OL Organic Letters

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Palladium-Catalyzed Tandem Dehydrogenative [4 + 2] Annulation of Terminal Olefins with *N*-Sulfonyl Amides via C−H Activations

Manman Sun, Weida Chen, Xiangyu Xia, Guodong Shen, Yongmin Ma, Jianguo Yang, Hanfeng Ding, and Zhiming Wang*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01011 Read Online

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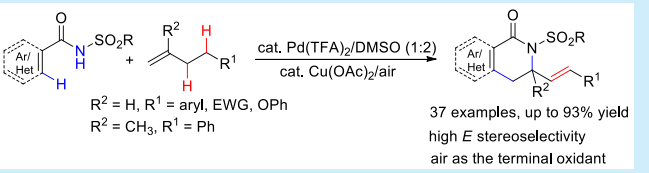
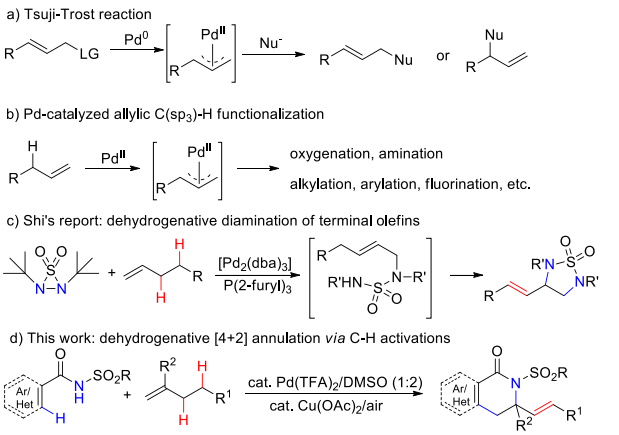
ABSTRACT: A palladium-catalyzed tandem dehydrogenative [4 + 2] annulation of terminal olefins with *N*-sulfonyl amides via C(sp^2)−H activation, allylic C(sp^3)−H activation, and homoallylic C(sp^3)−H elimination processes has been developed. Promoted by the DMSO ligand, various benzamides, heterocyclic arylamides, alkenyl carboxamides, and commercial olefins are found to be efficient substrates to construct important heterocyclic compounds bearing a vinyl substituent with high *E* stereoselectivity. Using air as the terminal oxidant also provides a great advantage regarding environmental friendliness.



The Tsuji−Trost reaction is well established as a powerful tool in organic synthesis, for the retained degree of unsaturation in the allylic products is easily manipulated to access various versatile functional groups (Scheme 1a).[1]

Scheme 1. Pd-Catalyzed Allylic Substitution Reactions

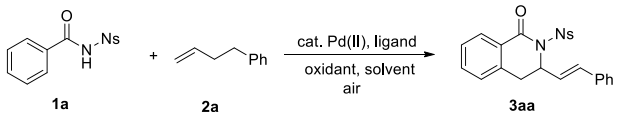


Compared with using the preactivated alkenes with an allylic leaving group (LG), such as ester, halide, carbonate, carbamate, and phosphate, directly oxidative allylic C(sp^3)−H cleavage of simple alkenes to generate the π-allyl palladium intermediates is more challenging, owing to the weak coordination ability of the C(sp^3)−H bond with palladium[2] and the competitive addition reaction of the carbon−carbon double bond with palladium.[3] Nevertheless, with the assistance of ligands[4] and/or by modification of reaction conditions,[5] numerous reactions including palladium-catalyzed allylic C-(sp^3)−H oxygenation,[4a,5c] amination,[4b,d] alkylation,[4e,i−m] arylation,[4h,5a] fluorination,[4c] and others[4g] have also been developed (Scheme 1b).[6] However, palladium-catalyzed tandem reactions involving allylic C(sp^3)−H functionalization are rarely reported.[7] In 2008, the Shi group reported a palladium-catalyzed tandem dehydrogenative diamination of terminal olefins (Scheme 1c).[8] In this report, the used *N*,*N*-di-*tert*-butylthiadiaziridine 1,1-dioxide was a dual nitrogen source. After allyl sulfamide was formed first, the retained N−H bond and carbon−carbon double bond subsequently underwent palladation and β-hydride elimination pathways, affording the cyclic diamine product. This tandem reaction shows great advantage in enabling the rapid construction of complexly cyclic compounds from simple starting materials. Hence, determining how to utilize a suitable substrate with dual nucleophilic centers to perform the dehydrogenative annulation with terminal olefins involving allylic C(sp^3)−H functionalization is challenging and rewarding.

Palladium-catalyzed directed C(sp^2)−H functionalization of amides is an appealing area,[9] especially the cascade cyclization reactions,[9b,10] since the CONHR group can serve not only as a directing group for C(sp^2)−H functionalization but also as a precursor to the C−N bond. Hence, we hypothesized that benzamides could be chosen as the dual nucleophilic sources to perform the dehydrogenative [4 + 2] annulation with terminal olefins. However, palladium-catalyzed [4 + 2] annulation of benzamides with isolated alkenes is still a

Received: March 19, 2020

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3aa

entry	catalyst	ligand	oxidant	yield (%)[b]
1	$Pd(TFA)_2$	–	$Cu(OAc)_2$	56
2	$Pd(OAc)_2$	–	$Cu(OAc)_2$	44
3	$PdCl_2$	–	$Cu(OAc)_2$	47
4	**$Pd(TFA)_2$**	**DMSO**	**$Cu(OAc)_2$**	**93**
5[c]	$Pd(TFA)_2$	–	$Cu(OAc)_2$	trace
6	$Pd(TFA)_2$	tetramethylene sulfoxide	$Cu(OAc)_2$	70
7	$Pd(TFA)_2$	diphenyl sulfoxide	$Cu(OAc)_2$	57
8	$Pd(TFA)_2$	methyl phenyl sulfone	$Cu(OAc)_2$	53
9	$Pd(TFA)_2$	PPh_3	$Cu(OAc)_2$	64
10	$Pd(TFA)_2$	2,5-dimethyl-1,4-benzoquinone	$Cu(OAc)_2$	46
11	$Pd(TFA)_2$	[1,1′-binaphthalene]-2,2′-diol	$Cu(OAc)_2$	44
12	$Pd(TFA)_2$	pyridine	$Cu(OAc)_2$	0
13	$Pd(TFA)_2$	phenanthroline	$Cu(OAc)_2$	8
14[d]	$Pd(TFA)_2$	DMSO	$Cu(OAc)_2$	72
15[e]	$Pd(TFA)_2$	DMSO	$Cu(OAc)_2$	56
16	$Pd(TFA)_2$	DMSO	–	10
17	$Pd(TFA)_2$	DMSO	BQ	8
18	$Pd(TFA)_2$	DMSO	Ag_2CO_3	62
19	$Pd(TFA)_2$	DMSO	$PhI(OAc)_2$	trace
20[f]	$Pd(TFA)_2$	DMSO	$Cu(OAc)_2$	27
21[g]	$Pd(TFA)_2$	DMSO	$Cu(OAc)_2$	51
22[h]	$Pd(TFA)_2$	DMSO	$Cu(OAc)_2$	23

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Pd-catalyst (0.02 mmol), ligand (0.04 mmol), oxidant (0.04 mmol), and solvent (2 mL) at 100 °C under air for 18 h. [b]Isolated yield. [c]The solvent is DMSO. [d]At 90 °C for 24 h. [e]$Pd(TFA)_2$ (0.01 mmol). [f]The solvent is 1,4-dioxane. [g]The solvent is PhCl. [h]The solvent is MeCN under refluxing.

challenge,[11] mostly tending to perform the $C(sp^2)$–H olefination/annulation processes.[12] Toward this goal, 1,3-dienes have been developed to successful substances to conduct the [4 + 2] annulation with amides through π-allyl palladium intermediate.[12a,13] However, the 1,3-dienes should be synthesized from corresponding aldehydes. Given the abundance of commercial terminal olefins (>1600) versus the relative scarcity of 1,3-dienes (120), we anticipated that if a carefully chosen Pd-catalytic system could promote the dehydrogenative [4 + 2] annulation of terminal olefins, a significant synthetic advantage in forming bioactively and medicinally important 3,4-dihydroisoquinolones would be provided.[14] Herein, we describe the palladium-catalyzed tandem dehydrogenative [4 + 2] annulation of terminal olefins with *N*-sulfonyl amides via $C(sp^2)$–H activation, allylic $C(sp^3)$–H activation, and homoallylic $C(sp^3)$–H elimination processes, in which the DMSO ligand plays a significant role (Scheme 1d). Moreover, the reaction proceeds by using air as the terminal oxidant, which avoids the waste of the oxidation and decreases the environmentally hazardous byproducts obtained with excessive oxidant.[15]

Substrates **1a** and **2a** were carried out to determine the optimal reaction conditions (Table 1). Initially, with 10 mol % $Pd(TFA)_2$ and 20 mol % $Cu(OAc)_2$, the two substrates afforded the desired dehydrogenative [4 + 2] annulation product **3aa** in 56% yield with *E* stereoselectivity in *p*-xylene at 100 °C for 18 h under air (entry 1). Examination of other Pd-catalysts showed that more electrophilic $Pd(TFA)_2$ had a higher yield than $Pd(OAc)_2$ and $PdCl_2$ (entries 2 and 3). Considering that sulfoxide ligands such as DMSO can promote the allylic $C(sp^3)$–H functionalization,[4a,6a] we added 20 mol % DMSO to the reaction. To our delight, an excellent 93% yield was obtained (entry 4). However, when the reaction was performed in DMSO, only trace product was detected (entry 5), which excluded the effect of the polarity of DMSO. Unfortunately, other sulfoxide ligands as well as sulfone, PPh_3, benzoquinone, and binaphthol ligands did not give a higher yield than DMSO (entries 6–11). Nitrogen-based ligands such as pyridine and phenanthroline were not suitable ligands for this reaction (entries 12 and 13). These results demonstrate the beneficial effect of the DMSO ligand. We consider that this effect may be due to the DMSO ligation to palladium.[16] The in situ formed $Pd(DMSO)_2(TFA)_2$ catalyst exhibits both hard *O*- and soft *S*-bound DMSO ligands,[16a] which may work cooperatively in the interconversion between the relatively hard Pd(II) and soft Pd(0) redox states.[16b] The *O*-DMSO ligand is kinetically labile, contrasting with the behavior of a nitrogen-based ligand, which might be important to enable weakly coordinating substrates to coordinate to Pd(II), such as the $C(sp^2)$–H bond and the allylic $C(sp^3)$–H bond, facilitating the electrophilic C–H cleavages.[6a] The kinetically labile nature also may be important to activate the π-allyl palladium intermediates, facilitating the nucleophilic π-allyl palladium functionalization.[4a] The *S*-DMSO ligand can stabilize the Pd(0) complex, which inhibits the formation of palladium black and facilitates the oxidation of the Pd(0) catalyst.[16c] The yield decreased to 72% when the temperature reduced to 90 °C for 24 h (entry 14). The yield decreased to 56% when the amount of $Pd(TFA)_2$ decreased to 5 mol % (entry 15). Omitting $Cu(OAc)_2$ led to a sharp decrease of the

https://dx.doi.org/10.1021/acs.orglett.0c01011
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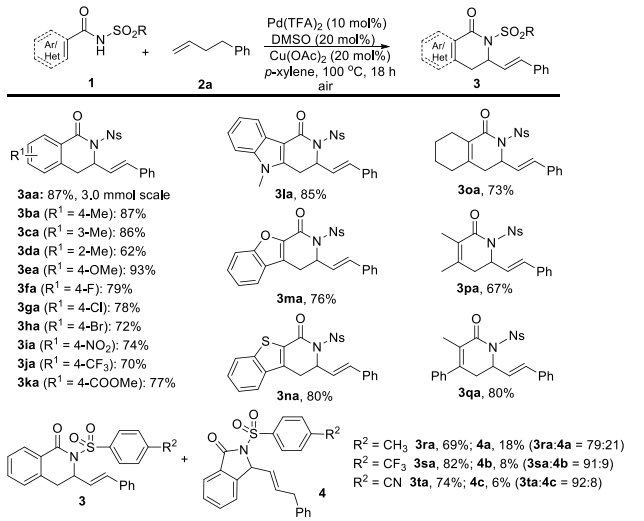
yield (entry 16). Changing the oxidant to BQ, Ag_2CO_3, $PhI(OAc)_2$ or solvent to 1,4-dioxane, PhCl, MeCN could not improve the reaction (entries 17−22). Eventually, satisfactory reaction conditions were obtained as shown in entry 4.

As shown in Scheme 2, a gram-scale reaction of substrates **1a** and **2a** was carried out under optimized reaction conditions.

Scheme 2. Dehydrogenative [4 + 2] Annulation of Amides with 2a

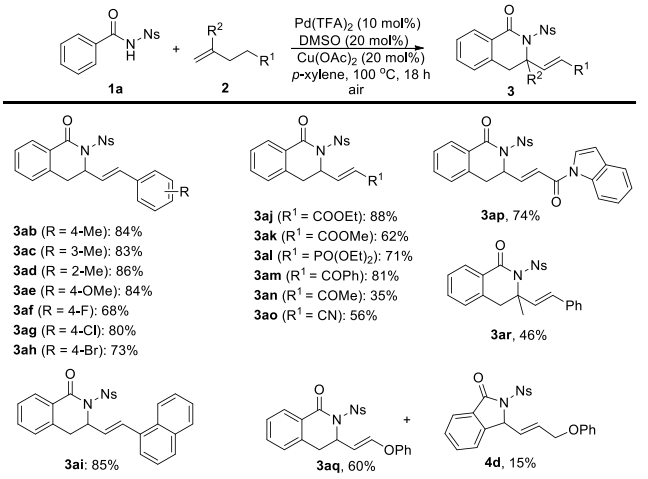


Gratifyingly, the reaction performed smoothly, affording desired product **3aa** in 87% yield. Then the scope was expanded to a variety of amides. Benzamides with both electron-donating and electron-withdrawing substituents functioned well, achieving desired products **3ba**−**3ka** in 62−93% yields. Electron-rich benzamides exhibited slightly better reactivities than electron-deficient benzamides (cf. **3ba**, **3ca**, **3ea** vs **3fa**−**3ka**). *meta*-Substituted benzamide **1c** afforded one regioisomer **3ca** in 86% yield. *ortho*-Substituted benzamide **1d** formed **3da** in 62% yield, slightly lower than the yields of **3ba** and **3ca**. The two reactions suggested that the steric factor could influence the Pd-catalyzed *ortho* C(sp^2)−H activation process. Heterocyclic arylamides were also compatible with this reaction. Products **3la**−**3na** were achieved in good yields. Furthermore, alkenyl carboxamides also worked well under those optimized conditions to synthesize another important type of heterocyclic compounds, 5,6-dihydropyridinones. Bicyclic product **3oa** was obtained in 73% yield. *α,β*-Disubstituted products **3pa** and **3qa** were obtained respectively in 67% and 80% yields.

The influence of a benzamide directing group was also explored. When *N*-tosylbenzamide **1r** was reacted with **2a**, dehydrogenative [4 + 2] annulation product **3ra** was obtained in 69% yield; however, the C−H olefination/annulation product **4a** was also obtained in relatively high ratio.[12b] Replacing the $-CH_3$ group with the $-CF_3$ or −CN group decreased the ratio of C−H olefination/annulation product **4b** or **4c**. These reactions demonstrated that the stronger acidity of the N−H bond benefited the dehydrogenative [4 + 2] annulation.

Subsequently, the scope was expanded to terminal olefins (Scheme 3). Both electron-donating and electron-withdrawing substituents on the phenyl ring of 4-phenyl-1-butenes were well tolerated, giving products **3ab**−**3ah** in 68−86% yields. 1-

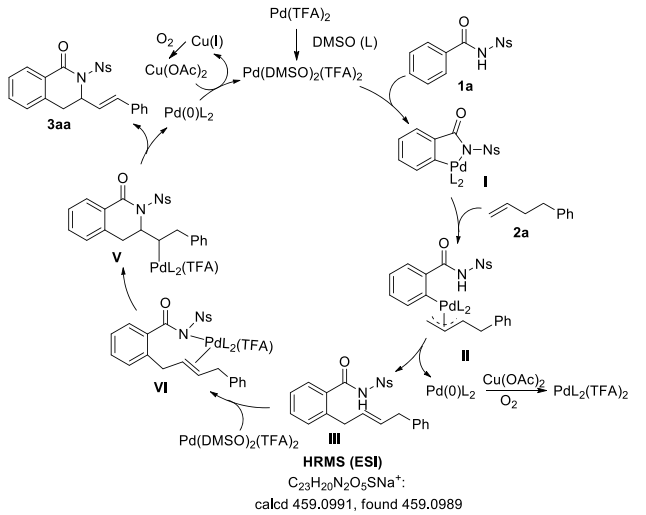
Scheme 3. Dehydrogenative [4 + 2] Annulation of Terminal Olefins with 1a



(3-Buten-1-yl)-naphthalene **2i** also worked smoothly, giving **3ai** in 85% yield. *γ,δ*-Unsaturated esters, ketones, nitrile, and amide were also applicable for the dehydrogenative [4 + 2] annulation. Products **3aj**−**3ap** were generated in 35−88% yields. The yield of **3an** was relatively low, which may be due to the relatively low boiling point of hex-5-en-2-one **2n**. When 4-phenoxy-1-butene **2q** was conducted in this reaction, the desired product **3aq** was obtained in 60% yield. However, the C−H olefination/annulation product **4d** was also obtained in 15% yield. We suspected that the homoallylic unsaturated bond benefited the dehydrogenative [4 + 2] annulation. Excitingly, the methyl group at the 2-position of olefin did not retard the dehydrogenative [4 + 2] annulation, and **3ar** was obtained in moderate yield.

According to all above-mentioned results and previous reports,[8,12b,16,17] a plausible mechanism was proposed as shown in Scheme 4. First, the catalyst $Pd(TFA)_2$ and ligand DMSO form a new $Pd(DMSO)_2(TFA)_2$ catalyst in situ,[16] which then complexes with the N−H bond and the C(sp^2)−H bond in **1a** to form a five-membered palladacycle **I**.[12b] After coordination of olefin to palladium and removal of an allylic hydrogen of **2a**, the *π*-allyl palladium complex **II** forms.[8]

Scheme 4. Proposed Plausible Mechanism

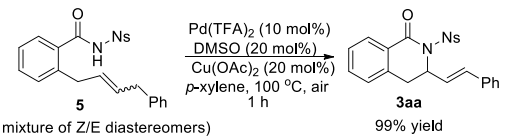


https://dx.doi.org/10.1021/acs.orglett.0c01011
Org. Lett. XXXX, XXX, XXX−XXX

Reductive elimination of **II** gives the allyl intermediate **III** and Pd(0) species. The intermediate **III** has been detected by high resolution mass spectra analysis. Subsequently, the coordination of Pd(II) catalyst with the N−H bond and retained carbon−carbon double bond in allyl intermediate **III** forms the complex **VI** which then undergos the nitrogen palladation of alkene to afford **V**.[16c] Finally, *β*-H elimination affords the dehydrogenative [4 + 2] annulation product **3aa** with regeneration of Pd(0) species. $Cu(OAc)_2$ and O_2 oxidize the Pd(0) species to a Pd(II) catalyst to participate in the next cycle.[16c]

Because the intermediate **III** was present at a trace level, 2-allyl benzamide **5** (a mixture of *Z*/*E* diastereomers) was prepared and subjected to the standard reaction conditions to gain more insight into the possible mechanism (Scheme 5).

Scheme 5. Cyclization of 2-Allyl Benzamide



5 (a mixture of Z/E diastereomers) **3aa** 99% yield

Quantitative product **3aa** could be obtained in just 1 h,[16b,c] which was in agreement with the proposed mechanism. The faster cyclization rate of 2-allyl benzamide compared to 2-alkenyl benzamide[12b] indicated that the stronger acidity of the N−H bond in the directing group and the homoallylic unsaturated bond in the terminal olefin benefited the competition of dehydrogenative [4 + 2] annulation from C−H olefination/annulation.

In summary, with the assistance of the DMSO ligand, we have developed the palladium-catalyzed tandem dehydrogenative [4 + 2] annulation of terminal olefins with *N*-sulfonyl amides via $C(sp^2)$−H activation, allylic $C(sp^3)$−H activation, and homoallylic $C(sp^3)$−H elimination processes. The mostly used commercial olefins represent an atom-efficient and step-efficient approach to synthesize bioactively important and medicinally important heterocyclic compounds bearing a vinyl substituent with high *E* stereoselectivity. Various substituted benzamides, heterocyclic arylamides, and alkenyl carboxamides are found to be efficient substrates. Using air as the terminal oxidant also provides a great advantage regarding environmental friendliness.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01011.

Experimental details, NMR (^1H, ^{13}C) spectra for all new compounds and high resolution mass spectra of intermediate **III** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Zhiming Wang − *Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou 318000, P. R. China;* orcid.org/0000-0002-6583-3826; Email: zhiming@tzc.edu.cn, wzmmol@hotmail.com

Authors

Manman Sun − *Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou 318000, P. R. China*

Weida Chen − *Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou 318000, P. R. China*

Xiangyu Xia − *Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou 318000, P. R. China*

Guodong Shen − *School of Chemistry and Chemical Engineering, School of Pharmacy, Liaocheng University, Liaocheng 252000, P. R. China;* orcid.org/0000-0002-0631-1913

Yongmin Ma − *Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou 318000, P. R. China*

Jianguo Yang − *Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou 318000, P. R. China;* orcid.org/0000-0003-4268-7384

Hanfeng Ding − *Department of Chemistry, Zhejiang University, Hangzhou 310058, P. R. China;* orcid.org/0000-0002-1781-4604

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c01011

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Natural Science foundation of Zhejiang Province (Nos. LQ20B020007, LY18B020002).

■ REFERENCES

(1) (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *6*, 4387. (b) Trost, B. M.; Fullerton, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 292. (c) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336. (d) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (e) Trost, B. M.; Machacek, M. R.; Aponick, A. *Acc. Chem. Res.* **2006**, *39*, 747. (f) Mishra, N. K.; Sharma, S.; Park, J.; Han, S.; Kim, I. S. *ACS Catal.* **2017**, *7*, 2821. (g) Bankar, S. K.; Singh, B.; Tung, P.; Ramasastry, S. S. V. *Angew. Chem., Int. Ed.* **2018**, *57*, 1678.

(2) For recent selected Pd-catalyzed $C(sp^3)$−H functionalization, see: (a) He, J.; Wasa, M.; Chan, K. S. L.; Shao, Q.; Yu, J.-Q. *Chem. Rev.* **2017**, *117*, 8754. (b) Chen, Z.; Rong, M.-Yu; Nie, J.; Zhu, X.-F.; Shi, B.-F.; Ma, J.-A *Chem. Soc. Rev.* **2019**, *48*, 4921. (c) Hong, G.; Nahide, P. D.; Neelam, U. K.; Amadeo, P.; Vijeta, A.; Curto, J. M.; Hendrick, C. E.; VanGelder, K. F.; Kozlowski, M. C. *ACS Catal.* **2019**, *9*, 3716. (d) Hu, Z.-Y.; Zhang, Y.; Li, X.-C.; Zi, J.; Guo, X.-X. *Org. Lett.* **2019**, *21*, 989. (e) Liu, L.; Liu, Y.-H.; Shi, B.-F. *Chem. Sci.* **2020**, *11*, 290.

(3) For recent selected examples, see: (a) Lu, M.-Z.; Chen, X.-R.; Xu, H.; Dai, H.-X.; Yu, J.-Q. *Chem. Sci.* **2018**, *9*, 1311. (b) Jeon, J.; Ryu, H.; Lee, C.; Cho, D.; Baik, M.-H; Hong, S. *J. Am. Chem. Soc.* **2019**, *141*, 10048. (c) Kathe, P. M.; Fleischer, I. *Org. Lett.* **2019**, *21*, 2213. (d) Wu, F.-P.; Li, D.; Peng, J.-B.; Wu, X.-F. *Org. Lett.* **2019**, *21*, 5699. (e) Ren, W.; Chu, J.; Sun, F.; Shi, Y. *Org. Lett.* **2019**, *21*, 5967.

(4) (a) Chen, M. S.; White, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 1346. (b) Yin, G.; Wu, Y.; Liu, G. *J. Am. Chem. Soc.* **2010**, *132*, 11978. (c) Braun, M.-G.; Doyle, A. G. *J. Am. Chem. Soc.* **2013**, *135*, 12990. (d) Strambeanu, I. I.; White, M. C. *J. Am. Chem. Soc.* **2013**, *135*, 12032. (e) Howell, J. M.; Liu, W.; Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2014**, *136*, 5750. (f) Ammann, S. E.; Rice, G. T.; White, M. C. *J. Am. Chem. Soc.* **2014**, *136*, 10834. (g) Wang, P.-S.; Lin, H.-C.; Zhou, X.-L.; Gong, L.-Z. *Org. Lett.* **2014**, *16*, 3332. (h) Wang, G.-W.; Zhou, A.-X.; Li, S.-X.; Yang, S.-D. *Org. Lett.* **2014**, *16*, 3118. (i) Trost, B. M.; Donckele, E. J.; Thaisrivongs, D. A.; Osipov, M.; Masters, J. T. *J. Am. Chem. Soc.* **2015**, *137*, 2776. (j) Hu, R.-B.; Wang, C.-H.; Ren, W.; Liu, Z.; Yang, S.-D. *ACS Catal.* **2017**, *7*, 7400. (k) Jin, M.; Ren,

W.; Qian, D.-W; Yang, S.-D *Org. Lett.* **2018**, *20*, 7015. (l) Lin, H.-C.; Xie, P.-P.; Dai, Z.-Y.; Zhang, S.-Q.; Wang, P.-S.; Chen, Y.-G.; Wang, T.-C.; Hong, X.; Gong, L.-Z. *J. Am. Chem. Soc.* **2019**, *141*, 5824. (m) Wang, T.-C.; Fan, L.-F.; Shen, Y.; Wang, P.-S.; Gong, L.-Z. *J. Am. Chem. Soc.* **2019**, *141*, 10616.

(5) (a) Mo, H.; Bao, W. *Adv. Synth. Catal.* **2009**, *351*, 2845. (b) Jiang, H.; Yang, W.; Chen, H.; Li, J.; Wu, W. *Chem. Commun.* **2014**, *50*, 7202. (c) Qi, X.; Chen, P.; Liu, G. *Angew. Chem., Int. Ed.* **2017**, *56*, 9517. (d) Li, C.; Chen, H.; Li, J.; Li, M.; Liao, J.; Wu, W.; Jiang, H. *Adv. Synth. Catal.* **2018**, *360*, 1600.

(6) For reviews, see: (a) Jensen, T.; Fristrup, P. *Chem. - Eur. J.* **2009**, *15*, 9632. (b) Liu, G.; Wu, Y. *Top. Curr. Chem.* **2009**, *292*, 195. (c) Liron, F.; Oble, J.; Lorion, M. M.; Poli, G. *Eur. J. Org. Chem.* **2014**, *2014*, 5863. (d) Tang, H.; Huo, X.; Meng, Q.; Zhang, W. *Huaxue Xuebao* **2016**, *74*, 219. (e) Wang, R.; Luan, Y.; Ye, M. *Chin. J. Chem.* **2019**, *37*, 720.

(7) For other metal catalyzed tandem reactions, see: (a) Archambeau, A.; Rovis, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 13337. (b) Liu, Y.; Yang, Y.; Wang, C.; Wang, Z.; You, J. *Chem. Commun.* **2019**, *55*, 1068. (c) Qin, L.; Sharique, M.; Tambar, U. K. *J. Am. Chem. Soc.* **2019**, *141*, 17305.

(8) Wang, B.; Du, H.; Shi, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 8224.

(9) (a) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 1107. (b) Zhu, R.-Y.; Farmer, M. E.; Chen, Y.-Q.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2016**, *55*, 10578. (c) Liao, G.; Chen, H.-M.; Shi, B.-F. *Chem. Commun.* **2018**, *54*, 10859. (d) Kong, W.-J.; Chen, X.; Wang, M.; Dai, H.-X.; Yu, J.-Q. *Org. Lett.* **2018**, *20*, 284. (e) Yang, Q.-L.; Wang, X.-Y.; Wang, T.-L.; Yang, X.; Liu, D.; Tong, X.; Wu, X.-Y.; Mei, T.-S. *Org. Lett.* **2019**, *21*, 2645. (f) Luo, Y.-C.; Yang, C.; Qiu, S.-Q.; Liang, Q.-J.; Xu, Y.-H.; Loh, T.-P. *ACS Catal.* **2019**, *9*, 4271.

(10) (a) Zhu, B.; Wang, G.-W. *Org. Lett.* **2009**, *11*, 4334. (b) Wang, G.-W.; Yuan, T.-T.; Li, D.-D. *Angew. Chem., Int. Ed.* **2011**, *50*, 1380. (c) Pimparkar, S.; Jeganmohan, M. *Chem. Commun.* **2014**, *50*, 12116. (d) Xia, X.-F.; Wang, Y.-Q.; Zhang, L.-L.; Song, X.-R.; Liu, X.-Y.; Liang, Y.-M. *Chem. - Eur. J.* **2014**, *20*, 5087. (e) Zhang, W.; Chen, P.; Liu, G. *Angew. Chem., Int. Ed.* **2017**, *56*, 5336. (f) Jing, K.; Yao, J.-P.; Li, Z.-Y.; Li, Q.-L.; Lin, H.-S.; Wang, G.-W. *J. Org. Chem.* **2017**, *82*, 12715. (g) Jing, K.; Wang, X.-N.; Wang, G.-W. *J. Org. Chem.* **2019**, *84*, 161. (h) Hussain, M.; Chen, M.; Yang, S.; Wang, G.-W. *Org. Lett.* **2019**, *21*, 8568.

(11) For Rh-catalyzed [4 + 2] annulations, see: (a) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350. (b) Guimond, N.; Gorelsky, S. I.; Fagnou, K. *J. Am. Chem. Soc.* **2011**, *133*, 6449. (c) Hyster, T. K.; Dalton, D. M.; Rovis, T. *Chem. Sci.* **2015**, *6*, 254. (d) Trifonova, E. A.; Ankudinov, N. M.; Kozlov, M. V.; Sharipov, M. Y.; Nelyubina, Y. V.; Perekalin, D. S. *Chem. - Eur. J.* **2018**, *24*, 16570. (e) Barber, J. S.; Scales, S.; Tran-Dubé, M.; Wang, F.; Sach, N. W.; Bernier, L.; Collins, M. R.; Zhu, J.; McAlpine, I. J.; Patman, R. L. *Org. Lett.* **2019**, *21*, 5689. For Co-catalyzed [4 + 2] annulations, see: (f) Yu, X.; Chen, K.; Wang, Q.; Zhang, W.; Zhu, J. *Org. Chem. Front.* **2018**, *5*, 994. (g) Ozols, K.; Jang, Y.-S.; Cramer, N. *J. Am. Chem. Soc.* **2019**, *141*, 5675.

(12) (a) Wrigglesworth, J. W.; Cox, B.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *Org. Lett.* **2011**, *13*, 5326. (b) Zhu, C.; Falck, J. R. *Org. Lett.* **2011**, *13*, 1214. (c) Li, D.-D.; Yuan, T.-T.; Wang, G.-W. *Chem. Commun.* **2011**, *47*, 12789. (d) Youn, S. W.; Ko, T. Y.; Kim, Y. H.; Kim, Y. A. *Org. Lett.* **2018**, *20*, 7869.

(13) (a) Watt, M. S.; Booker-Milburn, K. I. *Org. Lett.* **2016**, *18*, 5716. (b) Zhang, T.; Shen, H.-C.; Xu, J.-C.; Fan, T.; Han, Z.-Y.; Gong, L.-Z. *Org. Lett.* **2019**, *21*, 2048. (c) Sun, M.; Wu, H.; Xia, X.; Chen, W.; Wang, Z.; Yang, J. *J. Org. Chem.* **2019**, *84*, 12835. (d) Sun, M.; Li, J.; Chen, W.; Wu, H.; Yang, J.; Wang, Z. *Synthesis* **2019**, *51*, DOI: 10.1055/s-0039-1690219.

(14) (a) Zhang, S.-S.; Wu, J.-Q.; Liu, X.; Wang, H. *ACS Catal.* **2015**, *5*, 210. (b) Wu, X.; Ji, H. *J. Org. Chem.* **2018**, *83*, 12094. (c) Xu, Z.-Q.; Wang, C.; Li, L.; Duan, L.; Li, Y.-M. *J. Org. Chem.* **2018**, *83*, 9718. (d) Wang, J.; Sun, K.; Chen, X.; Chen, T.; Liu, Y.; Qu, L.; Zhao, Y.; Yu, B. *Org. Lett.* **2019**, *21*, 1863.

(15) (a) Wu, W.; Jiang, H. *Acc. Chem. Res.* **2012**, *45*, 1736. (b) Shi, Z.; Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3381.

(16) (a) Diao, T.; White, P.; Guzei, I.; Stahl, S. S. *Inorg. Chem.* **2012**, *51*, 11898. (b) McDonald, R. I.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 5529. (c) Lu, Z.; Stahl, S. S. *Org. Lett.* **2012**, *14*, 1234.

(17) Engelin, C.; Jensen, T.; Rodriguez-Rodriguez, S.; Fristrup, P. *ACS Catal.* **2013**, *3*, 294.

https://dx.doi.org/10.1021/acs.orglett.0c01011
Org. Lett. XXXX, XXX, XXX−XXX