Organic LETTERS

Letter

pubs.acs.org/OrgLett

Rhodium(III)-Catalyzed Acylation of C(sp^3)−H Bonds with Cyclopropenones

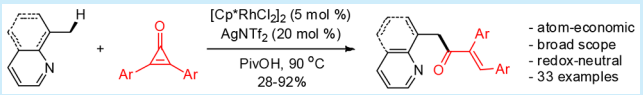
Lingheng Kong,[†,‡] Xukai Zhou,[†,‡] Youwei Xu,[†,‡] and Xingwei Li*[,†]

[†]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

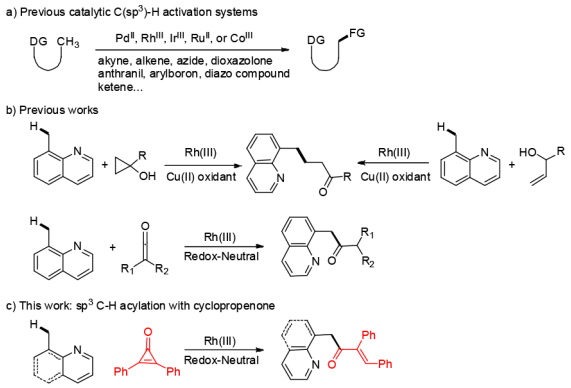
Supporting Information

ABSTRACT: Rh(III)-catalyzed activation and acylation of sp^3 C−H bonds has been realized with diarylcyclopropenone as an acylating reagent. Both benzylic C−H in 8-methylquinolines and unactivated C−H in 2-alkylpyridines are applicable in this C−H acylation reaction, providing enones in good yields under redox-neutral conditions.



Transition metal-catalyzed C−H activation reactions have witnessed rapid development and have provided straightforward approaches to deliver numerous important synthetic targets. A large array of C(sp^2)−H functionalization systems have been developed under metal catalysis in the past decades.[1] In contrast, much less attention has been directed to the activation of C(sp^3)−H bonds. This may be ascribed to the inherently low reactivity of a sp^3 C−H bond during the cleavage stage and the low reactivity of the resulting M-alkyl species toward the coupling partner. Nevertheless, significant achievements have been made in Pd-,[2] Rh-,[3] Co-,[4] Ir-,[5] and Ru[6]-catalyzed C(sp^3)−H activation (Scheme 1a). Various

Scheme 1. Transition Metal-Catalyzed Direct C−H Activation of C(sp^3/sp^2)−H Bonds



C(alkyl)−H substrates such as 8-methylquinolines, 2-alkylpyridines, *N*-alkylpyrazoles, and oxime ethers have been studied. However, the coupling partners of these substrates are mostly limited to polar unsaturated compounds such as azides, dioxazolones, anthranils, arylboron reagents, diazo compounds, and ketenes. Therefore, new synthetic options featuring high efficiency are still in high demand.

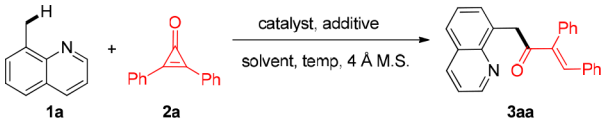
In recent years, the chemistry of strained rings, particularly three-membered rings, has been extensively investigated.[7] As a class of activated coupling partners, three-membered rings exhibited high activity in the coupling with some aryl and alkyl C−H bonds. Recently, we and others have successfully developed coupling of strained rings such as aziridines,[8] cyclopropenes,[9] vinylcyclopropanes,[10] methylenecyclopropanes,[11] vinyloxiranes,[12] cyclopropenones,[13] and cyclopropanols[3n] with various C−H bonds under Rh(III) or Co(III) catalysis. Despite these achievements, the scission of three-membered rings are mostly limited to C(sp^2)−H activation systems. Transition metal-catalyzed, especially Rh(III)-catalyzed, C(sp^3)−H activation, and coupling with strained rings remains largely underexplored. This is likely due to incompatibility between substrates: C(sp^3)−H substrates are generally less reactive, while strained rings can be so reactive that they may undergo decomposition. In 2016, our group reported in several examples rhodium-catalyzed oxidative coupling of 8-methylquinolines with cyclopropanols.[3n] The Kim group also obtained the same carbonyl compounds under Rh(III)-catalyzed C(sp^3)−H alkylation.[3o] What's more, direct acylation of sp^3 C−H bonds by Rh(III)-catalysis is also rare. In 2016, our group reported the redox-neutral C(sp^3)−H acylation of 8-methylquinolines with ketenes to deliver the carbonyl products (Scheme 1b).[3k] As a continuation of our efforts toward the Rh(III)-catalyzed C−H functionalization using strained rings, we now reported C(sp^3)−H activation and subsequent functionalization with cyclopropenones under redox-neutral conditions.

Our investigation was initiated with examination of the parameters of the coupling between 8-methylquinoline (**1a**) and cyclopropenone (**2a**, Table 1). Using [Cp*RhCl$_2$]$_2$/AgSbF$_6$ as a catalyst in the presence of PivOH and 4 Å MS as additives, a coupling occurred in DCE to afford enone **3aa** in 33% yield (entry 1). Screening of solvents (entries 2−6) revealed that chlorobenzene proved beneficial, affording product **3aa** in 40% yield (entry 6), while traces of the product were detected using a cationic catalyst [Cp*Rh-

Received: May 31, 2017
Published: June 23, 2017

DOI: 10.1021/acs.orglett.7b01650
Org. Lett. 2017, 19, 3644−3647

Table 1. Optimization Studies[a]



entry	cat. (mol %)	additive (2.0 equiv)	temp (°C)	solvent	yield (%)[b]
1	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	PivOH	80	DCE	33
2	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	PivOH	80	MeCN	<5
3	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	PivOH	80	1,4-dioxane	<5
4	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	PivOH	80	toluene	37
5	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	PivOH	80	TFE	<5
6	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	PivOH	80	PhCl	40
7	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5)	PivOH	80	PhCl	<5
8	$Cp^*Co(CO)I_2$ (10)/$AgNTf_2$(20)	PivOH	80	PhCl	<5
9	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	AcOH	80	PhCl	<5
10	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	MesCOOH	80	PhCl	22
11	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	AdCOOH	80	PhCl	30
12	$[Cp^*RhCl_2]_2$ (4)/$AgNTf_2$ (16)	PivOH	80	PhCl	43
13	$[Cp^*RhCl_2]_2$ (4)/$AgBF_4$ (16)	PivOH	80	PhCl	<5
14	$[Cp^*RhCl_2]_2$ (4)/AgOPiv (16)	PivOH	80	PhCl	24
15	$[Cp^*RhCl_2]_2$ (4)/$AgNTf_2$ (16)	PivOH	90	PhCl	49
16[c]	$[Cp^*RhCl_2]_2$ (4)/$AgNTf_2$ (16)	PivOH	90	PhCl/PhMe = 1:1	53
17[d]	$[Cp^*RhCl_2]_2$ (4)/$AgNTf_2$ (16)	PivOH	90	PhCl/PhMe = 1:1	56
18[d]	$[Cp^*RhCl_2]_2$ (5)/$AgNTf_2$ (20)	PivOH (0.2)	90	PhCl/PhMe = 1:1	73

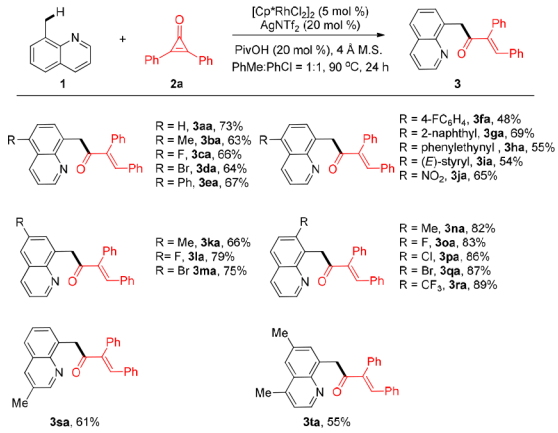
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), acid (2 equiv), solvent (2 mL), 4 Å MS (100 mg), 24 h, sealed tube under N_2. [b]Isolated yield after chromatography. [c]Solvent (4 mL). [d]**1a** (0.3 mmol), **2a** (0.2 mmol), and the solvent (4 mL) were used.

$(MeCN)_3][SbF_6]_2$ or $Cp^*Co(CO)I_2/AgNTf_2$ (entries 7, 8). Inferior results were also observed when PivOH was replaced by AcOH, MesCOOH, or AdCOOH (entries 9–11). Switching the silver salt to $AgNTf_2$ increased the yield to 43% (entries 12–14). A slightly higher yield was obtained when the reaction temperature was increased to 90 °C (entry 15). To our delight, switching the solvent to a mixed solvent of chlorobenzene and toluene (1:1) gave rise to 53% yield (entry 16), and an isolated yield of 56% was secured when the cyclopropenone was used as the limiting reagent (entry 17). Finally, decreasing the PivOH loading to 20 mol % and increasing the catalyst loading to 5 mol % improved the yield to 73% (entry 18). This may suggest the inhibitive effect of the PivOH additive at a higher concentration.

With the optimal reaction conditions in hand, we next explored the scope of 8-methylquinolines (Scheme 2). Introduction of both electron-donating and -withdrawing groups to the 5-position is fully tolerated (**1b–1j**, 48–69%). Of note, 8-methylquinolines bearing functional groups such as alkynyl and alkenyl were found to be coupled with **2a** to give the corresponding products in 55% and 54% yields (**3ha**, **3ia**). A 5-nitro group, which is often problematic in C–H activation systems, is also compatible, affording the product in 65% yield (**3ja**). Various 8-methylquinolines bearing a methyl (**1k**) or a halogen group (**1l–1m**) at the 6-position all reacted with moderate to good yields (66–79%). Moreover, coupling of diverse 7-substituted substrates also gave the corresponding products in high yields (82–89%), indicating the tolerance of steric hindrance and even steric assistance. 3-Methyl substituted (**1s**) and multisubstituted (**1t**) substrates can also react smoothly in the reaction system. Unfortunately, 8-ethylquinoline is ineffective under the standard reaction conditions.

We next investigated the scope of the cyclopropenones in the coupling with different methyl C–H bonds directed by a

Scheme 2. Scope of 8-Methylquinolines[a,b]

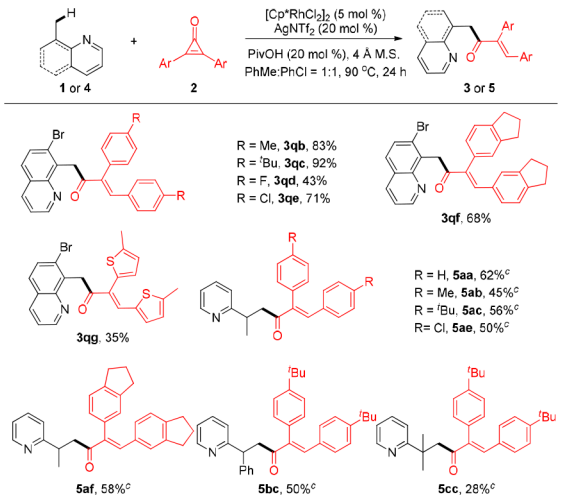


[a]Reaction conditions: **2a** (0.2 mmol), **1** (0.3 mmol), $[Cp^*RhCl_2]_2$/$AgSbF_6$ (5 mol %/ 20 mol %), PivOH (20 mol %), 4 Å MS (100 mg) in chlorobenzene and toluene (4.0 mL, 1:1) at 90 °C for 24 h in a sealed tube under N_2. [b]Isolated yield.

quinoline or pyridine group (Scheme 3). Variation of a series of cyclopropenones has been made by incorporation of both electron-withdrawing and -donating substituents, providing the corresponding products in 43–92% yields (**3qb–3qe**). A disubstituted substrate also reacted smoothly in the reaction system (**3qf**). In addition, 5-methylthienyl-substituted cyclopropenone was also applicable in this reaction (**3qg**). The directing group was also successfully extended to a pyridine ring at a higher temperature. 2-Isopropylpyridine coupled smoothly with various cyclopropenones, thus leading to desymmetrization in moderate to good yields (**5aa–af**). The C–H substrate has been extended to other 2-alkylpyridines (**5bc**, **5cc**).

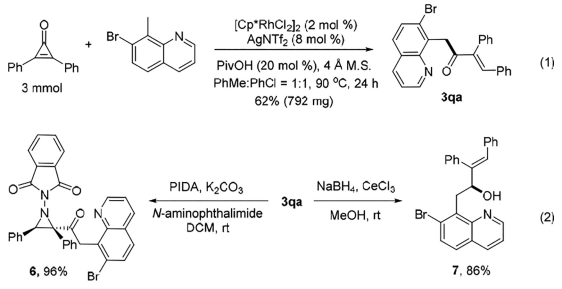
DOI: 10.1021/acs.orglett.7b01650
Org. Lett. 2017, 19, 3644–3647

Scheme 3. Scope of Cyclopropenones and 2-Alkylpyridines[a,b]



[a]Reaction conditions: **2** (0.2 mmol), **1** or **4** (0.3 mmol), $[Cp^*RhCl_2]_2/AgSbF_6$ (5 mol %/20 mol %), PivOH (20 mol %), 4 Å MS (100 mg) in PhCl and toluene (4.0 mL) at 90 °C for 24 h in a sealed tube under N_2. [b]Isolated yield. [c]At 110 °C.

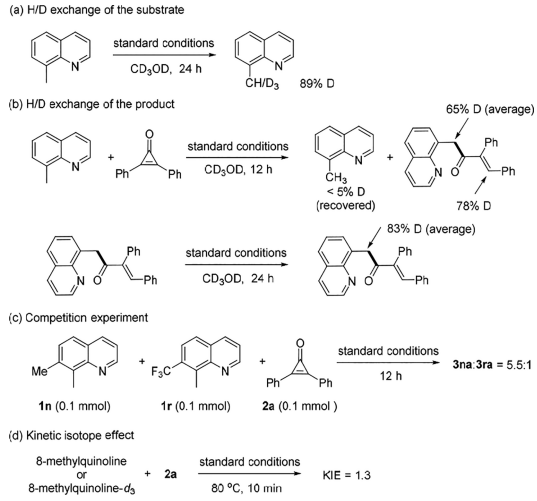
To highlight the robustness and practicality of this transformation, we successfully scaled up the reaction to 3 mmol with 2 mol % catalyst loading to give **3qa** in good yield (eq 1). Next, the synthetic utility of an enone product has



been briefly demonstrated (eq 2). Treatment of **3qa** with $PhI(OAc)_2/K_2CO_3$ at rt provided the aziridinated product **6** in 96% yield. Moreover, the chemoselective 1,2-reduction of **3qa** was carried out using $NaBH_4$ in combination with $CeCl_3$ to afford a functionalized allylic alcohol (**7**).

To gain mechanistic insight into this reaction, several experiments were conducted (Scheme 4). H/D exchange between **1a** and CD_3OD under the standard conditions led to deuteration at the methyl group, indicating reversibility of the C−H cleavage in the absence of any coupling partner (Scheme 4a). However, when the reaction was performed in the presence of **2a**, no deuteration was observed in the recovered starting material **1a**, and extensive H/D exchange was observed in the product **3aa** at the methylene (65% D) and the methine (78% D) positions, indicating that functionalization of the Rh−C(alkyl) bond should be faster than competitive protonolysis process. Meanwhile, a remarkable H/D exchange (83% D) was detected when the product **3aa** was allowed to undergo exchange with CD_3OD, suggesting that the α-C(sp^3)−H protons are sufficiently acidic to allow facile H/D exchange under the catalytic conditions (Scheme 4b). When 7-methylquinoline **1n** was run in competition with the 7-trifluoromethylquinoline **1r**, the

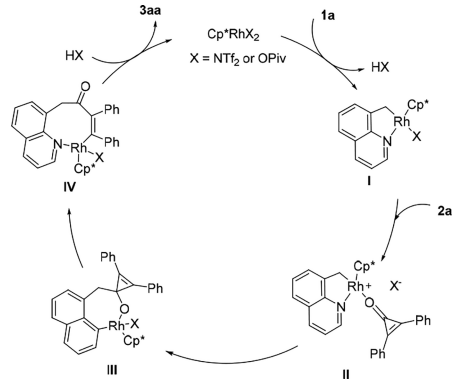
Scheme 4. Mechanistic Studies



reaction favors the electron-rich quinoline in a 5.5:1 ratio (Scheme 4c), indicating that an electrophilic-type rhodation might be involved in the catalytic cycle. Finally, a kinetic isotope effect (KIE) of k_H/k_D = 1.3 was obtained from parallel experiments, suggesting that the cleavage of the methyl C−H bond is probably not involved in the turnover-determining step (Scheme 4d).

Based on our experimental results and precedents of Rh(III)-catalyzed coupling of C(sp^2)−H bond with cyclopropenones,[13] the mechanism of this coupling is proposed in Scheme 5. First, a five-membered rhodacyclic intermediate **I** is

Scheme 5. Proposed Catalytic Cycle



formed via C(sp^3)−H bond activation, to which cyclopropenone **2a** coordinates to give intermediate **II**. The Rh−C bond undergoes migratory insertion into the carbonyl group of cyclopropenone, and subsequent β-carbon elimination gives a ring-opened alkenyl intermediate **IV**. Finally, protonolysis of **IV** furnishes the final product and regenerates the active rhodium species.

In summary, we have realized Rh(III)-catalyzed coupling of alkyl C−H bond with diarylcyclopropenones, leading to synthesis of enones under redox-neutral conditions. Both 8-methylquinolines and 2-alkylpyridines proved viable substrates. This process features good yield, broad substrate scope, functional group tolerance, and high atom-economy. Studies on activation and functionalization of other sp^3 C−H bonds are underway in our laboratories.

DOI: 10.1021/acs.orglett.7b01650
Org. Lett. 2017, 19, 3644−3647

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01650.

Detailed experimental procedures, characterization of new compounds, and copies of NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xwli@dicp.ac.cn.

ORCID

Xingwei Li: 0000-0002-1153-1558

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Final support from the NSFC (Nos. 21525208 and 21472186) and the fund for new technology of methanol conversion of Dalian Institute of Chemical Physics (Chinese Academy of Sciences) are gratefully acknowledged.

■ REFERENCES

(1) For a recent review on transition-metal-catalyzed direct C−H functionalization, see: (a) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (c) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (d) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (e) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (f) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (g) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936. (h) Li, B.-J.; Shi, Z.-J. *Chem. Soc. Rev.* **2012**, *41*, 5588. (i) Brückl, T.; Baxter, R. D.; Ishihara, Y.; Baran, P. S. *Acc. Chem. Res.* **2012**, *45*, 826. (j) Hartwig, J. F. *Acc. Chem. Res.* **2012**, *45*, 864. (k) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443. (l) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281. (m) Zhang, M.; Zhang, Y.; Jie, X.; Zhao, H.; Li, G.; Su, W. *Org. Chem. Front.* **2014**, *1*, 843. (n) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 1107. (o) Song, G.; Li, X. *Acc. Chem. Res.* **2015**, *48*, 1007. (p) Moselage, M.; Li, J.; Ackermann, L. *ACS Catal.* **2016**, *6*, 498. (q) Yoshino, T.; Matsunaga, S. *Adv. Synth. Catal.* **2017**, *359*, 1245. (r) Mishra, N. K.; Sharma, S.; Park, J.; Han, S.; Kim, I. S. *ACS Catal.* **2017**, *7*, 2821.

(2) (a) Shabashov, D.; Daugulis, O. *Org. Lett.* **2005**, *7*, 3657. (b) Chen, X.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 12634. (c) Thu, H.-Y.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9048. (d) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (e) Kalberer, E. W.; Whitfield, S. R.; Sanford, M. S. *J. Mol. Catal. A: Chem.* **2006**, *251*, 108. (f) Yu, W.-Y.; Sit, W. N.; Lai, K.-M.; Zhou, Z.-Y.; Chan, A. S. C. *J. Am. Chem. Soc.* **2008**, *130*, 3304. (g) Zhang, J.; Khaskin, E.; Anderson, N. P.; Zavalij, P. Y.; Vedernikov, A. N. *Chem. Commun.* **2008**, 3625. (h) Yu, W.-Y.; Sit, W. N.; Zhou, Z.; Chan, A. S.-C. *Org. Lett.* **2009**, *11*, 3174. (i) Iglesias, Á.; Álvarez, R.; de Lera, Á. R.; Muñiz, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 2225. (j) Wang, D.; Zavalij, P. Y.; Vedernikov, A. N. *Organometallics* **2013**, *32*, 4882. (k) Stowers, K. J.; Kubota, A.; Sanford, M. S. *Chem. Sci.* **2012**, *3*, 3192. (l) McMurtrey, K. B.; Racowski, J. M.; Sanford, M. S. *Org. Lett.* **2012**, *14*, 4094. (m) Gulia, N.; Daugulis, O. *Angew. Chem., Int. Ed.* **2017**, *56*, 3630.

(3) For selected reports on Rh(III)-catalyzed sp^3 C−H activation, see: (a) Liu, B.; Zhou, T.; Li, B.; Xu, S.; Song, H.; Wang, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 4191. (b) Wang, N.; Li, R.; Li, L.; Xu, S.; Song, H.; Wang, B. *J. Org. Chem.* **2014**, *79*, 5379. (c) Wang, X.; Yu, D.-G.; Glorius, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 10280. (d) Huang, X.; Wang, Y.; Lan, J.; You, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 9404. (e) Huang, X.; You, J. *Chem. Lett.* **2015**, *44*, 1685. (f) Wang, H.; Tang, G.; Li, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 13049. (g) Yu, S.; Tang, G.; Li, Y.; Zhou, X.; Lan, Y.; Li, X. *Angew. Chem., Int. Ed.* **2016**, *55*, 8696. (h) Tang, C.; Zou, M.; Liu, J.; Wen, X.; Sun, X.; Zhang, Y.; Jiao, N. *Chem. - Eur. J.* **2016**, *22*, 11165. (i) Hou, W.; Yang, Y.; Wu, Y.; Feng, H.; Li, Y.; Zhou, B. *Chem. Commun.* **2016**, *52*, 9672. (j) Wippich, J.; Truchan, N.; Bach, T. *Adv. Synth. Catal.* **2016**, *358*, 2083. (k) Yu, S.; Li, Y.; Kong, L.; Zhou, X.; Tang, G.; Lan, Y.; Li, X. *ACS Catal.* **2016**, *6*, 7744. (l) Han, S.; Park, J.; Kim, S.; Lee, S. H.; Sharma, S.; Mishra, N. K.; Jung, Y. H.; Kim, I. S. *Org. Lett.* **2016**, *18*, 4666. (m) Hu, X.-H.; Yang, X.-F.; Loh, T.-P. *ACS Catal.* **2016**, *6*, 5930. (n) Zhou, X.; Yu, S.; Kong, L.; Li, X. *ACS Catal.* **2016**, *6*, 647. (o) Kim, S.; Han, S.; Park, J.; Sharma, S.; Mishra, N. K.; Oh, H. J.; Kwak, H.; Kim, I. S. *Chem. Commun.* **2017**, *53*, 3006. (p) Yuan, C.; Tu, G.; Zhao, Y. *Org. Lett.* **2017**, *19*, 356. (q) Liu, B.; Hu, P.; Zhou, X.; Bai, D.; Chang, J.; Li, X. *Org. Lett.* **2017**, *19*, 2086. (r) Zhou, B.; Chen, Z.; Yang, Y.; Ai, W.; Tang, H.; Wu, Y.; Zhu, W.; Li, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 12121.

(4) For selected reports on Co(III)-catalyzed sp^3 C−H activation, see: (a) Sen, M.; Emayavaramban, B.; Barsu, N.; Premkumar, J. R.; Sundararaju, B. *ACS Catal.* **2016**, *6*, 2792. (b) Barsu, N.; Rahman, M. A.; Sen, M.; Sundararaju, B. *Chem. - Eur. J.* **2016**, *22*, 9135.

(5) For selected reports on Ir(III)-catalyzed sp^3 C−H activation, see: (a) Kang, T.; Kim, H.; Kim, J. G.; Chang, S. *Chem. Commun.* **2014**, *50*, 12073. (b) Kang, T.; Kim, Y.; Lee, D.; Wang, Z.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 4141. (c) Kim, H.; Park, G.; Park, J.; Chang, S. *ACS Catal.* **2016**, *6*, 5922. (d) Gao, P.; Guo, W.; Xue, J.; Zhao, Y.; Yuan, Y.; Xia, Y.; Shi, Z. *J. Am. Chem. Soc.* **2015**, *137*, 12231.

(6) Liu, B.; Li, B.; Wang, B. *Chem. Commun.* **2015**, *51*, 16334.

(7) (a) Rubin, M.; Rubina, M.; Gevorgyan, V. *Chem. Rev.* **2007**, *107*, 3117. (b) Zhu, Z.-B.; Wei, Y.; Shi, M. *Chem. Soc. Rev.* **2011**, *40*, 5534. (c) Shi, M.; Lu, J.-M.; Wei, Y.; Shao, L.-X. *Acc. Chem. Res.* **2012**, *45*, 641. (d) Zhang, D.-H.; Tang, X.-Y.; Shi, M. *Acc. Chem. Res.* **2014**, *47*, 913. (e) Marek, I.; Masarwa, A.; Delaye, P.-O.; Leibeling, M. *Angew. Chem.* **2015**, *54*, 414. (f) Arch-ambeau, A.; Miege, F.; Meyer, C.; Cossy, J. *Acc. Chem. Res.* **2015**, *48*, 1021. (g) Wang, F.; Yu, S.; Li, X. *Chem. Soc. Rev.* **2016**, *45*, 6462.

(8) Li, X.; Yu, S.; Wang, F.; Wan, B.; Yu, X. *Angew. Chem., Int. Ed.* **2013**, *52*, 2577.

(9) (a) Hyster, T. K.; Rovis, T. *Synlett* **2013**, *24*, 1842. (b) Zhang, H.; Wang, K.; Wang, B.; Yi, H.; Hu, F.; Li, C.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 13234.

(10) (a) Wu, J.-Q.; Qiu, Z.-P.; Zhang, S.-S.; Liu, J.-G.; Lao, Y.-X.; Gu, L.-Q.; Huang, Z.-S.; Li, J.; Wang, H. *Chem. Commun.* **2015**, *51*, 77. (b) Guo, W.; Xia, Y. *J. Org. Chem.* **2015**, *80*, 8113. (c) Zell, D.; Bu, Q.; Feldt, M.; Ackermann, L. *Angew. Chem., Int. Ed.* **2016**, *55*, 7408.

(11) (a) Cui, S.; Zhang, Y.; Wu, Q. *Chem. Sci.* **2013**, *4*, 3421. (b) Guo, W.; Zhou, T.; Xia, Y. *Organometallics* **2015**, *34*, 3012. (c) Chen, J.; Guo, W.; Xia, Y. *J. Org. Chem.* **2016**, *81*, 2635.

(12) (a) Yu, S.; Li, X. *Org. Lett.* **2014**, *16*, 1200. (b) Kong, L.; Yu, S.; Tang, G.; Wang, H.; Zhou, X.; Li, X. *Org. Lett.* **2016**, *18*, 3802.

(13) (a) Yu, S.; Li, X. *Org. Lett.* **2014**, *16*, 1220. (b) Xie, F.; Yu, S.; Qi, Z.; Li, X. *Angew. Chem., Int. Ed.* **2016**, *55*, 15351.

DOI: 10.1021/acs.orglett.7b01650
Org. Lett. 2017, 19, 3644−3647