Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

CO_2/Epoxides Ring-Opening Copolymerization Towards Hydroxy-Functionalized Polycarbonates

Nishant Chaudhary,[a,b] A. Stephen K. Hashmi,[b] Jean-François Carpentier,[a,*] Sophie M. Guillaume[a,*]

a. Univ. Rennes, CNRS, Institut des Sciences Chimiques de Rennes, UMR 6226, F-35042 Rennes, France. E-mail: sophie.guillaume@univ-rennes.fr; jean-francois.carpentier@univ-rennes.fr

b. Organisch-Chemisches Institut, Universität Heidelberg, Catalysis Research Laboratory (CaRLa), Im Neuenheimer Feld 271, D-69120 Heidelberg, Germany

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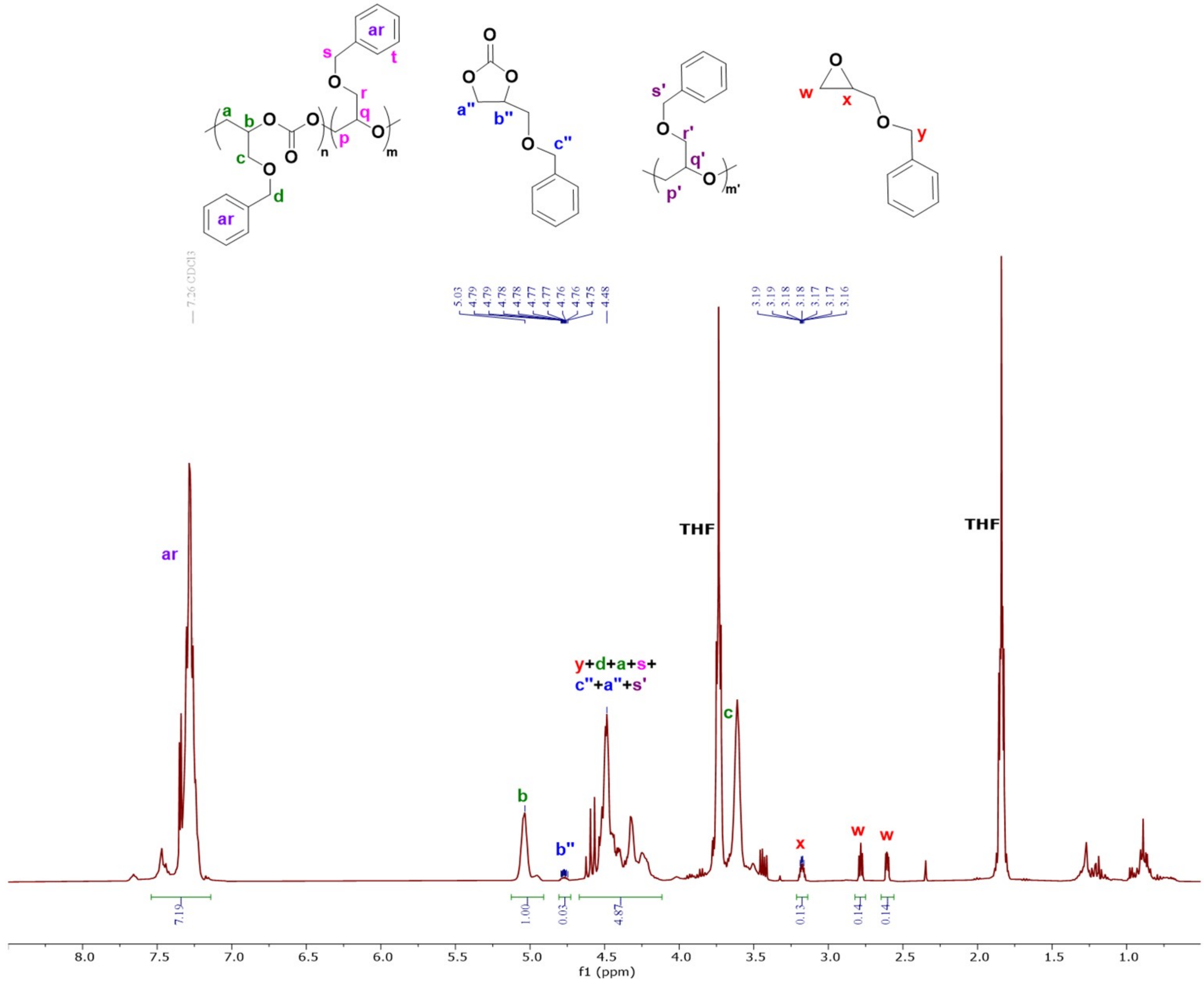


Figure S1. [1]H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of a crude reaction mixture resulting from the ROCOP of BnGE and CO_2 with the BEt_3/PPNCl system (Table S1, entry 7).

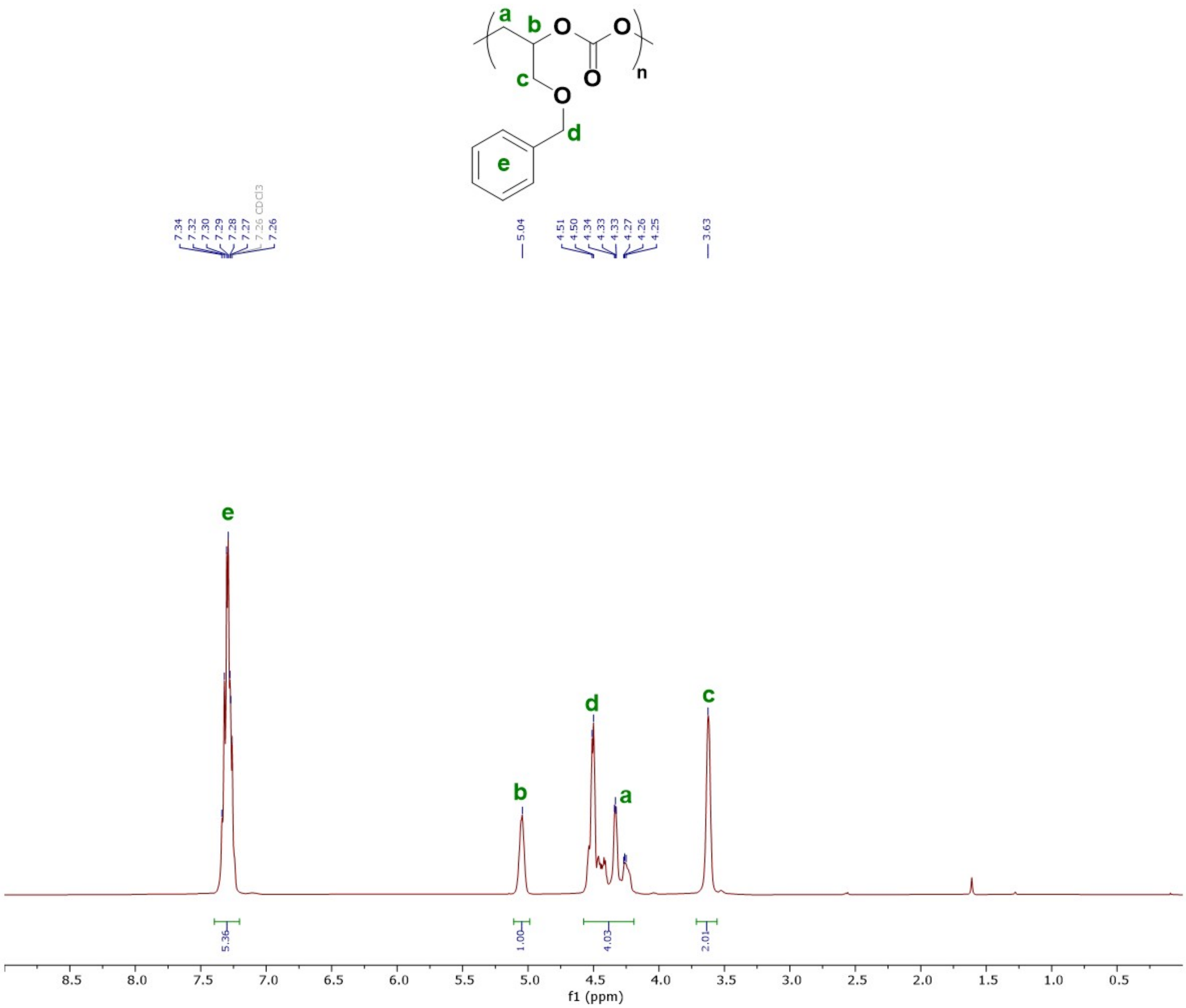


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of a PBnGEC synthesized with the SalphenCo(III)Cl/PPNCl system (Table 1, entry 3).

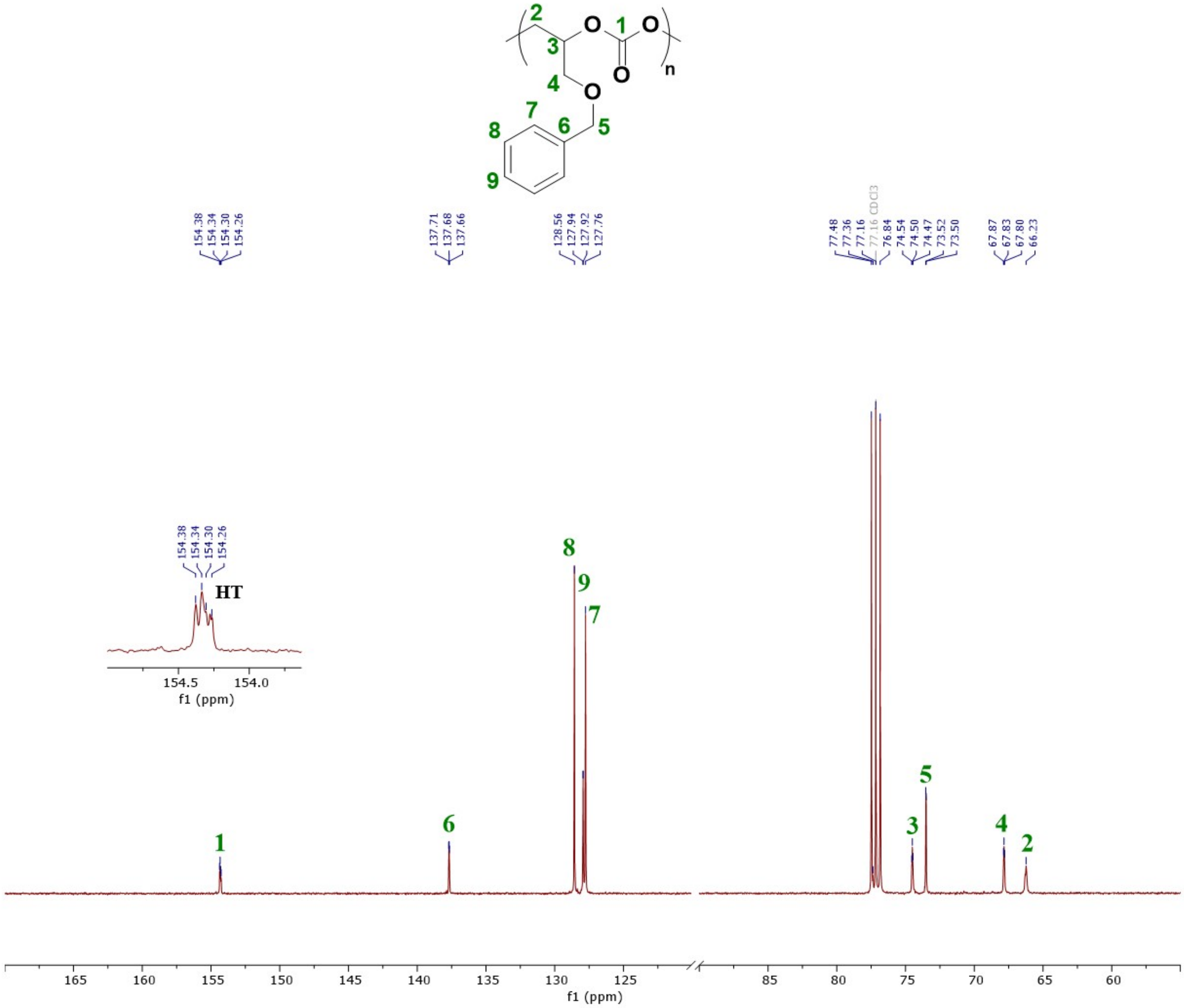


Figure S3. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 23 °C) spectrum of a PBnGEC synthesized with the SalphenCo(III)Cl/PPNCl system (Table 1, entry 3) showing a head-to-tail (HT) regiosequence of ca. 99%.

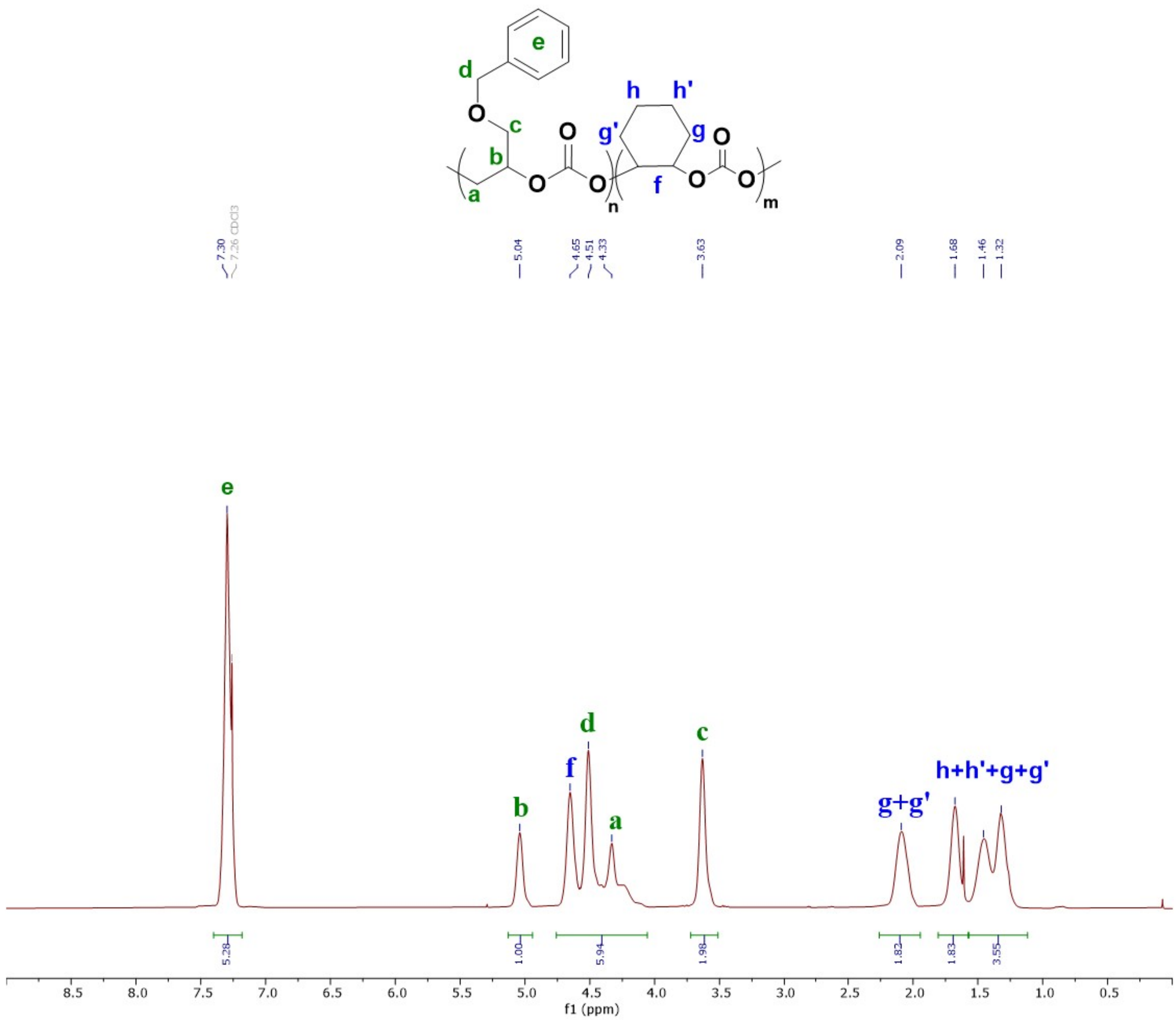


Figure S4. [1]H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of a P(BnGEC-*co*-CHC) synthesized with the SalphenCo(III)Cl/PPNCl system (Table 1, entry 7).

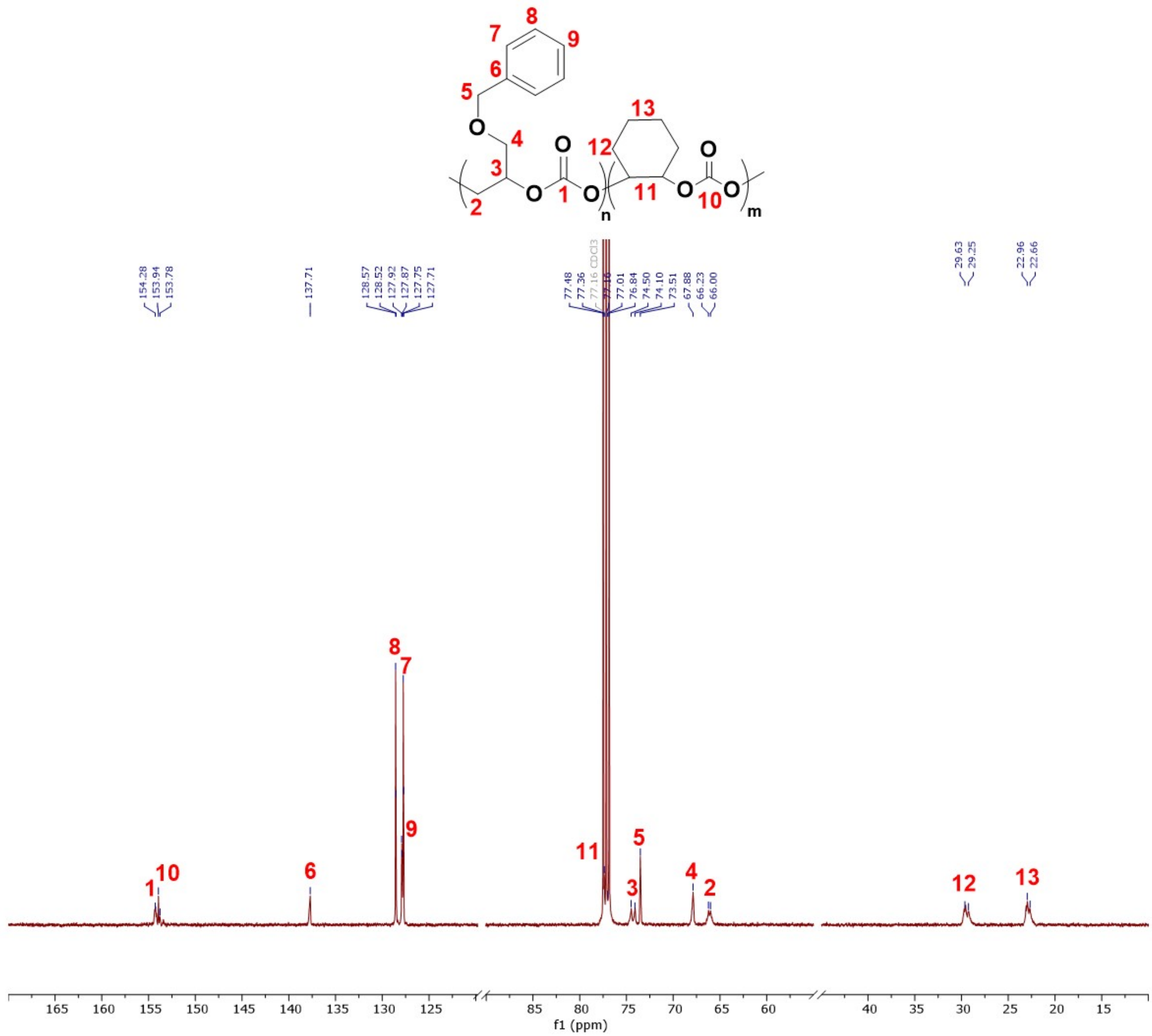


Figure S5. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 23 °C) spectrum of a P(BnGEC-*co*-CHC) synthesized with the SalphenCo(III)Cl/PPNCl system (Table 1, entry 7).

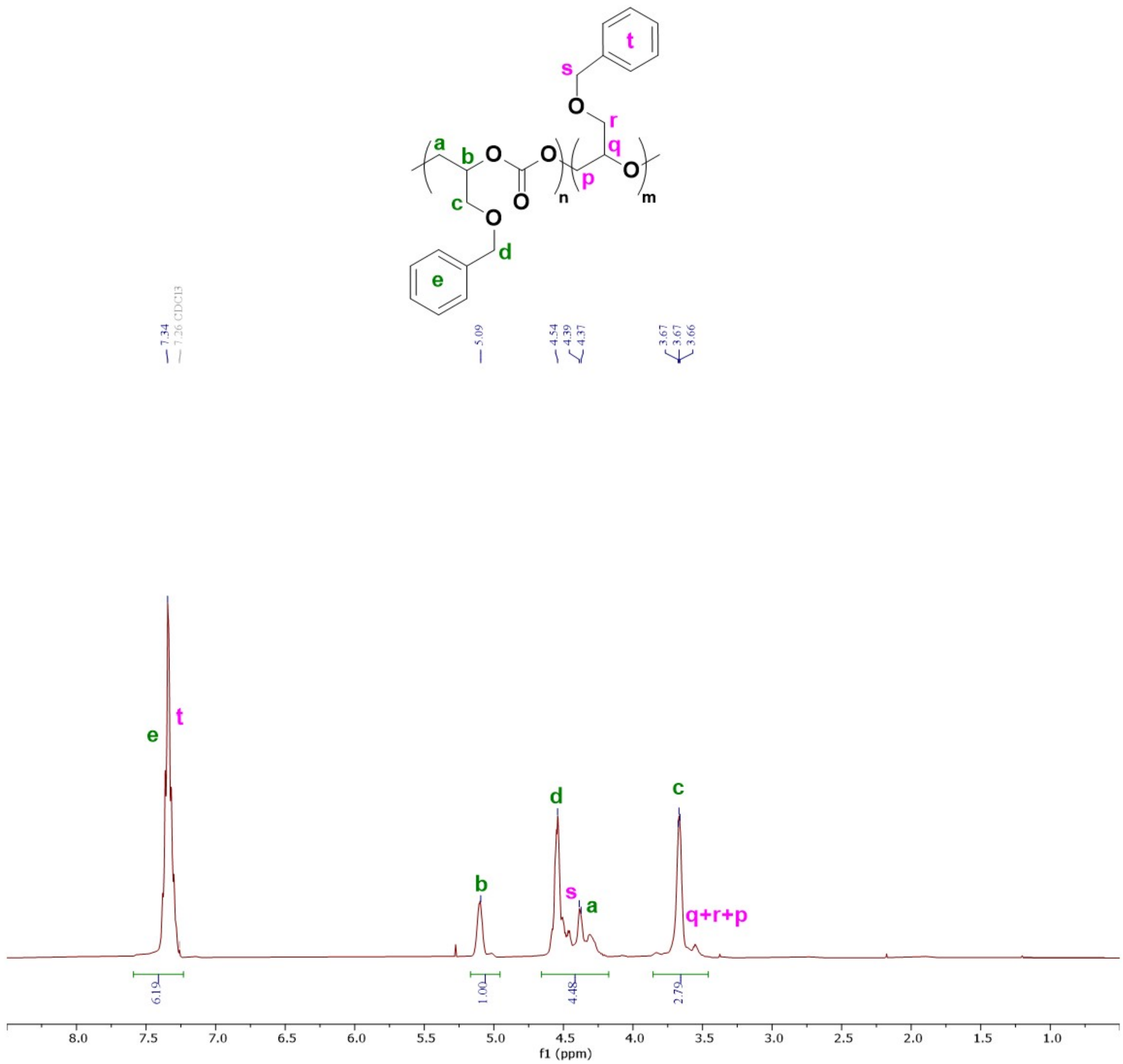


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of a PBnGEC synthesized with the BEt_3/PPNCl system (Table S1, entry 7).

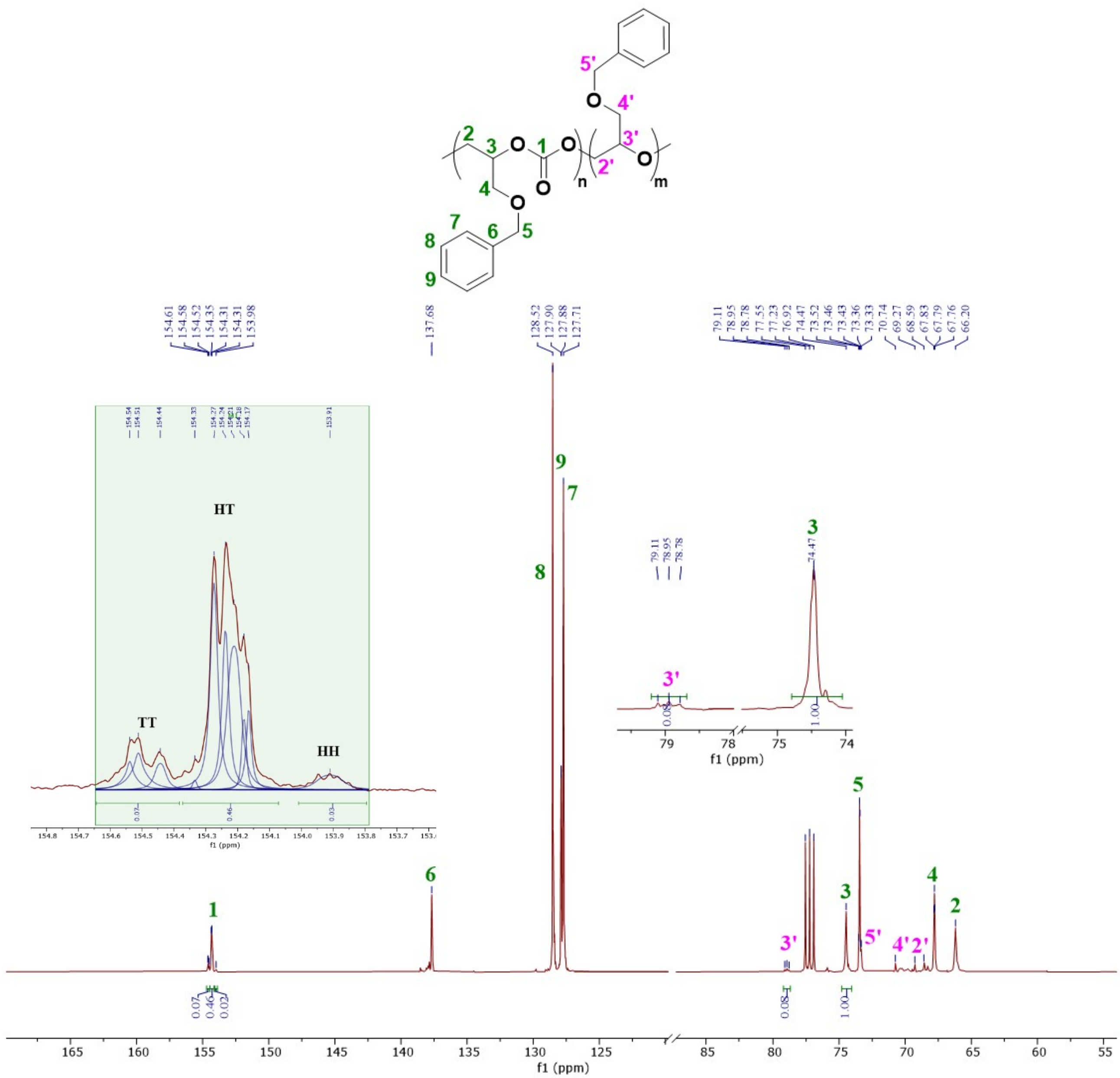


Figure S7. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 23 °C) spectrum of a PBnGEC synthesized with the BEt_3/PPNCl system (Table S1, entry 7) showing a head-to-tail (HT) regiosequence of ca. 84%. The left inset shows a magnified image of the carbonyl region, along with line fitting.

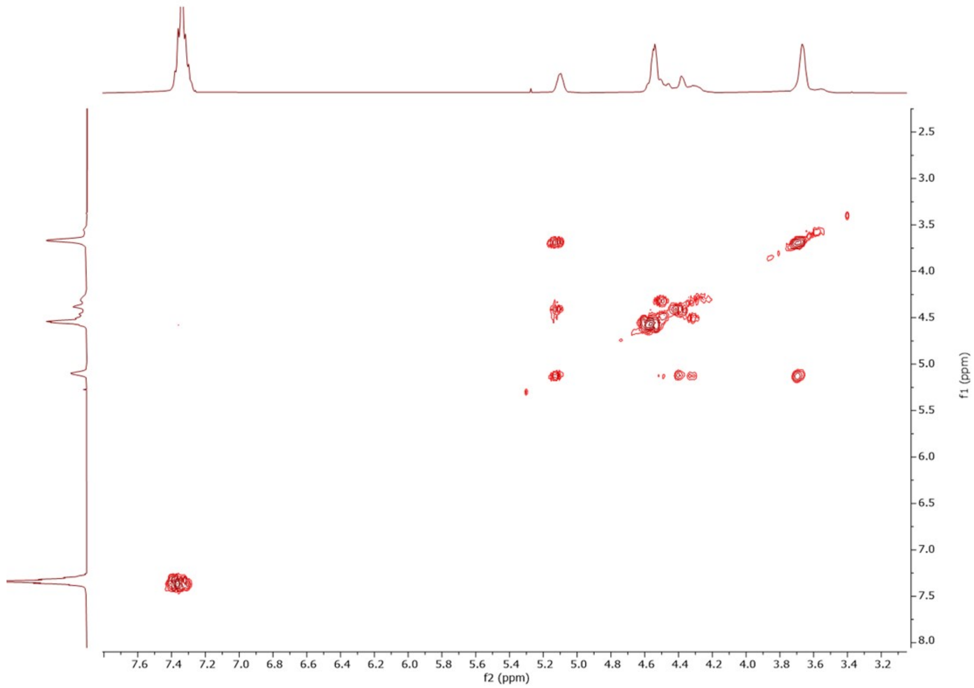


Figure S8. COSY (400 MHz, $CDCl_3$, 23 °C) spectrum of a PBnGEC synthesized with the BEt_3/PPNCl system (Table S1, entry 7).

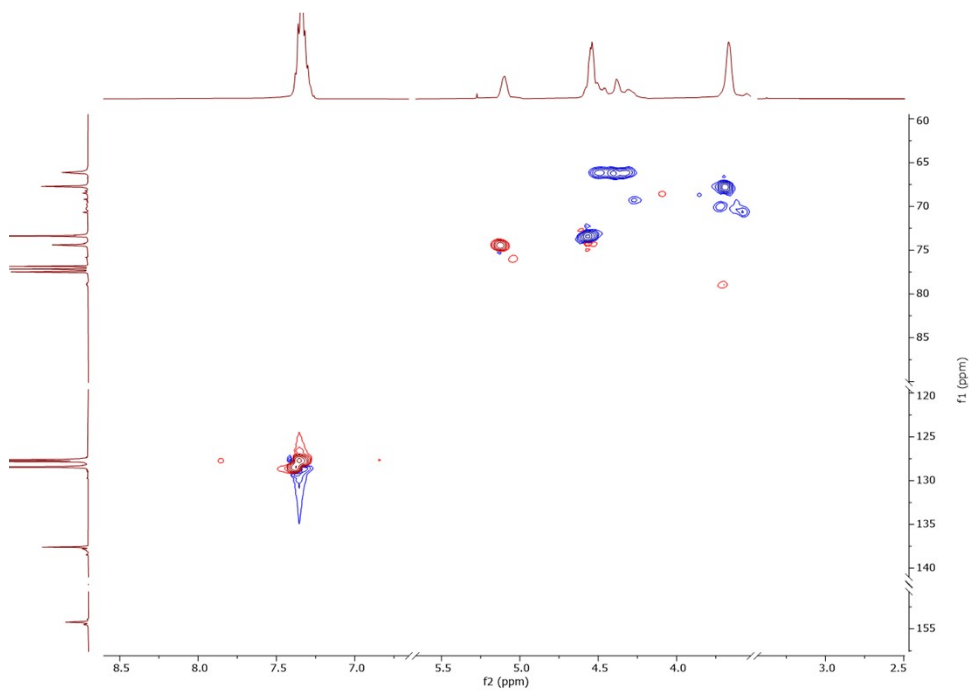


Figure S9. HSQC (400 MHz, $CDCl_3$, 23 °C) spectrum of a PBnGEC synthesized with the BEt_3/PPNCl system (Table S1, entry 7).

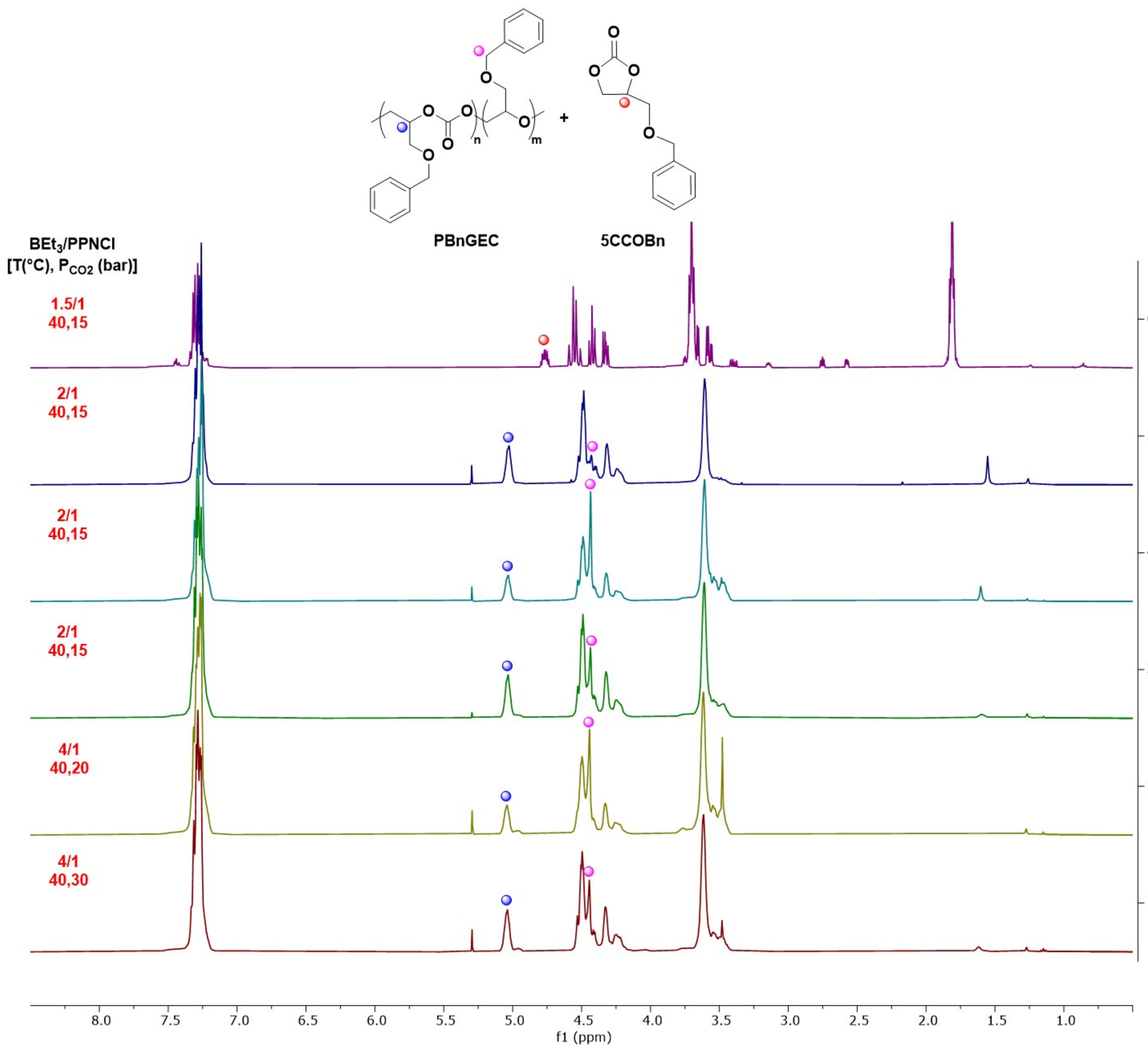


Figure S10. [1]H NMR stacked spectra (400 MHz, $CDCl_3$, 23 °C), showing the effect of BEt_3/PPNCl loadings on the selectivity of the reaction and composition of the isolated polymer synthesized with the BEt_3/PPNCl system.

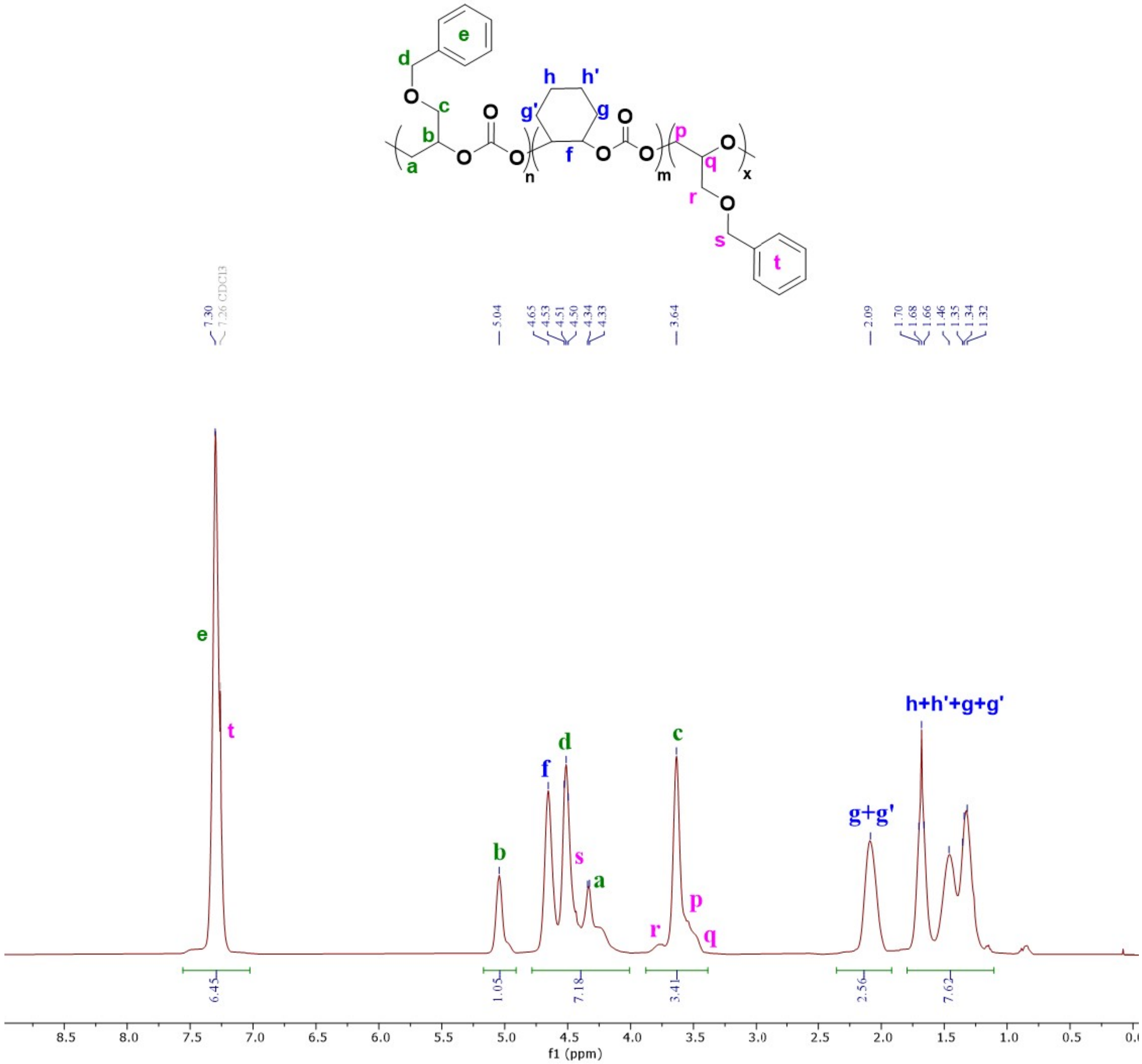


Figure S11. [1]H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of a P(BnGEC-*co*-CHC) synthesized with the BEt_3/PPNCl system (Table 3, entry 3).

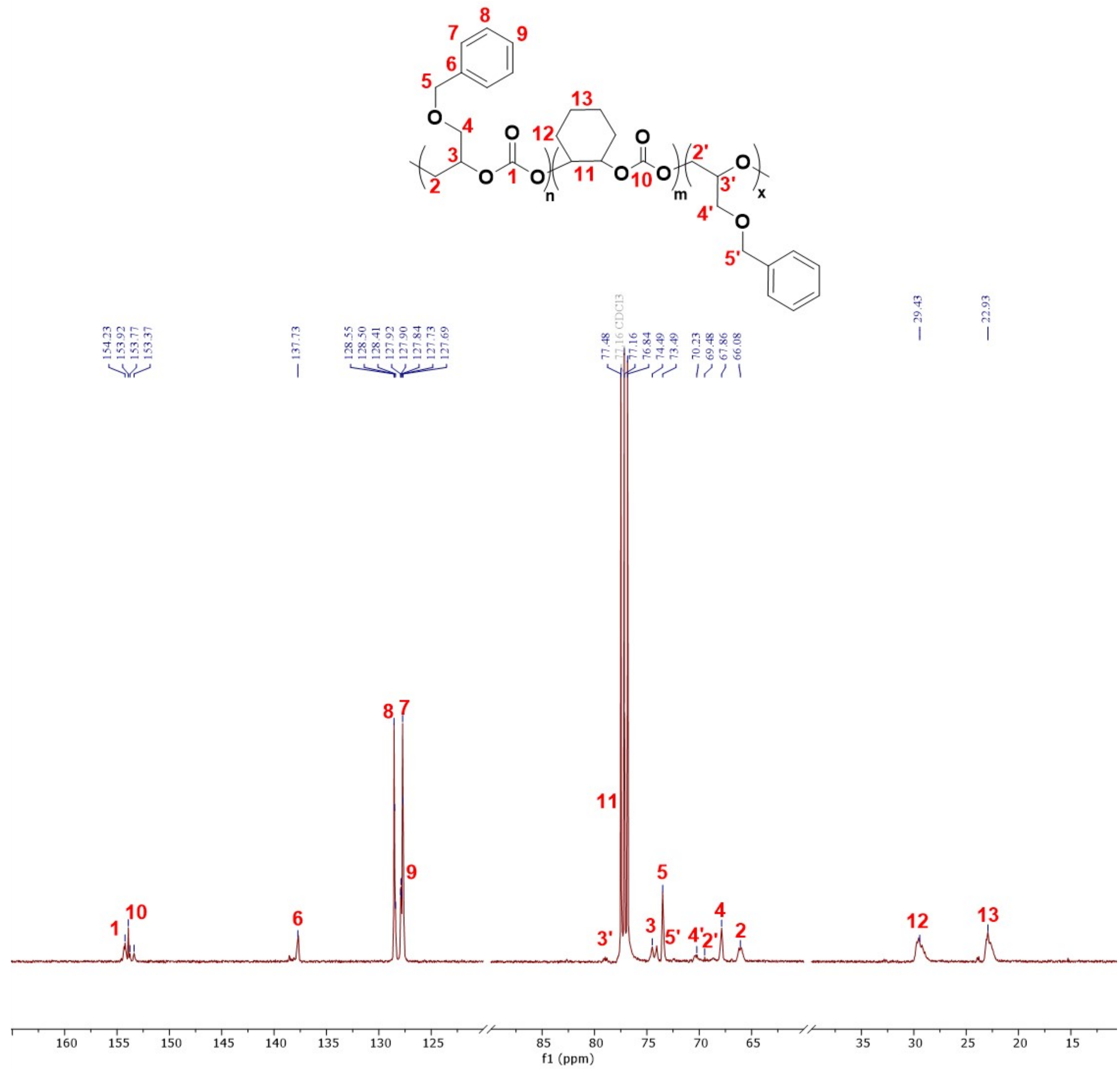


Figure S12. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 23 °C) spectrum of a P(BnGEC-*co*-CHC) synthesized with the BEt_3/PPNCl system (Table 3, entry 3).

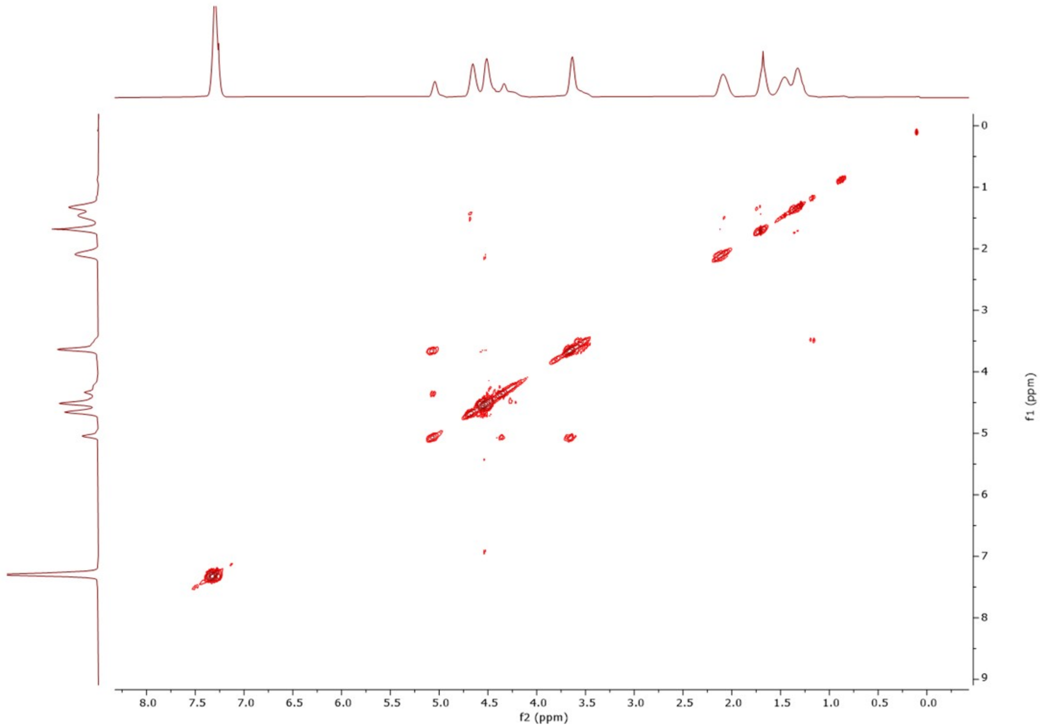


Figure S13. COSY (400 MHz, $CDCl_3$, 23 °C) spectrum of a P(BnGEC-*co*-CHC) synthesized with the BEt_3/PPNCl system (Table 3, entry 3).

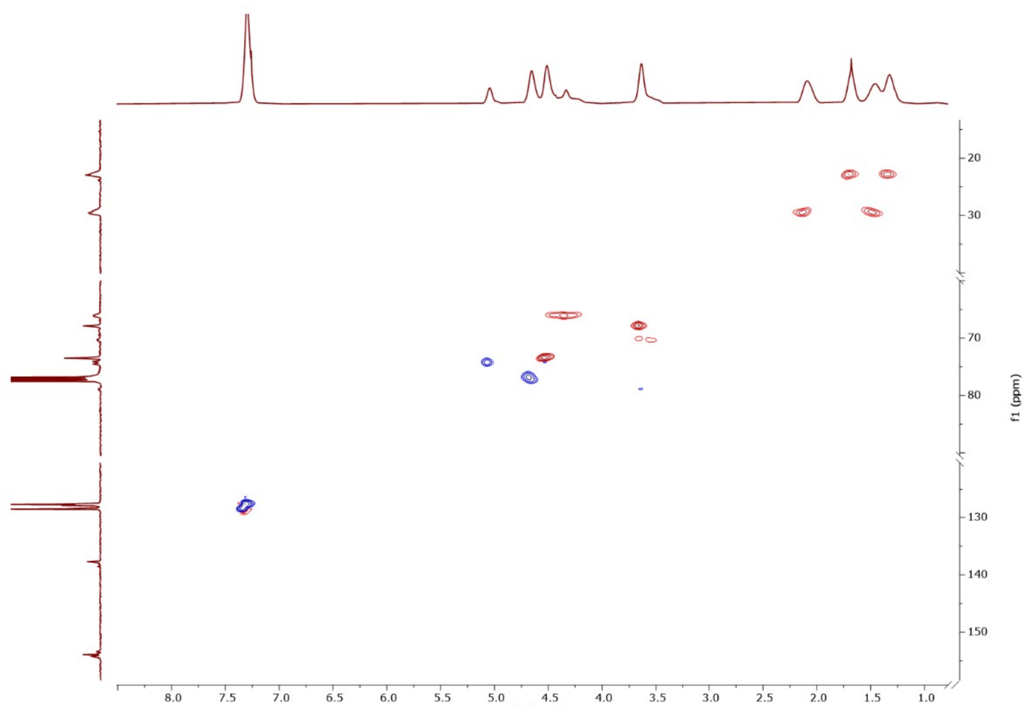


Figure S14. HSQC (400 MHz, $CDCl_3$, 23 °C) spectrum of a P(BnGEC-*co*-CHC) synthesized with the BEt_3/PPNCl system (Table 3, entry 3).

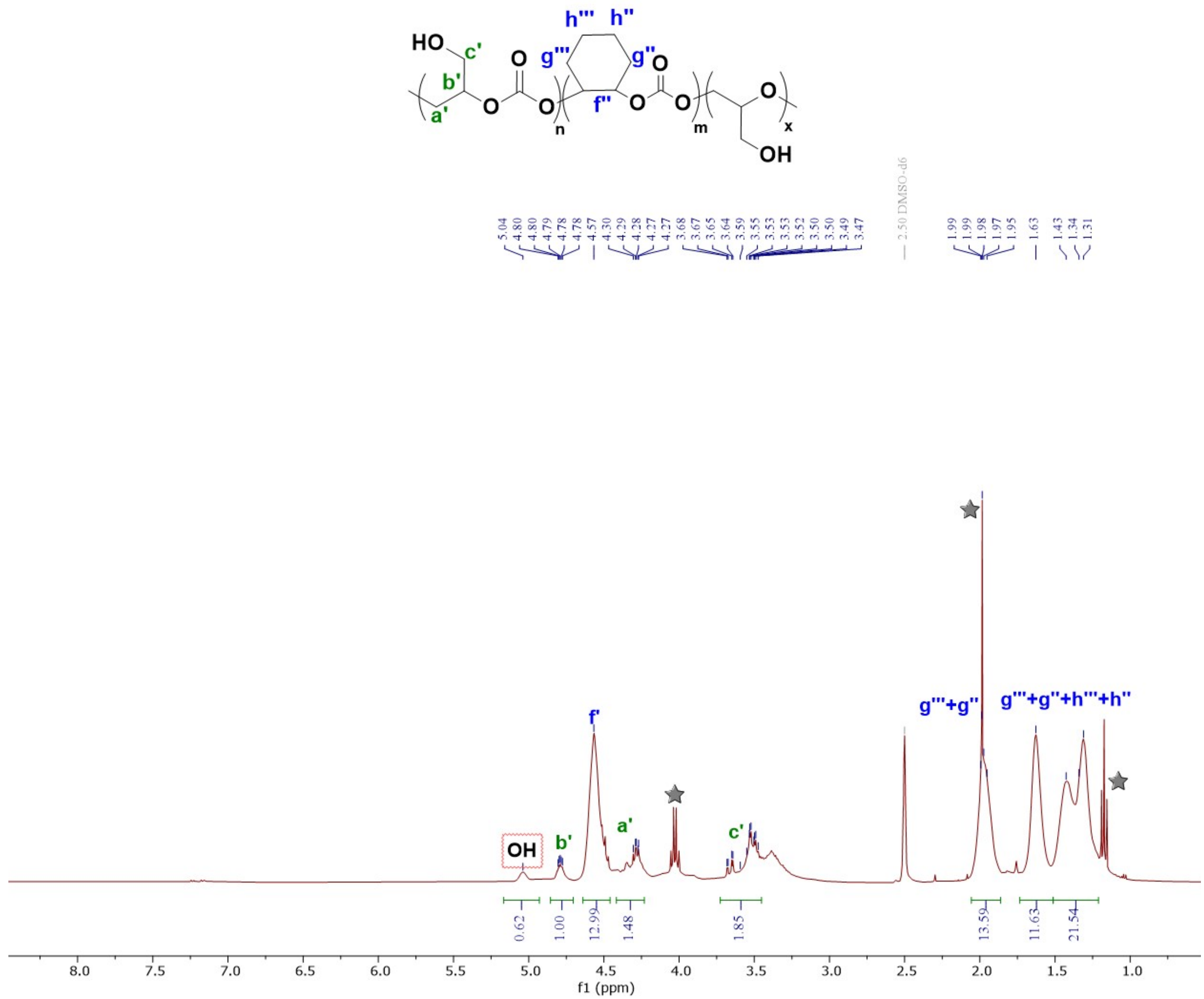


Figure S15. ^{1}H NMR (400 MHz, DMSO-d_6, 23 °C) spectrum of poly(glycidol-*co*-cyclohexene) carbonate, P(GC-*co*-CHC) resulting from deprotection of P(BnGEC-*co*-CHC) (Table 3, entry 4); ★ = residual solvent (ethyl acetate)

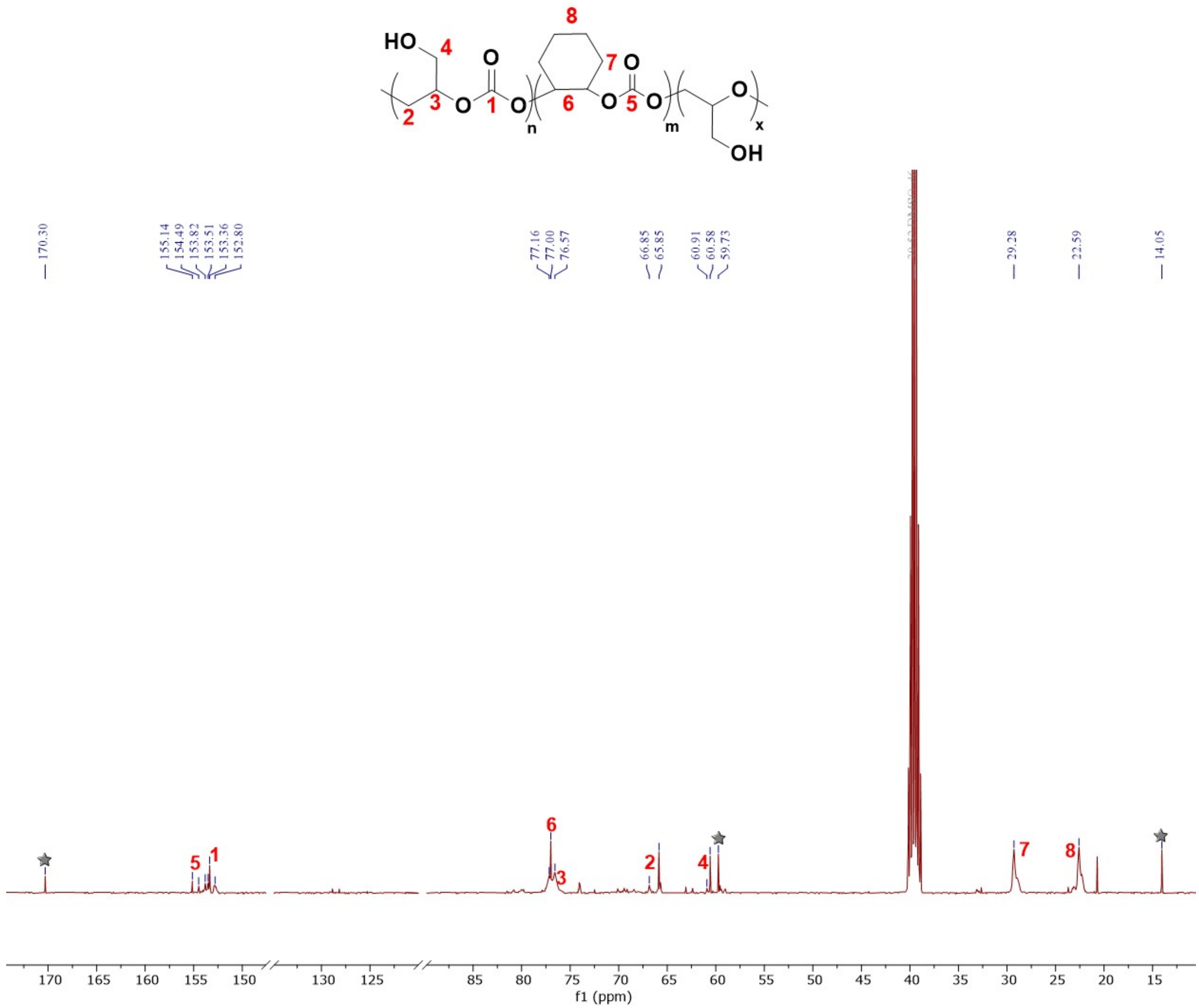


Figure S16. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6, 23 °C) spectrum of poly(glycidol-*co*-cyclohexene) carbonate, P(GC-*co*-CHC) resulting from deprotection of P(BnGEC-*co*-CHC) (Table 3, entry 4).

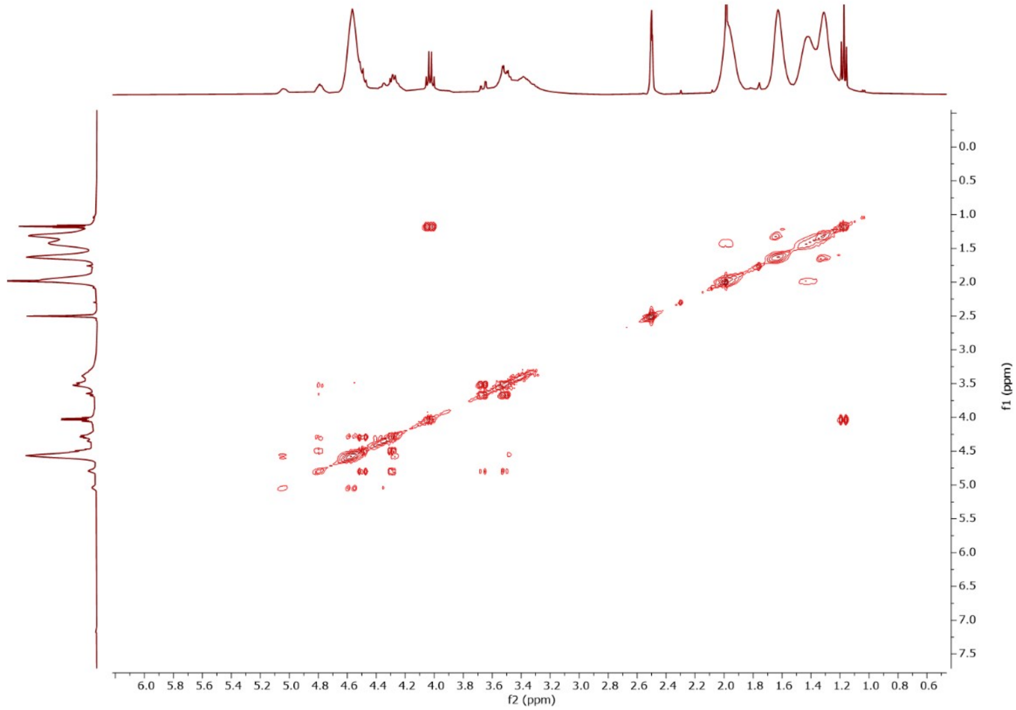


Figure S17. COSY (400 MHz, $CDCl_3$, 23 °C) spectrum of a P(GC-*co*-CHC) resulting from deprotection of P(BnGEC-*co*-CHC) (Table 3, entry 4).

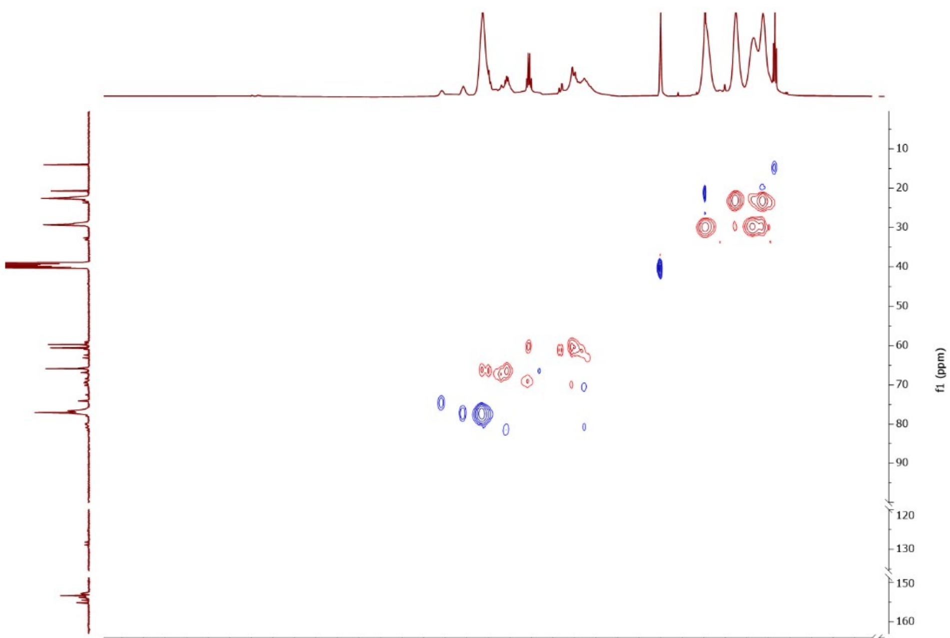
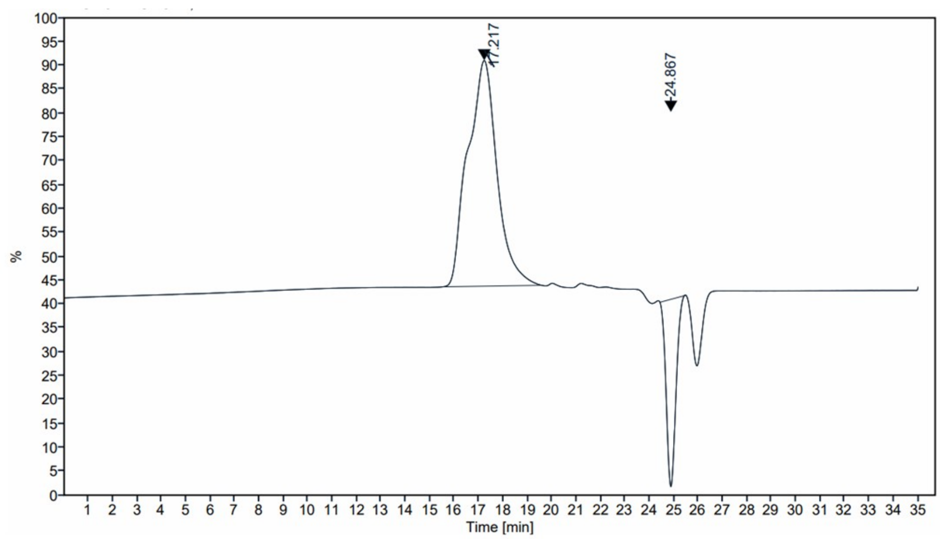
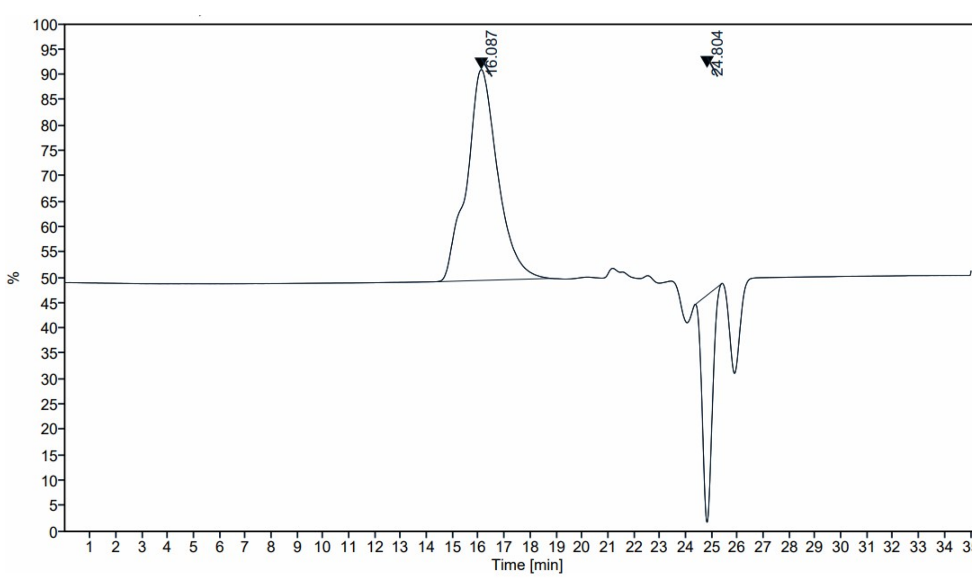


Figure S18. HSQC (400 MHz, $CDCl_3$, 23 °C) spectrum of a P(GC-*co*-CHC) resulting from deprotection of P(BnGEC-*co*-CHC) (Table 3, entry 4).



Peak	Retention Time (min)	*M*n	*M*w	*M*p	*M*z	*M*z+1	Dispersity
1	17.217	5500	6300	5700	7200	8000	1.16

Figure S19. SEC (DMF, 25 °C) trace of a PBnGEC synthesized with the BEt_3/PPNCl system (Table 2, entry 7).



Peak	Retention Time (min)	*M*n	*M*w	*M*p	*M*z	*M*z+1	Dispersity
1	16.087	10100	12100	11600	14200	16500	1.20

Figure S20. SEC (DMF, 25 °C) trace of a PCHC synthesized with the BEt_3/PPNCl system (Table S3, entry 10).

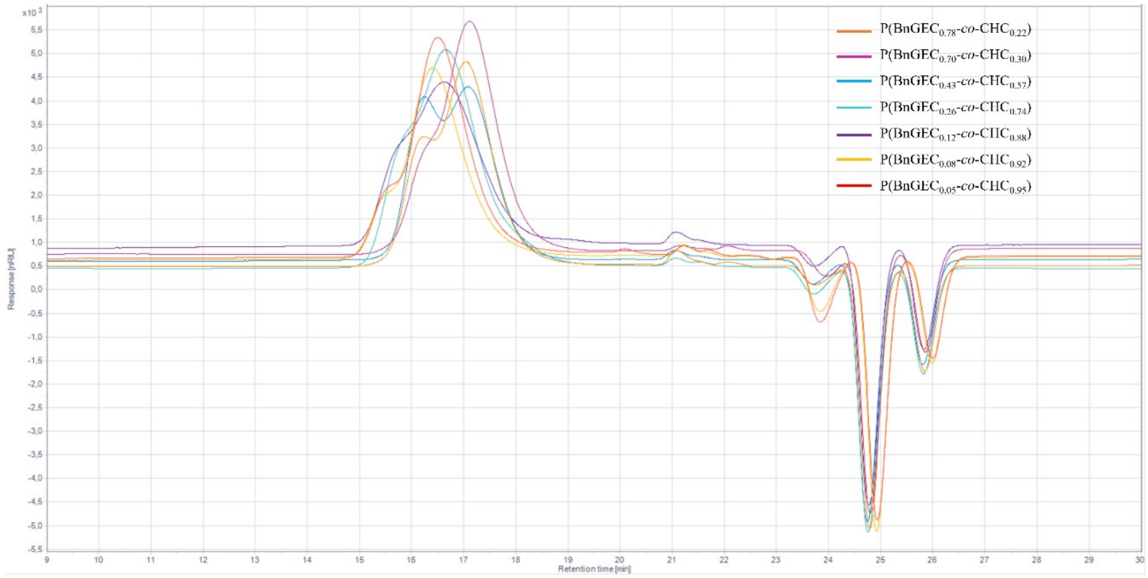
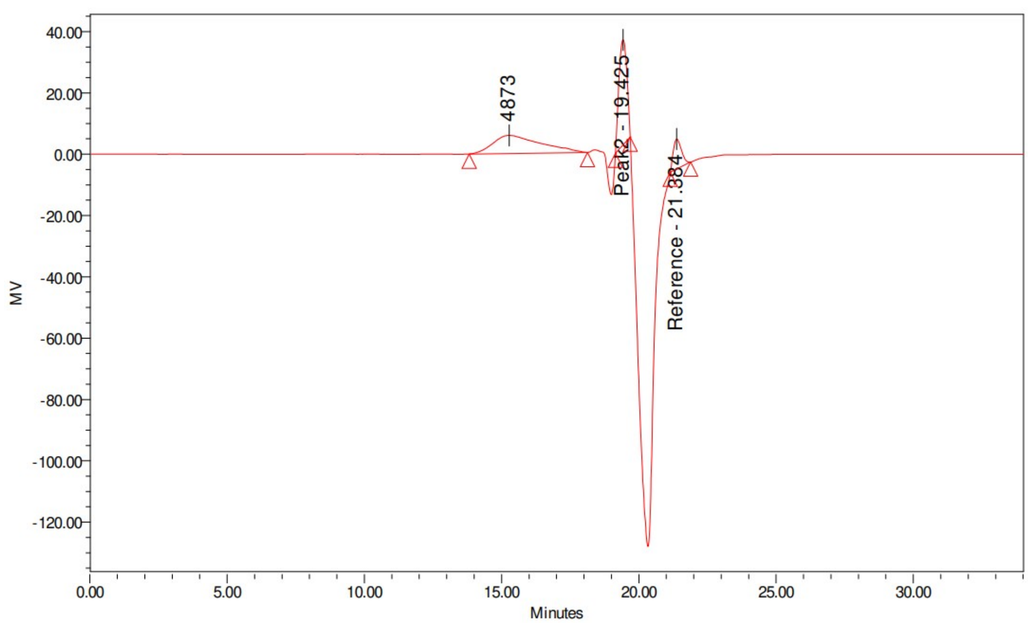
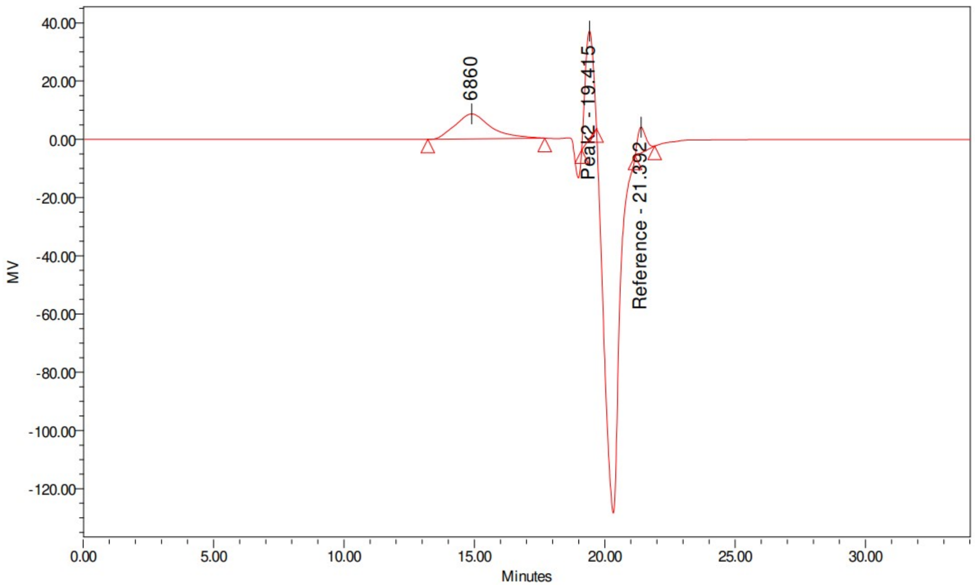


Figure S21. Superimposed SEC (THF, 25 °C) traces of all P(BnGEC-*co*-CHC) samples synthesized with the BEt_3/PPNCl system (Table 3, entry 1-7).



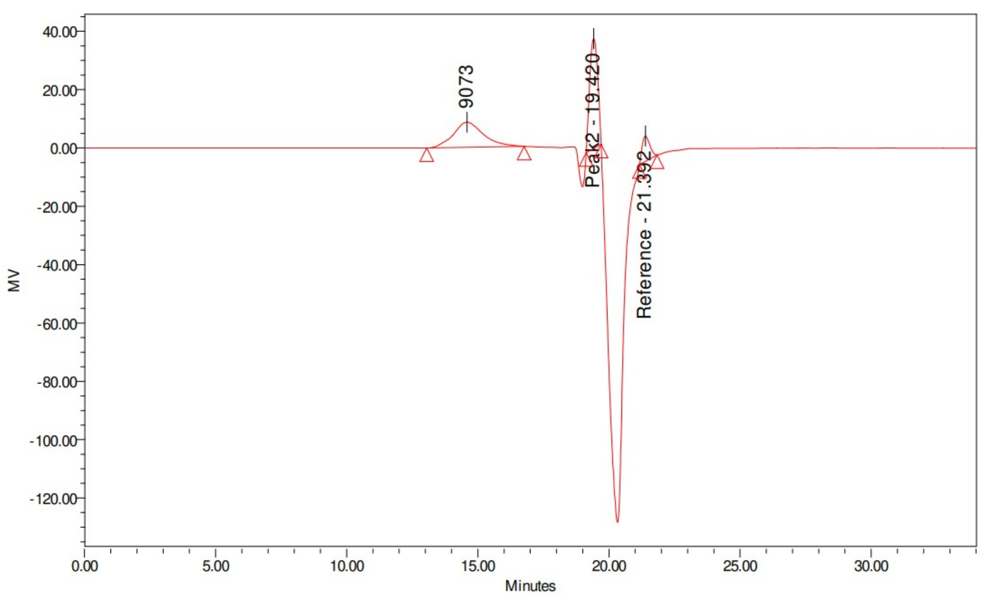
Peak	Retention Time (min)	*M*n	*M*w	*M*p	*M*z	*M*z+1	Dispersity
1	15.275	2600	4200	4900	6000	7650	1.62

Figure S22. SEC (DMF, 25 °C) trace of P(GC$_{0.23}$-*co*-CHC$_{0.77}$) resulting from deprotection of P(BnGEC$_{0.26}$-*co*-CHC$_{0.74}$) (Table 3, entry 4).



Peak	Retention Time (min)	Mn	Mw	Mp	Mz	Mz+1	Polydispersity
1	14.898	4900	7200	6900	9700	13000	1.49

Figure S23. SEC (DMF, 25 °C) trace of P(GC$_{0.11}$-*co*-CHC0$_{.89}$) resulting from deprotection of P(BnGEC$_{0.12}$-*co*-CHC$_{0.88}$) (Table 3, entry 5).



Peak	Retention Time (min)	Mn	Mw	Mp	Mz	Mz+1	Polydispersity
1	14.589	7100	9400	9100	11700	14200	1.31

Figure S24. SEC (DMF, 25 °C) trace of P(GC$_{0.07}$-*co*-CHC0$_{.93}$) resulting from deprotection of P(BnGEC$_{0.08}$-*co*-CHC$_{0.92}$) (Table 3, entry 6).

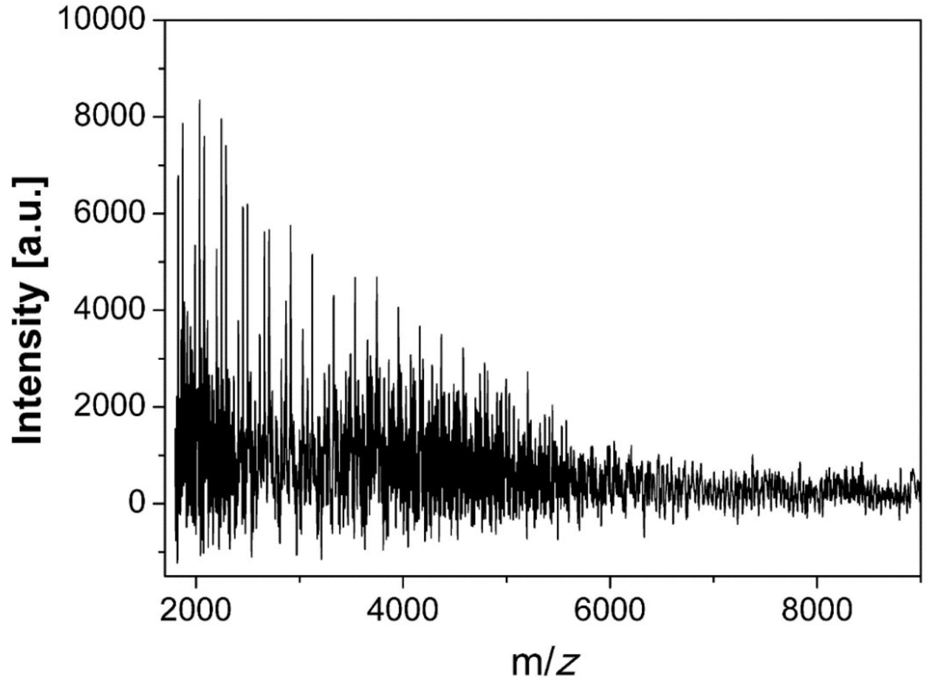


Figure S25. Representative MALDI-ToF mass spectrum (DHB matrix) of a PBnGEC synthesized with the BEt_3/PPNCl system (Table 2, entry 4) (see Figure S26 for a zoomed region with full assignment of the different observed signals).

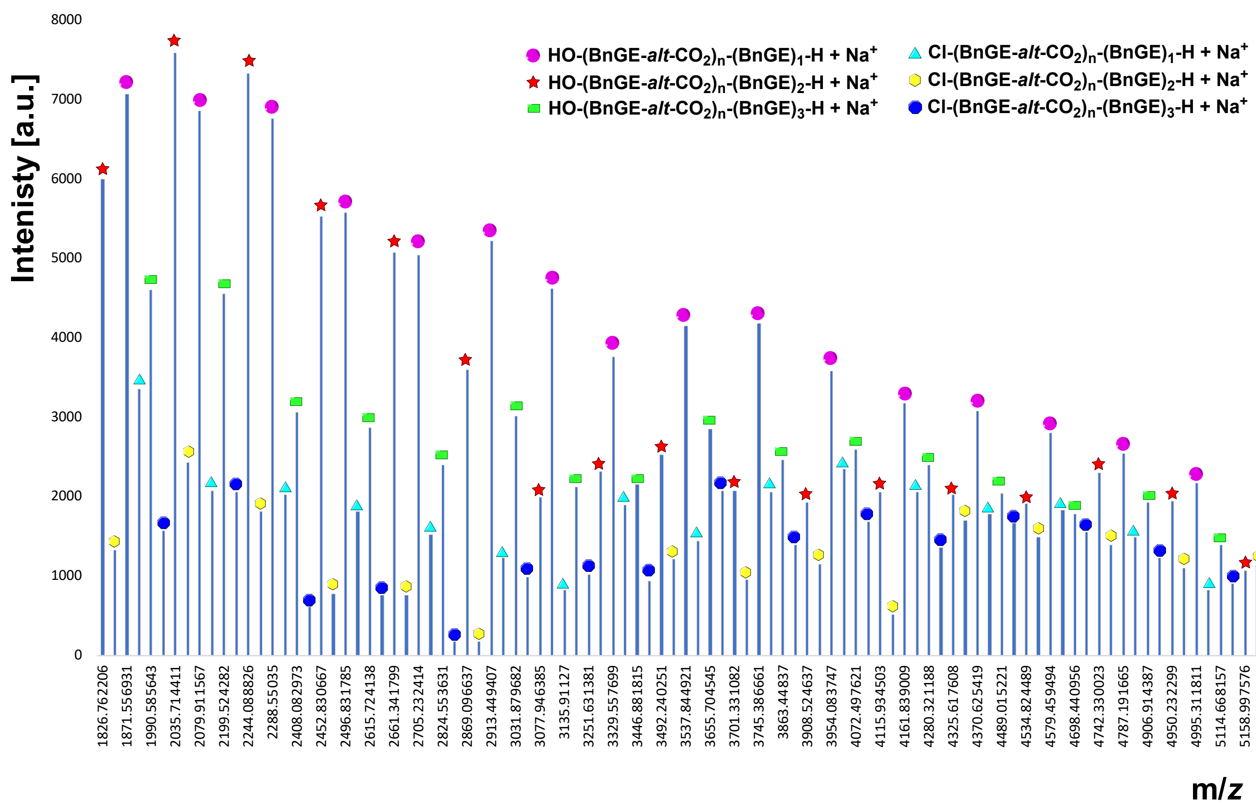


Figure S26. Zoomed region (*m/z* = *ca* 1800–5200 Da) of the above MALDI-TOF mass spectrum (DHB matrix) of a PBnGEC synthesized with the BEt_3/PPNCl system (Table 2, entry 4), with the assignment of the various copolymer fragment series displaying different chain-ends and composition.

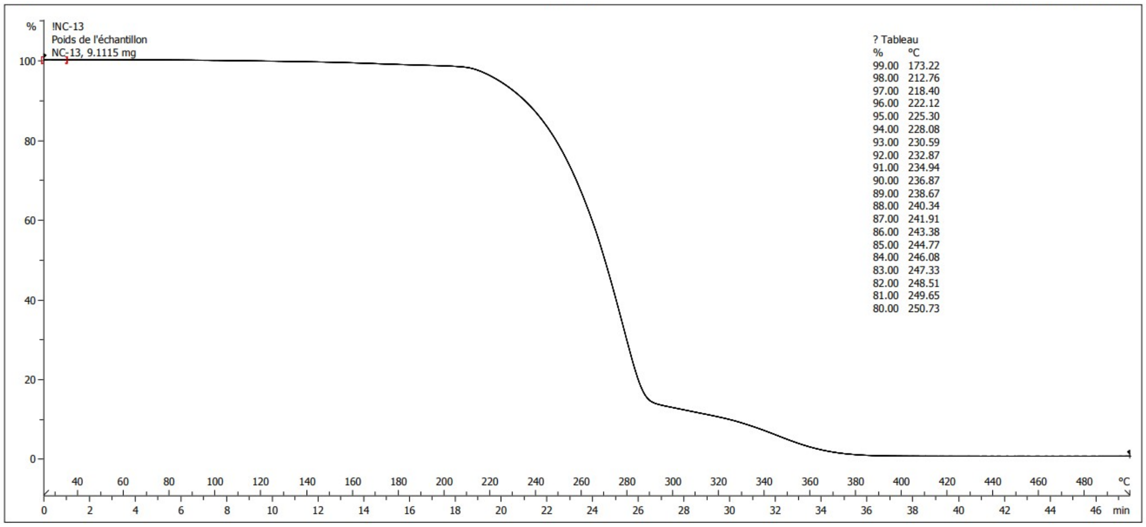


Figure S27. TGA trace (heating rate of 10 °C min^{-1}, from +25 to +500 °C) of a PBnGEC synthesized with the BEt_3/PPNCl system (Table 2, entry 7).

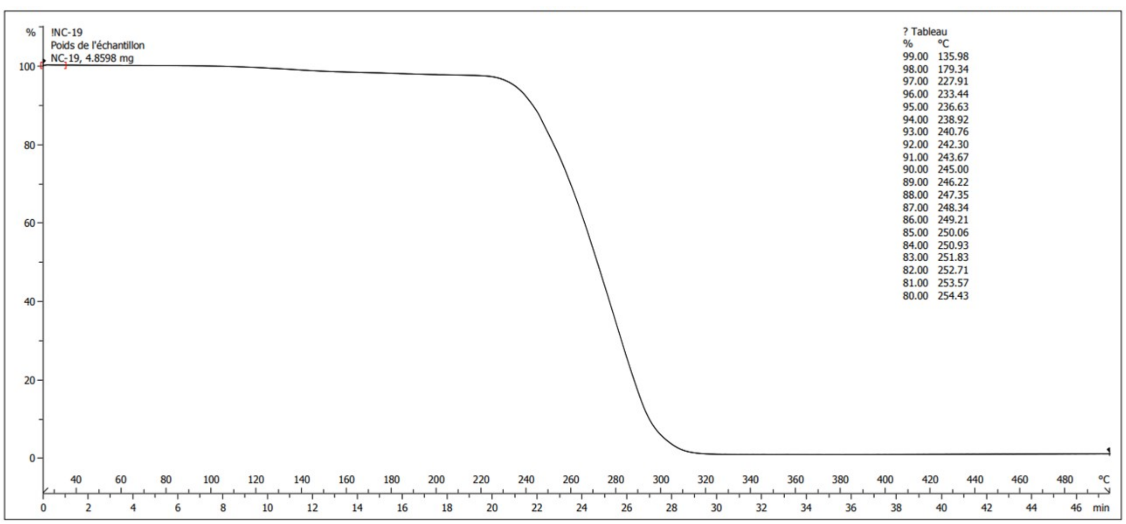


Figure S28. TGA trace (heating rate of 10 °C min^{-1}, from +25 to +500 °C) of a PCHC synthesized with the BEt_3/PPNCl system (Table S3, entry 10).

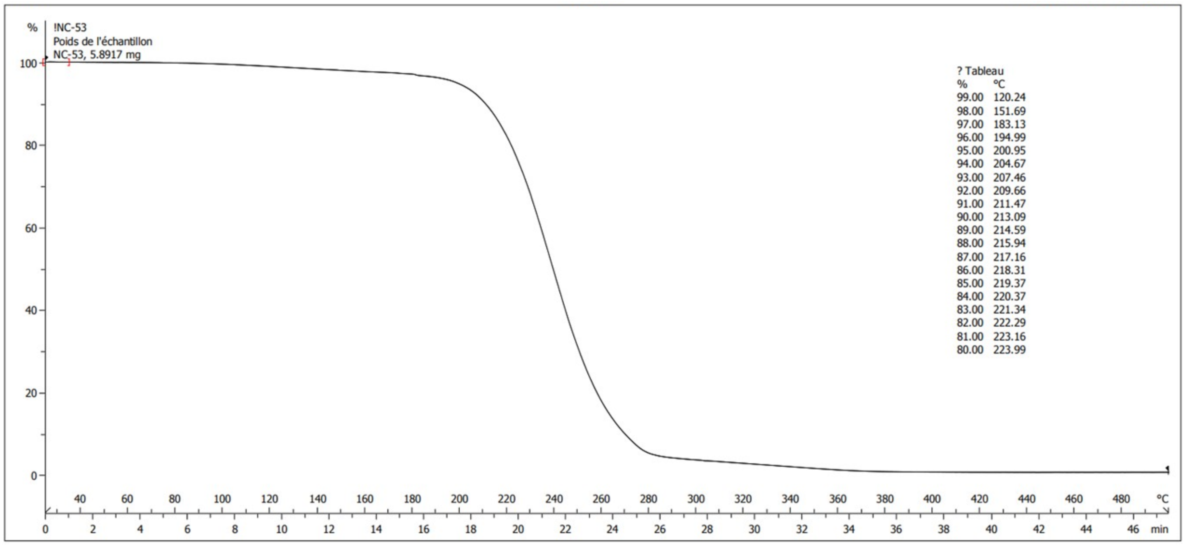


Figure S29. TGA trace (heating rate of 10 °C min^{-1}, from +25 to +500 °C) of a P(BnGEC$_{0.08}$-*co*-CHC$_{0.92}$) synthesized with the BEt$_3$/PPNCl system (Table 3, entry 6).

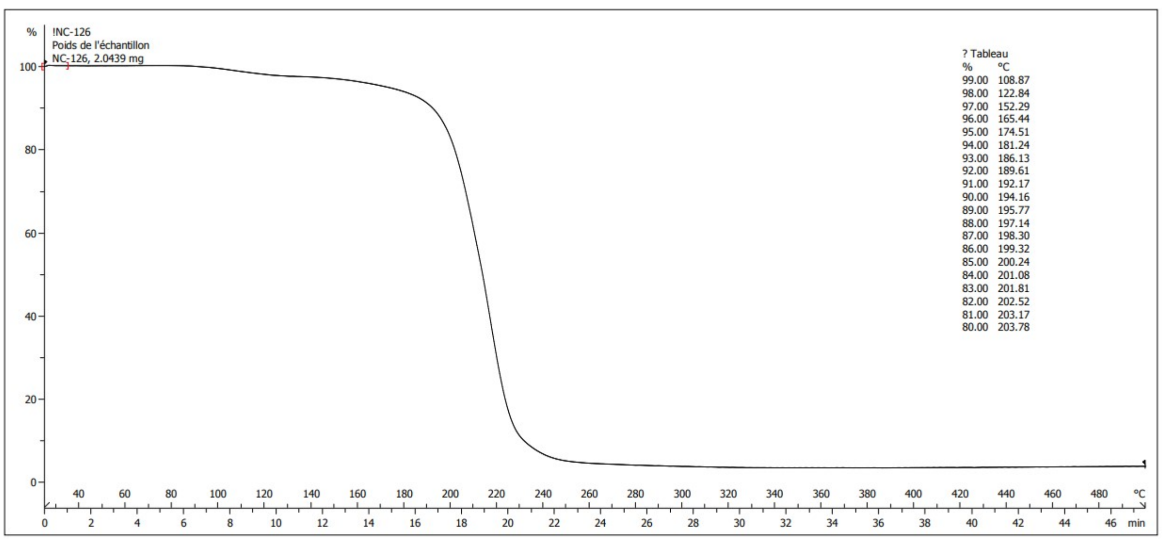


Figure S30. TGA trace (heating rate of 10 °C min^{-1}, from +25 to +500 °C) of a P(GC$_{0.11}$-*co*-CHC$_{0.89}$) synthesized with the BEt$_3$/PPNCl system (Table 3, entry 5).

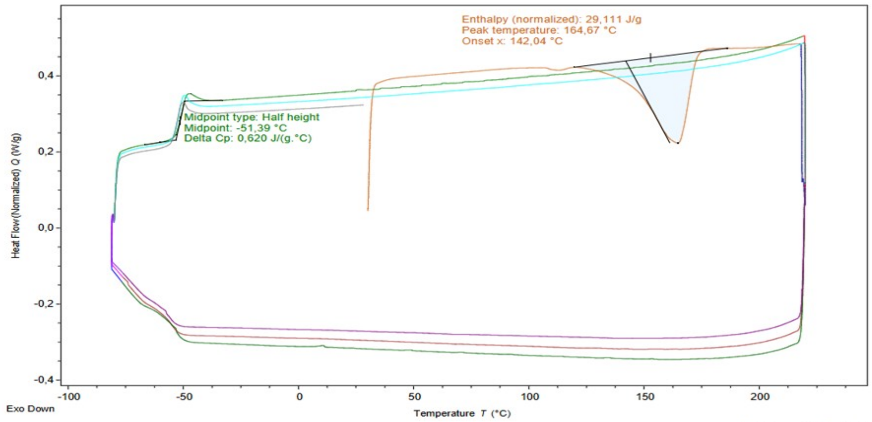


Figure S31. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +220 °C) of a PBnGEC synthesized with the BEt_3/PPNCl system (Table 2, entry 7).

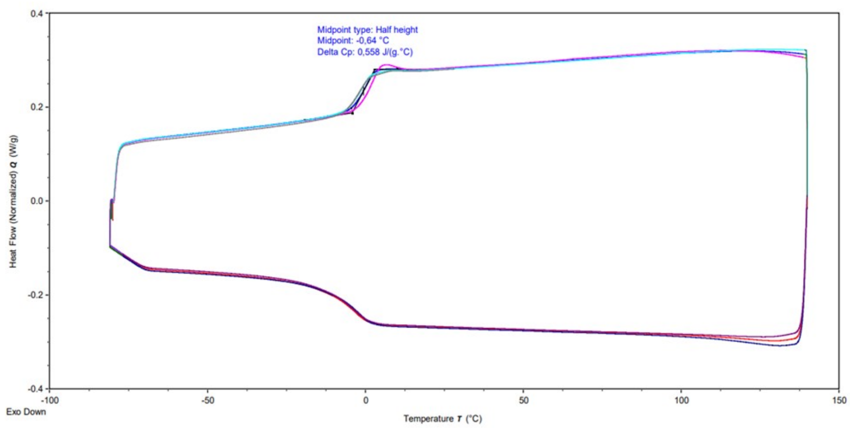


Figure S32. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +140 °C) of a PBnGEC synthesized with the BEt_3/PPNCl system (Table 2, entry 7).

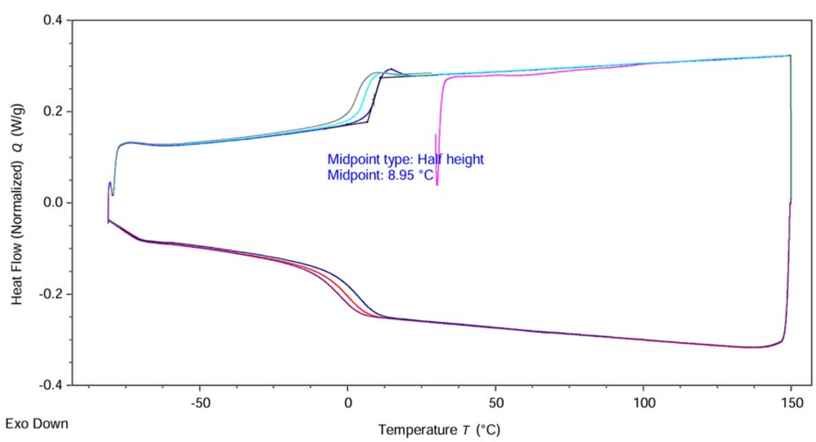


Figure S33. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +140 °C) of a PBnGEC synthesized with the SalphenCo(III)Cl/PPNCl system (Table 1, entry 3).

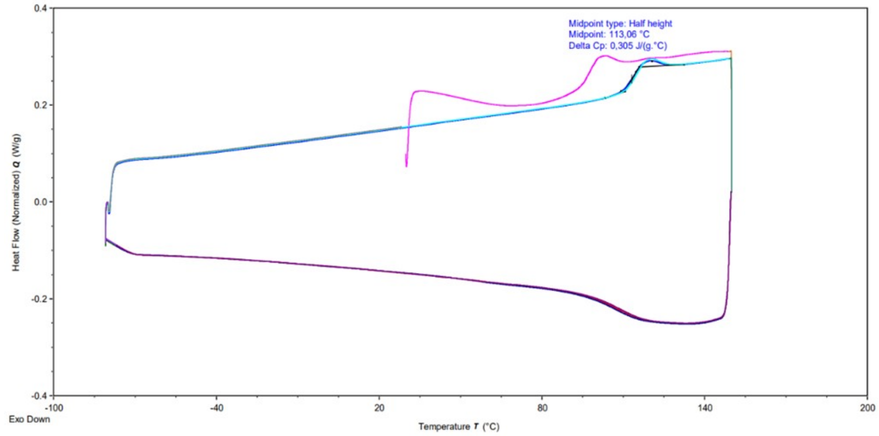


Figure S34. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C) of a PCHC synthesized with the BEt_3/PPNCl system (Table S3, entry 10).

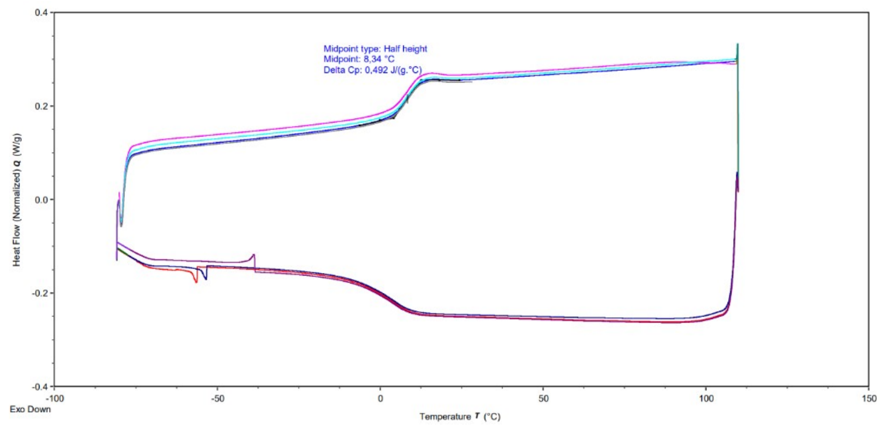


Figure S35. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +110 °C of a P(BnGEC$_{0.78}$-*co*-CHC$_{0.22}$) synthesized with the BEt_3/PPNCl system (Table 3, entry 1).

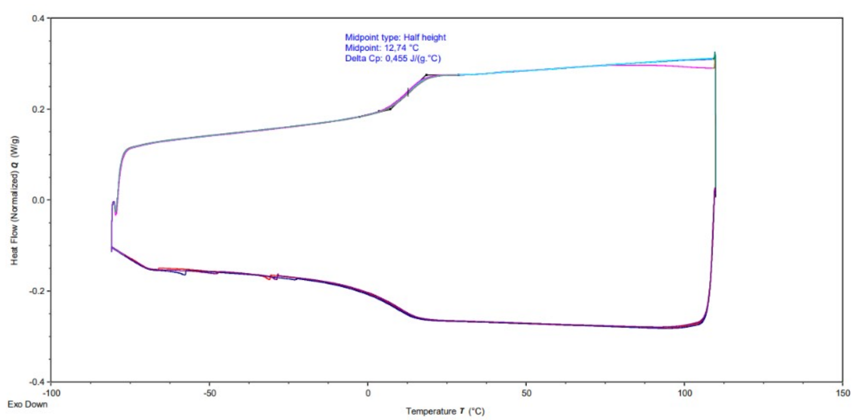


Figure S36. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +110 °C) of a P(BnGEC$_{0.70}$-*co*-CHC$_{0.30}$), synthesized with the BEt_3/PPNCl system (Table 3, entry 2).

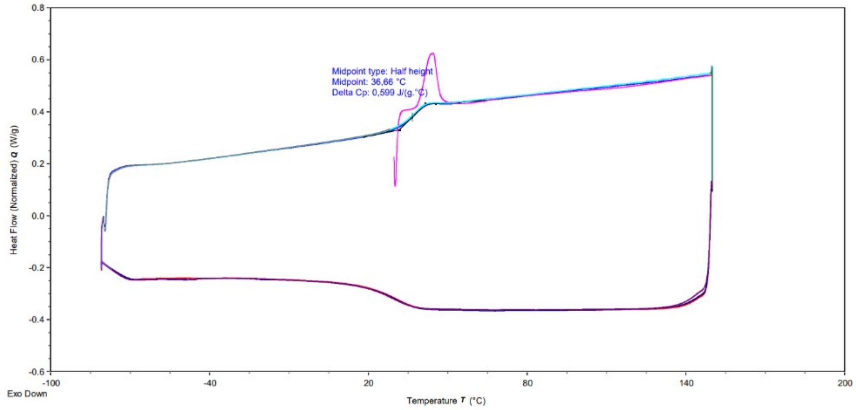


Figure S37. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C of a P($BnGEC_{0.43}$-*co*-$CHC_{0.57}$) synthesized with the BEt_3/PPNCl system (Table 3, entry 3).

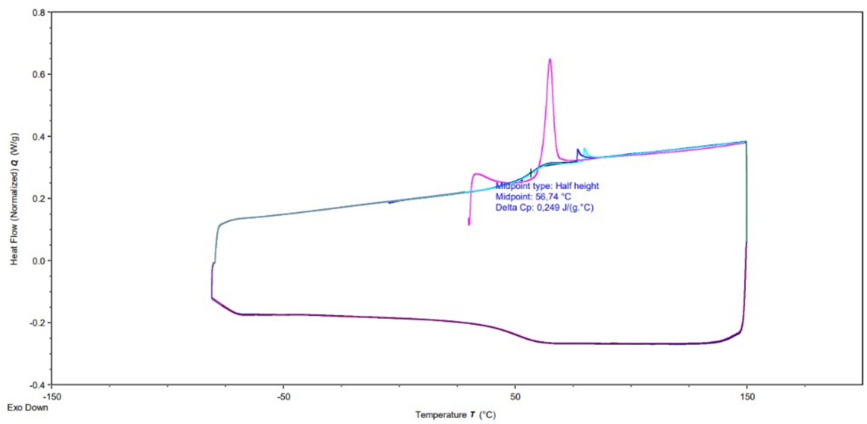


Figure S38. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C of a P($BnGEC_{0.26}$-*co*-$CHC_{0.74}$) synthesized with the BEt_3/PPNCl system (Table 3, entry 4).

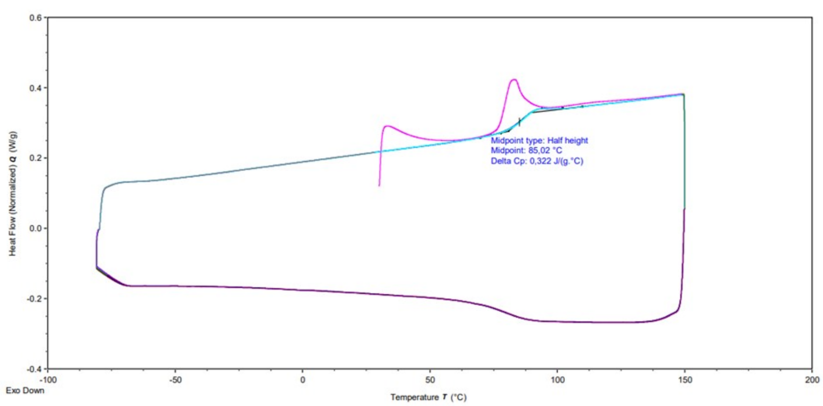


Figure S39. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C) of a P($BnGEC_{0.12}$-*co*-$CHC_{0.88}$) synthesized with the BEt_3/PPNCl system (Table 3, entry 5).

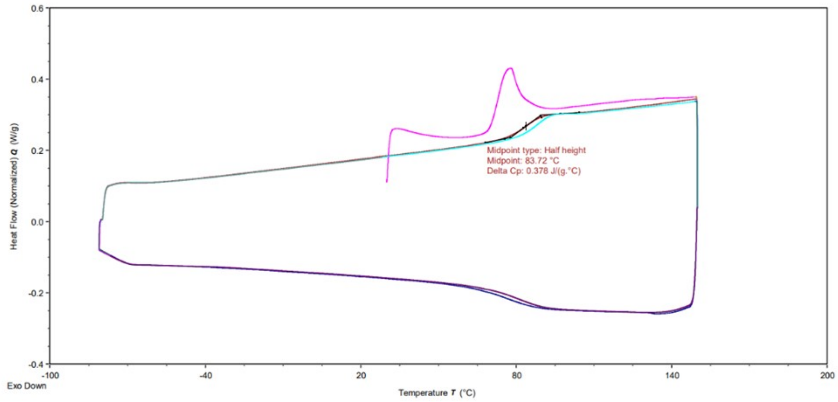


Figure S40. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C) of a P(BnGEC$_{0.08}$-*co*-CHC$_{0.92}$) synthesized with the BEt_3/PPNCl system (Table 3, entry 6).

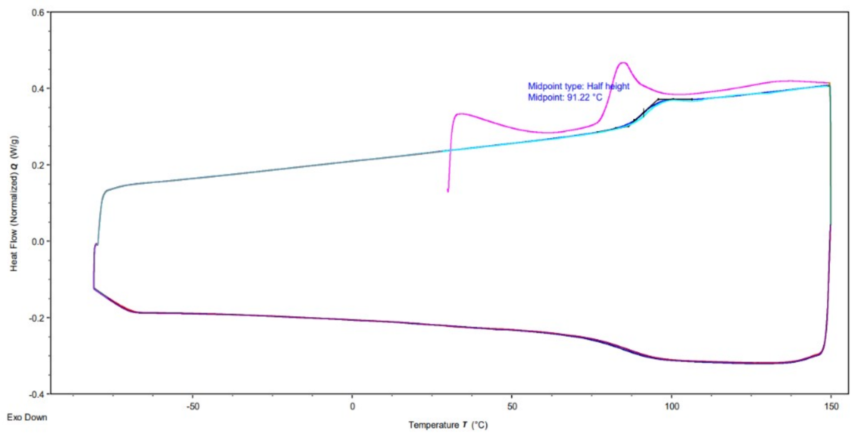


Figure S41. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C) of a P(BnGEC$_{0.05}$-*co*-CHC$_{0.95}$) synthesized with the BEt_3/PPNCl system (Table 3, entry 7).

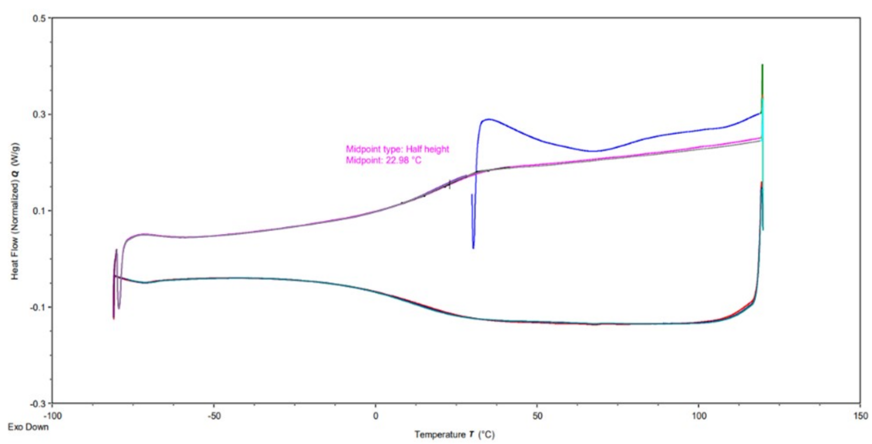


Figure S42. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +120 °C) of a P(GC$_{0.23}$-*co*-CHC$_{0.77}$) resulting from deprotection of P(BnGEC$_{0.26}$-*co*-CHC$_{0.74}$) (Table 3, entry 4).

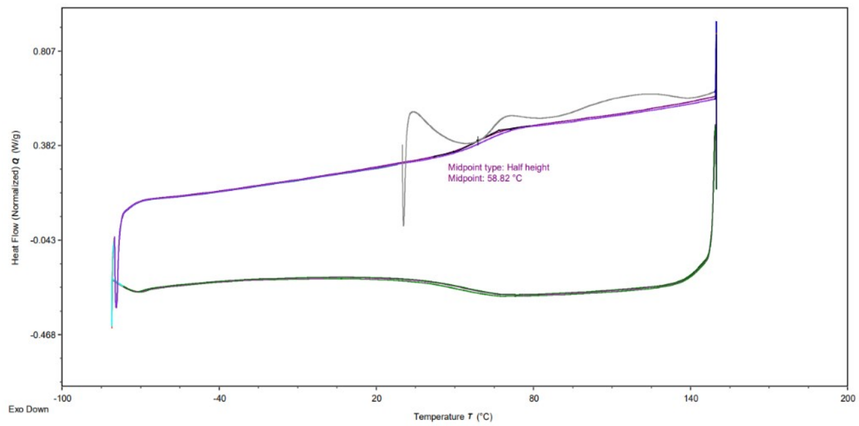


Figure S43. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C) of a P($GC_{0.11}$-*co*-$CHC_{0.89}$) resulting from deprotection of P($BnGEC_{0.12}$-*co*-$CHC_{0.88}$) (Table 3, entry 5).

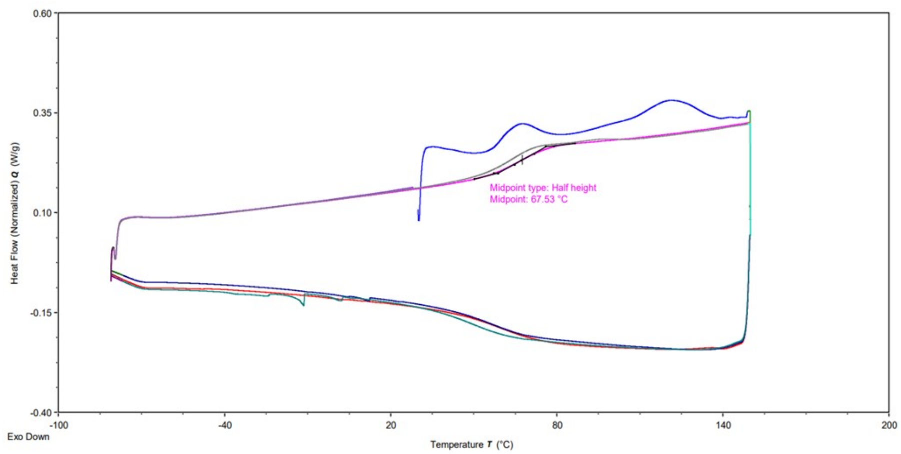


Figure S44. DSC thermogram (heating rate of 10 °C min^{-1}, from −80 to +150 °C) of a P($GC_{0.07}$-*co*-$CHC_{0.93}$) resulting from deprotection of P($BnGEC_{0.08}$-*co*-$CHC_{0.92}$) (Table 3, entry 6).

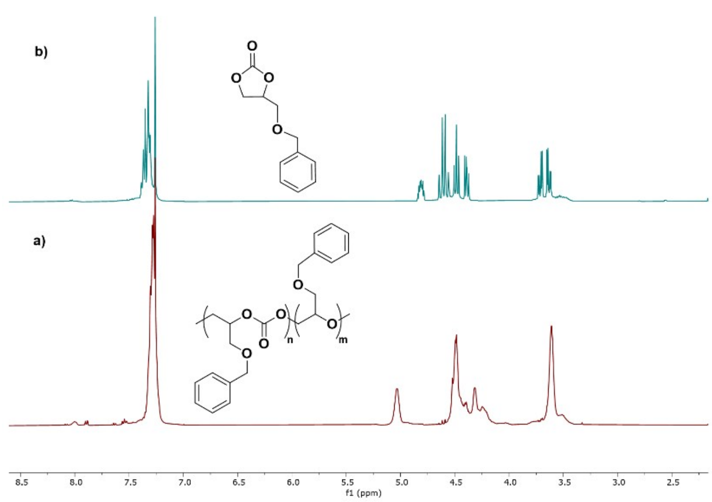


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) stacked spectra of a) a PBnGEC synthesized with the BEt_3/PPNCl system (Table 2, entry 7) after undergoing three heating-cooling cycles from –80 to +140 °C; b) after undergoing three heating-cooling cycles from –80 to +220 °C.

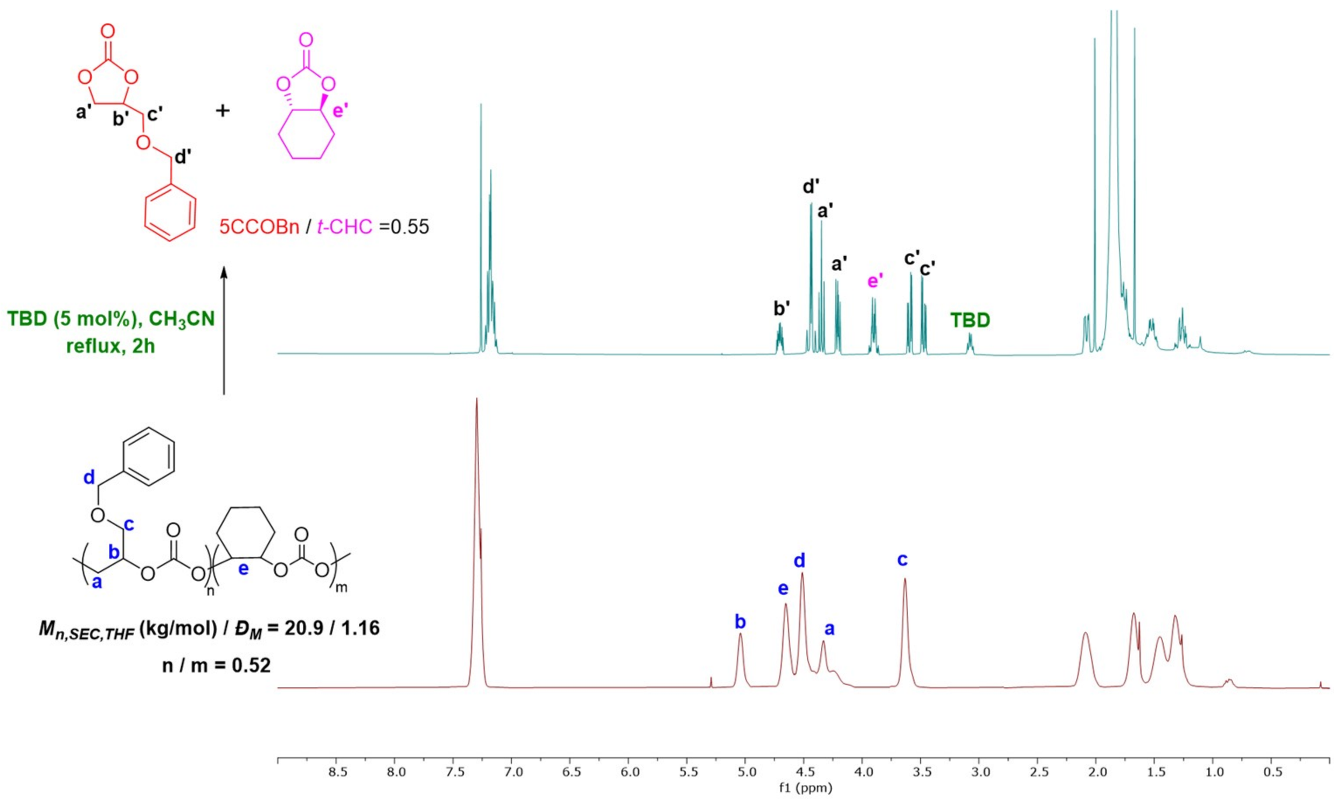
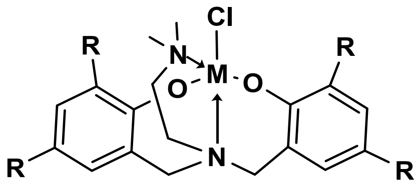


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) stacked spectra of (bottom) a P($BnGEC_{0.52}$-*co*-$CHC_{0.48}$) synthesized with the SalphenCo(III)Cl/PPNCl system (Table 1, entry 7); (top) after undergoing depolymerization to respective cyclic carbonates using 5 mol% TBD catalyst under acetonitrile reflux for 2h.

Table S1. ROCOP of BnGE/CO_2 using metal catalyst **1**,**2**, and **3**.



1 M = Al(III), R = ^{t}Bu
2 M = Al(III), R = Me
3 M = Fe(III), R = Cl

Entry	I/M	$[M]_o/[C]_o/[Co]_o$ [a]	Temp. (°C)	P_{CO2} (bar)	Time (h)	Conv. [b] (%)	Selectivity [c]
1	**1**/BnGE	100:1:0	40	30	16	-	No polym.
2	**1**/BnGE	100:1:1	30	50	22	10	CC
3	**1**/BnGE	100:1:1	40	30	16	22	CC
4	**1**/BnGE	200:1:1	60	40	16	90	CC
5	**1**/BnGE	200:1:0.5	40	30	20	6	CC
6	**2**/BnGE	100:1:1	30	50	22	40	CC
7	**2**/BnGE	200:1:1	25	15	24	47	CC
8	**3**/BnGE	200:1:0.5	40	30	20	9	CC
9	**3**/BnGE	200:1:1	60	55	18	75	CC
10	**3**/BnGE	200:1:1	40	30	16	27	CC
11	**3**/BnGE	200:1:0.5	40	30	18	19	CC
12	**3**/CHO	200:1:1	60	55	22	75	PCHC

[a] $[M]_o/[C]_o/[Co]_o$ = $[Monomer]_o/[catalyst]_o/[cocatalyst]_o$, where PPNCl was used as a cocatalyst and CH_2Cl_2 (1 mL) was used as solvent. [b, c] % Monomer conversion and CO_2 selectivity (CC = cyclic carbonate) determined by ^1H NMR analysis of the crude reaction mixture.

Table S2. Terpolymerization of CHO, BnGE, and CO_2 using metal catalyst **3**.

Entry	f_{BnGE} Substrate	$[M]_o/[C]_o/[Co]_o$ [a]	Temp. (°C)	P_{CO2} (bar)	Time (h)	Crude reaction mixture [b] Conv. (%)		Isolated polymer			
						BnGE	CHO	f_{BnGE} [c] P(BnGEC-*co*-CHC)	$M_{n, SEC}$ [d] (kg/mol) (Area%)	$Đ_M$ [e]	Yield [f] (%)
1	0.10	200:1:1	60	50	22	28	20	0.10			
2	0.50	200:1:1	60	55	23	2	6	-			
3	0.30	100:1:1	40	55	46	13	16	-			
4	0.25	100:1:1	60	55	17	33	37	0.13	2.7	1.24	
5	0.10	200:1:1	40	30	23	-	-				
6	0.10	200:1:1	50	40	23	-	-				
7	0.10	200:1:1	60	55	28	17	12	0.12			
8	0.10	100:1:1	60	55	46	83	85	0.05	7.0 (40) 3.1(60)	1.07 1.08	16

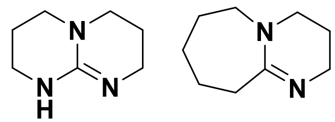
[a] $[M]_o/[C]_o/[Co]_o = [Monomer]_o/[catalyst]_o/[cocatalyst]_o$, where PPNCl was used as a cocatalyst and CH_2Cl_2 (1 mL) was used as solvent. [b] % Monomer conversion and CO_2 selectivity determined by ^1H NMR analysis of the crude reaction mixture. [c] Determined by ^1H NMR analysis of the isolated polymer. [d] Experimental molar mass of PBnGEC determined by SEC in THF with a calibration using polystyrene standards; the molar mass value is the average of the bimodal trace. [e] Dispersity value determined by SEC in THF. [f] Yield (%) = [Wt. of isolated polymer obtained(g)/ (monomer used + CO_2 consumed) (g)] × 100.

Table S3. ROCOP of CO_2/BnGE and CO_2/CHO in THF using the BEt_3/PPNCl system in 6:1 molar ratio.

Entry	M	$[M]_o/[A]_o/[I]_o$ (T, P_{CO_2})	Time (h)	Conv. [a] (%)	TOF [b] (h^{-1})	Selectivity of the Crude Reaction mixture [c]			Isolated Polymer					
						Polym.	CC	Polyether	Carbonate vs ether linkages [d] ^{1}H (^{13}C)	$M_{n,\ \mathrm{theo}}$ [e] (kg/mol)	$M_{n,\ \mathrm{SEC}}$ [f] (kg/mol)	$Đ_M$ [g]	Yield [h] (%)	T_g [i] (°C)
1	BnGE	100:6:1 (60,10)	5	95	19	77	13	10	75:25	14.4	8.9	1.15	38	
2	BnGE	100:6:1 (40,30)	15	89	6	97	3	0	82:18 (92:8)	17.3	5.4	1.16	65	-1
3	BnGE	100:6:1 (40,30)	15	82	5	98	2	0	84:16	16.1	7.9	1.16	67	
4	BnGE	100:6:1 (60,30)	5	91	18	98	2	0	77:23	17.6	9.2	1.12	72	
5	BnGE	250:6:1 (40,30)	24	71	7	97	1	1	77:23	34.2	5.6	1.19	50	
6	BnGE	250:6:1 (60,30)	5	63	32	86	14	0	72:28	26.4	4.8	1.18	40	
7	BnGE	500:6:1 (40,30)	24	40	8	84	8	8	82:18	34.09	n.d.[j]	n.d.[j]	n.d.[j]	
8	BnGE	500:6:1 (60,30)	23	68	15	50	43	7	80:20	34	5.1	1.19	27	
9	BnGE	1000:6:1 (40,30)	88	19	-	-	99	-	-	-			-	
10	CHO	100:6:1 (40,30)	15	97	6	99	0	0	99:1	13.8	10.0	1.20	72	113
11	CHO	1000:6:1 (40,30)	65	90	14	99	0	0	99:1	127.8	9.9	1.19	n.d.[j]	

M, A, I = Monomer (BnGE), Activator (BEt_3), Initiator (PPNCl). THF was used as solvent, introduced in a volume equal to that of the monomer. [a, c] % Monomer conversion and CO_2 selectivity determined by ^{1}H NMR analysis of the crude reaction mixture. [b] Turnover frequency (TOF) = mol(polymer).mol(PPNCl).(h^{-1}). [d] Determined by ^{1}H NMR analysis of the isolated PBnGEC. [e] $M_{n,\ \mathrm{theo}}$ = (No. of carbonate unit × 208) + (No. of ether unit × 164) + mass of end groups. [f] Experimental molar mass of PBnGEC determined by SEC in THF with a calibration using polystyrene standards; the molar mass value is the average of the bimodal trace. [g] Dispersity value determined by SEC in THF. [h] Yield (%) = [Wt. of isolated polymer obtained(g)/ (monomer used + CO_2 consumed) (g)] × 100. [i] Experimental glass transition temperature of copolymers measured by DSC. [j] Not determined.

Table S4. TBD- or DBU-organocatalyzed depolymerization of the PBnGEC and PCHC copolymers and P(BnGEC-*co*-CHC) terpolymers performed in



TBD **DBU**

refluxing acetonitrile (ACN) or toluene (Tol).

Entry	$f_{\mathbf{BnGE}}$ [a]	$M_{n,\text{ SEC, THF}}$ [b] (kg/mol) / $Đ_M$ [c]	**Catalyst, (mol%)**	**Solvent, temp. (°C)**	**Time (h)**	**Conv. (%)** [d]		$f_{\mathbf{5CCOBn}}$ [e]
						5CCOBn	***t*-CHC**	
1	1.00	6.6 / 1.16	TBD, 1	ACN, 82	2	23	-	1.00
2	1.00	4.9 / 1.13	TBD, 5	ACN, 82	2	99	-	1.00
3	0.80	18.3 / 1.22	TBD, 5	ACN, 82	2	99	99	0.82
4	0.79	6.6 / 1.19	TBD, 5	ACN, 82	2	99	99	0.82
5	0.52	20.9 / 1.16	TBD, 1	ACN, 82	2	99	73	0.55
6	0.52	20.9 / 1.16	TBD, 5	ACN, 82	2	99	99	0.55
7	0.44	5.9 / 1.14	TBD, 25	ACN, 82	0.25	99	99	0.49
8	0.44	5.9 / 1.14	TBD, 33	ACN, 82	0.25	99	99	0.51
9	0.44	5.9 / 1.14	TBD, 33	Tol, 111	0.25	99	85	0.56
10	0.44	5.9 / 1.14	TBD, 50	ACN, 82	0.25	99	99	0.56
11	0.26	7.0 / 1.24	TBD, 5	ACN, 82	2	99	99	0.28
12	0.26	7.0 / 1.24	DBU, 25	ACN, 82	0.25	99	18	0.35
13	0.26	7.0 / 1.24	DBU, 25	Tol, 111	0.25	0	0	-
14	0.07	8.9 / 1.19	TBD, 5	ACN, 82	2	99	99	0.09
15	0.00	10.1 / 1.20	TBD, 1	ACN, 82	2	-	18	0.00
16	0.00	10.1 / 1.20	TBD, 5	ACN, 82	2	-	84	0.00

[a] f_{BnGE} = molar fraction of PBnGEC vs PCHC in substrate(polymer). [b] Experimental molar mass of polymer determined by SEC in THF with a calibration using polystyrene standards; the molar mass value is the average value over the bimodal trace. [c] Dispersity value determined by SEC in THF. [d] % Polymer conversion to respective cyclic carbonates and selectivity determined by ^{1}H NMR analysis. [e] 5CCOBn molar fraction vs *t*-CHC and remaining polymer, determined by ^{1}H NMR analysis. ACN : acetonitrile, Tol : toluene.