

Supporting Information

**Controlled Ring-Opening Polymerization of *O*-Carboxyanhydrides
Using a β -Diiminate Zinc Catalyst**

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Contents:

Materials, instruments and general procedures

Table S1. Catalyst screening of various (BDI)Zn catalysts for the ROP of **1**.

Table S2. Dn/dc values for all homopolymers and block-copolymers.

Figure S1. GPC-LS traces of entry 1-4 in main text Table 1.

Figure S2. MALDI-TOF spectrum of poly(PheOCA) prepared with (BDI)Zn-1.

Figure S3. ¹H NMR spectrum of poly(PheOCA) prepared with (BDI)Zn-1

Figure S4. Homonuclear decoupled ¹H NMR spectrum of poly(PheOCA) prepared with (BDI)Zn-1

Figure S5. ¹³C NMR spectrum of poly(PheOCA) prepared with (BDI)Zn-1

Figure S6. ¹H NMR spectrum of poly(LacOCA) prepared with (BDI)Zn-1

Figure S7. Homonuclear decoupled ¹H NMR spectrum of poly(LacOCA) prepared with (BDI)Zn-1

Figure S8. ¹³C NMR spectrum of poly(LacOCA) prepared with (BDI)Zn-1

Figure S9. ¹H NMR spectrum of poly(Ser(Bn)OCA) prepared with (BDI)Zn-1

Figure S10. Homonuclear decoupled ¹H NMR spectrum of poly(Ser(Bn)OCA) prepared with (BDI)Zn-1

Figure S11. ¹³C NMR spectrum of poly(Ser(Bn)OCA) prepared with (BDI)Zn-1

Figure S12. ¹H NMR spectrum of poly(ManOCA) prepared with (BDI)Zn-1

Figure S13. ¹³C NMR spectrum of poly(ManOCA) prepared with (BDI)Zn-1

Figure S14. ¹H NMR spectrum of poly(Tyr(allyl)OCA) prepared with (BDI)Zn-1

Figure S15. Homonuclear decoupled ¹H NMR spectrum of poly(Tyr(allyl)OCA) prepared with (BDI)Zn-1

Figure S16. ¹³C NMR spectrum of poly(Tyr(allyl)OCA) prepared with (BDI)Zn-1

Figure S17. ¹H NMR spectrum of poly(LacOCA) prepared with DMAP/ⁱPrOH

Figure S18. Homonuclear decoupled ¹H NMR spectrum of poly(LacOCA) prepared with DMAP/ⁱPrOH

Figure S19. ¹H NMR spectrum of poly(PheOCA) prepared with DMAP/ⁱPrOH

Figure S20. Homonuclear decoupled ¹H NMR spectrum of poly(PheOCA) prepared with DMAP/ⁱPrOH

Figure S21. ¹H NMR spectrum of poly(Ser(Bn)OCA) prepared with DMAP/ⁱPrOH

Figure S22. Homonuclear decoupled ^1H NMR spectrum of poly(Ser(Bn)OCA) prepared with DMAP/ $i\text{PrOH}$

Figure S23. ^{13}C NMR spectrum of poly(Ser(Bn)OCA) prepared with DMAP/ $i\text{PrOH}$

Figure S24. ^1H NMR spectrum of poly(ManOCA) prepared with DMAP/ $i\text{PrOH}$

Figure S25. ^{13}C NMR spectrum of poly(ManOCA) prepared with DMAP/ $i\text{PrOH}$

Figure S26. GPC MAL-LS traces and RI traces of block copolymers of OCA and LA

Figure S27. Plot of $-\log[k_{app}]$ versus $-\log[\text{Zn}]$ for ROP of L-PheOCA prepared with (BDI)Zn-1.

Figure S28. ^1H NMR spectrum of (BDI)Zn-1.

Figure S29. ^1H NMR spectrum of (BDI)Zn-2.

Figure S30. Results of ROP of L-PheOCA prepared with (BDI)Zn-2.

Figure S31. ^1H NMR spectrum of mixing 1:1 equivalent of (BDI)Zn-2 and L-PheOCA for 4 h.

Figure S32. ^1H NMR spectrum of mixing 1:1 equivalent of (BDI)Zn-1 and L-PheOCA for 10 min.

Figure S33. Proposed Mechanism of ROP of OCA prepared with (BDI)Zn.

Materials: ALL chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) unless otherwise noted. L-Lactide (LLA) was purchased from TCI America (Portland, OR, USA). It was recrystallized three times in anhydrous toluene and stored at -30 °C in glove box. Anhydrous tetrahydrofuran (THF) was dried by an alumina column and stored in glove box. d₈-THF, isopropanol, and L-methyl lactate were dried by 4Å molecular sieve to remove trace amount of water. L-PheOCA,¹ L-LacOCA,² L-Ser(Bn)OCA,³ L-ManOCA,⁴ L-Tyr(allyl)OCA⁵ were synthesized according to the literature. All OCAs were recrystallized three times and stored at -30 °C in glove box. (BDI)Zn catalysts and precursor were synthesized according to the previous report using similar procedure.⁶

Instrumentation: NMR spectra were recorded on Varian U500 (500 MHz), VXR-500 (500 MHz), or Varian U600 (600 MHz) spectrometers. Infrared spectra were recorded on a Perkin Elmer 100 serial FT-IR spectrometer. Quantified FT-IR spectra were obtained using IR liquid transmission cell (Specac Inc., Swedesboro, NJ, USA). Gel permeation chromatography (GPC) experiments were performed on a system equipped with an isocratic pump (Model 1260, Agilent Technology, Santa Clara, CA, USA), a DAWN HELEOS multiangle laser light scattering (MALLS) detector, and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA, USA). The detection wavelength of HELEOS was set at 658 nm. Separations were performed using serially connected size exclusion columns (100 Å, 10³ Å, 10⁴ Å, 10⁵ Å, and 10⁶ Å Phenogel columns, 5 µm, 300 × 7.8 mm, Phenomenex, Torrance, CA, USA) at 60 °C using DMF containing 0.1 M LiBr as the mobile phase. The molecular weights of polymers were determined from the *dn/dc* value assuming 100% mass recovery using ASTRA software (Version 6.1.1, Wyatt Technology). MALDI-TOF spectra were taken on a Bruker Ultra Flex extreme equipped with a 337 nm nitrogen laser. An accelerating voltage of 23 kV was applied, acquiring 1000 shots for each sample. Samples were prepared using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) as the matrix (10 mg mL⁻¹ in THF), and sodium trifluoroacetate as the cationization agent (10 mg mL⁻¹ in THF). Samples were dissolved in THF (10 mg mL⁻¹). Solutions of matrix, salt, and polymer were mixed in a volume ratio of 4 : 1 : 1, respectively. The mixed solutions (0.5 µL) were hand spotted on a stainless steel MALDI target and allowed to dry completely. All spectra were recorded in reflectron mode.

General Polymerization Procedure using (BDI)Zn catalyst: In a glove box, (BDI)Zn catalyst (20 mM) and OCA (100 mM) were separately dissolved in anhydrous THF to obtain stock solution. (BDI)Zn solution (100 µL) was added into a 7-mL glass vial equipped with a magnetic stir bar and diluted with THF (1.0 mL). The OCA solution of pre-calculated volume (1.0 mL for

[OCA]:[Zn] = 50) was added into catalyst solution under stirring. After confirming fully conversion of monomer, resulting polymers were precipitated in hexane and dried to give final products. Yields were typically >80%. Trace amount of BDI ligand was washed away through precipitation in ether twice.

General Polymerization Procedure of DMAP/ⁱPrOH: In a glove box, DMAP catalyst (20 mM) ⁱPrOH (20 mM), and OCA (100 mM) were separately dissolved in anhydrous THF to obtain stock solution. DMAP solution (100 μ L) and ⁱPrOH solution (100 μ L) was added into a 7-mL glass vial equipped with a magnetic stir bar and diluted with THF (1.0 mL). The OCA solution (1.0 mL for [M]:[I] = 50) was added into catalyst solution under stirring. After reaction was complete, resulting polymers were precipitated in hexane and dried to give final products. Yields were typically >80%.

Poly(phenyllactic acid) (from _L-PheOCA): ¹H NMR (500 MHz, CDCl₃): δ 7.27 (m, 3H), 7.12 (d, 2H, J = 7.0 Hz), 5.27 (dd, 1H, J = 8.0, 8.5 Hz), 3.19 (dd, 1H, J = 8.0, 15 Hz), 3.05 (dd, 1H, J = 8.5, 15 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 168.30, 135.63, 129.56, 128.73, 127.33, 73.46, 37.11.

Poly(lactic acid) (from _L-LacOCA): ¹H NMR (500 MHz, CDCl₃): δ 5.15 (q, 1H, J = 7.0 Hz), 1.57 (d, 3H, J = 7.0 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 169.84, 69.24, 16.89.

Poly(benzyloxylactic acid) (from _L-Ser(Bn)OCA): ¹H NMR (500 MHz, CDCl₃): δ 7.26 (m, 5H), 5.46 (dd, 1H, J = 7.0 Hz), 4.53 (s, 2H), 3.95 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 166.72, 137.72, 128.62, 127.98, 127.96, 73.65, 73.01, 68.73.

Poly(mandalic acid) (from _L-ManOCA): ¹H NMR (500 MHz, CDCl₃): δ 7.28 (m, 5H), 5.98 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 167.03, 132.56, 129.61, 128.91, 128.06, 75.00.

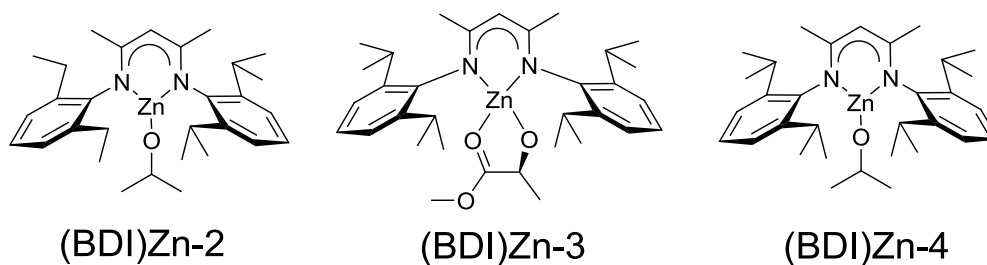
Poly(4-allyloxyphenyllactic acid) (from _L-Tyr(allyl)OCA): ¹H NMR (500 MHz, CDCl₃): δ 7.27 (m, 2H), 6.75 (m, 2H), 6.00 (m, 1H), 5.35 (d, 1H), 5.26 (d, 2H), 4.45 (t, 2H), 3.10 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 168.41, 157.94, 133.57, 130.66, 127.82, 117.81, 114.95, 73.61, 68.96, 36.34.

Conversion of Monomer: For confirming fully conversion purpose, a small aliquot was removed from reaction mixture and dipped onto a KBr salt plate. Disappearance of peak at 1812 cm⁻¹ indicated fully consumption of OCA monomers. For quantification, an aliquot of the reaction mixture (100 μ L) was quenched with 5% acetic acid THF solution (100 μ L). OCA concentration was quantified by FT-IR using pre-calibrated standard curve at 1812 cm⁻¹.

General Procedure for the Block Copolymerization of OCAs: The (BDI)Zn-1 catalyst in THF solution (50 μ L, 20 mM) was diluted in 500 μ L THF. L-PheOCA solution (0.5 mL, 19.2 mg/mL, 100 mM) was added and stirred at room temperature for 10 min. The complete monomer consumption was confirmed by FT-IR. L-Ser(Bn)OCA solution (0.5 mL, 22.2 mg/mL, 100 mM) was then added to the reaction mixture. The reaction mixture was stirred for another 10 min. After the fully consumption of both OCAs, resulting polymer was precipitated in hexane, dried and subjected to further analysis.

Procedure for the Block Copolymerization of L-PheOCA and L-lactide: The (BDI)Zn-1 in the THF solution (20 mM, 200 μ L) was diluted in 100 μ L THF. The L-PheOCA solution (1mL, 38 mg/mL, 200 mM) was added and stirred at room temperature for 10 min. The complete monomer consumption was confirmed by FT-IR. The L-lactide solution (1mL, 29 mg/mL, 200 mM) was then added to the reaction mixture. The reaction mixture was stirred for another 4 hour till the fully consumption of LLA. The resulting polymer was precipitated in hexane and dried to give final product.

Table S1. Catalyst screening of various (BDI)Zn catalysts for the ROP of **1**.

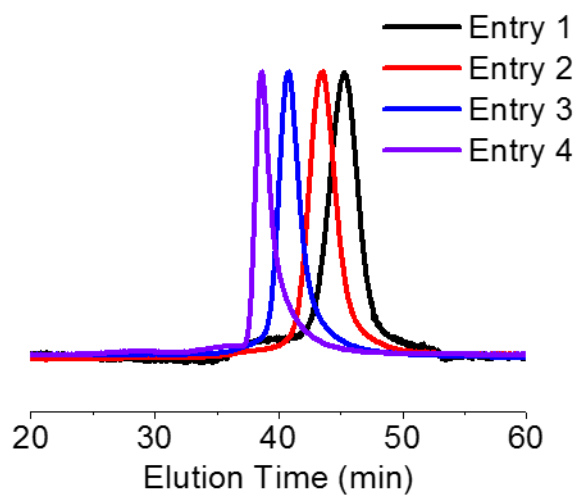


Entry	Catalyst	[M]/[I]	Time (h)	% Conv. ^a	M_n (exp.) (kDa) ^b	M_n (cal.) (kDa) ^c	PDI ^b
1	(BDI)Zn-1	50	0.5	>98	8.3	7.5	1.05
2	(BDI)Zn-2	50	24	>98	21.4	7.5	1.33
3	(BDI)Zn-3	50	0.5	>98	14.4	7.5	1.21
4	(BDI)Zn-4	50	0.5	>98	9.9	7.5	1.58

^aDetermined by FT-IR measurement of peak intensity at 1812 cm⁻¹ correspond to carbonyl groups in OCA ring. ^bDetermined by GPC analysis in DMF (0.1 M LiBr) using dn/dc = 0.103. ^cCalculated according to the feeding ratio of monomer to initiator.

Table S2. Dn/dc values for all homopolymers and block-copolymers calculated using 100% mass recovery methods from peaks.

Homopolymers		Block-copolymers	
monomer	dn/dc	polymer structure	dn/dc
1	0.103	1 ₅₀ -b- 2 ₅₀	0.073
2	0.025	1 ₅₀ -b- 3 ₅₀	0.091
3	0.093	2 ₅₀ -b- 3 ₅₀	0.058
4	0.095	1 ₅₀ -b-LA ₅₀	0.068
5	0.105	LA ₅₀ -b- 1 ₅₀	0.069
-	-	1 ₅₀ -b-LA ₅₀ -b- 1 ₁₀₀	0.090



Entry	Catalyst	[M]/[I]	Time (h)	% Conv. ^a	M_n (exp.) (kDa) ^b	M_n (cal.) (kDa) ^c	PDI ^b
1	(BDI)Zn-1	25	0.5	>98	3.7	3.8	1.06
2	(BDI)Zn-1	50	0.5	>98	8.3	7.5	1.05
3	(BDI)Zn-1	100	0.5	>98	16.4	14.9	1.07
4	(BDI)Zn-1	200	0.5	>98	33.1	29.7	1.02

^aDetermined by FT-IR measurement of peak intensity at 1812 cm^{-1} correspond to carbonyl groups in OCA ring. ^bDetermined by GPC analysis in DMF (0.1 M LiBr) using $dn/dc = 0.103$. ^cCalculated according to the feeding ratio of monomer to initiator.

Figure S1. GPC-LS traces of Entry 1-4 in main text Table 1.

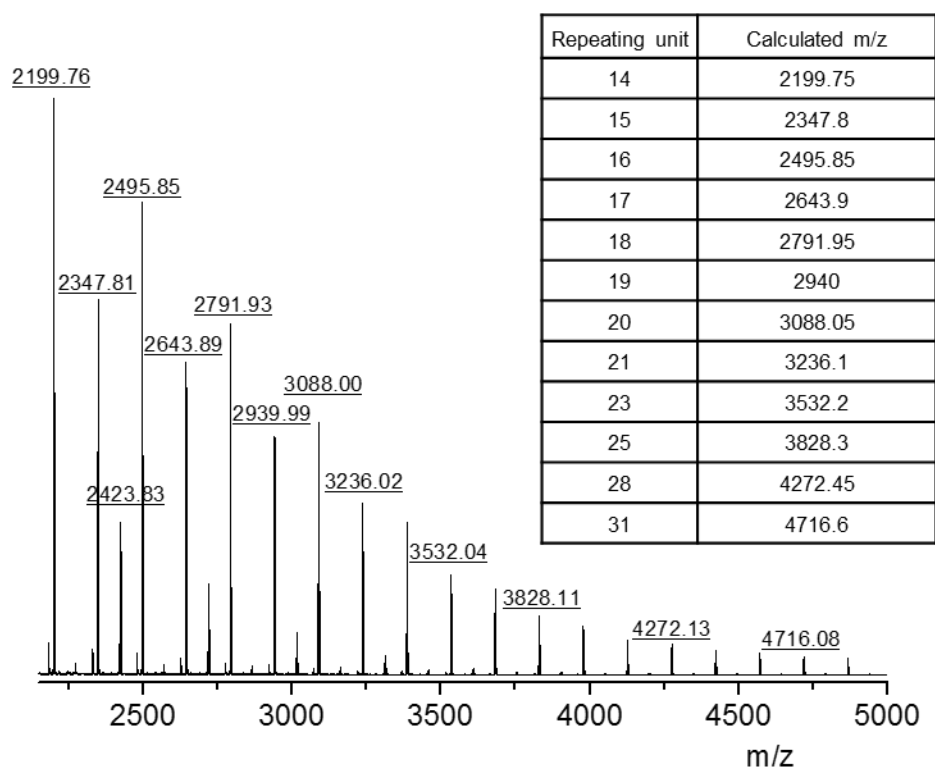


Figure S2. MALDI-TOF spectrum of poly(PheOCA) prepared with (BDI)Zn-1. Calculated $m/z = 104.05 + 22.99 + 148.05 \cdot n$. The extra set of peak (e.g. $m/z = 2423$) attributes to poly(PheOCA) initiated by trace amount of (BDI)Zn(OMe) as the impurity in the catalyst (see Figure S28).

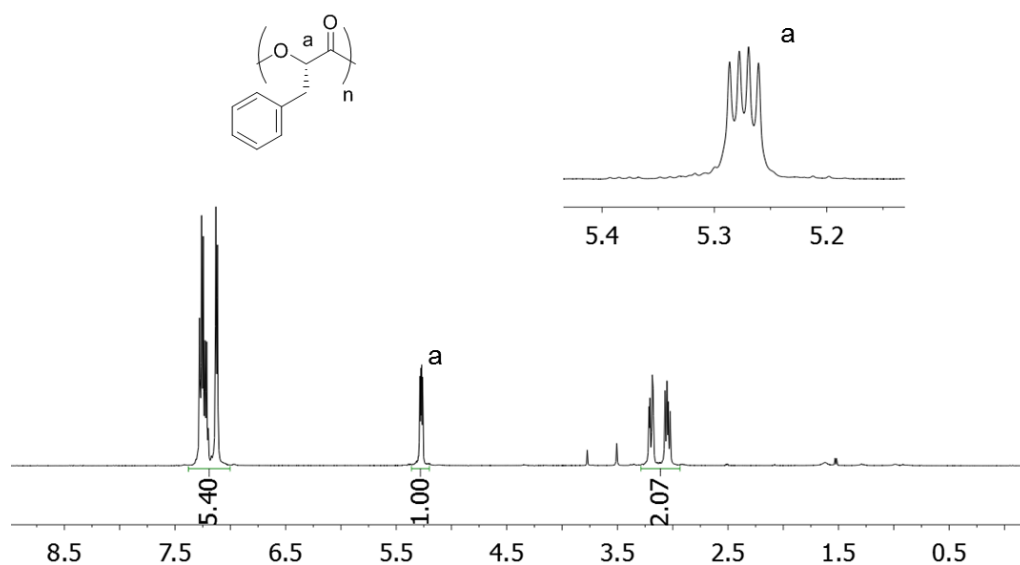


Figure S3. ^1H NMR spectrum of poly(PheOCA) prepared with (BDI)Zn-1 (500 MHz, CDCl_3).

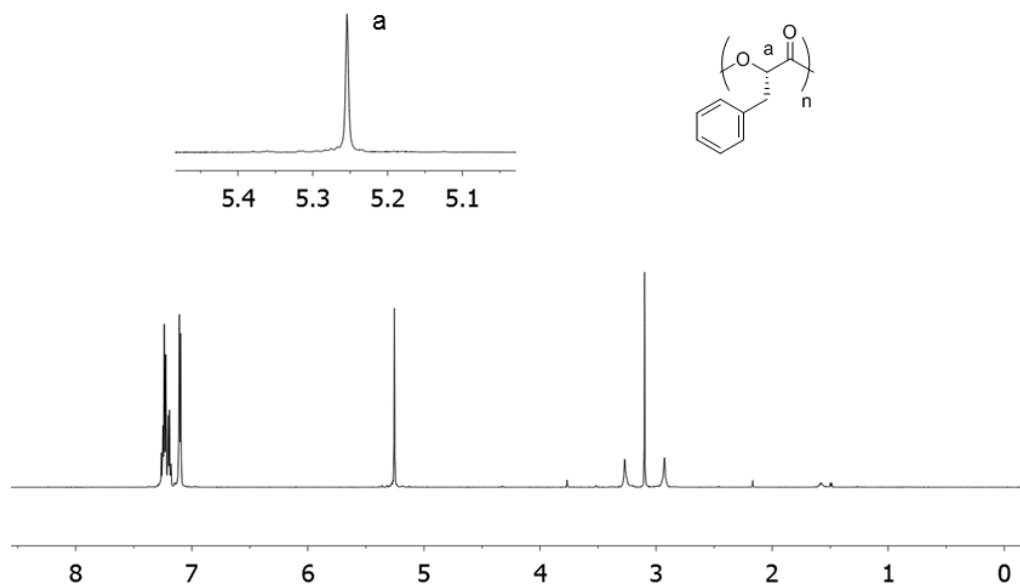


Figure S4. Homonuclear decoupled ^1H NMR spectrum of poly(PheOCA) prepared with (BDI)Zn-1 (600 MHz, CDCl_3).

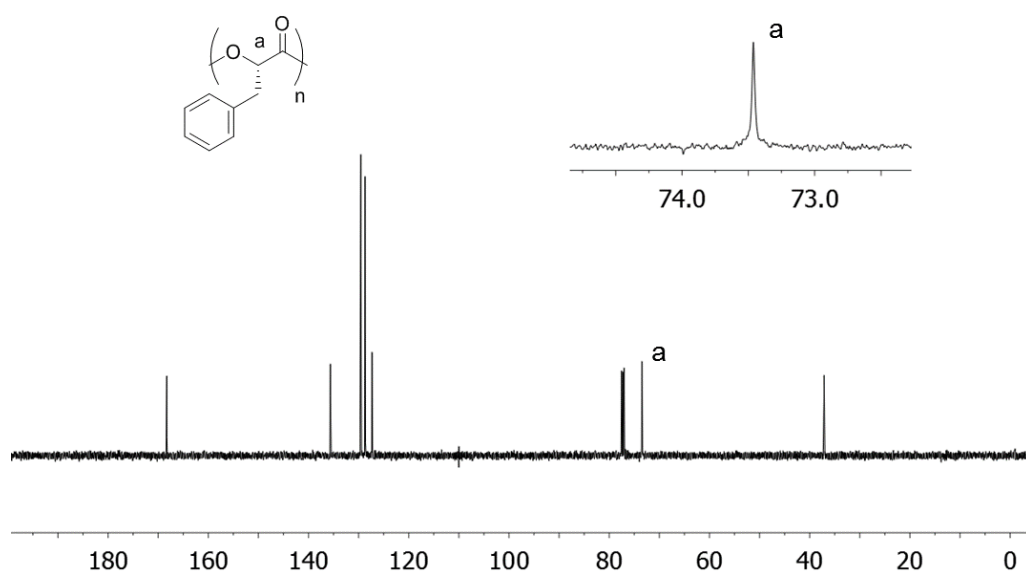


Figure S5. ^{13}C NMR spectrum of poly(PheOCA) prepared with BDIZn-1 (125 MHz, CDCl_3).

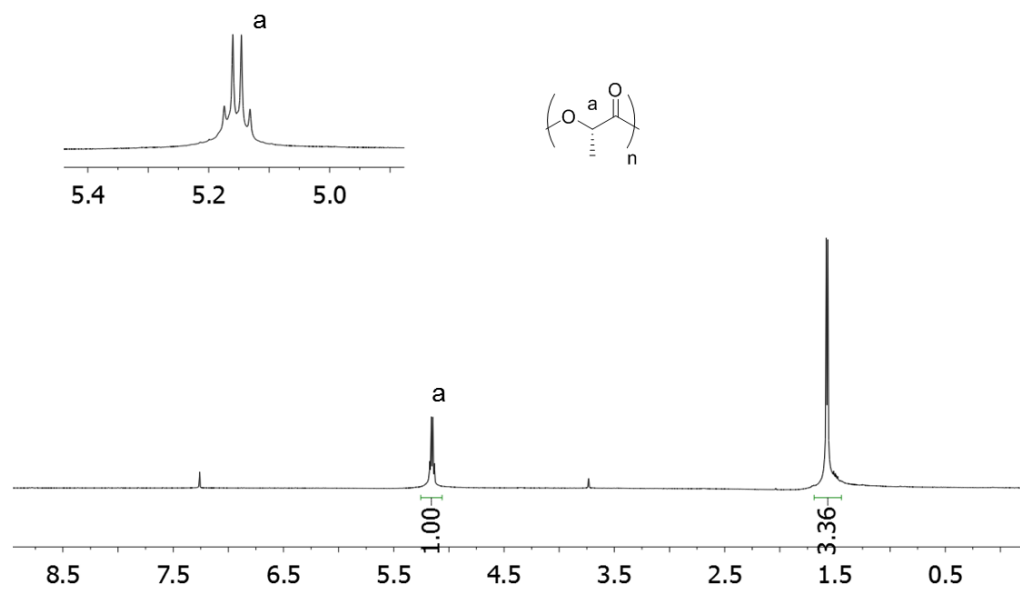


Figure S6. ^1H NMR spectrum of poly(LacOCA) prepared with (BDI)Zn-1 (500 MHz, CDCl_3).

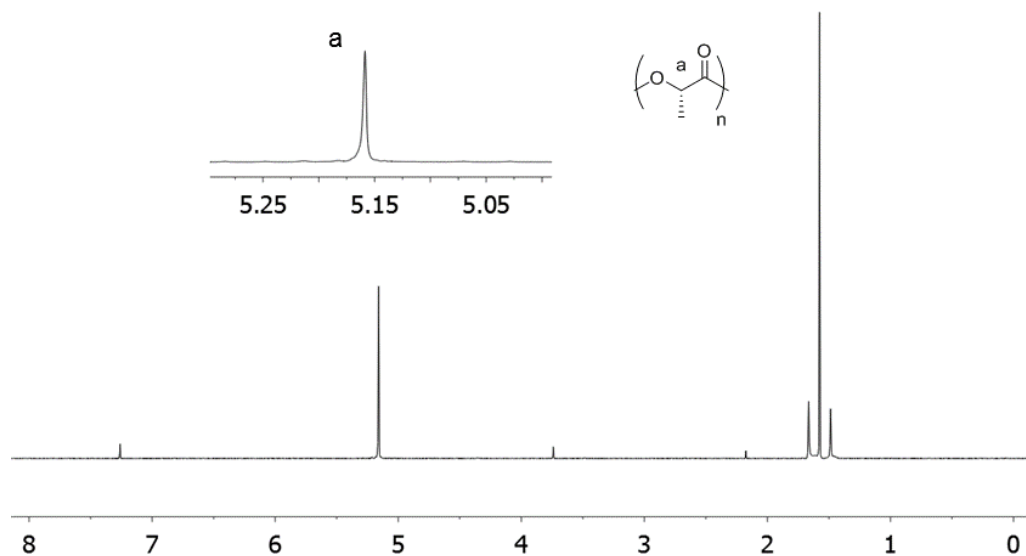


Figure S7. Homonuclear decoupled ¹H NMR spectrum of poly(LacOCA) prepared with (BDI)Zn-1 (600 MHz, CDCl₃).

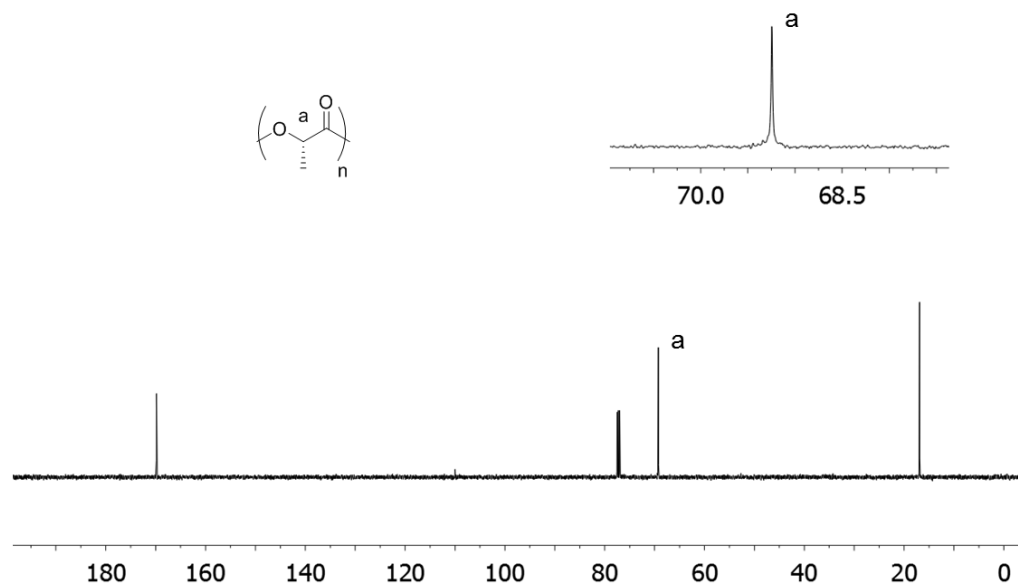


Figure S8. ¹³C NMR spectrum of poly(LacOCA) prepared with (BDI)Zn-1 (125 MHz, CDCl₃).

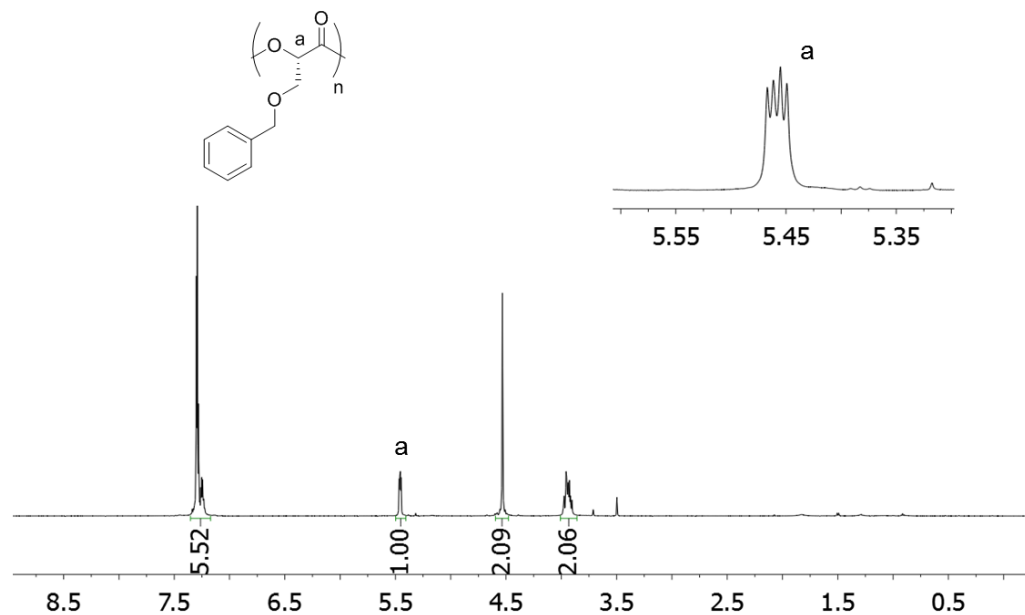


Figure S9. $^1\text{H NMR}$ spectrum of poly(Ser(Bn)OCA) prepared with (BDI)Zn-1 (500 MHz, CDCl_3).

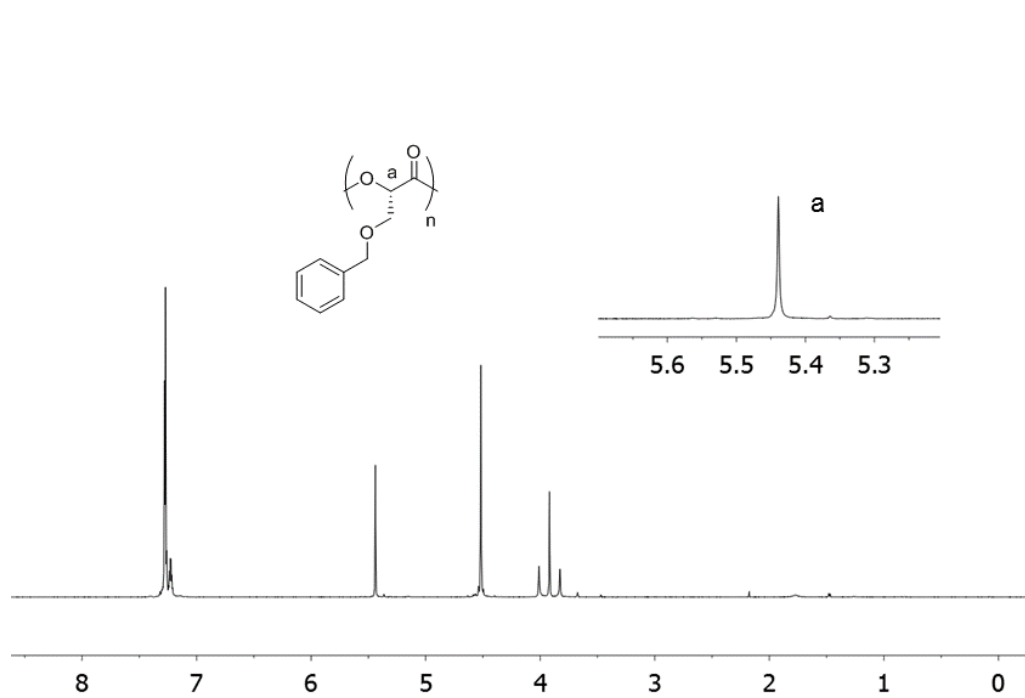


Figure S10. Homocoupled decoupled $^1\text{H NMR}$ spectrum of poly(Ser(Bn)OCA) prepared with (BDI)Zn-1 (600 MHz, CDCl_3).

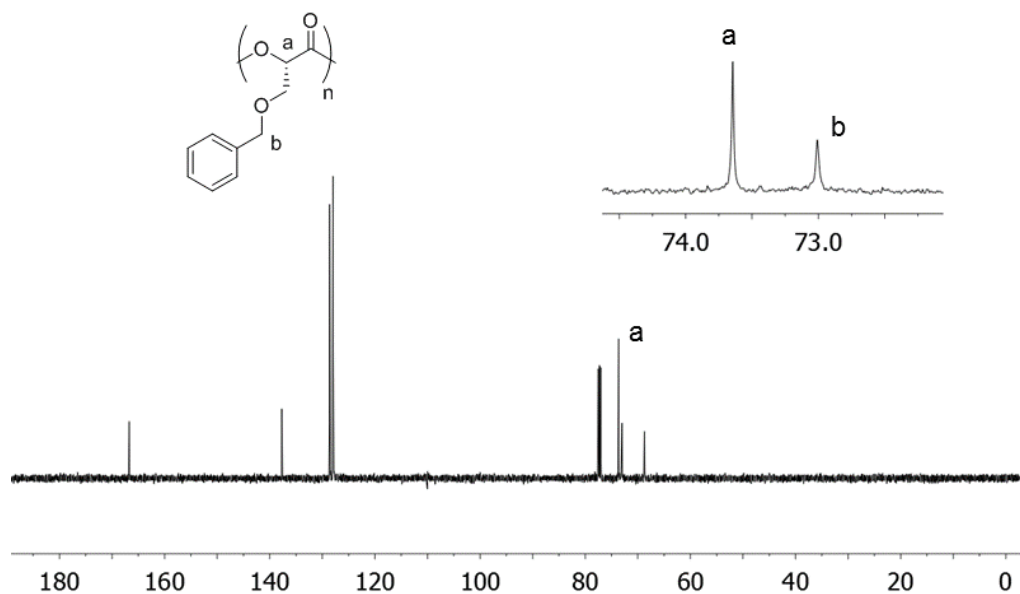


Figure S11. ^{13}C NMR spectrum of poly(Ser(Bn)OCA) prepared with (BDI)Zn-1 (125 MHz, CDCl_3).

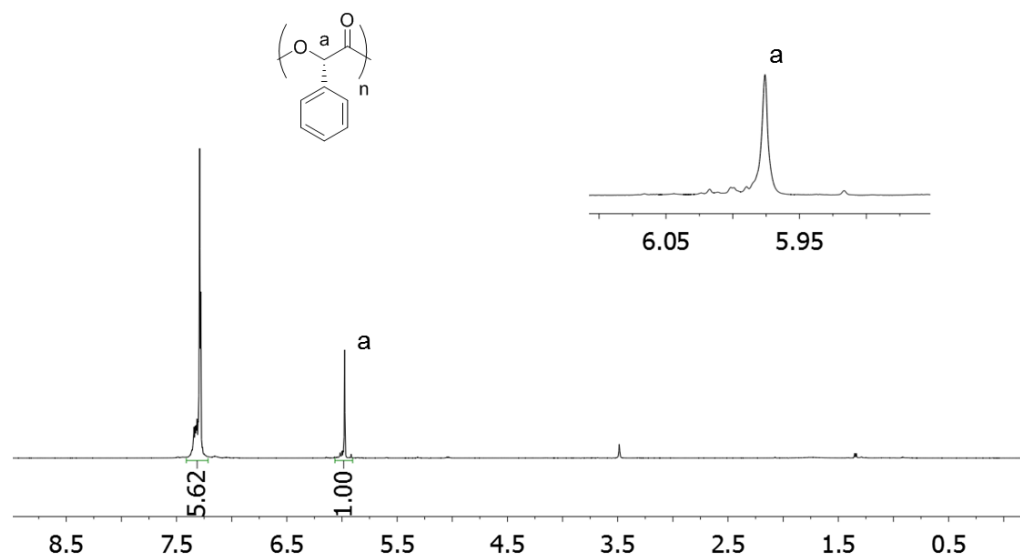


Figure S12. ^1H NMR spectrum of poly(ManOCA) prepared with (BDI)Zn-1 (500 MHz, CDCl_3).

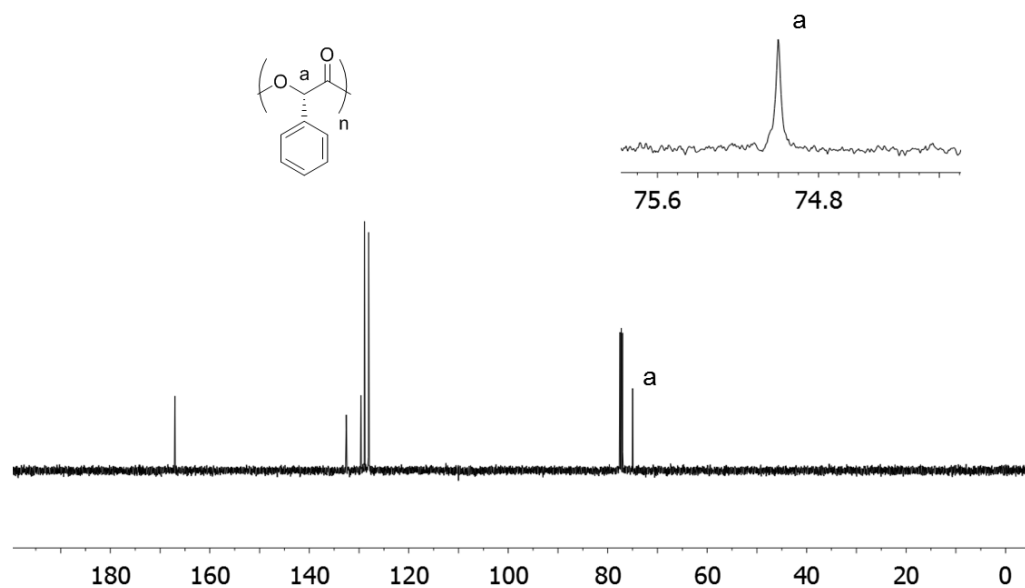


Figure S13. ^{13}C NMR spectrum of poly(ManOCA) prepared with (BDI)Zn-1 (125 MHz, CDCl_3).

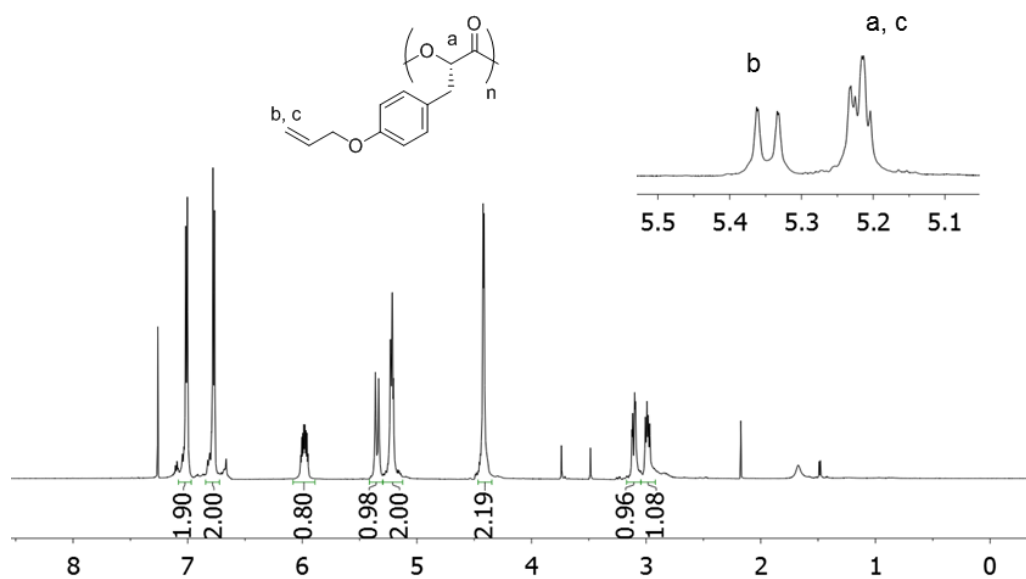


Figure S14. ^1H NMR spectrum of poly(Tyr(allyl)OCA) prepared with (BDI)Zn-1 (600 MHz, CDCl_3). (peak at 5.2 ppm is overlapped by a quartet (Ha) and a doublet (Hc))

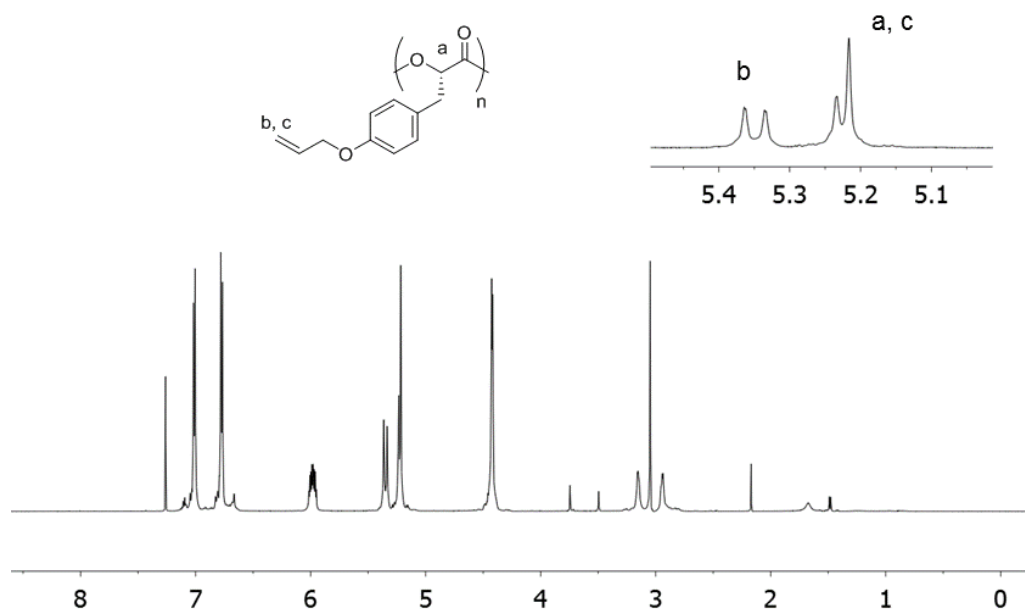


Figure S15. Homonuclear decoupled ^1H NMR spectrum of poly(Tyr(allyl)OCA) prepared with (BDI)Zn-1 (600 MHz, CDCl_3). (peak at 5.2 ppm is overlapped by a singlet (Ha) and a doublet (Hc))

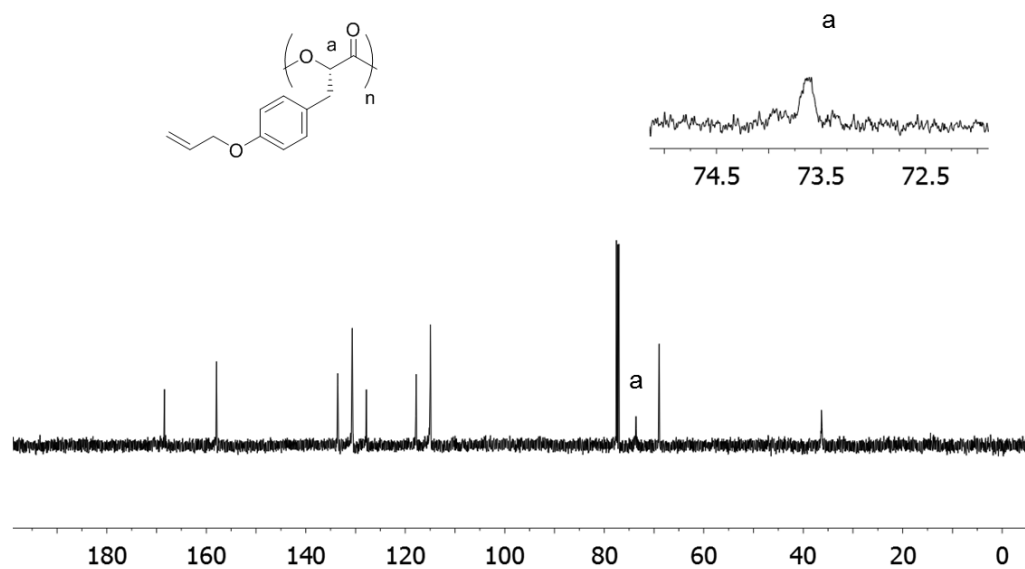


Figure S16. ^{13}C NMR spectrum of poly(Tyr(allyl)OCA) prepared with (BDI)Zn-1 (125 MHz, CDCl_3).

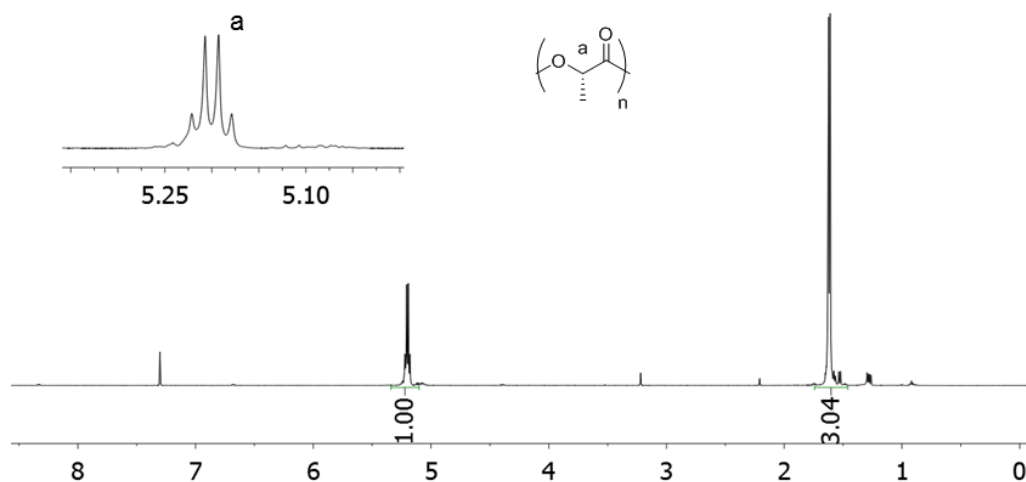


Figure S17. ^1H NMR spectrum of poly(LacOCA) prepared with DMAP/ i PrOH (500 MHz, CDCl_3).

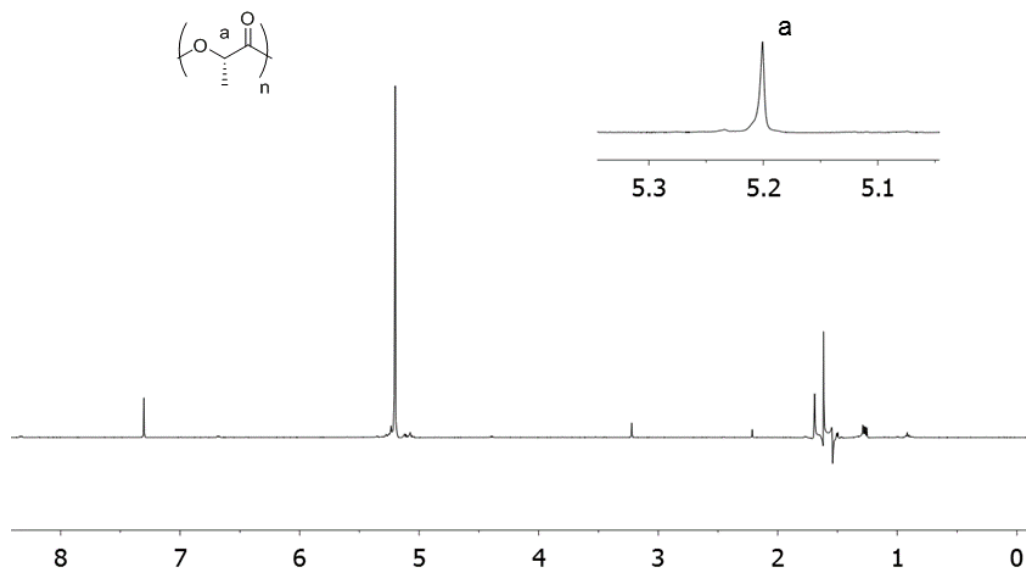


Figure S18. Homonuclear decoupled ^1H NMR spectrum of poly(LacOCA) prepared with DMAP/ i PrOH (500 MHz, CDCl_3).

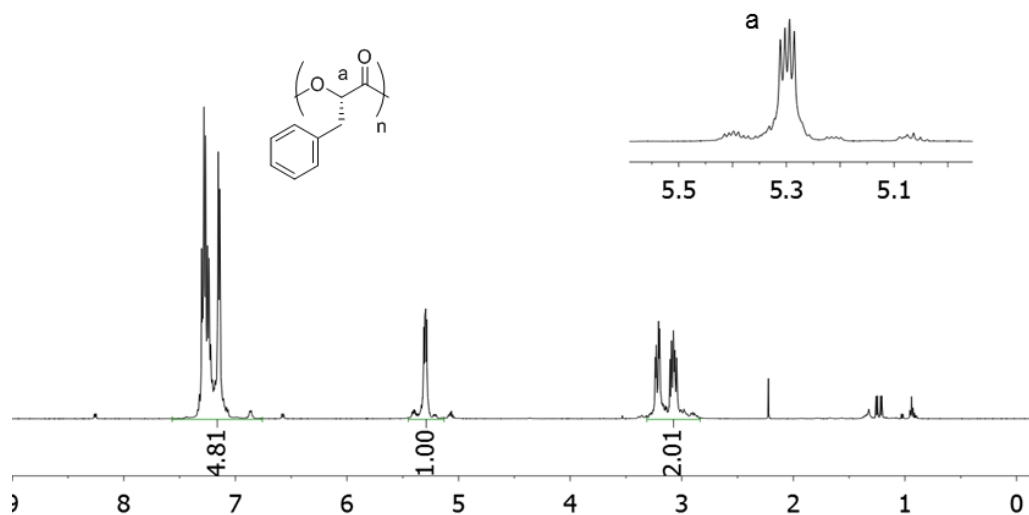


Figure S19. ¹H NMR spectrum of poly(PheOCA) prepared with DMAP/*i*PrOH (500 MHz, CDCl₃).

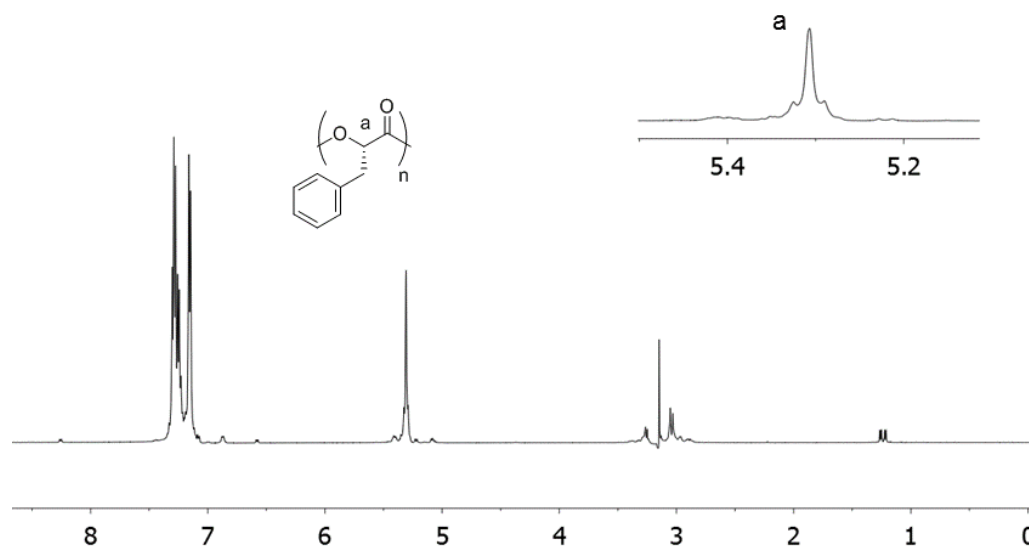


Figure S20. Homonuclear decoupled ¹H NMR spectrum of poly(PheOCA) prepared with DMAP/*i*PrOH (500 MHz, CDCl₃).

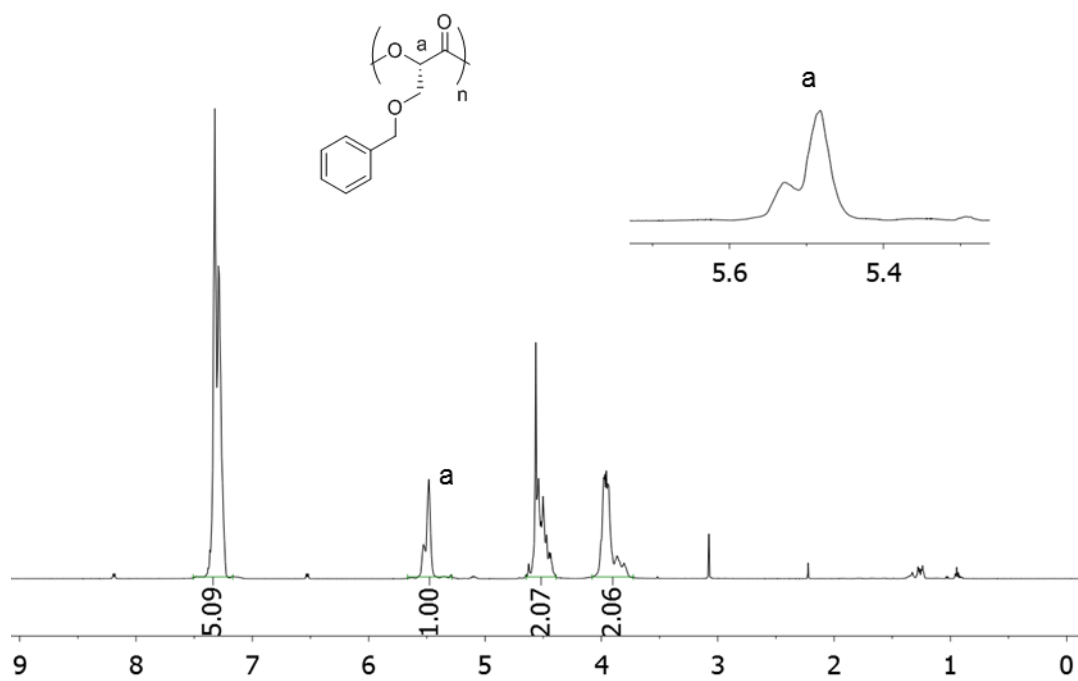


Figure S21. ¹H NMR spectrum of poly(Ser(Bn)OCA) prepared with DMAP/*i*PrOH (500 MHz, CDCl₃).

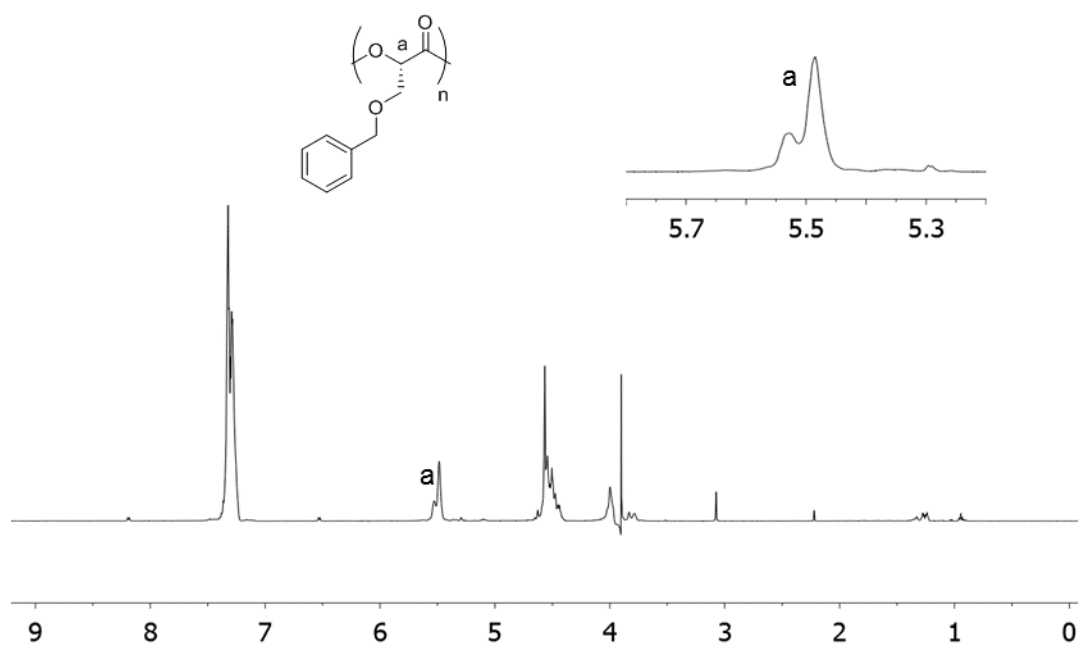


Figure S22. Homonuclear decoupled ¹H NMR spectrum of poly(Ser(Bn)OCA) prepared with DMAP/*i*PrOH (500 MHz, CDCl₃).

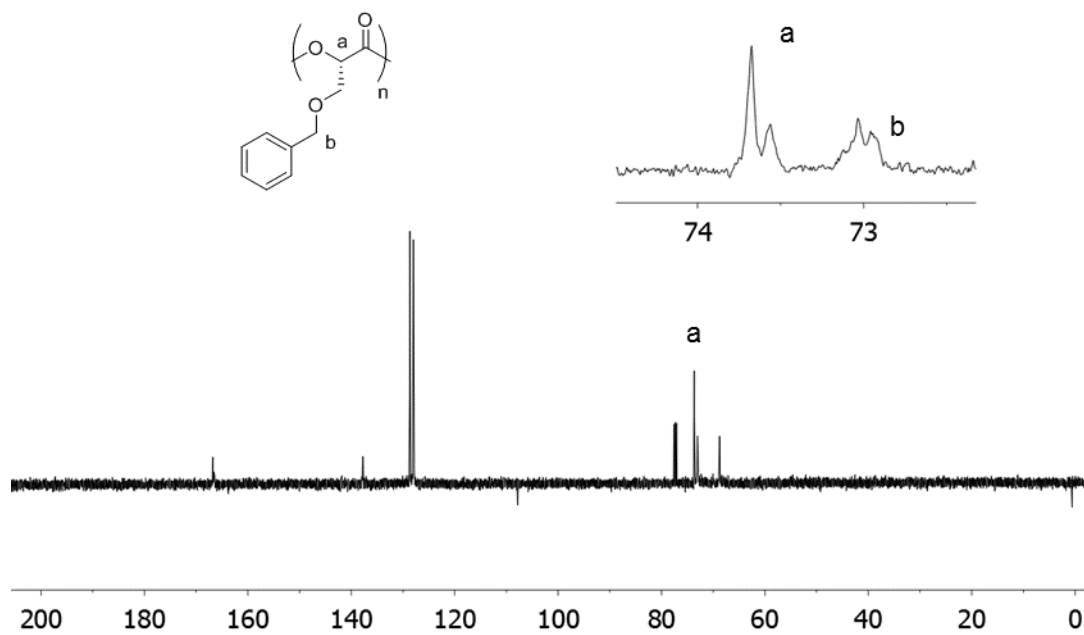


Figure S23. ^{13}C NMR spectrum of poly(Ser(Bn)OCA) prepared with DMAP/*i*PrOH (125 MHz, CDCl_3).

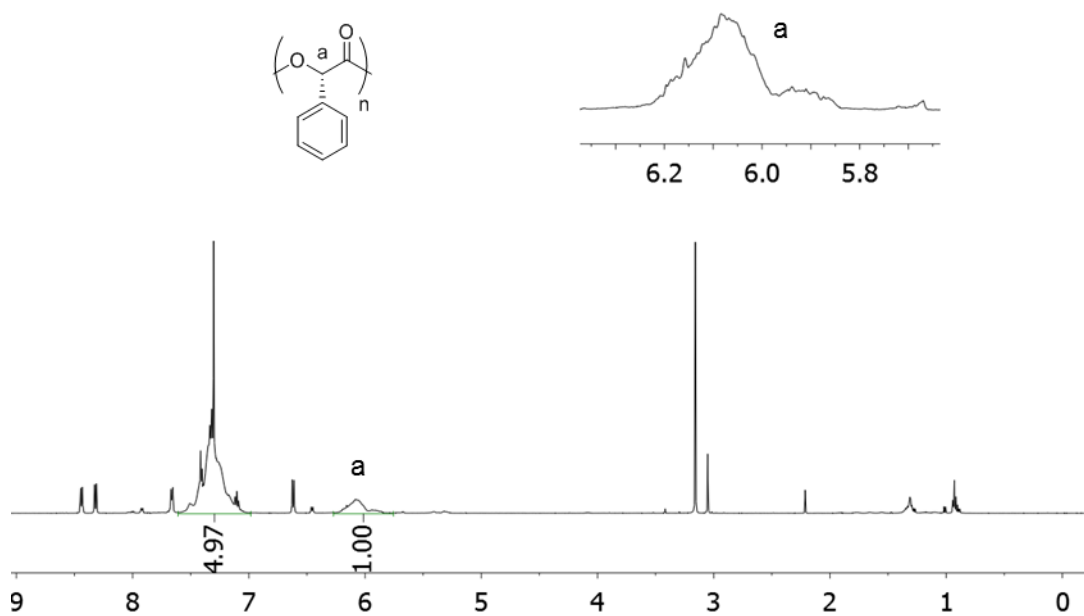


Figure S24. ^1H NMR spectrum of poly(ManOCA) prepared with DMAP/*i*PrOH (500 MHz, CDCl_3).

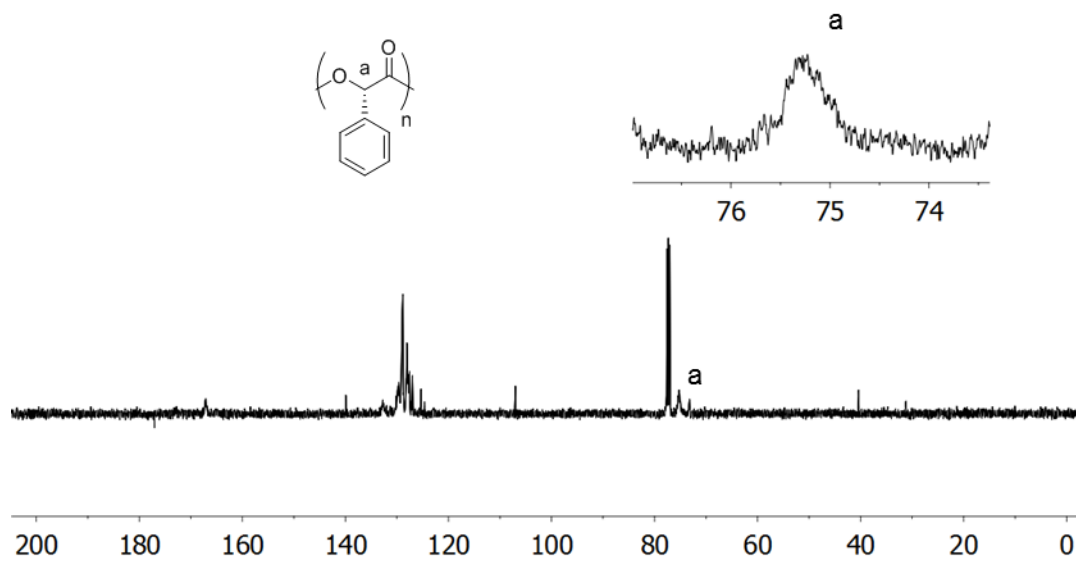


Figure S25. ¹³C NMR spectrum of poly(ManOCA) prepared with DMAP/*i*PrOH (125 MHz, CDCl₃).

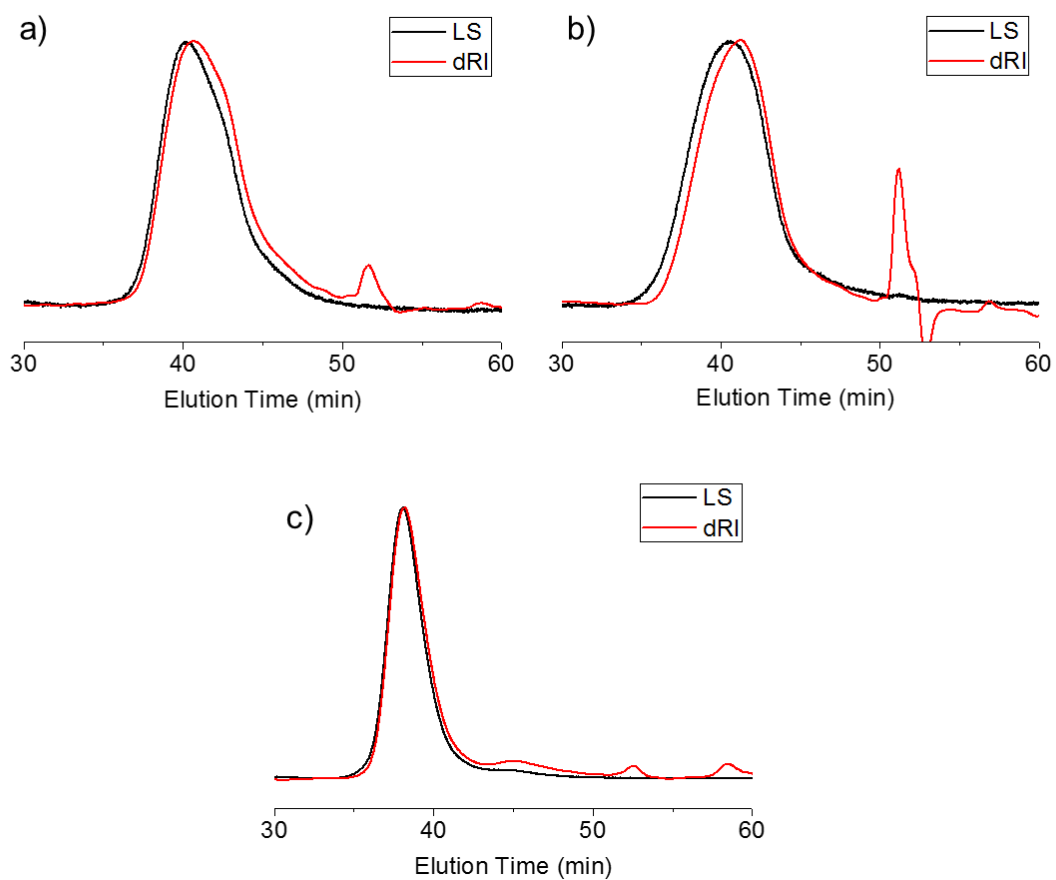


Figure S26. GPC MAL-LS traces and RI traces of block copolymers of OCA and LLA. a) Poly(1-LLA), b) Poly(LLA-b-1), c) Poly(1-b-LLA-b-1). Well overlapping between two traces indicate low PDI value for all polymers.

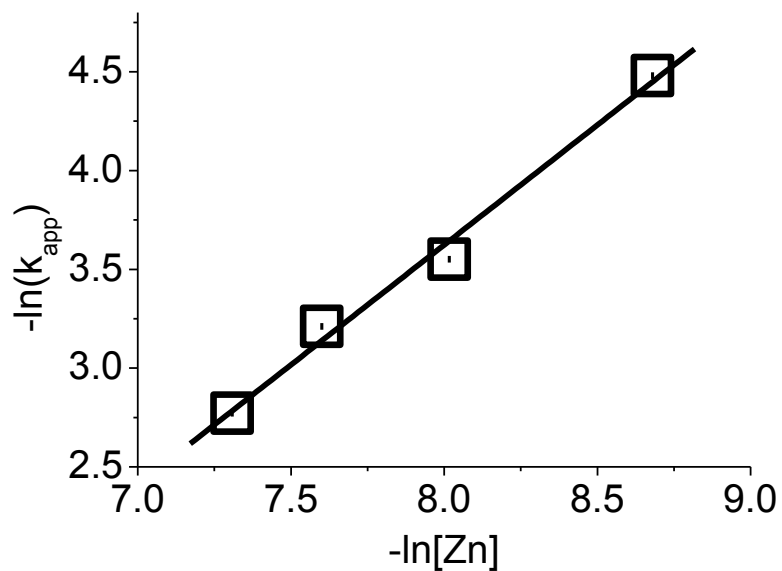


Figure S27. Plot of $-\ln(k_{app})$ versus $-\ln[\text{Zn}]$ for ROP of *L*-PheOCA prepared with (BDI)Zn-1. The reaction order for zinc catalyst is 1.21 from slope of the plot.

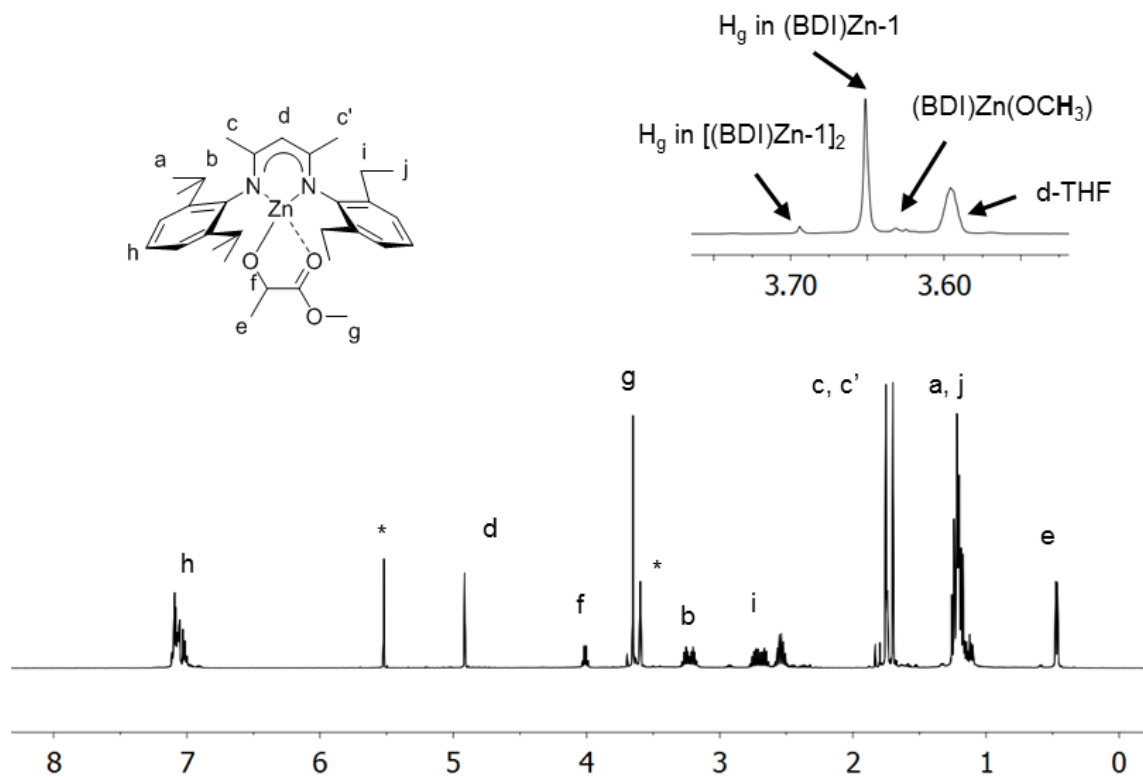


Figure S28. ¹H NMR spectrum of (BDI)Zn-1 (500 MHz, d₈-THF)

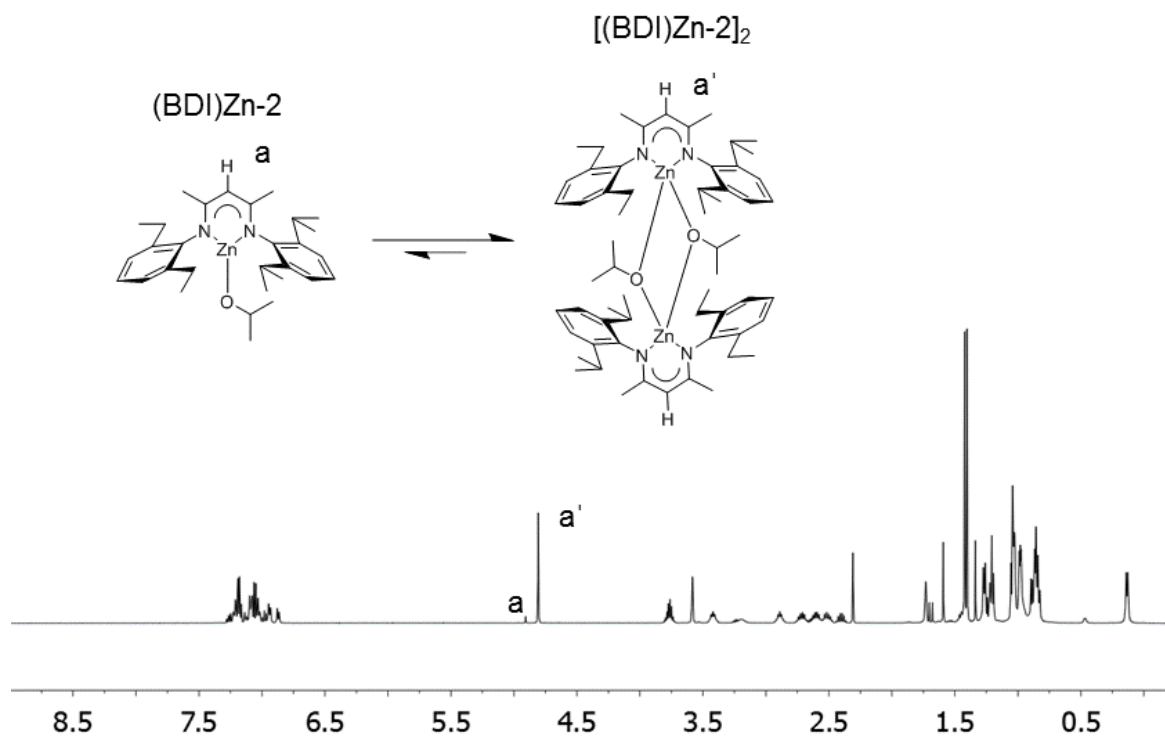
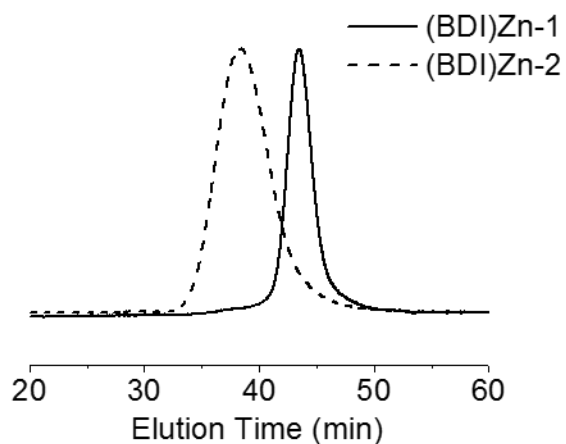


Figure S29. ^1H NMR spectrum of $(\text{BDI})\text{Zn-2}$ (500 MHz, $\text{d}_8\text{-THF}$). Two sets of peaks attributed to dimeric form of $(\text{BDI})\text{Zn-2}$, the ratio of dimeric form and monomeric form calculated from integral of peak a and a'.



Entry	Catalyst	[M]/[I]	Time (h)	% Conv. ^a	M_n (exp.) (kDa) ^b	M_n (cal.) (kDa) ^c	PDI ^b
1	(BDI)Zn-2	50	4	60	-	-	-
2	(BDI)Zn-2	50	24	>98	21.4	7.5	1.33
3	(BDI)Zn-1	50	0.5	>98	8.3	7.5	1.05

^aDetermined by FT-IR measurement of peak intensity at 1812 cm^{-1} correspond to carbonyl groups in OCA rings.

^bDetermined by GPC-RI analysis in DMF (0.1 M LiBr) ^cCalculated according to the feeding ratio of monomer to initiator.

Figure S30. Results of ROP of L-PheOCA prepared with (BDI)Zn-2

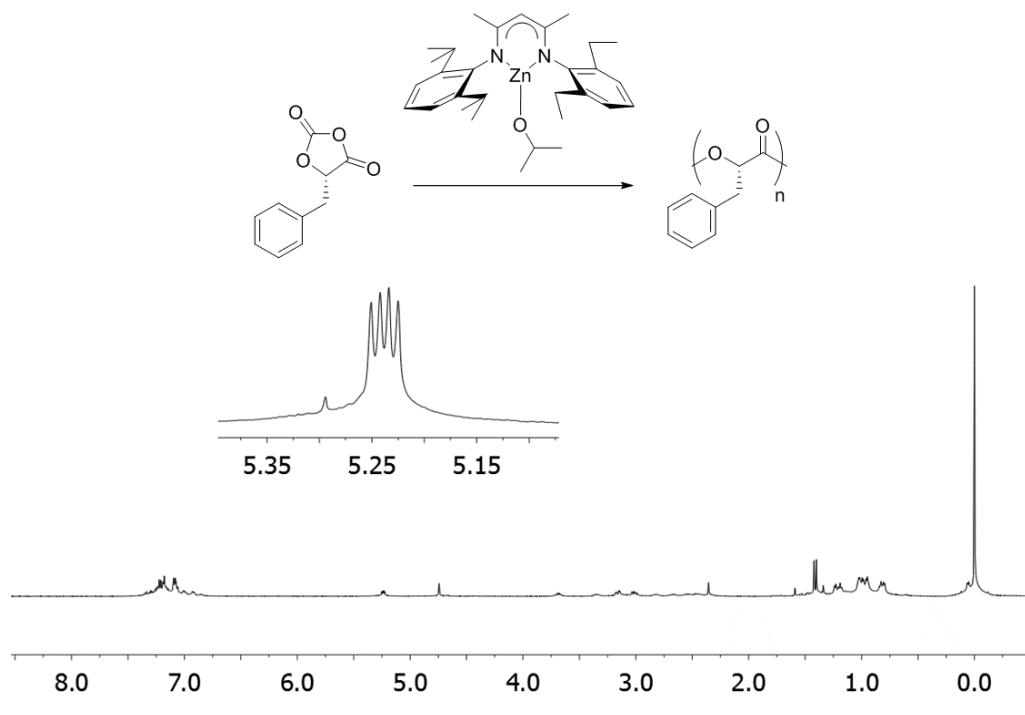


Figure S31. ^1H NMR spectrum of mixing 1:1 equivalent of (BDI)Zn-2 and PheOCA for 4 h (500 MHz, d_8 -THF). The quartet peak at 5.25 ppm indicated long isotactic PAHA formation.

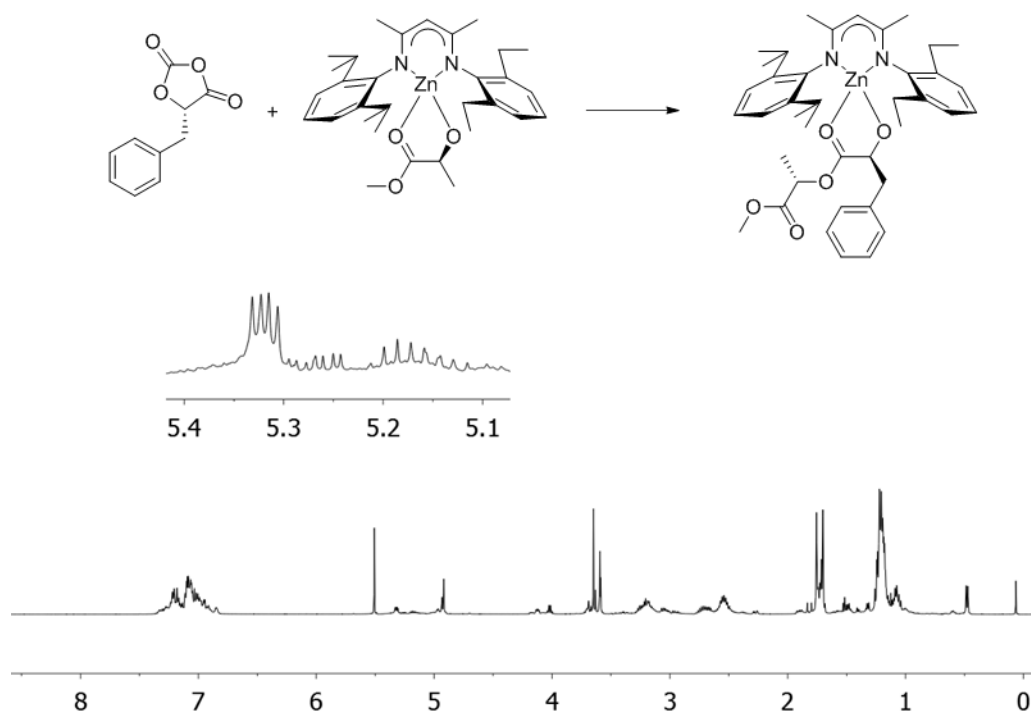


Figure S32. ¹H NMR spectrum of mixing 1:1 equivalent of (BDI)Zn-1 and L-PheOCA for 10 min (500 MHz, d₈-THF).

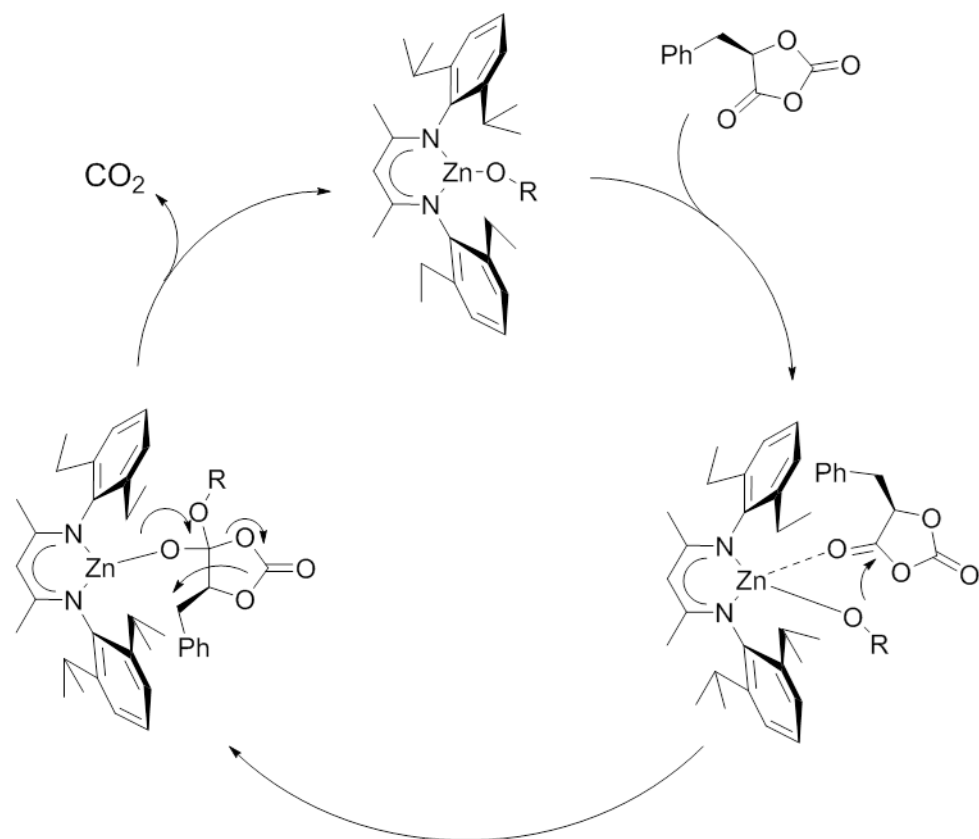


Figure S33. Proposed Mechanism of ROP of OCA prepared with (BDI)Zn

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