Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Dinuclear Chromium Complexes with [OSSO]-type ligands in the copolymerization of epoxides with CO_2 and with phthalic anhydride

Fatemeh Niknam, Alina Denk, Antonio Buonerba, Bernhard Rieger, Alfonso Grassi, Carmine Capacchione

Table of Contents

NMR Characterization

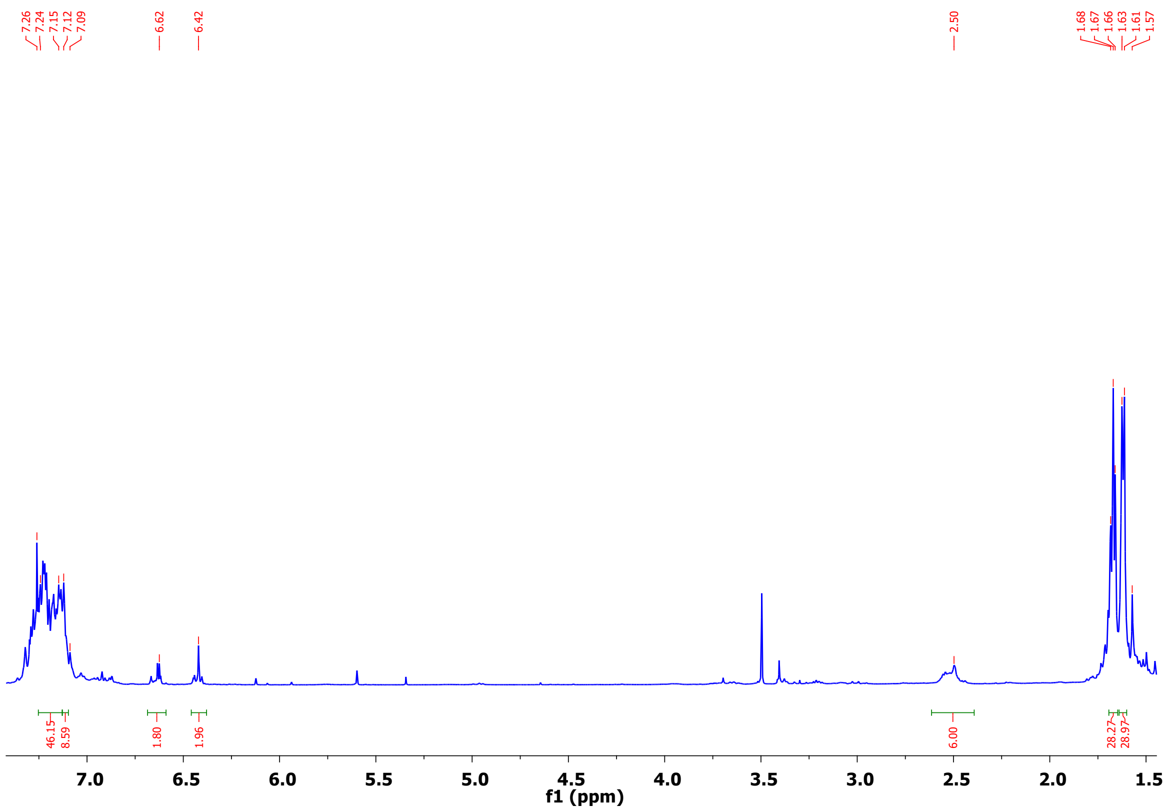


Figure S1. ^{1}H NMR spectrum of pro-ligand **L2** ($CDCl_3$, 600 MHz)

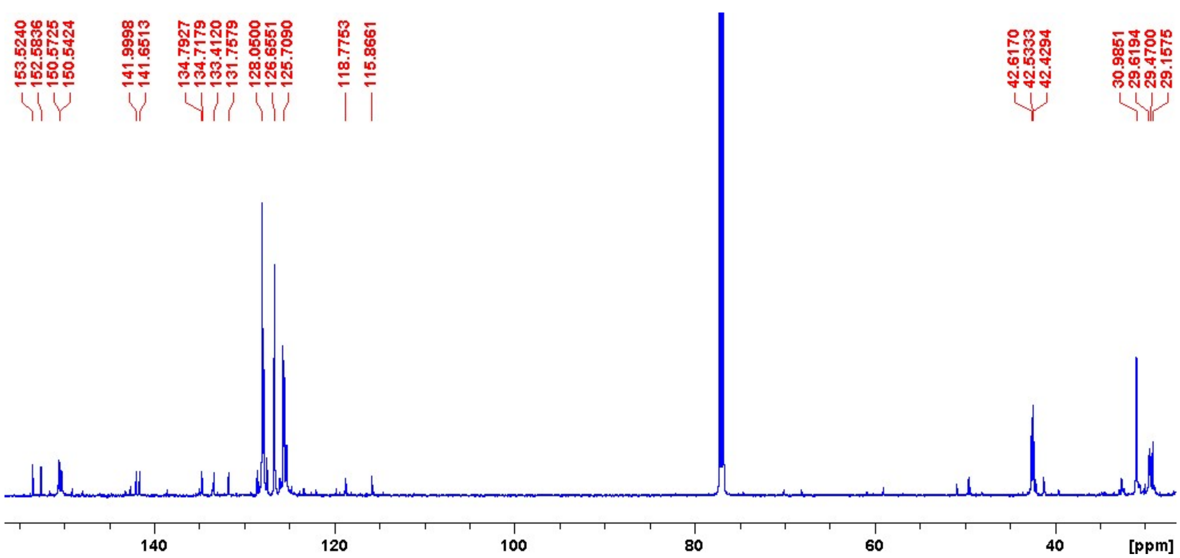


Figure S2. $^{13}C\{^{1}H\}$NMR spectrum of pro-ligand **L2** ($CDCl_3$, 600 MHz)

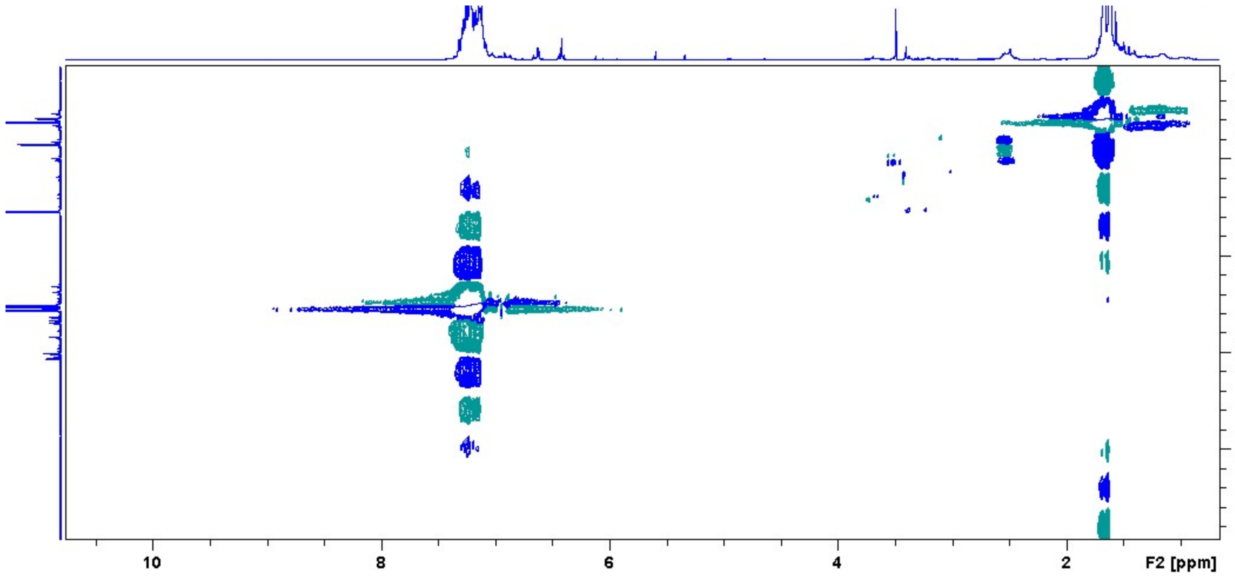


Figure S3. HSQC NMR spectrum of pro-ligand **L2** ($CDCl_3$, 600 MHz)

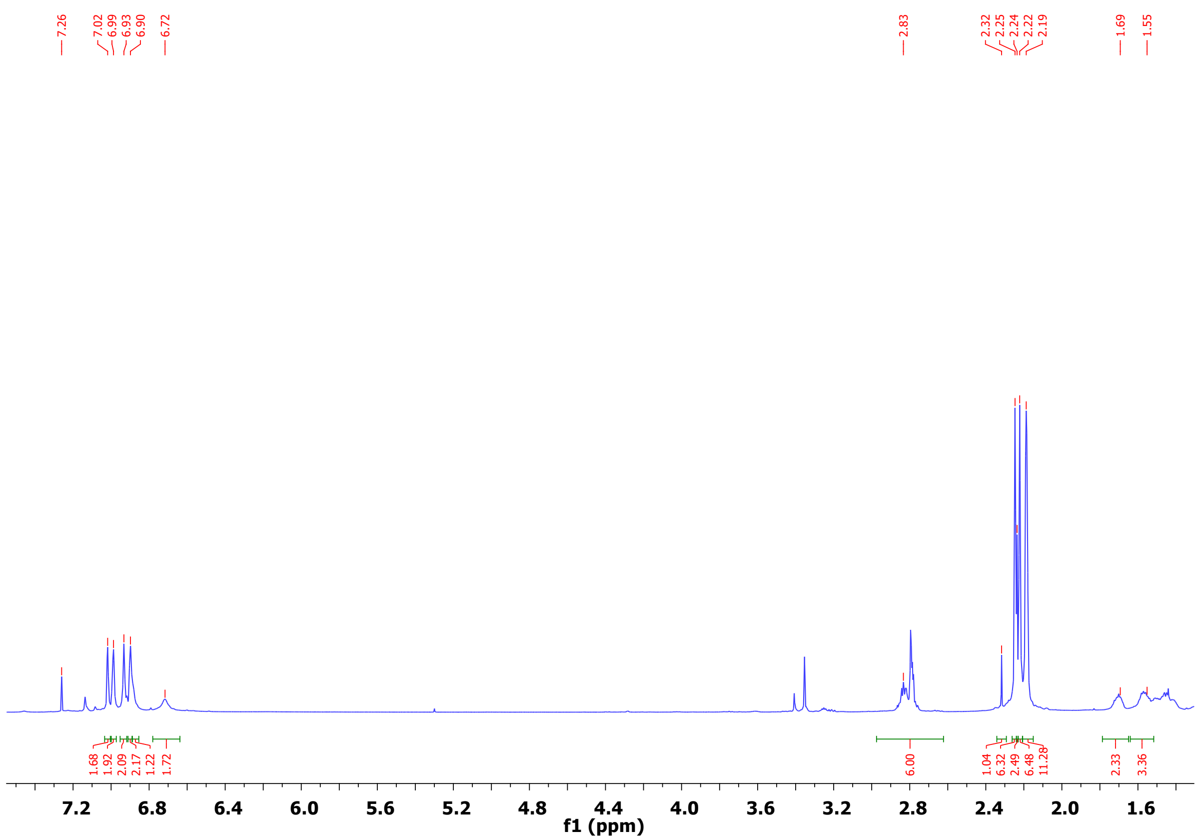


Figure S4. ^{1}H NMR spectrum of pro-ligand **L3** ($CDCl_3$, 600 MHz)

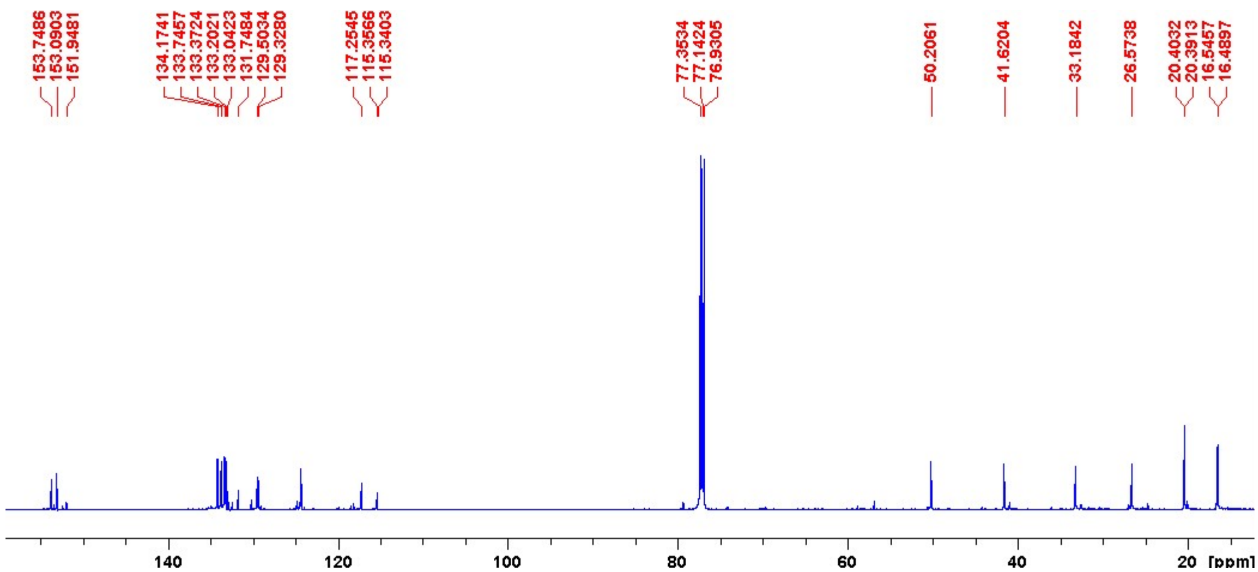


Figure S5. ^{13}C NMR spectrum of pro-ligand **L3** ($CDCl_3$, 600 MHz)

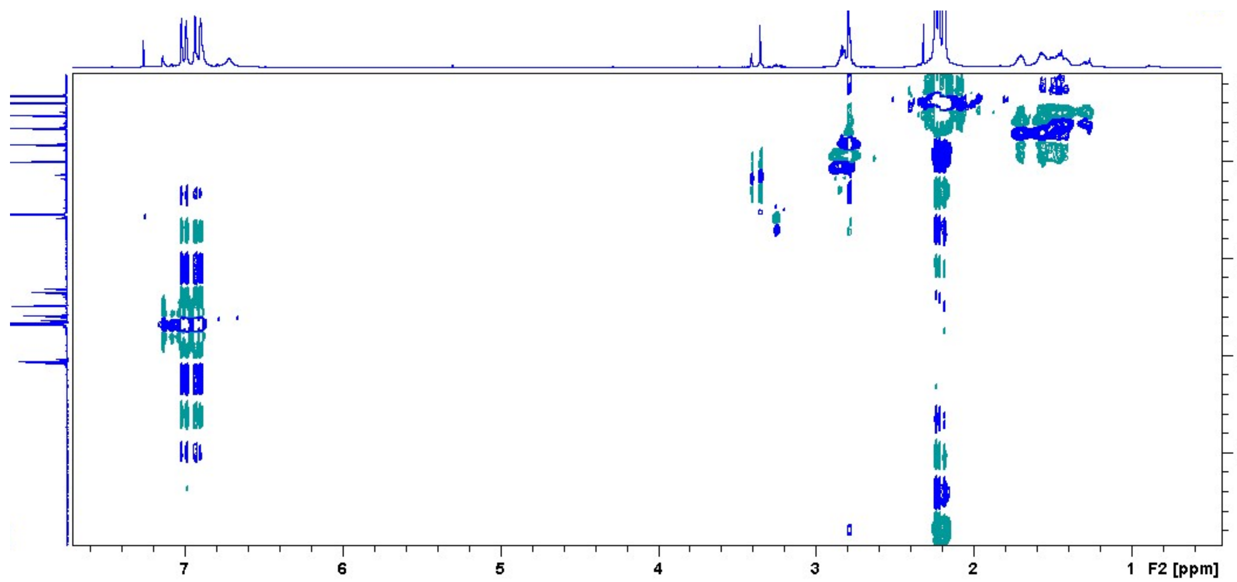


Figure S6. HSQC NMR spectrum of pro-ligand **L3** ($CDCl_3$, 600 MHz)

Mass Spectroscopy

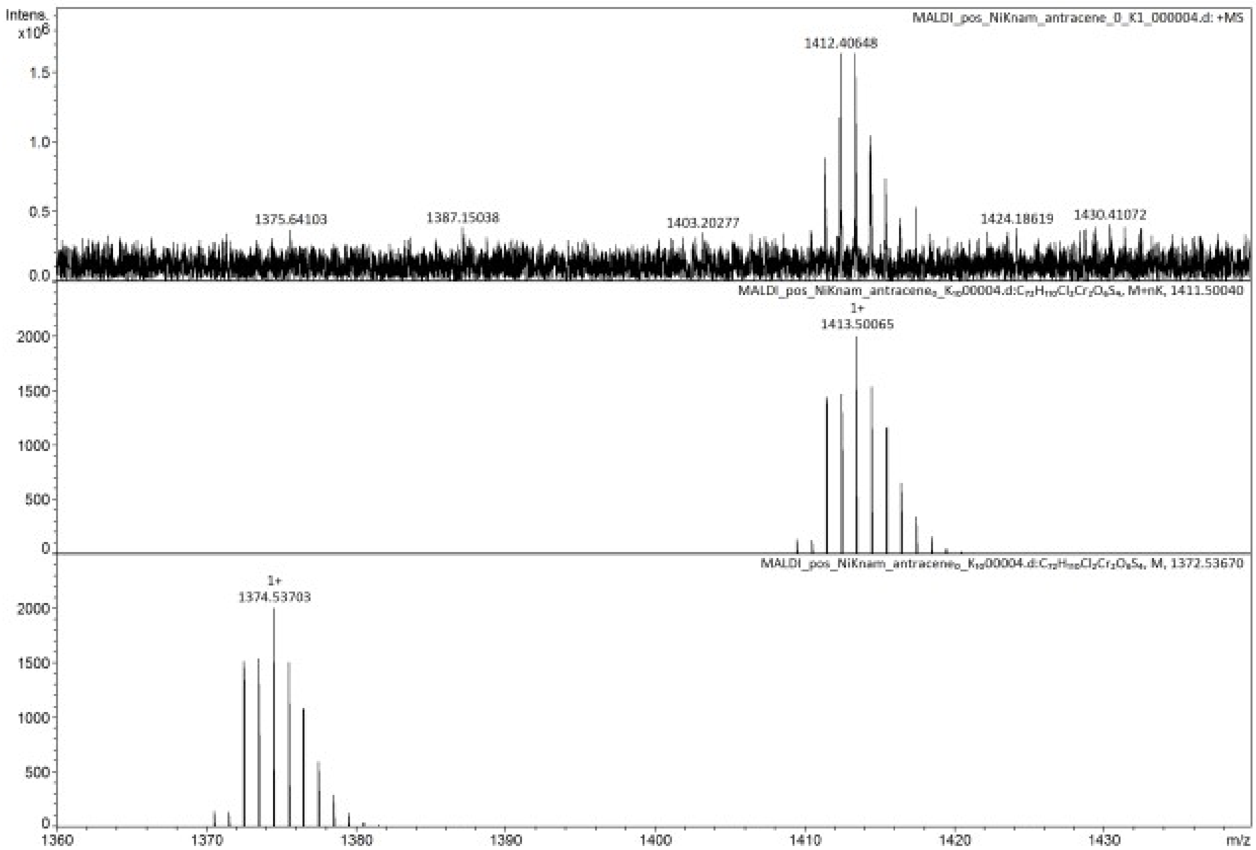


Figure S7. Mass spectrum of **1**: experimental (top), (**1**+K)$^+$calctd (middle), (**1**+H)$^+$ calctd (bottom)

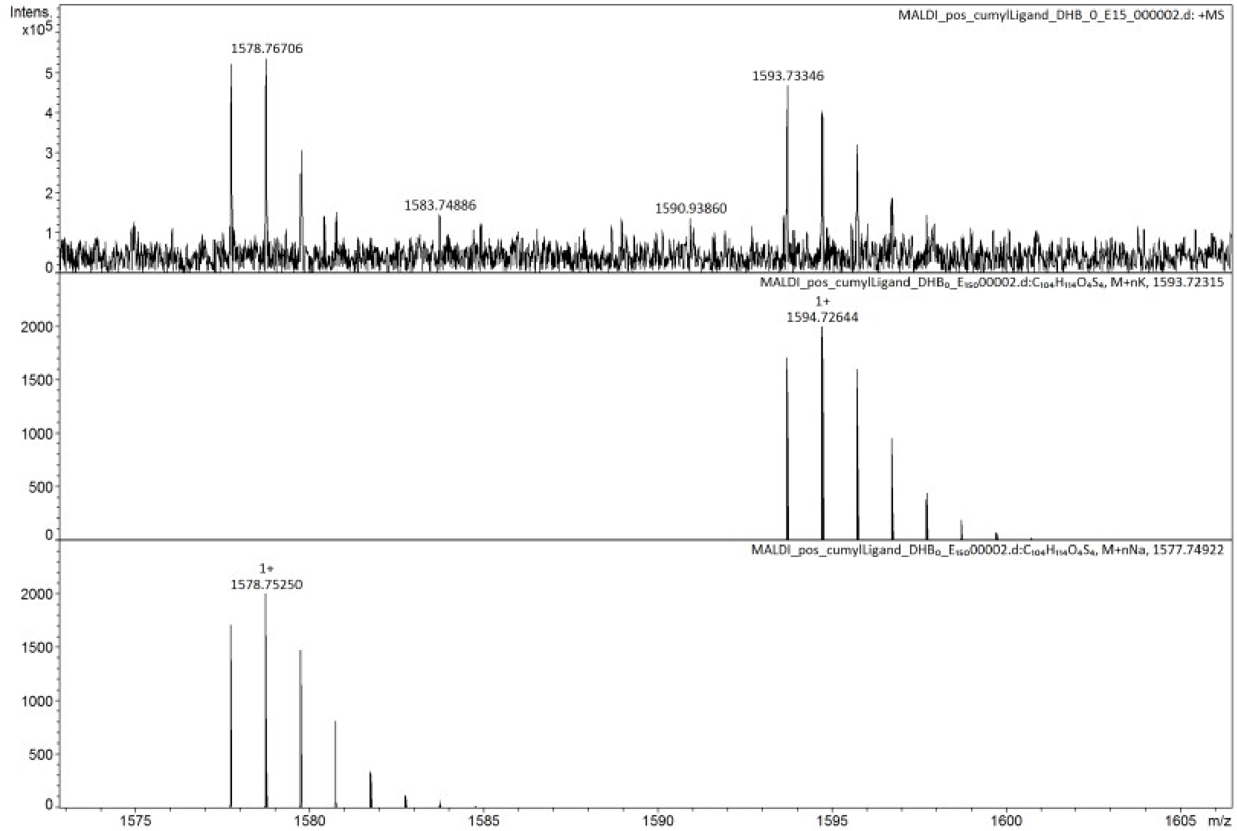


Figure S8. Mass spectrum of pro-ligand **L2**: experimental (top), (**L2**+K)$^+$calctd. (middle), (**L2**+Na)$^+$ calctd. (bottom)

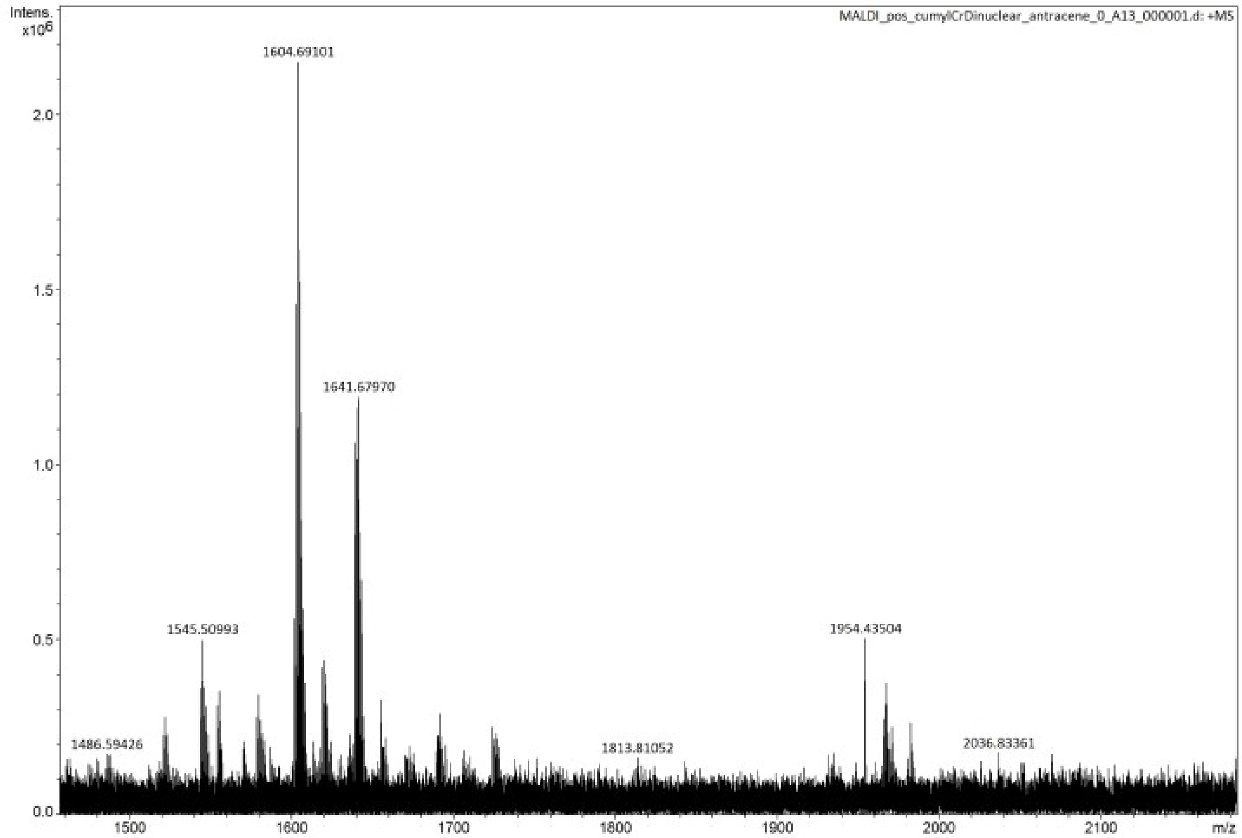


Figure S9. Mass experimental spectrum of Cr-complex **2**

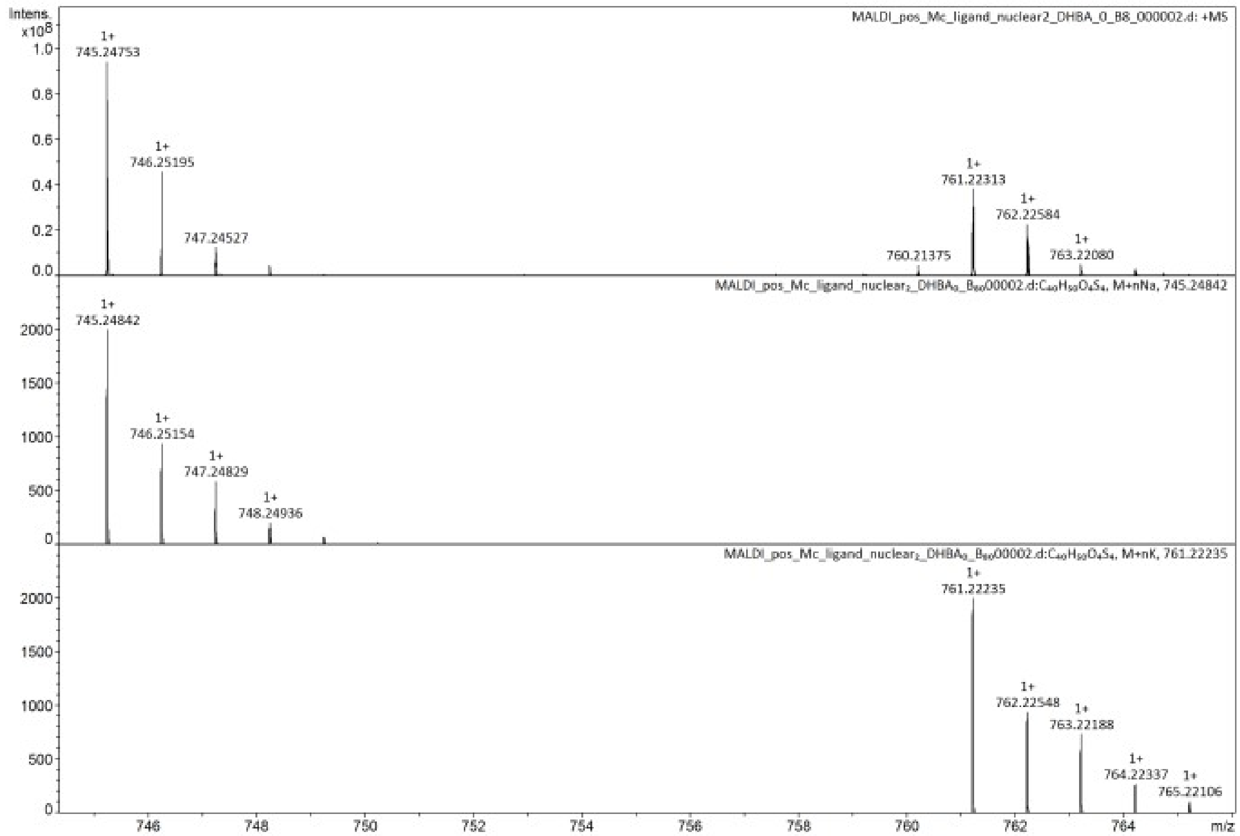


Figure S10. Mass spectrum of pro-ligand **L3**: experimental (top), (**L3**+Na)$^+$calctd. (middle), (**L3**+K)$^+$ calctd. (bottom)

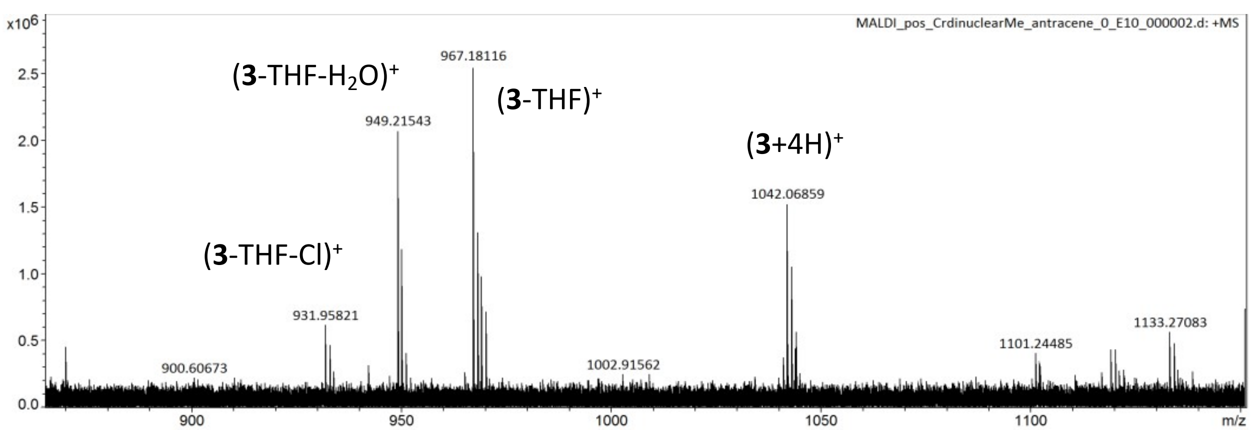


Figure S11. Mass experimental spectrum of Cr-complex **3**

FT-IR Analysis

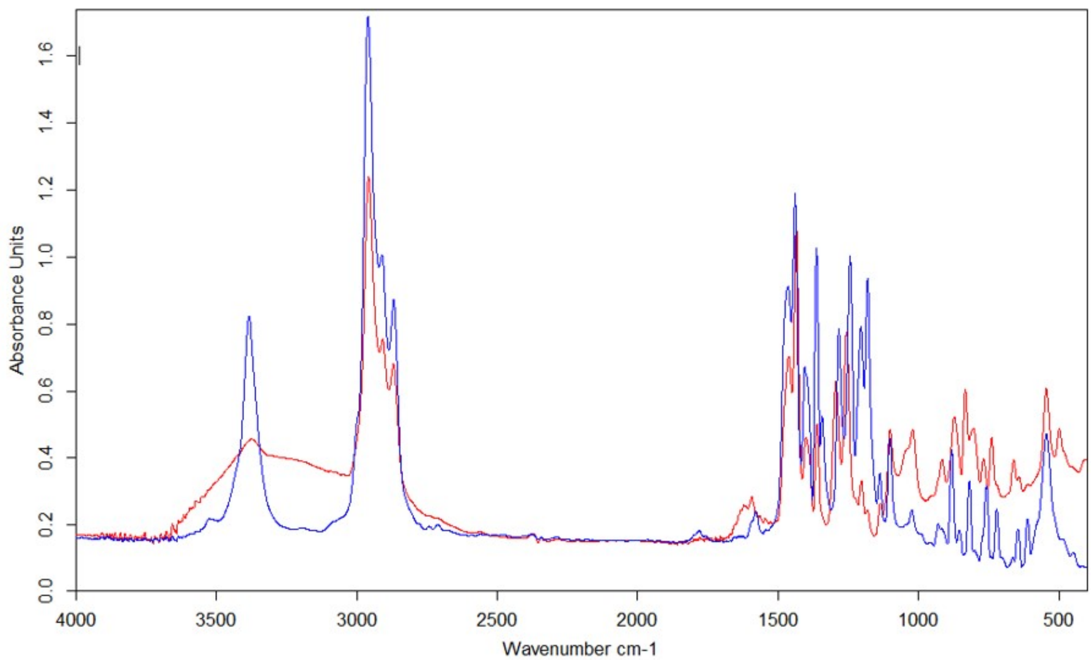


Figure S12. FT-IR pectrum of pro-ligand **L1** (blue) and **1** (red) (KBr disk)

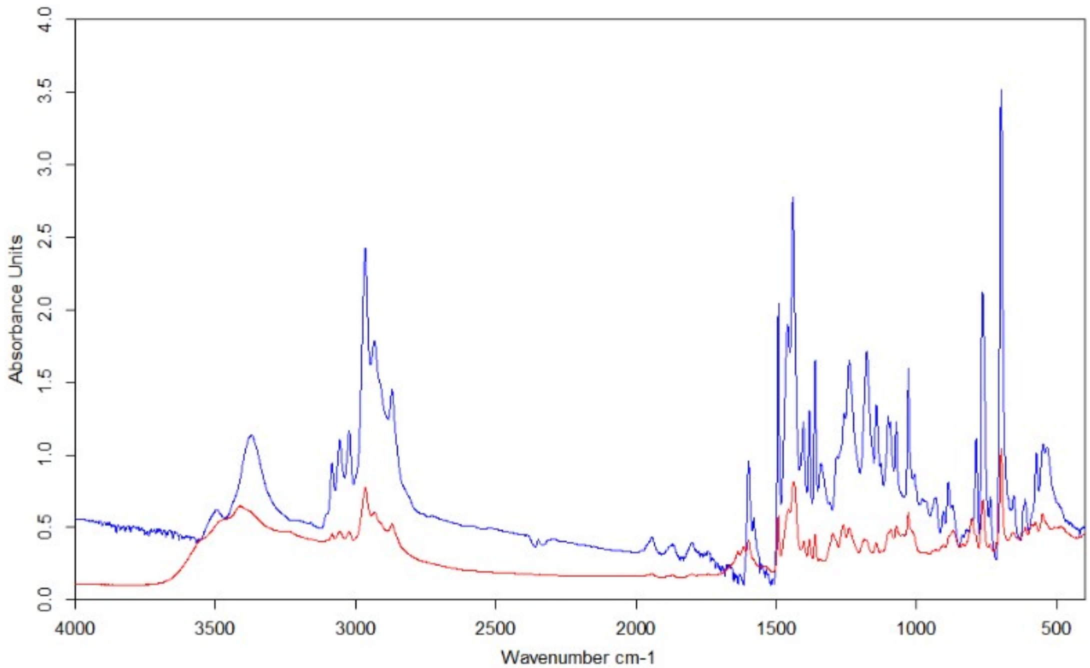


Figure S13. FT-IR spectrum of pro-ligand **L2** (blue) and **2** (red) (KBr disk)

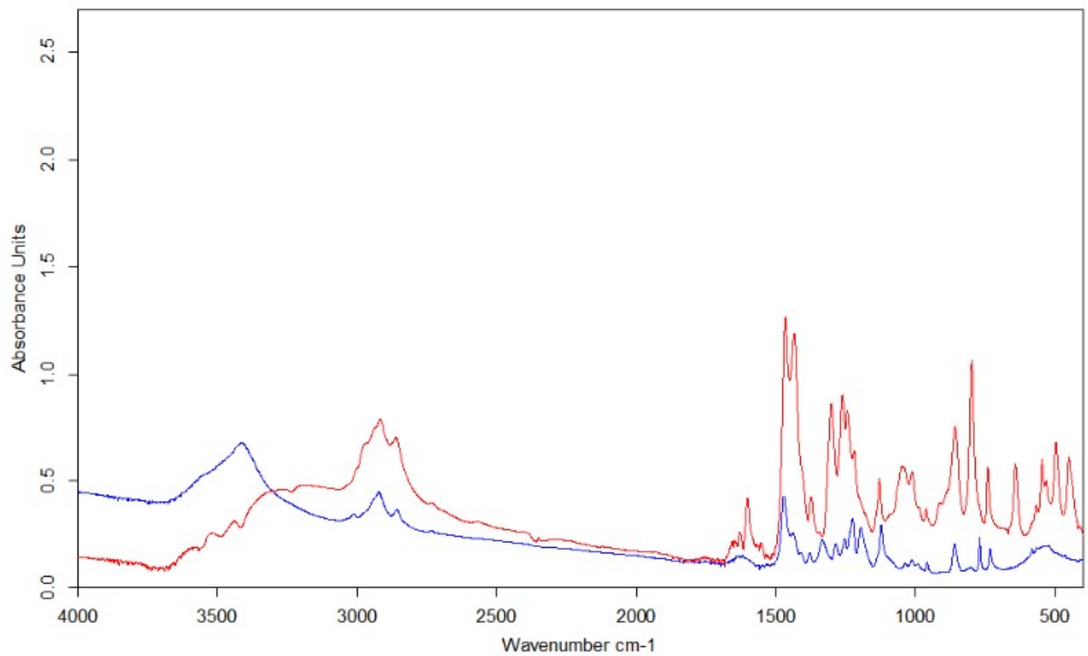
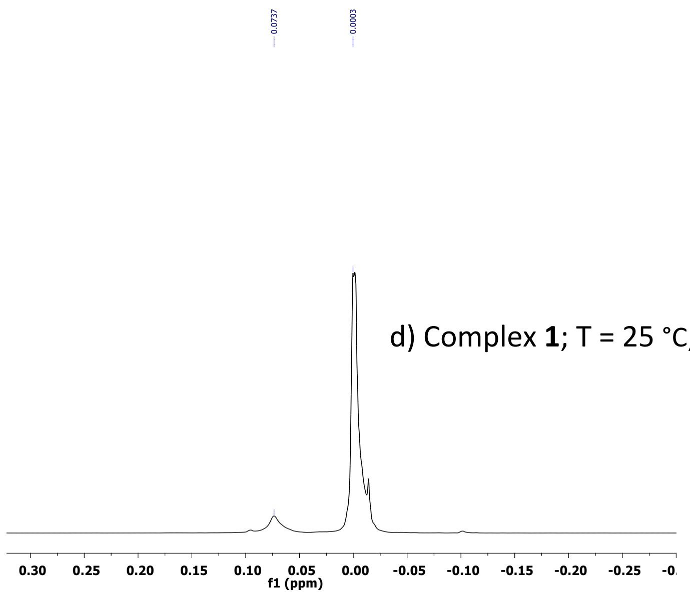
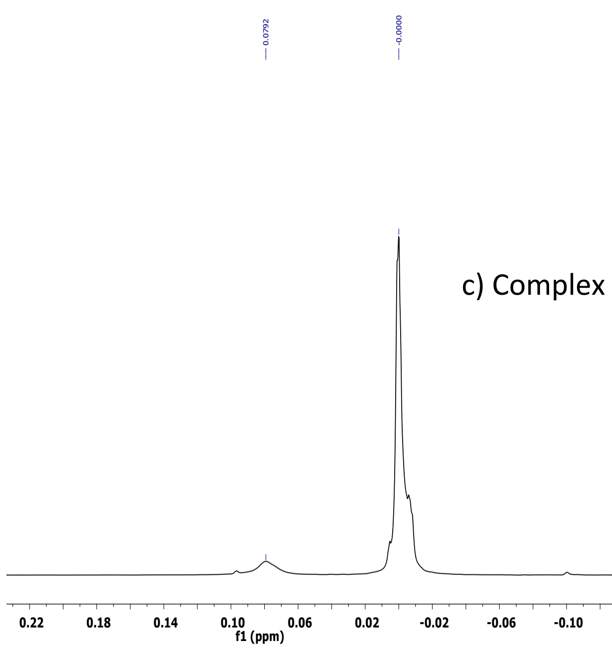


Figure S14. FT-IR spectrum of pro-ligand **L3** (blue) and **3** (red) (KBr disk)

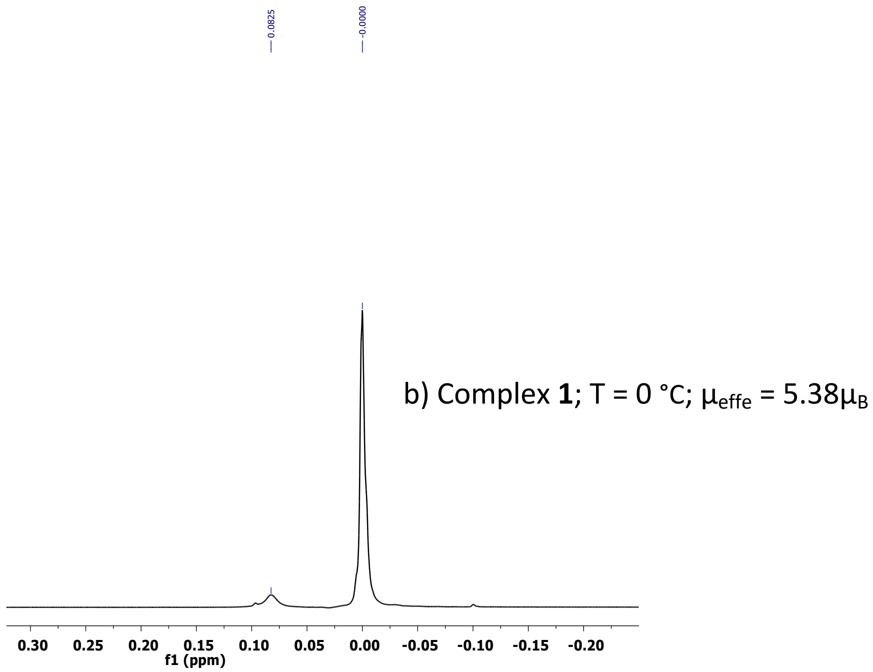
Evans Method Analysis



d) Complex **1**; T = 25 °C; μ_{effe} = 5.45μ_B



c) Complex **1**; T = 10 °C; μ_{effe} = 5.44μ_B



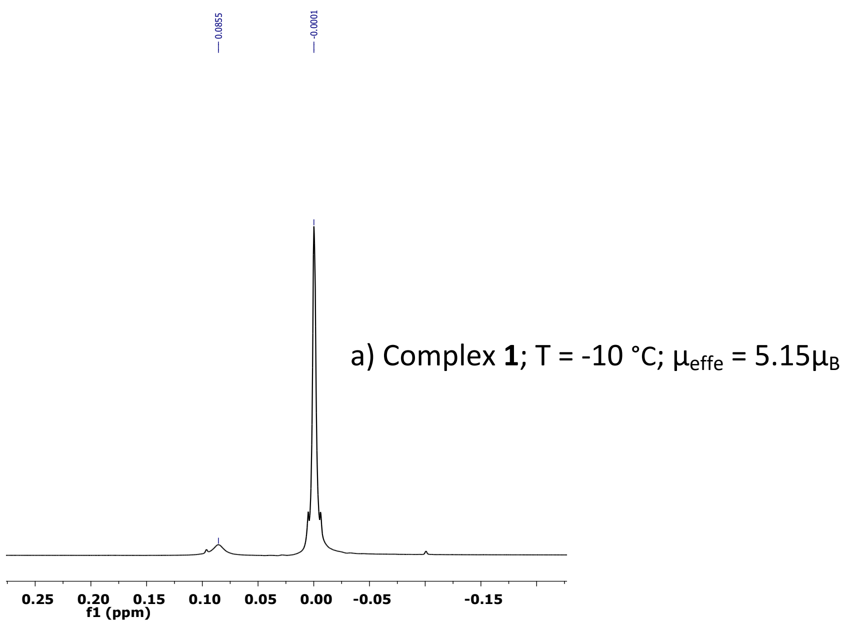
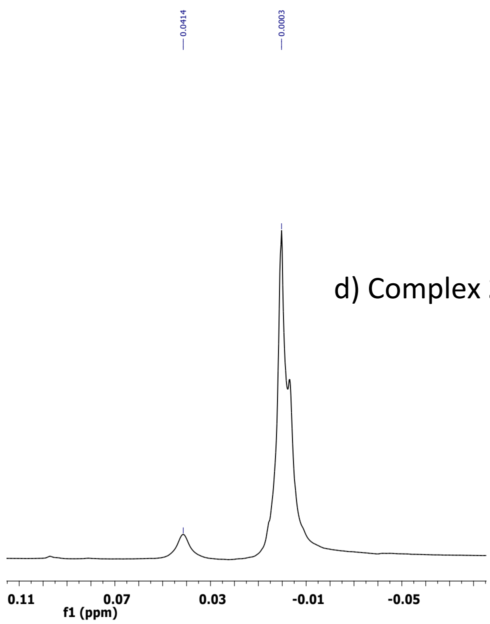
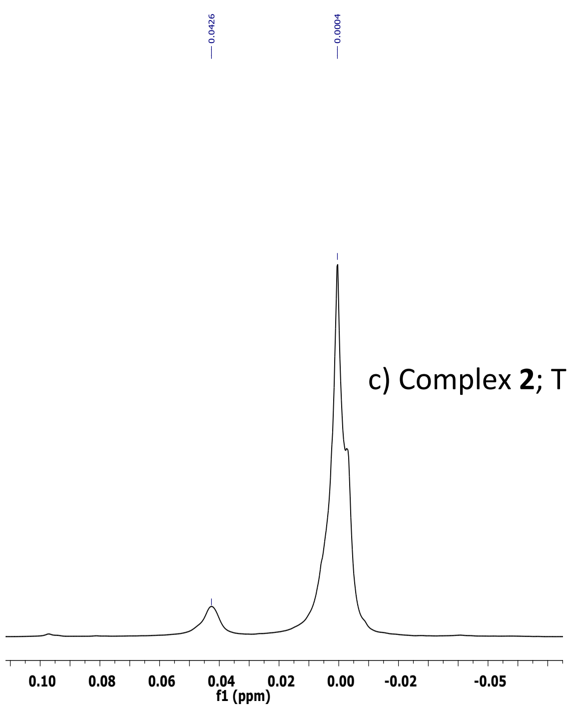


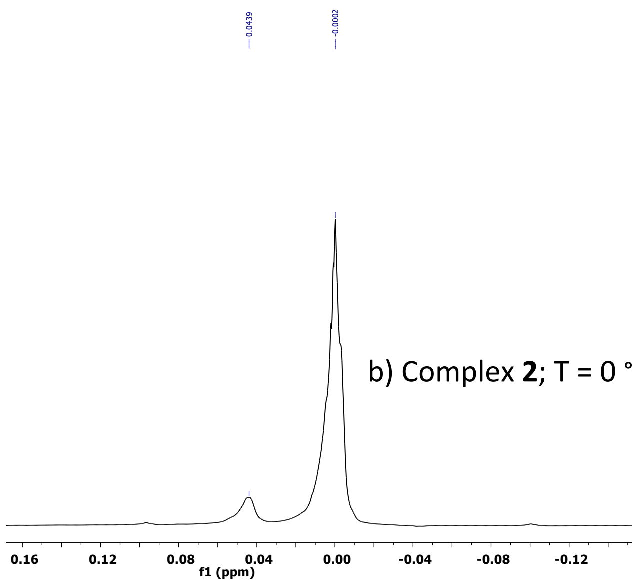
Figure S15. Plot of the ^{1}H-NMR spectra of the chromium(III) complex **1** (1.45 mM in DCM-d2) at different temperatures, for the determination of the solution magnetic susceptibility (μ_{eff}) by means of the method of Evans. a) -10 °C; b) 0 °C; c) 10 °C; d) 25 °C.



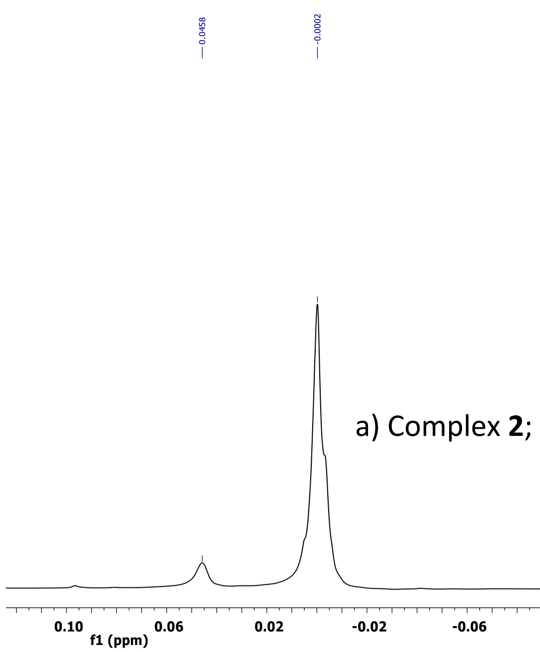
d) Complex **2**; T = 25 °C; μ_{effe} = 4.69μ_B



c) Complex **2**; T = 10 °C; μ_{effe} = 4.68μ_B

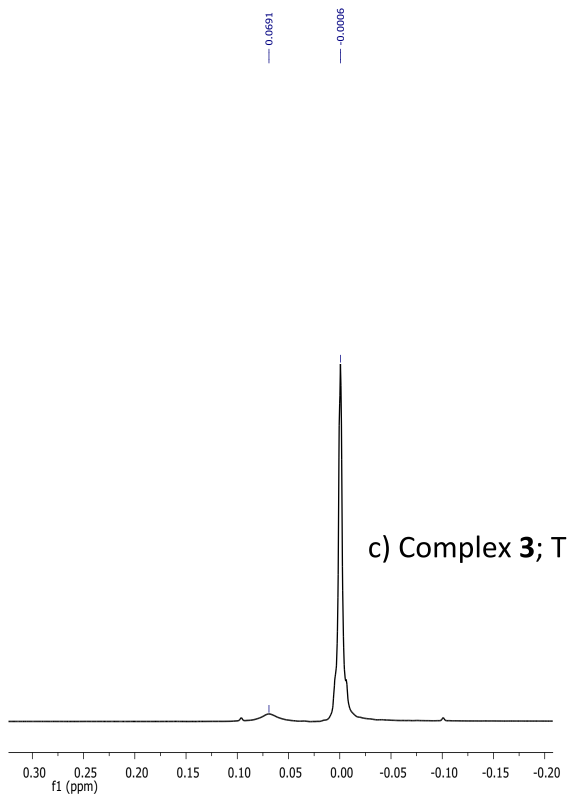


b) Complex **2**; T = 0 °C; μ_{effe} = 4.65μ_B

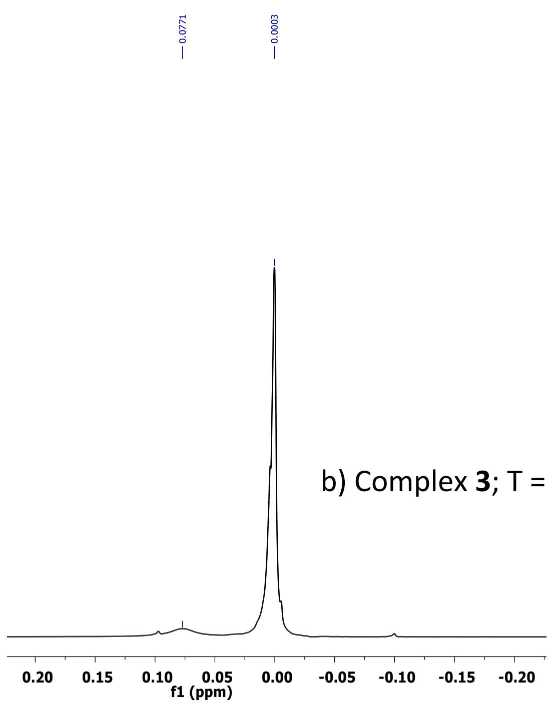


a) Complex **2**; T = -10 °C; μ_{effe} = 4.63μ_B

Figure S16. Plot of the ^{1}H-NMR spectra of the chromium(III) complex **2** (1.07 mM in DCM-d2) at different temperatures, for the determination of the solution magnetic susceptibility (μ_{eff}) by means of the method of Evans. a) -10 °C; b) 0 °C; c) 10 °C; d) 25 °C.



c) Complex **3**; T = 25 °C; μ_{effe} = 4.57μ_B



b) Complex **3**; T = 0 °C; μ_{effe} = 4.59μ_B

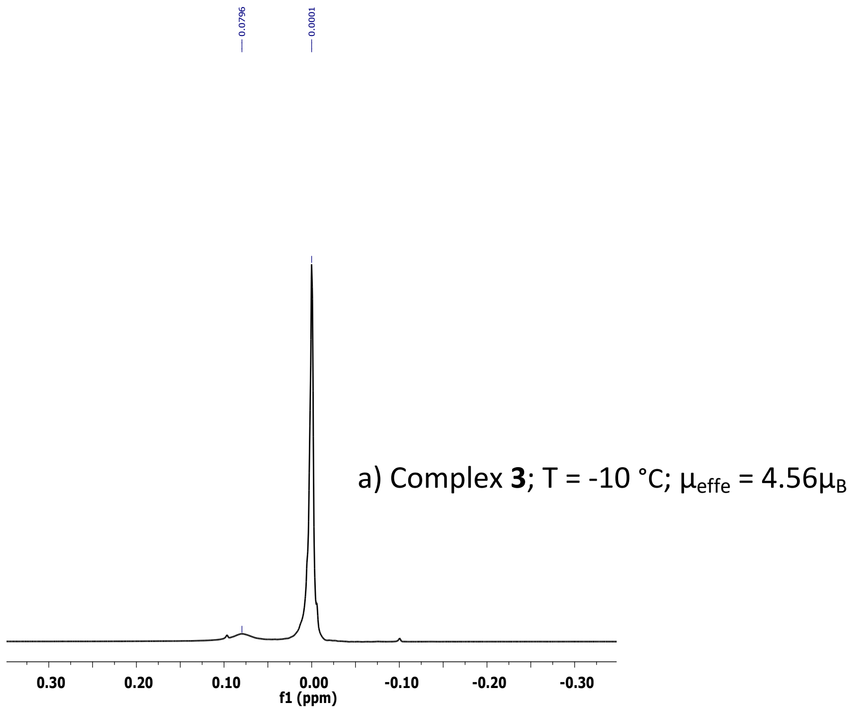


Figure S17. Plot of the ^{1}H-NMR spectra of the chromium(III) complex **3** (1.07 mM in DCM-d2) at different temperatures, for the determination of the solution magnetic susceptibility (μ_{eff}) by means of the method of Evans. a) -10 °C; b) 0 °C; c)25 °C.

Coupling of PO/CO_2

Table S1. Coupling of propylene oxide with carbon dioxide activated by catalyst **1**

Entry[a]	Cat (mol%)	Epoxide	T [°C]	Co-cat/Cat	Conv.[b] [%]	PC [%]*[b]	TOF [h^{-1}][c]
1	(0.025)	PO	70	2.0(TBAB)	36	19	60
2	(0.050)	PO	45	2.0(TBAB)	38	12	32
3	(0.050)	PO	70	2.0(TBAB)	48	24	40
4	(0.050)	PO	90	2.0(TBAB)	53	21	44

[a] Reaction conditions: PO=0.014 mol; time=24 h; pCO_2=20 bar;
co-catalyst = TBAB=Tetrabutylammonium bromide
[b] Determined by ^{1}H NMR spectroscopy
[c] TOF=(mol epoxide × conv)/(mol cat × time × 100)
* The complement to 100 is cyclic organic carbonate

DSC Analysis

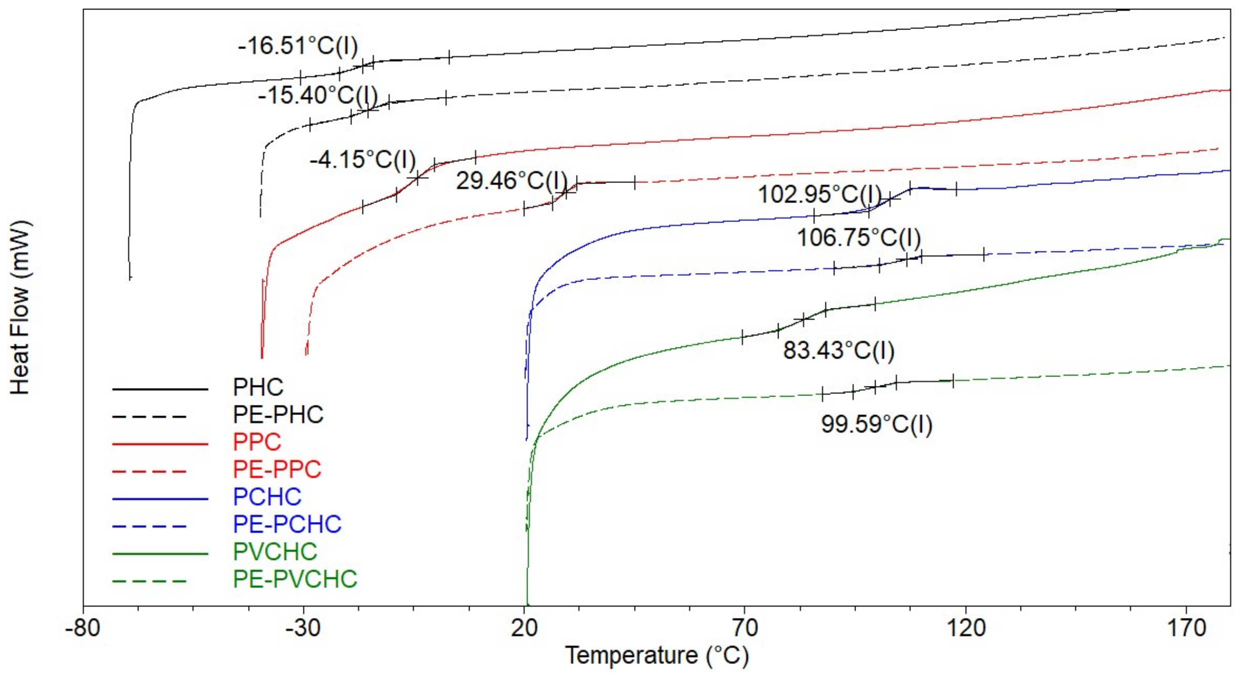


Figure S18. The differential scanning calorimetry (DSC) analysis of the polycarbonates and poly(ester-block-carbonate)s obtained by ctalyst **1**.

NMR Analysis of Products

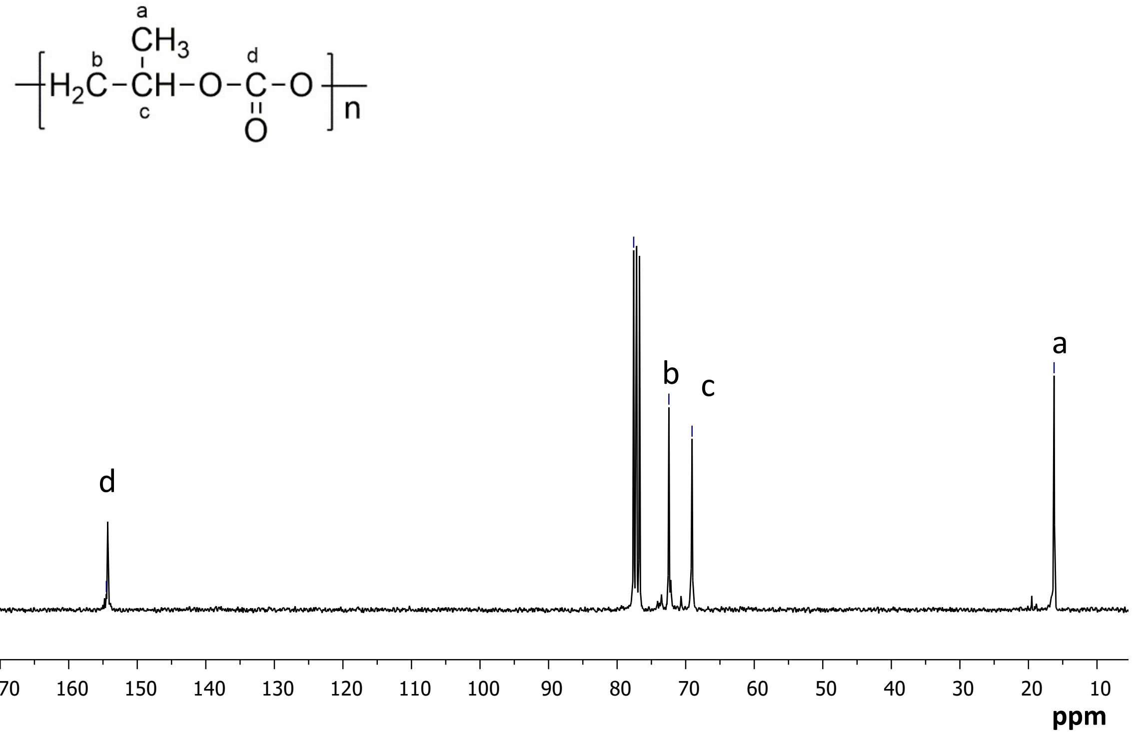


Figure S19.[13]C NMR spectra of purified **PPC** entry 1, Table 2 ($CDCl_3$, 600 MHz)

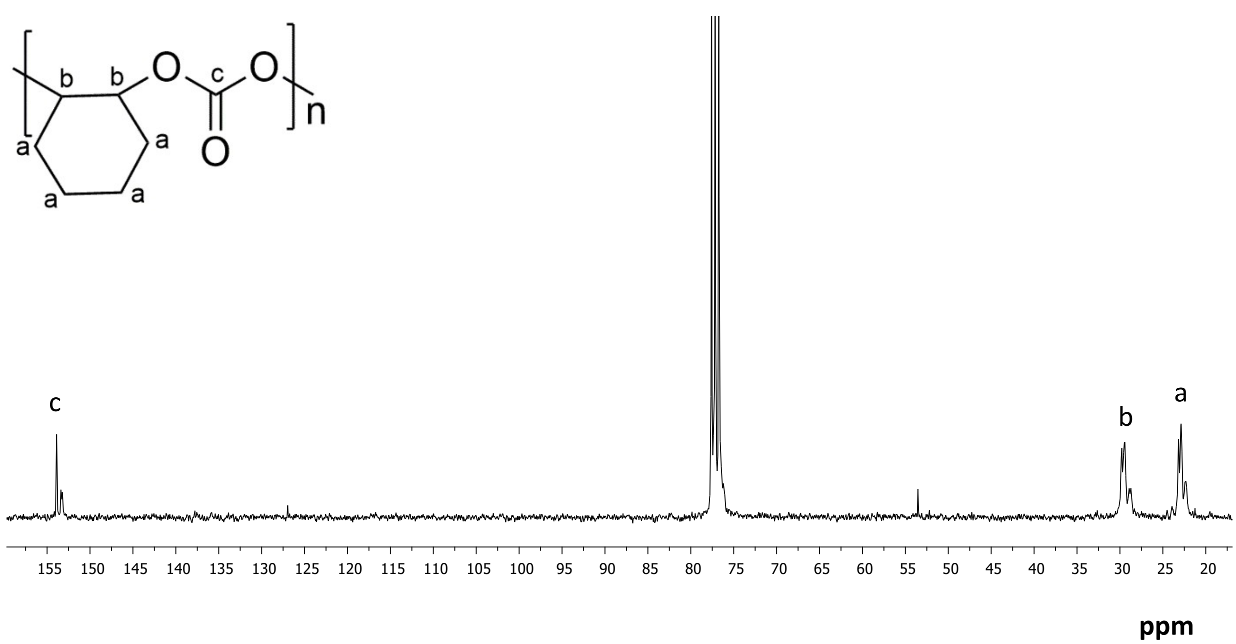


Figure S20.[13]C NMR spectra of purified **PCHC** entry 5, Table 2 ($CDCl_3$, 600 MHz)

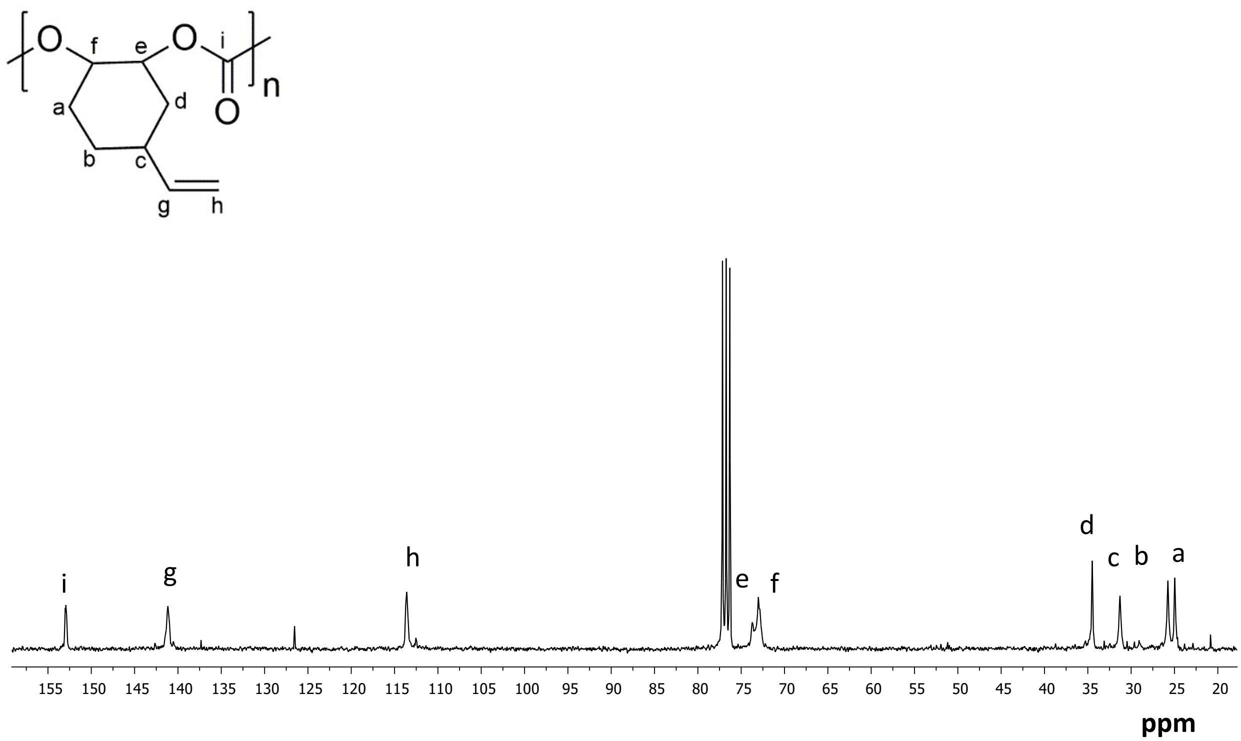


Figure S21.^{13}C NMR spectra of purified **PVCHC** entry 9, Table 2 ($CDCl_3$, 600 MHz)

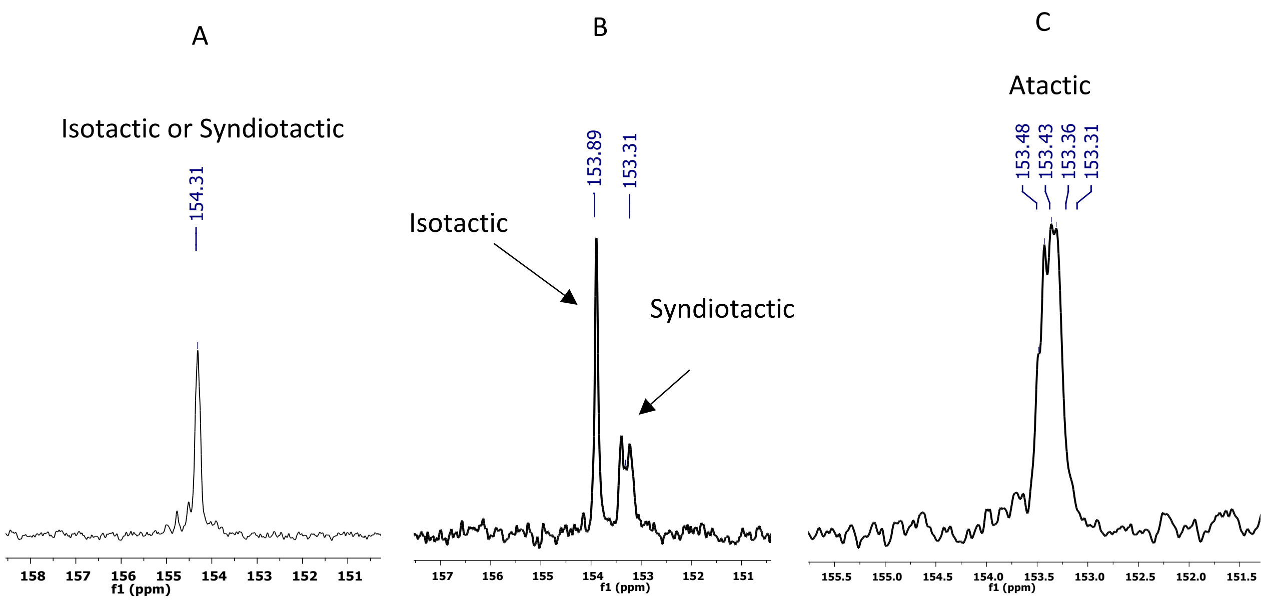


Figure S22. ^{13}C NMR spectrum of A) **PPC**, B) **PCHC**, and C) **PVCHC** in the carbonyl region ($CDCl_3$, 600 MHz)

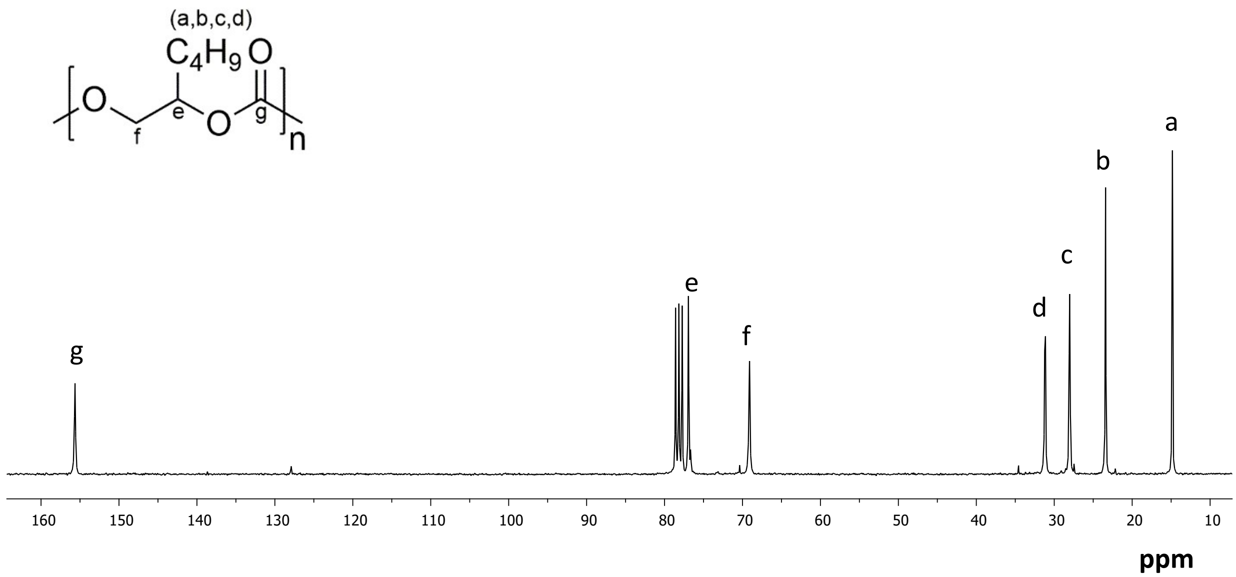


Figure S23.[13]C NMR spectra of purified **PHC** entry 13, Table 2 ($CDCl_3$, 600 MHz)

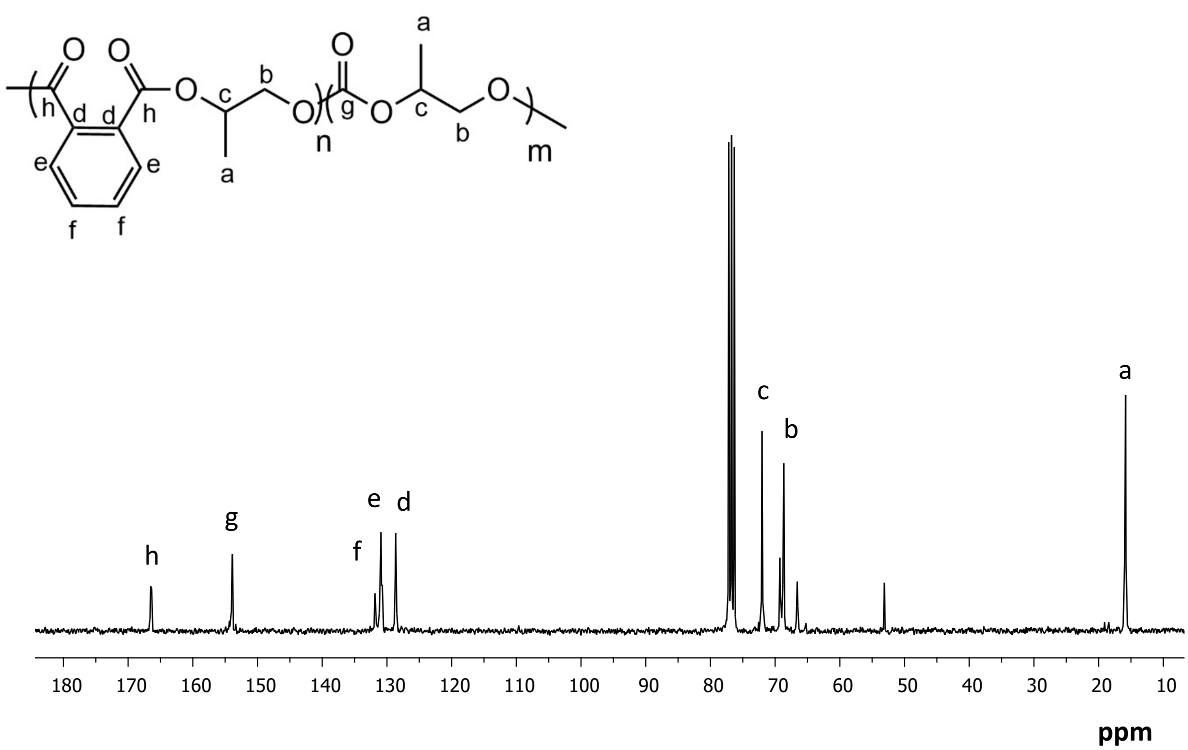


Figure S24.[13]C NMR spectra of purified **PO/PA/CO₂** in $CDCl_3$, entry 1, Table 3

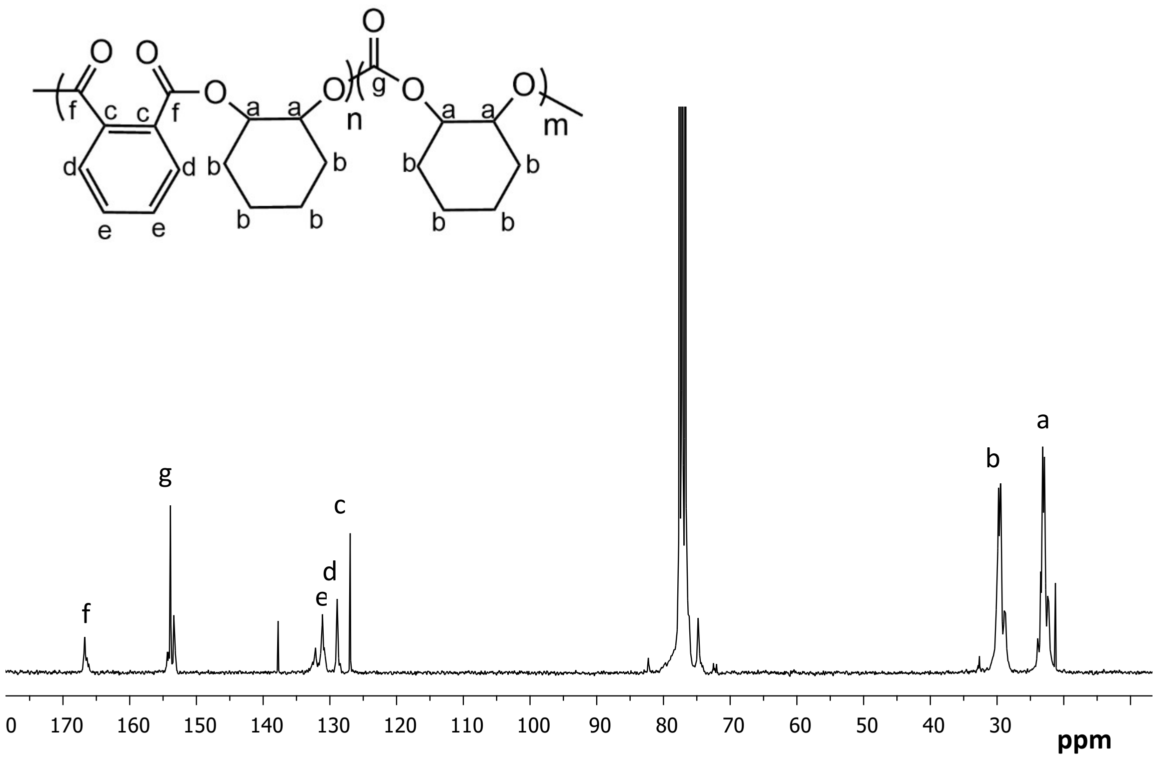


Figure S25. ^{13}C NMR spectra of purified **CHO/PA/CO₂** coupling entry 4, Table 3 ($CDCl_3$, 600 MHz)

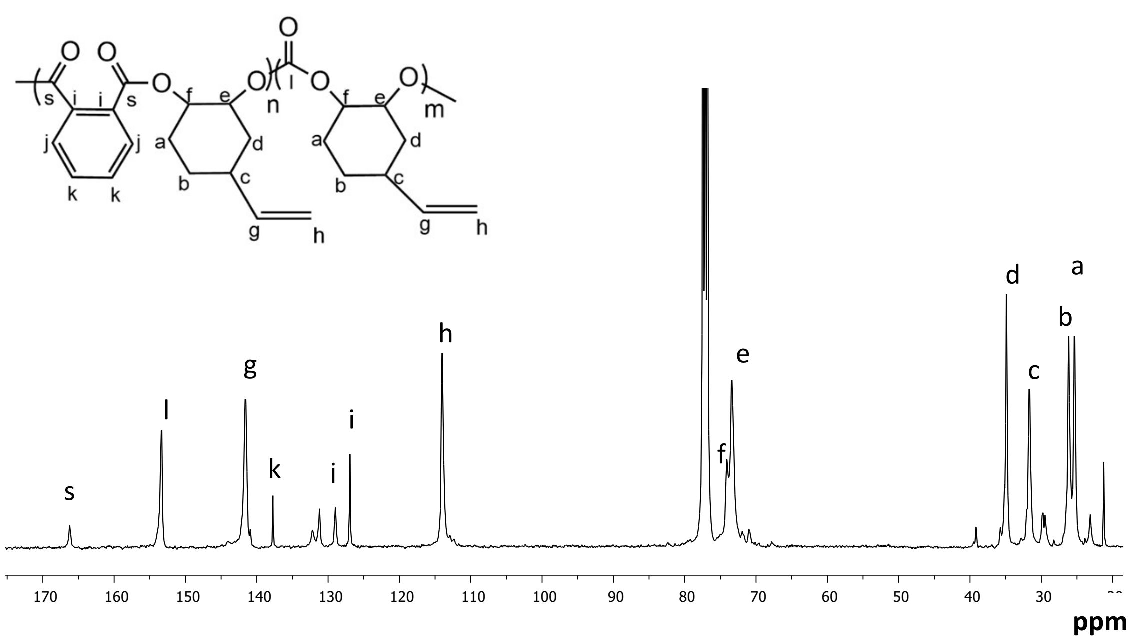


Figure S26. ^{13}C NMR spectra of purified **VCHO/PA/CO2** coupling entry 7, Table 3 (CDCl3, 600 MHz)

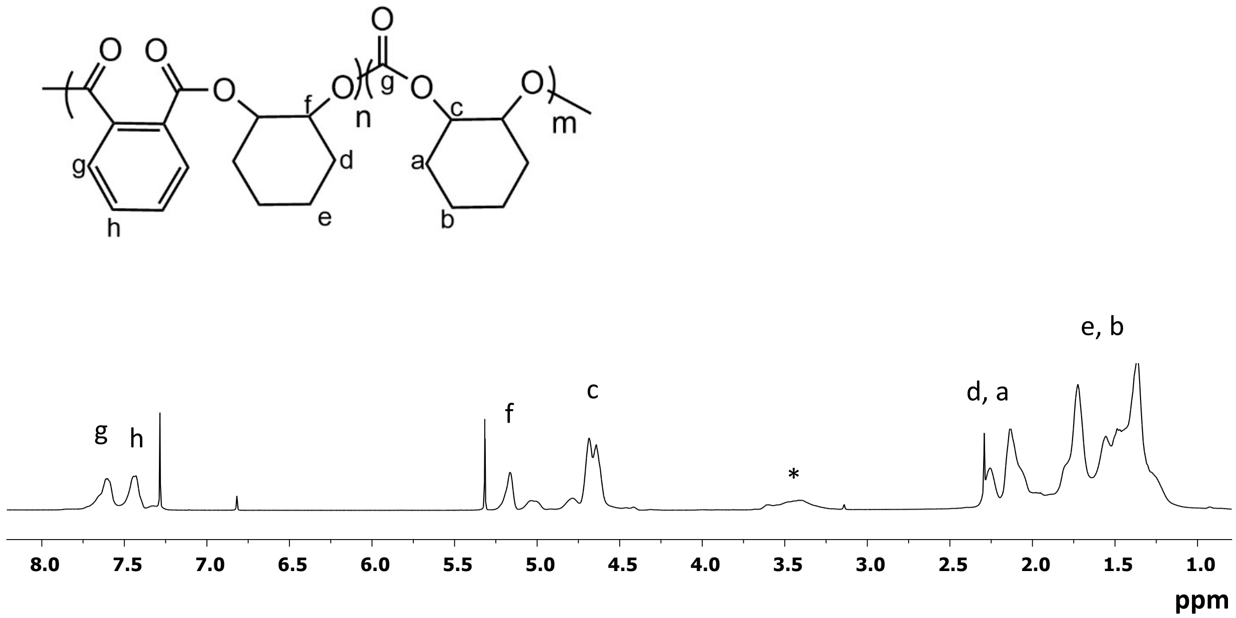


Figure S27. [1]H NMR spectra of purified **CHO/PA/CO_2** coupling in $CDCl_3$, entry 4, Table 3.* Trace amount of polyether as side product.

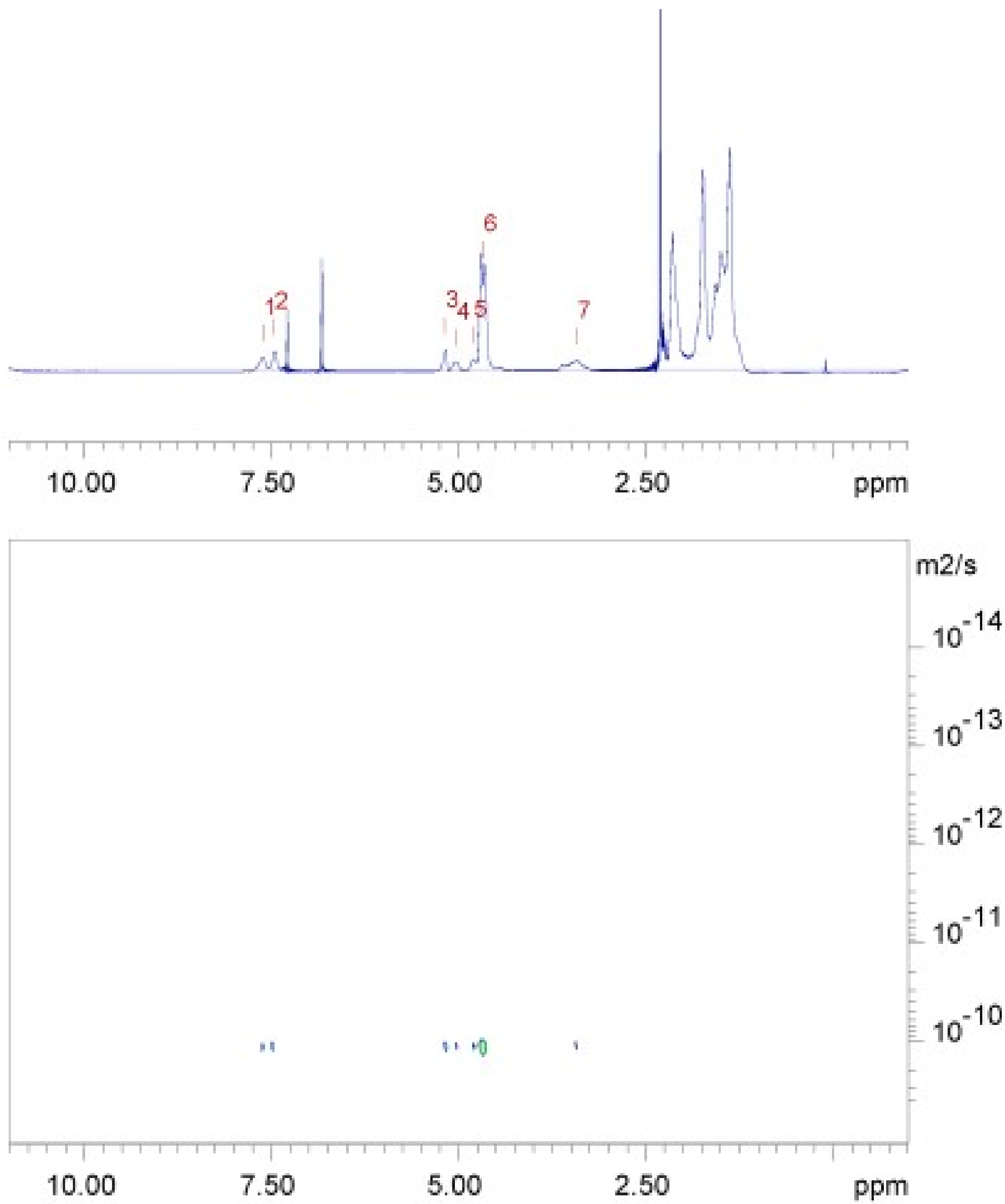


Figure S28. Dosy spectra of purified (**PE-*co*-PCHC**) in $CDCl_3$, entry 4, Table 3

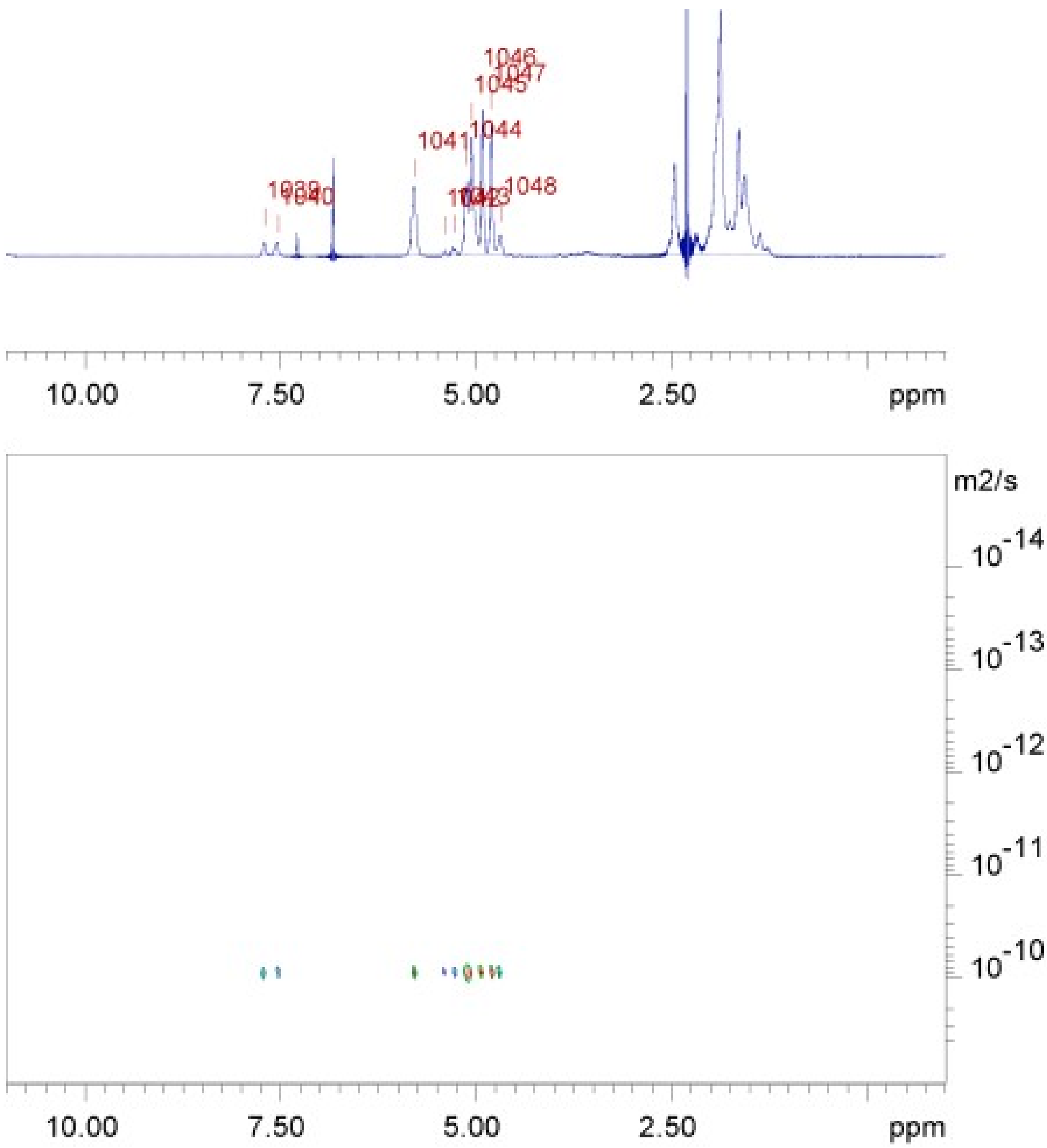
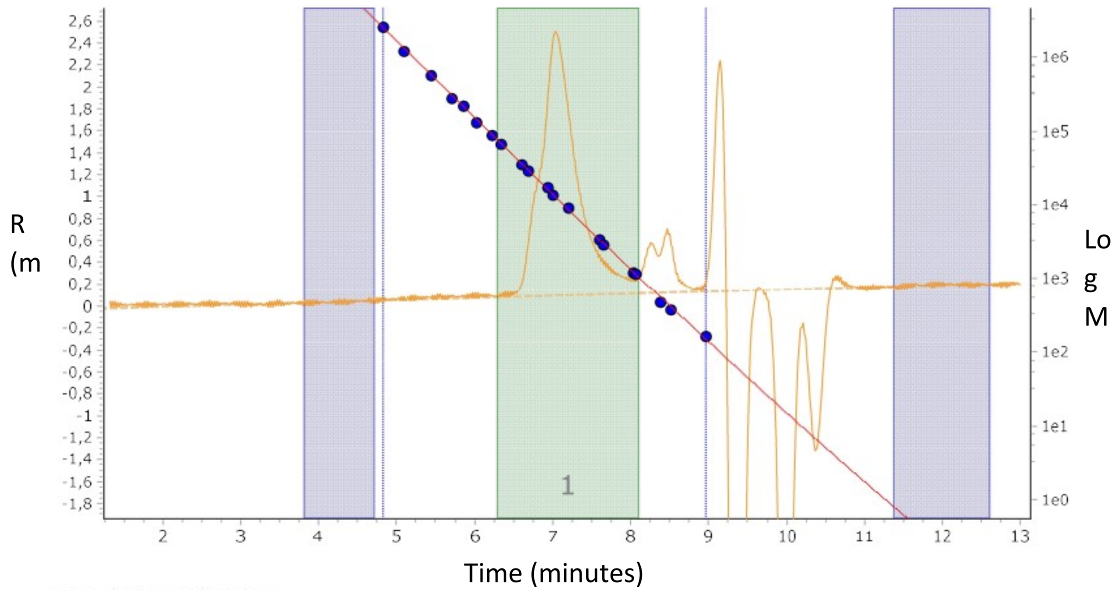


Figure S29.Dosy spectra of purified (**PE-*co*-PVCHC**) in $CDCl_3$, entry 7, Table 3

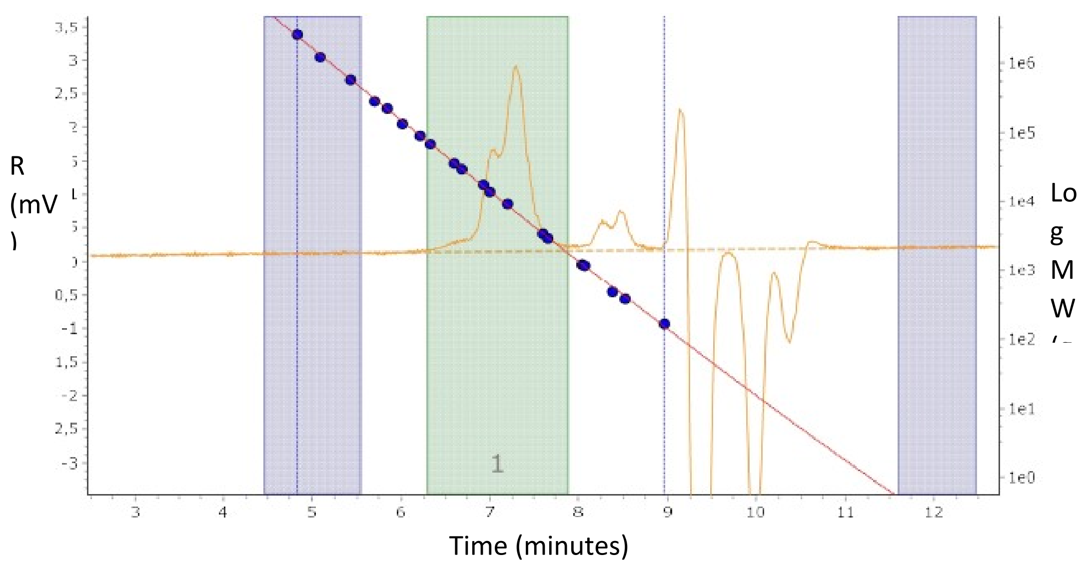
GPC Analysis



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	12651	7715	12519	17175	22658	11866	1,623

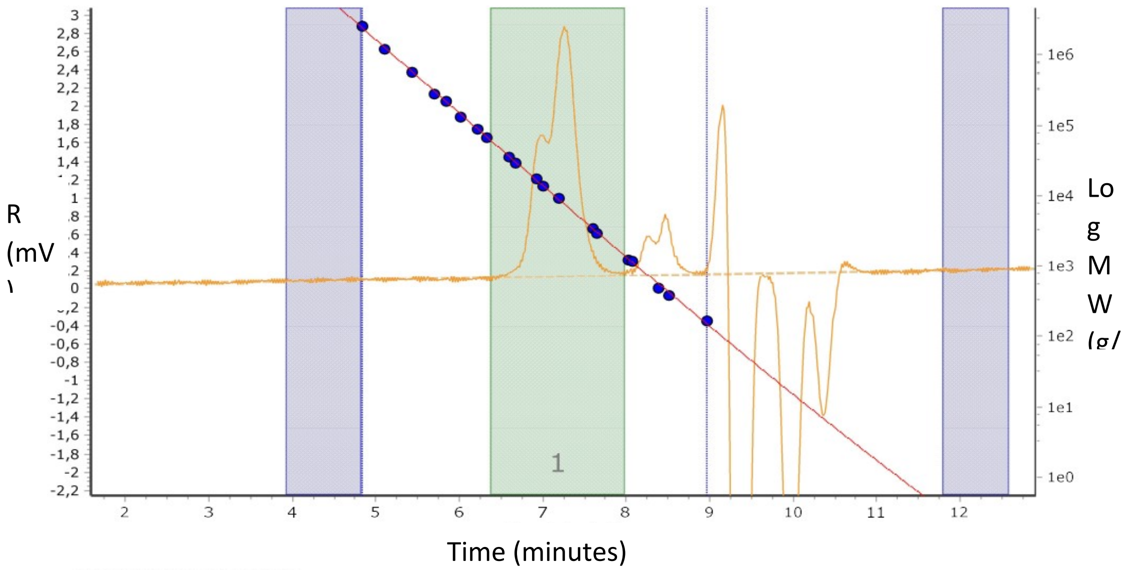
Figure S30. Chromatogram of purified **PPC**, entry 3, Table 1



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	6764	7475	10063	15354	25730	9539	1,346

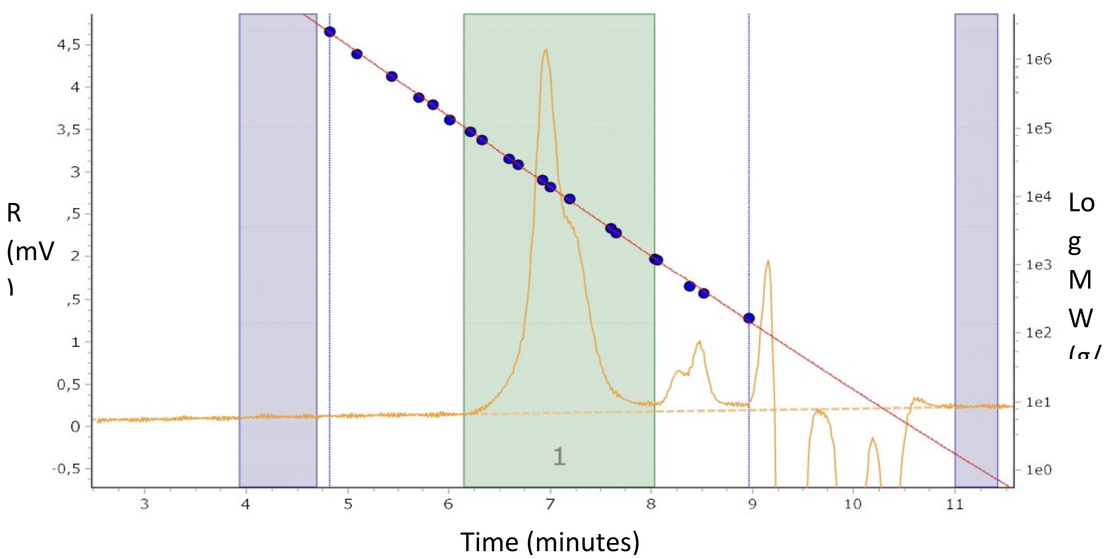
Figure S31. Chromatogram of purified **PPC**, entry 1, Table 1



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	7605	7871	10101	13042	17023	9727	1,283

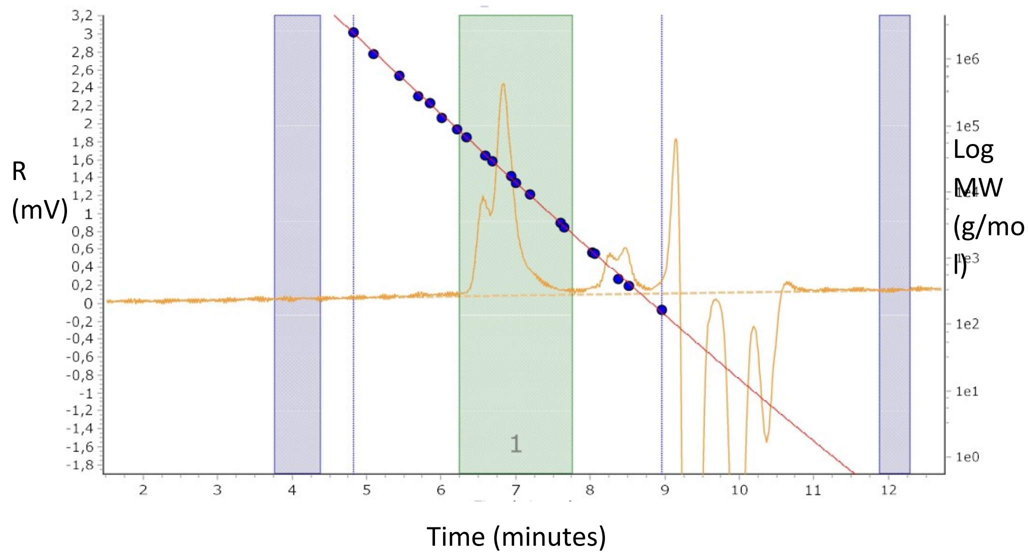
Figure S32. Chromatogram of purified **PCHC**, entry 5, Table 2



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	15392	9842	14251	19702	27839	13573	1,448

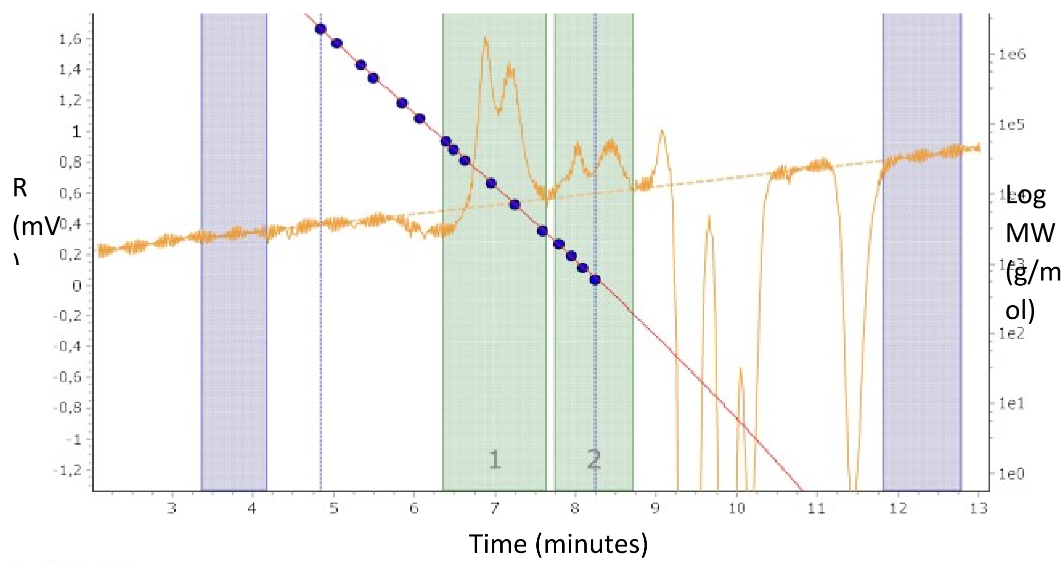
Figure S33. Chromatogram of purified **PVCHC**, entry 9, Table 2



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	19483	17174	23452	29192	34845	22609	1,366

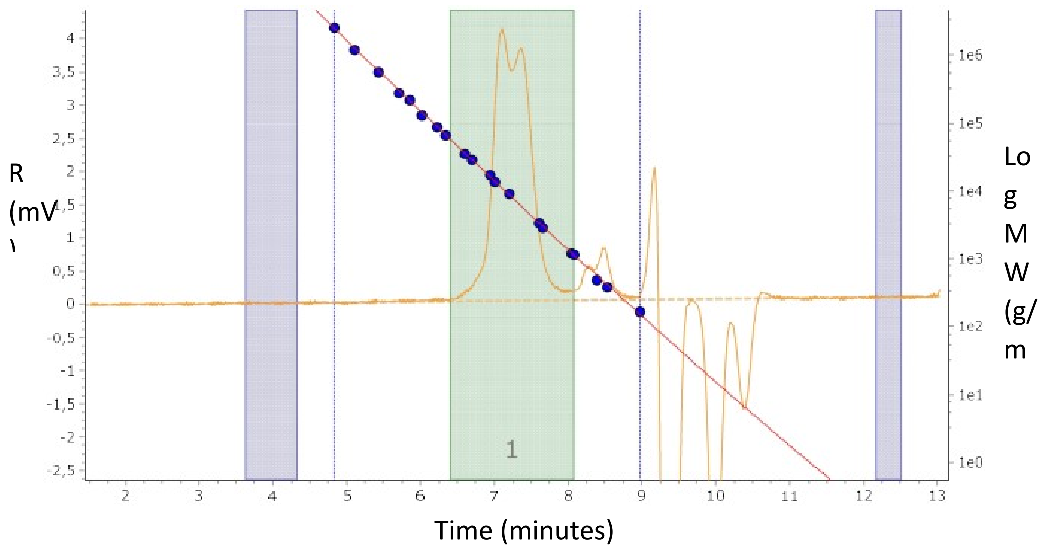
Figure S34. Chromatogram of purified **PHC**, entry 13, Table 2



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	17067	9876	12341	14778	16825	11971	1,25

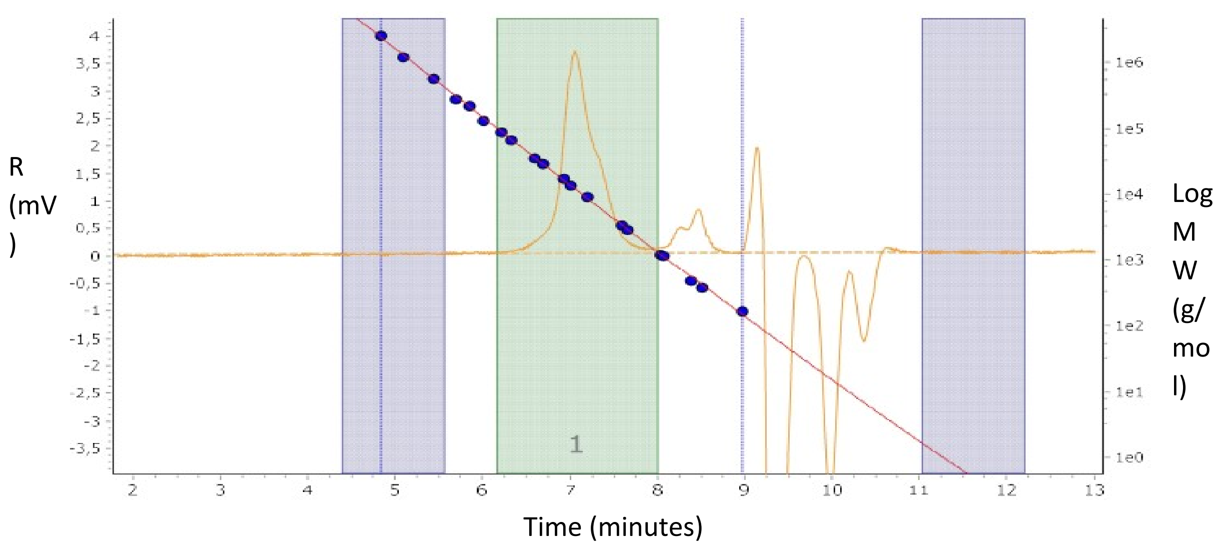
Figure S35. Chromatogram of purifed copoly(ester-carbonate) (**PE-*co*-PPC**), entry 1, Table 3



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	10815	6701	9146	12390	17238	8746	1,365

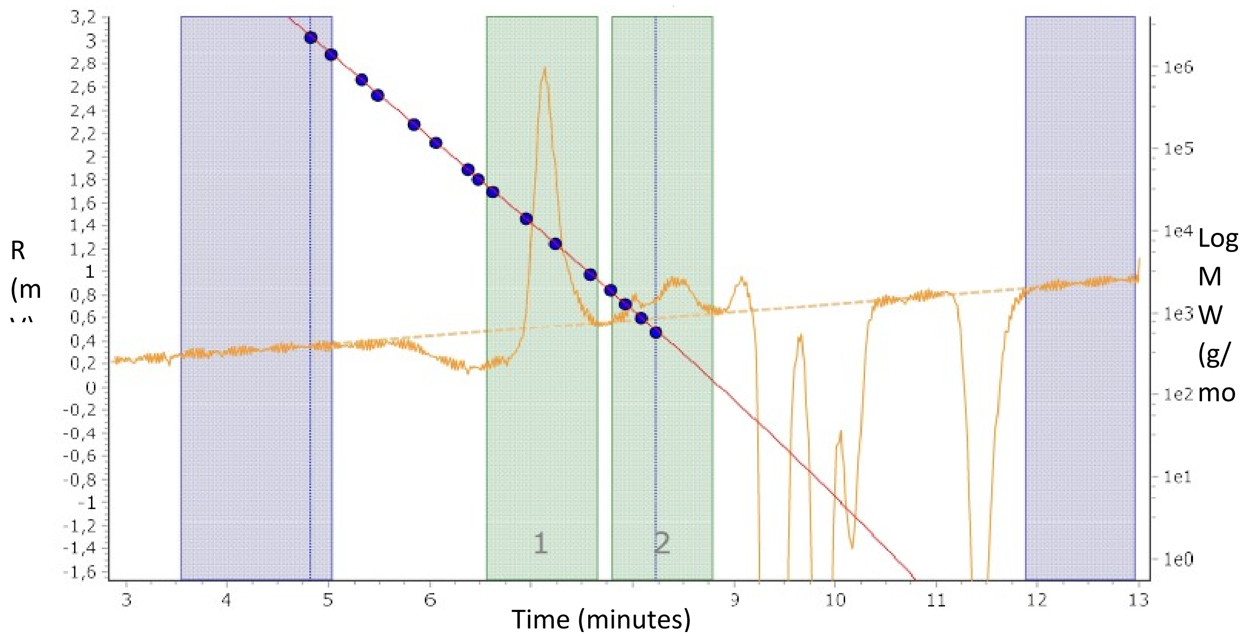
Figure S36. Chromatogram of purified copoly(ester-carbonate) (**PE-** ***co*****-PCHC**), entry 4, Table 3



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	12164	8703	12092	17341	27615	11518	1,389

Figure S37. Chromatogram of purified copoly(ester-carbonate) (**PE-*****co*****-PVCHC**), entry 7, Table 3



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	8987	7833	8565	9187	9717	8466	1,093

Figure S38. Chromatogram of purified copoly(ester-carbonate) (**PE-*co*-PHC**), entry 10, Table

Kinetic experiments for PPC formation promoted by cat/PPNCl

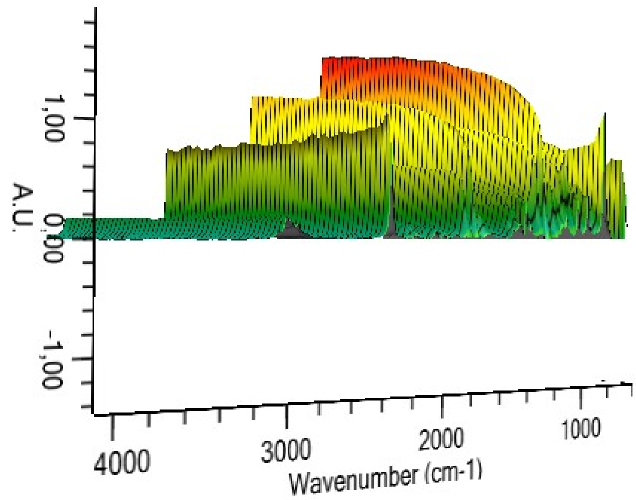
Table S2. Determination of the reaction order with respect to **1**

Entry	PO/PPNCl/**1**	[**1**] (mM)	V0 (l/s.10^4)
1	500/0.5/1	9.03	4.14
2	1000/1.0/1	4.51	2.00
3	1500/1.5/1	3.01	1.32
4	2000/2.0/1	2.26	1.08

Table S3. Determination of the reaction order with respect to **4**

Entry	PO/PPNCl/**4**	[**4**] (mM)	V0 (l/s.10^4)
1	250/0.25/1	18.05	7.98
2	370/0.37/1	12.20	5.86
3	700/0.7/1	6.45	1.59
4	1200/1.2/1	3.76	0.40

Reaction order with respect to [1]



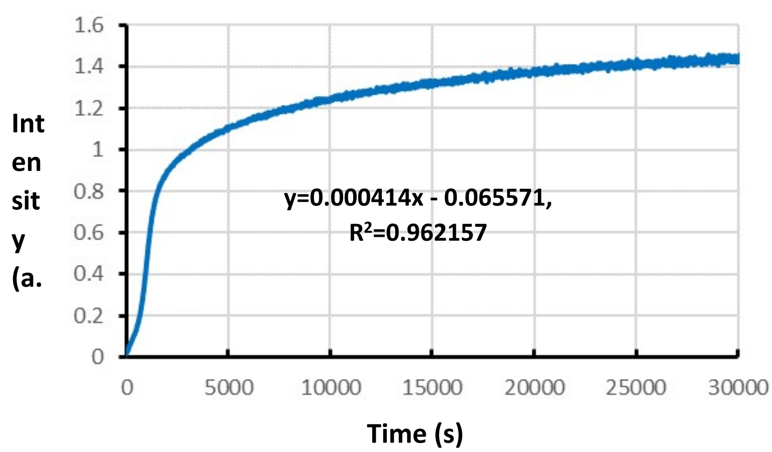
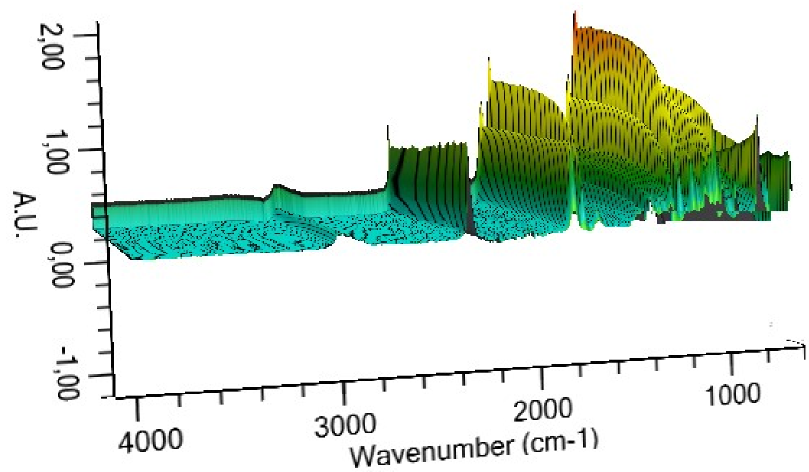


Figure S39. Carbonate signal of PPC grows at 1750 cm^{-1}. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; $P(CO_2)$ = 20 bar; **1** = 0.2 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 1, Table S2)



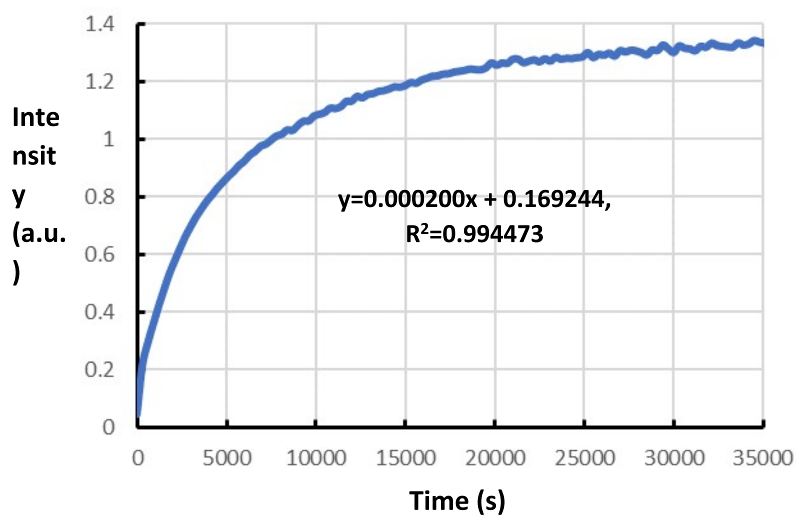
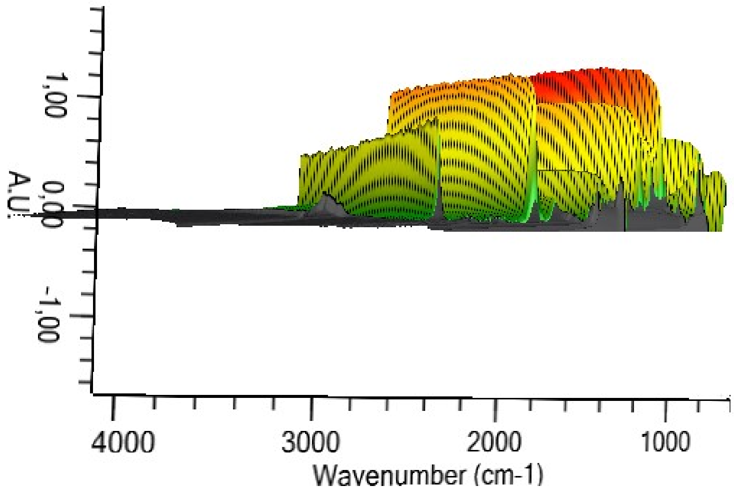


Figure S40. Carbonate signal of PPC grows at 1750 cm^{-1}. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; $P(CO_2)$ = 20 bar; **1** = 0.1 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 2, Table S2)



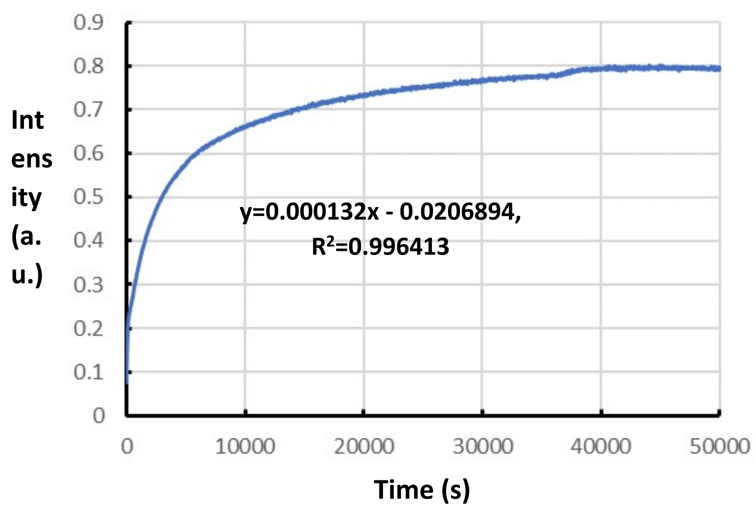
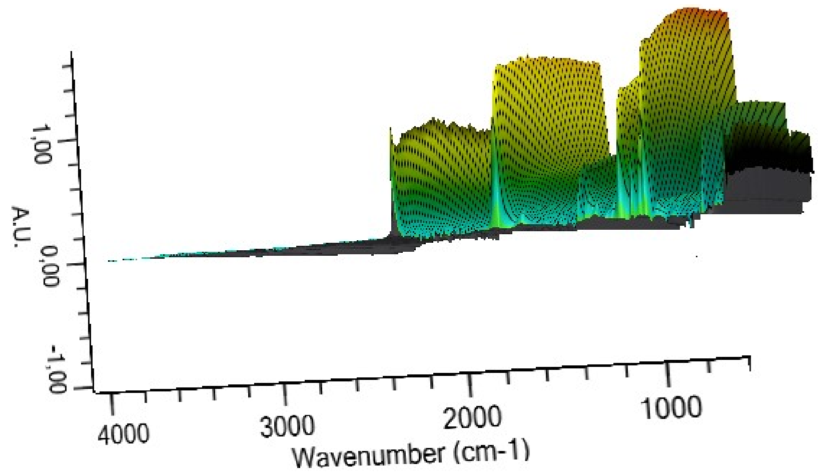


Figure S41. Carbonate signal of PPC grows at 1750 cm^{-1}. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; P(CO_2) = 20 bar; **1** = 0.066 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 3, Table S2)



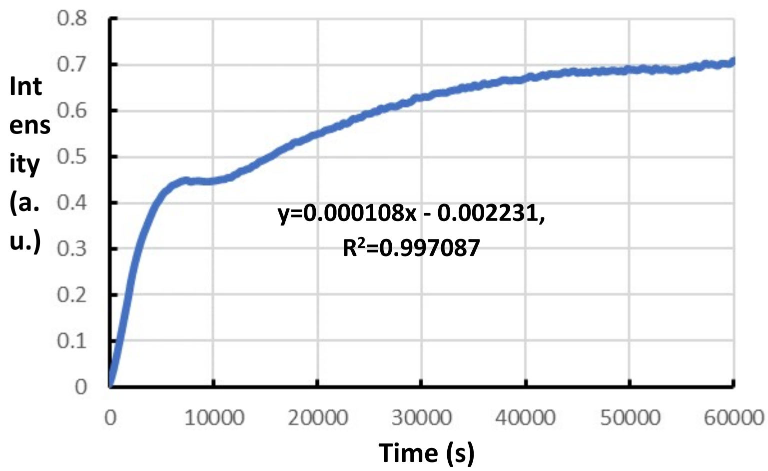
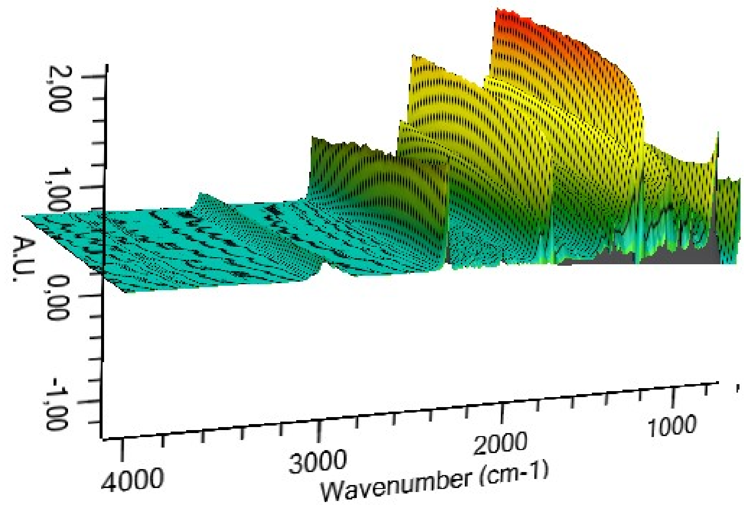


Figure S42. Carbonate signal of PPC grows at 1750 cm⁻¹. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; $P(CO_2)$ = 20 bar; **1** = 0.05 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 4, Table S2)

Reaction order with respect to [4]



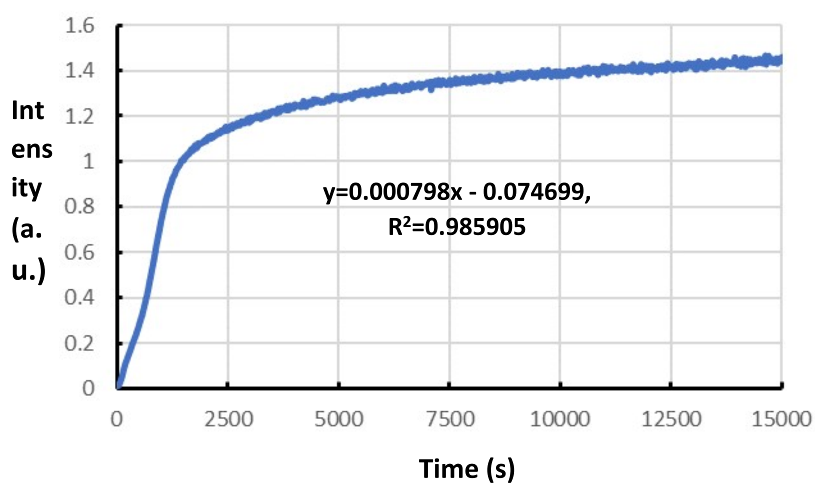
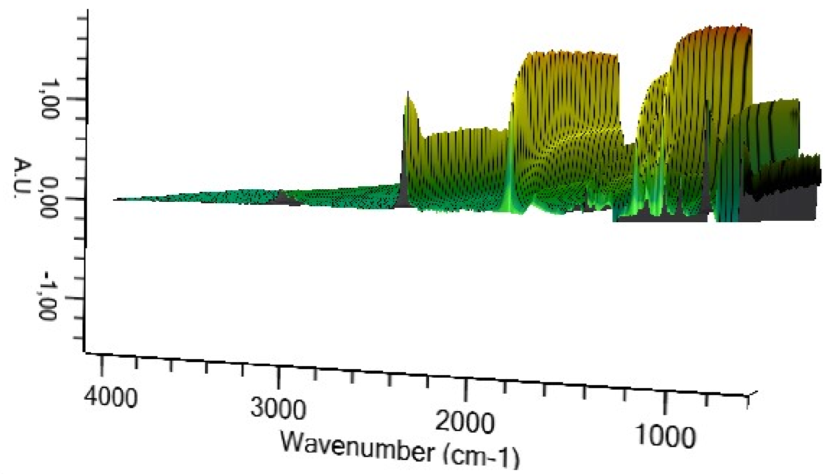


Figure S43. Carbonate signal of PPC grows at 1750 cm^{-1}. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; $P(CO_2)$ = 20 bar; **4** = 0.4 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 1, Table S3)



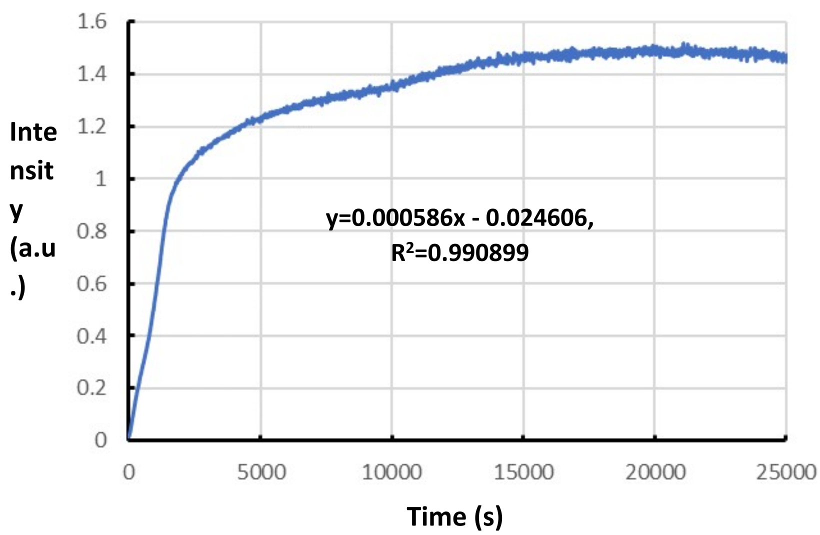
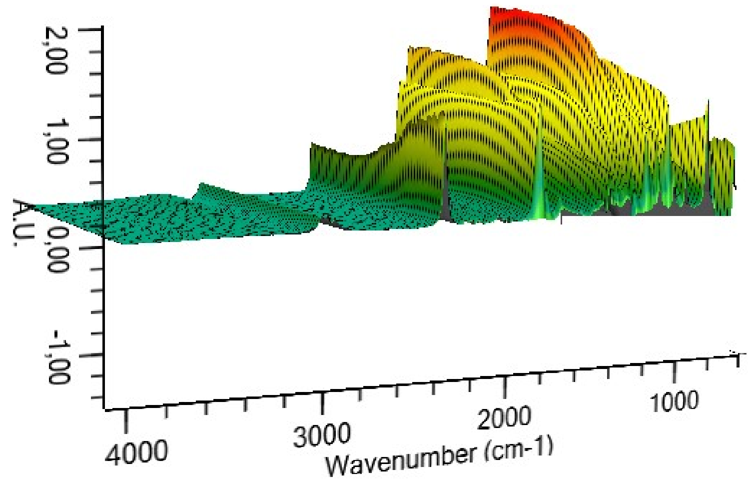


Figure S44. Carbonate signal of PPC grows at 1750 cm^{-1}. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; P(CO_2) = 20 bar; **4** = 0.27 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 2, Table S3)



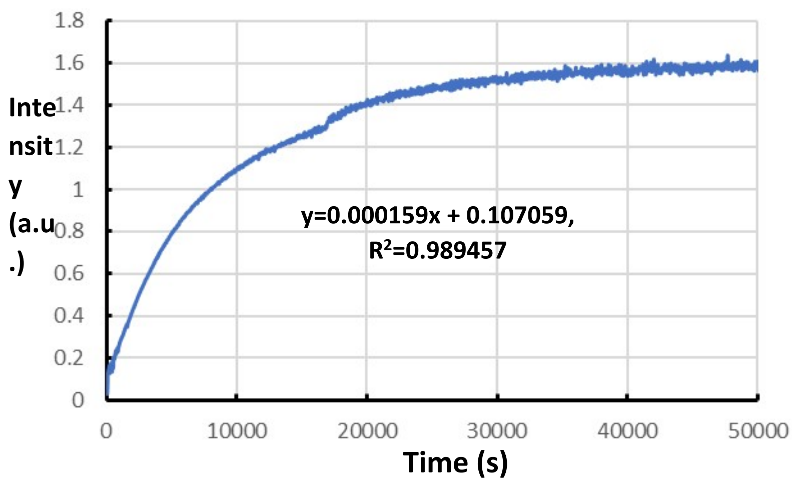
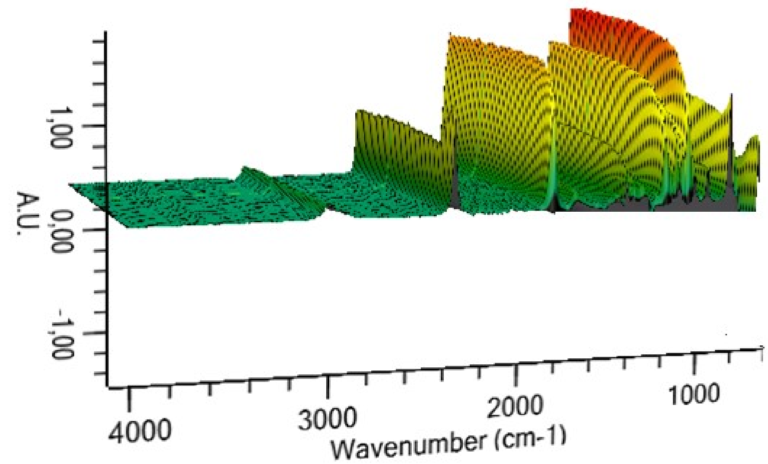


Figure S45. Carbonate signal of PPC grows at 1750 cm^{-1}. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; $P(CO_2)$ = 20 bar; **4** = 0.142 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 3, Table S3)



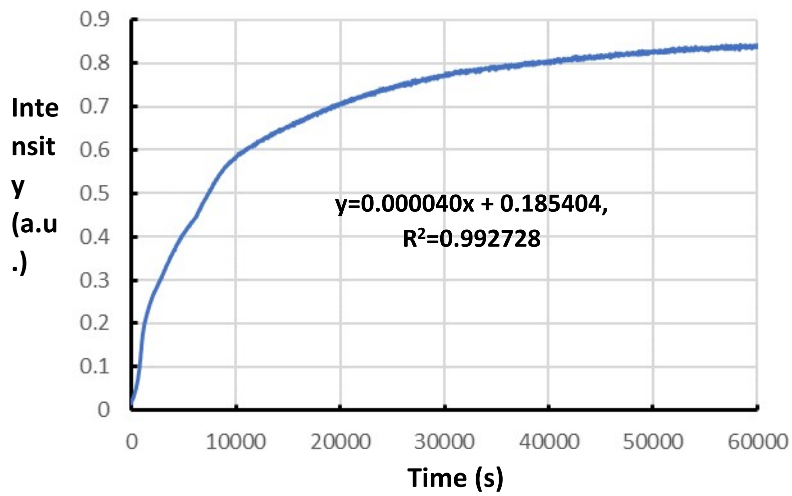


Figure S46. Carbonate signal of PPC grows at 1750 cm^{-1}. Reaction conditions: [PO] = 4.47 M in CH_2Cl_2; $P(CO_2)$ = 20 bar; **4** = 0.083 mol%; PPNCl = 0.1 mo%; T = 45°C, (entry 4, Table S3)

Purification of phthalic anhydride

A 250-mL flask equipped with a magnetic stirrer was charged with 10 g of phthalic anhydride and dried toluene under nitrogen. The solution was stirred over night to achieve maximum dissolution of phthalic anhydride. After that, the suspension solution was filtered through a PTFE tube into another flask. In the following, the solvent was removed by vacuum. The precipitated solids were dissolved in a minimum amount of anhydrous dichloromethane and kept in the fridge over night to allow the crystallization of phthalic anhydride. The additional solvent was transferred into another flask, and the residual crystals were dried under vacuum. Then the dried crystals were transferred to a tail tube (100 mL). The bottom of the tube was immersed in the bath oil, and with the aid of a vacuum at 80 °C, the crystals were sublimized. The white crystals were collected and kept in the glovebox.