Organic LETTERS

Letter

pubs.acs.org/OrgLett

Intramolecular, Site-Selective, Iodine-Mediated, Amination of Unactivated (sp^3)C−H Bonds for the Synthesis of Indoline Derivatives

Jinguo Long,[†] Xin Cao,[†] Longzhi Zhu,[†,‡] Renhua Qiu,[*,†,‡] Chak-Tong Au,[§] Shuang-Feng Yin,[*,†] Takanori Iwasaki,[‡] and Nobuaki Kambe[‡]

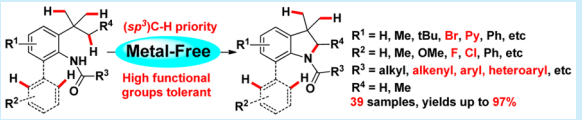
[†]State Key Laboratory of Chemo/Biosensing and Chemometrics,College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China

[‡]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

[§]College of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtang, China

S *Supporting Information*

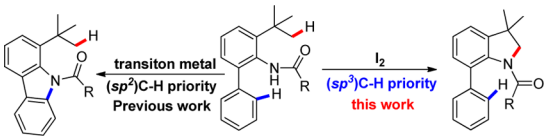
ABSTRACT: The Iodine-mediated oxidative intramolecular amination of anilines via cleavage of unactivated (sp^3)C−H and N−H bonds for the production of indolines is described. This transition-metal-free approach provides a straightforward strategy for producing (sp^3)C−N bonds for use in the preferential functionalization of unactivated (sp^3)C−H bonds over (sp^2)C−H bonds. The reaction could be performed on a gram scale for the synthesis of functionalized indolines.



Indolines, an extensive family of N-containing heterocycles, are structural motifs that are found in a number of biologically active natural products and are frequently employed as a key template in the synthesis of sophisticated structures by assembling various molecules.[1] Thus, the development of efficient methods for the preparation of indoline derivatives is an important issue. Intramolecular (sp^2)C−N bond formation by Buchwald−Hartwig amination[2a,b] was applied to the synthesis of *N*-substituted indolines via C−X bond activation.[2c,d] As a more elegant procedure, the transition-metal-catalyzed synthesis of *N*-substituted indolines via (sp^2)C−H bond activation was disclosed by Yu,[3a,b] Chen,[3c,d] Hirano, and Miura.[3e] Notably, Glorius,[4a] Chen,[3d] and Shi[4b] reported on the successful intramolecular amination of anilines via the concomitant cleavage of unactivated (sp^3)C−H and N−H bonds for the synthesis of indolines using Pd or Cu as catalysts. The synthesis of 2-acylindolines from ketones via (sp^3)C−H bond cleavage was disclosed by Zhang.[4c] Transition-metal-catalyzed oxidative C−H bond functionalization provides a powerful tool for step- and atom-economical synthetic transformations,[5] but sometimes suffers from undesired chemoselectivity. For example, in the above transition-metal-catalyzed indoline synthesis, (sp^2)C−N bond formation predominates over (sp^3)C−N bond formation when both (sp^2)C−H and (sp^3)C−H bonds are available at the appropriate positions (Scheme 1, left).[4a,b]

As an environmentally benign and less expensive methodology, the development of transition-metal-free systems has attracted considerable attention, recently.[6] Regarding C−H bonds activation,[6] iodine reagents, including hypervalent iodine derivatives, have been successfully used in oxidative C−C bond formation via dual C−H bond cleavage.[7] Similar oxidative C−N bond formation,[8] as well as the formation of C−O[9] and C−S[10] bonds, would provide a straightforward route to access the corresponding heteroatom molecules. However, these reactions could be used for the functionalization of only (sp)C−H bonds, (sp^2)C−H bonds, or activated (sp^3)C−H bonds, except for the case of the Hofmann−Löffler−Freytag (HLF) reaction, which affords pyrrolidines or pyrrolidones via 1,5-hydrogen radical transfer with the cleavage of unactivated (sp^3)C−H bonds by the aid of halogenes.[8l−o]

Scheme 1. Synthesis of Indolines via (sp^3)C−H Bond Activation



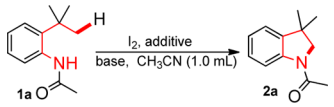
Herein, during the course of our study on C−H bond functionalization,[11] we report an iodine-mediated oxidative C−H/N−H bond coupling by the preferential functionalization of (sp^3)C−H over (sp^2)C−H bonds, giving rise to the selective formation of indolines and not carbazoles (Scheme 1, right), which is in sharp contrast to the transition-metal-catalyzed reactions.[4a,b]

We first examined the intramolecular cyclization of *N*-(2-*tert*-butylphenyl)acetamide (**1a**) and optimized the reaction conditions for this transformation (Table 1). The indoline **2a** was not produced in the absence of iodine (entry 1). The amount of iodine used in the reaction had a strong effect on reaction efficiency, as shown in entries 2−8. When 1.0 and 1.2 equiv of iodine were used, **2a** was formed in high yields, i.e., 93% and 97%, respectively (entries 6 and 7). In the absence of DTBP (di-*tert*-butylperoxide), **2a** was produced in only 43% yield, and without a base (entry 10),

Received: March 22, 2017

DOI: 10.1021/acs.orglett.7b00846
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization of Reaction Conditions



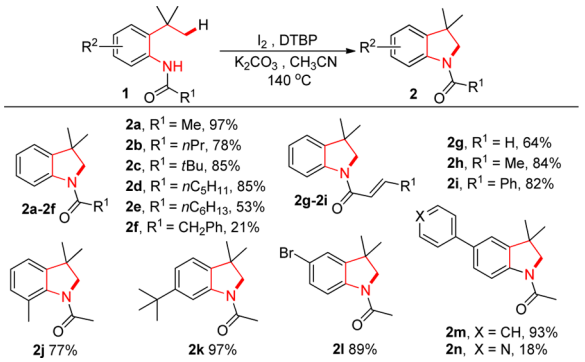
entry[a]	catalyst (equiv)	additive	base	yield (%)
1	–	DTBP	K_2CO_3	ND[b]
2	I_2 (0.1)	DTBP	K_2CO_3	14
3	I_2 (0.2)	DTBP	K_2CO_3	31
4	I_2 (0.4)	DTBP	K_2CO_3	47
5	I_2 (0.5)	DTBP	K_2CO_3	57
6	I_2 (1.0)	DTBP	K_2CO_3	93
7	**I_2 (1.2)**	**DTBP**	**K_2CO_3**	**97**
8	I_2 (1.5)	DTBP	K_2CO_3	91
9	I_2 (1.2)	–	K_2CO_3	43
10	I_2 (1.2)	DTBP	–	ND[b]

[a]Substrate **1a** (0.2 mmol, 1.0 equiv), additive (3.0 equiv), base (2.0 equiv), 24 h, 140 °C; isolated yield. [b]Not detected by ^1H NMR.

no **2a** was formed. Thus, the optimized conditions are substrate **1a** (1.0 equiv), I_2 (1.2 equiv), K_2CO_3 (2.0 equiv), and DTBP (3.0 equiv) in acetonitrile (1.0 mL) at 140 °C for 24 h.

We then examined the scope of substrates under the optimized reaction conditions (Schemes 2–4). Scheme 2 summarizes the

Scheme 2. Effect of Substrate at the Carbonyl Group and the Phenyl Ring[a]

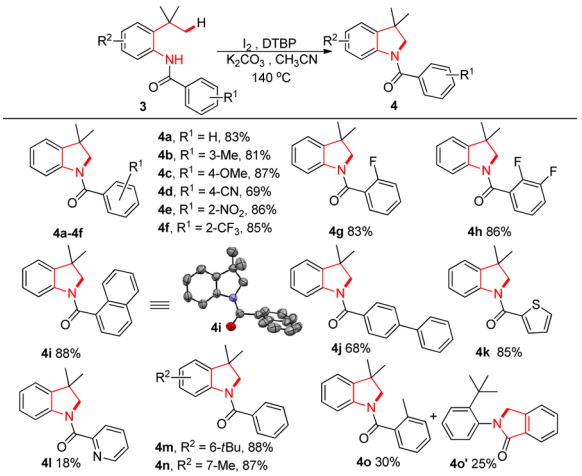


[a]Substrate **1** (0.2 mmol, 1.0 equiv), I_2 (1.2 equiv), DTBP (3.0 equiv), K_2CO_3 (2.0 equiv), CH_3CN (1.0 mL), 140 °C, 24 h; isolated yield of **2**.

effects of substituents at the carbonyl group and the phenyl ring. Alkyl amides with Me, *t*Bu, nC_3H_7, nC_5H_{11}, or nC_6H_{13} on the amide group afforded the corresponding products (**2a–2e**) in good yields. It should be noted that the present method could also be applied to a pivalamide **1c** which did not produce **2c** in a Pd-catalyzed reaction.[4a] Nonetheless, the benzyl amide **1f** afforded low yields of **2f** (21%) probably due to the weak benzylic C–H bond (*vide infra*). Alkenyl groups (**2g–2i**) showed high compatibility. This reaction was also compatible when various substituents were attached to the aromatic ring such as Me (**2j**, 77%), *t*Bu (**2k**, 97%), Br (**2l**, 89%), and Ph (**2m**, 93%). Unfortunately, 4-pyridylindoline **2n** was obtained in only 18% yield.

We then examined the synthesis of *N*-benzoyl indolines **4** using the present oxidative C–N coupling of **3**, because this transformation does not proceed in the case of the Pd-catalyzed system, probably because the (sp^2)C–H bond cleavage of the benzoyl group is faster than the (sp^3)C–H bond cleavage of the *t*Bu group.[4a] Gratifyingly, the desired products (**4a–4o**) were obtained in high yields in the metal-free iodine system, as shown in Scheme 3. Electron-donating (*m*-methyl **4b**, *p*-methoxy **4c**)

Scheme 3. Selective (sp^3)C–H Functionalization of Benzanilides[a]

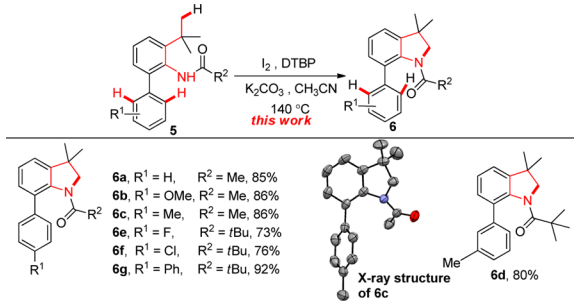


[a]Substrate **3** (0,2 mmol, 1.0 equiv), I_2 (1.2 equiv), DTBP (3.0 equiv), K_2CO_3 (2.0 equiv), CH_3CN (1.0 mL), 140 °C, 24 h; isolated yield of **4**.

and electron-withdrawing (CN **4d**, NO_2 **4e**, F **4f–4h**) groups exerted little influence on the efficiency of the reaction (**4b–4m**). Naphthyl and biphenyl substituted compounds, such as **4i** and **4j**, were produced in 88% and 68% yields, respectively. The heteroarene-substituted indoline **4k** containing a thienyl group was produced in 85% yield, but the reaction of a pyridyl substrate resulted in a low yield (**4l**, 18%). Me and *t*Bu substituents on the aniline ring gave high yields of the corresponding indolines (**4m**, 88%; **4n**, 87%). These results demonstrate that the iodine-mediated approach is superior to the Pd system[4a] for the synthesis of *N*-benzoyl substituted indolines. In the case of **3o**, which contains an *ortho*-methylbenzamide unit, there were two competing cyclization pathways giving rise to a mixture of indoline **4o** (30%) via unactivated C–H bond cleavage and isoindolinone **4o′** (25%) via benzylic C–H bond cleavage.

To investigate the selectivity of this method in more detail, the *ortho*-arylacetoanilide **5** having both (sp^2)C–H and (sp^3)C–H bonds at appropriate position were examined (Scheme 4). All of the substrates that were examined, including those bearing H,

Scheme 4. Competitive Experiments: (sp^2)C–H versus (sp^3)C–H[a]

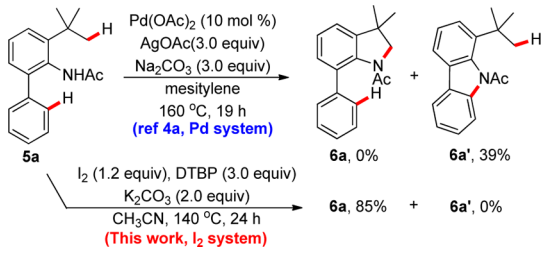


[a]Substrate **5** (0.2 mmol, 1.0 equiv), I_2 (1.2 equiv), K_2CO_3 (2.0 equiv), DTBP (3.0 equiv), CH_3CN (1.0 mL), 140 °C, 24 h; isolated yield of **6**.

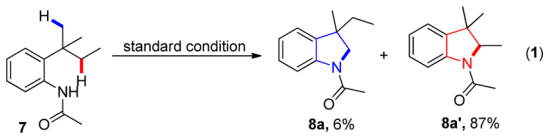
DOI: 10.1021/acs.orglett.7b00846
Org. Lett. XXXX, XXX, XXX–XXX

OMe, Me, F, Cl, or Ph groups, underwent (sp^3)C−H bond amination exclusively to give the target products (**6a**−**6g**) in good yields (73%−92%). This is again in sharp contrast to Pd-catalyzed reaction in which (sp^2)C−N amidation is the preferred route, forming the carbazole **6a′** (Scheme 5).[4a,b] This method offers a new route to the synthesis of C-7 arylated indolines via (sp^3)C−H amidation as a supplementary method to the Ar−H arylation of indlines.[12]

Scheme 5. Indoline Synthesis versus Carbazole Synthesis



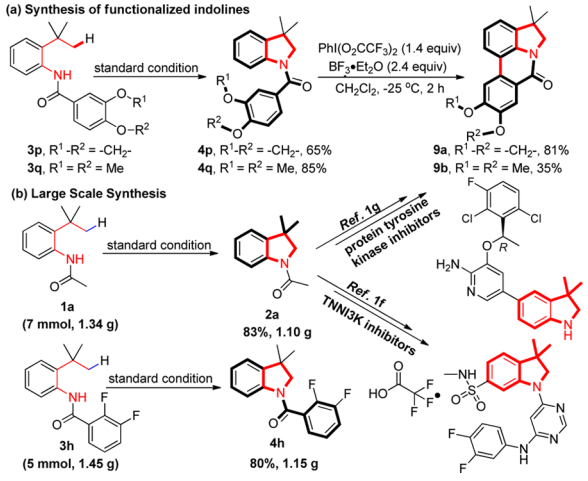
A comparison of the reactivities between primary C−H bonds and secondary C−H bonds was also made (eq 1). The product **8a**,



arising from the primary C−H bond cleavage, was formed in only 6% yield and the desired product **8a′** was produced in 87% yield. It was reported that Cu-catalyzed intramolecular C−H bond amidation afforded **8a′** in only moderate yield (57%).[4b]

We then attempted some synthetic applications, to access the potential of the procedure as a practical tool for the synthesis of functionalized indolines. Natural product precursors **4p** and **4q** were synthesized using our iodine approach in 65% and 85% yields from amides **3p** and **3q**, and subsequent oxidative cyclization led to the formation of the anhydrolycorinone and oxoassoanine derivatives **9a** and **9b** in 81% and 35% yields, respectively (Scheme 6a).[1b] In addition, a large scale synthesis of **2a**, a precursor of TNNI3k inhibitors[1f] and protein tyrosine kinase inhibitors,[1g] and **4h**, with a core skeleton of Mas receptor

Scheme 6. Application Experiments and Gram-Scale Synthesis

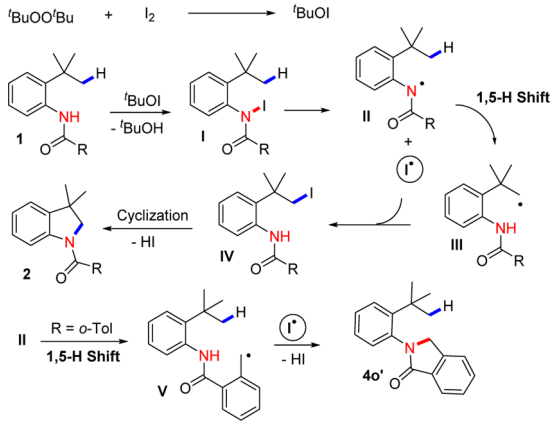


ligands,[1d,e] were successfully prepared in 83% (1.10 g) and 80% (1.15 g) yields, respectively (Scheme 6b).

To gain additional insight into the mechanisms of this reaction, the following experiments were performed (see Supporting Information (SI)). When the reaction was carried out in the presence of a radical inhibitor (2,2,6,6-tetramethylpiperidine-1-yl)oxidanyl (TEMPO), hydroquinone (HQ), or 2,6-diisopropyl-4-methylphenol (BHT),[8d] no **2a** was generated, suggesting the involvement of a radical pathway. When KI or KIO_3 was used in place of iodine, **2a** was not formed. This result suggests that "I^-" or IO_3^- is not likely to be the actual active species. When the reaction of **1a** was performed in the presence of indoline, only a trace amount of **2a** was formed. This result and the low yield of **4l** (Scheme 3) indicate that the reaction is affected by amines.

Based on the above findings and literature information,[8l−o,13] we propose the mechanism shown in Scheme 7. The initial

Scheme 7. Proposed Mechanism



reaction of DTBP with iodine leads to the formation of *t*BuOI[13] which reacts with the N−H bond to form the intermediate **I** and *t*BuOH. Cleavage of the N−I bond affords the nitrogen-centered radicals **II** at elevated temperatures. According to the Hofmann−Löffler−Freytag reaction,[8l−o] the *N*-radical induces a 1,5-H shift to give a carbon-centered radical **III** which can be readily quenched with an iodine radical to give the intermediate **IV**. The subsequent intramolecular substitution gives the indoline **2** furnishing (sp^3)C−N amidation. When R is an *o*-tolyl or benzyl group, a 1,5-H shift also occurs at the benzylic position leading to the formation of **4o′** as a minor product or resulting in a low yield of **2f**, respectively (Scheme 2).

In summary, we report on a novel method for the synthesis of *N*-acylindolines via intramolecular oxidative (sp^3)C−N cross-coupling. The reaction proceeds efficiently without a metal catalyst and shows good tolerance to a variety of substituents. This protocol opens a new avenue for the synthesis of nitrogen-containing heterocycles via the site-selective cleavage of (sp^3)C−H bonds over (sp^2)C−H bonds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00846.

Experimental procedures, screening of reaction conditions, and characterization data (PDF)
Crystallographic data for **4i** (CIF)
Crystallographic data for **6c** (CIF)

DOI: 10.1021/acs.orglett.7b00846
Org. Lett. XXXX, XXX, XXX−XXX

AUTHOR INFORMATION

Corresponding Authors

*E-mail: renhuaqiu@hnu.edu.cn.
*E-mail: sf_yin@hnu.edu.cn.

ORCID

Longzhi Zhu: 0000-0001-5161-9944
Renhua Qiu: 0000-0002-8423-9988
Takanori Iwasaki: 0000-0002-6663-3826

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors wish to thank the Natural Science Foundation of China (21373003 and 21676076), the Natural Science Foundation of Hunan Province, China (2016JJ3034), the Hunan Youth Talent (2016RS3023), and the Chinese Scholarship Council for financial support. We also wish to thank Prof. Akihiro Orita (Okayama University of Science), Prof. Wai-Yeung Wong (Hong Kong Polytechnic University), and Prof. Li.-Biao. Han (AIST, Tsukuba, Japan), for helpful discussions.

REFERENCES

(1) For selected reports on the synthesis of sophisticated structures with indoline templates, see: (a) Gruenfeld, N.; Stanton, J. L.; Yuan, A. M.; Ebetino, F. A.; Browne, L. J.; Gude, C.; Huebner, C. F. *J. Med. Chem.* **1983**, *26*, 1277. (b) Ganton, M. D.; Kerr, M. A. *Org. Lett.* **2005**, *7*, 4777. (c) Sirasani, G.; Paul, T.; Dougherty, W.; Kassel, S.; Andrade, R. B. *J. Org. Chem.* **2010**, *75*, 3529. (d) Boatman, D. P.; Adams, J. W.; Moody, J. V.; Babych, E. D.; Schrader, T. O. WO 2005063745. (e) Tran, T.-A.; Han, S. WO 2007002114. (f) Kallander, L. S.; Lawhorn, B. G.; Philip, J.; Zhao, Y. WO 2011088027. (g) Xi, N.; Wang, R.; Wang, L. WO 2014089324. (h) He, Y.-P.; Zhang, C.; Fan, M.; Wu, Z.; Ma, D. *Org. Lett.* **2015**, *17*, 496.

(2) For Buchwald−Hartwig amination, see: (a) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609. For selected synthesis of indolines via Buchwald−Hartwig amination, see: (b) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348. (c) Yamada, K.; Kubo, T.; Tokuyama, H.; Fukuyama, T. *Synlett* **2002**, *2002*, 231. (d) Omar-Amrani, R.; Thomas, A.; Brenner, E.; Schneider, R.; Fort, Y. *Org. Lett.* **2003**, *5*, 2311.

(3) For selected reports on (sp^2)C−H activation for the synthesis of indolines, see: (a) Mei, T.-S.; Wang, X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 10806. (b) Mei, T.-S.; Leow, D.; Xiao, H.; Laforteza, B. N.; Yu, J.-Q. *Org. Lett.* **2013**, *15*, 3058. (c) He, G.; Lu, C.; Zhao, Y.; Nack, W. A.; Chen, G. *Org. Lett.* **2012**, *14*, 2944. (d) He, G.; Zhao, Y.; Zhang, S.; Lu, C.; Chen, G. *J. Am. Chem. Soc.* **2012**, *134*, 3. (e) Takamatsu, K.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2015**, *80*, 3242.

(4) For selected reports on cleavage of (sp^3)C−H and N−H bonds for the synthesis of indolines, see: (a) Neumann, J. J.; Rakshit, S.; Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6892. (b) Pan, F.; Wu, B.; Shi, Z.-J. *Chem. - Eur. J.* **2016**, *22*, 6487. (c) Gao, W.-C.; Jiang, S.; Wang, R.-L.; Zhang, C. *Chem. Commun.* **2013**, *49*, 4890.

(5) For selected reviews on C−H activation: (a) Johannsen, M.; Jørgensen, K. *Chem. Rev.* **1998**, *98*, 1689. (b) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (c) Zalatan, D. N.; Bois, D. *Top. Curr. Chem.* **2009**, *292*, 347. (d) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (e) Misal-Castro, L. C.; Chatani, N. *Chem. Lett.* **2015**, *44*, 410. (f) Liu, C.; Yuan, J.; Gao, M.; Tang, S.; Li, W.; Shi, R.; Lei, A. *Chem. Rev.* **2015**, *115*, 12138. (g) Shin, K.; Kim, H.; Chang, S. *Acc. Chem. Res.* **2015**, *48*, 1040. (h) Liu, B.; Hu, F.; Shi, B.-F. *ACS Catal.* **2015**, *5*, 1863. (i) Yang, Y.; Lan, J.; You, J. *Chem. Rev.* **2017**, DOI: 10.1021/acs.chemrev.6b00567. (j) He, J.; Wasa, M.; Chan, K. S. L.; Shao, Q.; Yu, J.-Q. *Chem. Rev.* **2016**, DOI: 10.1021/acs.chemrev.6b00622.

(6) For selected reviews on transition-metal-free C−H functionalization, see: (a) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem.* **2013**, *2013*, 5769. (b) Finkbeiner, P.; Nachtsheim, B. J. *Synthesis* **2013**, *45*, 979. (c) Sun, C.-L.; Shi, Z.-J. *Chem. Rev.* **2014**, *114*, 9219. (d) Liu, D.; Lei, A. *Chem. - Asian J.* **2015**, *10*, 806.

(7) For selected reports on iodine reagent-mediated/-catalyzed C−C bond formation, see: (a) Ito, M.; Kubo, H.; Itani, I.; Morimoto, K.; Dohi, T.; Kita, Y. *J. Am. Chem. Soc.* **2013**, *135*, 14078. (b) Matcha, K.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 2082. (c) Moteki, S. A.; Usui, A.; Selvakumar, S.; Zhang, T.; Maruoka, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 11060. (d) Ghosh, S.; Chaudhuri, S.; Bisai, A. *Org. Lett.* **2015**, *17*, 1373. (e) Zhu, C.; Liang, Y.; Hong, X.; Sun, H.; Sun, W.-Y.; Houk, K. N.; Shi, Z. *J. Am. Chem. Soc.* **2015**, *137*, 7564. (f) Wu, X.; Gao, Q.; Geng, X.; Zhang, J.; Wu, Y.-D.; Wu, A.-X. *Org. Lett.* **2016**, *18*, 2507.

(8) For selected recent reports on the iodine reagent-mediated/-catalyzed C−N formation, see: (sp)C−H amination: (a) Souto, J.; Becker, P.; Iglesias, Á.; Muñiz, K. *J. Am. Chem. Soc.* **2012**, *134*, 15505. (sp^2)C−H amination: (b) Manna, S.; Matcha, K.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2014**, *53*, 8163. (c) Li, Y.-L.; Li, J.; Ma, A.-L.; Huang, Y.-N.; Deng, J. *J. Org. Chem.* **2015**, *80*, 3841. (d) Beukeaw, D.; Udomsasporn, K.; Yotphan, S. *J. Org. Chem.* **2015**, *80*, 3447. (e) Martínez, C.; Bosnidou, A. E.; Allmendinger, S.; Muñiz, K. *Chem. - Eur. J.* **2016**, *22*, 9929. (sp^3)C−H amination: (f) Ilangovan, A.; Satish, G. *J. Org. Chem.* **2014**, *79*, 4984. (g) Wu, X.; Gao, Q.; Liu, S.; Wu, A.-X. *Org. Lett.* **2014**, *16*, 2888. (h) Verma, A.; Patel, S.; Meenakshi; Kumar, A.; Yadav, A.; Kumar, S.; Jana, S.; Sharma, S.; Prasad, C. D.; Kumar, S. *Chem. Commun.* **2014**, *51*, 1371. (i) Martínez, C.; Muñiz, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 8287. (j) Zhu, C.; Liang, Y.; Hong, X.; Sun, H.; Sun, W.-Y.; Houk, K. N.; Shi, Z. *J. Am. Chem. Soc.* **2015**, *137*, 7564. (k) Kiyokawa, K.; Takemoto, K.; Minakata, S. *Chem. Commun.* **2016**, *52*, 13082. (l) Fan, R.; Pu, D.; Wen, F.; Wu, J. *J. Org. Chem.* **2007**, *72*, 8994. (m) Liu, T.; Mei, T.-S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 5871. (n) Sakic, D.; Zipse, H. *Adv. Synth. Catal.* **2016**, *358*, 3983. (o) Wappes, E. A.; Fosu, S. C.; Chopko, T. C.; Nagib, D. A. *Angew. Chem., Int. Ed.* **2016**, *55*, 9974.

(9) For selected iodine reagent-mediated/-catalyzed C−O formation, see: (a) Fujita, M.; Yoshida, Y.; Miyata, K.; Wakisaka, A.; Sugimura, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7068. (b) Wang, X.; Gallardo-Donaire, J.; Martin, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 11084. (c) Xu, W.; Nachtsheim, B. J. *Org. Lett.* **2015**, *17*, 1585. (d) Li, C.; Jin, T.; Zhang, X.; Li, C.; Jia, X.; Li, J. *Org. Lett.* **2016**, *18*, 1916. Oxidation of a methylene to a carbonyl group was also reported: (e) Moteki, S. A.; Usui, A.; Zhang, T.; Solorio Alvarado, C. R.; Maruoka, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 8657. (f) Moteki, S. A.; Selvakumar, S.; Zhang, T.; Usui, A.; Maruoka, K. *Asian J. Org. Chem.* **2014**, *3*, 932.

(10) For selected reports on iodine reagent-mediated/-catalyzed C−S formation, see: (a) Tang, S.; Wu, Y.; Liao, W.; Bai, R.; Liu, C.; Lei, A. *Chem. Commun.* **2014**, *50*, 4496. (b) Badsara, S. S.; Liu, Y.-C.; Hsieh, P.-A.; Zeng, J.-W.; Lu, S.-Y.; Liu, Y.-W.; Lee, C.-F. *Chem. Commun.* **2014**, *50*, 11374. (c) Kang, X.; Yan, R.; Yu, G.; Pang, X.; Liu, X.; Li, X.; Xiang, L.; Huang, G. J. *J. Org. Chem.* **2014**, *79*, 10605. (d) Liao, Y.; Jiang, P.; Chen, S.; Qi, H.; Deng, G.-J. *Green Chem.* **2013**, *15*, 3302.

(11) (a) Qiu, R.; Iwasaki, T.; Reddy, V. P.; Kambe, N. *J. Org. Chem.* **2015**, *80*, 367. (b) Wang, X.; Qiu, R.; Yan, C.; Reddy, V. P.; Zhu, L.; Xu, X.; Yin, S.-F. *Org. Lett.* **2015**, *17*, 1970. (c) Wang, X.; Zhu, L.; Chen, S.; Xu, X.; Au, C.-T.; Qiu, R. *Org. Lett.* **2015**, *17*, 5228. (d) Zhu, L.; Qiu, R.; Cao, X.; Xiao, S.; Xu, X.; Au, C. T.; Yin, S.-F. *Org. Lett.* **2015**, *17*, 5528. (e) Su, L.; Dong, J.; Liu, L.; Sun, M.; Qiu, R.; Zhou, Y.; Yin, S.-F. *J. Am. Chem. Soc.* **2016**, *138*, 12348.

(12) For selected synthesis of C-7 arylated indolines via C−H arylation, see: (a) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (b) Shi, Z.; Li, B.; Wan, X.; Cheng, J.; Fang, Z.; Cao, B.; Qin, C.; Wang, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5554. (c) Nishikata, T.; Abela, A. R.; Huang, S.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2010**, *132*, 4978. (d) Jiao, L. Y.; Oestreich, M. *Chem. - Eur. J.* **2013**, *19*, 10845. (e) Jiao, L. Y.; Smirnov, P.; Oestreich, M. *Org. Lett.* **2014**, *16*, 6020. (f) Luo, H.; Liu, H.; Zhang, Z.; Xiao, Y.; Wang, S.; Luo, X.; Wang, K. *RSC Adv.* **2016**, *6*, 39292.

(13) Luo, W.-K.; Shi, X.; Zhou, W.; Yang, L. *Org. Lett.* **2016**, *18*, 2036.

DOI: 10.1021/acs.orglett.7b00846
Org. Lett. XXXX, XXX, XXX−XXX