Electronic Supplementary Information

Cobalt Amino-bis(phenolate) Complexes for Coupling and Copolymerization of Epoxides with Carbon Dioxide

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MALDI-TOF-MS Characterization of complexes

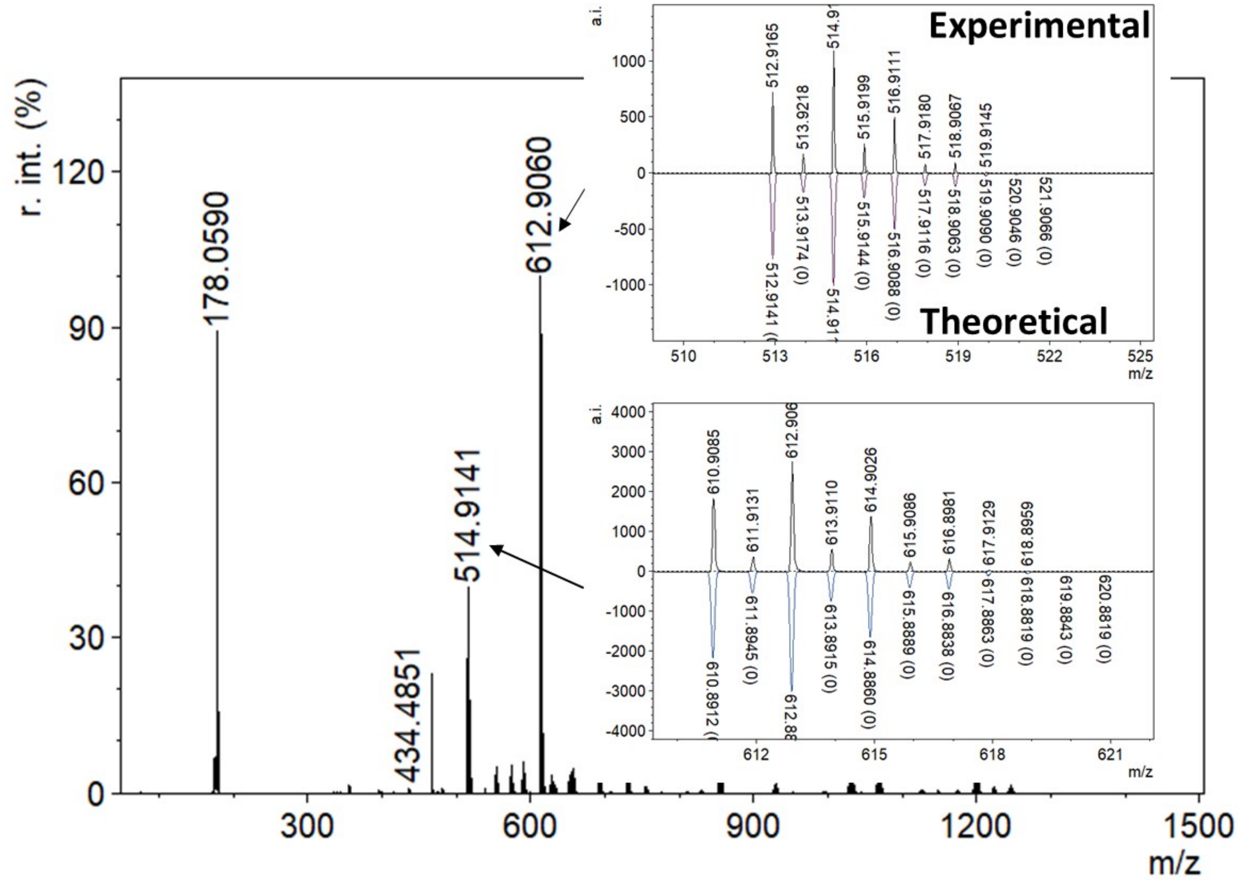

Figure S1: MALDI-TOF mass spectrum of **3** and comparison to calculated isotopic pattern.

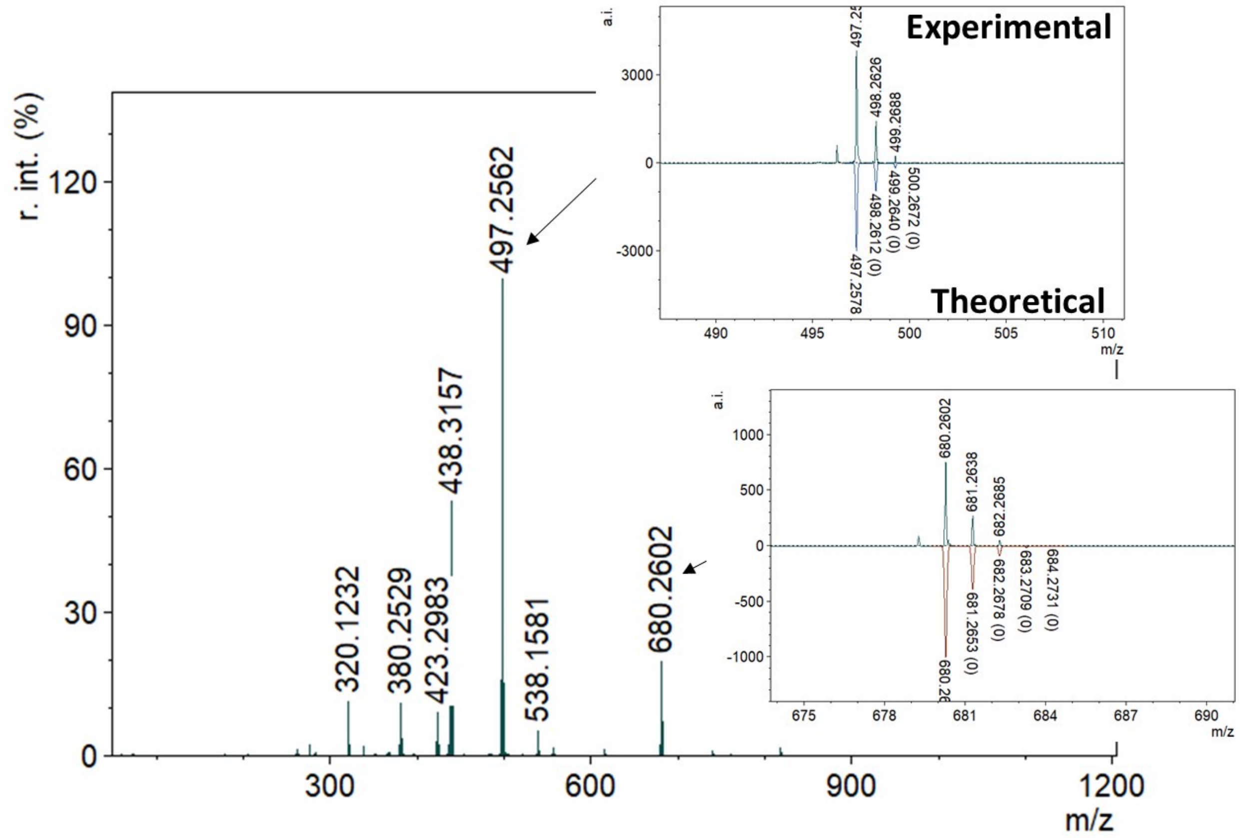

Figure S2: MALDI-TOF mass spectrum of **7** and comparison to calculated isotopic pattern.

NMR Characterization

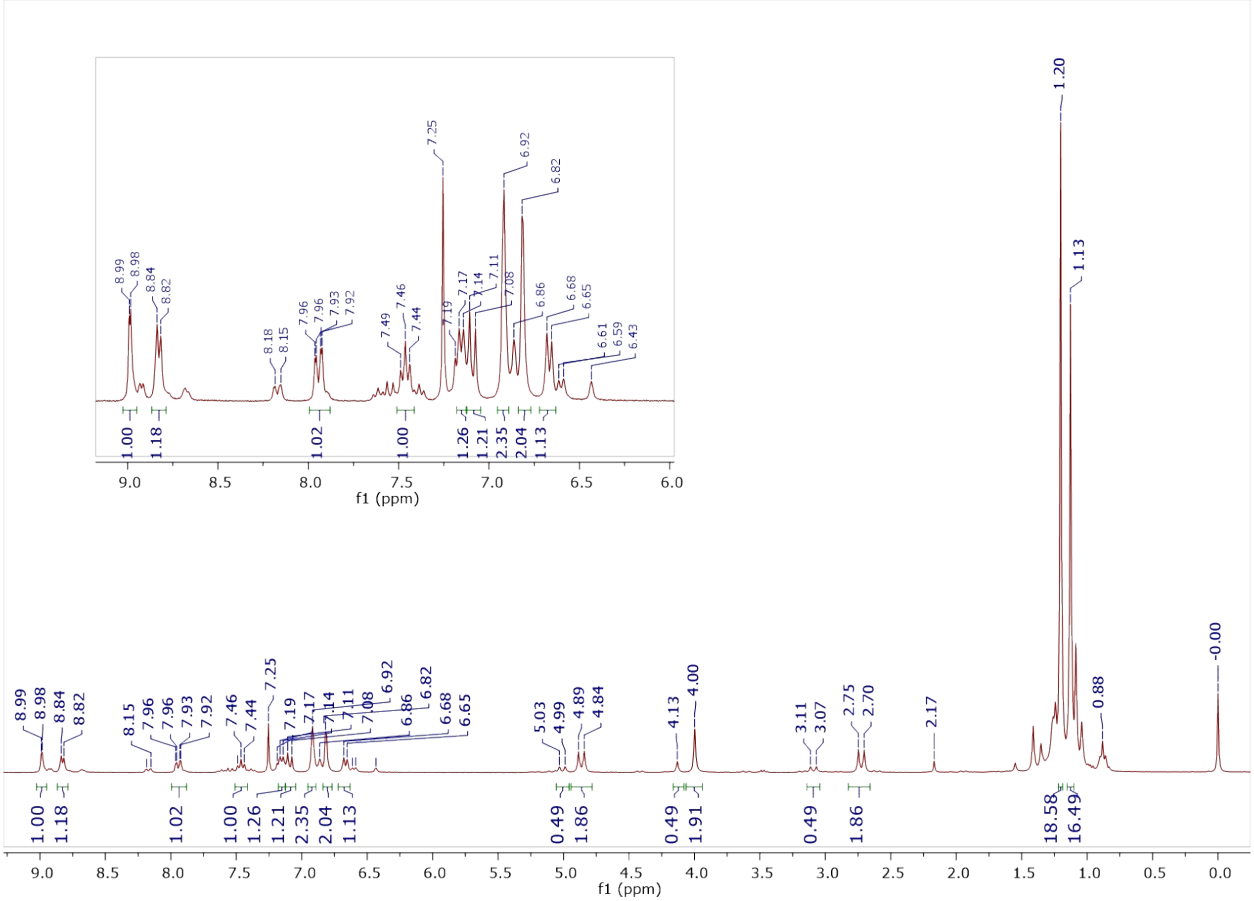

Figure S3: Representative ^{1}H NMR spectrum of **5** in $CDCl_3$.

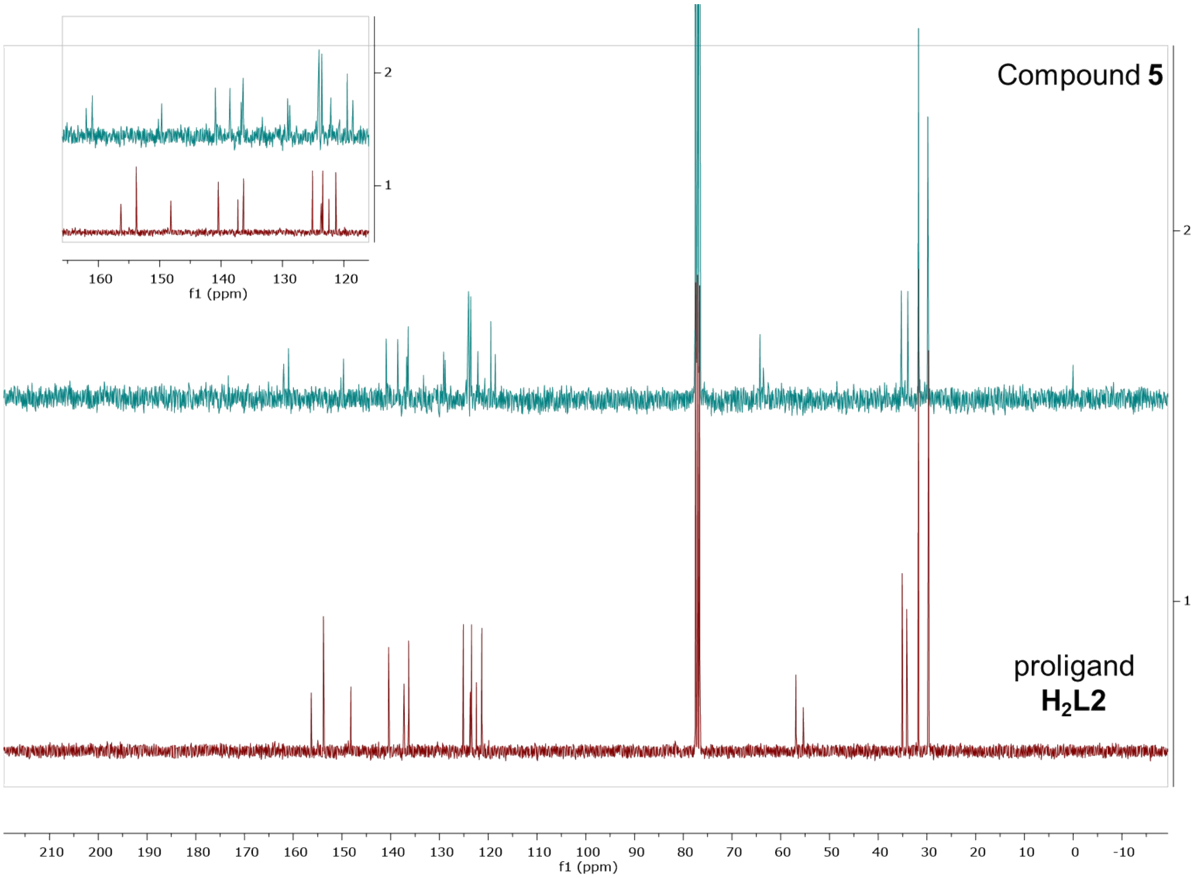

Figure S4: Stacked ^{13}C NMR spectra of **5** and proligand H_2**L2** in $CDCl_3$.

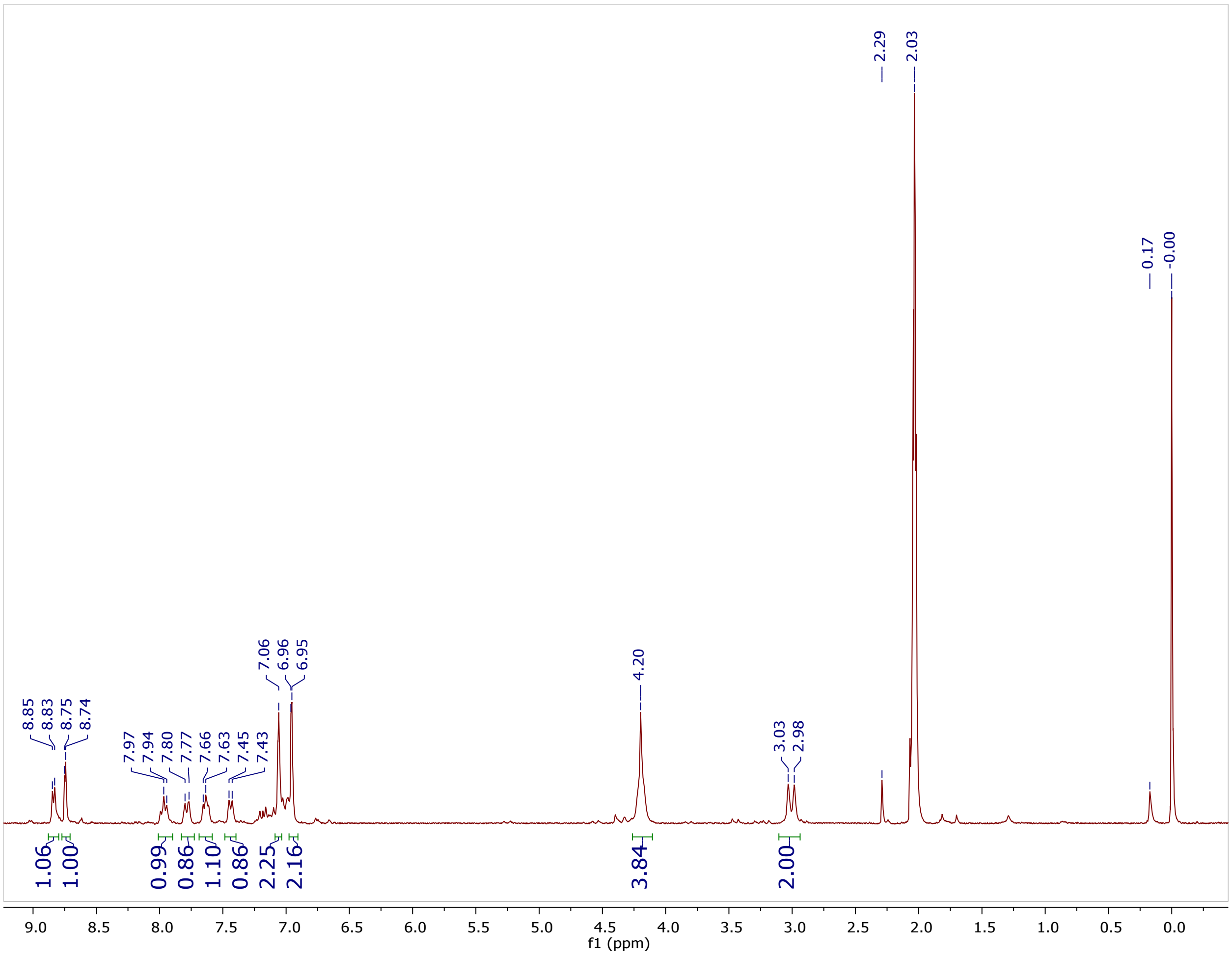

Figure S5: Representative ^{1}H NMR spectrum of **6** in acetone-d$_{6}$.

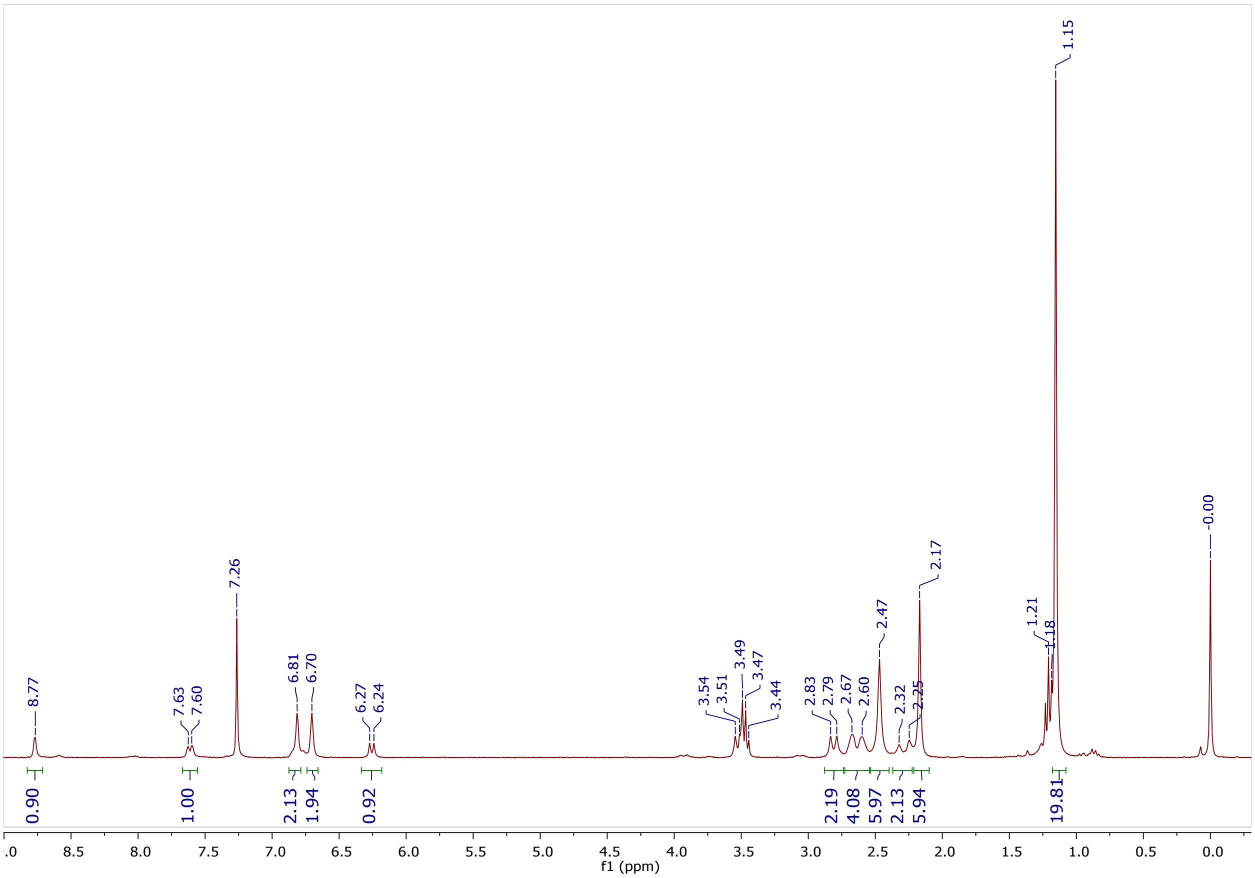

Figure S6: Representative ^{1}HNMR spectrum of **7** in $CDCl_3$.

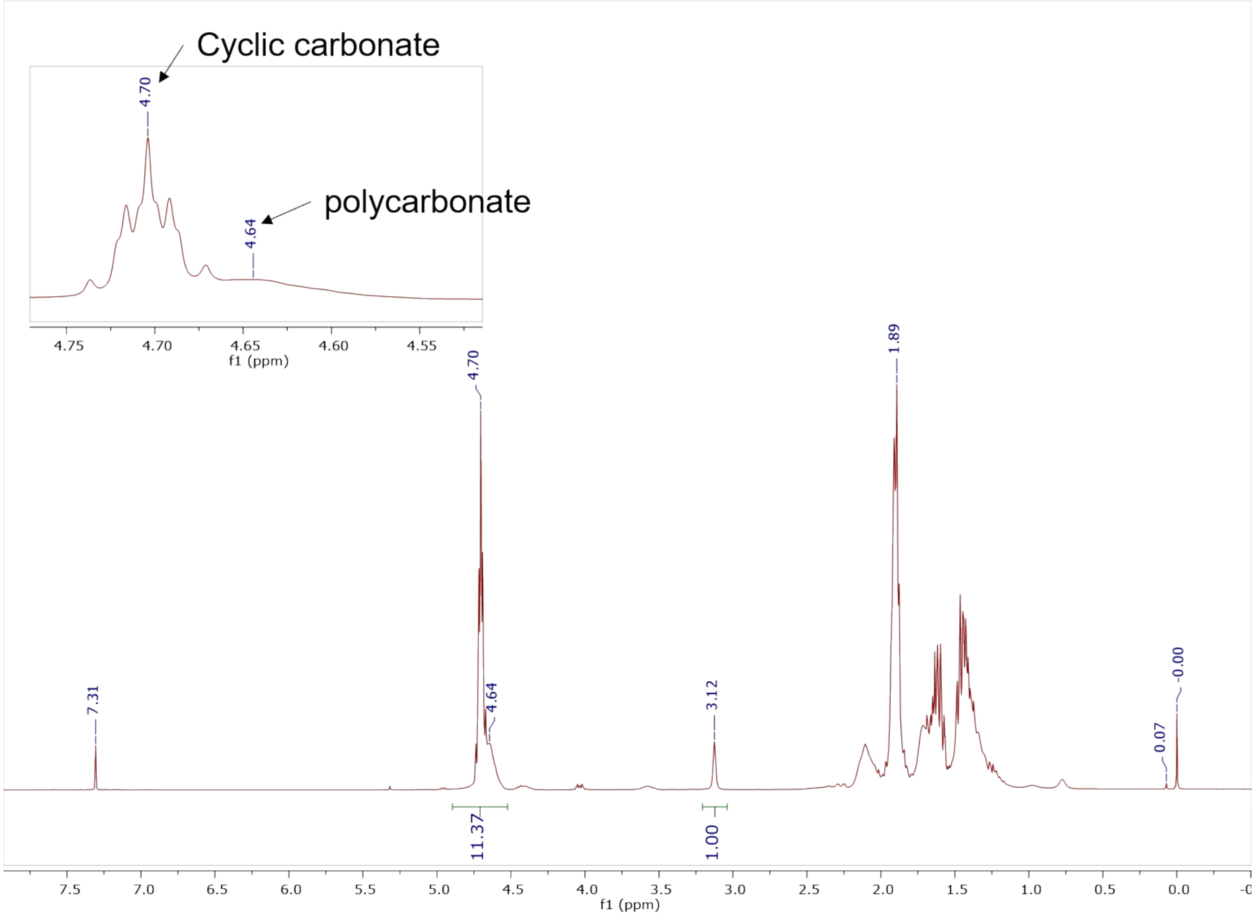

Figure S7: Representative ^{1}H NMR spectrum of aliquot taken immediately after reaction (Table 1, entry 7) in $CDCl_3$. % Conversion = integration of polymer/cyclic carbonate peaks (11.37 at 4.89 – 4.52 ppm) divided by the sum of cyclic carbonate/polymers (11.37 at 4.89 – 4.52 ppm) and monomer (1.00 at 3.12 ppm).

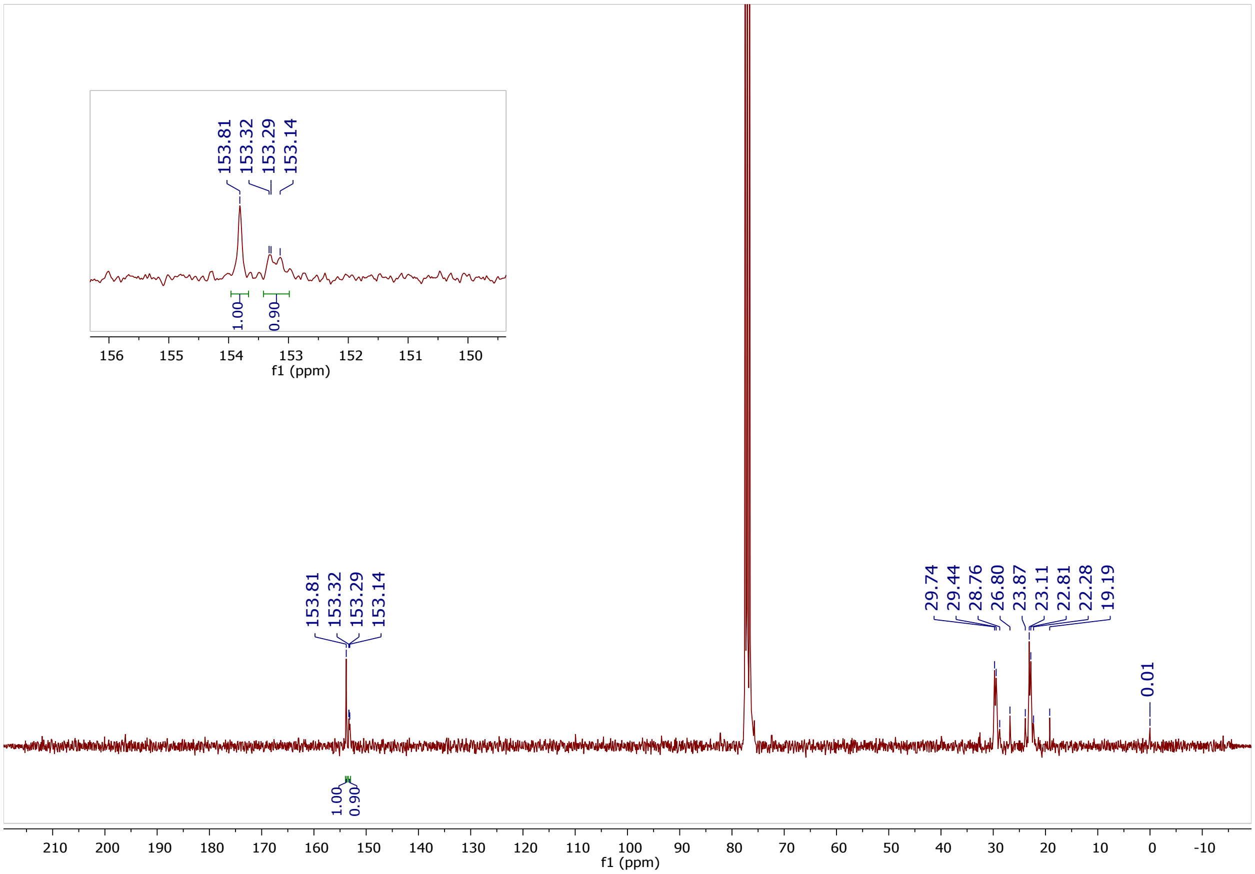

Figure S8: Representative ^{13}C NMR spectrum of aliquot taken immediately after reaction (Table 1, entry 1) in $CDCl_3$. Syndiotactic and isotactic diads observed at 153.2 and 153.8 ppm respectively. Integration ratios of 1:1 suggests atactic polymer.

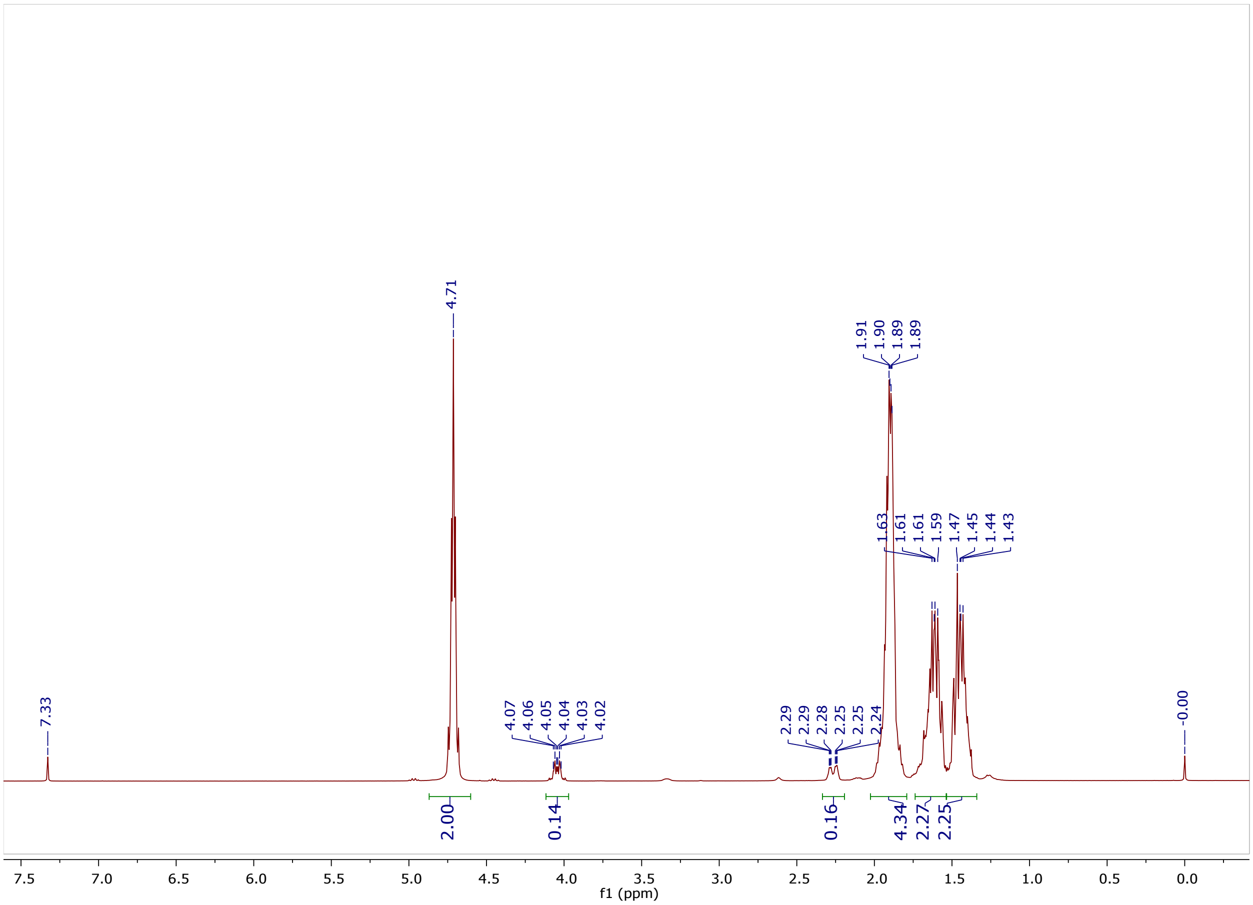

Figure S9: Representative ^{1}H NMR of isolated cyclohexene carbonate in $CDCl_3$. Peak at 4.71 ppm represents methine protons from *cis* isomer whereas multiplet at 4.02-4.07 ppm represents that of *trans* isomer.

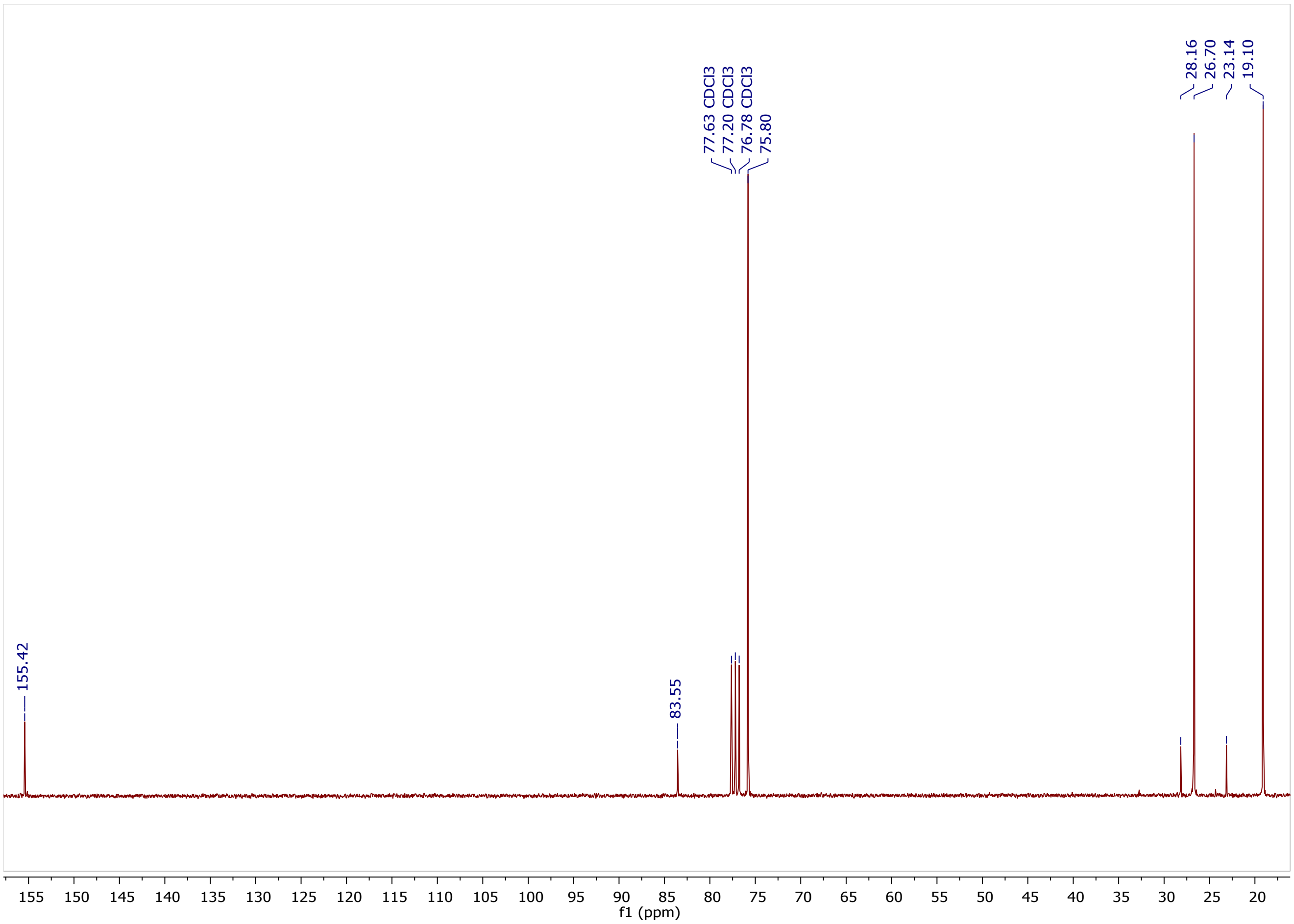

Figure S10: Representative ^{13}C NMR of isolated cyclohexene carbonate in $CDCl_3$. Peak at 75.80 ppm represents methine carbons from *cis* isomer whereas peak at 83.55 ppm represents that of residual *trans* isomer.

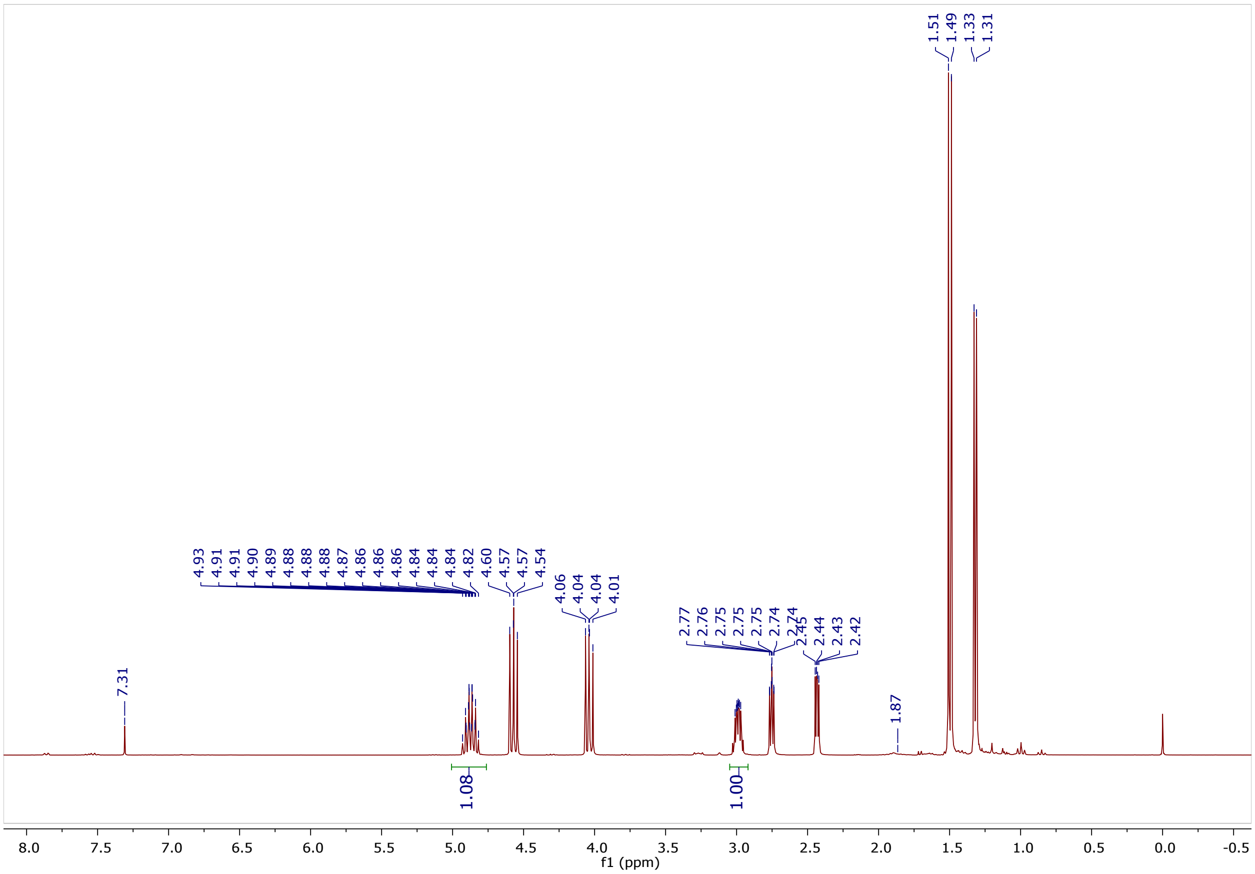

Figure S11: Representative ^{1}H NMR in $CDCl_3$ of aliquot taken immediately after reaction (table 2, entry 4). % Conversion = integration of cyclic carbonate methine multiplet (1.08 at 4.88 ppm) divided by the sum of cyclic carbonate methine multiplet (1.08 at 2.99 ppm) and monomer (1.00 at 2.99 ppm).

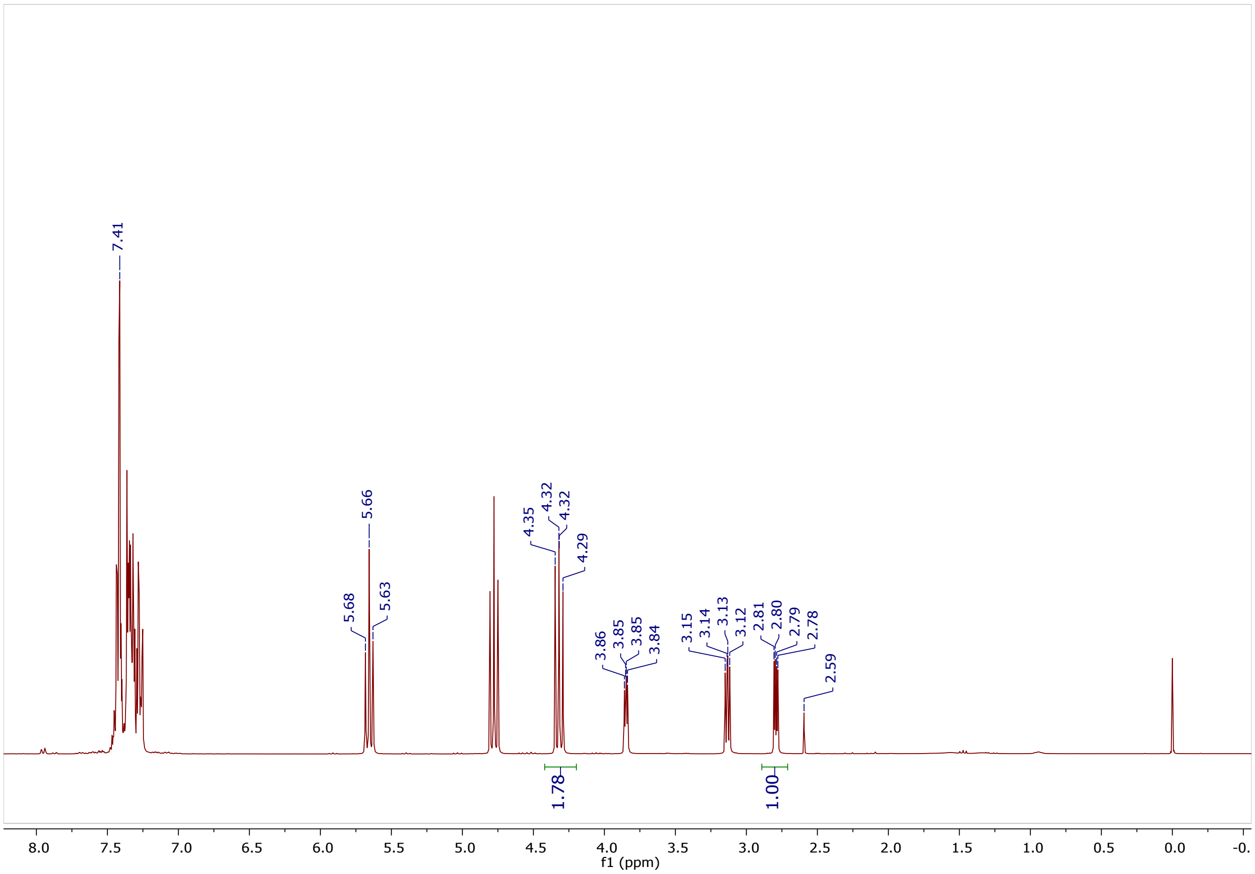

Figure S12: Representative ^{1}H NMR in $CDCl_3$ of aliquot taken immediately after reaction (Table 2, entry 9).

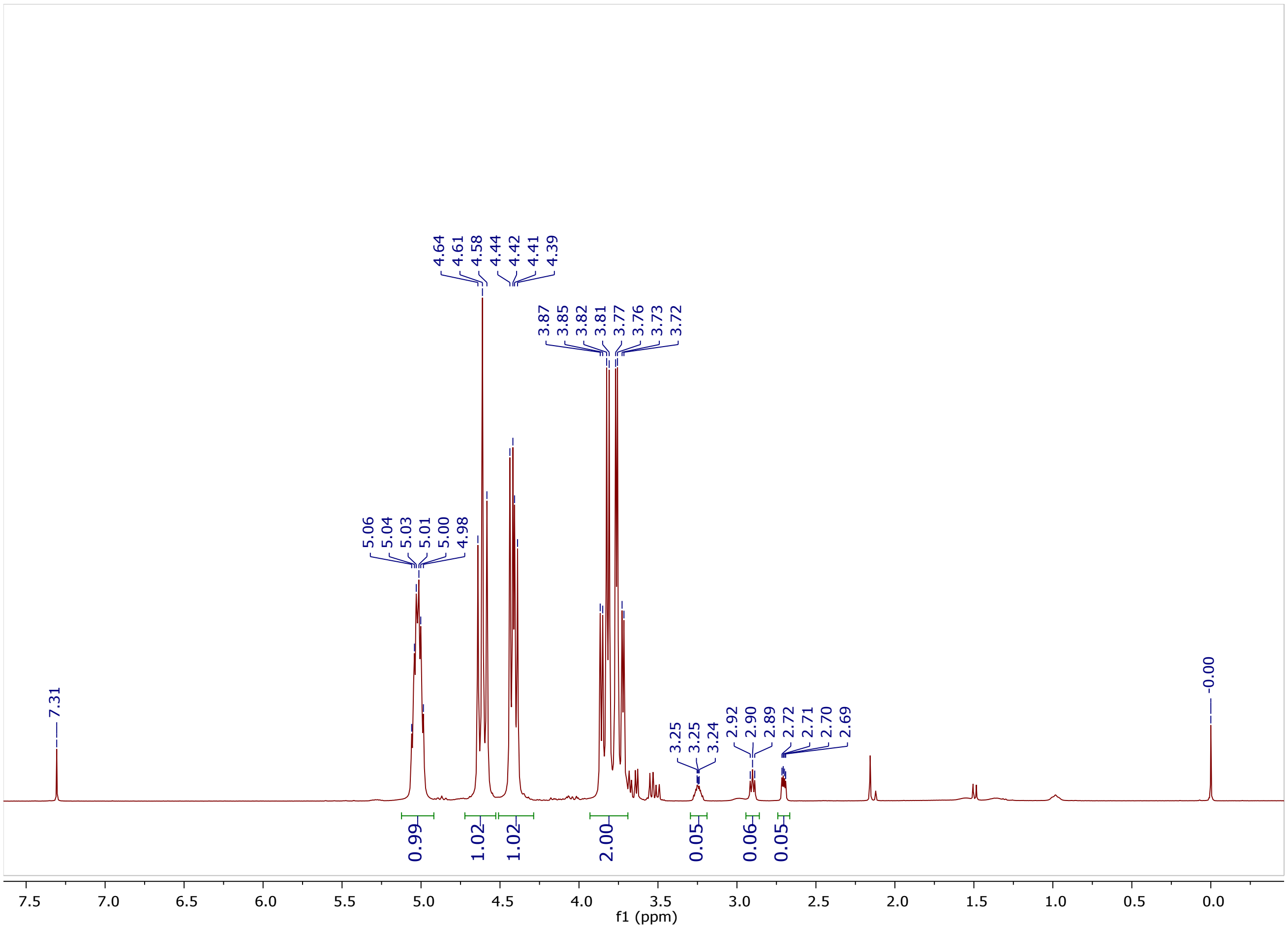

Figure S13: Representative ^{1}H NMR in $CDCl_3$ of aliquot taken immediately after reaction (Table 2, entry 10).

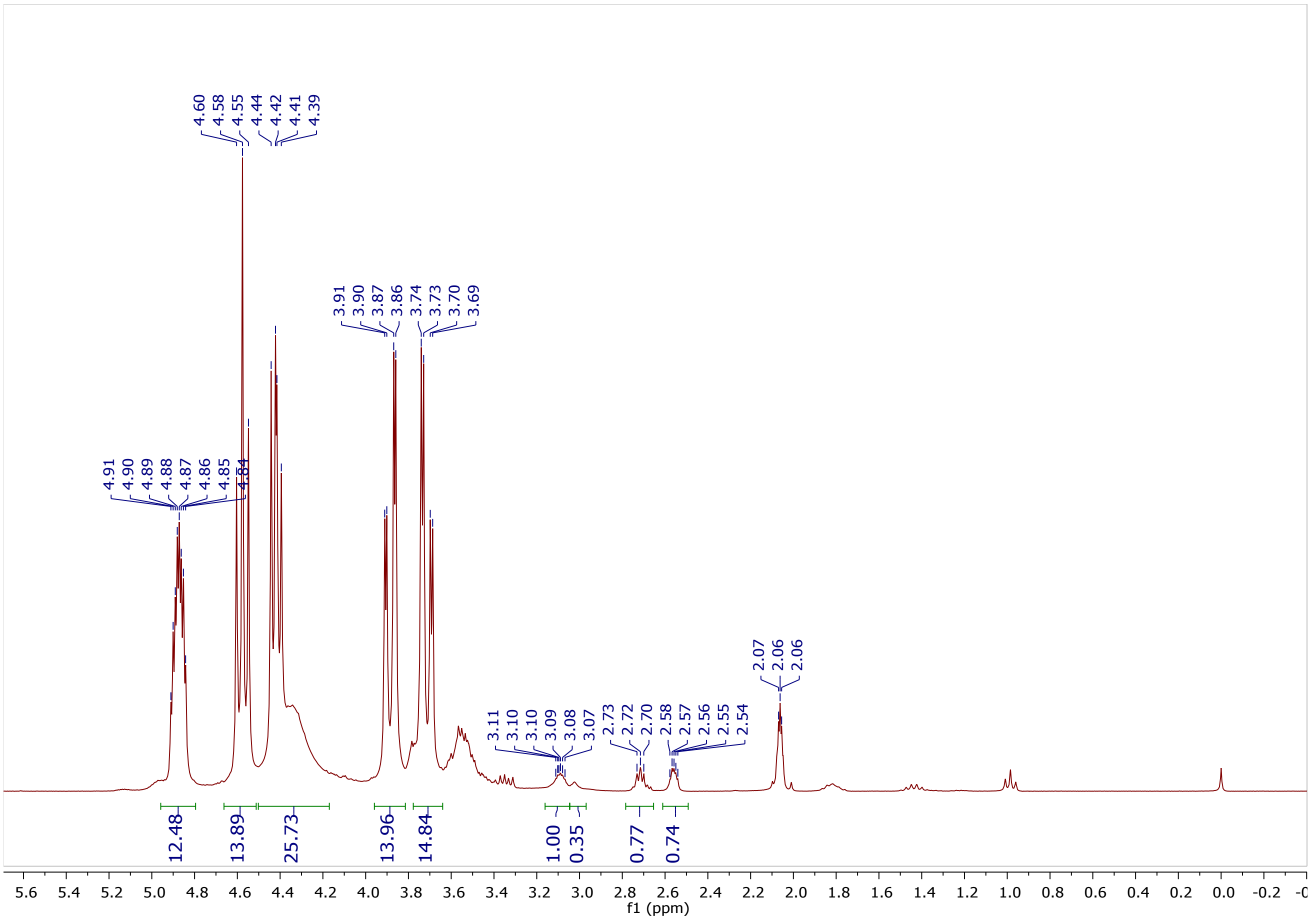

Figure S14: Representative ^{1}H NMR in $CDCl_3$ of aliquot taken immediately after reaction (Table 2, entry 11).

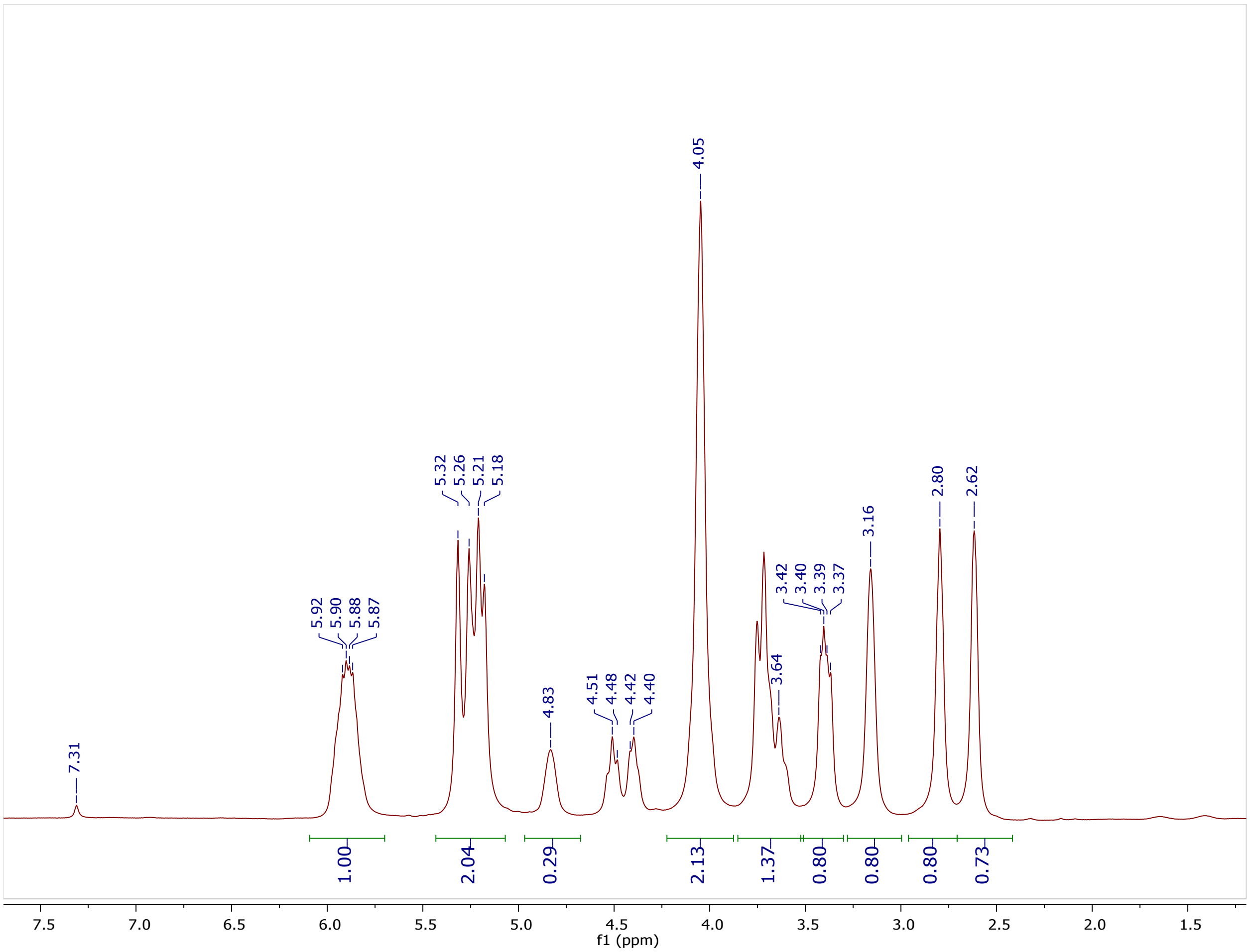

Figure S15: Representative ^{1}H NMR in $CDCl_3$ of aliquot taken immediately after reaction (Table 2, entry 12).

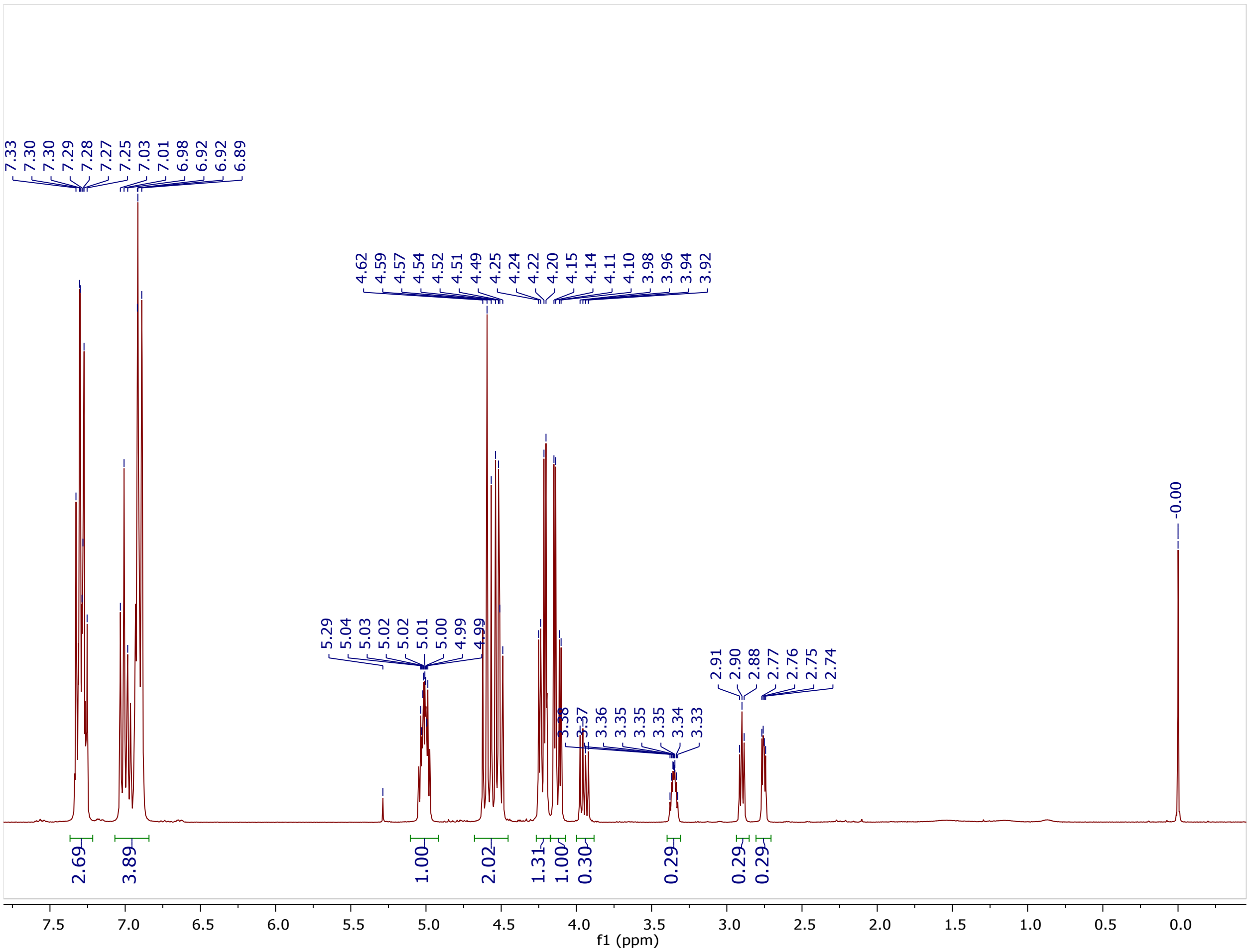

Figure S16: Representative ^{1}H NMR in $CDCl_3$ of aliquot taken immediately after reaction (Table 2, entry 13).

MALDI-TOF Characterization of polymers

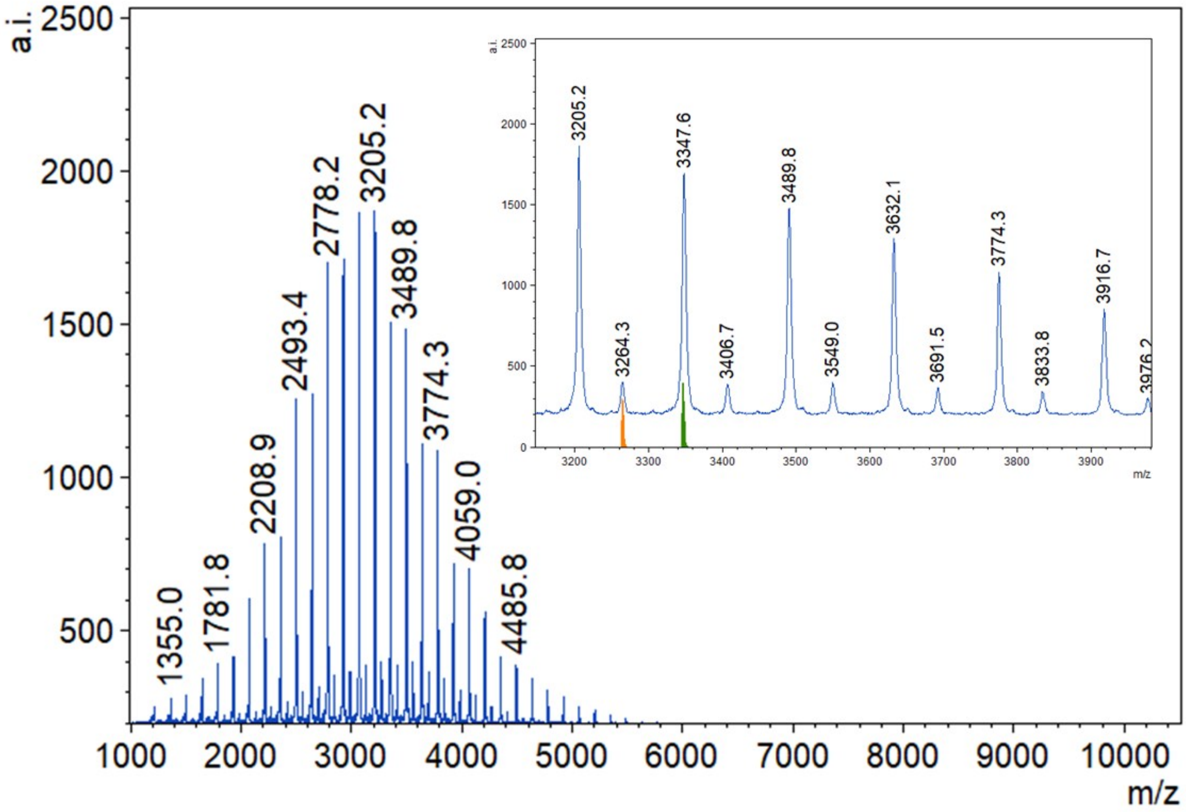

Figure S17: MALDI-TOF mass spectrum of polycarbonate obtained from Table 1, entry 1.

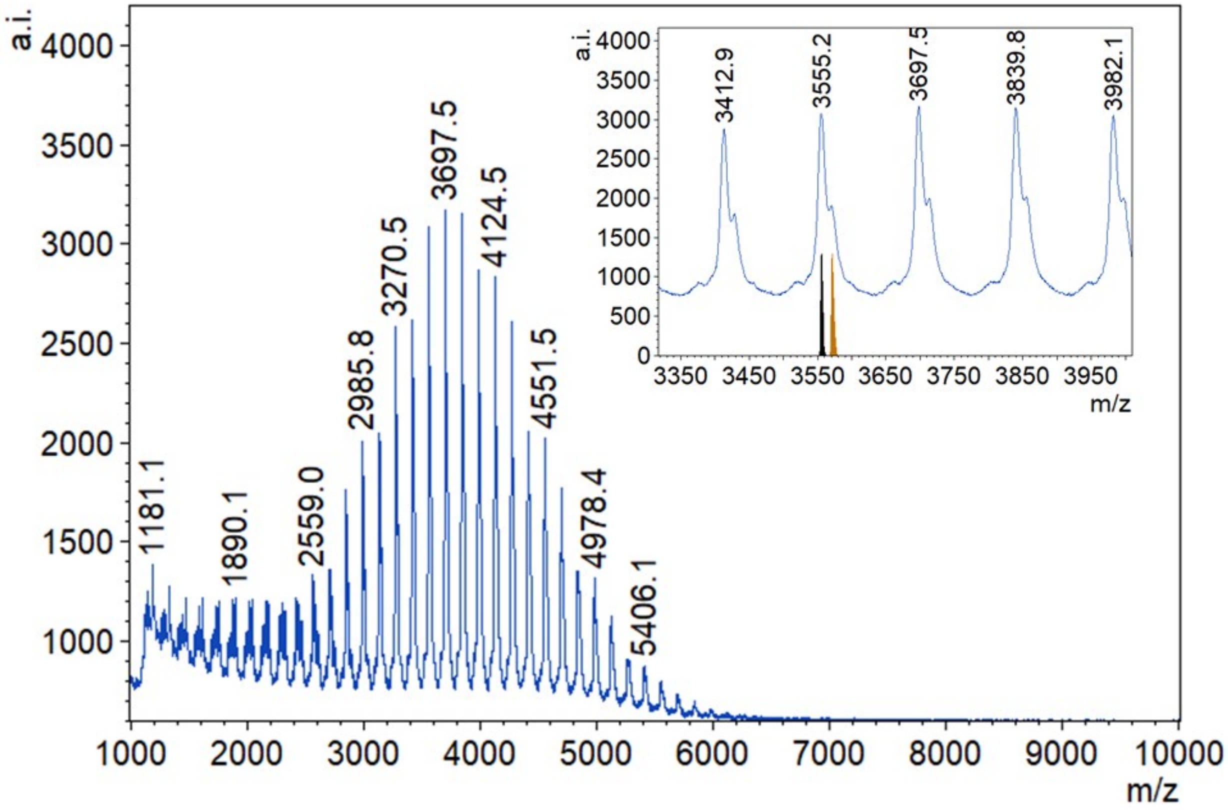

Figure S18: MALDI-TOF mass spectrum of polycarbonate obtained from Table 1, entry 9.

GPC traces of selected polymers

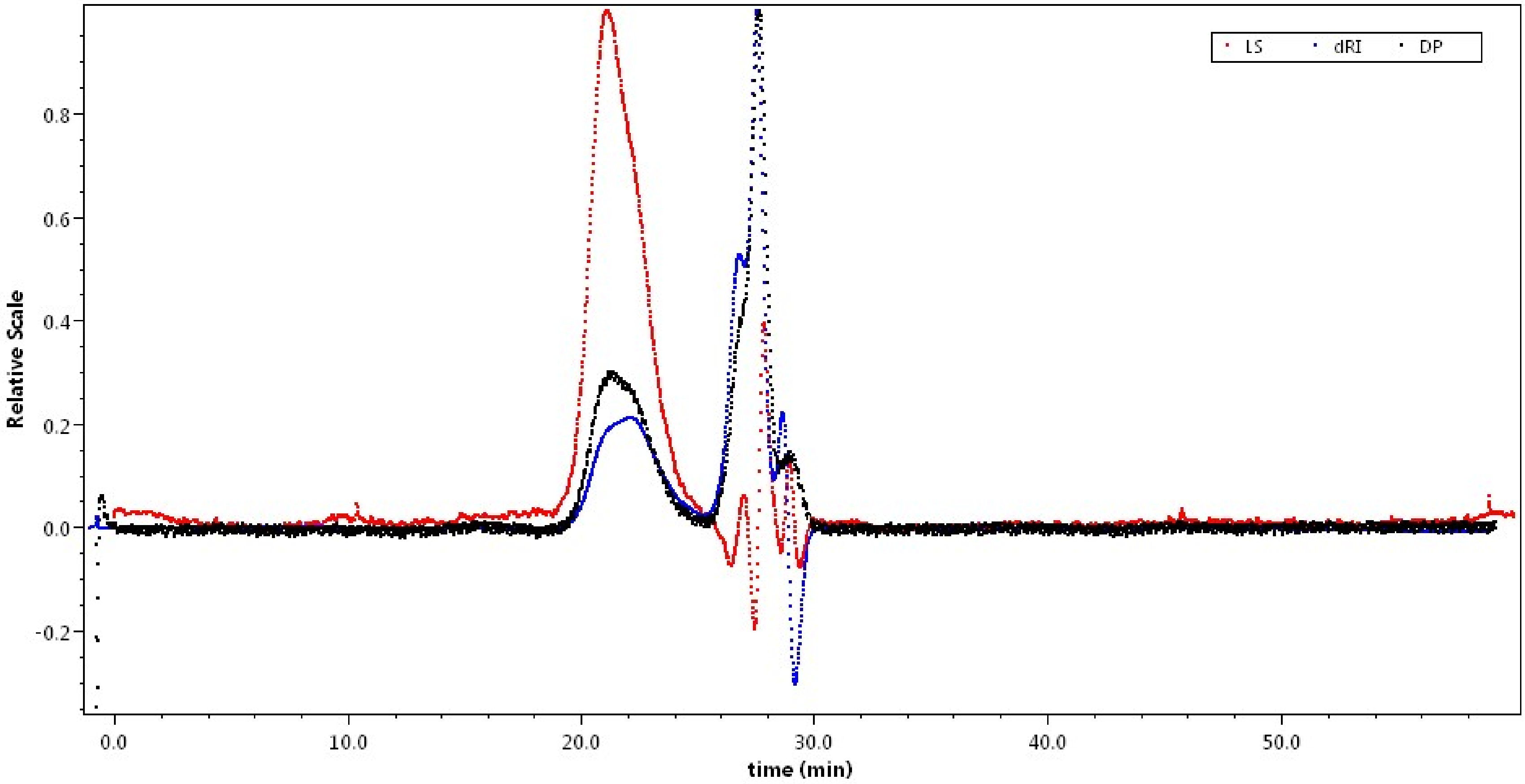

Figure S19: GPC traces for polymer using 3 (Table 1 entry 1). M_n = 6374 g mol^{-1}, Đ = 1.14.

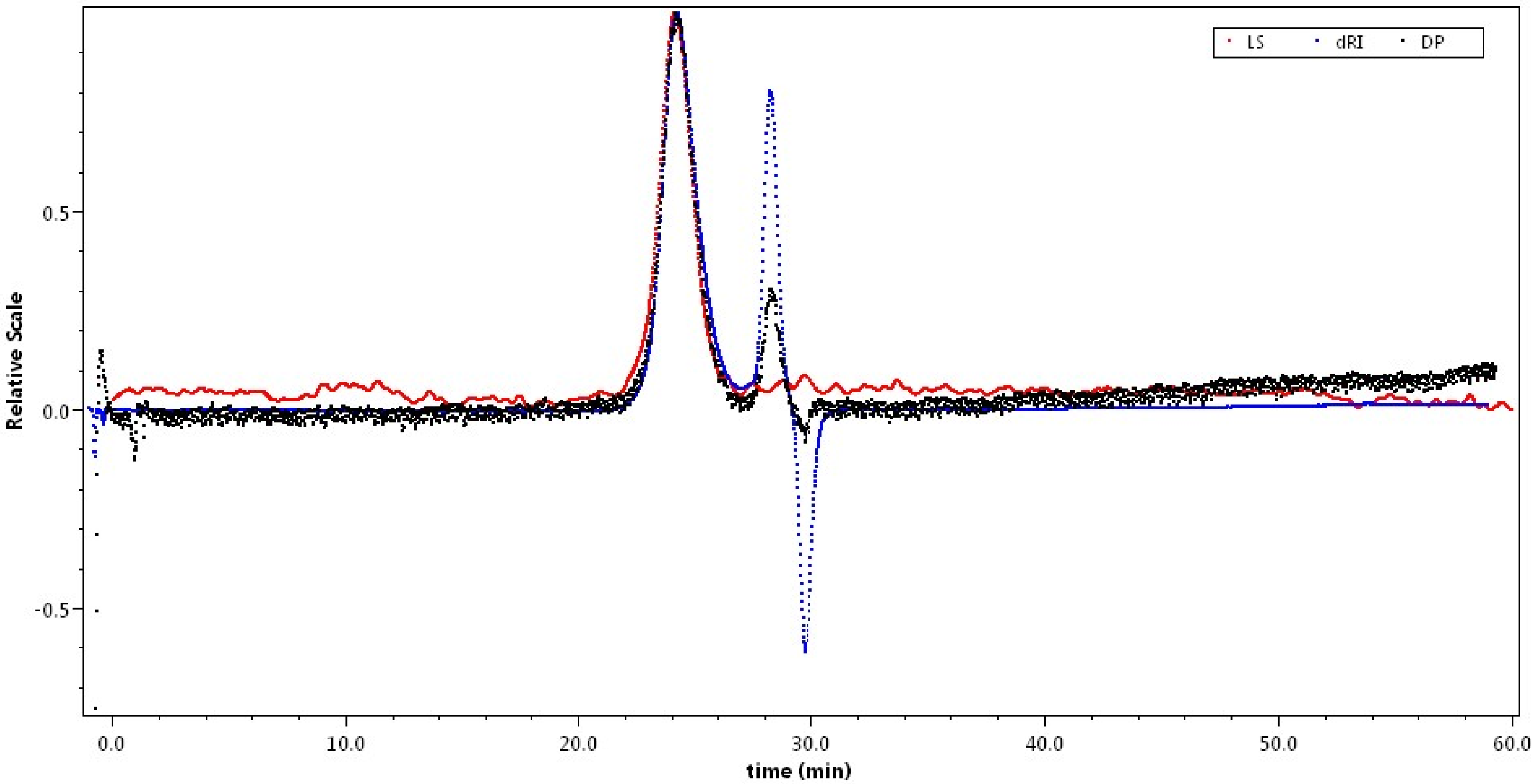

Figure S20: GPC traces for polymer produced using 3 (Table 1 entry 9). M_n = 5816 g mol^{-1}, Đ = 1.05.

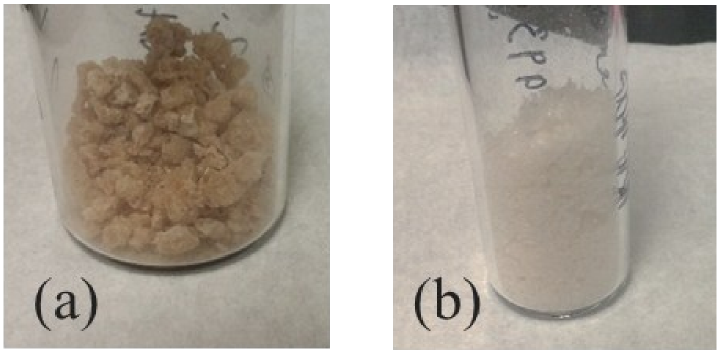

Figure S21: Isolated PCHC after precipitation by cold, acidified methanol (a) and after purification using decolourizing charcoal as described in Experimental (b).

Single Crystal X-Ray Characterization

Crystallography for compound **3** was performed by Katherine N. Robertson of the Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia B3H 3C3, Canada. Single crystals of $C_{66}H_{53}Cl_{12}Co_3K_3N_6O_{13}$, **3**, were crystallized from acetone and toluene. A suitable crystal was selected and placed in Paratone N oil, mounted in a nylon loop and data collected on a Bruker diffractometer equipped with an APEXII CCD detector.[1] The crystal was kept at 125(2) K during data collection.

The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, two ω-scan frame series were collected with 2.0° wide scans, 400 second frames and 105 frames per series at varying φ angles (φ = 26.41° and -62.05°). The crystal to detector distance was set to 6 cm and a single quadrant of data collected so that frame time could be maximized. Cell refinement and data reduction were performed with the Bruker SAINT software,[2] which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS).[3] The structure was solved using the program SHELXT [4] and refined using a full-matrix least-squares method on F^2 with SHELXL-2014 [5]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at $1.2U_{eq}$ of the parent carbon atom ($1.5U_{eq}$ was used for methyl hydrogens and for the hydrogens bonded to oxygen).

The best resolution that could be obtained in this data collection was only 1.06 Å (maximum θ angle of 19.55°). This resulted in a number of compromises that had to be made in the refinement process. All of the heavy atoms were refined anisotropically although this did result in a low data to parameter ratio. The thermal parameters were not generally well-behaved, so restraints were placed on all the heavy atoms to have them act more isotropically (ISOR 0.02) and several atoms (CL2, CL10 and C22) had to be more heavily restrained (ISOR 0.01). In addition, bonded atoms were restrained to have similar thermal parameters (SIMU 0.015) and to vibrate as rigid groups (RIGU 0.004). The bond lengths of all the bonds in the C6 aromatic rings were fixed to a distance of 1.39 (0.015) Å. In addition, other bonds of similar geometry throughout the molecule were restrained to be equal using SADI instructions. Three reflections having F*obs*^{2} much less than F*calc*^{2}, presumably since they were partially obscured by the beam stop, were omitted from the final refinement.

Once all the heavy atoms had been assigned to the molecular assembly (as included in the final refinement), it was obvious that there was significant residual density still present in the unit cell. However, no discrete solvent molecules could be identified. The program SQUEEZE, as implemented in the PLATON package [6], was used to remove this excess density. The total potential solvent accessible void volume was calculated to be 14898.2 Å^3, which was 54% of the total cell volume. After 14 cycles of refinement, the observed R-factor had dropped from 0.146 to 0.069 and 3899 electrons had been removed from the unit cell. This number was too large to accurately predict what solvent may have originally been present.

The Flack parameter calculated by SHELXL (Parson's method), 0.063(9), is in good agreement with the Hooft parameter calculated using PLATON, 0.069(10). This generates a Level B alert in the Checkcif file, "The Flack x is >> 0 - Do a BASF/TWIN Refinement". However, there is no evidence of twinning in the structure (TwinRotMax or Rotax). The values obtained are close to zero so it is more likely that the problem is lack of data for the analysis rather than a true problem with the absolute configuration.

Crystallography for compound **7** was performed by Julie Collins of the C-CART X-ray Diffraction Laboratory, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7, Canada. Single crystals of $C_{35}H_{47}Cl_2CoN_4O_7$, **7**, were crystallized from hexanes, diethyl ether and dichloromethane. A suitable crystal was selected and mounted in Paratone N on a MiTeGen MicroMount on a Rigaku Saturn70 (2x2 bin mode) diffractometer. The crystal was kept at 158 K during data collection. Using Olex2 [7], the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the ShelXL [5] refinement package using Least Squares minimization.

[1] APEX2 (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.
[2] SAINT (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.
[3] SADABS (Bruker, 2009) Bruker AXS Inc., Madison, Wisconsin, USA.
[4] G.M. Sheldrick, (2015). Acta Cryst., A71, 3–8.
[5] G.M. Sheldrick, (2008). *Acta Cryst.*, A64, 112-122.
[6] A.L. Spek, (2015). Acta Cryst. C71, 9-19.
[7] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst*. 42, 339-341.

Table S1: Crystal data and structure refinement of compounds **3** and **7.**

Compound	**3**	**7**
Empirical formula	$C_{66}H_{53}Cl_{12}Co_3K_3N_6O_{13}$	$C_{35}H_{47}Cl_2CoN_4O_7$
Formula weight	1857.63	765.59
Temperature/K	125(2)	158
Crystal system	tetragonal	triclinic
Space group	$P4_12_12$	P-1
a/Å	21.863(3)	11.7395(16)
b/Å	21.863(3)	13.1332(17)

c/Å	58.231(8)	13.2990(18)
α/°	90	77.736(6)
β/°	90	75.262(5)
γ/°	90	78.565(6)
Volume/Å^3	27833(9)	1915.0(4)
Z	8	2
ρ_{calc}g/cm^3	0.887	1.328
μ/mm^{-1}	0.708	0.637
F(000)	7496.0	804.0
Crystal size/mm^3	0.345 × 0.287 × 0.212	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71075)
2Θ range for data collection/°	2.33 to 39.112	6.244 to 52.744
Index ranges	$-20 \le h \le 16$, $-20 \le k \le 18$, $-54 \le l \le 52$	$-15 \le h \le 13$, $-16 \le k \le 16$, $-17 \le l \le 16$
Reflections collected	90364	19278
Independent reflections	10617 [R_{int} = 0.0872, R_{sigma} = 0.0945]	7787 [R_{int} = 0.0407, R_{sigma} = 0.0531]
Data/restraints/parameters	10617/2671/929	7787/18/479
Goodness-of-fit on F^2	1.032	1.150
Final R indexes [I>=2σ (I)]	R_1 = 0.0695, wR_2 = 0.1689	R_1 = 0.0738, wR_2 = 0.2069
Final R indexes [all data]	R_1 = 0.1250, wR_2 = 0.1974	R_1 = 0.0943, wR_2 = 0.2454
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27	2.59/-1.22
Flack parameter	0.063(9)	-
CCDC Reference number	1885982	1885983

Table S2: Selected bond lengths for **3**.

Selected Bond Lengths		
Atom	**Atom**	**Length/Å**
Co1	O2	1.886(13)
Co1	O1	1.959(13)
Co1	N2	2.045(15)
Co1	O3	2.051(13)
Co1	N1	2.207(16)
Co1	K3	3.590(5)
Co1	K1	3.808(5)
Co2	O5	1.934(13)
Co2	O6	1.973(12)
Co2	N4	2.069(17)
Co2	O7	2.098(12)
Co2	N3	2.180(16)
Co2	K2	3.589(5)
Co2	K1	3.808(5)
Co3	O9	2.033(13)
Co3	N6	2.086(17)
Co3	O10	2.097(13)
Co3	O11	2.114(12)
Co3	N5	2.210(17)

Co3	O8	2.220(12)
Co3	K2	3.544(5)
Co3	K3[1]	3.748(5)

Table S3: Selected bond angles for **3**.

Selected Bond Angles			
Atom	**Atom**	**Atom**	**Angle/°**
O2	Co1	O1	112.8(5)
O2	Co1	N2	122.9(6)
O1	Co1	N2	123.1(6)
O2	Co1	O3	90.9(5)
O1	Co1	O3	89.6(5)
N2	Co1	O3	99.6(6)
O2	Co1	N1	89.1(6)
O1	Co1	N1	90.9(6)
N2	Co1	N1	80.0(6)
O3	Co1	N1	179.5(6)
O2	Co1	K3	78.2(4)
O1	Co1	K3	49.8(4)
N2	Co1	K3	149.1(5)
O3	Co1	K3	54.4(4)
N1	Co1	K3	126.1(4)
O2	Co1	K1	47.0(4)
O1	Co1	K1	117.4(4)
N2	Co1	K1	108.5(4)
O3	Co1	K1	46.5(4)
N1	Co1	K1	133.3(5)
K3	Co1	K1	67.64(10)

Table S4: Selected bond lengths for **7**.

Selected bond Lengths		
Atom	**Atom**	**Length/Å**
Co1	O5	1.877(2)
Co1	O1	1.903(2)
Co1	O3	1.926(2)
Co1	O2	1.931(2)
Co1	N1	1.950(3)
Co1	N2	2.029(3)

Table S5: Selected bond angles for **7**.

Selected Bond Angles			
Atom	**Atom**	**Atom**	**Angle/°**
O5	Co1	O1	88.97(10)
O5	Co1	O3	93.21(9)
O5	Co1	O2	89.89(9)

O5	Co1	N1	91.42(10)
O5	Co1	N2	179.60(9)
O1	Co1	O3	86.36(9)
O1	Co1	O2	174.83(9)
O1	Co1	N1	92.06(10)
O1	Co1	N2	90.87(10)
O3	Co1	O2	88.67(9)
O3	Co1	N1	175.08(9)
O3	Co1	N2	87.14(10)
O2	Co1	N1	93.01(10)
O2	Co1	N2	90.30(10)
N1	Co1	N2	88.23(11)