Supporting Information for

An Alkaline-Resistant Ag(I)-Anchored Pyrazolate-Based Metal−Organic Frameworks for Chemical Fixation of CO_2

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General Methods

All starting chemicals and solvents were purchased from commercial suppliers (Aladdin, Adamas) and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded using a BRUKER D2 PHASER X-ray diffractometer equipped with a Cu sealed tube (λ = 1.54184 Å) at 30 kV and 10 mA with a scan speed of 1 s/step, a step size of 0.02° in 2θ, and a 2θ range of 5~40°; Elemental analyses (EA) for C, H, and N were operated on a FLASH EA 1112 element analyser. Fourier-transform infrared (FTIR) spectra were performed on a BRUKER ALPHA spectrophotometer in the region of 4000~400 cm^{-1} with a resolution of 2 cm^{-1}. Thermogravimetric analyses were carried out in N_2 stream (60 mL/min) on a NETZSCH STA 409 PC/PG differential thermal analyser running from room temperature to 700 °C with a heating rate of 10 °C/min. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were carried out on a BRUKER ARX400 spectrometer (400 MHz). Scanning Electron Microscopy (SEM) was carried out on a Hitachi S-4800 instrument using a 3 kV energy source under vacuum. Transmission Electron Microscopy (TEM) was carried out on a high-resolution transmission electron microscopy (HRTEM, Joel-2010) under 200 kV. X-ray Photoelectron Spectroscopy (XPS) was carried out on an AXIS ULTRA DLD instrument, and analyzed by the

XPSPEAK41 software. Inductive Coupled Plasma Emission Spectrometry (ICP) was collected on a PE 8300 Inductive Coupled Plasma Emission Spectrometer.

Experimental

Synthesise of 2-Nitro[1,4-bis(1H-pyrazol-4-yl)benzene] (H_2BDP-NO_2)

1,4-Bis(1H-pyrazol-4-yl)benzene (2.000 g, 9.52 mmol) and concentrated sulfuric acid (20 ml) was added in 50 ml flask. To the solution was then added dropwise 70% nitric acid (0.600 mL, 13.43 mmol) at 0 °C. After that, the mixture was stirred at room temperature for 12 h. The solution is diluted with crushed ice (10 g), and the precipitate was collected by centrifugation and neutralized with aqueous $NaHCO_3$, washed with 10 mL of water (2×5 mL), affording the pure ligand as a yellow solid (2.42 g, yield 99 %).

Synthesise of 2-Amino[1,4-bis(1H-pyrazol-4-yl)benzene] (H_2BDP-NH_2).

To a suspension of H_2BDP-NO_2 (0.600 g, 2.352 mmol) in DMF (10 mL) and ethanol (2 ml) was added Pd/C (10% wt., 35 mg) in 50 ml sealed flask at room temperature. H_2 was introduced into the bottle via a balloon. The reaction was allowed to stir for 6 h at 50 °C, after which the mixture was filtered off and a light yellow powder of H_2BDP-NH_2 was collected through rotary evaporation (529 mg, yield 99%).

Synthesis of NiBDP-NH_2

The NiBDP-NH_2 was synthesized after slight modification of the previous literature.[S1] BDP (27 mg, 0.124 mmol) and BDP-NH_2 (28 mg, 0.124 mmol) was introduced and dissolved in 5 mL DMF, followed by introduction of $Ni(OAc)_2$ (61 mg, 0.248 mmol). The mixture was reacted in a microwave reactor for 4 h. The resulting solid were isolated *via* centrifugation, rinsed with methanol (3×30 mL) to remove unreacted starting materials and dried in air, affording brown microcrystalline powders of NiBDP-NH_2 with a yield of 85% (0.54 g, based on the ligand).

Synthesis of NiBDP-SH

The NiBDP-NH_2 (50 mg, 0.124 mmol eq. of BDP) was immersed in CH_2Cl_2 (2 mL containing 0.28 mmol (26 mg) of mercaptoacetic acid. The mixture was left at room temperature to react for 12 h, and solids were isolated *via* centrifugation and washed thoroughly with fresh methanol (3×30 mL). After soaking in MeOH, the solids was isolated *via* centrifugation, and dried under vacuum.

Synthesis of NiBDP-AgS

The NiBDP-SH (24 mg, 0.05 mmol eq. of BDP) was introduced in a 4 mL aqueous solution containing $AgNO_3$ (8 mg, 0.5 mmol). The mixture was incubated for x h, and the solids was isolated by filtration and isolated *via* centrifugation. The solids was extensively washed with water (3×30 mL), and dried under air.

Gas Sorption

Freshly prepared NiBDP-NH_2, NiBDP-SH and NiBDP-AgS were soaked in 30 mL methanol (MeOH) for 3 days to achieve solvent exchange. Then, the MOFs were filtrated and dried under vacuum. 50 mg of activated sample was degassed at room temperature on a Micromeritics ASAP 2020 adsorption analyser for a minimum of 6 h or until the outgas rate was less than 5 mm Hg. Gas sorption isotherms were recorded volumetrically at 77K for N_2, 273K, 298K and 308K for CO_2, C_2H_2 and C_2H_6, respectively. BET surface area data were calculated using N_2 adsorption data at 77K. The exact surface area was averaged by the analyses of three independent samples. Isosteric heat of adsorption (Q_{st}) for were calculated by applying the Clausius-Clapeyron equation to two sets of adsorption data collected at two variable temperatures.

Catalytic Reaction

Cyclic CO_2 carboxylation of *N*-benzyl-propargylic amine: DBU (3.6 μl, 0.024 mmol or 72 μl, 0.48 mmol) and NiBDP-AgS (2.4 mg, 1.2 μmol) was added to a 1.2 mL DMSO solution containing *N*-benzyl-propargylic amine (34 mg, 0.24 mmol). After purging 1 atm CO_2, the reaction mixture was stirred at room temperature or 60 °C for

24 h. After 24 h, the mixture was filtered and the catalyst was washed by methanol for three times. The filtrate was extract by brine solution and $CDCl_3$. The organic layer of $CDCl_3$ solution was analyzed by ^{1}H-NMR.

Cyclic CO_2 carboxylation of propargyl amines: NiBDP-AgS (1.3 mg, 0.0065 mmol, 0.5 mol %) was introduced into a MeCN solution containing starting propargyl amines (0.13 mmol, 1.0 equiv) and DBU (0.0388 mL, 0.26 mmol, 2.0 equiv). After purging 1 atm CO_2, the reaction mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the mixture was filtered and the catalyst was washed by methanol for three times. The filtrate was extracted by the brine solution and $CDCl_3$. The organic layer of $CDCl_3$ solution was analyzed using ^{1}H-NMR.

Supporting Figures and Tables

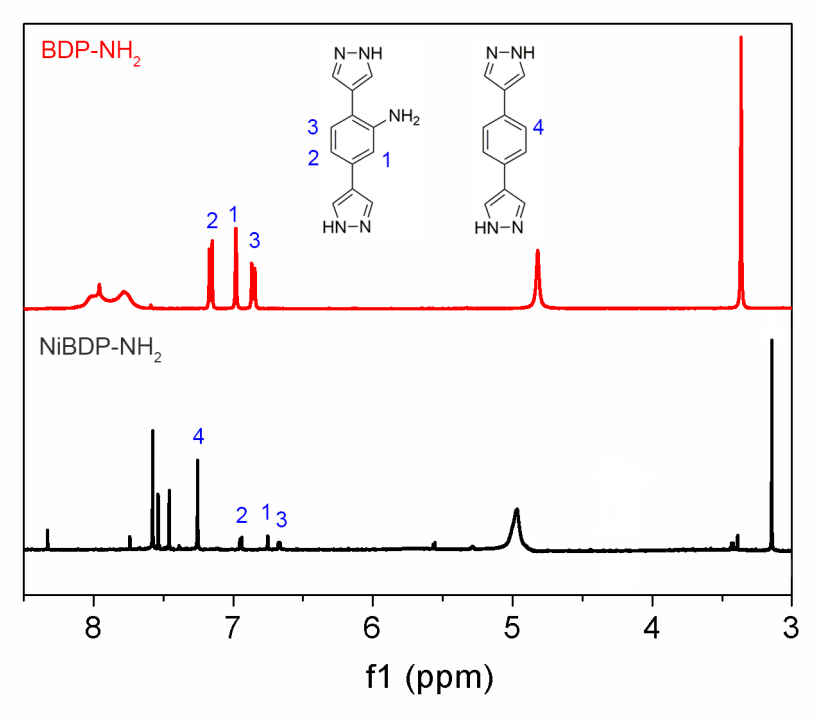


Figure S1. ^{1}H NMR pattern of NiBDP-NH_2.

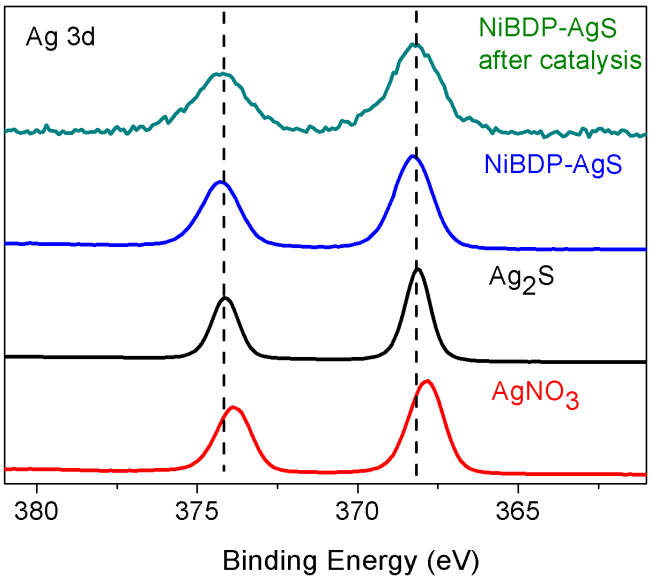


Figure S2. Ag(3d) XPS spectra of $AgNO_3$, Ag_2S, NiBDP-AgS before and after catalysis.

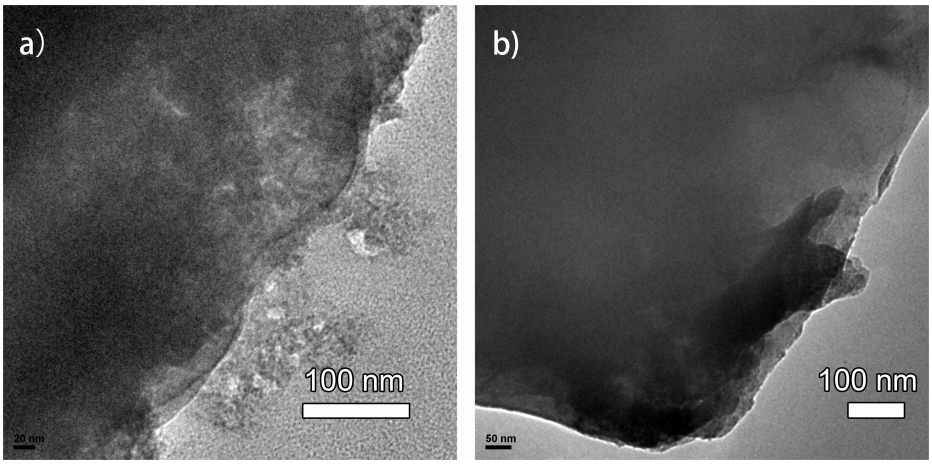


Figure S3. TEM images of NiBDP-AgS before catalysis (a) and after catalysis (b).

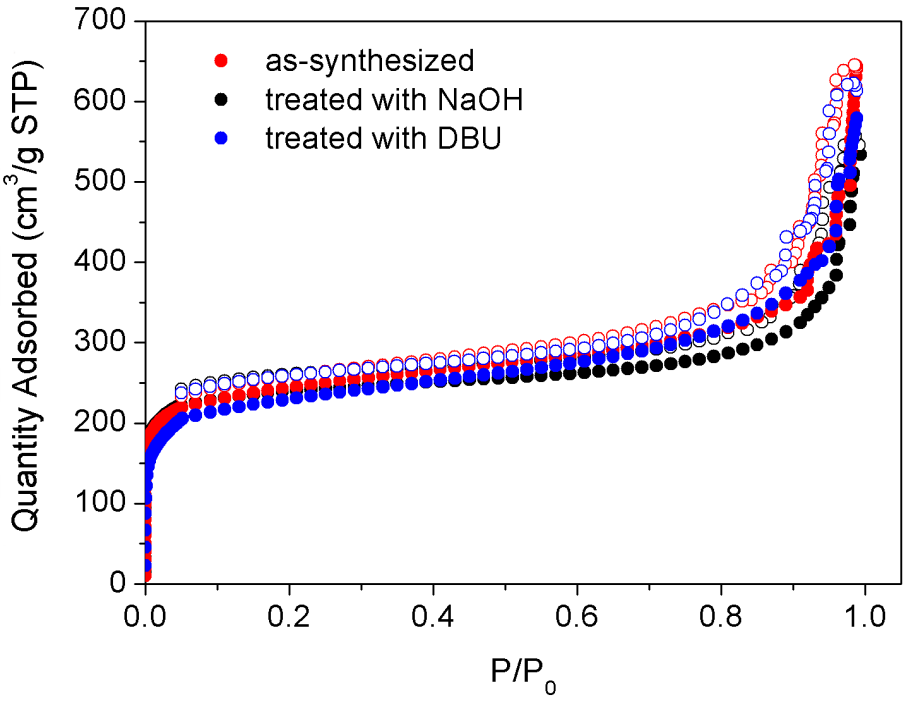


Figure S4. N_2 sorption isotherm of as-synthesized NiBDP-AgS (red), and NiBDP-AgS after treating with pH=13 NaOH aqueous solution (black) and 1M DBU solution (blue).

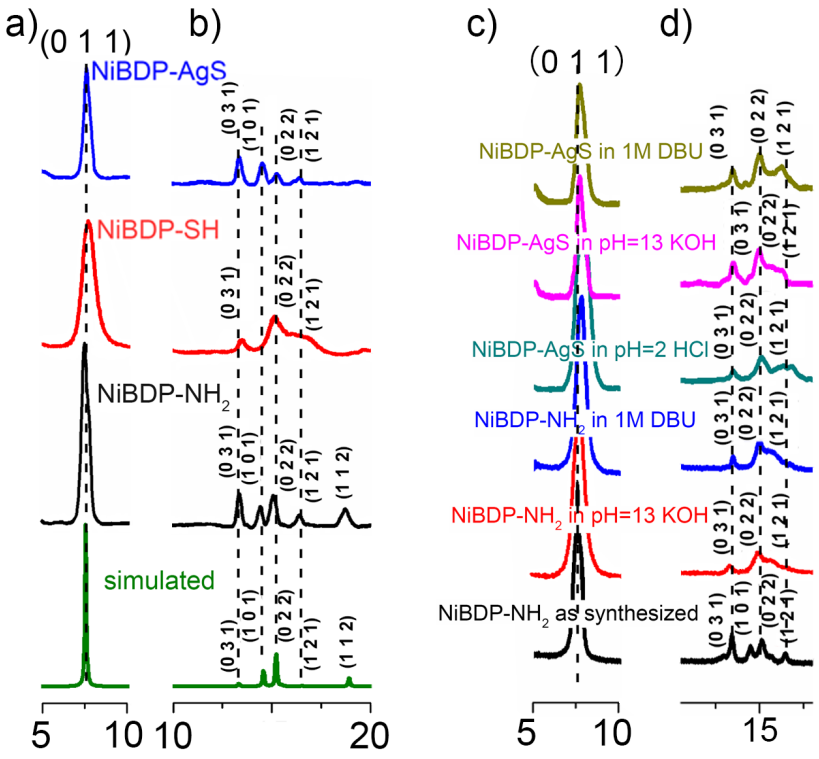


Figure S5. Zoom-in and the indexing of NiBDP before and after postsynthetic modification (a, left) and NiBDP after treating with different chemical conditions (b, right).

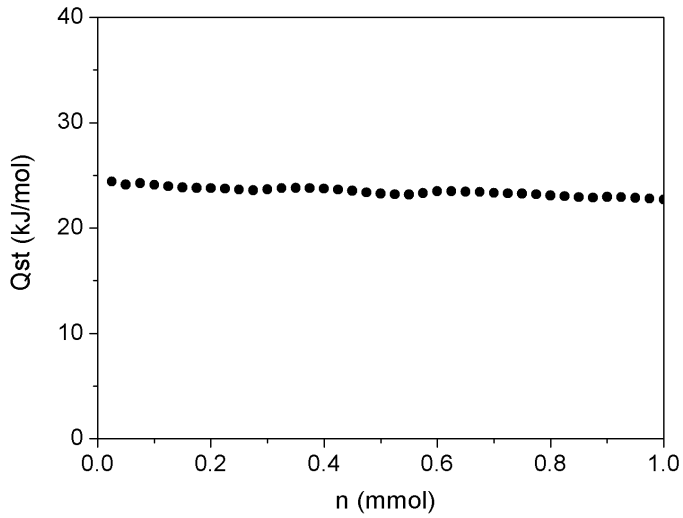


Figure S6. Q_{st} profile of NiBDP-AgS for CO2.

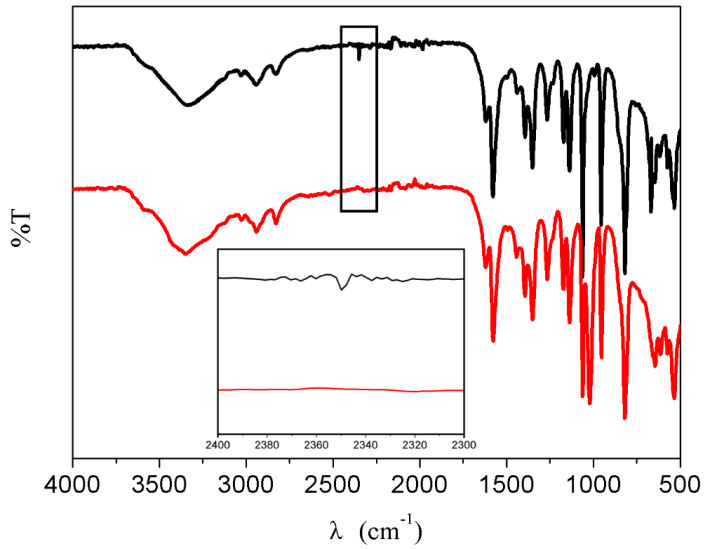


Figure S7. FTIR spectrum of NiBDP-AgS before and after CO_2 adsorption under room temperature and 1 atm.

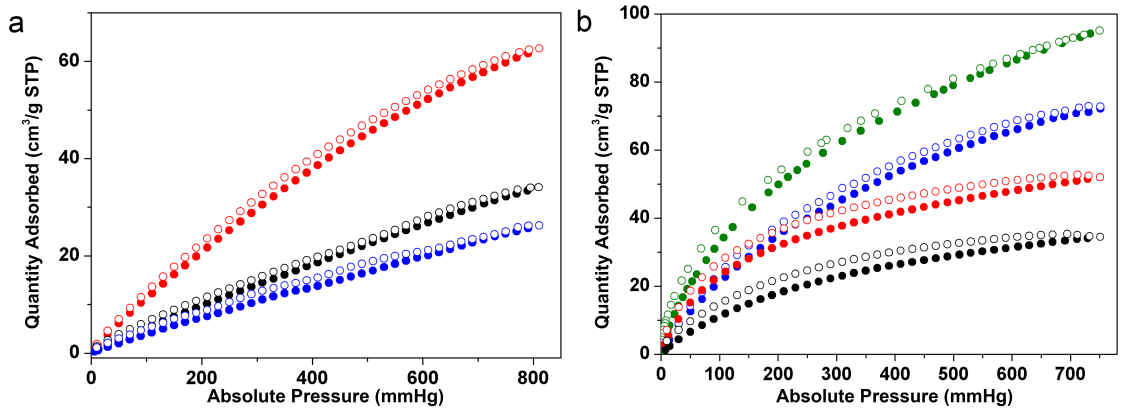


Figure S8. (a) CO_2 sorption isotherms of NiBDP-AgS at 273K (red), 298K (black) and 308K (blue). (b) C_2H_2 sorption isotherms of NiBDP-AgS at 273K (blue) and 298K (green) and C_2H_6 sorption isotherms of NiBDP-AgS at 273 (red) and 298K (black).

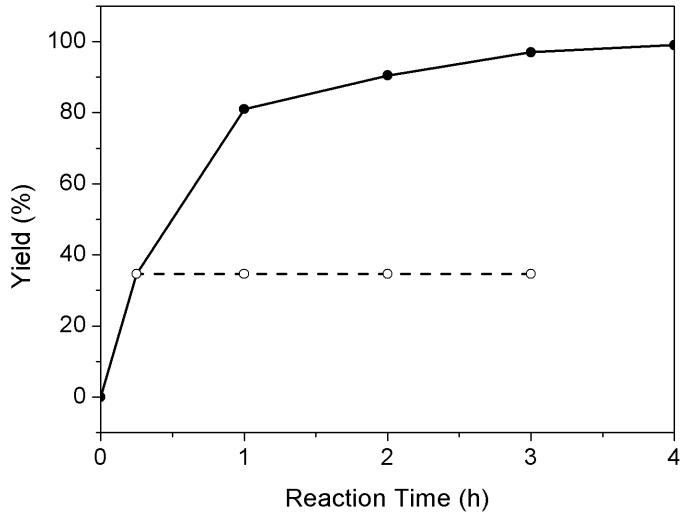


Figure S9. Time-dependent yields of the cyclic carboxylation of *N*-benzyl-propargylamine reaction and the dashed line indicate the reaction yield that the catalyst was removed after the first 15 min of the reaction.

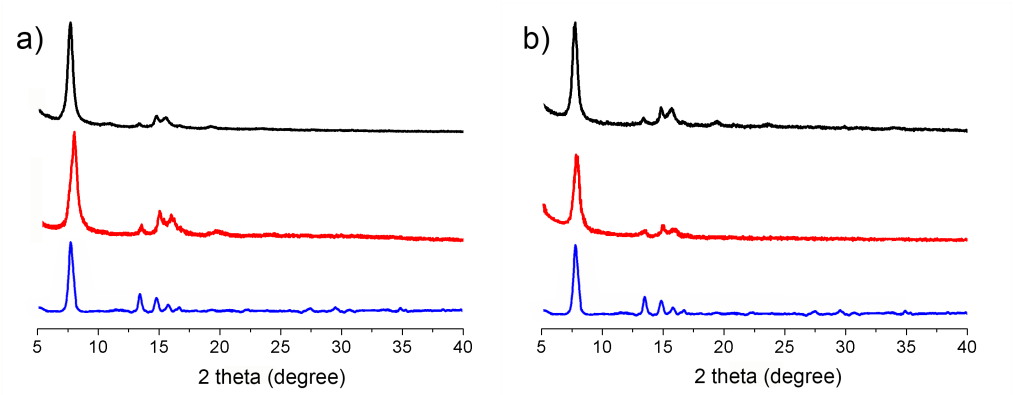


Figure S10. PXRD pattern of as-synthesized NiBDP-AgS (blue), after one-cycle catalysis (red) and ten-cycle catalysis (black) for cyclic carboxylation of propargyl amines (a, left) and cyclic carboxylation of N-benzyl-propargylamine (b, right).

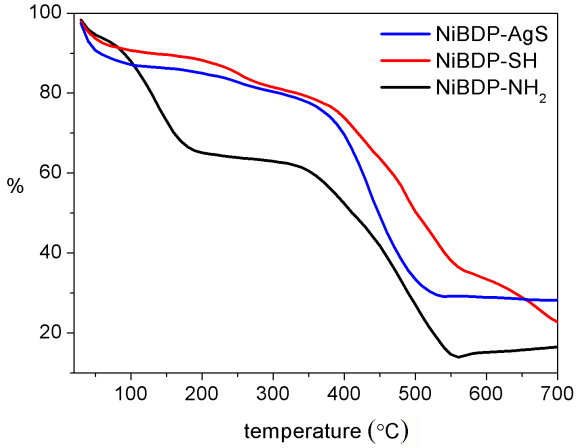


Figure S11. TGA of NiBDP-NH_2, NiBDP-SH and NiBDP-AgS.

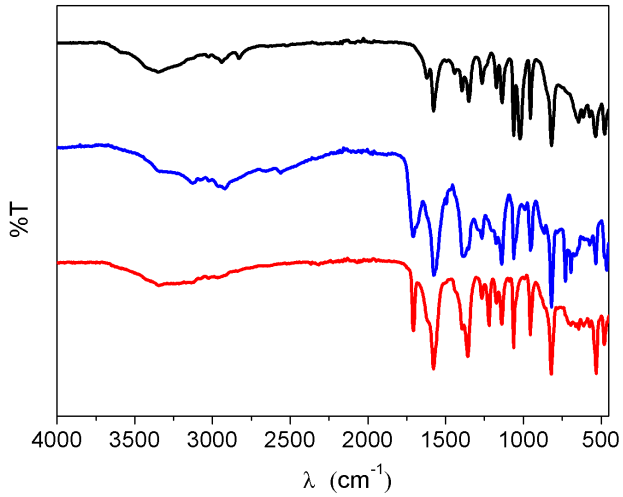


Figure S12. FTIR spectrum of NiBDP-NH_2 (red), NiBDP-SH (blue) and NiBDP-AgS (black).

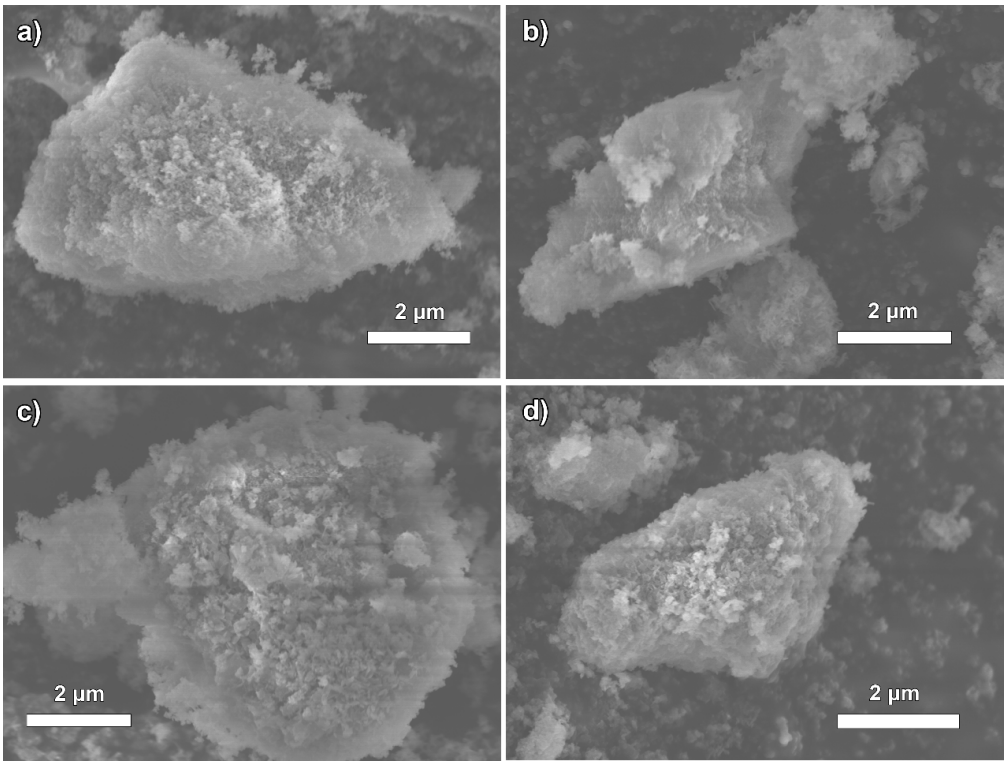


Figure S13. SEM pattern of NiBDP-NH_2 (a), NiBDP-SH (b), NiBDP-AgS (c), and NiBDP-AgS after catalysis (d).

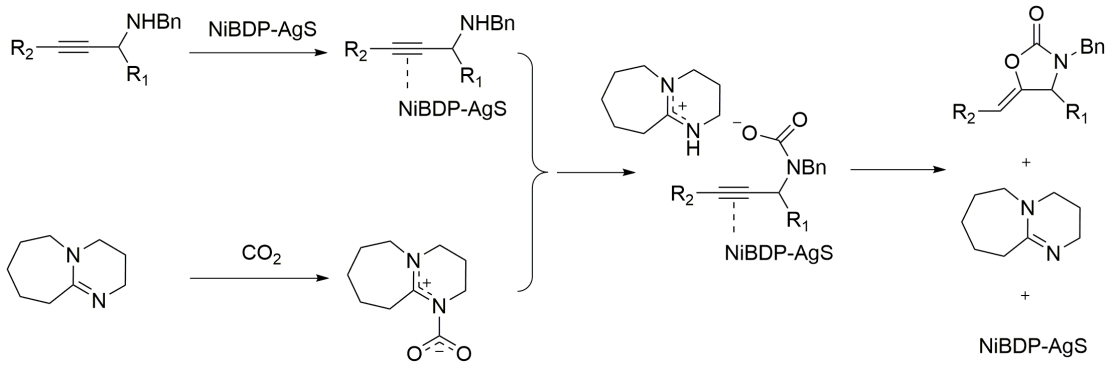


Figure S14. The proposed mechanism for the reaction of cyclic carboxylation of *N*-benzyl-propargylamine.

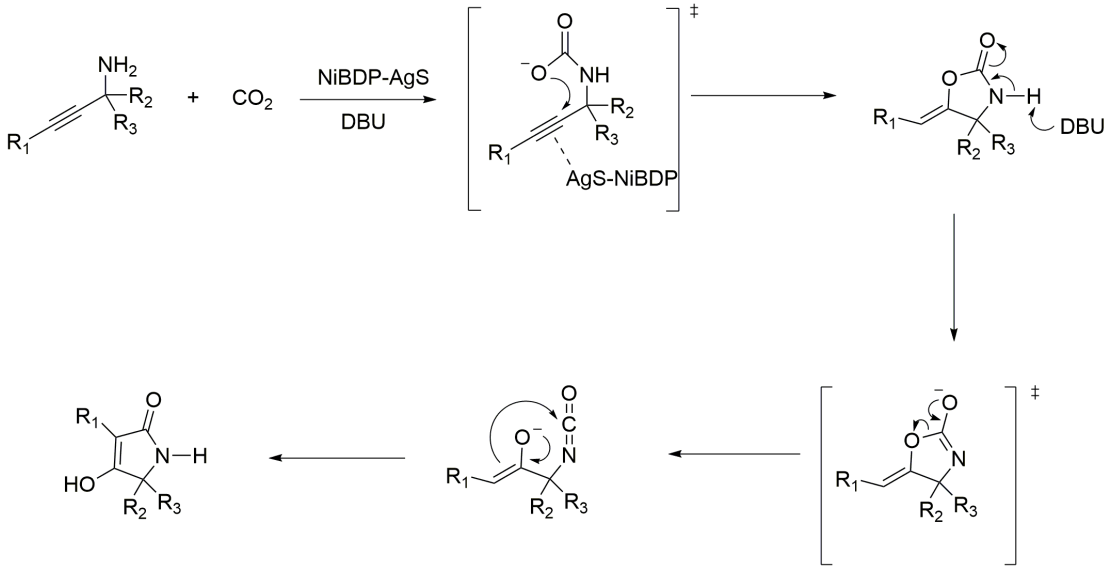


Figure S15. The proposed mechanism for the reaction of cyclic carboxylation of propargyl amine.

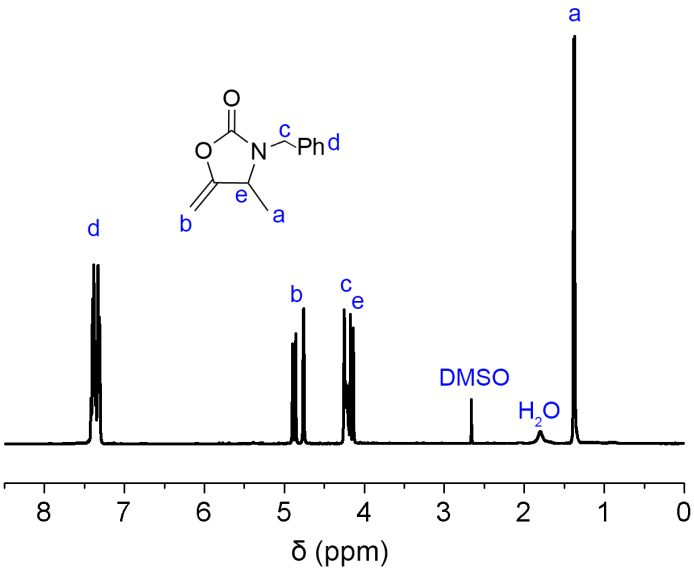


Figure S16. NMR spectrum of cyclic carboxylation of *N*-benzyl-propargylamine.

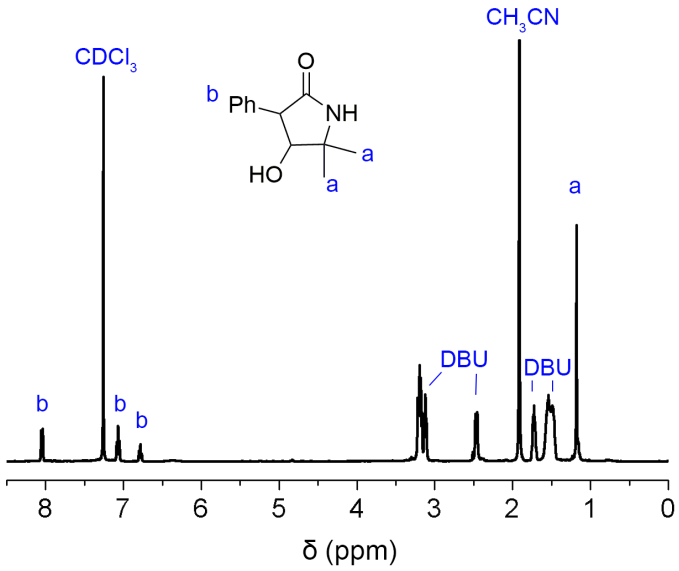


Figure S17. NMR spectrum of cyclic carboxylation of propargyl amines.

Table S1. Element analysis of NiBDP-NH_2 and NiBDP-SH.

	C%	N%	S%	H%
NiBDP-NH_2 (observed)	47.9	19.4	0.3	5.2
NiBDP-NH_2 (calculated)	48.3	19.4	0	5.23
NiBDP-SH (observed)	44.0	17.8	2.1	2.6
NiBDP-SH (calculated)	45.6	18.5	1.8	3.2

Table S2. Control reactions for cyclic carboxylation of *N*-benzyl-propargylamine.

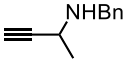
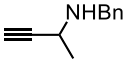
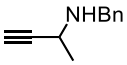
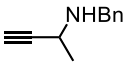
entry	Substrate	Catalyst	Time (h)	Yield (%)[e]
1		NiBDP	4	0
2		NiBDP-SH	4	0
3		200 mol% DBU	4	0
4		NiBDP-AgS	4	99

Table S3. Recyclability of NiBDP-AgS in ten successive runs of the catalysis. Yields are determined using NMR, average of two independent trials, error in parenthesis.

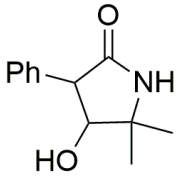
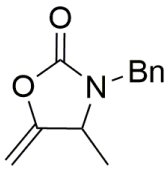
Run #	Product	
	1	2
		
1	97(8)	99
2	90(2)	99
3	91(0)	99
4	89(5)	99
5	89(8)	99
6	87(3)	99
7	92(6)	99
8	92(4)	99
9	91(3)	99
10	89(8)	99
Overall TON	1818	2000
Overall TOF	15.15 h^{-1}	50 h^{-1}

Table S4. TON and TOF of the cyclic carboxylation of *N*-benzyl-propargylamines.

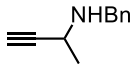
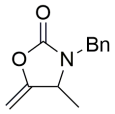
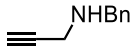
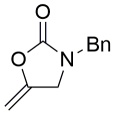
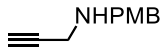
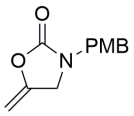
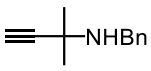
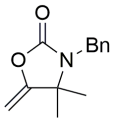
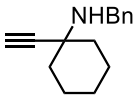
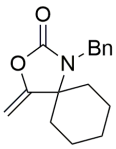
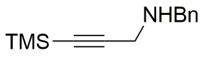
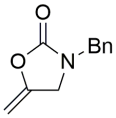
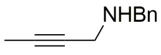
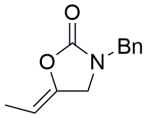
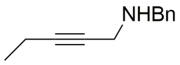
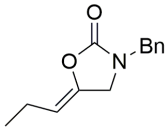
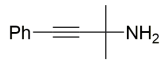
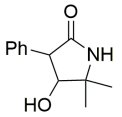
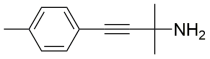
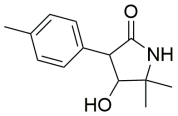
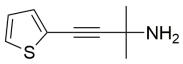
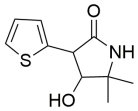
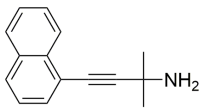
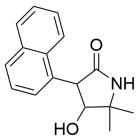
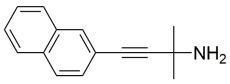
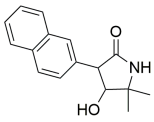
Substrate	Product	TON	TOF (h^{-1})
		200	50
		180	36
		200	50
		192	48
		106	4.4
		174	43.5
		17.5	1.45
		20.5	1.71

Table S5. TON and TOF of the cyclic carboxylation of propargyl amines.

Substrate	Product	TON	TOF (h^{-1})
		196	16.3
		175	14.6
		196	16.3
		189	15.8
		190	15.8

References

S1. V. Colombo, C. Montoro, A. Maspero, G. Palmisano, N. Masciocchi, S. Galli, E. Barea and J. A. R. Navarro, *J. Am. Chem. Soc.*, 2012, **134**, 12830-12843.