Articles

Poly(1,1′-bi-2-naphthol)s: Synthesis, Characterization, and Application in Lewis Acid Catalysis

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6,6′-Dibromo-1,1′-bi-2-naphthol derivatives, where the hydroxyl groups are protected by alkyl, methoxymethyl, and acyl groups, have been polymerized using nickel(0) or nickel(II) complexes as catalysts. The molecular weights of the resulting polymers have been analyzed by gel permeation chromatography and laser light scattering. Hydrolysis of these polymers has produced the optically active poly(1,1′-bi-2-naphthol)s [poly(BINOL)s]. The poly(BINOL)s are soluble in basic water solution and have been characterized by NMR, IR, UV, and CD spectroscopic methods. The reaction of a (*R*)-poly(BINOL) with diethylaluminum chloride, trimethylaluminum, and titanium tetraisopropoxide generates novel polymeric Lewis acid complexes. These complexes represent a new generation of polymeric catalysts where the catalytic centers are highly organized in an optically active and sterically regular polymer chain. When used to catalyze the Mukaiyama aldol condensation, the polymeric aluminum catalyst shows greatly enhanced catalytic activity over the monomeric complex.

Introduction

Due to the restricted rotation around the 1,1′-bond, 1,1′-binaphthyl molecules are chiral and the chirality of these compounds has been utilized in many asymmetric processes.[2−4] A number of chiral binaphthyl metal complexes have been demonstrated to be excellent catalysts for enantioselective organic transformations. Figure 1 lists several binaphthyl-based chiral metal complexes: the ruthenium binaphthylphosphine complex (*R*)-**1** is applied in asymmetric hydrogenations,[5] the aluminum binaphthyl complex (*R*)-**2** is used in asymmetric Diels-Alder reactions,[6] the titanium binaphthyl complex (*S*)-**3** is used in asymmetric aldol reactions,[7] and the trimeric binaphthyl lanthanum complex (*R*)-**4** is applied in asymmetric Michael reactions.[8] These catalysts have induced very good enantioselectivity in these reactions.
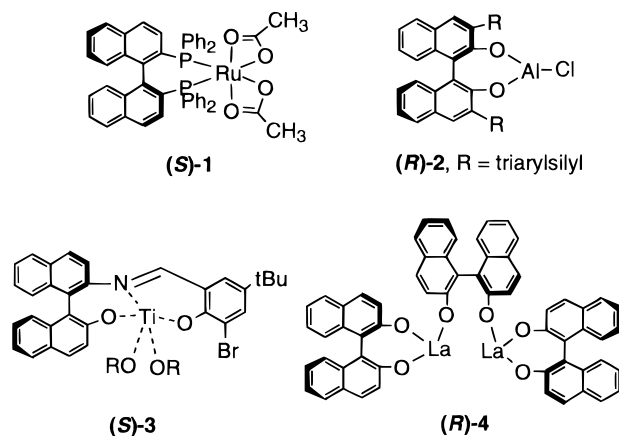

Figure 1. Examples of chiral binaphthyl catalysts.

On the basis of the unique structure of binaphthyl compounds, we have constructed novel main chain chiral conjugated polymers.[9−12] For example, propeller polymers such as (*R*)-**5** have been designed and synthesized in our laboratory.[12] In (*R*)-**5** (Chart 1), all of its binaphthyl units have a *R* configuration, and the dipole units of this polymer are expected to progressively rotate along the polymer axis to generate a fascinating three-dimensional propeller structure. Polymers of this structure may lead to interesting electrical and optical properties. Besides the development of the binaphthyl-based

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(1) (a) North Dakota State University. (b) The Chinese University of Hong Kong.

(2) (a) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503. (b) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581. (c) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977.

(3) (a) Takaya, H.; Ohta, T.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; pp 1. (b) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 3049. (c) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto. *J. Am. Chem. Soc.* **1988**, *110*, 310.

(4) Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: New York, 1995.

(5) Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.* **1987**, *52*, 3174.

(6) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

(7) (a) Carreira, E. M.; Lee, W.; Singer, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 3649. (b) Carreira, E. M.; Singer, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 12360.

(8) Sasai, H.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1994**, *116*, 1571.
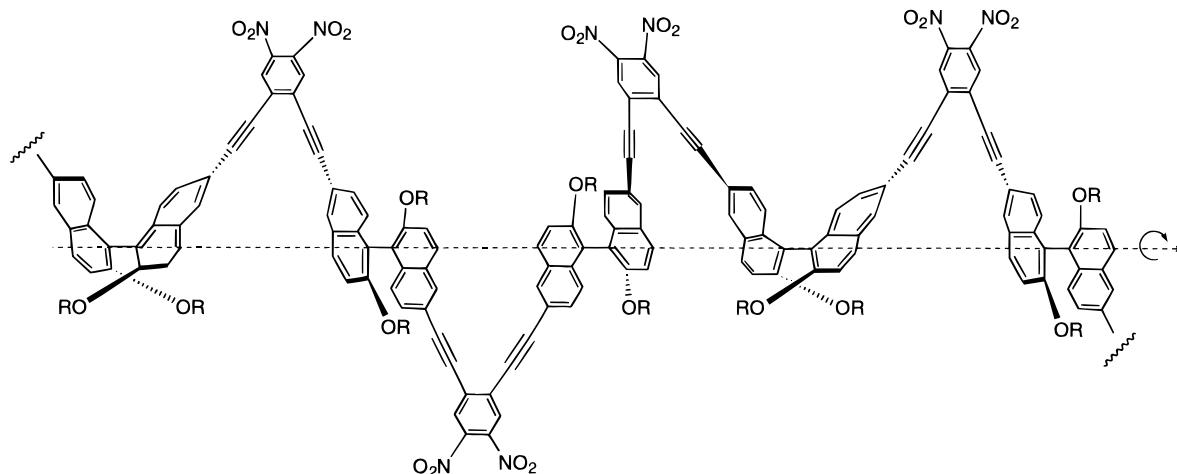
(9) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee, T. ; Pu, L. *Macromolecules* **1996**, *29*, 1082.

(10) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V.; Pu, L. *Macromolecules* **1996**, *29*, 5075.

(11) Ma, L.; Hu, Q.-S.; Musick, K.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1996**, *29*, 5083.

(12) (a) Ma, L.; Hu, Q.-S.; Pu, L. *Polymer Prepr.* **1996**, *37(2)*, 462. (b) Ma, L.; Hu, Q. -S.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. Manuscript submitted.

Chart 1

(*R*)-**5**, R = C$_{18}$H$_{37}$

polymers in electrical and optical applications, we are also interested in using these chiral materials in asymmetric catalysis. There are important advantages using polymer-supported catalysts in industrial processes.[13] For example, because of the easy separation of the polymeric catalysts from the reaction system, these catalysts can be used in flow reactor synthesis. Studies have shown that polymer-supported catalysts may have more durable catalytic activity than the monomeric metal complexes. Chiral polymeric catalysts have been studied before, but very few show good enantioselectivity. The traditional polymeric chiral catalysts are synthesized by covalently bonding a chiral metal complex to an achiral and sterically irregular polymer backbone. As shown by **6**, a polystyrene-supported chiral rhodium catalyst,[14] the catalytic centers in these catalysts are randomly oriented, and the influence of the microenviroment of the catalytic sites on the catalysis is difficulty to study. We have
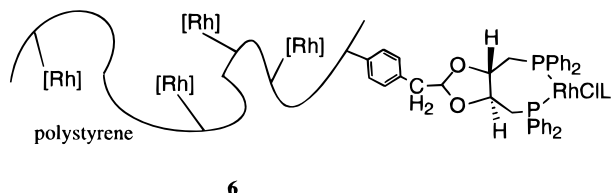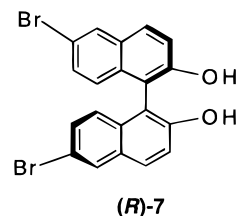

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carried out a program to introduce metal centers into the rigid and sterically regular polybinaphthyls to prepare a new generation of polymeric chiral catalysts. In this article, several strategies to prepare the optically active and sterically regular poly(1,1′-bi-2-naphthol)s [poly-(BINOL)s] are described. The hydroxyl functional groups in these polymers allow us to incorporate aluminum and titanium Lewis acid metal centers. The use of these polymeric complexes in the Mukaiyama aldol condensation is studied.[15]

Results and Discussion

In order to synthesize poly(BINOL)s, (*R*)-**7** is prepared from the bromination of (*R*)-1,1′-bi-2-naphthol in over 95% yield.[16,17] The attempt to directly polymerize this molecule using a catalytic amount of nickel(II) chloride and excess zinc produces mostly (*R*)-1,1′-bi-2-napthol with


(*R*)-**7**

less than 5% of oligomers. The hydroxyl groups of (*R*)-**7** are therefore protected with different protecting groups, and the resulting monomers are polymerized by using different coupling processes to make chiral polybinaphthyls. Removal of the protecting groups in the polymers gives the desired poly(BINOL) which are used to synthesize polymeric Lewis acid catalysts for the Mukaiyama aldol condensation.

1. Preparation of an Alkyl-Protected Poly-(BINOL). An alkyl-protected chiral binaphthyl monomer has been synthesized. The reaction of (*R*)-**7** with iodohexane in a refluxing acetone/K$_2$CO$_3$ mixture generates (*R*)-6,6′-dibromo-2,2′-bis(hexyloxy)-1,1′-binaphthyl, (*R*)-**8**.[9] The specific optical rotation of the monomer (*R*)-**8** is [α]$_D$ = +25.9° (*c* = 0.52, THF). (*R*)-**8** undergoes polymerization in the presence of a stoichiometric amount of bis(1,5-cyclooctadiene)nickel(0) (Scheme 1).[15b] The reaction is carried out in a DMF solution of (*R*)-**8** (1.42 mmol), bis(1,5-cyclooctadiene)nickel(0) (1.76 mmol), 2,2′-bipyridine (2.09 mmol), and 1,5-cyclooctadiene (4.9 mmol). After the mixture is heated at 70 °C under nitrogen for 21 h, a chiral polybinaphthyl (*R*)-**9** is obtained. Gel

(13) (a) Blossey, E. C.; Ford, W. T. In *Comprehensive Polymer Science. The Synthesis, Characterization, Reactions and Applications of Polymers;* Allen, G., Bevington, J. C., Ed.; Pergamon Press: New York. 1989; Vol. 6, p 81. (b) Pittman, C. U., Jr. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Ed.; Pergamon Press: Oxford, 1983; Vol. 8, p 553.
(14) (a) Dumont, W.; Poulin, J. C.; Dang, T. P.; Kagan. H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8295. (b) Dang, T. P.; Kagan, H. B. Fr. Pat. 1 199 756.

(15) Preliminary accounts of this work have been published: (a) Hu, Q.-S.; Zheng, X.-F.; Pu, L. *J. Org. Chem.* **1996**, *61*, 5200. (b) Vitharana, D.; Hu, Q.-S.; Pu, L. *Polymer Prepr.* **1996**, *37(1)*, 855.
(16) (a) Pradellok, W.; Kotas, A.; Walczyk, W.; Jedlinski, Z. *Chem. Abstr.* **1979**, *90*, 121289t. (b) Sogah, G. D. Y.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3035.
(17) An efficient resolution of 1,1′-2-naphthol has been developed in this laboratory: Hu, Q.-S.; Vitharana, D. R.; Pu, L. *Tetrahedron: Asymmetry* **1995**, *6*, 2123.

Scheme 1. Synthesis of an Optically Active Poly(binaphthyl) (*R*)-9

(*R*)-9, R = C$_6$H$_{13}$
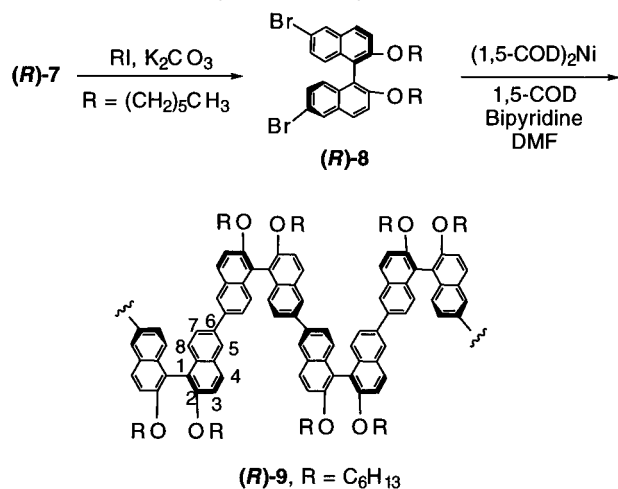
Table 1. UV Spectral Data of the Polymer (*R*)-9, 2,2′-Bis(hexyloxy)-1,1′-binaphthyl (10) and 2-(Hexyloxy)naphthalene (11)

|	(*R*)-9	10	11
λ_{max} (nm)	240 (sh), 262, 284, 316	252, 273 (sh), 284, 293 (sh), 328 (sh), 340	240, 266, 274, 318, 330

permeation chromatography (GPC) analysis shows that the molecular weight of (*R*)-9 is $M_w = 15\,000$ and $M_n = 6800$ (PDI = 2.2). The specific optical rotation of the polymer is $[\alpha]_D = -215°$ ($c = 0.52$, CH$_2$Cl$_2$). This polymer rotates the plane of polarized light to the opposite direction of the monomer with a much larger optical rotation.

The ^{1}H NMR spectrum of (*R*)-9 displays well-resolved proton signals with a few low intensity peaks probably arisen from the end groups. Based on analogy to substituted monomeric binaphthyl molecules, each peak in the aromatic region can be assigned. The ^{13}C NMR spectrum of (*R*)-9 is also well-resolved. The polymer has a glass transition temperature (Tg) at 119 °C as indicated by differential scanning calorimetry. The thermal stability of (*R*)-9 is very high. Thermogravimetric analysis shows that (*R*)-9 does not start to lose mass until ca. 392 °C.

The UV-vis spectrum of (*R*)-9 exhibits maximum absorptions at $\lambda_{max} = 240$ (sh), 262, 284, and 316 nm. Comparison of the UV spectrum of (*R*)-9 with those of 2,2′-bis(hexyloxy)-1,1′-binaphthyl, 10, and 2-(hexyloxy)-naphthalene, 11, can provide some insight on the main chain conformation of this class of polybinaphthyls. As shown in Table 1, the UV spectrum of the polymer (*R*)-9
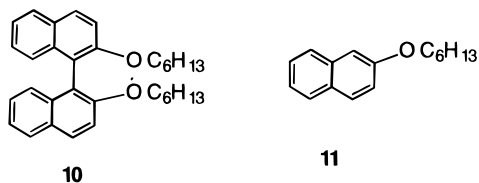
in methylene chloride solution resembles that of 11 more than it resembles that of 10. This indicates that there is no extended conjugation at both the α,α′-naphthyl connection and the β,β′-naphthyl connection in the polymer main chain. Therefore, all of the adjacent naphthalene rings in the polymer are most likely to be orthogonal to each other.

Scheme 2. The Suzuki Coupling Reaction to Prepare a Chiral Polybinaphthyl

(*R*)-12, R = C$_6$H$_{13}$
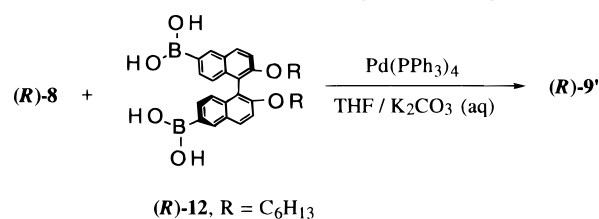
The circular dichroism spectrum of (*R*)-9 in methylene chloride exhibits very strong Cotton effects. The chiral configuration of this polymer is also quite stable. When a toluene solution of the polymer is heated at reflux for 24 h, only 6% loss of the optical rotation is observed.

The racemic monomer *rac*-8 has also been polymerized by using the nickel(0)-mediated polymerization. The resulting polymer *rac*-9 has a molecular weight of $M_w = 11\,000$ and $M_n = 4700$ (PDI = 2.3) as measured by GPC. The NMR and UV spectra of *rac*-9 are almost identical to those of (*R*)-9.

2. Using the Suzuki Coupling Reaction to Prepare the Polybinaphthyl. The Suzuki coupling reaction[19] has been utilized to prepare the chiral polybinaphthyl. When a 1:1 mixture of (*R*)-8 and (*R*)-12,[9] a diboronic acid monomer, is reacted in the presence of Pd(PPh$_3$)$_4$ catalyst, the Suzuki reaction occurs to generate (*R*)-9′ (Scheme 2). GPC analysis of (*R*)-9′ shows $M_w = 17\,600$ and $M_n = 7600$ (PDI = 2.3). $[\alpha]_D = -281°$ ($c = 0.50$, THF). The NMR and UV spectroscopic data (*R*)-9′ are essentially the same as those of (*R*)-9. Racemic monomers *rac*-8 and *rac*-12 also undergo the Suzuki coupling to generate polymer *rac*-9′. GPC analysis of *rac*-9′ shows $M_w = 21\,500$ and $M_n = 8100$ (PDI = 2.6). The Suzuki coupling reaction produces higher molecular weight polybinaphthyls than the nickel(0)-mediated polymerization.

In order to find out whether the polymerization of the racemic monomers *rac*-8 and *rac*-12 is stereoselective, and whether polymer *rac*-9′ is a stereoregular polymer or it is actually made of randomly distributed *R* and *S* binaphthyl units in the polymer chain, we have studied the Suzuki coupling of 2 equivalents of *rac*-8 with 1 equiv of (*R*)-12. After the reaction is completed, an oligomer 13 is obtained. GPC analysis of 13 shows $M_w = 3600$ and $M_n = 2300$ (PDI = 1.5). Its specific optical rotation is $[\alpha]_D = -97.7°$ ($c = 1.0$, THF). About 20% of unreacted *rac*-8 is recovered which shows the specific optical rotation is $[\alpha]_D = -0.7°$. Thus there is no enrichment of either *R* or *S* enantiomer after the reaction. On the basis of this experiment, we conclude that the coupling of *rac*-8 with *rac*-12 is not stereoselective and the polymer *rac*-9′ is made of randomly distributed *R* and *S* binaphthyl units.

3. Preparation of a Methoxymethyl Group Protected Poly(BINOL). A methoxy methyl protected chiral binaphthyl monomer is also synthesized (Scheme 3). In the presence of sodium hydride, the reaction of chloromethyl methyl ether with (*R*)-7 produces a chiral

(18) Maruyama, T.; Zhou, Z.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1992**, 643.

(19) Selected references on the Suzuki coupling reactions: (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (b) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (c) Huber, J.; Scherf, U. *Macromol. Rapid Commun.* **1994**, *15*, 897.

Scheme 3. Preparation of the Chiral Polybinaphthyl (R)-15

(R)-15
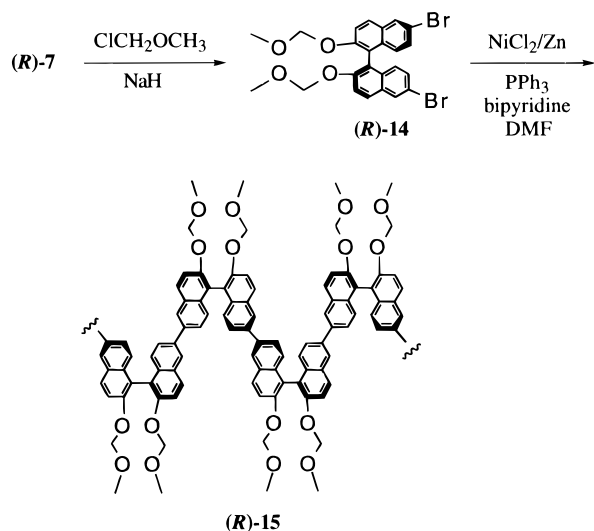
Table 2. Molecular Weights of the Polymers Prepared from the Polymerization of (R)-15 Using Different Amounts of NiCl₂ as the Catalysts

amount of NiCl$_2$ (mol %)	M_w	M_n	PDI
2	2400	1900	1.2
5	4400	2700	1.6
10	6000	3800	1.6
50	5400	3500	1.5

binaphthyl monomer (R)-**14**.[20] The specific optical rotation of (R)-**14** is $[\alpha]_D = +23.1°$ ($c = 1.0$, THF). The use of a catalytic amount of nickel(II) chloride and excess zinc[21] to carry out the polymerization of (R)-**14** is studied. The molecular weights of the resulting polybinaphthyl is found to be dependent on the amount of nickel(II) chloride. Table 2 summarizes the molecular weights of the polymers measured by GPC when different amount of nickel(II) chloride is used. In the presence of 10 mol % of nickel(II) chloride and excess zinc, the polymer (R)-**15** is obtained with a molecular weight of $M_w = 6000$ and $M_n = 3800$ (PDI = 1.6). (R)-**15** is soluble in common organic solvents such as THF, methylene chloride, and chloroform and has been characterized by spectroscopic methods including ^1H and ^{13}C NMR. Its specific optical rotation is $[\alpha]_D = -301.9°$ ($c = 1.0$, THF). The molecular weight of (R)-**15** is significantly lower than (R)-**9** and (R)-**9′**, but its optical rotation is much higher. This indicates that the methoxymethyl protecting groups have significant effects on the stereo and electronic structure of the polymer.

4. Preparation of an Acyl-Protected Poly(BINOL). An acyl-protected chiral binaphthyl monomer (R)-**16** is synthesized from the reaction of (R)-**7** with acetic anhydride in the presence of triethylamine. (R)-**16** is polymerized by using nickel(II) chloride and excess zinc (Scheme 4). The reaction is carried out under nitrogen by heating a mixture of (R)-**16** (18.0 mmol), zinc (61.2 mmol), NiCl₂ (1.80 mmol), PPh₃ (7.2 mmol), and bipyridine (1.8 mmol) in DMF at ca. 85 °C. The resulting polymer (R)-**17** is purified by dissolution in CH₂Cl₂ and precipitation with

Scheme 4. Preparation of the Chiral Polybinaphthyl (R)-17

(R)-17
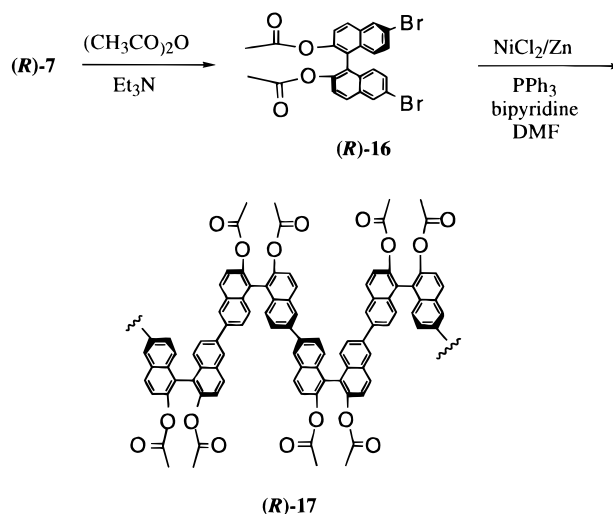
Scheme 5. Preparation of the Chiral Poly(1,1′-bi-2-naphthol) (R)-18

(R)-18
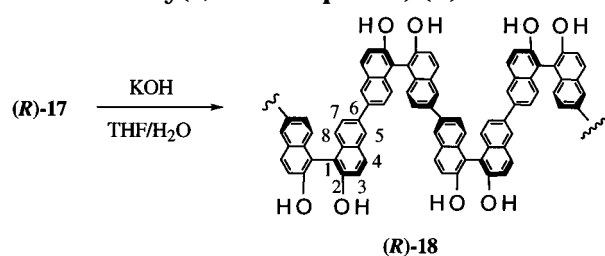
MeOH. The molecular weight of (R)-**17** is $M_w = 6400$ and $M_n = 3600$ (PDI = 1.8) as shown by GPC analysis. This polymer is soluble in methylene chloride, chloroform, and THF. The specific optical rotation of (R)-**16** is $[\alpha]_D = -353°$ ($c = 0.5$, THF). The racemic monomer *rac*-**16** has also been polymerized to generate *rac*-**17**. GPC analysis shows that the molecular weight of *rac*-**17** is $M_w = 7400$ and $M_n = 3200$ (PDI = 2.3).

All of the molecular weights of the polybinaphthyls described above are measured by GPC relative to polystyrene standards. Because the three-dimensional structure of the rigid polybinaphthyls are expected to be quite different from that of polystyrene, the GPC data may not reflect the actual molecular weights of these polymers. A laser light scattering (LLS) study of the polymers (R)-**17** and *rac*-**17** has been carried out to determine the absolute molecular weights of these polymers.[22] Table 3 summarizes the LLS study results and the GPC data. As shown in the table, the GPC data deviate ca. 10−20% from the LLS data. Since the difference is small, the GPC analysis using polystyrene standard can be used as a convenient and good estimate for the molecular weights of these polybinaphthyls.

5. Hydrolysis To Generate the Poly(BINOL)s. The acetate protecting groups of (R)-**17** can be easily hydrolyzed. Heating a mixture of the THF solution of (R)-**17** and aqueous potassium hydroxide at reflux generates the first optically active and sterically regular poly-(BINOL) (R)-**18** (Scheme 5). Although this polymer cannot be dissolved in organic solvents, it is soluble in

(20) Kitajima, H.; Aoki, Y.; Ito, K.; Katsuki, T. *Chem. Lett.* **1995**, 1113.

(21) (a) Wang, Y.; Quirk, R. P. *Macromolecules* **1995**, *28*, 3495. (b) Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 2354.

(22) (a) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1974. (b) Pecora, R.; Berne, B. J. *Dynamic Light Scattering*. Plenum Press: New York, 1976. (c) Wu, C.; Chan, K.; Xia, K. Q. *Macromolecules* **1995**, *28*, 1032.

Table 3. Comparison of the GPC Data and the LLS Study Results of the Polymers (R)-17 and rac-17

polymers	M_w (GPC)	M_n (GPC)	PDI (GPC)	M_w (LLS)	A_2 (mol cm^{-3} g^{-2})	$<D>$ (μm^2/s)	$<R_h>$ (nm)	$\mu_2\Gamma^2$	M_w/M_n (estimated)
(R)-**17**	6400	3600	1.79	7130	-2.86 E^{-3}	202	2.28	0.10	~1.4
rac-**17**	7400	3200	2.29	5930	-6.27 E^{-3}	205	2.24	0.089	~1.4

A_2 is the second virial coefficient; D is the translational diffusion coefficient; R_h is the hydrodynamic radius and $\mu_2/\langle\Gamma\rangle$ is the width of the line-width distribution.
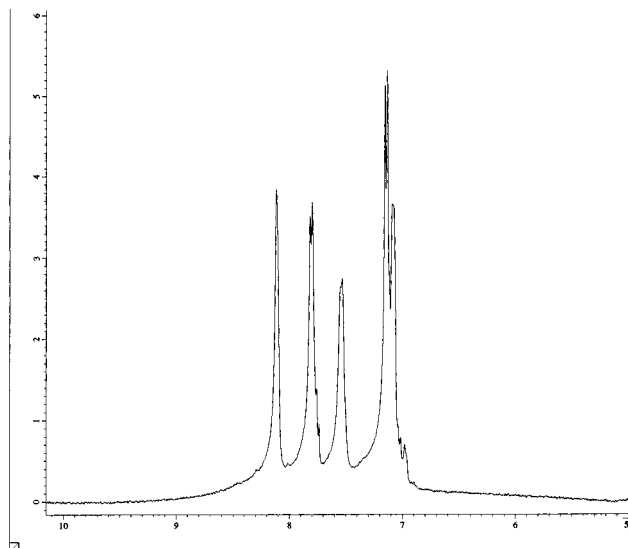
Figure 2. The ^{1}H NMR spectrum of (R)-**18** in a 0.5 M NaOD deuterium water solution.
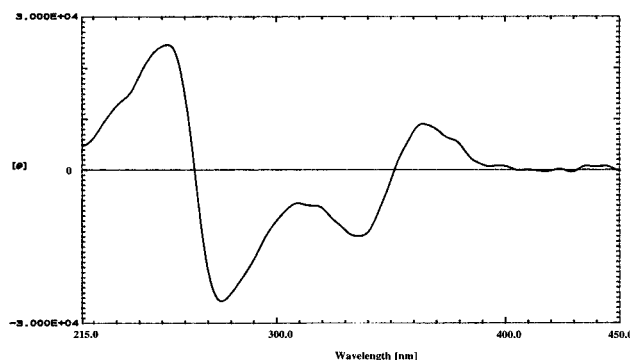
Figure 3. The CD spectrum of (R)-**18** in 0.5 M aqueous KOH solution.

basic water solution. It is purified by precipitation of its aqueous potassium hydroxide solution with hydrogen chloride. The specific optical rotation of (R)-**18** is [α]$_D$ = $-139.8°$ (c = 0.5, 0.5 M aqueous KOH). Figure 2 is the ^{1}H NMR spectrum of (R)-**18** in a D$_2$O solution of 0.5 M NaOD. A singlet at δ 8.12 corresponds to H-5 in the naphthalene ring. Four additional signals are observed for the remaining four protons on the aromatic ring. Smaller peaks in the spectrum are due to the end groups of the polymer. This relatively well-resolved NMR spectrum is consistent with the polymer structure. The UV spectrum of the polymer in 0.5 M aqueous KOH solution displays λ_{max} = 274 and 340 nm. The UV spectrum of (R)-**18** shows a significant red-shift of maximum absorptions from that of (R)-**9** due to the negative charges on the oxygen atoms of (R)-**18** in the strong basic solution. The circular dichroism spectrum of (R)-**18** in 0.5 M aqueous KOH solution is shown in Figure 3. Two positive and two negative Cotton effects are observed.

Scheme 6. The Mukaiyama Aldol Condensation of 19 and 20
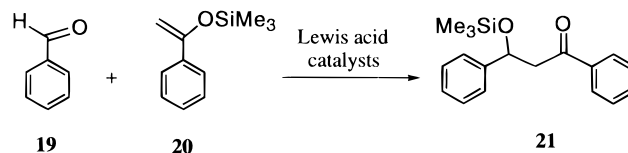
In the presence of hydrochloric acid, (R)-**15** undergoes facile hydrolysis to generate the optically active poly-(BINOL). The ether functional groups of (R)-**9** and (R)-**9**′ are difficult to hydrolyze. To convert these polymers to the poly(BINOL)s, (R)-**9** and (R)-**9**′ have to be treated with excess boron tribromide and followed by reaction with water.[23] Although both (R)-**9** and (R)-**9**′ have much higher molecular weights than (R)-**15** and (R)-**17**, the poly(BINOL)s prepared from them are still soluble in basic water solution. Among the methods we have described for the preparation of the optically active poly-(BINOL)s, the synthesis of (R)-**17** and its hydrolysis is the most practical one because of the readily available monomer, inexpensive catalysts, and easy hydrolysis.

6. Poly(BINOL) in Catalysis. We have used the chiral poly(BINOL) (R)-**18** to prepare novel polymeric Lewis acid catalysts for the Mukaiyama aldol reaction[24,25] of benzaldehyde, **19**, and 1-phenyl-1-(trimethylsilyloxy)-ethylene, **20**. The reaction of **19** and **20** can be catalyzed by Lewis acids to generate **21** (Scheme 6).[25] This class of reactions is very useful in the formation of carbon−carbon bonds between carbonyl compounds.

(R)-**18** can be converted to polyaluminum complexes (Scheme 7). The reaction (R)-**18** with diethylaluminum chloride produces a heterogeneous polymeric aluminum complex (R)-**22**.[26] The reaction of (R)-**18** with trimethyl-aluminum gives (R)-**23**. When these polymeric alumi-num complexes are used to catalyze the Mukaiyama condensation of **19** with **20** in methylene chloride solu-tion, (R)-**22** shows higher catalytic activity than (R)-**23**. At -78 °C, 100% conversion is observed in 3.5 h when the reaction is carried out in the presence of 16 mol % of (R)-**22**, but only ca. 30% conversion is observed when using 16 mol % of (R)-**23**. The catalytic activity of (R)-**22** is also much higher than its corresponding monomeric aluminum complex (R)-**24** made from the reaction of (R)-1,1′-bi-2-naphthol with diethylaluminum chloride. At -78 °C, there is only ca. 5% conversion for the reaction of **19** and **20** catalyzed by 16 mol % of (R)-**24**. Thus, there
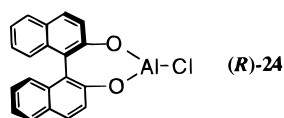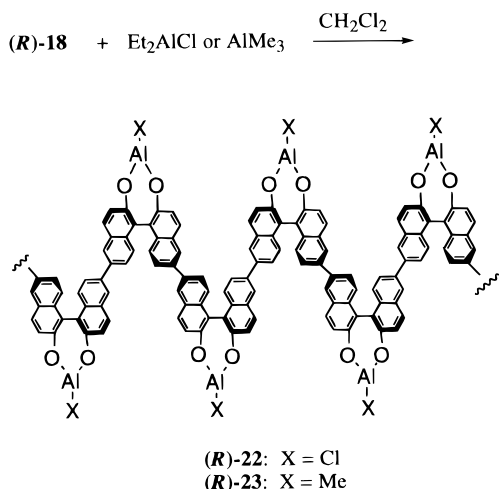
(23) Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org. Chem.* **1981**, *46*, 393.

(24) Selected references on Lewis acid-catalyzed asymmetric Mu-kaiyama aldol condensations: (a) a review: Bach, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 417. (b) Reetz, M. T.; Kyung, S.-H.; Bolm, C.; Zierke, T. *Chem. Ind.* **1986**, 824. (c) Mikami, K.; Matsukawa, S. *J. Am. Chem. Soc.* **1994**, *116*, 4077. (d) Parmee, E. R.; Hong, Y.; Tempkin, O.; Masamune, S. *Tetrahedron Lett.* **1992**, *33*, 1729. (e) Corey, E. J.; Cywin, C. L.; Roper, T. D. *Tetrahedron Lett.* **1992**, *33*, 6907.
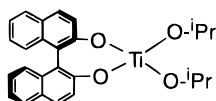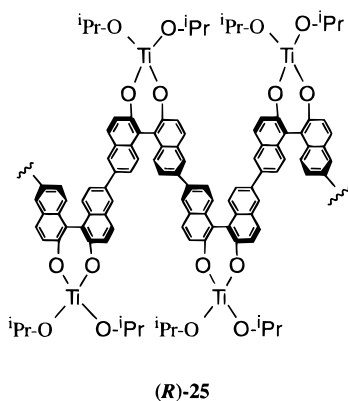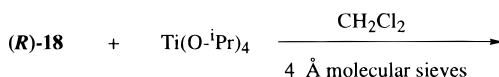
(25) Furuka, K.; Maruyama, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 1041.

(26) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

Scheme 7. Preparation of Polybinaphthol Aluminum(III) Catalysts (*R*)-22 and (*R*)-23

$$(R)\text{-}18 \quad + \quad Et_2AlCl \text{ or } AlMe_3 \quad \xrightarrow{\ CH_2Cl_2\ }$$

(*R*)-22: X = Cl
(*R*)-23: X = Me

(*R*)-24

Scheme 8. Synthesis of a Polymeric Titanium Complex (*R*)-25

$$(R)\text{-}18 \quad + \quad Ti(O\text{-}^iPr)_4 \quad \xrightarrow[\text{4 Å molecular sieves}]{\ CH_2Cl_2\ }$$

(*R*)-25

is a dramatic increase of catalytic activity from the monomeric complex to the polymeric complex.

However, when a polymeric titanium complex (*R*)-25, prepared from the reaction of (*R*)-18 with Ti(O-iPr)$_4$ in the presence of 4 Å molecular sieves (Scheme 8),[27] is used to catalyze the condensation of 19 and 20, no reaction occurs at all even in a refluxing methylene chloride solution for one day. In contrast, the monomeric titanium complex (*R*)-26, made from the reaction of (*R*)-1,1′-bi-2-naphthol with Ti(O-iPr)$_4$ in the presence of 4 Å molecular sieves,[27] can catalyze the reaction of 19 and 20 at rt.

This completely opposite behavior of the polybinaphthyl aluminum complex and the polybinaphthyl titanium complex provides additional insights on the mechanism of Lewis acid catalysis. It has been proposed that when a binaphthyl titanium complex such as (*R*)-26 is used to carry out organic transformations, the actual catalytically active species should be a dimeric complex.[28] Our observation that no reaction takes place when (*R*)-25 is used in the condensation of 19 and 20 supports this assumption. Because in the rigid polymer (*R*)-25, all of its titanium centers are isolated and the binaphthyl titanium units cannot dimerize to form the active catalyst for the reaction. On the other hand, the catalysis of aluminum complexes is believed to proceed through the coordination of substrates to the empty p orbital of the metal center. In solution, monomeric aluminum complexes such as (*R*)-24 can undergo oligomerization through the formation of stable Al−O−Al bridging bonds which reduces the Lewis acidity and deactivates the catalysts. However, in (*R*)-22, the rigid polymeric structure and its insolubility prevent the formation of such Al−O−Al bridging bonds. The empty p orbitals of the metal centers in this polyaluminum complex are therefore available to activate 19 for the Mukaiyama condensation. No enantioselectivity has been observed for this polymeric catalyst, and further modification of the catalyst is in progress.

Summary

The synthesis of polybinaphthyls containing alkoxyl, methoxymethoxyl, and acetyloxy substituents have been studied. We have shown that these polymers can be made by using nickel(0) or nickel(II) complexes mediated coupling processes as well as the Suzuki coupling reaction. GPC analysis and LLS study are used to analyze the molecular weights of these polymers. Hydrolysis of the functional groups of the polybinaphthyls leads to the first optically active and sterically regular poly(BINOL)s. These chiral poly(BINOL)s are soluble in basic water solution and have been characterized by different spectroscopic methods. The aluminum and titanium polymeric complexes are synthesized by using a poly(BINOL) as the precursor. A polymeric aluminum complex shows greatly enhanced catalytic activity over its monomeric binaphthyl complex when used in the Mukaiyama aldol condensation. The polybinaphthyl titanium complex, however, loses its catalytic activity while its monomeric complex is catalytically active. These studies have provided further understanding of the mechanism of Lewis acid catalysis in organic reactions.

Experimental Section

The general data about the analytical instruments and the LLS experiment were published.[10] THF and ether were dried with sodium benzophenone. Methylene chloride was dried

(27) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467.

(28) (a) Terada, M.; Mikami, K.; Nakai, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1623. (b) Mikami, K.; Terada, M. *Tetrahedron* **1992**, *48*, 5671. (c) Kitamoto, D. H.; Imma, H.; Nakai, T. *Tetrahedron Lett.* **1995**, *36*, 1861.

(29) References on Al−O−Al bridging bonds in aluminum alkoxide and aryloxide complexes: (a) Oliver, J. P.; Kumar, R.; Taghiof, M. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH Publishers: New York, 1993; p 167. (b) Jeffery, E. A.; Mole, T. *Aust. J. Chem.* **1968**, *21*, 2683. (c) Pasynkiewicz, S.; Starowieyski, K. B.; Skoweonska-Ptasinska, M. *J. Organomet. Chem.* **1973**, *52*, 269. (d) Pasynkiewicz, S.; Starowieyski, K. B.; Skoweonska-Ptasinska, M. *J. Organomet. Chem.* **1974**, *65*, 155.

with calcium hydride. 1,5-Cyclooctadiene, 2,2′-bipyridine, triphenylphosphine, and anhydrous DMF were purchased from Aldrich and used directly. Biscyclooctadienenickel(0), nickel-(II) chloride, and tetrakis(triphenylphosphine)palladium(0) were purchased from Strem and used directly. The optical purity of the binaphthyl monomers in this paper is larger than 99% as measured by HPLC using Chiralcel OD column made by Chiral Technologies Inc.

Preparation and Characterization of (R)-9. Under nitrogen, to a 50 mL Schlenk flask were added (R)-**8** (855 mg, 1.42 mmol), bis(cyclooctadiene)nickel(0) (489 mg, 1.76 mmol), 2,2′-bipyridine (330 mg, 2.09 mmol), and 1,5-cyclooctadiene (0.60 mL, 4.9 mmol) in DMF (9 mL), and the reaction mixture was heated at 70 °C for 21 h. Aqueous HCl (1 N, 25 mL) was then added to the reaction mixture at rt and was extracted with CH_2Cl_2 (2 × 25 mL). The Organic layer was passed through a plug of silica gel and concentrated under vacuum. The polymer was precipitated out with MeOH and isolated after centrifugation. The yield of (R)-**9** is 58%. GPC: $M_w = 15\,000$ and $M_n = 6800$ (PDI = 2.2). $[\alpha]_D = -215°$ (c = 0.52, CH_2Cl_2). FT-IR (KBr) cm^{-1} 2928 (s), 2858 (s), 1589 (s), 1491-(m), 1400 (m), 1327, 1271, 1244, 1093, 1083, 879, 819, 559. UV-vis (CH_2Cl_2) nm, $\lambda_{max} = 240$ (sh), 262, 284, 316. Fluorescence λ_{emi} (CH_2Cl_2) nm 408. ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.05 (s, 2H), 7.91 (d, J = 9.5 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 3.88 (m, 4H), 1.33 (br, 4H), 0.89 (br, 12H), 0.62 (br, 6H). ^{13}C NMR (270 MHz, CDCl$_3$) δ 154.61, 136.14, 133.31, 129.56, 129.35, 126.05, 125.91, 125.65, 120.58, 116.19, 69.79, 31.31, 29.36, 25.31, 22.46, 13.92. CD (CH_2Cl_2) $[\theta]_\lambda = +2.28 \times 10^5$ (253 nm), -1.85×10^5 (278 nm), -3.02×10^4 (318 nm), $+2.07 \times 10^4$ (340 nm). Anal. Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 83.91; H, 7.98.

Preparation and Characterization of rac-9. In a procedure similar to (R)-**9**, rac-**9** was prepared in 80% yield. GPC: $M_w = 11\,000$ and $M_n = 4700$ (PDI = 2.3). $[\alpha]_D = +12.2°$ (c = 0.50, CH_2Cl_2). UV-vis (CH_2Cl_2) nm, $\lambda_{max} = 240$ (sh), 262, 274, 280, 316. FT-IR (KBr) cm^{-1} 2931 (s), 2868 (s), 1591 (s), 1462 (s), 1400 (s), 1269 (m), 1093 (m), 802 (m). Fluorescence λ_{emi} (CH_2Cl_2) nm 408. ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.12 (s, 2H), 7.98 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 3.95 (m, 4H), 1.33 (br, 4H), 0.87 (br, 12H), 0.61 (br, 6H). ^{13}C NMR (270 MHz, CDCl$_3$) 154.58, 136.12, 133.28, 129.53, 129.32, 126.03, 125.91, 125.62, 120.52, 116.13, 69.76, 31.31, 29.32, 25.29, 22.45, 13.91.

Preparation of (R)-9′. Under nitrogen, to a mixture of (R)-**12** (135 mg, 0.25 mmol) and (R)-**8** (153 mg, 0.25 mmol) in THF (4 mL) and K_2CO_3 (5 mL, 1 M aqueous solution) was added a THF (1 mL) solution of Pd(PPh$_3$)$_4$ (10 mg, 0.0086 mmol, 3.5 mol %). After heated at reflux for 24 h, the reaction mixture was cooled to rt and the organic layer was separated and diluted with CH_2Cl_2 (50 mL). The organic solution was washed with 1 N HCl (15 mL) and then concentrated by rotary evaporation. Methanol was added to precipitate out the polymer. Centrifugation and removal of the solvent gave a solid which was redissolved in methylene chloride and precipitated with methanol. After centrifugation separation, the polymer (R)-**9′** was obtained and dried under vacuum at rt for 24 h. The yield of the polymer is 93% (210 mg). $[\alpha]_D = -281.3°$ (c = 0.5, THF). GPC: $M_w = 17\,600$ and $M_n = 7600$ (PDI = 2.3). The UV, IR, ^{1}H NMR and ^{13}C NMR data of (R)-**9′** are the same as those of (R)-**9**. Anal. Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.30; H, 7.89.

Preparation of rac-9′. rac-**9′** was prepared in a procedure similar to that of (R)-**9′** in 90% yield. GPC: $M_w = 21\,500$ and $M_n = 8100$ (PDI = 2.6). Anal. Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.06, H, 7.76.

Preparation of the Chiral Monomer (R)-14. Under nitrogen, to a THF solution (20 mL) of NaH (280 mg, 11.7 mmol) was slowly added (R)-**7** (2.0 g, 4.6 mmol) at 0 °C. After 5 min, chloromethyl methyl ether (0.88 mL, 11.6 mmol) was added. The mixture was stirred at rt for 12 h. A small amount of water was then slowly added to quench the reaction and the mixture was extracted with ethyl acetate and washed with brine. After removal of solvent by rotary evaporation, the product (R)-**14** was recrystallized from hexanes as a white solid

(70% yield). Mp 136−137 °C. $[\alpha]_D = +23.1°$ (c = 1.0, THF). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, 2H, J = 1.9 Hz), 7.86 (d, 2H, J = 9.1 Hz), 7.59 (d, 2H, J = 9.1 Hz), 7.28 (dd, 2H, J = 9.1, 1.9 Hz), 6.97 (d, 2H, J = 9.1 Hz), 5.08 (d, 2H, J = 6.7 Hz), 4.97 (d, 2H, J = 7.0 Hz), 3.15 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.98, 132.46, 130.93, 129.97, 129.80, 128.80, 127.21, 120.75, 118.10, 118.07, 95.05, 56.03. FT-IR (KBr) cm^{-1} 2991.8 (w), 2957.1 (m), 2901.1 (m), 2827.8 (w), 1585.6 (s), 1494.9 (s), 1363.8 (m), 1246.1 (s), 1192.1 (m), 1149.7 (s), 1064.8 (s), 1022.3 (s), 958.7 (m), 920.1 (m), 877.7 (m), 817.9 (m), 679.0 (w), 517.0 (w). Anal. Calcd for $C_{24}H_{20}O_4Br_2$: C, 54.14; H, 3.76. Found: C, 54.20; H, 3.71.

Preparation of the Polybinaphthyl (R)-15. Under nitrogen, a mixture of (R)-**14** (200 mg, 0.4 mmol), zinc (88 mg, 1.36 mmol), NiCl$_2$ (5.2 mg, 0.04 mmol), triphenylphosphine (42 mg, 0.16 mmol), and bipyridine (6 mg, 0.04 mmol) in DMF (10 mL) was stirred at 85−90 °C. After 24 h, CH_2Cl_2 (20 mL) was added and the mixture was filtered. The solution was concentrated and filtered again to remove some insoluble impurities. Methanol was added to the methylene chloride solution to precipitate out the polymer. This process was repeated twice to give (R)-**15** as a white solid in 90% yield. GPC: $M_w = 6000$ and $M_n = 3800$ (PDI = 1.6). $[\alpha]_D = -301.9°$ (c = 1.01, THF). ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.87, 136.61, 133.25, 130.27, 129.83, 126.26, 126.16, 125.89, 121.20, 117.79, 95.31, 55.99. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (s, 2H), 8.00 (m, 2H, small peaks at 7.94, 7.89), 7.60 (m, 2H), 7.26 (m, 4H, small peaks at 7.35, 7.22, 7.20), 5.10 (m, 2H), 5.00 (m, 2H), 3.16 (s, 6H) (small peaks are due to the end groups). FT-IR (KBr) cm^{-1} 2957.1 (w), 2916.6 (w), 1591.4 (m), 1473.7 (m), 1240.3 (s), 1151.6 (s), 1076.4 (m), 1016.6 (s), 922.3 (w), 821.7 (w). Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.42; H, 5.38. Found: C, 75.54; H, 5.45.

Preparation of the Chiral Monomer (R)-16. To a solution of (R)-**7** (9.31 g, 21.0 mmol) and Et$_3$N (20 mL) in CH_2Cl_2 was added Ac$_2$O (10 mL) at 0 °C. The mixture was stirred at 0 °C for 2 h and warmed up to rt for another 2 h. The reaction was monitored by ^{1}H NMR spectroscopy. After the reaction was complete, the mixture was poured into H$_2$O and extracted with EtOAc (3 × 150 mL). The combined organic layer was washed with brine (20 mL), 1 N HCl (2 × 50 mL), brine (20 mL), saturated sodium bicarbonate solution (20 mL), and brine (20 mL) and dried with Na$_2$SO$_4$. After evaporation of the solvent, the residue was recrystallized from EtOAc/hexanes (1:3) to give a white crystalline solid, (R)-**16** (10.5 g, 94.8%). Mp 182−183 °C. $[\alpha]_D = -77.2°$ (c = 1.0, THF). FT-IR (KBr) cm^{-1} 1772.7 (s), 1585.6 (m), 1493.0 (m), 1400 (w), 1367.6 (m), 1323.2 (w), 1188.2 (s), 1066.7 (m), 1012.7 (m), 937.5 (m), 877.7 (m). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.88 (s, 6H, CH_3), 7.02 (d, J = 8.8 Hz, 2H, H-8), 7.36 (dd, J = 1.9, 8.8 Hz, 2H, H-7), 7.45 (d, J = 9.2 Hz, 2H, H-3), 7.91 (d, J = 9.2 Hz, 2H, H-4), 8.10 (d, J = 1.9 Hz, 2H, H-5). ^{13}C NMR (CDCl$_3$, 400 MHz) δ 20.67, 120.2, 123.2, 123.3, 127.9, 129.0, 130.2, 130.4, 131.8, 132.7, 147.1, 169.3. Anal. Calcd for $C_{24}H_{16}O_4Br_2$: C, 54.57; H, 3.05. Found: C, 54.30; H, 3.01.

Preparation of the Chiral Polybinaphthyl (R)-17. Under nitrogen, to a mixture of (R)-**16** (9.5 g, 18.0 mmol), zinc (4.0 g, 61.2 mmol), NiCl$_2$ (0.234 g, 1.80 mmol), PPh$_3$ (1.872 g, 7.2 mmol), and bipyridine (0.288 g, 1.8 mmol) was added DMF (60 mL). The mixture was stirred at 80−90 °C for 24 h. It was then cooled to rt and diluted with CH_2Cl_2 (200 mL). After filtration, the solid was washed with CH_2Cl_2 (2 × 50 mL). The combined organic layer was washed with 1 N HCl (50 mL) and brine (2 × 30 mL). The solution was concentrated and precipitated with MeOH. Centrifugation and filtration gave a solid which was redissolved in CH_2Cl_2 and precipitated with MeOH twice. The resulting solid was dried under vacuum at rt for 24 h to give (R)-**17** as a white powder (4.85 g, 73.2%). $[\alpha]_D = -353.0°$ (c = 0.5, THF). IR (KBr) cm^{-1} 1765.0 (s), 1593.3 (m), 1500.7 (m), 1466.0 (m), 1429.3 (w), 1367.6 (s), 1331.0 (w), 1201.7 (s), 1082.1 (w), 1041.6 (w), 1012.7 (s), 884.4 (m), 821.7 (s). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.89 (s, 6H, CH_3), 7.31 (m, 2H), 7.46 (m, H-2), 7.65 (br s, 2H), 8.06 (m, 2H, H-4), 8.21 (br s, 2H, H-5). ^{13}C NMR (CDCl$_3$, 400 MHz) δ 20.77, 122.6, 123.4,

126.3, 126.6, 127.0, 130.0, 131.96, 132.7, 137.9, 147.0, 169.6. Anal. Calcd for $C_{24}H_{16}O_4$: C, 78.25; H, 4.38. Found: C, 77.30; H 4.47.

Preparation of the Chiral Polybinaphthol (*R*)-18. To a THF solution (150 mL) of (*R*)-17 (4.30 g) was added a water solution (50 mL) of KOH (5.0 g). The mixture was heated at reflux for 24 h. The aqueous layer was separated, and 1 N HCl (100 mL) was added to acidify the water solution. A precipitate was generated which was collected by filtration. The solid was then redissolved in 0.5 M KOH and precipitated with 1 N HCl again. After washed with H_2O, the solid was dried under vacuum at rt for 24 h to give (*R*)-18 as a light yellow powder (2.80 g, 85%). $[\alpha]_D = -139.8$ °C ($c = 0.5$, 0.5M aqueous KOH). IR (KBr) cm^{-1} 3421.9 (s), 1593.3 (s), 1500.7 (s), 1466.0 (s), 1381.1 (s), 1336.8 (s), 1250.0 (m), 1215.2 (s), 1157.4 (s), 943.2 (w), 819.8 (s). ^{1}H NMR (400 MHz, 0.5 M NaOD·D$_2$O) δ 7.09 (m, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 7.46 (m, 2H), 7.81 (d, $J = 8.8$ Hz, 2H), 8.12 (br s, 2H). UV (0.5 M aqueous KOH) λ_{max} 274, 340 nm. CD (0.5 M aqueous KOH) $[\theta]_\lambda = 2.45 \times 10^4$ (252 nm), -2.57×10^4 (276 nm), -1.30×10^4 (336 nm), 9.06×10^3 (364 nm) and 6.62×10^3 (377 [sh] nm).

Procedures for the Mukaiyama Aldol Condensation of 19 and 20 Using the Lewis Acid Catalysts. A: Under nitrogen, to a mixture of (*R*)-18 (56.8 mg, 0.2 mmol based on the repeat unit) and CH_2Cl_2 (5 mL) was added Et_2AlCl (19.3 mg, 0.16 mmol) at rt to prepare (*R*)-22. (This reaction was carried out in CD_2Cl_2 where the ^{1}H NMR spectrum had shown the complete consumption of Et_2AlCl after 3 h). After stirred at rt for 3 h, the mixture was cooled to -78 °C, and 19 (0.1 mL, 1 mmol) and 20 (0.25 mL, 1.2 mmol) were added. The reaction was complete within 3.5 h (monitored by TLC). Aqueous workup and flash chromatogrphy gave 21 as an oil

(275 mg, 92%). 21 is converted to its acetate derivative through desilylation with n-Bu$_4$NF followed by reaction with Ac_2O, and the ee of the acetate derivative is determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as the chiral shift reagent and by HPLC analysis using Chiralcel OD column.

Similar procedures were used for the reaction of 19 and 20 catalyzed by (*R*)-23 and (*R*)-24.

B: Under nitrogen, to a flask containing (*R*)-18 (56.8 mg, 0.2 mmol based on repeat unit) and 4 Å molecular sieves (450 mg) in CH_2Cl_2 (4 mL) was added Ti(O^{i}Pr)$_4$ (45.0 mg, 0.16 mmol), and the mixture was refluxed for 2 h. After cooled to rt, 19 (0.1 mL, 1 mmol) was added. After 10 min, the mixture was cooled to -78 °C and 20 (0.25 mL, 1.2 mmol) was added. No reaction was observed at -78 °C (24 h), at rt (18 h), and at reflux (24 h). A similar procedure was applied to prepare (*R*)-26 and to use it for the reaction of 19 and 20. Although no reaction was observed at -78 °C (24 h), about 50% conversion was observed after the reaction mixture was warmed up to rt for 18 h.