Supporting Information

Cu^{I}-Anchored Porous Covalent Organic Frameworks for Highly Efficient Conversion of Propargylic Amines with CO_2 from Flue Gas

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1. Materials and Methods

All starting materials and solvents were purchased from chemical reagent factory and used without further purification. Powder X-ray diffraction (PXRD) data were recorded by using a Bruker D8 Advance X-ray diffractometer at room temperature. The radiation used for diffraction was Cu Kα (α = 1.54 Å) and PXRD data were collected in the range of $2\theta = 2\text{-}40°$. Fourier transform infrared (FT-IR) spectra of the solid samples were collected on a Spectrum 400F spectrometer. All the data had been reported in wavenumber (cm^{-1}) scale. In order to analyze the thermal properties of the materials, thermogravimetric analysis (TGA) data were obtained on a STA449C under N_2 atmosphere from 50°C to 800°C along with a ramp rate of 10°C min^{-1}. Scanning electron microscopy (SEM) images were performed on a Hitachi SU8010 microscope operated at an accelerating voltage of 10.0kV. The nitrogen adsorption-desorption experiment was carried out on a ASiQwin Quantachrome instrument at 77 K. The samples were treated at 120°C for 12h before measurements. The surface area and pore size distribution were estimated from Brunauer–Emmett–Teller (BET) and non-local density functional theories (NLDFT), respectively. X-ray photoelectron spectra (XPS) in the region of O1s, N 1s, Cu2p were performed on an ESCALAB259Xi spectrometer. The ICP-MS of metal Cu was recorded on the Agilent 7700 spectrometer. Before measurement, the samples (10 mg) were soaked in concentrated nitric acid (10 mL) at 100 oC for 12 h. This solution was then diluted with deionised water and aqueous NaOH (3 M) to 100 mL (pH=5) and the metal content was analyzed.

Synthetic methods of TpBD-COF

A solution of 1,4-dioxane and mesitylene (1/4 v/v, 3 mL) was put into a 10 mL Pyrex tube, then 1,3,5-triformylphloroglucinol (Tp) (0.3 mmol, 63 mg) and [1,1'-Biphenyl] -4,4'-diamine (BD) (0.45 mmol, 82.9 mg) were added. The mixture was degassed and stirred at 120°C for 3 days in a sealed tube. The obtained solid was collected and washed with ethanol and tetrahydrofuran for three times, respectively. The product was dried at 100 °C for 24 h to get the corresponding TpBD (71 mg).

Synthetic methods of Cu^I-TpBD-COF

In order to introduce Cu^I ions into the pore walls of COF material, a mixture of

CuI(170 mg) and TpBD-COF (150 mg) of were put in a 50 mL round bottom flask, added 15 mL acetonitrile to reflux for 12 h in an N_2 atmosphere. The solid was washed with acetonitrile and acetone, and then immersed in DMSO for 48 h to eliminate the residual CuI. Finally, the dark brown powder Cu^I-TpBD-COF was obtained after drying at 60 °C for 12 h under vacuum.

General procedures for the synthesis of terminal propargylic amine

The corresponding amine (162 mmol) was placed in a three-necked flask, and propargylic bromide (3 mL, 27 mmol) was added to the amine via a constant pressure drop funnel at 0 °C, followed by stirring for 12 h at room temperature. The resulting mixture was then diluted with ethyl acetate, washed three times with saturated sodium bicarbonate solution, and dried with anhydrous sodium sulfate. The organic phase was concentrated and purified by petroleum ether: ethyl acetate (V/V=9:1) column chromatography to obtain the target product of pale yellow liquid.

The cycloaddition of CO_2 with propargylic amine catalyzed by Cu^I-TpBD-COF

Propargylic amine (0.5 mmol), DBU (0.5 mmol,76.12 mg) and Cu^I-TpBD-COF (5 mg) were successively added to a 10 mL Schlenk tube with 1mL acetonitrile. The Schlenk tube was placed in an oil bath and connected to a CO_2 balloon, then refluxed at 80 °C for 6 h. At the end of the reaction, the mixture was added with excess water; the organic phase was extracted with ethyl acetate, and then washed three times with saturated sodium chloride solution and water respectively. The target product was purified by petroleum ether: ethyl acetate (V/V=15:1) column chromatography.

2. Figures S1-13

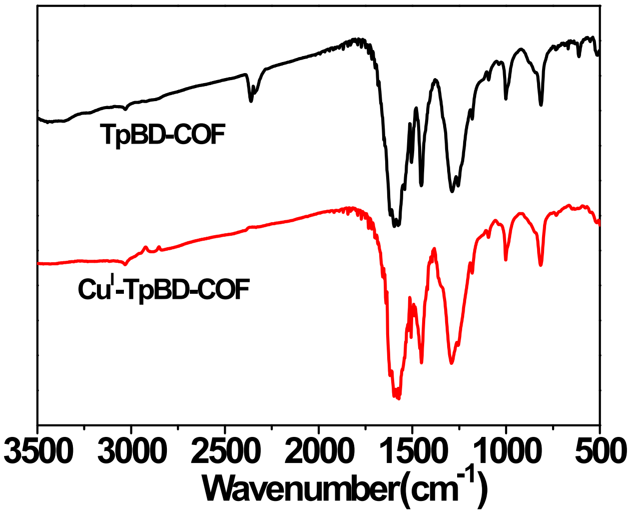

Figure S1. IR spectra of TpBD-COF and Cu^I-TpBD-COF.

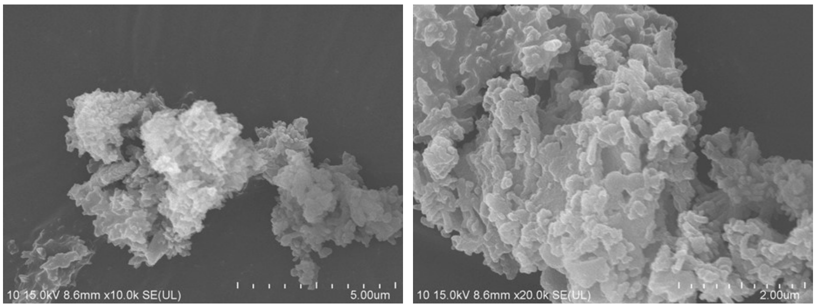

Figure S2. Scanning electron microscopy (SEM) images of TpBD-COF.

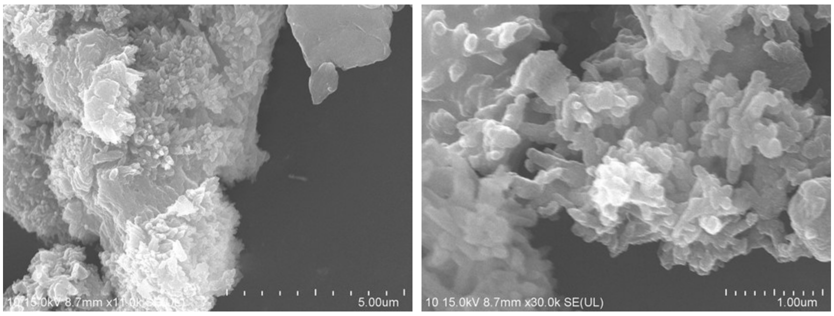

Figure S3. Scanning electron microscopy (SEM) images of Cu^I-TpBD-COF.

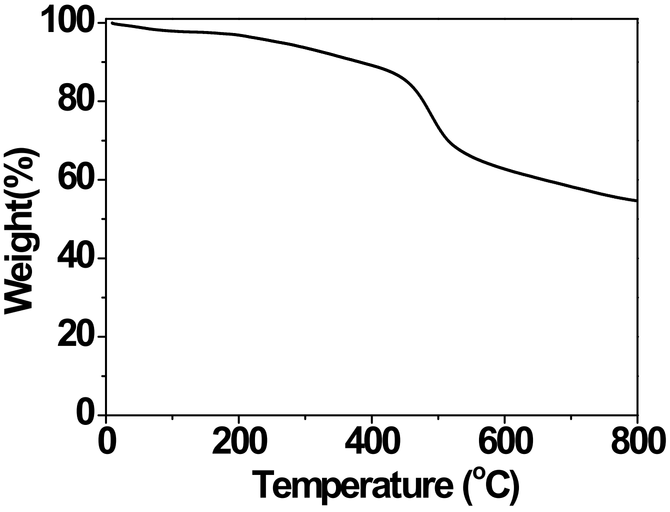

Figure S4. Thermo gravimetric analysis curve of TpBD-COF.

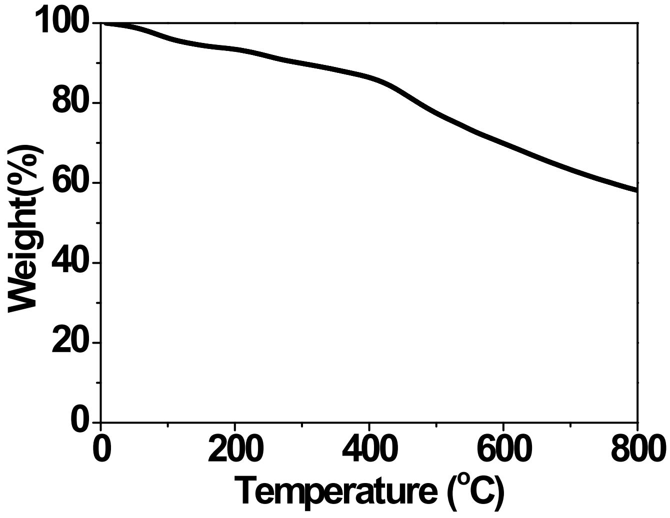

Figure S5. Thermo gravimetric analysis curve of Cu^I-TpBD-COF. The initial drop at 50-100 °C corresponds to the loss of residual solvents.

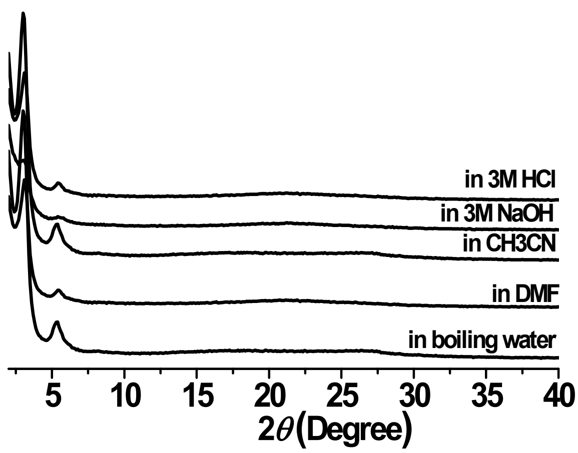

Figure S6. PXRD patterns of Cu^I-TpBD-COF treated with different solvents.

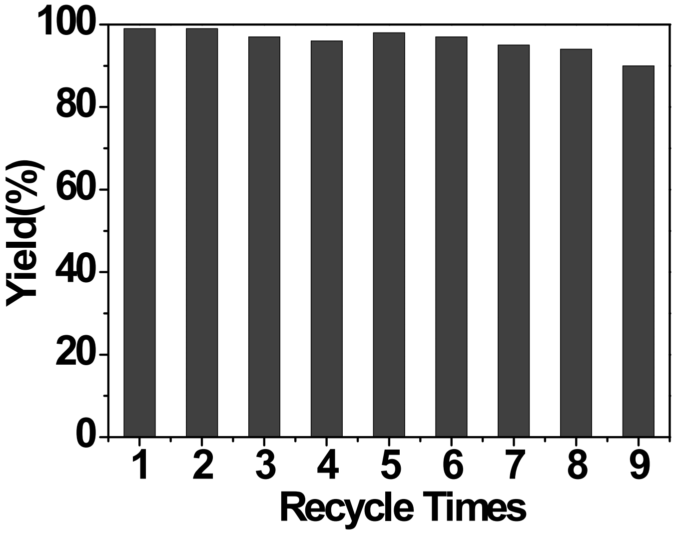

Figure S7. Cycling performance of Cu^{I}-TpBD-COF for catalyzing the reaction of CO_2 and propargylamine 1a.

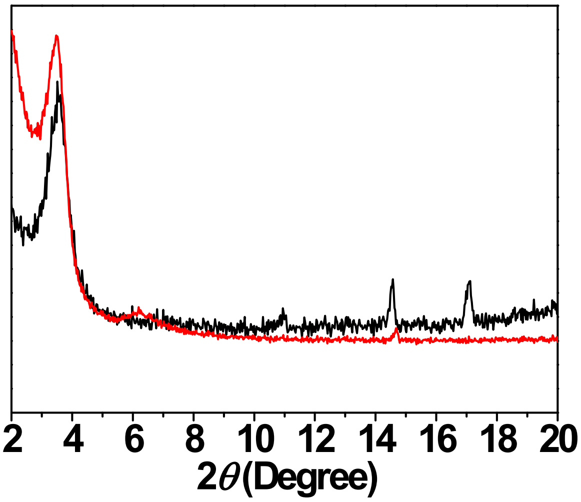

Figure S8. PXRD patterns of Cu^{I}-TpBD-COF before (red line) and after recycle 9 times (balck line).

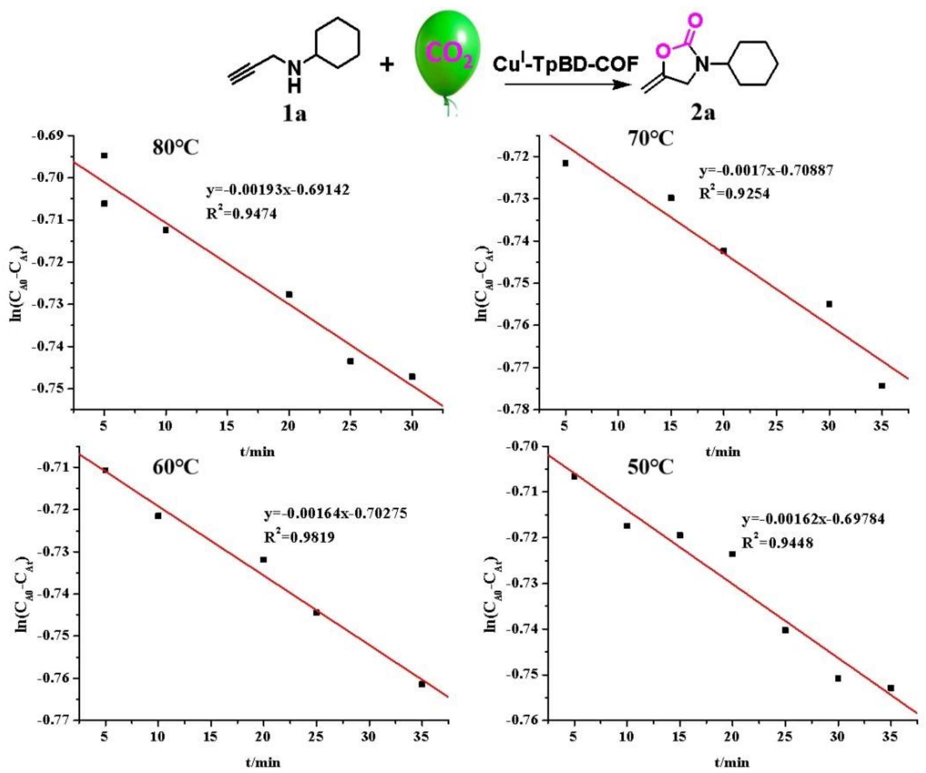

Figure S9. Linear relationship between reactant 1a concentration and reaction time at different reaction temperatures. Reaction conditions: Cu^{I}-TpBD-COF (5 mg), DBU (0.5 mmol), 1a (0.5 mmol), CO_2 balloon, carried out in acetonitile (1 mL).

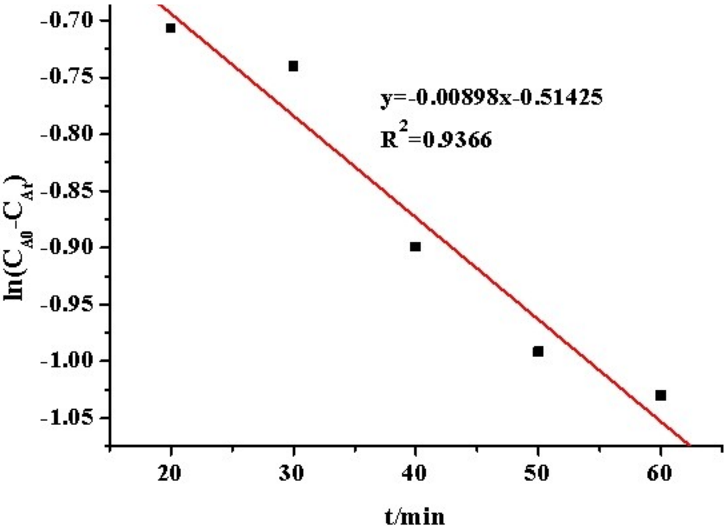

Figure S10. Linear relationship between reactant 1h concentration and reaction time. Reaction conditions: 1 h (0.5 mmol), Cu^{I}-TpBD-COF (5 mg), DBU (0.5 mmol), CO_2 balloon, carried out in acetonitile (1 mL) at 80 °C.

Figure S11. Linear relationship between reactant 1h-*d* concentration and reaction time. Reaction conditions: 1 h-*d* (0.5 mmol), Cu^{I}-TpBD-COF (5 mg), DBU (0.5 mmol), CO_2 balloon, carried out in acetonitile (1 mL) at 80 °C.

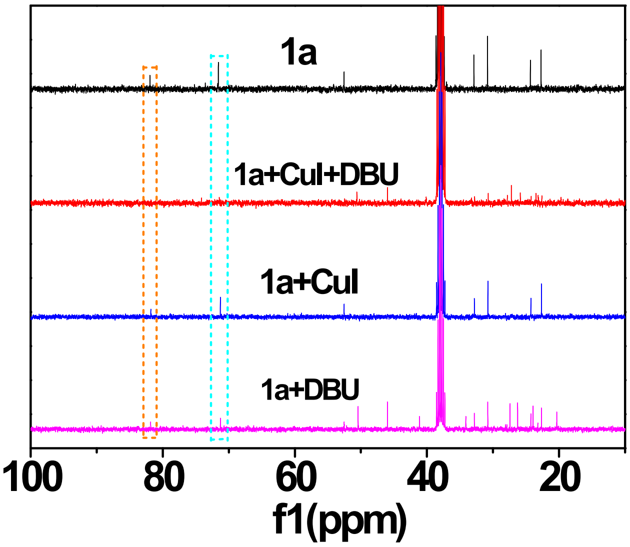

Figure S12. The ^{13}C NMR spectra for the activation of C≡C of substrate in different reaction systems.

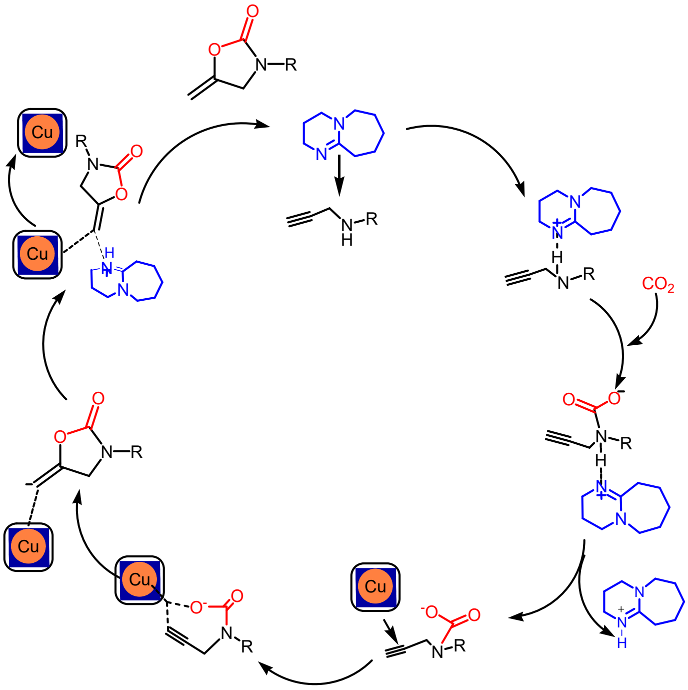

Figure S13. The potential reaction pathway for the cyclization reaction of CO_2 with propargylamine catalyzed by Cu^I-TpBD-COF.

3.Tables S1-2

Table S1. The comparison of the TOF with other catalysts.

Catalyst	Solvent	T(°C)	*P* (atm)	*t* (h)	TOF (h^{-1})	Reference
Cu^I-TpBD-COF	MeCN	80	1	6	1058	*This work*
Cu-based MOF **1**	--	30	1	0.17	230	1
[Ru]/PPh_3	Toluene	100	50	8	10	2
$Pd(OAc)_2$	Toluene	20	40	24	58	3
AgCl(IPr)	CH_3OH	40	1	15	3	4
CuI	DMSO	50	1	4	2.4	5
Bu_4NF	t-BuOH	110	5	12	8.3	6
TOS-Ag_8	MeCN	RT	1	24	4.1	7
TMOF-$_3$-Ag	DMSO	50	1	6	1.7	8
NiBDP-AgS	DMSO	60	1	4	49.5	9
MOF-1a	MeCN	60	5	24	10.3	10
Fe_4O_3/[Au]	H_2O	RT	15	12	1.2	11
CAT3	DMSO	60	1	10	0.8	12
HPG@[Au]	H_2O	RT	15	48	1.9	13
Ag-MOF-1	MeCN	RT	1	24	0.6	14
Ag@COF	--	40	1	2	41.8	15
Pd@BBA-2	DMSO	40	1	2	43.7	16
Cu-MC30	DMSO	40	1	20	0.2	17
Ag-HMP-2	MeCN	60	1	20	10.6	18
Cd-Bpy-COF	MeCN	60	1	2	6.9	19
Ag_4 NC	MeCN	25	1	2	2873.1	20

Table S2. The first order reaction rate constant *k* and the fitted correlation coefficient at different reaction temperatures for cyclization reaction of substrate 1a and CO_2.

T/°C	*k*/min^{-1}	R^2
50	0.00162	0.9448
60	0.00164	0.9819
70	0.00170	0.9254
80	0.00193	0.9474

4. Reference

[1] X. Jiang, Y. Jiao, S. Hou, L. Geng, H. Wang, B. Zhao, *Angew. Chem. Int. Ed*. 2021, 60, 20417– 20423.

[2] T. aki Mitsudo, Y. Hori, Y. Yamakawa, Y. Watanabe, *Tetrahedron Lett*., 1987, 28, 4417–4418.

[3] M. Shi, Y. M. Shen, *J. Org. Chem*., 2002, 67, 16–21.

[4] S. Hase, Y. Kayaki, T. Ikariya, *Organometallics*, 2013, 32, 5285–5288.

[5] Y. Zhao, J. Qiu, L. Tian, Z. Li, M. Fan, J. Wang, *ACS Sustain. Chem. Eng*., 2016, 4, 5553–5560.

[6] A. Fujii, J. C. Choi, K. ichi Fujita, *Tetrahedron Lett.*, 2017, 58, 4483–4486.

[7] Z. Chang, X. Jing, C. He, X. Liu, C. Duan, *ACS Catal*., 2018, 8, 1384–1391.

[8] G. Zhang, H. Yang, H. Fei, *ACS Catal*., 2018, 8, 2519–2525.

[9] H. Yang, X. Zhang, G. Zhang, H. Fei, *Chem. Commun*., 2018, 54, 4469–4472.

[10] D. Zhao, X. H. Liu, C. Zhu, Y. S. Kang, P. Wang, Z. Shi, Y. Lu, W. Y. Sun, *ChemCatChem*, 2017, 9, 4598–4606.

[11] S. M. Sadeghzadeh, *Appl. Organomet. Chem*., 2016, 30, 835–842.

[12] B. Yu, D. Kim, S. Kim, S. H. Hong, *ChemSusChem*, 2017, 10, 1080–1084.

[13] S. M. Sadeghzadeh, *J. Mol. Catal. A Chem*., 2016, 423, 216–223.

[14] X. Wang, Z. Chang, X. Jing, C. He, C. Duan, *ACS Omega*, 2019, 4, 10828–10833.

[15] S. Ghosh, T. S. Khan, A. Ghosh, A. H. Chowdhury, M. A. Haider, A. Khan, S. M. Islam, *ACS Sustain. Chem. Eng*., 2020, 8 (14), 5495–5513.

[16] S. Ghosh, S. Riyajuddin, S. Sarkar, K. Ghosh, S. M. Islam, *ChemNanoMat*, 2020, 6, 160–172.

[17] N. K. Kim, H. Sogawa, T. Takata, T*etrahedron Lett*., 2020, 61, 151966.

[18] S. Ghosh, A. Ghosh, S. Riyajuddin, S. Sarkar, A. H. Chowdhury, K. Ghosh, S. M. Islam, *ChemCatChem* 2020, 12, 1055–1067.

[19] Y. Zhang, H. Li, X. He, A. Wang, G. Bai, X. Lan, *Green Chem*., 2023, 25,5557.

[20] L. Li, Y. Lv, H. Sheng, Y. Du, H. Li, Y. Yun, Z. Zhang, H. Yu, M. Zhu, *Nat. Commun*., 2023, 14, 6989.