Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Alternating Copolymerization of Dihydrocoumarin and Epoxides Catalyzed by Chromium Salen Complexes: A New Route to Functional Polyesters

Nathan J. Van Zee and Geoffrey W. Coates*
Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University
Ithaca, NY 14853-1301, USA

I. General considerations

All manipulations of air and water sensitive compounds were carried out under dry nitrogen using an MBraun Labmaster glovebox or standard Schlenk line techniques. ^{1}H NMR spectra were recorded on a Varian INOVA 500 (^{1}H, 500 MHz) spectrometer and referenced to the residual non-deuterated $CHCl_3$ signal (7.26 ppm). ^{13}C NMR spectra were recorded on a Varian INOVA (^{13}C, 125 MHz) spectrometer and referenced to chloroform (77.23 ppm).

Gel permeation chromatography (GPC) analyses were carried out using an Agilent Technologies PL-GPC 50 Integrated GPC equipped with a UV detector and a refractive index detector as well as a Polymer Laboratories PL-AS RT GPC autosampler. The GPC used two PL gel Mini-MIX C columns (5 micron, 4.6 mm ID). The GPC columns were eluted with tetrahydrofuran at 30 °C at 0.3 mL/min and were calibrated using monodisperse polystyrene standards.

Differential scanning calorimetry (DSC) measurements of polymer samples were performed on a Mettler-Toledo Polymer DSC instrument equipped with a chiller and an autosampler. Standard DSC experiments were made in aluminum pans using the following heating program: −70 °C to 200 °C at 10 °C/min, 200 to −70 °C at 10 °C/min, and then −70 °C to 200 °C at 10 °C/min. Data was processed using StarE software. All reported glass and melting temperatures were observed on the second heating cycle.

Gas chromatography (GC) was performed on a Hewlett Packard 6890 GC equipped with a Chiraldex α-cyclodextrin trifluoroacetyl column and a flame ionization detector. Helium (Airgas, UHP grade) was used as carrier gas.

II. Materials

Hexane (Macron), methanol (Macron), methylene chloride (Fischer), and diethyl ether (J. T. Baker) were used as received. Dihydrocoumarin (DHC, ≥99%, Sigma-Aldrich) was dried over CaH_2 for three days, vacuum distilled, degassed through three freeze-pump-thaw cycles, and stored in the glovebox until use. All epoxides were obtained from Aldrich; they were all stirred over CaH_2 for three days, either vacuum transferred or vacuum distilled, degassed by three freeze-pump-thaw cycles, and stored in the glovebox prior to use. Bis(triphenylphosphine)iminium chloride (PPNCl, 97%, Aldrich) was recrystallized by layering a saturated methylene chloride solution with diethyl ether. The resulting crystals were crushed and then dried overnight at 60 °C under vacuum prior to use. (*R*,*R*)-(salcy)CrCl (**4**) (Strem) was used as received. (BDI)Zn(OAc) (**1**),[1] (TPP)AlCl (**2**),[2] (*R*,*R*)-(salcy)CoCl (**3**),[3] (salph)CoCl (**5**),[3] and (salph)CrCl (**6**)[4] were prepared according to literature procedures.

III. Representative Copolymerization Procedure

In a glovebox, catalyst (8.0 μmol, 1 equiv.) and PPNCl (8.0 μmol, 1 equiv.) were placed in a flame dried 4-mL vial equipped with a stir bar. DHC (2.0 mmol, 250 equiv.) was then added to the vial, followed by epoxide (4.0 mmol, 500 equiv.). The vial was sealed with a Teflon-lined cap, removed from the glovebox, and placed in an aluminum heating block preheated to 80 °C. After the appropriate amount of time, the vial was removed from the heating block and diluted with a small amount of $CDCl_3$. An aliquot was taken for ^1H NMR analysis to determine conversion of DHC. The reaction mixture was then diluted with dichloromethane and precipitated into a vial of hexanes with stirring. The hexane was decanted off, and the polymer was dried under vacuum with gentle heating.

IV. Regiochemistry of DHC-Based Polyesters

Nucleophilic attack of the propagating polymer phenoxide at the methylene of PO results in the 1,2-insertion of PO into the polymer chain (Figure S1, top). Conversely, the ring-opening at the methine of PO results in the 2,1-insertion of PO into the polymer chain (Figure S1, bottom). The ^1H NMR spectrum of isolated poly(propylene dihydrocoumarate) appeared to have a major set and two minor sets of signals. One of the minor sets of signals was very low in intensity; we propose that this set is due to polymer end groups. The two other sets could be most clearly seen in the methine and methylene region of the polymer (Figure S2). We tentatively assigned the major set to 1,2-insertion and the other minor set to 2,1 insertion. We chose to compare the integrations of the methine signals because they were the best resolved. The ratio of the integration of the methine signals corresponded to 93% regioselectivity for 1,2-insertion of PO. The ratio of the methylene signals corresponds to a 91% regioselectivity for 1,2-insertion; we suspect that this discrepancy is due to end group signals that overlap with the 2,1-insertion methylene signals. Furthermore, on the basis of our analysis of the hydrolyzed polymer (*vida infra*), the methine signals in the ^{1}H NMR spectrum of the polymer appear to be a good indicator of polymer regiochemistry.

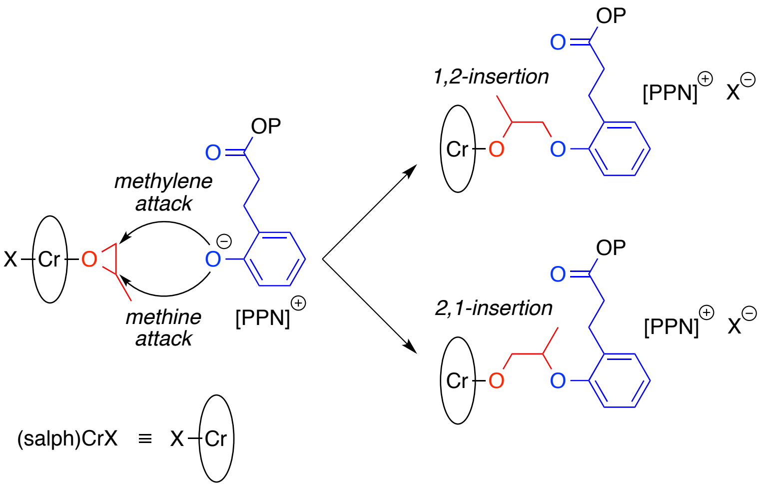


Figure S1. 1,2- and 2,1-insertion of PO when copolymerized with DHC using (salph)CrCl and PPNCl (OP = propagating polymer chain, X = chloride or propagating polymer chain).

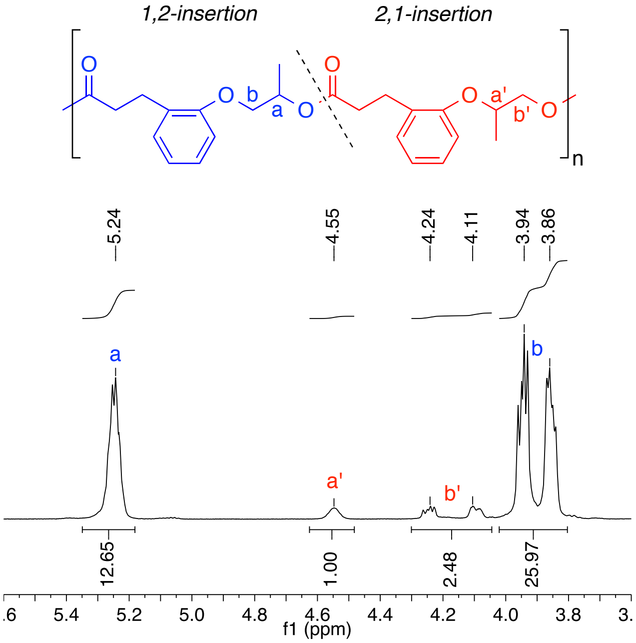


Figure S2. Methine and methylene region of the ^{1}H NMR spectrum of poly(propylene dihydrocoumarate) (93% 1,2 insertion).

To confirm that the minor set of signals was due to 2,1-insertion of PO, the polymer was hydrolyzed using the following procedure: 142 mg of poly(propylene dihydrocoumarate) were placed in a 20-mL scintillation vial with 10 mL MeOH, 0.6 g NaOH, and a stirbar. The vial was sealed with a Teflon-lined cap and placed in an aluminum heat block preheated to 60 °C. After stirring for 12 h, the homogenous mixture was neutralized with 7.7 mL 2M HCl and evaporated to dryness on a rotovap. The solids were extracted with 3 x 10 mL diethyl ether. The combined ether extracts were then dried with anhydrous $MgSO_4$, filtered, and evaporated to dryness to give 0.15 g of a brown oil that solidified upon standing.

The ^{1}H NMR spectrum of the crude mixture was acquired using the following parameters: scans = 32, relaxation delay = 90 s, pulse angle = 90°. The ^{1}H NMR spectrum is consistent with a mixture of two regioisomers (Figure S3; note that there is an unknown impurity at 3.66 ppm). While neither regioisomer is reported in the literature, their ^{1}H NMR spectra are consistent with the ^{1}H NMR spectra of similar molecules.[5,6] The major regioisomer is derived from the 1,2 insertion of PO, while the minor one is derived from the 2,1 insertion of PO. While most of the corresponding signals between the regioisomers overlap, the signals from the methine protons are well resolved. Integrating these gives 93% selectivity for the 1,2-insertion of PO. This procedure was also performed on a sample of poly(propylene dihydrcoumarate) made with (*S*)-PO; the ^{1}H NMR spectrum of the degradation products was consistent with 93% 1,2-insertion of PO.

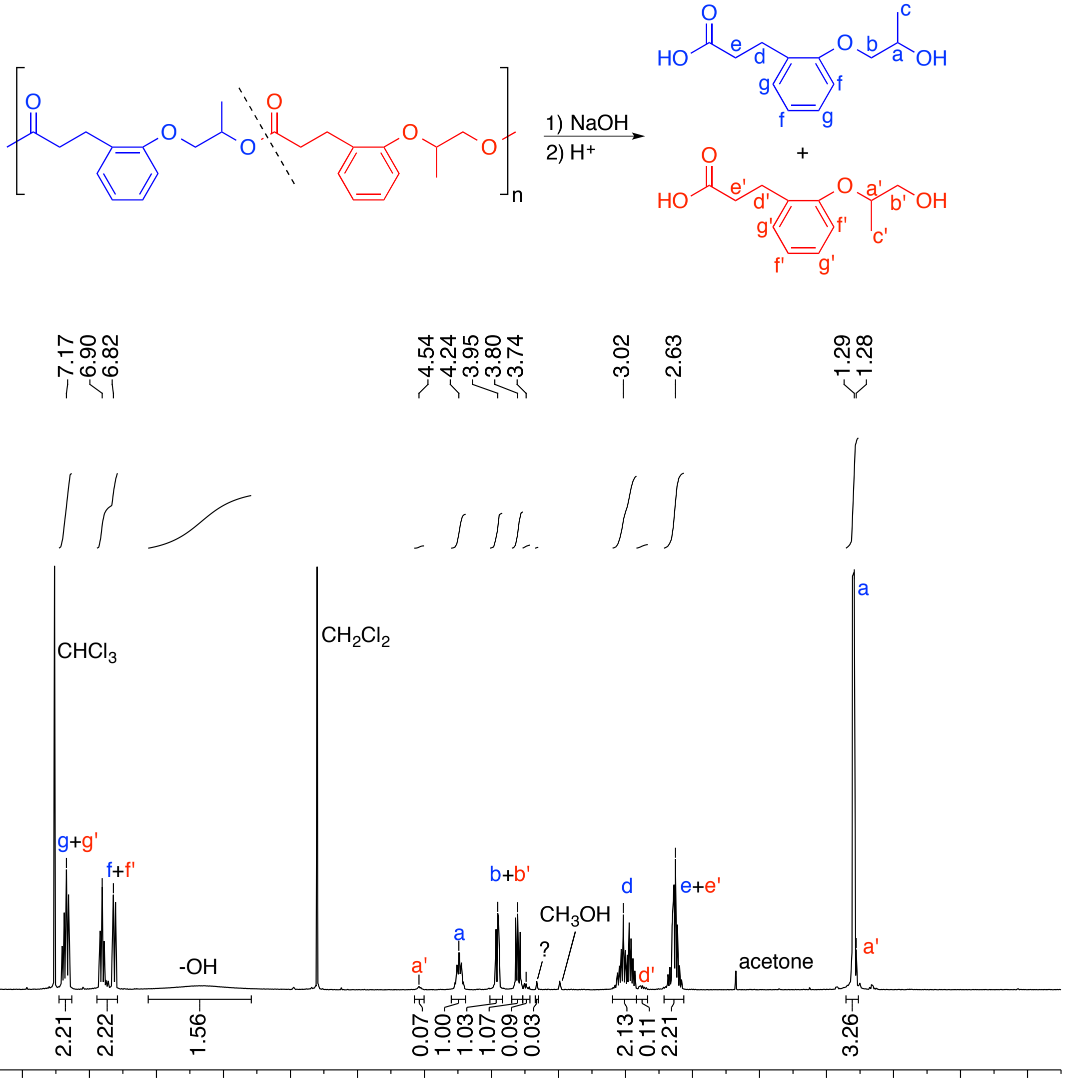


Figure S3. Crude ^{1}H NMR spectrum of the regioisomers obtained by hydrolysis of poly(propylene dihydrocoumarate).

The regioselectivity for other polymers derived from terminal epoxides was determined in a similar fashion. Major and minor sets of signals were observed in the ^{1}H

NMR spectra of the purified polymers (Figures S4-S8). The methine signals for the 1,2- and 2,1-insertion units were used in each case to calculate the regioselectivity because they were the best resolved. Based on the above analysis with poly(propylene dihydrocoumarate), we propose that the catalyst prefers 1,2-insertion of other epoxides as well. Assignments were based on literature assignments for similar polyesters.[7]

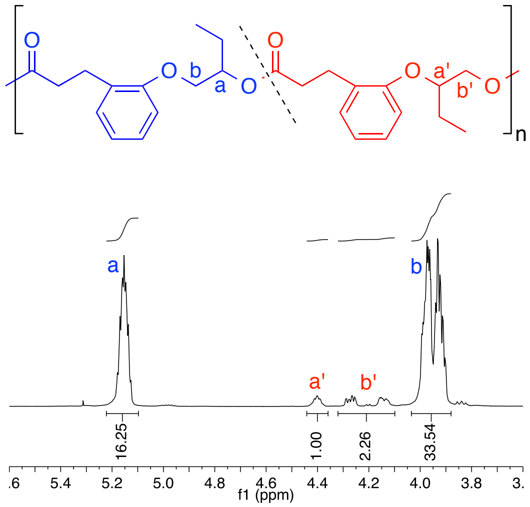


Figure S4. Methine and methylene region of the ^{1}H NMR spectrum of poly(1-butene-*alt*-dihydrocoumarate) (94% 1,2-insertion).

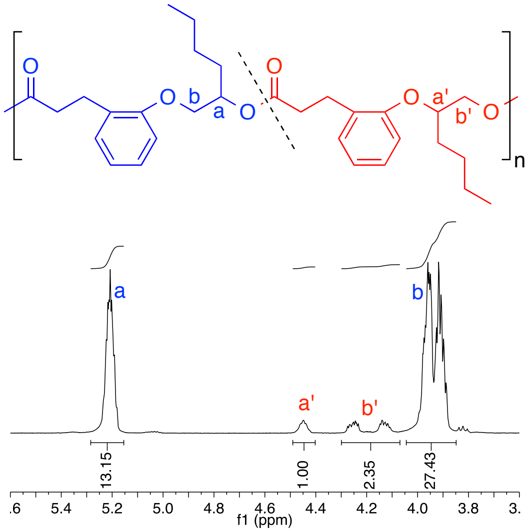


Figure S5. Methine and methylene region of the ^{1}H NMR spectrum of poly(1-hexene-*alt*-dihydrocoumarate) (93% 1,2-insertion).

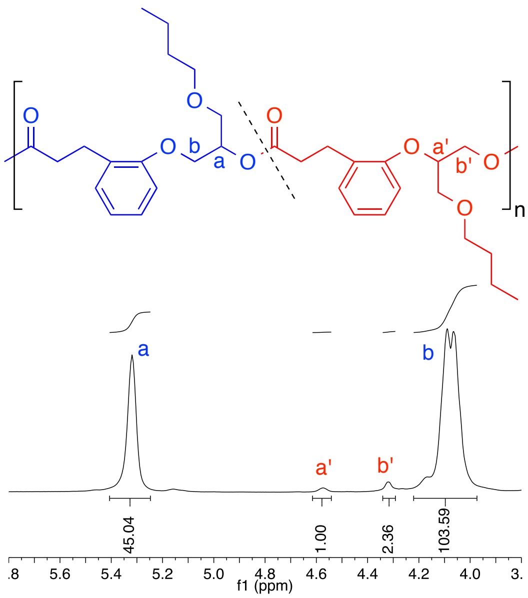


Figure S6. Methine and methylene region of the ^{1}H NMR spectrum of poly(3-*n*-butoxy-1-propene-*alt*-dihydrocoumarate) (98% 1,2-insertion).

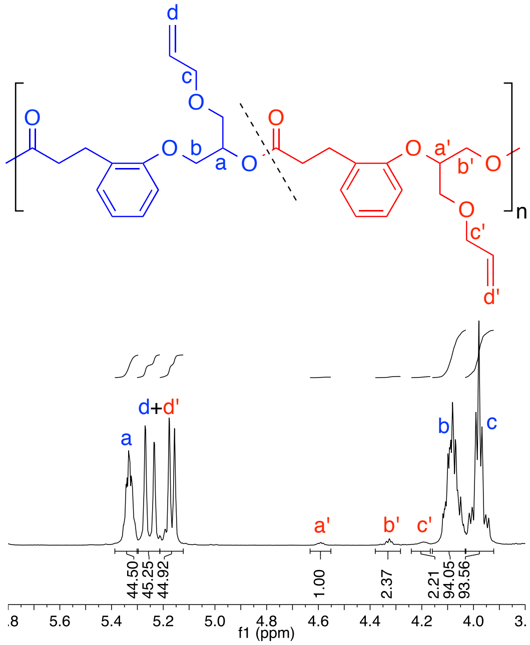


Figure S7. Methine and methylene region of the ^{1}H NMR spectrum of poly(3-allyloxy-1-propene-*alt*-dihydrocoumarate) (98% 1,2-insertion).

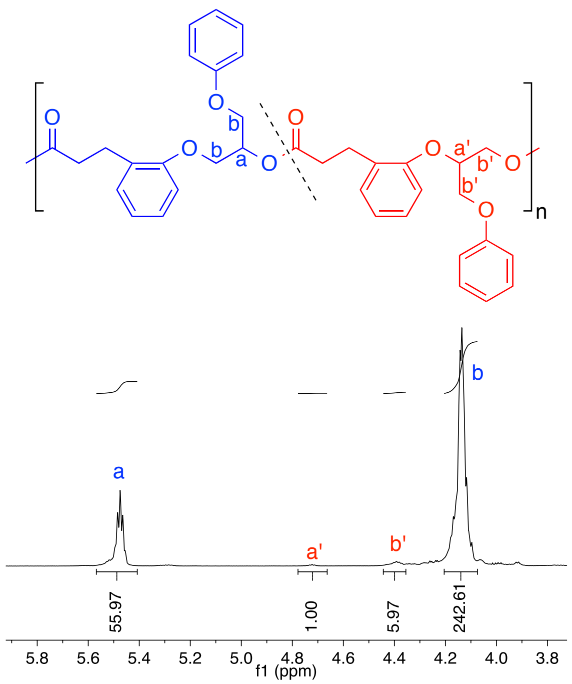


Figure S8. Methine and methylene region of the ^{1}H NMR spectrum of poly(3-phenoxy-1-propene-*alt*-dihydrocoumarate) (98% 1,2-insertion).

V. Kinetic Resolution Experiment with DHC and PO using (*R*,*R*)-(salcy)CrCl and PPNCl

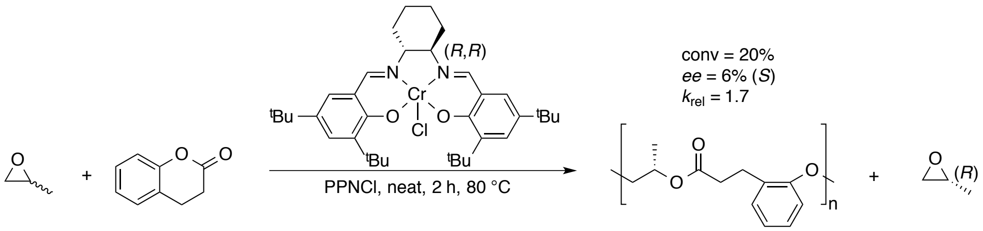


Figure S9. Kinetic resolution of PO with DHC using (*R*,*R*)-(salcy)CrCl and PPNCl.

The copolymerization procedure was modified for this experiment: the ratio of the monomers and catalyst was [PO]:[DHC]:[catalyst]:[PPNCl] = 250:250:1:1 and the scale was increased by a factor of 3.5. After 2 hours, the polymerization was cooled to 0 °C. An aliquot of the reaction mixture was taken for ^{1}H NMR analysis to determine conversion of PO (20%). The unreacted PO was isolated by vacuum transfer and analyzed by chiral GC, giving an ee of 6.0%. Based on the equation $k_{\mathrm{rel}} = \ln[(1-c)(1-ee)]$

/ ln[(1−c)(1+ee)], where c = 0.20 and ee = 0.060, (*R*,*R*)-(salcy)CrCl exhibited a k_{rel} of 1.7, preferentially consuming (*S*)-PO (Figure S9).

VI. Control experiments using (salph)CrCl and PPNCl to copolymerize DHC and PO

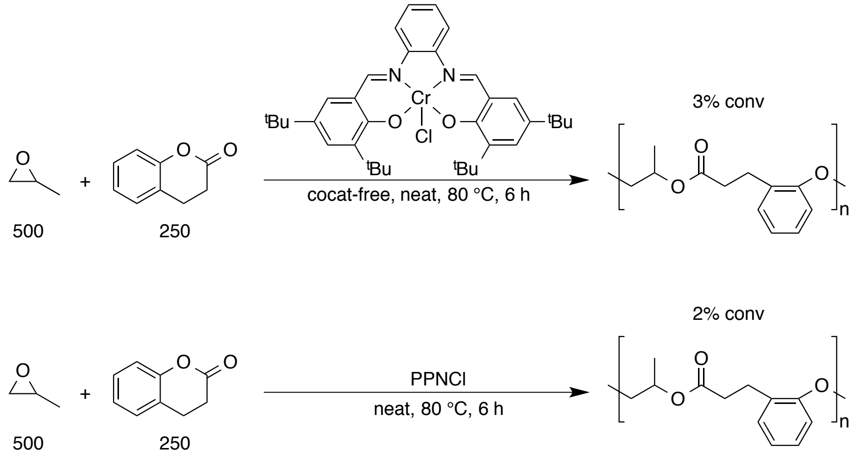


Figure S10. Control experiments where either the (salph)CrCl or PPNCl was left out.

A series of control experiments were performed with the copolymerization of PO and DHC. The standard representative copolymerization was used except that either one of the catalyst components (PPNCl or (salph)CrCl) or one of the monomers (PO or DHC) was left out. The polymerization reached very low conversion of dihydrocoumarin by ^{1}H NMR spectroscopy (<5%) when only (salph)CrCl or only PPNCl was used as a catalyst (Figure S10).

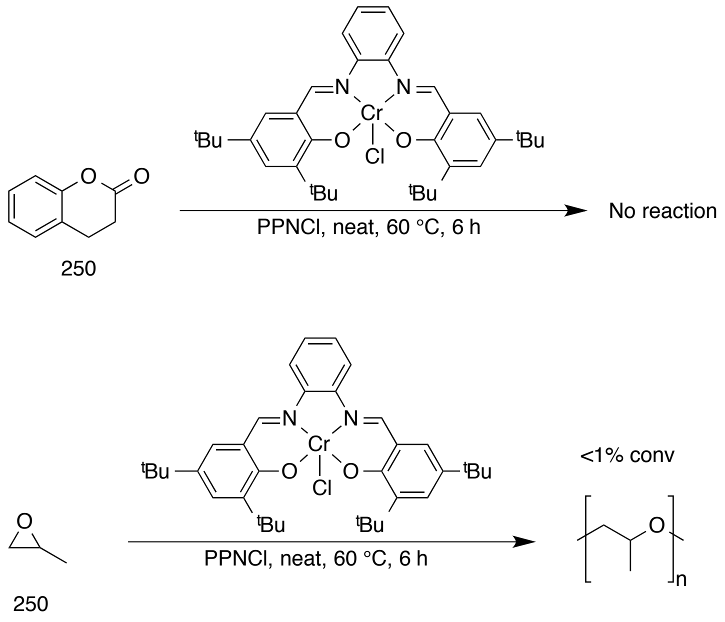


Figure S11. Control experiments where either DHC or PO was reacted with (salph)CrCl and PPNCl.

Homopolymerization of DHC was unsuccessful. Homopolymerization of PO (using 250 eq. instead of 500 eq. as in the representative copolymerization procedure) resulted in only a trace amount of poly(propylene oxide) by ^{1}H NMR spectroscopy (Figure S11).

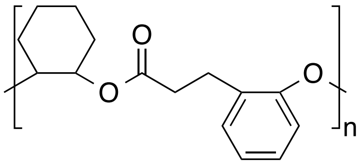
VII. Differential Scanning Calorimetry Experiments with Poly(cyclohexene coumarate) and Poly(cyclopentene coumarate)

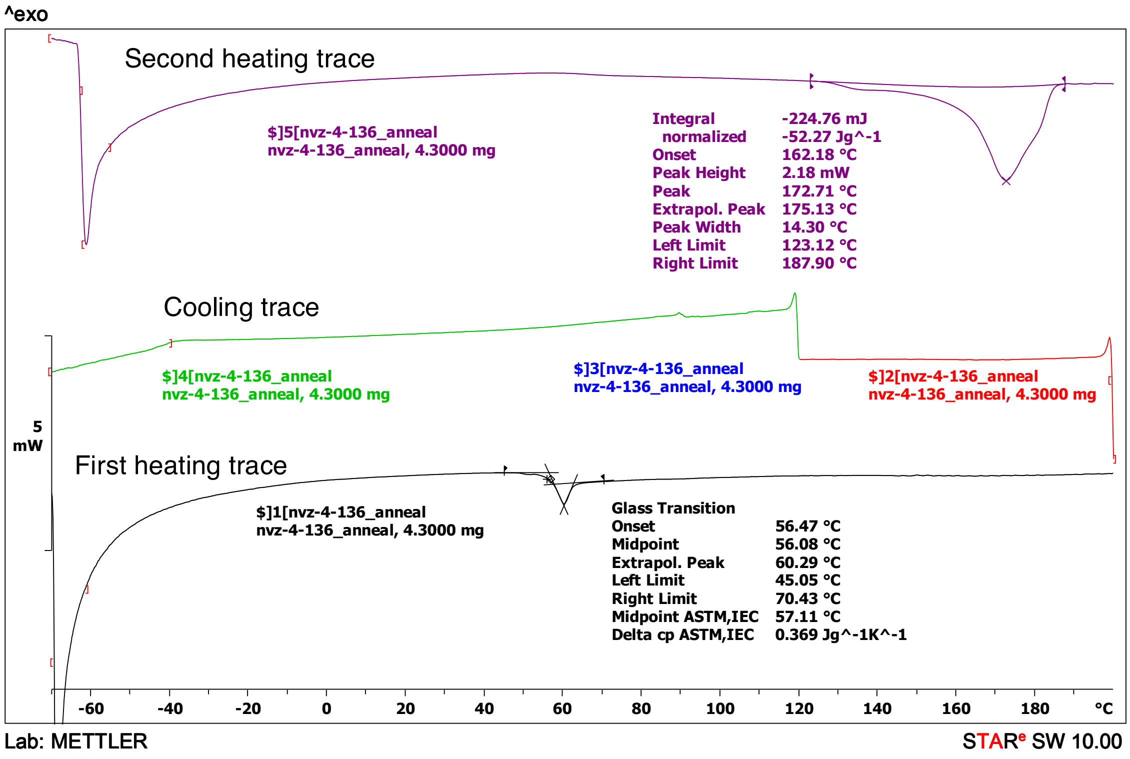
Both the poly(cyclohexene coumarate) and poly(cyclopentene coumarate) samples were melted in a previous DSC experiment prior to performing the annealing experiment. ^{1}H NMR analysis of the melted polymers revealed that they had not degraded after performing these DSC experiments.

For annealing poly(cyclohexene coumarate), the following heating program was used: −70 °C to 200 °C at 10 °C/min, 200 to 120 °C at 10 °C/min, hold 120 °C for 4 h, 120 °C to −70 °C at 10 °C/min, then finally −70 °C to 200 °C at 10 °C/min.

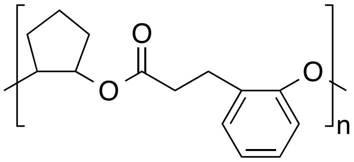
For annealing poly(cyclopentene coumarate), the following heating program was used: −70 °C to 200 °C at 10 °C/min, 200 to 90 °C at 10 °C/min, hold 90 °C for 4 h, 120 °C to −70 °C at 10 °C/min, then finally −70 °C to 200 °C at 10 °C/min.

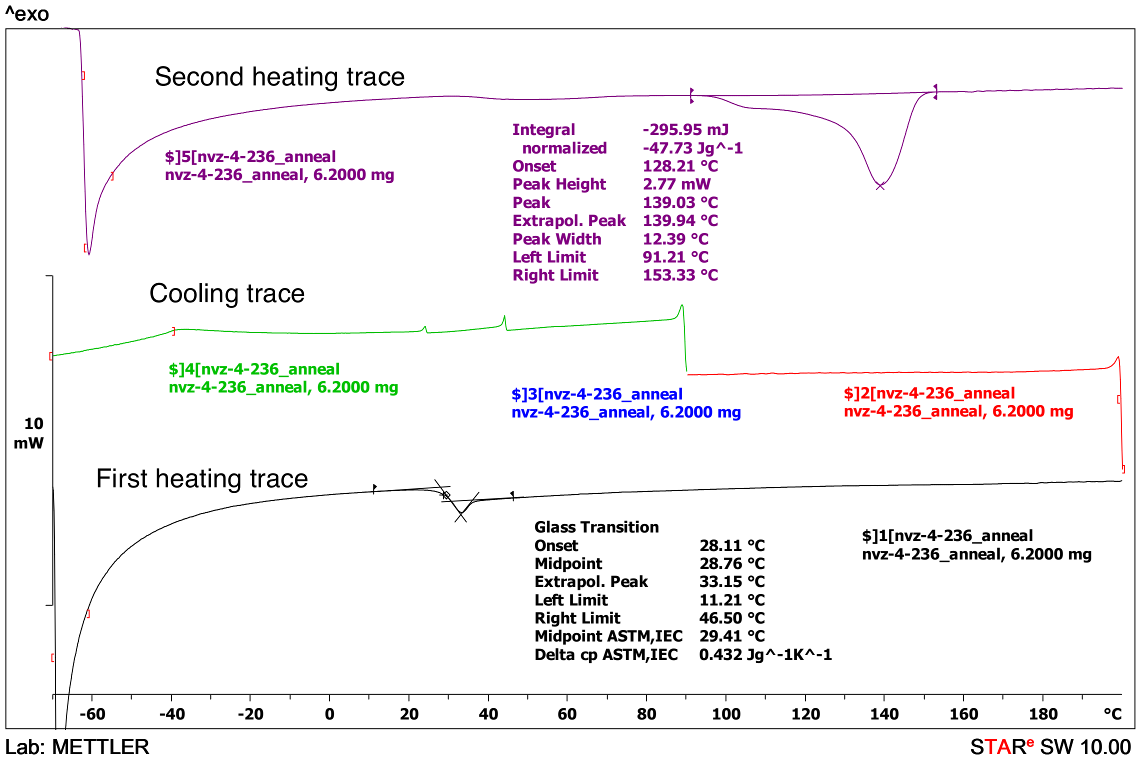
Poly(cyclohexene coumarate) (Table 2, entry 8)





Poly(cyclopentene coumarate) (Table 2, entry 7)

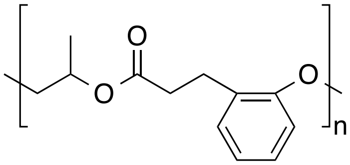




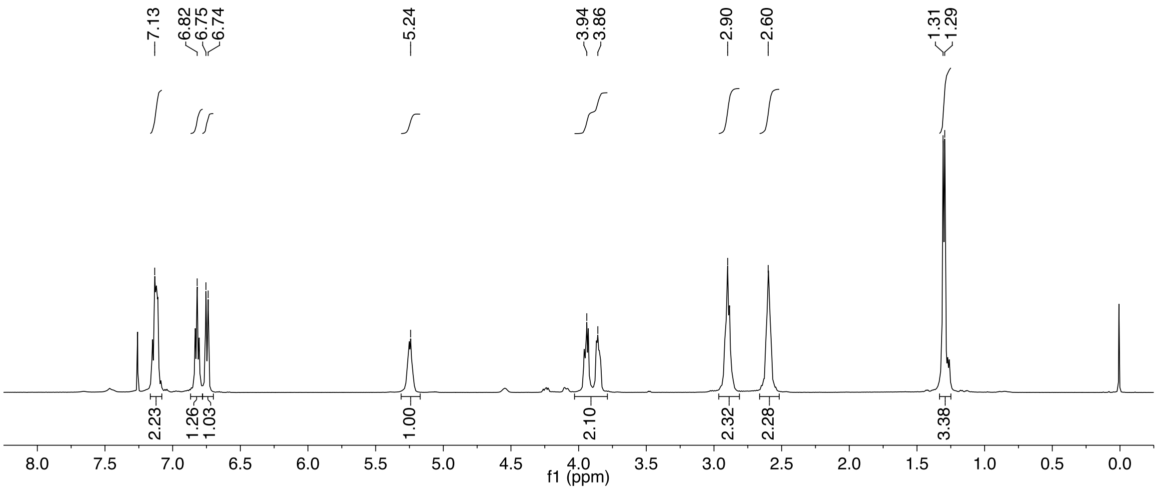
VIII. ^{1}H and ^{13}C NMR Spectra of Dihydrocoumarin/Epoxide Copolymers

All polymerizations were performed using the representative copolymerization procedure detailed above. The samples were prepared for NMR analysis by dissolving approximately 50 mg of polymer in 0.7 mL $CDCl_3$ and filtering the solutions through a plug of glass wool into an NMR tube. The ^{1}H NMR spectra were acquired using the following parameters: scans = 16, relaxation delay = 2 s, pulse angle = 45°. The ^{13}C NMR spectra were acquired using the following parameters: scans = 512, relaxation delay = 1 s, pulse angle = 45°.

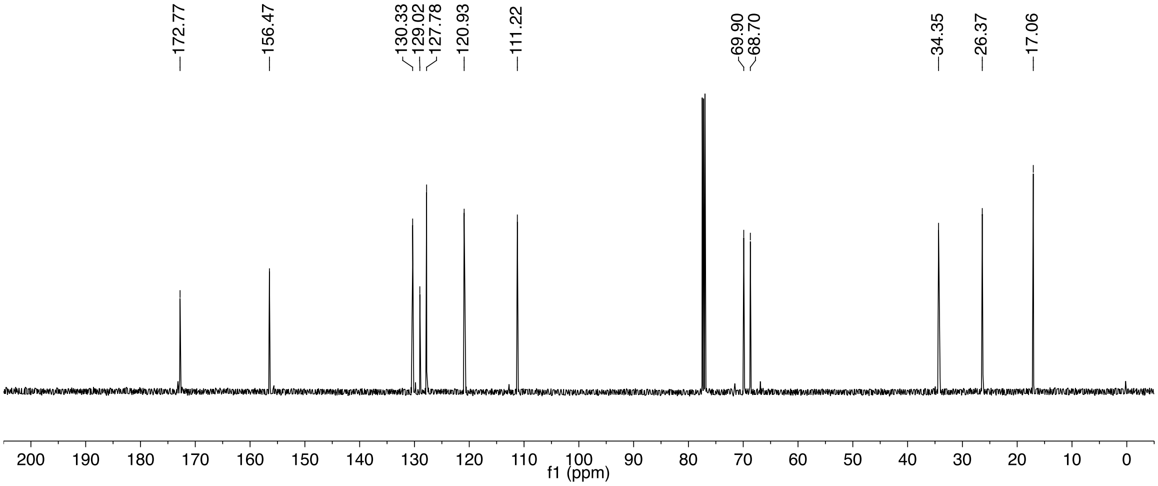
Poly(propylene dihydrocoumarate) (Table 2, entry 1)



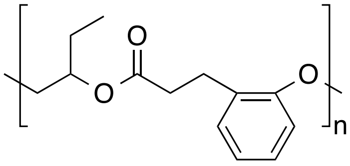
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.08-7.17 (m, 2H); 6.82 (t, *J* = 7.3 Hz, 1H); 7.45 (d, 8.1 Hz); 5.20-5.30 (m, 1H), 3.81-3.99 (m, 2H), 2.85-2.95 (m, 2H), 2.54-2.65 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 3H).



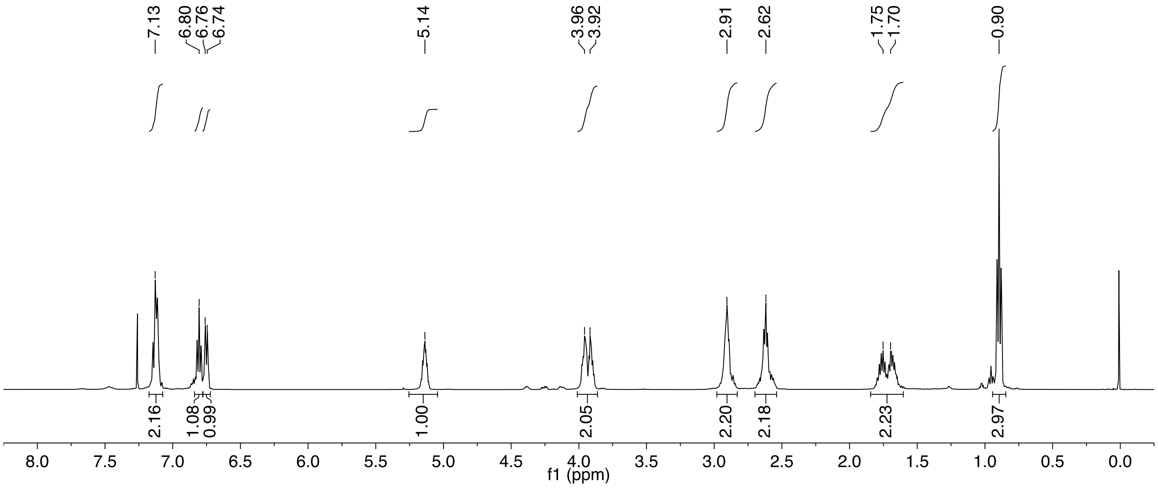
^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.77, 156.47, 130.33, 129.02, 127.78, 120.93, 111.22, 69.90, 68.70, 34.35, 26.37, 17.06.



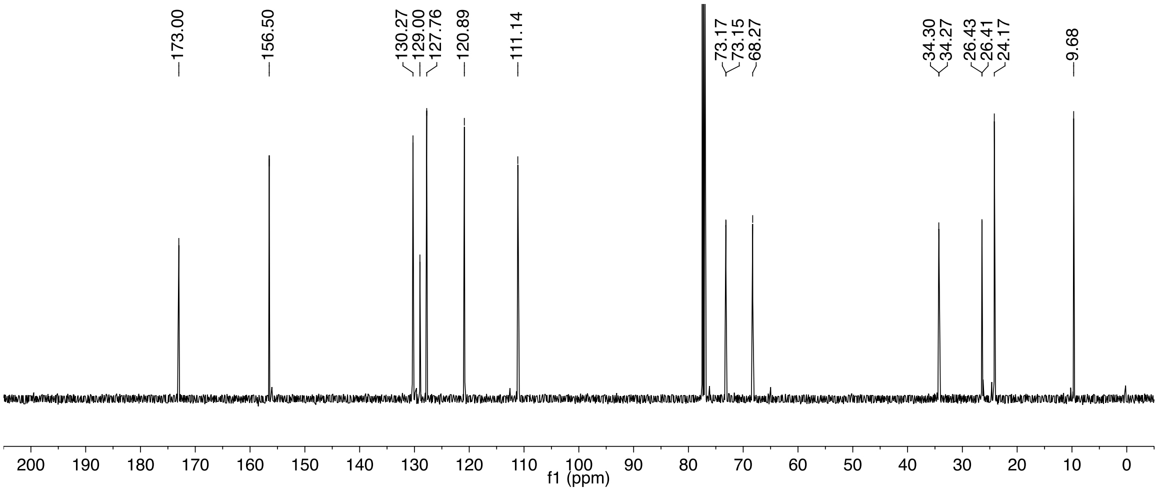
Poly(1-butene-*alt*-dihydrocoumarate) (Table 2, entry 2)



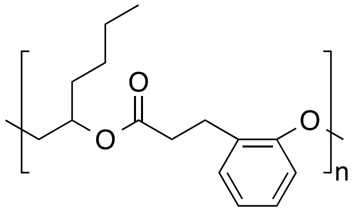
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.08-7.18 (m, 2H), 6.78-6.82 (m, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 5.09-5.17 (m, 1H), 3.87-3.99 (m, 2H), 2.86-2.96 (m, 2H), 2.54-2.69 (m, 2H), 1.62-1.81 (m, 2H), 0.89 (t, *J* = 7.6 Hz, 3H).



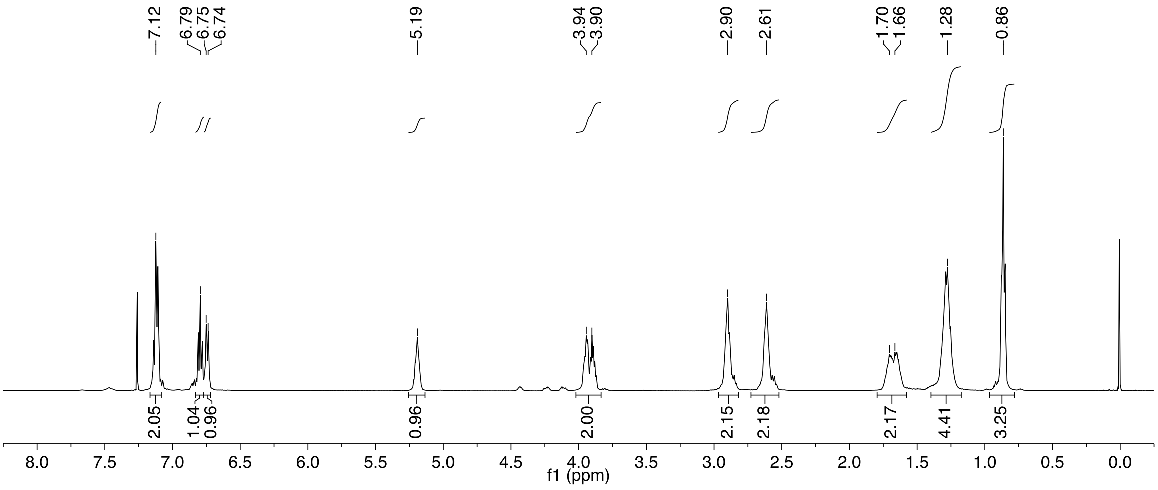
^{13}C NMR (CDCl$_3$, 125 MHz): δ 173.00, 156.50, 130.27, 129.00, 127.76, 120.89, 111.14, 73.16, 68.27, 34.28, 26.42, 24.17, 9.68.



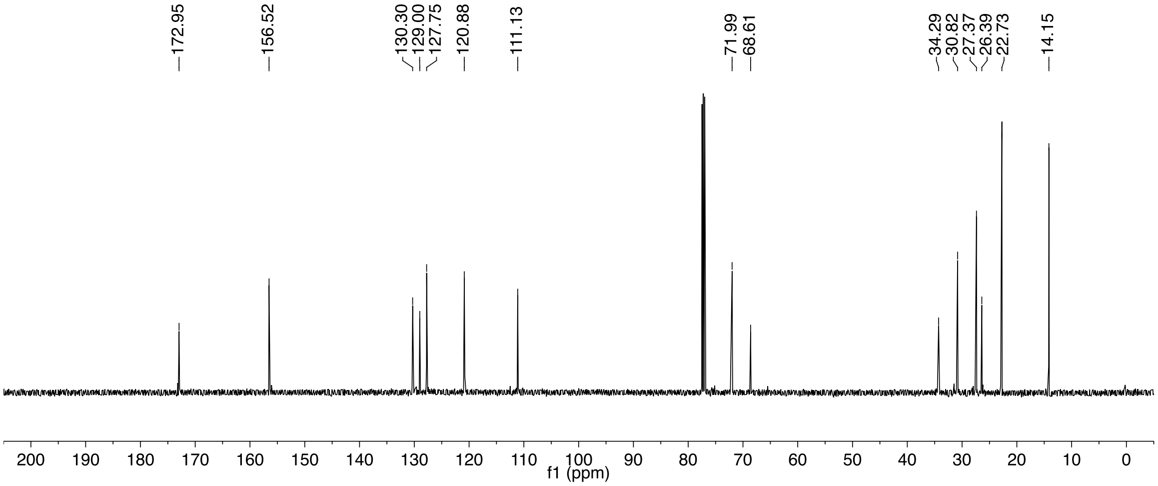
Poly(1-hexene-*alt*-dihydrocoumarate) (Table 2, entry 3)



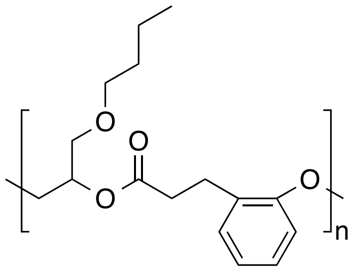
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.09-7.15 (m, 2H), 6.80 (t, *J* = 7.0 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.15-5.24 (m, 1H), 3.85-3.99 (m, 2H), 2.82-2.97 (m, 2H), 2.53-2.67 (m, 2H), 1.60-1.76 (m, 2H), 1.21-1.35 (m, 4H), 0.83-0.90 (m, 3H).



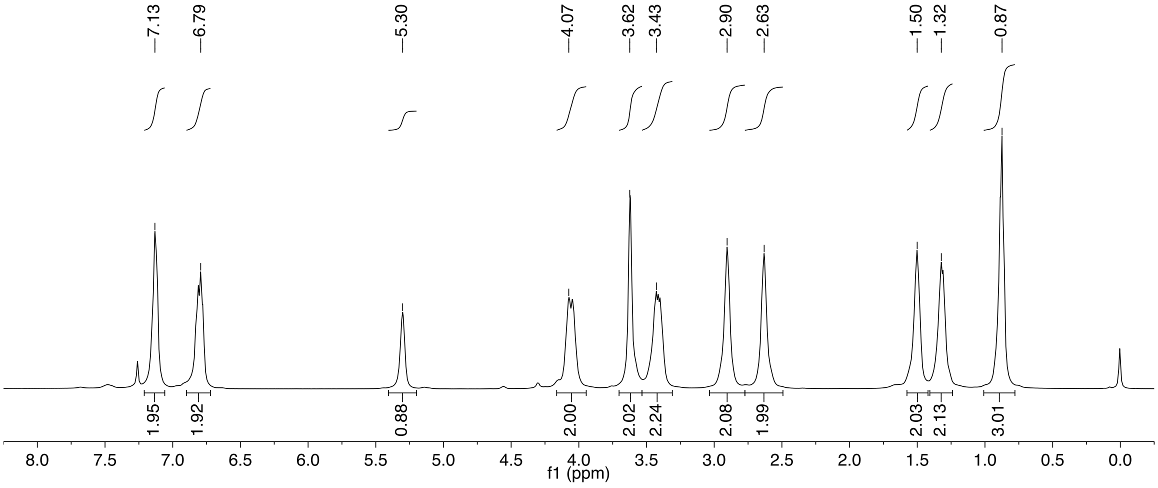
^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.95, 156.52, 130.30, 129.00, 127.75, 120.88, 111.13, 71.89, 68.61, 34.29, 30.82, 27.37, 26.39, 22.73, 14.15.



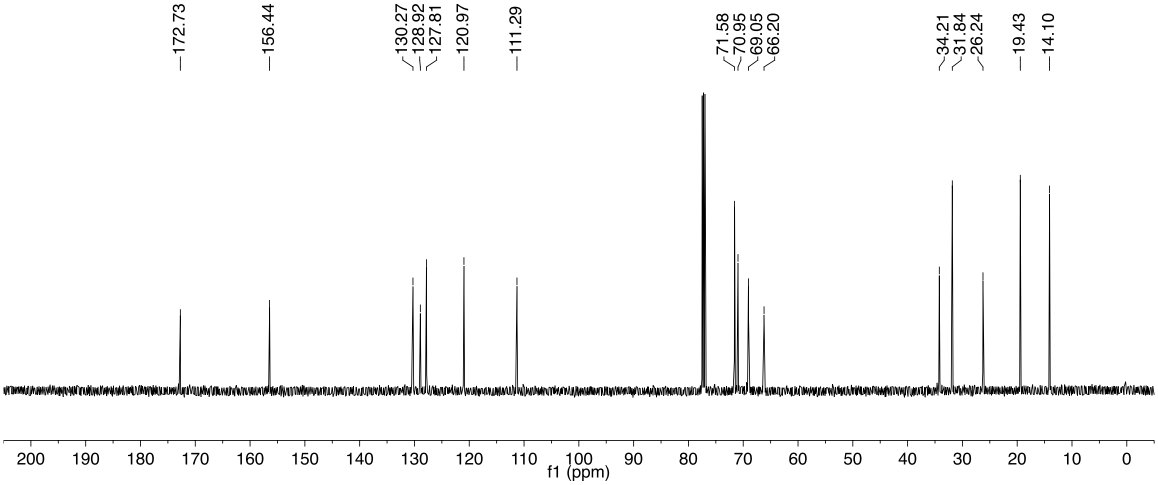
Poly(3-*n*-butoxy-1-propene-*alt*-dihydrocoumarate) (Table 2, entry 4)



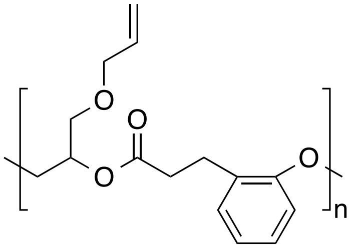
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.07-7.20 (m, 2H), 6.74-6.87 (m, 2H), 5.23-5.36 (m, 2H), 3.97-4.14 (m, 2H), 3.54-3.68 (m, 2H), 3.33-3.52 (m, 2H), 2.82-3.02 (m, 2H), 2.55-2.72 (m, 2H), 1.42-1.59 (m, 2H), 1.24-1.42 (m, 2H), 0.80-0.97 (m, 3H).



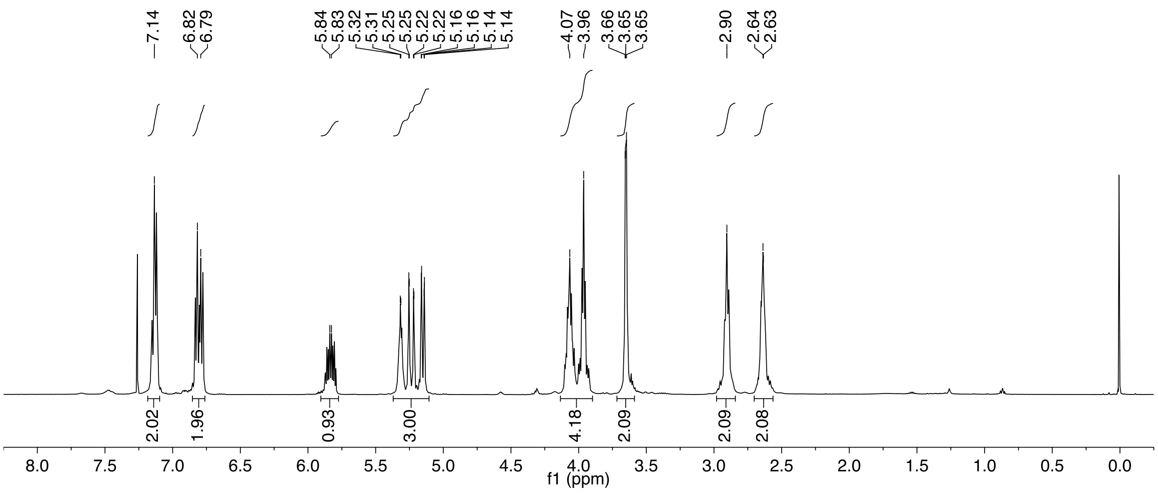
^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.73, 156.44, 130.27, 128.92, 127.81, 120.97, 111.29, 71.58, 70.95, 69.05, 66.20, 34.21, 31.84, 26.24, 19.43, 14.10.



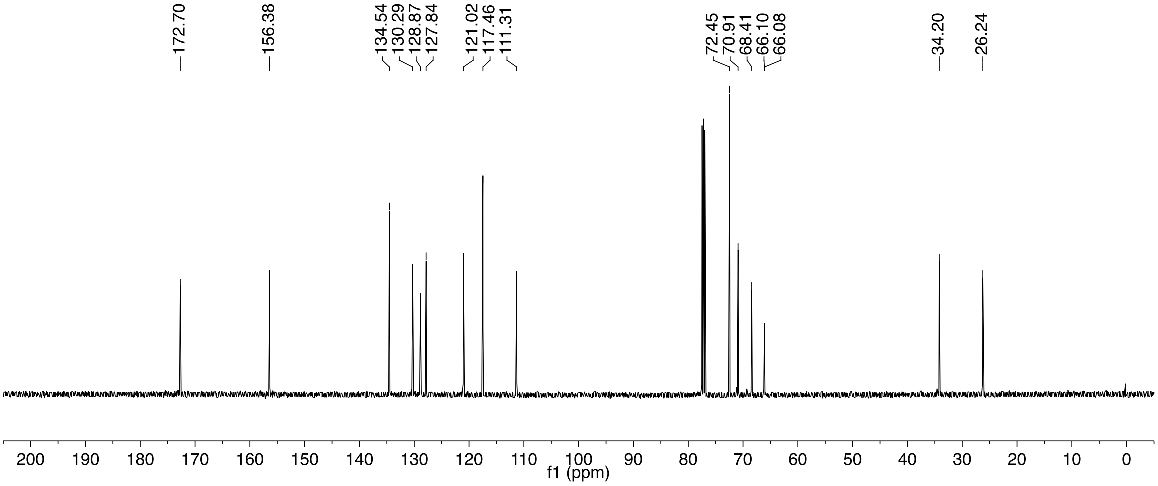
Poly(3-allyloxy-1-propene-*alt*-dihydrocoumarate) (Table 2, entry 5)



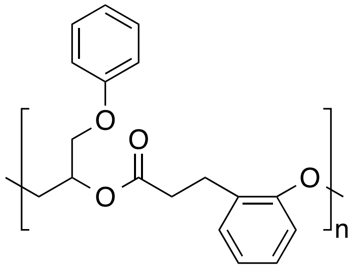
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.10-7.16 (m, 2H), 6.76-6.84 (m, 2H), 5.79-5.88 (m, 1H), 5.29-5.34 (m, 1H), 5.21-5.26 (m, 1H), 5.13-5.17 (m, 1H), 4.01-4.11 (m, 2H), 3.91-4.02 (m, 2H), 3.61-3.69 (m, 2H), 2.85-2.98 (m, 2H), 2.58-2.69 (m, 2H).



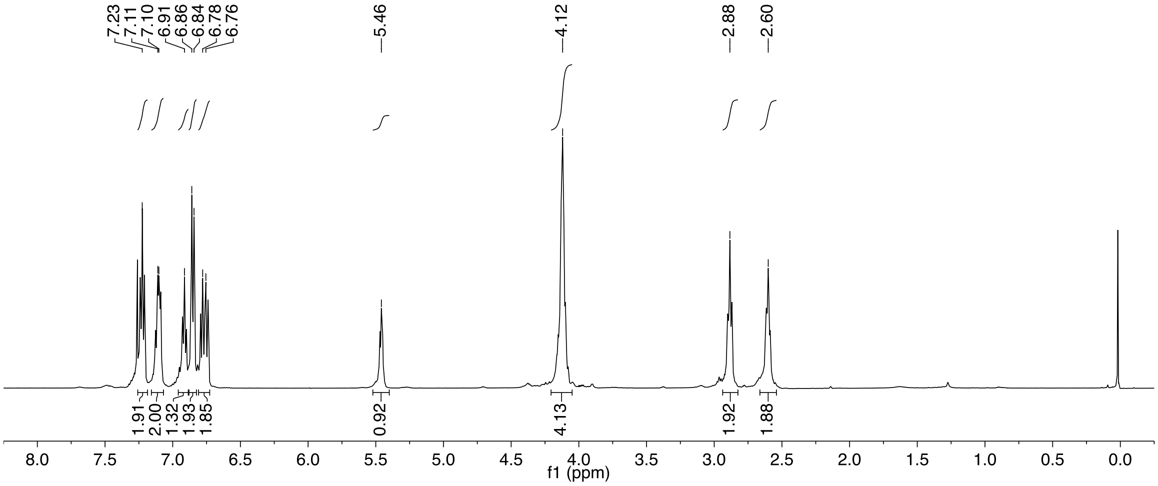
^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.70, 156.38, 134.54, 130.29, 128.87, 127.84, 121.02, 117.46, 111.31, 72.45, 70.91, 68.41, 66.09, 34.20, 26.24.



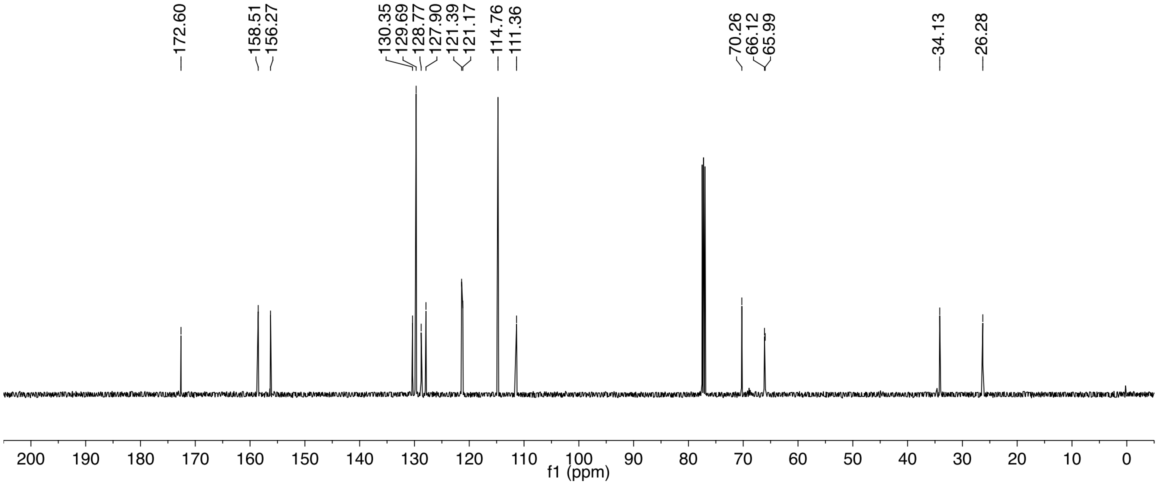
Poly(3-phenoxy-1-propene-*alt*-dihydrocoumarate) (Table 2, entry 6)



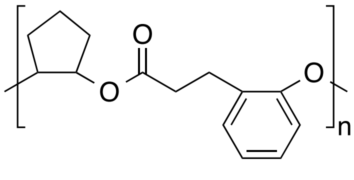
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.20-7.25 (m, 2H), 7.08-7.14 (m, 2H), 6.89-6.94 (m, 2H), 6.83-6.88 (m, 2H), 6.73-6.80 (m, 2H), 5.41-5.50 (m, 1H), 4.07-4.20 (m, 4H), 2.84-2.93 (m, 2H), 2.55-2.66 (m, 2H).



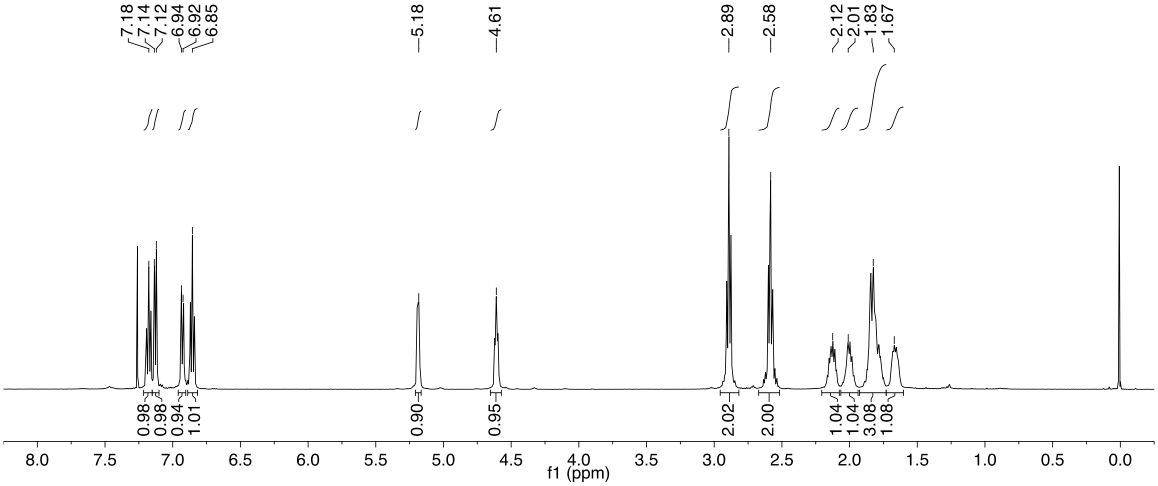
^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.60, 158.51, 156.27, 130.35, 129.69, 128.77, 127.90, 121.39, 121.17, 114.76, 111.36, 70.26, 66.12, 65.99, 34.13, 26.28.



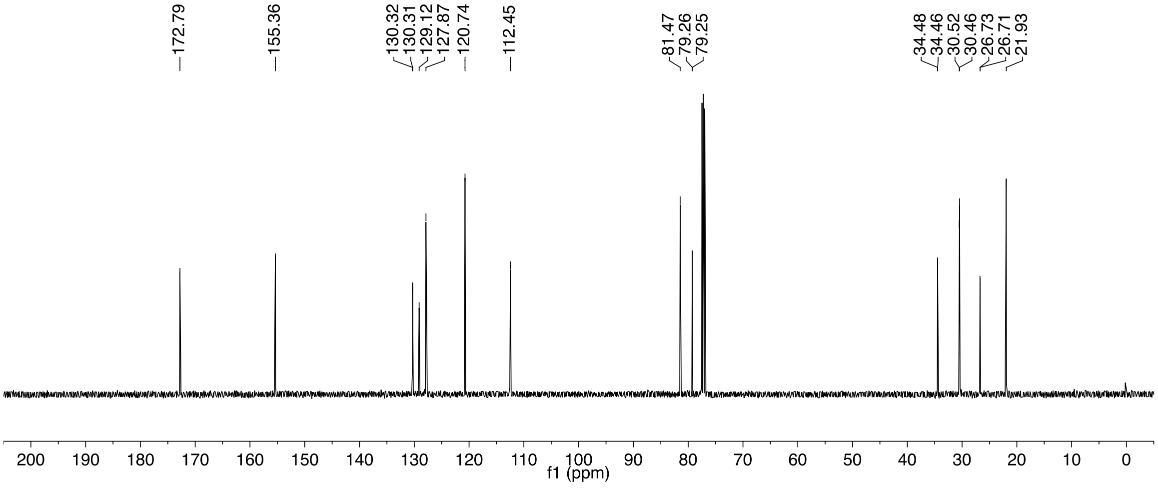
Poly(cyclopentene dihydrocoumarate) (Table 2, entry 7)



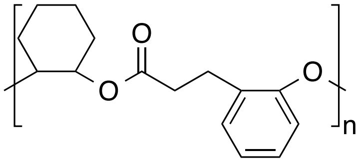
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.15-7.20 (m, 1H), 7.11-7.14 (m, 1H), 6.91-6.95 (m, 1H), 5.17-5.21 (m, 1H), 4.58-4.63 (m, 1H), 2.85-2.94 (m, 2H), 2.53-2.64 (m, 2H), 2.08-2.18 (m, 1H), 1.96-2.06 (m, 1H), 1.74-1.89 (m, 3H), 1.62-1.71 (m, 1H).



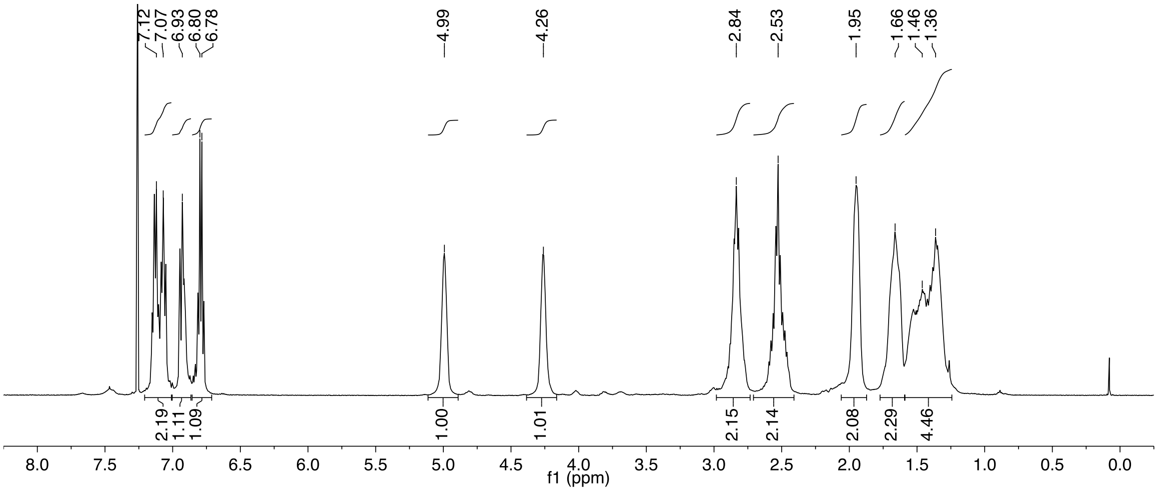
^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.79, 155.36, 130.32, 129.12, 127.87, 120.74, 112.45, 81.47, 79.26, 34.47, 30.50, 26.72, 21.93.



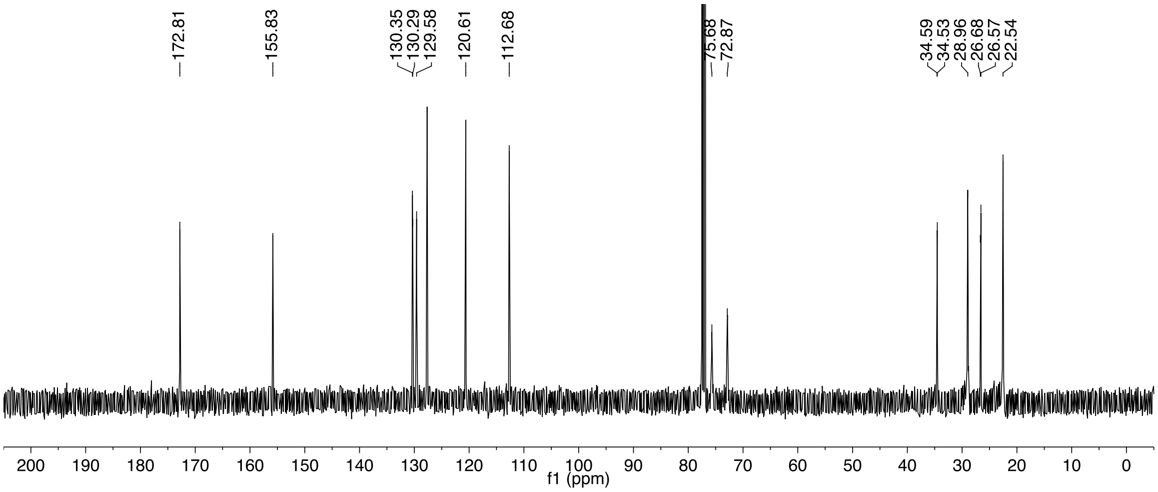
Poly(cyclohexene dihydrocoumarate) (Table 2, entry 8)



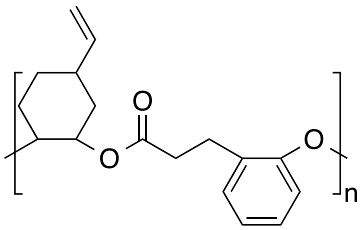
^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.04-7.16 (m, 2H), 6.89-6.96 (m, 1H), 6.76-6.83 (m, 1H), 4.94-5.05 (m, 1H), 4.21-4.31 (m, 1H), 2.75-2.92 (m, 2H), 2.43-2.61 (m, 2H), 1.89-2.02 (m, 2H), 1.60-1.78 (m, 2H), 1.24-1.59 (m, 4H).



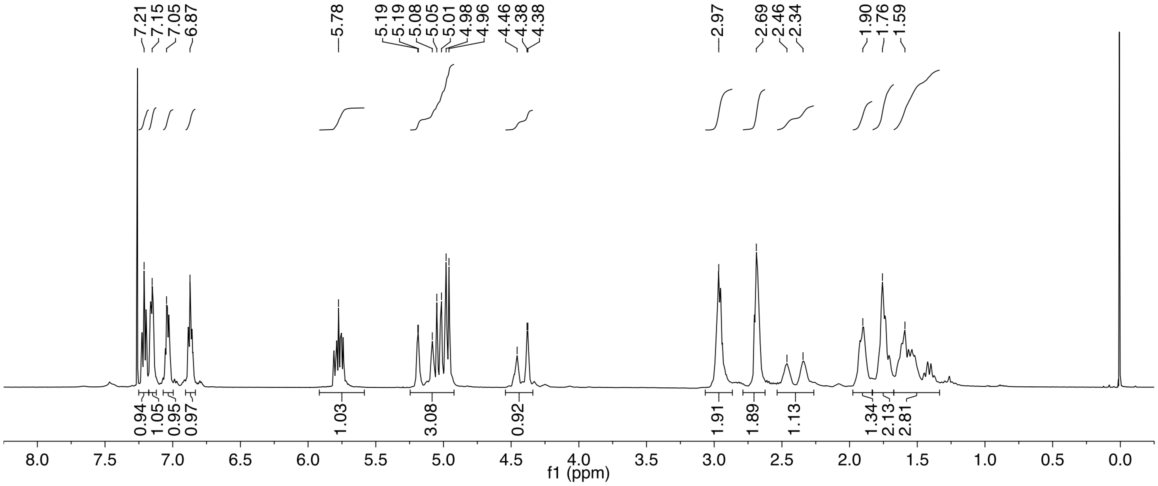
^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.81, 155.83, 130.32, 129.59, 127.67, 120.59, 112.68, 75.63, 72.87, 34.56, 28.95, 26.61, 22.51



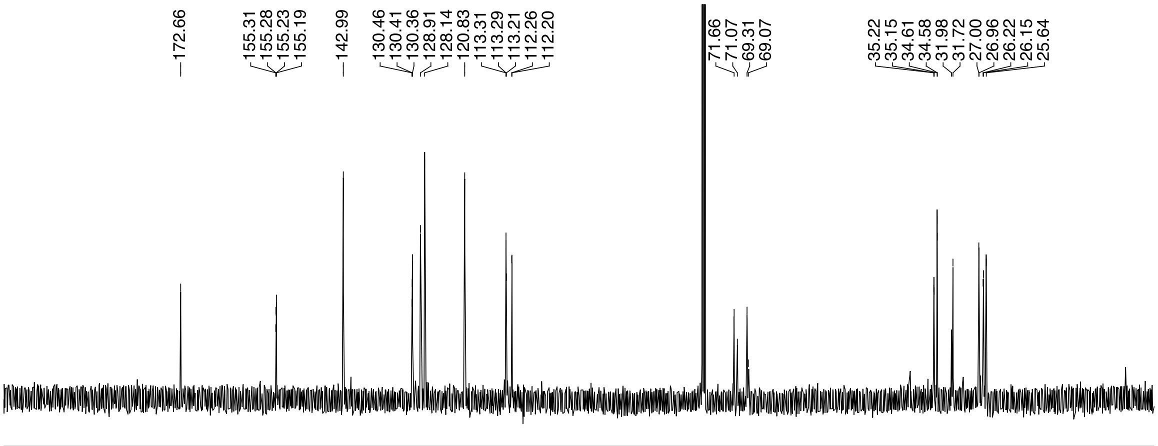
Poly(vinylcyclohexene dihydrocoumarate) (Table 2, entry 9)



^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.19-7.23 (m, 1H), 7.13-7.17 (m, 1H), 7.0-7.07 (m, 1H), 6.83-6.92 (m, 1H), 5.82-5.73 (m, 1H), 4.91-5.23 (m, 3H), 4.35-4.50 (m, 1H), 2.91-3.01 (m, 2H), 2.64-2.72 (m, 2H), 2.29-2.52 (m, 1H), 1.68-1.97 (m, 4H), 1.35-1.67 (m, 3H).



^{13}C NMR (CDCl$_3$, 125 MHz): δ 172.69, 155.25, 142.99, 130.41, 128.90, 128.14, 120.82, 113.26, 112.23, 71.66, 71.07, 69.31, 69.07, 35.18, 34.58, 31.98, 31.72, 26.99, 26.20, 25.62.



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