

Electronic Supplementary Information for

Highly selective pressure-dependent (transfer) hydrogenative depolymerization of polybutylene succinate

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General Information:

All reagents were purchased from Fisher Scientific Inc. or Sigma Aldrich Corporation and used as received. Tetrahydrofuran, 99.9%, anhydrous, stabilized with BHT and fitted AcroSeal,TM was transferred to Schlenk flask and used in nitrogen filled mBraun glove box. Hydrogen gas (HY 5.0UH, 99.999%) was purchased from Linde Gas and Equipment Inc. and used as received. Ru-MACHO-BH (**1**), Ru-MACHO catalyst precursor (**2**), and Milstein catalyst precursor (**3**) were purchased from STREM Chemicals Inc. and were stored in glove box. 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. NMR characterizations were performed neat using an Anasazi Instruments Eft-60 NMR Spectrometer. Samples of insufficient product volume to run neat had CDCl₃ added. Samples were analyzed using quantitative ¹³C methods and data was acquired for 2000 scans using a 60 degree pulse width. Spectra were analyzed using the SNAP software (Anasazi) with 0.5 Hz line broadening. Chemical shifts are referenced to tetramethylsilane at zero ppm. Gas Chromatography was performed on a Shimadzu 2014 gas chromatograph equipped with a 30 meter Zebron ZB-Wax plus column. Reaction products were compared to commercially purchased samples of *gamma*-butyrolactone (GBL) and 1,4-butanediol (BDO). Observed ¹³C NMR shifts for GBL are 178, 69, 28 and 22 ppm and BDO are 62 and 29 ppm. The relative integrations for peaks at 69 (GBL) and 62 (BDO) were selected for percent conversion calculations.

Initial Screening Conditions:

Catalyst screening followed our previously developed procedure,¹ Catalyst precursor (.023 mmol Ru), KO^tBu (2 eq), and solvent (1.5 mL THF, 1.5 mL anisole) were combined in a scintillation vial for 5 minutes, then transferred to a reactor bottom charged with magnetic stir bar and PBS (200 mg, 1.2 mmol). The reactor was sealed and purged with hydrogen gas (20.4 atm) for three pressurization/venting cycles with rapid stirring. Following the third cycle, the reactor was charged with 13.6 atm hydrogen and immersed in a silicone oil bath and heated to 150 °C for 24 hours. Following the designated time, the reactor was cooled to room temperature, vented, and then checked for residual polymeric solids. Samples without solids were analyzed by GC.

Table S1: Screening of commercially available ruthenium complexes for PBS depolymerization.

Catalyst	Mass (Ru, KO ^t Bu mg)	Result
Ru-MACHO-BH (1)	13.6 mg, 0 mg	Clear brown solution
Ru-MACHO (2)	14.1 mg, 5.2 mg	Polymer solids remain
Milstein Catalyst Precursor (3)	11.3 mg, 5.2 mg	Polymer solids remain

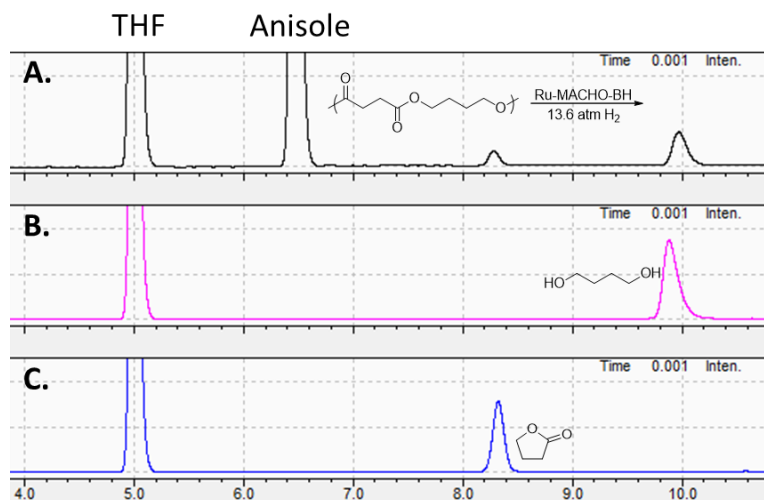


Figure S1. A. Chromatogram of the mixture following PBS reaction with Ru-MACHO-BH and 20.4 atm H₂. B. Chromatogram of BDO in THF. C. Chromatogram of GBL in THF.

General depolymerization procedure for reaction optimization:

Catalyst, PBS (1.0 g, 11.6 mmol carbonyl), and a magnetic stir bar were added directly into the pressure vessel containing a glass sleeve and charged with 1.0 mL of solvent *via* a disposable syringe in a nitrogen filled glovebox. The vessel was sealed, removed from the glovebox, and purged with hydrogen gas (20.4 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. The glass sleeve was removed, which contained any unreacted polymeric solids and catalyst residues. GBL and BDO distilled into the reactor bottom outside of the glass sleeve during the course of the reaction (Figure S2). Depolymerization products were quantitatively removed using an additional 5.0 mL of THF in four successive rinses to ensure products on the walls of the glass sleeve and the reactor bottom were recovered. These were combined, concentrated *via* rotary evaporation, and massed before transferring to an NMR tube for quantitative ^{13}C analysis. Percent conversions were calculated by the ratio between GBL and BDO/2 peaks. Percent yields were determined by isolated mass while considering the ratio between GBL and BDO when calculating the theoretical yields.

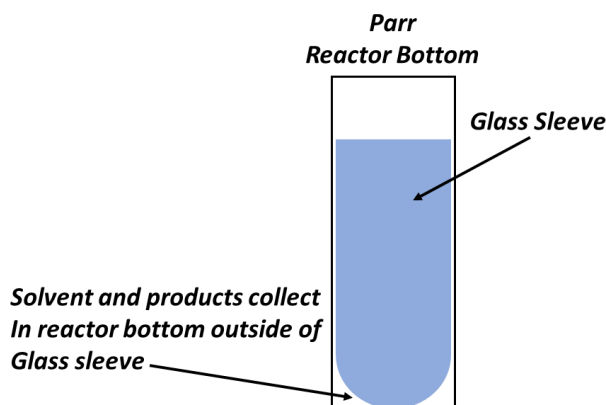


Figure S2. Schematic depicting shape of glass sleeve and where depolymerization products collect during the reaction

To ensure that quantitative ^{13}C NMR analysis accurately determined GBL:BDO mixtures, sample combinations were made from commercial standards, run for 2000 scans, and integrated. For example, a 99:1 GBL:BDO mixture was made from 8.52 mL GBL (112 mmol) and 0.1 mL BDO (1.1 mmol), mixed well, and added tetramethylsilane (Figure S3).

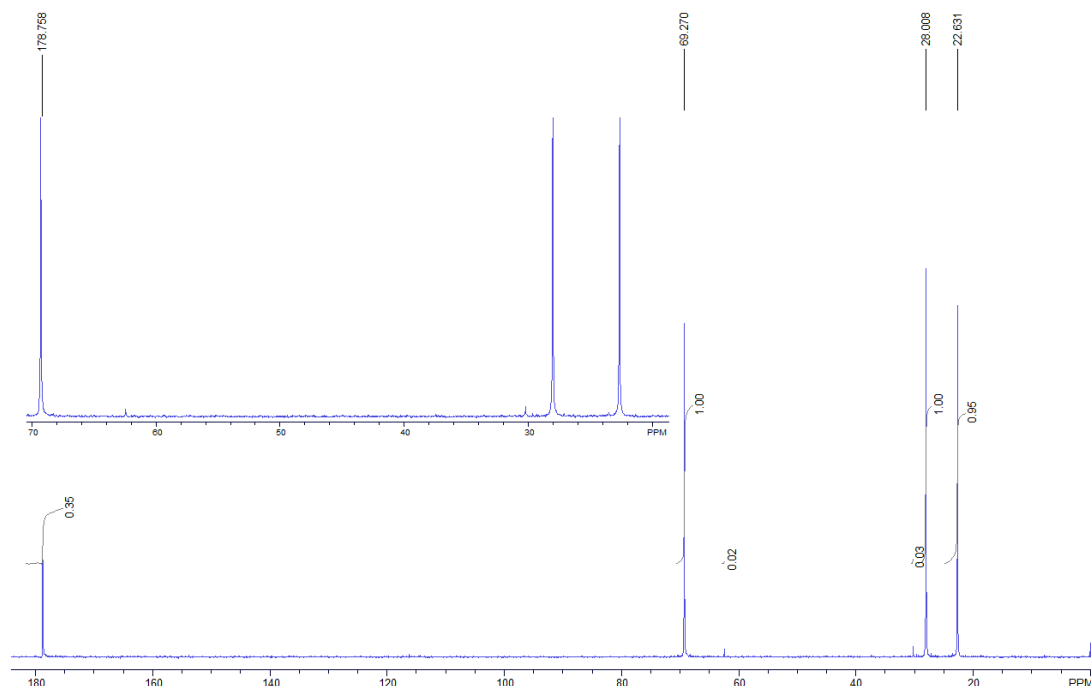


Figure S3. ^{13}C NMR spectrum of 99:1 mixture of GBL and BDO using commercial GBL and BDO. Integrating the peaks at 69 and 62 ppm leads to $1/1.01 = 99.0\%$ GBL.

Table S2. Optimization conditions for 20 h depolymerization of PBS to GBL or BDO.

Entry	Catalyst (mol %)	T (°C)	P _{initial} (atm gauge)	Solvent (mL)	%GBL ^a	%BDO ^a	% yield ^b
1	1, 1.0	160	3.4	THF (1.0)	93.0	7.0	91
2	1, 1.0	185	3.4	THF (1.0)	99.0	1.0	94
3	1, 0.5	185	3.4	THF (1.0)	90.1	9.9	40
4	1, 0.75	185	3.4	THF (1.0)	94.8	5.2	45
5 ^c	1, 1.0	185	0.0	THF (1.0)	99.5	0.5	96
6	1, 1.0	185	0.7	THF (1.0)	98.0	2.0	59
7	1, 1.0	185	1.4	THF (1.0)	99.0	1.0	95
8	1, 1.0	185	2.0	THF (1.0)	98.0	2.0	88
9	1, 1.0	185	2.7	THF (1.0)	98.0	1.0	95
10 ^d	1, 2.0	185	n.a.	THF (1.0)	>99.9	<0.01	70
11 ^e	n.a.	185	3.4	THF (1.0)	0	0	0
12	1, 1.0	185	3.4	Me-THF (1.0)	97.1	2.9	93
13	1, 1.0	185	3.4	THF (0.5)	95.7	4.3	93
14	1, 1.0	185	3.4	n. a. (0)	99.0	1.0	77
15	2, 1.0	185	3.4	THF (1.0)	97.1	2.9	83
16	3, 1.0	185	3.4	THF (1.0)	85.5	14.5	51
17	1, 1.0	185	5.1	THF (1.0)	96.6	3.4	79
18	1, 1.0	185	6.8	THF (1.0)	93.9	6.1	89
19	1, 1.0	185	13.6	THF (1.0)	69.4	30.6	83
20	1, 1.0	185	20.4	THF (1.0)	52.1	47.9	98
21	1, 1.0	185	27.2	THF (1.0)	34.2	65.8	93
22	1, 1.0	185	34.0	THF (1.0)	21.3	78.7	94
23	1, 1.0	185	40.8	THF (1.0)	14.7	85.3	95
24 ^f	1, 1.0	185	47.6	THF (1.0)	1.0	99.0	95
25 ^f	1, 1.0	185	47.6	Me-THF (1.0)	1.2	98.8	91

^a Determined by quantitative ^{13}C NMR. ^b Determined by mass, incorporating the ratio between GBL and BDO in the product. ^c 48 h reaction time. ^d Reaction under 0 atm gauge N_2 . ^e No catalyst. ^f 1 h reaction time.

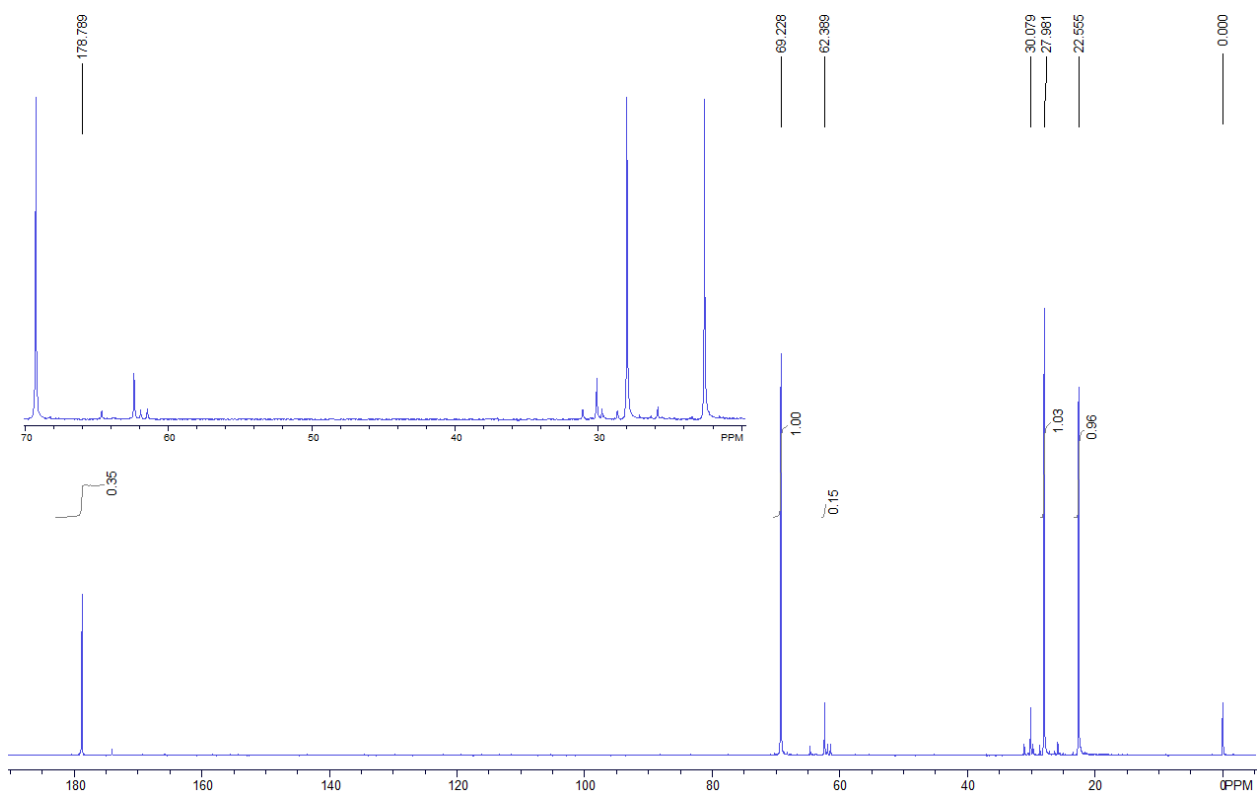


Figure S4. ^{13}C NMR spectrum for table 1, entry 1.

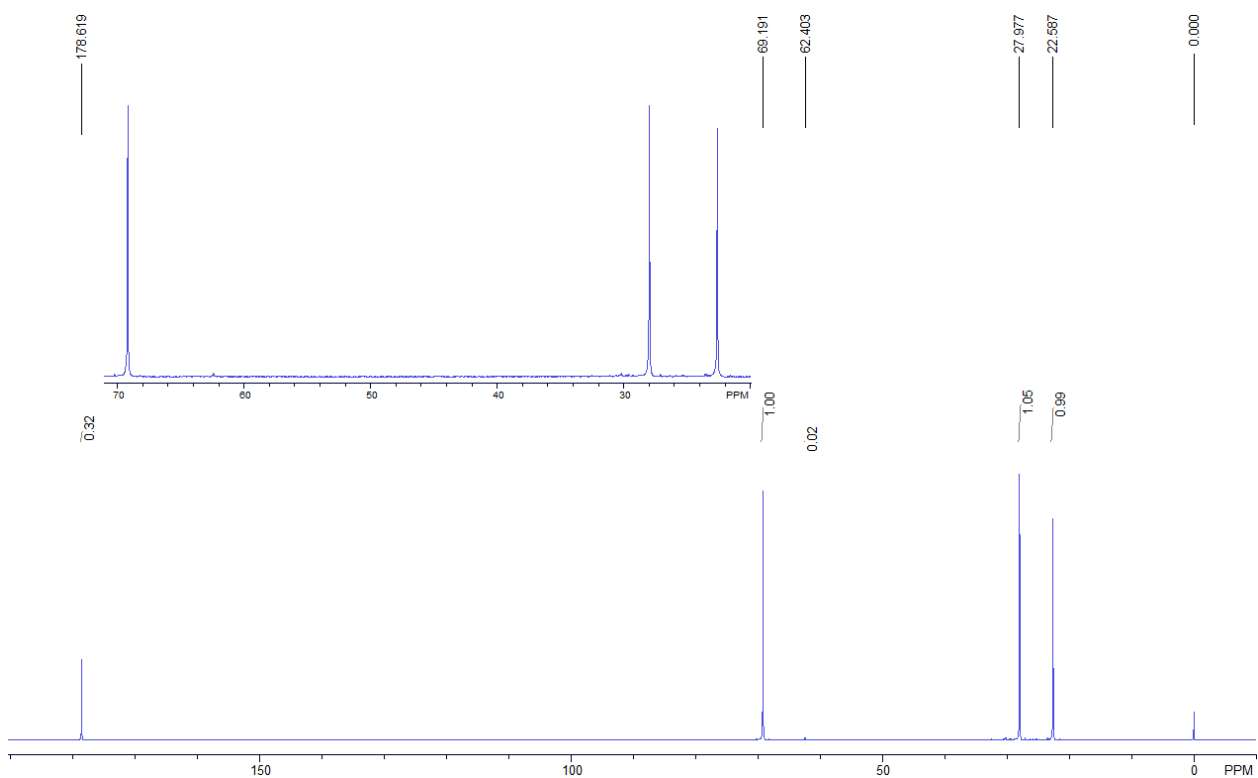


Figure S5. ^{13}C NMR spectrum for table 1, entry 2.

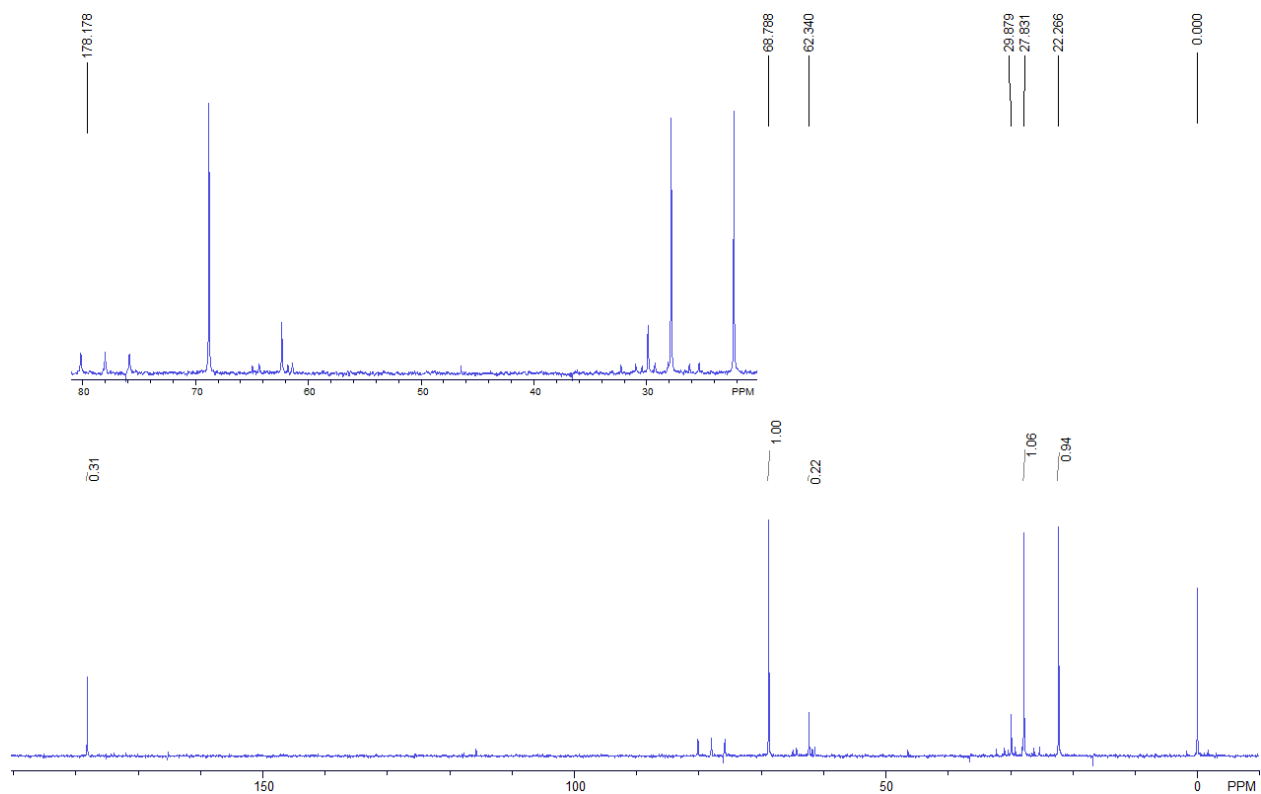


Figure S6. ^{13}C NMR spectrum for table 1, entry 3. CDCl_3 added to increase sample volume.

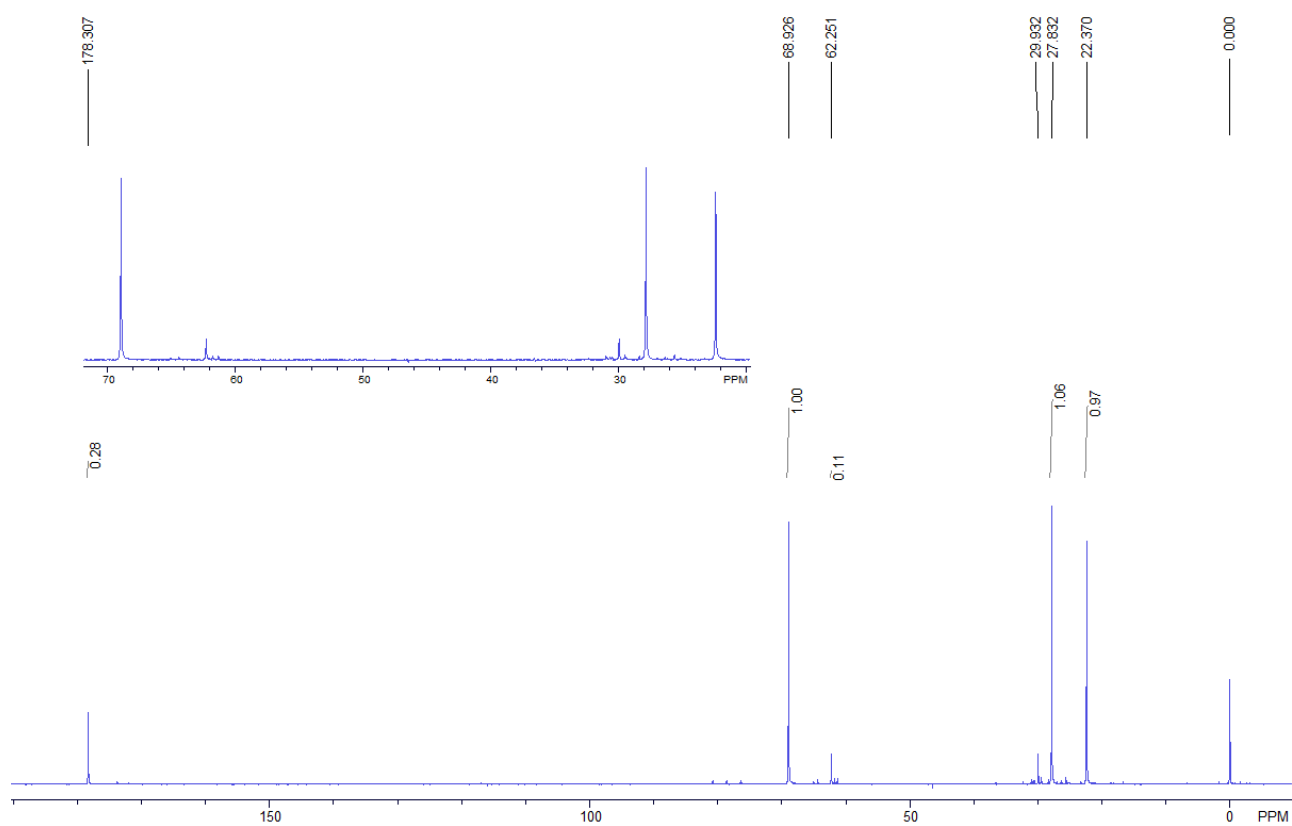


Figure S7. ^{13}C NMR spectrum for table 1, entry 4. CDCl_3 added to increase sample volume.

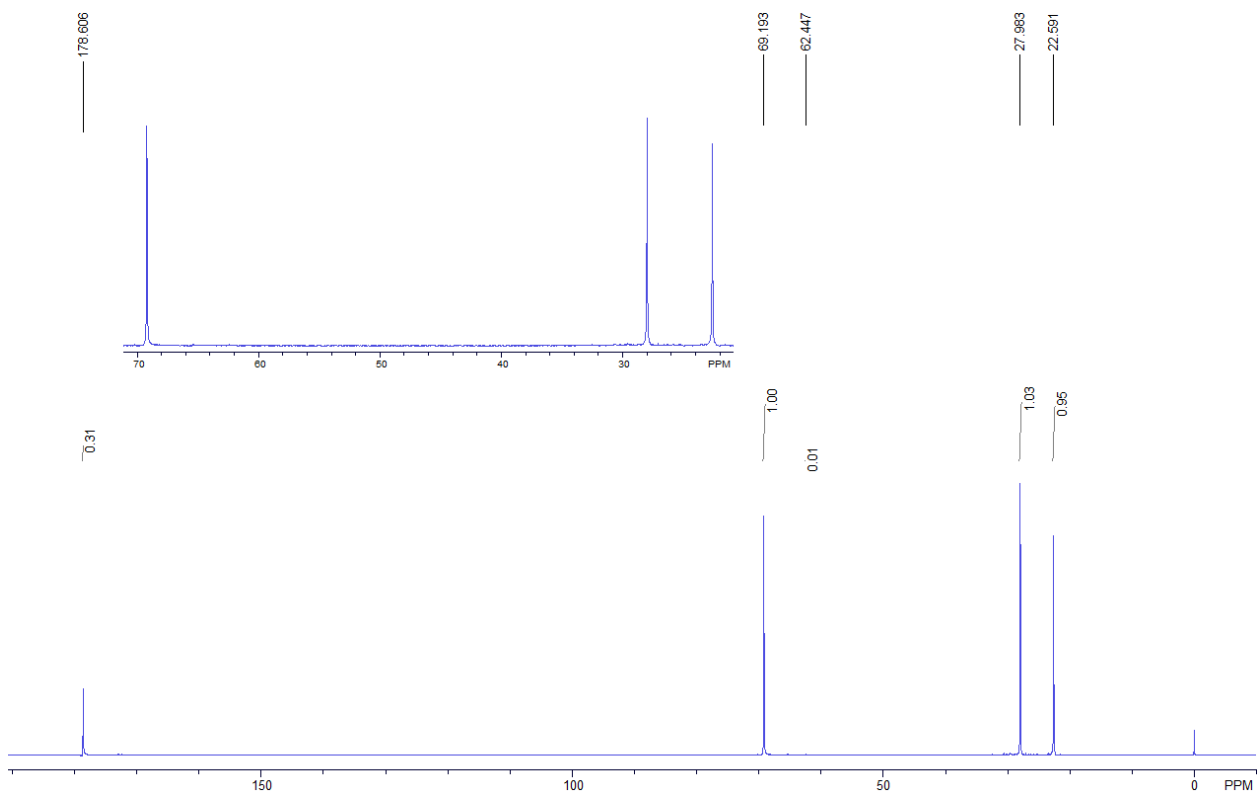


Figure S8. ^{13}C NMR spectrum for table 1, entry 5.

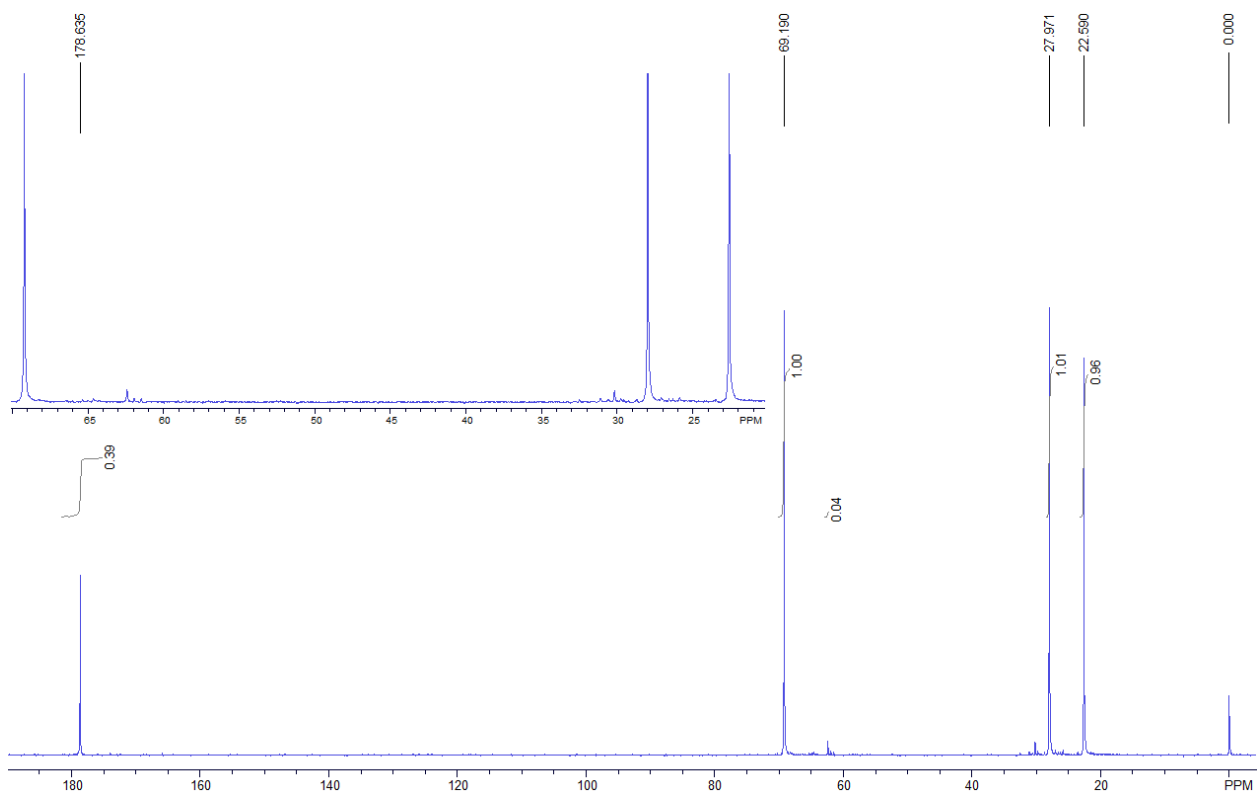


Figure S9. ^{13}C NMR spectrum for table 1, entry 6.

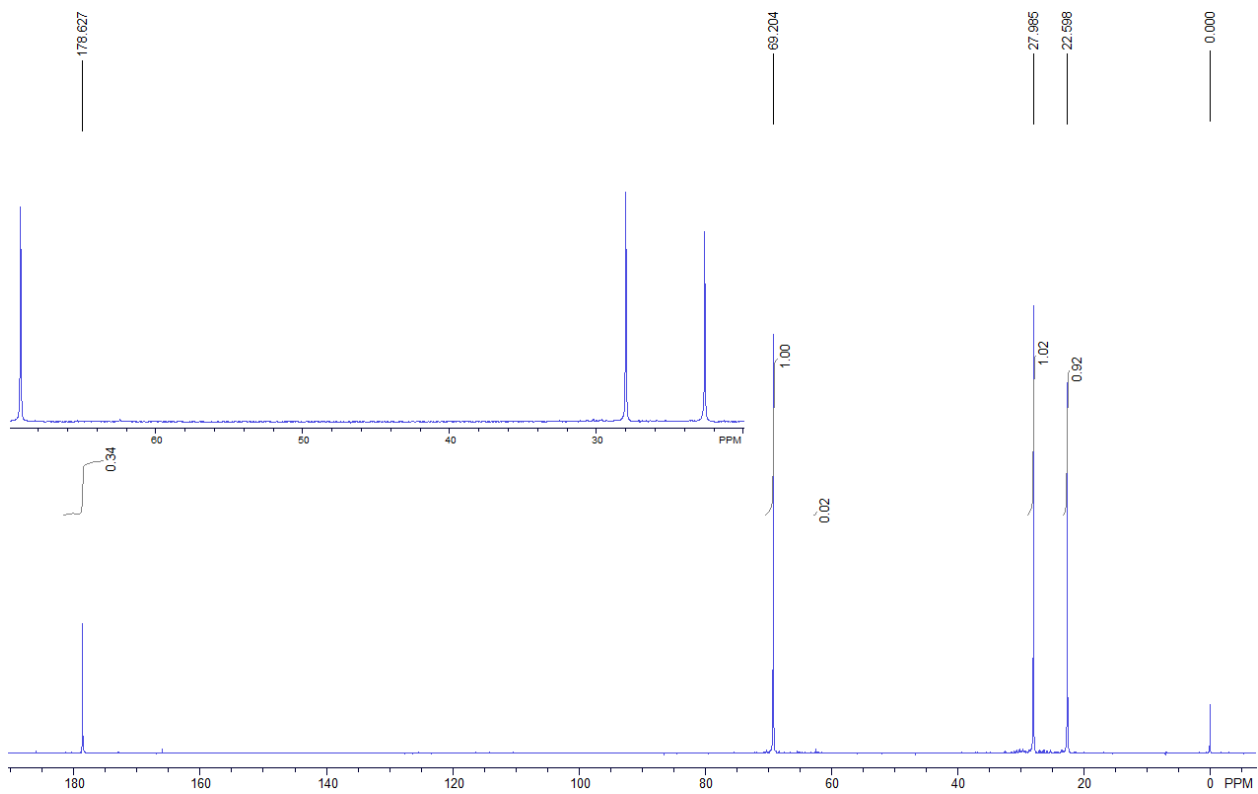


Figure S10. ^{13}C NMR spectrum for table 1, entry 7.

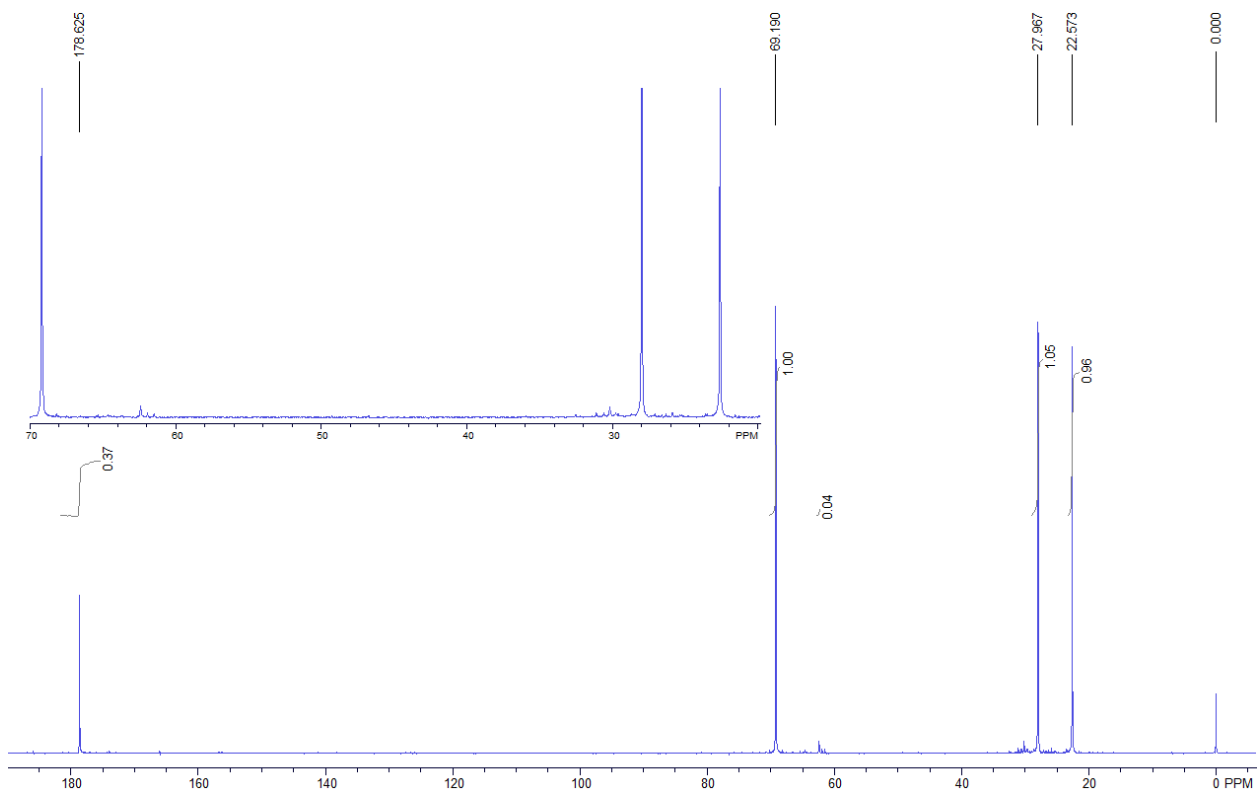


Figure S11. ^{13}C NMR spectrum for table 1, entry 8.

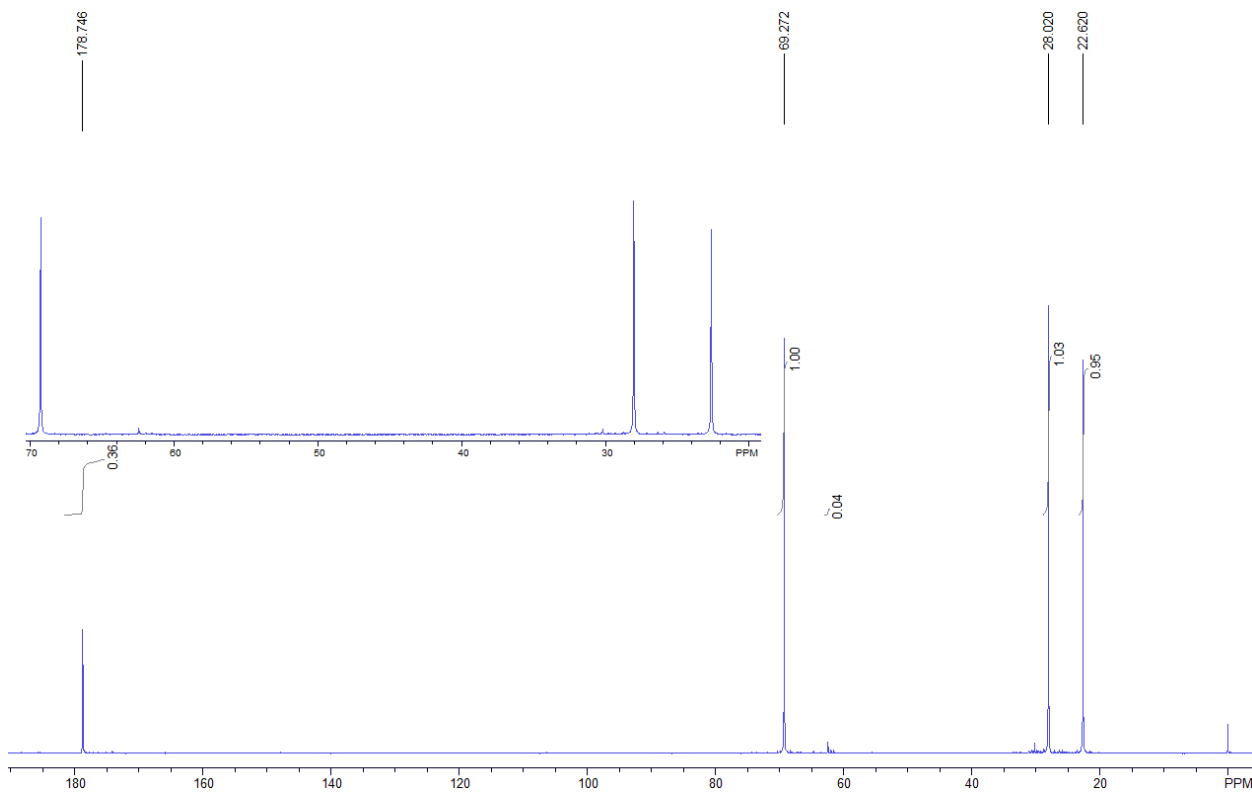


Figure S12. ^{13}C NMR spectrum for table 1, entry 9.

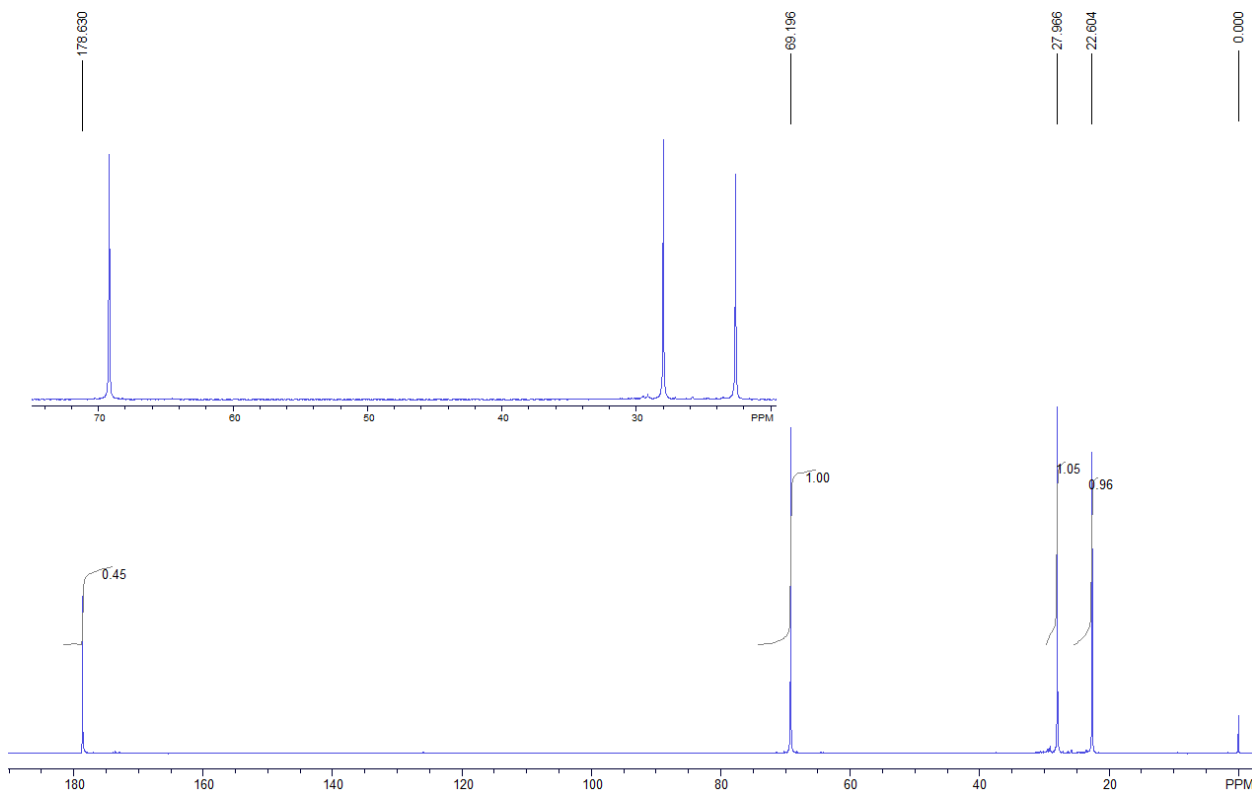


Figure S13. ^{13}C NMR spectrum for table 1, entry 10. No evident BDO signals.

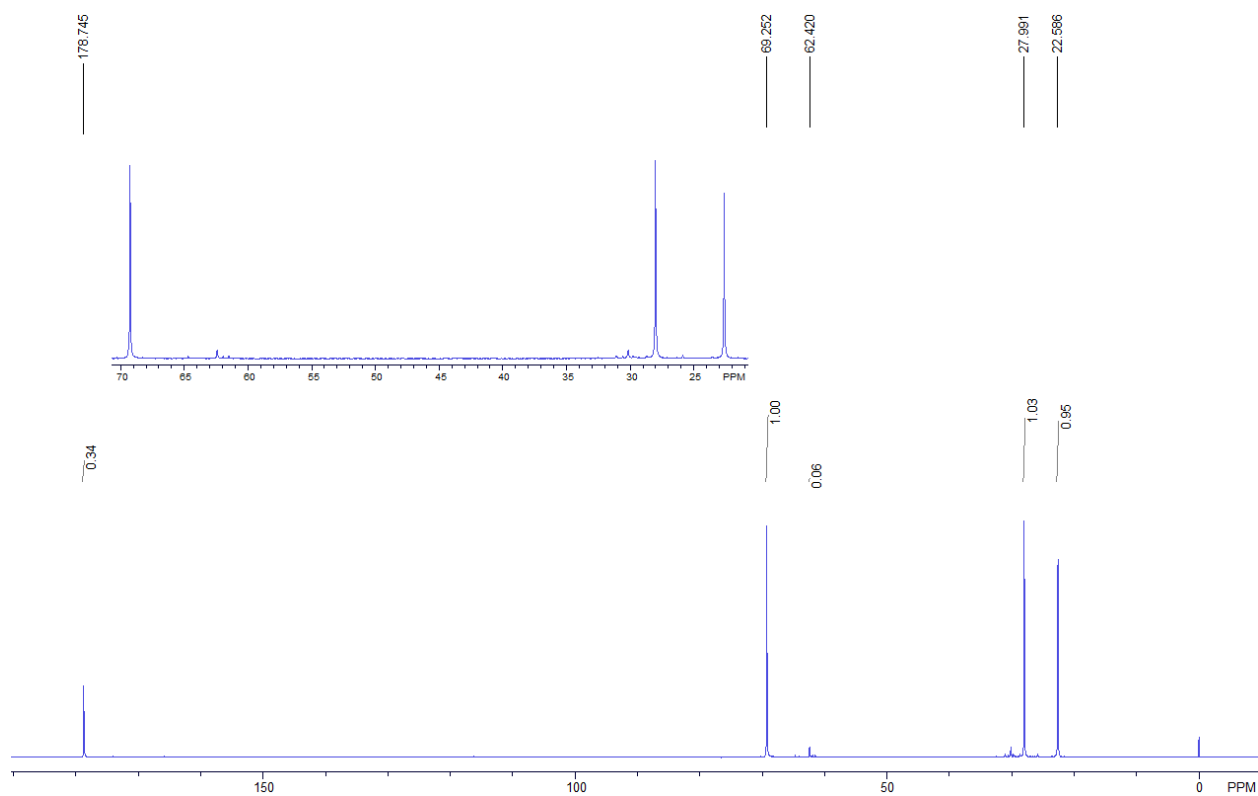


Figure S14. ^{13}C NMR spectrum for table 1, entry 12.

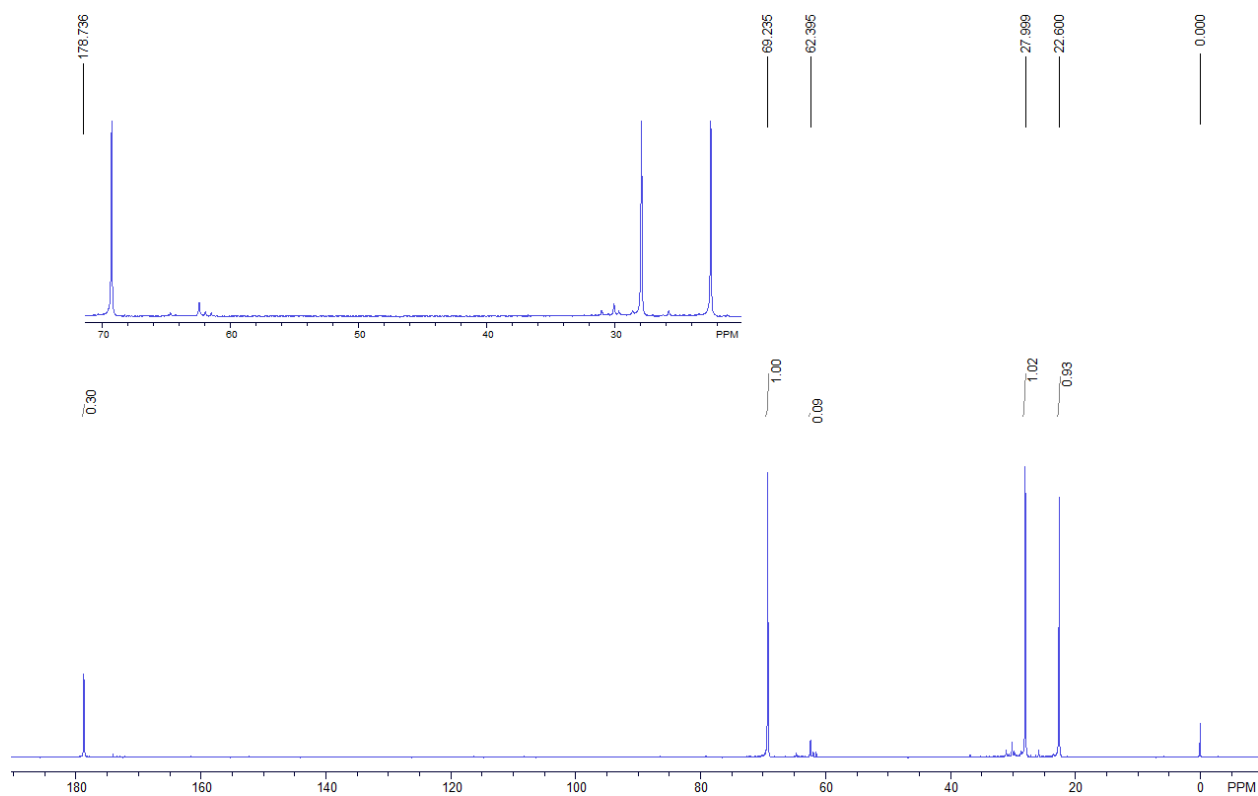


Figure S15. ^{13}C NMR spectrum for table 1, entry 13.

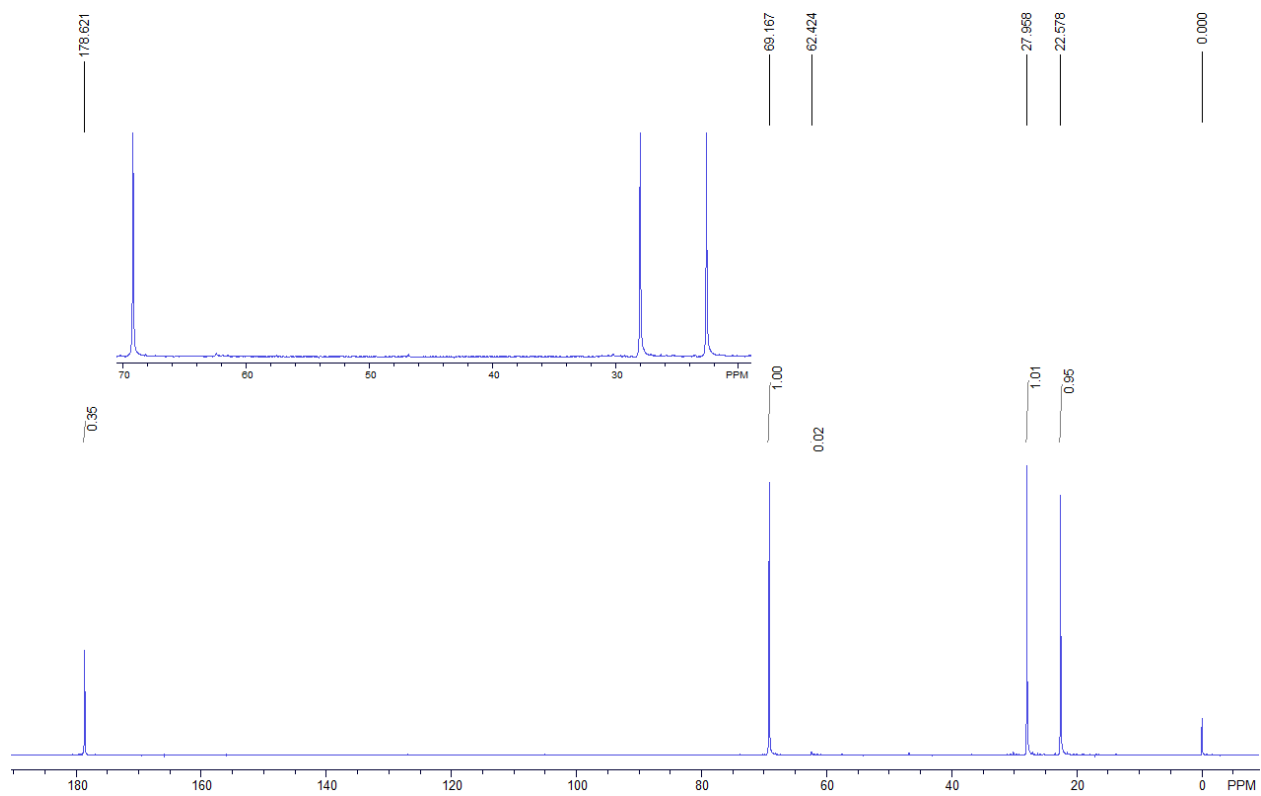


Figure S16. ^{13}C NMR spectrum for table 1, entry 14.

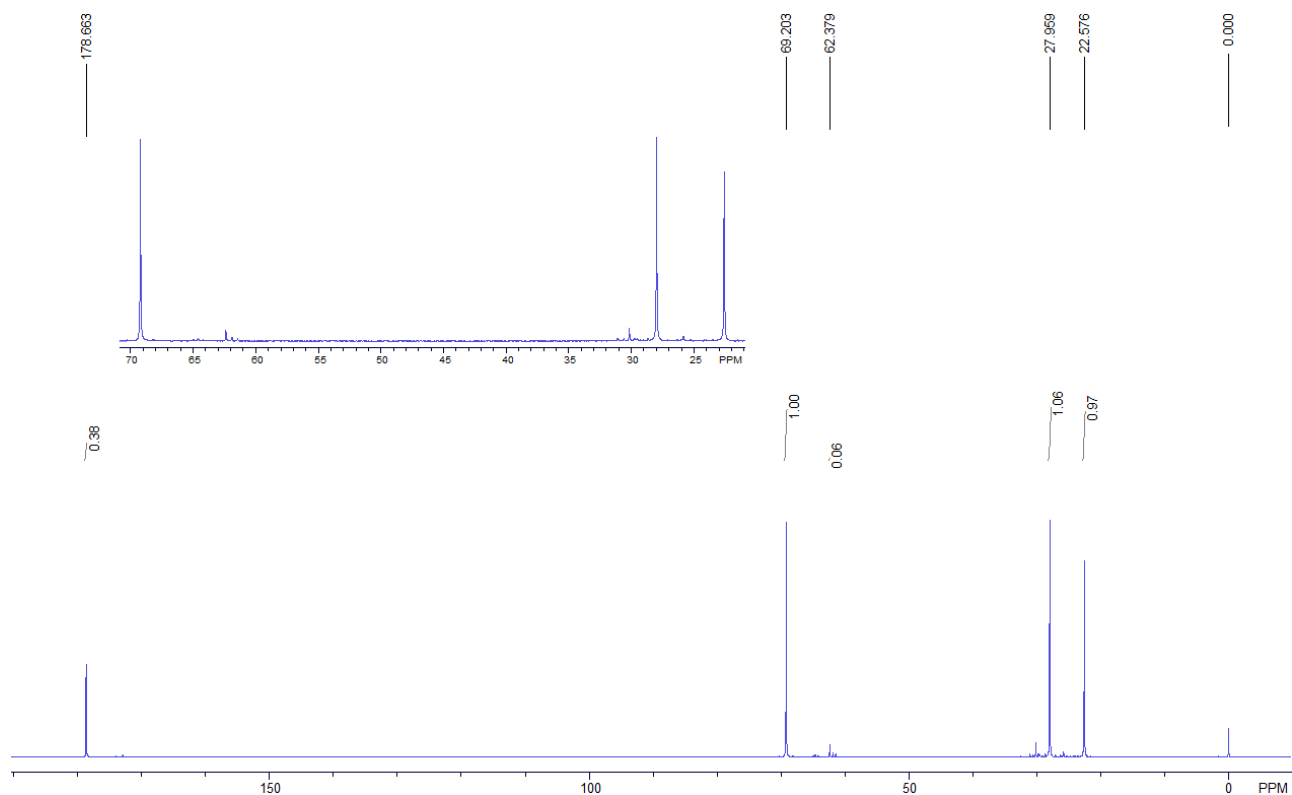


Figure S17. ^{13}C NMR spectrum for table 1, entry 15.

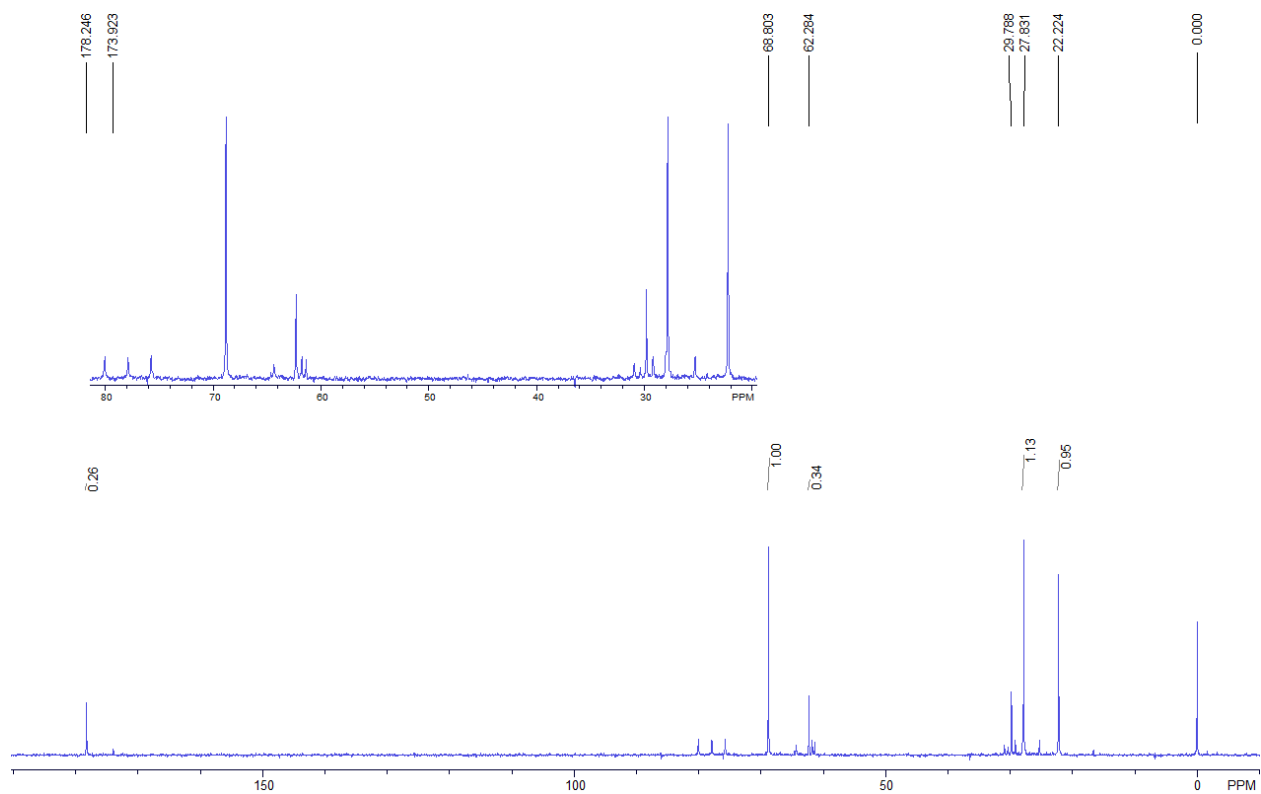


Figure S18. ¹³C NMR spectrum for table 1, entry 16. CDCl₃ added to increase sample volume.

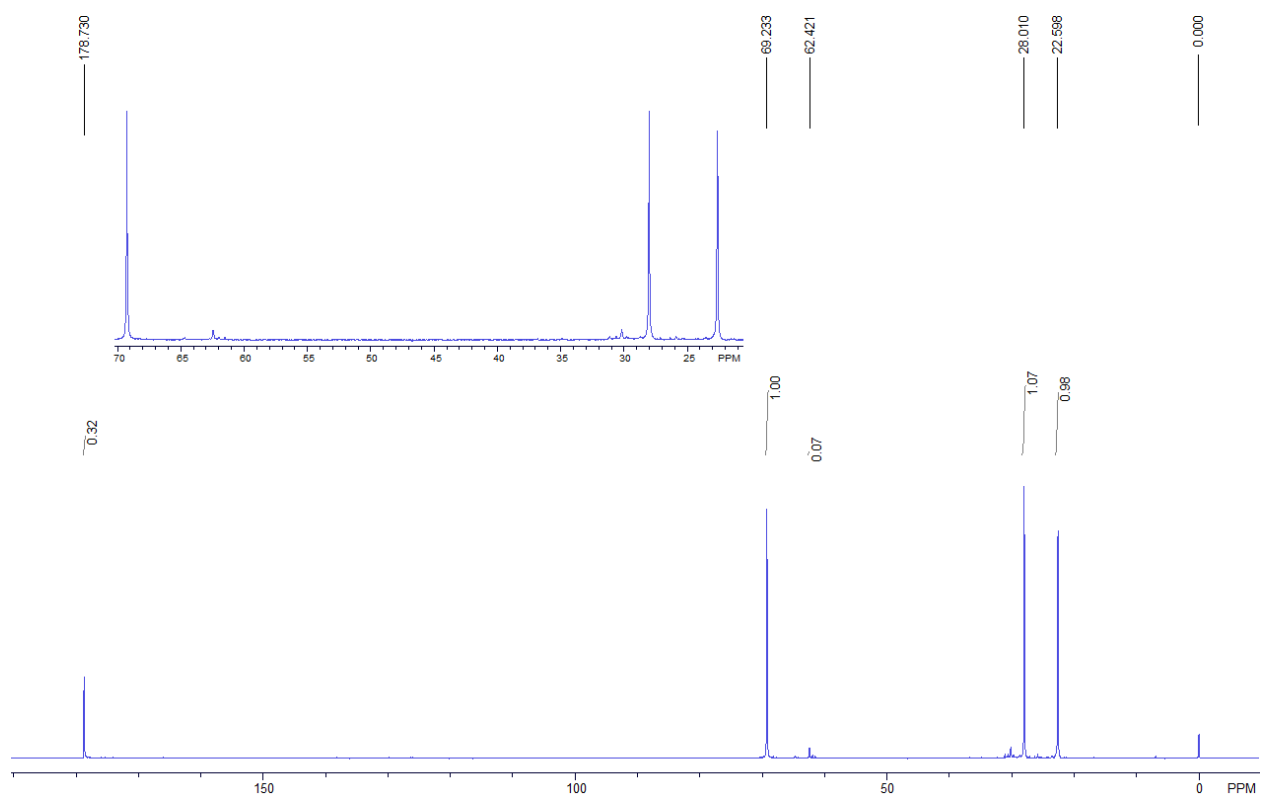


Figure S19. ¹³C NMR spectrum for table S2, entry 17.

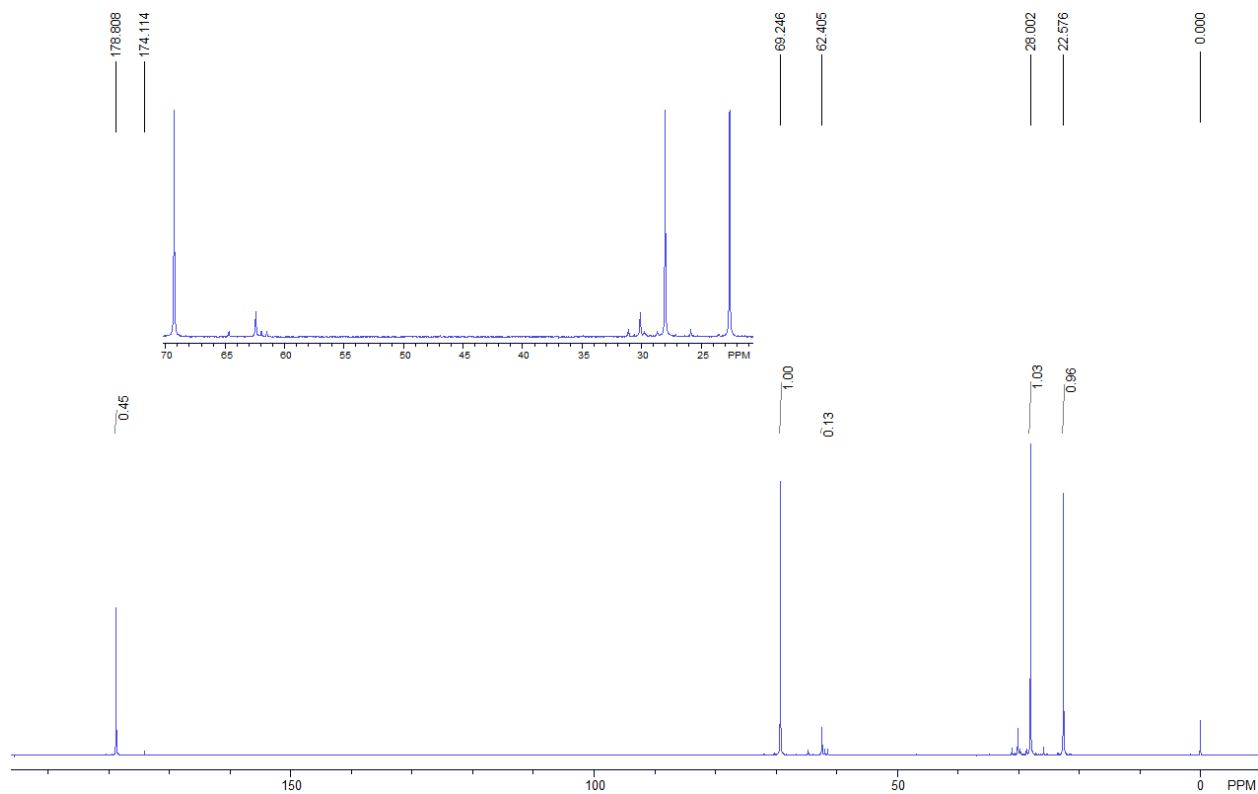


Figure S20. ^{13}C NMR spectrum for table S2, entry 18.

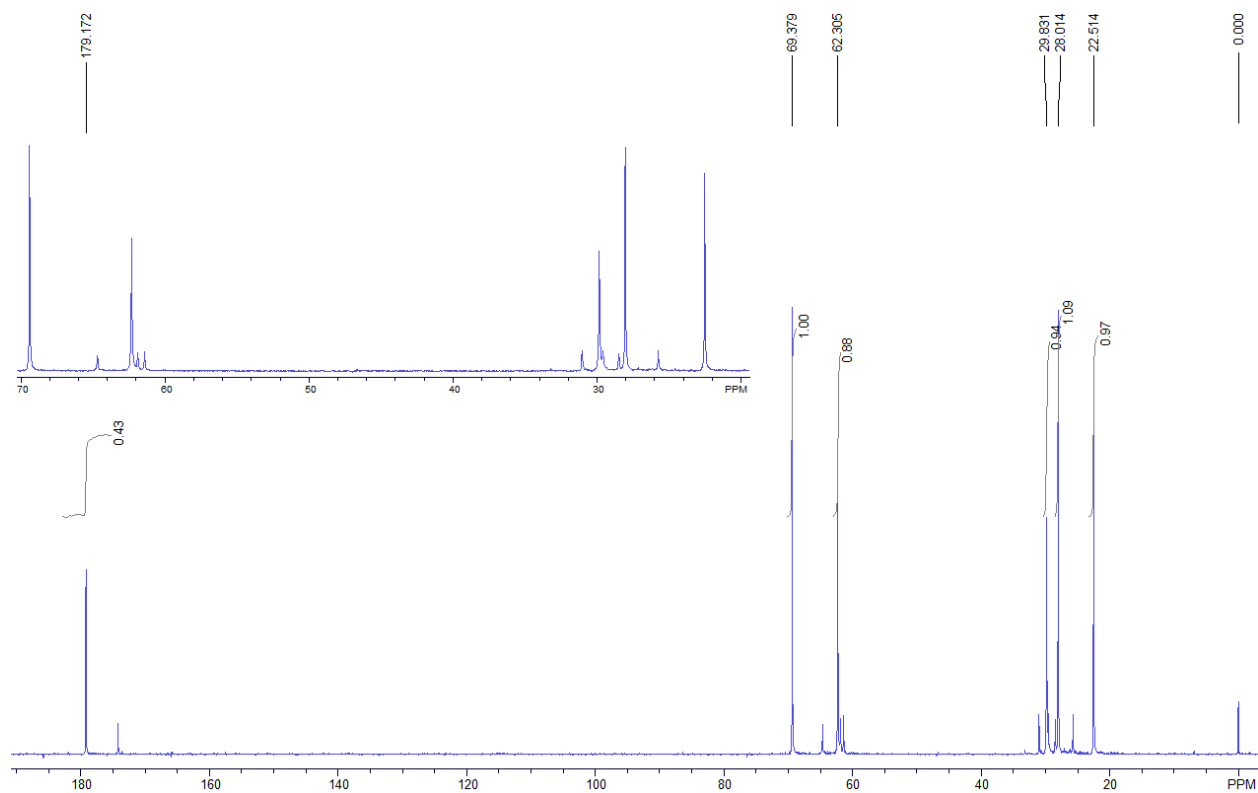


Figure S21. ^{13}C NMR spectrum for table S2, entry 19.

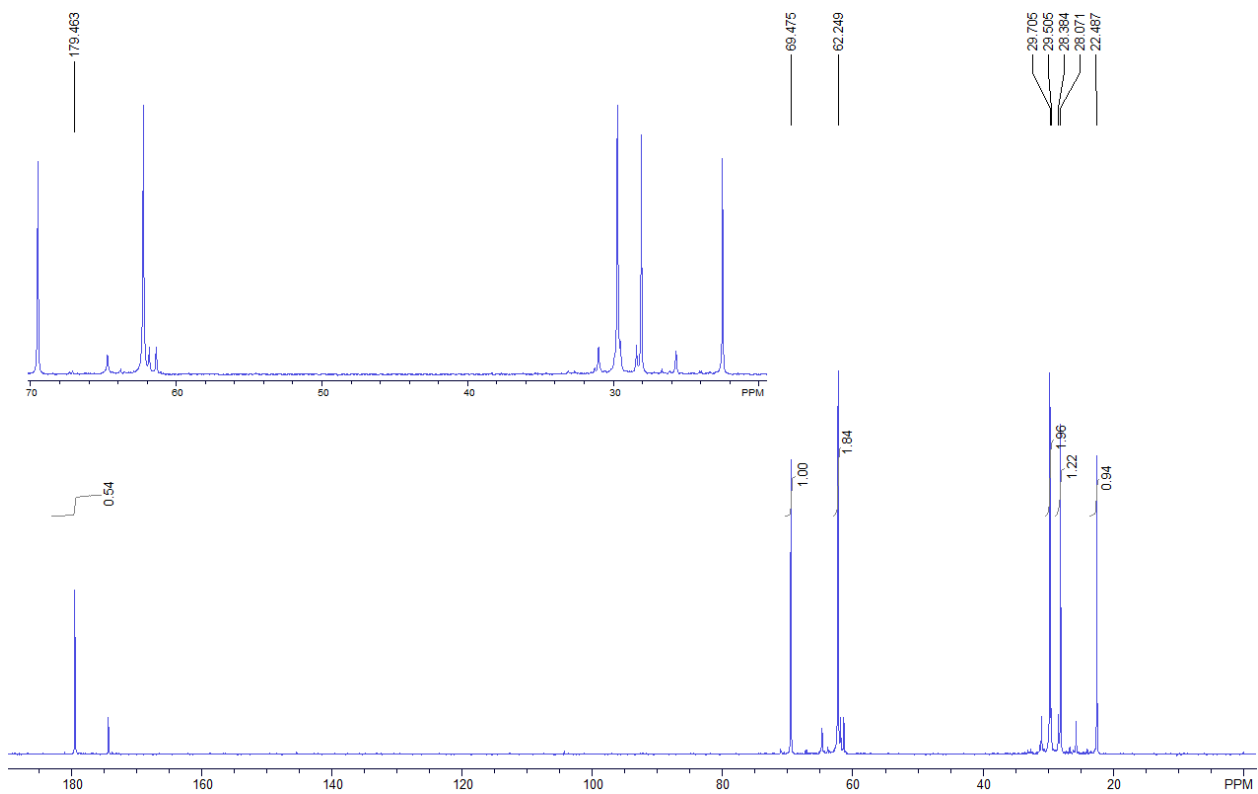


Figure S22. ^{13}C NMR spectrum for table S2, entry 20.

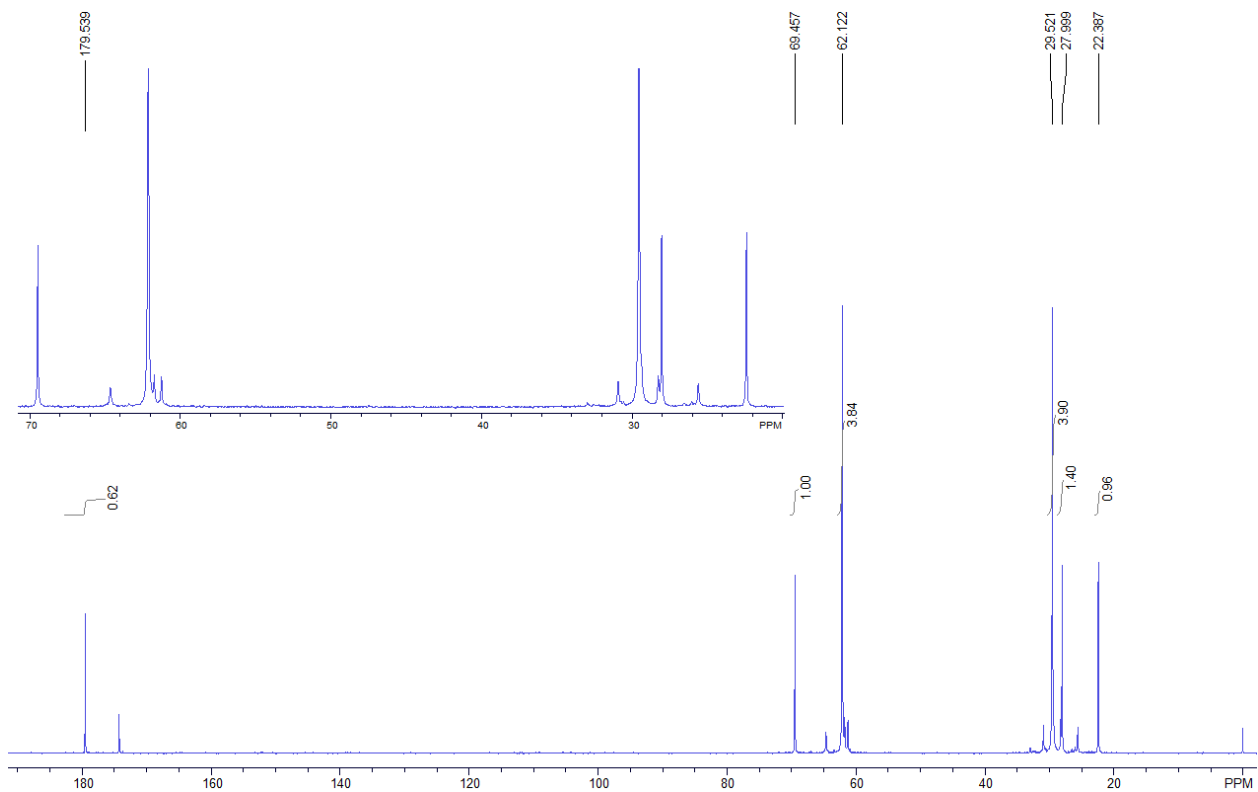


Figure S23. ^{13}C NMR spectrum for table S2, entry 21.

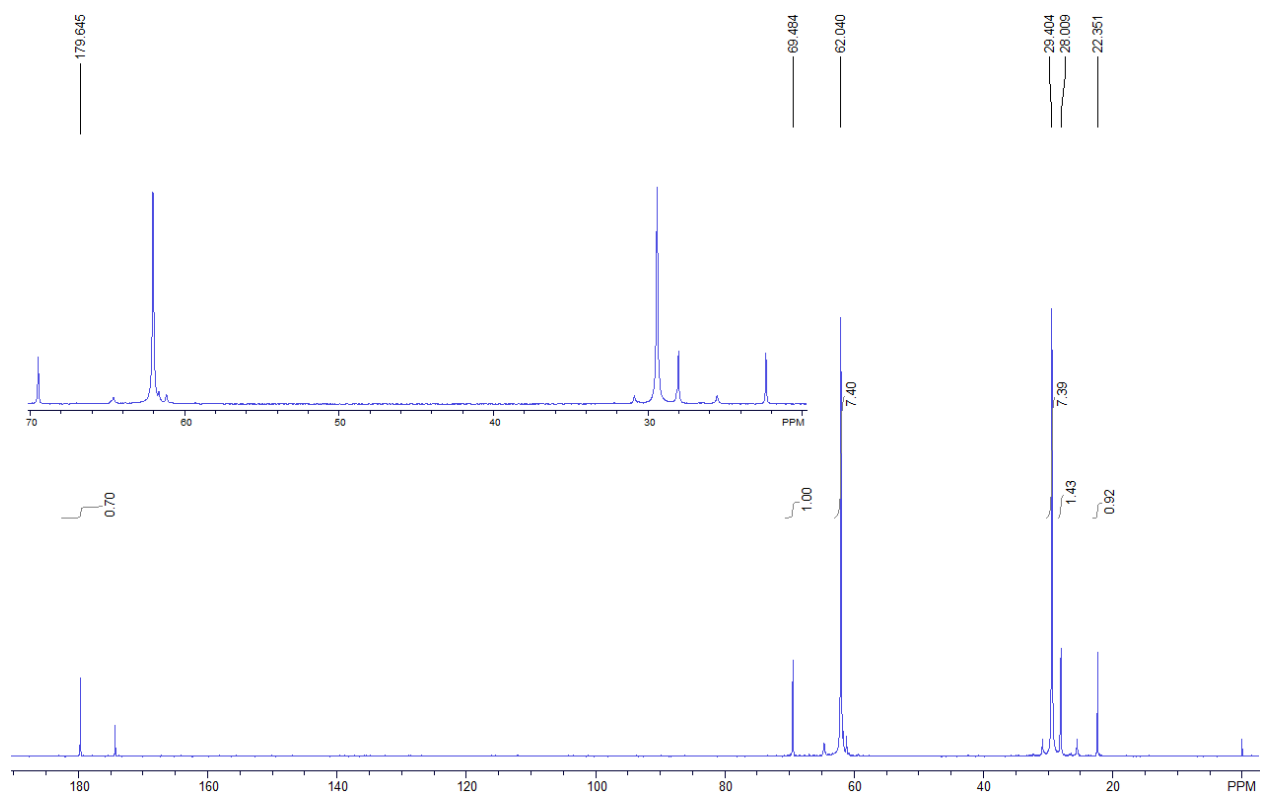


Figure S24. ^{13}C NMR spectrum for table S2, entry 22.

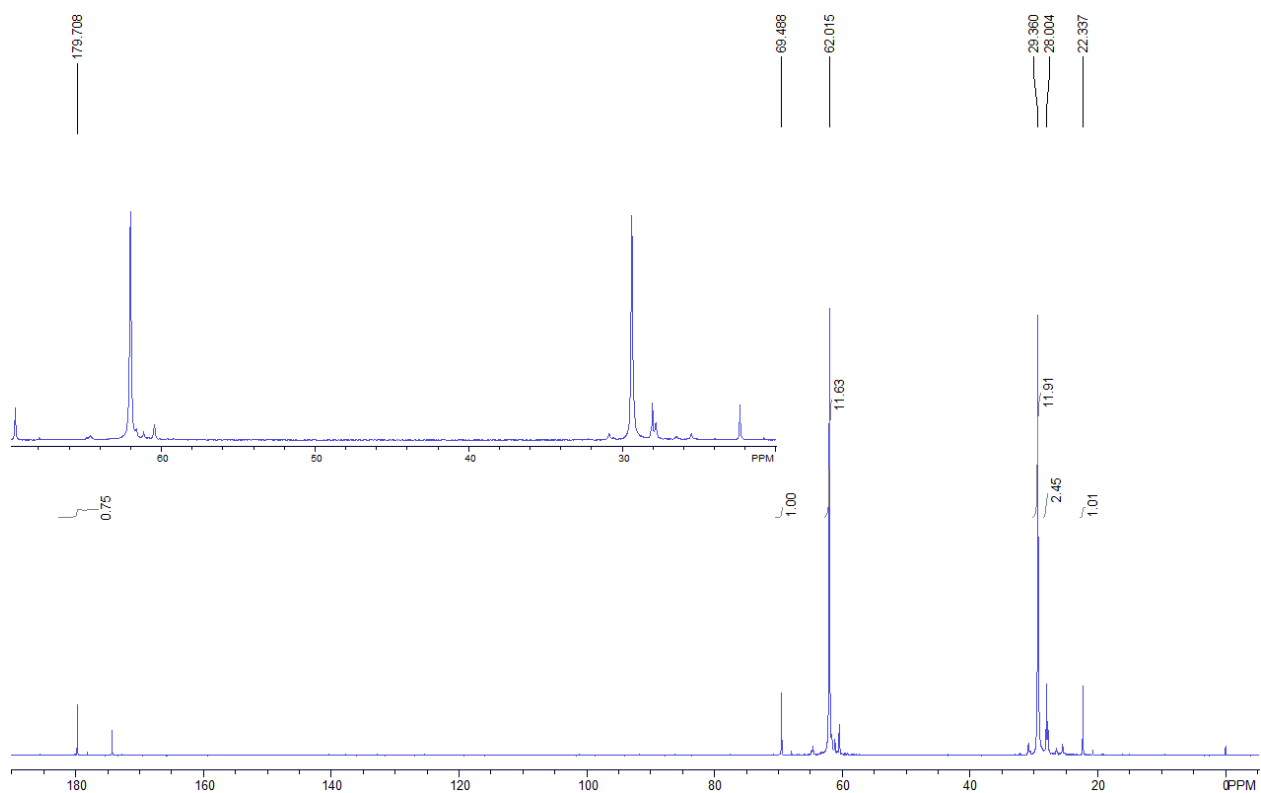


Figure S25. ^{13}C NMR spectrum for table S2, entry 23.

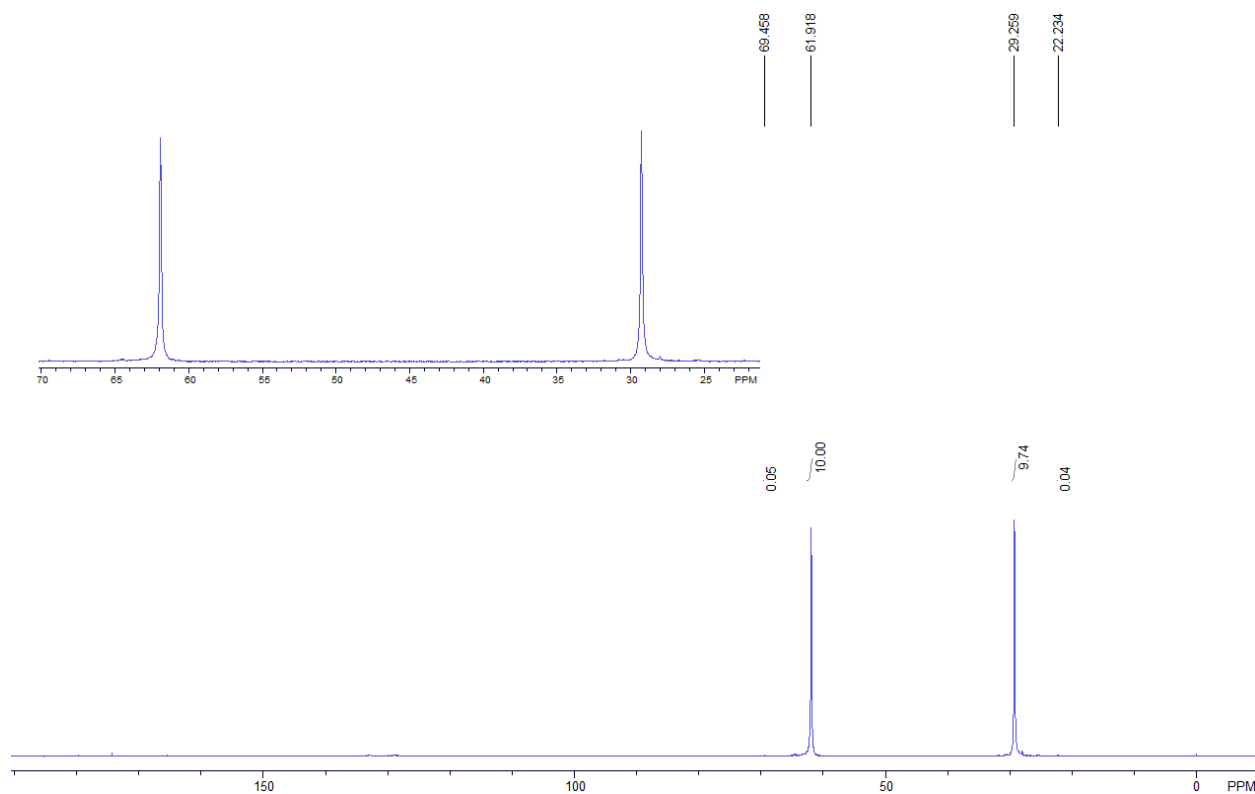


Figure S26. ¹³C NMR spectrum for table S2, entry 24.

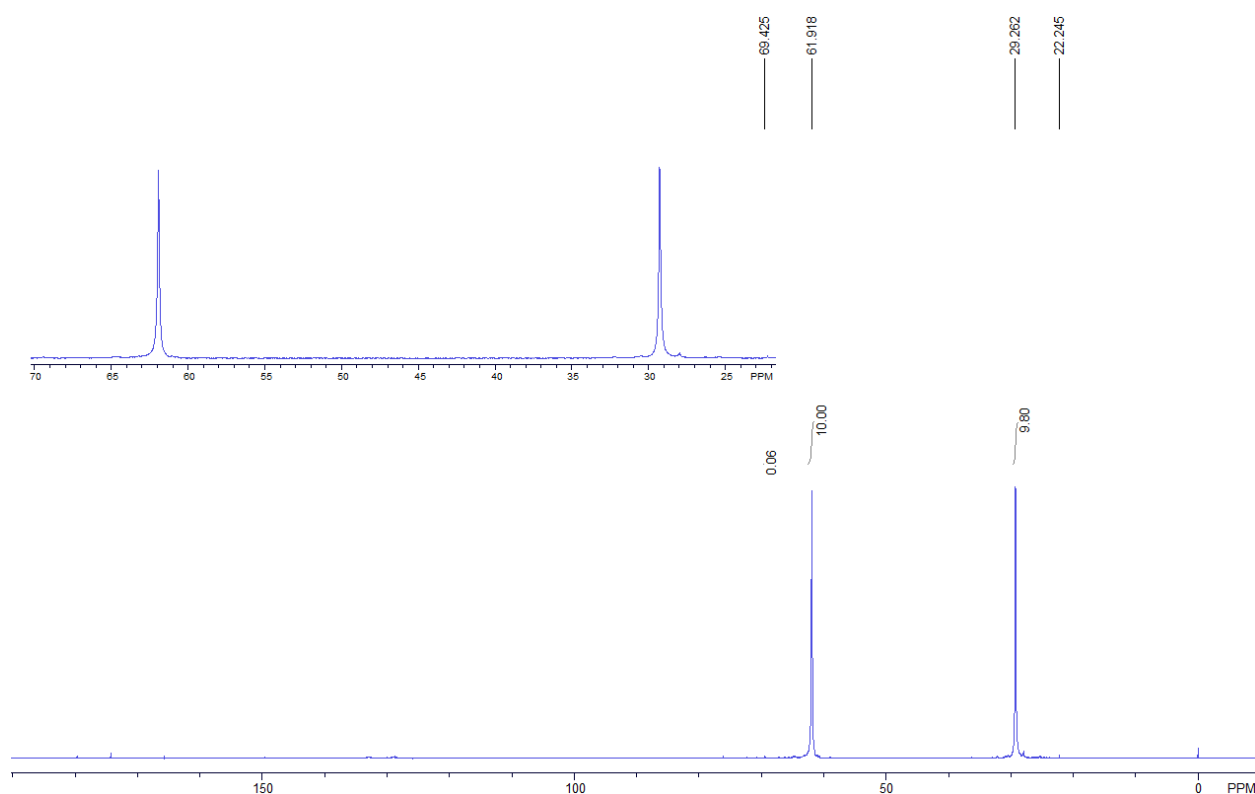


Figure S27. ¹³C NMR spectrum for table S2, entry 25.

Synthesis of polyesters *via* azeotropic distillation with Dean Stark reflux:

Diol (56.0 mmol) and diacid (54.0 mmol) were combined with *para*-toluenesulfonic acid monohydrate (0.28 mmol) in a round bottom equipped with a magnetic stir bar. Excess diol was used to ensure no free acid remained to impact **1**, which contains borohydride. A Dean-Stark

apparatus and condenser was attached to the flask and toluene (30 mL) was poured through the top of the condenser. The reaction was heated to reflux for 6 hours. After 3 hours, water was removed from the Dean-Stark trap. Following the designated time, the reaction mixture was poured into methanol (200 mL) containing triethylamine (2.0 mL) to generate a precipitate or oil. After stirring for 1 hour, it was filtered, resuspended in methanol, and filtered again. If polymer was an oil, it was extracted from the methanol solution. The resulting polymer was dried *in vacuo* at 50 °C for 24 hours. The resulting dried polymers were then used in depolymerization studies as is.

Table S3. Reagent quantities for polyester syntheses.

Diol (mass or mL, mmol)	Diacid (mass, mmol)	Percent Yield
1,4-butanediol (5.0 mL, 56.0)	Succinic acid (6.34 g, 54.0)	86%, white powder
1,5-pentanediol (5.9 mL, 56.0)	Glutaric acid (7.13 g, 54.0)	92%, viscous oil/waxy solid
1,6-hexanediol (6.62 g, 56.0)	Adipic acid (6.38 g, 54.0)	78%, white powder

Depolymerization of synthesized aliphatic polyesters.

Catalyst was weighed in the nitrogen filled glovebox and added to the reactors. The polyester, diol, or lactone of interest was added along with a stir bar and tetrahydrofuran (1.0 mL). The reactor was sealed and purged with hydrogen gas (20.4 atm) for three successive pressurization/venting cycles with rapid stirring. Following the third cycle of venting, the vessel was charged with hydrogen (3.4 atm), 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. The crude reaction mixture was removed for ^{13}C NMR analysis.

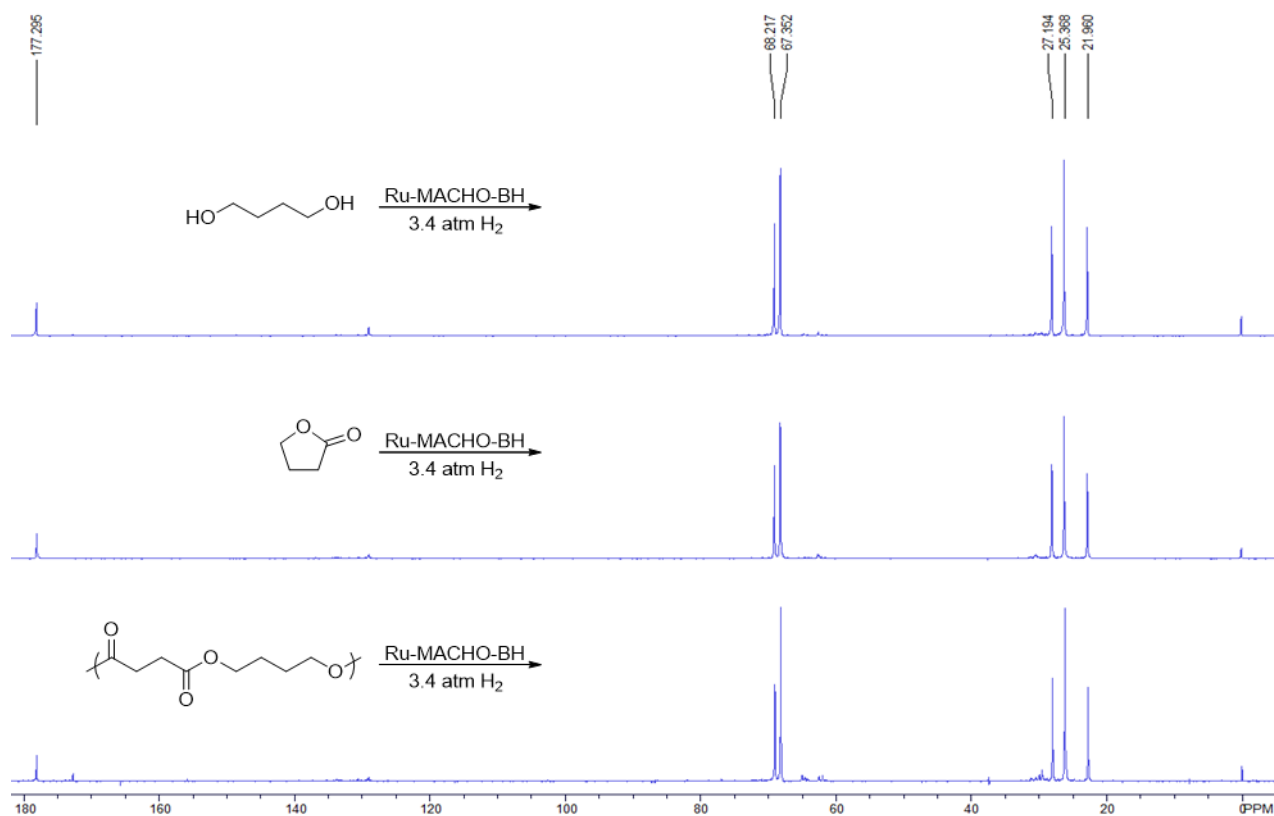


Figure S28. ^{13}C NMR spectra resulting from the hydrogenation of BDO, GBL, or synthesized PBS at 185 °C for 20 h all yield GBL as the predominant product as evidenced by signals at 22.5, 28.0, 69.2, and 178.6 ppm, with THF at 26 and 68 ppm. Results demonstrate that the synthetic approach used to prepare aliphatic polyesters does not inhibit conversion of PBS to form GBL.

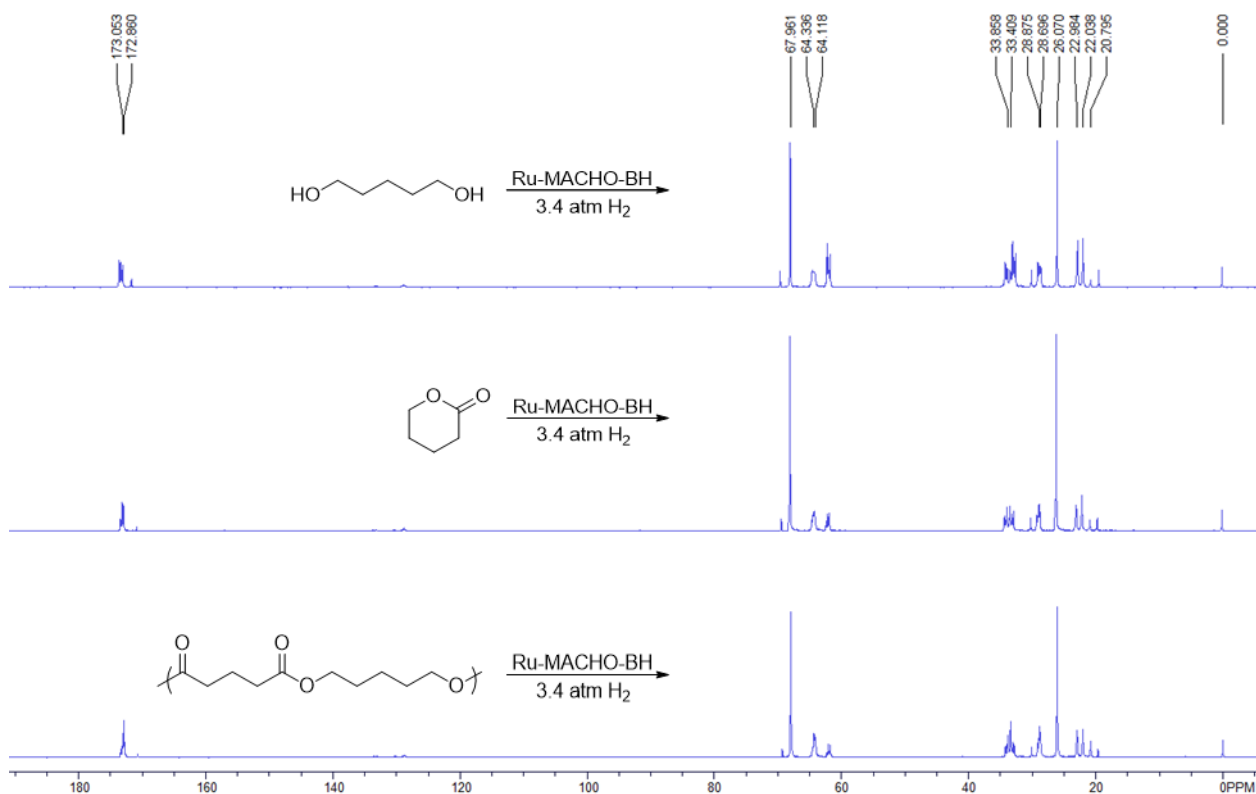


Figure S29. ^{13}C NMR spectra resulting from the hydrogenation of 1,5-pentenediol, δ -valerolactone, and poly(1,5-pentylene glutarate).

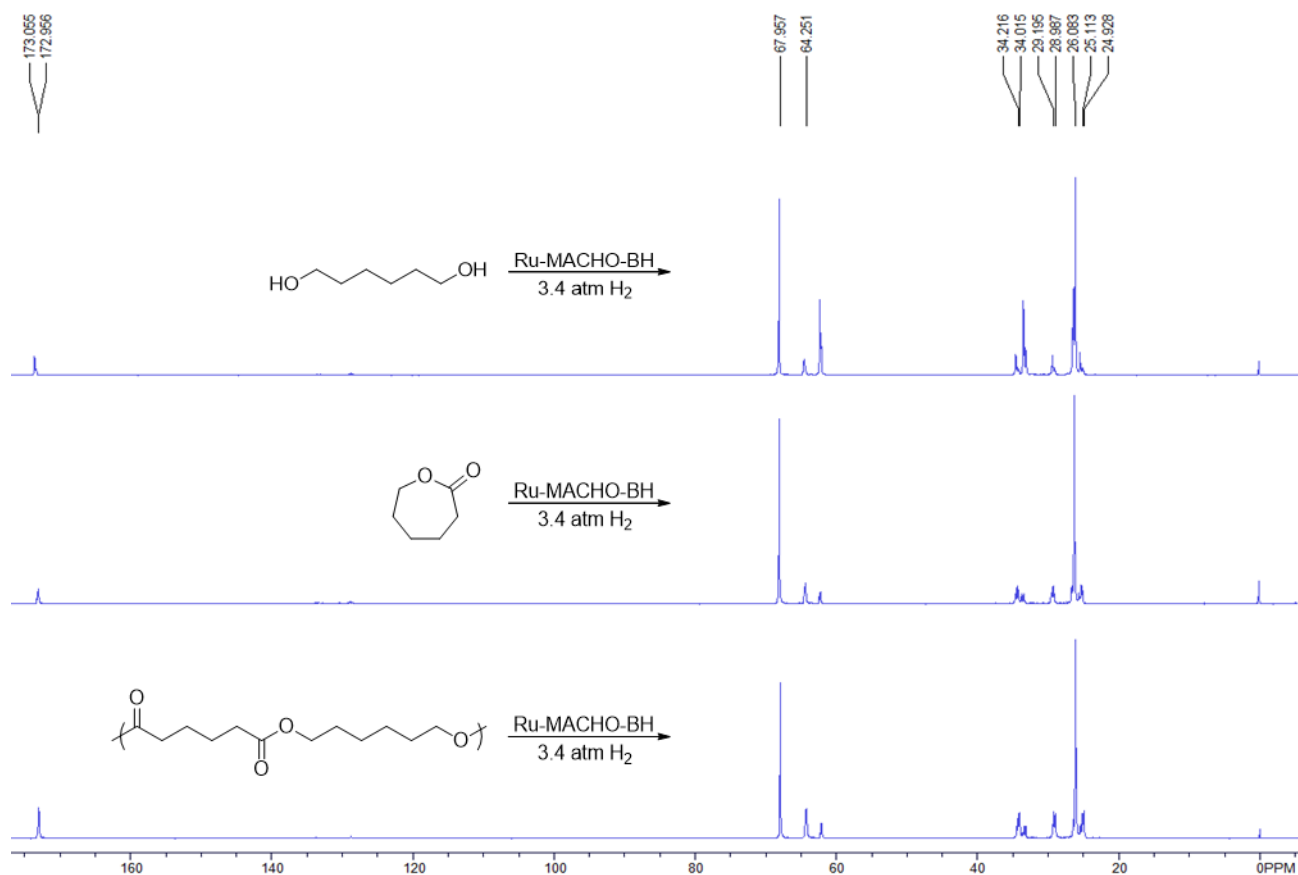


Figure S30. ^{13}C NMR spectra resulting from the hydrogenation of 1,6-hexanediol, ϵ -caprolactone, and poly(1,6-hexylene adipate) with 3.4 atm hydrogen.

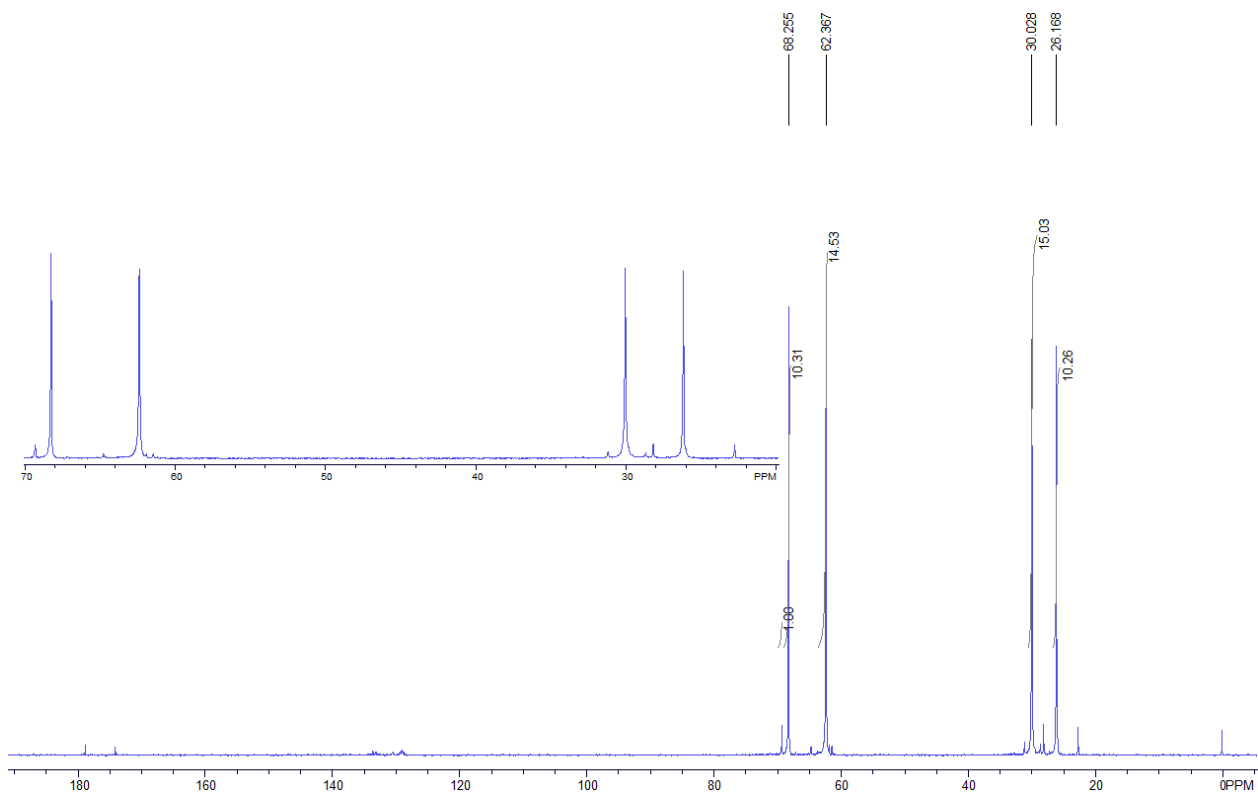


Figure S31. ^{13}C NMR spectrum resulting from the hydrogenation of synthesized PBS with 47.6 atm hydrogen.

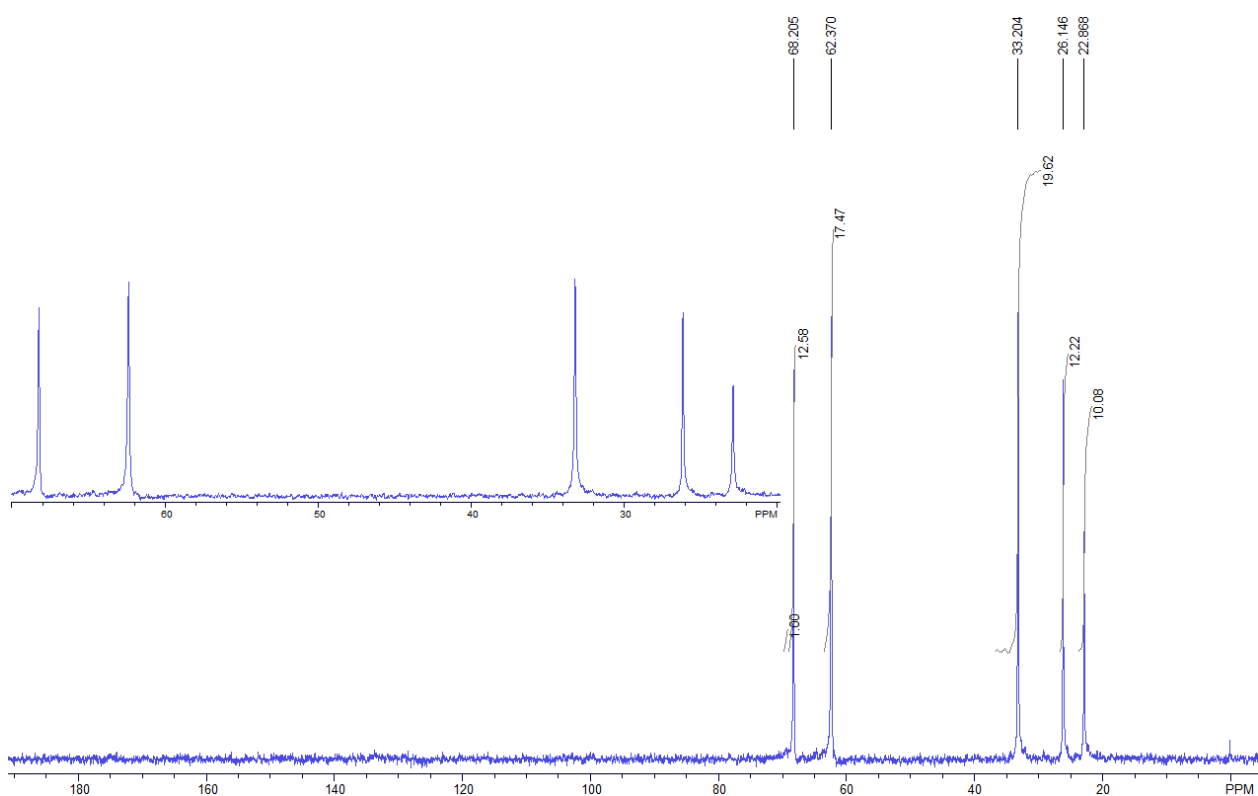


Figure S32. ^{13}C NMR spectrum resulting from the hydrogenation of poly(1,5-pentylene glutarate) with 47.6 atm hydrogen.

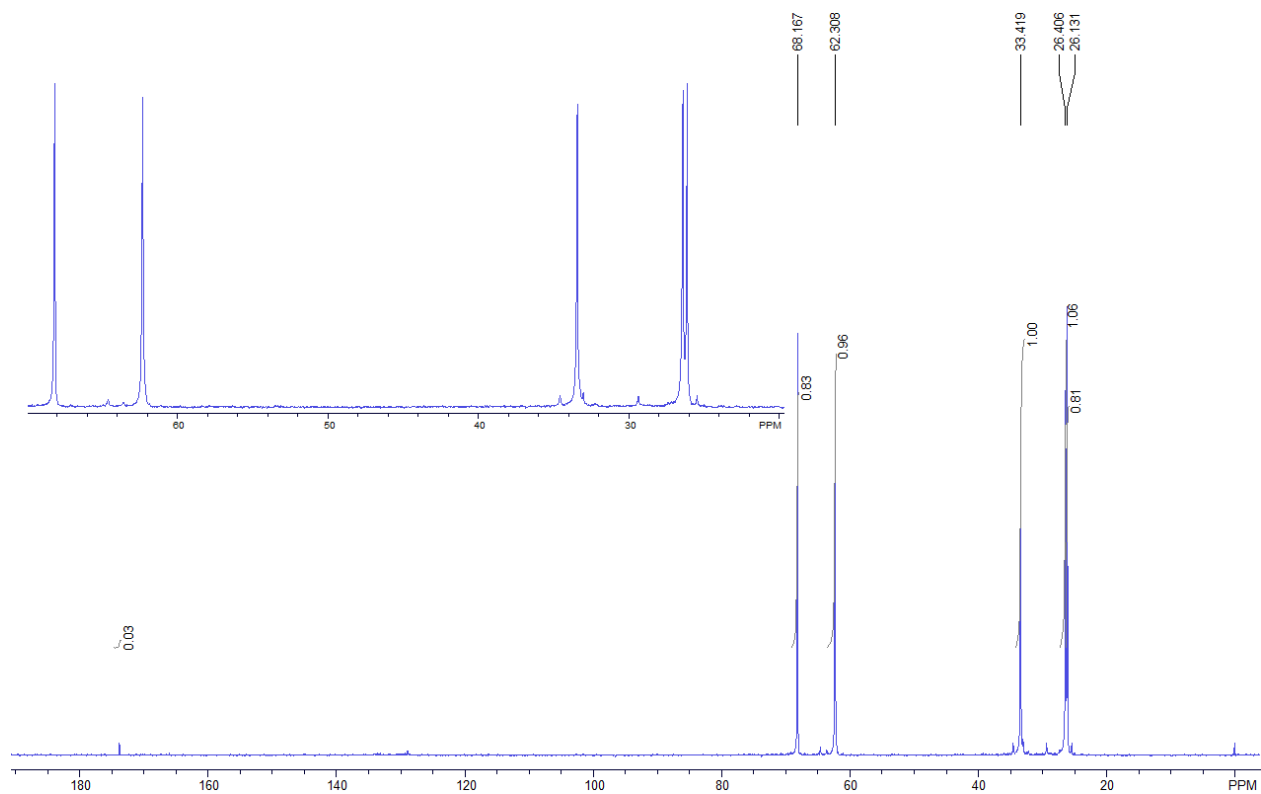


Figure S33. ^{13}C NMR spectrum resulting from the hydrogenation of poly(1,6-hexylene adipate) with 47.6 atm hydrogen.

References:

1. E. M. Krall, T. W. Klein, R. J. Andersen, A. J. Nett, R. W. Glasgow, D. S. Reader, B. C. Dauphinais, S. P. M. Ilrath, A. A. Fischer, M. J. Carney, D. J. Hudson and N. J. Robertson, *Chem. Commun.*, 2014, **50**, 4884.