

Electronic supplementary information

**Schiff-base molecules and COFs as metal-free catalysts or silver
supports for carboxylation of alkynes with CO₂**

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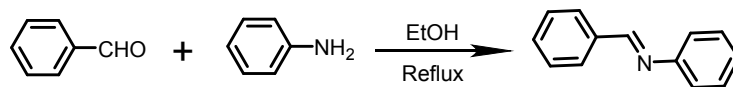
Materials

All the chemicals and reagents were purchased in analytical purity from commercial sources and used directly without further purification. Cs_2CO_3 , silver nitrate (AgNO_3), hydrazine hydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Dimethyl sulfoxide (DMSO), aniline, dichloromethane (CH_2Cl_2) were supplied by Tansoole Co., Ltd. Phloroglucinol, 1,3,5-trimethoxybenzene, *p*-toluene sulfonic acid monohydrate were bought from the Macklin Inc. Benzaldehyde, salicylaldehyde, terminal alkynes were obtained from Sinopharm Chemical Reagent Co., Ltd. 1,3,5-Triformylphloroglucinol (Tp) and 2,2'-bipyridine-5,5'-diamine (Bpyda) were synthesized according to literature methods.¹ 2,4,6-Trimethoxybenzene-1,3,5-tricarbaldehyde (TpOMe) was also synthesized according to reported method.²

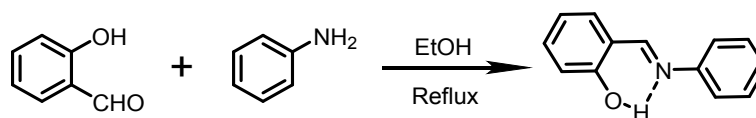
Measurements

X-ray diffraction (XRD) patterns of the samples were measured using a Rigaku D/Max-2500 diffractometer at 35kV, 25mA for a Cu-target tube and a graphite monochromator at ambient pressure. The FT-IR spectra were recorded in the range 400-4000 cm^{-1} using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. Scanning electron microscopy (SEM) images were carried out with a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were recorded using JEOL JEM-2100 TEM at an accelerating voltage of 200 kV. Nitrogen adsorption and desorption isotherm measurements were performed on a Micromeritics ASAP2020 analyzer at 77 K. Carbon dioxide adsorption and desorption isotherm measurements were performed on the same instrument at 273 K and 298 K. Thermal gravimetric analysis (TGA) was performed on a STA 449 F3 Simultaneous Thermal Analyzer in flowing air at 10 $^\circ\text{C}/\text{min}$. ^1H NMR spectra were recorded on Bruker Spectrometer at 25 $^\circ\text{C}$. The catalytic products were analyzed by gas chromatography (GC, Shimadzu: GC-2014) under the following conditions: injection volume 0.20 μL , oven temperature 150 $^\circ\text{C}$, start temperature 130 $^\circ\text{C}$ and remained 4 min, ramp 10 $^\circ\text{C}/\text{min}$, end temperature 250 $^\circ\text{C}$ and remained 3 min. X-ray photoelectron spectroscopy (XPS) analysis was conducted on SHIMADZU AXIS SUPRA, Ag content was determined by Optima 8300 inductively coupled plasma atomic emission spectrometer (ICP-AES).

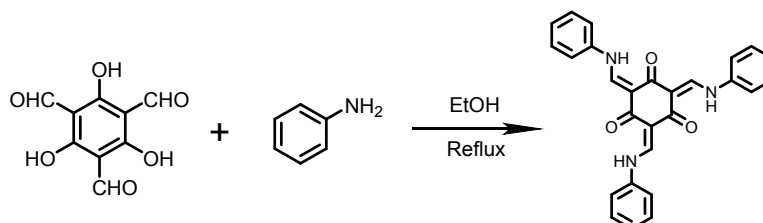
Synthetic and Experimental Procedures



Synthesis of diphenylmethanimine (PhAn). Benzaldehyde (1.02 mL, 10 mmol) and aniline (0.91 mL, 10 mmol) were dissolved together in EtOH (10 mL) and refluxed overnight. After cooling down to room temperature, the crude product was obtained by filtration. Recrystallization in EtOH gave white crystals. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.46 (s, 1H), 7.95 - 7.87 (m, 2H), 7.52 - 7.44 (m, 3H), 7.44 - 7.36 (m, 2H), 7.24 - 7.18 (m, 3H).



Synthesis of 2-((phenylimino)methyl)phenol (SaAn). This compound was obtained as faint yellow needle crystals using a similar method. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 13.10 (s, 1H), 8.97 (s, 1H), 7.67 (dd, 1H), 7.51 - 7.45 (m, 2H), 7.43 (td, 3H), 7.35 - 7.30 (m, 1H), 7.03 - 6.96 (m, 2H).



Synthesis of 2,4,6-tris((phenylamino)methylene)cyclohexane-1,3,5-trione (TpAn). Tp (0.163 g, 0.78 mmol) and aniline (0.5 mL, 5.37 mmol) were dissolved together in EtOH (70 mL), and the mixture was heated to reflux for 12 h. After cooling to room temperature, the precipitate was collected by filtration, washed with ethanol, and dried under vacuum to give a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 13.41 (d, 1H), 8.80 (d, 1H), 7.43 (dd, 2H), 7.38 - 7.30 (m, 2H), 7.22 (t, 1H).

Catalytic tests

Typically, the carboxylation reaction was carried out in a 10 mL Schlenk tube. The indicated amount of catalyst and DMSO (3 ml) were put into the tube, then Cs_2CO_3 (0.4778 g, 1.5 mmol) was added. After three times of atmosphere exchange with CO_2 , the reactor was equipped with a CO_2 balloon and heated to 60°C in an oil bath. Terminal alkyne (0.5 mmol) was injected under stirring to initiate the reaction. After reacting for a given time, the system was cooled to room temperature. After the addition of 20 mL water, the solid was separated by filtration and washed with water ($10\text{ mL} \times 3$). The filtrate was washed with CH_2Cl_2 ($3 \times 10\text{ mL}$), acidified with 1M HCl to $\text{pH} = 1$ and then extracted with ethyl acetate ($3 \times 40\text{ mL}$). The combined organic phase was washed with saturated NaCl solution and dried over anhydrous MgSO_4 . The solvent was removed under vacuum to obtain the carboxylic acid product, which was weighed for yield calculations.

For GC-based yield analysis, the filtrate obtained after removing water-insoluble solids or the reaction mixture diluted with 50 ml water (if no water-insoluble solids) was extracted with CH_2Cl_2 ($4 \times 30\text{ mL}$). The combined organic phase was washed with saturated brine. Toluene ($40\ \mu\text{l}$) was added as a standard. The amount of unreacted terminal alkyne was measured by GC.

For recycle tests, the used catalyst isolated from the last run was washed with acetone ($3 \times 10\text{ mL}$) and then heated under vacuum for 12 h.

For kinetics studies, the reactions were carried out in $\text{DMSO}-d_6$ under 50 and 60°C . In a given time interval, a small amount of reaction mixture was extracted with a syringe, and the catalyst was filtered off. The filtrate was analyzed by ^1H NMR to calculate the yield.

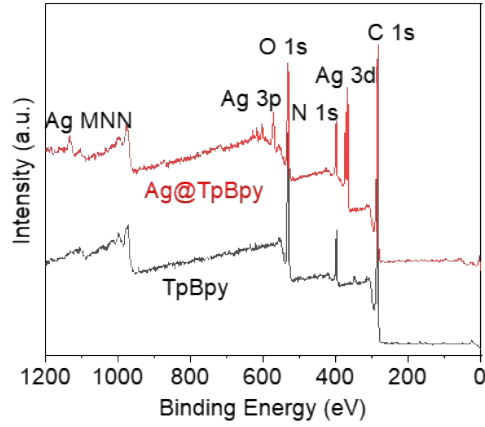


Fig S1. Full-range XPS spectra of TpBpy and Ag@TpBpy.

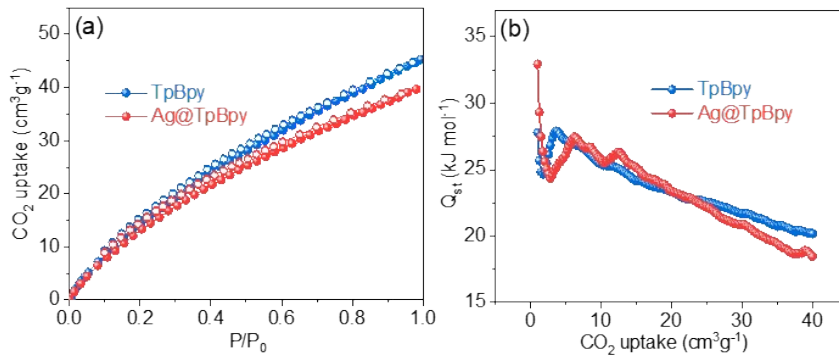


Fig S2. (a) CO₂ sorption isotherms at 298K. (b) CO₂ adsorption heat of TpBpy and Ag@TpBpy.

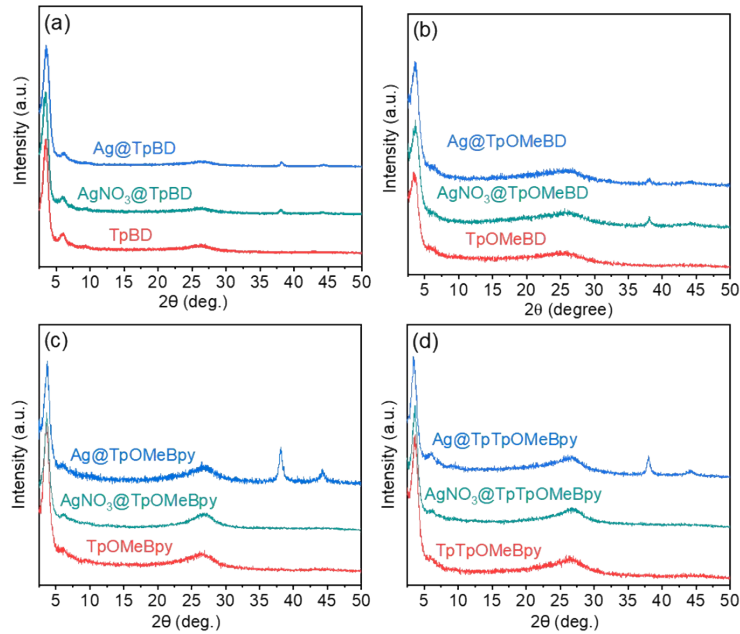


Fig S3. (a-d) XRD patterns of COFs, AgNO₃@COFs, and Ag@COFs

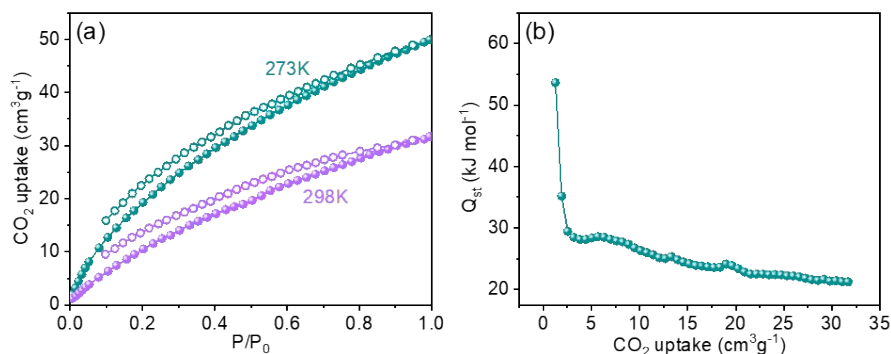


Fig S4. (a) CO₂ sorption isotherms of TpBpy treated with Cs₂CO₃ at 298 K and 273K. (b) CO₂ adsorption heat of TpBpy treated with Cs₂CO₃.

Table S1. Optimization for the catalytic carboxylation of phenylacetylene. ^a

Entry	Base	Solvent	Yield (%) ^b
1	Cs ₂ CO ₃	DMSO	67
2	Cs ₂ CO ₃	DMF	38
3	Cs ₂ CO ₃	PC	25
4	Cs ₂ CO ₃	CH ₃ CN	2
5	Cs ₂ CO ₃	Dioxane	7
6	-	DMSO	none
7	K ₂ CO ₃	DMSO	none
8	Na ₂ CO ₃	DMSO	none
9	KOH	DMSO	none
10	Triethylamine	DMSO	none

^a Reaction conditions: phenylacetylene (0.5 mmol), base (1.5 mmol), solvent (3 ml), CO₂ (1.0 atm), 60 °C, 6h. ^b Isolated yield. "none" means that no product is obtained through separation.

Table S2. Synthesis of 3-phenylpropionic acid from CO₂ and phenylacetylene with catalysts.

Entry	Catalyst (Ag, Cu/ wt%)	Reaction conditions	Yield (%)	TOF (h ⁻¹) ^a	ME (mmol/g/h) ^b	Ref.
1	bis-(NHC)-Cu(I) (9.0)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.2 mmol), CO ₂ (1 atm), DMSO (1 ml), 50 °C, 16 h	80	1.0	1.4	3
2	TpBpy-Cu-14 (13.6)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMSO (5 ml), 60 °C, 18 h	90	2.3	4.0	4
3	Cu-CN-8.0 (8.0)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.25 mmol), CO ₂ (1 atm), DMF (2 ml), 80 °C, 10 h	97	9.7	11.2	5
4	UiO-66 @UiO-67-Bpy-Ag (4.38)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMF (2 ml), 50 °C, 24 h	96	5.5	2.2	6
5	Ag/Schiff-SiO ₂ (1.45)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMSO (5 ml), 60 °C, 24 h	98	29	4.0	7

6	Ag@P-NHC (6.8)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.2 mmol), CO ₂ (1 atm), DMF (5 ml), 25 °C, 20 h	98	16	9.8	8
7	Ag-HMP-2 (3.21)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMF (5 ml), 80 °C, 12 h	98	6.8	2.0	9
8	Ag@MIL-101 (4.16)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMF (5 ml), 50 °C, 15 h	97	2.4	0.9	10
9	CTF-DCE-Ag (4.3)	phenylacetylene (1 mmol), Cs ₂ CO ₃ (2 mmol), CO ₂ (1 atm), DMF (5 ml), 50 °C, 20 h	90	11	4.5	11
10	Ag ⁰ @CTFN (1.37)	phenylacetylene (0.5 mmol), Cs ₂ CO ₃ (1 mmol), CO ₂ (1 atm), DMSO (3 ml), 60 °C, 24 h	97	5.3	0.7	12
11	Ag/PCNF-700 (3.69)	phenylacetylene (0.5 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMSO (3 ml), 25 °C, 18 h	90	3.7	1.3	13
12	Ag@TpBpy (1.9)	phenylacetylene (0.5 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMSO (3 ml), 60 °C, 6 h	93	22	3.9	This work
13	TpBpy (0)	phenylacetylene (0.5 mmol), Cs ₂ CO ₃ (1.5 mmol), CO ₂ (1 atm), DMSO (3 ml), 60 °C, 14 h	93	-	1.7	This work

^a TOF based on the metal center. ^b ME (mass efficiency) = the amount of product (mmol)/catalyst (g)/time (h).

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