Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Pillar[5]arene-segregated ion pairs for enhanced cycloaddition of epoxides with CO_2

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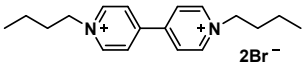
1. Materials and Methods

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz, ^{13}C: 100 MHz). $CDCl_3$ and CD_3OD were purchased from Cambridge Isotope Laboratories, and were used for the titration experiments without further drying. Chemical shifts are reported in δ values in ppm using tetramethylsilane (TMS) and coupling constants (*J*) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, and m = multiplet. All chemicals were obtained from commercial suppliers and were used as received unless otherwise noted. Column chromatography was carried out using silica gel (200 - 300 mesh). Solvents for chromatography were reagent grade. ESI mass spectra were recorded on a Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer. The conductivity measurements were performed with a conductometer DDS-307A. The CO_2 absorption experiments were performed with a CO_2 adsorption analyzer (Autosorb-1, Quantachrome, USA).

2. Synthesis

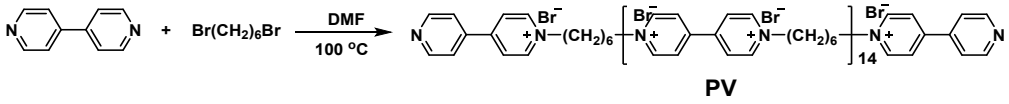
2.1 Synthesis of Guests PV and BP



BP

Guest bispyridinium (**BP)** was prepared according to the procedure in the literature. [1]

BP: ^{1}H NMR (400 MHz, D_2O, 298 K) δ 9.03 (d, *J* = 6.3 Hz, 4H), 8.45 (d, *J* = 6.3 Hz, 4H), 4.65 (t, *J* = 7.5 Hz, 4H), 2.02 -1.94 (m, 4H), 1.37 -1.28 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H)

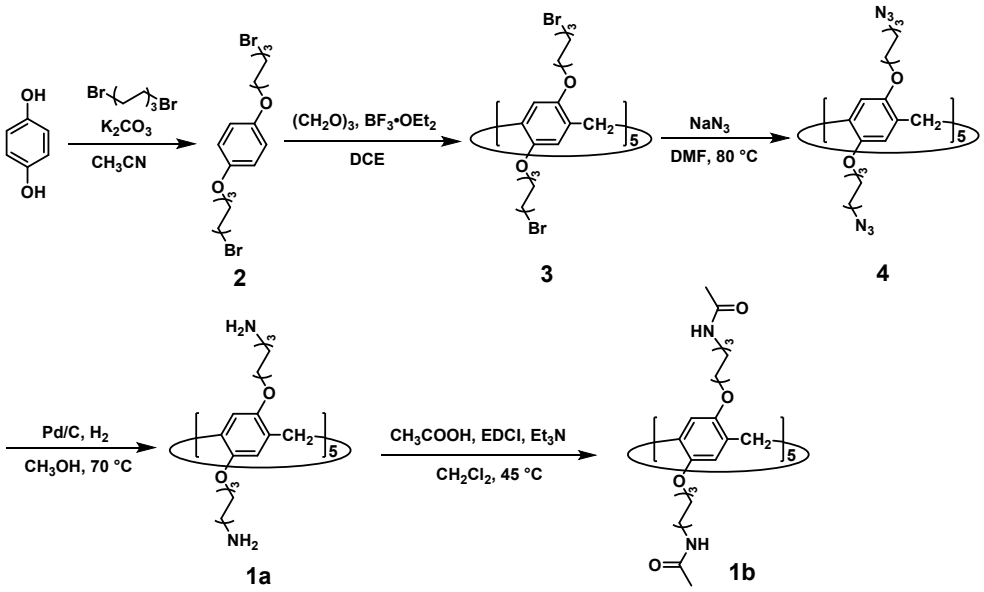


Scheme S1. Synthetic routes of the guest **PV**.

Polyviologen (**PV**) was prepared according to the reported procedure. [2]

PV: 1 ,6-Dibromohexane (5.00 g, 20.5 mmol) and 4,4' -bipyridine (3.35 g, 21.5 mmol) were dissolved in DMF (30 mL). The mixture was stirred at 100 °C for 20 h. An orange precipitate was collected and was dissolved in water and washed with chloroform to

remove unreacted starting materials. The solid was dried under high vacuum to afford **PV** as a brown solid (6.68 g, 80%). The average degree of polymerization (n) was determined by ^{1}H NMR spectroscopy to be 14 based on the signal integration ratio of the viologen proton signal to the proton signal from the end-group. The average molecular weight of **PV** is calculated to be 6158 g/mol. ^{1}H NMR (400 MHz, D_2O, 298 K) δ 9.05 (d, *J* = 6.7 Hz, 14H), 8.90 (d, *J* = 6.9 Hz, 1H), 8.69 (d, *J* = 5.2 Hz, 1H), 8.48 (d, *J* = 6.8 Hz, 14H), 8.33 (d, *J* = 6.9 Hz, 1H), 7.87 - 7.81 (m, 1H), 4.66 (m, *J* = 7.3 Hz, 14H), 2.07 -20.2 (m, 14H), 1.45 - 1.40 (m, 14H).



Scheme S2. Synthetic route of pillar[5]arenes **1a** and **1b**. **1a** was prepared according to the procedures in the literature. [3]

2: To a solution of hydroquinone (2.00 g, 18.2 mmol) and 1,6-dibromohexane (133 g, 0.55 mol) in acetonitrile (30 mL) was added anhydrous K_2CO_3 (37.7 g, 0.27 mol). The reaction mixture was stirred at 80 °C for 18 h under Ar atmosphere, and then cooled to room temperature. The insoluble excess anhydrous K_2CO_3 was filtered, and the solvent was concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, PE/DCM = 5:1, v/v) gave **2** as a white solid (5.92 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.67 (s, 2H), 3.77 (t, *J* = 6.9 Hz,6H), 3.33 (t, *J* = 6.7 Hz, 4H), 1.81-1.74 (m, 4H), 1.73 - 1.68 (m, 4H), 1.40 (t, *J* = 6.7 Hz, 8H).

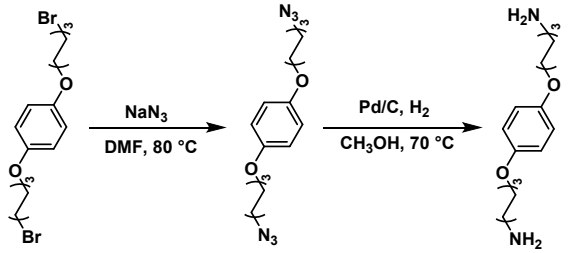
3: To a solution of **2** (2.00 g, 4.58 mmol) in dry dichloromethane (150 mL) was added 1,3,5-trioxane (165 mg, 1.83 mmol) under nitrogen atmosphere. Then boron trifluoride diethyl etherate (0.78 g, 5.50 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h. A dark green solution was obtained. After the solvent was removed, the resulting residue was dissolved in CH_2Cl_2 (100 mL) and washed twice with H_2O (2 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. The obtained solid was purified by column chromatography (SiO_2, PE/DCM from 4 : 1 to 1:1, v/v) to obtain **3** as a white solid (766 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.85 (s, 10H), 3.89 (s, 20H), 3.74 (s, 10H), 3.27 (s, 20H), 1.81-1.70 (m, 40H), 1.50-1.16 (m, 40H).

4: To a solution of **3** (100 mg, 37.3 μmol) in dry DMF (10 mL) was added sodium azide (48.5 mg, 0.70 mmol). After stirring at 80 ℃ for 24 h, the mixture was cooled to room temperature. The insoluble solid was filtered, and the solvent was concentrated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and washed twice with H_2O (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. The obtained light-yellow oil was used directly for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.83 (s, 10H), 3.88 (s, 20H), 3.74 (s, 10H), 3.12 (t, J = 6.8 Hz, 20H), 1.84 -1.76 (m, 20H), 1.51-1.40 (m, 40H), 1.38-1.28 (m, 20H).

1a: To a solution of **4** (100 mg, 44.8 μmol) in methanol (30 mL) was added Pd/C (20.0 mg, 20% wt.). The reaction mixture was stirred at 70 ℃ for 72 h under hydrogen atmosphere, and then cooled to room temperature. The insoluble Pd/C was filtered, and the solvent was concentrated under reduced pressure. A white solid compound **1a** was obtained (85.0 mg, 99%). ^{1}H NMR (400 MHz, CD_3OD, 298 K) δ 6.92 (s, 10H), 3.98 -3.75 (m, 30H), 2.70 - 2.36 (m, 20H), 1.87 -1.30 (m, 80H). ^{13}C NMR (100 MHz, CD_3OD) δ_C = 168.9 148.8, 127.5, 113.5, 66.7, 36.8, 28.6, 28.5, 25.3, 25.2.

1b: To a solution of **1a** (100 mg, 62.0 μmol) and EDCI (240 mg, 1.25 mmol) in DCM (50 mL) was added Et_3N (126 mg, 1.30 mmol) and acetic acid (150 mg, 2.50 mmol). The reaction mixture was stirred for 48 h at 45 ℃, and then cooled to room temperature. After

the solvent was removed, the resulting residue was dissolved in CH_2Cl_2 (50 mL) and washed twice with H_2O (2 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. The resultant solid was purified by column chromatography (SiO_2, DCM/MeOH, 10:1, v/v) to obtain **1b** as a white solid (90 mg, 71%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.80 (s, 10H), 3.98 (s, 10H), 3.75 - 3.57 (m, 20H), 3.08 - 2.98 (m, 20H), 1.78 (s, 10H), 1.76-1.70 (m, 40 H), 1.56 - 1.28 (m, 60H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C = 169.4, 149.6, 128.3, 114.4, 68.4, 39.0, 29.8, 29.6, 29.2, 27.0, 26.1, 23.0. HRESI-MS: m/z calcd for $[C_{115}H_{180}N_{10}O_{20} + 2H]^{2+}$ 1021.1777; found: 1021.1763.

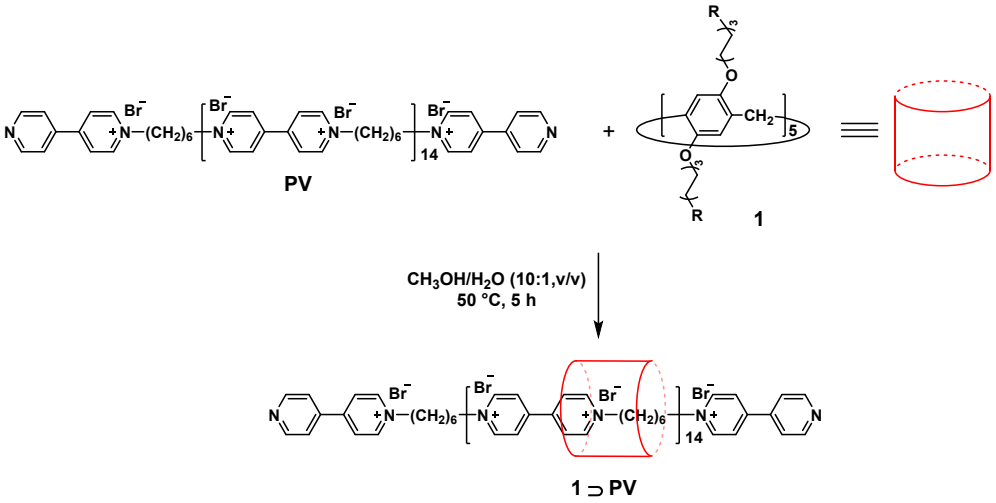


Scheme S3. Synthetic route of **1c**.

4: To a solution of **3** (200 mg, 0.55 mmol) in dry DMF (10 mL) was added sodium azide (108 mg, 1.66 mmol). After stirring at 80 ℃ for 24 h, the mixture was cooled to room temperature. The insoluble solid was filtered, and the solvent was concentrated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and washed twice with H_2O (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. The obtained light-yellow oil was used directly for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.82 (s, 4H), 3.91 (t, J = 6.4 Hz, 4H), 3.28 (t, J = 6.9 Hz, 4H), 1.80 - 1.74 (m, 4H), 1.68 - 1.59 (m, 4H), 1.54 - 1.40 (m, 8H).

1c: To a solution of **5** (171 mg, 0.55 mmol) in methanol (30 mL) was added Pd/C (34.0 mg, 20% wt.). The reaction mixture was stirred at 70 ℃ for 24 h under hydrogen atmosphere, and then cooled to room temperature. The insoluble Pd/C was filtered, and the solvent was concentrated under reduced pressure. A white solid compound **1c** was obtained (145 mg, 99%). ^{1}H NMR (400 MHz, CD_3OD, 298 K) δ 6.81 (s, 6.81, 4H), 3.94 - 3.90 (m, 4H), 2.64 - 2.45 (m, 4H), 1.87 - 1.18 (m, 16H).

2.2 Synthesis of Supramolecular Complex 1 ⊃ PV



Scheme S4. Synthetic route of supramolecular complex **1 ⊃ PV**.

General procedure for 1a ⊃ PV

PV (5.00 mg, 0.80 μmol) and **1a** (10.3 mg, 6.40 μmol) was dissolved in the mixed solvent of H_2O (0.1 mL) and MeOH (1.0 mL). The reaction mixture was stirred at 50 ℃ for 5 h, the solution gradually changed from light yellow to dark yellow. The mixture was cooled to room temperature. A yellow solid was obtained after removing the solvents, then dried under vacuum oven at 45 ℃. The obtained yellow solid was used directly for catalysis without further purification.

General procedure for 1b ⊃ PV

PV (5.00 mg, 0.80 μmol) and **1b** (12.5 mg, 6.40 μmol) was dissolved in the mixed solvent of H_2O (0.1 mL) and MeOH (1.0 mL). The reaction mixture was stirred at 50 ℃ for 5 h. The mixture was cooled to room temperature. A white solid was obtained after removing solvent, then dried under vacuum oven at 45 ℃. The obtained white solid was used directly for catalysis without further purification.

3. Spectroscopic Characterization

3.1 ^{1}H and ^{13}C NMR Spectra of Compounds

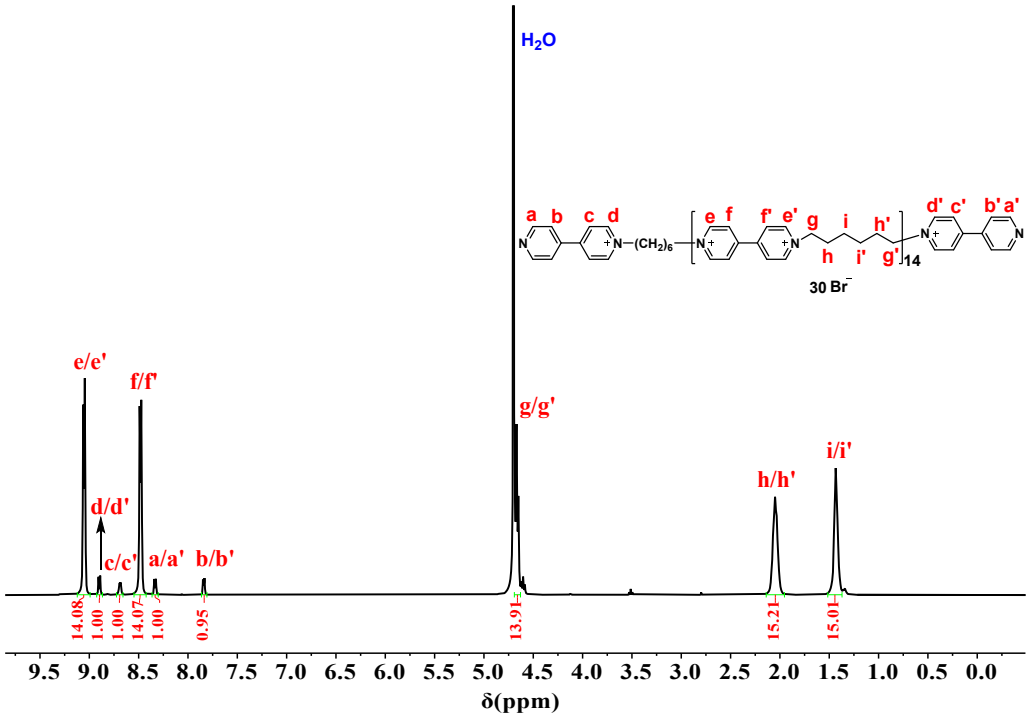


Figure S1 ^{1}H NMR spectrum of **PV** (400 MHz, D_2O, 298 K).

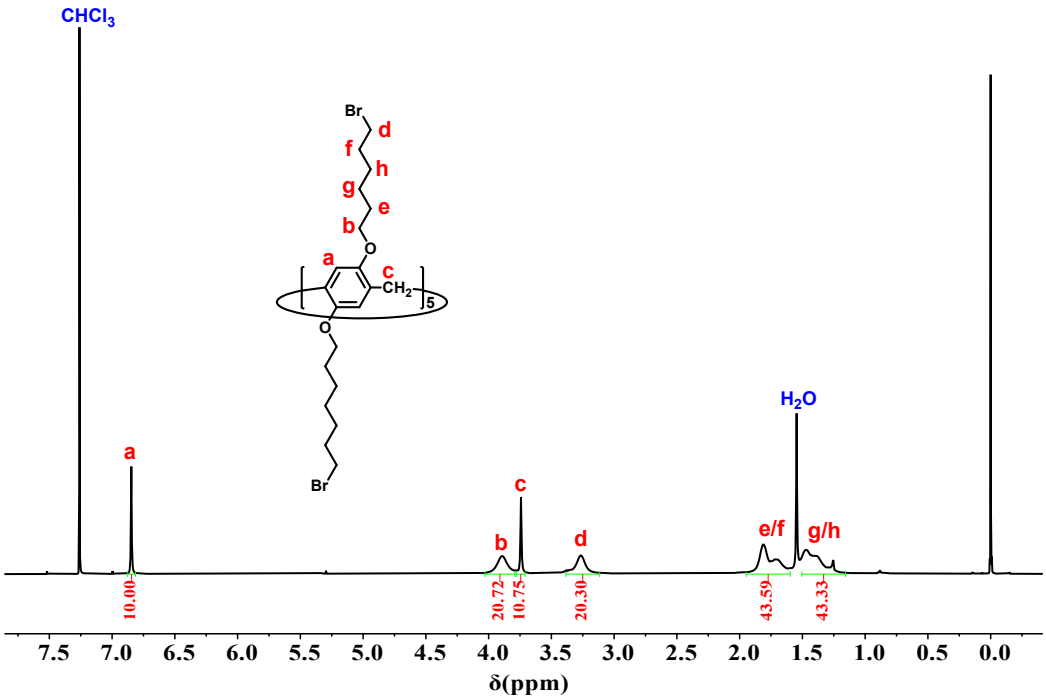


Figure S2 ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$, 298 K).

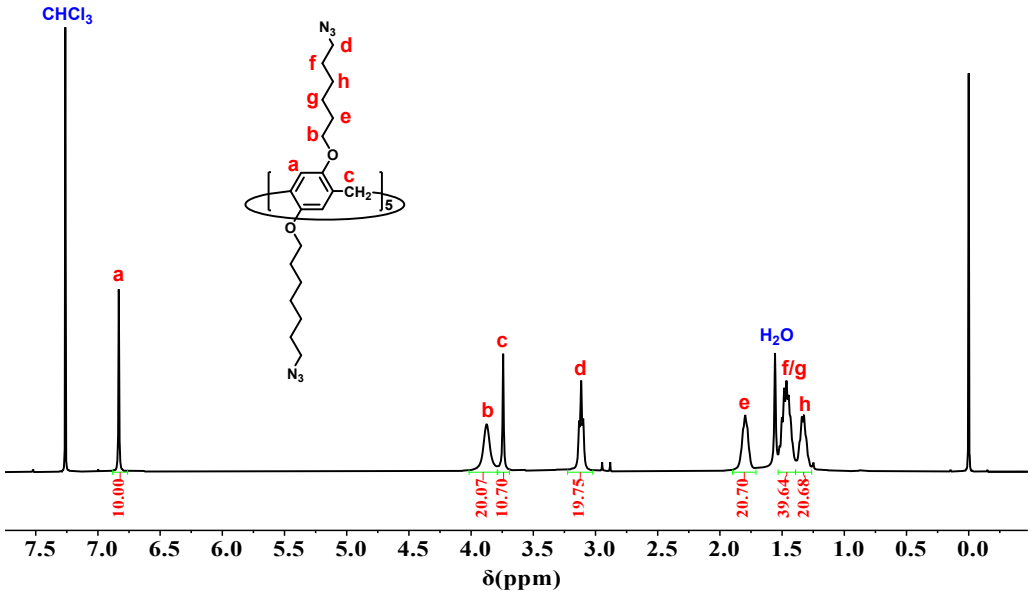


Figure S3 ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$, 298 K).

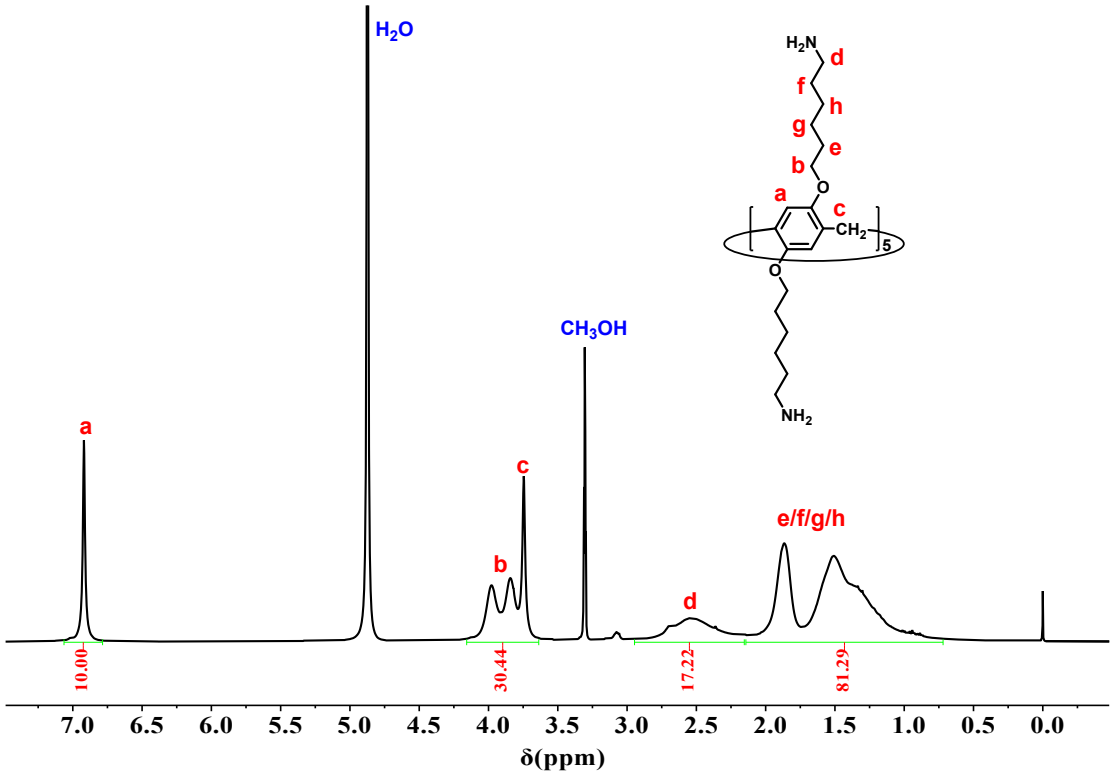


Figure S4 ^{1}H NMR spectrum of **1a** (400 MHz, CD_3OD, 298 K).

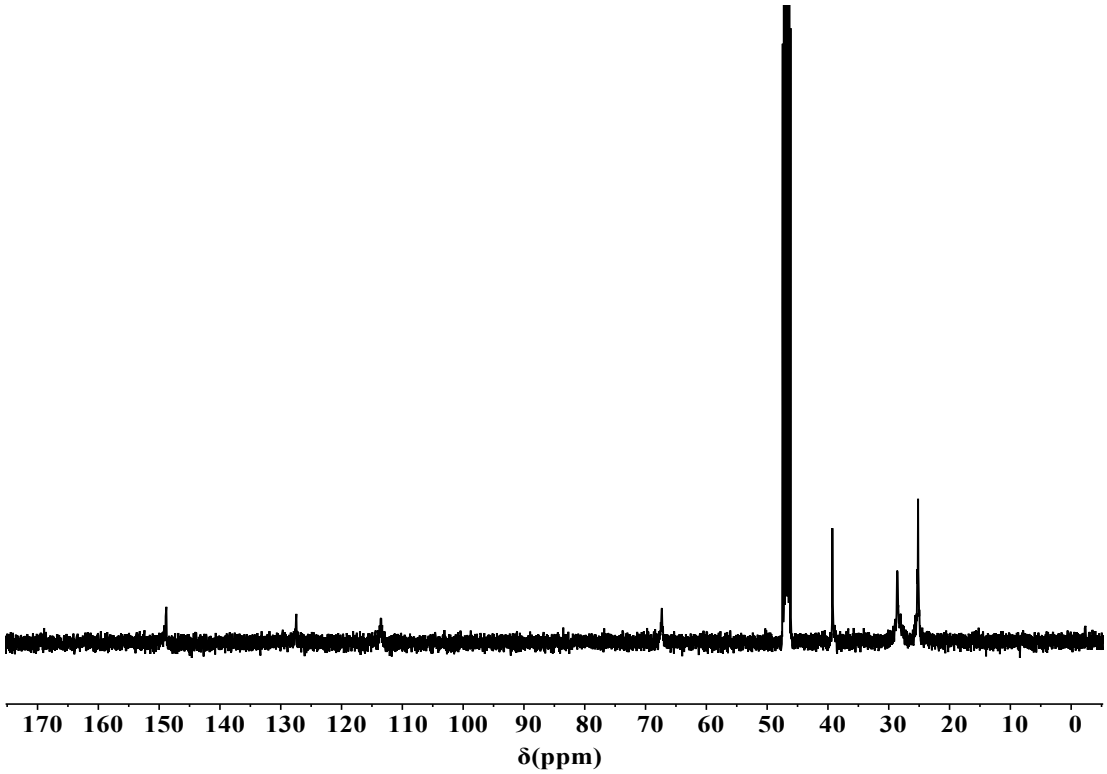


Figure S5 ^{13}C NMR spectrum of **1a** (100 MHz, CD_3OD, 298 K).

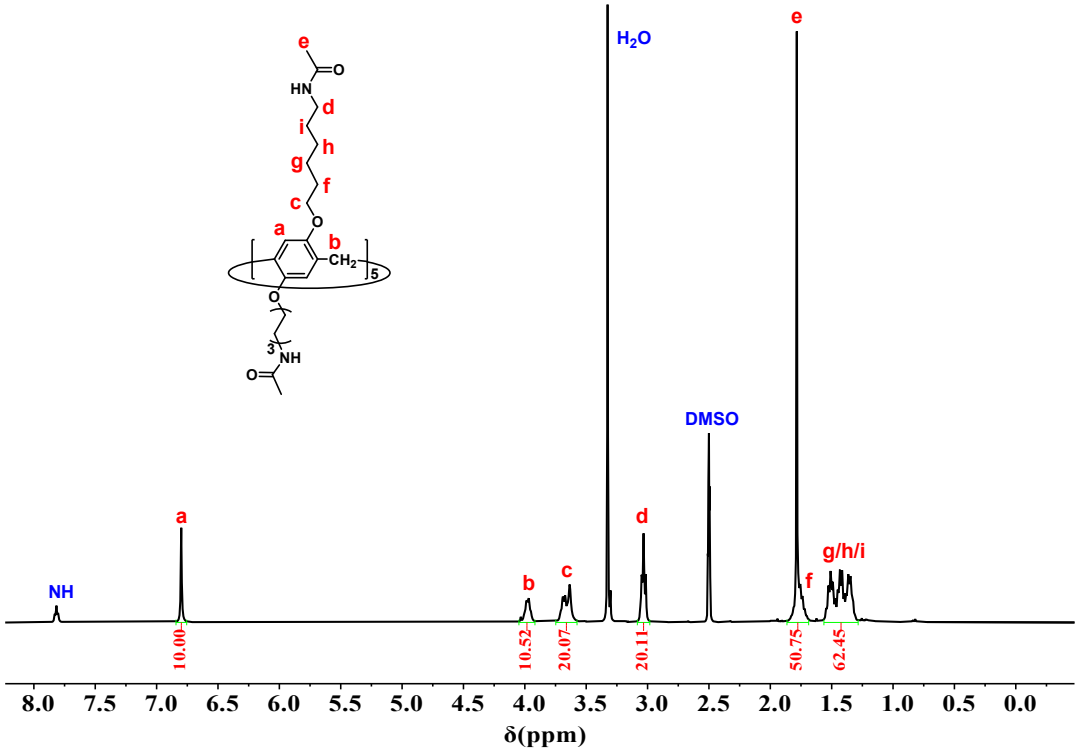


Figure S6 ^{1}H NMR spectrum of **1b** (400 MHz, DMSO-d_6, 298 K).

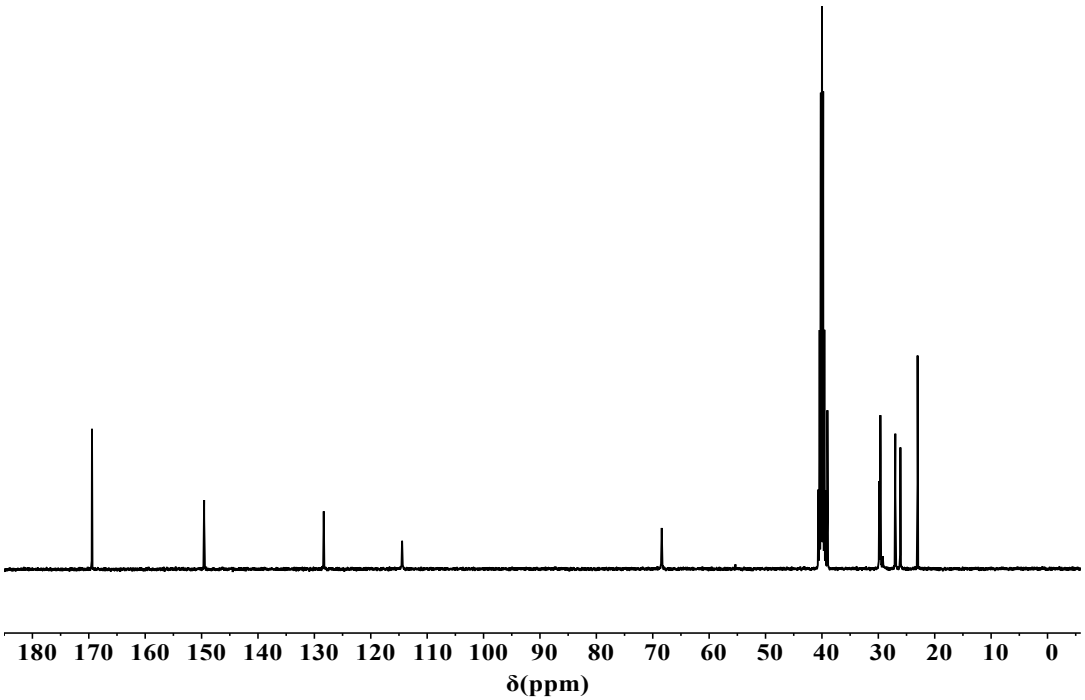


Figure S7 ^{13}C NMR spectrum of **1b** (100 MHz, DMSO-d_6, 298 K).

3.2 HRESI-MS Spectrum of Compound 1b

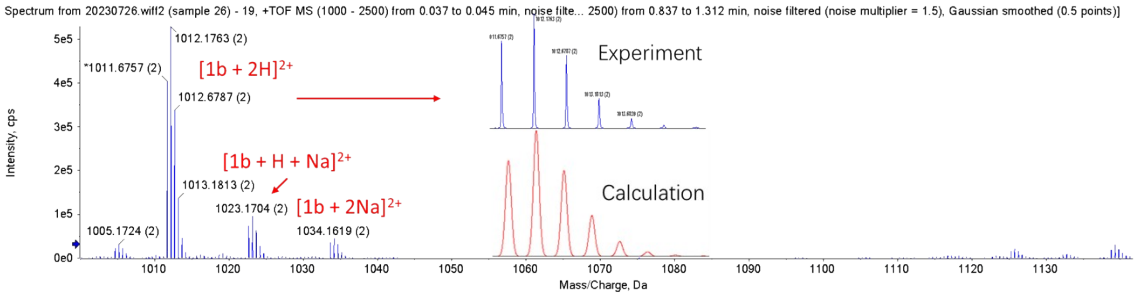


Figure S8 HRESI-MS spectrum of **1b**. The inserted images show the calculated isotope pattern *vs*. the experimental isotope pattern.

4. Host-Guest Complexation Study

4.1 Host-Guest Complexation of 1a and BP

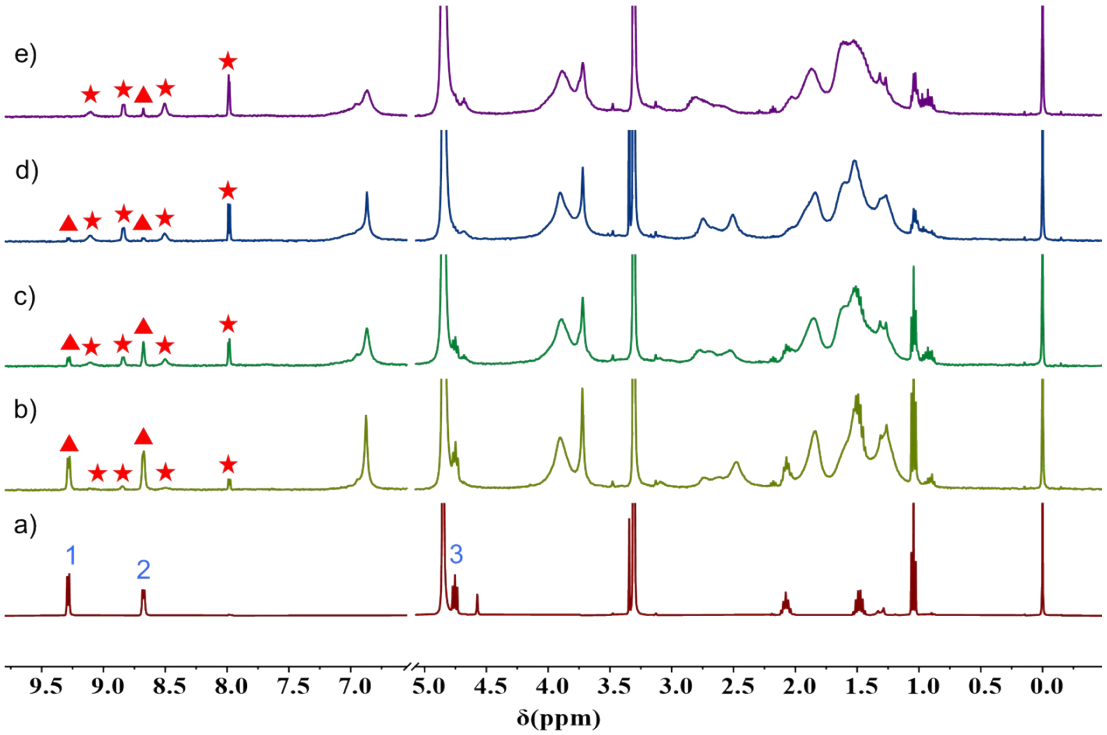


Figure S9 Stacked partial ^{1}H NMR spectra (400 MHz, CD_3OD, 298 K) of (a) **BP**, and (b-e) the mixing of **BP** and **1a** at indicating time. The mixing times for each spectrum (b) 1 hour, (c) 1 day, (d) 3 days, (e) 7 days. The proton signal of free **BP** (non-encapsulated) was marked by the triangle (▲), and the proton signal of encapsulated **BP** was marked by the star (★). [**BP**] = 2.0 mM, [**1a**] = 2.0 mM.

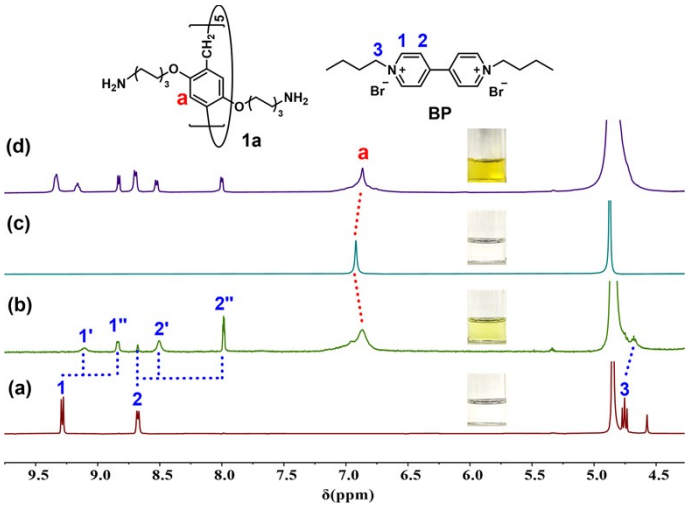


Figure S10 Partial ^{1}H NMR spectra (400 MHz, CD_3OD, 298 K) of (a) **BP**; (b) bipyridinium **BP** and **1a**; (c) **1a**; (d) **1a** ⊃ **PV** complex. [**BP**] = 2.0 mM, [**1a**] = 2.0 mM, [**1a** ⊃ **PV**] = 5.0 mM. The inserted images show the color change upon host-guest complexation.

4.2 Job Plot for Determination of Stoichiometry

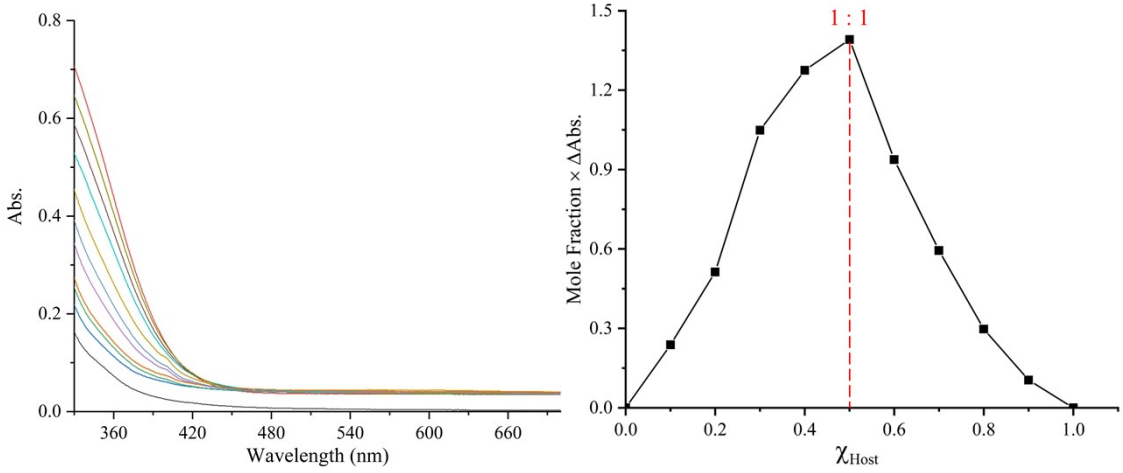


Figure S11 Job plot for the determination of stoichiometry of **1a** and **BP** based on the absorbance at 400 nm in $CHCl_3$:CH_3OH (10:1, v/v). [**1a**] + [**BP**] = 0.5 mM.

4.3 UV-vis Titration Experiments

The binding constant (K_a) of complex **1a** ⊃ **BP** were determined by probing the charge-transfer band of the complex by UV-vis spectroscopy and employing a titration method. UV-vis progressive titration experiments were performed in $CHCl_3$:CH_3OH (10:1,

v/v) at a constant concentration of **1a** (0.5 mM) and varying concentration of **BP**. For the titration, 25 data points were collected. Binding constants were calculated by a global fitting analysis according to a 1:1 binding model using the website (http://supramolecular.org/). Treatment of the collected absorbance data at λ = 380 nm, 390 nm and 400 nm with a non-linear curve-fitting program afforded the corresponding binding constant (K_a): (8.63 ± 0.07) × 10^3 M^{-1}.

The non-linear curve-fitting was based on the equation:

$A = (A_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a) - (0.5\ ([G]_0^2+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$ (Eq. S1)

Where A is the absorption intensity of the charge-transfer band at $[G]_0$, A_∞ is the absorption intensity of the charge-transfer band when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of the guest.

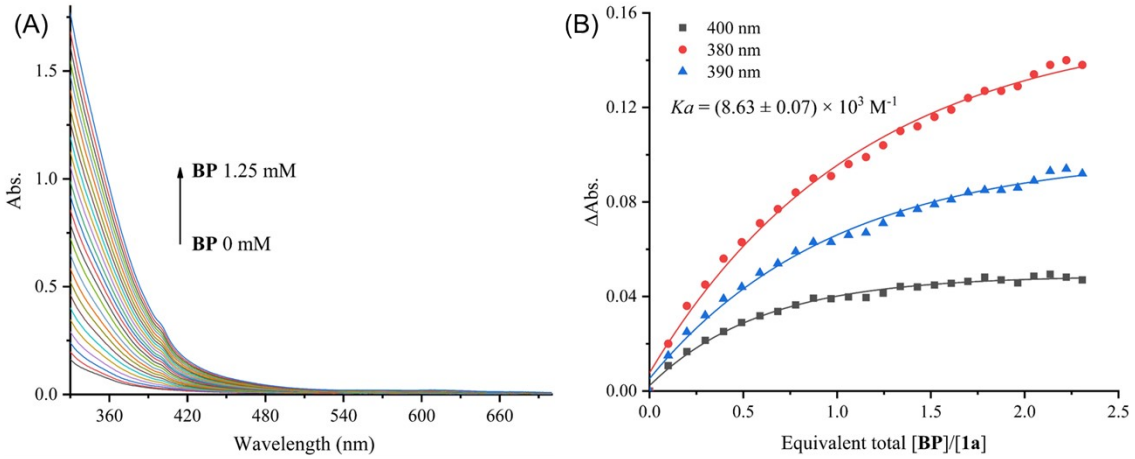


Figure S12 (A) Stacked UV-vis spectra of **1a** (0.5 mM) titrated with **BP** (0~1.25 mM) in $CHCl_3$:CH_3OH (10:1, v/v) at 298 K. (B) Determination of the binding constant of **1a** (0.5 mM) and **BP** in $CHCl_3$:CH_3OH (10:1, v/v). Fitting result based on the absorbance at 380 nm, 390 nm and 400 nm. The average binding constant (K_a) of **1a** and **BP** is calculated to be (8.63 ± 0.07) × 10^3 M^{-1}.

4.4 Charge Transfer Complex

The UV-vis spectra were used as evidence for the formation of a charge transfer complex via host-guest encapsulation. A C-T band was observed by UV-vis spectroscopy from 380-550 nm in CH_3OH at 298 K.

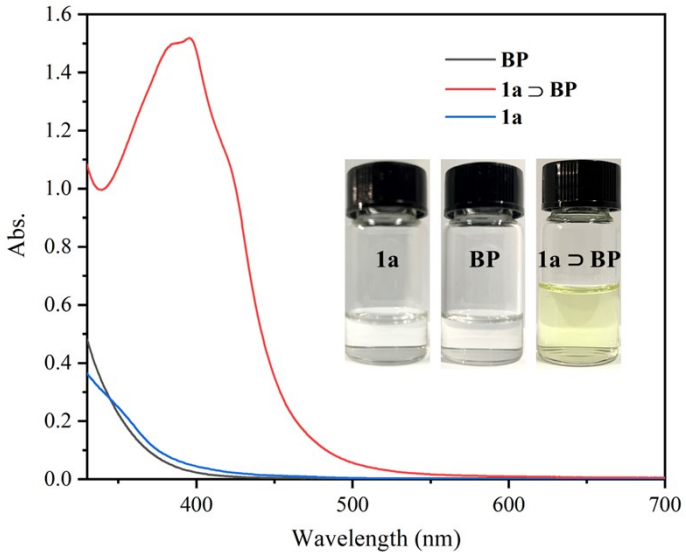


Figure S13 The UV-vis spectra of **1a** (2.0 mM, blue line), **BP** (2.0 mM, black line), and **1a ⊃ BP** complex (2.0 mM, mole ratio of **1a** and **BP** is 1:1, red line) in CH_3OH at 298 K.

4.5 HRESI-MS Spectrum of the Complex of 1b and BP

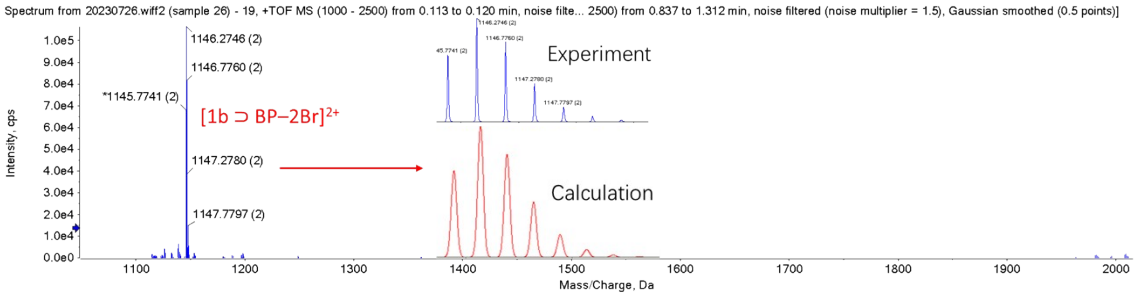


Figure S14 HRESI-MS spectrum of **1b ⊃ BP**. The inserted images show the calculated isotope pattern *vs.* the experimental isotope pattern. HRESI-MS: m/z calcd for [**1b ⊃ BP** – 2Br]$^{2+}$ 1146.2747; found: 1146.2746.

5. 2D ROESY Spectroscopy

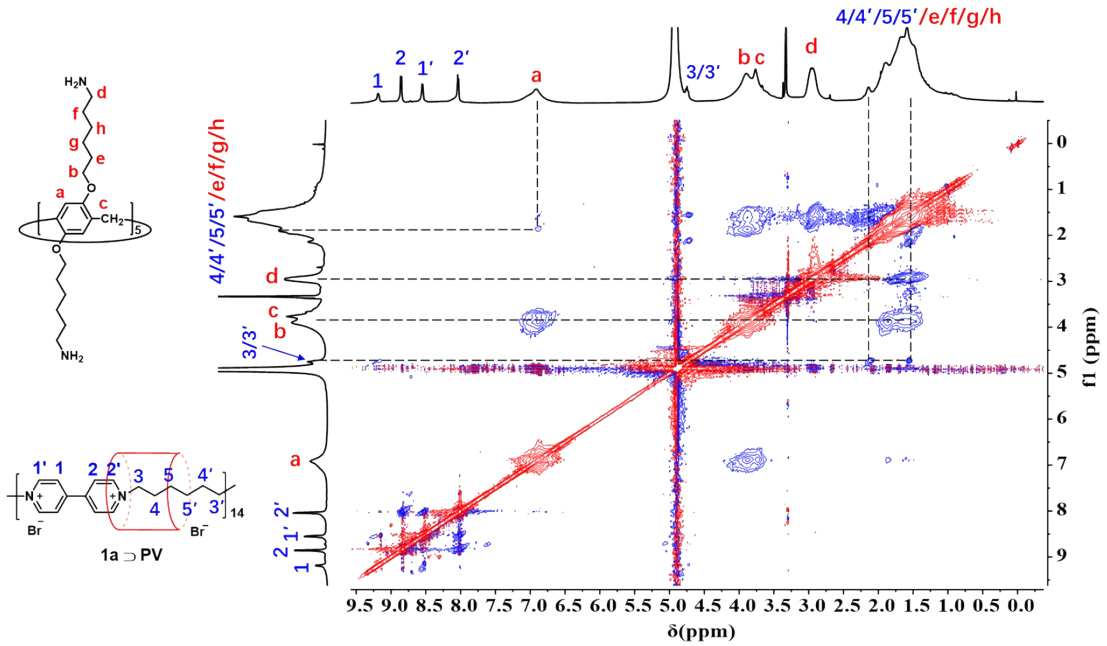


Figure S15 2D ROESY spectrum of **1a ⊃ PV** (400 MHz, CD_3OD, 298 K, 5 mM, mixing time = 0.4 s).

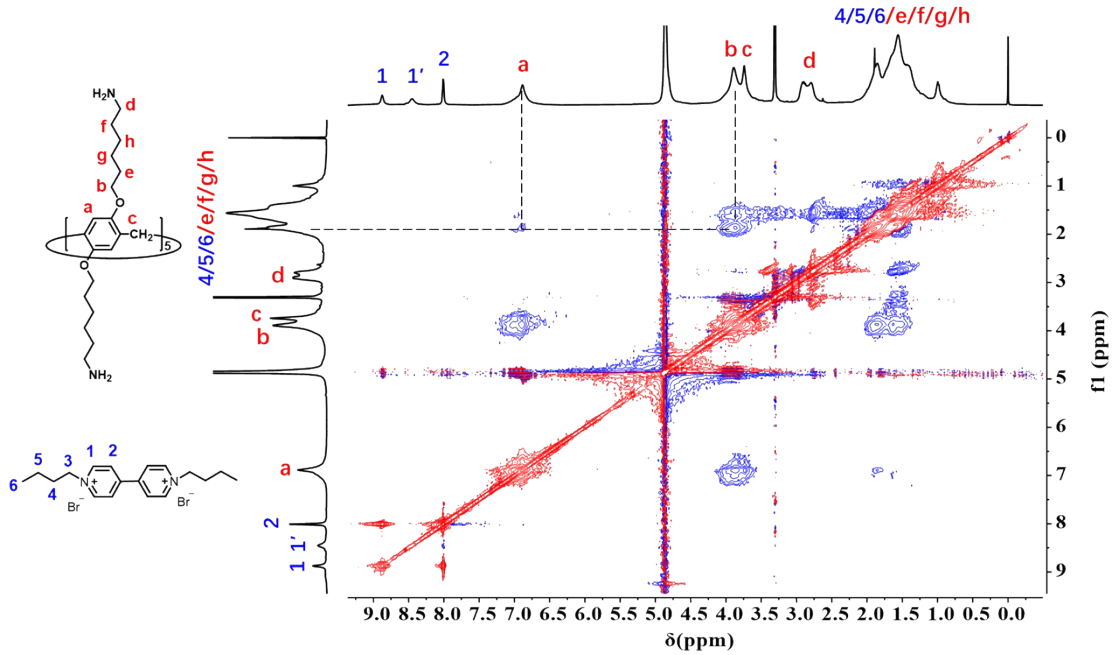


Figure S16 2D ROESY spectrum of **1a ⊃ BP** (400 MHz, CD_3OD, 298 K, 5 mM, mixing time = 0.4 s).

6. Electrical Conductivity

The conductivity measurements were performed with a conductometer (DDS-307A, cell constant=1.021 cm^{-1}) with an uncertainty of 1.0%, and a dipping-type conductivity cell with Pt electrodes (DJS-1VTC). A solution containing **PV** (5.0 mg) and **1a (**10 mg) in a mixed solvent (CH_3OH/H_2O, 9:2, HPLC) was placed in the conductivity cell. The temperature of the sample was maintained at 298 K. The specific conductance for the mixed solvent is 1.36 μS cm^{-1}. The electrical conductivities (σ) of the guest and complex are given in Table S1.

Table S1 The electrical conductivity values obtained in CH_3OH/H_2O (9:2, v/v) at 298 K.

Solution	**1a ⊃ PV**	**1a+PV**	**PV**	**1a**
σ/μS cm^{-1}	123.1±0.1	77.8±0.2	56.7±0.3	24.1±0.1

7. CO_2 Absorption Experiment

The BET analysis was conducted on **1a** to evaluate the surface area and CO_2 adsorption capacity.

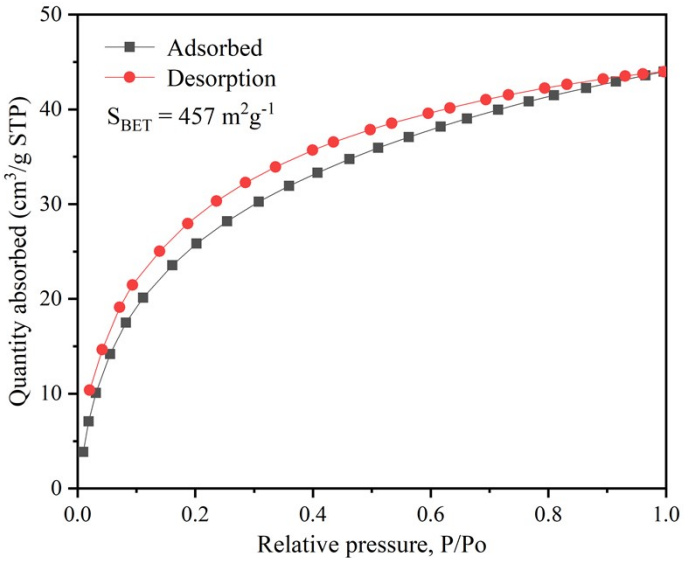


Figure S17 CO_2 adsorption-desorption isotherms of **1a** at 273 K.

8. Catalytic Cycloaddition Reactions of CO_2 with Epoxides

General experimental procedure: **1a** ⊃ **PV** (**1a**: 6.40 μmol, **PV**: 5.00 mg) and 2.4 mmol of epoxides were added into a Schlenk tube (10 mL), followed by capping it with a septum. After the Schlenk tube was evacuated, CO_2 (balloon) was introduced into the reaction mixture under stirring. The reaction mixture was stirred at 80 °C for 24 h. All the product yields were analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard with the reaction mixture after removing the residual catalyst by filtration.

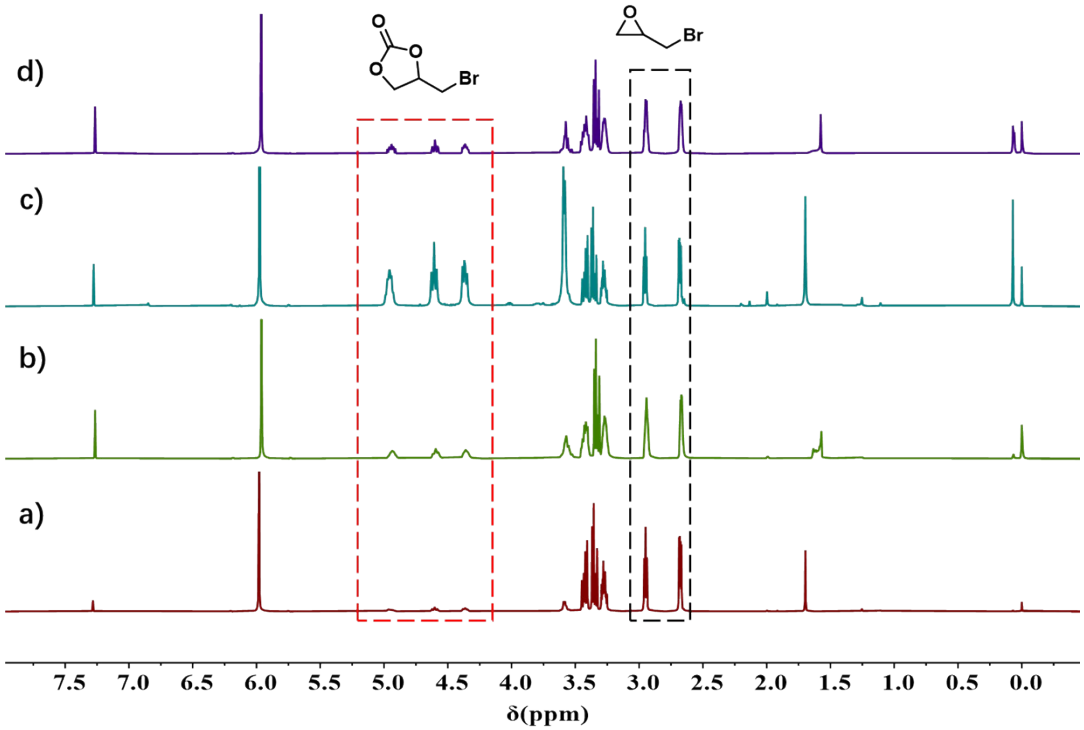


Figure S18 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with epibromohydrin as substrate using different catalysts: (a) **1b**, (b) **1b** + **PV**, (c) **1b** ⊃ **PV**, (d) **PV**.

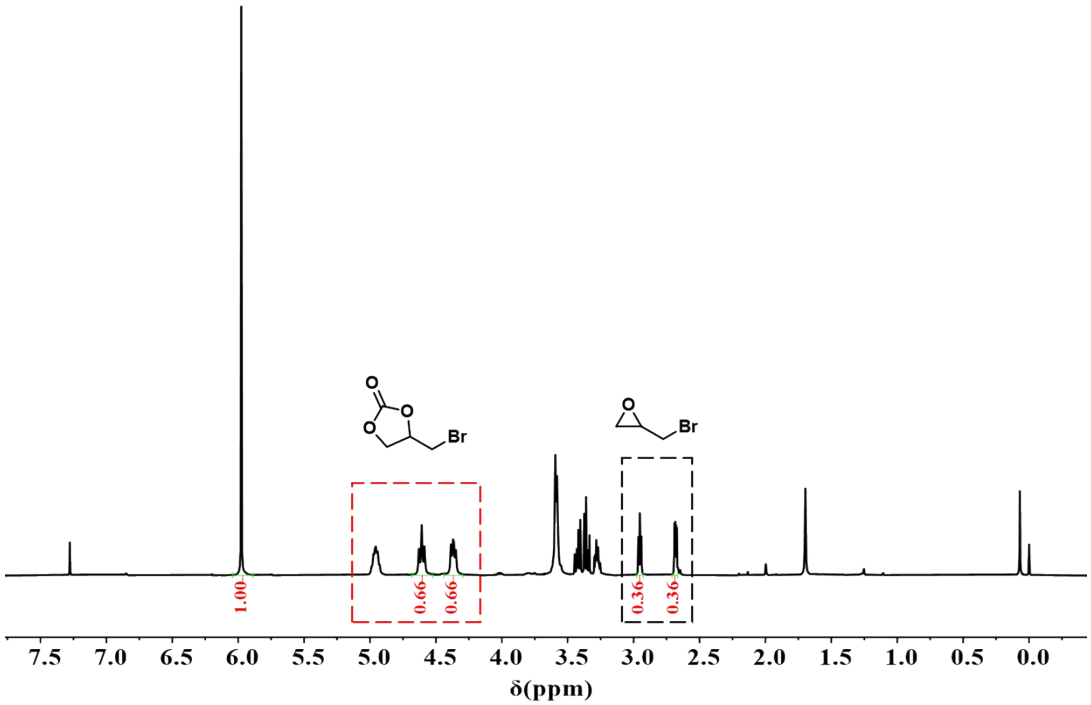


Figure S19 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with epibromohydrin as substrate using catalyst **1b** ⊃ **PV**.

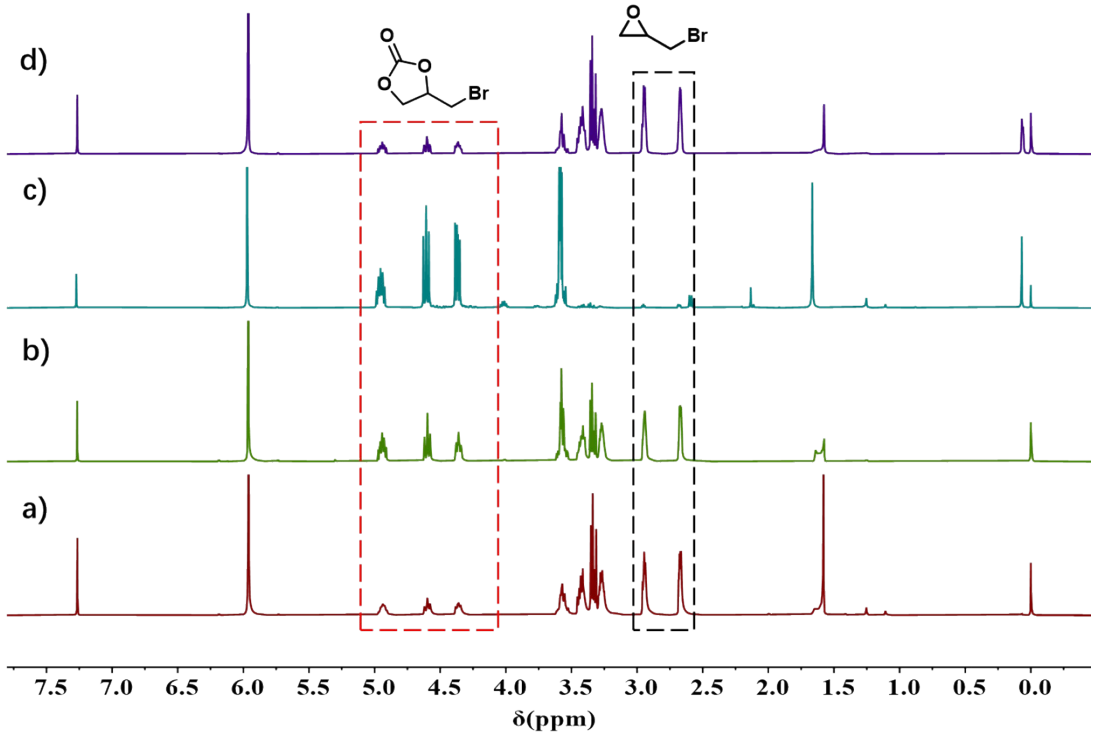


Figure S20 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with epibromohydrin as substrate using different catalysts: (a) **1a**, (b) **1a** + **PV**, (c) **1a** ⊃ **PV**, (d) **PV**.

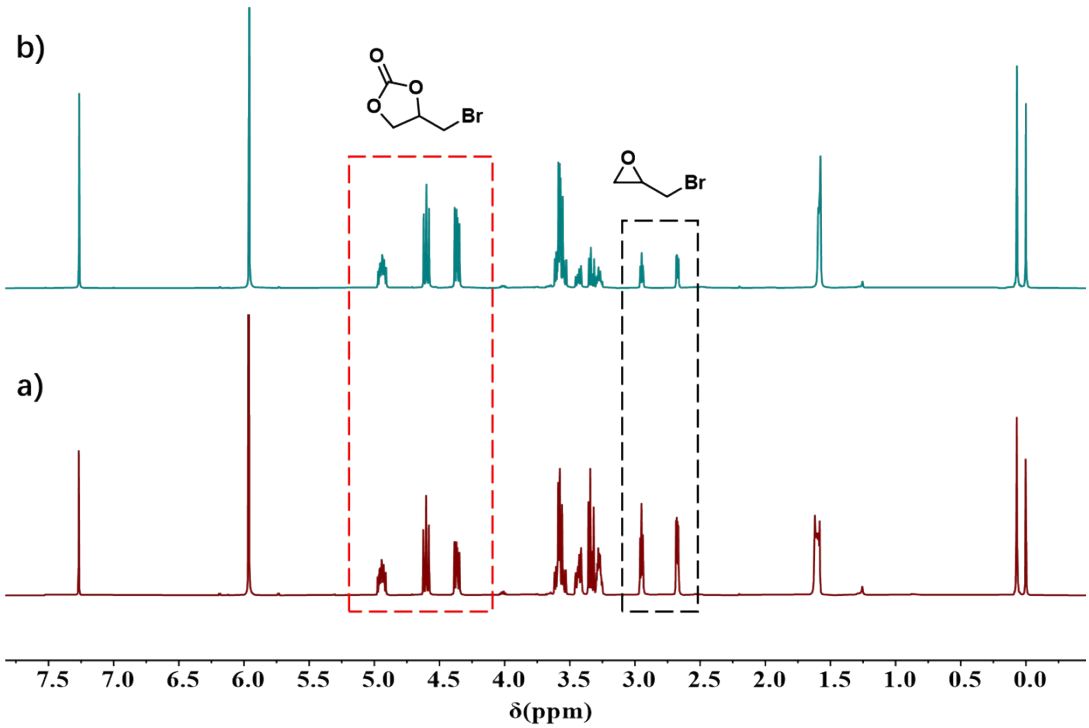


Figure S21 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with epibromohydrin as substrate using different catalysts: (a) **1c**, (b) **1c** + **PV**.

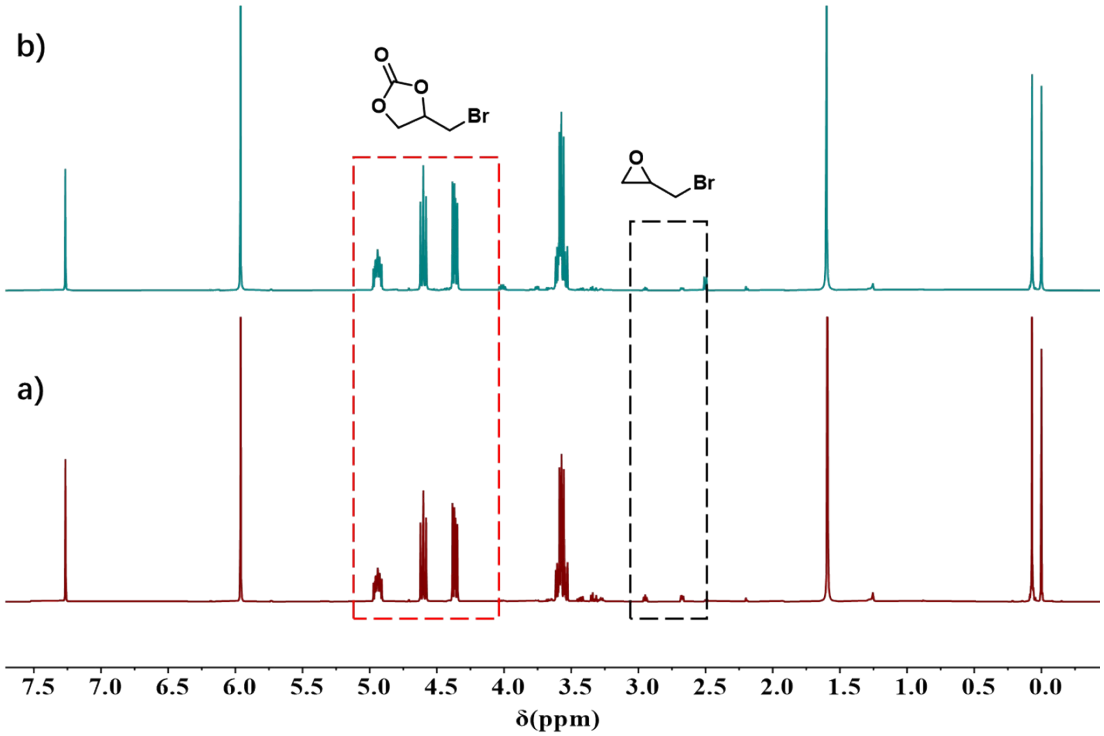


Figure S22 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with epibromohydrin as substrate using different catalysts: (a) **BP**, (b) **1a** ⊃ **BP**.

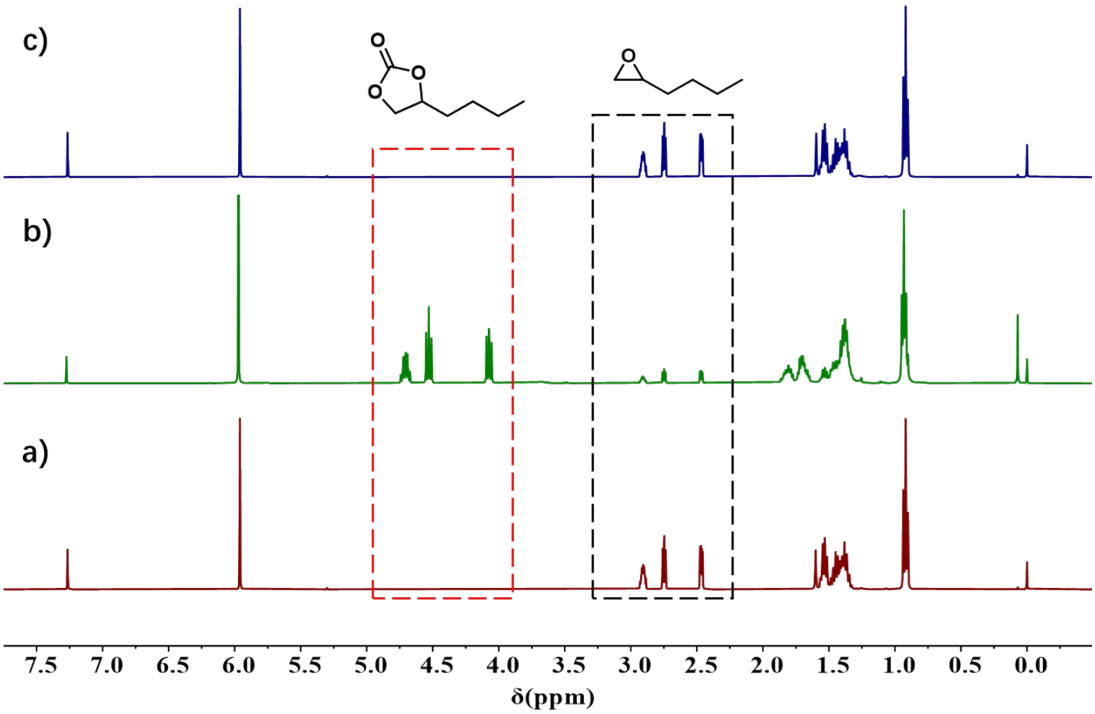


Figure S23 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with 1,2-epoxyhexane as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

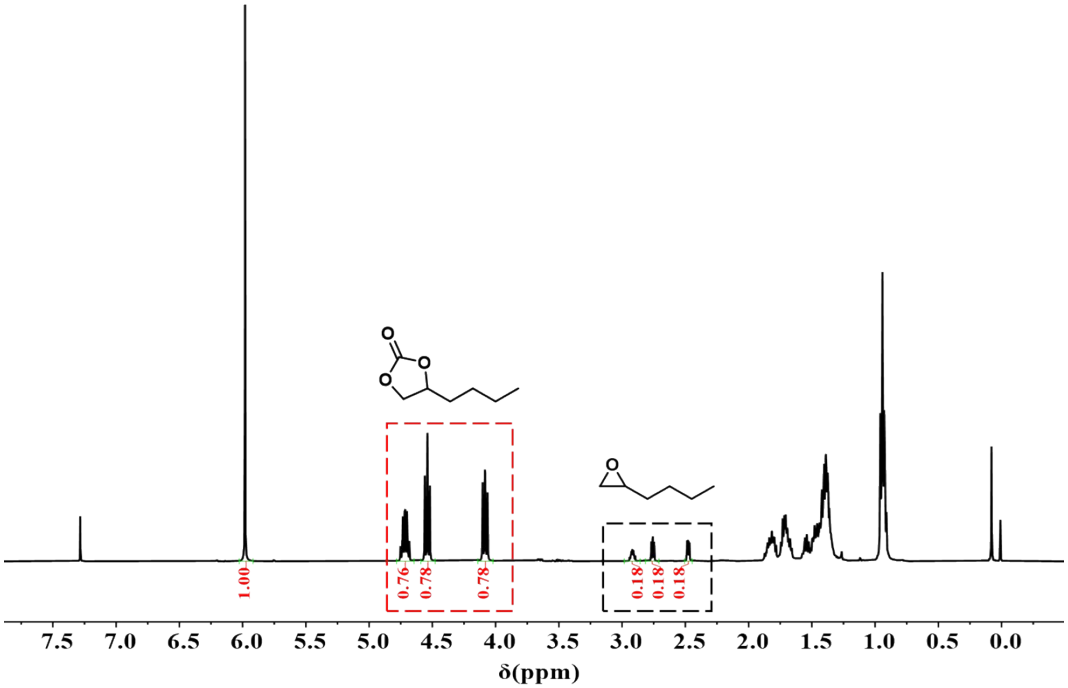


Figure S24 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with 1,2-epoxyhexane as substrate using catalyst **1a** ⊃ **PV**.

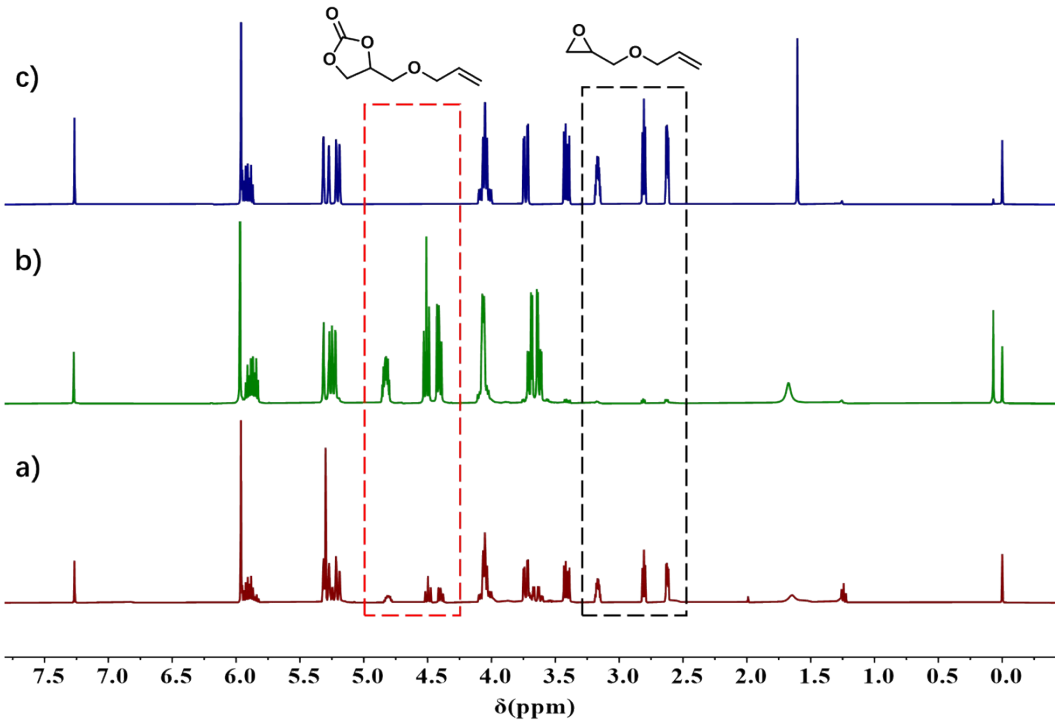


Figure S25 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with allyl glycidyl ether as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

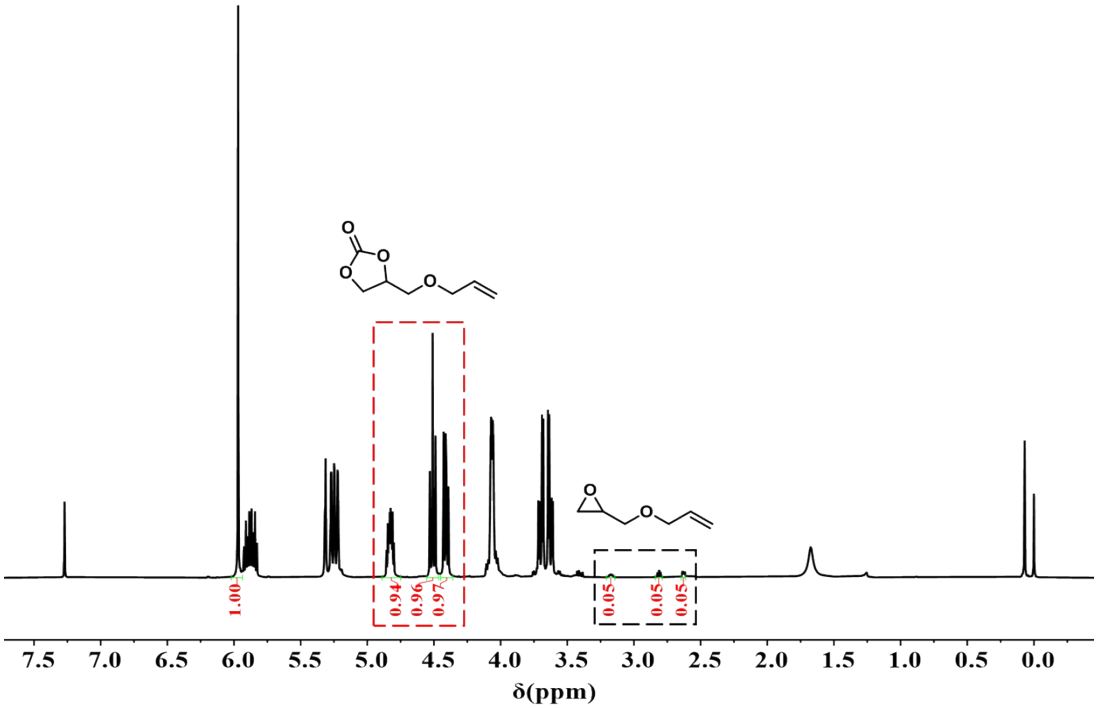


Figure S26 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with allyl glycidyl ether as substrate using catalyst **1a** ⊃ **PV**.

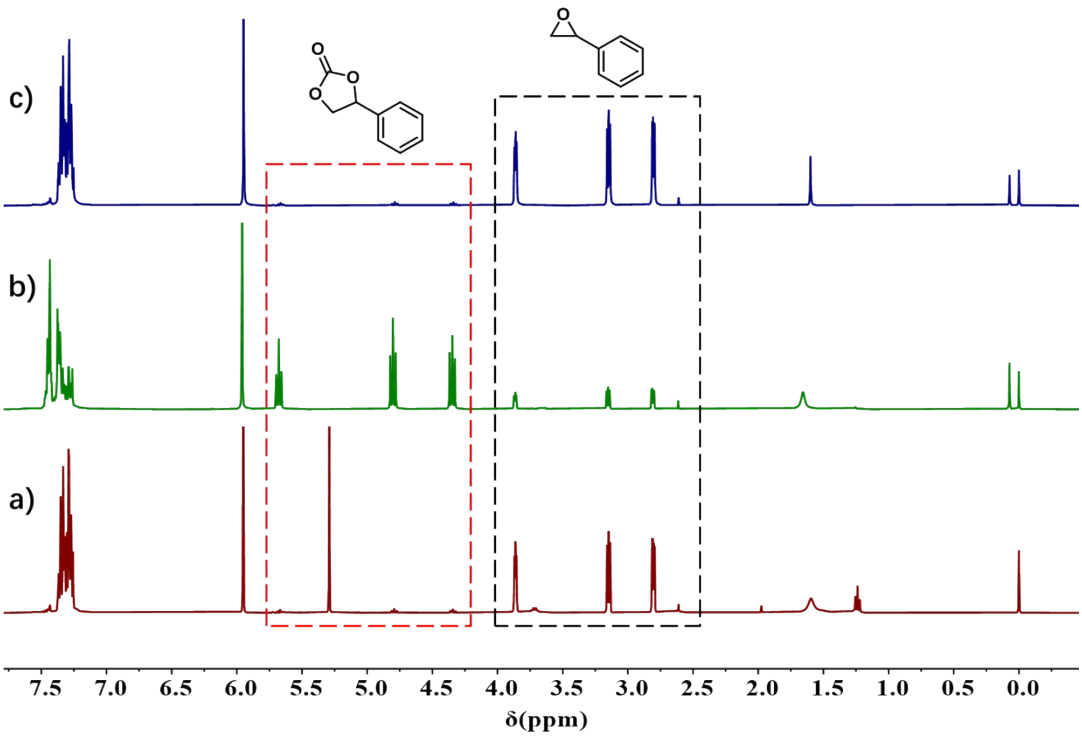


Figure S27 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with styrene oxide as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

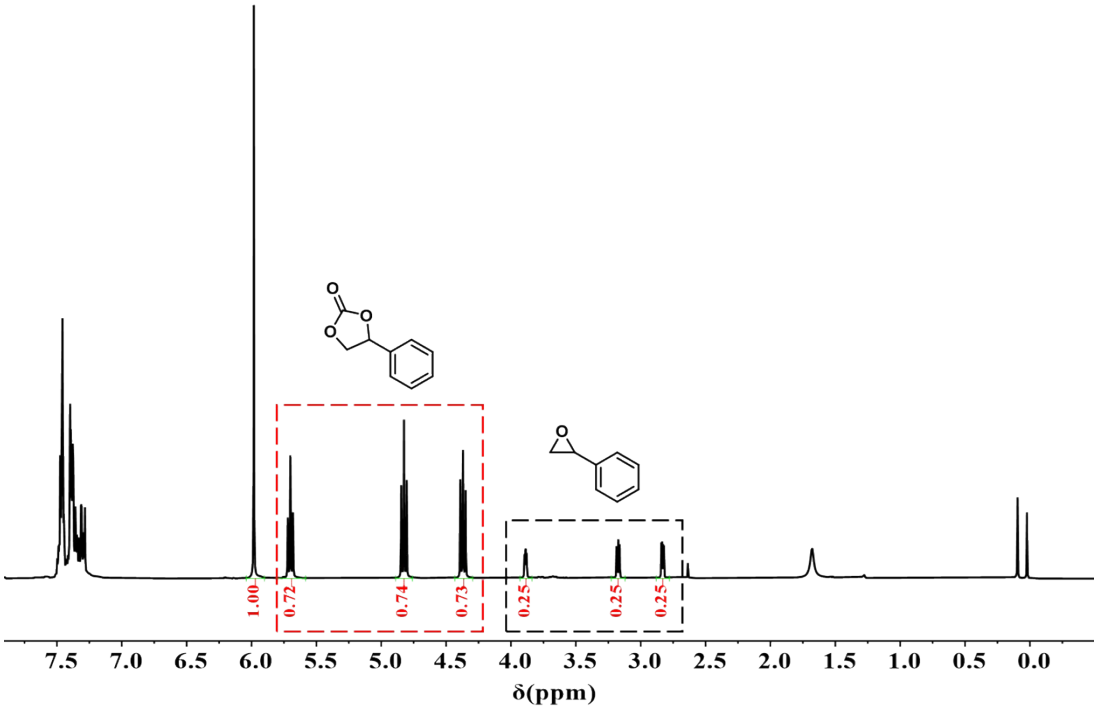


Figure S28 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with styrene oxide as substrate using catalyst **1a** ⊃ **PV**.

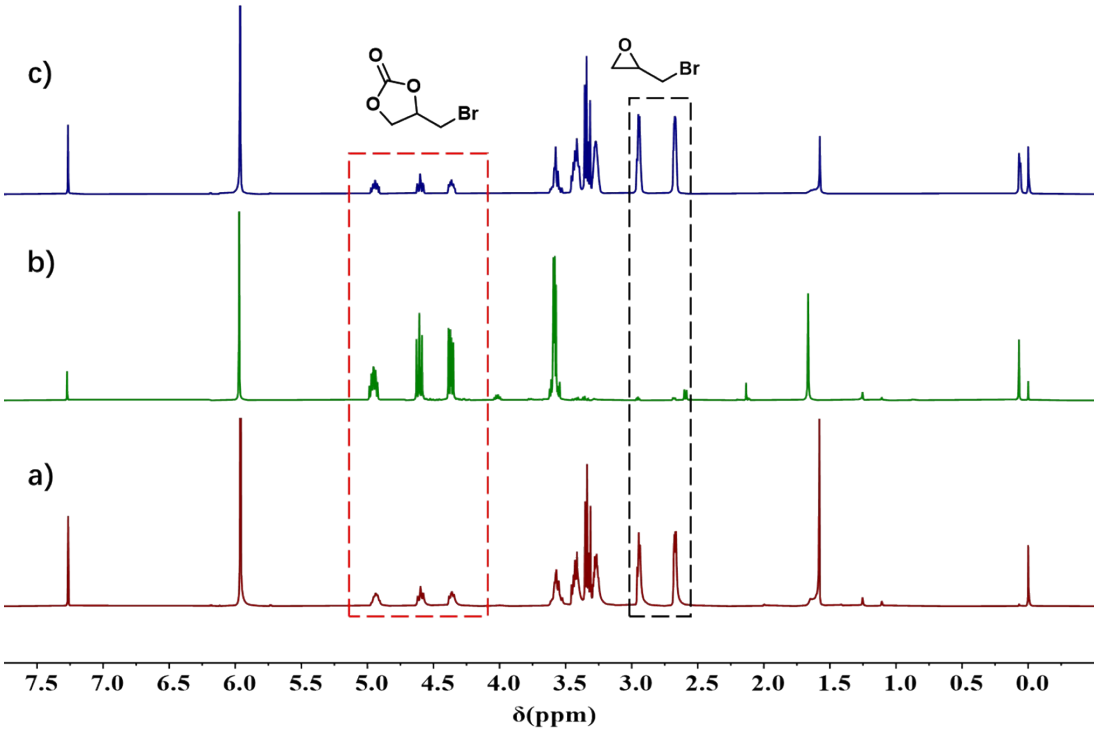


Figure S29 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with epibromohydrin as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

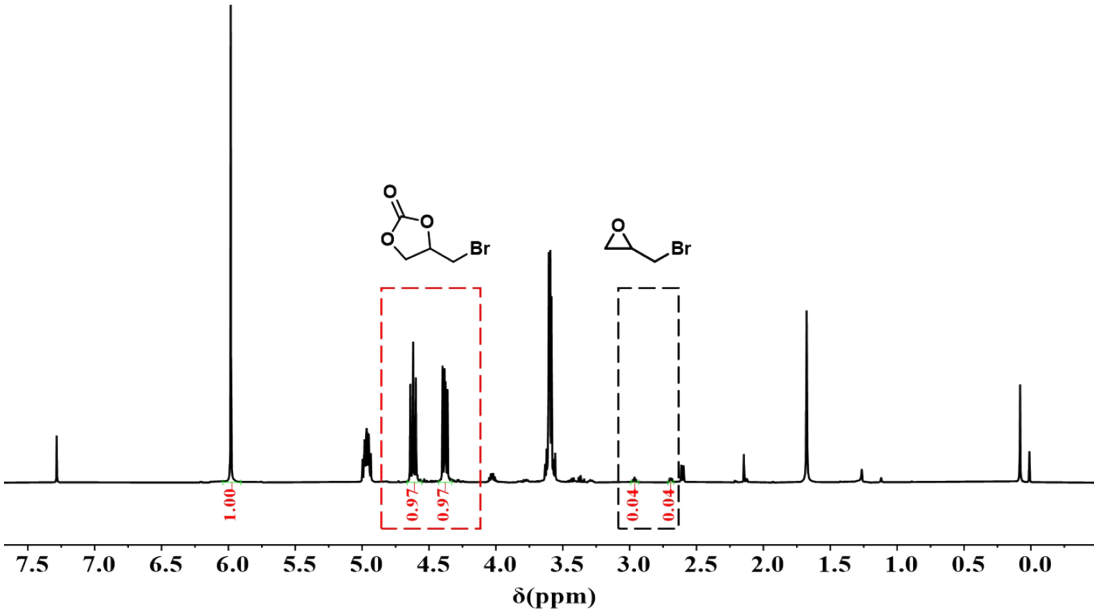


Figure S30 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with epibromohydrin as substrate using catalyst **1a** ⊃ **PV**.

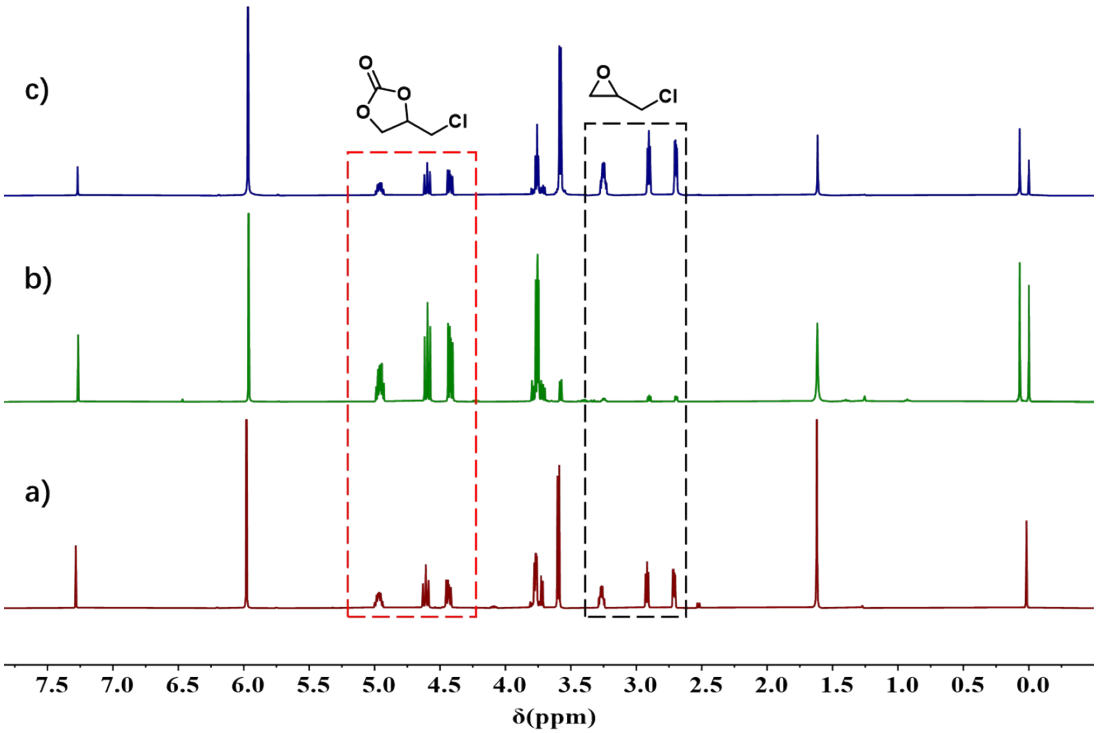


Figure S31 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with epichlorohydrin as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

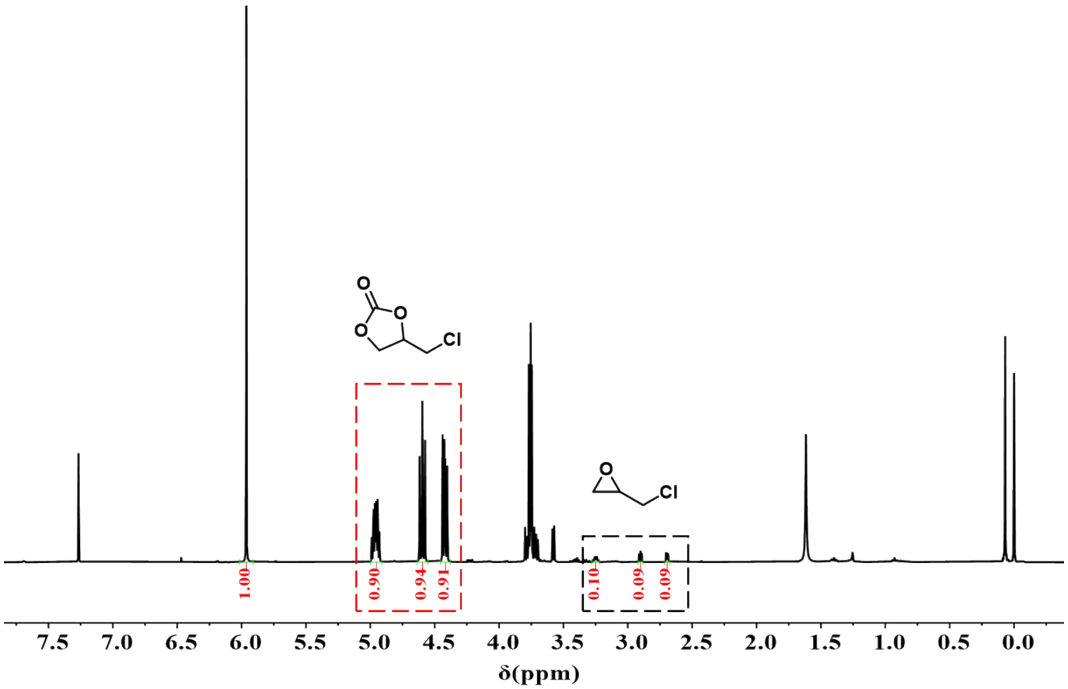


Figure S32 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with epichlorohydrin as substrate using catalyst **1a** ⊃ **PV**.

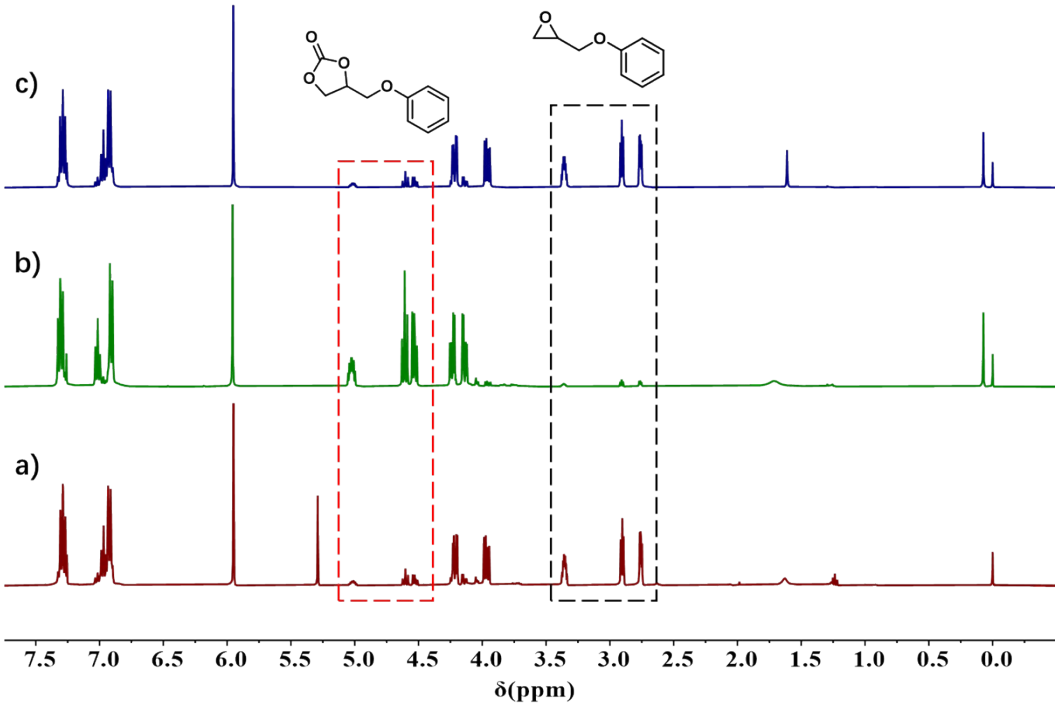


Figure S33 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with phenyl ether as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

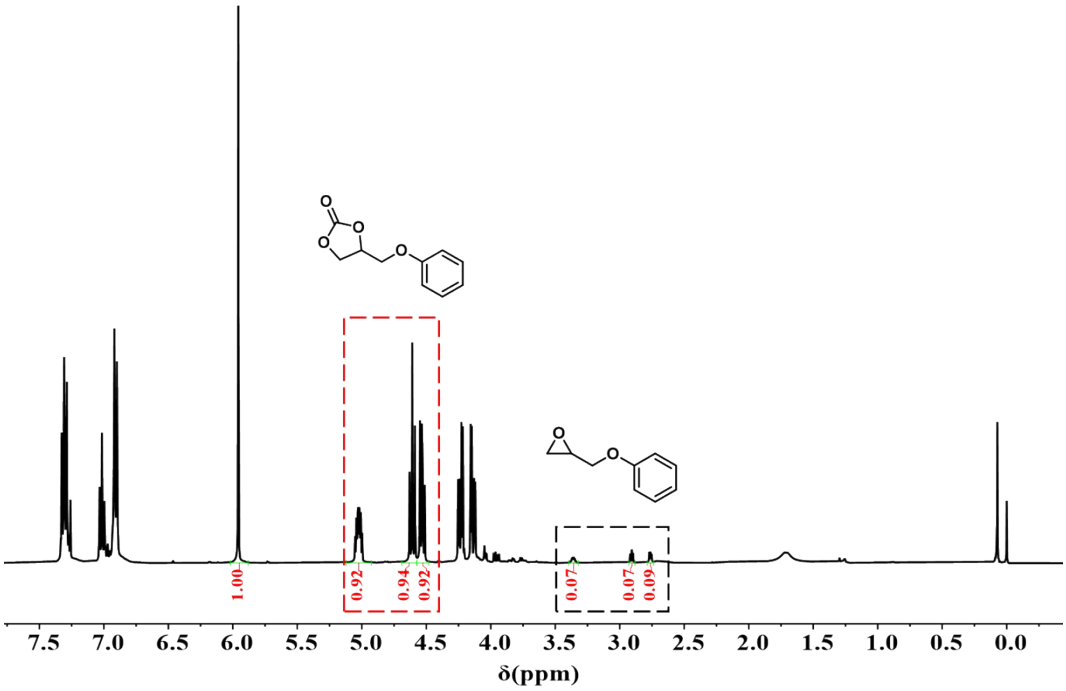


Figure S34 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with phenyl ether as substrate using catalyst **1a** ⊃ **PV**.

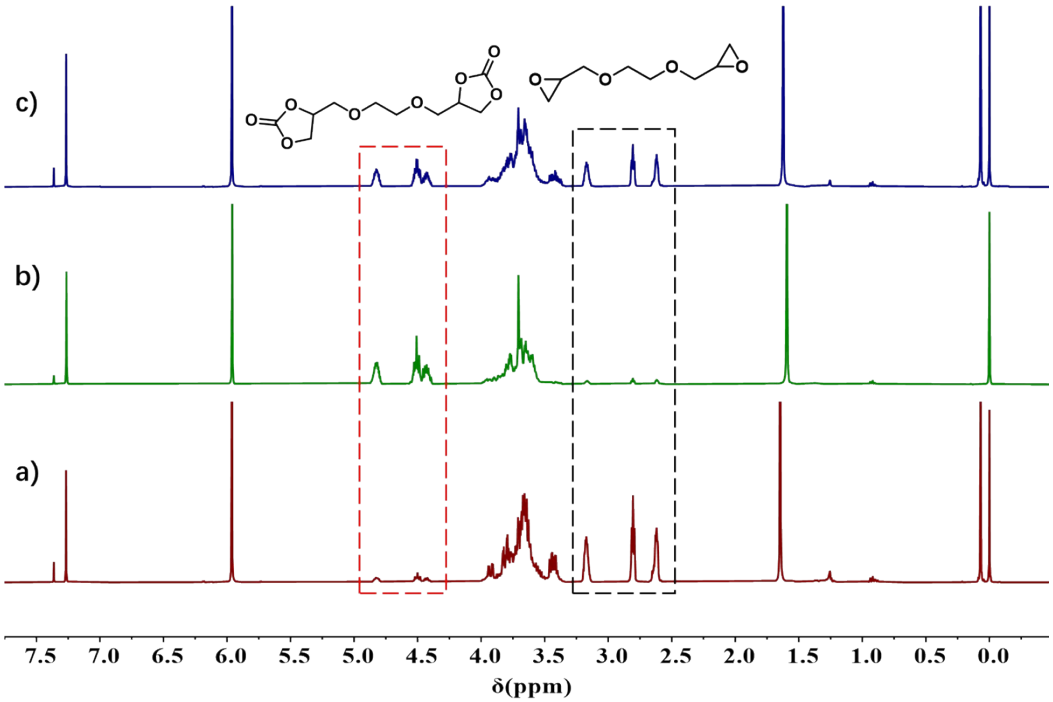


Figure S35 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with ethylene glycol diglycidyl as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

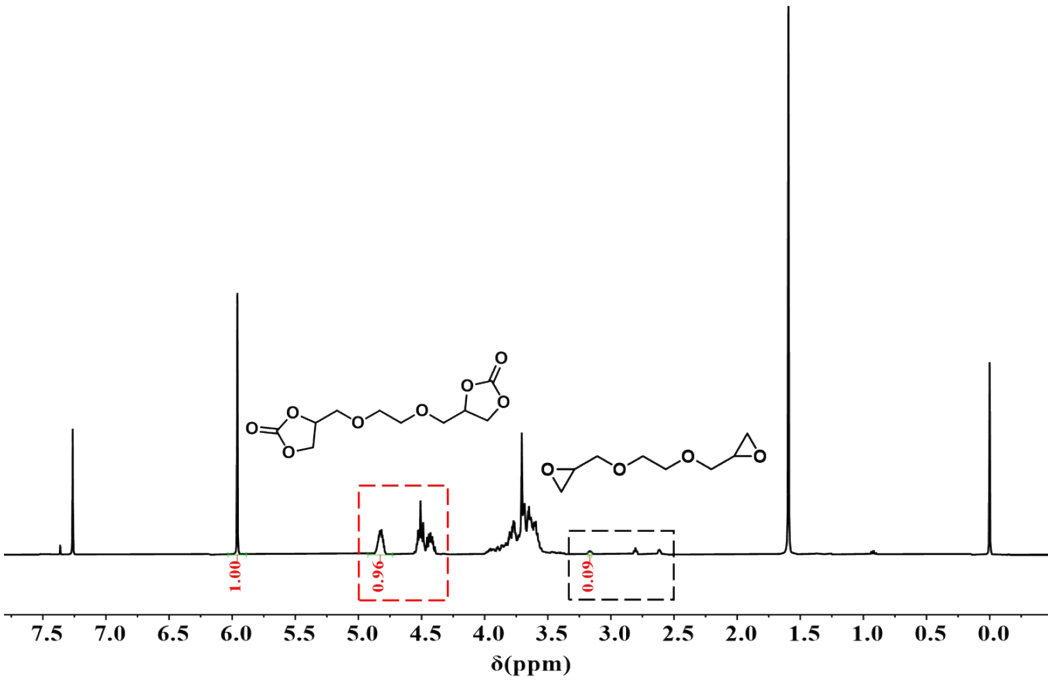


Figure S36 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with ethylene glycol diglycidyl as substrate using catalyst **1a** ⊃ **PV**.

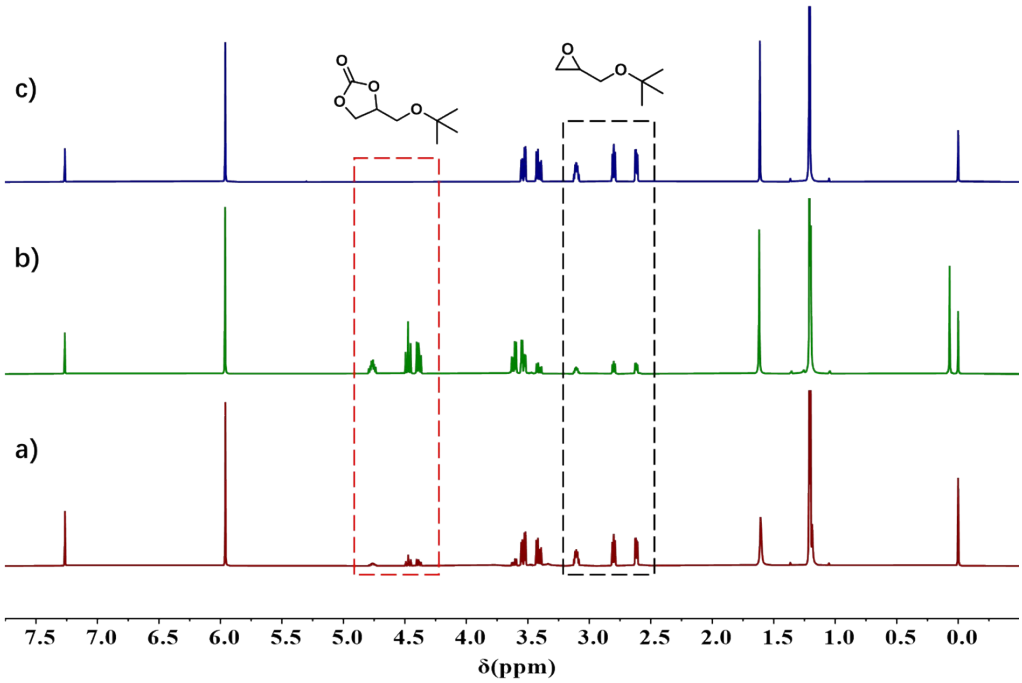


Figure S37 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the reaction mixtures with tert-butyl glycidyl ether as substrate using different catalysts: (a) **1a**, (b) **1a** ⊃ **PV**, (c) **PV**.

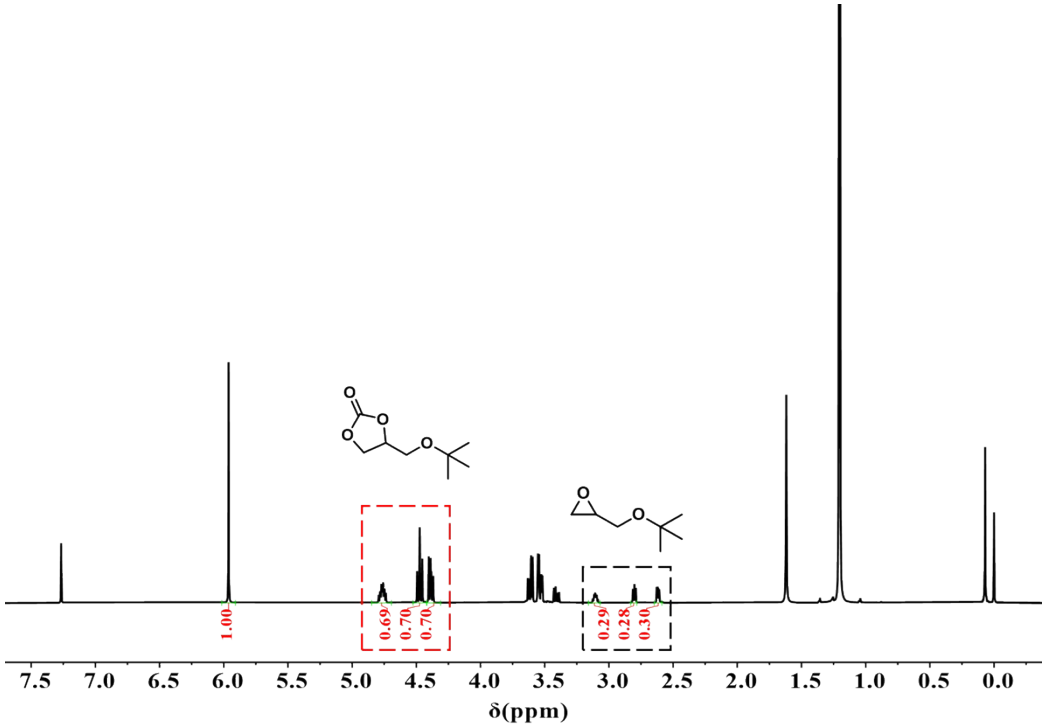
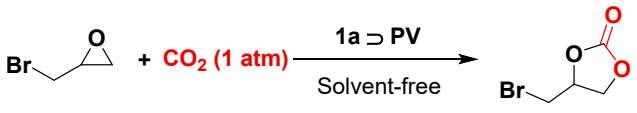


Figure S38 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the reaction mixture with tert-butyl glycidyl ether as substrate using catalyst **1a** ⊃ **PV**.

9. Kinetic Studies

Table S2 Kinetics experiments of CO_2 with epibromohydrin using different catalyst loading [a]



Entry	Cat. loading		Rate constant (min^{-1}) [b]
	1a (mol%)	**PV** (mg)	
1	0.062	3.57	$(7.56 \pm 0.38) \times 10^{-4}$
2	0.125	7.5	$(8.73 \pm 0.44) \times 10^{-4}$
3	0.250	15.0	$(8.45 \pm 0.42) \times 10^{-4}$
4	0.500	30.0	$(1.32 \pm 0.07) \times 10^{-3}$
5	--	--	n.r. [c]

[a] Reaction conditions: epibromohydrin (7.30 mmol), CO_2 (1 atm), catalyst is **1a** ⊃ **PV** solvent-free, 80 ˚C and 24 h. [b] The rate constant is fitted followed by a pseudo-first order dependence. [c] n.r. = no reaction.

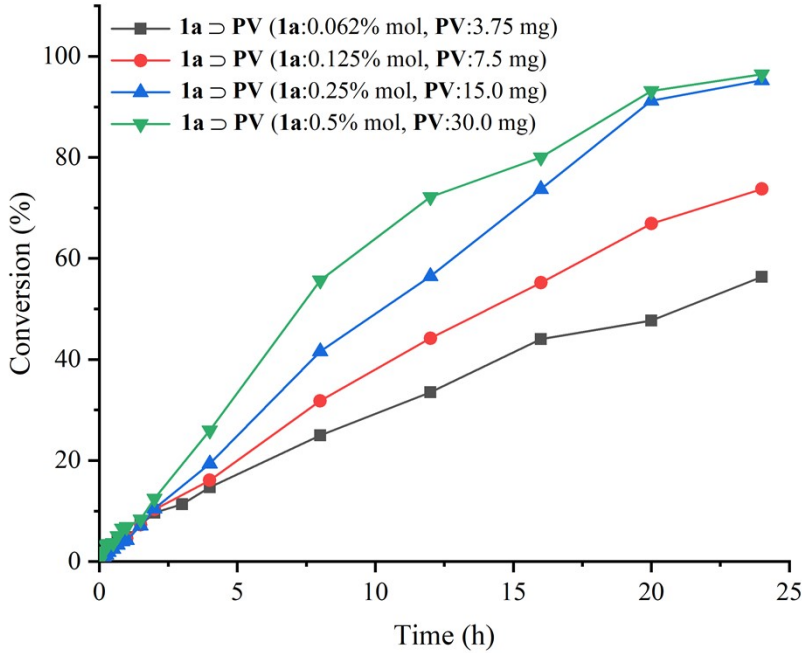


Figure S39 Kinetic profile for the cycloaddition reaction of CO_2 and epibromohydrin catalyzed by different catalyst loading **1a** ⊃ **PV**.

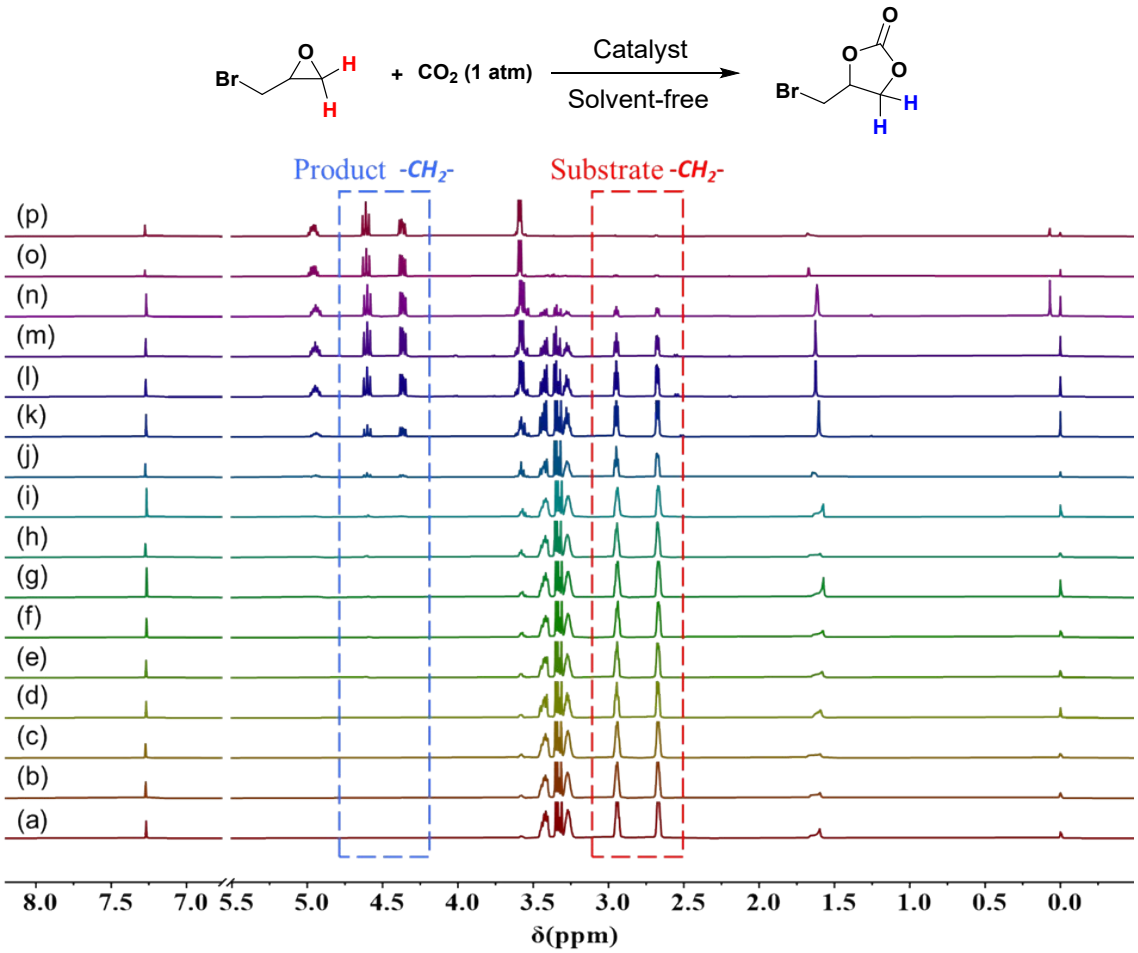


Figure S40 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, (f) 40 min, (g) 50 min, (h) 1 h, (i) 1.5 h, (j) 2 h, (k) 4 h, (l) 8 h, (m) 12 h, (n) 16 h, (o) 20 h, (p) 24 h. (**1a**: 0.25 mol%, **PV**: 15.0 mg)

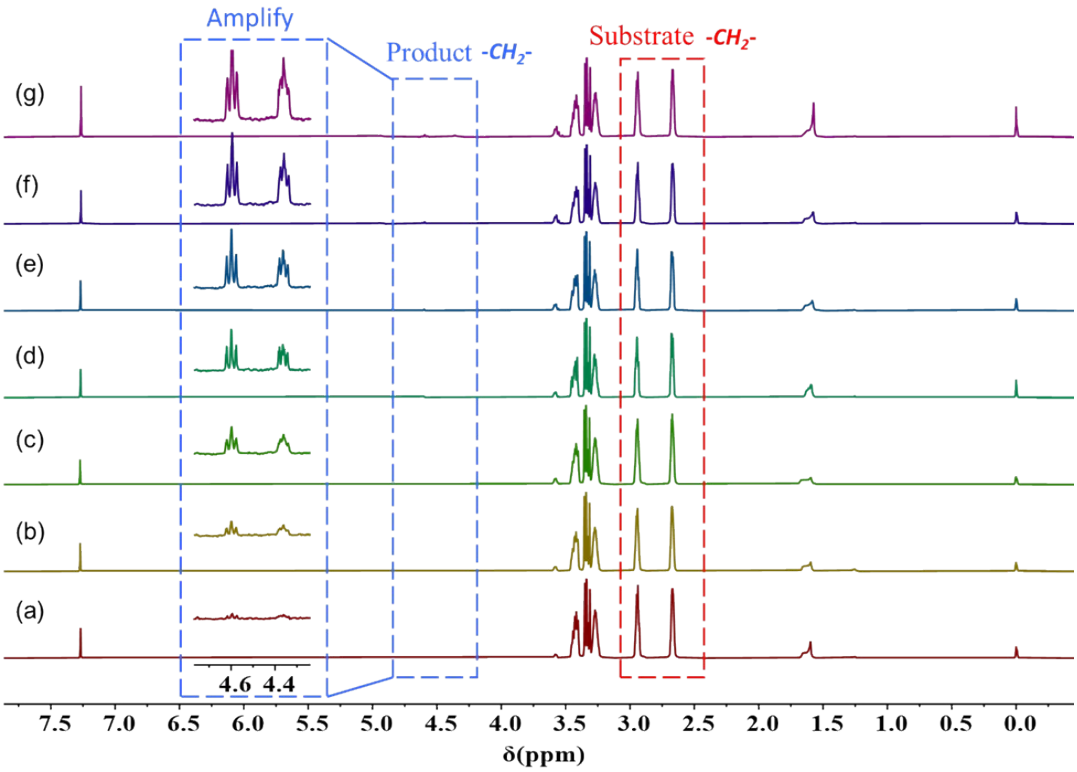


Figure S41 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, (f) 40 min, (g) 50 min. (**1a**: 0.25 mol%, **PV**: 15.0 mg)

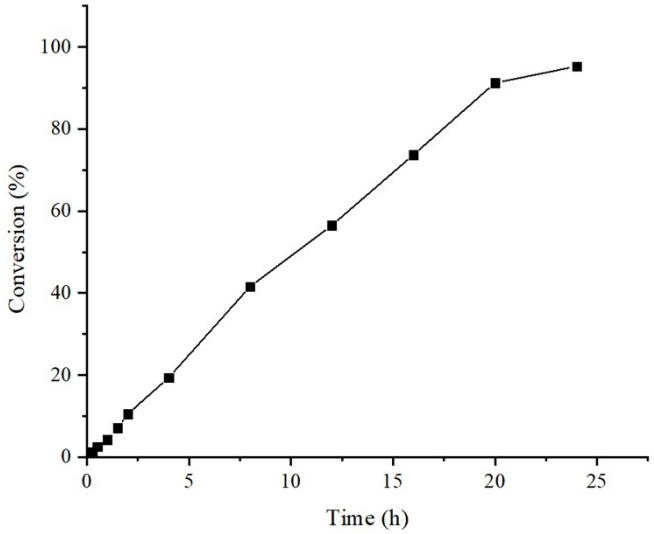


Figure S42 Kinetic profile for the cycloaddition reaction of CO_2 and epibromohydrin catalyzed by **1a** ⊃ **PV** under 1 atm CO_2 and 80 °C conditions. (**1a**: 0.25 mol%, **PV**: 15.0 mg)

Table S3 Kinetic study of epibromohydrin catalyzed by **1a** ⊃ **PV**

Entry	Time (min)	epibromohydrin (mmol)	ln ($n_{a,0}$ / n_a) [a]
a	5	7.2563	0.0061
b	10	7.2290	0.0098
c	15	7.2026	0.0135
d	20	7.1644	0.0188
e	30	7.1155	0.0257
f	40	7.0584	0.0337
g	50	7.0103	0.0406

[a] $n_{a,0}$ = 7.30 mmol. (**1a**: 0.25 mol%, **PV**: 15.0 mg)

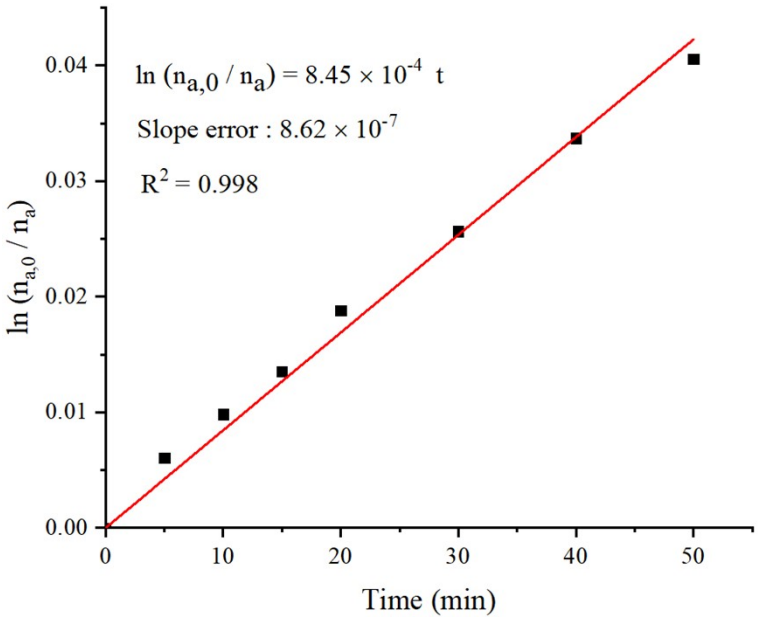


Figure S43 Linear curve fitting of the amount of substance of epibromohydrin against reaction time, indicating a pseudo-first order dependence of the reaction rate on epibromohydrin.

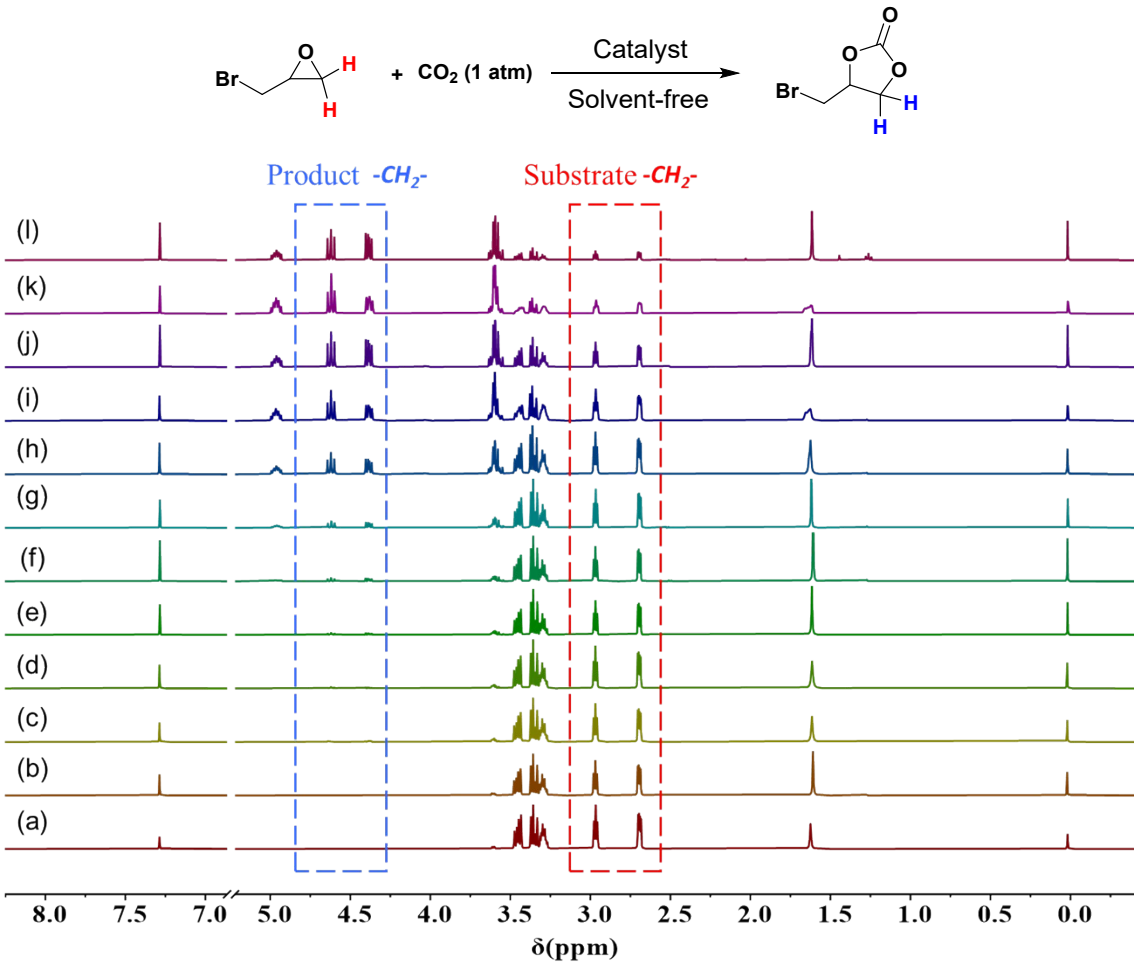


Figure S44 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 10 min, (b) 20 min, (c) 40 min, (d) 1 h, (e) 1.5 h, (f) 2 h, (g) 4 h, (h) 8 h, (i) 12 h, (j) 16 h, (k) 20 h, (l) 24 h. (**1a**: 0.125 mol%, **PV**: 7.5 mg)

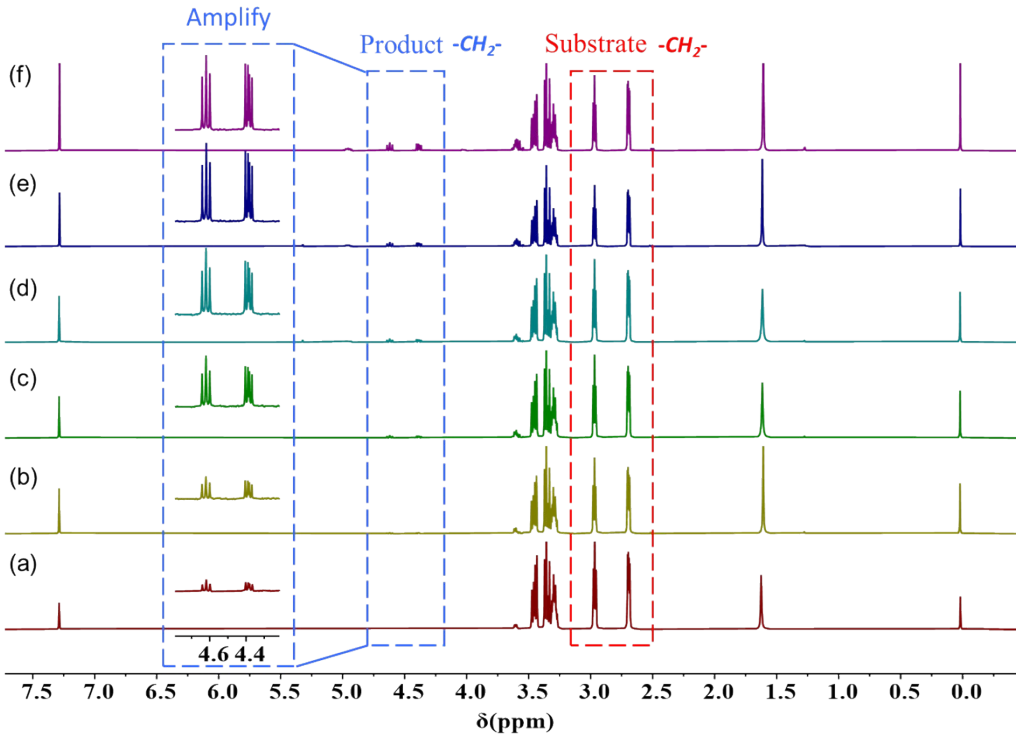


Figure S45 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 10 min, (b) 20 min, (c) 40 min, (d) 1 h, (e) 1.5 h, (f) 2 h. (**1a**: 0.125 mol%, **PV**: 7.5 mg)

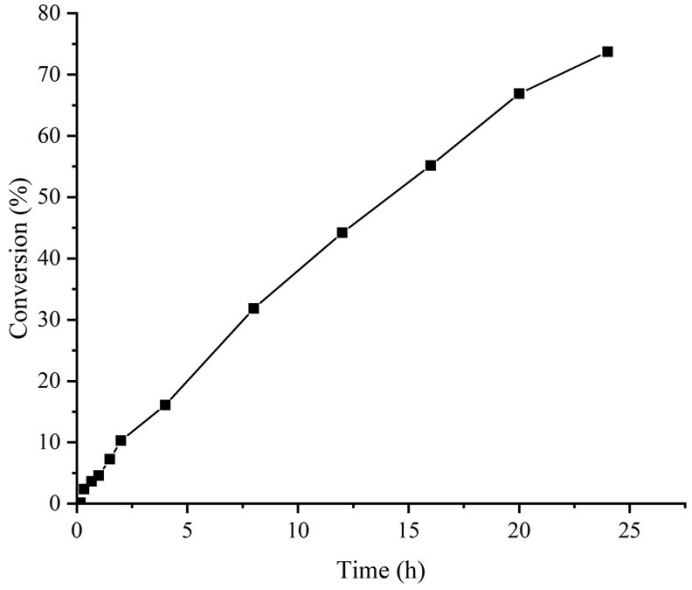


Figure S46 Kinetic profile for the cycloaddition reaction of CO_2 and epibromohydrin catalyzed by **1a** ⊃ **PV** under 1 atm CO_2 and 80 °C conditions. (**1a**: 0.125 mol%, **PV**: 7.5 mg)

Table S4 Kinetic study of epibromohydrin catalyzed by **1a** ⊃ **PV**

Entry	Time (min)	epibromohydrin (mmol)	ln ($n_{a,0}$ / n_a) [a]
a	10	7.2897	0.0015
b	20	7.1274	0.0240
c	40	7.0353	0.0370
d	60	6.9649	0.0471
e	90	6.7710	0.0753
f	120	6.5487	0.1087

[a] $n_{a,0}$ = 7.30 mmol. (**1a**: 0.125 mol%, **PV**: 7.5 mg)

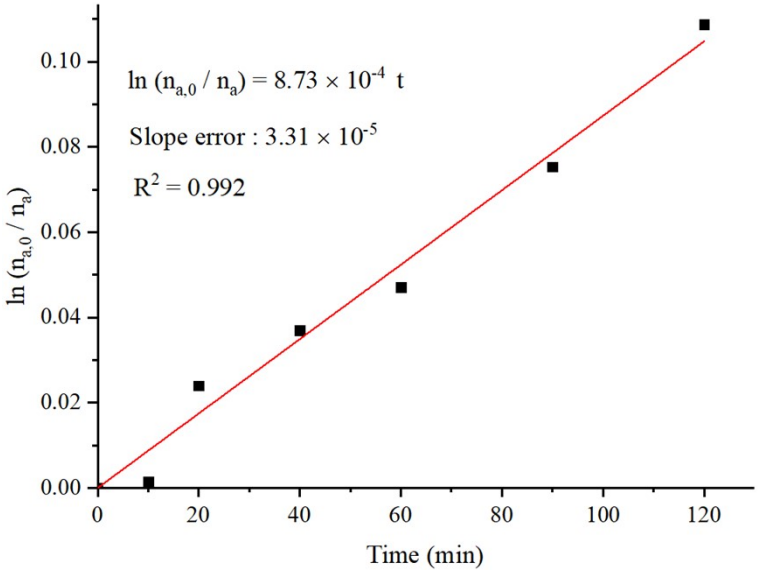


Figure S47 Linear curve fitting of amount of substance of epibromohydrin against reaction time, indicating a pseudo-first order dependence of the reaction rate on epibromohydrin.

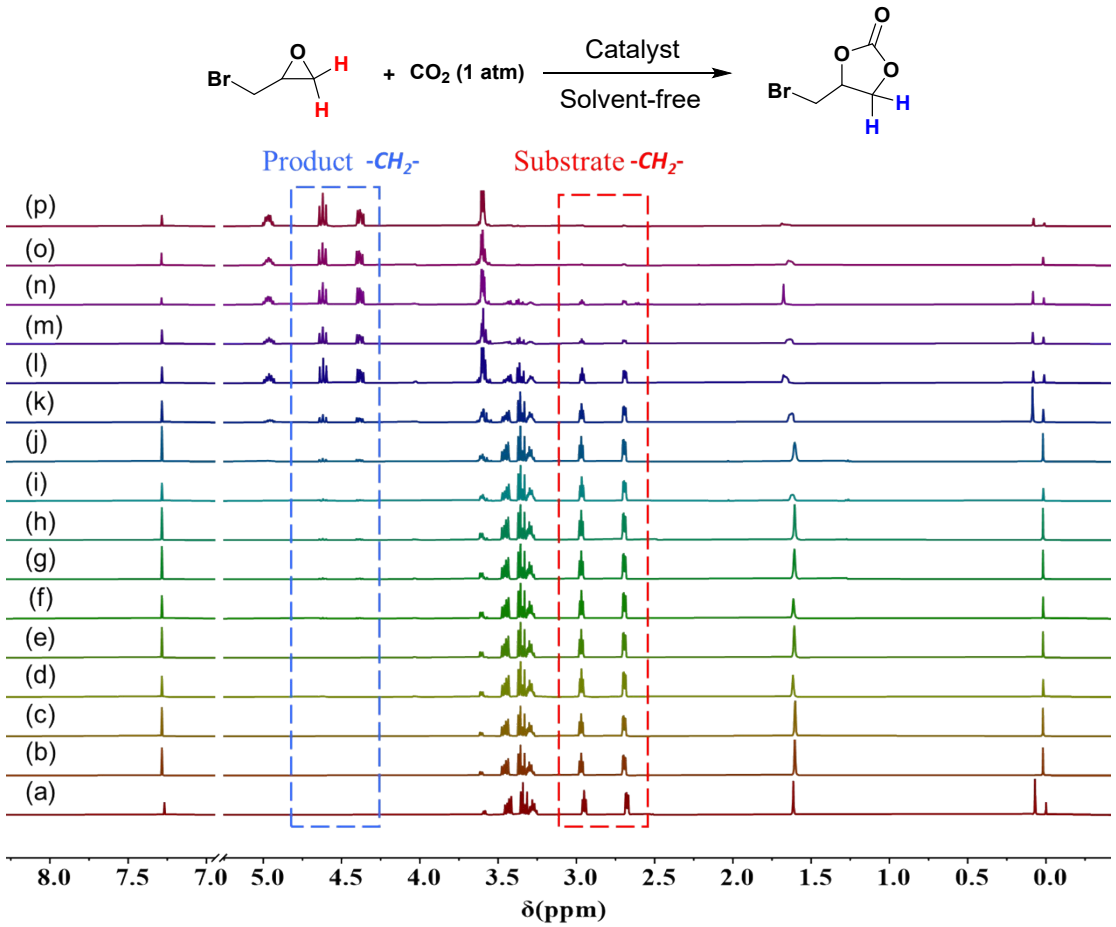


Figure S48 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, (f) 40 min, (g) 50 min, (h) 1 h, (i) 1.5 h, (j) 2 h, (k) 4 h, (l) 8 h, (m) 12 h, (n) 16 h, (o) 20 h, (p) 24 h. (**1a**: 0. 5 mol%, **PV**: 30.0 mg)

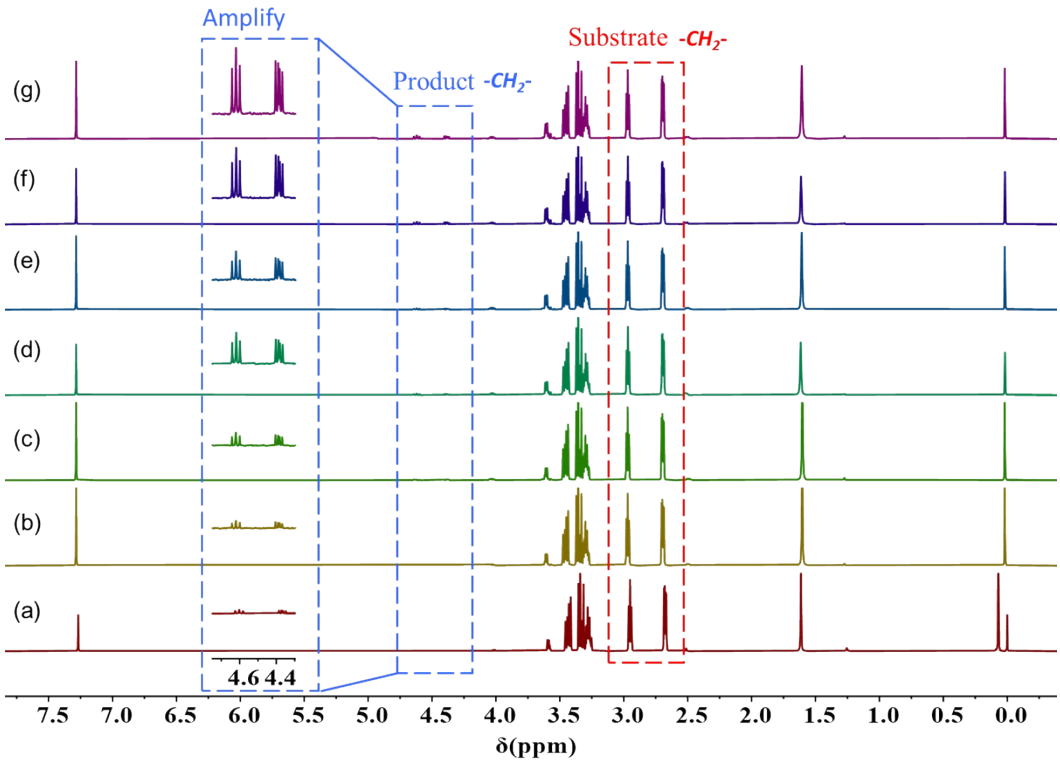


Figure S49 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 30 min, (f) 40 min, (g) 50 min. (**1a**: 0. 5 mol%, **PV**: 30.0 mg)

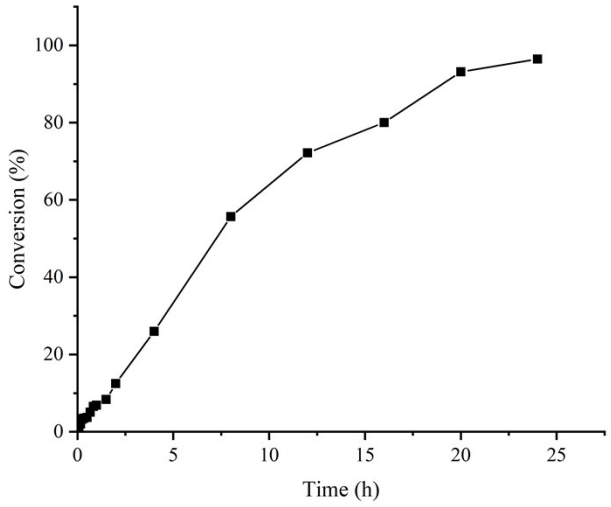


Figure S50 Kinetic profile for the cycloaddition reaction of CO_2 and epibromohydrin catalyzed by **1a** ⊃ **PV** under 1 atm CO_2 and 80 °C conditions. (**1a**: 0. 5 mol%, **PV**: 30.0 mg)

Table S5 Kinetic study of epibromohydrin catalyzed by **1a** ⊃ **PV**

Entry	Time (min)	epibromohydrin (mmol)	ln ($n_{a,0}$ / n_a) [a]
a	5	7.2126	0.0121
b	10	7.1526	0.0205
c	15	7.0619	0.0332
d	20	7.0462	0.0355
e	30	7.0306	0.0377
f	40	6.9325	0.0517
g	50	6.8242	0.0675

[a] $n_{a,0}$ = 7.30 mmol. (**1a**: 0. 5 mol%, **PV**: 30.0 mg)

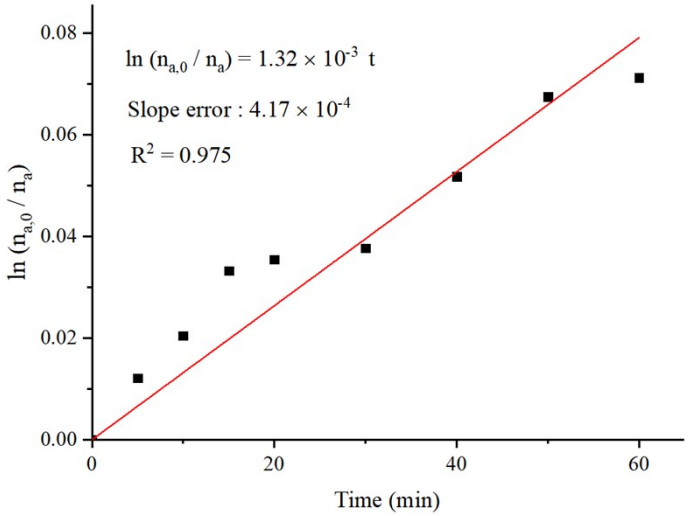


Figure S51 Linear curve fitting of the amount of substance of epibromohydrin against reaction time, indicating a pseudo-first order dependence of the reaction rate on epibromohydrin.

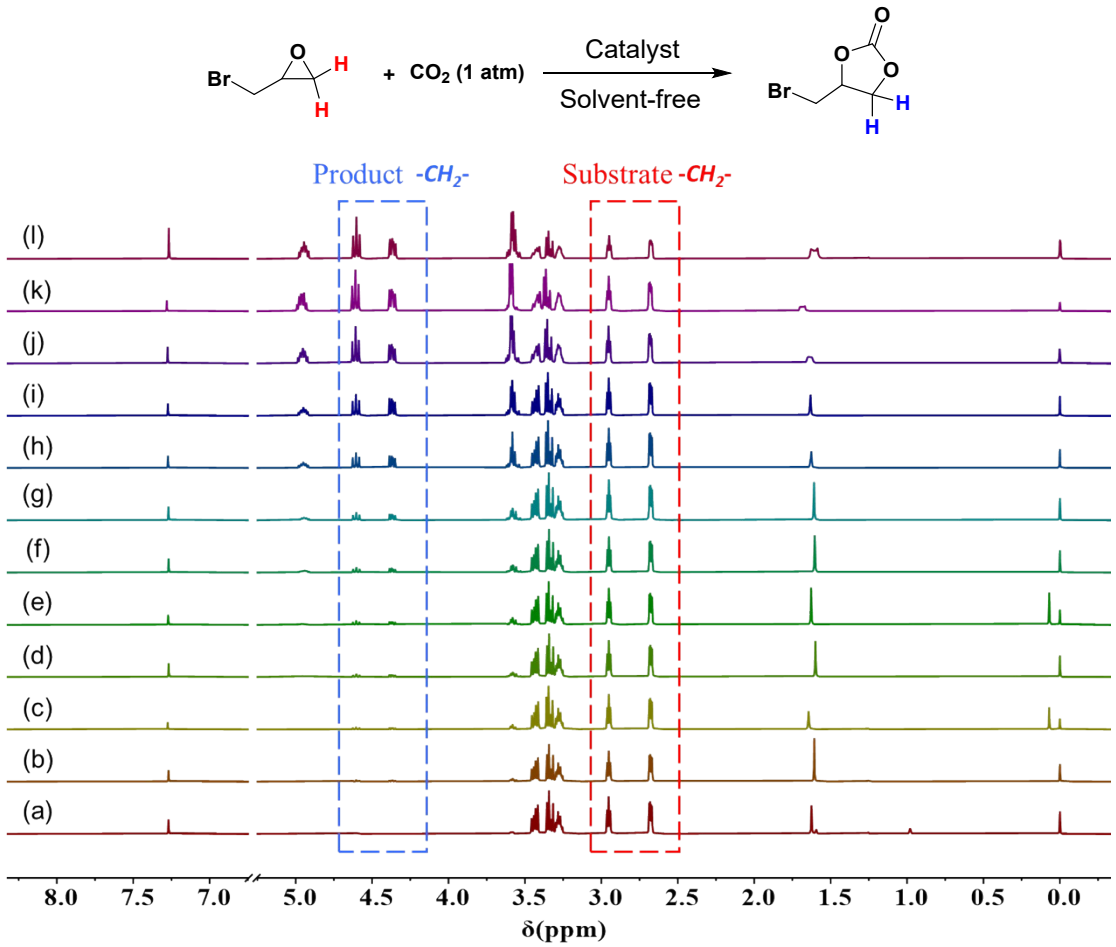


Figure S52 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 20 min, (b) 40 min, (c) 1 h, (d) 1.5 h, (e) 2 h, (f) 3 h, (g) 4 h, (h) 8 h, (i) 12 h, (j) 16 h, (k) 20 h, (l) 24 h. (**1a**: 0. 062 mol%, **PV**: 3.75 mg)

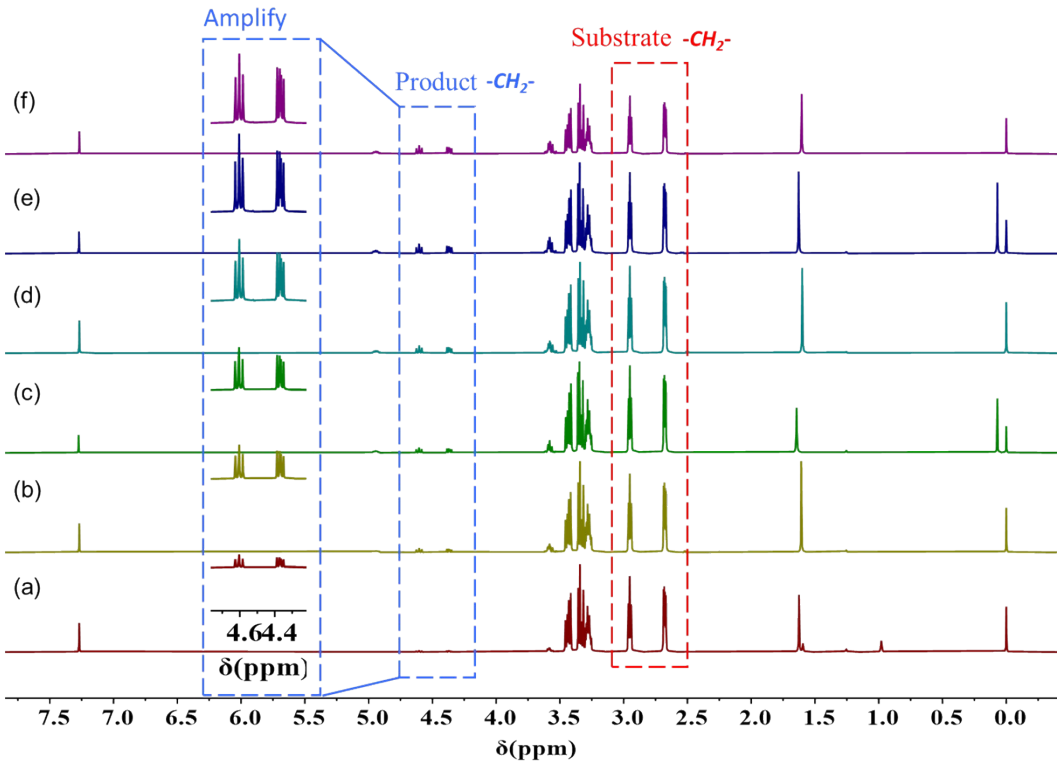


Figure S53 Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of conversions of epibromohydrin catalyzed by **1a** ⊃ **PV**. The spectra from bottom to top correspond to the reaction at (a) 20 min, (b) 40 min, (c) 1 h, (d) 1.5 h, (e) 2 h, (f) 3 h. (**1a**: 0. 062 mol%, **PV**: 3.75 mg)

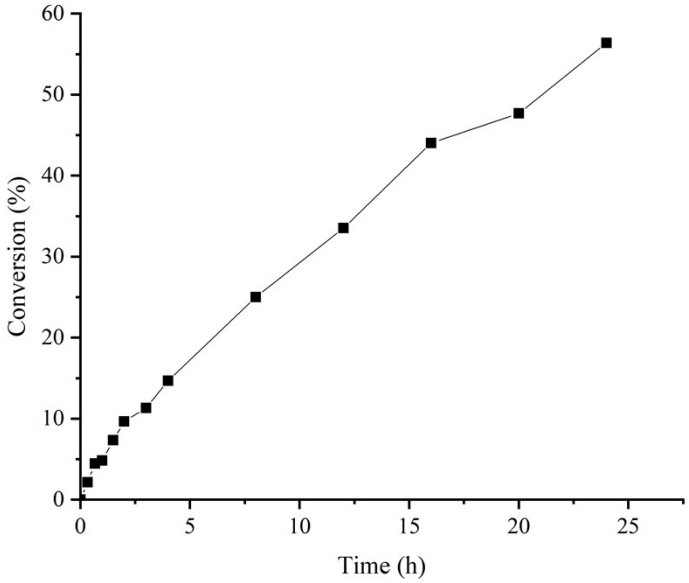


Figure S54 Kinetic profile for the cycloaddition reaction of CO_2 and epibromohydrin catalyzed by **1a** ⊃ **PV** under 1 atm CO_2 and 80 °C conditions. (**1a**: 0. 062 mol%, **PV**: 3.75 mg)

Table S6 Kinetic study of epibromohydrin catalyzed by **1a** ⊃ **PV**

Entry	Time (min)	epibromohydrin (mmol)	ln ($n_{a,0}$ / n_a) [a]
a	20	7.14216	0.02186
b	40	6.97497	0.04555
c	60	6.94841	0.04936
d	90	6.7649	0.07613
e	120	6.59619	0.10138
f	180	6.47393	0.12009

[a] $n_{a,0}$ = 7.30 mmol. (**1a**: 0. 062 mol%, **PV**: 3.75 mg)

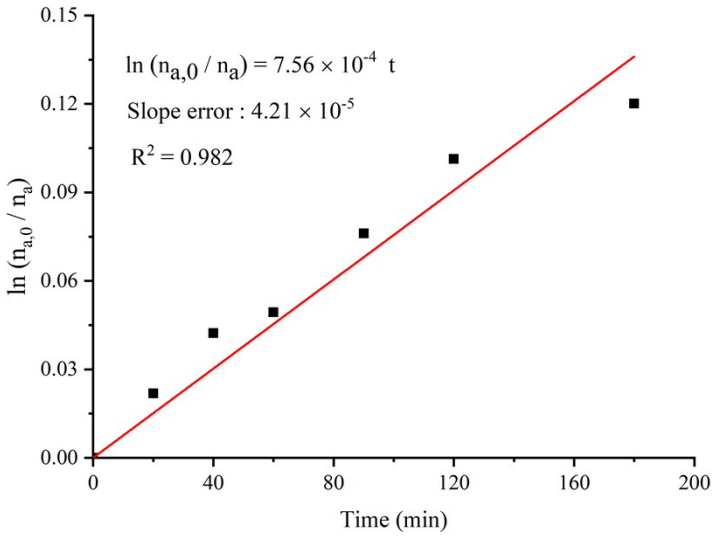


Figure S55 Linear curve fitting of the amount of substance of epibromohydrin against reaction time, indicating a pseudo-first order dependence of the reaction rate on epibromohydrin.

10. Recyclability of 1a ⊃ PV

Epoxide epibromohydrin was used as a substrate to test the recyclability of **1a ⊃ PV**. The catalyst was recovered by filtration, washed with dichloromethane and dried under vacuum for the next catalytic reaction.

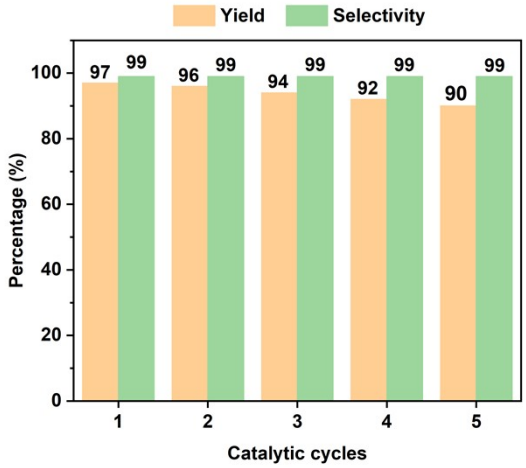


Figure S56 Catalytic reusability of **1a ⊃ PV** in the cycloaddition of CO_2 with epibromohydrin. Reaction conditions: epibromohydrin (2.4 mmol), CO_2 pressure (1 atm), the fresh catalyst **1a ⊃ PV** (6.4 μmol **1a** and 0.8 μmol **PV**), 80 °C, 24 h.

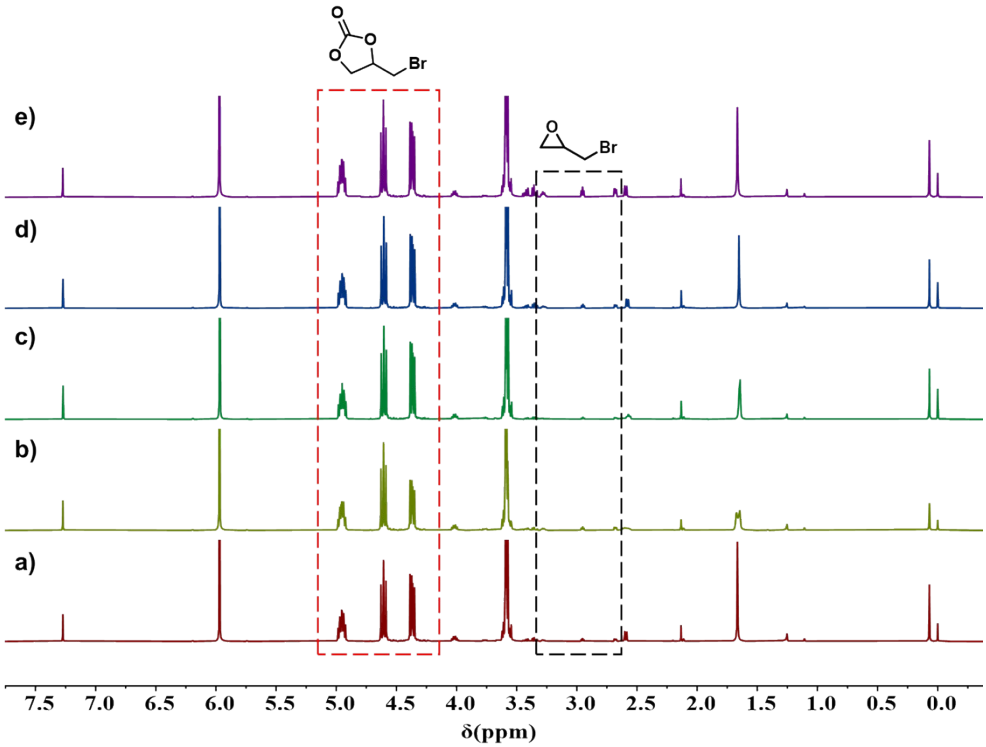


Figure S57 Stacked ^{1}H NMR spectra (a-e) (400 MHz, $CDCl_3$, 298 K) of reaction mixtures using epibromohydrin as the substrate and **1a ⊃ PV** as the catalyst for five catalytic cycles.

Reference

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