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Cooperative C(sp^3)−H and C(sp^2)−H Activation of 2-Ethylpyridines by Copper and Rhodium: A Route toward Quinolizinium Salts

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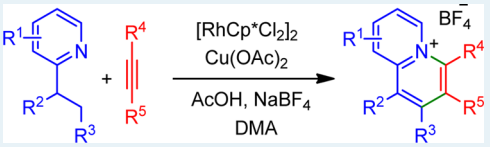
Supporting Information

ABSTRACT: A method for the synthesis of substituted quinolizinium salts from 2-ethylpyridines and alkynes is demonstrated. The transformation is conveniently achieved using 1 mol % of a Rh(III) catalyst along with an excess amount of copper(II) salt. The reaction gives high product yields with broad substrate scope and functional group tolerance. Detailed mechanistic studies suggest that 2-vinylpyridine is formed in situ from 2-ethylpyridine by a copper-promoted C(sp^3)−H hydroxylation, followed by dehydration. Later, a Rh(III)-catalyzed pyridine-directed vinylic C(sp^2)−H activation and annulation with alkynes provided the final product.



KEYWORDS: *rhodium, copper, C−H activation, dehydrogenation, quinolizinium salts, alkynes*

Synthesis of heterocyclic and carbocyclic compounds via transition-metal-catalyzed C−H activation has become an important tool in organic synthesis because the reactions use less-functionalized starting compounds, tolerate a wide range of functional groups, and are generally more step- and atom-economical.[1] Over the past three decades, great advances have been made in the area of C(sp^2)−H functionalization and are widely used in organic synthesis.[2] In particular, Rh(III)-catalyzed C(sp^2)−H activation and annulation reactions have become a powerful tool for the synthesis of heterocyclic compounds.[3] Similar annulation reactions via C(sp^3)−H activations are rare,[4,5] but recently, the dehydrogenative functionalization of aliphatic compounds into unsaturated or aromatic compounds has gradually emerged as a new strategy in organic synthesis.[6] It is attractive because of the in situ formation of unstable, unsaturated species from the stable and readily available starting compounds.

In this report, we disclose an interesting cooperative Cu^{II}-mediated C(sp^3)−H and a Rh^{III}-catalyzed C(sp^2)−H activation and annulation reaction for the synthesis of quinolizinium salts from 2-ethylpyridines and alkynes (Scheme 1).[7] Quinolizinium cation is an important core found in many natural and bioactive compounds[8] and materials.[9] They are also potential intermediates for the synthesis of heterocyclic compounds.[10] After a great effort to optimize the catalytic reaction (see Supporting Information), we found that diphenylacetylene (**1a**) (0.28 mmol) reacted with 2-ethylpyridine (**2a**) (0.56 mmol) in the presence of 1 mol % $[RhCl_2Cp^*]_2$, $Cu(OAc)_2$ (2.24 mmol), acetic acid (5.60 mmol), and $NaBF_4$ (0.28 mmol) in DMAc (3 mL) at 150 °C for 24 h to give quinolizinium salt **3a** in 89% isolated yield. The compound was thoroughly characterized by ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR, HRMS, and X-ray data.[11] In this catalytic reaction, the choice of oxidant, solvent, and acid is crucial. In the absence of rhodium(III) or copper(II), no product **3a** was observed. Moreover, a decrease in the amount of $Cu(OAc)_2$ lowers the product yields (See Table S3 for the detailed optimization studies). It might be due to the reduction of Cu^{II} to Cu^{I} by DMAc under the reaction conditions.[12] Among the various copper salts tested, $Cu(OAc)_2{\cdot}H_2O$, $Cu(BF_4)_2{\cdot}6H_2O$, and $Cu(OTf)_2$ afforded product **3a** in 82%, 45%, and 30% yields, respectively. The catalytic reaction is less effective with the other solvents tested. Notably, *o*-xylene, 2-ethoxyethanol, dimethylformamide, and dimethyl sulfoxide (DMSO) offered **3a** in 35, 57, 44, and 27% yields, respectively. The reaction also proceeded well with different anion sources. Quinolizinium salt **3a** containing different anions SbF_6^{-1}, $OSO_2CF_3^{-1}$, or PF_6^{-1} was isolated in 84%, 84%, and 76% yields, respectively.[11] Because of the lower cost and higher solubility of $NaBF_4$ relative to other anion sources, $NaBF_4$ was selected for all other studies. An acid additive is also crucial for a high product yield, and AcOH appears more appropriate in terms of the yield of **3a** than the other acids tested (see Supporting Information for the detailed optimization studies).

To understand the scope of the reaction, we examined the reaction of various symmetrical and unsymmetrical alkynes with 2-ethylpyridine (**2a**) under the optimized reaction conditions. The results are presented in Table 1. Thus, *p*-Me- and *p*-OMe-substituted diphenyl acetylenes (**1b−c**) reacted smoothly with **2a** to afford quinolizinium salts **3b** and **3c** in 83 and 81% yields,

Scheme 1. Quinolizinium Salt Formation via C−H Activation

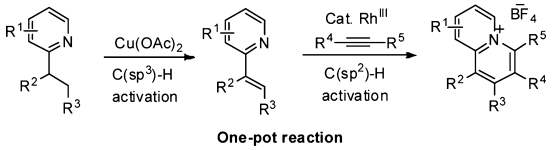


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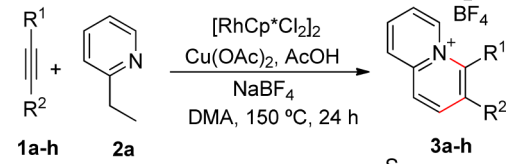
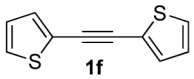
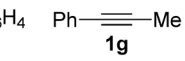
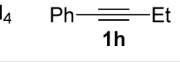
Table 1. Scope of Alkynes in the Formation of Quinolizinium Salts[a]



1a; $R^1 = R^2$ = Ph
1b; $R^1 = R^2$ = 4-MeC_6H_4
1c; $R^1 = R^2$ = 4-$MeOC_6H_4$
1d; $R^1 = R^2$ = 4-FC_6H_4
1e; $R^1 = R^2$ = 4-$F_3CC_6H_4$







entry	1	3	yield (%)[b]
1	**1a**	**3a**	89
2	**1b**	**3b**	83
3	**1c**	**3c**	81
4	**1d**	**3d**	60
5	**1e**	**3e**	58
6	**1f**	**3f**	69
7	**1g**	**3g**	79 (81:19)[c]
8	**1h**	**3h**	74 (76:24)[c]

[a]All reactions were carried out using alkyne **1** (0.28 mmol), 2-ethylpyridine **2a** (0.56 mmol), $[Cp^*RhCl_2]_2$ (1.0 mol %), $Cu(OAc)_2$ (2.24 mmol), AcOH (5.60 mmol), and $NaBF_4$ (0.28 mmol) in DMAc (3.0 mL) at 150 °C for 24 h. [b]Isolated yield. [c]The ratios of regioisomers are given in parentheses and were determined by ^1H NMR analysis; the major isomers are shown.

respectively (Table 1, entries 2 and 3). Similarly, electron-withdrawing 4-fluorophenyl- and 4-trifluoromethylphenyl-group-substituted alkynes **1d** and **1e** reacted with **2a** to give the respective salts **3d** and **3e** in good yields (entries 4 and 5). Thiophene-substituted alkyne **1f** is also compatible under the reaction conditions to afford the expected quinolizinium salt **3f** in 69% yield. Unsymmetrical alkynes were also successfully employed in this bimetal mediated C(sp^3)−H and C(sp^2)−H activation to form the corresponding quinolizinium salts in high regioselectivity. Thus, the reaction of 1-phenyl-1-propyne (**1g**) and 1-phenyl-1-butyne (**1h**) with **2a** effectively afforded the expected products **3g** and **3h** in high yields. Unfortunately, terminal alkynes and dialkyl alkyne failed to give the corresponding quinolizinium salt under the standard reaction conditions.

To further extend the scope of the present reaction, we examine the reaction of diphenylacetylene with different 2-alkyl substituted pyridines under the optimized reaction conditions (Table 2). First, we probed the effect of substituent at carbon-1 of the ethyl group in **2a** on the product yield by carrying out the reaction of 2-(hexan-2-yl)pyridine (**2b**), 2-(1- phenylpropan-2-yl)pyridine (**2c**), and 2-isopropylpyridine (**2d**) with **1a.** All three substrates gave the expected substituted quinolizinium salts **3i**−**3k** in moderate to good yields (entries 1−3). The reactions show excellent chemoselectivity; only the methyl group in the alkyl substituent is involved in the C−H bond activation to give the final products. The *n*-propyl group in **2b** and the phenyl group in **2c** likely prevent the C−H bond activation reaction from occurring at the attached methylene carbon (carbon-2) as a result of the very large steric effect of these moieties compared with a hydrogen.

Next, we investigated the effect of the substituent at carbon-2 on the ethyl group of **2**. 2-(*n*-Pentyl)pyridine (**2e**) reacted smoothly with **1a** to give product **3l** in 75% yield, implying that a long alkyl chain is compatible with the present catalytic reaction. Similarly, treatment of 2-phenethylpyridine (**2f**) with **1a** afforded the desired C−H bond activation product **3m** in moderate yields. Furthermore, 5-methyl-substituted 2-arylethylpyridines **2g** and **2h** also reacted with **1a** efficiently to furnish quinolizinium salts **3n** and **3o**, respectively, in good yields. Interestingly, 2-ethylbenzimidazole derivative **2i** also successfully underwent dehydrogenative C−H activation to give respective quinolizinium salt product **3p** (entry 8), but under the reaction conditions, 2-(*t*-butyl)-5-methylpyridine (**2j**) did not offer any C−H activation product (entry 9).

To understand the nature of the present catalytic transformation, we examined the reactions of diphenylacetylene (**1a**) with 2-vinylpyridine (**2A**) and 2-styrylpyridine (**2F**) under the reaction conditions similar to those shown in Tables 1 and 2. The reactions afforded products **3a** and **3m** in 91% and 65% yields, respectively (Scheme 2a). In the absence of Rh catalyst, no products were obtained for Scheme 2a. Next, we treated **2g** under the standard reaction conditions, but in the absence of acetylene **1a**. The reaction afforded dehydrogenation product **2G** in 33% yield along with unreacted **2g** in 50%. We then carried out the above reaction in the absence of $[RhCp^*Cl_2]_2$. Surprisingly, the dehydrogenation product **2G** was obtained in 35% yield with 38% unreacted **2g** recovered. Interestingly, treatment of **2g** under the standard catalytic conditions but in the absence of $Cu(OAc)_2$, 99% of **2g** was recovered and no dehydrogenation product **2G** was detected. Furthermore, when **2g** was treated with a stoichiometric amount of $[RhCp^*Cl_2]_2$ in the absence of $Cu(OAc)_2$, a quantitative amount of unreacted **2g** was recovered (Scheme 2b). The results suggest that the $Cu(OAc)_2$ plays the key role in the dehydrogenation of 2-ethylpyridine to 2-vinylpyridine.

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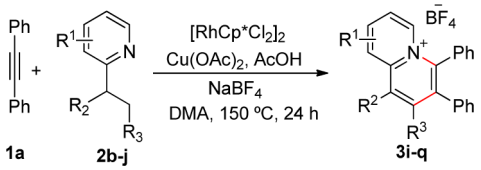
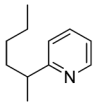
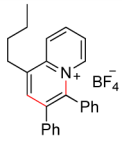
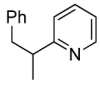
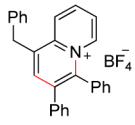
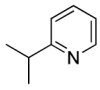
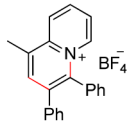
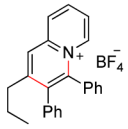
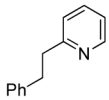
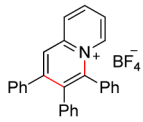
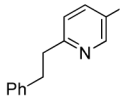
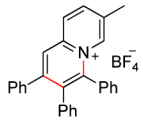
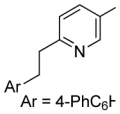
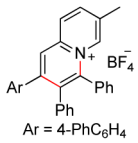
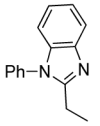
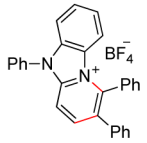
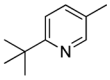
Table 2. Scope of 2-Alkylpyridines in the Catalytic Synthesis of Quinolizinium Salts[a]



entry	2		3		yield (%)[b]
1		2b		3i	48
2		2c		3j	39
3		2d		3k	79
4		2e		3l	75
5		2f		3m	57
6		2g		3n	61
7		2h		3o	63
8		2i		3p	72
9		2j	--	3q	--

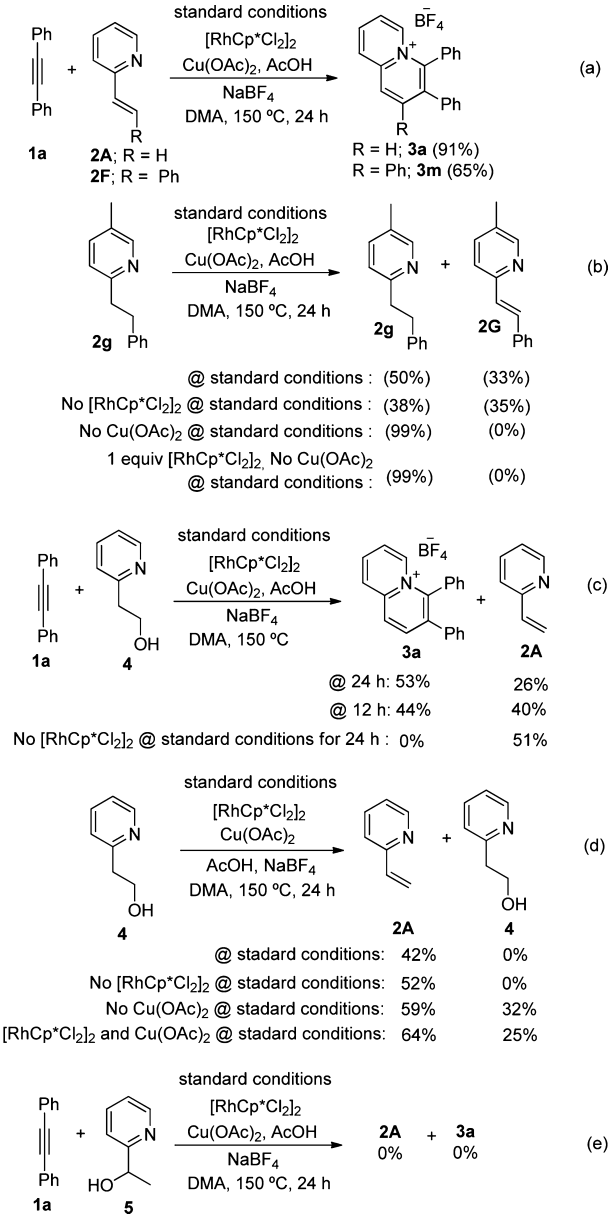
[a]All reactions were carried out using diphenylacetylene **1a** (0.28 mmol), 2-alkylpyridine **2** (0.56 mmol), $[Cp^*RhCl_2]_2$ (1.0 mol %), $Cu(OAc)_2$ (2.24 mmol), AcOH (5.60 mmol), and $NaBF_4$ (0.28 mmol) in DMAc (3.0 mL) at 150 °C for 24 h. [b]Isolated yield.

$[RhCp^*Cl_2]_2$ clearly is not involved in the dehydrogenation reaction to form intermediate **2A** from **2a**. The in situ-formed 2-vinylpyridine (**2A**) undergoes Rh(III)-catalyzed C−H activation and annulation with alkynes to give product **3a**. The formation of 2-vinylpyridine from 2-ethylpyridine probably occurs through a copper-mediated hydroxylation,[13] followed by dehydration; however, our attempt to isolate the hydroxylation/acetoxylation product from 2-ethylpyridine failed. The reaction of 2-(pyridin-2-yl)ethanol (**4**) with **1a** under the standard reaction conditions for 12 h afforded product **3a** in 44% and the intermediate product vinylpyridine (**2A**) in 40% yields. As the reaction time increased, the yield of **3a** increased along with the decrease of **2A**, and no salt product was formed in the absence of Rh^{III} (Scheme 2c).

We also tested several reaction conditions for the dehydration of 2-(pyridin-2-yl)ethanol (**4**) and found that no rhodium or copper is necessary for the dehydration (Scheme 2d). Interestingly, the reaction of 2-(1-hydroxyethyl)pyridine (**5**) with **2a** under the standard reaction conditions did not give either **2A** or **3a** at the end of the reaction (Scheme 2e). An alternative pathway for the in situ generation of vinylpyridine from 2-ethylpyridine through Cu-mediated $C(sp^3)$−H activation followed by β-hydride elimination cannot be ruled out.

On the basis of the results of the present catalytic reaction and the above mechanistic studies, a possible catalytic cycle is

Scheme 2. Mechanistic Studies



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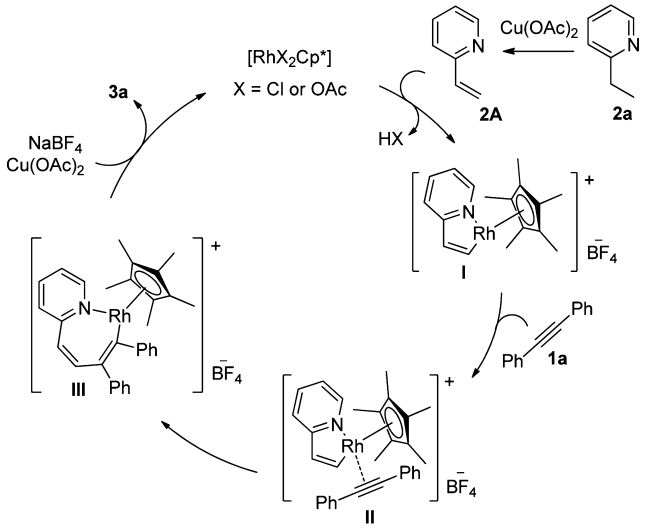
proposed, as shown in Scheme 3. The catalytic cycle is initiated by the dehydrogenation of 2-ethylpyridine by copper(II)

Scheme 3. Plausible Catalytic Cycle



acetate to 2-vinylpyridine. The coordination of this in situ-formed 2-vinylpyridine to the Rh(III) center, followed by cyclometalation via vinylic C(sp^2)−H bond cleavage, gives a five-membered ring rhodacycle that likely undergoes anion exchange with BF_4^- first and then forms cationic rhodacycle **I** with BF_4^- as the anion. Coordination of the alkyne to cationic rhodacycle **I** affords **II**, and subsequent insertion into the C−Rh bond provides seven-membered rhodacycle **III**, which then undergoes reductive elimination to give the final quinolizinium salt and Rh(I) species. The latter is reoxidized to Rh(III) by copper(II) to regenerate the active catalytic species.

In summary, we have demonstrated a catalytic dehydroannulation reaction of substituted 2-ethylpyridines with alkynes to afford the corresponding quinolizinium salts via cooperative C(sp^3)−H and C(sp^2)−H activation by copper and rhodium, respectively, as the key steps. Detailed mechanistic studies reveal that 2-vinylpyridines are formed from 2-ethylpyridines via C(sp^3)−H activation by copper(II) salt. Later, Rh(III)-catalyzed vinylic C(sp^2)−H activation and annulation with alkynes affords the quinolizinium salts. The applications of this approach to the synthesis of other heterocycles and useful compounds are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01244.

General experimental procedures, characterization details and ^1H and ^{13}C NMR spectra of new compounds (PDF)
Supplementary crystallographic data ($C_{21}H_{16}BF_4N$) (CIF)
Supplementary crystallographic data ($C_{22}H_{16}F_3NO_3S$) (CIF)
Supplementary crystallographic data ($C_{21}H_{16}F_6NSb$) (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Bond, G. C. *Metal-Catalysed Reactions of Hydrocarbons*; Kluwer Academic/Plenum Publishers: New York, 2005. (b) Dyker, G. *Handbook of C−H Transformations: Applications in Organic Synthesis*; Wiley-VCH: Weinheim, 2005. (c) Yu, J.-Q.; Ackermann, L.; Shi, Z. C−H *Activation*; Springer: Heidelberg; New York, 2010. (d) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792−9826. (e) Cho, H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068−5083. (f) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236−10254. (g) Li, B.; Dixneuf, P. H. *Chem. Soc. Rev.* **2013**, *42*, 5744−5767. (h) Gao, K.; Yoshikai, N. *Acc. Chem. Res.* **2014**, *47*, 1208−1219.

(2) For recent reviews: (a) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281−295. (b) Kakiuchi, F.; Kochi, T.; Murai, S. *Synlett* **2014**, *25*, 2390−2414. (c) Le Bras, J.; Muzart, J. *Synthesis* **2014**, *46*, 1555−1572. (d) Gigant, N.; Chausset-Boissarie, L.; Gillaizeau, I. *Chem. - Eur. J.* **2014**, *20*, 7548−7564. (e) He, R.; Huang, Z.-T.; Zheng, Q.-Y.; Wang, C. *Tetrahedron Lett.* **2014**, *55*, 5705−5713. (f) Mesganaw, T.; Ellman, J. A. *Org. Process Res. Dev.* **2014**, *18*, 1097−1104. (g) Qiu, G.; Kuang, J.; Wu, J. *Adv. Synth. Catal.* **2014**, *356*, 3483−3504. (h) Gandeepan, P.; Cheng, C.-H. *Chem. - Asian J.* **2015**, *10*, 824−838.

(3) (a) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814−825. (b) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443−1460. (c) Satoh, T.; Miura, M. *Chem. - Eur. J.* **2010**, *16*, 11212−11222. (d) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651−3678. (e) Du Bois, J. *Org. Process Res. Dev.* **2011**, *15*, 758−762. (f) Gandeepan, P.; Rajamalli, P.; Cheng, C.-H. *Chem. - Eur. J.* **2015**, *21*, 9198−9203.

(4) Selected reviews on C(sp^3)−H activation, see: (a) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem. - Eur. J.* **2010**, *16*, 2654−2672. (b) Wasa, M.; Engle, K. M.; Yu, J.-Q. *Isr. J. Chem.* **2010**, *50*, 605−616. (c) Li, H.; Li, B.-J.; Shi, Z.-J. *Catal. Sci. Technol.* **2011**, *1*, 191−206. (d) Franzoni, I.; Mazet, C. *Org. Biomol. Chem.* **2014**, *12*, 233−241. (e) Dastbaravardeh, N.; Christakakou, M.; Haider, M.; Schnürch, M. *Synthesis* **2014**, *46*, 1421−1439.

(5) For Rh-catalyzed C(sp^3)−H activation, see: (a) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585−9587. (b) Cochet, T.; Bellosta, V.; Roche, D.; Ortholand, J.-Y.; Greiner, A.; Cossy, J. *Chem. Commun.* **2012**, *48*, 10745−10747. (c) Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 12924−12927. (d) Tan, X.; Liu, B.; Li, X.; Li, B.; Xu, S.; Song, H.; Wang, B. *J. Am. Chem. Soc.* **2012**, *134*, 16163−16166. (e) Kuninobu, Y.; Nakahara, T.; Takeshima, H.; Takai, K. *Org. Lett.* **2013**, *15*, 426−428. (f) Liu, B.; Zhou, T.; Li, B.; Xu, S.; Song, H.; Wang, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 4191−4195. (g) Wang, N.; Li, R.; Li, L.; Xu, S.; Song, H.; Wang, B. *J. Org. Chem.* **2014**, *79*, 5379−5385.

(6) (a) Izawa, Y.; Pun, D.; Stahl, S. S. *Science* **2011**, *333*, 209−213. (b) Diao, T.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 14566−14569. (c) Moon, Y.; Kwon, D.; Hong, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 11333−11336. (d) Shang, Y.; Jie, X.; Zhou, J.; Hu, P.; Huang, S.; Su, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 1299−1303. (e) Gandeepan, P.; Rajamalli, P.; Cheng, C.-H. *ACS Catal.* **2014**, *4*, 4485−4489.

(7) (a) Luo, C.-Z.; Gandeepan, P.; Cheng, C.-H. *Chem. Commun.* **2013**, *49*, 8528−8530. (b) Luo, C.-Z.; Gandeepan, P.; Jayakumar, J.; Parthasarathy, K.; Chang, Y.-W.; Cheng, C.-H. *Chem. - Eur. J.* **2013**, *19*, 14181−14186. (c) Senthilkumar, N.; Gandeepan, P.; Jayakumar, J.; Cheng, C.-H. *Chem. Commun.* **2014**, *50*, 3106−3108. (d) Luo, C.-Z.; Jayakumar, J.; Gandeepan, P.; Wu, Y.-C.; Cheng, C.-H. *Org. Lett.* **2015**, *17*, 924−927.

DOI: 10.1021/acscatal.5b01244
ACS Catal. 2015, 5, 4837−4841

(8) (a) Lipińska, T. *Tetrahedron Lett.* **2002**, *43*, 9565−9567. (b) Martin, N.; Prado, S.; Lecellier, G.; Thomas, O.; Raharivelomanana, P. *Molecules* **2012**, *17*, 12015−12022. (c) Schmidt, A. *Adv. Heterocycl. Chem.* **2003**, *85*, 67−171. (d) Viola, G.; Dall'Acqua, F.; Gabellini, N.; Moro, S.; Vedaldi, D.; Ihmels, H. *ChemBioChem* **2002**, *3*, 550−558.
(9) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2084. (b) Facchetti, A.; Abbotto, A.; Beverina, L.; van der Boom, M. E.; Dutta, P.; Evmenenko, G.; Marks, T. J.; Pagani, G. A. *Chem. Mater.* **2002**, *14*, 4996−5005. (c) Seddon, K. R. *Nat. Mater.* **2003**, *2*, 363−365. (d) Chen, Z.; Zhang, S.; Qi, X.; Liu, S.; Zhang, Q.; Deng, Y. *J. Mater. Chem.* **2011**, *21*, 8979−8982.
(10) (a) Bradsher, C. K.; Jones, J. H. *J. Org. Chem.* **1958**, *23*, 430−431. (b) Matia, M. P.; Ezquerra, J.; García-Navío, J. L.; Vaquero, J. J.; Alvarez-Builla, J. *Tetrahedron Lett.* **1991**, *32*, 7575−7578. (c) Bull, J. A.; Mousseau, J. J.; Pelletier, G.; Charette, A. B. *Chem. Rev.* **2012**, *112*, 2642−2713.
(11) CCDC 1059785−1059787 contain the supplementary crystallographic data for this paper.
(12) (a) Wang, Y.-F.; Toh, K. K.; Lee, J.-Y.; Chiba, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 5927−5931. (b) Malkhasian, A. Y. S.; Finch, M. E.; Nikolovski, B.; Menon, A.; Kucera, B. E.; Chavez, F. A. *Inorg. Chem.* **2007**, *46*, 2950−2952. (c) Teo, J. J.; Chang, Y.; Zeng, H. C. *Langmuir* **2006**, *22*, 7369−7377.
(13) (a) Wang, Z.; Kuninobu, Y.; Kanai, M. *Org. Lett.* **2014**, *16*, 4790−4793. (b) Zhang, J.; Chen, H.; Wang, B.; Liu, Z.; Zhang, Y. *Org. Lett.* **2015**, *17*, 2768−2771. (c) Li, J.; John, M.; Ackermann, L. *Chem. - Eur. J.* **2014**, *20*, 5403−5408.

DOI: 10.1021/acscatal.5b01244
ACS Catal. 2015, 5, 4837−4841