

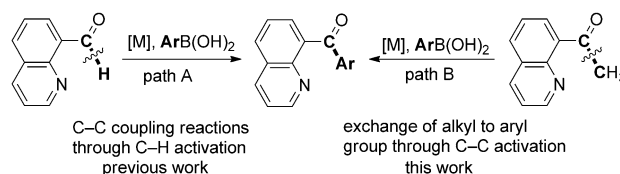
C–C Activation

Direct Exchange of a Ketone Methyl or Aryl Group to Another Aryl Group through C–C Bond Activation Assisted by Rhodium Chelation**

Jingjing Wang, Weiqiang Chen, Sujing Zuo, Lu Liu, Xinrui Zhang, and Jianhui Wang*

The development of transition-metal-catalyzed C–C bond cleavage has attracted much attention in recent years,^[1] because these reactions help chemists to form complex molecules through nontraditional retrosynthetic disconnections.^[2] Traditionally, C–C bond cleavage can be achieved by oxidative cyclometalation of three- or four-membered-ring compounds to form more stable metallacyclic complexes; these reactions are accompanied by the release of ring strain.^[3] For unstrained molecules, special driving forces are required to overcome the high kinetic barriers associated with the activation step of generating stable intermediates, such as the stability of the organometallic intermediates and the ketones that are produced during the catalytic selective C–C bond cleavage of tertiary alcohols.^[4] Directing a metal complex to a particular C–C bond using functional groups is another strategy that is commonly used for activation of unstrained C–C bond. This concept was first demonstrated in the early 1980s when a rhodium complex was used to catalyze the C–C bond cleavage of quinolinone derivatives at the 8 position;^[5] a five-membered ring (as favored in cyclometalation) was formed, and metal coordination to the nitrogen atoms in the ligands was directed to the α -ketone C–C bond. Since then, the idea of using assisted chelation for C–C activation has been extended to other systems.^[6d–g] Many important reaction models based on chelation-assisted C–C activation have been developed,^[2,6a–c,7] such as an intramolecular carboacylation reaction with acylquinolines,^[2] a catalytic decarbonylation reaction,^[7a] and a pyridinyl-directed alkenylation through bond cleavage of secondary arylmethanols.^[7c] The discovery of these reactions, which are based on C–C activation, has greatly enriched the methods available for the construction of complex molecules. However, compared with the diversity of synthetic methods that have been developed for C–H activation, reactions using C–C activation are relatively few. A variety of efficient methods for the activation of C–C bonds is highly desirable in order to use unstrained C–C σ bonds as versatile synthons for the formation of complex molecules, and there has been an intense focus in this area.

In contrast, transition-metal-catalyzed C–C bond formation through a coupling reaction of aryl halides and aryl boronic acids, called the Suzuki–Miyaura reaction,^[8] is an important synthetic tool for organic chemistry. Recently, many research groups have developed direct coupling reactions through transition-metal-catalyzed activation of aromatic C–H bonds directed by a functional group.^[9] For example, the reaction of a chelating aldehyde with iodoarenes or organostannanes in the presence of Pd and Ru as a cooperative catalyst gave the direct coupling products in high yields by means of C–H activation (Scheme 1,



Scheme 1. Coupling reactions through C–H or C–C activation.

path A).^[10] Similar to the recent emergence of C–H activation in synthetic chemistry, some articles have also reported C–C bond formation with arylboronic acid after cleavage of a C–CN or a C–COOR bond of a substrate.^[11] However, for reactions with olefins, there are only a few examples of C–C bond formations in ketones after chelation-assisted C–C activation.^[2,6] Herein, we report C–C bond formation in ketones through a chelation-assisted C–C activation. The ketone was reacted with arylboronic acid, which is the commonly used partner for coupling reactions (Scheme 1, path B). In a ketone that has an N-directing group, this reaction results in the direct exchange of a methyl or an aryl group to another aryl group.

To achieve this reaction, 1-(quinolin-8-yl)ethanone (**1a**) and phenylboronic acid (**2a**) were initially used as cross-coupling partners to optimize the reaction conditions (see the Supporting Information for details). The results show that the reaction gave the desired product **3a** in 93% yield when [Rh(PPh₃)₃Cl] (known as Wilkinson's catalyst) was used as the catalyst in combination with CuI (1 equiv) and K₂CO₃ (2 equiv) at 130 °C for 18 h. When Ru complexes were used as the catalyst, the desired product was obtained in less than 5% yield. These results clearly show the special reactivity of the Rh center for C–C activation.

Next, the reactions of **1a** with various arylboronic acids containing electron-donating or electron-withdrawing groups

[*] J.-J. Wang, W. Chen, S. Zuo, L. Liu, X. Zhang, Prof. Dr. J.-H. Wang
Department of Chemistry, College of Science Tianjin University
Tianjin 300072 (China)
E-mail: wjh@tju.edu.cn

[**] This work was supported by grants from the NSFC (21072149, 20872108).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201206693>.

Table 1: Catalytic coupling of acyl ketones with various arylboronic acids.^[a]

R^1-substituted quinoline-4-carbonyl + 2 R^2-B(OH)₂ $\xrightarrow[\text{xylene, air, 130}^\circ\text{C}]{[\text{Rh}(\text{PPh}_3)_3\text{Cl}], \text{K}_2\text{CO}_3, \text{CuI}}$ R^1-substituted quinoline-4-carbonyl-5-R^2 + Me-C₆H₄-R^2 (not isolated) X = C, or N							
3a (93%); (59%)^[b,c]	3b (85%)^[d]	3c (76%)^[d]	3d (83%)	3e (90%)^[d]	3f (87%)	3g (85%)	3h (74%)
3i (51%)	3j (94%)^[e]	3k (83%)^[e]	3l (57%)	3m (47%)	3n (57%)	3o (35%)	
3p (0%)	3q (0%)	3r (69%)^[c]	3s (65%)^[c]	3t (75%)^[c]	3u (81%)^[c]	3v (57%)^[c]	3w (89%)^[c]

[a] Reaction conditions: 1-(quinolin-8-yl)ethanone (0.10 mmol), substituted phenylboronic acid (0.25 mmol), CuI (0.20 mmol), K₂CO₃ (0.20 mmol), [Rh(PPh₃)₃Cl] (0.01 mmol, 10.0 mol%), xylene (0.5 mL), 130 °C, under air, 48 h; yields of isolated products are given based on **1a**. [b] Sodium tetraphenylborate was used as the substrate. [c] 18 h. [d] 36 h. [e] 24 h.

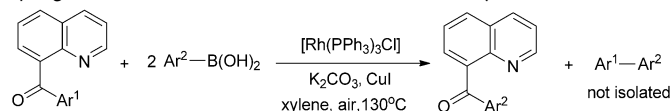
were explored using the optimized reaction conditions (Table 1). When **1a** was reacted with sodium tetraphenylborate, **3a** was obtained in 59% yield, however, the reaction of **1a** with phenylboronic acid gave **3a** in 93% yield. Longer reaction times (36 or 48 h) were required for arylboronic acids with electron-donating groups, but the reaction with **1a** gave the corresponding products **3b–3h** in good yields (74–90%). The reaction of **1a** with 3,4,5-trimethoxyphenylboronic acid gave the desired product **3i** in moderate yield (51%), because this boronic acid with its three strongly electron-donating groups is prone to be oxidized under the reaction conditions. β -Naphthaleneboronic acid also exhibited excellent reactivity under similar reaction conditions and gave the product **3j** in 94% yield. It should be noted that the arylboronic acids with halide substituents were stable in these coupling reactions. For example, arylboronic acids with a Cl, F, or Br substituent at the 4 position reacted with **1a** to give **3k**, **3l**, and **3m** in 83%, 57%, and 47% yield, respectively. Arylboronic acids with a strong electron-withdrawing group at the 4 position, such as COOEt or NO₂, gave products **3n** and **3o** in 57% and 35% yield, respectively, thus indicating that the electronic effect plays an important role in this reaction. Thiophen-2-ylboronic acid with its electron-rich heteroaromatic ring was also tested for the coupling reaction. The desired product **3p** was not isolated, which may be due to the strong complexation of the sulfur atom with the transition metal and its competition with the directing group of the substrate. Furthermore,

the arylboronic acid with a methyl group at the *ortho* position did not give product **3q**, thus indicating that these reactions are very sensitive to the steric hindrance of the boronic acid substrates. Substituents on the quinoline ring also affected the yield of the catalytic reaction. For example, the reaction of 1-(6-methylquinolin-8-yl)ethanone with phenylboronic acid gave product **3r** in 69% yield, which is significantly lower than the yield of the reaction with 1-(quinolin-8-yl)ethanone under similar conditions. When 1-(6-methoxyquinolin-8-yl)ethanone or 1-(5,6-dimethoxyquinolin-8-yl)ethanone were used, the quinoline rings of which bear one or two methoxy substituents, the substrates reacted with phenylboronic acid to give the desired products **3s** and **3t** in 65% and 75% yield, respectively. The reaction of 1-(5-chloroquinolin-8-yl)ethanone, which bears a Cl substituent at the 5 position of the quinoline ring, gave product **3u** in 81% yield. In addition, 1-(benzo[f]quinolin-5-yl)ethanone reacted with phenylboronic acid to give the desired product **3v** in 57% yield, and 1-(quinoxalin-5-yl)ethanone, which (as quinolines) also has an N atom at the appropriate position as a directing group, reacted with phenylboronic acid to give the desired product **3w** in 89% yield. These results clearly show that the direct exchange of a methyl to an aryl group can be achieved in ketones with an N-directing group, and that this reaction can occur with many different arylboronic acids under the optimized reaction conditions.

Further studies showed that phenyl(quinolin-8-yl)methanone (**3a**), which contains a C(sp²)–C bond, underwent similar conversions when it was reacted with substituted arylboronic acids under conditions similar to the above-mentioned studies. Rh-catalyzed coupling reactions of phenyl(quinolin-8-yl)methanone (**3a**) with an arylboronic acid that bears a methyl substituent at the *meta* or *para* position proceeded smoothly to give **3b** and **3c** in 52 % and 50 % yield, respectively (Table 2, entries 1 and 2). The reaction of arylboronic acids that bear different electron-donating

groups with phenyl ketone **3a** afforded the corresponding products **3d–3g** in 45–71 % yield (Table 2, entries 3–6). Furthermore, naphthalen-2-yl boronic acid reacted smoothly with **3a** to give the desired product **3j** in 55 % yield (Table 2, entry 7). However, no product was isolated when naphthalen-1-ylboronic acid was reacted with **3a**, again showing that steric hindrance has a significant impact on the reaction (Table 2, entry 8). Unfortunately, in sharp contrast to the electron-donating groups, an electron-withdrawing group on the aryl boronic acids inhibited the reaction of these

Table 2: The C(sp²)–C(sp²) bond coupling reaction of substituted ketones with various arylboronic acids.^[a]



Entry	Substrate	Product (Yield) ^[b]	Entry	Substrate	Product (Yield) ^[b]	Entry	Substrate	Product (Yield) ^[b]
1			8			15		
2			9			16		
3			10			17		
4			11			18		
5			12			19		
6			13			20		
7			14			21		

[a] Reactions conditions: (quinolin-8-yl)methanone (0.05 mmol), substituted phenylboronic acid (0.125 mmol, 2.5 equiv), CuI (0.10 mmol), K₂CO₃ (0.10 mmol), [Rh(PPh₃)₃Cl] (0.005 mmol, 10.0 mol %), xylene (0.5 mL), 130 °C, under air, 48 h. [b] Yields of isolated products are given. Biphenyl products were also observed, their yields are given in Table S3 in the Supporting Information.

substrates with **3a**. For example, an F-substituted aryl boronic acid displayed no reactivity under similar conditions (Table 2, entry 9) and again, an aryl boronic acid with an NO₂ substituent did not react with **3a** to give the desired product **3n**, thus indicating that the electronic effect has a strong impact on the outcome of the reaction (Table 2, entry 10).

A comparison of the reactivity of a specific arylborane with ketones **1** and **3** showed that the substituent of the ketone may also have a significant effect on the reaction. Thus, a series of substituted aryl ketones **3f–3o** were tested for the catalytic C–C bond grafting reaction with different arylboronic acids (Table 2, entries 11–21). Ketone **3f**, which bears an electron-donating methoxy group on the phenyl ring, was found to undergo a coupling reaction with 3,5-dimethylphenylboronic acid to form the desired product **3e** in 54% yield (Table 2, entry 11). It is worth noting that the yield of product **3c** increased to 95% when naphthalen-2-yl(quinolin-8-yl)methanone (**3j**) was reacted with 3-methylphenylboronic acid under standard reaction conditions (Table 2, entry 12). To gain further insight into the reaction, the reactions of some ketones with electron-withdrawing groups on the aromatic ring were also investigated. For instance, 4-chlorophenyl(quinolin-8-yl)methanone (**3k**) reacted with arylboronic acids that bear electron-donating groups to give the desired products in 66–72% yield (Table 2, entries 13–15). As in other Rh-catalyzed reactions,^[7a,12] a Cl substituent on the phenyl rings also worked in this catalytic system, which might allow further modification of the product. The reaction of 4-fluorophenyl(quinolin-8-yl)methanone (**3l**) with boronic acids that bear electron-donating groups proceeded smoothly to give the corresponding products in 61–70% yield (Table 2, entries 16–18). However, when 4-nitrophenylboronic acid, a substrate that bears a strong electron-withdrawing group, was used to react with the ketone **3l**, no product was obtained (Table 2, entry 19). In contrast, the reaction of 4-nitrophenyl(quinolin-8-yl)methanone (**3o**), a ketone that bears a strong electron-withdrawing group, with phenylboronic acid or 4-methoxyphenylboronic acid gave the desired products **3a** and **3f** in 93% and 91% yield, respectively (Table 2, entries 20 and 21).

Based on these findings and previous reports, the following reaction mechanism is proposed (Figure 1). First, a Rh^I complex activates an acetyl C–C bond of the chelating ketone **1a** to afford a five-membered cycloacyl Rh^{III} intermediate **A**.^[1,5,13] Transmetalation of **A** with arylboronic acid then gives intermediate **B**, in which the Rh center bears a methyl and an aryl group. Subsequent elimination of the methyl and phenyl groups on **B** lead to Rh^I intermediate **C** after a phosphine ligand insertion. The Rh^I complex **C** is then oxidized to Rh^{III} complex **D** by CuI in the presence of O₂.^[14] Another transmetalation of Rh^{III} complex **D** with arylboronic acid gives aryl Rh^{III} complex **E**. Finally, reductive elimination of **E** gave product **3a** and the Rh^I complex after the coordination of two phosphine ligands.

In this proposed mechanism, O₂ is the terminal oxidant. To prove this hypothesis, a catalytic reaction was conducted in an N₂ atmosphere using phenylboronic acid and **1a** as the reagents. In contrast to the 93% yield obtained in air, this reaction did not give **3a** in isolatable quantities, even after

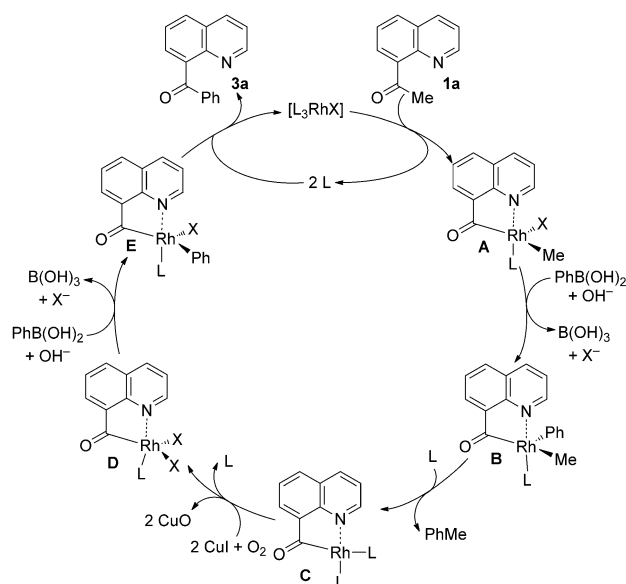
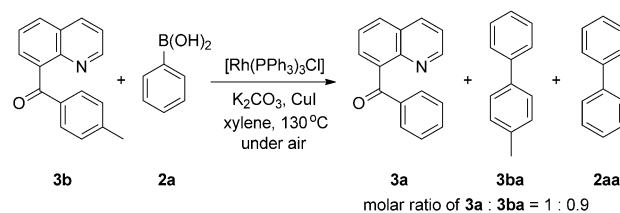


Figure 1. Proposed mechanism for the reaction of ketones with arylboronic acids catalyzed by [Rh(PPh₃)₃Cl].

a prolonged reaction time (48 h). On the other hand, the reaction proceeded very fast under an atmosphere of pure O₂ (1 atm); ketone **1a** was consumed completely in less than 12 h and the reaction gave **3a** in 72% yield along with some unidentified by-products. This evidence clearly points to the important role of O₂ in the catalytic cycle, and thus proves that the in situ oxidation of Rh^I to Rh^{III} by O₂ in the presence of CuI is the turnover-limiting step. Furthermore, the crude product mixture of **3b** and phenylboronic acid obtained under air was analyzed by ¹H NMR spectroscopy (Scheme 2). The integration results indicated that the crude product mixture contained **3a** and 4-methyl-1,1'-biphenyl (**3ba**) in a molar ratio of 1:0.9 (for the molar ratio of biphenyl and the substituted quinolinone derivative from other reaction systems, see Table S3 in the Supporting Information). This result proves that the reductive elimination of **B** to **C**, which is the key step, occurs (Figure 1). Although the key intermediates were not isolated, the above evidence confirm the proposed mechanism.

It should be noted that 8-benzoylquinolines have been frequently used as a core structure for the design of modern pharmaceuticals and related compounds,^[15] such as tubulin polymerization inhibitors,^[15a,b] cannabinoid (CB1) receptor ligands,^[15c] drugs for the treatment of bone metabolic disorders,^[15d] and antiulcer agents.^[15e] The current method



Scheme 2. Molar ratio of the product mixture.

offers a possible synthetic pathway to efficiently form similar compounds from readily available materials.

In conclusion, a new approach for ketone synthesis by a rhodium-catalyzed direct exchange of a ketone methyl or aryl group to another aryl group is described. A variety of different substituted quinolinone derivatives were obtained in moderate to good yields using commercially available quinolinone derivatives. Further efforts to expand the scope of this reaction are currently underway in our laboratories.

Received: August 18, 2012

Published online: November 4, 2012

Keywords: C–C activation · chelation · cross-coupling · quinolinones · rhodium

- [1] For reviews on C–C activation with a transition metal, see: a) S. M. Bonesi, M. Fagnoni, *Chem. Eur. J.* **2010**, *16*, 13572–13589; b) M. Tobisu, N. Chatani, *Chem. Soc. Rev.* **2008**, *37*, 300–307; c) D. Nečas, M. Kotora, *Curr. Org. Chem.* **2007**, *11*, 1566–1591; d) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610–618; e) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792; f) B. Rybtchinski, D. Milstein, *Angew. Chem.* **1999**, *111*, 918–932; *Angew. Chem. Int. Ed.* **1999**, *38*, 870–883; g) M. Murakami, Y. Ito, *Top. Organomet. Chem.* **1999**, *3*, 97–129; h) P. W. Jennings, L. L. Johnson, *Chem. Rev.* **1994**, *94*, 2241–2290.
- [2] A. M. Dreis, C. J. Douglas, *J. Am. Chem. Soc.* **2009**, *131*, 412–413.
- [3] Selected examples: a) T. Seiser, N. Cramer, *J. Am. Chem. Soc.* **2010**, *132*, 5340–5341; b) C. Winter, N. Krause, *Angew. Chem.* **2009**, *121*, 2497–2499; *Angew. Chem. Int. Ed.* **2009**, *48*, 2460–2462; c) H. Taniguchi, T. Ohmura, M. Sugimoto, *J. Am. Chem. Soc.* **2009**, *131*, 11298–11299; d) T. Matsuda, M. Shigeno, M. Murakami, *J. Am. Chem. Soc.* **2007**, *129*, 12086–12087; e) M. Murakami, S. Ashida, T. Matsuda, *J. Am. Chem. Soc.* **2005**, *127*, 6932–6933; f) S. C. Bart, P. J. Chirik, *J. Am. Chem. Soc.* **2003**, *125*, 886–887; g) S. Matsumura, Y. Maeda, T. Nishimura, S. Uemura, *J. Am. Chem. Soc.* **2003**, *125*, 8862–8869; h) S. Kim, D. Takeuchi, K. Osakada, *J. Am. Chem. Soc.* **2002**, *124*, 762–763; i) T. Nishimura, S. Uemura, *J. Am. Chem. Soc.* **2000**, *122*, 12049–12050.
- [4] a) M. Sai, H. Yorimitsu, K. Oshima, *Angew. Chem.* **2011**, *123*, 3352–3356; *Angew. Chem. Int. Ed.* **2011**, *50*, 3294–3298; b) M. Waibel, N. Cramer, *Angew. Chem.* **2010**, *122*, 4557–4560; *Angew. Chem. Int. Ed.* **2010**, *49*, 4455–4458; c) H. Miura, K. Wada, S. Hosokawa, M. Sai, T. Kondo, M. Inoue, *Chem. Commun.* **2009**, 4112–4114; d) R. Shintani, K. Takatsu, T. Hayashi, *Org. Lett.* **2008**, *10*, 1191–1193; e) T. Nishimura, H. Araki, Y. Maeda, S. Uemura, *Org. Lett.* **2003**, *5*, 2997–2999; f) Y. Terao, H. Wakui, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2001**, *123*, 10407–10408; g) T. Kondo, K. Kodoi, E. Nishinaga, T. Okada, Y. Morisaki, Y. Watanabe, T. Mitsudo, *J. Am. Chem. Soc.* **1998**, *120*, 5587–5588.
- [5] a) J. W. Suggs, C.-H. Jun, *J. Am. Chem. Soc.* **1986**, *108*, 4679–4681; b) J. W. Suggs, C.-H. Jun, *J. Am. Chem. Soc.* **1984**, *106*, 3054–3056; c) J. W. Suggs, S. D. Cox, *J. Organomet. Chem.* **1981**, *221*, 199–201.
- [6] a) J. P. Lutz, C. M. Rathbun, S. M. Stevenson, B. M. Powell, T. S. Boman, C. E. Baxter, J. M. Zona, J. B. Johnson, *J. Am. Chem. Soc.* **2012**, *134*, 715–722; b) C. M. Rathbun, J. B. Johnson, *J. Am. Chem. Soc.* **2011**, *133*, 2031–2033; c) M. T. Wentzel, V. J. Reddy, T. K. Hyster, C. J. Douglas, *Angew. Chem.* **2009**, *121*, 6237–6239; *Angew. Chem. Int. Ed.* **2009**, *48*, 6121–6123; d) Y. G. Park, J.-W. Park, C.-H. Jun, *Acc. Chem. Res.* **2008**, *41*, 222–234; e) C.-H. Jun, C. W. Moon, S.-G. Lim, H. Lee, *Org. Lett.* **2002**, *4*, 1595–1597; f) C.-H. Jun, H. Lee, S.-G. Lim, *J. Am. Chem. Soc.* **2001**, *123*, 751–752; g) C.-H. Jun, H. Lee, *J. Am. Chem. Soc.* **1999**, *121*, 880–881; h) J. W. Suggs, C.-H. Jun, *J. Chem. Soc. Chem. Commun.* **1985**, 92–93.
- [7] a) Z.-Q. Lei, H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, J. Sun, Z.-J. Shi, *Angew. Chem.* **2012**, *124*, 2744–2748; *Angew. Chem. Int. Ed.* **2012**, *51*, 2690–2694; b) K. Chen, H. Li, Y. Li, X.-S. Zhang, Z.-Q. Lei, Z.-J. Shi, *Chem. Sci.* **2012**, *3*, 1645–1649; c) H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, Z.-J. Shi, *J. Am. Chem. Soc.* **2011**, *133*, 15244–15247; d) D.-Y. Lee, B.-S. Hong, E.-G. Cho, H. Lee, C.-H. Jun, *J. Am. Chem. Soc.* **2003**, *125*, 6372–6373; e) D.-Y. Lee, I.-J. Kim, C.-H. Jun, *Angew. Chem.* **2002**, *114*, 3157–3159; *Angew. Chem. Int. Ed.* **2002**, *41*, 3031–3033; f) C.-H. Jun, H. Lee, C. W. Moon, H.-S. Hong, *J. Am. Chem. Soc.* **2001**, *123*, 8600–8601; g) C.-H. Jun, D.-Y. Lee, Y.-H. Kim, H. Lee, *Organometallics* **2001**, *20*, 2928–2931; h) N. Chatani, Y. Ie, F. Kakiuchi, S. Murai, *J. Am. Chem. Soc.* **1999**, *121*, 8645–8646.
- [8] a) C. Amatore, A. Jutand, G. LeDuc, *Angew. Chem.* **2012**, *124*, 1408–1411; *Angew. Chem. Int. Ed.* **2012**, *51*, 1379–1382; b) P.-P. Fang, A. Jutand, Z.-Q. Tian, C. Amatore, *Angew. Chem.* **2011**, *123*, 12392–12396; *Angew. Chem. Int. Ed.* **2011**, *50*, 12184–12188; c) P. J. Ellis, I. J. S. Fairlamb, S. F. J. Hackett, K. Wilson, A. F. Lee, *Angew. Chem.* **2010**, *122*, 1864–1868; *Angew. Chem. Int. Ed.* **2010**, *49*, 1820–1824; d) N. Hoshiya, M. Shimoda, H. Yoshikawa, Y. Yamashita, S. Shuto, M. Arisawa, *J. Am. Chem. Soc.* **2010**, *132*, 7270–7272; e) Y.-H. Chen, H.-H. Hung, M. H. Huang, *J. Am. Chem. Soc.* **2009**, *131*, 9114–9121; f) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147–168; g) N. Miyaura in *Advances in Metal-Organic Synthesis*, Vol. 6, JAI, London, **1998**, pp. 187–243.
- [9] a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655; b) M. C. Willis, *Chem. Rev.* **2010**, *110*, 725–748; c) G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447–2464; d) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074–1086; e) J. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013–1025; f) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238.
- [10] S. Ko, B. Kang, S. Chang, *Angew. Chem.* **2005**, *117*, 459–461; *Angew. Chem. Int. Ed.* **2005**, *44*, 455–457.
- [11] a) M. Tobisu, H. Kinuta, Y. Kita, E. Rémond, N. Chatani, *J. Am. Chem. Soc.* **2012**, *134*, 115–118; b) D. V. Gribkov, S. J. Pastine, M. Schnürch, D. Sames, *J. Am. Chem. Soc.* **2007**, *129*, 11750–11755.
- [12] a) D.-G. Yu, B.-J. Li, Z.-J. Shi, *Acc. Chem. Res.* **2010**, *43*, 1486–1495; b) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. deMeijere, F. Diederich), Wiley-VCH, New York, **2004**, and references therein; c) E. Negishi, *Handbook of Organopalladium Chemistry for Organic Synthesis*, Vol. 1 (Eds.: E. Negishi), Wiley-Interscience, New York, **2002**, pp. 213–1119.
- [13] a) D. Dowerah, L. J. Radonovich, N. F. Woolsey, *Organometallics* **1990**, *9*, 614–620; b) I. Omae, *Chem. Rev.* **1979**, *79*, 287–321.
- [14] a) K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, *72*, 5362–5367; b) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407–1409; c) J. M. Kisenyi, G. J. Sunley, J. A. Cabeza, A. J. Smith, H. Adams, N. J. Salt, P. M. Maitlis, *J. Chem. Soc. Dalton Trans.* **1987**, 2459–2466.
- [15] a) A. Zarghi, R. Ghodsi, *Bioorg. Med. Chem.* **2010**, *18*, 5855–5860; b) C.-Y. Nien, Y.-C. Chen, C.-C. Kuo, H.-P. Hsieh, C.-Y. Chang, J.-S. Wu, S.-Y. Wu, J.-P. Liou, J.-Y. Chang, *J. Med. Chem.* **2010**, *53*, 2309–2313; c) B. C. Thomas, C. A. James, D. E. Karol, S. Ulrich, *PCT Int. Appl.* 2002042248A2, **2002**; d) O. Teruo, S. Shigeki, I. Takayuki, U. Yasuji, Y. Tatsuya, Y. Noriko (Jpn. Kokai Tokkyo Koho), JP10291988A, **1998**; e) O. Yasuo, N. Juji, T. Haruki, S. Naokatsu, K. Hiroshi, Y. Shunei, I. Akio (Jpn. Kokai Tokkyo Koho), JP07173138A, **1995**.