Strategic design of a bifunctional Ag(I)-grafted NHC-MOF for efficient chemical fixation of CO_2 from dilute gas at ambient conditions

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Materials and methods

All reagents used in this study were commercially available and used as received without further purification. $Zn(NO_3)_2.6H_2O$, silver nitrate ($AgNO_3$), 4-aminobenzoic acid ($C_7H_7NO_2$), 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 Ag in the framework was determined by Agilent's microwave-plasma atomic emission spectrometer (MP-AES). The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific NEXSA photoemission spectrometer using Al Kα (1486.6 eV) X-ray radiation. The analysis of obtained data was carried out using advantage software. ^1H NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-ECS400 spectrometer operating at a frequency of 400 MHz.

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 the previous literature with a slight modification.[1] In a typical synthesis, 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 allowed to stir at ambient temperature for 24 h. The white solid formed was collected by filtration followed by washing with cold methanol, and dried in air (Compound L1). The compound L1 (1 g), was dissolved in anhydrous THF (10 mL) under N_2 atmosphere followed by the addition of a solution of paraformaldehyde (125 mg) in 12 N HCl (400 μL) in dioxane (1 mL) at 0 °C. The reaction mixture was stirred at room temperature for 4 h and the light pink precipitate formed was collected by filtration, washed with Et_2O, and dried under vacuum. Yield: 70%.

Synthesis of MOF-NHC

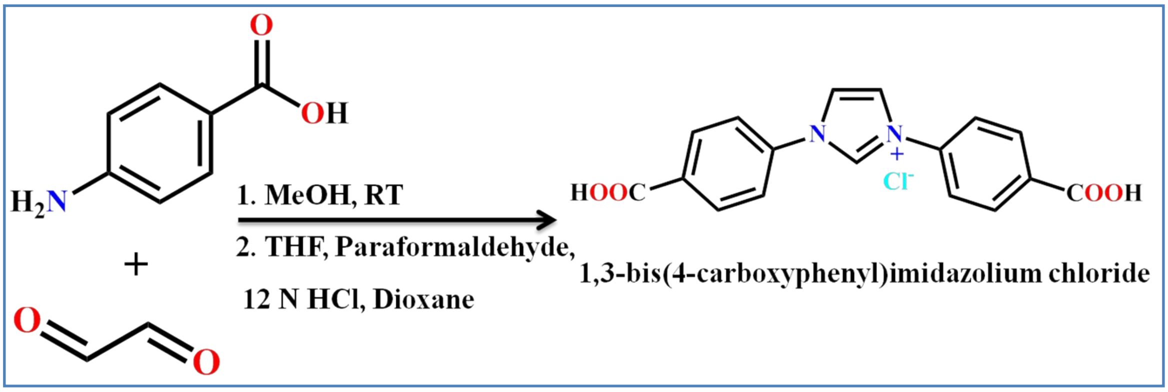
The 1,3-bis(4-carboxyphenyl)imidazolium chloride ($H_2L^+Cl^-$) ligand was synthesized by following the previously reported procedure with a slight modification and characterized by ^1H NMR analysis (Figure S1).[1] The MOF-NHC was synthesized by using the following procedure. The $Zn(NO_3)\cdot 6H_2O$ (2.0 mmol, 0.595 g) and $H_2L^+Cl^-$ (0.5 mmol, 0.172 g) were dissolved in 3 mL of dry DMF 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 crystalline solid of MOF obtained was collected by filtration, washed with DMF, and dried under vacuum at 120 °C overnight. Yield: 42%. The phase purity of MOF-NHC was confirmed by PXRD analysis (Figure 1a). FTIR (ν, cm^{-1}): 3088 (m), 1650 (w), 1608 (s), 1541 (s), 1380 (s) (Figure S3). Elemental analysis for MOF-NHC, 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 Ag(I)@MOF-NHC

In a typical procedure, anhydrous $AgNO_3$ (0.2 mmol, 0.034 g) was dissolved in 10 mL deionized water in a 30 mL culture tube and to this solution, MOF-NHC (0.01 mmol, 0.0488 g) was added. The tube was placed in an ice batch and was kept for constant *shaking* on a magnetic shaker for 2 h. After which time, the Ag(I)@MOF-NHC obtained was filtered and washed with water thoroughly, dried at 80 °C under vacuum for 12 h. The phase purity of the sample was confirmed by PXRD analysis (Figure 1a). FTIR (ν, cm^{-1}): 3085 (w), 1606 (s), 1382 (s), 1257 (m) (Figure S3).

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) at RT and 1 atm CO_2 (balloon) conditions. Prior to catalytic reactions, the catalyst was activated at 120 °C under vacuum for 12 h. The substrate (2 mmol), along with DBU (0.2 mmol), catalyst (0.01 mmol), and DMF (2 mL) were taken in a Schlenk tube and CO_2 was introduced with a commercially purchased balloon and the contents were stirred at RT. After 6 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 12 h and reused for the subsequent catalytic cycles.



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

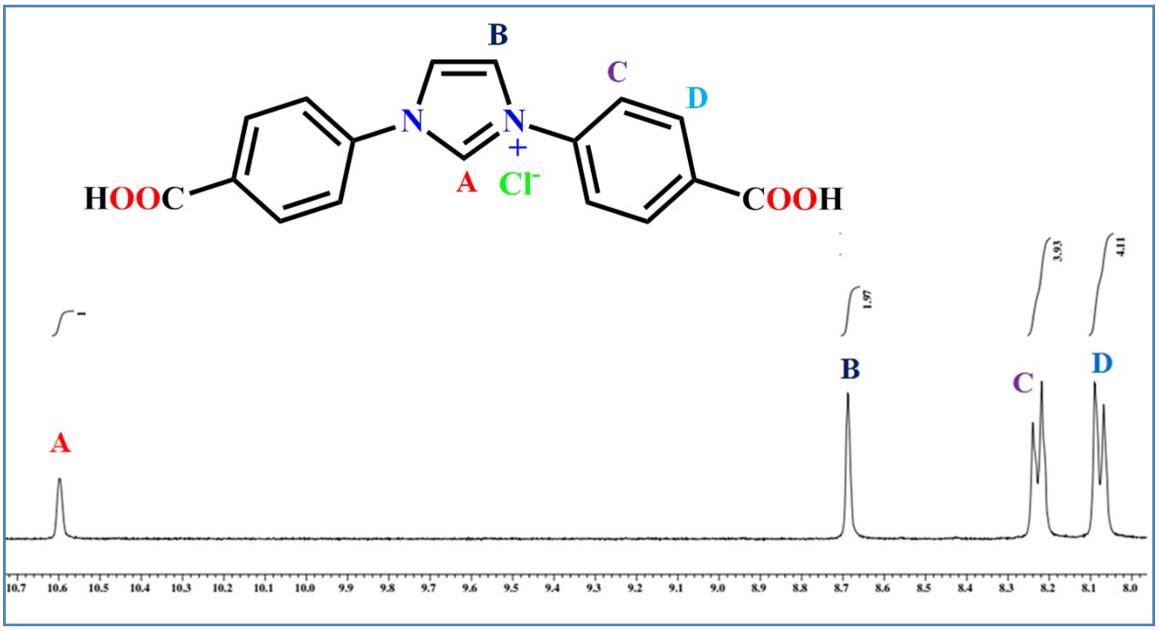


Figure S1. ^1H NMR spectrum of 1,3-bis(4-carboxyphenyl)imidazolium chloride ($H_2L^+Cl^-$).

Gas adsorption measurements

Gas adsorption measurements of MOF-NHC and Ag(I)@MOF-NHC were performed on a Quantachrome's QUADRASORB-SI automatic volumetric instrument using ultrapure (99.995%) N_2, CH_4, and CO_2 gases. Before starting the adsorption measurements, the sample (~ 0.10 g) was activated by heating at 120 °C under vacuum (18 mTorr) for 24 h. The N_2 adsorption measurements were carried out at 77K and CO_2 adsorption measurements were conducted at 273 K and 298K. The temperatures, 273 and 298 K were maintained by using a water chiller with appropriate coolants. The 77 K was achieved by using liquid N_2 and the dead volume of the sample cell was determined using He gas (99.995%).

Analysis of gas adsorption isotherms

Clausius-Clapeyron Equation[2] was used to determine the enthalpies of carbon dioxide adsorption and by using Langmuir Freundlich equation[3] an accurate fit was retrieved which gives a precise prediction of CO_2 adsorbed at saturation. A modified Clausius-Clapeyron equation was used for calculations.

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

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.

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

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)

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

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

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

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

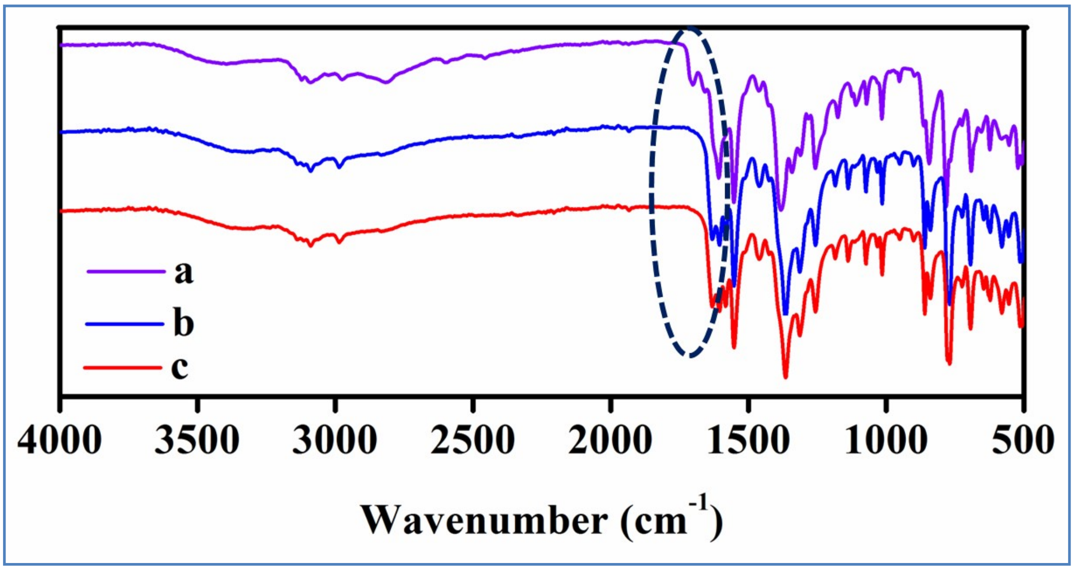


Figure S2. FT-IR spectra of (a) MOF-NHC, (b) Ag(I)@MOF-NHC , and (c) recycled sample of Ag(I)@MOF-NHC after five catalytic cycles.

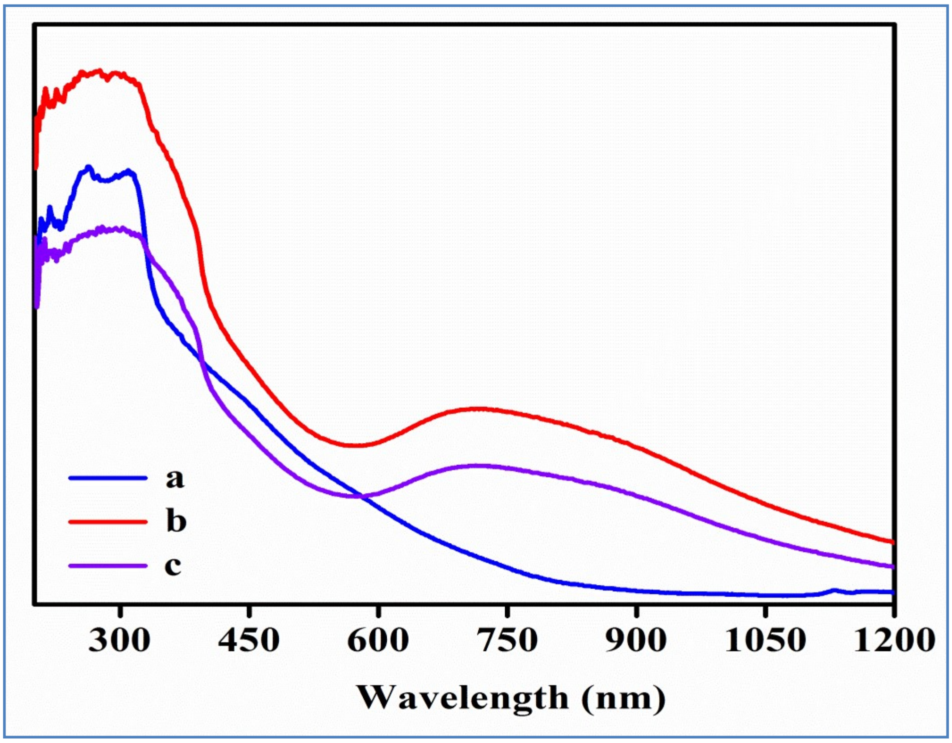
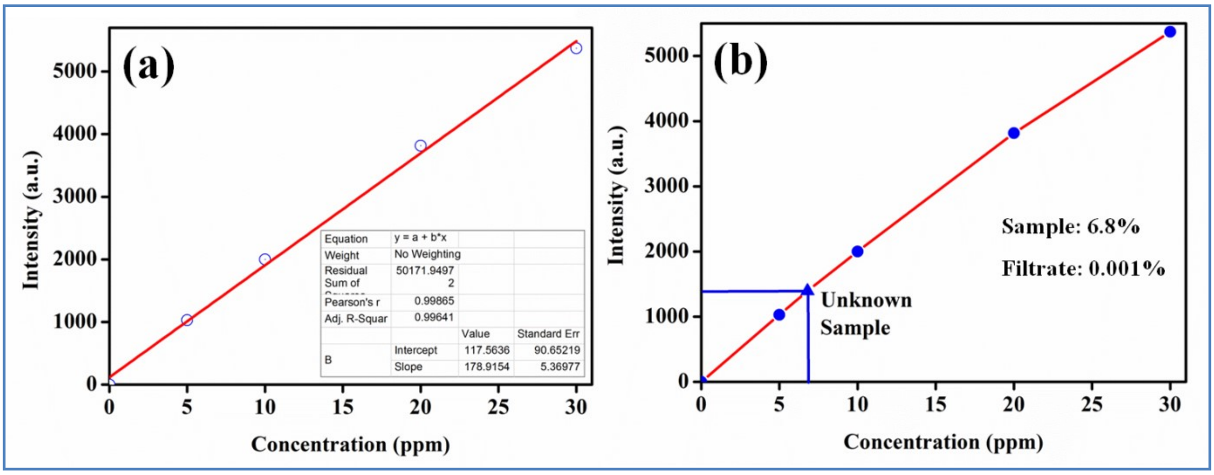


Figure S3. UV-Vis absorption spectra of (a) MOF-NHC, (b) Ag(I)@MOF-NHC and (c) recycled sample of Ag(I)@MOF-NHC after five catalytic cycles.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	50171.9497 2		
Pearson's r	0.99865		
Adj. R-Squar	0.99641		
		Value	Standard Err
B	Intercept	117.5636	90.65219
	Slope	178.9154	5.36977

Figure S4. (a) Calibration curve of MP-AES analysis, and (b) concentration of Ag in the Ag(I)@MOF-NHC.

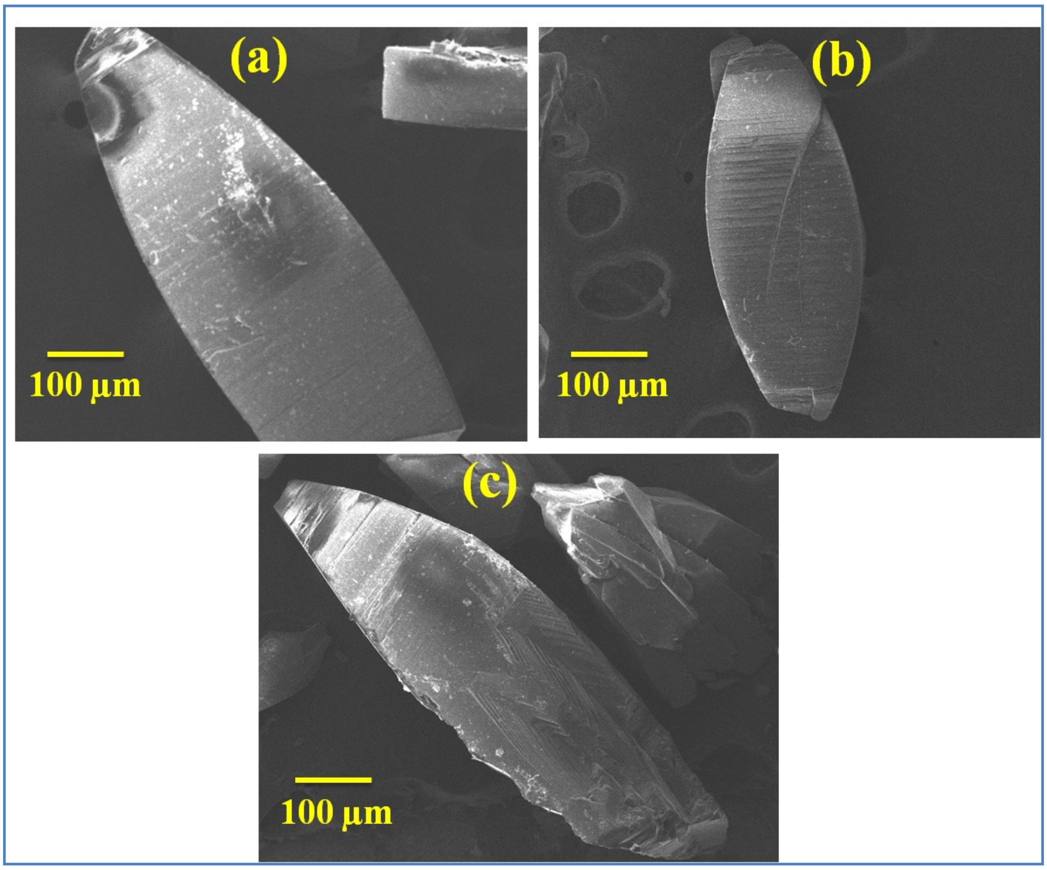


Figure S5. SEM image of (a) MOF-NHC, (b) Ag(I)@MOF-NHC , and (c) recycled sample of Ag(I)@MOF-NHC after five catalytic cycles.

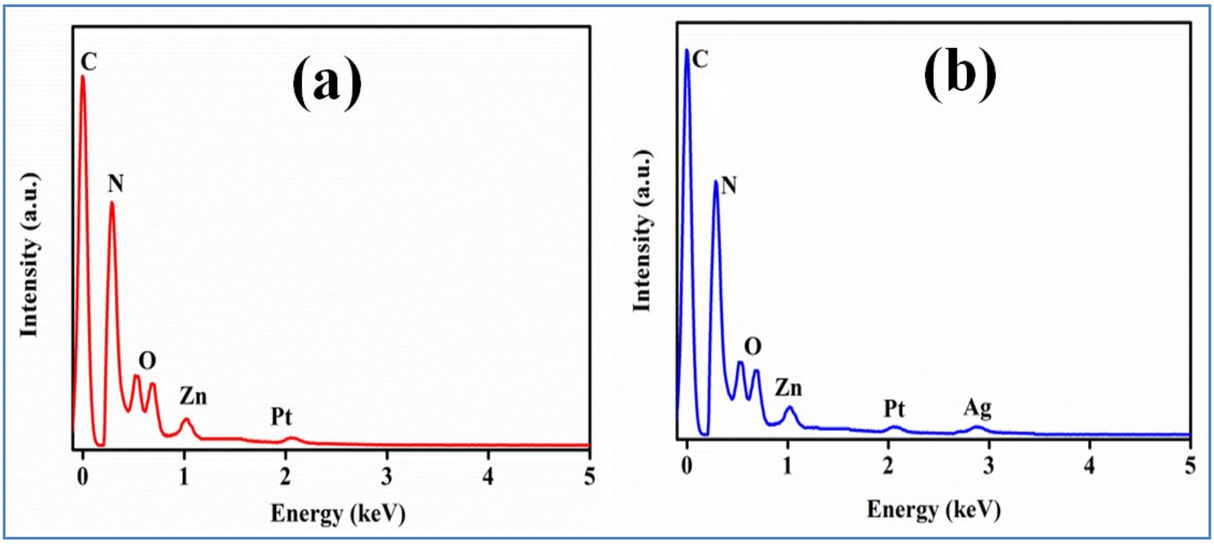


Figure S6. EDS plot of (a) MOF-NHC, and (b) Ag(I)@MOF-NHC.

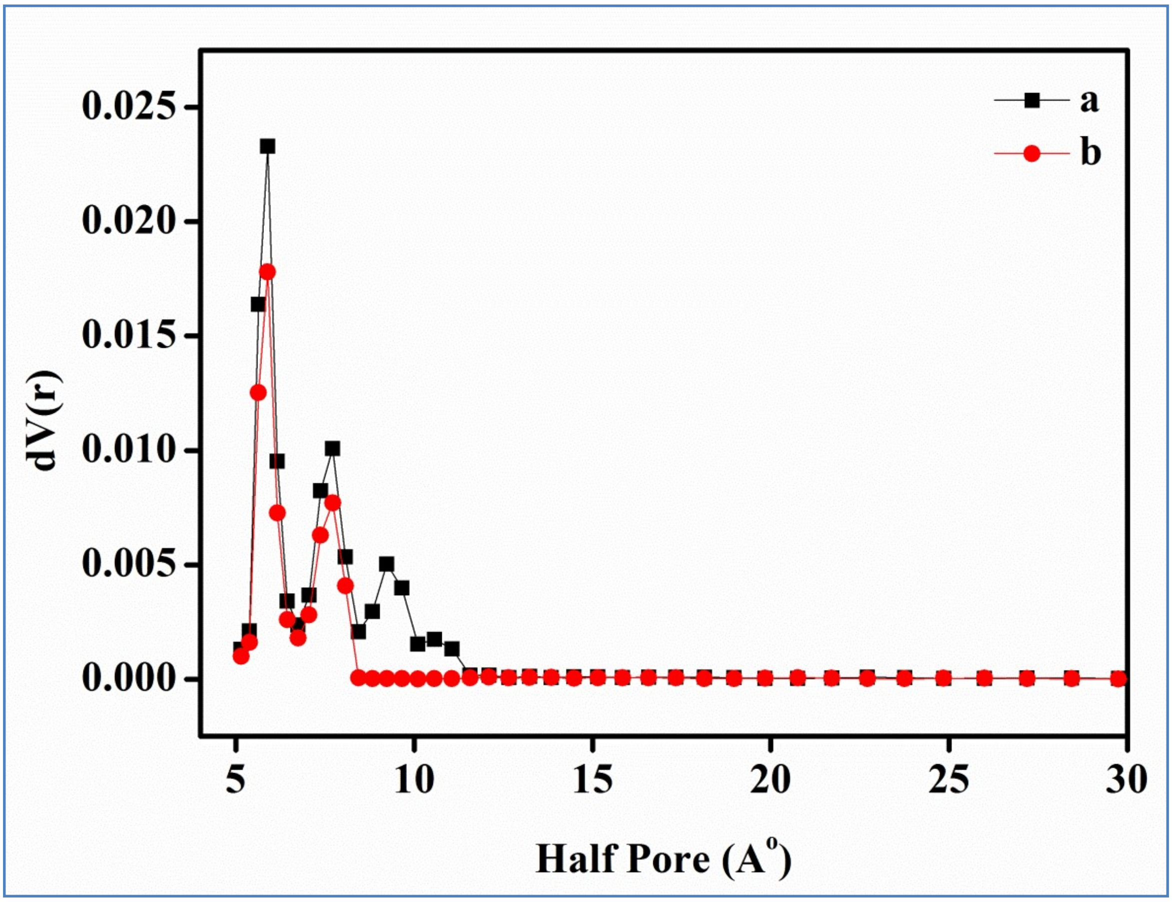


Figure 7. Pore size distribution plots estimated by using DFT for (a) MOF-NHC, and (b) Ag(I)@MOF-NHC.

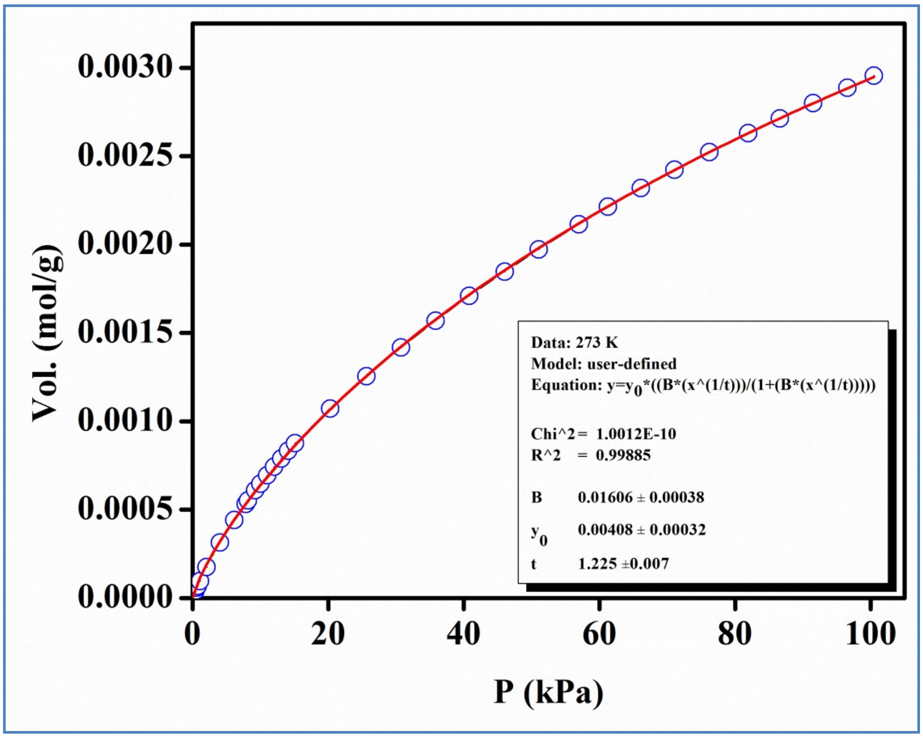


Figure S8. Carbon dioxide adsorption isotherm of Ag(I)@MOF-NHC carried out at 273 K (the solid line shows the best fit to the data using the Langmuir-Freundlich equation).

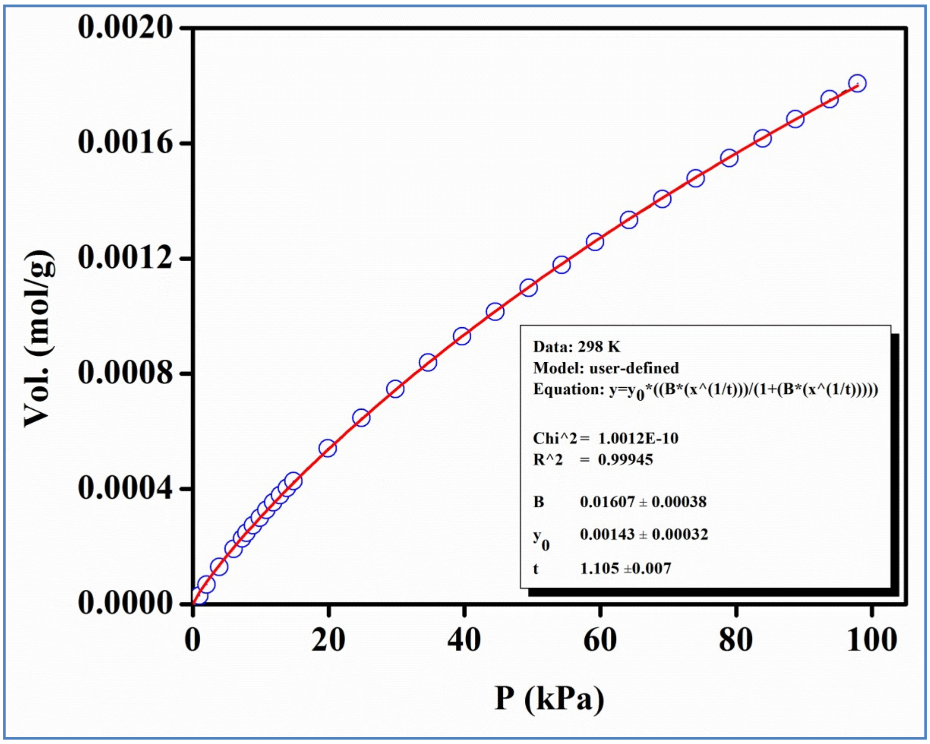


Figure S9. Carbon dioxide adsorption isotherm of Ag(I)@MOF-NHC carried out at 298 K (the solid line shows the best fit to the data using the Langmuir-Freundlich equation).

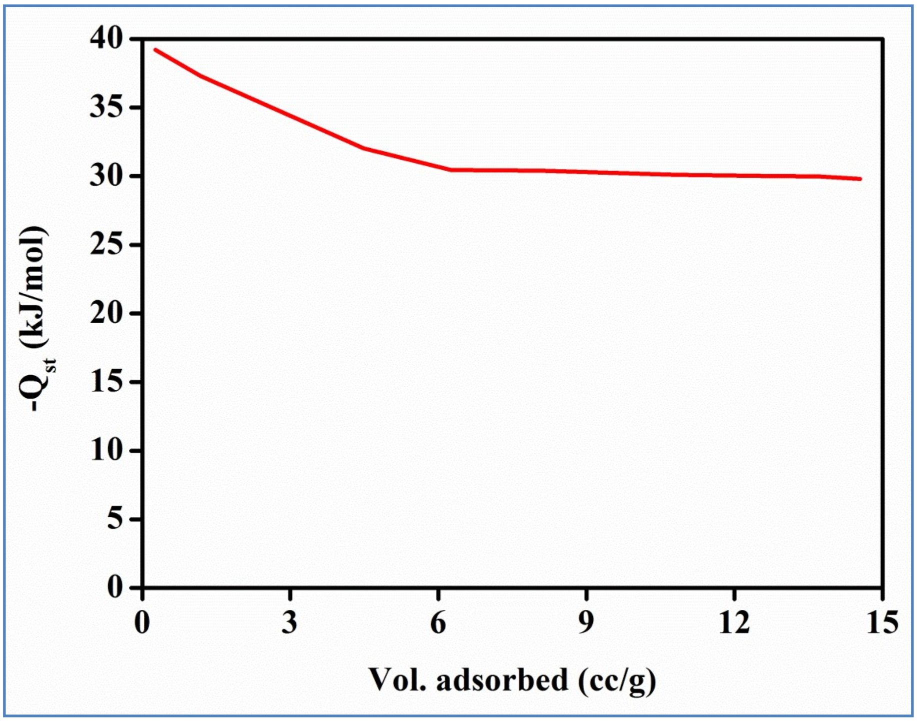


Figure S10. Enthalpy of carbon dioxide adsorption for Ag(I)@MOF-NHC determined using the Clausius-Clapeyron equation.

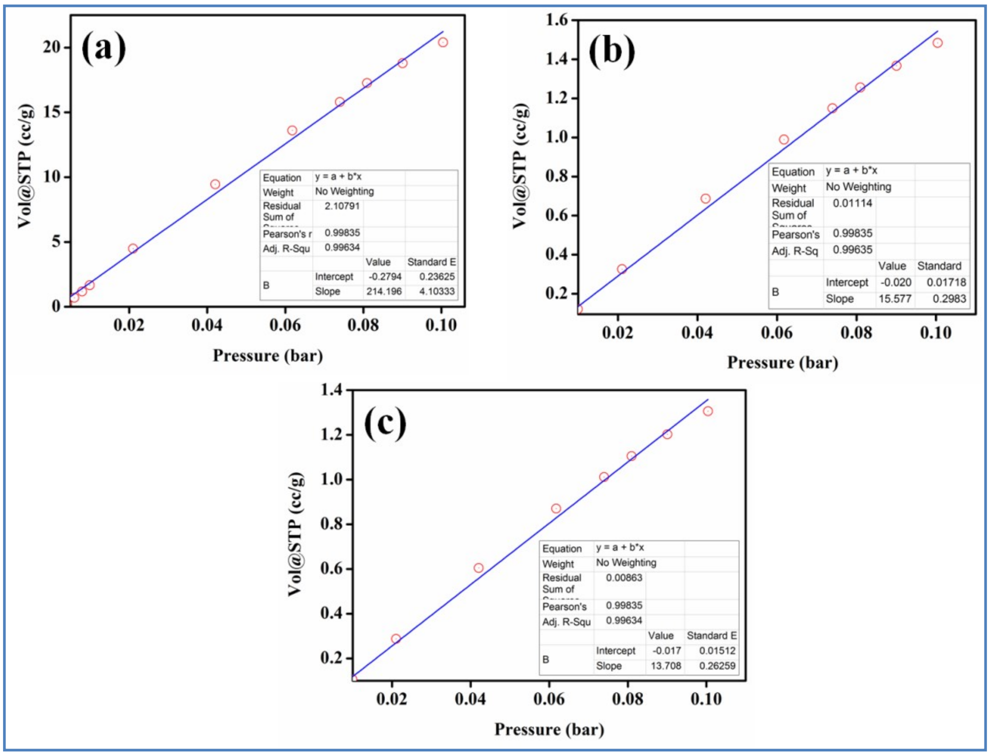


Figure S11. Calculation of Henry gas selectivity constants for gases (a) CO_2, (b) N_2, and (c) CH_4.

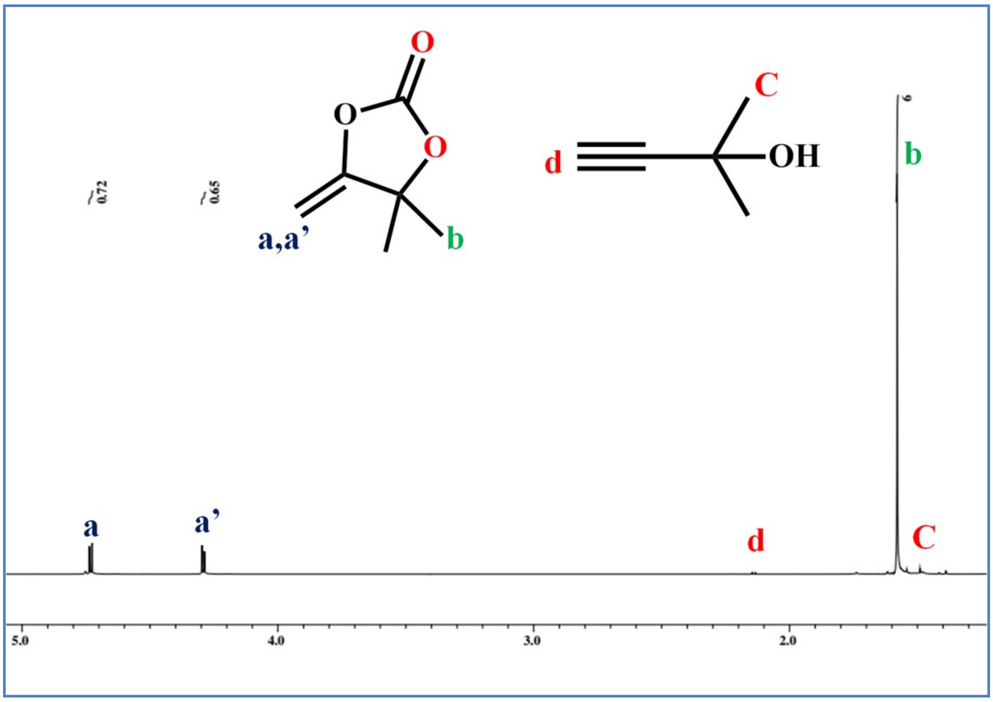


Figure S12. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Ag(I)@MOF-NHC .

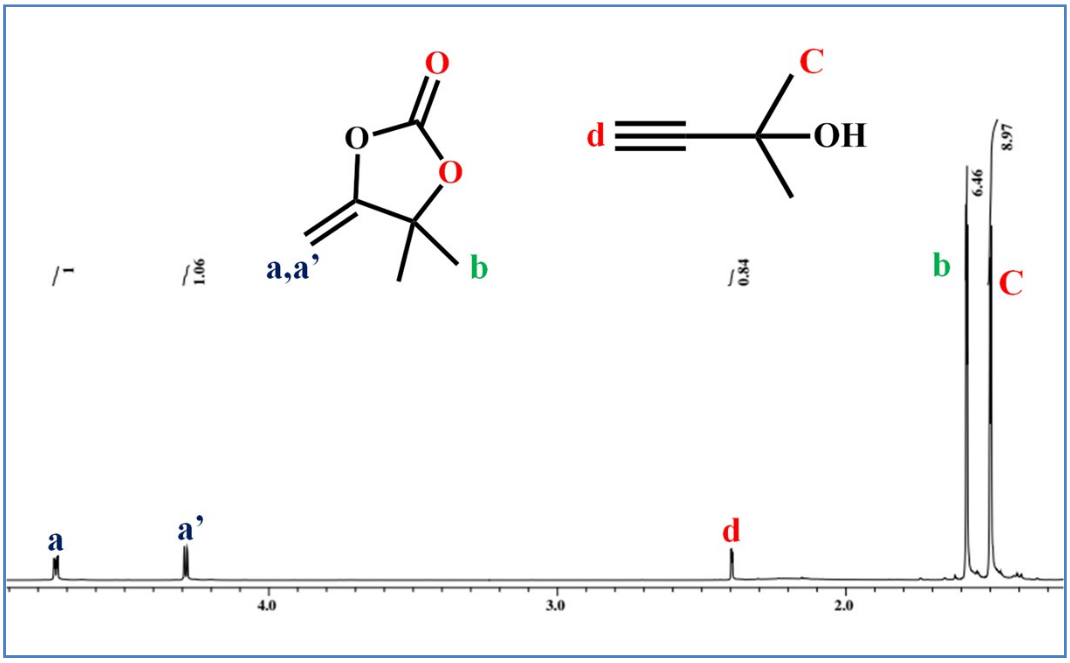


Figure S13. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by $AgNO_3$.

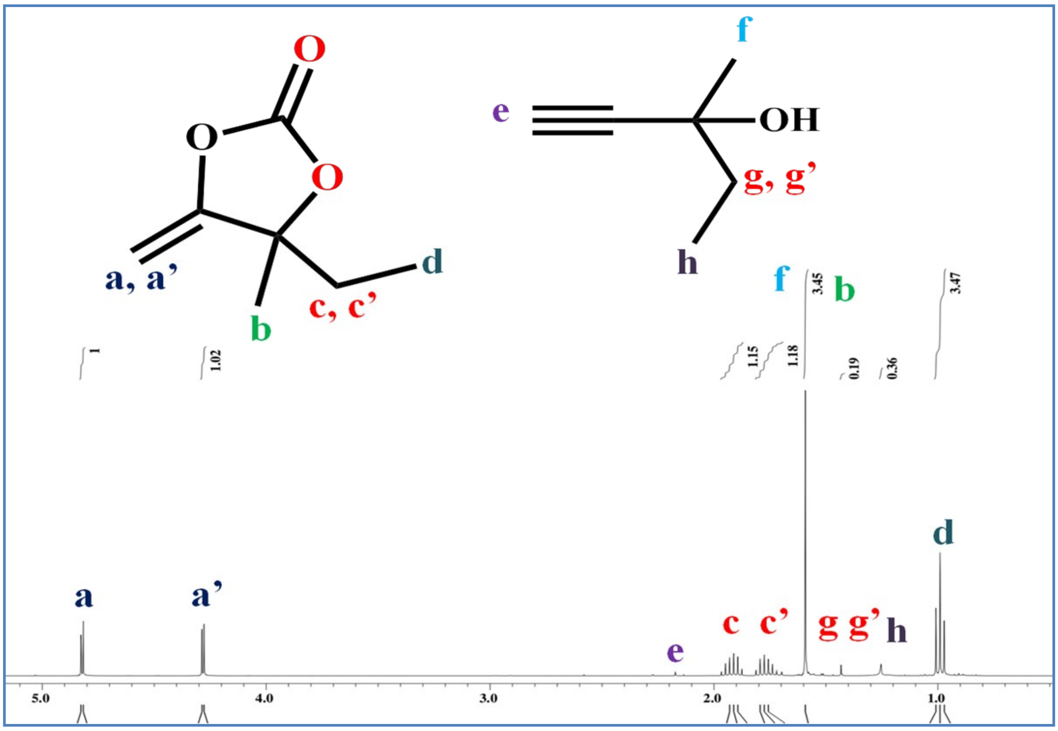


Figure S14. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-ethyl-3-butyn-2-ol catalysed by Ag(I)@MOF-NHC .

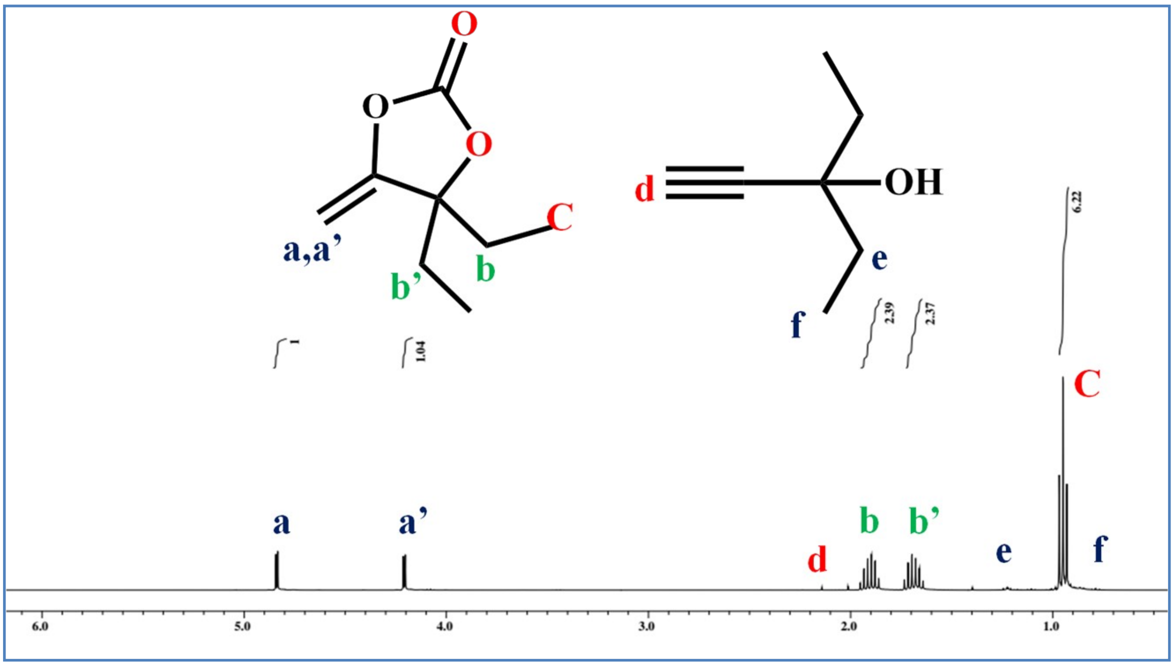


Figure S15. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 3-ethyl-1-pentyn-3-ol catalysed by Ag(I)@MOF-NHC .

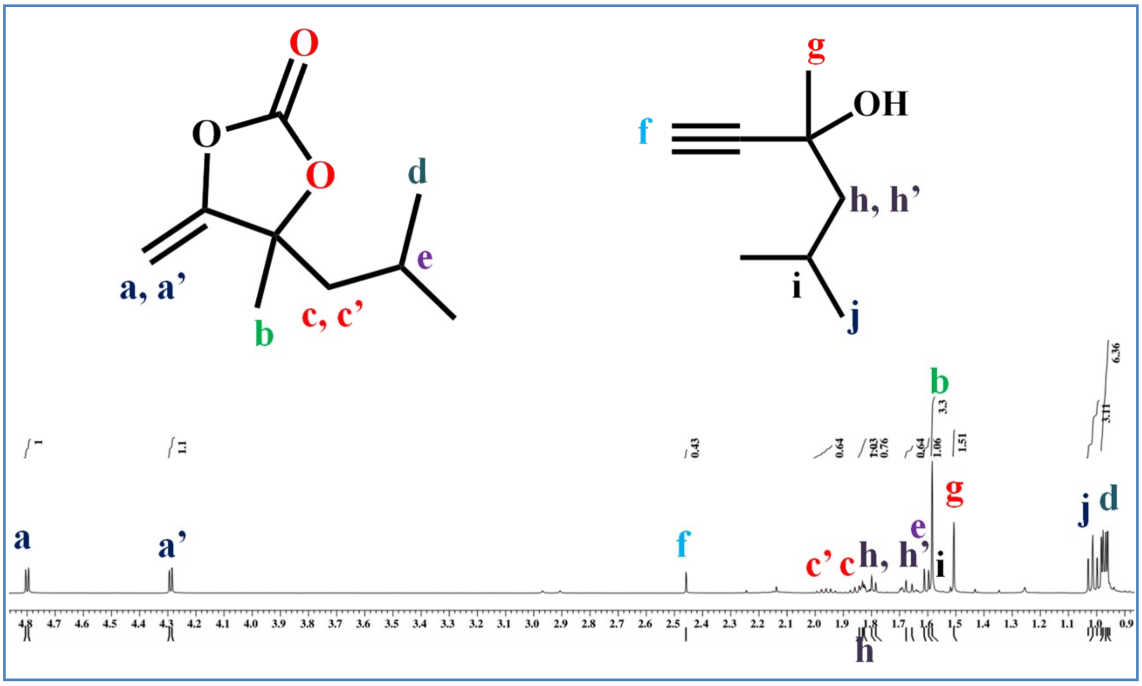


Figure S16. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-isobutyl-3-butyn-3-ol catalysed by Ag(I)@MOF-NHC.

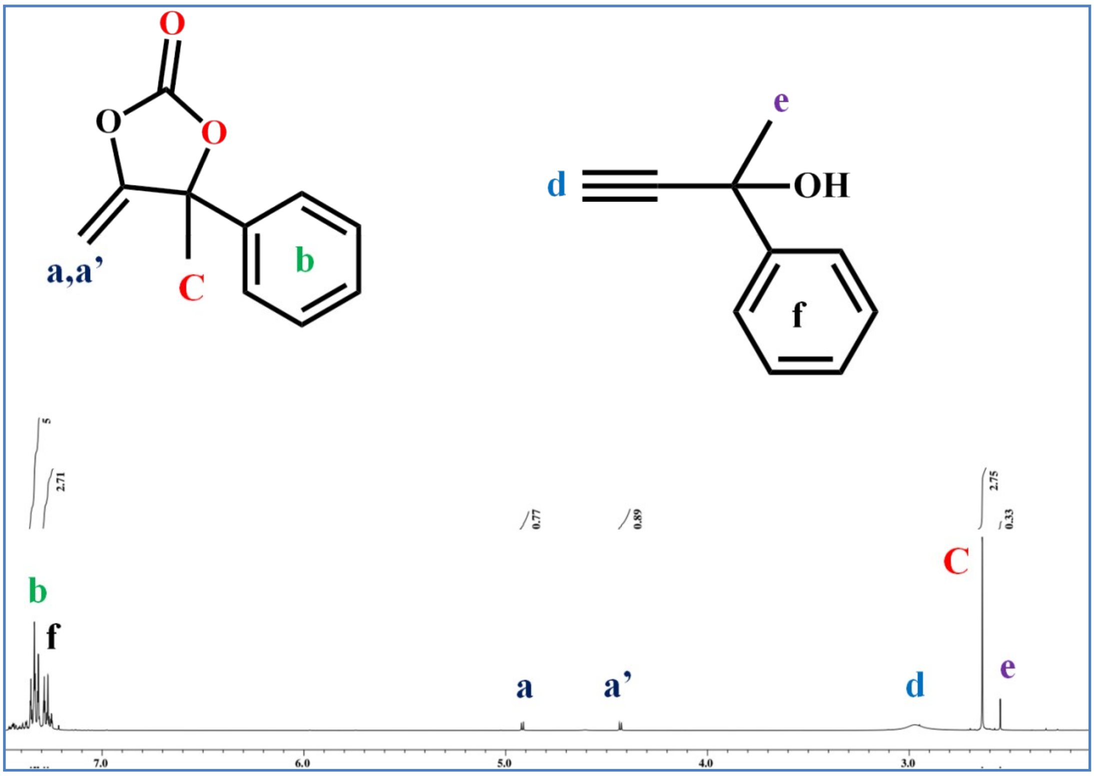
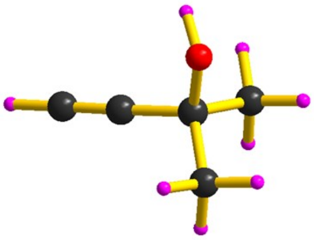
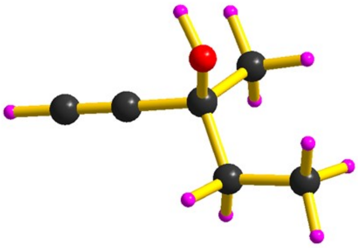
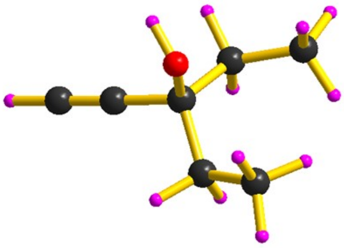
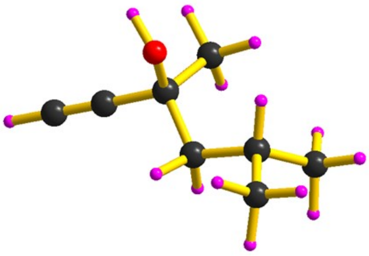
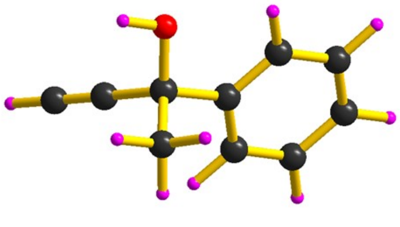


Figure S17. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-phenyl-butyn-2-ol catalysed by Ag(I)@MOF-NHC .

Table S1. Optimized geometries of propargylic alcohols using Gaussian09 at b3lyp/6-311g (d,p) level.[4]

Substrate	Optimized structure	Dimensions (Å^2)
2-methyl-3-butyn-2-ol		5.56 X 4.31
2-ethyl-3-butyn-2-ol		6.62 X 5.17
3-ethyl-1-pentyn-3-ol		6.56 X 5.35
2-isobutyl-3-butyn-3-ol		7.90 X 6.26
2-phenyl-butyn-2-ol		8.01 X 5.98

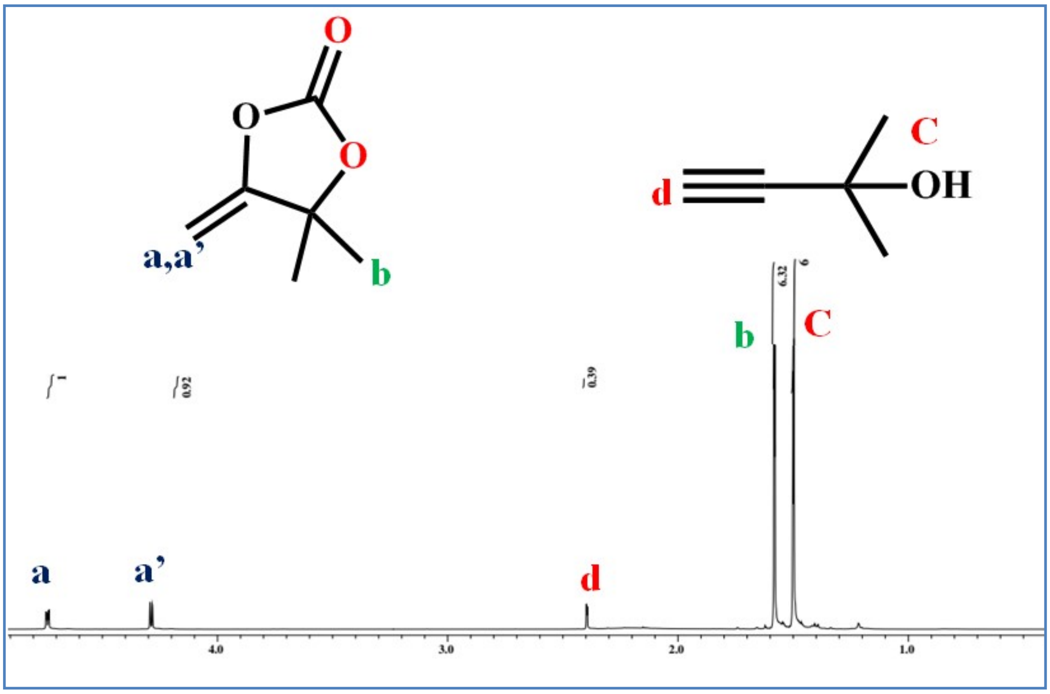


Figure S18. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Ag(I)@MOF-NHC using dilute CO_2 gas in 6 h.

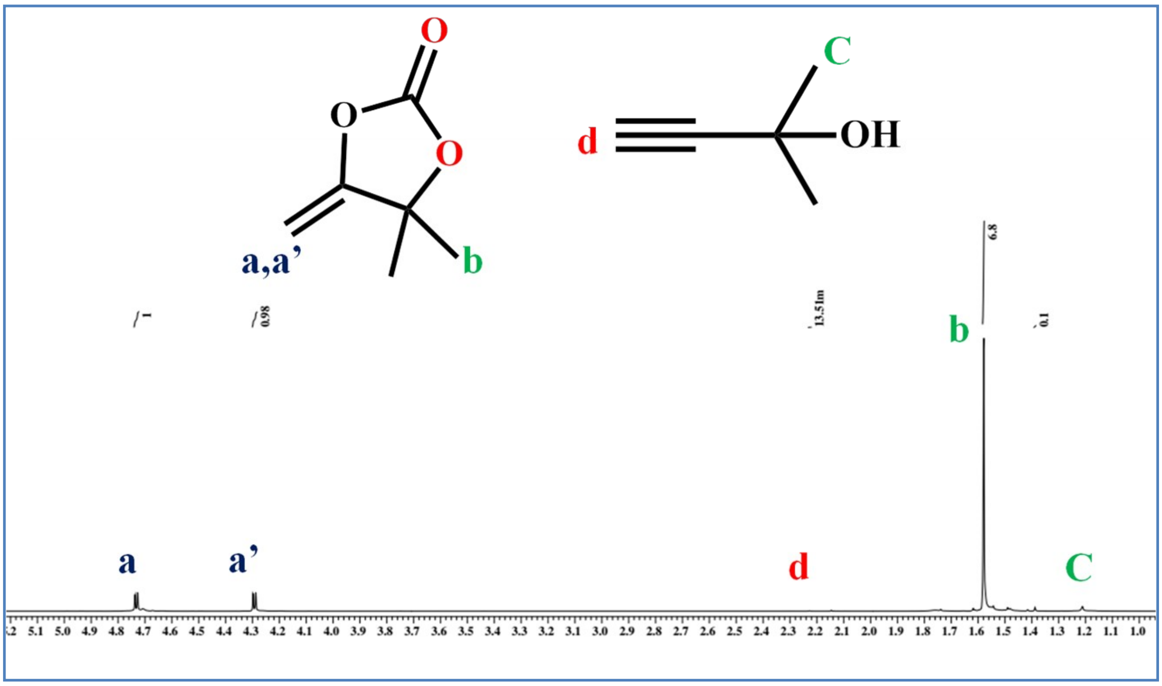


Figure S19. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Ag(I)@MOF-NHC using dilute CO_2 gas in 12 h.

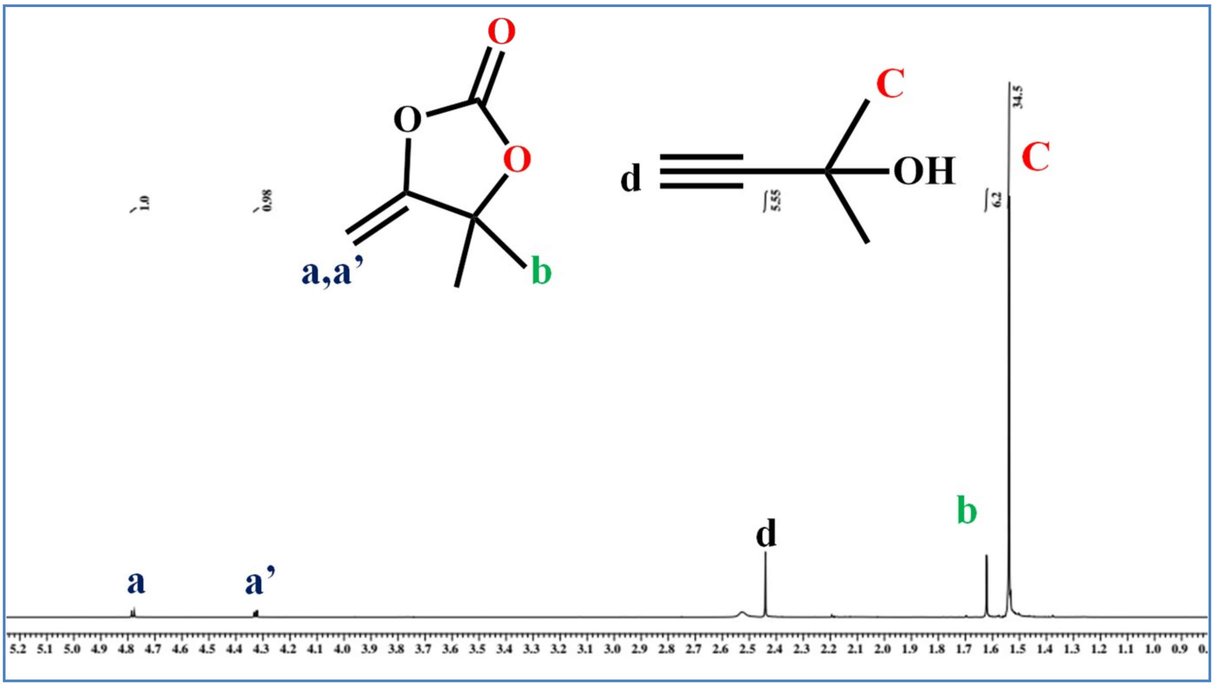


Figure S20. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Ag(I)@MOF-NHC using air as a source of CO_2.

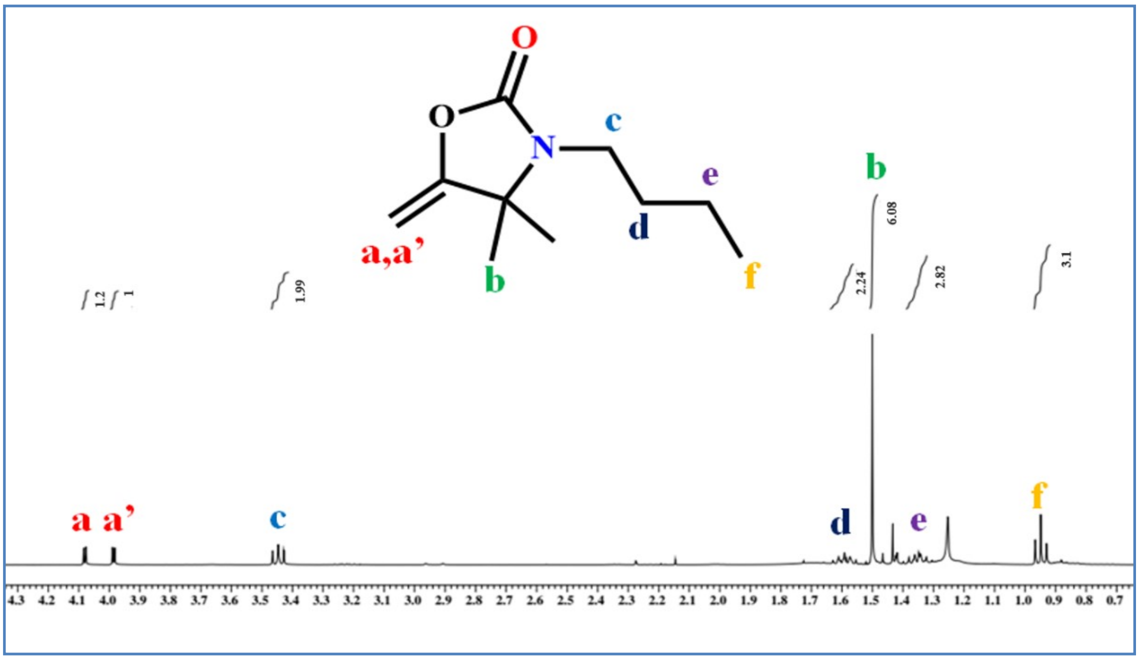


Figure S21. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for three-component reaction between CO_2, 2-methyl-3-butyn-2-ol and n-butylamine using Ag(I)@MOF-NHC as catalyst.

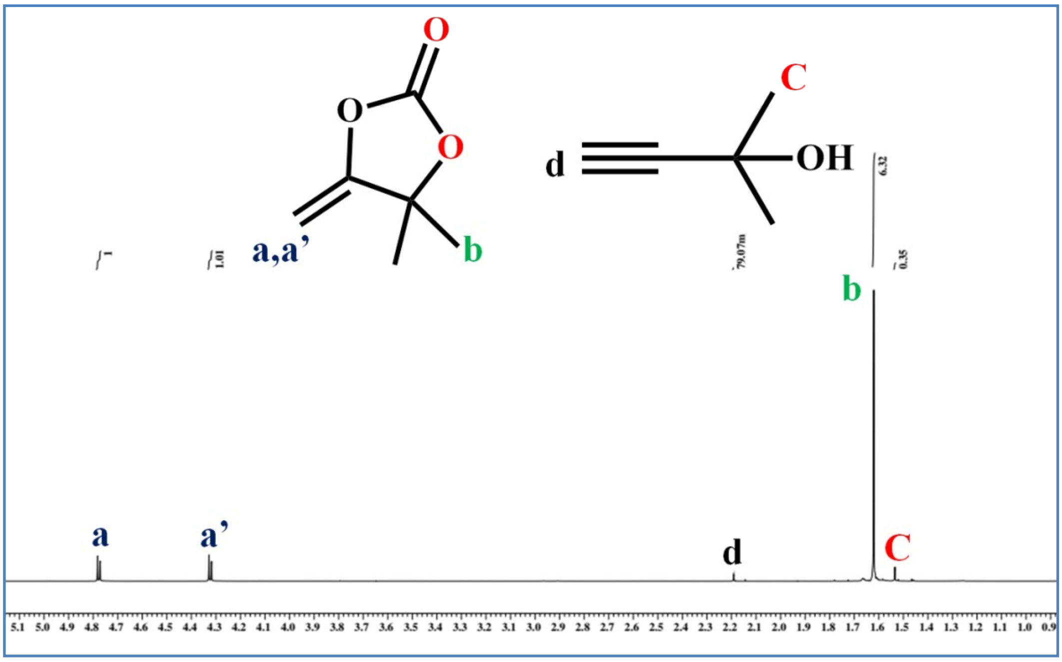


Figure S22. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for the cyclic carboxylation of 2-methyl-3-butyn-2-ol catalysed by Ag(I)@MOF-NHC after five cycles.

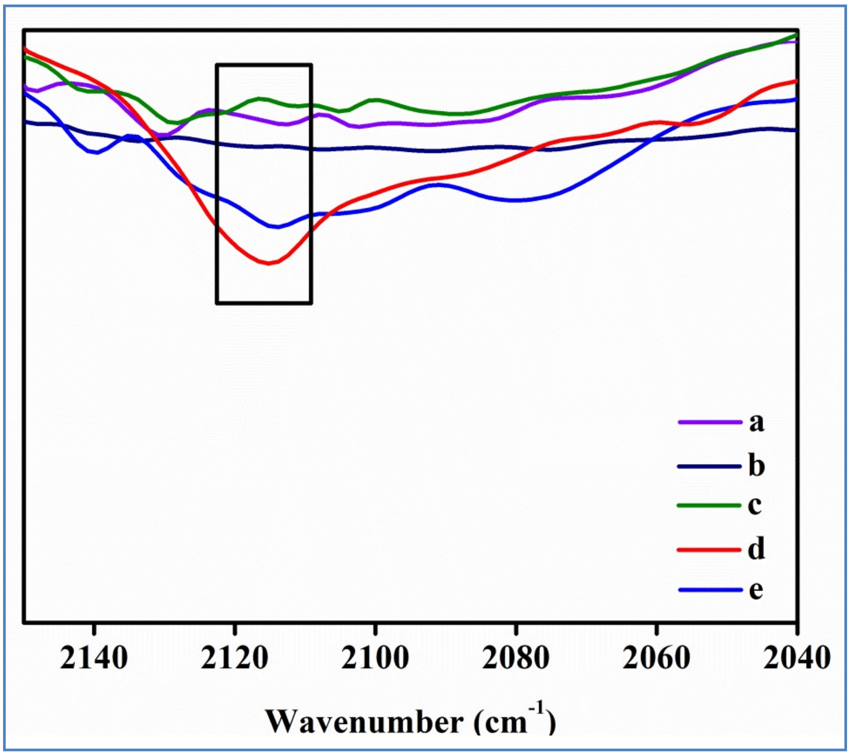
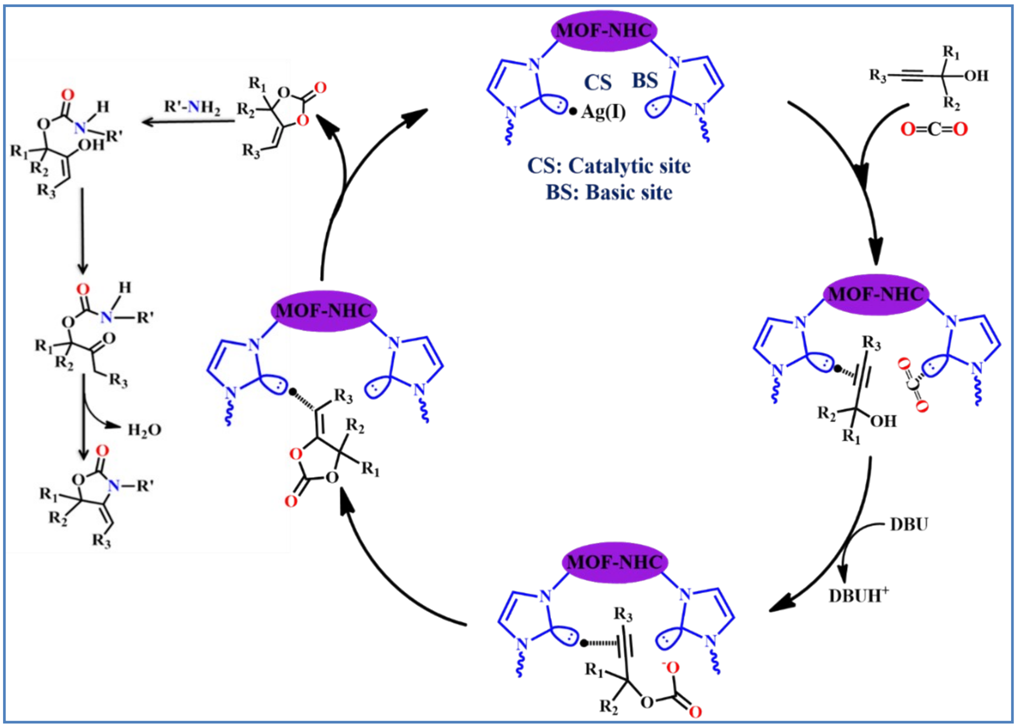


Figure S23. FT-IR spectra of (a) MOF-NHC, (b) Ag(I)@MOF-NHC , (c) 2-methyl-3-butyn-2-ol, (d) MOF-NHC treated with 2-methyl-3-butyn-2-ol, and (e) Ag(I)@MOF-NHC treated with 2-methyl-3-butyn-2-ol.



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

Reference

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

(4) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, Gaussian 09, Revision D.01,; Revision B.01,; Gaussian, Inc.: Wallingford CT, 2010.