Supporting Information

Active Ga-catalysts for the ring opening homo- and copolymerization of cyclic esters, and copolymerization of epoxide and anhydrides

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Content

Figure S30. GPC elugram of *rac*-PLA obtained by reaction of *rac*-LA and **1** in ratio [monomer]:[Cat.]:[BnOH] = 200:1:4 at 100 °C in toluene.

Figure S31. GPC elugram of PCL obtained by reaction of *ε*-CL and **1** in ratio [monomer]:[Cat.]:[BnOH] = 200:1:4 at 100 °C in toluene.

Figure S32. GPC elugram of PCL and PCL-*b*-PLLA obtained by the **1** in presence of BnOH at 100 °C in toluene.

Figure S33. GPC elugram of PLLA and PLLA-*b*-PCL obtained by the **1** in the presence of BnOH at 100 °C in toluene.

Figure S34. GPC elugram of poly(cyclohexenesuccinate) copolymer obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S35. DSC curve of PCL-*b*-PLLA obtained by reaction of *ε*-CL, *L*-LA and **1** in ratio [*ε*-CL]:[*L*-LA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S36. DOSY NMR (300 MHz, $CDCl_3$, 298 K) spectrum of PCL-b-PLLA diblock copolymer.

Figure S37. DOSY NMR (300 MHz, $CDCl_3$, 298 K) spectrum of poly[(cyclohexene succinate) copolymer.

Figure S38. DOSY NMR (300 MHz, $CDCl_3$, 298 K) spectrum of poly[(cyclohexene malonate) copolymer.

Figure S39. Plot of $M_n^{(obs)}$ (kg/mol) vs. conversion (%) for *rac*-LA and *ε*-CL using complex **1** in a ratio [Monomer]:[cat.]:[BnOH] = 200:200:1:4 in toluene at 100 °C.

Figure S40. GPC elugram of PLLA obtain by polymerization resumption experiment of enantiomeric pure *L*-LA and **1** in toluene at 100 °C, [monomer]:[cat.]:[BnOH] = (200^{1st} + 200^{2nd}):1:4.

Figure S41. GPC elugram of PCL obtain by polymerization resumption experiment of *ε*-CL and **1** in toluene at 100 °C, [monomer]:[cat.]:[BnOH] = (200^{1st} + 200^{2nd}):1:4.

Figure S42. COSY NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S43. HMBC NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S44. HSQC NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S45. COSY NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S46. HMBC NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S47. HSQC NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

Figure S48. ^{1}H NMR spectrum of **2** (blue color) and **catalyst-2-OBn (**red color**)** in CD_2Cl_2. C**atalyst-2-OBn** obtained by reaction of **catalyst -2** and BnOH in ratio [**Cat-2**]:[BnOH] = 1:4 at 23 °C in CD_2Cl_2.

Figure S49. ^{1}H NMR spectrum **catalyst-2-OBn** in CD_2Cl_2 obtained by reaction of **2** and BnOH in ratio [**Cat-2**]:[BnOH] = 1:4 at 23 °C in CD_2Cl_2.

Figure S50. MALDI-ToF spectrum of poly(cyclohexene succinate) copolymer obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 100:200:1:4 at 100 °C in toluene at 100 °C.

Table S2 ROP of *ε*-CL initiated by complex **1** with varying [monomer]:[cat.]:[BnOH] molar ratios in toluene at 100 °C.

I. Spectroscopic Characterization of 1-3

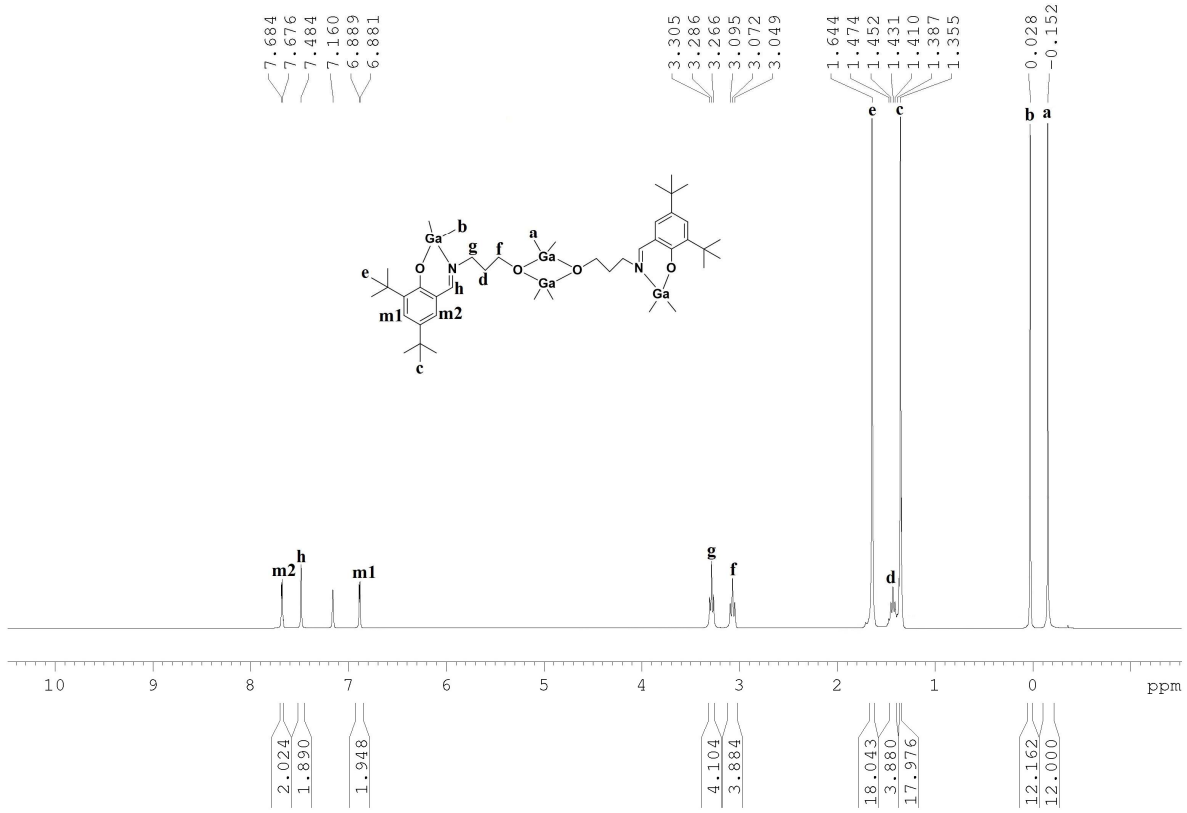

Figure S1: ^{1}H-NMR (300 MHz, C_6D_6, 300 K) spectrum of **1**

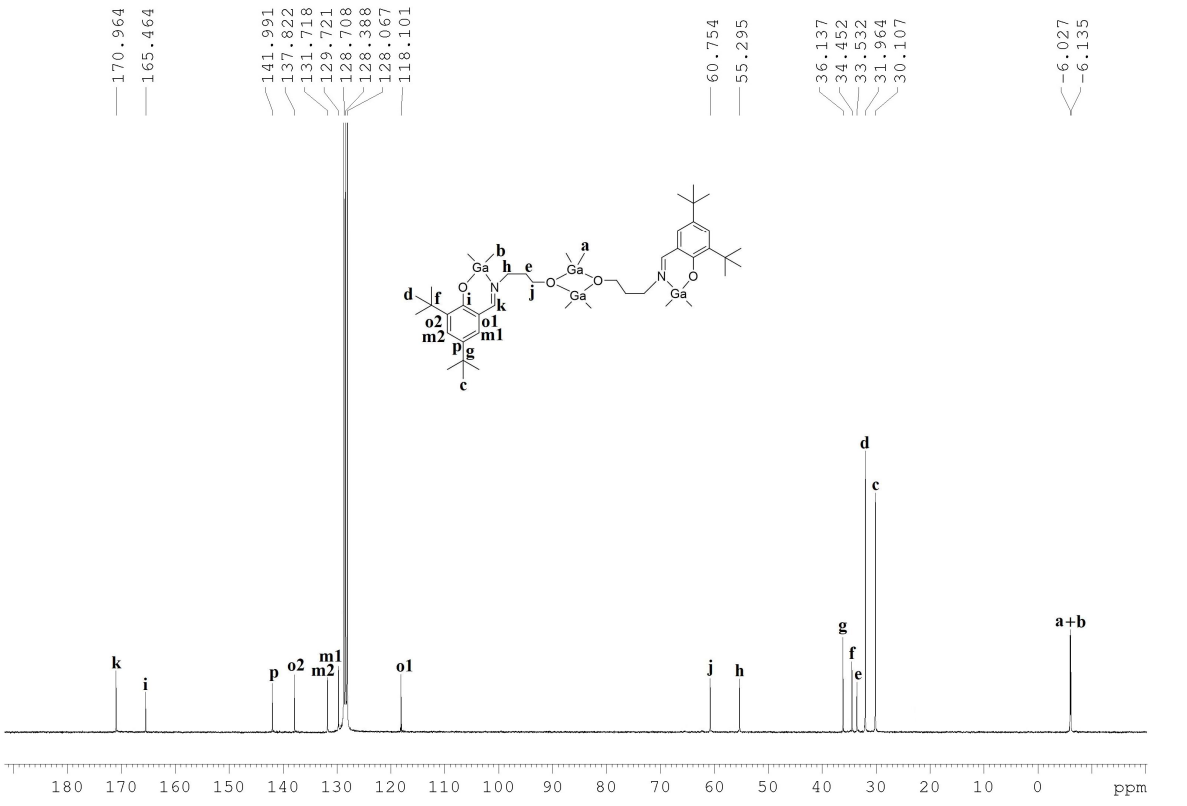

Figure S2: ^{13}C-NMR (75 MHz, C_6D_6, 300 K) spectrum of **1**

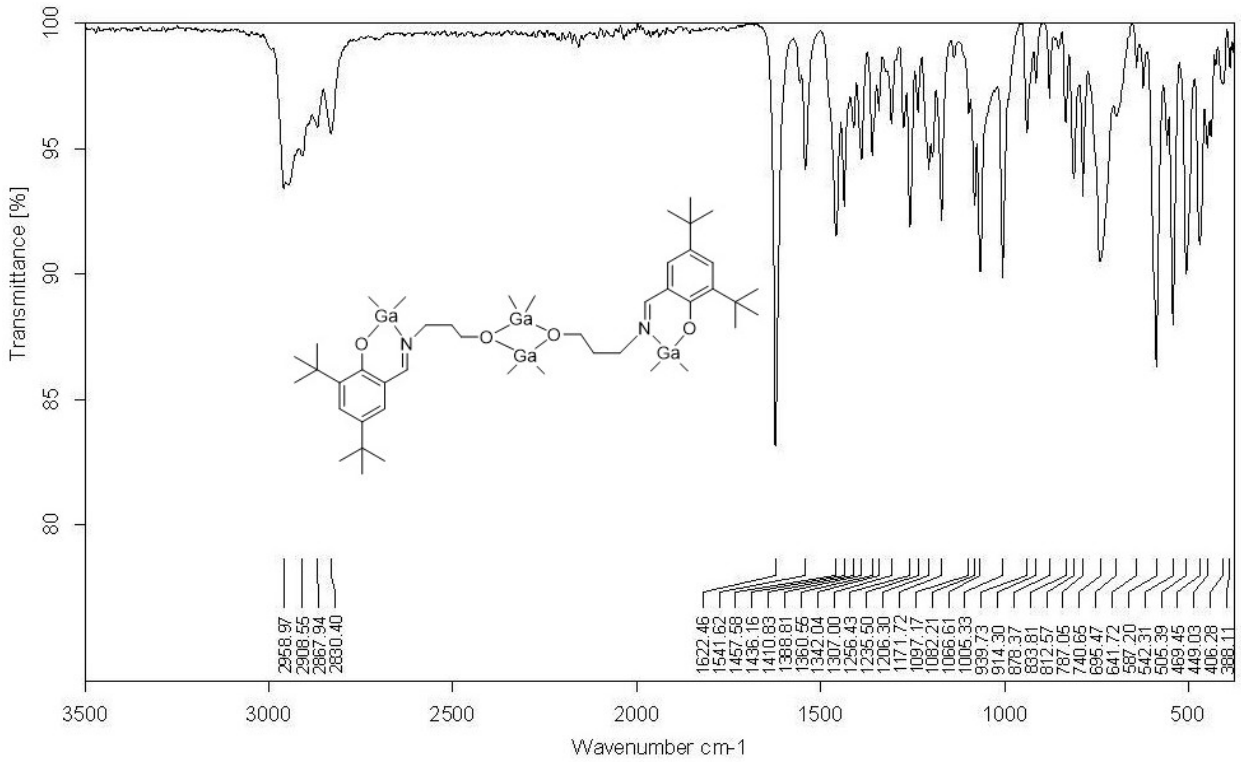

Figure S3: IR spectrum of **1**

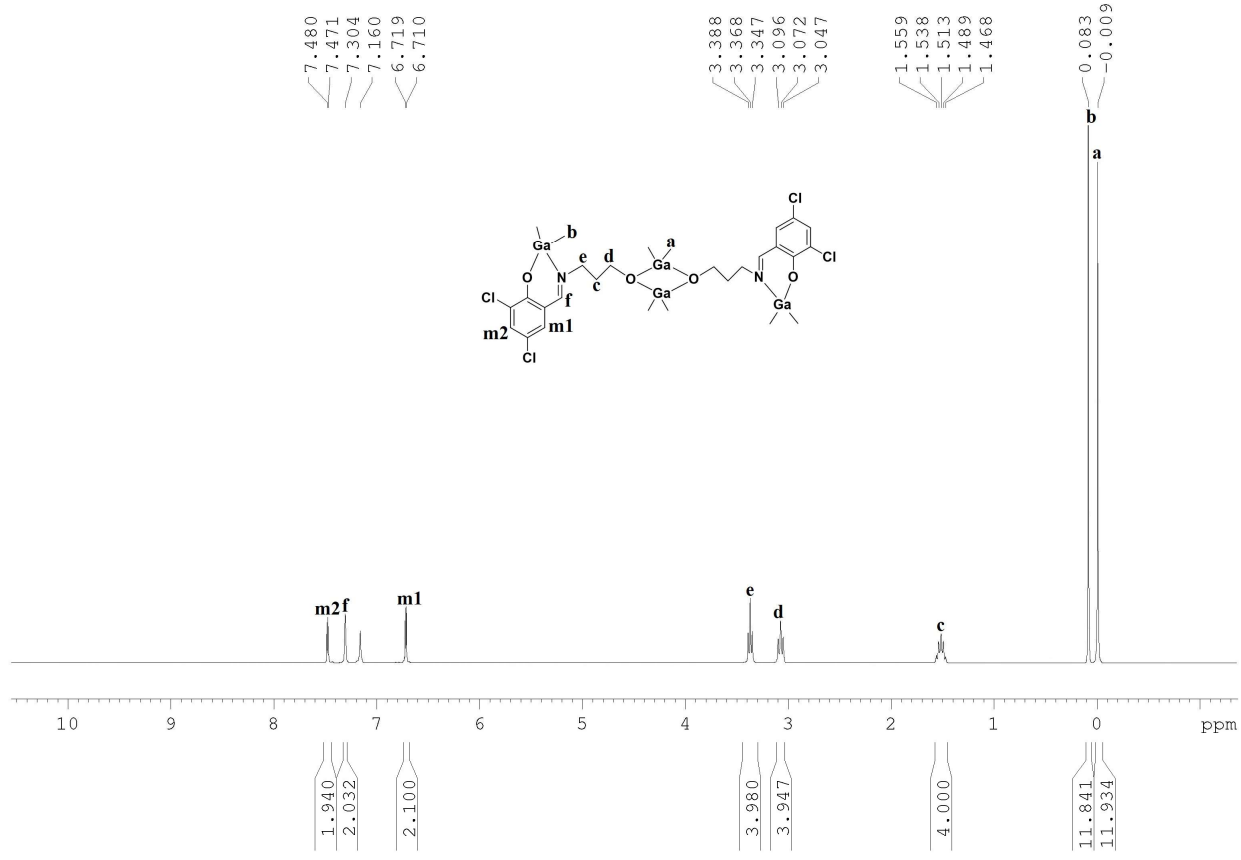

Figure S4: ^{1}H-NMR (300 MHz, C_6D_6, 300 K) spectrum of **2**

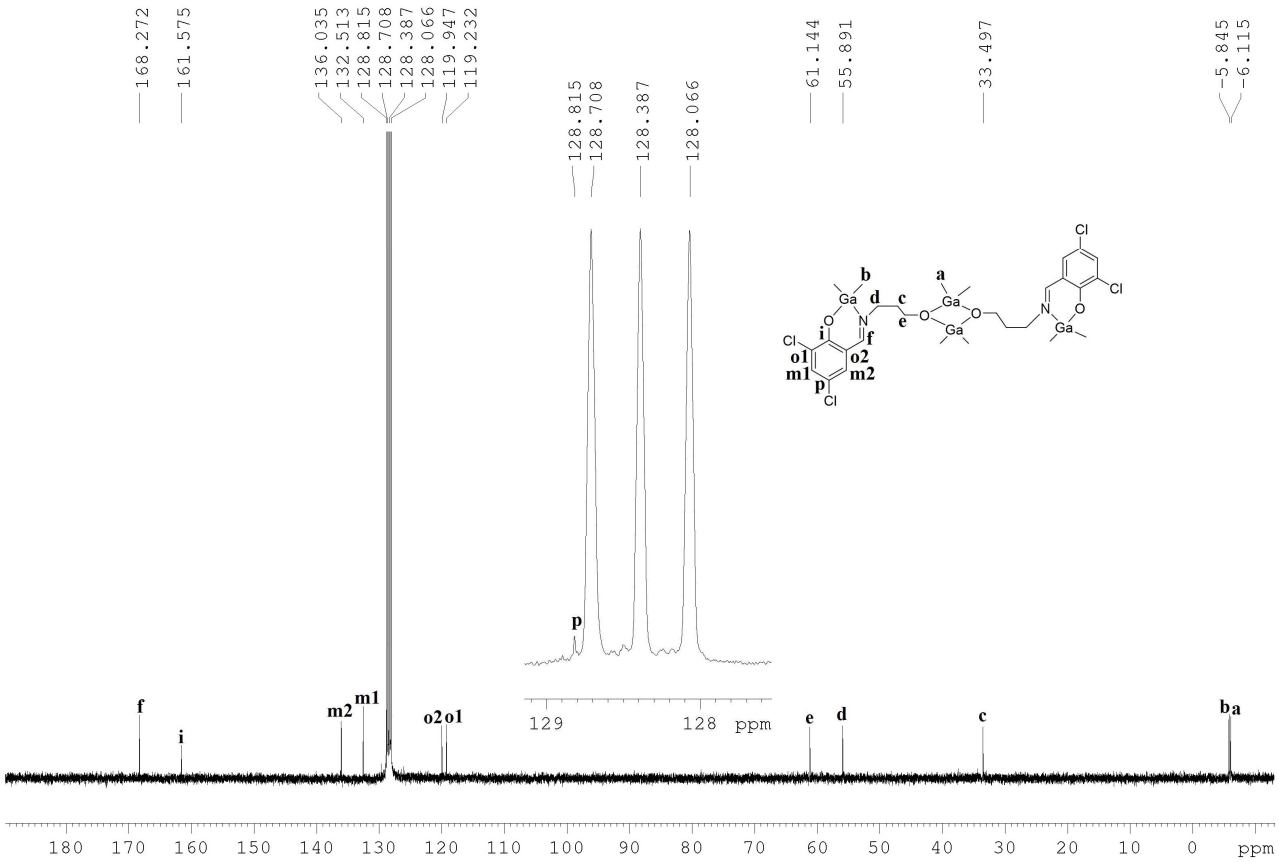

Figure S5: ^{13}C-NMR (75 MHz, C_6D_6, 300 K) spectrum of **2**

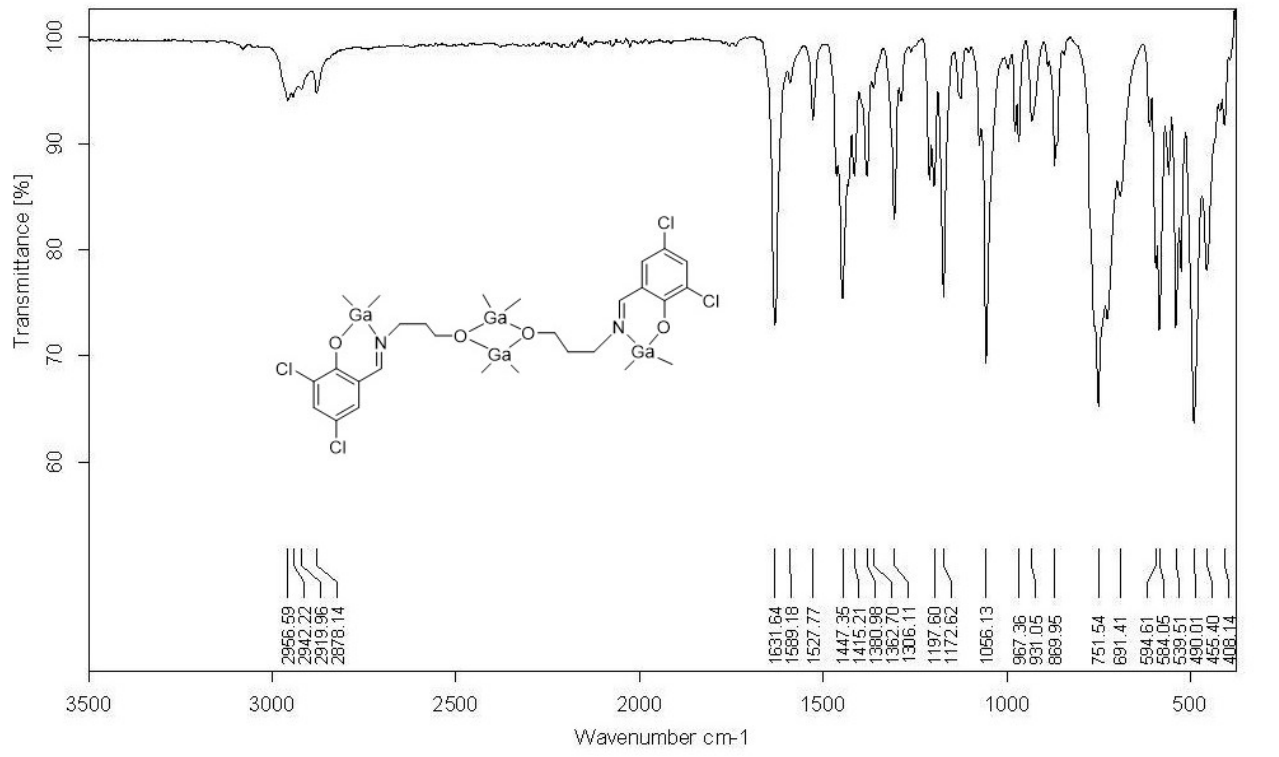

Figure S6: IR spectrum of **2**

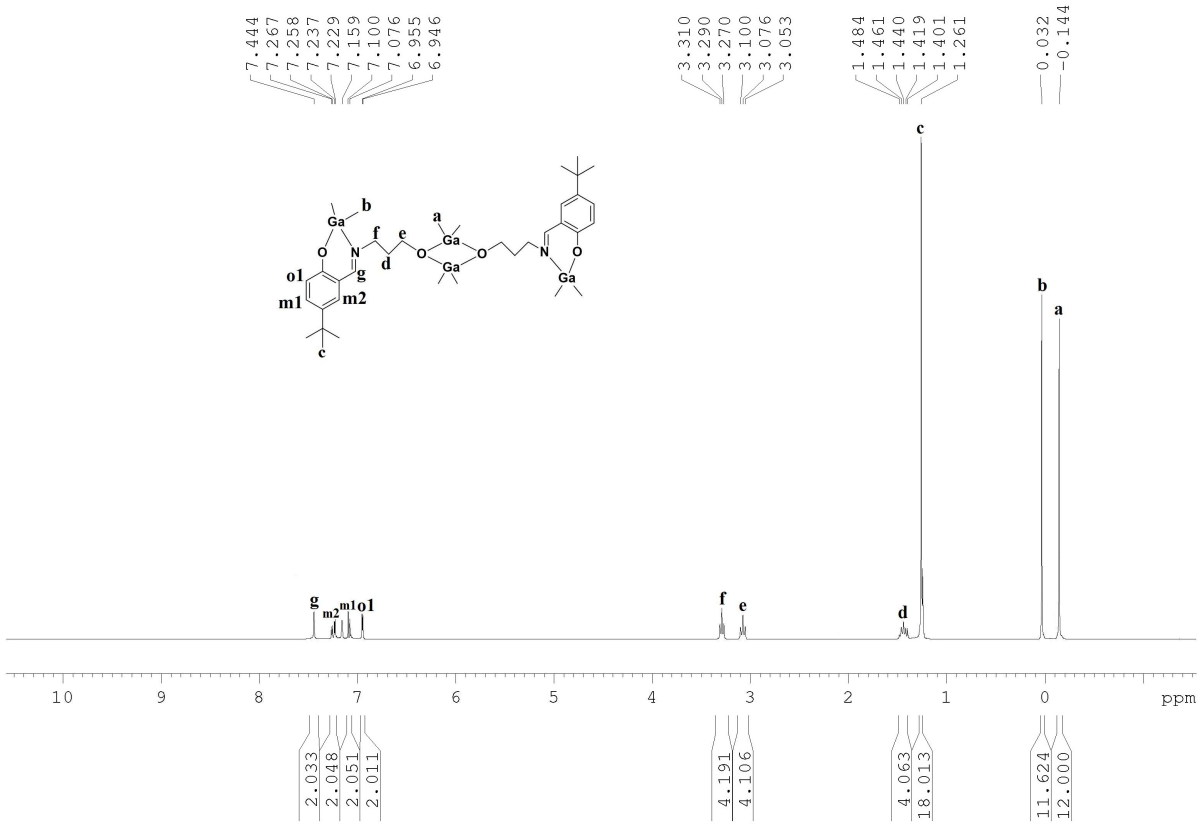

Figure S7: ^{1}H-NMR (300 MHz, C_6D_6, 300 K) spectrum of **3**

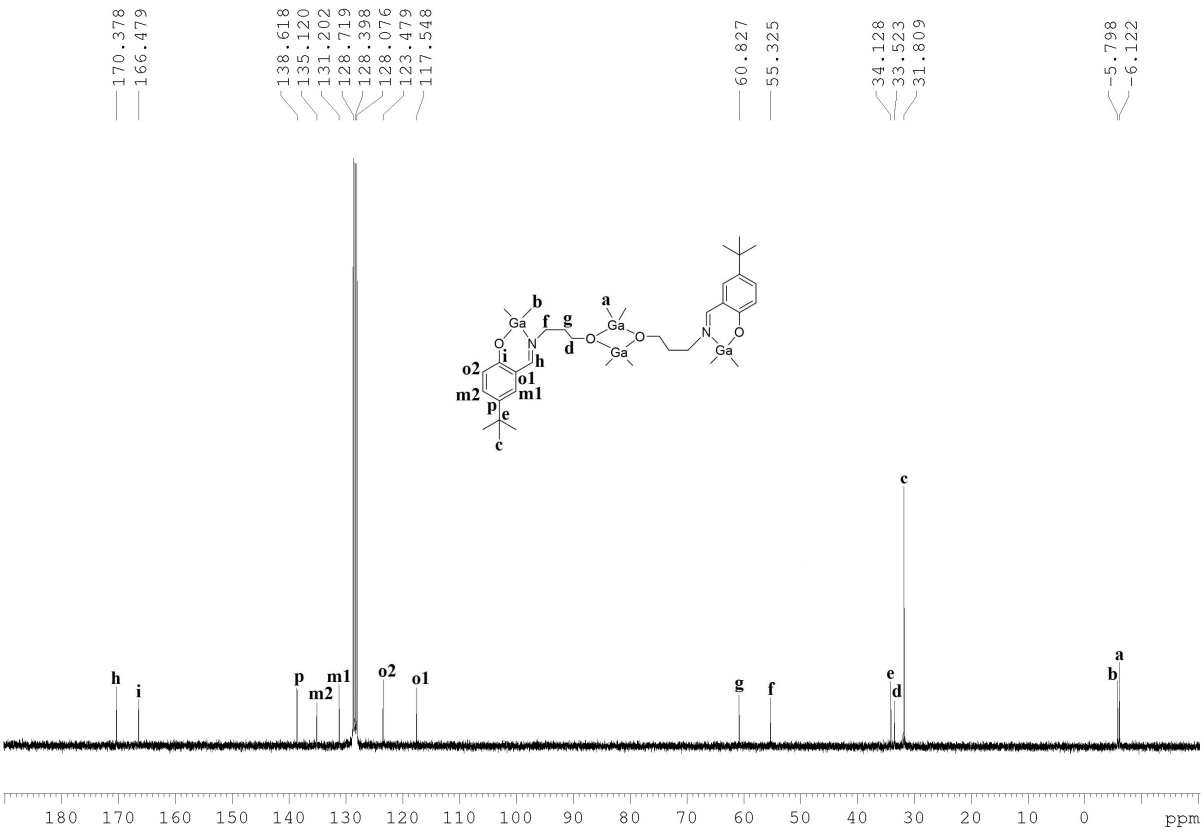

Figure S8: ^{13}C-NMR (75 MHz, C_6D_6, 300 K) spectrum of **3**

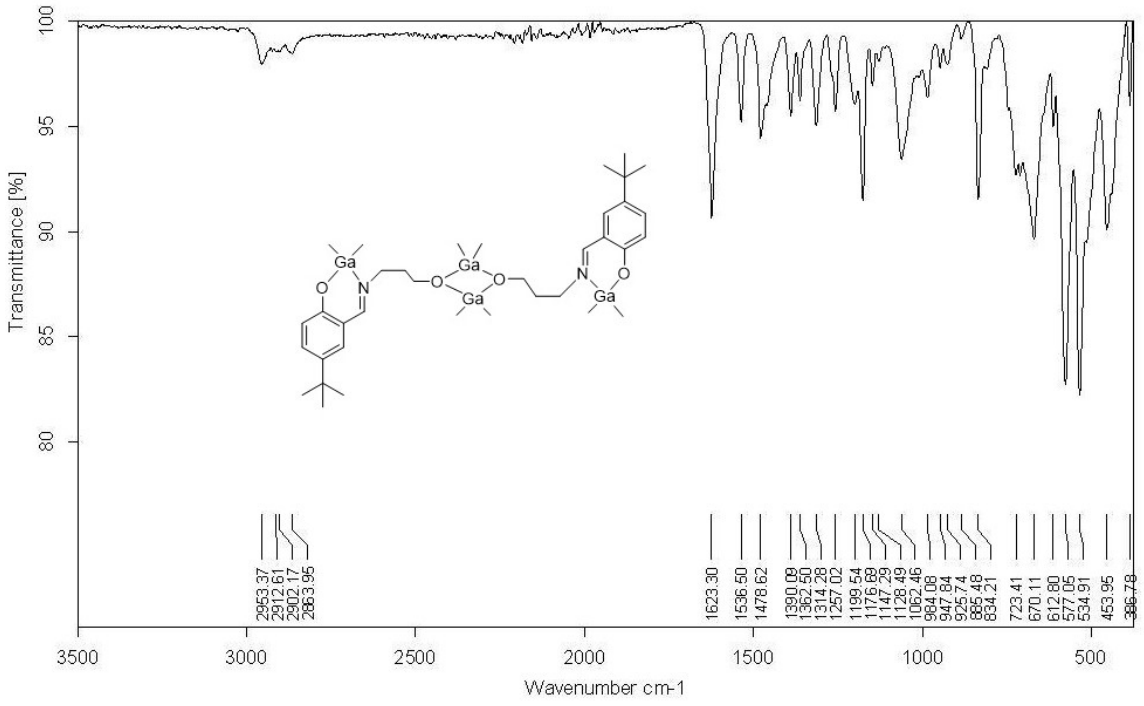

Figure S9: IR spectrum of **3**

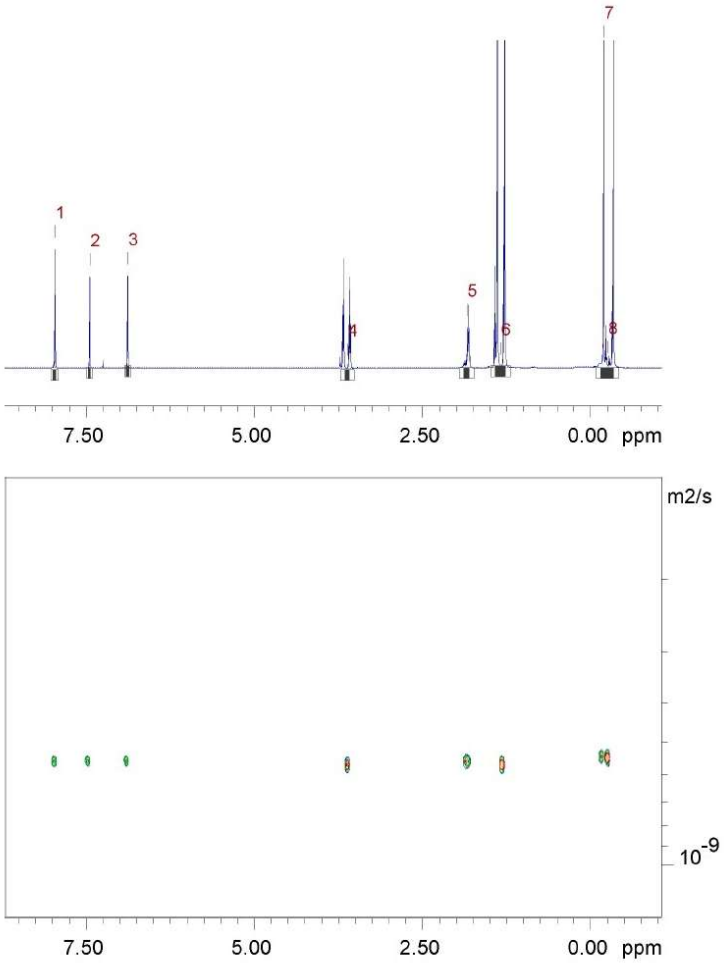

Figure S10. DOSY NMR spectrum of (300 MHz, $CDCl_3$, 298 K) spectrum of **1**

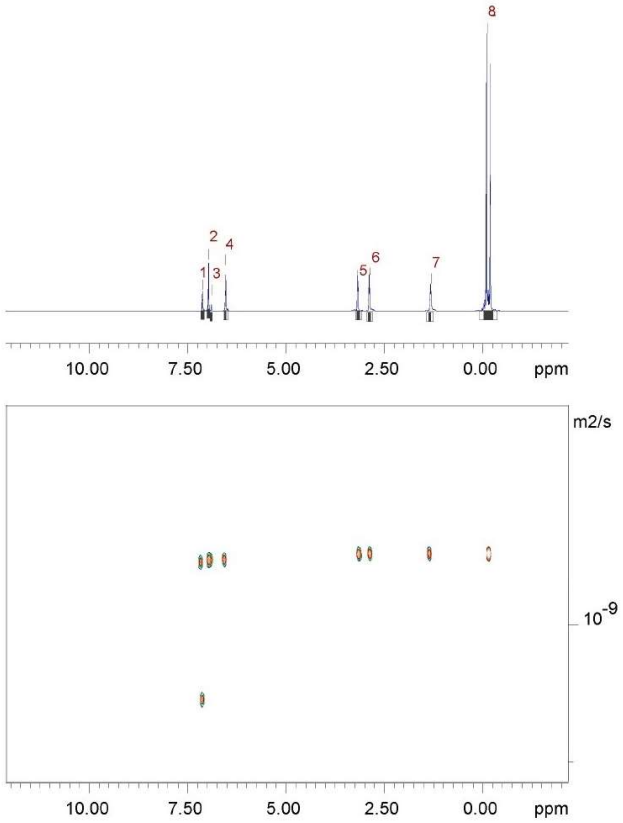

Figure S11. DOSY NMR spectrum of (300 MHz, C_6D_6, 298 K) spectrum of **2**

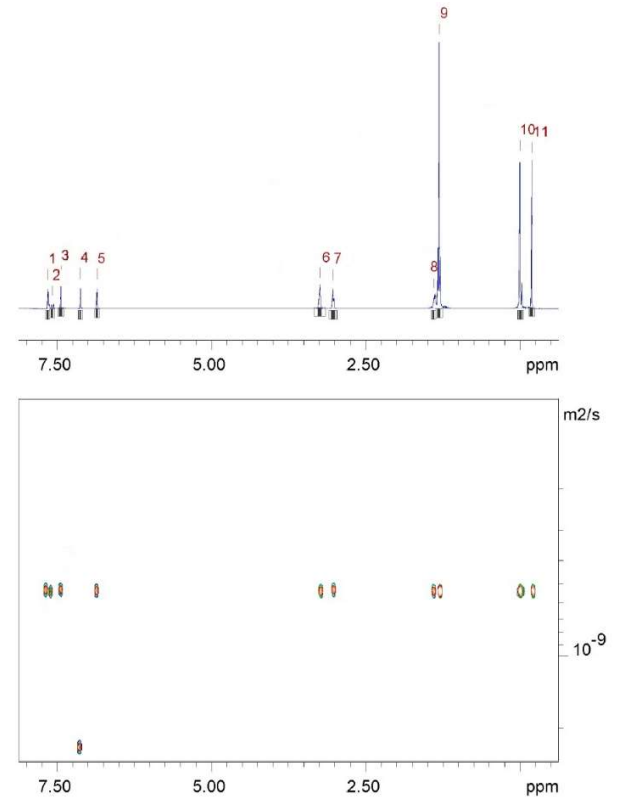

Figure S12. DOSY NMR spectrum of (300 MHz, C_6D_6, 298 K) spectrum of **3**

II. Crystallographic Details

Table S1 Crystal data for compound **1** and **2**

Compounds	**1**	**2**
Empirical formula	$C_{60.33}$ $H_{96.67}$ Ga_4 N_2 O_4	$C_{28}H_{42}Cl_4Ga_4N_2O_4$
Formula weight (Da)	1192.94	891.31
T /K	100(2)	100(2)
Wavelength (Å)	0.71073	1.54178
Crystal system,	trigonal	monoclinic
Space group	*R -3:H*	*P* 2_1*/n*
a /Å	39.314(7)	7.8895(8)
b /Å	39.314(7)	17.1647(17)
c /Å	10.636(2)	13.2719(13)
α (°)	90	90
β (°)	90	93.448(4)
γ (°)	120	90
V (Å^3)	14237(6)	1794.0(3
Z, Calculated density (g cm^{-3})	9, 1.252	2, 1.650
Absorption coefficient (mm^{-1})	1.727	6.447
Crystal size (mm)	0.275 × 0.215 × 0.186	0.151 × 0.089 × 0.044
Theta range for data collection (°)	1.794°- 33.288°	4.215°- 81.023°
Reflections collected	64996	54968
Independent reflections	11471	3917
Data/restraints/parameters	8827/216/451	3917 / 0 / 194
Goodness-of-fit on F^2	1.088	1.068
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0429	$R1$ = 0.0274
	$wR2$ = 0.0933	$wR2$ = 0.0718
R indices (all data)	$R1$ = 0.0633	$R1$ = 0.0293
	$wR2$ = 0.0997	$wR2$ = 0.0738

III. Polymerization Studies

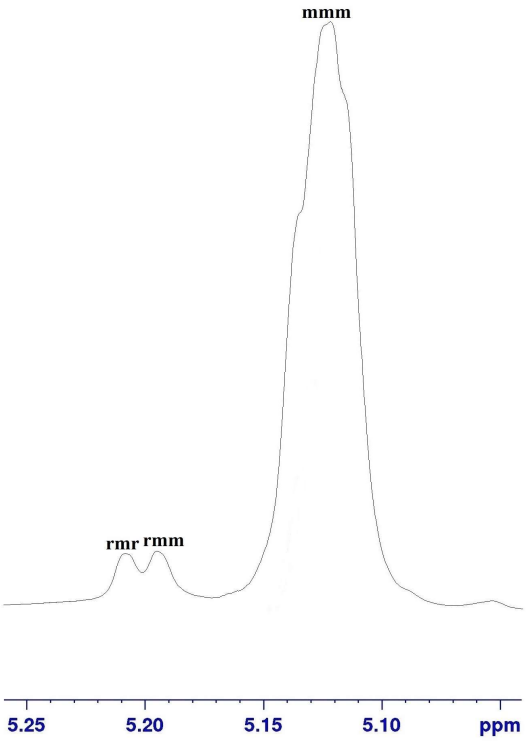

Figure S13. Homonuclear decoupled ^{1}H-NMR spectrum of *rac*-PLA in $CDCl_3$ (methine H-atom region) obtained by reaction of *rac*-LA and **1** in ratio [monomer]:[Cat.]:[BnOH] = 200:1:4 at 100 °C in toluene.

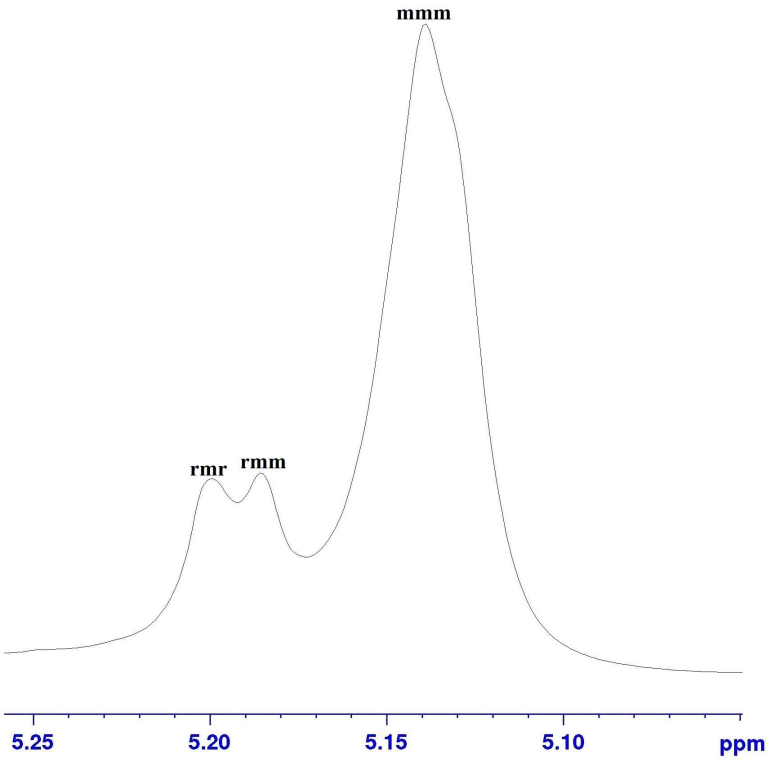

Figure S14. Homonuclear decoupled ^{1}H-NMR spectrum of *rac*-PLA in $CDCl_3$ (methine H-atom region) obtained by reaction of *rac*-LA and **2** in ratio [monomer]:[Cat.]:[BnOH] = 200:1:4 at 100 °C in toluene.

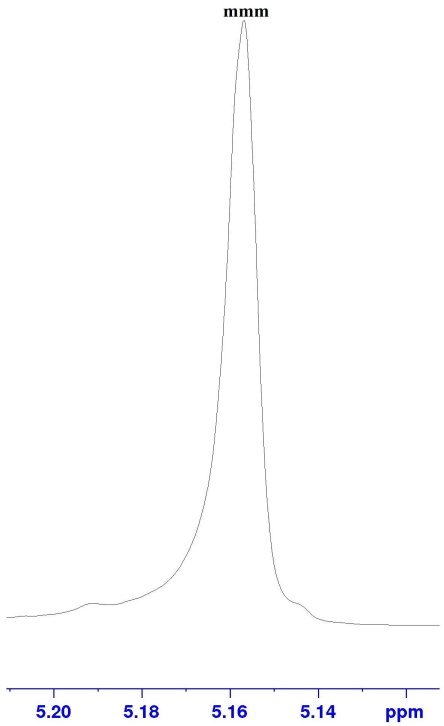

Figure S15. Homonuclear decoupled ^{1}H-NMR spectrum of *L*-PLA in $CDCl_3$ (methine H-atom region) obtained by reaction of *L*-LA and **1** in ratio [monomer]:[Cat.]:[BnOH] = 200:1:4 at 100 °C in toluene.

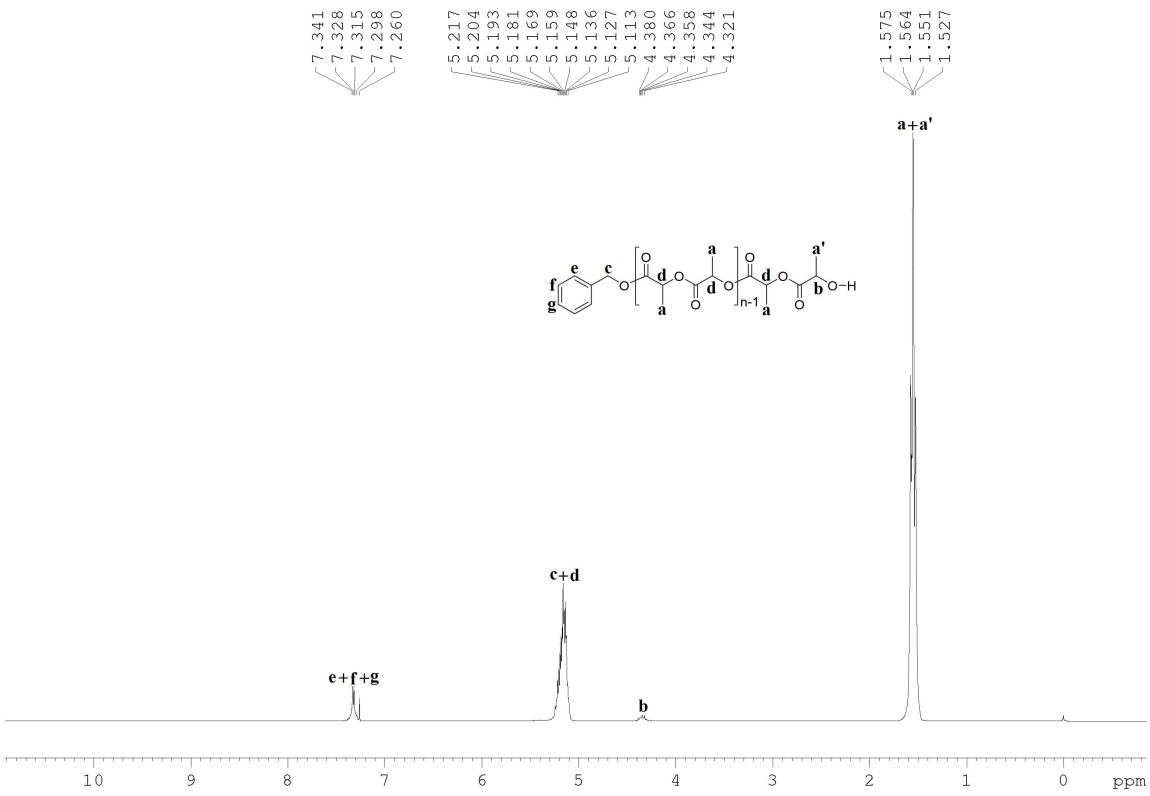

Figure S16. ^{1}H-NMR spectrum of *rac*-PLA in $CDCl_3$ obtained by reaction of *rac*-LA and **1** in ratio [monomer]:[Cat.]:[BnOH] = 100:1:4 at 100 °C in toluene.

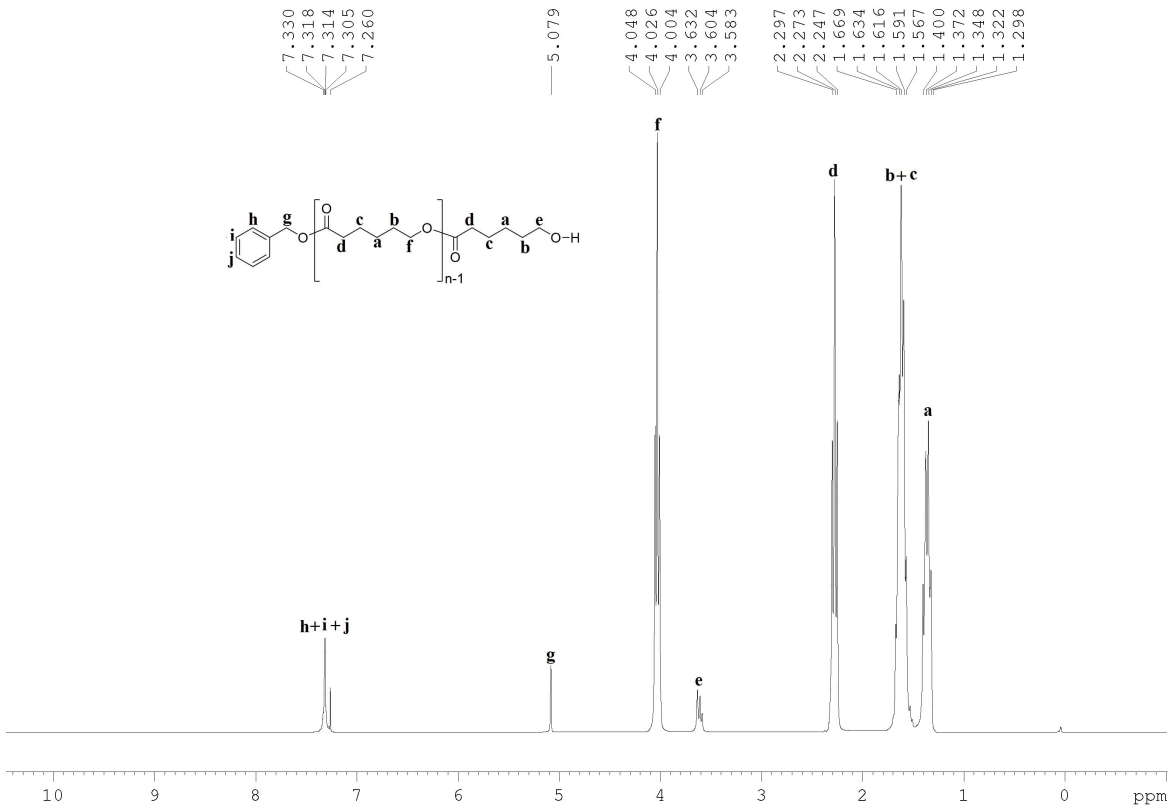

Figure S17. ^{1}H-NMR spectrum of PCL in $CDCl_3$ obtained by reaction of *ε*-CL and **1** in ratio [monomer]:[Cat.]:[BnOH] = 100:1:4 at 100 °C in toluene.

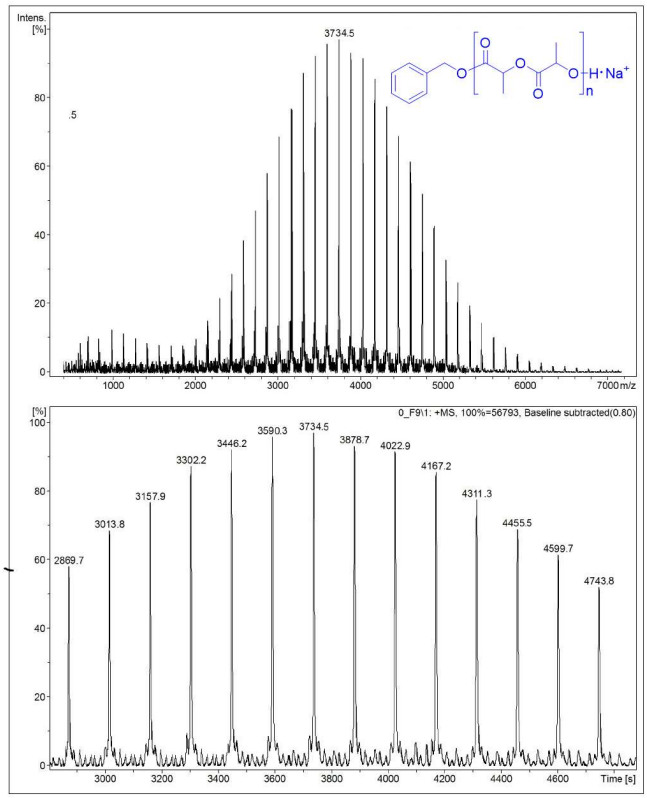

Figure S18. MALDI-ToF spectrum of *rac*-PLA obtained by reaction of *rac*-LA and **1** in ratio [monomer]:[Cat.]:[BnOH] = 100:1:4 at 100 °C in toluene.

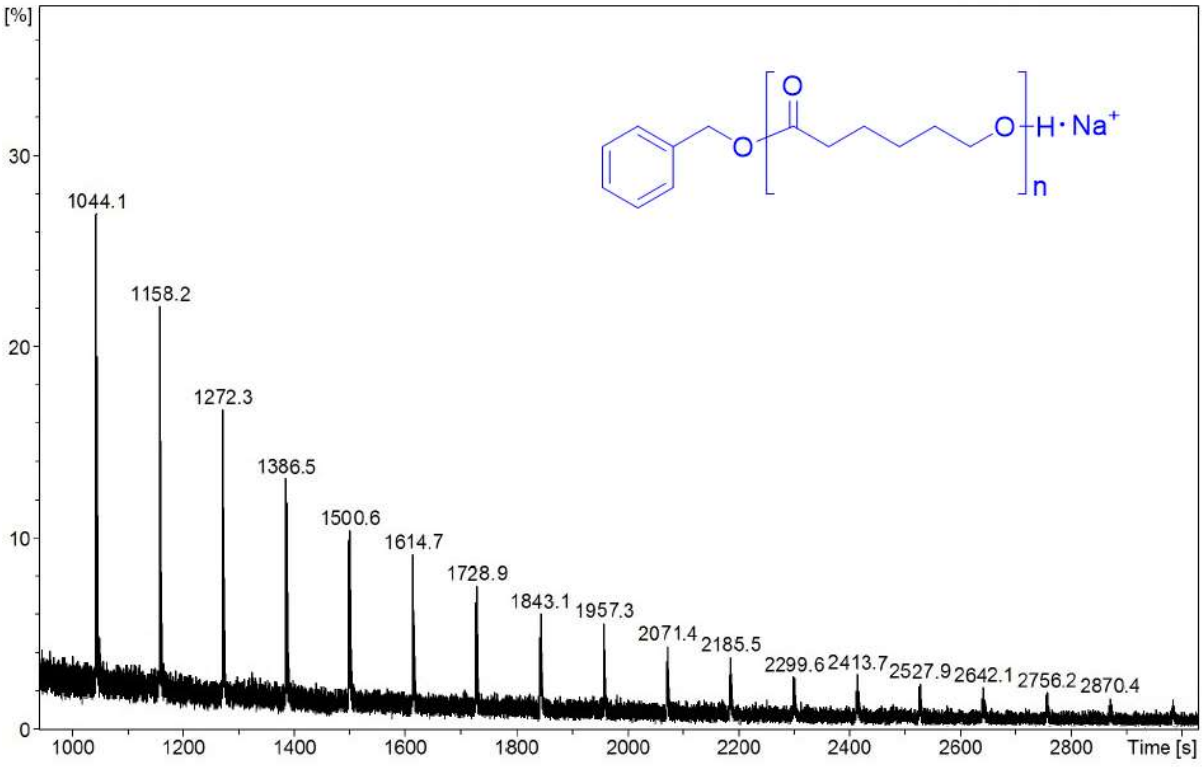

Figure S19. MALDI-ToF spectrum of ε-PCL obtained by reaction of ε-CL and **1** in ratio [monomer]:[Cat.]:[BnOH] = 100:1:4 at 100 °C in toluene.

Figure S20. IR spectrum of *rac*-PLA obtained by reaction of *rac*-LA and **1** in ratio [monomer]:[Cat.]:[BnOH] = 100:1:4 at 100 °C in toluene.

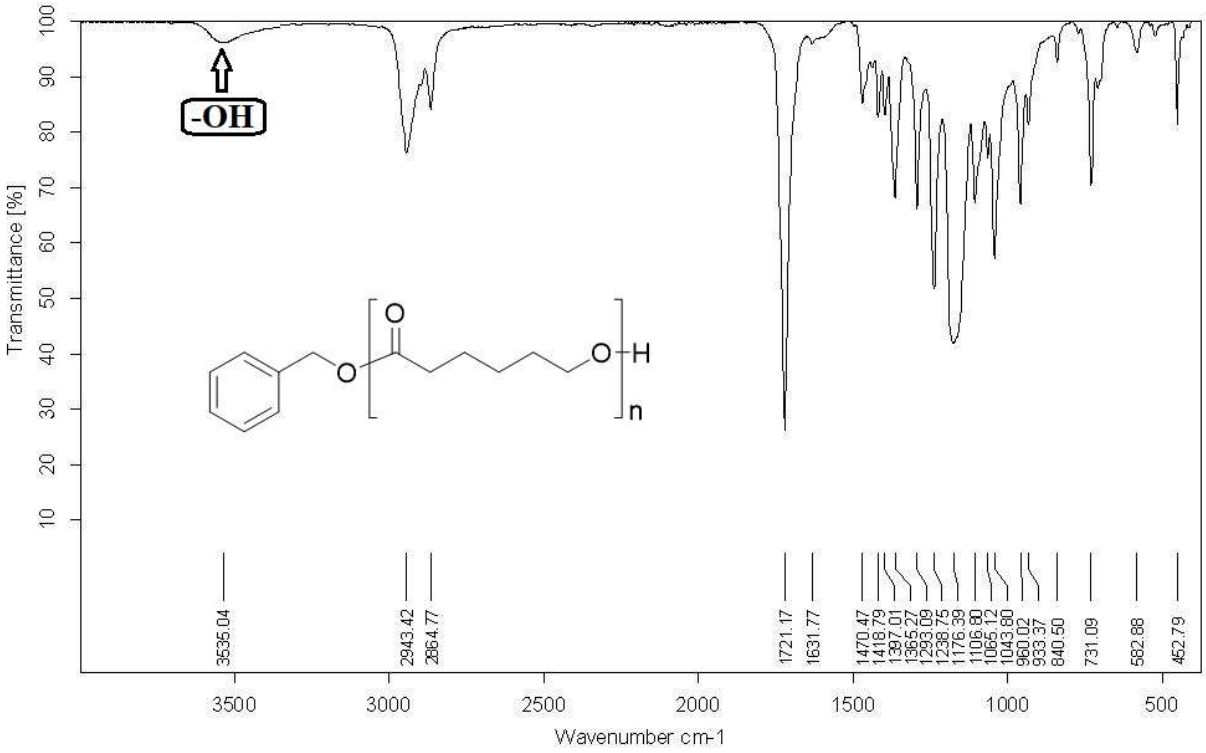

Figure S21. IR spectrum of of PCL in $CDCl_3$ obtained by reaction of ε-CL and **1** in ratio [monomer]:[Cat.]:[BnOH] = 100:1:4 at 100 °C in toluene.

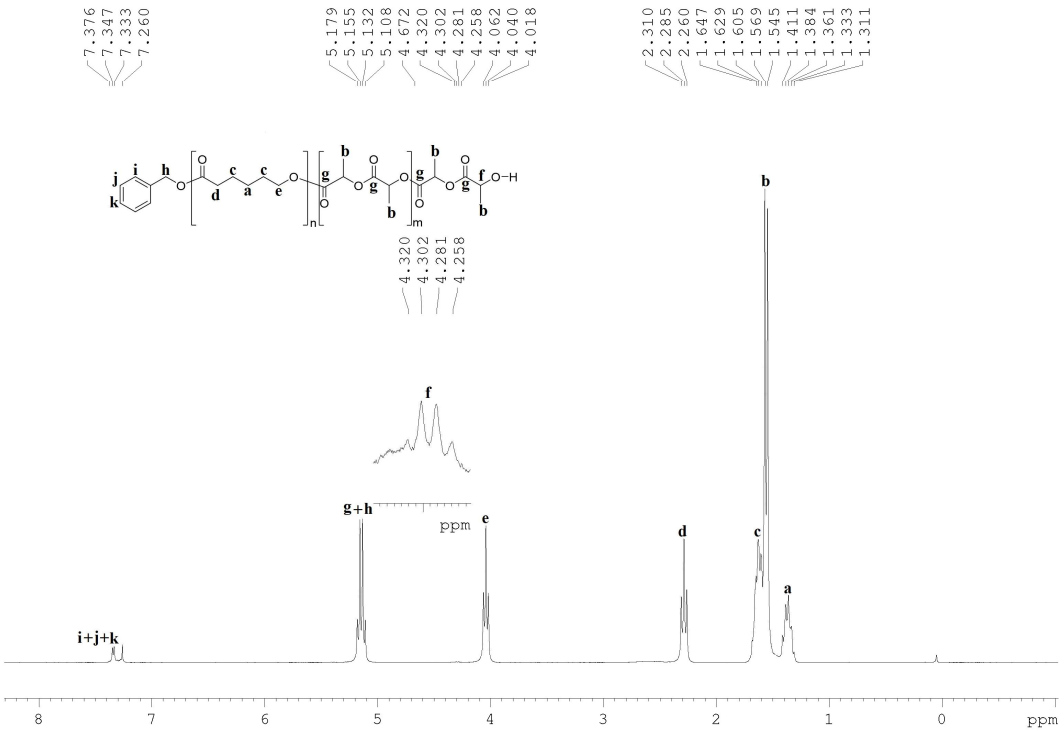

Figure S22. ^{1}H NMR spectrum of PCL-b-PLLA copolymer in $CDCl_3$ obtained by reaction of ε-CL, *L*-LA and **1** in ratio [ε-CL]:[*L*-LA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

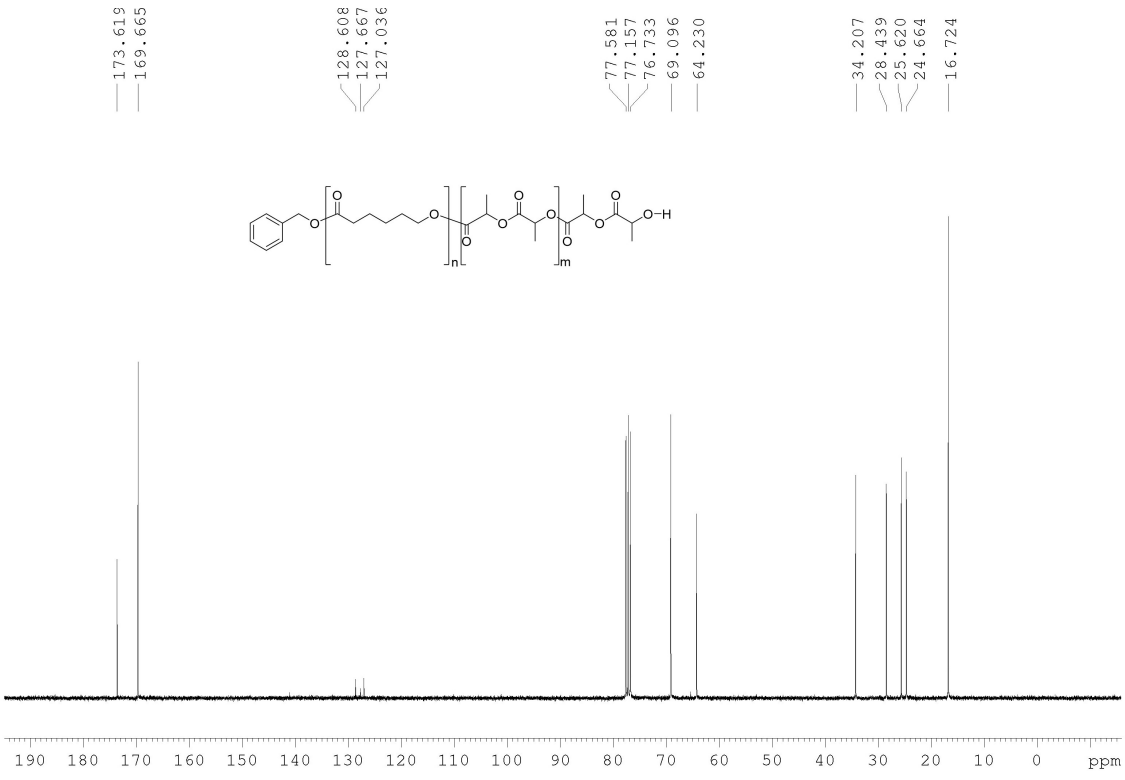

Figure S23. ^{13}C NMR spectrum of PCL-b-PLLA copolymer in $CDCl_3$ obtained by reaction of *ε*-CL, *L*-LA and **1** in ratio [*ε*-CL]:[*L*-LA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

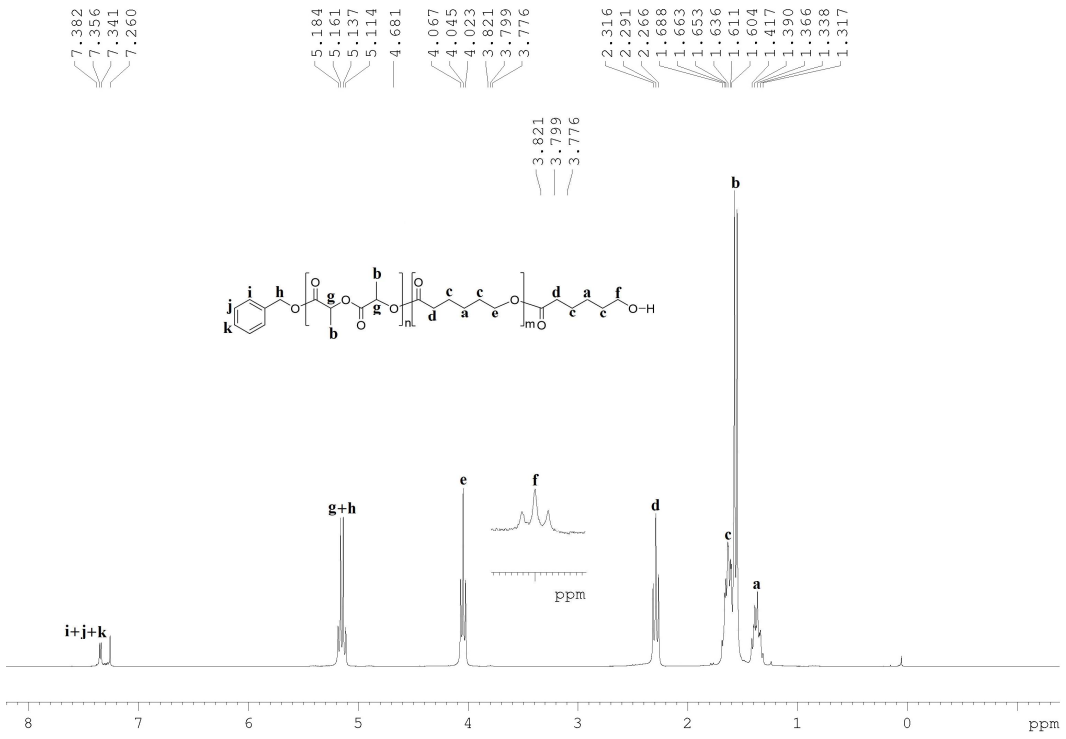

Figure S24. ^{1}H NMR spectrum of PLLA-b-PCL copolymer in $CDCl_3$ obtained by reaction of *L*-LA, *ε*-CL, and **1** in ratio [*L*-LA]:[*ε*-CL]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

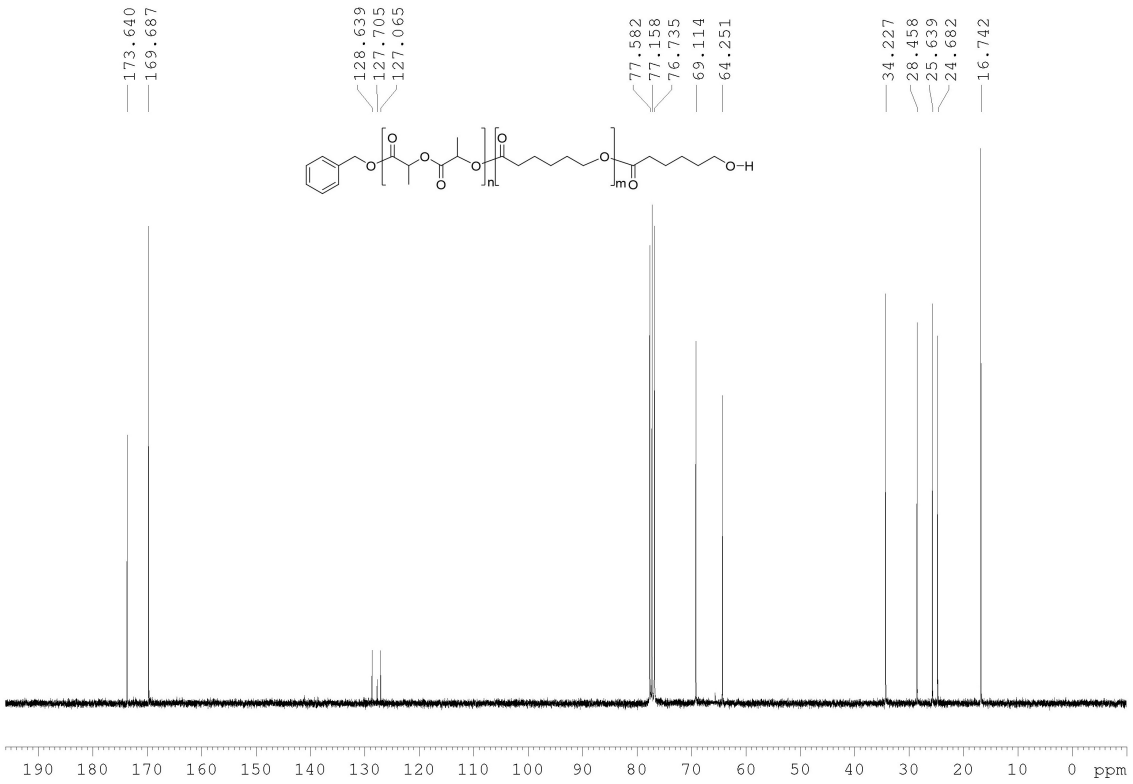

Figure S25. ^{13}C NMR spectrum of PLLA-b-PCL copolymer in $CDCl_3$ obtained by reaction of *L*-LA, *ε*-CL, and **1** in ratio [*L*-LA]:[*ε*-CL]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

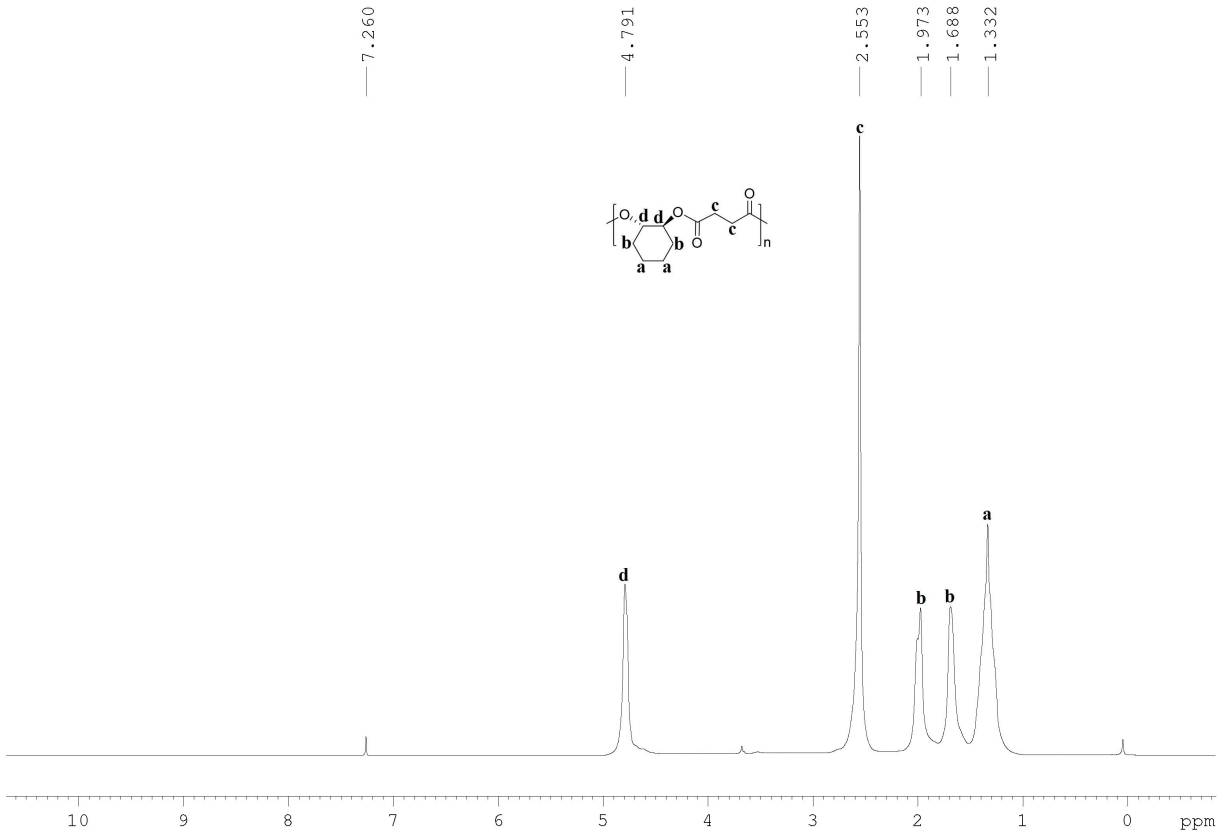

Figure S26. ^{1}H NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

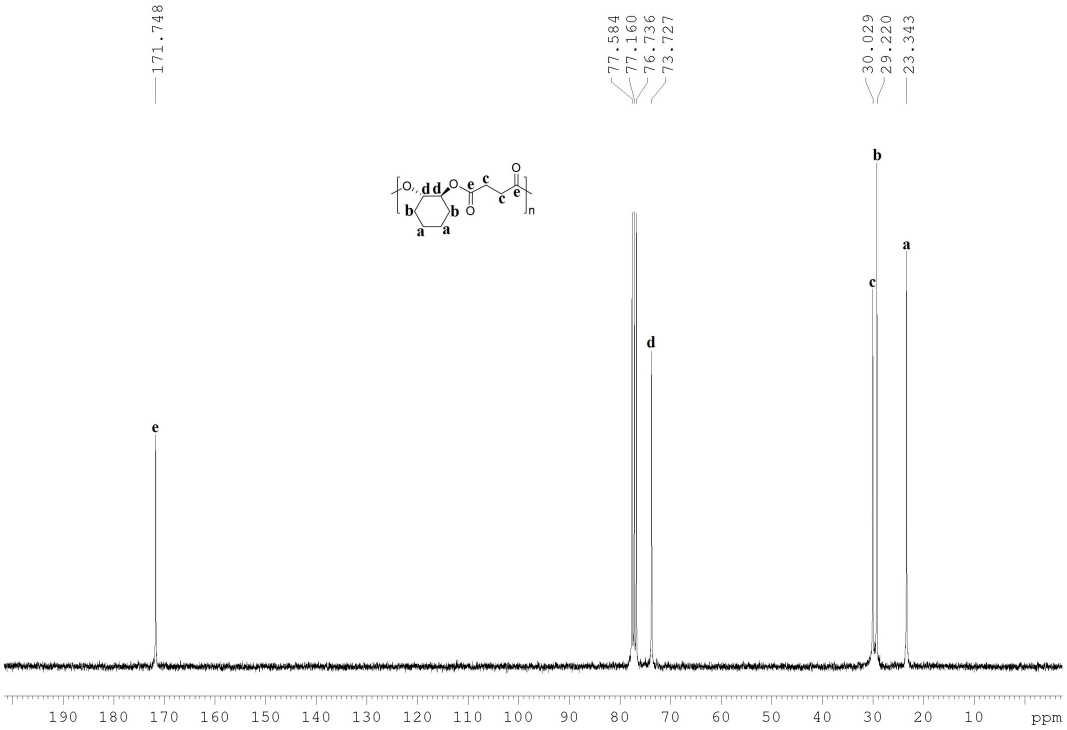

Figure S27. ^{13}C NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

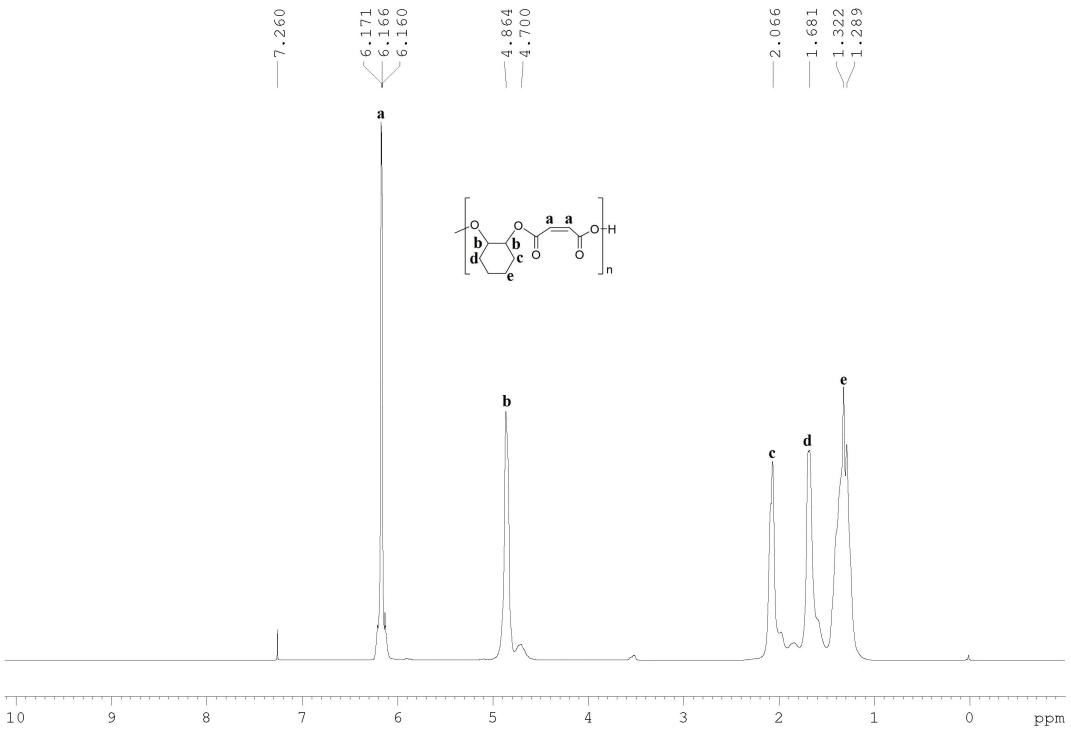

Figure S28. ^{1}H NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

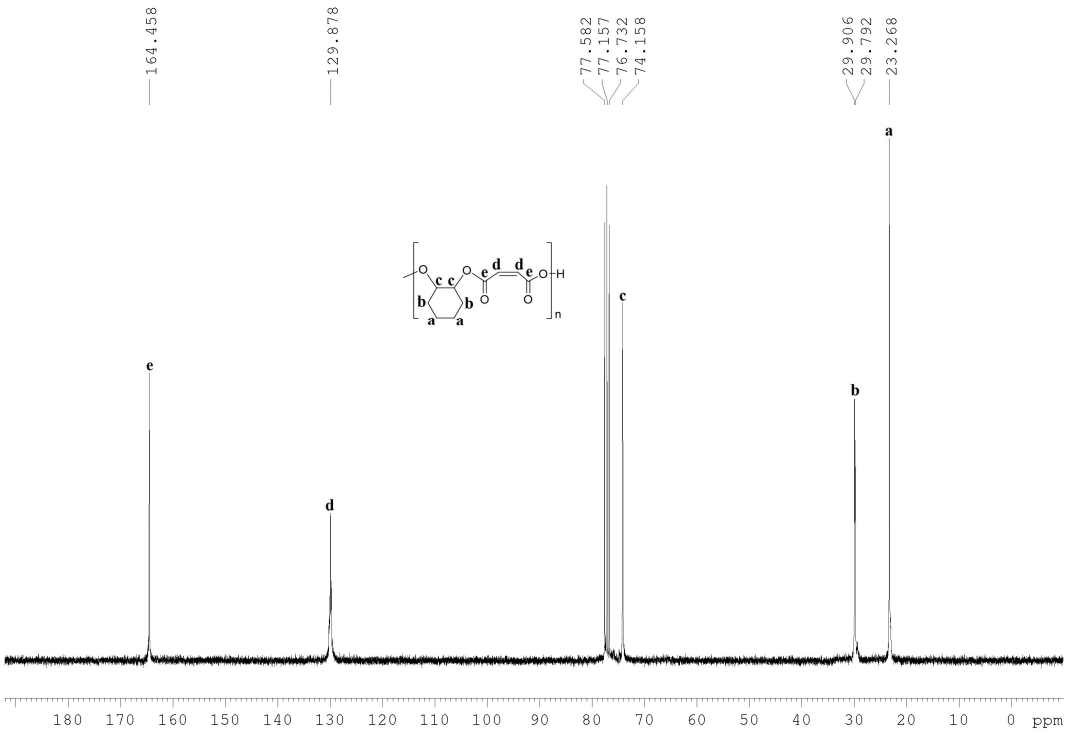

Figure S29. ^{13}C NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

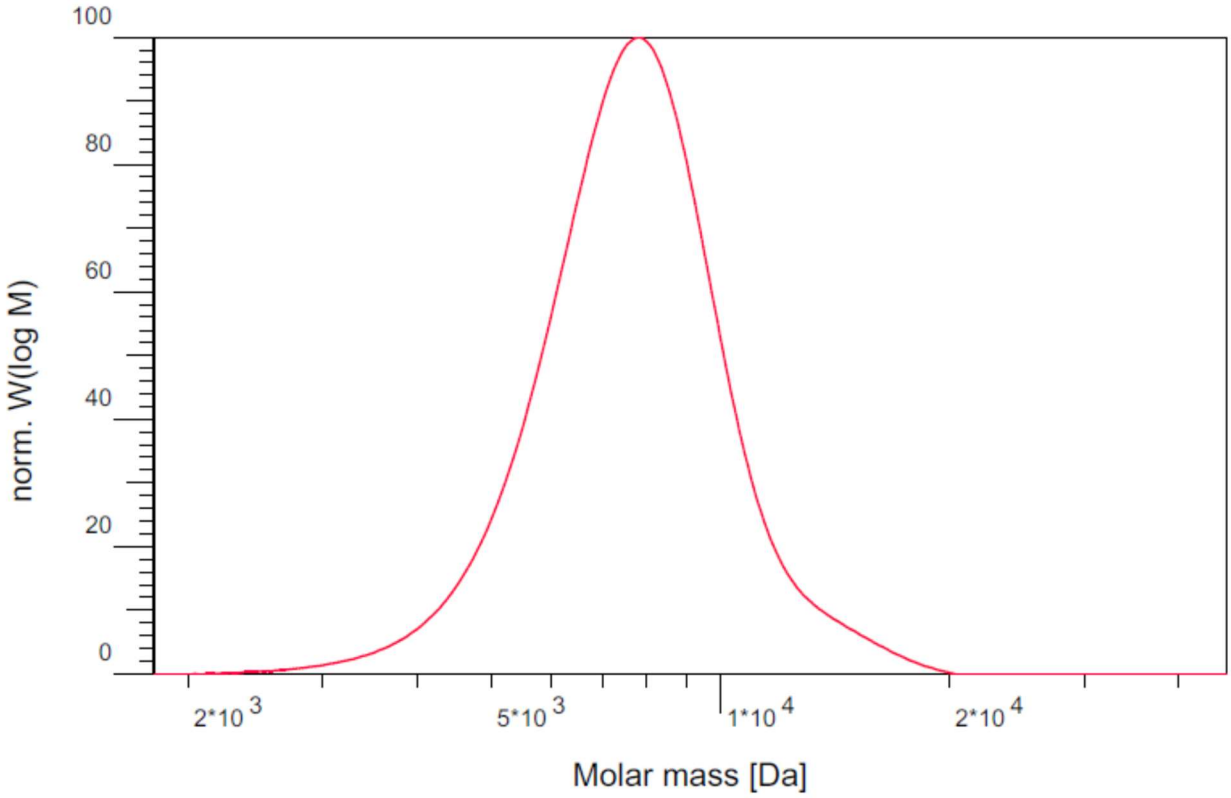

Figure S30. GPC elugram of *rac*-PLA obtained by reaction of *rac*-LA and **1** in ratio [monomer]:[Cat.]:[BnOH] = 200:1:4 at 100 °C in toluene.

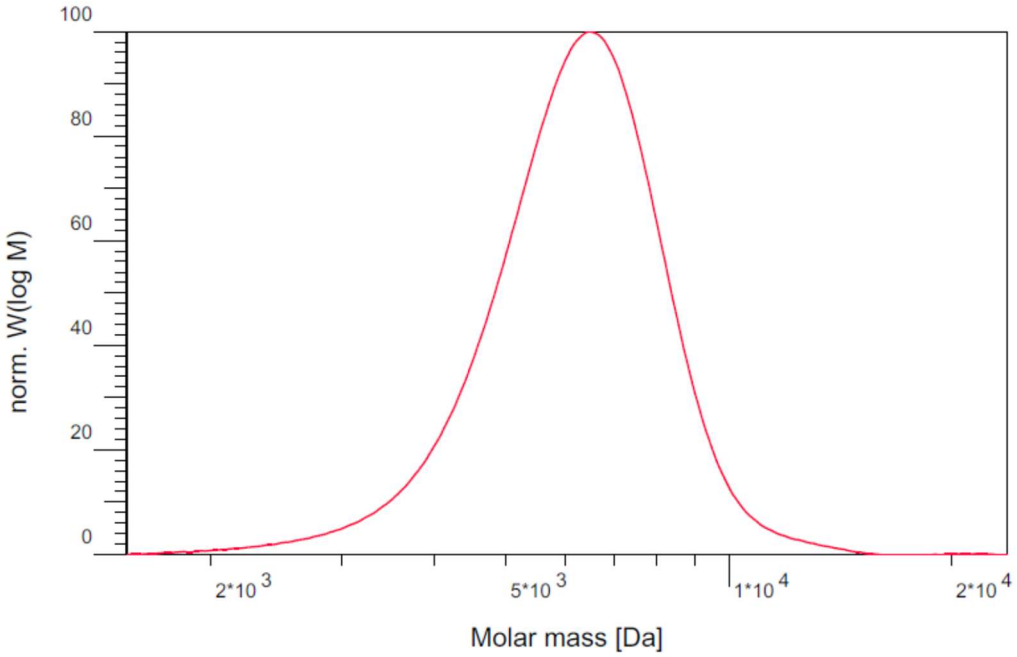

Figure S31. GPC elugram of PCL obtained by reaction of *ε*-CL and **1** in ratio [monomer]:[Cat.]:[BnOH] = 200:1:4 at 100 °C in toluene.

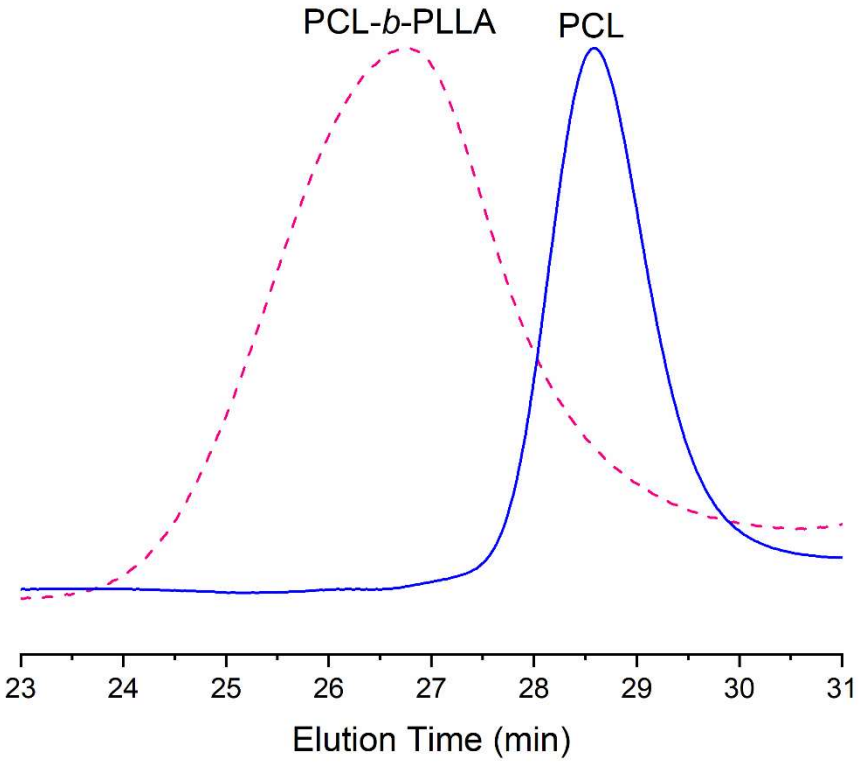

Figure S32. GPC elugram of PCL and PCL-*b*-PLLA obtained by the **1** in presence of BnOH at 100 °C in toluene.

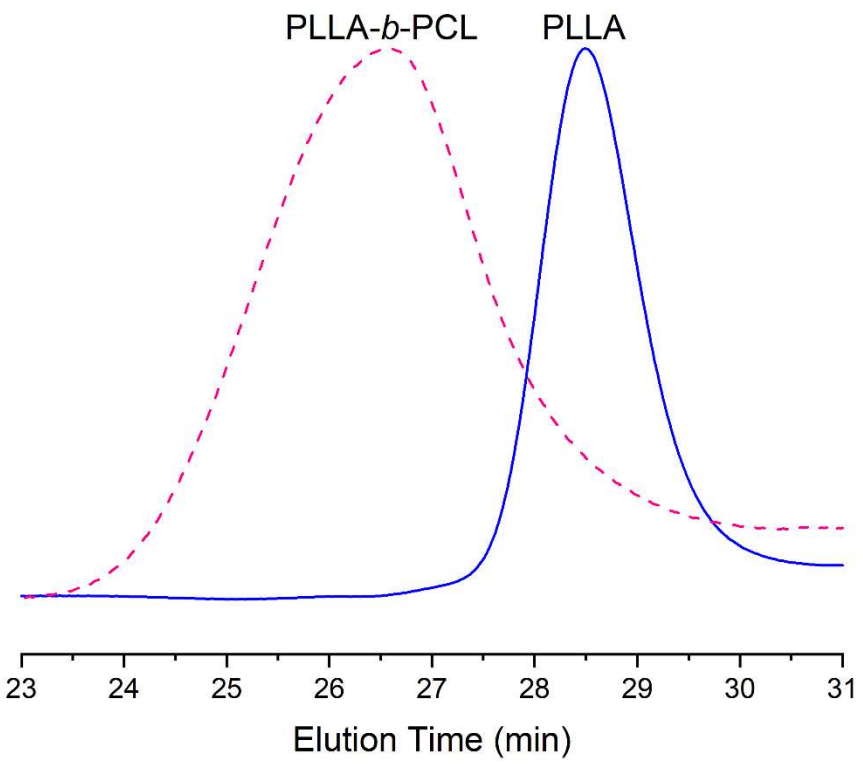

Figure S33. GPC elugram of PLLA and PLLA-*b*-PCL obtained by the **1** in the presence of BnOH at 100 °C in toluene.

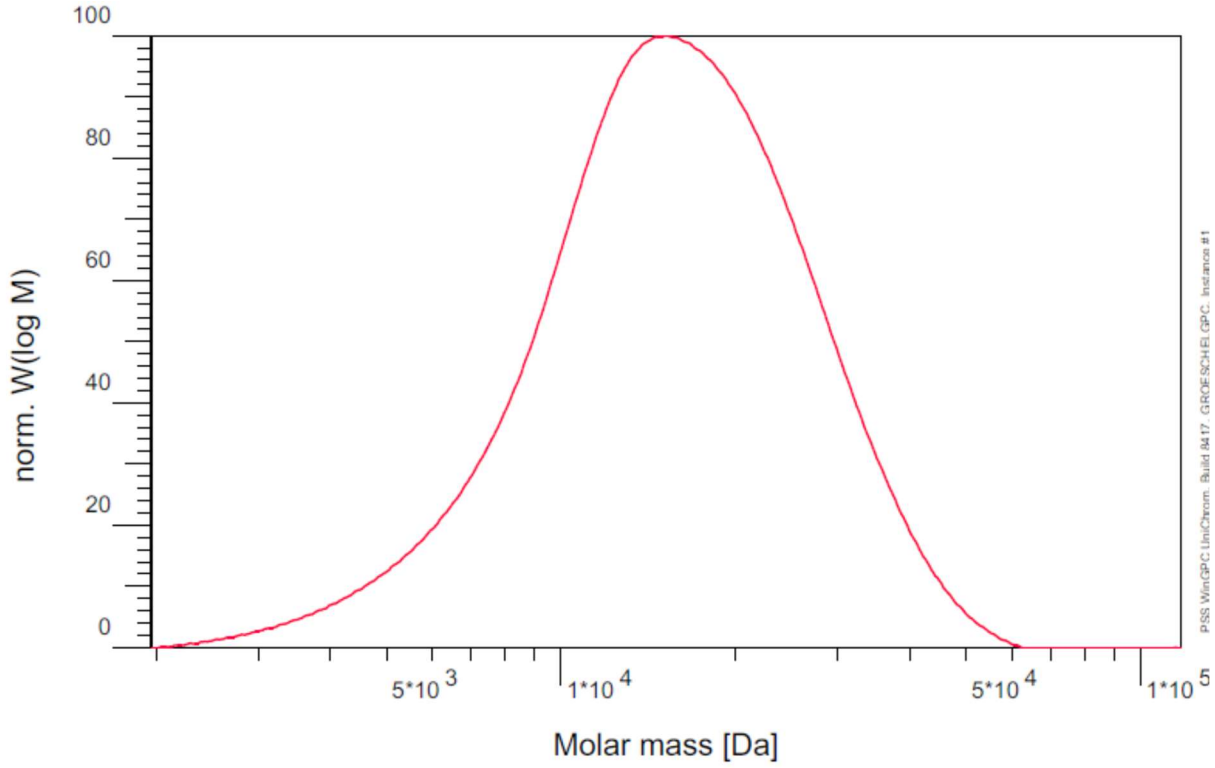

Figure S34. GPC elugram of poly(cyclohexenesuccinate) copolymer obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

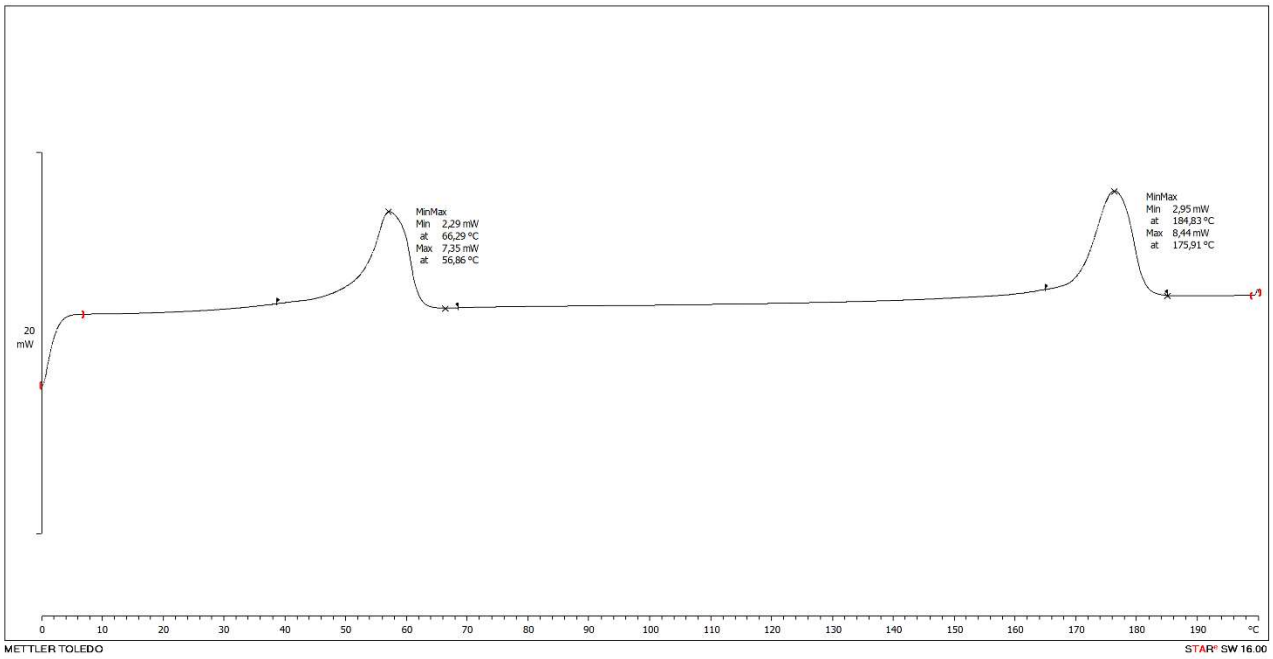

Figure S35. DSC curve of PCL-*b*-PLLA obtained by reaction of *ε*-CL, *L*-LA and **1** in ratio [*ε*-CL]:[*L*-LA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

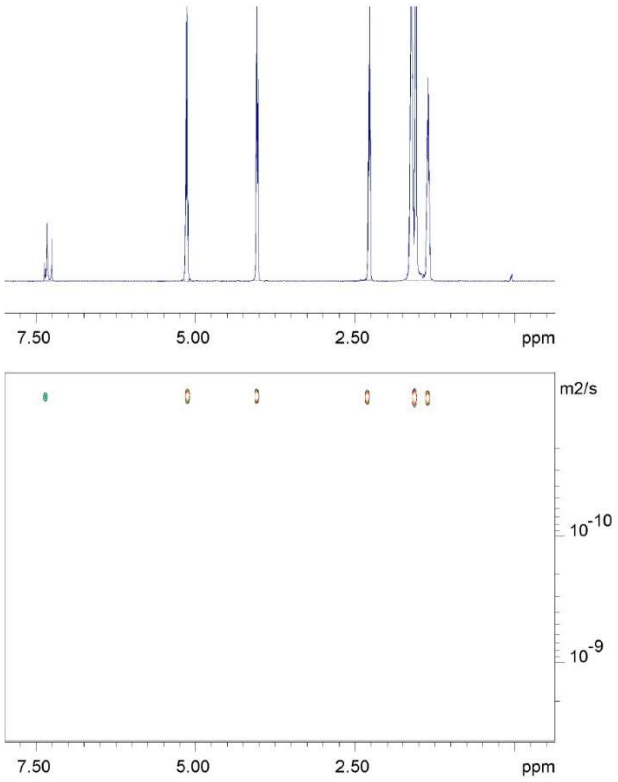

Figure S36. DOSY NMR (300 MHz, $CDCl_3$, 298 K) spectrum of PCL-b-PLLA diblock copolymer.

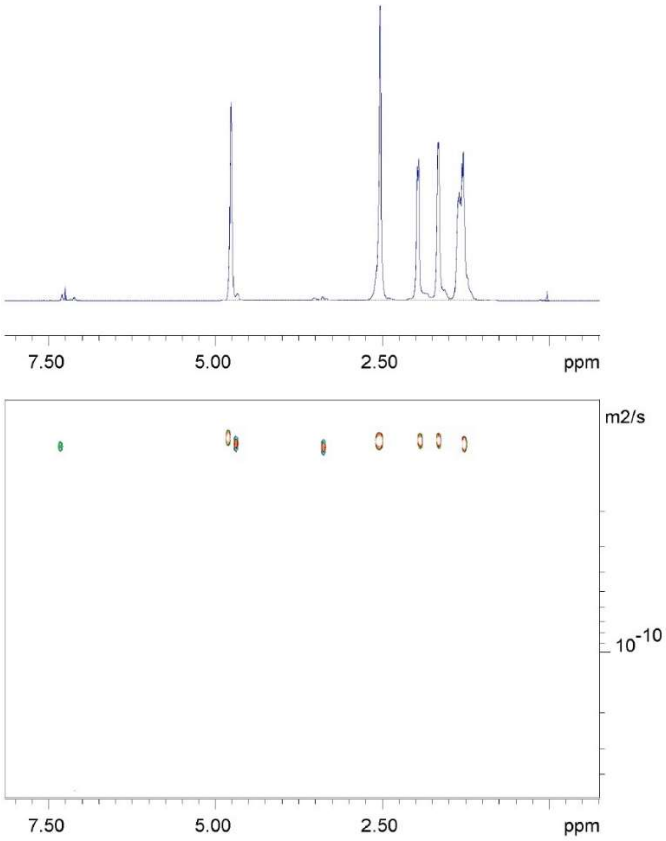

Figure S37. DOSY NMR (300 MHz, $CDCl_3$, 298 K) spectrum of poly[(cyclohexene succinate) copolymer.

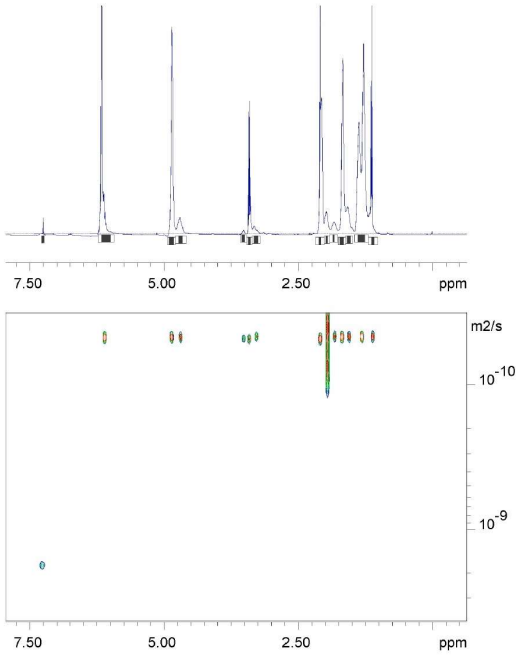

Figure S38. DOSY NMR (300 MHz, $CDCl_3$, 298 K) spectrum of poly[(cyclohexene malonate) copolymer.

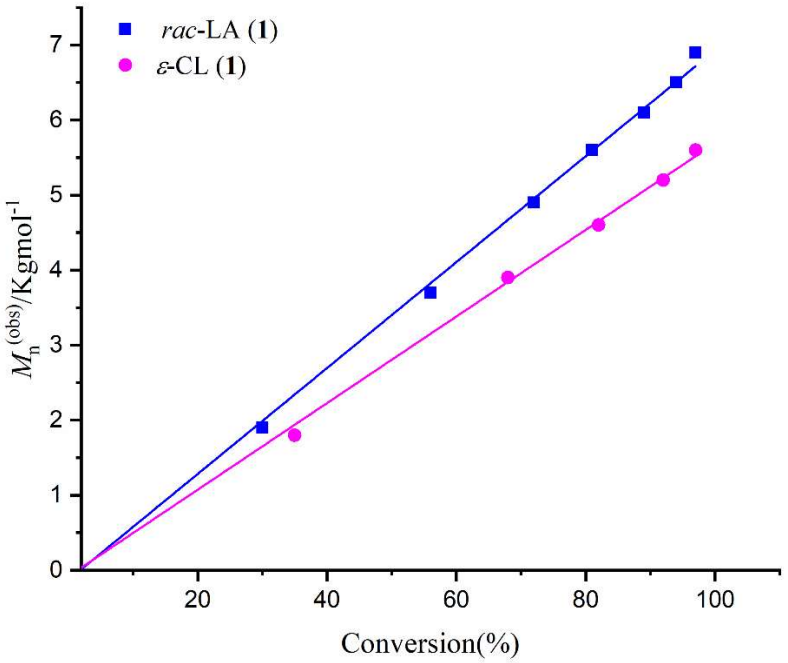

Figure S39. Plot of $M_n^{(obs)}$ (kg/mol) vs. conversion (%) for *rac*-LA and ε-CL using complex **1** in a ratio [Monomer]:[cat.]:[BnOH] = 200:200:1:4 in toluene at 100 °C.

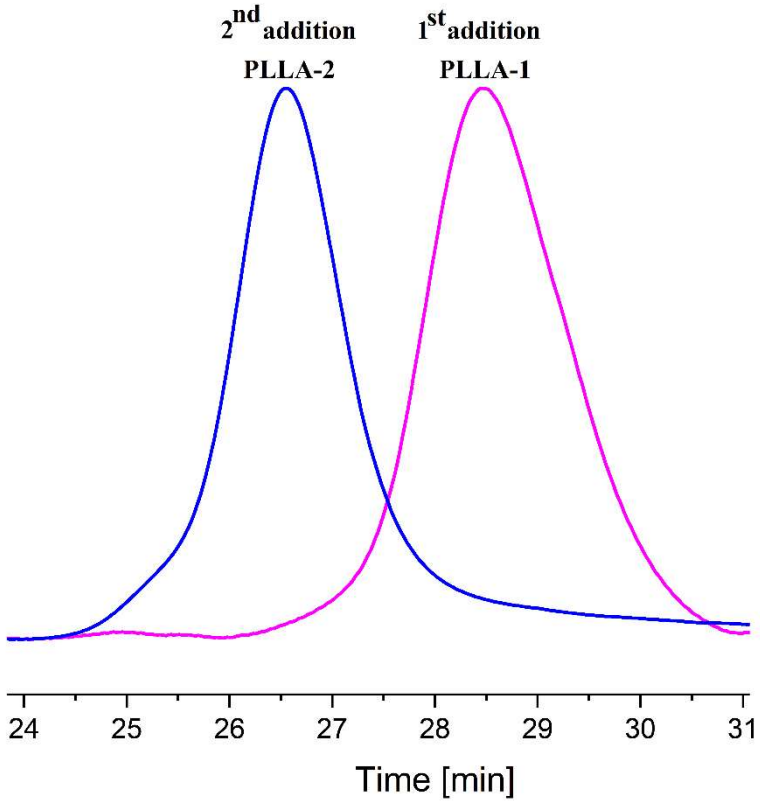

Figure S40. GPC elugram of PLLA obtain by polymerization resumption experiment of enantiomeric pure *L*-LA and **1** in toluene at 100 °C, [monomer]:[cat.]:[BnOH] = (200^{1st} + 200^{2nd}):1:4.

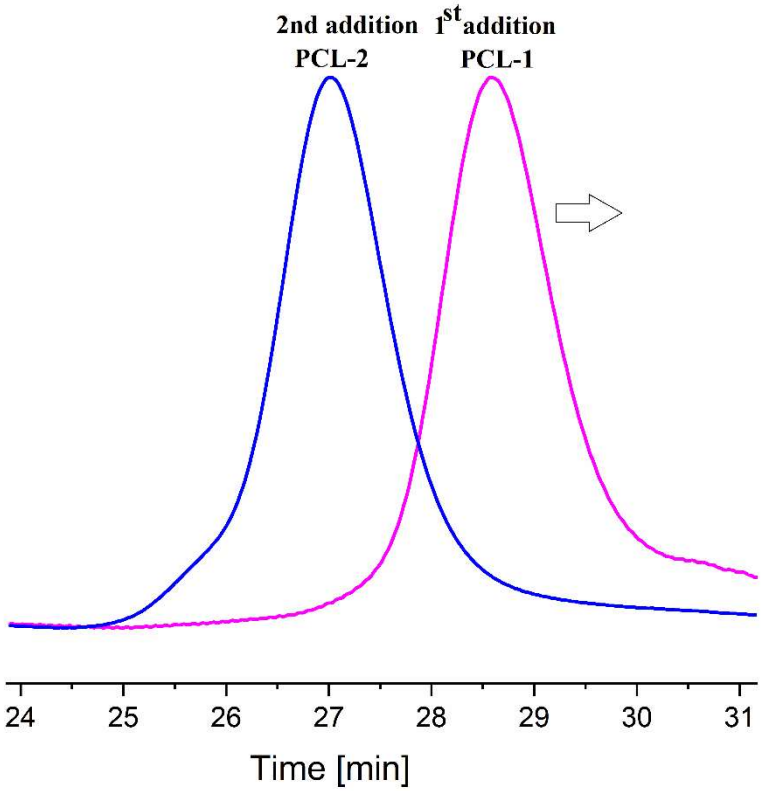

Figure S41. GPC elugram of PCL obtain by polymerization resumption experiment of ε-CL and **1** in toluene at 100 °C, [monomer]:[cat.]:[BnOH] = (200^{1st} + 200^{2nd}):1:4.

Figure S42. COSY NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

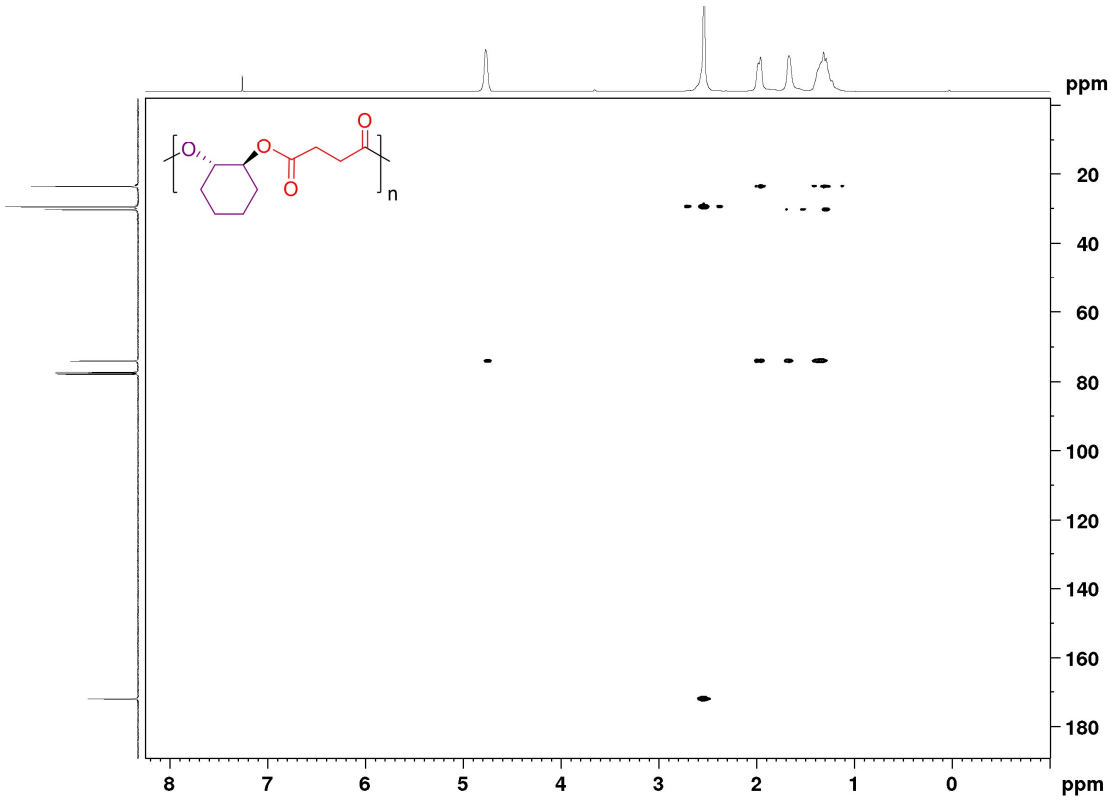

Figure S43. HMBC NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

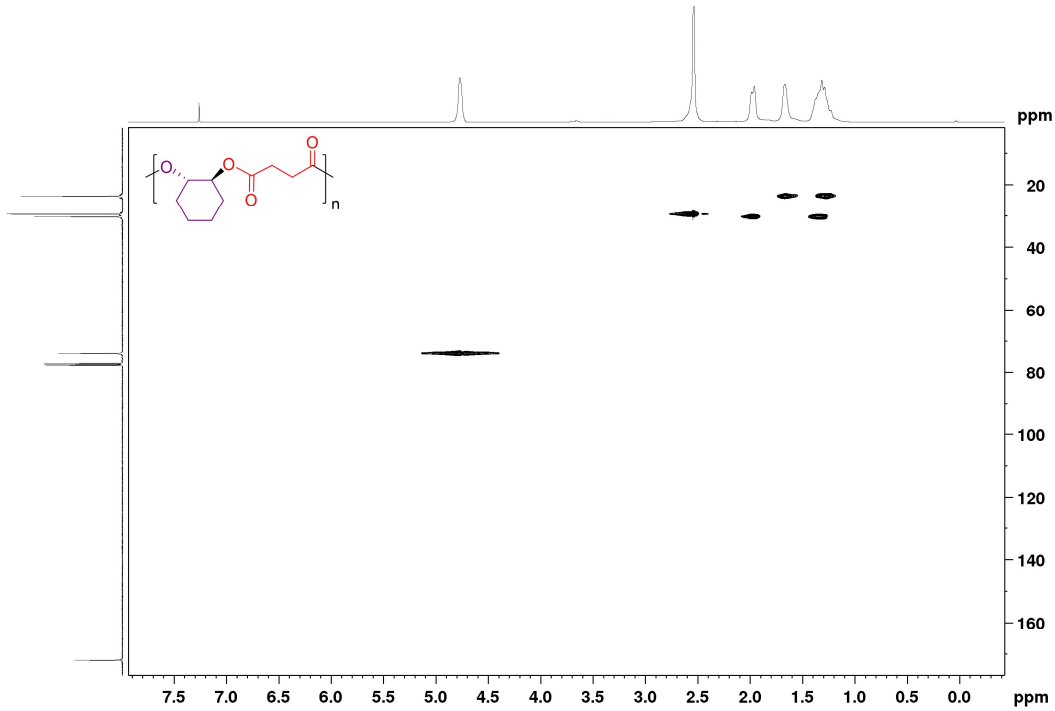

Figure S44. HSQC NMR spectrum of poly(cyclohexene succinate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

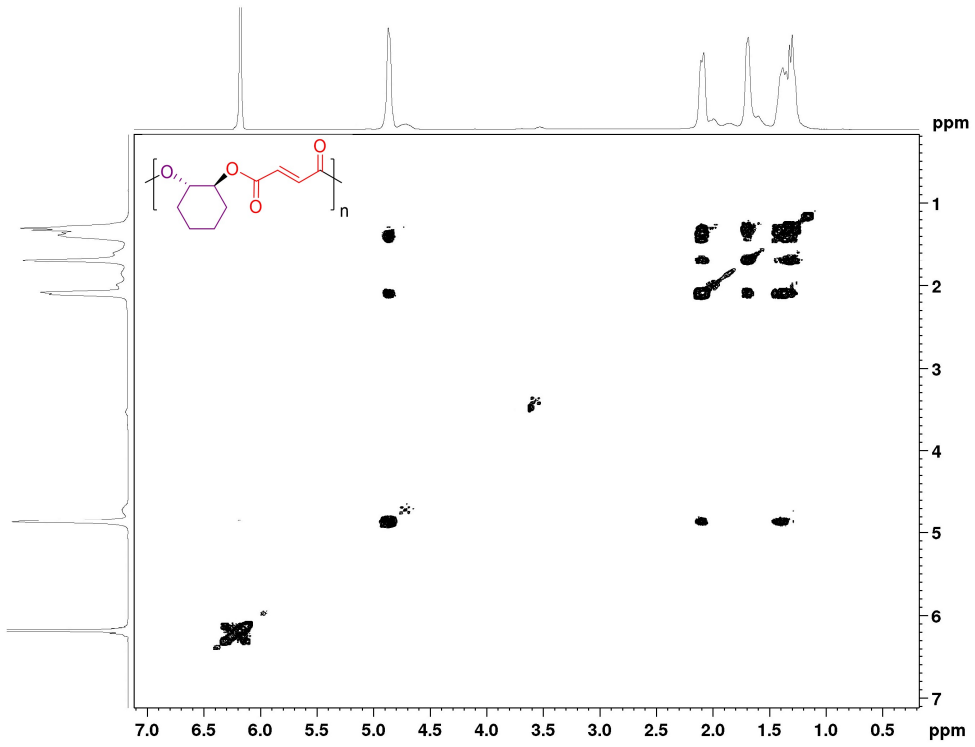

Figure S45. COSY NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

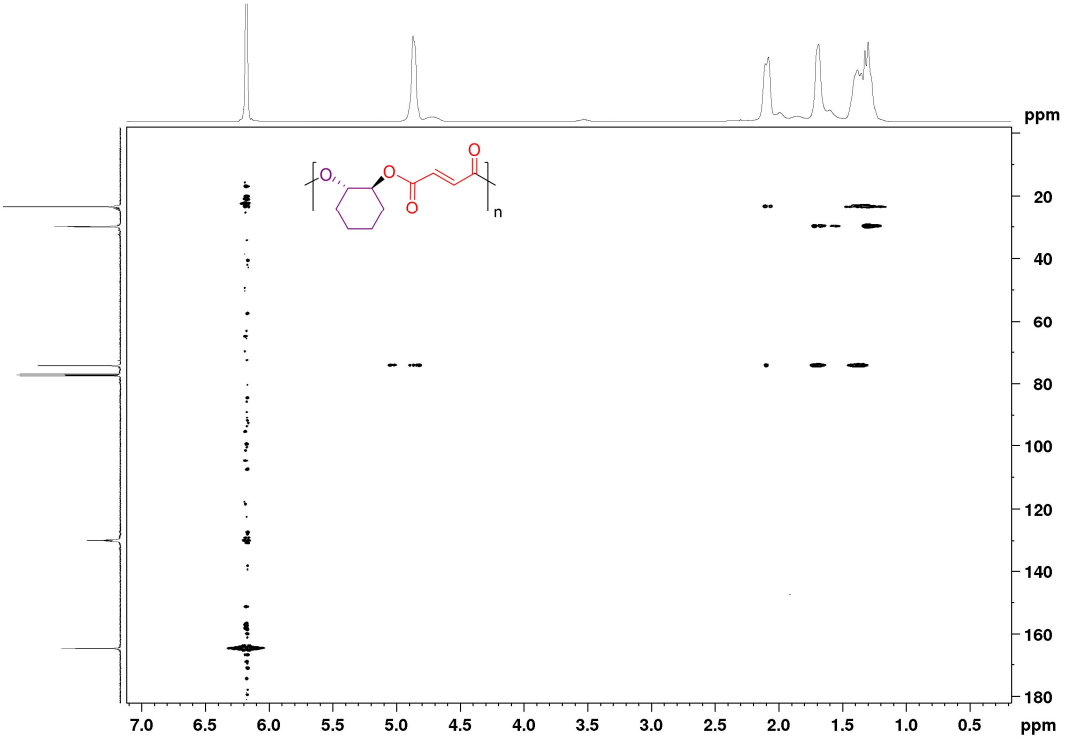

Figure S46. HMBC NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

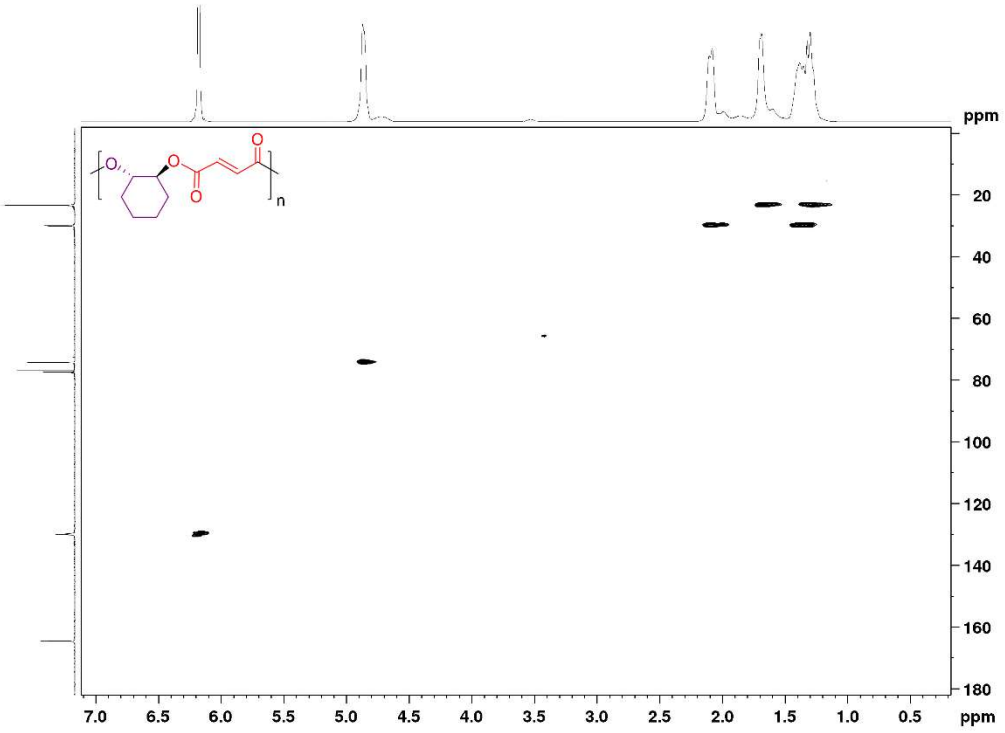

Figure S47. HSQC NMR spectrum of poly(cyclohexene malonate) copolymer in $CDCl_3$ obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[MA]:[cat.]:[BnOH] = 200:200:1:4 at 100 °C in toluene.

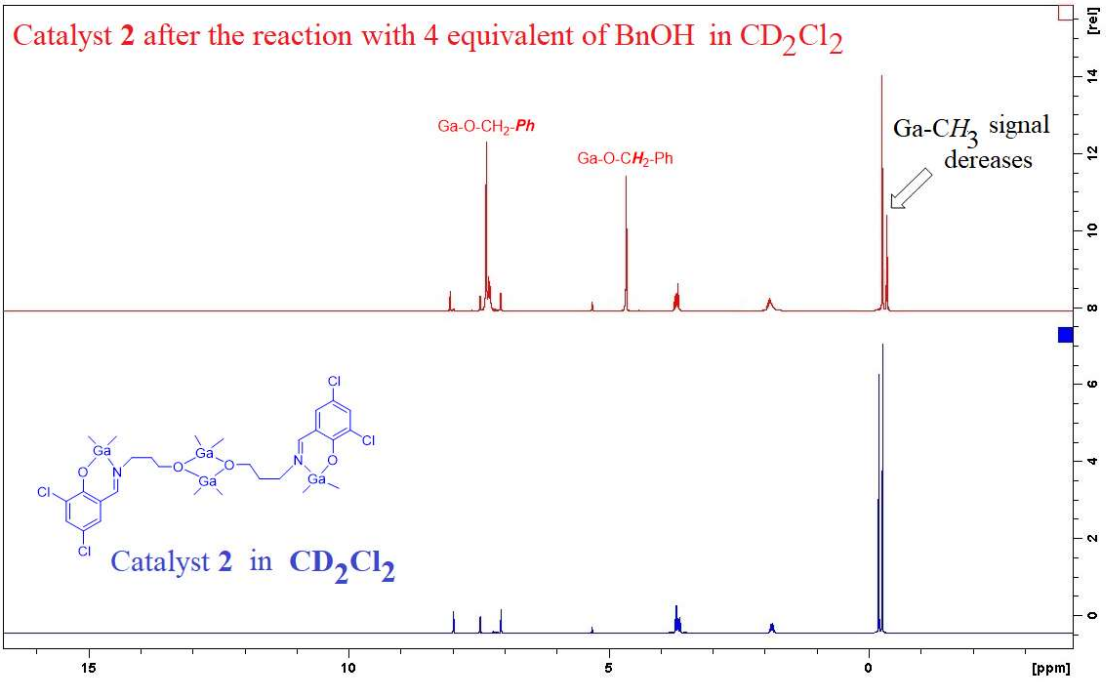

Figure S48. ^{1}H NMR spectrum of **2** (blue color) and **catalyst-2-OBn (**red color**)** in CD_2Cl_2. **Catalyst-2-OBn** obtained by reaction of **catalyst -2** and BnOH in ratio [**Cat-2**]:[BnOH] = 1:4 at 23 °C in CD_2Cl_2.

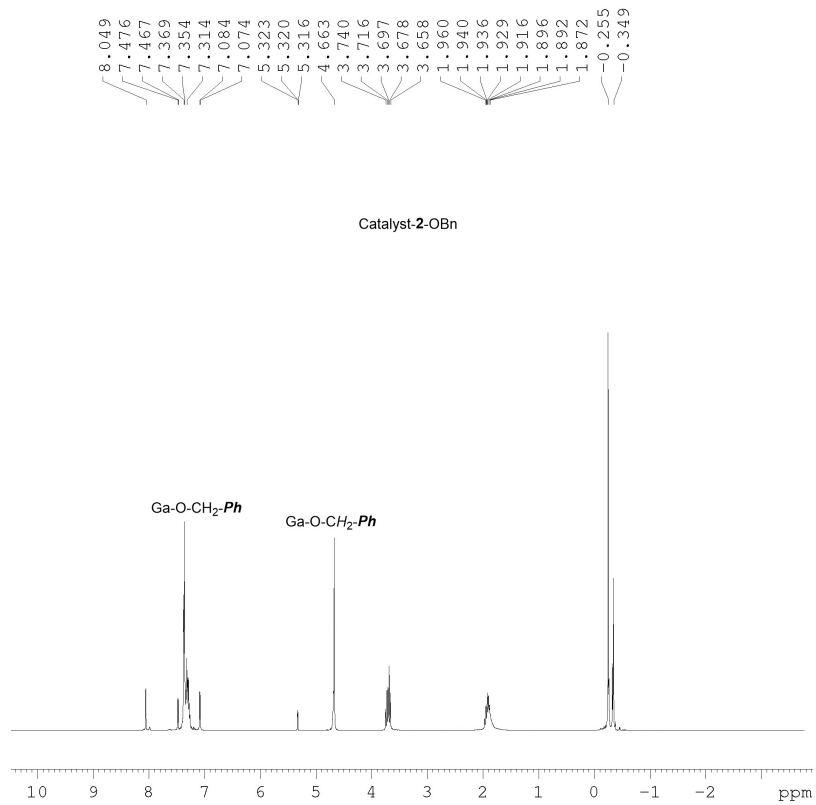

Figure S49. ^{1}H NMR spectrum **catalyst-2-OBn** in CD_2Cl_2 obtained by reaction of **2** and BnOH in ratio [**Cat-2**]:[BnOH] = 1:4 at 23 °C in CD_2Cl_2.

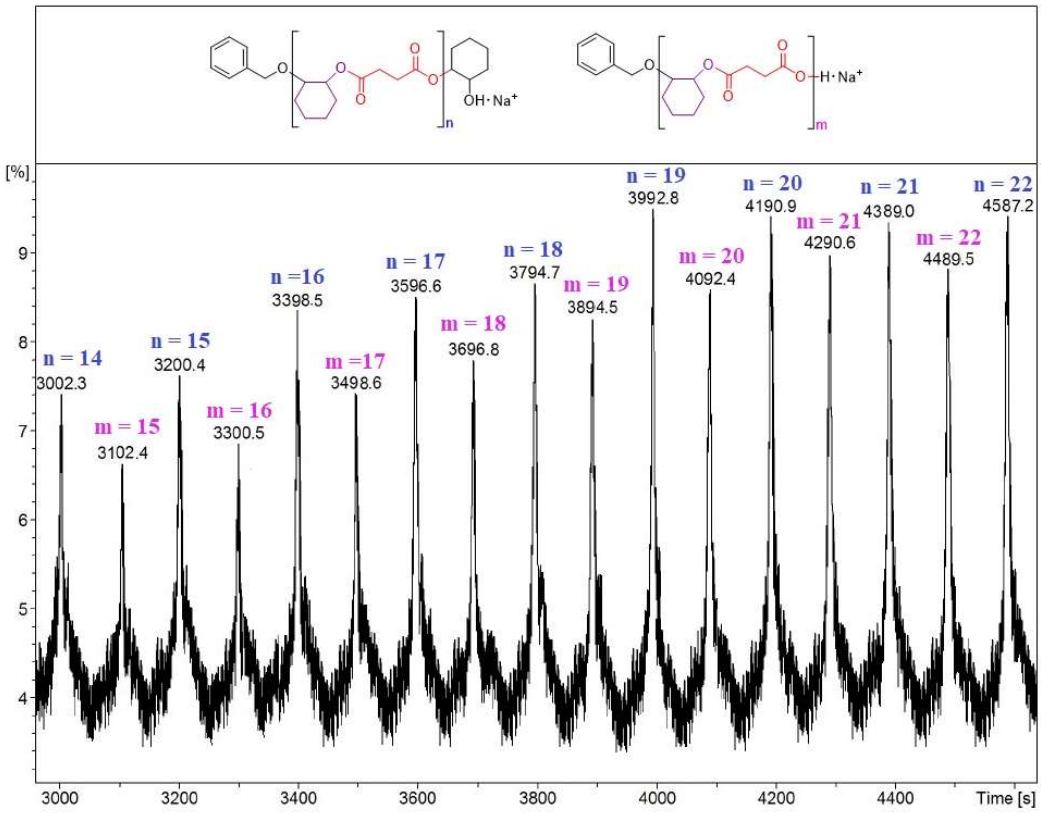

Figure S50. MALDI-ToF spectrum of poly(cyclohexene succinate) copolymer obtained by reaction of CHO, SA, and **1** in ratio [CHO]:[SA]:[cat.]:[BnOH] = 100:200:1:4 at 100 °C in toluene at 100 °C.

Table S2 ROP of *ε*-CL initiated by complex **1** with varying [monomer]:[cat.]:[BnOH] molar ratios in toluene at 100 °C.

Entry	[M]:[cat.]:[BnOH]	Time min	Conv.[a] %	$M_n^{b(theo)}$ Kg/mol	$M_n^{cal(GPC)c}$ Kg/mol	PDI
1	200:1:1	60	99	22.7	22.1	1.12
2	200:1:4	15	98	5.7	5.6	1.07
3	500:1:8	20	95	6.9	6.3	1.10
4	1000:1:10	40	95	10.9	10.2	1.13
5	5000:1:10	300	90	51.47	49.4	1.16
6	10000:1:10	720	90	102.8	100.3	1.18
7[d]	$(200^{1st} + 200^{2nd})$:1:4	$15^{1st} + 10^{2nd}$	97	5.7^{1st}, 11.1^{2nd}	5.6^{1st}, 10.9^{2nd}	1.07^{1st}, 1.09^{2nd}

[a]Monomer conversion as determined by ^{1}H NMR analysis. [b]$M_{n,}^{theo}$ = {[M_w(monomer) x [Monomer]/[Cat] x Conv./number eq of BnOH} + M_n(BnOH). [c]$M_n^{cal(GPC)}$ values were determined by GPC analysis in THF using polystyrene standards. [d]Polymerization resumption experiment of *ε*-CL in toluene at 100 °C, [monomer]:[cat.]:[BnOH] = $(200^{1st} + 200^{2nd})$:1:4.