Synthetic Methods

DOI: 10.1002/anie.200803230

C_1-Symmetric Monosubstituted Chiral Diene Ligands in Asymmetric Rhodium-Catalyzed 1,4-Addition Reactions**

*Thomas Gendrineau, Olivier Chuzel, Hendrik Eijsberg, Jean-Pierre Genet, and Sylvain Darses**

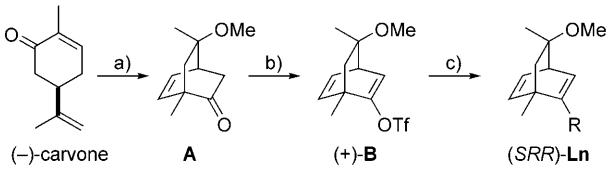
Asymmetric catalysis provides outstanding tools to introduce chiral information to a substrate by using only catalytic amounts of a chiral transition-metal complex.[1] The success of these efficient asymmetric processes relies on the development of chiral ligands that form a complex with the metal; until very recently phosphorus-, nitrogen-, and oxygen-containing chiral ligands were the only ones available. Recently, the groups of Hayashi and Carreira independently reported the use of chiral dienes in asymmetric catalysis:[2] high levels of enantioselectivity were achieved in both the iridium-catalyzed kinetic resolution of allyl carbonates[3] and the rhodium-catalyzed 1,4-additions of organoboron reagents to Michael acceptors.[4,5]

Major efforts in the development of these chiral diene ligands have been focused on the latter reaction and on the related rhodium-catalyzed addition of organoboron reagents to imines.[6] In comparison to the use of phosphorus ligands, diene ligands allowed reactions to be conducted at room temperature with low catalytic amounts of the rhodium catalyst. In the rhodium-catalyzed asymmetric 1,4-additions, only C_2-symmetric (or C_2-like) disubstituted dienes allowed high levels of enantioselectivity.[4,7–9] Although such dienes are easily accessed, their syntheses are generally low yielding,[6a,7e,n] requires either chiral chromatographic separation,[6b,c] asymmetric catalysis,[4] or the introduction of the first substituent early in the synthesis,[8] therefore preventing straightforward access to diene libraries. Moreover, it appeared that ligands derived from a bicyclo[2.2.1]heptadiene core showed moderate stability,[7a] and that the bicyclo-[2.2.2]octadiene framework was the most suitable for the rhodium-catalyzed addition of organometallic reagents to Michael acceptors in terms of the enantioselectivity.[2,7,8]

The space around the rhodium center coordinated to C_2-symmetric chiral dienes is quite similar to that of the rhodium coordinated to a conventional C_2-symmetric chiral phosphorous ligands such as 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (binap). In the bis(phosphanyl), chirality is frequently controlled by the face/edge orientation of the aryl substituents at the phosphorus atom; whereas for dienes, the chirality is controlled by the substituents attached to the double bonds.[4,7,8] Because of their straightforward preparation, we wondered if C_1-type diene ligands, bearing only one substituent could be employed in rhodium-catalyzed 1,4-addition reactions with comparable efficiency.[10] Actually, such C_1-type diene ligands proved useful only in the iridium-catalyzed kinetic resolution of allyl carbonates.[3]

In our continuing work on rhodium-catalyzed reactions involving organoboron reagents,[11] we report herein that the C_2-symmetry of a chiral diene ligand is not necessary to achieve high enantioselectivities in rhodium-catalyzed 1,4-additions, and that easily accessible (only four steps) monosubstituted dienes with C_1-symmetry compare favorably to these disubstituted dienes.

The synthesis of chiral monosubstituted diene ligands was inspired by the work of Carreira and co-workers.[3] Enantiopure ketone **A** (Scheme 1) was prepared in two steps on large scale by bromination of commercial (−)-carvone and subsequent cyclization and separation of the resulting diastereoisomers.[12] Triflation of the lithium enolate by using Comins reagent[13] afforded bicyclic triflate (+)-**B** in 81% yield. In contrast to a previous report involving organozinc reagents,[3] the diene substituent was introduced by a palladium-catalyzed cross-coupling reaction with either Grignard reagents, arylboronic acids, or potassium aryltrifluoroborates.[14] For the introduction of an aromatic substituent, the best conditions employed arylboronic acids as coupling partners ($PdCl_2$(dppf), K_2CO_3, DMF, 100 °C; dppf = 1,1′-bis(diphenylphosphanyl)ferrocene).[15] However, under these unoptimized conditions slightly lower yields were obtained by using *ortho*-substituted arylboronic acids. The monosubstituted chiral dienes ((*SRR*)-**Ln**)[16] were easily prepared in moderate to good yields from (−)-carvone by using this methodology.



R = Bn (**L1**), Ph (**L2**), 4-MeC_6H_4 (**L3**), 4-(*t*Bu)C_6H_4 (**L4**), 2-MeC_6H_4 (**L5**), 3,5-$(Me)_2C_6H_3$ (**L6**), 2,6-$(Me)_2C_6H_3$ (**L7**), 2,4,6-$(Me)_3C_6H_2$ (**L8**), 4-$MeOC_6H_4$ (**L9**), 4-$CF_3C_6H_4$ (**L10**), 4-FC_6H_4 (**L11**), 2-$CHOC_6H_4$ (**L12**), 1-naphthyl (**L13**), 2-naphthyl (**L14**)

Scheme 1. Preparation of monosubstituted chiral diene ligands. a) See reference [12]; b) LDA, Comins reagent, THF, −78 °C (81%); c) see the Supporting Information.

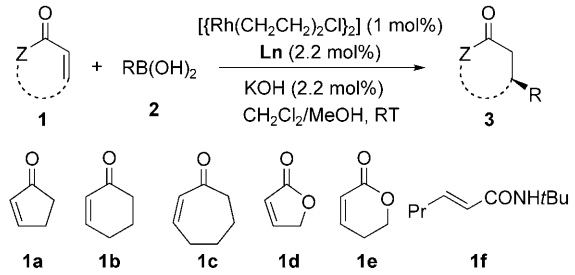
[*] T. Gendrineau, Dr. O. Chuzel, H. Eijsberg, Prof. J.-P. Genet, Dr. S. Darses
Laboratoire de Synthèse Sélective Organique (UMR 7573), Ecole Nationale Supérieure de Chimie de Paris
11 rue P&M Curie, 75231 Paris cedex 05 (France)
Fax: (+33) 1-4407-1062
E-mail: sylvain-darses@enscp.fr

[**] This work was support by the Centre National de la Recherche Scientifique (CNRS). T. Gendrineau thanks the Ministère de l'Education et de la Recherche for a grant.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803230.

Elements of diversity were introduced in the last step of the synthesis, allowing fast generation of a library of ligands. The enantiomers ((*RSS*)-**Ln**) were obtained in identical yields from (+)-carvone.

We evaluated the ability of these monosubstituted chiral diene ligands to control the enantioselectivity in the rhodium-catalyzed 1,4-addition of boronic acids to Michael acceptors. Gratifyingly, the reaction of cyclohexenone (**1b**) with phenylboronic acid (**2a**) was efficiently catalyzed by a rhodium complex generated from ligand **L3** and commercially available $[\{Rh(CH_2CH_2)_2Cl\}_2]$, and enantio-enriched product **3ba** was obtained with 92% enantiomeric excess by using previously reported conditions (Scheme 2).[4] An improved



R = Ph (**2a**), 4-$MeOC_6H_4$ (**2b**), 3-$MeOC_6H_4$ (**2c**), 4-FC_6H_4 (**2d**), 4-ClC_6H_4 (**2e**), 4-$CF_3C_6H_4$ (**2f**), 1-naphthyl (**2g**)

Scheme 2. Monosubstituted chiral dienes in rhodium-catalyzed 1,4-addtion of boronic acids to α,β-unsaturated substrates.

enantioselectivity (95% *ee* by using ligand **L3**) was achieved by conducting the reaction in methanol/dichloromethane (10:1; instead of the classical dioxane/water (10:1) solvent system).[17] The rhodium catalyst precursor was prepared by coordination of the chiral diene to commercial $[\{Rh(CH_2CH_2)_2Cl\}_2]$ in dichloromethane with subsequent treatment by a methanolic solution of KOH to generate the hydroxy–rhodium complex.

Under these optimized conditions, we evaluated the library of chiral diene ligands in the rhodium-catalyzed 1,4-addition of **2a** to cyclohexenone (**1b**; Table 1, Scheme 2). Overall, high enantioselectivities were obtained for the formation of **3ba** by using aryl-substituted dienes (from 85% to 98% *ee*). However, the presence of a methylene bridge in the ligand, such as in **L1**, resulted in moderate chiral induction. In contrast to C_2-like symmetric ligands where benzyl or alkyl substituents were perfectly suitable, a rigid and bulky substituent in the monosubstituted dienes is essential to achieve high enantioselectivity.[4,7,8] Among the aryl-substituted ligands evaluated, it appeared that the presence of *ortho* substituents was essential to access enantioselectivities above 95%. To our delight, an enantiomeric excess of 98% was obtained by using ligand **L7**, which had two *ortho*-methyl substituents on the aromatic ring. This result constitutes the highest enantiomeric excess reported for the phenylation of substrate **1b** by using chiral dienes. The electronic nature of the substituents on the aromatic ring does have some influence on the enantioselectivities: lower

Table 1: Ligand screening in the rhodium-catalyzed addition of $PhB(OH)_2$ (**2a**) to α,β-unsaturated substrates **1b** and **1d**.[a]

Entry[a]	Chiral diene	Yield [%] (*ee* [%])[b]	
		3ba	**3da**
1	**L1**	91 (39)	
2	**L2**	90 (90)	
3	**L3**	81 (95)	56 (90)
4	**L4**	87 (91)	58 (83)
5	**L5**	88 (96)	
6	**L6**	>99 (91)	57 (80)
7	**L7**	86 (98)	56 (90)
8	**L8**	82 (92)	
9	**L9**	93 (91)	69 (87)
10	**L10**	91 (85)	
11	**L11**	99 (89)	
12	**L12**	90 (93)	
13	**L13**	>99 (95)	
14	**L14**	93 (91)	

[a] Reactions conditions: **1** (0.5 mmol), **2** (2 equiv), $[\{Rh(CH_2CH_2)_2Cl\}_2]$ (2 mol% Rh), (*SRR*)-**Ln** (2.2 mol%; from (−)-carvone), and KOH (2.2 mol%) in $MeOH/CH_2Cl_2$ (10:1; 1 mL) at room temperature. [b] Yield of isolated product. The *ee* values shown in parentheses were determined by chiral HPLC methods.

ee values are observed with dienes bearing electron-withdrawing substituents (Table 1, entry 10). Some of these ligands were also evaluated in the 1,4-addition of **2a** to lactone **1d** (Table 1), and the highest enantioselectivity was achieved by using di-*ortho*-substituted chiral diene **L7** in the formation of 1,4-addition adduct **3da**. Compared to cyclohexenone, the enantioselectivity levels were lower (≤90%), but comparable to those obtained by using C_2-type disubstituted chiral diene ligands.[8a]

The scope of the reaction was evaluated by using diene (−)-**L7**, which was prepared from (−)-carvone (Table 2). Cyclic enones underwent clean reaction with different arylboronic acids at room temperature (Table 2, entries 1–11). Enantioselectivities ranging from 93 to 98% were achieved by using this chiral diene ligand and the *ee* values were within the range and even above those observed with C_2-type symmetry chiral dienes previously reported.[4,7–9] The enantiomer of **3ba** was obtained by using the enantiomer (+)-**L7** as the ligand (Table 2, entries 3 and 4). A slightly lower enantiomeric excess was observed in the reaction of cyclohexenone (**1b**) with *ortho*-substituted boronic acid **2g** (Table 2, entry 10). Good enantioselectivities were also achieved for the reaction of boronic acids with lactones (Table 2, entries 12–15). Higher *ee* values were observed for six-membered rings compared to five-membered rings; similar to observations made by others.[4,7,8] Indeed, enantioselectivities obtained for cyclic α,β-unsaturated substrates by using monosubstituted chiral diene **L7** compared favorably and even surpassed those obtained with previously reported dienes. A preliminary result concerning the addition of phenylboronic acid (**2a**) to linear α,β-unsaturated amide **1f**, was encouraging; the expected 1,4-addition adduct was formed in good yield and with an enantioselectivity of 90% (Table 2, entry 16).

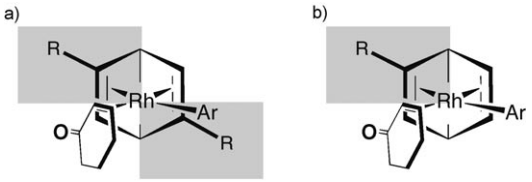
A monosubstitution of the chiral diene ligand is sufficient to achieve high enantioselectivity in the rhodium-catalyzed

Table 2: Monosubstituted chiral diene (−)-(*SRR*)-**L7** in rhodium-catalyzed 1,4-addition of boronic acids to α,β-unsaturated substrates.[a]

Entry	**1**	$RB(OH)_2$	Yield [%][b]	*ee* [%][c]
1	**1a**	**2a**	95 (**3aa**)	96 (*S*)
2	**1a**	**2c**	85 (**3ac**)	96
3	**1b**	**2a**	>99 (**3ba**)	98 (*S*)
4	**1b**	**2a**	89 (**3ba**)	97 (*R*)[d]
5	**1b**	**2b**	83 (**3bb**)	98
6	**1b**	**2c**	93 (**3bc**)	95
7	**1b**	**2d**	84 (**3bd**)	98
8	**1b**	**2e**	77 (**3be**)	93
9	**1b**	**2f**	66 (**3bf**)	98
10	**1b**	**2g**	45 (**3bg**)	75 (*S*)
11	**1c**	**2a**	53[e] (**3ca**)	93
12	**1d**	**2a**	56 (**3da**)	90
13	**1e**	**2g**	95 (**3eg**)	86
14	**1e**	**2b**	95 (**3eb**)	97
15	**1e**	**2a**	95 (**3ea**)	97
16	**1f**	**2a**	40 (**3fa**)	90

[a] Reactions conditions: **1** (0.5 mmol), **2** (2 equiv), $[\{Rh(CH_2CH_2)_2Cl\}_2]$ (2 mol% Rh), (−)-(*SRR*)-**L7** (2.2 mol%), KOH (2.2 mol%) in MeOH/CH_2Cl_2 (10:1; 1 mL) at room temperature. [b] Yield of isolated product. [c] The *ee* values were determined by chiral HPLC methods. [d] (+)-(*RSS*)-**L7** used as ligand. [e] Used 3 equivalents of arylboronic acid.

addition of boronic acids to α,β-unsaturated substrates, which is similar to the observation by Carreira and co-workers in the iridium-catalyzed kinetic resolution of allyl carbonates.[3] These observations can be readily explained by considering that coordination of the unsaturated substrate to rhodium occurs after the transmetalation of the organoborane so that an aryl substituent is present on the rhodium center.[18] This aryl group blocks one of the substituents of the disubstituted chiral diene, suggesting that the substituent has little effect on selectivity (Scheme 3a). Only one substituent on the diene is sufficient for chiral recognition (steric interaction) of one face of the incoming α,β-unsaturated substrate (Scheme 3b).



Scheme 3. Origin of the enantioselectivity: disubstituted (a) versus monosubstituted (b) chiral diene ligands.

We have demonstrated, for the first time, that monosubstituted chiral dienes are well-suited ligands in the rhodium-catalyzed asymmetric 1,4-addition of boronic acids to α,β-unsaturated substrates. These ligands can be easily accessed (four steps from commercially available carvones), and allow high enantioselectivities to be obtained for the formation of a new C–C bond in the β position of Michael acceptors. The preparation of this monosubstituted ligand is straightforward and high yielding, permitting access to a large library of chiral ligands derived from either enantiomer of cheap, commercially available carvones, which will be of great interest in asymmetric catalysis.

Experimental Section

Typical procedure for the rhodium-catalyzed 1,4-addition of boronic acids to α,β-unsaturated substrates: A septum-capped vial, equipped with a magnetic stirring bar, was charged with $[\{Rh(CH_2CH_2)_2Cl\}_2]$ (2.0 mg, 2 mol% Rh) and chiral diene **L7** (3.0 mg, 2.2 mol%). The vial was closed, evacuated under vacuum and placed under an argon atmosphere. Degassed dichloromethane (100 μL) was added and the mixture was stirred for 15 min at room temperature. A methanolic KOH solution (0.22 M, 50 μL, 2.2 mol%) was added to the mixture which was then stirred for 15 min at room temperature. Another septum-capped vial, equipped with a magnetic stirring bar, was charged with the α,β-unsaturated substrate (0.5 mmol) and arylboronic acid (1 mmol). The vial was closed, evacuated under vacuum and placed under an argon atmosphere. Degassed methanol (850 μL) and the previously prepared catalyst solution were added and the mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the crude residue was purified by using column chromatography with silica gel to afford pure 1,4-addition adduct.

Received: July 3, 2008
Published online: September 4, 2008

Keywords: asymmetric synthesis · boron · diene ligands · Michael addition · rhodium

[1] a) *Asymmetric Catalysis in Organic Synthesis* (Ed.: R. Noyori), Wiley, New York, **1994**; b) *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), Wiley, New York, **2000**.
[2] Review: C. Defieber, H. Grützmacher, E. M. Carreira, *Angew. Chem.* **2008**, *120*, 4558–4579; *Angew. Chem. Int. Ed.* **2008**, *47*, 4482–4502.
[3] C. Fischer, C. Defieber, T. Suzuki, E. M. Carreira, *J. Am. Chem. Soc.* **2004**, *126*, 1628–1629.
[4] T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 11508–11509.
[5] Rhodium-catalyzed 1,4-additions by using chiral phosphorous ligands: a) M. Sakai, H. Hayashi, N. Miyaura, *Organometallics* **1997**, *16*, 4229–4231; b) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura, *J. Am. Chem. Soc.* **1998**, *120*, 5579–5580. Reviews on rhodium-catalyzed asymmetric 1,4-addition: c) T. Hayashi, *Synlett* **2001**, 879–887; d) T. Hayashi, K. Yamasaki, *Chem. Rev.* **2003**, *103*, 2829–2844; e) T. Hayashi, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 13–21; f) T. Hayashi, *Pure Appl. Chem.* **2004**, *76*, 465–475.
[6] The use of C_2-symmetric chiral dienes in asymmetric rhodium-catalyzed addition to imines: a) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2004**, *126*, 13584–13585; b) Y. Otomaru, N. Tokunaga, R. Shintani, T. Hayashi, *Org. Lett.* **2005**, *7*, 307–310; c) Y. Otomaru, A. Kina, R. Shintani, T. Hayashi, *Tetrahedron: Asymmetry* **2005**, *16*, 1673–1679; d) T. Nishimura, Y. Yasuhara, T. Hayashi, *Org. Lett.* **2006**, *8*, 979–981.
[7] Ligands derived from bicyclo[2.2.1]heptane structures: a) G. Berthon-Gelloz, T. Hayashi, *J. Org. Chem.* **2006**, *71*, 8957–8960; b) T. Noel, K. Vandyck, J. Van der Eycken, *Tetrahedron* **2007**, *63*, 12961–12967. Bicyclo[2.2.2]octadienes: c) R. Shintani, A. Tsurusaki, K. Okamoto, T. Hayashi, *Angew. Chem.* **2005**, *117*, 3977–3980; *Angew. Chem. Int. Ed.* **2005**, *44*, 3909–3912; d) T. Hayashi, N. Tokunaga, K. Okamoto, R. Shintani, *Chem. Lett.* **2005**, *34*, 1480–1481; e) Y. Otomaru, K. Okamoto, R. Shintani, T. Hayashi, *J. Org. Chem.* **2005**, *70*, 2503–2508; f) R. Shintani, K. Okamoto, T. Hayashi, *Org. Lett.* **2005**, *7*, 4757–4759; g) F. Chen, A. Kina, T. Hayashi, *Org. Lett.* **2006**, *8*, 341–344; h) Y. Nakao, J. Chen, H. Imanaka, T. Hiyama, Y. Ichikawa, W. L. Duan, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 9137–9143;

i) W. L. Duan, Y. Imazaki, R. Shintani, T. Hayashi, *Tetrahedron* **2007**, *63*, 8529 – 8536; j) R. Shintani, Y. Ichikawa, T. Hayashi, J. Chen, Y. Nakao, T. Hiyama, *Org. Lett.* **2007**, *9*, 4643 – 4645; k) S. Sörgel, N. Tokunaga, K. Sasaki, K. Okamoto, T. Hayashi, *Org. Lett.* **2008**, *10*, 589 – 592. Bicyclo[3.3.1]nona-2,6-diene: l) Y. Otomaru, A. Kina, R. Shintani, T. Hayashi, *Tetrahedron: Asymmetry* **2005**, *16*, 1673 – 1679; m) Y. Nakao, M. Takeda, J. Chen, T. Hiyama, Y. Ichikawa, R. Shintani, T. Hayashi, *Chem. Lett.* **2008**, *37*, 290 – 291. 1,5-cyclooctadiene: n) A. Kina, K. Ueyama, T. Hayashi, *Org. Lett.* **2005**, *7*, 5889 – 5892.

[8] C_2-type symmetric bicyclo[2.2.2]octadienes derived from (−)-carvone: a) C. Defieber, J. Paquin, S. Serna, E. M. Carreira, *Org. Lett.* **2004**, *6*, 3873 – 3876; b) J. Paquin, C. Defieber, C. R. J. Stephenson, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 10850 – 10851; c) J. Paquin, C. R. J. Stephenson, C. Defieber, E. M. Carreira, *Org. Lett.* **2005**, *7*, 3821 – 3824.

[9] Bicyclo[3.3.0]octa-2,5-dienes: a) S. Helbig, S. Sauer, N. Cramer, S. Laschat, A. Baro, W. Frey, *Adv. Synth. Catal.* **2007**, *349*, 2331 – 2337; b) Z. Wang, C. G. Feng, M. Xu, G. Q. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 5336 – 5337.

[10] An example of C_1-symmetric chiral diene in rhodium-catalyzed 1,4-addition (moderate *ee* values observed): F. Läng, F. Breher, D. Stein, H. Grützmacher, *Organometallics* **2005**, *24*, 2997 – 3007. Carreira and co-workers also reported the low efficiency of such monosubstituted chiral dienes: see reference [8a].

[11] a) M. Pucheault, S. Darses, J. P. Genet, *Eur. J. Org. Chem.* **2002**, 3552 – 3557; b) L. Navarre, S. Darses, J. P. Genet, *Angew. Chem.* **2004**, *116*, 737 – 741; *Angew. Chem. Int. Ed.* **2004**, *43*, 719 – 723; c) L. Navarre, S. Darses, J. P. Genet, *Chem. Commun.* **2004**, 1108 – 1109; d) M. Pucheault, S. Darses, J. P. Genet, *J. Am. Chem. Soc.* **2004**, *126*, 15356 – 15357; e) M. Pucheault, S. Darses, J. P. Genet, *Chem. Commun.* **2005**, 4714 – 4716; f) G. Mora, S. Darses, J. P. Genet, *Adv. Synth. Catal.* **2007**, *349*, 1180 – 1184; g) R. Martinez, F. Voica, J. P. Genet, S. Darses, *Org. Lett.* **2007**, *9*, 3213 – 3216.

[12] A. Srikrishna, G. V. R. Sharma, S. Danieldoss, P. Hemamalini, *J. Chem. Soc. Perkin Trans. 1* **1996**, 1305 – 1311.

[13] D. L. Comins, A. Dehghani, *Tetrahedron Lett.* **1992**, *33*, 6299 – 6302.

[14] a) G. A. Molander, D. E. Petrillo, N. R. Landzberg, J. C. Rohanna, B. Biolatto, *Synlett* **2005**, 1763 – 1766; b) S. Darses, J. P. Genet, *Chem. Rev.* **2008**, *108*, 288 – 325; c) H. A. Stefani, R. Cella, A. S. Vieira, *Tetrahedron* **2007**, *63*, 3623 – 3658; d) G. A. Molander, N. M. Ellis, *Acc. Chem. Res.* **2007**, *40*, 275 – 286; e) G. A. Molander, R. Figueroa, *Aldrichimica Acta* **2005**, *38*, 49 – 56; f) S. Darses, J. P. Genet, *Eur. J. Org. Chem.* **2003**, 4313 – 4327.

[15] Review: N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457 – 2483.

[16] (*SRR*)-**Ln** corresponds to (1*S*,4*R*,5*R*)-**Ln** for **L1**–**L11** and **L13**–**L14** and to (1*S*,4*R*,8*R*)-**Ln** for **L12**.

[17] Improved reaction efficiency was also observed by using an alcoholic solvent instead of water in a related reaction: S. Brock, D. R. J. Hose, J. D. Moseley, A. J. Parker, I. Patel, A. J. Williams, *Org. Process Res. Dev.* **2008**, *12*, 496 – 502.

[18] T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **2002**, *124*, 5052 – 5058.

