C–H Activation

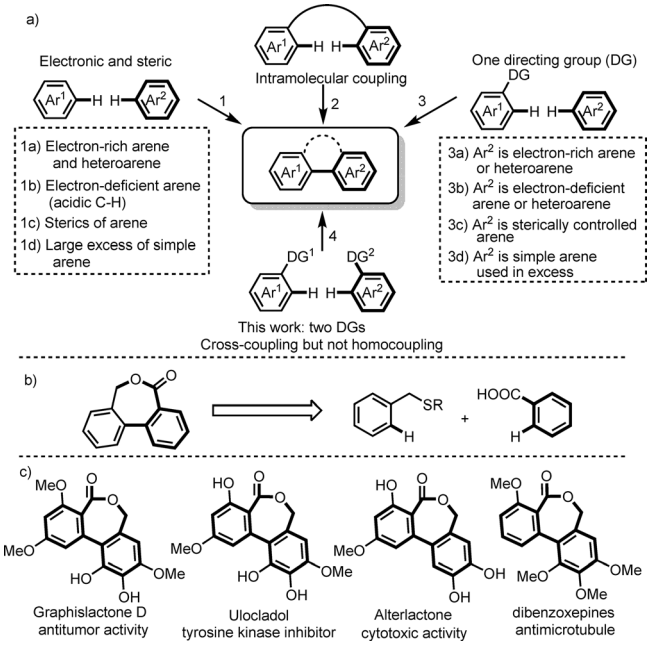
International Edition: DOI: 10.1002/anie.201500486
German Edition: DOI: 10.1002/ange.201500486

Synthesis of Dibenzo[c,e]oxepin-5(7*H*)-ones from Benzyl Thioethers and Carboxylic Acids: Rhodium-Catalyzed Double C–H Activation Controlled by Different Directing Groups**

*Xi-Sha Zhang, Yun-Fei Zhang, Zhao-Wei Li, Fei-Xian Luo, and Zhang-Jie Shi**

Abstract: *A rhodium(III)-catalyzed cross-coupling of benzyl thioethers and aryl carboxylic acids through the two directing groups is reported. Useful structures with diverse substituents were efficiently synthesized in one step with the cleavage of four bonds (C–H, C–S, O–H) and the formation of two bonds (C–C, C–O). The formed structure is the privileged core in natural products and bioactive molecules. This work highlights the power of using two different directing groups to enhance the selectivity of a double C–H activation, the first of such examples in cross-oxidative coupling.*

Biaryl compounds are important structures in organic synthesis, materials chemistry, and drug molecules.[1] In biaryl synthesis, the use of selective double C–H bond activation[2] usually leads to a mixture of regioisomers. However, nondirecting strategies can be utilized,[3] including the control of electronics,[4] sterics,[5] and use of an excess[6] of substrates (Scheme 1a, see 1a–d). To further control the regioselectivity and enhance the reactivity, an intramolecular strategy was designed and applied to construct fused rings[7,8] (Scheme 1a, see 2). Another efficient and widely used strategy is the introduction of a directing group to one of the two partners (Scheme 1a, see 3). Having controlled the regioselectivity of C–H activation in one arene, the selectivity of the second C–H activation was always ensured by selection of electron-rich,[9] electron-deficient,[10] or bulky[11] substrates (Scheme 1a, see 3a–c). All these strategies suffer from the limitation of either substrate scope or relatively poor regioselectivity. Our hypothesis to solve this problem was to control the selectivity of a double C–H bond activation by using two directing groups, thus introducing a second directing group to the second arene partner (Scheme 1a, see 4). This novel approach is unknown, although there are a few examples of the homocoupling of arenes with directing groups.[12]



Scheme 1. New strategy to for the direct oxidative coupling of two different arenes based on control by two directing groups.

Herein we use a thioether and carboxylic acid as directing groups in the designed double C–H cross-coupling reaction. Our choice in directing group derives from the wide application of carboxylic acids as directing groups in palladium[13] and rhodium[14] catalysis, and our previous interest in the development of thioethers as directing groups in C–H activation,[15] especially in rhodium catalysis[16] (Scheme 1b). More interestingly, during our study we finally found that after the double C–H coupling, in situ intramolecular cyclization generated a dibenzo[*c*,*e*]oxepin-5(7*H*)-one. From this aspect, this reaction was ideal because after the reaction the thioether directing group could be removed in situ[17] and the carboxylic acid group became part of the product.[18]

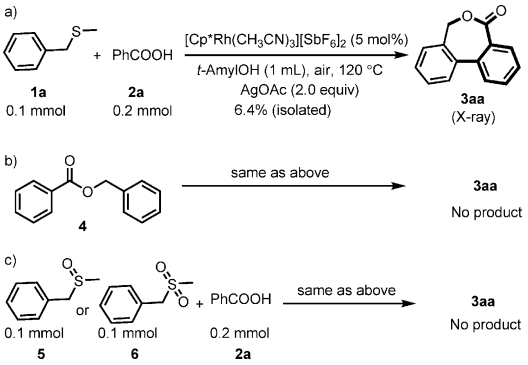
Dibenzooxepinones and their analogues can be found in natural products and bioactive molecules (Scheme 1c).[19] Antitumor activity,[19a] tyrosine kinase inhibition activity,[19b,d] cytotoxic activity,[19c,20] and antimicrotubule activity[21] have been investigated for some of these molecules. Traditionally, this dibenzo[*c*,*e*]oxepin-5(7*H*)-one structure was constructed by a sequence of conventional cross-coupling and C–O bond-forming cyclization. For example, the biphenyl structure was mainly constructed from organohalides and/or organometal-

[*] X.-S. Zhang, Y.-F. Zhang, Z.-W. Li, F.-X. Luo, 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/anie.201500486.

lic reagents.[19b,20–22] For the cyclization step, it is essential that two functional groups be installed at the *ortho* positions.[19b,22,23] The multistep sequence and the prefunctionalization of starting materials make the synthesis complicated and non-economical. Herein, with our direct one-step method, the starting materials are very simple and readily available. Notably, prefunctionalization to prepare organohalides and organometallic reagents was avoided.

Our initial studies indicated that the oxidative coupling product **3aa** was observed in 6% yield upon isolation from the reaction of the thioether (**1a**) and benzoic acid (**2a**), with $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ as the catalyst and AgOAc as oxidant (Scheme 2a). The structure of **3aa** was unambiguously determined by X-ray crystallography of its single crystal. Basically, this designed product may arise from the intramolecular double C–H coupling of benzyl benzoate (**4**), however such an ester cannot be transformed into the desired product under the same reaction conditions (Scheme 2b), thus further confirming our double directing group strategy. Control experiments with the sufoxide **5** and sulfone **6** also resulted in no product (Scheme 2c), thus ruling out the possibility of sulfoxide or sulfone as actual directing groups (see the Supporting Information for the control experiments run under standard reaction conditions).

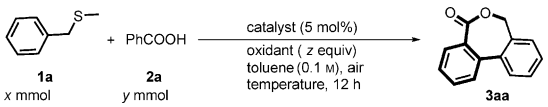


Scheme 2. Initial results and some control experiments. Cp* = C_5Me_5.

Based on our initial result, we continued to optimize the reaction conditions (Table 1). After systematic screening, we found that the oxidant and solvent played a vital role and $AgNO_3$, and toluene provided the optimal combination (entries 3 and 4). By changing the ratio between the two partners, with the thioether in excess, the yield was elevated to 41% (entry 6). The yield can be further increased to 66% by increasing the temperature to 160 °C (entry 8). By changing the cationic rhodium catalyst to a combination of $[\{Cp^*RhCl_2\}_2]$ and $AgSbF_6$ and increasing $AgNO_3$ to 4.0 equivalents, a more reproducible yield of 71% was obtained (entry 11). The reaction cannot proceed in the absence of the rhodium catalyst (entry 12).

With the optimal reaction conditions in hand, we first investigated the substrate scope of the aryl carboxylic acids (Table 2). A series of electron-neutral acids reacted smoothly, thus giving the products in good yields (**3aa**, **3ab**, **3ac**, **3ah**). However, electron-rich (**3ad**) and electron-poor (**3ae**, **3af**, **3ag**) acids showed reduced reactivity (see the Supporting Information for potential side reactions). The *ortho*- and *meta*-substituted substrates also reacted smoothly, although sterically encumbered ones showed lower efficiency (**3ai**, **3aj**). It should be noted that halides like F, Cl, and Br could be tolerated in this reaction to and resulted in moderate yields (**3af–ah**, **3ak–ao**, **3aq**), thus revealing the possibility of further functionalization. Apart from monosubstituted benzoic acids, disubstituted benzoic acids and naphthoic acids (**3al–aq**) could also be used as suitable substrates.

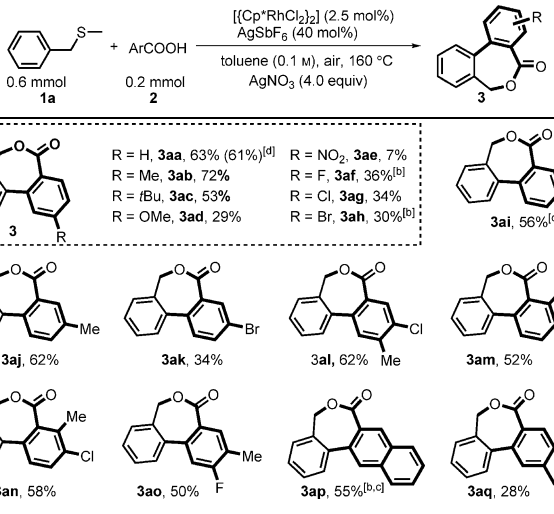
Table 1: Screening of reaction conditions for the coupling of thioethers with carboxylic acids.



Entry	*x*	*y*	Oxidant (*z*)	*T* [°C]	Yield [%][a]
1[c]	0.1	0.2	AgOAc (2.0)	120	(6)[b]
2[c]	0.1	0.2	$AgNO_3$ (2.0)	120	(11)[b]
3[c]	0.1	0.2	$AgNO_3$ (3.0)	120	19 (13)[b]
4	0.1	0.2	$AgNO_3$ (3.0)	120	23
5	0.2	0.1	$AgNO_3$ (3.0)	120	35
6	0.3	0.1	$AgNO_3$ (3.0)	120	41
7	0.3	0.1	$AgNO_3$ (3.0)	140	52
8	0.3	0.1	$AgNO_3$ (3.0)	160	66
9[d]	0.3	0.1	$AgNO_3$ (3.0)	160	70 (53–68)[b]
10[d]	0.6	0.2	$AgNO_3$ (3.0)	160	71
11[d]	0.6	0.2	$AgNO_3$ (4.0)	160	71 (63)[b]
12[e]	0.6	0.2	$AgNO_3$ (4.0)	160	0

[a] Determined by NMR spectroscopy using BnOMe as an internal standard. [b] Yield of isolated product. [c] *t*AmylOH as solvent. [d] $[\{Cp^*RhCl_2\}_2]$ (2.5 mol%) + $AgSbF_6$ (40 mol%) instead of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$. [e] No catalyst.

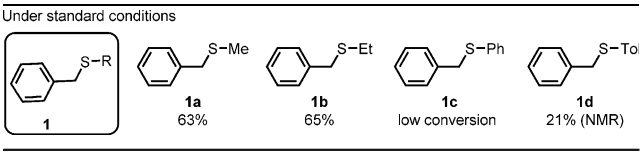
Table 2: Substrate scope for aryl carboxylic acids.[a]



[a] Reaction conditions: $[\{Cp^*RhCl_2\}_2]$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (27.6 mg, 0.08 mmol), $AgNO_3$ (136.0 mg, 0.8 mmol), carboxylic acid (**2**, 0.2 mmol), and thioether (**1a**; 83.0 mg, 81.6 μL, 0.6 mmol) were added to a 50 mL Wattecs reaction tube before adding solvent (toluene, 2 mL). Then the tube was sealed and heated at 160 °C for 8–12 h. [b] Some inseparable contaminant was observed in the ^{13}C NMR spectrum. [c] Used 5 mol% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ as catalyst. [d] Run on 0.5 mmol scale at 160 °C for 10 h, then 140 °C for 15 h.

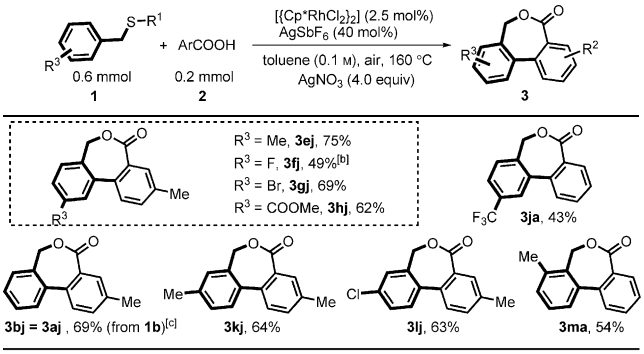
We then investigated the substrate scope of the thioethers. Firstly, we found that the substituents on the S atom played a vital role in enhancing the efficiency. Alkyl groups gave very good yields (**1a**,**b**) while aryl groups (**1c**,**d**) showed very low efficiency (Table 3). With the methyl group as a substituent on

Table 3: The effect of substituents on sulfur atom.



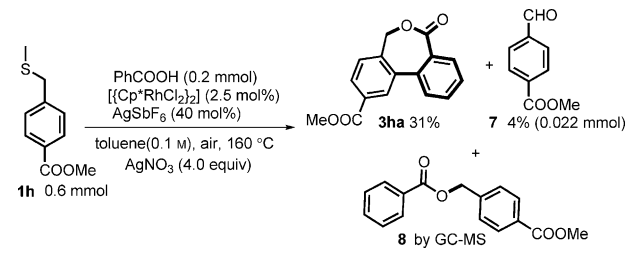
S, we further investigated the reactivity of substituted thioethers (Table 4). Different functional groups, such as F, Cl, Br, COOMe, OMe, CF_3, etc., all tolerated the reaction conditions and gave the desired products in moderate to good yields (**3ej–gj**, **3ha–ja**, **3lj**). Again, electron-neutral substrates showed the best efficiency. In addition, substrates having *ortho* and *meta* substituents also reacted well (**3kj–lj**, **3ma**).

Table 4: Substrate scope for thioether derivatives.[a]



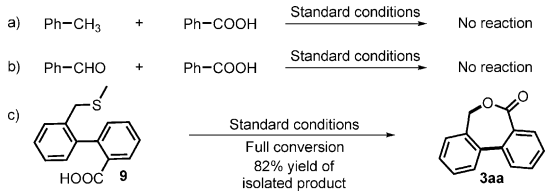
[a] Reaction conditions: $[\{Cp^*RhCl_2\}_2]$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (27.6 mg, 0.08 mmol), $AgNO_3$ (136.0 mg, 0.8 mmol), carboxylic acid (**2**, 0.2 mmol), and thioether **1** (0.6 mmol) were added to a 50 mL Wattecs reaction tube before adding solvent (toluene, 2 mL). Then the tube was sealed and heated to 160 °C for 8–12 h. [b] Used 2.4 equiv of **1f**. [c] Benzyl(ethyl)sulfane (**1b**).

With **1h** as a substrate, we observed small amounts of both the aldehyde **7** (derived from **1h**) and ester **8** (derived from **1h** and **2**; Scheme 3). As a result, the relatively low efficiency arises in part from esterification. In addition, in the presence of the silver salt at high temperature, the decarboxylation of



Scheme 3. Byproduct analysis.

carboxylic acids might occur, thus reducing the yield.[24] However, by either replacing the thioether with benzaldehyde or running the reaction in the absence of thioether, the reaction did not occur, thus indicating the aldehyde was not the key intermediate and the thioether was essential (Scheme 4a,b). The desired product was not obtained from **4** under



Scheme 4. Control experiments and intermediate study.

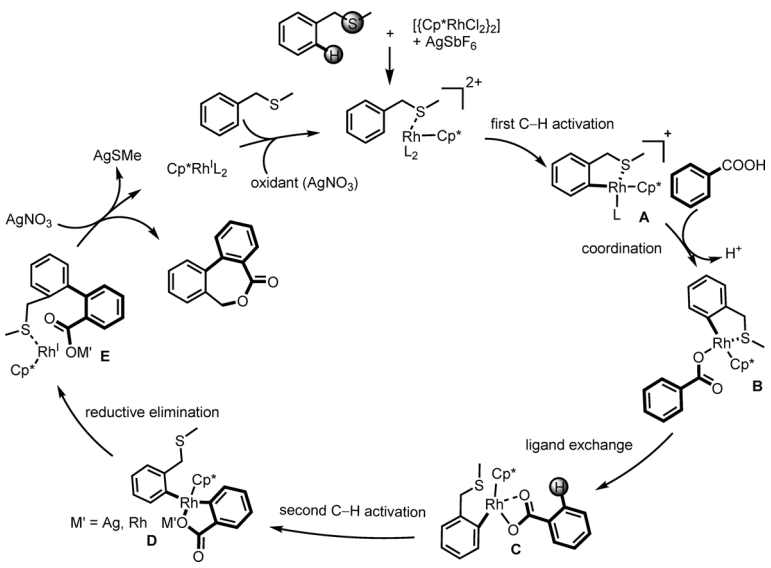
the standard reaction conditions (see Scheme 2b; also see the Supporting Information). To further investigate the intermediate, we synthesized **9**. Indeed, it was transformed into the desired product in high yield under the standard reaction conditions (Scheme 4c), thus indicating it might be a key intermediate in the catalytic cycle. This cyclization step can be promoted by either the rhodium catalyst or silver salt.[25] Further efforts showed that the kinetic isotope effect (KIE) of the carboxylic acid and thioether were 2.0 and 4.9, respectively, thus indicating that C–H activation for both arenes was possibly involved in the rate-determining step (see the Supporting Information).

Based on these mechanistic studies, we proposed the mechanism shown in Scheme 5. The first thioether-directed rate-determining first C–H bond activation forms the intermediate **A**. Carboxylic acid coordination and ligand exchange then forms the intermediate **C**, from which a relatively facile second C–H bond activation occurrs to form the intermediate **D**. Reductive elimination forms the C–C bond coupling intermediate **E** and rhodium(I) species. With the assistance of the rhodium catalyst or silver salt, **E** is cyclized to the final product. Reoxidation of rhodium(I) into rhodium(III) by $AgNO_3$ completes the catalytic cycle. The intermediates **A** and **D** were detected by ESI-HRMS (see the Supporting Information). At this stage the carboxylic acid C–H activation/thioether C–H activation sequence cannot be ruled out.

In summary, we have developed a rhodium-catalyzed double C–H bond coupling reaction between benzyl thioethers and aryl carboxylic acids to synthesize dibenzooxepinones. Here, two directing groups were used and they were either incoorporated into the product or removed in situ after the reaction. The substrate scope is good and several functional groups could be tolerated. The synthetic application of this method in useful natural products and further investigation of the mechanism are underway.

Experimental Section

General procedures: $[\{Cp^*RhCl_2\}_2]$ (3.1 mg, 0.005 mmol), $AgSbF_6$ (27.6 mg, 0.08 mmol), $AgNO_3$ (136.0 mg, 0.8 mmol), and carboxylic acid (**2a**; 24.4 mg, 0.2 mmol) were added to a 50 mL Wattecs reaction tube (sealed tube) under an atmosphere of air. Then the thioether



Scheme 5. Proposed mechanism.

(**1a**; 83.0 mg, 81.6 μL, 0.6 mmol) was added by using a microinjector before adding solvent (toluene, 2 mL). After that, the tube was sealed and the Wattecs parallel reactor heated to 160 °C for 12 h. After the reaction, the system was cooled to room temperature and the reaction mixture concentrated under vacuum before purification by flash chromatography on silica gel with petroleum ether/EtOAc (10:1 to 6:1) to give the product **3aa**.

Supporting information for this article is available on the WWW under http://www.angewandte.org. CCDC 1040225 (**3aa**) 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.

Keywords: C–H activation · carboxylic acids · cross-coupling · rhodium · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5478–5482
Angew. Chem. **2015**, *127*, 5568–5572

[1] a) M. Miura, T. Satoh, *Top. Organomet. Chem.* **2005**, *14*, 55–83; b) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238.

[2] a) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826; *Angew. Chem.* **2009**, *121*, 9976–10011; b) J. Bouffard, K. Itami, *Top. Curr. Chem.* **2010**, *292*, 231–280; c) S.-l. You, J.-B. Xia, *Top. Curr. Chem.* **2010**, *292*, 165–194; d) D. R. Stuart, K. Fagnou, *Top. Organomet. Chem.* **2013**, *44*, 91–120.

[3] a) K. Fagnou, *Top. Curr. Chem.* **2010**, *292*, 35–56; b) D. Zhao, J. You, C. Hu, *Chem. Eur. J.* **2011**, *17*, 5466–5492; c) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236–10254; *Angew. Chem.* **2012**, *124*, 10382–10401.

[4] a) D. R. Stuart, K. Fagnou, *Science* **2007**, *316*, 1172–1175; b) P. Xi, F. Yang, S. Qin, D. Zhao, J. Lan, G. Gao, C. Hu, J. You, *J. Am. Chem. Soc.* **2010**, *132*, 1822–1824; c) N. Kuhl, M. N. Hopkinson, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 8230–8234; *Angew. Chem.* **2012**, *124*, 8354–8358; d) X. C. Cambeiro, T. C. Boorman, P. Lu, I. Larrosa, *Angew. Chem. Int. Ed.* **2013**, *52*, 1781–1784; *Angew. Chem.* **2013**, *125*, 1825–1828.

[5] a) A. Kar, N. Mangu, H. M. Kaiser, M. K. Tse, *J. Organomet. Chem.* **2009**, *694*, 524–537; b) Y. Izawa, S. S. Stahl, *Adv. Synth. Catal.* **2010**, *352*, 3223–3229.

[6] R. Li, J. Li, W. Lu, *Organometallics* **2006**, *25*, 5973–5975.

[7] H.-J. Knölker, *Chem. Lett.* **2009**, *38*, 8–13.

[8] a) A. Shiotani, H. Itatani, *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 471–472; *Angew. Chem.* **1974**, *86*, 478–479; b) B. Akermark, L. Eberson, E. Jonsson, E. Pettersson, *J. Org. Chem.* **1975**, *40*, 1365–1367; c) H. Hagelin, J. D. Oslob, B. Åkermark, *Chem. Eur. J.* **1999**, *5*, 2413–2416; d) D. G. Pintori, M. F. Greaney, *J. Am. Chem. Soc.* **2011**, *133*, 1209–1211.

[9] a) L.-Y. Jiao, M. Oestreich, *Chem. Eur. J.* **2013**, *19*, 10845–10848; b) V. P. Reddy, R. Qiu, T. Iwasaki, N. Kambe, *Org. Lett.* **2013**, *15*, 1290–1293.

[10] a) M. Kitahara, N. Umeda, K. Hirano, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2011**, *133*, 2160–2162; b) Z. Wang, F. Song, Y. Zhao, Y. Huang, L. Yang, D. Zhao, J. Lan, J. You, *Chem. Eur. J.* **2012**, *18*, 16616–16620.

[11] a) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 11904–11905; b) G. Brasche, J. Garcia-Fortanet, S. L. Buchwald, *Org. Lett.* **2008**, *10*, 2207–2210; c) B.-J. Li, S.-L. Tian, Z. Fang, Z.-J. Shi, *Angew. Chem. Int. Ed.* **2008**, *47*, 1115–1118; *Angew. Chem.* **2008**, *120*, 1131–1134; d) X. Zhao, C. S. Yeung, V. M. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 5837–5844; e) J. Karthikeyan, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2011**, *50*, 9880–9883; *Angew. Chem.* **2011**, *123*, 10054–10057; f) X. Wang, D. Leow, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 13864–13867; g) J. Wencel-Delord, C. Nimphius, F. W. Patureau, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 2247–2251; *Angew. Chem.* **2012**, *124*, 2290–2294; h) M. Ito, H. Kubo, I. Itani, K. Morimoto, T. Dohi, Y. Kita, *J. Am. Chem. Soc.* **2013**, *135*, 14078–14081.

[12] a) K. L. Hull, E. L. Lanni, M. S. Sanford, *J. Am. Chem. Soc.* **2006**, *128*, 14047–14049; b) X. Chen, G. Dobereiner, X.-S. Hao, R. Giri, N. Maugel, J.-Q. Yu, *Tetrahedron* **2009**, *65*, 3085–3089; c) D. G. Pintori, M. F. Greaney, *Org. Lett.* **2011**, *13*, 5713–5715; d) S. Oi, H. Sato, S. Sugawara, Y. Inoue, *Org. Lett.* **2008**, *10*, 1823–1826; e) X. Guo, G. Deng, C.-J. Li, *Adv. Synth. Catal.* **2009**, *351*, 2071–2074; f) L. Ackermann, P. Novak, R. Vicente, V. Pirovano, H. K. Potukuchi, *Synthesis* **2010**, 2245–2253.

[13] K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788–802.

[14] a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407–1409; b) X. Shi, C.-J. Li, *Adv. Synth. Catal.* **2012**, *354*, 2933–2938.

[15] a) B. Sezen, R. Franz, D. Sames, *J. Am. Chem. Soc.* **2002**, *124*, 13372–13373; b) D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2010**, *132*, 3965–3972; c) J. Yao, M. Yu, Y. Zhang, *Adv. Synth. Catal.* **2012**, *354*, 3205–3210; d) M. Yu, Y. Xie, C. Xie, Y. Zhang, *Org. Lett.* **2012**, *14*, 2164–2167; e) X.-S. Zhang, Q.-L. Zhu, Y.-F. Zhang, Y.-B. Li, Z.-J. Shi, *Chem. Eur. J.* **2013**, *19*, 11898–11903.

[16] a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2009**, *110*, 624–655; b) J. Bouffard, K. Itami in *C-H Activation*, *Vol. 292* (Eds.: J.-Q. Yu, Z. Shi), Springer, Berlin, **2010**, pp. 231–280; c) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212–11222; d) F. W. Patureau, J. Wencel-Delord, F. Glorius, *Aldrichimica Acta* **2012**, *45*, 31–41; e) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651–3678; f) X.-S. Zhang, K. Chen, Z.-J. Shi, *Chem. Sci.* **2014**, *5*, 2146–2159.

[17] a) Y. Wang, G. Cheng, X. Cui, *Chin. J. Org. Chem.* **2012**, *32*, 2018; b) C. Wang, Y. Huang, *Synlett* **2013**, 145–149; c) E. M. Ferreira, *Nat. Chem.* **2014**, *6*, 94–96; d) W. Zhang, J. Zhang, Y. Liu, *Chin. J. Org. Chem.* **2014**, *34*, 36.

[18] a) P. Thansandote, M. Lautens, *Chem. Eur. J.* **2009**, *15*, 5874–5883; b) T.-S. Mei, L. Kou, S. Ma, K. M. Engle, J.-Q. Yu, *Synthesis* **2012**, 1778–1791; c) C. Zhu, R. Wang, J. R. Falck, *Chem. Asian J.* **2012**, *7*, 1502–1514; d) N. Yoshikai, Y. Wei,

Asian J. Org. Chem. **2013**, *2*, 466 – 478; e) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281 – 295.

[19] a) H. Abe, K. Nishioka, S. Takeda, M. Arai, Y. Takeuchi, T. Harayama, *Tetrahedron Lett.* **2005**, *46*, 3197 – 3200; b) M. Altemöller, T. Gehring, J. Cudaj, J. Podlech, H. Goesmann, C. Feldmann, A. Rothenberger, *Eur. J. Org. Chem.* **2009**, 2130 – 2140; c) A. H. Aly, R. Edrada-Ebel, I. D. Indriani, V. Wray, W. E. G. Mueller, F. Totzke, U. Zirrgiebel, C. Schaechtele, M. H. G. Kubbutat, W. H. Lin, P. Proksch, R. Ebel, *J. Nat. Prod.* **2008**, *71*, 972 – 980; d) U. Höller, G. Konig, A. D. Wright, *Eur. J. Org. Chem.* **1999**, 2949 – 2955; e) U. Höller, A. D. Wright, G. F. Matthee, G. M. Konig, S. Draeger, H.-J. Aust, B. Schulz, *Mycol. Res.* **2000**, *104*, 1354 – 1365; f) T. Tanahashi, Y. Takenaka, N. Nagakura, N. Hamada, *Phytochemistry* **2003**, *62*, 71 – 75.

[20] G. Wu, H.-F. Guo, K. Gao, Y.-N. Liu, K. F. Bastow, S. L. Morris-Natschke, K.-H. Lee, L. Xie, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 5272 – 5276.

[21] V. Colombel, A. Joncour, S. Thoret, J. Dubois, J. Bignon, J. Wdzieczak-Bakala, O. Baudoin, *Tetrahedron Lett.* **2010**, *51*, 3127 – 3129.

[22] F. Büttner, S. Bergemann, D. Guenard, R. Gust, G. Seitz, S. Thoret, *Bioorg. Med. Chem.* **2005**, *13*, 3497 – 3511.

[23] a) Y. Kamochi, T. Kudo, *Chem. Lett.* **1993**, 1495 – 1498; b) S. Kobayashi, F. Senoo, M. Kihara, K. Sakata, A. Miura, *Chem. Pharm. Bull.* **1971**, *19*, 1262 – 1267; c) S. Omura, T. Fukuyama, Y. Murakami, H. Okamoto, I. Ryu, *Chem. Commun.* **2009**, 6741 – 6743.

[24] a) L. J. Goossen, K. Goossen, *Top. Organomet. Chem.* **2013**, *44*, 121 – 142; b) L. J. Goossen, N. Rodriguez, K. Goossen, *Angew. Chem. Int. Ed.* **2008**, *47*, 3100 – 3120; *Angew. Chem.* **2008**, *120*, 3144 – 3164.

[25] a) N. Barbero, R. Martin, *Org. Lett.* **2012**, *14*, 796 – 799; b) F. Pan, Z.-J. Shi, *ACS Catal.* **2014**, *4*, 280 – 288; c) K. M. Wager, M. H. Daniels, *Org. Lett.* **2011**, *13*, 4052 – 4055.

Received: January 18, 2015
Published online: March 10, 2015

