Organic LETTERS

Letter

pubs.acs.org/OrgLett

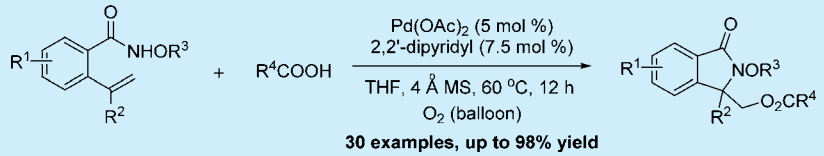
Palladium-Catalyzed Aerobic Aminooxygenation of Alkenes for Preparation of Isoindolinones

Xuezhen Kou,[†] Yu Li,[‡] Liang Wu,[†] Xinghua Zhang,[‡] Guoqiang Yang,*[,†] and Wanbin Zhang*[,†]

[†]School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

[‡]School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, China

Supporting Information

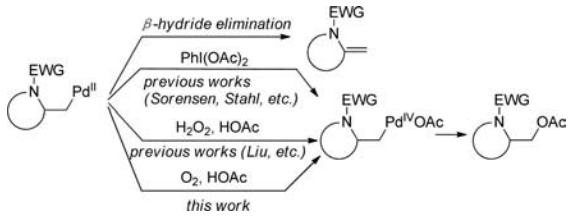


ABSTRACT: A palladium-catalyzed intramolecular isoindolinone-forming aminooxygenation of alkenes with 1 atm of oxygen as oxidant is reported. A variety of functionalized alkenes and carboxylic acids can be used, and high yields were observed. Preliminary mechanistic studies revealed that the aminooxygenation products were formed through the oxidation of a C−Pd^{II} species using a strong oxidant, peroxide, which is generated in situ from a Pd(OAc)$_2$/bpy/O$_2$/HOAc catalytic system.

The oxidative functionalization of alkenes is one of the most powerful and fundamental transformations known in organic synthesis.[1] Palladium catalyst systems have enabled a wide variety of practical and broadly used oxidative reactions.[2] Among them, the palladium-catalyzed addition of nitrogen nucleophiles to alkenes is a well-developed strategy for the construction of C−N bonds.[3] Although methods for the direct functionalization of alkyl Pd^{II} intermediates exist,[4] β-hydride elimination can be a rapid process (Scheme 1),[3a,5] while transformations involving alkyl Pd^{IV} intermediates can readily undergo reductive elimination reactions to realize a palladium-catalyzed difunctionalization of olefins.[6] Recently, Sorensen,[7a] Stahl,[7b] Sanford,[7c,d] Muñiz,[7e] Dong,[7f] and Liu[7g] reported that the palladium-catalyzed aminooxygenation of alkenes could be achieved using PhI(OAc)$_2$ as a strong oxidant. This oxidant traps the Pd−C bond and oxidizes Pd^{II} to high-valent Pd^{IV} to facilitate C−O[7a−h] (also C−C,[7i−k] C−N,[7l−n] C−F[7o]) bond formation (Scheme 1). Additionally, Liu and co-workers have shown that hydrogen peroxide can be used as the sole oxidant to oxidize Pd^{II} to Pd^{IV} for the construction of C−Cl[8a,b] and C−O[8c,d] bonds with a palladium catalyst (Scheme 1). Furthermore, NFSI,[9a,b] Oxone,[9c,d] PhICl$_2$,[9e−g] and NXS[9h,i] can also be used as strong oxidants to generate Pd^{IV} species.[9] Unfortunately, stoichiometric quantities of these wasteful high-energy oxidants often produce large quantities of byproducts.

Recently, the development of environmentally sustainable oxidants for use in oxidative transformations has gained increased prominence.[9l,10] Molecular O$_2$ should be an ideal oxidant because it is environmentally benign, economical, practical, and readily available. Compared to the oxidation of Pd^0 to Pd^{II}, strategies that utilize molecular O$_2$ for the oxidation of Pd^{II} to Pd^{IV} are underdeveloped. Therefore, using O$_2$ as a sole oxidant remains a tremendous challenge in palladium-catalyzed oxidation reactions.[3g,11] Recently, Grubbs,[12a] Loh,[12b] and Jiang[12c] disclosed the palladium-catalyzed dioxygenation of alkenes with O$_2$ as an oxidant using high-valent palladium catalysis. However, palladium-catalyzed aminooxygenations of alkenes that utilize O$_2$ as the sole oxidant have not been reported.[13] Herein, we report an efficient palladium-catalyzed intramolecular isoindolinone-forming aminooxygenation of alkenes with 1 atm of O$_2$ as oxidant (Scheme 1). These reactions may proceed through a mechanism involving the oxidation of Pd^{II} to Pd^{IV} by oxidants (hydrogen peroxide and organic peroxyacids) generated in situ from O$_2$.

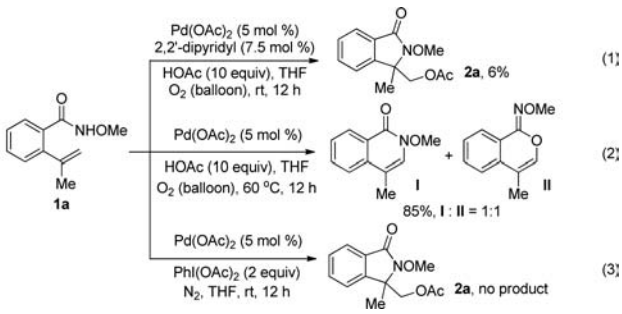
Scheme 1. Pathways for Oxidation via Alkyl C−Pd^{II} Intermediates



During our initial studies on palladium-catalyzed asymmetric aerobic aza-Wacker-type cyclization of alkenes,[14] we found that treatment of **1a** with 5 mol % Pd(OAc)$_2$, 7.5 mol % 2,2′-dipyridyl, and 10 equiv of HOAc under 1 atm of O$_2$ afforded aminoacetoxylation product **2a** in very low yield (6%). The reaction was carried out at room temperature for 12 h (eq 1). Although the reaction yield was very low, no six-membered ring olefin products (**I** and **II**)[15] arising from an aerobic aza-Wacker cyclization were observed. The aza-Wacker cyclization products (**I** and **II**) were obtained as the major products in the absence of ligand bpy (eq 2). However, the reaction failed to give aminooxygenation product **2a** when PhI(OAc)$_2$ was employed as the oxidant under a nitrogen atmosphere (eq 3), an oxidant

Received: September 17, 2015
Published: November 2, 2015

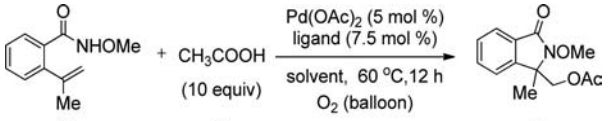
DOI: 10.1021/acs.orglett.5b02703
Org. Lett. 2015, 17, 5566−5569



that has been widely used in palladium-catalyzed C−O bond forming reactions.[7a−h]

Further optimization of the reaction conditions for palladium-catalyzed intramolecular aminooxygenation of alkenes revealed that the yield of **2a** improved to 93% when the temperature was raised from room temperature to 60 °C (Table 1, entry 1). To facilitate the desired aminooxygenation, a series of monodentate and bidentate pyridine ligands were examined; however, yields of **2a** failed to improve (entries 2−6). 1,10-Phenanthroline was also tested as a ligand and gave the desired product in moderate yield (entry 7). According to these results, different solvents were screened, showing that the type of solvent noticeably affects the reaction efficiency (entries 8−11). THF was found to be the best solvent for the aminooxygenation. Conversely, polar solvents such as DMF and CH_3CN were incompatible with our reaction system. Reaction under 1 atm of air provided **2a** in 83% yield using THF as a solvent (entry 12). To our delight, the efficiency of this reaction could be further enhanced by the addition of 4 Å molecular sieves (MS, 80 mg, entry 13).

Table 1. Optimization of Reaction Conditions[a]

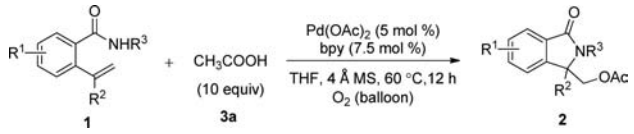


entry	ligand	solvent	yield[b] (%)
1	bpy	THF	93
2	pyridine[c]	THF	86
3	4,4′-Me-bpy	THF	54
4	4,4′-OMe-bpy	THF	60
5	4,4′-^{t}Bu-bpy	THF	78
6	5,5′-Me-bpy	THF	74
7	1,10-phenanthroline	THF	66
8	bpy	MeOH	44
9	bpy	DMF	0
10	bpy	DCE	26
11	bpy	CH_3CN	trace
12[d]	bpy	THF	83
13[e]	bpy	THF	98

[a]Reaction conditions: **1a** (0.2 mmol), **3a** (2 mmol), $Pd(OAc)_2$ (5 mol %), ligand (7.5 mol %), THF (1.5 mL), at 60 °C for 12 h under O_2 (1 atm). [b]Isolated yield. [c]Pyridine (0.06 mmol). [d]Under air. [e]4 Å MS (80 mg) was added. bpy = 2,2′-dipyridyl, DMF = *N*,*N*-dimethylformamide, DCE = dichloroethane, THF = tetrahydrofuran.

With the optimized reaction conditions in hand, a variety of alkene substrates were examined (Table 2). First, substrates with various functional groups on the benzene ring were surveyed. Substrates bearing benzene rings with electron-withdrawing substituents such as fluoro (**1b** and **1c**), chloro (**1d** and **1e**), and trifluoromethyl (**1f**) groups gave their corresponding products

Table 2. Alkene Substrate Scope[a]



entry	substrate	product	yield (%)[b]
1	**1a**, R^1= H	**2a**	98
2	**1b**, R^1 = 5-F	**2b**	91
3	**1c**, R^1 = 4-F	**2c**	94
4	**1d**, R^1 = 5-Cl	**2d**	91
5	**1e**, R^1 = 4-Cl	**2e**	96
6	**1f**, R^1 = 4-CF_3	**2f**	94
7	**1g**, R^1 = 4-OMe	**2g**	92
8[c]	**1h**, R^1 = 4,5-dimethoxyl	**2h**	90
9[c]	**1i**	**2i**	70
10	**1j**, R^2 = Et	**2j**	98
11	**1k**, R^2 = *n*-hexyl	**2k**	90
12	**1l**, R^2 = cyclopentyl	**2l**	95
13	**1m**, R^2 = cyclohexyl	**2m**	91
14	**1n**, R^2 = phenethyl	**2n**	93
15	**1o**, R^2 = phenylpropyl	**2o**	97
16	**1p**, R^3 = benzyloxyl	**2p**	87
17	**1q**, R^3 = Ts	**2q**	0
18	**1r**, R^3 = Boc	**2r**	0
19	**1s**, R^3 = benzyl	**2s**	0
20	**1t**, R^3 = phenyl	**2t**	0
21	**1u**, R^3 = ^{n}Bu	**2u**	0

[a]Reaction conditions: **1** (0.2 mmol), **3a** (2 mmol), $Pd(OAc)_2$ (5 mol %), bpy (7.5 mol %), THF (1.5 mL), 4 Å MS (80 mg) at 60 °C for 12 h under O_2 (1 atm). [b]Isolated yield. [c]24 h.

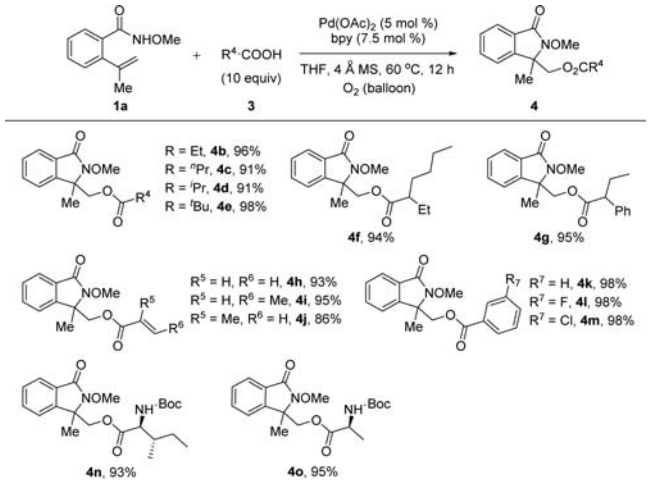
2b−f in excellent yields with high efficiency. Strongly electron-donating substituents reduced the reactivity of the substrates (**1h** and **1i** vs **1g**). To our disappointment, reaction of substrate **1i** bearing a 4,5-methylenedioxyl group only gave its corresponding product **2i** in modest yield and was accompanied by many byproducts. By varying R^2, substrates **1j−o** bearing different substituents were tested, and the reactions proceeded well to provide the corresponding products **2j−o** in excellent yields. Replacement of R^2 from a methyl group (**1a**) to ethyl (**1j**), cyclopentyl (**1l**), and phenylpropyl (**1o**) groups had little influence on the aminoacetoxylation of alkenes, while the presence of *n*-hexyl (**1k**), cyclohexyl (**1m**), and phenethyl (**1n**) groups led to a slight decrease in yield. Furthermore, substrates bearing various protecting groups on the nitrogen were surveyed. Substrate **1p** possessing a benzyloxyl protecting group gave its corresponding product **2p** in good yield. However, the introduction of Ts (**1q**), Boc (**1r**), benzyl (**1s**), phenyl (**1t**), or butyl (**1u**) groups at R^3 prevented any reaction from occurring.

To further explore the applicability of the $Pd(OAc)_2$/bpy/O_2 catalytic system, we investigated whether this methodology was suitable for different types of carboxylic acids. As shown in Scheme 2, reactions with alkyl carboxylic acids proceeded very well to provide the desired products (**4b−g**) in excellent yields. Interestingly, acrylic acid substrates gave their corresponding products (**4h−j**) in good to excellent yields. It is worth noting that aryl carboxylic acids were also tolerated (**4k−m**). Importantly, the present strategy was also successfully applied to amino acid substrates (**4n** and **4o**).

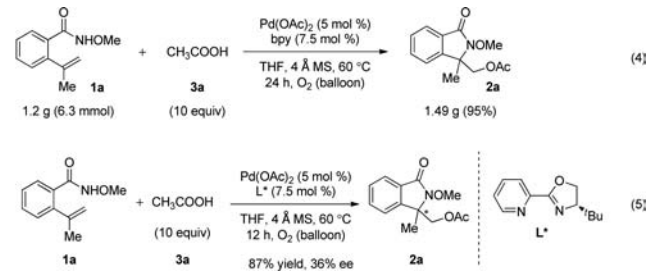
To test the practicality of our methodology, a gram-scale reaction using substrate **1a** and HOAc was carried out (eq 4). The product **2a** was obtained with results comparable to those shown in Table 2. When a chiral ligand **L*** was added to this

DOI: 10.1021/acs.orglett.5b02703
Org. Lett. 2015, 17, 5566−5569

Scheme 2. Carboxylic Acid Substrate Scope[a,b]

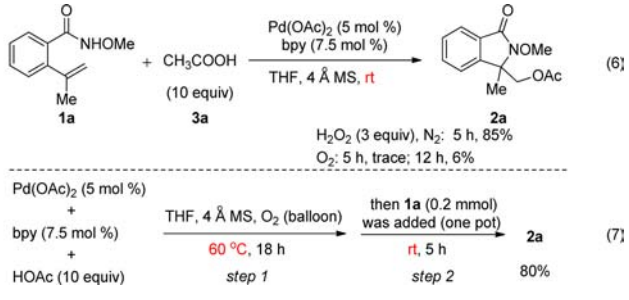


[a]Reaction conditions: **1** (0.2 mmol), **3a** (2 mmol), $Pd(OAc)_2$ (5 mol %), bpy (7.5 mol %), THF (1.5 mL), 4 Å MS (80 mg) at 60 °C for 12 h under 1 atm O_2. [b]Isolated yield.



catalytic system, product **2a** could be isolated in 87% yield and 36% ee (eq 5).

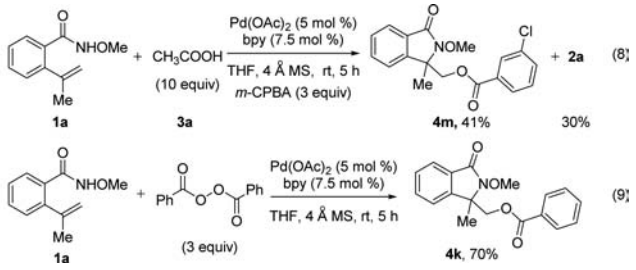
To gain more insight into the mechanism of the aminooxygenation process, several experiments were conducted. No reaction occurred when **1a** was treated with stoichiometric amounts of $Pd(OAc)_2$ and ligand in the absence of O_2 or air. Similar results with O_2 were observed (**2a**, 85%) when H_2O_2 was used as an oxidant at room temperature for 5 h under a N_2 atmosphere (eq 6). Furthermore, the reductive elimination of



C−Pd−OAc intermediates to form C−O bond is often observed in $Pd^{II/IV}$-catalyzed oxidative transformations.[7a−h,8c,11a,12c] Thus, a $Pd^{II/IV}$-catalyzed aminooxygenation of alkenes seems to be more probable than $Pd^{0/II}$ catalysis.

With the above results in hand, we questioned whether O_2 was able to act as a strong enough oxidant to directly oxidize Pd^{II} to Pd^{IV}. Control experiments showed that reaction of **1a** at room temperature afforded only a trace amount of **2a** after 5 h (eq 6). Interestingly, a stepwise experiment provided results similar to experiments using H_2O_2 as an oxidant (eq 7). Furthermore, H_2O_2 can be generated in situ from Pd/ligand/O_2 catalytic systems.[3g,8b] On the basis of these experiments, we assume that the most feasible reagent for the oxidation of Pd^{II} to Pd^{IV} is H_2O_2, generated in situ from O_2.

We also wanted to address whether or not organic peroxyacids, which could potentially be formed in situ from H_2O_2 and carboxylic acid, were able to serve as oxidants. The addition of 3 equiv of *m*-CPBA to the reaction mixture successfully gave the product **4m** in 41% yield and **2a** in 30% yield at room temperature after 5 h (eq 8). A similar experiment was carried

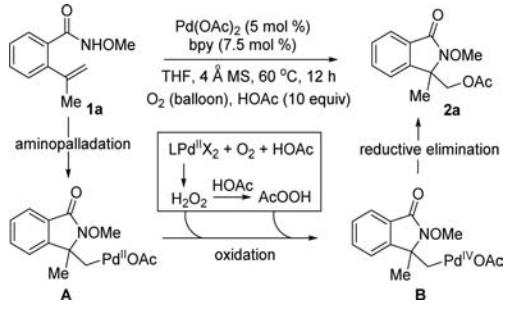


out with 3 equiv of benzoyl peroxide at room temperature, giving product **4k** in 70% yield (eq 9). Thus, peroxyacids acting as the active oxidants cannot be completely excluded,[16] even though H_2O_2 is also an efficient oxidant.

When radical inhibitors such as TEMPO and 1,4-dinitrobenzene were added to the standard reaction conditions, product **2a** was isolated in low yield, while a BHT additive strongly inhibited the aminooxygenation (see the Supporting Information). Since the chiral ligand can induce enantioselectivity (36% ee) in the product (eq 5), we believe that the C−N bond formation step is an aminopalladation process and not a radical process, but a radical process cannot be definitely excluded for the steps of the generation of peroxide and the steps after the C−N bond formation.

In light of these results, we propose a reaction pathway in which aminopalladation of **1a** is followed by oxidation of a Pd^{II} intermediate **A** to Pd^{IV} intermediate **B** via the in situ generation of H_2O_2 or AcOOH from O_2. This high-valent palladium intermediate **B** then undergoes reductive elimination to generate product **2a** (Scheme 3).

Scheme 3. Possible Pd^{II}/Pd^{IV} Mechanism with O_2 as Oxidant



In summary, we have developed a palladium-catalyzed intramolecular benzoheterocyclic ring forming aminooxygenation of alkenes using environmentally benign O_2 (1 atm) as the sole oxidant. The reaction is proposed to proceed through a challenging C−O bond-forming reductive elimination from a high-valent Pd^{IV} intermediate. On the basis of mechanistic studies, we assume that the Pd^{IV} intermediate is generated from the oxidation of Pd^{II} via the in situ generation of H_2O_2 and/or organic peroxyacid from O_2.

DOI: 10.1021/acs.orglett.5b02703
Org. Lett. 2015, 17, 5566−5569

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02703.

Experimental procedures, characterization details, and additional data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: gqyang@sjtu.edu.cn.
*E-mail: wanbin@sjtu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partly supported by the National Nature Science Foundation of China (Nos. 21302124, 21232004, 21172144), China Postdoctoral Science Foundation (No. 2012M520882), Shanghai Chenguang Project (14CG11), Nippon Chemical Industrial Co. Ltd., and Shanghai Jiao Tong University (SJTU). We thank Prof. Tsuneo Imamoto and Dr. Masashi Sugiya of Nippon Chemical Industrial Co., Ltd., for helpful discussions and the Instrumental Analysis Center of SJTU.

■ REFERENCES

(1) For recent reviews, see: (a) de Figueiredo, R. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 1190. (b) Cardona, F.; Goti, A. *Nat. Chem.* **2009**, *1*, 269. (c) Stanley, L. M.; Sibi, M. P. *Chem. Rev.* **2008**, *108*, 2887. (d) Wolfe, J. P. *Synlett* **2008**, *2008*, 2913. (e) Li, G.; Kotti, S. R. S. S.; Timmons, C. *Eur. J. Org. Chem.* **2007**, *2007*, 2745. (f) Minatti, A.; Muñiz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142. (g) Chemler, S. R.; Fuller, P. H. *Chem. Soc. Rev.* **2007**, *36*, 1153. (h) Takacs, J. M.; Jiang, X.-T. *Curr. Org. Chem.* **2003**, *7*, 369.

(2) (a) Tsuji, J. *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*; Wiley: Hoboken, 2004. (b) Bäckvall, J. E. *Modern Oxidation Methods*; Wiley-VCH: Weinheim, 2004.

(3) (a) Hosokawa, T. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-I., Ed.; John Wiley & Sons: New York, 2002; Vol. 2, pp 2211−2225. (b) Tamaru, Y.; Kimura, M. *Synlett* **1997**, *1997*, 749. (c) Chen, P.; Liu, G.; Engle, K. M.; Yu, J.-Q. In *Science of Synthesis: Organometallic Complexes of Palladium*; Stoltz, B. M., Ed.; Thieme: Stuttgart, 2013; Vol. *1*, p 63. (d) McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981. (e) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (f) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400. (g) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368. (h) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800.

(4) (a) Lei, A.; Lu, X.; Liu, G. *Tetrahedron Lett.* **2004**, *45*, 1785. (b) Manzoni, M. R.; Zabawa, T. P.; Kasi, D.; Chemler, S. R. *Organometallics* **2004**, *23*, 5618. (c) Harayama, H.; Abe, A.; Sakado, T.; Kimura, M.; Fugami, K.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1997**, *62*, 2113. (d) Hegedus, L. S.; Allen, G. F.; Olsen, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 3583.

(5) (a) Brice, J. L.; Harang, J. E.; Timokhin, V. I.; Anastasi, N. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2005**, *127*, 2868. (b) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415.

(6) For reviews, see: (a) Martínez, C.; Wu, Y.; Weinstein, A. B.; Stahl, S. S.; Liu, G.; Muñiz, K. *J. Org. Chem.* **2013**, *78*, 6309. (b) Jensen, K. H.; Sigman, M. S. *Org. Biomol. Chem.* **2008**, *6*, 4083. (c) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924. (d) Kotov, V.; Scarborough, C. C.; Stahl, S. S. *Inorg. Chem.* **2007**, *46*, 1910.

(7) For selected examples on palladium-catalyzed C−X (X = O, C, N, Cl, F) bond formation of alkenes, see: (a) Alexanian, E. J.; Lee, C.; Sorensen, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 7690. (b) Liu, G.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 7179. (c) Desai, L.; Sanford, M. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5737. (d) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300. (e) Hovelmann, C. H.; Streuff, J.; Brelot, L.; Muñiz, K. *Chem. Commun.* **2008**, 2334. (f) Li, Y.; Song, D.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 2962. (g) Chen, S.; Wu, T.; Liu, G.; Zhen, X. *Synlett* **2011**, *7*, 891. (h) Rao, W.-H.; Yin, X.-S.; Shi, B.-F. *Org. Lett.* **2015**, *17*, 3758. (i) Tang, S.; Peng, P.; Wang, Z.-Q.; Tang, B.-X.; Deng, C.-L.; Li, J.-H.; Zhong, P.; Wang, N.-X. *Org. Lett.* **2008**, *10*, 1875. (j) Welbes, L. L.; Lyons, T. W.; Cychosz, K. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 5836. (k) Tong, X.; Beller, M.; Tse, M. K. *J. Am. Chem. Soc.* **2007**, *129*, 4906. (l) Muñiz, K.; Hövelmann, C. H.; Streuff, J. *J. Am. Chem. Soc.* **2008**, *130*, 763. (m) Muñiz, K. *J. Am. Chem. Soc.* **2007**, *129*, 14542. (n) Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2005**, *127*, 14586. (o) Wu, T.; Yin, G.; Liu, G. *J. Am. Chem. Soc.* **2009**, *131*, 16354.

(8) (a) Yin, G.; Wu, T.; Liu, G. *Chem. - Eur. J.* **2012**, *18*, 451. (b) Yin, G.; Liu, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5442. (c) Zhu, H.; Chen, P.; Liu, G. *Org. Lett.* **2015**, *17*, 1485. (d) Zhu, H.; Chen, P.; Liu, G. *J. Am. Chem. Soc.* **2014**, *136*, 1766.

(9) (a) Liskin, D. V.; Sibbald, P. A.; Rosewall, C. F.; Michael, F. E. *J. Org. Chem.* **2010**, *75*, 6294. (b) Rosewall, C. F.; Sibbald, P. A.; Liskin, D. V.; Michael, F. E. *J. Am. Chem. Soc.* **2009**, *131*, 9488. (c) Wang, G.-W.; Yuan, T.-T.; Wu, X.-L. *J. Org. Chem.* **2008**, *73*, 4717. (d) Desai, L. V.; Malik, H. A.; Sanford, M. S. *Org. Lett.* **2006**, *8*, 1141. (e) Muñiz, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 9412. (f) Kalyani, D.; Sanford, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 2150. (g) Whitfield, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 15142. (h) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712. (i) Michael, F. E.; Sibbald, P. A.; Cochran, B. M. *Org. Lett.* **2008**, *10*, 793. (j) Hickman, A. J.; Sanford, M. S. *Nature* **2012**, *484*, 177. (k) Powers, D. C.; Ritter, T. *Acc. Chem. Res.* **2012**, *45*, 840. (l) Vedernikov, A. N. *Acc. Chem. Res.* **2012**, *45*, 803. (m) Powers, D. C.; Ritter, T. *Top. Organomet. Chem.* **2011**, *503*, 129. (n) Engle, K. M.; Mei, T.-S.; Wang, X.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2011**, *50*, 1478. (o) Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824.

(10) For selected reviews, see: (a) Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**, *45*, 851. (b) Piera, J.; Backvall, J.-E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3506. (c) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977.

(11) For examples on palladium-catalyzed reactions with oxygen, see: (a) Zhang, Y.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 14654. (b) Vedernikov, A. N. *Chem. Commun.* **2009**, 4781. (c) Liu, G.; Yin, G.; Wu, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4733. (d) Wang, A.; Jiang, H. *J. Am. Chem. Soc.* **2008**, *130*, 5030. (e) Zhang, J.; Khaskin, E.; Anderson, N. P.; Zavalij, P. Y.; Vedernikov, A. N. *Chem. Commun.* **2008**, 3625. (f) Gligorich, K. M.; Sigman, M. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 6612. (g) Trend, R. M.; Ramtohul, Y. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 17778.

(12) (a) Wickens, Z. K.; Guzmán, P. E.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2015**, *54*, 236. (b) Zhu, M.-K.; Zhao, J.-F.; Loh, T.-P. *J. Am. Chem. Soc.* **2010**, *132*, 6284. (c) Wang, A.; Jiang, H.; Chen, H. *J. Am. Chem. Soc.* **2009**, *131*, 3846.

(13) Chemler, S. R.; Copeland, D. A. *Sythesis of Saturated Heterocyles via Metal-Catalyzed Alkene Diamination, Aminoalkoxylation, or Dialkoxylation Reactions*; Wolfe, J. P., Ed.; Springer: Berlin, 2013; Vol. *32*, pp 39−75.

(14) (a) Jiang, F.; Wu, Z.; Zhang, W. *Tetrahedron Lett.* **2010**, *51*, 5124. (b) Yang, G.; Shen, C.; Zhang, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 9141. (c) Butt, N. A.; Zhang, W. *Sythesis of Heterocyles via Palladium-Catalyzed Wacker-Type Oxidative Cyclization Reactions of Hydroxy- and Amino-Alkenes*; Wolfe, J. P., Ed.; Springer: Berlin, 2013; Vol. *32*, pp 77−107.

(15) Yang, G.; Zhang, W. *Org. Lett.* **2012**, *14*, 268.

(16) Giri, R.; Liang, J.; Lei, J.-G.; Li, J.-J.; Wang, D.-H.; Chen, X.; Naggar, I. C.; Guo, C.; Foxman, B. M.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2005**, *44*, 7420.

DOI: 10.1021/acs.orglett.5b02703
Org. Lett. 2015, 17, 5566−5569