Organic LETTERS

Letter

pubs.acs.org/OrgLett

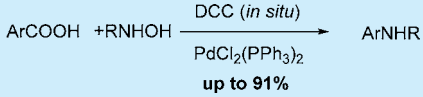
Palladium-Catalyzed Decarboxylative Synthesis of Arylamines

Qipu Dai,*[,†] Peihe Li,[†] Nuannuan Ma, and Changwen Hu*

Key Laboratory of Cluster Science of Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic, School of Chemistry, Beijing Institute of Technology, Beijing 100081, People's Republic of China

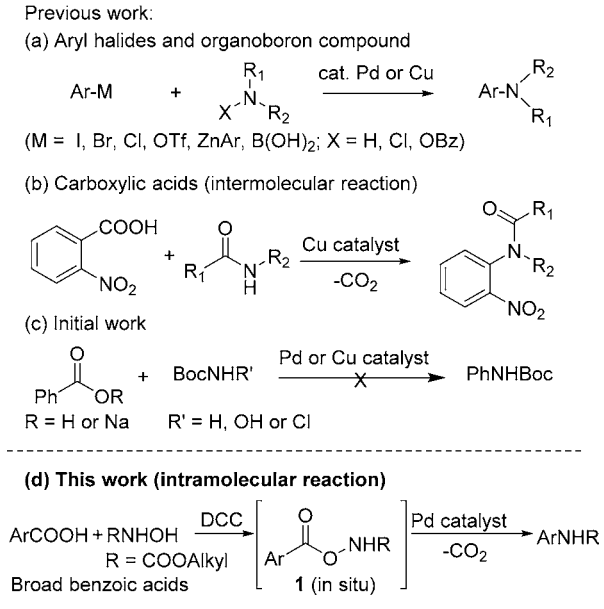
Supporting Information

ABSTRACT: A novel approach has been developed for the synthesis of arylamines via the palladium-catalyzed intramolecular decarboxylative coupling (IDC) of aroyloxycarbamates, obtained in situ by reacting aryl carboxylic acids with hydroxycarbamates. The reaction offers facile access to structurally diverse arylamines with the site-specific formation of the C(sp^2)-N bond under mild conditions.



Arylamine is an important structural motif that can be found in many natural products, synthetic pharmaceuticals, agrochemicals, and important synthetic building blocks.[1] Due to arylamine usefulness, many elegant methods based on the formation of the C(sp^2)-N bonds via the intermolecular cross-coupling reactions, have been reported for the synthesis of arylamines, such as the Buchwald-Hartwig cross-coupling,[2] the Ullmann reaction of arylamine,[3] the Chan-Lam coupling,[4] and the direct C−H amination of arenes.[5] Aryl halides,[2,3] arylboronic acids,[4,6] and arenes[7] have been used as the coupling partners in these reactions (Scheme 1a). Despite this progress, the development of a new method that relies on inexpensive and readily available starting materials is still warranted. Arylcarboxylic acids are cheap and readily available raw materials. The decarboxylative cross-coupling reactions of aryl carboxylic acids has attracted a lot interest in the past decade.[8] The reaction involves the cleavage of the C(sp^2)-COOH bond, which allows the site-specific introduction of a functional group into the substrate molecule.[9] Various C−C bond-forming transformations have been developed based on this strategy, using aryl carboxylate salts as the source of the carbon nucleophiles.[10] In contrast, there are only a few reports in which this protocol is used for the formation of a carbon−nitrogen bond.[7,11] Mainolfi and co-workers[7a] reported the first example of C(sp^2)-N bond formation reaction employing aryl carboxylic acids as the stable, inexpensive, and widely available arylating reagents. More recently, Jia and co-workers[7b] also established a Cu(II)-catalyzed intermolecular decarboxylative reaction of aryl carboxylic acids for the synthesis of tertiary amides (Scheme 1b). While these two reactions are very valuable synthetic tools, we believe more work can still be done along these lines to further increase the utility of these decarboxylative coupling reactions. Herein, we report a novel intramolecular decarboxylative coupling (IDC) reaction for the synthesis of arylamines by using carboxylic acids together with alkyl hydroxycarbamate derivatives.

Scheme 1. Metal-Catalyzed C(sp^2)−N Bond Formation

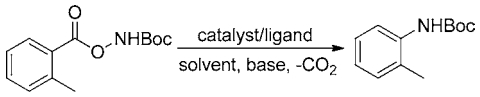


We initially attempted a metal-catalyzed intermolecular reaction between alkyl hydroxycarbamates and carboxylic acid or carboxylates; however, these reactions did not deliver the desired products (Scheme 1c). We then turned our attention to the intramolecular reaction. In pursuit of such an IDC protocol for the synthesis of arylamines, we conceived a catalytic redox design based on the Tsuji-Trost's intramolecular decarboxylative allylation reaction, which has been used successfully for the C−C bond formation.[12] Thus, we first examined the reaction of aroyloxycarbamates **1** as the *N*-arylation precursor for the synthesis of the arylamines. To our delight, the reaction catalyzed by palladium gave the desired arylcarbamates **2** in high yields and regioselectivity, with CO_2 as the only byproduct of this reaction. In addition, we found the reactive aroyloxycarbamates **1** could be obtained by reacting carboxylic acids with alkyl hydroxycarbamate in situ so that a one-pot synthesis of arylamines can be achieved in high yields (Scheme 1d and Table 2, entry 1). The detailed results are summarized in Table 1.

Received: September 18, 2016
Published: October 18, 2016

DOI: 10.1021/acs.orglett.6b02724
Org. Lett. 2016, 18, 5560−5563

Table 1. Optimization of the Reaction Conditions[a]



1a 2a

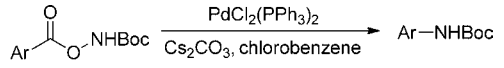
entry	catalyst	ligand	base	solvent	yield[b] (%)
1	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	MCB	68
2	$Pd(TFA)_2$	PPh_3	Cs_2CO_3	MCB	56
3	$Pd(dba)_2$	PPh_3	Cs_2CO_3	MCB	58
4	$PdCl_2$	PPh_3	Cs_2CO_3	MCB	78
5	$PdCl_2$		Cs_2CO_3	MCB	trace
6	$PdCl_2$	TTBP	Cs_2CO_3	MCB	80
7	$PdCl_2$	$P(o\text{-tol})_3$	Cs_2CO_3	MCB	76
8	$PdCl_2$	BINAP	Cs_2CO_3	MCB	45
9	$PdCl_2$	XantPhos	Cs_2CO_3	MCB	63
10	**$PdCl_2(PPh_3)_2$**		**Cs_2CO_3**	**MCB**	**88 (86)**[c]
11	$Pd(PPh_3)_4$		Cs_2CO_3	MCB	78
12	$Pd(dppf)Cl_2$		Cs_2CO_3	MCB	45
13	No		Cs_2CO_3	MCB	trace
14	$PdCl_2(PPh_3)_2$			MCB	0
15	$PdCl_2(PPh_3)_2$		K_3PO_4	MCB	41
16	$PdCl_2(PPh_3)_2$		NaO^tBu	MCB	67
17	$PdCl_2(PPh_3)_2$		KO^tBu	MCB	68
18	$PdCl_2(PPh_3)_2$		K_2CO_3	MCB	56
19	$PdCl_2(PPh_3)_2$		Et_3N	MCB	39
20	$PdCl_2(PPh_3)_2$		Cs_2CO_3	toluene	80
21	$PdCl_2(PPh_3)_2$		Cs_2CO_3	xylene	78
22	$PdCl_2(PPh_3)_2$		Cs_2CO_3	DMF	48
23	$PdCl_2(PPh_3)_2$		Cs_2CO_3	THF	65
24	$PdCl_2(PPh_3)_2$		Cs_2CO_3	*tert*-butyl alcohol	79

[a]Reaction conditions: **1a** (0.20 mmol), catalyst (5 mol %), ligand (10 mol %), base (0.40 mmol) in chlorobenzene (MCB) (1.2 mL) at 85 °C for 1 h. [b]Unless otherwise noted, the yields were determined by GC analysis using biphenyl as internal standard. [c]The yield of the isolated product is shown in parentheses.

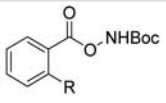
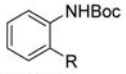
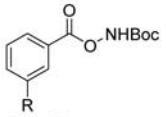
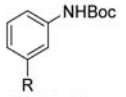
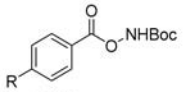
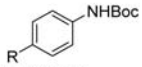
As shown in Table 1, with $Pd(OAc)_2$ (5 mol %) as the catalyst in the presence of PPh_3 (10 mol %) as ligand, the IDC reaction of *t*-butyl [(2-methylbenzoyl)oxy)]carbamate **1a** gave the corresponding *t*-butyl *o*-tolylcarbamate **2a** in 68% yield, when the reaction was conducted at 85 °C in chlorobenzene (MCB) with Cs_2CO_3 (2 equiv) as the base. (Table 1, entry 1). Other Pd sources are also capable of catalyzing the desired reaction in the presence of PPh_3 (Table 1, entries 2−4), with $PdCl_2$ gave the best results (Table 1, entry 4). However, only trace amount product was obtained if the phosphine ligand was absent (Table 1, entry 5). Next the phosphine ligands with different steric and electronic environments were screened (Table 1, entries 6−9). An electron-rich phosphine ligand TTBP was found to give a slightly higher yield of the desired coupling product (Table 1, entry 6). Further screening revealed that using $PdCl_2(PPh_3)_2$ (Table 1, entry 10) is more efficient than using $PdCl_2$ and PPh_3 separately. However, other ligand-containing Pd sources, such as $Pd(PPh_3)_4$ and $Pd(dppf)Cl_2$, are less effective (Table 1, entries 11−12). In addition, the reaction did not proceed without either the Pd catalyst or the Cs_2CO_3 base (Table 1, entries 13−14). The results of other inorganic and organic bases screened in this reaction (Table 1, entries, 14−19) indicate that Cs_2CO_3 is the base of choice for this reaction (Table 1, entry 12). Further investigations on the solvent effects showed that several common solvents such as toluene, DMF, xylene, THF, and *t*-butanol all led to the formation of the product **2a** in good yields (Table 1, entries 20−24), with MCB gave the best results in terms of yield and regioselectivity. On the other hand, increasing the amount of the catalyst and reaction time did not improve the yield (data not shown).

With the optimized reaction parameters for this newly developed IDC reaction, we then examined the scope of this reaction (Table 2). As shown in Table 2, many functional

Table 2. Substrate Scope[a]



1 2

entry	substrate	product (time)	yield (%)[b]
			
1	**1a**, 2-Me	**2a** (1 h)	86(83)
2[c]	**1b**, H	**2b** (2.5 h)	45
3	**1c**, 2-MeO	**2c** (1 h)	83
4	**1d**, 2-F	**2d** (1 h)	70
5	**1e**, 2-Cl	**2e** (1 h)	91
6	**1f**, 2-NO_2	**2f** (1 h)	87
7	**1g**, 2-(CF_3)	**2g** (1 h)	83
8	**1h**, 2-Ph	**2h** (1.5 h)	90
			
9[c]	**1i**, 3-Cl	**2i** (2.5 h)	88
10[c]	**1j**, 2,3-Me_2	**2j** (1 h)	73
11[c]	**1k**, 2,4,6-Cl_3	**2k** (2.5 h)	61
			
12[c]	**1l**, 4-Me	**2l** (2.5 h)	75
13[c]	**1m** 4-MeO	**2m** (2.5 h)	71
14[c]	**1n**, 4-Cl	**2n** (2.5 h)	72
15[c]	**1o**, 4-NO_2	**2o** (2.5 h)	60
16[c]	**1p**, 4-Ph	**2p** (3 h)	45
17[c]	**1q**, 4-MeOOC	**2q** (3 h)	42

[a]Reaction conditions: **1** (0.50 mmol), $PdCl_2(PPh_3)_2$ (5 mol %), Cs_2CO_3 (1.0 mmol) in chlorobenzene (MCB) (3 mL) at 85 °C. [b]Yield of isolated product. The in situ yield is shown in parentheses. [c]Conducted with Cs_2CO_3 (0.50 mmol) at 120 °C.

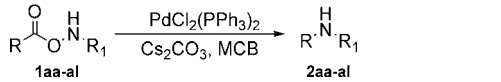
groups, such as the nitro (**1f**, **1o**), ester (**1q**), alkoxy (**1c**, **1m**), and halide groups (**1d**, **1e**, **1i**, **1k**, and **1n**), are compatible with this transformation. Sterically more hindered *ortho*-substituted carboxylic acids gave high yields of the desired products (Table 2, entries 1, 3−8, and 10−11). Nonetheless, although *t*-butyl benzoyloxycarbamate **1b** derived from benzoic acid could successfully be transformed into **2b**, the yield was much lower (Table 2, entry 2). We also found that the *meta*-, and *para*-substituted substrates react more slowly under the optimized conditions. Fortunately, full conversions were achieved when the reactions were carried out at 120 °C with just 1 equiv of Cs_2CO_3. Under these new conditions, the corresponding *meta*-, *para*-substituted **2** may be obtained in good yields. In general, the yields obtained for *ortho*-substituted carboxylates are slightly higher than those *meta*-, *para*-substituted ones, possibly

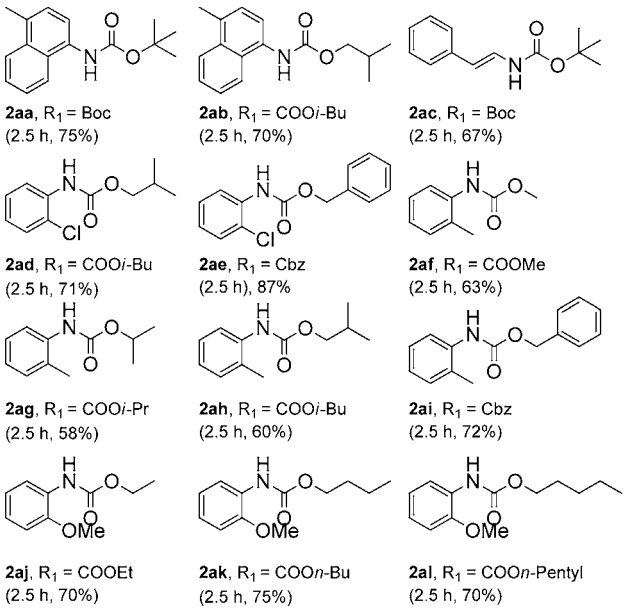
DOI: 10.1021/acs.orglett.6b02724
Org. Lett. 2016, 18, 5560−5563

because of the steric hindrance and/or interaction of the substituent with the palladium catalyst in the transition state.

To demonstrate further the scope and the versatility of this catalytic system, we next evaluated the reaction of 4-methyl-1-naphthoic acid, *trans*-cinnamic acid, and various hydroxycarbamates (Table 3). As the results show, 4-methyl-1-naphthoic acid is well tolerated, and the desired coupling product **2aa** was obtained in 75% yield. Similarly, a good yield was obtained for the IDC product corresponding to *trans*-cinnamic acid **2ac**. In the case of hydroxycarbamates, the reaction proceeds well with hydroxycarbamates that has a primary, secondary, or tertiary ester alkyl group (Table 3). Moreover, when *ortho*-substituted benzoic acids **1ad**-**1al** were subjected to this reaction under the standard reaction conditions, the expected IDC products were obtained in good to high yields (Table 3).

Table 3. Substrate Scope[a]

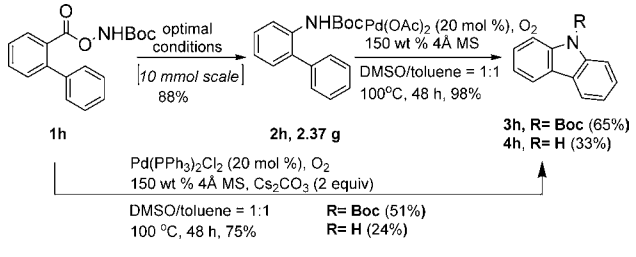




[a]Reaction conditions: **1** (0.50 mmol), $PdCl_2(PPh_3)_2$ (5 mol %), Cs_2CO_3 (0.50 mmol) in chlorobenzene (MCB) (3 mL) at 120 °C. Yield of isolated product shown.

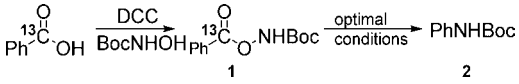
To demonstrate the practical utility of this novel method, the reaction of *t*-butyl [(1,1′-biphenyl)-2-carbonyl]oxycarbamate (**1h**) was performed at the 10 mmol scale. The desired *t*-butyl (1,1′-biphenyl)-2-yl carbamate (**2h**) was formed in 88% yield (Scheme 2). This result is comparable with that obtained previously at 0.5 mmol scale (Table, 2, entry 8). Compound **2h** can be effectively converted to the carbazoles **3h** and **4h** in 98% yield, with a 2:1 ratio of **3h** to **4h** (Scheme 2). In contrast, the direct C−H amination of **1h** only gave a total yield of 75% for these two products with a product ratio of 68:32 (Scheme 2). In addition, there are some reports for the synthesis of indole using phenylcarbamates as a versatile synthon.[13]

Scheme 2. Large-Scale Synthesis of 2a and Its Application



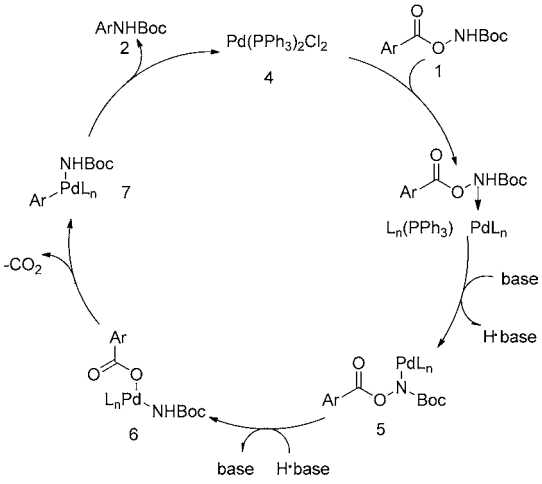
To probe the catalytic pathway, some additional investigations were conducted. First, we investigated the gas phase of the reaction mixture and carbon dioxide was detected by GC (see the Supporting Information). When the decarboxylation was carried out in deuterated benzoic acid, which suggested that a possible process of decarboxylation and coupling reaction existed. From isotopic labeling experiments, it was also strongly suggesting that the rate-determining step for the IDC reaction is most probably the decarboxylation from the benzoic acid (Scheme 3). Thus, the observed selectivity is understandable.

Scheme 3. Isotopic Labeling Experiments



On the basis of the current results and the reported mechanistic proposals for the Buchwald−Hartwig cross-coupling and the Gooßen's decarboxylative Heck reaction,[2,10] a plausible pathway of the IDC reaction is proposed (Scheme 4). As shown in Scheme 4, the first step of the catalytic cycle is the reaction of the Pd species with **1** to generate the complex **5** through deprotonation with the assistance of the base. Then the N−O bond cleavage affords the acyl carboxylate−Pd intermediate **6**. Previous reports on the use of aroyloxycarbamates for amidation reactions supports this hypothesis.[12,5b,d] The complex **7** is then generated through decarboxylation of **6**, and finally, reductive elimination produces the desired product **2** with the regeneration of catalyst and completes the catalytic cycle.

Scheme 4. Proposed IDC Pd Catalytic Cycle



In summary, we have developed a direct synthesis of arylamines via a palladium-catalyzed *N*-arylation that works through an intramolecular decarboxylative coupling of aroyloxycarbamates that may generated in situ from inexpensive, readily available, and nontoxic carboxylic acids and hydroxycarbamates. The corresponding arylamines may be obtained

DOI: 10.1021/acs.orglett.6b02724
Org. Lett. 2016, 18, 5560−5563

with high regioselectivities and good to high yields under mild thermal conditions. In addition, the method reported here can be successfully applied to a broad range of carboxylic acids and hydroxycarbamates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02724.

General procedures, characterization data, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: daiqipu@bit.edu.cn.
*E-mail: cwhu@bit.edu.cn.

Author Contributions

†Q.D. and P.L. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Excellent Young Scholars Research Fund of Beijing Institute of Technology (319-0012331518, 3190012331523), the National Natural Science Foundation of China (21231002, 21276026), and the 973 Program (2014CB932103). We are grateful to Dr. John C.-G. Zhao at the University of Texas at San Antonio for helpful discussions.

■ REFERENCES

(1) (a) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893−930. (b) Lygaitis, R.; Getautis, V.; Grazulevicius, J. V. *Chem. Soc. Rev.* **2008**, *37*, 770−788. (c) Liang, M.; Chen, J. *Chem. Soc. Rev.* **2013**, *42*, 3453−3488.

(2) (a) Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, *12*, 927−928. (b) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901−7902. (c) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348−1350. (d) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609−3612. (e) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805−818. (f) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860. (g) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534−1544. (h) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338−6361. (i) Maiti, D.; Fors, B. P.; Henderson, J. L.; Nakamura, Y.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 57−68. (j) Brusoe, A. T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 8460−8468. (k) Smith, S. M.; Buchwald, S. L. *Org. Lett.* **2016**, *18*, 2180−2183.

(3) (a) Ullmann, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2382−2384. (b) Cortes-Salva, M.; Garvin, C.; Antilla, J. C. *J. Org. Chem.* **2011**, *76*, 1456−1459. (c) Jiao, J.; Zhang, X.-R.; Chang, N.-H.; Wang, J.; Wei, J.-F.; Shi, X.-Y.; Chen, Z.-G. *J. Org. Chem.* **2011**, *76*, 1180−1183. (d) Zhang, Y.; Yang, X.; Yao, Q.; Ma, D. *Org. Lett.* **2012**, *14*, 3056−3059. (e) Louillat, M.-L.; Patureau, F. W. *Chem. Soc. Rev.* **2014**, *43*, 901−910.

(4) (a) Chan, D. M. T.; Monaco, K. L.; Wang, R.-P.; Winters, M. P. *Tetrahedron Lett.* **1998**, *39*, 2933−2936. (b) Lam, P. Y. S.; Clark, C. G.; Saubern, S.; Adams, J.; Winters, M. P.; Chan, D. M. T.; Combs, A. *Tetrahedron Lett.* **1998**, *39*, 2941−2944. (c) Quach, T. D.; Batey, R. A. *Org. Lett.* **2003**, *5*, 4397−4400. (d) Kantam, M. L.; Venkanna, G. T.; Sridhar, C.; Sreedhar, B.; Choudary, B. M. *J. Org. Chem.* **2006**, *71*, 9522−9524. (e) Raghuvanshi, D. S.; Gupta, A. K.; Singh, K. N. *Org. Lett.* **2012**, *14*, 4326−4329. (f) Jiang, Y.; Huang, S. *Synlett* **2014**, *25*, 407−410. (g) Gao, J.; Shao, Y.; Zhu, J.; Mao, H.; Wang, X.; Lv, X. *J. Org. Chem.* **2014**, *79*, 9000−9008. (h) Moon, S.-Y.; Nam, J.; Rathwell, K.; Kim, W.-S. *Org. Lett.* **2014**, *16*, 338−341.

(5) (a) Ng, K.-H.; Chan, A. S. C.; Yu, W.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 12862−12864. (b) Grohmann, C.; Wang, H.; Glorius, F. *Org. Lett.* **2013**, *15*, 3014−3017. (c) Shi, J.; Zhao, G.; Wang, X.; Xu, H. E.; Yi, W. *Org. Biomol. Chem.* **2014**, *12*, 6831−6836. (d) Patel, P.; Chang, S. *Org. Lett.* **2014**, *16*, 3328−3331. (e) Patel, P.; Chang, S. *ACS Catal.* **2015**, *5*, 853−858. (f) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Soc. Rev.* **2016**, *45*, 2044−2056.

(6) (a) Berman, A. M.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 5680−5681. (b) Campbell, M. J.; Johnson, J. S. *Org. Lett.* **2007**, *9*, 1521−1524. (c) He, C.; Chen, C.; Cheng, J.; Liu, C.; Liu, W.; Li, Q.; Lei, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6414−6417. (d) Barker, T. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2009**, *131*, 15598−15599. (e) Barker, T. J.; Jarvo, E. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 8325−8328. (f) Matsuda, N.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3642−3645. (g) Rucker, R. P.; Whittaker, A. M.; Dang, H.; Lalic, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 3953−3956.

(7) (a) Zhang, Y.; Patel, S.; Mainolfi, N. *Chem. Sci.* **2012**, *3*, 3196−3199. (b) Sheng, W.-J.; Ye, Q.; Yu, W.-B.; Liu, R.-R.; Xu, M.; Gao, J.-R.; Jia, Y.-X. *Tetrahedron Lett.* **2015**, *56*, 599−601.

(8) (a) Weaver, J. D.; Recio, A.; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846−1913. (b) Dzik, W. I.; Lange, P. P.; Gooßen, L. J. *Chem. Sci.* **2012**, *3*, 2671−2678.

(9) (a) Becht, J.-M.; Catala, C.; Le Drian, C.; Wagner, A. *Org. Lett.* **2007**, *9*, 1781−1783. (b) Gooßen, L. J.; Rodríguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248−15249. (c) Gooßen, L. J.; Zimmermann, B.; Linder, C.; Rodríguez, N.; Lange, P. P.; Hartung, J. *Adv. Synth. Catal.* **2009**, *351*, 2667−2674. (d) Gooßen, L. J.; Linder, C.; Rodríguez, N.; Lange, P. P. *Chem. - Eur. J.* **2009**, *15*, 9336−9349. (e) Gooßen, L. J.; Lange, P. P.; Rodríguez, N.; Linder, C. *Chem. - Eur. J.* **2010**, *16*, 3906−3909.

(10) (a) Gooßen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662−664. (b) Gooßen, L. J.; Rodríguez, N.; Gooßen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100−3120. (c) Rodríguez, N.; Gooßen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030−5048. (d) Shang, R.; Liu, L. *Sci. China: Chem.* **2011**, *54*, 1670−1687. (e) Cornella, J.; Larrosa, I. *Synthesis* **2012**, *44*, 653−676. (f) Tang, J.; Biafora, A.; Goossen, L. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 13130−13133. (g) Zuo, Z.; Cong, H.; Li, W.; Choi, J.; Fu, G. C.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2016**, *138*, 1832−1835.

(11) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000−2003.

(12) (a) Hazelden, I. R.; Ma, X.; Langer, T.; Bower, J. F. *Angew. Chem., Int. Ed.* **2016**, *55*, 11198. (b) Chen, C.; Hou, L.; Cheng, M.; Su, J.; Tong, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 3092−3096. (c) Fromm, A.; van Wüllen, C.; Hackenberger, D.; Gooßen, L. J. *J. Am. Chem. Soc.* **2014**, *136*, 10007−10023.

(13) (a) Li, P.; Wang, L.; Wang, M.; You, F. *Eur. J. Org. Chem.* **2008**, *2008*, 5946−5951. (b) Schmid, M.; Waldner, B.; Schnürch, M.; Mihovilovic, M. D.; Stanetty, P. *Tetrahedron* **2011**, *67*, 2895−2904.

DOI: 10.1021/acs.orglett.6b02724
Org. Lett. 2016, 18, 5560−5563