C–H Activation

DOI: 10.1002/ange.201206890

Rhodium(III)-Catalyzed Oxidative C–H Coupling of *N*-Methoxybenzamides with Aryl Boronic Acids: One-Pot Synthesis of Phenanthridinones**

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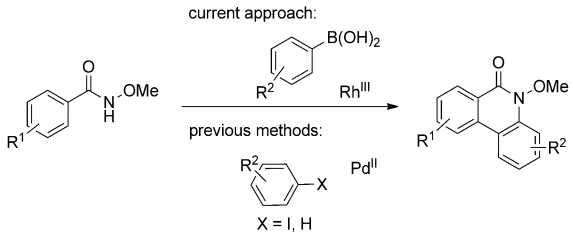
In recent years, transition-metal-catalyzed directing-group-assisted C–H activation has emerged as a sustainable and intriguing protocol for the construction of C–C, C–N, C–O, and C–X bonds.[1] In particular, one-pot C–C/C–N bond-forming reactions have been used as key steps for the synthesis of nitrogen-containing natural products and heterocycles in drug discovery.[2] In this context, rhodium catalysts have proven valuable for applications in the step-economical synthesis of complex molecular scaffolds.[3] Although a vast number of rhodium(III)-catalyzed directing-group-assisted C–H activation reactions of alkenes[4] and alkynes[5] and nucleophilic addition reactions[6] have been reported, rhodium(III)-catalyzed oxidative C–H coupling reactions between arenes or between an arene and an organometallic reagent remain relatively unexplored.[7,8]

Organoboron reagents are stable and powerful reagents for versatile transformations, including the well-known Suzuki–Miyaura coupling. However, very few examples of the use of organoboron reagents as the coupling reagents in palladium- and rhodium(I)-catalyzed C–H activation reactions are known.[9,10] In 2009, Miura and co-workers reported a rhodium(III)-catalyzed oxidative coupling of aryl boronic acids with alkynes to give naphthalenes and anthracenes.[11]

We have become interested in the use of *N*-methoxybenzamides as an important motif for rapid access to phenanthridinone derivatives, which are well-represented in natural products and drugs.[12] Recently, Wang et al. and our research group reported the palladium-catalyzed synthesis of phenanthridinone derivatives from *N*-methoxybenzamides with iodoarenes[13a] and simple arenes,[13b] respectively. Although a variety of methods have been documented, a more straightforward alternative method with wide scope under mild conditions is desired for the synthesis of phenanthridinones. Our continuing efforts in metal-catalyzed C–H bond activation and cyclization reactions[13b,14] prompted us to explore the reaction of *N*-methoxybenzamides with aryl boronic acids. Herein we report the Rh^{III}-catalyzed regioselective synthesis of phenanthridinones from *N*-methoxybenzamides and aryl boronic acids through one-pot C–C/C–N bond formation under mild conditions. To the best of our knowledge, this is the first rhodium-catalyzed dual oxidative C–H bond coupling of two aromatic[4h,15] compounds to give a formal [4+2] cyclization product (Scheme 1).



Scheme 1. Synthesis of phenanthridinone derivatives.

The treatment of *N*-methoxybenzamide (**1a**) and phenylboronic acid (**2a**) with $[\{RhCp^*Cl_2\}_2]$ ($Cp^* = Me_5C_5$; 2 mol%) and Ag_2O (4 equiv) in methanol at 60 °C for 3 h afforded phenanthridinone **3a** in 94% yield (Table 1, entry 1). Control experiments revealed that the reaction did not proceed in the absence of rhodium. The presence of a silver salt is crucial to the reaction. We examined various silver salts and found that **3a** was formed in the highest yield with Ag_2O. A combination of Ag_2O (2 equiv) and oxygen (1 atm) afforded **3a** in 82% yield. A series of solvents or solvent combinations and oxidants were examined for the reaction of **1a** with **2a**. The reaction in MeOH gave the best result (Table 1, entry 1). Other solvents tested were less effective or totally ineffective (see the Supporting Information).

We examined the reaction of various substituted *N*-methoxybenzamides **1b–q** with phenylboronic acid (**2a**) under the optimized reaction conditions. Gratifyingly, excellent yields and regioselectivity were generally observed for these substrates with electron-donating or electron-withdrawing groups (Table 1, entries 2–17).

C–H bond activation at C2 in **1** is less likely than activation at C6 if a *meta* substituent is present owing to the stronger steric repulsion between the substituent and the complex (see Table 1, entries 3, 4, 6, 11, and 16). In contrast, in the case of 3,4-methylenedioxy-*N*-methoxybenzamide (**1g**), C–H bond activation occurred at C2 instead of C6 to afford **3g** in 82% yield (Table 1, entry 7). In the C–H bond activation of **1g**, coordination of both the 3-oxy and the *N*-methoxycarboxamide group probably occurs to cause activation at the C2 site.[14f]

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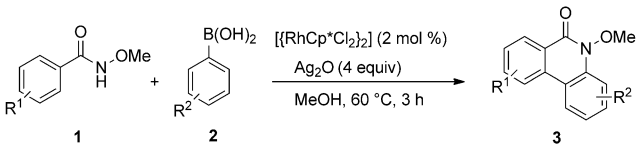
[**] We thank the National Science Council of the Republic of China (NSC 98-2119-M-007-002-MY3) for support of this research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206890.

Table 1: Rhodium-catalyzed dual C–H activation of *N*-methoxybenzamides with aryl boronic acids.[a]



1 **2** **3**

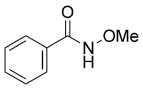
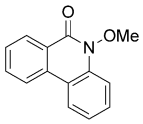
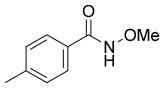
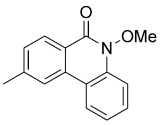
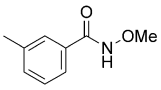
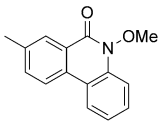
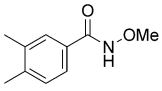
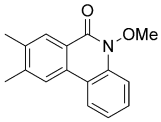
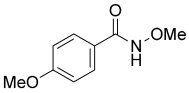
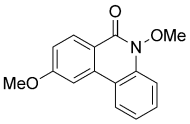
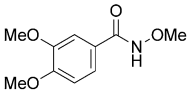
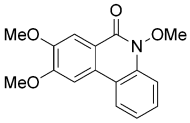
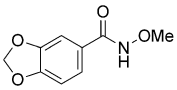
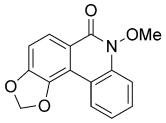
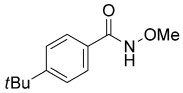
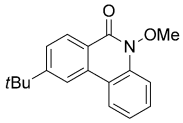
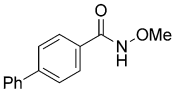
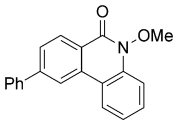
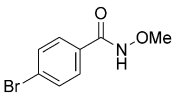
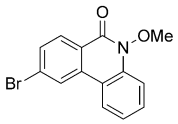
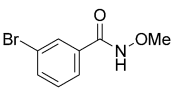
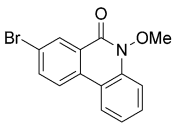
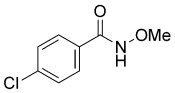
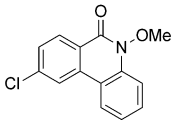
Entry	**1**		**2**	Product **3**		Yield [%][b]
1		**1a**	**2a**		**3a**	94
2		**1b**	**2a**		**3b**	91
3		**1c**	**2a**		**3c**	84
4		**1d**	**2a**		**3d**	82
5		**1e**	**2a**		**3e**	87
6		**1f**	**2a**		**3f**	85
7		**1g**	**2a**		**3g**	82
8		**1h**	**2a**		**3h**	86
9		**1i**	**2a**		**3i**	83
10		**1j**	**2a**		**3j**	86
11		**1k**	**2a**		**3k**	81
12		**1l**	**2a**		**3l**	89

Table 1: (Continued)

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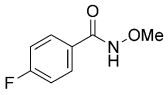
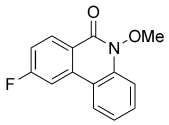
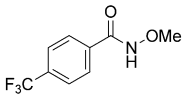
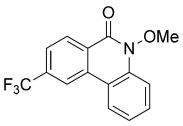
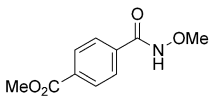
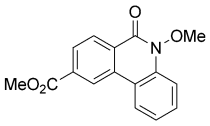
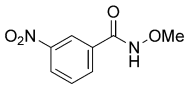
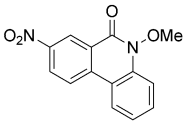
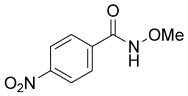
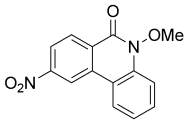
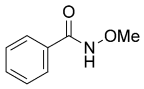
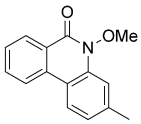
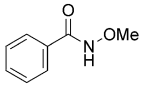
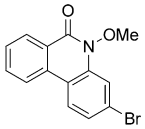
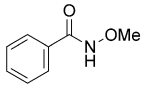
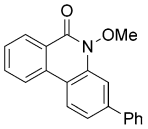
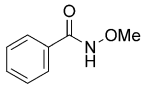
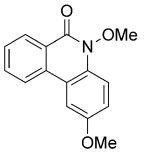
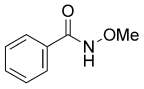
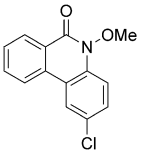
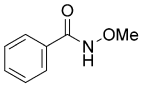
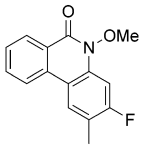
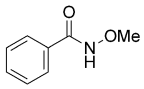
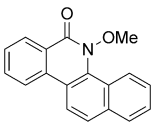
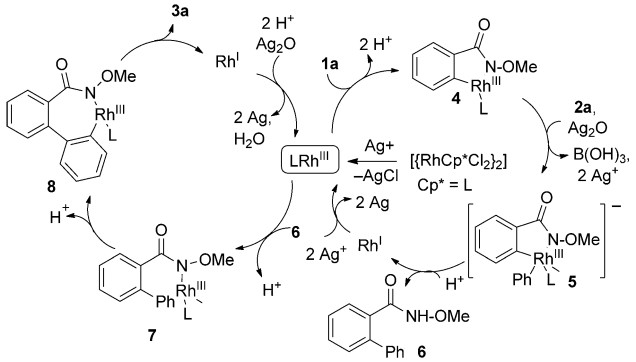
13		**1m**	**2a**		**3m**	91
14		**1n**	**2a**		**3n**	84
15		**1o**	**2a**		**3o**	87
16		**1p**	**2a**		**3p**	76
17		**1q**	**2a**		**3q**	79
18		**1a**	**2b**		**3r**	90
19		**1a**	**2c**		**3s**	84
20		**1a**	**2d**		**3t**	77
21		**1a**	**2e**		**3u**	84
22		**1a**	**2f**		**3v**	72
23		**1a**	**2g**		**3w**	85
24		**1a**	**2h**		**3x**	83

[a] Reactions conditions: **1** (0.60 mmol), **2** (1.20 mmol), [{RhCp*Cl$_2$}$_2$] (2.0 mol%), Ag_2O (2.40 mmol), MeOH (3 mL), 60°C, 3 h. [b] Yield of the isolated product.

To further explore the scope of the reaction, we investigated the reaction of various aryl boronic acids **2b–h** with **1a** under the optimized conditions. Thus, the treatment of **1a** with 4-methylphenyl-, 4-bromophenyl-, and 4-biphenylboronic acid (**2b–d**) provided phenanthridinones **3q–s** in 77–90% yield (Table 1, entries 18–20). The reactions of 3-methoxyphenyl-, 3-chlorophenyl-, and 3-methyl-4-fluorophenylboronic acid also proceeded with high regioselectivity to give the less-hindered regioisomeric products **3u–w** in good yields (Table 1, entries 21–23). Notably, products **3u–w** could not be made by the previously reported palladium-catalyzed reaction (Scheme 1) from **1** and an arene coupling partner owing to the *para* reactivity of the arenes.[13b] Finally, 2-naphthylboronic acid reacted with **1a** to give the sterically more hindered product **3x** in 83% yield (Table 1, entry 24).

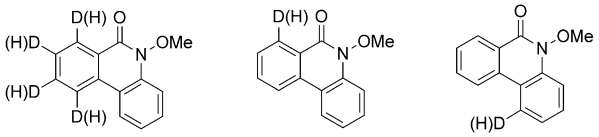
A plausible mechanism to account for the present reaction of **1a** with **2a** to give **3a** is proposed in Scheme 2. The catalytic



Scheme 2. A proposed mechanism for the catalytic reaction.

cycle is probably initiated by the removal of a chloride ligand from [{RhCp*Cl_2}$_2$] by Ag^+, followed by N-metalation and a turnover-limiting C–H activation to form a five-membered rhodacycle **4**. Transmetalation with **2a** then leads to intermediate **5**, which undergoes reductive elimination to give the *ortho*-arylated product **6** and a Rh^I species. Rh^I is reoxidized to Rh^{III} by Ag_2O. Subsequent deprotonative coordination of the nitrogen atom in **6** to Rh^{III} forms intermediate **7**. Further C–H activation to give the seven-membered rhodacycle **8** is followed by reductive elimination to afford **3a** and Rh^I, which is oxidized by Ag_2O to regenerate the active Rh^{III} species for the next cycle. Strong evidence in support of **6** as a catalytic intermediate was provided by the observation that when compound **6** was heated under the catalytic conditions, product **3a** was formed in 94% yield (see the Supporting Information for details).

To gain further understanding of the mechanistic details of this catalytic reaction, we measured the kinetic isotopic effects (KIEs) of the reaction by carrying out inter- and intramolecular competition reactions (Scheme 3). An intermolecular KIE of $k_H/k_D = 1.40$ was observed for the competitive reaction of **1a** and deuterium-labeled [D_5]**1a** with **2a** to give **3a**. On the other hand, an intramolecular competition experiment with [D_1]**1a** and **2a** showed $k_H/k_D = 3.6$. These



Scheme 3. Kinetic isotope effects for the rhodium-catalyzed oxidative coupling of **1a** with **2a**.

results are in agreement with the proposed mechanism (Scheme 2), according to which the binding of substrate **1a** (probably through the amide nitrogen atom) to rhodium occurs prior to an irreversible C–H bond cleavage to form **4**.[16] The substrate-binding step would not show selectivity for **1a** or [D_5]**1a**, but different rates would be observed for the following C–H bond-cleavage step. As a result, a small KIE of 1.40 was observed for the intermolecular competition experiment. In contrast, for the intramolecular H/D competition experiment, the irreversible C–H bond cleavage would be the product-determining step, and a primary KIE was observed. Finally, we conducted an intramolecular competition experiment with the aryl boronic acid [D_1]**2a** and **1a** as substrates for the formation of product [D_1]**3a**. The KIE value k_H/k_D was only 1.28. This observation indicates that the C–H bond cleavage of [D_1]**2a** is not the product-determining step to form intermediate **8**; binding of the phenyl ring to the rhodium center, which would not show selectivity for a C–H or C–D bond of [D_1]**2a**, probably occurs before the C–H bond cleavage.

In conclusion, we have successfully demonstrated a rhodium-catalyzed dual C–H activation of *N*-methoxybenzamides with aryl boronic acids under mild conditions. The catalytic reaction proceeds with high regioselectivity and provides various substituted phenanthridinones through C–C and C–N bond formation in very good yields. This method is complementary to previously reported methods based on the use of palladium catalysts.[13] Further application of this methodology in natural product synthesis is in progress.

Experimental Section

General procedure: A sealed tube (20 mL) containing [{RhCp*Cl_2}$_2$] (8.5 mg, 0.012 mmol, 2.0 mol%), **1** (0.60 mmol), **2** (1.20 mmol), and Ag_2O (556 mg, 2.40 mmol) was evacuated and purged with nitrogen gas three times. Methanol (3.00 mL) was then added with a syringe. The reaction mixture was stirred at 60 °C for 3 h, then diluted with dichloromethane (30 mL) and stirred in air for 10 min. The mixture was filtered through a Celite and silica-gel pad and washed with dichloromethane. Concentration of the filtrate and purification of the residue on a silica-gel column with hexane/ethyl acetate as the eluent afforded the desired product **3**.

Received: August 25, 2012
Published online: October 26, 2012

Keywords: C–H activation · cross-coupling · homogeneous catalysis · phenanthridinones · rhodium

[1] a) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; b) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; c) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; d) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074; e) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; for reviews focused on oxidative coupling, see: f) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; g) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* **2011**, *111*, 1780.

[2] a) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885; b) C. Zhu, R. Wang, J. R. Falck, *Chem. Asian J.* **2012**, *7*, 1502.

[3] For reviews on rhodium-catalyzed C–H activation, see: a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; b) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; c) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2012**, *45*, 814.

[4] For selected examples of Rh^{III}-catalyzed oxidative coupling with alkenes, see: a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407; b) N. Umeda, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 7094; c) J. Chen, G. Song, C.-L. Pan, X. Li, *Org. Lett.* **2010**, *12*, 5426; d) F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9982; e) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 3024; f) X. Li, M. Zhao, *J. Org. Chem.* **2011**, *76*, 8530; g) A. S. Tsai, M. Brasse, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2011**, *13*, 540; h) S. H. Park, J. Y. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2372; i) F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem.* **2011**, *123*, 1096; *Angew. Chem. Int. Ed.* **2011**, *50*, 1064; j) H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, Z.-J. Shi, *J. Am. Chem. Soc.* **2011**, *133*, 15244; k) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350.

[5] For selected examples of Rh^{III}-catalyzed oxidative coupling with alkynes, see: a) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, *Angew. Chem.* **2008**, *120*, 4083; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019; b) S. Mochida, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2010**, *39*, 744; c) P. C. Too, Y.-F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688; d) T. K. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565; e) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585; f) N. Umeda, K. Hirano, T. Satoh, N. Shibata, H. Sato, M. Miura, *J. Org. Chem.* **2011**, *76*, 13; g) M. P. Huestis, L. Chan, D. R. Stuart, K. Fagnou, *Angew. Chem.* **2011**, *123*, 1374; *Angew. Chem. Int. Ed.* **2011**, *50*, 1338; h) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; i) F. W. Patureau, T. Besset, N. Kuhl, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2154; j) T. K. Hyster, T. Rovis, *Chem. Commun.* **2011**, *47*, 11846; k) B.-J. Li, H.-Y. Wang, Q.-L. Zhu, Z.-J. Shi, *Angew. Chem.* **2012**, *124*, 4014; *Angew. Chem. Int. Ed.* **2012**, *51*, 3948; l) K. Muralirajan, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2011**, *123*, 4255; *Angew. Chem. Int. Ed.* **2011**, *50*, 4169; m) J. Jayakumar, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2012**, *124*, 201; *Angew. Chem. Int. Ed.* **2012**, *51*, 197; n) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6908.

[6] a) A. S. Tsai, M. E. Tauchert, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2011**, *133*, 1248; b) Y. Li, B.-J. Li, W.-H. Wang, W.-P. Huang, X.-S. Zhang, K. Chen, Z.-J. Shi, *Angew. Chem.* **2011**, *123*, 2163; *Angew. Chem. Int. Ed.* **2011**, *50*, 2115; c) M. E. Tauchert, C. D. Incarvito, A. L. Rheingold, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2012**, *134*, 1482; d) Y. Li, X.-S. Zhang, H. Li, W.-H. Wang, K. Chen, B.-J. Li, Z.-J. Shi, *Chem. Sci.* **2012**, *3*, 1634; e) Y. Du, T. K. Hyster, T. Rovis, *Chem. Commun.* **2011**, *47*, 12074; f) K. D. Hesp, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2011**, *133*, 11430; g) C. Zhu, R. Wang, J. R. Falck, *Chem. Eur. J.* **2011**, *17*, 12591; h) J. Park, E. Park, A. Kim, Y. Lee, K.-W. Chi, J. H. Kwak, Y. H. Jung, I. S. Kim, *Org. Lett.* **2011**, *13*, 4390; i) L. Yang, C. A. Correia, C.-J. Li, *Adv. Synth. Catal.* **2011**, *353*, 1269; j) Y. Li, X.-S. Zhang, K. Chen, K.-H. He, F. Pan, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2012**, *14*, 636.

[7] K. Chen, H. Li, Y. Li, X.-S. Zhang, Z.-Q. Lei, Z.-J. Shi, *Chem. Sci.* **2012**, *3*, 1645.

[8] J. Wencel-Delord, C. Nimphius, F. W. Patureau, F. Glorius, *Angew. Chem.* **2012**, *124*, 2290; *Angew. Chem. Int. Ed.* **2012**, *51*, 2247.

[9] For selected examples of Pd-catalyzed C–H activation reactions with organoboron reagents, see: a) X. Chen, J. J. Li, C. E. Goodhue, J. Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 12634; b) R. Giri, N. Maugel, J.-J. Li, D.-H. Wang, S. P. Breazzano, L. B. Saunders, J.-Q. Yu, *J. Am. Chem. Soc.* **2007**, *129*, 3510; c) D. H. Wang, T. S. Mei, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 17676; d) S. D. Yang, C. L. Sun, Z. Fang, B. J. Li, Y.-Z. Li, Z.-J. Shi, *Angew. Chem.* **2008**, *120*, 1495; *Angew. Chem. Int. Ed.* **2008**, *47*, 1473; e) C.-L. Sun, N. Liu, B.-J. Li, D.-G. Yu, Y. Wang, Z.-J. Shi, *Org. Lett.* **2010**, *12*, 184; f) T. Nishikata, A. R. Abela, S. Huang, B. H. Lipshutz, *J. Am. Chem. Soc.* **2010**, *132*, 4978; g) M. J. Tredwell, M. Gulias, N. G. Bremeyer, C. C. C. Johansson, B. S. L. Collins, M. J. Gaunt, *Angew. Chem.* **2011**, *123*, 1108; *Angew. Chem. Int. Ed.* **2011**, *50*, 1076; h) Z. Shi, B. Li, X. Wan, J. Cheng, Z. Fang, B. Cao, C. Qin, Y. Wang, *Angew. Chem.* **2007**, *119*, 5650; *Angew. Chem. Int. Ed.* **2007**, *46*, 5554.

[10] a) N. Umeda, K. Hirano, T. Satoh, N. Shibata, H. Sato, M. Miura, *Org. Lett.* **2005**, *7*, 2229; b) S. Miyamura, H. Tsurugi, T. Satoh, M. Miura, *J. Organomet. Chem.* **2008**, *693*, 2438; c) T. Vogler, A. Studer, *Org. Lett.* **2008**, *10*, 129.

[11] a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2009**, *11*, 5198; b) T. Fukutani, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 2867.

[12] a) D. Weltin, V. Picard, K. Aupeix, M. Varin, D. Oth, J. Marchal, P. Dufour, P. Bischoff, *Int. J. Immunopharmac.* **1995**, *17*, 265; b) T. Harayama, H. Akamatsu, K. Okamura, T. Miyagoe, T. Akiyama, H. Abe, Y. Takeuchi, *J. Chem. Soc. Perkin Trans. 1* **2001**, 523; c) T. Harayama, T. Akiyama, Y. Nakano, K. Shibaike, H. Akamatsu, A. Hori, H. Abe, Y. Takeuchi, *Synthesis* **2002**, 237.

[13] a) G.-W. Wang, T.-T. Yuan, D.-D. Li, *Angew. Chem.* **2011**, *123*, 1416; *Angew. Chem. Int. Ed.* **2011**, *50*, 1380; b) J. Karthikeyan, C.-H. Cheng, *Angew. Chem.* **2011**, *123*, 10054; *Angew. Chem. Int. Ed.* **2011**, *50*, 9880.

[14] a) K. Parthasarathy, M. Jeganmohan, C.-H. Cheng, *Org. Lett.* **2008**, *10*, 325; b) V. S. Thirunavukkarasu, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2008**, *120*, 9604; *Angew. Chem. Int. Ed.* **2008**, *47*, 9462; c) V. S. Thirunavukkarasu, K. Parthasarathy, C.-H. Cheng, *Chem. Eur. J.* **2010**, *16*, 1436; d) P. Gandeepan, K. Parthasarathy, C.-H. Cheng, *J. Am. Chem. Soc.* **2010**, *132*, 8569; e) P. Gandeepan, C.-H. Cheng, *J. Am. Chem. Soc.* **2012**, *134*, 5738; f) K. Parthasarathy, N. Senthilkumar, J. Jayakumar, C.-H. Cheng, *Org. Lett.* **2012**, *14*, 3478.

[15] a) L. Li, W. W. Brennessel, W. D. Jones, *Organometallics* **2009**, *28*, 3492; b) L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 12414; c) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326.

[16] E. M. Simmons, J. F. Hartwig, *Angew. Chem.* **2012**, *124*, 3120; *Angew. Chem. Int. Ed.* **2012**, *51*, 3066.

