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The First Enantioselective Addition of Diethylzinc to Aldehydes in Ionic Liquids Catalysed by a Recyclable Ion-Tagged Diphenylprolinol

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Room-temperature ionic liquids (RTILs) have received a growing attention over the past decade, particularly in the field of chemical synthesis and catalysis.[1] The structural diversity and the tuneable miscibility with organic solvents and water make RTILs promising candidates for multiphase homogeneous catalysis, in which the immobilization of the catalyst in a well-defined phase of a multiphase system makes both product separation and catalyst recycling easier.[2,3] The confinement of a catalyst or ligand in a RTIL may be optimized by the presence of an ion-tag on its frame; moreover, the ionic nature could ideally make the catalyst (or ligand) insoluble in organic solvents from which the product is easily extracted, leaving a recyclable, catalyst-containing phase.[4] Catalyst immobilization in a RTIL phase by ionic tagging was recently exploited in our lab in organocatalytic asymmetric aldol reactions[5a] and in Pd-catalyzed Suzuki–Miyaura cross-coupling reactions.[5b]

While the use of tailored catalysts for metathesis,[6] cross-coupling[7] and hydroformylation[8,1b] reactions in RTILs has been thoroughly explored, the nucleophilic addition of simple organometallic compounds to carbonyl compounds in these media has received, so far, less attention.[9] The examples reported simply transpose organometallic reactions into RTILs as the solvent.[10a] Among these, a few asymmetric organometallic additions have also been reported: 1) the allylation of aldehydes[10b] and ketones[10c] with allyltributyltin catalyzed by a chiral indium(III)–PYBOX catalyst, 2) the enantioselective addition of alkynes to imines catalyzed by chiral copper(I)–BOX complexes,[10d] and 3) the asymmetric synthesis of cyanohydrins catalyzed by VO–salen complexes (PYBOX = pyridylbisoxazoline, BOX = bisoxazoline, salen = *N*,*N*′-bis(salicylidene)ethylenediamine).[10e]

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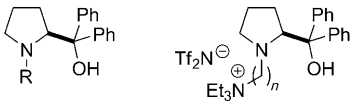
Pure diethylzinc was also reported by Chan to react with aldehydes in RTILs, 1-butylpyridinium tetrafluoroborate ([bpy][BF_4]) being the best solvent, with no need of catalytic activation.[9b] However, when we sought to alkylate benzaldehyde in [bpy][BF_4] using a commercial solution of diethylzinc in *n*-hexane, the reaction was so sluggish that only a negligible amount of alkylation product was recovered after 12 h at 20 °C. This observation attracted our attention, since it inspired us to exploit ligand accelerated catalysis (LAC)[11] and to put into play the ionic-tagging strategy to design a recyclable catalysts soluble in RTILs.

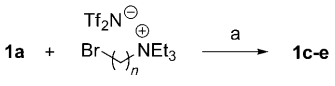
Among the variety of optically active aminoalcohol derivatives reported in the literature to catalyze the enantioselective addition of dialkylzinc to carbonyl compounds,[12] diphenylprolinol (**1a**) represented an attractive option, since the installation of an ion-tagged chain can be easily achieved by a simple nitrogen alkylation step. Moreover, optically pure diphenylprolinol is easily available in multigram scale starting from simple L-proline.[13]



1a: R = H
1b: R = CH_3

1c: *n* = 3
1d: *n* = 4
1e: *n* = 6

We prepared a few ion-tagged tertiary aminoalcohols **1c**–**e**, by reacting **1a** with alkyl bromides **2c**–**e**, as reported in Scheme 1. A simple trialkylammonium tag was selected instead of the widely used imidazolium ion, to avoid the possible *N*-heterocyclic carbene formation during reaction

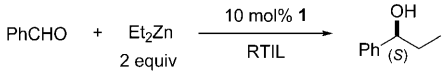


Scheme 1. Synthesis of ion-tagged ligands **1c**–**e**. Conditions: a) 1. CH_3CN, NaI, 80 °C, 24 h; 2. H_2O, NaOH. 80–90 %.

with diethylzinc.[14,10b] The choice of bis(trifluoromethylsulfonyl)imide (Tf_2N) as counter ion was dictated by solubility (very low in water) and stability reasons.

With ligands **1c–e** in our hands, we started testing the simple addition of diethylzinc to benzaldehyde as the benchmark reaction in different RTILs. The results are reported in Table 1.

Table 1. Addition of diethylzinc to benzaldehyde in different RTILs catalyzed by ligands **1**.



Entry	RTIL	**1**	T [°C]	t [h]	Yield [%][a]	*ee* [%][b]
1	–	**1d**	0	3	90	23
2	[bpy][BF_4][c]	**1d**	0	3	92	30
3	[bpy][NTf_2]	**1d**	0	3	88	69
4	[bmpy][NTf_2][d]	**1d**	0	3	92	89
5	[bmpy][OTf]	**1d**	0	3	90	87
6	[bmpy][NTf_2][e]	**1d**	0	4.5	80	89
7	[bmpy][NTf_2]	**1d**	20	2	85	75
8	[bmpy][NTf_2]	**1d**[f]	20	2	91	95
9	[bmpy][NTf_2]	**1c**	0	3	92	72
10	[bmpy][NTf_2]	**1e**	0	3	90	80
11	[bmpy][NTf_2]	**1a**	0	24	91	38
12	[bmpy][NTf_2]	**1b**	0	3	75	78

[a] Yield of isolated product. [b] The absolute configuration was assigned by comparison of the optical rotation with that of the known product. The *ee* was determined by HPLC analysis (chiralcel OD column). [c] bpy = 1-butylpyridinium. [d] bmpy = 1-butyl-1-methylpyrrolidinium. [e] 5 mol% of ligand was used. [f] 20 mol% of ligand was used.

We first compared the effect of the RTIL structure on reactivity and selectivity using 10 mol% of ligand **1d** at 0°C (Table 1, entries 1–5). Yields were independent of the RTIL used (88–92%), while the enantiomeric excesses (*ee*'s) were strongly affected by its structure. As a matter of fact, the electrostatic environment associated to the RTIL seems essential for selectivity, since the reaction in *n*-hexane (Table 1, entry 1) delivered a 23% *ee*. Using 1-butylpyridinium RTILs, the effect of the counter anion on selectivity was apparent, since tetrafluoroborate gave a 30% *ee* (entry 2), while NTf_2^- ensured a 40% gain (entry 3). The best enantioselectivity was achieved by combining the pyrrolidinium cation and NTf_2^- anion (entry 4) or triflate (entry 5).

Since [bmpy][NTf_2] is much more easily synthesized and handled with respect to the corresponding triflate, it was elected as the solvent of choice in the next study.

When the catalyst loading was decreased to 5 mol%, 80% isolated yield after 4.5 h at 0°C was obtained, with identical *ee* with respect to the use of 10 mol% ligand (Table 1, entry 6). When the reaction was catalyzed by **1d** at 20°C, we recorded a 10% loss in *ee* (Table 1, entry 7), but using the ligand in 20 mol%, a 95% *ee* and 91% isolated yield was obtained within 2 h (Table 1, entry 8).

The different length of the alkyl spacer (**1c**,**e**) did not affect the high yields, but reflected in lower enantioselectivities with respect to the use of **1d** (Table 1, entries 9, 10).

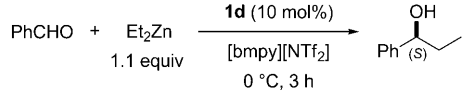
The efficiency of ion-tagged ligands was then compared to that of simple diphenylprolinol (**1a**) and *N*-methyl-diphenylprolinol (**1b**).[15] The former required longer reaction times to ensure a good conversion but with only a 38% *ee* (Table 1, entry 11). The latter was less efficient both in terms of yield and selectivity (Table 1, entry 12) with respect to ligand **1d**.

Using the protocol of entry 4, we attempted the reaction adding only a slightly excess amount of diethylzinc (1.1 equiv), and we were delighted to obtain essentially the same results, both in terms of yield and selectivity (87%, 90% *ee*), with respect to the use of a larger excess of the organometallic reagent.

Having defined entry 4 as an optimized protocol, process refinement required to focus on catalyst recycling. This task was efficiently addressed when a very simple workup was developed to easily remove the inorganic zinc salts formed during the aqueous workup and to quantitatively recover the alkylation product.

In detail, the reaction mixture was quenched with a basic aqueous solution of sodium salt of ethylenediamine tetraacetic acid (EDTA), washed with water and extracted with Et_2O. The ligand-containing IL phase was dried by heating for 2–3 h at 70°C under reduced pressure (~0.1 mmHg), and eventually reloaded with diethylzinc and the appropriate aldehyde. Results obtained in ten consecutive cycles are reported in Table 2.

Table 2. Recycling experiments.



Cycle	Yield [%][a]	*ee* [%][b]	Cycle	Yield [%][a]	*ee* [%][b]
1	96	89	6	96	89
2	94	89	7	98	88
3	95	90	8	95	90
4	98	89	9	98	88
5	96	89	10	96	90

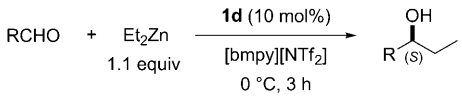
[a] Yield of isolated product. [b] Determined by HPLC analysis (chiralcel OD column).

An outstanding reproducibility was displayed and no loss of activity and stereoselectivity was apparent up to the tenth cycle.

Finally, we performed an aldehyde screen to explore the scope of this catalytic system, by applying the same optimized protocol reported for the recycling experiments. Results are summarized in Table 3.

Very good yields and enantioselectivities were obtained with aromatic aldehydes substituted in the *para* position with electron-withdrawing or donating groups (Table 3, entries 1–7), while 2-substituted aromatic aldehydes (Table 3, entries 8, 9), α,β-unsaturated aldehydes (Table 3, entries 10, 11) and aliphatic aldehydes (Table 3, entry 12) afforded lower *ee*'s.

Table 3. Scope of addition reaction.



Entry	R	Yield [%][a]	*ee* [%][b]
1	4-F-C_6H_4	90	92[c]
2	4-Br-C_6H_4	92	92[d]
3	4-Cl-C_6H_4	94	90[e]
4	4-Me-C_6H_4	92	91[c]
5	4-MeO-C_6H_4	95	92[e]
6	4-CN-C_6H_4	98	94[f]
7	2-naphthyl	99	91[e]
8	2-Br-C_6H_4	92	80[c]
9	2-MeO-C_6H_4	97	66[e]
10	(*E*)-Ph-CH=CH	90	70[e]
11	Ph-C≡C	99	55[d]
12	$PhCH_2CH_2$	50	85[e]

[a] Yield of isolated product. [b] The absolute configuration was assigned by comparison of the optical rotation with that of the known products. [c] Determined by GC analysis (Megadex cyclodextrin chiral column). [d] Determined by HPLC analysis (chiralcel OJ column). [e] Determined by HPLC analysis (chiralcel OD column). [f] Determined by HPLC analysis (chiralpak AD column).

In conclusion, we have developed a new procedure for the asymmetric addition of diethylzinc to aryl aldehydes in RTILs. Remarkable is the use of only a slight excess of diethylzinc to obtain $\geq$ 90% isolated yields of alkylation products. Adopting the ionic-tag concept aimed at tailoring ligands capable to provide metal complexes soluble in RTILs, we envisaged diphenylprolinol-derived **1d** as a promising candidate to accelerate the asymmetric addition of diethylzinc to aromatic aldehydes. Besides to the operational simplicity and efficiency, the catalytic system was easily recyclable, making the use of 10 mol% loading of **1d** a minor problem.

Experimental Section

Typical Procedure: A solution of diethylzinc (1.0 M in hexanes, 0.6 mL, 0.6 mmol) was added to a solution of catalyst **1d** (35.9 mg, 0.05 mmol) in [bmpy][NTf_2] (1.0 mL) and the mixture was stirred at RT for 5 min. Benzaldehyde (0.051 mL, 0.5 mmol) was then added at 0°C and the solution was stirred until thin-layer chromatography (TLC) showed the disappearance of the starting aldehyde (3 h). The reaction was quenched with a few drops of water and the resulting mixture was directly charged on the top of a silica gel column diluting with CH_2Cl_2. Elution with 9:1 cyclohexane/AcOEt afforded the alcohol adduct (0.067 g, 98%) as a colorless oil. The *ee* value (90%) was determined by high-performance liquid chromatography (HPLC) by using a Chiralcel OD column: *n*-hexane/*i*PrOH 99:1, 0.8 mL min^{-1}, t_R = 28.4 min (minor), 31.2 min (major). The absolute *S* configuration was assigned by comparison of the optical rotation with that of the known product: $[\alpha]_D^{22} = -42.0$ (c = 1.9 in $CHCl_3$), 90% *ee*; literature value: *S* isomer, $[\alpha]_D^{21} = -45.6°$, (c = 5.55 in $CHCl_3$), 95.4% *ee*.[16]

Recycling procedure: The experimental procedure for the recycling of catalyst and ionic liquid was the same as described above, except the reaction was quenched by adding a solution of EDTA disodium salt (0.57 g, 1.5 mmol) and NaOH (0,08 g, 2 mmol) in H_2O (2 mL). The aqueous phase was removed with a syringe and the ionic liquid was further washed with H_2O (2×2 mL). The alcohol adduct was then extracted with Et_2O (5×2 mL), and the combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure. The title product was purified by flash-chromatography on silica eluting with cyclohexane/EtOAc 9:1. The ionic liquid was dried by heating at 70°C under vacuum (~0.1 mmHg) for 2–3 h and directly reloaded with the starting reagents.

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Keywords: asymmetric synthesis · diethylzinc · ionic liquids · homogeneous catalysis · recycling

[1] a) H. Weingärtner, *Angew. Chem.* **2008**, *120*, 664–682; *Angew. Chem. Int. Ed.* **2008**, *47*, 654–670; b) M. Haumann, A. Riisager, *Chem. Rev.* **2008**, *108*, 1474–1497; c) M. A. P. Martins, C. P. Frizzo, D. N. Moreira, N. Zanatta, H. G. Bonacorso, *Chem. Rev.* **2008**, *108*, 2015–2050; d) T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206–237; e) *Green Chemical Reactions* (Eds.: P. Tundo, V. Esposito), Springer, Heidelberg, **2008**; f) *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, **2007**; g) F. van Rantwijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757–2785; h) K. Binnemans, *Chem. Rev.* **2007**, *107*, 2592–2614; i) J. Ranke, S. Stolte, R. Stormann, J. Arning, B. Jastorff, *Chem. Rev.* **2007**, *107*, 2183–2206; j) V. I. Parvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615–2665; k) *Metal Catalyzed Reactions in Ionic Liquids*, (Eds.: P. J. Dyson, T. J. Geldbach), Springer, Heidelberg, **2005**; l) *Chemistry In Alternative Reaction Media* (Eds.: D. Adams, P. J. Dyson, S. Tavener), Wiley, Chichester, **2004**; m) Y.-F. Hu, C.-M. Xu, R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792–793; n) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3692; o) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2084.

[2] a) P. Migowski, J. Dupont, *Chem. Eur. J.* **2007**, *13*, 32–39; b) Z. Fei, T. J. Geldbach, D. Zhao, P. J. Dyson, *Chem. Eur. J.* **2006**, *12*, 2122–2130; c) *Multiphase Homogeneous Catalysis* (Eds.: B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt), Wiley-VCH, Weinheim, **2005**.

[3] D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702–1706.

[4] For a recent review on ion-tagged catalysts and their use in RTILs, see: R. Šebesta, I. Kmentová, Š. Toma, *Green Chem.* **2008**, *10*, 484–496.

[5] a) M. Lombardo, F. Pasi, S. Easwar, C. Trombini, *Adv. Synth. Catal.* **2007**, *349*, 2061–2065; b) M. Lombardo, M. Chiarucci, C. Trombini, submitted.

[6] a) H. Clavier, S. P. Nolan, M. Mauduit, *Organometallics* **2008**, *27*, 2287–2292; b) G. Liu, J. Zhang, B. Wu, J. Wang, *Org. Lett.* **2007**, *9*, 4263–4266; c) Y. S. Vygodskii, A. S. Shaplov, E. I. Lozinskaya, O. A. Filippov, E. S. Shubina, R. Bandari, M. R. Buchmeiser, *Macromolecules* **2006**, *39*, 7821–7830; d) A. Stark, M. Ajam, M. Green, H. G. Raubenheimer, A. Ranwell, B. Ondruschka, *Adv. Synth. Catal.* **2006**, *348*, 1934–1941; e) D. B. G. Williams, M. Ajam, A. Ranwell, *Organometallics* **2006**, *25*, 3088–3090; f) Q. Yao, M. Sheet, *J. Organomet. Chem.* **2005**, *690*, 3577–3584; g) H. Clavier, N. Audic, J. C. Guillemin, M. Mauduit, *J. Organomet. Chem.* **2005**, *690*, 3585–3599; h) V. Martinez, J. C. Blais, G. Bravic, D. Astruc, *Organometallics* **2004**, *23*, 861–874; i) H. Clavier, L. Boulanger, N. Audic, L. Toupet, M. Mauduit, J. C. Guillemin, *Chem. Commun.* **2004**, 1224–1225; j) N. Audic, H. Clavier, M. Mauduit, J.-C. Guillemin, *J. Am. Chem. Soc.* **2003**, *125*, 9248–9249; k) K. E. Gutowski, G. A. Broker, H. D. Willauer, J. G. Huddleston, R. P. Swatloski, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2003**, *125*, 6632–6633; l) Q. W. Yao, Y. L. Zhang, *Angew. Chem.* **2003**, *115*, 3517–3520; *Angew. Chem. Int. Ed.* **2003**, *42*, 3395–3398; m) D. Semeril, H. Oliver-Bourbigou, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **2002**, 146–147; n) K. G. Mayo,

E. H. Nearhoof, J. J. Kiddle, *Org. Lett.* **2002**, *4*, 1567–1570; o) S. Csihony, C. Fischmeister, C. Bruneau, I. T. Horvath, P. H. Dixneuf, *New J. Chem.* **2002**, *26*, 1667–1670; p) R. C. Buijsman, E. van Vuuren, J. G. Sterrenburg, *Org. Lett.* **2001**, *3*, 3785–3787.

[7] a) X. Yang, Z. Fei, D. Zhao, W. H. Ang, Y. Li, P. J. Dyson, *Inorg. Chem.* **2008**, *47*, 3292–3297; b) Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe, P. J. Dyson, *Organometallics* **2007**, *26*, 1588–1598; c) J.-C. Hierso, J. Boudon, M. Picquet, P. Meunier, *Eur. J. Org. Chem.* **2007**, 583–587; d) J.-H. Li, B.-X. Tang, L.-M. Tao, Y.-X. Xie, Y. Liang, M.-B Zhang, *J. Org. Chem.* **2006**, *71*, 7488–7490; e) L. Durán Pachón, C. J. Elsevier, G. Rothenberg, *Adv. Synth. Catal.* **2006**, *348*, 1705–1710; f) K. Bica, P. Gaertner, *Org. Lett.* **2006**, *8*, 733–735; g) R. Wang, B. Twamley, J. M. Shreeve, *J. Org. Chem.* **2006**, *71*, 426–429; h) C. Chiappe, D. Pieraccini, D. Zhao, Z. Fei, P. J. Dyson, *Adv. Synth. Catal.* **2006**, *348*, 68–74; i) J.-C. Xiao, C. Ye, J. M. Shreeve, *Org. Lett.* **2005**, *7*, 1963–1965; j) J.-C. Xiao, J. M. Shreeve, *J. Org. Chem.* **2005**, *70*, 3072–3078; k) V. Calo, A. Nacci, A. Monopoli, F. Montingelli, *J. Org. Chem.* **2005**, *70*, 6040–6044; l) D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876–15882; m) F. McLachlan, C. J. Mathews, P. J. Smith, T. Welton, *Organometallics* **2003**, *22*, 5350–5357; n) G. W. Kabalka, G. Dong, B. Venkataiah, *Org. Lett.* **2003**, *5*, 893–895; o) W. Miao, T. H. Chan, *Org. Lett.* **2003**, *5*, 5003–5005; p) J. D. Revell, A. Ganesan, *Org. Lett.* **2002**, *4*, 3071–3073.

[8] a) L. Leclercq, I. Suisse, F. Agbossou-Niedercorn, *Chem. Commun.* **2008**, 311–313; b) K. Hamza, J. Blum, *Eur. J. Org. Chem.* **2007**, 4706–4710; c) S. Paganelli, A. Perosa, M. Selva, *Adv. Synth. Catal.* **2007**, *349*, 1858–1862; d) M. Haumann, K. Dentler, J. Joni, A. Riisager, P. Wasserscheid, *Adv. Synth. Catal.* **2007**, *349*, 425–431; e) D. B. G. Williams, M. Ajam, A. Ranwell, *Organometallics* **2007**, *26*, 4692–4695; f) J. J. Kim, H. Alper, *Chem. Commun.* **2005**, 3059–3061; g) A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann, P. Wasserscheid *Angew. Chem.* **2005**, *117, 826–830; Angew. Chem. Int. Ed.* **2005**, 44, 815–819; *Angew. Chem. Int. Ed.* **2005**, *44*, 815–819; h) R. P. J. Bronger, S. M. Silva, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Dalton Trans.* **2004**, 1590–1596; i) P. B. Webb, M. F. Sellin, T. E. Kunene, S. Williamson, A. M. Z. Slawin, D. J. Cole-Hamilton, *J. Am. Chem. Soc.* **2003**, *125*, 15577–15588; j) M. Marchetti, C. Botteghi, S. Paganelli, M. Taddei *Adv. Synth. Catal.* **2003**, *345*, 1229–1236; k) C. P. Mehnert, R. A. Cook, N. C. Dispenziere, M. Afeworki, *J. Am. Chem. Soc.* **2002**, *124*, 12932–12933; l) C. C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, *Organometallics* **2000**, *19*, 3818–3823; m) Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem.* **1995**, *107*, 2941–2943; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2698–2700.

[9] a) M. C. Law, K.-Y. Wong, T. H. Chan, *Chem. Commun.* **2006**, 2457–2459; b) M. C. Law, K.-Y. Wong, T. H. Chan, *Green Chem.* **2004**, *6*, 241–244; c) C. M. Gordon, C. Ritchie, *Green Chem.* **2002**, *4*, 124–128; d) G. W. Kabalka, B. Venkataiah, B. C. Das, *Green Chem.* **2002**, *4*, 472–473; e) M. C. Law, K.-Y. Wong, T. H. Chan, *Green Chem.* **2002**, *4*, 161–164; f) G. W. Kabalka, R. R. Malladi, *Chem. Commun.* **2000**, 2191–2192; g) C. M. Gordon, A. McCluskey, *Chem. Commun.* **1999**, 1431–1432.

[10] a) For a recent review on asymmetric catalysis in RTILs, see: S. V. Malhotra, V. Kumar, V. S. Parmar, *Curr. Org. Synth.* **2007**, *4*, 370–380; b) J. Lu, S.-J. Ji, T.-P. Loh, *Chem. Commun.* **2005**, 2345–2347; c) J. Lu, S.-J. Ji, Y.-C. Teo, T.-P. Loh, *Tetrahedron Lett.* **2005**, *46*, 7435–7437; d) J. N. Rosa, A. G. Santos, C. A. M. Afonso, *J. Mol. Catal. A* **2004**, *214*, 161–165; e) C. Baleizão, B. Gigante, H. Garcia, A. Corma, *Green Chem.* **2002**, *4*, 272–274.

[11] a) K. Mikami, M. Terada, T. Korenaga, Y. Matsumoto, M. Ueki, R. Angelaud, *Angew. Chem.* **2000**, *112*, 3676–3701; *Angew. Chem. Int. Ed.* **2000**, *39*, 3532–3556; b) D. J. Berrisford, C. Bolm, K. B. Sharpless, *Angew. Chem.* **1995**, *107*, 1159–1171; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1059–1070.

[12] a) J.-C. Kizirian, *Chem. Rev.* **2008**, *108*, 140–205; L. Pu, H.-B. Yu, *Chem. Rev.* **2001**, *101*, 757–824.

[13] J. V. B. Kanth, M. Periasamy, *Tetrahedron* **1993**, *49*, 5127–5132.

[14] T. R. Jensena, C. P. Schallerb, M. A. Hillmyera, W. B. Tolman, *J. Organomet. Chem.* **2005**, *690*, 5881–5891.

[15] K. Soai, C. Shimada, M. Takeuchi, M. Itabashi, *J. Chem. Soc. Chem. Commun.* **1994**, 567–568.

[16] M. Kitamura, H. Oka, S. Suga, R. Noyori, *Org. Synth.*, **2002**, *79*, 139–142.

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