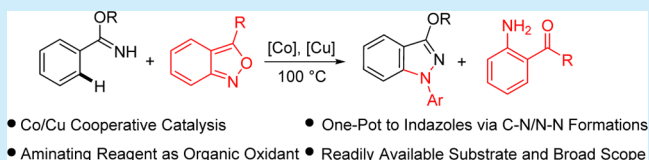


Cooperative Co(III)/Cu(II)-Catalyzed C–N/N–N Coupling of Imidates with Anthranils: Access to 1*H*-Indazoles via C–H ActivationLei Li,[†] He Wang,[†] Songjie Yu, Xifa Yang, and Xingwei Li^{*}

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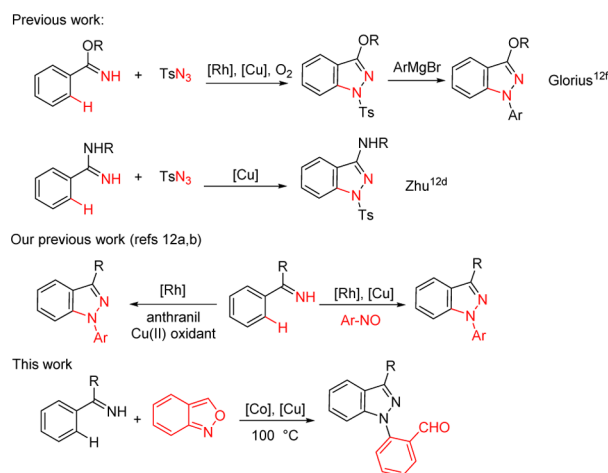
Supporting Information

ABSTRACT: Cooperative cobalt- and copper-catalyzed C–H activation of imidate esters and oxidative coupling with anthranils allowed efficient synthesis of 1*H*-indazoles in the absence of metal oxidants. The anthranil acts as a convenient aminating reagent as well as an organic oxidant in this transformation. The copper catalyst likely functions at the stage of N–N formation.



Transition-metal-catalyzed direct C–H functionalization of arenes has been extensively employed over the past decades as a powerful strategy in organic synthesis¹ owing to high atom- and step-economy.^{2,3} Despite the high activity of various second- and third-row transition-metal catalysts, applications of cost-effective, earth-abundant, and functionally unique first-row metal catalysts are highly desirable. Pioneered by Kanai and Matsunaga,⁴ the higher Lewis acidity and catalytic activity of stable Cp^{*}Co(III) complexes have allowed the development of new catalytic systems of C–H activation. This was made possible by the enhanced metal–ligand cooperation in the catalytic cycle. Afterward, the groups of Glorius,⁵ Ackermann,⁶ Ellman,⁷ Daugulis,⁸ Chang,⁹ and others¹⁰ have made progress in cobalt-catalyzed C–H activation. These catalytic systems can stay complementary to those enabled by the rhodium(III) congeners in terms of substrate scope, activity, and selectivity.

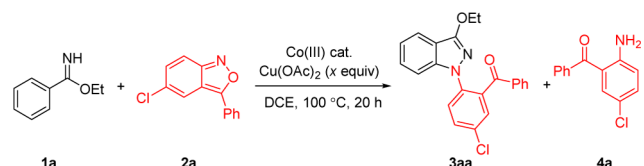
1*H*-Indazoles are known as an important skeleton that has shown a wide range of pharmacological activities,¹¹ including anti-inflammatory, antiviral, antimicrobial, and anticancer activities. Therefore, the development of inexpensive and efficient methods to access 1*H*-indazoles in a green and step-economic fashion is highly desirable. In this regard, the strategy of transition-metal-catalyzed C–H bond activation/functionalization has exhibited significant potentials in indazole synthesis.¹² For example, Glorius reported a Rh(III)-catalyzed oxidative annulation between imidates and sulfonyl azides to deliver 1*H*-indazoles.^{12f} Subsequently, copper-catalyzed 1*H*-indazole synthesis via C–N/N–N bond formations has been disclosed by the group of Zhu.^{12d} We recently developed two distinctive methods to construct indazoles via Rh(III)-catalyzed C–H activation of imidates under both oxidative and redox-neutral conditions (Scheme 1).^{12a,b} While we have briefly applied anthranil as an aminating reagent in one report, both expensive rhodium(III) catalysts and a stoichiometric amount of Cu(II) oxidant were necessary.^{12a} Thus, direct access to these synthetically useful substituted indazoles via base metal catalysis needs further exploration. We now reported synergistic cobalt- and copper-catalyzed synthesis of 1*H*-indazoles via C–

Scheme 1. Intermolecular Synthesis of 1*H*-Indazoles

H activation and C–N/N–N bond formations, where anthranils¹³ act as both an aminating reagent and an organic oxidant.^{12d}

We commenced our investigation with the screening of reaction parameters for the coupling between imidates (**1a**) and 5-chloro-3-phenylbenzo[*c*]isoxazole (**2a**, Table 1). Using [Cp^{*}Co(CO)I₂] (10 mol %)/AgSbF₆ (20 mol %) as a catalyst, a coupling occurred and the desired indazole product **3aa** was isolated in 60% yield in the presence of Cu(OAc)₂ (2.1 equiv, entry 1). Switching the catalyst to [Cp^{*}Co(MeCN)₃](SbF₆)₂ slightly improved the yield (entry 2). When the amount of **2a** was increased from 1.5 to 3.0 equiv, the yield of **3aa** was improved to 92% (entry 3), but lowering the catalyst loading resulted in diminished yields (entries 4 and 5). We noted that in some cases anthranil decomposed to a 2-aminobenzophenone in rhodium-catalyzed reactions, so we reasoned that it might act as an organic oxidant. Indeed, the reaction proceeded

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Table 1. Optimization of the Reaction Conditions^a


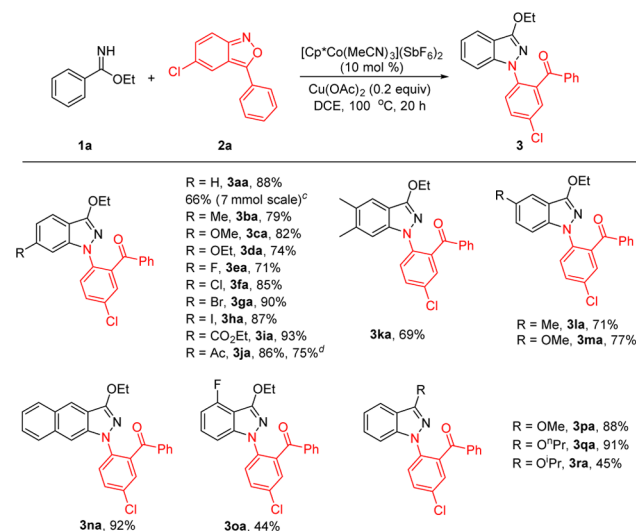
entry	cat. (mol %)	<i>x</i>	yield ^b (%)
1	[Cp*Co(Co)I ₂] ₂ (10)/AgSbF ₆ (20)	2.1	60 ^c
2	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	2.1	66 ^c
3	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	2.1	92
4	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (8)	2.1	85
5	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (5)	2.1	60
6	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	2.1	56 ^d
7	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	0.2	88
8	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	0.2	56 ^e
9	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	0.2	81 ^f
10	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	0.2	84 ^g
11	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	0	ND
12	[Cp*Co(MeCN) ₃](SbF ₆) ₂ (10)	0.2	ND

^aThe reaction was carried out using imidate ester **1a** (0.2 mmol), **2a** (0.6 mmol), Co catalyst, and Cu(OAc)₂ in DCE (3 mL) at 100 °C (sealed tube) under N₂. ^bIsolated yield after column chromatography. ^c**2a** (0.3 mmol). ^d80 °C. ^eReaction was performed with **2a** (0.3 mmol) under 1 atm of O₂. ^f**2a** (0.4 mmol). ^g**2a** (0.5 mmol).

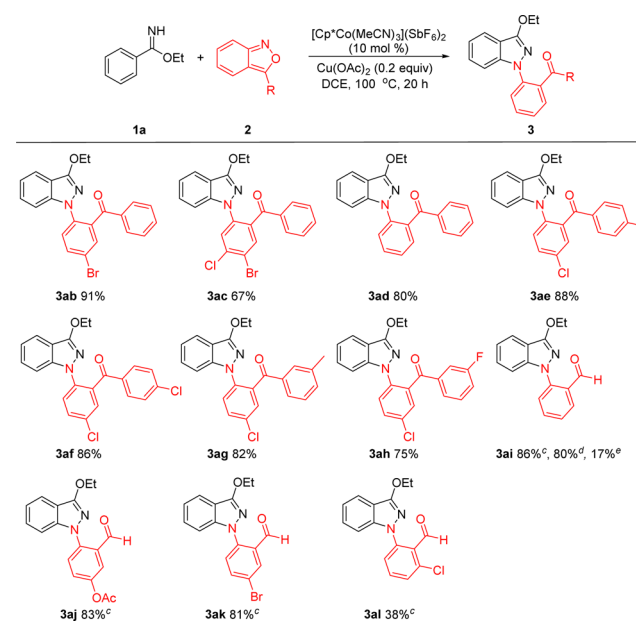
with comparable efficiency (88% yield) in the presence of 20 mol % of Cu(OAc)₂ (entry 7), and the reduced coproduct **4a** was isolated yield (45% based on **2a** and 130% based on **1a**). However, further decreasing the amount of **2a** gave inferior results even in the presence of O₂ (entry 8). It was found that 3.0 equiv of **2a** was the optimal loading (entries 7, 9, and 10). Control experiments indicated that no desired reaction occurred when either the Co(III) catalyst or Cu(OAc)₂ was omitted (entries 11 and 12).

With the optimized reaction conditions in hand, the scope and generality with respect to imidates were next examined in the coupling of **2a** (Scheme 2). Thus, imidates bearing both electron-donating and -withdrawing groups at the *para* position of the phenyl ring all coupled in good to excellent yields (**3aa–ja**). It was observed that the electronic properties of imidates had no apparent effect on the reaction. In addition, *meta*-substituted or disubstituted imidates (**3ka–na**) coupled in moderate to excellent yields in high site selectivity, where C–H functionalization occurred at the less hindered site. Introduction of an *o*-fluoro group was also tolerated, delivering **3oa** in 44% yield. Besides the ethyl ester, other alkyl esters also coupled smoothly in excellent yields (**3pa,qa**), although the isopropyl imidate reacted with diminished efficiency (**3ra**).

We next examined the scope of the anthranil substrate. As given in Scheme 3, introduction of functional groups such as halogens (**3ab,ac**) and phenyl (**3ad**) to different positions of the anthranil ring was compatible. In addition, introduction of a substituted phenyl group into the 3-position of the anthranil ring was fully tolerated (**3ae–ah**). However, when the unsubstituted anthranil was applied under the standard conditions, the reaction became sluggish. To our delight, further introduction of PivOH regained the coupling efficiency (**3ai**), which likely facilitated the C–H activation process. In comparison, a poor result was observed when the aminating reagent was replaced by 2-azidobenzaldehyde, indicating the intrinsic reactivity of anthranils. Thus, several substituted

Scheme 2. Substrate Scope of Imidates^{a,b}

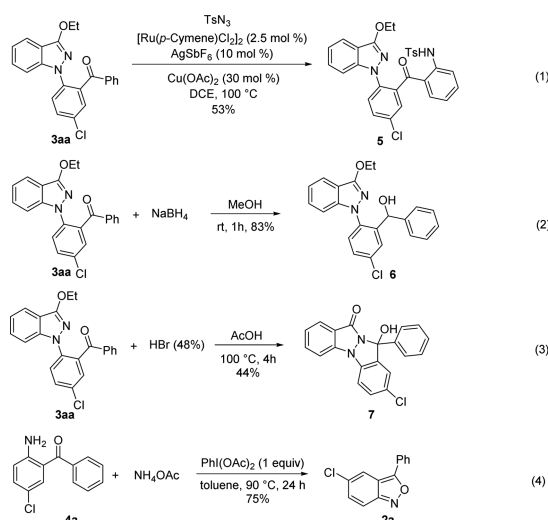
^aThe reaction was carried out using imidate ester (0.2 mmol), **2a** (0.6 mmol), the cobalt catalyst (0.02 mmol), and Cu(OAc)₂ (0.04 mmol) in DCE (3 mL) at 100 °C (sealed tube) under N₂. ^bIsolated yield after column chromatography. ^cReaction was performed with 7 mmol of **1a**. ^d**2a** (0.5 mmol).

Scheme 3. Scope of Anthranils in Indazole Synthesis^{a,b}

^aThe reaction was carried out using **1a** (0.2 mmol), anthranil (0.6 mmol), the Co catalyst (0.02 mmol), and Cu(OAc)₂ (0.04 mmol) in DCE (3 mL) at 100 °C (sealed tube) under N₂ for 20 h. ^bIsolated yield after column chromatography. ^cPivOH (0.2 mmol). ^dPivOH (0.2 mmol) and anthranil (0.5 mmol). ^eReaction was performed with 2-azidobenzaldehyde.

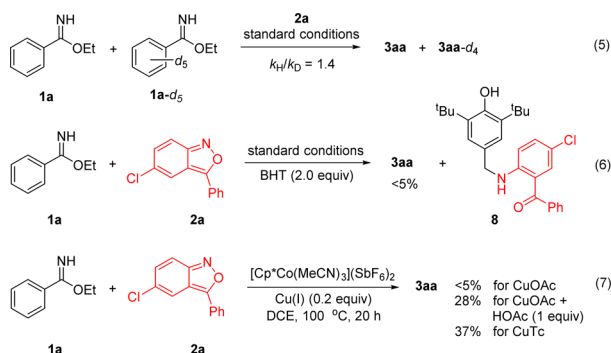
anthranils coupled smoothly in high yields (**3aj,ak**) in the presence of PivOH, although introduction of a 4-chloro group reduced the reaction efficiency likely due to steric effects (**3al**).

To access a functionalized product, a derivatization reaction was carried out (eq 1). Using TsN₃ as an amidating reagent, product **5** was isolated in moderate yield via a Ru(II)-catalyzed C–H amidation process.¹⁴ Reduction of **3aa** with NaBH₄ afforded alcohol **6** in 83% yield (eq 2). Moreover, acid



treatment of **3aa** led to deprotection of the ether^{12f} followed by intramolecular nucleophilic addition to give hemiaminal **7** in 44% yield (eq 3). Recycling of coproduct **4a** has been briefly explored.¹⁵ Satisfyingly, when a stoichiometric amount of $\text{PhI}(\text{OAc})_2$ was used as an oxidant, the anthranil **2a** was isolated in 75% yield (eq 4).

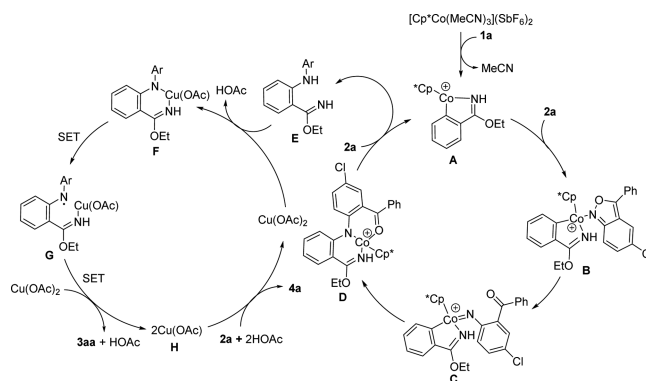
To gain mechanistic insight into the catalytic system, two side-by-side parallel reactions were carried out for coupling of **1a** and **1a-d₅** with anthranil **2a** at a low conversion. A small value of $k_{\text{H}}/k_{\text{D}} = 1.4$ was obtained on the basis of ^1H NMR analysis (eq 5), indicating that C–H bond cleavage is likely not



involved in the turnover-limiting step. To explore the intermediacy of radical species and hence the possibility of single-electron transfer in N–N bond formation,^{12f} the amination reaction was performed in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT, eq 6). The reaction was inhibited, but an amine (**8**) was isolated in 30% yield, suggesting that a radical pathway is probably involved in this reaction. To further probe the formation of N–N bond, the $\text{Cu}(\text{OAc})_2$ was replaced by CuOAc for the coupling of **1a** and **2a**, and **3aa** was isolated in 28% yield in the presence of AcOH (eq 7). Switching to CuTc (0.2 equiv) gave rise to **3aa** in 37% yield, thus indicating that a Cu(I) species might be involved in the N–N formation process.

On the basis of our preliminary results and relevant reports,^{12a,b,d,f} a plausible catalytic cycle is proposed in Scheme 4 (see the SI for alternative mechanisms). The reaction is initiated by cyclometalation of the imidate to furnish a five-membered metallacyclic intermediate **A** to which anthranil coordinates to afford intermediate **B**, which undergoes intramolecular N–O bond cleavage to deliver a nitrene

Scheme 4. Proposed Mechanism



intermediate **C**. Migratory insertion of the Co–aryl bond into the nitrene gives a tripodal intermediate **D**. Coordination of an imidate to **D** and subsequent C–H activation releases the aminated intermediate **E** with the regeneration of cobalt(III) **A**. In a sequential copper-catalyzed cycle, coordination of $\text{Cu}(\text{OAc})_2$ to **E** with extrusion of HOAc gives a Cu(II) species **F**, which undergoes double single-electron transfer to generate indazole **3aa** and Cu(I) intermediate **H**. This intermediate could be oxidized by another molecule of **2a** in the presence of AcOH to regenerate the $\text{Cu}(\text{OAc})_2$. In this process, reductive opening of the anthranil ring generates a nitrogen radical that is trappable by BHT. However, an alternative $\text{Cu(II)}\text{--Cu(0)}\text{--Cu(II)}$ pathway remains possible in which intermediate **F** reductively eliminates the product **3aa** and HOAc to give a Cu(0) . Oxidation of Cu(0) by anthranil to Cu(II) then regenerates the active copper catalyst.

In summary, we have developed a synergistic Co/Cu-catalyzed system to construct substituted 1*H*-indazoles from easily available imidates and anthranils via a C–H activation pathway where anthranils also serve as an organic oxidant. This catalytic system tolerates a wide range of substrates with high reaction efficiency. Meanwhile, mechanistic studies indicated that the N–N formation likely involved nitrogen radical species. Moreover, the reduced coproduct could be recycled to the anthranil substrate under oxidative conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01716.

Experimental procedures, characterization data, alternative mechanism, and ^1H and ^{13}C NMR spectra (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 1107. (b) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281. (c) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936. (d) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788. (e) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (f) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (g) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (h) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (i) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (j) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (k) Mkhali, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. (l) Godula, K.; Sames, D. *Science* **2006**, *312*, 67.
- (2) Trost, B. M. *Science* **1991**, *254*, 1471.
- (3) Wender, P. A.; Miller, B. L. *Nature* **2009**, *460*, 197.
- (4) (a) Sun, B.; Yoshino, T.; Kanai, M.; Matsunaga, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 12968. (b) Suzuki, Y.; Sun, B.; Sakata, K.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 9944. (c) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Chem. Commun.* **2015**, *51*, 4659. (d) Ikemoto, H.; Yoshino, T.; Sakata, K.; Matsunaga, S.; Kanai, M. *J. Am. Chem. Soc.* **2014**, *136*, 5424. (e) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal.* **2014**, *356*, 1491. (f) Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Chem. - Eur. J.* **2013**, *19*, 9142. (g) Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 2207.
- (5) (a) Wang, X.; Lerchen, A.; Glorius, F. *Org. Lett.* **2016**, *18*, 2090. (b) Kim, J. H.; Greßes, S.; Glorius, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 5577. (c) Lu, Q.; Vásquez-Céspedes, S.; Gensch, T.; Glorius, F. *ACS Catal.* **2016**, *6*, 2352. (d) Lerchen, A.; Vásquez-Céspedes, S.; Glorius, F. *Angew. Chem., Int. Ed.* **2016**, *55*, 3208. (e) Gensch, T.; Vásquez-Céspedes, S.; Yu, D.-G.; Glorius, F. *Org. Lett.* **2015**, *17*, 3714. (f) Zhao, D.; Kim, J. H.; Stegemann, L.; Strasser, C. A.; Glorius, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 4508. (g) Gensch, T.; Vásquez-Céspedes, S.; Yu, D.-G.; Glorius, F. *Org. Lett.* **2015**, *17*, 3714. (h) Yu, D.-G.; Gensch, T.; de Azambuja, F.; Vásquez-Céspedes, S.; Glorius, F. *J. Am. Chem. Soc.* **2014**, *136*, 17722.
- (6) (a) Li, J.; Tang, M.; Zang, L.; Zhang, X.; Zhang, Z.; Ackermann, L. *Org. Lett.* **2016**, *18*, 2742. (b) Mei, R.; Wang, H.; Warratz, S.; Macgregor, S. A.; Ackermann, L. *Chem. - Eur. J.* **2016**, *22*, 6759. (c) Wang, H.; Moselage, M.; González, M. J.; Ackermann, L. *ACS Catal.* **2016**, *6*, 2705. (d) Mei, R.; Loup, J.; Ackermann, L. *ACS Catal.* **2016**, *6*, 793. (e) Moselage, M.; Li, J.; Ackermann, L. *ACS Catal.* **2016**, *6*, 498. (f) Sauermann, N.; González, M. J.; Ackermann, L. *Org. Lett.* **2015**, *17*, 5316. (g) Wang, H.; Koeller, J.; Liu, W.; Ackermann, L. *Chem. - Eur. J.* **2015**, *21*, 15525. (h) Li, J.; Ackermann, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 8551. (i) Moselage, M.; Sauermann, N.; Koeller, J.; Liu, W.; Gelman, D.; Ackermann, L. *Synlett* **2015**, *26*, 1596. (j) Ma, W.; Ackermann, L. *ACS Catal.* **2015**, *5*, 2822. (k) Li, J.; Ackermann, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 3635.
- (7) (a) Hummel, J. R.; Ellman, J. A. *Org. Lett.* **2015**, *17*, 2400. (b) Hummel, J. R.; Ellman, J. A. *J. Am. Chem. Soc.* **2015**, *137*, 490.
- (8) (a) Nguyen, T. T.; Grigorjeva, L.; Daugulis, O. *ACS Catal.* **2016**, *6*, 551. (b) Grigorjeva, L.; Daugulis, O. *Org. Lett.* **2015**, *17*, 1204. (c) Grigorjeva, L.; Daugulis, O. *Angew. Chem., Int. Ed.* **2014**, *53*, 10209.
- (9) (a) Park, J.; Chang, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 14103. (b) Pawar, A. B.; Chang, S. *Org. Lett.* **2015**, *17*, 660. (c) Patel, P.; Chang, S. *ACS Catal.* **2015**, *5*, 853.
- (10) (a) Prakash, S.; Muralirajan, K.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2016**, *55*, 1844. (b) Yu, W.; Zhang, W.; Liu, Z.; Zhang, Y. *Chem. Commun.* **2016**, *52*, 6837. (c) Sen, M.; Emayavaramban, B.; Barsu, N.; Premkumar, J. R.; Sundararaju, B. *ACS Catal.* **2016**, *6*, 2792. (d) Barsu, N.; Sen, M.; Premkumar, J. R.; Sundararaju, B. *Chem. Commun.* **2016**, *52*, 1338. (e) Wang, F.; Wang, H.; Wang, Q.; Yu, S.; Li, X. *Org. Lett.* **2016**, *18*, 1306. (f) Kong, L.; Yu, S.; Zhou, X.; Li, X. *Org. Lett.* **2016**, *18*, 588. (g) Liang, Y.; Jiao, N. *Angew. Chem., Int. Ed.* **2016**, *55*, 4035. (h) Liang, Y.; Liang, Y.-F.; Tang, C.; Yuan, Y.; Jiao, N. *Chem. - Eur. J.* **2015**, *21*, 16395. (i) Zhang, Z.-Z.; Liu, B.; Wang, C.-Y.; Shi, B.-F. *Org. Lett.* **2015**, *17*, 4094. (j) Liu, X. G.; Zhang, S. S.; Jiang, C. Y.; Wu, J. Q.; Li, Q.; Wang, H. *Org. Lett.* **2015**, *17*, 5404.
- (11) (a) Dolzhenko, A. V.; Chui, W. K. *Heterocycles* **2008**, *75*, 1575. (b) Sun, J.-H.; Teleha, C. A.; Yan, J.-S.; Rodgers, J. D.; Nugiel, D. A. *J. Org. Chem.* **1997**, *62*, 5627. (c) Rodgers, J. D.; Johnson, B. L.; Wang, H.; Greenberg, R. A.; Erickson-Viitanen, S.; Klabe, R. M.; Cordova, B. C.; Rayner, M. M.; Lam, G. N.; Chang, C.-H. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2919. (d) Turnbull, R. S. *J. Can. Dent. Assoc.* **1995**, *61*, 127. (e) Bermudez, J.; Fake, C. S.; Joiner, G. F.; Joiner, K. A.; King, F. D.; Miner, W. D.; Sanger, G. J. *J. Med. Chem.* **1990**, *33*, 1924.
- (12) (a) Yu, S.; Tang, G.; Li, Y.; Zhou, X.; Lan, Y.; Li, X. *Angew. Chem., Int. Ed.* **2016**, *55*, 8696. (b) Wang, Q.; Li, X. *Org. Lett.* **2016**, *18*, 2102. (c) Hummel, J. R.; Ellman, J. A. *J. Am. Chem. Soc.* **2015**, *137*, 490. (d) Peng, J.; Xie, Z.; Chen, M.; Wang, J.; Zhu, Q. *Org. Lett.* **2014**, *16*, 4702. (e) Hu, J.; Xu, H.; Nie, P.; Xie, X.; Nie, Z.; Rao, Y. *Chem. - Eur. J.* **2014**, *20*, 3932. (f) Yu, D.-G.; Suri, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 8802. (g) Li, X.; He, L.; Chen, H.; Wu, W.; Jiang, H. *J. Org. Chem.* **2013**, *78*, 3636. (h) Zhang, T.; Bao, W. *J. Org. Chem.* **2013**, *78*, 1317. (i) Lian, Y.; Bergman, R. G.; Lavis, L. D.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7122. (j) Hu, J.; Cheng, Y.; Yang, Y.; Rao, Y. *Chem. Commun.* **2011**, *47*, 10133. (k) Inamoto, K.; Saito, T.; Katsuno, M.; Sakamoto, T.; Hiroya, K. *Org. Lett.* **2007**, *9*, 2931.
- (13) (a) Yu, S.; Li, Y.; Zhou, X.; Wang, H.; Kong, L.; Li, X. *Org. Lett.* **2016**, *18*, 2812. (b) Shi, L.; Wang, B. *Org. Lett.* **2016**, *18*, 2820. (c) Zou, M.; Liu, J.; Tang, C.; Jiao, N. *Org. Lett.* **2016**, *18*, 3030. (d) Tang, C.; Zou, M.; Liu, J.; Wen, X.; Sun, X.; Zhang, Y.; Jiao, N. *Chem. - Eur. J.* **2016**, DOI: 10.1002/chem.201602556. (e) Jin, H.; Huang, L.; Xie, J.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2016**, *55*, 794. (f) Baum, J. S.; Condon, M. E.; Shook, D. A. *J. Org. Chem.* **1987**, *52*, 2983.
- (14) (a) Zheng, Q.-Z.; Liang, Y.-F.; Qin, C.; Jiao, N. *Chem. Commun.* **2013**, *49*, 5654. (b) Bhanuchandra, M.; Ramu Yadav, M.; Rit, R. K.; Kuram, M. R.; Sahoo, A. K. *Chem. Commun.* **2013**, *49*, 5225. (c) Kim, J.; Kim, J.; Chang, S. *Chem. - Eur. J.* **2013**, *19*, 7328.
- (15) Zhao, D.; Shen, Q.; Li, J.-X. *Adv. Synth. Catal.* **2015**, *357*, 339.