

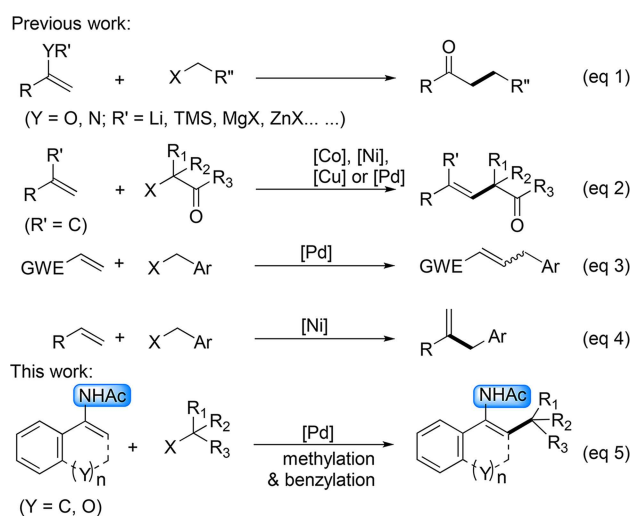
## Palladium Catalysis

# Palladium-Catalyzed Direct Methylation and Benzylation of Enamides Using Iodomethane and Benzyl Halides with Retention of Alkenyl Moiety

Ran Ding<sup>\*[a]</sup> and Borong Yu<sup>[b]</sup>

**Abstract:** A palladium-catalyzed direct methylation and benzylation of enamides at  $\beta$ -position with iodomethane and various benzyl halides was developed. The corresponding multisubstituted enamide products could be obtained in good yields under mild reaction conditions.

Alkylation of lithium enolates,<sup>[1]</sup> enol silyl ethers,<sup>[2]</sup> metalloenamines<sup>[3]</sup> and metal enamides<sup>[4]</sup> with alkyl halides has been well developed as a fundamental reaction for efficient construction of carbon-carbon bonds in organic synthesis. Consequently, various alkyl substituents can be introduced at the  $\alpha$ -position of carbonyl groups with concomitant loss of the original alkenyl moiety in the starting materials (Scheme 1, eq 1). From the view



**Scheme 1.** Alkylation reactions of double bonds with alkyl halides.

point of potential application, conservation of the double bond during this transformation is more preferable yet challenging. Moreover, further functionalization could be easily performed for the precursors with retention of the double bond.

It is well known that enamides are versatile functional groups widely applied in synthesis of complex nitrogen-containing compounds,<sup>[5]</sup> and the key subunits in many natural products and bioactive molecules.<sup>[6]</sup> Therefore, the development of efficient methodologies for preparation of functionalized enamids is highly desirable.

Recently, the direct alkenyl alkylation with retention of the double bond has emerged as a powerful tool for synthesis of multi-substituted alkenes.<sup>[7]</sup> Among them, the reported methods, the use of transition metal catalysts including Co,<sup>[8]</sup> Pd,<sup>[9]</sup> Cu,<sup>[10]</sup> Ni,<sup>[11]</sup> etc., as well as photocatalysts<sup>[12]</sup> have been elegantly applied for the coupling reactions between alkenes and  $\alpha$ -halide carbonyls (Scheme 1, eq 2). However, only limited scopes of substrates have ever been explored thus far. Therefore, the development of efficient catalytic systems and accommodation of expanding various functional alkenes still remain of broad prospect in thisfield. It is well known that benzylic halides and methyl iodide can be employed in coupling reactions with organometallic reagents or aryl C–H bonds<sup>[13]</sup> with the help of transition-metal catalysts. However, only few examples of direct methylation and benzylation of alkenyl C–H bonds have ever been explored (Scheme 1, eqs 3 and 4).<sup>[14]</sup> Herein, we communicate the results on palladium mediated direct methylation and benzylation reactions of enamide for synthesis of multi-substituted functional alkenes (Scheme 1, eq 5).<sup>[15]</sup>

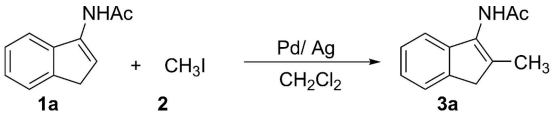
Initially, enamide **1a** and iodomethane **2** were chosen as the model reaction to optimize the reaction conditions. The results are summarized in Table 1. Fortunately, the system of Pd(TFA)<sub>2</sub> with AgOAc afforded the desired product **3a** in 83% yield. Further screening of various palladium catalysts showed that Pd(TFA)<sub>2</sub> was more efficient (Table 1, entry 1 to entry 9), while other silver salts proved to be less efficient to promote the formation of the desired product (Table 1, entry 10 to entry 13). Following that, the catalyst loading and reaction temperature were also examined. When the catalyst loading was reduced to 5 mol%, a slightly decreased yield of the product was obtained (Table 1, entry 16). It was found that either higher or lower reaction temperature decreased the product yield (Table 1, entries 18 and 19) also. It is noteworthy that adding PPh<sub>3</sub> (20 mol%) ligand into the reaction greatly suppress the product's formation. Moreover, control experi-

[a] Prof. Dr. R. Ding  
College of Chemistry and Materials Engineering, Anhui Science and Technology University, Bengbu, Anhui, 233100, P. R.China.  
E-mail: dingran128@126.com

[b] B. Yu  
Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, P. R. China

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/ajoc.201800535>

**Table 1.** Optimization of reaction conditions of alkylation of enamide **1a** with iodomethane.<sup>[a]</sup>

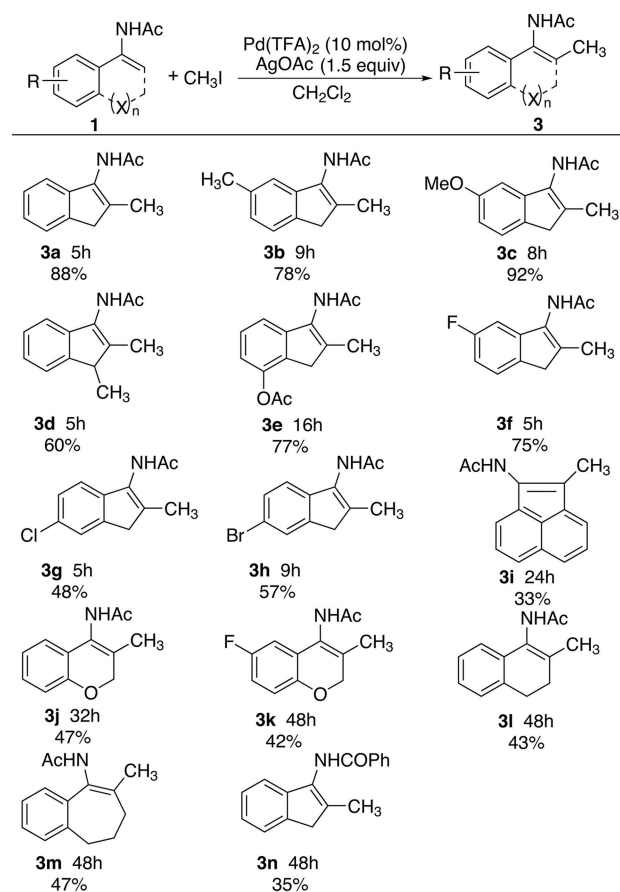


entry	Cat (10 mol%)	AgX (2.0 eq)	T (°C)	time (h)	yield <sup>[g]</sup>
1	Pd(TFA) <sub>2</sub>	AgOAc	80	9	83%
2	Pd(PhCN) <sub>2</sub> Cl <sub>2</sub>	AgOAc	80	9	57%
3	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	AgOAc	80	9	69%
4	Pd <sub>2</sub> (dba) <sub>3</sub>	AgOAc	80	9	trace
5	PdCl <sub>2</sub>	AgOAc	80	9	66%
6	[Pd(allyl)Cl] <sub>2</sub>	AgOAc	80	9	12%
7	Pd(OPiv) <sub>2</sub>	AgOAc	80	9	74%
8	Pd(acac) <sub>2</sub>	AgOAc	80	9	20%
9	Pd(OAc) <sub>2</sub>	AgOAc	80	9	64%
10	Pd(TFA) <sub>2</sub>	AgOTf	80	9	trace
11	Pd(TFA) <sub>2</sub>	AgOTs	80	9	trace
12	Pd(TFA) <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	80	9	trace
13	Pd(TFA) <sub>2</sub>	AgTFA	80	9	trace
14	Pd(TFA) <sub>2</sub>	—	80	9	trace
15	—	AgOAc	80	9	16%
16 <sup>b</sup>	Pd(TFA) <sub>2</sub>	AgOAc	80	9	74%
17 <sup>c</sup>	Pd(TFA) <sub>2</sub>	AgOAc	80	9	trace
18	Pd(TFA) <sub>2</sub>	AgOAc	70	9	81%
19	Pd(TFA) <sub>2</sub>	AgOAc	90	9	82%
20 <sup>d</sup>	Pd(TFA) <sub>2</sub>	AgOAc	80	9	87%
21 <sup>d</sup>	Pd(TFA) <sub>2</sub>	AgOAc	80	5	88%
22 <sup>e</sup>	Pd(TFA) <sub>2</sub>	AgOAc	80	9	75%
23 <sup>f</sup>	—	AgOAc	80	5	14%

<sup>[a]</sup> Reaction conditions: To a mixture of **1a** (0.3 mmol, 1 equiv), **2** (0.6 mmol, 2 equiv), catalyst, ligand, additive and solvent (1 mL) in the sealed tube under air. <sup>[b]</sup> Pd(TFA)<sub>2</sub> (5 mmol %). <sup>[c]</sup> PPh<sub>3</sub> (20 mmol%). <sup>[d]</sup> AgOAc (0.45 mmol, 1.5 equiv). <sup>[e]</sup> AgOAc (0.3 mmol, 1.0 equiv). <sup>[f]</sup> TFA (0.06 mmol, 0.2 equiv). <sup>[g]</sup> Isolated yields.

ments displayed that the presence of palladium catalyst and AgOAc were necessary for providing the desired product in good yield (Table 1, entries 14, 15 and 23). Finally, the optimized reaction conditions are summarized as following: 10 mol% Pd(TFA)<sub>2</sub> as catalyst, 1.5 equiv. AgOAc as additive in DCM(dichloromethane) at 80 °C under air atmosphere.

After optimization of the reaction conditions, the substrate scope of different enamides was tested (Scheme 2). When various substituted cyclic enamides were subjected to this reaction, it was found that the substrates with electron-donating groups would give the products in high yields (**3b** and **3e**, **3c**). However, only moderate yields of desired products could be achieved when the substrates with electron-withdrawing were applied in reactions (**3g**, **3h** and **3f**). It was observed that only 60% yield of **3d** was obtained when the reaction of substituted *N*-(1-methyl-1H-inden-3-yl)acetamide was examined. It is notable that **3i** was also obtained in 33% isolated yield. Further studies showed that only moderate yields of the corresponding products (**3j** and **3k**) were observed when the *N*-(2*H*-chromen-4-yl)acetamide and its derivatives were applied in reactions. Other cyclic enamides such as *N*-(3,4-dihydronaphthalen-1-yl)acetamide and *N*-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)acetamide were also tolerated in this cou-



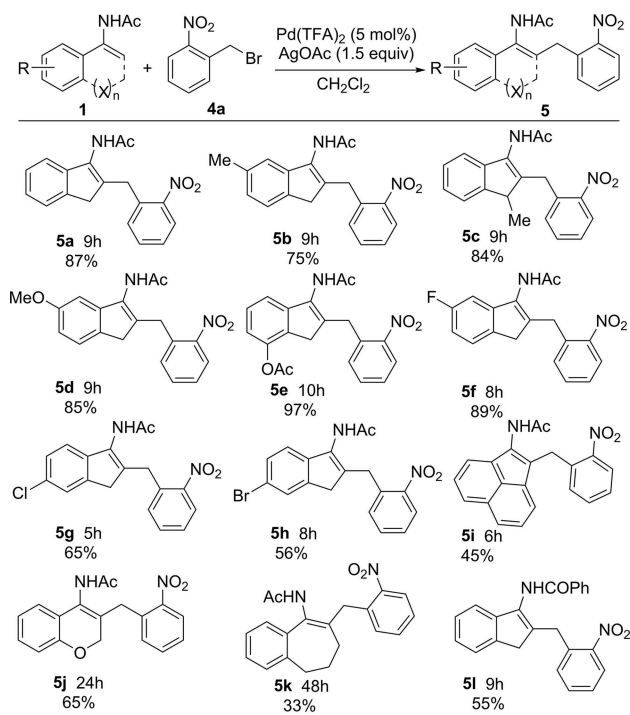
<sup>a</sup> Reaction conditions: To a mixture of **1** (0.3 mmol, 1 equiv), **2** (0.6 mmol, 2 equiv), Pd(TFA)<sub>2</sub> (0.03 mmol, 10 mol %), AgOAc (0.45 mmol, 1.5 equiv) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in the sealed tube at 80 °C under air. <sup>b</sup> Isolated yields.

**Scheme 2.** Palladium-catalyzed methylation of different enamides.<sup>[a,b]</sup>

pling reaction, with only moderate yields of the products(**3i** and **3m**) obtained. Finally, it was found that the change of acetal group to benzoyl group decreased the product yield significantly (**3n**).

We next turned our attention to investigate the reaction of the enamide with 1-(bromomethyl)-2-nitrobenzene (Scheme 3). Based on the conditions established for methylation reaction, subsequently the reaction could proceed smoothly by using 5 mol% Pd(TFA)<sub>2</sub>. Then various enamides were subjected to this benzylation reaction. Generally, both electron-rich and electron-deficient cyclic enamides were well tolerated to give the corresponding products in moderate to high yields (**5a** to **5i**). Meanwhile, *N*-(2*H*-chromen-4-yl)acetamide, *N*-(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)acetamide and benzoyl group protected enamides were further proved to be less efficient to afford the corresponding products (**5j**, **5k** and **5l** respectively).

Different benzyl bromides were then investigated in this benzylation reaction (Scheme 4). A wide range of functional groups including electron-donating (**6f**) and electron-withdrawing groups, such as F, Cl, CF<sub>3</sub>, NO<sub>2</sub>, acetal and ester all could be well tolerated in reaction under the standard reaction conditions (**6a–6h**, and **6m**, **6n**). Inspired by the positive results of primary benzyl halides, we attempted to employ more sterically



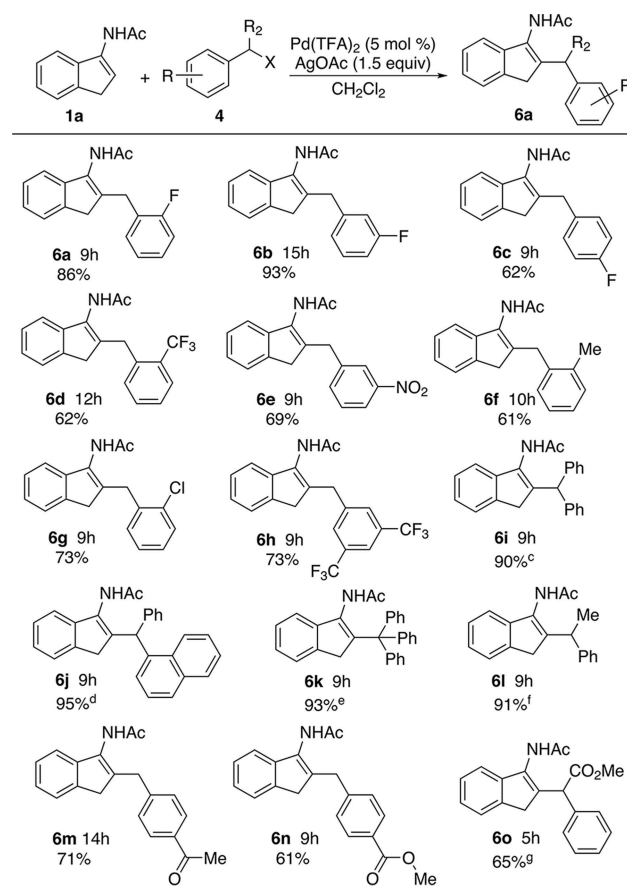
<sup>a</sup> Reaction conditions: To a mixture of **1** (0.3 mmol, 1 equiv), **4a** (0.6 mmol, 2 equiv), Pd(TFA)<sub>2</sub> (5 mol %), AgOAc (0.45 mmol, 1.5 equiv) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in the sealed tube at 80 °C under air. <sup>b</sup> Isolated yields.

**Scheme 3.** Palladium-catalyzed benzylation of various enamides.<sup>[a,b]</sup>

hindered chlorides (Scheme 4). Both secondary benzyl chloride and bromide could be used as coupling partners smoothly. Moreover, when tertiary triphenylchloromethane was used, the product **6j** also could be obtained in excellent yield.

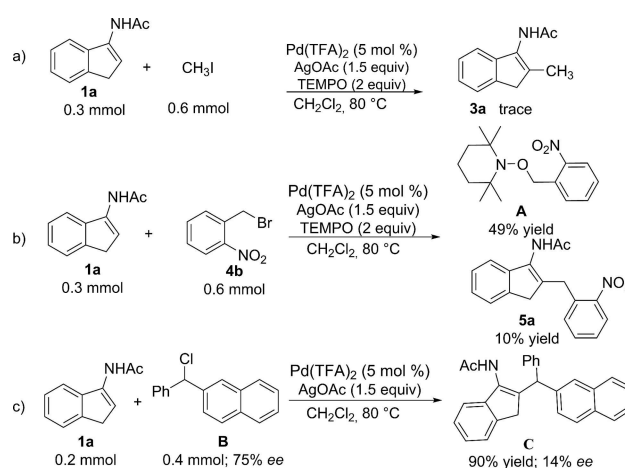
To gain more insight into the benzylation and methylation reaction, 2 equivalents of TEMPO were introduced into this reaction under the standard reaction conditions. It was found that compound **A** could be isolated in 49% yield along with product **5a** in 10% yield (Scheme 5a). Furthermore, enantio-enriched 2-(chloro(phenyl)methyl)naphthalene **B** was prepared and subjected to this benzylation reaction (Scheme 5b). Finally, the coupling product **C** could be obtained in 90% yield with retention of 14% enantiopurity (Scheme 5c). Comparing with this, only 67% yield of product **C** along with complete racemization could be observed in the absence of palladium catalyst. These results show that the palladium catalyst plays a significant role during the cleavage of C–X bond in this benzylation reaction. On the basis of all above results and previous reports,<sup>[15g]</sup> a radical processes is still the most reasonable proposal for this transformation (for possible catalytic cycles, see the Supporting Information).

In conclusion, we have described a palladium-mediated methylation and benzylation of enamides with iodomethane and various benzylic halides, and the corresponding products could be obtained in moderate to good yields, which provide a simple and general method for synthesis of functional multi-substituted enamides.



<sup>a</sup> Reaction conditions: To a mixture of **1** (0.3 mmol, 1 equiv), **4** (0.6 mmol, 2 equiv), Pd(TFA)<sub>2</sub> (5 mol %), AgOAc (0.45 mmol, 1.5 equiv) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in the sealed tube at 80 °C under air. <sup>b</sup> Isolated yields. <sup>c</sup> **4** = (Ph)<sub>2</sub>CHCl. <sup>d</sup> **4** = (Ph)(Nap)CHCl. <sup>e</sup> **4** = (Ph)<sub>3</sub>CHCl. <sup>f</sup> **4** = (Ph)(Me)CHBr. <sup>g</sup> **4** = (Ph)(CO<sub>2</sub>Me)CHBr.

**Scheme 4.** Palladium-catalyzed benzylation with different benzylic halides.<sup>[a,b]</sup>



**Scheme 5.** Reactions in the presence of TEMPO and with a chiral substrate.

## Acknowledgements

The authors gratefully acknowledge the funding support of the Materials Science and Engineering Key Discipline Foundation

(No. AKZDXK2015A01) and the funding support of the Institute of material chemistry.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** alkylation · alkenes ·  $\alpha$ -bromo carbonyls · enamides · palladium

- [1] a) G. Stork, P. Rosen, N. L. Goldman, *J. Am. Chem. Soc.* **1961**, *83*, 2965; b) T. A. Spencer, R. W. Britton, D. S. Watt, *J. Am. Chem. Soc.* **1967**, *89*, 5727; c) H. O. House, M. Gall, H. D. Olmstead, *J. Org. Chem.* **1971**, *36*, 2361.
- [2] a) G. Stork, P. E. Hudrlik, *J. Am. Chem. Soc.* **1968**, *90*, 4464; b) I. Kuwajima, E. Nakamura, *J. Am. Chem. Soc.* **1975**, *97*, 3257; c) I. Kuwajima, E. Nakamura, M. Shimizu, *J. Am. Chem. Soc.* **1982**, *104*, 1025.
- [3] a) I. Marek, F. Normant, *Chem. Rev.* **1996**, *96*, 3241; b) J. D. Dixon, V. S. Ley, F. R. Rodriguez, *Angew. Chem., Int. Ed.* **2001**, *40*, 4763.
- [4] a) T. Hatakeyama, S. Ito, M. Nakamura, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 14192; Examples on alkylation reaction of metal enamides with using alkenes, please see: b) M. Nakamura, T. Hatakeyama, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 11820; c) M. Nakamura, T. Hatakeyama, K. Hara, H. Fukudome, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 14344.
- [5] a) R. Matsubara, S. Kobayashi, *Acc. Chem. Res.* **2008**, *41*, 292; b) M. Terada, K. Machioka, K. Sorimachi, *Angew. Chem. Int. Ed.* **2006**, *45*, 2254; c) K. Terada, K. Machioka, K. Sorimachi, *J. Am. Chem. Soc.* **2007**, *129*, 1033; d) J. Wu, W. Xu, Z.-X. Yu, J. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 9489; e) N. Gigant, L. Chausset-Boissarie, I. Gillaizeau, *Chem. Eur. J.* **2014**, *20*, 7548.
- [6] For recent reviews of enamides, see: a) K. Gopalaiah, H. B. Kagan, *Chem. Rev.* **2011**, *111*, 4599; b) J.-H. Xie, S.-F. Zhu, Q.-L. Zhou, *Chem. Rev.* **2011**, *111*, 1713. For convergent synthesis of *N*-vinyl and *N*-aryl amides, see: c) A. R. Muci, S. L. Buchwald, *Topics in Current Chemistry*; Springer-Verlag: Berlin, **2002**; Vol 219, p 131; d) J. F. Hartwig, In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Ed: E. Negishi, Wiley-Interscience: New York, **2002**; p 1051; e) I. P. Beletskaya, A. V. Cheprakov, *Coord. Chem. Rev.* **2004**, *248*, 2337; f) J. R. Dehli, J. Legros, C. Bolm, *Chem. Commun.* **2005**, 973; g) T. Courant, G. Dagousset, G. Masson, *Synthesis-stuttgart*. **2015**, *13*, 1799. h) M.-X. Wang, *Chem. Commun.* **2015**, *51*, 6039.
- [7] For recent reviews, see: a) S. Tang, K. Liu, C. Liu, A. Lei, *Chem. Soc. Rev.* **2015**, *44*, 1070; b) N. Gigant, L. Chausset Boissarie, I. Gillaizeau, *Chem. Eur. J.* **2014**, *20*, 7548.
- [8] a) B. P. Branchaud, W. D. Detlefsen, *Tetrahedron Lett.* **1991**, *32*, 6273; b) S. Bräse, B. Waegell, A. de Meijere, *Synthesis*. **1998**, 148; c) Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2002**, *124*, 6514; d) T. Fujioka, T. Nakamura, H. Yorimitsu, K. Oshima, *Org. Lett.* **2002**, *4*, 2257; e) W. Affo, H. Ohmiya, T. Fujioka, Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, Y. Imamura, T. Mizuta, K. Miyoshi, *J. Am. Chem. Soc.* **2006**, *128*, 8068.
- [9] a) M. Mori, I. Oda, Y. Ban, *Tetrahedron Lett.* **1982**, *23*, 5315; b) F. Glorius, *Tetrahedron Lett.* **2003**, *44*, 5751; c) C. Fischer, S. W. Smith, D. A. Powell, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 1472; d) L. Firmansjah, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 11340; e) X.-J. Wu, J. W. T. See, K. Xu, H. Hirao, J. Roger, J.-C. Hierso, J.-R. Zhou, *Angew. Chem. Int. Ed.* **2014**, *53*, 13573; f) X. Wu, C. Lei, G. Yue, J. Zhou, *Angew. Chem. Int. Ed.* **2015**, *54*, 9601; g) Y.-J. Zou, J.-R. Zhou, *Chem. Commun.* **2014**, *50*, 3725; h) C. M. McMahon, E. J. Alexanian, *Angew. Chem. Int. Ed.* **2014**, *53*, 5974; i) K. S. Bloome, R. L. McMahan, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 20146; j) C. M. McMahon, E. J. Alexanian, *Angew. Chem. Int. Ed.* **2014**, *53*, 5974.
- [10] a) T. Nishikata, Y. Noda, R. Fujimoto, T. Sakashita, *J. Am. Chem. Soc.* **2013**, *135*, 16372; b) T. W. Liwosz, R. Chemler, *J. Am. Chem. Soc.* **2012**, *134*, 2020; c) X. Zhang, H. Yi, Z. Liao, G. Zhang, C. Fan, C. Qin, J. Liu, A. Lei, *Org. Biomol. Chem.* **2014**, *12*, 6790; d) J. Yuan, L. Zheng, L. Meng, A. Lei, *Angew. Chem. Int. Ed.* **2012**, *51*, 3638; e) M. R. Harris, M. O. Konev, E. R. Jarvo, *J. Am. Chem. Soc.* **2014**, *136*, 7825.
- [11] a) S. A. Lebedev, V. S. Lopatina, E. S. Petrov, I. P. Beletskaya, *J. Organomet. Chem.* **1988**, *344*, 253; b) R. Matsubara, A. C. Gutierrez, T. F. Jamison, *J. Am. Chem. Soc.* **2011**, *133*, 19020; c) E. A. Standley, T. F. Jamison, *J. Am. Chem. Soc.* **2013**, *135*, 1585; d) C. Liu, S. Tang, D. Liu, J. Yuan, L. Zheng, L. Meng, A. Lei, *Angew. Chem. Int. Ed.* **2012**, *51*, 3638; e) M. R. Harris, M. O. Konev, E. R. Jarvo, *J. Am. Chem. Soc.* **2014**, *136*, 7825.
- [12] Q. Liu, H. Yi, J. Liu, Y. Yang, X. Zhang, Z. Zeng, A. Lei, *Chem. Eur. J.* **2013**, *19*, 5120.
- [13] For recent reviews: a) S. Messaoudi, J.-D. Brion, M. Alami, *Eur. J. Org. Chem.* **2010**, 6495; b) B. M. Trost, L. C. Czabaniuk, *Angew. Chem. Int. Ed.* **2014**, *53*, 2826; c) G. Yan, A. J. Borah, L. Wang, M. Yang, *Adv. Synth. Catal.* **2015**, *357*, 1333; For benzylic halides or methyl iodide couple with aryl C-H bonds see: d) S. J. Tremont, *J. Am. Chem. Soc.* **1984**, *106*, 5759; e) M. J. Jang, S. W. Youn, *Bull. Korean Chem. Soc.* **2011**, *32*, 2865; f) S. Bae, H.-L. Jang, H. Jung, J. M. Joo, *J. Org. Chem.* **2015**, *80*, 690; g) L. Ackermann, P. Novák, *Org. Lett.* **2009**, *11*, 4966; h) S. J. Hwang, S. H. Cho, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 16158; i) M. Bao, H. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **2001**, *123*, 759; j) W. Mai, J. Yuan, Z. Li, *Synlett.* **2012**, *6*, 938. k) S. J. Hwang, S. H. Cho, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 16158. l) T. Mukai, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 1360; m) D. Lapointe, K. Fagnou, *Org. Lett.* **2009**, *11*, 4160; For benzylic halides or methyl iodide couple with organometallic reagents see: n) F. Zhao, Q. Tan, F. Xiao, S. Zhang, G.-J. Deng, *Org. Lett.* **2013**, *15*, 1520; o) T. O. Ronson, J. R. Carney, A. C. Whitwood, R. J. K. Taylor, I. J. S. Fairlamb, *Chem. Commun.* **2015**, *51*, 3466; p) G. A. Molander, M. D. Elia, *J. Org. Chem.* **2006**, *71*, 9198; q) A. Lopez-Pérez, J. Adrio, J. Carretero, *Org. Lett.* **2009**, *11*, 5514; r) Y.-Y. Sun, J. Yi, X. Lu, Z.-Q. Zhang, B. Xiao, Y. Fu, *Chem. Commun.* **2014**, *50*, 11060; s) X. Chen, L. M. Zhou, Y. Li, T. Xie, S. Zhou, *J. Org. Chem.* **2014**, *79*, 230; t) D. Srimani, A. Bej, A. Sarkar, *J. Org. Chem.* **2010**, *75*, 4296; u) V. Colombel, F. Rombouts, D. Oehlrich, G. A. Molander, *J. Org. Chem.* **2012**, *77*, 2966; v) M. J. Burns, I. J. S. Fairlamb, A. R. Kapdi, P. Sehna, R. J. K. Taylor, *Org. Lett.* **2009**, *11*, 5514.
- [14] a) R. F. Heck, J. P. Nolley, *J. Org. Chem.* **1972**, *37*, 2320; b) G.-Z. Wu, F. Lamaty, E.-i. Negishi, *J. Org. Chem.* **1989**, *54*, 2507; c) W. Rauf, J. M. Brown, *Angew. Chem. Int. Ed.* **2008**, *47*, 4228; d) Y. Pan, Z. Zhang, H. Hu, *Synth. Commun.* **1992**, *22*, 2019; e) Pan, Y. Zhang, H. Hu, *Synthesis* **1995**, 245; f) P. Kumar, *Org. Prep. Proced. Int.* **1997**, *29*, 477; g) L. Wang, Y. Pan, X. Jiang, H. Hu, *Tetrahedron Lett.* **2000**, *41*, 725; h) K. Higuchi, K. Sawada, H. Nambu, T. Shogaki, Y. Kita, *Org. Lett.* **2003**, *5*, 3703; i) A. Narahashi, H. Yamamoto, I. Shimizu, *Chem. Lett.* **2004**, *33*, 348; j) H. Narahashi, I. Shimizu, A. Yamamoto, *J. Organomet. Chem.* **2008**, *693*, 283; k) R. Matsubara, A. C. Gutierrez, T. F. Jamison, *J. Am. Chem. Soc.* **2011**, *133*, 19020; l) S. J. Gharpure, Y. G. Shelke, S. Raja Bhushan Reddy, *RSC Adv.* **2014**, *4*, 46962; m) G. W. Waldhart, N. P. Mankad, *J. Organomet. Chem.* **2015**, *793*, 171.
- [15] a) H. Zhou, W.-J. Chung, Y.-H. Xu, T.-P. Loh, *Chem. Commun.* **2009**, 45, 3472; b) H. Zhou, Y.-H. Xu, W.-J. Chung, T.-P. Loh, *Angew. Chem. Int. Ed.* **2009**, *48*, 5355; c) Y.-H. Xu, Y.-K. Chok, T.-P. Loh, *Chem. Sci.* **2011**, *2*, 1822; d) S. Pankajakshan, Y.-H. Xu, J.-K. Cheng, M.-T. Low, T.-P. Loh, *Angew. Chem. Int. Ed.* **2012**, *51*, 5701; e) C. Feng, T.-P. Loh, *Chem. Sci.* **2012**, *3*, 3458; f) Y.-H. Xu, T. He, Q.-C. Zhang, T.-P. Loh, *Chem. Commun.* **2014**, *50*, 2784; g) R. Ding, Q.-C. Zhang, Y.-H. Xu, T.-P. Loh, *Chem. Commun.* **2014**, *50*, 11661; h) Y.-H. Xu, Q.-C. Zhang, T. He, T.-P. Loh, *Adv. Synth. Catal.* **2014**, *356*, 1539; i) M. Wang, X. Zhang, Y.-X. Zhuang, Y.-H. Xu, T.-P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 1341; j) R. Ding, Z.-D. Huang, Z.-L. Liu, T.-X. Wang, Y.-H. Xu, T.-P. Loh, *Chem. Commun.* **2016**, *50*, 5617.

Manuscript received: September 7, 2018

Accepted manuscript online: September 24, 2018

Version of record online: October 9, 2018