

Rh(III)-Catalyzed *meta*-C–H Olefination Directed by a Nitrile Template

Hua-Jin Xu,[†] Yi Lu,^{*,†} Marcus E. Farmer,[‡] Huai-Wei Wang,[†] Dan Zhao,[†] Yan-Shang Kang,[†] Wei-Yin Sun,^{*,†} and Jin-Quan Yu^{*,‡}

[†]Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, China

[‡]Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037, United States

S Supporting Information

ABSTRACT: A range of Rh(III)-catalyzed *ortho*-C–H functionalizations have been developed; however, extension of this reactivity to remote C–H functionalizations through large-ring rhodacyclic intermediates has yet to be demonstrated. Herein we report the first example of the use of a U-shaped nitrile template to direct Rh(III)-catalyzed remote *meta*-C–H activation via a postulated 12-membered macrocyclic intermediate. Because the ligands used for Rh(III) catalysts are significantly different from those of Pd(II) catalysts, this offers new opportunities for future development of ligand-promoted *meta*-C–H activation reactions.

Transition-metal-catalyzed C–H functionalization has been an area of significant interest because of the ability of these reactions to convert previously considered inert C–H bonds into a diverse range of C–C and C–heteroatom bonds. Directed C–H functionalization has been of particular interest, as the precoordination of a given functional group to the transition metal catalyst enables highly selective C–H activation in a general and predictable manner.¹ This strategy has been demonstrated to be a useful tactic with a wide variety of metals and has been shown to be particularly versatile when using Pd(II), Ru(II), and Rh(III) as catalysts.¹ The use of other catalysts, including Cu(II) and Ir(III), has also been demonstrated.¹ Directed C–H activation typically proceeds via five- or six-membered cyclometalation processes, precluding the functionalization of remote *meta*- or *para*-C–H bonds. As one of several approaches toward *meta*-C–H functionalization of aromatics,^{2–5} the development of a U-shaped directing template has successfully achieved a number of remote C–H activation reactions with several different classes of substrates.⁶ Key to the success of this approach was the use of a nitrile embedded in the template that serves as a linear end-on directing group. The linearity of the nitrile group prevents the assembly of the classical cyclic pretransition state required for *ortho*-C–H activation and instead positions the Pd catalyst near the remote *meta*-C–H bond. This allows a macrocyclic cyclophane-like transition state to be preferentially assembled, resulting in a *meta*-C–H-functionalized product. Such precise recognition of distance and geometry has proven to be rather general in terms of substrate and reaction type.^{6,7} Furthermore,

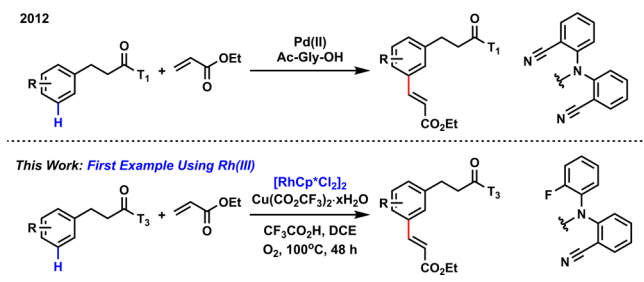
this approach has been demonstrated to be compatible with both Pd(II)/(0) and Pd(II)/(IV) catalysis⁶ and has been utilized to achieve *para*-C–H activation by modification of the template.⁷

In light of the recent and rapid development of Rh(III)-catalyzed *ortho*-C–H functionalizations,^{1g–j,8} it is highly desirable to extend the templating approach to Rh(III)-catalyzed *meta*-C–H activation processes for a number of reasons. First, both the substrate and reaction type can be complementary to that of Pd(II)-catalyzed *meta*-C–H functionalizations. Second, the ligands used for Rh(III) and Pd(II) are often different, which could offer new opportunities for developing ligand-controlled, enantioselective remote C–H activation reactions. Third, the oxidation potentials for the reoxidation of low-valent metal species are different, which may lead to the use of more practical oxidants for closing the catalytic cycle. Herein, we report the first example of using a Rh(III) catalyst in the presence of a guiding template to provide a *meta*-selective C–H olefination of hydrocinnamic acids. The use of Cu(II) as the co-oxidant is an advantage compared to the Ag oxidant required for the related Pd chemistry. The generality of this approach is also demonstrated by accomplishing *meta*-C–H olefination of aniline and indoline substrates bearing templates previously developed for Pd(II) catalysts.^{6b,c}

On the basis of previous Pd(II)-catalyzed *meta*-selective C–H bond activation studies using a nitrile-containing template,^{6a} we initiated efforts to develop a [RhCp*Cl₂]₂-catalyzed *meta*-C–H olefination of hydrocinnamic acid (Scheme 1). We selected hydrocinnamic acid-derived compound **1'** (Table 1) as our initial substrate for optimization because it is a benchmark substrate for the analogous Pd(II) chemistry. Our studies began using Cu(OAc)₂ as a terminal oxidant for the reaction in dry toluene under an atmosphere of O₂ at 100 °C. With these conditions, we were delighted to find our desired product in trace quantities. A thorough solvent screen was undertaken and DCE was found to be optimal, allowing the formation of the desired product in 18% yield. A brief study of the temperature dependence of this reaction indicated that at 120 °C a yield of 25% could be obtained. Though 140 °C provided a higher

Received: December 26, 2016

Published: January 27, 2017

Scheme 1. Directed *meta*-C–H FunctionalizationTable 1. Optimization of the Reaction Conditions^a

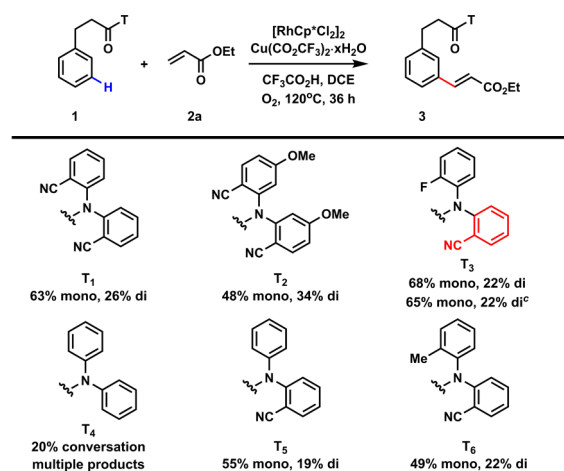
Entry	Oxidant	Additive (1 equiv)	Yield (%) [mono:di]	Entry	Oxidant	Additive (1 equiv)	Yield (%) [mono:di]
1	Cu(OAc) ₂	—	25 [25:0]	9	Cu(BF ₄) ₂	—	NR
2	AgOAc	—	NR	10	Cu(CO ₂ CF ₃) ₂ ·xH ₂ O	—	50 [45:5]
3	Ag ₂ CO ₃	—	NR	11 ^b	Cu(CO ₂ CF ₃) ₂ ·xH ₂ O	—	77 [62:15]
4	AgPF ₆	—	NR	12 ^{b,c}	Cu(CO ₂ CF ₃) ₂ ·xH ₂ O	—	55 [47:8]
5	Ag ₂ O	—	NR	13 ^b	Cu(CO ₂ CF ₃) ₂ ·xH ₂ O	HOAc	66 [54:12]
6	PhI(OAc) ₂	—	NR	14 ^b	Cu(CO ₂ CF ₃) ₂ ·xH ₂ O	PivOH	81 [55:26]
7	Cu(SO ₃ CF ₃) ₂	—	NR	15 ^b	Cu(CO ₂ CF ₃) ₂ ·xH ₂ O	CF ₃ CO ₂ H	89 [63:26]
8	CuCl ₂	—	NR	16 ^b	Cu(CO ₂ CF ₃) ₂ ·xH ₂ O	AcONa	23 [23:trace]

^aReaction conditions: **1'** (0.1 mmol), **2a** (0.6 mmol), [RhCp*Cl₂]₂ (5 mol %), oxidant (0.2 mmol), additive (0.1 mmol), dry DCE (2 mL), O₂, 36 h, 120 °C. Yields were determined by ¹H NMR analysis using CH₂Br₂ as the internal standard. ^bCu(CO₂CF₃)₂·xH₂O (0.1 mmol). ^cAir was used instead of O₂.

yield, the reaction profile was not as clean, and we therefore decided to move forward with the optimization using 120 °C. No distinct difference was observed when the reaction time was extended to 48 h, indicating that the catalyst was no longer functional after 36 h. A wide variety of oxidants were evaluated, and Cu(O₂CCF₃)₂·xH₂O was found to be far superior to the others, enhancing the yield to 50%, with 5% being disubstituted product. Interestingly, when we decreased the amount of Cu(O₂CCF₃)₂·xH₂O to 1 equiv, a significant increase in the total yield to 77% was obtained. Presumably, excess Cu(II) species could outcompete Rh(III) for coordination with the nitrile template. We next examined the role of the oxidants in this transformation. First, since O₂ can potentially turn over copper oxidation catalysts, we attempted the reaction under an atmosphere of oxygen with only 0.5 equiv of Cu(O₂CCF₃)₂·xH₂O and found that the yield decreased to 44%. This led us to evaluate the reaction under a nitrogen atmosphere in the presence of 1 equiv of Cu(O₂CCF₃)₂·xH₂O; however, the yield of the desired products under these conditions was a mere 13%, indicating that O₂ is also necessary for this transformation (see the Supporting Information (SI)). Further optimization of additives revealed that addition of 1 equiv of CF₃CO₂H improved the yield to 89%. The use of a Cu(II) oxidant is a practical advantage over Pd(II) methods as Ag(I) salts are often needed in Pd(II)-catalyzed remote C–H functionalizations using nitrile templates.⁶

Since the disubstituted product was non-negligible under the standard conditions, we endeavored to search for a suitable

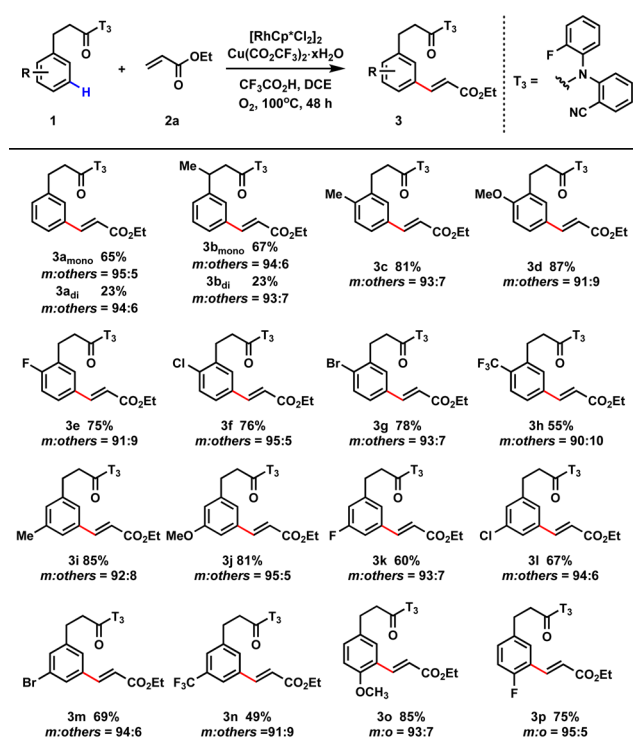
directing group that could inhibit the generation of disubstituted product. A brief evaluation of templates revealed that use of T₃ containing a single nitrile group (Table 2) could

Table 2. Investigation of Templates^{a,b}

^aReaction conditions: **1** (0.1 mmol), **2a** (0.6 mmol), [RhCp*Cl₂]₂ (5 mol %), Cu(CO₂CF₃)₂·xH₂O (0.1 mmol), CF₃CO₂H (0.1 mmol), dry DCE (2 mL), O₂, 36 h, 120 °C. ^bYields were determined by ¹H NMR analysis using CH₂Br₂ as the internal standard. ^cIsolated yield of the reaction run at 100 °C for 48 h.

slightly improve the mono:di ratio, enabling the mono- and disubstituted products to be obtained in 68% and 22% yield, respectively. On the basis of these results, we selected template T₃ as our final template. Importantly, the nitrile is key to achieving high selectivity, as indicated by the mixture of products obtained with T₄. At this point, we attempted to lower the reaction temperature. As can be seen in Table 2, using the optimized conditions and template at 100 °C provided a comparable yield of the desired product. Under these milder conditions, the catalyst was active for over 36 h, and the optimal reaction time was extended to 48 h.

With the optimized conditions in hand, we examined the scope of hydrocinnamic acid derivatives using ethyl acrylate (**2a**) as the coupling partner (Table 3). Unsubstituted compounds **1a** and **1b** provided the highest total yields of 88% and 90%, respectively. It is worth noting that there were no disubstituted products for the substrates with substituents at the *ortho*, *meta*, or *para* positions. For *ortho*-substituted substrates, both electron-donating groups (**3c**, **3d**) and halogens (**3e–g**) were well-tolerated, with the desired products being obtained in good yield. Substrate **1h** containing an *ortho*-trifluoromethyl group could be coupled to provide the desired product in a modest although synthetically useful yield of 55%. For *meta*-substituted substrates, those bearing electron-donating groups at the *meta*-position (**1i**, **1j**) worked well in the reaction, cleanly affording the desired products in 85% (**3i**) and 81% (**3j**) yield with good *meta* selectivity. Substitution of the *meta*-position with halogens (**3k–m**; Table 3) provided a slight depreciation of the yield, though the selectivity remained high. *meta*-Trifluoromethyl-substituted substrate **1n** gave the desired product **3n** in a modest yield of 49%. Either methoxy or fluoride substitution at the *para* position does not hamper this reaction (**3o**, **3p**). However, it is noteworthy that this reaction is somewhat sensitive to both sterics and electronics at the 4-position of the aromatic. We attempted reactions using 4-*tert*-

Table 3. Rh(III)-Catalyzed *meta*-C–H Olefination of Hydrocinnamic Acid Derivatives^{a,b}

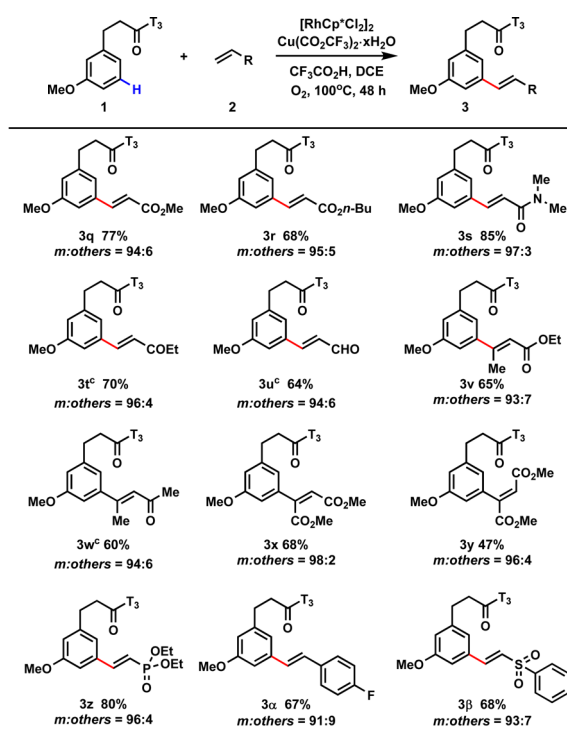
^aReaction conditions: **1** (0.1 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $Cu(CO_2CF_3)_2 \cdot xH_2O$ (0.1 mmol), CF_3CO_2H (0.1 mmol), dry DCE (2 mL), O_2 , 48 h, 100 °C. ^bIsolated yields are shown.

butyl- and 4-nitrohydrocinnamic acid-derived substrates, but neither provided significant quantities of olefination products.

To investigate the generality of this reaction, the scope of olefin coupling partners was evaluated. As can be seen in Table 4, a wide range of olefin coupling partners can be employed in this transformation. Methyl acrylate, butyl acrylate, dimethyl acrylamide, ethyl vinyl ketone, acrolein, and diethylvinyl phosphonate could all be effectively coupled, providing the desired products in good yield. A β -substituted enone and styrene derivatives were also compatible with this reaction, with electron-withdrawing groups on the aromatic ring of styrene being favored. Phenyl vinyl sulfone also coupled well in this reaction.

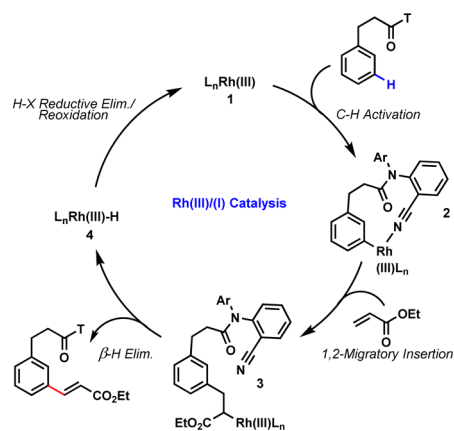
Given the generality of this templating approach with Pd(II) catalysis, we sought to examine whether this Rh(III) system can be extended to other types of substrates. A brief examination of templates that have previously been utilized for Pd(II) catalysis^{6b,c} indicated that indeed, Rh(III)-catalyzed *meta*-C–H functionalization using this strategy will likely prove to be highly general. Both indoline and *N*-methylaniline were successfully olefinated at the *meta*-position using a template originally developed for Pd(II)-catalyzed olefination of indolines (see Supporting Information for details).^{6e} Interestingly, it was found that in these cases the addition of TFA to the reaction mixture hampered the reactivity of the catalyst. Further work on improving the scope and efficiency of this transformation using Rh(III), as well as other transition metal catalysts, is currently underway and will be reported in due course.

A plausible reaction mechanism for this reaction is proposed in Scheme 2. Coordination of the nitrile to the $[Rh(III)]$

Table 4. Scope of Olefin Coupling Partners^{a,b}

^aReaction conditions: **1** (0.1 mmol), **2** (0.6 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $Cu(CO_2CF_3)_2 \cdot xH_2O$ (0.1 mmol), CF_3CO_2H (0.1 mmol), dry DCE (2 mL), O_2 , 48 h, 100 °C. ^bIsolated yields are shown. ^cThe reaction was run in the absence of the TFA additive.

Scheme 2. Simplified Mechanism of the Olefination Reaction



catalyst is followed by *meta*-C–H bond activation to give the corresponding 12-membered rhodacyclic intermediate **2**. Subsequent coordination to the olefin coupling partner followed by 1,2-migratory insertion would yield intermediate **3**. β -Hydride elimination yields the desired product and Rh(III) hydride **4**. Reductive elimination followed by reoxidation of $[Rh(I)]$ to $[Rh(III)]$ by $Cu(CO_2CF_3)_2 \cdot xH_2O$ and O_2 would restore the active catalyst, completing the catalytic cycle. In an attempt to probe whether C–H activation is rate-determining in this catalytic cycle, we conducted experiments to determine the kinetic isotope effect (KIE) for parallel experiments. The KIE ($k_H/k_D = 1.8$) revealed that the *meta*-C–H bond cleavage may be the rate-determining step (see the SI for details).

We next attempted the reaction on a gram scale. Refluxing the reaction mixture in toluene for 48 h under O₂ (balloon) gave a 75% yield (55% mono, 20% di, isolated) of the desired product (see the SI for details).

In summary, we have developed a Rh(III)-catalyzed *meta*-C–H olefination of hydrocinnamic acid derivatives using a modified mononitrile template. The identification of Cu(CO₂CF₃)₂·xH₂O as an oxidant was crucial for this reaction. These results pave the way for further development of new ligands for Rh(III)-catalyzed remote C–H functionalizations.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13269.

Experimental procedures and spectral data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*luyi@nju.edu.cn

*sunwy@nju.edu.cn

*yu200@scripps.edu

ORCID

Wei-Yin Sun: 0000-0001-8966-9728

Jin-Quan Yu: 0000-0003-3560-5774

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (21201100, 21671097, and 21331002) and the National Science Foundation (CHE-1465292) for support.

■ REFERENCES

(1) Reviews of C–H activation: (a) Daugulis, O.; Do, H. Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (b) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (c) Engle, K. M.; Yu, J.-Q. *J. Org. Chem.* **2013**, *78*, 8927. (d) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (e) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281. (f) Mkhaliid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. Reviews pertaining to Rh(III) C–H activation: (g) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (h) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (i) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (j) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichimica Acta* **2012**, *45*, 31.

(2) Examples of nondirected *meta*-C–H borylation and silylation: (a) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III. *Science* **2002**, *295*, 305. (b) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (c) Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056. (d) Murphy, J. M.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 15434. (e) Mkhaliid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. (f) Kuninobu, Y.; Ida, H.; Nishi, M.; Kanai, M. *Nat. Chem.* **2015**, *7*, 712. (g) Maleczka, R. E., Jr.; Shi, F.; Holmes, D.; Smith, M. R., III. *J. Am. Chem. Soc.* **2003**, *125*, 7792. (h) Holmes, D.; Chotana, G. A.; Maleczka, R. E., Jr.; Smith, M. R., III. *Org. Lett.* **2006**, *8*, 1407. (i) Hurst, T. E.; Macklin, T. K.; Becker, M.; Hartmann, E.; Kuegel, W.; Parisienne-La Salle, J.-C.; Batsanov, A. S.; Marder, T. B.; Snieckus, V. *Chem. - Eur. J.* **2010**, *16*, 8155. Examples of regioselective C–H metalation without the need for 1,3-disubstitution: (j) Cheng, C.; Hartwig, J. F. *Science* **2014**, *343*, 853. (k) Saito, Y.; Segawa, Y.;

Itami, K. *J. Am. Chem. Soc.* **2015**, *137*, 5193. (l) Kuninobu, Y.; Ida, H.; Nishi, M.; Kanai, M. *Nat. Chem.* **2015**, *7*, 712.

(3) (a) Saidi, O.; Marafie, J.; Ledger, A. E. W.; Liu, P. M.; Mahon, M. F.; Kociok-Koehn, G.; Whittlesey, M. K.; Frost, C. G. *J. Am. Chem. Soc.* **2011**, *133*, 19298. (b) Hofmann, N.; Ackermann, L. *J. Am. Chem. Soc.* **2013**, *135*, 5877. (c) Li, J.; Warratz, S.; Zell, D.; De Sarkar, S.; Ishikawa, E. E.; Ackermann, L. *J. Am. Chem. Soc.* **2015**, *137*, 13894. (d) Teskey, C. J.; Lui, A. Y. W.; Greaney, M. F. *Angew. Chem., Int. Ed.* **2015**, *54*, 11677. (e) Paterson, A. J.; St John-Campbell, S.; Mahon, M. F.; Press, N. J.; Frost, C. G. *Chem. Commun.* **2015**, *51*, 12807.

(4) (a) Wang, X. C.; Gong, W.; Fang, L. Z.; Zhu, R. Y.; Li, S. H.; Engle, K. M.; Yu, J. Q. *Nature* **2015**, *519*, 334. (b) Dong, Z.; Wang, J. C.; Dong, G. B. *J. Am. Chem. Soc.* **2015**, *137*, 5887. (c) Shen, P.-X.; Wang, X.-C.; Wang, P.; Zhu, R.-Y.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 11574. (d) Han, J.; Zhang, L.; Zhu, Y.; Zheng, Y.; Chen, X.; Huang, Z.-B.; Shi, D.-Q.; Zhao, Y. *Chem. Commun.* **2016**, *52*, 6903. (e) Wang, P.; Farmer, M. E.; Huo, X.; Jain, P.; Shen, P.-X.; Ishoey, M.; Bradner, J. E.; Wisniewski, S. R.; Eastgate, M. D.; Yu, J.-Q. *J. Am. Chem. Soc.* **2016**, *138*, 9269.

(5) Examples using copper and aryl iodoniums to achieve *meta*-C–H arylation: (a) Phipps, R. J.; Gaunt, M. J. *Science* **2009**, *323*, 1593. (b) Duong, H. A.; Gilligan, R. E.; Cooke, M. L.; Phipps, R. J.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 463. (c) Yang, Y.; Li, R.; Zhao, Y.; Zhao, D.; Shi, Z. *J. Am. Chem. Soc.* **2016**, *138*, 8734. Example using CO₂ as a traceless directing group: (d) Luo, J.; Preciado, S.; Larrosa, I. *J. Am. Chem. Soc.* **2014**, *136*, 4109. Example using deprotonation to achieve *meta* functionalization: (e) Martinez-Martinez, A. J.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T. *Science* **2014**, *346*, 834.

(6) Examples of Pd-catalyzed *meta*-C–H functionalization using nitrile-based templates: (a) Leow, D.; Li, G.; Mei, T.-S.; Yu, J.-Q. *Nature* **2012**, *486*, 518. (b) Tang, R.-Y.; Li, G.; Yu, J.-Q. *Nature* **2014**, *507*, 215. (c) Yang, G. Q.; Lindovska, P.; Zhu, D. J.; Kim, J.; Wang, P.; Tang, R. Y.; Movassaghi, M.; Yu, J. Q. *J. Am. Chem. Soc.* **2014**, *136*, 10807. (d) Lee, S.; Lee, H.; Tan, K. L. *J. Am. Chem. Soc.* **2013**, *135*, 18778. (e) Li, S. D.; Ji, H. F.; Cai, L.; Li, G. *Chem. Sci.* **2015**, *6*, 5595. (f) Bera, M.; Maji, A.; Sahoo, S. K.; Maiti, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 8515. (g) Chu, L.; Shang, M.; Tanaka, K.; Chen, Q.; Pissarnitski, N.; Streckfuss, E.; Yu, J.-Q. *ACS Cent. Sci.* **2015**, *1*, 394.

(7) (a) Bag, S.; Patra, T.; Modak, A.; Deb, A.; Maity, S.; Dutta, U.; Dey, A.; Kancherla, R.; Maji, A.; Hazra, A.; Bera, M.; Maiti, D. *J. Am. Chem. Soc.* **2015**, *137*, 11888. (b) Patra, T.; Bag, S.; Kancherla, R.; Mondal, A.; Dey, A.; Pimparkar, S.; Agasti, S.; Modak, A.; Maiti, D. *Angew. Chem., Int. Ed.* **2016**, *55*, 7751.

(8) Examples of Rh(III)-catalyzed *ortho*-C–H olefination: (a) Mishra, N. K.; Park, J.; Sharma, S.; Han, S.; Kim, M.; Shin, Y.; Jang, J.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.* **2014**, *50*, 2350. (b) Wang, N.-J.; Mei, S.-T.; Shuai, L.; Yuan, Y.; Wei, Y. *Org. Lett.* **2014**, *16*, 3040. (c) Zhang, X.-S.; Zhu, Q.-L.; Zhang, Y.-F.; Li, Y.-B.; Shi, Z.-J. *Chem. - Eur. J.* **2013**, *19*, 11898. (d) Li, B.; Ma, J.; Xie, W.; Song, H.; Xu, S.; Wang, B. *Chem. - Eur. J.* **2013**, *19*, 11863. (e) Liu, B.; Fan, Y.; Gao, Y.; Sun, C.; Xu, C.; Zhu, J. *J. Am. Chem. Soc.* **2013**, *135*, 468. (f) Feng, C.; Feng, D.; Loh, T.-P. *Org. Lett.* **2013**, *15*, 3670. (g) Zhou, J.; Li, B.; Hu, F.; Shi, B.-F. *Org. Lett.* **2013**, *15*, 3460. (h) Presset, M.; Oehlich, D.; Rombouts, F.; Molander, G. A. *Org. Lett.* **2013**, *15*, 1528. (i) Cui, S.; Zhang, Y.; Wu, Q. *Chem. Sci.* **2013**, *4*, 3421. (j) Shen, Y.; Liu, G.; Zhou, Z.; Lu, X. *Org. Lett.* **2013**, *15*, 3366. (k) Ye, B.; Cramer, N. *Science* **2012**, *338*, 504. (l) Zhu, C.; Falck, J. R. *Chem. Commun.* **2012**, *48*, 1674. (m) Li, G.; Ding, Z.; Xu, B. *Org. Lett.* **2012**, *14*, 5338. (n) Kwon, K.-H.; Lee, D. W.; Yi, C. S. *Organometallics* **2012**, *31*, 495. (o) Hyster, T. K.; Knörr, L.; Ward, T. R.; Rovis, T. *Science* **2012**, *338*, 500. (p) Tsai, A. S.; Brasse, M.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2011**, *13*, 540. (q) Park, S.; Kim, J. Y.; Chang, S. *Org. Lett.* **2011**, *13*, 2372. (r) Li, X.; Zhao, M. *J. Org. Chem.* **2011**, *76*, 8530. (s) Wang, F.; Song, G.; Li, X. *Org. Lett.* **2010**, *12*, 5430. (t) Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9982. (u) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2007**, *9*, 1407.