JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Catalytic Asymmetric Hydrogenation of N-Boc-Imidazoles and Oxazoles

Ryoichi Kuwano,* Nao Kameyama, and Ryuhei Ikeda

Department of Chemistry, Graduate School of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Supporting Information

ABSTRACT: Substituted imidazoles and oxazoles were respectively hydrogenated into the corresponding chiral imidazolines and oxazolines (up to 99% ee). The highly enantioselective hydrogenation was achieved by using the chiral ruthenium catalyst, which is generated from Ru(η^3-methallyl)$_2$(cod) and a trans-chelating chiral bisphosphine ligand, PhTRAP. This is the first successful catalytic asymmetric reduction of 5-membered aromatic rings containing two or more heteroatoms.

Highly enantioselective hydrogenation of heteroaromatic compounds would be a powerful approach to constructing optically active heterocycles.[1] Indoles,[2,3] pyrroles,[4] quinolines,[5] quinoxalines,[6] pyridines,[7] and furans[8] have been successfully reduced with high enantioselectivity through asymmetric catalysis. However, asymmetric hydrogenation of other heteroaromatics remains one of unsettled subjects in organic chemistry. To the best of our knowledge, catalytic asymmetric hydrogenations of 5-membered aromatic rings containing two or more heteroatoms are still unknown in literature. In this communication, we disclose the first successful catalytic asymmetric hydrogenations of imidazoles and oxazoles. The asymmetric transformations will be a new straightforward access to optically active imidazolines[9] and oxazolines,[10] which are often present in various natural products and biologically acitive molecules. Furthermore, the imidazolines and oxazolines can be converted through hydrogenolysis or acid hydrolysis to 1,2-diamines[11] and β-amino alcohols,[12] respectively.

In our previous report, 2,3,5-trisubstituted *N*-Boc-pyrroles were hydrogenated with high enantioselectivity by PhTRAP[13]—ruthenium catalyst (Chart 1).[4] The structure of 2,4,5-trisubstituted *N*-Boc-imidazole is closely related to that of the pyrrole substrates. The structural similarity inspired us to apply the ruthenium catalyst to the enantioselective hydrogenation of *N*-Boc-imidazoles. At the initial attempt, we conducted the hydrogenation of *N*-Boc-4,5-dimethyl-2-phenylimidazole (**1**) under the conditions identical to those used for the asymmetric hydrogenation of pyrroles,[4] but no reaction was observed. We were pleased that Ru(η^3-methallyl)$_2$(cod)—(*R*,*R*)-(*S*,*S*)-PhTRAP catalyzed the selective hydrogenation of *N*-Boc-4-methyl-2-phenylimidazole (**2a**), which has no substituent at its 5-position. The imidazole substrate **2a** was quantitatively converted to *N*-Boc-imidazoline (*S*)-**3a** with 97% ee (Table 1, entry 1). No overhydrogenation product such as imidazolidine was detected in the reaction mixture. The enantiomeric product was obtained from the reaction using (*S*,*S*)-(*R*,*R*)-PhTRAP (entry 2). The PhTRAP—ruthenium catalyst exhibited high enantioselectivities in the hydrogenations of *N*-Boc-imidazoles bearing a secondary as well as primary alkyl group at the 4-position (entries 3—5). Electron-withdrawing trifluoromethyl group of **3e** did not decrease the reaction rate nor the stereoselectivity (entry 6). Unfortunately, 2,4-diarylimidazoles were converted to the desired imidazolines in less than 15% yield. The replacement of phenyl by ethyl group at the 2-position resulted in deterioration in the reaction rate as well as the stereoselectivity (entry 7).

As with the reaction of imidazoles, the asymmetric hydrogenation of 2,4-disubstituted oxazoles **4** proceeded with high enantioselectivity in the presence of PhTRAP—ruthenium catalyst. 2,4-Diphenyloxazole (**4a**) was transformed into (*R*)-2,4-diphenyloxazoline **5a** with 98% ee when (*S*,*S*)-(*R*,*R*)-PhTRAP was used as the chiral ligand (Table 2, entry 1). Variations in reaction conditions barely disturbed the stereoselectivity, while solvent affected the catalytic activity of the ruthenium complex.[14] Isobutyl alcohol was the solvent of choice. Although the hydrogenation of imidazoles **2** required a base for efficient production of **3**, the product **5a** could be obtained from the oxazole **4a** in high yield without the additional base (entry 2). The substrate **4b**, which has an electron-donating group on its 4-aryl ring, was also hydrogenated to **5b** in high yield under base-free conditions (entry 3). However, the electron-deficient substrates **4c** and **4d** required *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG) additive for their rapid conversion (entries 4—6). The PhTRAP—ruthenium catalyst is effective for the asymmetric hydrogenation of 4-alkylated as well as 4-arylated substrates. Use of TMG allowed the reaction of **4e** to produce the desired oxazoline in high yield (entries 7 and 8). Cyclohexyl-substituted oxazole **4f** was also reduced to oxazoline **5f** with 88% ee (entry 9). However, the tertiary alkyl group in **4g** caused a steric hindrance to the catalytic hydrogenation (entry 10). The chiral catalyst could produce oxazoline-4-carboxylate **5h** from **4h**, but the ee value was moderate (entry 11). Use of base or protic solvent induced the racemization of the chiral product **5h**. The asymmetric hydrogenation of 2-methyloxazole **4i** proceeded at a rate comparable to that of 2-phenyloxazole **4a** (entry 12). However, the enantiomeric excess of **5i** was less than that of **5a**.

PhTRAP—ruthenium complex is useful for the catalytic asymmetric hydrogenation of 2,5-disubstituted oxazoles **6**. The chiral catalyst transformed 2,5-diphenyloxazole **6a** into *R*-enriched oxazoline **7a** with 95% ee under the conditions optimized for the hydrogenation of **4a** regardless of the addition of TMG

Received: February 18, 2011
Published: April 27, 2011

dx.doi.org/10.1021/ja201543h | *J. Am. Chem. Soc.* 2011, 133, 7312–7315

Chart 1. Structure of PhTRAP

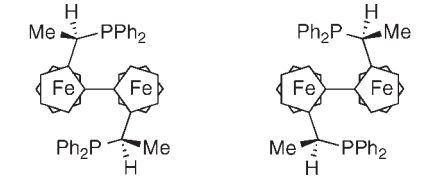
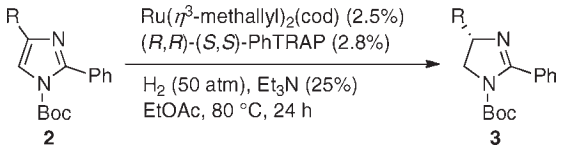


Table 1. Catalytic Asymmetric Hydrogenation of *N*-Boc-4-alkyl-2-phenylimidazoles 2[a]



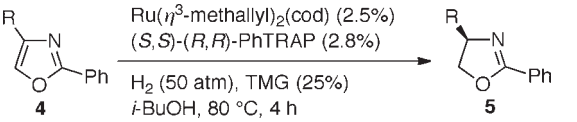
entry	R (**2**)	product	yield[b] (%)	ee[c] (%)
1[d]	Me (**2a**)	**3a**	97	97 (*S*)
2[d,e]	Me (**2a**)	**3a**	85	97 (*R*)
3	Et (**2b**)	**3b**	99	96
4	*n*-C_6H_{13} (**2c**)	**3c**	90	97
5	*c*-C_6H_{11} (**2d**)	**3d**	97	97
6	CF_3 (**2e**)	**3e**	89	99
7	Me (**2f**)[f]	**3f**[f]	35[g]	86

[a] Reactions were conducted on a 0.2 mmol scale in 1.0 mL of EtOAc. The ratio of **2**:[Ru]:PhTRAP:Et_3N was 40:1:1.1:10. The ^1H NMR analyses of the crude products indicated full conversion of **2** unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC analysis. [d] Reactions were conducted at 60 °C. [e] (*S,S*)-(*R,R*)-PhTRAP was used. [f] Compounds have an ethyl group in place of the phenyl one at the 2-position. [g] Conversion of **2f** was 45%.

(Table 3, entries 1 and 2). The enantiomeric excess of **7a** was slightly enhanced to 97% ee by using toluene in place of isobutyl alcohol, but the aprotic solvent caused a decrease in the catalytic activity (entry 3). The desired product was obtained in high yield by exposing the reaction mixture to hydrogen for 24 h (entry 4). Electron-rich substrate **6b** was converted to oxazoline **7b** with 95% ee in high yield, but the reaction failed to reach full conversion of the oxazoline at 4 h (entry 5). In this case, prolonged reaction caused generation of an unidentified side product. The electron-withdrawing substituents of **6c** and **6d** did not cause significant deterioration of enantioselectivity (entries 6 and 7). 5-Methyloxazole **6e** was transformed into (*R*)-**7e** with 86% ee by the chiral ruthenium catalyst (entry 8). The catalyst loading can be reduced to 0.5 mol % without serious loss of the ee value (entry 9). The asymmetric catalysis would be affected by the size of the alkyl substituent on the 5-carbon. The reaction of cyclohexyloxazole **6f** produced **7f** in high yield, but the enantiomeric excess of **7f** was considerably lower than that of **7e** (entry 10). *tert*-Butyl group in **6g** obstructed the catalytic hydrogenation (entry 11). In contrast to the hydrogenation of **4**, the 2-methyl group of **6h** caused low yield of **7h**, while the enantioselectivity was not affected by the replacement of the 2-substituent (entry 12).

The stereochemical features of the above asymmetric hydrogenations are summarized as follows. First, the oxazoles **4** and **6** are hydrogenated with high enantioselectivity despite no Boc

Table 2. Catalytic Asymmetric Hydrogenation of 4-Substituted 2-Phenyloxazoles 4[a]



entry	R (**4**)	product	convn.[b] (%)	yield[c] (%)	ee[d] (%)
1	Ph (**4a**)	**5a**	100	>99	98 (*R*)
2[e]	Ph (**4a**)	**5a**	100	86	98 (*R*)
3[e]	*p*-$CH_3OC_6H_4$ (**4b**)	**5b**	100	93	97 (*R*)
4	*p*-FC_6H_4 (**4c**)	**5c**	100	92	97
5[e]	*p*-FC_6H_4 (**4c**)	**5c**	23	13	97
6	*p*-$CF_3C_6H_4$ (**4d**)	**5d**	100	90	93
7	Me (**4e**)	**5e**	100	88	91 (*R*)
8[e]	Me (**4e**)	**5e**	23	—[f]	84 (*R*)
9	*c*-C_6H_{11} (**4f**)	**5f**	100	91	88
10	*t*-Bu (**4g**)	**5g**	5	—	—
11[e,g]	CO_2Me (**4h**)	**5h**	100	89	50 (*S*)
12[h]	Ph (**4i**)[i]	**5i**[i]	100	78	90 (*S*)

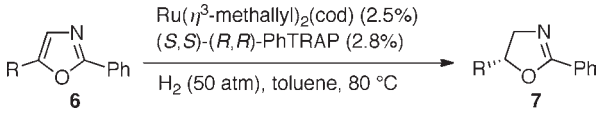
[a] Reactions were conducted on a 0.2 mmol scale in 1.0 mL of *i*-BuOH. The ratio of **4**:[Ru]:PhTRAP:TMG was 40:1:1.1:10. [b] Determined by ^1H NMR analysis. In all cases, no side product was detected. [c] Isolated yield. [d] Determined by HPLC or GC analyses. The absolute configuration of major enantiomer is indicated in parentheses. [e] Reactions were conducted in the absence of TMG. [f] **5e** could not separated from **4e**. [g] Reaction was conducted in toluene for 24 h. [h] (*R,R*)-(*S,S*)-PhTRAP was used. [i] Compounds have a methyl group in place of the phenyl one at the 2-position.

group on their oxygen atom. Although amide carbonyl is commonly known to function as a directing group to attain high stereoselectivity in asymmetric hydrogenation of enamides,[15] the Boc group hardly participates in the chiral induction during the PhTRAP−ruthenium-catalyzed hydrogenation of **2**. Second, the (*S,S*)-(*R,R*)-PhTRAP−ruthenium complex induces the attack of hydrogen to **2** and **4** from below and to **6** from above, when these substrates are arranged as shown in Figure 1, where their Ph−C═N moieties overlap one another. The outcomes suggest that the enantiofacial discrimination arises independently of the electronic properties of two heteroatoms on each carbon atom of the reduced C4−C5 double bond. The chiral catalyst recognizes the relative positions of the substituent R and C4−C5 bond. The PhTRAP ligand on the ruthenium may create steric hindrances to block the substituents on the 5-position of **2** in Figure 1a. The steric hindrance might inhibit 4,5-disubstituted imidazole **1** from undergoing the hydrogenation. In a similar manner to **2**, substrates **4** can approach to the ruthenium catalyst. In contrast, the attack of the metal center to **6** from below is obstructed by the steric repulsion between the 5-substituent and the chiral ligand. To avoid the steric repulsion, the chiral catalyst will attack on the heteroaromatic ring from above, leading to preferential formation of the *R*-product in the asymmetric hydrogenation of **6**.

The optically active imidazoline **3a**, which was obtained from the catalytic asymmetric hydrogenation of **2a**, was transformed to acyclic chiral 1,2-diamine thorough palladium-catalyzed hydrogenolysis in high yield (Scheme 1). The hydrogenation of C−N double bond in **2a** occurred along with successive hydrogenolysis of benzylidene moiety, affording the ring-opening product **8**.

dx.doi.org/10.1021/ja201543h |*J. Am. Chem. Soc.* 2011, 133, 7312–7315

Table 3. Catalytic Asymmetric Hydrogenation of 5-Substituted 2-Phenyloxazoles 6[a]



entry	R (6)	time (h)	product	convn.[b] (%)	yield[c] (%)	ee[d] (%)
1[e,f]	Ph (**6a**)	2	**7a**	100	>99	95 (*R*)
2[f]	Ph (**6a**)	2	**7a**	100	97	95 (*R*)
3	Ph (**6a**)	2	**7a**	50	40	97 (*R*)
4	Ph (**6a**)	24	**7a**	100	97	97 (*R*)
5	*p*-MeOC$_6$H$_4$ (**6b**)	4	**7b**	92	88	95
6	*p*-FC$_6$H$_4$ (**6c**)	24	**7c**	100	>99	93 (*R*)
7	*p*-CF$_3$C$_6$H$_4$ (**6d**)	24	**7d**	100	>99	85 (*R*)
8	Me (**6e**)	4	**7e**	100	85	86 (*R*)
9[g]	Me (**6e**)	4	**7e**	100	97	84 (*R*)
10	*c*-C$_6$H$_{11}$ (**6f**)	4	**7f**	100	99	72 (*R*)
11	*t*-Bu (**6g**)	4	**7g**	5	—	—
12[h]	Ph (**6h**)[i]	4	**7h**[i]	38	36	96

[a] Reactions were conducted on a 0.2 mmol scale in 1.0 mL of toluene. The ratio of **6**:[Ru]:PhTRAP:TMG was 40:1:1.1:10. [b] Determined by ^{1}H NMR analysis. In all cases, no side product was detected. [c] Isolated yield. [d] Determined by HPLC analysis. The absolute configuration of major enantiomer is indicated in parentheses. [e] Reaction was conducted in the presence of TMG. [f] Reactions were conducted in *i*-BuOH. [g] Reaction was conducted with 0.5 mol % catalyst loading. [h] (*R*,*R*)-(*S*,*S*)-PhTRAP was used. [i] Compounds have a methyl group in place of the phenyl one at the 2-position.

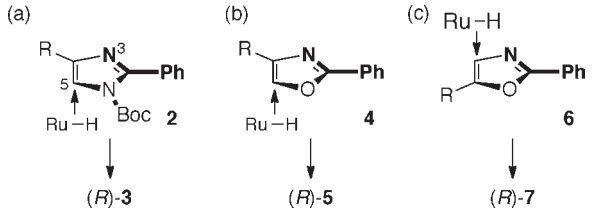
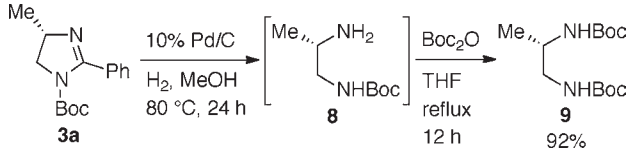


Figure 1. Stereochemistry of the asymmetric hydrogenations using (*S*,*S*)-(*R*,*R*)-PhTRAP. (a) For the reaction of 4-substituted imidazoles **2**. (b) For the reaction of 4-substituted oxazoles **4**. (c) For the reaction of 5-substituted oxazoles **6**.

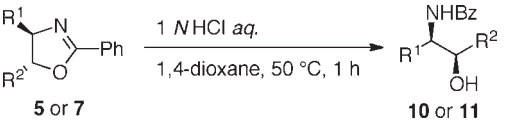
Scheme 1. Transformation of Imidazoline 3a to 1,2-Diamine



To isolate the ring-opening product in high yield, the amino group of **8** was treated with Boc_2O to give Boc-protected diamine **9** in 92% yield.

Various β-amino alcohols, which are frequently used as chiral auxiliaries[16] in organic synthesis and medicinal drugs such as β blockers, were prepared through the catalytic asymmetric hydrogenation of oxazoles. The hydrolysis of the hydrogenation products **5** with hydrochloric acid[17] afforded *N*-benzoyl β-amino alcohols **10**, which possess a chiral center at the β-position (Table 4, entries 1−4). Similarly, β-amido alcohols **11** having a chiral α-carbon were obtained from **7** (entries 5−10). The enantiopurities of the oxazolines were scarcely lost during the course of the hydrolytic transformation in most cases. However, complete racemization took place in the hydrolysis of oxazoline **7b**. Its electron-donating *p*-methoxy group may induce the dissociation of the C5−O bond to form the benzylic cation. Therefore, the acid hydrolysis of **7b** might proceed through S_N1 pathway.

Table 4. Transformation of Oxazolines 5 and 7 to β-Amido Alcohols[a]



entry	substrate	R^1	R^2	product	yield[b] (%)
1	**5a**	Ph	H	**10a**	>99
2	**5b**	4-MeOC$_6$H$_4$	H	**10b**	90
3	**5e**	Me	H	**10e**	28
4	**5f**	Cy	H	**10f**	67
5	**7a**	H	Ph	**11a**	98
6	**7b**	H	4-MeOC$_6$H$_4$	**11b**	95[c]
7	**7c**	H	4-FC$_6$H$_4$	**11c**	86
8	**7d**	H	4-CF$_3$C$_6$H$_4$	**11d**	81
9	**7e**	H	Me	**11e**	72
10	**7f**	H	Cy	**11f**	96

[a] Reactions were conducted at 50 °C for 1 h. See the detailed conditions and the enantiomeric excesses of the products in SI. [b] Isolated yield. [c] **11b** was obtained as racemic form.

We successfully developed the highly enantioselective hydrogenations of imidazoles and oxazoles by using the chiral catalyst, Ru(η^3-methallyl)$_2$(cod)−PhTRAP complex. In the asymmetric hydrogenation, the 5-membered heteroaromatic rings react with one molar equivalent of hydrogen molecule, giving the corresponding imidazolines or oxazolines with high enantiomeric excess. The optically active hydrogenation products can be converted to chiral 1,2-diamines or β-amido alcohols through the hydrogenolysis or acidic hydrolysis without loss of their enantiopurities. Further studies on the asymmetric hydrogenation of other heteroaromatics are in progress.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
rkuwano@chem.kyushu-univ.jp

■ ACKNOWLEDGMENT

This work was supported by Takeda Science Foundation, Nagase Science and Technology Foundation, and a Grant-in-Aid for the Global COE Program, "Science for Future Molecular Systems" from MEXT.

REFERENCES

(1) Reviews: (a) Glorius, F. *Org. Biomol. Chem.* **2005**, *3*, 4171–4175. (b) Zhou, Y.-G. *Acc. Chem. Res.* **2007**, *40*, 1357–1366. (c) Kuwano, R. *Heterocycles* **2008**, *76*, 909–922.

(2) (a) Kuwano, R.; Sato, K.; Kurokawa, T.; Karube, D.; Ito, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7614–7615. (b) Kuwano, R.; Kaneda, K.; Ito, T.; Sato, K.; Kurokawa, T.; Ito, Y. *Org. Lett.* **2004**, *6*, 2213–2215. (c) Kuwano, R.; Kashiwabara, M.; Sato, K.; Ito, T.; Kaneda, K.; Ito, Y. *Tetrahedron: Asymmetry* **2006**, *17*, 521–535. (d) Kuwano, R.; Kashiwabara, M. *Org. Lett.* **2006**, *8*, 2653–2655.

(3) (a) Baeza, A.; Pfaltz, A. *Chem.—Eur. J.* **2010**, *16*, 2036–2039. (b) Wang, D.-S.; Chen, Q.-A.; Li, W.; Yu, C.-B.; Zhou, Y.-G.; Zhang, X. *J. Am. Chem. Soc.* **2010**, *132*, 8909–8911.

(4) Kuwano, R.; Kashiwabara, M.; Ohsumi, M.; Kusano, H. *J. Am. Chem. Soc.* **2008**, *130*, 808–809.

(5) Representative examples, see: (a) Wang, W.-B.; Lu, S.-M.; Yang, P.-Y.; Han, X.-W.; Zhou, Y.-G. *J. Am. Chem. Soc.* **2003**, *125*, 10536–10537. (b) Lu, S.-M.; Wang, Y.-Q.; Han, X.-W.; Zhou, Y.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2260–2263.

(6) (a) Bianchini, C.; Barbaro, P.; Scapacci, G.; Farnetti, E.; Graziani, M. *Organometallics* **1998**, *17*, 3308–3310. (b) Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 9135–9138. (c) Mršić, N.; Jerphagnon, T.; Minnaard, A. J.; Feringa, B. L.; de Vries, J. G. *Adv. Synth. Catal.* **2009**, *351*, 2549–2552. (d) Cartigny, D.; Nagano, T.; Ayad, T.; Genêt, J.-P.; Ohshima, T.; Mashima, K.; Ratovelomanana-Vidal, V. *Adv. Synth. Catal.* **2010**, *352*, 1886–1891.

(7) (a) Legault, C. Y.; Charette, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 8966–8967. (b) Rueping, M.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 4562–4565. (c) Wang, X.-B.; Zeng, W.; Zhou, Y.-G. *Tetrahedron Lett.* **2008**, *49*, 4922–4924. (d) Tang, W.; Sun, Y.; Xu, L.; Wang, T.; Fan, Q.; Lam, K.-H.; Chan, A. S. C. *Org. Biomol. Chem.* **2010**, *8*, 3464–3471.

(8) Kaiser, S.; Smidt, S. P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 5194–5197.

(9) Examples, see: (a) Bao, B.; Sun, Q.; Yao, X.; Hong, J.; Lee, C.-O.; Cho, H. Y.; Jung, J. H. *J. Nat. Prod.* **2007**, *70*, 2–8. (b) Capon, R. J.; Rooney, F.; Murray, L. M.; Collins, E.; Sim, A. T. R.; Rostas, J. A. P.; Butler, M. S.; Carroll, A. R. *J. Nat. Prod.* **1998**, *61*, 660–662.

(10) Examples, see: (a) Morris, L. A.; Jaspars, M.; Kettenes-van den Bosch, J. J.; Versluis, K.; Heck, A. J. R.; Kelly, S. M.; Price, N. C. *Tetrahedron* **2001**, *57*, 3185–3197. (b) Tsuda, M.; Yamakawa, M.; Oka, S.; Tanaka, Y.; Hoshino, Y.; Mikami, Y.; Sato, A.; Fujiwara, H.; Ohizumi, Y.; Kobayashi, J. *J. Nat. Prod.* **2005**, *68*, 462–464. (c) Motohashi, K.; Takagi, M.; Shin-ya, K. *J. Nat. Prod.* **2010**, *73*, 226–228.

(11) Recent examples, see: (a) Braddock, D. C.; Redmond, J. M.; Hermitage, S. A.; White, A. J. P. *Adv. Synth. Catal.* **2006**, *348*, 911–916. (b) Park, Y.; Kang, S.; Lee, Y. J.; Kim, T.-S.; Jeong, B.-S.; Park, H.-g.; Jew, S.-s. *Org. Lett.* **2009**, *11*, 3738–3741.

(12) Examples, see: (a) Nishimura, M.; Minakata, S.; Takahashi, T.; Oderaotoshi, Y.; Komatsu, M. *J. Org. Chem.* **2002**, *67*, 2101–2110. (b) Cheung, F. K.; Hayes, A. M.; Hannedouche, J.; Yim, A. S. Y.; Wills, M. *J. Org. Chem.* **2005**, *70*, 3118–3197.

(13) (a) Sawamura, M.; Hamashima, H.; Sugawara, M.; Kuwano, R.; Ito, Y. *Organometallics* **1995**, *14*, 4549–4558.(b) Kuwano, R.; Sawamura, M. In *Regio- and Stereo-controlled Oxidations and Reductions*; Roberts, S. M.; Whittall, J., Eds.; Catalysts for Fine Chemical Synthesis, Vol. 5; John Wiley & Sons: West Sussex, 2007; pp 73−86.

(14) See Supporting Information.

(15) (a) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952–5954. (b) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746–1754. (c) Brown, J. M.; Chaloner, P. A. *J. Am. Chem. Soc.* **1980**, *102*, 3040–3048.

(16) A review, see: Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835–876.

(17) Liu, C.; Tamm, M.; Nötzel, M. W.; Rauch, K.; de Meijere, A.; Schilling, J. K.; Lakdawala, A.; Snyder, J. P.; Bane, S. L.; Shanker, N.; Ravindra, R.; Kingston, D. G. I. *Eur. J. Org. Chem.* **2005**, 3962–3972.