C–H Activation

DOI: 10.1002/anie.201409751

Cobalt-Catalyzed C(sp^2)–H Alkoxylation of Aromatic and Olefinic Carboxamides**

Lin-Bao Zhang, Xin-Qi Hao, Shou-Kun Zhang, Zhan-Jiang Liu, Xin-Xiang Zheng, Jun-Fang Gong, Jun-Long Niu, and Mao-Ping Song**

Abstract: *The cobalt-catalyzed alkoxylation of C(sp^2)–H bonds in aromatic and olefinic carboxamides has been developed. The reaction proceeded under mild conditions in the presence of $Co(OAc)_2{\cdot}4H_2O$ as the catalyst and tolerates a wide range of both alcohols and benzamide substrates, including even olefinic carboxamides. In addition, this reaction is the first example of the direct alkoxylation of alkenes through C–H bond activation.*

The direct C–H bond functionalization method has emerged as a practical strategy for the synthesis of natural products and medicinal compounds.[1] The synthesis of C–O bonds is one of the fundamental reactions in organic chemistry, and ether-containing compounds are widely employed in the synthesis of pharmaceuticals and functional materials.[2]. Comparing the continuous development of direct hydroxylation,[3] acetoxylation,[8a,4] and phenoxylation,[4d,5] reports on the more challenging C–H bond alkoxylation are scarce because of the fact that alkanols are easily transformed to the corresponding aldehydes or ketones through cationic or radical mechanisms.[6] Moreover, the alkoxyl–metal intermediates formed tend to undergo β-hydride elimination.[7] Consequently, direct C–H bond alkoxylation is largely restricted to using an established palladium-[8] or copper-catalyzed system.[9,10a]

Recently, the chelation-assisted C–H bond functionalization strategy has attracted widespread attention as a result of the pioneering work of Daugulis and co-workers[10] on the use of 8-aminoquinoline, picolinamide, and 2-pyridinylmethylamine compounds. Other groups have extensively applied this strategy to various Pd-, Ru-, Fe-, Ni-, and Cu-catalyzed reactions.[11] On the other hand, the use of a cobalt catalyst in C–C bond-forming reactions has attracted significant attention[12] since the chelation-assisted direct metalation of azobenzene was reported by Murahashi and Horiie in 1956.[13] Furthermore, Daugulis and Grigorjeva recently reported Co/Mn-catalyzed coupling of alkynes with C(sp^2)–H bonds by using 8-aminoquinoline and picolinic acid compounds.[14] Thereafter, they employed this catalyst system for the coupling of alkynes and the carbonylation of C(sp^2)–H bonds.[15] However, to our knowledge, no application of a cobalt catalyst for C–O bond formation has been reported. We speculated that a cobalt catalyst might also promote the alkoxylation of 2-aminopyridine-1-oxide benzamides on the basis of the following factors: a) cobalt salts could activate C(sp^2)–H bonds,[16] b) alkoxyl cobaltacycle intermediates have been reported in enantioselective hydroacylation reactions,[17] c) 2-aminopyridine-1-oxide benzamide ligands could stabilize Co intermediates, as seen for 8-aminoquinoline benzamides. As part of our interest in the field,[18] we present a simple C–H alkoxylation of aromatic and olefinic carboxamides using a $Co(OAc)_2{\cdot}4H_2O$ catalyst which provides a new method for C–O bond formation.

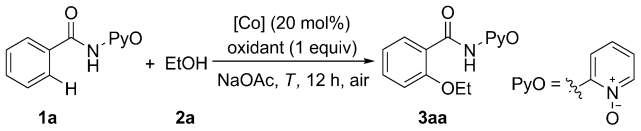
To probe the feasibility of this approach, we initiated our study with the reaction between ethanol (**2a**) and 2-benzamidopyridine 1-oxide (**1a**). To our delight, the desired ethoxylated product **3aa** was obtained in 17% yield when a solution of benzamide (**1a**) in ethanol was treated with a stoichiometric amount of $Co(OAc)_2{\cdot}4H_2O$, NaOAc (2 equiv), and $PhI(OAc)_2$ (1 equiv) under an air atmosphere at 80 °C (Table 1, entry 1). A decrease in the catalyst loading only resulted in a slightly decreased yield (Table 1, entry 2). The catalyst loading was decreased to 20 mol% of $Co(OAc)_2{\cdot}4H_2O$ and various oxidants were investigated, with Ag_2O proving to be most effective (Table 1, entries 3–11). This is in agreement with findings by Gooßen and co-workers.[9] Alternative cobalt catalysts (Table 1, entries 12–14) were found to be inferior compared to $Co(OAc)_2{\cdot}4H_2O$. The replacement of NaOAc with other bases and the addition of various cosolvents did not promote the efficiency of the reaction (see the Supporting Information). However, lowering the reaction temperature substantially influenced the yields (Table 1, entry 15). We speculated that a decrease of temperature could slow down the decomposition of the starting material and diminish the formation of by-products (a trace amount of the homocoupled product of **1a** was detected by HRMS analysis under the reaction conditions at 80 °C). A decrease in the reaction temperature to room temperature and a longer reaction time failed to afford an ideal result as a large portion of the starting materials were unreacted. By screening the reaction temperature, we found that 60 °C was the optimal temperature and afforded the ethoxylated product in 82% yield. Control experiments revealed that the cobalt catalyst is essential, as no reaction takes place in the absence of the $Co(OAc)_2{\cdot}4H_2O$ catalyst. Notably, using other bidentate coordinating groups (Figure 1, **A**–**C**), the

[*] L.-B. Zhang, Dr. X.-Q. Hao, S.-K. Zhang, Z.-J. Liu, X.-X. Zheng, Dr. J.-F. Gong, Dr. J.-L. Niu, Prof. M.-P. Song
The College of Chemistry and Molecular Engineering
Henan Key Laboratory of Chemical Biology and Organic Chemistry
Zhengzhou University, Kexue Avenue 100
Zhengzhou, Henan 450001 (P. R. China)
E-mail: niujunlong@zzu.edu.cn
mpsong@zzu.edu.cn

[**] We are grateful to the National Natural Science Foundation of China (Nos. 21072177 and 21272217) for financial support of this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201409751.

Table 1: Optimization of cobalt-catalyzed alkoxylation reaction between substrates **1a** and **2a**.[a]



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

Entry	Catalyst	*T* [°C]	Oxidant	Yield [%]
1[b]	$Co(OAc)_2{\cdot}4H_2O$	80	$PhI(OAc)_2$	17
2	$Co(OAc)_2{\cdot}4H_2O$	80	$PhI(OAc)_2$	15
3	$Co(OAc)_2{\cdot}4H_2O$	80	$K_2S_2O_8$	18
4	$Co(OAc)_2{\cdot}4H_2O$	80	$Mn(OAc)_3{\cdot}2H_2O$	45
5	$Co(OAc)_2{\cdot}4H_2O$	80	$NaIO_4$	26
6	$Co(OAc)_2{\cdot}4H_2O$	80	NMO	n.r.
7	$Co(OAc)_2{\cdot}4H_2O$	80	BQ	n.r.
8	$Co(OAc)_2{\cdot}4H_2O$	80	O_2	n.r.
9	$Co(OAc)_2{\cdot}4H_2O$	80	Ag_2CO_3	18
10	$Co(OAc)_2{\cdot}4H_2O$	80	AgOTf	27
11	$Co(OAc)_2{\cdot}4H_2O$	80	Ag_2O	67
12	$Co(acac)_2$	80	Ag_2O	42
13	$Co(acac)_3$	80	Ag_2O	25
14	$CoSO_4{\cdot}6H_2O$	80	Ag_2O	29
15	$Co(OAc)_2{\cdot}4H_2O$	50	Ag_2O	75
16	**$Co(OAc)_2{\cdot}4H_2O$**	**60**	**Ag_2O**	**82**
17	$Co(OAc)_2{\cdot}4H_2O$	70	Ag_2O	71
18[c]	$Co(OAc)_2{\cdot}4H_2O$	RT	Ag_2O	26
19	none	60	Ag_2O	n.r.

[a] reaction conditions: **1a** (0.2 mmol), **2a** (1.5 mL), [Co] (20 mol%), NaOAc (2.0 equiv), in air. Yield indicates yield of isolated product. [b] $Co(OAc)_2{\cdot}4H_2O$ (0.2 mmol). [c] 24 h. NMO = *N*-methylmorpholine oxide, BQ = 1,4-benzoquinone, acac = acetylacetonate. OTf = trifluoromethanesulfonate. n.r. = no reaction.

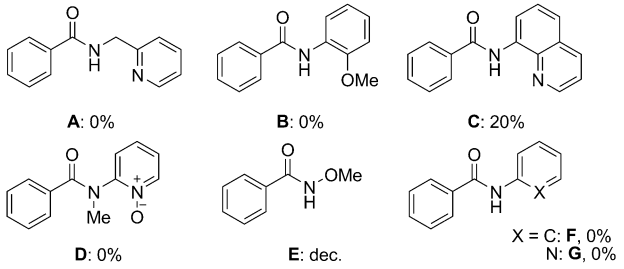
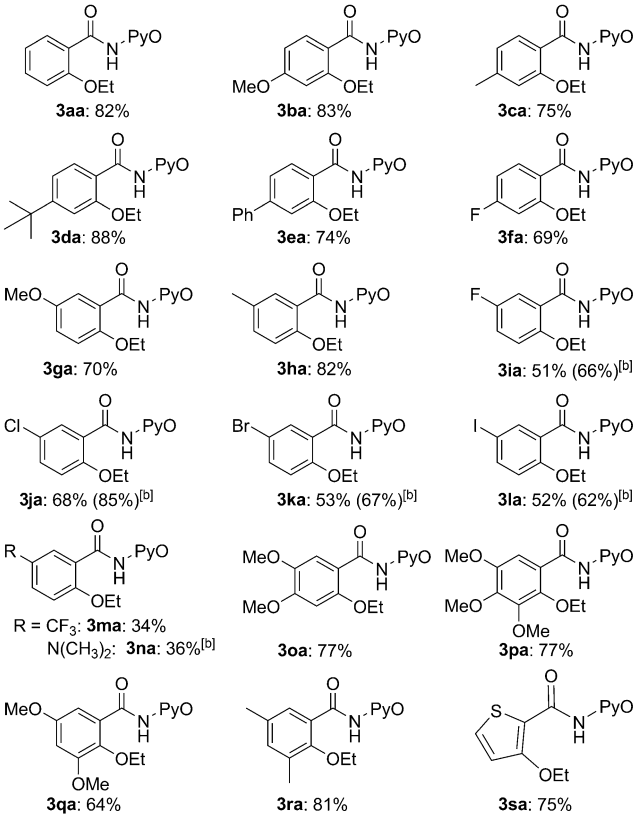


Figure 1. Screening of directing groups for the alkoxylation reaction. Dec. = decomposed.

reaction was inefficient under the same optimized reaction conditions. Notably, 8-aminoquinolinebenzamide (**C**) did not give a satisfactory yield in our system. No reaction was detected in the case of the structurally similar but monodentate directing groups (**D**–**G**), highlighting the unique property of the *N*,*O*-bidentate coordinating group (Figure 1).

With these optimized reaction conditions in hand, we probed the substrate scope in the ethoxylation of benzamides **1**. As shown in Table 2, a wide variety of functionalized benzamides were tolerated by the cobalt catalyst to give rise to the desired products **3**. The reactions proceeded successfully for both electron-rich and electron-poor amides. In all cases studied, bisethoxylated products were not obtained. The benzamides which have electron-rich functional groups in the *para* position afforded coupling products in good yields (**3ba**–**3ea**). The electron-poor amide **1f** bearing a fluoro functional

Table 2: Cobalt-catalyzed ethoxylation of benzamide derivatives **1** with ethanol (**2a**).[a]

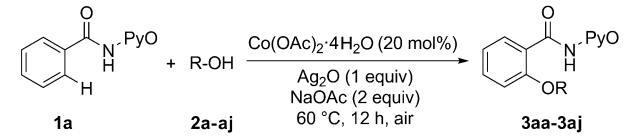


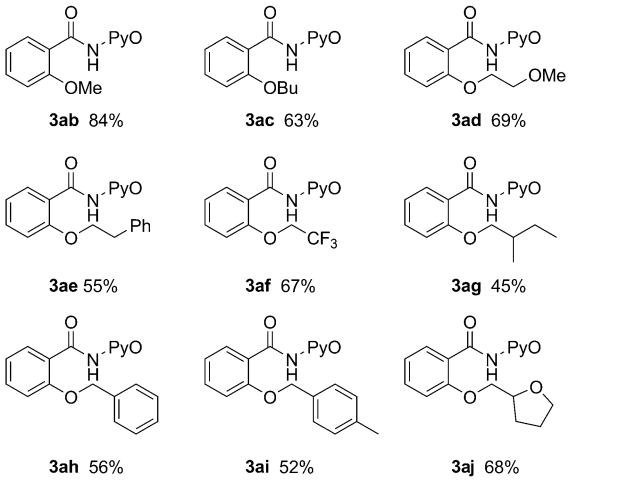
[a] Reaction conditions: **1** (0.2 mmol), ethanol **2a** (1.5 mL), $Co(OAc)_2{\cdot}4H_2O$ (20 mol%), Ag_2O (0.2 mmol), NaOAc (2.0 equiv), under air, 60 °C, 12 h. [b] Ag_2O (0.3 mmol).

group also underwent reacted under these conditions to form **3fa** in 69% yield. The ethoxylation of *ortho*-methoxylbenzamide took place sluggishly with a yield of 19% (data not shown). For *meta*-substituted substrates (**1g**–**1n**), the reactions proceeded with high regioselectivity, with the reaction in each case occurring exclusively at the less-hindered position of the arenes. Notably, the fluoro, chloro, bromo, and even iodo halogen functional groups on the arene derivatives remained intact under these reaction conditions. Moreover, increasing the amount of the oxidant Ag_2O was beneficial in these transformations (**3ia**–**3la**). Disubstituted substrates (**1o**, **1q**, and **1r**) bearing methyl and methoxy groups provided the ethoxylated products (**3oa**, **3qa**, and **3ra**) in good yields. The trisubstituted benzamide **1p** also underwent reaction to form the corresponding product **3pa** in 77% yield. To our delight, the heterocyclic substrate **1s** underwent ethoxylation to produce product **3sa** in 75% yield.

Next, we explored various alkanol substrates in the cobalt-catalyzed alkoxylation and found that the procedure can be widely applied (Table 3). A variety of linear and branched alcohols were efficiently coupled with benzamide **1** to give products **3aa**–**3aj**. Simple primary alkyl alcohols, such as methanol and butanol, afforded good yields (**3ab**–**3ac**). The successful formation of products **3ad** and **3ae** showed that ether- and phenyl-containing alcohol substrates are well tolerated in the reaction. Trifluoroethanol (**2f**)

Table 3: Cobalt-catalyzed alkoxylation of benzamide **1a** with various alcohol substrates **2a**–**2j**.[a]





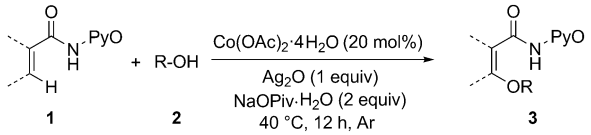
[a] Reaction conditions: **1a** (0.2 mmol), alkanols **2** (1.5 mL), $Co(OAc)_2 \cdot 4H_2O$ (20 mol%), Ag_2O (0.2 mmol), NaOAc (2.0 equiv), under air, 60°C, 12 h.

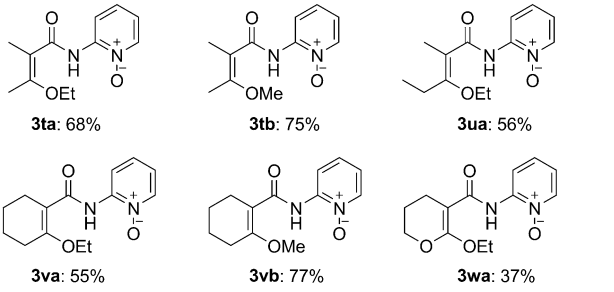
underwent reaction with **1a** to form the desired product **3af** which was isolated in 67% yield. The sterically hindered alcohol **2g** was employed to provide corresponding ether product **3ag**, albeit in a lower yield. Benzyl alcohols **2h** and **2i** were also transformed into the corresponding benzyl ether derivatives **3ah** and **3ai** in synthetically useful yields, despite the fact that they are sensitive to oxidation.[6a] The heterocyclic compound tetrahydrofurfuryl alcohol (**2j**) underwent alkoxylation upon reaction with **1a** to yield **3aj** in 68% yield. Unfortunately, the use of secondary alcohols such as isopropanol in the reaction was unsuccessful under these reaction conditions.

Furthermore, the reactions were not restricted to aromatic amides. 2-aminopyridine-1-oxide olefinic carboxamides also served as valuable substrates for the cobalt-catalyzed C–H bond alkoxylation (Table 4). In these reactions, a lower temperature was employed. As part of our investigations, we found that NaOPiv·H_2O (OPiv = pivalate) was a more effective base compared to NaOAc. The reaction afforded a higher yield under an atmosphere of argon (see the Supporting Information). These necessary changes indicate that olefinic carboxamides in this reaction are more sensitive to the reaction conditions compared with aromatic amides. For example, α,β-unsaturated amide **1t** was treated with methanol (**2b**) and the methoxylation product **3tb** was isolated in 75% yield.

The mechanistic details of the cobalt-catalyzed alkoxylation of C–H bonds are unclear. Our control experiments revealed that the addition of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 1.5 equiv) as a radical quencher inhibited the reaction. Moreover, the experimental EPR spectrum of the

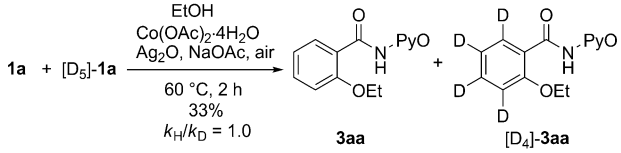
Table 4: Cobalt-catalyzed alkoxylation of olefinic carboxamides **1**.[a]





[a] Reaction conditions: **1** (0.2 mmol), alkanols **2** (1.5 mL), $Co(OAc)_2 \cdot 4H_2O$ (20 mol%), Ag_2O (0.2 mmol), NaOPiv·H_2O (2.0 equiv), under Ar, 40°C, 12 h. Piv = pivalate.

reaction system showed the existence of the free radical ($g = 2.00905$, see the Supporting Information). These results indicate that a radical pathway is involved. A 1:1 mixture of **1a** and [D_5]-**1a** was then treated with ethanol. No kinetic isotope effect (KIE; $k_H/k_D \approx 1.0$) was obtained (Scheme 1),

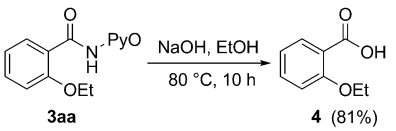


Scheme 1. Determination of the kinetic isotope effect.

suggesting that C–H bond cleavage of arenes is not the rate-limiting step. On the basis of the seminal studies by Kochi et al. on the oxidation of aromatic compounds by Co^{III}[19] and the chelation-directed chlorination reactions of 2-phenylpyridine reported by Yu and co-workers[4d] in which a low KIE (= 1.0) was measured, we speculate that an oxidative substitution of arenes mediated by single-electron transfer (SET) is very possible in the cobalt-catalyzed alkoxylation. However, the exact oxidation state of the catalytic Co species (Co^{II} or Co^{III}) is for now unclear.

Finally, the 2-aminopyridine-1-oxide (PyO) directing group can be easily removed. As shown in Scheme 2, the ethoxylated product **3aa** was treated with NaOH in EtOH at 80°C to obtain 2-ethoxybenzoic acid (**4**) in a high yield.

In conclusion, we have developed the first cobalt-catalyzed alkoxylation of C(sp^2)–H bonds using 2-aminopyridine-1-oxide as an *N*,*O*-bidentate directing group. The



Scheme 2. Removal of the 2-aminopyridine-1-oxide (PyO) directing group.

method is synthetically simple and suitable for a wide range of alcohols and benzamide substrates bearing a variety of electron-rich and electron-poor groups, such as halogen, ether, methoxy, trifluoromethyl, and *N*,*N*-dimethyl substituents. Moreover, this reaction is the first example of the direct alkoxylation of alkenes through C–H bond activation. This method provides a unique reaction procedure among the otherwise broadly applicable palladium- or copper-catalyzed C–H alkoxylation reactions, thus extending the scope of cobalt-catalyzed C–H functionalization reactions. Moreover, the *N*,*O*-bidentate directing group can be easily removed. Further exploration of the detailed mechanism is currently ongoing in our laboratory.

Received: October 3, 2014
Published online: ■■ ■■, ■■■■

Keywords: alkoxylation · C–H activation · cobalt · directing groups · transition-metal catalysis

[1] For recent reviews, see: a) K. M. Engle, J.-Q. Yu, *J. Org. Chem.* **2013**, *78*, 8927 – 8955; b) K. Collins, F. Glorius, *Nat. Chem.* **2013**, *5*, 597 – 601; c) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960 – 9009; *Angew. Chem.* **2012**, *124*, 9092 – 9142; d) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879 – 5918; e) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315 – 1345; f) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147 – 1169; g) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215 – 1292; h) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335 – 344; i) B.-J. Li, Z.-J. Shi, *Chem. Soc. Rev.* **2012**, *41*, 5588 – 5598.

[2] a) S. Enthaler, A. Company, *Chem. Soc. Rev.* **2011**, *40*, 4912 – 4924; b) J. J. Li, D. S. Johnson, *Modern Drug Synthesis*, Wiley, Hoboken, **2010**; c) J. J. Li, D. S. Johnson, D. R. Sliskovic, B. D. Roth, *Contemporary Drug Synthesis*, Wiley, Hoboken, **2004**; d) F. Müller, *Agrochemicals*, Wiley-VCH, Weinheim, **1999**; e) H.-G. Elias, *An Introduction to Polymer Science*, Wiley-VCH, Weinheim, **1997**.

[3] a) Y. Yan, P. Feng, Q.-Z. Zheng, Y.-F. Liang, J.-F. Lu, Y. Cui, N. Jiao, *Angew. Chem. Int. Ed.* **2013**, *52*, 5827 – 5831; *Angew. Chem.* **2013**, *125*, 5939 – 5943; b) Y.-H. Zhang, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 14654 – 14655; c) X. Li, Y.-H. Liu, W.-J. Gu, B. Li, F.-J. Chen, B.-F. Shi, *Org. Lett.* **2014**, *16*, 3904 – 3907.

[4] a) X.-F. Cheng, Y. Li, Y.-M. Su, F. Yin, J.-Y. Wang, J. Sheng, H. U. Vora, X.-S. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2013**, *135*, 1236 – 1239; b) M. H. Emmert, A. K. Cook, Y. J. Xie, M. S. Sanford, *Angew. Chem. Int. Ed.* **2011**, *50*, 9409 – 9412; *Angew. Chem.* **2011**, *123*, 9581 – 9584; c) W. Wang, F. Luo, S. Zhang, J. Cheng, *J. Org. Chem.* **2010**, *75*, 2415 – 2418; d) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790 – 6791; e) A. R. Dick, K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2004**, *126*, 2300 – 2301.

[5] a) J. Zhao, Y. Wang, Y. He, L. Liu, Q. Zhu, *Org. Lett.* **2012**, *14*, 1078 – 1081; b) B. Xiao, T.-J. Gong, Z.-J. Liu, J.-H. Liu, D.-F. Luo, J. Xu, L. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 9250 – 9253; c) Y. Wei, N. Yoshikai, *Org. Lett.* **2011**, *13*, 5504 – 5507.

[6] a) J. M. Hoover, B. L. Ryland, S. S. Stahl, *J. Am. Chem. Soc.* **2013**, *135*, 2357 – 2367; b) R. I. Khusnutdinov, A. R. Bayguzina, L. I. Gimaletdinova, U. M. Dzhemilev, *Russ. J. Org. Chem.* **2012**, *48*, 1191 – 1196. See the Supporting Information for complete citations.

[7] a) X. Wu, B. P. Fors, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 9943 – 9947; *Angew. Chem.* **2011**, *123*, 10117 – 10121; b) S. Gowrisankar, A. G. Sergeev, P. Anbarasan, A. Spannenberg, H. Neumann, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 11592 – 11598; c) K. E. Torraca, X. Huang, C. A. Parrish, S. L. Buchwald, *J. Am. Chem. Soc.* **2001**, *123*, 10770 – 10771.

[8] a) L. V. Desai, H. A. Malik, M. S. Sanford, *Org. Lett.* **2006**, *8*, 1141 – 1144; b) W. Li, P. Sun, *J. Org. Chem.* **2012**, *77*, 8362 – 8366; c) T.-S. Jiang, G.-W. Wang, *J. Org. Chem.* **2012**, *77*, 9504 – 9509. See the Supporting Information for complete citations.

[9] a) S. Bhadra, W. I. Dzik, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2013**, *52*, 2959 – 2962; *Angew. Chem.* **2013**, *125*, 3031 – 3035; b) S. Bhadra, C. Matheis, D. Katayev, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2013**, *52*, 9279 – 9283; *Angew. Chem.* **2013**, *125*, 9449 – 9453; c) S. Bhadra, W. I. Dzik, L. J. Gooßen, *J. Am. Chem. Soc.* **2012**, *134*, 9938 – 9941.

[10] a) J. Roane, O. Daugulis, *Org. Lett.* **2013**, *15*, 5842 – 5845; b) T. Truong, K. Klimovica, O. Daugulis, *J. Am. Chem. Soc.* **2013**, *135*, 9342 – 9345; c) L. D. Tran, J. Roane, O. Daugulis, *Angew. Chem. Int. Ed.* **2013**, *52*, 6043 – 6046; *Angew. Chem.* **2013**, *125*, 6159 – 6162; d) V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2005**, *127*, 13154 – 13155.

[11] Some selected examples with different metal centers. Pd: a) S.-Y. Zhang, G. He, W. A. Nack, Y. Zhao, Q. Li, G. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 2124 – 2127; b) G. He, G. Chen, *Angew. Chem. Int. Ed.* **2011**, *50*, 5192 – 5196; *Angew. Chem.* **2011**, *123*, 5298 – 5302; c) G. He, S.-Y. Zhang, W. A. Nack, Q. Li, G. Chen, *Angew. Chem. Int. Ed.* **2013**, *52*, 11124 – 11128; *Angew. Chem.* **2013**, *125*, 11330 – 11334; d) Q. Zhang, K. Chen, W. Rao, Y. Zhang, F.-J. Chen, B.-F. Shi, *Angew. Chem. Int. Ed.* **2013**, *52*, 13588 – 13592; *Angew. Chem.* **2013**, *125*, 13833 – 13837; e) K. S. Kanyiva, Y. Kuninobu, M. Kanai, *Org. Lett.* **2014**, *16*, 1968 – 1971; f) K. Chen, F. Hu, S.-Q. Zhang, B.-F. Shi, *Chem. Sci.* **2013**, *4*, 3906 – 3911; Ru: g) G. Rouquet, N. Chatani, *Chem. Sci.* **2013**, *4*, 2201 – 2208; h) Y. Aihara, N. Chatani, *Chem. Sci.* **2013**, *4*, 664 – 670; Fe: i) S. Asako, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* **2013**, *135*, 17755 – 17757; j) T. Matsubara, S. Asako, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* **2014**, *136*, 646 – 649; Ni: k) Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2014**, *136*, 898 – 901; l) W. Song, S. Lackner, L. Ackermann, *Angew. Chem. Int. Ed.* **2014**, *53*, 2477 – 2480; *Angew. Chem.* **2014**, *126*, 2510 – 2513; Cu: m) M. Nishino, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2013**, *52*, 4457 – 4461; *Angew. Chem.* **2013**, *125*, 4553 – 4557; n) M. Shang, S.-Z. Sun, H.-L. Wang, B. N. Laforteza, H.-X. Dai, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2014**, *53*, 10439 – 10442; *Angew. Chem.* **2014**, *126*, 10607 – 10610.

[12] a) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208 – 1219; b) G. Cahiez, A. Moyeux, *Chem. Rev.* **2010**, *110*, 1435 – 1462; c) K. Gao, N. Yoshikai, *J. Am. Chem. Soc.* **2013**, *135*, 9279 – 9282; d) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2013**, *52*, 2207 – 2211; *Angew. Chem.* **2013**, *125*, 2263 – 2267.

[13] S. Murahashi, S. Horiie, *J. Am. Chem. Soc.* **1956**, *78*, 4816 – 4817.

[14] L. Grigorjeva, O. Daugulis, *Angew. Chem. Int. Ed.* **2014**, *53*, 10209 – 10212; *Angew. Chem.* **2014**, *126*, 10373 – 10376.

[15] a) L. Grigorjeva, O. Daugulis, *Org. Lett.* **2014**, *16*, 4684 – 4687; b) L. Grigorjeva, O. Daugulis, *Org. Lett.* **2014**, *16*, 4688 – 4690.

[16] a) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Chem. Eur. J.* **2013**, *19*, 9142 – 9146; b) H. Pellissier, H. Clavier, *Chem. Rev.* **2014**, *114*, 2775 – 2823; c) L. Ackermann, *J. Org. Chem.* **2014**, *79*, 8948 – 8954.

[17] Q.-A. Chen, D. K. Kim, V. M. Dong, *J. Am. Chem. Soc.* **2014**, *136*, 3772 – 3775.

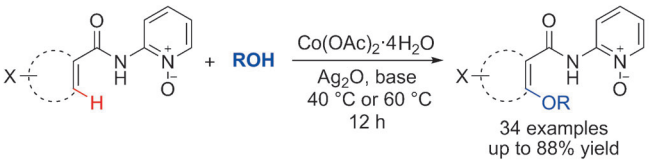
[18] X.-Q. Hao, L.-J. Chen, B. Ren, L.-Y. Li, X.-Y. Yang, J.-F. Gong, J.-L. Niu, M.-P. Song, *Org. Lett.* **2014**, *16*, 1104 – 1107.

[19] J. K. Kochi, R. T. Tang, T. Bernath, *J. Am. Chem. Soc.* **1973**, *95*, 7114 – 7123.

Communications

C–H Activation

L.-B. Zhang, X.-Q. Hao, S.-K. Zhang, Z.-J. Liu, X.-X. Zheng, J.-F. Gong, J.-L. Niu,* M.-P. Song* ____ ■■■■–■■■■



Cobalt-Catalyzed C(sp^2)–H Alkoxylation of Aromatic and Olefinic Carboxamides

Alcohols in action: A wide range of alcohols and benzamide substrates functionalized with electron-rich orelectron-poor substituents are tolerated in the title reaction. This practical reaction occurs under mild conditions.