

Electronic Supplementary Information

Location matters: cooperativity of catalytic partners in porous organic polymers for enhanced CO₂ transformation

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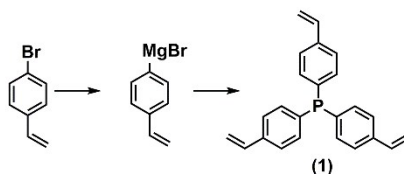
Experimental Details

Chemicals

4-Bromostyrene was purified by distillation over CaH_2 under reduced pressure. Other commercially available reagents were purchased in high purity and used without further purification. Solvents were purified according to standard laboratory methods.

Material synthesis

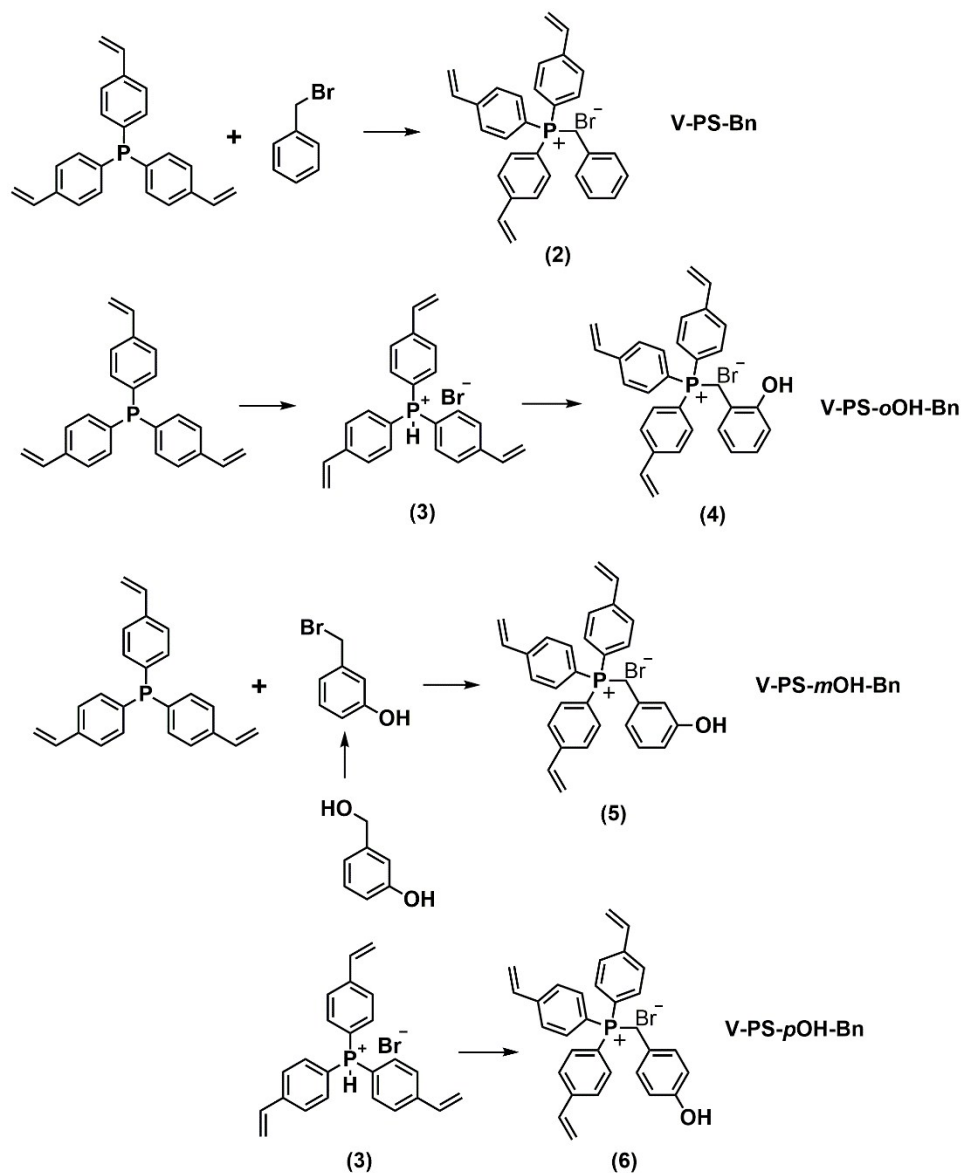
Synthesis of tris-(4-vinylphenyl)-phosphine (1)



The title compound was synthesized according to our previously established procedures.^[1] ^1H NMR (400 MHz, CDCl_3 , 298 K, TMS): δ 7.37 (d, 6H), 7.22-7.31 (m, 6H), 6.64-6.75 (m, 3H), 5.75 (d, 3H), 5.27 (d, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 114.7, 126.28, 126.35, 133.78, 133.97, 136.35, 136.53, 136.63, 138.00 ppm. ^{31}P NMR (162 MHz): δ -6.72 ppm.

Synthesis of vinyl-functionalized phosphonium salts (V-PS)

Synthesis of benzyltris(4-vinylphenyl)phosphonium bromide (V-PS-Bn, 2). Benzyl bromide (0.75 g) was introduced into a solution of tris-(4-vinylphenyl)-phosphine (1.5 g) and acetone (25 mL). The mixture was heated to 60 °C for 3 d under N_2 atmosphere, then cooled to room temperature. A solid product was precipitated out in ether and was then filtered and dissolved in ethanol, whereby the insoluble materials were removed by filtration over Celite. This process was repeated twice and the final product as a white solid was obtained by evaporation under vacuum. Yield: 1.15 g (51%). ^1H NMR (400 MHz, d^6 -DMSO, 298 K, TMS): δ 7.83-7.86 (m, 6H), 7.63-7.68 (m, 6H), 7.24-7.32 (m, 3H), 7.04 (d, 2H), 6.86-6.93 (m, 3H), 6.16 (d, 3H), 5.57 (d, 3H), 5.22 (d, 2H) ppm. ^{13}C NMR (100 MHz, d^6 -DMSO): δ 28.41, 28.90, 116.62, 117.48, 120.07, 127.88, 128.01, 128.50, 128.58, 128.81, 128.85, 129.31, 129.34, 131.32, 131.39, 134.86, 134.96, 135.57, 135.58, 143.75, 143.78 ppm. ^{31}P NMR (162 MHz): δ 22.30 ppm.



Synthesis of (2-hydroxybenzyl)tris(4-vinylphenyl)phosphonium bromide (V-PS-oOH-Bn, 4). To target the title material, an intermediate compound tris(4-vinylphenyl)phosphonium bromide was first synthesized as follows. Tris(4-vinylphenyl)-phosphine (1 g) was slowly added into 48% HBr aqueous solution (6 mL). The resulting mixture was stirred at room temperature for 30 min and then heated at 75 °C for a further 7 min. The residue was extracted with CHCl₃, dried over Na₂SO₄, and evaporated under reduced pressure to give the crude compound which was purified by washing with ethyl acetate to afford **3** as a yellow solid (0.5 g). ¹H NMR (400 MHz, d⁶-DMSO, 298 K, TMS): δ 8.34 (s, 1H), 7.57-7.66 (m, 12H), 6.77-6.84 (m, 3H), 5.98 (d, 3H), 5.42 (d, 3H) ppm. ³¹P NMR (162 MHz): δ 25.04 ppm. The yielded **3** and 2-hydroxybenzyl alcohol (0.2 g) was dissolved in anhydrous acetonitrile (10 mL), and the resulting mixture was refluxed under N₂ atmosphere for 2 h. After cooling to room temperature, the solution was filtered over Celite. A solid product was precipitated out in ether and was then filtered

and dissolved in dichloromethane. This process was repeated twice and the final product as a white solid was obtained by evaporation under vacuum. Yield: 0.2 g (32%). ^1H NMR (400 MHz, $\text{d}^6\text{-DMSO}$, 298 K, TMS): δ 9.78 (s, 1H), 7.80-7.83 (m, 6H), 7.60-7.65 (m, 6H), 7.11-7.15 (m, 1H), 6.85-6.93 (m, 4H), 6.75 (d, 2H), 6.66 (t, 1H), 6.14 (d, 3H), 5.56 (d, 3H), 4.90 (d, 2H) ppm. ^{13}C NMR (100 MHz, $\text{d}^6\text{-DMSO}$): δ 23.65, 24.13, 114.20, 114.28, 115.91, 117.18, 118.05, 119.59, 119.62, 119.65, 119.91, 127.75, 127.87, 130.32, 132.10, 132.14, 134.73, 134.83, 135.62, 143.57, 143.60, 156.51, 156.57 ppm. ^{31}P NMR (162 MHz): δ 20.84 ppm.

Synthesis of (3-hydroxybenzyl)tris(4-vinylphenyl)phosphonium bromide (V-PS-mOH-Bn, 5). 3-(Bromomethyl)phenol (0.8 g) was introduced to a solution of tris-(4-vinylphenyl)-phosphine (1.6 g) and acetone (25 mL). The mixture was heated to 60 °C for 3 d under N_2 atmosphere, then cooled to room temperature. A solid product was precipitated out in ether and was then filtered and dissolved in ethanol, whereby the insoluble materials were removed by filtration over Celite. This process was repeated twice and the final product as a white solid was obtained by evaporation under vacuum. Yield: 1.5 g (60%). ^1H NMR (400 MHz, $\text{d}^6\text{-DMSO}$, 298 K, TMS): δ 9.57 (s, 1H), 7.83-7.86 (m, 6H), 7.61-7.66 (m, 6H), 7.04 (t, 1H), 6.86-6.93 (m, 3H), 6.72 (d, 1H), 6.42-6.48 (m, 2H), 6.16 (d, 3H), 5.57 (d, 3H), 5.08 (d, 2H) ppm. ^{13}C NMR (100 MHz, $\text{d}^6\text{-DMSO}$): δ 28.58, 29.05, 115.48, 115.82, 116.77, 117.65, 118.25, 118.30, 120.01, 121.87, 121.92, 127.86, 127.99, 129.58, 129.67, 130.23, 130.26, 134.82, 134.93, 135.6, 143.71, 143.74, 157.99, 158.03 ppm. ^{31}P NMR (162 MHz): δ 22.07 ppm. The used 3-(bromomethyl)phenol was synthesized as follows. The mixture of PBr_3 (0.42 mL) and CHCl_3 (5 mL) was slowly added into the suspension of 3-hydroxybenzyl alcohol (1.1 g) in CHCl_3 (6.5 mL) at 0 °C, after which the reaction mixture was stirred at room temperature for another hour. The reaction was quenched by pouring into ice water and the residue was extracted with CHCl_3 , washed with water, dried over Na_2SO_4 , and evaporated under reduced pressure to give the crude compound which was purified by flash chromatography with hexane/ethyl acetate (3:1) as eluent to afford the title compound as a white solid. Yield: 0.89 g (53%). ^1H NMR (500 MHz, CDCl_3 , 298 K, TMS): δ 7.20 (t, 1H), 6.96 (d, 1H), 6.87 (t, 1H), 6.76 (d, 1H), 4.98 (br, 1H), 4.43 (s, 2H) ppm.

Synthesis of (4-hydroxybenzyl)tris(4-vinylphenyl)phosphonium bromide (V-PS-pOH-Bn, 6). **3** and 4-hydroxybenzyl alcohol (0.2 g) was dissolved in anhydrous acetonitrile (10 mL), and the resulting mixture was refluxed under N_2 atmosphere for 2 h. After cooling to room temperature, a solid product was precipitated out and was then filtered and dissolved in ethanol, whereby the insoluble materials were removed by filtration over Celite. A solid product was precipitated out in ether and was then filtered and dissolved in dichloromethane. This process was repeated twice and the final product as a white solid was obtained by evaporation under vacuum. Yield: 0.24 g (38%). ^1H NMR (400 MHz, $\text{d}^6\text{-DMSO}$, 298 K, TMS): δ 9.97 (s, 1H), 7.83-7.85 (m, 6H), 7.61-7.66 (m, 6H), 6.80-6.93 (m, 5H), 6.69 (d, 2H), 6.15 (d, 3H), 5.56 (d, 3H), 5.07 (d, 2H) ppm. ^{13}C NMR (100 MHz, $\text{d}^6\text{-DMSO}$): δ 28.04, 28.50, 116.16, 116.19, 116.90, 117.45, 117.53, 117.77, 119.96, 127.82, 127.96, 132.39, 132.44, 134.88, 134.98, 135.60, 143.64, 143.67, 158.13, 158.17 ppm. ^{31}P NMR (162 MHz): δ 21.3 ppm.

Synthesis of polymeric phosphonium salts (PPS)

PPS-Bn. As a typical procedure, 1 g of V-PS-Bn was dissolved in 10 mL of DMF, followed by the addition of 25 mg of AIBN. The mixture was transferred into an autoclave at 100 °C for 24 h. The title polymer was obtained after being washed with ethanol and evaporated under vacuum.

PPS-oOH-Bn. PPS-oOH-Bn was obtained following a similar procedure as that of PPS-Bn except that 1 g of V-PS-oOH-Bn was used instead of V-PS-Bn.

PPS-mOH-Bn. PPS-mOH-Bn was obtained following a similar procedure as that of PPS-Bn except that 1 g of V-PS-mOH-Bn was used instead of V-PS-Bn.

PPS-pOH-Bn. PPS-pOH-Bn was obtained following a similar procedure as that of PPS-Bn except that 1 g of V-PS-pOH-Bn was used instead of V-PS-Bn.

Catalytic Tests

The reactions were performed in a 25 mL Schlenk tube with a magnetic stirrer. As a typical run, epoxide (10 mmol) and catalyst (0.05 mmol based on the amount of phosphonium salt moieties) were added. After sealing and purging with CO₂ using a balloon, the tube was placed in a preheated oil bath and stirred for a desired time. After the reaction, the catalyst was taken out from the system by centrifugation and the product was analyzed by ¹H-NMR.

The TOF value was defined as follows:

TOF = moles of product yield at a certain time (T) / (moles of catalyst used x T)

For recycling, the catalyst was separated from the reaction system by centrifugation and washing with excessive of ethanol and dried under vacuum for the next run.

Computational Methods

Quantum chemical calculations were performed with the Gaussian 09 C.01 software.^[2] We adopted the density functional theory (DFT) approach for our calculations using the classical B3LYP hybrid density functional^[3,4] with the 6-31G(d)^[5,6] basis set for all the light atoms. Frequency calculations were performed at the B3LYP/6-31G(d) level to ensure that all the geometries in the gas phase (optimized at the same B3LYP/6-31G(d) level) were minima. Frequency calculations were performed at the B3LYP/6-31G(d) level to ensure that all the reactants, intermediates and products in the gas phase were minima. The transition state search function was used to explore accurate transition state with a single imaginary frequency. Then the intrinsic reaction coordinate (IRC) theory was used to verify that the given transition states were well connected to the desired adjacent minima.

Characterization

Nitrogen sorption isotherms were measured at 77 K using Micromeritics ASAP 2020M and Tristar system after treating the samples under vacuum at 100 °C for 10 h. Thermogravimetric analysis (TG) was performed with a SDT Q600 V8.2 Build 100 instrument under N₂ atmosphere with a heating rate of 10 °C min⁻¹. Powder X-ray diffraction (PXRD) patterns were collected with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using Cu K α ($\lambda=1.5406$ Å) radiation. Scanning electron microscopy (SEM) images were collected using a Hitachi SU 8010. Transmission electron microscopy (TEM) images were collected using a Hitachi HT-7700. The solution NMR spectra were recorded with a Bruker Avance-400 spectrometer and Bruker Avance-500 spectrometer. Chemical shifts are expressed in ppm downfield from TMS at $\delta=0$ ppm. ¹³C cross-polarization magic-angle spinning (CP-MAS), and ³¹P MAS solid-state NMR experiments were recorded on a Varian infinity plus 600 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO₂ rotor, whereby (NH₄)₂HPO₄ was chosen as reference with ³¹P chemical shift at 1.0 ppm.

Table S1 PPS-*m*OH-Bn-catalyzed cycloaddition reactions of epoxides with atmospheric CO₂ to cyclic carbonates.^[a]

Entry	Epoxides	Products	T (°C)	Yields (%) ^[b]
1			50	98
2			80	92
3 ^[c]			80	90
4			50	78
5 ^[d]			80	90
6			100	88

[a] Reaction conditions: epoxides (10 mmol), CO₂ (1 atm), PPS-*m*OH-Bn (0.5 mol%), and 3 d. [b] Yields were determined by ¹H NMR. [c] 6 d. [d] 10 d.

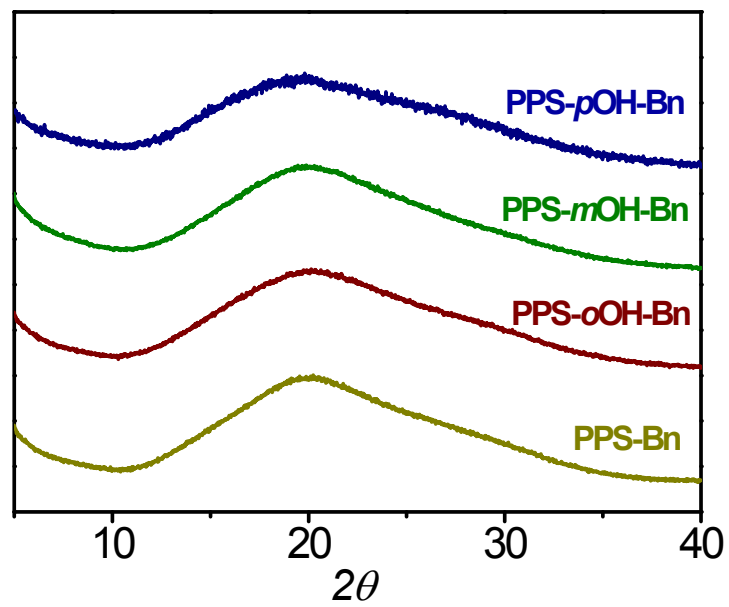
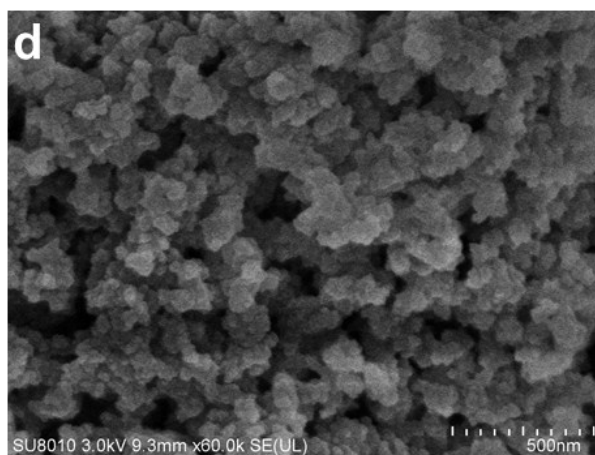
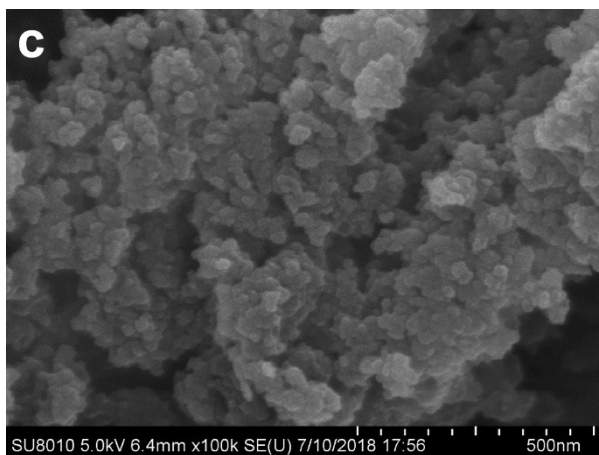
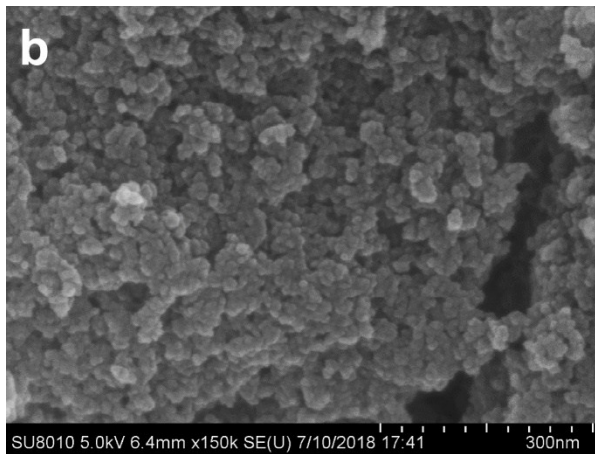
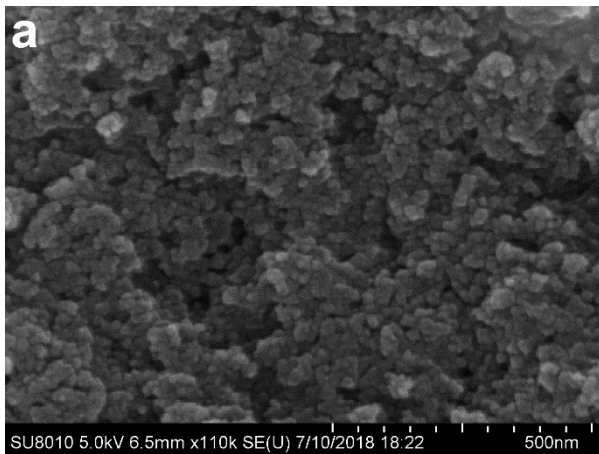


Fig. S1 PXR D patterns of PPS-Bn, PPS-*o*OH-Bn, PPS-*m*OH-Bn, and PPS-*p*OH-Bn.



respectively.

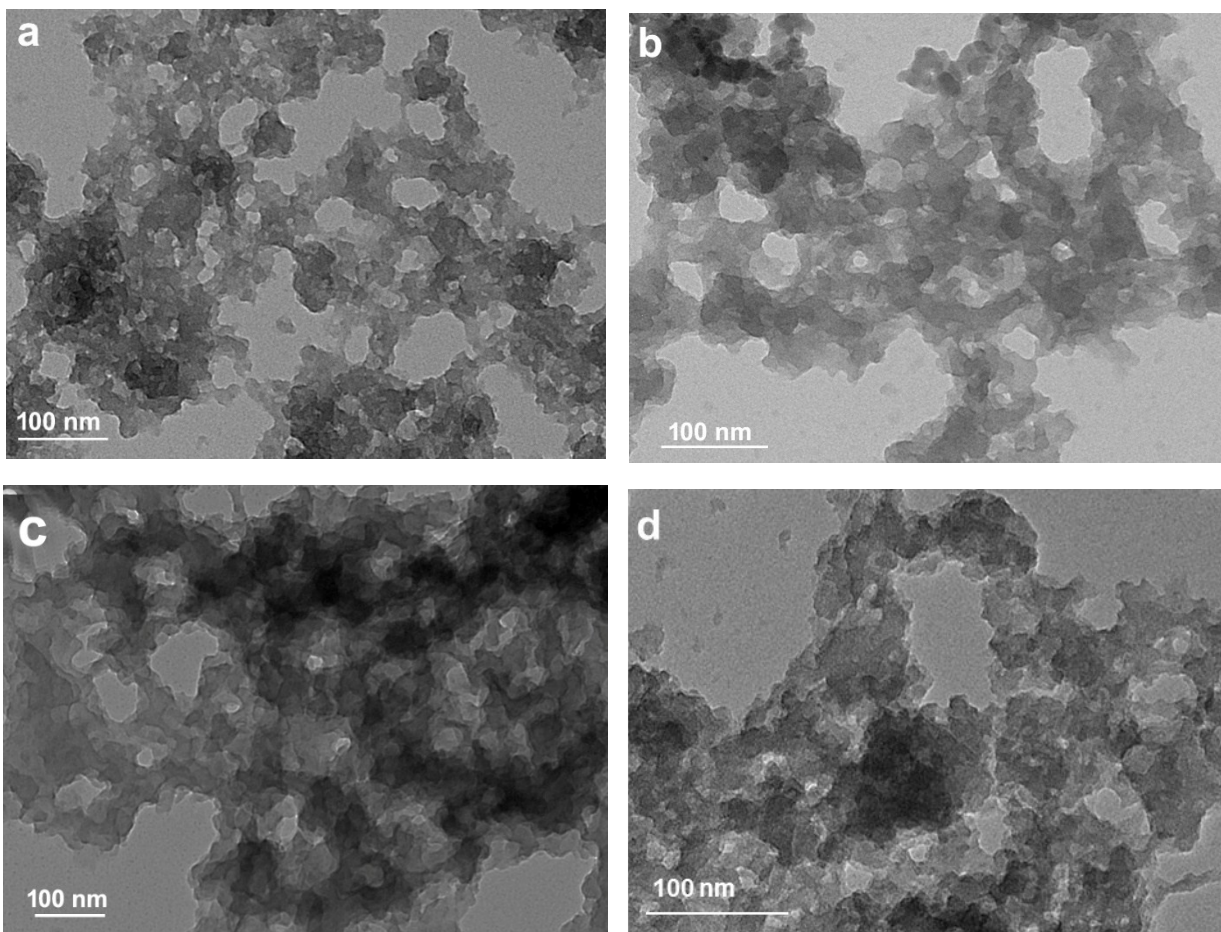


Fig. S3 TEM images of (a) PPS-Bn, (b) PPS-*o*OH-Bn, (c) PPS-*m*OH-Bn, and (d) PPS-*p*OH-Bn, respectively.

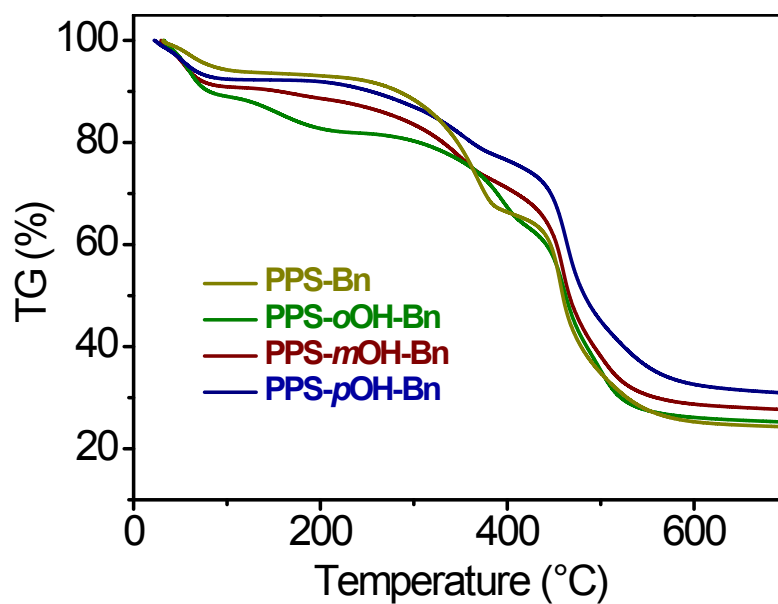


Fig. S4 TGA curves of PPS-Bn, PPS-oOH-Bn, PPS-mOH-Bn, and PPS-pOH-Bn, respectively.

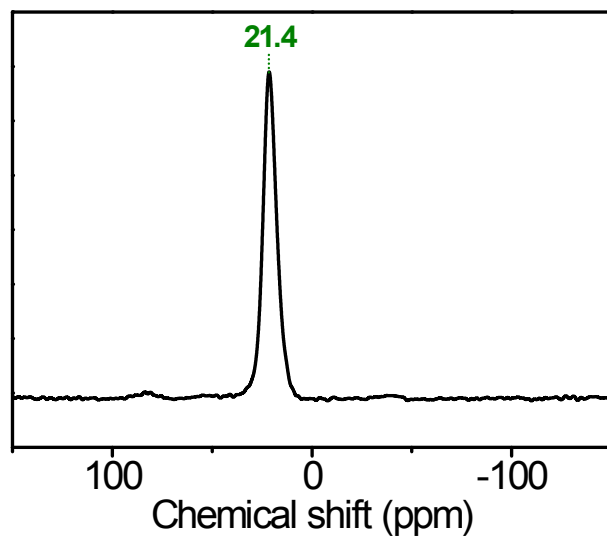
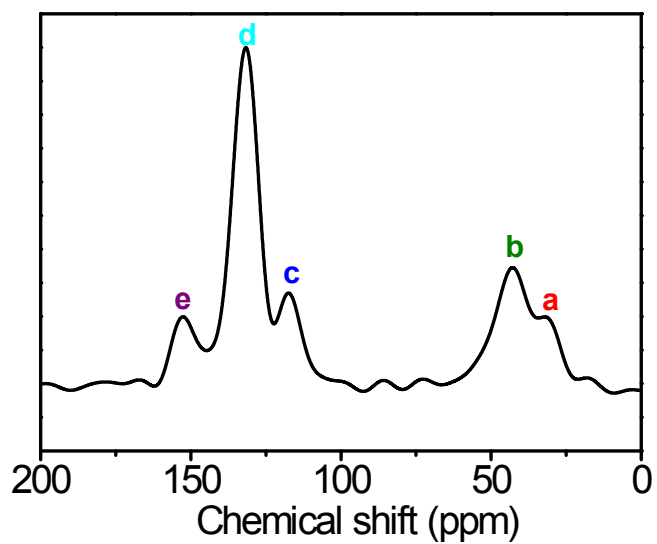
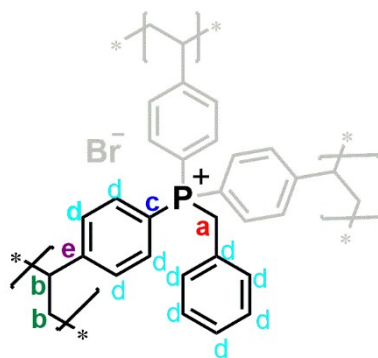


Fig. S5 Solid-state ^{13}C and ^{31}P NMR spectra of PPS-Bn.

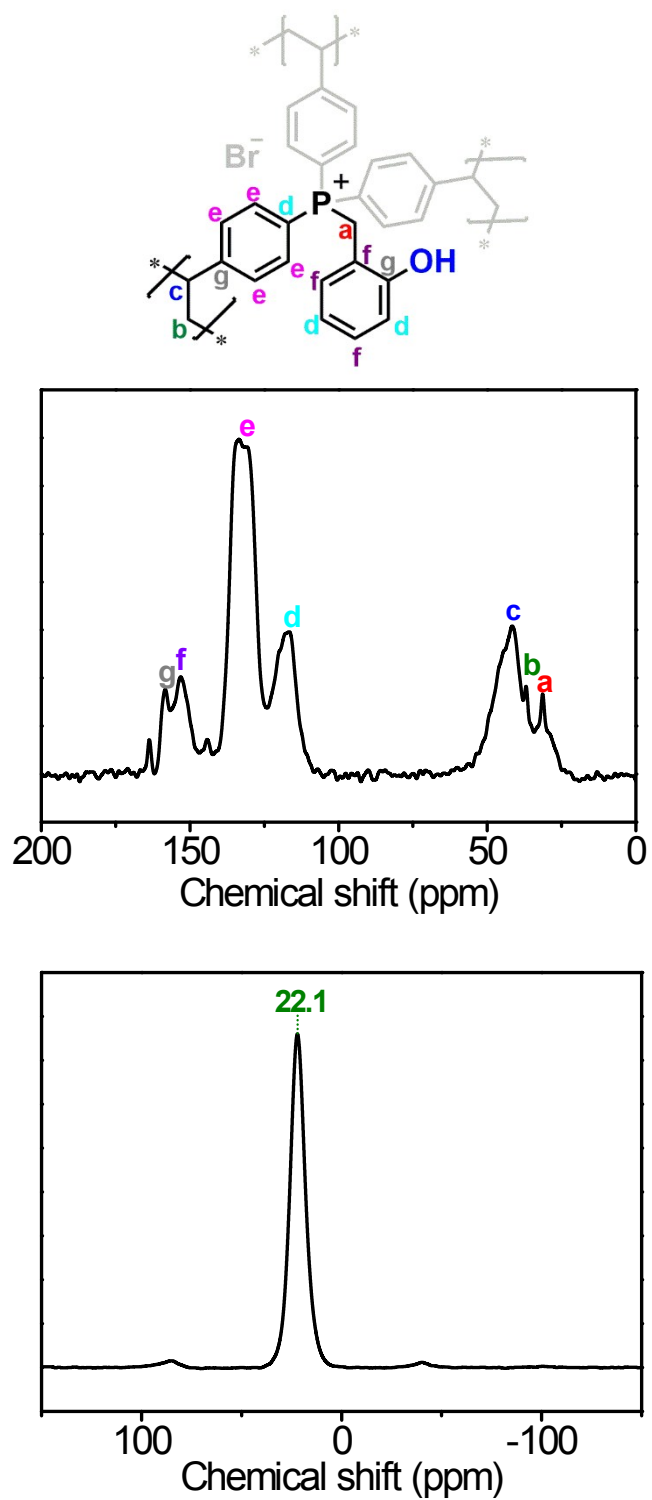


Fig. S6 Solid-state ^{13}C and ^{31}P NMR spectra of PPS-oOH-Bn.

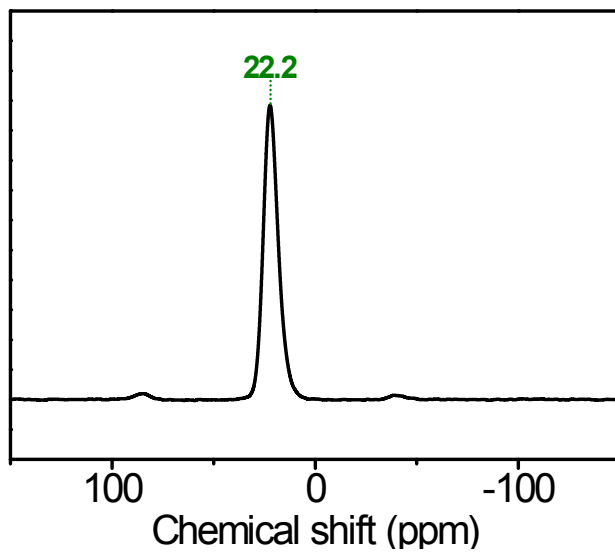
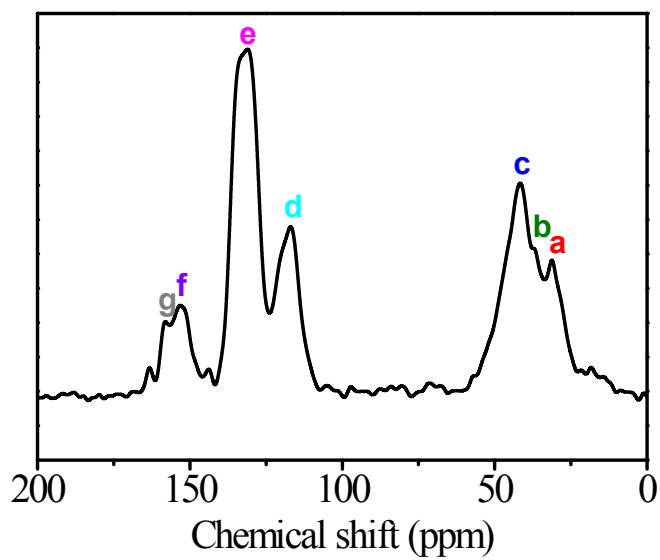
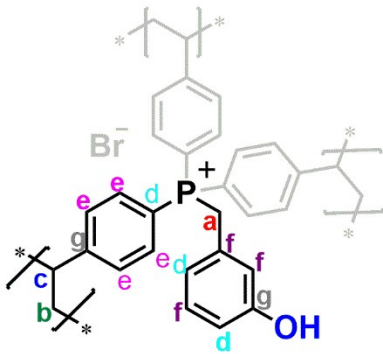


Fig. S7 Solid-state ^{13}C and ^{31}P NMR spectra of PPS-*m*OH-Bn.

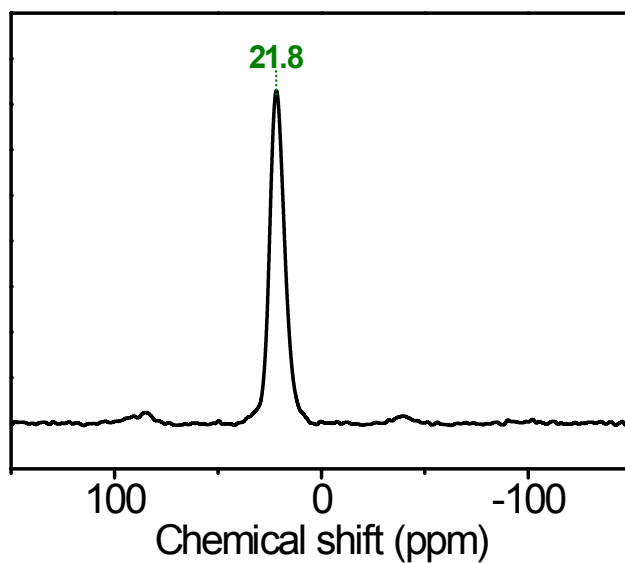
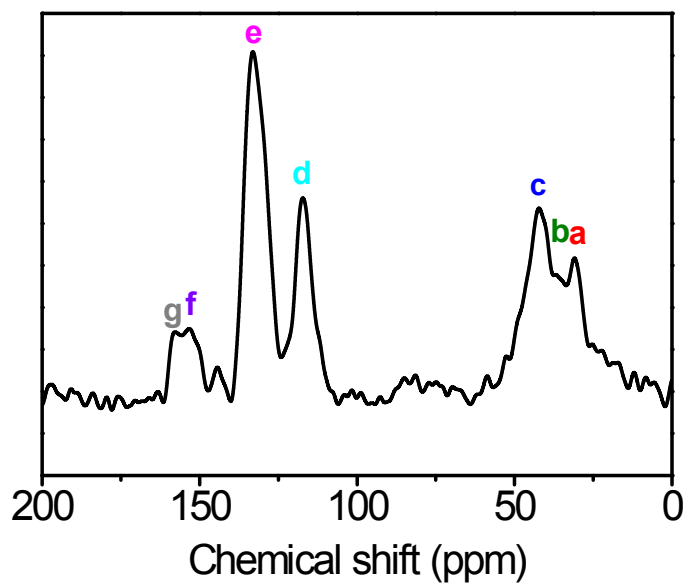
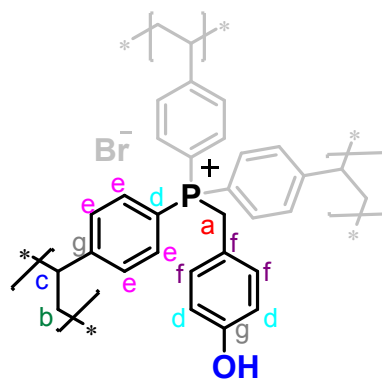


Fig. S8 Solid-state ^{13}C and ^{31}P NMR spectra of PPS-*p*OH-Bn.

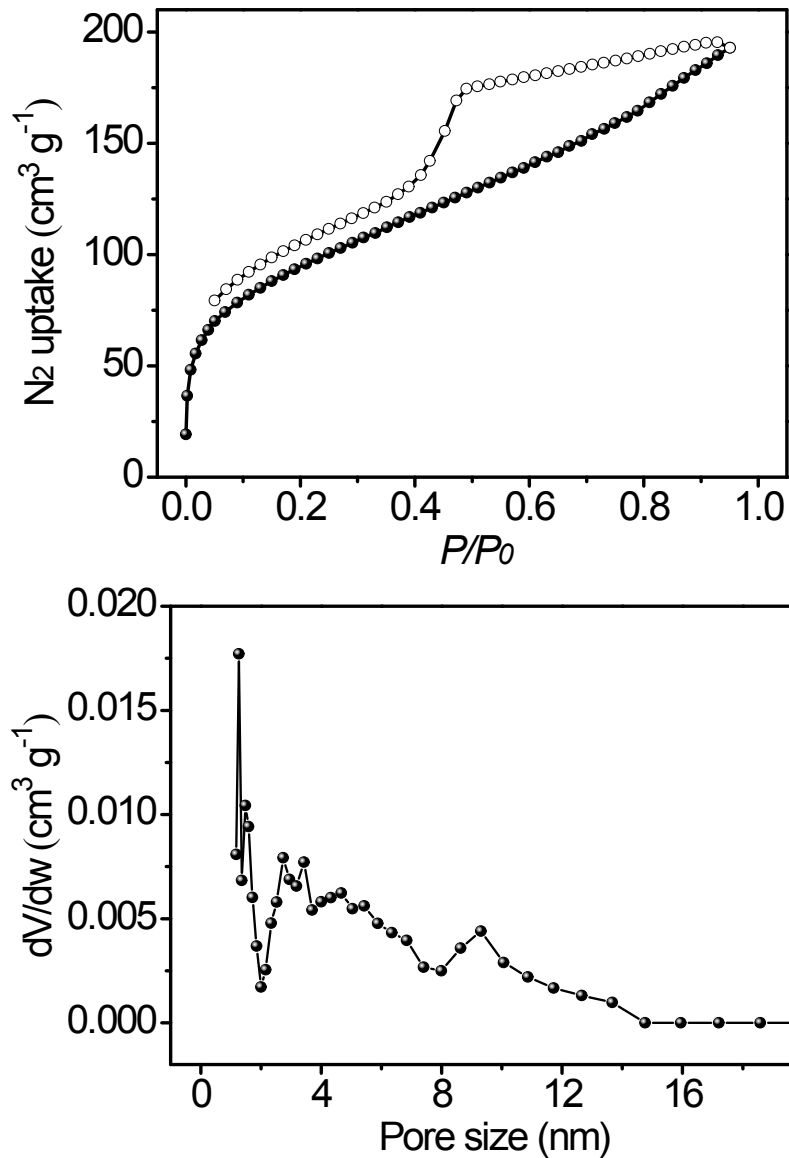


Fig. S9 N₂ sorption isotherms and corresponding DFT pore size distribution of PPS-Bn. The BET surface area and pore volume were calculated to be 314 m² g⁻¹ and 0.3 cm³ g⁻¹. It is noteworthy that PPS-Bn exhibits a sorption behavior of type I plus type IV, suggesting its hierarchical porous structure comprised of both micropores and mesopores. The adsorption at low pressure ($P/P_0 < 0.01$) is due to the filling of micropores, while the hysteresis loops at higher relative pressure ($P/P_0 = 0.4 \sim 0.9$) is assigned to the presence of mesoporosity in the sample. Pore size distribution analysis indicates a peak at the lower bound of detection, centered at 1.3 nm, as well as a broad distribution of mesopores.

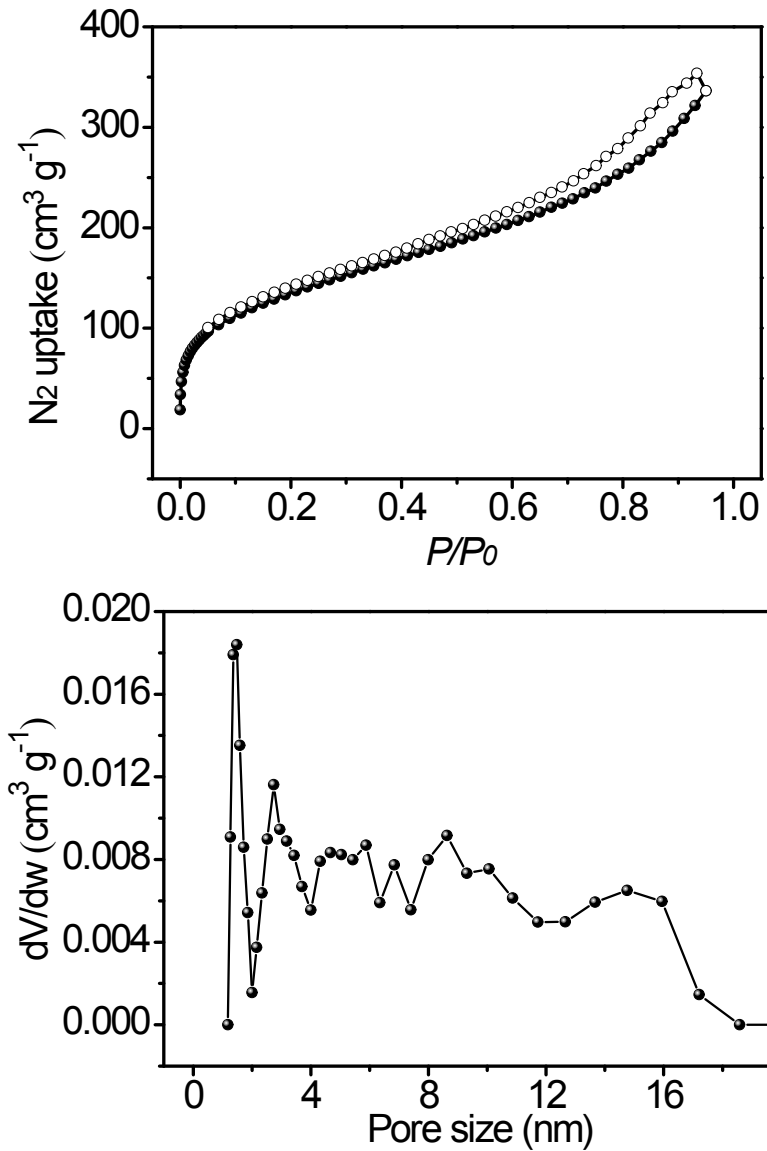


Fig. S10 N₂ sorption isotherms and corresponding DFT pore size distribution of PPS-oOH-Bn. The BET surface area and pore volume were calculated to be 440 m² g⁻¹ and 0.52 cm³ g⁻¹.

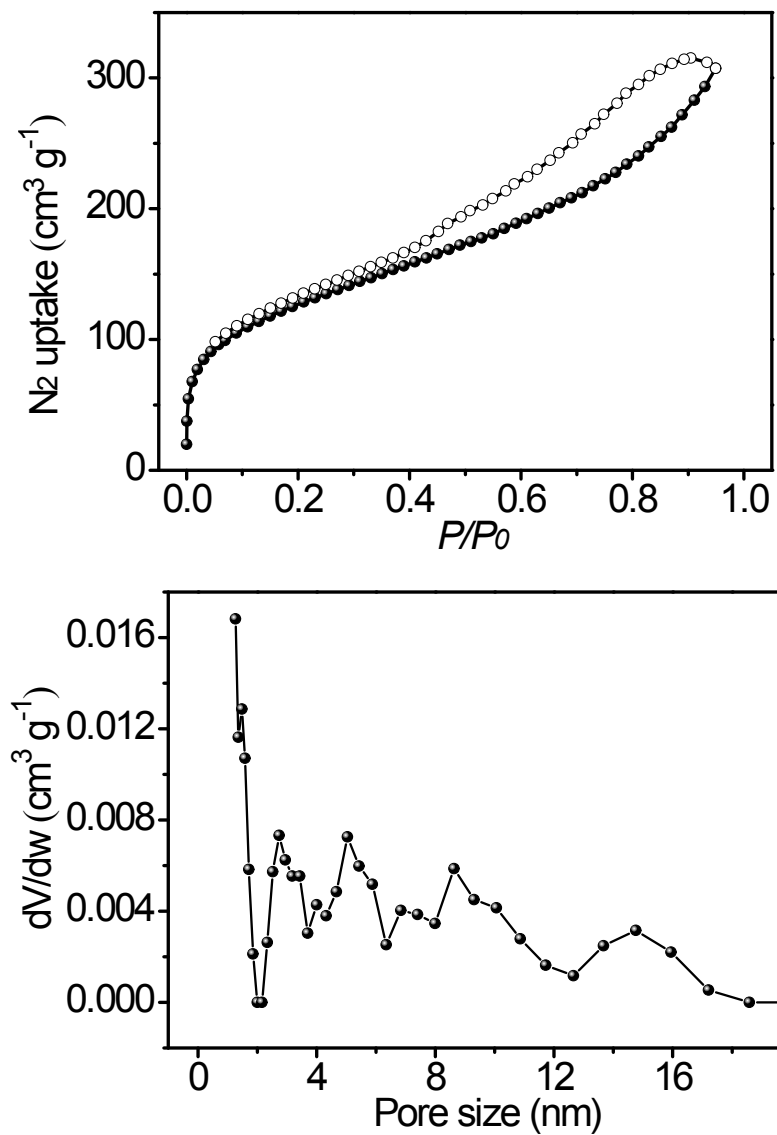


Fig. S11 N₂ sorption isotherms and corresponding DFT pore size distribution of PPS-*m*OH-Bn. The BET surface area and pore volume were calculated to be 420 m² g⁻¹ and 0.48 cm³ g⁻¹.

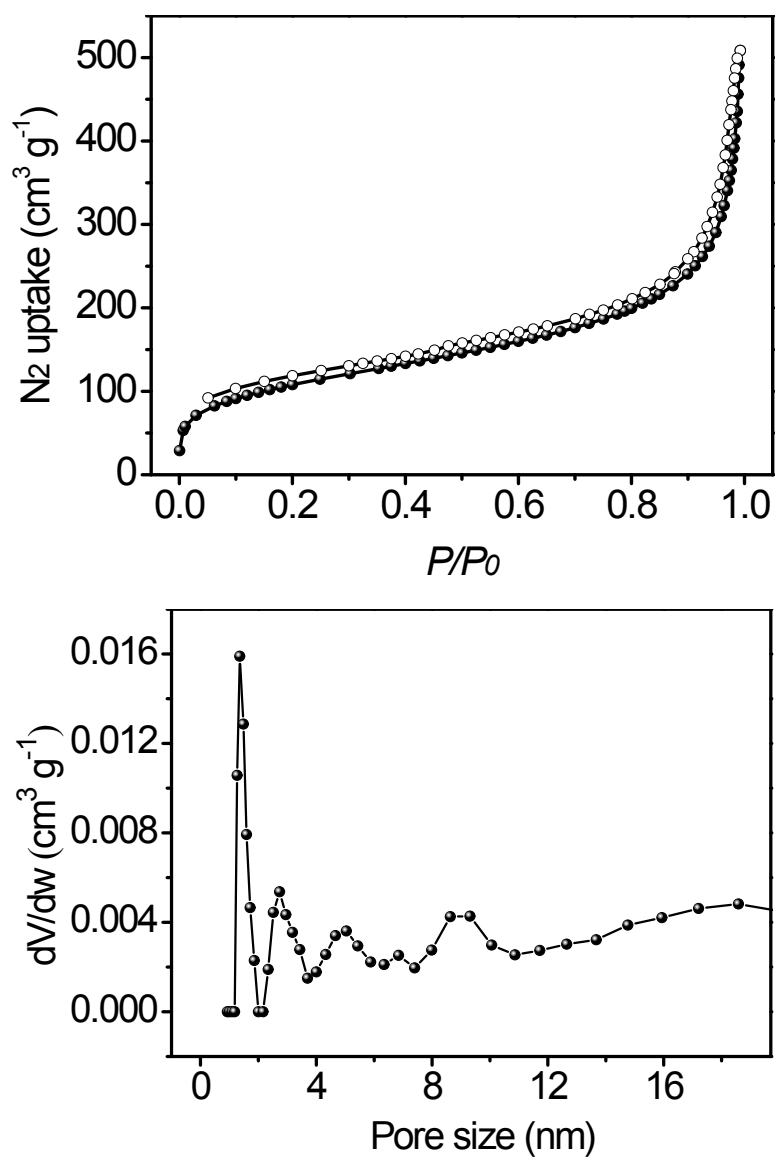


Fig. S12 N₂ sorption isotherms and corresponding DFT pore size distribution of PPS-*p*OH-Bn. The BET surface area and pore volume were calculated to be 394 m² g⁻¹ and 0.62 cm³ g⁻¹.

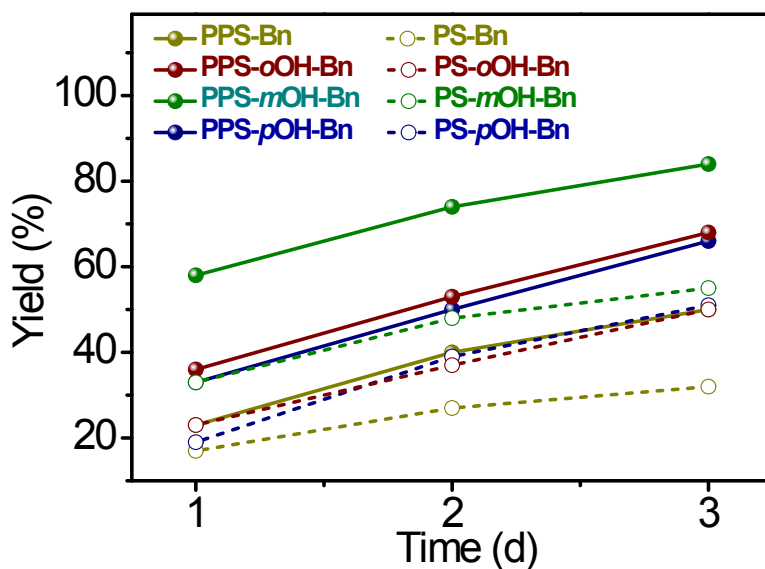


Fig. S13 Plots of yield of the carbonate product over various catalysts. Reaction conditions: 2-(butoxymethyl)oxirane (10 mmol), catalyst (0.05 mmol, based on the amount of phosphonium moieties), CO₂ (1 atm), and 80 °C.

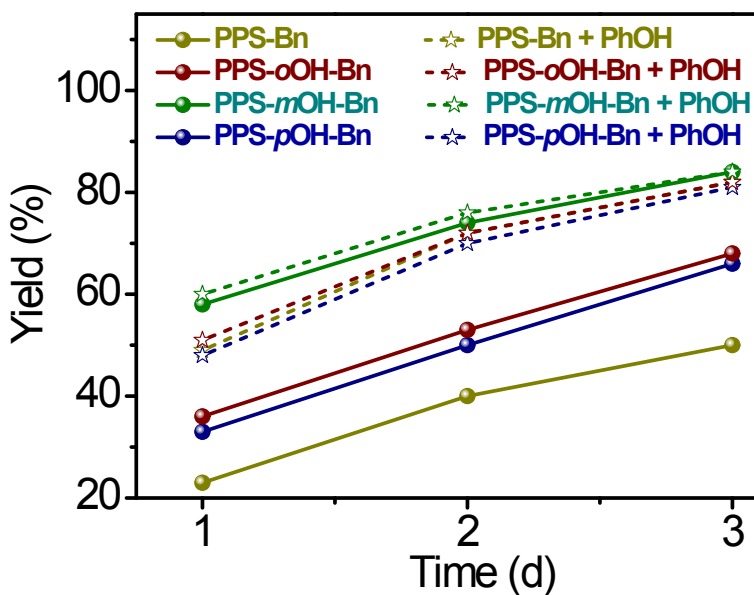


Fig. S14 The effect of phenol on the activity of various catalysts in catalyzing the cycloaddition of 2-(butoxymethyl)oxirane and CO₂. Reaction conditions: 2-(butoxymethyl)oxirane (10 mmol), catalyst (0.05 mmol, based on the amount of phosphonium moieties), phenol (0.05 mmol), CO₂ (1 atm), and 80 °C.

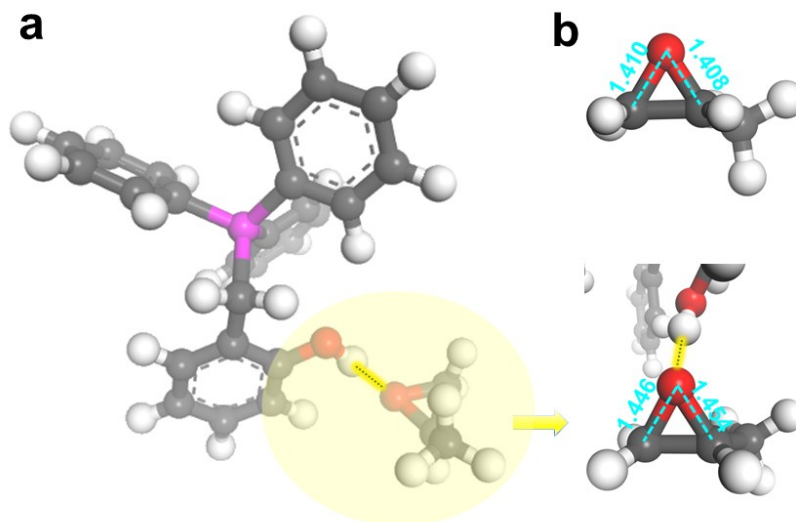


Fig. S15 (a) Hydrogen bond interaction between the cationic moiety in PPS-*o*OH-Bn and propylene oxide (atom colors in geometries: H: white, C: dark gray, O: red, P: pink). (b) The comparisons of C-O bond lengths in propylene oxide and that with the hydrogen bond interaction with the phenolic hydroxyl group. The unit of bond length is Å.

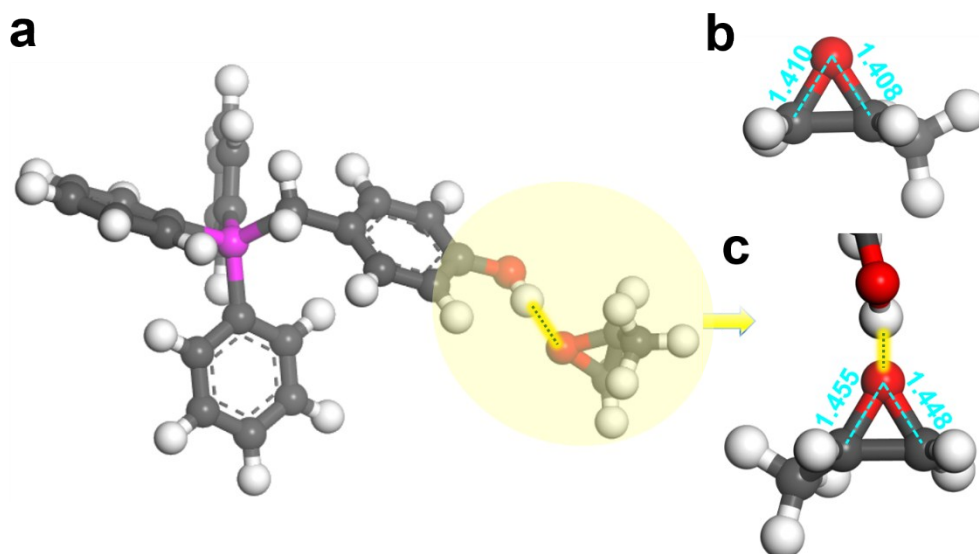


Fig. S16 (a) Hydrogen bond interaction between the cationic moiety in PPS-*p*OH-Bn and propylene oxide (atom colors in geometries: H: white, C: dark gray, O: red, P: pink). (b) The comparisons of C-O bond lengths in propylene oxide and that with the hydrogen bond interaction with the phenolic hydroxyl group. The unit of bond length is Å.

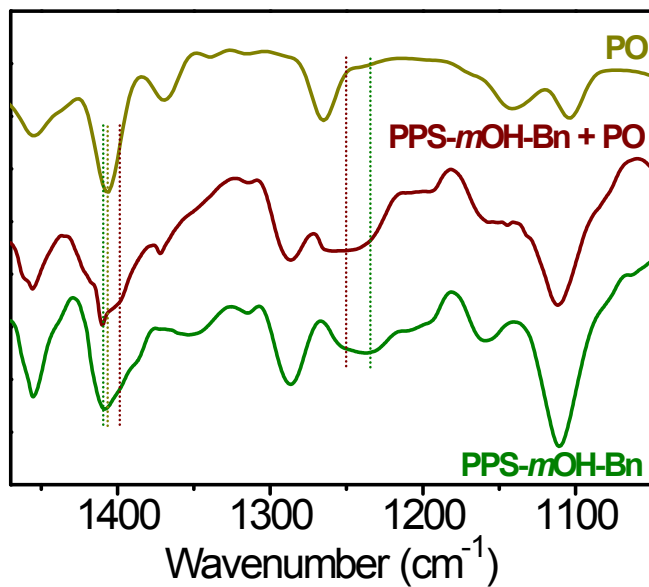


Fig. S17 IR spectra of PPS-*m*OH-Bn, propylene oxide (PO), and composite of well mixed PPS-*m*OH-Bn and PO (PPS-*m*OH-Bn + PO).

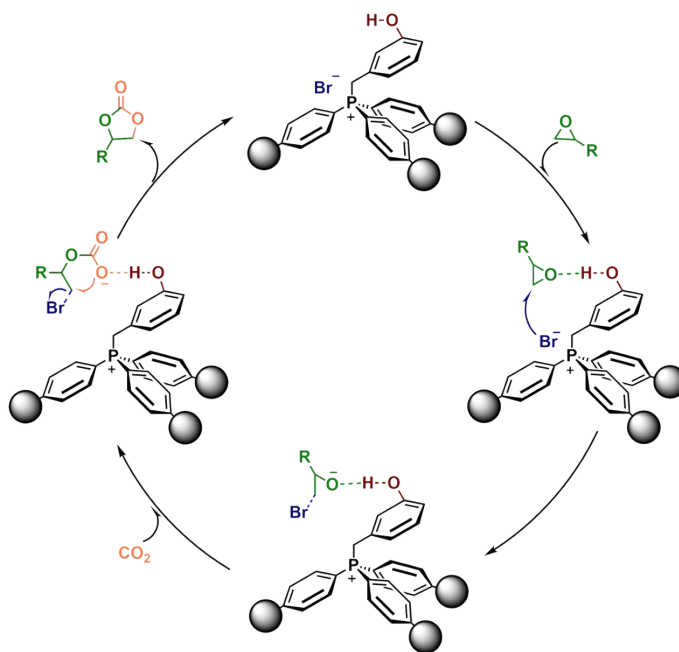


Fig. S18 Schematic illustration of the tentatively proposed catalytic mechanism for the cycloaddition of epoxide and CO₂ into cyclic carbonate catalyzed by PPS-*m*OH-Bn.

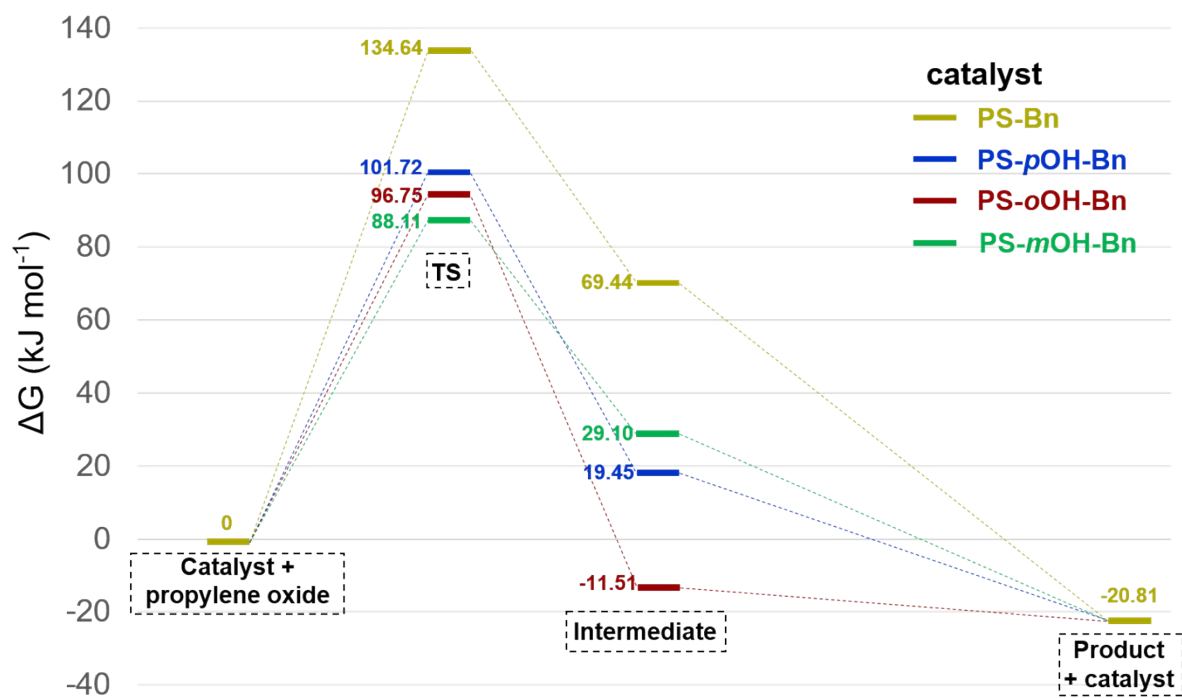


Fig. S19 Potential energy profiles for the PS-Bn, PS-*p*OH-Bn, PS-*o*OH-Bn, and PS-*m*OH-Bn catalyzed reactions of propylene oxide with CO₂ in the ring opening step.

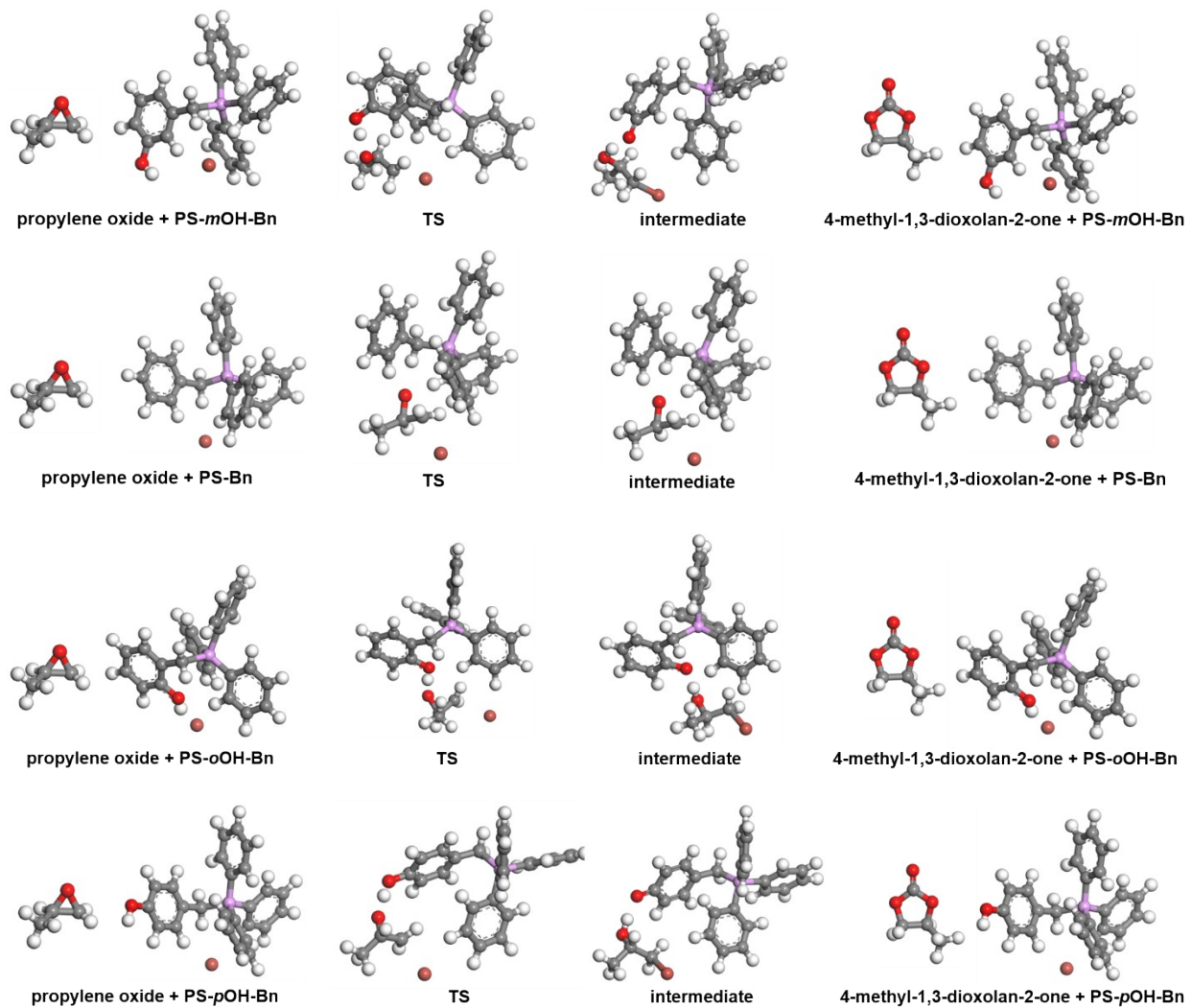


Fig. S20 Optimized structures of various steps corresponding to Fig. S18.

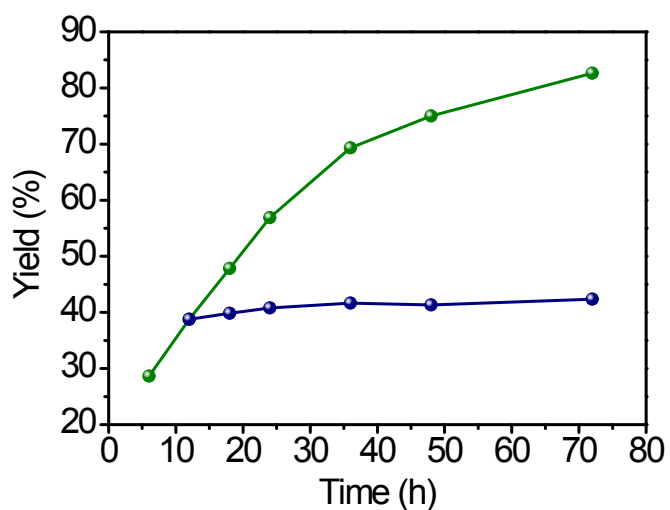


Fig. S21 4-(Butoxymethyl)-1,3-dioxolan-2-one yield verse time plots in the presence of PPS-*m*OH-Bn (olive) and with catalyst removal after 12 h (navy). Reaction conditions: 2-(butoxymethyl)oxirane (10 mmol), catalyst (0.05 mmol, based on the amount of phosphonium moieties), CO₂ (1 atm), and 80 °C.

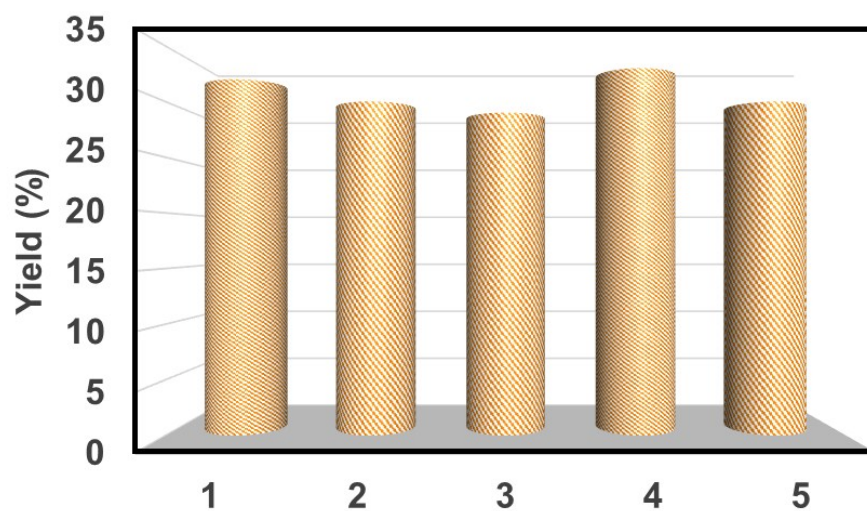


Fig. S22 Recycling tests for PPS-*m*OH-Bn in the cycloaddition of 1,2-epoxybutane and CO₂. Reaction conditions: 1,2-epoxybutane (10.0 mmol), catalyst (0.05 mmol, based on the amount of phosphonium moieties), CO₂ (1 atm), and 50 °C for 24 h.

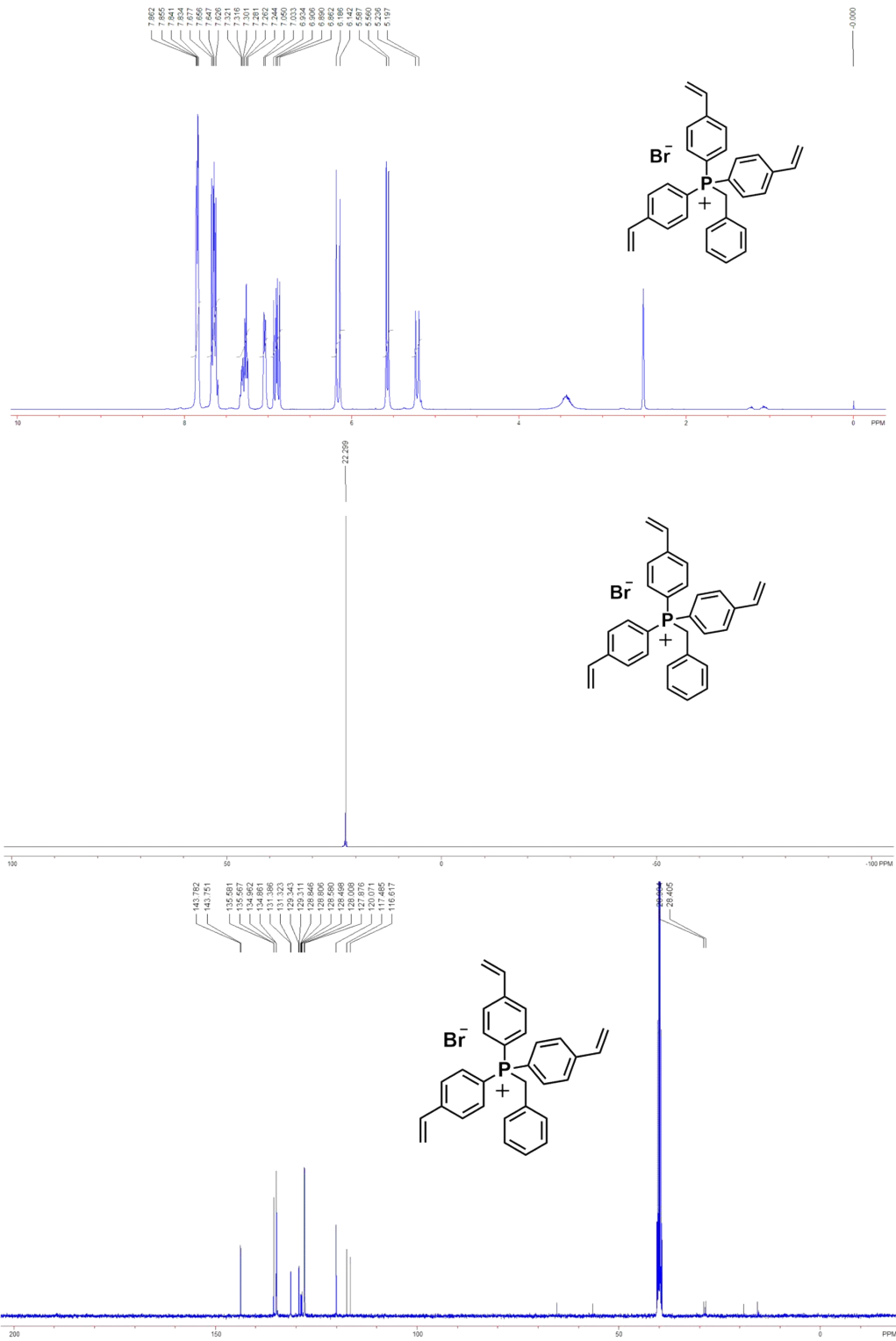


Fig. S23 ¹H, ³¹P, and ¹³C NMR spectra of V-PS-Bn.

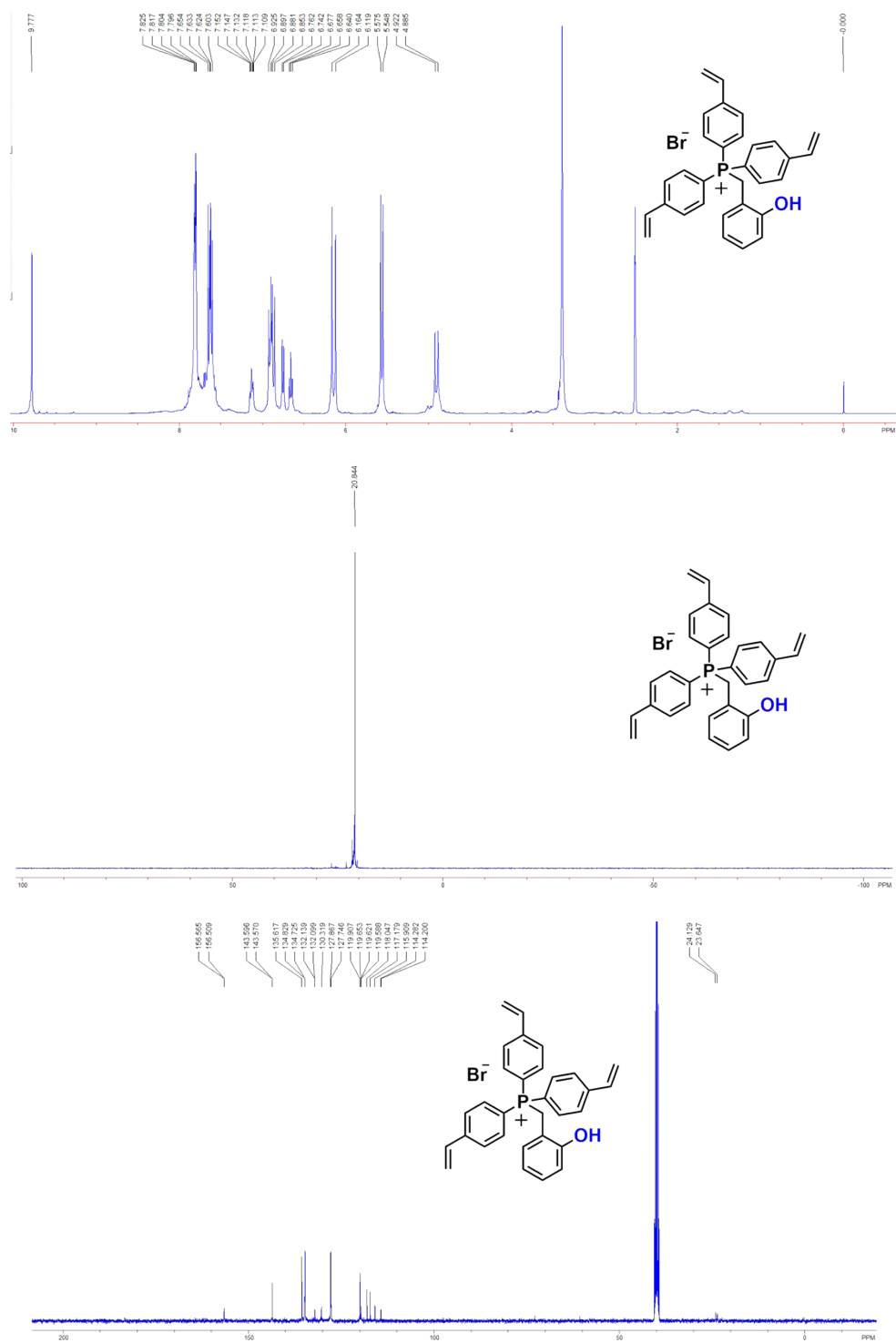


Fig. S24 ¹H, ³¹P, and ¹³C NMR spectra of V-PS-oOH-Bn.

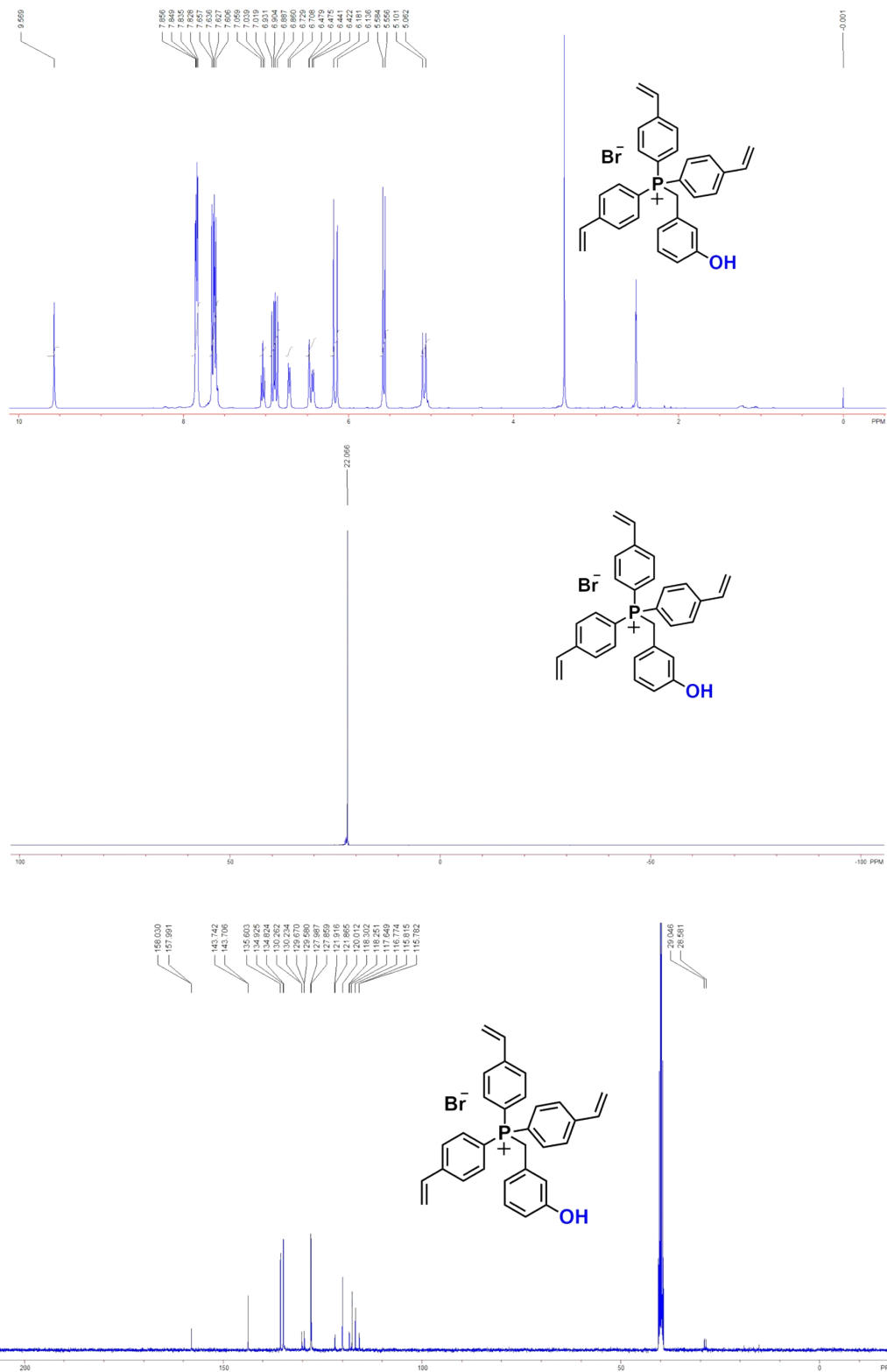


Fig. 25 ^1H , ^{31}P , and ^{13}C NMR spectra of V-PS-mOH-Bn.

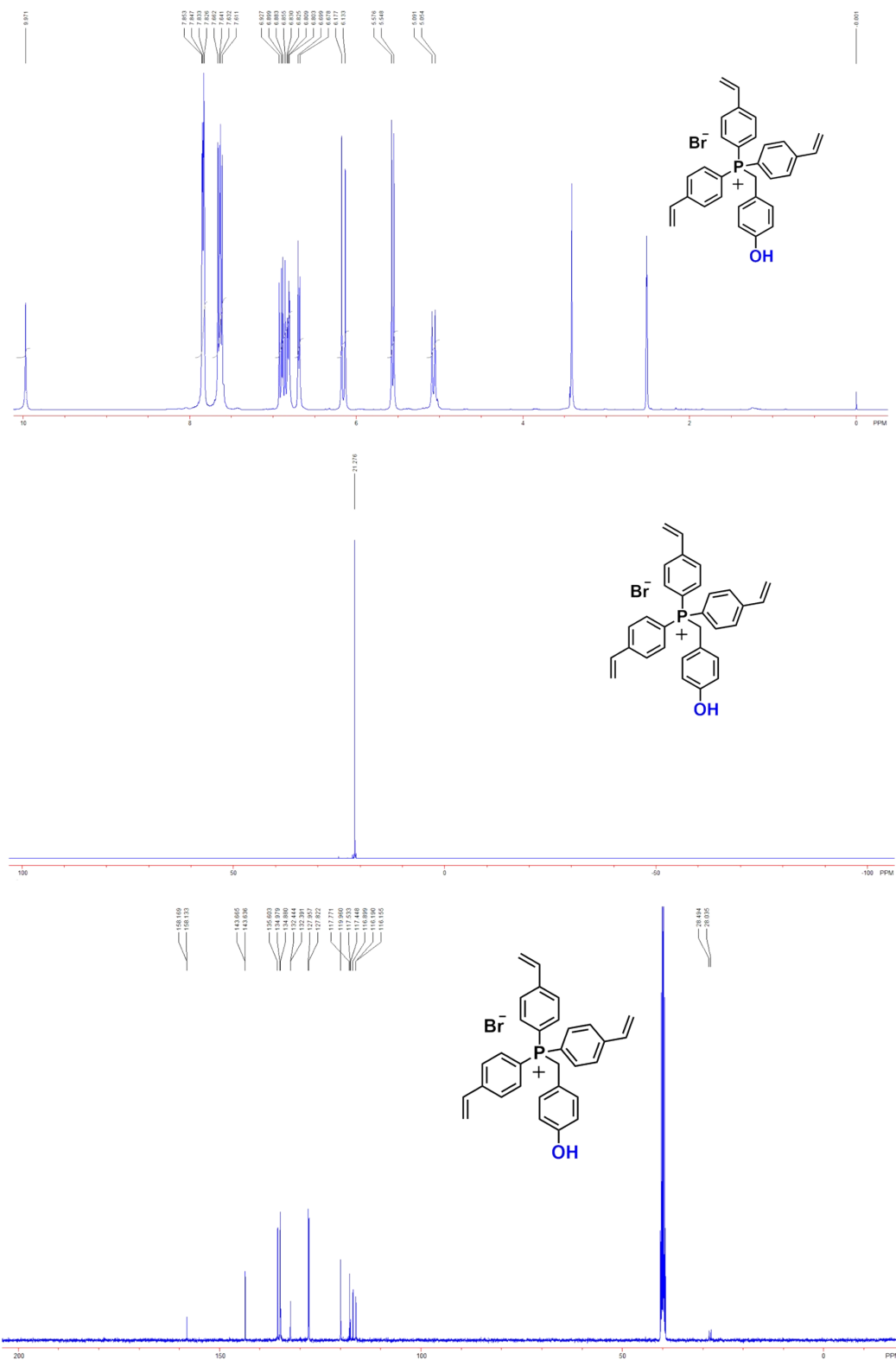


Fig. 26 ¹H, ³¹P, and ¹³C NMR spectra of V-PS-pOH-Bn.

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