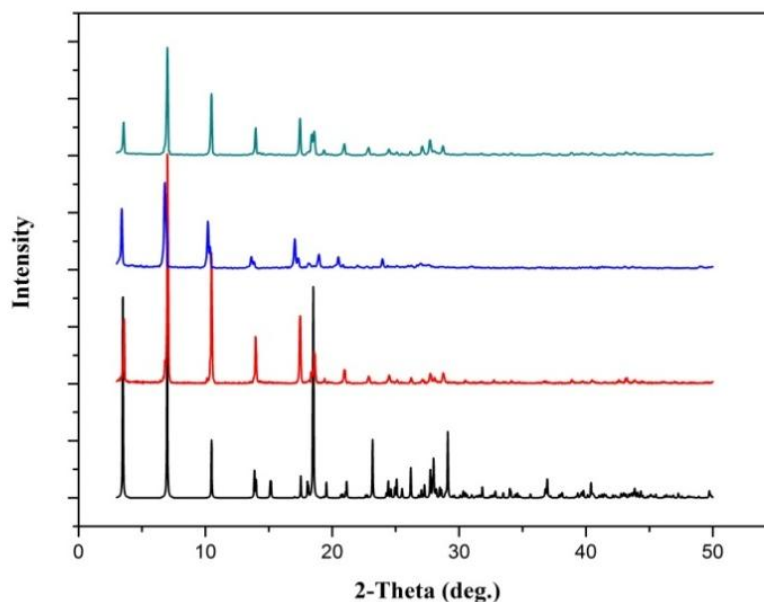


Figure S2. The PXRD patterns of the simulated (black), as-made (red), water-free (blue) and water-regenerated (green) samples.

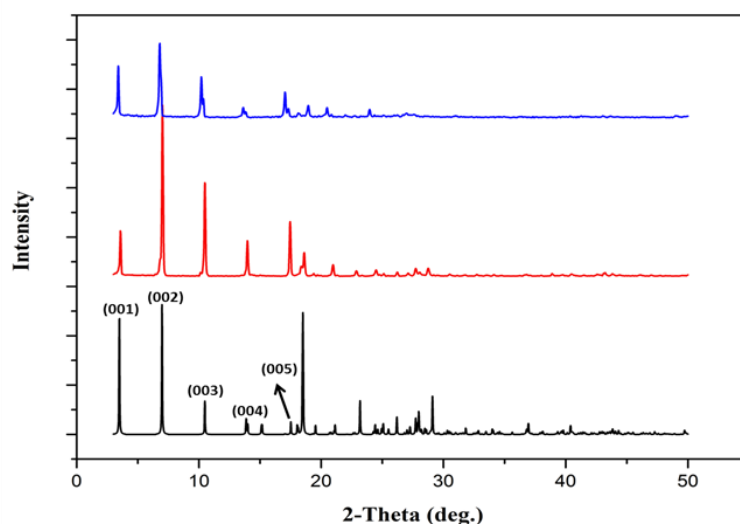


Figure S3. PXRD patterns of simulated (black), as-made (**1**, red) and water-free (**1'**, blue, after heating to remove all the water molecules) samples.

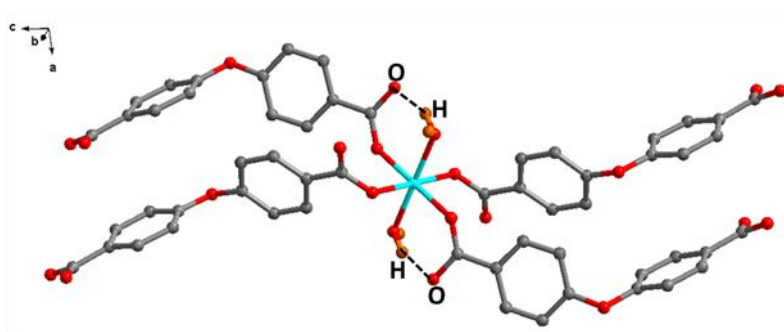


Figure S4. Hydrogen bonds between water molecules and carboxylate groups in an as-made sample.

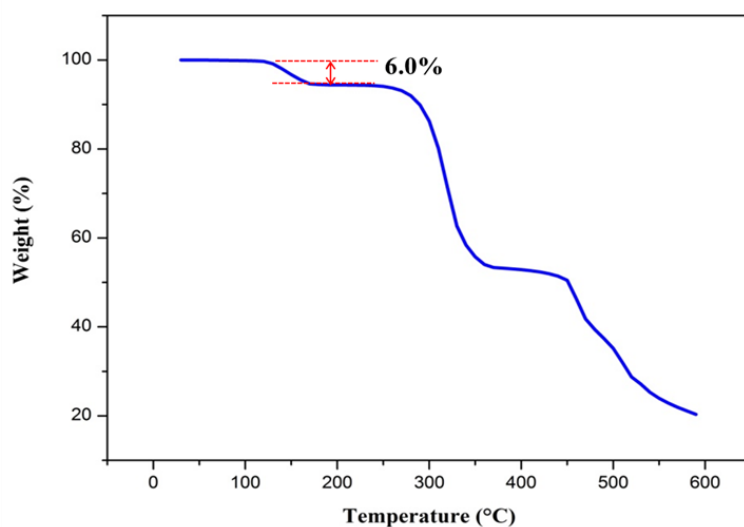


Figure S5. Thermogravimetric analysis of a freshly prepared sample of **1** showing a good match of the observed weight loss of water with the calculated value.

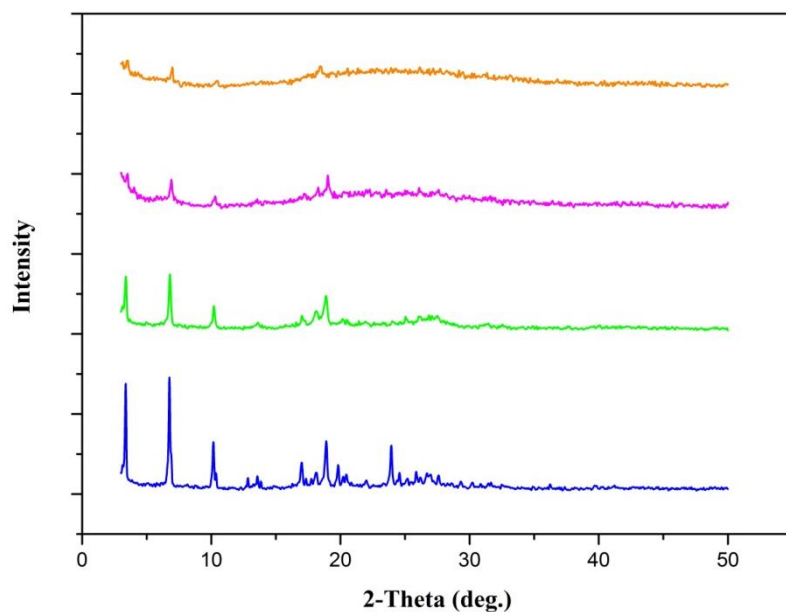


Figure S6. PXRD patterns of **1'** (blue), **1'** after 1st (green), 2nd (pink), and 4th (orange) cycle of catalytic reaction in acetonitrile.

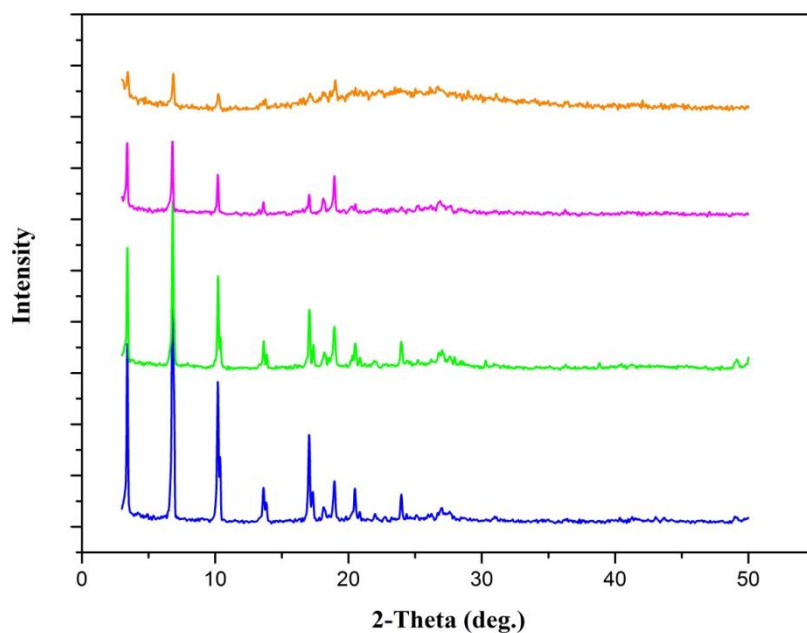


Figure S7. PXRD patterns of **1'** (blue), **1'** after 1st (green), 2nd (pink), and 4th (orange) cycle of catalytic reaction under "solvent-free" conditions.

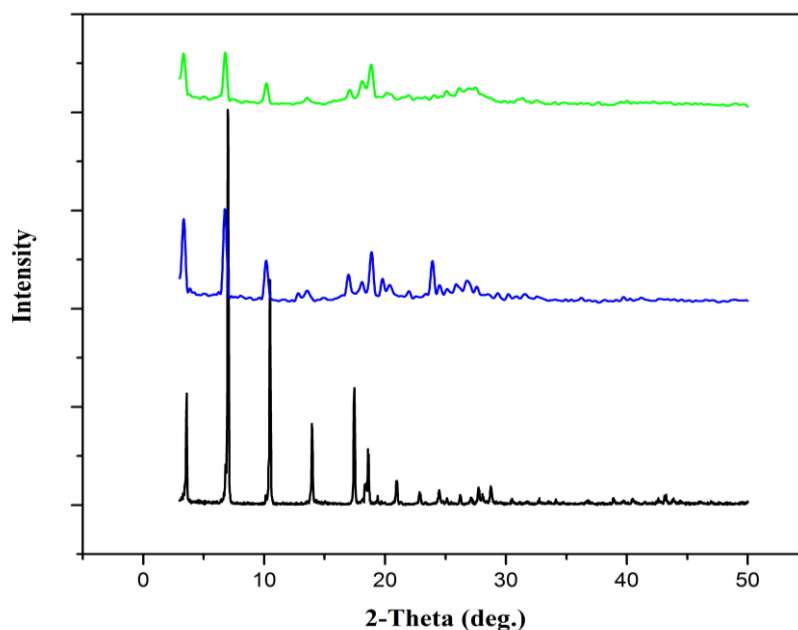


Figure S8. PXRD patterns of **1** (black), **1'** (blue), **1'** after 1st (green) cycle of catalytic reaction under "solvent-free" conditions.

III. Catalytic Activity Tests of **1'**

Experimental: In a typical reaction, a 50 mL three-neck round bottom flask, was charged with the desired amount of reactant, oxidant, catalyst, internal standard (chlorobenzene) and solvent (if needed) were charged. The reaction mixture was then immersed in a preheated oil bath at the desired temperature (75 °C) and the reaction was initiated by stirring with a magnetic stir bar. The reaction was carried out under atmospheric air. The progress of the reaction was monitored by withdrawing aliquot samples at a selected time intervals and then analyzing them by GC and GC-MS.

The catalytic activities of both **1** and **1'** were tested in solvent-free condition and the results are shown in Table S1.

Table S1. Comparison of catalytic activities between **1** and **1'** under "solvent-free" condition^a

Entry	Catalyst	Conversion (%)	Selectivity (%)	
			A	B
1	1	70	90	10
2	1'	96	96	4

^a Reaction condition: Styrene: 50 mmol; TBHP (5.5 M in decane): 100 mmol; catalyst (**1** or **1'**), 15 mg (0.05 mol %); internal standard (chlorobenzene); 15 mmol; Temperature: 75°C; and time: 6 h. The selectivity is only based on the two major products A and B.

The effect of solvents in epoxidation reactions catalyzed by **1'** was also investigated (Table S2). When a non-polar solvent such as toluene was used, no reaction was observed (Table S2, Entry 1). When polar solvents MeOH and DMSO were used, high conversions of 92% and 84%, respectively, were obtained. (Table S2, Entries 2 and 3) Interestingly, however, the selectivities of the reaction products were remarkably different. Reaction in MeOH resulted in styrene oxide as the main product (74% selectivity), whereas the same reaction in DMSO produced 61% benzaldehyde as the major product

(Table S2, Entries 2 and 3). While conversion rate and catalytic activity are both relatively high with these two solvents, **1'** dissolves in both of the reaction mixtures, and cannot be recovered at the end of the reaction through centrifugation. This is not uncommon as numerous MOFs can be dissolved in solvents of high dielectric constant and high polarity, including DMSO and MeOH. Furthermore, since Co(II) is a relatively hard Lewis acid, it is readily soluble in O-donor solvent such as DMSO and MeOH.¹ On the other hand, when the catalytic reaction was performed in acetonitrile, the MOF catalyst can be fully recovered along with a good conversion of styrene (69%) and selectivity to epoxide (78%). (Table S2, Entry 4). Notably, the highest performance (96% conversion of styrene and 96% selectivity to styrene epoxide) was obtained using "solvent-free" conditions. (Table S2, Entry 5) The comparison of catalytic activity between **1'** and Au₂₅-HAP², Au-SBA15³ and Co(OOCC₆H₅)₂ is summarized in Table S5. Au₂₅-HAP and Au-SBA15³ have the best performance in the epoxidation of styrene.

Table S2. MOF **1'** catalyzed epoxidation of styrene in various other solvents^a and under "solvent-free"^{a,b} conditions.

Entry	Solvent	Conversion (%)	Selectivity (%)	
			A	B
1	Toluene	0	0	0
2	Methanol	92	74	26
3	Dimethylsulfoxide	84	39	61
4	Acetonitrile	69	78	22
5	"Solvent-free"	96	96	4

Reaction conditions: ^a Styrene: 1 mmol; TBHP (5.5 M in decane): 2 mmol; catalyst (**1'**): 15 mg (2.5 mol%); Chlorobenzene (internal standard): 15 mmol; Solvent (10 mL); Temperature: 75 °C; and Reaction time: 6 h. ^b Styrene: 50 mmol; TBHP (5.5 M in decane): 100 mmol; catalyst (**1'**): 15 mg (0.5 mol%); Chlorobenzene (internal standard): 15 mmol; Temperature: 75 °C; and Reaction time: 6 h. The selectivity is only based on the two major products A and B.

Catalyst Recycling Test: The recyclability tests of **1'** were carried out using acetonitrile as a solvent, and under "solvent-free" conditions; the results are summarized in Table S3 and S4. To demonstrate the heterogeneous nature of the catalyst, the following hot filtration experiment was performed: after reacting for 2h, the catalyst was removed from the reaction mixture by centrifugation and the resulting supernatant was allowed to react for an additional 4h without the catalyst. The results were summarized in Figure S9.

Table S3. Recyclability test of **1'** using acetonitrile as solvent.^a

Cycle	Conversion (%)	% Selectivity	
		A	B
1	70	70	30
2	83	59	41
3	84	58	42

4	82	59	41
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^a Styrene: 1 mmol; TBHP (5.5 M in decane), 2 mmol; catalyst (**1'**): 15 mg (2.5 mol%); Internal standard (chlorobenzene): 15 mmol; Solvent: acetonitrile (10 mL); Temperature: 75 °C; and Reaction time: 6 h. After each reaction cycle, the catalyst was re-weighed, and the amount of styrene and TBHP was scaled appropriately based on the mole of the catalyst in order to make the relative concentration of substrate to catalyst ratio the same in each cycle. The selectivity is only based on the two major products A and B.

Table S4. Recyclability test of **1'** under "solvent-free"^a conditions.^a

Cycle	Conversion (%)	% Selectivity	
		A	B
1	96	96	4
2	95	95	5
3	93	88	12
4	93	81	19

^a Styrene: 50 mmol; TBHP (5.5 M in decane), 100 mmol; catalyst (**1'**): 15 mg (0.05 mol%); Internal standard (chlorobenzene): 15 mmol; Temperature: 75 °C; and Reaction time: 6 h. After each reaction cycle, the catalyst was re-weighed, and the amount of styrene and TBHP was scaled appropriately based on the mole of the catalyst in order to make the relative concentration of substrate to catalyst ratio the same in each cycle. The selectivity is only based on the two major products A and B.

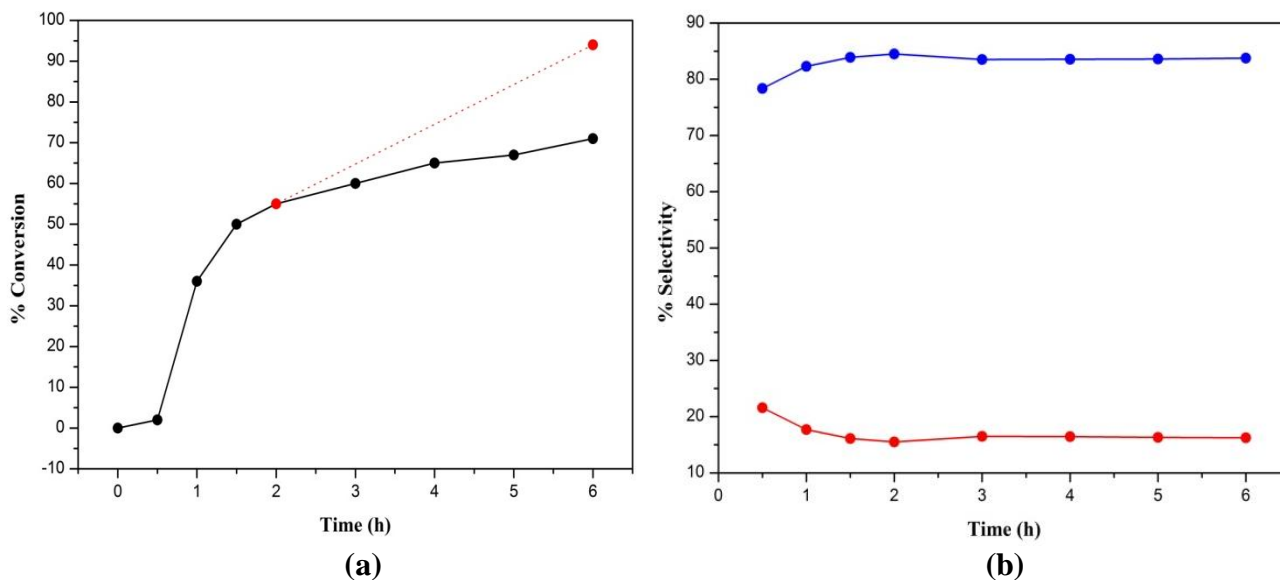


Figure S9. Test of heterogeneous nature of catalyst **1'**. (a) % conversion versus reaction time of epoxidation of styrene oxide catalyzed by **1'**. After 2 h, the catalyst was filtered off and the reaction continued. This has resulted in a substantial decrease in the rate of the reaction, indicating that catalyst **1'** is mainly responsible for the catalysis. (b) % selectivity versus reaction time epoxidation of styrene oxide catalyzed by **1'** (red: aldehyde and, blue: epoxide).

Table S5. Comparison of catalytic activity of **1'** with respect to Au₂₅-HAP, Au/SBA15 and Co(OOCC₆H₅)₂, previously reported catalysts for styrene epoxidation

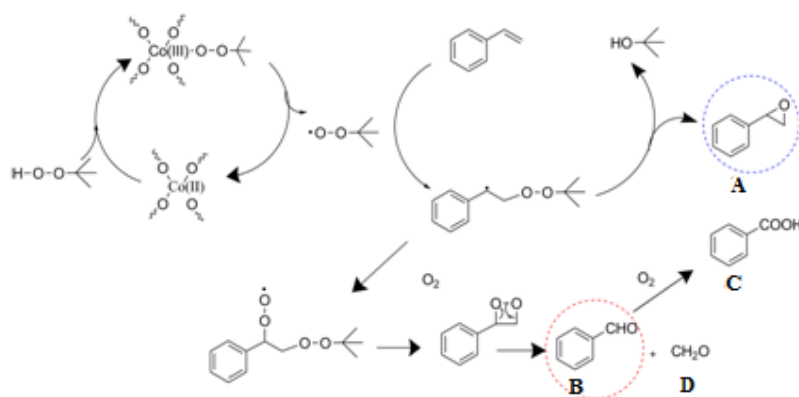
Entry	Catalyst	Conversion (%)	Selectivity (%)	
			A	B
1	1'	96	96	4
2	Au ₂₅ -HAP ²	100	92	8
3	Au/SBA15 ^{3,b}	98	96	NA
4	Co(OOCC ₆ H ₅) ₂ ^a	60	8	92

^a Styrene: 50 mmol; TBHP (5.5 M in decane), 100 mmol; Catalyst (Co(OOCC₆H₅)₂), 7.5 mg (0.05 mol%); Internal standard (chlorobenzene): 15 mmol; Temperature: 75 °C and Reaction time: 6 h. The selectivity is only based on the two major products A and B.

^b The substrate they used is 4-chlorostyrene.

Mechanism study:

To determine whether the reaction proceeds through radical intermediates, the presence of radicals in the reaction mixture was analyzed. 20 mmol styrene, 40 mmol oxidant (TBHP-5.5M in decane) and 15 mmol internal standard (chlorobenzene) were charged to a 50 mL three-neck round bottom flask and the solution was stirred with a magnetic stir bar. The reaction mixture was heated at 75 °C for 2h. 40 mmol of the radical scavenger butyl-hydroxyl-toluene (BHT) was then added to the reaction mixture and the reaction was allowed to continue for another 4 h. For the control reaction, the reaction was performed using the same procedure, minus the addition of BHT. The reaction was monitored by withdrawing aliquot samples at selected time intervals and analyzed by GC. The products were confirmed by GC-MS. In addition, pure oxygen and argon protected catalytic reactions were carried out under the same conditions and the results are summarized in Table S6 below. And the proposed mechanism is shown in Scheme S2.



Scheme 2. Proposed reaction mechanism of epoxidation catalyzed by **1**.

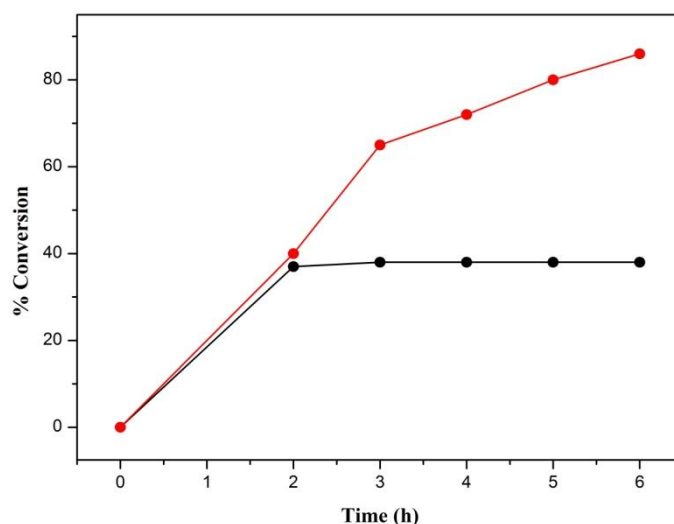


Figure S10. % conversion vs. time for comparison between reactions with radical scavenger (black) and control reaction without adding radical scavenger (red).

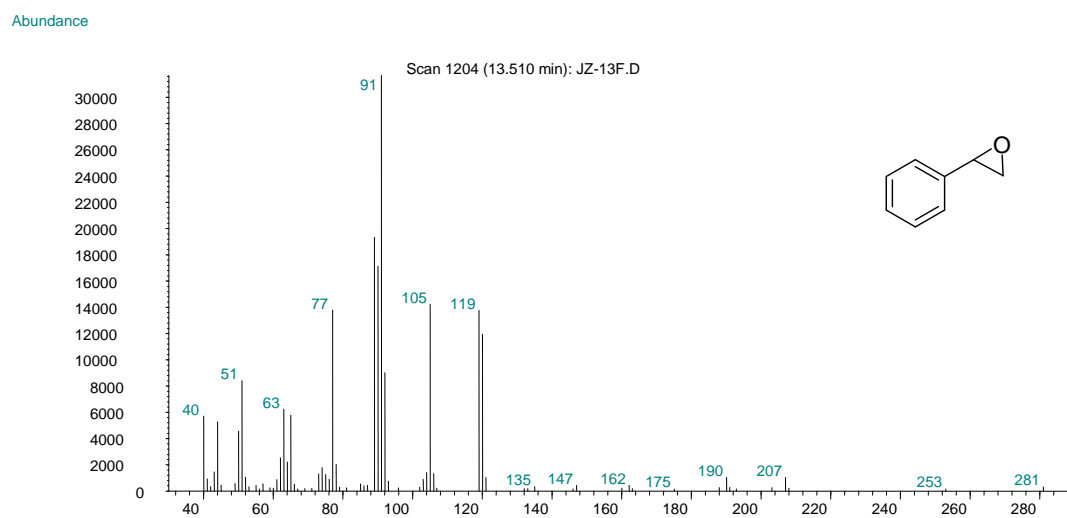
Table S6. Comparison of catalytic activity between pure oxygen environment and argon protected environment.^a

Entry	Environment	Conversion (%)	Selectivity (%)		
			A	B	C
1	Oxygen	100	33	25	42
2	Argon	56	96	4	0

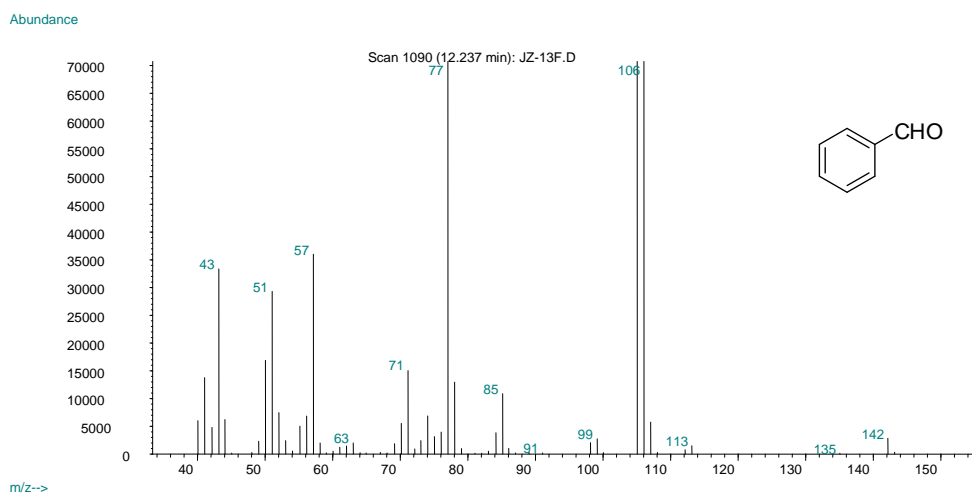
^a Styrene: 25 mmol; TBHP (5.5 M in decane): 50 mmol; catalyst (**1'**):15 mg (0.05 mol%); internal standard (chlorobenzene), 15 mmol ; temperature:75 °C; and Reaction time: 6 h. The selectivity of the reaction is based only on the major products, A, B and C.

GC-MS Spectra:

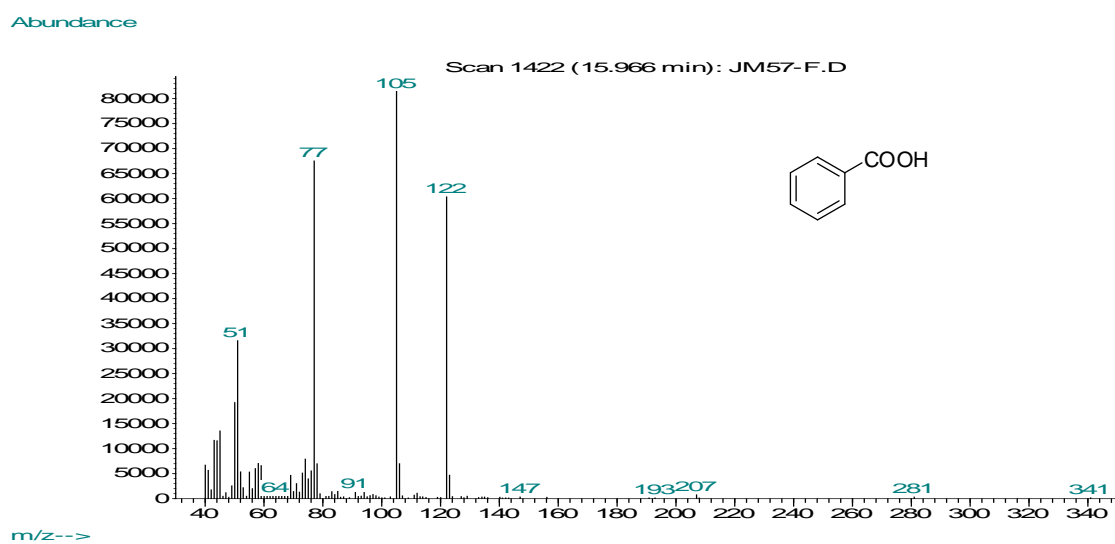
(A) Styrene oxide



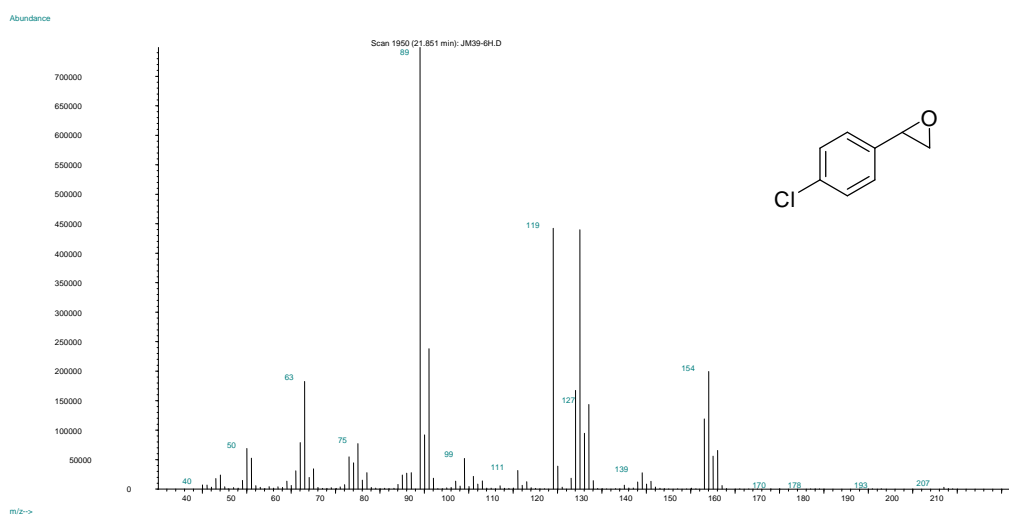
(B) Benzaldehyde



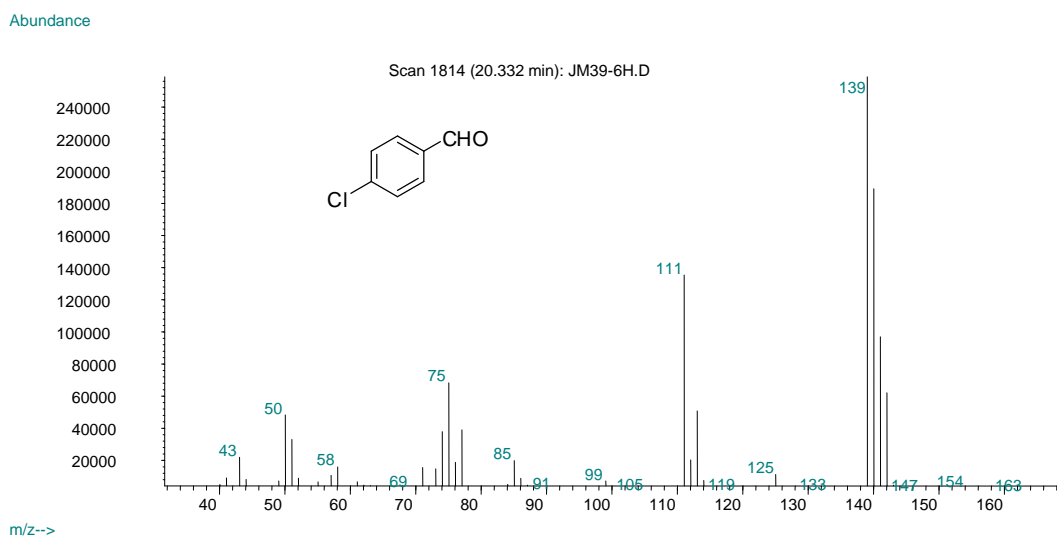
(C) Benzoic acid



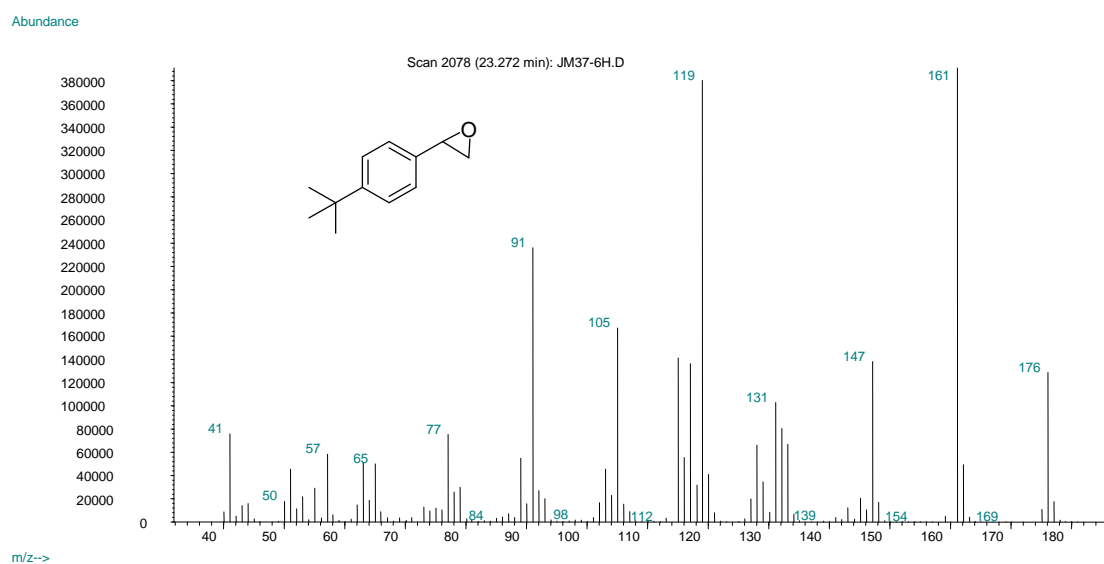
(D) 2-(4-chlorophenyl)oxirane



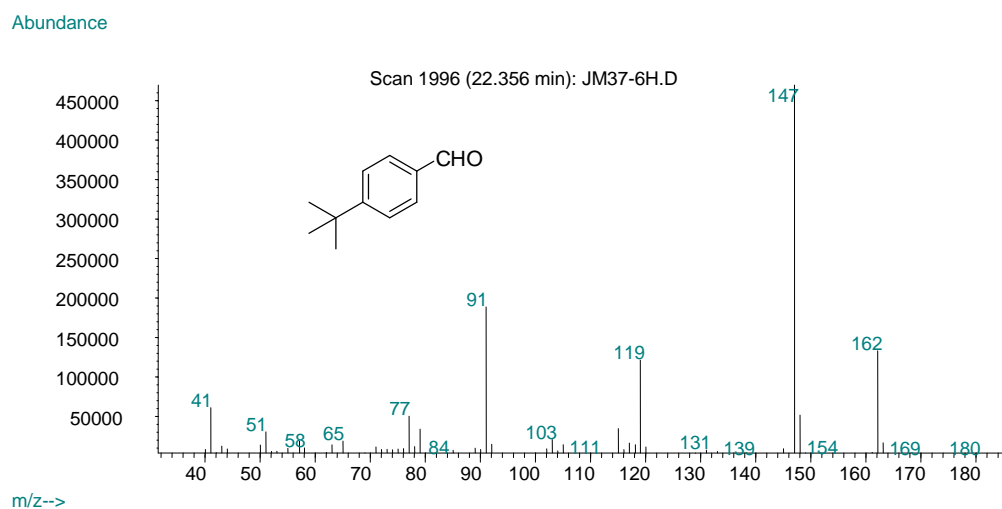
(E) 4-chlorobenzaldehyde



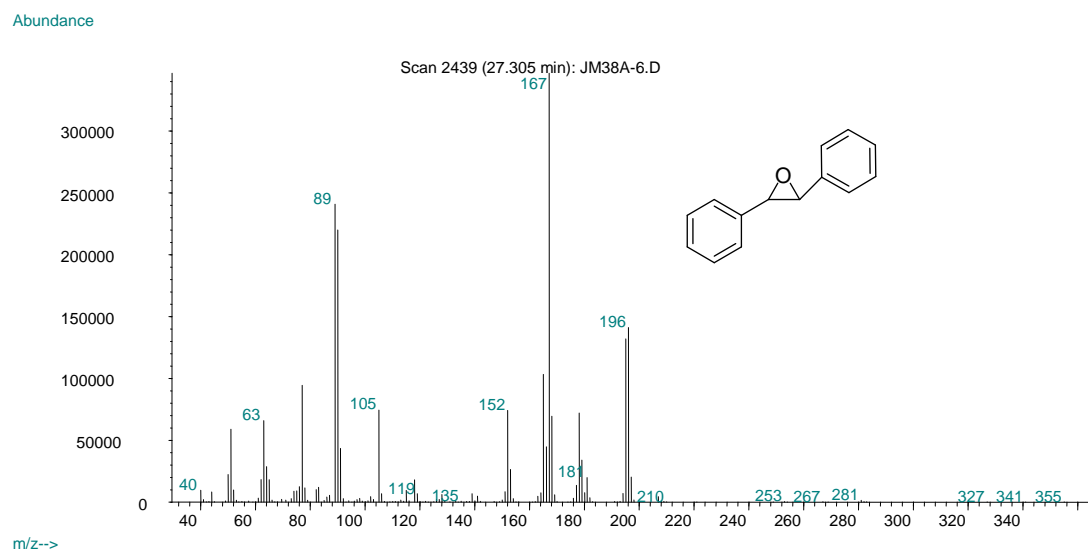
(F) 2-(4-tert-butylphenyl)oxirane



(G) 4-tert-butylbenzaldehyde



(H) 2,3-diphenyloxirane



(I) Ethyl 3-phenyl oxirane-2-carboxylate

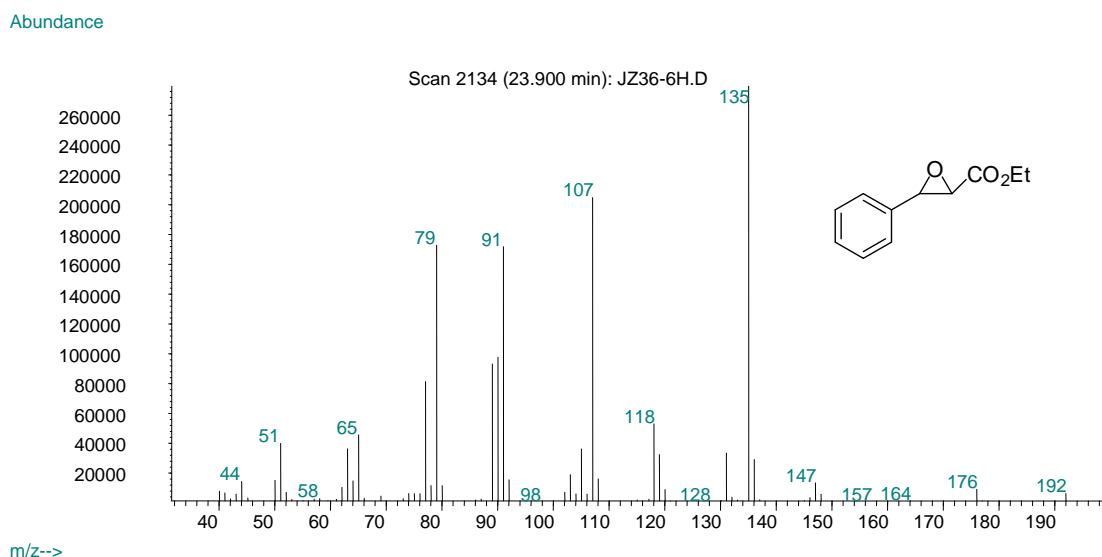


Figure S11. GC-MS spectra of selected products from Co-MOF catalyzed epoxidation reactions: (A) Styrene oxide, (B) Benzaldehyde, (C) Benzoic acid, (D) 2-(4-chlorophenyl)oxirane, (E) 4-chlorobenzaldehyde, (F) 2-(4-tert-butylphenyl)oxirane, (G) 4-tert-butylbenzaldehyde, (H) 2,3-diphenyloxirane and (I) Ethyl 3-phenyl oxirane-2-carboxylate.

IV. Crystal Structure Data

Crystal data of 1: C₂₈H₂₂CoO₁₂, FW = 609.39, triclinic, P-1: a = 6.5938(6), b = 7.3333(7), c = 25.306(2), α = 88.223(1)° β = 89.712(2)° γ = 89.770(2)°, V = 1223.1(2) Å³, Z = 2, D_c = 1.655 g cm⁻³, λ (Mo-K α) = 0.71073 Å, μ = 1.222. Measurements were made on a SMART CCD area detector at 100(2) K with graphite-monochromated Mo-K α radiation. A total of 15,498 reflections were collected (8044 unique, R(int) = 0.0288) between a θ of 2.42° to 31.62° (97.6% completeness). R1 = 0.0662 (I > 2 θ (I)), wR = 0.1785 (all data), and GOF = 1.033 (all data). Largest diff. Peak and hole 3.418 and -0.592e Å⁻³ (See SI for details). CCDC 807547 contains supplementary crystallographic data. These data can be

obtained free of charge from the Cambridge Crystallographic Data Centre via
 www.ccdc.cam.ac.uk/data_request/cif.

Table S7. Selected crystallographic data for **1**.

Empirical formula	C ₂₈ H ₂₂ Co O ₁₂	
Formula weight	609.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.5938(6) Å	α = 88.223(1)°
	b = 7.3333(7) Å	β = 89.712(2)°
	c = 25.306(2) Å	γ = 89.770(2)°
Volume	1223.1(2) Å ³	
Z	2	
Density (calculated)	1.655 Mg/m ³	
Absorption coefficient	0.774 mm ⁻¹	
F(000)	626	
Crystal size	0.20 x 0.11 x 0.05 mm ³	
Theta range for data collection	2.42 to 31.62°	
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -36 ≤ l ≤ 37	
Reflections collected	15498	
Independent reflections	8044 [R(int) = 0.0288]	
Completeness to theta = 31.62°	97.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9623 and 0.8605	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8044 / 0 / 391	
Goodness-of-fit on F ²	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0662, wR2 = 0.1667	
R indices (all data)	R1 = 0.0814, wR2 = 0.1785	
Largest diff. peak and hole	3.418 and -0.592 e.Å ⁻³	

Table S8. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å³ × 10³) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	5000	0	0	4(1)
Co(2)	0	5000	0	5(1)
O(1)	1184(3)	-3412(3)	-629(1)	12(1)
O(2)	4221(3)	-2469(2)	-357(1)	10(1)
O(3)	2559(3)	-5284(3)	-4899(1)	16(1)
O(4)	3803(3)	-7601(3)	-4400(1)	16(1)
O(5)	5099(3)	-1139(3)	-2844(1)	15(1)
O(6)	3841(3)	1589(2)	-633(1)	12(1)
O(7)	780(3)	2515(2)	-358(1)	10(1)
O(8)	-1298(3)	-2592(3)	-4361(1)	16(1)

O(9)	-2426(3)	-273(3)	-4876(1)	16(1)
O(10)	-45(3)	3980(2)	-2837(1)	14(1)
O(1W)	7783(3)	-99(3)	-380(1)	11(1)
O(2W)	-2769(3)	4914(2)	-378(1)	11(1)
C(1)	3498(4)	-2334(3)	-1285(1)	10(1)
C(2)	2099(4)	-2606(3)	-1687(1)	12(1)
C(3)	2627(4)	-2277(4)	-2211(1)	14(1)
C(4)	4585(4)	-1649(3)	-2332(1)	13(1)
C(5)	5985(4)	-1382(4)	-1939(1)	15(1)
C(6)	5444(4)	-1736(3)	-1412(1)	13(1)
C(7)	2903(4)	-2756(3)	-722(1)	9(1)
C(8)	3885(4)	-4660(3)	-4054(1)	10(1)
C(9)	3684(4)	-2770(3)	-4134(1)	12(1)
C(10)	4087(4)	-1607(3)	-3725(1)	12(1)
C(11)	4679(4)	-2347(3)	-3238(1)	11(1)
C(12)	4923(4)	-4221(3)	-3156(1)	14(1)
C(13)	4522(4)	-5376(4)	-3566(1)	13(1)
C(14)	3372(4)	-5884(3)	-4487(1)	11(1)
C(15)	1521(4)	2650(3)	-1285(1)	10(1)
C(16)	2940(4)	2430(3)	-1690(1)	12(1)
C(17)	2412(4)	2796(4)	-2214(1)	15(1)
C(18)	465(4)	3408(3)	-2328(1)	14(1)
C(19)	-980(4)	3603(4)	-1932(1)	15(1)
C(20)	-438(4)	3215(4)	-1409(1)	13(1)
C(21)	2114(4)	2232(3)	-724(1)	9(1)
C(22)	-1139(4)	365(3)	-4027(1)	10(1)
C(23)	-678(4)	-337(3)	-3524(1)	12(1)
C(24)	-286(4)	839(3)	-3115(1)	12(1)
C(25)	-336(4)	2709(3)	-3219(1)	10(1)
C(26)	-747(4)	3429(3)	-3723(1)	12(1)
C(27)	-1174(4)	2252(3)	-4124(1)	11(1)
C(28)	-1669(4)	-870(3)	-4456(1)	11(1)

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4. This reaction is said to be "solvent-free" to indicate that there is no additional solvent added into the reaction mixture other than decane in the TBHP solution.