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Asymmetric addition of phenylacetylene to aldehydes catalyzed by soluble optically active polybinaphthols ligand

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Abstract

A chiral polymer ligand was synthesized by the polymerization of (*S*)-5,5′-dibromo-6,6′-dibutyl-2,2′-binaphthol (***S*-M-1**) with (*S*)-2,2′-bishexyloxy-1,1′-binaphthyl-6,6′-boronic acid (***S*-M-2**) via Pd-catalyzed Suzuki reaction. The application of the chiral polymer ligand to the asymmetric addition of phenylethynyl zinc to various aldehydes has been studied. The results show that the soluble chiral polybinaphthols ligand in combination with Et_2Zn and $Ti(O^iPr)_4$ can exhibit excellent enantioselectivity for phenylacetylene addition to both aromatic and aliphatic aldehydes. The catalytically active center of the repeating unit ***S*-1** used as a catalyst produced the opposite configuration of the propargylic alcohols to that of ***S*-1**, on the contrary, the chiral polymer gave the same configuration as the optically active binaphthol moiety of the polybinaphthols ligand. Moreover, the chiral polymer ligand can be easily recovered and reused without loss of catalytic activity as well as enantioselectivity.

Keywords: (*S*)-2,2′-Binaphthol; Suzuki coupling; Asymmetric enantioselectivity

1. Introduction

Optically active 1,1′-bi-2-naphthol (BINOL) and its derivatives have attracted particular interests because their versatile backbone can be systematically modified by the introduction of functional groups based on steric and electronic properties.[1] According to the reported literature, the skeletal structure of BINOL can be selectively halogenated at the 3,3′- or 6,6′-positions of binaphthyl, leading to a variety of binaphthyl derivatives.[2] But so far there have been few reports on halogenation of BINOL at the 5,5′-positions except that Shimada and Lemaire reported the direct and facile synthesis of 5,5′-diiodo-/5,5′-dibromo-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl (BINAP), and Pirkle described the synthesis and chiral resolution of racemic 5,5′-dibromo-6,6′,7,7′-tetramethyl-2,2′-binaphthol.[3] Based on our current study, (*S*)-BINOL can be specifically brominated at 5,5′-positions in a mild condition to afford a pure product in an excellent yield when 6,6′-positions are occupied by *n*-butyl groups. 5,5′-Dibromo-6,6′-dialkyl-2,2′-binaphthol can further be used as an entry into a wide range of other derivatives by strategic placement of substituents at the well-defined molecular level, which will lead to the outcome of a new generation of novel binaphthyl-based derivatives for applications in asymmetric catalysis, chiral fluorescent sensors, and electro-optical devices.

In the past 10 years, Pu et al. have proposed and designed a series of novel chiral polymer ligands based on polybinaphthols as the Lewis acid to carry out highly enantioselective organic reactions, such as the additions to aldehydes, hetero-Diels–Alder reactions, 1,3-dipolar cycloadditions, reductions of ketones, and others.[4] Unlike the traditional polymeric chiral catalysts, which are prepared by anchoring a chiral ligand to a flexible and sterically irregular achiral polymer backbone, these stereoregular chiral BINOL-based polymer ligands can generate regularly oriented catalytic sites along the polybinaphthols chain backbone and produce a well-defined microenvironment around the

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catalytically chiral centers. Therefore it is possible to systematically adjust the microenvironment of the catalytic sites in these chiral polymer ligands to achieve the desired catalytic activity and stereoselectivity.[5] Chan et al. also reported earlier the soluble polymer-supported catalysts incorporating the chiral BINAP units in the polymer main chain, which showed high activity and stereoselectivity in asymmetric hydrogenation.[6] The use of soluble chiral polymer catalysts in asymmetric synthesis has important practical advantages. These soluble chiral polymers can catalyse asymmetric reactions in a homogeneous manner and thus have similar catalytic activity and stereoselectivity as the homogeneous parent system. When the reaction is completed, polymeric catalysts can beeasily separated from the reaction mixture by simple filtration or precipitation upon the addition of methanol. In addition, the recycling and recovery of chiral catalyst is particularly important since it is often more expensive to obtain these optically pure ligands.[5b,7]

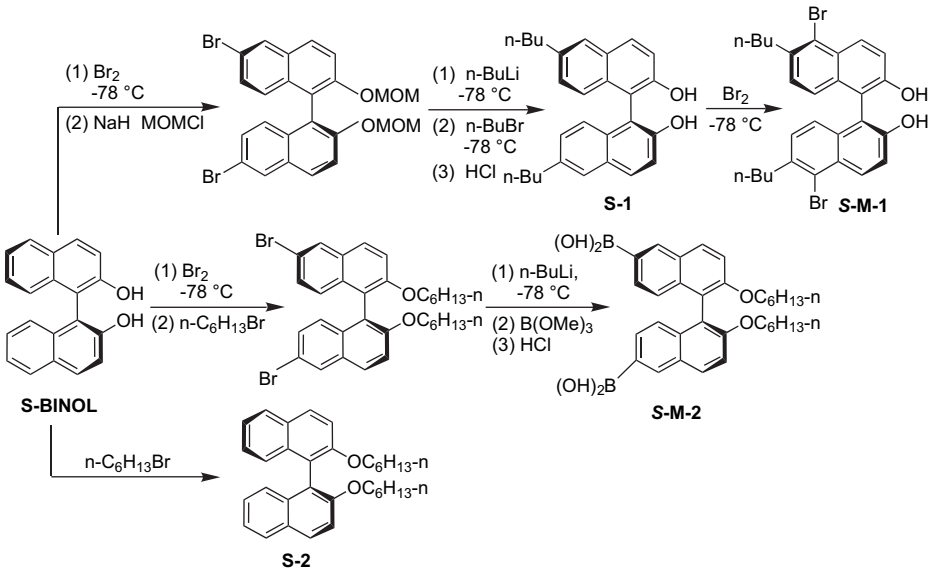
The enantioselective alkynylzinc addition to aldehydes is a very useful method for the synthesis of chiral propargyl alcohols, which are important versatile building blocks for asymmetric synthesis.[8] Since Ishizaki and Hoshino reported the first addition of alkynylzinc reagents to aldehydes in 1994,[9] some chiral ligands, such as *N*-methylephedrine,[8c] sulfonamide alcohol,[10] BINOL, and its derivatives,[11] have successfully been applied to this reaction in recent years. The BINOL derivative ligands show excellent enantioselectivity for the alkynylzinc addition to aromatic aldehydes. In this paper, we report the synthesis and asymmetric enantioselectivity of a soluble chiral polymer ligand incorporating the alternative (*S*)-2,2′-binaphthol at 5,5′-positions and (*S*)-1,1′-binaphthyl at 6,6′-positions. The chiral moieties of (*S*)-2,2′-bishexyloxy-1,1′-binaphthyl and (*S*)-6,6′-dibutyl-2,2′-binaphthol can regularly distribute along the polymer chain. This kind of polybinaphthols ligand substituted at 5,5′-positions of (*S*)-2,2′-binaphthol has not been reported so far. When the resulting chiral polymer was used to catalyze the addition reactions of phenylethynyl zinc to both aromatic and aliphatic aldehydes, the resulting products were obtained in excellent enantioselectivity. Moreover, the chiral polymer ligand can be easily recovered and reused without loss of catalytic activity as well as enantioselectivity.

2. Results and discussion

2.1. Syntheses and features of monomers and polymer

The chiral repeating units ***S*-1**, ***S*-2**, and the chiral monomers ***S*-M-1**, ***S*-M-2** were synthesized from the starting product (*S*)-BINOL (Scheme 1). ***S*-M-1** was prepared in an overall yield of 46% by a five-step synthesis. The hydroxyl groups of 6,6′-dibromo-2,2′-binaphthol were first protected by methoxymethyl chloride (MOMCl) according to the literature.[2d–f,12] (*S*)-6,6′-Dibutyl-2,2′-binaphthol (***S*-1**) could be obtained by deprotection of MOM groups of (*S*)-6,6′-dibutyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl, which was obtained by the reaction of (*S*)-6,6′-dibromo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl with *n*-butyllithium at −78 °C under a N_2 atmosphere, and followed by the addition of *n*-butyl bromide at −78 °C. ***S*-M-1** can be directly obtained by electrophilic aromatic bromination of (*S*)-6,6′-dibutyl-2,2′-binaphthol (***S*-1**) at 5,5′-positions in CH_2Cl_2 at −78 °C with 1.05 equiv of bromine without any further purification in a very high yield of 99%. ^{1}H NMR of (*S*)-6,6′-dibutyl-2,2′-binaphthol has a single peak of 5,5′-position protons at 7.66 ppm, but this single peak disappears in the ^{1}H NMR of ***S*-M-1**, which can be attributed to bromination at 5,5′-positions of (*S*)-6,6′-dibutyl-2,2′-binaphthol. The repeating unit ***S*-2** can be synthesized by the etherification of hydroxyl groups of (*S*)-BINOL with *n*-hexyl bromide in the presence of K_2CO_3 in refluxing CH_3CN solution. ***S*-M-2** can be obtained from (*S*)-6,6′-dibromo-2,2′-bishexyloxy-1,1′-binaphthyl according to the reported literatures.[13]

Based on Lin's report,[12b,14] while (*S*)-6,6′-dichloro-2,2′-bisethoxy-1,1′-binaphthyl was chosen as the starting material, bromination could undergo at 4,4′-positions in CH_2Cl_2 at

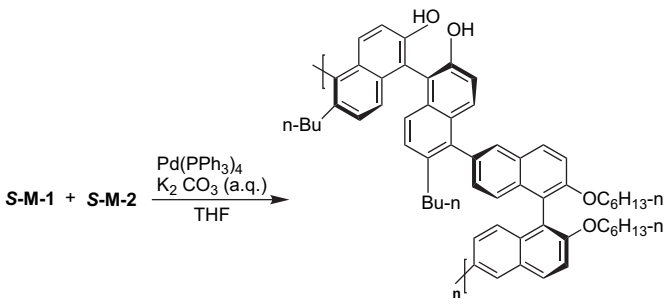


Scheme 1. Synthesis procedures of ***S*-1**, ***S*-2**, ***S*-M-1**, and ***S*-M-2**.

−78 °C with 10 equiv of bromine to directly afford a pure product 4,4′-dibromo-6,6′-dichloro-2,2′-bisethoxy-1,1′-binaphthyl in a very high yield of 98%. Pu also reported preparation of (*R*)- or (*S*)-4,4′,6,6′-tetrabromo-2,2′-bishexyloxy-1,1′-binaphthyl in AcOH under room temperature with 10 equiv of bromine when optically pure 2,2′-bishexyloxy-1,1′-binaphthyl was used as a starting material.[14b] Herein, (*S*)-6,6′-dibutyl-2,2′-binaphthol can undergo bromination substitution at 5,5′-positions at lower temperature with almost equivalent bromine because the butyl substituent groups at 6,6′-positions of BINOL will directly affect the reactivity and regioselectivity of 5,5′-positions. The reactivity of BINOL toward electrophile will be greatly enhanced by *n*-butyl substituent groups, which donate electron density to the BINOL. The bromination activating effect can be attributed to the large increase of electron density at 5,5′-positions of BINOL. Therefore, orientation of bromination is predominated by the only choice of 5,5′-positions.

A typical Suzuki reaction condition was applied to the polymerization (Scheme 2).[15] The C−C cross coupling process was easily carried out in THF and 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 a N_2 atmosphere. The polymerization went on in a good yield (95.3%) after 48 h. In this paper, the GPC result of the polymer shows the moderate molecular weight. This kind of soluble polymer ligand used as the catalyst for asymmetric addition of alkynylzinc to benzaldehyde can undergo homogeneous reaction. Generally, the soluble polymer ligands can afford higher catalytic activity and enantioselectivity than the insoluble polymer polybinaphthols catalysts due to the homogeneous asymmetric reaction.[5b,16] The recovered and reused polymer ligand could still show similar enantioselectivity (entries 4 and 9).

The polymer ligand is an air stable solid with pale color and shows good solubility in some common solvents such as THF, CH_2Cl_2, $CHCl_3$, toluene, and DMF, which can be attributed to the nonplanarity of the twisted polymer in the main-chain backbone and the flexible *n*-butyl or *n*-hexyloxy substitutent groups as the side chain of the polymer. Polymer ligand shows no glass transition temperature (T_g). Thermogravimetric analysis (TGA) of the polymer catalyst was carried out under a N_2 atmosphere at a heating rate of 10 °C/min. According to Figure 1, there is no loss of weight before 280 °C. However, polymer ligand undergoes an apparent one-step degradation at temperature ranging from 350 to 580 °C,



Scheme 2. Synthesis procedure of the chiral polymer ligand.

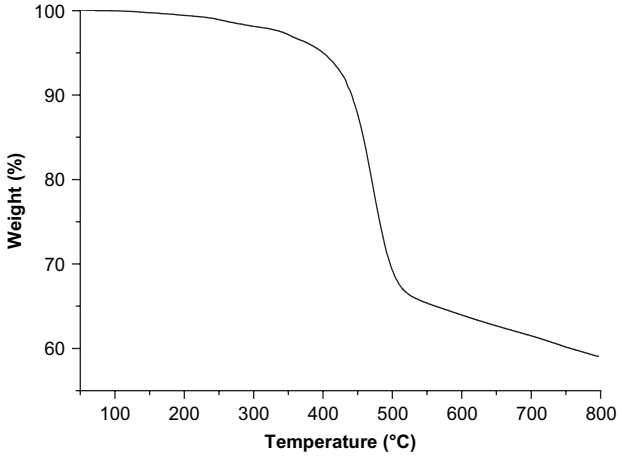


Figure 1. TGA curve of the chiral polymer ligand.

and tends to completely decompose at 700 °C. A total loss of about 41% is observed when the polymer was heated to 800 °C.

2.2. CD spectra

The specific rotation values ($[\alpha]_D^{20}$) of the repeating units (*S*)-6,6′-dibutyl-2,2′-binaphthol (***S*-1**) and (*S*)-2,2′-bishexyloxy-1,1′-binaphthyl (***S*-2**) are +82.9 (*c* 0.31, CH_2Cl_2) and −88.9 (*c* 0.72, CH_2Cl_2), but $[\alpha]_D^{20}$ of the chiral polymer ligand is +20 (*c* 0.5, CH_2Cl_2). CD spectral data of ***S*-1**, ***S*-2**, and the chiral polymer ligand in CH_2Cl_2 are listed in Table 1. ***S*-1**, ***S*-2**, and the polymer ligand exhibit intense CD signals with negative and positive Cotton effects in their CD spectra (Fig. 2). We can find great difference from CD spectra of ***S*-1**, ***S*-2**, and the chiral polymer ligand. ^1L_a band position of the chiral ligand polymer is almost similar as the chiral repeating units ***S*-1** and ***S*-2**. On the contrary, ^1L_a and ^1B_b band intensities of the repeating units ***S*-1** and ***S*-2** are as more than two times as that of the chiral polymer ligand. ^1B_b bands of ***S*-1** and ***S*-2** appear at 238 and 240 nm, but the chiral polymer ligand appears at 250 nm and shows red-shift of about 10 nm relative to ***S*-1** and ***S*-2**. Herein, we first report the synthesis of a soluble chiral polymer ligand incorporating the alternative (*S*)-2,2′-binaphthol at 5,5′-positions and (*S*)-1,1′-binaphthyl at 6,6′-positions. The chiral moieties of (*S*)-2,2′-bishexyloxy-1,1′-binaphthyl and (*S*)-6,6′-dibutyl-2,2′-binaphthol are alternatively organized in a regular chiral polymer chain. But the resulting polymer ligand has smaller specific rotation value, which can be attributed to the counteracting result of the opposite specific rotation signal of the repeating units ***S*-1** and ***S*-2** in the regular arrangement of the main-chain backbone.

Table 1
CD spectral data of the repeating units ***S*-1**, ***S*-2**, and the polymer ligand

	***S*-1** ($\times 10^6$)	***S*-2** ($\times 10^6$)	***P*-1** ($\times 10^5$)
$[\theta]$	−1.29 (226.0)	−0.776 (227.9)	−4.06 (224.0)
(λ_{max} in nm)	+1.59 (238.0)	+1.09 (240.1)	+3.82 (250.3)

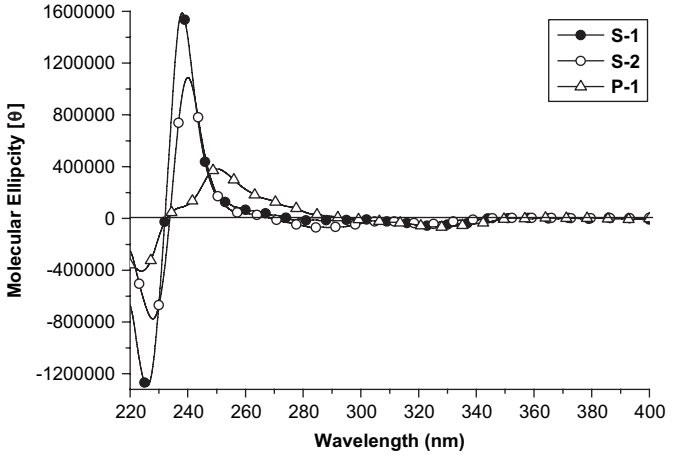
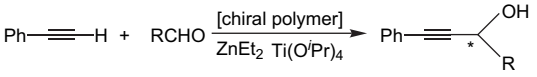


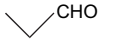
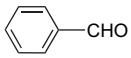
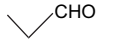
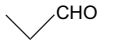
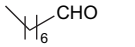
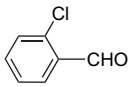
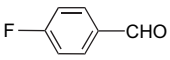
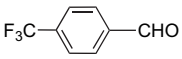
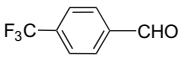
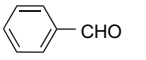
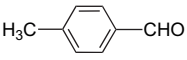
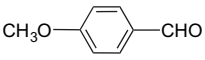
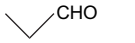
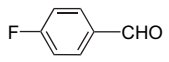
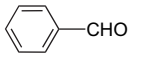
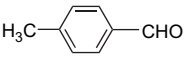
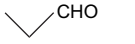
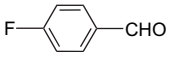
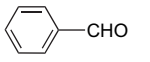
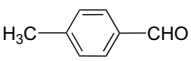
Figure 2. CD spectra of the repeating units ***S*-1**, ***S*-2**, and the chiral polymer ligand.

2.3. Asymmetric addition reactions of phenylacetylene with aldehydes

The asymmetric addition reactions of phenylacetylene with aldehydes in combination with Et_2Zn and $Ti(O^iPr)_4$ were carried out in the presence of the chiral polymer ligand in different solvents. The reactions were conducted at room temperature using phenylacetylene, Et_2Zn, $Ti(O^iPr)_4$, chiral polymer ligand (based on the repeating unit), and aldehyde with a molar ratio of 4:4:1:0.1:1. Chiral ligand (10 mol %) in combination with Et_2Zn and $Ti(O^iPr)_4$ were used as the addition reaction catalyst. In order to evaluate the efficiency of the chiral ligand for enantioselectivity of asymmetric addition, a variety of aldehydes were chosen as substrates in THF, CH_2Cl_2, and toluene. The enantioselective data are summarized in Table 2. The polymer catalyst shows excellent solubility in toluene, THF, and CH_2Cl_2, but quantitatively precipitated upon the addition of methanol. The different solubility provided a convenient and reliable method for the recycling of the chiral polymeric ligand. According to Table 2, we can find that this kind of soluble polybinaphthols ligand shows to be a good catalyst for the addition reactions of aldehydes with an excellent enantioselectivity and a moderate yield. The main side products of the asymmetric addition reaction can be attributed to the competitive reaction of diethylzinc and alkynylzinc to aldehydes. The results show that the resulting chiral polymer is an excellent enantioselective catalyst not only for the alkynylzinc addition to aromatic aldehydes, but also for the alkynylzinc addition to aliphatic aldehydes in the three solvents. Traditionally, polymeric chiral catalysts are prepared by anchoring a chiral ligand to a flexible and sterically irregular achiral polymer backbone. It is generally observed that the polymer-supported chiral catalysts are usually less efficient than their monomeric version, which 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 the traditional polymeric

Table 2
Reaction of phenylacetylene with aldehyde in the presence of chiral ligand[a]



Entry	Solvent	Aldehyde	Yield[b] (%)	ee[c] (%)	Configuration[d]
1[e]	Toluene		70	76	*R*
2[e]	Toluene		73	82	*R*
3	Toluene		83	87	*S*
4[f]	Toluene		75	85	*S*
5	Toluene		76	96	*S*
6	Toluene		85	67	*S*
7	Toluene		80	89	*S*
8	Toluene		90	81	*S*
9[f]	Toluene		89	92	*S*
10	Toluene		79	90	*S*
11	Toluene		84	97	*S*
12	Toluene		86	61	*S*
13	THF		80	98	*S*
14	THF		90	98	*S*
15	THF		86	57	*S*
16	THF		85	96	*S*
17	CH_2Cl_2		80	94	*S*
18	CH_2Cl_2		84	87	*S*
19	CH_2Cl_2		84	91	*S*
20	CH_2Cl_2		78	96	*S*

[a] Phenylacetylene/Et_2Zn/$Ti(O^iPr)_4$/ligand (based on the repeating unit)/aldehyde=4:4:1:0.1:1.
[b] Isolated yields.
[c] Determined by HPLC on Chiralcel OD-H column eluted with hexane/2-propanol (90:10, v/v) at 1.0 mL/min and detected at 254 nm.
[d] Absolute configuration of the corresponding propargylic alcohols.
[e] ***S*-1** was used as the ligand.
[f] The chiral polymer catalyst was reused.

chiral catalysts generates randomly oriented catalytic sites, which can not be systematically modified to achieve the desired catalytic active center and stereoselectivity.[17] Based on our study, the polymer catalyst incorporating optically active (*S*)-6,6′-dibutyl-2,2′-binaphthol moiety in the polymer main chain can show higher enantioselectivity than the catalytically active center of the repeating unit ***S*-1** (entries 1, 3 and 2, 10).

When the polymer ligand was used as the catalyst, the absolute configuration of the corresponding propargylic alcohol products is assigned as *S* by comparing its HPLC data with those previously reported literature,[11b,18] which is the same as the optically active binaphthol moiety of the polymer catalyst. On the contrary, while the small molecule ligands, such as optically active BINOL or the modified BINOL derivatives, were used as the catalyst for the enantioselective alkynylzinc addition to aldehydes, the resulting configuration of the propargylic alcohols is opposite to the configuration of the chiral catalyst. [11a,b,18] Based on our study, we draw the same conclusion that the *R* configuration of the propargylic alcohols can be obtained (entries 1 and 2) when the catalytically active center of the repeating unit ***S*-1** was used as the enantioselective catalyst for asymmetric addition reactions of phenylethynyl zinc to propionaldehyde and benzaldehyde in toluene. Currently, we are further doing the study on the change feature of the configuration of the propargylic alcohols based on other asymmetric addition reactions using the small molecule BINOL derivative catalysts and polybinaphthols ligands. In this paper, when the recycled chiral polymer ligand was reused for the asymmetric addition reaction of phenylethynyl zinc to propionaldehyde and *p*-trifluoromethylbenzaldehyde in toluene, 85% and 92% ee could be obtained (entries 4 and 9). The results show that the recycled polymer catalyst can keep similar enantioselectivity as the original chiral polymer ligand.

3. Conclusion

Pd-catalyzed Suzuki reaction was found to offer a simple access to the optically active polybinaphthols ligand. The chiral polymer ligand shows good solubility in some common solvents due to the nonplanarity of the twisted polymers in the main-chain backbone and flexible hexyloxy and *n*-butyl group substitutent on naphthyl rings as side chain of the polymer ligand, so that the asymmetric addition reactions can be carried out in homogeneous solution. The results indicate that the chiral polymer in combination with Et_2Zn and $Ti(O^iPr)_4$ can catalyze the asymmetric phenylacetylene addition to both aromatic and aliphatic aldehydes with high enantioselectivity to produce the chiral propargyl alcohols. Small molecule BINOL derivative catalyst produced the opposite configuration of the propargylic alcohols to that of the derivative, but the chiral polymer ligand incorporating 6,6′-dibutyl-2,2′-binaphthol moiety at 5,5′-positions afforded the same configuration as the catalytically active center. The chiral polymer ligand can be easily recovered and reused without loss of catalytic activity as well as enantioselectivity.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectral measurements were recorded on a 300-Bruker spectrometer with TMS as an internal standard. FTIR spectra were taken on a Nexus 870 FT-IR spectrometer. Specific rotation was determined with a Rudolph Research Analytical Autopol I apparatus. The ee value determination was carried out using chiral P–E Series200 HPLC with a Chiralpak OD-H column on a Waters chromatograph with a P–E Series200 UV/vis-detector. All solvents and reagents were of commercially available A.R. grade. (*S*)-2,2′-Binaphthol (BINOL) was purchased from Aldrich and directly used without purification. All reactions were performed under a N_2 atmosphere using Schlenk tube techniques. THF and toluene were purified by distillation from sodium in the presence of benzophenone. CH_2Cl_2 was distilled from P_2O_5.

4.2. Synthesis of (S)-6,6′-dibutyl-2,2′-binaphthol (*S*-1)

(*S*)-6,6′-Dibromo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (2.0 g, 3.8 mmol) was dissolved in anhydrous THF (30.0 mL). *n*-BuLi (3.8 mL, 2.5 M in hexanes, 9.5 mmol) was added by syringe injection at −78 °C under N_2 atmosphere. After the reaction mixture was stirred for 10 min, *n*-C_4H_9Br (2.1 g, 15.2 mmol) was added to the above solution at −78 °C under a N_2 atmosphere. The reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was extracted with ethyl acetate (2×50 mL). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate) (30:1, v/v) to afford a colorless viscous product (0.93 g, 51% yield). The product was dissolved in the mixed solvents of 10 mL THF and 10 mL methanol. Hydrochloric acid (15 mL, 12 M) solution was added to the above solution. The solution was stirred at room temperature for 8 h. After the removal of all solvents under reduced pressure, the residue was extracted with ethyl acetate (2×30 mL). The combined organic layers were washed with 2 M $NaHCO_3$ solution and brine twice, and then dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) (20:1, v/v) to afford a white solid product (0.71 g, 93.4% yield). Mp: 72–74 °C. $[\alpha]_D^{20}$ +82.9 (*c* 0.31, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J=8.9 Hz, 2H), 7.66 (s, 2H), 7.34 (d, J=8.9 Hz, 2H), 7.14 (dd, J=8.6 Hz, 2H), 7.08 (d, J=8.6 Hz, 2H), 4.96 (s, 2H), 2.72 (t, J=7.7 Hz, 4H), 1.68–1.60 (m, 4H), 1.42–1.34 (m, 4H), 0.93 (t, J=7.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 139.0, 132.1, 131.2, 130.0, 129.4, 127.3, 124.6, 118.0, 111.3, 35.9, 33.9, 22.8, 14.4. ν_{max} (KBr) 3503.4, 3421.9, 2950.1, 2921.8, 1598.1, 1507.3, 1474.1, 1363.7, 1214.1, 1142.6, 1124.5, 952.2, 880.6, 827.1 cm^{-1}.

4.3. Synthesis of (S)-5,5′-dibromo-6,6′-dibutyl-2,2′-binaphthol (*S*-M-1)

Bromine (0.14 mL, 2.8 mmol in 5 mL CH_2Cl_2) was slowly added to a solution of (*R*)-6,6′-dibutyl-2,2′-binaphthol (0.52 g, 1.33 mmol) in CH_2Cl_2 (10 mL) at −78 °C over 1 h. The solution was stirred overnight and gradually warmed to room temperature. The reaction was quenched with saturated $NaHSO_3$ solution (15 mL). The mixture was extracted with CH_2Cl_2 (2×30 mL). The combined organic layers were washed with water and saturated brine, and then dried over anhydrous Na_2SO_4. After the removal of solvent, a pure solid product ***S*-M-1** can directly be obtained in the yield of 99% (0.73 g) without further purification. Mp: 48–50 °C. $[\alpha]_D^{20}$ −13.3 (*c* 0.23, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J*=9.0 Hz, 2H), 7.46 (d, *J*=9.6 Hz, 2H), 7.17 (d, *J*=8.4 Hz, 2H), 7.01 (d, *J*=8.7 Hz, 2H), 5.04 (s, 2H), 2.93–2.92 (m, 4H), 1.67–1.62 (m, 4H), 1.49–1.42 (m, 4H), 0.99–0.94 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 139.1, 133.4, 131.5, 130.2, 128.9, 124.6, 124.0, 119.2, 111.3, 37.3, 32.7, 23.0, 14.3. ν_{max} (KBr) 3530.2, 3027.4, 2956.5, 2928.9, 1597.9, 1567.3, 1467.1, 1367.7, 1248.7, 1212.0, 1154.1, 1132.9, 970.7, 819.2 cm^{-1}. MS (ESI) *m*/*z*=554.4 (M+1). Anal. Calcd for $C_{28}H_{28}Br_2O_2$: C, 60.45; H, 5.07. Found: C, 60.41; H, 5.11.

4.4. Synthesis of the chiral polymer ligand

A mixture of ***S*-M-1** (420 mg, 0.76 mmol), ***S*-M-2** (389 mg, 0.76 mmol), and $Pd(PPh_3)_4$ (44 mg, 0.038 mmol, 5 mol %) was dissolved in THF (10 mL) and K_2CO_3 (15 mL, 1 M aqueous solution) and kept stirring at 85 °C under N_2. After refluxing for 48 h, the reaction mixture was cooled to room temperature, and the organic layer was 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. Methanol (100 mL) was added to precipitate the polymer. A pale solid was filtered off and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CH_2Cl_2 to precipitate in methanol again. ***P*-1** was dried under vacuum at room temperature for 24 h. The final yield was 95.3% (610 mg). $[\alpha]_D^{20}$ +20.0 (*c* 0.1, THF). M_w=10,760, M_n=9950, PDI=1.08. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (br, 12H), 1.18 (br, 20H), 1.50 (br, 8H), 4.09 (d, 4H), 5.06 (s, 2H), 7.32 (br, 6H), 7.43–7.77 (m, 8H), 7.88 (d, 2H), 8.03 (s, 2H). ν_{max} (KBr) 3532.2, 3406.5, 3059.2, 2953.1, 2925.9, 2856.4, 1909.8, 1777.1, 1657.3, 1592.9, 1463.5, 1382.7, 1338.0, 1243.1, 1149.3, 1089.0, 1045.8, 890.0, 820.8, 745.7 cm^{-1}.

4.5. Typical procedure for asymmetric alkynylation reactions

Phenylacetylene (1.0 mmol) was added into a 10 mL Schlenk flask containing 1 mL toluene at room temperature under a N_2 atmosphere. The mixture was stirred and followed by the addition of a 2.0 M solution of diethylzinc in toluene (1.0 mmol). The resulting solution was stirred for 1 h, and then $Ti(O^iPr)_4$ (0.25 mmol) was added to the above solution. After the solution was stirred for 0.5 h, the chiral catalyst (based on the BINOL unit) (0.025 mmol, 10 mol %) was added to the solution. The homogenous solution was stirred at room temperature for 1 h, and then aldehyde (0.25 mmol) was added via syringe. The resulting mixture was stirred at room temperature for 24 h. The solution was quenched by adding saturated NH_4Cl (2 mL). The solution was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. The CH_2Cl_2 solution was concentrated in vacuo and treated with MeOH, and then the polymer was filtrated and washed with water. The chiral polymer was washed with 1 N HCl several times to recover the chiral ligand for the next reaction of phenylacetylene to aldehydes. The MeOH solution was concentrated under reduced pressure, and the crude product can be purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) (18:1, v/v) to afford a pure product. Enantiomeric excess values were determined by HPLC with a Chiralcel OD-H column.

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