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(Pentamethylcyclopentadienyl)cobalt(III)-Catalyzed Oxidative [4+2] Annulation of N–H Imines with Alkynes: Straightforward Synthesis of Multisubstituted Isoquinolines

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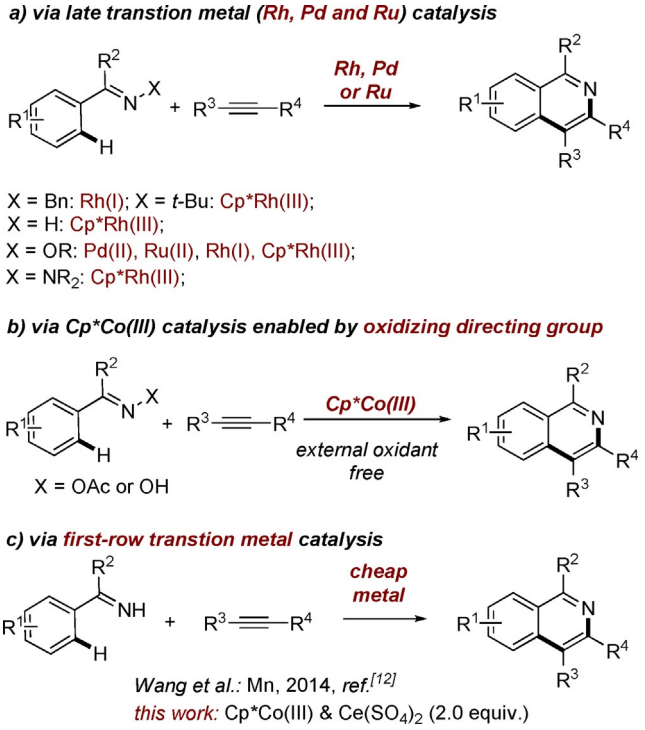
Abstract: A synthetic method for isoquinoline synthesis *via* a [4+2] annulation of N–H imines with alkynes using the high-valent (pentamethylcyclopentadienyl)cobalt(III) [Cp*Co(III)] catalyst is described. Cerium(IV) sulfate was found to be an efficient oxidant in lieu of the commonly used copper or silver salts. Broad substrate scope, high functional group tolerance, and generally good yields were observed.

Keywords: annulation; cerium salts; C–H activation; cobalt; isoquinolines

Isoquinolines are frequently encountered in a diverse array of functional molecules, such as phosphorescent materials,[1] fluorosensors,[2] and ligands for metal catalysis.[3] In particular, a number of biologically important compounds contain the isoquinoline motif.[4] The classical protocols for isoquinoline synthesis, as represented by the Bischler–Napieralski, Pomeranz–Fritsch, and Pictet–Gams reactions, suffer from disadvantages such as lack of easy availability of the substrate/reagent, harsh reaction conditions, limited product diversity, and/or low yields.[5] Recently, with the advent of transition metal-catalyzed C–H activation reactions,[6] several synthetic methodologies toward isoquinolines based on straightforward oxidative C–H annulations were elegantly developed (Scheme 1).[7–10] The majority of these methods take the advantage of the high reactivities of late transition metals, such as rhodium,[8] ruthenium[9] and palladium,[10] with the existence of an external oxidant or by using an oxidizing directing group (Scheme 1a). While these methods are effective, their synthetic application may be compromised by the high cost of the metal catalyst. From the sustainable chemistry point of view, there is an intensive need for cheap metal catalysts in lieu of the often used but precious late transition metals. In this regard, great advances have been realized on earth-abundant first-row transition metals catalysis (for instance, iron, cobalt, nickel, and copper), which effects similar, and more importantly, complementary reactivities for C–H activation reaction.[11] For isoquinoline synthesis, Wang recently reported an elegant [4+2] annulation of imines with alkynes under the catalysis of manganese (Scheme 1c).[12]

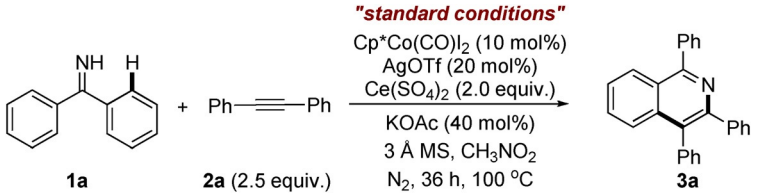


Scheme 1. Isoquinoline synthesis *via* direct C–H annulation.

Pioneered by Kanai and Matsunaga, high-valent Cp*Co(III) complexes have recently been recognized as efficient catalysts for a number of C–H activation reactions.[13,14] It is intriguing that in contrast to its congener Cp*Rh(III), Cp*Co(III) seems to favour redox-neutral C–H addition reactions, probably driven by the relatively higher basicity of the Co–C bond. In fact, only three examples of oxidative C–H functionalization promoted by Cp*Co(III) were known,[14w–y] wherein silver and/or copper salts were used as terminal oxidants. In continuation of our ongoing exploration of cheap metal catalysis, we herein report a Cp*Co(III)-catalyzed oxidative C–H annulation of imines with various alkynes (Scheme 1c).[14p,y] We identified in this reaction that $Ce(SO_4)_2$ is an efficient oxidant for Cp*Co(III) regeneration. We anticipate that the discovery of this new oxidant $Ce(SO_4)_2$ might extend the scope of Cp*Co(III)-catalyzed C–H activation reactions. In addition, various substituted alkynes including terminal alkynes were well tolerated in this reaction. During the preparation of this manuscript, the groups of Kanai and Matsunaga,[15a] Ackermann,[15b] and Sundararaju[15c] reported that multisubstituted isoquinolines could be accessed *via* Cp*Co(III)-catalyzed annulation reaction using an oxidizing oxime or its ester as directing group (Scheme 1b).

We commenced our studies by reacting diphenylmethanimine (**1a**) with 1,2-diphenylethyne (**2a**) using $Cp^*Co(CO)I_2$ as catalyst (Table 1). It should be noted that the starting materials – ketimines – are easily accessible *via* organometallic addition to benzonitriles. To our delight, after extensive exploration, we were able to obtain the desired product 1,3,4-triphenylisoquinoline (**3a**) in 83% isolated yield under the reaction conditions of $Cp^*Co(CO)I_2$ (10 mol%), $Ce(SO_4)_2$ (2.0 equiv.), AgOTf (20 mol%) and KOAc (40 mol%) in nitromethane (0.2 M) at 100 °C under an N_2 atmosphere (Table 1, entry 1). Control experiments indicated that $Cp^*Co(CO)I_2$ is essential for the reactivity (entry 2). The omission of iodide scavenger AgOTf gave a lower yield of 44% (entry 3). In addition, the absence of oxidant $Ce(SO_4)_2$ led to a much lower yield of 30% (entry 4). The attempts to use copper or silver salts, which were effective in other Cp*Co(III)-catalyzed oxidative C–H activation reactions,[14w–y] were proven to be unsuccessful in the current transformation (entries 5–8). Another cerium salt CAN $[Ce(NH_4)_2(NO_3)_6]$ shut down the reactivity completely (entry 9). Interestingly, the replacement of KOAc

Table 1. Optimization of the reaction conditions.[a]

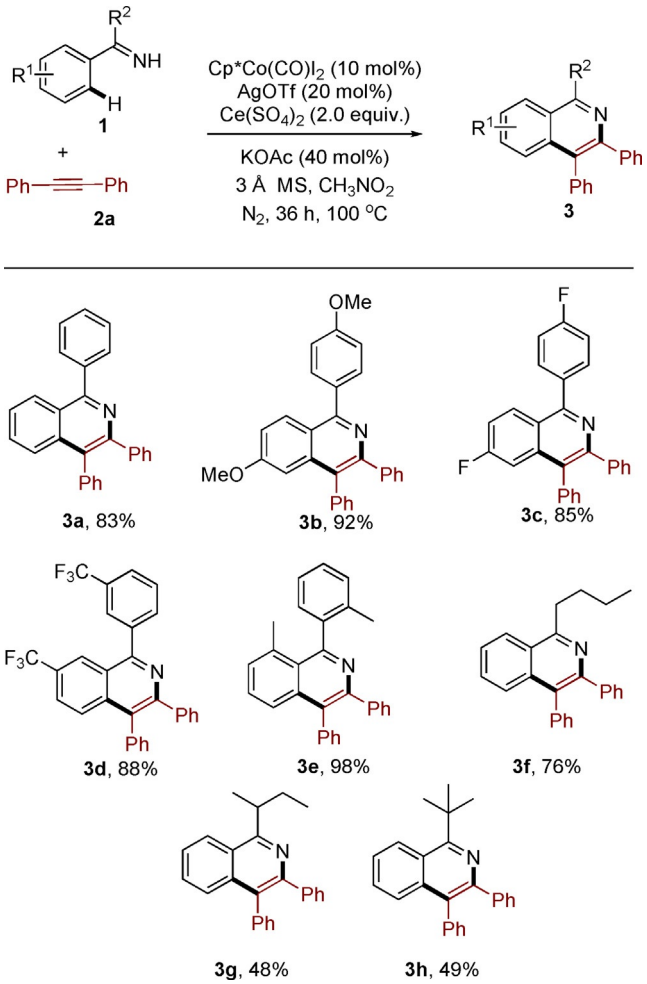


Entry	Variation from the standard conditions	Yield [%][b]
1	none	89 (83)[c]
2	without $Cp^*Co(CO)I_2$	0
3	without AgOTf	44
4	without $Ce(SO_4)_2$	30
5	$Cu(OAc)_2$ instead of $Ce(SO_4)_2$	24
6	AgOAc instead of $Ce(SO_4)_2$	0
7	$Cu(OAc)_2{\cdot}H_2O/Ag_2CO_3$ instead of $Ce(SO_4)_2$	13
8	Ag_2O instead of $Ce(SO_4)_2$	7
9	CAN instead of $Ce(SO_4)_2$	0
10	without KOAc	13
11	NaOAc instead of KOAc	70
12	PivOH instead of KOAc	76
13	5 mol% of $Cp^*Co(CO)I_2$	68
14	DCE instead of CH_3NO_2	53
15	MeOH instead of CH_3NO_2	65
16	DMF instead of CH_3NO_2	trace
17	80 °C instead of 100 °C	75

[a] *Reaction conditions:* **1a** (0.2 mmol), $Cp^*Co(CO)I_2$ (10 mol%), AgOTf (20 mol%), $Ce(SO_4)_2$ (2.0 equiv.), KOAc (40 mol%), 3 Å MS (300 mg) in CH_3NO_2 (1.0 mL) at 100 °C for 32 h.
[b] Yield determined by ^1H NMR using 1-iodo-4-methoxybenzene as internal standard.
[c] Isolated yield.

with either basic NaOAc or acidic PivOH gave slightly lower yields (entries 11 and 12); the omission of KOAc, however, led to a significantly lower efficiency (entry 10). The importance of carboxylate for this transformation might be rationalized by a carboxylate assisted C–H activation mechanism.[16] When 5 mol% of Cp*Co(CO)I_2 were employed, a lower yield (68%) was obtained (entry 13). Other solvents, such as DCE, MeOH and DMF, gave inferior results (entries 14–16). A lower temperature of 80 °C led to the incomplete conversion of **1a** (entry 17).

With the optimized reaction conditions established, we first investigated the scope and limitation of this transformation by reacting 1,2-diphenylethyne (**2a**) with a variety of imines. As shown in Scheme 2, it turned out that diaryl ketimines bearing different substituents regardless of their electronic properties such as methoxy (**3b**), fluoro (**3c**), trifluoromethyl (**3d**) and methyl (**3e**) groups underwent the reactions smoothly. An *ortho*-substitutent did not hamper the efficiency (**3e**). In addition, a *meta*-trifluomethylated aryl ketimine provided a single regioisomeric product, favouring the reaction at the less sterically hindered position (**3d**). Importantly, we were pleased to find that aryl alkyl ketimines are also compatible with the current reaction conditions even though lower yields were obtained, thus greatly broadening the scope of this reaction (**3f–h**).

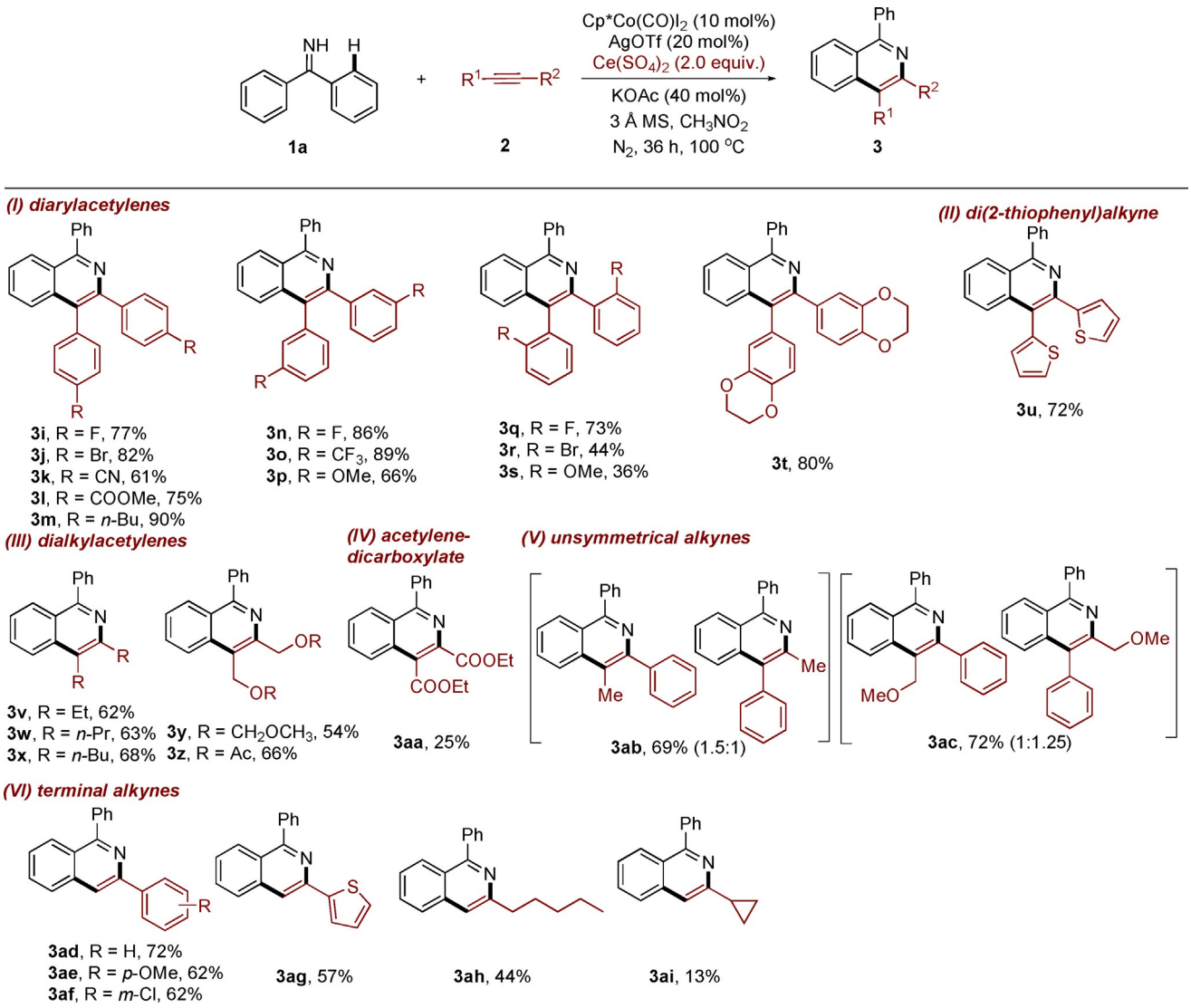


Scheme 2. Scope of imines.

The scope of the alkynes was also examined (Scheme 3). It was found that not only diarylacetylenes (**3i–u**), but also dialkylacetylenes (**3v–z**) were suitable coupling partners for this transformation, forming the corresponding multisubstituted isoquinolines in generally good yields. Numerous commonly encountered functional groups were well tolerated. In addition, diethyl acetylenedicarboxylate also gave the desired product in 25% yield (**3aa**). Terminal alkynes are often problematic coupling partners in oxidative C–H activation reactions, especially when copper or silver are used as oxidant due to the unproductive Glaser–Hay coupling reaction. We were delighted to find that terminal alkynes including aromatic, heteroaromatic and aliphatic alkynes reacted smoothly to give the annulation products with the substituents positioned exclusively next to the nitrogen atom.

A kinetic isotope effect (KIE) study was carried out to give clues on the mechanism. A small KIE value of 1.2 was observed, indicating that C–H bond cleavage is not involved in the turnover-limiting step (see the Supporting Information for details). In addition, no *cis*-stilbene derived from reduction of the alkyne was found, indicating a different reaction pathway from the manganese-catalyzed version.[12] Based on this observation and other relevant reports on Cp*Co(III)- and Cp*Rh(III)-catalyzed[8,14,15] oxidation annulation reactions, a plausible mechanism is outlined in Scheme 4. Firstly, the proposed active cationic catalyst **I** [Cp*Co(III)OAc]$^+$ was formed *via* halogen abstraction and ligand exchanges. Coordination of the ketimine is followed by a C–H activation to form a cyclocobalt species **III** (path A). The cleavage of the C–H bond might be assisted by the acetate and is not turnover-limiting. A subsequent migratory insertion of alkyne delivers a seven-membered ring intermediate **VI**. The isoquinoline product was formed upon C–N reductive elimination. The reduced Cp*Co(I) species is then oxidized by $Ce(SO_4)_2$ to complete the catalytic cycle.

Another mechanistic scenario featuring an intramolecular single electron transfer (SET) might be also evoked based on a recent theoretical study (path B).[14x] After the coordination of imine to Cp*Co(III), an intramolecular SET might occur to deliver a radical cation **IV**. A radical addition of **IV** to alkyne **2a** is followed by the radical combination with Cp*Co(II) to regenerate a Cp*Co(III) species. This Wheland intermediate **V** is then deprotonated to give the same species **VI** as path A. Radical scavenger experiments using TEMPO (2,2,6,6-tetramethylpiperidinyl 1-oxy)



Scheme 3. Scope of the alkynes.

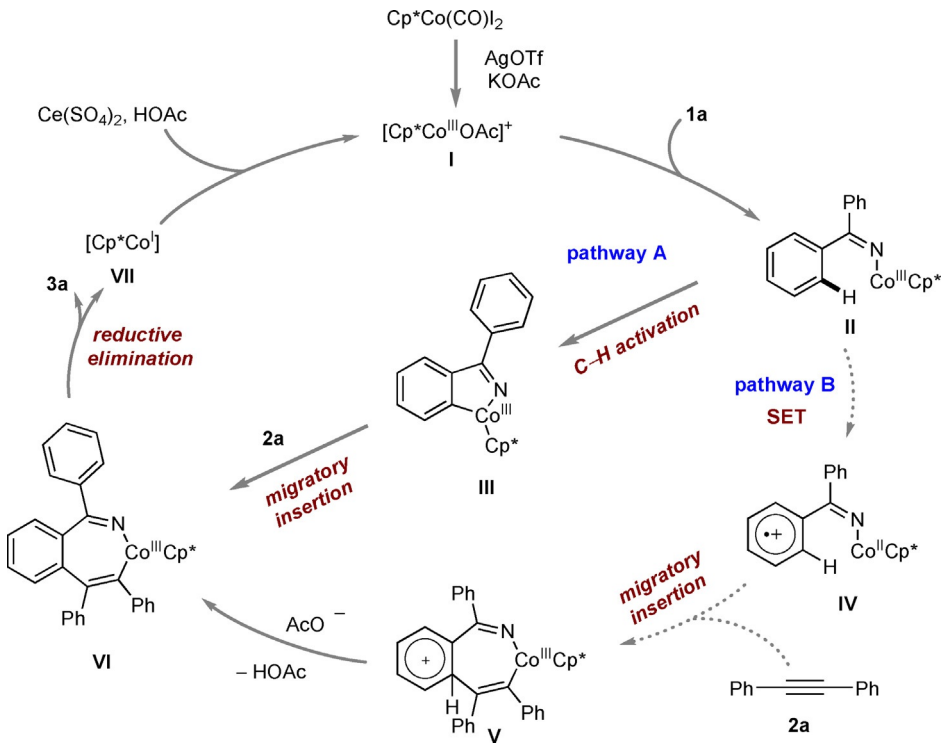
or BHT (butylated hydroxytoluene) as radical inhibiter did not hamper the reactivity. These results might suggest that pathway B is less likely.

In summary, we have successfully developed a cheap metal-catalyzed [4+2] annulation reaction of N–H imines with alkynes for the construction of multisubstituted isoquinolines. The reaction is catalyzed by a high valent [Cp*Co(III)] complex. $Ce(SO_4)_2$ was identified as an efficient oxidant for this transformation. This finding is important given that the commonly used copper or silver salts may cause undesired chemical processes due to their diverse reactivies in synthetic chemistry. Broad substrate scope, high functional group tolerance, and generally good yields were found.

Experimental Section

General Procedure

To an oven-dried Schlenk tube, under a stream of argon, were added imine **1** (0.2 mmol, 1.0 equiv.), alkyne **2** (0.5 mmol, 2.5 equiv.), $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 10.0 mol%), AgOTf (10.3 mg, 0.04 mmol, 0.2 equiv.), KOAc (7.8 mg, 0.08 mmol, 0.4 equiv.), $Ce(SO_4)_2$ (133.0 mg, 0.4 mmol, 2.0 equiv.), 3 Å molecular sieves (300.0 mg) and anhydrous CH_3NO_2 (1.0 mL). The mixture was stirred at 100 °C for 36 h. The reaction mixture was then diluted with DCM (10 mL) and washed with brine. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude product was purified by flash column chromatography on silica gel with an appropriate solvent to afford the pure product **3**.



Scheme 4. Proposed mechanism.

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References

[1] a) A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979; b) C.-L. Ho, W.-Y. Wong, Z.-Q. Gao, C.-H. Chen, K.-W. Cheah, B. Yao, Z. Xie, Q. Wang, D. Ma, L. Wang, X.-M. Yu, H.-S. Kwok, Z.-Y. Lin, *Adv. Funct. Mater.* **2008**, *18*, 319–331.

[2] D. Collado, E. Perez-Inestrosa, R. Suau, J.-P. Desvergne, H. Bouas-Laurent, *Org. Lett.* **2002**, *4*, 855–858.

[3] a) N. W. Alcock, J. M. Brown, G. I. Hulmes, *Tetrahedron: Asymmetry* **1993**, *4*, 743–756; b) C. W. Lim, O. Tissot, A. Mattison, M. W. Hooper, J. M. Brown, A. R. Cowley, D. I. Hulmes, A. J. Blacker, *Org. Process Res. Dev.* **2003**, *7*, 379–384; c) B. A. Sweetman, H. Müller-Bunz, P. J. Guiry, *Tetrahedron Lett.* **2005**, *46*, 4643–4646; d) F. Durola, J.-P. Sauvage, O. S. Wenger, *Chem. Commun.* **2006**, 171–173.

[4] a) K. W. Bentley, *Nat. Prod. Rep.* **2004**, *21*, 395; b) K. W. Bentley, *Nat. Prod. Rep.* **2006**, *23*, 444–463; c) Y. L. Janin, D. Decaudin, C. Monneret, M.-F. Poupon, *Tetrahedron* **2004**, *60*, 5481–5485.

[5] J. J. Li, E. J. Corey, *Name Reactions in Heterocyclic Chemistry*, John Wiley & Sons, Hoboken, NJ, **2005**, pp 375–494.

[6] For selected reviews, see: a) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074–1086; b) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242–3272; c) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147–1169; d) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655; e) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740–4761; f) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879–5918; g) B.-J. Li, Z.-J. Shi, *Chem. Soc. Rev.* **2012**, *41*, 5588–5598; h) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281–295; i) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007–1020.

[7] For a review, see: R. He, Z.-T. Huang, Q.-Y. Zheng, C. Wang, *Tetrahedron Lett.* **2014**, *55*, 5705–5713.

[8] Rhodium as catalyst: a) S.-G. Lim, J. H. Lee, C. W. Moon, J.-B. Hong, C.-H. Jun, *Org. Lett.* **2003**, *5*, 2759–2761; b) N. Guimond, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 12050–12051; c) K. Parthasarathy, C.-H. Cheng, *J. Org. Chem.* **2009**, *74*, 9359–9364; d) T. Fukutani, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Commun.* **2009**, *45*, 5141–5143; e) P. C. Too, Y.-F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688–5691; f) X. Zhang, D. Chen, M. Zhao, J. Zhao, A. Jia, X. Li, *Adv. Synth. Catal.* **2011**, *353*, 719–723; g) T. K. Hyster, T. Rovis, *Chem. Commun.* **2011**, *47*, 11846–11848; h) P. C. Too, S. H. Chua, S. H. Wong, S. Chiba, *J. Org. Chem.* **2011**, *76*, 6159–6168; i) X. Wei, M. Zhao, Z. Du, X. Li, *Org. Lett.* **2011**, *13*, 4636–4639; j) Y.-F. Wang, K. K. Toh, J.-Y. Lee, S. Chiba, *Angew. Chem.* **2011**, *123*,

6049–6053; *Angew. Chem. Int. Ed.* **2011**, *50*, 5927–5931; k) K. Morimoto, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2011**, *40*, 600–602; l) L. Zheng, J. Ju, Y. Bin, R. Hua, *J. Org. Chem.* **2012**, *77*, 5794–5800; m) S.-C. Chuang, P. Gandeepan, C.-H. Cheng, *Org. Lett.* **2013**, *15*, 5750–5753; n) W. Liu, X. Hong, B. Xu, *Synthesis* **2013**, *45*, 2137–2149; o) D.-S. Kim, J.-W. Park, C.-H. Jun, *Adv. Synth. Catal.* **2013**, *355*, 2667–2679; p) D. Zhao, F. Lied, F. Glorius, *Chem. Sci.* **2014**, *5*, 2869–2873; q) J. Zhang, H. Qian, Z. Liu, C. Xiong, Y. Zhang, *Eur. J. Org. Chem.* **2014**, 8110–8118; r) X.-C. Huang, X.-H. Yang, R.-J. Song, J.-H. Li, *J. Org. Chem.* **2014**, *79*, 1025–1031; s) W. Han, G. Zhang, G. Li, H. Huang, *Org. Lett.* **2014**, *16*, 3532–3535.

[9] Ruthenium as catalyst: a) C. Kornhaaß, J. Li, L. Ackermann, *J. Org. Chem.* **2012**, *77*, 9190–9198; b) R. K. Chinnagolla, S. Pimparkar, M. Jeganmohan, *Org. Lett.* **2012**, *14*, 3032–3035; c) R. K. Chinnagolla, S. Pimparkar, M. Jeganmohan, *Chem. Commun.* **2013**, *49*, 3703–3705; d) P. Villuendas, E. P. Urriolabeitia, *J. Org. Chem.* **2013**, *78*, 5254–5263; e) S. Gupta, J. Han, Y. Kim, S. W. Lee, Y. H. Rhee, J. Park, *J. Org. Chem.* **2014**, *79*, 9094–9103.

[10] Palladium as catalyst: a) T. Gerfaud, L. Neuville, J. Zhu, *Angew. Chem.* **2009**, *121*, 580–585; *Angew. Chem. Int. Ed.* **2009**, *48*, 572–577; b) D. A. Candito, M. Lautens, *Angew. Chem.* **2009**, *121*, 6841–6844; *Angew. Chem. Int. Ed.* **2009**, *48*, 6713–6716; c) M. Blanchot, D. A. Candito, F. Larnaud, M. Lautens, *Org. Lett.* **2011**, *13*, 1486–1489. Nickel as catalyst: d) Y. Yoshida, T. Kurahashi, S. Matsubara, *Chem. Lett.* **2011**, *40*, 1140–1142.

[11] For reviews, see: a) A. A. Kulkarni, O. Daugulis, *Synthesis* **2009**, 4087–4109; b) P. Kumar, J. Louie, *Angew. Chem.* **2011**, *123*, 10956–10958; *Angew. Chem. Int. Ed.* **2011**, *50*, 10768–10769; c) J. J. Mousseau, A. B. Charette, *Acc. Chem. Res.* **2013**, *46*, 412–424; d) C. Wang, *Synlett* **2013**, *24*, 1606–1613; e) D. Tilly, G. Dayaker, P. Bachu, *Catal. Sci. Technol.* **2014**, *4*, 2756–2777; f) L. Ackermann, *J. Org. Chem.* **2014**, *79*, 8948–8954; g) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208–1219; h) F. Jia, Z. Li, *Org. Chem. Front.* **2014**, *1*, 194–214; i) W. Liu, J. T. Groves, *Acc. Chem. Res.* **2015**, *48*, 1727–1735; j) J. Miao, H. Ge, *Eur. J. Org. Chem.* **2015**, 7859–7868; k) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498–525.

[12] R. He, Z.-T. Huang, Q.-Y. Zheng, C. Wang, *Angew. Chem.* **2014**, *126*, 5050–5053; *Angew. Chem. Int. Ed.* **2014**, *53*, 4950–4953.

[13] For a review, see: T. K. Hyster, *Catal. Lett.* **2015**, *145*, 458–467.

[14] For selected examples, see: a) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem.* **2013**, *125*, 2263–2267; *Angew. Chem. Int. Ed.* **2013**, *52*, 2207–2211; b) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Chem. Eur. J.* **2013**, *19*, 9142–9146; c) H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.* **2014**, *136*, 5424–5431; d) B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Adv. Synth. Catal.* **2014**, *356*, 1491–1495; e) T. M. Figg, S. Park, J. Park, S. Chang, D. G. Musaev, *Organometallics* **2014**, *33*, 4076–4085; f) J. Li, L. Ackermann, *Angew. Chem.* **2015**, *127*, 3706–3709; *Angew. Chem. Int. Ed.* **2015**, *54*, 3635–3638; g) D.-G. Yu, T. Gensch, F. de Azambuja, S. Vásquez-Céspedes, F. Glorius, *J. Am. Chem. Soc.* **2014**, *136*, 17722–17725; h) J. R. Hummel, J. A. Ellman, *J. Am. Chem. Soc.* **2015**, *137*, 490–498; i) P. Patel, S. Chang, *ACS Catal.* **2015**, *5*, 853–858; j) A. B. Pawar, S. Chang, *Org. Lett.* **2015**, *17*, 660–663; k) N. Yoshikai, *ChemCatChem* **2015**, *7*, 732–734; l) B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Chem. Commun.* **2015**, *51*, 4659–4661; m) D. Zhao, J. H. Kim, L. Stegemann, C. A. Strassert, F. Glorius, *Angew. Chem.* **2015**, *127*, 4591–4594; *Angew. Chem. Int. Ed.* **2015**, *54*, 4508–4511; n) J. R. Hummel, J. A. Ellman, *Org. Lett.* **2015**, *17*, 2400–2403; o) J. Li, L. Ackermann, *Angew. Chem.* **2015**, *127*, 8671–8674; *Angew. Chem. Int. Ed.* **2015**, *54*, 8551–8554; p) X.-G. Liu, S.-S. Zhang, J.-Q. Wu, Q. Li, H. Wang, *Tetrahedron Lett.* **2015**, *56*, 4093–4095; q) M. Moselage, N. Sauermann, J. Koeller, W. Liu, D. Gelman, L. Ackermann, *Synlett* **2015**, *26*, 1596–1600; r) Y. Suzuki, B. Sun, K. Sakata, T. Yoshino, S. Matsunaga, M. Kanai, *Angew. Chem.* **2015**, *127*, 10082–10085; *Angew. Chem. Int. Ed.* **2015**, *54*, 9944–9947; s) N. Sauermann, M. J. Gonzalez, L. Ackermann, *Org. Lett.* **2015**, *17*, 5316–5319; t) T. Gensch, S. Vásquez-Céspedes, D.-G. Yu, F. Glorius, *Org. Lett.* **2015**, *17*, 3714–3717; u) Z.-Z. Zhang, B. Liu, C.-Y. Wang, B.-F. Shi, *Org. Lett.* **2015**, *17*, 4094–4097; v) E. Ozkal, B. Cacherat, B. Morandi, *ACS Catal.* **2015**, *5*, 6458–6462; w) Y. Suzuki, B. Sun, T. Yoshino, M. Kanai, S. Matsunaga, *Tetrahedron* **2015**, *71*, 4552–4556; x) X.-K. Guo, L.-B. Zhang, D. Wei, J.-L. Niu, *Chem. Sci.* **2015**, *6*, 7059–7071; y) X.-G. Liu, S.-S. Zhang, C.-Y. Jiang, J.-Q. Wu, Q. Li, H. Wang, *Org. Lett.* **2015**, *17*, 5404–5407; z) J. Park, S. Chang, *Angew. Chem.* **2015**, *127*, 14309–14313; *Angew. Chem. Int. Ed.* **2015**, *54*, 14103–14107; aa) Y. Liang, Y.-F. Liang, C. Tang, Y. Yuan, N. Jiao, *Chem. Eur. J.* **2015**, *21*, 16395–16399.

[15] a) B. Sun, T. Yoshino, M. Kanai, S. Matsunaga, *Angew. Chem.* **2015**, *127*, 13160–13164; *Angew. Chem. Int. Ed.* **2015**, *54*, 12968–12972; b) H. Wang, J. Koeller, W. Liu, L. Ackermann, *Chem. Eur. J.* **2015**, *21*, 15525–15528; c) M. Sen, D. Kalsi, B. Sundararaju, *Chem. Eur. J.* **2015**, *21*, 15529–15533.

[16] a) K. Fagnou, *Top. Curr. Chem.* **2009**, *292*, 35–56; b) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315–1345.

