Palladium-Catalyzed Controllable Reductive/Oxidative Heck Coupling between Cyclic Enones and Thiophenes via C−H Activation

Zhen-Kang Wen,*,[†] Ze-Kai Zhao,[†] Ning-Jing Wang,[†] Zi-Ling Chen,[†] Jian-Bin Chao,[‡] and Li-Heng Feng*,[†]

[†]School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China
[‡]Scientific Instrument Center, Shanxi University, Taiyuan 030006, China

ⓢ Supporting Information

ABSTRACT: Herein, we report a straightforward, environmentally friendly, and controllable palladium/ligand catalytic system to enable reductive/oxidative Heck reactions of cyclic enones with thiophene or furan derivatives via C−H activation. The key to this tunable reaction is the appropriate intercepting thienyl-Pd(II)-enolate during the enolization process. Such a controllable and economic protocol would not only provide efficient methods to construct various value-added β-heteroarylated cyclic ketones/enones but also shed light on developing other conjugate addition reactions via C−H activation.
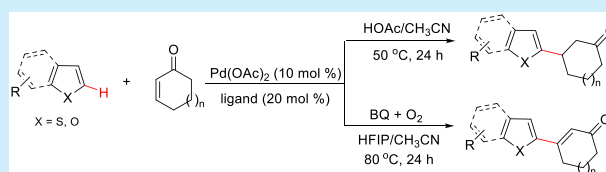
Transition-metal-catalyzed C−H activation chemistry has greatly accelerated the development of synthetic diversifications, thus delivering unconventional synthetic disconnections to the rapid preparation of complex molecules in an atom- and step-economical fashion.[1] In this regard, the well-established Fujiwara−Moritani−Heck reaction,[2] also identified as an oxidative Heck reaction (Scheme 1a), holds a unique position in direct C−H olefination[3] of a wide range of arenes as well as heteroarenes through a palladium-catalyzed C−H functionalization strategy, as witnessed by explosively growth of this type of transformations during the past several decades. On the stark contrary, the synthetically more appealing reductive Heck reaction (Scheme 1a), which starts from the identical starting materials, but delivering formally alkene hydroarylation products[4] through C−H activation without atom waste, has remained undeveloped yet.

Mechanistically, the most daunting challenge of reductive Heck reaction is intrinsic rapid syn-β-hydride elimination of the key alkyl-Pd-X intermediate (Scheme 1b), which ultimately results in oxidative Heck coupling products retaining the olefin functionality. Thus, intercepting alkyl-Pd-X with a suitable hydrogenation reagent that outcompetes β-hydride elimination would be a critical concern to access the desired hydroarylation products. In this context, trapping alkyl-Pd-X with formic salts to produce alkyl-Pd-H is a commonly used strategy to access olefin hydroarylation, which follows a sequence of anion exchange of formic anion with X, CO_2 release to give alkyl-Pd-H and reductive elimination to afford hydroarylation product and regenerate Pd(0) catalyst. For example, Cacchi[5] disclosed the first reductive Heck coupling of aryl iodides with conjugated enones in 1983, and then after, Minnaard,[6] Lee,[7] Hagiwara,[8] Loh,[9] and Engle[10] have greatly extended the scope

Scheme 1. Overview and Context of Work
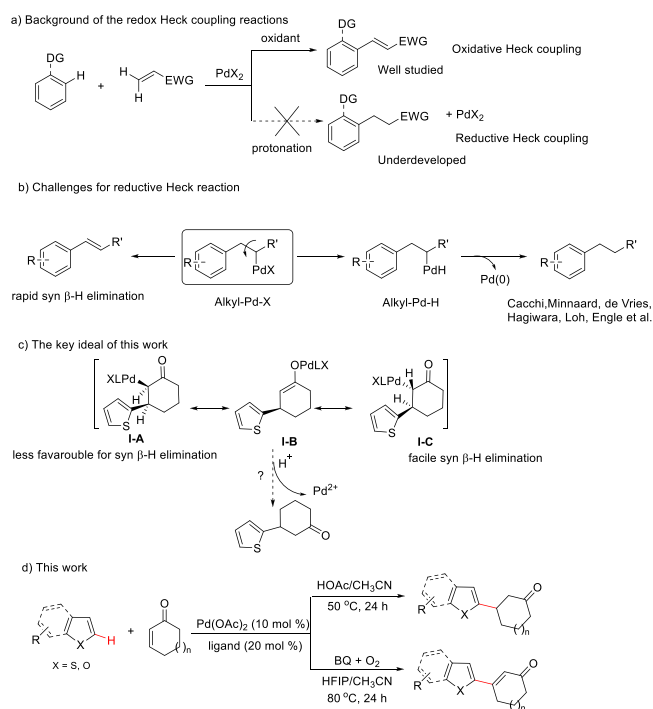
of substrate including a wide range of aryl halides, aryl triflates, and aryl boronic acids as arylation reagents to react with various conjugated enones or directing groups assisted
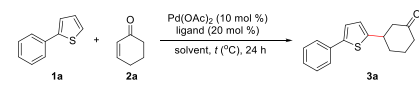
aliphatic alkenes. Despite these advances, to the best of our knowledge, the most straightforward palladium-catalyzed C−H activation strategy leads to direct reductive Heck coupling between simple (hetero)arenes and alkenes has not been reported to date, presumably because difficulties in suppressing rapid β-hydride elimination side reaction of the alkyl palladium intermediate as well as precise designing suitable catalytic system that can efficiently promote C−H activation, olefin insertion, and hydrogenation in a tandem order.

Recently, we have successfully enabled direct coupling of thiophenes with cyclic enones[11] which have been known as problematic substrates in many palladium(II)-catalyzed C−H olefination reactions.[12] Mechanistic study revealed that a rapid enolization process of thienyl-Pd(II)-enolate (**I-A**, **I-B**, **I-C**) was involved for facile syn-β-hydride elimination to accomplish oxidative Heck coupling (Scheme 1c). We postulated that such an enolization process would offer a potential opportunity to enable other useful transformations through intercepting the thienyl-Pd(II)-enolate, for example, whether a suitable protic acid would hydrolyze the enol-O-Pd bond of thienyl-Pd(II)-enolate (**I-B**) to give conjugate addition product and restore the active Pd(II) catalyst. Additionally, we also hypothesized whether a tunable reductive/oxidative Heck reaction could be attained through concise control over enolization process. Within our ongoing program to address the proposed hypothesis, herein we report a palladium/ligand-catalyzed controllable reductive/oxidative Heck coupling of commercially available cyclic enones with thiophene or furan derivatives (Scheme 1d). Both of the reactions proceeded under mild and environmentally friendly conditions starting from a C−H activation strategy. A key feature of our reductive Heck process is that acetic acids served as proton cation source effectively trap thienyl-Pd(II)-enolate (**I-B**) to accomplish the conjugate addition of thiophene to cyclic enones in the absence of stoichiometric oxidants, which remains in sharp contrast to the previously reported strategy involving alkyl-Pd-H. On the other hand, by replacing acetic acid with HFIP as solvents and using catalytic benzoquinone as oxidants under oxygen gas, a more eco-friendly oxidative Heck coupling reaction condition is established where commonly used metal oxidants such as silver salts are not required. Moreover, this operationally simple and economically flexible protocol not only provides a straightforward route to synthesize valuable β-functionalized cyclic ketones[13] from easily accessible starting materials but also initiates a promising alternative to traditional conjugate addition reactions, avoiding utilization of air- and moisture-sensitive organometal reagents[14] as well as preformed aryl boronic acids.[15]

To test the feasibility of our envisioned approach of trapping thienyl-Pd-enolate that was generated in situ through migratory insertion of palladated thiophene to double bonds of cyclic enone, the reaction of 2-phenylthiophene with cyclohexenone in acetic acid at 90 °C was chosen as a model reaction system in the presence of catalytic Pd(OAc)$_2$. Initial screening revealed that acetic acid served as proton cation to hydrolyze Pd-enolate albeit with low yields (Table 1, entry 1). Note that the employment of ligand has been realized to play an important role in C−H activation chemistry.[16] To our delight, after examining various types of ligand (entry 2−8), we found that use of 20 mol % of 4,5-diazafluoren-9-one (entry 5) greatly increased the yield up to 60%. In addition, addition of acetonitrile as a minor solvent (entry 12) is found to facilitate the reaction likely because of the coordination

Table 1. Identification of Reaction Conditions[a,b]

entry	ligand	solvent	temp (°C)	yield[b] (%)
1	−	HOAc	90	8
2	L1	HOAc	90	trace
3	L2	HOAc	90	trace
4	L3	HOAc	90	30
5	L4	HOAc	90	60
6	L5	HOAc	90	31
7	L6	HOAc	90	24
8	L7	HOAc	90	19
9	L4	dioxane/HOAc (1:20)	90	56
10	L4	DCE/HOAc (1:20)	90	50
11	L4	DMF/HOAc (1:20)	90	45
12	L4	CH$_3$CN/HOAc (1:20)	90	64
13	**L4**	**CH$_3$CN/HOAc**(1:20)	**50**	**69**
14[c]	L4	CH$_3$CN/HOAc (1:20)	rt (25)	60
15[d]	L4	CH$_3$CN/HOAc (1:20)	50	0

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), Pd(OAc)$_2$ (10 mol %), ligand (20 mol %) in solvent (1 mL), stirred for 24 h. [b]Isolated yield. [c]48 h. [d]In the absence of Pd(OAc)$_2$.
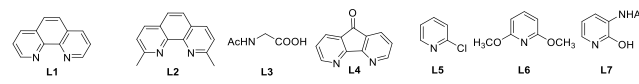
effect to stabilize the palladium center, and other solvents proved to be less effective (entry 9−11). Finally, lowering the reaction temperature to 50 °C also furnished the reaction in slightly increased yields (entry 13). Interestingly, the reaction also proceeded smoothly at room temperature to give the desired product in 60% yield, but a longer reaction time was required (entry 14). Control experiments revealed that Pd(OAc)$_2$ plays a pivotal role in this transformation (entry 15), the absence of which led to no coupling product formation. Thus, the optimal conditions of reductive Heck coupling between cyclohexenone and thiophene are established as follows: combining the substrates with 10 mol % of Pd(OAc)$_2$ and 20 mol % of 4,5-diazafluoren-9-one in mixed CH$_3$CN/HOAc (1:20) solvent at 50 °C and stirred for 24 h.
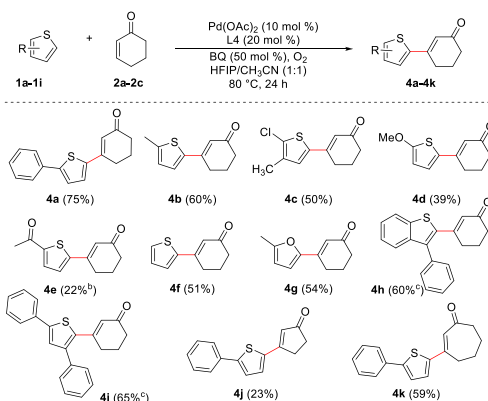
Having established the optimized reaction conditions, we then examined the substrate scope of this reductive Heck reaction. As shown in Scheme 2, a variety of thiophene or furan derivatives reacted exclusively at the α-position with cyclohexenone to afford the conjugate addition products in moderate to high yields. Changing the phenyl moiety at the α position of thiophene to methyl, methoxyl, bromo, or chloro could deliver the desired products in good yields (**3a−3e**), with the exception of acetyl and ester functional groups (**3f**, **3g**), gave the corresponding products in relatively low yields. Di- or trisubstituted thiophenes also furnished the corresponding products in good yields (**3h−3l**). Note that unsubstituted thiophene possessing two identical α hydrogen atoms provided mono and 2-fold conjugate addition products (**3ma**, **3mb**) in 28% and 55% yields, respectively. Two equivalents of thiophene analogues was used in order to obtain single conjugate addition products when reactions of 3,4- and 3-substituted thiophene with cyclohexenone were performed (**3n−3q**). Furthermore, other heteroarenes such as 2-methylfuran (**3r**) and benzothiophene (**3s**) also proved to be suitable substrates in this transformation. Finally, the scope of

Scheme 2. Scope of the Reductive Heck Coupling between Substituted Thiophenes with Cyclic Enones[a]
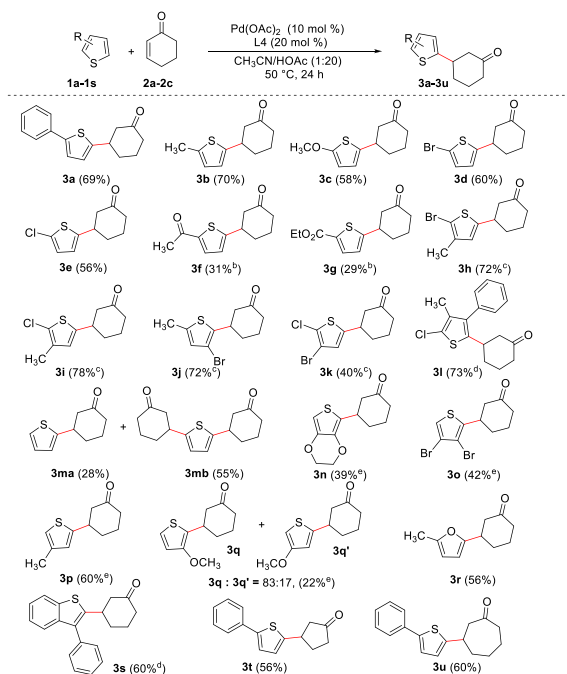
[a]Reaction conditions: cyclic enones (0.5 mmol), thiophene homologues (0.25 mmol), Pd(OAc)$_2$ (10 mol %), ligand (20 mol %), HOAc (0.6 mL), CH$_3$CN (0.03 mL), 50 °C, 24 h. [b]110 °C, 48 h. [c]36 h. [d]48 h, yields are based on recovery of starting materials. [e]Thiophene derivatives (0.5 mmol), cyclohexenone (0.25 mmol), 36 h.

Scheme 3. Scope of the Oxidative Heck Coupling between Substituted Thiophenes with Cyclic Enones[a]

[a]Reaction conditions: cyclic enones (0.5 mmol), thiophene homologues (0.25 mmol), Pd(OAc)$_2$ (10 mol %), ligand (20 mol %), HFIP (0.5 mL), CH$_3$CN (0.5 mL), BQ (50 mol %), O$_2$ balloon, 80 °C, 24 h. [b]36 h. [c]36 h, yields are based on recovery of starting materials.

cyclic enones was also investigated, and reactions of 2-phenylthiophene with cyclopentenone (**3t**) or cycloheptenone (**3u**) also gave the desired products in synthetically useful yields.

Noteworthy, during the reductive Heck reaction of 2-phenylthiophene with cyclohexenone, about 10% yield of oxidative Heck product (**4a**) was detected in the absence of oxidant; this encouraging finding motivated us to modulate the reaction pathway from reductive to oxidative Heck coupling of cyclic enones with thiophenes. Gratifyingly, by changing the solvent of CH$_3$CN/HOAc (1:20) to CH$_3$CN/HFIP (1:1) and employing 0.5 equiv of BQ and oxygen gas as oxidants, a more economical and practical method to synthesize β-heteroarylated cyclic enones was established under mild conditions. The scope of the substrate for this reaction is depicted in Scheme 3. Generally, thiophenes bearing a phenyl, methyl, chloro, or methoxyl functional group can participate in this reaction and afford the corresponding dehydrogenative coupling products in synthetically useful yields (**4a**−**4d**), while 2-acetylthiophene (**4e**) gave the coupling product in poor yield. Mono- and disubstituted thiophenes were all tolerated (**4i**) in this dehydrogenative cross-coupling reaction. In addition, unsubstituted thiophene (**4f**) bearing two accessible reaction sites only gave the singly coupling product in moderate yields. Other heteroarenes such as 2-methylfuran (**4g**) and benzothiophene (**4h**) were also compatible to this protocol to give the corresponding products in synthetically useful yields. Furthermore, under the dehydrogenative coupling conditions, 2-phenylthiophene can couple with cyclopente-

none (**4j**) or cycloheptenone (**4k**) to access the desired products in reasonable yields.

The practicality of our controllable redox Heck reaction was further demonstrated by the following scale-up operations (eqs 1 and 2). To verify our hypothesis of the mechanism,
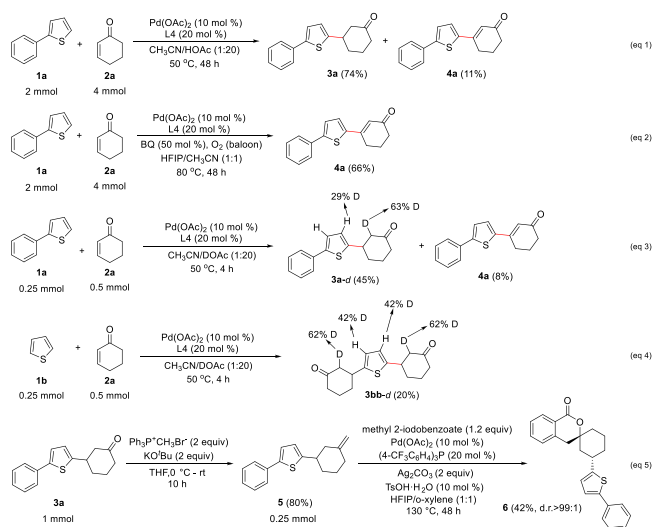
deuterium-labeling control experiments were conducted, and the results revealed that the additional α-hydrogen atom at the carbonyl group of conjugate addition product came from proton cation of acetic acid, with concomitant exchanges of H/D in thiophenes during these process (eqs 3 and 4); such results were consistent with our proposed envision. In addition, the absence of deuterium in dehydrogenative cross-coupling byproduct (**4a**) indicated that its formation did not occur through dehydrogenation of the conjugate product, thus suggesting our controllable redox process underwent two different pathways that did not transformed to each other. Moreover, derivatization of the reductive Heck coupling product to synthesize valuable isochromanone (**6**) containing heterocycles by using our recently developed method[17] was also communicated (eq 5).

In conclusion, we have developed palladium-catalyzed controllable redox Heck coupling reactions of cyclic enones with thiophene or furan under mild conditions. A variety of β-heteroarylated cyclic ketones/enones could be rapidly accessed by this streamlined strategy. Efforts on extending these controllable transformations to other aromatic substrates and olefins as well as systematic understanding mechanisms are in progress in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03721.

Detailed experimental procedures and spectral data for all products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: zkwen@sxu.edu.cn.
*E-mail: lhfeng@sxu.edu.cn.
ORCID Ⓞ
Zhen-Kang Wen: 0000-0003-1253-9583
Li-Heng Feng: 0000-0003-3829-2136
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) For selective reviews, see: (a) Sambiagio, C.; Schönbauer, D.; Blieck, R.; Dao-Huy, T.; Pototschnig, G.; Schaaf, P.; Wiesinger, T.; Zia, M. F.; Wencel-Delord, J.; Besset, T.; Maes, B. U. W.; Schnürch, M. Chem. Soc. Rev. 2018, 47, 6603. (b) Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J. Chem. Soc. Rev. 2016, 45, 2900. (c) Engle, K. M.; Mei, T. S.; Wasa, M.; Yu, J. Q. Acc. Chem. Res. 2012, 45, 788. (d) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. Angew. Chem., Int. Ed. 2012, 51, 8960. (e) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. Chem. Rev. 2012, 112, 5879. (f) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. Acc. Chem. Res. 2012, 45, 814. (g) Lyons, T. W.; Sanford, M. S. Chem. Rev. 2010, 110, 1147.

(2) For selected reviews and examples, see: (a) Sherikar, M. S.; Kapanaiah, R.; Lanke, V.; Prabhu, K. R. Chem. Commun. 2018, 54, 11200. (b) Zhou, L. H.; Lu, W. J. Chem. - Eur. J. 2014, 20, 634. (c) Shang, X. J.; Liu, Z. Q. Chem. Soc. Rev. 2013, 42, 3253. (d) Rauf, W.; Brown, J. M. Chem. Commun. 2013, 49, 8430. (e) Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M. J. Am. Chem. Soc. 2002, 124, 1586. (f) Weissman, H.; Song, X. P.; Milstein, D. J. Am. Chem. Soc. 2001, 123, 337.

(3) For selected reviews and examples, see: (a) Zhang, L.; Chen, C. P.; Han, J.; Huang, Z. B.; Zhao, Y. S. Org. Chem. Front. 2016, 3, 1271. (b) Wang, Q.; Han, J.; Wang, C.; Zhang, J. Y.; Huang, Z. B.; Shi, D. Q.; Zhao, Y. S. Chem. Sci. 2014, 5, 4962. (c) Sigman, M. S.; Werner, E. W. Acc. Chem. Res. 2012, 45, 874. (d) Le Bras, J.; Muzart, J. Chem. Rev. 2011, 111, 1170. (e) Ye, M.; Gao, G. L.; Yu, J. Q. J. Am. Chem. Soc. 2011, 133, 6964. (f) Engle, K. M.; Wang, D. H.; Yu, J. Q. J. Am. Chem. Soc. 2010, 132, 14137. (g) Engle, K. M.; Wang, D. H.; Yu, J. Q. Angew. Chem., Int. Ed. 2010, 49, 6169. (h) Wang, D. H.; Engle, K. M.; Shi, B. F.; Yu, J. Q. Science 2010, 327, 315. (i) Jia, C. G.; Kitamura, T.; Fujiwara, Y. Acc. Chem. Res. 2001, 34, 633. (j) Beletskaya, I. P.; Cheprakov, A. V. Chem. Rev. 2000, 100, 3009. (k) Jia, C. G.; Piao, D. P.; Oyamada, J.; Lu, W. J.; Kitamura, T.; Fujiwara, Y. Science 2000, 287, 1992. (l) Jia, C. G.; Lu, W. J.; Kitamura, T.; Fujiwara, Y. Org. Lett. 1999, 1, 2097.

(4) For representative reviews and examples, see: (a) Nguyen, J.; Chong, A.; Lalic, G. Chem. Sci. 2019, 10, 3231. (b) Li, T. Y.; Shen, C.; Sun, Y. L.; Zhang, J.; Xiang, P. J.; Lu, X. N.; Zhong, G. F. Org. Lett. 2019, 21, 7772. (c) Jin, L. Q.; Qian, J. X.; Sun, N.; Hu, B. X.; Shen, Z. L.; Hu, X. Q. Chem. Commun. 2018, 54, 5752. (d) Friis, S. D.; Pirnot, M. T.; Dupuis, L. N.; Buchwald, S. L. Angew. Chem., Int. Ed. 2017, 56, 7242. (e) Dong, Z.; Ren, Z.; Thompson, S. J.; Xu, Y.; Dong, G. B. Chem. Rev. 2017, 117, 9333. (f) Semba, K.; Ariyama, K.; Zheng, H.; Kameyama, R.; Sakaki, S.; Nakao, Y. Angew. Chem., Int. Ed. 2016, 55, 6275.

(5) Cacchi, S.; Arcadi, A. J. Org. Chem. 1983, 48, 4236.

(6) (a) Raoufmoghaddam, S.; Mannathan, S.; Minnaard, A. J.; de Vries, J. G.; Reek, J. N. H. Chem. - Eur. J. 2015, 21, 18811. (b) Gottumukkala, A. L.; de Vries, J. G.; Minnaard, A. J. Chem. - Eur. J. 2011, 17, 3091.

(7) Walker, S. E.; Boehnke, J.; Glen, P. E.; Levey, S.; Patrick, L.; Jordan-Hore, J. A.; Lee, A. L. Org. Lett. 2013, 15, 1886.

(8) Hagiwara, H.; Eda, Y.; Morohashi, K.; Suzuki, T.; Ando, M.; Ito, N. Tetrahedron Lett. 1998, 39, 4055.

(9) Wang, C. D.; Xiao, G. L.; Guo, T.; Ding, Y. L.; Wu, X. J.; Loh, T. P. J. Am. Chem. Soc. 2018, 140, 9332.

(10) (a) Gurak, J. A., Jr; Engle, K. M. ACS Catal. 2018, 8, 8987. (b) Tran, V. T.; Gurak, J. A., Jr; Yang, K. S.; Engle, K. M. Nat. Chem. 2018, 10, 1126.

(11) Wen, Z. K.; Song, T. T.; Liu, Y. F.; Chao, J. B. Chem. Commun. 2018, 54, 3668.

(12) (a) Chung, L. G. Y.; Juwaini, N. A. B.; Seayad, J. ChemCatChem 2015, 7, 1270. (b) Gigant, N.; Bäckvall, J. E. Chem. - Eur. J. 2014, 20, 5890. (c) Li, Y. M.; Qi, Z. S.; Wang, H. F.; Fu, X. M.; Duan, C. Y. J. Org. Chem. 2012, 77, 2053. (d) Gottumukkala, A. L.; Teichert, J. F.; Heijnen, D.; Eisink, N.; van Dijik, S.; Ferrer, C.; van den Hoogenband, A.; Minnaard, A. J. J. Org. Chem. 2011, 76, 3498.

(13) For recent examples, see: (a) Koizumi, Y.; Jin, X. J.; Yatabe, T.; Miyazaki, R.; Hasegawa, J. Y.; Nozaki, K.; Mizuno, N.; Yamaguchi, K. Angew. Chem., Int. Ed. 2019, 58, 10893. (b) Boibessot, T.; Zschiedrich, C. P.; Lebeau, A.; Bénimèlis, D.; Dunyach-Rémy, C.; Lavigne, J. P.; Szurmant, H.; Benfodda, Z.; Meffre, P. J. Med. Chem. 2016, 59, 8830. (c) Radomkit, S.; Hoveyda, A. H. Angew. Chem., Int. Ed. 2014, 53, 3387. (d) Diao, T. N.; Pun, D.; Stahl, S. S. J. Am. Chem. Soc. 2013, 135, 8205. (e) Izawa, Y.; Zheng, C. W.; Stahl, S. S. Angew. Chem., Int. Ed. 2013, 52, 3672. (f) Simon, M. Q.; Girard, S. A.; Li, C. J. Angew. Chem., Int. Ed. 2012, 51, 7537. (g) Quideau, S.; Deffieux, D.; Douat-Casassus, C.; Pouységu, L. Angew. Chem., Int. Ed. 2011, 50, 586. (h) Kehrli, S.; Martin, D.; Rix, D.; Mauduit, M.; Alexakis, A. Chem. - Eur. J. 2010, 16, 9890. (i) Jimenez, M. E.; Bush, K.; Pawlik, J.; Sower, L.; Peterson, J. W.; Gilbertson, S. R. Bioorg. Med. Chem. Lett. 2008, 18, 4215.

(14) (a) Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. Angew. Chem., Int. Ed. 2012, 51, 5062. (b) Jerphagnon, T.; Pizzuti, M. G.; Minnaard, A. J.; Feringa, B. L. Chem. Soc. Rev. 2009, 38, 1039. (c) Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J.; Feringa, B. L. Chem. Rev. 2008, 108, 2824.

(15) (a) He, Q.; Xie, F.; Fu, G. H.; Quan, M.; Shen, C. R.; Yang, G. Q.; Gridnev, I. D.; Zhang, W. B. Org. Lett. 2015, 17, 2250. (b) Wang, F. J.; Chen, F.; Qu, M. L.; Li, T.; Liu, Y. L.; Shi, M. Chem. Commun. 2013, 49, 3360. (c) Gottumukkala, A. L.; Matcha, K.; Lutz, M.; de Vries, J. G.; Minnaard, A. J. Chem. - Eur. J. 2012, 18, 6907. (d) Kikushima, K.; Holder, J. C.; Gatti, M.; Stoltz, B. M. J. Am. Chem.

Soc. **2011**, *133*, 6902. (e) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Adv. Synth. Catal.* **2007**, *349*, 1759.

(16) (a) Chen, Y. Q.; Wang, Z.; Wu, Y. W.; Wisniewski, S. R.; Qiao, J. X.; Ewing, W. R.; Eastgate, M. D.; Yu, J. Q. *J. Am. Chem. Soc.* **2018**, *140*, 17884. (b) Lu, M. Z.; Chen, X. R.; Xu, H.; Dai, H. X.; Yu, J. Q. *Chem. Sci.* **2018**, *9*, 1311. (c) Wang, P.; Verma, P.; Xia, G. Q.; Shi, J.; Qiao, J. X.; Tao, S. W.; Cheng, P. T. W.; Poss, M. A.; Farmer, M. E.; Yeung, K. S.; Yu, J. Q. *Nature* **2017**, *551*, 489. (d) White, P. B.; Jaworski, J. N.; Geyunjian, H. Z.; Stahl, S. S. *ACS Catal.* **2016**, *6*, 3340. (e) White, P. B.; Jaworski, J. N.; Fry, C. G.; Dolinar, B. S.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2016**, *138*, 4869.

(17) Wen, Z. K.; Ge, X. M.; Zhao, Z. K.; Chao, J. B. *Adv. Synth. Catal.* **2019**, *361*, 983.