Conjugated Polycycles

International Edition: DOI: 10.1002/anie.201411994
German Edition: DOI: 10.1002/ange.201411994

Cobalt(III)-Catalyzed Directed C–H Coupling with Diazo Compounds: Straightforward Access towards Extended π-Systems**

Dongbing Zhao, Ju Hyun Kim, Linda Stegemann, Cristian A. Strassert, and Frank Glorius**

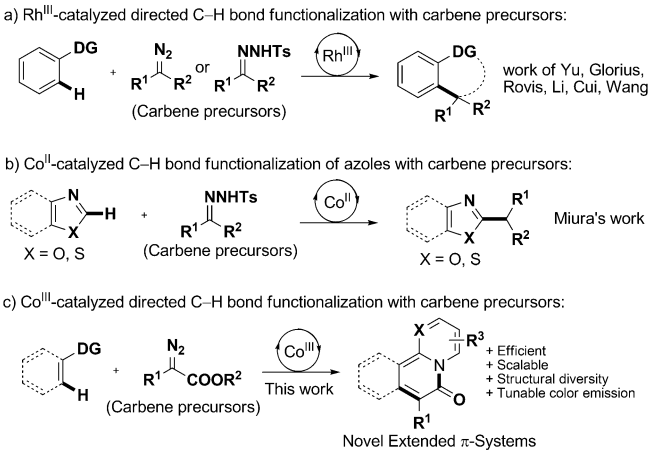
Dedicated to Professor Günther Wilke on the occasion of his 90th birthday

Abstract: *The first highly efficient and scalable cobalt-catalyzed directed C–H functionalization with carbene precursors is presented. This methodology provides a modular route towards a new class of conjugated polycyclic hydrocarbons with tunable emission wavelengths both in solution and in the solid state.*

Conjugated polycyclic hydrocarbons have received widespread attention in recent years because of their interesting and varied electronic, optoelectronic, and magnetic properties.[1] The design and synthesis of novel ring-fused conjugated polycyclic hydrocarbons to access systems with attractive electronic structures and solid-state packing properties is strongly desired. Direct π-extension of simple aromatics using C–H activation strategies is one of the most rapid, efficient, and convenient ways to obtain diverse fused π-conjugated polycyclic hydrocarbons.[2]

In recent years, noble-metal-catalyzed directed C–H functionalization has emerged as a versatile approach in organic synthesis.[3] However, because of the relatively high cost of these noble metals, the development of inexpensive earth-abundant first-row transition metals as alternative catalysts is attracting increasing attention in directed C–H functionalization.[4] For example, Co^{II}-catalyzed C–H activation pioneered by Nakamura, Ackermann, and Yoshikai has recently been applied in various transformations traditionally catalyzed by Rh, Ru, and Pd.[5,6] Furthermore, these first-row transition-metal-based catalysts may demonstrate unique reactivity not observed with noble-metal-based catalytic systems and expand the scope of directed C–H functionalization.

Carbenoid insertion into C–H bonds is a well-established method to functionalize inert C–H bonds.[7] However, directed C–H bond functionalization involving C–H metalation, metal-carbene formation, and migratory insertion still has limited precedent.[8] In 2012 Yu demonstrated the first example with an *ortho*-alkylation of directing-group-containing arene C–H bonds with diazomalonates using a Rh^{III} catalyst (Scheme 1a).[9] More recently, Rovis, Li, Glorius, Wang, and Cui have demonstrated the successful exploration of diazo compounds in Rh^{III}-catalyzed directed C–H functionalizations (Scheme 1a).[10] However, although Co is more earth-abundant and less expensive than Rh, cobalt-catalyzed directed C–H functionalization with carbene precursors has never been reported. Until now only cobalt-catalyzed C–H functionalization of 1,3-azoles with carbene precursors has been reported (Scheme 1b).[11]



Scheme 1. Directed C–H bond functionalization with carbene precursors.

Very recently, Kanai, Ackermann, Ellman, and Glorius demonstrated that the Cp^*Co^{III} catalyst could promote some reactions already established with Cp^*Rh^{III} catalysts to access the identical products.[12] More interestingly, Kanai further proved that a Cp^*Co^{III} catalyst could also trigger reactivity differing from that of the related Cp^*Rh^{III} catalysts because of the large difference in electronegativity between Co and Rh,[13] demonstrating the potential utility of Cp^*Co^{III} catal-

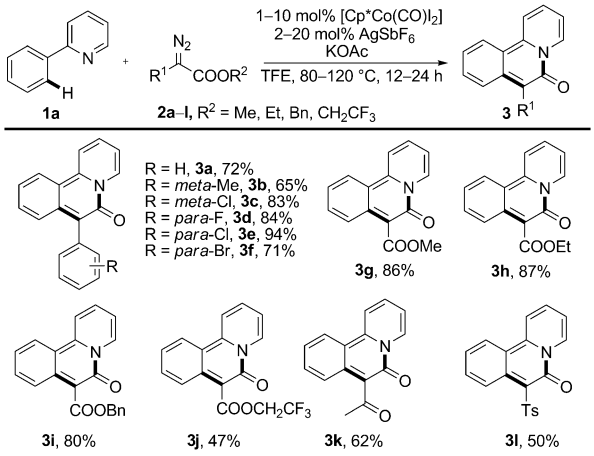
[*] Dr. D. Zhao,[+] Dr. J. H. Kim,[+] Prof. Dr. F. Glorius
Organisch-Chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
E-mail: dongbing.zhao@uni-muenster.de
glorius@uni-muenster.de
L. Stegemann, Dr. C. A. Strassert
Physikalisches Institut and Center for Nanotechnology (CeNTech)
Westfälische Wilhelms-Universität Münster (Germany)
[+] These authors contributed equally to this work.

[**] This work was supported by the Alexander von Humboldt Foundation (D.Z.), the Korea Research Foundation (NRF-2014R1A6A3A03057520, J.H.K.), the European Research Council under the European Community's Seventh Framework Program (FP7 2007-2013)/ERC Grant Agreement 25936 and by the DFG (Leibniz Award). We thank Dr. Constantin G. Daniliuc for X-ray crystallographic analysis and Prof. Shigehiro Yamaguchi (Nagoya University), Dr. Chang Guo, Dr. Matthew Hopkinson, and Tobias Gensch (all WWU Münster) for helpful discussions.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411994.

ysis. Based on these results and our previous work, we speculated that a cobalt(III) catalyst might also promote directed C–H functionalization with carbene precursors to give products distinctly different from those obtained with the related Rh^{III} catalytic systems. Herein, we disclose the first cobalt-catalyzed directed C–H functionalization with carbene precursors, which is highly efficient and scalable and provides a modular route for the assembly of an interesting class of structurally diverse conjugated polycyclic hydrocarbons, which have tunable emission wavelengths both in solution and in the solid state (Scheme 1c).

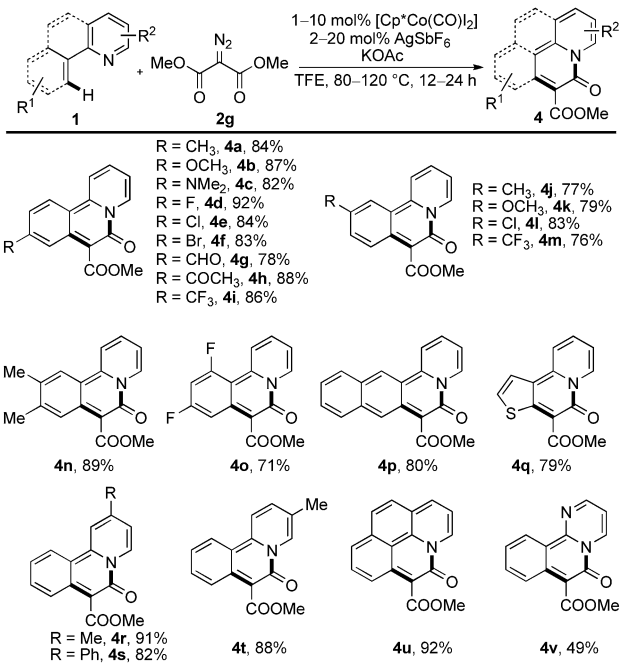
In preliminary experiments, 2-phenylpyridine **1a** was treated with $[Cp^*Co(CO)I_2]$ (5 mol%), $AgSbF_6$ (10 mol%), KOAc (20 mol%), and diazo ester **2a** (1.5 equiv) in methanol (1 mL) at 100 °C for 24 h. Unfortunately no coupled product was observed under these conditions and a survey of different solvents was carried out (Table S1). When we used 2,2,2-trifluoroethanol (TFE) as the solvent, product **3a** was obtained in 33% yield. We also attempted reactions with Cp^*Rh^{III} species in the presence and absence of KOAc, but in all cases only the alkylated products were obtained as the main products (entries 5–8, Table S1).[9] Increasing the amount of $[Cp^*Co(CO)I_2]$ and the reaction temperature to 120 °C improved the yield of **3a** to 72% (see the Supporting Information).

Subsequently, the scope of the diazo esters was investigated using 2-phenylpyridine **1a** as the substrate. As shown in Scheme 2, a series of 6*H*-pyrido[2,1-*a*]isoquinolin-6-ones bearing diverse substituents at the C7 position were synthesized in good to excellent yields. It is important to stress that these reactions using diazomalonates as substrates only worked smoothly with $[Cp^*Co(CO)I_2]$ (2.5 mol%), $AgSbF_6$ (5 mol%), and KOAc (10 mol%) as co-catalysts in TFE (Scheme 2, **3g–i**). For the coupling of 2-phenylpyridine **1a** and dimethyl diazomalonate **2g**, the catalyst loading could be further decreased to 1 mol% without a significant decrease in yield (81%). The structure of **3f** was confirmed by X-ray crystal analysis.[14] In addition, the reaction can be conducted on a gram scale (1 g of **3g**, 82% yield).



Scheme 2. Scope of diazo esters. For reaction conditions, see the Supporting Information.

We next examined the scope of N-heteroarylarenes in the C–H bond annulation (Scheme 3). First, various 2-arylpyridines proceeded smoothly to afford the desired products in satisfactory yields irrespective of the substrate electronics (Scheme 3, **4a–t**). Secondly, our method is suitable for not

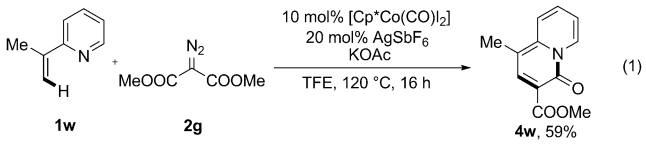


Scheme 3. Scope of arenes and heteroarenes in the tandem C–H bond activation/annulations. For reaction conditions, see the Supporting Information.

only diverse monosubstituted 2-arylpyridines, but also for disubstituted 2-arylpyridines (Scheme 3, **4n–p**). Additionally, the arene is not limited to a benzene platform; heteroarenes also undergo the same reaction with excellent levels of positional selectivity (Scheme 3, **4q**). Moreover, a variation of the substitution pattern on the pyridine moiety proved to be tolerated without significantly affecting the catalytic efficacy (Scheme 3, **4r–t**). Benzo[*h*]quinoline also showed high reactivity in this transformation (Scheme 3, **4u**). We were pleased to observe that pyrimidine could also be utilized as a directing group to obtain the corresponding cyclic product **4v** (Scheme 3). In contrast, when 1-(pyrimidin-2-yl)-1*H*-indoles were employed as substrates, the alkylated products **5** were obtained in high yields (see Scheme S1).

Gratifyingly, the C–H coupling of diazo compounds occurred not only with N-heteroarylarenes but also with olefins via alkenyl C–H activation. 2-(Propenyl)pyridine **1w** showed good reactivity in this reaction selectively delivering the 4*H*-quinolizin-4-one core, which is emerging as a key pharmacophores in a range of biological targets [Eq. (1)].[15]

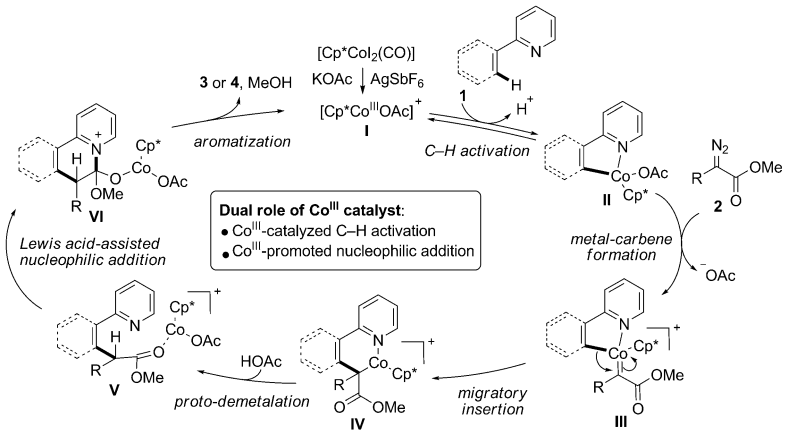
To probe the reaction mechanism, a series of experiments were carried out (see the Supporting Information). Competition experiments were used to determine the electronic preference of the reaction. When *p*-Cl-phenylpyridine **1e** was run in competition with **1a**, the reaction favored **3g** in a 3.15:1 ratio, implying that an electrophilic C–H activation may be



(1)

operating. The use of a deuterated co-solvent proved that the C–H activation was reversible. The value of $k_H/k_D = 1.0$ from two parallel reactions indicated that the C–H metalation step is not rate-determining. A competition experiment was also used to determine the preference for electronically different diazo compounds. The result suggests that migratory insertion favors a more electron-deficient diazo substrate (see the Supporting Information).

Based on previous reports and our preliminarily mechanistic experiments,[9,10,12,13] we propose a directed reversible C–H bond cleavage to form cobaltacycle **II** as the first step after generation of the active Cp*Co^{III} catalyst **I**. Then further reaction with the diazo compound might occur to form the metal–carbene intermediate **III** by dediazonization (Scheme 4). Subsequently, cobalt-carbene migratory insertion in intermediate **III** affords the cobaltacyclic intermediate **IV**,



Scheme 4. Proposed reaction mechanism.

which undergoes proto-demetalation and Lewis acid promoted nucleophilic addition to form intermediate **VI**. Finally, aromatization gives the desired product and regenerates the active species **I**. The dual role of cobalt as a transition metal and a Lewis acid catalyst might be vital to the C–H activation step and sequential cyclization in this transformation.

All of the synthesized compounds are brightly fluorescent. To further understand the photophysical properties of the involved electronic excited states, we characterized a series of representative derivatives in solution at RT, in frozen glassy matrices at 77 K, and in the solid state (powders). The absorption and excitation maxima, the molar absorption coefficients (ε), the photoluminescence (PL) maxima and quantum yields (Φ_F), as well as the excited state lifetimes (τ_F) of these compounds in CH_2Cl_2 solution, frozen matrices, and in the solid state, are listed in Tables S2 and S3, whereas the corresponding absorption, excitation, and emission spectra

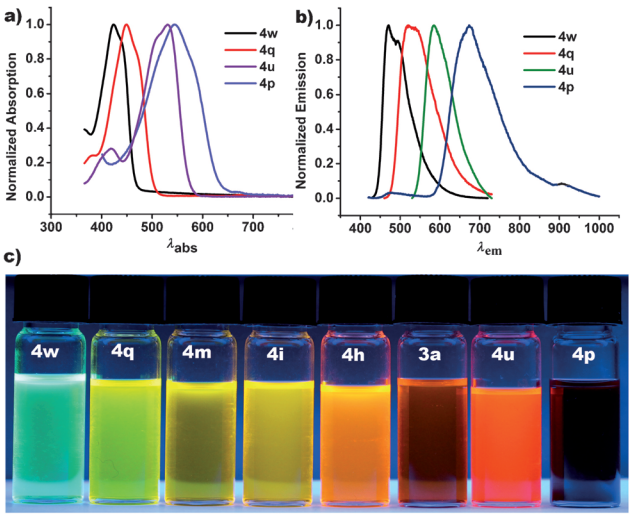


Figure 1. Absorption (a) and emission (b) spectra in CH_2Cl_2 at RT (10^{-5} M). Observed fluorescence under UV excitation (365 nm) (c).

are depicted in Figure 1 and Figures S1–S4. The PL range covers the whole visible region, offering a broad palette of colors both in CH_2Cl_2 (λ_{em}: 471–727 nm, Table S2 and Figure 1c) and in the solid state (λ_{em}: 567–714 nm, Table S3). Most of these compounds display high ε values ($\approx 10^4\,M^{-1}cm^{-1}$) for the lowest electronic transitions. Extension of the π-conjugated systems leads to significant bathochromic shifts in emission (**4u** and **4p**, Table S2 and Figure 1).[16]

In conclusion, we have successfully developed a cobalt(III)-catalyzed coupling of diazo compounds with aromatic and heteroaromatic compounds via C–H activation. The observed difference in the catalytic reactivity and activity between the Cp*Co^{III} and Cp*Rh^{III} complexes points to the dual role of the Co species as a transition metal and a Lewis acid catalyst. Furthermore, this facile synthetic approach resulted in the discovery of a new family of extended π-systems. Most of these compounds have broad and intense absorption and emission bands, and exhibit high extinction coefficients and large Stokes shifts.

Keywords: carbenes · C–H activation · cobalt · heterocycles · π-systems

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 4508–4511
Angew. Chem. **2015**, *127*, 4591–4594

[1] For recent books and reviews, see: a) R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, Weinheim, **1997**; b) *Carbon-Rich Compounds* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**; c) V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* **2004**, *303*, 1644; d) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891; e) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028; f) J. E. Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452; *Angew. Chem.*

2008, *120*, 460; g) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Angew. Chem. Int. Ed.* **2008**, *47*, 4070; *Angew. Chem.* **2008**, *120*, 4138; h) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2011**, *111*, 2208; i) M. Watanabe, K.-Y. Chen, Y. J. Chang, T. J. Chow, *Acc. Chem. Res.* **2013**, *46*, 1606; j) J. Mei, Y. Diao, A. L. Appleton, L. Fang, Z. Bao, *J. Am. Chem. Soc.* **2013**, *135*, 6724; k) Z. Sun, Z. Zeng, J. Wu, *Acc. Chem. Res.* **2014**, *47*, 2582.

[2] Latest review: a) Y. Segawa, T. Maekawa, K. Itami, *Angew. Chem. Int. Ed.* **2015**, *54*, 66; *Angew. Chem.* **2015**, *127*, 68. Selected examples: b) Y. Kawamata, S. Tokuji, H. Yorimitsu, A. Osuka, *Angew. Chem. Int. Ed.* **2011**, *50*, 8867; *Angew. Chem.* **2011**, *123*, 9029; c) W. Yue, A. Lv, J. Gao, W. Jiang, L. Hao, C. Li, Y. Li, L. E. Polander, S. Barlow, W. Hu, S. D. Motta, F. Negri, S. R. Marder, Z. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 5770; d) S.-Y. Liu, M.-M. Shi, J.-C. Huang, Z.-N. Jin, X.-L. Hu, J.-Y. Pan, H.-Y. Li, A. K. Y. Jen, H.-Z. Chen, *J. Mater. Chem. A* **2013**, *1*, 2795; e) J. Zhang, W. Chen, A. J. Rojas, E. V. Jucov, T. V. Timofeeva, T. C. Parker, S. Barlow, S. R. Marder, *J. Am. Chem. Soc.* **2013**, *135*, 16376; f) K. Ozaki, H. Zhang, H. Ito, A. Lei, K. Itami, *Chem. Sci.* **2013**, *4*, 3416; g) J. Dong, Z. Long, F. Song, N. Wu, Q. Guo, J. Lan, J. You, *Angew. Chem. Int. Ed.* **2013**, *52*, 580; *Angew. Chem.* **2013**, *125*, 608; h) X. Huang, J. Huang, C. Du, X. Zhang, F. Song, J. You, *Angew. Chem. Int. Ed.* **2013**, *52*, 12970; *Angew. Chem.* **2013**, *125*, 13208; i) Y. Huang, D. Wu, J. Huang, Q. Guo, J. Li, J. You, *Angew. Chem. Int. Ed.* **2014**, *53*, 12158; *Angew. Chem.* **2014**, *126*, 12354.

[3] Some recent reviews on C–H activation: a) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; *Angew. Chem.* **2009**, *121*, 9976; b) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; *Angew. Chem.* **2009**, *121*, 5196; c) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242; d) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654; e) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212; f) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; g) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; h) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; i) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315; j) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; k) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2011**, *44*, 814; l) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; m) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960; *Angew. Chem.* **2012**, *124*, 9092; n) S. R. Neufeldt, M. S. Sanford, *Acc. Chem. Res.* **2012**, *45*, 936; o) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281; p) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369; q) S. A. Girard, T. Knauber, C.-J. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 74; *Angew. Chem.* **2014**, *126*, 76.

[4] For reviews, see: a) A. A. Kulkarni, O. Daugulis, *Synthesis* **2009**, 4087; b) E. Nakamura, N. Yoshikai, *J. Org. Chem.* **2010**, *75*, 6061; c) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293; d) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem. Int. Ed.* **2011**, *50*, 11062; *Angew. Chem.* **2011**, *123*, 11256; e) C. Zhang, C. Tang, N. Jiao, *Chem. Soc. Rev.* **2012**, *41*, 3464; f) J. Yamaguchi, K. Mito, K. Itami, *Eur. J. Org. Chem.* **2013**, 19; g) J. J. Mousseau, A. B. Charette, *Acc. Chem. Res.* **2013**, *46*, 412.

[5] For reviews, see: a) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208; b) L. Ackermann, *J. Org. Chem.* **2014**, *79*, 8948. For representative examples, see: c) K. Gao, P.-S. Lee, T. Fujita, N. Yoshikai, *J. Am. Chem. Soc.* **2010**, *132*, 12249; d) J. Y. Kim, S. H. Cho, J. Joseph, S. Chang, *Angew. Chem. Int. Ed.* **2010**, *49*, 9899; *Angew. Chem.* **2010**, *122*, 10095; e) L. Ilies, Q. Chen, X. Zeng, E. Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 5221; f) P.-S. Lee, T. Fujita, N. Yoshikai, *J. Am. Chem. Soc.* **2011**, *133*, 17283; g) B. Li, Z.-H. Wu, Y.-F. Gu, C.-L. Sun, B.-Q. Wang, Z.-J. Shi, *Angew. Chem. Int. Ed.* **2011**, *50*, 1109; *Angew. Chem.* **2011**, *123*, 1141; h) Z. Ding, N. Yoshikai, *Angew. Chem. Int. Ed.* **2012**, *51*, 4698; *Angew. Chem.* **2012**, *124*, 4776; i) T. Andou, Y. Saga, H. Komai, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2013**, *52*, 3213; *Angew. Chem.* **2013**, *125*, 3295; j) H. Lu, C. Li, H. Jiang, C. L. Lizardi, X. P. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 7028; *Angew. Chem.* **2014**, *126*, 7148; k) L. Grigorjeva, O. Daugulis, *Angew. Chem. Int. Ed.* **2014**, *53*, 10209; *Angew. Chem.* **2014**, *126*, 10373; l) T. M. Figg, S. Park, J. Park, S. Chang, D. G. Musaev, *Organometallics* **2014**, *33*, 4076; m) L.-B. Zhang, X.-Q. Hao, S.-K. Zhang, Z.-J. Liu, X.-X. Zheng, J.-F. Gong, J.-L. Niu, M.-P. Song, *Angew. Chem. Int. Ed.* **2015**, *54*, 272; *Angew. Chem.* **2015**, *127*, 274; n) J. V. Obligacion, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 4133.

[6] a) Q. Chen, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 428; b) W. Liu, H. Cao, J. Xin, L. Jin, A. Lei, *Chem. Eur. J.* **2011**, *17*, 3588; c) H. Li, C.-L. Sun, M. Yu, D.-G. Yu, B.-J. Li, Z.-J. Shi, *Chem. Eur. J.* **2011**, *17*, 3593; d) W. Song, L. Ackermann, *Angew. Chem. Int. Ed.* **2012**, *51*, 8251; *Angew. Chem.* **2012**, *124*, 8376; e) K. Gao, P.-S. Lee, C. Long, N. Yoshikai, *Org. Lett.* **2012**, *14*, 4234; f) B. Punji, W. Song, G. Shevchenko, L. Ackermann, *Chem. Eur. J.* **2013**, *19*, 10605; g) K. Gao, N. Yoshikai, *J. Am. Chem. Soc.* **2013**, *135*, 9279.

[7] For recent reviews, see: a) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2012**, *112*, 704; b) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417.

[8] For a review, see: Z. Liu, J. Wang, *J. Org. Chem.* **2013**, *78*, 10024.

[9] W.-W. Chan, S.-F. Lo, Z. Zhou, W.-Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565.

[10] a) T. K. Hyster, K. E. Ruhl, T. Rovis, *J. Am. Chem. Soc.* **2013**, *135*, 5364; b) X. Yu, S. Yu, J. Xiao, B. Wan, X. Li, *J. Org. Chem.* **2013**, *78*, 5444; c) Z. Shi, D. C. Koester, M. Boultadakis-Arapinis, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 12204; d) S. Cui, Y. Zhang, D. Wang, Q. Wu, *Chem. Sci.* **2013**, *4*, 3912; e) F. Hu, Y. Xia, F. Ye, Z. Liu, C. Ma, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 1364; *Angew. Chem.* **2014**, *126*, 1388; f) Y. Xia, Z. Liu, S. Feng, Y. Zhang, J. Wang, *J. Org. Chem.* **2015**, *80*, 223.

[11] T. Yao, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 775; *Angew. Chem.* **2012**, *124*, 799.

[12] a) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2013**, *52*, 2207; *Angew. Chem.* **2013**, *125*, 2263; b) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Chem. Eur. J.* **2013**, *19*, 9142; c) B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Adv. Synth. Catal.* **2014**, *356*, 1491; d) J. Li, L. Ackermann, *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201409247; *Angew. Chem.* **2014**, DOI: 10.1002/ange.201409247; e) D.-G. Yu, T. Gensch, F. de Azambuja, S. Vásquez-Céspedes, F. Glorius, *J. Am. Chem. Soc.* **2014**, DOI: 10.1021/ja511011m; f) J. R. Hummel, J. A. Ellman, *J. Am. Chem. Soc.* **2015**, *137*, 490.

[13] H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.* **2014**, *136*, 5424.

[14] CCDC 1038977 (**3 f**) 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.

[15] a) S. D. Kuduk, C. N. Di Marco, WO 2010042347, **2010**; b) S. D. Kuduk, R. K. Chang, C. N. Di Marco, W. J. Ray, L. Ma, M. Wittmann, M. A. Seager, K. A. Koeplinger, C. D. Thompson, G. D. Hartman, M. T. Bilodeau, *ACS Med. Chem. Lett.* **2010**, *1*, 263.

[16] For a more detailed discussion of the photophysical data, see the Supporting Information.

Received: December 14, 2015
Published online: February 20, 2015

