

# Electronic Supplementary Information

## Clean and Rapid Synthesis of Double Metal Cyanide Complexes Using Mechanochemistry

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## Experimental details

### Materials

Carbon dioxide of 99.9% purity was directly used without further purification. Potassium hexacyanoferrate(III) [K<sub>3</sub>Fe(CN)<sub>6</sub>], potassium hexacyanocobaltate(III) [K<sub>3</sub>Co(CN)<sub>6</sub>], zinc chloride (ZnCl<sub>2</sub>), and tertiary butyl alcohol (tBuOH) were analytical purity and directly used unless otherwise mentioned. Propylene oxide (PO) was analytical purity and immersed in 4Å molecular sieves for 2 days before use.

A series of liquids used in this work:

liquid	purity	liquid	purity
cyclohexane	A R	N,N-dimethyl formamide (DMF)	A R
ethanol (EtOH)	A R	methanol (MeOH)	A R
chloroform (CHCl <sub>3</sub> )	A R	dimethyl sulfoxide (DMSO)	A R
acetone	A R	H <sub>2</sub> O (de-ionized water)	/
acetonitrile (ACN)	A R	1,1,1,2,3,4,4,5,5,5-decafluoropentane (DFP)	/

Polarity order of the used liquids was H<sub>2</sub>O > DMSO > MeOH > DMF > ACN > acetone > chloroform > EtOH > DFP > cyclohexane.

### Mechanochemical synthesis of complex 1

Reactions were carried out with a SPEX 8000M shaker mill, by placing a mol ratio 5:1 mixture of ZnCl<sub>2</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> into a 65 mL stainless steel jar, along with the grinding liquid and one 12.70 mm and two 6.35 mm steel balls. The mixture was ground at 50 Hz for the specified time. After the reaction finished, the products were washed by 15 mL de-ionized water to remove excessive ZnCl<sub>2</sub>, the final precipitates were dried under vacuum at 40 °C. After each use, the steel balls and jar were washed though solvent-free grinding a small amount of anhydrous sodium sulfate to ensure a clean reaction surface for the next reaction.

### Mechanochemical synthesis of complex 2

Based on a number of exploratory experiments, an intermittent grind way was found to synthesize complex 2: a mol ratio 5:1 mixture of ZnCl<sub>2</sub> and K<sub>3</sub>Co(CN)<sub>6</sub> were ground with liquids for 3 min and then paused for 7 min; such a process repeated 3 times and the total grinding time was 9 min, the next processing steps were as described above.

### Conventional solvent-based synthesis of DMC

For comparison, complexes 1 and 2 were also synthesized following the conventional ways according to the literature,<sup>1,2</sup> respectively.

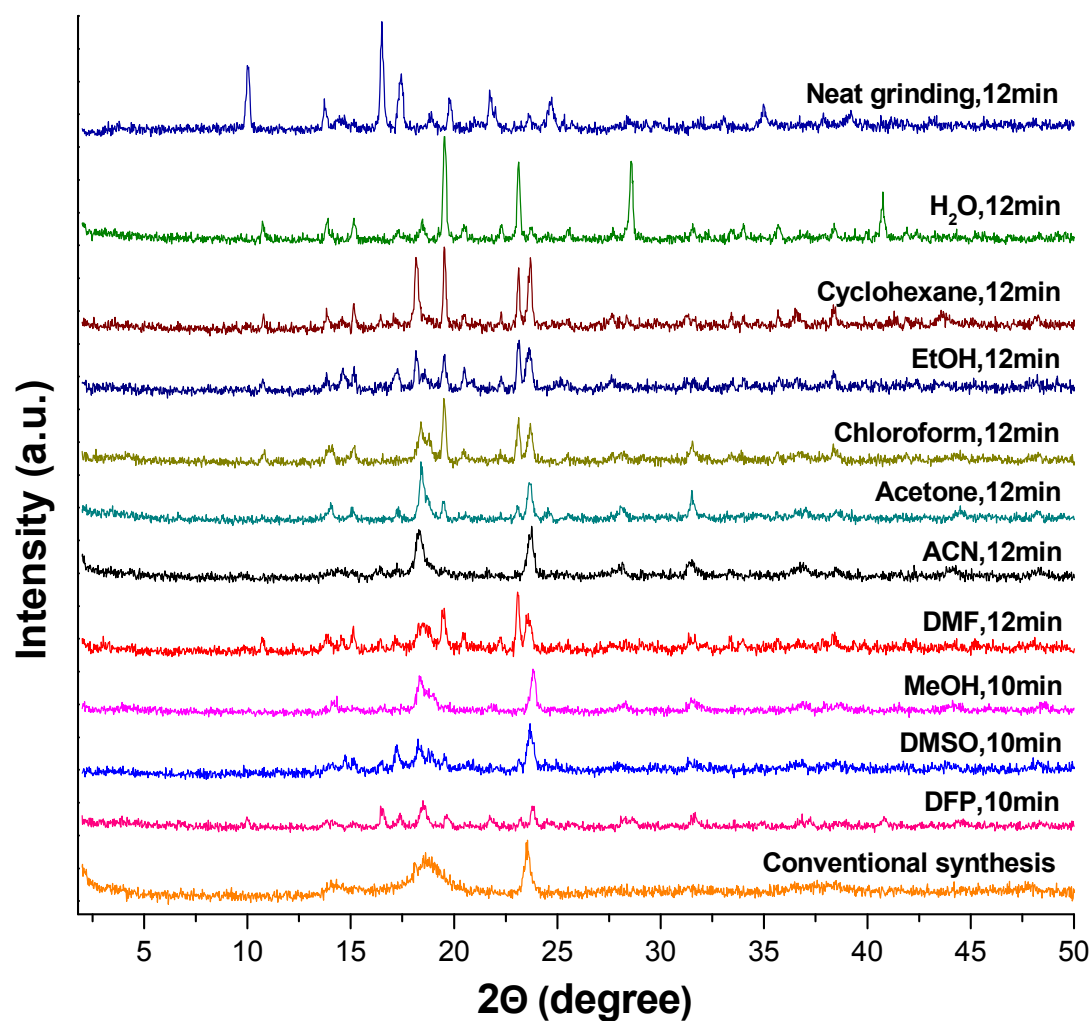
### Copolymerization of CO<sub>2</sub> and PO with DMC as catalysts

Copolymerization of CO<sub>2</sub> and PO was carried out in a 500 mL steel autoclave equipped with a magnetic stirrer, water bath heating and a check valve. Dried DMC was added into the autoclave, followed by adding a desired amount of purified PO under vacuum conditions. The autoclave was pressurized to 20 bar with CO<sub>2</sub>. Then the autoclave was heated at desired temperature with stirring. At the conclusion of copolymerization, the autoclave was cooled down to room temperature, slowly depressurized, and opened. The obtained polymer products were dissolved in acetone, stirred for 15 min, then poured into water, isolated, and dried under vacuum at 55 °C.

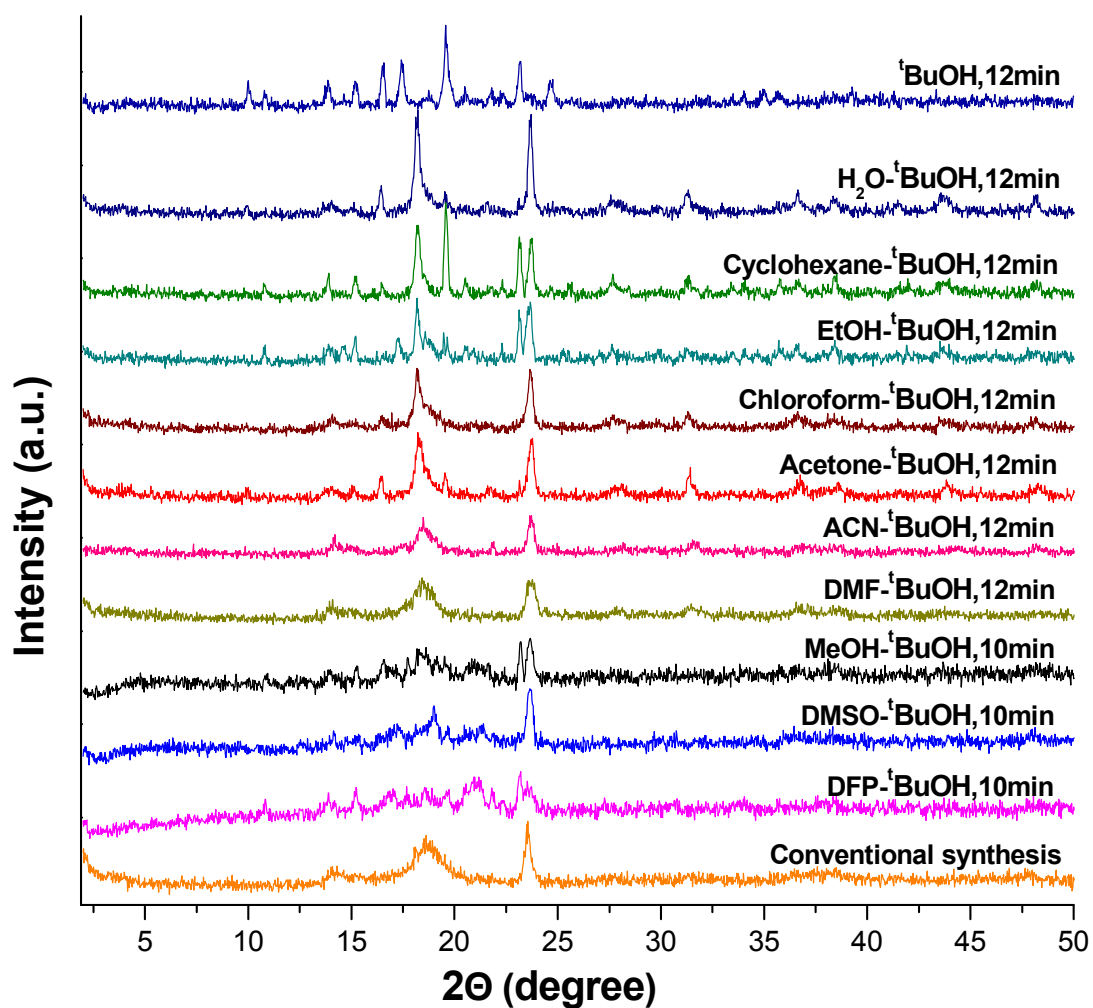
## Characterization

X-ray diffraction measurement was performed on a Bruker AXS/D8 Advance diffractometer using Cu K $\alpha$  radiation at 40 kV and 30 mA. The data were collected from 1.5° to 60° 2 $\theta$  with a step size of 0.025° 2 $\theta$  and a counting time of 0.5 s per step.

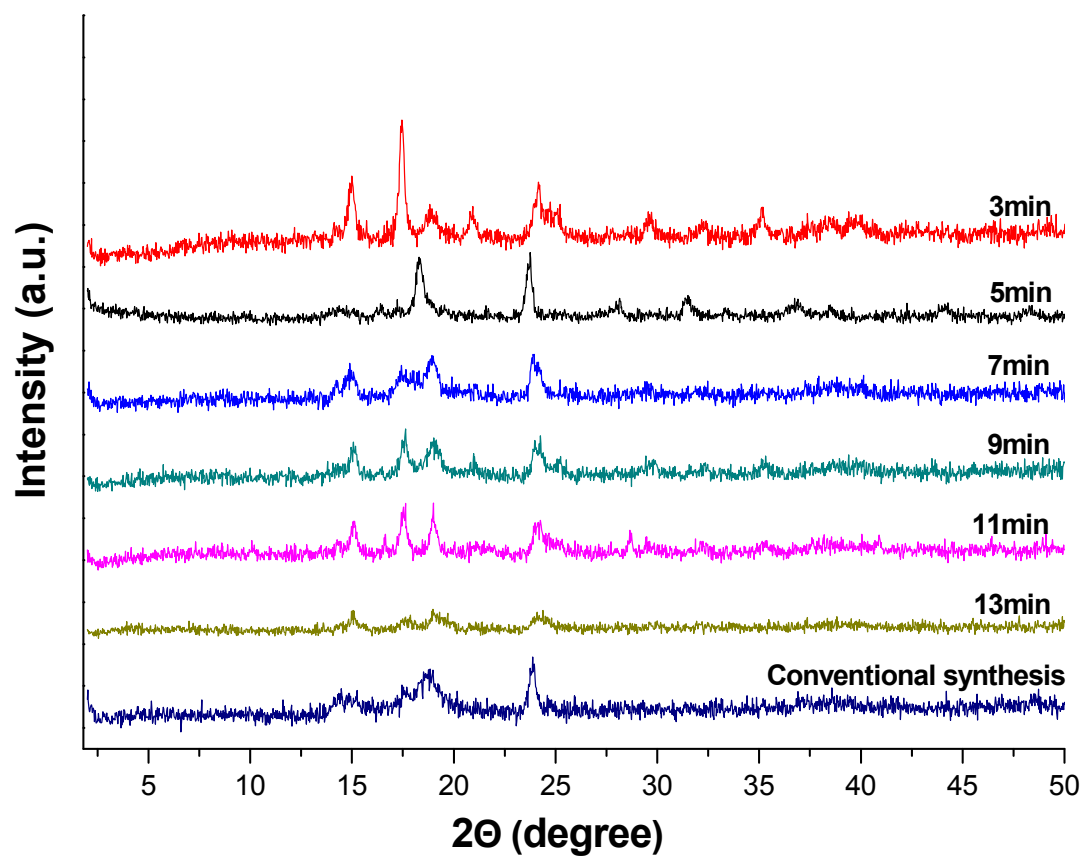
Spectroscopic analyses of polymer products were performed using a Bruker NMR spectrometer (Model: Bruker AV 400 MHz) with  $^1\text{H}$  and  $^{13}\text{C}$  probes,  $\text{CDCl}_3$  as the solvent. Number average molecular weight ( $M_n$ ) and polydispersity index (PDI) of polymer products were estimated using a gel permeation chromatography (GPC) system (Waters HPLC Pump, Waters 1515 detector) with a set of three columns (Waters Styragel 500A, 10,000A and 100,000A). The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02 supplied from Shodex Inc. Tetrahydrofuran (THF, HPLC grade) was used as an eluent.



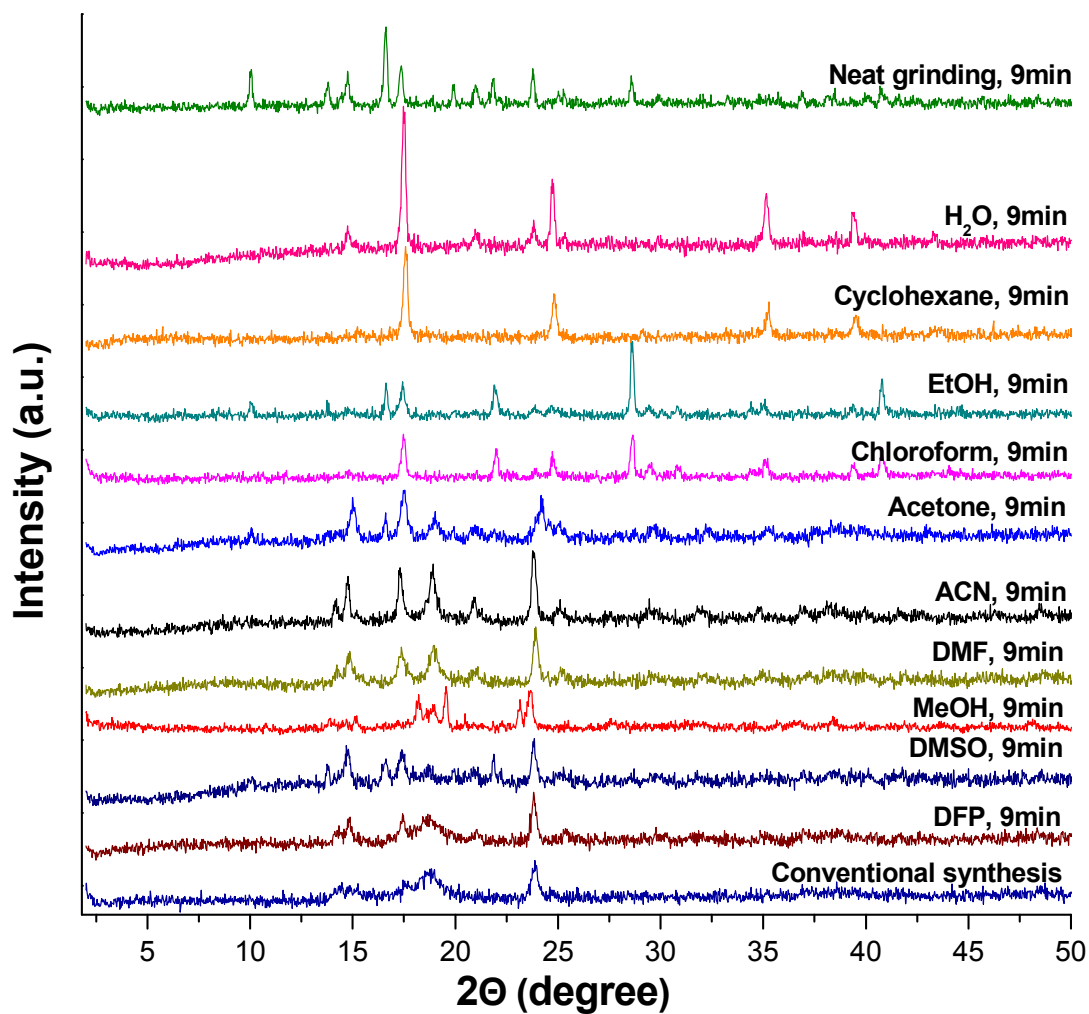
**Figure S1** Comparisons of XRPD patterns for synthesis of **1** by grinding ZnCl<sub>2</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> using LAG at 50 Hz. The volume of the added solvent is 300 μL. <sup>t</sup>BuOH-after way is used.



**Figure S2** Comparisons of XRPD patterns for synthesis of **1** by grinding ZnCl<sub>2</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> using LAG at 50 Hz. <sup>t</sup>BuOH-with way is used with a <sup>t</sup>BuOH to liquid volume ratio of 1:1. The total volume of the added solvent is 300 μL.

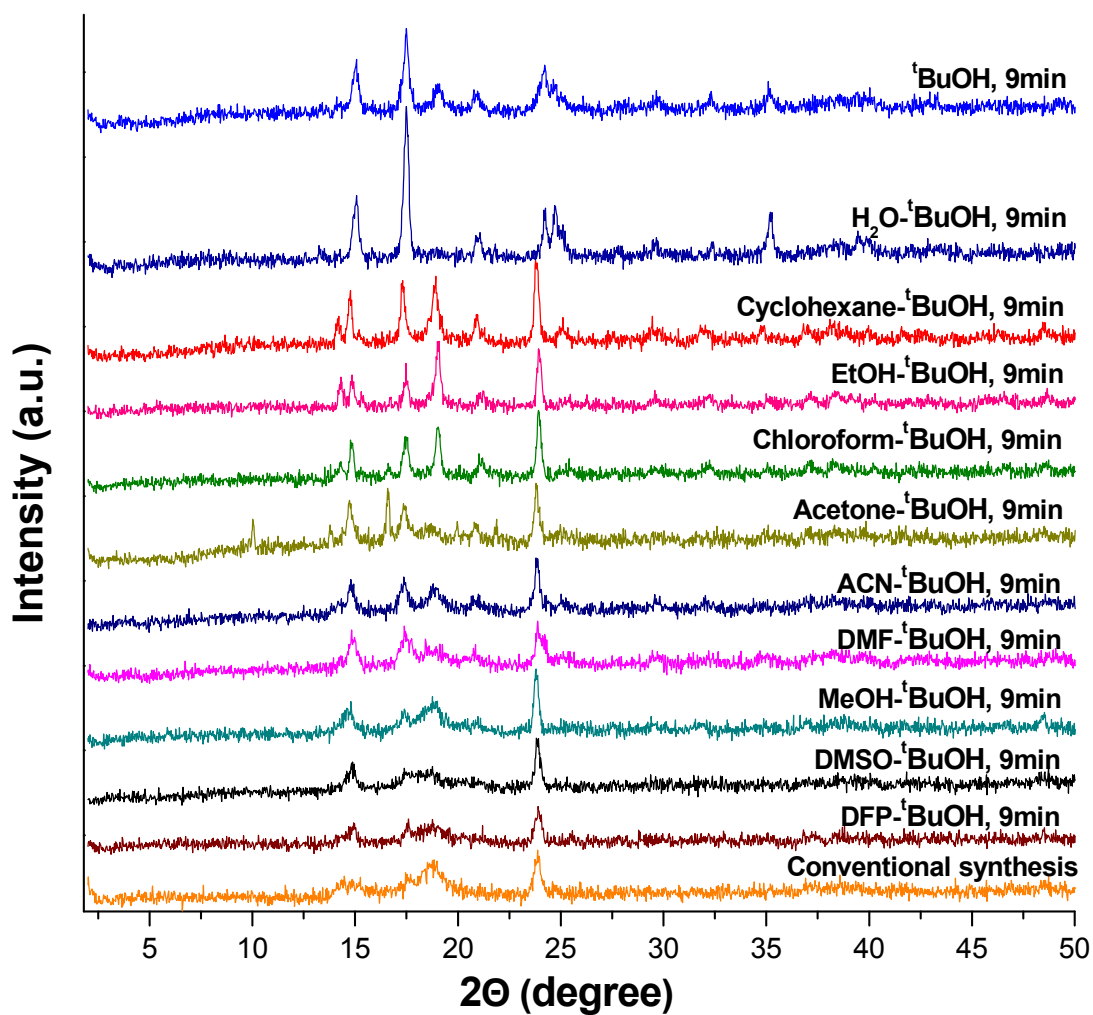


**Figure S3** XRPD patterns for mechanochemical reactions between  $\text{ZnCl}_2$  and  $\text{K}_3\text{Co}(\text{CN})_6$  using LAG at 50 Hz.  $t$ BuOH-with way is used with a  $t$ BuOH to DFP volume ratio of 1:1. The total volume of the added solvent is 250  $\mu\text{L}$ .



**Figure S4** Comparisons of XRPD patterns for synthesis of **2** by grinding ZnCl<sub>2</sub> and K<sub>3</sub>Co(CN)<sub>6</sub> using LAG at 50 Hz. The volume of the added solvent is 250  $\mu$ L. *t*BuOH-after way is used.



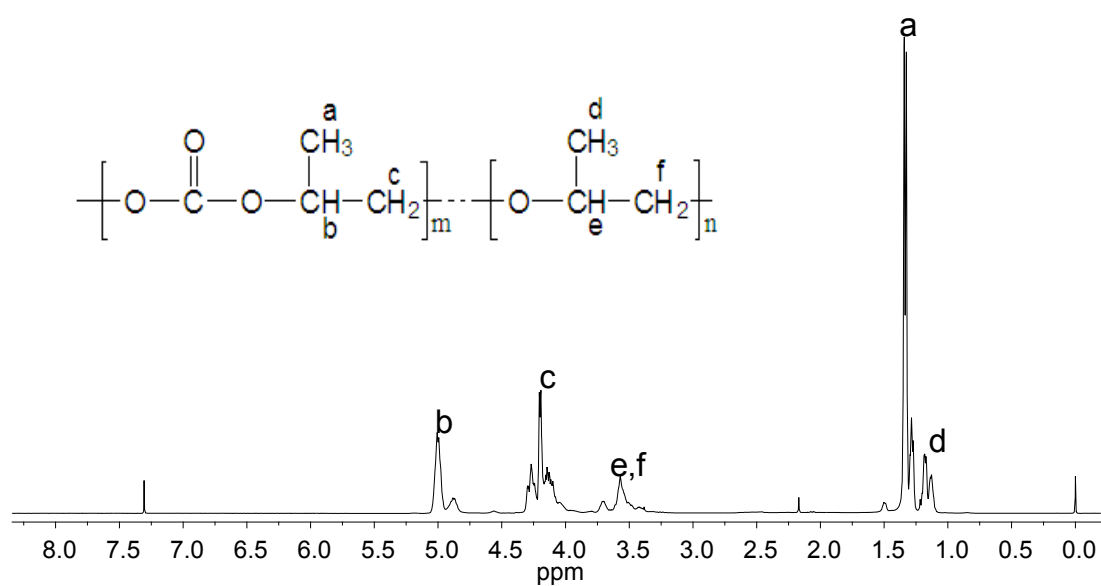


**Figure S5** Comparisons of XRPD patterns for synthesis of **2** by grinding ZnCl<sub>2</sub> and K<sub>3</sub>Co(CN)<sub>6</sub> using LAG at 50 Hz.  $t$ BuOH-with way is used with a  $t$ BuOH to liquid volume ratio of 1:1. The total volume of the added solvent is 250  $\mu$ L.

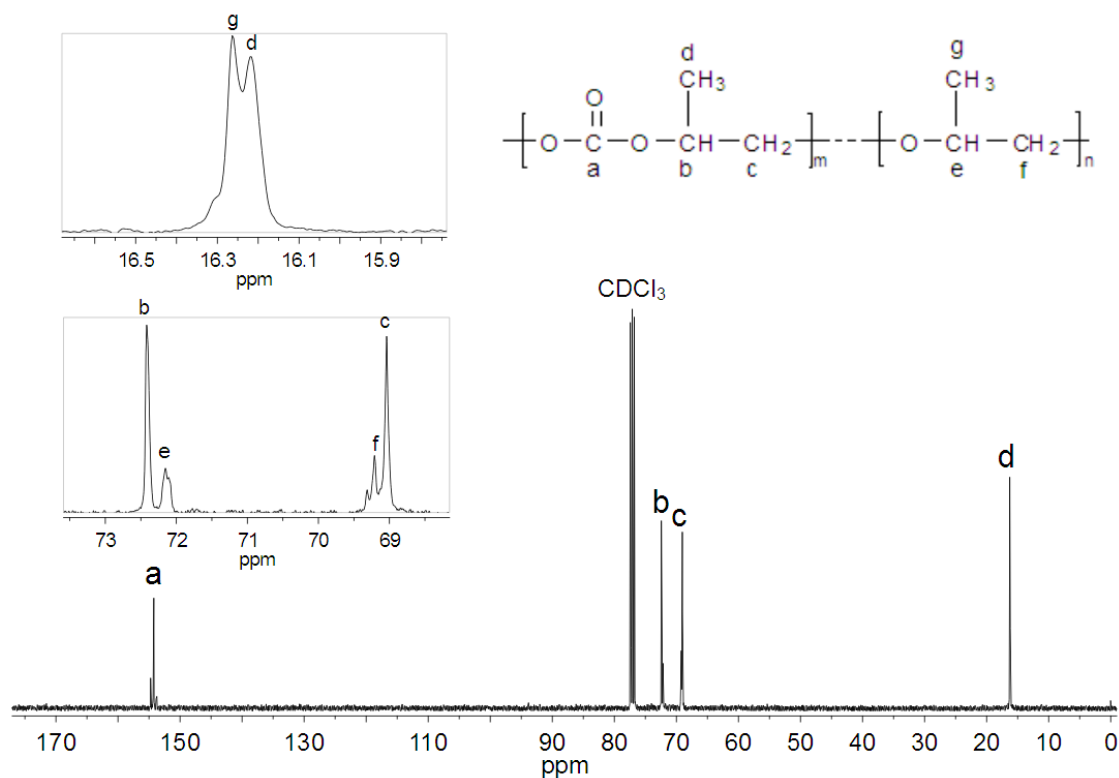
**Table S1** Propylene Oxide and CO<sub>2</sub> Copolymerization Results<sup>a</sup>

Entry	Complex	Grinding time (min)	TOF	Selectivity (% PPC)	$M_n$ ( $\times 10^3$ )	PDI $M_w/M_n$	$w_{CO_2}$
1	1-DFP	10	22.9	92	83.2	1.87	0.39
2	1-DMSO	10	20.0	90	72.0	2.12	0.39
3	1-DMF	12	15.3	88	61.9	2.36	0.36
4	1-ACN	12	16.6	84	64.2	1.91	0.34
5	1-Acetone	12	12.3	80	51.4	2.55	0.33
6	1-CHCl <sub>3</sub>	12	9.4	82	57.0	2.91	0.33
7	1-MeOH	12	7.5	70	19.2	4.02	0.22
8	1-EtOH	12	5.1	66	13.6	5.25	0.20
9	1-cyclohexane	12	4.4	62	9.5	4.32	0.22
10	1-H <sub>2</sub> O	12	5.2	55	4.3	4.73	0.19
11	1-Neat grinding	12	3.0	41	NA <sup>b</sup>	NA <sup>b</sup>	0.15
12	2-DFP	9	69.4	>95	23.5	2.16	0.42
13	2-DMSO	9	61.6	>95	16.1	1.95	0.41
14	2-MeOH	9	17.8	71	3.9	4.50	0.23
15	2-DMF	9	52.2	91	11.2	2.37	0.38
16	2-ACN	9	54.9	89	9.0	2.12	0.34
17	2-Acetone	9	42.5	85	7.4	2.73	0.37
18	2-CHCl <sub>3</sub>	9	27.6	85	9.9	3.35	0.32
19	2-EtOH	9	11.2	61	4.5	5.70	0.19
20	2-cyclohexane	9	9.2	52	2.3	5.32	0.20
21	2-H <sub>2</sub> O	9	3.0	44	NA <sup>b</sup>	NA <sup>b</sup>	0.17
22	2-Neat grinding	9	< 1	37	NA <sup>b</sup>	NA <sup>b</sup>	0.11

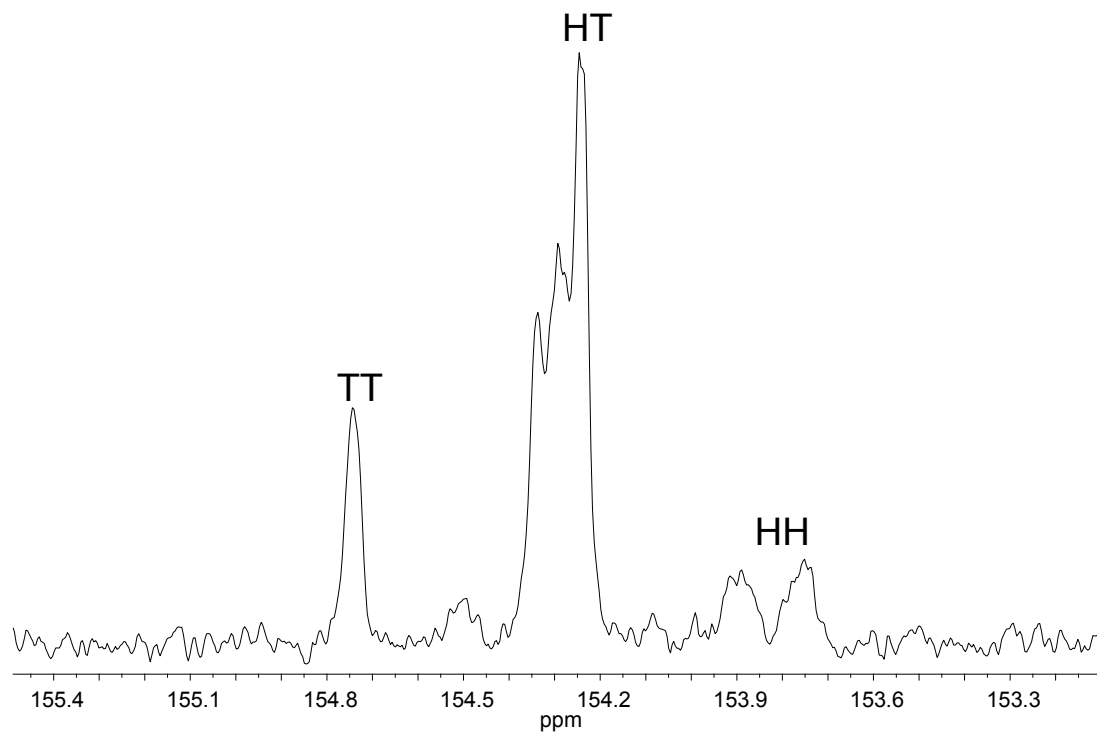
<sup>a</sup> Complexes **1** and **2** were synthesized by using LAG method with <sup>t</sup>BuOH-with way. <sup>b</sup> Not available.



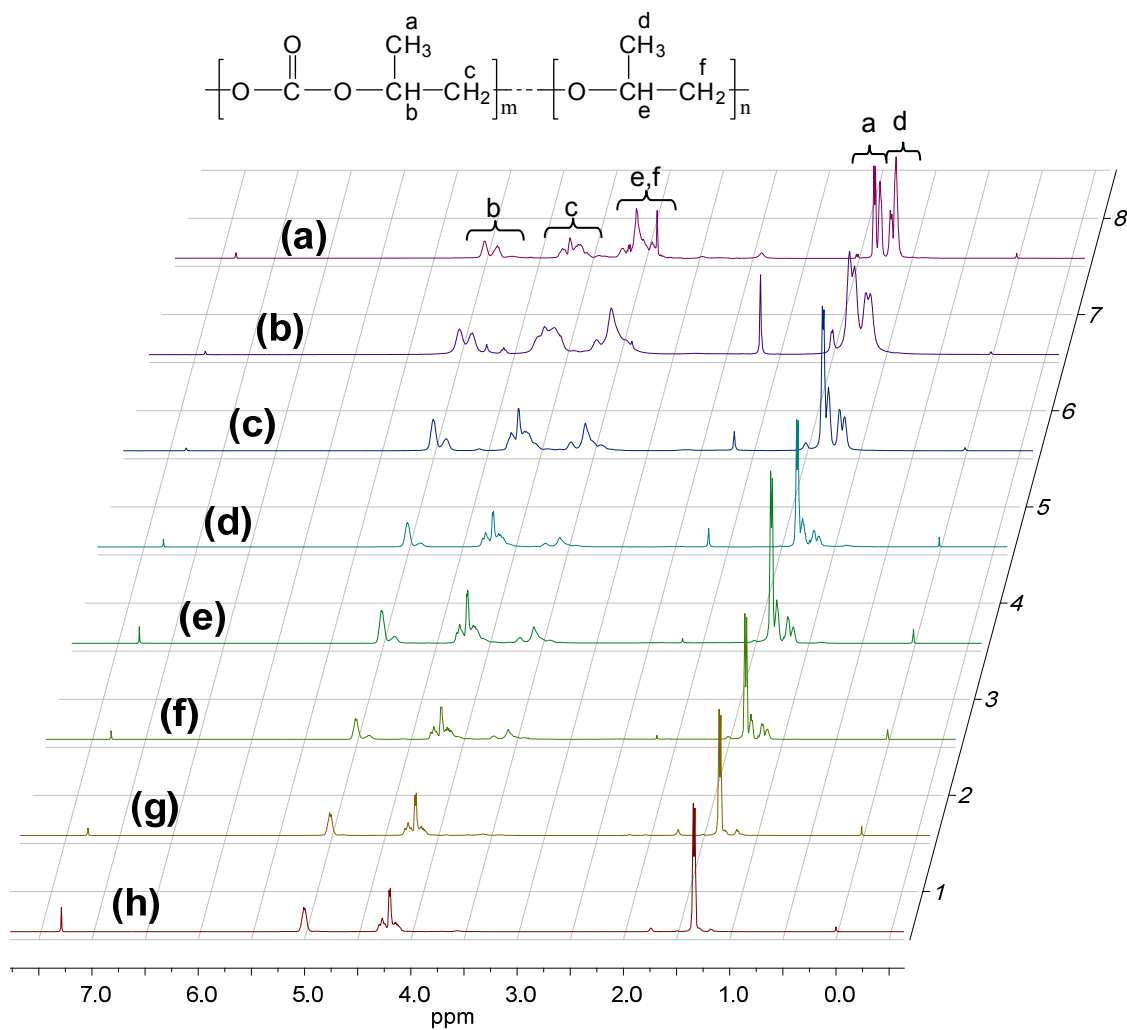
**Figure S6** <sup>1</sup>H NMR spectrum of a representative sample of poly(propylene carbonate) in CDCl<sub>3</sub>



**Figure S7**  $^{13}\text{C}$  NMR spectrum of a representative sample of poly(propylene carbonate) in  $\text{CDCl}_3$



**Figure S8**  $^{13}\text{C}$  NMR spectrum (carbonyl region) of representative sample of poly(propylene carbonate).



**Figure S9** Comparisons of <sup>1</sup>H NMR spectrum of PPC produced by 2 with different liquids. (a) 2-neat grinding; (b) 2-H<sub>2</sub>O; (c) 2-cyclohexane; (d) 2-chloroform; (e) 2-conventional synthesis; (f) 2-DMF; (g) 2-DMSO; (h) 2-DFP.

### Discussion of NMR spectra

For the polymer products PPC  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained as shown in Figures S6 and S7. For PPC, chemical shifts of the carbonate units were detected in  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ), 1.34 (3H;  $\text{CH}_3$ ), 4.19 (2H;  $\text{CH}_2\text{CH}$ ), 5.00 (1H;  $\text{CH}_2\text{CH}$ );  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ), 16.3 ( $\text{CH}_3$ ), 69.1 ( $\text{CH}_2\text{CH}$ ), 72.4 ( $\text{CH}_2\text{CH}$ ), 154.3 ( $\text{OCOO}$ ). Chemical shifts of ether units were detected in  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ), 1.17 (3H;  $\text{CH}_3$ ), 3.71 (2H;  $\text{CH}_2\text{CH}$ ), 3.56 (1H;  $\text{CH}_2\text{CH}$ );  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ), 16.2 ( $\text{CH}_3$ ), 69.2 ( $\text{CH}_2\text{CH}$ ), 72.1 ( $\text{CH}_2\text{CH}$ ). Therefore, these spectroscopic results suggest that the polymer product is the alternating poly(propylene carbonate) (PPC). The ether unit is present in the polymer product with reasonable amount (Figure S6).  $^{13}\text{C}$  NMR investigation on the carbonate carbon signals in the obtained PPC revealed the ratio of tail-to-tail (TT), head-to-tail (HT), and head-to-head (HH) junctions<sup>3</sup> in the order of 16.9 : 71.8 : 11.3 (Figure S8). Such a microstructure is consistent with a near region-random ring-opening of PO and is similar to polymers catalyzed by [(BDI)ZnOAc] complexes<sup>4</sup> (~54% head-to-tail linkages) and zinc glutamate<sup>3</sup> (~60% head-to-tail linkages).

Figure S9 illustrates proportions of carbonate and ether in PPC catalyzed by **2** in the presence or absence of grinding liquids, indicating that the polar liquid played a positive role in reducing the ether linkage in the copolymers. The intensity of ether units detected at 1.17, 3.71 and 3.56 ppm decreased significantly with increasing liquid polarity used under LAG conditions. According to the calculation results from  $^1\text{H}$  NMR spectra, the carbonate content of PPC produced by **2**-DPF or **2**-DMSO was found to be more than 95.0%, which was in contrast to PPC catalyzed by **2** using conventional solvent-based synthesis (87.1%) and **2**-cyclohexane (51.8%). The improvement of the alternating ratio of PPC was deduced that the liquid polarity had a significant impact on the active metal center of the formation of the complex, and therefore labilized the metal Zn-N bond and facilitated the insertion of  $\text{CO}_2$ .<sup>5-8</sup>

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