Supplementary Information

Borane-catalysed cyclodepolymerization of CO_2-derived polycarbonates

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1. Liquid-assisted grinding PPC depolymerization procedure

Stainless steel mixer mill vessel equipped with 5 stainless steel balls were brought into the glovebox. ~100 mg PPC was added to vessel with ~1.5 mL of BCF solution (~16 mg/mL in toluene). Vessel was placed on mixer mill for 20 min with 20 min cooling cycle, twice (40 min total shaking). Dissolved in CH_2Cl_2 and crude ^1H NMR (300 MHz, $CDCl_3$) taken. No conversion was observed.

Table S1. Depolymerization of terpolymers and polymer mixtures containing varying ratios of PCHC and PPC.[a]

Entry	CHO: PO	% conv. PCHC[b]	% conv. PPC[b]
1	4:1	98	>99
2	1:2	>99	>99
3[c]	4:1	70	70
4[c]	1:1	62	59
5[d]	25:1	64	n.d.

[a]All depolymerizations performed at 5 mol% BCF catalyst with respect to the repeat unit molar mass of PCHC. Performed in 20 mL toluene, at 105 °C for 2 h, under nitrogen. [b]Total % conversion to cyclic carbonate observed via ^1H NMR spectroscopy after 2 h. ^1H NMR spectra were collected in $CDCl_3$ at 298 K. [c]Depolymerizations performed using mixtures of polycarbonates (PPC and PCHC) rather than block copolymers derived from PO, CHO, and CO_2. [d]% conversion of PPC to PC could not be determined by ^1H NMR spectroscopy due to masking of peaks by PCHC/CHC peaks.

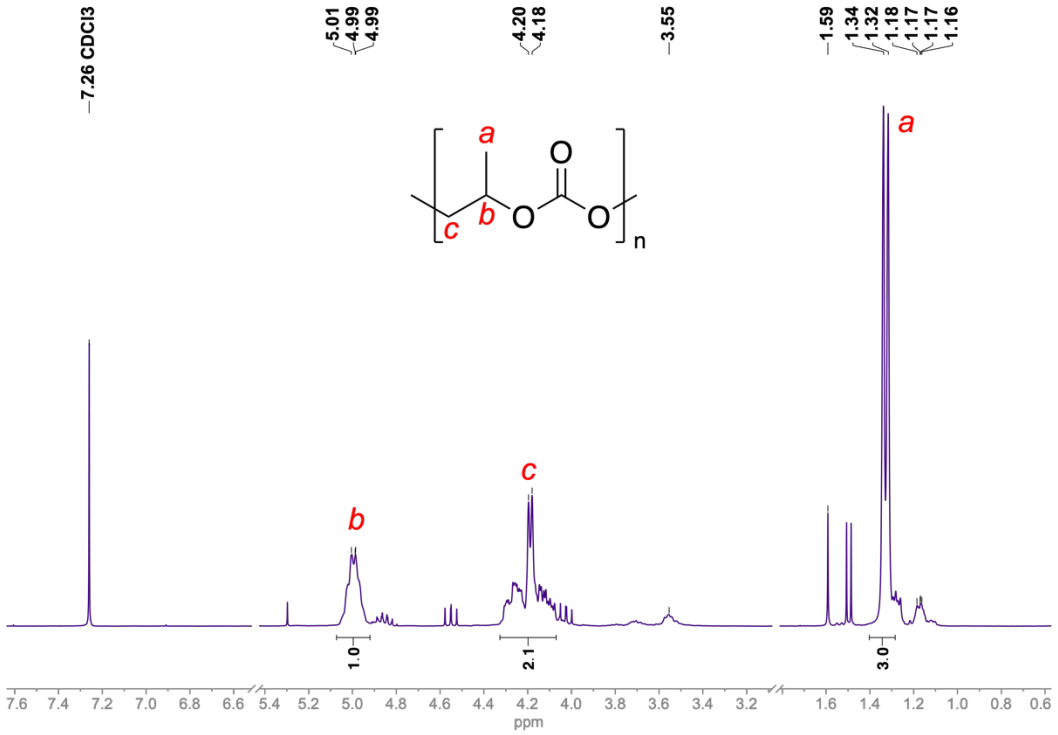

Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(propylene carbonate) (PPC).

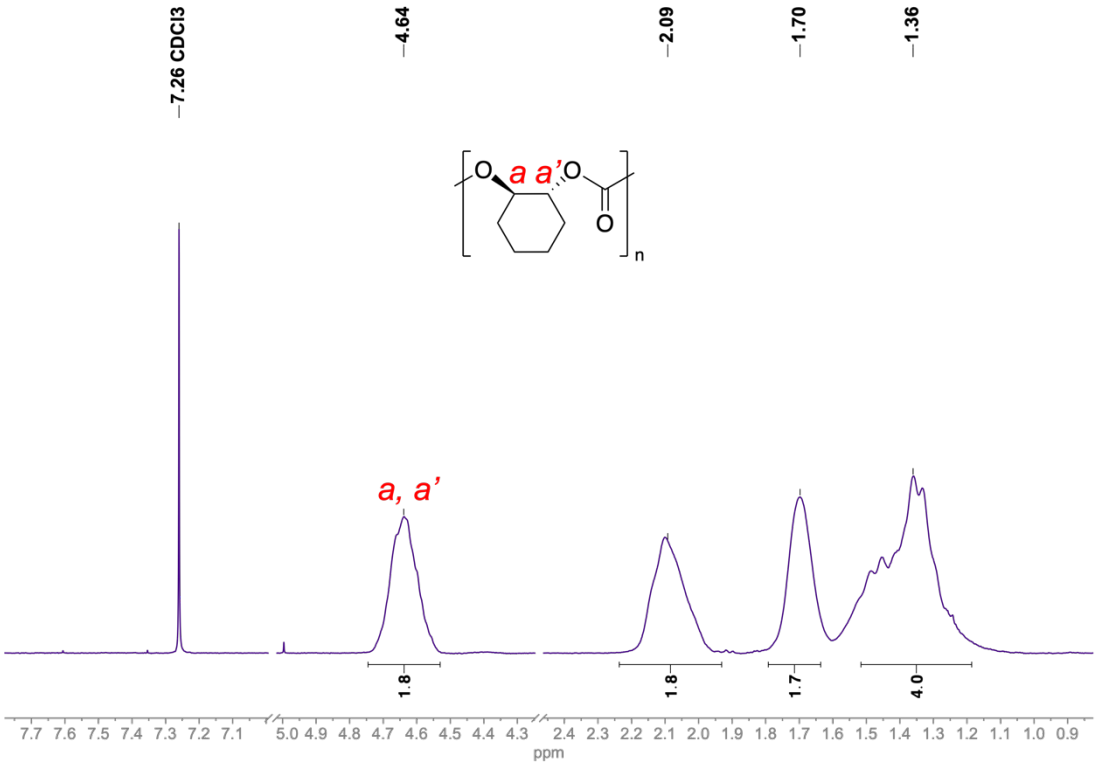

Figure S2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly(cyclohexene carbonate) (PCHC).

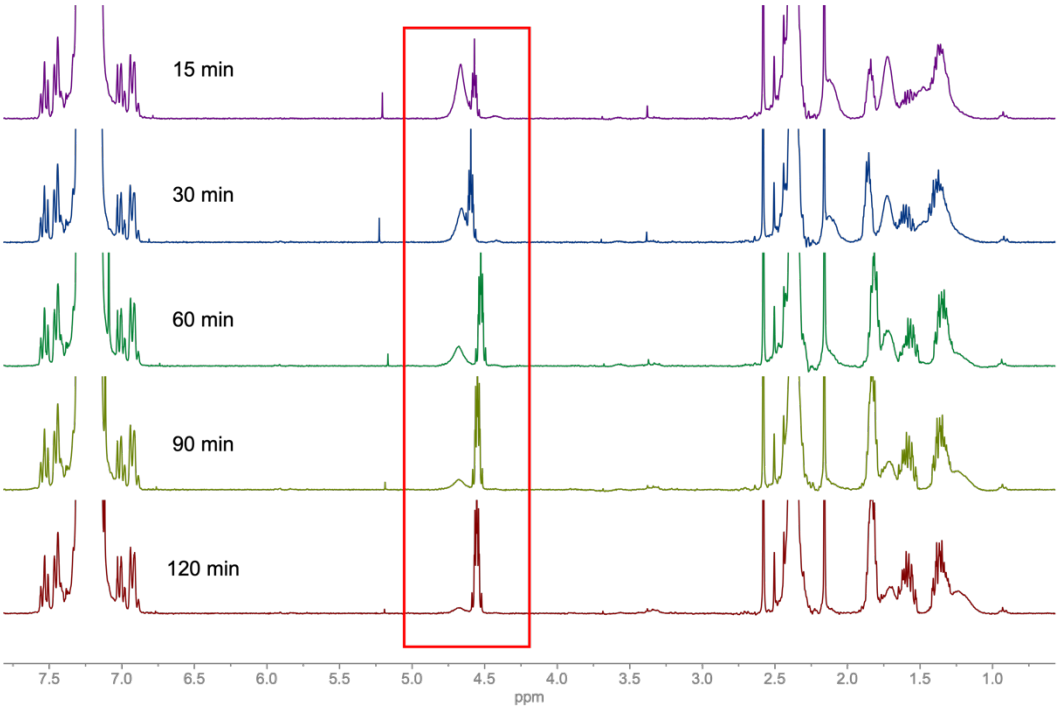

Figure S3. Stacked ^{1}H NMR spectra (300 MHz, $CDCl_3$) of PCHC depolymerization progression (10 mol% BCF at 105 °C for 2 h). 15 min (top, purple), 30 min (second, blue), 60 min (third, green), 90 min (fourth, green/yellow), 120 min (bottom, red).

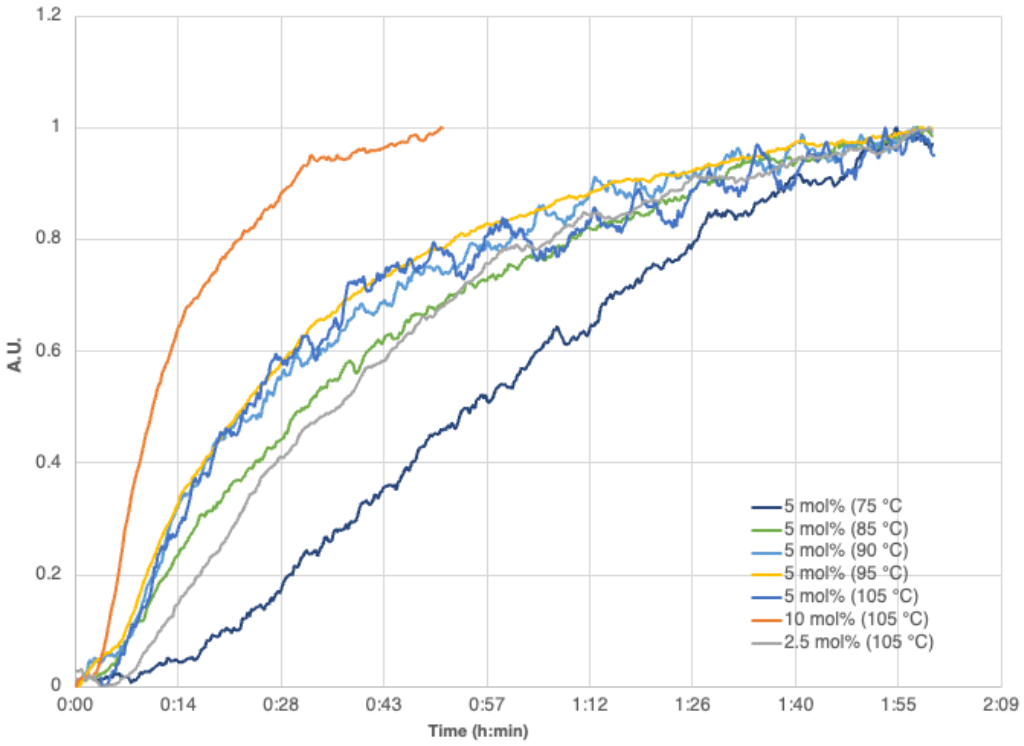

Figure S4. Overlay of normalized two-dimensional *in situ* FTIR spectra from CDP kinetic studies of PPC

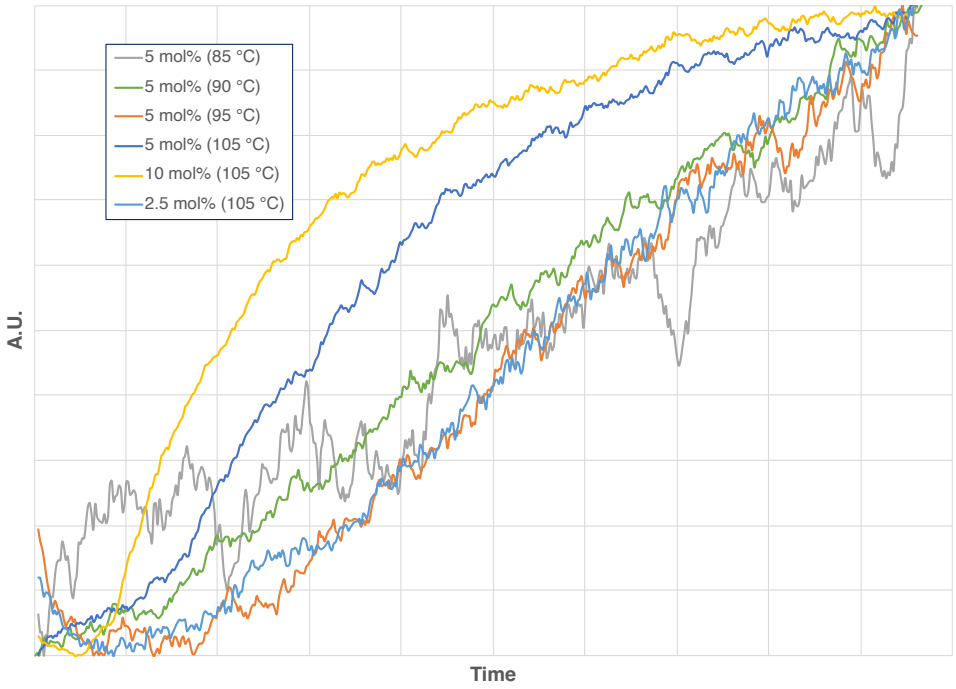

Figure S5. Overlay of normalized two-dimensional *in situ* FTIR spectra from CDP kinetic studies of PCHC

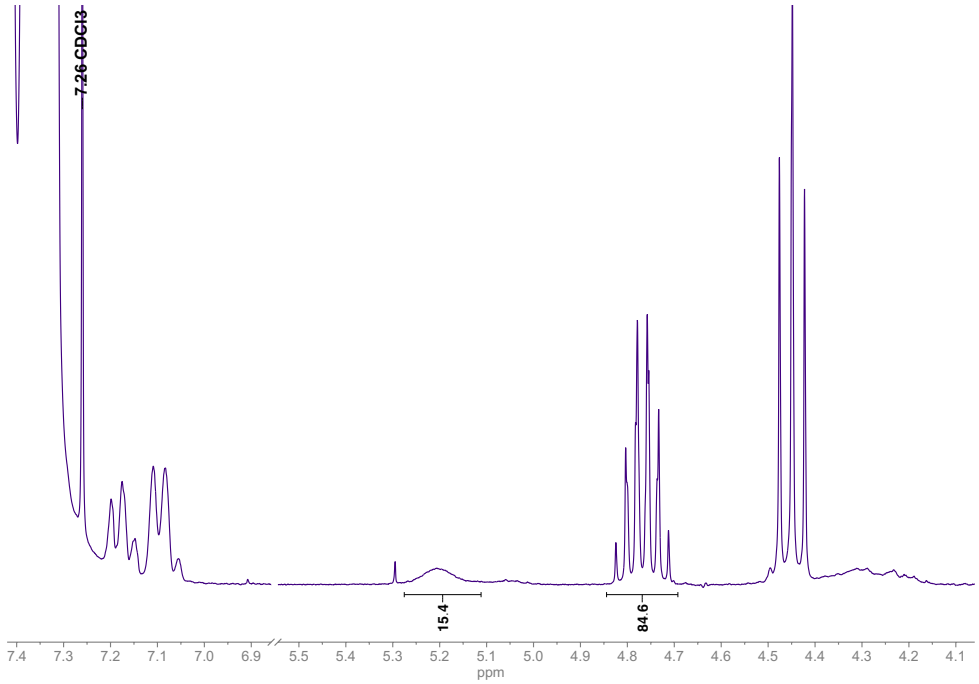

Figure S6. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PPC depolymerization with propylene carbonate impurity present. (1:1 PPC:PC, 2 h, 105 °C, 5 mol% BCF). % Conversion to PC = 70% [Initial conditions 50% PPC and 50% PC, Final conditions, 15% PPC and 85% PC. % Conversion = (50-15)/0.5 = 70%]

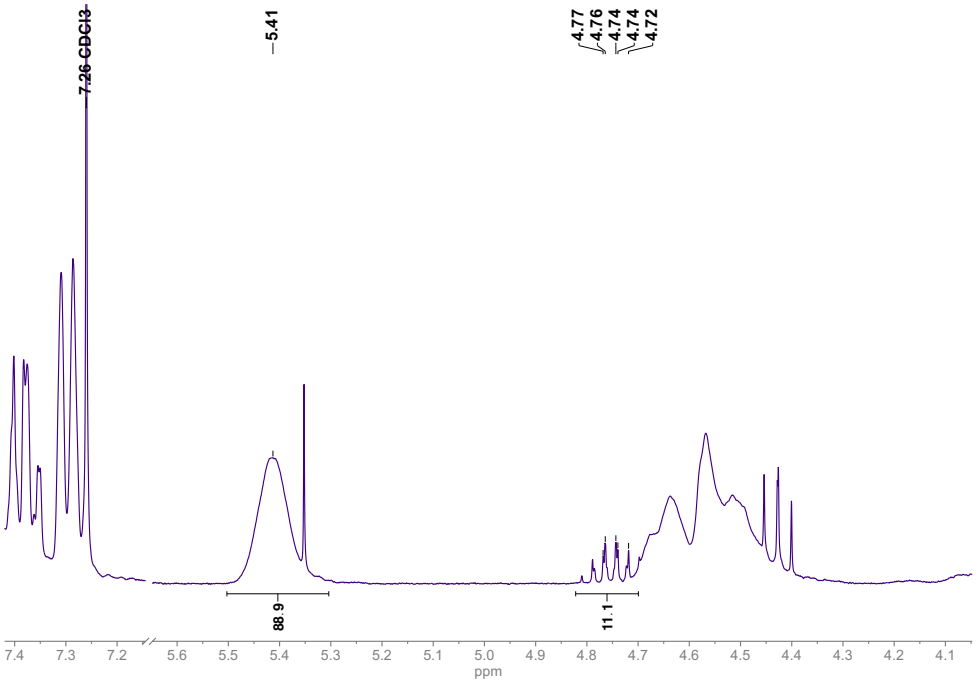

Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PPC after BCF was exposed to air (2 h, 105 °C, 5 mol% BCF). % Conversion of PPC to PC = 11% [Initial conditions 100% PPC and 0% PC, Final conditions, 89% PPC and 11% PC. % Conversion = (100-89)/1 = 11%]

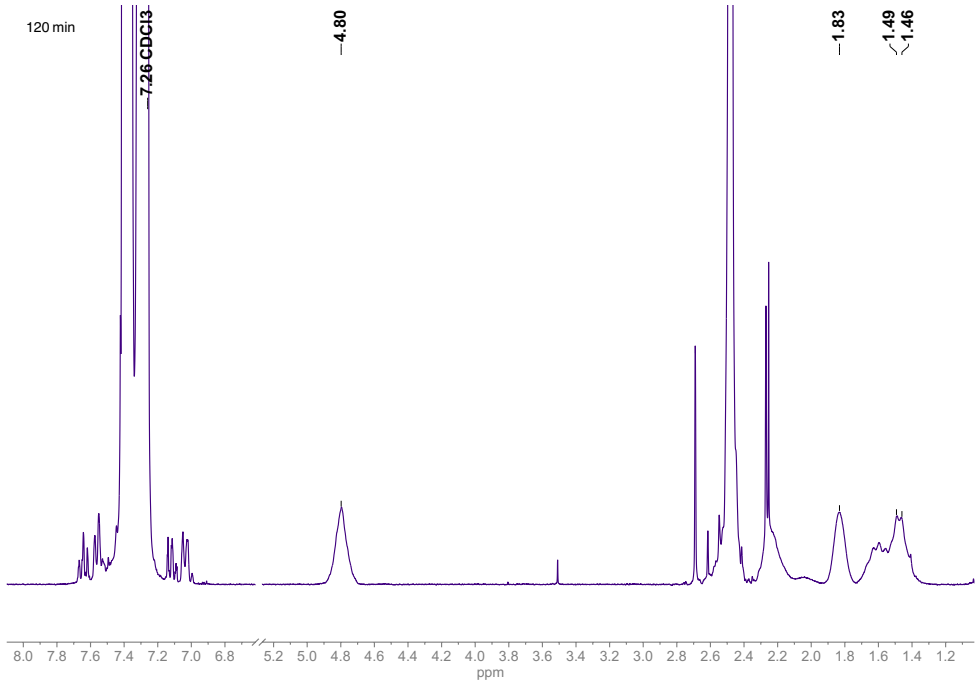

Figure S8. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PCHC depolymerization with 1 mol% H_2O impurity present. (2 h, 105 °C, 5 mol% BCF). % Conversion of PCHC to CHC = <1% [Initial conditions 100% PCHC, Final conditions, 100% PCHC, no CHC detected]

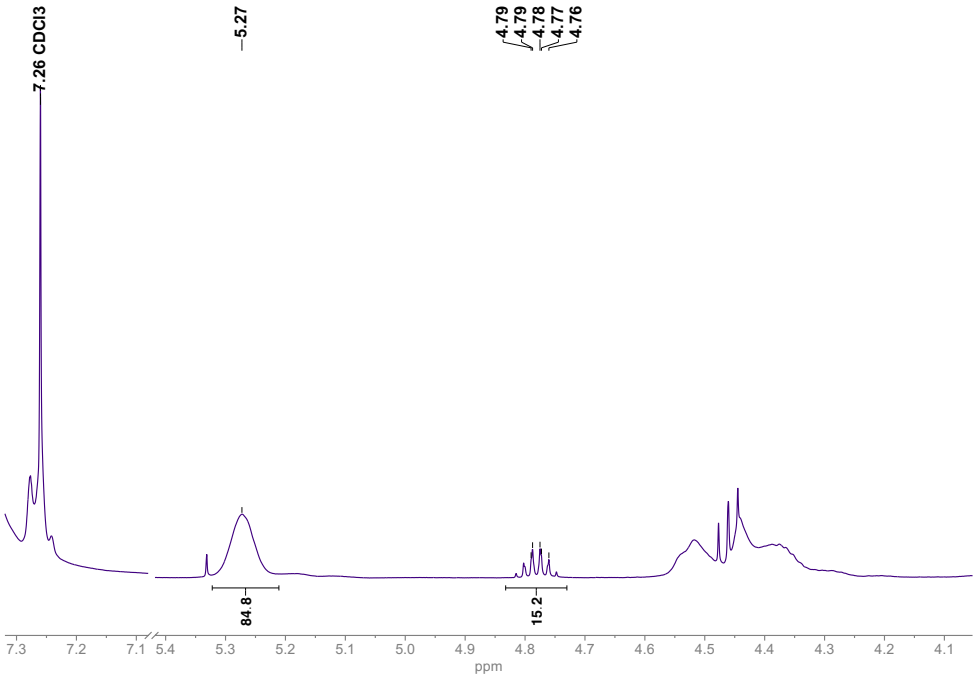

Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PPC depolymerization with CO_2 impurity present. (2 h, 105 °C, 5 mol% BCF, 40 bar CO_2). % Conversion of PPC to PC = 15% [Initial conditions 100% PPC and 0% PC, Final conditions, 85% PPC and 15% PC. % Conversion = (100-85)/1 = 15%]

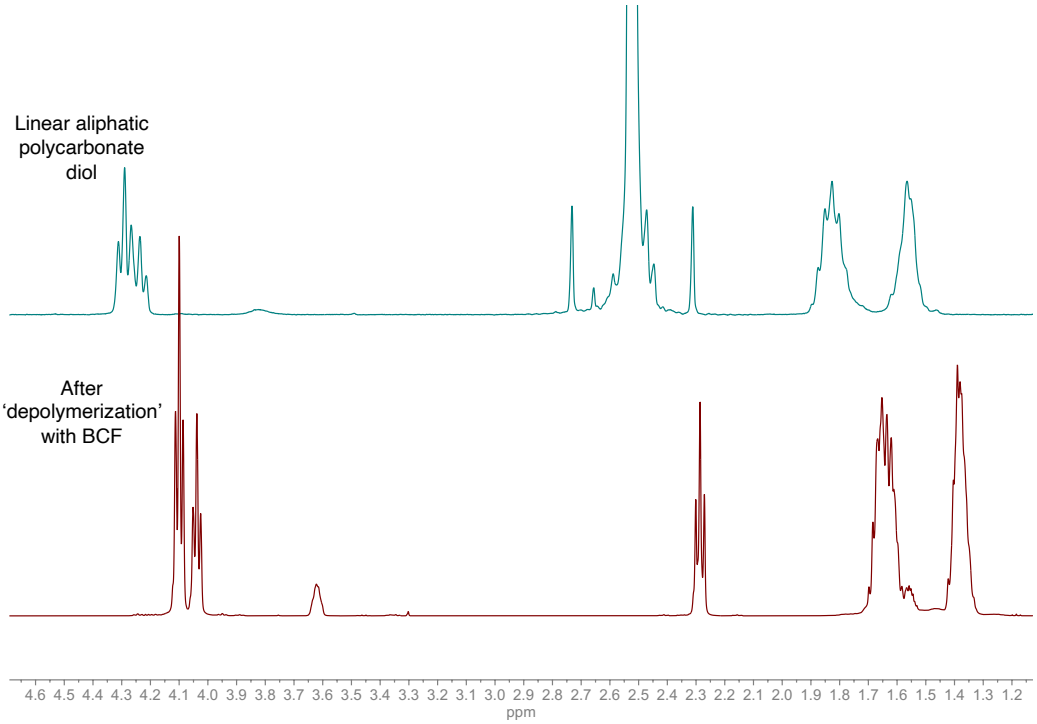

Figure S10. Stacked ^{1}H NMR spectra (300 MHz, $CDCl_3$)of starting commerical polycarbonate diol Desmorphen C1200 (top, blue) and after 18 h depolymerization with BCF (5 mol%, 105 °C) in toluene.

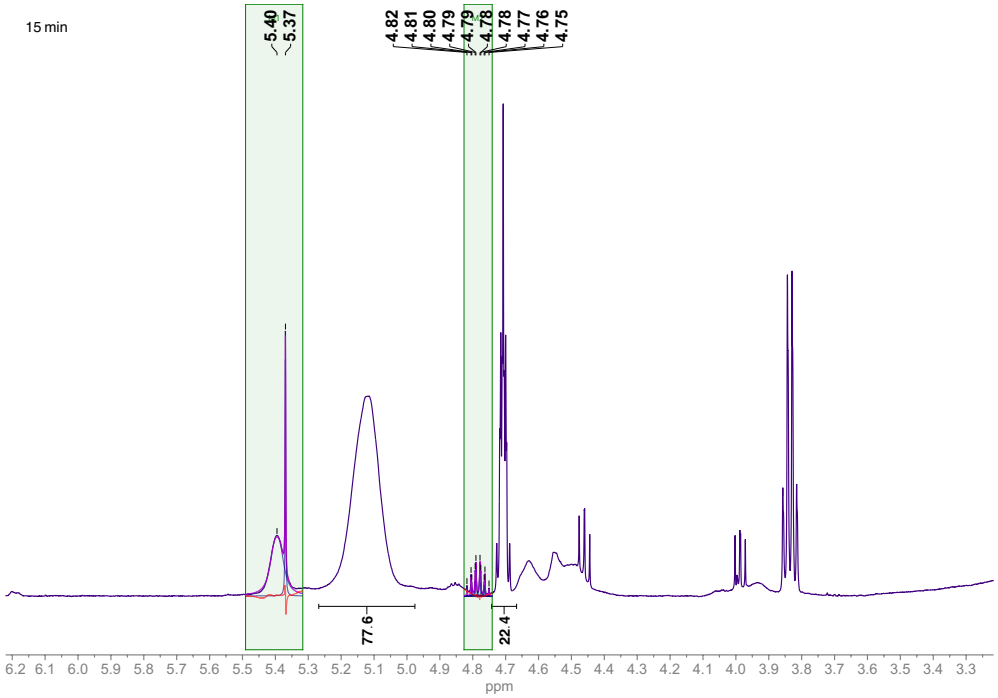

Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PCHC and PPC mixture (4:1 PCHC: PPC, 5 mol% BCF, 105 °C) after 15 min. Line fitting was used to calculated % conversions. % conversion of PCHC to CHC = 22% (Table 3, entry 3)

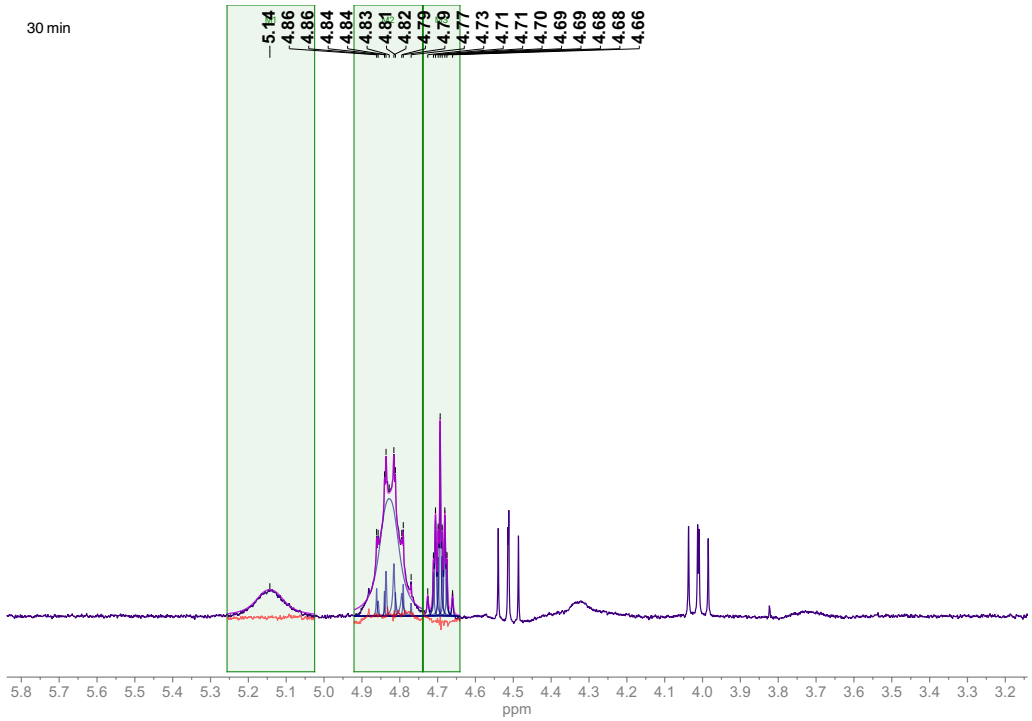

Figure S12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of terpolymer depolymerization (4:1 PCHC:PPC, 105 °C, 5 mol% BCF) after 30 min. Line fitting was used to calculated % conversions (Table 3, entry 1)

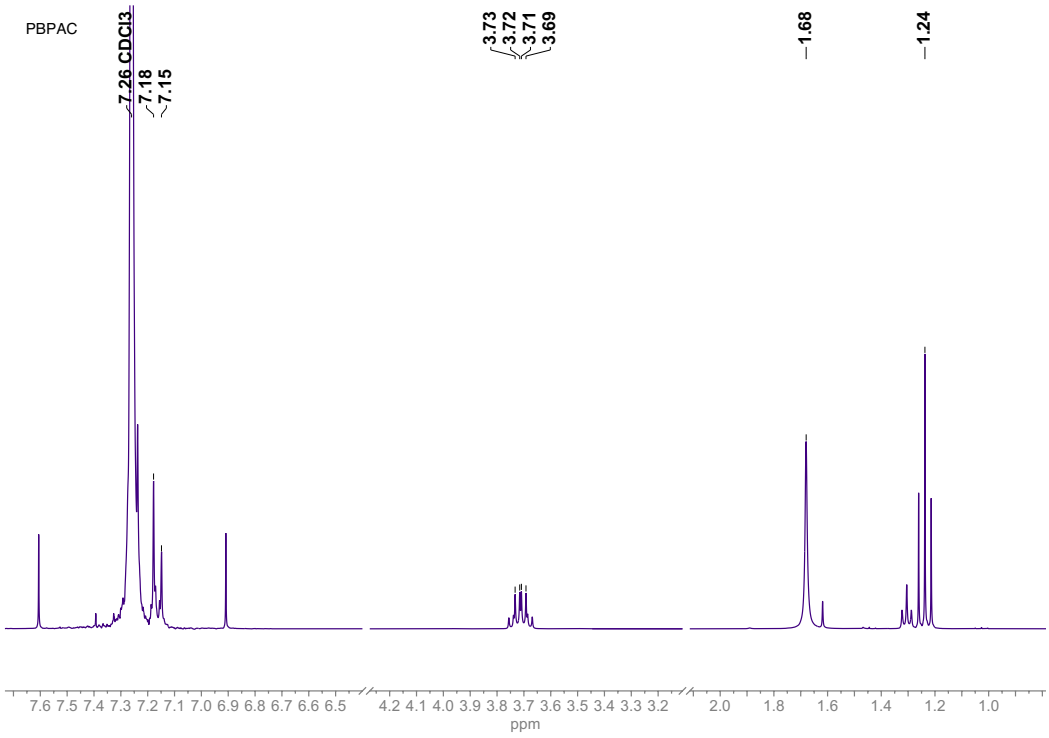

Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of poly(bisphenol A carbonate) (PBPAC)

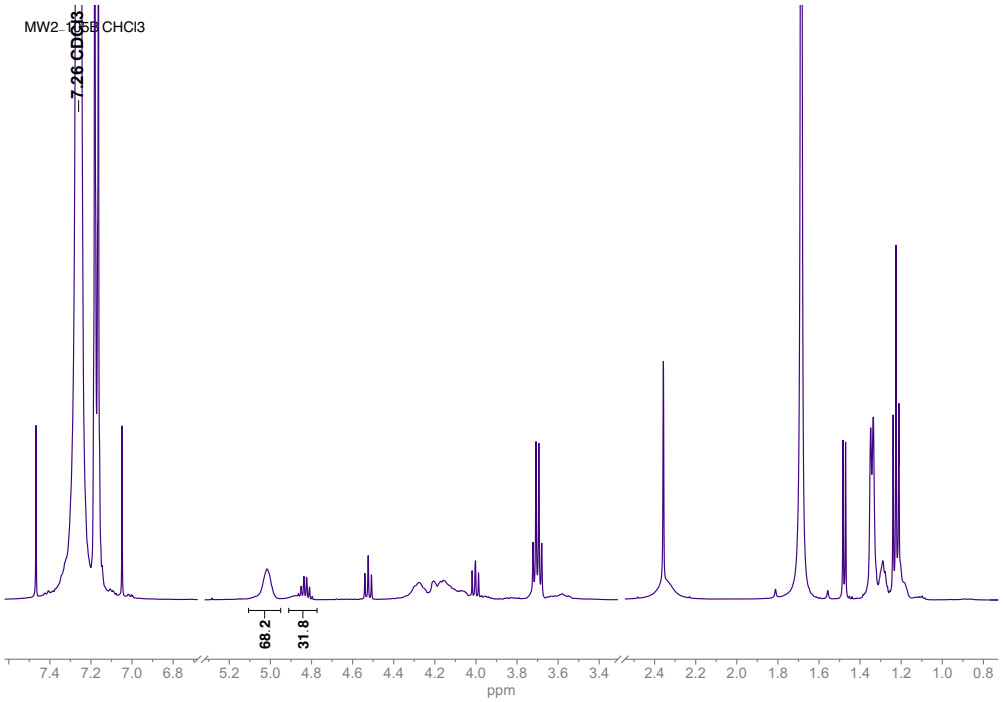

Figure S14. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PBPAC and PPC mixture after 2 h depolymerization (5 mol% BCF to PPC, 105 °C)