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Graphical Abstract

Preparation of several BINOL-based polymeric ligands for the enantioselective addition of triethylaluminium to aromatic aldehydes Dacai Liu, Kunbing Ouyang *, Nianfa Yang * OH Poly-BINOL/Ti(O-*i*-Pr)₄ THF, 0 °C, 24 h CHO R Up to 93% ee Up to 96% yield



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Preparation of several BINOL-based polymeric ligands for the enantioselective addition of triethylaluminium to aromatic aldehydes

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ABSTRACT

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1. Introduction

Asymmetric catalysis is an area of utmost importance in organic chemistry.¹ Adaptation of small chiral molecule catalyst to enantioselective synthesis has been well-studied in past decades.² In the contrast, the application of chiral polymeric ligands remains rare. The inherent advantages of chiral polymeric catalysts such as easy separation of product from reaction mixture, readily recovery and reuse of the expensive chiral catalyst ³ have made chiral polymeric ligands a promising area in both green chemistry and combinatorial chemistry.⁴ In addition, the employment of polymeric catalysts makes it possible to conduct reactions in flow reactors or in flow membrane reactors for large-scale production.⁵ Therefore, the development of polymeric ligand for asymmetric catalysts has long been attractive and of great significance.

Optically active 1,1'-binaphthol (BINOL) and its derivatives are widely used in asymmetric reactions, such as asymmetric alkylation, asymmetric hydrogenation, Diels-Alder reaction, asymmetric epoxidation of α , β -unsaturated ketone, etc.⁶ Many BINOL-based polymeric chiral ligands have been developed and successfully applied as chiral catalyst in these model reactions.⁷ Traditional approach for the preparation of polymers involves the development of a monomer and then anchored it to an achiral and sterically irregular polymer backbone. Although many polymersupported catalysts have been obtained in this way, a significant drop of enantioselectivity is often observed when a monomeric

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The synthesis of several polystyrene-supported BINOL (1,1-binaphthol) ligands via radical polymerization is described. These BINOL-based polymeric ligands were applied to the enantioselective addition of triethylaluminium to aromatic aldehyde in the presence of titanium isopropoxide. The products were obtained with up to 93% enantiomeric excess (ee) in good to excellent yield. The ligands were easily recovered and reused without losing their catalytic activity as well as enantioselectivity.

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chiral catalyst is attached to a polymer support due to the changes in the microenvironment of the catalytic sites.⁸

We have been working on asymmetric syntheses based on polymeric chiral catalysts for many years and have made significant progress in many asymmetric reactions.⁹ However, almost no polymeric ligands performed efficiently in the asymmetric addition of triethylaluminium to aromatic aldehyde in the past decades. Herein, we report the synthesis of several chiral polymers bearing BINOL that exhibited high catalytic activity and enantioselectivity in the addition of triethylaluminium to aromatic aldehyde. The products were obtained in good yields with high enantioselectivity. The polymeric catalysts were also proven to be more efficient with higher selectivity than its monomeric unit.

2. Results and discussion

Four polymeric ligands were successfully synthesized from commercially available (*S*)-BINOL as depicted in Scheme **1**. Chiral (*S*)-BINOL reacted with chloromethyl ether to give (*S*)-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene **1**.¹⁰ (*S*)-3-iodo-2,2'-bis(methoxymethyl)-1,1'-binaphthalene **2** was easily prepared from readily accessible **1** through a lithiation-iodination sequence.¹¹ The coupling of (*S*)-**2** with 4-vinyphenyl boronic acid was successfully carried out using Pd(PPh₃)₄ as catalyst in dioxane to afford the monomer (*S*)-3-(4-vinyphenyl)-2,2'-bis(methoxymethyl)-1,1'- binaphthalene (**3**) in good yield (93%).

Tetrahedron

Poly-4a, Poly-4b and Poly-4c were obtained by free radical M copolymerization of (*S*)-3 with styrene.

The purpose of copolymerization of (*S*)-**3** with styrene was to improve the solubility of the polymer in organic solvent so that the catalytic reaction could be carried out in various solvents such as toluene, CH₂Cl₂, THF and so on.^{12,3b} In addition, a component of the non-cross-linked copolymer backbones might affect the catalytic activity and enantioselectivity.¹³ The protecting groups were removed by treatment of acid to afford Poly-**5a** (M_n = 1.05 × 10⁴, PDI = M_w/M_n = 1.42), Poly-**5b** (M_n = 6.70×10^3 , PDI = M_w/M_n = 1.47) and Poly-**5c** (M_n = 3.80 × 10³, PDI = M_w/M_n = 1.57). All of these polymers are well soluble in solvents such as CH₂Cl₂, toluene, THF and ethyl acetate, and could be readily precipitate by adding the solution to methanol. By being precipitated in methanol for several times, the monomer could be completely removed. The structure and purity of the polymers were determined by ¹H NMR spectra.



Scheme 1. Synthesis of polymer 5a, 5b, 5c and 10

We were also interested in similar systems wherein the 4vinyphenyl was attached to the BINOL core at the 6 positions of BINOL, which are sufficiently far apart from the catalytic active center so that primary steric effect becomes an unimportant factor. Poly-**10** ($M_n = 6.52 \times 10^3$, PDI = $M_w/M_n = 1.46$) was synthesized in a similar way as presented in Scheme **1**. (*S*)-**6** and (*S*)-**7** were obtained for further use as reported.¹⁴ Later, compound (*S*)-**7** was subsequently coupled with 4vinyphenylborionic acid to give the 6-substituted monomer (*S*)-6-(4-vinyphenyl)-2,2'-bis(methoxymethyl)-1,1'-binaphthalene (**8**). The copolymerization of (*S*)-**8** with styrene was carried out in toluene using 2,2-azobisisobutyronitrile (AIBN) as initiator, followed by deprotection of the group -CH₂OCH₃ to afford Poly-**10** in high yield (89%) with good solubility.

Almost all of the reported works on asymmetric addition of triethylaluminium (Et₃Al) to aromatic aldehyde focused on small molecular catalysts.¹⁵ The study of polymeric ligands remains rare as mentioned above. As our continued interest in chiral catalysts, we tried to apply the polymeric ligands in this asymmetric addition reaction. Initially, we tested the reaction of triethylaluminium and benzaldehyde as a model example. To evaluate efficiency of the soluble polymeric ligands, the reactions were carried out in the presence of the polymeric ligands (5 mol%), with Et₃Al (3 equiv) and titanium tetraisopropoxide (1.4 equiv) in THF at 0 °C (Table 1). After 24 h, (S)-1phenylpropanol was obtained in moderate yields with moderate selectivity. Poly-5a possessed the highest level of enantioselective induction (61% ee) in 75% yield (Table 1, entry 1) among the three catalysts. Polymeric catalyst Poly-5b with a lower loading of BINOL led to a decrease in both ee (57%) and yield (72%) (Table 1, entry 2). The employment of Poly-5c (Table 1, entry 3), which contained the lowest loading of BINOL, gave similar result to that of Poly-5b. These results suggested that the reaction was majorly promoted by the BINOL moiety on the polymer chain. The chiral polymeric catalyst 6-substitued BINOL Poly-10 gave lowest enantioselectivity (37%) and yield (43%) (Table 1, entry 4) as expected. It can be inferred that the substituent on the 6-position of BINOL would lead to a drop in the catalytic activity of the ligand.

Table 1. Asymmetric reaction of Et_3Al with benzaldehyde catalyzed by various ligands

	PhCHO + Et₃Al ^{Ti(O-}	i-Pr)₄/ Ligand OH THF Ph	
Entry ^a	Ligand	Yield (%) ^b	ee ^c (%)
1	Poly-5a	75	61
2	Poly-5b	72	57
3	Poly-5c	70	56
4	Poly-10	43	37

^a Reactions were carried out with 5 mol% of catalyst, 1.0 mmol benzaldehyde, 3.0 mmol Et₃Al, 1.4 mmol Ti(O-*i*-Pr)₄, in 5 mL THF at 0 °C for 24 h. ^b Isolated yield. ^c Determined by HPLC using Chiralcel OD-H column.

It is well known that the enantioselectivity of asymmetric reactions are strongly affected by solvent, temperature, and the amount of catalyst. To evaluate these effects, we investigated the asymmetric reaction of Et₃Al with benzaldehyde catalyzed by the chiral polymeric ligand Poly-5a under various reaction activity conditions, and compared the catalytic and enantioselectivity with its monomeric unit. The results are summarized in Table 2. We chose THF, DCM and toluene to examine the solvent effects. The reaction carried out in toluene led to the formation of (S)-1-phenylpropan-1-ol with only 33% ee in 45% yield (Table 2, entry 2), while the reaction preformed in DCM gained a slightly higher yield and ee (Table 2, entry 1). To our delight, when THF was used as the solvent, the ee increased to 61% in 75% yield (Table 2, entry 3). Ti(O-i-Pr)₄ was proven to be crucial to both ee and yield (Table 2, entries 3-7). The addition of 3.0 eq. of Ti(O-*i*-Pr)₄ afforded expected product in 90% yield with up to 83% ee. Increasing the amount of $Ti(O-i-Pr)_4$ to 4.0 eq. resulted in a better yield with a slight drop of ee (Table 2, entry 7). Different amount of Et₃Al was then screened (Table 2, entries 7-9). When 2.0 eq. of Et₃Al was used, the yield was only 57% (Table 2, entry 8). The yield rapidly increased to 98% when 4.0 eq. of Et_3Al was employed while the ee dropped to 76% (Table 2, entry 9). When the reaction was carried out at 25 °C, the desired product was obtained in 78% yield with 75% ee. However, the reaction system became more complex (Table 2, entry 10). When the reaction temperature lowered to -15 °C, the product was

Table 2. Asymmetric reaction of Et_3AI with benzaldehyde catalyzed by Poly-5a PhCHO + Et_3AI $\frac{Ti(O-i-Pr)_4/Ligand}{Solvent}$ Ph							
Entry	Solvent	Et ₃ Al/(eq.)	Ti(O- <i>i</i> -Pr) ₄ (eq.)	T/(°C)	catalyst /(mol%)	Yield/(%) ^a	ee/(%) ^b
1	CH ₂ Cl ₂	3.0	1.4	0	5	51	41
2	Toluene	3.0	1.4	0	5	45	33
3	THF	3.0	1.4	0	5	75	61
4	THF	3.0	2.0	0	5	82	79
6	THF	3.0	3.0	0	5	90	83
7	THF	3.0	4.0	0	5	95	78
8	THF	2.0	3.0	0	5	57	82
9	THF	4.0	3.0	0	5	98	76
10	THF	3.0	3.0	25	5	78	75
11	THF	3.0	3.0	-15	5	80	79
12	THF	3.0	3.0	0	10	92	91
13	THF	3.0	3.0	0	15	87	85
14 ^c	THF	3.0	3.0	0	10	95	87
15	THF	3.0	3.0	0	0	85	0

Isolated yield. ^b Determined by HPLC using Chiralcel OD-H column. ^c The monomeric unit 12 was used as catalyst.

achieved in 80% yield with 79% ee (Table 2, entry 11). The yield and selectivity of the product were found be sensitive to the amount of catalyst. An increase in the catalyst loading from 5 mol% to 10 mol% at 0 °C resulted in a large increase in the enantioselectivity (91% ee) and a slight increase of yield (92%, Table 2, entry 12). The product was obtained with a slight loss of both the ee and yield when 15 mol% catalyst was used (Table 2, entry 13). When the reaction was carried out without any ligand, no enantioselectivity was observed (Table 2, entry 15). For comparison with Poly-5a, the monomeric unit (S)-3-(4vinyphenyl)-1,1'-binaphthalene (12), which was synthesized via a simple catalytic hydrogenation reaction (Scheme 2), was induced to the model reaction. The product was obtained in 95% yield with a slight loss of ee 87% (Table 2, entry 14). In consideration of the unrecyclable nature of compound 12, the optimized combination for the asymmetric addition of Et₃Al to benzaldehyde was realized: 10 mol% of Poly-5a, 1.0 mmol aldehyde, 3.0 eq. of Et₃Al 3.0 eq. of Ti(O-*i*-Pr)₄, and THF as the solvent, and the reaction was set at 0 °C for 24 h.



Scheme 2 Synthesis of (S)-3-(4-ethyl)-2,2'-bis(methoxymethyl)-1,1'- binaphthalene 12

With the optimized condition in hand, we examined the scope of the enantioselective addition of aldehydes to study the generality of the ligand Poly-**5a**. The results are summarized in Table **3**. As presented in Table **3**, Poly-**5a** showed a satisfying level of enantioselective for most aromatic aldehydes. The position of the electron-donating -OCH₃ substituent on the aromatic ring (Table **3**, entries 2 and 3) had little effect on the ee of the product. Asymmetric Addition of the aryl aldehyde proceeded with excellent enantioselectivity. The ethylation of 4-phenylbenzaldehyde gave the highest ee 93% (Table **3**, entry 8).

Table 3. Enantioselective addition of Et_3Al to various aromatic aldehydes catalyzed by Poly-5a

R-CHO + Et ₃ AI	Ti(O-i-Pr) ₄ / Poly-5a	OH
	THF. 0 ℃. 24 h	

1				
Entry ^a	R	Yield	ee ^c	Config. ^d
		(%) ^b	(%) ^c	
1	Phenyl	92	91	S
2	2-Methoxyphenyl	94	89	S
3	3-Methoxyphenyl	93	88	S
4	4-Chlorophenyl	92	86	S
5	4-Bromophenyl	87	85	S
6	2-Phenylvinyl	93	73	S
7	3-Phenylpropyl	75	77	S
8	4-Phenylphenyl	90	93	S
9	1-Naphthyl	96	91	S
10	2- Naphthyl	95	86	S
11	9-Anthryl	94	85	S

^a Reactions were carried out with 10 mol% of Poly-**5a** (as a BINOL monomer), 1.0 mmol aldehyde, 3.0 mmol Et₃Al, 3.0 mmol Ti(O-*i*-Pr)₄, in 5 mL THF at 0 °C for 24 h. ^b Isolated yield. ^c Determined by HPLC using a Chiralcel OD-H column. ^d Absolute configurations were determined by comparison with the sign of specific rotations reported in the literature.¹⁶

Electron-withdrawing groups (Table **3**, entries 4 and 5) resulted in little differences in both the ee and yield. The reaction of 1-, 2naphthaldehyde and 9-anthracene resulted in excellent yield (94%-96%) with good ee (85%-91%), respectively (Table **3**, entries 9-11). It was also noteworthy that the addition of cinnamyl aldehyde or benzenepropanal also furnished the corresponding alcohol smoothly with relatively lower ee 73% and 77% (Table 3, entries 6 and 7). These observations M suggested that the ligand Poly-**5a** would not work efficiently in the asymmetric addition of aliphatic aldehyde with Et_3Al . In summary, a series of secondary alcohols could be efficiently prepared by asymmetric addition of the aldehyde in good yields with high enantioselectivities in the presence of Poly-**5a**.

It is remarkable that the chiral ligand Poly-5a can be easily separated and recycled. The recovered Poly-5a was used for the asymmetric addition of Et₃Al to benzaldehyde repeatedly (Table 4). The results show that ligand Poly-5a could be reused at least four times without obvious loss of catalytic activity as well as enantioselectivity.

Table 4 Asymmetric reaction of Et_3Al with benzaldehyde catalyzed by the recovered Poly-5a a

Cycle	1	2	3	4
Yield (%) ^b	91	90	92	89
Ee (%) ^c	90	88	89	90

^a Reactions were carried out with 10 mol% of recovered catalyst, 1.0 mmol benzaldehyde, 3.0 mmol Et₃Al, 3.0 mmol Ti(O-*i*-Pr)₄, in 5 mL THF at 0 °C for 24 h. ^b Isolated yield. ^c Determined by HPLC using a Chiralcel OD-H column.

3. Conclusions

In summary, four new chiral polymeric ligands have been synthesized from commercial available BINOL and styrene. Its activity in catalytic asymmetric addition of triethylaluminum to aryl aldehyde was studied. The products were obtained with up to 93% ee and 96% yield. Meanwhile, Poly-**5a** exhibited good activity even after being used four times. The development of other asymmetric reactions using these polymeric ligands is currently ongoing in our group.

4. Experimental

General

¹H NMR and ¹³C NMR spectra were performed on a Bruker ARX 400 MHz spectrometer using deuterated chloroform as solvent and tetramethylsilane (TMS) as the internal standard. Optical rotation data were measured on a Perkin Elmer Model 341 LC Polarimeter at 365 nm. GPC analysis was performed with a J ASCO-GPC system consisting of DG-1580-53 degasser, PU-980 HPLC pump, UV-970 UV/Vis detector, RI-930 RI detector and CO-2065-plus column oven (at 38°C) using two connected Shodex GPC-KF-804L columns in THF (sample concentration = 1 wt %; flow rate = 1.0 mL/min). The molecular weight was calibrated with commercially available polystyrene. All reagents were used as supplied commercially unless otherwise noted. THF and toluene were distilled from sodium under N₂ before use.

Synthesis of (S)-3-(4-vinyphenyl)-2,2'-bis(methoxymethyl)-1,1'- binaphthalene (S-3)

A mixture of (S)-3-iodo-2,2'-bis(methoxy(methoxy))-1,1'binaphthalene (2.001 g, 4.0 mmol), 4-vinyphenylborionic acid (0.888 g, 6.0 mmol) and Pd(PPh₃)₄ (0.230 g, 0.2 mmol) in aqueous 2 M Na₂CO₃ (5 mL) and 1,4-dioxane (30 mL) was heated under reflux for 24 h under argon atmosphere. The reaction mixture was poured into water and extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate (MgSO₄) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (using 10 % ethyl acetate in toluene as eluent) to give 1.701 g (93% yield) of (*S*)-3-(4-vinyphenyl)-2,2'bis(methoxymethoxy) -1,1'- binaphthalene (*S*-3) as a white solid. m.p. 65.2 - 67.2 °C. $[\alpha]_{365}^{25} = -486$ (c = 1 mg/mL, THF). Elem. Anal. Calcd. for C₃₂H₂₈O₄: C 80.65, H 5.92; Found: C 80.62, H 5.94. IR: 3052, 2823, 1939, 1621, 1131, 993 cm⁻¹; ¹H NMR (400 MHz) δ 8.00 - 7.83 (m, 4H), 7.71 (d, *J* = 6.9 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.44 - 7.34 (m, 2H), 7.26 (m, 4H), 6.78 (dd, *J* = 17.0, 11.2 Hz, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 5.19 (d, *J* = 5.7 Hz, 1H), 5.08 (d, *J* = 6.5 Hz, 1H), 4.34 (d, *J* = 15.7 Hz, 2H), 3.23 (s, 3H), 2.29 (s, 3H). ¹³C NMR (100 MHz) δ 153.02, 151.17, 138.71, 136.60, 135.26, 134.21, 133.45, 131.12, 130.29, 129.92, 129.82, 129.77, 128.13, 127.92, 126.63, 126.51, 126.35, 126.27, 126.02, 125.93, 125.30, 124.22, 121.28, 116.84, 114.02, 98.81, 95.13, 56.04.

Synthesis of Poly-4a, Poly-4b and Poly-4c

2,2'-Azobisisobutyronitrile (AIBN, 0.048 g, 5 mol%) and (S)-3 (0.500 g) was added to a small dry Schlenk flask. The flask was thoroughly purged with nitrogen for three times and then a toluene solution of styrene (0.500 g in 2 mL) was added via degassed syringes. The mixture was stirred for 36 h at 85 °C. After cooling to room temperature the polymer was precipitated by addition to 50 mL methanol for several times. The precipitate was filtered and dried in vacuo at 40 °C for 4h to give 0.930 g of (93% yield) Poly- 4a as a white powder. $[\alpha]_{365}^{25} = -411$ (c = 1 mg/mL , THF). $M_n = 1.20 \times 10^4$, PDI = $M_w/M_n = 1.38$. IR: 3086, 2919, 2343, 1651, 1414, 975 cm⁻¹; ¹H NMR (400 MHz) δ 7.94 (br), 7.86 (br), 7.22 (br), 6.56 (br), 5.10 (br), 4.22 (br), 3.20 (br), 2.13 (br), 1.44 (br). Poly-4b (95% yield) was prepared according to the procedure mentioned above using 2.0 eq. styrene, $[\alpha]_{365}^{25} = -$ 378 (c = 1 mg/mLl, THF), $M_n = 8.20 \times 10^3$, PDI = $M_w/M_n = 1.40$. Poly-4c (93% yield) was prepared according to the procedure mentioned above using 5.0 eq. styrene, $\left[\alpha\right]_{365}^{25} = -102$ (c =1 mg/mL, THF), $M_n = 4.08 \times 10^3$, PDI = $M_w/M_n = 1.48$.

Synthesis of Poly-5a, Poly-5b and Poly-5c

4 mL of concentrated hydrochloric acid was added to a THF (50 mL) solution of Poly-4a (0.501 g) at 0°C. The mixture was then stirred at room temperature for 24 h. The mixture was extracted with CH₂Cl₂, the extractive was washed with saturated NaHCO₃ and then was poured into methanol to precipitate polymer. The polymer was precipitated in 50 mL methanol twice. The polymer was filtered and dried in vacuo at 40 °C for 4 h to give 0.431 g (86% yield) of Poly-**5a** as a white powder. $[\alpha]_{365}^{25} = -$ 578 (c =1 mg/mL, THF). $M_n = 1.05 \times 10^4$, PDI = $M_w/M_n = 1.42$. IR: 3524, 2985, 2356, 1601, 1311, 999 cm⁻¹; ¹H NMR (400 MHz) δ: 7.86 (br), 7.05 (br), 6.57 (br), 5.15 (br), 1.85 (br), 1.45 (br). Similarity, Poly-5b and Poly-5c was prepared according to the procedure mentioned above method. For Poly-**5b**: $\left[\alpha\right]_{365}^{25} = -415$ (c = 1 mg/mL, THF). $M_n = 6.70 \times 10^3$, PDI = $M_w/M_n = 1.47$. For Poly-5c: $[\alpha]_{365}^{25} = -134$ (c = 1 mg/mL, THF). $M_n = 3.80 \times 10^3$, PDI $= M_w/M_n = 1.57.$

Synthesis of (*S*)-6-(4-vinyphenyl)-2,2'-bis(methoxymethyl)-1,1'- binaphthalene (*S*-8)

A mixture of (*S*)-6-bromo-2,2'-bis(methoxymethoxy)-1,1'binaphthalene (2.260 g, 5.0 mmol), 4-vinyphenylborionic acid (1.480 g, 10.0 mmol), and Pd(PPh₃)₄ (0.446 g, 0.4 mmol) in aqueous 2 M Na₂CO₃ (5 mL) and 1,4-dioxane (30 mL) was heated to reflux for 48 h under argon atmosphere. The reaction mixture was poured into water and extracted with CH₂Cl₂ (2 × 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate (MgSO₄) and concentrated in vacuo. The residue was purified by flash column chromatography on silica

(59 % yield) of (S)-6-(4-vinyphenyl)-2,2'-1.400 g bis(methoxymethoxy)-1,1'-binaphthalene (S-8) as a white powder. m.p. 85.1 - 86.9 °C. $[\alpha]_{365}^{25} = -351$ (c = 1 mg/mL, THF). Elem. Anal. Calcd. for C₃₂H₂₈O₄: C 80.65, H 5.92; Found: C 80.64, H 5.95. IR: 2903, 2819, 2354, 1620, 1239, 1012 cm⁻¹; ¹H NMR (400 MHz) δ 8.09 (s, 1H), 7.99 (dd, *J* = 15.8, 9.0 Hz, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.67-7.57 (m, 4H), 7.49 (d, J = 8.0 Hz, 3H), 7.36 (t, J = 7.2 Hz, 1H), 7.26-7.19 (m, 3H), 6.76 (dd, J = 17.5, 10.9 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.9 Hz, 1H), 5.10 (d, J = 6.7 Hz, 2H), 5.02-4.97 (m, 2H), 3.18 (s, 3H) 3.16 (s, 3H). ¹³C NMR (100 MHz) δ 152.96, 152.82, 140.45, 136.54, 136.28, 134.14, 133.41, 130.22, 130.01, 129.84, 129.59, 128.05, 127.35, 126.82, 126.49, 126.30, 125.86, 125.66, 125.63, 124.23, 121.25, 121.25, 117.77, 117.38, 113.92, 95.26, 95.22, 55.95.

Synthesis of Poly-9

To a toluene solution of **6** (0.303 g) was added AIBN (0.029 g) and styrene (0.601 g). The solution was purged with argon thoroughly for three times. Polymerization continued for 48 h at 85°C. After cooling to room temperature the polymer was precipitated by pouring into 50 mL methanol to obtain precipitate. The obtained precipitate was precipitated in methanol for several times. Then the precipitate was filtered and dried in vacuo at 40°C for 4 h to give 0.765 g (85% yield) of Poly-**9** as a white powder. $[\alpha]_{365}^{25} = -242$ (c = 1 mg/mL, THF). $M_n = 7.95 \times 10^3$, PDI = $M_w/M_n = 1.35$. IR: 3010, 2921, 2348, 1603, 1489, 1012 cm⁻¹; ¹H NMR (400 MHz) δ 7.98 (br), 7.6 (br), 7.22 (br), 6.57 (br), 5.05 (br), 3.16 (br), 1.85 (br), 1.42 (br).

Synthesis of Poly-10

4 mL of concentrated hydrochloric acid was added to a THF (in 50 mL) solution of Poly-**9** (0.503 g) at 0 °C. The mixture was then stirred at room temperature for 24 h. The mixture was extracted with CH₂Cl₂. The extractive was washed with saturated NaHCO₃ and precipitated into 50 mL methanol twice. The precipitate was filtered and dried in vacuo at 40 °C for 4 h to give 0.445 g of (89 % yield) Poly-**10** as a white powder. $[\alpha]_{365}^{25} = -299$ (c =1 mg/mL, THF). M_n = 6.52×10^3 , PDI = M_w/M_n = 1.46. IR: 3523, 3022, 2921, 2354, 1501, 1006 cm⁻¹; ¹H NMR (400 MHz) δ 7.95 (br), 7.38 (br), 7.05 (br), 6.58 (br), 5.08 (br), 1.84 (br), 1.42 (br).

Synthesis of (S)-3-(4-vinyphenyl)-2,2'-bis(methoxymethyl)-1,1'- binaphthalene (S-11)

A mixture of (S)-3 (0.301 g) and 10 mol% Pd-C catalyst (0.021 g) in 10 mL THF was add to a small autoclave. The mixture was filled with hydrogen (0.3 MPa). The reaction continued for 24 h at 110 °C. After being cooled to room temperature, the mixture was filtrated and the filtrate was evaporated in vacuo to afford the pure product 0.291 g (98% yield) of (S)-3-(4-vinyphenyl)-2,2'-bis(methoxymethyl)-1,1'binaphthalene (11) as a white crystal. m.p. 79.3-81.1 °C. $[\alpha]_{365}^{25} = -$ 436(c = 1 mg/mL, THF). Elem. Anal. Calcd. for $C_{32}H_{30}O_4$: C 80.31, H 6.32; Found: C 80.29, H 6.33. IR: 3046, 2944, 2354, 1716, 1233, 1000 cm⁻¹; ¹H NMR (400 MHz) δ 7.97-7.85 (m, 4H), 7.62 (dd, J = 18.1, 8.3 Hz, 3H), 7.37 (dd, J = 13.3, 5.5 Hz, 2H), 7.32-7.21 (m, 6H), 5.17 (d, J = 6.7 Hz, 1H), 5.07 (d, J = 6.8 Hz, 1H), 4.35 (d, J = 5.5 Hz, 1H), 4.30 (d, J = 5.6 Hz, 1H), 3.22 (s, 3H), 2.74 - 2.68 (m, 2H), 2.28 (s, 3H), 1.28 (t, J = 7.5 Hz, 3H). ¹³C NMR (100 MHz) δ 153.04, 151.25, 143.40, 136.47, 135.65, 134.26, 133.32, 131.15, 130.32, 129.84, 129.71, 129.68, 128.07,

gel (using 10 % ethyl acetate in petroleum ether as eluent) to give M A27.90, 126.60, 126.37, 126.18, 126.00, 125.20, 124.21, 121.47, 1.400 g (59 % yield) of (S)-6-(4-vinyphenyl)-2,2'- 116.92, 98.71, 95.19, 56.01, 55.99, 28.73, 15.75.

Synthesis of (S)-3-(4-vinyphenyl) -1,1'- binaphthalene (S-12)

5 mL of concentrated hydrochloric acid was added to a solution of (S)-10 (0.501 g) in THF (20 mL) at 0°C. The mixture was stirred at room temperature for 6 h and the reaction was quenched with water. Then the mixture was extracted with ethyl acetate (2 \times 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate (MgSO₄) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (using 20 % ethyl acetate in petroleum ether as eluent) to afford 0.371 g (90% yield) of pure (S)-3-(4-vinyphenyl) -1,1'- binaphthalene (S-12) as a yellow bubble. $\left[\alpha\right]_{365}^{25} = -678$ (c = 1 mg/mL, THF). Elem. Anal. Calcd. for C₂₈H₂₂O₂: C 86.13, H 5.68; Found: C 86.15, H 5.65. IR: 3494, 2957, 2360, 1609, 1120, 744 cm⁻¹; ¹H NMR (400 MHz) δ 8.06-7.95 (m, 2H), 7.90 (t, J = 7.1 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.47-7.19 (m, 8H), 7.15 (d, J = 8.3 Hz, 1H), 5.30 (s, 1H), 5.12 (s, 1H), 2.73 (q, J = 7.5 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz) δ 152.73, 150.52, 144.06, 134.83, 133.60, 133.05, 131.35, 130.85, 129.69, 129.60, 128.50, 128.21, 127.48, 127.38, 124.50, 124.43, 124.34, 124.07, 117.91, 111.96, 111.81, 28.81, 15.73.

A typical asymmetric addition reaction of triethylaluminium with aldehydes catalyzed Poly-5a

Titanium tetraisopropoxide (1.0 mL, 3.0 mmol) was added to a solution of Poly-5a (86.5 mg, 0.1 mmol as a BINOL monomer) in THF (5 mL) at room temperature under argon atmosphere. The mixture was stirred for 15 min at room temperature. Then triethylaluminium (3 mL, 1M in hexane, 3.0 mmol) was added to this mixture at 0 °C. The mixture was stirred at room temperature for another 15 min. After that benzaldehyde (1 mL, 1.0 mmol) was added to this mixture at 0 °C. After being stirred for 24 h, the reaction mixture was quenched with aqueous 3 M HCl and extracted with ethyl acetate twice. The combined organic layer were washed with aqueous 5% NaHCO₃, dried over MgSO₄ and concentrated in vacuo. The residue was added into 20 mL of methanol. Then, the mixture was filtrated. The filtrated cake was recovered for recycling. The filtrate was evaporated in vacuo and residue was purified by column chromatography on silica gel to afford the pure product. The structure of all products were confirmed by comparison of characterization data to reported literature.16

Recovery experiment of Poly-5a

The recovered filtrated cake (1.0 g) was ground into powder and redissolved in 10 mL THF. The mixture was filtrated, the filtrate was poured into 100 mL methanol. The precipitate was washed with methanol several times and dried in vacuo at 40 °C for 4 h to obtain the recovered Poly-5a, yield 95%. The recovered Poly-5a was used for the asymmetric addition experiment again to study the catalytic activity.

Determination of alcohol enantiomeric excesses

The ee of the product was determined by chiral HPLC analysis using a chiral stationary phase column (Chiralcel OD-H).

For 1-Phenyl-1-propanol: *n*-hexane/isopropanol = 99/1, f = 0.8 mL/min, $t_R = 10.335$ min, $t_S = 13.723$ min. For 1-(2-Methoxyphenyl)-1-propanol: *n*-hexane/isopropanol = 98/2, f = 0.8 mL/min, $t_R = 10.505$ min, $t_S = 9.007$ min. For 1-(3-Methoxyphenyl)-1-propanol: *n*-hexane/isopropanol= 99/1, f = 1 mL/min, $t_R = 18.693$ min, $t_S = 21.602$ min. For 1-(4-Chlorophenyl)-1-propanol: *n*-hexane/isopropanol = 99.8/0.2, f =

0.7 mL/min, $t_R = 14.587$ min, $t_S = 24.387$ min. For 1-(4-MAN4.5 Bromo)-1-propanol: n-hexane/isopropanol = 99.8/0.2, f = mL/min, $t_R = 9.380$ min, $t_S = 10.590$ min. For 1-Phenyl-1-penten-3-ol: *n*-hexane/isopropanol = 90/10, f = 1.0 mL/min, t_R = 10.432min, $t_s = 16.580$ min. For 1-Phenyl-3-pentanol: *n*hexane/isopropanol = 90/10, f = 1.0 mL/min, t_R = 4.468 min, t_S = 1-(4-Phenylphenyl)-1-propanol: min. For 7.115 nhexane/isopropanol = 99.5/0.5, f = 0.5 mL/min, t_R = 70.11 min, t_S 63.532 For 1-(1-Naphthyl)-1-propanol: min. = nhexane/isopropanol = 90/10, f = 1.0 mL/min, t_R = 18.898 min, t_S 1-(2-Naphthyl)-1-propanol: 11.665 min. For nhexane/isopropanol = 98/2, f = 0.8 mL/min, t_R = 28.120 min, t_S = 22.698 For 1-(9-Anthracy)-1-propanol: min. nhexane/isopropanol = 99/1, f = 0.6 mL/min, t_R = 35.621 min, t_S = 51.842min.

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Supplementary data

Supplementary data (1 H NMR , 13 C NMR and IR spectra of the new compounds) associated with this article can be found in the online version, at http://dx.doi.org/.

References

- 1. Ohkuma, T.; Kitamura, M.; Noyori, R. in: I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, second ed., Wiley-VCH, Weinheim, **2000**.
- Blaser, H.U.; Pugin, B.; Spindler, F. J. Mol. Catal. A: Chem. 2005, 231, 1-20.
- (a) Benaglia, M.; Puglisi, A.; Cozzi, F. Chem. Rev. 2003, 103, 3401-3430. (b) Jayaprakash, D.; Kobayashi, Y.; Watanabe, S.; Arai, T.; Sasai, H. Tetrahedron: Asymmetry 2003, 14, 1587-1592.
 (c) Buchmeiser, M. R. Chem. Rev. 2009, 109, 303-321. (d) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. Chem. Rev. 2009, 109, 6102-6211.

- 4. S (a) Dickerson, T.J.; Reed, N. N.; Reed, K. D. Janda, *Chem. Rev.* 2002, 102, 3325-3544; (b) Fan, Q. H.; Li, Y. M.; Chan, A. S. C. *Chem. Rev.* 2002, 102, 3385-3446
- An, W. K.; Han, M. Y.; Wang, C. A.; Yu, S. M.; Zhang, Y.; Bai, S.; Wang, W. Chem. Eur. J. 2014, 20, 11019-11028.
- Chen, Y.; Yekta, S.; Yudin, A. K. Chem. Rev. 2003, 103, 3155-3211.
- (a) Fan, Q. H.; Ren, C. Y.; Yeung, C. H.; Hu, W. H.; Chan, A. S. C. J. Am. Chem. Soc. **1999**, *121*, 7407-7408. (b) Jayaprakash, D.; Sasai, H.; *Tetrahedron: Asymmetry* **2001**, *12*, 2589-2595. (c) Jayaprakash, D.; Kobayashi, Y.; Arai, T.; Hu, Q. H.; Zheng, X. F; Pu, L.; Sasai, H. J. Mol. Catal. A: Chem. **2003**, *196*, 145-149. (d) Arai, T.; Hu, Q. H.; Zheng, X. F; Pu, L.; Sasai, H. Org. Lett. **2000**. *26*. 4261-4263.
- (a)Yu, H. B.; Hu, Q. S.; Pu, L. Tetrahedron Lett. 2000, 41, 1681-1685. (b) L. Pu, Chem. Rev. 1998, 98, 2405-2494.
- (a) Zhang, A. L.; Yu, Z. D.; Yang, L. W.; Yang, N. F. Tetrahedron: Asymmetry 2015, 26, 173-179. (b) Zhang, A. L.; Yu, Z. D.; Yang, L. W.; Yang, N. F.; Peng, D. J. Mol. Catal. A: Chem. 2015, 398, 407-412. (c) Cheng, Y. H.; Qin, G. C.; Yang, L. W.; Yang, N. F. Chin. J. Chem. 2015, 33, 436-466. (d) Huang, C.W.; Yang, N. F.; Zhang, A. L.; Yang, L. W. Polymer 2012, 53, 3514-3519.
- 10. Recsei, C.; McErlean, C. S. P. Tetrahedron 2012, 68, 464-480.
- Yang, F.; Wei, S. P.; Chen, C. A.; Xi, P. H.; Yang, L.; Lan, J. B.; Gau, H. M.; You, J. S. *Chem. Eur. J.* **2008**, 14, 2223-2231.
- Rueping, M; Suqiono, E.; Steck, A.; Theissmann, T. Adv. Synth. Catal. 2010. 352, 281-287.
- 13. Yamada, Y. M. A.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Tetrahedron Lett.* **2002**, *43*, 3431-3434.
- 14. Liu, G. H.; Tang, W. J.; Fan, Q. H. *Tetrahedron* **2003**, *59*, 8603-8611.
- (a)Fernández-Mateos, E.; Maciá, B.; Yus. M. Tetrahedron: Asymmetry 2012, 23, 789-794. (b)Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S.; Angew. Chem. Int. Ed. 2005, 44, 2232-2234. (c) Chen, Q.; Ou, J.; Chen, G. S.; Liu, T. H.; Xie, B.; Liang, H, B.; Xie, L. Q.; Chen, Y. X. Chirality 2014, 26, 268-271.
- (a) Zhang, A. L.; Liu, Y. L.; Yang, N. F.; Yang, L. W. *Tetrahedron: Asymmetry* **2014**, *25*, 289-297. (b) Okamoto, k.; Kimachi, T.; Ibuka, T.; Yakemoto, Y. *Tetrahedron: Asymmetry* **2001**, *12*, 463-476. (c) Prasad, K. R.; Revu, O. *Tetrahedron* **2013**, *69*, 8422-8428.