Synthesis and Enantioselectivities of Soluble Polymers Incorporating Optically Active Binaphthyl and Binaphthol

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ABSTRACT: A polymer (**P-1**) was synthesized through the polymerization of (*S*)-6,6′-dibromo-3,3′-dibutyl-1,1′-binaphthol with (*S*)-2,2′-dioctoxy-1,1′-binaphthyl-6,6′-boronic acid in a Pd-catalyzed Suzuki reaction, and another polymer (**P-2**) was synthesized through the polymerization of (*S*)-6,6′-dibromo-3,3′-dibutyl-1,1′-binaphthol with (*S*)-6,6′-diethynyl-2,2′-dioctoxy-1,1′-binaphthyl in a Pd-catalyzed Sonogashira reaction. The two polymers showed good solubility in some common solvents and were characterized with NMR, Fourier transform infrared, gel permeation chromatography, and circular dichroism spectroscopy. The application of the chiral monomers and polymers in the asymmetric addition of diethyl zinc to benzaldehyde was studied. The results indicated that **P-1**, **P-2**, and the monomer (*S*)-3,3′-dibutyl-1,1′-binaphthol were efficient ligands in the asymmetric addition of diethyl zinc to benzaldehyde. The chiral polymer ligands **P-1** and **P-2** were more efficient than their monomeric version, (*S*)-3,3′-dibutyl-1,1′-binaphthol, and could be easily recovered and reused without a loss of catalytic activity or enantioselectivity. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 821–827, 2007

Key words: molecular recognition; self-assembly; structure-property relations; synthesis

INTRODUCTION

Optically active 1,1′-bi-2-naphthol (BINOL) and its derivatives have attracted particular interest because their versatile backbones can be modified.[1–4] Although BINOL was reported early in 1926, its application for asymmetric reaction catalysis was first recognized in 1979 by Noyori in the reduction of aromatic ketones and aldehydes.[5,6] BINOL itself does not always produce satisfactory results in asymmetric catalytic reactions. Since Noyori's discovery, there has been ongoing research on modified BINOL ligands. The outcome of a given asymmetric transformation depends on both the steric and electronic properties of the chiral ligand. Therefore, the strategic placement of substituents within the framework of a given BINOL derivative may lead to improved catalysts. In the past 10 years, Pu and coworkers[7–9] further investigated the design and synthesis of a series of novel binaphthyl-based chiral conjugated polymers used as Lewis acids to carry out highly enantioselective organic reactions, such as the additions of aldehydes, hetero Diels–Alder reactions, 1,3-dipolar cycloadditions, and reductions of ketones.[7–9] These rigid and sterically chiral polybinaphthyl polymers also represent a new generation of materials for applications in asymmetric catalysis, chiral sensors, polarized light emissions, and nonlinear optical materials.[2,10,11]

Chiral polybinaphthyls and polybinaphthols are often used to coordinate with metal centers such as Al(III), Ti(IV), Zn(II), and Ln(III) to generate highly enantioselective Lewis acid catalysts for many asymmetric organic transformations.[3,4,12–14] Polymer-bound or polymerized asymmetric catalysts have been the focus of many researchers for the recovery and reuse of expensive chiral catalysts in recent years, and BINOL has been one of the most widely studied.[15–17] The use of soluble chiral polymer catalysts in asymmetric synthesis has important practical advantages. Chiral polymers used as asymmetric synthesis catalysts can be employed in a homogeneous manner and thus may have catalytic activity and stereoselectivity similar to those of the homogeneous parent system. When the reaction is completed, the polymeric reagents or catalysts can be easily separated from the reaction mixture by simple filtration or precipitation with the addition of a nonsolvent. In addition, the recycling and recovery of chiral catalysts is particularly important because it is often quite expensive to obtain these optically pure materials. Traditionally, polymeric chiral catalysts are prepared by the anchoring of a chiral ligand to a flexible and sterically irregular achiral polymer back-

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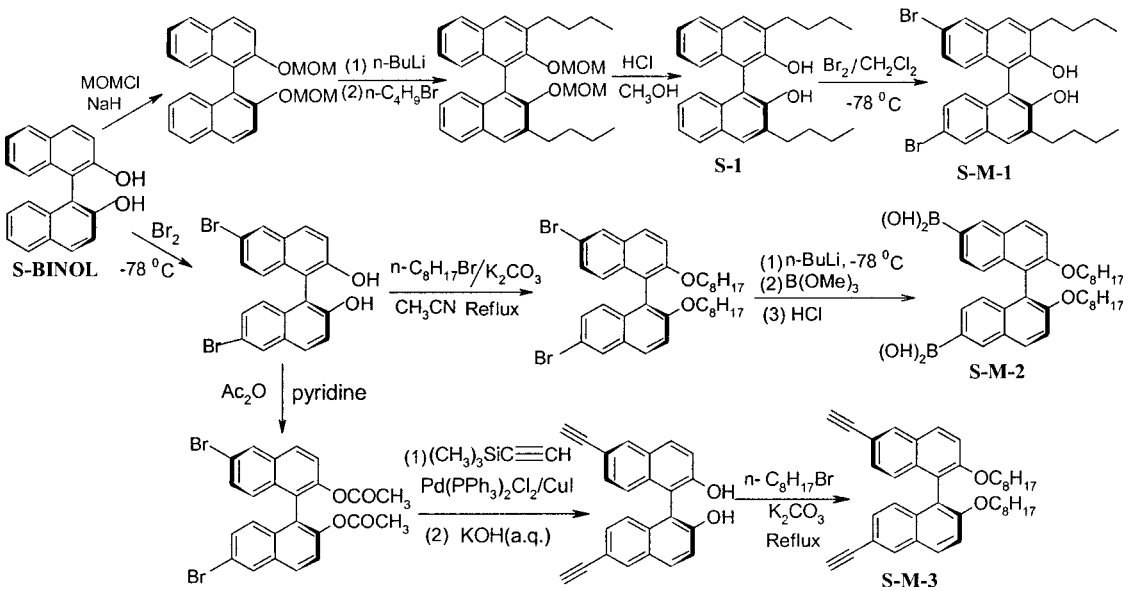
bone.[18–21] It has been generally observed that polymer-supported chiral catalysts are usually less efficient than their monomeric versions, and this indicates that the microenvironment of the catalytic sites in the polymers is very important for their effectiveness in steric control. The flexible and sterically irregular polymer backbone of traditional polymeric chiral catalysts generates randomly oriented catalytic sites that cannot be systematically modified to achieve the desired catalytic active center or stereoselectivity.

In this article, we report preliminary results for the synthesis and asymmetric enantioselective addition of two soluble polymers substituted on the 6,6′-positions of (*S*)-3,3′-dibutyl-1,1′-binaphthol (**S-1**) by Pd-catalyzed Suzuki and Sonogashira cross-coupling reactions. The chiral units **S-1** and (*S*)-2,2′-dioctoxy-1,1′-binaphthyl (**S-2**) were alternatively organized in a regular chiral polymer chain. The key feature of this kind of bifunctional ligand is that octoxy and butyl group substituents on the binaphthyl and binaphthol as side chains of the polymers can greatly improve the solubility in organic solvents so that the asymmetric addition reaction of diethyl zinc to benzaldehyde can be carried out in a homogeneous solution. When these two chiral polymers (**P-1** and **P-2**) were used to catalyze diethyl zinc addition to benzaldehyde, they produced 1-phenylpropanol with 90 and 83% enantiomeric excess (ee), and the recovered polymers also exhibited similar catalytic activity and enantioselectivity.

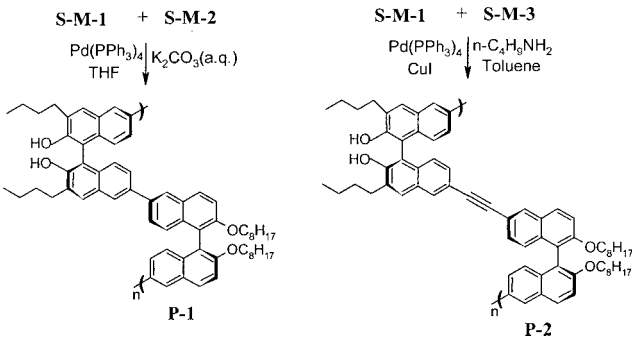
RESULTS AND DISCUSSION

Syntheses and features of the monomers and polymers

S-1, **S-2**, (*S*)-6,6′-dibromo-3,3′-dibutyl-1,1′-binaphthol (**S-M-1**), (*S*)-2,2′-dioctoxy-1,1′-binaphthyl-6,6′-boronic acid (**S-M-2**), and (*S*)-6,6′-diethynyl-2,2′-dioctoxy-1,1′-binaphthyl (**S-M-3**) were synthesized from the starting product (*S*)-BINOL (Scheme 1). **S-M-1** was prepared in an overall yield of 46% by a four-step synthesis. The hydroxyl groups were first protected by a reaction with methoxymethyl chloride according to the literature,[22,23] **S-1** was obtained through the deprotection of methoxymethyl groups of (*S*)-3,3′-dibutyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl, which was synthesized through the reaction of (*S*)-2,2′-bis (methoxymethoxy)-1,1′-binaphthyl with *n*-butyllithium (*n*-BuLi) at room temperature under N_2 and followed by the addition of *n*-butyl bromide at 0°C. The etherification of hydroxyl groups of **S-2** could be carried out through a reaction with *n*-octyl bromide in the presence of K_2CO_3 in a refluxing CH_3CN solution.[24–26] **S-M-2** was synthesized according to the literature,[27,28] and **S-M-3** was synthesized according to the literature.[29,30] **S-M-1**, **S-M-2**, and **S-M-3** could serve as the monomers for the synthesis of the desired chiral polymers. They could also be used as the starting materials or building blocks for preparing the novel chiral catalysts. In this article, chiral polymer ligand **P-1** was synthesized with **S-M-1** and **S-M-2** in a Pd-catalyzed Suzuki reaction.[31–33] **P-2** was obtained with **S-M-1** and **S-M-3** in a Pd-catalyzed Sonogashira reaction (Scheme 2).[34–36] The C—C cross-coupling process of **P-1** between **S-M-1** and **S-M-2** was easily carried out in tetrahydrofuran (THF) and an aqueous K_2CO_3 solution in the presence of a catalytic amount (5 mol %) of $Pd(PPh_3)_4$ at 85°C under the protection of an N_2 atmosphere. The cross-coupling process of **P-2** between **S-M-1** and **S-M-3** was carried out in toluene and an *n*-butylamine solution in the presence of a catalytic amount (5 mol %) of $Pd(PPh_3)_4$ and CuI (20 mol %) at 110°C under the protection of an N_2



Scheme 1 Synthesis procedures of **S-1, S-M-1, S-M-2,** and **S-M-3.**



Scheme 2 Synthesis procedures of **P-1** and **P-2.**

atmosphere. CuI was used as a cocatalyst and can play an important role in Sonogashira coupling reactions because of the poor activity of aryl bromide for polymerization.[34,36] The polymers showed good solubility in some common solvents such as THF, CH_2Cl_2, $CHCl_3$, toluene, and DMF, and this could be attributed to the nonplanarity of the twisted polymers in the main-chain backbone and the flexible octoxy and butyl group substituents on binaphthyl and binaphthol units as side chains of the polymers. The two soluble polymers were air-stable brown solids. The gel permeation chromatography (GPC) results for the two polymers showed moderate molecular weights. The GPC analysis and specific rotation results for the two polymers are listed in Table I. According to Kobayashi's previous investigations designed to examine the catalyst–substrate interaction, including the reaction course, and to improve the selectivities, the results indicated that the substituents on the 3,3′-positions of the BINOL ligand greatly influenced the enantioselectivities.[37–39] In this study, considering the microenvironment of the catalytic active sites of the Ti(IV) Lewis acid for their effectiveness in steric control and the electronic properties of the chiral polymer ligands, we introduced an *n*-butyl group into the 3,3′-position of binaphthol. Generally, soluble polymer ligands can produce higher catalytic activity and enantioselectivity than insoluble polybinaphthol catalysts because of the homogeneous asymmetric reaction.[14,40–42] The recovered and reused ligands (**P-1** and **P-2**) could still show similar enantioselectivity and reactivity (entries 7 and 9).

Circular dichroism (CD) spectra

Specific rotation ($[\alpha]_D^{20}$) data for **P-1** and **P-2** in CH_2Cl_2 are listed in Table I. Although the specific rotation values of the repeating units **S-1**, **S-2**, and **S-M-3** were −56.8 (concentration = 0.2, CH_2Cl_2), −62.6 (concentration = 0.3, CH_2Cl_2), and +10.5 (concentration = 0.5, CH_2Cl_2), those for **P-1** and **P-2** (concentration = 0.1, CH_2Cl_2) were +103.3 and +202.5, respectively. The absolute values of $[\alpha]_D^{20}$ for the two polymers were larger than those of their corresponding monomers and the chiral center units. **P-1** and **P-2** exhibited intense CD signals with negative and positive Cotton effects in their CD spectra (Table II and Fig. 1). The major differences in the CD spectra of **P-1** and **P-2** were from the split of ^1B_b in **P-2**, even though their molar ellipticity values were nearly of the same magnitude. ^1B_b and ^1L_a bands of **P-1** appeared around 237 and 275 nm. The split peaks of the ^1B_b band of **P-2** appeared at 226 and 237 nm with the reversed signal.

Asymmetric addition of diethyl zinc to benzaldehyde

The asymmetric enantioselective addition reactions of diethyl zinc to benzaldehyde were carried out with **S-1, P-1**, and **P-2** in THF, CH_2Cl_2, and toluene, respectively.[9,14,43–45] The reactions were conducted at 20°C with benzaldehyde, chiral ligands, $Ti(O^iPr)_4$, and Et_2Zn with a molar ratio of 1.0:0.05:1.2:4. The two polymers showed good solubility in common organic solvents such as THF, CH_2Cl_2, and toluene, but they quantitatively precipitated upon the addition of methanol (MeOH). The different solubilities provided a convenient and reliable method for the characterization and recycling of the chiral polymeric ligands. To evaluate the efficiency of these chiral ligands for asymmetric enantioselectivity, the addition reaction of diethyl zinc to benzaldehyde was chosen as a model reaction, and THF, CH_2Cl_2, and toluene were selected as solvents for this type of reaction. All the enantioselective data are summarized in Table III. The results showed that 10 mol % chiral ligands in toluene were best for the asymmetric enantioselective addition reactions of diethyl zinc to benzaldehyde. In this study, when chiral polymeric ligands **P-1** and **P-2** were used as the catalysts, higher ee values were obtained than those of the corresponding monomer **S-M-1** (entries 6 and 8). When the recycled chiral polymer ligands were reused for the reaction catalyst, the results showed similar enantioselectivities (entries 7 and 9). The results showed that 95% ee and an 85% yield could be obtained when recycled **P-2** was used

TABLE I
Polymerization Results and Characterization of P-1 and P-2

	Yield (%)	M_w[a]	M_n[a]	PDI[a]	$[\alpha]_D$[b]
P-1	51	10,700	4,640	2.31	+103.3
P-2	58	13,300	6,200	2.15	+202.5

[a] The weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI) values of **P-1** and **P-2** were determined by GPC with polystyrene standards in THF.

[b] At 20°C with CH_2Cl_2 as the solvent (concentration = 0.1).

TABLE II
CD Spectroscopy Data of S-1, S-M-3, S-2, P-1, and P-2 (in CH_2Cl_2)

	S-1 ($\times 10^5$)	**S-M-3** ($\times 10^5$)	**S-2** ($\times 10^5$)	**P-1** ($\times 10^5$)	**P-2** ($\times 10^5$)
[θ]	−4.16 (227.0 nm)	−9.79 (243.4 nm)	−4.74 (228.0 nm)	−4.20 (236.5 nm)	−8.34 (226.2 nm)
(α_{max})	+5.47 (239.7 nm)	+14.3 (259.4 nm)	+6.72 (240.1 nm)	+4.64 (274.9 nm)	+4.61 (236.7 nm)
		−0.95 (310.9 nm)			+1.64 (279.6 nm)

θ, molar ellipticity values of CD signal; α_{max}, maximal wavelength of CD signal.

as a catalyst ligand for the addition reaction of diethyl zinc to benzaldehyde at 20°C in toluene. Pu and coworkers[14,46] reported a chiral polybinaphthol as a catalyst for the addition reaction of diethyl zinc with benzaldehyde to afford 1-phenylpropanol at room temperature in CH_2Cl_2, but only 13% ee could be produced. In addition, a significant amount of the side product, benzyl alcohol, was also observed. Because poly(1,1′-bi-2-naphthol) was insoluble in the reaction solvent, Pu and coworkers prepared the soluble binaphthyl polymer containing the enantiomeric binaphthyl units and flexible hexyloxyl groups at the 6,6′-positions. When this polymer was used to catalyze the diethyl zinc addition to benzaldehyde, it produced 1-phenylpropanol with 40% ee. Pu and coworkers designed another kind of polymer through the polymerization of the binaphthyl units at the 3,3′-positions with a phenylene dialkoxy linker. Its steric and electronic environments in the binaphthyl units were different from those of the two polymers.[14,46] The results demonstrated that this kind of chiral ligand at 3,3′-substituents of BINOL could show high enantioselectivity for the reaction of diethyl zinc addition to benzaldehyde (92% ee). However, when a longer rigid phenylene linker was incorporated into the chiral polybinaphthol main chain, this kind of ligand exhibited very high enantioselectivity (98% ee).[9]

In this study, when ligands **P-1** and **P-2** were used as catalysts for the addition reaction of diethyl zinc to benzaldehyde at room temperature in toluene, 1-phenylpropanol could be produced with 90 and 83% ee, respectively. The recycled and recovered polymer ligand **P-2** could even produce 95% ee and an 86% yield. Chiral ligands **P-1** and **P-2** could show high enantioselectivity for the addition reaction of diethyl zinc with benzaldehyde. This result could be ascribed to the microenvironment change and steric control around the Lewis acid catalytic sites of Ti(IV) centers, whereas the *n*-butyl group was introduced into the binaphthol unit at the 3,3′-position. In addition, the octoxy and *n*-butyl group substituents on the binaphthyl and binaphthol as side chains of the polymers could greatly improve solubility in the organic solvents, and asymmetry addition could be carried out in the homogeneous solution.

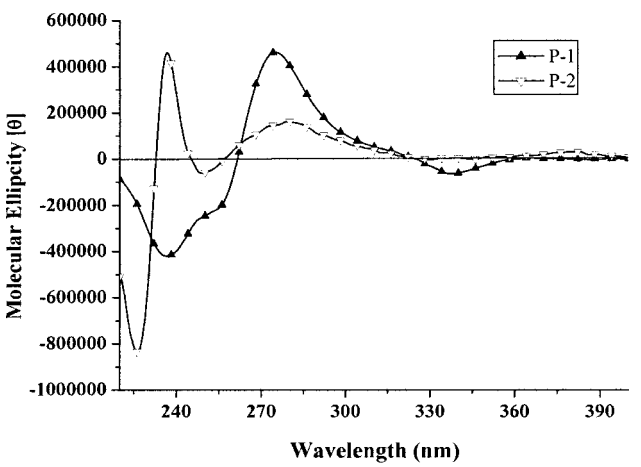
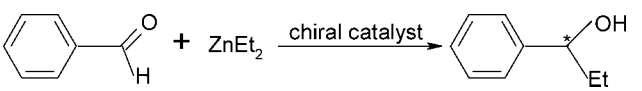


Figure 1 CD spectra of **P-1** and **P-2.**

TABLE III
Reaction of Benzaldehyde with Diethyl Zinc in the Presence of Chiral Polymer Ligands[a]



Entry	Ligand	Solvent	Conversion (%)[b]	ee (%)[c]	Conformation
1	**S-1**	CH_2Cl_2	71	38	*S*
2	**S-1**	THF	75	75	*S*
3	**S-1**	Toluene	94	81	*S*
4[d]	**S-1**	Toluene	88	14	*S*
5[e]	**S-1**	Toluene	95	43	*S*
6	**P-1**	Toluene	82	90	*S*
7[f]	**P-1**	Toluene	85	80	*S*
8	**P-2**	Toluene	81	83	*S*
9[g]	**P-2**	Toluene	86	95	*S*

[a] A benzaldehyde/ligand/$Ti(O^iPr)_4$/$ZnEt_2$ molar ratio of 1.0 : 0.05 : 1.2 : 4 and 10% chiral catalyst were used. The reaction temperature was 20°C, and the reaction time was 36 h.
[b] Isolated yield.
[c] Determined by HPLC on a Chiralcel OD-H column eluted with hexanes/2-propanol (97.5 : 2.5) at 1.0 mL/min and detected at 219 nm.
[d] 5% **S-1** was used.
[e] 20% **S-1** was used.
[f] Recycled **P-1** from entry 6 was used.
[g] Recycled **P-2** from entry 8 was used.

CONCLUSIONS

Pd-catalyzed Suzuki and Sonogashira reactions were found to offer simple access to chiral polymers. The polymers showed good solubility in some common solvents because of the nonplanarity of the twisted polymers in the main-chain backbone and flexible alkyl substituents on naphthyl rings as side chains of the polymers. All the chiral ligands showed good results in the asymmetric enantioselectivities, and chiral polymer catalysts **P-1** and **P-2** were more efficient than their corresponding monomeric version **S-1.** The recycled and recovered polymers also showed similar asymmetric enantioselectivities as before. The results showed that **P-1** and **P-2** were active chiral ligands for the enantioselectivity of diethyl zinc addition to benzaldehyde.

EXPERIMENTAL

General

^{1}H- and ^{13}C-NMR spectroscopy measurements were recorded on a Bruker 300 spectrometer (Bruker, Kleve, Germany) with tetramethylsilane (TMS) as the internal standard. Fourier transform infrared (FTIR) spectra were taken on a Nexus 870 FTIR spectrometer (Nicolet, Madison, WI). CD was determined with a Jasco J-810 spectropolarimeter (Tokyo, Japan). The molecular weight was determined by GPC with a Waters 244 high-performance liquid chromatography (HPLC) pump (Waters Co., Milford, MA), and THF was used as a solvent along with polystyrene standards. The ee determination was carried out with a Perkin Elmer chiral series 200 HPLC apparatus (Boston, MA) with a Chiralpak OD-H column on a Waters chromatograph with a PerkinElmer series 200 ultraviolet–visible detector. All solvents and reagents were commercially available and analytical-reagent-grade. BINOL was purchased from Aldrich (Milwaukee, WI) and used directly without purification. All reactions were performed under N_2 with a Schlenk technique. THF, *n*-butylamine, and toluene were purified by distillation from sodium in the presence of benzophenone. CH_2Cl_2 and CH_3CN were distilled from P_2O_5.

Preparation of S-M-1

Preparation of **S-1**

(*S*)-2,2′-Bis(methoxymethoxy)-1,1′-binaphthyl (3.14 g, 8.4 mmol) was dissolved in dry THF (40 mL) in a 50-mL Schlenk flask under an N_2 atmosphere. To the mixture with stirring was added *n*-BuLi (13.5 mL, 2.2*M* in hexanes, 29.7 mmol) at room temperature by syringe injection. After the reaction mixture was kept stirring for 6 h, *n*-C_4H_9Br (4 mL, 37.3 mmol) was injected into the flask at 0°C and then allowed to warm up to room temperature, and the mixture was stirred overnight. A mixture of MeOH (40 mL) and HCl (60 mL) was added to the solution, and the mixture was stirred at room temperature for 12 h. After the solvent was removed *in vacuo*, the residue was extracted with CH_2Cl_2 (2 × 60 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel with petroleum ether as an eluent. As a colorless, viscous product, **S-1** (2.0 g, 60% yield) was obtained.

$[\alpha]_D^{20} = -56.8$ (concentration = 0.2, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.91 (t, J = 7.3 Hz, 6H), 1.39 (m, 4H), 1.67 (m, 4H), 2.80 (t, J = 7.7 Hz, 4H), 5.03 (s, 2H), 6.99 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 8.1 Hz, 4H), 7.26 (t, J = 7.4 Hz, 2H), 7.72 (d, 2H), 7.75 (d, J = 8.0 Hz, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$): 152.3, 132.5, 132.0, 130.3, 129.9, 128.1, 126.8, 124.4, 124.3, 111.0, 32.3, 31.0, 23.1, 14.5.

Preparation of **S-M-1**

To a CH_2Cl_2 (30 mL) solution of **S-1** (0.7 g, 1.76 mmol) at −78°C was slowly added a CH_2Cl_2 (10 mL) solution of Br_2 (0.2 mL, 3.9 mmol). The mixture was stirred at −78°C for 30 min and then allowed to warm up to room temperature for 12 h. A saturated solution of $NaHSO_3$ (50 mL) was added, and stirring was continued for 2 h. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL). The combined organic layers were washed with saturated brine (2 × 60 mL) and then dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (20:1 v/v petroleum ether/ethyl acetate) to afford **S-M-1** as a light yellow, viscous product (0.9 g, 92% yield).

$[\alpha]_D^{20} = +12.5$ (concentration = 0.1, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.89 (t, J = 7.3 Hz, 6H), 1.40 (m, 4H), 1.66 (m, 4H), 2.79 (t, J = 7.7 Hz, 4H), 5.00 (s, 2H), 6.80 (d, J = 8.9 Hz, 2H), 7.23 (dd, J = 8.9, 1.9 Hz, 4H), 7.63 (s, 2H), 7.91 (d, J = 1.8 Hz, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$): 152.5, 133.4, 131.0, 130.9, 130.2, 129.5, 126.0, 118.2, 110.8, 32.1, 30.9, 23.1, 14.4.

Preparation of **S-M-2**

To a THF (75 mL) solution of (*S*)-6,6′-dibromo-2,2′-dioctoxy-1,1′-binaphthyl (5.7 g, 8.5 mmol) at −78°C was slowly added *n*-BuLi (11.6 mL, 2.2*M* in hexanes, 25.5 mmol). After it was stirred at −78°C for 30 min, the resulting brown solution was cannulated to a solution of $B(OMe)_3$ (4.4 mL, 38.3 mmol) in THF (25 mL). The mixture was then stirred overnight while the temperature was allowed to warm up to room temperature. The reaction was quenched with

2*N* HCl (40 mL) at 0°C and stirred for 3 h. Upon being evaporated to dryness, the residue was extracted with ethyl acetate and washed with aqueous $NaHCO_3$ and water twice. After being dried over anhydrous $MgSO_4$, the crude product was purified by chromatography on silica gel (1:1 v/v petroleum ether/ethyl acetate) to afford pure **S-M-2** as a pale yellow solid (2.05 g, 40.3% yield).

$[\alpha]_D^{20} = -24.0$ (concentration = 0.1, MeOH). ^{1}H-NMR (300 MHz, DMSO): δ 0.81 (t, J = 7.3 Hz, 6H), 1.03–1.21 (m, 24H), 3.33–3.40 (m, 4H), 6.84 (d, J = 8.5 Hz, 2H), 7.54 (t, J = 9.2 Hz, 4H), 7.99 (d, J = 8.9 Hz, 2H), 8.02 (s, 4H), 8.38 (s, 2H).

Preparation of S-M-3

Preparation of (*S*)-6,6′-dibromo-2,2′-diacetyl-1,1′-binaphthyl

To a solution of (*S*)-6,6′-dibromo-1,1′-binaphthol (4.44 g, 10 mmol) in CH_2Cl_2 (60 mL) were added acetic anhydride (4.7 mL, 50 mmol) and pyridine (4.0 mL, 50 mmol). The mixture was stirred at room temperature for 24 h. The mixture was extracted with CH_2Cl_2 (2 × 60 mL) and washed with water twice. The organic layer was dried over anhydrous Na_2SO_4. After the evaporation of organic volatiles, the residue was purified by column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate) to give (*S*)-6,6′-dibromo-2,2′-diacetyl-1,1′-binaphthyl as a light yellow solid (4.23 g, 80% yield).

Preparation of (*S*)-6,6′-diethynyl-1,1′-binaphthol

To a solution of (*S*)-6,6′-dibromo-2,2′-diacetyl-1,1′-binaphthyl (1.59 g, 3 mmol) and $Pd(PPh_3)_2Cl_2$ (213 mg, 0.3 mmol) in benzene (15 mL) and triethyl amine (20 mL) were added trimethyl silyl acetylene (6 mL, 42 mmol) and CuI (115 mg, 0.6 mmol). After refluxing for 48 h, the reaction mixture was cooled to room temperature. The solid was filtered off, and the filtrate was evaporated to dryness. The residue was dissolved in THF (25 mL) and MeOH (25 mL), and this was followed by the addition of a 2*M* aqueous sodium hydroxide solution (6 mL). After stirring for 2 h, the solution was extracted with CH_2Cl_2 (2 × 50 mL) and washed with water twice. The organic layer was dried over anhydrous Na_2SO_4 and was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate) to give (*S*)-6,6′-diethynyl-1,1′-binaphthol as a light yellow solid (0.7 g, 70% yield).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.04 (s, 2H), 5.07 (s, 2H), 6.98 (d, J = 8.7 Hz, 2H), 5.00 (s, 2H), 7.29 (dd, J = 8.7 Hz, 1.6 Hz, 4H), 7.33 (d, J = 9.0 Hz, 2H), 7.80 (d, J = 9.0 Hz, 2H), 7.96 (s, 2H).

Preparation of **S-M-3**

A mixture of (*S*)-6,6′-diethynyl-1,1′-binaphthol (1.1 g, 3.3 mmol), K_2CO_3 (3.3 g, 24 mmol), and n-$C_8H_{17}Br$ (2.4 g, 12.5 mmol) in 50 mL of CH_3CN was refluxed overnight. Upon being evaporated to dryness, the residue was poured into 5% aqueous NaOH (50 mL), and the solution was extracted by petroleum ether (3 × 20 mL). The combined organic layers were washed with saturated brine twice and then dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel with petroleum ether as an eluent. **S-M-3** was obtained as a yellow, viscous product in a 94% yield (1.7 g).

$[\alpha]_D^{20} = +10.5$ (concentration = 0.5, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.81 (m, 5H), 0.99 (m, 6H), 1.15 (m, 2H), 1.31 (m, 2H), 3.00 (s, 2H), 3.86 (m, 2H), 6.99 (d, J = 8.7 Hz, 2H), 7.23 (dd, J = 8.9, 1.9 Hz, 4H), 8.00 (s, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$): 155.8, 134.2, 132.8, 129.6, 129.2, 128.8, 125.8, 120.3, 117.1, 116.3, 84.7, 69.8, 32.1, 29.7, 29.6, 29.5, 26.0, 23.1, 14.5.

Preparation of polymers P-1 and P-2

Preparation of P-1

To a mixture of **S-M-1** (333 mg, 0.6 mmol) and **S-M-2** (358 mg, 0.6 mmol) in THF (10 mL) and K_2CO_3 (12 mL, 1*M* aqueous solution) was added a THF (2 mL) solution of $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 5 mol %) under N_2. After refluxing for 48 h, the reaction mixture was cooled to room temperature, and the organic layer was separated and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with 1*N* HCl (40 mL) and then concentrated by rotary evaporation. MeOH (100 mL) was added to precipitate the polymer. A fuscous solid was filtered off and was washed with MeOH several times. Further purification was conducted through the dissolution of the polymer in CH_2Cl_2 to precipitate in MeOH again. **P-1** was dried *in vacuo* at room temperature for 24 h. The yield was 51% (274 mg).

$[\alpha]_D^{20} = +103.3$ (concentration = 0.1, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.80 (m, 12H), 10.01 (m, 16H), 1.50 (m, 12H), 1.78 (m, 4H), 2.90 (m, 4H), 3.98 (m, 4H), 5.20 (m, 4H), 7.10 (br, 2H), 7.20 (m, 2H), 7.30 (m, 2H), 7.34 (m, 2H), 7.45 (m, 2H), 7.80 (m, 2H), 8.01 (br, 2H), 8.14 (br, 2H).

Preparation of **P-2**

To a mixture of $Pd(PPh_3)_4$ (28 mg, 0.024 mmol, 4 mol %) and CuI (24 mg, 0.12 mmol) in toluene (10 mL) and n-butylamine (15 mL) was added a toluene solution (5 mL) of **S-M-1** (333 mg, 0.6 mmol) and **S-M-3** (334 mg, 0.6 mmol) under N_2. After refluxing for 72 h, the reaction mixture was concentrated by rotary evap-

oration. The residue was dissolved in 1 mL of THF and added to 100 mL of MeOH to precipitate the polymer. Further purification was conducted through the dissolution of the polymer in CH_2Cl_2 to precipitate in MeOH again. **P-2** was dried *in vacuo* at room temperature for 24 h. The yield was 58% (330 mg).

$[\alpha]_D^{20} = +202.5$ (concentration = 0.1, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87 (m, 12H), 1.00 (m, 16H), 1.26 (m, 6H), 1.41 (m, 4H), 1.70 (m, 8H), 2.88 (br, 2H), 3.95 (br, 4H), 5.15 (br, 2H), 7.12 (m, 2H), 7.42 (m, 4H), 7.50 (m, 2H), 7.91 (m, 4H), 8.09 (m, 4H).

General procedure for the asymmetric addition of diethyl zinc to benzaldehyde

To a 10-mL Schlenk flask containing toluene (3 mL) were added **P-1** (27 mg, 0.03 mmol) and 0.10 mL of titanium tetraisopropoxide (0.36 mmol) under N_2 at room temperature. The mixture was stirred for 30 min. To this solution was added 0.6 mL of a 2.0*M* solution of diethyl zinc in hexane (1.2 mmol), and the mixture was stirred for 1 h. A 2.0*M* solution (0.15 mL) of benzaldehyde in toluene (0.3 mmol) was added to the solution. After the mixture was stirred at room temperature for 36 h, the reaction was quenched with 1*N* HCl, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed with brine twice and then dried over anhydrous Na_2SO_4. The ether solution was concentrated *in vacuo* and treated with MeOH, and then the polymer was filtered and washed with water. **P-1** was washed with 1*N* HCl several times to recover the chiral ligand for the next reaction of benzaldehyde with diethyl zinc. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (20:1 v/v petroleum ether/ethyl acetate) to afford the product 1-phenylpropanol as a colorless liquid.

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