

Synthesis of Optically Active Dendrimers Having Chiral Bisphosphine as a Core

Yuko Ouchi, Yasuhiro Morisaki, Yoshiki Chujo 

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
E-mail: chujo@chujo.synchem.kyoto-u.ac.jp

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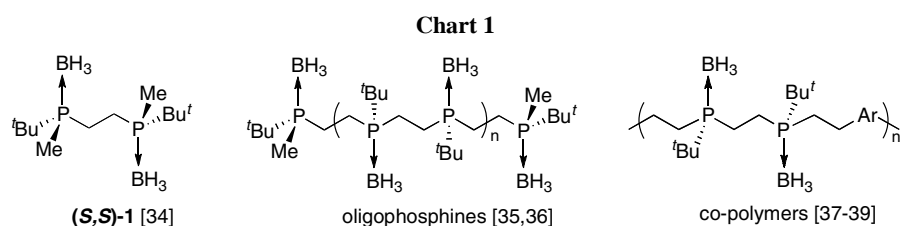
Summary

First and second generation chiral dendrimers **P-1G1**, **P-2G1**, **P-1G2** and **P-2G2** containing chiral bisphosphine as a core were synthesized via a reaction of chiral bisphosphine compound (**S,S**)-**1** with benzyl ether dendrons. This is the first example of chiral dendrimers containing chiral phosphorus atoms. To investigate the effect of chiral phosphorus atoms on their conformations, optically inactive dendrimer **P'-2G1** was synthesized as well using optically inactive initiator **1'** which was the mixture of *rac*-**1** ((**S,S**)-**1** and (**R,R**)-**1**) and *meso*-**1**. Their structures were characterized by ¹H, ¹³C, ³¹P NMR, and HRMS. According to CD measurement, optically active dendrimers exhibited the Cotton effect induced by the chirality of phosphorus atoms, while optically inactive dendrimer **P'-2G1** showed no Cotton effect.

Introduction

Dendrimers represent a new class of polymers that possess not only regular and highly branched skeletons but also monodispersed and well-defined structures [1-5]. These interesting macromolecules consist of a central core and branching units. A large number of dendrimers have been synthesized due to their numerous intriguing properties in diverse fields such as biology [6] and catalytic chemistry [7-10]. One of the most synthetically challenging areas in the field of dendrimer chemistry is preparation of chiral dendrimers [7,8,11-14], which open the possibility to study the effect of the chirality in macromolecular systems. In addition, potential applications of chiral dendrimers, *e.g.*, molecular recognition [12], sensor technology [13,14], and catalyst [7,8], have been investigated in detail. Most of chiral dendrimers reported till date possess chiral carbon atoms or chiral axes. However, no example of synthesis of chiral dendrimers consisting of chiral phosphorus atoms as chiral components has been reported so far, in spite of several reports on catalytic use of phosphorus-containing dendrimers [15-17]. Therefore, we have focused on chiral phosphorus atoms for construction of chiral dendrimers. Not only in dendrimer chemistry but also in synthetic polymer chemistry, little is known about chiral polymers having heteroatom chirality [18-21], though many optically active polymers with chiral carbons or chiral axes have been reported to date [22-28]. Polymers and dendrimers

containing phosphorus atoms are expected to exhibit the specific properties such as plasticity, flame resistance, and coordination ability to transition metals. In addition, as same as carbon atoms, pentavalent and trivalent phosphorus atoms are utilized as chiral centers because they have a tetrahedral conformation with sp^3 hybridization. Especially, trivalent phosphorus atoms exhibit the tetrahedral structure with a lone pair at one apex. The inversion energy of trivalent phosphorus atom is known to depend on the functional groups on the phosphorus atom, which is, in general, much larger than that of nitrogen atoms [29]. Since chiral phosphine compounds with bulky functional groups were found to exhibit a long half-life period of racemization, numerous number of chiral phosphine compounds have been reported so far [30-33]. Among them, chiral phosphine compound (*S,S*)-1,2-bis(boranato(*t*-butyl)methylphosphino)ethane (*S,S*)-**1** (Chart 1) [34] was chosen as a chiral key component for preparation of chiral phosphine polymers and dendrimers due to easy preparation with high enantiomer excess ($ee > 99\%$). In our previous works, we have synthesized optically active oligophosphines [35,36] and co-polymers consisting of chiral phosphorus atoms which were found to exhibit the chiral higher-ordered structure derived from the chirality of phosphorus atoms [37-39] (Chart1).



Helical induction and chiral amplification of optically inactive polymers by chiral additives [40] have been extensively studied. It implies that only small amounts of chiral components efficiently affect the conformation of the polymer and induce the helical structure. Herein, we report synthesis of chiral dendrimers containing chiral bisphosphine as a core. Their characterization and conformational studies are discussed in detail.

Results and Discussion

Synthesis of dendrimers P-1G1 and P-2G1

The first generation chiral dendrimers were synthesized according to Scheme 1. A THF solution of (*S,S*)-**1** was added into a THF solution of 2 equiv. of *sec*-BuLi under nitrogen atmosphere to generate anions of (*S,S*)-**1**. Then, a THF solution of **G1-Br** was added into the reaction mixture. Chiral dendrimers **P-1G1** and **P-2G1** having one and two **G1** units were obtained in 18% and 64% yield after purification by recycling preparative high-performance liquid chromatography (HPLC), respectively. Chiral dendrimers **P-1G1** and **P-2G1** were characterized by ¹H, ¹³C, ³¹P NMR, and HRMS. The ¹H NMR spectrum of **P-2G1** is shown in Figure 1. The broad peak for the BH₃ groups was observed at around δ 0.4 ppm. The doublet peak for the *tert*-butyl groups coupling with phosphorus atoms appeared at δ 1.2 ppm. Two kinds of ethylene protons, -PCH₂- and -CH₂-Ar-, were observed at around δ 1.9 and δ 2.8 ppm,

Scheme 1

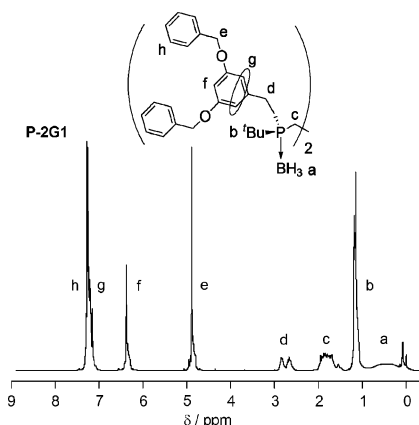
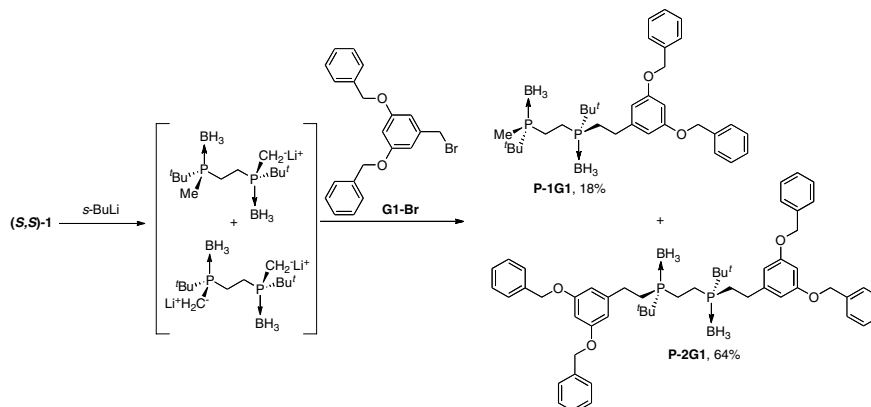


Figure 1. ^1H NMR spectrum of P-2G1 (CDCl_3).

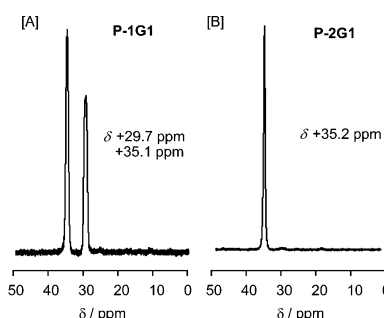


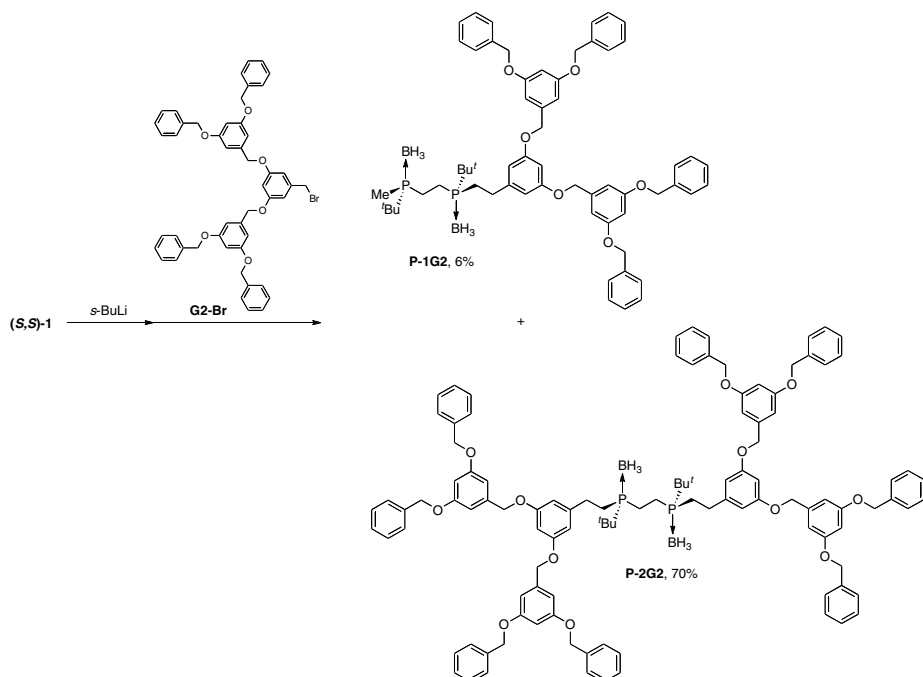
Figure 2. ^{31}P NMR spectra of [A] P-1G1 and [B] P-2G1 (CDCl_3).

respectively. The ^{31}P NMR spectrum of P-1G1 exhibited single peaks at $\delta +29.7$ and $\delta +35.1$ ppm in Figure 2A. Considering the chemical shift of (*S,S*)-1 ($\delta +30.6$ ppm), the peak at $\delta +29.7$ ppm was assigned to the unreacted phosphine unit, and the peak at $\delta +35.1$ ppm was ascribed to the phosphorus atom next to the dendron. In the case of P-2G1, a single phosphorus peak was observed at $\delta +35.2$ ppm in Figure 2B.

Synthesis of dendrimers P-1G2 and P-2G2

The second generation chiral dendrimers P-1G2 and P-2G2 were synthesized according to the same procedure as the preparation of P-1G1 and P-2G1 using the second generation dendron G2-Br (Scheme 2). Although the lithiation step was not an asymmetric reaction, (–)-sparteine was utilized only for activation of *sec*-BuLi in this case. After the purification by HPLC, chiral dendrimers P-1G2 and P-2G2 were obtained as colorless solids. The structures of P-1G2 and P-2G2 were confirmed by ^1H , ^{13}C , ^{31}P NMR, and HRMS. Similarly to those of the first generation dendrimers,

Scheme 2

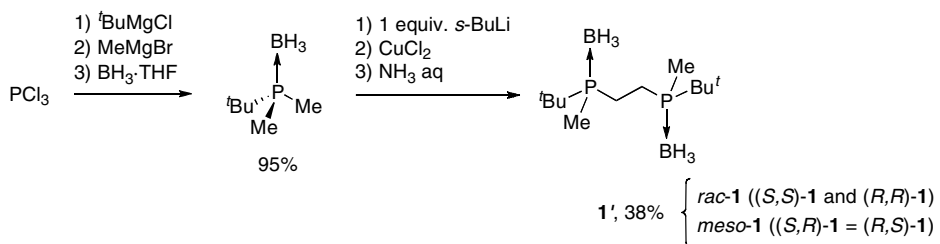


two single peaks were observed at $\delta +29.8$ and $\delta +35.1$ in the ^{31}P NMR spectrum of **P-1G2** and one single peak appeared at $\delta +35.6$ in that of **P-2G2**. The peak at $\delta +29.8$ was assigned to the unreacted phosphine unit and the other peak was derived from the reacted phosphine unit with the dendron unit.

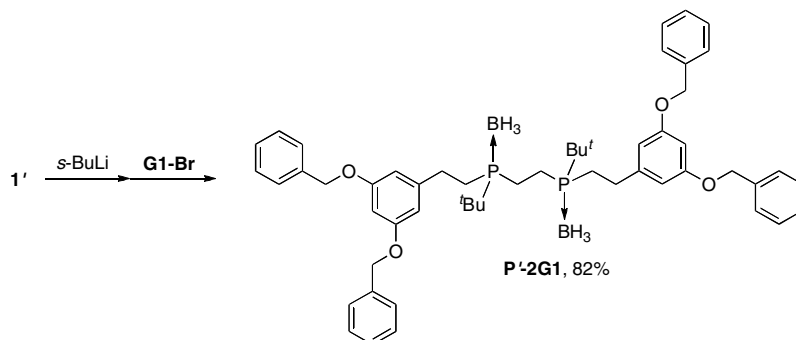
Synthesis of optically inactive dendrimer **P'-2G1**

The optically inactive phosphine compound **1'** was synthesized according to Scheme 3. The reaction was the same as that of **(S,S)-1** except absence of using chiral agent, (–)-sparteine. The compound **1'** was obtained as a mixture of *rac*-**1** (**(S,S)-1** and **(R,R)-1**) and *meso*-**1** (**(S,R)-1** = **(R,S)-1**) after purification by column chromatography on silica gel. Optically inactive dendrimer **P'-2G1** was synthesized according to the same procedure of the preparation of the optically active dendrimers (Scheme 4). The dendrimer having one **G1** unit was not obtained. The structure of **P'-2G1** was

Scheme 3



Scheme 4



characterized by ^1H , ^{13}C , ^{31}P NMR, and HRMS. As same as optically active dendrimers, **P'-2G1** exhibited one single phosphorus peak at $\delta +34.1$ in the ^{31}P NMR spectrum. In addition, chiral phosphine compound **2** was prepared as a model compound. The all obtained compounds were air and moisture stable due to coordination of borane to the phosphorus atom preventing its oxidation.

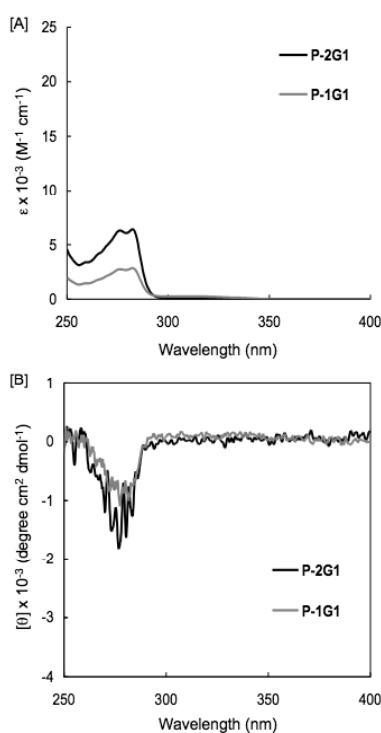
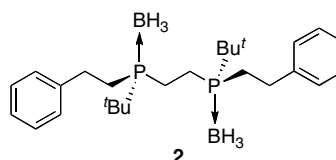


Figure 4. UV [A] and CD [B] spectra of **P-1G1** and **P-2G1** in CHCl_3 .

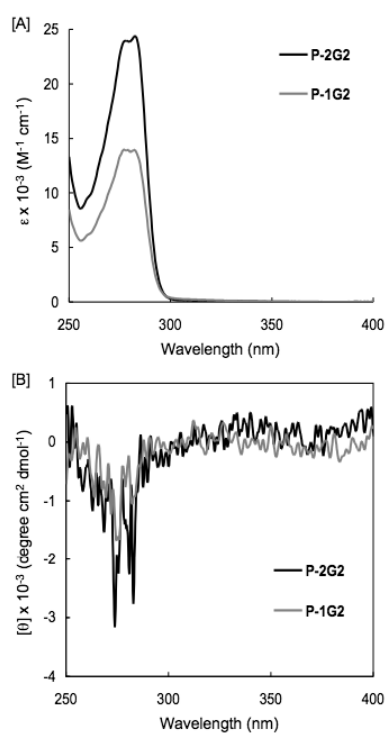


Figure 5. UV [A] and CD [B] spectra of **P-1G2** and **P-2G2** in CHCl_3 .

UV and CD measurements of optically active and optically inactive dendrimers

UV-vis absorption spectra were obtained in dilute chloroform solution. All compounds exhibited an absorption band at around 280 nm in the range of the π - π^* band of the benzene ring (Figures 4-7). The molar absorption coefficient (ϵ) became larger as the number of benzene rings was increasing linearly. The molar absorption coefficient of **P'-2G1** was the same as that of **P-2G1** independent on the enantiomeric purity (Figures 6).

As shown in Figures 4 and 5, all optically active dendrimers **P-1G1**, **P-2G1**, **P-1G2** and **P-2G2** in chloroform solution exhibited the negative Cotton effect at around 280 nm. On the other hand, no Cotton effect was observed in optically inactive dendrimer **P'-2G1** (Figure 6B). These results indicate that the chirality of dendrimers was induced by the chiral phosphorus atoms. It is thought that dendrons are twisted due to the chirality of phosphorus atoms and the steric hindrance. In all the cases of optically active dendrimers, the values of the observed molar ellipticity (θ) were almost the same in spite of the different molar absorption coefficient (ϵ). In addition, surprisingly, model compound **2**, a smallest generation of dendrimer, exhibited no clear Cotton effect in the range of the π - π^* band of the benzene ring (Figure 7B). These results indicate that the first and second generations are more suitable sizes for chiral induction by the chirality of phosphorus atoms as a core than **2**.

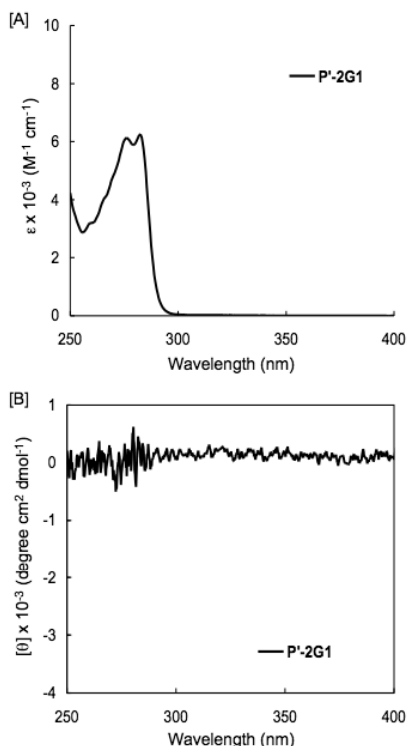


Figure 6. UV [A] and CD [B] spectra of **P'-2G1** in CHCl_3 .

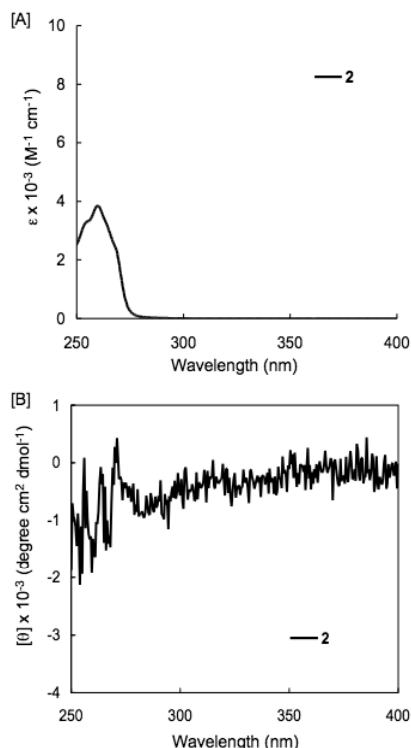


Figure 7. UV [A] and CD [B] spectra of **2** in CHCl_3 .

Conclusion

Optically active dendrimers **P-1G1**, **P-2G1**, **P-1G2** and **P-2G2** were synthesized by the reaction of benzyl ether type dendrons with phosphorus compound (**S,S**)-**1** having two chiral phosphorus atoms. Optically inactive dendrimer **P'-2G1** was prepared as well. Their structures were characterized by ^1H , ^{13}C , ^{31}P NMR, and HRMS. According to CD measurement, optically active dendrimers exhibited the Cotton effect induced by the chirality of phosphorus atoms as the core at around 280 nm which was π - π^* absorption band of the benzene ring. In view of the fact that model compound **2** exhibited no clear Cotton effect, the first and second generations are the proper sizes of chiral induction by the chirality of phosphorus atoms. After removal of BH_3 groups, the phosphorus atoms can coordinate with transition metals, and the complexation can act as a trigger of drastic changes in chiral structure. Therefore, chiral phosphorus dendrimers possess promising possibilities to be applied for a novel type of tunable host material and chiral ligand for transition metals.

Experimental Section

General

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX400 spectrometer, and samples were analyzed in CDCl_3 using Me_4Si as an internal standard. ^{31}P (161.9 MHz) NMR spectra were also recorded on a JEOL EX400 spectrometer, and samples were analyzed in CDCl_3 using H_3PO_4 as an external standard. The following abbreviations are used; s: singlet, d: doublet, q: quartet, m: multiplet, and br: broad. The UV-vis absorption spectra were obtained on a JASCO V-530 spectrometer with CHCl_3 as a solvent. The circular dichroism (CD) spectra were recorded on a JASCO J-600 spectropolarimeter with CHCl_3 as a solvent. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. The purification of each dendrimer was carried out on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using CHCl_3 as an eluent.

Materials

THF was distilled from sodium benzophenone ketyl under nitrogen. (–)-Sparteine was distilled from KOH under nitrogen. 3,5-Dibenzyloxybenzyl bromide **G-1-Br** 3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyl bromide **G-2-Br** were obtained commercially and used as received. *t*-Butyl(dimethyl)phosphine-borane and (**S,S**)-1,2-bis(boranato(*t*-butyl)methylphosphino)ethane (**S,S**)-**1** were prepared as described in the literature [34]. Model compound **2** was prepared according to the procedure described in the literature [37]. The other materials were used as received without further purification. All reactions were performed under nitrogen atmosphere using standard Schlenk techniques.

Synthesis of dendrimers P-1G1 and P-2G1

To a THF (15 mL) solution with stirring, *sec*-BuLi (0.98 M in cyclohexane and *n*-hexane solution, 1.2 mL, 1.2 mmol) was added by a syringe at $-78\text{ }^\circ\text{C}$ under nitrogen atmosphere. To this solution, a THF (4.0 mL) solution of (**S,S**)-**1** (0.13 g,

0.50 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$. After the stirring at $-78\text{ }^{\circ}\text{C}$ over 3 h, a solution of **G-1-Br** (0.45 g, 1.2 mmol) in THF (2.0 mL) was added, and the reaction mixture was allowed to slowly warm to room temperature. After 15 h, the reaction was quenched by the addition of 2 M HCl and extracted with CH_2Cl_2 (20 mL x 3). The combined extracts were washed with aqueous NaHSO_3 and brine. The organic layer was dried over MgSO_4 . After the solvent was removed under reduced pressure, the crude products were purified by a recycling preparative HPLC to obtain **P-1G1** in 18% yield (0.049 g, 0.086 mmol) and **P-2G1** in 64% yield (0.27g, 0.31 mmol), respectively, as white solids.

P-1G1: ^1H NMR (400 MHz, CDCl_3) δ -0.10-0.88 (br, $-\text{BH}_3$, 6H), 1.14 (d, $^3J = 13.6$ Hz, $-t\text{-Bu}$, 9H), 1.18 (d, $^3J = 13.2$ Hz, $-t\text{-Bu}$, 9H), 1.24 (d, $^2J = 9.6$ Hz, $-\text{PCH}_3$, 3H), 1.60-2.12 (br, $-\text{PCH}_2$ -, 6H), 2.65-3.00 (br, $-\text{CH}_2\text{-C}_6\text{H}_4$ -, 2H), 5.01 (s, $-\text{OCH}_2\text{-C}_6\text{H}_5$, 4H), 6.47 (s, ArH , 3H), 7.15-7.49 (m, $-\text{C}_6\text{H}_5$, 10H) ppm; ^{13}C NMR (CDCl_3) δ 4.73 (d, $-\text{PCH}_3$, $J_{\text{CP}} = 33.7$ Hz), 14.1 (d, $-\text{PCH}_2$ -, $J_{\text{CP}} = 29.0$ Hz), 15.9 (d, $-\text{PCH}_2$ -, $J_{\text{CP}} = 30.4$ Hz), 22.5 (d, $-\text{CH}_2\text{-CH}_2\text{-C}_6\text{H}_4$ -, $J_{\text{CP}} = 29.6$ Hz), 24.7 ($(\text{CH}_3)_3\text{C}$ -), 25.1 ($(\text{CH}_3)_3\text{C}$ -), 27.2 (d, $(\text{CH}_3)_3\text{C}$ -, $J_{\text{CP}} = 32.9$ Hz), 28.5 (d, $(\text{CH}_3)_3\text{C}$ -, $J_{\text{CP}} = 32.1$ Hz), 29.6 ($-\text{CH}_2\text{-C}_6\text{H}_4$ -), 69.7 ($-\text{OCH}_2$ -), 99.6, 107.0 (Ar C), 127.2, 127.7, 128.2 (Ph CH), 136.4, 143.3, 159.8 (Ph C and Ar CH) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ +29.7, +35.1 ppm; HRMS (FAB) calcd for $\text{C}_{33}\text{H}_{51}\text{O}_2\text{B}_2\text{P}_2$ $[\text{M-H}]^+$: 563.3550, found 563.3553.

P-2G1: ^1H NMR (400 MHz, CDCl_3) δ -0.10-0.89 (br, $-\text{BH}_3$, 6H), 1.18 (d, $^3J = 13.2$ Hz, $-t\text{-Bu}$, 18H), 1.60-2.01 (br, $-\text{PCH}_2$ -, 8H), 2.60-2.94 (br, $-\text{CH}_2\text{-C}_6\text{H}_4$ -, 4H), 4.94 (s, $-\text{OCH}_2\text{-C}_6\text{H}_5$, 8H), 6.46 (s, ArH , 6H), 7.23-7.36 (m, $-\text{C}_6\text{H}_5$, 20H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 15.0 (d, $-\text{PCH}_2$ -, $J_{\text{CP}} = 29.5$ Hz), 22.6 (d, $-\text{CH}_2\text{-CH}_2\text{-C}_6\text{H}_4$ -, $J_{\text{CP}} = 28.7$ Hz), 25.4 ($(\text{CH}_3)_3\text{C}$ -), 28.6 (d, $(\text{CH}_3)_3\text{C}$ -, $J_{\text{CP}} = 32.0$ Hz), 30.0 ($-\text{CH}_2\text{-C}_6\text{H}_4$ -), 69.8 ($-\text{OCH}_2$ -), 99.9, 107.2 (Ar C), 127.4, 127.8, 128.4 (Ph CH), 136.6, 143.6, 160.0 (Ph C and Ar CH) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ +35.4 ppm; HRMS (FAB) calcd for $\text{C}_{54}\text{H}_{69}\text{O}_4\text{B}_2\text{P}_2$ $[\text{M-H}]^+$: 865.4857, found 865.4857.

Synthesis of dendrimers P-1G2 and P-2G2

To a solution of (–)-sparteine (0.17 mL, 0.75 mmol) in THF (8 mL) with stirring, *sec*-BuLi (1.01 M in cyclohexane and n-hexane solution, 0.74 mL, 0.75 mmol) was added by a syringe at $-78\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. After 15 minutes with stirring at $-78\text{ }^{\circ}\text{C}$, a THF (2.0 mL) solution of (*S,S*)-**1** (0.082 g, 0.31 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$. After stirring at $-78\text{ }^{\circ}\text{C}$ over 3 h, a solution of **G-2-Br** (0.50 g, 0.62 mmol) in THF (2.0 mL) was added, and the reaction mixture was allowed to slowly warm to room temperature. After 15 h, the reaction was quenched by the addition of 2 M HCl and extracted with CH_2Cl_2 (20 mL x 3). The combined extracts were washed with aqueous NaHSO_3 and brine. The organic layer was dried over MgSO_4 . After the solvent was removed under reduced pressure, the crude products were purified by a recycling preparative HPLC to obtain **P-1G2** in 6% yield (0.019 g, 0.019 mmol) and **P-2G2** in 70% yield (0.38 g, 0.22 mmol), respectively, as white solids.

P-1G2: ^1H NMR (400 MHz, CDCl_3) δ 0.00-0.89 (br, $-\text{BH}_3$, 6H), 1.15 (d, $^3J = 14.4$ Hz, $-t\text{-Bu}$, 9H), 1.18 (d, $^3J = 14.0$ Hz, $-t\text{-Bu}$, 9H), 1.24 (d, $^2J = 10.0$ Hz, $-\text{PCH}_3$, 3H), 1.60-2.12 (br, $-\text{PCH}_2$ -, 6H), 2.65-3.03 (br, $-\text{CH}_2\text{-C}_6\text{H}_4$ -, 2H), 4.95 (s, $-\text{OCH}_2\text{-Ar}$, 4H), 5.02 (s, $-\text{OCH}_2\text{-C}_6\text{H}_5$, 8H), 6.43 (s, ArH , 1H), 6.46 (s, ArH , 2H), 6.57 (s, ArH , 2H), 6.68 (s, ArH , 4H), 7.24-7.42 (m, $-\text{C}_6\text{H}_5$, 20H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 4.82 (d, $-\text{PCH}_3$, $J_{\text{CP}} = 36.1$ Hz), 14.2 (d, $-\text{PCH}_2$ -, $J_{\text{CP}} = 32.9$ Hz), 15.9 (d, $-\text{PCH}_2$ -, $J_{\text{CP}} = 35.4$ Hz), 22.5 (d, $-\text{CH}_2\text{-CH}_2\text{-C}_6\text{H}_4$ -, $J_{\text{CP}} = 32.1$ Hz), 24.7 ($(\text{CH}_3)_3\text{C}$ -), 25.2 ($(\text{CH}_3)_3\text{C}$ -), 27.2 (d,

(CH₃)₃C-, $J_{CP} = 33.7$ Hz), 28.5 (d, (CH₃)₃C-, $J_{CP} = 32.1$ Hz), 29.4 (-CH₂-C₆H₄-), 69.6 (-OCH₂-), 69.8 (-OCH₂-), 99.6, 101.2, 107.0, 107.1 (Ar C), 127.2, 127.7, 128.3 (Ph CH), 136.4, 138.8, 143.4, 159.8, 159.9 (Ph C and Ar CH) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ +29.8, +35.1 ppm; HRMS (FAB) calcd for C₆₁H₇₅O₆B₂P₂ [M-H]⁺: 987.5225, found 987.5221.

P-2G2: ¹H NMR (400 MHz, CDCl₃) δ 0.04-0.85 (br, -BH₃, 6H), 1.15 (d, ³J = 12.8 Hz, -*t*-Bu, 18H), 1.65-2.05 (br, -PCH₂-, 8H), 2.67-2.98 (br, -CH₂-C₆H₄-, 4H), 4.81 (s, -OCH₂-Ar, 8H), 4.91 (s, -OCH₂-C₆H₅, 16H), 6.39 (s, ArH, 2H), 6.45 (s, ArH, 4H), 6.50 (s, ArH, 4H), 6.61 (s, ArH, 8H), 7.24-7.42 (m, -C₆H₅, 40H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 16.0 (-PCH₂-), 22.8 (-CH₂-CH₂-C₆H₄-), 25.8 ((CH₃)₃C-), 29.0 ((CH₃)₃C-), 30.6 (-CH₂-C₆H₄-), 70.1 (-OCH₂-), 70.3 (-OCH₂-), 102-108 (Ar C), 127-129 (Ph CH), 137-138, 159-160 (Ph C and Ar CH) ppm; ³¹P{¹H} NMR (161.9 MHz, CDCl₃) δ +35.6 ppm; HRMS (FAB) calcd for C₁₁₀H₁₁₇O₁₂B₂P₂ [M-H]⁺: 1713.8207, found 1713.8191.

Synthesis of **1'**

An Et₂O solution (28 mL) was cooled to -78 °C under nitrogen atmosphere. To a stirred this solution, *sec*-BuLi (1.0 M in cyclohexane and n-hexane solution, 19.0 mL, 19.0 mmol) was added by a syringe. After 15 minutes, a solution of *t*-butyl(dimethyl)phosphine-borane (1.48 g, 11.2 mmol) in Et₂O (11 mL) was added dropwise, and the mixture was stirred at -78 °C over 3 h. Dry CuCl₂ (2.3 g, 16.8 mmol) was added in one portion with vigorous stirring, and the mixture was allowed to slowly warm to room temperature. After 15 h, the reaction was quenched by the addition of 28% aqueous ammonia (15 mL), and extracted with CH₂Cl₂ (3 x 40 mL). The combined extracts were washed with 5% aqueous ammonia, 2M HCl, and brine, and then dried over MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexane:CH₂Cl₂ = 1:1) to give **1'** (0.56 g, 2.1 mmol, 38%) as a colorless solid.

¹H NMR (CDCl₃) δ 0.39 (q, $J_{HB} = 94.7$ Hz, -BH₃, 6H), 1.16 (d, ³J_{HP} = 13.7 Hz, -*t*-Bu, 9H), 1.18 (d, ³J_{HP} = 14.0 Hz, -*t*-Bu, 9H), 1.23 (d, ²J_{HP} = 9.8 Hz, -PCH₃, 6H), 1.52-1.70 (m, -PCH₂-, 2H), 1.85-1.21 (m, -PCH₂-, 2H) ppm; ¹³C NMR (CDCl₃) δ 4.78 (d, $J_{CP} = 33.9$ Hz, -PCH₃), δ 5.79 (d, $J_{CP} = 34.8$ Hz, -PCH₃) 14.9 (d, $J_{CP} = 29.8$ Hz, -PCH₂-), 16.1 (d, $J_{CP} = 30.6$ Hz, -PCH₂-), 25.1 (s, -PC(CH₃)₃), 25.2 (s, -PC(CH₃)₃), 27.6 (d, $J_{CP} = 34.0$ Hz, -PC(CH₃)₃), 27.8 (d, $J_{CP} = 34.0$ Hz, -PC(CH₃)₃) ppm; ³¹P{¹H}NMR (CDCl₃) δ +29.9 ppm.

Synthesis of dendrimer **P'-2G1**

To a THF (8 mL) solution with stirring, *sec*-BuLi (1.01 M in cyclohexane and n-hexane solution, 0.41 mL, 0.41 mmol) was added by a syringe at -78 °C under nitrogen atmosphere. To this solution, a THF (2 mL) solution of **1'** (0.045 g, 0.17 mmol) was added dropwise at -78 °C. After stirring at -78 °C over 3 h, a solution of **G-1-Br** (0.28 g, 0.34 mmol) in THF (2 mL) was added, and the reaction mixture was allowed to slowly warm to room temperature. After 15 h, the reaction was quenched by the addition of 2 M HCl and extracted with CH₂Cl₂ (20 mL x 3). The combined extracts were washed with aqueous NaHSO₃ and brine. The organic layer was dried over MgSO₄. After the solvent was removed under reduced pressure, the crude product was purified by a recycling preparative HPLC to obtain **P'-2G1** in 82% yield (0.12 g, 0.14 mmol) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 0.00-0.95 (br, $-\text{BH}_3$, 6H), 1.17 (m, $-t\text{-Bu}$, 18H), 1.65-2.08 (br, $-\text{PCH}_2-$, 8H), 2.62-2.95 (br, $-\text{CH}_2-\text{C}_6\text{H}_4-$, 4H), 4.94 (s, $-\text{OCH}_2-\text{C}_6\text{H}_5$, 8H), 6.46 (s, ArH , 6H), 7.25-7.46 (m, $-\text{C}_6\text{H}_5$, 20H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 15.0 (d, $-\text{PCH}_2-$, $J_{\text{CP}} = 28.8$ Hz), 22.6 (d, $-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_4-$, $J_{\text{CP}} = 28.8$ Hz), 25.4 (s, $(\text{CH}_3)_3\text{C}-$), 28.6 (d, $(\text{CH}_3)_3\text{C}-$, $J_{\text{CP}} = 32.1$ Hz), 30.1 ($-\text{CH}_2-\text{C}_6\text{H}_4-$), 69.9 ($-\text{OCH}_2-$), 100, 107 (Ar C), 127, 128, 128 (Ph CH), 137, 144, 160 (Ph C and Ar CH) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3) δ +34.1 ppm; HRMS (FAB) calcd for $\text{C}_{54}\text{H}_{69}\text{O}_4\text{B}_2\text{P}_2$ $[\text{M}-\text{H}]^+$: 865.4857, found 865.4858.

UV and CD measurement

UV and CD measurements were performed in a CHCl_3 solution (10 mm-length cell); **P-1G1** (4.34×10^{-4} mol/L), **P-2G1** (2.53×10^{-4} mol/L), **P-1G2** (3.49×10^{-5} mol/L), **P-2G2** (8.72×10^{-5} mol/L), **P'-2G1** (2.25×10^{-4} mol/L), and model compound **2** (1.81×10^{-4} mol/L).

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References and Notes

- Tomalia DA, Baker H, Dwald J, Hall M, Kallos G, Martin S, Roeck J, Ryder J, Smith P (1985) *Polym J* 17:117
- Newkome GR, Yao Z, Baker GR, Gupta VK (1985) *J Org Chem* 50:2004
- Hawker CJ, Fréchet JMJ (1990) *J Am Chem Soc* 112:7638
- Newkome GR, Moorfield CN, Vögtle F (1996) *Dendritic Molecules. Concepts, Synthesis, Perspectives*, VCH, Weinheim
- Fréchet JMJ, Hawker CJ (1996) *Comprehensive Polymer Science*, 2nd suppl. In Aggarwal SL, Russo S, (eds) Oxford, Pergamprn (pp.71-132)
- Boas U, Heegaard PMH (2004) *Chem Soc Rev* 37:341
- Kreiter R, Kleij AW, Gebbink RJM, van Koten G (2001) *Top Curr Chem* 217:163
- Astruc D, Chardac F (2001) *Chem Rev* 101:2991
- van Heerbeek R, Kamer PCJ, van Leeuwen PWNM, Reek JNH (2002) *Chem Rev* 102:3717
- Dijkstra HP, van Klink GPM, van Koten G (2002) *Acc Chem Res* 35:789
- Rheiner PB, Seebach D, Greiveldinger G, Butz T, Sellner H (1998) *Top Curr Chem* 197:127
- Lee YC, Lee RT (1995) *Acc Chem Res* 28:321
- Hu Q-S, Pugh V, Sabat M, Pu L (1999) *J Org Chem* 64:7528
- Pugh VJ, Hu Q-S, Pu L (2000) *Angew Chem Int Ed* 39:3638
- Majoral JP, Caminade AM (1999) *Chem Rev* 99:845
- Majoral JP, Caminade AM (2003) *Top Curr Chem* 223:111
- Caminade AM, Laurent R, Chaudret B, Majoral JP (1998) *Coord Chem Rev* 178-180:793
- Kawakami Y, Takeyama K, Komuro K, Ooi O (1998) *Macromolecules* 31:551
- Kawakami Y, Zhou D (2005) *Macromolecules* 38:6902
- Oyama T, Chujo Y (1999) *Macromolecules* 32:7732
- Angeloni A, Laus M, Caretti D, Chiellini E, Galli G (1990) *Makromol Chem* 191:2787
- Okamoto Y, Nakano T (1994) *Chem Rev* 94:349
- Okamoto Y, Nakano T (2001) *Chem Rev* 101:4013
- Cornelissen JJLM, Rowan AE, Nolte RJM, Sommerdijk NAJM (2001) *Chem Rev* 101:4039
- Pu L (1997) *Chem Rev* 98:2405

26. Piguet C, Bernardinelli G, Hopfgartner G (1997) *Chem Rev* 97:2005
27. Hill DJ, Mio MJ, Prince RB, Hughes TS, Moore JS (2001) *Chem Rev* 101:3893
28. Lam JWY, Tang BZ (2005) *Acc Chem Res* 38:745
29. Weston RE (1954,) *J Am Chem Soc* 76:2645
30. Noyori R (1994) *Asymmetric Catalyst in Organic Synthesis*, John Wiley & Sons, New York
31. Pitrusiewicz KM, Zablocki M (1994) *Chem Rev* 94:1375
32. Ojima I (ed) (2000) *Catalytic Asymmetric Synthesis*, John Wiley & Sons, New York
33. Knowles WS (1983) *Acc Chem Res* 16:106
34. Imamoto T, Watanabe J, Wada Y, Masuda H, Yamada H, Tsuruta H, Matsukawa S, Yamaguchi K (1998) *J Am Chem Soc* 120:1635
35. Morisaki Y, Ouchi Y, Fukui T, Naka K, Chujo Y (2005) *Tetrahedron Lett* 46:7011
36. Morisaki Y, Ouchi Y, Fukui T, Naka K, Chujo Y (2007) *Tetrahedron Lett* 48:1451
37. Morisaki Y, Ouchi Y, Tsurui K, Chujo Y (2007) *J Polym Sci Part A Polym Chem* 45:866
38. Morisaki Y, Ouchi Y, Tsurui K, Chujo Y (2007) *Polym Bull* 58:665
39. Ouchi Y, Morisaki Y, Ogoshi T, Chujo Y (2007) *Chem Asian J* 2:397
40. Yashima E, Maeda K, Okamoto Y (1999) *Nature* 399:449