Supplementary Information for:

Streamlining the Conversion of Biomass to Polyesters: Bicyclic Monomers with Continuous Flow

Deivasagayam Dakshinamoothy,[1] Stewart P. Lewis,[1,≠] Michael P. Cavazza,[1] Aaron M. Hoover,[1] David F. Iwig,[3] Krishnan Damodaran,[2] Robert T. Mathers[1]*

[1]Department of Chemistry, The Pennsylvania State University, New Kensington, Pennsylvania 15068. [2]Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. [3]Alcoa Technical Center, 100 Technical Drive, Alcoa Center, Pennsylvania 15069.

*To whom correspondence should be addressed. E-mail: rtm11@psu.edu.

Table of Contents

Figure S8	^{1}H NMR spectrum (700 MHz, $CDCl_3$) for the product (**2**) resulting from the hydrogenation of the Diels Alder adduct (**1**) in ethyl acetate using Pd/C and hydrogen (20 psi).
Figure S9	^{13}C NMR spectrum (700 MHz, $CDCl_3$) for the product (**2**) resulting from the hydrogenation of the Diels Alder adduct (**1**) in ethyl acetate using Pd/C and hydrogen (20 psi).
Figure S10	Differential scanning calorimetry (DSC) data (20 °C/min) for the product (**2**) resulting from the hydrogenation of the Diels Alder adduct.
Figure S11	FTIR data for the product (**2**) resulting from the hydrogenation of the Diels Alder adduct (**1**) in ethyl acetate using Pd/C and hydrogen (20 psi).
Figure S12	LC/MS data for the product resulting from the hydrogenation of the Diels Alder adduct in ethyl acetate using Pd/C and hydrogen (20 psi).
Figure S13	Overlay FTIR spectrum of the disappearance of the alkene C-H absorbance (3055 cm^{-1}) for the hydrogenation of Diels Alder product (monomer **1**).
Figure S14	Comparison of continuous flow hydrogenation data for a) cyclooctene and b) Diels Alder product (monomer **1**).
Figure S15	Continuous flow hydrogenation of Diels Alder product (monomer **1**) with 0.30 g of Pd/C and 125 psi hydrogen.
Figure S16	^{1}H NMR spectrum (700 MHz, $CDCl_3$) of polyester synthesized from bicyclic anhydride **2** and glycerol after 24 h at 120 °C.
Figure S17	^{13}C NMR spectrum (700 MHz, $CDCl_3$) of polyester synthesized from bicyclic anhydride **2** and glycerol after 24 h at 120 °C.

Figure S18 Dependence of glass transition temperature on M_w for the polymerization of glycerol with anhydride **2** ([glycerol]/[anhydride **2**] = 1).

Figure S19 Correlation between the glass transition temperature and the reaction time for the polymerization of glycerol with anhydride **2** ([glycerol]/[anhydride **2**] = 1).

Table S1: Solubility studies for cyclohexadiene, maleic anhydride, and monomer **1**.[a]

	Acetone	Ethanol	Ethyl acetate	Hexanes	Methanol	Toluene	DI water	Tetrahydrofuran
Maleic anhydride	2.317	0.246	0.595	insoluble	0.979	semi-soluble	0.579	1.392
1,3-CHD	soluble	soluble	soluble	soluble	soluble	soluble	insoluble	soluble
Monomer **1**	soluble	0.0338	0.196	insoluble	0.0396	0.104	insoluble	0.422

[a] Solubility studies were conducted at ambient temperature with stirred solutions. Solubility values are given in grams solute/gram solvent.

Table S2. Influence of time and temperature on the alkene isomerization reaction.[a]

Entry	Reaction[b]	Temp (° C)	Time (min)	Flow rate (mL/min)	Residence time (sec)	[1,3-CHD]/ [1,4-CHD][c]	Benzene (%)[c]	Abs_{3036}/ Abs_{3091}[d]
1	Continuous	25	-	1.5±1	13±1	1.9	68	1.96
2	Continuous	11	-	1.3±1	15±1	1.8	13	5.2
3	Continuous	0	-	1.5±1	13±1	1.1	7	6.7
4	Batch	5	5	-	-	1.7	3	-
5	Batch	5	15	-	-	1.8	6	-
6	Batch	5	45	-	-	1.8	10	-
7	Batch	5	140	-	-	1.8	14	-
9	Batch	5	260	-	-	1.8	14	-

[a] All reactions were conducted with neat 1,4-CHD derived from soybean oil that contained ~20 % dodecene isomers which result from monounsaturated triglycerides. [b] Continuous flow reactions flushed 2 mL of 1,4-CHD through a catalyst tube (ID 2.1 mm x 100 mm) with 100 mg of $Na_2O/Na/Al_2O_3$ catalyst. Batch reactions used 2 mL of 1,4-CHD and 17 mg of $Na_2O/Na/Al_2O_3$ catalyst in a vial under nitrogen. [c] Based on GC analysis of product mixtures indicating lower temperature and shorter reactions times are beneficial. [d] FTIR data for ratio of 1,3-CHD absorbance at 3036cm^{-1} and benzene absorbance at 3091 cm^{-1}.

Table S3. Yield data as a function of temperature for neat Diels-Alder reaction between 1,3-CHD and maleic anhydride.

Entry	T (°C)	Time (h)	% Yield based on MA
1	25	12	6.5
2	25	24	9.1
3	30	12	11.8
4	30	24	13.6
5	30	24	12.2
6	40	24	85.0
7	40	24	84.5
8	50	24	88.2
9	50	24	82.7
10	60	24	88.0

[MA] = 12.6 mmol
[CHD] = 19.3 mmol

Table S4: Comparison of polymerization of anhydride **2** with glycerol and 1,4-BDO.[a]

Entry	Monomers	M_w (g/mol)[b]	M_w/M_n [b]	[η][b] (mL/g)	Abs_{1726}/Abs_{1776} [c]	T_g [d] (°C)	T_d [e] (°C)	X_n [f]
1	1,4-BDO	8730	1.4	6.8	1.9	13	185	25
2	glycerol	9350	2.2	6.7	10	57	286	17

[a] Polymerizations were conducted at 120°C for 24 h under dynamic vacuum (150 mbar) with [glycerol or 1,4-BDO]/[**2**] = 1. [b] Measured by GPC in THF at 35°C using light scattering and viscometer detectors. [c] Absorbance ratios of ester (1726 cm^{-1}) and anhydride (1776 cm^{-1}) peaks determined by FTIR spectroscopy. [d] Measured by DSC (20 °C/min) under nitrogen. [e] Decomposition temperature reflects 5 % weight loss as measured by TGA (20 °C/min) under nitrogen. [f] Number-average degree of polymerization calculated from GPC data.

Table S5: Influence of catalyst choice on polymerization of **2** and glycerol.[a]

Entry	Catalyst	M_w (g/mol)[b]	M_w/M_n[b]	[η][b] (mL/g)	Abs_{1726}/Abs_{1776}[c]	T_g[d] (°C)	T_d[e] (°C)	X_n[f]
1	none	2560	2.6	3.0	1.4	-nd-	137	4
2	$Zn(OAc)_2$	4960	5.0	3.1	1.3	-9	154	4
3	$Ti(OBu)_4$	5040	4.9	3.2	1.6	-10	162	4
4	PTSA	9350	2.2	6.7	10	57	286	17

[a]Polymerizations conducted with catalyst (0.2 mol %) at 120°C for 24 h under dynamic vacuum (150 mbar) with [glycerol]/[**2**] = 1. [b]Measured by GPC in THF at 35°C using light scattering and viscometer detectors. [c]Absorbance ratios of ester (1726 cm^{-1}) and anhydride (1776 cm^{-1}) peaks determined by FTIR spectroscopy. [d]Determined by DSC (20 °C/min). [e]T_d values reflect 5 % weight loss as measured by TGA (20 °C/min) under nitrogen. [f]Number-average degree of polymerization calculated from GPC data.

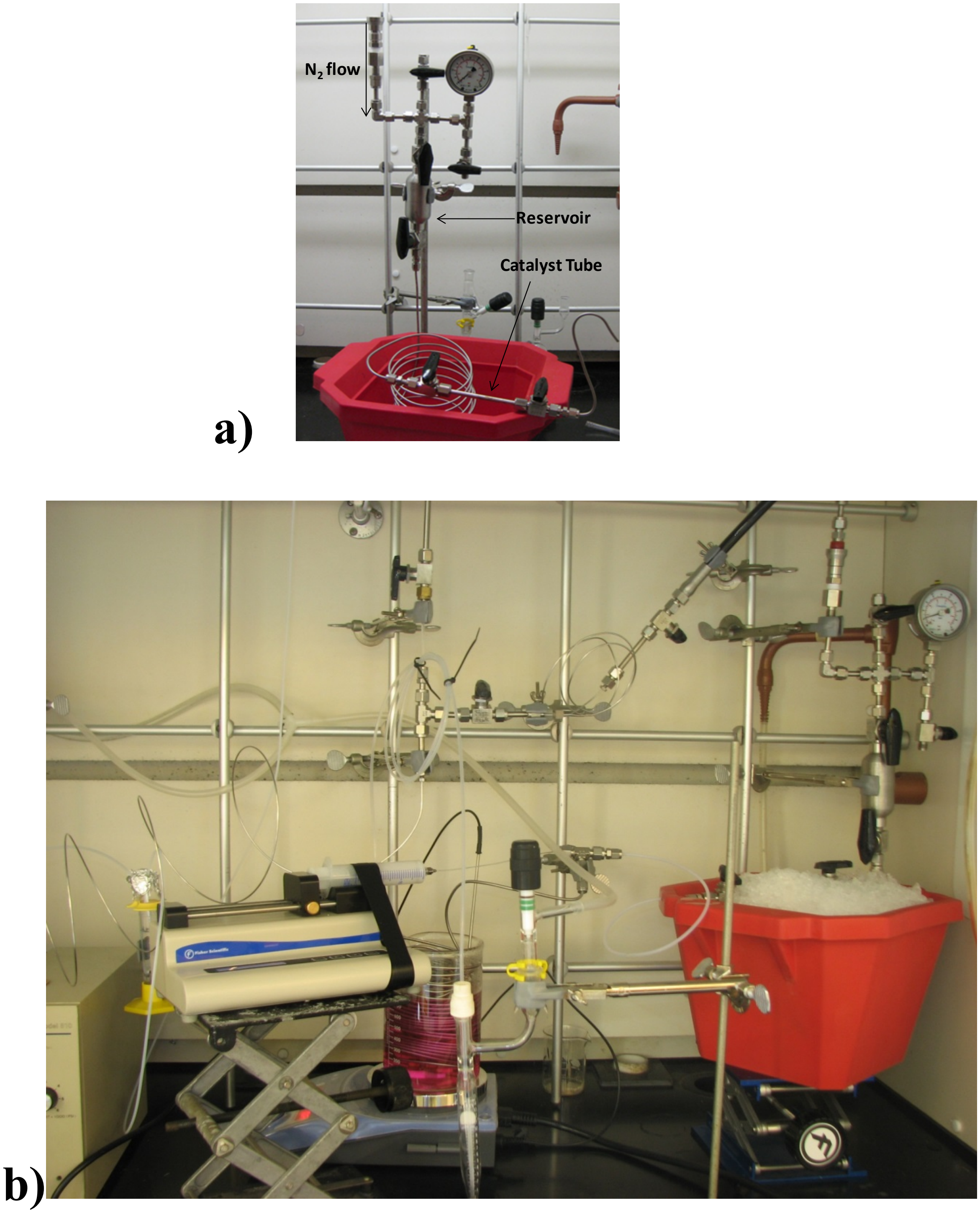


Figure S1. Continuous flow setup showing close-up of alkene isomerization reactor (top picture). The bottom picture shows the three step synthesis involving alkene isomerization reactor (on right), syringe pump for MA solution (on left), heating bath for Diels-Alder reaction, and vertical hydrogenation tube (on top) with hydrogen inlet.

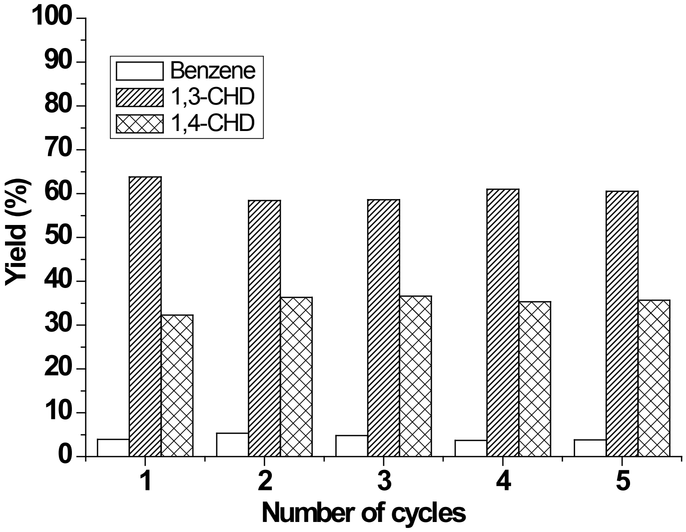


Figure S2. Recycling of catalyst (Na/Na_2O) for the isomerization of 1,4-CHD to 1,3-CHD. The catalyst (100 mg) was subjected to sequential injections of 1,4-CHD (2 mL). The 1,3-CHD:1,4,CHD ratio reflects the thermodynamic stability of the isomers at 0°C.

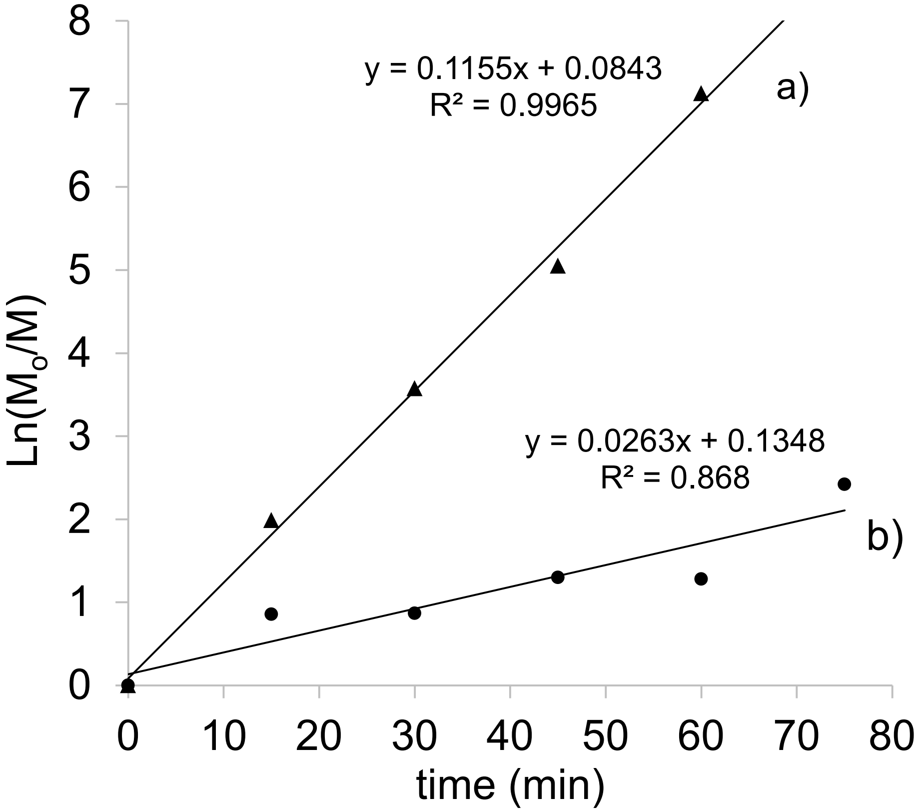
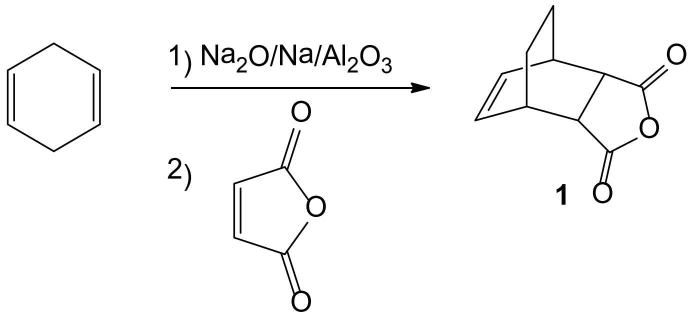


Figure S3. Comparison of Diels Alder reaction of maleic anhydride and 1,3-cyclohexadiene at a) 75 °C and b) 50 °C. The reaction was conducted with MA (1.66 g) in ethyl acetate (12 mL) with 1,3-CHD (4 mL). Data collected by examining the disappearance of the alkene C-H absorbance for maleic anhydride with FTIR spectroscopy.



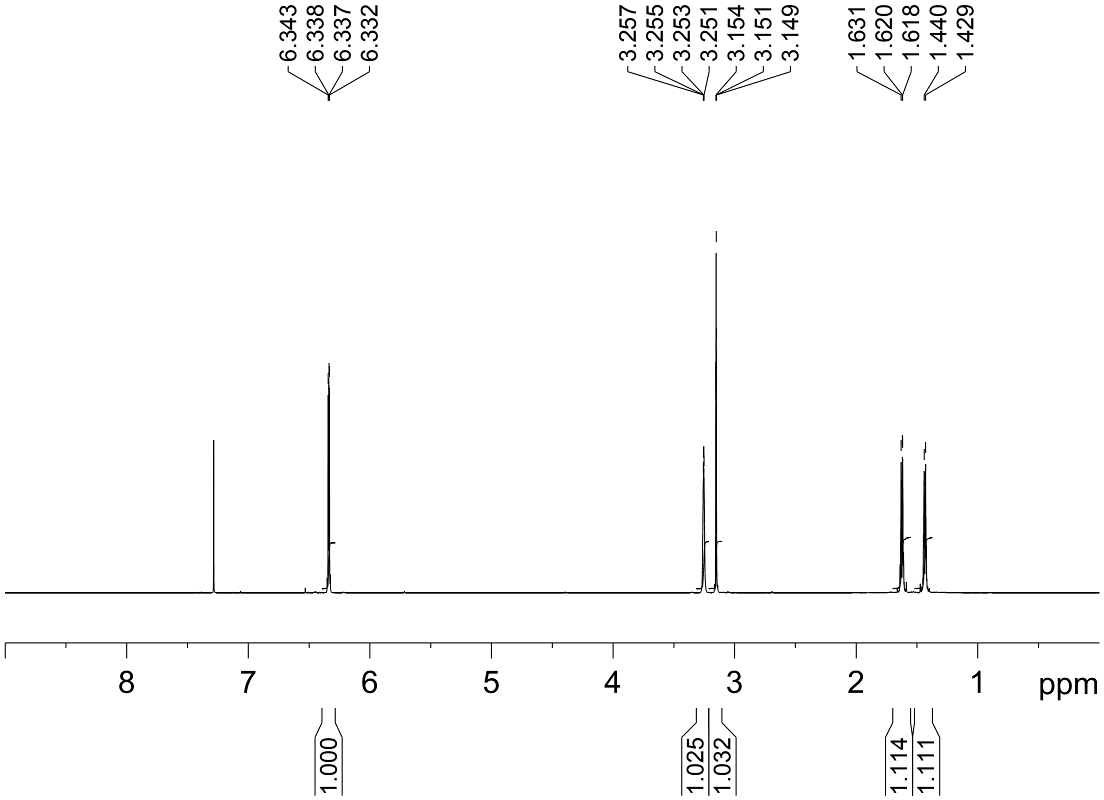
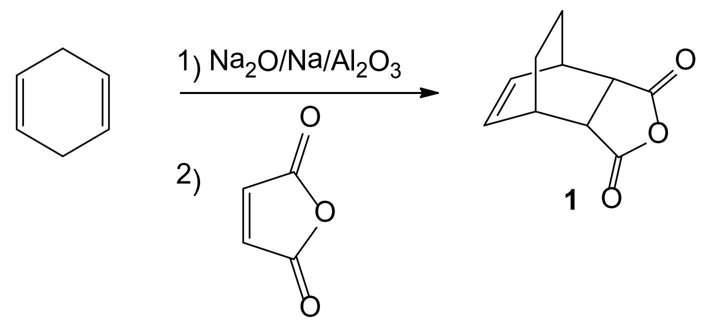


Figure S4. ^{1}H NMR spectrum (700 MHz, CDCl$_3$) for the Diels Alder product (**1**) of maleic anhydride and 1,3-cyclohexadiene. Initially, the 1,4-cyclohexadiene was isomerized at 0°C before adding to the maleic anhydride. The Diels Alder reaction was conducted without additional solvent at 60°C for 3 h before recovering the product in 88 % yield.



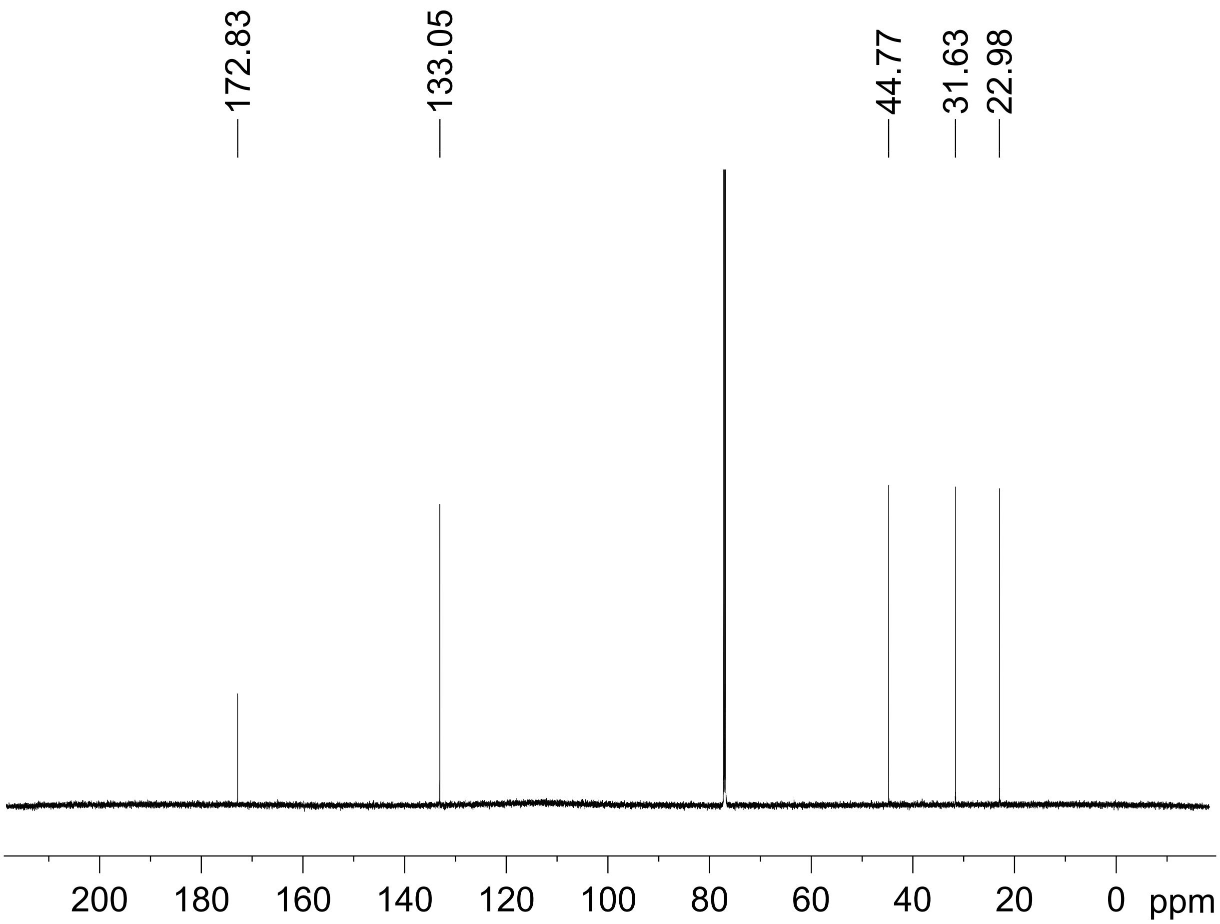
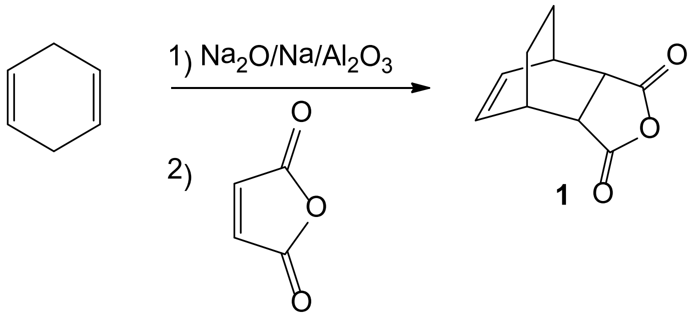


Figure S5. ^{13}C NMR spectrum (700 MHz, $CDCl_3$) for the Diels Alder product (**1**) of maleic anhydride and 1,3-cyclohexadiene.



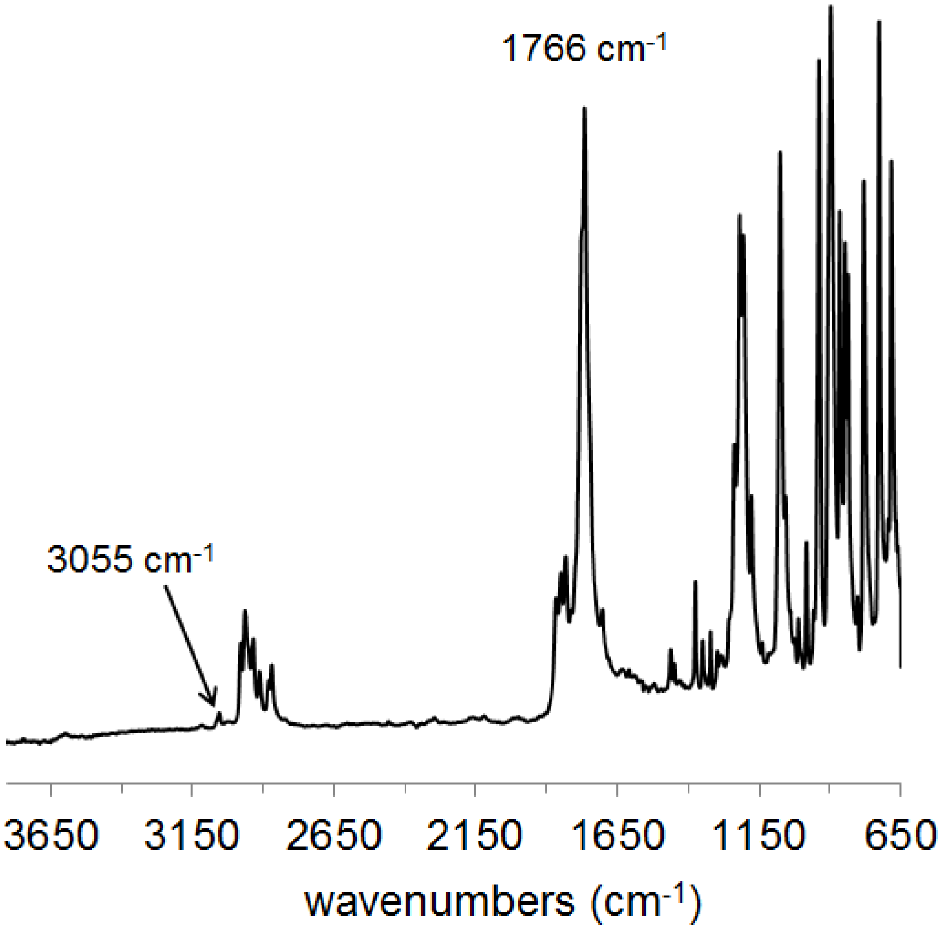
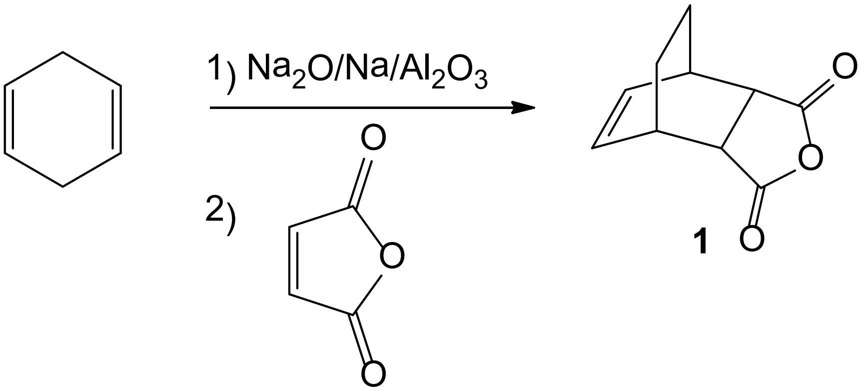
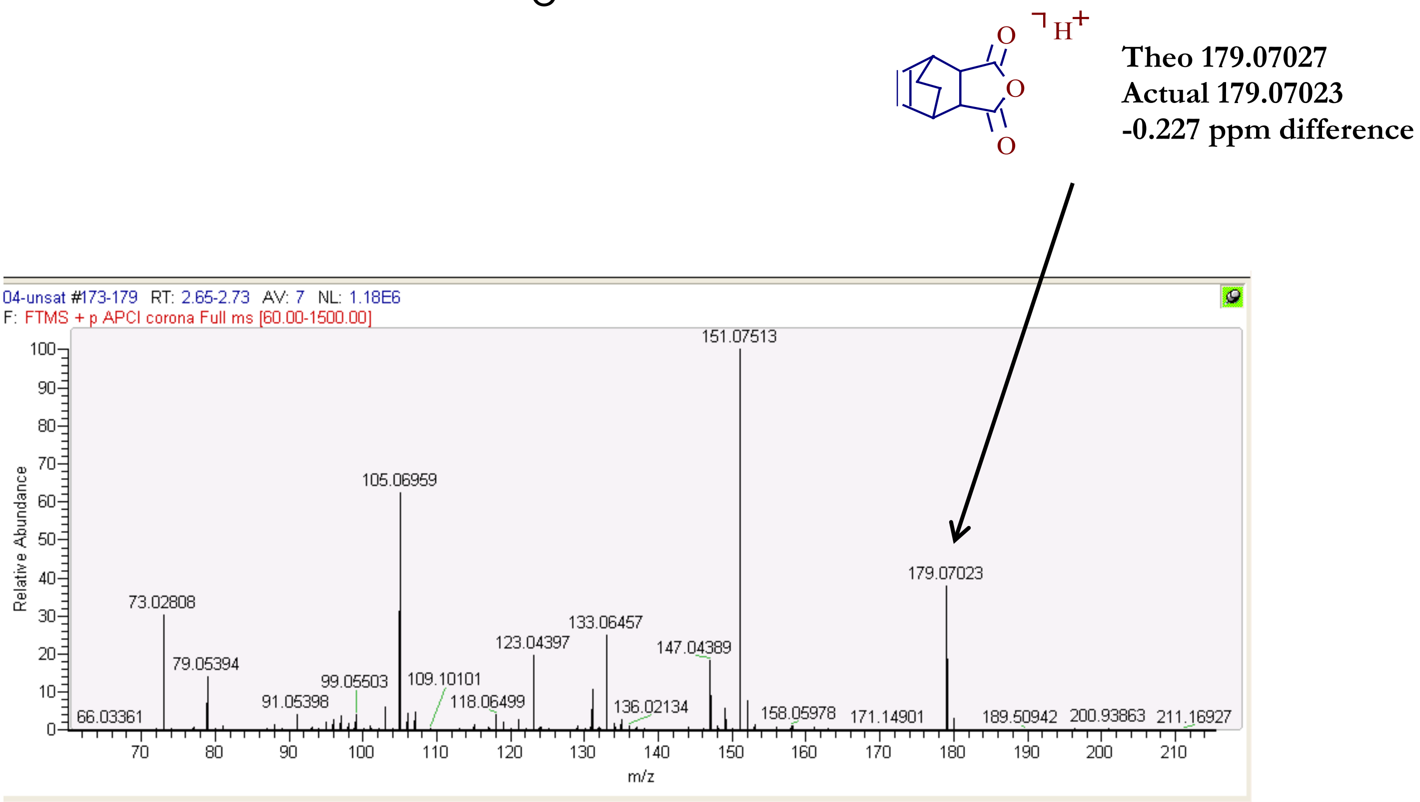


Figure S6. FTIR data for the Diels Alder product (**1**) of maleic anhydride and 1,3-cyclohexadiene. The Diels Alder reaction was conducted under neat conditions at 60°C for 3 h before recovering the product in 88 % yield. The alkene C-H absorbance was detected at 3055 cm^{-1}.

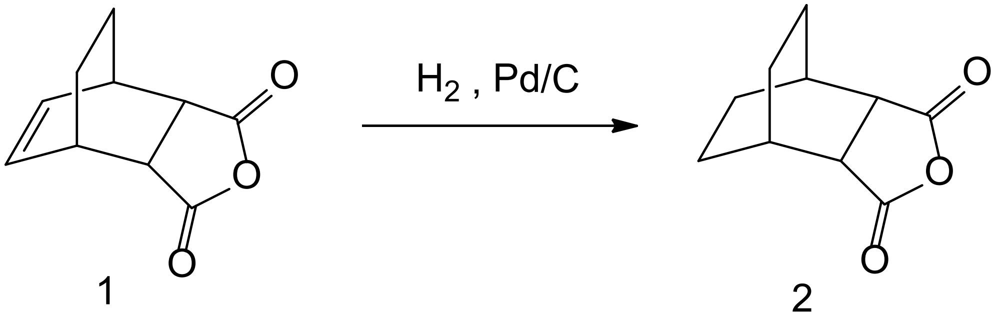


1



Theo 179.07027
Actual 179.07023
-0.227 ppm difference

Figure S7. LC/MS data for the Diels Alder adduct (**1**) of maleic anhydride and 1,3-cyclohexadiene.



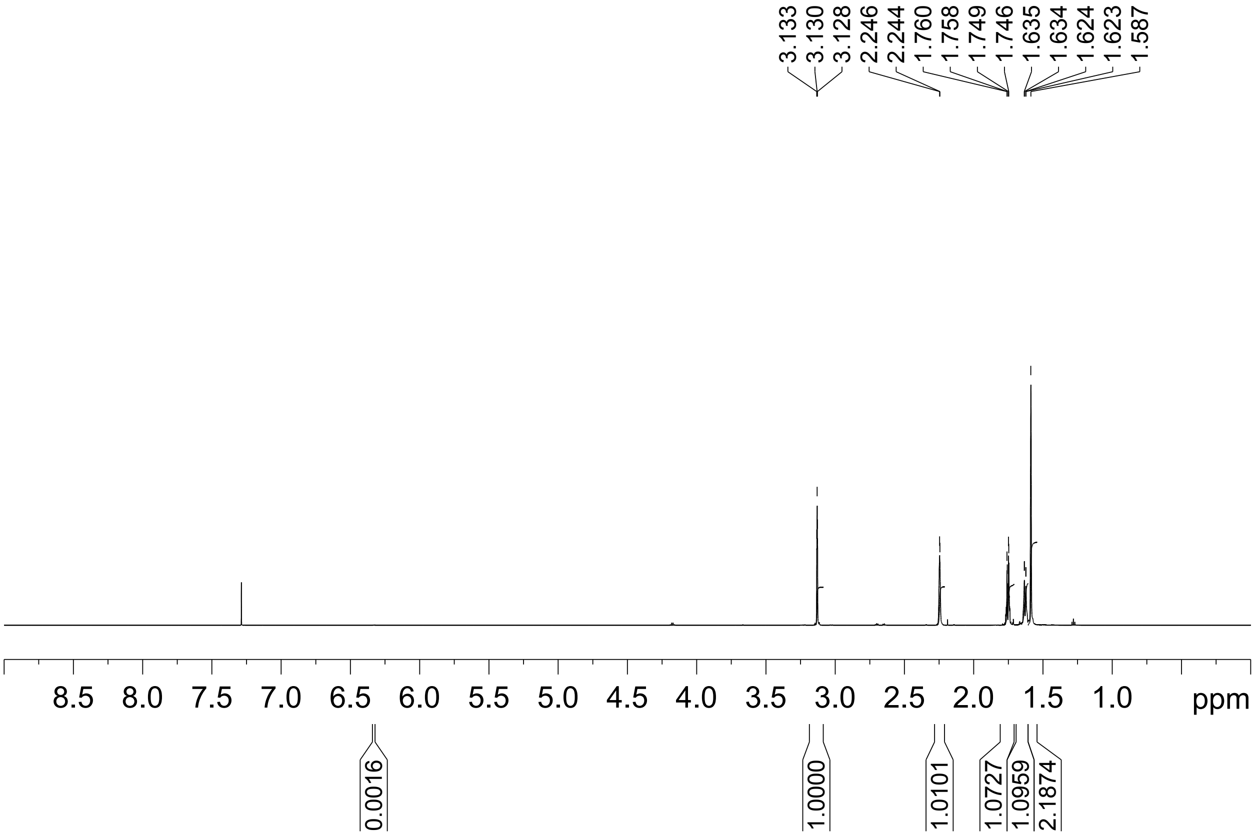
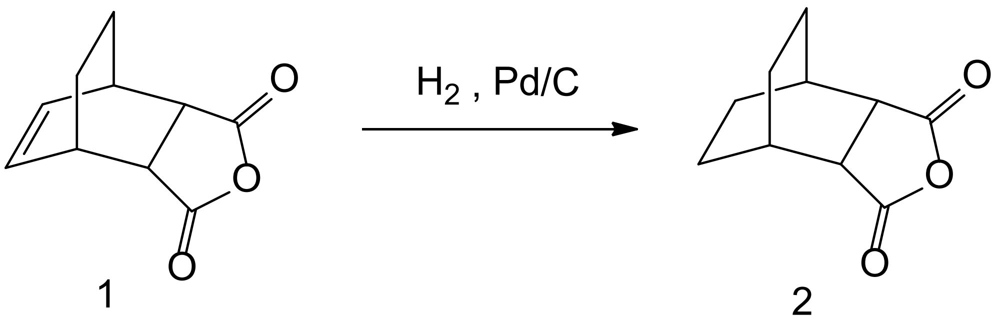


Figure S8. ^{1}H NMR spectrum (700 MHz, $CDCl_3$) for the product (**2**) resulting from the hydrogenation of the Diels Alder adduct (**1**) in ethyl acetate using Pd/C and hydrogen (20 psi). The reaction was conducted at ambient temperature for 1 day before recovering the product in 95% yield. Based on the disappearance of the alkene integration at δ 6.3 ppm, the hydrogenation was > 99.8 %.



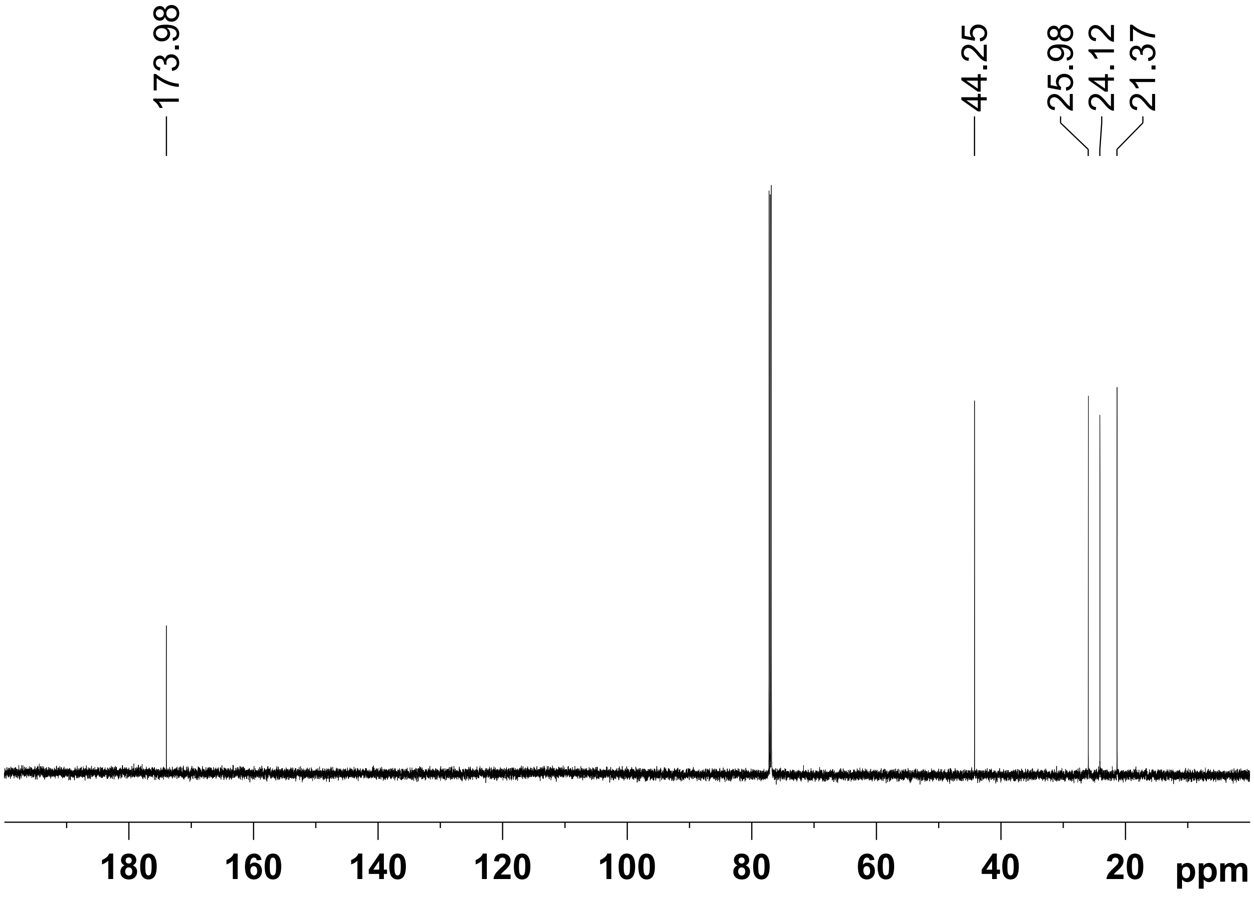
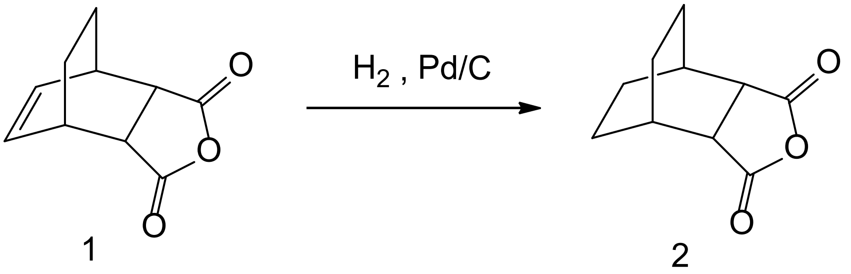


Figure S9. ^{13}C NMR spectrum (700 MHz, $CDCl_3$) for the product (**2**) resulting from the hydrogenation of the Diels Alder adduct (**1**) in ethyl acetate using Pd/C and hydrogen (20 psi).



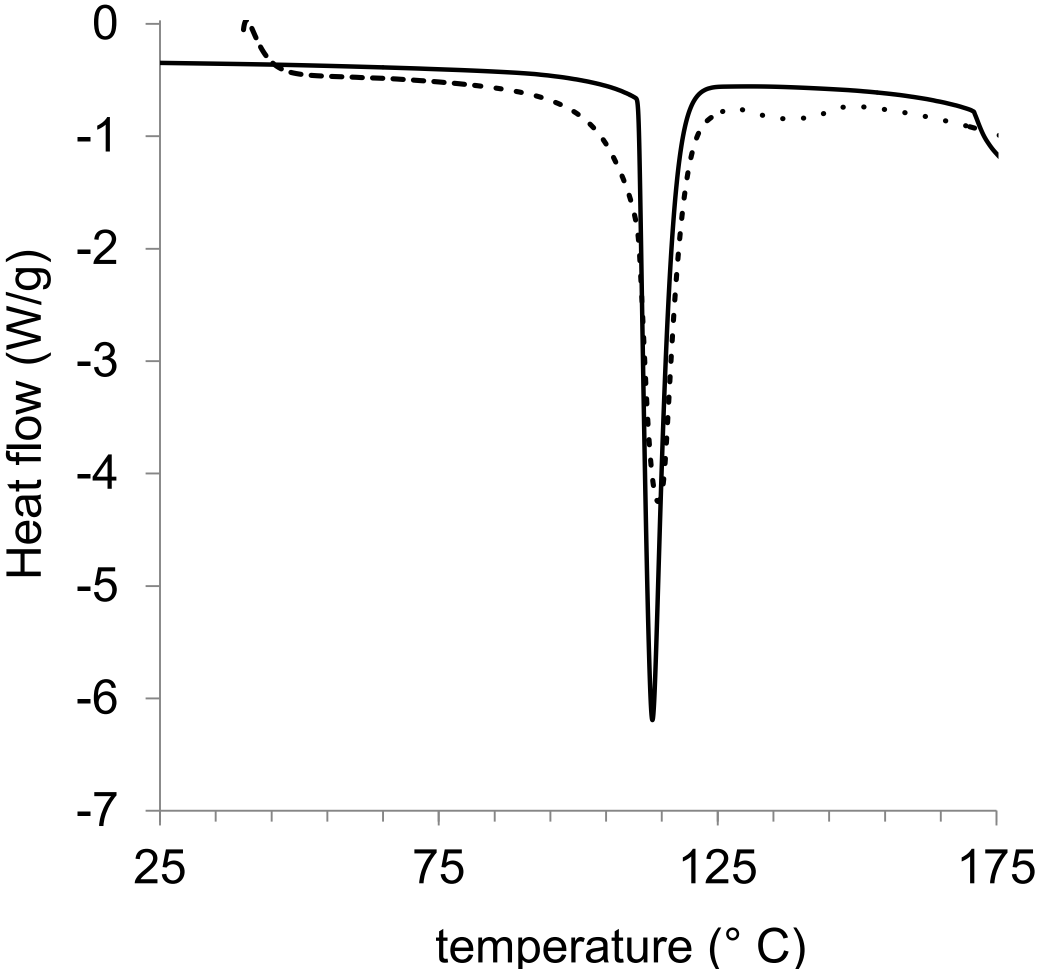
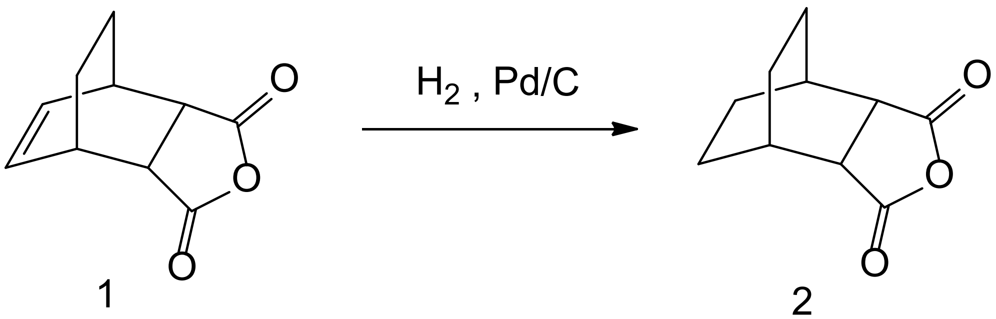


Figure S10. Differential scanning calorimetry (DSC) data (20 °C/min) for the product (solid line, **2**) resulting from the hydrogenation of the Diels Alder adduct (dashed line, **1**) in ethyl acetate using Pd/C and hydrogen (20 psi). The reaction was conducted at ambient temperature for 1 day before filtering the Pd/C and recovering the product in 95% yield.



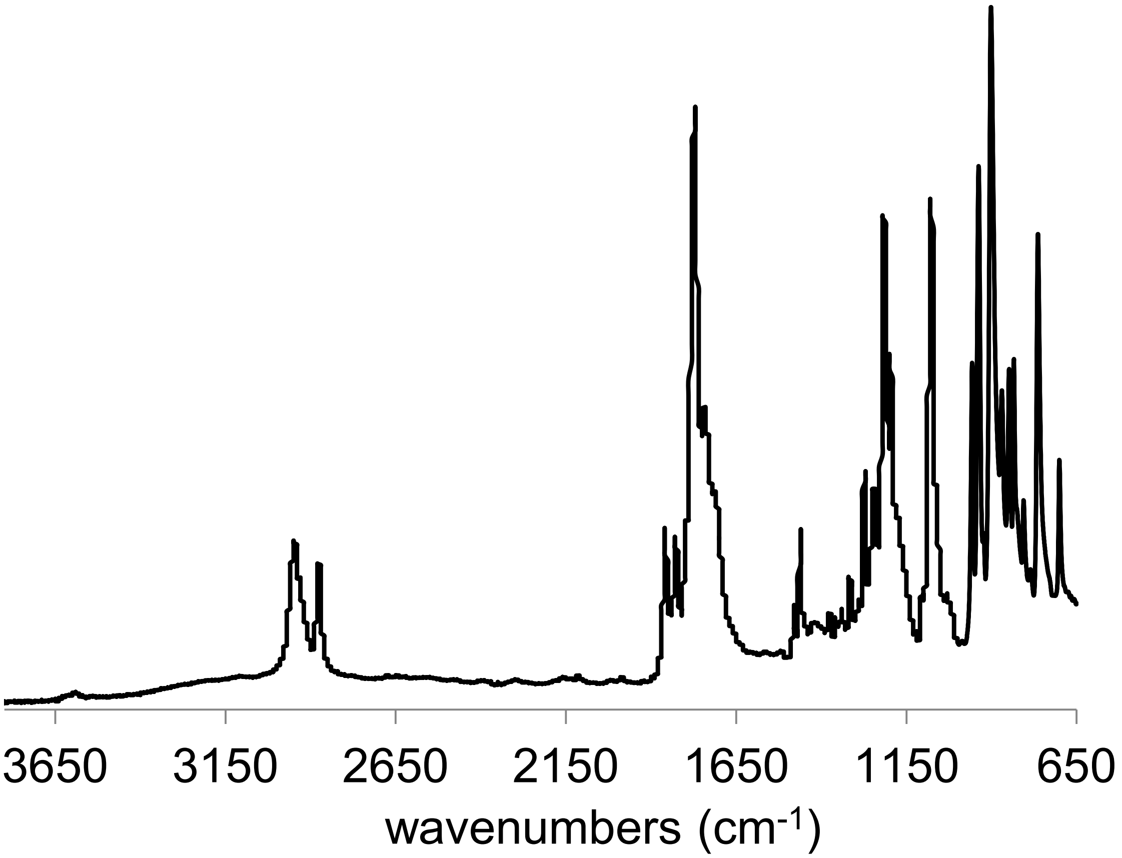
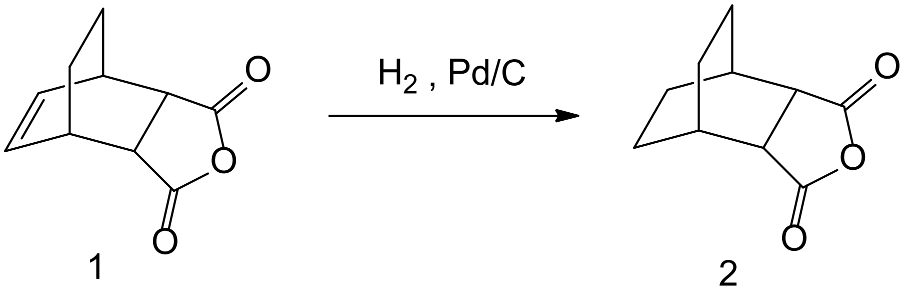
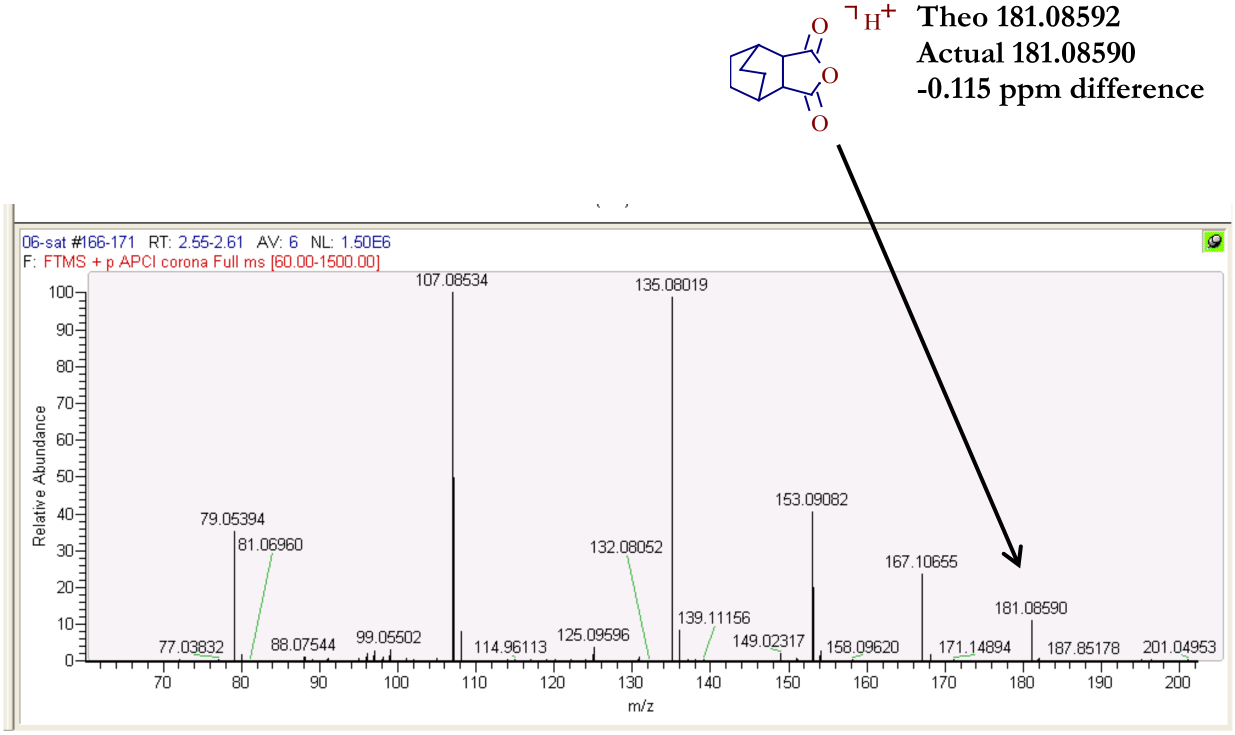


Figure S11. FTIR data for the product (**2**) resulting from the hydrogenation of the Diels Alder adduct (**1**) in ethyl acetate using Pd/C and hydrogen (20 psi). The reaction was conducted at ambient temperature for 2 days before filtering the Pd/C and recovering the product in 95% yield.





Theo 181.08592
Actual 181.08590
-0.115 ppm difference

Figure S12. LC/MS data for the product resulting from the hydrogenation of the Diels Alder adduct in ethyl acetate using Pd/C and hydrogen (20 psi).

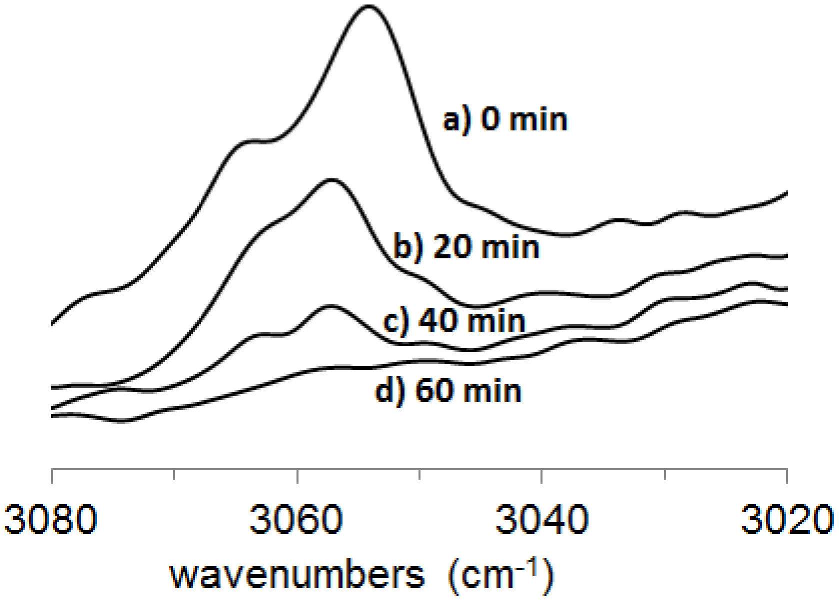


Figure S13. Overlay of FTIR spectra showing the disappearance of the alkene C-H absorbance (3055 cm^{-1}) at different time intervals during the hydrogenation of Diels Alder product (**1**). The data was used in Figure S14b.

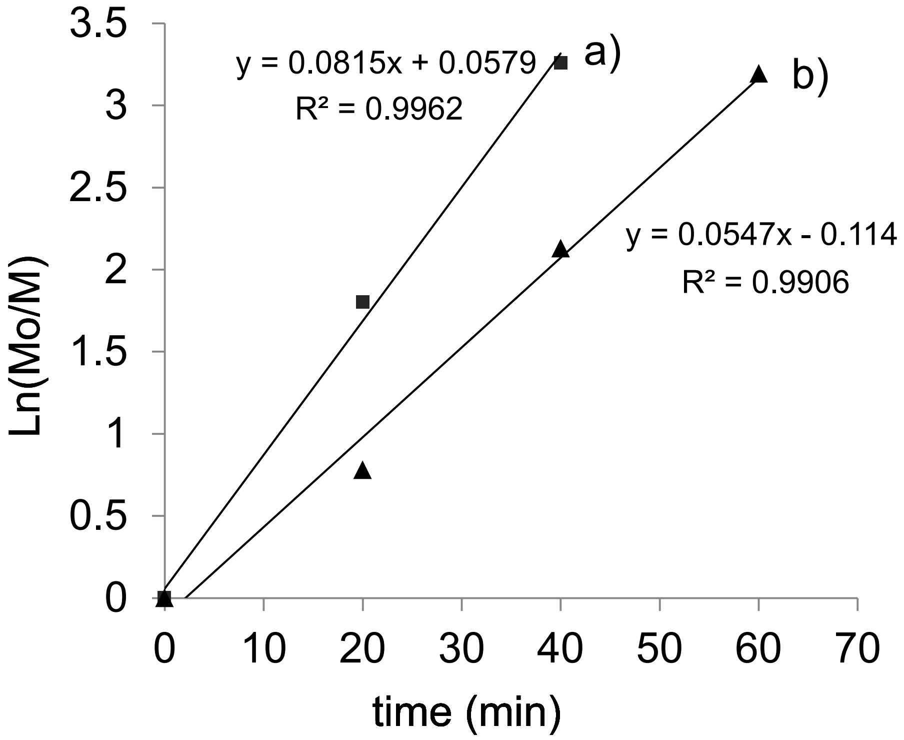


Figure S14. Comparison of continuous flow hydrogenation data for the hydrogenation of a) cyclooctene with b) Diels Alder product (monomer **1**). Both reactions were conducted in ethyl acetate at a concentration of 0.06 g/mL. The comparison of monomer **1** and cyclooctene used a continuous flow setup (1.8 mL/min) at ambient temperature with 0.50 g Pd/C and 125 psi hydrogen. Data for hydrogenation was collected and analyzed with GC (cyclooctene) and FTIR (monomer **1**).

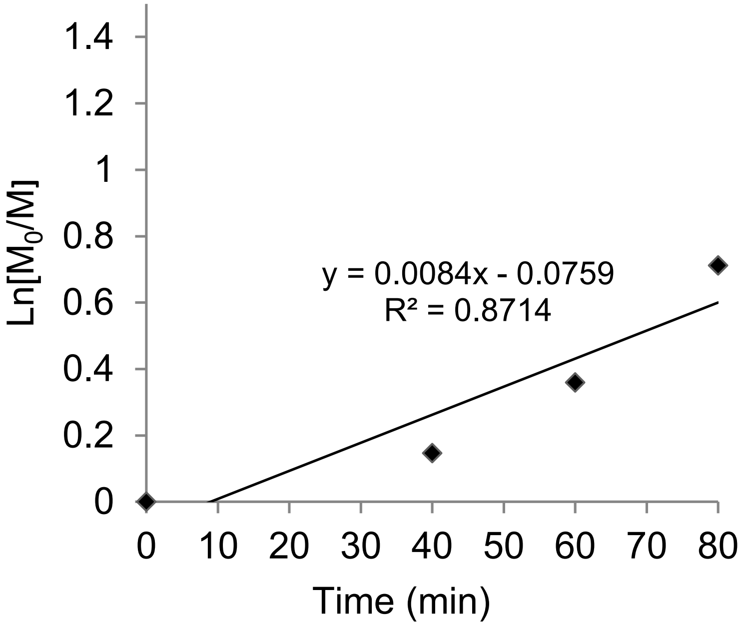


Figure S15. Continuous flow hydrogenation of Diels Alder product (monomer **1**) with less Pd/C than Figure S14. The reaction was conducted in ethyl acetate at a concentration of 0.06 g/mL and flow rate of 1.8 mL/min at ambient temperature with 0.30 g Pd/C and 125 psi hydrogen. The decrease in catalyst loading in Figure S15 gave a slower hydrogenation rate (k_{rel} = 1) compared to Figure S14b (k_{rel} = 6.5).

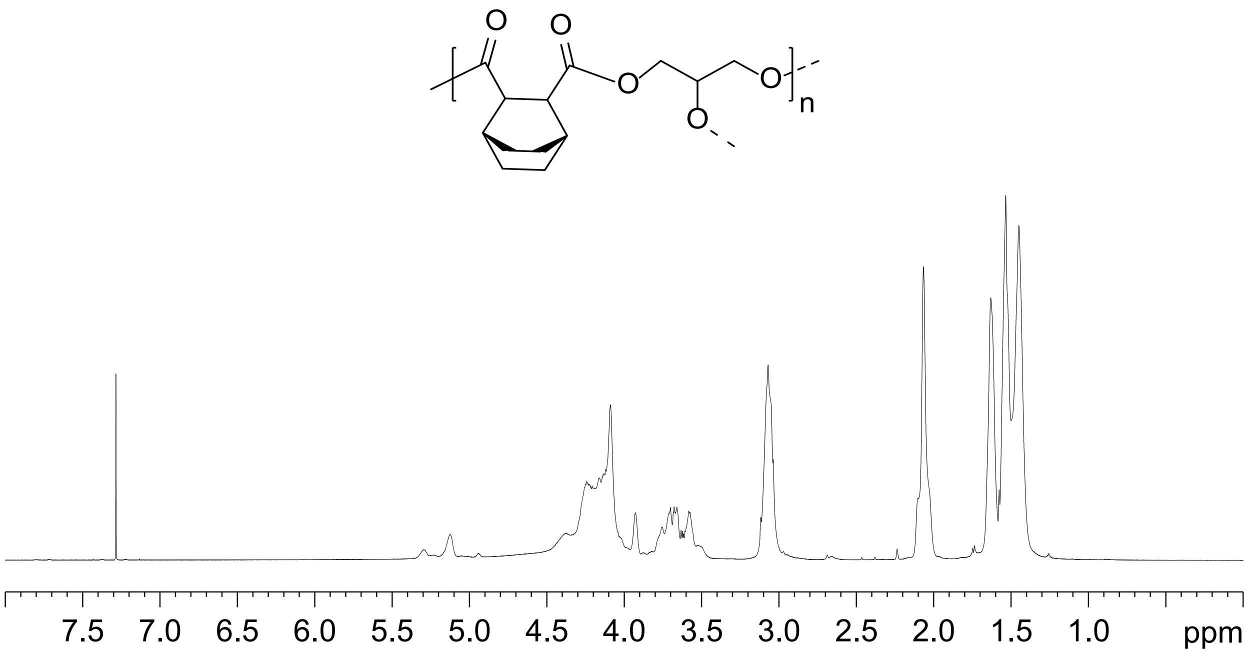


Figure S16. ^{1}H NMR spectrum (700 MHz, $CDCl_3$) of polyester synthesized from bicyclic anhydride **2** and glycerol after 24 h at 120 °C under dynamic vacuum (150 mbar).

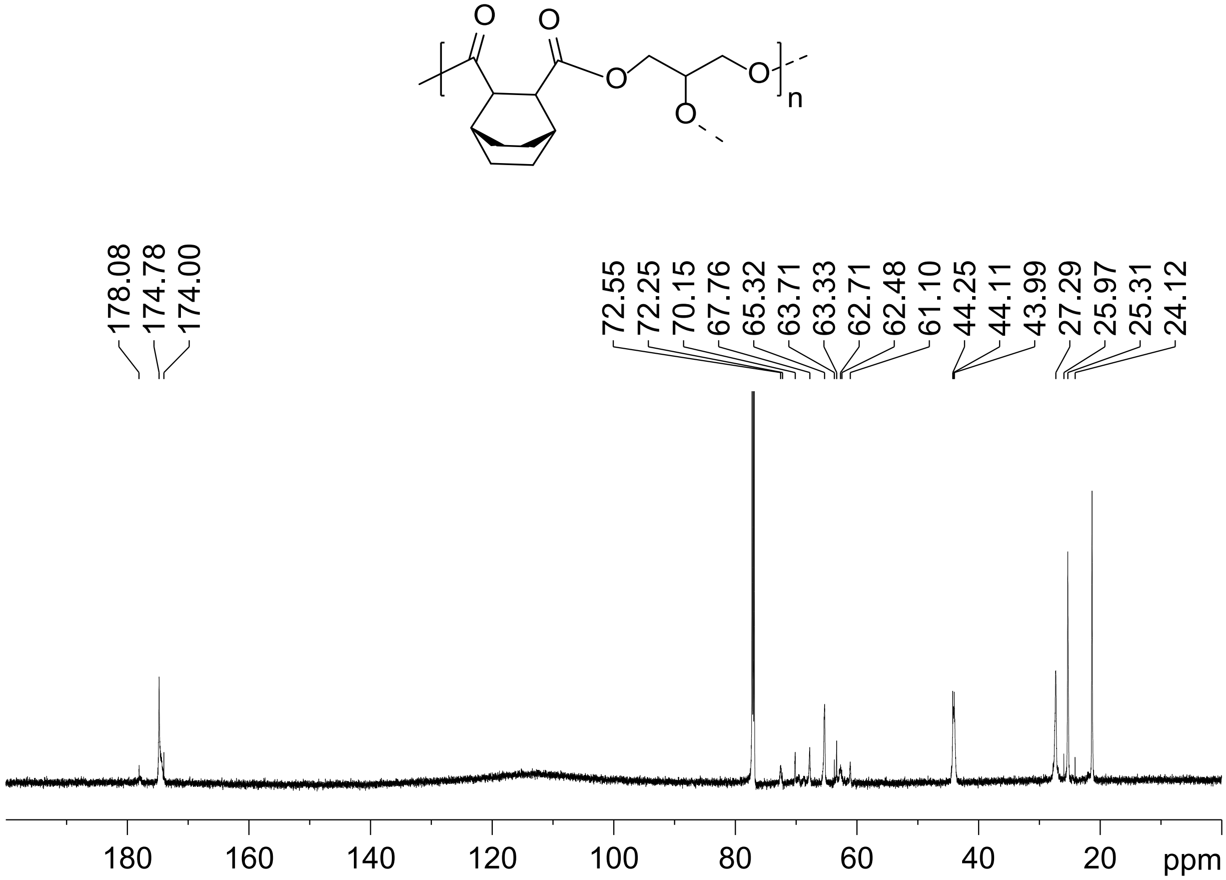


Figure S17. ^{13}C NMR spectrum (700 MHz, $CDCl_3$) of polyester synthesized from bicyclic anhydride **2** and glycerol after 24 h at 120 °C under dynamic vacuum (150 mbar).

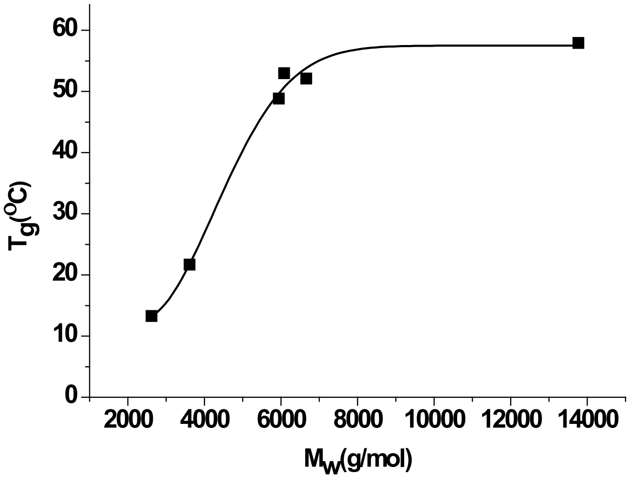


Figure S18. Dependence of glass transition temperature on M_w for the polymerization of glycerol with anhydride **2** ([glycerol]/[anhydride **2**] = 1).

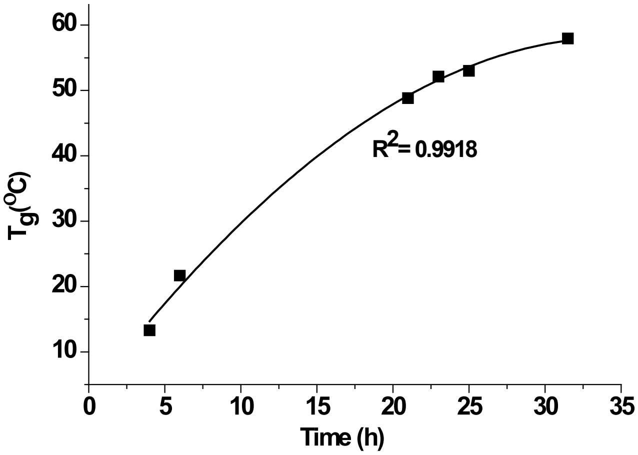


Figure S19. Correlation between the glass transition temperature and the reaction time for the polymerization of glycerol with anhydride **2** ([glycerol]/[anhydride **2**] = 1).