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Dendritic BINOL ligands for asymmetric catalysis: effect of the linking positions and generations of the dendritic wedges on catalyst properties

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Abstract—Three types of new chiral BINOL ligands (**2**, **3** and **4**) bearing dendritic wedges have been synthesized through coupling reaction between 3-hydroxymethyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol (**7**), 6,6′-dihydroxymethyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol (**12**), 6-hydroxymethyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol (**15**) and Fréchet-type polyether dendritic benzyl bromide, followed by deprotection of methoxymethyl groups by ^{i}PrOH/HCl, respectively. These new ligands obtained were assessed in enantioselective Lewis acid-catalyzed addition of diethylzinc to benzaldehyde. Compared to the enantioselectivity observed with dendrimer **1** bearing the dendritic wedges at 3,3′-positions of the binaphthyl backbone, higher enantioselectivity for all these ligands was observed. Difference in the effect of linking positions and generations on enantioselectivity and/or activity for all three kinds of dendritic ligand-derived catalysts was observed. Among these dendritic ligands, (*R*)-**3**/Ti(IV) catalyst with the dendritic wedges at 6,6′-positions of BINOL gave the highest enantioselectivity (up to 87% ee).

1. Introduction

Dendrimers are highly branched macromolecules which have precisely defined molecular structures with a nanoscale size. Since the pioneering work of van Koten et al. reported in 1994,[1] dendritic catalysts have become a subject of intensive research.[2] Such novel catalysts can be used under homogeneous conditions and be readily recovered via simple precipitation or nanofiltration methods. Dendritic catalysts can also be used in flow-through reactors where they are retained by a membrane. Compared to the linear soluble polymeric chiral catalysts, the dendrimer architecture might offer better control of the disposition of the catalytic species than soluble polymer-based catalysts. Thus, it is possible to fine-tune the catalytic properties of the dendritic catalysts through the adjustment of their structure, size, shape, and solubility. Although a number of dendritic catalysts have been described, so far relatively few reports on catalytic asymmetric catalysis employing chiral dendritic catalysts are available.[3]

Optically active binaphthyl-containing ligands have been extensively applied in asymmetric catalysis.[4] Recently, we have developed two types of chiral dendritic ligands for asymmetric catalysis through the incorporation of BINAP[5] and BINOL[6] into the core of the Fréchet-type dendrimers, respectively. For both cases, it was found that the size of the dendritic wedges influenced the reactivity and/or the enantioselectivity of the dendritic catalysts. The 'dendritic effects' were probably due to the space-filling nature of the dendritic wedges near the metal center, which would alter the structure of the metal complex and thus possibly influence the reactivity of the catalyst and/or the substrate selectivity of the catalytic reaction with increasing generation. For example, the dendritic BINOL ligands[6] **1** bearing the dendritic wedges at 3,3′-positions of the binaphthyl backbone were found to be highly effective in the enantioselective addition of diethylzinc to benzaldehyde both in the presence and in the absence of Ti($O^{i}Pr$)$_4$, albeit gave lower enantioselectivity with the increasing generation of the dendrimer. This indicated that the microenvironment of the catalytic sites in the dendrimers was very important for their effectiveness in steric control. Although several types of chiral dendritic BINOL ligands bearing dendritic wedges have been recently described, however, no precedents exist concerning the effect of both the linking positions and the generations of the dendritic wedges on the catalyst properties.[7] As an extension of our previous study,[6] we herein report the synthesis of three types of BINOL ligand bearing dendritic wedges on 3-position (**2**), 6,6′-positions (**3**) and 6-position (**4**) of the binaphthyl backbone.

Keywords: chiral dendrimer; asymmetric catalysis; alkylation; BINOL.
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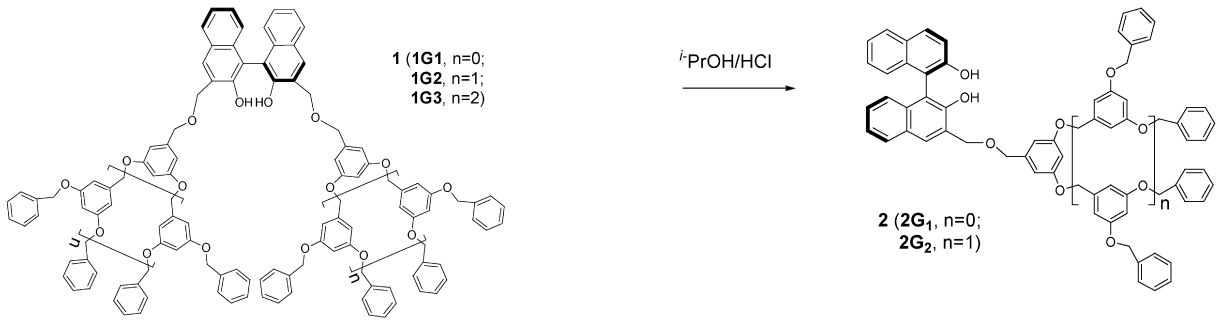


Their asymmetric induction was evaluated by choosing the enantioselective addition of diethylzinc to benzaldehyde as the model reaction. In this context the three new dendritic BINOLs have been found to be superior ligands to **1**. It has also been demonstrated that the linking positions and the generations of the dendritic wedges influenced the catalyst properties.

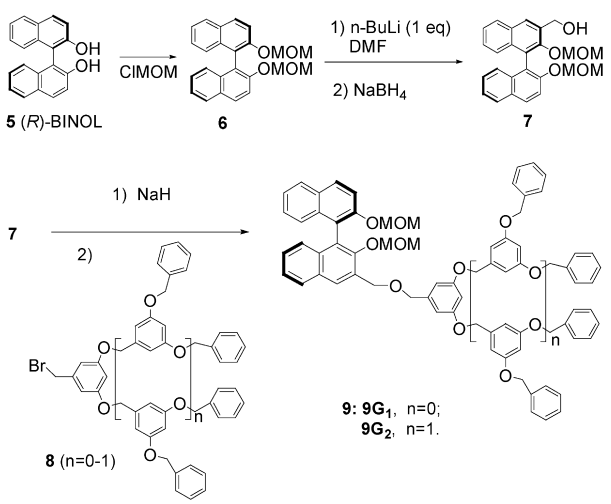
2. Results and discussion

2.1. Synthesis of dendritic BINOL ligands 2-(G_1–G_2), 3-(G_0–G_3) and 4-(G_0–G_3)

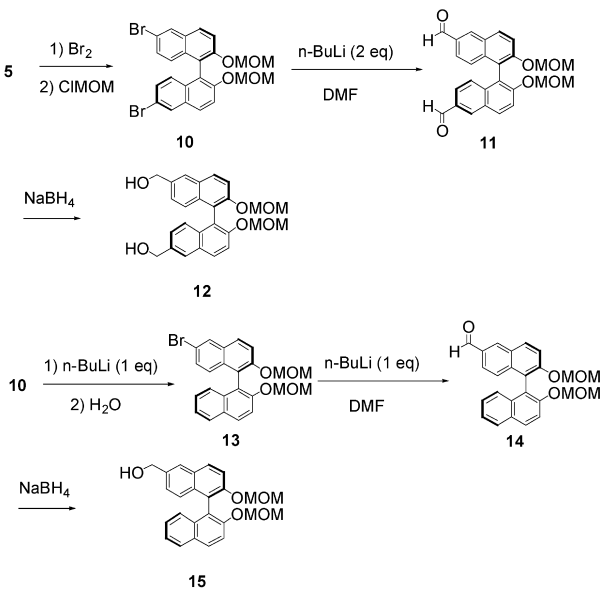
According to our previous study on the synthesis of dendritic BINOL ligands **1**,[6] BINOL derivatives (**2**) bearing dendritic wedge on the 3-position of the binaphthyl backbone were synthesized by using a similar method. 3-Hydroxymethyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol **7** was readily prepared following the literature procedure from commercially available (*R*)-BINOL **5** (Scheme 1).[8] The coupling of dendritic benzyl bromide[9] **8** with **7** was successfully carried out using NaH as the depronation reagent, followed by deprotection of the MOM group to afford $\mathbf{2G_1}$ and $\mathbf{2G_2}$ in moderate yields, respectively (Scheme 1).

We were also interested in similar systems wherein the dendritic segments are attached to the BINOL core at the 6,6′- or 6 positions which are sufficiently far apart from the catalytic active center so that primary steric effect is an unimportant factor. Accordingly **3** and **4** were synthesised as outlined in Schemes 2 and 3. BINOL was first brominated selectively at the 6,6′-positions,[10] followed by MOM-protection of the OH groups to give BINOL derivative **10**. Subsequent bis-formylation was carried out by reaction of **10** with *n*-BuLi followed by DMF to afford BINOL derivative **11**. The key BINOL derivative, 6,6′-dihydroxymethyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol **12** was then synthesized by reducing **11** with $NaBH_4$ (Scheme 2). One of the bromine atoms of **10** was removed to form **13** in 75% yield by using 1 equiv. of *n*-BuLi, followed by quenching with H_2O. This compound was then converted into 6-formyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol **14** according to the method described above. Reduction of **14** with $NaBH_4$ produced 6-hydroxymethyl-2,2′-bis(methoxymethyl)-1,1′-binaphthol **15** in quantitative yield.

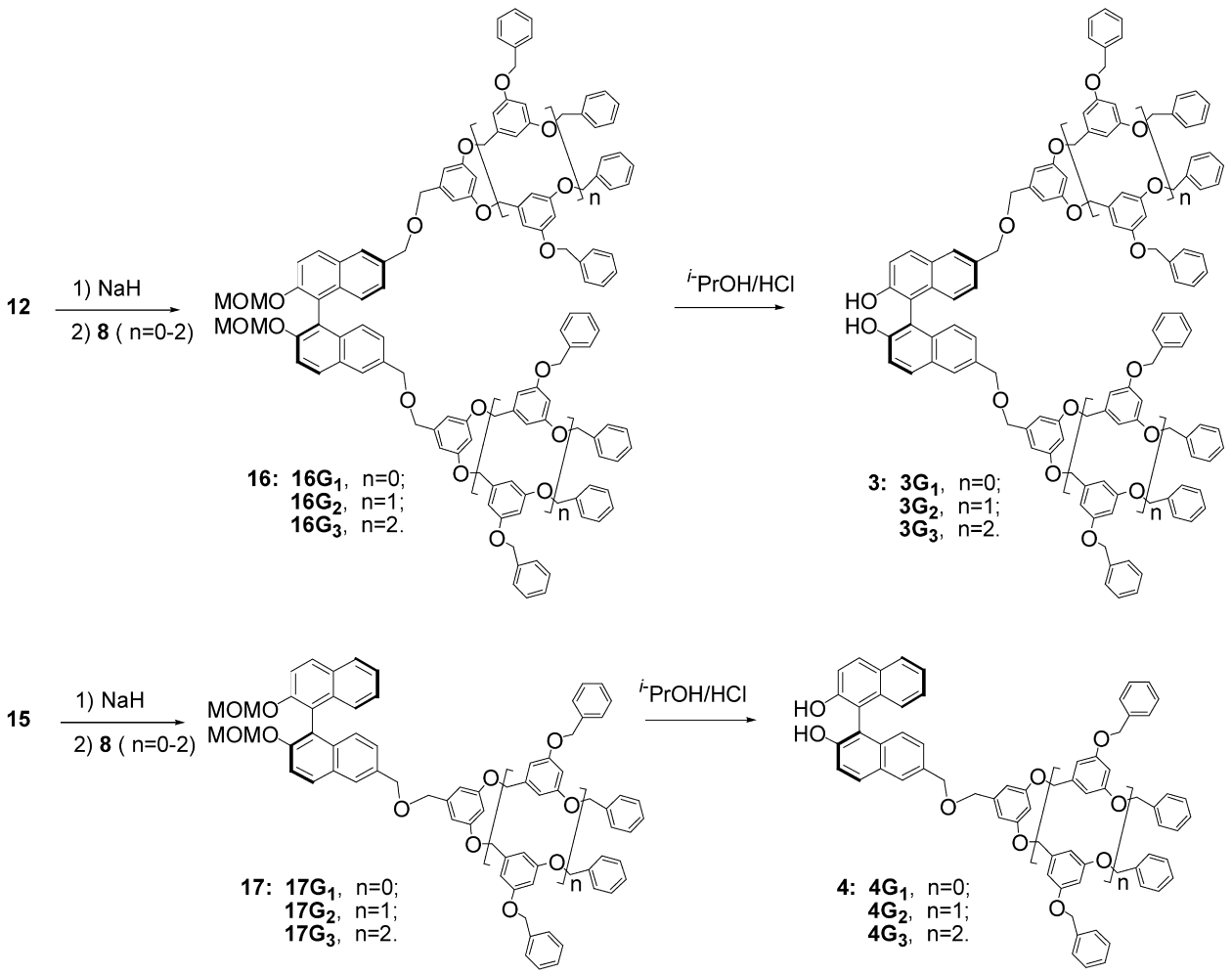
Finally, MOM-protected dendritic BINOL derivatives were synthesized through the coupling of dendrons **8** with the corresponding BINOL derivatives (**12** and **15**) using NaH as the deprotonation reagent in moderate to high yields, respectively. Deprotection of the MOM group in compounds **16** and **17** by ^{i}PrOH/HCl afforded dendritic BINOL



Scheme 1.



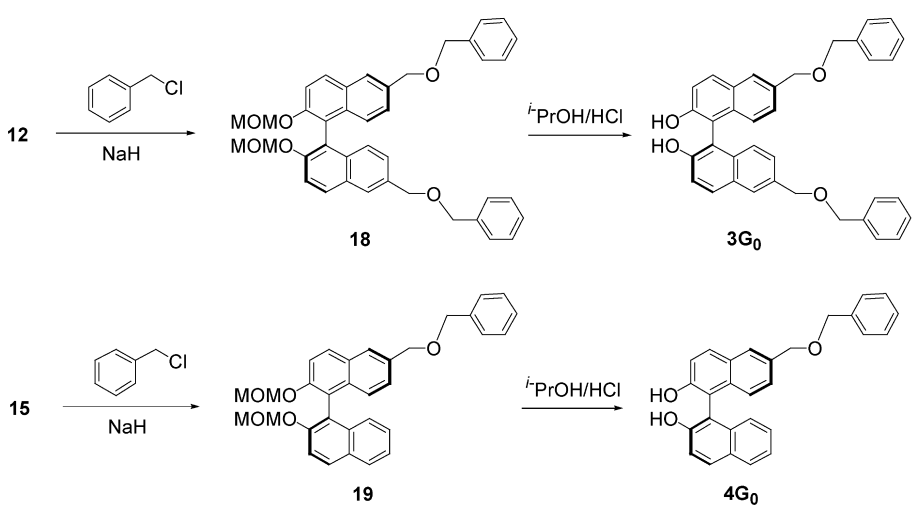
Scheme 2.



Scheme 3.

ligands **3**($\mathbf{G_1}$–$\mathbf{G_3}$) and **4**($\mathbf{G_1}$–$\mathbf{G_3}$) in high yields, respectively (Scheme 3). For comparison, model compounds of small molecules $\mathbf{3G_0}$ and $\mathbf{4G_0}$ were also synthesized using the same method (Scheme 4).

The structures of these dendrimer ligands were confirmed by IR, elemental analysis, ^{1}H NMR as well as MALDI mass spectra. It is noteworthy that the specific optical rotation of individual chiral dendrimers decreased with increasing dendrimer generation. Most interestingly, (*R*)-**3** gave a negative sign of the rotation, which was opposite to those of (*R*)-BINOL, (*R*)-**1**, (R)-**2** and (*R*)-**4**. The molar rotation was



Scheme 4.

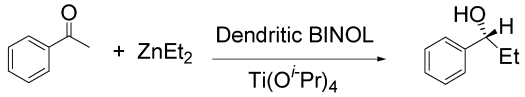
almost identical regardless of the generation and linking positions of the dendritic wedges.

2.2. Asymmetric induction of the dendritic BINOL ligands in the enantioselective addition of $ZnEt_2$ to benzaldehyde in the presence of $Ti(O^iPr)_4$

In recent years the catalytic enantioselective addition of diethylzinc to aldehydes has attracted much attention because of its potential in the preparation of a variety of high value non-racemic chiral alcohols.[11] More recently titanium complexes of BINOL and H_8-BINOL were reported to be effective catalysts for the asymmetric addition of diethylzinc to aldehydes by Chan et al. and Nakai et al., respectively.[12] In this study, in order to compare the performance of our dendritic BINOL ligands and fine-tune the catalytic efficiency through systematically adjusting the linking positions and generations of the dendritic wedges, we chose the titanium catalyzed enantioselective addition of diethylzinc to benzaldehyde as the model reaction. According to the previous study,[6] toluene was chosen as the reaction solvent, and the molar ratio of benzaldehyde/ligand/$Ti(O^iPr)_4$/$ZnEt_2$ being 1.0/0.2/0.8/3 as the reaction conditions. The experimental results are summarized in Table 1. The catalysts derived from all these dendritic BINOL ligands (**2**, **3** and **4**) were tested in this reaction and found to be effective in the presence of $Ti(O^iPr)_4$. High conversion (up to 99%) and good enantioselectivities were observed. As compared with the dendritic BINOL ligand **1**, these dendrimers (**2**, **3** and **4**) gave higher enantioselectivity.

As shown in Table 1, (*R*)-**2** gave high enantioselectivity, which was only slightly lower than that of (*R*)-BINOL (entries 2 and 3 vs 1). As compared to (*R*)-**1** with dendritic wedges at 3,3′-positions (entries 2 and 3, data shown in bracket),[6] improved enantioselectivity was achieved by using (*R*)-**2** as ligands. This was probably due to the relatively opening space around the active site of (*R*)-**2**, which may decrease the negative effect of the sterically bulky dendritic wedges. In order to further investigate the 'dendrimer effect', we also studied the enantioselective addition of diethyl zinc to benzaldehyde in the absence of $Ti(O^iPr)_4$. These ligands were found to give lower conversions and enantioselectivities than (*R*)-**1** (entries 14 and 15). Furthermore, the enantioselectivity also decreased with increasing generation. However, less effect by the generation (from 39 to 33% vs from 62 to 50%) was observed as compared to (*R*)-**1** (entries 14 and 15).

Table 1. Asymmetric addition of diethylzinc to benzaldehyde catalyzed by (*R*)-BINOL and dendritic BINOL ligands in the presence of $Ti(O^i\text{-}Pr)_4$[a]



Entry	Ligand	Conv. (%)[b]	ee.(%)[b]
1	(*R*)-BINOL	98	85
2	(*R*)-**2G$_1$**	>99	80 (74)[c]
3	(*R*)-**2G$_2$**	>99	80 (54)[c]
4	(*R*)-**3G$_0$**	>99	84 (84)[c]
5	(*R*)-**3G$_1$**	>99	85 (74)[c]
6	(*R*)-**3G$_2$**	>99	87 (54)[c]
7	(*R*)-**3G$_3$**	>99	86 (52)[c]
8	(*R*)-**3G$_3$**	>99	86[d]
9	(*R*)-**4G$_0$**	>99	83
10	(*R*)-**4G$_1$**	>99	83
11	(*R*)-**4G$_2$**	>99	79
12	(*R*)-**4G$_3$**	>99	77
13[e]	(*R*)-BINOL	19	5
14[e]	(*R*)-**2G$_1$**	80 (98)[c]	39 (62)[c]
15[e]	(*R*)-**2G$_2$**	65 (78)[c]	33 (50)[c]
16[e]	(*R*)-**3G$_0$**	69 (98)[c]	6 (66)[c]

[a] Reactions were carried out in toluene under the reaction conditions: benzaldehyde/ligand/$Ti(O^i\text{-}Pr)_4$/$ZnEt_2$=1.0:0.2:0.8:3 (molar ratio); reaction temperature=0°C; reaction time=7 h.
[b] Determined by chiral GC analysis. The absolute configuration of the product is *R*.
[c] Data in the brackets were obtained by using (*R*)-**1** as ligands.[6]
[d] Recovered (*R*)-**3G$_3$** was used.
[e] Recotions were carried out in the absence of $Ti(O^i\text{-}Pr)_4$.

Unlike dendrimers (*R*)-**1** and (*R*)-**2**, ligands (*R*)-**3** and (*R*)-**4** bear dendritic wedges at the 6,6′-positions or 6-position on the binaphthyl backbone, which are situated at a large enough distance from the catalytic center so as not to cause any steric hindrance. As expected, ligands (*R*)-**3G$_0$**–(*R*)-**3G$_3$** gave high enantioselectivity (up to 87%), which are similar to that of BINOL (entries 4–7 vs 1). As compared with that of (*R*)-**1**, the enantioselectivity increased significantly for all generation-derived catalysts (comparing the data shown in entries 5–7 and the data in the corresponding brackets). When this reaction was carried out in the absence of $Ti(O^iPr)_4$ using (*R*)-**3G$_0$** as ligand, similar enantioselectivity (6% vs. 5%), albeit higher conversions (69% vs 19%) was obtained as compared to those of BINOL (entries 13 and 16), which, however, are much lower than those of (*R*)-**1** (6% vs 66%, shown in entry 16). Ligand (*R*)-**4** without C_2-symmetry gave only slightly lower enantioselectivity as compared to those of (*R*)-**3** and BINOL (entries 9–12). For both dendritic ligands (*R*)-**3** and (*R*)-**4**, the generation did not show significantly effect on enantioselectivity.

Although the relationship between dendritic structure and catalyst properties is complex, the following two factors could be taken into consideration. Firstly, the potentially coordinating ether linkage at the 3-position on the binaphthyl backbone played an important role on the catalytic activity and enantioselectivity. Similar results were observed by Pu, Katsuki and co-workers,[14–15] in which BINOL derivatives bearing oxygen or nitrogen atom-containing substituents at 3,3′-positions were found to be highly effective in asymmetric addition of diethyl zinc to aldehydes in the absence of $Ti(O^iPr)_4$. Secondly, the dendritic wedges attached onto 3, 3′- or 6, 6′-positions may probably interact with each other due to the steric effect with increasing generation, which possibly affects the dihedral angle of the two naphthalene rings on dendritic BINOL and thus affects the activity and selectivity. Yoshida and co-workers[7a] recently reported very similar dendritic BINOL ligands for asymmetric allylation, in which the dihedral angle obtained from the computer-generated folded structure was slightly decreased with increasing generation. Therefore, as compared with (*R*)-**1** and (*R*)-**2**, much lower catalytic activity and enantioselectivity in the absence of $Ti(O^iPr)_4$ for (*R*)-**3** and (*R*)-**4** were probably due to the lack of the linkage coordination effect. The difference in the

effect of generation on enantioselectivity between (*R*)-**1** and (*R*)-**2**, (*R*)-**3** and (*R*)-**4**, were partially the reflection of the possible cooperation between the two dendritic wedges on the 6,6′- or 3,3′-positions on the binaphthyl backbone.

An important feature of the design of soluble dendrimer-based catalyst, on the other hand, is the easy and reliable separation of the chiral catalyst. The high generations of the dendrimers are expected to achieve quantitative recovery of the ligand/catalyst from the reaction mixtures based on the large molecular size and different solubility in various organic solvents. In this study, for example, the third generation ligand (*R*)-**3G$_3$** was used to carry out the recycling experiment. Upon the completion of the reaction, (*R*)-**3G$_3$** was quantitatively precipitated by the addition of methanol and recovered via filtration. The recovered ligand showed almost the same reactivity and enantioselectivity (entry 8 in Table 1).

3. Conclution

In this paper, we reported the preparation of three kinds of new chiral BINOL derivatives bearing dendritic wedges located at 3-, 6,6′- and 6-positions of the binaphthyl backbone for a study on effect of the linking positions and generations of the dendritic wedges on the catalyst properties. Dendritic catalysts derived from these new ligands were found to be highly effective in enantioselective Lewis acid catalyzed addition of diethylzinc to benzaldehyde, which are superior to those of (*R*)-1/Ti(IV) catalyst with the dendritic wedges at 3,3′-positions of the binaphthyl backbone. Difference in the effect of linking positions and generations on enantioselectivity and/or activity for all three kinds of dendritic ligand-derived catalysts was observed. Among these dendritic ligands, (*R*)-3/Ti(IV) catalyst with the dendritic wedges at 6,6′-positions of BINOL gave the highest enantioselectivity (up to 87% ee).

4. Experimental

4.1. General

All experiments, which are sensitive to moisture or air, were carried out under a nitrogen atmosphere using standard Schlenk technique. Commercial reagents were used as received without further purification unless otherwise noted. Toluene and THF were distilled from sodium benzophenone ketyl, benzaldehyde was distilled from calcium hydride before use. Compounds (*R*)-**6**,[8] (R)-**7**,[8] (R)-**8**[9] and (R)-**10**[13] were prepared according to the reported procedures.

IR spectra were recorded on a Bruker IFS 25 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker DM 300 spectrometer in $CDCl_3$ with TMS as internal standard. MALDI-TOF mass spectra were obtained on an Instrum III spectrometer with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. Elemental analysis was performed with a Carlo Erba 1106 Elemental Analyzer. Optical rotations were measured with AA-10R automatic polarimeter. The ee values were determined by GLC using a Supelco-Dex 120 chiral column (30 m×0.25 mm (i.d.), 0.25 m film).

4.1.1. Preparation of (*R*)-6,6′-diformyl-2,2′-bis(methoxymethy)-1,1′-binaphthol (*R*)-11. To a stirred solution of (*R*)-**10** (2.83 g, 5.30 mmol) in THF (20 mL) was added *n*-BuLi (11.9 mL, 19.0 mmol, 1.60 M in hexane) at room temperature. The mixture was stirred for 2 h at the same temperature. After cooling down to 0°C, DMF (1.76 mL, 22.4 mmol) was added dropwise over 15 min. The mixture was then warmed up to room temperature and stirred for further 2 h. Sat. aq. NH_4Cl was added to quench the reaction. After neutralization, the reaction mixture was extracted with ethyl acetate several times. The combined organic layer was washed subsequently with water and brine, and dried over anhydrous Na_2SO_4. Evaporation of solvent gave the crude product, which was further purified by flash column chromatography on silica gel (hexane–ethyl acetate, 4:1) to yield (*R*)-**11** (1.82 g, 80%) as white solid. $[\alpha]_D^{20}$=0–66.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 1687, 1620, 1236, 1164, 1014 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 Hz): δ 10.10 (s, 2H, –CHO), 8.38 (s, 2H, Ar-H), 8.14 (d, *J*=9.1 Hz, 2H, Ar-H), 7.69 (d, *J*=9.1 Hz, 4H, Ar-H), 7.18 (d, *J*=4.1 Hz, 2H, Ar-H), 5.16–5.03 (m, 4H, –OCH_2O–), 3.17 (s, 6H, –OCH_3); ^{13}C NMR ($CDCl_3$, 75 Hz): δ 191.8, 155.1, 136.9, 134.7, 132.4, 131.4, 128.5, 125.9, 123.2, 120.1, 117.1, 94.2, 55.9; MS (EI) *m*/*z* (%): 431(1.7) $[M+1]^+$, 430(6.2) $[M]^+$, 354(20.1), 326(11.8), 397(4.7), 269(5.5), 239(3.2), 45(100), 32(43.7); Anal. calcd for $C_{26}H_{22}O_6$: C, 72.55; H, 5.15. Found C, 72.48; H, 5.37.

4.1.2. Preparation of (*R*)-6,6′-bis(hydroxymethyl)-2,2′-bis(methoxymethy)-1,1′- binaphthol (*R*)-12. $NaBH_4$ (0.18 g, 4.65 mmol) was added to a solution of (*R*)-**11** (1.0 g, 2.31 mmol) in THF (20 mL) at 0°C. After 30 min, sat. aq NH_4Cl was added to quench the reaction. After most of the organic solvent was removed under reduced pressure, ethyl acetate (20 mL) was added to the mixture. The organic layer was then separated and the aqueous layer was extracted with ethyl acetate several times. The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. Evaporation of solvent gave the crude product, which was further purified by flash column chromatography on silica gel (hexane–ethyl acetate, 4:1) to afford (*R*)-**12** (1.0 g, 99%) as white solid. $[\alpha]_D^{20}$=+108.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 3346, 1597, 1482, 1240, 1148, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 Hz): δ 7.93 (d, *J*=9.0 Hz, 2H, Ar-H), 7.83 (s, 2H, Ar-H), 7.56 (d, *J*=9.0 Hz, 2H, Ar-H), 7.21 (d, *J*=8.7 Hz, 2H, Ar-H), 7.11 (d, *J*=8.7 Hz, 2H, Ar-H), 5.06–4.94 (m, 4H, –OCH_2O–), 4.78 (s, 4H, BINOL–CH_2), 3.13 (s, 6H, –OCH_3); ^{13}C NMR ($CDCl_3$, 75 Hz): δ 152.5, 136.3, 133.3, 129.5, 129.2, 125.7, 125.6, 125.5, 121.0, 117.3, 94.9, 65.1, 55.6; MS (EI) *m*/*z* (%): 435(4.9) $[M+1]^+$, 434(12.0) $[M]^+$, 372(5.0), 354(24.0), 340(8.6), 326(16.2), 311(25.1), 297(12.5), 281(10.8), 269(18.0), 252(6.9), 239(8.6), 226(4.0), 45(100), 32(86.2); Anal. calcd for $C_{26}H_{26}O_6$: C, 71.87; H, 6.03. Found: C, 71.82; H, 6.06.

4.1.3. Preparation of (*R*)-6-bromo-2,2′-bis(methoxymethy)-1,1′-binaphthol (*R*)-13. To a stirred solution of (*R*)-**10** (4.0 g, 7.6 mmol) in THF (80 mL) was added *n*-BuLi (5.2 mL, 8.4 mmol, 6.4 M in hexane) over 30 min at −78°C. The mixture was stirred for 2 h at the same temperature. Then sat. aq NH_4Cl was added to quench the reaction. After neutralization, the reaction mixture was worked-up as described above. The residue was further purified by

column chromatography on silica gel (hexane–ethyl acetate, 4:1) to afford (*R*)-**13** (2.6 g, 75%) as white solid. $[\alpha]_D^{20}$=+108.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 1618, 1593, 1213, 1147 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.99 (d, *J*=9.0 Hz, 2H, Ar-H), 7.90 (d, *J*=8.1 Hz, 2H, Ar-H), 7.61 (d, *J*=9.0 Hz, 2H, Ar-H), 7.40–7.35 (m, 2H, Ar-H), 7.28–7.17 (m, 3H, Ar-H), 5.13–5.00 (m, 4H, $-OCH_2O-$), 3.17 (s, 6H, $-OCH_3$); ^{13}C NMR ($CDCl_3$, 75 Hz): δ 152.4, 133.8, 129.7, 129.2, 127.7, 126.1, 125.4, 123.9, 117.1, 95.0, 55.6; MS(EI) *m/z* (%): 374(31.4) $[M-Br]^+$, 311(4.1), 298(53.1), 282(9.8), 281(9.7), 270(39.5), 269(46.1), 253(10.4), 239 (12.8), 226(6.6), 45(100), 32(37.6).

4.1.4. Preparation of (*R*)-6-hydroxymethyl-2,2′-bis-(methoxymethy)-1,1′-binaphthol (*R*)-15. To a stirred solution of (*R*)-**13** (2.0 g, 4.4 mmol) in THF (20 mL) was added *n*-BuLi (5.6 mL, 8.8 mmol, 1.60 M in hexane) over 30 min at −78°C. The mixture was stirred for 4 h at the same temperature. After cooling down to −50°C, DMF (6.8 mL, 26.4 mmol) was added dropwise over 15 min. The mixture was stirred for 2 h at the same temperature. Sat. aq NH_4Cl was added to quench the reaction. After neutralization, the reaction mixture was extracted with ethyl acetate several times. The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. Evaporation of solvent under reduced pressure gave (*R*)-**14** as white solid. (*R*)-**14** was then dissolved in THF (20 mL). After the solution was cooled to 0°C, $NaBH_4$(0.36 g, 9.3 mmol) was added. After 30 min, sat. aq NH_4Cl was added to quench the reaction. After most of the organic solvent was removed under reduced pressure, ethyl acetate (20 mL) was added to the mixture. The organic layer was then separated and the aqueous layer was extracted with ethyl acetate several times. The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. Evaporation of solvent gave the crude product, which was further purified by flash column chromatography (hexane–ethyl acetate, 4:1) to afford (*R*)-**15** (1.56 g, 88%) as colorless oil. $[\alpha]_D^{20}$=+4.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 1619, 1594, 1213, 1148 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.01–7.98 (m, 2H, Ar-H), 7.90 (d, *J*=8.1 Hz, 2H, Ar-H), 7.60 (d, *J*=9.1 Hz, 1H, Ar-H), 7.43–7.35 (m, 2H, Ar-H), 7.30–7.16 (m, 4H, Ar-H), 5.15–4.47 (m, 2H, $-OCH_2O-$), 4.92 (d, *J*=4.4 Hz, 2H, BINOL–CH_2), 3.27 (s, 3H, $-OCH_3$), 3.15 (s, 3H, $-OCH_3$); ^{13}C NMR ($CDCl_3$, 75 Hz): δ 153.0, 152.9, 134.5, 133.8, 133.7, 131.1, 130.1, 129.7, 129.0, 128.1, 128.0, 126.9, 126.3, 125.7, 125.5, 125.4, 125.2, 124.3, 120.4, 116.4, 99.3, 94.7, 61.9, 56.0, 55,9; MS(EI) *m/z* (%): 405(1.2) $[M+1]^+$, 404(4.7) $[M]^+$, 372(8.6), 342(7.3), 328(10.4), 310(12.2), 298(38.6), 281(19.8), 269(27.4), 253(14.8), 239(15.1), 226(4.8), 120(6.7), 75(9.5), 45(100), 32(29.5).

4.1.5. Synthesis of MOM-protected dendritic BINOL ligands (*R*)-9, (*R*)-16 and (*R*)-17. Typical procedure: To a mixture of sodium hydride (0.034 g, 0.74 mmol, 52% dispersion in mineral oil) in THF (5 mL) and DMF (4 mL) under nitrogen was slowly added a solution of (*R*)-**7** (0.2 g, 0.5 mmol) in THF (2 mL) over 15 min at 0°C. The mixture was warmed up to room temperature and stirred for 1 h. To this mixture was then slowly added a solution of **8** (*n*=1, 0.22 g, 0.58 mmol) in 2 mL of THF over 10 min at 0°C. The mixture was then warmed up to room temperature and stirred for another 4 h. Water (5 mL) was added at 0°C to quench the reaction. The solution was extracted with CH_2Cl_2 several times. The combined organic layer was washed with water and brine, and then dried over Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography on silica gel (hexane–CH_2Cl_2, 1:2) to give (*R*)-**9G$_1$** (56 mg, 16%) as a white foam. $[\alpha]_D^{20}$=+34.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 1594, 1450, 1154, 1052 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.17 (s, 1H, Ar-H), 8.05–7.92 (m, 2H, Ar-H), 7.65 (d, *J*=9.0 Hz, 1H, Ar-H), 7.50–7.27 (m, 17H, Ar-H), 6.81 (s, 2H, Ar-H), 6.65 (s, 1H, Ar-H), 5.12 (s, 4H, Ph–CH_2), 5.19–4.62 (m, 4H, $-OCH_2O-$), 4.98 (s, 2H, BINOL–CH_2), 4.77 (s, 2H, Ph–CH_2), 3.22 (s, 3H, $-OCH_3$), 2.90 (s, 3H, $-OCH_3$); MALDI-TOF-MS *m/z*: 729.17 $[M+Na]^+$, 745.13 $[M+K]^+$.

4.1.6. Compound (*R*)-9G$_2$. (Hexane–CH_2Cl_2, 1:2). A white foam. Yield 27%; $[\alpha]_D^{20}$=+10.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 1592, 1450, 1152, 1051 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.14 (s, 1H, Ar-H), 7.99–7.89 (m, 2H, Ar-H), 7.64 (d, *J*=9.0 Hz, 1H, Ar-H), 7.45–7.20 (m, 27H, Ar-H), 6.76–6.60 (m, 9H, Ar-H), 5.08 (s, 8H, Ph–CH_2), 5.03 (s, 4H, Ph–CH_2), 5.16–4.59 (m, 4H, $-OCH_2O-$), 4.96 (s, 2H, BINOL–CH_2), 4.74 (s, 2H, Ph–CH_2), 3.19 (s, 3H, $-OCH_3$), 2.88 (s, 3H, $-OCH_3$); MALDI-TOF-MS *m/z*: 1154.5 $[M+Na]^+$, 1170.5 $[M+K]^+$.

4.1.7. Compound (*R*)-16G$_1$. (Hexane–CH_2Cl_2, 1:2). A white foam. Yield 73%; $[\alpha]_D^{20}$=+8.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 1594, 1451, 1148, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.95 (d, *J*=9.0 Hz, 2H, Ar-H), 7.84 (s, 2H, Ar-H), 7.59 (d, *J*=9.0 Hz, 2H, Ar-H), 7.42–7.11 (m, 24H, Ar-H), 6.63 (s, 4H, Ar-H), 6.56 (s, 2H, Ar-H), 5.02 (s, 8H, Ph–CH_2), 5.08–4.97 (m, 4H, $-OCH_2O-$), 4.63 (s, 4H, BINOL–CH_2), 4.52 (s, 4H, Ph–CH_2), 3.16 (s, 6H, $-OCH_3$); Anal. calcd for $C_{68}H_{62}O_{10}$: C, 78.59; H, 6.01. Found: C, 78.63; H, 6.05.

4.1.8. Compound (*R*)-16G$_2$. (Hexane–CH_2Cl_2, 1:3). A white foam. Yield 73%; $[\alpha]_D^{20}$=+4.0 (*c* 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 1594, 1450, 1154, 1052 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.91 (d, *J*=9.0 Hz, 2H, Ar-H), 7.82 (s, 2H, Ar-H), 7.54 (d, *J*=9.0 Hz, 2H, Ar-H), 7.40–7.10 (m, 44H, Ar-H), 6.66–6.52 (m, 18H, Ar-H), 5.02 (s, 16H, Ph–CH_2), 4.97 (s, 8H, Ph–CH_2), 5.05–4.93 (m, 4H, $-OCH_2O-$), 4.63 (s, 4H, BINOL–CH_2), 4.52 (s, 4H, Ph–CH_2), 3.15 (s, 6H, $-OCH_3$); Anal. calcd for $C_{124}H_{110}O_{18}$: C, 78.88; H, 5.87. Found: C, 78.79; H, 5.86.

4.1.9. Compound (*R*)-16G$_3$. (Hexane–CH_2Cl_2, 1:3). A white foam. Yield 72%; $[\alpha]_D^{20}$=+1.0 (*c* 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 1594, 1449, 1153, 1051 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.91 (d, *J*=9.0 Hz, 2H, Ar-H), 7.81 (s, 2H, Ar-H), 7.52, 7.39 (d, *J*=9.0 Hz, 2H, Ar-H), 7.40–7.11 (m, 84H, Ar-H), 6.66–6.55 (m, 42H, Ar-H), 5.00 (s, 32H, Ph–CH_2), 4.93 (s, 16H, Ph–CH_2), 4.93 (s, 8H, Ph–CH_2), 5.05–4.93 (m, 4H, $-OCH_2O-$), 4.63 (s, 4H, BINOL–CH_2), 4.52 (s, 4H, Ph–CH_2), 3.11 (s, 6H, $-OCH_3$); Anal. calcd for $C_{236}H_{206}O_{34}$: C, 79.04; H, 5.79. Found: C, 79.24; H, 5.96.

4.1.10. Compound (*R*)-18. (Hexane–ethyl acetate, 4:1). Colorless viscous oil. Yield 74%; $[\alpha]_D^{20}$=+10.0 (*c* 1.0,

CH_2Cl_2); IR (KBr) ν_{max}: 1617, 1595, 1395, 1208, 1065 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.99 (d, J= 9.1 Hz, 2H, Ar-H), 7.91 (s, 2H, Ar-H), 7.64 (d, J=9.0 Hz, 2H, Ar-H), 7.42–7.20 (m, 14H, Ar-H), 5.14–5.02 (m, 4H, $-OCH_2O-$), 4.71 (s, 4H, BINOL$-CH_2$), 4.63 (s, 4H, Ph$-CH_2$), 3.20 (s, 6H, $-OCH_3$); MS(EI) m/z (%): 615(0.2) $[M+1]^+$, 614(0.5) $[M]^+$, 462(13.8), 400(14.7), 340(100), 311(23.8), 310(24.4), 309(13.9), 283(16.6), 282(24.9), 281(23.7), 254(12.7), 253(23.7), 91(99.9), 77(13.4), 45(57.7).

4.1.11. Compound (*R*)-17G$_1$. (Hexane–CH_2Cl_2, 1:2). A white foam. Yield 92%; $[\alpha]_D^{20}$=+48.0 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 1595, 1450, 1149, 1058 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.10 (s, 1H, Ar-H), 7.99–7.86 (m, 3H, Ar-H), 7.59 (d, J=9.0 Hz, 1H, Ar-H), 7.44–7.20 (m, 15H, Ar-H), 6.74 (s, 2H, Ar-H), 6.58 (s, 1H, Ar-H), 5.06 (s, 4H, Ph$-CH_2$), 5.13–4.55 (m, 4H, $-OCH_2O-$), 5.01 (s, 2H, BINOL$-CH_2$), 4.91 (s, 2H, Ph$-CH_2$), 3.15 (s, 3H, $-OCH_3$), 2.84 (s, 3H, $-OCH_3$); MALDI-TOF-MS m/z: 729.9 $[M+Na]^+$, 745.8 $[M+K]^+$.

4.1.12. Compound (*R*)-17G$_2$. (Hexane–CH_2Cl_2, 1:2). A white foam. Yield 92%; $[\alpha]_D^{20}$=+27.0 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 1594, 1449, 1153, 1027 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.12 (s, 1H, Ar-H), 7.98–7.86 (m, 3H, Ar-H), 7.60 (d, J=9.0 Hz, 1H, Ar-H), 7.45–7.21 (m, 26H, Ar-H), 6.75–6.58 (m, 9H, Ar-H), 5.06 (s, 8H, Ph$-CH_2$), 5.03 (s, 4H, Ph$-CH_2$), 5.14–4.57 (m, 4H, $-OCH_2O-$), 5.00 (s, 2H, BINOL$-CH_2$), 4.71 (s, 2H, Ph$-CH_2$), 3.17 (s, 3H, $-OCH_3$), 2.86 (s, 3H, $-OCH_3$); MALDI-TOF-MS m/z: 1154.6 $[M+Na]^+$, 1170.6 $[M+K]^+$.

4.1.13. Compound (*R*)-17G$_3$. (Hexane–CH_2Cl_2, 1:2). A white foam. Yield 79.9%; $[\alpha]_D^{20}$=+16.0 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 1594, 1450, 1154, 1052 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.08 (s, 1H, Ar-H), 7.98–7.84 (m, 3H, Ar-H), 7.56 (d, J=9.0 Hz, 1H, Ar-H), 7.41–7.18 (m, 46H, Ar-H), 6.72–6.54 (m, 21H, Ar-H), 5.01 (s, 16H, Ph$-CH_2$), 5.00 (s, 8H, Ph$-CH_2$), 4.99 (s, 4H, Ph$-CH_2$), 5.07–4.53 (m, 4H, $-OCH_2O-$), 4.95 (s, 2H, BINOL$-CH_2$), 4.68 (s, 2H, Ph$-CH_2$), 3.12 (s, 3H, $-OCH_3$), 2.82 (s, 3H, $-OCH_3$); MALDI-TOF-MS m/z: 2003.8 $[M+Na]^+$, 2019.7 $[M+K]^+$.

4.1.14. Compound (*R*)-19. (Hexane–ethyl acetate, 4:1). Colorless viscous oil. Yield 85.2%; $[\alpha]_D^{20}$=+73.0 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 1595, 1450, 1149, 1058 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.12 (s, 1H, Ar-H), 7.99–7.87 (m, 3H, Ar-H), 7.60 (d, J=9.0 Hz, 1H, Ar-H), 7.47–7.20 (m, 11H, Ar-H), 5.32–4.55 (m, 4H, $-OCH_2O-$), 4.93 (s, 2H, BINOL$-CH_2$), 4.77 (s, 2H, Ph$-CH_2$), 3.19 (s, 3H, $-OCH_3$), 2.85 (s, 3H, $-OCH_3$); MS (EI) m/z (%): 495(5.8) $[M+1]^+$, 494(16.8) $[M]^+$, 388(26.8), 343(25.2), 342(100), 311(34.7), 310(73.6), 298(34.4), 297(48.5), 282(85.9), 281(53.7), 269(67.7), 253(22.6), 239(21.4), 91(55.1), 45(62.9).

4.1.15. Synthesis of dendritic BINOL ligands (*R*)-2, (*R*)-3 and (*R*)-4. Typical procedure: To a stirred solution of (*R*)-**9G$_1$** (0.48 g, 0.78 mmol) in CH_2Cl_2 (5 mL) was added ^{i}PrOH/HCl (6 N, 5 mL). After stirring overnight at 40°C and evaporation most of the solvent, the residue was diluted with CH_2Cl_2 and washed with water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried over Na_2SO_4. After removing the solvent, the residue was further purified by column chromatography on silica gel (hexane–CH_2Cl_2, 1:2) to give (*R*)-**2G$_1$** (390 mg, 94%) as a white foam. $[\alpha]_D^{20}$=+20.0 (c 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 3442 (–OH), 1594, 1450, 1154, 1052 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.96–7.85 (m, 4H, Ar-H), 7.40–7.29 (m, 15H, Ar-H), 7.14 (t, J= 7.04 Hz, 2H, Ar-H), 6.65–6.57 (m, 3H, Ar-H; 1H, –OH), 5.04 (s, 1H, –OH), 5.01 (s, 4H, Ph$-CH_2$), 4.90 (s, 2H, BINOL$-CH_2$), 4.64 (s, 2H, Ph$-CH_2$); MALDI-TOF-MS m/z: 641.4 $[M+Na]^+$, 657.4 $[M+K]^+$; Anal. calcd for $C_{42}H_{34}O_5$: C, 81.53; H, 5.54. Found: C, 81.54; H, 5.71.

4.1.16. Compound (*R*)-2G$_2$. (Hexane–CH_2Cl_2, 1:3). A white foam. Yield 90%; $[\alpha]_D^{20}$=+13.0 (c 1.0, CH_2Cl_2); IR (KBr) ν_{max}: 3441 (–OH), 1592, 1450, 1152, 1051 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.94–7.85 (m, 4H, Ar-H), 7.43–7.28 (m, 25H, Ar-H), 7.15 (t, J=7.13 Hz, 2H, Ar-H), 6.68–6.57 (m, 9H, Ar-H; 1H, –OH), 5.06–4.97 (m, 12H, Ph$-CH_2$, 1H, –OH), 4.92 (s, 2H, BINOL$-CH_2$), 4.67 (s, 2H, Ph$-CH_2$); MALDI-TOF-MS m/z: 1065.16 $[M+Na]^+$, 1081.14 $[M+K]^+$; Anal. calcd for $C_{70}H_{58}O_9$: C, 80.59; H, 5.60. Found: C, 80.21; H, 5.94.

4.1.17. Compound (*R*)-3G$_0$. (Hexane–ethyl acetate, 4:1). A colorless oil. Yield 94%. $[\alpha]_D^{20}$=–82 (c 2.0,CH_2Cl_2); IR (KBr) ν_{max}: 3493, 1617, 1595, 1395, 1208, 1065 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.89 (d, J=8.9 Hz, 2H, Ar-H), 7.80 (s, 2H, Ar-H), 7.32–7.18 (m, 14H, Ar-H), 7.06 (d, J= 8.5 Hz, 2H, Ar-H), 4.99 (s, 2H, –OH), 4.71 (s, 4H, BINOL$-CH_2$), 4.63 (s, 4H, Ph$-CH_2$); MS (EI) m/z(%): 527(30.7) $[M+1]^+$, 526(75.7) $[M]^+$, 434(12.6), 420(40.6), 328(31.6), 314(30.8), 299(31.1), 281(14.5), 158(18.0), 157(62.8), 108(29.4), 107(23.3), 105(24.2), 91(100), 77(39.9); Anal. calcd for $C_{36}H_{30}O_4$.0.5 H_2O: C, 80.73; H, 5.65. Found: C, 80.96; H, 5.43.

4.1.18. Compound (*R*)-3G$_1$. (Hexane–CH_2Cl_2, 1:2). A white foam. Yield 92%. $[\alpha]_D^{20}$=–47 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 3503, 1594, 1451, 1148, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.89 (d, J=9.0 Hz, 2H, Ar-H), 7.78 (s, 2H, Ar-H), 7.33–7.18 (m, 24H, Ar-H), 7.04 (d, J=9.0 Hz, 2H, Ar-H), 6.55 (s, 4H, Ar-H), 6.48 (s, 2H, Ar-H), 4.96 (s, 2H, –OH), 4.94 (s, 8H, Ph$-CH_2$), 4.56 (s, 4H, BINOL$-CH_2$), 4.45 (s, 4H, Ph$-CH_2$); MALDI-TOF-MS m/z: 973.6 $[M+Na]^+$, 989.7 $[M+K]^+$; Anal. calcd for $C_{64}H_{54}O_8$: C, 80.82; H, 5.72. Found: C, 80.47; H, 5.58.

4.1.19. Compound (*R*)-3G$_2$. (Hexane–CH_2Cl_2, 1:3). A white foam. Yield 86%. $[\alpha]_D^{20}$=–24 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 3511, 1594, 1450, 1154, 1052 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.95 (d, J=9.0 Hz, 2H, Ar-H), 7.85 (s, 2H, Ar-H), 7.40–7.26 (m, 44H, Ar-H), 7.13 (d, J=9.0 Hz, 2H, Ar-H), 6.66–6.52 (m, 18H, Ar-H), 5.04 (s, 2H, –OH), 5.00 (s, 16H, Ph$-CH_2$), 4.95 (s, 8H, Ph$-CH_2$), 4.63 (s, 4H, BINOL$-CH_2$), 4.52 (s, 4H, Ph$-CH_2$); MALDI-TOF-MS m/z: 1821.6 $[M+Na]^+$, 1837.5 $[M+K]^+$, Anal. calcd for $C_{120}H_{102}O_{16}$: C, 80.07; H, 5.71. Found: C, 79.88; H, 5.77.

4.1.20. Compound (*R*)-3G$_3$. (Hexane–CH_2Cl_2, 1:4). A white foam. Yield 51%. $[\alpha]_D^{20}$=–13 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 3513, 1594, 1449, 1153, 1051 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.88 (d, J=9.0 Hz, 2H, Ar-H), 7.74 (s,

2H, Ar-H), 7.34–7.20 (m, 84H, Ar-H), 7.06 (d, J=9.0 Hz, 2H, Ar-H), 6.57–6.46 (m, 42H, Ar-H), 5.00 (s, 2H, –OH), 4.91 (s, 32H, Ph–CH_2), 4.84 (s, 16H, Ph–CH_2), 4.83 (s, 8H, Ph–CH_2), 4.63 (s, 4H, BINOL–CH_2), 4.52 (s, 4H, Ph–CH_2); MALDI-TOF-MS m/z: 3518.7 $[M+Na]^+$; Anal. calcd for $C_{232}H_{198}O_{32}$: C, 79.66; H, 5.70. Found: C, 79.54; H, 5.51.

4.1.21. Compound (*R*)-4G$_0$. (Hexane–ethyl acetate, 4:1). A colorless oil. Yield 92%; $[\alpha]_D^{20}$=+60.0 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 3510, 1595, 1450, 1149, 1058 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 8.05–7.95 (m, 4H, Ar-H), 7.74–7.34 (m, 10H, Ar-H), 7.25–7.21 (m, 2H, Ar-H), 6.76 (s, 1H, –OH), 5.10 (s, 1H, –OH), 5.02 (s, 2H, BINOL–CH_2), 4.81 (s, 2H, Ph–CH_2); MS(EI) m/z (%): 407(8.7) $[M+1]^+$, 406(27.7) $[M]^+$, 299(26.0), 298(100), 281(14.1), 269(41.2), 253(28.7), 239(25.3), 226(8.4), 108(16.1), 91(32.6), 77(20.2).

4.1.22. Compound (*R*)-4G$_1$. (Hexane–CH_2Cl_2, 1:2). A white foam. Yield 84%. $[\alpha]_D^{20}$=+36 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 3503, 1595, 1450, 1149, 1058 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.96–7.89 (m, 4H, Ar-H), 7.44–7.29 (m, 15H, Ar-H), 7.18 (t, J=5.96 Hz, 2H, Ar-H), 6.68–6.60 (m, 3H, Ar-H, 1H, –OH), 5.33 (s, 1H, –OH), 5.04 (s, 4H, Ph–CH_2), 4.93 (s, 2H, BINOL–CH_2), 4.68 (s, 2H, Ph–CH_2); MALDI-TOF-MS m/z: 641.2 $[M+Na]^+$; Anal. calcd for $C_{42}H_{34}O_5$: C, 81.53; H, 5.54. Found: C, 81.29; H, 5.57.

4.1.23. Compound (*R*)-4G$_2$. (Hexane–CH_2Cl_2, 1:3). A white foam. Yield 75%. $[\alpha]_D^{20}$=+18 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 3510, 1594, 1449, 1153, 1027 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.97–7.87 (m, 4H, Ar-H), 7.41–7.29 (m, 25H, Ar-H), 7.17 (t, J=5.96 Hz, 2H, Ar-H), 6.69–6.59 (m, 9H, Ar-H; 1H, –OH), 5.33 (s, 1H, –OH), 5.04 (s, 8H, Ph–CH_2), 4.98 (s, 4H, Ph–CH_2), 4.93 (s, 2H, BINOL–CH_2), 4.68 (s, 2H, Ph–CH_2); MALDI-TOF-MS m/z: 1065.7 $[M+Na]^+$, 1081.6 $[M+K]^+$; Anal. calcd for $C_{70}H_{58}O_9$: C, 80.59; H, 5.60. Found: C, 80.44; H, 5.72.

4.1.24. Compound (*R*)-4G$_3$. (Hexane–CH_2Cl_2, 1:4). A white foam. Yield 85%. $[\alpha]_D^{20}$=+11 (c 2.0, CH_2Cl_2); IR (KBr) ν_{max}: 3514, 1594, 1450, 1154, 1053 cm^{-1}; ^1H NMR ($CDCl_3$, 300 Hz): δ 7.94–7.80 (m, 4H, Ar-H), 7.31–7.17 (m, 45H, Ar-H), 7.17 (t, J=5.96 Hz, 2H, Ar-H), 6.57–6.43 (m, 21H, Ar-H; 1H, –OH), 5.04 (s, 1H, –OH), 4.91 (s, 16H, Ph–CH_2), 4.90 (s, 8H, Ph–CH_2), 4.89 (s, 4H, Ph–CH_2), 4.79 (s, 2H, BINOL–CH_2), 4.54 (s, 2H, Ph–CH_2); MALDI-TOF-MS m/z: 1912.9 $[M+Na]^+$, 1928.9 $[M+K]^+$; Anal. calcd for $C_{126}H_{106}O_{17}$: C, 79.98; H, 5.65. Found: C, 79.79; H, 5.55.

4.2. General procedure for asymmetric addition of diethylzinc to benzaldehyde

Under nitrogen, Ti(O^{i}Pr)$_4$ (34 μL, 0.10 mmol) was added to a solution of (*R*)-**2G$_1$** (15.5 mg, 0.025 mmol) in 1 mL of toluene at room temperature and the mixture was stirred at ambient temperature for 10 min followed by the addition of diethylzinc (1.0 M in hexane, 0.375 mL) under stirring. After 10 min, benzaldehyde (13 μL, 0.125 mmol) was added with a microsyringe at 0°C. The reaction mixture was allowed to stir at 0°C for a given time. The reaction mixture was quenched with 2.0 mL of 1.0N hydrochloric acid solution, filtered through a short pad of Celite to remove the insoluble material, and extracted with 2×1.0 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was further purified by flash column chromatography on silica gel to afford 1-phenyl-1-propanol as a colorless liquid. The conversion and enantioselectivity of the product were determined by GLC using a Supelco β-Dex 120 chiral column (30 m×0.25 mm (i.d.), 0.25 μm film) and the absolution configuration was determined by comparing the retention times with those of authentic samples.

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