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Supporting Information

Rose Bengal-Functionalized Porous Organic Polymer for Carboxylative Cyclization of Propargyl Alcohols with CO_2

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1. General experimental methods

Materials

All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise.

Instrumentation

Liquid ^{1}H and ^{13}C NMR spectra were recorded on Bruck 400 spectrometer. Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm^{-1}. Gas sorption isotherms were obtained with Micromeritics TriStar II 3020 and Micromeritics ASAP 2020 M+C accelerated surface area and porosimetry analyzers at certain temperature. The samples were outgassed at 140 ^{o}C for 8 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi SU8020 microscope operated at an accelerating voltage of 15.0 kV. (HR) Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 and JEM-2100F instrument operated at 200 kV. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA PT1600 Linseis) over the temperature range of 25 to 800 °C under air with a heating rate of 10 °C/min. The content of Ag in the **Ag@RB-POP** was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES VISTA-MPX). X-ray photoelectron spectroscopy (XPS) was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of ~3×10^{-9} mbar (1 mbar = 100 Pa) using Al Ka as the excitation source (1486.6 eV) and operated at 15 kV and 20 mA. The binding energies were referenced to the C_{1s} line at 284.8 eV from adventitious carbon. The XRD analysis was performed on a D/MAX-RC diffractometer operating at 30 kV and 100 mA with $Cu_{K\alpha}$ radiation.

2. Synthetic procedures

(1) Synthetic procedure for RB-POP

Typically, Rose bengal (1 mmol), 1,4-diethynylbenzene (2 mmol), tetrakis(triphenylphosphine) palladium (20 mg) and cuprous iodide (10 mg) were dissolved in the mixture of 4 mL of N,N-dimethylformamide and 4 mL of triethanolamine. Then the reaction mixture was heated to 90 ^{o}C and stirred for 72 h under a nitrogen atmosphere. After cooling down to room temperature, the solid was collected by filtration and washed with distilled water, tetrahydrofuran and ethanol for three times. After being extracted in a Soxhlet extractor with ethanol, H_2O and THF (1: 1: 1) for 48 h, **RB-POP** as deep red solid was collected and dried in vacuum oven at 80 °C for 24 h. The yield was 88% for **RB-POP.**

(2) Synthetic procedure for Ag@RB-POP

In a round-bottom flask equipped with a nitrogen inlet and a reflux condenser, $AgBF_4$ (6 mg) dissolved in 20 mL of THF and **RB-POP** (300 mg) were added under nitrogen. The mixture was kept stirring for 24 h at 80 ^{o}C in dark. The resulting solid was isolated by filtration and washed with THF, and then purified using Soxhlet extraction (THF) for 24 h. **Ag@RB-POP** was obtained as a brown

powder after drying at 80 °C under vacuum for 12 h. The **Ag@porous carbon** was prepared in the same way using various supports.

(3) General procedure for carboxylative cyclization reaction

Typically, propargyl alcohols (i.e., **1a-1k,** 0.5 mmol), **Ag@RB-POP** (20 mg), DBU (0.5 mmol) and CH_3CN (2 mL) were successively added into a stainless steel autoclave with a Teflon tube (16 mL inner volume) under N_2 atmosphere. The autoclave was sealed and charged with CO_2 up to 1 MPa at room temperature, then was moved to an oil bath of 30 °C and stirred for 12 h. After reaction, the yield of **2a~2k** were determined by NMR using mesitylene as an internal standard and $CDCl_3$ as the solvent. The pure products of **2a~2i** was obtained by column chromatography on silica gel using petroleum ether/ethyl acetate (from 10:1 to 1:1) as eluent and identified by NMR spectra.

(4) Recycling test of Ag@RB-POP

After reaction, the catalyst was recycled by filtration, washed with 50 mL CH_2Cl_2, and then dried under vacuum at 40 °C for 24 h. The recycled catalyst was reused for the next run without further purification.

3. Supplementary Figures

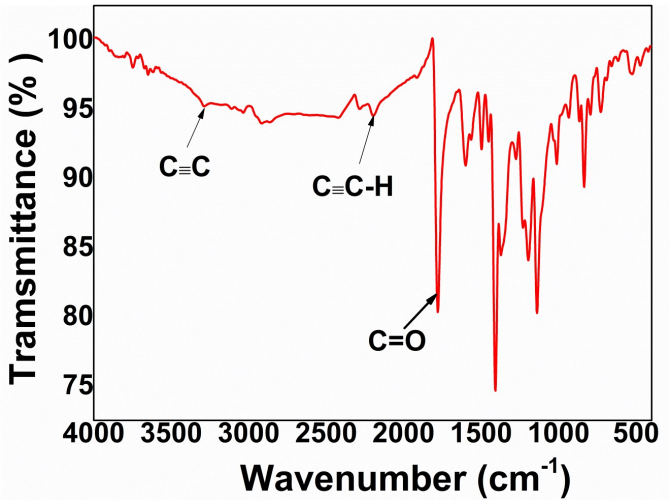


Figure S1 FTIR spectrum of **RB-POP.** The spectrum was recorded as KBr pellets.

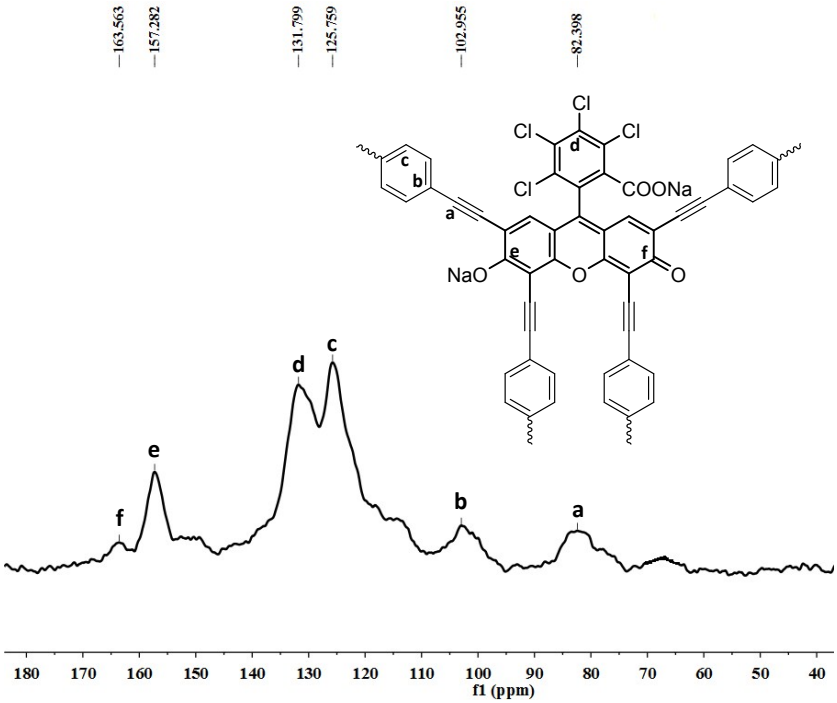


Figure S2 CP/MAS ^{13}C NMR spectrum for **RB-POP**.

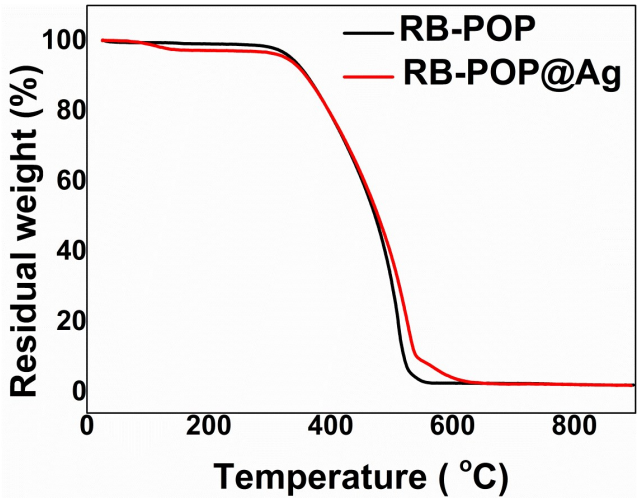


Figure S3 TGA analysis on **RB-POP** and **Ag@RB-POP** in air, with a ramping rate of 10 °C min.

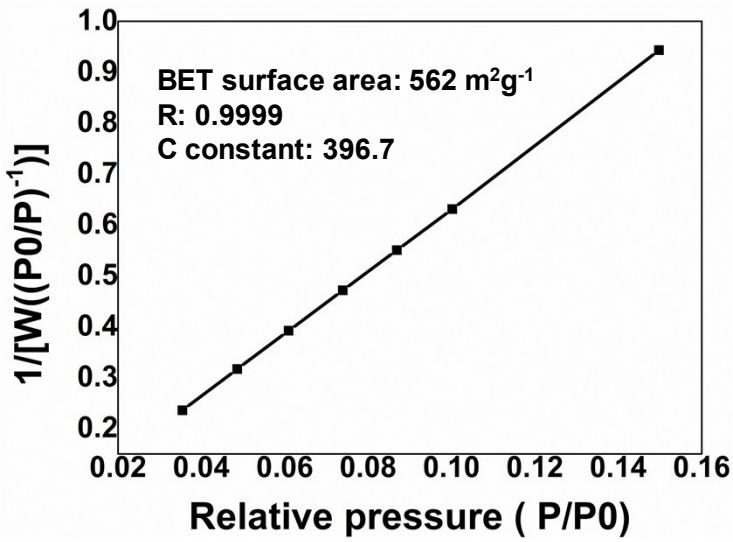


Figure S4 BET plot of **RB-POP.**

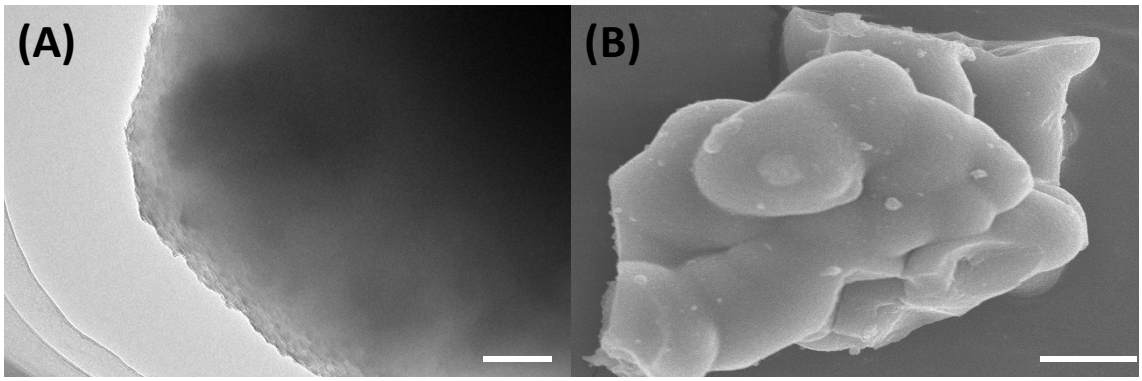


Figure S5 (a) SEM and (b) TEM images of **RB-POP**. Scale bar, (a) 200 nm, (b) 20 μm.

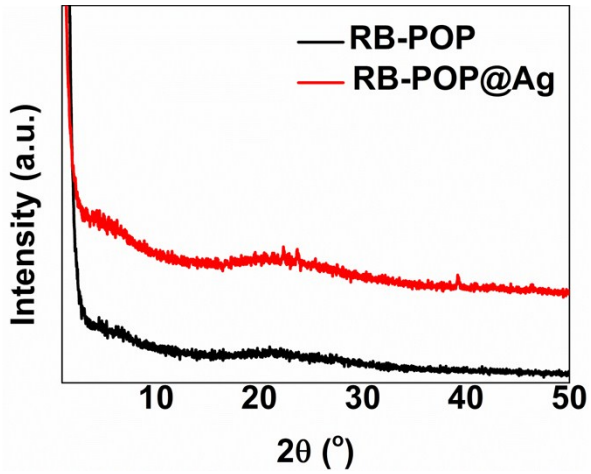


Figure S6 PXRD-pattern of **RB-POP and Ag@RB-POP.**

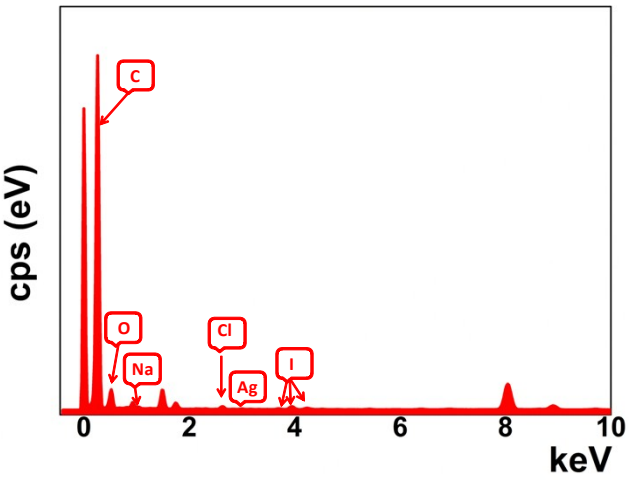


Figure S7 EDS profile of **Ag@RB-POP**

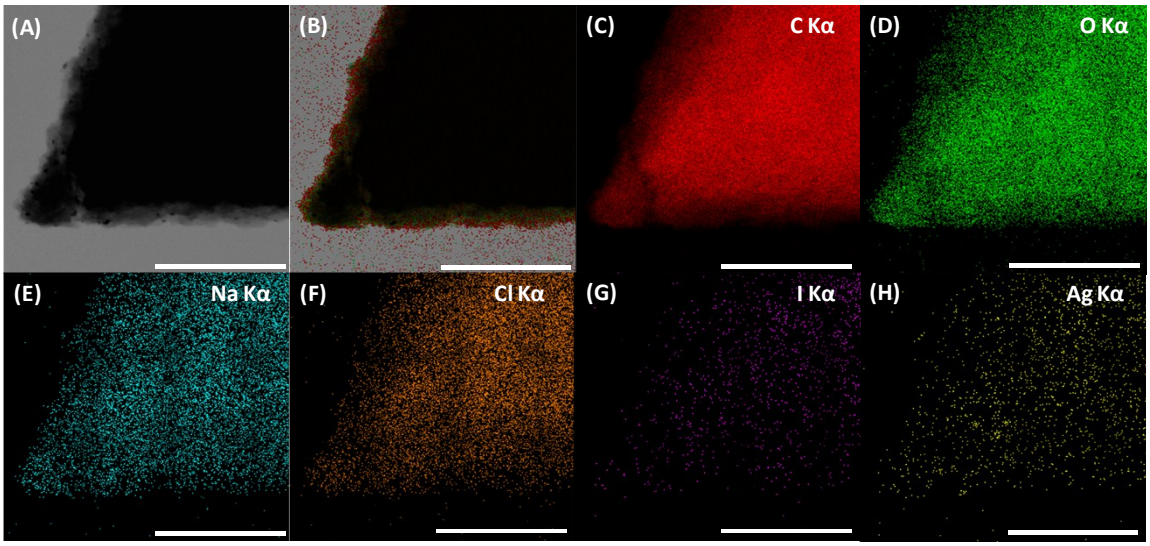


Figure S8 (A) The(HR)TEM of **Ag@RB-POP,** Scale bar 200 nm, (B) to (H) are the compositional EDS mapping of **Ag@RB-POP** using scanning transmission electron microscopy. Scale bar 200 nm.

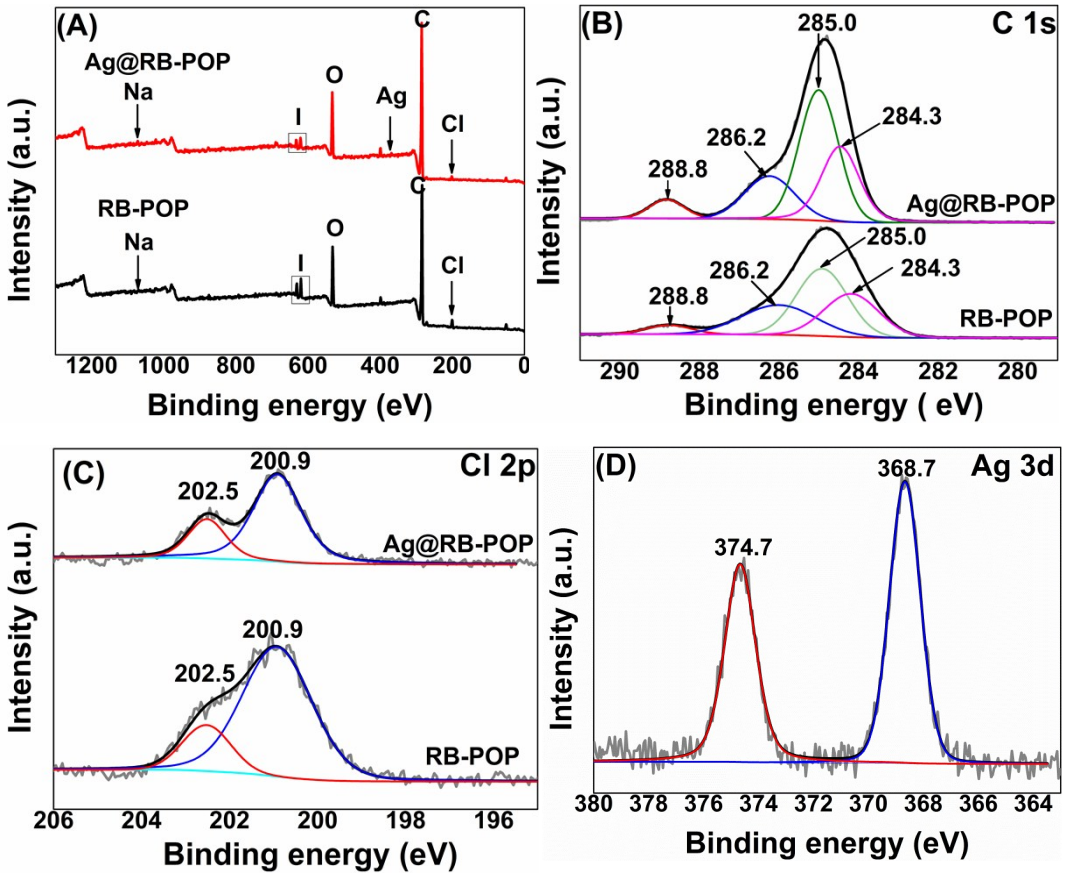


Figure S9. XPS spectra: (A) survey spectra, (B) C1s, (C) Cl1s for **RB-POP** and **Ag@RB-POP** (D) Ag 3d for **Ag@RB-POP -After**

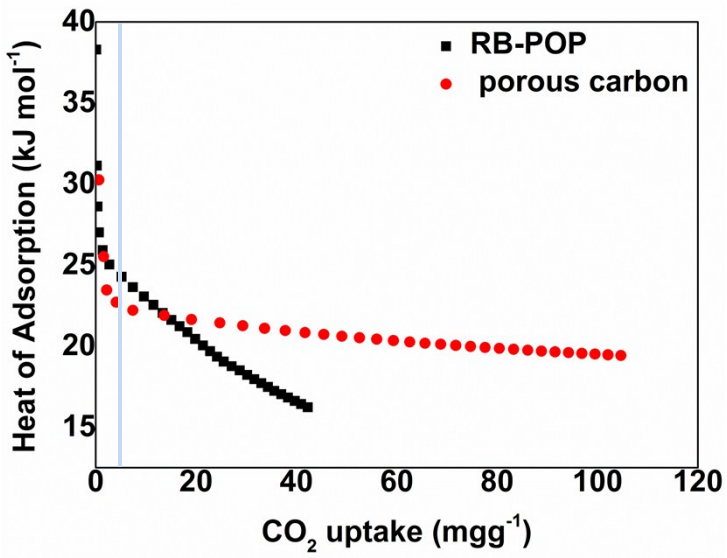


Figure S10 Isosteric heats of adsorption (Qst) for CO_2 adsorption by RB-POP and porous carbon. The isosteric heats of adsorption (Qst) are calculated by fitting the CO_2 adsorption isotherms at 273 K and 298 K and applying of the Clausius-Clapeyron equation.

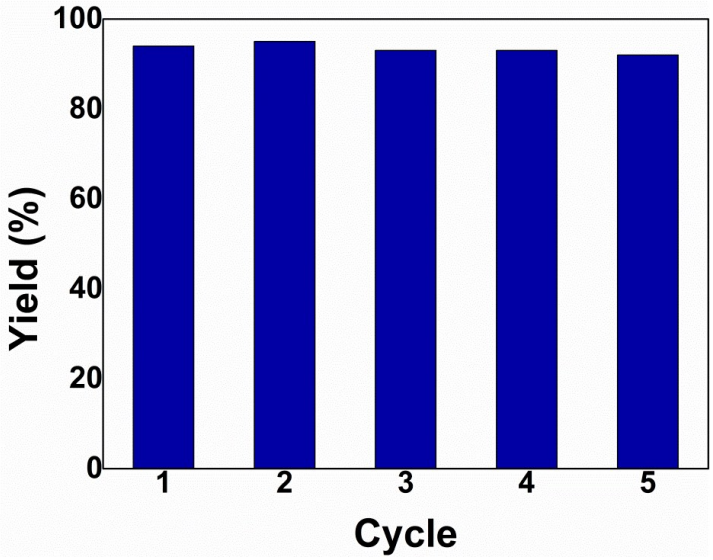
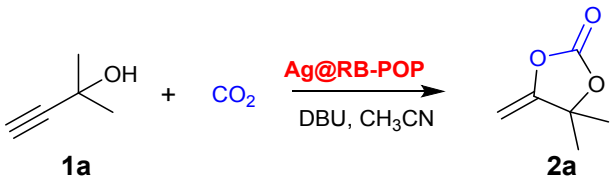


Figure S11 Recyclability test of **Ag@RB-POP**. Reaction conditions: **1a**, 0.5 mmol; **Ag@RB-POP**, 20 mg (Ag was 0.01 mol% based on **1a**); DBU, 0.5 mmol; CO_2 1 MPa; CH_3CN, 2 mL; 30 °C, 12 h. [b] Determined by ^1H NMR ($CDCl_3$, 400 MHz) using mesitylene as an internal standard.

Table S1 Base screening[a]

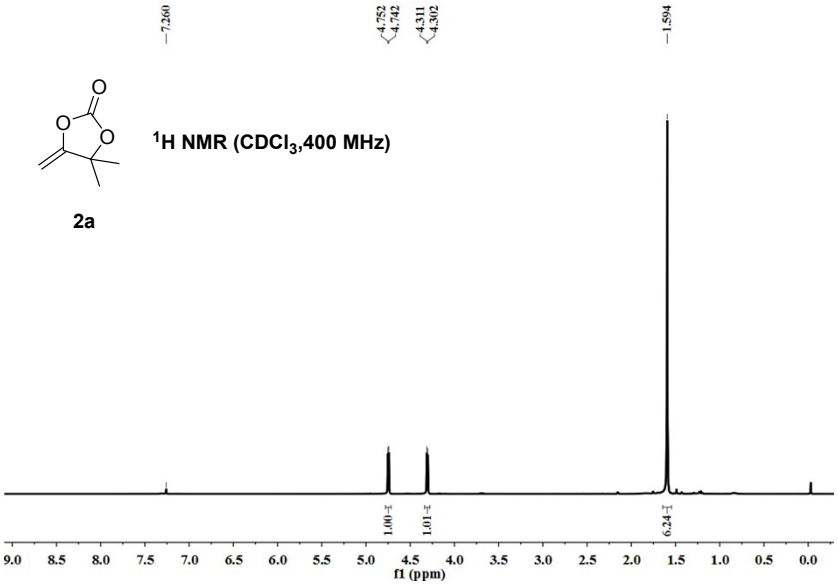


1a **2a**

Entry	Base	Catalyst	Yield/%[b]
1	DBU	**Ag@RB-POP**	94
2	t-BuOK	**Ag@RB-POP**	<1
3	KOH	**Ag@RB-POP**	<1
4	K_2CO_3	**Ag@RB-POP**	24
5	K_3PO_4	**Ag@RB-POP**	<1
6	Cs_2CO_3	**Ag@RB-POP**	56

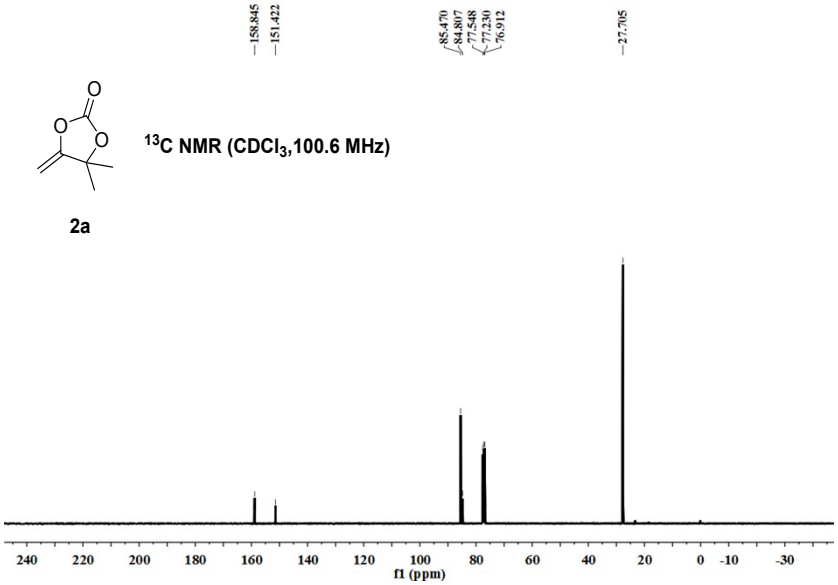
[a] Reaction condition: **1a**, 0.5 mmol; **Ag@ RB-POP**, 20 mg (Ag was 0.01 mol% based on **1a**); base, 0.5 mmol; CO_2 1 MPa; CH_3CN, 2 mL; 30 ^oC, 12 h. [b] Determined by ^1H NMR ($CDCl_3$, 400 MHz) using mesitylene as an internal standard.

4. Charactrization (NMR) of the products of carboxylative cyclization of propargyl alcohols with CO_2.



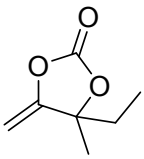
^{1}H NMR ($CDCl_3$,400 MHz)

2a



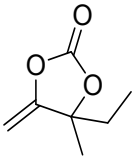
^{13}C NMR ($CDCl_3$,100.6 MHz)

2a



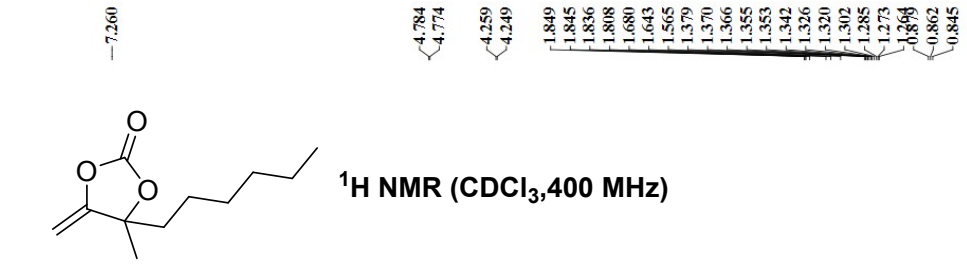
^{1}H NMR ($CDCl_3$,400 MHz)

2b



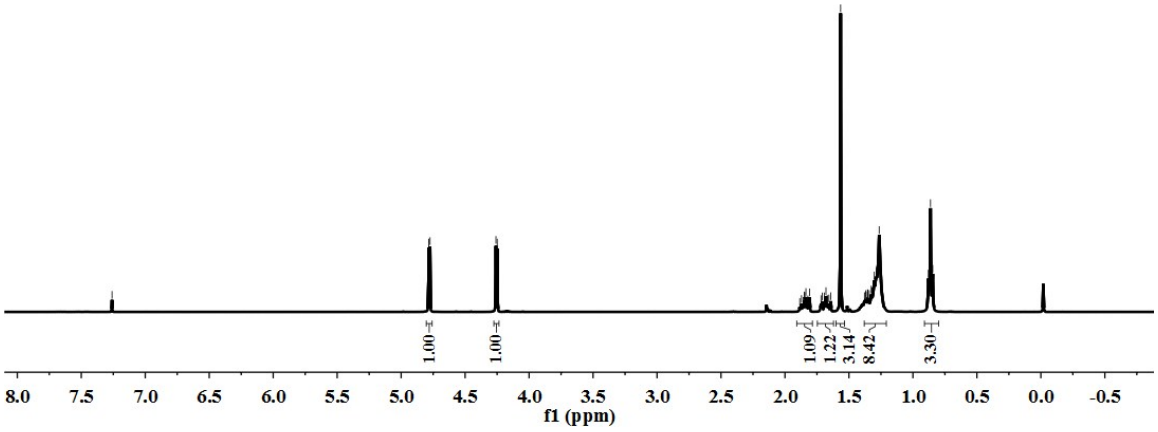
^{13}C NMR ($CDCl_3$,100.6 MHz)

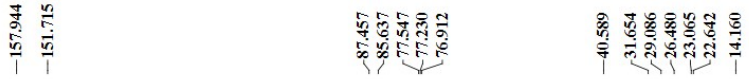
2b

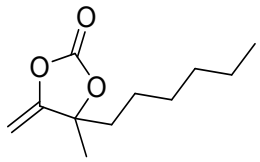


^{1}H NMR ($CDCl_3$,400 MHz)

2c

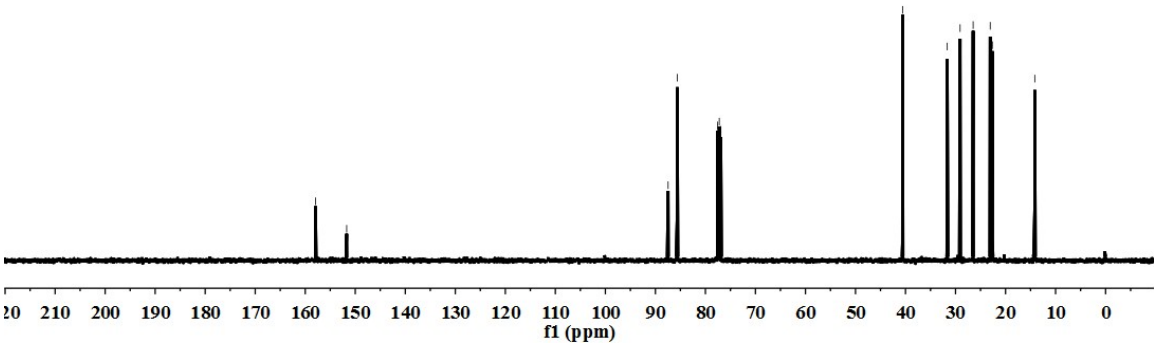


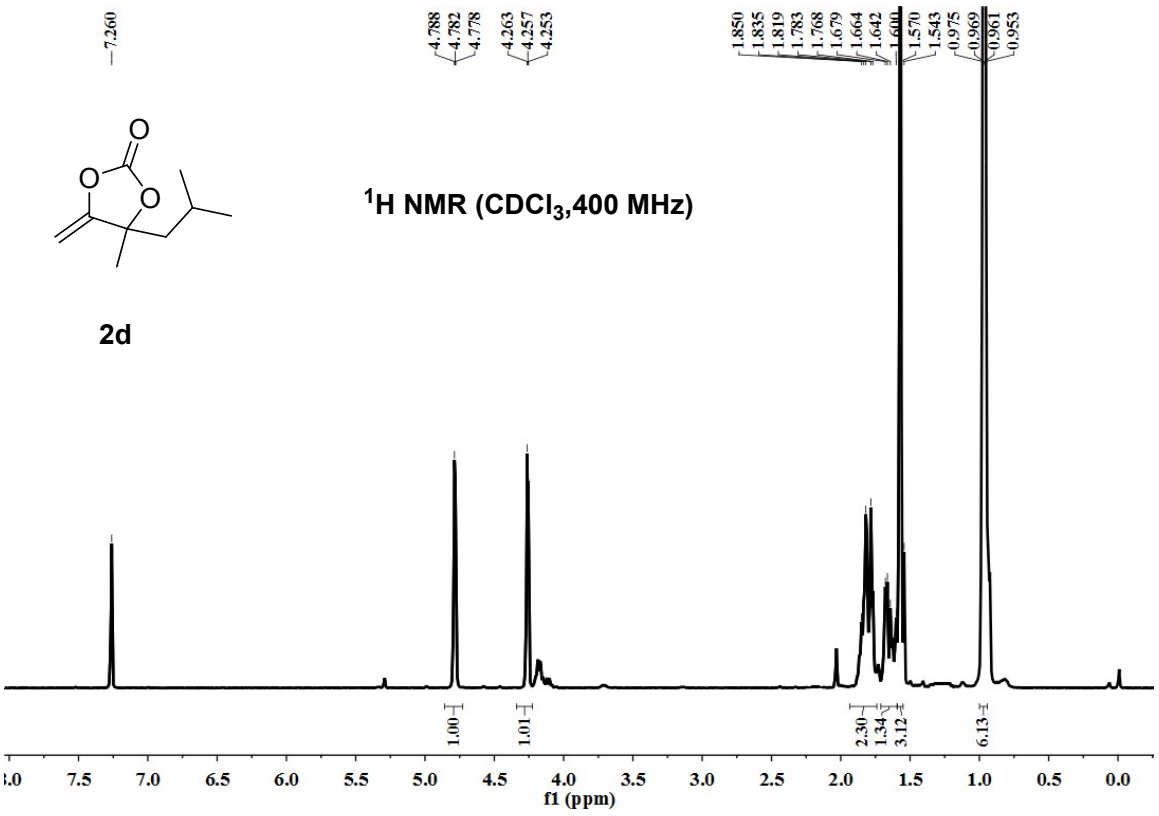




^{13}C NMR ($CDCl_3$,100.6 MHz)

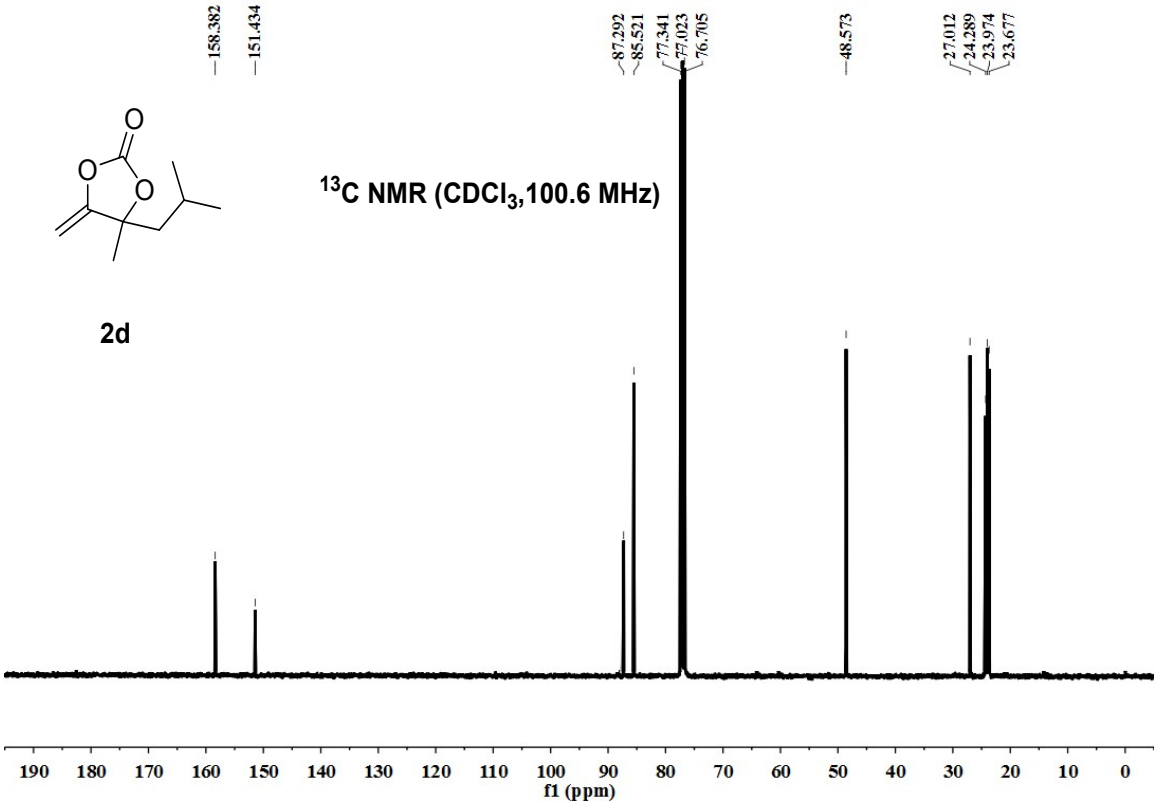
2c





^{1}H NMR ($CDCl_3$,400 MHz)

2d



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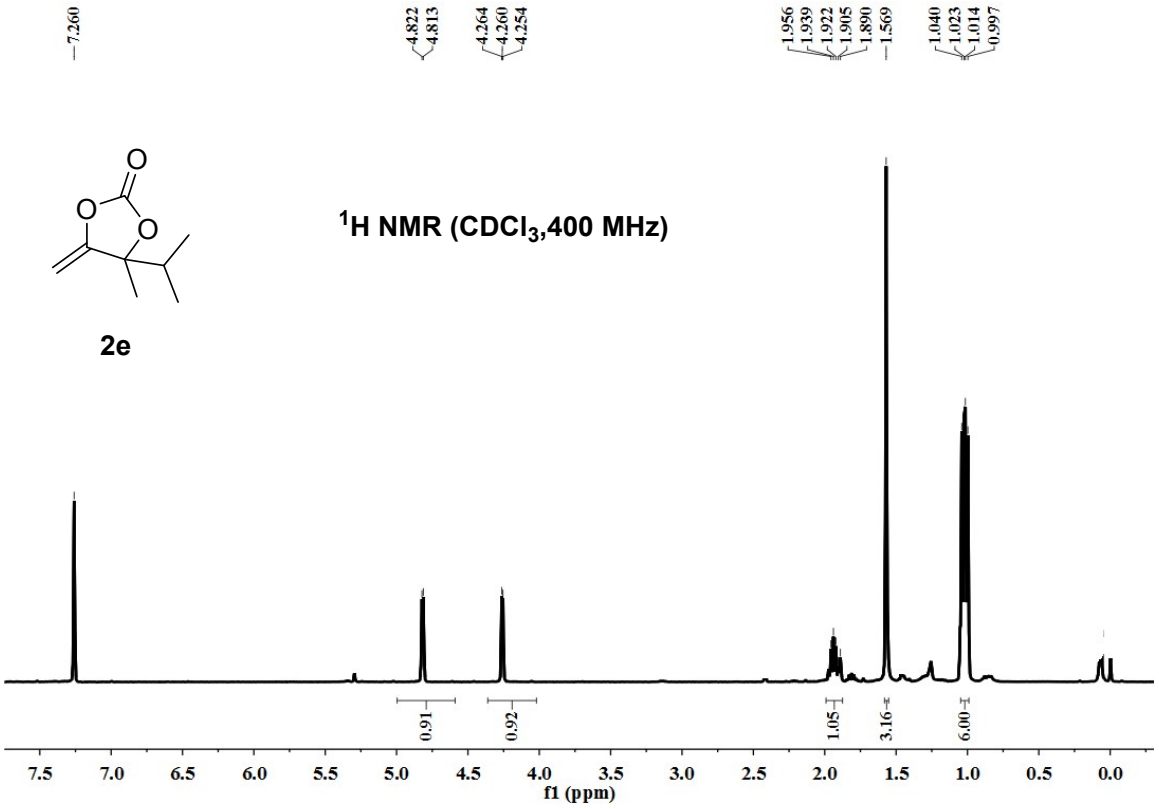
2d



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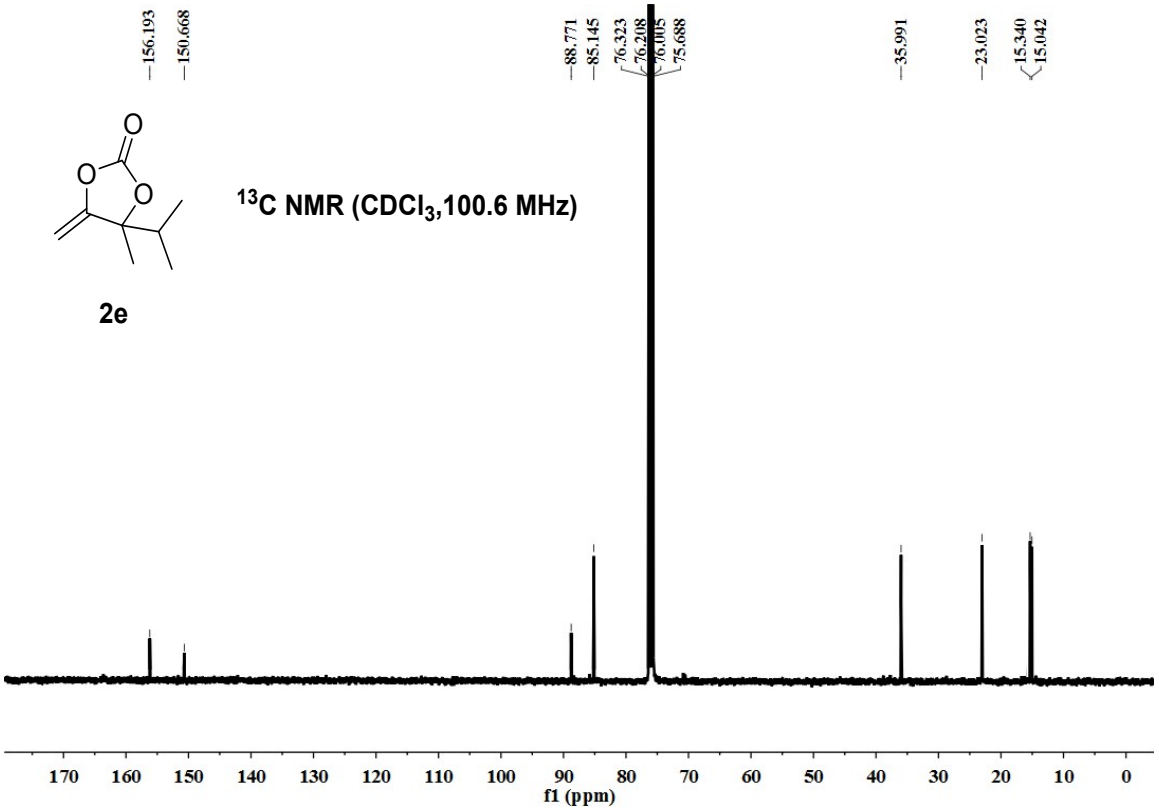
2e



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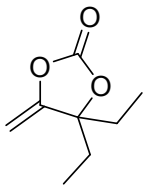
2e



2f

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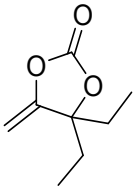

2f

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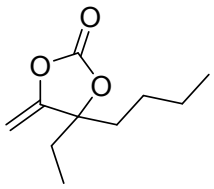

2g

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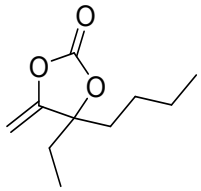

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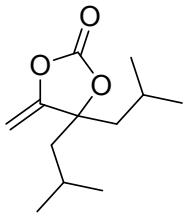

2h

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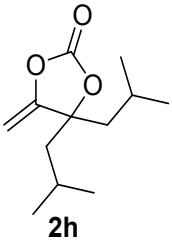

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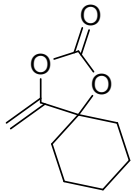

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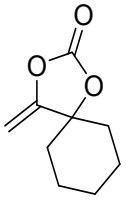

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