Letter

Oxazolinyl-Assisted C-H Amidation by Cobalt(III) Catalysis

Ruhuai Mei, Joachim Loup, and Lutz Ackermann

ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.5b02661 • Publication Date (Web): 22 Dec 2015

Oxazolinyl-Assisted C−H Amidation by Cobalt(III) Catalysis

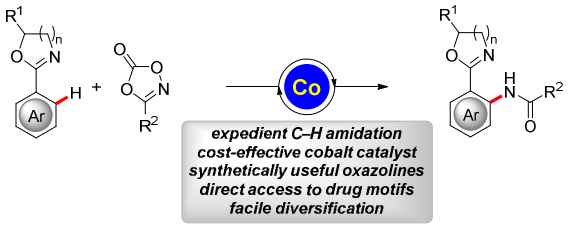
Ruhuai Mei,[¶] Joachim Loup,[¶] and Lutz Ackermann*

Institut für Organische und Biomolekulare Chemie, Georg-August-Universität,
Tammannstraße 2, 37077 Göttingen, Germany

Supporting Information Placeholder

[¶] *R.M. and J.L. contributed equally.*

ABSTRACT: Cobalt-catalyzed C–H activation by means of oxazolinyl assistance set the stage for versatile direct amidations with ample substrate scope. Thus, a high-valent cobalt(III) catalyst enabled C–H amidations with excellent levels of positional and chemo-selectivities. Mechanistic studies provided strong support for a kinetically relevant C–H functionalization.



KEYWORDS: *amidation, C–H activation, cobalt, mechanism, oxazolines*

Substituted oxazolines are omnipresent structural motifs of numerous bioactive compounds of relevance to crop protection and medicinal chemistry (Figure 1).[1] Moreover, oxazolines are easily accessible and can be converted into a plethora of valuable functionalities,[2] which renders them key intermediates in organic synthesis and useful ligands in metal catalysis. As a consequence there is a continued strong demand for flexible methods that provide general access to substituted oxazolines.[2] While directed *ortho*-metalation strategies have been developed, they require stoichiometric mounts of strong bases.[3] In contrast, transition metal-catalyzed C–H functionalization[4] technology has provided means for the atom- and step-economical diversification by oxazolinyl assistance.[5] In spite of these undisputed advances, catalytic C–H amidations on aryl oxazolines are as of yet restricted to the use of precious rhodium and iridium catalysts, as elegantly developed by Chang, among others.[6] In consideration of the attractive features associated with naturally abundant 3d transition metals, recent focus has shifted to inexpensive base metal catalysts for C–H activation chemistry.[7] In this context, major progress has been achieved with versatile high-valent cobalt-catalyzed C–H functionalizations, as were reported by Kanai,[8] Ackermann,[9] Daugulis,[10] Glorius,[11] Ellman,[12] and Chang,[13] among others.[14] Within our program on cobalt-catalyzed C–H activation,[15] we have developed the first oxazolinyl-assisted cobalt-catalyzed C–H functionalization, which set the stage for expedient direct amidations with ample substrate scope. Recent independent reports by Jiao[16] and Chang[17] on cobalt-catalyzed amidations with rather strongly-coordinating amides and pyridines prompted us to now report our findings on an effective protocol for cobalt(III)-catalyzed C–H amidations of synthetically useful aryl oxazolines by the action of dioxazolones[18] as user-friendly amidating reagents. Notable features of our strategy include (*i*) the first cobalt(III)-catalyzed C–H activation on aryl oxazolines and oxazines, (*ii*) high functional group tolerance, (*iii*) robust C–H amidations on indoles and pyrroles within a removable[19] directing group strategy, and (*iv*) key mechanistic insights on the crucial C–H cobaltation step. Further, our approach provides modular and step-economical access to 2-amido-substituted 2-aryloxazolines – the key scaffold of Yu's powerful bidentate auxiliary.[20]

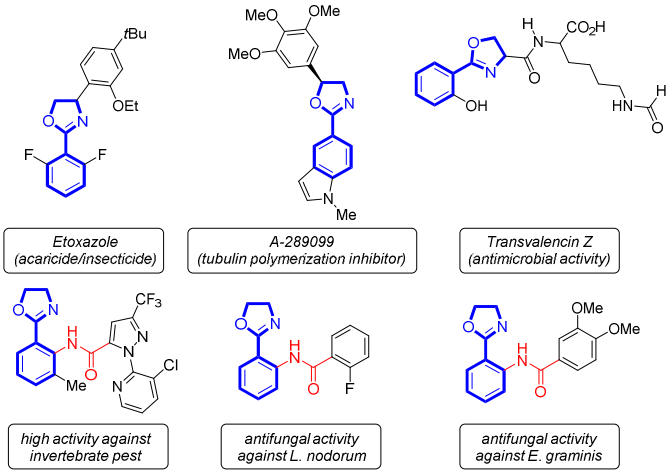


Figure 1. Selected bioactive 2-aryl oxazolines.

At the outset of our studies, we explored the feasibility of the envisioned cobalt-catalyzed C–H amidation of aryl oxazoline **1a** with dioxazolone **2a** (Table 1). Preliminary observations revealed that aprotic solvents enabled the desired C–H amidation, with DCE being optimal (entries 1–3). Among a variety of additives, NaOAc proved to be most effective (entries 3–10), highlighting the importance of carboxylate assistance in the C–H functionalization regime (*vide infra*).[21] Interestingly, the sodium salt of a protected amino acid generated a

less effective cobalt catalyst (entry 9). Different cobalt(III) complexes were explored thereafter (entries 10–14), and Cp*Co(CO)I_2 emerged as the most powerful catalyst, while the analogous cyclopentadienyl complex CpCo(CO)I_2 or simple cobalt salt $CoCl_2$ only performed poorly (entries 12 and 13). It is noteworthy that in contrast to Jiao's observation,[16] the cationic [Cp*Co(MeCN)$_3$](SbF$_6$)$_2$ was found to be inferior in the oxazoline-assisted C–H activation (entry 14). With the optimized reaction conditions identified, we verified the beneficial effect of the carboxylate additive, and showed the cobalt complex to be essential for the C–H activation process (entries 15 and 16).

Table 1. Oxazoline-Assisted C–H Amidation [a]

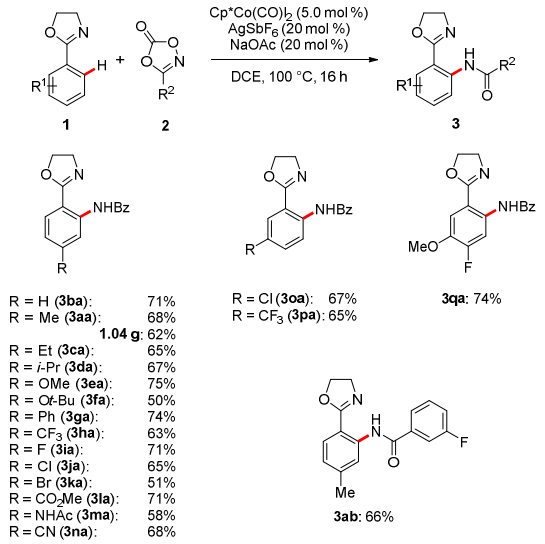
1a 2a 3aa

entry	[Co]	solvent	additive	**3aa** (%)
1	Cp*Co(CO)I_2	TFE	NaOAc	–
2	Cp*Co(CO)I_2	$PhCF_3$	NaOAc	53
3	**Cp*Co(CO)I_2**	**DCE**	**NaOAc**	**65**
4	Cp*Co(CO)I_2	DCE	KOAc	47
5	Cp*Co(CO)I_2	DCE	PivOH	58
6	Cp*Co(CO)I_2	DCE	NaOPiv	63
7	Cp*Co(CO)I_2	DCE	NaO_2CMes	3
8	Cp*Co(CO)I_2	DCE	NaO_2CAd	44
9	Cp*Co(CO)I_2	DCE	NaO_2C-Ile-Ac	17
10	**Cp*Co(CO)I_2**	**DCE**	**NaOAc**	**68**[b]
11	$[Cp^*CoI_2]_2$	DCE	NaOAc	61[b]
12	CpCo(CO)I_2	DCE	NaOAc	–
13	$CoCl_2$	DCE	NaOAc	–
14	[Cp*Co(MeCN)$_3$](SbF$_6$)$_2$	DCE	–	54
15	Cp*Co(CO)I_2	DCE	–	35
16	–	DCE	NaOAc	–

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (1.2 equiv), [Co] (5.0 mol %), $AgSbF_6$ (10 mol %), additive (10 mol %), solvent (2 mL), 100 °C, 16 h. [b] $AgSbF_6$ (20 mol %), NaOAc (20 mol %).

Subsequently, we tested the versatility of the cobalt(III) catalyst in the C–H amidation of various aryl oxazolines **1** (Scheme 1). The cobalt(III) complex was found to be highly chemo-selective as was reflected by a remarkable functional group tolerance that included chloro, bromo, cyano, ester and amide substituents. The robustness of the protocol was moreover illustrated by the gram-scale synthesis of amide **3aa**. In intramolecular competition experiments with *meta*-substituted arenes **1o**–**1q** featuring two inequivalent *ortho*-C–H bonds an excellent positional selectivity was observed, that was fully controlled by oxazolinyl assistance and secondary steric interactions.

Scheme 1. Scope of Oxazolinyl-Assisted C–H Amidation



R = H (**3ba**): 71%
R = Me (**3aa**): 68%
1.04 g: 62%
R = Et (**3ca**): 65%
R = *i*-Pr (**3da**): 67%
R = OMe (**3ea**): 75%
R = O*t*-Bu (**3fa**): 50%
R = Ph (**3ga**): 74%
R = CF_3 (**3ha**): 63%
R = F (**3ia**): 71%
R = Cl (**3ja**): 65%
R = Br (**3ka**): 51%
R = CO_2Me (**3la**): 71%
R = NHAc (**3ma**): 58%
R = CN (**3na**): 68%

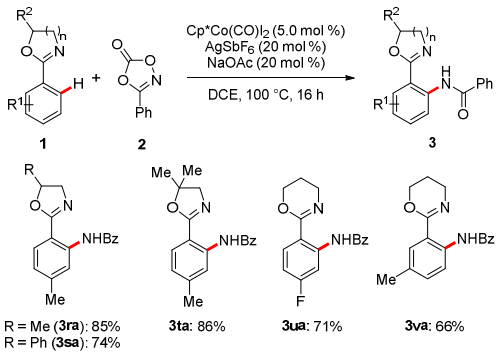
R = Cl (**3oa**): 67%
R = CF_3 (**3pa**): 65%

3qa: 74%

3ab: 66%

Thereafter, we put the influence of the oxazoline substitution pattern on the C–H amidation process to a test (Scheme 2). Thus, oxazolines **1** derived from different β-aminoalcohols delivered the desired products **3ra**–**3ta** with synthetically useful yields. Notably, the versatile cobalt(III) catalyst was not limited to oxazoline substrates. Indeed, aryl 1,3-oxazines **1v** and **1u** smoothly delivered the desired amidated products **3ua**–**3va** as well.

Scheme 2. Substituted Oxazolines and Oxazines 1 for C–H Amidation



R = Me (**3ra**): 85%
R = Ph (**3sa**): 74%

3ta: 86%

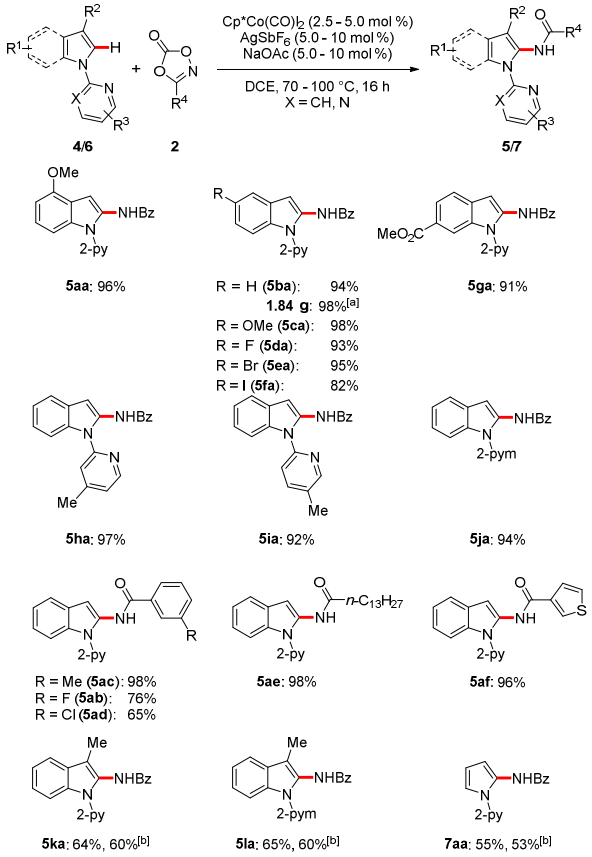
3ua: 71%

3va: 66%

The scope of the Cp*Co(CO)I_2-catalyzed C–H amidation beyond oxazolines and oxazines **1** was showcased by the C–H functionalization of indoles **4**[22] bearing removable pyridyl (py) and pyrimidyl (pym) entities (Scheme 3). Here, the chemoselective cobalt(III) catalyst was again characterized by a remarkable tolerance of valuable electrophilic functional groups, as illustrated for fluoro, chloro, bromo, iodo, ester or thiophene substituents (**5aa**–**5ja**/**5af**). At the same time, the user-friendly protocol allowed for the introduction of aryl, heteroaryl and alkyl amides in a step-economical manner. The gram-scale synthesis of amidated indole **5ba** occurred efficiently at low catalyst loading of only 1.0 mol %. Likewise, sterically hindered 1,3-disubstituted indoles **4k** and **4l** were converted with high efficacy. The catalyst was not limited to

indole substrates, but also enabled the unprecedented cobalt-catalyzed C–H nitrogenation of pyrroles (**7aa**).

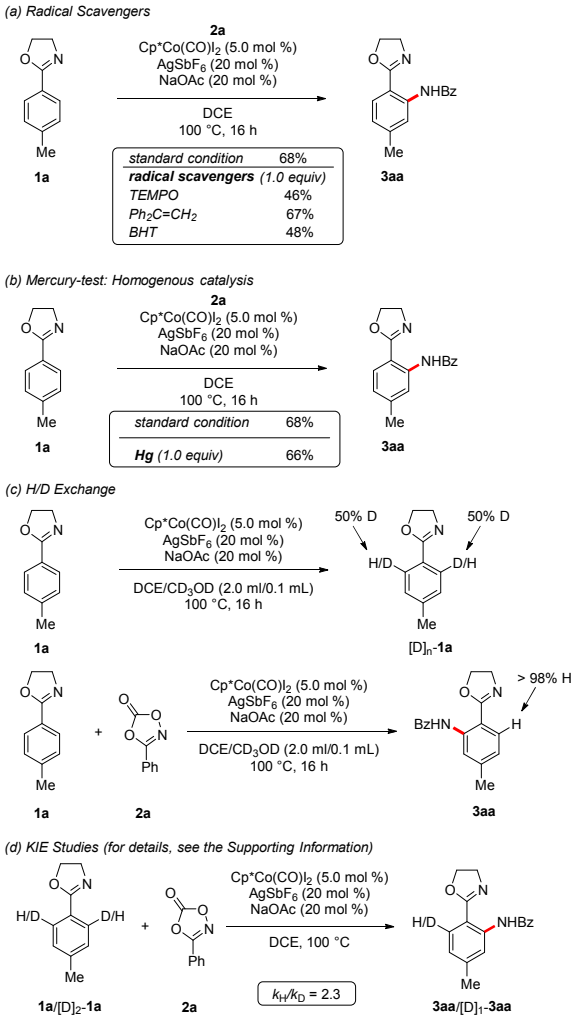
Scheme 3. Cobalt(III)-Catalyzed C–H Nitrogenation of Indoles 4 and Pyrroles 6



[a] Cp*Co(CO)I_2 (1.0 mol %). [b] Without NaOAc.

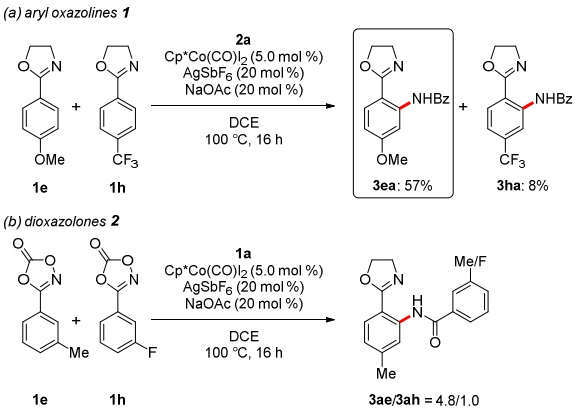
Given the versatility of the cobalt(III)-catalyzed C–H amidation, we conducted mechanistic studies to delineate its mode of action. To this end, C–H functionalizations performed in the presence of typical radical scavengers gave the amidated product **3aa** with only a minor loss in catalytic activity (Scheme 4a). Thus, in contrast to a recent mechanistic study on cobalt(III)-catalyzed oxygenations,[23] our findings do not provide support for a radical-based mechanism. Furthermore, a mercury-test confirmed the cobalt catalysis to be homogenous in nature (Scheme 4b). Reactions performed with an isotopically labeled co-solvent highlighted a considerable H/D scrambling, yet only occurring in the absence of the dioxazolinones **2** (Scheme 4c). The kinetic isotope effect (KIE) of $k_H/k_D \approx 2.3$ by independent measurements (Scheme 4d) indicated the C–H cobaltation to be kinetically relevant.

Scheme 4. Mechanistic Findings



Intermolecular competition reactions between differently decorated substrates revealed electron-rich arenes **1** and electron-rich dioxazolones **2** to be functionalized preferentially (Scheme 5). These findings can be rationalized in terms of the key C–H activation step occurring by a base(acetate)-assisted, intermolecular electrophilic substitution-type (BIES) C–H metalation event.[24]

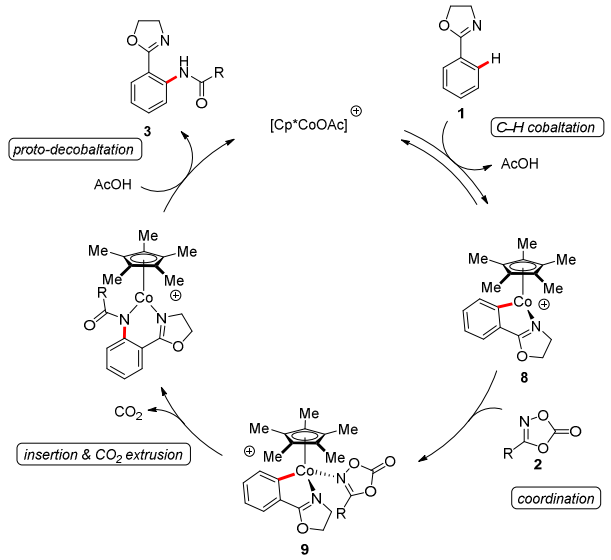
Scheme 5. Intermolecular Competition Experiments[a]



[a] ^{1}H NMR with 1,3,5-$(MeO)_3C_6H_3$ as the internal standard.

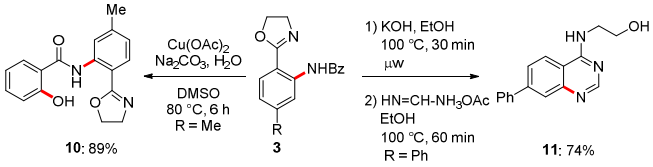
Based on our mechanistic studies and previous reports, we propose a plausible catalytic cycle that commences by a kinetically-relevant, acetate-assisted C–H cobaltation to generate metallacyle **8** (Scheme 6). Subsequent coordination of the dioxazolones **2** forms the intermediate **9**, which then undergoes CO_2 extrusion. Thereafter, proto-decobaltation by the formed HOAc regenerates the catalytically active cobalt(III) carboxylate and yields the desired product **3**.

Scheme 6. Plausible Catalytic Cycle



The synthetic utility of the cobalt(III)-catalyzed C–H amidation by means of oxazolinyl assistance was exploited for the post-synthetic diversification of the thus obtained amides **3** (Scheme 7). Hence, the chemo-selective deliberation of the free primary amine was easily accomplished, while a copper-catalyzed C–H oxygenation proved viable adopting Yu's protocol.[25] Moreover, following a modified procedure,[6a] novel quinazolinone **11** could be prepared in a step-economical fashion as well.

Scheme 7. Diversification of 2-Amidoaryloxazolines 3



In conclusion, we have reported on the first cobalt-catalyzed C–H functionalization by the assistance of synthetically useful oxazolines. Thus, a versatile cobalt(III) catalyst allowed for the direct amidation using robust dioxazolones with ample substrate scope, which also proved amenable to C–H functionalizations on indoles as well as pyrroles with removable directing groups. The power of the oxazolinyl-assisted C–H amidation strategy was further illustrated by late-stage diversification of the thus-obtained *ortho*-amidated aryl oxazolines. Mechanistic studies provided strong support for a kinetically-relevant C–H cobaltation by carboxylate assistance.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* Lutz.Ackermann@chemie.uni-goettingen.de

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Support by the European Research Council under the European Community's Seventh Framework Program (FP7 2007–2013)/ERC Grant agreement no. 307535, the DFG (SPP 1807), and the CSC (fellowship to M.R.) is gratefully acknowledged.

REFERENCES

1. Representative examples: (a) Mukai, A.; Fukai, T.; Matsumoto, M.; Ishikawa, J.; Hoshino, Y.; Yazawa, K.; Harada, K.; Mikami, Y. *J. Antibiot*. **2006**, *59*, 366-369. (b) Li, Q.; Woods, K. W.; Claiborne, A.; Gwaltney, S. L.; Barr, K. J.; Liu, G.; Gehrke, L.; Credo, R. B.; Hui, Y. H.; Lee, J.; Warner, R. B.; Kovar, P.; Nukkala, M. A.; Zielinski, N. A.; Tahir, S. K.; Fitzgerald, M.; Kim, K. H.; Marsh, K.; Frost, D.; Ng, S.-C.; Rosenberg, S.; Sham, H. L. *Bioorg. Med. Chem. Lett.* **2002**, *22*, 465-469. (c) Clark, D.; Finkelstein, B.; Lahm, G.; Selby, T.; Stevenson, T. WO 2003016304 A1., 2003. (d) Suzuki, J.; Ishida, T.; Shibuya, I.; Toda, K. *J. Pestic. Sci*. **2001**, *26*, 215-223.
2. Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297-2360.
3. For a review, see: (a) Hartung, C. G.; Snieckus, V., In *Modern Arene Chemistry* Astruc, D., Ed. Wiley-VCH: Weinheim, 2002; pp 330-367. Selected examples: (b) Gupta, L.; Hoepker, A. C.; Singh, K. J.; Collum, D. B. *J. Org. Chem.* **2009**, *74*, 2231-2233. (c) Wehman, E.; Van Koten, G.; Jastrzebski, J. T. B. H.; Rotteveel, M. A.; Stam, C. H. *Organometallics* **1988**, *7*, 1477-1485, and references cited therein.
4. Representative recent reviews on C–H activation: (a) Ye, B.; Cramer, N. *Acc. Chem. Res*. **2015**, *48*, 1308-1318. (b) Shin, K.; Kim, H.; Chang, S. *Acc. Chem. Res.* **2015**, *48*, 1040-1052. (c) Daugulis, O.; Roane, J.; Tran, L. D. *Acc. Chem. Res.* **2015**, *48*, 1053-1064. (d) Segawa, Y.; Maekawa, T.; Itami, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 66-81. (e) Thirunavukkarasu, V. S.; Kozhushkov, S. I.; Ackermann, L. *Chem. Commun.* **2014**, *50*, 29-39. (f) Kuhl, N.; Schroeder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443-1460. (g) Mesganaw, T.; Ellman, J. A. *Org. Process Res. Dev*. **2014**, *18*, 1097-1104. (h) Girard, S. A.; Knauber, T.; Li, C.-J. *Angew. Chem., Int. Ed.* **2014**, *53*, 74-100. (i) Yeung, C. S.; Dong, V. M. *Chem. Rev*. **2011**, *111*, 1215-1292. (j) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068-5083. (k) Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 11212-11222. (l) Daugulis, O. *Top. Curr. Chem*. **2010**, *292*, 57-84. (m) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242-3272. (n) Ackermann, L.; Vicente, R.; Kapdi, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9792-9826. (o) Chen, X.;

Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed*. **2009**, *48*, 5094-5115 and references cited therein.

5. For selected examples, see: (a) Ebe, Y.; Nishimura, T. *J. Am. Chem. Soc.* **2015**, *137*, 5899-5902. (b) Xie, F.; Qi, Z.; Yu, S.; Li, X. *J. Am. Chem. Soc*. **2014**, *136*, 4780-4787. (c) Ogiwara, Y.; Tamura, M.; Kochi, T.; Matsuura, Y.; Chatani, N.; Kakiuchi, F. *Organometallics* **2014**, *33*, 402-420. (d) Gong, T.-J.; Xiao, B.; Cheng, W.-M.; W.Su; Xu, J.; Liu, Z.-J.; Liu, L.; Fu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 10630-10633. (e) Ackermann, L.; Kozhushkov, S. I.; Yufit, D. S. *Chem. Eur. J.* **2012**, *18*, 12068-12077. (f) Ouellet, S. G.; Roy, A.; Molinaro, C.; Angelaud, R.; Marcoux, J.-F.; O'Shea, P. D.; Davies, I. W. *J. Org. Chem.* **2011**, *76*, 1436-1439. (g) Kim, M.; Kwak, J.; Chang, S. *Angew. Chem. Int. Ed*. **2009**, *48*, 8935-8939. (h) Chen, X.; Li, J.-J.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 78-79. (i) Ackermann, L.; Althammer, A.; Born, R. *Angew. Chem. Int. Ed*. **2006**, *45*, 2619-2622. (j) Oi, S.; Aizawa, E.; Ogino, Y.; Inoue, Y. *J. Org. Chem*. **2005**, *70*, 3113–3119, and references cited therein.

6. (a) Maiden, T. M. M.; Swanson, S.; Procopiou, P. A.; Harrity, J. P. A. *Chem. Eur. J.* **2015**, *21*, 14342-14346. (b) Zhao, H.; Shang, Y.; Su, W. *Org. Lett.* **2013**, *15*, 5106-5109. (c) Patel, P.; Chang, S. *Org. Lett.* **2014**, *16*, 3328-3331. (d) Lee, D.; Kim, Y.; Chang, S. *J. Org. Chem* **2013**, *78*, 11102-11109.

7. Recent authorative reviews on the use of inexpensive first-row transition metal catalysts for C–H bond functionalization: (a) Nakamura, E.; Hatakeyama, T.; Ito, S.; Ishizuka, K.; Ilies, L.; Nakamura, M. *Org. React.* **2014**, *83*, 1-209. (b) Ackermann, L. *J. Org. Chem*. **2014**, *79*, 8948-8954. (c) Yamaguchi, J.; Muto, K.; Itami, K. *Eur. J. Org. Chem.* **2013**, 19-30. (d) Yoshikai, N. *Synlett* **2011**, 1047-1051. (e) Nakao, Y. *Chem. Rec.* **2011**, *11*, 242-251. (f) Kulkarni, A.; Daugulis, O. *Synthesis* **2009**, 4087-4109, and references cited therein.

8. (a) Suzuki, Y.; Sun, B.; Sakata, K.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 9944-9947. (b) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Chem. Commun.* **2015**, *51*, 4659-4661. (c) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal.* **2014**, *356*, 1491-1495. (d) Ikemoto, H.; Yoshino, T.; Sakata, K.; Matsunaga, S.; Kanai, M. *J. Am. Chem. Soc.* **2014**, *136*, 5424-5431. (e) Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Chem. Eur. J.* **2013**, *19*, 9142-9146. (f) Andou, T.; Saga, Y.; Komai, H.; Matsunaga, S.; Kanai, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 3213-3216. (g) Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 2207-2211.

9. (a) Wang, H.; Koeller, J.; Liu, W.; Ackermann, L. *Chem. Eur. J.* **2015**, *21*, 15525-15528. (b) Sauermann, N.; González, M. J.; Ackermann, L. *Org. Lett.* **2015**, *17*, 5316-5319. (c) Li, J.; Ackermann, L. *Angew. Chem. Int. Ed.* **2015**, *54*, 8551-8554. (d) Moselage, M.; Sauermann, N.; Koeller, J.; Liu, W.; Gelman, D.; Ackermann, L. *Synlett* **2015**, 1596-1600. (e) Ma, W.; Ackermann, L. *ACS Catal.* **2015**, *5*, 2822-2825. (f) Li, J.; Ackermann, L. *Angew. Chem. Int. Ed.* **2015**, *54*, 3635-3638.

10. (a) Grigorjeva, L.; Daugulis, O. *Org. Lett.* **2015**, *17*, 1204-1207. (b) Grigorjeva, L.; Daugulis, O. *Angew. Chem. Int. Ed.* **2014**, *53*, 10209-10212.

11. (a) Zhao, D.; Kim, J. H.; Stegemann, L.; Strassert, C. A.; Glorius, F. *Angew. Chem. Int. Ed.* **2015**, *54*, 4508-4511. (b) Gensch, T.; Vasquez-Cespedes, S.; Yu, D.-G.; Glorius, F. *Org. Lett.* **2015**, *17*, 3714-3717. (c) Yu, D.-G.; Gensch, T.; Azambuja, F. d.; Vásquez-Céspedes, S.; Glorius, F. *J. Am. Chem. Soc.* **2014**, *136*, 17722-17725.

12. (a) Hummel, J. R.; Ellman, J. A. *Org. Lett.* **2015**, *17*, 2400-2403. (b) Hummel, J. R.; Ellman, J. A. *J. Am. Chem. Soc.* **2015**, *137*, 490-498.

13. (a) Pawar, A. B.; Chang, S. *Org. Lett.* **2015**, *17*, 660-663. (b) Patel, P.; Chang, S. *ACS Catal.* **2015**, *5*, 853-858. (c) Figg, T. M.; Park, S.; Park, J.; Chang, S.; Musaev, D. G. *Organometallics* **2014**, *33*, 4076-4085.

14. (a) Zhang, Z.-Z.; Liu, B.; Wang, C.-Y.; Shi, B.-F. *Org. Lett.* **2015**, *17*, 4094-4097. (b) Zhang, L.-B.; Hao, X.-Q.; Liu, Z.-J.; Zheng, X.-X.; Zhang, S.-K.; Niu, J.-L.; Song, M.-P. *Angew. Chem. Int. Ed.* **2015**, *54*, 10012-10015. (c) Zhang, L.-B.; Hao, X.-Q.; Zhang, S.-K.; Liu, Z.-J.; Zheng, X.-X.; Gong, J.-F.; Niu, J.-L.; Song, M.-P. *Angew. Chem. Int. Ed.* **2015**, *54*, 272-275. (d) Wu, X.; Yang, K.; Zhao, Y.; Sun, H.; Li, G.; Ge, H. *Nat. Commun.* **2015**, *6*, 6462. (e) Yang, K.; Chen, X.; Wang, Y.; Li, W.; Kadi, A. A.; Fun, H.-K.; Sun, H.; Zhang, Y.; Li, G.; Lu, H. *J. Org. Chem* **2015**, *80*, 11065-11072. (f) Planas, O.; Whiteoak, C. J.; Company, A.; Ribas, X. *Adv. Synth. Catal.* **2015**, *357*, 4003-4012. (g) Kalsi, D.; Sundararaju, B. *Org. Lett.* **2015**, *17*, 6118-6121.

15. For representative examples on complementary low-valent cobalt catalysis, see: (a) Moselage, M.; Sauermann, N.; Richter, S. C.; Ackermann, L. *Angew. Chem. Int. Ed*. **2015**, *54*, 6352-6355. (b) Li, J.; Ackermann, L. *Chem. Eur. J.* **2015**, *21*, 5718-5722. (c) Punji, B.; Song, W.; Shevchenko, G. A.; Ackermann, L. *Chem. Eur. J.* **2013**, *19*, 10605-10610. (d) Song, W.; Ackermann, L. *Angew. Chem. Int. Ed*. **2012**, *51*, 8251-8254.

16. Liang, Y.; Liang, Y.-F.; Tang, C.; Yuan, Y.; Jiao, N. *Chem. Eur. J.* **2015**, *21*, 16395-16399.

17. Park, J.; Chang, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 14103-14107.

18. For the use of dioxazolones, see: (a) Park, Y.; Park, K. T.; Kim, J. G.; Chang, S. *J. Am. Chem. Soc*. **2015**, *137*, 4534-4542. (b) Bizet, V.; Bolm, C. *Eur. J. Org. Chem*. **2015**, 2854-2860. (c) Park, Y.; Jee, S.; Kim, J. G.; Chang, S. *Org. Process Res. Dev.* **2015**, *19*, 1024-1029. (d) Bizet, V.; Buglioni, L.; Bolm, C. *Angew. Chem. Int. Ed.* **2014**, *53*, 5639-5642. See also: (e) Zhong, C. L.; Tang, B. Y.; Yin, P.; Chen, Y.; He, L. *J. Org. Chem.* **2012**, *77*, 4271-4277. (f) Eibler, E.; Käsbauer, J.; Pohl, H.; Sauer, J. *Tetrahedron Lett*. **1987**, *28*, 1097-1100. (g) Middleton, W. J. *J. Org. Chem.* **1983**, *48*, 3845-3847. (h) Sauer, J.; Mayer, K. K. *Tetrahedron Lett.* **1968**, *9*, 319-324, and references cited therein.

19. (a) Rousseau, G.; Breit, B. *Angew. Chem. Int. Ed.* **2011**, *50*, 2450-2494. (b) Zhang, F.; Spring, D. R. *Chem. Soc. Rev.* **2014**, *43*, 6906-6919.

20. (a) Wang, H.-L.; Shang, M.; Sun, S.-Z.; Zhou, Z.-L.; Laforteza, B. N.; Dai, H.-X.; Yu, J.-Q. *Org. Lett.* **2015**, *17*, 1228-1231. (b) Shang, M.; Sun, S.-Z.; Dai, H.-X.; Yu, J.-Q. *Org. Lett.* **2014**, *16*, 5666-5669. (c) Shang, M.; Sun, S.-Z.; Wang, H.-L.; Laforteza, B. N.; Dai, H.-X.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2014**, *53*, 10439-10442. (d) Shang, M.; Wang, H.-L.; Sun, S.-Z.; Dai, H.-X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 11590-11593.

21. Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315-1345.

22. Ackermann, L.; Lygin, A. V. *Org. Lett.* **2011**, *13*, 3332-3335.

23. Guo, X.-K.; Zhang, L.-B.; Wei, D.; Niu, J.-L. *Chem. Sci.* **2015**, *6*, 7059-7071.

24. (a) Tirler, C.; Ackermann, L. *Tetrahedron* **2015**, 4543-4551. (b) Ma, W.; Mei, R.; Tenti, G.; Ackermann, L. *Chem. Eur. J.* **2014**, *20*, 15248-15251.

25. Sun, S.-Z.; Shang, M.; Wang, H.-L.; Lin, H.-X.; Dai, H.-X.; Yu, J.-Q. *J. Org. Chem* **2015**, *80*, 8843-8848.