Asymmetric Catalysis

DOI: 10.1002/ange.201304591

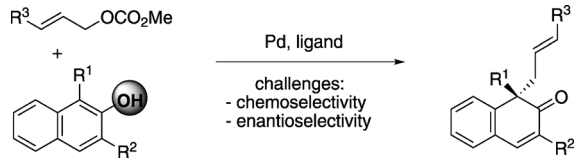
Palladium-Catalyzed Intermolecular Asymmetric Allylic Dearomatization Reaction of Naphthol Derivatives**

*Chun-Xiang Zhuo and Shu-Li You**

Dearomatization reactions are widely recognized as powerful methods for the synthesis of highly functionalized three-dimensional structures from simple planar aromatic compounds.[1] Recently, great efforts have been devoted to the development of catalytic asymmetric dearomatization processes.[2]

Phenols are a readily available chemical feedstock and widely used as starting materials in organic synthesis.[3] Dearomatization reactions of phenols are of wide interest because of their potential for the preparation of cyclohexadienones, which often serve as structural cores prevalent in various biologically active natural products and pharmaceuticals, or as valuable synthetic intermediates. However, because of the competitive O alkylation and the Friedel–Crafts alkylation reaction pathways, it is very challenging to develop efficient methods with high levels of chemoselectivity and stereoselectivity. Compared with recent achievements in the area of asymmetric dearomatization of phenols, which were focused on oxidative protocols,[4] limited examples are reported involving the catalytic asymmetric dearomatization of phenol derivatives under non-oxidative conditions.[5–8]

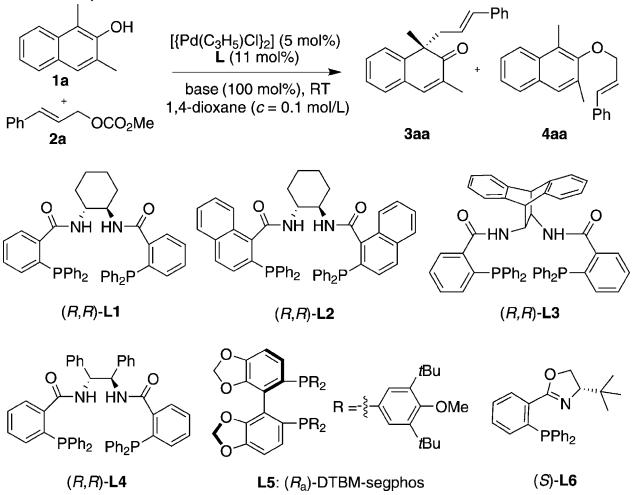
In transition-metal-catalyzed allylic substitution reactions, phenols are usually used as oxygen nucleophiles[9] and a limited number of examples of C allylation are reported.[10] Very recently, Hamada and co-workers and our group reported the dearomatization of phenols by palladium- and iridium-catalyzed, respectively, intramolecular asymmetric allylic substitution reactions.[6,7] The intramolecular design involving separating the OH group and the allylic electrophile avoided the competition of the O alkylation, and the spirocyclohexadienones were obtained in excellent yields and enantioselectivity. However, for the intermolecular catalytically asymmetric allylic dearomatization of phenol derivatives, no example has been reported thus far.[11] Herein we describe the first palladium-catalyzed intermolecular asymmetric allylic dearomatization of naphthol derivatives with excellent control of chemoselectivity and enantioselectivity (Scheme 1).



Scheme 1. Palladium-catalyzed intermolecular asymmetric allylic dearomatization reaction of naphthol derivatives.

The study was launched by utilizing 1,3-dimethyl-2-naphthol (**1a**) and cinnamyl carbonate (**2a**) as the model substrates to optimize the reaction conditions. Firstly, different chiral ligands were tested. As shown in Table 1, with 5 mol% [{Pd(C_3H_5)Cl}$_2$] and 11 mol% of the Trost ligand **L1**, the asymmetric allylic dearomatization reaction proceeded smoothly with good conversion, chemoselectivity, and enan-

Table 1: Optimization of the reaction conditions.[a]



Entry	L	Base	*t* [h]	Conv. [%][b]	**3aa**/**4aa**[b]	*ee* [%][c]
1	**L1**	Li_2CO_3	28	>95	77:23	83
2	**L2**	Li_2CO_3	28	>95	81:19	28
3	**L3**	Li_2CO_3	28	>95	69:31	−31
4	**L4**	Li_2CO_3	28	23	77:23	n.d.
5	**L5**	Li_2CO_3	28	>95	>95:5	0
6	**L6**	Li_2CO_3	28	18	38:62	n.d.
7	**L1**	DBU	23	>95	>95:5	83
8[d]	**L1**	DBU	4	>95 (84)	>95:5	90

[a] Reaction conditions: 5 mol% [{Pd(C_3H_5)Cl}$_2$], 11 mol% of ligand, 0.2 mmol of **1a** and **2a**, 0.2 mmol of base in 2.0 mL 1,4-dioxane at RT. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Determined by HPLC analysis. [d] Used 2 equiv of **1a** and DBU, $c = 0.025$ mol L^{-1} and yield of isolated **3aa** is given within the parenthesis. DBU = 1,8-diaza- bicyclo[5.4.0] undec-7-ene.

[*] C.-X. Zhuo, Prof. Dr. S.-L. You
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Lu, Shanghai 200032 (China)
E-mail: slyou@sioc.ac.cn
Homepage: http://shuliyou.sioc.ac.cn/

[**] We thank the NSFC (20923005, 21025209, 21121062), the National Basic Research Program of China (973 Program 2010CB833300), and the Chinese Academy of Sciences for generous financial support.

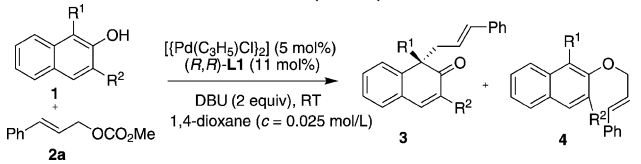
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304591.

tioselectivity (entry 1, Table 1). The ligands **L2** and **L3** could be also used to promote the reaction with good conversions and chemoselectivity, but with low enantioselectivity (entries 2 and 3). The reactions with either the ligand **L4** or **L6** proceeded with low conversions (entries 4 and 6). With the ligand **L5**, the reaction occurred smoothly but with no enantioselective control (entry 5). Taking **L1** as the optimal ligand, different bases such as Na_2CO_3, K_2CO_3, Cs_2CO_3, KOAc, K_3PO_4, and DBU were tested, and DBU was found to be a good choice concerning both chemoselectivity and enantioselectivity (entry 7). Next, examination of the solvents, substrate concentration, and ratio of the substrates led to the optimal reaction conditions: 5 mol% of [{Pd(C_3H_5)Cl}$_2$], 11 mol% **L1**, 2.0 equivalents of **1a** and DBU, 1.0 equivalent of **2a** at room temperature in 1,4-dioxane (0.025 mol L^{-1}), thus providing **3aa** in 84% yield and 90% *ee* (entry 8; for comprehensive data on optimization of the reaction conditions, see the Supporting Information).

Under the optimized reaction conditions, various β-naphthol derivatives (**1b–i**) were reacted with cinnamyl carbonate (**2a**) to examine the generality of the process (Table 2). When the substituent in the 1-position of 2-naphthol was changed to bulkier groups such as ethyl (**1b**) and allyl (**1c**), the reactions occurred smoothly in excellent chemoselectivity (>95:5) and enantioselectivity (90–94% *ee*), but with slightly decreased yields (66–71%; entries 2 and 3, Table 2). 1-Methyl-2-naphthol derivatives bearing 3-Et (**1d**), 3-allyl (**1e**), and 3-Cl (**1f**) groups (entries 4–6) generally led to the corresponding dearomatized products in excellent chemoselectivity (>95:5) with moderate to good yields (67–78%) and good enantioselectivity (81–84% *ee*). Interestingly, when 1-methyl-3-bromo-2-naphthol (**1g**) was utilized, the reaction occurred with excellent chemoselectivity (>95:5), enantioselectivity (96% *ee*), and yield (91%) to give the corresponding α-bromo-substituted enone **3ga**, which could be further functionalized by cross-coupling reactions[12] (entry 7). It is noteworthy that a 1-methyl-2-naphthol derivative bearing a 3-phenylethynyl group could also undergo the dearomatization reaction with a high level of chemo- and enantiocontrol (entry 8). The asymmetric allylic dearomatization reaction also occured with 1-methyl-2-naphthol (**1i**) with good enantioselectivity, but low yield and moderate chemoselectivity (entry 9). Gratifyingly, the yield could be significantly improved by running the reaction in cyclohexane and benzene using K_2CO_3 as a base (entry 10).

In addition, various substituted allylic carbonates (**2**) were tested in this reaction. The results are summarized in Table 3.

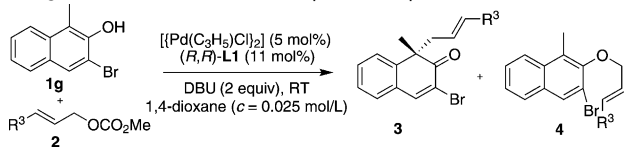
Table 2: The reaction substrate scope: Naphthols.[a]



Entry	**1**, R^1, R^2	*t* [h]	**3**/**4**[b]	Yield [%][c]	*ee* [%][d]
1	**1a**, Me, Me	4	>95:5	**3aa**, 84	90
2	**1b**, Et, Me	4	>95:5	**3ba**, 71	90
3[e]	**1c**, allyl, Me	24	>95:5	**3ca**, 67	94
4	**1d**, Me, Et	5	>95:5	**3da**, 67	84
5[f]	**1e**, Me, allyl	11	>95:5	**3ea**, 78	83
6	**1f**, Me, Cl	4	>95:5	**3fa**, 66	81
7	**1g**, Me, Br	5	>95:5	**3ga**, 91	96
8	**1h**, Me,	4	>95:5	**3ha**, 74	97
9[g]	**1i**, Me, H	19	64:36	**3ia**, 17	81
10[h]	**1i**, Me, H	24	70:30	**3ia**, 65	85

[a] Reaction conditions: 5 mol% [{Pd(C_3H_5)Cl}$_2$], 11 mol% (*R*,*R*)-**L1**, 0.4 mmol **1**, 0.2 mmol **2a**, 0.4 mmol DBU in 1,4-dioxane (8.0 mL) at RT. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Yield of isolated product. [d] Determined by HPLC analysis. [e] Reaction was conducted with 1.1 equiv of **1c** and DBU. [f] Reaction was conducted with 1.5 equiv of **1e** and 0.9 equiv of DBU. [g] Reaction was conducted with 1 equiv of **1i** and DBU. [h] Reaction conditions: 5 mol% of [{Pd(C_3H_5)Cl}$_2$], 11 mol% (*R*,*R*)-**L1**, 0.4 mmol **1i**, 0.2 mmol **2a**, 0.4 mmol of K_2CO_3 in degassed cyclohexane (4.0 mL) and benzene (1.0 mL) at 0°C.

Table 3: The reaction substrate scope: Electrophiles.[a]

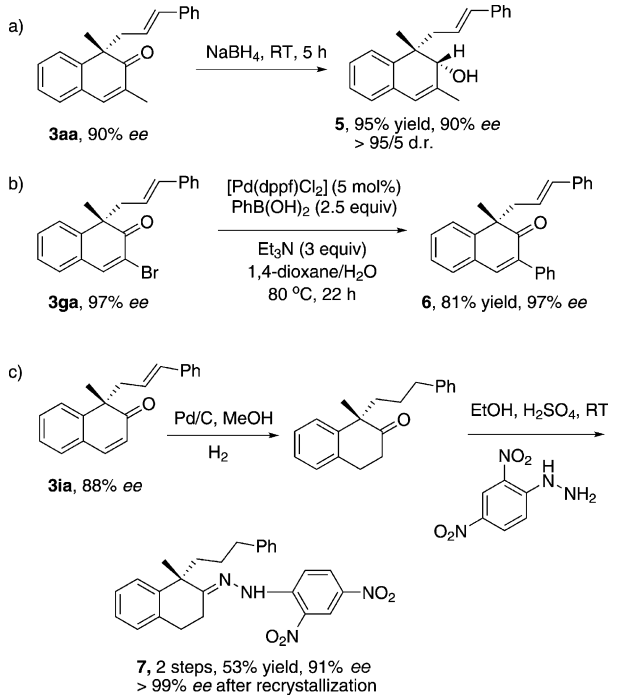


Entry	**2**, R^3	*t* [h]	**3**/**4**[b]	Yield [%][c]	*ee* [%][d]
1	**2a**, Ph	5	>95:5	**3ga**, 91	96
2[e]	**2a**, Ph	4.5	>95:5	**3ga**, 86	97
3	**2b**, 4-MeC_6H_4	5	>95:5	**3gb**, 72	96
4	**2c**, 4-MeOC_6H_4	5	>95:5	**3gc**, 71	96
5[f]	**2d**, 4-FC_6H_4	15	>95:5	**3gd**, 76	97
6	**2e**, 4-Cl-C_6H_4	5	>95:5	**3ge**, 68	93
7	**2f**, 4-BrC_6H_4	5	>95:5	**3gf**, 82	92
8	**2g**, 2-thienyl	5	>95:5	**3gg**, 82	97
9[g]	**2h**, Me	4.5	>95:5	**3gh**, 50	96

[a] Reaction conditions: 5 mol% [{Pd(C_3H_5)Cl}$_2$], 11 mol% **L1**, 0.4 mmol **1g**, 0.2 mmol **2**, 0.4 mmol DBU in1,4- dioxane (8.0 mL) at RT. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Yield of isolated product. [d] Determined by HPLC analysis. [e] Reaction was conducted with 1 equiv of **1g** and DBU on a 0.8 mmol scale. [f] Reaction was conducted with 1 equiv of **1g** and DBU. [g] The *ee* value was determined by Agilent SFC analysis.

Reactions of allylic carbonates containing *para*-methylphenyl and *para*-methoxyphenyl groups (**2b–c**) occurred smoothly to give the desired products (**3gb–gc**) in good yields with excellent enantioselectivity (entries 3 and 4, Table 3). Aromatic allylic carbonates containing an electron-withdrawing group (**2d–f**) were tolerated to afford the dearomatized products **3gd–gf** in good yields with excellent enantioselectivity (entries 5–7). The reaction of 2-thienyl allylic carbonate (**2g**) with **1g** afforded the product **3gg** in 82% yield with 97% *ee* (entry 8). When crotyl carbonate (**2h**) was used, the reaction also proceeded smoothly in 50% yield and 96% *ee* (entry 9). Notably, the reaction of **2a** with 1 equivalent of **1g** on a 0.8 mmol scale gave an 86% yield with 97% *ee* (entry 2).

To demonstrate the synthetic utility of the newly developed methodology, several transformations of the 2-naphthalenone products were carried out. The ketone group could be reduced with $NaBH_4$ to afford the allylic alcohol **5** in



Scheme 2. Transformation of the products. dppf = 1,1′-bis(diphenylphosphino)ferrocene.

excellent yield and diastereoselectivity (Scheme 2a). The bromo-containing product **3ga** underwent a Suzuki coupling with $PhB(OH)_2$ in the presence of 5 mol% of $[Pd(dppf)Cl_2]$, thus providing 1-methyl-3-phenyl-2-naphthalenone (**6**) in 81% yield and 97% *ee* (Scheme 2b). To determine the absolute configuration of the dearomatized products, 1-methyl-2-naphthalenone (**3ia**) was converted into the corresponding hydrazone **7** through a two-step transformation (Scheme 2c).[13] A single crystal of the enantiopure hydrazone **7** suitable for X-ray diffraction was obtained. An X-ray crystallographic analysis disclosed the absolute configuration of **7** as *S*.[14]

In summary, we have achieved the first palladium-catalyzed intermolecular asymmetric allylic dearomatization reaction of β-naphthol derivatives. The β-naphthalenones bearing an all-carbon quaternary chiral center could be easily accessed from simple aromatic naphthol derivatives in good to excellent yields, and excellent chemo- and enantioselectivity. Further studies of the reaction scope and applications of the highly enantioenriched β-naphthalenone derivatives are currently under investigation in our laboratory.

Experimental Section

General procedure for the palladium-catalyzed intermolecular asymmetric allylic dearomatization reaction: Two flame-dried Schlenk tubes were cooled to room temperature and filled with argon. $[\{Pd(C_3H_5)Cl\}_2]$ (0.010 mmol, 5 mol%) and (*R*, *R*)-**L1** (0.022 mmol, 11 mol%) were added to one flask. The flask was evacuated and refilled with argon, and then freshly distilled 1,4-dioxane (4 mL) was added and the resultant solution was stirred at 25 °C for 30 min. The β-naphthol derivative **1** (0.40 mmol, 200 mol%) was added to another dry Schlenk tube. The flask was evacuated and refilled with argon and placed under argon atmosphere. The catalyst solution, DBU (0.40 mmol, 200 mol%), allyl carbonate **2** (0.20 mmol, 100 mol%), and freshly distilled 1,4-dioxane (4 mL) were then added to this flask. The reaction mixture was stirred at 25 °C. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through celite and washed with ethyl acetate, then the solvents were removed under reduced pressure. The ratio of **3**/**4** was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. The residue was then purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the desired product **3**.

Received: May 28, 2013
Published online: August 9, 2013

Keywords: allylic dearomatization · arenes · asymmetric catalysis · palladium · synthetic methods

[1] For recent reviews, see: a) A. R. Pape, K. P. Kaliappan, E. P. Kündig, *Chem. Rev.* **2000**, *100*, 2917; b) A. Pelter, R. S. Ward, *Tetrahedron* **2001**, *57*, 273; c) E. P. Kündig, A. R. Pape, *Top. Organomet. Chem.* **2004**, *7*, 71; d) W. D. Harman, *Top. Organomet. Chem.* **2004**, *7*, 95; e) S. Quideau, L. Pouységu, D. Deffieux, *Curr. Org. Chem.* **2004**, *8*, 113; f) F. López Ortiz, M. J. Iglesias, I. Fernández, C. M. Andújar Sánchez, G. R. Gómez, *Chem. Rev.* **2007**, *107*, 1580; g) S. P. Roche, J. A. Porco Jr., *Angew. Chem.* **2011**, *123*, 4154; *Angew. Chem. Int. Ed.* **2011**, *50*, 4068.

[2] For a recent review, see: a) C.-X. Zhuo, W. Zhang, S.-L. You, *Angew. Chem.* **2012**, *124*, 12834; *Angew. Chem. Int. Ed.* **2012**, *51*, 12662. Selected examples: b) M. Takamura, K. Funabashi, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2000**, *122*, 6327; c) K. Funabashi, H. Ratni, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2001**, *123*, 10784; d) E. Ichikawa, M. Suzuki, K. Yabu, M. Albert, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 11808; e) J. F. Austin, S.-G. Kim, C. J. Sinz, W.-J. Xiao, D. W. C. MacMillan, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5482; f) C. Y. Legault, A. B. Charette, *J. Am. Chem. Soc.* **2005**, *127*, 8966; g) B. M. Trost, J. Quancard, *J. Am. Chem. Soc.* **2006**, *128*, 6314; h) R. P. Reddy, H. M. L. Davies, *J. Am. Chem. Soc.* **2007**, *129*, 10312; i) J. García-Fortanet, F. Kessler, S. L. Buchwald, *J. Am. Chem. Soc.* **2009**, *131*, 6676; j) S. B. Jones, B. Simmons, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 13606; k) J. Qi, A. B. Beeler, Q. Zhang, J. A. Porco Jr., *J. Am. Chem. Soc.* **2010**, *132*, 13642; l) Q.-F. Wu, H. He, W.-B. Liu, S.-L. You, *J. Am. Chem. Soc.* **2010**, *132*, 11418; m) L. M. Repka, J. Ni, S. E. Reisman, *J. Am. Chem. Soc.* **2010**, *132*, 14418; n) O. Lozano, G. Blessley, T. M. del Campo, A. L. Thompson, G. T. Giuffredi, M. Bettati, M. Walker, R. Borman, V. Gouverneur, *Angew. Chem.* **2011**, *123*, 8255; *Angew. Chem. Int. Ed.* **2011**, *50*, 8105; o) R. Leon, A. Jawalekar, T. Redert, M. J. Gaunt, *Chem. Sci.* **2011**, *2*, 1487; p) Q. Cai, C. Zheng, J.-W. Zhang, S.-L. You, *Angew. Chem.* **2011**, *123*, 8824; *Angew. Chem. Int. Ed.* **2011**, *50*, 8665; q) C.-X. Zhuo, W.-B. Liu, Q.-F. Wu, S.-L. You, *Chem. Sci.* **2012**, *3*, 205; r) Q.-F. Wu, C. Zheng, S.-L. You, *Angew. Chem.* **2012**, *124*, 1712; *Angew. Chem. Int. Ed.* **2012**, *51*, 1680; s) G. Cera, M. Chiarucci, A. Mazzanti, M. Mancinelli, M. Bandini, *Org. Lett.* **2012**, *14*, 1350; t) S. Zhu, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2012**, *134*, 10815; u) J. E. Spangler, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 6802; v) H. Xiong, H. Xu, S. Liao, Z. Xie, Y. Tang, *J. Am. Chem. Soc.* **2013**, *135*, 7851.

[3] M. Weber, M. Weber, M. Kleine-Boymann, *"Phenol" in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2004**.

[4] For reviews, see: a) S. Quideau, L. Pouységu, D. Deffieux, *Synlett* **2008**, 467; b) L. Pouységu, D. Deffieux, S. Quideau, *Tetrahedron* **2010**, *66*, 2235. Selected examples: c) S. Dong, J. Zhu, J. A. Porco, Jr., *J. Am. Chem. Soc.* **2008**, *130*, 2738; d) T. Dohi, A.

Maruyama, N. Takenaga, K. Senami, Y. Minamitsuji, H. Fujioka, S. B. Caemmerer, Y. Kita, *Angew. Chem.* **2008**, *120*, 3847; *Angew. Chem. Int. Ed.* **2008**, *47*, 3787; e) J. K. Boppisetti, V. B. Birman, *Org. Lett.* **2009**, *11*, 1221; f) S. Quideau, G. Lyvinec, M. Marguerit, K. Bathany, A. Ozanne-Beaudenon, T. Buffeteau, D. Cavagnat, A. Chénedé, *Angew. Chem.* **2009**, *121*, 4675; *Angew. Chem. Int. Ed.* **2009**, *48*, 4605; g) M. Uyanik, T. Yasui, K, Ishihara, *Angew. Chem.* **2010**, *122*, 2221; *Angew. Chem. Int. Ed.* **2010**, *49*, 2175; h) M. Uyanik, T. Yasui, K. Ishihara, *Tetrahedron* **2010**, *66*, 5841; i) A. Rudolph, P. H. Bos, A. Meetsma, A. J. MInnaard, B. L. Feringa, *Angew. Chem.* **2011**, *123*, 5956; *Angew. Chem. Int. Ed.* **2011**, *50*, 5834; j) T. Oguma, T. Katsuki, *J. Am. Chem. Soc.* **2012**, *134*, 20017; k) T. Dohi, N. Takenaga, T. Nakae, Y. Toyoda, M. Yamasaki, M. Shiro, H. Fujioka, A. Maruyama, Y. Kita, *J. Am. Chem. Soc.* **2013**, *135*, 4558.

[5] S. Rousseaux, J. García-Fortanet, M. A. Del Aguila Sanchez, S. L. Buchwald, *J. Am. Chem. Soc.* **2011**, *133*, 9282.

[6] a) T. Nemoto, Y. Ishige, M. Yoshida, Y. Kohno, M. Kanematsu, Y. Hamada, *Org. Lett.* **2010**, *12*, 5020; b) M. Yoshida, T. Nemoto, Z. Zhao, Y. Ishige, Y. Hamada, *Tetrahedron: Asymmetry* **2012**, *23*, 859.

[7] Q.-F. Wu, W.-B. Liu, C.-X. Zhuo, Z.-Q. Rong, K.-Y. Ye, S.-L. You, *Angew. Chem.* **2011**, *123*, 4547; *Angew. Chem. Int. Ed.* **2011**, *50*, 4455.

[8] R. J. Phipps, F. D. Toste, *J. Am. Chem. Soc.* **2013**, *135*, 1268.

[9] For reviews: a) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921; b) Z. Lu, S. Ma, *Angew. Chem.* **2008**, *120*, 264; *Angew. Chem. Int. Ed.* **2008**, *47*, 258; c) B. M. Trost, T. Zhang, J. D. Sieber, *Chem. Sci.* **2010**, *1*, 427. Selected examples: d) C. Goux, M. Massacret, P. Lhoste, D. Sinou, *Organometallics* **1995**, *14*, 4585; e) T. Satoh, M. Ikeda, M. Miura, M. Nomura, *J. Org. Chem.* **1997**, *62*, 4877; f) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1998**, *120*, 815; g) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1999**, *121*, 4545; h) B. Nay, J.-F. Peyrat, J. Vercauteren, *Eur. J. Org. Chem.* **1999**, 2231; i) P. A. Evans, D. K. Leahy, *J. Am. Chem. Soc.* **2000**, *122*, 5012; j) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 3090; k) F. López, T. Ohmura, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 3426; l) C. Fischer, C. Defieber, T. Suzuki, E. M. Carreira, *J. Am. Chem. Soc.* **2004**, *126*, 1628; m) B. M. Trost, M. L. Crawley, *Chem. Eur. J.* **2004**, *10*, 2237; n) M. Kimura, Y. Uozumi, *J. Org. Chem.* **2007**, *72*, 707; o) J. A. van Rijn, M. Lutz, L. S. von Chrzanowski, A. L. Spek, E. Bouwman, E. Drent, *Adv. Synth. Catal.* **2009**, *351*, 1637; p) J. A. van Rijn, M. A. Siegler, A. L. Spek, E. Bouwman, E. Drent, *Organometallics* **2009**, *28*, 7006.

[10] a) A. V. Malkov, S. L. Davis, I. R. Baxendale, W. L. Mitchell, P. Kočovský, *J. Org. Chem.* **1999**, *64*, 2751; b) A. V. Malkov, P. Spoor, V. Vinader, P. Kočovský, *J. Org. Chem.* **1999**, *64*, 5308; c) S. B. Hallagudi, C. S. Sajanikumari, N. K. K. Raj, S. S. Deshande, M. P. Degaonfar, *J. Mol. Catal. A* **2001**, *175*, 161; d) N. Tsukada, Y. Yagura, T. Sato, Y. Inoue, *Synlett* **2003**, 1431; e) I. Fernández, R. Hermatschweiler, F. Breher, P. S. Pregosin, L. F. Veiros, M. J. Calhorda, *Angew. Chem.* **2006**, *118*, 6535; *Angew. Chem. Int. Ed.* **2006**, *45*, 6386; f) M. Kimura, M. Fukasaka, Y. Tamaru, *Synthesis* **2006**, 3611; g) E. Kuntz, A. Amgoune, C. Lucas, G. Godard, *J. Mol. Catal. A* **2006**, *244*, 124; h) I. Fernández, D. Schott, S. Gruber, P. S. Pregosin, *Helv. Chim. Acta* **2007**, *90*, 271; i) Y. Yamamoto, K. Itonaga, *Org. Lett.* **2009**, *11*, 717; j) Y. Suzuki, T. Nemoto, K. Kakugawa, A. Hamajima, Y. Hamada, *Org. Lett.* **2012**, *14*, 2350; k) Q.-L. Xu, L.-X. Dai, S.-L. You, *Org. Lett.* **2012**, *14*, 2579.

[11] For stereoselective alkylation of naphthols using chiral lithium reagent, see: M. A. Lovchik, A. Goeke, G. Fráter, *Tetrahedron: Asymmetry* **2006**, *17*, 1693.

[12] F. Diederich, P. J. Stang, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, **1997**.

[13] a) J. He, K. Tchabanenko, R. M. Adlington, A. R. Cowley, J. E. Baldwin, *Eur. J. Org. Chem.* **2006**, 4003. For synthetic utility of β-naphthalenone, also see: b) B. M. Trost, G. M. Schroeder, J. Kristensen, *Angew. Chem.* **2002**, *114*, 3642; *Angew. Chem. Int. Ed.* **2002**, *41*, 3492.

[14] CCDC 913331 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. Using the working model to predict the absolute configuration, see: B. M. Trost, M. R. Machacek, A. Aponick, *Acc. Chem. Res.* **2006**, *39*, 747. For details, see the Supporting Information.

