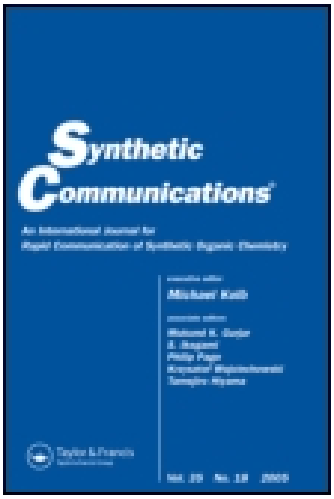

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NICKEL-CATALYZED REDUCTIVE ALKYLATION OF HALOGENATED PYRIDINES WITH SECONDARY ALKYL BROMIDES

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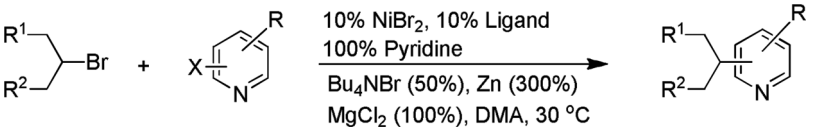
GRAPHICAL ABSTRACT



Abstract *This article highlights Ni-catalyzed cross-electrophile coupling of halogenated pyridines with secondary alkyl bromides using zinc as the terminal reductant. With this protocol, we have successfully achieved different alkyl-substituted pyridines in moderate to excellent yields.*

Keywords Alkylation; cross-coupling; Ni-catalyzed; pyridines; zinc

INTRODUCTION

Many pyridine derivatives are known as bioactive and medicinally important compounds and have been widely used as the agricultural products.[1] The pyridines are also recognized as important ligands in organometallic processes. As a result, numerous methods have been developed for the functionalization of pyridine rings. In particular, decoration of pyridine rings with alkyl moieties has attracted increasing attention. Conventionally, alkylated pyridines can be synthetized via transition-metal-catalyzed cross-coupling reactions of alkyl-metallic reagents with pyridyl electrophiles and pyridyl-metallic reagents with alkyl electrophiles.[2,3] However, both these approaches require the synthesis of functionalized organometallic reagents, which not only need additional steps but also constrain functional-group

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Authors Huiyan Liu and Zhuye Liang contributed equally to this work.

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compatibility. Furthermore, the cross coupling of an alkyl halide with a pyridyl organometallic reagent is often problematic.[3b] Recently, the alkylation of pyridyl C-H bonds has also received pronounced attention, which provides *ortho*-substituted alkyl pyridine effectively.[4] However, although this strategy is ideal in term of atom economy, it generally requires Pd and is limited to *ortho* C-H bonds. In addition, alkylated pyridines can be made through decarboxylative coupling reactions or using an alkylation/double decarboxylation strategy.[5]

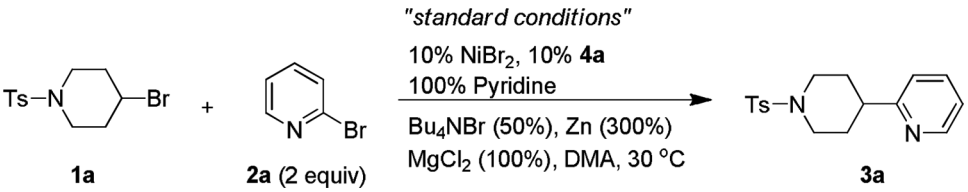
On the other hand, we and others have disclosed the transition-metal-catalyzed reductive coupling reactions of two electrophiles, which afford an alternative choice by facile carbon–carbon bond formation without prepreparation of organometallic nucleophiles.[6,7] The pre-installation of halides on to the specific pyridyl carbon position allows easy access to differently substituted pyridines.[7h,8] In 2012, our group reported an efficient Ni-catalyzed method for the reductive coupling of aryl halides with secondary alkyl bromides, in which 2-bromopyridine, as an example of heteroaromatic compound, provided a yield of 38% of the desired product.[8] Following this work, Weix and coworkers revealed a similar Ni-catalyzed cross-electrophile coupling of halogenated pyridines with alkylated halides.[9] However, Weix's work is mainly limited to primary bromides; there is only one example of secondary alkyl bromide, namely, cyclohexyl bromide, which was disclosed for the coupling with 2-bromopyridine. With 2 equiv of cylcohexyl bromide, 2-cyclohexylpyridine was obtained in 48% yield. This is not surprising, as secondary alkyl halides are generally more difficult in the transition-metal-catalyzed reactions due partially to sterically more hindrance. In addition, the use of bromopyridines in that work appears to be less effective; only 26% yield for the coupling of 2-bromopyridine with 1-bromooctane was obtained.[7h]

Considering the potential value of application of alkylated pyridines, further studies of the alkylation of halogenated pyridines with emphasis on more sterically hindered secondary alkyl halides are nontrivial. In this article, we present our continuing efforts to the studies of Ni-catalyzed reductive coupling of secondary alkyl bromides with a variety of bromo-substituted pyridine derivatives. Our results are complementary to the concurrent reductive alkylation of halo-pyridines with alkyl halides.

RESULTS AND DISCUSSION

To begin with, the coupling of 2-bromopyridine (**1a**) with 4-bromo-1-tosylpiperidine (**2a**) was chosen as the model reaction. After considerable efforts, we eventually determined the optimal conditions, namely, 1 equiv of **1a** and 2 equiv of **2a** in the presence of $NiBr_2$ (10 mol%), 4,4′-di-tert-butyl-2,2′-bipyridine **4a** (10 mol%), and additives $MgCl_2$ (100 mol%)/pyridine (1:1) and Bu_4NBr (50 mol%) in dimethylacetamide (DMA) at 30 °C. These conditions provided the coupling product **(3a)** in a 70% yield (shown in Table 1, entry 1). With 1.0 equiv. of Bu_4NBr, other ligands such as **4b**–**9** (shown in Fig. 1) were less effective than **4a**, which was able to generate the desired product in 58% yield (entries 2–13). When the ligand loading was reduced to half (from 20% to 10%), the yield only showed a little decrease (from 58% to 55%, entries 13 and 14). Therefore, 10 mol% of ligand loading was chosen, due to lower cost. Other nickel sources such as $Ni(COD)_2$ were not

Table 1. Screening of conditions[a]



Entry	Variation from the "standard" conditions	Yield of **3a** (%)[b]
1	None	70
2[c]	1 equiv. of Bu_4NBr; **4b** instead of **4a**	51
3[c]	1 equiv. of Bu_4NBr; **4c** instead of **4a**	51
4[c]	1 equiv. of Bu_4NBr; **4d** instead of **4a**	50
5[c]	1 equiv. of Bu_4NBr; **5a** instead of **4a**	56
6[c]	1 equiv. of Bu_4NBr; **5b** instead of **4a**	49
7[c]	1 equiv. of Bu_4NBr; **5c** instead of **4a**	41
8[c]	1 equiv. of Bu_4NBr; **6** instead of **4a**	36
9[c]	1 equiv. of Bu_4NBr; **7a** instead of **4a**	52
10[c]	1 equiv. of Bu_4NBr; **7b** instead of **4a**	46
11[c]	1 equiv. of Bu_4NBr; **8** instead of **4a**	55
12[c]	1 equiv. of Bu_4NBr; **9** instead of **4a**	20
13[c]	1 equiv. of Bu_4NBr	58
14	1 equiv. of Bu_4NBr	55
15	1 equiv. of Bu_4NBr; $Ni(COD)_2$ instead of $NiBr_2$	46
16	1 equiv. of Bu_4NBr; DMF instead of DMA	45
17	1 equiv. of Bu_4NBr; THF instead of DMA	Trace
18	Reaction run at 0 °C	40
19	Reaction run at 50 °C	46
20	0.5 equiv. of pyridine	50
21	1.5 equiv. of pyridine	59
22	No $MgCl_2$	12
23	0.1 equiv. of Bu_4NBr	43

[a]Reaction conditions: **1a** (0.15 mmol, 100 mol%), **2a** (0.30 mmol, 200 mol%), $NiBr_2$ (10 mol%), ligand (10 mol%), Zn (300 mol%), Bu_4NBr (50 mol%), $MgCl_2$ (0.15 mmol)–pyridine (1:1), and DMA (1 mL).
[b]Isolated yield.
[c]20% ligand was used.

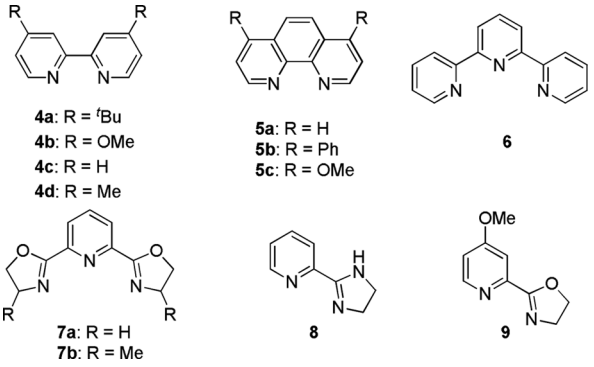
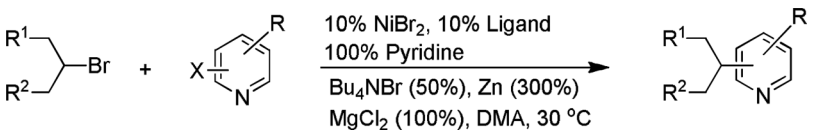


Figure 1. Structures of the ligands.

Table 2. Scope of the cross coupling of halogenated pyridines with secondary alkyl bromides[a]



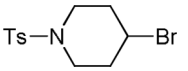
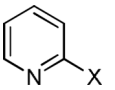
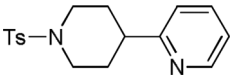
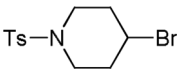
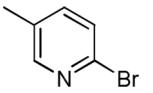
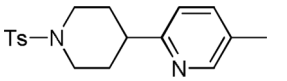
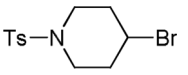
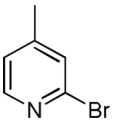
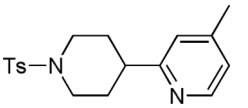
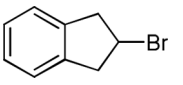
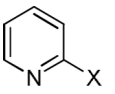
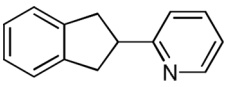
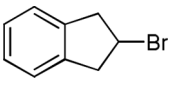
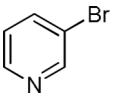
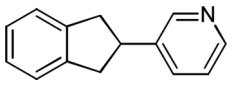
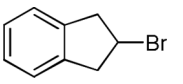
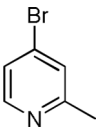
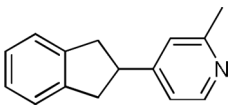
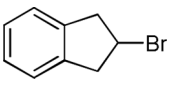
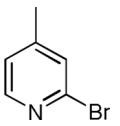
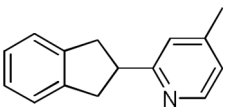
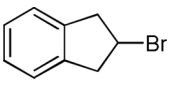
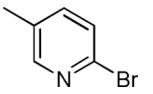
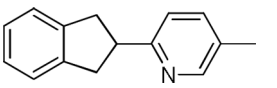
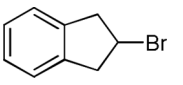
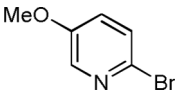
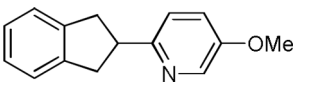
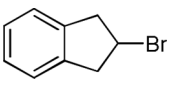
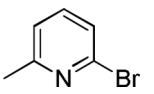
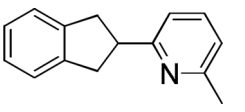
Entry	Reactant	Halopyridine	Product	Yield (%)[b]
1 2				X = Br 70 X=Cl 42
3				45
4				41
5 6				X = Br 68 X = Cl 38
7				61
8				60
9				50
10				64
11				55
12				27

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Table 2. Continued

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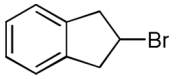
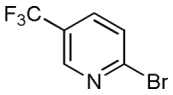
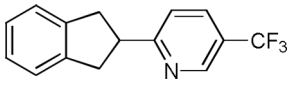
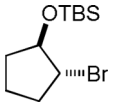
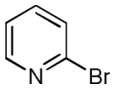
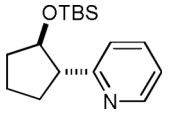
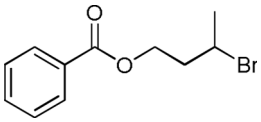
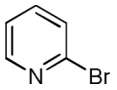
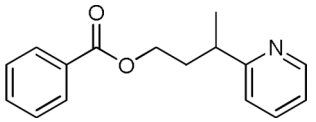
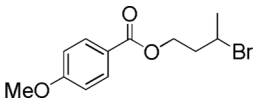
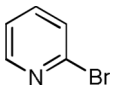
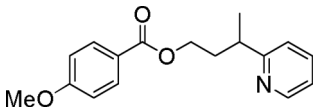
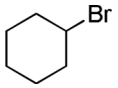
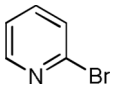
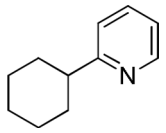
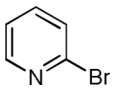
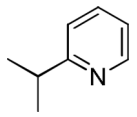
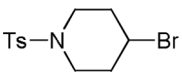
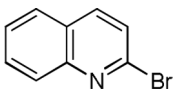
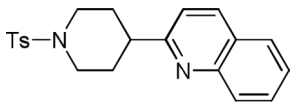
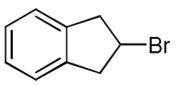
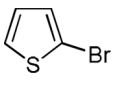
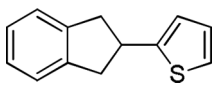
13				21
14				18 (dr > 20:1)
15				27
16				31
17				<10
18				<10
19				Trace
20				Trace

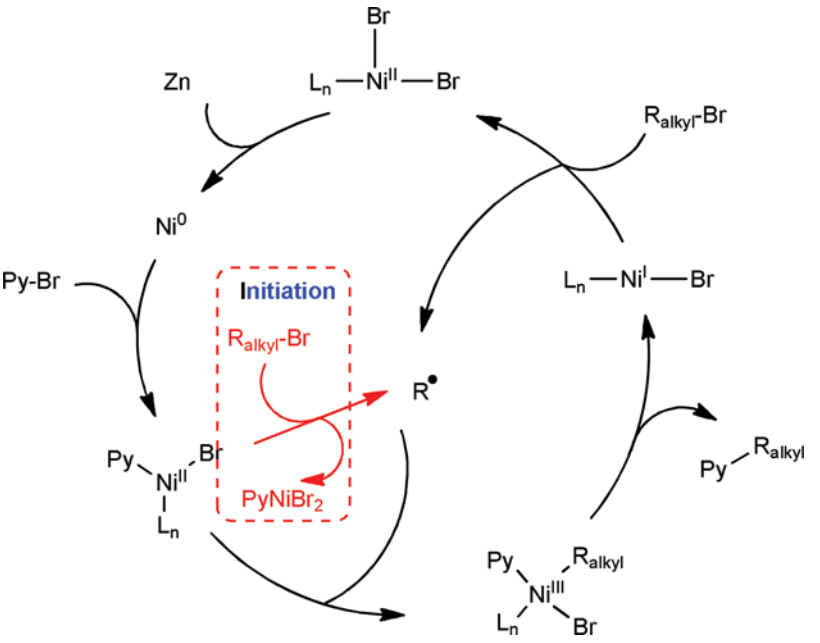
[a]Reaction conditions: alkyl bromide (0.15 mmol), halogenated pyridine (0.30 mmol, 200 mol%), $NiBr_2$ (10 mol%), ligand (10 mol%), Zn (300 mol%), Bu_4NBr (50 mol%), $MgCl_2$ (0.15 mmol)–pyridine (1:1), DMA (1 mL).

[b]Isolated yield.

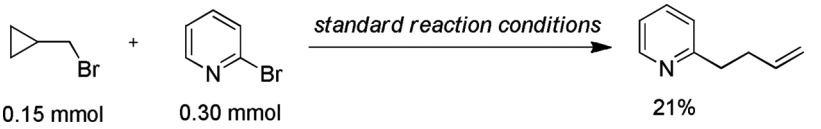
satisfactory (entry 15). The use of solvents other than DMA gave the product in poor yields or with trace amount (entries 16 and 17). Varying the reaction temperature was not successful (entries 18 and 19). Use of 1.5 equiv pyridine gave the product **3a** in 59% yield, which was greater than that with 0.5 equiv of pyridine (entries 20 and 21). We reasoned that pyridine here also serves to promote the reactivity through the combination with a bidentate ligand.[8] Without $MgCl_2$, a significant decrease of the yield was observed (entry 22). Finally, variation of the loading of

Bu_4NBr with 0.1 equiv and 0.5 equiv disclosed that the latter resulted in a dramatic increase of the yield to 70% (entries 1 and 23). We speculated that the role of $MgCl_2$ and Bu_4NBr is possibly to activate zinc powder by removal salts on its surface. However, it is also possible that $MgCl_2$ can affect the dielectric nature of the solvent, and possibly coordinates with the Ni intermediates.[10]

With the optimized conditions in hand, the limitation and scope of the halogenated pyridines were examined, as shown in Table 2. In general, chloropyridines were less effective (entries 2 and 6). The coupling of **1a** with 2-bromo-3- and 2-bromo-4-mehtyl pyridines gave moderate yields (entries 3 and 4). When 2-bromo-2,3-dihydro-1*H*-indene was exposed to 2-bromopyridine, the yields had an increase about 10% (entries 7 and 10). For the cross coupling of 2-bromo-2,3-dihydro-1H-indene with 2-bromopyridine, the yield was comparable to that obtained from **1a** (entry 5). For 3-bromopyridine and 2-methyl-4-bromopryidine, 68% and 61% of the coupling products were obtained (entries 7 and 8). With 2-bromopyridines bearing 4-methyl, 5-methyl, and 5-methoxy substituents, good results were generated (entries 9–11). However, 6-methyl-2-bromopyridines only gave rise to a very poor yield, probably due to the sterical hindrance (entry 12). In contrast, when electron-withdrawing groups such as CF_3 were introduced, the coupling yield was reduced significantly; the product was obtained in only 21% yield (entry 13). The sterically more hindered *trans*-2-bromocyclopentyloxy (*tert*-butyl) dimethylsilane only yielded the desired product in 18% yield (entry 14). The open-chain secondary bromide seemed to be less efficient (entries 15 and 16). Next, we also compared the coupling efficiency for the coupling of bromocyclohexane with 2-bromopyridine using our conditions with Weix's result. Unfortunately, a very poor



Scheme 1. Proposed reaction mechanism for Py-R_{alkyl} formation.



Scheme 2. Reductive coupling of bromomethylcyclopropane with 1-bromopyridine.

yield was observed (entries 17), suggesting that this reductive coupling conditions were substrate sensitive, with those alkyl halides bearing electronegative functionalities being more effective. Indeed the coupling of 2-bromopropane revealed similar result as that from bromocyclohexane (entry 18). Finally, we also tested the compatibility of other heteroaryl halides such as 2-bromoquinoline and 2-bromothiophene, and only trace amounts of the desired products were detected (entries 19 and 20). Overall, it appears that the coupling conditions are sensitive to the both alkyl halides and pyridyl bromides with different substitution patterns and electronic properties. Given the difficulties of preparation of alkylated pyridines, this work may still find interesting applications for compounds of interest.

According to the recent mechanistic studies from Weix's Ni-catalyzed reductive coupling of aryl and alkyl halides, it appears that oxidative addition of pyridyl bromide to Ni(0) forming Py-Ni(II)-Br proceeds faster than that of alkyl bromide to Ni(0).[11] Initiation of the reaction was achieved when the Py-Ni(II)-Br intermediate abstracts bromine from alkyl bromide to generate Py-Ni(III)-$(Br)_2$, and the alkyl radical then adds to Py-Ni(II)-Br, giving Py-Ni(III)-(alkyl)-Br, which undergoes reductive elimination to give the Py-alkyl product and Ni(I). Halide abstraction of alkyl bromide by the Ni(I) produces Ni(II)-Br_2 and alkyl radical. While the alkyl radical undergoes radial addition to Py-Ni(II)-Br, the Ni(II)-Br_2 is reduced by Zn to regenerate Ni(0), which undergoes oxidative addition by Py-Br (Scheme 1). Indeed the radical property of this coupling event was evidenced in the coupling of bromomethylcyclopropane with 1-bromopyridine where only a ring opening product was observed, albeit with a poor yield (Scheme 2).

CONCLUSIONS

In conclusion, we have disclosed a method for the cross coupling of differently substituted pyridines with secondary alkyl bromides, which provides a complementary solution to the unreported examples in the previous studies on alkylation of halo-pyridines. Although the alkyl substrate scope has limited to those bearing electronegative functional groups, the current conditions are still convenient for relevant pyridine ring alkylation.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. All NMR spectra were recorded on Bruker Avance 500-MHz spectrometer at STP unless otherwise indicated. High-resolution mass spectra (HRMS) were obtained using an Agilent 7890-5975. Melting points were recorded on a micro-melting-point

apparatus (X-4, Yuhua Co., Ltd, Gongyi, China). Column chromatography was performed using silica gel, 300–400 mesh (purchased from Qingdao-Haiyang Co. China) as the solid support. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. 4-Bromo-1-tosylpiperidine and 2-bromo-2,3-dihydro-1H-indene were synthesized according to the literature procedures.

A flame-dried Schlenk tube equipped with a magnetic stir bar was loaded with alkyl bromide (0.15 mmol, 100 mol%, solid), halogenated pyridine (0.30 mmol, 300 mol%, solid), ligand (0.015 mmol, 10 mol%), and zinc powder (0.45 mmol, 300 mol%). The tube was capped with a rubber septum and moved to a dry glove box, to which $NiBr_2$ (0.015 mmol, 10 mol%), $MgCl_2$ (0.15 mmol, 100 mol%), and Bu_4NBr (0.075 mmol, 50 mol%) were added. Then the tube was moved out of the glove box. Alkyl bromide (0.15 mmol, 100 mol%, liquid), halogenated pyridine (0.30 mmol, 300 mol%, liquid), pyridine (0.15 mmol, 100 mol%), and DMA (1.0 mL) were added via syringe. After the reaction mixture was allowed to stir overnight under N_2 atmosphere at 30 °C, it was directly loaded onto a silica column without workup. The residue in the reaction vessel was rinsed with small amount of DCM or eluent. Flash column chromatography provided the product as solid or oil.

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SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website.

REFERENCES

1. (a) Daly, J. W.; Garraffo, H. M.; Spande, T. F. In *Alkaloids: Chemical and Biological Perspectives*; W. Pelletier (Ed.); Elsevier: New York, 1999; vol. 13, p. 92; (b) Raju, S. V. N.; Purandhar, K.; Reddy, P. P.; Reddy, G. M.; Reddy, L. A.; Reddy, K. S.; Sreenath, K.; Mukkanti, K.; Reddy, G. S. *Org. Process Res. Dev.* **2005**, *10*, 33–35; (c) Turner, K. *Org. Process Res. Dev.* **2009**, *13*, 381–390; (d) Pyridine and pyridine derivatives: *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; John Wiley & Sons: New York, 2006, vol. 20.
2. (a) Hesp, K. D.; Fernando, D. P.; Jiao, W. H.; Londregan, A. T. *Org. Lett.* **2014**, *16*, 413–415; (b) Girijavallabhan, V.; Arasappan, A.; Bennett, F.; Huang, Y.; Njoroge, F. G.; MacCoss, M. *Tetrahedron Lett.* **2010**, *51*, 2797–2799; (c) Joubert, N.; Pohl, R.;

Klepetářová, B.; Hocek, M. *J. Org. Chem.* **2007**, *72*, 6797–6805; (d) Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863.

3. (a) Nakamura, M.; Ito, S.; Matsuo, K.; Nakamura, E. *Synlett* **2005**, 1794–1798; (b) Suzuki, M.; Sumi, K.; Koyama, H.; Siqin Hosoya, T.; Takashima-Hirano, M.; Doi, H. *Chem. Eur. J.* **2009**, *15*, 12489–12495; (b) Vechorkin, O.; Proust, V.; Hu, X. L. *J. Am. Chem. Soc.* **2009**, *131*, 9756–9766.
4. For alkylation of pyridine via C-H activation, see (a) Xiao, Q.; Ling, L.; Ye, F.; Tan, R. C.; Tian, L. M.; Zhang, Y.; Li, Y. X.; Wang, J. B. *J. Org. Chem.* **2013**, *78*, 3879–3885; (b) Xiao, B.; Liu, Z. J.; Liu, L.; Fu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 616–619; (c) Guan, B. T.; Hou, Z. H. *J. Am. Chem. Soc.* **2011**, *133*, 18086–18089; (d) Nakao, Y.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 2448–2449; (e) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 5332–5333; (f) Godula, K.; Sezen, B.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 3648–3649.
5. (a) Shang, R.; Yang, Z. W.; Wang, Y.; Zhang, S. L.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 14391–14393; (b) Donald, C.; Boyd, S. *Tetrahedron Lett.* **2012**, *53*, 3853–3856.
6. Our group's work: (a) Tan, Z. Z.; Wan, X. L.; Zang, Z. H.; Qian, Q.; Deng, W.; Gong, H. G. *Chem. Commun.* **2014**, *50*, 3827–3830; (b) Xu, H. L.; Zhao, C. L.; Qian, Q.; Deng, W.; Gong, H. G. *Chem. Sci.* **2013**, *4*, 4022–4029; (c) Yin, H.; Zhao, C.; You, H.; Lin, K.; Gong, H. G. *Chem. Commun.* **2012**, *48*, 7034–7036; (d) Dai, Y.; Wu, F.; Zang, Z.; You, H.; Gong, H. *Chem. Eur. J.* **2012**, *18*, 808–812; (e) Yu, X.; Yang, T.; Wang, S.; Xu, H.; Gong, H. *Org. Lett.* **2011**, *13*, 2138–2141.
7. Others' work: (a) Wang, L.; Zhang, Y.; Liu, L.; Wang, Y. *J. Org. Chem.* **2006**, *71*, 1284–1287; (b) Amatore, M.; Gosmini, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 2089–2092; (c) Krasovskiy, A.; Duplais, C.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2009**, *131*, 15592–15593; (d) Czaplik, W. M.; Mayer, M.; von Wangelin, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 607–610; (e) Goldup, S. M.; Leigh, D. A.; McBurney, R. T.; McGonigal, P. R.; Plant, A. *Chem. Sci.* **2010**, *1*, 383–386; (f) Everson, D. A.; Shrestha, R.; Weix, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 920–921; (g) Shrestha, R.; Weix, D. J. *Org. Lett.* **2011**, *13*, 2766–2769; (h) Everson, D. A.; Jones, B. A.; Weix, D. J. *J. Am. Chem. Soc.* **2012**, *134*, 6146–6159; (i) Shrestha, R.; Dorn, S. C. M.; Weix, D. J. *J. Am. Chem. Soc.* **2012**, *135*, 751–762.
8. Wang, S.L.; Qian, Q.; Gong, H. G. *Org. Lett.* **2012**, *14*, 3352–3355.
9. Everson, D. A.; Buonomo, J. A.; Weix, D. J. *Synlett* **2014**, *25*, 233–238.
10. (a) Macann, L. C.; Organ, M. G. *Angew. Chem., Int. Ed.* **2014**, *53*, 4386–4389; (b) Jin, L.; Liu, C.; Liu, J.; Hu, F.; Lan, Y.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B.; Lei, A. *J. Am. Chem. Soc.* **2009**, *131*, 16656–16657.
11. (a) Biswas, S.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135*, 16192–16197; (b) Zhao, Y.; Weix, D. J. *J. Am. Chem. Soc.* **2014**, *136*, 48–51.