Organic LETTERS

Letter

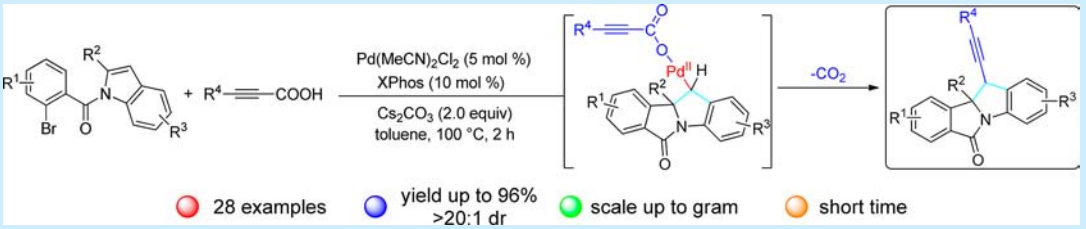
pubs.acs.org/OrgLett

Palladium-Catalyzed Intramolecular Dearomatization of Indoles via Decarboxylative Alkynyl Termination

Si Chen, Xin-Xing Wu, Jia Wang, Xin-Hua Hao, Yu Xia, Yi Shen, Huanwang Jing,* and Yong-Min Liang*

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China

Supporting Information



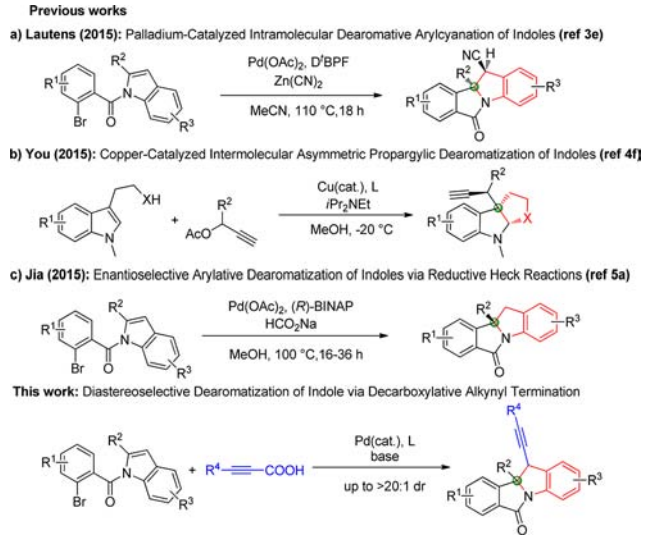
ABSTRACT: A highly diastereoselective dearomatization of indoles via palladium-catalyzed decarboxylative alkynyl termination was developed. This protocol provides dissimilar tetracyclic and tetrasubstituted indoline scaffolds bearing congested stereocenters, which led to operationally simple conditions, short time, and broad substrate scope. Additionally, this reaction system could be scaled to gram quantities in a satisfactory yield and diastereoselectivity.

Diastereoselective dearomative cyclizations have emerged as a chemical transformation of rudimentary value in synthetic organic chemistry. The heterocyclic scaffolds prepared in this manner comprise key moieties of complex biological targets and pharmaceuticals.[1] Specifically, dearomative indoles represent important structural units among them. For example, the natural product brevianamide E is used to treat myasthenia gravis, glaucoma, and orthostatic hypotension. Hinckdentine A and (+)-aspidospermidine are considered as the construction of substituted C-centers at the C2 and C3 positions of the indole core (Figure 1),[2] yet ordinary catalyst systems that easily build complex cores with this desirable pattern remain scarce in the scientific research field.

Pioneering works by the groups of Lautens,[3] You,[4] Jia,[5] and others[6] have demonstrated novel strategies toward this challenge. In 2015, Lautens et al. described the palladium-catalyzed intramolecular dearomative arylcyanation of indoles (Scheme 1, 1a).[3e] Soon after, You and co-workers developed an unprecedented, copper-catalyzed intermolecular dearomatization of *N*-substituted tryptophol and tryptamine derivatives to provide furoindolines and pyrroloindolines (Scheme 1, 1b).[4f] Recently, Jia's group used a convenient $Pd(OAc)_2$/(*R*)-BINAP catalyst system to realize the novel asymmetric dearomatization of indole, which proceeded via an intramolecular reductive Heck reaction (Scheme 1, 1c).[5a,7] As a result of these contributions, the transition-metal catalyzed dearomatization of (hetero)arenes has become a conspicuous strategy in the area of synthesis.

Figure 1. Complex indoline-based natural products bearing C-stereocenters at C2 and C3.

Scheme 1. Methods toward Diverse Indoline Scaffolds via Pd-Catalyzed Indole Dearomatizations

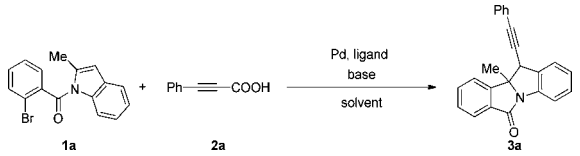


Equally important are decarboxylative couplings, which have become efficient instruments for constructing carbon−carbon and carbon−heteroatom bonds with high selectivity.[8] In 2006, Myers[9] and Goossen[10] reported a redox-neutral decarboxylative

Received: June 23, 2016
Published: August 10, 2016

DOI: 10.1021/acs.orglett.6b01711
Org. Lett. 2016, 18, 4016−4019

Table 1. Optimization of Reaction Conditions[a]



entry	[Pd]	ligand	yield[b] (%)	dr[c]
1	$Pd(OAc)_2$	PPh_3	66	15:1
2	$Pd(OAc)_2$	SPhos	70	19:1
3	$Pd(OAc)_2$	Xantphos	21	13:1
4	$Pd(OAc)_2$	$P(2\text{-furyl})_3$	48	16:1
5	$Pd(OAc)_2$	dppf	0	
6	$Pd(OAc)_2$	XPhos	81	>20:1
7	$Pd(MeCN)_2Cl_2$	XPhos	84	>20:1
8	$PdCl_2$	XPhos	7	13:1
9	$Pd(PPh_3)_2Cl_2$	XPhos	63	18:1
10	$Pd(PPh_3)_4$	and	65	17:1
11	$Pd(TFA)_2$	XPhos	81	19:1
12[d]	$Pd(MeCN)_2Cl_2$	XPhos	0	
13[e]	$Pd(MeCN)_2Cl_2$	XPhos	78	>20:1
14[f]	$Pd(MeCN)_2Cl_2$	XPhos	83	>20:1
15[g]	$Pd(MeCN)_2Cl_2$	XPhos	46	>20:1
16[h]	**$Pd(MeCN)_2Cl_2$**	**XPhos**	**87**	**>20:1**
17[i]	$Pd(MeCN)_2Cl_2$	XPhos	79	>20:1

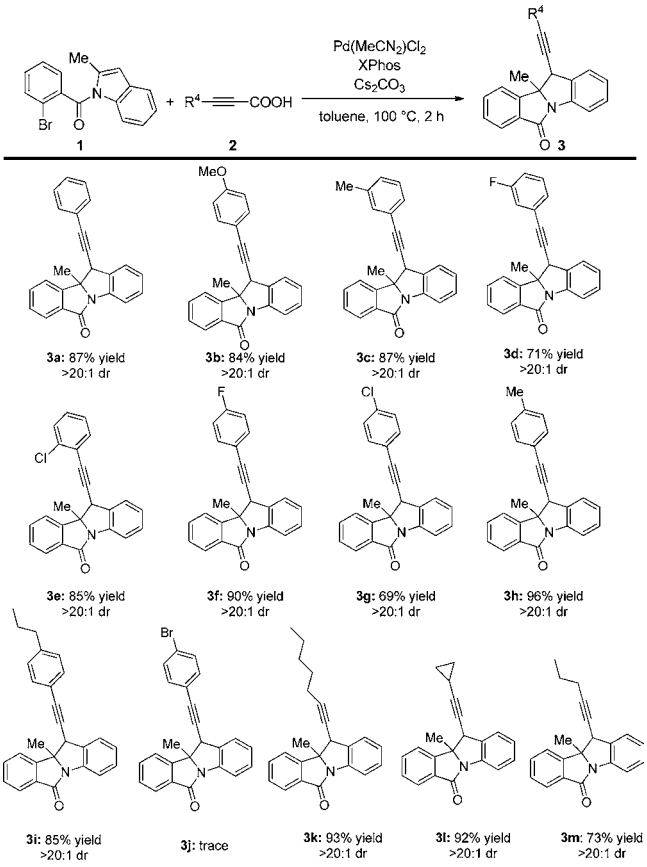
[a]Reactions were carried out using **1a** (0.2 mmol), **2a** (0.3 mmol), [Pd] (10 mol %), ligand (20 mol %), Cs_2CO_3 (2.0 equiv), solvent (2.0 mL), 100 °C, 2 h. [b]Isolated yields. [c]Determined by ^1H NMR analysis of the crude reaction mixture. [d]Absence of palladium catalyst, ligand, or base failed to afford the desired product **3a**. [e]At 80 °C. [f]ArI instead of ArBr. [g]ArCl instead of ArBr. [h]$Pd(MeCN)_2Cl_2$ (5.0 mol %), XPhos (10 mol %). [i]$Pd(MeCN)_2Cl_2$ (2.5 mol %), XPhos (5 mol %).

biaryl synthesis via aromatic carboxylic acids with a Pd/Cu bimetallic catalyst system.[11] Since then, Pd-, Cu-, and Rh-catalyzed decarboxylative reactions were all discovered.[12] Recently, Gu,[13] Chen, and Wu[14] et al. reported powerful reagents in coupling reactions via protected alkynes by release of some micromolecules. Meanwhile, the different substrates react smoothly and have broad scope. The concepts of decarboxylative couplings possess apparent advantages over conventional cross-coupling reaction with cheap and broadly available carboxylates, displacing expensive and toxic organometallic reagents.

By taking into consideration our current interest in the synthesis of dearomative indole compounds,[15] as well as the continued anticipation of novel approaches to indoline scaffolds, we designed the diastereoselective dearomative indole synthesis through the decarboxylative alkynyl termination by using available alkynyl carboxylic acids and unsubstituted indoles. To the best of our knowledge, it is the first example of combining decarboxylative reactions of alkynoic acids with dearomative indole synthesis.

The initial exploration for our anticipation was begun by employing compound **1a** as the model substrate with the 3-phenylpropiolic acid **2a**. As shown in Table 1, **1a** was treated with $Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %), and Cs_2CO_3 (2.0 equiv) in toluene (2.0 mL) at 100 °C for 2 h, affording the anticipated product **3a** in 66% yield with 15:1 dr (Table 1, entry 1). Subsequently, various phosphine ligands were screened. Other ligands such as Xantphos, $P(2\text{-furyl})_3$, and dppf were found to be ineffective or less efficient except SPhos (entries 2−5). The reaction with XPhos provided the higher

Scheme 2. Substrate Scope with Alkynyl Carboxylic Acids[a,b]



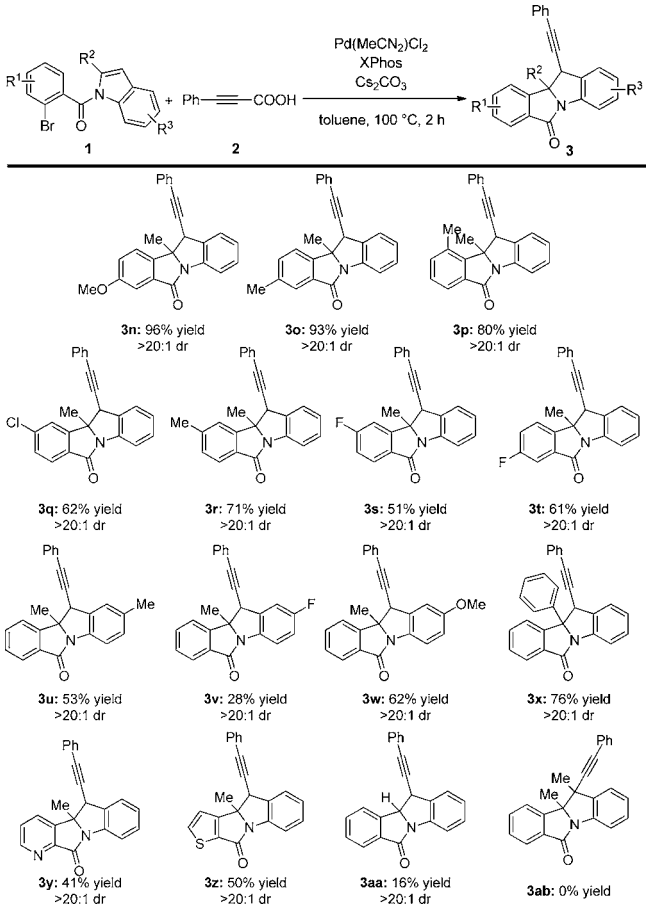
[a]Reaction conditions unless otherwise noted: **1** (0.2 mmol), **2** (0.3 mmol), $Pd(MeCN)_2Cl_2$ (5 mol %), XPhos (10 mol %), Cs_2CO_3 (2.0 equiv), toluene (2.0 mL), 100 °C, 2 h. Isolated yields are shown. [b]The dr values were determined by ^1H NMR analysis of the crude reaction mixture.

isolated yield of **3a** (81% yield with >20:1 dr, entry 6). A subsequent brief survey on various representative solvents showed toluene still performed most efficiently. No better results were obtained after further study on the effect of base (see the Supporting Information). Next, we examined palladium catalysts and found that $Pd(MeCN)_2Cl_2$ provided a higher isolated yield of **3a** (84% with >20:1 dr, entry 7). Other catalysts, such as $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, and $Pd(TFA)_2$, provided lower yields and dr (entries 8−11). An additional control experiment indicated palladium, ligand, and base were all necessary (entry 12). Ultimately, subsequent adjustment of the reaction temperature, catalyst/ligand ratio of loadings, and use of the iodo-substituted or chlorine-substituted reactant became the optimal conditions for the formation of product **3a** (entries 13−17).

The conditions optimized for **1a** were tested on a series of indole substrates possessing sterically and electronically diverse alkynyl carboxylic acids (Scheme 2). Electronic effects were investigated by changing the substituent of the 3-phenylpropiolic acids. With electron-donating groups at the *para*-positions and *meta*-positions, good to excellent yields and dr could be achieved (products **3b**, **3c**, **3h**, and **3i**). Electron-withdrawing groups on the 3-phenylpropiolic acids gave slightly lower yields than electron-donating substituents (products **3d**, **3e**, **3f**, **3g**). Unfortunately, substrate **3j** failed to give the corresponding product due to the presence of the bromide in

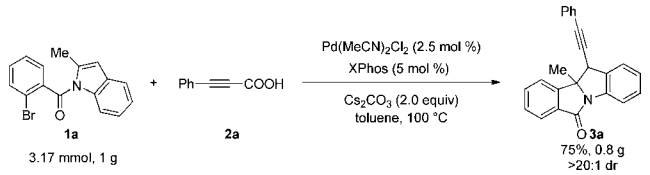
DOI: 10.1021/acs.orglett.6b01711
Org. Lett. 2016, 18, 4016−4019

Scheme 3. Substrate Scope with *o*-Bromobenzoyl Groups and Indoles[a,b]



[a]Reaction conditions unless otherwise noted: **1** (0.2 mmol), **2** (0.3 mmol), $Pd(MeCN)_2Cl_2$ (5 mol %), XPhos (10 mol %), Cs_2CO_3 (2.0 equiv), toluene (2.0 mL), 100 °C, 2 h. Isolated yields are shown. [b]The dr values were determined by ^1H NMR analysis of the crude reaction mixture.

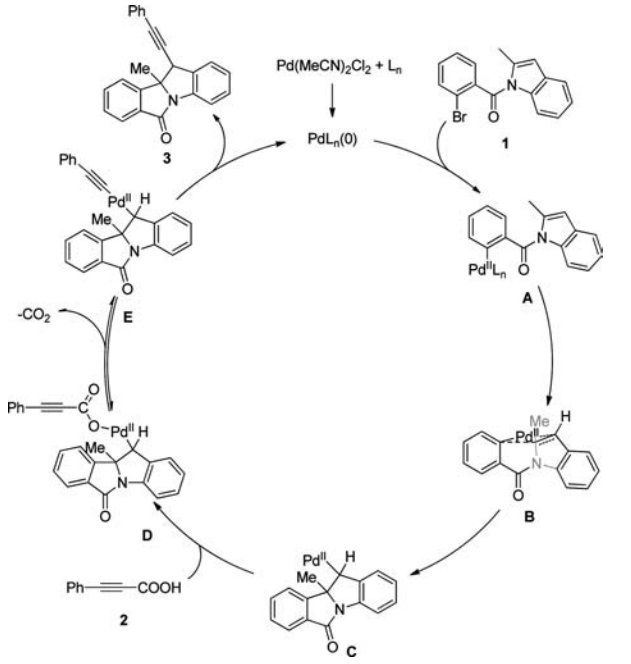
Scheme 4. Scale-up Experiments



the 3-phenylpropiolic acid. It was noteworthy that substrates with aliphatic alkynes were also striking, showing significant advantages over the previous method. For example, oct-2-ynoic acid, hex-2-ynoic acid, and 3-cyclopropylpropiolic acid proceeded smoothly to give the corresponding products in 73%−93% yields (products **3k**−**m**). In addition, the structure of **3a** was confirmed by X-ray crystal structure analysis (see the Supporting Information).

To ascertain the scope of this method further, a variety of *o*-bromobenzoyl groups were investigated (Scheme 3). Sterically hindered aryl bromide **1p** was found to function exceptionally well in this reaction, and **3p** was obtained in 80% yield with >20:1 dr. Gratifyingly, electron-rich aryl bromides could be converted to the corresponding products in good to excellent yields (products **3n**, **3o**, **3p**, and **3r**), which were much better

Scheme 5. Proposed Reaction Mechanisms



than electron-deficient substrates in yield (products **3q**, **3s**, and **3t**). Subsequently, to test the electronic effects of the indole components of **1** (Scheme 3), substrates **1u**, **1v**, and **1w** were synthesized and subjected to the standard conditions. Both electron-poor (**1v**) and electron-rich (**1u** and **1w**) indoles led to the desired products (**3u**−**w**), albeit in lower yield than the parent substrates. The 2-arylindole (**1x**) was well tolerated under the reaction conditions, and the corresponding product (**3x**) could be obtained in good yield. In an effort to incorporate heteroaromatic groups into the product framework, pyridine- or thiophene-containing substrates (**1y** and **1z**) were tested. They were found to provide the desired products in 41% and 50% yields, respectively.

Finally, some limitations of the reaction were noted. When unsubstituted indole **1aa** was subjected to the reaction conditions, only 16% of the desired indoline product **3aa** could be afforded. Substrate **1ab** possessing a 2,3-dimethylindole motif was also tested. Unfortunately, this reaction failed to produce the desired indoline **3ab**, while only the palladium-catalyzed cross-coupling at the C−Br site product was observed.

A prominent advantage of the method is that the reaction could be scaled up to gram quantities; a 75% yield of product **3a** was isolated on the gram scale using $Pd(MeCN)_2Cl_2$ (2.5 mol %) and XPhos (5 mol %), which might provide a potential application for this protocol in industry (Scheme 4).

On the basis of the above observations, a plausible mechanism that is consistent with the experimental results and previous literature is proposed in Scheme 4.[16] The in situ formed Pd(0) undergoes oxidative addition with the C−Br bond in **1**, affording intermediate **A**, which then undergoes intramolecular coordination of the olefin of the indole subunit to the palladium center and transmetalation to provide dearomatized secondary Pd^{II} intermediate **C** through transition state **B**. Next, anion exchange of **C** with the 3-phenylpropiolic acid forms alkoxypalladium **D**, which generates alkynylpalladium **E** in situ by releasing a molecule of carbon dioxide.

DOI: 10.1021/acs.orglett.6b01711
Org. Lett. 2016, 18, 4016−4019

Finally, the reaction delivered the product **3** via reductive elimination (Scheme 5).

In summary, we have developed a distinct palladium-catalyzed intramolecular Heck decarboxylative alkynylation via dearomatization of indoles, thus affording the dearomative alkynyl products in moderate to excellent yields under mild conditions. In addition, a series of indolines bearing C2 and C3 stereogenic centers were provided with high diastereoselectivity. Moreover, the new method has been demonstrated by the applicability to a wide range of indole substrates and a large reaction scale for potential applications in further industrial production.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01711.

X-ray data for **3a** (CIF)

Experimental procedures, product characterizations, crystallographic data, and ^{1}H and ^{13}C spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: hwjing@lzu.edu.cn.

*E-mail: liangym@lzu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support was received from the National Science Foundation (NSF21272101, NSF21472073, NSF21472074, NSFC21173106, and NSF21302076) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1138 and IRT15R28).

■ REFERENCES

(1) (a) Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917. (b) Lopez Ortiz, F.; Iglesias, M. J.; Fernández, I.; Andujar Sanchez, C. M.; Ruiz Gómez, G. *Chem. Rev.* **2007**, *107*, 1580. (c) García-Fortanet, J.; Kessler, F.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 6676. (d) Rousseaux, S.; García-Fortanet, J.; Del Aguila Sanchez, M. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2011**, *133*, 9282. (e) Tang, S. Y.; Guo, Q. X.; Fu, Y. *Chem. - Eur. J.* **2011**, *17*, 13866. (f) Kieffer, M. E.; Chuang, K. V.; Reisman, S. E. *Chem. Sci.* **2012**, *3*, 3170. (g) Zhuo, C. X.; Zhang, W.; You, S. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 12662. (h) Zhuo, C.-X.; Zheng, C.; You, S.-L. *Acc. Chem. Res.* **2014**, *47*, 2558.

(2) (a) Christoffers, J.; Mann, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4591. (b) Christoffers, J.; Baro, A. *Adv. Synth. Catal.* **2005**, *347*, 1473. (c) Liu, J.-F.; Jiang, Z.-Y.; Wang, R.-R.; Zheng, Y.-T.; Chen, J.-J.; Zhang, X.-M.; Ma, Y.-B. *Org. Lett.* **2007**, *9*, 4127. (d) Tan, C.-J.; Di, Y.-T.; Wang, Y.-H.; Zhang, Y.; Si, Y.-K.; Zhang, Q.; Gao, S.; Hu, X.-J.; Fang, X.; Li, S.-F. *Org. Lett.* **2010**, *12*, 2370. (e) Roche, S. P.; Porco, J. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 4068. (f) Ruiz-Sanchis, P.; Savina, S. A.; Albericio, F.; Álvarez, M. *Chem. - Eur. J.* **2011**, *17*, 1388. (g) Quasdorf, K. W.; Overman, L. E. *Nature* **2014**, *516*, 181.

(3) (a) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2011**, *133*, 1778. (b) Jia, X.; Petrone, D. A.; Lautens, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 9870. (c) Petrone, D. A.; Lischka, M.; Lautens, M. *Angew. Chem.* **2013**, *125*, 10829. (d) Yoon, H.; Petrone, D. A.; Lautens, M. *Org. Lett.* **2014**, *16*, 6420. (e) Le, C. M.; Hou, X.; Sperger, T.; Schoenebeck, F.; Lautens, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 15897. (f) Petrone, D. A.; Yen, A.; Zeidan, N.; Lautens, M. *Org. Lett.* **2015**, *17*, 4838.

(4) (a) Liu, C.; Zhang, W.; Dai, L.-X.; You, S.-L. *Org. Lett.* **2012**, *14*, 4525. (b) Wu, K.-J.; Dai, L.-X.; You, S.-L. *Org. Lett.* **2012**, *14*, 3772. (c) Wu, K.-J.; Dai, L.-X.; You, S.-L. *Chem. Commun.* **2013**, *49*, 8620. (d) Xu, R.-Q.; Gu, Q.; Wu, W.-T.; Zhao, Z.-A.; You, S.-L. *J. Am. Chem. Soc.* **2014**, *136*, 15469. (e) Shao, W.; Li, H.; Liu, C.; Liu, C. J.; You, S. L. *Angew. Chem., Int. Ed.* **2015**, *54*, 7684. (f) Zhang, X.; Liu, W.-B.; Tu, H.-F.; You, S.-L. *Chem. Sci.* **2015**, *6*, 4525. (g) Wu, W.-T.; Zhang, L.; You, S.-L. *Chem. Soc. Rev.* **2016**, *45*, 1570.

(5) (a) Shen, C.; Liu, R.-R.; Fan, R.-J.; Li, Y.-L.; Xu, T.-F.; Gao, J.-R.; Jia, Y.-X. *J. Am. Chem. Soc.* **2015**, *137*, 4936. (b) Liu, R.-R.; Li, B.-L.; Lu, J.; Shen, C.; Gao, J.-R.; Jia, Y.-X. *J. Am. Chem. Soc.* **2016**, *138*, 5198.

(6) (a) Beck, E. M.; Grimster, N. P.; Hatley, R.; Gaunt, M. *J. Am. Chem. Soc.* **2006**, *128*, 2528. (b) Trost, B. M.; Zhang, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4590. (c) García-Fortanet, J.; Kessler, F.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 6676. (d) Nakanishi, M.; Katayev, D.; Besnard, C.; Kündig, E. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 7438. (e) Kieffer, M. E.; Chuang, K. V.; Reisman, S. E. *Chem. Sci.* **2012**, *3*, 3170. (f) Zhu, S.; MacMillan, D. W. *J. Am. Chem. Soc.* **2012**, *134*, 10815. (g) Du, K.; Guo, P.; Chen, Y.; Cao, Z.; Wang, Z.; Tang, W. *Angew. Chem., Int. Ed.* **2015**, *54*, 3033.

(7) (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (b) Minatti, A.; Zheng, X.; Buchwald, S. L. *J. Org. Chem.* **2007**, *72*, 9253. (c) Wang, D.-S.; Chen, Q.-A.; Li, W.; Yu, C.-B.; Zhou, Y.-G.; Zhang, X. *J. Am. Chem. Soc.* **2010**, *132*, 8909. (d) Wang, D.-S.; Chen, Q.-A.; Lu, S.-M.; Zhou, Y.-G. *Chem. Rev.* **2012**, *112*, 2557.

(8) (a) Moon, J.; Jang, M.; Lee, S. *J. Org. Chem.* **2009**, *74*, 1403. (b) Moon, J.; Jeong, M.; Nam, H.; Ju, J.; Moon, J. H.; Jung, H. M.; Lee, S. *Org. Lett.* **2008**, *10*, 945. (c) Xie, K.; Yang, Z.; Zhou, X.; Li, X.; Wang, S.; Tan, Z.; An, X.; Guo, C.-C. *Org. Lett.* **2010**, *12*, 1564. (d) Zhao, D.; Gao, C.; Su, X.; He, Y.; You, J.; Xue, Y. *Chem. Commun.* **2010**, *46*, 9049. (e) Hu, P.; Zhang, M.; Jie, X.; Su, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 227. (f) Fromm, A.; van Wüllen, C.; Hackenberger, D.; Gooßen, L. J. *J. Am. Chem. Soc.* **2014**, *136*, 10007.

(9) (a) Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**, *6*, 433. (b) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323.

(10) (a) Goossen, L. J.; Rodríguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824. (b) Gooßen, L. J.; Rudolphi, F.; Oppel, C.; Rodriguez, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 3043. (c) Gooßen, L. J.; Zimmermann, B.; Knauber, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7103. (d) Gooßen, L. J.; Rodríguez, N.; Lange, P. P.; Linder, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 1111. (e) Song, B.; Knauber, T.; Gooßen, L. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 2954.

(11) Gooßen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662.

(12) (a) Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H. Z.; Liu, L. *Angew. Chem.* **2009**, *121*, 9514. (b) Sun, Z. M.; Zhao, P. *Angew. Chem.* **2009**, *121*, 6854. (c) Weaver, J. D.; Recio, A., III; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846.

(13) (a) Ma, S.; Gu, Z. *J. Am. Chem. Soc.* **2005**, *127*, 6182. (b) Chen, G.; Zeng, R.; Gu, Z.; Fu, C.; Ma, S. *Org. Lett.* **2008**, *10*, 4235. (c) Sun, F.; Gu, Z. *Org. Lett.* **2015**, *17*, 2222. (d) Sun, F.; Li, M.; Gu, Z. *Org. Chem. Front.* **2016**, *3*, 309.

(14) Pan, S.; Ma, X.; Zhong, D.; Chen, W.; Liu, M.; Wu, H. *Adv. Synth. Catal.* **2015**, *357*, 3052.

(15) (a) Ali, S.; Li, Y.-X.; Anwar, S.; Yang, F.; Chen, Z.-S.; Liang, Y.-M. *J. Org. Chem.* **2012**, *77*, 424. (b) Li, Y.-X.; Wang, H.-X.; Ali, S.; Xia, X.-F.; Liang, Y.-M. *Chem. Commun.* **2012**, *48*, 2343. (c) Wang, J.; Zhu, H.-T.; Qiu, Y.-F.; Niu, Y.; Chen, S.; Li, Y.-X.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2015**, *17*, 3186. (d) Wu, X.-X.; Shen, Y.; Chen, W.-L.; Chen, S.; Xu, P.-F.; Liang, Y.-M. *Chem. Commun.* **2015**, *51*, 16798. (e) Wu, X.-X.; Chen, W.-L.; Shen, Y.; Chen, S.; Xu, P.-F.; Liang, Y.-M. *Org. Lett.* **2016**, *18*, 1784.

(16) (a) Zhao, L.; Li, Z.; Chang, L.; Xu, J.; Yao, H.; Wu, X. *Org. Lett.* **2012**, *14*, 2066. (b) Vachhani, D. D.; Butani, H. H.; Sharma, N.; Bhoya, U. C.; Shah, A. K.; Van der Eycken, E. V. *Chem. Commun.* **2015**, *51*, 14862. (c) Sharma, U. K.; Sharma, N.; Kumar, Y.; Singh, B. K.; Van der Eycken, E. V. *Chem. - Eur. J.* **2016**, *22*, 481.

DOI: 10.1021/acs.orglett.6b01711
Org. Lett. 2016, 18, 4016−4019