OL | Organic Letters

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

Letter

pubs.acs.org/OrgLett

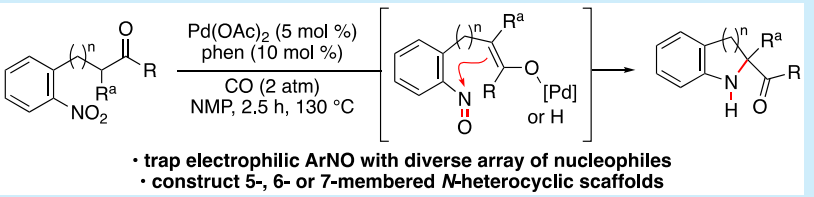
Intramolecular Pd-Catalyzed Reductive Amination of Enolizable sp^3-C−H Bonds

Russell L. Ford,[†] Isabel Alt,[†,‡] Navendu Jana,[†] and Tom G. Driver*[,†]

[†]Department of Chemistry, University at Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607, United States

[‡]Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, DE-70569 Stuttgart, Germany

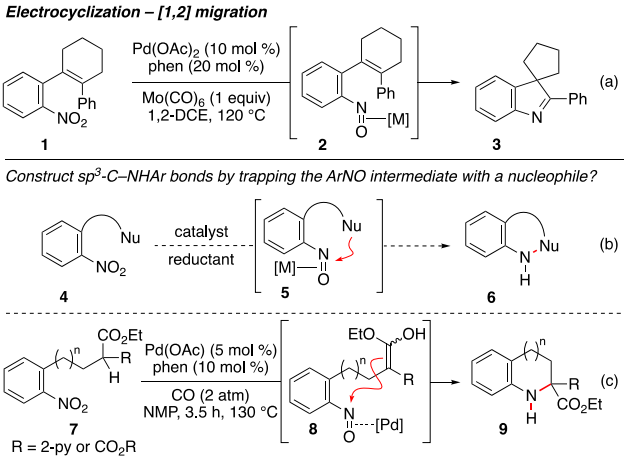
Supporting Information



ABSTRACT: A palladium-catalyzed reductive cyclization of nitroarenes has been designed to construct sp^3-C−NHAr bonds from sp^3-C−H bonds by using an enolizable nucleophile to intercept a nitrosoarene intermediate. Exposure of *ortho*-substituted nitroarenes to 5 mol % of $Pd(OAc)_2$ and 10 mol % of phenanthroline under 2 atm of CO constructs partially saturated 5-, 6-, or 7-membered *N*-heterocycles using α-pyridyl carboxylates, malonates, 1,3-dimethylbarbituric acid, 1,3-diones, or difurans as the nucleophile.

The amination of sp^3-C−H bonds continues to spur significant research development, because of the atom- and step-economy of this desirable transformation.[1] Despite the many advances in this field, the formation of sp^3-C−N bonds from sp^3-C−H bonds generally requires the use of strong *N*-electron-withdrawing substituents with an oxidant or the use of activated nitrene-precursors, such as an oxycarbamates or azides.[2−4] While sp^3-C−N bonds can be constructed from nitrosoarenes through ene-[5] and α-amination reactions,[6] the instability of nitrosoarenes limits their availability.[7] This challenge has encouraged the development of methods to generate nitrosoarenes in situ from readily accessible precursors. While it is possible to access nitrosoarenes through the oxidation of *N*-hydroxyanilines,[8] most efforts have focused on their reductive generation from nitroarenes.[9] Using nitroarenes as precursors to nitrosoarenes is an attractive synthetic strategy, since these compounds are benchtop stable, the nitro group is easy to install, and many examples are commercially available. We previously established that new C−N bonds can be formed by electrocyclic trapping of nitrosoarenes generated in situ from Pd- or Fe-catalyzed reduction of nitroarenes **1** to synthesize 3*H*-indoles **3** through a cyclization-migration reaction (see Scheme 1a).[10] We were curious if sp^3-C−NHAr bonds could be constructed by using a similar strategy to trap nitrososarenes generated from nitroarenes with a tethered nucleophile (see Scheme 1b). Herein, we report that 5- or 6-membered *N*-heterocyclic scaffolds can be efficiently constructed through a Pd-catalyzed reductive sp^3-C−N bond forming reaction from readily accessible 2-substituted nitroarenes using CO as the terminal reductant. A diverse array of nucleophiles are shown to intercept the electrophilic nitrosoarene intermediate to synthesize a broad range of *N*-heterocycles (see Scheme 1c).

Scheme 1. Formation of sp^3-C−N Bonds from Nitroarenes

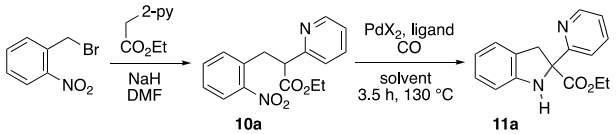


To test our hypothesis that sp^3-C−H bond amination could be achieved with nitroarenes under reductive conditions, the reactivity of **10a** was examined in the presence of a metal catalyst and reductant (see Table 1). This substrate is readily prepared in one step from commercially available reagents 2-nitrobenzyl bromide and 2-pyridylacetic acid ethyl ester through a NaH-mediated alkylation. While no reaction occurred when **10a** was exposed to the combination $Pd(OAc)_2$, phenanthroline and $Mo(CO)_6$,[11] changing the identity of the reductant to carbon monoxide produced indoline **11a** in 70% yield (Table 1, entry 1). A screen of polar aprotic solvents revealed NMP to be the

Received: September 30, 2019

DOI: 10.1021/acs.orglett.9b03458
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Development of Optimal Conditions



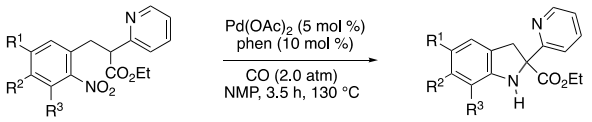
entry	PdX_2 (mol %)	ligand (mol %)	CO pressure (atm)	solvent	**11a** content[a] (%)
1	$Pd(OAc)_2$ (10)	phen (20)	2.0	DMF	70
2	$Pd(OAc)_2$ (10)	phen (20)	2.0	DMSO	53
3	$Pd(OAc)_2$ (10)	phen (20)	2.0	NMP	76
4	$Pd(OAc)_2$ (5)	phen (10)	2.0	NMP	83
5[b]	$Pd(OAc)_2$ (1)	phen (2)	2.0	NMP	0
6	$Pd(OAc)_2$ (5)	phen (10)	1.0	NMP	72
7	$Pd(OAc)_2$ (5)	tmphen (20)	2.0	NMP	30
8	$Pd(OAc)_2$ (5)	4,7-$(MeO)_2$ phen (10)	2.0	NMP	71
9	$Pd(OAc)_2$ (5)	Bphen (10)	2.0	NMP	42
10	$PdCl_2$ (5)	phen (10)	2.0	NMP	n.r.
11	$Pd(TFA)_2$ (5)	phen (10)	2.0	NMP	n.r.

[a]As determined via ^{1}H NMR spectroscopy, using CH_2Br_2 as an internal standard. [b]16 h reaction time.

optimal reaction medium for the transformation (Table 1, entries 1−3). Diminishing the catalyst loading to 5 mol % resulted in a small increase in the yield of **11a**, but further reduction impeded indoline formation (Table 1, entries 3−5). While the pressure of CO could be reduced to 1 atm and afford indoline in good yield (Table 1, entry 6), using 2.0 atm gave the best result. Deviation from the use of the phenanthroline ligand and testing of alternative palladium salts did not further improve the synthesis of **11a** from **10a** and therefore, the conditions shown in entry 4 in Table 1 were selected to interrogate the scope of the transformation (Table 1, entries 7−11).

Using these optimal conditions, we examined the scope and limitations of palladium-catalyzed reductive cyclization reaction by changing the electronic and steric nature of the nitroarene (see Table 2). Although Pd-catalyzed reduction of nitroarenes using CO was reported to be attenuated by electron-releasing substituents,[12] we found that the reaction is fairly insensitive to the electronic nature of the nitroarene (Table 2, entries 2−9). While the reaction tolerated a range of electron-rich or moderately electron-poor R^1 or R^2 substituents, lower yields were observed with stronger electron-withdrawing groups such as CF_3, and the addition of an R^3-substituent impeded the transformation to suggest coordination of the metal catalyst to the nitro-group (Table 2, entry 10).[13]

Table 2. Scope and Limitations of the Nitroarene Moiety



entry	#	R^1	R^2	R^3	yield[a] (%)
1	**a**	H	H	H	83 (68)[b]
2	**b**	Cl	H	H	65
3	**c**	F	H	H	72
4	**d**	Me	H	H	80
5	**e**	H	CF_3	H	50
6	**f**	H	Cl	H	65
7	**g**	H	F	H	80
8	**h**	H	Me	H	85
9	**i**	H	OMe	H	61
10	**j**	H	H	Me	n.r.

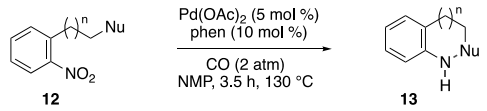
[a]Isolated yield of **11** after silica gel chromatography. [b]1 mmol scale.

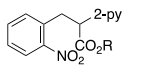
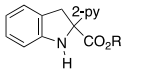
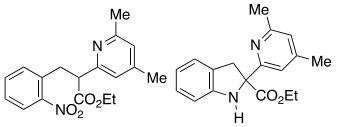
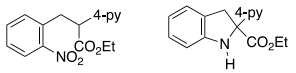
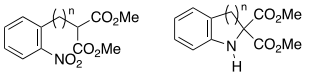
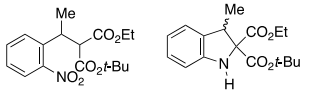
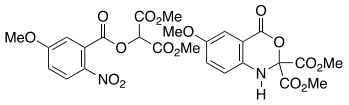
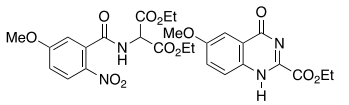
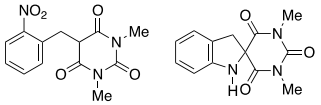
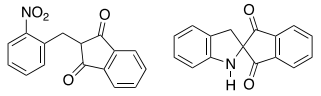
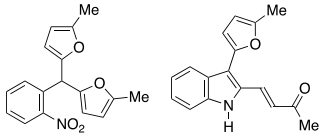
To investigate the breadth of the reactivity of the in-situ-generated nitrosoarene, we explored nitroarenes bearing a variety of nucleophiles to showcase the diverse *N*-heterocyclic scaffolds that could be constructed through the reductive sp^3-C−N bond forming reaction (see Table 3). Through simple modification of our initial test substrate, we determined that the yield of the cyclization was dependent on the size of the ester substituent and independent of the steric environment around the pyridyl nitrogen (Table 3, entries 1−3). Changing the position of the pyridyl-nitrogen to the 4-position, however, resulted in no indoline formation and confirmed our suspicion that the orientation of the Lewis basic functionality plays an important role in enol stabilization for trapping of the nitrosoarene intermediate (Table 3, entry 4). Gratifyingly, pyridine was not required for successful cyclization (Table 3, entries 5−12). Malonate **12e** was smoothly converted to indoline **13e** (Table 3, entry 5). To our delight, cyclization was not limited to the formation of 5-membered *N*-heterocycles: tetrahydroquinoline **13f** was formed in 68% and even tetrahydrobenzoazepine **13g** could be accessed in attenuated yield (Table 3, entries 6 and 7). While the cyclization of malonate **12h** was determined not to be diastereoselective (see Table 3, entry 8), heteroatoms could be incorporated into the tether to smoothly afford more-complex heterocycles such as benzo-1,3-oxazine **13i** and dihydroquinazoline **13j** (Table 3, entries 9 and 10). Beyond malonate and 2-pyridylacetic acid ethyl esters, enolizable nuclophiles such as 1,3-dimethylbarbituric acid-derived **12k** and 1,3-indanedione-derived **12l** smoothly formed new sp^3-C−N bonds (Table 3, entries 11 and 12),[14] and even difuran **12m** underwent reductive cyclization and ring-opening to give indole **13m** (see Table 3, entry 13).[15] These studies established the generality of this reductive cyclization method for the construction of a variety of partially saturated *N*-heterocyclic compounds from simple *ortho*-substituted nitroarenes.

To account for cyclization by sp^3-C−N bond formation of *ortho*-substituted nitroarenes under reductive conditions, we have outlined a potential catalytic cycle in Scheme 2 and included potential alternative pathways for consideration.

DOI: 10.1021/acs.orglett.9b03458
Org. Lett. XXXX, XXX, XXX−XXX

Table 3. Investigation of Nucleophile Scope

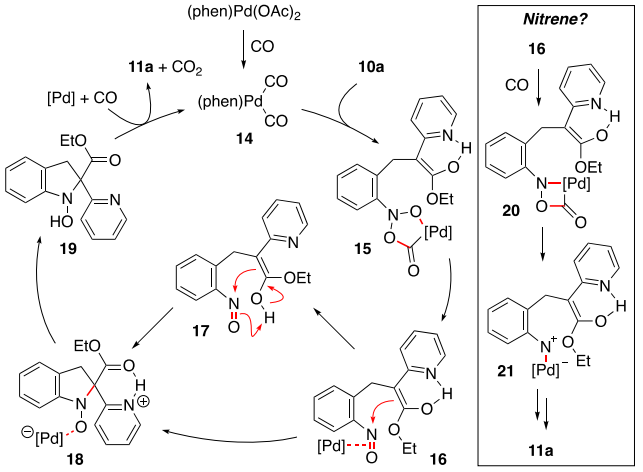


entry	#	12	13	%, yield[a]
1 2	a b			64, R = Bn 44, R = *t*-Bu
3	c			70
5	d			0
6 7 8	e f g			88, n = 1 62, n = 2 14, n =3
9	h			44
10	i			50
11	j			51
12	k			78
13	l			61
14	m			61

[a]Isolated yield of **13** after silica gel chromatography.

Because our reaction requires enolizable groups, this suggests that cyclization occurs through nucleophilic attack on an enol onto a nitrosoarene. The active catalyst for nitroarene reduction and cyclization could be generated from CO-mediated reduction of the palladium(II) precatalyst. Oxidative addition of nitroarene **10a** could then form palladacycle **15**.[16] Loss of CO_2 could generate nitrosoarene **16**,[17] which could be attacked by the pendant enol (or palladium enolate) to construct the sp^3-C−NAr bond.[18] Alternatively, the nitrosoarene could dissociate from palladium before nucleophilic attack.[8g,19] This dissociation could facilitate an ene-reaction to afford *N*-hydroxy indoline **18**.[5,20] Irrespective of how **18** is formed, reduction of the *N*-hydroxyindoline occurs to form **11a**.[21] A metal nitrene mechanism is also potentially possible for C−N bond formation. Reaction of the nitrosoarene with an additional CO ligand on palladium could produce palladacyclebutane **20**, which has been

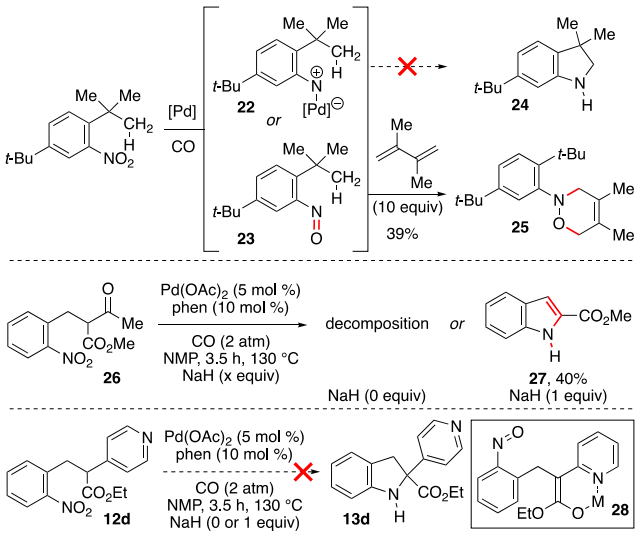
Scheme 2. Proposed Mechanism for Pd-Catalyzed sp^3-C−H Bond Formation To Access *N*-Heterocycles



characterized by X-ray crystallography by Osborn and co-workers in their studies into the mechanism of palladium-catalyzed carbonylation of nitroarenes.[22] A loss of CO_2 would produce palladium *N*-aryl nitrene **21**, which could react with the proximal enol to produce the *N*-heterocyclic product.

Several experiments were performed to test our proposed mechanism for reductive cyclization (see Scheme 3). To test for

Scheme 3. Mechanistic Probes



potential radical intermediates, TEMPO was examined as an additive for the cyclization of **10a**. Its addition to the reaction mixture did not significantly impact the yield of the transformation, suggesting that radical intermediates are not formed or do not escape the solvent shell in the catalytic cycle. To determine if an *N*-aryl nitrene such as **21** plays a critical role in these transformations, 2,5-di-*tert*-butylnitroarene was examined; however, only reduction to the corresponding aniline was observed. The 2,5-di-*tert*-butylnitrosoarene intermediate could be intercepted by 2,3-butadiene to afford oxazine **25**, suggesting that the nitrosoarene intermediate is not bound to palladium.[8b,c,23] Examination of acetoacetate-derived **26** provided insight into the effect of acidity and enolization on the reaction outcome.[24] Only decomposition was obtained when **26** was

DOI: 10.1021/acs.orglett.9b03458
Org. Lett. XXXX, XXX, XXX−XXX

subjected to the reaction conditions. The increased acidity of **26** appears to be responsible for the decomposition: deprotonation of **26** with NaH resulted in amination to form the deacylated indole **27**.[25] While deprotonation rescued the reactivity of **26**, deprotonation of 4-pyridyl **12d** did not result in *N*-heterocycle formation using palladium and CO. Since the use of an α-4-pyridyl group should not preclude an ene-reaction, we interpret this data as evidence that sp^3-C−N bond formation does not occur through an ene-reaction and that a bidentate chelation of the pyridyl group and the carboxylate to the metal ion (or proton) is critical for bond formation.

In conclusion, we have developed a palladium-catalyzed reductive cyclization of nitroarenes that converts a sp^3-C−H bond to a sp^3-C−N bond. By constructing the C−N bond through nucleophile attack onto a nitrosoarene catalytic intermediate, this reaction is mechanistically distinct from C−H bond amination reactions to enable synthesis of a variety of ring sizes and *N*-heterocycles by simply changing the identity of the nucleophile and tether length. Our future investigations will further probe the synthetic potential of each class of initially explored nucleophiles to define the fundamental electrophilicity of the nitrosoarene intermediate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03458.

Experimental procedures and analytical data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tgd@uic.edu.

ORCID

Navendu Jana: 0000-0002-7356-5382

Tom G. Driver: 0000-0001-7001-342X

Author Contributions

The manuscript was written through the contributions of all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Science Foundation (No. CHE-1564959) for their generous financial support. I.A. thanks the DAAD scholarship program for support. We thank Mr. Furong Sun (UIUC) for HRMS data.

■ REFERENCES

(1) (a) Du Bois, J. *Org. Process Res. Dev.* **2011**, *15*, 758. (b) Collet, F.; Lescot, C.; Dauban, P. *Chem. Soc. Rev.* **2011**, *40*, 1926. (c) Lu, H.; Zhang, X. P. *Chem. Soc. Rev.* **2011**, *40*, 1899. (d) Shin, K.; Kim, H.; Chang, S. *Acc. Chem. Res.* **2015**, *48*, 1040. (e) Jiao, J.; Murakami, K.; Itami, K. *ACS Catal.* **2016**, *6*, 610. (f) Park, Y.; Kim, Y.; Chang, S. *Chem. Rev.* **2017**, *117*, 9247.

(2) (a) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6728. (b) Espino, C. G.; Du Bois, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 598. (c) Espino, C. G.; Wehn, P. M.; Chow, J.; Du Bois, J. *J. Am. Chem. Soc.* **2001**, *123*, 6935. (d) Espino, C. G.; Fiori, K. W.; Kim, M.; Du Bois, J. *J. Am. Chem. Soc.* **2004**, *126*, 15378. (e) Fiori, K. W.; Du Bois, J. *J. Am. Chem. Soc.* **2007**, *129*, 562. (f) Milczek, E.; Boudet, N.; Blakey, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6825. (g) Kornecki, K. P.; Berry, J. F. *Chem. Commun.* **2012**, *48*, 12097.

(3) (a) Lebel, H. n.; Huard, K.; Lectard, S. *J. Am. Chem. Soc.* **2005**, *127*, 14198. (b) Huard, K.; Lebel, H. *Chem. - Eur. J.* **2008**, *14*, 6222. (c) Lebel, H.; Trudel, C.; Spitz, C. *Chem. Commun.* **2012**, *48*, 7799.

(4) (a) Lu, H.; Subbarayan, V.; Tao, J.; Zhang, X. P. *Organometallics* **2010**, *29*, 389. (b) Lu, H.; Jiang, H.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2010**, *49*, 10192. (c) Nguyen, Q.; Sun, K.; Driver, T. G. *J. Am. Chem. Soc.* **2012**, *134*, 7262. (d) Ryu, J.; Kwak, J.; Shin, K.; Lee, D.; Chang, S. *J. Am. Chem. Soc.* **2013**, *135*, 12861. (e) Shin, K.; Baek, Y.; Chang, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 8031. (f) Shin, K.; Ryu, J.; Chang, S. *Org. Lett.* **2014**, *16*, 2022. (g) Jiang, H.; Lang, K.; Lu, H.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 11604. (h) Lu, H.; Lang, K.; Jiang, H.; Wojtas, L.; Zhang, X. P. *Chem. Sci.* **2016**, *7*, 6934. (i) Kong, C.; Jana, N.; Jones, C.; Driver, T. G. *J. Am. Chem. Soc.* **2016**, *138*, 13271.

(5) (a) Adam, W.; Krebs, O. *Chem. Rev.* **2003**, *103*, 4131. (b) Srivastava, R. S.; Tarver, N. R.; Nicholas, K. M. *J. Am. Chem. Soc.* **2007**, *129*, 15250. (c) Penoni, A.; Palmisano, G.; Zhao, Y.-L.; Houk, K. N.; Volkman, J.; Nicholas, K. M. *J. Am. Chem. Soc.* **2009**, *131*, 653.

(6) (a) Momiyama, N.; Yamamoto, H. *J. Am. Chem. Soc.* **2003**, *125*, 6038. (b) Momiyama, N.; Torii, H.; Saito, S.; Yamamoto, H. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 5374. (c) Yamamoto, H.; Momiyama, N. *Chem. Commun.* **2005**, 3514.

(7) (a) Beaudoin, D.; Wuest, J. D. *Chem. Rev.* **2016**, *116*, 258. (b) Zuman, P.; Shah, B. *Chem. Rev.* **1994**, *94*, 1621. (c) Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Rev.* **2004**, *104*, 3315. (d) Priewisch, B.; Rück-Braun, K. *J. Org. Chem.* **2005**, *70*, 2350.

(8) (a) Srivastava, A.; Ma, Y.-A.; Pankayatselvan, R.; Dinges, W.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 853. (b) Johannsen, M.; Jorgensen, K. A. *J. Org. Chem.* **1994**, *59*, 214. (c) Srivastava, R. S.; Nicholas, K. M. *J. Org. Chem.* **1994**, *59*, 5365. (d) Johannsen, M.; Jorgensen, K. A. *J. Org. Chem.* **1995**, *60*, 5979. (e) Srivastava, R. S.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1996**, *118*, 3311. (f) Srivastava, R. S.; Nicholas, K. M. *Chem. Commun.* **1996**, 2335. (g) Srivastava, R. S.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 3302. (h) Murru, S.; Srivastava, R. S. *Eur. J. Org. Chem.* **2014**, *2014*, 2174. (i) Porter, D.; Poon, B. M. L.; Rutledge, P. J. *Beilstein J. Org. Chem.* **2015**, *11*, 2549.

(9) (a) Cenini, S.; Ragaini, F.; Tollari, S.; Paone, D. *J. Am. Chem. Soc.* **1996**, *118*, 11964. (b) Srivastava, R. S.; Nicholas, K. M. *Chem. Commun.* **1998**, 2705. (c) Ragaini, F.; Cenini, S.; Borsani, E.; Dompé, M.; Gallo, E.; Moret, M. *Organometallics* **2001**, *20*, 3390. (d) Ragaini, F.; Cenini, S.; Brignoli, D.; Gasperini, M.; Gallo, E. *J. Org. Chem.* **2003**, *68*, 460. (e) Formenti, D.; Ferretti, F.; Ragaini, F. *ChemCatChem* **2018**, *10*, 148.

(10) (a) Jana, N.; Zhou, F.; Driver, T. G. *J. Am. Chem. Soc.* **2015**, *137*, 6738. (b) Shevlin, M.; Guan, X.; Driver, T. G. *ACS Catal.* **2017**, *7*, 5518. (c) Zhou, F.; Wang, D.-S.; Guan, X.; Driver, T. G. *Angew. Chem., Int. Ed.* **2017**, *56*, 4530.

(11) Åkerbladh, L.; Odell, L. R.; Larhed, M. *Synlett* **2019**, *30*, 141.

(12) Wehman, P.; Borst, L.; Kamer, P. C. J.; Leeuwen, P. W. N. M. V. *Chem. Ber.* **1997**, *130*, 13.

(13) In ref 12, van Leeuwen and co-workers reported that the TOF of $(phen)_2Pd(OTf)_2$ diminished from 241 mol/mol h to 47 mol/mol h when the F_3C group was moved from the *para*-position to the *ortho*-position.

(14) In contrast, exposure of α-cyano- or α-nitro-substituted carboxylates to reaction conditions resulted in decomposition.

(15) For a discussion of the scope and limitations of $SnCl_2$-mediated reductive cyclization of difuryl-substituted nitroarenes, see: Uchuskin, M. G.; Molodtsova, N. V.; Abaev, V. T.; Trushkov, I. V.; Butin, A. V. *Tetrahedron* **2012**, *68*, 4252.

(16) (a) Paul, F.; Osborn, J. A.; Fischer, J.; Ochsenbein, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1638. (b) Paul, F.; Fischer, J.; Ochsenbein, P.; Osborn, J. A. *Organometallics* **1998**, *17*, 2199.

(17) Little, R. G.; Doedens, R. J. *Inorg. Chem.* **1973**, *12*, 537.

(18) (a) Albéniz, A. C.; Catalina, N. M.; Espinet, P.; Redón, R. *Organometallics* **1999**, *18*, 5571. (b) Sodeoka, M.; Hamashima, Y. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 941. (c) Cámpora, J.; Maya, C. M.; Palma, P.;

DOI: 10.1021/acs.orglett.9b03458
Org. Lett. XXXX, XXX, XXX−XXX

Carmona, E.; Gutiérrez, E.; Ruiz, C.; Graiff, C.; Tiripicchio, A. *Chem. - Eur. J.* **2005**, *11*, 6889. (d) Muñiz, K.; Streuff, J.; Chávez, P.; Hövelmann, C. H. *Chem. - Asian J.* **2008**, *3*, 1248.
(19) (a) Kolel-Veetil, M.; Khan, M. A.; Nicholas, K. M. *Organometallics* **2000**, *19*, 3754. (b) Srivastava, R. S.; Nicholas, K. M. *Organometallics* **2005**, *24*, 1563.
(20) Alternatively, sp^3-C−N bond formation in **17** could occur via stepwise attack of the enol nucleophile.
(21) (a) Penoni, A.; Volkmann, J.; Nicholas, K. M. *Org. Lett.* **2002**, *4*, 699. (b) Belley, M.; Sauer, E.; Beaudoin, D.; Duspara, P.; Trimble, L. A.; Dubé, P. *Tetrahedron Lett.* **2006**, *47*, 159. (c) Hirschhäuser, C.; Parker, J. S.; Perry, M. W. D.; Haddow, M. F.; Gallagher, T. *Org. Lett.* **2012**, *14*, 4846. (d) Yang, L.; Shi, L.; Xing, Q.; Huang, K.-W.; Xia, C.; Li, F. *ACS Catal.* **2018**, *8*, 10340.
(22) Leconte, P.; Metz, F.; Mortreux, A.; Osborn, J. A.; Paul, F.; Petit, F.; Pillot, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1616.
(23) Srivastava, R. S.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **2005**, *127*, 7278.
(24) (a) Tollari, S.; Cenini, S.; Crotti, C.; Gianella, E. *J. Mol. Catal.* **1994**, *87*, 203. (b) Wehman, P.; Borst, L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Mol. Catal. A: Chem.* **1996**, *112*, 23. (c) Ragaini, F.; Gasperini, M.; Cenini, S. *Adv. Synth. Catal.* **2004**, *346*, 63. (d) Gasperini, M.; Ragaini, F.; Cazzaniga, C.; Cenini, S. *Adv. Synth. Catal.* **2005**, *347*, 105. (e) Mooibroek, T. J.; Bouwman, E.; Drent, E. *Organometallics* **2012**, *31*, 4142.
(25) Huang, H.; Yang, Y.; Zhang, X.; Zeng, W.; Liang, Y. *Tetrahedron Lett.* **2013**, *54*, 6049.

DOI: 10.1021/acs.orglett.9b03458
Org. Lett. XXXX, XXX, XXX−XXX