JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Decarbonylative Diaryl Ether Synthesis by Pd and Ni Catalysis

Ryosuke Takise,[†] Ryota Isshiki,[‡] Kei Muto,[‡] Kenichiro Itami,*[,†,§] and Junichiro Yamaguchi*[,‡]

[†]Institute of Transformative Bio-Molecules (WPI-ITbM) and Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

[‡]Department of Applied Chemistry, Waseda University, 3-4-1 Ohkubo, Shinjuku, Tokyo 169-8555, Japan

[§]JST-ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Chikusa, Nagoya 464-8602, Japan

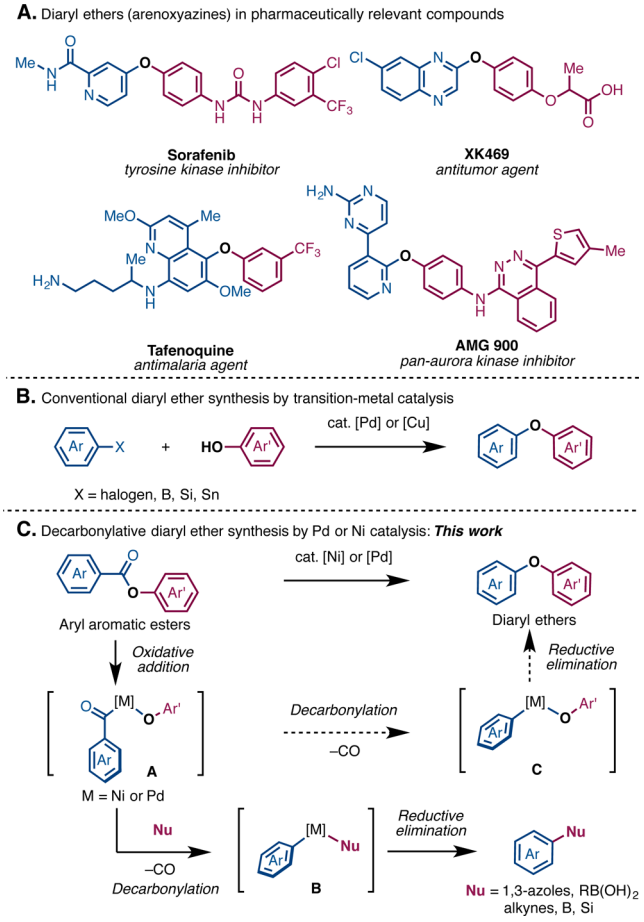
Supporting Information

ABSTRACT: Because diaryl ethers are present as an important motif in pharmaceuticals and natural products, extensive studies for the development of novel methods have been conducted. A conventional method for the construction of the diaryl ether moiety is the intermolecular cross-coupling reaction of aryl halides and phenols with a copper or palladium catalyst. We developed a catalytic decarbonylative etherification of aromatic esters using a palladium or nickel catalyst with our enabling diphosphine ligand to give the corresponding diaryl ethers. The present reaction can be conducted on gram scale in excellent yield. This reaction not only functions in an intramolecular setting but also allows for a cross-etherification using other phenols.

The diaryl ether scaffold has often been seen in pharmaceuticals and natural products, and particularly, arenoxyazine frameworks are observed in pharmaceutically relevant compounds such as Sorafenib, XK469, Tafenoquine, and AMG900 (Scheme 1A).[1,2] Therefore, the development of methods for diaryl ether synthesis is in high demand. Classically, the copper-mediated Ullmann ether synthesis is known to be one of the most reliable methods for the synthesis of diaryl ethers.[3] However, over the past few decades, palladium- and copper-catalyzed cross-coupling of aryl halides with phenols has been developed extensively and is now considered to be a "conventional" route (Scheme 1B).[4,5] Additionally, copper-mediated or catalyzed Chan–Lam–Evans-type Ar–B/Ar–OH couplings are well-established methods for diaryl ether synthesis.[6]

In related work, our group and others have recently developed a range of decarbonylative coupling reactions using nickel or palladium catalysts (Scheme 1C).[7,8] These reactions proceed through ester C–O bond activation by a metal catalyst (intermediate **A**), after which nucleophiles attack the metal center and decarbonylation produces intermediate **B**. Finally, reductive elimination from **B** can form coupling products. However, in an alternative pathway from intermediate **A**, if decarbonylation occurred without an external nucleophile, diaryl ethers could be obtained by reductive elimination through intermediate **C**. Capitalizing on this blueprint, we herein report a de novo synthesis of diaryl ethers by decarbonylation from aromatic esters.

Scheme 1. (A) Diaryl Ethers in Pharmaceutically Relevant Compounds; (B) Conventional Diaryl Ether Synthesis by Transition-Metal Catalysis; (C) Decarbonylative Coupling Reaction and Diaryl Ether Synthesis by Ni or Pd Catalysis



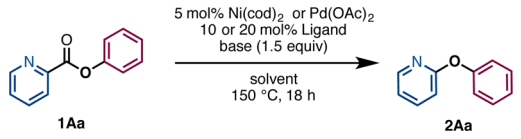
First, we attempted to react many aromatic esters under our catalytic nickel protocol[7] without additional nucleophiles. After extensive screening, we found that phenyl picolinate (**1Aa**) was converted to 2-phenoxypyridine (**2Aa**) under $Ni(cod)_2$ (5 mol %), dcype [1,2-bis(dicyclohexyl)phosphino]ethane, 10 mol %], and K_3PO_4 (1.5 equiv) in toluene at 150 °C for 18 h in 37%

Received: January 3, 2017
Published: February 19, 2017

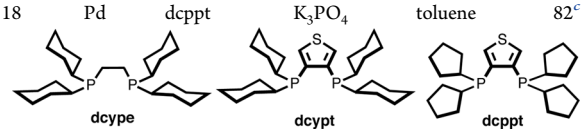
DOI: 10.1021/jacs.7b00049
J. Am. Chem. Soc. 2017, 139, 3340–3343

isolated yield (Table 1, entry 1).[9] When we changed the ligand to other diphosphine ligands such as dppf (entry 2) and BINAP

Table 1. Screening of the Reaction Conditions[a]



entry	metal	ligand	base	solvent	**2Aa** (%)[b]
1	Ni	dcype	K_3PO_4	toluene	37
2	Ni	dppf	K_3PO_4	toluene	0
3	Ni	BINAP	K_3PO_4	toluene	0
4	Ni	PPh_3	K_3PO_4	toluene	0
5	Ni	PCy_3	K_3PO_4	toluene	0
6	Ni	P(*n*-Bu)$_3$	K_3PO_4	toluene	0
7	Ni	bipy	K_3PO_4	toluene	0
8	Ni	IPr	K_3PO_4	toluene	0
9	Ni	ICy	K_3PO_4	toluene	0
10	Ni	dcypt	K_3PO_4	toluene	90
11	Ni	dcypt	K_3PO_4	dioxane	79
12	Ni	dcypt	K_3PO_4	THF	67
13	Ni	dcypt	K_3PO_4	DMF	20
14	Ni	dcypt	CsF	toluene	90
15	Ni	dcypt	Na_2CO_3	toluene	82
16	Ni	dcypt	–	toluene	74
17	Pd	dcypt	CsF	toluene	62
18	Pd	dcppt	K_3PO_4	toluene	82[c]



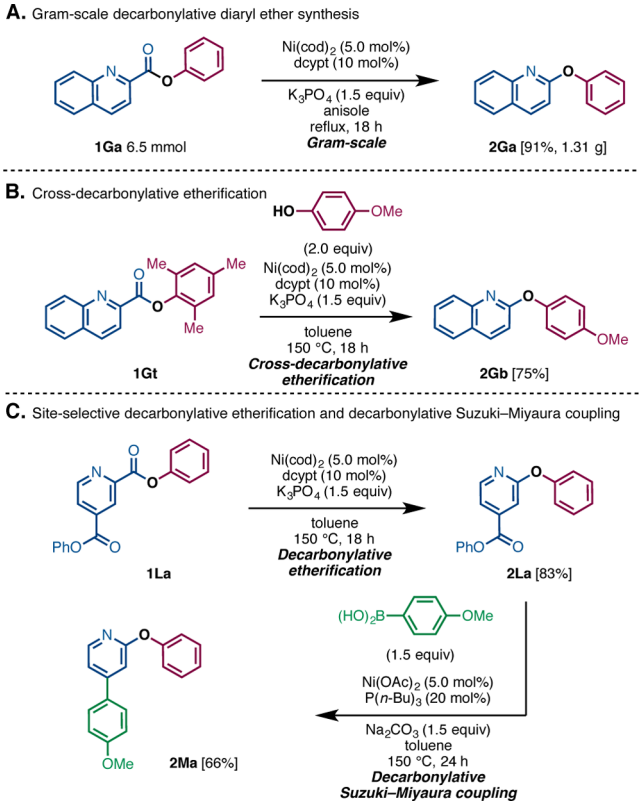
[a]Unless otherwise noted, the reactions conditions were as follows: **1Aa** (0.40 mmol), Ni(cod)$_2$ (5 mol %) or Pd(OAc)$_2$ (10 mol %), ligand (bidentate, 10 mol %; monodentate, 20 mol %), base (1.5 equiv), solvent (1.6 mL), 150 °C for 18 h. [b]Isolated yield. [c]140 °C for 12 h.

(entry 3), the reaction completely shut down, and only starting material was recovered. Monophosphines PPh_3 (entry 4), PCy_3 (entry 5), and P(*n*-Bu)$_3$ (entry 6) as well as bipy (entry 7) also led to no reaction. Although NHC ligands, e.g., IPr and ICy were reported to be effective for the C–heteroatom bond activation,[8h,9] they did not work at all in this reaction (entries 8 and 9). Finally, dcypt [3,4-bis(dicyclohexylphosphino)-thiophene], which was developed by our group,[10] was found to increase dramatically the yield, affording **2Aa** in 90% yield (entry 10).

Regarding the solvent, it can be changed to 1,4-dioxane, THF, and DMF, albeit in decreased yields (entries 11–13). When the base was changed CsF (entry 14) and Na_2CO_3 (entry 15), the yield was the same or slightly decreased, and even without base, the desired product **2Aa** can be obtained in 74% yield (entry 16). When the metal catalyst was changed from nickel to palladium [Pd(OAc$_2$)] (same conditions as entry 13), **2Aa** was obtained in 62% yield (entry 17), but after optimizing the reaction conditions further, dcppt [3,4-bis-(dicyclopentylphosphino)thiophene] as the ligand and K_3PO_4 as the base led to **2Aa** in 82% yield (entry 18).[11]

Under the established conditions, the substrate scope for this nickel- or palladium-catalyzed decarbonylative diaryl ether synthesis was examined (Table 2). The phenyl group on the picolinate was changed to 4-methoxyphenyl, 4-fluorophenyl, 4-

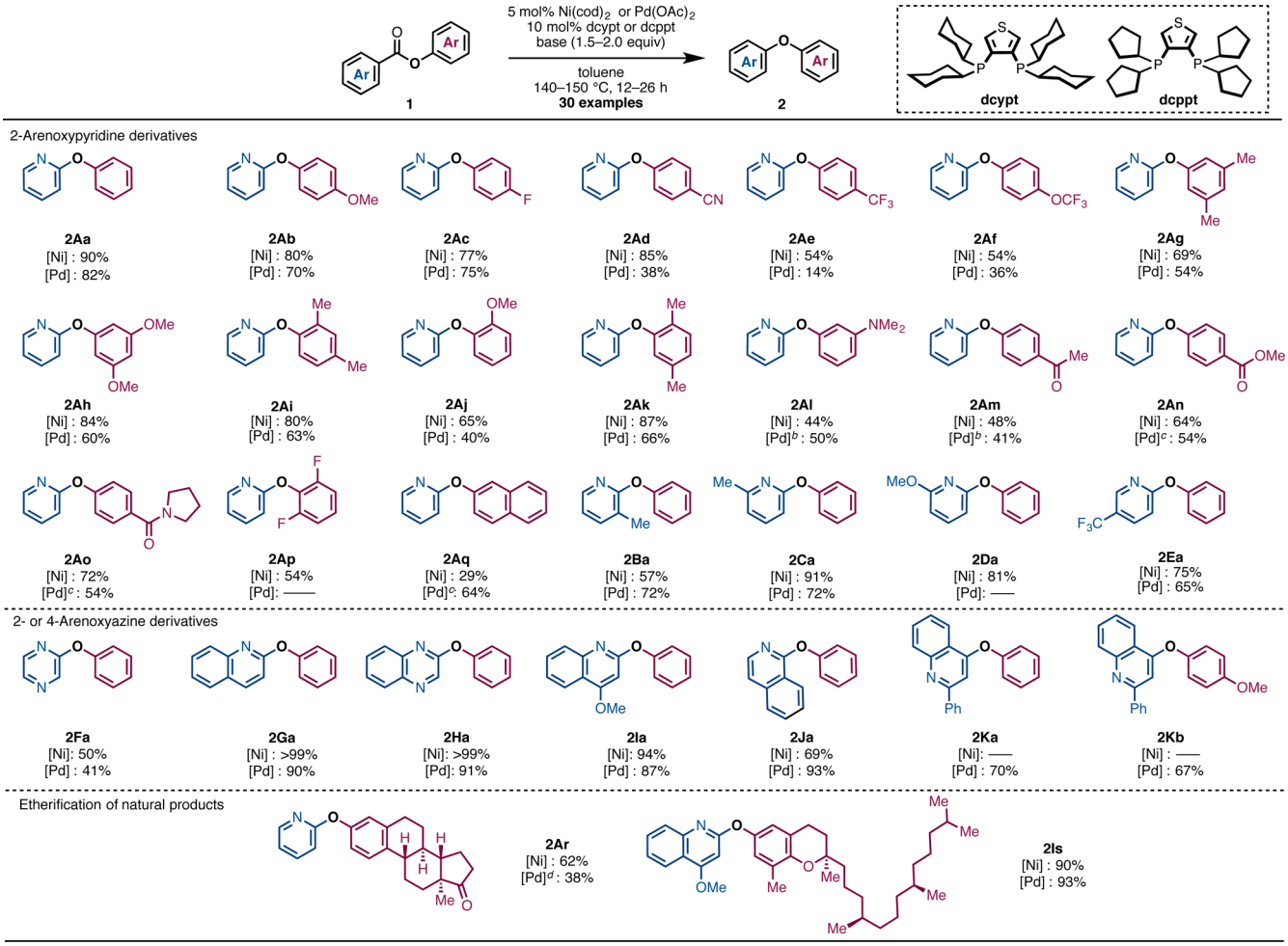
Scheme 2. (A) Gram-Scale Decarbonylative Diaryl Ether Synthesis; (B) Cross-Decarbonylative Etherification; (C) Site-Selective Decarbonylative Etherification and Decarbonylative Suzuki–Miyaura Coupling



cyanophenyl, 4-trifluoromethylphenyl, and 4-trifluoromethyloxyphenyl to give 2-arenoxypyridines (**2Ab–2Af**) in good to moderate yields. Disubstituted aryl groups on the picolinate such as 3,5-dimethylphenyl and 3,5-dimethoxyphenyl worked well to afford arenoxypyridines **2Ag** (69% by Ni) and **2Af** (80% by Ni). Even if the aryl group has a substituent on the *ortho* position, decarbonylative etherification proceeded to furnish the corresponding products **2Ai–2Ak**. Reactive functional groups on the aryl moiety such as amines, ketones, methyl esters, and amides were tolerated to give diaryl ethers **2Am–2Ao** in good yields. For these substrates, dcypt instead of dcppt, and different bases (CsF or KF) for palladium catalysis gave better yields. Additionally, electron-deficient aryl groups such as 2,6-difluorophenyl, as well as a naphthalenyl group still reacted to form **2Ap** (54% by Ni) and **2Aq** (64% by Pd), respectively. Substituents on the pyridine portion of the starting material such as 3-methyl, 6-methyl, 6-methoxy, and 5-trifluoromethyl gave the corresponding diaryl ethers **2Ba**, **2Ca**, **2 Da**, and **2Ea** in good to excellent yields. Next, we screened other phenyl azinecarboxylates. Although phenyl pyrazinecarboxylate gave **2Fa** in moderate yield, quinoline, quinoxaline, and their derivatives afforded the corresponding 2-phenoxyazines **2Ga**, **2Ha**, **2Ia**, and **2Ja** in nearly quantitative yields. Unfortunately, this reaction only proceeds generally on aryl 2-azinecarboxylates, but specific aryl 4-azinecarboxylates did react under palladium catalysis to give **2Ka** and **2Kb** in good yields. Furthermore, azinecarboxylates derived from natural products such as estrone and tocopherol can be etherified under the standard conditions to form diaryl ethers **2Ar** (62% by Ni) and **2Is** (93% by Pd), respectively. Although palladium catalysis

DOI: 10.1021/jacs.7b00049
J. Am. Chem. Soc. 2017, 139, 3340–3343

Table 2. Decarbonylative Diaryl Ether Synthesis[a]



[a]Unless otherwise noted, reactions conditions were as follows: [Ni]: **1** (0.40 mmol), $Ni(cod)_2$ (5 mol %), dcypt (10 mol %), K_3PO_4 (1.5 equiv), toluene (1.6 mL), 150 °C, 18 h. [Pd]: **1** (0.40 mmol), $Pd(OAc)_2$ (5 mol %), dcppt (10 mol %), K_3PO_4 (1.5 equiv), toluene (1.6 mL), 150 °C, 18 h. [b]dcypt (5 mol %) was used instead of dcppt. CsF (2.0 equiv) was used instead of K_3PO_4 (1.5 equiv). [c]dcypt (5 mol %) was used instead of dcppt. KF (2.0 equiv) was used instead of K_3PO_4 (1.5 equiv). MS 3 Å was used as an additive. [d]170 °C.

generally gave slightly lower yields compared to nickel catalysis, both modes of catalysis gave the desired product, otherwise the starting material was recovered. Although it remains unclear why 2-azinecarboxylates discretely work well in this reaction, a plausible reason can be elaborated as follows: (i) typically, reductive elimination from Ar−M−OAr′ intermediate **C** is the rate-determining step for the formation of Ar−OAr′; and (ii) it is known that the reductive elimination is faster using 2-azine−M−OR than for 3-azine and 4-azine,[12] possibly accelerated by the electron-withdrawing nature of a 2-azinyl group bestowing a greater positive charge and destabilizing the metal center.

Next, we conducted experiments to showcase the utility of this reaction in a variety of settings (Scheme 2). This decarbonylative etherification can be applied on gram-scale (Scheme 2A). For example, **1Ga** (6.5 mmol) was subjected to this reaction under Ni catalysis using anisole as solvent to afford the desired product **2Ga** in 91% yield (1.31 g of product).

Additionally, when an azinecarboxylate with bulky aryl substituents such as **1Gt** was used, cross-etherification was made possible with 4-methoxyphenol to furnish **2Gb** in 75% yield (Scheme 2B). Finally, site-selective decarbonylative etherification was achieved (Scheme 2C): a diphenyl azinedicarboxylate was treated under nickel catalysis to afford aryl ether **2La** in 83% yield with exclusive C2-selectivity. Subsequently, **2La** was reacted with 4-methoxyphenyl boronic acid using a $Ni(OAc)_2/P(n\text{-}Bu)_3$ catalyst and Na_2CO_3 in toluene to give coupling product **2Ma** in 66% yield by a de(phenoxy)carbonylative Suzuki−Miyaura cross-coupling.[7b]

In conclusion, we have developed the first decarbonylative ether synthesis by nickel or palladium catalysis. Use of our in-house ligands, dcypt and dcppt, were critical for this reaction, in which a variety of aryl azinecarboxylates lead to the corresponding 2-arenoxyazines by decarbonylation. Further optimization of reaction conditions to achieve a broader scope is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b00049.

Detailed experimental procedures, and spectral data for all compounds, including scanned images of ^1H, ^{13}C NMR spectra (DOCX)

DOI: 10.1021/jacs.7b00049
J. Am. Chem. Soc. 2017, 139, 3340−3343

AUTHOR INFORMATION

Corresponding Authors

*itami@chem.nagoya-u.ac.jp

*junyamaguchi@waseda.jp

ORCID

Kei Muto: 0000-0001-8301-4384

Junichiro Yamaguchi: 0000-0002-3896-5882

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Number JP16H01011, and JP16H04148 (to J.Y.), the ERATO program from JST (to K.I.), the Early Bird Program of Waseda University (to K.M.), and a JSPS research fellowship for young scientists (to R.T.). We thank Dr. Yoshihiro Ishihara (Vertex Pharmaceuticals) for fruitful discussion and critical comments. ITbM is supported by the World Premier International Research Center (WPI) Initiative, Japan.

REFERENCES

(1) Selected review: (a) Nicolaou, K. C.; Boddy, C. N. C.; Bräse, S.; Winssinger, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2096. (b) Cristau, P.; Vors, J.-P.; Zhu, J. *Tetrahedron* **2003**, *59*, 7859. (c) Corbett, J. W.; Rauckhorst, M. R.; Qian, F.; Hoffman, R. L.; Knauer, C. S.; Fitzgerald, L. W. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6250. (d) Pitsinos, E. N.; Vidali, V. P.; Couladouros, E. A. *Eur. J. Org. Chem.* **2011**, *2011*, 1207. (e) Bedos-Belval, F.; Rouch, A.; Vanucci-Bacqué, C.; Baltas, M. *MedChemComm* **2012**, *3*, 1356.

(2) (a) LoRusso, P. M.; Parchment, R.; Demchik, L.; Knight, J.; Polin, L.; Dzubow, J.; Behrens, C.; Harrison, B. A.; Trainor, G.; Corbett, T. H. *Invest. New Drugs* **1999**, *16*, 287. (b) Peters, W. *J. R. Soc. Med.* **1999**, *92*, 345. (c) Wilhelm, S. M.; Adnane, L.; Newell, P.; Villanueva, A.; Llovet, J. M.; Lynch, M. *Mol. Cancer Ther.* **2008**, *7*, 3129. (d) Geuns-Meyer, S.; Cee, V. J.; Deak, H. L.; Du, B.; Hodous, B. L.; Nguyen, H. N.; Olivieri, P. R.; Schenkel, L. B.; Vaida, K. R.; Andrews, P.; Bak, A.; Be, X.; Beltran, P. J.; Bush, T. L.; Chaves, M. K.; Chung, G.; Dai, Y.; Eden, P.; Hanestad, K.; Huang, L.; Lin, M.-H. J.; Tang, J.; Ziegler, B.; Radinsky, R.; Kendall, R.; Patel, V. F.; Payton, M. *J. Med. Chem.* **2015**, *58*, 5189.

(3) (a) Ullmann, F. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 853. (b) Lindley, J. *Tetrahedron* **1984**, *40*, 1433. (c) Theil, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 2345. (d) Sawyer, J. S. *Tetrahedron* **2000**, *56*, 5045. (e) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400. (f) Frlan, R.; Kikelj, D. *Synthesis* **2006**, *2006*, 2271. (g) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054.

(4) For selected examples for Pd-catalyzed diaryl ether synthesis, see: (a) Mann, G.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 5413. (b) Mann, G.; Incarvito, C.; Rheingold, A. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 3224. (c) Aranyos, A.; Old, D. W.; Kiyomori, A.; Wolfe, J. P.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4369. (d) Shelby, Q.; Kataoka, N.; Mann, G.; Hartwig, J. *J. Am. Chem. Soc.* **2000**, *122*, 10718. (e) Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775. (f) Harkal, S.; Kumar, K.; Michalik, D.; Zapf, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Beller, M. *Tetrahedron Lett.* **2005**, *46*, 3237. (g) Burgos, C. H.; Barder, T. E.; Huang, X.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 4321. (h) Hu, T.; Schulz, T.; Torborg, C.; Chen, X.; Wang, J.; Beller, M.; Huang, J. *Chem. Commun.* **2009**, 7330. (i) Platon, M.; Cui, L.; Mom, S.; Richard, P.; Saeys, M.; Hierso, J.-C. *Adv. Synth. Catal.* **2011**, *353*, 3403. (j) Salvi, L.; Davis, N. R.; Ali, S. Z.; Buchwald, S. L. *Org. Lett.* **2012**, *14*, 170.

(5) For selected examples for Cu-catalyzed diaryl ether synthesis, see: (a) Marcoux, J.-F.; Doye, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 10539. (b) Buck, E.; Song, Z. J.; Tschaen, D.; Dormer, P. G.; Volante, R. P.; Reider, P. J. *Org. Lett.* **2002**, *4*, 1623. (c) Ma, D.; Cai, Q. *Org. Lett.* **2003**, *5*, 3799. (d) Cristau, H.-J.; Cellier, P. P.; Hamada, S.; Spindler, J.-F.; Taillefer, M. *Org. Lett.* **2004**, *6*, 913. (e) Cai, Q.; Zou, B.; Ma, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1276. (f) Rao, H.; Jin, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Chem. - Eur. J.* **2006**, *12*, 3636. (g) Lv, X.; Bao, W. *J. Org. Chem.* **2007**, *72*, 3863. (h) Altman, R. A.; Shafir, A.; Choi, A.; Lichtor, P. A.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 284. (i) Xia, N.; Taillefer, M. *Chem. - Eur. J.* **2008**, *14*, 6037. (j) Zhang, Q.; Wang, D.; Wang, X.; Ding, K. *J. Org. Chem.* **2009**, *74*, 7187. (k) Liu, Y.; Li, G.; Yang, L. *Tetrahedron Lett.* **2009**, *50*, 343. (l) Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 6954. (m) Maiti, D.; Buchwald, S. L. *J. Org. Chem.* **2010**, *75*, 1791. (n) Fan, M.; Zhou, W.; Jiang, Y.; Ma, D. *Angew. Chem., Int. Ed.* **2016**, *55*, 6211.

(6) (a) Chan, D. M. T.; Winters, M. P.; Monaco, K. L.; Wang, R. *Tetrahedron Lett.* **1998**, *39*, 2933. (b) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett.* **1998**, *39*, 2937. (c) Jung, M. E.; Lazarova, T. I. *J. Org. Chem.* **1999**, *64*, 2976. (d) Decicco, C. P.; Song, S.; Evans, D. A. *Org. Lett.* **2001**, *3*, 1029. (e) Lam, P. Y. S.; Vincent, G.; Clark, C.; Deudon, S.; Jadhav, P. K. *Tetrahedron Lett.* **2001**, *42*, 3415. (f) Chan, D. M. T.; Monaco, K. L.; Li, R.; Bonne, D.; Clark, C. G.; Lam, P. Y. S. *Tetrahedron Lett.* **2003**, *44*, 3863. (g) Qiao, J. X.; Lam, P. Y. S. *Synthesis* **2011**, *2011*, 829.

(7) (a) Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 13573. (b) Muto, K.; Yamaguchi, J.; Musaev, D. G.; Itami, K. *Nat. Commun.* **2015**, *6*, 7508. (c) Amaike, K.; Itami, K.; Yamaguchi, J. *Chem. - Eur. J.* **2016**, *22*, 4384. (d) Muto, K.; Hatakeyama, T.; Itami, K.; Yamaguchi, J. *Org. Lett.* **2016**, *18*, 5106. (e) Okita, T.; Kumazawa, K.; Takise, R.; Muto, K.; Itami, K.; Yamaguchi, J. *Chem. Lett.* **2017**, *46*, 218.

(8) (a) Gooßen, L. J.; Paetzold, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1237. (b) Gooßen, L. J.; Paetzold, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1095. (c) Wang, J.; Liu, B.; Zhao, H.; Wang, J. *Organometallics* **2012**, *31*, 8598. (d) Correa, A.; Cornella, J.; Martin, R. *Angew. Chem., Int. Ed.* **2013**, *52*, 1878. (e) Hong, X.; Liang, Y.; Houk, K. N. *J. Am. Chem. Soc.* **2014**, *136*, 2017. (f) Lu, Q.; Yu, H.; Fu, Y. *J. Am. Chem. Soc.* **2014**, *136*, 8252. (g) LaBerge, N. A.; Love, J. A. *Eur. J. Org. Chem.* **2015**, *2015*, 5546. (h) Guo, L.; Chatupheeraphat, A.; Rueping, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 11810. (i) Pu, X.; Hu, J.; Zhao, Y.; Shi, Z. *ACS Catal.* **2016**, *6*, 6692. (j) Guo, L.; Rueping, M. *Chem. - Eur. J.* **2016**, *22*, 16787.

(9) Recent examples: (a) Hie, L.; Fine Nathel, N. F.; Shah, T. K.; Baker, E. L.; Hong, X.; Yang, Y.-F.; Liu, P.; Houk, K. N.; Garg, N. K. *Nature* **2015**, *524*, 79. (b) Nakamura, K.; Tobisu, M.; Chatani, N. *Org. Lett.* **2015**, *17*, 6142.

(10) dcype and dcypt: (a) Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 169. (b) Meng, L.; Kamada, Y.; Muto, K.; Yamaguchi, J.; Itami, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 10048. (c) Muto, K.; Yamaguchi, J.; Lei, A.; Itami, K. *J. Am. Chem. Soc.* **2013**, *135*, 16384. (d) Xu, H.; Muto, K.; Yamaguchi, J.; Zhao, C.; Itami, K.; Musaev, D. G. *J. Am. Chem. Soc.* **2014**, *136*, 14834. (e) Muto, K.; Hatakeyama, T.; Yamaguchi, J.; Itami, K. *Chem. Sci.* **2015**, *6*, 6792. (f) Takise, R.; Muto, K.; Yamaguchi, J.; Itami, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 6791. (g) Koch, E.; Takise, R.; Studer, A.; Yamaguchi, J.; Itami, K. *Chem. Commun.* **2015**, *51*, 855. (h) Takise, R.; Itami, K.; Yamaguchi, J. *Org. Lett.* **2016**, *18*, 4428.

(11) See Supporting Information for further experimental details.

(12) Shen, Q.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 7734.

DOI: 10.1021/jacs.7b00049
J. Am. Chem. Soc. 2017, 139, 3340−3343