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Regioselective Synthesis of 5-Aminooxazoles via Cp*Co(III)-Catalyzed Formal [3 + 2] Cycloaddition of *N*-(Pivaloyloxy)amides with Ynamides

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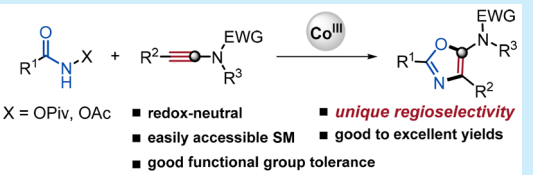
Supporting Information

ABSTRACT: A simple and efficient protocol for the regioselective synthesis of 5-aminooxazoles is disclosed. The reaction, catalyzed by a cheap Cp*Co(III) catalyst, starts from easily accessible *N*-(pivaloyloxy)-amides and ynamides. Mild reaction conditions, a broad substrate scope, good functional group tolerance, and good to excellent yields were observed.



Oxazoles represent one of the most important heterocycles found in naturally occurring products and pharmaceutically relevant molecules.[1] They also serve as versatile building blocks for efficient organic synthesis.[2] Consequently, a variety of methods,[3] including the traditional Fischer,[4] Robinson-Gabriel,[5] and van Leusen[6] oxazole syntheses, have been developed for their preparation.[7] Recently, with the development of organometallic chemistry, transition-metal-catalyzed bimolecular cycloaddition reactions provide an alternative method, which allows the synthesis to take place under mild reaction conditions with a broader substrate scope.[3c]

Alkynes, due to their versatile reactivities toward transition metals, have been utilized as two-carbon synthons in the construction of oxazoles under the catalysis of Ru,[7o] Pd,[7i] Hg,[7s] Ag,[7j] Cu,[7k,q] or Au.[7a,g,l,p] Specifically, 1-amido-alkynes (ynamides), which could be activated by acids to form the corresponding keteniminium ion species,[8] have proven to be versatile building blocks in organic synthesis, especially in heterocyclic scaffolds synthesis.[9] For instance, in oxazole synthesis, Davies and co-workers disclosed a Au(III)-catalyzed intermolecular formal [3 + 2] cycloaddition of pyridine-*N*-aminides with ynamides, providing oxazoles with a useful amino substituent (Scheme 1a).[10] Very recently, similar [3 + 2] cycloadditions catalyzed by Au(I)[11] or Tf_2NH[12] using dioxazoles as a nucleophilic *N*-acyl nitrene equivalent with ynamides had been achieved (Scheme 1b). It should be mentioned that, in all these cases, the same regioselectivity was observed, resulting in the formation of 4-aminooxazoles exclusively.

In recent years, the cobalt-based complexes have been widely utilized in the assembly of diverse C−C and C−X bonds.[13] It has been reported that the cobalt-catalyzed coupling reaction of benzamide derivatives with alkynes could lead to the formation of isoquinolones via C−H activation/annulation processes (Scheme 1c and 1d).[14] In continuation of our interest in Cp*Co(III) catalysis as well as in the application of a functionalized unsaturated carbon−carbon bond in C−H activation reactions,[15] we envisioned that the amino-substituted isoquinolone might be accessible via a cobalt-catalyzed C−H annulation of *N*-(pivaloyloxy)amide with ynamide (Scheme 1e, path A). Interestingly, however, an unexpected 5-aminooxazole product was obtained as the sole product (Scheme 1e, path B). Importantly, the regioselectivity in this reaction was in contrast to the previous observations wherein ynamides were used as

Scheme 1. Oxazoles Synthesis Using Ynamides and Cobalt-Catalyzed Annulation of Benzamides with Alkynes

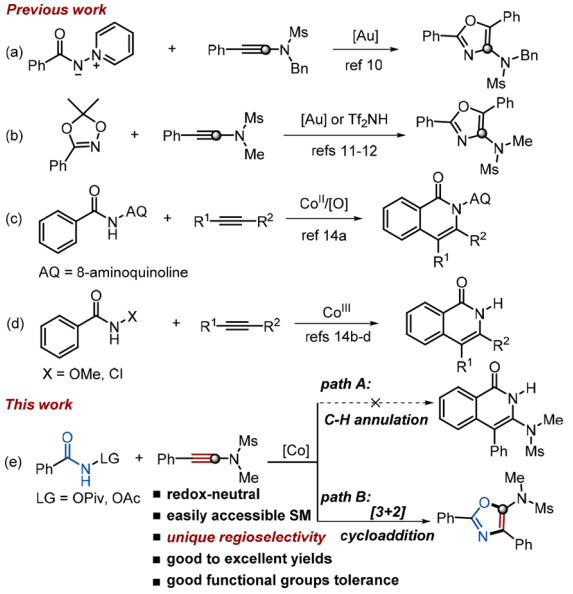


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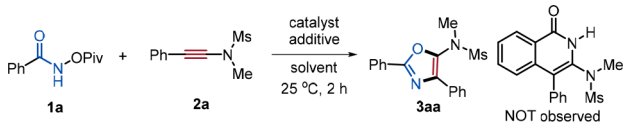
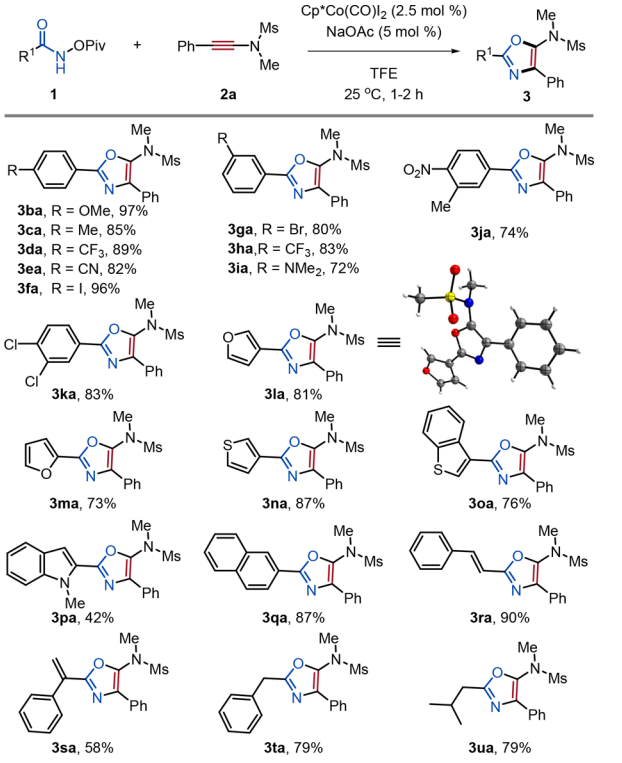
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst (x mol %)	additive (y mol %)	solvent	yield (%)[b]
1	Cp*Co(CO)I_2 (10)	NaOAc (20)	TFE	76
2	$Co_2(CO)_8$ (10)	NaOAc (20)	TFE	0
3	$Co(OAc)_2$ (10)	NaOAc (20)	TFE	0
4	**Cp*Co(CO)I_2 (2.5)**	**NaOAc (5)**	**TFE**	**88**
5	Cp*Co(CO)I_2 (1)	NaOAc (5)	TFE	71
6	$[Cp^*RhCl_2]_2$ (2.5)	NaOAc (5)	TFE	0
7	$[Ir(COD)Cl]_2$ (2.5)	NaOAc (5)	TFE	0
8	$Cu(OTf)_2$ (10)	NaOAc (10)	TFE	0
9	AgOTf (10)	NaOAc (10)	TFE	0
10	IPrAuNTf_2 (10)	NaOAc (10)	TFE	0
11	IPrAuNTf_2 (5)	–	DCE	0
12	Tf_2NH (5)	–	DCE	0
13	$Sc(OTf)_3$ (5)	–	DCE	0
14	Cp*Co(CO)I_2 (2.5)	NaOAc (5)	HFIP	65
15	Cp*Co(CO)I_2 (2.5)	NaOAc (5)	MeCN	0
16	Cp*Co(CO)I_2 (2.5)	NaOAc (5)	DCE	0
17	Cp*Co(CO)I_2 (2.5)	NaOAc (5)	HOAc	0
18	Cp*Co(CO)I_2 (2.5)	NaOAc (5)	MeOH	0
19	–	NaOAc (5)	TFE	0
20	Cp*Co(CO)I_2 (2.5)	–	TFE	62

[a]General reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.24 mmol, 1.2 equiv), catalyst (x mol %), additive (y mol %), solvent (2.0 mL), 25 °C, 2 h. [b]Isolated yield.

Scheme 2. Substrates Scope of *N*-(Pivaloyloxy)amides[a]



[a]General reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2a** (0.24 mmol, 1.2 equiv), Cp*Co(CO)I_2 (2.5 mol %), NaOAc (5.0 mol %), TFE (2.0 mL), 25 °C, 1–2 h under air, isolated yield.

coupling partners (Scheme 1a and 1b).[10−12] Herein, we disclose our studies on the polysubstituted oxazole synthesis via a redox-neutral Co(III)-catalyzed formal [3 + 2] cycloaddition of *N*-(pivaloyloxy)amides with ynamides. The reaction proceeds under mild reaction conditions, and a broad substrate scope, good to excellent yields, and high regioselectivities are observed.

Initially, the reaction of *N*-(pivaloyloxy)benzamide **1a** and *N*-methyl-*N*-(phenylethynyl)methanesulfonamide **2a** was studied. Under the conditions of Cp*Co(CO)I_2 (10 mol %), NaOAc (20 mol %), TFE (2 mL), 25 °C, 2 h (Table 1, entry 1), oxazole **3aa** was obtained in 76% isolated yield, with no formation of amino-substituted isoquinolone being detected. Other cobalt catalysts tested such as $Co_2(CO)_8$ or $Co(OAc)_2$ were ineffective for the cycloaddition (entries 2 and 3). Interestingly, a higher yield was obtained while lowering the loadings of both the catalyst (to 2.5 mol %) and additive (to 5 mol %) (entries 4 and 5). Further studies demonstrated that some catalysts based on the siblings (Rh and Ir) of cobalt and its neighbors (Cu, Ag, and Au) were found to be inefficient (entries 6−10). Lewis acids such as IPrAuNTf_2, Tf_2NH, and $Sc(OTf)_3$, which were reported to be effective in related cyclization reactions,[11,12] showed no reactivities for the transformation (entries 11−13). The solvent effect was also examined. Hexafluoroisopropanol (HFIP) exhibited less efficiency (entry 14), and there was no desired product obtained in other solvents, such as acetonitrile, dichloroethane, acetic acid, and methanol (entries 15−18).[16] Control experiments showed that both the catalyst and additive NaOAc were important for this transformation. The omission of catalyst resulted in no formation of the oxazole product (entry 19), whereas the exclusion of NaOAc led to a lower yield (entry 20). Note that the transformation proceeded in a highly regioselective manner. The regioisomer 4-aminoxazole of **3aa** was not formed in our protocol.

With the optimized conditions in hand (Table 1, entry 4), we next explored the substrate scope of the cycloaddition reaction. The scope of *N*-(pivaloyloxy)amides **1** was first investigated by reacting with ynamide **2a**. As shown in Scheme 2, the reaction was found to be very general and robust. A number of commonly encountered functional groups, regardless of the electronic nature, at different positions of the benzamide ring were well tolerated, giving the corresponding products in generally good to excellent yields (**3ba**−**3ka**). Substituents such as ether (**3ba**), cyano (**3ea**), halides (**3fa**, **3ga**, **3ka**), and nitro (**3ja**) were valuable functional handles for further derivatization. Heteroaryl-substituted amides, such as furyl (**3la**, **3ma**), thienyl (**3na**), benzothienyl (**3oa**), and indolyl-substituted (**3pa**) substrates, were also compatible with the reaction conditions, delivering a bis-heteroaryl axis architecture. The regioselectivity of the intermolecular cycloaddition was unambiguously confirmed by X-ray analysis of compounds **3aa** and **3la**.[17] The cycloaddition of 2-naphthyl (**3qa**) or alkenyl (**3ra** and **3sa**) substituted amides with **2a** produced the desired oxazoles in good yields. In addition, aliphatic substituents could be installed to the 2-position of oxazoles (**3ta** and **3ua**) by using alkyl-substituted amides.

Subsequently, the scope on the ynamides was also investigated and the results were summarized in Scheme 3. The effect of the R^1 group at the terminal alkyne was first examined. A wide range of substituents, such as OMe, *t*-Bu, F, CN, Br, and Cl, at different positions of the phenyl ring were all suitable for this process, furnishing **3bb**−**3bi** in 64−97% yields. It was noted that a lower 64% yield for **3bi** was observed when *o*-Cl-phenyl alkyne was employed, probably due to steric reasons. 2-Thienyl-substituted

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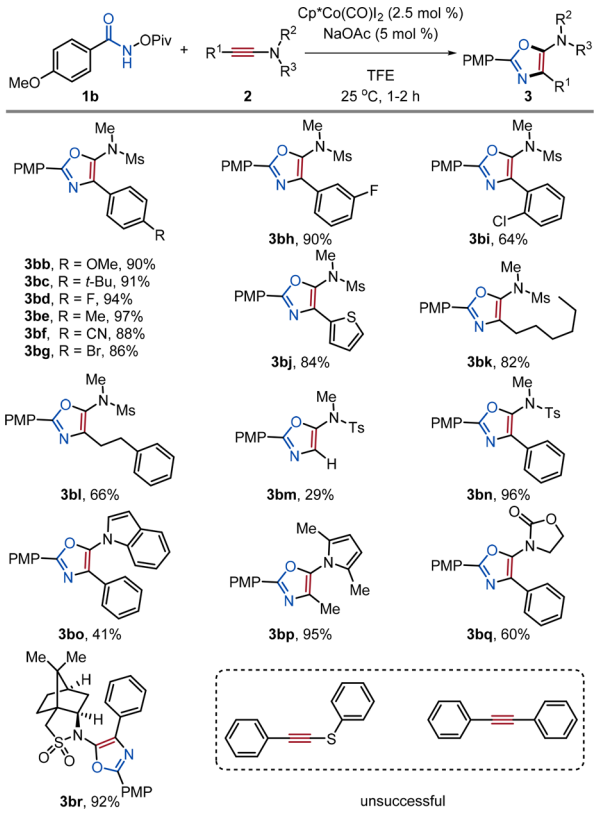
Scheme 3. Substrates Scope of Ynamides[a]

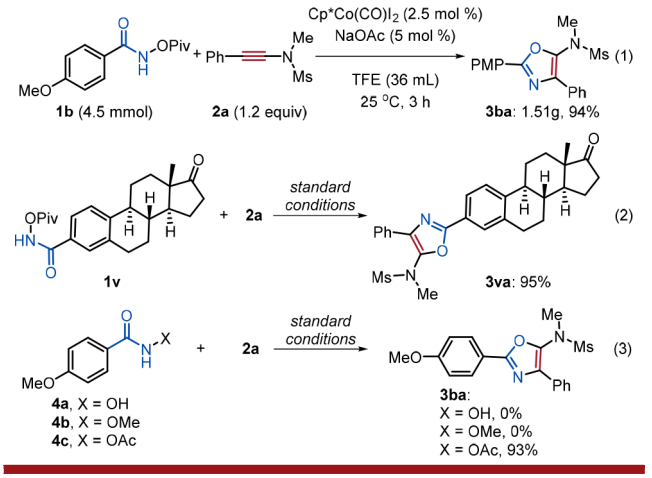


[a]General reaction conditions: **1b** (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), Cp*Co(CO)I_2 (2.5 mol %), NaOAc (5.0 mol %), TFE (2.0 mL), 25 °C, 1−2 h under air, isolated yield.

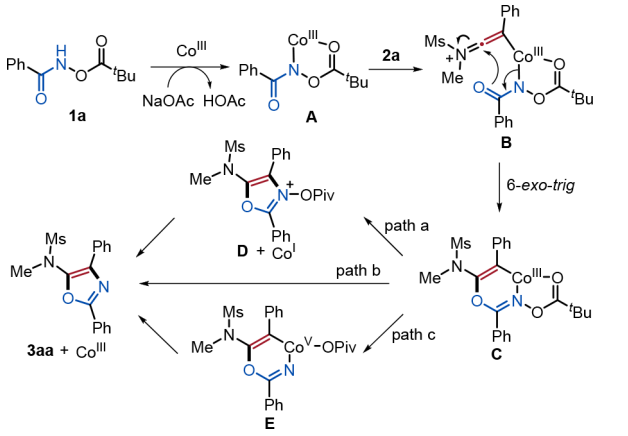
alkyne was smoothly converted into the corresponding oxazole **3bj** in high yield. Furthermore, alkyl-substituted ynamides could also undergo reaction efficiently (**3bk**, **3bl**). Most notably, the desired oxazole was also formed by using terminal ynamide as a reaction partner, albeit in a lower yield (**3bm**, 29%). Finally, the R^2 and R^3 groups at the nitrogen atom were explored. The reaction of *N*-tosyl ynamide **2n** with **1b** proceeded successfully, giving **3bn** in excellent yield. The 5-indolyl or pyrrolyl oxazole could be prepared by switching ynamide to the corresponding alkyne (**3bo**, **3bp**). The more electron-rich ynamide **2q** with an oxazolidine group was also applicable to the transformation, affording the corresponding oxazole **3bq** in a moderate yield. The chiral cyclic ynamide was also amenable for annulation (**3br**). Disappointedly, the reaction of sulfur-substituted alkyne or diphenyl acetylene did not give the corresponding oxazoles, only with near-quantitative recovery of the starting materials.

The potential synthetic utility was demonstrated by a gram-scale synthesis. Thus, 1.51 g of oxazole **3ba** was obtained (94% yield) via the cycloaddition of amide **1b** with ynamide **2a** under the standard reaction conditions with a slightly prolonged reaction time (to 3 h, eq 1). Remarkably, by using our protocol, the oxazole moiety could be introduced to estrone in an excellent 95% yield (**3va**, eq 2). The reaction was also conducted with different leaving groups on the nitrogen atom of amide. While the use of OAc as the leaving group delivered a comparable yield, the use of OH or OMe led to no reaction at all, indicating the leaving ability of the substituent on nitrogen was important for reaction.

On the basis of the results obtained and preceding reports,[14d,18] the possible reaction pathways are outlined in Scheme 4. Initially,



Scheme 4. Possible Reaction Pathways for the Formation of Oxazole 3aa



the coordination of *N*-(pivaloyloxy)benzamide **1a** to the Co^{III} catalyst delivers the amido complex **A**. Thereafter, the nucleophilic attack of ynamide **2a** to **A** leads to the formation of keteniminium ion species **B**. An intramolecular 6-*exo*-*trig* cyclization generates a cyclocobalt species **C**. At this stage, the reductive elimination would generate the *N*-pivaloyloxy oxazole cation **D** and a Co^{I} species. The Co^{I} is then oxidized to Co^{III} by the N−O bond (path a). Alternatively, the nucleophilic displacement of the N−O bond with a Co−C bond could produce **3aa** and release the catalyst directly (path b). Another possibility is that the Co^{III} might be oxidized to Co^{V} prior to a C−N bond reductive elimination (path c).

In conclusion, we have developed a simple and efficient method for the synthesis of 5-aminooxazoles by using a Cp*Co(III)-catalyzed regioselective formal [3 + 2] cycloaddition reaction of *N*-(pivaloyloxy)amides with ynamides. The reaction proceeds under mild reaction conditions, with good tolerance to a variety of functional groups and good to excellent yields being observed. In consideration of the ready availability of the starting materials and the importance of the products, we anticipate this method will find applications in organic synthesis and medicinal chemistry.

■ ASSOCIATED CONTENT

Supporting Information

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Detailed experimental procedures, characterization of all reported compounds, and ^{1}H, ^{13}C NMR spectra (PDF)
Crystallographic data for **3aa** (CIF)
Crystallographic data for **3la** (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For selected examples, see: (a) Hulin, B.; Clark, D. A.; Goldstein, S. W.; McDermott, R. E.; Dambek, P. J.; Kappeler, W. H.; Lamphere, C. H.; Lewis, D. M.; Rizzi, J. P. *J. Med. Chem.* **1992**, *35*, 1853. (b) Wipf, P. *Chem. Rev.* **1995**, *95*, 2115. (c) Li, Y. M.; Milne, J. C.; Madison, L. L.; Kolter, R.; Walsh, C. T. *Science* **1996**, *274*, 1188. (d) Davyt, D.; Serra, G. *Mar. Drugs* **2010**, *8*, 2755. (e) Yeh, V. S. C. *Tetrahedron* **2004**, *60*, 11995. (f) Jin, Z. *Nat. Prod. Rep.* **2016**, *33*, 1268.

(2) For selected reviews and books, see: (a) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. (b) Palmer, D. C.; Venkatraman, S. *Oxazoles: Synthesis, Reactions and Spectroscopy, Part A*; J. Wiley & Sons: Hoboken, NJ, 2003. (c) Palmer, D. C.; Taylor, E. C. *The Chemistry of Heterocyclic Compounds. Oxazoles: Synthesis, Reactions, and Spectroscopy*; Wiley: Hoboken, NJ, 2004; Vol. *60*.

(3) For some recent reviews on oxazole synthesis, see: (a) Turner, C. D.; Liang, H. S. *Curr. Org. Chem.* **2011**, *15*, 2846. (b) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084. (c) Bresciani, S.; Tomkinson, N. C. O. *Heterocycles* **2014**, *89*, 2479. (d) Xiao, L.; Zhang, G.; Jing, X.; Zhou, Q.; Feng, R. *Youji Huaxue* **2016**, *36*, 1000. (e) Ibrar, A.; Khan, I.; Abbas, N.; Farooq, U.; Khan, A. *RSC Adv.* **2016**, *6*, 93016.

(4) Fischer, E. *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 205.

(5) (a) Robinson, R. *J. Chem. Soc., Trans.* **1909**, *95*, 2167. (b) Gabriel, S. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1283.

(6) van Leusen, A. M.; Hoogenboom, B. E.; Siderius, H. *Tetrahedron Lett.* **1972**, *13*, 2369.

(7) For selected recent references for oxazole synthesis, see: (a) Reddy, R. J.; Ball-Jones, M. P.; Davies, P. W. *Angew. Chem., Int. Ed.* **2017**, *56*, 13310. (b) Yagyu, T.; Takemoto, Y.; Yoshimura, A.; Zhdankin, V. V.; Saito, A. *Org. Lett.* **2017**, *19*, 2506. (c) Duan, X.; Yang, K.; Lu, J.; Kong, X.; Liu, N.; Ma, J. *Org. Lett.* **2017**, *19*, 3370. (d) Wu, X.; Geng, X.; Zhao, P.; Zhang, J.; Wu, Y.-d.; Wu, A.-x. *Chem. Commun.* **2017**, *53*, 3438. (e) Soeta, T.; Matsumoto, A.; Sakata, Y.; Ukaji, Y. *J. Org. Chem.* **2017**, *82*, 4930. (f) Chao, I.; Lujan-Montelongo, J. A.; Fleming, F. F. *Org. Lett.* **2016**, *18*, 3062. (g) Peng, H.; Akhmedov, N. G.; Liang, Y.-F.; Jiao, N.; Shi, X. *J. Am. Chem. Soc.* **2015**, *137*, 8912. (h) Zeng, T.-T.; Xuan, J.; Ding, W.; Wang, K.; Lu, L.-Q.; Xiao, W.-J. *Org. Lett.* **2015**, *17*, 4070. (i) Zheng, J.; Zhang, M.; Huang, L.; Hu, X.; Wu, W.; Huang, H.; Jiang, H. *Chem. Commun.* **2014**, *50*, 3609. (j) Hu, Y.; Yi, R.; Wu, F.; Wan, B. *J. Org. Chem.* **2013**, *78*, 7714. (k) Li, X.; Huang, L.; Chen, H.; Wu, W.; Huang, H.; Jiang, H. *Chem. Sci.* **2012**, *3*, 3463. (l) Luo, Y.; Ji, K.; Li, Y.; Zhang, L. *J. Am. Chem. Soc.* **2012**, *134*, 17412. (m) Xu, Z.; Zhang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 11367. (n) Zhou, W.; Xie, C.; Han, J.; Pan, Y. *Org. Lett.* **2012**, *14*, 4766. (o) Zhong, C. L.; Tang, B. Y.; Yin, P.; Chen, Y.; He, L. *J. Org. Chem.* **2012**, *77*, 4271. (p) He, W.; Li, C.; Zhang, L. *J. Am. Chem. Soc.* **2011**, *133*, 8482. (q) Cano, I.; Álvarez, E.; Nicasio, M. C.; Pérez, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 191. (r) Egorova, O. A.; Seo, H.; Kim, Y.; Moon, D.; Rhee, Y. M.; Ahn, K. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 11446. (s) Lee, H.; Kim, H.-J. *Tetrahedron Lett.* **2011**, *52*, 4775. (t) Wan, C.; Zhang, J.; Wang, S.; Fan, J.; Wang, Z. *Org. Lett.* **2010**, *12*, 2338.

(8) Evano, G.; Lecomte, M.; Thilmany, P.; Theunissen, C. *Synthesis* **2017**, *49*, 3183.

(9) For some reviews: (a) Evano, G.; Coste, A.; Jouvin, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2840. (b) DeKorver, K. A.; Li, H.; Lohse, A. G.; Hayashi, R.; Lu, Z.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2010**, *110*, 5064. (c) Wang, X.-N.; Yeom, H.-S.; Fang, L.-C.; He, S.; Ma, Z.-X.; Kedrowski, B. L.; Hsung, R. P. *Acc. Chem. Res.* **2014**, *47*, 560. (d) Pan, F.; Shu, C.; Ye, L. W. *Org. Biomol. Chem.* **2016**, *14*, 9456. (e) Hu, L.; Zhao, J. *Synlett* **2017**, *28*, 1663.

(10) (a) Davies, P. W.; Cremonesi, A.; Dumitrescu, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8931. (b) Gillie, A. D.; Reddy, R. J.; Davies, P. W. *Adv. Synth. Catal.* **2016**, *358*, 226.

(11) Chen, M.; Sun, N.; Chen, H.; Liu, Y. *Chem. Commun.* **2016**, *52*, 6324.

(12) Zhao, Y.; Hu, Y.; Wang, C.; Li, X.; Wan, B. *J. Org. Chem.* **2017**, *82*, 3935.

(13) For the pioneering works of Cp*Co(III) in C−H activation reactions, see: (a) Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 2207. (b) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal.* **2014**, *356*, 1491. For some reviews, see: (c) Yoshino, T.; Matsunaga, S. *Adv. Synth. Catal.* **2017**, *359*, 1245. (d) Wang, S.; Chen, S.-Y. *Chem. Commun.* **2017**, *53*, 3165. (e) Hammann, J. M.; Hofmayer, M. S.; Lutter, F. H.; Thomas, L.; Knochel, P. *Synthesis* **2017**, *49*, 3887. (f) Usman, M.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. *Synthesis* **2017**, *49*, 1419. (g) Wei, D.; Zhu, X.; Niu, J.-L.; Song, M.-P. *ChemCatChem* **2016**, *8*, 1242. (h) Moselage, M.; Li, J.; Ackermann, L. *ACS Catal.* **2016**, *6*, 498. (i) Pellissier, H.; Clavier, H. *Chem. Rev.* **2014**, *114*, 2775. (j) Brennan, M. R.; Kim, D.; Fout, A. R. *Chem. Sci.* **2014**, *5*, 4831. (k) Cahiez, G.; Moyeux, A. *Chem. Rev.* **2010**, *110*, 1435. (l) Gosmini, C.; Bégouin, J.-M.; Moncomble, A. *Chem. Commun.* **2008**, 3221.

(14) (a) Grigorjeva, L.; Daugulis, O. *Angew. Chem., Int. Ed.* **2014**, *53*, 10209. (b) Chavan, L. N.; Gollapelli, K. K.; Chegondi, R.; Pawar, A. B. *Org. Lett.* **2017**, *19*, 2186. (c) Sivakumar, G.; Vijeta, A.; Jeganmohan, M. *Chem. - Eur. J.* **2016**, *22*, 5899. (d) Yu, X.; Chen, K.; Guo, S.; Shi, P.; Song, C.; Zhu, J. *Org. Lett.* **2017**, *19*, 5348.

(15) (a) Liu, X.-G.; Li, Q.; Wang, H. *Adv. Synth. Catal.* **2017**, *359*, 1942. (b) Lao, Y.-X.; Zhang, S.-S.; Liu, X.-G.; Jiang, C.-Y.; Wu, J.-Q.; Chen, S.-Y.; Li, Q.; Huang, Z.-S.; Wang, H. *Adv. Synth. Catal.* **2016**, *358*, 2186. (c) Zhang, S.-S.; Liu, X.-G.; Chen, S.-Y.; Tan, D.-H.; Jiang, C.-Y.; Wu, J.-Q.; Li, Q.; Wang, H. *Adv. Synth. Catal.* **2016**, *358*, 1705. (d) Liu, X.-G.; Zhang, S.-S.; Jiang, C.-Y.; Wu, J.-Q.; Li, Q.; Wang, H. *Org. Lett.* **2015**, *17*, 5404. (e) Liu, X.-G.; Zhang, S.-S.; Wu, J.-Q.; Li, Q.; Wang, H. *Tetrahedron Lett.* **2015**, *56*, 4093.

(16) Preliminary studies showed that fluorinated alcohol solvent exhibited high reactivity in high-valent cobalt catalysis reactions; see: Bunno, Y.; Murakami, N.; Suzuki, Y.; Kanai, M.; Yoshino, T.; Matsunaga, S. *Org. Lett.* **2016**, *18*, 2216 and references cited therein.

(17) CCDC 1578645 (**3aa**) and 1558135 (**3la**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

(18) (a) Zhang, Z.-Z.; Liu, B.; Wang, C.-Y.; Shi, B.-F. *Org. Lett.* **2015**, *17*, 4094. (b) Sun, B.; Yoshino, T.; Kanai, M.; Matsunaga, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 12968.

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