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Supplementary Information

Binaphthol-Derived Phosphoric Acid as an Efficient Chiral Organocatalyst for the Enantiomer-Selective Polymerization of *rac*-Lactide

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1. Experimental section

Materials. *rac*-Lactide (*rac*-LA; >98%, Tokyo Kasei Kogyo Co., Ltd. (TCI)), L-lactide (LLA; >98%, TCI), and D-lactide (DLA; >99%, Musashino Chemical Co., Ltd.) were purified by two recrystallizations from dry toluene before use. 3-Phenyl-1-propanol (PPA; >98%, TCI) was distilled over CaH_2 under an argon atmosphere. (*R*)-3,3'-Bis(pentafluorophenyl)-1,1'-binaphtyl-2,2'-diyl-hydrogenphosphate ((*R*)-**1a**) was synthesized via a previously reported technique.[1] (*R*)-3,3'-Bis[3,5-bis(trifluoromethyl)phenyl]-1,1'-binaphtyl-2,2'-diyl-hydrogenphosphate ((*R*)-**1b**; 95%, Sigma Aldrich), (*R*)-3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphtyl-2,2'-diyl-hydrogenphosphate ((*R*)-**1c**; >97.5%, Sigma Aldrich), methyl DL-lactate (>96.0 %, Kanto Chemical Co., Inc.), and a weak base anion exchange resin, Amberlyst A21 (Organo Co., Ltd.) were used as received. Toluene (>99.5 %; water content, <0.001 %, Kanto Chemical Co., Inc.) was distilled over sodium benzophenone ketyl under an argon atmosphere. All other reagents were of synthetic grade and used without further purification.

Instruments. The number-average molecular weight ($M_{n,NMR}$) was determined from the recorded ^1H NMR spectra using a JEOL JNM-A400II instrument. The polymerization was carried out in an MBRAUN stainless steel glove box equipped with a gas purification system (molecular sieves and copper catalyst) and a dry argon atmosphere (H_2O, O_2 <1 ppm). The moisture and oxygen contents in the glove box were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. The size exclusion chromatography (SEC) was performed at 40 °C in $CHCl_3$ (0.8 mL min^{-1}) using a Jasco GPC-900 system equipped with a set of two Shodex KF-805L columns (linear, 8 mm × 300 mm). The polydispersity index (M_w/M_n) of the polymers was calculated on the basis of a polystyrene calibration. The preparative SEC was performed in $CHCl_3$ (3.5 mL min^{-1}) at 23 °C using a JAI LC-9201 equipped with a JAI JAIGEL-3H column (20 mm × 600 mm; exclusion limit, 7×10^4) and a JAI RI-50s refractive index detector.

Polymerization of *rac*-lactide (*rac*-LA) catalyzed by (*R*)-3,3'-bis(pentafluorophenyl)-1,1'-binaphtyl-2,2'-diyl-hydrogenphosphate ((*R*)-1a). A typical procedure for the polymerization is as follows: *rac*-LA (144 mg, 1.0 mmol) and (*R*)-**1a** (13.6 mg, 20.0 μmol) were added to toluene (0.312 mL), then a stock solution of PPA (20.0 μL, 20.0 μmol) was added to initiate the polymerization under an argon atmosphere at 75 °C in an oil bath. After 18 h, the polymerization was quenched by the addition of Amberlyst A21. Before the addition of the Amberlyst A21, we obtained a portion of the polymerization mixtures and then added a small amount of triethylamine to the mixtures for determining the monomer conversion that was directly determined by the ^1H NMR measurements of the polymerization mixtures. The polymer was isolated by preparative SEC (eluent, $CHCl_3$) to remove the remaining residue. Yield, 21.0 %; $M_{n,NMR}$, 3730 g mol^{-1}; $M_{n,SEC}$, 4130 (2400)[2] g mol^{-1}; M_w/M_n, 1.13; ^1H NMR ($CDCl_3$) δ (ppm), 1.57 (*m*, 3H × *n*, $(\text{-C}H_3)_n$), 1.95 (*q*, 2H, *J* = 8.8, $\text{ArCH}_2\text{C}H_2\text{-}$), 2.66 (*t*, 2H, *J* = 8.0, $\text{ArC}H_2\text{-}$), 4.14 (*m*, 2H,$\text{ArCH}_2\text{CH}_2\text{C}H_2\text{-}$), 4.34 (*q*, 1H, *J* = 6.8, $\text{-C}H(\text{CH}_3)\text{OH}$), 5.10-5.23 (*m*, 1H × n-1, , $(\text{-C}H(\text{CH}_3)\text{O-})_{n-1}$), 7.14-7.29 (*m*, 5H, aromatic).

HPLC measurement

For determining of the enantiomer ratio of the unreacted monomer after the polymerization, the recovered materials were measured by chiral HPLC. The quenched compounds were evaporated to remove the solvent, and the unreacted monomer was collected as the hexane/isopropanol = 1/1 soluble part. The HPLC measurement of the unreacted monomer was carried out using hexane/isopropanol (7/3) (column, Chiralpak IA (linear, 4.6 mm × 250 mm); flow, 0.5 mL min^{-1}) and the enantiomeric excess (*ee*) of the unreacted monomer was determined from the ratio of the peak areas, as shown in Fig. 1. The selectivity factor (k_D/k_L) was determined by $k_D/k_L = \{\ln[(1\text{-conv.})(1\text{-}ee)]\}/\{\ln[(1\text{-conv.})(1+ee)]\}$.

2. Detailed polymerization results at 75°C

Table S1 listed the data of samples obtained at 75°C. The polymer produced through high enantiomer-selectivity (*ee* of 80.6, run 3) was highly isotactic polylactide with P_m of 0.86. For runs 8 and 10, P_m values decreased with the decreasing *ee*.

Table S1. Enantiomer-selective Ring-opening Polymerization of *rac*-Lactide using (*R*)-**1** as Organocatalyst [a]

run	catalyst	conv. (%) [b]	$M_{n,calcd}$ (g mol^{-1}) [c]	$M_{n,NMR}$ (g mol^{-1}) [b]	M_w/M_n [d]	*ee* (%) [e]	k_D/k_L [f]	P_m [g]
3	(*R*)-**1a**	49.0	3670	3730	1.13	80.6	28.3	0.86
8	(*R*)-**1b**	45.7	3430	3310	1.16	62.3	12.6	0.78
10	(*R*)-**1c**	56.1	4180	3660	1.06	0.09	1.00	0.48

[a] Solvent, toluene; time, 18 h; temperature, 75 °C; initiator (I), 3-phenyl-1-propanol (PPA); $[rac\text{-LA}]_0/[\text{PPA}]_0/[\text{cat.}]_0$, 50/1/1; $[rac\text{-LA}]_0$, 3.0 mol L^{-1}. [b] Determined by ^{1}H NMR in CDCl_3. [c] Calculated from ($[rac\text{-LA}]_0/[\text{PPA}]_0$) × conv. × (M.W. of *rac*-LA) + (M.W. of PPA). [d] Determined by SEC in CHCl_3 using PSt standards. [e] Enantiomeric excess of unreacted monomer measured by chiral HPLC. [f] Calculated from $\{\ln[(1\text{-conv.})(1\text{-}ee)]\}/\{\ln[(1\text{-conv.})(1+ee)]\}$. [g] P_m was equated from the methie region of ^{13}C NMR spectra (ref 3).

3. Determination of polymerization mechanism

In contrast to DLA with (*R*)-**1a** (Fig. 2), the carbonyl carbon of LLA in the presence of (*R*)-**1a** shifted upfield in the ^{13}C NMR spectrum of Fig. S1a, which implied that the carbonyl group was deactivated whereas the deactivating mechanism was indeterminable. The result was also supported by the IR spectrum in Fig. S1b.

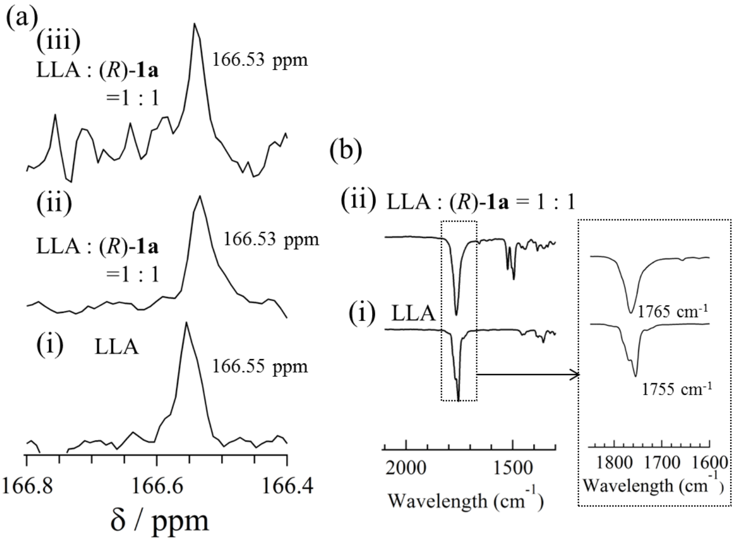

Fig. S1. (a) ^{13}C NMR spectra at 75°C in toluene-d$_8$ and (b) IR spectra of the carbonyl carbon signals of (i) LLA, (ii) a 1:1 mixture of LLA and (*R*)-**1a**, and (iii) 1:3 mixture of LLA and (*R*)-**1a**.

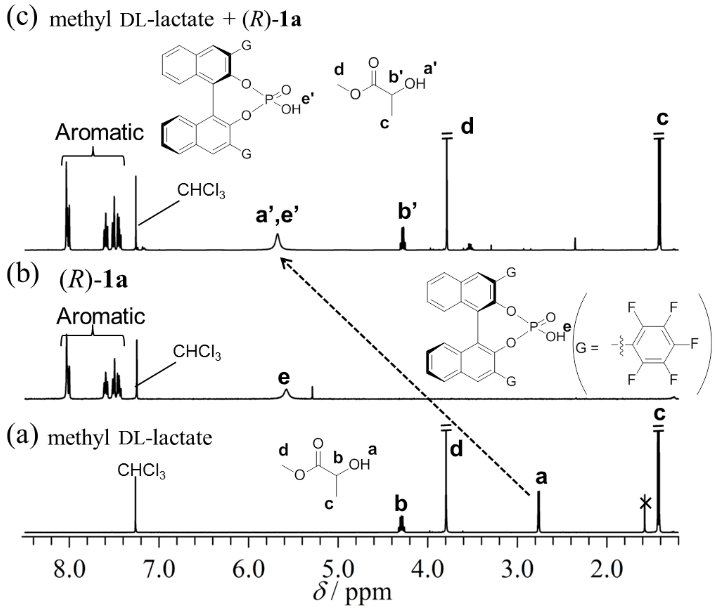

Fig. S2. ^{1}H NMR spectra of the hydroxyl proton signals for (a) methyl DL-lactate, (b) (*R*)-**1a**, and (c) the 1:1 mixture of methyl DL-lactate with (*R*)-**1a** in CDCl$_3$.

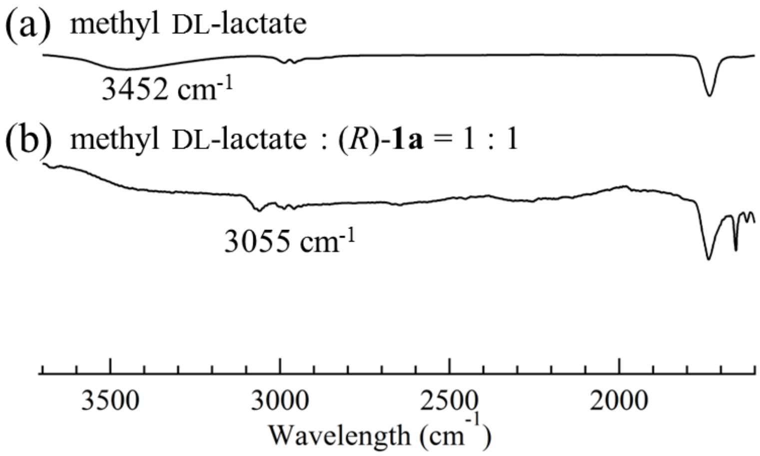

Fig. S3. IR spectra of (a) methyl DL-lactate and (b) a 1:1 mixture of methyl DL-lactate and (*R*)-**1a**.

4. Characterization of the obtained polylactide

For determining the chemical structure of the obtained polymer (Table 1, run 3), we measured the ^{1}H and ^{13}C NMR spectra (Fig. S4). For the ^{1}H NMR measurement, the characteristic peaks due to the polymer main chain were clearly observed at 5.10 to 5.23 and 1.57 ppm and those of chain-end were observed at 7.14 to 7.29, 4.34, 4.14, 2.66, and 1.95 ppm, respectively, which supported the fact that the chemical structure of the obtained polymer was assigned to the polylactide (PLA). Additionally, the ^{13}C NMR spectrum also revealed the exact structure and showed isotactic enrichment of the PLA (P_m up to 0.93),[3] which was elucidated by the *mrm* tetrad peak of the methine region, as shown in Fig. S6. This result suggested that the obtained polymer was mainly composed of DLA. Size exclusion chromatography (SEC) of the obtained polymers showed monomodal shapes with the narrow polydispersity index of 1.13 (Fig. S7). More importantly, the number-average molecular weight ($M_{n,NMR}$) of the obtained polymer fairly well agreed with the calculated value ($M_{n,calcd}$); the $M_{n,NMR}$ and $M_{n,calcd}$ values were 3730 g mol^{-1} and 3670 g mol^{-1}, respectively. These results strongly suggested that the polymerization proceeded with not only an enantiomer-selective, but also controlled/living fashion.

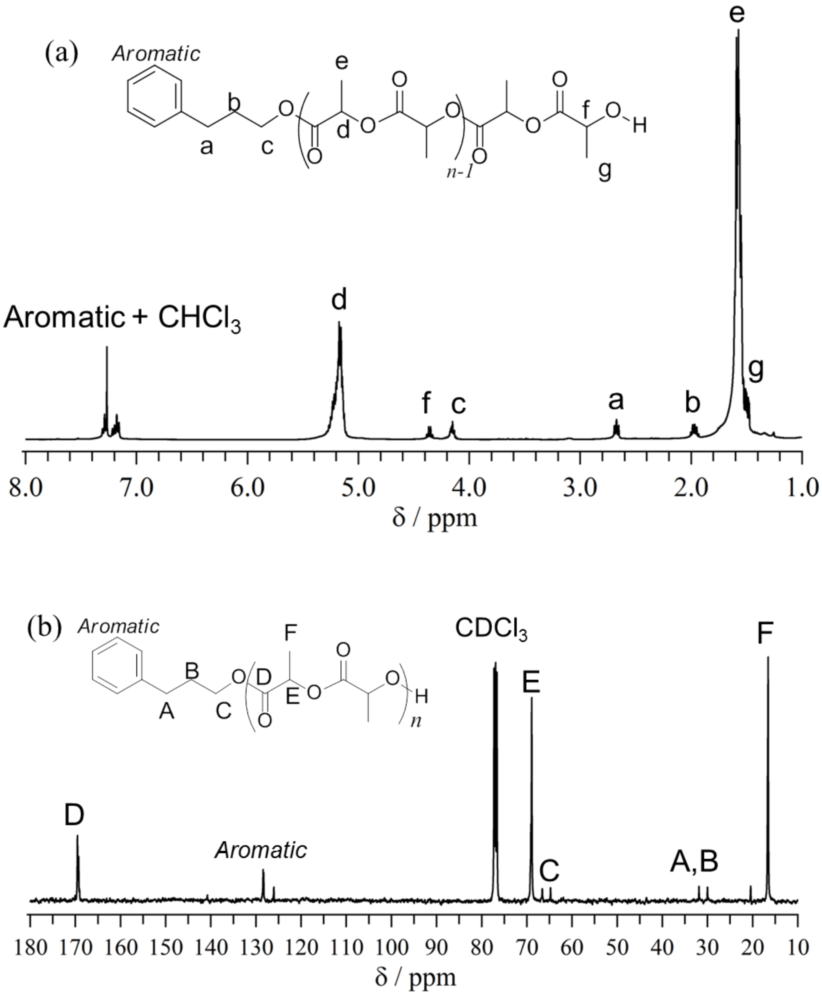

Fig. S4. (a) ^{1}H and (b) ^{13}C NMR spectrum of the obtained PLA (Table 1, run 3) ($CDCl_3$).

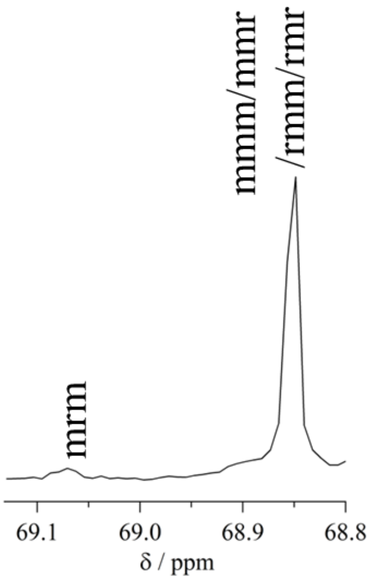

Fig. S5. Methine region of ^{13}C NMR spectrum of the obtained polylactide prepared with [*rac*-LA]$_0$/[PPA]$_0$ = 50 at 75 °C (conv., 37.1%; P_m, 0.93) (100 MHz, $CDCl_3$).

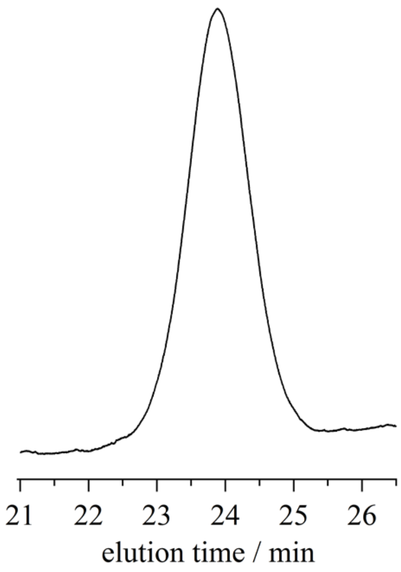

Fig. S6. SEC trace of the obtained polylactide (Table 1, run 3) (eluent, $CHCl_3$; flow rate, 0.8 mL min^{-1}).

4. Reference and Note

1. N. Momiyama, H. Nishimoto, and M. Terada, *Org. Lett.,* **2011**, *13*, 2126-2129.

2. $M_{n,SEC}$ was corrected using correction factor. See the following article; J.-C. Wu, B.-H. Huang, M.-L. Hsueh, S.-L. Lai, and C.-C. Lin, *Polymer* **2005**, *46*, 9784-9792.

3. The probability of meso linkage (P_m) was equated from the methie region of ^{13}C NMR spectrum: [*mmm*] = $P_m(P_m+1)/2$; [*mmr*] = $P_m(1- P_m)/2$; [*rmm*] = P_m $(1-P_m)/2$; [*rmr*] = $(1-P_m)2/2$; [*mrm*] = $(1-P_m)/2$.