Asymmetric Catalysis

DOI: 10.1002/anie.201102586

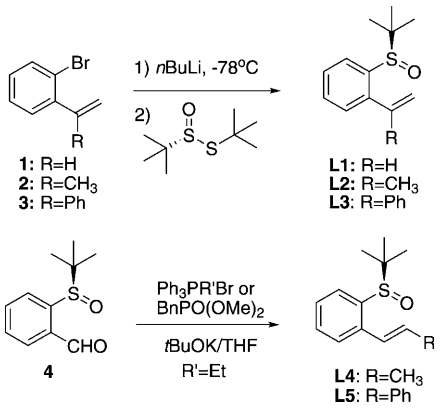
# Chiral Sulfoxide-Olefin Ligands: Completely Switchable Stereoselectivity in Rhodium-Catalyzed Asymmetric Conjugate Additions**

*Guihua Chen, Jiangyang Gui, Liangchun Li, and Jian Liao**

The design and synthesis of novel chiral ligands is an important part of developing enantioselective transition-metal-catalyzed reactions[1] which provide access to both enantiomers.[2] Reaction parameters (such as pressure, solvent, counterions, and additives),[3] the choice of metal,[4] tunable ligands,[5] and so on,[6,7] play a critical role in the optimization of a particular asymmetric transformation. Among these criteria, the design of different ligands from a single easily accessible chiral source is an attractive strategy.

As a ubiquitous structural element, olefins have attracted intense attention as ligands in organometallic chemistry,[8] owing to the independent contributions of Hayashi et al. and Carreira and co-workers.[9] Several novel cyclic chiral dienes were developed that exhibit unique and exciting properties in transition-metal-catalyzed asymmetric reactions.[10] Recently, Du and co-workers as well as Yu and co-workers independently reported two types of acyclic chiral diene ligands that provide good to excellent enantioselectivity in asymmetric reactions.[11] Furthermore, olefins were also successfully utilized in the design of hybrid bidentate ligands, such as olefin-phosphine[12] and olefin-nitrogen ligands.[13] Nevertheless, we are unaware of hybrid chiral sulfoxide-olefin ligands.[14] Sulfoxides have a long history in asymmetric catalysis,[15] and these compounds were recently highlighted by Dorta and co-workers.[16] We have focused on the design of chiral ligands based on the *tert*-butylsulfinyl moiety[17] since these ligands provide encouraging results in transition-metal-catalyzed asymmetric reactions.[18] Inspired by the previous reports in this area, we elected to prepare a hydrid ligand from the combination of an olefin with a *tert*-butylsulfinyl moiety. Interestingly, the relative size of the substituents attached to the C=C bonds in a diene ligand is considered to be the key factor for the origin of stereocontrol. We believe that the position of the substituents on the olefin may also be very important for asymmetric induction, particularly for asymmetric hybrid ligands, which could potentially control the absolute configuration of the product. Herein, we describe the development of a novel class of hybrid sulfoxide-olefin ligands and evaluate the efficiency and selectivity of this type of ligand in the rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids to electron-deficient olefins; a reaction which was originally reported by Miyaura, Hayashi, and co-workers and is considered as one of the most important methods for asymmetric C–C bond formation.[19]

The synthesis of the sulfoxide-olefin ligands **L1**–**L5** is outlined in Scheme 1. (*R*)-*tert*-Butyl *tert*-butanethiosulfinate was added to the 1-bromo-2-vinylbenzenes **1**–**3** after a standard halogen-metal exchange at low temperature, to furnish the styrene-type ligand **L1** and the branched olefin ligands **L2** and **L3** in 38-77% yield. Similarly, the synthesis of linear olefin ligands **L4**[20] and **L5** was also accomplished from (*R*)-2-(*tert*-butylsulfinyl)benzaldehyde (**4**) in a single step, in 71% and 79% yield, respectively, by using a Wittig and a Horner–Wadsworth–Emmons reaction.




***Scheme 1.*** Synthesis of chiral sulfoxide-olefin ligands **L1**–**L5**. Bn = benzyl, THF = tetrahydrofuran.

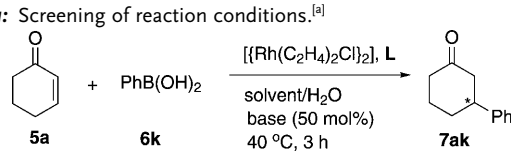
To test these ligands, we initiated our studies with the rhodium-catalyzed conjugate addition of phenylboronic acid (**5a**) to cyclohexenone (**6k**). As illustrated in Table 1, ligand screening revealed that all the sulfoxide-olefins tested were effective ligands for this transformation in the context of the reaction efficiency (74–93% yield). The most striking feature of this study was the effect that the substituents on the olefin had on enantioselectivity. For example, the monosubstituted olefin **L1**, provided only modest enantioselectivity (Table 1, entry 1), whereas the disubstituted ligands **L2**–**L5** provided good to excellent selectivities. Interestingly, the opposite

[*] G. Chen, J. Gui, Dr. L. Li, Prof. Dr. J. Liao
Natural Products Research Center, Chengdu Institute of Biology
Chinese Academy of Sciences, Chengdu 610041 (China)
and
Chengdu Institute of Organic Chemistry
Chinese Academy of Sciences, Chengdu, 610041 (China)
and
Graduate School of Chinese Academy of Sciences
Beijing 100049 (China)
E-mail: jliao@cib.ac.cn

[**] We thank the NSFC(No. 21072186 and 20872139), CAS, Chengdu Institute of Biology of CAS (Y0B1051100), the Major State Basic Research Development Program (973 program, 2010CB833300), and Jiangxi Key Laboratory of Functional Organic Molecules.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201102586.

***Table 1:*** Screening of reaction conditions.[a]



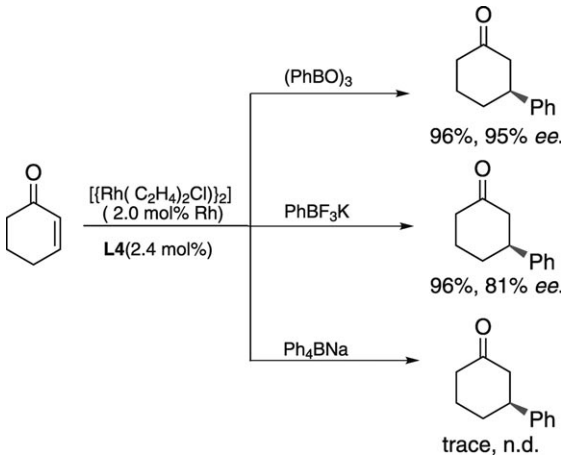

**5a** **6k** **7ak**

| Entry | L | Solvent | Base | Yield [%][b] | *ee* [%][c] |
|---|---|---|---|---|---|
| 1 | **L1** | dioxane | KOH | 91 | 20 (*R*) |
| 2 | **L2** | dioxane | KOH | 93 | 94 (*R*) |
| 3 | **L3** | dioxane | KOH | 74 | 94 (*R*) |
| 4 | **L4** | dioxane | KOH | 91 | 88 (*S*) |
| 5 | **L5** | dioxane | KOH | 78 | 96 (*S*) |
| 6 | **L4** | THF | KOH | 95 | 84 (*S*) |
| 7 | **L4** | toluene | KOH | 88 | 46 (*S*) |
| 8 | **L4** | $CH_2Cl_2$ | KOH | 95 | 48 (*S*) |
| 9 | **L4** | MeOH | KOH | 98 | 95 (*S*) |
| 10 | **L4** | EtOH | KOH | 96 | 91 (*S*) |
| 11[d] | **L4** | MeOH | $Et_3N$ | 98 | 88 (*S*) |
| 12 | **L4** | MeOH | KF | 93 | 98 (*S*) |

[a] Reaction conditions: 0.3 mmol of **5a**, 0.6 mmol of **6k**, 1.2 mg of $[\{Rh(C_2H_4)_2Cl\}_2]$ (0.003 mmol, 2.0 mol% of Rh), 0.0072 mmol of **L**, 0.6 mL of solvent, 50 mol% of base, 40°C, 3 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. The absolute configuration was determined by comparison with literature data. [d] $Et_3N$ was used neat.

absolute configuration of **7ak** was obtained using the branched **L2** and **L3** olefin ligands (*R*, up to 94% *ee*) and linear **L4** and **L5** olefin ligands (*S*, up to 96% *ee*; Table 1, entries 2–5). In additional studies, **L4** was utilized to screen the reaction conditions, and these studies demonstrated that the nature of the solvent and base dramatically affect the selectivity; excellent enantioselectivity (98% *ee*) was achieved using methanol and potassium fluoride (Table 1, entry 12).[21]

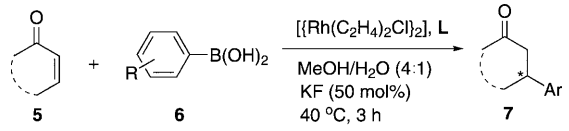
We next examined other common arylboronic reagents in this system, and these studies demonstrated that phenyboroxine and potassium trifluoroborate provided excellent yields and good enantioselectivities. However, when sodium tetraphenylborate was used, only a trace amount of the product was obtained (Scheme 2).



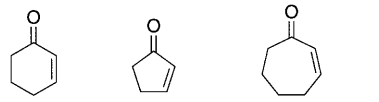

***Scheme 2.*** Evaluation of other arylboronic reagents.

With the optimized reaction conditions established, a wide range of arylboronic acids, cyclic/linear enones, and cyclic esters were examined to investigate the scope of the switch in stereochemistry (Table 2). Herein, **L2** (Me) and **L4** (Me), and **L3** (Ph) and **L5** (Ph) are defined as reversal ligand pairs (RLPs), according to the substituents on the ligands

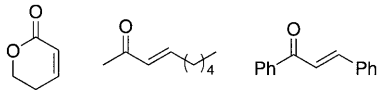
***Table 2:*** Substrate scope of the rhodium-catalyzed 1,4-addition of arylboronic acid to electron-deficient olefins.[a]




**5** **6** **7**



**5a** **5b** **5c**




**5d** **5e** **5f**

| Entry | 5 | R | L | Yield [%][b] | *ee* [%][c] |
|---|---|---|---|---|---|
| 1 | **5a** | H (**6k**) | **L2** | 98 | >99 (*R*) |
| | | | **L4** | 93 | 98 (*S*) |
| 2 | | | **L3** | 98 | 95 (*R*) |
| | | | **L5** | 97 | 97 (*S*) |
| 3 | **5a** | *p*-$CH_3$ (**6l**) | **L2** | 98 | >99 (*R*) |
| | | | **L4** | 90 | 97 (*S*) |
| 4 | **5a** | *m*-$CH_3$ (**6m**) | **L2** | 98 | 99 (*R*) |
| | | | **L4** | 96 | 96 (*S*) |
| 5 | **5a** | *o*-$CH_3$ (**6n**) | **L2** | 98 | 94 (*R*) |
| | | | **L4** | 97 | 97 (*S*) |
| 6 | **5a** | *p*-$CH_3O$ (**6o**) | **L2** | 80 | >99 (*R*) |
| | | | **L4** | 82 | 98 (*S*) |
| 7 | **5a** | *m*-$CH_3O$ (**6p**) | **L2** | 93 | 99 (*R*) |
| | | | **L4** | 85 | 97 (*S*) |
| 8 | **5a** | *o*-$CH_3O$ (**6q**) | **L2** | 98 | 98 (*R*) |
| | | | **L4** | 98 | 66 (*S*) |
| 9 | | | **L3** | 82 | 90 (*R*) |
| | | | **L5** | 82 | 81 (*S*) |
| 10 | **5a** | *p*-*t*Bu (**6r**) | **L2** | 97 | 99 (*R*) |
| | | | **L4** | 98 | 97 (*S*) |
| 11 | **5a** | 3,5-$CH_3$ (**6s**) | **L2** | 81 | >99 (*R*) |
| | | | **L4** | 97 | 97 (*S*) |
| 12 | **5a** | *p*-F (**6t**) | **L2** | 98 | >99 (*R*) |
| | | | **L4** | 97 | 96 (*S*) |
| 13 | **5a** | *p*-$CF_3$ (**6u**) | **L2** | 98 | >99 (*R*) |
| | | | **L4** | 98 | 85 (*S*) |
| 14 | **5a** | *p*-Cl (**6v**) | **L2** | 97 | >99 (*R*) |
| | | | **L4** | 94 | 95 (*S*) |
| 15 | **5a** | *m*-Cl (**6w**) | **L2** | 98 | 90 (*R*) |
| | | | **L4** | 97 | 96 (*S*) |
| 16 | **5a** | 1-naph (**6x**) | **L2** | 83 | 94 (*R*) |
| | | | **L4** | 97 | 92 (*S*) |
| 17 | **5a** | 2-naph (**6y**) | **L2** | 98 | 99 (*R*) |
| | | | **L4** | 91 | 64 (*S*) |
| 18 | | | **L3** | 97 | 97 (*R*) |
| | | | **L5** | 99 | 87 (*S*) |
| 19 | **5a** | (*E*)-PhCH=CH (**6z**) | **L2** | 57 | 93 (*R*) |
| | | | **L4** | 30 | 42 (*S*) |

*Table 2:* (Continued)

| Entry | 5 | R | L | Yield [%][b] | *ee* [%][c] |
|---|---|---|---|---|---|
| 20 | **5b** | H (**6k**) | **L2** | 98 | 96 (*R*) |
| | | | **L4** | 98 | 26 (*S*) |
| 21 | | | **L3** | 90 | 77 (*R*) |
| | | | **L5** | 97 | 93 (*S*) |
| 22 | **5c** | H (**6k**) | **L2** | 97 | 98 (*R*) |
| 23 | **5d** | H (**6k**) | **L2** | 71 | 87 (*R*) |
| | | | **L4** | 85 | 78 (*S*) |
| 24 | **5e** | H (**6k**) | **L2** | 96 | 44 (S) |
| 25 | **5f** | *p*-$CH_3$ (**6l**) | **L2** | 95 | 65 (+) |

[a] Reaction conditions: 0.3 mmol of 5, 0.6 mmol of **6**, 1.2 mg [{Rh-$(C_2H_4)_2Cl\}_2$] (0.003 mmol, 2.0 mol% of Rh), 0.0072 mmol of **L**, 0.6 mL of MeOH, 50 mol% of KF, 40°C, 3 h. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. The absolute configuration was determined by comparison with literature data. naph = naphthyl.

(R = Me or Ph; Scheme 1), and each pair could induce the formation of both absolute configurations in the products. To our delight, complete reversal of enantioselectivity was observed for most of the substrates, with up to >99% *ee* (*R*) and 98% *ee* (*S*) when the **L2** and **L4** RLP was used (Table 2, entries 1 and 6). In some specific cases the **L2** and **L4** RLP did not work well (Table 2, entry 20; **L2** 96% *ee*, *R* isomer; **L4** 26% *ee*, *S* isomer), but complementary results could be achieved with the **L3** and **L5** RLP (Table 2, entry 21; **L3** 77% *ee*, *R* isomer; **L5** 93% *ee*, *S* isomer). For the cycloheptenone **5c**, **L2** furnished excellent enantioselectivity, but the related ligands **L4** and **L5** failed to provide inversion, and only a trace amount of the product was formed (Table 2, entry 22). Furthermore, modest yields and enantioselectivities were obtained when the cyclic ester **5d** was used as the substrate (Table 2, entry 23). Similar to **5c**, acyclic enone **5e** and chalcone **5f** could smoothly react in the presence of **L2** to give the corresponding adducts with excellent yields and modest enantioselectivities (Table 2, entries 24 and 25).[22]

To gain insight into this interesting phenomenon, some structural information on the catalyst was obtained. Treatment of **L3** with [{$Rh(C_2H_4)_2Cl\}_2$] in dichloromethane at 25°C for 30 minutes gave the corresponding sulfoxide-olefin/rhodium complex, [(**L3**RhCl)$_2$]. Suitable crystals of this complex for X-ray crystal-structure analysis were obtained by recrystallization from dichloromethane/*n*-hexane (Figure 1).[23] In this structure, the sulfur atom and the carbon-carbon double bond of **L3** coordinate to the rhodium atom, and notably the rhodium atom coordinates with the α-*Si* face of the α-phenylvinyl group. The phenyl and *tert*-butyl groups provide an excellent stereoenvironment that presumably results in the high enantioselectivity in the 1,4-addition. On the basis of the switch in configuration, which is attributed to the olefin substitution, the stereochemical pathway with Rh/**L3** and Rh/**L5** can be rationalized as outlined in Figure 2. Thus, the initial coordination of the rhodium species results in a *trans* relationship between the phenyl group and the olefin moiety, and the substrate 2-cyclohexen-1-one binds to the rhodium center at the position *cis* to the olefin ligand, because of steric repulsion between the alkyl or phenyl group of the ligand with

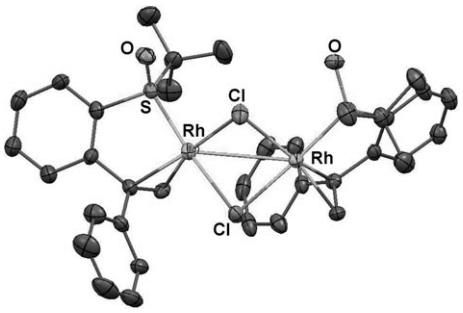



***Figure 1.*** ORTEP illustration of [(**L3**RhCl)$_2$] with thermal ellipsoids drawn at the 50% probability level.

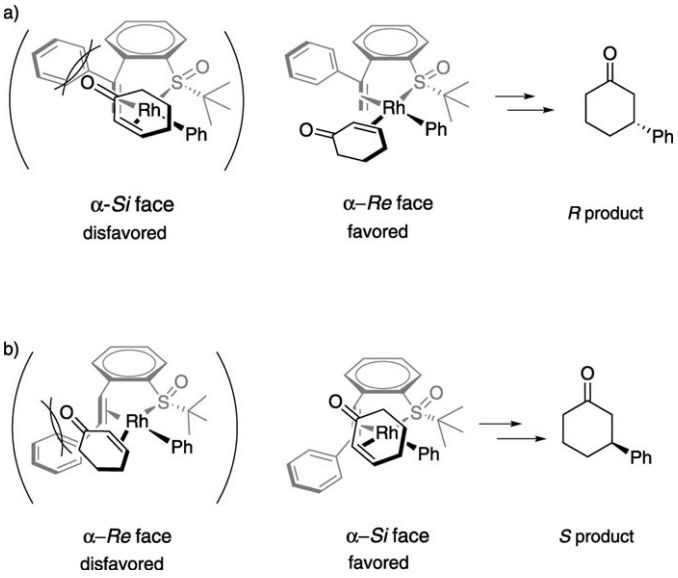



***Figure 2.*** Proposed stereochemical pathway showing the facial coordination of the rhodium atom with the enone substrate: a) Using **L3**, b) using **L5**.

the carbonyl moiety, thus leading to the 1,4-adduct with the desired configuration.

In conclusion, we have successfully developed a new family of chiral sulfoxide-olefin ligands from a single chiral source through a concise synthetic route, and evaluated these ligands in the rhodium-catalyzed 1,4-addition of arylboronic acids to electron-deficient olefins. These ligands demonstrated that the olefin geometry can completely reverse the absolute configuration of the product, thus simplifying the process of accessing either enantiomer.

## *Experimental Section*

In an argon atmosphere, at room temperature, [{$Rh(C_2H_4)_2Cl\}_2$] (1.2 mg, 0.003 mmol) and the sulfoxide-olefin ligand (1.6 mg, 0.0072 mmol) were added to a 10 mL Schlenk tube followed by $CH_2Cl_2$ (0.50 mL). The reaction mixture was stirred at room temperature for 30 min, then the $CH_2Cl_2$ was removed and the arylboronic acid (0.60 mmol) was added. After purging the mixture with argon, enone (0.30 mmol), methanol (0.60 mL) and KF (0.15 mL, 1.0 M in $H_2O$, 0.15 mmol) were added sequentially. The reaction mixture was stirred at 40°C for 3 h, then the solvent was removed in vacuo and the

residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate 20:1 as eluent to afford the adduct.

Received: April 14, 2011
Published online: June 17, 2011

**Keywords:** chirality · conjugate addition · rhodium · S ligands · stereoselectivity reversal

[1] a) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**; b) S. P. Jacqueline, *Chiral Auxiliaries and ligands in Asymmetric Synthesis*, Wiley, New York, **1995**; c) E. N. Jacobsen, A. Pfaltz, H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Vols. 1–3, Springer, Berlin, **1999**; d) I. Ojima, *Catalytic Asymmetric Synthesis*, 2nd ed., Wiley, New York, **2000**; e) K. Mikami, M. Lautens, *New Frontiers in Asymmetric Catalysis*, Wiley, New York, **2007**.

[2] For reviews, see: a) Y. M. Kim, *Acc. Chem. Res.* **2001**, *34*, 955; b) M. P. Sibi, M. Liu, *Curr. Org. Chem.* **2001**, *5*, 719; c) G. Zanoni, F. Castronovo, M. Franzini, G. Vidari, E. Giannini, *Chem. Soc. Rev.* **2003**, *32*, 115; d) T. Tanaka, M. Hayashi, *Synthesis* **2008**, 3361; e) M. Bartók, *Chem. Rev.* **2010**, *110*, 1663.

[3] For selected examples, see: a) S. Kobayashi, H. Ishitani, *J. Am. Chem. Soc.* **1994**, *116*, 4083; b) J. P. G. Seerden, M. M. M. Kuypers, H. W. Scheeren, *Tetrahedron: Asymmetry* **1995**, *6*, 1441; c) K. V. Gothelf, R. G. Hazell, K. A. Jørgensen, *J. Org. Chem.* **1998**, *63*, 5483; d) D. A. Evans, M. C. Kozlowski, J. A. Murry, C. S. Burgey, K. R. Campos, B. T. Connell, R. J. Staples, *J. Am. Chem. Soc.* **1999**, *121*, 669; e) M. Kawamura, S. Kobayashi, *Tetrahedron Lett.* **1999**, *40*, 3213; f) R. Kuwano, M. Sawamura, Y. Ito, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2571; g) M. C. Perry, X. H. Cui, M. T. Powell, D. R. Hou, J. H. Reibenspies, K. Burgess, *J. Am. Chem. Soc.* **2003**, *125*, 113; h) C. P. Casey, S. C. Martins, M. A. Fagan, *J. Am. Chem. Soc.* **2004**, *126*, 5585; i) J. Zhou, M. C. Ye, Z. Z. Huang, Y. Tang, *J. Org. Chem.* **2004**, *69*, 1309; j) N. Shibata, M. Okamoto, Y. Yamamoto, S. Sakaguchi, *J. Org. Chem.* **2010**, *75*, 5707.

[4] For selected examples, see: a) F. Bertozzi, M. Pineschi, F. Macchia, L. A. Arnold, A. J. Minnaard, B. L. Feringa, *Org. Lett.* **2002**, *4*, 2703; b) D. M. Du, S. F. Lu, T. Fang, J. X. Xu, *J. Org. Chem.* **2005**, *70*, 3712; c) A. Frölander, C. Moberg, *Org. Lett.* **2007**, *9*, 1371; d) K. Y. Spangler, C. Wolf, *Org. Lett.* **2009**, *11*, 4724; e) H. Y. Kim, H. J. Shih, W. E. Knabe, K. Oh, *Angew. Chem.* **2009**, *121*, 7556; *Angew. Chem. Int. Ed.* **2009**, *48*, 7420; f) Y. L. Liu, D. J. Shang, X. Zhou, Y. Zhu, L. L. Lin, X. H. Liu, X. M. Feng, *Org. Lett.* **2010**, *12*, 180.

[5] For selected examples, see: a) S. Kobayashi, M. Horibe, *J. Am. Chem. Soc.* **1994**, *116*, 9805; b) H. Ait-Haddou, J. C. Daran, D. Cramailere, G. G. A. Balavoine, *Organometallics* **1999**, *18*, 4718; c) S. Kobayashi, K. Kusakabe, S. Komiyama, H. Ishitani, *J. Org. Chem.* **1999**, *64*, 4220; d) D. S. Clyne, Y. C. Mermet-Bouvier, N. Nomura, T. V. RajanBabu, *J. Org. Chem.* **1999**, *64*, 7601; e) J. C. Anderson, R. J. Cubbon, J. D. Harling, *Tetrahedron: Asymmetry* **1999**, *10*, 2829; f) W. Zeng, G. Y. Chen, Y. G. Zhou, Y. X. Li, *J. Am. Chem. Soc.* **2007**, *129*, 750; g) W. Q. Wu, Q. Peng, D. X. Dong, X. L. Hou, Y. D. Wu, *J. Am. Chem. Soc.* **2008**, *130*, 9717; h) X. X. Yan, Q. Peng, Q. Li, K. Zhang, J. Yao, X. L. Hou, Y. D. Wu, *J. Am. Chem. Soc.* **2008**, *130*, 14362; i) S. Mouri, Z. H. Chen, H. Mitsunuma, M. Furutachi, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2010**, *132*, 1255; j) R. Robles-Machín, M. Gonzalez-Esguevillas, J. Adrio, J. C. Carretero, *J. Org. Chem.* **2010**, *75*, 233.

[6] For selected examples, see: a) B. M. Hackman, P. J. Lombardi, J. L. Leighton, *Org. Lett.* **2004**, *6*, 4375; b) N. N. Reed, T. J. Dickerson, G. E. Boldt, K. D. Janda, *J. Org. Chem.* **2005**, *70*, 1728; c) A. B. Zaitsev, H. Adolfsson, *Org. Lett.* **2006**, *8*, 5129; d) J. D. Huber, J. L. Leighton, *J. Am. Chem. Soc.* **2007**, *129*, 14552; e) M. I. Burguete, M. Collado, J. Escorihuela, S. V. Luis, *Angew. Chem.* **2007**, *119*, 9160; *Angew. Chem. Int. Ed.* **2007**, *46*, 9002.

[7] For selected references on stereocontrolled inversions in organocatalytic reactions, see: a) S. E. Denmark, X. P. Su, Y. Nishigaichi, *J. Am. Chem. Soc.* **1998**, *120*, 12990; b) S. E. Denmark, R. A. Stavenger, *J. Am. Chem. Soc.* **2000**, *122*, 8837; c) G. S. Cortez, S. H. Oh, D. Romo, *Synthesis* **2001**, 1731; d) X. J. Li, G. W. Zhang, L. Wang, M. Q. Hua, J. A. Ma, *Synlett* **2008**, 1255; e) K. Nakayama, K. Maruoka, *J. Am. Chem. Soc.* **2008**, *130*, 17666; f) N. Li, X. H. Chen, J. Song, S. W. Luo, W. Fan, L. Z. Gong, *J. Am. Chem. Soc.* **2009**, *131*, 15301; g) D. G. Blackmond, A. Moran, M. Hughes, A. Armstrong, *J. Am. Chem. Soc.* **2010**, *132*, 7598; h) M. Messerer, H. Wennemers, *Synlett* **2011**, 499; i) J. B. Wang, B. L. Feringa, *Science* **2011**, *331*, 1429.

[8] For reviews on chiral olefin ligands, see: a) F. Glorius, *Angew. Chem.* **2004**, *116*, 3444; *Angew. Chem. Int. Ed.* **2004**, *43*, 3364; b) J. B. Johnson, T. Rovis, *Angew. Chem.* **2008**, *120*, 852; *Angew. Chem. Int. Ed.* **2008**, *47*, 840; c) C. Defieber, H. Grutzmacher, E. M. Carreira, *Angew. Chem.* **2008**, *120*, 4558; *Angew. Chem. Int. Ed.* **2008**, *47*, 4482; d) R. Shintani, T. Hayashi, *Aldrichimica Acta* **2009**, *42*, 31.

[9] a) T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 11508; b) C. Fischer, C. Defieber, T. Suzuki, E. M. Carreira, *J. Am. Chem. Soc.* **2004**, *126*, 1628.

[10] For selected examples, see: a) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2004**, *126*, 13584; b) C. Defieber, J. F. Paquin, S. Serna, E. M. Carreira, *Org. Lett.* **2004**, *6*, 3873; c) F. Läng, F. Breher, D. Stein, H. Grutzmacher, *Organometallics* **2005**, *24*, 2997; d) S. Helbig, S. Sauer, N. Cramer, S. Laschat, A. Baro, W. Frey, *Adv. Synth. Catal.* **2007**, *349*, 2331; e) Z. Q. Wang, C. G. Feng, M. H. Xu, G. Q. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 5336; f) K. Okamoto, T. Hayashi, V. H. Rawal, *Org. Lett.* **2008**, *10*, 4387; g) T. Gendrineau, O. Chuzel, H. Eijsberg, J. P. Genet, S. Darses, *Angew. Chem.* **2008**, *120*, 7783; *Angew. Chem. Int. Ed.* **2008**, *47*, 7669; h) T. Nishimura, H. Kumamoto, M. Nagaosa, T. Hayashi, *Chem. Commun.* **2009**, 5713; i) M. K. Brown, E. J. Corey, *Org. Lett.* **2010**, *12*, 172; j) G. Pattison, G. Piraux, H. W. Lam, *J. Am. Chem. Soc.* **2010**, *132*, 14373.

[11] For selected examples, see: a) X. C. Hu, M. Zhuang, Z. P. Cao, H. F. Du, *Org. Lett.* **2009**, *11*, 4744; b) Y. Z. Wang, X. C. Hu, H. F. Du, *Org. Lett.* **2010**, *12*, 5482; c) Q. Li, Z. Dong, Z. X. Yu, *Org. Lett.* **2011**, *13*, 1122.

[12] For selected example of phosphine-alkene hybrid ligands, see: a) P. Maire, S. Deblon, F. Breher, J. Geier, C. Bohler, H. Ruegger, H. Schonberg, H. Grutzmacher, *Chem. Eur. J.* **2004**, *10*, 4198; b) R. Shintani, W. L. Duan, T. Nagano, A. Okada, T. Hayashi, *Angew. Chem.* **2005**, *117*, 4687; *Angew. Chem. Int. Ed.* **2005**, *44*, 4611; c) P. Kasák, V. B. Arion, M. Widhalm, *Tetrahedron: Asymmetry* **2006**, *17*, 3084; d) G. Mora, S. V. Zutphen, C. Thoumazet, X. F. L. Goff, L. Ricard, H. Grutzmacher, P. L. Floch, *Organometallics* **2006**, *25*, 5528; e) W. L. Duan, H. Iwamura, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 2130; f) C. Defieber, M. A. Ariger, P. Moriel, E. M. Carreira, *Angew. Chem.* **2007**, *119*, 3200; *Angew. Chem. Int. Ed.* **2007**, *46*, 3139; g) R. T. Stemmler, C. Bolm, *Synlett* **2007**, 1365; h) P. Štěpnička, M. Lamac, I. Cisarova, *J. Organomet. Chem.* **2008**, *693*, 446; i) R. Mariz, A. Briceno, R. Dorta, R. Dorta, *Organometallics* **2008**, *27*, 6605; j) E. Drinkel, A. Briceno, R. Dorta, R. Dorta, *Organometallics* **2010**, *29*, 2503; k) T. Minuth, M. M. K. Boysen, *Org. Lett.* **2009**, *11*, 4212; l) Z. Q. Liu, H. F. Du, *Org. Lett.* **2010**, *12*, 3054.

[13] For selected examples, see: a) P. Maire, F. Breher, H. Schonberg, H. Grutzmacher, *Organometallics* **2005**, *24*, 3207; b) B. T. Hahn, F. Tewes, R. Frohlich, F. Glorius, *Angew. Chem.* **2010**, *122*, 1161; *Angew. Chem. Int. Ed.* **2010**, *49*, 1143.

[14] For racemic sulfoxide-olefin ligands, see: A. Szadkowska, A. Makal, K. Woźniak, R. Kadyrov, K. Grela, *Organometallics* **2009**, *28*, 2693.

[15] For selected examples, see: a) B. R. James, R. S. McMillan, *Can. J. Chem.* **1977**, *55*, 3927; b) N. Khiar, I. Fernandez, F. Alcudia, *Tetrahedron Lett.* **1993**, *34*, 123; c) R. Tokunoh, M. Sodeoka, K. Aoe, M. Shibasaki, *Tetrahedron Lett.* **1995**, *36*, 8035; d) B. Delouvrié, L. Fensterbank, F. Najera, M. Malacria, *Eur. J. Org. Chem.* **2002**, 3507; e) K. Hiroi, T. Sone, *Curr. Org. Synth.* **2008**, *5*, 305; f) M. C. Carreño, G. Hernandez-Torres, M. Ribagorda, A. Urbano, *Chem. Commun.* **2009**, 6129.

[16] a) R. Mariz, X. J. Luan, M. Gatti, A. Linden, R. Dorta, *J. Am. Chem. Soc.* **2008**, *130*, 2172; b) J. J. Bürgi, R. Mariz, M. Gatti, E. Drinkel, X. J. Luan, S. Blumentritt, A. Linden, R. Dorta, *Angew. Chem.* **2009**, *121*, 2806; *Angew. Chem. Int. Ed.* **2009**, *48*, 2768; c) R. Mariz, A. Poater, M. Gatti, E. Drinkel, J. J. Burgi, X. J. Luan, S. Blumentritt, A. Linden, L. Cavallo, R. Dorta, *Chem. Eur. J.* **2010**, *16*, 14335; d) A. Poater, F. Ragone, R. Mariz, R. Dorta, L. Cavallo, *Chem. Eur. J.* **2010**, *16*, 14348.

[17] For reviews on the use of the *tert*-butylsulfinyl moiety as a chiral auxiliary, see: a) J. A. Ellman, T. D. Owens, T. P. Tang, *Acc. Chem. Res.* **2002**, *35*, 984; b) G. Q. Lin, M. H. Xu, Y. W. Zhong, X. W. Sun, *Acc. Chem. Res.* **2008**, *41*, 831; c) F. Ferreira, C. Botuha, F. Chemla, A. Perez-Luna, *Chem. Soc. Rev.* **2009**, *38*, 1162; d) M. A. T. Robak, M. A. Herbage, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 3600.

[18] For our studies on the use of the *tert*-butylsulfinyl moiety in ligands, see: a) J. M. Chen, D. Li, H. F. Ma, L. F. Cun, J. Zhu, J. G. Deng, J. Liao, *Tetrahedron Lett.* **2008**, *49*, 6921; b) P. Wang, J. M. Chen, L. F. Cun, J. G. Deng, J. Zhu, J. Liao, *Org. Biomol. Chem.* **2009**, *7*, 3741; c) J. M. Chen, F. Lang, D. Li, L. F. Cun, J. Zhu, J. G. Deng, J. Liao, *Tetrahedron: Asymmetry* **2009**, *20*, 1953; d) F. Lang, D. Li, J. M. Chen, J. Chen, L. C. Li, L. F. Cun, J. Zhu, J. G. Deng, J. Liao, *Adv. Synth. Catal.* **2010**, *352*, 843; e) J. Chen, J. M. Chen, F. Lang, X. Y. Zhang, L. F. Cun, J. Zhu, J. G. Deng, J. Liao, *J. Am. Chem. Soc.* **2010**, *132*, 4552; f) F. Z. Han, J. Chen, X. Y. Zhang, J. B. Liu, L. F. Cun, J. Zhu, J. G. Deng, J. Liao, *Tetrahedron Lett.* **2011**, *52*, 830; g) X. Y. Zhang, J. Chen, F. Z. Han, L. F. Cun, J. Liao, *Eur. J. Org. Chem.* **2011**, 1443; h) F. Lang, G. H. Chen, L. C. Li, J. W. Xing, F. Z. Han, L. F. Cun, J. Liao, *Chem. Eur. J.* **2011**, *17*, 5242.

[19] For selected examples, see: a) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura, *J. Am. Chem. Soc.* **1998**, *120*, 5579; b) J. G. Boiteau, F. Imbos, A. J. Minnaard, B. L. Feringa, *Org. Lett.* **2003**, *5*, 681; for reviews, see: c) "Organoboranes for Synthesis": N. Miyaura, *ACS Symp. Ser.* **2001**, *783*, 94–107; d) T. Hayashi, K. Yamasaki, *Chem. Rev.* **2003**, *103*, 2829; e) T. Hayashi, *Pure Appl. Chem.* **2004**, *76*, 465; f) T. Hayashi, *Synlett* **2001**, 879; g) K. Yoshida, T. Hayashi in *Modern Rhodium-Catalyzed Organic Reactions*, (Ed.: P. A. Evans), Wiley-VCH, Weinheim, **2005**, pp. 55–77; h) H. J. Edwards, J. D. Hargrave, S. D. Penrose, C. G. Frost, *Chem. Soc. Rev.* **2010**, *39*, 2093.

[20] The *Z* isomer (< 5%) of **L4** was observed by $^1$H NMR analysis of the crude product.

[21] For the detailed screening of the reaction conditions, see the Supporting Information.

[22] The absolute configuration of adduct **7ek** was *S*, which is probably influenced by the geometry of the C=C bond of the substrate. We attempted to prove this and (*Z*)-**5f** was used, however, only 50% conversion was achieved (64% *ee* for (+)-**7fl**) and 50% of (*E*)-**5f** was obtained. For selected examples of the reversal of stereoselectivity determined by the configuration of olefins, see: a) T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **1999**, *121*, 11591; b) R. Shintani, Y. Tsutsumi, M. Nagaosa, T. Nishimura, T. Hayashi, *J. Am. Chem. Soc.* **2009**, *131*, 13588; c) R. Shintani, T. Hayashi, *Org. Lett.* **2010**, *12*, 350.

[23] CCDC 824876 ([(**L3**RhCl)$_2$]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.