Supporting Information for

Polymeric Bis(triphenylphosphine)iminium Chloride as a Recyclable Catalyst

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Materials, Reagents and Methods

General considerations

The synthesis of all compounds with air and/or water-sensitive reactants was performed in an argon-filled glovebox or with the standard Schlenk techniques under dry nitrogen.

Materials

All chemicals were used as received unless otherwise mentioned. *p*-(diphenylphosphino)styrene (Sigma-Aldrich), n-Butyllithium (1.6 M in hexane, Sigma-Aldrich), triphenylphosphine (Sigma-Aldrich), hydroxylamine-O-sulfonic acid (Sigma-Aldrich), hexachloroethane (Fluorochem), bis(triphenylphosphine)iminium chloride (Alfa), 1-chloro-4-nitrobenzene (Thermo Scientific Acros), 4-Chlorobenzonitrile (Thermo Scientific Acros), 1-Chloro-4-(trifluoromethyl)benzene (Thermo Scientific Acros), 4-Chlorobenzamide (Thermo Scientific Acros), 4-Chlorobenzenesulfonic acid (Thermo Scientific Acros), 3-Chloro-N,N-dimethylbenzenamine (Thermo Scientific Acros), 1,3,5-trimethoxybenzene (Sigma-Aldrich), bromobenzene (Fluorochem), boron trifluoride etherate (Acros Organics), hydrogen chloride solution (2M in diethyl ether) (Alfa Aesar), 4-chlorostyrene (Fluorochem), 2-aminoethyl diphenylborinate (Sigma-Aldrich), 2-phenyl-2-propyl benzodithioate (Sigma-Aldrich), potassium fluoride (Thermo Scientific Chemicals), magnesium sulfate (Thermo Scientific Chemicals), ammonium chloride (Aldrich), sodium chloride (Sigma-Aldrich), were used as received. Anhydrous toluene, tetrahydrofuran, dichloromethane, methanol, diethyl ether, hexanes were obtained from an MBraun 7 Solvent Purification System containing alumina and copper catalysts and degassed by three successive freeze-pump-thaw cycles prior to use. Styrene (Aldrich), glycidyl chloride (Fluorochem), propylene oxide (Fluorochem), styrene

oxide (Sigma-Aldrich), 1,2-epoxybutane (Sigma-Aldrich), 1,2-epoxyhexane (Thermo Scientific Chemicals), cyclohexene oxide (Sigma-Aldrich) and deuterated solvents (Sigma-Aldrich, Flurochem) were all stirred over calcium hydride (99.9%, Aldrich) for 16 h and then distilled under reduced pressure. Magnesium turnings (Sigma-Aldrich) were dried in an oven at 200 °C for a minimum of 3 days prior to their use in Grignard reactions. Carbon dioxide (N5.0, research grade, 99.999% purity) was purchased from BOC.

Triphenylborane (BPh_3) and poly(BPh_3) were synthesized according to previous reports by our group.[1-3]

Instrumentation

All NMR experiments were performed at 298 K on either a 400MHz Bruker AVIII spectrometer or a 500 MHz Bruker AVIII HD spectrometer. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the chemical shift of the residual solvent resonances ($CDCl_3$ [1]H: δ=7.26 ppm, [13]C: δ=77.2 ppm).

Molecular weights and molecular weight distributions of polymers were measured by using an Agilent 1260 Infinity II Multi-Detector Gel Permeation Chromatography (GPC)/Size Exclusion Chromatography System through PLgel 5 μm columns packed with PSDVB beads. The GPC was run at a flow rate of 1.0 mL min^{-1} with THF as the eluent at 35 °C. The sample concentration was about 6.5 mg mL^{-1}, and the injection volume was 100 μL. The molecular weight molecular and weight distributions were obtained using triple detection based on a calibration prepared with monodisperse polystyrene standards covering the molecular weight range from 580 to 460000 Da.

Thermogravimetry analysis (TGA) measurements were performed in the TA SDT650 analyser to measure the change in mass with an increase in temperature, thermal stability, and maximum degradation temperature for the samples. All samples were heated in sealed aluminium sample pans at a heating rate of 10 °C min^{-1} in the temperature range of 25–600 °C under an air atmosphere with a flow rate of 50 mL min^{-1}. The mass of the analysed samples varied between 5 and 10 mg.

The differential scanning calorimeter (DSC) measurements were employed to determine the glass transition temperatures, which were carried out in TA DSC2500 under a nitrogen atmosphere. Samples weighing between 5 and 10 mg were sealed in aluminium pans and first heated from -80 °C to 180 °C to 180 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere to eliminate the thermal history. At the end of the first run, the samples were cooled down to -80 °C and run up to 180 °C again at a rate of 10 °C min^{-1} under a nitrogen atmosphere. The second-run DSC curve was the reference for determining the glass transition temperature.

A Fourier transform infrared spectrometer (Agilent 4500a) equipped with an attenuated total-reflection diamond crystal accessory (ATR) was used to obtain the spectra in the wavenumber range of 4000–650 cm^{-1} at room temperature.

Synthetic Procedures for poly(PPNCl)

General procedure for the synthesis of P1

P1
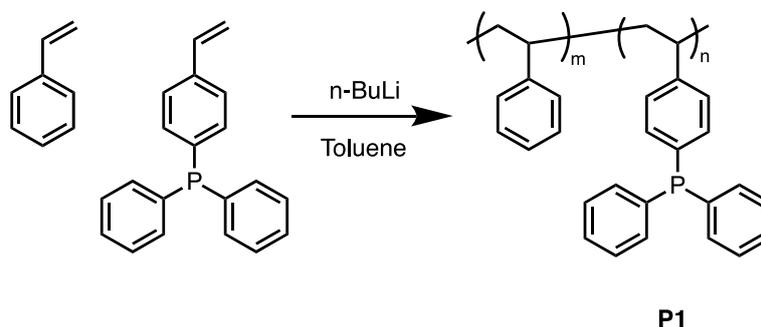
The synthetic procedure of P1 is referenced to our previous work.[3] Styrene (3.0 g, 28.8 mmol) and diphenylphosphino styrene (0.44 g, 1.5 mmol) were combined in toluene (35 mL). A solution of n-butyllithium (0.11 mL, 0.17 mmol) in hexane (1.6 M) was then added to the mixture at -78 °C under N_2 before warming to room temperature. After 3 hours, a drop of methanol was added to quench the reaction. A small aliquot was removed for ^{1}H NMR analysis to calculate the conversion of styrene and diphenylphosphino styrene. The residue solution was concentrated under vacuum and then dissolved in THF. The product was obtained by precipitation in methanol and dried in vacuum. The NMR results of the product matched our previous report.

Yield: 3.3 g, 96 %.

¹H NMR (400 MHz, 298 K, CDCl$_3$) δ/ppm = 7.40-6.80, 6.16-6.76 (br, aryl), 2.20 − 1.67 (m, br, alkyl), 1.60 - 1.16 (br, alkyl).

³¹P NMR (162 MHz, 295 K, CDCl$_3$) δ/ppm = -6.30 (br).

GPC Data: M_n = 19300 g/mol, Đ = 1.1.

General procedure for the synthesis of P2

P1   **P2**
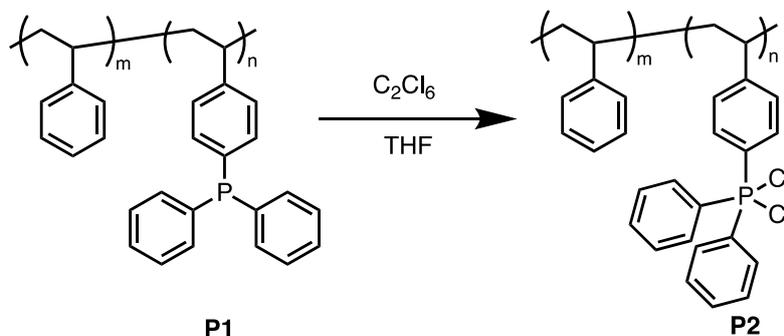
The synthetic procedure of P2 is referenced to the work reported previously.[4] A solution of hexachloroethane (0.36 g, 1.5 mmol) in THF (2 mL) was added dropwise to the solution of P1 (3.2 g, 0.16 mmol) in THF (10 mL). The mixture was stirred for another 3 h and a small aliquot was removed for ¹H NMR analysis to calculate the conversion of P1. The remaining mixture was then added to cold hexane and the precipitate was collected by filtration. The precipitate was washed with hexane for three times and dried in vacuum. The ³¹P NMR results of P2 share a similar chemical shift with its small molecule PPh$_3$Cl$_2$ as reported in the literature.[5]

Yield: 3.2 g, 90 %

¹H NMR (400 MHz, 298 K, CDCl3) δ/ppm =8.10-7.50, 7.40-6.80, 6.16-6.76 (br, aryl), 2.20 − 1.67 (m, br, alkyl), 1.60 - 1.16 (br, alkyl).

³¹P NMR (162 MHz, 295 K, CDCl$_3$) δ/ppm =63.2 (br).

GPC Data: M_n = 18700 g/mol, Đ = 1.2

General procedure for the synthesis of amino(triphenyl)phosphonium chloride
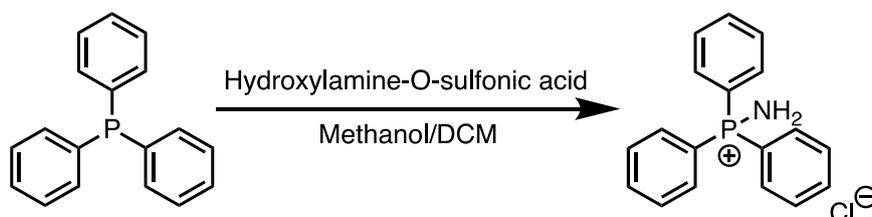
A solution of hydroxylamine-O-sulfonic acid (2.26 g, 8.80 mmol) in methanol (10 mL) and DCM (8 mL) was added to a solution of triphenylphosphine (1.00 g, 8.80 mmol) in DCM (14 mL) via

cannula under nitrogen atmosphere. The mixture was then stirred for another 1 hour and diluted in DCM, washed with a saturated solution of sodium chloride, and the organic layer was dried over magnesium sulphate and dried in vacuum.

Yield: 2.6 g, 80 %.

^{1}H NMR (400 MHz, 298 K, CDCl$_3$) δ/ppm = 7.70 – 7.40 (m, aryl), 7.82 (dd, aryl)

^{31}P NMR (162 MHz, 298 K, CDCl$_3$) δ/ppm = 35.7.

General procedure for the synthesis of poly(PPNCl)
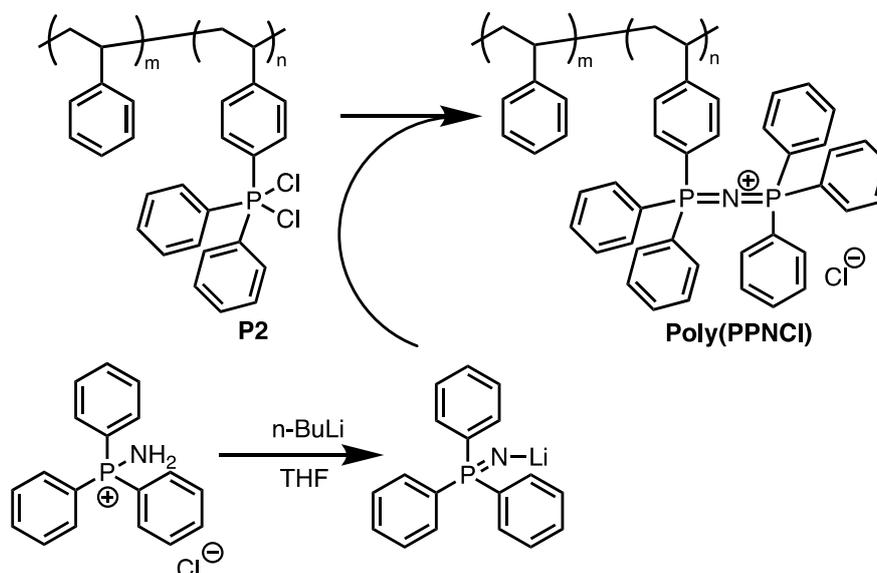
A solution of n-Butyllithium (1.6 M in hexane, 1.6 mL, 2.64 mmol) was added dropwise to a solution of P3 (0.41 g, 1.32 mmol) in THF (15 mL) at -50 °C under N$_2$. The mixture was stirred at -15 °C for another 2 h before adding a solution of P2 (3.0 g, 1.2 mmol P moieties) in THF (15 mL) under a nitrogen atmosphere at -15 °C. The reaction solution was warmed to room temperature and stirred overnight. Drops of denoised water was added to quench the reaction. The mixture was diluted in dichloromethane and washed with a saturated solution of sodium chloride three times. The organic layer was dried with magnesium sulphate, filtered and evaporated. The residue was dissolved in THF and precipitated out in hexane. Upon filtration and rinsing with hexane, crude poly(PPNCl) was obtained. Dialysis was attempted to remove the small molecular impurities in the crude poly(PPNCl). The crude poly(PPNCl) was dissolved in DCM and then transferred to the dialysis membrane with a pore size of 1000 Da. The dialysis membrane was immersed in the buffer, which was made of dichloromethane and methanol with a volume ratio of 2: 1. The mixture was stirred for 8 hours at room temperature

to reach equilibrium. The solution in the dialysis membrane was collected and precipitated in hexane. The purified poly(PPNCl) was obtained as the precipitate and dried under vacuum to remove solvent.

Yield: 2.3 g, 69 %

^{1}H NMR (400 MHz, 298 K, CDCl$_3$) δ/ppm = 6.23-7.78 (br, aryl), 2.20 – 1.67 (m, br, alkyl), 1.60 - 1.16 (br, alkyl).

^{31}P NMR (162 MHz, 295 K, CDCl$_3$) δ/ppm =20.7 (br).

GPC Data: M_n = 17800 g/mol, Đ = 1.20.

Summary of polymerisation data

Table S1. Summary of polymerisation data and example of mol% calculation for catalysis.

	Feed ratio		Average units per chain (theoretical)		M_n (theoretical)	M_n (GPC)	Đ
	Styrene	Functional Monomer	Styrene	Functional Monomer			
Poly(PPNCl)-5	95	5	152	8[a]	20500	17800	1.2
Poly(PPNCl)-10	90	10	144	16[a]	24300	19600	1.2
Poly(BPh$_3$)	95	5	91	10[b]	14100	15600	1.3

[a] In the absence of detectable unpolymerised monomer signals in the crude NMR spectra of poly(PPNCl)-5 and poly(PPNCl)-10, complete conversion was assumed. Theoretical average units were consequently determined using molar feed ratios.

[b] Calculated considering conversions found in crude NMR spectra relative to the internal standard.

All mol% values reported for catalytic reactions utilised the theoretical average units of functional monomer.
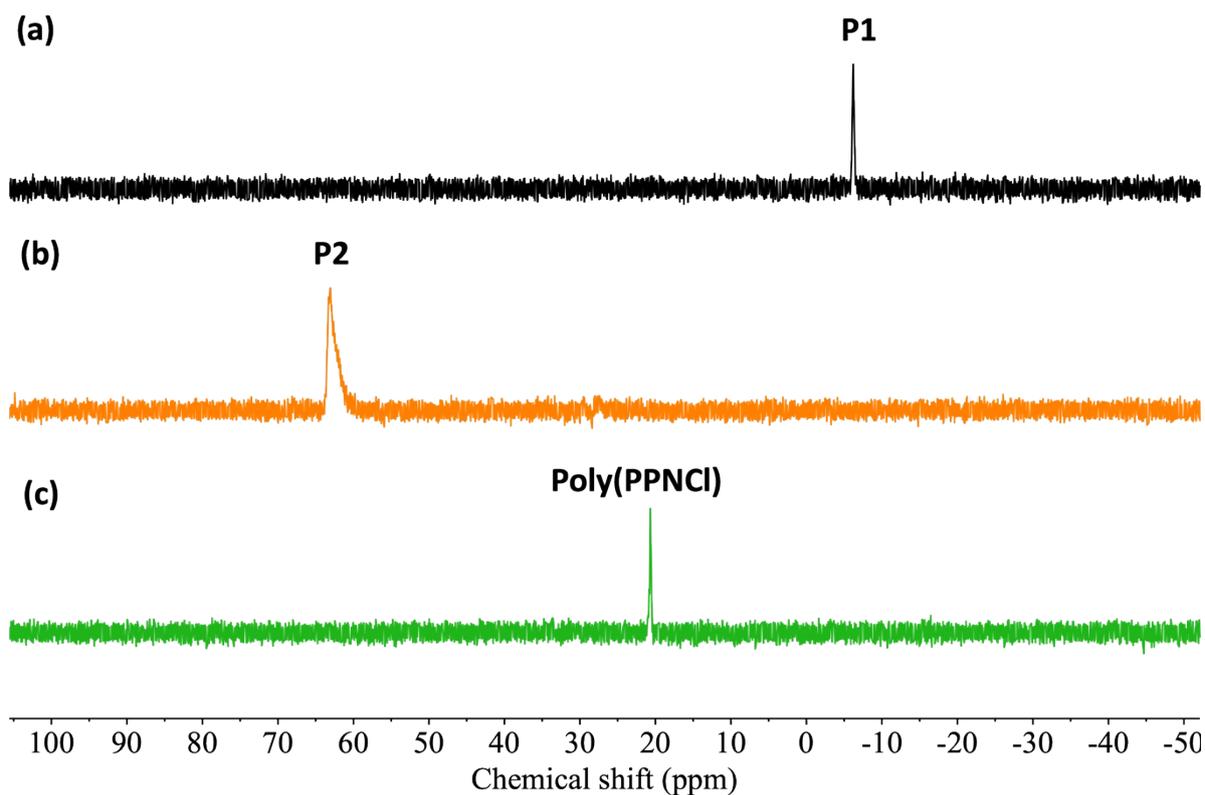
Figure S1. ^{31}P NMR spectroscopy in CDCl$_3$ of (a) **P1**; (b) **P2** and (c) **poly(PPNCl)-10**.
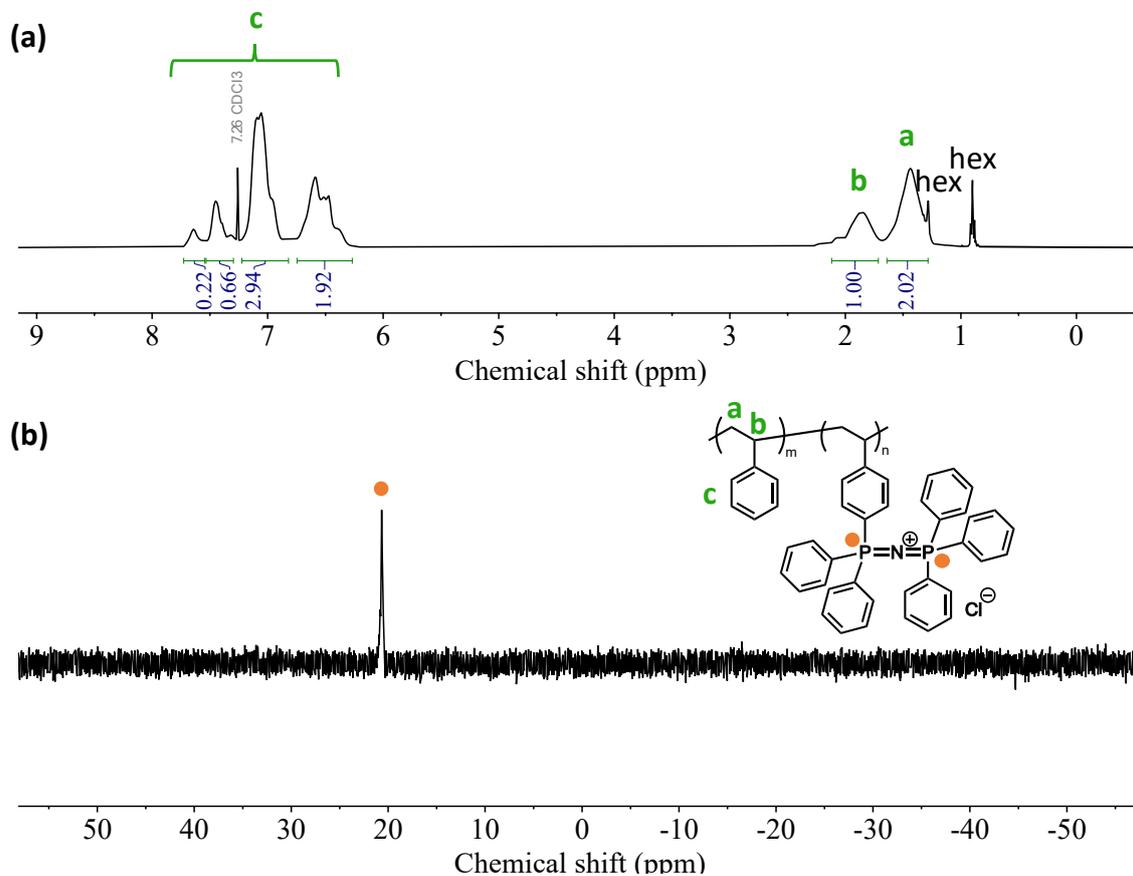
Figure S2. NMR spectroscopy of purified **poly(PPNCl)-10** in CDCl$_3$ (a) ^{1}H NMR and (b) ^{31}P NMR.
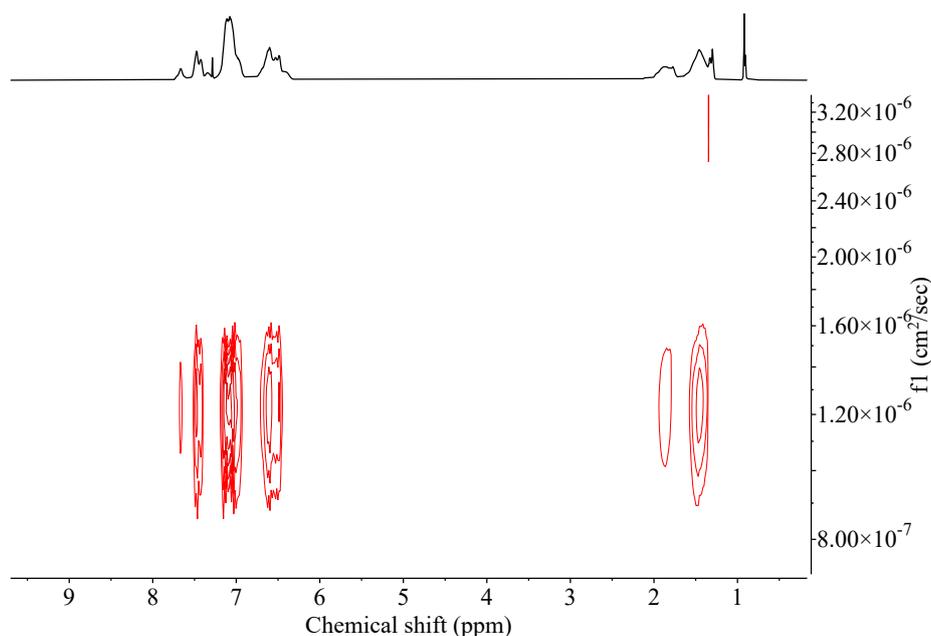
Figure S3. Diffusion order spectroscopy (DOSY) of **poly(PPNCl)-10** in CDCl$_3$.

For further identification of poly(PPNCl), a series of characterisations were performed. The GPC traces are given in Figure S4a to determine the number-molecular weight (M$_n$). The chromatogram displays that both **poly(PPNCl)-5** and **poly(PPNCl)-10** show a monodisperse distribution and their polymerisation data are summarised in Table S1. TGA was carried out to determine the degradation behaviour as depicted in Figure S4b. For **poly(PPNCl)-10**, two distinct stages of change can be observed: the first stage of mass loss from 300 to 450 °C represents the degradation of the polymer backbone, and the second stage started around 450 °C and reached a maximum degradation temperature at 600 °C, which attributed to the pyrolysis of PPNCl group in the side chains. Compared to **poly(PPNCl)-10**, **poly(PPNCl)-5** has a lower temperature at around 400 °C for the start of the second stage due to the fewer PPNCl loading in the polymer chains. As DSC curves shown in Figure S4c, **poly(PPNCl)-5** and **poly(PPNCl)-10** exhibit a glass-transition temperature at around 108 °C and 115 °C, respectively. A shoulder at 112 °C was observed in both conditions which may be attributed to the blocky nature of poly(PPNCl). The FTIR spectrum of poly(PPNCl) was presented in Figure S4d. It was observed that there is not much difference between **poly(PPNCl)-5** and **poly(PPNCl)-10**. The two absorptions in the region between 3020 and 3080 cm^{-1} are related to the vibrations of C-H bonds on the phenyl ring. The peaks ranging from 2840 to 2920 cm^{-1} are attributed to the existence of methylene and methine vibrations in the polymer backbone. Resonances around 1500 cm^{-1} are due to the aromatic C=C stretching vibration. The bands

around 750 cm^{-1} are assigned to C-H out-of-plane bending. Importantly, the evident absorptions in the region between 1100 and 1480 cm^{-1} correspond to the vibration of P=N bonds according to similar observations reported in the literature,[6] further indicating the formation of poly(PPNCl).
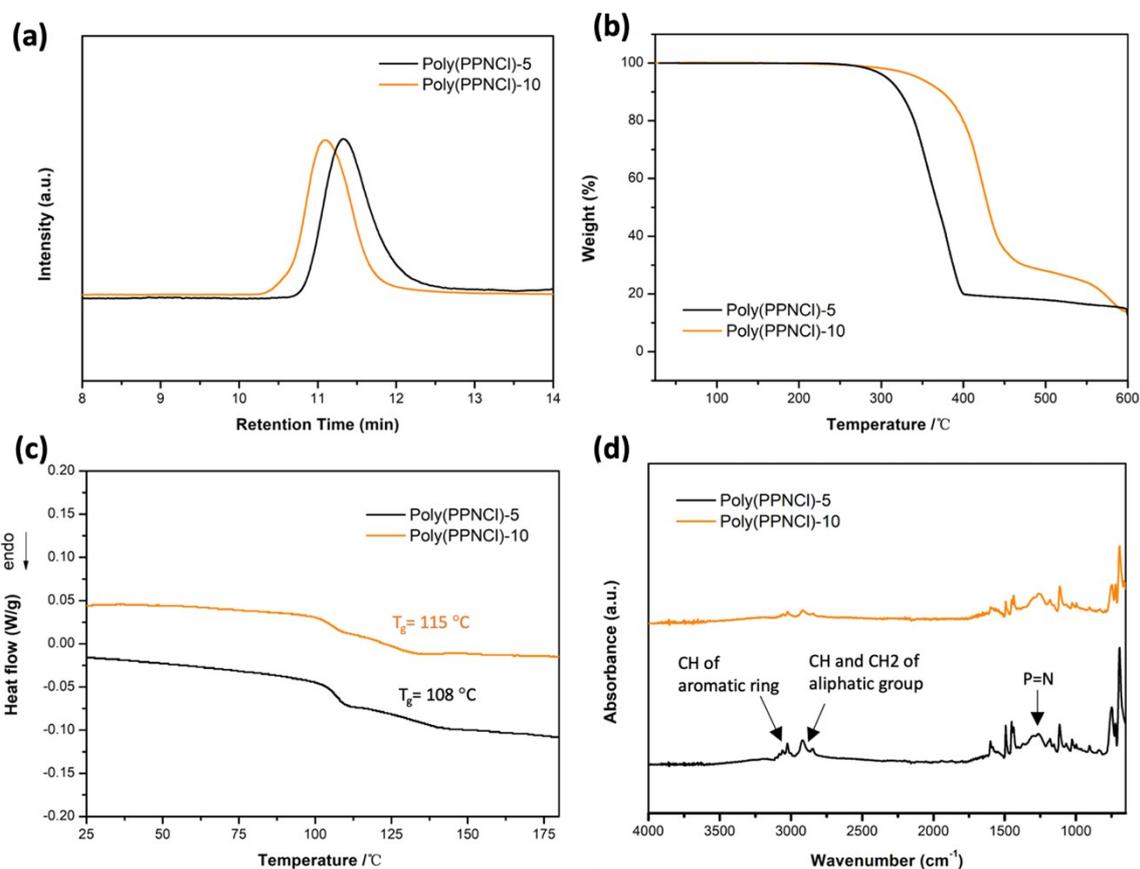
Figure S4. Poly(PPNCl) characterization (a) Gel permeation chromatography (GPC) trace; (b) Thermogravimetric analysis (TGA); (c) The second-run curve of Differential scanning calorimetry (DSC); and (d) Fourier transform infrared spectroscopy (FTIR).

Halogen-exchange reaction

General procedure for halogen-exchange reaction

In a glovebox, 4-chloronitrobenzene (158 mg, 1.0 mmol), potassium fluoride (70 mg, 1.2 mmol), poly(PPNCl) and dimethyl sulfoxide were mixed in a vial. Then the vial was sealed and removed to a fume hood and heated at 150 °C for 8 h. After cooling, a small amount of the crude product was used for NMR spectroscopy to determine the conversion.

Table S2. Catalytic Data for the halogen-exchange reaction catalysed by poly(PPNCl)

Entry	Catalyst	CNB Concentration (M)	Solvent	Conversion (%) [a]
1	PPNCl	2	DMSO	81
2	Poly(PPNCl)-10	2	DMSO	64
3	Poly(PPNCl)-5	2	DMSO	80
4 [b]	Poly(PPNCl)-5	2	DMSO	82
5 [c]	Poly(PPNCl)-5	2	DMSO	89
6	Poly(PPNCl)-5	2	MeOH	33
7	Poly(PPNCl)-5	2	DMF	66
8	Poly(PPNCl)-5	0.5	DMSO	44
9	Poly(PPNCl)-5	1	DMSO	62
10	Poly(PPNCl)-5	3	DMSO	63
11	Poly(PPNCl)-5	4	DMSO	54

General reaction conditions: all reactions were conducted at 150 °C for 8 h, the feed ratio of CNB: KF: Catalyst= 1: 1.2: 0.04. [a] Determined by ^{1}H NMR spectroscopy; [b] The feed ratio of CNB: KF: Catalyst= 1: 1.5: 0.04; [c] The feed ratio of CNB: KF: Catalyst= 1: 1.5: 0.02.
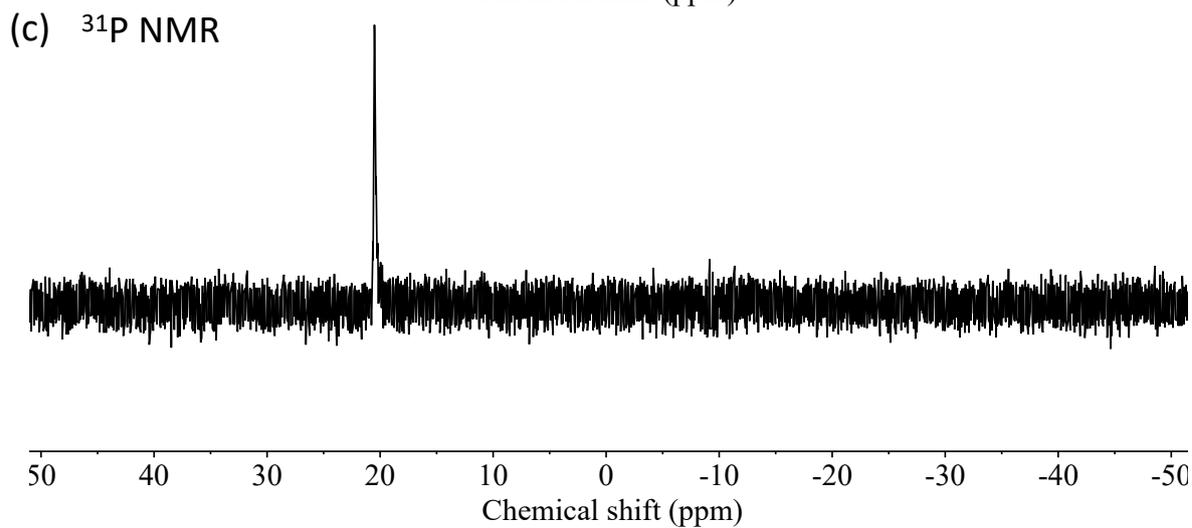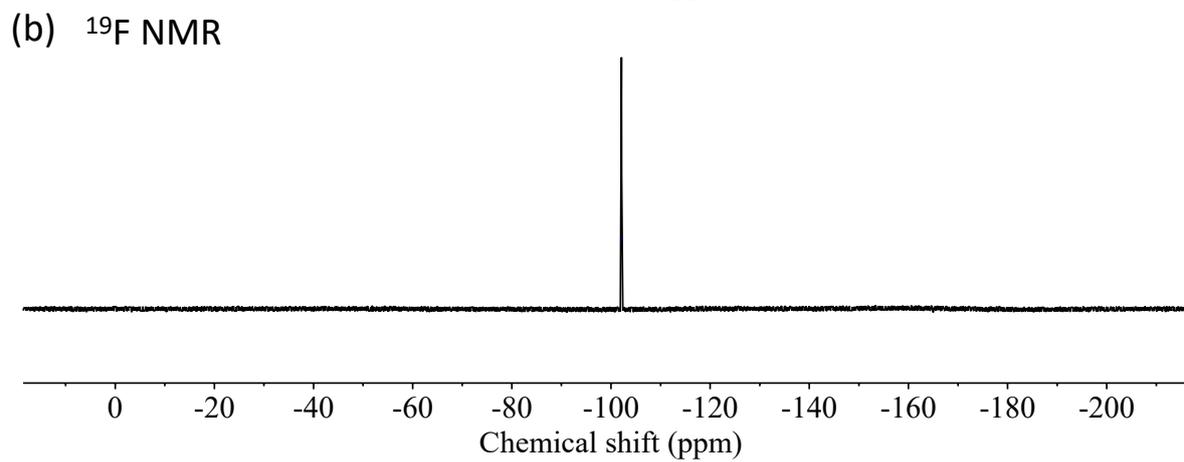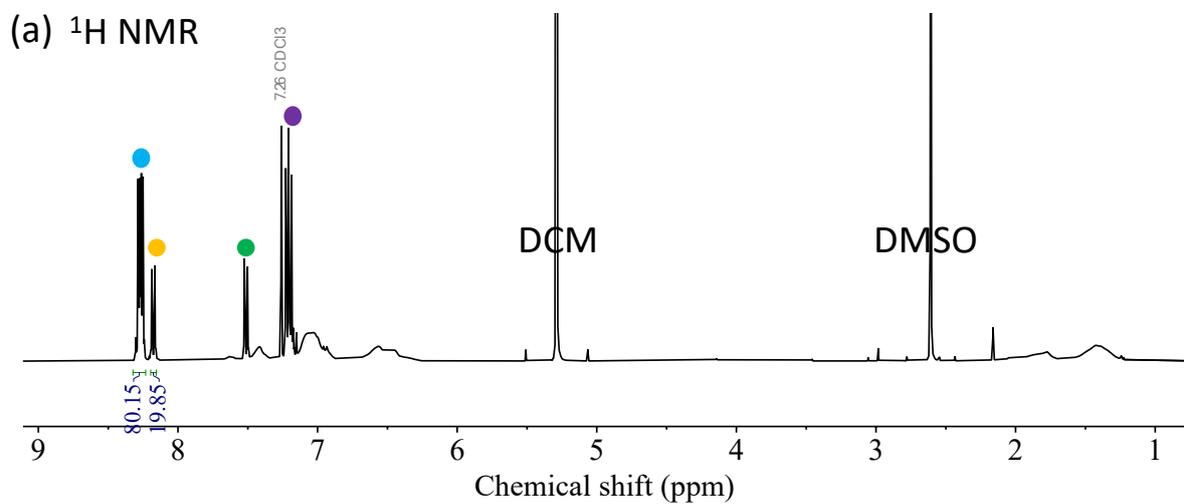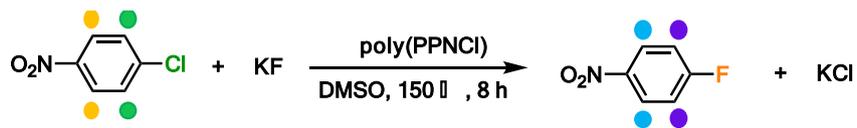
Figure S5. NMR spectroscopy of crude product in CDCl$_3$ in Table S2, Entry 3. (a) ^{1}H NMR; (b) ^{19}F NMR; (c) ^{31}P NMR.

Substrate Screen

(a) 89%

(b) 5%

(c) N.R.

(d) N.R.

(e) N.R.

(f) N.R.
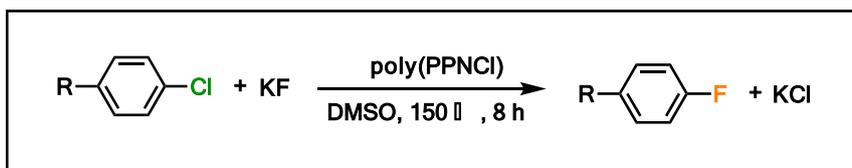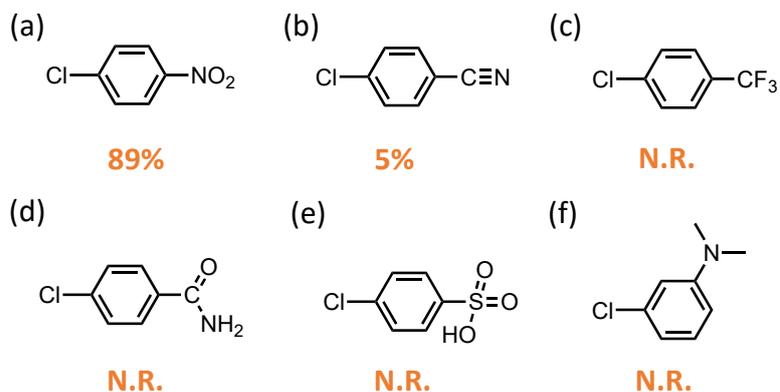
Figure S6. Substrate screen in the halogen-exchange reaction. (a) 1-chloro-4-nitrobenzene (b) 4-Chlorobenzonitrile (c) 1-Chloro-4-(trifluoromethyl)benzene (d) 4-Chlorobenzamide (e) 4-Chlorobenzenesulfonic acid (f) 3-Chloro-N,N-dimethylbenzenamine; General reaction conditions: all reactions were conducted at 150 °C for 8 h. Substrate: KF: poly(PPNCl) = 1: 1.2: 0.02. Conversion of substrates was in orange and determined by ^{1}H NMR spectroscopy (N.R. = no reaction).
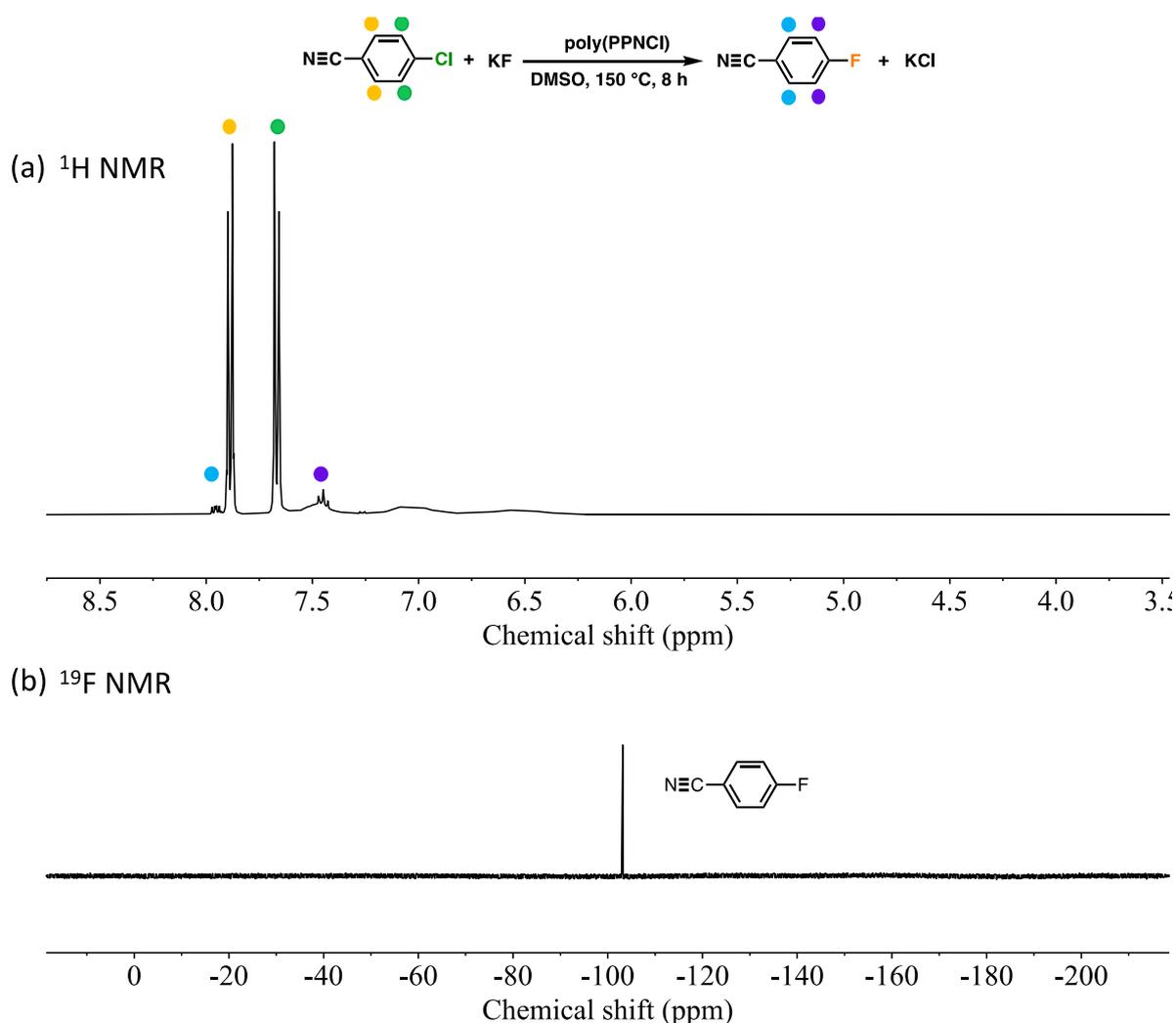
Figure S7. NMR spectroscopy of crude product in CDCl₃ (a) ¹H NMR; (b) ¹⁹F NMR.

CO$_2$ coupling reactions with epoxides

General procedure for CO$_2$ coupling reactions with epoxides

In a glovebox, poly(PPNCl) (40.1 mg, 1.28 μmol PPNCl moieties) and 1,3,5-trimethoxybenzene internal standard (0.11 g, 0.70 mmol) (resonances at 6.1 and 3.7ppm in ¹H NMR spectroscopy) were charged in a round-bottom ampoule before addition of desired cyclic ether substrate (12.8 mmol). A small portion was taken and diluted for t_0 analysis by ¹H NMR spectroscopy. The ampoule was then sealed with a Young's tap and removed from the glovebox and was then linked to a Schlenk line connected to a CO$_2$ cylinder through a 3-way joint. The reaction mixture underwent three freeze-pump-thaw cycles to remove gas before returning to room temperature. CO$_2$ was then introduced and the ampoule was sealed before being placed in an oil bath at 100 °C for the required reaction duration.
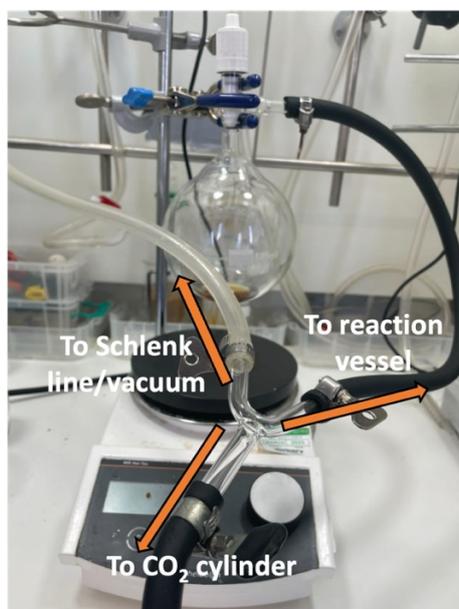
Figure S8. Reaction setup for CO_2 loading to the reaction vessel containing catalyst and epoxide substrate (Note: A balloon would be insufficient due to the variation of CO_2).

CO_2 coupling reactions with GC

Table S3. Catalytic data for CO_2 insertion to GC

Entry	Poly(PPNCl) (mol%)	CO_2 pressure (bar)	Reaction time (h)	Conversion (%) [a]
1	0	1	24	0
2	0.1	1	24	66
3	0.2	1	24	83
4	0.4	1	24	98
5	0.1	1.5	24	67
6	0.1	2	24	66
7	0.1	5	24	61
8 [b]	0	1	24	0
9 [c]	0.1	1	24	48
10	0.1	1	3	22
11	0.1	1	6	32
12	0.1	1	12	40
13	0.1	1	15	50
14	0.1	1	18	55
15	0.1	1	48	89
16 [d]	0.1	1	24	66

General reaction conditions: reactions were carried out in a sealed ampoule on a 12.8 mmol scale of GC and poly(PPNCl) without additional solvent (mol% as calculated from the number of expected active functional

groups) at 100°C; [a] Determined by ^1H NMR spectroscopy; [b] Conducted with only 0.1 mol% BPh_3 as a catalyst; [c] Conducted 0.1 mol% poly(PPNCl) and 0.1 mol% BPh_3. [d] Setup under ambient atmosphere.
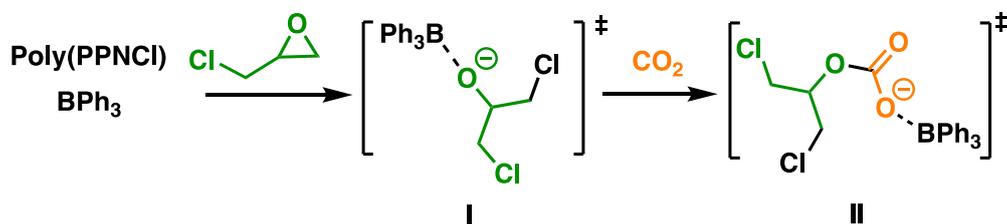
Figure S9. Proposed catalytic process in the GC/ poly(PPNCl)/ BPh_3 system.
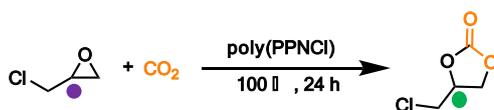
(a) ^1H NMR
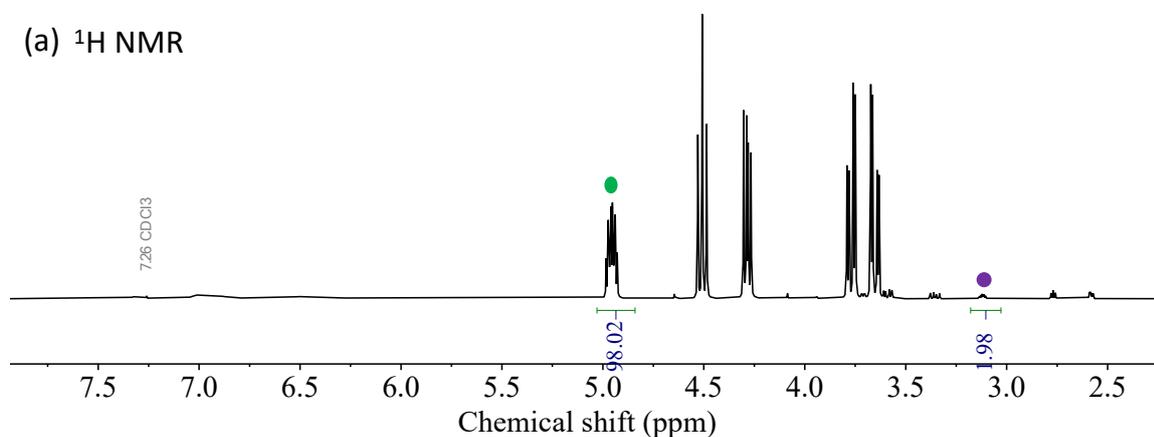
(b) ^{31}P NMR
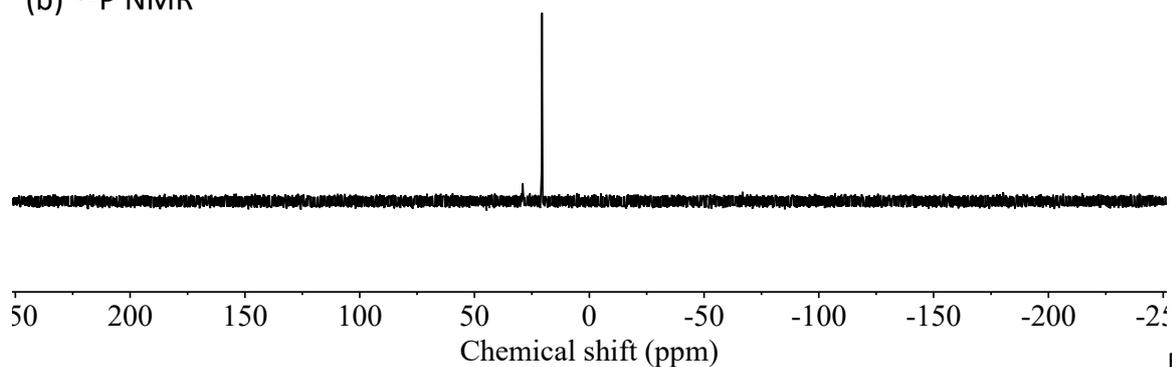
re S10. NMR spectroscopy of crude cyclic product (Table S2, Entry 4) in $CDCl_3$. (a) ^1H NMR; (b) ^{31}P NMR.

Kinetic study of CO₂/GC coupling reaction

Reactions for the kinetic study of GC/CO_2 coupling were carried out in a sealed ampoule on a 12.8 mmol scale of GC and 0.1 mol% poly(PPNCl) without additional solvent (mol% as calculated from the number of expected active functional groups) at 100°C for desired time.

After cooling, a small amount of the crude product was taken for ^{1}H NMR spectroscopy to determine the conversion of GC. The kinetic studies data is summarized in Figure S11.
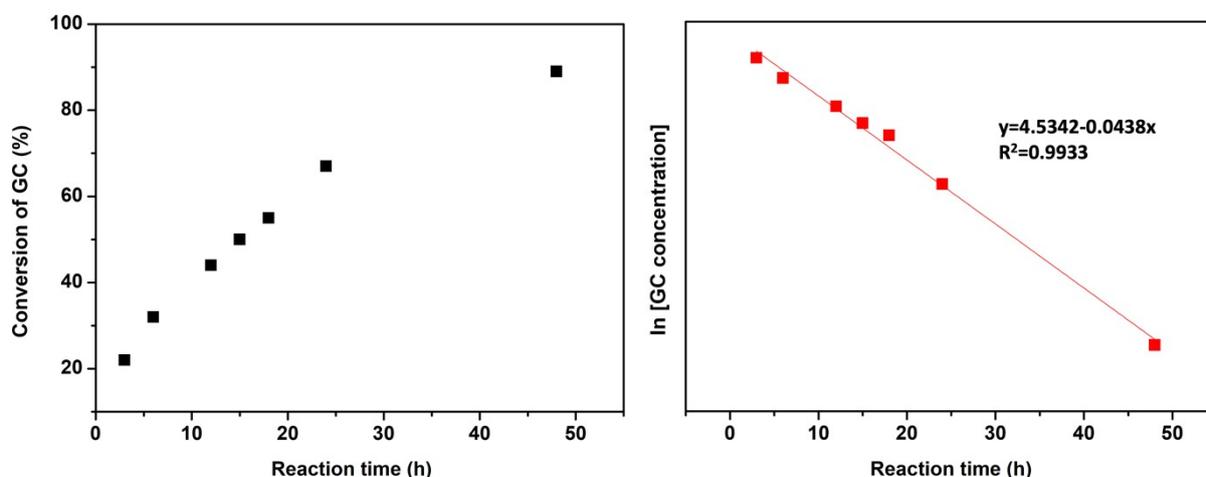
Figure S11. Kinetic studies of GC/CO$_2$ coupling reactions. (a) GC conversion vs reaction time (b) Curve fitting of In[GC] as a function of reaction time.

In the CO$_2$/epoxides coupling reaction, Cl$^-$ acts as the nucleophilic group, while both PPN$^+$ in polymer and BPh$_3$ can activate the epoxide through coordination. However, the PPN$^+$ was less able to interact with the epoxides compared to BPh$_3$, due to its steric bulk and the larger radius of the phosphorus atom. Here, we propose a catalytic mechanism for the GC/poly(PPNCl) system as shown in Scheme S1. The poly(PPN$^+$) activates GC by the interaction of the PPN$^+$ phosphorus ion with the oxygen atom (Step 1), Cl$^-$ then attacks the less-hindered electrophilic carbon atom of GC, opening the epoxide ring to form a dichlorinated intermediate (Step 2). The dichlorinated intermediate then attacks the electrophilic carbon of CO$_2$ to form the carbonate anion intermediate (Step 3). The carbonate anion intermediate then undergoes intramolecular nucleophilic addition to the chlorine-attached carbon atom to form the cyclic carbonate product with the elimination of the chloride anion nucleophile and PPN cation (Step 4).
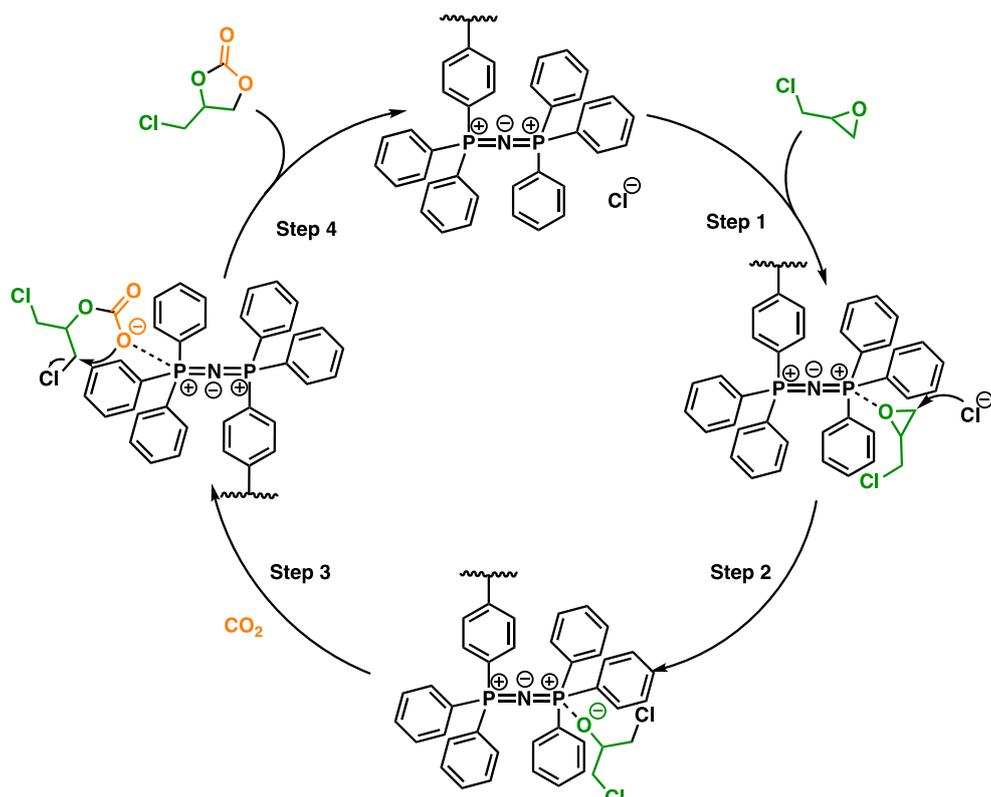
Scheme S1. A proposed catalytic mechanism in the CO_2 coupling reactions with GC catalysed by poly(PPNCl).

CO_2 coupling reactions with PO

Table S4. Catalytic data for CO_2 insertion to PO

Entry	Poly(PPNCl) (mol%)	BPh₃ (mol%)	CO₂ pressure (bar)	Conversion (%) [a]
1	0.1	0	1	2
2	0.1	0	1	9
3	0	0.1	1	0
4	0.1	0.1	1	48
5 [b]	0.1	0.1	1	63
6	0.1	0.1	1.5	43
7	0.1	0.1	2	49
8	0.1	0.1	5	47
9	0.2	0.2	1	71
10	0.1	0.1 [c]	1	50

General reaction conditions: reactions were carried out in a sealed ampoule on a 12.8 mmol scale of PO and poly(PPNCl)/BPh₃ (mol% as calculated from the number of expected active functional groups) in 1 mL toluene (to prevent evaporation of PO during the reaction) at 100°C for 24 h; [a] Determined by ^1H NMR spectroscopy; [b] Reaction time = 48 h; [c] Poly(BPh₃) used in place of BPh₃.

Due to the lower reactivity of PO, the addition of BPh_3 is necessary to better activate it (Table S4, Entry 4). The catalytic mechanism in the presence of both poly(PPNCl) and BPh_3 was proposed as shown in Scheme S2.
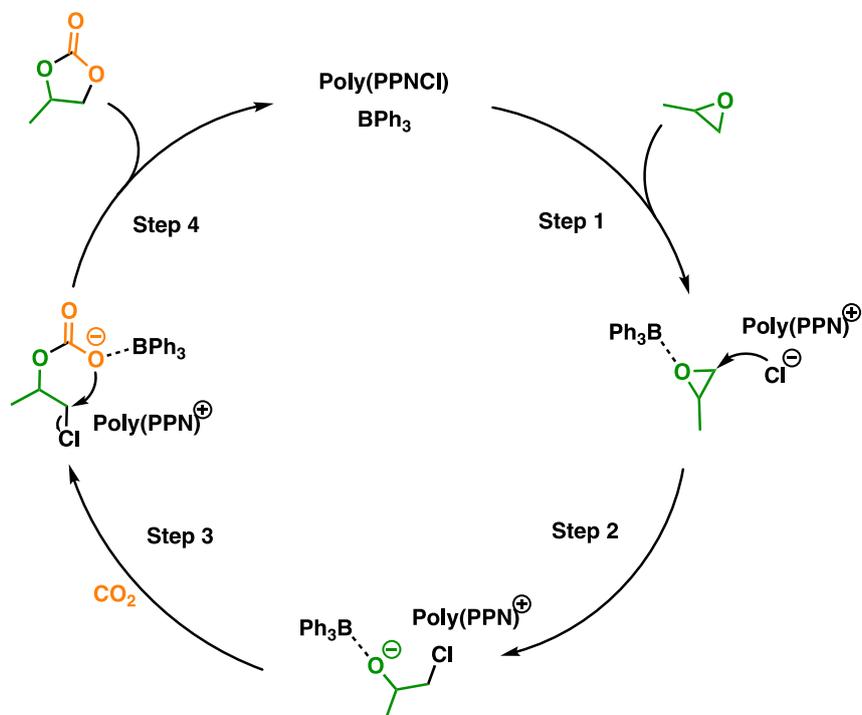
Scheme S2. A proposed catalytic mechanism in the CO_2 coupling reactions with PO catalysed by poly(PPNCl)/BPh_3

(a) ^1H NMR
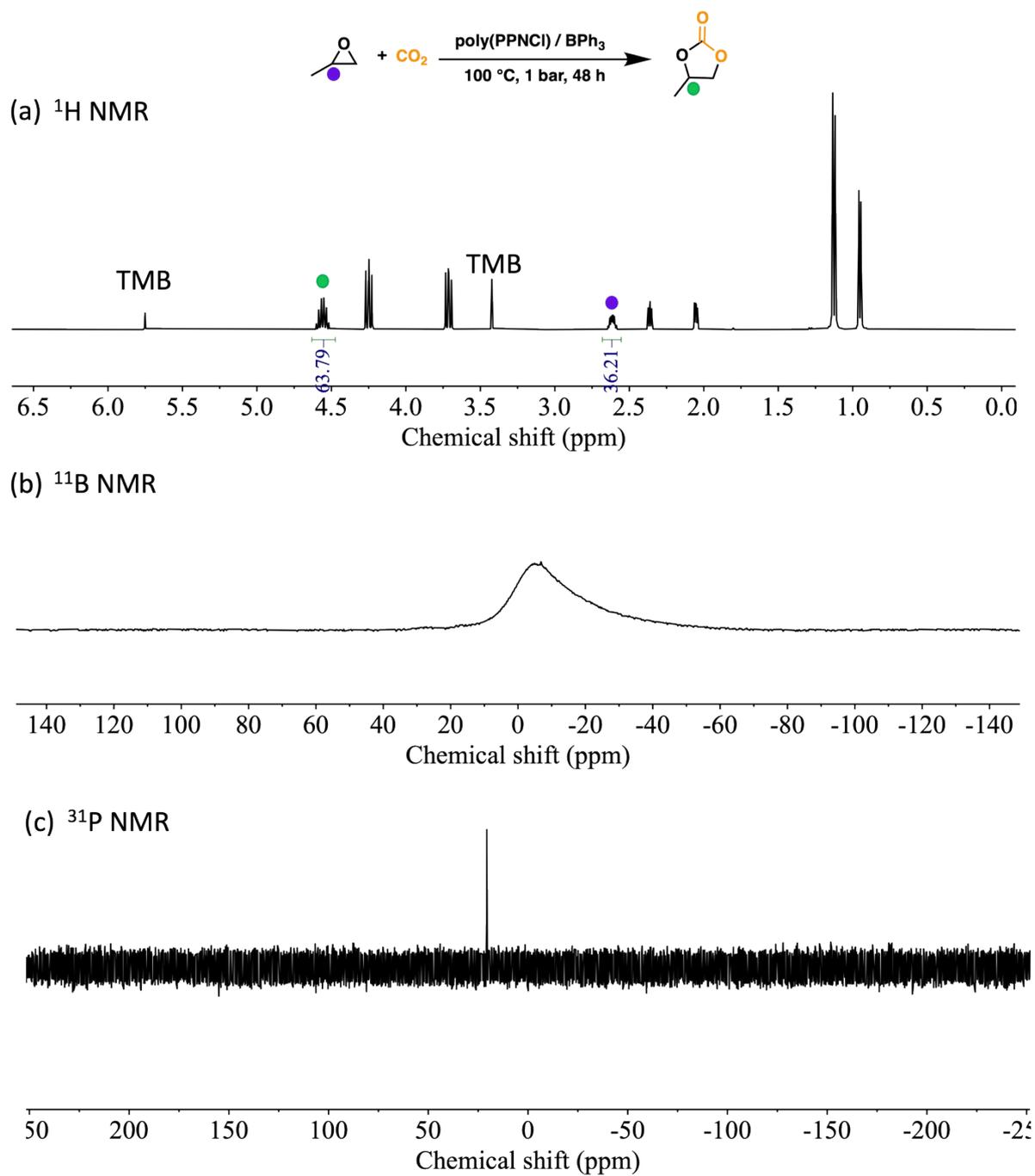
(b) ^{11}B NMR

(c) ^{31}P NMR

Figure S12. NMR spectroscopy of crude product (Table S4, Entry 5) in CDCl$_3$. (a) ^1H NMR; (b) ^{11}B NMR; (c) ^{31}P NMR.

Substrate screen

For the poly(PPNCl)/BPh₃ catalytic system, it was observed that the conversion of all epoxides screened increased when prolonging reaction times to 48 h, as shown in Table S5. Due to the lack of differences observed in GC and PO reactions in Figure S3, the experiments in Table S5 were only run once.

Table S5. Conversion of epoxides catalysed by poly(PPNCl)/BPh₃

Entry	Substrate	Conversion (%)
1	Cl—epoxide	66
2	epoxide	61
3	Ph—epoxide	52
4	epoxide	37
5	epoxide	50
6	cyclohexene oxide	12
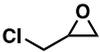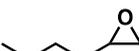
General reaction conditions: reactions were carried out in a sealed ampoule on a 12.8 mmol scale of epoxide and 0.1 mol% poly(PPNCl)/BPh₃ at 100°C for 48 h. Conversion was determined by ^1H NMR spectroscopy.
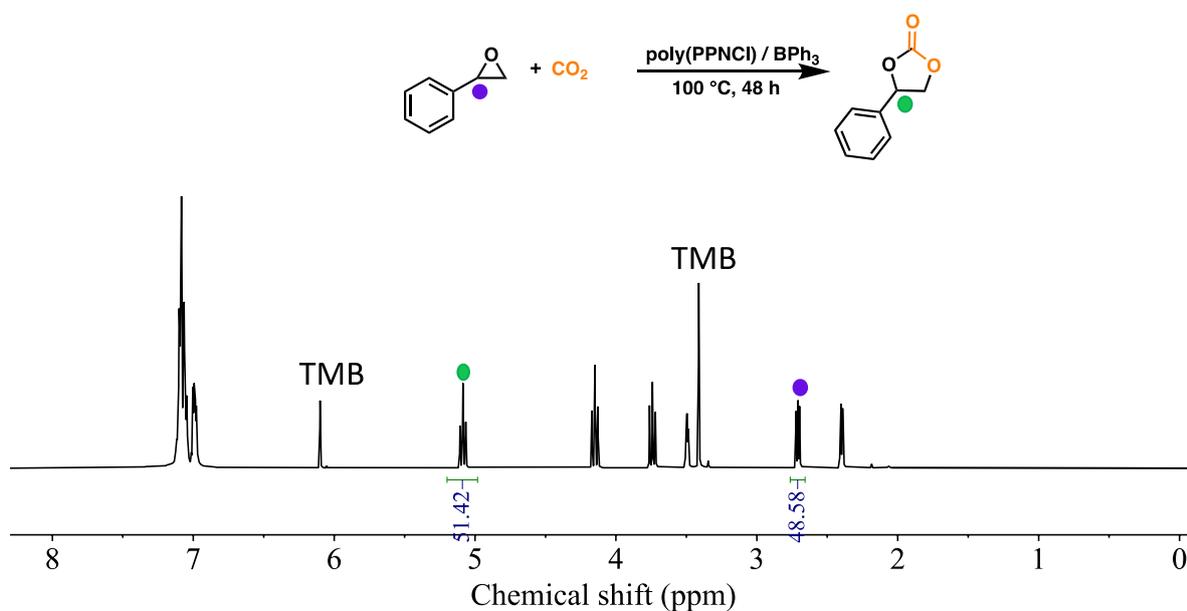
Figure S13. ^1H NMR spectroscopy of crude cyclic product (Table S5, Entry 3) in CDCl₃.
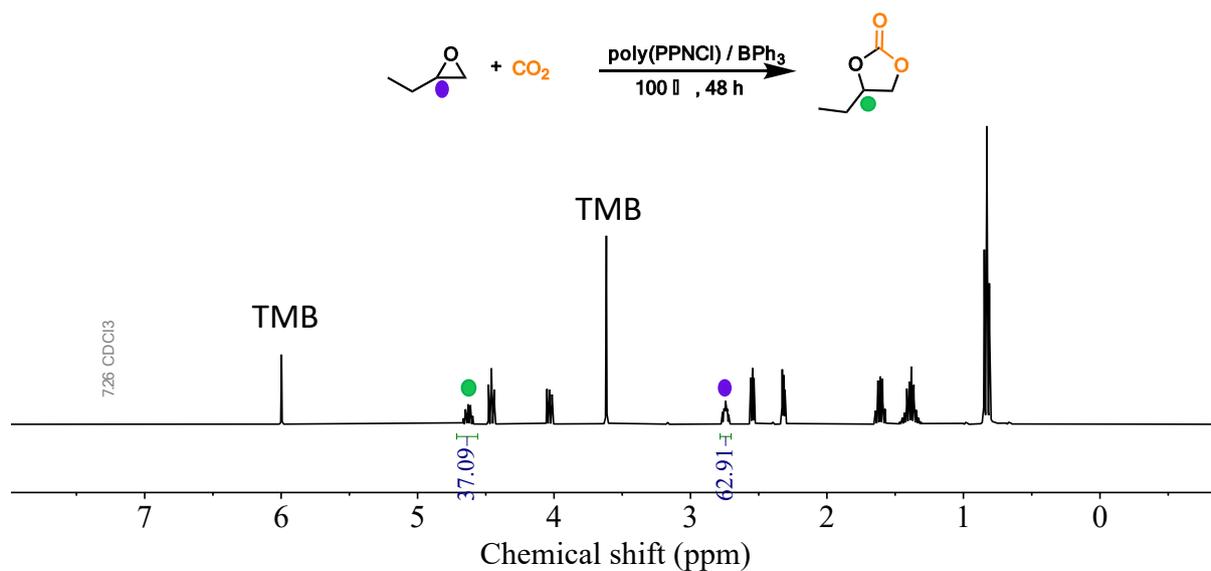
Figure S14. ^{1}H NMR spectroscopy of crude cyclic product (Table S5, Entry 4) in CDCl$_3$.
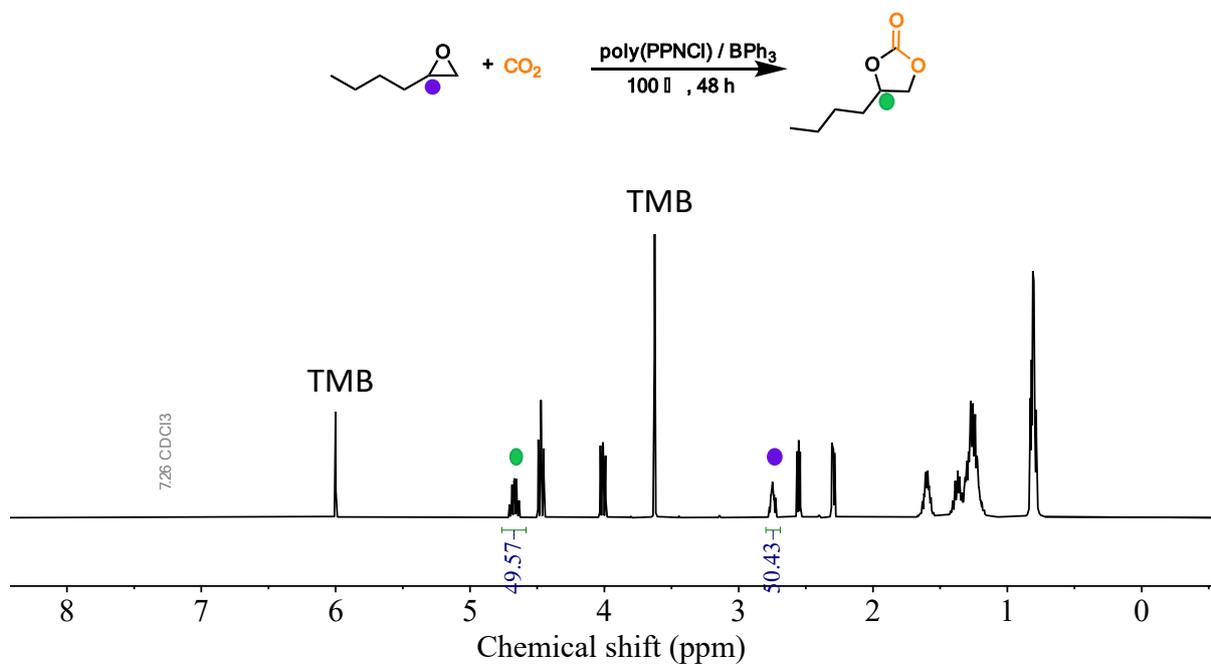
Figure S15. ^{1}H NMR spectroscopy of crude cyclic product (Table S5, Entry 5) in CDCl$_3$.
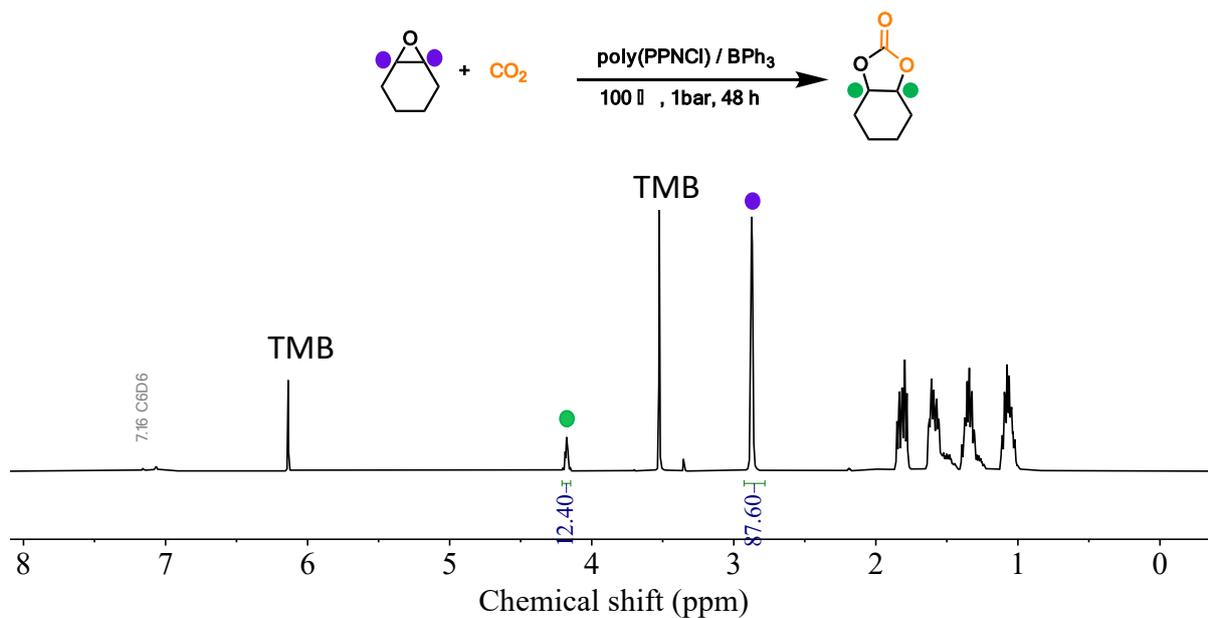
Figure S16. ^{1}H NMR spectroscopy of crude cyclic product (Table S5, Entry 5) in CDCl$_3$.
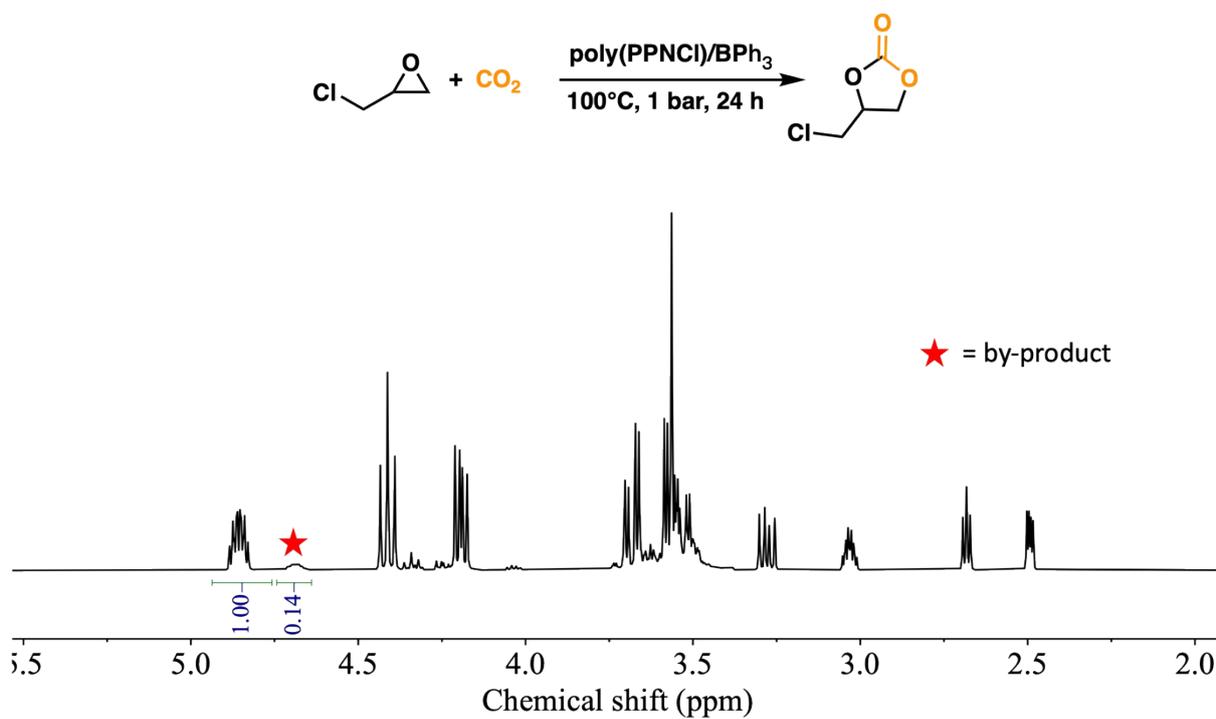
Figure S17. ^{1}H NMR spectroscopy of crude cyclic product (Table S3, Entry 9) in CDCl$_3$.
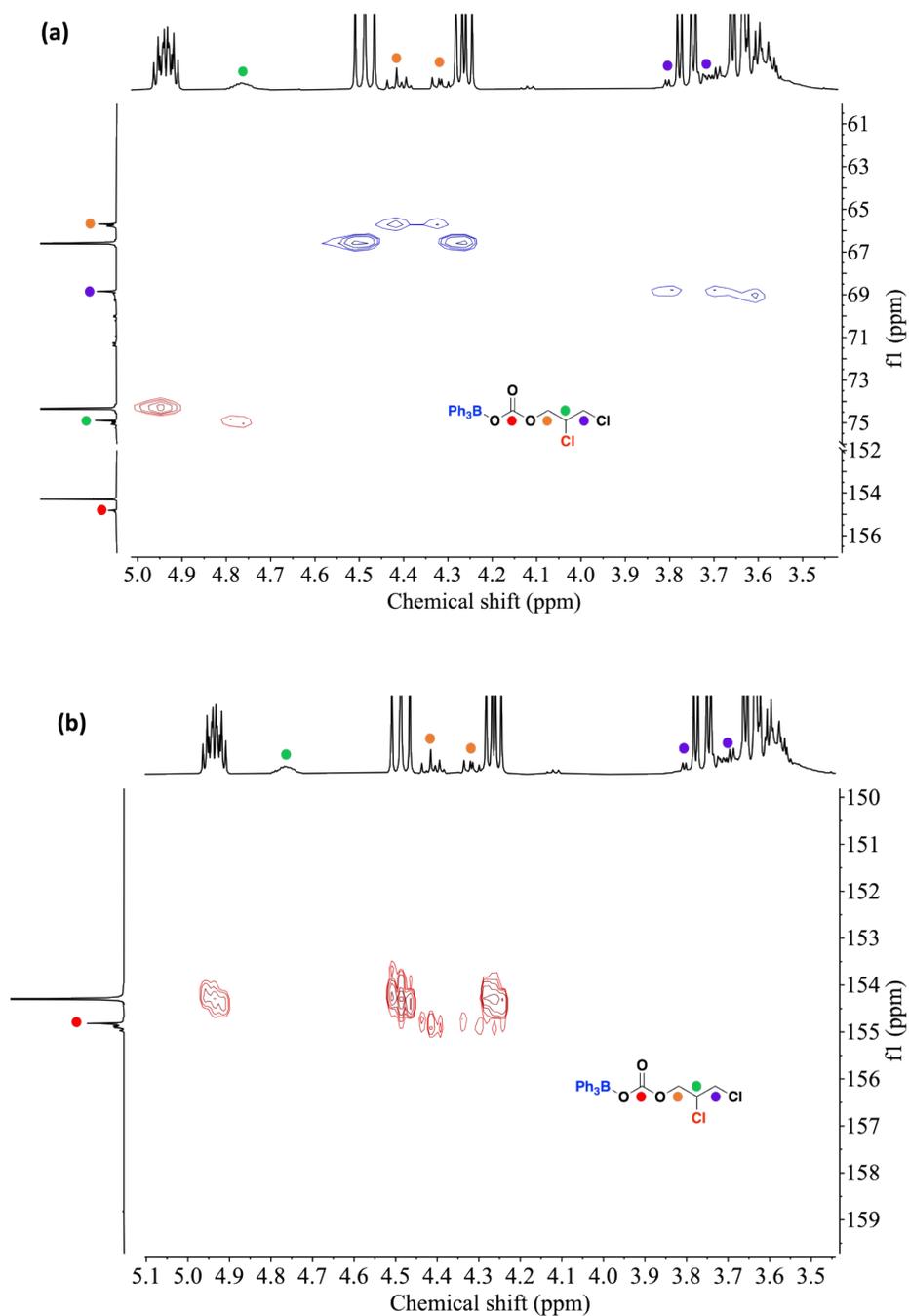
Figure S18. 2D NMR analysis of crude chloropropene carbonate in Entry 9, Table S3. (a) HSQC analysis. (b) HMBC analysis, attack of chloride ion observed at more hindered carbon.

Catalytic selectivity towards GC and PO

GC, PO and poly(PPNCl) were combined in an ampoule with the feed ratio of 1000: 1000: 4 and performed at 1 bar CO_2 for 24 h. 4 equivalent amount of BPh_3 was then added to the ampoule and refilled with 1 bar CO_2 for another 24 h. Before the addition of BPh_3, a conversion of 97% of GC to chloropropene carbonate was achieved and 2% of PO was converted to propylene carbonate. After the addition of BPh_3, the residue GC was completely

converted to chloropropene carbonate, and the PO conversion was 74%, as shown in Scheme 3.

Catalyst recycling

The recycling of poly(PPNCl) was conducted using the halogen-exchange reaction from CNB to FNB and GC/CO_2 coupling reaction. Catalyst recycling of poly(PPNCl)/poly(BPh$_3$) binary catalytic systems was performed using the PO/CO_2 coupling reaction. According to the ^{31}P NMR spectrum of recycled poly(PPNCl) with a single resonance at the same chemical shift with the original poly(PPNCl), the decomposition of PPN during the process of catalyst recovery did not occur.

General procedure for catalyst recycling in halogen-exchange reaction

For the halogen-exchange reaction (Table S2, Entry 3) and GC/CO_2 coupling reaction (Table S3, Entry 2) used in this work, poly(PPNCl) can be isolated from the crude product by simple precipitation in n-hexane or diethyl ether under ambient atmosphere. The precipitate was subsequently filtered and rinsed with more solvent and dried under vacuum prior to weighing between each cycle.

General procedure for catalyst recycling in CO_2/epoxide coupling reaction

The recovery of poly(PPNCl) in the GC/CO_2 coupling reaction (Table S3, Entry 2) is performed in a glovebox in order to keep consistency with the recovery of the air-sensitive poly(PPNCl)/poly(BPh3) in the PO/CO_2 coupling reaction (Table S4, Entry 10). Cold anhydrous n-hexane was added to the ampoule with a reaction mixture to obtain the precipitate. Extra n-hexane in the ampoule was then removed once the precipitate settled. The precipitate (recycled catalyst) in the ampoule was subsequently rinsed with more n-hexane before drying under vacuum. The recovered catalyst in the ampoule was then used in the next reaction cycle.

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