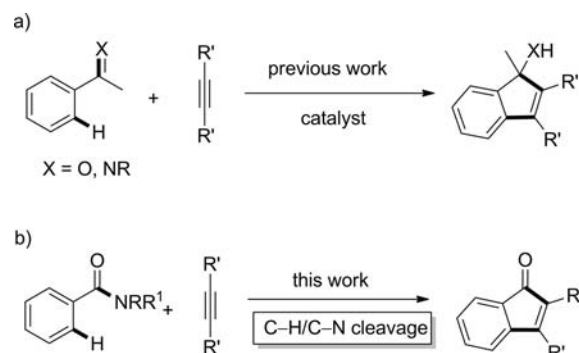


Rhodium/Copper-Catalyzed Annulation of Benzimides with Internal Alkynes: Indenone Synthesis through Sequential C–H and C–N Cleavage**

Bi-Jie Li, Hao-Yuan Wang, Qi-Lei Zhu, and Zhang-Jie Shi*

Indenones are valuable synthetic intermediates for natural products, ligand scaffolds, and material science.^[1] Traditional synthetic routes to indenones usually require multiple steps or have limited scope.^[2] Transition metal catalyzed approaches have begun to address some of these issues by providing various direct routes for their synthesis.^[3,4] Among these methods, several direct annulation reactions between alkyne and *ortho*-functionalized aldehydes, esters, or nitriles have developed as important synthetic entries,^[4] and some of them have been applied to organic synthesis.^[1a,f] However, these approaches require preactivation of the substrates, and this is both time and cost consuming in a synthetic sequence. Therefore, the development of a facile synthetic pathway to indenone from easily available starting materials is highly desirable.

The underlying synthetic logic of C–H functionalization would meet these requirements.^[5] In particular, catalytic direct annulations of phenyl imine and phenone with alkynes have been developed for the synthesis of indenyl amine and indenol, respectively (Scheme 1a).^[6] Inspired by these developments, we envisioned that by using a directing group at the ester or amide oxidation level, annulation with an alkyne would directly provide the indenone product (Scheme 1b). However, the choice of a proper directing group for the designed annulation is challenging. First, the ester or amide should have sufficient electron density to coordinate with the metal center to facilitate *ortho* metallation and, at the same time, exhibit substantial electrophilicity to react with the C–M bond obtained by alkyne insertion. Second, although the addition of transition-metal organometallic species to a carbonyl group is well known,^[7] its reaction with less reactive electrophiles such as ester or amide groups is more difficult.^[8] In fact, transition metal catalyzed C–N bond



Scheme 1. a) Addition of C–M bond to ketone/imine through C–H cleavage. b) Addition of C–M bond to imide through C–H and C–N cleavage.

cleavage in amides or imides is particularly rare.^[9] Finally, the reaction of an organometallic reagent with ester or amide generates a ketone product which is typically more reactive than the starting material, thus further complicating such an addition process. Nonetheless, if the desired annulation is successfully implemented, this process would allow the straightforward synthesis of diverse indenones from abundant and essentially unfunctionalized benzoic acid derivatives. Given our continuing interest in the addition of C–H bonds to polar functionalities,^[10,11] we report herein a rhodium(III)-catalyzed annulation of benzimides with alkynes for the synthesis of indenones which involves an uncommon acylation of organorhodium(III) with an imide motif.

At the outset of our study, we realized that the choice of a proper directing group would be crucial for the reaction development (Table 1). A cationic rhodium complex was selected as the catalyst because of its established diverse reactivity.^[12–14] As expected, simple benzamides did not undergo the desired annulation reaction since they are good substrates for either C–H/N–H annulation or hydroarylation (entries 1 and 2).^[12,13b] The use of *N*-acylbenzamides as the substrates, however, provided some indenone product albeit in low to moderate yields (entries 3 and 4). A higher yield was obtained by using *N*-benzoyloxazolidinone as the substrate, thus indicating that it has the appropriate balance between directing ability and electrophilicity (entry 5). Interestingly, *N*-acyloxazolidinone has rarely been used as a directing group for C–H functionalization.^[5] In addition, the oxazolidinone auxiliary is quite stable. It can be carried through a multistep synthesis,^[15] and generally requires the addition of organolithium or Grignard reagents to cleave the C–N bond for C–C formation.^[16] A catalytic amount of copper acetate as an

[*] B.-J. Li, H.-Y. Wang, Q.-L. Zhu, Prof. Dr. Z.-J. Shi
Beijing National Laboratory of Molecular Sciences (BNLMS) and
Key Laboratory of Bioorganic Chemistry and Molecular Engineering
of Ministry of Education, College of Chemistry and Molecular
Engineering and Green Chemistry Center
Peking University, Beijing, 100871 (China)
E-mail: zshi@pku.edu.cn

Prof. Dr. Z.-J. Shi
State Key Laboratory of Organometallic Chemistry
Chinese Academy of Sciences, Shanghai 200032 (China)

[**] Support of this work by the “973” Project from the MOST of China (2009CB825300) and NSFC (Nos. 20925207, and 21002001) is gratefully acknowledged.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201200271>.

Table 1: Reaction development.

Entry	NRR'	Additive	Solvent	Yield [%] ^[b]
1	NHMe	Cu(OAc) ₂	decalin	0
2	NMe ₂	Cu(OAc) ₂	decalin	0
3	NMe(Ac)	Cu(OAc) ₂	decalin	5
4		Cu(OAc) ₂	decalin	32
5		Cu(OAc) ₂	decalin	80 (76)
6		AgOAc	decalin	20
7		HOAc	decalin	10
8		–	decalin	< 5
9		Cu(OAc) ₂	toluene	< 5
10		Cu(OAc) ₂	PhCF ₃	74
11		Cu(OAc) ₂	dioxane	42
12		Cu(OAc) ₂	<i>t</i> -AmylOH	< 5

[a] Reaction conditions: 0.2 mmol of **1**, 0.3 mmol of **2a**, 0.01 mmol Rh catalyst, 0.04 mmol of additive, 2 mL of solvent, 12 h. [b] Yields determined by GC analysis using *n*-dodecane as an internal standard. Yield of isolated product given within parentheses. Decalin = decahydronaphthalene, Cp* = C₅Me₅.

additive is sufficient for the reaction, but its absence or a change to other additives provided either no product or low yields (entries 6–8). We have also tested several other Lewis acids such as Zn(OTf)₂, Cu(OTf)₂, Sc(OTf)₃, but none of them gave the desired product, presumably because of the lack of an OAc anion, which is essential for C–H cleavage. The reaction worked better in nonpolar solvents than in polar ones (entries 9–12). No reaction occurred in the absence of a rhodium catalyst.

Having the optimized reaction conditions, we tested various benzimidides (Table 2). Electron-donating groups at the *para* position of the aryl ring slightly decreased the yield, presumably because of the decreased electrophilicity of the imide which slows the addition of the C–Rh intermediate to the carbonyl group (**3a–f**). Electron-withdrawing groups and various halides including fluoro, chloro, and bromo groups were well tolerated (**3g–j**). Acetate and benzoate ester groups, which are at the same oxidation level as imide, were also accommodated (**3k,l**). The reaction of *meta*-methyl- or bromo-substituted benzimidide gave a single regioisomer (**3m,n**). The annulation selectively occurred at the less sterically hindered position. Multisubstituted indenones were also easily accessible by the annulation process, regardless of the presence of an electron-donating or electron-withdrawing groups (**3o–p'**). Interestingly, 3,5-difluorobenzimidide reacted faster than the unsubstituted one, thus suggesting a potential concerted metallation/deprotonation mechanism for C–H cleavage.^[17] The synthesis of the functionalized indenone product **3p'** is of particular interest because it closely resembles the synthetic intermediate for pauciflorol F,^[1a] thus illustrating the synthetic potential of the reaction. An *ortho*-methyl substituent significantly lowered

Table 2: Substrate scope for benzimidides.^[a]

3a: R = H, 76% 3b: R = Me, 71% 3c: R = <i>i</i> Bu, 68% 3d: R = Ph, 64% 3e: R = OPh, 69% 3f: R = OMe, 61% 3g: R = CF ₃ , 60% 3h: R = F, 73% 3i: R = Cl, 71% 3j: R = Br, 76% 3k: R = OAc, 74% 3l: R = CO ₂ Me, 50%				
3m: 63% 3n: 60% 3o: 89%				
3p: Ar = Ph, 85% 3p': Ar = 4-MeOC ₆ H ₄ , 90% 3q: 12%				
3r: 54%				

[a] Reaction conditions: 0.2 mmol of **1**, 0.3 mmol of **2a**, 0.01 mmol of Rh catalyst, 0.04 mmol of Cu(OAc)₂, 2 mL of decalin. Yields are reported for the isolated products.

the yield (**3q**). In comparison, an improved yield was obtained by using a less bulky methoxy group at the *ortho* position (**3r**).

Next we investigated the scope of the alkynes (Table 3). Diarylalkynes having various electron-donating and electron-withdrawing groups reacted without incident to give high yields, except *ortho*-substituted diphenylacetylene, wherein the steric hindrance largely inhibited the reaction (**3s–ab**). Functional groups such as methoxy and halide groups were

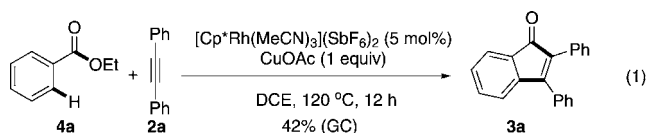
Table 3: Substrate scope for alkynes.^[a]

3s: Ar = 2-MeC ₆ H ₄ , <10% 3t: Ar = 3-MeC ₆ H ₄ , 80% 3u: Ar = 3,5-Me ₂ C ₆ H ₃ , 70% 3v: Ar = 3-ClC ₆ H ₄ , 81% 3w: Ar = 4-MeOC ₆ H ₄ , 85% 3x: Ar = 4-MeC ₆ H ₄ , 73% 3y: Ar = 4-FC ₆ H ₄ , 84% 3z: Ar = 4-ClC ₆ H ₄ , 79% 3aa: Ar = 4-BrC ₆ H ₄ , 77% 3ab: Ar = 4-CF ₃ C ₆ H ₄ , 79%				
3ac: 46% (6.7:1) ^[b] 3ad: 81% (5.8:1) 3ae: 78% (3.3:1)				
3af: 44% (>20:1) 3ag: 67% (2.2:1) 3ah: < 10%				

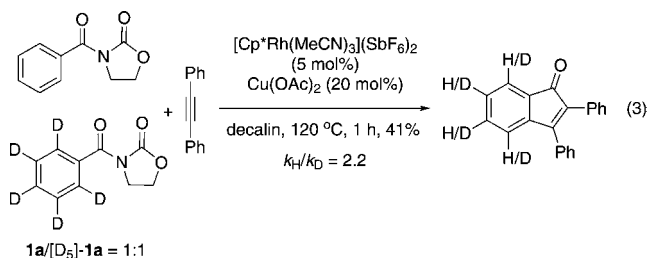
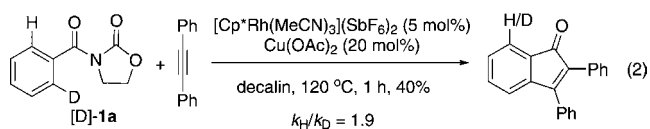
[a] Reaction conditions: 0.2 mmol of **1a**, 0.3 mmol of **2**, 0.01 mmol of Rh catalyst, 0.04 mmol of Cu(OAc)₂, 2 mL of decalin. Yields are reported for the isolated products. Ratios of regioisomers are given within parentheses and were determined by NMR analysis. Major isomers are shown. [b] 10 mol % catalyst.

tolerated. An aryl alkyl alkyne, however, exhibited lower reactivity (**3ac**). By using the more reactive 3,5-difluorobenzimide substrate, the reaction with 1-phenylpropyne and 1-phenylpentyne proceeded with high yields and moderate selectivity (**3ad**, **ae**). Presumably as a result of its increased bulkiness, the reaction of 1-phenylcyclopropylacetylene gave decreased yield but with exclusive regioselectivity (**3af**). A conjugated enyne also participated in the annulation, thus providing a 2:1 ratio of regioisomers (**3ag**). The ratio could be attributed to the similarity in the electronic effects of phenyl and vinyl groups. In the reactions of these unsymmetrical alkynes, the phenyl group is selectively placed in proximity to the carbonyl group, which is in agreement with previous annulation reactions.^[12] A dialkyl alkyne, which lacks a phenyl substituent as the activating group through conjugation, failed to undergo the desired reaction (**3ah**). Trimethylsilyl-substituted phenylacetylene did not react, either.

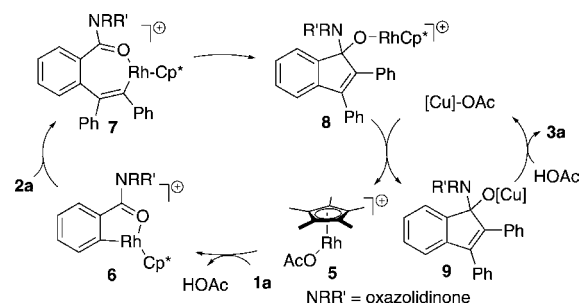
Although benzoic ester was tolerated in the current catalytic system (**3i**), a switch in the copper salt and solvent also allows it to engage in the annulation reaction, albeit in moderate yield [Eq. (1)]. This is the first example of direct annulation of benzoic ester with an alkyne through directed C–H functionalization.



To gain insight into the mechanism, we performed deuterium-labeling experiments [Eqs. (2) and (3)]. The intramolecular and intermolecular kinetic isotopic effects were determined to be 1.9 and 2.2, respectively, thus suggesting that C–H cleavage was involved in the rate-determining step.



Although the reaction mechanism remains to be elucidated, we tentatively propose the following reaction pathway (Scheme 2). Coordination of benzimide to the cationic rhodium species **5** and subsequent C–H cleavage forms the five-membered rhodacycle **6**. Then alkyne insertion gives the



Scheme 2. Mechanistic proposal.

seven-membered intermediate **7**, which undergoes an intramolecular insertion of the carbonyl group into the vinyl–Rh bond. Transmetalation between copper acetate and the rhodium alkoxide **8** takes place to regenerate the catalyst with formation of the copper alkoxide **9**, which decomposes to form the product and release the copper species. The beneficial effect of copper salt may also originate from the increased electrophilicity of imide moiety upon coordination with copper,^[18] thus facilitating the insertion of the carbonyl group into the C–Rh bond.

In conclusion, we have developed a cationic rhodium-catalyzed annulation between benzimides and alkynes for the synthesis of indenones. The proper directing ability and electrophilicity of the imide group provides a handle for the annulation with concomitant C–H and C–N cleavage. Starting from easily available benzimide derivatives, a range of functionalized indenone products are obtained. Since the reaction is redox neutral, only catalytic amounts of rhodium and copper salts are required. The reaction involves a challenging nucleophilic addition of an organorhodium species to an imide. We expect that more synthetically useful and mechanistically novel transformations can be developed through exploitation of the nucleophilicity of organometallic species generated by C–H activation.

Experimental Section

General procedures: *N*-benzoyloxazolidin-2-one **1a** (0.20 mmol, 38.2 mg), diphenylacetylene **2a** (0.30 mmol, 53.4 mg), [Cp*Rh(MeCN)₃](SbF₆)₂ (5 mol %, 0.01 mmol, 8.3 mg), Cu(OAc)₂ (20 mol %, 0.04 mmol, 7.3 mg) were weighed in the air and charged into an oven-dried 25 mL Schlenk tube. The tube was evacuated and refilled with N₂, which was repeated for three times. After addition of 2 mL of decalin under a positive pressure of N₂ via syringe, the sealed tube was placed in a 120 °C oil bath and stirred for 12 h. After completion, the reaction mixture was cooled down to room temperature and directly purified by flash column chromatography eluting with CH₂Cl₂ and petroleum ether (1:2).

Received: January 11, 2012

Published online: March 6, 2012

Keywords: annulation · C–H activation · heterocycles · rhodium · synthetic methods

[1] a) J. L. Jeffrey, R. Sarpong, *Org. Lett.* **2009**, *11*, 5450; b) W. M. Clark, A. M. Tickner-Eldridge, G. K. Huang, L. N. Pridgen,

- M. A. Olsen, R. J. Mills, I. Lantos, N. H. Baine, *J. Am. Chem. Soc.* **1998**, *120*, 4550; c) G. M. Anstead, S. R. Wilson, J. A. Katzenellenbogen, *J. Med. Chem.* **1989**, *32*, 2163; d) Q. Xi, W. Zhang, X. Zhang, *Synlett* **2006**, 945; e) E. V. Banide, C. O'Connor, N. Fortune, Y. Ortin, S. Milosevic, H. Müller-Bunz, M. J. McGlinchey, *Org. Biomol. Chem.* **2010**, *8*, 3997; f) K. Morinaka, T. Ubukata, Y. Yokoyama, *Org. Lett.* **2009**, *11*, 3890.
- [2] a) C. S. Marvel, C. W. Hinman, *J. Am. Chem. Soc.* **1954**, *76*, 5435; b) H. Martens, G. Hoornaert, *Tetrahedron* **1974**, *30*, 3641; c) M. B. Floyd, G. R. Allen, Jr., *J. Org. Chem.* **1970**, *35*, 2647; d) P. Galatsis, J. J. Manwell, J. M. Blackwell, *Can. J. Chem.* **1994**, *72*, 1656.
- [3] a) Y. Kuninobu, T. Matsuki, K. Takai, *Org. Lett.* **2010**, *12*, 2948; b) Y. Harada, J. Nakanishi, H. Fujihara, M. Tobisu, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2007**, *129*, 5766; c) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani, T. Nishioka, *Org. Lett.* **2009**, *11*, 1777; d) T. Fukuyama, N. Chatani, F. Kakiuchi, S. Murai, *J. Org. Chem.* **1997**, *62*, 5647; e) K. Kokubo, K. Matsumasa, M. Miura, M. Nomura, *J. Org. Chem.* **1996**, *61*, 6941; f) A. Padwa, D. J. Austin, Y. Gareau, J. M. Kassir, S. L. Xu, *J. Am. Chem. Soc.* **1993**, *115*, 2637; g) N. P. Robinson, G. J. Depree, R. W. de Wit, L. Main, B. K. Nicholson, *J. Organomet. Chem.* **2005**, *690*, 3827; h) N. P. Robinson, L. Main, B. K. Nicholson, *J. Organomet. Chem.* **1989**, *364*, C37.
- [4] a) R. C. Larock, M. J. Doty, *J. Org. Chem.* **1993**, *58*, 4579; b) R. C. Larock, Q. Tian, A. A. Pletnev, *J. Am. Chem. Soc.* **1999**, *121*, 3238; c) T. Miura, M. Murakami, *Org. Lett.* **2005**, *7*, 3339; d) H. Tsukamoto, Y. Kondo, *Org. Lett.* **2007**, *9*, 4227.
- [5] a) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633; b) M. Miura, M. Nomura, *Top. Curr. Chem.* **2002**, *219*, 211; c) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731; d) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; e) K. Godula, D. Sames, *Science* **2006**, *312*, 67; f) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173; g) M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; h) M. S. Chen, M. C. White, *Science* **2007**, *318*, 783; i) X. Chen, K. M. Engle, D. H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; j) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074; k) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; l) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335; m) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; n) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; o) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677; p) R. Jazzar, H. Julien, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654; q) I. A. I. Mkhali, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890; r) W. R. Gutekunst, P. S. Baran, *Chem. Soc. Rev.* **2011**, *40*, 1976; s) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; t) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; u) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; v) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* **2011**, *111*, 1780.
- [6] a) F. W. Patureau, T. Besset, N. Kuhl, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2154; b) K. Muralirajan, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2011**, *123*, 4255; *Angew. Chem. Int. Ed.* **2011**, *50*, 4169; c) Y. Kuninobu, Y. Tokunaga, A. Kawata, K. Takai, *J. Am. Chem. Soc.* **2006**, *128*, 202; d) Z.-M. Sun, S.-P. Chen, P. Zhao, *Chem. Eur. J.* **2010**, *16*, 2619; e) D. N. Tran, N. Cramer, *Angew. Chem.* **2011**, *123*, 11294; *Angew. Chem. Int. Ed.* **2011**, *50*, 11098. For related annulation: f) T. Fukutani, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Commun.* **2009**, 5141; g) D. N. Tran, N. Cramer, *Angew. Chem.* **2010**, *122*, 8357; *Angew. Chem. Int. Ed.* **2010**, *49*, 8181.
- [7] a) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763; b) M. Sakai, M. Ueda, N. Miyaoura, *Angew. Chem.* **1998**, *110*, 3475; *Angew. Chem. Int. Ed.* **1998**, *37*, 3279; c) H. Nakamura, K. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 4242; d) C. Krug, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 1674; e) G. Liu, X. Lu, *J. Am. Chem. Soc.* **2006**, *128*, 16504.
- [8] a) H. Urabe, K. Suzuki, F. Sato, *J. Am. Chem. Soc.* **1997**, *119*, 10014; b) R. Shintani, K. Okamoto, Y. Otomaru, K. Ueyama, T. Hayashi, *J. Am. Chem. Soc.* **2005**, *127*, 54; c) T. Miura, T. Sasaki, H. Nakazawa, M. Murakami, *J. Am. Chem. Soc.* **2005**, *127*, 1390; d) D. Solé, O. Serrano, *Angew. Chem.* **2007**, *119*, 7408; *Angew. Chem. Int. Ed.* **2007**, *46*, 7270; e) Y.-B. Zhao, B. Mariampillai, D. A. Candito, B. Laleu, M. Li, M. Lautens, *Angew. Chem.* **2009**, *121*, 1881; *Angew. Chem. Int. Ed.* **2009**, *48*, 1849; f) M. Ohashi, T. Taniguchi, S. Ogoshi, *J. Am. Chem. Soc.* **2011**, *133*, 14900.
- [9] Ni: a) A. D. Jenkins, A. Herath, M. Song, J. Montgomery, *J. Am. Chem. Soc.* **2011**, *133*, 14460; b) Y. Kajita, S. Matsubara, T. Kurahashi, *J. Am. Chem. Soc.* **2008**, *130*, 6058; Pd: c) D. Solé, O. Serrano, *J. Org. Chem.* **2008**, *73*, 9372.
- [10] a) 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; b) B.-J. Li, Z.-J. Shi, *Chem. Sci.* **2011**, *2*, 488; c) Y. Li, X.-S. Zhang, K. Chen, K.-H. He, F. Pan, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2012**, *14*, 636; d) Y. Li, X.-S. Zhang, H. Li, W.-H. Wang, K. Chen, B.-J. Li, Z.-J. Shi, *Chem. Sci.* **2012**, DOI: 10.1039/C2SC01081J.
- [11] a) W. D. Jones, G. P. Foster, J. M. Putinas, *J. Am. Chem. Soc.* **1987**, *109*, 5047; b) Y. Fukumoto, K. Sawada, M. Hagihara, N. Chatani, S. Murai, *Angew. Chem.* **2002**, *114*, 2903; *Angew. Chem. Int. Ed.* **2002**, *41*, 2779; c) C. Zhou, R. C. Larock, *J. Am. Chem. Soc.* **2004**, *126*, 2302; d) Y. Kuninobu, Y. Nishina, C. Nakagawa, K. Takai, *J. Am. Chem. Soc.* **2006**, *128*, 12376; e) Y. Kuninobu, Y. Nishina, T. Takeuchi, K. Takai, *Angew. Chem.* **2007**, *119*, 6638; *Angew. Chem. Int. Ed.* **2007**, *46*, 6518; f) Y. Kuninobu, Y. Fujii, T. Matsuki, Y. Nishina, K. Takai, *Org. Lett.* **2009**, *11*, 2711; g) K. Tsuchikama, Y. Hashimoto, K. Endo, T. Shibata, *Adv. Synth. Catal.* **2009**, *351*, 2850; h) B. Qian, S. Guo, J. Shao, Q. Zhu, L. Yang, C. Xia, H. Huang, *J. Am. Chem. Soc.* **2010**, *132*, 3650; i) Y. Tan, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 3676; j) H. Mizuno, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 1251; k) A. S. Tsai, M. E. Tauchert, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2011**, *133*, 1248; l) K. D. Hesp, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2011**, *133*, 11430; m) L. Yang, C. A. Correia, C.-J. Li, *Adv. Synth. Catal.* **2011**, *353*, 1269.
- [12] For a review: a) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212. For heterocycle synthesis: b) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407; c) L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 12414; d) N. Guimond, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 12050; e) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585; f) T. K. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565; g) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326; h) K. Morimoto, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 2068; i) J. Chen, G. Song, C.-L. Pan, X. Li, *Org. Lett.* **2010**, *12*, 5426; j) P. C. Too, Y.-F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688; k) M. P. Huestis, L. Chan, D. R. Stuart, K. Fagnou, *Angew. Chem.* **2011**, *123*, 1374; *Angew. Chem. Int. Ed.* **2011**, *50*, 1338; l) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; m) T. K. Hyster, T. Rovis, *Chem. Sci.* **2011**, *2*, 1606.
- [13] a) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, *Angew. Chem.* **2008**, *120*, 4083; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019; b) D. J. Schipper, M. Hutchinson, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6910; c) F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem.* **2011**, *123*, 1096; *Angew. Chem. Int. Ed.* **2011**, *50*, 1064; d) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350; e) A. S. Tsai, M. Brasse, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2011**, *13*, 540; f) S. H. Park, J. Y. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2372; g) T.-J. Gong, B. Xiao, Z.-J. Liu,

- J. Wan, J. Xu, D.-F. Luo, Y. Fu, L. Liu, *Org. Lett.* **2011**, *13*, 3235; 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.
- [14] For selected other metal-catalyzed annulations: a) L. Ackermann, A. V. Lygin, N. Hofmann, *Angew. Chem.* **2011**, *123*, 6503; *Angew. Chem. Int. Ed.* **2011**, *50*, 6379; b) Z. Shi, S. Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 8035; *Angew. Chem. Int. Ed.* **2009**, *48*, 7895; c) R. Bernini, G. Fabrizi, A. Sferrazza, S. Cacchi, *Angew. Chem.* **2009**, *121*, 8222; *Angew. Chem. Int. Ed.* **2009**, *48*, 8078; d) B. Li, H. Feng, S. Xu, B. Wang, *Chem. Eur. J.* **2011**, *17*, 12573; e) P. Hu, S. Huang, J. Xu, Z.-J. Shi, W. Su, *Angew. Chem.* **2011**, *123*, 10100; *Angew. Chem. Int. Ed.* **2011**, *50*, 9926.
- [15] D. J. Ager, I. Prakash, D. R. Schaad, *Chem. Rev.* **1996**, *96*, 835.
- [16] a) M.-R. Tsai, B.-F. Chen, C.-C. Cheng, N.-C. Chang, *J. Org. Chem.* **2005**, *70*, 1780; b) S. Mantecón, J. J. Vaquero, J. Alvarez-Builla, M. L. Puente, J. F. Espinosa, J. Ezquerro, *Org. Lett.* **2003**, *5*, 3791; c) E. García, S. Arrasate, E. Lete, N. Sotomayor, *J. Org. Chem.* **2005**, *70*, 10368; d) A. Giovannini, D. Savoia, A. Umani-Ronchi, *J. Org. Chem.* **1989**, *54*, 228; e) C. M. Jensen, K. B. Lindsay, R. H. Taaning, J. Karaffa, A. M. Hansen, T. Skrydstrup, *J. Am. Chem. Soc.* **2005**, *127*, 6544.
- [17] a) D. Lapointe, K. Fagnou, *Chem. Lett.* **2010**, *39*, 1118; b) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315; c) D. L. Davies, S. M. A. Donald, S. A. Macgregor, *J. Am. Chem. Soc.* **2005**, *127*, 13754; d) D. L. Davies, S. M. A. Donald, O. Al-Duaij, S. A. Macgregor, M. Pölleth, *J. Am. Chem. Soc.* **2006**, *128*, 4210; e) L. Li, W. W. Brennessel, W. D. Jones, *Organometallics* **2009**, *28*, 3492.
- [18] D. A. Evans, S. J. Miller, T. Lectka, P. von Matt, *J. Am. Chem. Soc.* **1999**, *121*, 7559.