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Synthesis and application of peripherally alkyl-functionalized dendritic pyrphos ligands: Homogeneous-supported catalysts for enantioselective hydrogenation

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ABSTRACT

A new series of dendritic ligands with a chiral diphosphine located at the focal point have been synthesized through coupling of (R,R)-3,4-bis(biphenylphosphino)pyrrolidine (pyrphos) with peripherally alkyl-functionalized benzoic acid dendrons. These ligands were employed in the Rh-catalyzed asymmetric hydrogenation of prochiral dehydroamino acids, exhibiting excellent catalytic activities and enantioselectivities. The second-generation dendritic catalyst could be recovered by simple liquid–liquid biphasic separation and reused four times without serious loss of its activity and selectivity.

1. Introduction

Dendrimer chemistry has been extremely popular in the past decades, and several potential applications of dendrimers have been explored and are well documented in various reviews [1–6]. Unlike traditionary polymers, dendrimers can be characterized by their elaborate structure, which allows us to precisely control their molecular size, shape, and the numbers and positions of functional groups. Recently, dendrimers as ideal scaffolds employed in catalysis have received considerable attention. The dendrimer catalysts are soluble in most common organic solvents, allowing the catalytic reactions to be carried out in a homogeneous manner under appropriate reaction conditions. On the other hand, such novel nano-sized catalyst can be easily recycled via supra-filtration or solvent precipitation methods. Thus, dendritic catalysts may bridge the gap between homogeneous and heterogeneous catalysis. So far, a number of organometallic dendrimers with catalytic sites at either their core or their periphery have been reported [7–10]. For the immobilization of chiral catalysts, even subtle conformational changes may significantly influence the catalytic behavior of the active sites [11–23]. In the case of the core-functionalized dendrimers, it is expected that the steric shielding or blocking effect of the specific microenvironment created by the branched shell could modulate the catalytic behavior of the core. Recently, Fan and co-workers reported a kind of BINAP-cored dendrimers for asymmetric catalytic reaction of prochiral substrates. It was found that the rate of the reaction increased by using the high-generation dendritic catalysts [11,16]. In contrast, dendritic catalysts with a chiral diphosphine pyrphos located at the focal point showed a dramatic decrease in catalytic activity on going from generation 3 to generation 4. This negative effect might be due to the steric shielding effect of the dendritic shell [22]. In addition, the solubility and physical properties of dendrimers can be altered by peripheral modification, which may facilitate the recycling of catalysts [9,24–26]. For example, introduction of hydrophilic groups to the peripheral layer of a hydrophobic dendron can result in water-soluble dendritic unimolecular micelles [27–29]. Most recently, Fan and co-workers reported a new kind of apolar dendritic Ru-BINAP catalysts functionalized with alkyl chain at the periphery. These catalysts were employed for the homogeneous asymmetric hydrogenation by using ethanol–hexane as solvent, and could be easily recycled at the end of reaction via a liquid–liquid biphasic separation method [30]. Inspired by this finding, in this paper, we designed and synthesized a new kind of dendritic pyrphos ligands (Scheme 1) bearing alkyl chains at the periphery for the Rh-catalyzed asymmetric hydrogenation of dehydroamino acids. In contrast to the poly(benzyl ether) dendron-supported catalysts [22], excellent catalytic performance (100% conversion and up to 97.8% ee) and facile catalyst recycling have been achieved.

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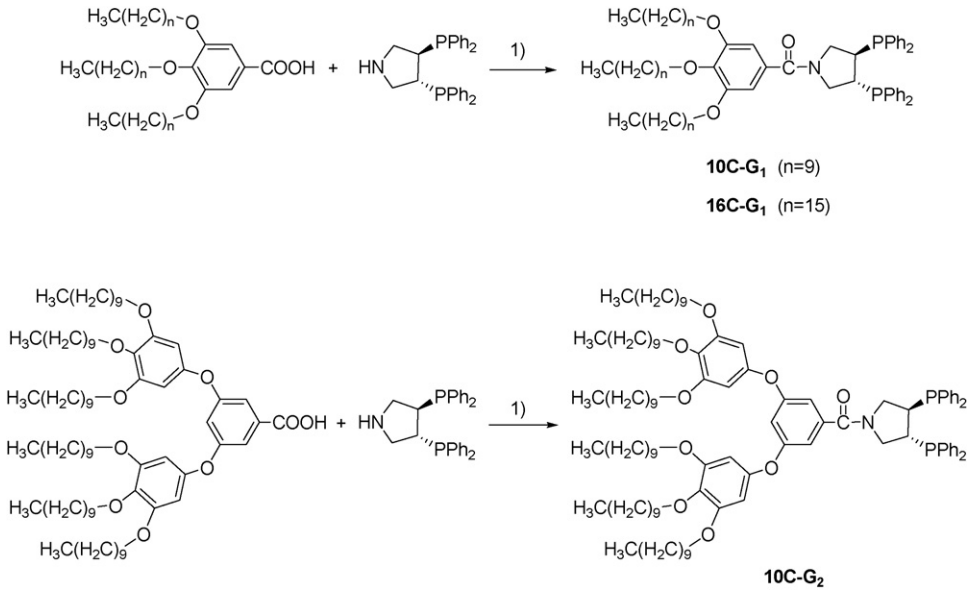


Scheme 1. Synthesis of chiral dendritic pyrphos ligands. (1) DCC, DMAP, CH_2Cl_2, r.t.

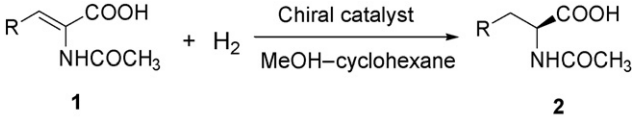
2. Results and discussions

The preparation of new dendritic chiral pyrphos ligands was conducted according to the recently reported procedure [22]. Condensation reaction of pyrphos [31] with peripherally alkyl-functionalized dendritic wedges with carboxyl groups located at the focal point in the presence of 1,3-dicyclohexylcarbodiimine (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane at room temperature gave the chiral dendritic ligands with good reaction yields (Scheme 1). All these ligands were purified by flash column chromatography and characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, elemental analyses and/or HRMS, and MALDI-TOF mass spectrometry. All results are in full agreement with the proposed structures.

The rhodium catalysts were prepared from the corresponding ligands and $[Rh(COD)_2]^+BF_4^-$ (COD = 1,5-cyclooctadiene) at an equal molar ratio in dichloromethane at room temperature. The metalation was complete within minutes, which was evident from the change of their colour from brown red to orange-yellow. The above metallodendrimers can be directly used in the hydrogenation reactions without further purification.

With these chiral dendritic catalysts in hand, we chose the asymmetric hydrogenation of acetamido cinnamic acid **1a** as a standard reference system for comparing their catalytic performance. Methanol was initially chosen as the solvent for this reaction. The preliminary results are summarized in Table 1. As we expected, the number and length of the alkyl end groups of the dendritic wedges influenced the reaction performance and the results depended on

Table 1
Asymmetric hydrogenation of dehydroamino acids catalyzed by the dendritic pyrphos-Rh(I) catalysts[a].



1 2

Entry	Substrate (R)	Ligand	Solvent (v/v)	T/h	[b]Conv./%	[b]E.e./%
1	**1a** (C_6H_5)	**10C-G$_1$**	MeOH	4	100	95.6
2	**1a** (C_6H_5)	**16C-G$_1$**	MeOH	4	94.0	95.2
3	**1a** (C_6H_5)	**10C-G$_2$**	MeOH	4	65.0	95.2
4	**1a** (C_6H_5)	**10C-G$_1$**	MeOH/cyclohexane (1/1)	2	100	97.3
5	**1a** (C_6H_5)	**16C-G$_1$**	MeOH/cyclohexane (1/1)	2	100	97.1
6	**1a** (C_6H_5)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	2	100	97.2
7	**1a** (C_6H_5)	**10C-G$_2$**	MeOH/cyclohexane (2/3)	2	98.2	97.0
8	**1a** (C_6H_5)	**10C-G$_2$**	MeOH/cyclohexane (3/2)	2	100	97.1
9[c]	**1a** (C_6H_5)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	1	86.7	97.2
10	**1b** (2-Cl–C_6H_4)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	3	100	96.8
11	**1c** (3-Cl–C_6H_4)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	2	100	96.1
12	**1d** (4-Cl–C_6H_4)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	3	100	96.7
13	**1f** (4-NO_2–C_6H_4)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	3	100	96.4
14	**1g** (4-CH_3O–C_6H_4)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	2	100	97.5
15	**1h** (4-CH_3–C_6H_4)	**10C-G$_2$**	MeOH/cyclohexane (1/1)	2	100	97.8

[a] Hydrogenations were carried out in 0.032 M solution of substrate **1** (0.0975 mmol) under the following conditions: substrate/catalyst = 200:1; 60 atm hydrogen pressure; 20 °C.

[b] Based on GC analysis with a 25 m × 0.25 mm Chrompack Chirasil L-Val column. The absolute configuration of product is (S), which were determined by comparison of the optical rotation with the literature value.

[c] 0.975 mmol of substrate **1a** and 30 ml of reaction solvent with a substrate/catalyst molar ratio of 800 were used under otherwise identical conditions.

the solubility of the dendrimer in solvent. Full conversion and high enantioselectivity (up to 95.6% ee) for the first generation dendrimer ligand **10C-G_1** was observed (entry 1), which are similar to those for the soluble polymer-supported catalyst (95.5% ee) [32]. However, the dendritic ligand **16C-G_1**, which linked with hexadecoxy chain at the periphery, gave lower conversion and slightly lower enantioselectivity (entry 2). Much lower activity was obtained with the second-generation dendritic ligand **10C-G_2** (entry 3). The low reactivity was due to the poor solubility of the latter two catalysts in methanol. Thus, a binary solvent system was chosen as the reaction medium in order to sustain homogeneous reaction conditions for all generation/size dendritic catalysts. In comparison with those in methanol, utilizing an equal volume mixture of methanol and cyclohexane as solvent gave better reactivity and higher enantioselectivity (100% conversion and up to 97.3% ee) for all of the dendritic pyrphos Rh(I)-catalysts among the chosen binary solvent system (entries 4–6), which were much higher than those of the soluble MeO-PEG-supported pyrphos-rhodium(I) catalyst [32]. This confirmed the value of catalysts with a well-defined dendritic wedge. The further experimental results showed that similar conversion and enantioselectivity were obtained in the Rh(**10C-G_2**) catalyzed hydrogenation when a mixture of methanol/cyclohexane was used in different ratios as solvent (entries 7–8). Notably, the dendritic catalyst was found to be highly effective even under low catalyst loading. For example, the hydrogenation of **1a** with a substrate/catalyst molar ratio of 800 and under 60 atm H_2 pressure at 20 °C gave 86.7% conversion and 97.2% ee in 1 h with TOF of 694 h^{-1} (entry 9). Encouraged by these excellent results, we decided to further investigate the applications of the dendritic catalyst in the asymmetric hydrogenation of other dehydroamino acid derivatives using **10C-G_2** as the ligand. In all cases, full conversion and high enantioselectivities (96.1–97.8%) were observed (entries 10–15).

An important feature of the design of peripherally alkyl-modified dendritic ligands was the easy and reliable catalyst recycling *via* liquid–liquid biphasic separation technique. It was found that these dendrimer-based catalysts with alkyl tailed at the periphery preferred to dissolve in a non-polar solvent system. In the case of the second-generation dendritic ligand **10C-G_2**, more than 99% of its Rh complex could be extracted to the non-polar cyclohexane phase in a methanol/cyclohexane (2.0% H_2O) biphasic system. For example, upon completion of the catalytic hydrogenation reaction, a small amount of water (2.0%) was added to the reaction mixture to induce phase separation. The cyclohexane layer, which contained the catalyst **10C-G_2**-Rh(I), was separated and reused in the next run of reaction. The recovered catalyst was reused five times with similar enantioselectivity, albeit decreased activity until the fourth cycle (Table 2, entry 4). To the methanol layer, which contained the reduced product, was added some new substrate, and then subjected to hydrogenation under otherwise identical conditions. No hydrogenation of the newly added substrate was observed. However, when this reaction was carried out for 24 h, some of substrate was found to be reduced, indicating that a small amount of the catalyst might remain dissolved in the methanol layer. Further determination of the Rh content in the product by using inductively coupled plasma (ICP) spectroscopy showed that less than 0.35% Rh was leached into the methanol layer.

Table 2
Recycling of the catalyst **10C-G_2**-Rh(I) in the asymmetric hydrogenation of acetamido cinnamic acid (**1a**)[a].

Entry	Cycle	[b]Conv./%	[b]E.e./%
1	First	100	97.0
2	Second	99	97.1
3	Third	97	97.0
4	Fourth	83	96.8
5	Fifth	56	96.5

[a] Hydrogenations were carried out in 0.032 M solution of substrate **1a** (20 mg) under the following conditions: solvent = MeOH/cyclohexane (1/1, v/v); substrate/catalyst = 100:1; 60 atm hydrogen pressure; 20 °C; 2 h for cycles 1–2, 6 h for cycles 3–4, 24 h for cycle 5.

[b] Based on GC analysis with a 25 m × 0.25 mm Chrompack Chirasil L-Val column.

3. Conclusions

A practical protocol for the effective asymmetric hydrogenation of prochiral dehydroamino acids and the recycling of catalyst by simple liquid–liquid biphasic separation has been developed, as summarized as follows: (1) peripherally alkyl-functionalized dendritic Rh(pyrphos) catalysts have been synthesized and applied in the asymmetric hydrogenation of acetamido cinnamic acids using a mixture of methanol/cyclohexane as reaction medium, affording better enantioselectivity and catalytic activity than those of the soluble polymer-supported catalyst; (2) the combination of chiral dendritic catalyst and organic biphasic system provided facile catalyst recycling. The recovered catalyst could be recycled four times without significant loss of catalytic activity and enantioselectivity. No obvious Rh leaching was observed during the recycling of catalyst via liquid–liquid biphasic separation.

4. Experimental

Unless otherwise noted, all experiments were carried out under an inert atmosphere by using standard Schlenk-type techniques, or performed in a nitrogen-filled glovebox. All solvents were dried using standard, published methods and were distilled under a nitrogen atmosphere before use. Pyrphos was synthesized according to the reported procedures [31]. Peripherally alkyl-functionalized Fréchet-type dendrimers with carboxyl groups at the focal points were prepared by using the convergent approach according to literature [33,34]. $[Rh(COD)_2]BF_4$ [35] and $[Rh(COD)Cl]_2$ [36] were synthesized according to the literature.

^1H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 300 Spectrometer (^1H 300 MHz, ^{31}P 121 MHz and ^{13}C 75 MHz, respectively). Chemical shift (δ) is given in ppm and is referenced to residual solvent peaks (^1H and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR). Infrared spectra were recorded on a Bruker Tensor 27 spectrophotometer. MALDI-TOF mass spectra were obtained on a BIFLEX III instrument with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. High resolution mass spectra were recorded on a GCT or a APEX II spectrometer. Elemental analyses were performed on a Flash EA 1112 Elemental Analyzer. Optical rotations were measured on an AA-10R automatic polarimeter in the solvent indicated. All enantiomeric excess values were obtained from GC analysis on a Varian-6000 chromatograph with a Chrompack Chirasil L-VAL chiral column.

4.1. General procedure for the synthesis of dendritic pyrphos ligands

Typical procedure: 3,4,5-tri(decoxy)benzoic acid (36 mg, 0.061 mmol), (3*R*,4*R*)-pyrphos hydrochloride (34.3 mg, 0.072 mmol), DCC (20 mg, 0.097 mmol), and DAMP (15 mg, 0.122 mmol) were combined in dry, degassed CH_2Cl_2 (5 ml) at ambient temperature. The mixture was stirred for 12 h at the same temperature (TLC monitoring), and the hydrated DCC adduct dicyclohexylurea (DCU) precipitate was removed by filtration through celite. After a usual work-up, the crude product was purified by column chromatography on silica gel (petroleum ether:ethyl acetate 2:1,v/v) to afford **10C-G_1** as white grease. (58 mg, 94%); R_f = 0.27 (4:1 petroleum ether/ethyl acetate); $[\alpha]_D^{20}$ = +60.0 (C

1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74–7.10 (m, 18H), 7.02–6.99 (m, 2H), 6.55 (s, 2H), 4.19–4.07 (m, 1H), 3.94–3.90 (m, 1H), 3.89–3.78 (m, 6H), 3.59 (pseudo-t, J = 13.5 Hz, 1H), 3.32 (pseudo-t, J = 11.4 Hz, 1H), 2.90–2.85 (m, 1H), 2.76–2.71 (m, 1H), 1.72–1.61 (m, 6H), 1.38–1.31 (m, 42H), 0.81 (t, J = 7.1 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$):δ 168.8, 151.9, 138.3, 134.5 (m), 132.7 (m), 132.4 (m), 130.6, 128.4, 128.2, 127.6 (m), 104.6, 72.4, 68.1, 50.4 (m), 47.4 (m), 38.7 (m), 36.3 (m), 30.9, 29.3, 28.7, 28.6, 28.5, 28.4, 28.3, 25.0, 21.7, 13.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ −11.7, −12.4 (J = 7 Hz); IR (KBr): ν (cm^{-1}) 1635.5, 1580.0; MALDI-TOF MS: m/z 1012.8 (M^+); HRMS (ESI) m/z found: 1012.6508, $C_{65}H_{91}NO_4P_2$ ([M+H]$^+$) requires: 1012.6522.

Compound **10C-G$_2$**: a procedure similar to that for the preparation of **10C-G$_1$** was used to prepare **10C-G$_2$** from peripherally decyl-functionalized generation 2 acid and (3*R*,4*R*)-pyrphos hydrochloride. The resulting residue was purified by column chromatography on silica gel (petroleum ether:ethyl acetate 2:1) to afford **10C-G$_2$** as white grease. Yield 80%; R_f = 0.34 (1:1 petroleum ether/dichloromethane); $[\alpha]_D^{20}$ = +49.0 (C 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.18 (m, 18H), 7.08–7.04 (m, 2H), 6.73 (s, 2H), 6.62 (s, 5H), 4.89 (m, 4H), 4.27–4.02 (m, 2H), 4.01–3.94 (m, 12H), 3.68 (pseudo-t, J = 13.2 Hz, 1H), 3.38 (pseudo-t, J = 11.7 Hz, 1H), 2.98–2.96 (m, 1H), 2.84–2.80 (m, 1H), 1.86–1.72 (m, 12H), 1.49–1.28 (m, 84H), 0.89 (t, J = 6.6 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$):δ 169.4, 159.8, 153.4, 138.7, 138.0, 136.3 (m), 135.5 (m), 133.6 (m), 131.4, 129.5, 129.2 (m), 129.0 (m), 106.2, 103.7, 73.5, 70.7, 69.2, 51.4 (m), 48.6 (m), 39.4 (m), 37.5 (m), 32.0, 30.4, 29.8, 29.7, 29.5, 26.2, 22.8, 14.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ −12.1, −12.3 (J = 7 Hz); IR (KBr): ν (cm^{-1}) 1636.7, 1591.2; MALDI-TOF MS: m/z 1693.3 (M^+); HRMS (ESI) m/z found: 1665.1536, $C_{107}H_{159}NO_9P_2$ (M^+) requires: 1665.1524.

Compound **16C-G$_1$**: a procedure similar to that for the preparation of **10C-G$_1$** was used to prepare **16C-G$_1$** from 3,4,5-tri(hexadecoxy)benzoic acid and (3*R*,4*R*)-pyrphos hydrochloride. The resulting residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate 6:1) to afford **16C-G$_1$** as white grease. Yield 67%; R_f = 0.31 (6:1 petroleum ether/ethyl acetate); $[\alpha]_D^{20}$ = +57.0 (C 1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61–7.10 (m, 21H), 6.66 (s, 2H), 4.31–4.18 (m, 1H), 4.14–3.99 (m, 1H), 3.97–3.82 (m, 6H), 3.70 (pseudo-t, J = 13.5 Hz, 1H), 3.43 (pseudo-t, J = 11.7 Hz, 1H), 2.99–2.92 (m, 1H), 2.86–2.84 (m, 1H), 1.85–1.70 (m, 6H), 1.48–1.29 (m, 78H), 0.91 (t, J = 6.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$):δ 169.8, 152.9, 139.3, 136.1 (m), 135.4 (m), 133.6 (m), 131.7, 129.4, 129.2, 128.7 (m), 105.7, 73.4, 69.2, 51.4 (m), 48.6 (m), 39.4 (m), 37.7 (m), 32.0, 30.3, 29.8, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.2; ^{31}P NMR (121 MHz, $CDCl_3$): δ −11.6, −12.3 (J = 7 Hz); IR (KBr): ν (cm^{-1}) 1631.7, 1579.5; MALDI-TOF MS: m/z 1265.0 (M^+); HRMS (ESI) m/z found: 1264.9284, $C_{83}H_{127}NO_4P_2$ (M^+) requires: 1264.9312.

4.2. General procedure for the hydrogenation and catalyst recycling experiments

In a glovebox under a nitrogen atmosphere, a 45 ml glass-lined stainless steel reactor with a magnetic stirring bar was charged with substrate (0.0975 mmol), the calculated amount of catalyst and methanol–cyclohexane (1:1, v/v, 3 ml). The inert gas in the autoclave was displaced with hydrogen. The pressure was set at 60 atm and the reaction started by stirring. The temperature was kept constant at about 20 °C with an oil-bath. After carefully venting hydrogen, 0.06 ml degassed distilled-water was added to the reaction mixture under inert atmosphere to induce complete phase separation. The cyclohexane layer, which contained the catalyst, was separated, and reused in the next catalytic cycle after dried with anhydrous $MgSO_4$. The conversion and ee value of product were determined by chromatography using a 25 m Chiralsi L-Val capillary column after the acids had been transformed into the corresponding methyl esters.

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References

[1] A.D. Schlüter, Top. Curr. Chem. 197 (1998) 165–191.
[2] J.P. Majoral, A.M. Caminade, Chem. Rev. 99 (1999) 845–880.
[3] A.W. Bosman, H.M. Janssen, E.W. Meijer, Chem. Rev. 99 (1999) 1665–1688.
[4] A.D. Schlüter, J.P. Rabe, Angew. Chem., Int. Ed. 39 (2000) 864–883.
[5] H. Frauenrath, Prog. Polym. Sci. 30 (2005) 325–384.
[6] A.D. Schlüter, Top. Curr. Chem. 245 (2005) 151–191.
[7] G.E. Oosterom, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Angew. Chem., Int. Ed. 40 (2001) 1828–1849.
[8] D. Astruc, F. Chardac, Chem. Rev. 101 (2001) 2991–3023.
[9] R. van Heerbeek, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, Chem. Rev. 102 (2002) 3717–3724.
[10] Q.H. Fan, G.J. Deng, Y. Feng, Y.M. He, Enantioselective catalysis using dendrimer supports, in: K. Ding, Y. Uozumi (Eds.), Handbook of Asymmetric Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2008, pp. 131–180.
[11] Q.H. Fan, Y.M. Chen, X.M. Chen, D.Z. Jiang, F. Xi, A.S.C. Chan, Chem. Commun. (2000) 789–790.
[12] R. Breinbauer, E.N. Jacobsen, Angew. Chem., Int. Ed. 39 (2000) 3604–3607.
[13] Y. Ribourdouille, G.D. Engel, M. Richard-Plouet, L.H. Gade, Chem. Commun. (2003) 1228–1229.
[14] G.J. Deng, Q.H. Fan, X.M. Chen, G.H. Liu, J. Mol. Catal. A: Chem. 193 (2003) 21–25.
[15] Y. Wu, Y. Zhang, M. Yu, G. Zhao, S. Wang, Org. Lett. 8 (2006) 4417–4420.
[16] Z.J. Wang, G.J. Deng, Y. Li, Y.M. He, W.J. Tang, Q.H. Fan, Org. Lett. 9 (2007) 1243–1246.
[17] J.K. Kassube, H. Wadepohl, L.H. Gade, Adv. Synth. Catal. 350 (2008) 1155–1162.
[18] A.V. Gaikwad, V. Boffa, J.E. ten Elshof, G. Rothenberg, Angew. Chem., Int. Ed. 47 (2008) 5407–5410.
[19] F. Zhang, Y. Li, Z.W. Li, Y.M. He, S.F. Zhu, Q.H. Fan, Q.L. Zhou, Chem. Commun. (2008) 6048–6050.
[20] A.W. Kleij, R.A. Gossage, R.J.M.K. Gebbink, N. Brinkmann, Ed.J. Reijerse, U. Kragl, M. Lutz, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 122 (2000) 12112–12124.
[21] G.D. Engel, L.H. Gade, Chem. Eur. J. 8 (2002) 4319–4329.
[22] B. Yi, Q.H. Fan, G.J. Deng, Y.M. Li, L.Q. Qiu, A.S.C. Chan, Org. Lett. 6 (2004) 1361–1364.
[23] A.A. El-Shehawy, K. Sugiyama, A. Hirao, Tetrahedron: Asymm. 19 (2008) 425–434.
[24] V. Chechik, R.M. Crooks, J. Am. Chem. Soc. 122 (2000) 1243–1244.
[25] M. Ooe, M. Murata, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 126 (2004) 1604–1605.
[26] Y.Y. Huang, Y.M. He, H.F. Zhou, L. Wu, B.L. Li, Q.H. Fan, J. Org. Chem. 71 (2006) 2874–2877.
[27] J.J. Lee, W.T. Ford, Macromolecules 27 (1994) 4632–4634.
[28] L.Z. Gong, L. Pu, Tetrahedron Lett. 42 (2001) 7337–7340.
[29] H. Hattori, K. Fujita, T. Muraki, A. Sakaba, Tetrahedron Lett. 48 (2007) 6817–6820.
[30] G.J. Deng, Q.H. Fan, X.M. Chen, D.S. Liu, A.S.C. Chan, Chem. Commun. (2002) 1570–1571.
[31] Pyrphos was first reported by Nagel and co-workers. See: U. Nagel, E. Kinzel, J. Andrade, G. Prescher, Chem. Ber. 119 (1986) 3326–3343.
[32] Q.H. Fan, G.J. Deng, C.C. Lin, A.S.C. Chan, Tetrahedron: Asymm. 12 (2001) 1241–1247.
[33] C.J. Hawker, J.M.J. Fréchet, J. Am. Chem. Soc. 112 (1990) 7638–7647.
[34] K.L. Wooley, C.J. Hawker, J.M.J. Fréchet, J. Am. Chem. Soc. 113 (1991) 4252–4261.
[35] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 93 (1971) 3089–3090.
[36] G. Giordano, R.H. Crabtree, R.M. Heintz, D. Forster, D.E. Morris, Inorg. Synth. 19 (1970) 218–220.