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Selective Synthesis of 3-Aryl Quinolin-2(1*H*)-ones and 3-(1-Arylmethylene)oxindoles Involving a 2-Fold Arene C−H Activation Process

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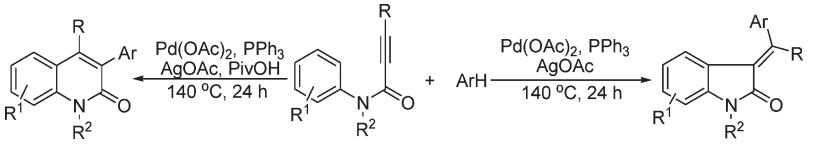

A novel and selective palladium-catalyzed C−H activation protocol has been developed for the synthesis of 3-aryl quinolin-2(1*H*)-ones and 3-(1-arylmethylene)oxindoles with use of PivOH as the switch. In the presence of $Pd(OAc)_2$, AgOAc, and PivOH, a variety of *N*-methyl anilides reacted with arenes to afford the corresponding 3-aryl quinolin-2(1*H*)-ones in moderate yields, whereas the selectivity was shifted toward 3-(1-arylmethylene)oxindoles in the absence of PivOH.

Introduction

Palladium-catalyzed addition of an arene C−H bond to a carbon−carbon triple bond has proven to be a powerful carbon−carbon forming reaction.[1−5] However, much attention has been given to the hydroarylation of alkynes since it was first reported by Fujiwara.[1−4] The hydroarylation of alkynes under acidic conditions usually proceeds via the intramolecular 6-*endo*-*dig* hydroarylation process. Fujiwara and co-workers, for example, first found that arylalkynes could undergo the palladium-catalyzed intramolecular hydroarylation reaction in acids to afford the *endo*-six-membered heterocycles (Scheme 1).[1,2] Recently, Gevorgyan and Chemyak reported an interesting Pd-catalyzed exclusive 5-*exo*-*dig* hydroarylation of *o*-alkyne biaryls under neutral conditions. However, all the methods are limited because they only introduced one carbon and one hydrogen atom into a carbon−carbon triple bond to form a carbon−carbon bond and a hydrogen−carbon bond. According to the mechanism, a novel strategy for capturing the C−Pd σ-bonds in intermediates **B** or **C** by other groups instead of

(1) For reviews, see: (a) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Soc.* **2001**, *34*, 633. (b) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167. (c) Fairlamb, I. J. S. *Annu. Rep. Prog. Chem., Sect. B* **2006**, *102*, 50.

(2) For palladium-catalyzed hydroarylation of alkynes, see: (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992. (b) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252. (c) Jia, C.; Piao, D.; Kitamura, T.; Fujiwara, Y. *J. Org. Chem.* **2000**, *65*, 7516. (d) Lu, W.; Jia, C.; Kitamura, T.; Fujiwara, Y. *Org. Lett.* **2000**, *2*, 2927. (e) Trost, B. M.; Toste, F. D.; Greenman, K. *J. Am. Chem. Soc.* **2003**, *125*, 4518. (f) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752. (g) Ahlquist, M.; Fabrizi, G.; Cacchi, S.; Norrby, P.-O. *J. Am. Chem. Soc.* **2006**, *128*, 12785. (h) Chernyak, N.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 5636.

(3) For other transition metal-catalyzed hydroarylation of alkynes, see: (a) Tunge, J. A.; Foresee, L. N. *Organometallics* **2005**, *24*, 6440. (b) Soriano, E.; Marco-Contelles, J. *Organometallics* **2006**, *25*, 4542. Pt: (c) Pastine, S. J.; Youn, S. W.; Sames, D. *Org. Lett.* **2003**, *5*, 1055. (d) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556. (e) Nevado, C.; Echavarren, A. M. *Chem.—Eur. J.* **2005**, *11*, 3155. Au: (f) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485. (g) Shi, Z.; He, C. *J. Org. Chem.* **2004**, *69*, 3669. (h) England, D. B.; Padwa, A. *Org. Lett.* **2008**, *10*, 3631. Fe: (i) Li, R.; Wang, S. R.; Lu, W. *Org. Lett.* **2007**, *9*, 2219. Re (j) Kuninobu, Y.; Kikuchi, K.; Tokunaga, Y.; Nishina, Y.; Takai, K. *Tetrahedron* **2008**, *64*, 5974. Rh: (k) Hong, P.; Cho, B.-R.; Yamazaki, H. *Chem. Lett.* **1980**, 507. (l) Yamazaki, H.; Hong, P. *J. Mol. Catal.* **1983**, *21*, 133. (m) Tokunaga, Y.; Sakakura, T.; Tanaka, M. *J. Mol. Catal.* **1989**, *56*, 305. (n) Boese, W. T.; Goldman, A. S. *Organometallics* **1991**, *10*, 782. (o) Aulwurm, U. R.; Melchinger, J. U.; Kisch, H. *Organometallics* **1995**, *14*, 3385. Ru: (p) Hong, P.; Cho, B.-R.; Yamazaki, H. *Chem. Lett.* **1979**, 339. (q) Kakiuchi, F.; Yamamoto, Y.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 681.

(4) For Lewis acid-catalyzed hydroarylation of alkynes, see: (a) Song, C. E.; Jung, D.-u.; Choung, S. Y.; Roh, E. J.; Lee, S.-g. *Angew. Chem., Int. Ed.* **2004**, *43*, 6183. (b) Yoon, M. Y.; Kim, J. H.; Choi, D. S.; Shin, U. S.; Lee, J. Y.; Song, C. E. *Adv. Synth. Catal.* **2007**, *349*, 1725.

(5) (a) Pinto, A.; Neuville, L.; Retailleau, P.; Zhu, J. *Org. Lett.* **2006**, *8*, 4927. (b) Pinto, A.; Neuville, L.; Zhu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 3291. (c) Pinto, A.; Neuville, L.; Zhu, J. *Tetrahedron Lett.* **2009**, *50*, 3602. (d) Song, R.-J.; Liu, Y.; Li, R.-J.; Li, J.-H. *Tetrahedron Lett.* **2009**, *50*, 3912. (e) Tang, S.; Peng, P.; Pi, S.-F.; Liang, Y.; Wang, N.-X.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1179. (f) Tang, S.; Peng, P.; Wang, Z.-Q.; Tang, B.-X.; Deng, C.-L.; Li, J.-H.; Zhong, P.; Wang, N.-X. *Org. Lett.* **2008**, *10*, 1875. (g) Tang, S.; Peng, P.; Zhong, P.; Li, J.-H. *J. Org. Chem.* **2008**, *73*, 5476. (h) Peng, P.; Tang, B.-X.; Pi, S.-F.; Liang, Y.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 3569.

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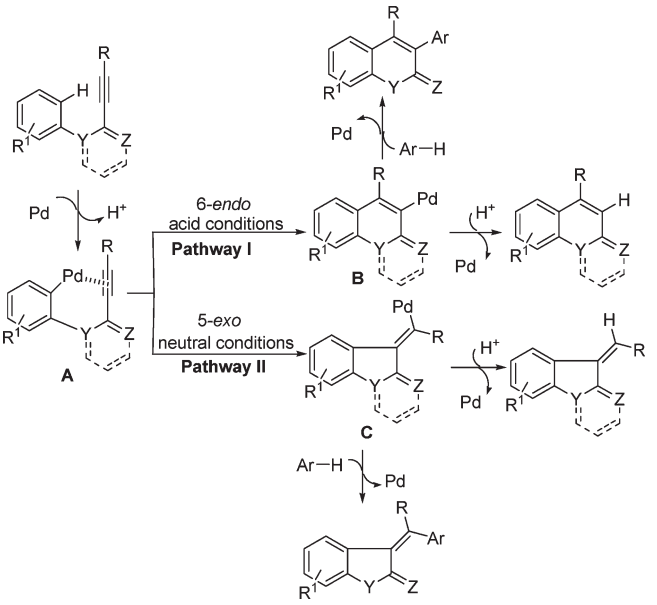
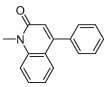
SCHEME 1



hydrogen would be highly desirable. Zhu and co-workers have reported an interesting palladium-catalyzed domino reaction of arylalkynes with electrophilic aryl iodides to afford the *exo*-five-membered heterocycles under basic conditions.[5a−c] We also discovered that *exo*-five-membered heterocycles were prepared by the palladium-catalyzed oxidative C−H functionalization of arylalkynes with nucleophiles,[5d−h] and the selectivity was not affected by the conditions (acidic or basic). Recently, transition metal-catalyzed activation of sp^2 C−H bonds of arenes have been widely investigated, and emerged as a promising method for carbon−carbon bond formation.[6] These prompted us to examine the feasibility of arenes as an alternative to hydrogen to capture the C−Pd σ-bonds. After a series of trials, we were delighted to find that selective 5-*exo-dig* and 6-*endo-dig* diarylation of *N*-arylpropiolamides with arenes could be conducted successfully via a 2-fold arene C−H activation pathway, and the switch of the selectivity is PivOH (Scheme 1).

Results and Discussion

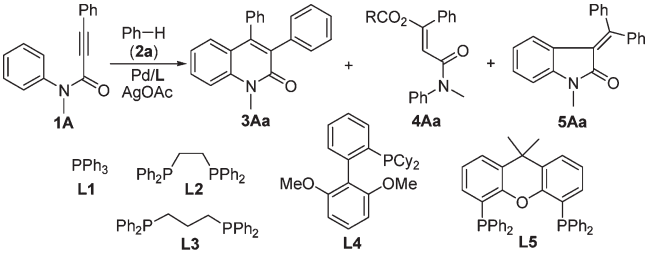
The reaction of *N*-methyl-*N*,3-diphenylpropiolamide (**1A**) with benzene (**2a**) was carried out to optimize the reaction conditions (Table 1). Our investigation began with an attempt at diarylation of amide **1A** with 60 equiv of benzene (**2a**), 5 mol % of $Pd(OAc)_2$, 3 equiv of AgOAc, and 6 equiv of CF_3COOH at 110 °C. However, only 1-methyl-4-phenylquinolin-2(1*H*)-one (**6Aa**),



the reported hydroarylation product, was isolated in 80% yield (entry 1). To our delight, the target product **3Aa** was obtained in 34% yield along with 41% yield of another hydropivaloyloxylation product **4Aa** with use of PivOH instead of CF_3COOH (entry 2). Identical results were observed by using 4-nitrobenzoic acid (entry 3). However, both HOAc and benzoic acid have no activity (entries 4 and 5). Subsequently, other conditions, such as ligand and reaction temperature, were screened to enhance the yield. Among the ligand and temperature examination, PPh_3 (**L1**) combined with 140 °C gave the best results (entries 6−11). We found that $PdCl_2(Ph_3P)_2$ was less effective than the $Pd(OAc)_2/Ph_3P$ system (entry 12). It was interesting to disclose that the amount of PivOH affected the selectivity, and the selectivity toward the 5-*exo-dig* diarylation occurred along with decreasing loading of PivOH (entries 13−17). We found that a trace amount of the 5-*exo-dig* diarylation product **5Aa** was observed in the presence of 4 equiv of PivOH (entry 13), and the yield of **5Aa** was enhanced to 30% at 0.1 equiv of PivOH (entry 16). Gratifyingly, the product **5Aa** was obtained exclusively in 59% yield without PivOH (entry 17). It is noted that PivOCs has no effect on the reaction (entry 18), and no product was observed in the absence of Pd or Ag catalysts (entries 19 and 20). Finally, two other Ag salts were tested, and they were less effective (entries 21 and 22).

With the optimal conditions in hand, we decided to explore the anilide scope for the 6-*endo-dig* diarylation

TABLE 1. Screening Optimal Conditions[a]

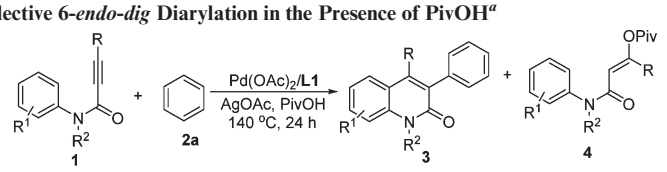


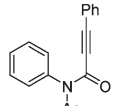
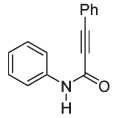
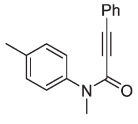
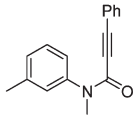
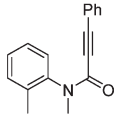
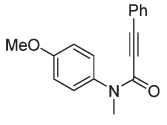
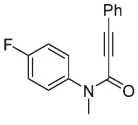
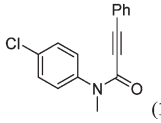
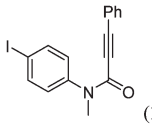
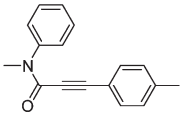
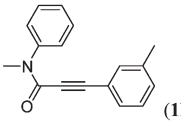
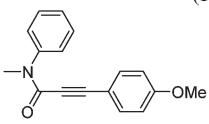
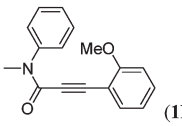
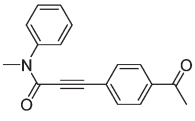
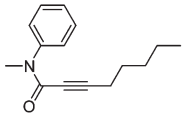
					yield (%)		
entry	ligand	[Ag]	additive (equiv)	t (°C)[b]	**3Aa**	**4Aa**	**5Aa**
1[c]		AgOAc	CF_3COOH (6)	110	0	trace	0
2		AgOAc	PivOH (6)	110	34	41	0
3		AgOAc	4-$NO_2C_6H_4CO_2H$	110	32	10	0
4		AgOAc	AcOH	110	trace	trace	0
5		AgOAc	$C_6H_5CO_2H$	110	trace	trace	0
6	**L1**	AgOAc	PivOH (6)	110	43	35	0
7	**L2**	AgOAc	PivOH (6)	110	17	53	0
8	**L3**	AgOAc	PivOH (6)	110	15	50	0
9	**L4**	AgOAc	PivOH (6)	110	33	39	0
10	**L5**	AgOAc	PivOH (6)	110	23	51	0
11	**L1**	AgOAc	PivOH (6)	140	47	33	0
12[d]		AgOAc	PivOH (6)	140	40	41	0
13	**L1**	AgOAc	PivOH (4)	140	38	32	trace
14	**L1**	AgOAc	PivOH (1.5)	140	23	47	14
15	**L1**	AgOAc	PivOH (0.3)	140	14	trace	25
16	**L1**	AgOAc	PivOH (0.1)	140	10	trace	30
17	**L1**	AgOAc		140	trace	0	59
18	**L1**	AgOAc	PivOCs (2)	140	0	0	0
19	**L1**		PivOH (6)	110	trace	trace	0
20[e]	**L1**	AgOAc	PivOH (6)	140	0	0	0
21	**L1**	Ag_2CO_3	PivOH (6)	110	trace	trace	0
22	**L1**	$AgSbF_6$	PivOH (6)	110	trace	trace	0

[a]Reaction conditions: **1A** (0.2 mmol), benzene **2a** (60 equiv), $Pd(OAc)_2$ (5 mol %), ligand (10 mol %), AgOAc (3 equiv), and additive under Ar atmosphere for 24 h. Substrate **1A** was consumed completely, and some side products via the decomposition of the two C−N bonds were observed by GC-MS analysis. [b]Oil-bath temperature. [c]**6Aa** was isolated in 80% yields. [d]$PdCl_2(Ph_3P)_2$ instead of $Pd(OAc)_2$. [e]Without Pd catalysts.

(6) For selected reviews, see: (a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (b) Campeau, L.-C.; Fagnou, K. *Chem. Commun.* **2006**, 1253. (c) Beccalli, E. M.; Gianluigi Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318.

TABLE 2. $Pd(OAc)_2$-Catalyzed Selective 6-*endo-dig* Diarylation in the Presence of PivOH[a]

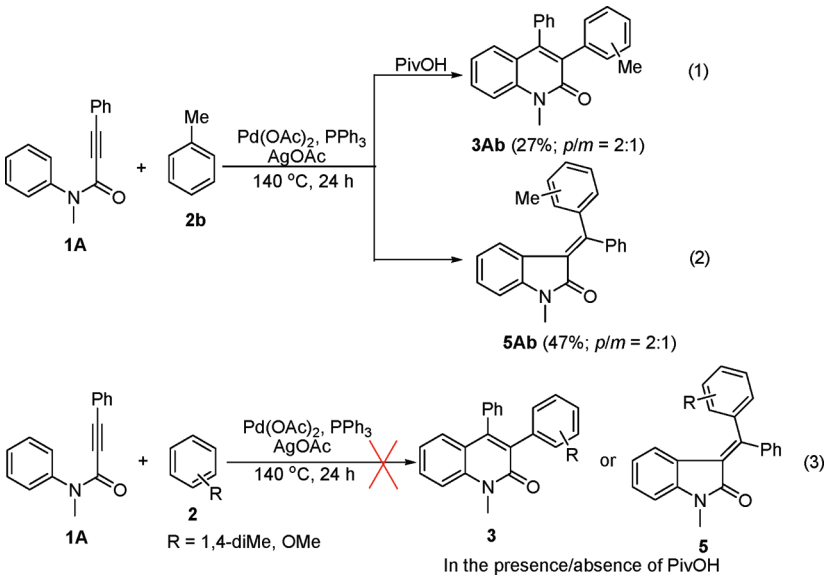


Entry	Amide **1**	Yield (%)[b] **3**	Yield (%)[b] **4**
1	 (**1B**)	trace (**3Ba**)	trace (**4Ba**)
2	 (**1C**)	trace (**3Ca**)	trace (**4Ca**)
3	 (**1D**)	51 (**3Da**)	36 (**4Da**)
4[c]	 (**1E**)	47 (**3Ea**)	34 (**4Ea**)
5	 (**1F**)	34 (**3Fa**)	44 (**4Fa**)
6	 (**1G**)	43 (**3Ga**)	43 (**4Ga**)
7	 (**1H**)	51 (**3Ha**)	36 (**4Ha**)
8	 (**1I**)	36 (**3Ia**)	26 (**4Ia**)
9	 (**1J**)	12 (**3Ja**)	trace (**4Ja**)
10	 (**1K**)	44 (**3Ka**)	47 (**4Ka**)
11	 (**1L**)	45 (**3La**)	39 (**4La**)
12	 (**1M**)	49 (**3Ma**)	43 (**4Ma**)
13	 (**1N**)	trace (**3Na**)	trace (**4Na**)
14	 (**1O**)	34 (**3Oa**)	40 (**4Oa**)
15	 (**1P**)	trace (**3Pa**)	trace (**4Pa**)

[a]Reaction conditions: **1** (0.2 mmol), benzene **2a** (60 equiv), $Pd(OAc)_2$ (5 mol %), PPh_3 (**L1**; 10 mol %), AgOAc (3 equiv), and PivOH (6 equiv) at 140 °C under argon atmosphere for 24 h. [b]Substrate **1** was consumed completely, and some side products via the decomposition of the two C−N bonds were observed by GC-MS analysis.

reaction with benzene (**2a**) first (Table 2). The results demonstrated that the analogous amides with the *N*-methyl group replaced by either a hydrogen atom or an acetyl group were unsuitable substrates (entries 1 and 2). Consequently, a variety of *N*-methyl anilides **1D**−**P** were investigated in the presence of $Pd(OAc)_2$, AgOAc, and PivOH (entries 3−15). We were pleased to find that several functional groups, such as methyl, methoxy, fluoro, or chloro groups, on the *N*-aromatic ring were perfectly tolerated, but both the iodo group and the steric hindrance effect disfavored the reaction (entries 3−9). While substrate **1D** bearing a methyl at the para-position gave the corresponding products **3Da** in 51% yield and **4Da** in 36% yield under the standard conditions (entry 3), substrate **1F** having an *o*-methyl group reduced the yield of the desired product **3Fa** to 34% together with the product **4Fa** in 44% yield (entry 5). It is worthy noting that the 6-positon arene C−H activated product **3Ea** is selectively obtained from *N*-methyl-3-phenyl-*N*-*m*-tolylpropiolamide (**1E**) (entry 4). The results revealed that the properties of halide groups affected the yields of the products **3**, with the order of the yields being F > Cl > I (entries 7−9). Substitutents at the terminal alkyne moiety of *N*-methyl-*N*-phenylpropiolamides were also evaluated. It was found that both para- and meta-substituted aryl groups, either electron

SCHEME 2. Cyclization Reactions of Amide 1A with Toluene (2b)



deficient or electron rich, were effective for the reaction in good total yields under the standard conditions (entries 10−12 and 14), but *o*-methoxyphenyl and alkyl groups have no activity (entries 13 and 15). Amide **1M** bearing a *p*-methoxyphenyl group, for example, was treated with benzene (**2a**), $Pd(OAc)_2$, AgOAc, and PivOHto afford a 49% yield of the target product **3Ma** and 43% yield of **4Ma** (entry 12), and 74% total yield was still achieved from substrate **1O** with a *p*-acetylphenyl group (entry 14).

Next, 5-*exo*-*dig* diarylation of *N*-arylpropiolamides with benzene (**1a**) was evaluated with $Pd(OAc)_2$, PPh_3, and AgOAc in the absence of PivOH (Table 2). We found that substrates **1B** and **1C** were still unsuitable for the 5-*exo*-*dig* diarylation reaction under the standard conditions (entries 1 and 2). However, *N*-methyl-substituted substrate **1D** underwent the 5-*exo*-*dig* diarylation reaction with $Pd(OAc)_2$, PPh_3, and AgOAc smoothly to afford the corresponding 5-*exo*-*dig* product **5Da** in 65% yield (entry 3). Identical results were obtained from the reactions of amides **1E**−**I**, **1M**, and **1O**, bearing electron-donating or electron-withdrawing groups on the aryl moiety, under the same conditions (entries 4−10), but 5-*exo*-*dig* diarylation of *N*-methyl-*N*-phenyloct-2-ynamide **1P** was unsuccessful (entry 11). Substrate **1F** bearing an *o*-methyl group, for instance, was treated $Pd(OAc)_2$, PPh_3 and AgOAc efficiently to afford the target product **5Fa** in moderate yield (entry 5). To our delight, the standard conditions were also compatible with amides **1H** and **1I** with a halo-substituted aryl group (entries 7 and 8).

Another arene, toluene (**2b**), was also tested under the standard conditions. As shown in Scheme 2, the reaction of *N*-methyl-*N*,3-diphenylpropiolamide (**1A**) with toluene (**2b**), $Pd(OAc)_2$, AgOAc, and PivOH was carried out smoothly to afford the corresponding product **3Ab** in 27% yield (p/m = 2:1; eq 1 in Scheme 2), and the 5-*exo*-*dig* product **5Ab** was isolated in 47% yield without PivOH (p/m = 2:1; eq 2 in Scheme 2) (Table 3). However, the reactions of amide **1A** with *p*-xylene (**2c**) or anisole (**2d**) were unsuccessful under the same conditions (eq 3 in Scheme 2).

To elucidate the mechanism, some controlled experiments, including the kinetic isotope effect experiments, were conducted (Scheme 3). We found that without arenes a mixture of products, including the hydropivaloyloxylation product **4Aa** and the decomposition products, were observed by GC-MS analysis from the reaction of substrate **1A** with $Pd(OAc)_2$, AgOAc, and PivOH (eq 4 in Scheme 3). The product **4** can be obtained without arenes, which suggests the competition between the C−H activation and the hydropivaloyloxylation reaction in the present 6-*endo*-*dig* diarylation process. For the 6-*endo*-*dig* diarylation reaction, intermolecular and intramolecular kinetic isotope effects of 3.2 and 1.6, respectively, were found, which is among the range of the C−H activation.[3a,6,7] On the other hand, we found that the hydrogen/deuterium kinetic isotope effects for the 5-*exo*-*dig* diarylation reaction were 1 (intermolecular) and 2.1 (intramolecular). This result indicated that the C−H functionalization was not the rate-determining step of this present process, and the mechanism of C−H activation was incompatible with the SEAr mechanism.[3a,5−7]

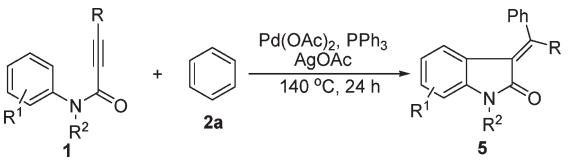
Consequently, the possible mechanisms as outlined in Scheme 4 were proposed on the basis of the reported mechanism and the present results.[1−8] The reaction of Pd

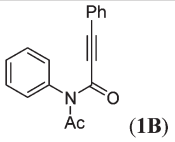
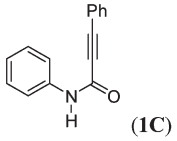
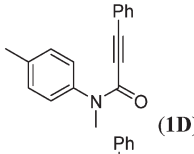
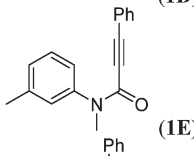
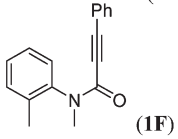
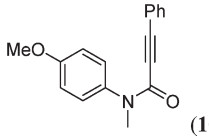
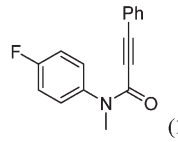
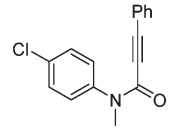
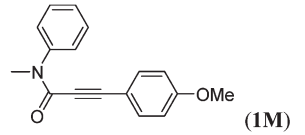
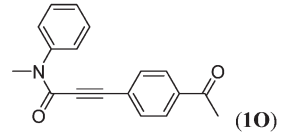
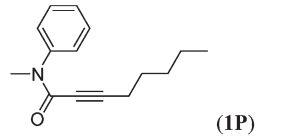
(7) For selected papers on the kinetic isotope effect studies, see: (a) Shue, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 7116. (b) Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.* **2002**, *124*, 1586. (c) Hennessy, E. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 12084. (d) Tunge, A. A.; Foresee, L. N. *Organometallics* **2005**, *24*, 6640. (e) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581. (f) García-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880.

(8) (a) Davies, D.; Donald, S. M. A.; Macgregor, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13754. (b) Lafrance, M.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 16496. (c) Lebrasseur, N.; Larrosa, I. *J. Am. Chem. Soc.* **2008**, *130*, 2926. (d) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 10848. (e) Lafrance, M.; Lapointe, D.; Fagnou, K. *Tetrahedron* **2008**, *64*, 6015. (f) Stuart, D. R.; Fagnou, K. *Science* **2007**, *316*, 1172. (g) Cárdenas, D. J.; Martín-Matute, B.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 5033. (h) Pascual, S.; de Mendoza, P.; Braga a, A. A.C.; Maseras, F.; Echavarren, A. M. *Tetrahedron* **2008**, *64*, 6021. (i) Potavathri, S.; Dumas, A. S.; Dwight, T. A.; Naumiec, G. R.; Hammann, J. M.; DeBoef, B. *Tetrahedron Lett.* **2008**, *49*, 4050 and references cited therein. (j) Chen, X.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 12634. (k) Giri, R.; Maugel, N.; Li, J.-J.; Wang, D.-H.; Breazzano, S. P.; Saunders, L. B.; Yu, J.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 3510. (l) Li, J.-J.; Mei, T.-S.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 6452.

(9) Wang, Z.; Fan, R.; Wu, J. *Adv. Synth. Catal.* **2007**, *349*, 1943.

TABLE 3. $Pd(OAc)_2$-Catalyzed Selective 5-*exo-dig* Diarylation in the Absence of PivOH[a]



Entry	Substrate **1**	Yield (%)[b]
1	 (**1B**)	trace (**5Ba**)
2	 (**1C**)	trace (**5Ca**)
3	 (**1D**)	65 (**5Da**)
4	 (**1E**)	49 (**5Ea**)
5	 (**1F**)	51 (**5Fa**)
6	 (**1G**)	63 (**5Ga**)
7	 (**1H**)	53 (**5Ha**)
8	 (**1I**)	57 (**5Ia**)
9	 (**1M**)	57 (**5Ma**)
10	 (**1O**)	56 (**5Oa**)
11	 (**1P**)	trace (**5Pa**)

[a]Reaction conditions: **1** (0.2 mmol), benzene **2a** (60 equiv), $Pd(OAc)_2$ (5 mol %), PPh_3 (**L1**; 10 mol %), AgOAc (3 equiv), and PivOH (6 equiv) at 140 °C under argon atmosphere for 24 h. [b]Substrate **1** was consumed completely, and some side products via the decomposition of the two C−N bonds were observed by GC-MS analysis.

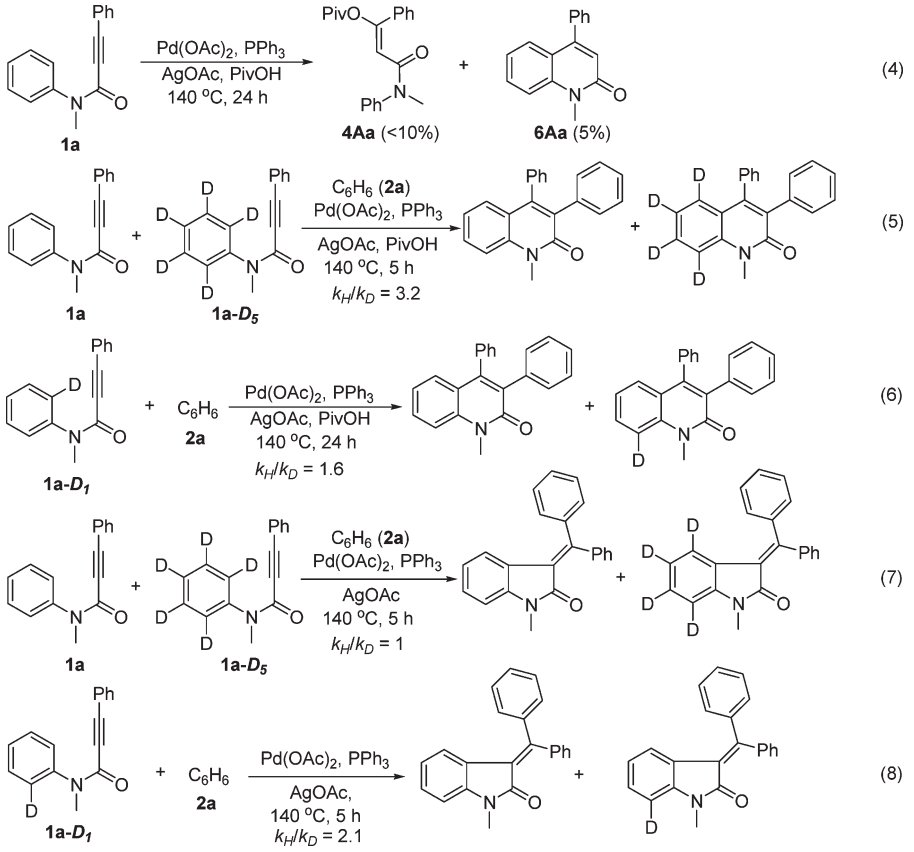
with ArH affords intermediate **D** with the aid of AgOAc.[6,8] Subsequently, two pathways may take place: (1) amide-assisted *o*-C−H activation of the anilide is induced by intermediate **E** in the presence of in situ generated pivalate (by the action of acetate anion), followed by *trans*-carbopalladation[2a] across the triple bond, which might lead to the 6-*endo-dig* intermediate **G**. Reductive elimination of intermediate **G** provides the corresponding products **3** and regenerates the active Pd(0) species. (2) A complex of intermediate **D** with a triple bond occurs to yield the 5-*exo-dig* intermediate **H**, followed by cis-addition to give intermediate **I**. Intermediate **I** undergoes the second C−H activation/cyclization reaction to afford the product **5**, which may undergo the same process as those of Zhu according to the kinetic isotope effect experiments.[5a−c] Under basic conditions, another **F** → **J** pathway cannot be ruled out on the base of the kinetic isotope effect experiments, and the 5-*exo-dig* intermediate **J** may undergo the same process as those of Zhu[5a−c] to afford the product **5**.

In summary, we describe here the first example of selectively constructing 3-aryl quinolin-2(1*H*)-ones and 3-(1-arylmethylene)oxindoles via a $Pd(OAc)_2$-catalyzed 2-fold arene C−H activation/annulation of the *N*-arylpropiolamide process. A mechanism has also been proposed for this transformation on the basis of the observed values of kinetic isotope effects.

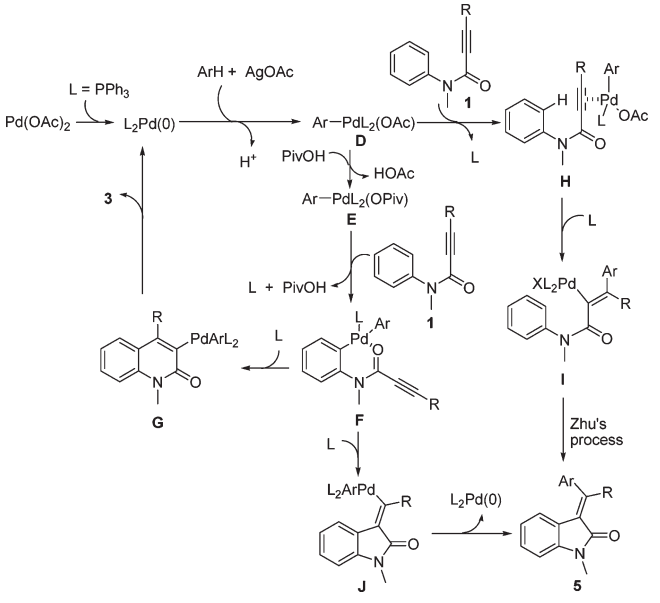
Experimental Section

Typical Experimental Procedure for the $Pd(OAc)_2$-Catalyzed Selective 6-*endo-dig* Diarylation in the Presence of PivOH. A mixture of aniline **1** (0.2 mmol), arene **2** (60 equiv), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), AgOAc (3 equiv), and PivOH (6 equiv) was stirred in a Schlenk tube at 140 °C for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was poured into diethyl ether, which was washed with brine. The aqueous layer was extracted with diethyl ether and the combined organic layer was dried over anhydrous

SCHEME 3. Some Controlled Reactions Including the Kinetic Isotope Effect Experiments



SCHEME 4. Possible Mechanisms



Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford products **3** and **4**.

1-Methyl-3,4-diphenylquinolin-2(1*H*)-one (3Aa):[9] yellow solid, mp 192.7−194.3 °C (uncorrected); ^{1}H NMR (500 MHz) δ 7.57 (t, J = 10.0 Hz, 1H), 7.46 (d, J = 10.0 Hz, 1H), 7.44−7.29 (m, 2H), 7.27−7.25 (m, 2H), 7.16−714 (m, 2H), 7.13−7.09 (m, 6H), 3.85 (s, 3H); ^{13}C NMR (125 MHz) δ 161.8, 147.7, 139.5, 136.3, 135.9, 132,0, 130.6, 130.3, 129.9, 128.5, 127.9, 127.5, 127.4, 126.8, 121.9, 121.5, 114.0, 29.7; IR (KBr, cm^{-1}) 1635, 1587; LRMS (EI, 70 eV) m/z (%) 311 (M$^+$, 49), 310 (100), 267 (11).

(*E*)-2-(*N*-Methyl-*N*-phenylcarbamoyl)-1-phenylvinyl pivalate (4Aa): yellow oil; ^{1}H NMR (500 MHz) δ 7.41 (t, J = 7.5 Hz, 2H), 7.34−7.26 (m, 7H), 6.01 (s, 1H), 3.34 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (125 MHz) δ 175.7, 163.9, 153.9, 143.7, 134.6, 129.8, 129.5, 128.5, 127.3, 127.0, 126.8, 125.5, 108.6, 39.2, 36.9, 27.2; IR (KBr, cm^{-1}) 1752, 1667, 1630; LRMS (EI, 70 eV) m/z (%) 252 (M$^+$ − PivO, 10), 236 (48), 43 (100); HRMS (EI) for $C_{21}H_{23}NO_3$ (M$^+$) calcd 337.1678, found 337.1676.

Typical Experimental Procedure for the Pd(OAc)$_2$-Catalyzed Selective 5-*exo-dig* Diarylation in the Absence of PivOH. A mixture of aniline **1** (0.2 mmol), arene **2** (60 equiv), Pd(OAc)$_2$ (5 mol %), PPh_3 (10 mol %), and AgOAc (3 equiv) was stirred in a Schlenk tube at 140 °C for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was poured into diethyl ether, which was washed with brine. The aqueous layer was extracted with diethyl ether and the combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the product **5**.

1-Methyl-3-(diphenylmethylene)indolin-2-one (5Aa):[5] yellow solid; ^{1}H NMR (500 MHz) δ 7.44−7.42 (m, 3H), 7.40−7.32 (m, 7H), 7.17 (t, J = 8.0 Hz, 1H), 6.77 (d, J = 7.5 Hz, 1H), 6.68 (t, J = 7.5 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (125 MHz) δ 166.8, 154.6, 143.3, 141.3, 140.0, 130.0, 129.3, 129.2, 129.1, 128.9, 128.8, 128.5, 127.8, 123.3, 123.2, 121.4, 107.7, 25.9; LRMS (EI, 70 eV) m/z (%) 310 (M$^+$ − 1, 100).

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Supporting Information Available: General experimental procedures, compounds characterization data for **3**, **4**, **5**, and **6**, and copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.