

C–H Activation

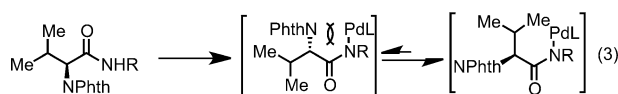
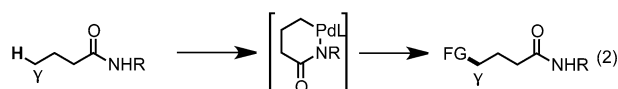
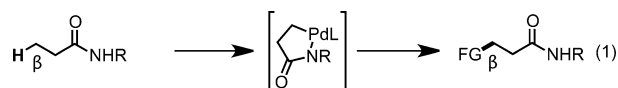
Deutsche Ausgabe: DOI: 10.1002/ange.201512020
Internationale Ausgabe: DOI: 10.1002/anie.201512020Ligand-Enabled Arylation of γ -C–H Bonds

Suhua Li, Ru-Yi Zhu, Kai-Jiong Xiao, and Jin-Quan Yu*

Abstract: Pd^{II}-catalyzed arylation of γ -C(sp³)–H bonds of aliphatic acid-derived amides was developed by using quinoline-based ligands. Various γ -aryl- α -amino acids were prepared from natural amino acids using this method. The influence of ligand structure on reactivity was also systematically investigated.

Transition metal-catalyzed C–H functionalization of readily accessible and structurally simple chemicals provides a compelling method for expanding molecular diversity.^[1] The diverse reactivity of the carbon–palladium bond renders Pd^{II}-catalyzed C–H functionalization reactions highly suitable for this endeavor. In this context, late-stage functionalization of sp² C–H bonds has been demonstrated.^[2] Great efforts have also been made towards directed C(sp³)–H activation over the past decade, specifically, functionalization of carboxylic acids and derivatives,^[3] amines,^[3c,4] and imines^[5] by five-membered metallacycles have been extensively demonstrated. Development of C–H activation reactions by six-membered metallacycles to functionalize more distal carbon centers will significantly broaden the synthetic utility of C(sp³)–H activation reactions. For example, γ -C–H functionalizations and β -C–H functionalizations of carboxylic acid derivatives provide two distinct synthetic disconnections, respectively [Eq. (1–2)]. While substantial progress has been made towards β -C–H activation using Pd catalysts, γ -C–H activation has met with difficulties owing to the less favored six-membered cyclopalladation of alkyl C–H bonds. Corey et al. established that the presence of a phthalimido group at the α -position was beneficial for the arylation of γ -C–H bonds in valine using a bidentate directing group [Eq. (3)].^[6] The sterically bulky phthalimido group could favor the assembly of the desired conformation, as shown in Eq. (3). An improved procedure for γ -C–H arylation of phthalimido-protected valine was also reported more recently.^[7] However, γ -C–H arylation of simple carboxylic acids derivatives not containing a sterically bulky phthalimido group has not been reported to date. Herein, we report a ligand-enabled γ -arylation of primary C–H bonds attached to quaternary carbon centers of simple aliphatic acids derivatives. The method was also successfully applied to the diversification of valine, isoleucine, and *tert*-leucine.

Our initial effort was focused on the γ -arylation of simple aliphatic acids. We chose 3,3-dimethyl-butanamide **1a** as the model substrate because it contains nine γ -C–H bonds which



would result in better reactivity. However, only trace amount of product was formed using 20 mol % of Pd(OAc)₂ under various conditions. Encouraged by our recent results of γ -olefination of amide derivatives that were enabled by ligands in combination with a weakly coordinating amide directing group (CONHAr_F, Ar_F = 2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl),^[8] we wondered whether these types of ligands would promote arylation of the γ -C–H bond. Systematic ligand screening was carried out using pyridine, quinoline, acridine, and phenanthroline derivatives (Table 1). Various substituted pyridines (**L1–L2**) were tested and gave no noticeable improvement. To our delight, quinoline significantly promoted the reaction to give mono-arylated and di-arylated products in 46 % total yield (**L3**). The yield was improved when an alkoxy group was introduced to the 2-position of quinoline (**L4–L6**).^[9] The 2,4-dialkoxy-substituted quinolines (**L7–L9**) further increased the yield, indicating that electron-donating substituents enhance the efficiency of the ligand. Therefore, we tested tricyclic quinolines (**L10–L14**) with the 2-alkoxy moiety constrained in the ring such that one of the oxygen lone pairs is parallel to the π -system of the quinoline ring. This conformational orientation will result in a more electron-rich ligand.^[10] After a systematic examination of the tricyclic quinolines, ligand **L10** was found to be the most effective. Simple acridine (**L15**) also gave moderate yield, while dimethylamine-substituted acridine (**L16**) decreased the efficiency. Bidentate 1,10-phenanthroline (**L17**) inhibited the reaction. Using the most effective ligand **L10**, we performed extensive optimization and found that this γ -C–H arylation can proceed with 10 mol % Pd catalyst under an oxygen atmosphere at 90 °C to give comparable yield (Supporting Information). The ligand could also be recycled. The replacement of air by molecular oxygen is crucial. A range of other amide directing groups were also tested with these new conditions and gave significantly inferior results (Supporting Information). While the rationalization of the

[*] Dr. S. Li, R.-Y. Zhu, Dr. K.-J. Xiao, Prof. Dr. J.-Q. Yu
Department of Chemistry, The Scripps Research Institute (TSRI)
10550 North Torrey Pines Road, La Jolla, CA 92037 (USA)
E-mail: yu200@scripps.edu

Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201512020>.

Table 1: Ligand effects.^[a]

$\text{Me}_2\text{C}(\text{Me})\text{C}(\text{NHAr}_F) + \text{PhI} \xrightarrow[\text{Ag}_2\text{CO}_3 (3 \text{ equiv}), t\text{-AmylOH}, 120^\circ\text{C}, 20 \text{ h}]{\text{Pd}(\text{OAc})_2 (20 \text{ mol}\%), \text{ligand} (40 \text{ mol}\%)}$ Ar_F = (4-CF₃)C₆F₄		
no ligand 4/0	L1, 5/0	L2, 19/2
L3, 30/16	L4, 37/12	L5, 33/38
L6, 25/32	L7, 32/32	L8, 29/48
L9, 27/46	L10, 34/50 (38/46) ^[b]	L11, 41/20
L12, 31/36	L13, 46/27	L14, 36/43
L15, 21/40	L16, 24/3	L17, <1

[a] Reaction conditions: 0.1 mmol of substrate, 0.4 mmol of PhI (45 μ L), 0.02 mmol of Pd(OAc)₂ (20 mol%), 0.04 mmol of Ligand (40 mol%), 0.3 mmol of Ag₂CO₃, 1 mL of *t*-AmylOH, air, 50 mL sealed tube, 120 °C (oil), 20 h. Yield was determined by the ¹H NMR spectroscopy using CH₂Br₂ as the internal standard. The ratios are the yields of mono-arylated product to di-arylated product (2a%/2a'%). [b] 0.2 mmol of substrate, 0.8 mmol of PhI (90 μ L), 0.02 mmol of Pd(OAc)₂ (10 mol%), 0.04 mmol of Ligand (20 mol%), 0.6 mmol of Ag₂CO₃, 1 mL of *t*-AmylOH, O₂ (1 atm), 50 mL sealed tube, 90 °C (oil), 20 h.

ligand effect would need further investigations, the observed influence of the ligand structure on this reaction indicates the superiority of electron-rich quinoline ligands. These types of ligands have also been shown to accelerate the C–H activation step in the C(sp³)–H borylation reaction.^[11]

With these optimized conditions in hand, we proceeded to survey the substrate scope of the reaction (Table 2). This procedure is compatible with substrates containing one or two β -methyl groups, and afforded comparable yields (2b and 2b', 2c). Phenyl and benzyl groups at the β -positions were also tolerated affording the desired products in moderate yields (2d, 2e). The single methyl group in the cyclic substrates could also be arylated to give the desired products in 45–73 % yields (2f–h). Notably, tetrahydropyran and substituted norbornane structural motif were also compatible with this

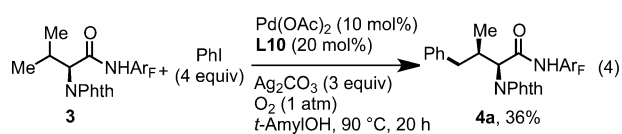
Table 2: Substrate scope.^[a]

$\text{Me}_2\text{C}(\text{R}')\text{C}(\text{R}'')\text{C}(\text{NHAr}_F) + \text{Arl} \xrightarrow[\text{Ag}_2\text{CO}_3 (3 \text{ equiv}), \text{O}_2 (1 \text{ atm}), t\text{-AmylOH}, 90^\circ\text{C}, 20 \text{ h}]{\text{Pd}(\text{OAc})_2 (10 \text{ mol}\%), \text{L10} (20 \text{ mol}\%)}$		
2a, 35%	2b, 50%	2c, 60% ^[b]
2a', 43%	2b', 17%	
2d, 45% ^[b]	2e, 57% ^[b]	2f, 45%
2g, 72%	2h, 73% ^[b]	2i, 86% d.r. = 2:1 ^[c]

[a] 0.2 mmol of substrate, 0.8 mmol of ArI, 0.02 mmol of Pd(OAc)₂ (10 mol%), 0.04 mmol of L10 (20 mol%), 0.6 mmol of Ag₂CO₃, 1 mL of *t*-AmylOH, 50 mL sealed tube, 90 °C (oil), 20 h. The yields are isolated yields. [b] 1 equiv of AgO₂CⁿBu was added and the reaction temperature was 100 °C. [c] The d.r. value of 1i is 2:1. The configuration in the table is the major isomer.

arylation procedure (2h, 2i), affording 73 % and 86 % yields, respectively. Unfortunately, the amide derived from 3-methylbutanoic acid was not reactive, which is consistent with the well-known Thorpe–Ingold effect. Further development of the ligand will be required to overcome this limitation.

In light of the broad interests in modifying natural amino acids^[3p, 4, 6, 7, 12] and oligopeptides,^[13] we performed the γ -functionalization of valine under these conditions. Unfortunately, only 36 % of arylated product was obtained under the newly established conditions [Eq. (4)].



However, the dramatic ligand effect indicated by the control experiment (no product was formed in the absence of ligand) (Table 3) encouraged us to further optimize the ligand effect. We found that reducing the ligand/palladium ratio from 2:1 to 1:1 increased the yield to 61 % (see supporting information). Using these new conditions, we re-investigated a series of ligands. 2-picoline (L18) and 2,6-lutidine (L19) are poor ligands. Acridine (L20–L22) ligands gave the arylated products in 30–40 % yields. While 2-alkoxyl or 2,4-dialkoxyl quinolines (L6, L8) did not improve further, the tricyclic quinoline ligand 10 afforded 61 % yield. Thus, we prepared additional substituted tricyclic quinoline ligands to establish

Table 3: Ligand development.^[a]

$\text{Me-CH(Me)-CH(NHArF)-C(=O)NPhth} + \text{PhI} \xrightarrow[\text{AgOAc (3 equiv), } t\text{-AmylOH, } 80^\circ\text{C, 20 h}]{\text{Pd(OAc)}_2 \text{ (10 mol\%), Ligand (10 mol\%)}}$		
without ligand		
NR	L18 , 10%	L19 , 13%
L20 , 38%	L21 , 40%	L22 , 33%
L6 , 33%	L8 , 41%	L10 , 61%
L14 , 69%, (81%) ^[b]	L23 , 24%	L24 , 52%
L25 , 57%	L26 , 28%	L27 , 20%
L11 , 11%	L28 , 69%	L29 , 67%

[a] Reaction conditions: 0.1 mmol of substrate, 0.4 mmol of PhI (45 μL), 0.01 mmol of $\text{Pd}(\text{OAc})_2$ (10 mol%), 0.01 mmol of Ligand (10 mol%), 0.3 mmol of AgOAc , 0.5 mL of $t\text{-AmylOH}$, 10 mL sealed tube, 80°C (oil), 20 h. Yield was determined by the ^1H NMR spectroscopy using CH_2Br_2 as the internal standard. [b] 0.1 mmol of substrate, 0.4 mmol of ArI, 0.01 mmol of $\text{Pd}(\text{OAc})_2$ (10 mol%), 0.01 mmol of Ligand (10 mol%), 0.2 mmol of AgOAc , 0.1 mmol of $\text{AgO}_2\text{C}^t\text{Bu}$, 0.5 mL of $t\text{-AmylOH}$, 10 mL sealed tube, 90°C (oil), 20 h.

the structure–reactivity relationship. The electron-donating and bulky *tert*-butyl-substituted at 7-position ligand (**L14**) could enhance the reactivity. On the other hand, the extremely bulky 2,6-diisopropyl phenyl substituent at the same position (**L23**) decreased the effectiveness. Quinolines containing amino groups at the 7-positions (**L24–25**) gave moderate yields. Both electron-withdrawing (**L26**) and electron-donating groups (**L27**, **L11**) at 8-position decreased the yields. However, ligands containing either electron-donating or -withdrawing groups at the 9-positions (**L28**, **L29**) are comparable to the best ligand **L14**. Through further screening, we found that the use of one equivalent of $\text{AgO}_2\text{C}^t\text{Bu}$ and raising reaction temperature to 90°C increased the yield to 81% (Supporting Information).

Various substituted aryl iodides are compatible with this ligand-enabled $\gamma\text{-C-H}$ arylation reaction (Table 4). Aryl iodides containing methyl and methoxy groups reacted well under the standard conditions, giving the products in good to excellent yields (**4a–4d**). Fluoro, chloro, bromo, and trifluoro-

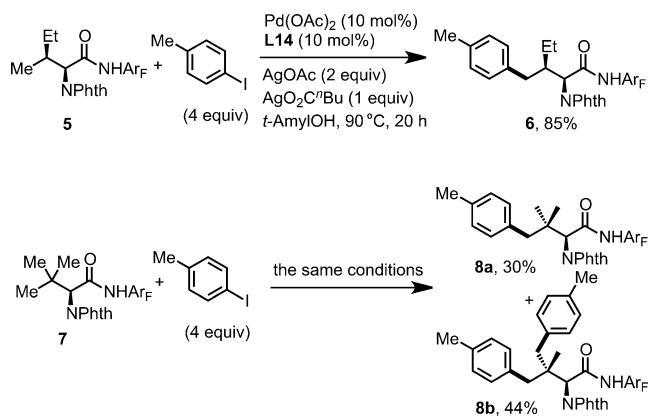
Table 4: Arylation of valine.^[a]

$\text{Me-CH(Me)-CH(NHArF)-C(=O)NPhth} + \text{ArI} \xrightarrow[\text{AgOAc (2 equiv), } \text{AgO}_2\text{C}^t\text{Bu (1 equiv), } t\text{-AmylOH, } 90^\circ\text{C, 20 h}]{\text{Pd(OAc)}_2 \text{ (10 mol\%), L14 (10 mol\%)}}$		
4a , 78%	4b , 90%	4c , 83%
4d , 74%	4e , 59%	4f , 74%
4g , 75%	4h , 66%	4i , 76%
4j , 73%	4k , 62%	4l , 65%
4m , 61%	4n , 73%	4o , 66%
4p , 65%	4q , 69%	4r , 57%

[a] Reaction conditions: 0.1 mmol of substrate, 0.4 mmol of ArI, 0.01 mmol of $\text{Pd}(\text{OAc})_2$ (10 mol%), 0.01 mmol of **L14** (10 mol%), 0.2 mmol of AgOAc , 0.1 mmol of $\text{AgO}_2\text{C}^t\text{Bu}$, 0.5 mL of $t\text{-AmylOH}$, 10 mL sealed tube, 90°C (oil), 20 h. The yields are isolated yields. d.r. > 20:1 in all examples.

methyl substituents produced moderate to good yields of modified valine derivatives. These halide substituents could be used for further transformation (**4e–4i**). The 4-iodo-1,1'-biphenyl and 2-iodonaphthalene worked well in the reaction (**4j–4k**). A range of common functional groups, including ester, ketone, and acetate, were also compatible, affording 61–73% of the desired products (**4l–4o**). A number of heterocyclic moieties were successfully attached to valine through this arylation reaction (**4p–4r**).

4-Aryl isoleucine **6** could also be prepared by arylation of the $\gamma\text{-C-H}$ bond of isoleucine in good yield (Scheme 1). Arylation of *tert*-leucine produced 30% of the mono-arylated product (**8a**), and 44% of the di-arylated product (**8b**). In these arylation reactions, the stereochemistry of the α -chiral center was maintained (*ee* > 98%; Supporting Information). In addition, high diastereoselectivity (d.r. > 20:1) was obtained in the arylation reaction, owing to the favored *trans*-conformation and disfavored *cis*-conformation regarding the methyl and phthalimide groups (Figure 1). The amide auxiliary could be converted to thioester in high yield using LiSEt [Eq. (5)]. Alternatively, formation of the carbamate



Scheme 1. Arylation of amino acids.

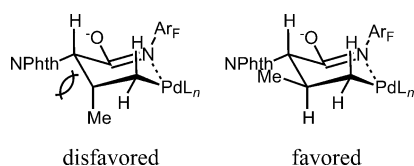
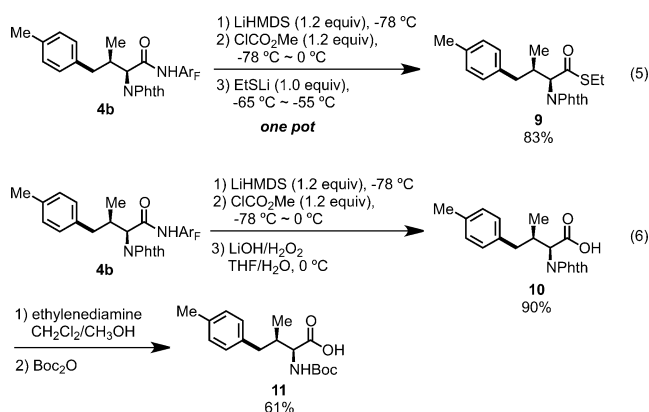


Figure 1. The origin of the high diastereoselectivity.

followed by treatment with LiOH/H₂O₂ afforded the carboxylic acid **10** [Eq. (6)]. The phthalimide group was readily removed by treating with ethylenediamine to generate the free amine, and subsequent protection with Boc₂O gave **11**.



In summary, we have developed a procedure for γ -arylation of simple aliphatic acids containing β -quaternary carbon centers, as well as amino acids including valine, isoleucine, and *tert*-leucine. The use of tricyclic quinoline ligands was crucial for the reactivity, providing useful information for developing more efficient ligands that will enable γ -C–H activation.

Acknowledgements

We gratefully acknowledge The Scripps Research Institute, the NIH (NIGMS, 2R01GM084019) and Novartis for financial support.

Keywords: arylation · carboxylic acids · palladium · quinoline ligand · γ -C–H activation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4317–4321
Angew. Chem. **2016**, *128*, 4389–4393

- [1] K. M. Engle, J.-Q. Yu, *J. Org. Chem.* **2013**, *78*, 8927.
- [2] For selected examples, see: a) D.-H. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 5767; b) H.-X. Dai, A. F. Stepan, M. S. Plummer, Y.-H. Zhang, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 7222; c) B. R. Rosen, L. R. Simke, P. S. Thuy-Boun, D. D. Dixon, J.-Q. Yu, P. S. Baran, *Angew. Chem. Int. Ed.* **2013**, *52*, 7317; *Angew. Chem.* **2013**, *125*, 7458; d) G. Yang, P. Lindovska, D. Zhu, J. Kim, P. Wang, R.-Y. Tang, M. Movassaghi, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 10807; e) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369.
- [3] For selected examples, see: a) R. Giri, X. Chen, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2005**, *44*, 2112; *Angew. Chem.* **2005**, *117*, 2150; b) R. Giri, J. Liang, J.-G. Lei, J.-J. Li, D.-H. Wang, X. Chen, I. C. Naggari, C. Guo, B. M. Foxman, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2005**, *44*, 7420; *Angew. Chem.* **2005**, *117*, 7586; c) V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2005**, *127*, 13154; d) R. Giri, N. Mangel, J.-J. Li, D.-H. Wang, S. P. Breazzano, L. B. Saunders, J.-Q. Yu, *J. Am. Chem. Soc.* **2007**, *129*, 3510; e) D.-H. Wang, M. Wasa, R. Giri, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 7190; f) E. J. Yoo, M. Wasa, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 17378; g) D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2010**, *132*, 3965; h) N. Hasegawa, V. Charra, S. Inoue, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 8070; i) E. T. Nades, G. I. F. Santos, D. Shabashov, O. Daugulis, *J. Org. Chem.* **2013**, *78*, 9689; j) S.-Y. Zhang, Q. Li, G. He, W. A. Nack, G. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 12135; k) F.-J. Chen, S. Zhao, F. Hu, K. Chen, Q. Zhang, S.-Q. Zhang, B.-F. Shi, *Chem. Sci.* **2013**, *4*, 4187; l) R. Shang, L. Ilies, A. Matsumoto, E. Nakamura, *J. Am. Chem. Soc.* **2013**, *135*, 6030; m) L. Zhou, W. Lu, *Org. Lett.* **2014**, *16*, 508; n) Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2014**, *136*, 898; o) X. Wu, Y. Zhao, H. Ge, *J. Am. Chem. Soc.* **2014**, *136*, 1789; p) G. Chen, T. Shigenari, P. Jain, Z. Zhang, Z. Jin, J. He, S. Li, C. Mapelli, M. M. Miller, M. A. Poss, P. M. Scolia, K.-S. Yeung, J.-Q. Yu, *J. Am. Chem. Soc.* **2015**, *137*, 3338.
- [4] For selected examples, see: a) G. He, G. Chen, *Angew. Chem. Int. Ed.* **2011**, *50*, 5192; *Angew. Chem.* **2011**, *123*, 5298; b) G. He, Y. Zhao, S. Zhang, C. Lu, G. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 3; c) S.-Y. Zhang, G. He, W. A. Nack, Y. Zhao, Q. Li, G. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 2124; d) S.-Y. Zhang, G. He, Y. Zhao, K. Wright, W. A. Nack, G. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 7313; e) N. Rodríguez, J. A. Romero-Revilla, M. Á. Fernández-Ibáñez, J. C. Carretero, *Chem. Sci.* **2013**, *4*, 175; f) M. Fan, D. Ma, *Angew. Chem. Int. Ed.* **2013**, *52*, 12152; *Angew. Chem.* **2013**, *125*, 12374; g) K. S. L. Chan, M. Wasa, L. Chu, B. N. Laforteza, M. Miura, J.-Q. Yu, *Nat. Chem.* **2014**, *6*, 146.
- [5] a) L. V. Desai, K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2004**, *126*, 9542; b) T. Kang, Y. Kim, D. Lee, Z. Wang, S. Chang, *J. Am. Chem. Soc.* **2014**, *136*, 4141; c) Z. Ren, F. Mo, G. Dong, *J. Am. Chem. Soc.* **2012**, *134*, 16991; d) S. J. Thompson, D. Q. Thach, G. Dong, *J. Am. Chem. Soc.* **2015**, *137*, 11586.
- [6] B. V. S. Reddy, L. R. Reddy, E. J. Corey, *Org. Lett.* **2006**, *8*, 3391.
- [7] a) G. He, S.-Y. Zhang, W. A. Nack, Q. Li, G. Chen, *Angew. Chem. Int. Ed.* **2013**, *52*, 11124; *Angew. Chem.* **2013**, *125*, 11330; b) G. He, S.-Y. Zhang, W. A. Nack, R. Pearson, J. Rabb-Lynch, G. Chen, *Org. Lett.* **2014**, *16*, 6488.
- [8] S. Li, G. Chen, C.-G. Feng, W. Gong, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 5267.
- [9] M. Wasa, K. S. L. Chan, X.-G. Zhang, J. He, M. Miura, J.-Q. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 18570.

- [10] For insightful discussions on the conformation of 2-methoxy-pyridine: R.-J. Chein, E. J. Corey, *Org. Lett.* **2010**, *12*, 132.
- [11] J. He, H. Jiang, R. Takise, R.-Y. Zhu, G. Chen, H.-X. Dai, T. G. M. Dhar, J. Shi, H. Zhang, P. T. W. Cheng, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 785; *Angew. Chem.* **2016**, *128*, 795.
- [12] For selected examples, see: a) B. D. Dangel, J. A. Johnson, D. Sames, *J. Am. Chem. Soc.* **2001**, *123*, 8149; b) Q. Li, S.-Y. Zhang, G. He, W. A. Nack, G. Chen, *Adv. Synth. Catal.* **2014**, *356*, 1544; c) L. D. Tran, O. Daugulis, *Angew. Chem. Int. Ed.* **2012**, *51*, 5188; *Angew. Chem.* **2012**, *124*, 5278; d) S. Aspin, A.-S. Goutierre, P. Larini, R. Jazzar, O. Baudoin, *Angew. Chem. Int. Ed.* **2012**, *51*, 10808; *Angew. Chem.* **2012**, *124*, 10966; e) L.-S. Zhang, G. Chen, X. Wang, Q.-Y. Guo, X.-S. Zhang, F. Pan, K. Chen, Z.-J. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 3899; *Angew. Chem.* **2014**, *126*, 3980; f) Q. Zhang, K. Chen, W. Rao, Y. Zhang, F.-J. Chen, B.-F. Shi, *Angew. Chem. Int. Ed.* **2013**, *52*, 13588; *Angew. Chem.* **2013**, *125*, 13833; g) K. Chen, B.-F. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 11950; *Angew. Chem.* **2014**, *126*, 12144; h) Q. Zhang, X.-S. Yin, K. Chen, S.-Q. Zhang, B.-F. Shi, *J. Am. Chem. Soc.* **2015**, *137*, 8219; i) K. Chen, S.-Q. Zhang, H.-Z. Jiang, J.-W. Xu, B.-F. Shi, *Chem. Eur. J.* **2015**, *21*, 3264; j) J. He, S. Li, Y. Deng, H. Fu, B. N. Laforteza, J. E. Spangler, A. Homs, J.-Q. Yu, *Science* **2014**, *343*, 1216; k) R.-Y. Zhu, J. He, X.-C. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 13194; l) R.-Y. Zhu, K. Tanaka, G.-C. Li, J. He, H.-Y. Fu, S. Li, J.-Q. Yu, *J. Am. Chem. Soc.* **2015**, *137*, 7067.
- [13] W. Gong, G. Zhang, T. Liu, R. Giri, J.-Q. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 16940.

Received: December 30, 2015

Revised: February 2, 2016

Published online: February 25, 2016