Electronic Supplementary Material (ESI) for Green Chemistry.

SEMI-AROMATIC BIO-BASED POLYESTERS DERIVED FROM LIGNIN AND CYCLIC CARBONATES

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Supporting Information

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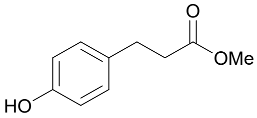
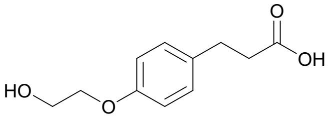
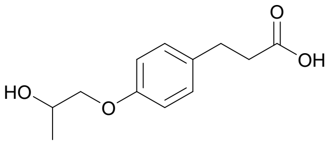
Monomer Preparation



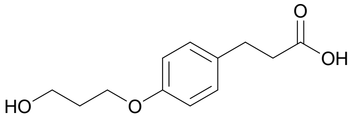
100 g (601 mmol) of phloretic acid were dissolved into 150 mL of methanol. A catalytic amount of sulfuric acid was added, and the reaction was heated to reflux for 6 hours. Upon cooling, the reaction was concentrated and taken up in ethyl acetate and washed with saturated sodium bicarbonate followed by brine. The organic layer was dried over magnesium sulfate and filtered. Removal of solvent yielded 108.44 g of product as a white solid in quantitative yield. ^{1}H NMR (300 MHz, cdcl$_3$) δ 7.07 (d 2H), 6.76 (d 2H), 4.99 (s -OH) 3.67 (s 3H), 2.91 (t, 2H) 2.63 (t, 2H)



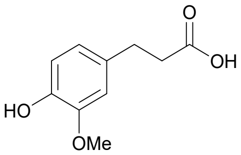
M1 60.0 g (333 mmol) of methyl 3-(4-hydroxyphenyl)propanoate, 2.30 g (16.65 mmol) of potassium carbonate, and 29.33 g (366 mmol) of ethylene carbonate were added into a 3-neck round bottom flask equipped with a N_2 inlet and gas relief valve. The flask was backfilled with N_2 three times and then heated to 160°C and stirred for 1 hour. The mixture was then allowed to cool bellow 100 °C. 270 mL of 2M NaOH were added, and a reflux condenser was equipped to the round bottom flask. The heterogeneous mixture was allowed to reflux overnight. Once the mixture became homogenous, it was then cooled in an ice bath and acidified. The resultant solid was collected by vacuum filtration and washed with excess water. 67.2 g of white solid were obtained in a 96% yield and used without further purification. ^{1}H NMR (300 MHz, dmso) δ 7.13 (d 2H), 6.84 (d 2H), 4.86 (t -OH), 3.95, 3.93 (t 2H), 3.71 (t 2H) 3.66, 2.77 (t 2H), 2.45 (m 2H). ^{13}C NMR (75 MHz, dmso) δ 173.79, 156.99, 132.70, 129.17, 114.28, 69.41, 59.58, 35.61, 29.51.



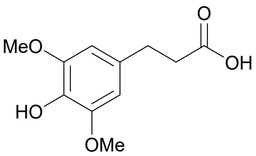
M2 3-(4-(2-hydroxypropoxy)phenyl)propanoic acid was synthesized in the same manner with propylene carbonate in 83% yield. ^{1}H NMR (300 MHz, cdcl$_3$) δ 7.11 (d 2H), 6.86 (d 2H), 4.20 (m 1H), 3.93 (m 1H), 3.77 (m 1H), 2.91 (t 2H), 2.65 (t 2H), 1.29 (d 3H). ^{13}C NMR (75 MHz, cdcl$_3$) δ 178.82, 157.31, 133.01, 129.51, 114.87, 73.50, 66.55, 36.03, 29.96, 18.89.



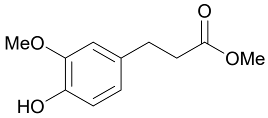
M3 83 g (500 mmol) of phloretic acid, 50 g (1.25 mol) of NaOH, and 22.5 g (150 mmol) of NaI were dissolved in 500 mL of water. After all solids were dissolved, 63 mL (750 mmol) of 3-Chloro-1-propanol were added slowly by addition funnel to avoid exotherming. After addition the solution was allowed to reflux for 12 hours. After reflux, the solution was distilled to approximately half volume, then cooled in an ice bath. The solution was acidified, and the resultant solids were collected by vacuum filtration. After washing with cold ethanol and water, 48.23 g of crude product containing monomer and dimers were obtained in 50% yield. The product was used without purification. ^{1}H NMR (300 MHz, cdcl$_3$) δ 7.11 (m 2H), 6.83 (m 2H), 4.24 (t 1H), 4.11 (t 1H), 3.87 (t 1H), 2.91 (m 2H), 2.65 (m 2H), 2.04 (m 2H). ^{13}C NMR (75 MHz, cdcl$_3$) δ 178.28, 173.20, 157.48, 132.77, 129.46, 114.76, 65.98, 64.46, 61.53, 60.73, 36.31, 35.99, 32.11, 30.29, 29.99, 28.84.



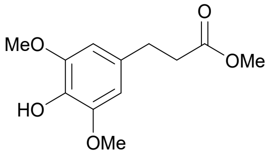
In a 3-neck round bottom flask, 72.3 g (372 mmol) of ferulic acid and 7.92 g (74.47 mmol) of 10% Pd/C were added. The round bottom was equipped with a N_2 inlet, reflux condenser, and addition funnel, then backfilled with N_2 three times. 370 mL of acetic acid was added under positive N_2 pressure, and the solution was heated until ferulic acid dissolved. 90.5 ml of limonene was then added dropwise by addition funnel, followed by reflux until the reaction was complete by TLC. The mixture was cooled to room temperature and filtered through a celite. After removal of solvent, the crude solid was taken up in methyl ethyl ketone and extracted with 1 M NaOH. The aqueous layer was cooled in an ice bath and acidified. The resultant white precipitate was collected by vacuum filtration and washed with water. 59.22 g, 95% yield. ^{1}H NMR (300 MHz, cdcl$_3$) δ 6.83 (d 1H), 6.72 (s 1H), 6.69 (s 1H), 3.87 (s 3H), 2.90 (t 3H), 2.65 (t 3H).



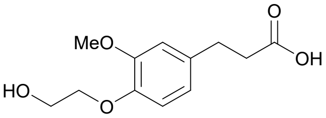
3-(4-hydroxy-3,5-dimethoxyphenyl)propanoic acid was synthesized in the same manner in 83% yield. ^{1}H NMR (300 MHz, dmso) δ 8.05 (s 2H), 3.72 (s 6H), 2.72 (t 2H), 2.47 (m 2H).



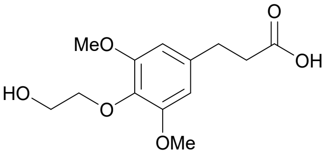
Methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate was synthesized by the esterification described above in quantitative yield. ^{1}H NMR (300 MHz, cdcl$_3$) δ 6.82 (d 1H), 6.70 (s 1H), 6.68 (s 1H), 3.87 (s 3H), 3.67 (s 3H), 2.88 (t 2H), 2.61 (t 2H).



Methyl 3-(4-hydroxy-3,5-dimethoxyphenyl)propanoate was synthesized by the esterification described above in quantitative yield. ^{1}H NMR (300 MHz, cdcl$_3$) δ 6.42 (s 2H), 3.87 (S 6H), 3.68 (s 3H), 2.91 (t 2H), 2.61 (t 2H).



M4 3-(4-(2-hydroxyethoxy)-3-methoxyphenyl)propanoic acid was synthesized by the alkylation described above in 92% yield. ^{1}H NMR (500 MHz, cdcl$_3$) δ 6.86 (d 2H), 6.75 (s 1H), 6.73 (s 1H), 4.11 (t 2H), 3.91 (t 2H), 3.83 (s 3H), 2.91 (t 2H), 2.67 (t 2H). ^{13}C NMR (75 MHz, cdcl$_3$) δ 178.50, 149.98, 146.69, 134.42, 120.63, 115.42, 112.35, 71.77, 61.42, 55.98, 35.96, 30.50.



M5 3-(4-(2-hydroxyethoxy)-3,5-dimethoxyphenyl)propanoic acid was synthesized by the alkylation described above in 94% yield. ^{1}H NMR (500 MHz, cdcl$_3$) δ 6.44 (s 2H), 4.12 (t 2H), 3.85 (s 6H), 3.70 (t 2H), 2.93 (t 2H), 2.70 (t 2H). ^{13}C NMR (75 MHz, cdcl$_3$) δ 178.17, 153.38, 136.67, 134.82, 105.39, 75.37, 61.53, 56.27, 35.83, 31.26.

Monomer	Total yield (%)
M1	96
M2	83
M3	50
M4	87
M5	78

NMR Spectra

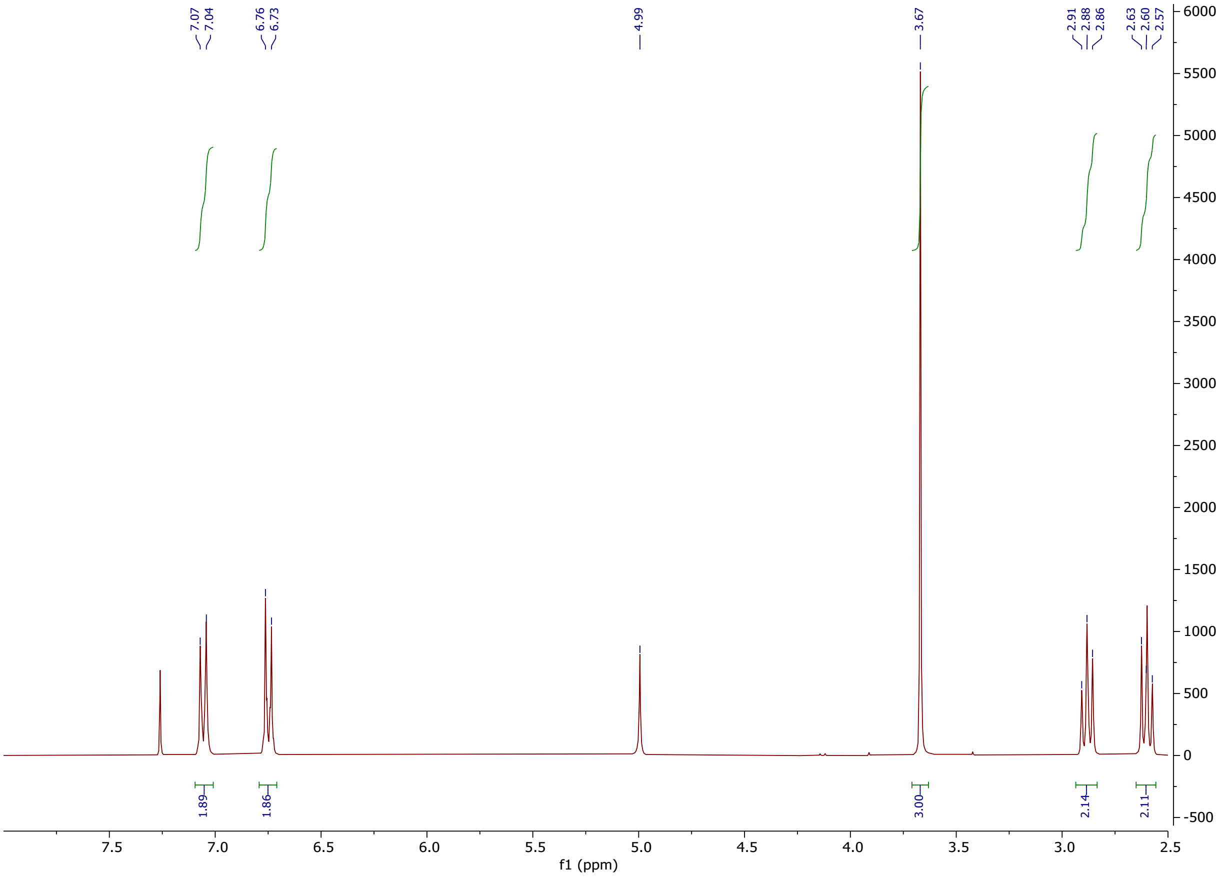


Figure S 1 ^{1}H NMR spectrum of methyl 3-(4-hydroxyphenyl)propanoate

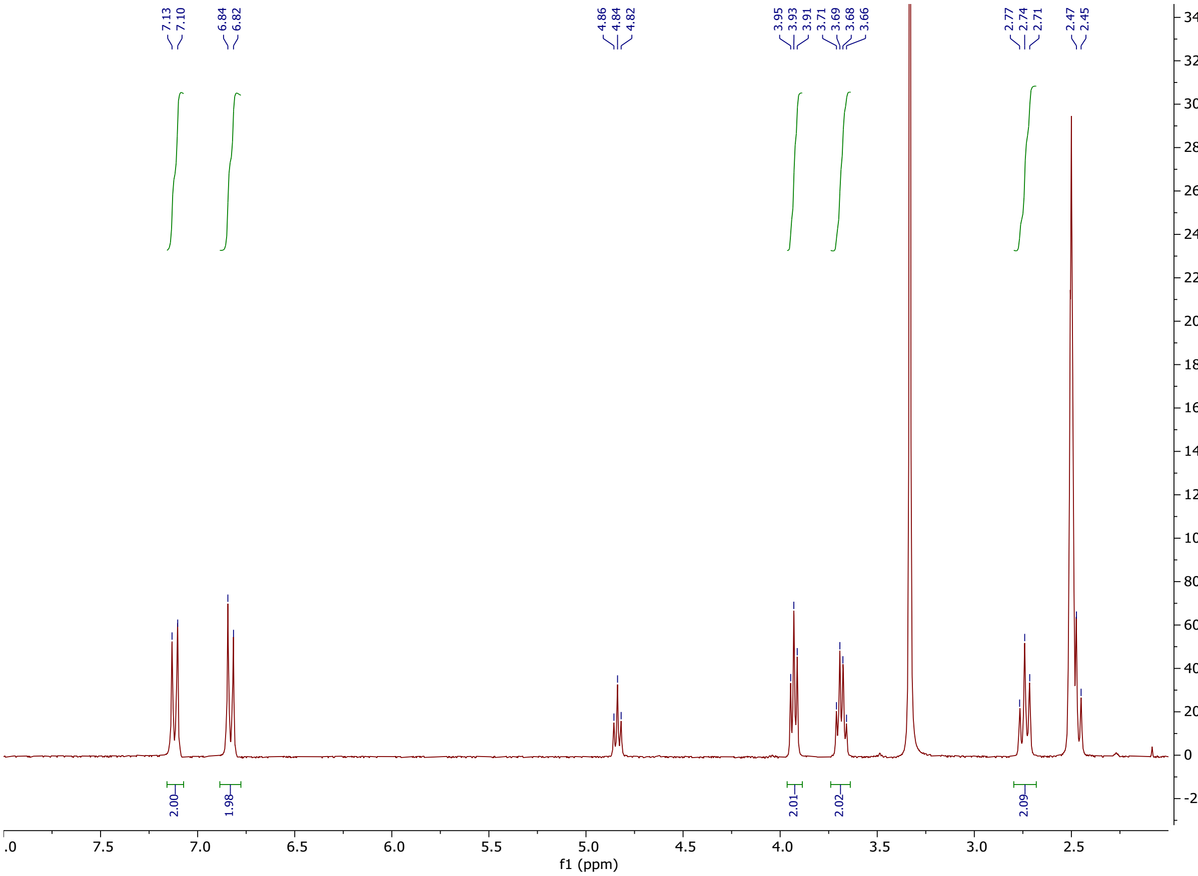


Figure S 2 ^{1}H NMR spectrum of 4-(2-hydroxyethoxy)phenylpropanoic acid

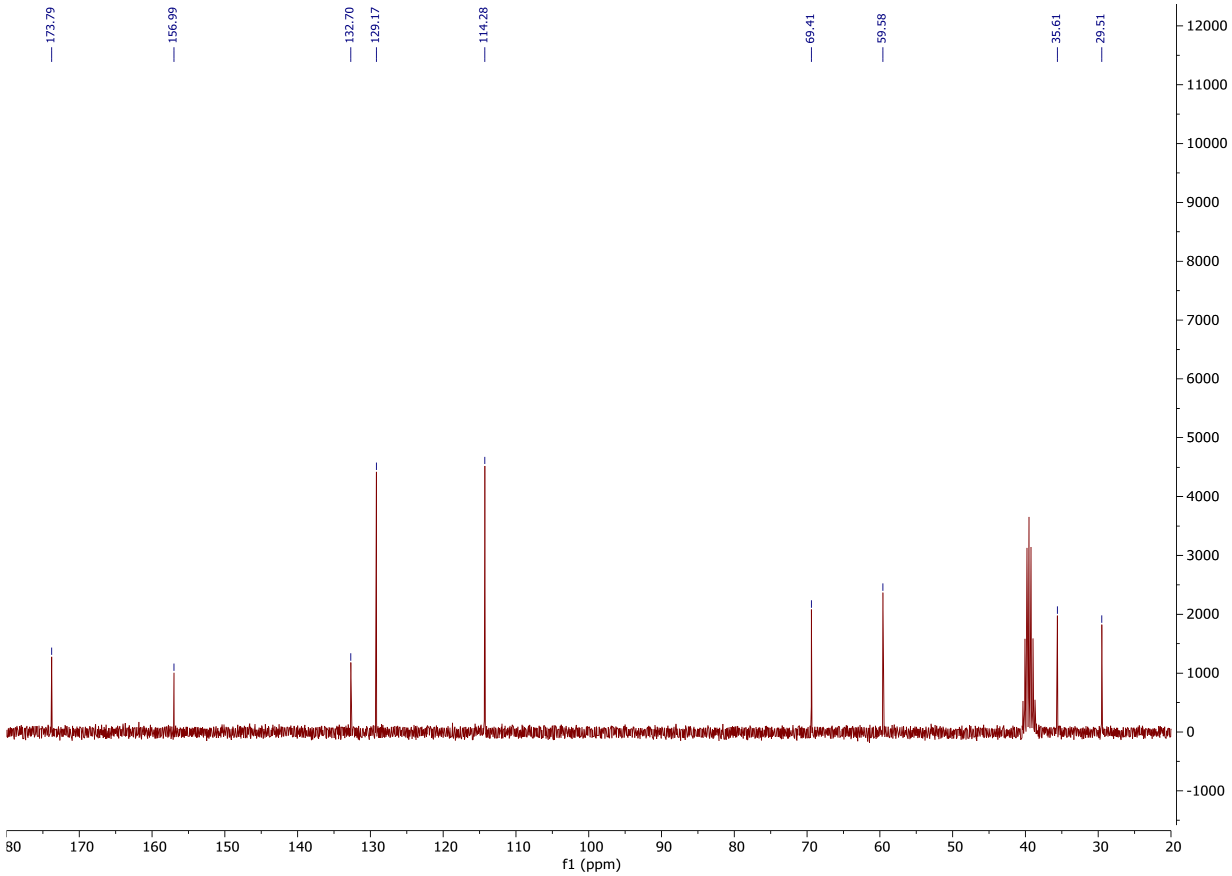


Figure S 3 ^{13}C NMR spectrum of 4-(2-hydroxyethoxy)phenylpropanoic acid

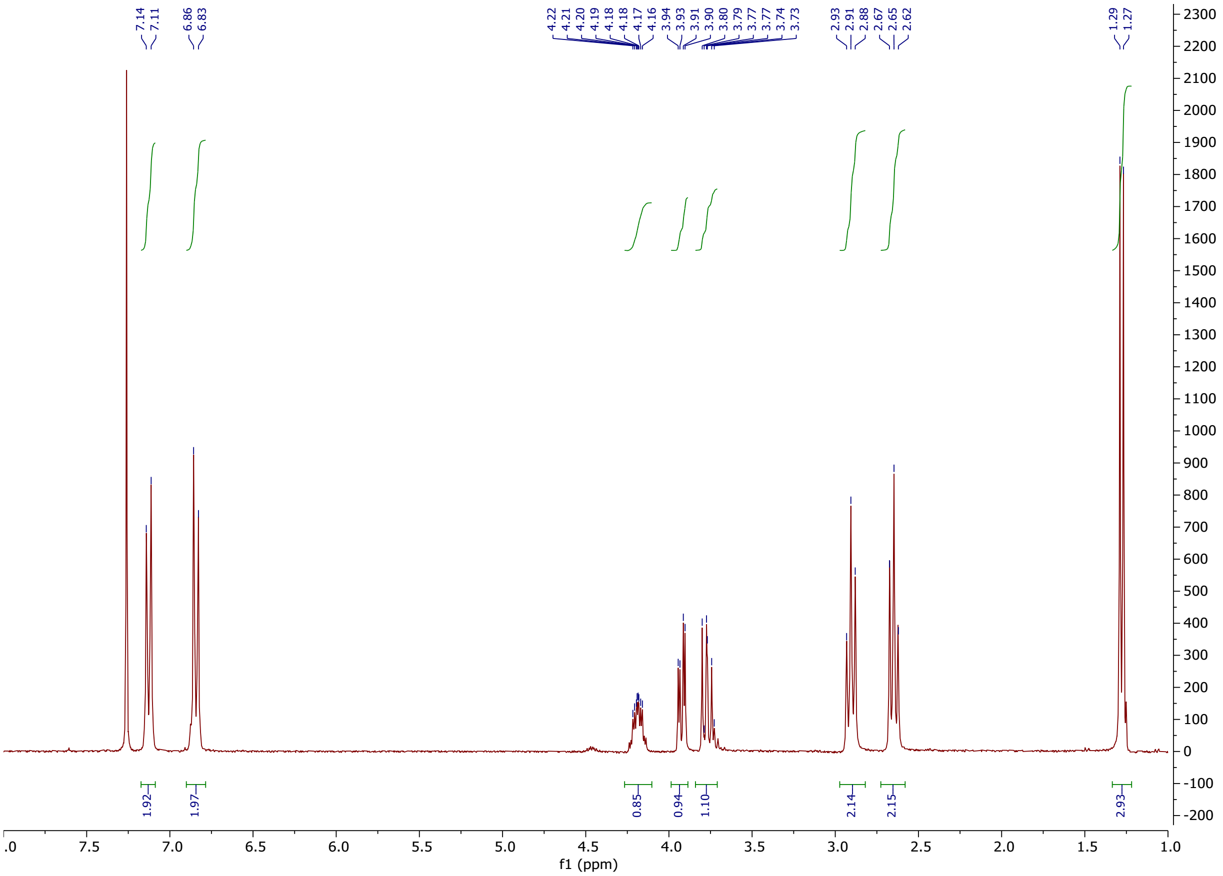


Figure S 4 ^{1}H NMR spectrum of 3-(4-(2-hydroxypropoxy)phenyl)propanoic acid

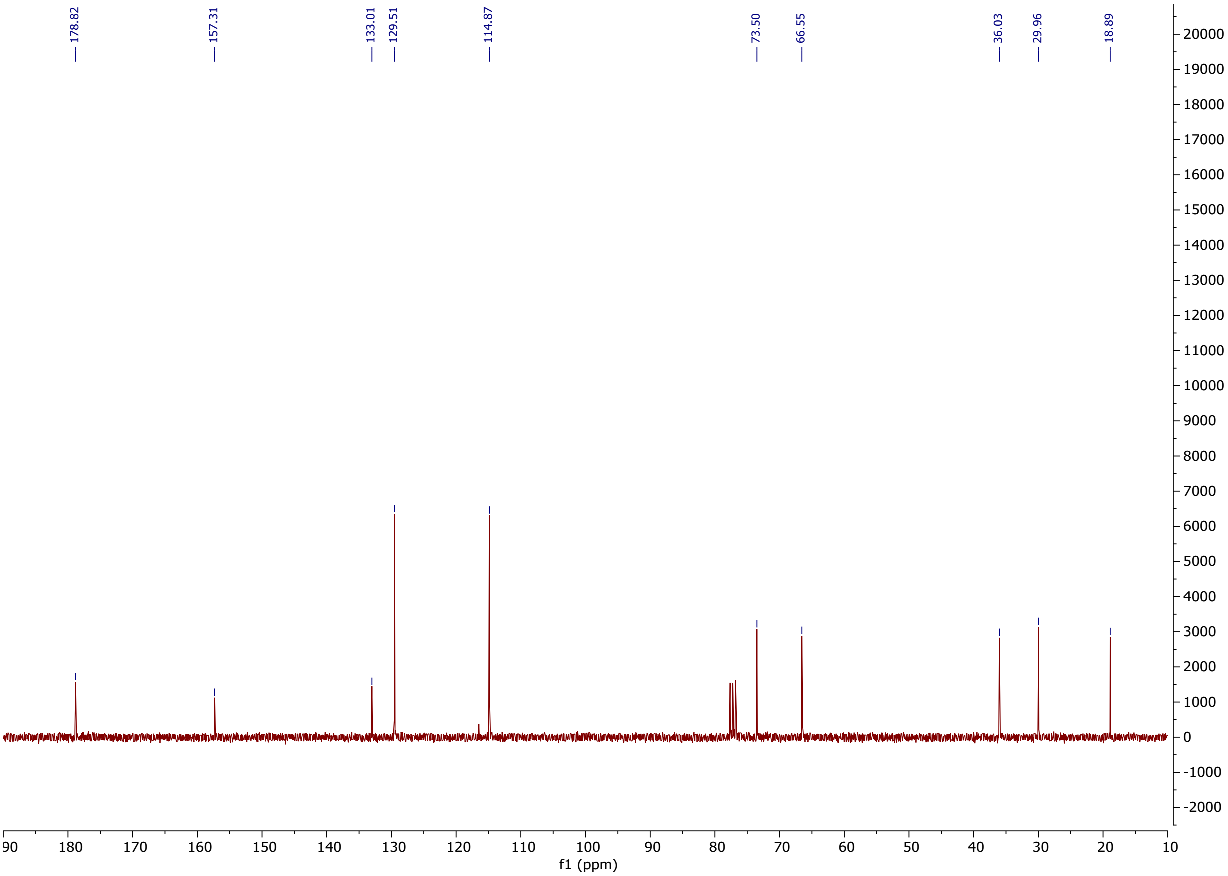


Figure S 5 ^{13}C NMR spectrum of 3-(4-(2-hydroxypropoxy)phenyl)propanoic acid

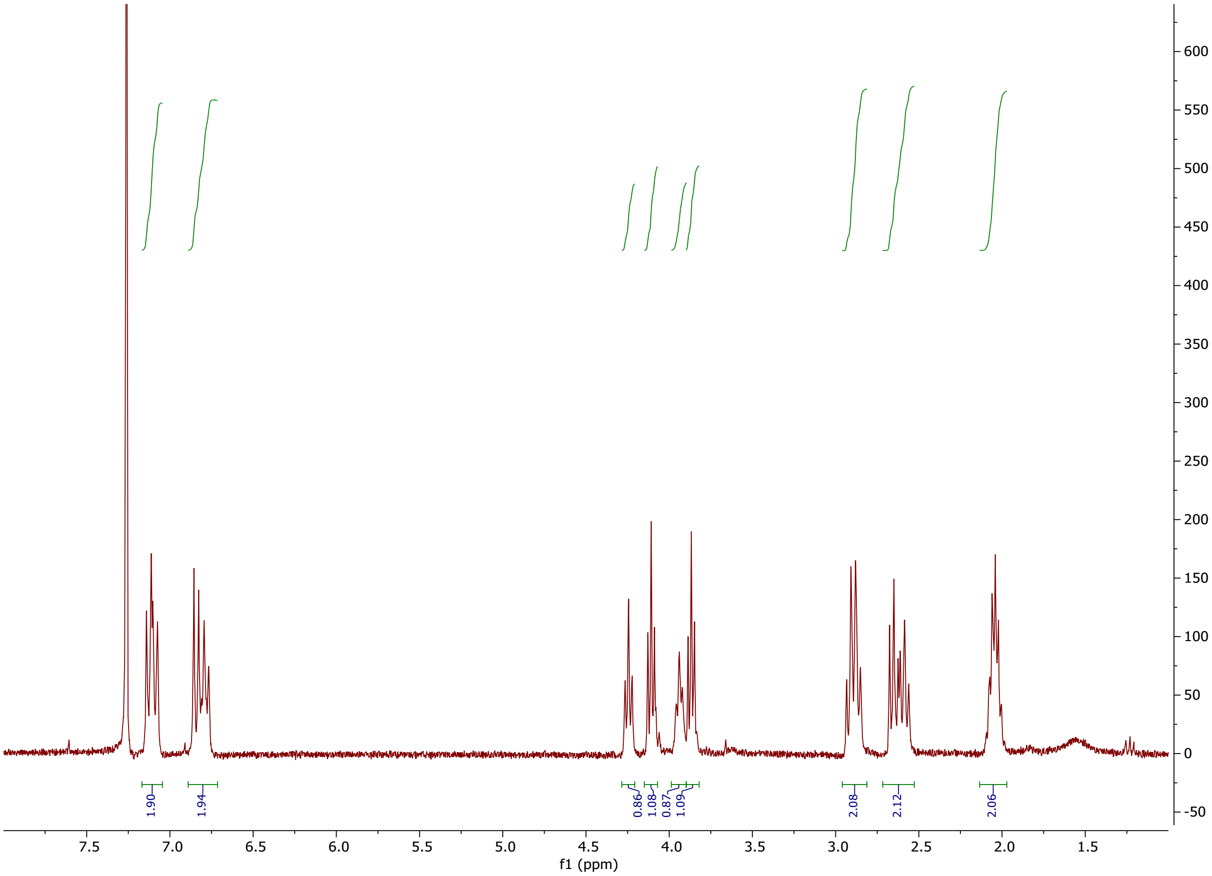


Figure S 6 ^{1}H NMR spectrum of 4-(3-hydroxypropoxy)phenylpropanoic acid

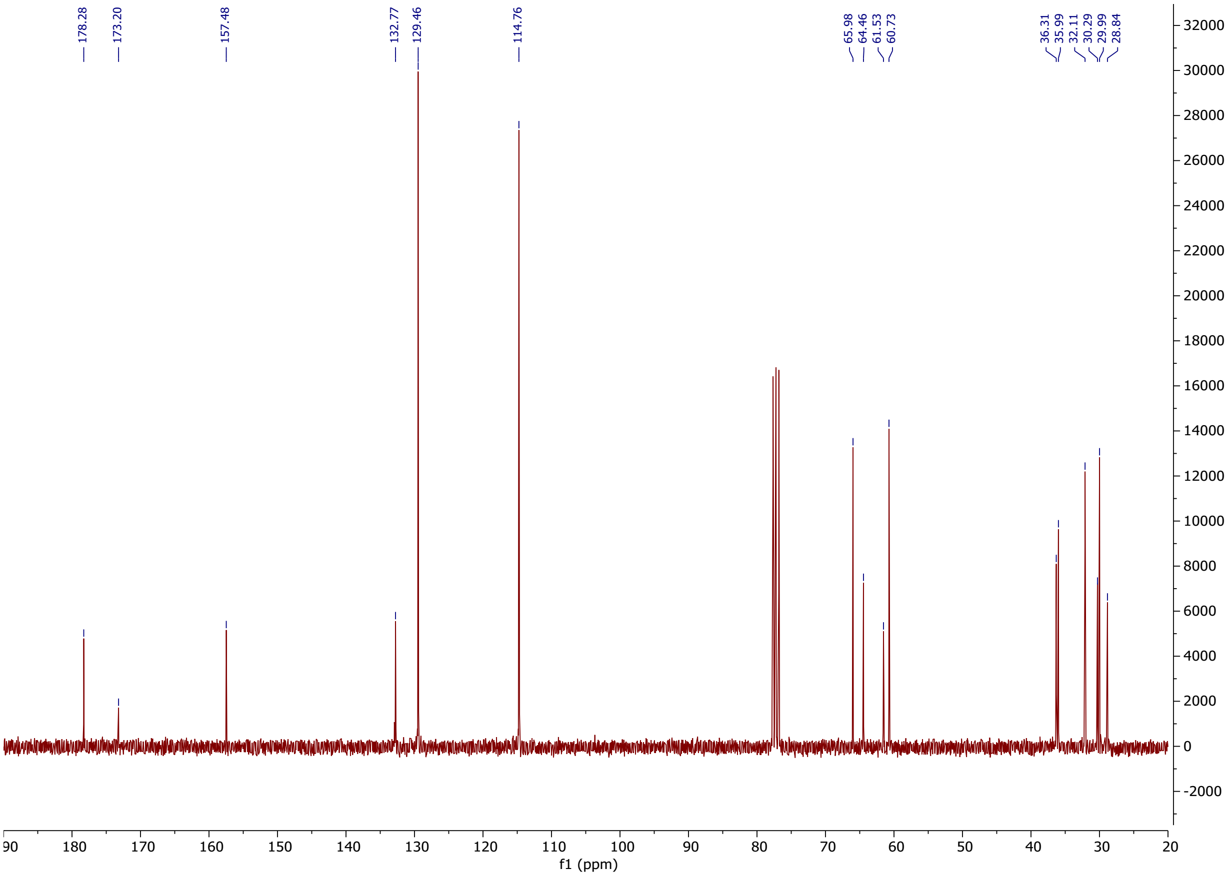


Figure S 7 ^{13}C NMR spectrum of 4-(3-hydroxypropoxy)phenylpropanoic acid

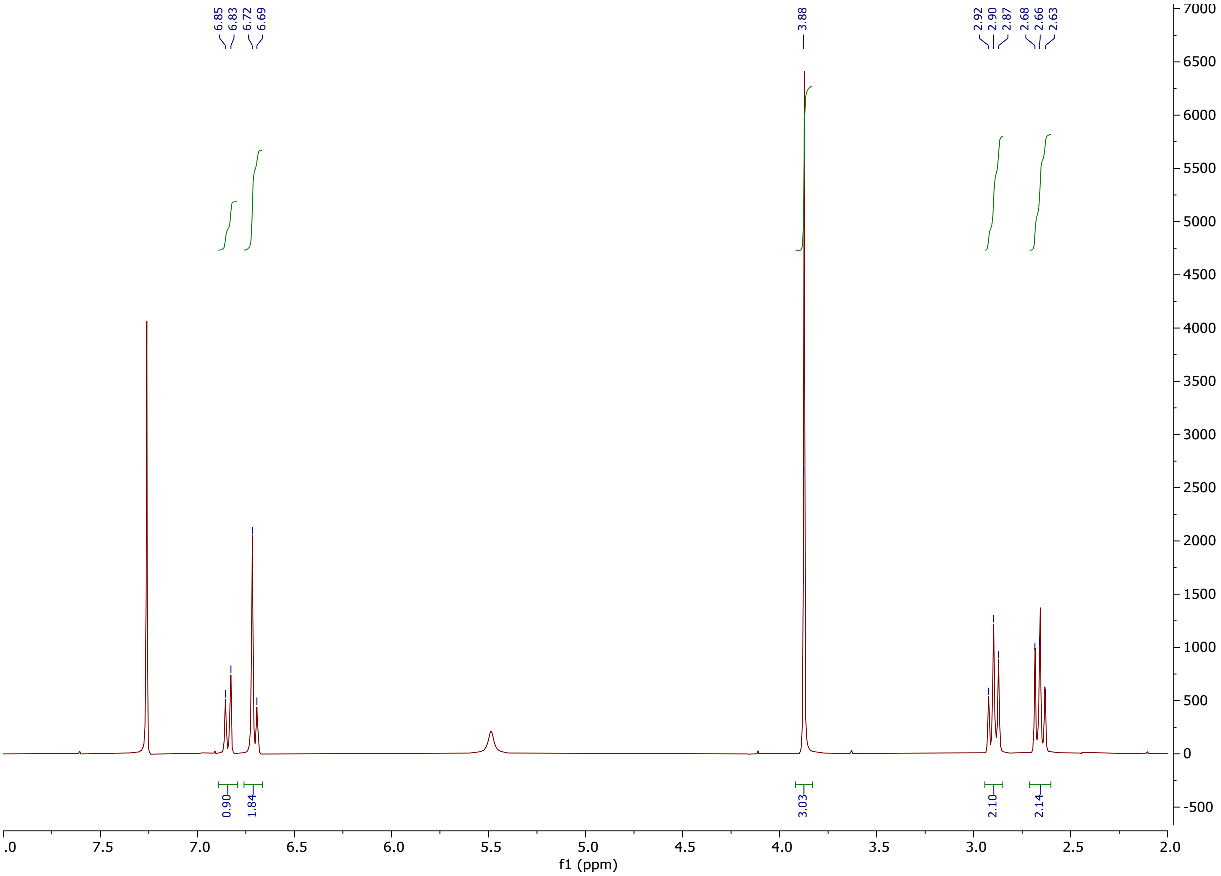


Figure S 8 ^{1}H NMR spectrum of 3-(4-hydroxy-3-methoxyphenyl)propionic Acid

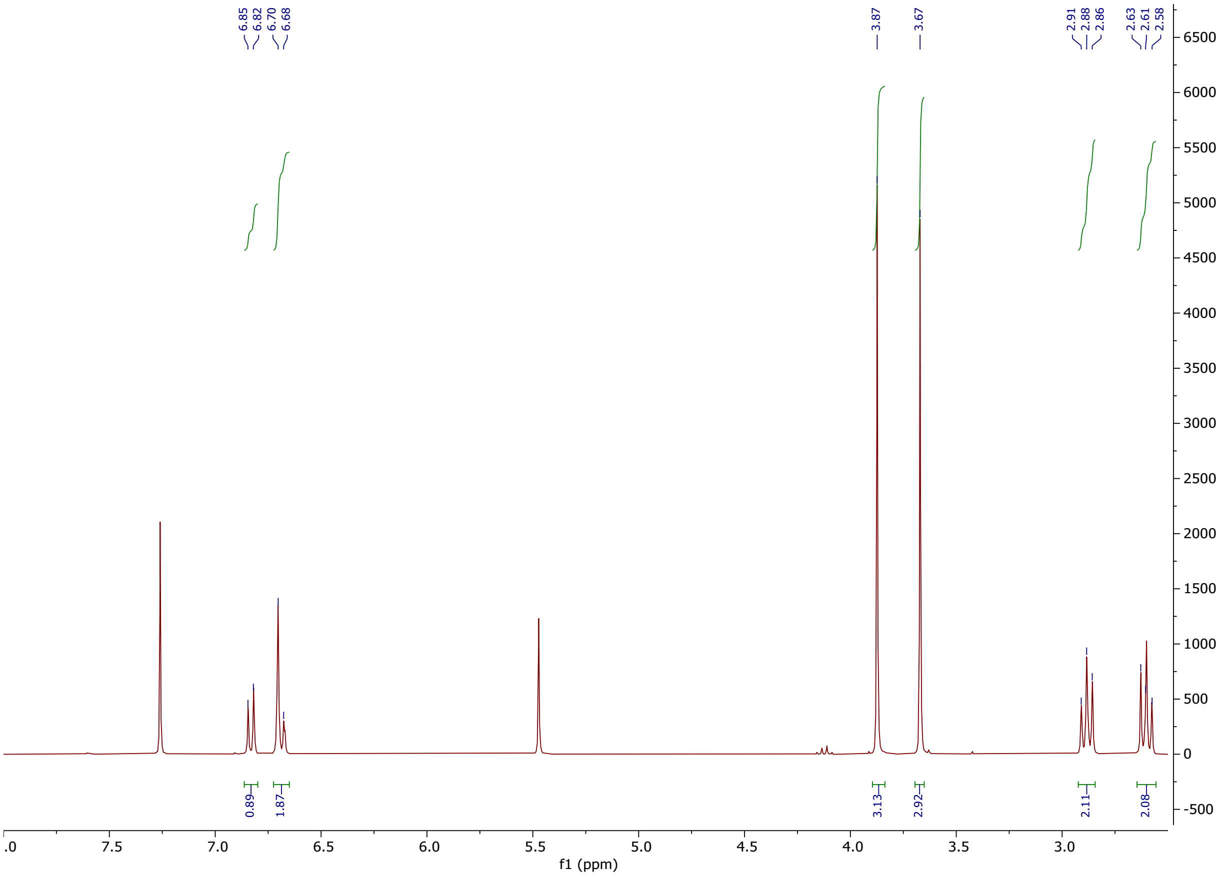


Figure S 9 ^{1}H NMR spectrum of methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate

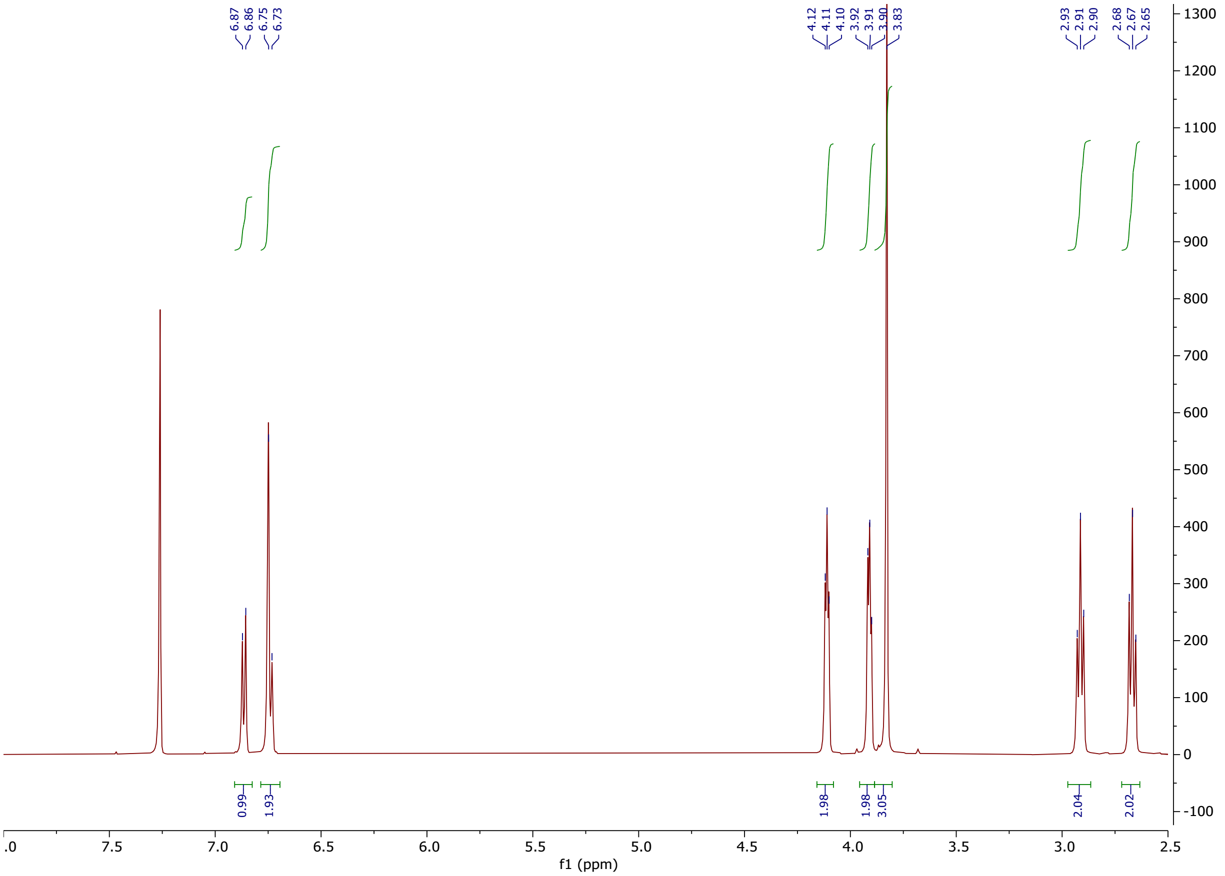


Figure S 10 ^1H NMR spectrum of 3-(4-(2-hydroxyethoxy)-3-methoxyphenyl)propanoic acid

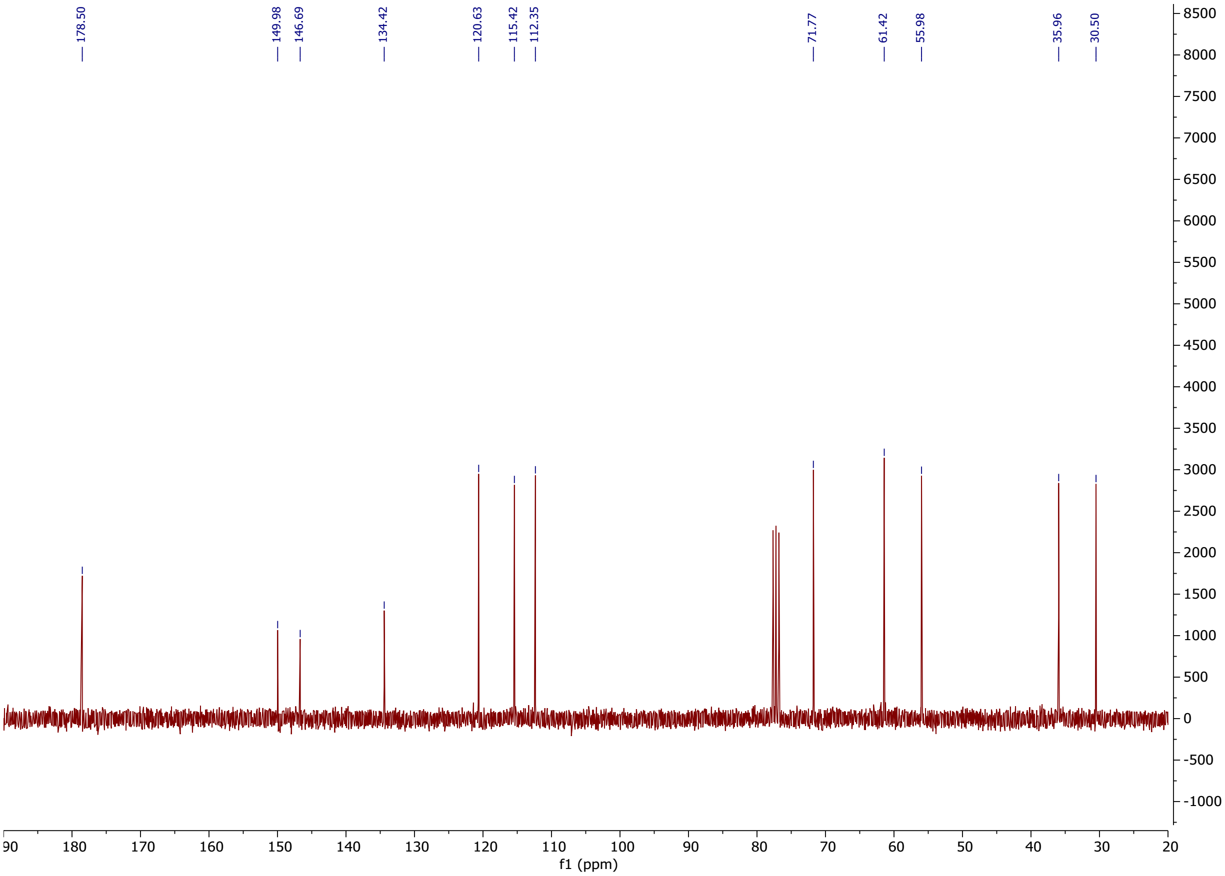


Figure S 11 ^{13}C NMR spectrum of 3-(4-(2-hydroxyethoxy)-3-methoxyphenyl)propanoic acid

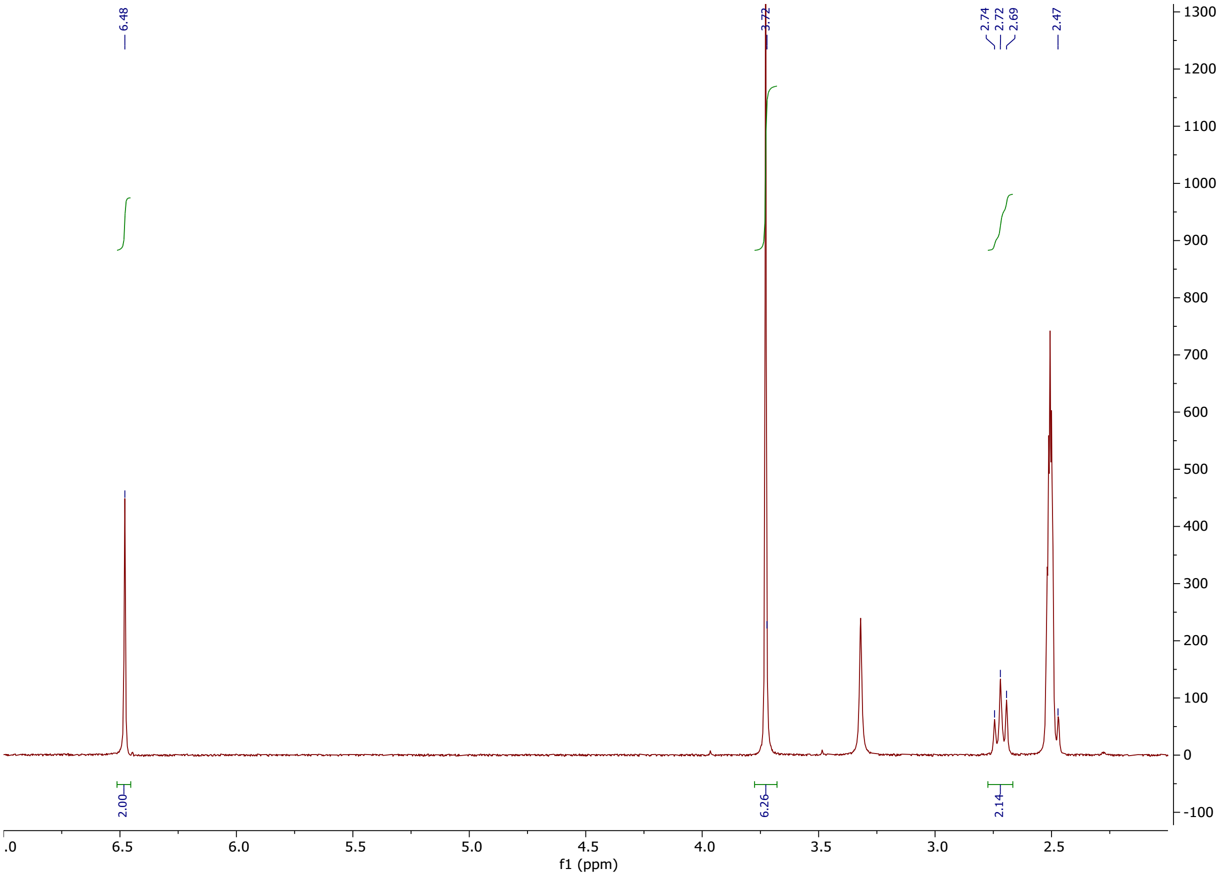


Figure S 12 ^{1}H NMR spectrum of 3-(4-hydroxy-3,5-dimethoxyphenyl)propanoic acid

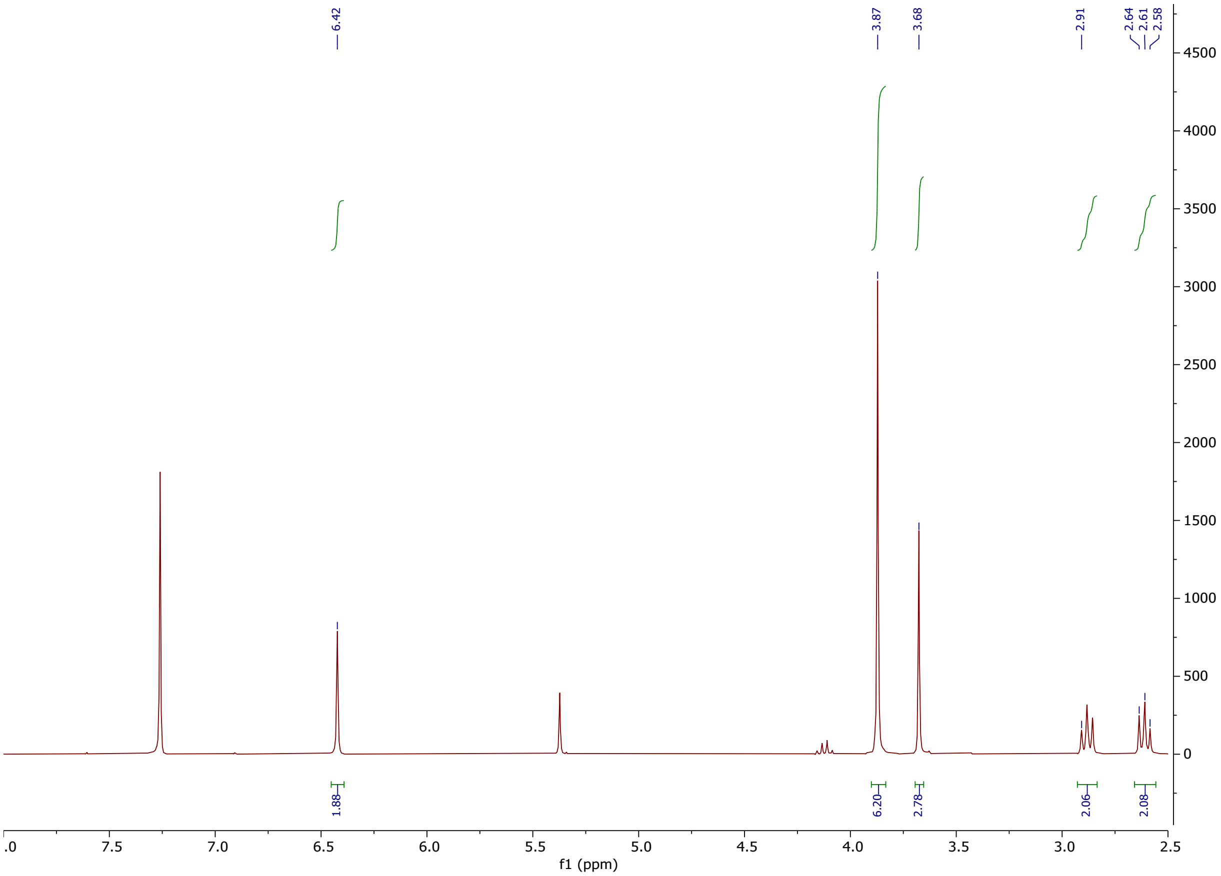


Figure S 13 ^{1}H NMR spectrum of methyl 3-(4-hydroxy-3,5-dimethoxyphenyl)propanoate

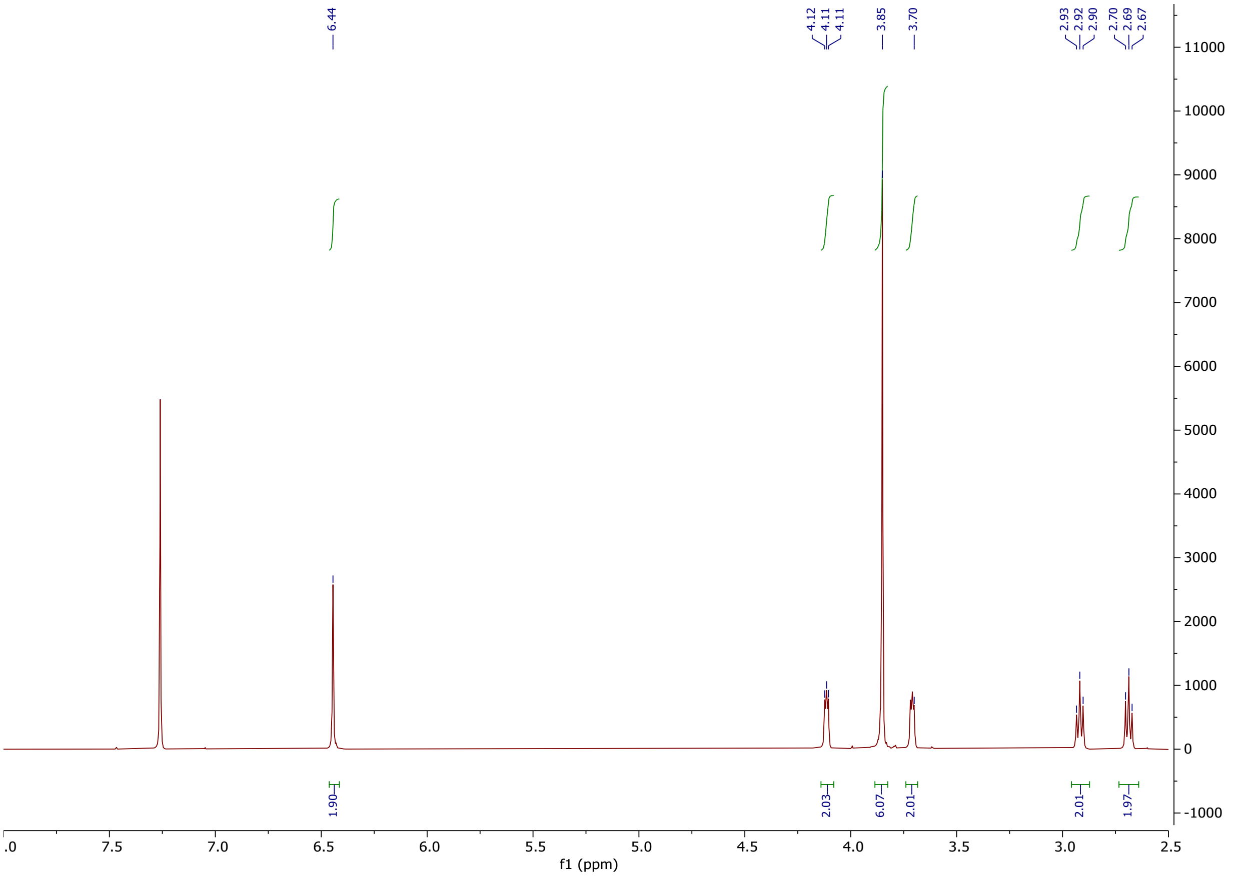


Figure S 14 ^{1}H NMR spectrum of 3-(4-(2-hydroxyethoxy)-3,5-dimethoxyphenyl)propanoic acid

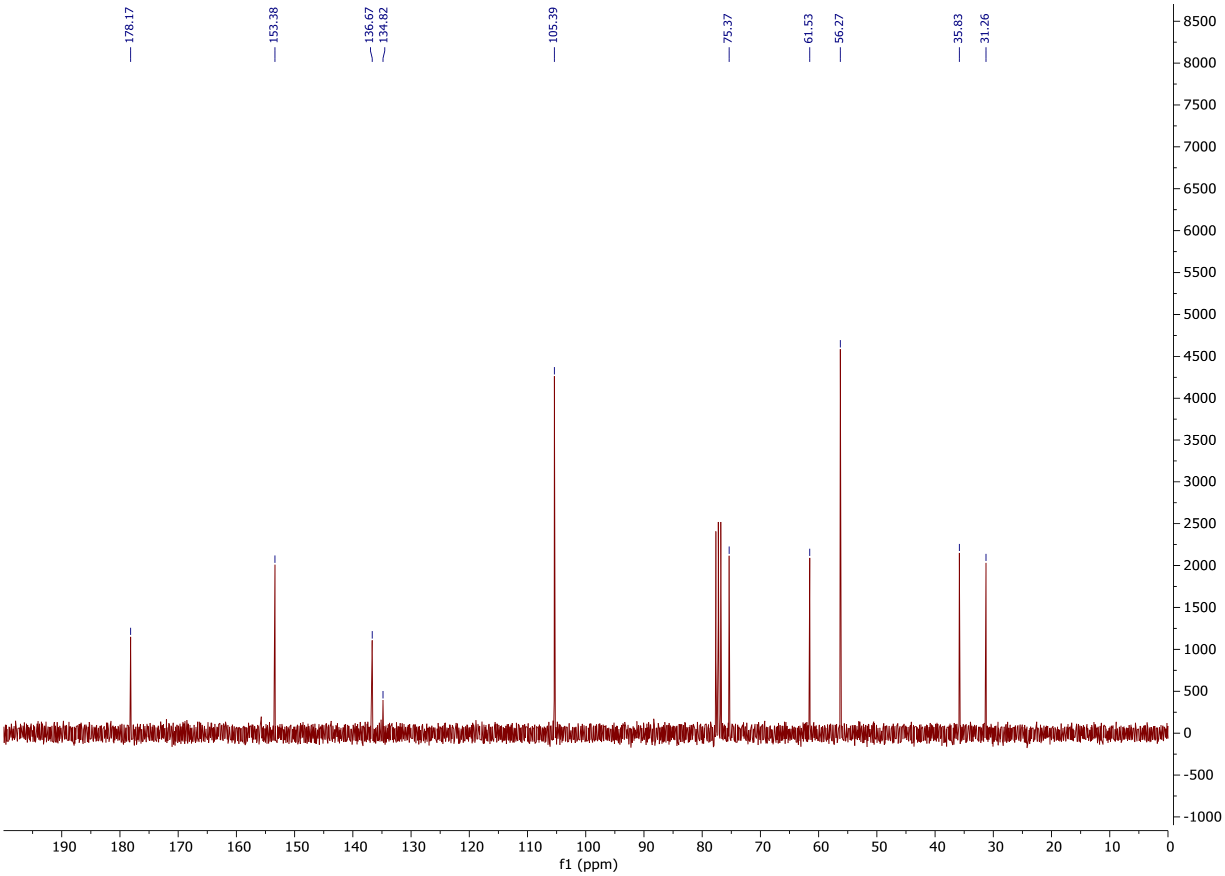


Figure S 15 ^{13}C NMR spectrum of 3-(4-(2-hydroxyethoxy)-3,5-dimethoxyphenyl)propanoic acid

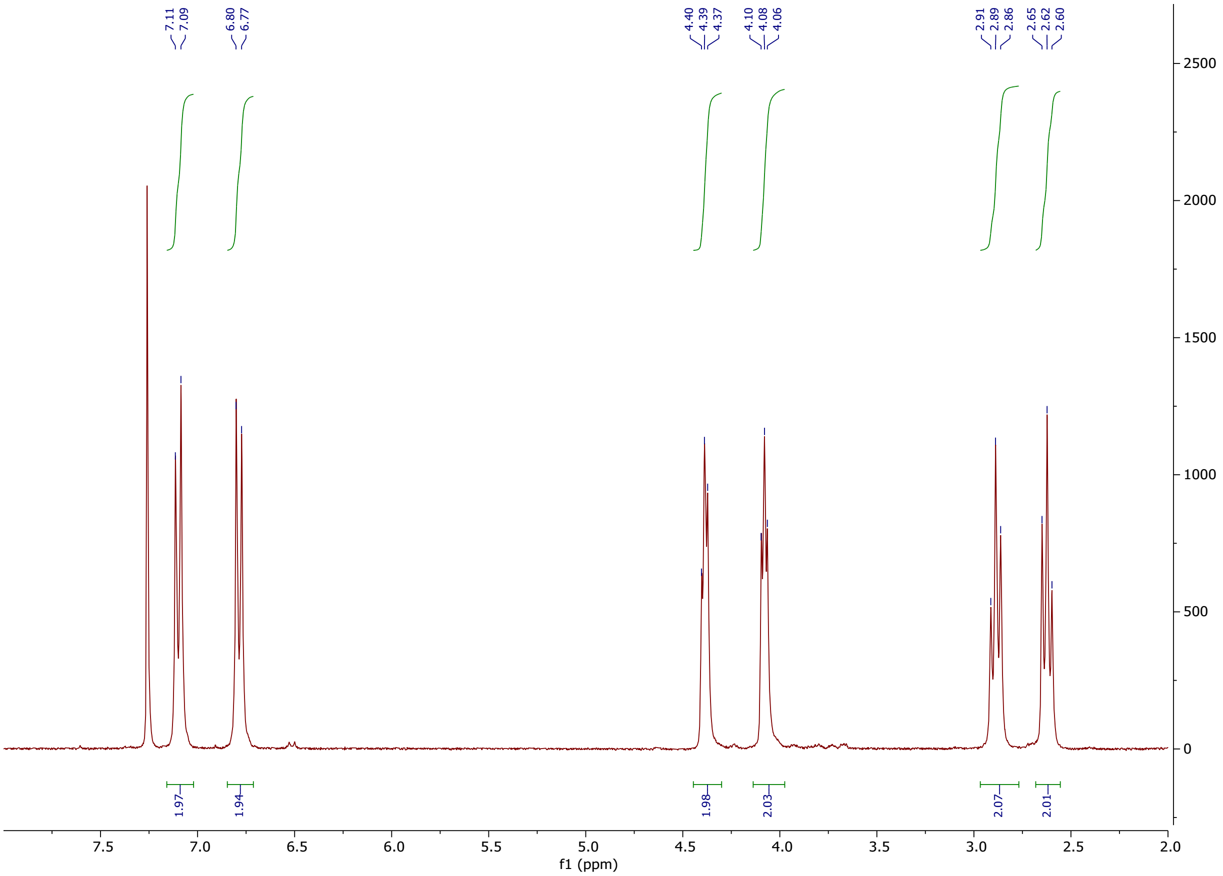


Figure S 16 ^{1}H NMR spectrum of polyethylene phloretate

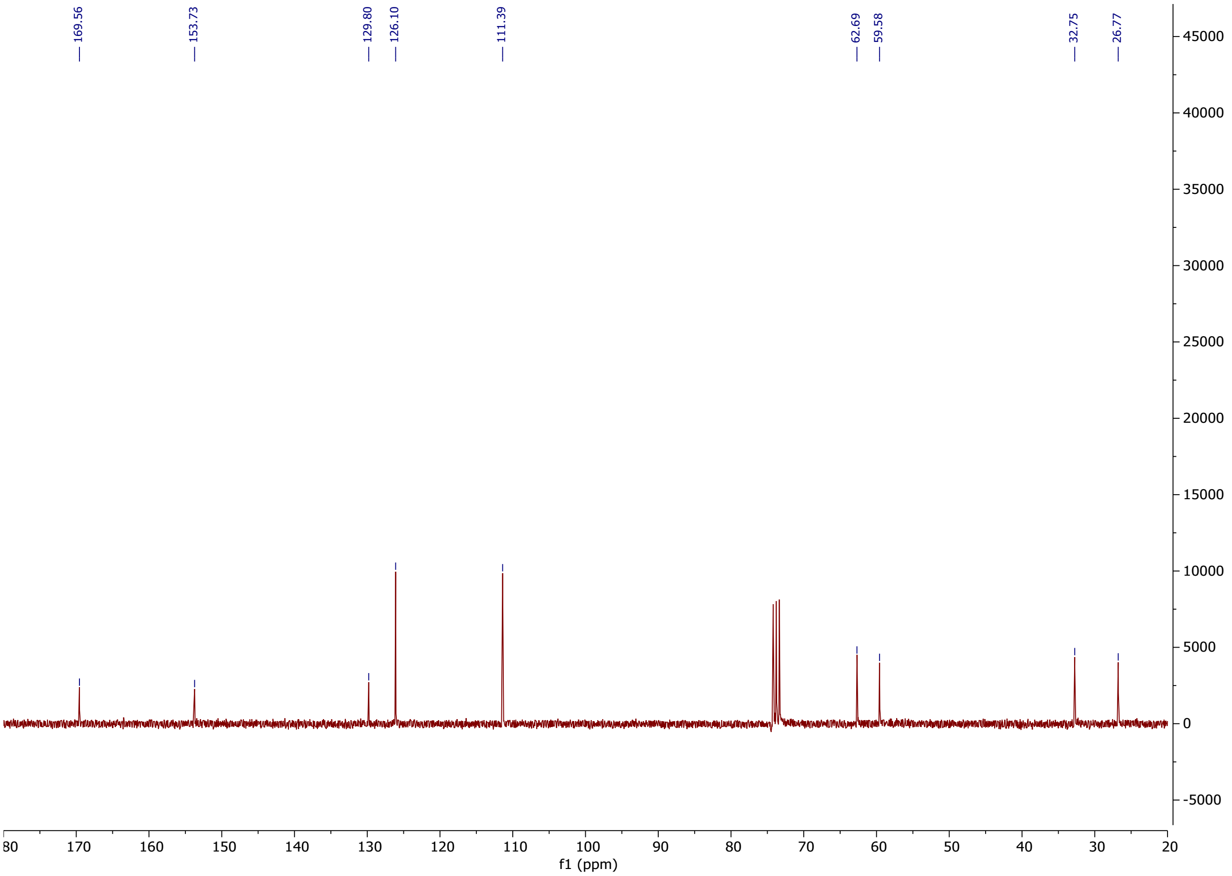


Figure S 17 ^{13}C NMR spectrum of polyethylene phloretate

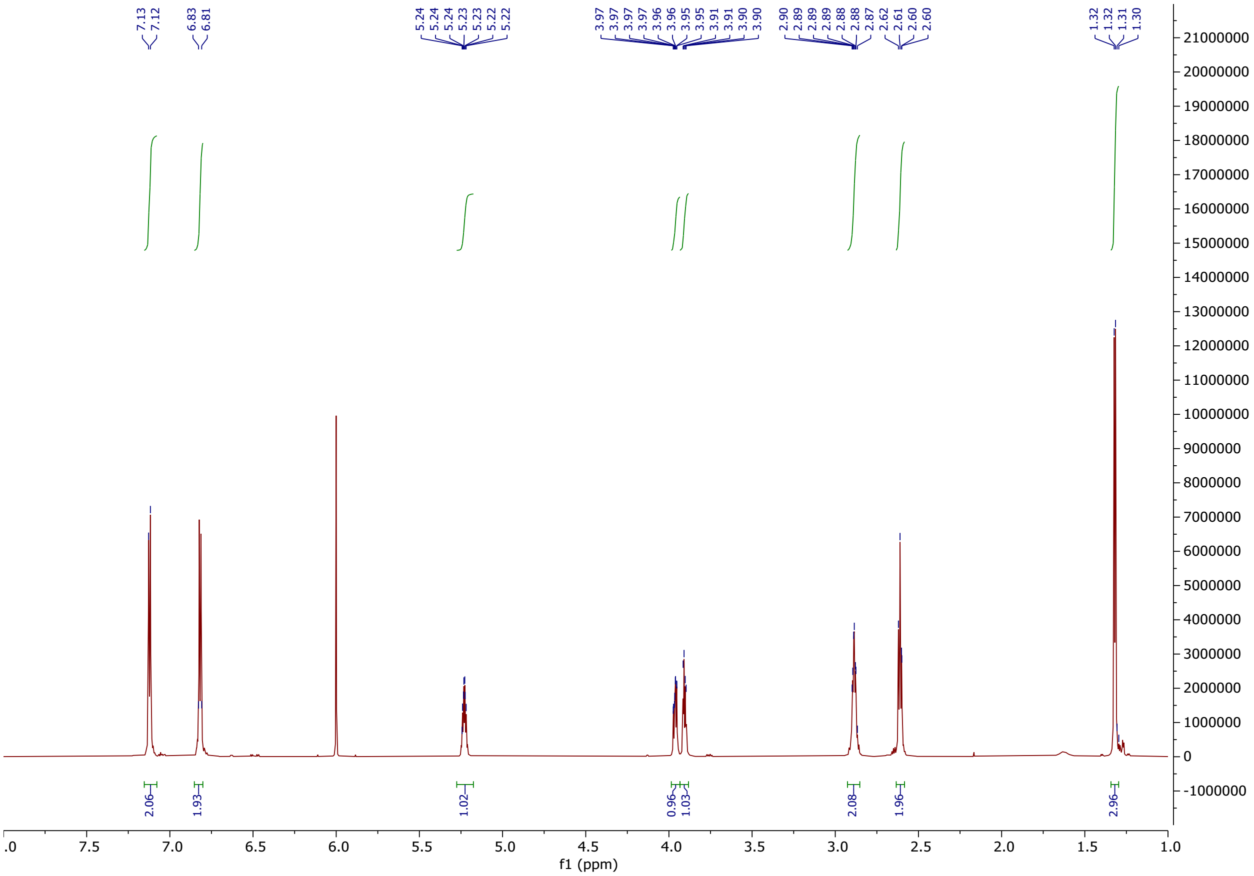


Figure S 18 ^{1}H NMR spectrum of polyisopropyl phloretate (PiPP)

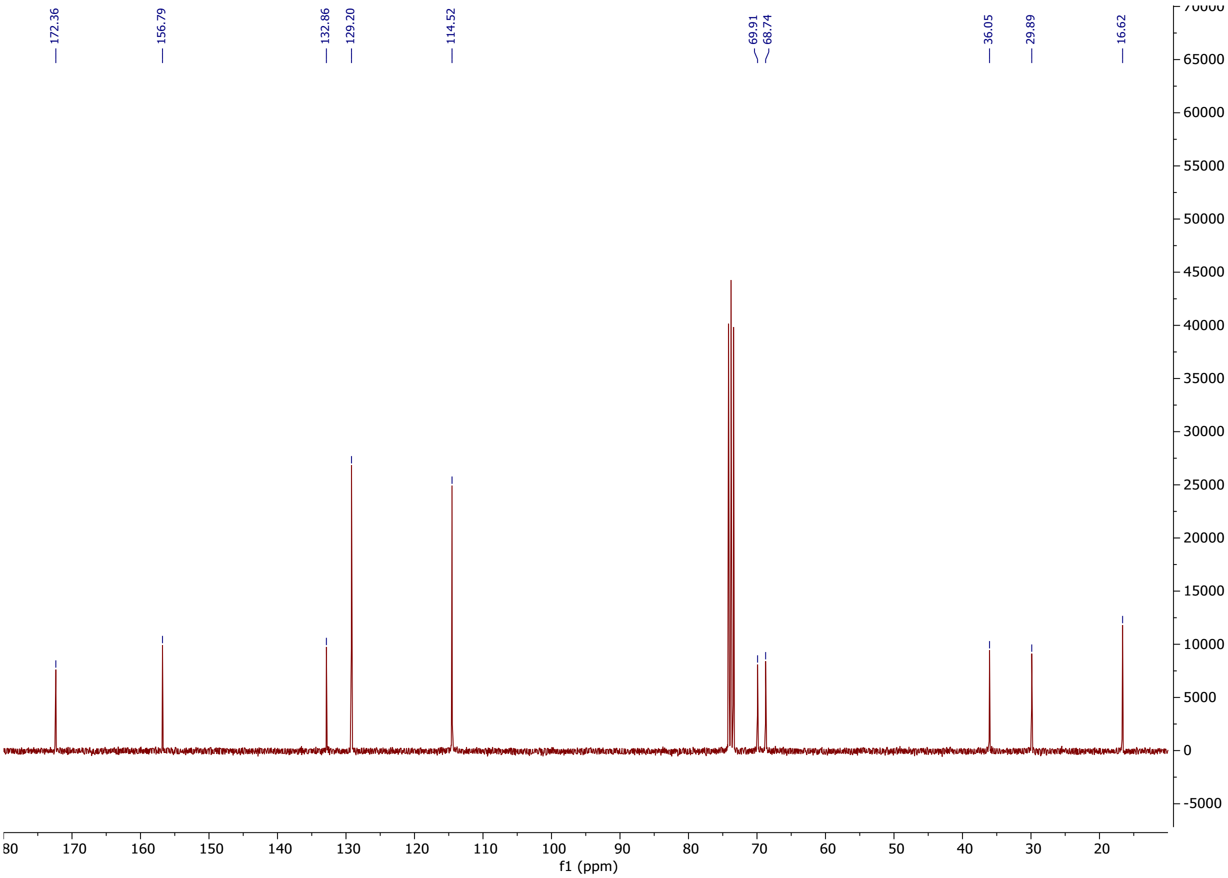


Figure S 19 ^{13}C NMR spectrum of polyisopropyl phloretate (PiPP)

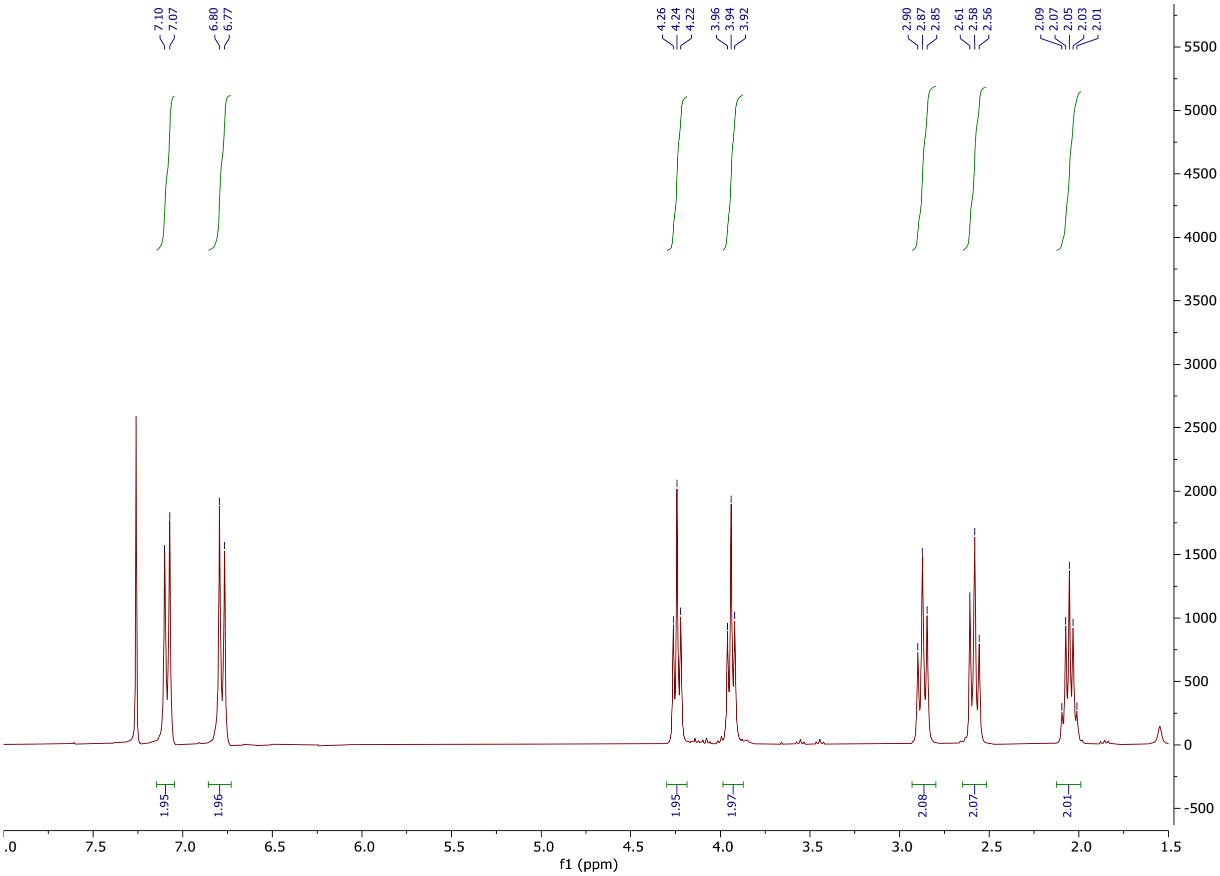


Figure S 20 ^{1}H NMR spectrum of polypropylene phloretate (PPP)

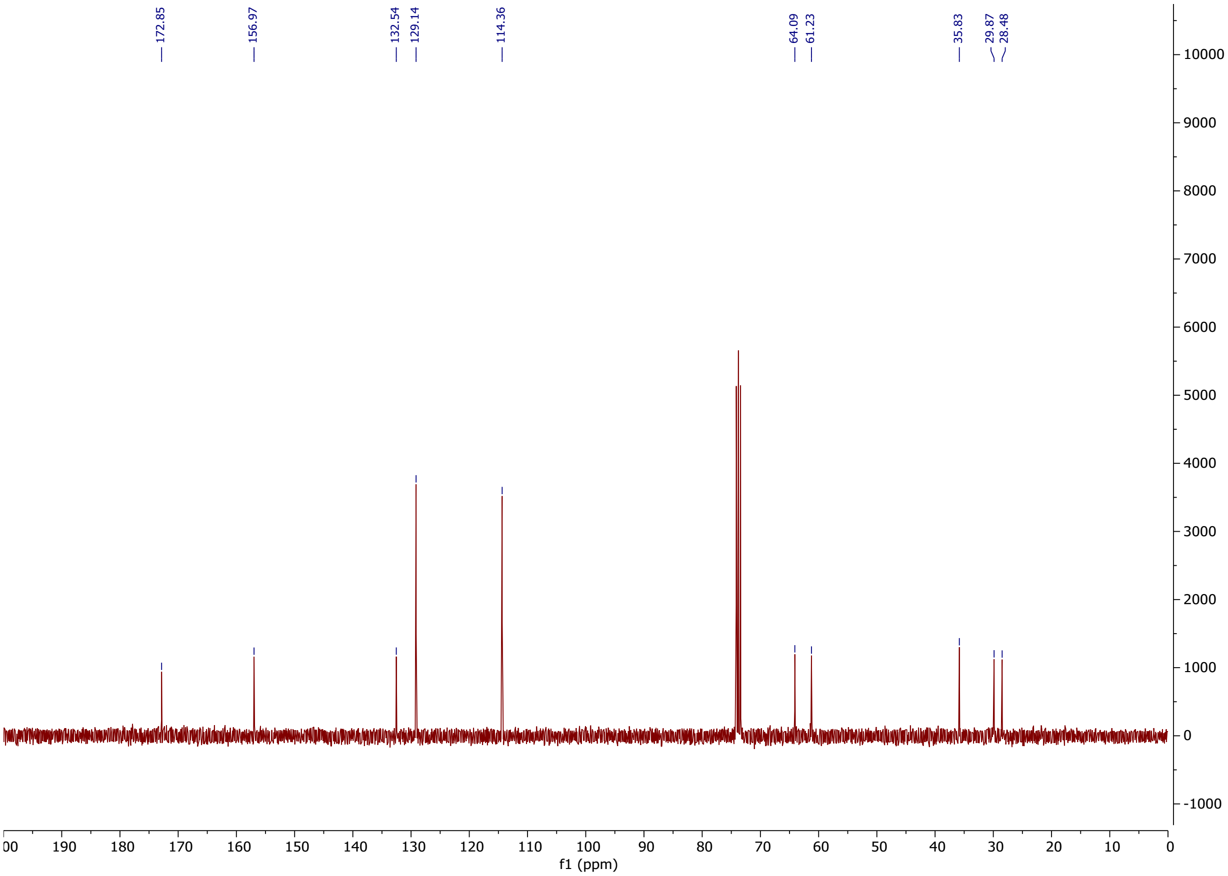


Figure S 21 ^{13}C NMR spectrum of polypropylene phloretate (PPP)

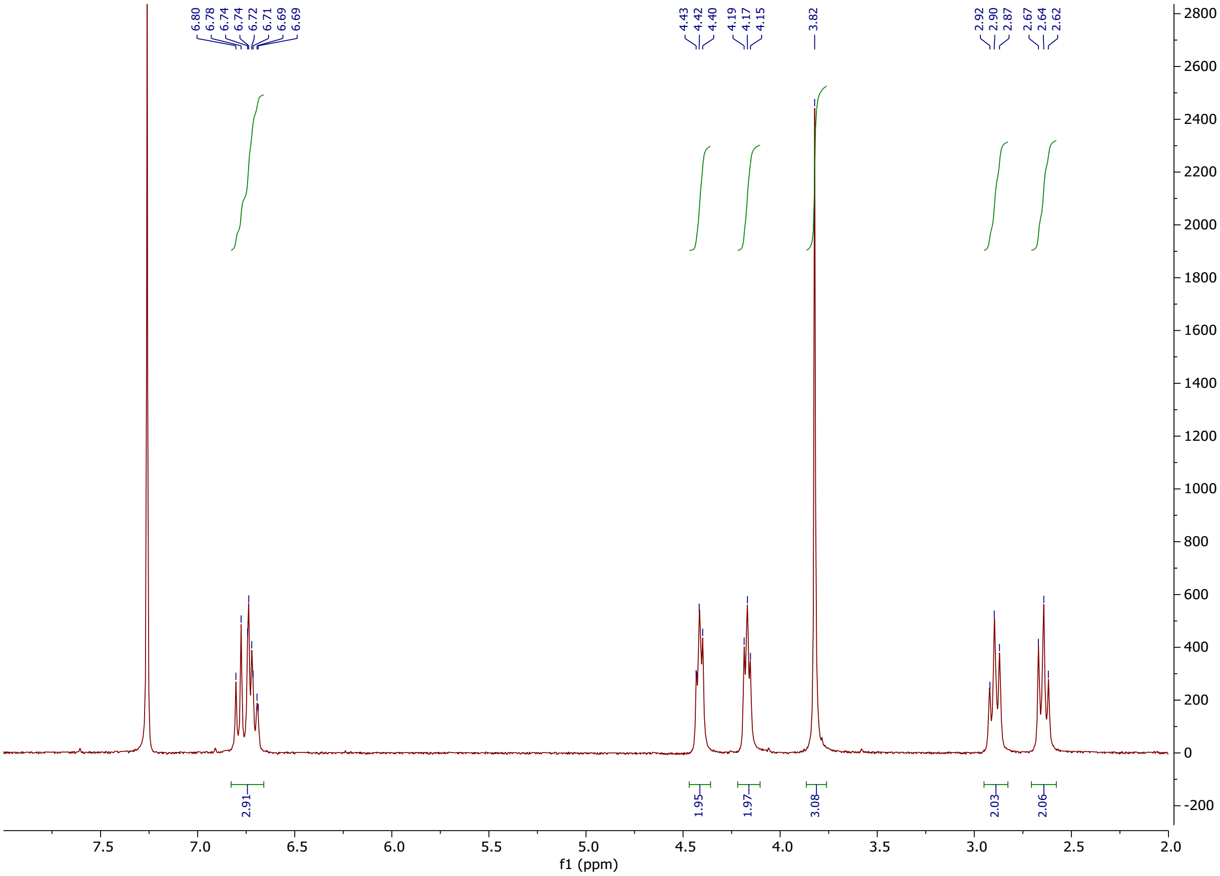


Figure S 22 ^{1}H NMR spectrum of polyethylene dihydroferulate

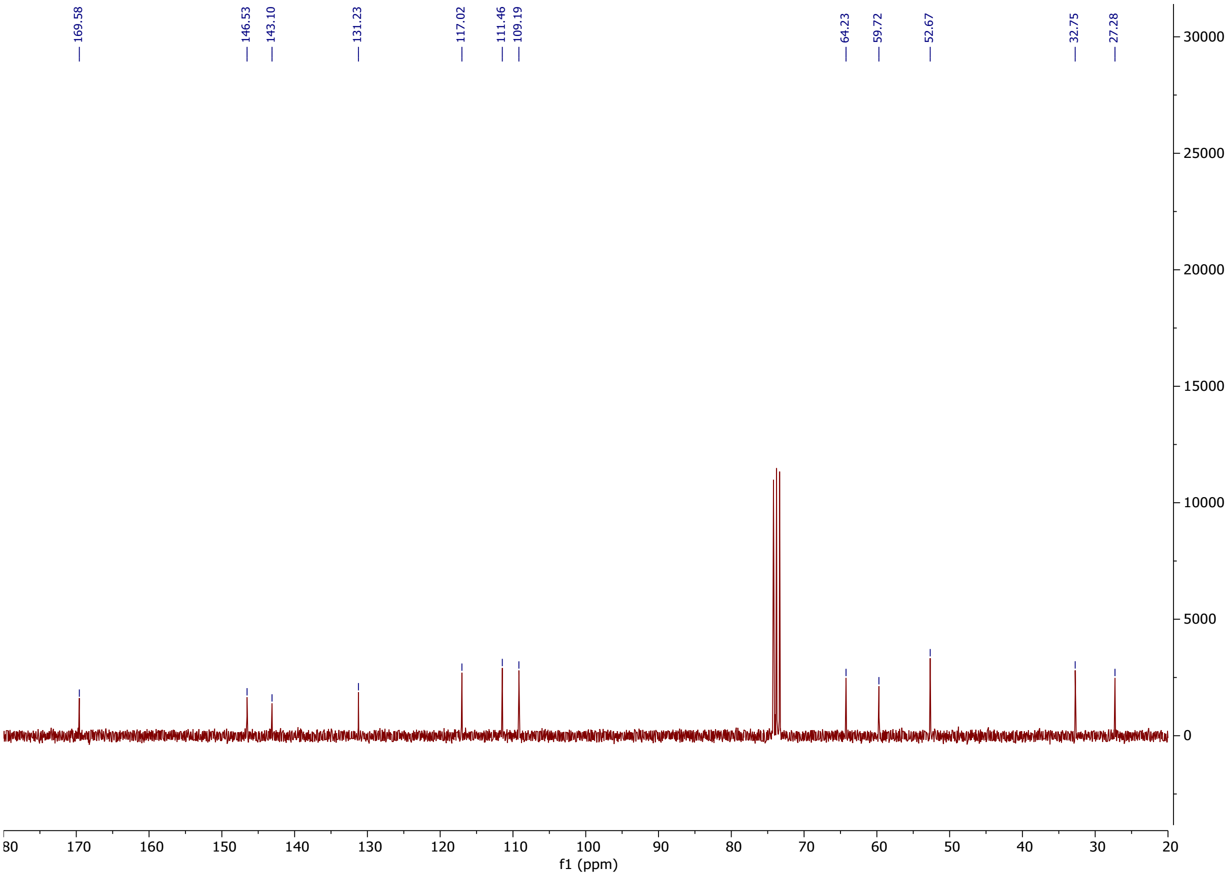


Figure S 23 ^{13}C NMR spectrum of polyethylene dihydroferulate

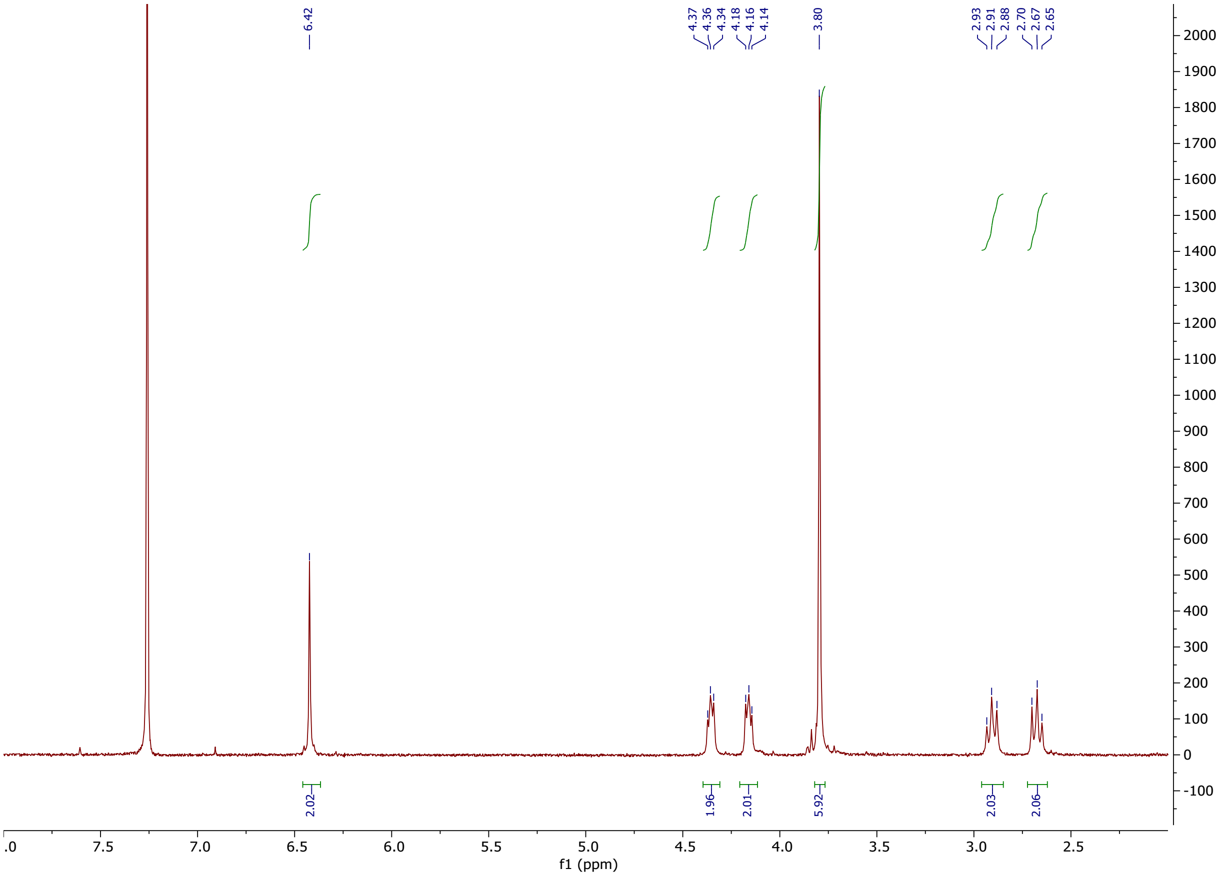


Figure S 24 ^{1}H NMR spectrum for polyethylene dihydrosinapate

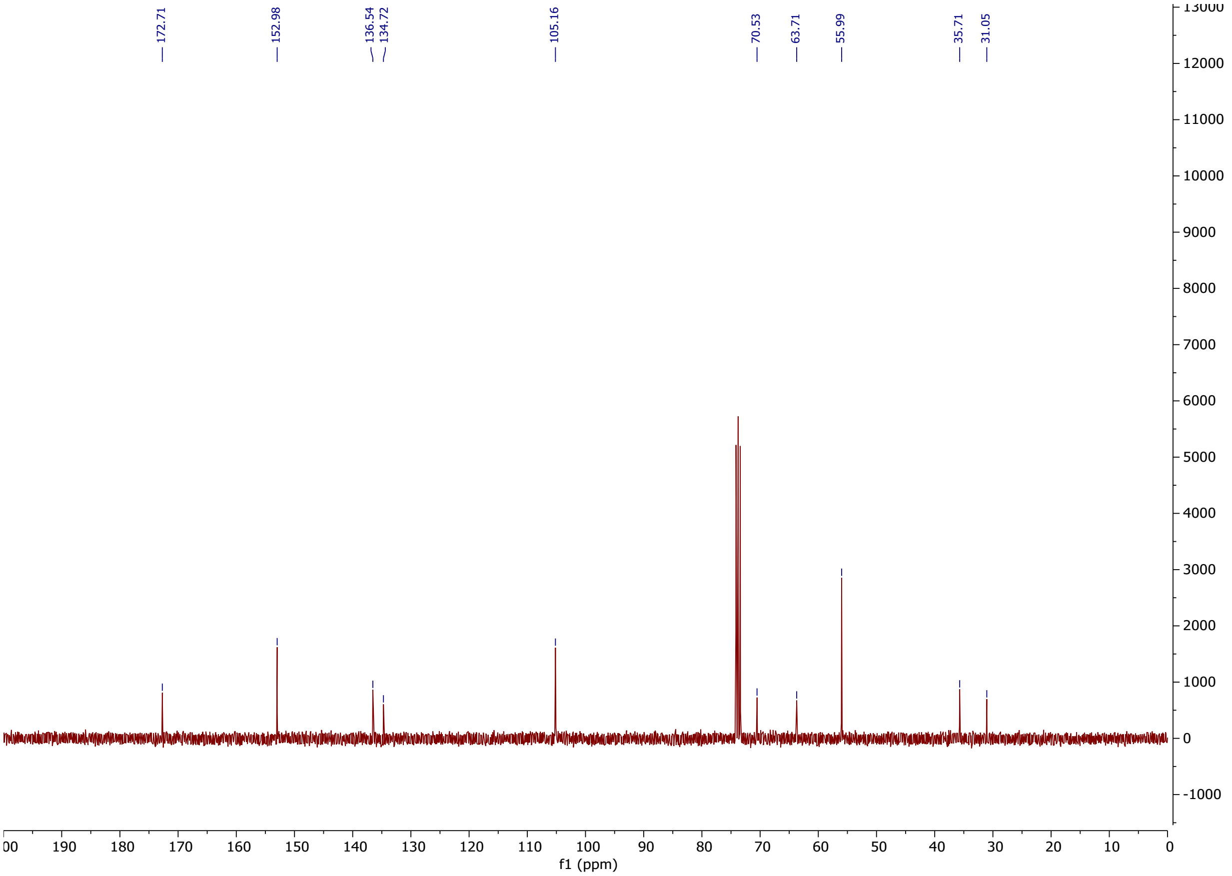


Figure S 25 ^{13}C NMR spectrum of polyethylene dihydrosinapate

Green Metrics

The E-Factor for the synthesis of 4-(2-hydroxyethoxy)phenylpropanoic acid by ethylene carbonate and 1-chloroethanol is present below.

$$E - Factor = \frac{Mass\ of\ Inputs - Mass\ of\ Products\ (g)}{Mass\ of\ Products\ (g)}$$ (Equation S1)

Table S 1 Alkylation via cyclic carbonate over two steps. Sulfuric acid assumed to be negligible

Product	Input Material	Input Weight (g)	Product Weight (g)	E Factor	Process E Factor
PA Methyl Ester	Phloretic acid	50.00	53.61	0	0.97
	MeOH	118.80			
	Sulfuric Acid				
EP monomer	PA Methyl Ester	53.61	50.25	0.97	

	Ethylene carbonate	22.10			
	Potassium Carbonate	1.65			
	NaOH	21.60			
	H2O	270.00			

Table S 2 Alkylation via halo alcohol

Halo alcohol route	Phloretic acid	166.00	132.45	2.26
EP Monomer	NaOH	100.00		
	NaI	45.00		
	2chloro ethanol	120.77		
	H20	1000.00		

The general rubric for Eco-Scale for both routes is shown below.

$$EcoScale = 100 - Penalty\ Points \quad \text{(Equation S2)}$$

Excellent: 75-100
Acceptable: 50-74
Inadequate: 0-49

Table S 3 Eco-Scale Rubric

1. Yield	**Penalty Points**
(100-%yield)/2	.5-50
2. Price (for 10 mmol product)	
<$10	0
$10-$50	3
>$50	5
3. Safety (sum all that apply)	
N- dangerous for environment	5
T- toxic	5
F- flammable	5
E- explosive	10
F+ extremely flammable	10
T+ extremely toxic	10
4. Set up (sum all that apply)	
common	0

Controlled addition	1
Unconventional activation	2
Pressure equipment >1atm	3
additional special glassware	1
inert atmospere	1
glove box	3
5. Temp/Time (sum all that apply)	
rt<1hr	0
rt<24hr	1
heat <1hr	2
heat>1hr	3
cool to 0C	4
Cool < 0C	5
6. Workup/purification (sum all that apply)	
none	0
Cool to rt	0
Adding solvent	0
simple filtration	0
removal of solvent bp <150C	0
Crystallization/filtration	1
removal of solvent bp>150C	2
solid phase extraction	2
distillation	3
sublimation	3
liquid-liquid extraction	3
Chromatography	10

Table S 4 Alkylation with ethylene carbonate

Parameter	Assessment	Penalty Points
1. Yield	(100-96)/2	2
2. Price PMeEster Ethylene Carbonate K2CO3	 $ 1.80/10 mmol $ 0.97/10 mmol $ 0.69/10 mmol	0
3. Safety	Toxic (ethylene carbonate)	5
4. Set up	Additional special glassware Inert atmosphere	2
5. Temp/Time	heat>1hr	3
6. Workup	Crystallization/Filtration	1
Total Penalty Points		13

Eco-Scale	100-13	**87**

Table S 5 Alkylation with 2-chloroethanol

Parameter	Assessment	Penalty Points
1. Yield	(100-63)/2	18.5
2. Price Phloretic Acid NaOH NaI 2-chloro ethanol	 $ 1.66/10 mmol $ 1.00/10 mmol $ 0.45/10 mmol $ 1.21/10mmol	0
3. Safety	Dangerous for the environment, flammable, extremely toxic (2-chloroethanol)	20
4. Set up	Controlled addition	1
5. Temp/Time	heat>1hr	3
6. Workup	Crystallization/Filtration Liquid-liquid extraction	4
Total Penalty Points		46.5
Eco-Scale	100-46.5	**53.5**

DSC Thermograms

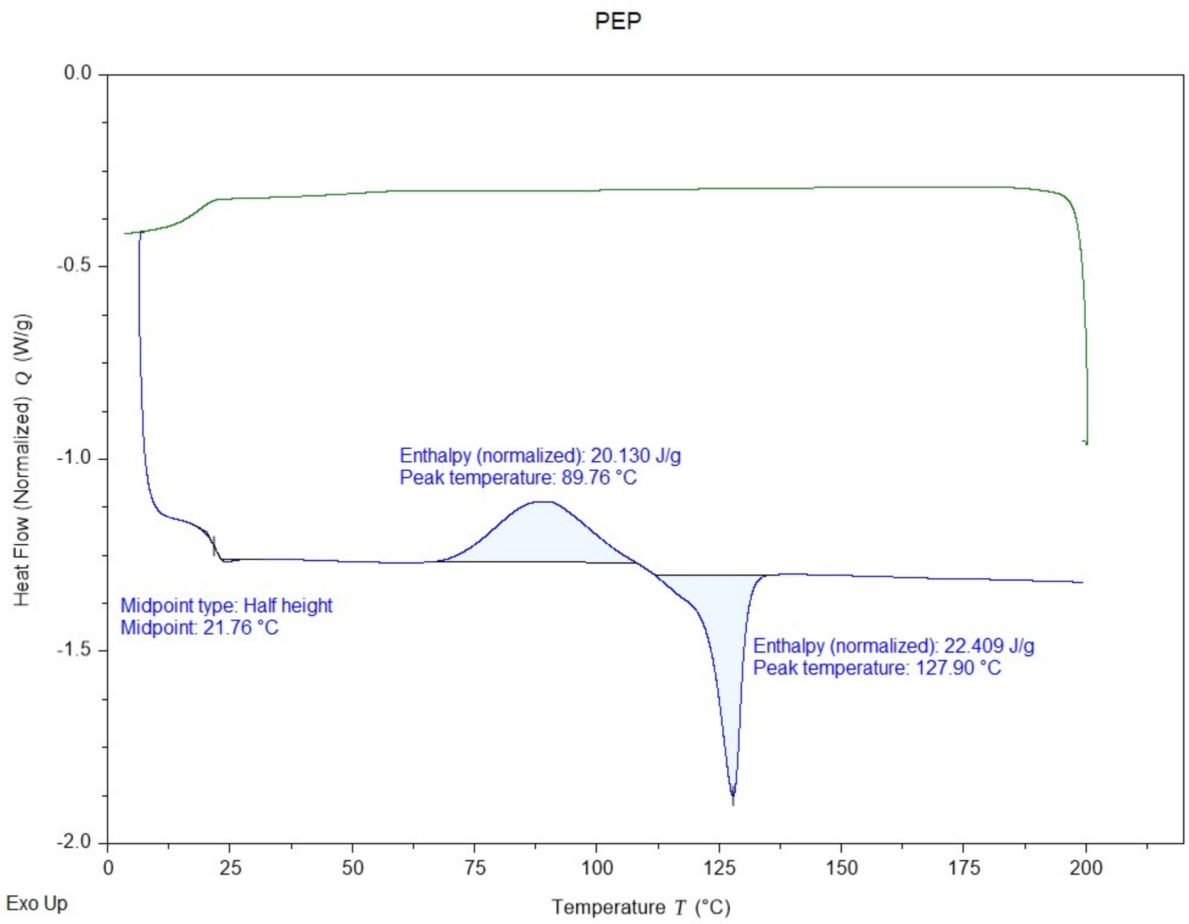


Figure S 26 Second heating and cooling cycle of PEP

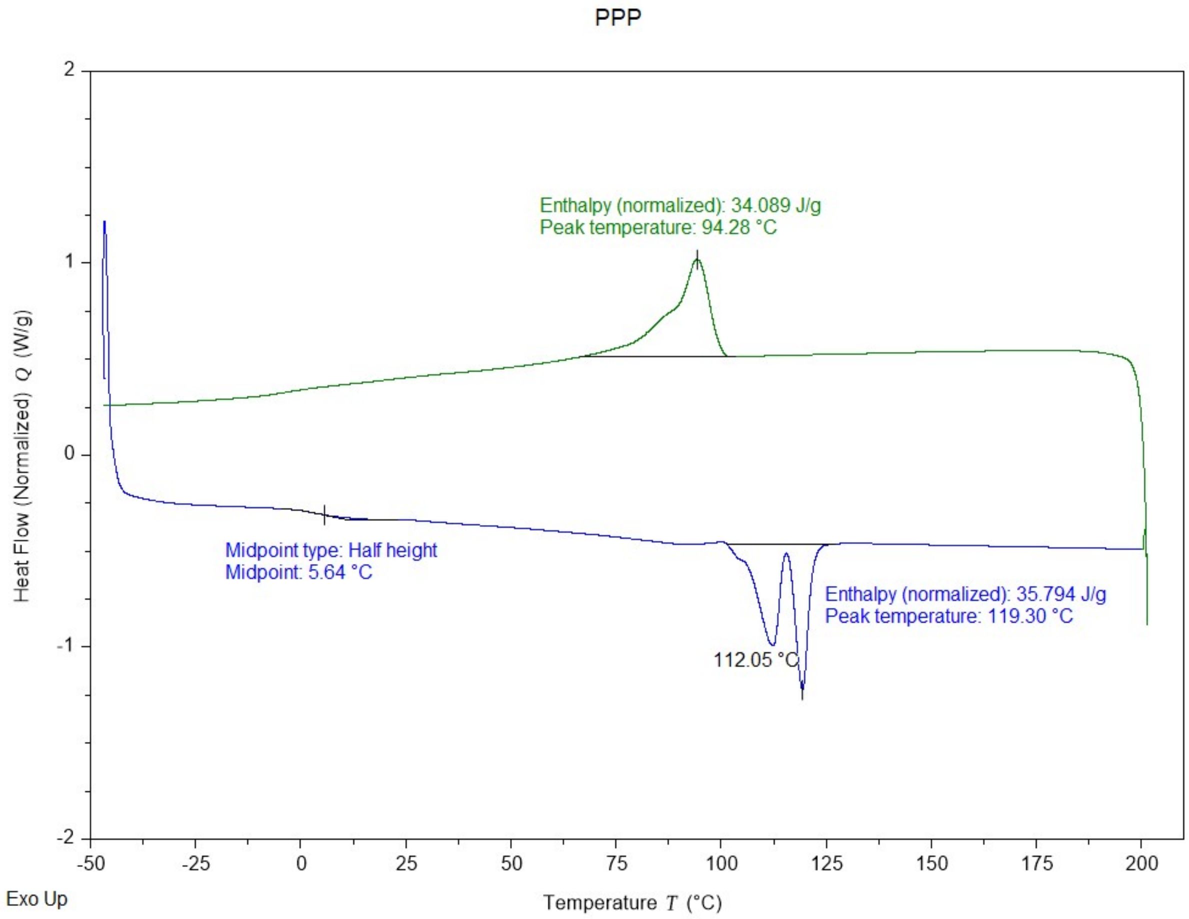


Figure S 27 Second heating and cooling cycle of PPP

Tensile Testing

Table S 6 Tensile properties of PiPP tested at different rates

Rate (mm/min)	Elastic Modulus (MPa)	Tensile Strength (MPa)	Ultimate Elongation (%)
20	3.77	5.40	428.95
50	2.39	2.93	249.80
80	4.76	4.25	273.57

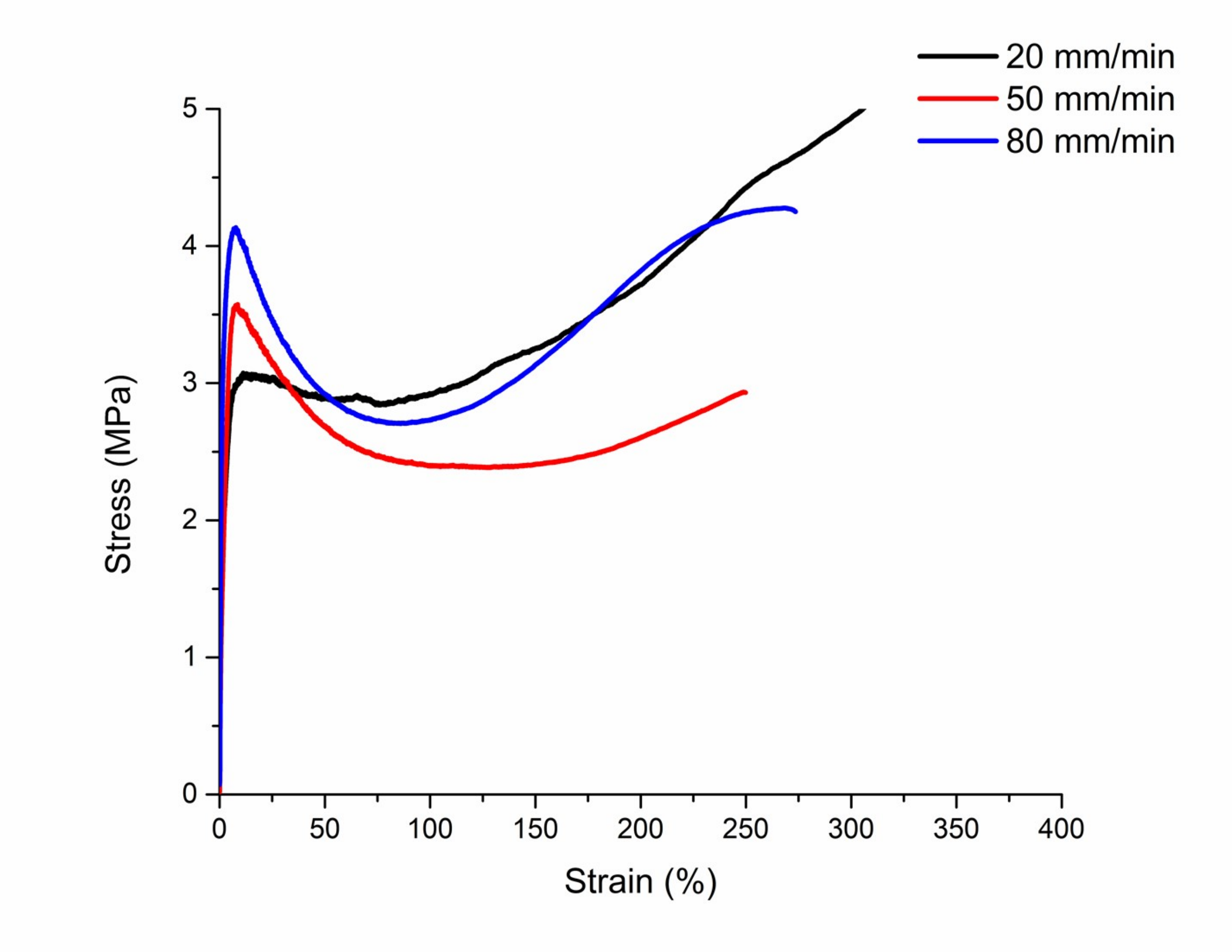


Figure S 28 Stress/Strain curve of PiPP tested at different rates

Composting

The evolved biogas of each sample was calculated daily by the difference of each sample to the average CO_2 contribution from the blank and negative controls as described by Equation 3.

$$Sample_{CO_2} = R_{CO_2} - B_{CO_2} \quad \text{(Equation S3)}$$

Where $Sample_{CO2}$ is the cumulative CO_2 production (mg) from the sample specimen on the *n*th day of operation determined from each replicate reactor CO_2 evolution, R_{CO2} (mg). No negative control was used in respirometry experiments. Each replicate $Sample_{CO2}$ is calculated from the average of the CO_2 evolved from the triplicate control blanks, B_{CO2} (mg). The calculated evolved

CO_2 for each sample was then used to calculate the daily absolute biodegradation (%), according to Equation 4.

$$Absolute\ Biodegradation\ (\%) = \frac{Sample_{CO_2}}{m \times c \times 44.01/12.01} \qquad \text{(Equation S4)}$$

Where the sample mass, *m* (mg) and the percent organic carbon of the sample, *c (%)*, was used to determine the carbon contributions to CO_2 for each sample. The dimensionless value of 44.01/12.01 is used to account for the carbon mass in CO_2 generated from each reactor. Methane concentrations were monitored to ensure aerobic conditions were maintained throughout the experiment.

These datasets were normalized according to the standard normalization Equation 5.

$$y = a + \frac{(y - A)(b - a)}{(B - A)} \qquad \text{(Equation S5)}$$

Where *a* is the minimum value 0, *b* is the maximum value of 1, *A* is the dataset minimum value, 0, and *B* is the dataset maximum value for the absolute biodegradation calculations.

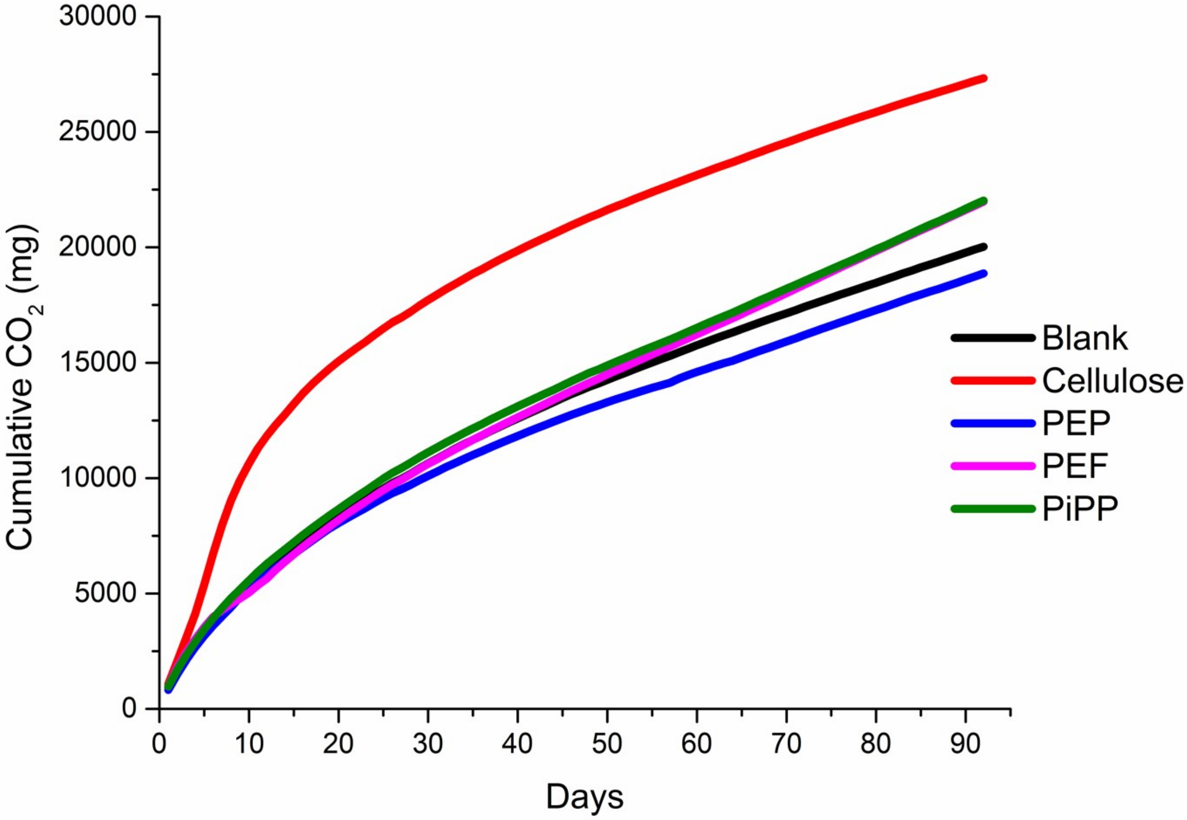


Figure S 29 Cumulative CO$_2$ production of compost without sample (blank), cellulose positive control, and tested samples

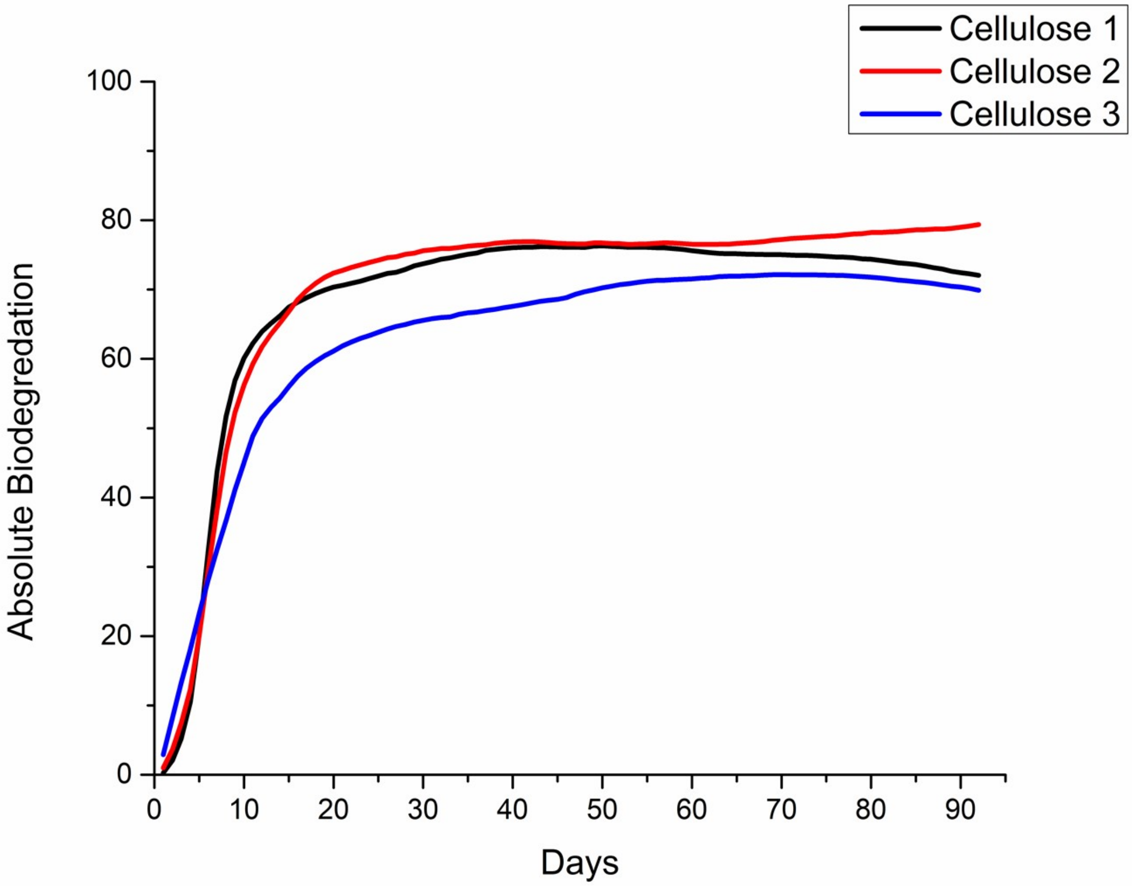


Figure S 30 Absolute biodegradation of cellulose triplicates

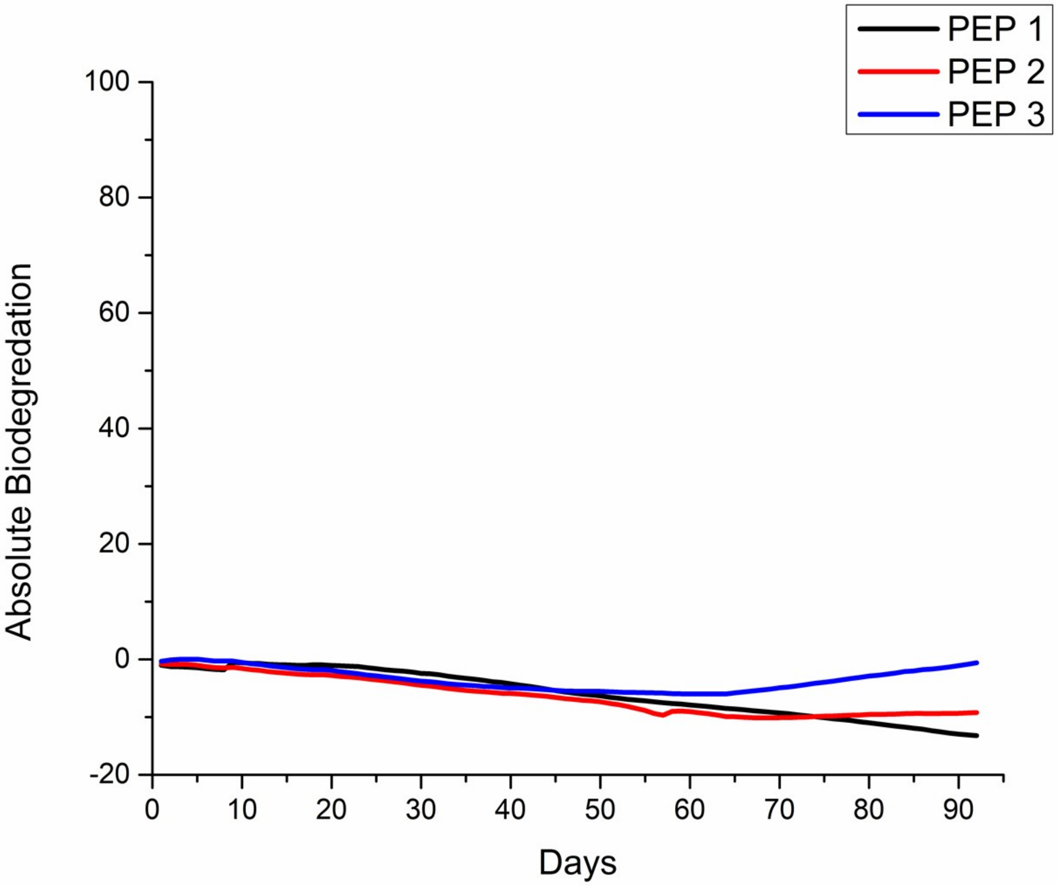


Figure S 31 Absolute biodegradation of PEP triplicates

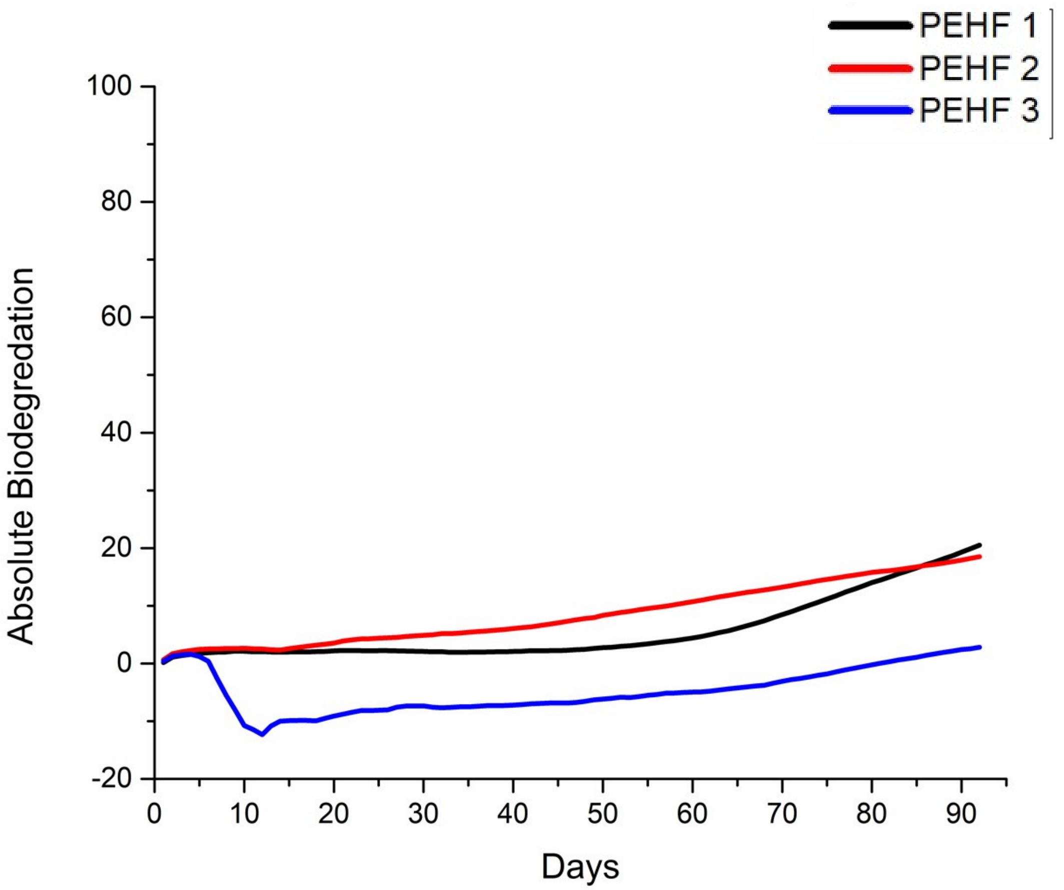


Figure S 32 Absolute biodegradation of PEHF

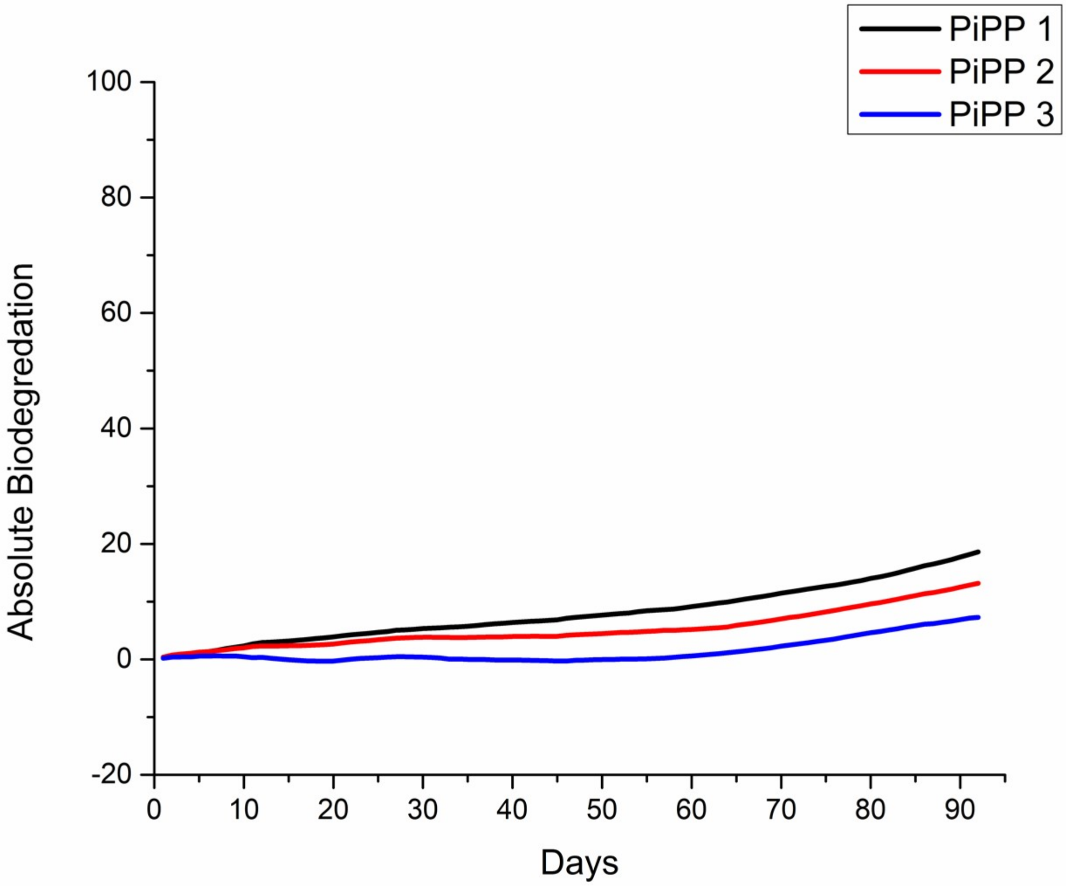


Figure S 33 Absolute biodegradation of PiPP