C–H/C–C Activation

International Edition: DOI: 10.1002/anie.201601778
German Edition: DOI: 10.1002/ange.201601778

Mild C–H/C–C Activation by *Z*-Selective Cobalt Catalysis

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Abstract: *Cationic cobalt complexes enable unprecedented cobalt-catalyzed C–H/C–C functionalizations with unique selectivity features. The versatile cobalt catalyst proved broadly applicable, enabled efficient C–H/C–C cleavage at room temperature, and delivered Z-alkenes with excellent diastereocontrol.*

Catalyzed C–H functionalizations have been identified as a transformative approach for step-economical organic syntheses,[1] with applications in natural product chemistry,[2] the pharmaceutical industry,[3] and material sciences,[4] among others. Considerable impetus has very recently been gained by merging C–H activation with challenging C–C[5] cleavage[6] methods. In spite of undisputed advances, catalytic[7] C–H/C–C activations continue to be scarce, with all the reported examples requiring the precious transition metal rhodium.[8] The recent years have witnessed increasing interest in the use of naturally abundant 3d transition metal catalysts for C–H functionalizations.[9] Particularly, cobalt(III) complexes have emerged as versatile tools,[10] with key contributions by Matsunaga/Kanai,[11] Ellman,[12] Chang,[13] Glorius,[14] Shi,[15] Jiao,[16] and Ackermann,[17] among others.[18] As part of our research on base-metal-catalyzed C–H activation,[19] we have now developed the first cobalt-catalyzed C–H/C–C functionalization. Notable features of our strategy include 1) the first C–H/C–C functionalizations by cobalt catalysis, 2) high catalytic efficacy at room temperature, 3) unique levels of positional selectivity that contrasts with expensive rhodium catalysts,[8a] and 4) unprecedented diastereoselectivity towards thermodynamically less stable *Z* alkenes (Figure 1), which was rationalized by means of DFT calculations.

To start with, we probed reaction conditions for the envisioned cobalt-catalyzed C–H/C–C activation of indole **1a** with vinylcyclopropane **2a** (Table 1 and Table S1 in the Supporting Information).[20] Indeed, the desired transformation proved viable, with carboxylates[21] emerging as particularly powerful additives (entries 1–5). The sterically hindered pivalate additive was the most effective (entries 6–10), and [Cp*Co(CO)I_2] proved to be optimal among a variety of cobalt complexes (entries 8, and 11–14). It is noteworthy that the optimized cobalt(III) catalysts delivered the thermodynamically less stable *Z* isomer *Z*-**3aa** with an excellent *E*/*Z* diastereoselectivity of 1:11. In contrast, rhodium(III) complexes predominantly furnished the *E* product with an overall poor *E*/*Z* selectivity of only 2:1 under otherwise identical reaction conditions,[20] while pyrimidyl-substituted indoles gave an *E*/*Z* ratio of 5:1.[8a] The catalytic efficacy of the cationic cobalt complex was highlighted by successful C–H/C–C activation under exceedingly mild reaction conditions, that is at room temperature (25 °C; entry 15).

With the optimized catalyst in hand, we explored its versatility in the cobalt(III)-catalyzed C–H/C–C functionalization process with cyclopropanes **2** (Scheme 1). The robustness of this widely applicable cationic cobalt(III) catalyst is reflected by its tolerance of a variety of valuable functional

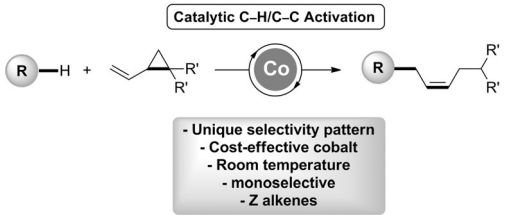
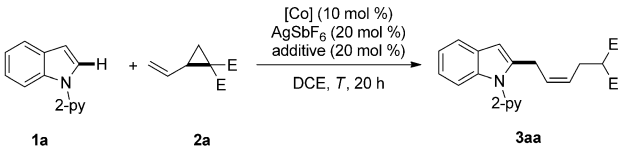


Figure 1. *Z*-Selective C–H/C–C activation by cobalt catalysis.

Table 1: Cobalt-catalyzed C–H/C–C activation.[a]



1a **2a** **3aa**

Entry	[Co]	Additive	*T* [°C]	**3aa** [%][b]
1	[Cp*Co(CO)I_2]	LiOAc	50	74
2	[Cp*Co(CO)I_2]	NaOAc	50	88
3	[Cp*Co(CO)I_2]	CsOAc	50	11
4	[Cp*Co(CO)I_2]	$NaO_2C(3\text{-}CF_3)C_6H_4$	50	68
5	[Cp*Co(CO)I_2]	Na(O-Piv-Val)	50	84
6	[Cp*Co(CO)I_2]	LiOPiv	50	61
7	[Cp*Co(CO)I_2]	$Mg(OPiv)_2$	50	70[c]
8	**[Cp*Co(CO)I_2]**	**NaOPiv**	50	**93**
9	[Cp*Co(CO)I_2]	KOPiv	50	51
10	[Cp*Co(CO)I_2]	CsOPiv	50	39
11	–	NaOPiv	50	–
12	[CpCo(CO)I_2]	NaOPiv	50	10[d]
13	[1,3-(tBu)$_2$$C_5H_3$Co(CO)$I_2$]	NaOPiv	50	18[d]
14	$[Cp^*Co(CH_3CN)_3](SbF_6)_2$	NaOPiv	50	91[e]
15	[Cp*Co(CO)I_2]	NaOPiv	25	64

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.60 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgSbF_6$ (20 mol %), additive (20 mol %), dichloroethane (DCE; 1.0 mL), 20 h. Yields of isolated product are given. py = pyridyl, E = CO_2Me. [b] *E*/*Z* ratio = 1:11. [c] $Mg(OPiv)_2$ (10 mol %). [d] *E*/*Z* ratio = 8:1. [e] Without $AgSbF_6$.

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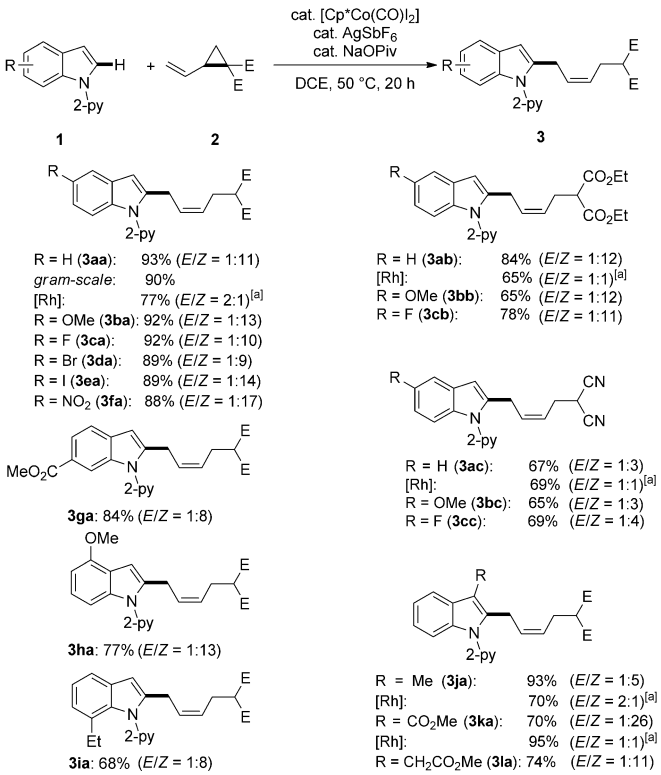
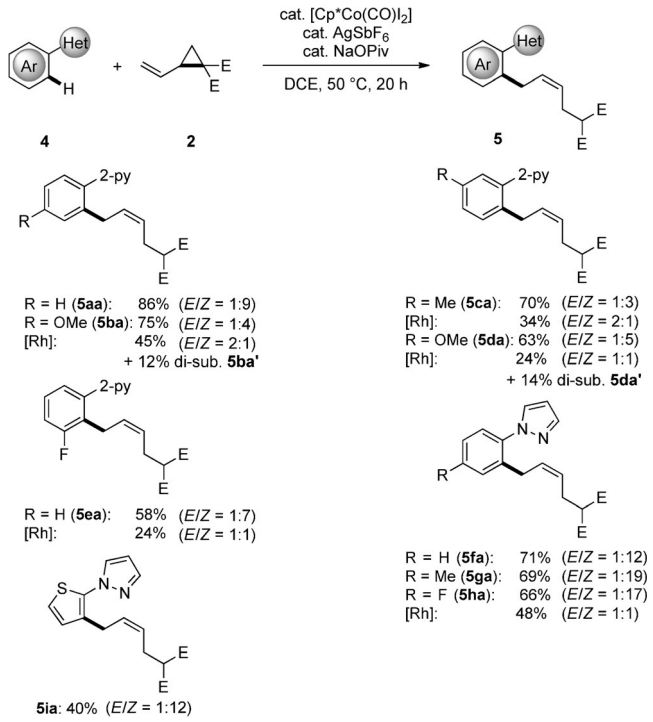
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201601778.



Scheme 1. *Z*-Selective cobalt-catalyzed C–H/C–C activation.
[a] $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ was used as the catalyst.



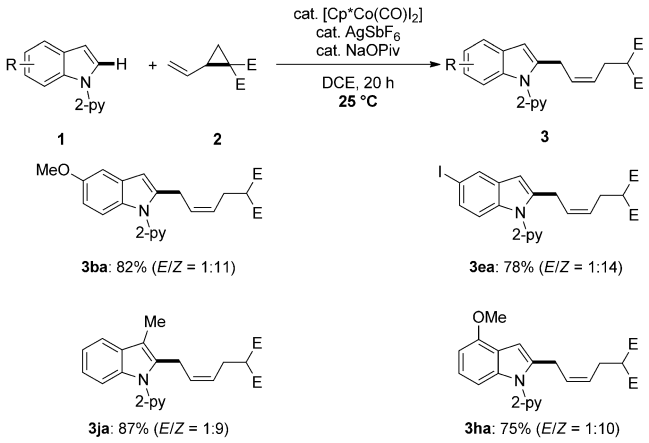
Scheme 2. Cobalt-catalyzed arene C–H/C–C functionalization.

groups, such as ester, nitrile, bromo, iodo, and nitro substituents. Diverse substitution was well accepted at all positions of the indole nucleus. It is particularly noteworthy that in all cases the less stable *Z* diastereomers were formed with high to excellent selectivity. In stark contrast, rhodium(III) complexes delivered difficult-to-separate mixtures of the *E*/*Z* diastereomers, with a minor bias for the *E* diastereomer.

The broadly applicable cobalt catalyst was not restricted to the functionalization of inherently electron-rich heteroarenes **1**. Indeed, heteroarene-assisted diversification of arenes **4** proved viable and proceeded with outstanding *Z*-diastereoselectivity. It is important to note that the cobalt catalyst was characterized by excellent chemoselectivity in that the monofunctionalized arenes **5** were formed as the sole products. By contrast, rhodium(III) catalysts gave mixtures of mono- and di-substituted arenes **5** with overall low selectivity. The wide substrate scope of the cationic cobalt catalyst was illustrated by the efficient transformation of both electron-rich and electron-deficient arenes **4** into the desired products **5** (Scheme 2).

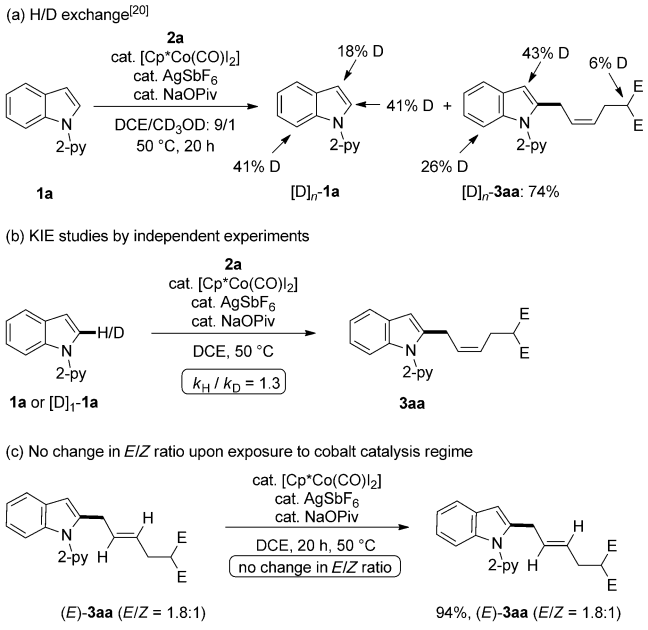
The synthetic utility of the cobalt-catalyzed C–H/C–C functionalization was highlighted by late-stage diversification of products **3** (Schemes S1–S3 in the Supporting Information),[20] as well as by high-yielding C–H/C–C transformations at room temperature (25 °C; Scheme 3).

Given the unique selectivity pattern of the cobalt-catalyzed C–H/C–C activation, and considering the related rhodium(III)-catalyzed transformation,[8a] we became interested in rationalizing its mode of action. To this end, catalytic



Scheme 3. Cobalt-catalyzed C–H/C–C activation at room temperature.

reactions were carried out in the presence of isotopically labelled cosolvent $[D]_4$-MeOH, and the results clearly reveal the reversible nature of the C–H cobaltation event (Scheme 4a).[20] Moreover, independent kinetic experiments with substrate **1a** and its isotopically labelled analogue $[D]_1$-**1a** showed a minor kinetic isotope effect (KIE) of $k_H/k_D \approx 1.3$ (Scheme 4b),[20] which is suggestive of a facile C–H metalation event. Interestingly, the *E*/*Z* ratio of the product isolated from the rhodium(III)-catalyzed transformation was found to be unaltered upon exposure to the cobalt catalysis procedure (Scheme 4c),[20] thereby excluding a post-C–C-cleavage isomerization process. Likewise, the product of the cobalt-catalyzed C–H allylation did not undergo isomerization in the presence of the rhodium catalyst.[20]



Scheme 4. Summary of key mechanistic findings.

In order to unravel the origin of the unique selectivity features, density functional theory (DFT)[20] calculations using B3LYP[22,23] and Grimme's D3 dispersion correction[24,25] were conducted (Figure 2).

It was found that both cobalt and rhodium catalysts follow the mechanism that was proposed earlier.[8a] The reaction is initiated by migratory insertion of the double bond of vinylcyclopropane **2** into the Co–C bond via the transition state Ts(**I**-**II**). Thereafter, oxygen coordinates to the metal center, thereby leading to the intermediate **III**. Finally, the key C–C cleavage of vinylcyclopropane in intermediate **III** takes place to form the intermediate **IV** via the transition state Ts(**III**-**IV**). Our calculations were indicative of the C–C cleavage being the rate- and diastereoselectivity-determining step. Furthermore, when comparing the energetic span[20,26] for this step, the *Z* diastereomer is clearly preferred under cobalt(III) catalysis (Figure 2), with an activation barrier of 13.1 kcal mol^{-1} compared to 19.6 kcal mol^{-1} for the *E* diastereomer. By contrast, with the rhodium(III) catalyst (Figure S1) the energy difference is in favor of the *E* diastereomer with an energetic span of 20.9 kcal mol^{-1} compared to 23.2 kcal mol^{-1} for the *Z* diastereomer (Figure S-2). This observation is likely due to the significantly shorter Co–C bonds translating into more compact organometallic species (Figure 3). As for cobalt triplet states, the substrate did not even coordinate to the cobalt center here.

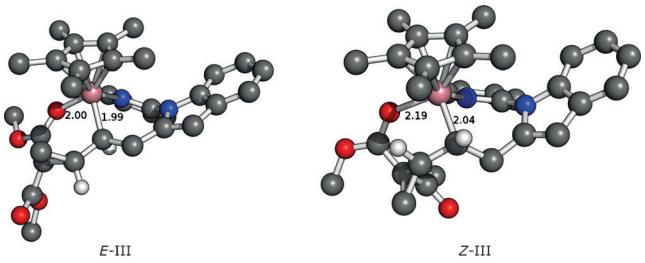


Figure 3. Computed intermediate structures associated with the C–C activation step with key distances in Å (H atoms omitted for clarity).

In summary, we have developed the first cobalt-catalyzed C–H/C–C activation. A cationic cobalt(III) catalyst enabled efficient C–H activation with vinylcyclopropanes[27] in a reaction featuring unique levels of chemo- and diastereoselectivity, as well as a broad scope. The efficacy of the cost-effective cobalt catalyst was reflected by successful C–H/C–C activation under exceedingly mild reaction conditions[28] at room temperature. Notably, the C–H/C–C functionalization delivered the thermodynamically less stable *Z* alkenes with excellent diastereocontrol.

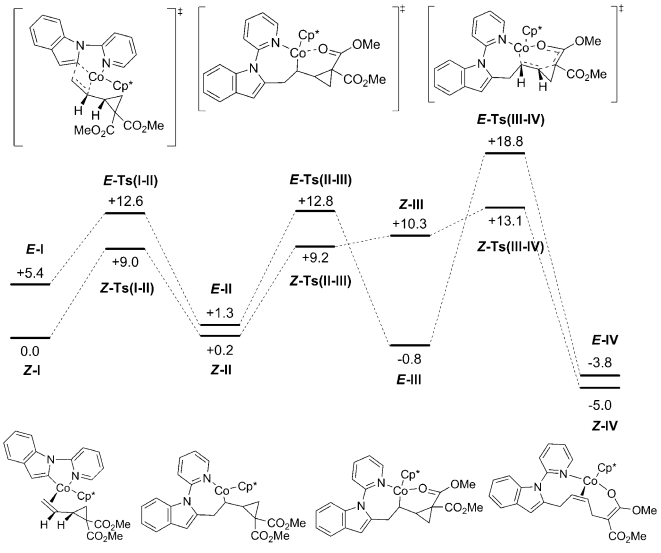


Figure 2. Computed reaction profile in DCE with energies given in kcal mol^{-1}.

Acknowledgements

Generous 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 Q.B.) is gratefully acknowledged.

Keywords: C–C cleavage · C–H activation · cobalt · homogeneous catalysis · stereoselectivity

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 7408–7412
Angew. Chem. **2016**, *128*, 7534–7538

[1] Representative recent reviews on C–H activation: a) J. K. Kim, K. Shin, S. Chang, *Top. Organomet. Chem.* **2016**, *55*, 29–51; b) C. Borie, L. Ackermann, M. Nechab, *Chem. Soc. Rev.* **2016**, *45*, 1368–1386; c) O. Daugulis, J. Roane, L. D. Tran, *Acc. Chem. Res.* **2015**, *48*, 1053–1064; d) J. Li, L. Ackermann, *Nat. Chem.* **2015**, *7*, 686–687; e) K. Shin, H. Kim, S. Chang, *Acc. Chem. Res.* **2015**, *48*, 1040–1052; f) Y. Segawa, T. Maekawa, K. Itami,

Angew. Chem. Int. Ed. **2015**, *54*, 66 – 81; *Angew. Chem.* **2015**, *127*, 68 – 83; g) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007 – 1020; h) N. Kuhl, N. Schroeder, F. Glorius, *Adv. Synth. Catal.* **2014**, *356*, 1443 – 1460; i) S. A. Girard, T. Knauber, C.-J. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 74 – 100; *Angew. Chem.* **2014**, *126*, 76 – 103; j) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369 – 375; k) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212 – 11222; l) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242 – 3272; m) L. Ackermann, R. Vicente, A. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792 – 9826; *Angew. Chem.* **2009**, *121*, 9976 – 10011; n) R. G. Bergman, *Nature* **2007**, *446*, 391 – 393, and references therein.

[2] J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960 – 9009; *Angew. Chem.* **2012**, *124*, 9092 – 9142.

[3] L. Ackermann, *Org. Process Res. Dev.* **2015**, *19*, 260 – 269.

[4] L. G. Mercier, M. Leclerc, *Acc. Chem. Res.* **2013**, *46*, 1597 – 1605.

[5] Recent reviews: a) L. Souillart, N. Cramer, *Chem. Rev.* **2015**, *115*, 9410 – 9464; b) T. Seiser, T. Saget, D. N. Tran, N. Cramer, *Angew. Chem. Int. Ed.* **2011**, *50*, 7740 – 7752; *Angew. Chem.* **2011**, *123*, 7884 – 7896; c) M. Murakami, T. Matsuda, *Chem. Commun.* **2011**, *47*, 1100 – 1105; d) T. Xu, A. Dermenci, G. Dong, *Top. Curr. Chem.* **2014**, *346*, 233 – 257; e) a recent elegant example of cobalt-catalyzed C–C functionalization: E. Ozkal, B. Cacherat, B. Morandi, *ACS Catal.* **2015**, *5*, 6458 – 6462.

[6] Examples of C–C activation by means of rhodium catalysis: a) T. Matsuda, K. Kato, T. Goya, S. Shimada, M. Murakami, *Chem. Eur. J.* **2016**, *22*, 1941 – 1943; b) L. Deng, T. Xu, H. Li, G. Dong, *J. Am. Chem. Soc.* **2016**, *138*, 369 – 374; c) X. Zhou, G. Dong, *J. Am. Chem. Soc.* **2015**, *137*, 13715 – 13721; d) R. Zeng, G. Dong, *J. Am. Chem. Soc.* **2015**, *137*, 1408 – 1411; e) A. Yada, S. Fujita, M. Murakami, *J. Am. Chem. Soc.* **2014**, *136*, 7217 – 7220; f) H. M. Ko, G. Dong, *Nat. Chem.* **2014**, *6*, 739 – 744; g) N. Ishida, W. Ikemoto, M. Murakami, *J. Am. Chem. Soc.* **2014**, *136*, 5912 – 5915; h) L. Souillart, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 9640 – 9644; *Angew. Chem.* **2014**, *126*, 9794 – 9798; i) L. Ding, N. Ishida, M. Murakami, K. Morokuma, *J. Am. Chem. Soc.* **2014**, *136*, 169 – 178; j) L. Souillart, E. Parker, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 3001 – 3005; *Angew. Chem.* **2014**, *126*, 3045 – 3049; k) L. Souillart, N. Cramer, *Chem. Sci.* **2014**, *5*, 837 – 840; l) Y. Masuda, M. Hasegawa, M. Yamashita, K. Nozaki, N. Ishida, M. Murakami, *J. Am. Chem. Soc.* **2013**, *135*, 7142 – 7145; m) N. Ishida, S. Sawano, Y. Masuda, M. Murakami, *J. Am. Chem. Soc.* **2012**, *134*, 17502 – 17504; n) T. Seiser, N. Cramer, *J. Am. Chem. Soc.* **2010**, *132*, 5340 – 5341; o) L. Liu, N. Ishida, M. Murakami, *Angew. Chem. Int. Ed.* **2012**, *51*, 2485 – 2488; *Angew. Chem.* **2012**, *124*, 2535 – 2538; p) M. Murakami, H. Amii, Y. Ito, *Nature* **1994**, *370*, 540 – 541, and references therein.

[7] A. Masarwa, D. Didier, T. Zabrodski, M. Schinkel, L. Ackermann, I. Marek, *Nature* **2014**, *505*, 199 – 203.

[8] a) J.-Q. Wu, Z.-P. Qiu, S.-S. Zhang, J.-G. Liu, Y.-X. Lao, L.-Q. Gu, Z.-S. Huang, J. Li, H. Wang, *Chem. Commun.* **2015**, *51*, 77 – 80; b) A. Masarwa, M. Weber, R. Sarpong, *J. Am. Chem. Soc.* **2015**, *137*, 6327 – 6334; c) T. Seiser, O. A. Roth, N. Cramer, *Angew. Chem. Int. Ed.* **2009**, *48*, 6320 – 6323; *Angew. Chem.* **2009**, *121*, 6438 – 6441; d) C. Aïssa, A. Fürstner, *J. Am. Chem. Soc.* **2007**, *129*, 14836 – 14837.

[9] Recent authoritative reviews on the use of inexpensive first-row transition metal catalysts for C–H bond functionalization: a) E. Nakamura, T. Hatakeyama, S. Ito, K. Ishizuka, L. Ilies, M. Nakamura, *Org. React.* **2014**, *83*, 1 – 209; b) L. Ackermann, *J. Org. Chem.* **2014**, *79*, 8948 – 8954; c) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208 – 1219; d) N. Yoshikai, *Synlett* **2011**, 1047 – 1051; e) Y. Nakao, *Chem. Rec.* **2011**, *11*, 242 – 251; f) E. Nakamura, N. Yoshikai, *J. Org. Chem.* **2010**, *75*, 6061 – 6067; g) A. Kulkarni, O. Daugulis, *Synthesis* **2009**, 4087 – 4109, and references therein.

[10] M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498 – 525.

[11] a) B. Sun, T. Yoshino, M. Kanai, S. Matsunaga, *Angew. Chem. Int. Ed.* **2015**, *54*, 12968 – 12972; *Angew. Chem.* **2015**, *127*, 13160 – 13164; b) Y. Suzuki, B. Sun, T. Yoshino, M. Kanai, S. Matsunaga, *Tetrahedron* **2015**, *71*, 4552 – 4556; c) Y. Suzuki, B. Sun, K. Sakata, T. Yoshino, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2015**, *54*, 9944 – 9947; *Angew. Chem.* **2015**, *127*, 10082 – 10085; d) B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Chem. Commun.* **2015**, *51*, 4659 – 4661; e) H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.* **2014**, *136*, 5424 – 5431; f) B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Adv. Synth. Catal.* **2014**, *356*, 1491 – 1495; g) T. Andou, Y. Saga, H. Komai, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2013**, *52*, 3213 – 3216; *Angew. Chem.* **2013**, *125*, 3295 – 3298; h) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2013**, *52*, 2207 – 2211; *Angew. Chem.* **2013**, *125*, 2263 – 2267.

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

[13] a) A. B. Pawar, S. Chang, *Org. Lett.* **2015**, *17*, 660 – 663; b) P. Patel, S. Chang, *ACS Catal.* **2015**, *5*, 853 – 858; c) J. Park, S. Chang, *Angew. Chem. Int. Ed.* **2015**, *54*, 14103 – 14107; *Angew. Chem.* **2015**, *127*, 14309 – 14313.

[14] a) A. Lerchen, S. Vásquez-Céspedes, F. Glorius, *Angew. Chem. Int. Ed.* **2016**, *55*, 3208 – 3211; *Angew. Chem.* **2016**, *128*, 3261 – 3265; b) D. Zhao, J. H. Kim, L. Stegemann, C. A. Strassert, F. Glorius, *Angew. Chem. Int. Ed.* **2015**, *54*, 4508 – 4511; *Angew. Chem.* **2015**, *127*, 4591 – 4594; c) T. Gensch, S. Vasquez-Cespedes, D.-G. Yu, F. Glorius, *Org. Lett.* **2015**, *17*, 3714 – 3717; d) D.-G. Yu, T. Gensch, F. D. Azambuja, S. Vásquez-Céspedes, F. Glorius, *J. Am. Chem. Soc.* **2014**, *136*, 17722 – 17725.

[15] Z.-Z. Zhang, B. Liu, C.-Y. Wang, B.-F. Shi, *Org. Lett.* **2015**, *17*, 4094 – 4097.

[16] a) Y. Liang, N. Jiao, *Angew. Chem. Int. Ed.* **2016**, *55*, 4035 – 4039; *Angew. Chem.* **2016**, *128*, 4103 – 4107; b) Y. Liang, Y.-F. Liang, C. Tang, Y. Yuan, N. Jiao, *Chem. Eur. J.* **2015**, *21*, 16395 – 16399.

[17] a) R. Mei, H. Wang, S. Warratz, S. A. Macgregor, L. Ackermann, *Chem. Eur. J.* **2016**, *22*, DOI: 10.1002/chem.201601101; b) R. Mei, J. Loup, L. Ackermann, *ACS Catal.* **2016**, *6*, 793 – 797; c) J. Li, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 8551 – 8554; *Angew. Chem.* **2015**, *127*, 8671 – 8674; d) M. Moselage, N. Sauermann, J. Koeller, W. Liu, D. Gelman, L. Ackermann, *Synlett* **2015**, 1596 – 1600; e) N. Sauermann, M. J. González, L. Ackermann, *Org. Lett.* **2015**, *17*, 5316 – 5319; f) W. Ma, L. Ackermann, *ACS Catal.* **2015**, *5*, 2822 – 2825; g) J. Li, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 3635 – 3638; *Angew. Chem.* **2015**, *127*, 3706 – 3709.

[18] a) S. Prakash, K. Muralirajan, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2016**, *55*, 1844 – 1848; *Angew. Chem.* **2016**, *128*, 1876 – 1880; b) T. T. Nguyen, L. Grigorjeva, O. Daugulis, *ACS Catal.* **2016**, *6*, 551 – 554; c) N. Barsu, M. Sen, J. R. Premkumar, B. Sundararaju, *Chem. Commun.* **2016**, *52*, 1338 – 1341; d) L.-B. Zhang, X.-Q. Hao, Z.-J. Liu, X.-X. Zheng, S.-K. Zhang, J.-L. Niu, M.-P. Song, *Angew. Chem. Int. Ed.* **2015**, *54*, 10012 – 10015; *Angew. Chem.* **2015**, *127*, 10150 – 10153; e) 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 – 275; *Angew. Chem.* **2015**, *127*, 274 – 277; f) X. Wu, K. Yang, Y. Zhao, H. Sun, G. Li, H. Ge, *Nat. Commun.* **2015**, *6*, 6462; g) L. Grigorjeva, O. Daugulis, *Org. Lett.* **2015**, *17*, 1204 – 1207; h) L. Grigorjeva, O. Daugulis, *Angew. Chem. Int. Ed.* **2014**, *53*, 10209 – 10212; *Angew. Chem.* **2014**, *126*, 10373 – 10376, and references therein.

[19] a) M. Moselage, N. Sauermann, S. C. Richter, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 6352 – 6355; *Angew. Chem.* **2015**, *127*, 6450 – 6453; b) W. Song, L. Ackermann, *Angew. Chem. Int. Ed.* **2012**, *51*, 8251 – 8254; *Angew. Chem.* **2012**, *124*, 8376 – 8379.

[20] For detailed information, see the Supporting Information.

[21] a) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281 – 295; b) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315 – 1345.
[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[23] P. Stephens, F. J. Devlin, C. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623 – 11627.
[24] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456 – 1465.
[25] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
[26] S. Kozuch, S. Shaik, *Acc. Chem. Res.* **2011**, *44*, 101 – 110.
[27] Vinylcyclopropanes **2** lacking electron-withdrawing groups gave only unsatisfactory yields.
[28] J. Wencel-Delord, T. Droege, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740 – 4761.

Received: February 19, 2016
Published online: May 4, 2016

