

Supporting Information

Novel porous organic polymers functionalized by metalloporphyrin and phosphonium salt for efficient synergistic catalysis of CO₂ conversion under mild conditions

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EXPERIMENT SECTION

Synthesis of 4-vinylbenzaldehyde. 4-Vinylbenzaldehyde was synthesized according to the previous reports [1]. Typically, magnesite powders (4.25 g, 170 mmol, 1.7 eq) was placed in a 250 mL round-bottom flask equipped with a magnetic stirring bar. After addition of anhydrous THF (50 mL) under N₂ atmosphere, 4-bromostyrene (18.32 g, 100 mmol, 1 eq) was slowly added into the flask in an ice water bath, followed by stirring at room temperature for 2 h. Then, DMF (7.32 g, 100 mmol, 1 eq) was slowly added into the solution in an ice water bath, and stirred at room temperature overnight. The reaction was quenched using saturated aqueous solution of NH₄Cl, and the mixture was extracted by Ethyl acetate. The organic layer was filtered and concentrated. The residue was purified by silica gel chromatography (petroleum ether: ethyl acetate =10:1 v/v) to give 4-vinylbenzaldehyde as yellowish oil (9.78 g, 74.07% yield). 4-vinylbenzaldehyde was checked through ¹H NMR measurement, as illustrated in **Figure S3** in the Supporting Information. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.91 (d, J = 17.6 Hz, 1H), 5.44 (d, J = 10.9 Hz, 1H) ppm.

Synthesis of quaternized poly(4-(diphenylphosphino)-styrene) (PPh₂PStD). A typical protocol is as follows: Ph₂PSt (2.00 g, 7 mmol) and AIBN (12.3 mg, 0.075 mmol) were introduced into a round-bottomed flask with 10 mL DMF. After three freeze-thaw cycles under reduced pressure, the flask was recharged with nitrogen and placed in a preheated oil bath with a stirring bar. The polymerization was conducted at 65 °C for 24 h under N₂ atmosphere. Then, the solution was cooled down to room temperature. To afford the product, the as-obtained viscous solution was poured into abundant diethyl ether. White solid was produced and the raw product was collected by filtration. The product (PPh₂PSt 1.64 g, 81.67% yield) was obtained after washing with diethyl ether and dried on vacuum at 50 °C overnight.

PPh₂PSt (1.00 g) and 1-bromododecane (3.5 g, 14 mmol) were introduced into a round-bottomed flask with 10 mL DMF. The operation is the same as above. The final product (PPh₂PStD 1.54 g, 89.28% yield) was obtained after washing with diethyl ether and dried on vacuum at 50 °C overnight.

Synthesis of metalized PVPP (PCoVPP). In a typical protocol, VPP (0.69 g, 0.9 mmol) were dissolved in NMP (5 mL), followed by the addition of AIBN (20 mg, 0.12 mmol). After treatment in an autoclave at 200 °C for 72 h, the reaction mixture was washed with DMF and purified using Soxhlet extraction (DCM, 72 h) to give the dark-purple product, which was denoted as PVPP (0.6814 g, 98.85% yield).

Typically, PVPP (0.30 g) and DMF (10 mL) were added into a 50 mL two neck round-bottom flask. After refluxing at 100 °C, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.51 g, 2.1 mmol) was added into the flask, and stirred at 100 °C overnight. After cooling down to room temperature, HCl (3.0 M, 60 mL) was added under air atmosphere to oxidize Co^{2+} . After reacted for 5 h, the product was obtained by filtration and washing with water several times. The solvent was removed and the as-obtained product (0.27 g, 88.9% yield) was dried in vacuum for 10 h at 80 °C.

Leaching experiment on reactions of epoxides and CO_2 . The coupling reactions of CO_2 with epoxides were performed in the 25 mL Schlenk tubes with CO_2 balloons and magnetic stirrers. In a 25 mL Shrek tube was charged with catalyst and epoxide. The reaction mixture was degassed using three freeze-pump-thaw cycles, then a CO_2 balloon was added to the tube and the reaction was stirred at 80°C for 24 hours. The catalyst was removed by filtration, the filtrate was added to a clean Shrek tube, the reaction mixture was degassed using three freeze-pump-thaw cycles, then a CO_2 balloon was added to the tube, stirred at 80 °C and the reaction continued for 24 hours. ^1H NMR confirmed the selectivity and conversion of the target product.

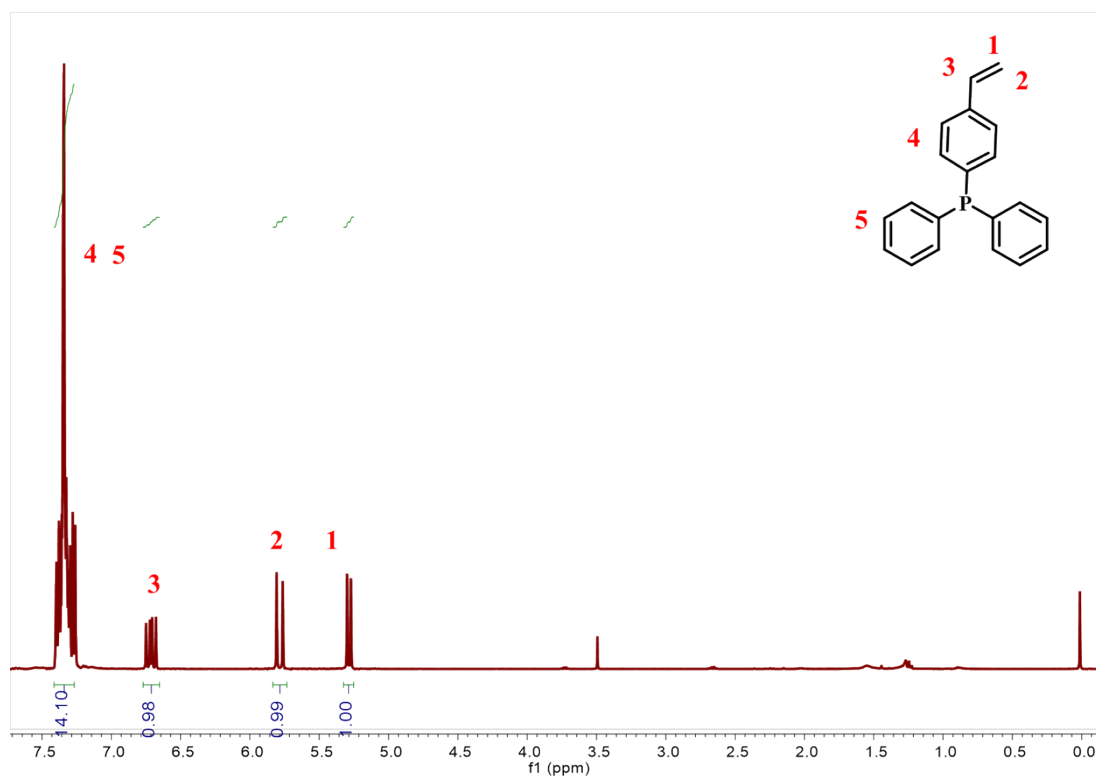


Figure S1 ¹H NMR of the vinyl-functionalized phosphonium monomer 4-(diphenylphosphino) styrene (Ph₂PSt).

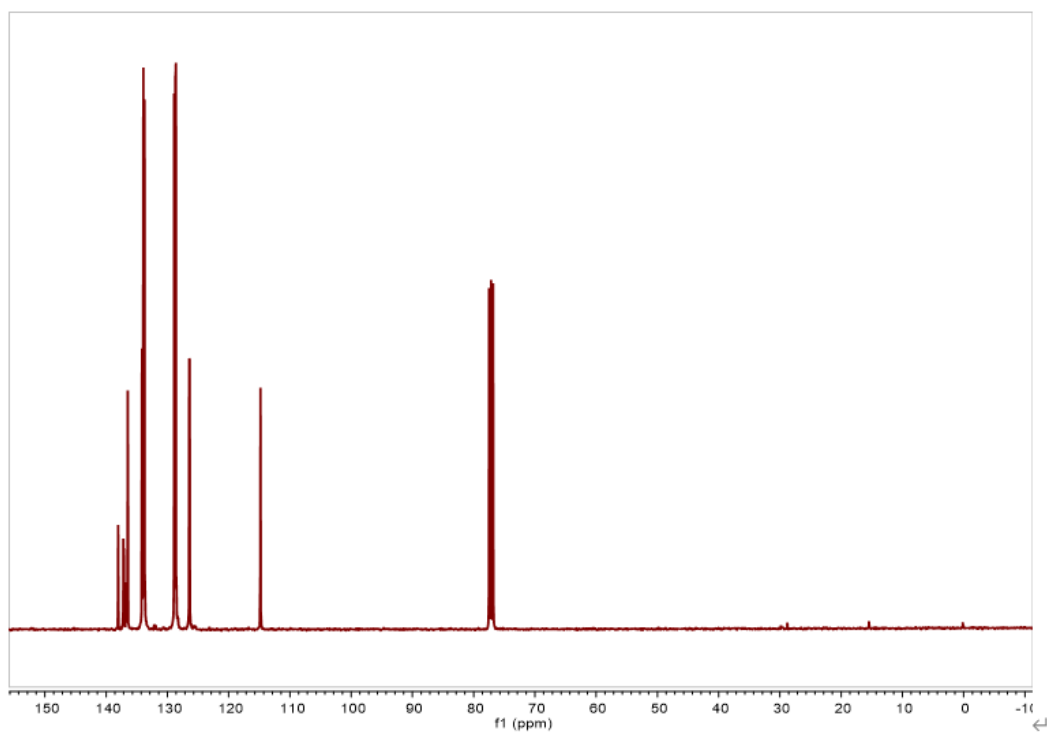


Figure S2 ¹³C NMR of the vinyl-functionalized phosphonium monomer 4-(diphenylphosphino) styrene (Ph₂PSt).

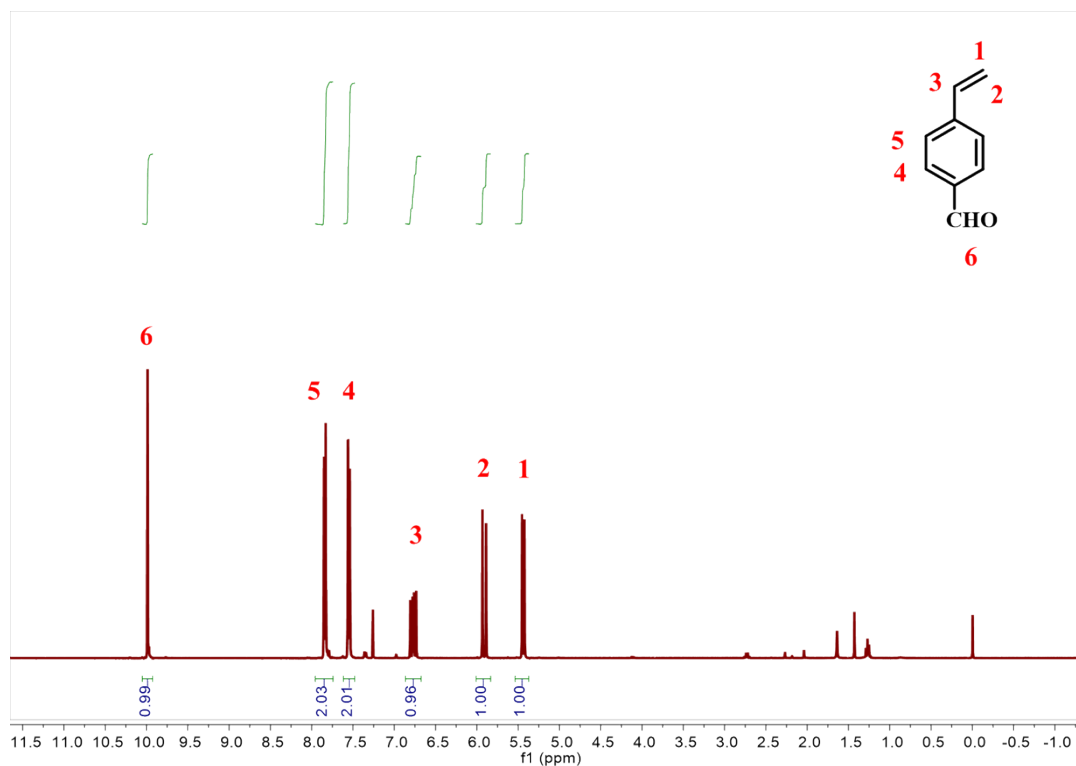


Figure S3 ^1H NMR of the vinyl-functionalized porphyrin monomer 4-vinylbenzaldehyde.

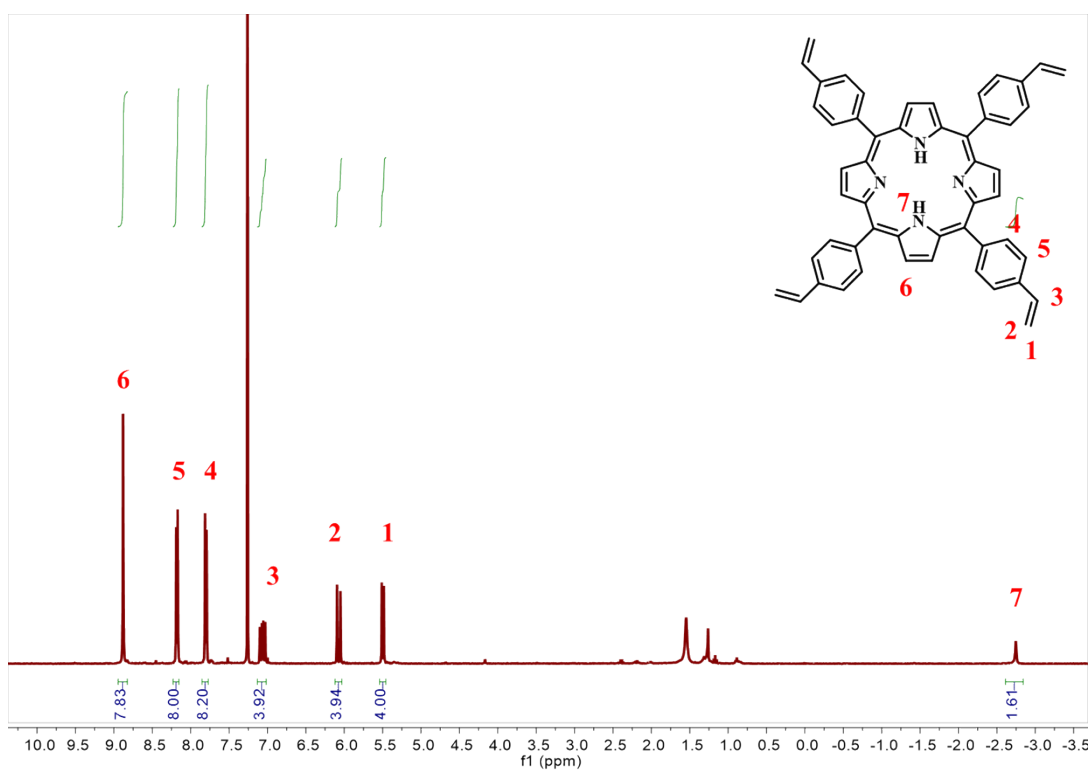


Figure S4 ^1H NMR of the vinyl-functionalized porphyrin monomer 5,10,15,20-tetrakis(4-vinylphenyl)-21H,23H-porphyrin (VPP).

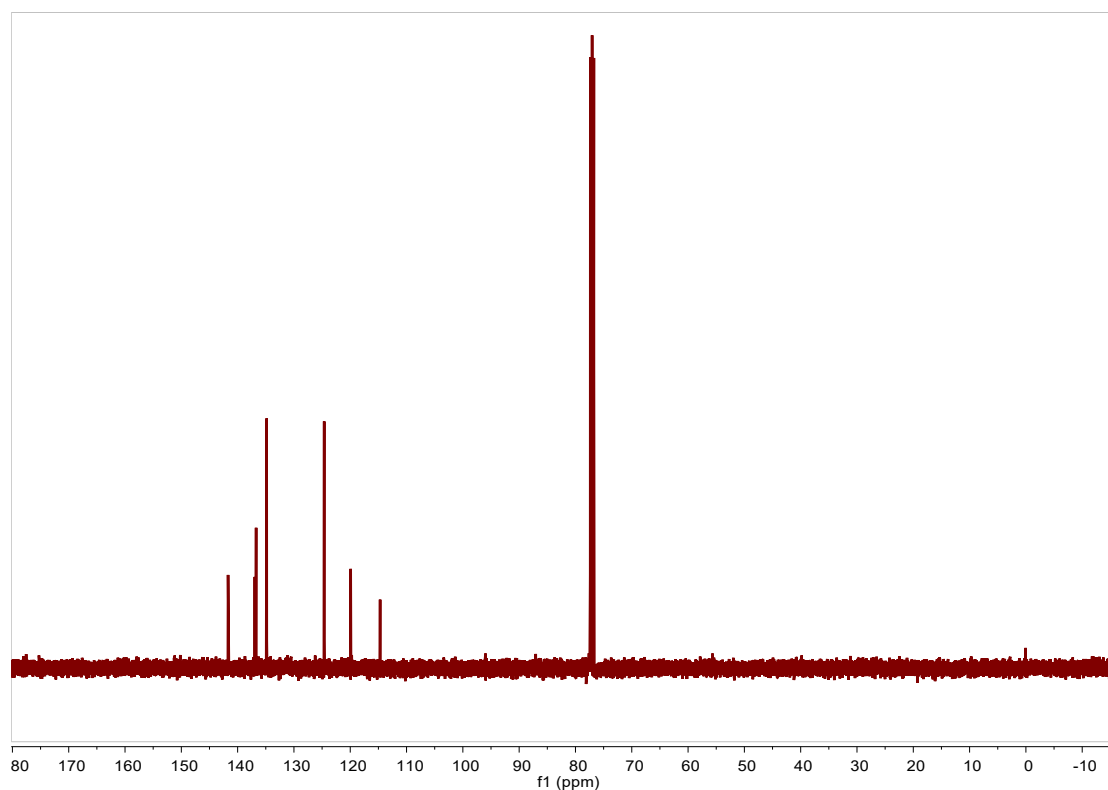


Figure S5 ^{13}C NMR of the vinyl-functionalized porphyrin monomer 5,10,15,20-tetrakis(4-vinylphenyl)-21H,23H-porphyrin (VPP).

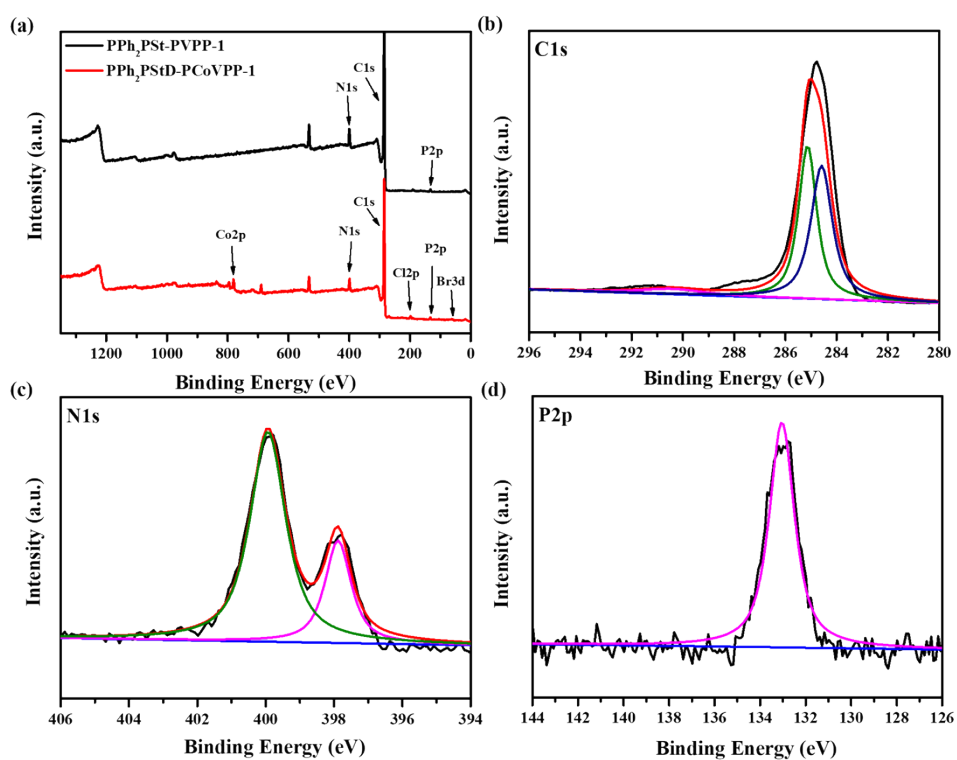


Figure S6 (a) XPS full spectra of $\text{PPh}_2\text{PSt-PVPP-1}$ and $\text{PPh}_2\text{PStD-PCoVPP-1}$; (b) C1s

spectrum, (c) N1s spectrum, (d) P2p spectrum of PPh₂PS_t-PVPP-1.

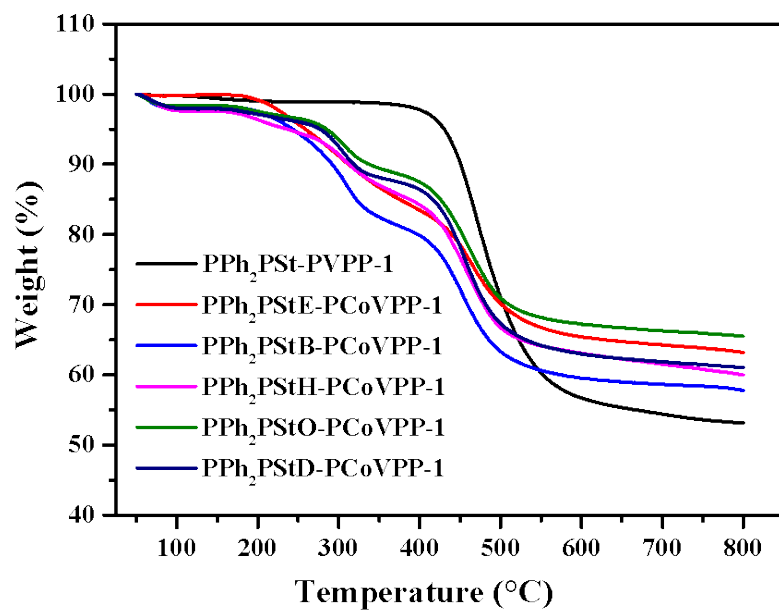


Figure S7 TG curves of PPh₂PS_t-PVPP-1 and PPh₂PS_tR-PCoVPP-1.

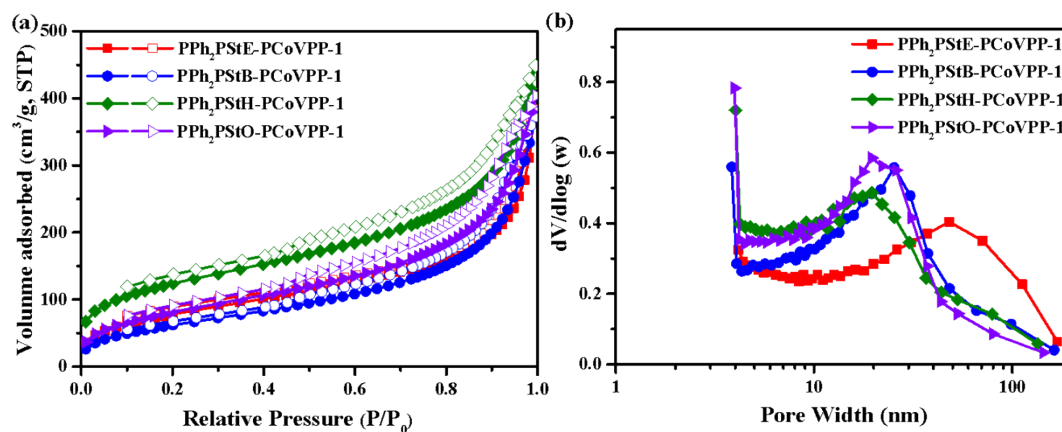


Figure S8 N₂ sorption isotherms (a) and pore size distribution (b) of PPh₂PS_tE-PCoVPP-1, PPh₂PS_tB-PCoVPP-1, PPh₂PS_tH-PCoVPP-1 and PPh₂PS_tO-PCoVPP-1.

Table S1 Textural parameters of heterogeneous catalysts.

Entry	Catalysts	BET surface area (m ² /g)	Average pore width (nm)	Pore volume (cm ³ /g)
1	PPh ₂ PSt-PVPP-1	654.64	6.00	0.95
2	PPh ₂ PStE-PCoVPP-1	291.88	8.15	0.59
3	PPh ₂ PStB-PCoVPP-1	233.96	9.84	0.58
4	PPh ₂ PStH-PCoVPP-1	450.09	6.17	0.69
5	PPh ₂ PStO-PCoVPP-1	305.24	8.19	0.63
6	PPh ₂ PStD-PCoVPP-1	380.57	6.96	0.64

Table S2 The relative content of each element of catalysts.

Catalysts	Element (%)					
	C	N	P	Co	Cl	Br
PPh ₂ PSt-PVPP-1	92.37	6.75	0.88	-	-	-
PPh ₂ PStD-PCoVPP-1	90.1	6.22	1.31	1.16	1.04	0.17

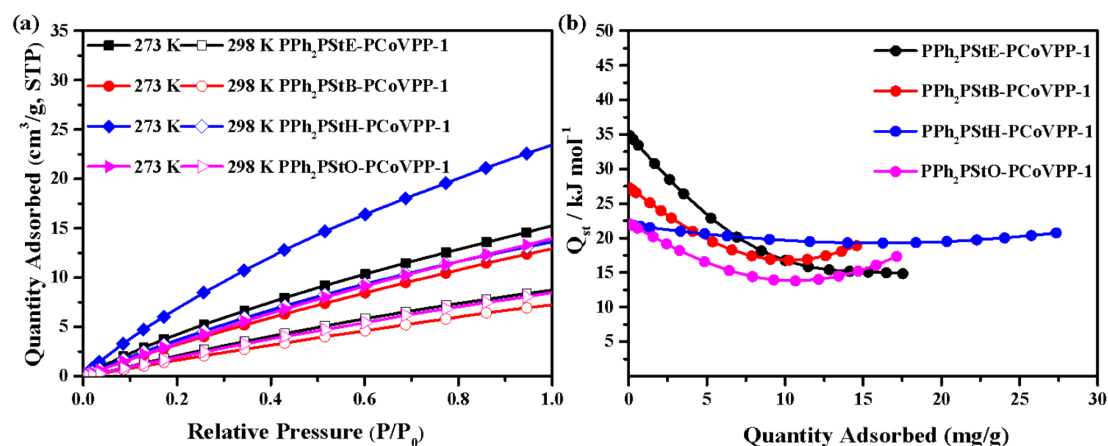


Figure S9 (a) Gas sorption isotherm curves of different polymeric catalysts at 273 K (solid icons) and 298 K (hollow icons); (b) Isothermic heat (Q_{st}) of CO₂ adsorption of PPh₂PStE-PCoVPP-1, PPh₂PStB-PCoVPP-1, PPh₂PStH-PCoVPP-1 and PPh₂PStO-PCoVPP-1.

Table S3 Catalytic Performance of Catalysts in the Synthesis of Cyclic Carbonate with epoxides and CO₂.

Entry	Catalysts	Conversion (%)	TON	TOF (h ⁻¹)	Ref
1 ^a	PPh ₂ PStD-PCoVPP-1	98.9	594.15	12.38	This work
2 ^b	SILP-5	89	19.1	2.7	Ref [4]
3 ^c	CILs-POF _{0.3}	83.6	279	11.6	Ref [5]
4 ^d	MFM-KUST	99.9	83.3	11.6	Ref [6]
5 ^e	Phenc ⁺ -PHP-2	83	18.44	0.26	Ref [7]
6 ^f	ZnTCPPc(Br ⁻)Etim- UiO-66 (0.95)	91.1	95	6.8	Ref [8]
7 ^g	[APmim][LAc]	94	188	13	Ref [9]

TON (turnover number) = [moles of initial substrate × conversion]/ [moles of active sites]. TOF (turnover frequency) = [mmol (product)]/ [mmol (active sites) × (reaction time)]

^a Reaction conditions: ECH (20 mmol), catalyst (n_{CO₃⁺})=0.0424 mmol, 0.1 MPa of CO₂, 80 °C, 48 h. ^b Performed with a flow rate of 2 mL/min (1.98 mL/min scCO₂ and 0.02 mL/min propylene oxide/n-hexane 1:1; column: 4.5 mm ID × 150 mm). Column length 4.5 mm ID × 250 mm. ^c Reaction conditions: ECH (10 mmol), catalysts (30 μmol ionic sites), CO₂ pressure 10 bar, 90 °C, and 24 h. ^d Reaction conditions: catalyst (61.3 mg), epichlorohydrin (50 mmol), temperature (110 °C), CO₂ pressure (1.0 MPa), time (6.0 h), magnetic stirring rate (280 rpm). ^e Reaction conditions: epichlorohydrin (2 mmol), CO₂ pressure (0.1 MPa), the catalyst (40 mg), temperature (T = 60 °C), time (t = 72 h). ^f Reaction conditions: solvent free, Phenyl Glycidyl Ether (5 mmol), catalyst (0.95 mol % based on imidazolium), CO₂ (constant 1 bar), 140 °C, 14 h. ^g Reaction conditions: epichlorohydrin 5.0 mL, catalyst 0.5 mol%, 0.3 MPa, 80 °C, 14 h.

Table S4. Cycloaddition of epichlorohydrin with carbon dioxide catalyzed by PPh₂PStD-PCoVPP-1 catalyst used for different run times ^a

Entry	Catalysts	Co Loading (mmol/g) ^b	Conv. (%) ^c	Sele. (%) ^c
1	PPh ₂ PStD-PCoVPP-1 (Run 1)	0.581	93.05	>99
2	PPh ₂ PStD-PCoVPP-1 (Run 2)	0.535	87.81	>99
3	PPh ₂ PStD-PCoVPP-1 (Run 3)	0.517	85.61	>99
4	PPh ₂ PStD-PCoVPP-1 (Run 4)	0.506	85.07	>99

^a Reaction conditions: epichlorohydrin (20 mmol), catalyst (57.3 mg), 48 h, 80 °C, 1 atm CO₂; ^b Co (mmol)/catalyst (g), determined by ICP; ^c Determined by ¹H NMR.

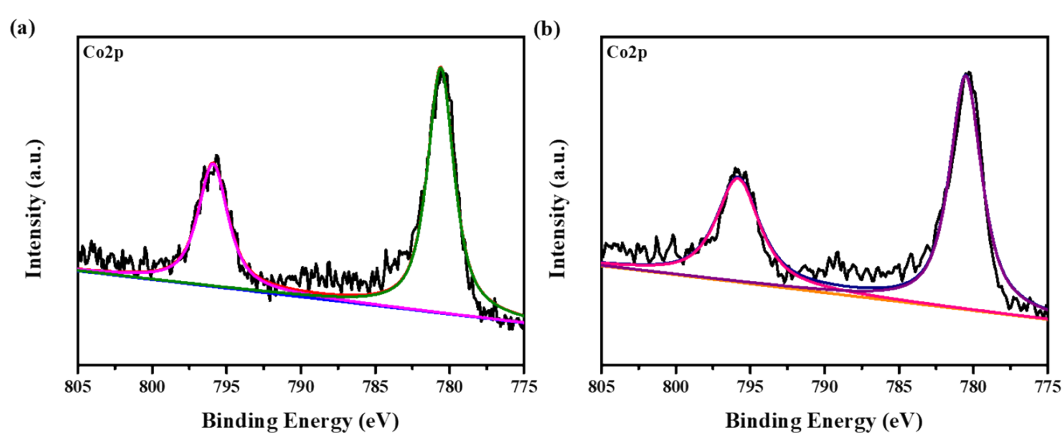


Figure S10 Co2p XPS spectra of fresh(a) and recovered(b) PPh₂PStD-PCoVPP-1.



Figure S11 The picture of fresh and recovered PPh₂PStD-PCoVPP-1.

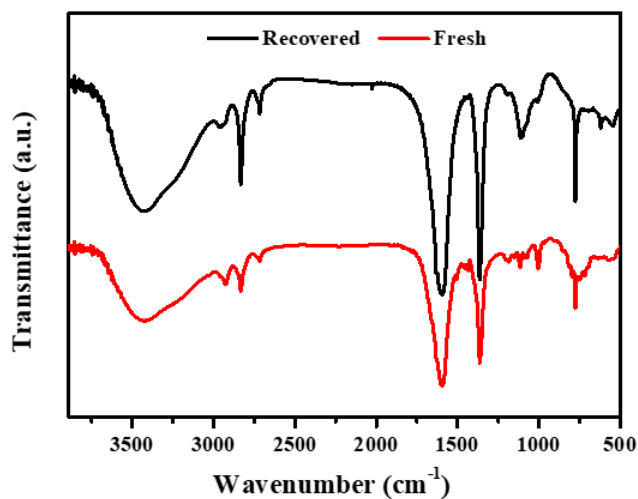


Figure S12 FT-IR spectra of fresh and recovered PPh₂PStD-PCoVPP-1.

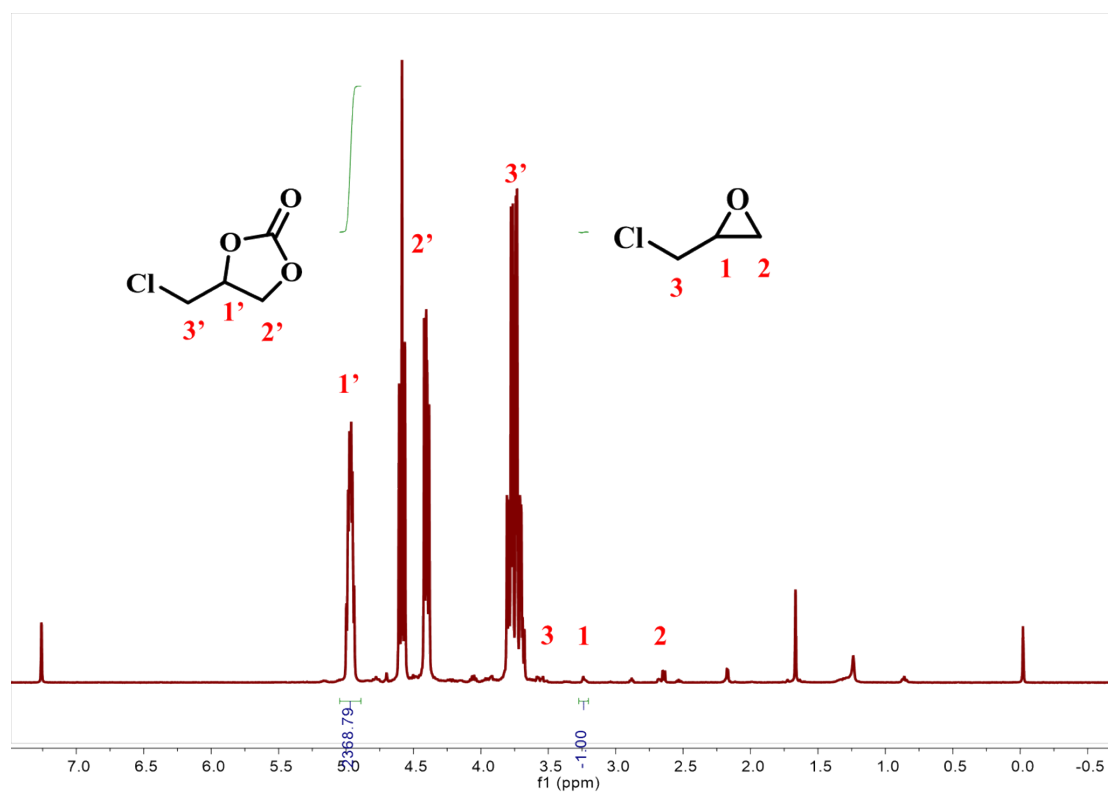


Figure S13 ¹H liquid NMR of the crude products in the cycloaddition reaction catalyzed by the PPh₂PStD-PCoVPP-1 catalyst with epichlorohydrin (ECH) as a substrate.

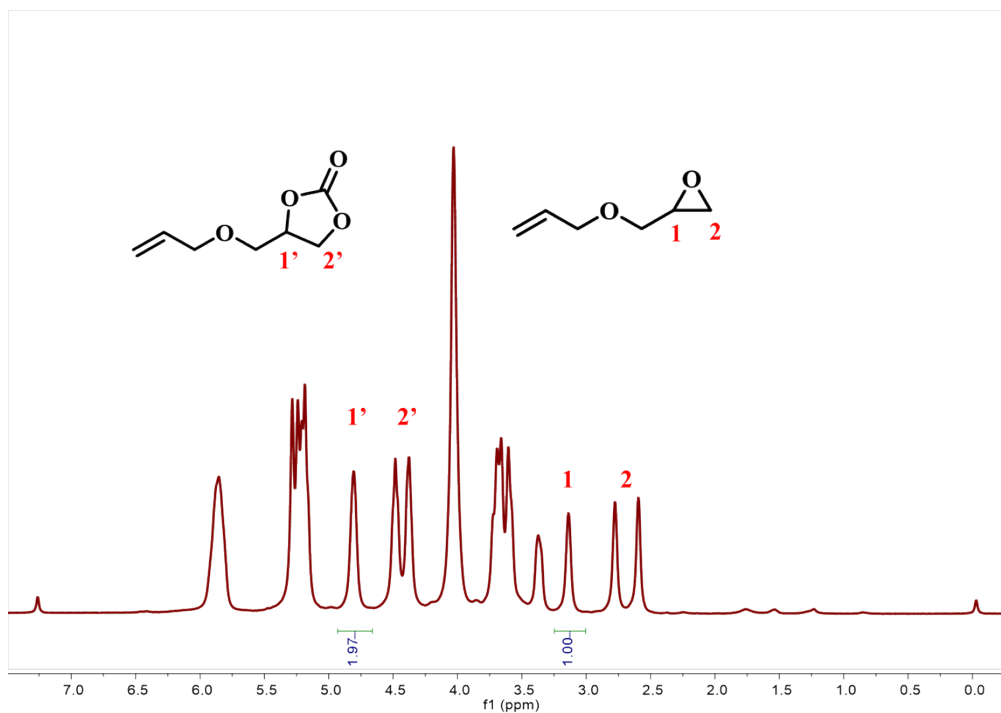


Figure S14 ¹H liquid NMR of the crude products in the cycloaddition reaction catalyzed by the PPh₂PStD-PCoVPP-1 catalyst with allyl glycidyl ether as a substrate.

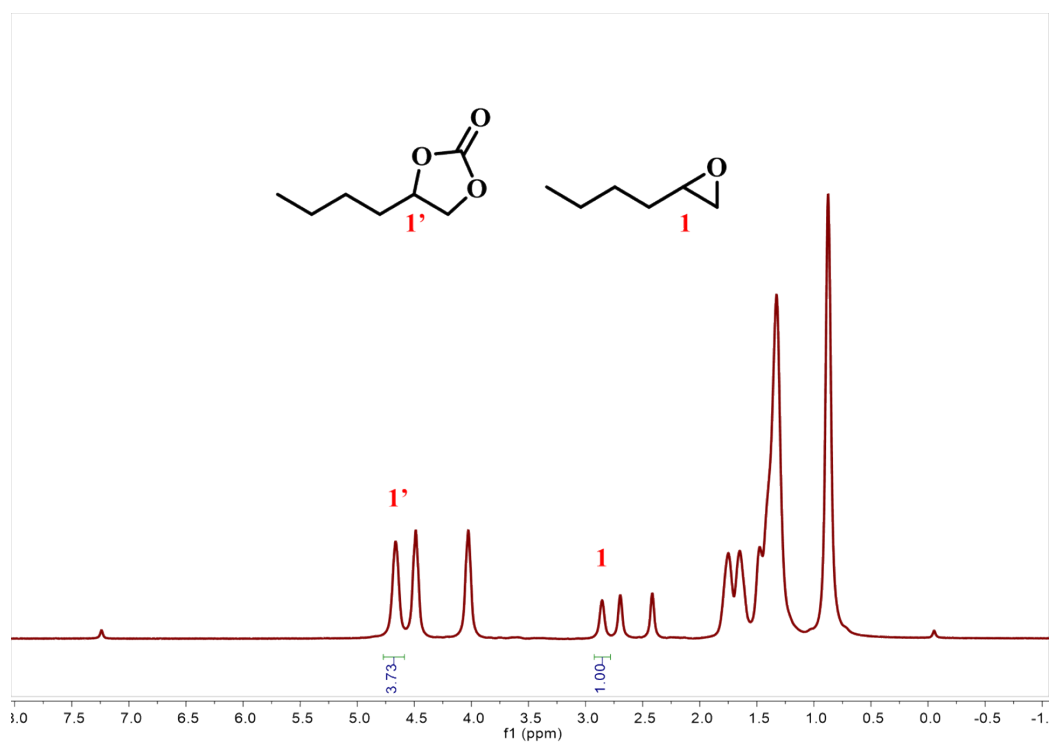


Figure S15 ¹H liquid NMR of the crude products in the cycloaddition reaction catalyzed by the PPh₂PStD-PCoVPP-1 catalyst with 1,2-hexylene oxide as a substrate.

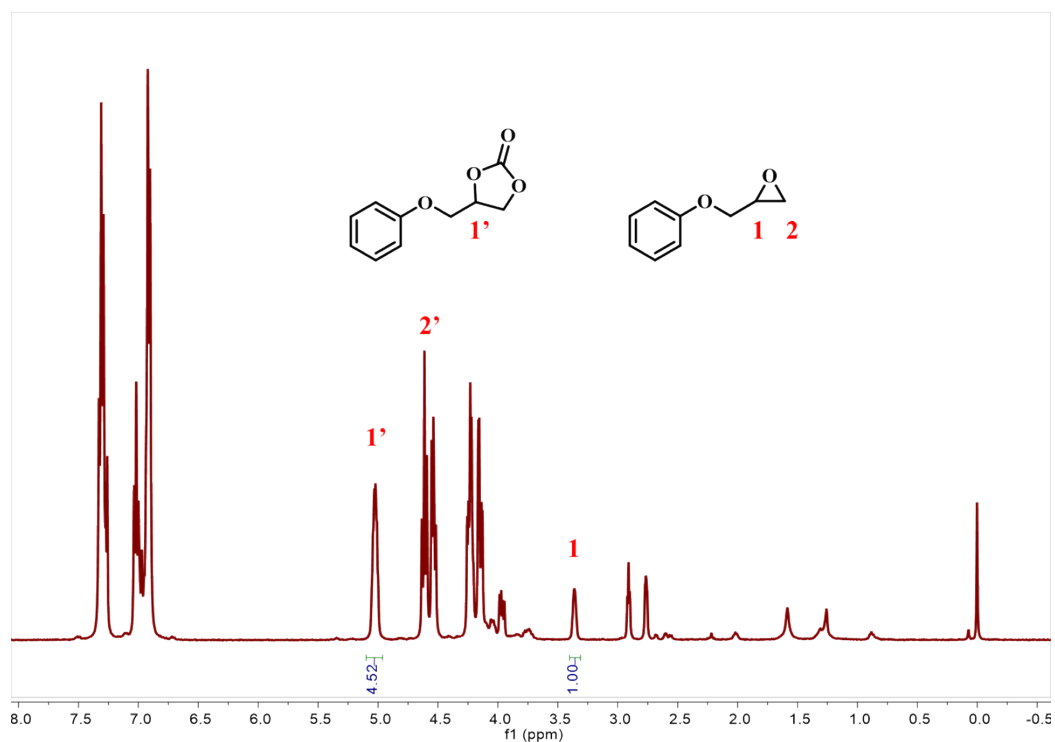


Figure S16 ¹H liquid NMR of the crude products in the cycloaddition reaction catalyzed by the PPh₂PStD-PCoVPP-1 catalyst with allyl glycidyl ether as a substrate.

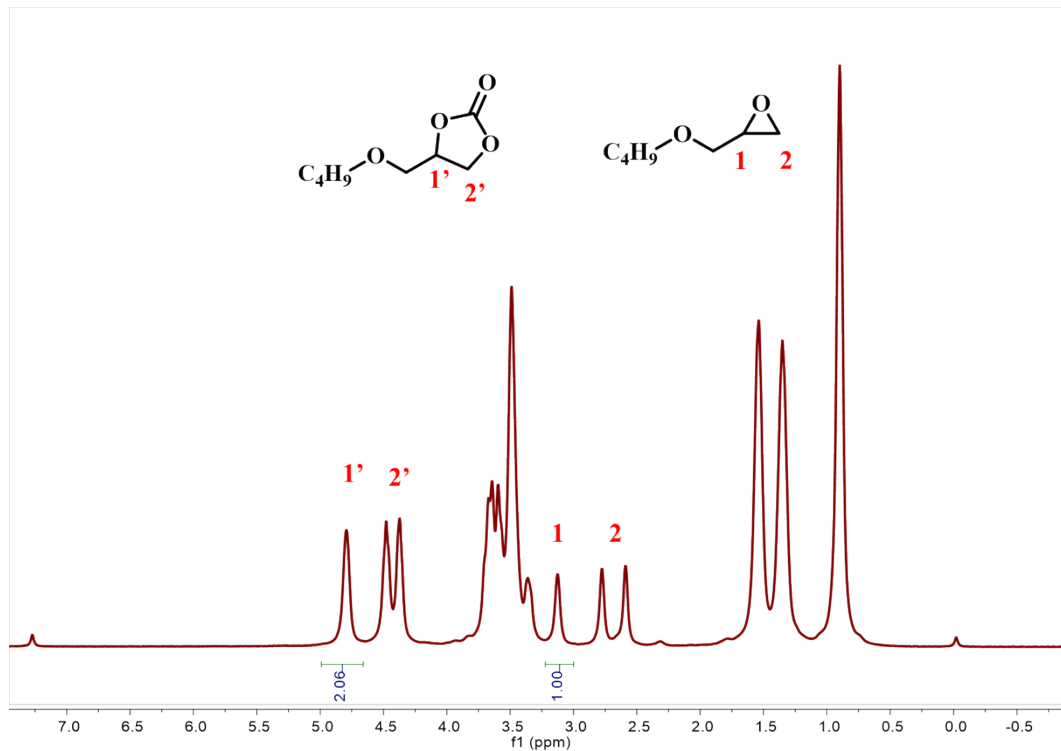


Figure S17 ¹H liquid NMR of the crude products in the cycloaddition reaction catalyzed by the PPh₂PStD-PCoVPP-1 catalyst with butyl glycidyl ether as a substrate.

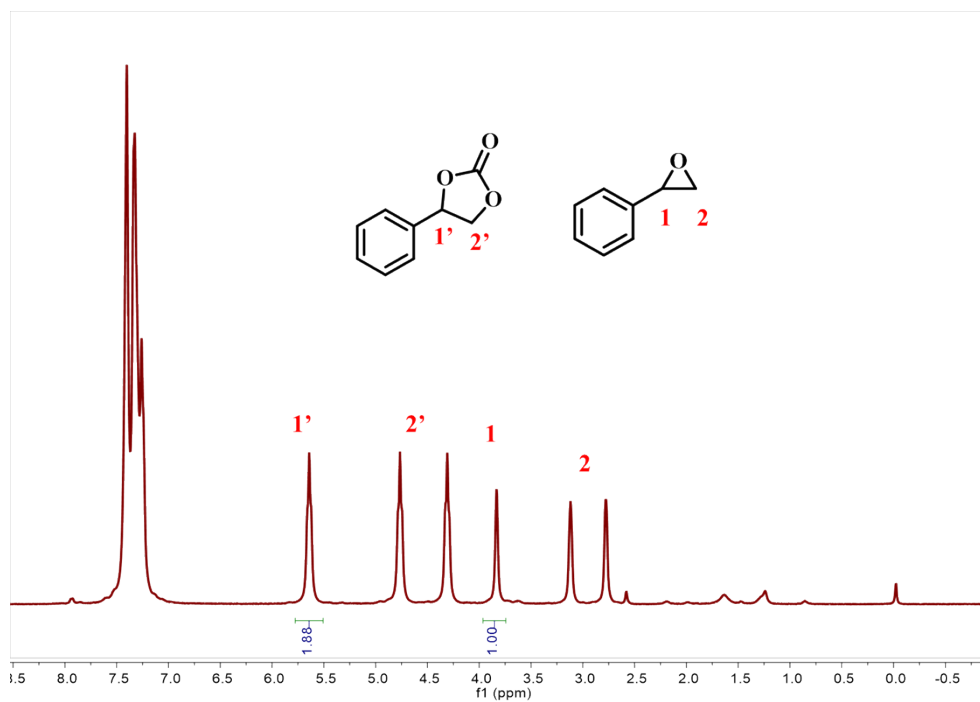


Figure S18 ^1H NMR of the crude products in the cycloaddition reaction catalyzed by the $\text{PPh}_2\text{PStD-PCoVPP-1}$ catalyst with styrene oxide as a substrate.

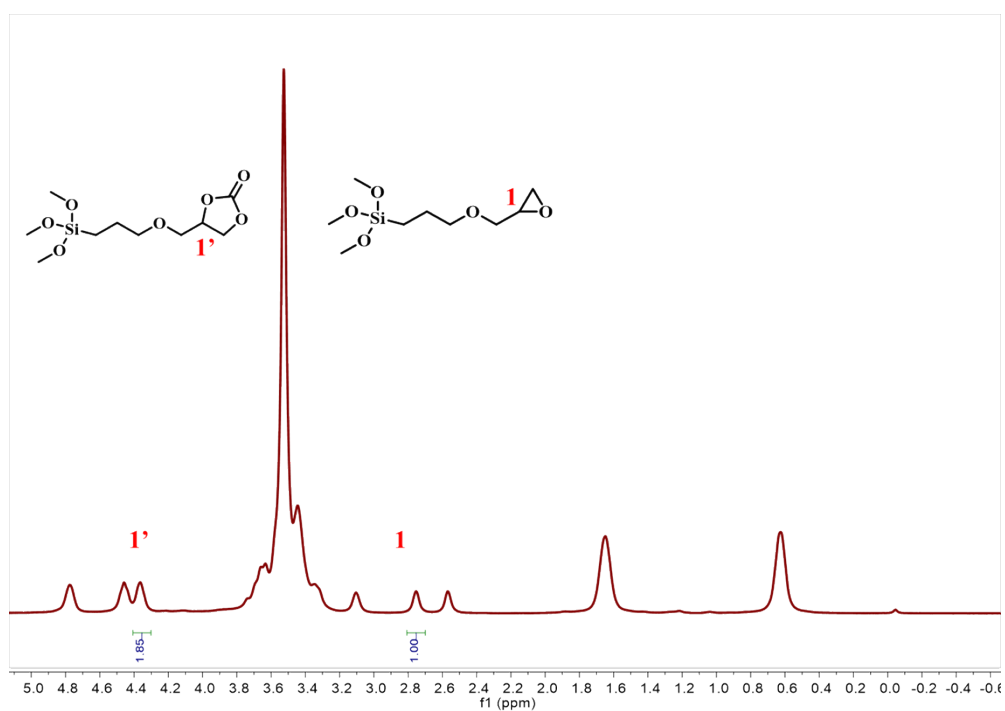


Figure S19 ^1H NMR of the crude products in the cycloaddition reaction catalyzed by the $\text{PPh}_2\text{PStD-PCoVPP-1}$ catalyst with 3-glycidoxypropyltrimethoxysilane as a substrate.

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