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Rhodium(III)-Catalyzed C−C Bond Formation of Quinoline *N*-Oxides at the C-8 Position under Mild Conditions

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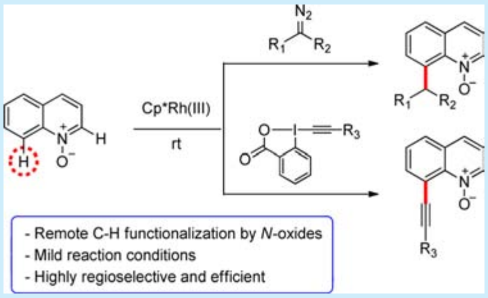
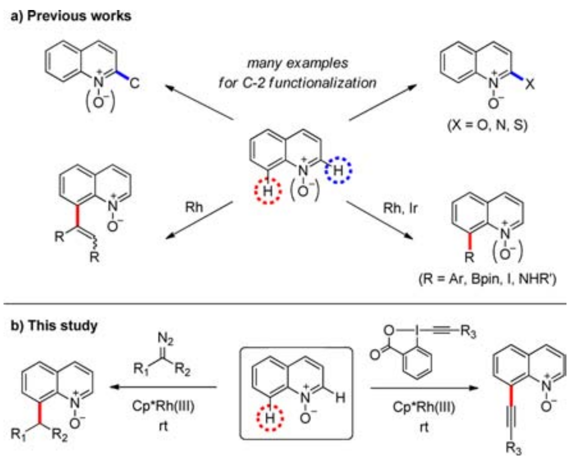
S *Supporting Information*

ABSTRACT: The Rh(III)-catalyzed C-8 selective direct alkylation and alkynylation of quinoline *N*-oxides has been developed. The reactions proceeded highly efficiently at room temperature over a broad range of substrates with excellent regioselectivity and functional group tolerance. This development demonstrates the synthetic utility of the *N*-oxide directing group as a stepping stone for remote C−H functionalization of quinolines.



Quinolines and their analogues are an important class of *N*-heterocycles widely utilized in medicinal and materials chemistry.[1] As a result, the derivatization of quinolines has been an intensive research focus in synthetic chemistry.[2] Recent advances in selective C−H bond activation as a promising tool for the direct functionalization of readily available hydrocarbon commodities have led to efficient synthetic methods[3] that can be successfully applied to the short-step preparation of diverse heteroarenes.[4] In this regard, a range of 2-substituted quinolines (or their *N*-oxides) are easily accessed by the catalytic C−H functionalization[5] of quinolines (*N*-oxides) such as arylation,[6] alkenylation,[7] alkylation,[8] acetoxylation,[9] amidation,[10] and sulfonylation[11] (Scheme 1a). In contrast, only a few examples have been reported for the selective C-8 functionalization of quinolines (*N*-oxides) including our own contribution.[12]

Scheme 1. C−H Functionalization of Quinolines (*N*-Oxides)



In our continuing efforts for the development of direct C−H functionalization of quinolines, we recently disclosed the Rh- and Ir-catalyzed regioselective installation of heteroatoms at the C-8 position of quinoline *N*-oxides using *N*-oxide as a directing group.[13] We were also intrigued by the possibility of developing additional C-8 functionalizations of quinoline *N*-oxides, especially aiming at C−C bond formation.[14] Since the interconversion of quinolines and their *N*-oxides is highly facile, we anticipated that our successful results in this regard would greatly widen the derivatization of quinolines, thereby further expanding the utility of quinolines in medicinal and materials chemistry as well as in total synthesis. Herein, we describe the first example of room temperature introduction of alkyl and alkynyl groups at the C-8 position of quinoline *N*-oxides by using a rhodium catalyst system (Scheme 1b).

Inspired by Yu's work on the Cp*Rh(III)-catalyzed direct C−H coupling of arenes with diazocarbonyl compounds,[15] several research groups have elegantly demonstrated the synthetic utility of carbenoid chemistry in direct C−H annulation reactions to obtain various heterocycles such as isoindolinones, isoquinoline *N*-oxides, azepinones, and 1-aminoindoles.[16]

Motivated by these pioneering works as well as our own interest in developing the C-8 selective C−C bond formation of quinolines (*N*-oxides) and the potential uses of 8-alkylated products,[17] we initiated our study in a model reaction of 6-methylquinoline *N*-oxide (**1b**) with diazomalonate (1.1 equiv, **2a**) to find optimal conditions (Table 1).[18] While no conversion was observed in the absence of rhodium (entry 1), a cationic rhodium species generated in situ from $[RhCp^*Cl_2]_2$ and $AgSbF_6$ displayed catalytic activity that was found to be dependent on the reaction temperatures, leading to 75% yield

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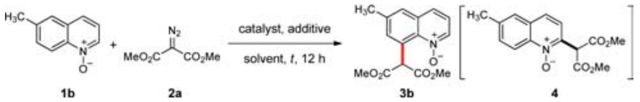
Table 1. Optimization of C-8 Alkylation Reaction[a]



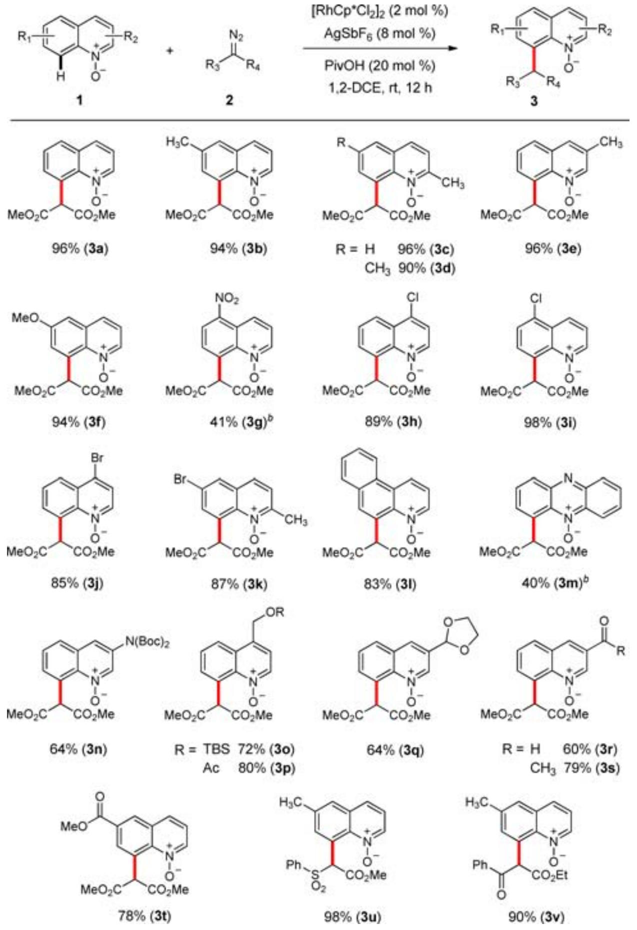
entry	catalyst (mol %)	additive (mol %)	solvent	temp (°C)	yield[b] (%)
1	none	none	1,2-DCE	25	0
2	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	none	1,2-DCE	25	11
3	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	none	1,2-DCE	40	41
4	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	none	1,2-DCE	50	76
5	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	none	1,2-DCE	60	75
6	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	none	toluene	50	5
7	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	none	dioxane	50	19
8	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	none	MeCN	50	11
9	$[RhCp^*Cl_2]_2$ (4) /$AgSbF_6$ (16)	AcOH (20)	1,2-DCE	40	74
10	**$[RhCp^*Cl_2]_2$ (2) /$AgSbF_6$ (8)**	**PivOH (20)**	**1,2-DCE**	**25**	**96 (94)**
11	$[RhCp^*Cl_2]_2$ (1) /$AgSbF_6$ (4)	PivOH (20)	1,2-DCE	25	71
12	$[IrCp^*Cl_2]_2$ (4) /$AgNTf_2$ (16)	PivOH (20)	1,2-DCE	25	<5
13	$[Ru(p\text{-cymene})Cl_2]_2$ (4) /$AgNTf_2$ (16)	PivOH (20)	1,2-DCE	25	<5

[a] Reaction conditions: **1b** (0.1 mmol) and **2a** (1.1 equiv) in solvent (0.5 mL) for 12 h. [b] ^{1}H NMR yield of crude reaction mixture (1,1,2,2-tetrachloroethane as an internal standard); isolated yield is in parentheses.

at 60 °C (entries 2–5). 1,2-Dichloroethane was the most effective solvent among others examined (entries 6–8). We were pleased to see that the reaction efficiency was significantly increased by the addition of acid additives (entries 9 and 10). Indeed, excellent product yield was obtained at 25 °C in the presence of pivalic acid (0.2 equiv) even with a lower loading of catalyst precursor (2 mol %) to give **3b** in 94% isolated yield (entry 10). Reaction with 1 mol % of catalyst resulted in slightly lower yield (entry 11). On the other hand, only trace amounts of product were formed with $[IrCp^*Cl_2]_2$ or $[Ru(p\text{-cymene})Cl_2]_2$ (entries 12 and 13). It should be noted that a regioisomeric product **4** was not detected under the present reaction conditions.

With the optimized conditions in hand, we subsequently examined the scope of quinoline *N*-oxides and diazo compounds to explore this carbenoid functionalization strategy (Scheme 2). Significantly, the reaction proceeded smoothly with most substrates examined leading to products in good to excellent yields. Regardless of the position of alkyl substituents in quinoline *N*-oxides, the reaction proceeded highly efficiently (**3b–e**). A potentially reactive benzylic sp^3 C–H bond *ortho* to *N*-oxide remained intact (**3c,d**). While the reaction of a substrate bearing an electron-donating group (**3f**) was facile, 5-nitroquinoline *N*-oxide underwent the alkylation with moderate yield (**3g**). Halogenated substrates were readily alkylated regardless of the position of halide substituents (**3h–k**), thus allowing for further functionalizations through cross-coupling reactions. Reaction of polyaromatic heterocycles such as benzo[*f*]quinoline *N*-oxide (**3l**) and phenazine mono-oxide (**3m**) was also regioselective. Functional groups commonly used in synthetic chemistry such as carbamate (**3n**), silyloxy (**3o**), acetoxy (**3p**), acetal (**3q**), aldehyde (**3r**), ketone (**3s**), and ester (**3t**) were all compatible with the present reaction conditions. While diazo compounds substituted with a phenylsulfonyl (**3u**) or a benzoyl group (**3v**) were found to be suitable for this reaction to afford the corresponding products in excellent yields, diazo derivatives bearing a diethyl phosphonate, nitrile, or nitro group were not reactive.

Scheme 2. Scope of C-8 Alkylation Reaction[a]

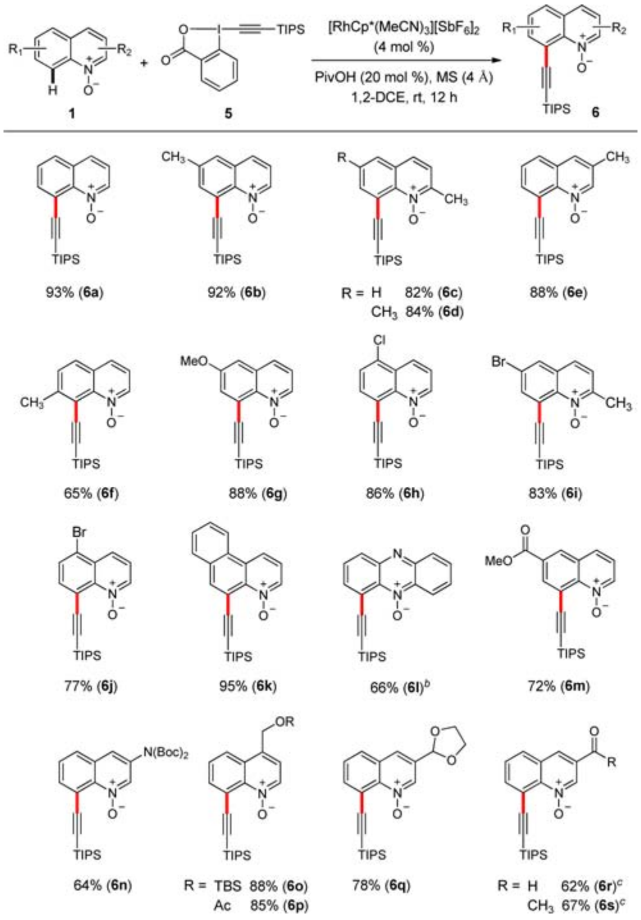


[a] Reaction conditions: **1** (0.1 mmol), **2** (1.1 equiv), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), and PivOH (20 mol %) in 1,2-DCE (0.5 mL); isolated yields are given. [b] At 50 °C for 24 h.

After successful exploration of the regioselective C-8 alkylation of quinoline *N*-oxides with diazo compounds, we turned our attention to the introduction of a new type of functionality at the same position. We decided to examine an alkynylation reaction since 8-alkynylquinoline derivatives have found utility in various areas including coordination chemistry.[19,20] In this regard, the Loh, Li, and Glorius groups independently reported the Rh(III)-catalyzed direct C–H alkynylation of arenes or alkenes by employing 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) as a viable alkynyl source.[21] In addition, this alkynylated hypervalent iodine reagent was previously utilized for the C–H alkynylation of electron-rich (hetero)arenes under Au catalytic conditions.[22]

We were pleased to see that the desired C–H alkynylation of quinoline *N*-oxides occurred smoothly with TIPS-EBX (**5**) to afford the corresponding products in good to excellent yields at room temperature (Scheme 3). Upon screening the reaction conditions, the alkynylation was observed to be more facile by using a pregenerated cationic species $[RhCp^*(MeCN)_3][SbF_6]_2$ (see the Supporting Information for details). In addition, the addition of molecular sieves (4 Å) gave higher product yields in the C-8 alkynylation reaction.

Scheme 3. Scope of C-8 Alkynylation Reaction[a]



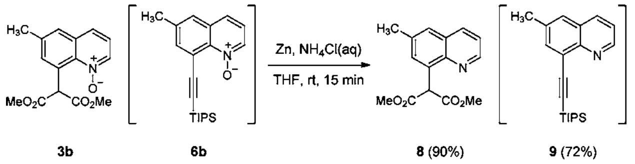
[a] Reaction conditions: **1** (0.1 mmol), **5** (1.1 equiv), $[RhCp^*(MeCN)_3][SbF_6]_2$ (4 mol %), PivOH (20 mol %), and molecular sieves (4 Å) in 1,2-DCE (0.5 mL); isolated yields are given. [b] At 50 °C. [c] At 60 °C.

An alkyl substituent at the different positions of quinoline *N*-oxides did not cause any problem in alkynylation (**6b–f**), and the reaction efficiency was not affected by the electronic variation of substrates (**6g–j**). Products bearing halide groups could be obtained in high yields (**6h–j**), and polyaromatic heterocycles also participated in the reaction (**6k,l**). A wide range of functional groups were well tolerated under the present reaction conditions, such as ester, carbamate, silyloxy, acetoxy, acetal, aldehyde, and ketone (**6m–s**).

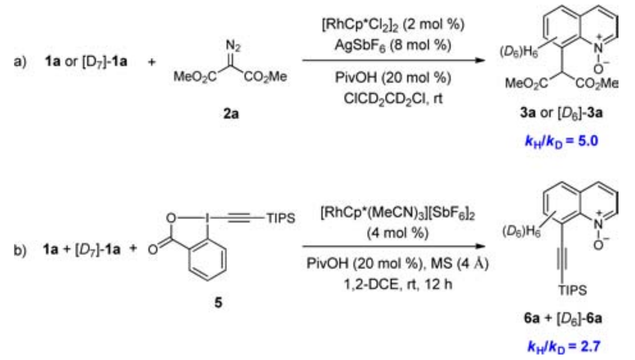
It was shown that the resultant alkylated and alkynylated quinoline *N*-oxides could easily be deoxygenated leading to the corresponding quinoline derivatives with the use of zinc reagent under mild conditions (Scheme 4), thus demonstrating that the present protocol is a highly attractive route to the C-8 functionalization of quinolines.

To gain a mechanistic insight into the present C–C bond-forming reactions, isotope-labeling experiments were conducted with a deuterium-labeled quinoline *N*-oxide under the standard conditions (Scheme 5). Significant primary kinetic isotope effects (KIE) were observed from parallel carbenoid reactions ($k_H/k_D = 5.0$, Scheme 5a) and competitive alkynylation reactions ($k_H/k_D = 2.7$, Scheme 5b). These KIE values led us to propose that the C–H bond cleavage would be involved in the turnover-limiting step in both reactions, although the exact reason for the different range of KIEs is not clearly understood at this stage.

Scheme 4. Deoxygenation of Quinoline *N*-Oxide Products

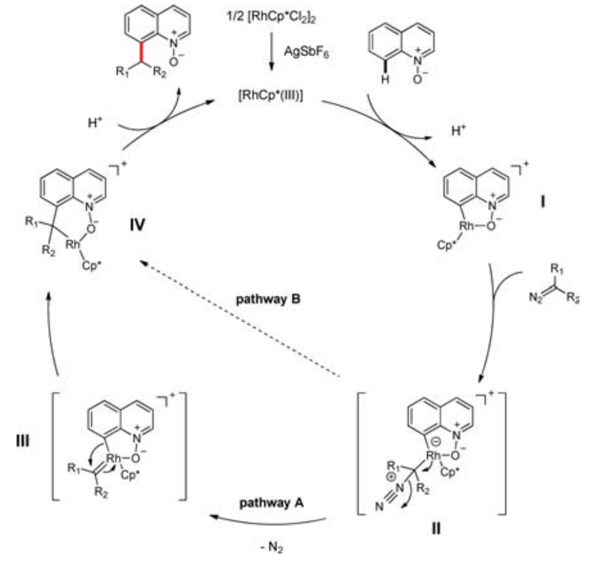


Scheme 5. Kinetic Isotope Studies of C-8 Alkylation and Alkynylation of Quinoline *N*-Oxides



On the basis of the above experiments and precedent literature,[15,16] a plausible alkylation pathway is shown in Scheme 6. First, a cationic Rh(III) catalyst reacts with a substrate through the C–H activation to generate a five-membered rhodacycle intermediate **I**. It is then proposed that coordination of a diazo species to **I** and then release of N_2 will afford a metal–carbenoid intermediate **III** through **II** (pathway A). Subsequent migratory insertion would generate a 6-membered rhodacycle species **IV** that will be finally protonated to give the desired product. However, an alternative route (pathway B) that does not involve

Scheme 6. Proposed Pathway of C-8 Alkylation



a discrete metal−carbenoid intermediate for the formation of the rhodacycle **IV** cannot completely be ruled out at the present stage.

In conclusion, the Rh(III)-catalyzed direct alkylation and alkynylation of quinoline *N*-oxides has been accomplished for C-8 selective C−C bond formation. The reactions proceeded highly efficiently and selectively at room temperature over a broad range of substrates with excellent functional group tolerance. This example demonstrates the synthetic utility of the *N*-oxide directing group as a stepping stone for remote C−H functionalization of quinolines.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure and characterization of new compounds (^{1}H, ^{13}C NMR spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Egan, T. J.; Ross, D. C.; Adams, P. A. *FEBS Lett.* **1994**, *352*, 54. (b) Foley, M.; Tilley, L. *Pharmacol. Ther.* **1998**, *79*, 55. (c) Eicher, T.; Hauptmann, S. *The Chemistry of Heterocycles*, 2nd ed.; Wiley-VCH: Weinheim, 2003. (d) Hughes, G.; Bryce, M. R. *J. Mater. Chem.* **2005**, *15*, 94. (e) Kimyonok, A.; Wang, X. Y.; Weck, M. *Polym. Rev.* **2006**, *46*, 47. (f) Michael, J. P. *Nat. Prod. Rep.* **2008**, *25*, 166. (g) Solomon, V. R.; Lee, H. *Curr. Med. Chem.* **2011**, *18*, 1488.

(2) (a) *Chemistry of Heterocyclic Compounds: Quinolines*; Jones, G., Ed.; Wiley: Chichester, U.K., 1977 (Part I), 1982 (Part II), 1990 (Part III); Vol. 32. (b) Mongin, F.; Queguiner, G. *Tetrahedron* **2001**, *57*, 4059. (c) Youssef, M. S. K.; Ahmed, R. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2006**, *181*, 1123. (d) Mphahlele, M. J.; Lesenyeho, L. G. *J. Heterocycl. Chem.* **2013**, *50*, 1.

(3) For selected reviews, see: (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (c) Bergman, R. G. *Nature* **2007**, *446*, 391. (d) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (e) Li, C.-J. *Acc. Chem. Res.* **2009**, *42*, 335. (f) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (g) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 677. (h) Daugulis, O. *Top. Curr. Chem.* **2010**, *292*, 57. (i) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (j) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. (k) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (l) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (m) White, M. C. *Science* **2012**, *335*, 807. (n) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (o) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (p) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788. (q) Hartwig, J. F. *Acc. Chem. Res.* **2012**, *45*, 864. (r) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936. (s) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (t) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (u) Rouquet, G.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 11726. (v) Pan, S.; Shibata, T. *ACS Catal.* **2013**, *3*, 704. (w) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443.

(4) For selected reviews, see: (a) Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 11212. (b) Zhu, C.; Wang, R.; Falck, J. R. *Chem.—Asian J.* **2012**, *7*, 1502.

(5) Yan, G.; Borah, A. J.; Yang, M. *Adv. Synth. Catal.* **2014**, *356*, 2375.

(6) (a) Cho, S. H.; Hwang, S. J.; Chang, S. *J. Am. Chem. Soc.* **2008**, *130*, 9254. (b) Campeau, L.-C.; Stuart, D.-R.; Leclerc, J.-P.; Bertrand-Laperle, M.; Villemure, E.; Sun, H.-Y.; Lasserre, S.; Guimond, N.; Lecavallier, M.; Fagnou, K. *J. Am. Chem. Soc.* **2009**, *131*, 3291. (c) Zhao, D.; Wang, W.; Yang, F.; Lan, J.; Yang, L.; Gao, G.; You, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 3296. (d) Xi, P.; Yang, F.; Qin, S.; Zhao, D.; Lan, J.; Gao, G.; Hu, C.; You, J. *J. Am. Chem. Soc.* **2010**, *132*, 1822. (e) Gong, X.; Song, G.; Zhang, H.; Li, X. *Org. Lett.* **2011**, *13*, 1766.

(7) (a) Wu, J.; Cui, X.; Chen, L.; Jiang, G.; Wu, Y. *J. Am. Chem. Soc.* **2009**, *131*, 13888. (b) Wen, P.; Li, Y.; Zhou, K.; Ma, C.; Lan, X.; Ma, C.; Huang, G. *Adv. Synth. Catal.* **2012**, *354*, 2135.

(8) (a) Ryu, J.; Cho, S. H.; Chang, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3677. (b) Xiao, B.; Liu, Z.-J.; Liu, L.; Fu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 616. (c) Wu, Z.; Pi, C.; Cui, X.; Bai, J.; Wu, Y. *Adv. Synth. Catal.* **2013**, *355*, 1971. (d) Larionov, O. V.; Stephens, D.; Mfuh, A.; Chavez, G. *Org. Lett.* **2014**, *16*, 864.

(9) Chen, X.; Zhu, C.; Cui, X.; Wu, Y. *Chem. Commun.* **2013**, *49*, 6900.

(10) (a) Li, G.; Jia, C.; Sun, K. *Org. Lett.* **2013**, *15*, 5198. For C−H aminations, see: (b) Zhu, C.; Yi, M.; Wei, D.; Chen, X.; Wu, Y.; Cui, X. *Org. Lett.* **2014**, *16*, 1840.

(11) Wu, Z.; Song, H.; Cui, X.; Pi, C.; Du, W.; Wu, Y. *Org. Lett.* **2013**, *15*, 1270.

(12) (a) Kwak, J.; Kim, M.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 3780. (b) Konishi, S.; Kawamorita, S.; Iwai, T.; Steel, P. G.; Marder, T. B.; Sawamura, M. *Chem.—Asian J.* **2014**, *9*, 434.

(13) Hwang, H.; Kim, J.; Jeong, J.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 10770.

(14) Shibata, T.; Matsuo, Y. *Adv. Synth. Catal.* **2014**, *356*, 1516.

(15) Chan, W.-W.; Lo, S.-F.; Zhou, Z.; Yu, W.-Y. *J. Am. Chem. Soc.* **2012**, *134*, 13565.

(16) (a) Hyster, T. K.; Ruhl, K. E.; Rovis, T. *J. Am. Chem. Soc.* **2013**, *135*, 5364. (b) Yu, X.; Yu, S.; Xiao, J.; Wan, B.; Li, X. *J. Org. Chem.* **2013**, *78*, 5444. (c) Shi, Z.; Koester, D. C.; Boultadakis-Arapinis, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 12204. (d) Cui, S.; Zhang, Y.; Wang, D.; Wu, Q. *Chem. Sci.* **2013**, *4*, 3912. (e) Hu, F.; Xia, Y.; Ye, F.; Liu, Z.; Ma, C.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 1364. (f) Shi, J.; Yan, Y.; Li, Q.; Xu, H. E.; Yi, W. *Chem. Commun.* **2014**, *50*, 6483. (g) Lam, H.-W.; Man, K.-Y.; Chan, W.-W.; Zhou, Z.; Yu, W.-Y. *Org. Biomol. Chem.* **2014**, *12*, 4112. (h) Liang, Y.; Yu, K.; Li, B.; Xu, S.; Song, H.; Wang, B. *Chem. Commun.* **2014**, *50*, 6130. (i) Ye, B.; Cramer, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 7896.

(17) Parnes, J. S.; Carter, D. S.; Kurz, L. J.; Flippin, L. A. *J. Org. Chem.* **1994**, *59*, 3497.

(18) For our previous works on the carbenoid chemistry, see: (a) Park, E. J.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2008**, *130*, 17268. (b) Park, E. J.; Lee, S.; Chang, S. *J. Org. Chem.* **2010**, *75*, 2760. (c) Kim, J.; Ohk, Y.; Park, S. H.; Jung, Y.; Chang, S. *Chem.—Asian J.* **2011**, *6*, 2040.

(19) (a) Consorti, C. S.; Ebeling, G.; Rodembusch, F.; Stefani, V.; Livotto, P. R.; Rominger, F.; Quina, F. H.; Yihwa, C.; Dupont, J. *Inorg. Chem.* **2004**, *43*, 530. (b) Greco, N. J.; Hysell, M.; Goldenberg, J. R.; Rheingold, A. L.; Tor, Y. *Dalton Trans.* **2006**, 2288.

(20) For our previous studies on the C−H alkynylation reaction, see: (a) Kim, S. H.; Chang, S. *Org. Lett.* **2010**, *12*, 1868. (b) Kim, S. H.; Yoon, J.; Chang, S. *Org. Lett.* **2011**, *13*, 1474. (c) Kim, S. H.; Park, S. H.; Chang, S. *Tetrahedron* **2012**, *68*, 5162.

(21) (a) Feng, C.; Loh, T.-P. *Angew. Chem., Int. Ed.* **2014**, *53*, 2722. (b) Xie, F.; Qi, Z.; Yu, S.; Li, X. *J. Am. Chem. Soc.* **2014**, *136*, 4780. (c) Collins, K. D.; Lied, F.; Glorius, F. *Chem. Commun.* **2014**, *50*, 4459. (d) Feng, C.; Feng, D.; Loh, T.-P. *Chem. Commun.* **2014**, *50*, 9865.

(22) (a) Brand, J. P.; Charpentier, J.; Waser, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9346. (b) Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 7304. (c) Li, Y.; Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 6743.