Electronic Supplementary Information for

Controlled Hydrogenative Depolymerization of Polyesters and Polycarbonates Catalyzed by Ruthenium(II) PNN Pincer Complexes

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General Information:

All reagents were purchased from Fisher Scientific Inc. or Sigma Aldrich Corporation and used as received unless otherwise stated. Anisole (99%) was stored over 4Å molecular sieves. Tetrahydrofuran, 99.9%, anhydrous, stabilized with BHT and fitted AcroSeal,™ was measured *via* syringe under nitrogen atmosphere. Hydrogen gas (HY 5.0UH, 99.999%) was purchased from Praxair Technology Inc. and used as received. The Milstein catalyst precursor (**1**) was purchased from STREM and the catalyst precursor (**3**) was prepared according to a literature procedure;[1] both were stored in a nitrogen filled Vacuum Atmospheres glove box. Complexes **2** and **4** were generated *in situ* using potassium *tert*-butoxide. Linear aliphatic polyesters were prepared using the procedure we previously reported.[2] Polyethylene terephthalate (PET) pieces (approx. 0.5 x 0.5 cm) were cut from a used Dasani™ water bottle and added to the reactor without additional treatment. Poly(lactic acid) (PLA) pieces (approx. 0.5 x 0.5 cm) were cut from an Earth Choice® beverage cup stamped by Ingeo. Poly(R-3-hydroxybutryic acid) (PHB) was purchased from Sigma Aldrich. Poly(3-hydroxypropionic acid) (P3HP, M_n = 135 kg/mol, PDI = 1.3) was generously donated by the Coates Lab at Cornell University. Polyethylene carbonate (PEC, M_w = 129 kg/mol) and polypropylene carbonate (PPC, M_n = 150 kg/mol) were graciously donated by Empower Materials Inc. and Novomer Inc., respectively.

Depolymerizations were carried out in a Parr Instrument Co. 4714 pressure vessel (45 mL capacity) fitted with a 4316 gauge block assembly (0-1000 psi gauge, 1000 psi rupture disc) immersed in a silicone oil bath. Product characterization was performed in $CDCl_3$ using a Bruker 400 MHz

Avance II NMR Spectrometer. The spectrometer is a three-channel instrument equipped with a variable-temperature unit and 5 mm TXI/Z-gradient three-channel indirect detection probe. Spectra were analyzed using TopSpin, Sparky and iNMR. A known amount (3.2 mmol) of CH_2Cl_2 was added to the reactor contents at the end of the reaction to serve as an internal standard. Percent conversions were determined by ^1H NMR integration of product (diol or carboxylic acid) resonances versus the 5.2 ppm resonance of CH_2Cl_2.

General Depolymerization Procedure (see Table S1 for details):

Catalyst precursor and potassium *tert*-butoxide were combined in a scintillation vial and fitted with a rubber septum in a nitrogen filled glovebox. The vial was removed from the glovebox and charged with 2.0 mL of solvent *via* a disposable syringe. The solution was agitated for 5 minutes, opened to the atmosphere and transferred to the pressure vessel containing the polymer and a magnetic stir bar. The additional solvent was used to wash all remaining catalyst from the vial into the reactor. The reactor was sealed and purged with hydrogen gas (13.6 atm) for three successive pressurization/venting cycles with rapid stirring. Following the third cycle of venting, the vessel was charged with the appropriate amount of hydrogen, sealed, immersed in a silicone oil bath and heated to the target temperature. Following the designated time period, the reactor was raised from the oil bath, allowed to cool to room temperature and vented. Dichloromethane (3.2 mmol) was added to the reaction mixture for use as an internal standard. An aliquot was removed for NMR analyses and to check for precipitation in MeOH.

Table S1. Experimental details corresponding to entries listed in Table 1[a]

Entry	Catalyst	Solvent (mL)	Catalyst precursor (mg, mmol)	KO^{t}Bu (mg, mmol)	Polymer mass (g, mmol polymer repeat unit)	$p(H_2)$ initial (atm)
1	**2**	Anisole (5.0)	14.6, 0.030	3.4, 0.030	0.523, 3.0	11.2
2	**4**	THF (3.0)	21.6, 0.045	5.1, 0.045	0.256, 2.2	40.8
3	**4**	Anisole, THF (2.0, 2.0)	15.0, 0.031	7.0, 0.062	0.300, 1.6	40.8
4	**4**	Anisole, THF (2.0, 2.0)	20.0, 0.042	9.4, 0.084	0.150, 2.1	40.8
5a[b]	**2**	Anisole, THF (2.0, 2.0)	15.5, 0.032	7.1, 0.063	0.326, 3.2	40.8
5b[b]	**4**	Anisole, THF (2.0, 2.0)	15.0, 0.031	7.0, 0.062	0.323, 3.2	40.8
6a[b]	**2**	Anisole, THF (2.0, 2.0)	17.5, 0.036	8.1, 0.072	0.318, 3.6	40.8
6b[b]	**4**	Anisole, THF (2.0, 2.0)	16.6, 0.035	7.7, 0.069	0.306, 3.5	40.8
7	**4**	Anisole, THF (2.0, 2.0)	18.6, 0.039	8.6, 0.077	0.170, 2.0	40.8
8	**4**	Anisole, THF (2.0, 2.0)	30.1, 0.063	14.3, 0.127	0.232, 3.2	40.8

[a] All hydrogenations were prepared following the general outline described above. [b] Catalysts **2** and **4** exhibited the same performance for PPC and PEC.

Characterization of Depolymerizations:

^{13}C NMR spectra of crude reaction mixtures contain anisole and/or THF. Anisole: (100 MHz, $CDCl_3$, δ): 159.6, 129.5, 120.7, 113.9, 55.1. THF: (100 MHz, $CDCl_3$, δ): 67.9, 25.6.

Poly(1,10-Decanediol) depolymerization, Table 1, entry 1: An aliquot was removed for NMR analyses and the remaining solution was cooled to 0 °C, filtered, and the white crystals were washed with 3.0 mL of cold anisole. The solid was dried *in vacuo* for 24 hours (.421 g, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.60 (t, 4H), 1.54 (m, 4H), 1.47 (br s, 2H, OH), 1.29 (m, 12H).

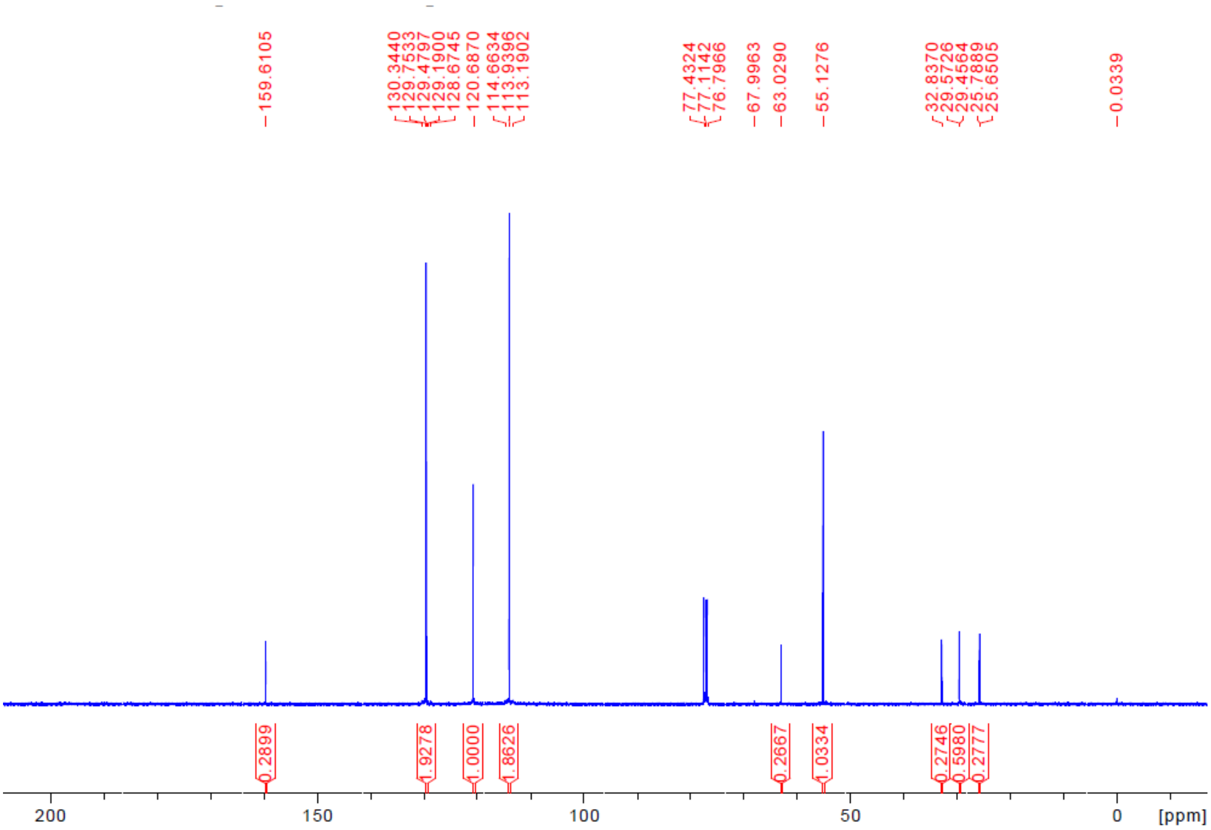

Fig. S1 ^{13}C NMR of crude reaction mixture of poly(1,10-decanediol) depolymerization. (100 MHz, $CDCl_3$, δ): 63.0, 32.8, 29.6, 29.5, 25.8 align with a commercially purchased standard of 1,10-decanediol. ^{13}C NMR demonstrates absence of carbonyl-containing products. Anisole: 159.6, 129.5, 120.7, 113.9, 55.1.

Caprolactone hydrogenation, Table 1, entry 2: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.59 (t, 4H), 2.90 (br s, 2H, OH), 1.56 (m, 4H), 1.39 (m, 4H).

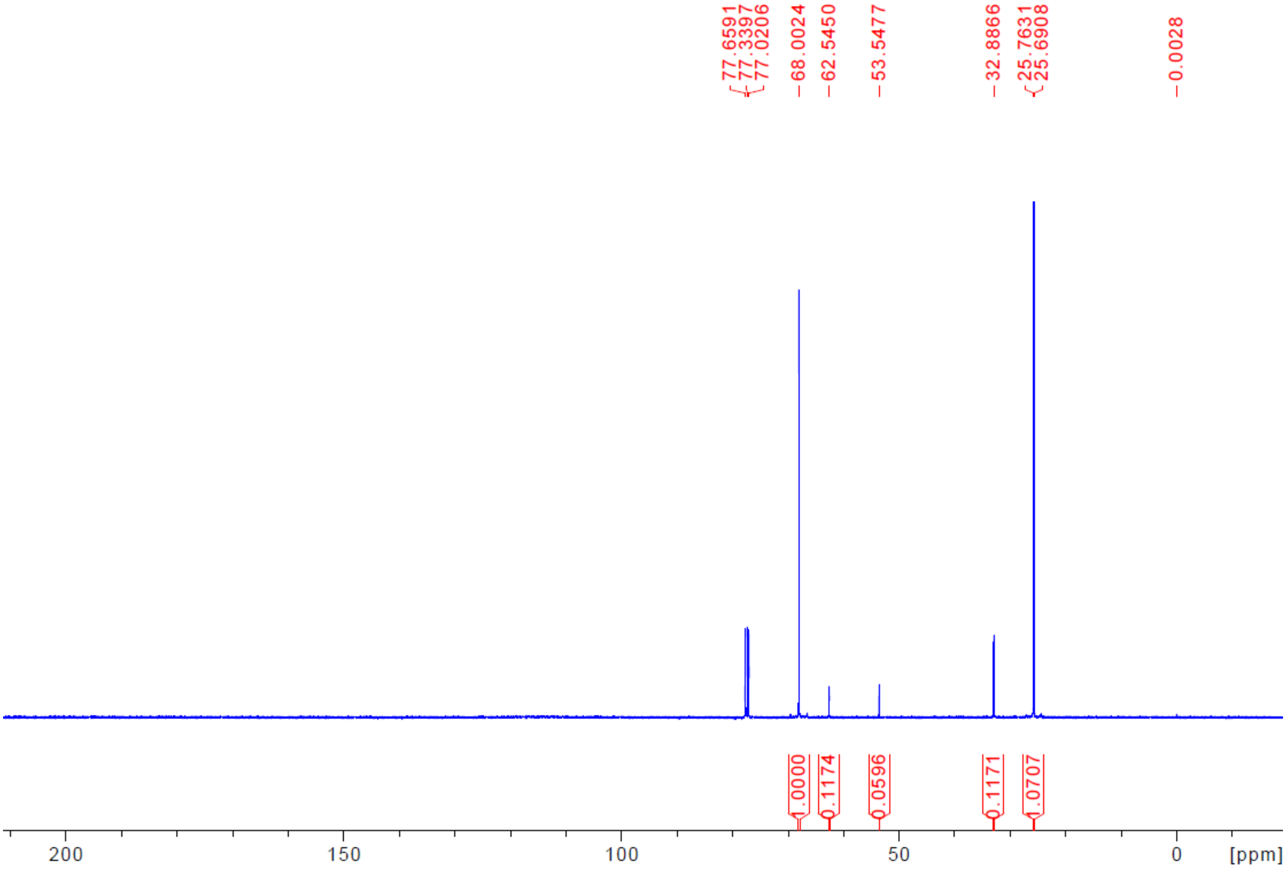

Fig. S2 ^{13}C NMR of crude reaction mixture of caprolactone hydrogenation. (100 MHz, $CDCl_3$, δ): 62.5, 32.9, 25.8 align with commercially purchased standard of 1,6-hexanediol (53.5 is CH_2Cl_2 reference). THF: 68.0, 25.7. ^{13}C NMR demonstrates absence of carbonyl-containing products.

Polyethylene terephthalate depolymerization, Table 1, entry 3: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31 (s, 4H, BDM), 4.62 (s, 4H, BDM), 3.63 (s, 4H, EG), 3.14 (br s, 2H, OH), 3.03 (br s, 2H, OH). >99% conversion.

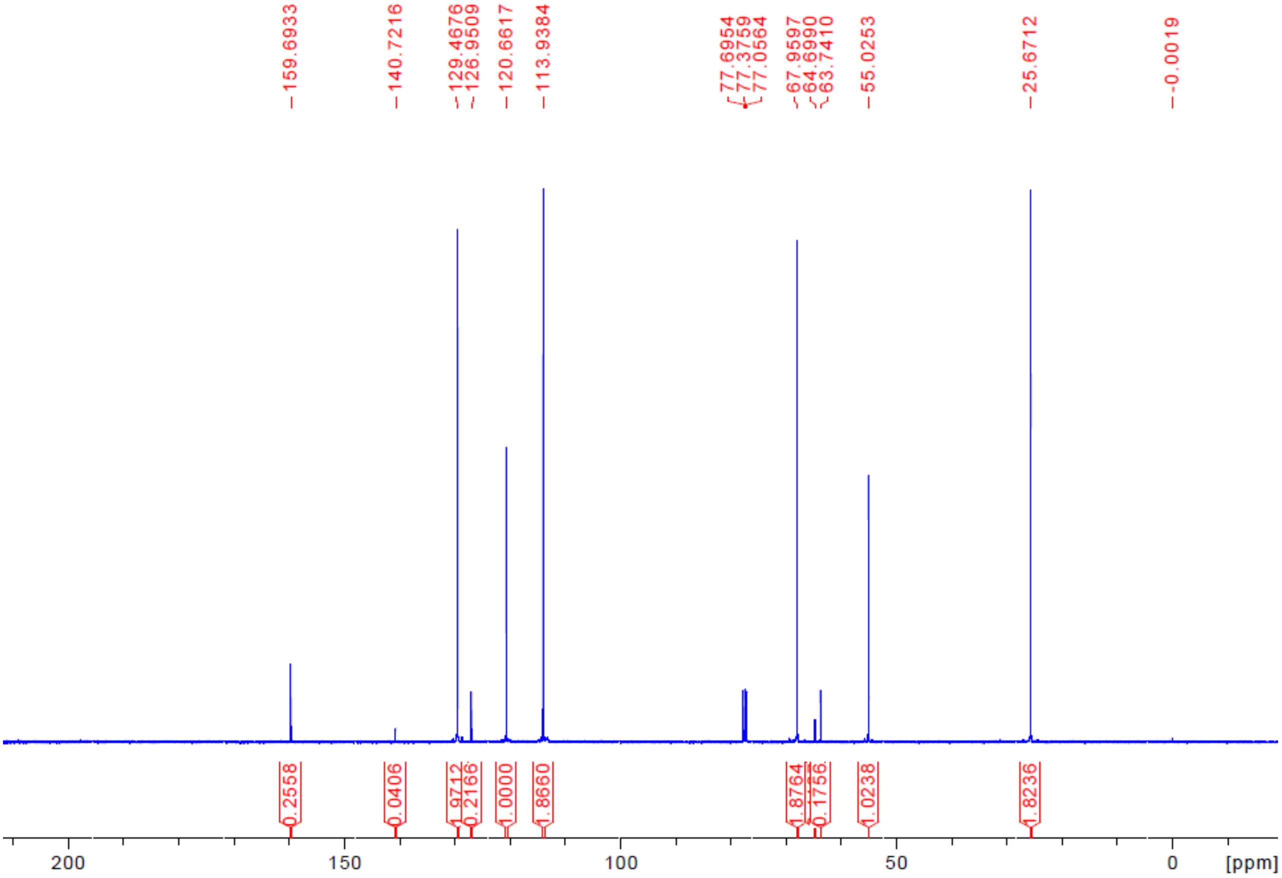

Fig. S3 ^{13}C NMR of crude reaction mixture of PET depolymerization. (100 MHz, $CDCl_3$, δ): 140.7 (BDM), 127.0 (BDM), 64.7 (BDM), 63.7 (EG) align with standards of 1,4-benzenedimethanol and ethylene glycol. Anisole: 159.7, 129.5, 120.7, 113.9, 55.1. THF: 67.9, 25.7. ^{13}C NMR demonstrates absence of carbonyl-containing products.

Poly(lactic acid) depolymerization, Table 1, entry 4: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.85 (m, 1H), 3.56 (m, 1H), 3.36 (m, 1H), 2.37 (br s, 2H, OH), 1.14, (d, 3H). >99% conversion.

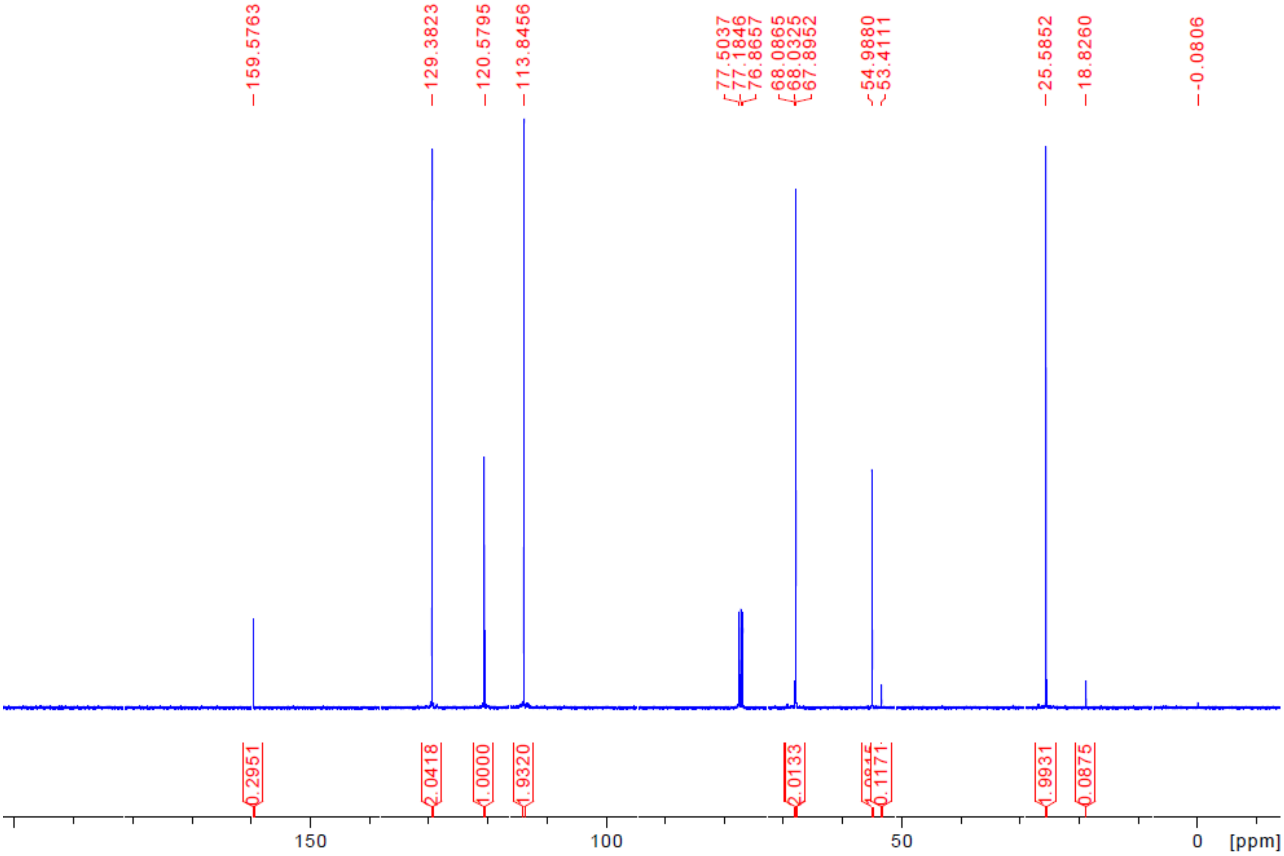

Fig. S4 ^{13}C NMR of crude reaction mixture of PLA depolymerization. (100 MHz, $CDCl_3$, δ): 68.1, 68.0, 18.8 aligns with standard of propylene glycol (53.4 is CH_2Cl_2 reference). Anisole: 159.6, 129.4, 120.6, 113.8, 55.0. THF: 67.9, 25.6. ^{13}C NMR demonstrates absence of carbonyl-containing products.

Polypropylene carbonate depolymerization, Table 1, entry 5: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.85 (m, 1H, PG), 3.56 (m, 1H, PG), 3.41 (s, 3H, MeOH), 3.34 (m, 1H, PG), 3.18 (br s, 2H, PG OH), 1.12 (d, 3H, PG). >99% conversion.

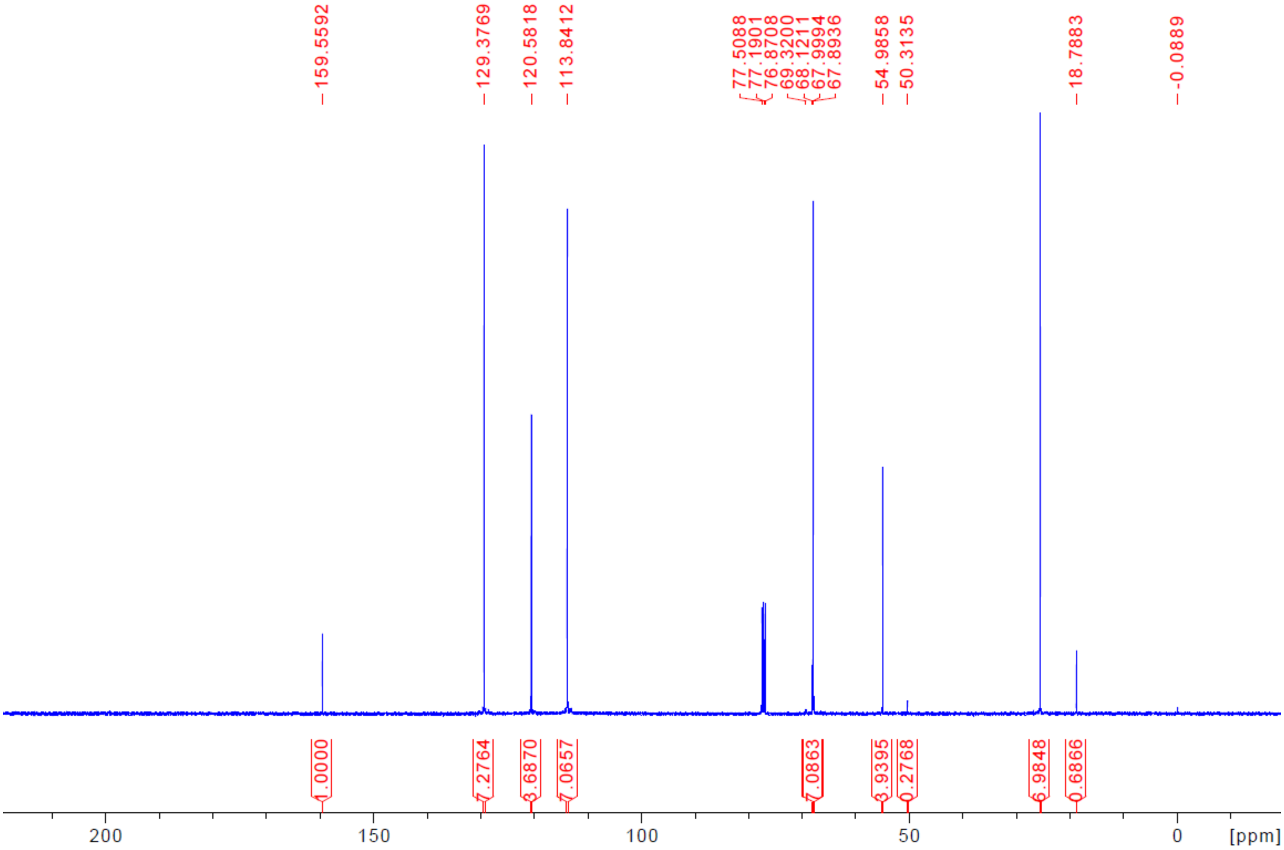

Fig. S5 ^{13}C NMR of crude reaction mixture of PPC depolymerization. (100 MHz, $CDCl_3$, δ): 68.1 (PPC), 68.0 (PPC), 50.3 (MeOH), 18.8 (PG) align with standards of propylene glycol and methanol. Anisole: 159.6, 129.4, 120.6, 113.8, 55.0. THF: 67.9, 25.6. ^{13}C NMR demonstrates absence of carbonyl-containing products.

Polyethylene carbonate depolymerization, Table 1, entry 6: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.64 (s, 4H, EG), 3.39 (s, 3H, MeOH), 3.00 (br s, 2H, EG OH), 2.51 (br s, 1H, MeOH). 91% conversion.

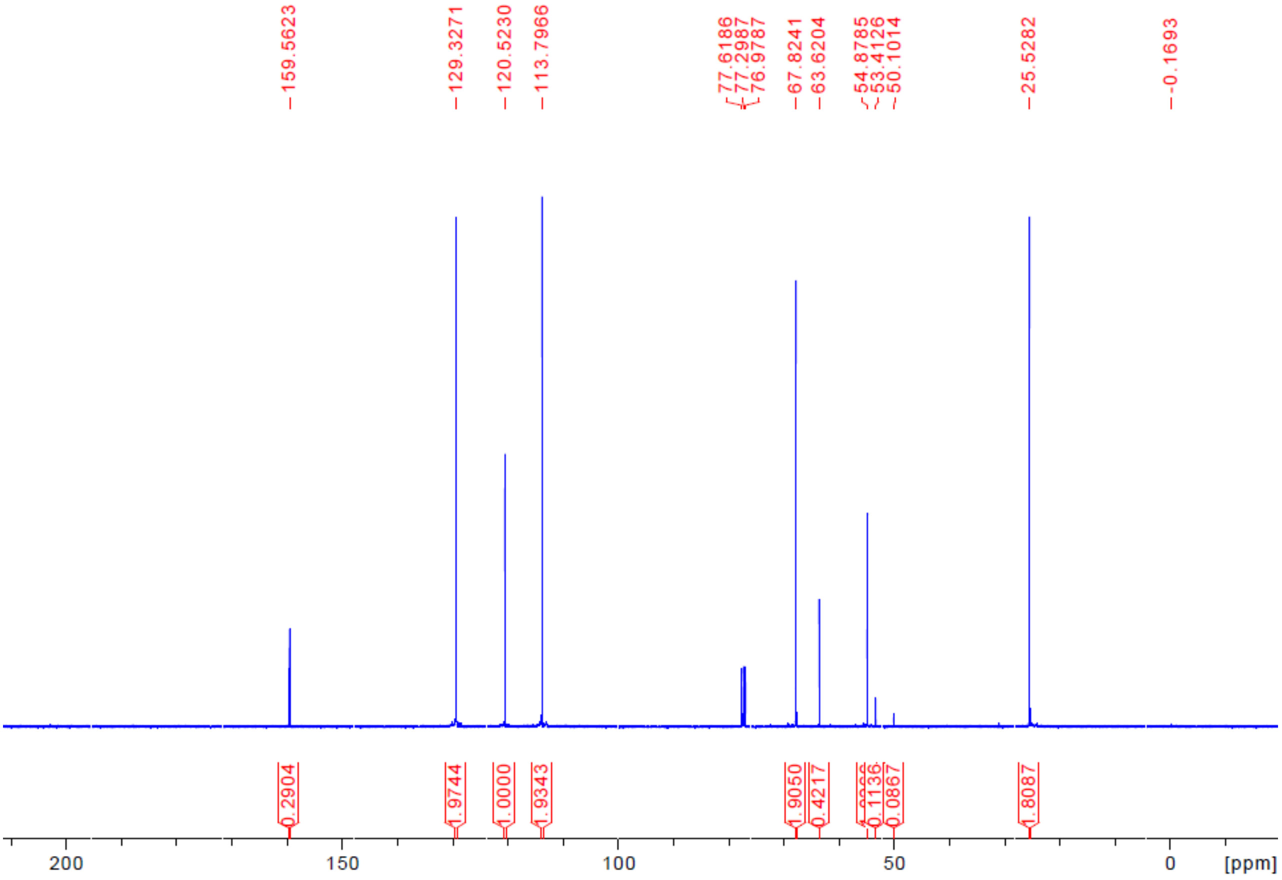

Fig. S6 ^{13}C NMR of crude reaction mixture of PEC depolymerization. (100 MHz, $CDCl_3$, δ): 63.6 (PEC), 50.1 (MeOH) align with standards of ethylene glycol and methanol (53.4 is CH_2Cl_2 reference). Anisole: 159.6, 129.3, 120.5, 113.8, 54.9. THF: 67.8, 25.5. ^{13}C NMR demonstrates absence of carbonyl-containing products.

Poly(*R*-3-hydroxybutyric acid) depolymerization, Table 1, entry 7: ^{1}H NMR (400 MHz, CDCl$_3$, δ): 2.29 (t, 2H), 1.65 (m, 2H), 0.96 (t, 3H). 88% conversion

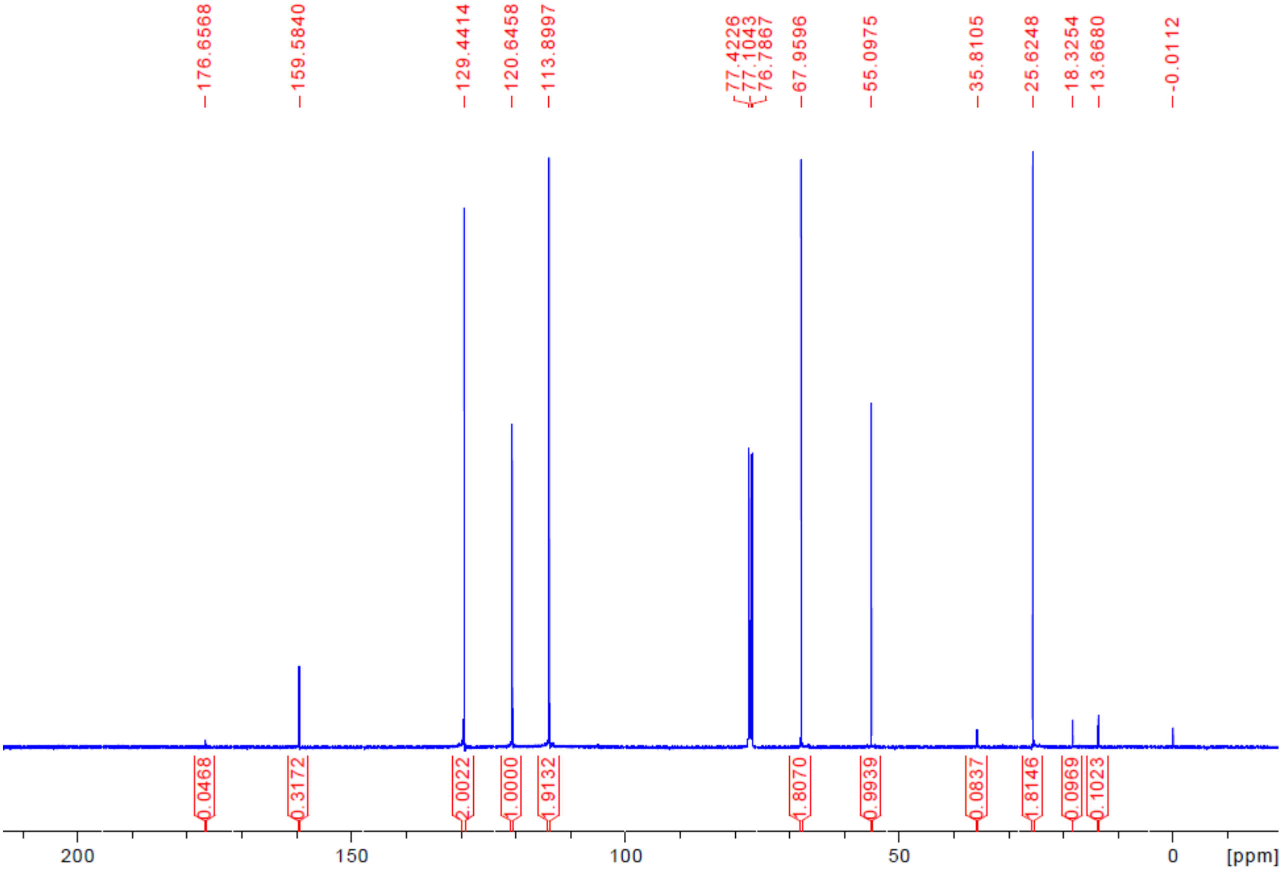

Fig. S7 ^{13}C NMR of crude reaction mixture of PHB depolymerization. (100 MHz, CDCl$_3$, δ): 176.7, 35.8, 18.3, 13.7 aligns with standard of butyric acid. Anisole: 159.6, 129.4, 120.6, 113.9, 55.1. THF: 67.9, 25.6.

Poly(3-hydroxypropionic acid), Table 1, entry 8: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.31 (q, 2H), 1.12 (t, 3H). 90% conversion

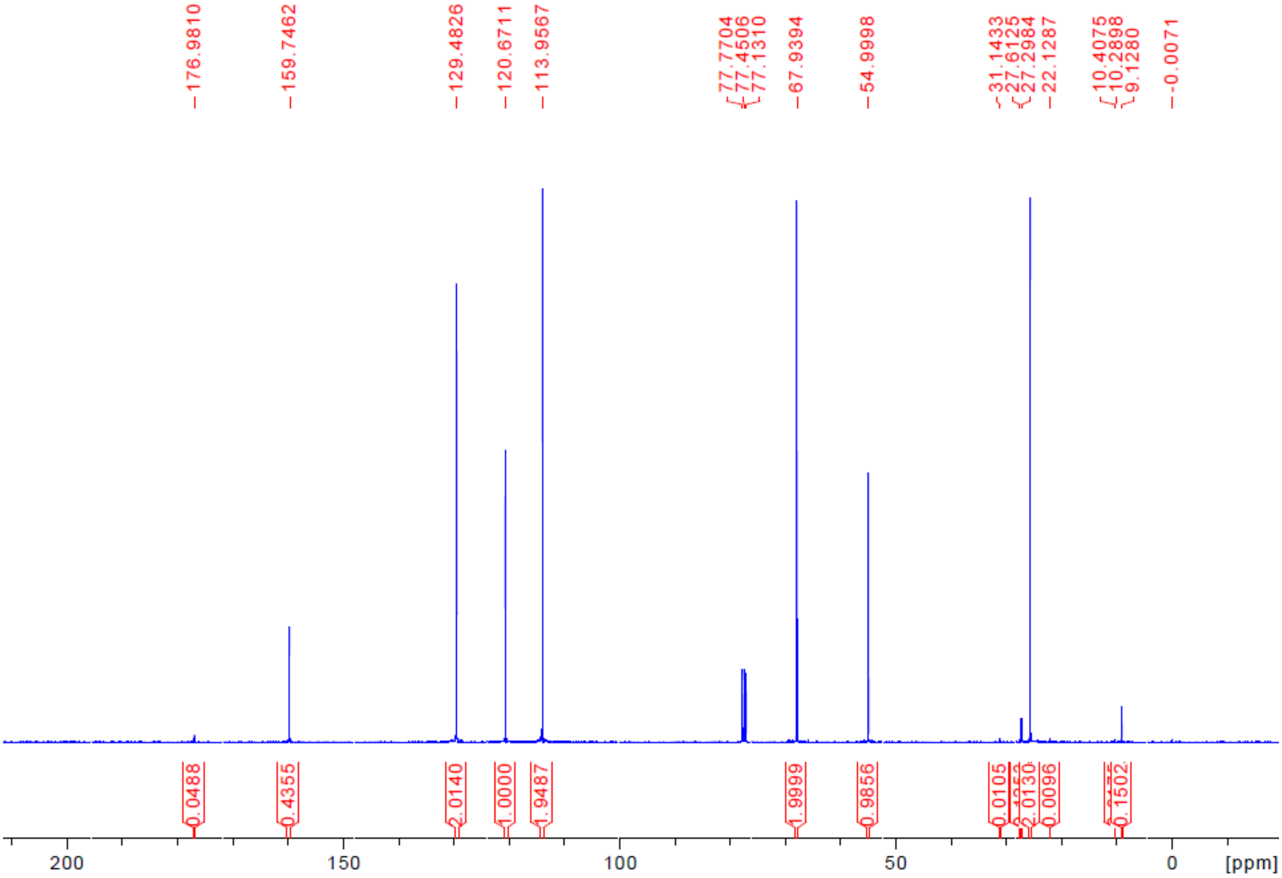

Fig. S8 ^{13}C NMR of crude reaction mixture of P3HP depolymerization. (100 MHz, $CDCl_3$, δ): 177.0, 27.3, 9.1 aligns with standard of propionic acid. Anisole: 159.7, 129.5, 120.7, 113.9, 55.0. THF: 67.9, 25.6.

References:

1 E. Balaraman, B. Gnanaprakasam, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2010, **132**, 16756.

2 D. M. Hunsicker, B. C. Dauphinais, S. P. Mc Ilrath and N. J. Robertson, *Macromol. Rapid Commun.*, 2012, **33**, 232.