ORGANIC LETTERS

2012
Vol. 14, No. 17
4594–4597

Direct Carbo-Acylation Reactions of 2-Arylpyridines with α-Diketones via Pd-Catalyzed C−H Activation and Selective C(sp2)−C(sp2) Cleavage

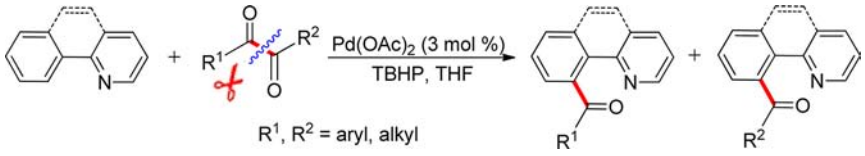
Wei Zhou,[†] Hongji Li,[†] and Lei Wang*[,†,‡]

Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, P. R. China

leiwang@chnu.edu.cn

Received July 25, 2012

ABSTRACT



An efficient carbo-acylation reaction of 2-arylpyridines with α-diketones via Pd-catalyzed C−H bond activation and C−C bond cleavage in the presence of TBHP was developed that generated aryl ketones in good yields. The highly selective formation of aryl ketones was observed when 2-arylpyridines reacted with aromatic/aliphatic α-diketones.

In past years, the transition-metal-catalyzed carbon−carbon bond cleavage has attracted considerable attention for its broad applications in organic synthesis.[1] To the best of our knowledge, three modes of the C−C bond cleavage process have been developed, i.e., formation of a stable complex by chelation,[1b,2] relief of ring strain,[3] and the selective cleavage of substrates with functional groups as leaving groups such as carboxylic acids,[4] nitriles,[5] carbonyls[6] and so on.[7] In general, Rh, Ru, Fe, Pd,[1−7] and Cu[6b,8] are often used to activate the inert C−C bonds and behave in high activity. Different from the selective C−C cleavage of tertiary[1c,d] and secondary alcohols,[7d] β-diketones,[6b] epoxides,[7f] and others,[4,5] the C−C cleavage of α-diketones has not so far been reported.

[†] Huaibei Normal University.
[‡] Shanghai Institute of Organic Chemistry.

(1) For selected reviews, see: (a) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222. (b) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610. For selected examples, see: (c) Zhao, P.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 3124. (d) Iwasaki, M.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4463. (e) Niwa, T.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 2643.

(2) For selected examples, see: (a) Liou, S.-Y.; Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687. (b) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1999**, *121*, 8645. (c) Jun, C.-H.; Moon, C. W.; Lee, D.-Y. *Chem.—Eur. J.* **2002**, *8*, 2422.

(3) For selected examples, see: (a) Bart, S. C.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 886. (b) Winter, C.; Krause, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 2460. (c) Seiser, T.; Cramer, N. *J. Am. Chem. Soc.* **2010**, *132*, 5340.

(4) For selected examples, see: (a) Gooβen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662. (b) Cicchillo, R. M.; Zhang, H.; Blodgett, J. A. V.; Whitteck, J. T.; Li, G.; Nair, S. K.; Donk, W. A.; Metcalf, W. W. *Nature* **2009**, *459*, 871. (c) Pusterla, I.; Bode, J. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 513.

(5) For selected examples, see: (a) Hirata, Y.; Yada, A.; Morita, E.; Nakao, Y.; Hiyama, T.; Ohashi, M.; Ogoshi, S. *J. Am. Chem. Soc.* **2010**, *132*, 10070. (b) Tobisu, M.; Kinuta, H.; Kita, Y.; Remond, E.; Chatani, N. *J. Am. Chem. Soc.* **2012**, *134*, 115.

(6) For selected examples, see: (a) Mecinovic, J.; Hamed, R. B.; Schofield, C. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2796. (b) He, C.; Gou, S.; Huang, L.; Lei, A. *J. Am. Chem. Soc.* **2010**, *132*, 8273.

(7) (a) Waibel, M.; Cramer, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 4455. (b) Li, H.; Li, W.; Liu, W.; He, Z.; Li, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 2975. (c) Baidya, M.; Yamamoto, H. *J. Am. Chem. Soc.* **2011**, *133*, 13880. (d) Li, H.; Li, Y.; Zhang, X.-S.; Chen, K.; Wang, X.; Shi, Z.-J. *J. Am. Chem. Soc.* **2011**, *133*, 15244. (e) Tiwari, B.; Zhang, J.; Chi, Y. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 1911. (f) Zhang, Y.; Wang, M.; Li, P.; Wang, L. *Org. Lett.* **2012**, *14*, 2206.

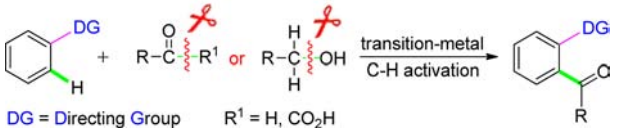
(8) Sai, M.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3294.

(9) (a) *Activation and Functionalization of C−H Bond*; Goldberg, K. I., Goldman, A. S., Eds.; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004. (b) Dyker, G. *Handbook of C−H Transformations: Applications in Organic Synthesis*; Wiley−VCH: Weinheim, 2005. (c) Yu, J. Q.; Shi, Z. J. *C−H Activation*; Springer: Berlin, Germany, 2010.

10.1021/ol3020557
Published on Web 08/27/2012

Recently, C−H activation has become a hot topic[9] because of its economic advantages and it provides a direct route for C−C bond formations.[10] A wide range of transition-metal catalysts, such as Pd^{II}, Cu^{II}, Rh^{III}, and Co^{II} complexes have been applied in the direct C−C cross-coupling via C(sp^2)−H functionalization.[11] These C−H bond activation reactions often require a suitable catalyst, functionalized partner, and oxidant.[12] Importantly, the functionalized partner containing a directing group played an important role in the reactions because the C−H bond adjacent to a heteroatom can be selectively activated.[11] Several directing groups, including pyridines, oximes, amides, amines, alcohols, carboxylic acids, esters, ketones, aldehdyes, and triazenes, were effective to realize the *ortho*-selective C−H functionalizations.[13] It is noteworthy that aryl ketones could be directly synthesized through transition-metal-catalyzed C−H activation (Scheme 1), and carbonyl sources, such as aldehydes, alcohols, and α-ketone acids, were needed.[14] However, α-diketone as a coupling partner[15] and a potential carbonyl source via C−C cleavage to form arylketones was rarely reported. In continuing our efforts on the organic reactions through C−H activation,[16] herein, we wish to report a novel approach to aryl ketones from arylpyridines and α-diketones via Pd-catalyzed C−H bond activation of 2-arylpyridine and selective C(sp^2)−C(sp^2) bond cleavage of α-diketones in the presence of *tert*-butyl hydroperoxide.

Scheme 1. Transition-Metal-Catalyzed Carbo-acylations



In our initial attempts to realize the carbo-acylation reaction of 2-phenylpyridine (**1a**) with α-diphenyl ketone (**2a**), the catalyst screening was first investigated. As shown in Table 1, all Pd/TBHP systems could catalyze the model reaction in THF. To our delight, $Pd(OAc)_2$ exhibited the highest activity among the Pd sources in Table 1, and the desired product **3a** was isolated in 82% yield (Table 1, entry 1). Other Pd catalysts, such as $Pd(CH_3CN)_2Cl_2$, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $PdCl_2$ were inferior and generated **3a** in 34−62% yields (Table 1, entries 2−5). Next, a variety of oxidants were examined on the model reaction to further optimize the reaction conditions. TBHP was found to be the best one among the oxidants tested in Table 1. Other organic oxidizers, such as di-*tert*-butyl peroxide (DTBP), α,α-dimethylbenzyl hydroperoxide (DBHP), dicumyl peroxide (DCP), *tert*-butyl peroxybenzoate (TBPB), and peroxyacetic acid (PAA), gave the inferior yields of **3a** in 21−50% (Table 1, entries 6−10). However, the inorganic oxidants $K_2S_2O_8$ and $Cu(OAc)_2$ showed very poor performance (Table 1, entries 11 and 12). In addition, the effect of solvent on the reaction was also investigated, and the results indicated that THF was the best medium among the screened solvents in Table S1 (see the Supporting Information).

Under the optimized reaction conditions, the scope of the carbo-acylation reactions between the substituted arylpyridines with various α-diketones was investigated. As can be seen from Scheme 2, the reaction of arylpyridines with α-diketones gave the corresponding products in good yields. A variety of arylpyridines bearing substituents on the benzene rings were examined. The results indicated that the functional groups, including electron-donating and -withdrawing ones, were tolerated.

2-Phenylpyridines with the electron-rich groups on the phenyl rings, such as MeO, Me groups, reacted smoothly with α-diphenyl ketone and gave the corresponding carbo-acylation products **3b**−**f** in 67−83% yields. Meanwhile, 2-phenylpyridines with the electron-poor groups on the phenyl rings, such as Cl and F groups, also reacted with α-diphenyl ketone and generated **3h** and **3i** in 74% and 68% yields respectively. The reaction of 2-((1,1′-biphenyl)-4-yl)-pyridine with **2a** provided the corresponding product **3g** in 70% yield. On the other hand, α-diaryl ketones bearing

(10) For selected reviews, see: (a) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (d) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (c) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (d) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (e) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2008**, *41*, 1013. (f) Diaz-Requejo, M. M.; Perez, P. *J. Chem. Rev.* **2008**, *108*, 3379. (g) Giri, R.; Shi, B.; Engle, K.; Maugel, N.; Yu, J. Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (h) Mkhalid, I.; Barnard, J.; Marder, T.; Murphy, J.; Hartwig, J. *Chem. Rev.* **2010**, *110*, 890. (i) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.

(11) For recent examples, see: (a) Zhao, L.; Baslé, O.; Li, C.-J. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 4106. (b) Gao, K.; Lee, P. S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2010**, *132*, 12249. (c) Wang, X.; Truesdale, L.; Yu, J. Q. *J. Am. Chem. Soc.* **2010**, *132*, 3648. (d) Tang, B. X.; Song, R. J.; Wu, C. Y.; Liu, Y.; Zhou, M. B.; Wei, W. T.; Deng, G. B.; Yin, D. L.; Li, J. H. *J. Am. Chem. Soc.* **2010**, *132*, 8900. (e) Kim, J. Y.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110. (f) Xie, P.; Xie, Y.; Qian, B.; Zhou, H.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 9902.

(12) For recent examples, see: (a) Garca-Rubia, A.; Arrays, R. G.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 6511. (b) Engle, K. M.; Wang, D. H.; Yu, J. Q. *J. Am. Chem. Soc.* **2010**, *132*, 14137. (c) Engle, K. M.; Wang, D. H.; Yu., J. Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 6169. (d) Feng, C.; Loh, T. P. *Chem. Commun.* **2011**, *47*, 10458. (e) Wang, C.; Ge, H. B. *Chem.—Eur. J.* **2011**, *17*, 14371. (f) Gandeepan, P.; Cheng, C. H. *J. Am. Chem. Soc.* **2012**, *134*, 5738.

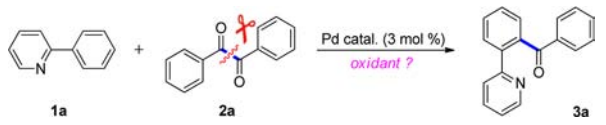
(13) For selected examples, see: (a) Wang, D. H.; Engle, K. M.; Shi, B. F.; Yu, J. Q. *Science* **2010**, *327*, 315. (b) Lu, Y.; Wang, D. H.; Engle, K. M.; Yu, J. Q. *J. Am. Chem. Soc.* **2010**, *132*, 5916. (c) Wasa, M.; Engle, K. M.; Yu, J. Q. *J. Am. Chem. Soc.* **2010**, *132*, 3680. (d) Patureau, F. W.; Besset, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1064. (e) Dai, H. X.; Stepan, A. F.; Plummer, M. S.; Zhang, Y. H.; Yu, J. Q. *J. Am. Chem. Soc.* **2011**, *133*, 7222. (f) Garca-Rubia, A.; Urones, B.; Arrays, R. G.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 10927. (g) Huang, C. H.; Chattopadhyay, B.; Gevorgyan, V. *J. Am. Chem. Soc.* **2011**, *133*, 12406. (h) Mewald, M.; Schiffner, J. A.; Oestreich, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 1763. (i) Wang, C. M.; Chen, H.; Wang, Z. F.; Chen, J.; Huang, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 7242.

(14) (a) Jia, X. F.; Zhang, S. H.; Wang, W. H.; Luo, F.; Cheng, J. *Org. Lett.* **2009**, *11*, 3120. (b) Baslé, O.; Bidange, J.; Shuai, Q.; Li, C.-J. *Adv. Synth. Catal.* **2010**, *352*, 1145. (c) Li, M. Z.; Ge, H. B. *Org. Lett.* **2010**, *12*, 3464. (d) Chan, C. W.; Zhou, Z. Y.; Chan, A. S. C.; Yu, W. Y. *Org. Lett.* **2010**, *12*, 3926. (e) Xiao, F. H.; Shuai, Q.; Zhao, F.; Baslé, O.; Deng, G. J.; Li, C.-J. *Org. Lett.* **2011**, *13*, 1614.

(15) (a) Takano, S.; Hatakeyama, S.; Ogasawara, K. *J. Am. Chem. Soc.* **1979**, *101*, 6414. (b) Takano, S.; Hatakeyama, S; Ogasawara, K. *J. Am. Chem. Soc.* **1976**, *98*, 3022.

(16) (a) Li, C.; Wang, L.; Li, P.; Zhou., W. *Chem.—Eur. J.* **2011**, *17*, 10208. (b) He, T.; Li, H.; Li, P.; Wang, L. *Chem. Commun.* **2011**, *47*, 8946. (c) Li, C.; Li, P.; Yang, J.; Wang, L. *Chem. Commun.* **2012**, *48*, 4214. (d) He, T.; Yu, L.; Zhang, L.; Wang, L.; Wang., M. *Org. Lett.* **2011**, *13*, 5016.

Table 1. Optimization of the Reaction Conditions[a]



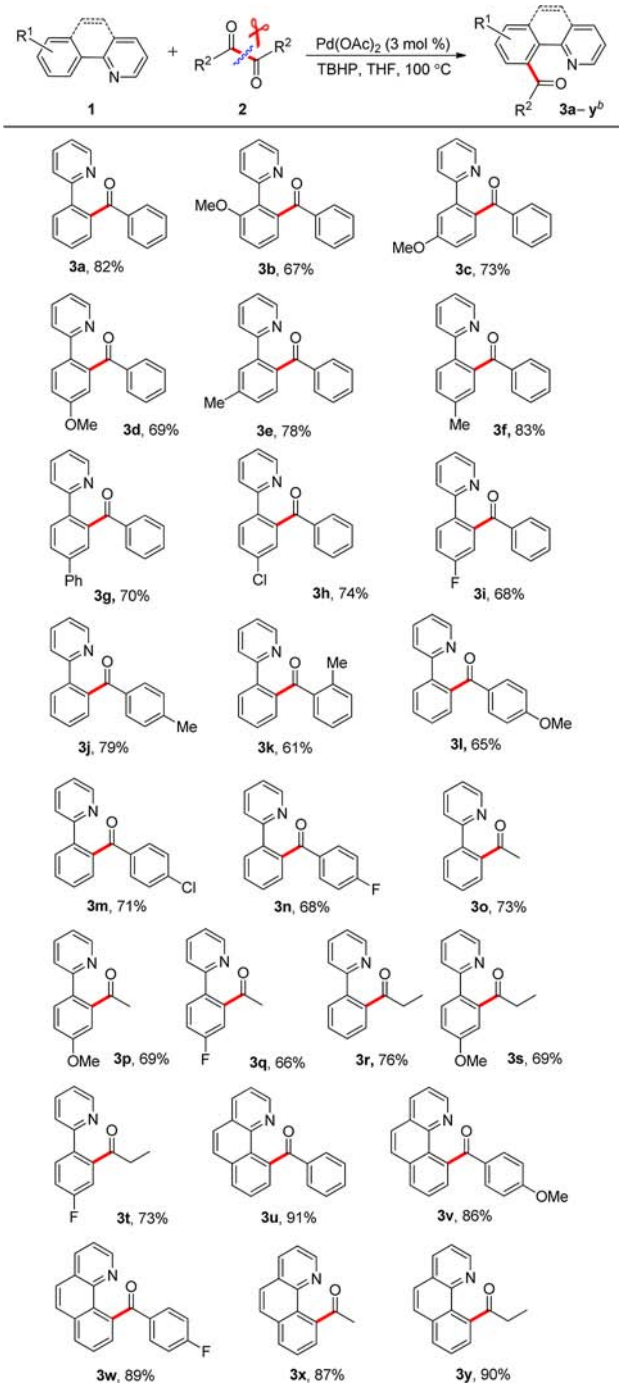
entry	Pd source	oxidant	yield[b] (%)
1	$Pd(OAc)_2$	TBHP	82
2	$Pd(CH_3CN)_2Cl_2$	TBHP	62
3	$Pd(PPh_3)_4$	TBHP	56
4	$Pd(PPh_3)_2Cl_2$	TBHP	40
5	$PdCl_2$	TBHP	34
6	$Pd(OAc)_2$	DTBP	21
7	$Pd(OAc)_2$	DBHP	50
8	$Pd(OAc)_2$	DCP	29
9	$Pd(OAc)_2$	TBPB	22
10	$Pd(OAc)_2$	PAA	48
11	$Pd(OAc)_2$	$K_2S_2O_8$	trace
12	$Pd(OAc)_2$	$Cu(OAc)_2$	0

[a] Reaction conditions: 2-phenylpyridine (**1a**, 0.50 mmol), α-diphenyl ketone (**2a**, 0.75 mmol), Pd source (3 mol %), oxidant (1.5 mmol), THF (2.0 mL), sealed tube, 100 °C, air, 12 h. [b] Isolated yields.

with different substituted groups on the benzene rings, such as Me, MeO, F, and Cl, could react with 2-phenylpyridine, affording the products **3k**−**n** in good yields. We were delighted to find that the reactions of 2-phenylpyridine with challenging α-di(aliphatic)ketones also proceeded well. For example, α-dimethyl ketone and α-diethyl ketone showed almost the comparable reactivity with α-diaryl ketones in the carbo-acylation reactions and offered the satisfactory yields of the corresponding products **3o**−**t**. It is important to note that it provides an efficient route to introduce an aliphatic carbonyl group, such as acetyl or propionyl to 2-arylpyridines, comparing with the reported C−H functionalizations.[14] To extend the scope of arylpyridines, the cross-coupling reaction of benzo[*h*]quinoline with α-diarylketones and α-di(aliphatic)ketones was examined and the excellent yields of the products **3u**−**y** were obtained. The factor for the improved yields may result from the planar structure of benzo[*h*]quinoline.[14b,17]

Interestingly, the highly selective formation of the derivatives of ketones was investigated when 2-arylpyridines reacted with asymmetric α-diketones. The results in Table 2 indicate that asymmetric aromatic α-diketones with an electron-donating group (MeO) and electron-withdrawing one (F) on the benzene rings showed the selective formation of arylketones with the ratio of 27:56 to 25:47 (Table 2, entry 1 vs 2). However, asymmetric aromatic/aliphatic

Scheme 2. Scope of the Direct Carbo-acylation of Arylpyridines with α-Diketones[a]



[a] Reaction conditions: 2-arylpyridine (**1**, 0.50 mmol), α-diketone (**2a**, 0.75 mmol), $Pd(OAc)_2$ (3 mol %), TBHP (1.5 mmol), THF (2.0 mL), sealed tube, 100 °C, air, 12 h. [b] Isolated yields.

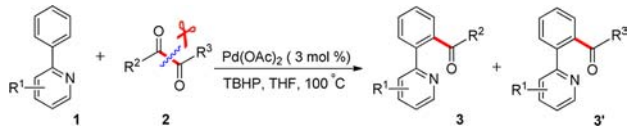
α-diketones, such as 1- phenylpropane-1,2-dione and 1-phenylbutane-1,2-dione, reacted with 2-phenylpyridine, 2-(*p*-methoxyphenyl)pyridine, and 2-(*p*-fluorophenyl)pyridine smoothly and generated the products in good yields with high selectivity (Table 2, entries 3−6). Aliphatic/aromatic ketones were obtained in majority, comparing to aromatic/aromatic ones in the selective formation of arylketones,

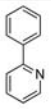
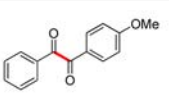
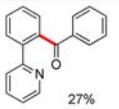
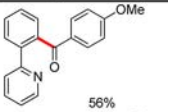
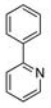
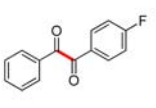
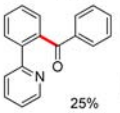
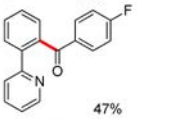
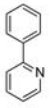
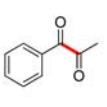
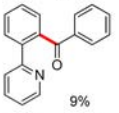
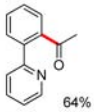
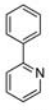
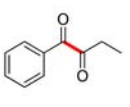
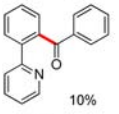
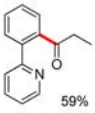
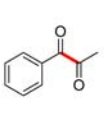
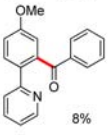
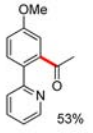
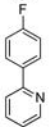
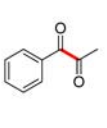
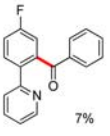
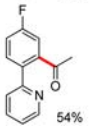
(17) Dick, A. R.; Remy, M. S.; Kampf, J. W.; Sanford, M. S. *Organometallics* **2007**, *26*, 1365.

(18) (a) Adam, W.; Oestrich, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3455. (b) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991. (c) Bentrude, W. G.; Darnall, K. R. *J. Am. Chem. Soc.* **1968**, *90*, 3588.

(19) (a) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300. (b) Arnold, P. L.; Sanford, M. S.; Pearson, S. M. *J. Am. Chem. Soc.* **2009**, *131*, 13912.

Table 2. Selective Cleavage of Asymmetric α-Diketones in the Carbo-acylation Reactions[a]



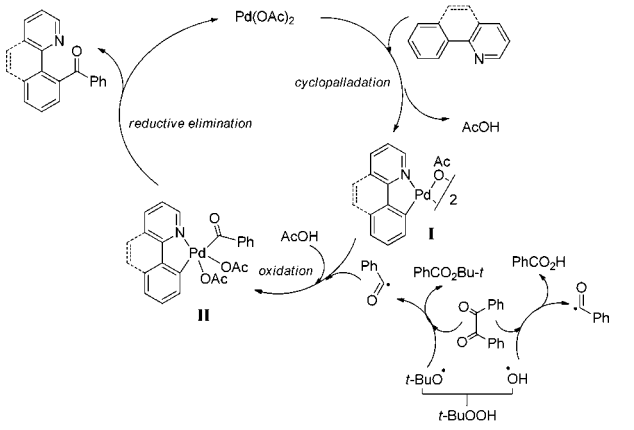
entry	1	2	3, yield [%][b]	3', yield [%][b]
1			 27%	 56%
2			 25%	 47%
3			 9%	 64%
4			 10%	 59%
5			 8%	 53%
6			 7%	 54%

[a] Reaction conditions: 2-arylpyridine (**1**, 0.50 mmol), α-diketone (**2**, 0.75 mmol), $Pd(OAc)_2$ (3 mol %), TBHP (1.5 mmol), THF (2.0 mL), sealed tube, 100 °C, air, 12 h. [b] Isolated yields.

providing the ratio of 59/10 to 64/9. The reason of this selectivity between alkyl ketone vs aryl ketone for unsymmetric diketone is probably that the reactivity of arylcarbonyl reacted with free radical is superior to that of alkylcarbonyl with same radical.[18]

A proposed mechanism of the palladium-catalyzed carbo-acylation reaction of 2-arylpyridine with α-diketone via direct C−H bond activation and $C(sp^2)$−$C(sp^2)$ cleavage in the presence of TBHP is shown in Scheme 3. The reaction probably proceeds involving (i) the formation of a cyclopalladated dimer intermediate (**I**)[19] by chelate-directed C−H activation of the benzene ring of 2-arylpyridine with $Pd(OAc)_2$, (ii) the reaction of **I** with benzoyl radical, which was generated in situ by the reaction of α-diphenyl ketone with TBHP,[18] providing reactive Pd^{IV} intermediate (**II**),[14b,16a,20] and finally, (iii) carbon−carbon bond formation via reductive elimination of **II** affording the acylation product of 2-arylpyridine and regenerating the Pd^{II} species for next run. It should be noted that *tert*-butyl benzoate and benzoic acid were isolated during the reaction of **1a** with **2a**. In addition, the carbo-acylation did not occur in the presence of a radical scavenger, such as TEMPO (2,2,6,6-tetramethylpiperidyl-1-oxyl) or ascorbic acid up to 2 equiv.[14d,21]

Scheme 3. Proposed Reaction Mechanism



In summary, we have developed a direct carbo-acylation reaction of arylpyridines with α-diketones via palladium-catalyzed C−H bond activation and selective cleavage of the C−C bond in the presence of TBHP. 2-Arylpyridines could react with diverse symmetric and asymmetric α-diketones in the presence of $Pd(OAc)_2$ and TBHP in THF and generated arylketones in good yields. It is important to note that the highly selective formation of arylketones was observed when 2-arylpyridines reacted with asymmetric aromatic/aliphatic α-diketones. A detailed mechanistic study is currently underway.

Acknowledgment. This work was financially supported by the National Science Foundation of China (Nos. 21172092, 20972057).

Supporting Information Available. Analytical data and spectra (^1H and ^{13}C NMR) for all products; typical procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

(20) (a) Deprez, N. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 11234. (b) Racowski, J. M.; Dick, A. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974. (c) Rosewall, C. F.; Sibbald, P. A.; Liskin, D. V.; Michael, F. E. *J. Am. Chem. Soc.* **2009**, *131*, 9488. (d) Sibbald, P. A.; Rosewall, C. F.; Swartz, R. D.; Michael, F. E. *J. Am. Chem. Soc.* **2009**, *131*, 15945.

(21) (a) Warren, J. J.; Mayer, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 7784. (b) Liu, W.; Cao, H.; Zhang, H.; Zhang, H.; Chung, K. H.; He, C.; Wang, H.; Kwong, F. Y.; Lei, A. *J. Am. Chem. Soc.* **2010**, *132*, 16737.