Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Titanium−Oxide Cluster with Rutile Unit Doped Divalent Lead Ions for Efficient Photocatalytic Applications

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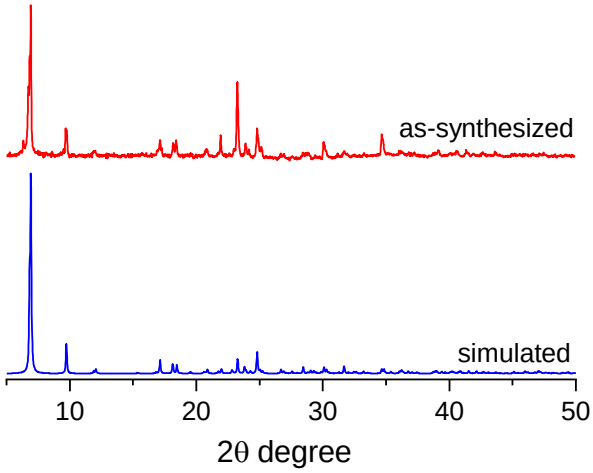


Fig. S1 Powder X-ray diffraction and simulated XRD pattern of $\mathbf{Ti_{12}Pb_2}$.

Discussion: The phase stability of $\mathbf{Ti_{12}Pb_2}$ was confirmed by powder XRD analysis. It can be seen from the PXRD spectra that the experimentally obtained PXRD data are consistent with the simulated spectra obtained from the crystal structure of $\mathbf{Ti_{12}Pb_2}$.

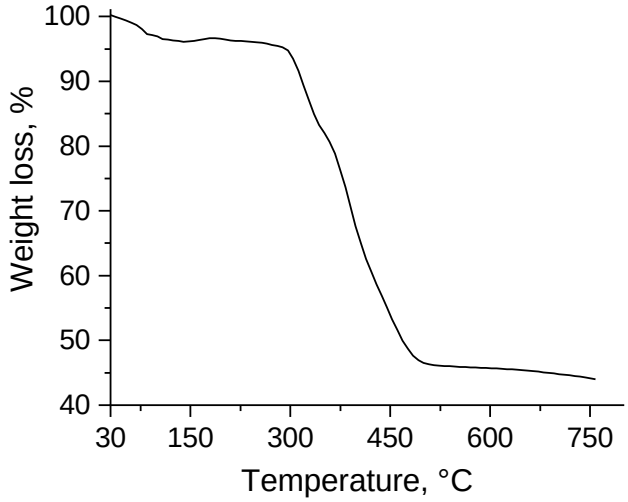


Fig. S2 Thermal decomposition analysis of crystalline $\mathbf{Ti_{12}Pb_2}$.

Discussion: Thermogravimetric analysis (TGA) of the crystalline sample revealed that the $\mathbf{Ti_{12}Pb_2}$ cluster structure could be preserved upto 430 °C, although some disordered ligand molecules might be lost before the cluster decomposition.

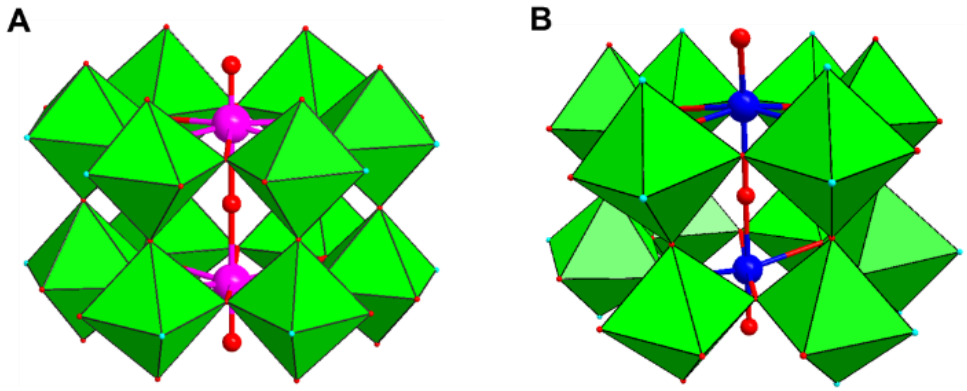


Fig. S3 Core structural of (**A**) **$Ti_{12}Pb_2$** and (**B**) **Ti_{14}**. Color scheme: green polyhedral, TiO_5N; purple, Pb; blue, Ti; red, O; and cyan, N. The ligands are omitted for clarity.

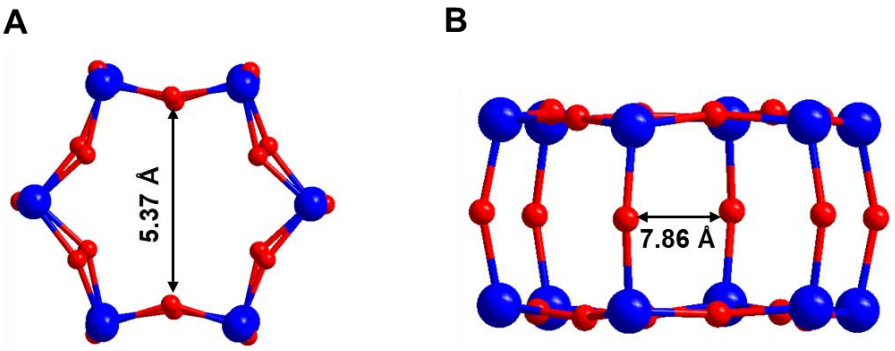
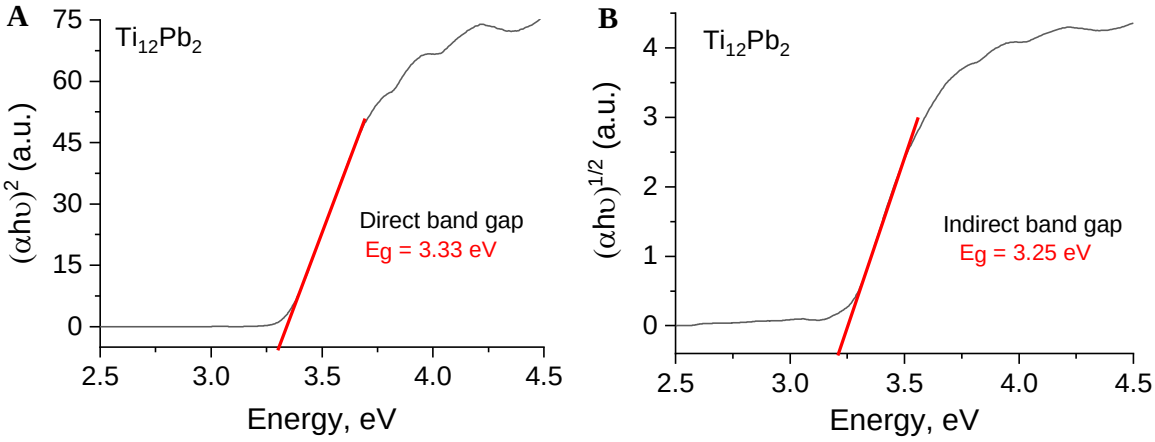


Fig. S4 Ball-and-stick view of the $Ti_{12}O_{18}$ framework. Color scheme: blue, Ti; and red, O.



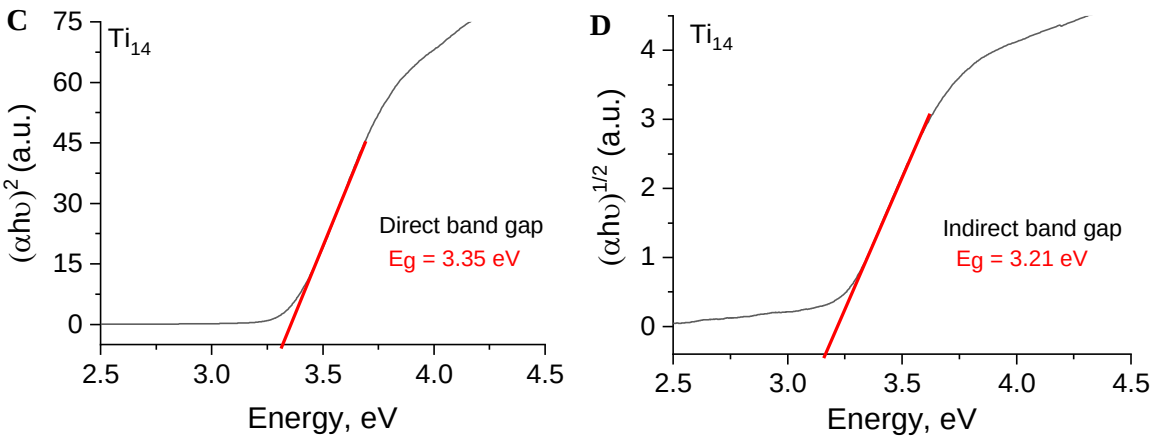


Fig. S5 Calculations of the direct and indirect bandgap energies values based on solid−state UV−vis diffuse reflectance spectra of **$Ti_{12}Pb_2$** and **Ti_{14}**.

Discussion: The Kubelka−Munk function for calculation of the bandgap:

$$(\alpha hv)^{1/n} = A(hv - E_g)$$

Here, α is the absorption coefficient, h is the Planck constant; v is frequency; A is constant; and Eg is the bandgap value of the semiconductor.

The index n is directly related to the type of semiconductor:

For direct bandgap: n = 1/2; for indirect bandgap: n = 2.

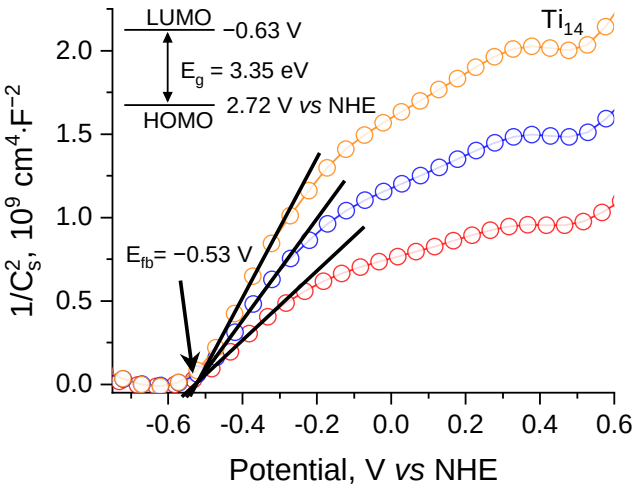


Fig. S6 The Mott−Schottky plot of **Ti_{14}** at different frequencies (the inset is the diagram of the HOMO−LUMO energy level).

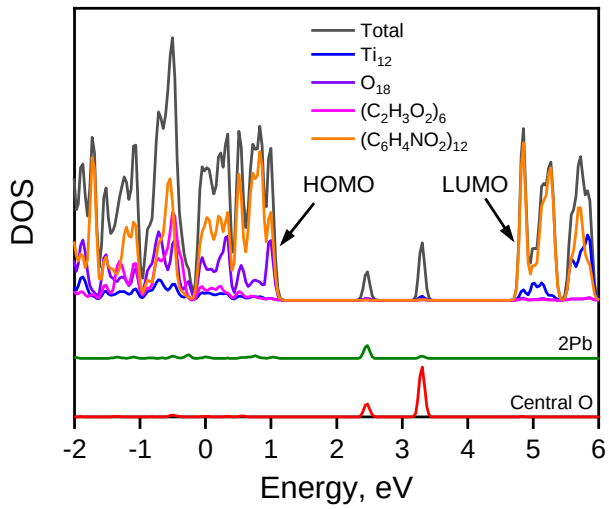
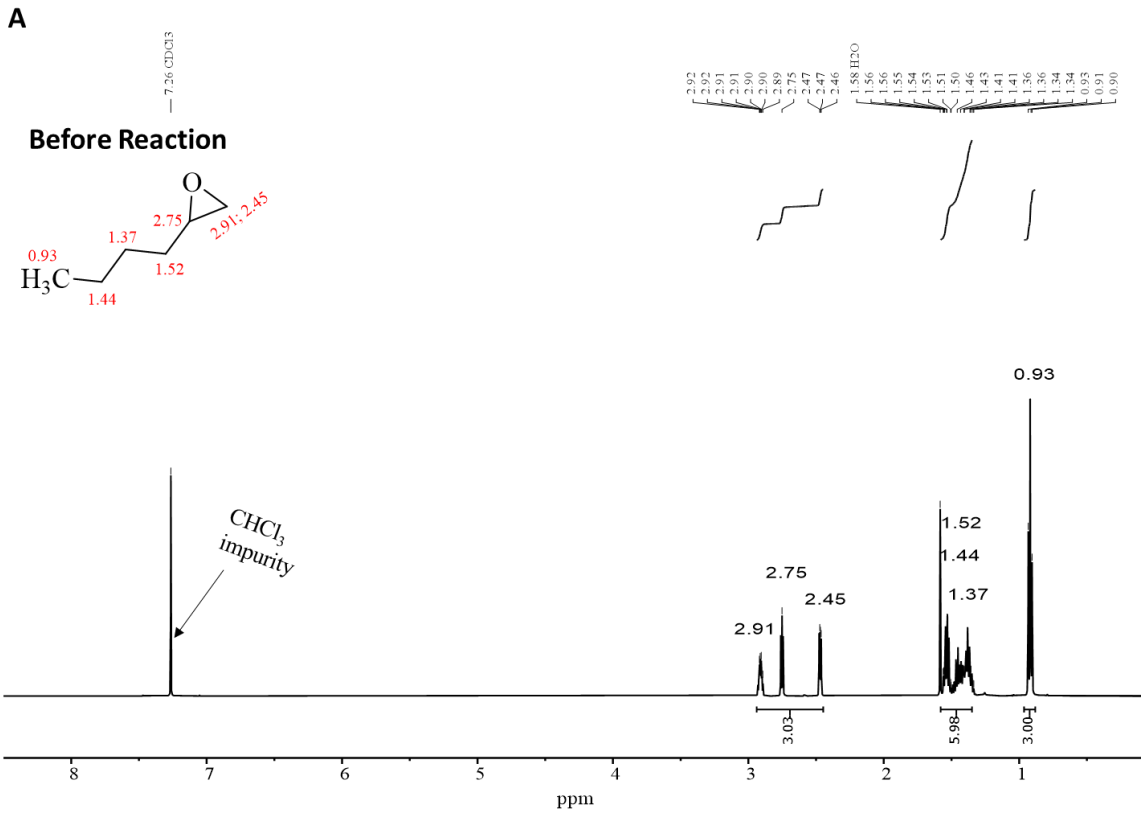


Figure S7. The density of state (DOS) plots of $\mathbf{Ti_{12}Pb_2}$.



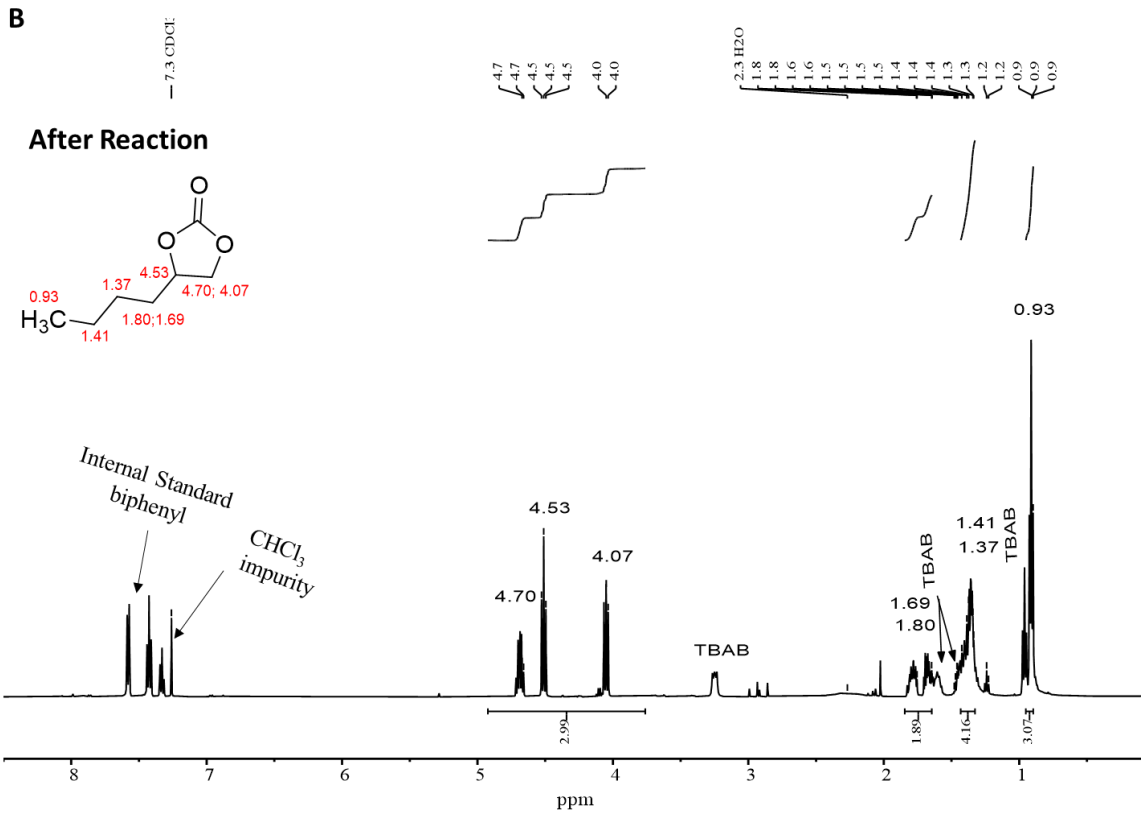


Fig. S8 ^{1}H NMR spectra of CO_2 cycloaddition to epoxide before and after the catalytic reaction.

Discussion: The ^{1}H NMR spectra were measured using an Avance−400 MHz NMR spectrometer (Bruker, Switzerland) at room temperature using chloroform−d as the deuterated solvent. The ^{1}H NMR spectra show that the epoxide at 2.45, 2.75 and 2.91 ppm were observed before the reaction (Figure S8A). After the reaction, the peaks of epoxide at 2.45, 2.75 and 2.91 ppm probably diminished along with the production of new broad peaks of cyclic carbonate at 4.07, 4.53 and 4.70 ppm (Figure S8B). It shows that epoxide conversion into cyclic carbonate approached near completion after 24 h under simulated light irradiation in CO_2 atm at 20 °C.

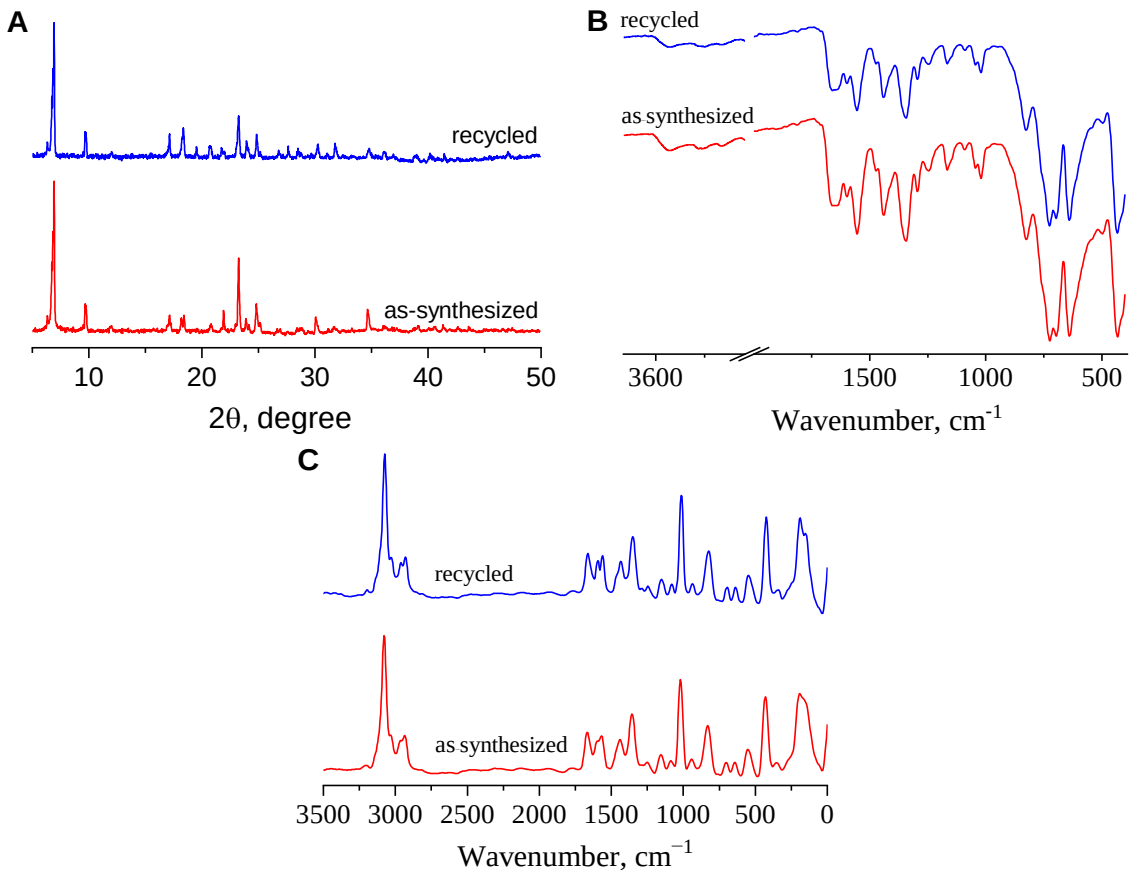


Fig. S9 (**A**) The PXRD patterns, (**B**) FTIR analysis, and (**C**) Raman analysis of the $\mathbf{Ti_{12}Pb_2}$ as-synthesized and recycled after photocatalytic CO_2 cycloaddition to epoxide.

Table S1 Comparison of various catalysts used for the CO_2 cycloaddition to epoxide.

Catalyst	Reaction conditions	Time, h	Conv., %	Yield, %	No. of substrate	References
$Ti_{12}Pb_2$	Catalyst (23 μmol); TBAB (0.5 mmol); epoxide (3 mmol); 1 atm CO_2; 20 ºC; simulated solar light.	24 h	100	>99	6	***This work***
$Ti_{12}Pb_2$	Catalyst (23 μmol); TBAB (0.5 mmol); epoxide (3 mmol); 1 atm CO_2; 80 ºC; simulated solar light.	4 h	100	>99	6	***This work***
Zn-NTTA	Catalyst (5 μmol); TBAB (0.3 mmol); epoxide (20 mmol); 10 bar CO_2; 100 ºC.	8 h	-	98.2	4	*ACS Appl. Mater. Interfaces*, **2016**, *8*, 31746-56.
Al–N_4–C	Catalyst (20 mmol); TBAB (0.8 mmol); epoxide (0.67 mmol); DMF; 1 bar CO_2; visible light.	60 h	-	80	5	*Adv. Mater.*, **2021**, *33*, 2103186.
MOF-801 (D)	Catalyst (0.6 mol%); TBAB (0.5 mol%); epoxide (19.2 mmol); 0.1 MPa CO_2; 80 °C.	15 h	92.4	92.4	5	*J. Mate. Chem. A*, **2022**, *10*, 10051–10061.
V_8-1	Catalyst (2 mol %); TBAB (0.5 mmol, 2.5 mol %); epoxide (28 mmol); CO_2 (0.5 Mpa); 70 °C.	16 h	-	>99	6	*J. Am. Chem. Soc.*, **2019**, *141*, 19487−19497.
Ni−TCPE1	Catalyst (10 μmol; based on Ni); epoxide (20 mmol); TBAB (0.3 mmol); CO_2 (1 MPa), 100 °C.	12 h	-	>99	4	*J. Am. Chem. Soc.*, **2015**, *137*, 15066−15069.
Mn-MOF	Catalyst (10 mg); TBAB (0.028 mmol); epoxide (1.429 mmol); 1 bar CO_2; visible-light; 80 °C.	24 h	-	90	6	*ACS Omega*, **2022**, *7*, 9958-9963.
PMo_{12}@Zr-Fc MOFs	catalyst (5 mg, 10.26 wt%); TBAB (0.25 mmol); epoxide (12.5 mmol); 1 atm CO_2; 80 °C; 900 rpm.	8 h	80	86.77	1	Appl. Catal. B, **2021**, *296*, 120329.
$CoPc/TiO_2$	Catalyst (100 mg); TBAB (0.1 mmol); epoxide (1.0 mmol); 1 bar CO_2; solvent (CH_3CN+MeOH); 20 W white cold LED, 25 °C.	24 h	96.7	94	7	*ACS Sustain. Chem. Eng.*, **2018**, *6*, 7799–7809.
Bi-PCN-224	Catalyst (30 mg); TBAB (0.5 mmol); epoxide (4.5 mmol); 1 bar CO_2; 300 W Xenon lamp.	6 h	>99	-	1	*ACS Catal.*, **2021,** *11*, 1988-1994.

$\{Cu_4[(C_{57}H_{32}N_{12})(COO)_8]\}_n$	Catalyst (0.2 mol%); TBAB (0.65 g, 10 mol %); CO_2 (1 atm); r.t.	48 h	-	96	4	*J. Am. Chem. Soc.*, **2016**, *138*, 2142−2145.
$Au_{19}Ag_4(S\text{-}Adm)_{15}$	Catalyst (5 mg); TBAB (10 mol%); epoxide (0.3 mmol); 3 ml solvent; 60 °C.	24 h	-	78	3	*Angew. Chem. Int. Ed.*, **2021**, *60*, 10573–10576.
IHEP-9	Catalyst (0.05 mmol); TBAB (0.5 mmol); epoxide (1 mmol); 1 bar CO_2; visible-light; r.t.	12 h	-	>99	5	*Inorg. Chem.*, **2021**, *60*, 651-659.
Zr-MOF	Catalyst (30 mg); TBAB (0.5 mmol); epoxide (4.5 mmol); 1 bar CO_2; Xe lamp; r.t.	6 h	>99	-	5	*ACS Catal*. **2021**, *11*, 1988.
$Ti_{18}Bi_4$	Catalyst (100 mg); TBAB (0.5 mmol); epoxide (3.0 mmol); 1 bar CO_2; Xe lamp, r.t.	14 h	100	>99	6	*ACS Catal.*, ***2022***, *12*, 8202−8213.
$BiNbO_4$/r-GO	Catalyst (50 mg); TBAB (9 mg); epoxide (100 μl); CO_2 (1.48 MPa); 353 K.	24 h	-	65	1	*ACS Sustain. Chem. Engin.*, **2020**, *8*, 12072-12079.
NUC-38Yb	Catalyst (0.5 mol %); TBAB (4 mol%); epoxide (20 mmol); CO_2 (1 atm); 60 °C.	10 h	-	96	8	*ACS Catal.*, **2021**, *11*, 14916−14925.