

Supporting Information

Chromium Diamino-bis(phenolate) Complexes as Catalysts for Ring-Opening Copolymerization of Cyclohexene Oxide and Carbon Dioxide

Kenson Ambrose, Jennifer N. Murphy, Christopher M. Kozak*

Department of Chemistry, Memorial University of Newfoundland,
St. John's, NL, Canada A1B 3X7

* Author to whom correspondence should be addressed. E-mail: ckozak@mun.ca

Table S1: Crystal data and structure refinement of Cr(III) amino-bis(phenolate) complexes.	S3
Table S2: Bond lengths from structural data of 1	S4
Table S3: Bond angles from structural data of 1	S4
Table S4: Bond lengths from structural data of 1'	S5
Table S5: Bond angles from structural data of 1'	S6
Table S6: Bond lengths from structural data of 2	S8
Table S7: Bond angles from structural data of 2	S8
Table S8: Bond lengths from structural data of 3	S9
Table S9: Bond angles from structural data of 3	S10
Figure S1: MALDI-TOF mass spectrum of 1 in positive reflectron mode showing complex monomeric fragments.	12
Figure S2: MALDI-TOF mass spectrum of 1 collected in positive reflectron mode, showing higher mass region and proposed Cr(III) complex fragments.	13
Figure S3: MALDI-TOF mass spectrum of 1 in negative reflectron mode.....	14
Figure S4: Representative crude ^1H NMR spectrum of PCHC in CDCl_3 from Table 1, entry 1 with enlarged area showing characteristic polymer signal (4.66 and 4.61 ppm).....	15

Figure S5: Representative crude ^{13}C NMR spectrum of PCHC in CDCl_3 from Table 1, entry 1 (top) and entry 7 (bottom) with insets showing characteristic polymer syndiotactic (153.1 ppm) and isotactic diads (153.8 ppm).....	16
Figure S6: MALDI-TOF mass spectrum of polycarbonate obtained from Table 1, entry 2.	17
Figure S7: Magnified MALDI-TOF mass spectrum (higher mass region, m/z 10350 – 12250) of PCHC obtained from Table 1, entry 2. Proposed polymer structure shown.....	18
Figure S8: MALDI-TOF mass spectrum of polycarbonate obtained from Table 1 entry 3.	18
Figure S9: Magnified MALDI-TOF mass spectrum (higher mass region, m/z 8040 – 10250) of PCHC obtained from Table 1, entry 3. Proposed polymer structures shown.	19
Figure S10: GPC chromatograms (from refractive index) for polymers obtained under conditions shown in Table 1, entry 1 (A), entry 2 (B), entry 3 (C) and entry 7 (D).	20

Crystallographic data

Table S1: Crystal data and structure refinement of Cr(III) amino-bis(phenolate) complexes.

	1	1'	2	3
Empirical formula	C ₄₇ H ₆₂ Cl ₄ Cr ₂ N ₄ O ₄	(C ₄₆ H ₆₀ Cl ₂ Cr ₂ N ₄ O ₄) ₂ (CH ₂ Cl ₂) ₃	C ₄₈ H ₆₅ Cr ₂ N ₅ O ₆	C ₂₅ H ₃₆ Cl ₄ CrN ₅ O ₃
Crystal colour	Green	Pink	Green	Green
Formula weight	992.80	2070.53	912.05	648.39
Temperature/K	100	100	100	100
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	I2/a	P-1	I2/a	P-1
a/Å	26.0093(7)	12.0398(4)	24.6373(7)	11.6364(11)
b/Å	8.2812(2)	15.4044(6)	8.4395(2)	12.1029(14)
c/Å	21.1095(6)	16.2569(7)	21.4764(6)	12.7523(9)
α/°	90	110.922(4)	90	117.065(9)
β/°	94.158(3)	98.112(3)	95.014(3)	110.298(8)
γ/°	90	97.931(3)	90	91.107(9)
Volume/Å ³	4534.8(2)	2729.7(2)	4448.4(2)	1465.8(3)
Z	4	1	4	2
ρ _{calc} g/cm ³	1.454	1.260	1.362	1.469
μ/mm ⁻¹	0.764	0.685	0.544	0.791
F(000)	2080.0	1082.0	1936.0	674.0
Crystal size/mm ³	0.2 × 0.15 × 0.1	0.3 × 0.3 × 0.1	0.1 × 0.1 × 0.01	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.804 to 51.364	3.97 to 51.36	4.828 to 51.352	4.238 to 51.358
Index ranges	-31 ≤ h ≤ 31, -10 ≤ k ≤ 10, -25 ≤ l ≤ 25	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19	-30 ≤ h ≤ 30, -10 ≤ k ≤ 10, -26 ≤ l ≤ 26	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	29027	35731	28725	11612
Independent reflections	4299 [R _{int} = 0.0972, R _{sigma} = 0.0589]	10364 [R _{int} = 0.0866, R _{sigma} = 0.0943]	4233 [R _{int} = 0.1047, R _{sigma} = 0.0535]	11612 [R _{int} = 0.4856, R _{sigma} = 0.1609]
Data/restraints/parameters	4299/3/280	10364/0/585	4233/10/295	11612/26/376
Goodness-of-fit on F ²	1.051	1.032	1.096	0.892
Final R indexes [I>=2σ (I)]	R ₁ = 0.0671, wR ₂ = 0.1512	R ₁ = 0.0830, wR ₂ = 0.2043	R ₁ = 0.0660, wR ₂ = 0.1533	R ₁ = 0.0877, wR ₂ = 0.2204
Final R indexes [all data]	R ₁ = 0.0876, wR ₂ = 0.1659	R ₁ = 0.1188, wR ₂ = 0.2356	R ₁ = 0.0783, wR ₂ = 0.1634	R ₁ = 0.1611, wR ₂ = 0.2376
Largest diff. peak/hole / e Å ⁻³	0.71/-0.77	0.89/-0.55	0.83/-0.53	1.66/-0.74
CCDC Reference No.	2019770	2019771	2019772	2019773

Table S2: Bond lengths from structural data of **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	Cl1	2.3805(12)	C4	C5	1.393(6)
Cr1	Cl1 ¹	2.4244(12)	C4	C8	1.502(6)
Cr1	O1	1.903(3)	C5	C6	1.395(6)
Cr1	O2	1.923(3)	C6	C7	1.397(6)
Cr1	N1	2.131(3)	C6	C9	1.509(6)
Cr1	N2	2.106(3)	C10	C11	1.522(5)
O1	C16	1.343(4)	C11	C12	1.396(5)
O2	C3	1.345(5)	C11	C16	1.406(5)
N1	C10	1.482(5)	C12	C13	1.381(6)
N1	C19	1.504(5)	C13	C14	1.406(5)
N1	C23	1.495(5)	C13	C17	1.502(6)
N2	C1	1.498(5)	C14	C15	1.383(5)
N2	C20	1.489(5)	C15	C16	1.420(5)
N2	C21	1.504(5)	C15	C18	1.497(5)
C1	C2	1.506(5)	C19	C20	1.537(5)
C2	C3	1.402(6)	C21	C22	1.529(5)
C2	C7	1.389(6)	C22	C23	1.533(6)
C3	C4	1.413(6)	Cl2	C24	1.750(4)

¹ 3/2-X, 1/2-Y, 3/2-Z

Table S3: Bond angles from structural data of **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Cr1	Cl1 ¹	83.15(4)	C7	C2	C3	119.9(4)
O1	Cr1	Cl1	88.54(8)	O2	C3	C2	120.3(3)
O1	Cr1	Cl1 ¹	171.68(9)	O2	C3	C4	119.6(4)
O1	Cr1	O2	93.08(11)	C2	C3	C4	120.1(4)
O1	Cr1	N1	82.65(11)	C3	C4	C8	119.9(4)
O1	Cr1	N2	95.33(12)	C5	C4	C3	117.8(4)
O2	Cr1	Cl1 ¹	87.15(9)	C5	C4	C8	122.2(4)
O2	Cr1	Cl1	92.89(9)	C4	C5	C6	123.1(4)
O2	Cr1	N1	166.48(12)	C5	C6	C7	117.6(4)
O2	Cr1	N2	92.22(12)	C5	C6	C9	120.4(4)
N1	Cr1	Cl1 ¹	98.93(9)	C7	C6	C9	121.9(4)
N1	Cr1	Cl1	99.78(9)	C2	C7	C6	121.4(4)
N2	Cr1	Cl1 ¹	92.97(9)	N1	C10	C11	112.6(3)
N2	Cr1	Cl1	173.41(9)	C12	C11	C10	117.8(3)
N2	Cr1	N1	75.50(12)	C12	C11	C16	119.3(3)

Cr1	Cl1	Cr1 ¹	96.85(4)	C16	C11	C10	122.7(3)
C16	O1	Cr1	126.4(2)	C13	C12	C11	122.8(4)
C3	O2	Cr1	113.1(2)	C12	C13	C14	117.1(4)
C10	N1	Cr1	108.9(2)	C12	C13	C17	120.7(4)
C10	N1	C19	110.7(3)	C14	C13	C17	122.2(4)
C10	N1	C23	110.0(3)	C15	C14	C13	122.3(4)
C19	N1	Cr1	107.5(2)	C14	C15	C16	119.5(4)
C23	N1	Cr1	110.8(2)	C14	C15	C18	121.7(4)
C23	N1	C19	109.0(3)	C16	C15	C18	118.9(3)
C1	N2	Cr1	111.5(2)	O1	C16	C11	124.2(3)
C1	N2	C21	108.2(3)	O1	C16	C15	116.8(3)
C20	N2	Cr1	105.3(2)	C11	C16	C15	118.9(3)
C20	N2	C1	110.4(3)	N1	C19	C20	110.5(3)
C20	N2	C21	109.5(3)	N2	C20	C19	110.4(3)
C21	N2	Cr1	112.0(2)	N2	C21	C22	115.9(3)
N2	C1	C2	114.1(3)	C21	C22	C23	118.0(3)
C3	C2	C1	117.6(4)	N1	C23	C22	111.7(3)
C7	C2	C1	122.4(4)	Cl2 ²	C24	Cl2	111.1(4)

¹ 3/2-X, 1/2-Y, 3/2-Z

Table S4: Bond lengths from structural data of **1'**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	Cl1	2.4065(15)	C11	C12	1.407(7)
Cr1	Cl2	2.3240(15)	C11	C16	1.384(8)
Cr1	O1	1.912(3)	C12	C13	1.423(8)
Cr1	O2	2.011(3)	C13	C14	1.381(8)
Cr1	N1	2.130(4)	C13	C17	1.521(8)
Cr1	N2	2.147(4)	C14	C15	1.401(8)
Cr2	Cl1	2.4316(15)	C15	C16	1.380(8)
Cr2	O2	2.076(3)	C15	C18	1.513(9)
Cr2	O3	1.926(3)	C19	C20	1.555(7)
Cr2	O4	1.897(3)	C21	C22	1.516(7)
Cr2	N3	2.159(4)	C22	C23	1.535(7)
Cr2	N4	2.149(4)	C24	C25	1.479(7)
O1	C12	1.350(6)	C25	C26	1.415(7)
O2	C3	1.380(6)	C25	C30	1.405(7)
O3	C35	1.340(6)	C26	C27	1.420(7)
O4	C26	1.341(6)	C27	C28	1.398(7)
N1	C10	1.505(6)	C27	C32	1.499(8)
N1	C20	1.488(7)	C28	C29	1.385(8)

N1	C21	1.509(6)	C29	C30	1.379(8)
N2	C1	1.488(6)	C29	C31	1.521(8)
N2	C19	1.491(6)	C33	C34	1.505(8)
N2	C23	1.489(6)	C34	C35	1.412(7)
N3	C24	1.495(7)	C34	C39	1.414(8)
N3	C42	1.494(6)	C35	C36	1.412(7)
N3	C46	1.508(6)	C36	C37	1.393(7)
N4	C33	1.479(7)	C36	C41	1.504(7)
N4	C43	1.498(6)	C37	C38	1.406(8)
N4	C44	1.502(7)	C38	C39	1.376(8)
C1	C2	1.511(7)	C38	C40	1.512(8)
C2	C3	1.412(7)	C42	C43	1.529(8)
C2	C7	1.394(7)	C44	C45	1.501(9)
C3	C4	1.398(7)	C45	C46	1.537(9)
C4	C5	1.399(7)	Cl3	C47	1.724(7)
C4	C9	1.493(7)	Cl4	C47	1.797(8)
C5	C6	1.383(8)	Cl6	Cl6 ¹	1.365(7)
C6	C7	1.399(8)	Cl6	C48	1.789(11)
C6	C8	1.515(7)	Cl5	C48	1.676(13)
C10	C11	1.481(8)			

¹ 2-X, -Y, 2-Z

Table S5: Bond angles from structural data of **1'**.

Atom	Atom	Atom	Angle/ [°]	Atom	Atom	Atom	Angle/ [°]
Cl2	Cr1	Cl1	169.90(6)	C4	C3	C2	119.5(4)
O1	Cr1	Cl1	88.43(12)	C3	C4	C5	118.1(5)
O1	Cr1	Cl2	88.68(12)	C3	C4	C9	123.2(5)
O1	Cr1	O2	97.15(14)	C5	C4	C9	118.5(5)
O1	Cr1	N1	93.60(15)	C6	C5	C4	123.7(5)
O1	Cr1	N2	167.94(16)	C5	C6	C7	116.9(5)
O2	Cr1	Cl1	79.85(10)	C5	C6	C8	121.4(5)
O2	Cr1	Cl2	90.92(10)	C7	C6	C8	121.7(5)
O2	Cr1	N1	166.05(15)	C2	C7	C6	121.6(5)
O2	Cr1	N2	93.75(14)	C11	C10	N1	113.6(4)
N1	Cr1	Cl1	91.63(12)	C12	C11	C10	117.1(5)
N1	Cr1	Cl2	98.22(12)	C16	C11	C10	123.3(5)
N1	Cr1	N2	74.85(15)	C16	C11	C12	119.5(5)
N2	Cr1	Cl1	88.45(11)	O1	C12	C11	121.2(5)
N2	Cr1	Cl2	96.28(11)	O1	C12	C13	120.0(5)
O2	Cr2	Cl1	78.02(10)	C11	C12	C13	118.8(5)

O2	Cr2	N3	105.46(15)	C12	C13	C17	119.6(5)
O2	Cr2	N4	166.61(15)	C14	C13	C12	118.8(5)
O3	Cr2	C11	92.28(11)	C14	C13	C17	121.6(5)
O3	Cr2	O2	92.47(14)	C13	C14	C15	123.0(6)
O3	Cr2	N3	160.79(16)	C14	C15	C18	121.1(6)
O3	Cr2	N4	90.21(16)	C16	C15	C14	116.8(6)
O4	Cr2	C11	171.42(11)	C16	C15	C18	122.0(6)
O4	Cr2	O2	93.41(14)	C15	C16	C11	123.0(5)
O4	Cr2	O3	88.58(14)	N2	C19	C20	110.3(4)
O4	Cr2	N3	83.64(15)	N1	C20	C19	110.8(4)
O4	Cr2	N4	99.76(15)	N1	C21	C22	113.3(4)
N3	Cr2	C11	98.03(12)	C21	C22	C23	116.9(4)
N4	Cr2	C11	88.77(12)	N2	C23	C22	114.0(4)
N4	Cr2	N3	73.94(17)	C25	C24	N3	112.7(4)
Cr1	C11	Cr2	88.63(5)	C26	C25	C24	122.4(4)
C12	O1	Cr1	118.1(3)	C30	C25	C24	119.5(5)
Cr1	O2	Cr2	111.55(15)	C30	C25	C26	118.0(5)
C3	O2	Cr1	112.5(3)	O4	C26	C25	122.8(5)
C3	O2	Cr2	124.7(3)	O4	C26	C27	117.3(5)
C35	O3	Cr2	117.6(3)	C25	C26	C27	119.9(5)
C26	O4	Cr2	131.0(3)	C26	C27	C32	118.9(5)
C10	N1	Cr1	108.4(3)	C28	C27	C26	118.7(5)
C10	N1	C21	110.5(4)	C28	C27	C32	122.3(5)
C20	N1	Cr1	107.5(3)	C29	C28	C27	122.3(5)
C20	N1	C10	110.9(4)	C28	C29	C31	120.4(5)
C20	N1	C21	108.1(4)	C30	C29	C28	118.1(5)
C21	N1	Cr1	111.4(3)	C30	C29	C31	121.5(6)
C1	N2	Cr1	110.0(3)	C29	C30	C25	122.9(5)
C1	N2	C19	109.4(4)	N4	C33	C34	114.4(4)
C1	N2	C23	110.9(4)	C35	C34	C33	117.7(5)
C19	N2	Cr1	107.4(3)	C35	C34	C39	120.4(5)
C23	N2	Cr1	111.4(3)	C39	C34	C33	121.8(5)
C23	N2	C19	107.6(4)	O3	C35	C34	119.5(5)
C24	N3	Cr2	107.4(3)	O3	C35	C36	121.7(4)
C24	N3	C46	110.7(4)	C36	C35	C34	118.7(5)
C42	N3	Cr2	108.5(3)	C35	C36	C41	119.1(5)
C42	N3	C24	110.0(4)	C37	C36	C35	119.6(5)
C42	N3	C46	108.0(4)	C37	C36	C41	121.3(5)
C46	N3	Cr2	112.2(3)	C36	C37	C38	121.8(6)
C33	N4	Cr2	112.4(3)	C37	C38	C40	119.6(6)
C33	N4	C43	111.1(4)	C39	C38	C37	118.9(5)
C33	N4	C44	107.3(4)	C39	C38	C40	121.5(5)

C43	N4	Cr2	103.5(3)	C38	C39	C34	120.7(5)
C43	N4	C44	107.8(4)	N3	C42	C43	110.4(4)
C44	N4	Cr2	114.8(3)	N4	C43	C42	110.0(4)
N2	C1	C2	112.2(4)	C45	C44	N4	117.7(5)
C3	C2	C1	120.3(4)	C44	C45	C46	119.7(5)
C7	C2	C1	120.0(4)	N3	C46	C45	110.0(5)
C7	C2	C3	119.7(5)	Cl3	C47	Cl4	110.6(4)
O2	C3	C2	119.8(4)	Cl6 ¹	Cl6	C48	176.2(6)
O2	C3	C4	120.6(4)	Cl5	C48	Cl6	113.9(6)

¹ 2-X, -Y, 2-Z

Table S6: Bond lengths from structural data of **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	O1	2.003(2)	C3	C4	1.394(5)
Cr1	O1*	1.988(2)	C4	C5	1.385(5)
Cr1	O2	1.933(2)	C4	C9	1.511(5)
Cr1	O3	1.920(2)	C5	C6	1.382(4)
Cr1	N1	2.125(3)	C6	C7	1.418(4)
Cr1	N2	2.120(3)	C6	C8	1.498(5)
O2	C7	1.338(4)	C10	C11	1.520(4)
O3	C12	1.335(4)	C11	C12	1.415(4)
N1	C1	1.492(4)	C11	C16	1.396(4)
N1	C19	1.479(4)	C12	C13	1.414(4)
N1	C23	1.498(4)	C13	C14	1.390(4)
N2	C10	1.486(4)	C13	C17	1.506(4)
N2	C20	1.496(4)	C14	C15	1.398(4)
N2	C21	1.487(4)	C15	C16	1.386(5)
N3	C25	1.1623	C15	C18	1.506(4)
C25	C26	1.4533	C19	C20	1.536(4)
C1	C2	1.508(4)	C21	C22	1.520(4)
C2	C3	1.395(4)	C22	C23	1.529(5)
C2	C7	1.403(4)			

¹ 3/2-X, 3/2-Y, 3/2-Z

Table S7: Bond angles from structural data of **2**.

Atom	Atom	Atom	Angle/ [°]	Atom	Atom	Atom	Angle/ [°]
O1 ¹	Cr1	O1	77.17(10)	C3	C2	C7	120.0(3)
O1	Cr1	N1	95.03(9)	C7	C2	C1	118.4(3)
O1 ¹	Cr1	N1	170.23(9)	C4	C3	C2	121.6(3)
O1 ¹	Cr1	N2	99.99(9)	C3	C4	C9	121.8(3)

O1	Cr1	N2	97.52(9)	C5	C4	C3	117.2(3)
O2	Cr1	O1 ¹	94.57(9)	C5	C4	C9	121.0(3)
O2	Cr1	O1	90.41(9)	C6	C5	C4	123.7(3)
O2	Cr1	N1	91.33(9)	C5	C6	C7	118.4(3)
O2	Cr1	N2	164.64(9)	C5	C6	C8	122.3(3)
O3	Cr1	O1	169.49(9)	C7	C6	C8	119.2(3)
O3	Cr1	O1 ¹	92.44(9)	O2	C7	C2	120.4(3)
O3	Cr1	O2	92.02(9)	O2	C7	C6	120.5(3)
O3	Cr1	N1	95.13(9)	C2	C7	C6	119.1(3)
O3	Cr1	N2	82.57(9)	N2	C10	C11	113.0(2)
N2	Cr1	N1	74.94(10)	C12	C11	C10	123.2(3)
Cr1 ¹	O1	Cr1	102.83(10)	C16	C11	C10	117.4(3)
C7	O2	Cr1	114.82(18)	C16	C11	C12	119.2(3)
C12	O3	Cr1	125.21(18)	O3	C12	C11	124.0(3)
C1	N1	Cr1	112.61(18)	O3	C12	C13	117.6(3)
C1	N1	C23	107.3(2)	C13	C12	C11	118.4(3)
C19	N1	Cr1	105.53(18)	C12	C13	C17	118.3(3)
C19	N1	C1	110.4(2)	C14	C13	C12	120.0(3)
C19	N1	C23	110.3(2)	C14	C13	C17	121.7(3)
C23	N1	Cr1	110.71(18)	C13	C14	C15	122.3(3)
C10	N2	Cr1	109.24(18)	C14	C15	C18	121.9(3)
C10	N2	C20	110.2(2)	C16	C15	C14	117.0(3)
C10	N2	C21	109.4(2)	C16	C15	C18	121.1(3)
C20	N2	Cr1	107.78(17)	C15	C16	C11	123.0(3)
C21	N2	Cr1	110.79(18)	N1	C19	C20	110.3(2)
C21	N2	C20	109.5(2)	N2	C20	C19	110.6(2)
N3	C25	C26	180.0	N2	C21	C22	111.4(2)
N1	C1	C2	114.3(3)	C21	C22	C23	117.0(3)
C3	C2	C1	121.5(3)	N1	C23	C22	115.0(3)

¹ 3/2-X, 3/2-Y, 3/2-Z

Table S8: Bond lengths from structural data of **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	O1	1.944(5)	C10	C11	1.473(9)
Cr1	O2	1.946(4)	C11	C12	1.400(9)
Cr1	O3	2.036(4)	C11	C16	1.408(9)
Cr1	N1	2.085(5)	C12	C13	1.412(9)
Cr1	N2	2.104(6)	C13	C14	1.390(10)
Cr1	N3	2.007(6)	C13	C18	1.457(10)
O1	C7	1.346(7)	C14	C15	1.378(10)
O2	C12	1.342(8)	C15	C16	1.379(10)

N1	C1	1.485(8)	C15	C17	1.513(10)
N1	C20	1.506(8)	C19	C20	1.521(9)
N1	C21	1.477(8)	C21	C22	1.520(9)
N2	C10	1.500(8)	C22	C23	1.518(9)
N2	C19	1.506(8)	C13	C25	1.779(13)
N2	C23	1.477(8)	C13	C15	2.216(13)
N3	N4	1.158(7)	C14	C25	1.744(16)
N4	N5	1.177(8)	C14	C16	2.339(9)
C1	C2	1.475(9)	C14	C15	0.967(12)
C2	C3	1.389(9)	C14	C26	1.62(3)
C2	C7	1.400(9)	C25	C15	1.536(18)
C3	C4	1.361(10)	C25	C26	0.71(2)
C4	C5	1.392(10)	C11	C24	1.760(8)
C4	C8	1.516(9)	C12	C24	1.704(9)
C5	C6	1.367(9)	C16	C26	1.67(3)
C6	C7	1.404(9)	C15	C26	1.70(3)
C6	C9	1.509(9)			

Table S9: Bond angles from structural data of **3**.

Atom	Atom	Atom	Angle/ [°]	Atom	Atom	Atom	Angle/ [°]
O1	Cr1	O2	95.94(18)	C12	C11	C10	120.0(7)
O1	Cr1	O3	87.15(18)	C12	C11	C16	118.8(6)
O1	Cr1	N1	93.8(2)	C16	C11	C10	121.0(6)
O1	Cr1	N2	169.6(2)	O2	C12	C11	119.9(6)
O1	Cr1	N3	90.3(2)	O2	C12	C13	119.9(6)
O2	Cr1	O3	86.15(18)	C11	C12	C13	120.2(7)
O2	Cr1	N1	169.0(2)	C12	C13	C18	119.8(6)
O2	Cr1	N2	93.8(2)	C14	C13	C12	117.7(7)
O2	Cr1	N3	90.8(2)	C14	C13	C18	122.5(6)
O3	Cr1	N1	89.20(19)	C15	C14	C13	123.6(7)
O3	Cr1	N2	89.9(2)	C14	C15	C16	117.8(7)
N1	Cr1	N2	76.2(2)	C14	C15	C17	119.7(7)
N3	Cr1	O3	175.8(2)	C16	C15	C17	122.5(7)
N3	Cr1	N1	94.3(2)	C15	C16	C11	121.8(7)
N3	Cr1	N2	93.2(2)	N2	C19	C20	110.9(5)
C7	O1	Cr1	121.6(4)	N1	C20	C19	110.4(5)
C12	O2	Cr1	120.7(4)	N1	C21	C22	112.9(5)
C1	N1	Cr1	110.7(4)	C23	C22	C21	117.3(6)
C1	N1	C20	109.2(5)	N2	C23	C22	113.2(6)
C20	N1	Cr1	106.2(4)	C25	C13	C15	43.5(5)

C21	N1	Cr1	112.3(4)	C25	Cl4	Cl6	69.3(5)
C21	N1	C1	109.6(5)	Cl5	Cl4	C25	61.4(8)
C21	N1	C20	108.9(5)	Cl5	Cl4	Cl6	115.7(8)
C10	N2	Cr1	109.8(4)	Cl5	Cl4	C26	77.5(13)
C10	N2	C19	110.2(5)	C26	Cl4	C25	24.0(9)
C19	N2	Cr1	105.7(4)	C26	Cl4	Cl6	45.7(10)
C23	N2	Cr1	111.3(4)	Cl4	C25	Cl3	110.1(9)
C23	N2	C10	110.9(5)	Cl5	C25	Cl3	83.6(8)
C23	N2	C19	108.8(5)	Cl5	C25	Cl4	33.5(5)
N4	N3	Cr1	122.0(5)	C26	C25	Cl3	169(4)
N3	N4	N5	175.2(7)	C26	C25	Cl4	68(3)
C2	C1	N1	114.2(6)	C26	C25	Cl5	90(3)
C3	C2	C1	121.4(6)	Cl2	C24	Cl1	113.2(5)
C3	C2	C7	118.2(7)	C26	Cl6	Cl4	43.8(11)
C7	C2	C1	119.9(6)	Cl4	Cl5	Cl3	125.5(10)
C4	C3	C2	123.4(7)	Cl4	Cl5	C25	85.1(9)
C3	C4	C5	117.3(7)	Cl4	Cl5	C26	68.7(13)
C3	C4	C8	121.1(7)	C25	Cl5	Cl3	52.9(6)
C5	C4	C8	121.5(7)	C25	Cl5	C26	24.7(9)
C6	C5	C4	122.1(7)	C26	Cl5	Cl3	77.4(10)
C5	C6	C7	119.6(7)	Cl4	C26	Cl6	90.5(16)
C5	C6	C9	120.7(7)	Cl4	C26	Cl5	33.8(7)
C7	C6	C9	119.7(6)	C25	C26	Cl4	88(4)
O1	C7	C2	120.0(6)	C25	C26	Cl6	168(5)
O1	C7	C6	120.6(6)	C25	C26	Cl5	65(3)
C2	C7	C6	119.4(6)	Cl6	C26	Cl5	118.2(19)
C11	C10	N2	114.9(6)				

Spectroscopic Data

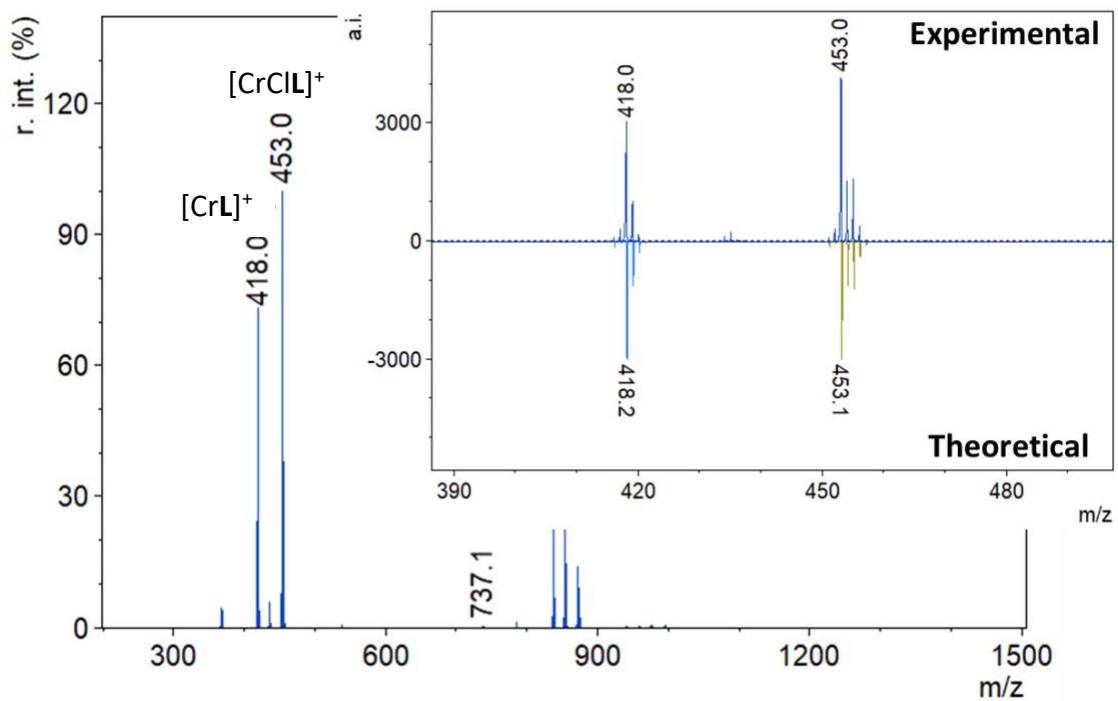


Figure S1: MALDI-TOF mass spectrum of **1** in positive reflectron mode showing complex monomeric fragments.

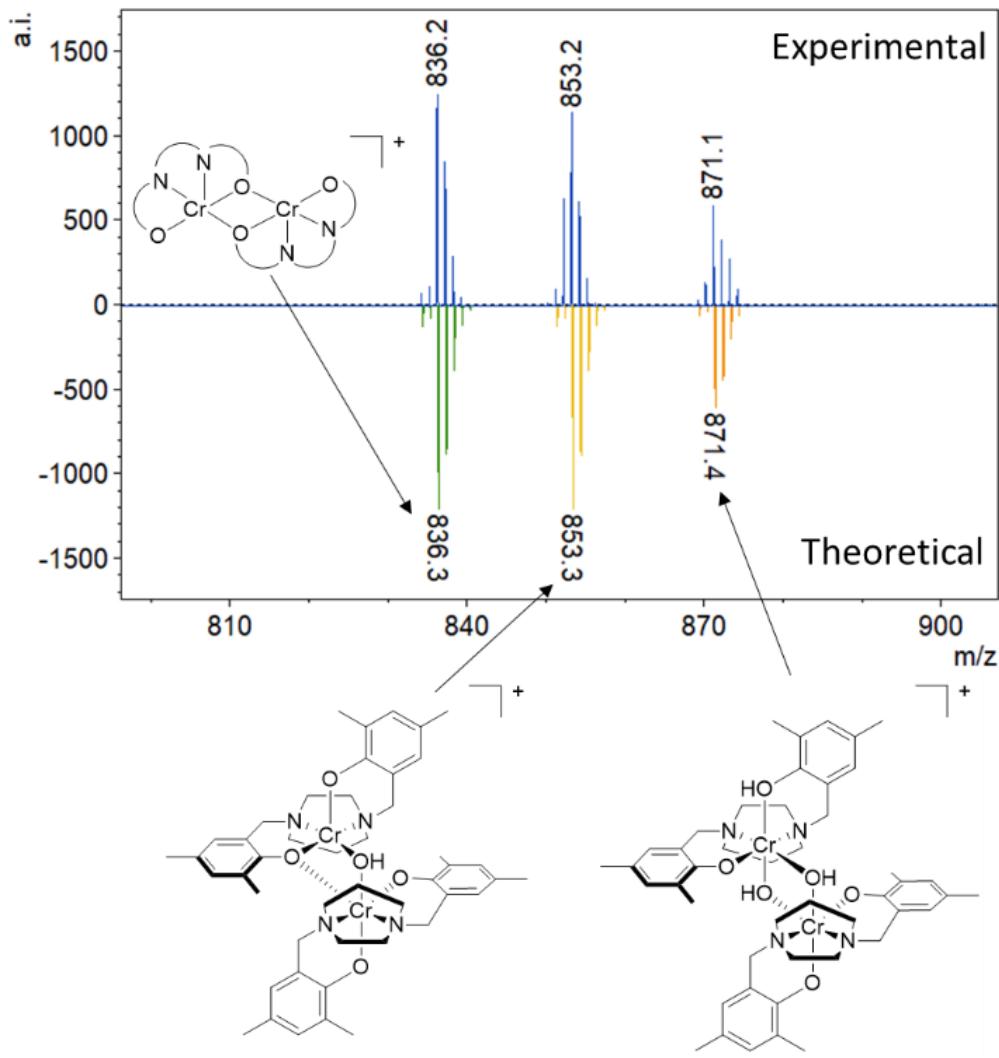


Figure S2: MALDI-TOF mass spectrum of **1** collected in positive reflectron mode, showing higher mass region and proposed Cr(III) complex fragments. The isotopic patterns of the experimental and theoretical distributions are in good agreement with each other for $[Cr_2L_2]^+$. The isotopic patterns at m/z 853.2 and 871.1 correspond to two overlapping ions. For m/z 853.2, the pattern corresponds to $[Cr_2L_2O + H]^+$ (shown) and $[Cr_2L_2O]^+$. For m/z 871.1, the pattern corresponds to $[Cr_2L_2(OH)_2 + H]^+$ and $[Cr_2L_2(OH)_2]^+$ (shown). The observed C, H, and N percentages for crude **1** that was analyzed by MALDI-TOF MS can be rationalized by incorporating co-crystallized solvent to the formula for **1** or by incorporating a mixture of **1** and **2**. The experimental percentage found for crude product gave C 62.66%, H 7.10% and N 6.41%, which can be closely matched for a mixture containing 40% **1** with 60% **2**, giving C 62.67%, H 7.02% and N 6.36%. Thus, when exposed to air the product is obtained as a mixture of the two derivatives that can be isolated by crystallization.

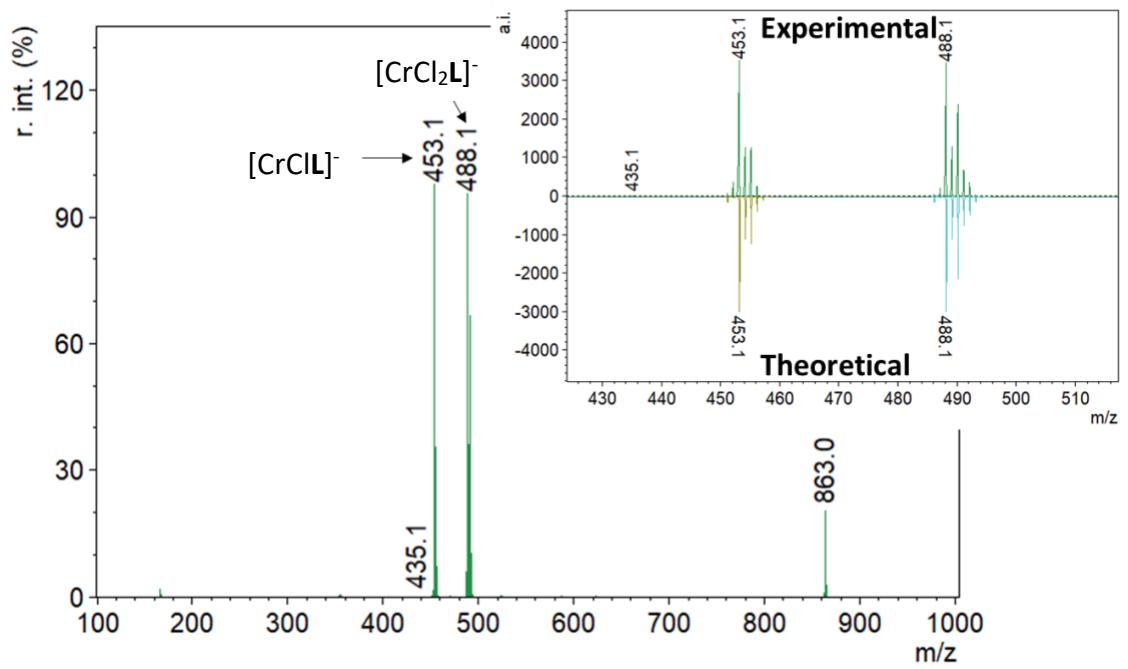


Figure S3: MALDI-TOF mass spectrum of **1** in negative reflectron mode.

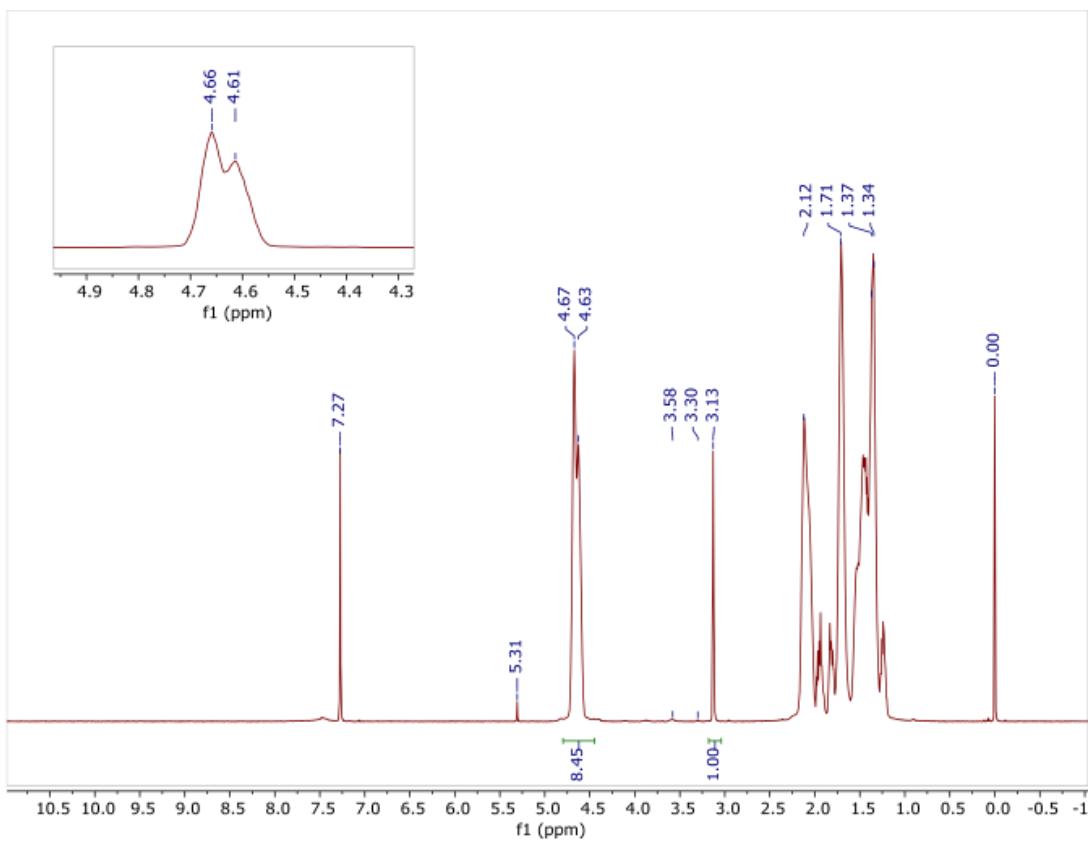


Figure S4: Representative crude ¹H NMR spectrum of PCHC in CDCl₃ from Table 1, entry 1 with enlarged area showing characteristic polymer signal (4.66 and 4.61 ppm).

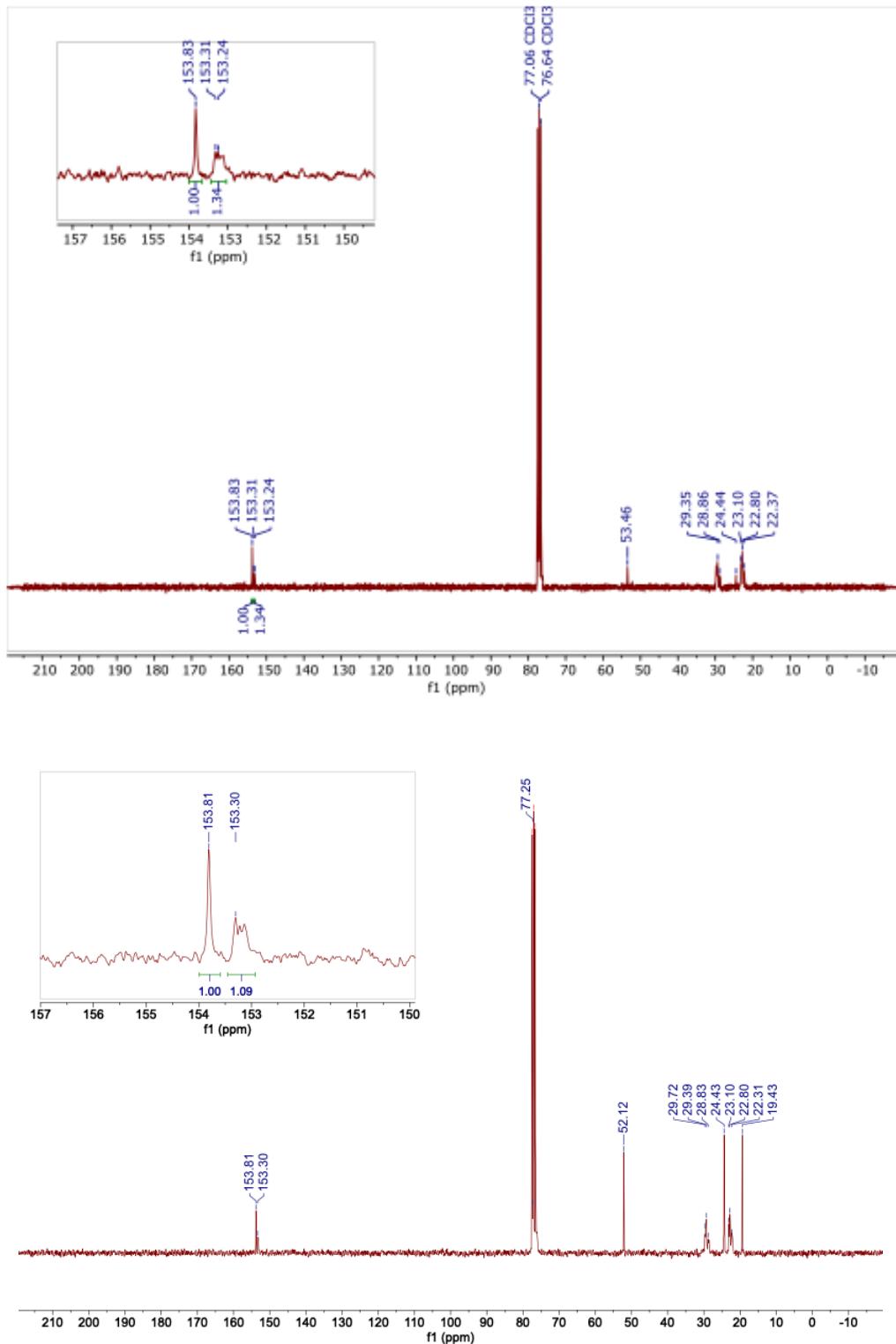


Figure S5: Representative crude ^{13}C NMR spectrum of PCHC in CDCl_3 from Table 1, entry 1 (top) and entry 7 (bottom) with insets showing characteristic polymer syndiotactic (153.1 ppm) and isotactic diads (153.8 ppm).

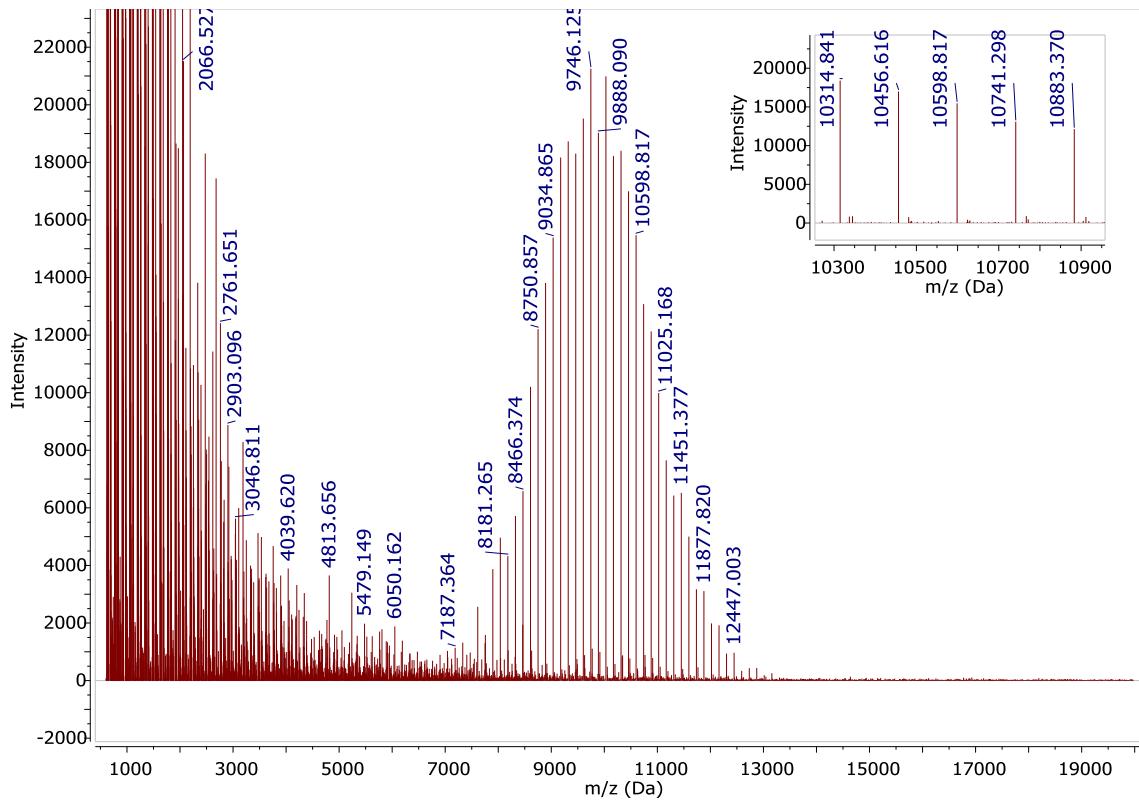


Figure S6: MALDI-TOF mass spectrum of polycarbonate obtained from Table 1, entry 2.

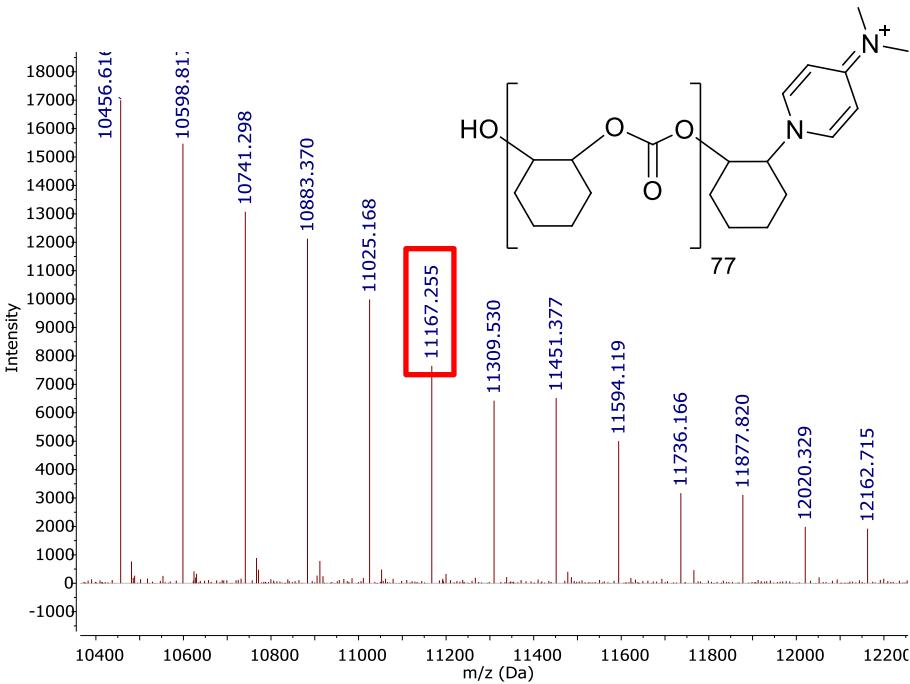


Figure S7: Magnified MALDI-TOF mass spectrum (higher mass region, m/z 10350 – 12250) of PCHC obtained from Table 1, entry 2. Proposed polymer structure shown.

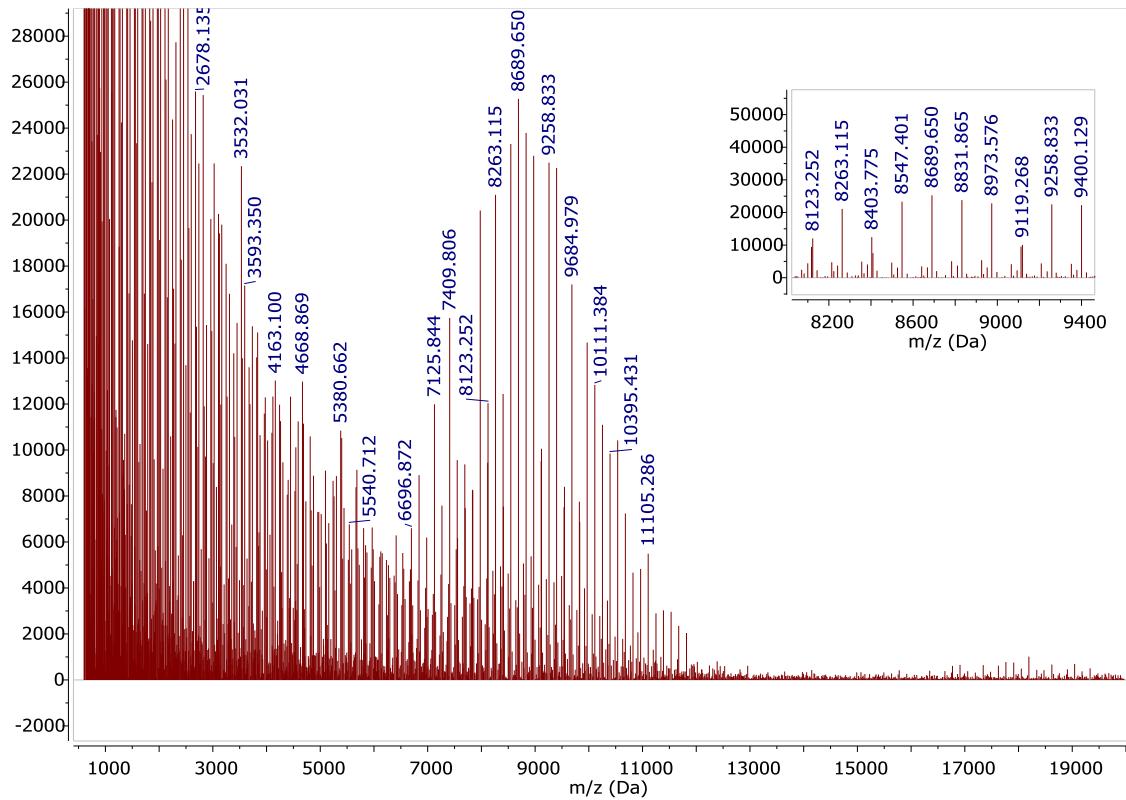


Figure S8: MALDI-TOF mass spectrum of polycarbonate obtained from Table 1 entry 3.

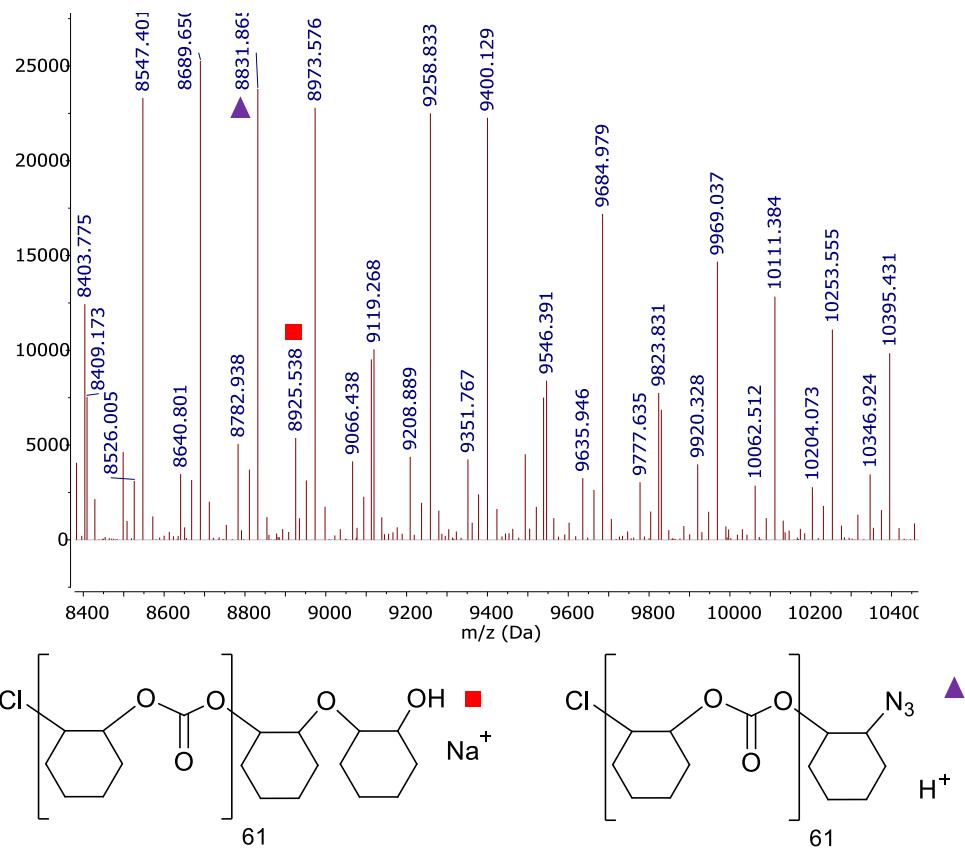


Figure S9: Magnified MALDI-TOF mass spectrum (higher mass region, m/z 8040 – 10250) of PCHC obtained from Table 1, entry 3. Proposed polymer structures shown.

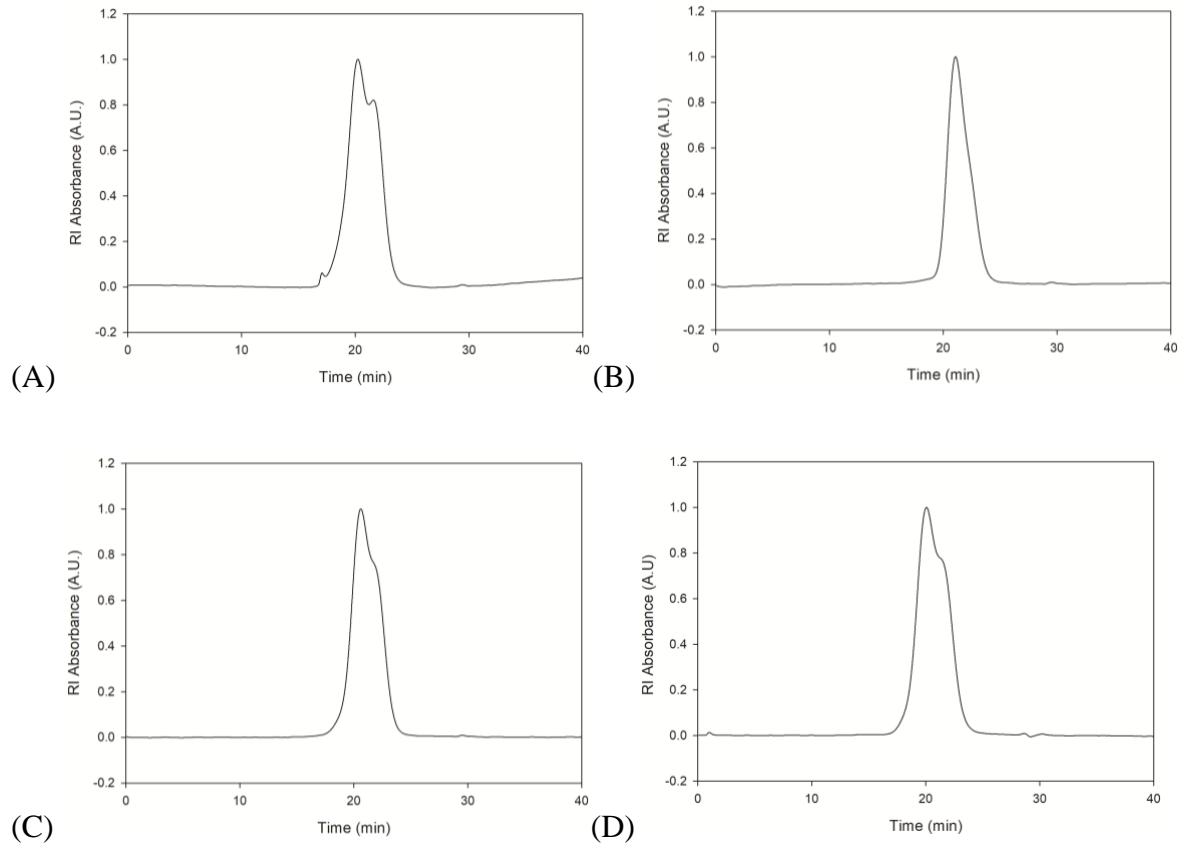


Figure S10: GPC chromatograms (from refractive index) for polymers obtained under conditions shown in Table 1, entry 1 (A), entry 2 (B), entry 3 (C) and entry 7 (D).