Electronic Supplementary Material (ESI) for Green Chemistry.

Noble metal-free Cu(I)-anchored NHC-based MOF for highly recyclable fixation of CO_2 under RT and atmospheric pressure conditions

Rajesh Das and C. M. Nagaraja*

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001,

Punjab, India. Tel: 91-1881-242229. Email: cmnraja@iitrpr.ac.in

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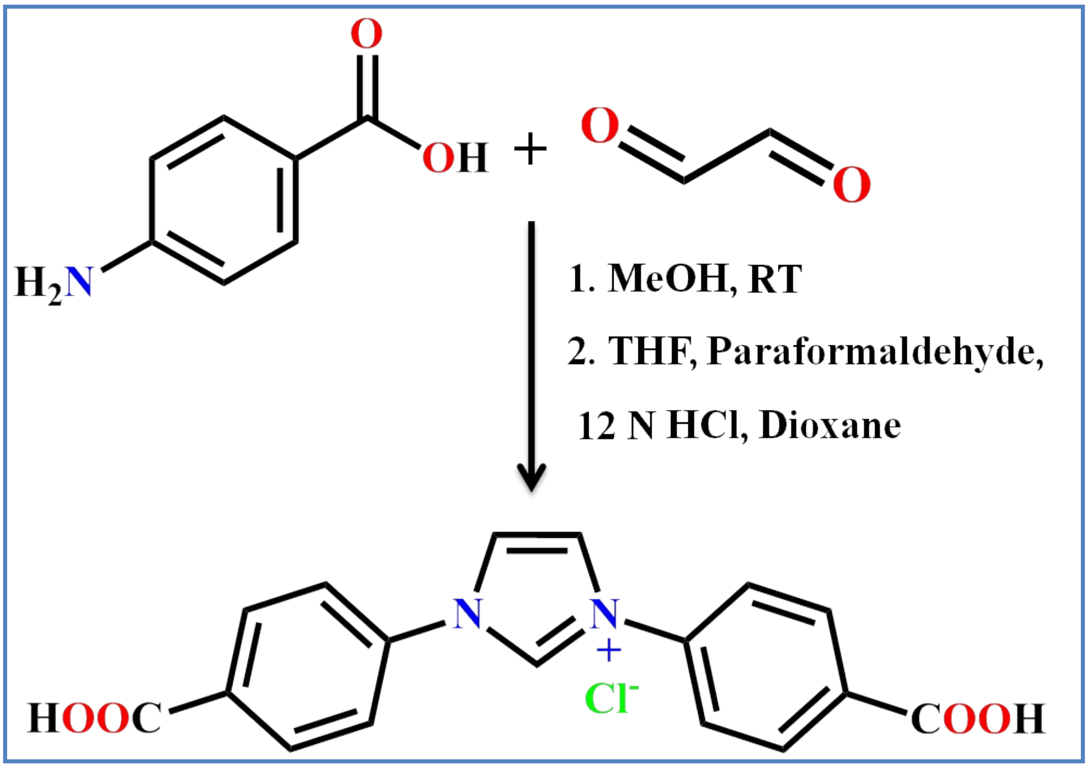
Materials and methods

All reagents used in this study were commercially available and used as received without further purification. $Zn(NO_3)_2.H_2O$, CuCl, 4-aminobenzoic acid and propargylic alcohols were purchased from Sigma Aldrich Chemical Co. The phase-purity of the MOF samples was confirmed by powder XRD analysis, recorded on a PANalytical's X'PERT PRO diffractometer using CuK_α radiation (k = 1.542 Å; 40 kV, 20 MA). Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Perkin Elmer FTIR spectrometer. UV−Vis (Diffuse Reflectance) spectra were recorded on a Shimadzu spectrophotometer using $BaSO_4$ as reference. The metal content of Zn and Cu in the framework was determined by Agilent's microwave-plasma atomic emission spectrometer (MP-AES). The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo Fisher Scientific NEXSA photoemission spectrometer using Al Kα (1486.6 eV) X-ray radiation, and analysis of the obtained data was performed using advantage software. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-ECS400 spectrometer operating at a frequency of 400 MHz and 100 MHz, respectively.

Experimental section

Synthesis of 1,3-bis(4-carboxyphenyl)imidazolium chloride ($H_2L^+Cl^-$)

The 1,3-bis(4-carboxyphenyl)imidazolium chloride ($H_2L^+Cl^-$) ligand was synthesized by following previous literature with slight modification.[1] Briefly, 4-aminobenzoic acid (5 g, 2.0 equiv.) was dissolved in methanol (15 mL) followed by the addition of 2 drops of formic acid and 40% aqueous solution of glyoxal (2.5 mL, 1.0 equiv.) and the solution was stirred at ambient temperature for 24 h. The white solid formed was collected by filtration, washed with cold methanol, and dried in air (Compound L1). The compound L1 (1 g), was dissolved in anhydrous THF (10 mL) under an inert atmosphere followed by the addition of a solution of paraformaldehyde (125 mg) in 12 N HCl (400 microlitter) in dioxane (1 mL) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The light pink precipitate formed was collected by filtration, washed with Et_2O, and dried under vacuum. Yield: 70%.



Scheme S1. Synthesis of 1,3-bis(4-carboxyphenyl)imidazolium chloride ($H_2L^+Cl^-$).

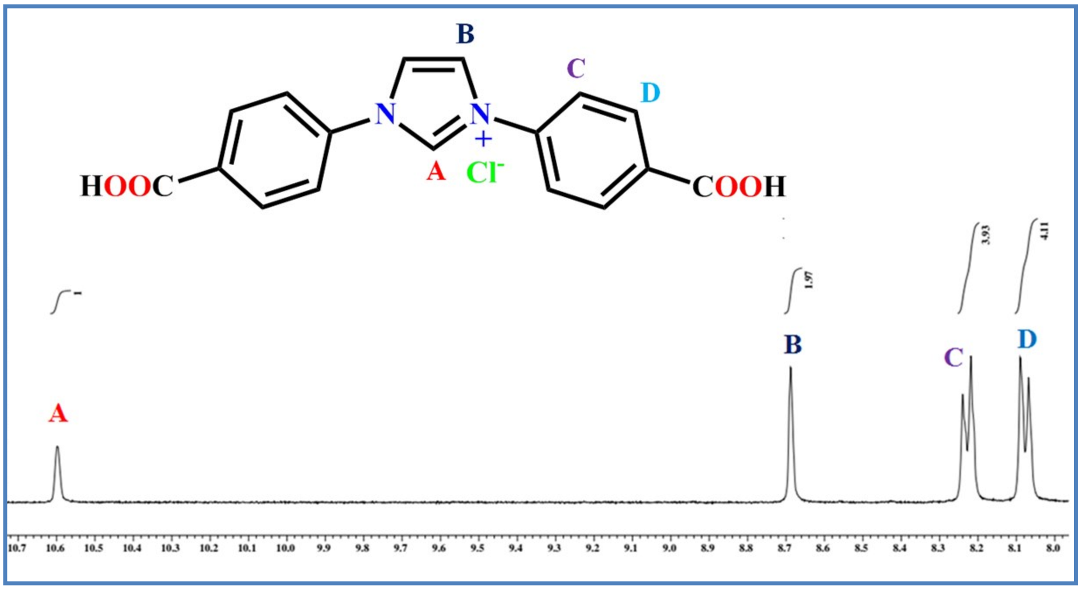


Figure S1. ${}^1H$ NMR of 1,3-bis(4-carboxyphenyl)imidazolium chloride ($H_2L^+Cl^-$).

Synthesis of NHC-MOF

The NHC-MOF was synthesized by following the procedure reported before with a slight modification.[1] Briefly, $Zn(NO_3)\cdot 6H_2O$ (2.0 mmol, 0.5950 g) and $H_2L^+Cl^-$ (0.5 mmol, 0.1724 g) were dissolved by 3 mL dry DMF solvent in a 50 mL Teflon-lined autoclave. Then it was heated under autogenous pressure to 120 °C for 48 h followed by cooling to ambient temperature slowly. The as-synthesized sample was collected by filtration, washed with DMF and dried under vacuum at 120 °C overnight. Yield: 42%. The phase purity of NHC-MOF was confirmed by PXRD analysis (Figure 1a). FTIR (cm^{-1}) : 3088 (m), 1650 (w), 1608 (s), 1541 (s), 1380 (s) (Figure S3). Elemental analysis for NHC-MOF, calculated for $[Zn_8(L)_{12}(H_2O)_{29}(DMF)_{69}(NO_3)_2]_n$: C: 49.74, H: 7.08, N:13.41 and found C: 49.02, H: 6.28, N: 12.85.

Synthesis of Cu(I)@NHC-MOF

CuCl (0.05 mmol, 5 mg) was dissolved by 10 mL dry methanol and NHC-MOF (0.01 mmol, 48.8 mg) was added to it. The resulting reaction mixture was stirred at 60 °C for 30 min under an inert atmosphere. Then the mixture was cooled down to room temperature and washed by DMA and methanol thoroughly, dried under vacuum at 80 °C for 12 h. The phase purity of Cu(I)@NHC-MOF was confirmed by PXRD analysis (Figure 1a). FTIR (cm^{-1}) : 3085 (w), 1606 (s), 1382 (s), 1257 (m) (Figure S3). Elemental analysis for Cu(I)@NHC-MOF, Calculated for $[Zn_8Cu_4(L)_{12}(H_2O)_{29}(DMF)_{69}Cl_4]_n$: C: 49.03, H: 6.94, N: 12.25 and found C: 48.36, H: 6.14, N: 11.97.

Gas adsorption measurements

Gas adsorption measurements of the samples were performed on a Quantachrome's QUADRASORB-SI automatic volumetric instrument using ultrapure (99.995%) N_2, O_2 and

CO_2 gases. Prior to adsorption measurements, the MOF sample (~ 0.10 g) was activated by heating at 120 °C under vacuum (18 mTorr) for 24 h. N_2 adsorption measurements are carried out at 77K and CO_2 adsorption measurements were done at 273 K and 298K. The temperatures, 273 and 298 K were achieved by using a water chiller with appropriate coolants. Whereas 77 K was achieved by using liquid nitrogen and the dead volume of the sample cell was determined using He gas (99.995%).

Catalytic cycloaddition reactions of CO_2 with propargylic alcohols

Catalytic cyclic carboxylation reactions of alkyne molecules (propargylic alcohols) and primary amines with CO_2 were carried out in a Schlenk tube (50 mL) under RT and 1 atm CO_2 (balloon). Before catalytic reactions, the catalyst was activated at 120 °C under vacuum for 24 h to remove guest solvent molecules. The MOF catalyst (0.005 mmol), propargylic alcohol (4 mmol), DBU (0.05 equiv.) in 2 mL of DMF were taken in the Schlenk tube at RT, CO_2 was introduced using a balloon and the contents were stirred at RT. After 12 h, the catalyst was separated from the reaction mixture by filtration and the catalytic conversions were determined by ^1H NMR spectra of the filtrate using $CDCl_3$ solvent. The recovered catalyst was washed with methanol thoroughly and activated at 120 °C under vacuum for 24 h and reused for subsequent catalytic cycles.

Analysis of gas adsorption isotherms

Clausius-Clapeyron Equation[2] was used to calculate the enthalpies of carbon dioxide adsorption and by using Langmuir Freundlich equation[3] an accurate fit was retrieved which gives a precise prediction of carbon dioxide adsorbed at saturation. A modified Clausius-Clapeyron equation was used for calculations.

$$ln(P1/P2) = \Delta H_{ads}(T2 - T1/R.T1.T2) \text{.......}(1)$$

where P_1 and P_2 = Pressures for isotherm at 273K and 298K, respectively.

T_1 and T_2 = Temperatures for isotherm at 273K and 298K, respectively.

ΔH_{ads} = Enthalpy of adsorption.

R = Universal gas constant = 8.314 J/K/mol.

The pressure is a function of the amount of gas adsorbed which was determined by using the Langmuir-Freundlich fit.

$$Q/Q_m = B.P^{(1/t)}/1 + (B.P^{(1/t)}) \quad \ldots\ldots\ldots (2)$$

where Q = moles of gas adsorbed.

Q_m = moles of gas adsorbed at saturation.

B and t = constants.

P = Pressure.

By rearranging equation (2) we get equation (3)

$$P = [(Q/Q_m)/\{B - (B.(Q/Q_m)\}]^t \quad \ldots\ldots\ldots(3)$$

Substituting equation (3) into equation (1) we get

$$\Delta H_{ads} = \{R.T1.T2/(T2 - T1)\}.ln\frac{[(Q/Q_{m1})/\{B - (B.Q/Q_{m1})\}]^{t1}}{[(Q/Q_{m2})/\{B - (B.Q/Q_{m2})\}]^{t2}} \quad \ldots\ldots\ldots(4)$$

In equation (4), subscript 1 and 2 are representing data corresponding to 273K and 298K in case of carbon dioxide gas.

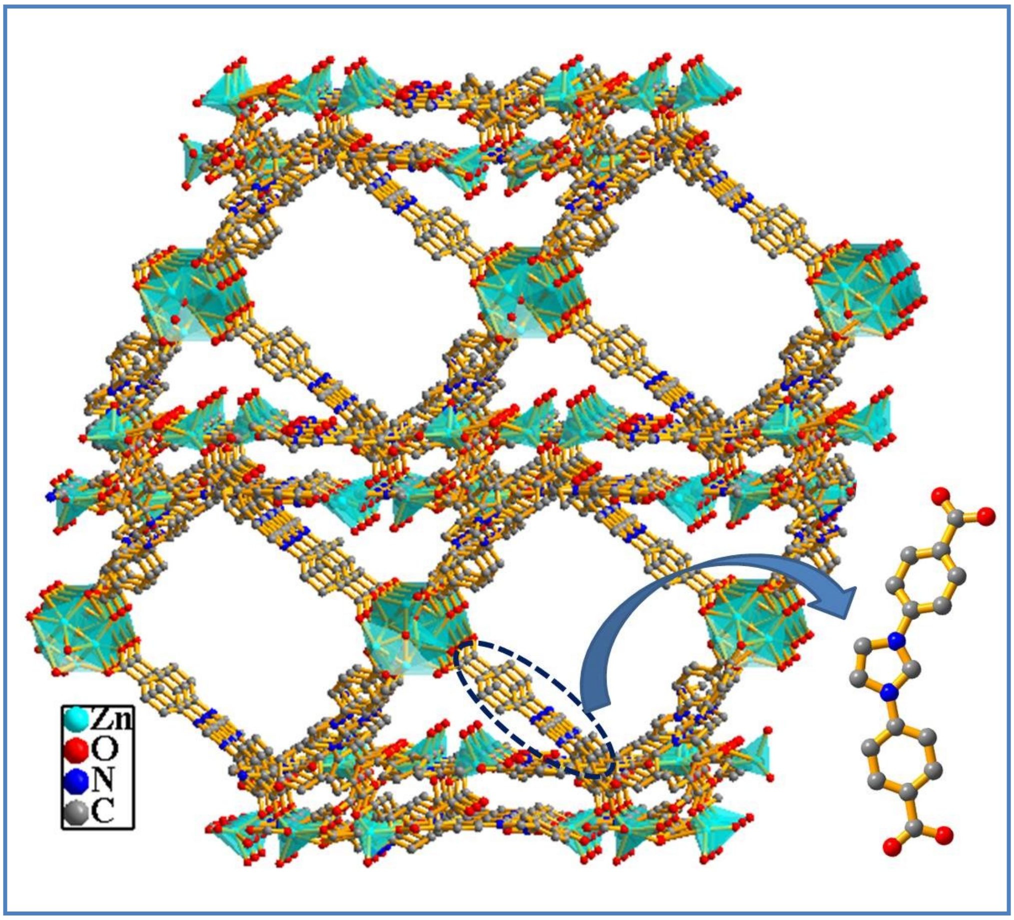


Figure S2. View of one-dimensional pore along *b*-axis containing NHC sites.

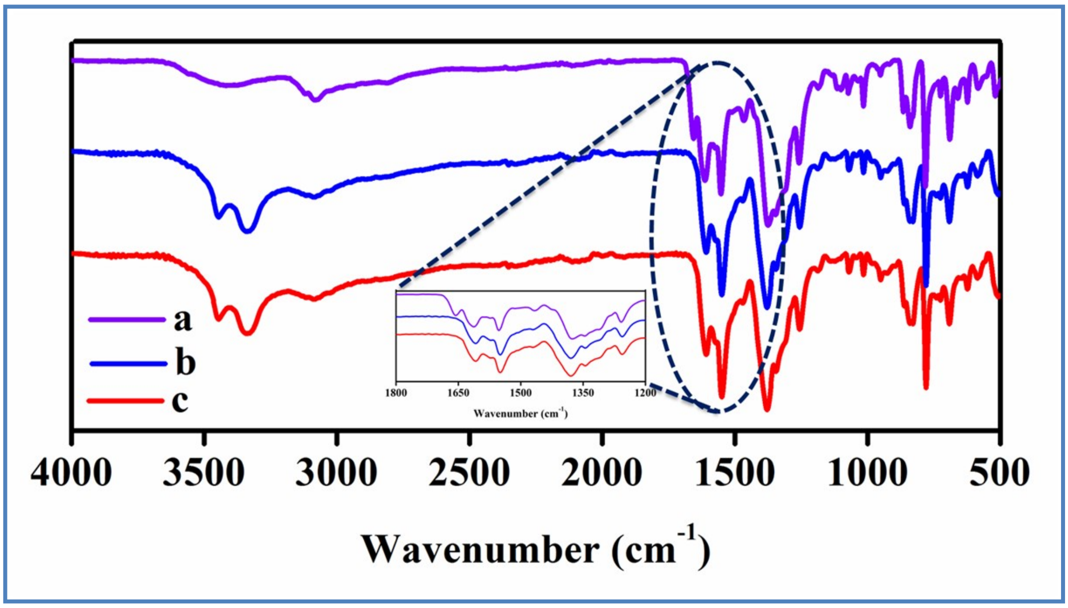


Figure S3. FT-IR spectra of (a) NHC-MOF, (b) Cu(I)@NHC-MOF and (c) recycled sample of Cu(I)@NHC-MOF after ten catalytic cycles.

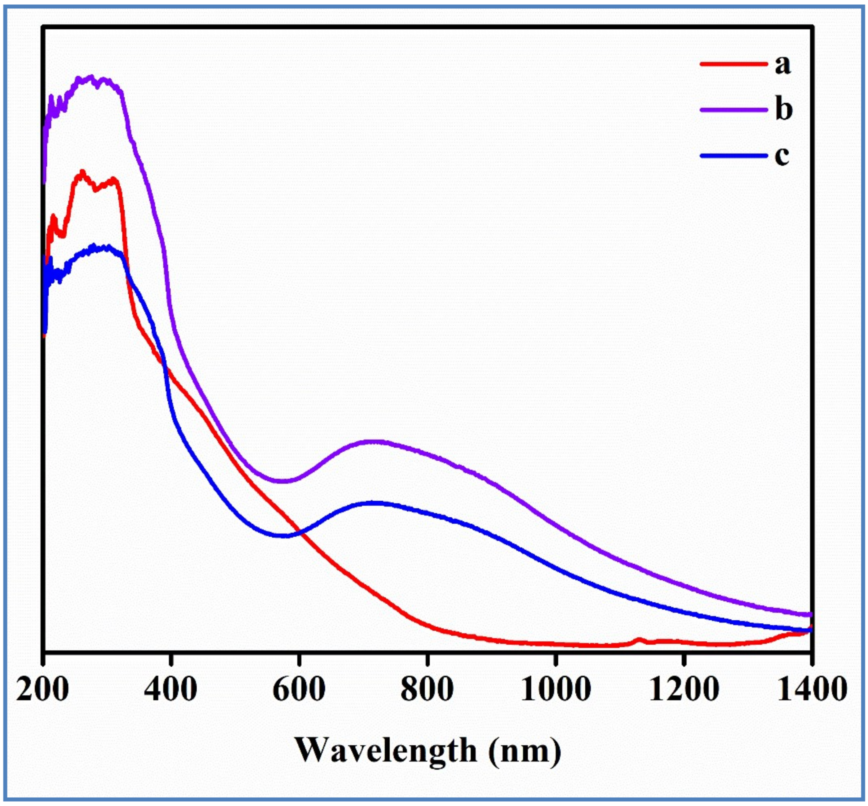
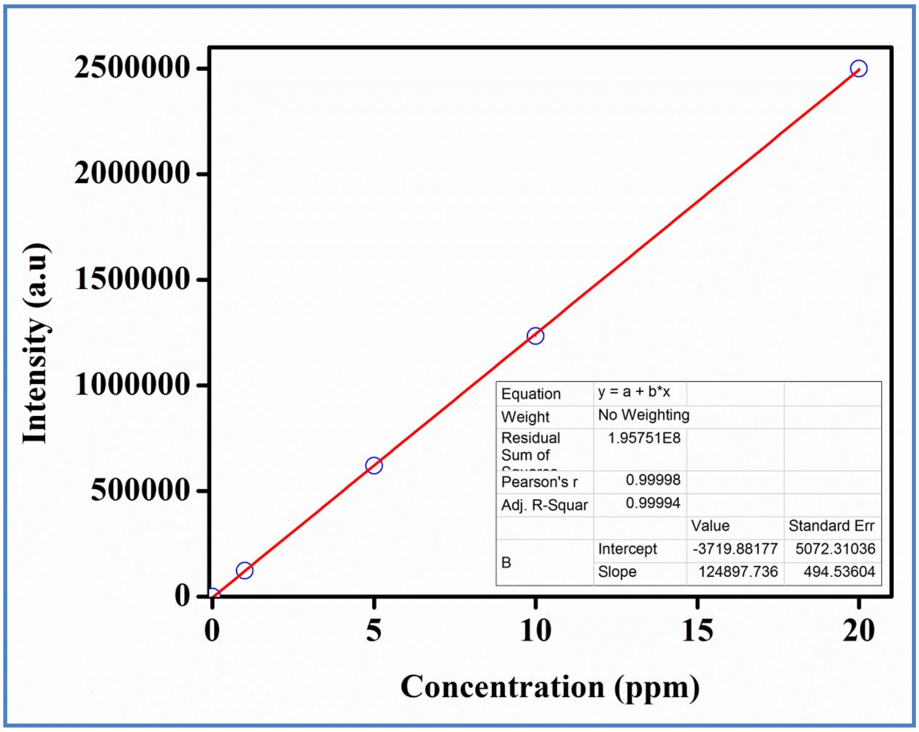


Figure S4. UV-Vis absorption spectra of (a) NHC-MOF, (b) Cu(I)@NHC-MOF and (c) recycled sample of Cu(I)@NHC-MOF after ten catalytic cycles.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of	1.95751E8		
Pearson's r	0.99998		
Adj. R-Squar	0.99994		
		Value	Standard Err
B	Intercept	-3719.88177	5072.31036
	Slope	124897.736	494.53604

Figure S5. Calibration curve of MP-AES analysis for Cu(I)@NHC-MOF.

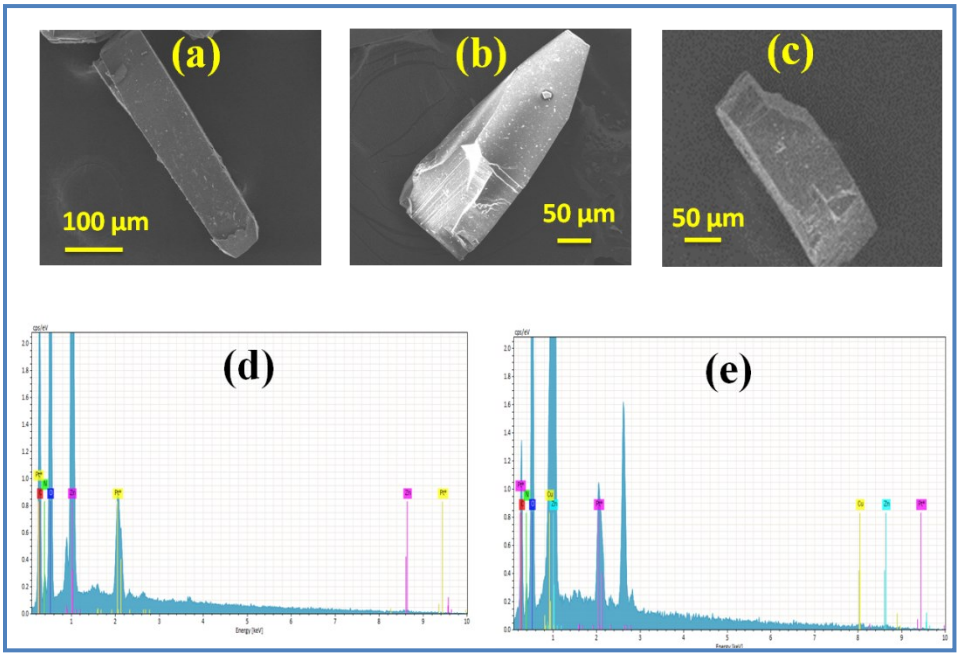


Figure S6. SEM image of (a) NHC-MOF, (b) Cu(I)@NHC-MOF, (c) recycled sample of Cu(I)@NHC-MOF after ten catalytic cycles, EDS plot of (d) NHC-MOF and (e) Cu(I)@NHC-MOF.

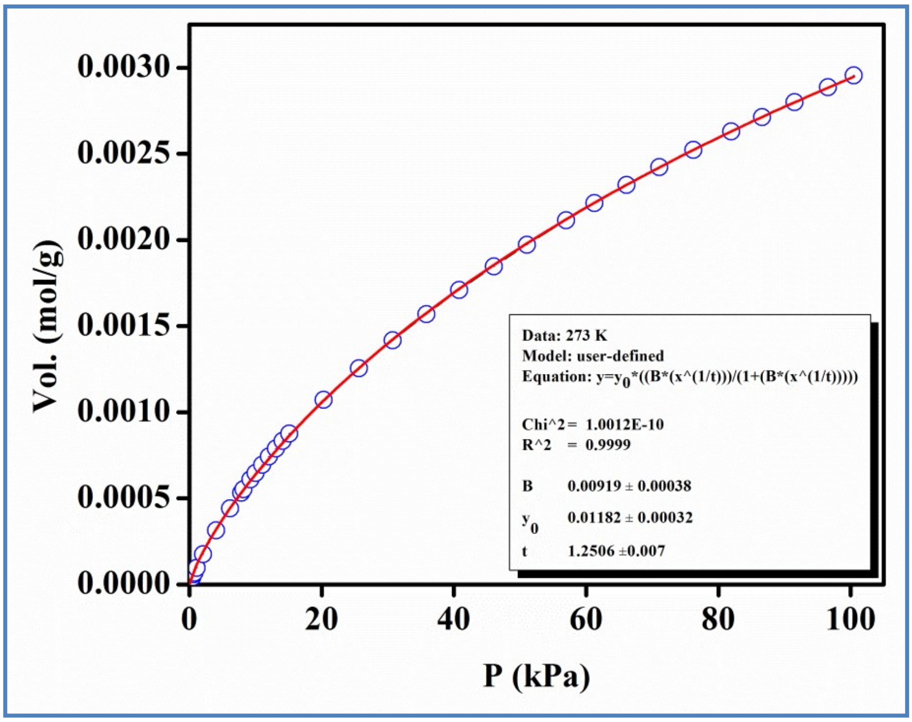


Figure S7. Carbon dioxide adsorption isotherm of Cu(I)@NHC-MOF carried out at 273 K. The solid line shows the best fit to the data using the Langmuir-Freundlich equation.

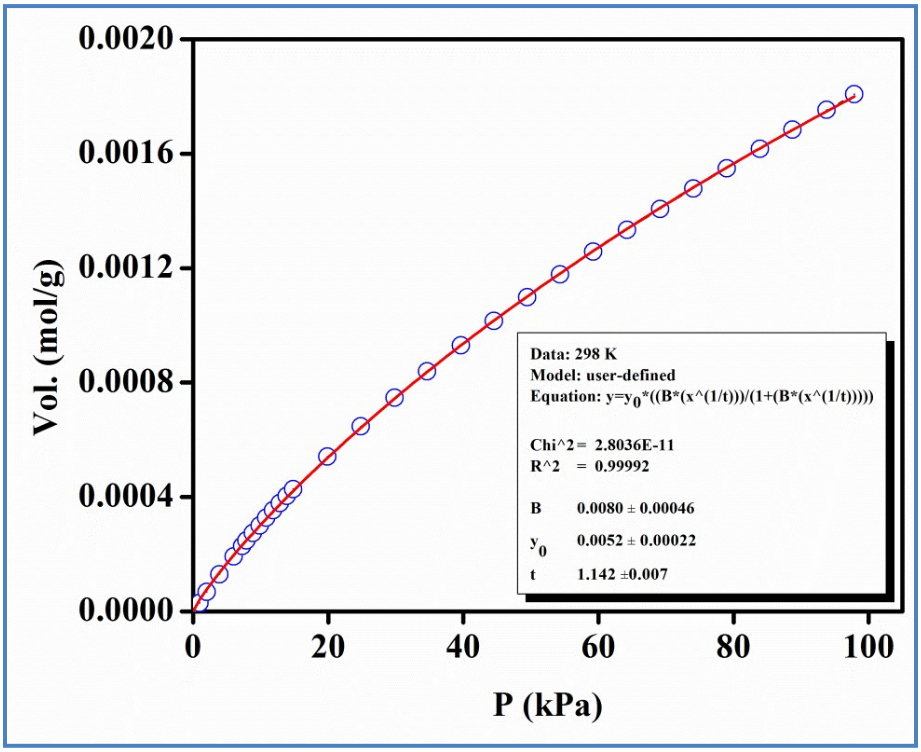


Figure S8. Carbon dioxide adsorption isotherm of Cu(I)@NHC-MOF carried out at 298 K. The solid line shows the best fit to the data using the Langmuir-Freundlich equation.

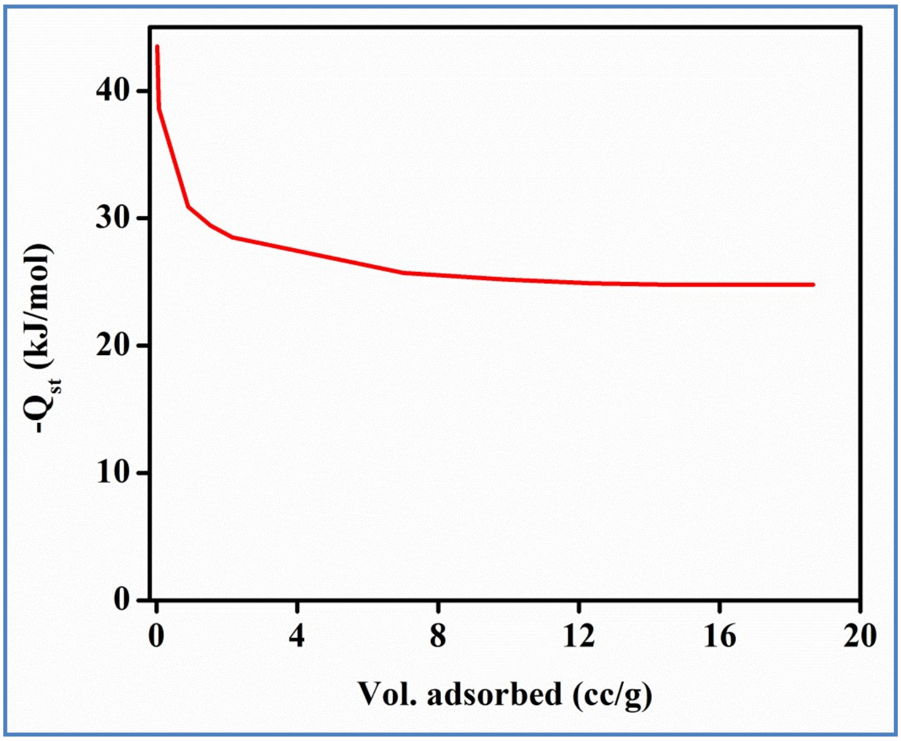


Figure S9. Enthalpy of carbon dioxide adsorption for Cu(I)@NHC-MOF determined using the Clausius-Clapeyron equation.

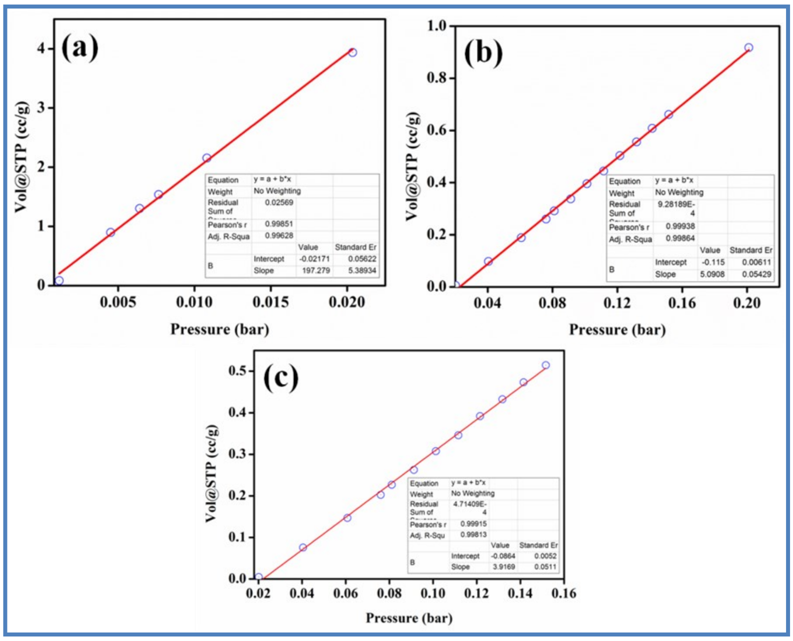
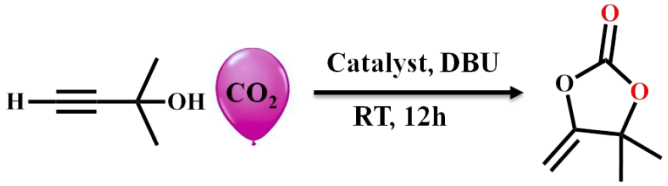


Figure S10. Calculation of Henry gas selectivity constants for gases (a) CO_2, (b) N_2 and (c) O_2.

Table S1. Catalyst optimization towards carboxylation of 2-methyl-3-butyn-2ol.[a]



Sl. No.	Catalyst	Pressure	Conversion (%)[c]
1	-	1 atm CO_2	-
2	NHC-MOF	1 atm CO_2	-
3	$Cu(NO_3)_2.6H_2O$	1 atm CO_2	-
4	CuCl	1 atm CO_2	78
5	Cu(I)@NHC-MOF	Bubbling of laboratory air	21
6	Cu(I)@NHC-MOF	1 atm (CO_2:N_2 = 13:87)	67
7	Cu(I)@NHC-MOF	1 atm CO_2	88[b]
8	Cu(I)@NHC-MOF	1 atm CO_2	99

Reaction Conditions, a: 2-methyl-3-butyn-2-ol (4 mmol), catalyst (0.005 mmol), DBU (0.05 equivalent), DMF (2 mL), temperature (RT), time (12 h), b: time (10h) and c: The percentage of conversion was determined by ^{1}H NMR analysis.

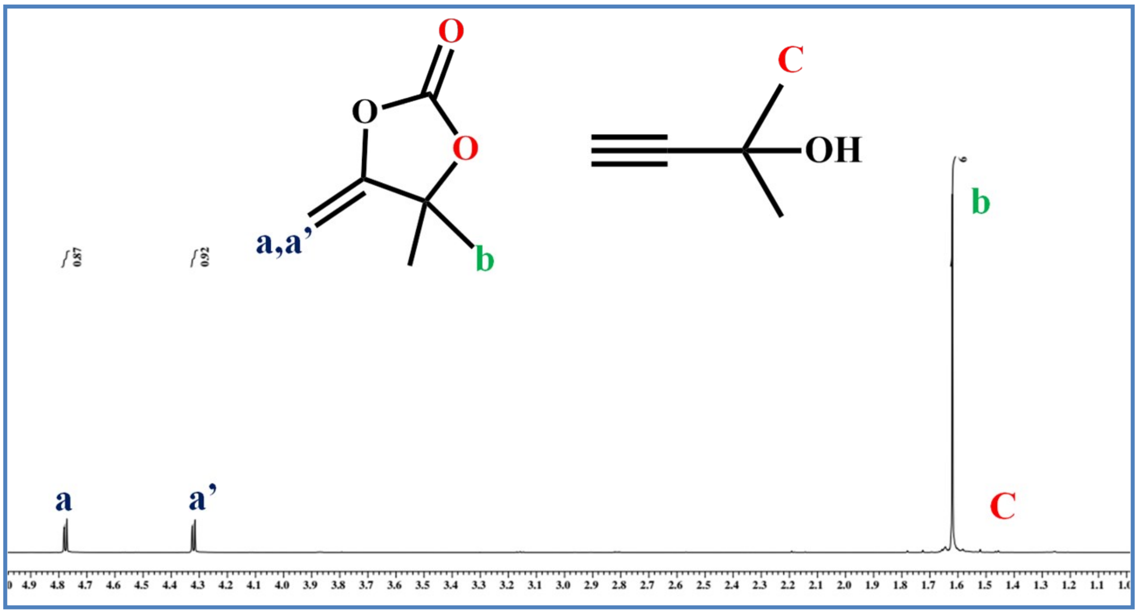


Figure S11. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Cu(I)@NHC-MOF.

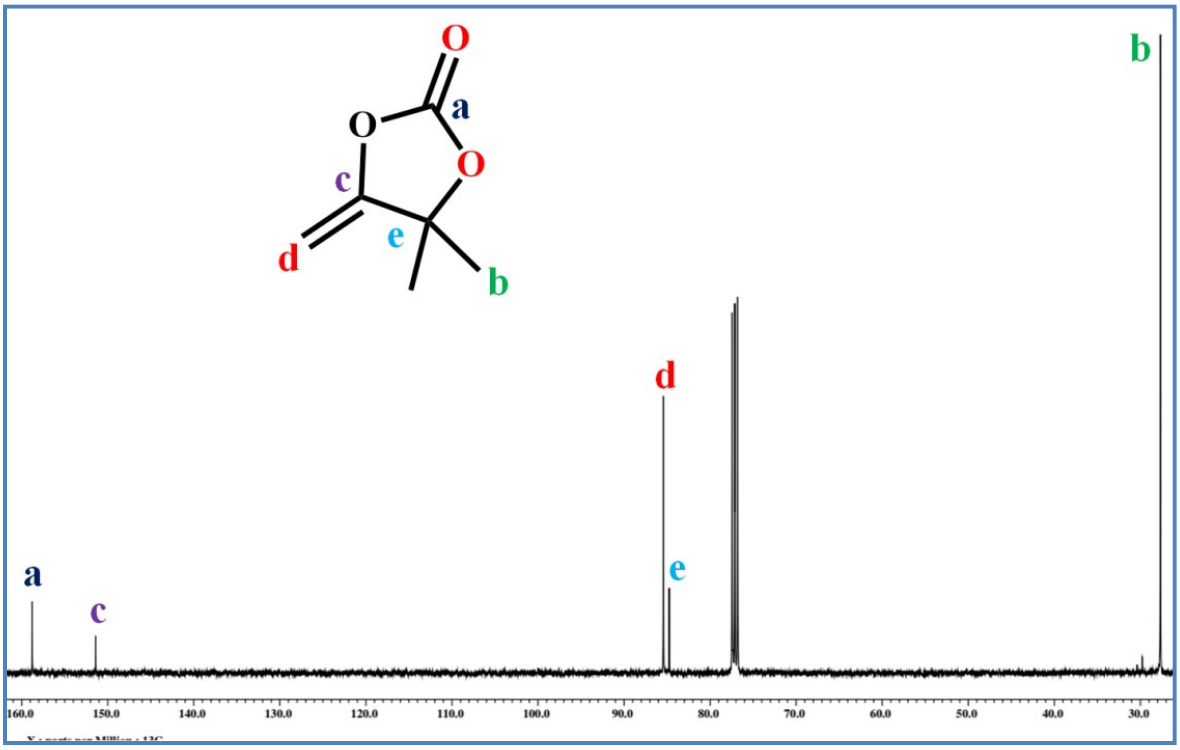


Figure S12. ^{13}C NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Cu(I)@NHC-MOF.

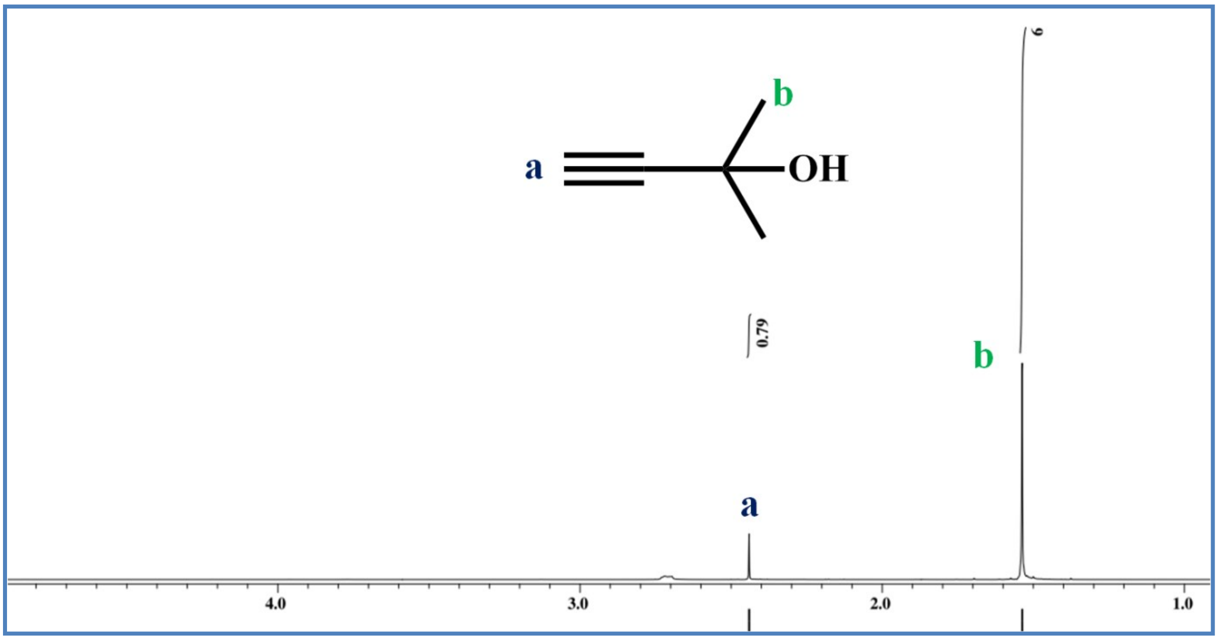


Figure S13. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by NHC-MOF.

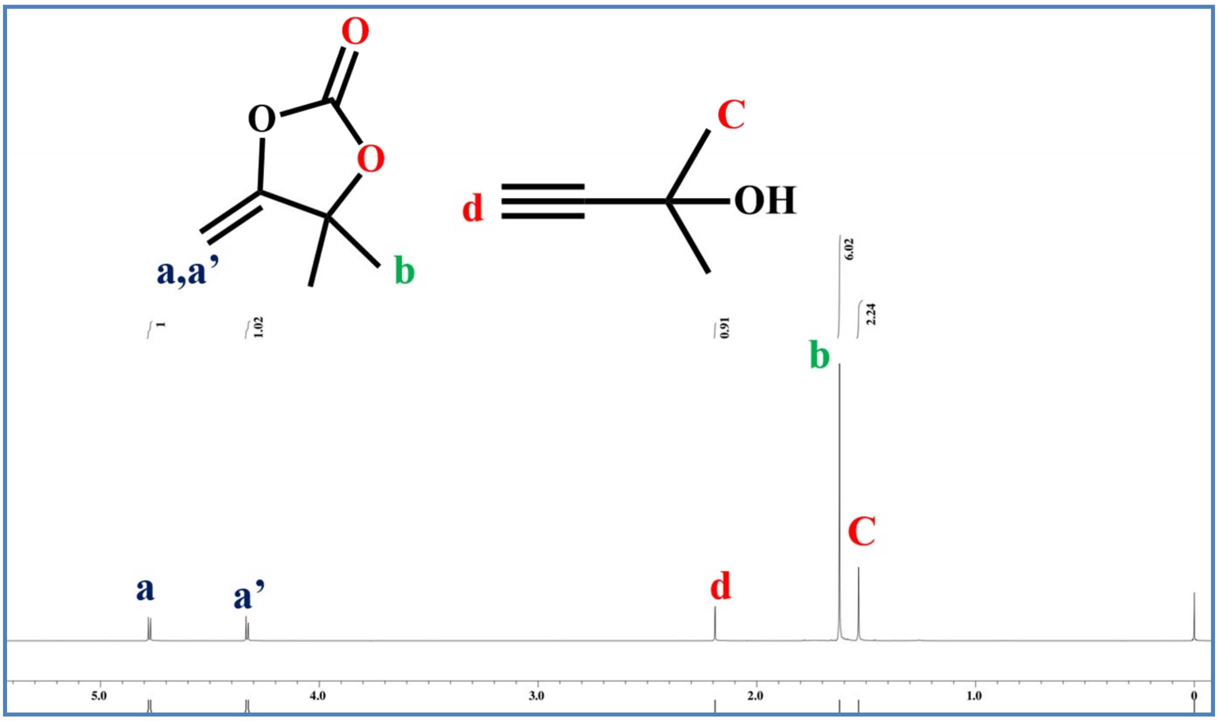


Figure S14. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Cu(I)@NHC-MOF using simulated dry flue gas CO_2:N_2 (13:87) gas.

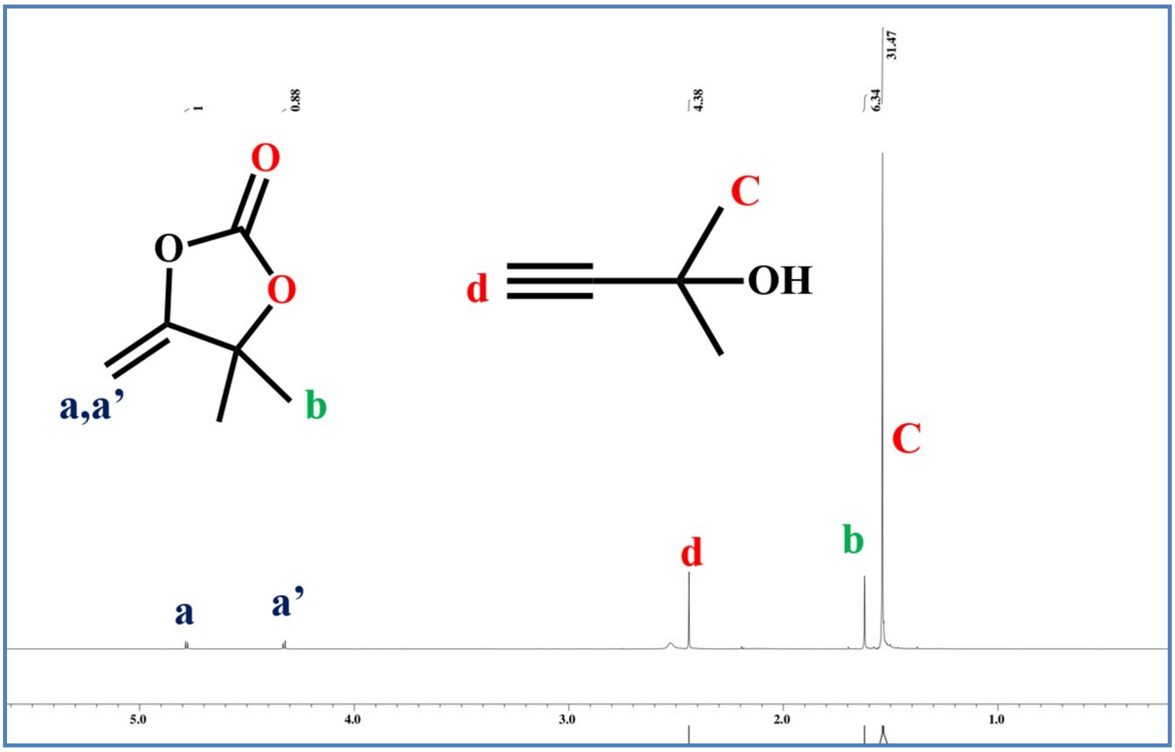


Figure S15. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Cu(I)@NHC-MOF by bubbling of laboratory air as source of CO_2.

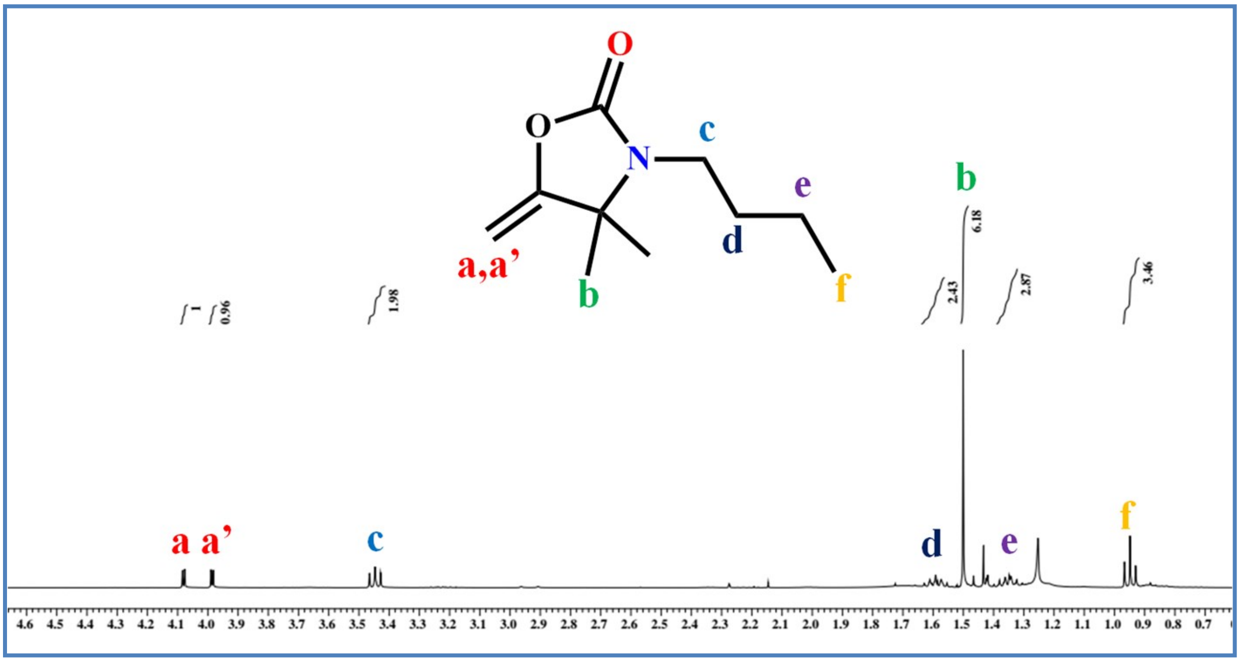


Figure S16. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for three-component reaction between CO_2, 2-methyl-3-butyn-2-ol and n-butylamine using Cu(I)@NHC-MOF as catalyst.

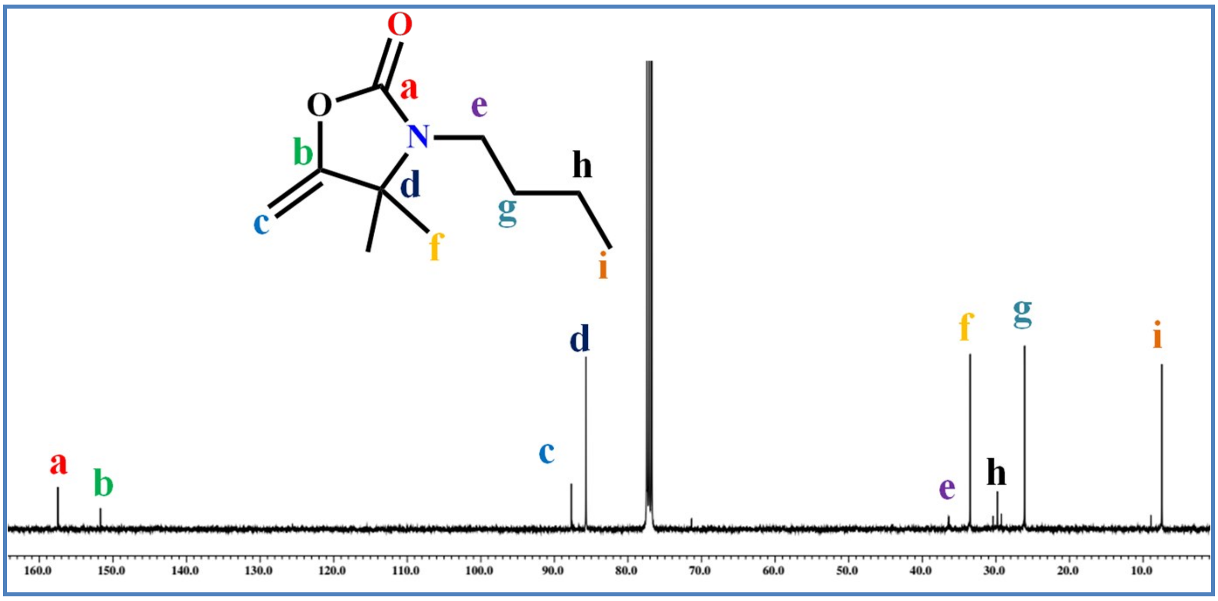


Figure S17. ^{13}C NMR ($CDCl_3$, 400 MHz) spectra for three-component reaction between CO_2, 2-methyl-3-butyn-2-ol and n-butylamine using Cu(I)@NHC-MOF as catalyst.

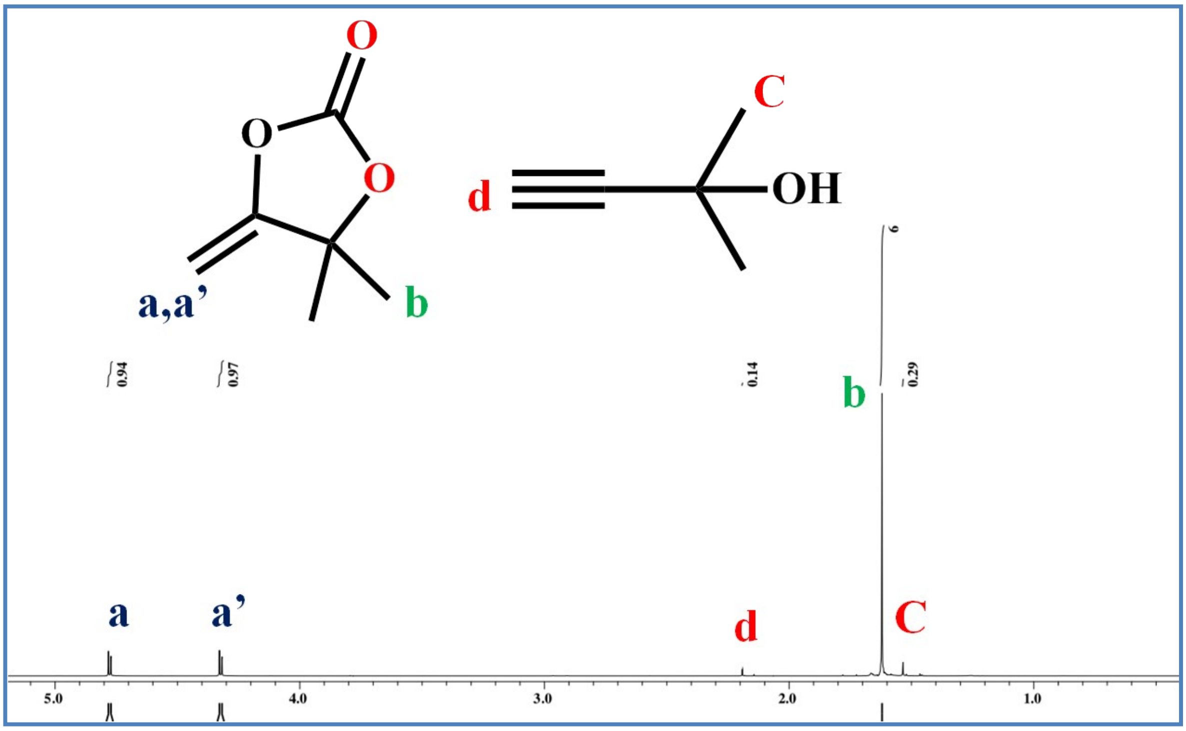


Figure S18. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Cu(I)@NHC-MOF after ten cycles.

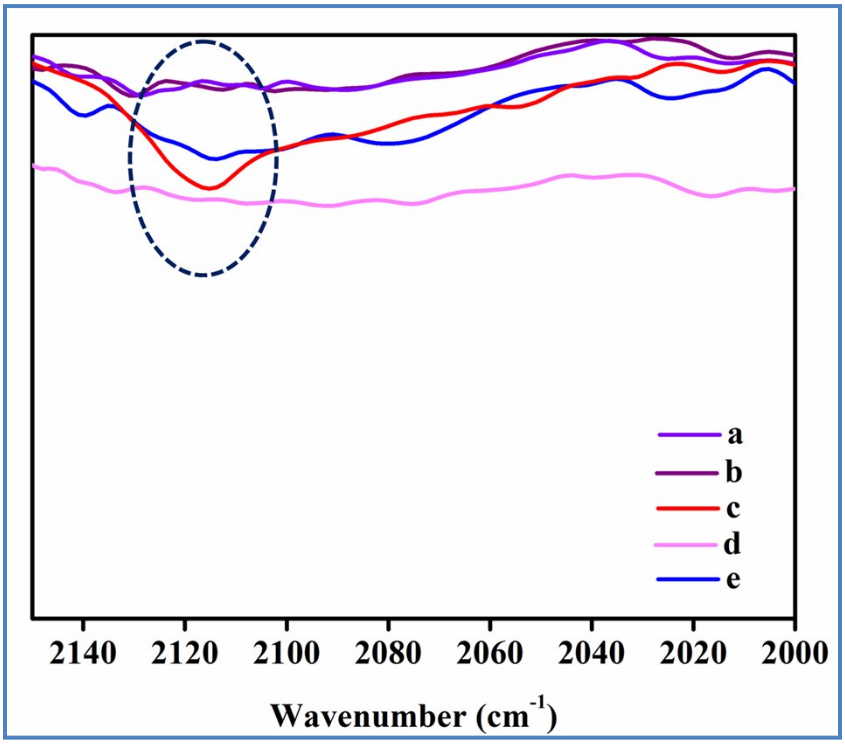
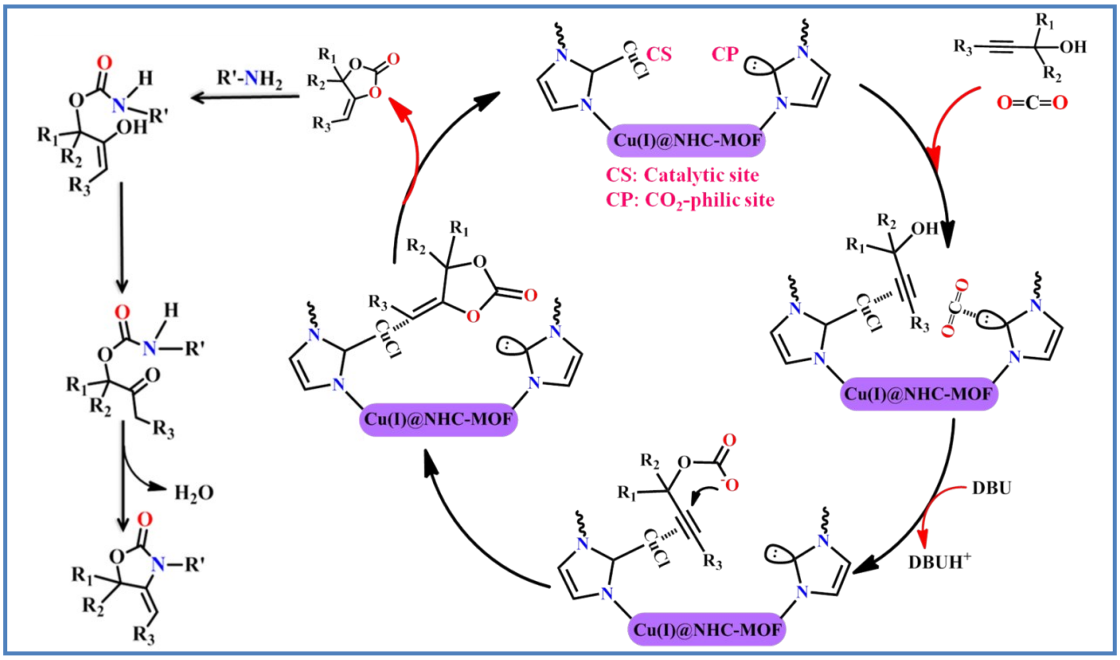


Figure S19. FT-IR spectra of (a) NHC-MOF, (b) Cu(I)@NHC-MOF, (c) 2-methyl-3-butyn-2-ol, (d) NHC-MOF treated with 2-methyl-3-butyn-2-ol, and (e) Cu(I)@NHC-MOF treated with 2-methyl-3-butyn-2-ol.



Scheme S2. A plausible mechanism for the three-component reaction between CO_2, propargylic alcohol and primary amine catalysed by Cu(I)@NHC-MOF.

References

(1) S. Sen, N. N. Nair, T. Yamada, H. Kitagawa, P. K. Bharadwaj, High Proton Conductivity by a Metal-Organic Framework Incorporating Zn_8O Clusters with Aligned Imidazolium Groups Decorating the Channels. *J. Am. Chem. Soc*., 2012, **134**, 19432-19437.

(2) H. Pan, J. A. Ritter, P. B. Balbuena, Examination of the Approximations Used in Determining the Isosteric Heat of Adsorption from the Clausius−Clapeyron Equation. *Langmuir*, 1998, **14**, 6323-6327.

(3) R. T. Yang, Gas Separation by Adsorption Processes, Butterworth, Boston, 1997.