

# The coupling reaction of epoxides with carbon dioxide catalyzed by functional cross-linked polystyrenes and metal salts/functional polystyrenes systems

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## EXPERIMENTAL SECTION

**General Procedures.** All manipulations involving air- and moisture-sensitive compounds were performed under an atmosphere of dried and purified argon using standard vacuum-line, Schlenk, or glovebox techniques.

**Materials.** Triethylamine (TEA), 4-vinylbenzylchloride (VBC), 1-bromohexene, 1-bromobutane, 1-methylimidazole, anhydrous ethanol, petroleum ether, ethyl acetate, diethyl ether, imidazole, ammonium hexafluorophosphate ( $\text{NH}_4\text{PF}_6$ ), aqueous dimethylamine solution (40 wt%) were purchased from Energy Chemical (Anqing, China) and used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purified by recrystallization from methanol before use. Divinylbenzene (DVB, 80%), propylene oxide (PO), epichlorohydrin, glycidol, styrene oxide were purchased from Energy Chemical (Anqing, China). All organic liquids were dried over 4 Å molecular sieves for a week and distilled over  $\text{CaH}_2$  before use.  $\text{CO}_2$  (99.999% purity) was purchased from Shenyang Hongsheng Gas Limited Corporation.

**Measurements.** NMR spectra of styrene derivatives were performed on Bruker AVANCE III 500 MHz instruments in  $\text{CDCl}_3$  using TMS as a reference. TGA were

performed at Analytical Research Centre of Shenyang University of Chemical Technology. Spectra of solid state  $^{13}\text{C}$  NMR of **CP1-5** were conducted in the Analytic Research Center of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

### Preparation of functional styrenes 1~5

Preparation of triethyl-(4-vinylbenzyl)ammonium chloride **1**: VBC ( 3.05 g, 20 mmol) and TEA (3.04 g, 30 mmol) and hydroquinone (0.003 g, 0.027 mmol ) were dissolved in 30 mL of THF in a 100 mL of three neck round bottom flask equipped with a condenser and a balloon filled with argon. The mixtures were stirred and heated to reflux for 12 h, resulting in a pale yellow suspension. The desired product was isolated as yellowish solids after filtration and washed with diethyl ether for 3 times (3×15 mL). Yield: 4.347 g, 83.7%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.34 (m, 4H), 6.70 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.91 -5.63 (m, 1H), 5.58 – 5.22 (m, 1H), 4.90 (d,  $J = 57.1$  Hz, 2H), 3.78 -3.25 (m, 6H), 1.47 (d,  $J = 14.5$  Hz, 7H), 1.37 (d,  $J = 7.1$  Hz, 2H).

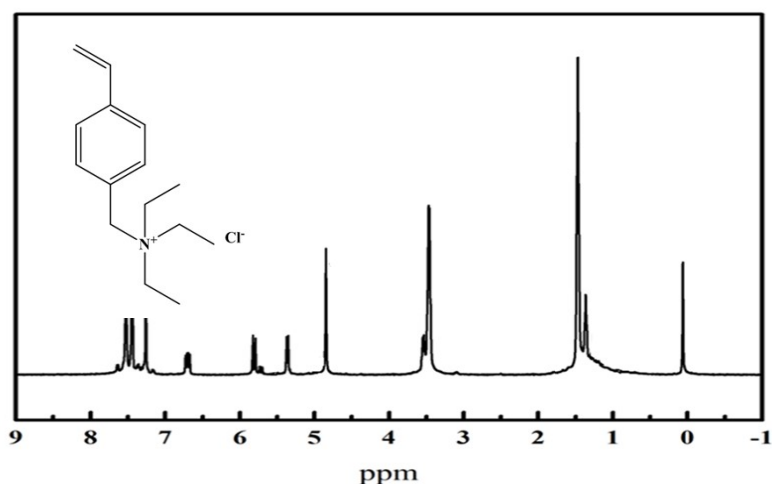


Figure S1.  $^1\text{H}$  NMR spectrum of **1**

Preparation of dimethyl-(4-vinylbenzyl)amine<sup>2</sup>: VBC (3.05 g, 20 mmol), aqueous dimethylamine solution (3.61 g, 80 mmol) K<sub>2</sub>CO<sub>3</sub> (5.528 g, 40 mmol) and 30 mL of ethanol was added into a 50 mL of round bottom flask. Then the flask was placed into 50 °C oil bath and stirred for 2 days. The reaction mixtures were concentrated by rotary evaporation. The desired product DMVBA were isolated as a yellowish liquid using column chromatography using petroleum ether and ethyl acetate (9/1) as eluent. Yield: 2.56 g, 80%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (d, J = 17.5 Hz, 1H), 5.21 (d, J = 10.8 Hz, 1H), 3.41 (s, 2H), 2.23 (s, 6H).

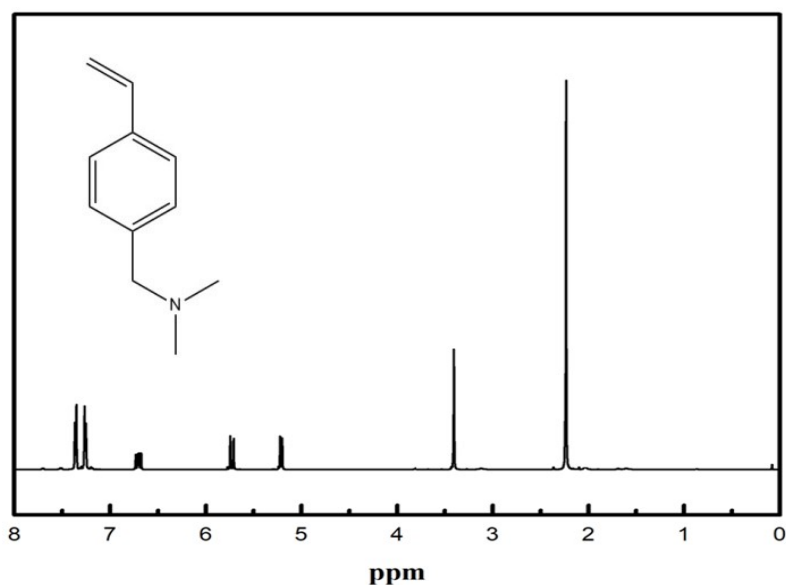


Figure S2. <sup>1</sup>H NMR spectrum of 2

Preparation of triethyl-(4-vinylbenzyl)ammonium hexafluorophosphate (3)<sup>3</sup>: triethyl-(4-vinylbenzyl)ammonium chloride (1 g, 3.94 mmol) and NH<sub>4</sub>PF<sub>6</sub> (0.64 g, 3.94 mmol) were independently dissolved in 2 mL of water. Then the aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added into the solution of triethyl-(4-vinylbenzyl)ammonium chloride under vigorous agitation for 1 h. The desired

ammonium salt was isolated as viscous yellow oil by suction filtration followed by washing with water for 3 times. Yield: 1.26 g, 88%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 2.0$  Hz, 4H), 6.64 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.76 (d,  $J = 17.6$  Hz, 1H), 5.32 -5.25 (m, 1H), 4.45 (s, 2H), 3.22 (q,  $J = 7.2$  Hz, 6H), 1.34 (d,  $J = 14.4$  Hz, 9H).

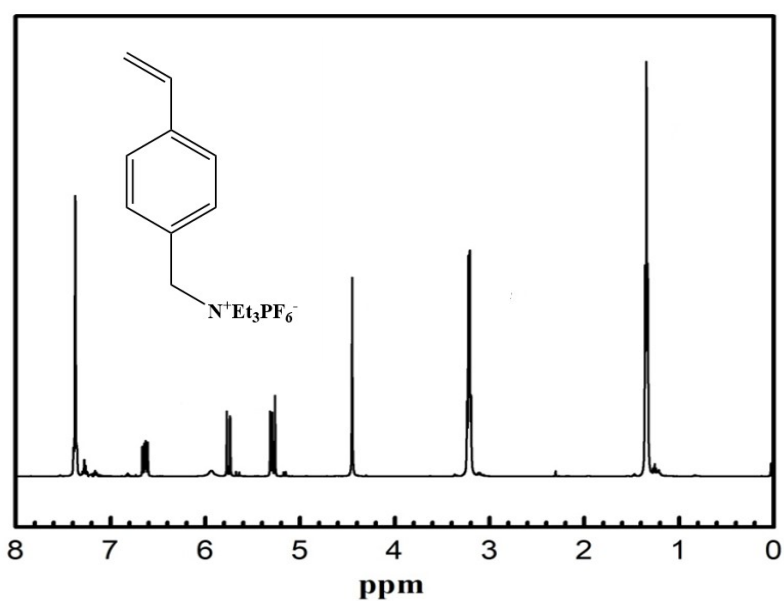
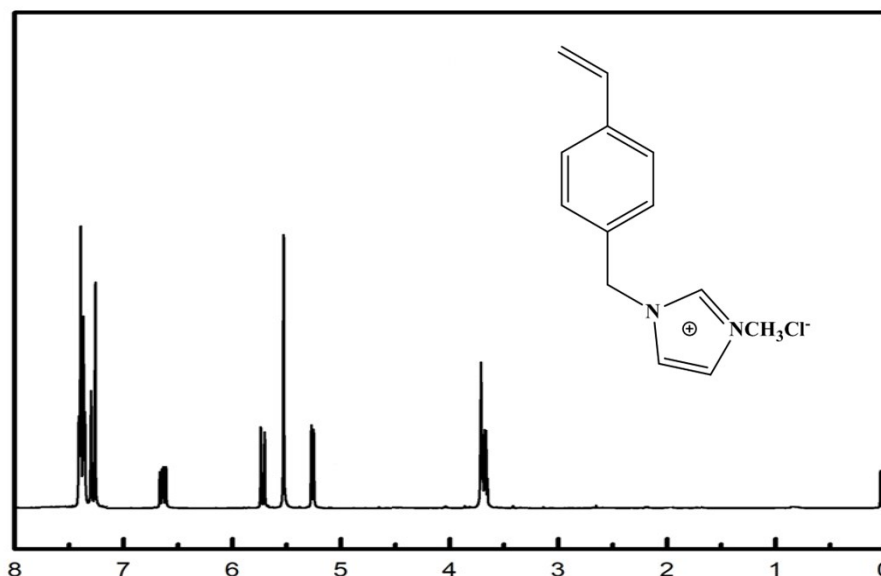


Figure S3.  $^1\text{H}$  NMR spectrum of **3**

Preparation of 1-methyl-3-(4-vinylbenzyl)-imidazolium chloride (**4**):<sup>1</sup> VBC (1.52 g, 10 mmol) and 1-methylimidazole (0.82 g, 10 mmol) and hydroquinone



(0.002 g, 0.18 mmol) were dissolved in 5 mL of anhydrous THF in a 100 mL of three neck round bottom flask equipped with a condenser and a balloon filled with argon. The mixtures were stirred and heated to reflux for 1 day. The target product was isolated as yellow viscous oil after washing by petroleum in 75% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.33 (m, 6H), 7.30 (s, 1H), 6.67 – 6.59 (m, 1H), 5.72 (dd, J = 17.7, 1.4 Hz, 1H), 5.53 (s, 2H), 5.26 (dd, J = 10.9, 1.4 Hz, 1H), 3.75 – 3.64 (m, 3H).

Figure S4. <sup>1</sup>H NMR spectrum of **4**

Preparation of 1-(4-vinylbenzyl)-3-(n-butyl)imidazolium bromide (**5**)<sup>2</sup>: K<sub>2</sub>CO<sub>3</sub> (5.528 g, 40 mmol) · 30mL of alcohol · VBC(3.04 g, 20 mmol)imidazole (1.36 g, 20 mmol) were added to a flask equipped with condenser and magnetic stirrer. The mixtures were stirred and heated to 50 °C for 2 days. The volatiles were removed by rotary evaporation. 2.86 g of 1-(4-

vinylbenzyl)imidazole was isolated by using column chromatography with petroleum ether and ethyl acetate (3/1) as eluent (yield: 77.9%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 7.9$  Hz, 2H), 6.72 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.75 (d,  $J = 17.6$  Hz, 1H), 5.24 (d,  $J = 10.9$  Hz, 1H), 4.45 (s, 2H), 3.38 (s, 3H)

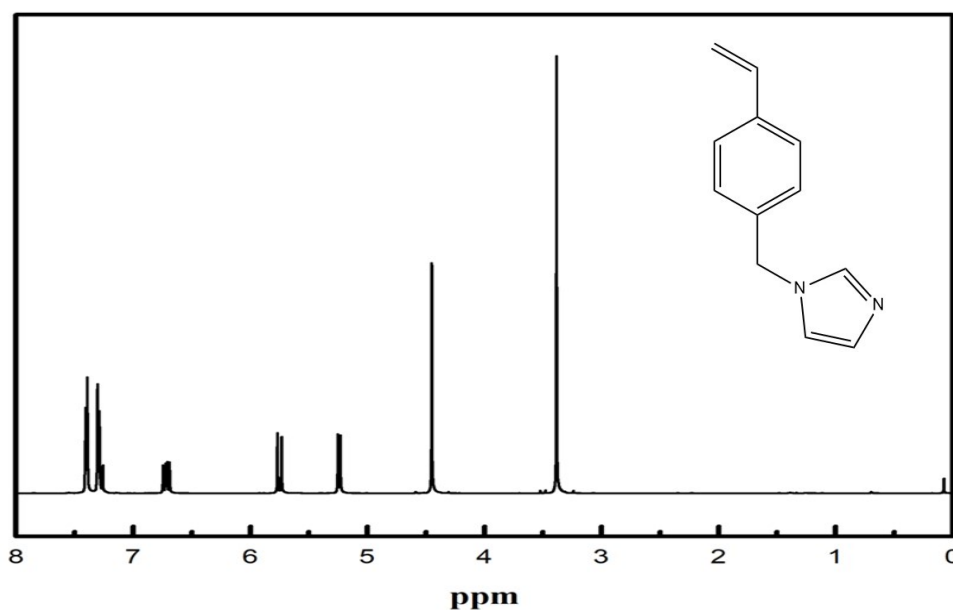


Figure S5.  $^1\text{H}$  NMR spectrum of 1-(4-vinylbenzyl)imidazole

Hydroquinone (0.001 g, 0.009 mmol), 1-(4-vinylbenzyl)imidazole (1 g, 5.5 mmol), 1-bromohexane (0.9 g, 5.5 mmol) were dissolved in 5mL of THF. The reaction mixtures were stirred and heated to reflux for 2 days. The target bromide product **5** was isolated as viscous oil by washing with petroleum ether for 3 times<sup>1</sup>. Yield: 1.214 g, 63.2% .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.41 (m, 5H), 7.32 (d,  $J = 7.7$  Hz, 2H), 6.60 (dd,  $J = 17.5, 10.9$  Hz, 1H), 5.70- 5.62 (m, 1H), 5.56 (s, 2H), 5.22 (d,  $J = 10.9$  Hz, 1H), 1.83 (q,  $J = 10.3, 8.8$  Hz, 3H), 1.30 -1.10 (m, 10H).

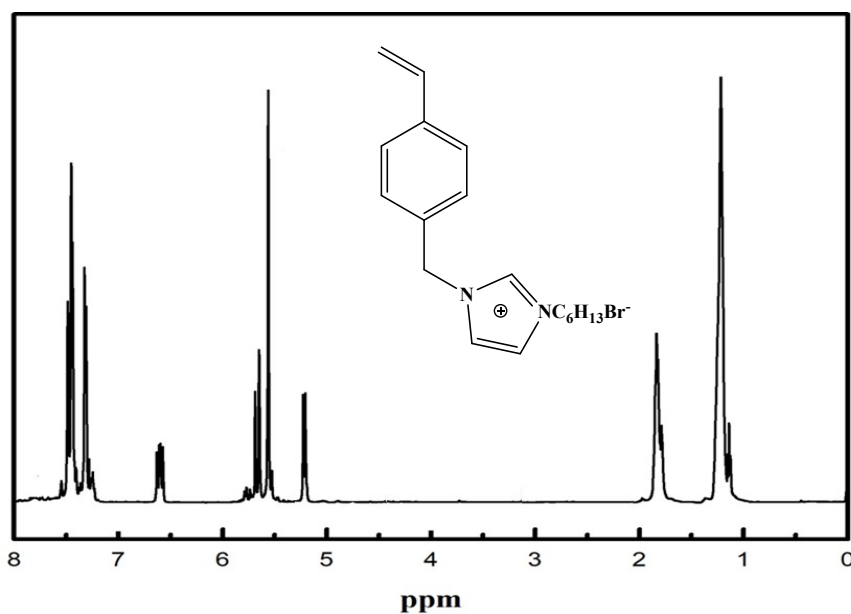


Figure S6.  $^1\text{H}$  NMR spectrum of **5**

#### Preparation of cross-linked polymers CP1~CP5

**Typical copolymerization procedure for the preparation of cross-linked polystyrene CP14:** DVB (0.19 g, 1.18 mmol), **1** (0.3 g, 1.18 mmol) and AIBN (0.013 g, 0.079 mmol) were weighed into a 50 mL of round bottom flask. Then 30 mL of chloroform was injected into the flask. The mixtures were heated to 100 °C and stirred overnight. After cooling, white solids were separated by filtration and washed by THF and  $\text{CHCl}_3$ . The resulting cross-linked polymers were dried at 40 °C under reduced pressure till constant weight. Yield: 0.45 g,

100%. IR: 2922  $\text{cm}^{-1}$   $\nu(-\text{CH}_2-)$ , 1603  $\text{cm}^{-1}$   $\nu_{\text{Ar}}(\text{C}=\text{C})$ , 1152  $\text{cm}^{-1}$   $\nu(\text{C}-\text{N})$ , 826  $\text{cm}^{-1}$   $\nu_{\text{Ar}}(\text{C}-\text{H})$ .

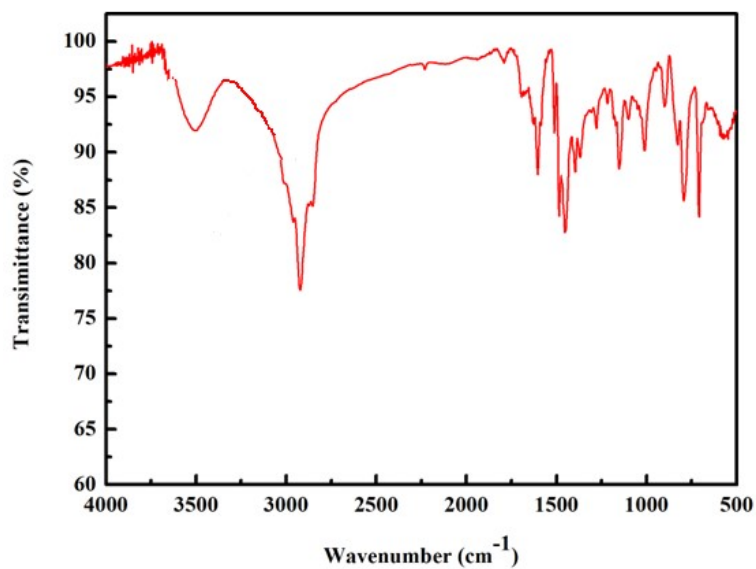


Figure S7. FT IR spectrum of **CP1**

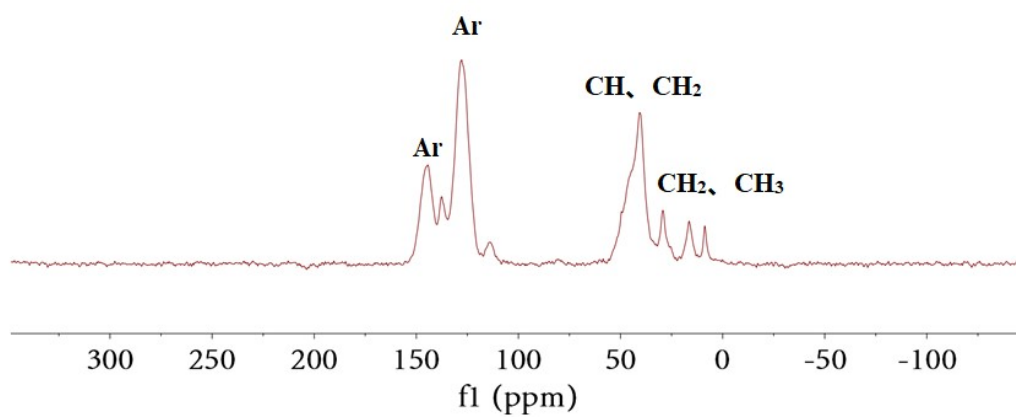


Figure S8. Solid-state  $^{13}\text{C}$  NMR spectrum of **CP1**



**CP2: yield: 100%. IR:** 2925  $\text{cm}^{-1}$   $\nu(-\text{CH}_2-)$ , 1509  $\text{cm}^{-1}$   $\nu_{\text{Ar}}(\text{C}=\text{C})$ , 1198  $\text{cm}^{-1}$   $\nu(\text{C}-\text{N})$ , 829  $\text{cm}^{-1}$   $\gamma_{\text{Ar}}(\text{C}-\text{H})$ .

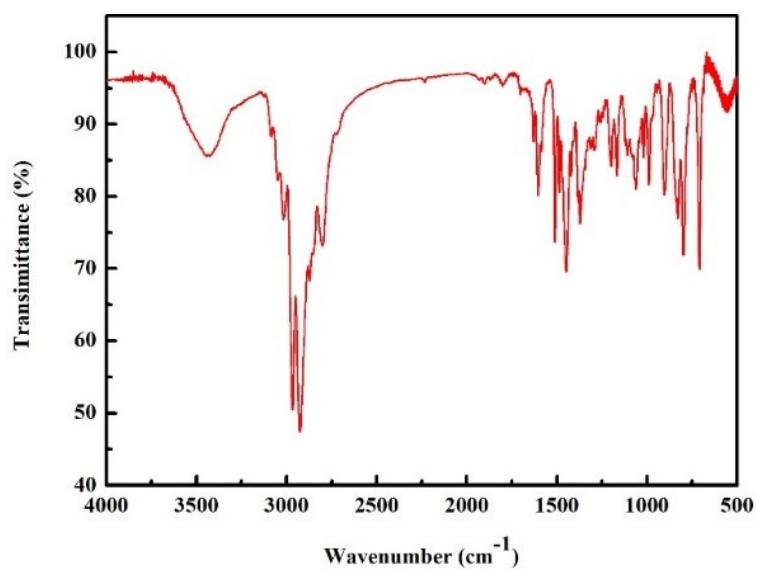


Figure S9. FT IR spectrum of **CP2**

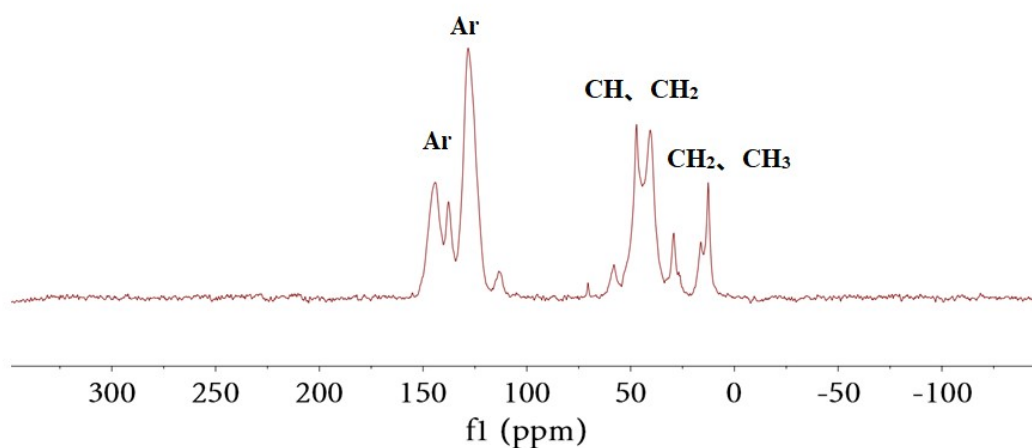


Figure S10. Solid-state  $^{13}\text{C}$  NMR spectrum of **CP2**

**Cp3: yield: 100%. IR:** 2927  $\text{cm}^{-1}$   $\nu(-\text{CH}_2-)$ , 1604  $\text{cm}^{-1}$   $\nu_{\text{Ar}}(\text{C}=\text{C})$ , , 1157  $\text{cm}^{-1}$   $\nu(\text{C}-\text{N})$ , 841  $\text{cm}^{-1}$   $\gamma_{\text{Ar}}(\text{C}-\text{H})$ .

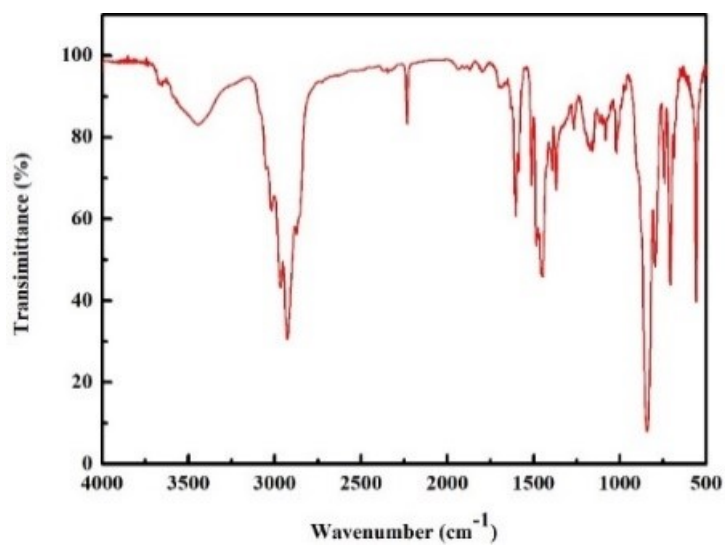


Figure S11. FT IR spectrum of **CP3**

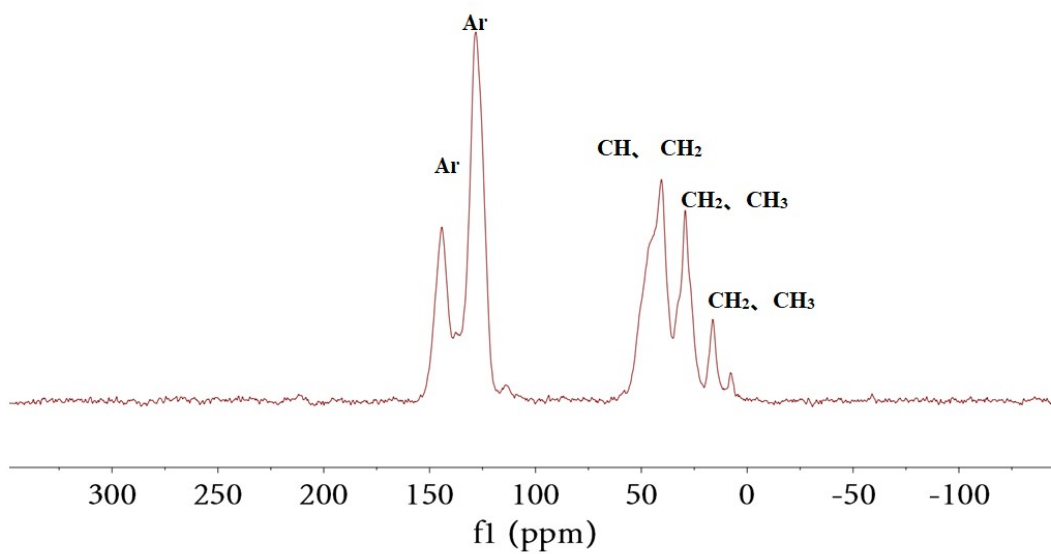


Figure S12. Solid-state  $^{13}\text{C}$  NMR spectrum of **CP3**

**CP4: yield: 100%. IR:** 2815  $\text{cm}^{-1}$   $\nu(-\text{CH}_2-)$ , 1550  $\text{cm}^{-1}$   $\nu_{\text{Ar}}(\text{C}=\text{C})$ , 1217  $\text{cm}^{-1}$   $\nu(\text{C}-\text{N})$ , 1134  $\text{cm}^{-1}$   $\nu(\text{C}-\text{C})$ , 861  $\text{cm}^{-1}$   $\gamma_{\text{Ar}}(\text{C}-\text{H})$ .

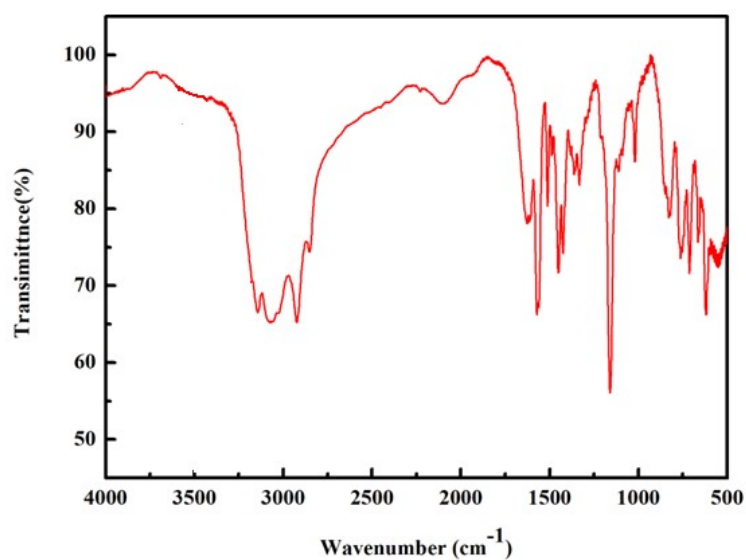


Figure S13. FT IR spectrum of CP4

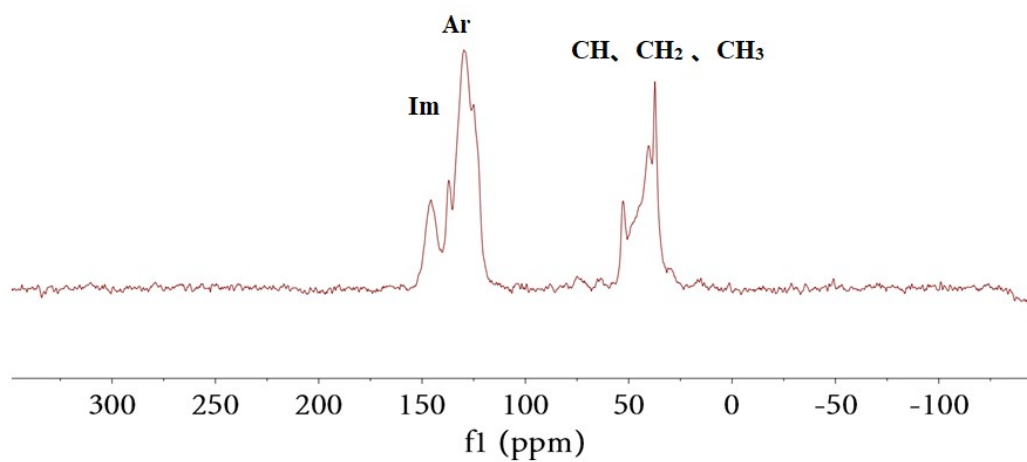


Figure S14. Solid-state  $^{13}\text{C}$  NMR spectrum of CP4

**CP5: yield: 100%. IR:** 2945  $\text{cm}^{-1}$   $\nu(-\text{CH}_2-)$ , 1620  $\text{cm}^{-1}$   $\nu_{\text{Ar}}(\text{C}=\text{C})$ , 1260  $\text{cm}^{-1}$   $\nu(\text{C}-\text{N})$ , 1126  $\text{cm}^{-1}$   $\nu(\text{C}-\text{C})$ . 805  $\text{cm}^{-1}$   $\gamma_{\text{Ar}}(\text{C}-\text{H})$ .

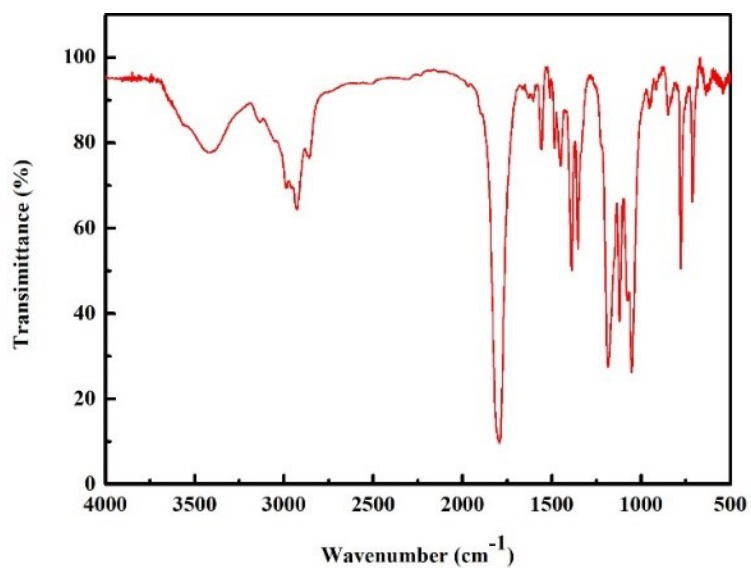


Figure S15. FT IR spectrum of **CP5**

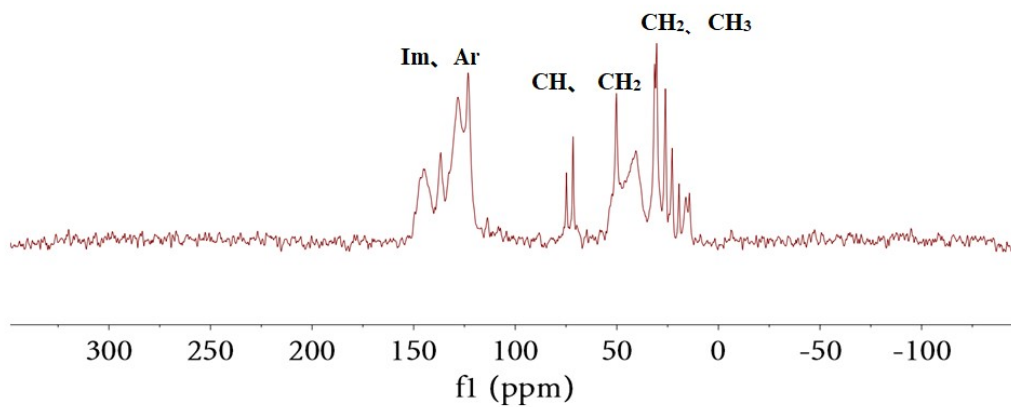


Figure S16. Solid-state <sup>13</sup>C NMR spectrum of **CP5**

### **Catalytic coupling of CO<sub>2</sub> with epoxide by functional cross-linked polymers**

Typical procedure for the coupling of PO with CO<sub>2</sub> by cross-linked polymer **CP1**. **CP1** (0.09 g, 0.233 mmol based on Cl<sup>-</sup>) was weighed into a pre-dried autoclave. Then the autoclave was evacuated using a vacuum pump and recharged with CO<sub>2</sub> for 3 times. Then dry propylene oxide (PO, 2.03 g, 35 mmol) was transferred into the autoclave using syringe. The autoclave was then pressured with CO<sub>2</sub> to 1.5 MPa and heated. After the designated time, the autoclave was cooled in an ice bath. The excess of the CO<sub>2</sub> was vented out. The cross-linked polymer **CP1** was isolated by suction filtration and washed with dichloromethane (15 mL). Cyclic propylene carbonate was produced as the sole product without discovery of poly(propylene carbonate) as evidenced by <sup>1</sup>H NMR. The yield of propylene carbonate (PC) was calculated on the basis of weight.

Typical procedure for the coupling of PO with CO<sub>2</sub> by cross-linked polymer **CP1/FeCl<sub>3</sub>** composite catalyst.

**CP1/FeCl<sub>3</sub>**(0.128 g, 0.233 mmol for **CP1** and 0.038 g, 0.233 mmol for FeCl<sub>3</sub> ), was weighed into a pre-dried autoclave. Then the autoclave was evacuated using a vacuum pump and recharged with CO<sub>2</sub> for 3 times. Then anhydrous propylene oxide (PO) (5.411 g, 93.3 mmol) was transferred into the autoclave using syringe. The autoclave was then pressured with CO<sub>2</sub> to 1.5 MPa and heated. After the designated time, the autoclave was cooled in an ice bath. The excess of the CO<sub>2</sub> was vented out. The **CP1/FeCl<sub>3</sub>** was isolated by suction filtration and washed with dichloromethane

(15 mL). Cyclic propylene carbonate was produced as the sole product without discovery of poly(propylene carbonate) as evidenced by  $^1\text{H}$  NMR. The yield of propylene carbonate (PC) was calculated on the basis of weight.

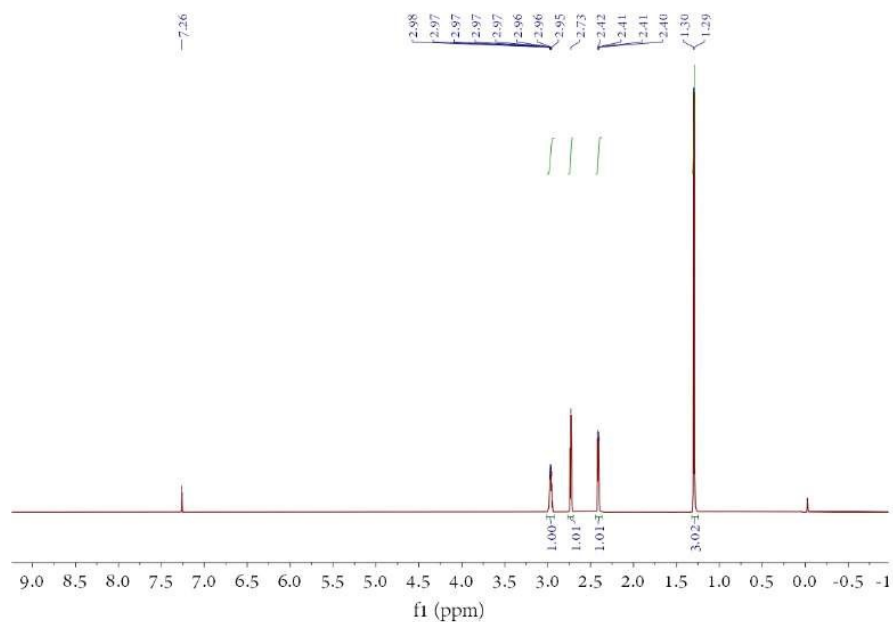


Figure S17.  $^1\text{H}$  NMR spectrum of propylene oxide

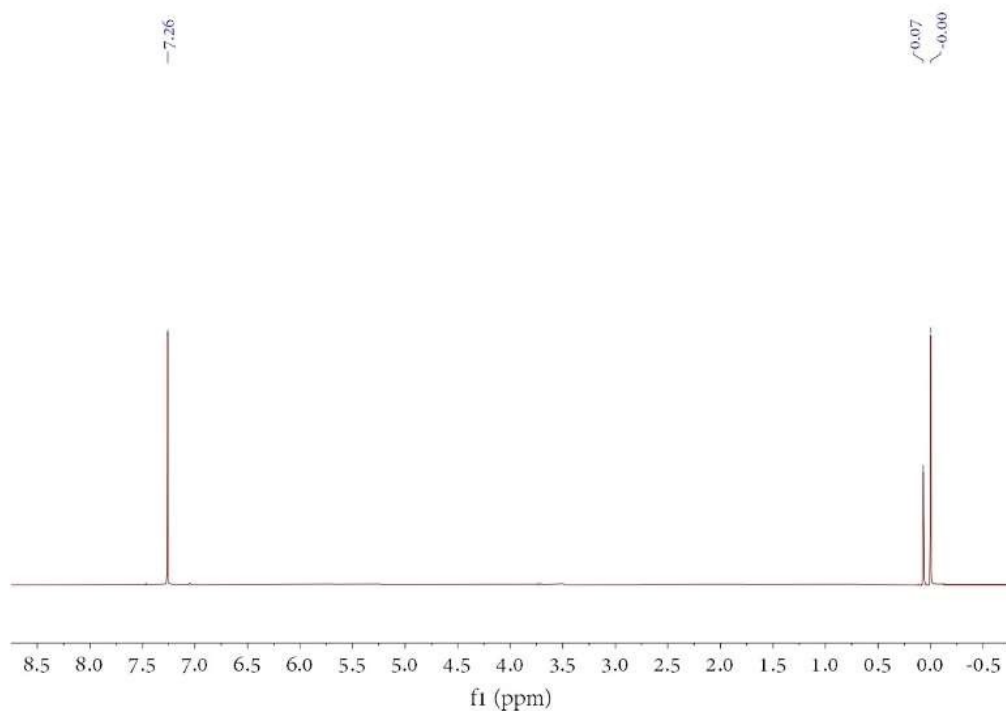


Figure S18.  $^1\text{H}$  NMR spectrum of  $\text{AlCl}_3$

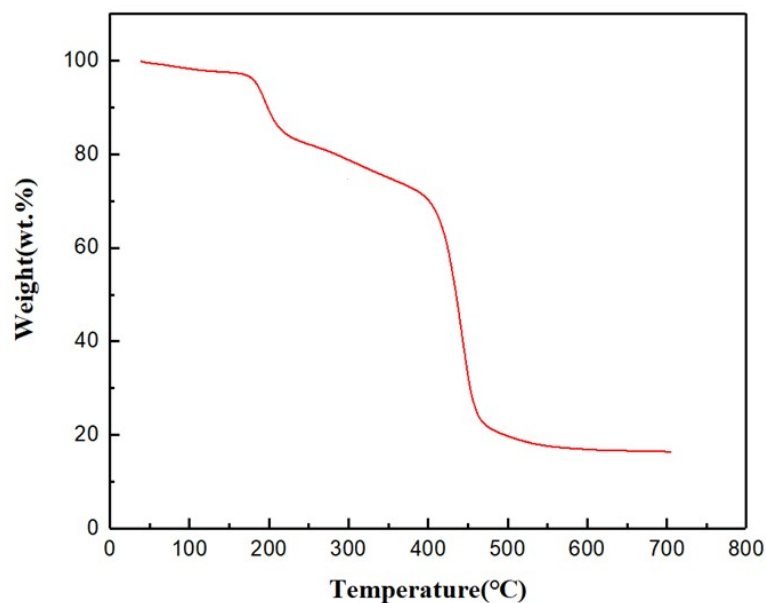


Chart S1. TGA curves of Cross-linked copolymer 1.

Table S1. Cycloaddition of CO<sub>2</sub> to epoxides catalyzed by **CP1** catalyst<sup>a</sup>

| entry | epoxide         | Yield (%) |
|-------|-----------------|-----------|
| 1     | epichlorohydrin | 84        |
| 2     | styrene oxide   | 83        |
| 3     | glycidol        | 50        |

<sup>a</sup> Conditions:  $n_{\text{(epoxide)}} = 35$  mmol;  $n_{\text{(epoxide)}}/n_{\text{(Cl)}} = 150$ , temperature: 130 °C, time: 10h,  $P_{\text{(CO}_2\text{)}} = 1.5$  MPa.

#### References

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