Asymmetric Synthesis of *N*-(Diphenylphosphinyl)amines Promoted by Chiral Carbosilane Dendritic Ligands in The Enantioselective Addition of Dialkylzinc Compounds to *N*-(Diphenylphosphinyl)imines

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The enantioselective addition of dialkylzinc compounds to *N*-(diphenylphosphinyl)imines by using chiral dendrimers with flexible carbosilane backbones gives enantiomerically enriched *N*-(diphenylphosphinyl)amines with up to 92% *ee*.

Introduction

The enantioselective addition of organometallic reagents to imines is a useful method to obtain chiral amines.[1] However, compared to the corresponding addition reaction to aldehydes,[2] much less attention has been paid to the enantioselective addition of dialkylzinc reagents to imines. We have developed an enantioselective addition of dialkylzinc compounds to *N*-(diphenylphosphinyl)imines in the presence of chiral β-amino alcohols for the formation of enantiomerically enriched *N*-(diphenylphosphinyl)amines.[3,4] Subsequent removal of the diphenylphosphinyl group by an acid hydrolysis[5] affords enantiomerically enriched secondary amines.

The synthetic application of dendrimers, which are polymers with particular molecular weights and structures, are of current interest.[6] Hyperbranched chain ends are able to load chiral functionalities such as β-amino alcohols, and the resulting chiral macromolecule works as a dendritic chiral ligand in asymmetric synthesis.[7,8] Compared to other polymer-bound chiral ligands,[9] dendritic chiral ligands possess superior applicabilities in: i) high activities of every chiral sites due to their location at the periphery; ii) high enantioselectivity induced by approximately the same chiral circumstances of each chiral site. We have developed PAMAM-based chiral dendrimers[10a] and chiral poly(phenylethyne) dendrimers.[10b,11a] Chiral poly(phenylethyne) dendrimers with rigid backbones act as chiral ligands for the enantioselective addition of diethylzinc to *N*-(diphenylphosphinyl)imines.

On the other hand, the backbone of carbosilane dendrimers[12] is flexible and it hardly coordinates with organometallic reagents. When chiral dendrimers with flexible backbones are used as chiral ligands, the flexibility of the backbones may cause unfavorable interactions between the chiral sites and may reduce enantioselectivity.[10a] Thus, highly enantioselective synthesis utilizing chiral dendrimers with flexible backbones has been a challenge. We report here a highly enantioselective addition of dialkylzinc compounds to *N*-(diphenylphosphinyl)imines by using dendritic chiral ligands composed of flexible carbosilane backbones bearing four or twelve chiral β-amino alcohols (Figure 1).

Results and Discussion

The enantioselective addition of dialkylzinc compounds to *N*-(diphenylphosphinyl)imines was examined in the presence of chiral dendritic ligands **1**, **2,** and a chiral dimer **3** (Scheme 1 and Table 1). When the chiral dendrimer **1**,[11b] containing four chiral sites, was used as the chiral ligand, the enantioselective addition of Et_2Zn to *N*-(diphenylphosphinyl)imine (**4a**) gave (*R*)-*N*-(diphenylphosphinyl)amine (**5a**) with 92% *ee* in 78% yield (Table 1, entry 1).[13] The yield and enantioselectivity with chiral dendrimer **1** are similar to those of the chiral poly(phenylethyne) dendrimers with rigid backbones.[10b] Reaction with *N*-(diphenylphosphinyl)imine **4b** affords *N*-(diphenylphosphinyl)amine **5b** with 90% *ee* (entry 2). Addition of iPr_2Zn to *N*-(diphenylphosphinyl)imine **4c** proceeded with slightly higher enantioselectivity — to give (*R*)-*N*-(diphenylphosphinyl)-amine **6** with 89% *ee* — than the corresponding addition of diethylzinc to **4c**, giving *N*-(diphenylphosphinyl)amine **5c** with 82% *ee* (entries 3 and 4). On the other hand, *N*-(diphenylphosphinyl)imines **4d** gave chiral *N*-(diphenylphosphinyl)amines **5d** (88% *ee*, entry 5). The chiral dendrimer **1** can be recovered and reused.[14] Recovered **1** gave *N*-(diphenylphosphinyl)amine **5a** with 91% *ee* without any loss of enantioselectivity (entry 6). Chiral dendrimer **2,** with 12

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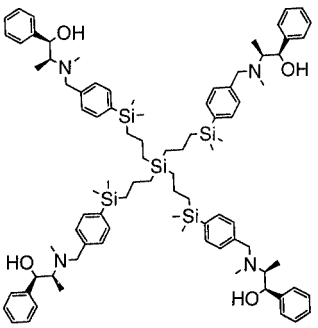

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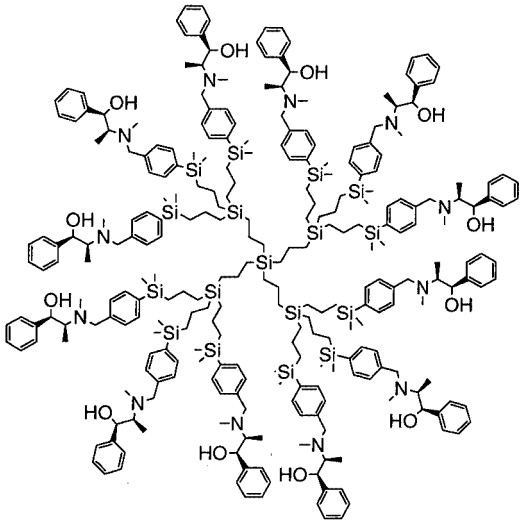

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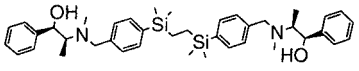
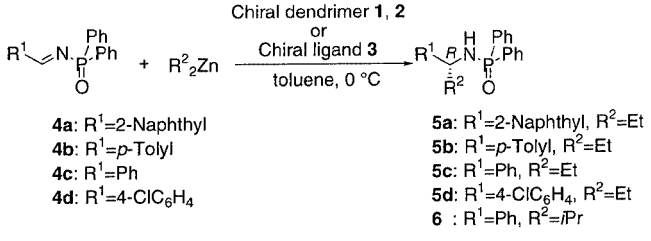


3

Figure 1. Chiral dendrimers **1**, **2** and chiral dimer **3**



Scheme 1

chiral sites,[11b] also works as a highly enantioselective chiral ligand in the enantioselective addition of Et_2Zn to *N*-(diphenylphosphinyl)imine (**4a**). Thus, *N*-(diphenylphosphinyl)amine **5a** was obtained with 92% and 90% *ee* in the reactions with 0.13 and 0.083 molar equiv. of chiral dendrimer **2**, respectively (entries 7 and 8). The enantioselectivity of chiral dendrimer **2** is comparable to that of chiral dendrimer **1** (entry 1) and chiral dimer **3** (entry 12). Addition of Et_2Zn to *N*-(diphenylphosphinyl)imines **4b** and **4d** using chiral dendrimer **2** proceeded with high enantioselectivity to give chiral *N*-(diphenylphosphinyl)amines **5b** (84% *ee*) and **5d** (85% *ee*), respectively (entries 9 and 10). Isopropylation of *N*-(diphenylphosphinyl)imine **4c** afforded *N*-(diphenylphosphinyl)amine **6** with 86% *ee* in 70% yield (entry 11).

In summary, chiral dendrimers **1** and **2** with flexible backbone are effective chiral ligands in the enantioselective synthesis of chiral *N*-(diphenylphosphinyl)amines by the addition of dialkylzinc reagents to *N*-(diphenylphosphinyl)-imines.

Experimental Section

According to the literature,[11b] chiral dendrimer **1** was synthesized by the reaction between lithiated (1*R*,2*S*)-*N*-(4-bromobenzyl)-*O*-(*tert*-butyldimethylsilyl)ephedrine[11b] and tetrakis[3-(chlorodimethylsilyl)propyl]silane[12a] followed by the cleavage of the silyl ether.[11b] Chiral dendrimer **2** was prepared from tetrakis[3-{tris[3-(chlorodimethylsilyl)propyl]silyl}propyl]silane[12a] and (1*R*,2*S*)-*N*-(4-bromobenzyl)-*O*-(trimethylsilyl)ephedrine.[11b] Chiral dimer **3** was derived from commarcially available 1,3-(chlorodimethylsilyl)ethane and (1*R*,2*S*)-*N*-(4-bromobenzyl)-*O*-(*tert*-butyldimethylsilyl)ephedrine.[11b] Compounds **4a**,[3a,15] **4b**,[3a,10a] **4c**[3a,15] and **4d**[15] were prepared according to a literature procedure.[15] Compounds **5a**,[3a,16] **5b**,[3a][10a] **5c**,[3a,16] **5d**[4a] and **6**[17] are known compounds.

Dendrimer 1: Colorless oil. $[\alpha]_D^{25} = -26.8$ (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 24 H), 0.54 (m, 8 H), 0.80 (m, 8 H), 0.99 (d, J = 6.8 Hz, 12 H), 1.34 (m, 8 H,), 2.20 (s, 12 H,), 2.93 (qd, J = 6.8, 5.4 Hz, 4 H), 3.60 (d, J = 13.5 Hz, 4 H), 3.63 (d, J = 13.5 Hz, 4 H), 4.90 (d, J = 5.4 Hz, 4 H), 7.2−7.5 (m, 36 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = −2.8, 9.9, 17.4, 18.5, 20.6, 38.7, 59.1, 63.4, 73.5, 126.1, 126.9, 128.0, 128.1, 133.5, 138.2, 140.0, 142.5 ppm. FT-IR (neat): $\tilde{\nu}$ = 3432 cm^{-1}, 2792, 1450, 1249. HR MS (FAB^+) calcd. for $C_{88}H_{129}N_4O_4Si_5$ [M + H]: 1445.886; found 1445.886.

Dendrimer 2: Colorless oil. $[\alpha]_D^{22} = -21.5$ (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.23 (s, 72 H), 0.58 (m, 40 H), 0.80 (m, 24 H), 0.97 (d, J = 6.6 Hz, 36 H), 1.21 (m, 32 H), 2.17 (s, 36 H), 2.90 (m, 12 H), 3.58 (d, J = 13.9 Hz, 12 H), 3.62 (d, J = 13.9 Hz, 12 H), 4.89 (d, J = 4.0 Hz, 12 H), 7.2−7.5 (m, 108 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = −2.8, 9.8, 17.4, 18.6, 20.6, 38.7, 59.1, 63.6, 73.4, 126.1, 126.9, 128.0, 128.1, 133.5, 138.2, 139.8, 142.5 ppm. FT-IR (neat): $\tilde{\nu}$ = 3382 cm^{-1}, 2915, 1450, 1250. MALDI-TOF MS (α-CHCA): m/z = 4564.7 $[M + H]^+$.

Dimer 3: Colorless powder; m.p. 78 °C (hexane). $[\alpha]_D^{25} = -36.9$ (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 12 H), 0.68 (s, 4 H), 1.01 (d, J = 6.8 Hz, 6 H), 2.22 (s, 6 H), 2.95 (qd, J = 6.8, 4.8 Hz, 2 H), 3.63 (d, J = 13.6 Hz, 2 H), 3.64 (d, J = 13.6 Hz, 2 H), 4.90 (d, J = 4.8 Hz, 2 H), 7.2−7.5 (m, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = −3.5, 7.8, 9.9, 38.8, 59.1, 63.4, 73.5, 126.2, 126.9, 128.0, 128.0, 133.7, 137.8, 140.0, 142.4 ppm. FT-IR (neat):

Table 1. Highly enantioselective synthesis of *N*-(diphenylphosphinyl)amines by the addition of dialkylzinc compounds to *N*-(diphenylphosphinyl)imines using chiral dendrimers **1**, **2** or chiral dimer **3**

Entry[a]	*N*-(diphenylphosphinyl)imine R^1		Chiral dendrimer	(mol. equiv.)	R^2	*N*-(diphenylphosphinyl)amine	yield [%][b]	*ee* [%][c]
1	2-naphthyl	**4a**	**1**	(0.25)	Et	**5a**	78	92
2	*p*-tolyl	**4b**	**1**	(0.25)	Et	**5b**	71	90
3	phenyl	**4c**	**1**	(0.25)	*i*Pr	**6**	79	89
4	phenyl	**4c**	**1**	(0.25)	Et	**5c**	81	82
5	4-ClC_6H_4	**4d**	**1**	(0.25)	Et	**5d**	72	88
6	2-naphthyl	**4a**	**1**	(0.25)[d]	Et	**5a**	77	91
7	2-naphthyl	**4a**	**2**	(0.13)	Et	**5a**	70	92
8	2-naphthyl	**4a**	**2**	(0.083)	Et	**5a**	70	90
9	*p*-tolyl	**4b**	**2**	(0.13)	Et	**5b**	71	84
10	4-ClC_6H_4	**4d**	**2**	(0.13)	Et	**5d**	74	85
11	phenyl	**4c**	**2**	(0.13)	*i*Pr	**6**	70	86
12	2-naphthyl	**4a**	**3**	(0.50)	Et	**5a**	71	94
13	phenyl	**4c**	**3**	(0.50)	*i*Pr	**6**	81	90
14	phenyl	**4c**	**3**	(0.50)	Et	**5c**	80	86

[a] Reactions were run in toluene at 0 °C for 48 h using 3 molar equiv. of dialkylzinc compounds. [b] Isolated yields.[c] Determined by HPLC analysis on a chiral stationary phase. [d] Recovered chiral dendrimer was used.

$\tilde{\nu}$ = 3394 cm^{-1}, 2951, 2842, 2788, 1454, 1392. HR MS (FAB^+) calcd. for $C_{40}H_{57}N_2O_2Si_2$ [M + H]: 653.3959; found 653.3962.

***N*-(4-Methybenzylidene)-*P,P*-diphenylphosphinamide (4b):** Colorless powder; m.p. 154 °C (hexane/toluene). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 7.30 (m, 2 H), 7.4−7.5 (m, 6 H), 7.8−7.9 (m, 6 H), 9.38 (d, *J* = 34.8 Hz, 1 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1630 cm^{-1}, 1195. HR-MS calcd. for $C_{22}H_{24}ONP$ [M^+]: 319.1126; found 319.1117.

Representative Procedure for the Enantioselective Addition of Dialkylzinc Compounds to *N*-(diphenylphosphinyl)imine 4a in the Presence of Chiral Dendrimer 3: A 1 M toluene solution of Et_2Zn (0.3 mL, 0.3 mmol) at 0 °C was added to a mixture of *N*-(diphenylphosphinyl)imine **4a** (35.5 mg, 0.1 mmol) and dendritic chiral ligand **3** (38.0 mg, 0.0083 mmol) in toluene (2 mL). After stirring the mixture for 48 h at 0 °C, the reaction was quenched by adding sat. aq. ammonium chloride (3 mL). The mixture was filtered through celite and the separated aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate and the solvents evaporated. Purification of the residue by thin layer chromatography (eluent: dichloromethane/acetone, 5:1) gave *N*-(diphenylphosphinyl)amine **5a** (27.1 mg, 70%). The *ee* value was determined to be 90% by HPLC analysis using a chiral stationary phase (Chiralcel OD; 4.6 × 250 mm; 254 nm UV detector; eluent: 3% 2-propanol in hexane; flow rate: 1.0 mL/min; retention time: 27 min for *R*-isomer, 44 min for *S*-isomer).

(+)-*N*-[1-(4-Methylphenyl)propyl]-*P,P*-diphenylphosphinamide (5b):[3a,10a] Colorless needles; m.p. 139 °C (hexane/dichloromethane, 96% *ee*). $[\alpha]_D^{24}$ = +43.5 (*c* = 1.00, MeOH, 96% *ee*). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.77 (t, *J* = 7.3 Hz, 3 H), 1.79 (m, 1 H), 2.00 (m, 1 H), 2.33 (s, 3 H), 3.23 (m, 1 H), 4.04 (m, 1 H), 7.03 (m, 2 H), 7.10 (m, 2 H), 7.3−7.5 (m, 6 H), 7.80 (m, 4 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1}, 1185. HR-MS calcd. for $C_{22}H_{24}NOP$ [M^+] 349.1596; found 349.1598. HPLC conditions: Chiralcel AD; 4.6 × 250 mm; 254 nm UV detector; eluent: 10% 2-propanol in hexane; flow rate: 1.0 mL/min; retention time: 16 min for *R*-isomer, 20 min for *S*-isomer.

***N*-(1-Phenylpropyl)-*P,P*-diphenylphosphinamide (5c):**[3a,16] HPLC conditions: Chiralcel OD; 4.6 × 250 mm; 254 nm UV detector; eluent: 3% 2-propanol in hexane; flow rate: 1.0 mL/min; retention time: 15 min for *R*-isomer, 24 min for *S*-isomer.

***N*-[1-(4-Chlorophenyl)propyl]-*P,P*-diphenylphosphinamide (5d):**[4a] HPLC conditions: Chiralpak AD; 4.6 × 250 mm; 254 nm UV detector; eluent: 10% 2-propanol in hexane; flow rate: 1.0 mL/min; retention time: 20 min for *R*-isomer, 24 min for *S*-isomer.

(+)-*N*-(2-Methyl-1-phenylpropyl)-*P,P*-diphenylphosphinamide (6):[17] Colorless needles; m.p. 155 °C (hexane/dichloromethane, 87% *ee*). $[\alpha]_D^{25}$ = +35.3 (*c* = 1.00, MeOH, 87% *ee*). HPLC conditions: Chiralcel OD; 4.6 × 250 mm; 254 nm UV detector; eluent: 2% 2-propanol in hexane; flow rate: 1.0 mL/ min; retention time: 24 min for *R*-isomer, 34 min for *S*-isomer.

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[1] For alkyllithiums see: [1a] K. Tomioka, I. Inoue, M. Shindo, K. Koga, *Tetrahedron Lett.* **1990**, *31*, 6681−6684. [1b] S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, *J. Am. Chem. Soc.* **1994**, *116*, 8797−8798. [1c] S. Itsuno, M. Sasaki, S. Kuroda, K. Ito, *Tetrahedron: Asymmetry* **1995**, *6*, 1507−1510. For organozinc reagents see: [1d] A. R. Katritzky, P. A. Harris, *Tetrahedron: Asymmetry* **1992**, *3*, 437−442. [1e] M. Nakamura, A. Hirai, E. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 8489−8490. [1f] S. Hanessian, R.-Y. Yang, *Tetrahedron Lett.* **1996**, *37*, 8997−9000. [1g] Y. Ukaji, Y. Shimizu, Y. Kenmoku, A. Ahmed, K. Inomata, *Chem. Lett.* **1997**, 59−60. [1h] H. Fujihara, K. Nagai, K. Tomioka, *J. Am. Chem. Soc.* **2000**, *122*, 12055−12056. [1i] J. R. Porter, J. F. Traverse, A. H. Hoveyda, M. L. Snapper, *J. Am. Chem. Soc.* **2001**, *123*, 984−985. For organomagnesium reagents see: [1j] F. L. Merchan, P. Merino, I. Rojo, T. Tejero, A. Dondoni, *Tetrahedron: Asymmetry* **1996**, *7*, 667−670. Reviews: [1k] S. E. Denmark, O. J.-C. Nicaise, *Chem. Commun.*

1996, 999−1004. [1l] D. Enders, U. Reinhold, *Tetrahedron: Asymmetry* **1997**, *8*, 1895−1946. [1m] R. Bloch, *Chem. Rev.* **1998**, *98*, 1407−1438.

[2] Reviews: [2a] K. Soai, S. Niwa, *Chem. Rev.* **1992**, *92*, 833−856. [2b] R. Noyori, M. Kitamura, *Angew. Chem.* **1990**, *102*, 34−55; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49−69. [2c] L. Pu, H.-B. Yu, *Chem. Rev.* **2001**, *101*, 757−824.

[3] [3a] K. Soai, T. Hatanaka, T. Miyazawa, *J. Chem. Soc., Chem. Commun.* **1992**, 1097−1098. [3b] T. Hayase, Y. Inoue, T. Shibata, K. Soai, *Tetrahedron: Asymmetry* **1996**, *7*, 2509−2510. [3c] T. Suzuki, N. Narisada, T. Shibata, K. Soai, *Tetrahedron: Asymmetry* **1996**, *7*, 2519−2522.

[4] For related reactions: [4a] P. G. Andersson, D. Guijarro, D. Tanner, *J. Org. Chem.* **1997**, *62*, 7364−7375. [4b] C. Jimeno, K. S. Reddy, L. Solà, A. Moyano, M. A. Pericàs, A. Riera, *Org. Lett.* **2000**, *2*, 3157−3159. [4c] X. Zhang, L. Gong, A. Mi, X. Cui, Y. Jiang, M. C. K. Choi, A. S. C. Chan, *Tetrahedron Lett.* **2001**, *42*, 6369−6372.

[5] [5a] R. Ramage, D. Hopton, M. J. Parrott, G. W. Kenner, G. A. Moore, *J. Chem. Soc., Perkin Trans. 1* **1984**, 1357−1370. [5b] T. W. Green, P. G. M. Wutz, *Protective Groups in Organic Synthesis, Third edition*, Wiley, New York, **1999**, p 598.

[6] Reviews: [6a] D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991−3023. [6b] G. E. Oosterom, J. N. H. Reek, P. W. N. M. van Leeuwen, *Angew. Chem.* **2001**, *113*, 1878−1901; *Angew. Chem. Int. Ed.* **2001**, *40*, 1828−1849. [6c] R. Kreiter, A. W. Klej, R. J. M. K. Gebbink, G. van Koten, *Top. Curr. Chem.* **2001**, *217*, 163−199. [6d] S. Hechet, J. M. J. Fréchet, *Angew. Chem.* **2001**, *113*, 76−94; *Angew. Chem. Int. Ed.* **2001**, *40*, 74−91. [6e] A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665−1688. [6f] M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem.* **1997**, *109*, 1559−1562; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1526−1529.

[7] Asymmetric synthesis using chiral dendritic ligands: [7a] D. Seebach, R. E. Marti, T. Hintermann, *Helv. Chim. Acta* **1996**, *79*. 1710−1740.[7b] H. W. I. Peerlings, E. W. Meijer, *Chem. Eur. J.* **1997**, *3*, 1563−1570. [7c] C. Köllner, B. Pugin, A. Togni, *J. Am. Chem. Soc.* **1998**, *120*, 10274−10275. [7d] R. Breinbauer, E. N. Jacobsen, *Angew. Chem.* **2000**, *112*, 3750−3753; *Angew. Chem. Int. Ed.* **2000**, *39*, 3604−3607. [7e] C. Köllner, A. Togni, *Can. J. Chem.* **2001**, *79*, 1762−1774. [7f] A. R. Schmitzer, S. Franceshi, E. Perez, I. Rico-Lattes, A. Lattes, L. Thion, M. Erard, C. Vidal, *J. Am. Chem. Soc.* **2001**, *123*, 5956−5961. [7g] Y.-M. Chung, H.-K. Rhee, *Chem. Commun.* **2002**, 238−239.

[8] For the ligands with one chiral site possessing dendritic substituents: [8a] H. Brunner, S. Altmann, *Chem. Ber.* **1994**, *127*, 2285−2296. [8b] H. Brunner, *J. Organomet. Chem.* **1995**, *500*, 39−46. [8c] C. Bolm, N. Derrien, A. Seger, *Synlett* **1996**, 387−388. [8d] P. B. Rheiner, H. Sellner, D. Seebach, *Helv. Chim. Acta* **1997**, *80*, 2027−2032. [8e] S. Yamago, M. Furukawa, A. Azuma, J. Yoshida, *Tetrahedron Lett.* **1998**, *39*, 3783−3786. [8f] P. B. Rheiner, D. Seebach, *Chem. Eur. J.* **1999**, *5*, 3221−3236. [8g] C. Bolm, N. Derrien, A. Seger, *Chem. Commun.* **1999**, 2087−2088. [8h] Q.-S. Hu, V. Pugh, M. Sabat, L. Pu, *J. Org. Chem.* **1999**, *64*, 7528−7536. [8i] Q.-H. Fan, Y.-M. Chen, X.-M. Chen, D.-Z Jiang, F. Xi, A. S. C. Chan, *Chem. Commun.* **2000**, 789−790.

[9] For example: [9a] T. Suzuki, N. Narisada, T. Shibata, K. Soai, *Polym. Adv. Technol.* **1999**, *10*, 30−38. [9b] S. Itsuno, Y. Sakurai, K. Ito, T. Maruyama, S. Nakahama, J. M. J. Fréchet, *J. Org. Chem.* **1990**, *55*, 304−310. [9c] M. Watanabe, K. Soai, *J. Chem. Soc., Perkin Trans. 1* **1994**, 837−842. [9d] H. Sellner, D. Seebach, *Angew. Chem.* **1999**, *111*, 2039−2041; *Angew. Chem. Int. Ed.* **1999**, *38*, 1918−1920.

[10] [10a] T. Suzuki, Y. Hirokawa, K. Ohtake, T. Shibata, K. Soai, *Tetrahedron: Asymmetry* **1997**, *8*, 4033−4040. [10b] I. Sato, R. Kodaka, T. Shibata, Y. Hirokawa, N. Shirai, K. Ohtake, K. Soai, *Tetrahedron: Asymmetry* **2000**, *11*, 2271−2275.

[11] For our application of chiral dendrimers to the enantioselective alkylation of aldehydes, see: [11a] I. Sato, T. Shibata, K. Ohtake, R. Kodaka, Y. Hirokawa, N. Shirai, K. Soai, *Tetrahedron Lett.* **2000**, *41*, 3123−3126. [11b] I. Sato, R. Kodaka, K. Hosoi, K. Soai, *Tetrahedron: Asymmetry* **2002**, *13*, 805−808.

[12] For carbosilane dendrimers, see: [12a] J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659−663. [12b] D. Seyferth, D. Y. Son, A. L. Rheingold, R. L. Ostrander, *Organometallics* **1994**, *13*, 2682−2690. [12c] A. W. van der Made, P. W. N. M. van Leeuwen, *J. Chem. Soc., Chem. Commun.* **1992**, 1400−1441. [12d] S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168−8179. Reviews: [12e] J. W. Kriesel, T. D. Tilley, *Adv. Mater.* **2001**, *13*, 1645−1648. [12f] F. Holger, S. Christian, *Top. Curr. Chem.* **2000**, *210*, 69−129.

[13] A monomeric chiral ligand, (1*S*,2*R*)-2-morpholino-1-phenylpropan-1-ol gave (*S*)-*N*-(diphenylphosphinyl)amine (**5a**) with 91% *ee* in 84% yield (0 °C, 112 h).[3a]

[14] After purification by thin layer chromatography, dendritic ligand **1** was recovered in 88% yield. Similarly, dendritic ligand **2** was recovered in 87%.

[15] W. B. Jennings, C. J. Lovely, *Tetrahedron* **1991**, *47*, 5516−5568.

[16] T. Suzuki, T. Shibata, K. Soai, *J. Chem. Soc., Perkin Trans. 1* **1997**, 2757−2760.

[17] [17a] I. Sato, R. Kodaka, K. Soai, *J. Chem. Soc., Perkin Trans. 1* **2001**, 2912−2914. [17b] R. O. Hutchins, A. Abdel-Magid, Y. P. Stercho, A. Wambsgans, *J. Org. Chem.* **1987**, *52*, 704−706.

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