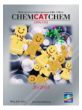
ChemPubSoc Europe
DOI: 10.1002/cctc.201500842
CHEMCATCHEM Communications



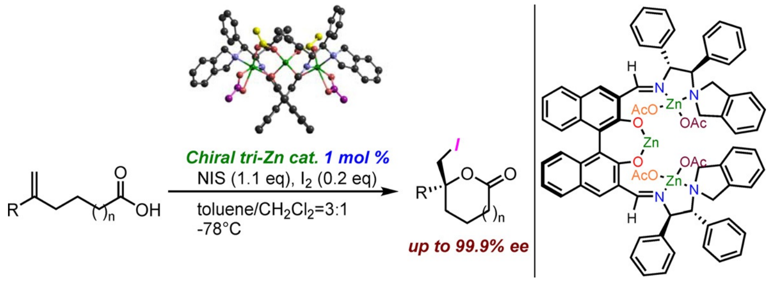
Recyclable Poly-$Zn_3(OAc)_4$–3,3′-Bis(aminoimino)binaphthoxide Catalyst for Asymmetric Iodolactonization

Takayoshi Arai,*[a] Takahiro Kojima,[a] Ohji Watanabe,[a] Tsutomu Itoh,[b] and Hirofumi Kanoh[c]

On the basis of the structure of the unimolecular $Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide complex, a poly-$Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide (poly-**Zn**) complex was prepared from 3,3′-diformylbinaphthol, tetramine, and $Zn(OAc)_2$. The first-generation poly-**Zn** catalyst (poly-**Zn1**) was prepared from poly(aminoiminobinaphthol) and $Zn(OAc)_2$. Although poly-**Zn1** showed high catalytic activity for iodolactonization, the catalyst could not be reused. The second-generation poly-Zn catalyst (poly-**Zn2**) was prepared by the self-organization of 3,3′-diformylbinaphthol, tetramine, and $Zn(OAc)_2$. This produced a stable and active poly-**Zn2** catalyst for asymmetric iodolactonization that was reused over five cycles.

The construction of reusable catalyst systems is important for sustainable organic syntheses, especially for expensive asymmetric catalysts. Although polymer-supported catalysts[1] have been used widely for the recovery and reuse of asymmetric catalysts, the polymer backbone often causes significant negative effects on the activity of the catalyst and the stereoselectivity of the target reaction. To overcome these drawbacks, approaches such as ion-supported catalysts,[2] fluorous catalysts,[3] and dendritic catalysts[4] have been developed to maintain the original stereoselectivity. Comparing these soluble recyclable catalysts, heterogeneous catalysts are still fundamentally advantageous, because they can be separated from the product by simple filtration. Polymeric ligands not containing a polymer backbone would be an ideal insoluble recyclable catalyst system, though successful examples are limited.[5] This report describes the development of poly-$Zn_3(OAc)_4$–3,3′-bis(aminoimino) binaphthoxide (poly-**Zn**), based on the unimolecular $Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide complex,[6] as a recyclable catalyst for asymmetric iodolactonization.[7]

In 2014, we reported a $Zn_3(OAc)_4$–3,3′-bis(aminoimino) binaphthoxide complex for catalytic asymmetric iodolactonization.[6] It was shown that trinuclear $Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide (**tri-Zn**, 1 mol %) could catalyze asymmetric iodolactonization with up to 99.9 % *ee* (Scheme 1).



Scheme 1. The unimolecular $Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide (**tri-Zn**) catalyst for asymmetric iodolactonization.

The 3,3′-bis(aminoimino)binaphthol ligand (**C**) was synthesized by condensation of (*R*)-3,3′-diformylbinaphthol (**A**) with (1*R*,2*R*)-2-(isoindolin-2-yl)-1,2-diphenylethyrene diamine (**B**) (Scheme 2 a). Polymeric ligand poly-**L1** was designed by joining the isoindoline ring of **D** to the original 3,3′-bis(aminoimino)-binaphthol ligand (Scheme 2 b). Thus, condensation of **A** with (*R*,*R*)-diphenylethylenediamine-derived tetramine **D** in EtOH under reflux for 38 h gave soluble polymeric 3,3′-bis(aminoimino)binaphthol ligand poly-**L1 a** (Table 1, entry 1).

Gel-permeation chromatography (GPC) of poly-**L1 a** indicated a molecular weight of approximately 5500, which corresponds to the 6-mers of the monomeric structure described in Scheme 2 b. Condensation conducted in dioxane under reflux for 120 h gave insoluble poly-**L1 b** corresponding to the 40-mers (Table 1, entry 2). Using these polymeric ligands, corresponding poly-$Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide catalysts poly-**Zn1 a** and poly-**Zn1 b** were prepared, and their

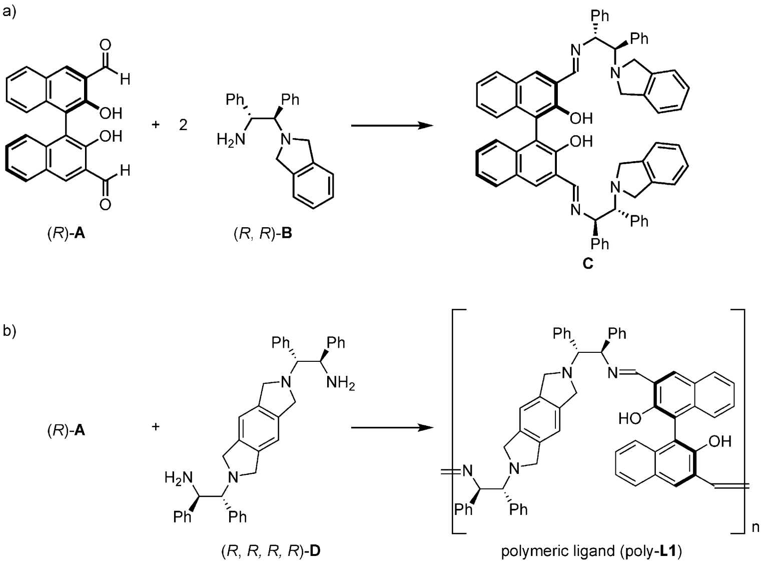
---

[a] Prof. Dr. T. Arai, T. Kojima, O. Watanabe
Molecular Chirality Research Center
Synthetic Organic Chemistry
Department of Chemistry
Graduate School of Science
Chiba University
1-33 Yayoi, Inage, Chiba 263-8522 (Japan)
E-mail: tarai@faculty.chiba-u.jp

[b] Dr. T. Itoh
Center for Analytical Instrumentation
Chiba University
1-33 Yayoi, Inage, Chiba 263-8522 (Japan)

[c] Prof. Dr. H. Kanoh
Molecular Chemistry, Department of Chemistry
Graduate School of Science
Chiba University
1-33 Yayoi, Inage, Chiba 263-8522 (Japan)

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500842.



Scheme 2. a) Synthesis of the 3,3′-bis(aminoimino)binaphthol ligand, and b) design of the polymeric 3,3′-bis(aminoimino)binaphthol ligand.

Table 1. Preparation of polymeric 3,3′-bis(aminoimino)binaphthol ligands.

(*R*)-**A**+(*R*,*R*,*R*,*R*)-**D** → polymeric ligand (poly-**L1**)

Entry	Polymer	Solvent	*t* [h]	M_w[a] (n[b])	M_w/M_n[c]
1	poly-**L1 a**	EtOH	38	5490 (6)	6.6
2	poly-**L1 b**	1,4-dioxane	120	35 780 (40)	13.1

[a] Analyzed by GPC. M_w = weight-average molecular weight. [b] Estimated degree of polymerization. [c] M_n = number-average molecular weight.

catalyst activity was examined in the standard iodolactonization of 5-phenylhex-5-enoic acid (**1 a**) (Table 2).

Soluble catalyst poly-**Zn1 a** prepared from poly-**L1 a** smoothly catalyzed the asymmetric iodolactonization reaction to give product **2 a** in 99% yield with 99% *ee*, whereas insoluble catalyst poly-**Zn1 b** prepared from poly-**L1 b** gave **2 a** with 22% *ee*. Although asymmetric induction of catalyst poly-**Zn1 b** was low, analysis of poly-**Zn1 b** was done by using XRD and SEM. The XRD pattern (Figure 1) revealed several unique peaks for complex poly-**Zn1 b**, even though poly-**L1 b** did not produce significant peaks, which suggests that the conformational lock was provided in the formation of multinuclear Zn complexes on poly-**L1 b**. Figure 1 c shows the peaks observed in parent powder complex **tri-Zn** (green and yellow circles). The peak at $2\theta = 25.51^\circ$ ($d = 3.49$ Å) was assigned to the distance between a central Zn atom and an outer Zn atom, whereas the peak at $2\theta = 12.84^\circ$ ($d = 6.89$ Å) was assigned to the distance between two outer Zn atoms in the **tri-Zn** complex.

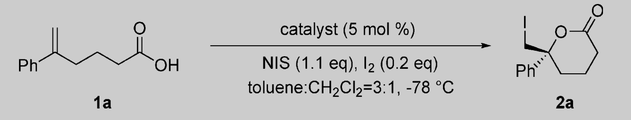
Identification of the other peaks (red circles) was accomplished by preparing symmetrically connected binaphthols **E** on (*R*,*R*)-diphenylethylene diamine-derived tetramine **D** and by obtaining the XRD pattern of **E-Zn** (Figure 1 d). The XRD pattern of poly-**Zn1 b** can be explained as the summation of the XRD patterns of **tri-Zn** and **E-Zn**. Interestingly, complex **E-Zn** was also an efficient asymmetric catalyst for the iodolactonization reaction, and it gave **2 a** in >99% yield with 97% *ee* (Table 2, entry 4).

The crystalline nature of poly-**Zn1 b** was suggested by the SEM images (Figure 2). Comparison of the SEM image of poly-**L1 b** (amorphous structure) with that of poly-**Zn1 b** revealed that poly-**Zn1 b** adopts a plate structure, which results in a limited effective surface of the insoluble catalyst.

Although the conditions for the catalytic asymmetric iodolactonization reaction with the use of poly-**Zn1 b** were further optimized, it was difficult to improve the stereoselectivity of the poly-**Zn1 b**-catalyzed iodolactonization.[8]

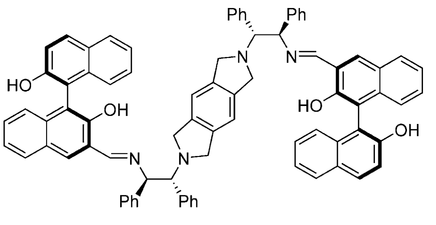
To obtain effectively workable poly-Zn catalysts, the preparation of the polymeric catalyst was reinvestigated. Second-generation poly-**Zn2** was then prepared directly from a mixture of **A**, **D**, and $Zn(OAc)_2$, as shown in Scheme 3.

Table 2. Asymmetric iodolactonization by using the poly-$Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide (poly-**Zn 1 a** and poly-**Zn1 b**) catalysts.



Entry	Catalyst	*t* [h]	Yield [%]	*ee* [%]
1	poly-**Zn1 a**	15	99	99
2	poly-**Zn1 b**	22	>99	22
3	**tri-Zn**[a]	20	>99	99.5
4	**E-Zn**[b]	25	>99	97

[a] 1 mol% catalyst. [b] Ligand **E**



E

Poly-**Zn2 a** was generated in 1,4-dioxane at 80 °C after 3 days, whereas poly-**Zn2 b** was generated in 1,4-dioxane under reflux after 7 days. Poly-**Zn2 b** was insoluble in 1,4-dioxane. The catalytic activity of newly prepared poly-**Zn2** was examined in the asymmetric iodolactonization reaction (Table 3).

Not only poly-**Zn2 a** but also insoluble poly-**Zn2 b** smoothly catalyzed the iodolactonization reaction, and surprisingly, **2 a** was obtained with 96% *ee* (Table 3, entry 2). Poly-**Zn2** was characterized by using XRD (Figure 3). The XRD pattern of poly-**Zn2 a** contains clear peaks, which suggest that poly-**Zn2 a** is more crystalline in nature than poly-**Zn1 b** (Figure 3 a, c), owing to the smooth introduction of $Zn(OAc)_2$ in the polymer structure.

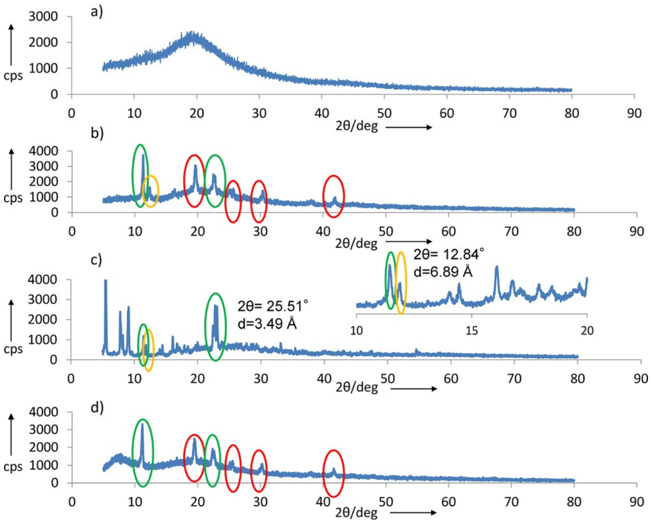


Figure 1. XRD analysis of a) poly-**L1 b**, b) poly-**Zn1 b**, c) **tri-Zn**, and d) **E-Zn**.

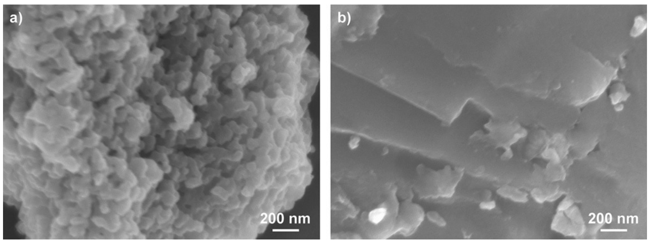


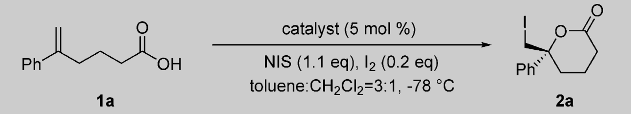
Figure 2. SEM images of a) poly-**L1 b** and b) poly-**Zn1 b**.

$$\mathbf{A} + \mathbf{D} + \mathrm{Zn(OAc)_2} \xrightarrow[\text{1,4-dioxane}]{} \text{poly-}\mathbf{Zn2}\text{ cat}$$

80 °C, 3 days: poly-**Zn2a** (ca. 60%)
reflux, 7 days: poly-**Zn2b** (ca. 86%)

Scheme 3. Revised method for preparing poly-Zn catalysts.

Table 3. Asymmetric iodolactonization by using catalyst poly-**Zn2**.



Entry	Catalyst	*t* [h]	Yield [%]	*ee* [%]
1	poly-**Zn2 a**	15	>99	97
2	poly-**Zn2 b**	15	>99	96

Interestingly, the XRD pattern of poly-**Zn2 b** shows broad peaks, even though insoluble poly-**Zn2 b** is an effective catalyst for asymmetric iodolactonization. Thus, poly-**Zn2 b** would be formed via poly-**Zn2 a** in refluxing 1,4-dioxane. These differences are also supported by the SEM images (Figure 4).

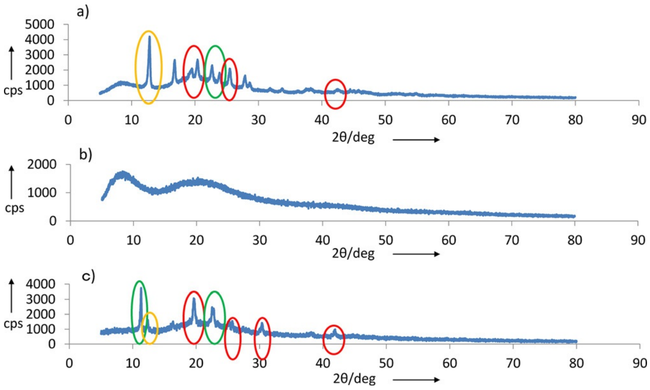


Figure 3. XRD analysis of a) poly-**Zn2 a**, b) poly-**Zn2 b**, and c) poly-**Zn1 b**.

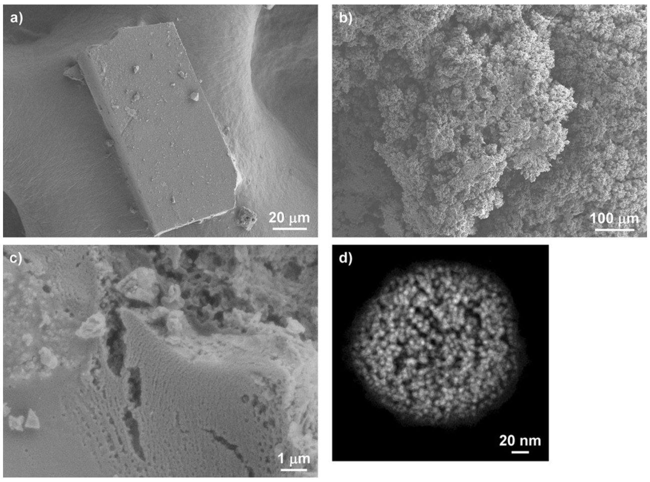


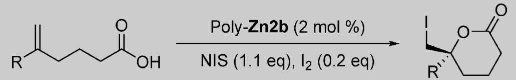
Figure 4. SEM images of a) poly-**Zn2 a**, b) poly-**Zn2 b**, and c) poly-**Zn2 a** (expansion) and d) HAADF-STEM image of a poly-**Zn2 a** particle.

Poly-**Zn2 a** was obtained as a rectangular block, whereas poly-**Zn2 b** was an amorphous solid having a large surface (Figure 4 a, b). Poly-**Zn2 a** was formed by the agglomeration of small particles (Figure 4 c). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of poly-**Zn2 a** reveals a uniform distribution of Zn atoms in the particles (Figure 4 d, enhanced by white color).

Next, the generality of the asymmetric iodolactonization was examined by using insoluble poly-**Zn2 b** (2 mol %) (Table 4). For 5-arylhex-5-enoic acids, various substituents including electron-withdrawing and electron-donating functionalities on the benzene ring were successfully employed to produce iodolactones **2 a**–**f** with stereoselectivities ranging from 91 to 97 % *ee*. Dimethyl substituents on the alkyl chain resulted in **2 g** with 93 % *ee*. Replacement of the phenyl group with alkyl groups successfully provided **2 h** and **2 i** with high stereoselectivities of 79 and 95 % *ee*, respectively.

Finally, catalyst recovery and reuse were examined for catalyst poly-**Zn2 b**. After recovery of the catalyst by centrifugation after the first use, the second use of poly-**Zn2 b** gave **2 a** in 94 % yield with 92 % *ee*. Catalyst poly-**Zn2 b** was transformed into a paste after the first iodolactonization; the tiny amount of poly-**Zn2 b** that was used made its recovery difficult. To overcome this difficulty, the addition of an external support

Table 4. Asymmetric iodolactonization by using catalyst poly-**Zn2 b**.



1 **2**

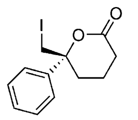
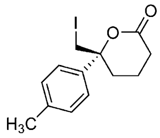
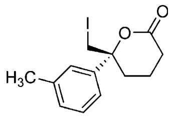
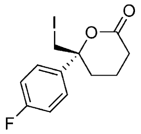
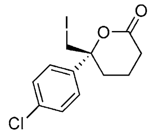
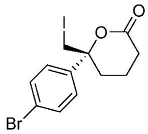
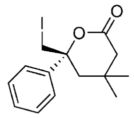
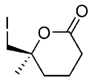
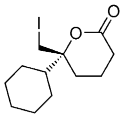
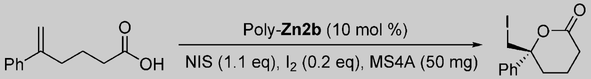
 **2a**, 15 h >99% yield, 96% ee	 **2b**, 14 h >99% yield, 91% ee	 **2c**, 16 h >99% yield, 96% ee
 **2d**, 17 h 92% yield, 94% ee	 **2e**, 11 h >99% yield, 97% ee	 **2f**, 14 h 94% yield, 97% ee
 **2g**, 12 h >99% yield, 93% ee	 **2h**, 18 h 84% yield, 79% ee	 **2i**, 18 h >99% yield, 95% ee

Table 5. Reuse of catalyst poly-**Zn2 b**.



1a **2a**

Run	Yield [%]	*ee* [%]
1	>99	99
2	>99	96
3	>99	94
4	97	95
5	>99	97

was investigated.[9] Among the external supports examined, 4 Å molecular sieves (MS4A) enabled easy recovery of poly-**Zn2 b** (see the effects of other external supports in the Supporting Information). Upon the addition of 4 Å molecular sieves (50 mg) to poly-**Zn2 b** (0.01 mmol), the asymmetric iodolactonization reaction was catalyzed smoothly to give **2 a** in >99% yield with 99% *ee* after the first use (Table 5). Catalyst poly-**Zn2 b**–MS4 Å was recovered quantitatively by filtration and was reused over five cycles.

In conclusion, polymeric $Zn_3(OAc)_4$–3,3′-bis(aminoimino)binaphthoxide (poly-**Zn2 b**) was prepared by the self-assembly of 3,3′-diformylbinaphthol, tetramine, and $Zn(OAc)_2$ in one pot. Poly-**Zn2 b** was found to be a stable and active catalyst for asymmetric iodolactonization. The development of additional approaches for asymmetric catalysis by using self-organization methods is underway.

Acknowledgements

This work was supported by Tokuyama Science Foundation and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Japan).

Keywords: asymmetric catalysis · heterogeneous catalysis · iodolactonization · polymers · zinc

[1] Recent examples of the application of polymer-supported catalysts: a) S. M. Nicolle, C. J. Hayes, C. J. Moody, *Chem. Eur. J.* **2015**, *21*, 4576; b) Q. Song, X. An, T. Xia, X. Zhou, T. Shen, *C. R. Chim.* **2015**, *18*, 215; c) R. Pedrosa, J. M. Andres, D. P. Avila, M. Ceballos, R. Pindado, *Green Chem.* **2015**, *17*, 2217; d) R. P. Jumde, A. D. Pietro, A. Manariti, A. Mandoli, *Chem. Asian J.* **2015**, *10*, 397; e) B. J. Khairnar, B. M. Bhanage, *Synthesis* **2014**, *46*, 1236; f) J. Yadax, G. R. Stanton, X. Fan, J. R. Robinson, E. J. Schelter, P. J. Walsh, M. A. Pericas, *Chem. Eur. J.* **2014**, *20*, 7122; g) A. H. Henseler, C. Ayats, M. A. Pericas, *Adv. Synth. Catal.* **2014**, *356*, 1795; h) R. Martín-Rapún, S. Sayalero, M. A. Pericas, *Green Chem.* **2013**, *15*, 3295; i) Q. Sun, Z. Lv, Y. Du, Q. Wu, L. Wang, L. Zhu, X. Menng, W. Chen, F. S. Xiao, *Chem. Asian J.* **2013**, *8*, 2822; j) R. Almansa, J. F. Collados, D. Guijarro, M. Yus, *Tetrahedron: Asymmetry* **2013**, *24*, 116.

[2] Recent examples of the application of ion-supported catalysts: a) Y. Xie, H. Pan, *Phosphorus Sulfur Silicon* **2014**, *189*, 98; b) Y. Kawagoe, K. Moriyama, H. Togo, *Tetrahedron* **2013**, *69*, 3971; c) Y. Imura, N. Shimojuh, Y. Kawano, H. Togo, *Tetrahedron* **2010**, *66*, 3421; d) Y. Ishiwata, H. Togo, *Tetrahedron Lett.* **2009**, *50*, 5354; e) W. Qian, E. Jin, W. Bao, Y. Zhang, *Tetrahedron* **2006**, *62*, 556.

[3] Recent examples of the application of fluorous catalysts: a) T. Deng, C. Cai, *J. Fluorine Chem.* **2013**, *156*, 183; b) J. L. Qian, W. B. Yi, C. Cai, *Tetrahedron Lett.* **2013**, *54*, 7100; c) Y. W. Zhu, J. L. Qian, W. B. Yi, C. Cai, *Tetrahedron Lett.* **2013**, *54*, 638; d) M. Ikram, R. J. Baker, *J. Fluorine Chem.* **2012**, *139*, 58; e) L. Wan, C. Cai, *Catal. Lett.* **2011**, *141*, 839; f) M. Matsugi, Y. Kobayashi, N. Suzumura, Y. Tsuchiya, T. Shioiri, *J. Org. Chem.* **2010**, *75*, 7905; g) S. Dordonne, B. Crousse, D. Bonnet-Delpon, J. Legros, *Chem. Commun.* **2011**, *47*, 5855; h) B. Gourdet, K. Singh, A. M. Stuart, J. A. Vidal, *J. Fluorine Chem.* **2010**, *131*, 1133; i) Q. Yao, Y. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 74.

[4] Recent examples of the application of dendritic catalysts: a) L. Garcia, A. Roglans, R. Laurent, J. P. Majoral, A. Pla-Quintana, A. M. Caminade, *Chem. Commun.* **2012**, *48*, 9248; b) M. Keller, A. Hameau, G. Spataro, S. Ladeira, A. M. Caminade, J. P. Majoral, A. Ouali, *Green Chem.* **2012**, *14*, 2807; c) M. Keller, V. Colliere, O. Reiser, A. M. Caminade, J. P. Maloral, A. Ouali, *Angew. Chem. Int. Ed.* **2013**, *52*, 3626; *Angew. Chem.* **2013**, *125*, 3714; d) B. Ma, Z. Ding, J. Liu, Y. He, Q. H. Fan, *Chem. Asian J.* **2013**, *8*, 1101; e) R. S. Bagul, N. Jayaraman, *Inorg. Chim. Acta* **2014**, *409*, 34; f) L. Wu, J. Ling, Z. O. Wu, *Adv. Synth. Catal.* **2011**, *353*, 1452; g) K. Fujita, M. Yamazaki, T. Ainoya, T. Tsuchimoto, H. Yasuda, *Tetrahedron* **2010**, *66*, 8536.

[5] For a book of polymer-based chiral catalysts, see a) S. Itsuno, *Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis*, Wiley, Hoboken, **2011**; for helically chiral polymer catalysts, see b) M. Reggelin, M. Schultz, M. Holbach, *Angew. Chem. Int. Ed.* **2002**, *41*, 1614; *Angew. Chem.* **2002**, *114*, 1684; c) M. Reggelin, S. Doerr, M. Klussmann, M. Schultz, M. Holbach, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5461; d) G. Roelfes, B. L. Feringa, *Angew. Chem. Int. Ed.* **2005**, *44*, 3230; *Angew. Chem.* **2005**, *117*, 3294; e) A. J. Boersma, B. L. Feringa, G. Roelfes, *Org. Lett.* **2007**, *9*, 3647; f) D. Coquière, B. Feringa, G. Roelfes, *Angew. Chem. Int. Ed.* **2007**, *46*, 9308; *Angew. Chem.* **2007**, *119*, 9468; g) T. Yamamoto, M. Suginome, *Angew. Chem. Int. Ed.* **2009**, *48*, 539; *Angew. Chem.* **2009**, *121*, 547; h) A. J. Boersma, B. L. Feringa, G. Roelfes, *Angew. Chem. Int. Ed.* **2009**, *48*, 3346; *Angew. Chem.* **2009**, *121*, 3396; i) A. J. Boersma, R. P. Megens, B. L. Feringa, G. Roelfes, *Chem. Soc. Rev.* **2010**, *39*, 2083; j) T. Yamamoto, T. Yamada, Y. Nagata, M. Suginome, *J. Am. Chem. Soc.* **2010**, *132*, 7899; k) G. M. Miyake, H. Iida, H.-Y. Hu, Z. Tang, E. Y.-X. Chen, E. Yashima, *J. Polym. Sci. Part A* **2011**, *49*, 5192; l) T. Yamamoto, Y. Akai, Y. Nagata, M. Suginome, *Angew. Chem. Int. Ed.* **2011**, *50*, 8844; *Angew. Chem.* **2011**, *123*, 9006; m) Y. Akai, T. Yamamoto, Y. Nagata, T. Ohmura, M. Suginome, *J. Am. Chem. Soc.* **2012**, *134*, 11092; n) Y. Nagata, T. Yamada, T. Adachi, Y. Akai, T. Yamamoto,

M. Suginome, *J. Am. Chem. Soc.* **2013**, *135*, 10104; o) T. Yamamoto, Y. Akai, M. Suginome, *Angew. Chem. Int. Ed.* **2014**, *53*, 12785; *Angew. Chem.* **2014**, *126*, 12999; p) E. Yashima, K. Maeda, H. Iida, Y. Furusho, K. Nagai, *Chem. Rev.* **2009**, *109*, 6102; q) R. P. Megens, G. Roelfes, *Chem. Eur. J.* **2011**, *17*, 8514.

[6] T. Arai, N. Sugiyama, H. Masu, S. Kado, S. Yabe, M. Yamanaka, *Chem. Commun.* **2014**, *50*, 8287.

[7] a) G. E. Veitch, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2010**, *49*, 7332; *Angew. Chem.* **2010**, *122*, 7490; b) M. C. Dobish, J. N. Johnston, *J. Am. Chem. Soc.* **2012**, *134*, 6068; c) Z. Ning, R. Jin, J. Ding, L. Gao, *Synlett* **2009**, 22914; d) H. Nakatsuji, Y. Sawamura, A. Sakakura, K. Ishihara, *Angew. Chem. Int. Ed.* **2014**, *53*, 6974; *Angew. Chem.* **2014**, *126*, 7094; e) J. E. Tungen, J. M. J. Nolsøe, T. V. Hansen, *Org. Lett.* **2012**, *14*, 5884; f) L. Filippova, Y. Stenstrom, T. V. Hansen, *Tetrahedron Lett.* **2014**, *55*, 419; g) T. Arai, S. Kajikawa, E. Matsumura, *Synlett* **2013**, 2045; h) K. Murai, N. Shimizu, H. Fujioka, *Chem. Commun.* **2014**, *50*, 12530.

[8] Trial on the recovery and reuse of soluble poly-Zn**1a** resulted in failure.

[9] Examples on the addition of external support: a) T. Yasukawa, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.* **2012**, *134*, 16963; b) Y.-X. Tan, Y.-P. He, J. Zhang, *Chem. Mater.* **2012**, *24*, 4711; c) R. Jin, K. Liu, D. Xia, Q. Qian, G. Liu, H. Li, *Adv. Synth. Catal.* **2012**, *354*, 3265; d) Z.-H. Li, Z.-M. Zhou, X.-Y. Hao, J. Zhang, Z. Dong, Y.-Q. Liu, *Chirality* **2012**, *24*, 1092; e) Y. Xu, T. Cheng, J. Long, K. Liu, Q. Qian, F. Gao, G. Liu, H. Li, *Adv. Synth. Catal.* **2012**, *354*, 3250; f) H. Miyamura, S. Kobayashi, *Acc. Chem. Res.* **2014**, *47*, 1054; g) T. Ogawa, N. Kumagai, M. Shibasaki, *Angew. Chem. Int. Ed.* **2013**, *52*, 6196; *Angew. Chem.* **2013**, *125*, 6316; h) D. Sureshkumar, K. Hashimoto, N. Kumagai, M. Shibasaki, *J. Org. Chem.* **2013**, *78*, 11494; i) K. Hashimoto, N. Kumagai, M. Shibasaki, *Org. Lett.* **2014**, *16*, 3496; j) K. Hashimoto, N. Kumagai, M. Shibasaki, *Chem. Eur. J.* **2015**, *21*, 4262; k) T. Tsubogo, H. Oyamada, S. Kobayashi, *Nature* **2015**, *520*, 329.

Received: July 28, 2015