ChemPubSoc Europe

DOI: 10.1002/chem.201500816

CHEMISTRY
A European Journal
Communication

Asymmetric Catalysis |Hot Paper|

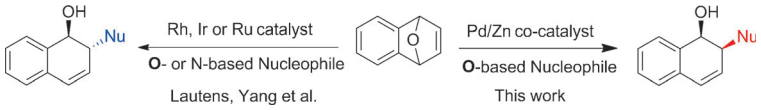
Palladium/Zinc Co-Catalyzed *syn*-Stereoselectively Asymmetric Ring-Opening Reaction of Oxabenzonorbornadienes with Phenols

Sifeng Li,[b] Jianbin Xu,[a] Baomin Fan,*[a, d] Zhiwu Lu,[a] Chaoyuan Zeng,[a] Zhaoxiang Bian,[c] Yongyun Zhou,[a] and Jun Wang*[b]

Abstract: A new palladium/zinc co-catalyst system associated with chiral (*R*)-Difluorphos for asymmetric ring-opening reaction of oxabenzonorbornadienes with phenols is reported. This catalyst system allows the formation of *cis*-2-aryloxy-1,2-dihydronaphthalen-1-ol products in good yields (up to 95% yield) with excellent enantioselectivities (up to 99% *ee*). The *cis*-configuration of the product has been confirmed by X-ray crystal structure analysis. To the best of our knowledge, it represents the first example in ring-opening reactions of bicycloalkenes with heteronucleophiles in a *syn*-stereoselective manner.

Transition metal-catalyzed asymmetric ring-opening (ARO) reactions of oxabenzonorbornadienes have attracted continuous interest and extensive study due to their advantages of straightforward access to chiral hydronaphthalenes, in which they are widely exist as the subunit in natural products and bioactive molecules.[1] Considerable progresses have been made for this type of reactions since Lautens's initial work. With the aid of various chiral transition-metal catalysts, a variety of carbo-[2–6] and heteroatom nucleophiles[7–11] reacted with oxabenzonorbornadienes successfully leading to substituted hydroxyl-dihydronaphthalenes. In the ring-opening addition of carbonucleophiles to oxabenzonorbornadienes, both *cis* and *trans* configured products can be obtained in a highly diastereoselective and enantioselective manners by choosing different metal catalysts, such as Rh,[6b,12] Cu,[2e,3a,b] Pd,[2a,b,f,6c,13] Pt[14] and Ni.[15] Yet, for the ring-opening addition of oxabenzonorbornadienes with oxygen- or nitrogen-based nucleophiles, only *trans*-configuration products were generally observed with Rh, Ir or Ru catalysts.[7,8,10,11,16] To the best of our knowledge, there has been no example in ring-opening reaction of oxabenzonorbornadienes with heteroatom nucleophiles to afford *cis*-2-aryloxy-1,2-dihydronaphthalen-1-ol. In fact, they are important scaffolds for total synthesis of many bioactive compounds.[17]

Recent literatures showed that *cis*-2-aryloxy-1,2-dihydronaphthalen-1-ols could be accessed by cross-coupling of *cis*-1,2-dihydronaphthalen-1,2-diol with $ArBF_3K$ in the presence of copper(II) acetate.[18] The parent *cis*-1,2-dihydronaphthalen-1,2-diol could be afforded by bacterial oxidation of aromatic molecules[19] or by multi-step synthesis from *ortho*-vinylbenzaldehyde.[20] Indeed, a general and stereocontrolled method for easy access of *cis*-dihydronaphthalen-1,2-diols with various substituents is still in demand. In this regard, the ARO pathway leading to *cis*-2-aryloxy-1,2-dihydronaphthalen-1-ol products in one step would be a desirable approach.



Scheme 1. Asymmetric ring-opening reaction of oxabenzonorbornadienes with O- or N-based nucleophiles.

In continuing our research interest of ring-opening reaction using carbonucleophiles,[21,22] herein we report a transition metal/Lewis acid co-catalyst system for asymmetric ring-opening reaction of oxabenzonorbornadienes with phenolic or naphtholic nucleophiles. Remarkably, this method gave exclusive *syn*-selective outcome the first time, in which it is complementary to previous methods for *trans*-configuration product formation (Scheme 1).

We embarked this investigation using oxabenzonorbornadiene **1a** and phenol **2a** as benchmark substrates with $Pd(OAc)_2$ catalyst and Lewis acid $Zn(OTf)_2$ as co-catalyst in combination with a range of chiral diphosphine ligands (Table 1). Gratifyingly, commercially available ligand (*R*)-Binap gave *cis*-2-phyloxy-1,2-dihydronaphthalen-1-ol **3aa** in 66% yield with 76% *ee* in DCE at room temperature for 12 h (Table 1, entry 1). The best product enantioselectivity was obtained by employ-

[a] J. Xu,[+] Prof. B. Fan, Z. Lu, C. Zeng, Y. Zhou
YMU-HKBU Joint Laboratory of Traditional Natural Medicine
Yunnan Minzu University, Kunming 650500 (P. R. China)
E-mail: adams.bmf@hotmail.com

[b] S. Li,[+] Prof. J. Wang
Department of Chemistry
South University of Science and Technology of China
Shenzhen, Guangdong, 518055 (P. R. China)
E-mail: wang.j@sustc.edu.cn

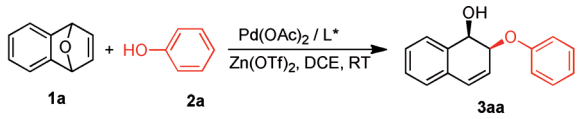
[c] Prof. Z. Bian
School of Chinese Medicine
Hong Kong Baptist University

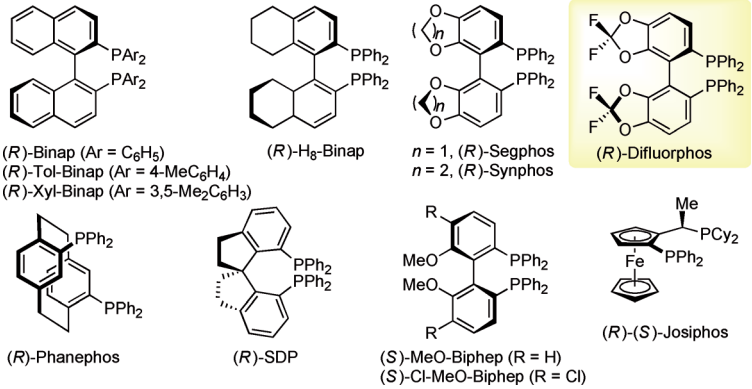
[d] Prof. B. Fan
State Key Laboratory of Elemento-organic Chemistry
Nankai University, Tinajim, 300071 (P. R. China)

[+] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201500816.

Table 1. Ligand screening for Pd/Zn-catalyzed ARO reaction of oxabenzonorbornadiene **1a** with phenol **2a**.[a]





Entry	Ligand	*t* [h]	Yield [%][b]	*ee* [%][c]
1	(*R*)-Binap	12	66	76
2	(*R*)-Tol-Binap	20	66	50
3	(*R*)-xylyl-Binap	16	71	8
4	(*R*)-H_8-Binap	10	55	28
5	(*R*)-Synphos	32	51	66
6	(*R*)-Segphos	20	63	72
7	(*R*)-Difluorphos	3	66	94
8	(*R*)- Phanephos	96	trace	ND
9	(*S*)-MeO-Biphep	20	70	77
10	(*S*)-Cl-MeO-Biphep	6	80	81
11	(*R*)-SDP	52	64	−61
12	(*R*)-(*S*)-Josiphos	60	91	35

[a] Reaction conditions: $Pd(OAc)_2$ (3.0 mol%), $Zn(OTf)_2$ (6.0 mol%), and ligand (3.6 mol%) in DCE (2 mL) was stirred at room temperature for 30 min under Ar atm. **1a** (0.3 mmol) and **2a** (1.5 mmol) were added, and the reaction mixture was stirred at room temperature for indicated period of time. [b] Yield of isolated product. [c] Determined by HPLC analysis. DCE = 1,2-dichloroethane. ND = not determined.

ing (*R*)-Difluorphos as the ligand (Table 1, entry 7). (*R*)-(*S*)-Josiphos gave high yield but inferior enantioselectivity (entry 12). Thus, we chose (*R*)-Difluorphos as the ligand of choice for further optimization.

The reaction conditions for this $Pd(OAc)_2/Zn(OTf)_2$ co-catalyzed asymmetric ring-opening reaction were further surveyed (Table 2). Solvents such as CH_2Cl_2, THF, toluene, DME, dioxane, THP and MTBE resulted in moderate-to-good yields with high *ee* values (Table 2, entries 2–8). The highest *ee* of **3aa** (97%) along with a good yield (84%) was afforded in toluene (entry 4). The effects of the temperature were investigated. Increasing the reaction temperature to 50 °C, decreased the yield of **3aa** to 46% without affecting the *ee* (entry 9). Lowering the reaction temperature to 0 °C resulted in a similar yield and enantioselectivity, but 32 h was required for full conversion (entry 10). The addition of $Zn(OTf)_2$ is crucial for the reaction to proceed. When the reaction was carried out in the absence of $Zn(OTf)_2$, only trace amount of product was detected (Table 2, entry 11). Formation of product **3aa** was not observed when the reaction was co-catalyzed by Lewis acid AgOTf, $AgPF_6$, $AgBF_4$, or $Cu(OTf)_2$, while 1-naphthol only was obtained as the main product (Table 2, entries 12, 14–16).[23] Compared with $Zn(OTf)_2$, $AgSbF_6$ resulted in a higher product yield but a lower enantioselectivity (Table 2, entry 13). CuOTf gave almost the same performance as $Zn(OTf)_2$ (Table 2, entry 17). The reaction still proceeded well even the catalyst loading was decreased to 1.5 mol% $Pd(OAc)_2$ (Table 2, entry 18).

The substrate scope were compiled in Table 3. No significant effect on phenolic nucleophile as the corresponding ring-opening products **3aa**–**3aj** could be obtained in good yields (78–95%) with good enantioselectivities (88–97%). Sterically hindered 1-naphthol **2k** resulted in moderate yield (50%) with good *ee* (91%). 2-Naphthol and 7-methoxyl-2-naphthol also reacted with **1a** smoothly, and afforded the desired product in good yield with high *ee* (entries 12–13). The *cis*-configuration of the product was confirmed by X-ray crystal structure analysis (**3ad**, Figure 1).[24]

To further extend the substrate scope of this transformation, substituted oxabenzonorbornadienes **1b**–**f** with various substituents were examined (Table 4). The addition of phenol **2a** to oxabenzonorbornadienes **1b**–**f** proceeded smoothly to afford the corresponding ring-opening products in good yields and excellent enantioselectivities. Particularly noteworthy is that the steric hindrance caused by the substituents at the oxabenzonorbornadienes **1b** and **1c** did not have deleterious effect on both yields and *ees* of the products (Table 4, entries 1 and 2). The bromo group remained intact under these reaction conditions (Table 4, entry 5), that allows further potential functionalization using traditional cross-coupling methods. Remarkably, all the ring-opening products were exclusively in *cis*-configuration with 70–84% yield and 97–99% *ee* values.

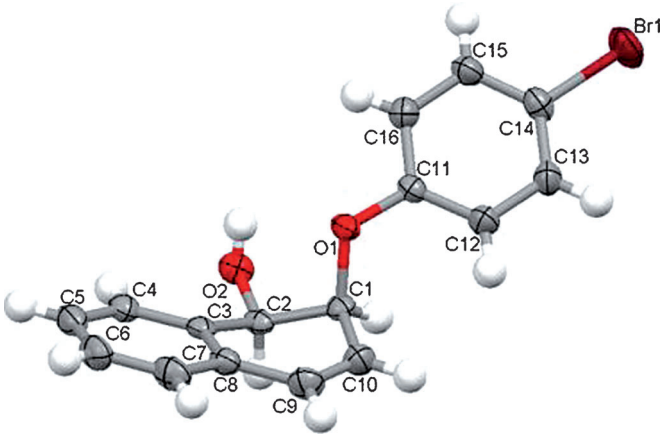
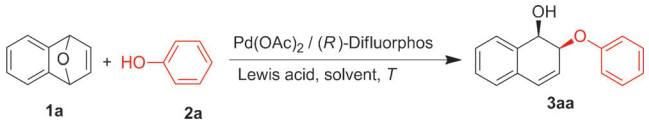


Figure 1. ORTEP drawing of **3ad**.

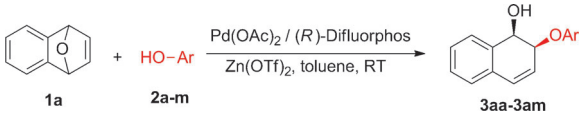
Table 2. Optimization of reaction conditions.[a]

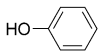
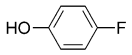
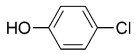
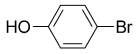
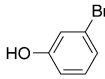
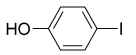
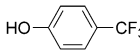
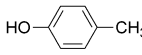
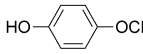
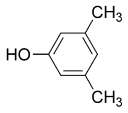
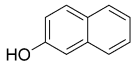
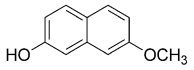


Entry	Solvent	T [°C]	Lewis acid	t [h]	Yield [%][b]	*ee* [%][c]
1	DCE	RT	$Zn(OTf)_2$	3	66	94
2	CH_2Cl_2	RT	$Zn(OTf)_2$	6	42	94
3	THF	RT	$Zn(OTf)_2$	8	76	95
4	toluene	RT	$Zn(OTf)_2$	8	84	97
5	DME	RT	$Zn(OTf)_2$	3	73	96
6	dioxane	RT	$Zn(OTf)_2$	96	63	96
7	THP	RT	$Zn(OTf)_2$	5	64	96
8	MTBE	RT	$Zn(OTf)_2$	96	60	96
9	toluene	50	$Zn(OTf)_2$	1	46	96
10	toluene	0	$Zn(OTf)_2$	32	81	97
11	toluene	RT	–	96	trace	ND
12[d]	toluene	RT	AgOTf	96	trace	ND
13	toluene	RT	$AgSbF_6$	20	90	90
14[d]	toluene	RT	$AgPF_6$	96	trace	ND
15[d]	toluene	RT	$AgBF_4$	96	trace	ND
16[d]	toluene	RT	$Cu(OTf)_2$	96	trace	ND
17	toluene	RT	CuOTf	10	83	97
18[e]	toluene	RT	$Zn(OTf)_2$	8	84	97

[a] Reaction conditions: $Pd(OAc)_2$ (3.0 mol%), Lewis acid (6.0 mol%), and (*R*)-Difluorphos (3.6 mol%) in solvent (2 mL) was stirred at room temperature for 30 min under Ar atm. **1a** (0.3 mmol) and **2a** (1.5 mmol) were added, and the reaction mixture was stirred at room temperature for indicated period of time. [b] Yield of isolated product. [c] Determined by HPLC analysis. [d] 1-Naphthol was obtained as main product. [e] 1.5 mol% $Pd(OAc)_2$ and 1.8 mol% (*R*)-Difluorphos were used instead. DCE = dichloroethane, THF = tetrahydrofuran, DME = dimethoxyethane, THP = tetrahydrapyran, MTBE = methyl *tert*-butyl ether. ND = not determined.

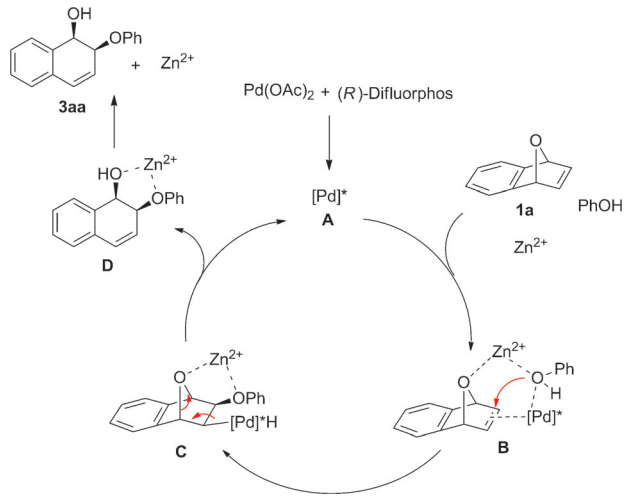
Table 3. Pd/Zn-catalyzed ARO reaction of **1a** with various phenols and naphthols.[a]



Entry	Aryl phenols		t [h]	Yield [%][b]	*ee* [%][c]
1		**2a**	8	84	97
2		**2b**	8	79	96
3		**2c**	8	92	94
4		**2d**	8	80	93
5		**2e**	12	78	89
6		**2f**	8	95	93
7		**2g**	8	96	88
8		**2h**	8	91	96
9		**2i**	8	95	95
10		**2j**	24	87	96
11		**2k**	24	50	91
12		**2l**	12	96	89
13		**2m**	48	90	95

[a] Reaction conditions: $Pd(OAc)_2$ (1.5 mol%), $Zn(OTf)_2$ (6.0 mol%), and (*R*)-Difluorphos (1.8 mol%) in toluene (2 mL) was stirred at room temperature for 30 min under Ar atm. **1a** (0.3 mmol) and **2a–m** (1.5 mmol) were added, and the reaction mixture was stirred at room temperature for indicated period of time. [b] Yield of isolated product. [c] Determined by HPLC analysis.

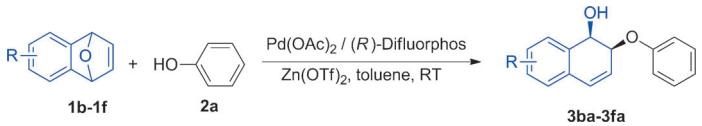
On the basis of results, a proposed mechanism is shown in Scheme 2. Chiral palladium **A** generated by $Pd(OAc)_2$ and (*R*)-Difluorphos coordinates with oxabenzonorbornadiene **1a** and phenol to form intermediate **B**. Pd inserts to the O–H bond of phenol to give the intermediate **C**. Then β-elimination of oxygen opens the furyl ring and gives the ring-opened species **D**. Subsequent hydrolysis liberates ring-opened product **3aa**. The Pd complex **A** is regenerated. It should be noted that in this proposed mechanism, $Zn(OTf)_2$ is important for the reactivity and stereoselectivity.



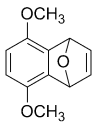
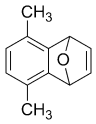
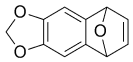
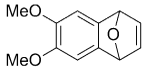
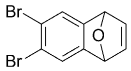
Scheme 2. Proposed mechanism for the Pd/Zn co-catalyzed asymmetric ring-opening reaction.

In conclusion, we have successfully developed a new Pd/Zn catalyst system associated with chiral (*R*)-Difluorphos for asymmetric ring-opening addition of oxabenzonorbornadienes with phenolic or naphtholic nucleophiles. This protocol has the characteristic of mild reaction conditons (e.g., room temperature) and broad substrate scope. The *cis*-2-aryloxy-1,2-dihydronaphthalen-1-ol products were generally obtained in good

Table 4. Pd/Zn-catalyzed ARO reaction of substituted oxabenzonorbornadienes with phenol.[a]



1b-1f 2a 3ba-3fa

Entry	Oxabenzonorbornadien		*t* [h]	Yield [%][b]	*ee* [%][c]
1		**1b**	12	79	97
2		**1c**	24	82	96
3		**1d**	18	70	99
4		**1e**	18	67	97
5		**1f**	64	78	97

[a] Reaction conditions: $Pd(OAc)_2$ (1.5 mol%), (*R*)-Difluorphos (1.8 mol%) and $Zn(OTf)_2$ (6.0 mol%), in toluene (2 mL) was stirred at room temperature for 30 min under Ar atm. **1a–f** (0.3 mmol) and **2a** (1.5 mmol) were added, and the reaction mixture was stirred at room temperature for indicated period of time. [b] Yield of isolated product. [c] Determined by HPLC analysis.

yields (up to 95% yield) with high level of enantioselectivities (up to 99% *ee*). To the best of our knowledge, it represents the first example in ring-opening reaction of oxabenzonorbornadienes with oxygen-based nucleophiles giving exclusive *cis*-product. Further investigations are underway to clarify the mechanism and to explore the scope of the asymmetric ring-opening (ARO) reactions.[25]

Keywords: asymmetric catalysis · oxabenzonorbornadienes · phenols · ring-opening reaction · *syn*-stereoselectivity

[1] For selected references: a) J. P. Freeman, E. T. Michalson, S. V. D'Andrea, L. Baczynskyj, P. F. VonVoigtlander, R. A. Lahti, M. W. Smith, C. F. Lawson, T. A. Scahill, S. A. Mizsak, J. Szmuszkovicz, *J. Med. Chem.* **1991**, *34*, 1891; b) J. H. Jones, P. S. Anderson, J. J. Baldwin, B. V. Clineschmidt, D. E. McClure, G. F. Lundell, W. C. Randall, G. E. Martin, M. Williams, J. M. Hirshfield, G. Smith, P. K. Lumma, *J. Med. Chem.* **1984**, *27*, 1607;c) A. Kamal, L. Gayatri, *Tetrahedron Lett.* **1996**, *37*, 3359; d) W. M. Welch, A. R. Kraska, R. Sarges, B. K. Keo, *J. Med. Chem.* **1984**, *27*, 1508; e) S. E. Snyder, F. A. Aviles-Garay, R. Chakraborti, D. E. Nichols, V. J. Watts, R. B. Mailman, *J. Med. Chem.* **1995**, *38*, 2395; f) A. Saito, Y. Kayama, T. Watanabe, H. Fukushima, T. Hara, *J. Med. Chem.* **1980**, *23*, 1364; g) A. Sobti, K, Kim, J. A. Sulikowski, *J. Org. Chem.* **1996**, *61*, 6; h) F. A. Davis, C. Clark, A. Kumar, B.-C. Chen, *J. Org. Chem.* **1994**, *59*, 1184; i) T. Kaneko, H. Wong, *Tetrahedron Lett.* **1987**, *28*, 517; j) R. Perrone, *J. Med. Chem.* **1995**, *38*, 942; k) J. Tsoung, K. Kramer, A. Zajdlik, C. Liebert, M. Lautens, *J. Org. Chem.* **2011**, *76*, 9031.

[2] For selected references of zinc reagents: a) M. Lautens, J. Renaud, S. Hiebert, *J. Am. Chem. Soc.* **2000**, *122*, 1804; b) M. Lautens, S. Hiebert, *J. Am. Chem. Soc.* **2004**, *126*, 1437; c) S. Cabrera, R. G. Arrayas, I. Alonso, J. C. Carretero, *J. Am. Chem. Soc.* **2005**, *127*, 17938; d) S. Cabrera, R. G. Arrayas, J. C. Carretero, *Angew. Chem. Int. Ed.* **2004**, *43*, 3944; *Angew. Chem.* **2004**, *116*, 4034; e) F. Bertozzi, M. Pineschi, F. Macchia, L. A. Arnold, A. J. Minnaard, B. L. Feringa, *Org. Lett.* **2002**, *4*, 2703; f) M. Li, X.-X. Yan, W. Hong, X.-Z. Zhu, B.-X. Cao, J. Sun, X.-L. Hou, *Org. Lett.* **2004**, *6*, 2833; g) T. Imamoto, K. Sugita, K. Yoshida, *J. Am. Chem. Soc.* **2005**, *127*, 11934; h) T. Imamoto, Y. Saitoh, A. Koide, T. Ogura, K. Yoshida, *Angew. Chem. Int. Ed.* **2007**, *46*, 8636; *Angew. Chem.* **2007**, *119*, 8790; i) K. Endo, K. Tanaka, M. Ogawa, T. Shibata, *Org. Lett.* **2011**, *13*, 868.

[3] For selected references of Grignard reagents: a) R. G. Arrayás, S. Cabrera, J. C. Carretero, *Org. Lett.* **2003**, *5*, 1333; b) W. Zhang, L.-X. Wang, W.-J. Shi, Q.-L. Zhou, *J. Org. Chem.* **2005**, *70*, 3734; c) W. Zhang, S.-F. Zhu, X.-C. Qiao, Q.-L. Zhou, *Chem. Asian J.* **2008**, *3*, 2105; d) R. Millet, L. Gremaud, T. Bernardez, L. Palais, A. Alexakis, *Synthesis* **2009**, 2101.

[4] For selected references of aluminum reagents: a) R. Millet, T. Bernardez, L. Palais, A. Alexakis, *Tetrahedron Lett.* **2009**, *50*, 3474; b) C. Ladjel, N. Fuchs, J.-K. Zhao, G. Bernardinelli, A. Alexakis, *Eur. J. Org. Chem.* **2009**, 4949.

[5] For lithium reagents: P. H. Bos, A. Rudolph, M. Perez, M. Fananas-Mastral, S. R. Harutyunyan, B. L. Feringa, *Chem. Commun.* **2012**, *48*, 1748.

[6] For selected references of organoboronic acids: a) M. Murakami, H. Igawa, *Chem. Commun.* **2002**, 390; b) M. Lautens, C. Dockendorff, K. Fagnou, A. Malicki, *Org. Lett.* **2002**, *4*, 1311; c) M. Lautens, C. Dockendorff, *Org. Lett.* **2003**, *5*, 3695; d) T.-K. Zhang, D.-L. Mo, L.-X. Dai, X.-L. Hou, *Org. Lett.* **2008**, *10*, 3689.

[7] For selected references of phenols and alcohols: a) M. Lautens, K. Fagnou, M. Taylor, *Org. Lett.* **2000**, *2*, 1677; b) M. Lautens, K. Fagnou, T. Rovis, *J. Am. Chem. Soc.* **2000**, *122*, 5650; c) M. Lautens, K. Fagnou, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5455; d) H.-C. Cheng, D.-Q. Yang, *J. Org. Chem.* **2012**, *77*, 9756; e) W. Braun, W. Muller, B. Calmuschi, A. Salzer, *J. Organomet. Chem.* **2005**, *690*, 1166; f) S.-F. Li, H.-L. Chen, Q.-J. Yang, L. Yu, C.-L. Fan, Y.-Y. Zhou, J. Wang, B.-M. Fan, *Asian J. Org. Chem.* **2013**, *2*, 494.

[8] For selected references of amines: a) M. Lautens, K. Fagnou, D.-Q. Yang, *J. Am. Chem. Soc.* **2003**, *125*, 14884; b) R. Webster, C. Boing, M. Lautens, *J. Am. Chem. Soc.* **2009**, *131*, 444; c) A. Boyer, M. Lautens, *Angew. Chem. Int. Ed.* **2011**, *50*, 7346; *Angew. Chem.* **2011**, *123*, 7484; d) D.-Q. Yang, P. Hu, Y.-H. Long, Y.-J. Wu, H.-P. Zeng, H. Wang, X.-J. Zuo, *Beilstein J. Org. Chem.* **2009**, *5*, 53; e) D.-Q. Yang, Y.-H. Long, J.-F. Zhang, H.-P. Zeng, S.-Y. Wang, C.-R. Li, *Organometallics* **2010**, *29*, 3477; f) L. Yu, Y.-Y. Zhou, X. Xu, S.-F. Li, J.-B. Xu, B.-M. Fan, C.-Y. Lin, Z.-X. Bian, A. S. C. Chan, *Tetrahedron Lett.* **2014**, *55*, 6315.

[9] For thiols: P. Leong, M. Lautens, *J. Org. Chem.* **2004**, *69*, 2194.

[10] For carboxylate: M. Lautens, K. Fagnou, *Tetrahedron* **2001**, *57*, 5067.

[11] For water: G. C. Tsui, M. Lautens, *Angew. Chem. Int. Ed.* **2012**, *51*, 5400; *Angew. Chem.* **2012**, *124*, 5496.

[12] a) A. Preetz, C. Kohrt, H.-J. Drexler, A. Torrens, H. Buschmann, M. G. Lopez, D. Heller, *Adv. Synth. Catal.* **2010**, *352*, 2073; b) C. Dockendorff, S.-J. Jin, M. Olsen, M. Lautens, M. Coupal, L. Hodzic, N. Spear, K. Payza, C. Walpole, M. J. Tomaszewski, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 1228.

[13] a) J. Priego, O. G. Mancheño, S. Cabrera, R. G. Arrayás, T. Llama, J. C. Carretero, *Chem. Commun.* **2002**, 2512; b) K. Yoshida, T. Toyoshima, N. Akashi, T. Imamoto, A. Yanagisawa, *Chem. Commun.* **2009**, 2923; c) M. Lautens, S. Hiebert, J.-L. Renaud, *J. Am. Chem. Soc.* **2001**, *123*, 6834; d) C.-L. Chen, S. F. Martin, *Org. Lett.* **2004**, *6*, 3581; e) C. Moinet, J.-C. Fiaud, *Tetrahedron Lett.* **1995**, *36*, 2051.

[14] X.-J. Pan, G.-B. Huang, Y.-H. Long, X.-J. Zuo, X. Xu, F.-L. Gu, D.-Q. Yang, *J. Org. Chem.* **2014**, *79*, 187.

[15] a) M.-S. Wu, D. K. Rayabarapu, C.-H. Cheng, *J. Org. Chem.* **2005**, *70*, 8407; b) D. K. Rayabarapu, C.-F. Chiou, C.-H. Cheng, *Org. Lett.* **2002**, *4*, 1679.

[16] a) M. Lautens, G. A. Schmid, A. Chau, *J. Org. Chem.* **2002**, *67*, 8043; b) Y.-H. Long, S.-Q. Zhao, H.-P. Zeng, D.-Q. Yang, *Catal. Lett.* **2010**, *138*, 124; c) D.-Q. Yang, H.-P. Zeng, *Chin. Chem. Lett.* **2003**, *14*, 697; d) M. Lautens, K. Fagnou, *J. Am. Chem. Soc.* **2001**, *123*, 7170; e) R. Webster, A. Boyer, M. J. Fleming, M. Lautens, *Org. Lett.* **2010**, *12*, 5418; f) Y.-F. Han, D.-Q. Yang, E.-C. Liu, J.-X. Dong, *Chin. Chem. Lett.* **2006**, *17*, 296; g) M. Lautens, K. Fagnou, M. Taylor, T. Rovis, *J. Organomet. Chem.* **2001**, *624*, 259;

h) G. C. Tsui, P. Dougan, M. Lautens, *Org. Lett.* **2013**, *15*, 2652; i) K. Jack, E. Fatila, C. Hillis, W. Tam, *Synth. Commun.* **2013**, *43*, 1181.

[17] a) G. Gianninia, S. Pencoa, C. Pisanoa, T. Riccionia, G. Nasinib, G. Candianib, *Fitoterapia* **2003**, *74*, 323; b) D. Jiménez-Teja, M. Daoubi, I. G. Collado, R. Hernández-Galán, *Tetrahedron* **2009**, *65*, 3392.

[18] J. S. Kudavalli, D. Coyne, R. A. M. O'Ferrall, *J. Org. Chem.* **2012**, *77*, 563.

[19] For selected references: a) D. M. Jerina, J. W. Daly, A. M. Jeffrey, D. T. Gibson, *Arch. Biochem. Biophys.* **1971**, *142*, 394; b) A. Bosetti, D. Bianchi, N. Andriollo, D. Cidaria, P. Cesti, *J. Chem. Technol. Biotechnol.* **1996**, *66*, 375; c) R. E. Parales, M. D. Emig, N. A. Lynch, D. T. Gibson, *J. Bacteriol.* **1998**, *180*, 2337; d) J. V. Parales, R. E. Parales, S. M. Resnick, D. T. Gibson, *J. Bacteriol.* **1998**, *180*, 1194; e) H. Nojiri, J.-W. Nam, M. Kosaka, K.-I. Morii, T. Takemura, K. Furihata, H. Yamane, T. Omori, *J. Bacteriol.* **1999**, *181*, 3105; f) M. Kwit, J. Gawronski, Derek. R. Boyd, N. D. Sharma, M. Kaik, R. A. M. O'Ferrall, J. S. Kudavalli, *Chem. Eur. J.* **2008**, *14*, 11500.

[20] a) P. Mukherjee, S. J. S. Roy, T. K. Sarkar, *Org. Lett.* **2010**, *12*, 2472; b) P. Mukherjee, T. K. Sarkar, *Org. Biomol. Chem.* **2012**, *10*, 3060.

[21] B.-M. Fan, S.-F. Li, H.-L. Chen, Z.-W. Lu, S.-S. Liu, Q.-J. Yang, L. Yu, J. B. Xu, Y.-Y. Zhou, J. Wang, *Adv. Synth. Catal.* **2013**, *355*, 2827.

[22] S.-S. Liu, S.-F. Li, H.-L. Chen, Q.-J. Yang, J. B. Xu, Y.-Y. Zhou, M.-L. Yuan, W.-M. Zeng, B.-M. Fan, *Adv. Synth. Catal.* **2014**, *356*, 2960.

[23] F.-Z. Peng, B.-M. Fan, Z.-H. Shao, X.-W. Pu, P.-H. Li, H.-B. Zhang, *Synthesis* **2008**, 3043.

[24] CCDC 1038727 [for **3ad**] 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..

[25] A related paper using a platinum catalyst, appeared during the revision of the manuscript. L. Meng, W. Yang, X.-J. Pan, M. Tao, G. Cheng, S.-Y. Wang, H.-P. Zeng, Y.-H. Long, D.-Q. Yang, *J. Org. Chem.* **2015**, *80*, 2503.

Received: December 22, 2014
Revised: February 27, 2015
Published online on ■■ ▮▮, 0000

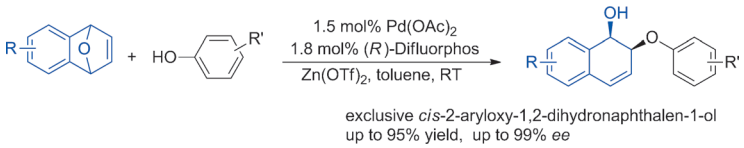
COMMUNICATION

Asymmetric Catalysis

S. Li, J. Xu, B. Fan, Z. Lu, C. Zeng, Z. Bian, Y. Zhou, J. Wang**

■■ – ■■

Palladium/Zinc Co-Catalyzed *syn*-Stereoselectively Asymmetric Ring-Opening Reaction of Oxabenzonorbornadienes with Phenols



Open the ring: A new palladium/zinc co-catalyst associated with chiral (*R*)-Difluorphos for asymmetric ring-opening reaction of oxabenzonorbornadienes with phenolic or naphtholic nucleophiles was developed, which afforded corresponding *cis*-2-aryloxy-1,2-dihydronaphthalen-1-ol products in good yields (up to 95% yield) with excellent enantioselectivities (up to 99% *ee*).

An Asymmetric Ring-Opening Reaction

For the ring-opening addition of oxabenzonorbornadienes with oxygen- or nitrogen-based nucleophiles, only *trans*-configuration products were observed generally with Rh, Ir or Ru catalysts. In the Communication by B. Fan, J. Wang and co-workers on page ■■ ff., a new palladium/zinc co-catalyst associated with chiral (*R*)-Difluorphos for asymmetric ring-opening reaction of oxabenzonorbornadienes with phenol was developed, which afforded corresponding *cis*-2-aryloxy-1,2-dihydronaphthalen-1-ol products in good yields (up to 95% yield) with excellent enantioselectivities (up to 99% *ee*).