C–H Activation

International Edition: DOI: 10.1002/anie.201506397
German Edition: DOI: 10.1002/ange.201506397

Ortho C–H Acylation of Aryl Iodides by Palladium/Norbornene Catalysis

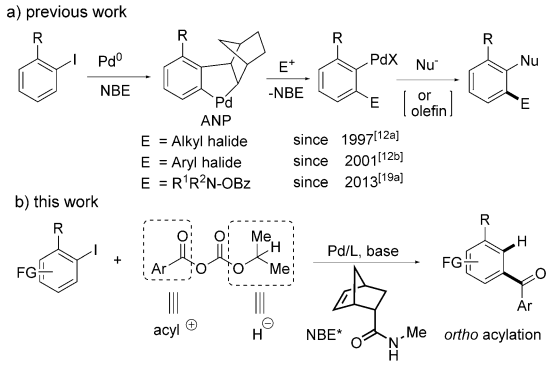
*Zhe Dong, Jianchun Wang, Zhi Ren, and Guangbin Dong**

Dedicated to Professor Stephen L. Buchwald on the occasion of his 60th birthday

Abstract: *Reported herein is a palladium/norbornene-catalyzed ortho-arene acylation of aryl iodides by a Catellani-type C–H functionalization. This transformation is enabled by isopropyl carbonate anhydrides, which serve as both an acyl cation equivalent and a hydride source.*

Aromatic ketones are widely found in pharmaceuticals,[1] agrochemicals,[2] organic electrons,[3] and polymers.[4] They have also been frequently utilized as dyes,[5] photolabels,[6] and photosensitizers.[4a,7] Further transformation of the carbonyl group provides a generic entry to compounds containing a benzylic functionality. Conventionally, aryl ketones are synthesized by the Friedel–Crafts acylation[8] of arenes using strong Lewis acids. Generally, the site selectivity is dominated by the electronic preference of the substrates. Addition of aryl nucleophiles to carbonyl compounds[9] and carbonylative cross-couplings[10] represent two effective methods to prepare aryl ketones from prefunctionalized arenes (e.g. aryl halides) to give *ipso*-substituted products. Transition-metal-catalyzed arene C–H activation/acylation offers a distinct approach, but use of a directing group[11] is usually critical. Given the wide availability of aryl halides, here, a complementary strategy for aryl ketone synthesis was sought through introducing an acyl group to the *ortho*-position of iodoarenes by using palladium/norbornene (NBE) catalysis.

The Pd/NBE chemistry, originally discovered by Catellani et al.,[12] allows activation of both the *ipso* and *ortho*-positions of arenes with aryl halides as substrates (Scheme 1a).[12c–e,13] This reaction is initiated by palladium(0) oxidative addition to the Ar–X bond[14] and subsequent NBE-mediated vicinal C–H metalation to generate a unique electron-rich aryl/NBE palladacycle (ANP),[15] which can react with an electrophile to introduce a functional group (FG) at the *ortho*-position (Figure 1).[16] Subsequent de-insertion of NBE through β-carbon elimination gives back an aryl palladium (Ar-Pd-X) species (**G**), which can then be trapped by a nucleophile (or an olefin) to furnish the *ipso* functionalization and regenerate the palladium(0) catalyst.[12a] Seminal work by the groups of Catellani and Lautens[12a,b,17] showed that a variety of FGs can be installed at the *ipso*-carbon atom by choosing different nucleophiles. However, functionalization at the *ortho*-position was previously restricted to alkylation and arylation.[12a,18] Recently, *ortho* amination was realized by using benzoyloxyamines as the reagent.[19] Nevertheless, introduction of other FGs at the *ortho*-position remains challenging, mainly because of the difficulty of selective oxidation of the ANP intermediate versus the initial palladium(0) catalyst.



Scheme 1. Palladium/norbornene catalysis. Bz = benzoyl, FG = functional group.

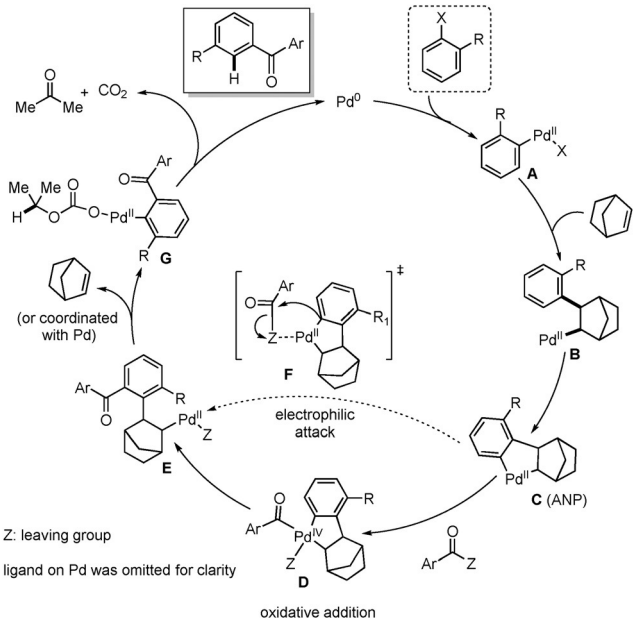


Figure 1. Proposed catalytic cycle.

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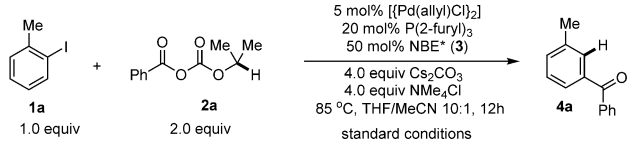
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201506397.

We hypothesized that a properly masked acyl cation could selectively react with the electron-rich ANP intermediate to form the *ortho* aryl–acyl bond through either a palladium(IV) intermediate or direct electrophilic substitution (Figure 1). In the presence of a suitable hydride source, hydrogen would be introduced at the *ipso*-position to complete the *ortho* acylation. Meanwhile, palladium(0) would be regenerated. To examine this hypothesis, benzoyl chloride and anhydride were employed as the initial acyl source, and isopropyl alcohol was used as the hydride source because of our previous success with this reductant.[19a] Not surprisingly, this combination in the presence of a base led to severe esterification without producing any desired *ortho*-acylation product.[20] A survey of other common hydride sources, such as formate salts,[17e] alkyl boronic acids,[21] and tributyltin hydride, was unfruitful. Thus, in contrast to the previous reductive *ortho*-amination reaction,[19a] the compatibility between the acyl electrophile and the reductant became a new challenge. The key was to produce the hydride for palladium in the absence of alcohol nucleophiles.

To address the aforementioned challenge, a unique isopropyl carbonate anhydride (**2a**; see Table 1), available in one step from the corresponding carboxylic acid,[22] was sought as a bifunctional reagent. The expected benefits are twofold: 1) the isopropoxide was masked in the form of a carbonate, thus minimizing the esterification side reaction; 2) the reagent contains both the acyl electrophile and hydride source in a single molecule, thus the operation is simplified. Indeed, by using **2a** as the coupling partner, the desired *ortho*-acylation product **4a** can be obtained in up to 76% yield when using [{Pd(allyl)Cl}$_2$] and tri(2-furyl)phosphine as the metal/ligand combination (Table 1; entry 1). A series of control experiments indicated that the palladium, phosphine ligand,[17b] NBE, and base were all essential for this transformation (entries 2–4 and 6). While a simple NBE can promote the desired transformation (entry 5), use of the amide-substituted NBE **3** (NBE*; for structure see Scheme 1) was found to give an enhanced yield, and importantly ease of isolation of the desired product from NBE-containing byproducts.[23] The use of NMe_4Cl as an additive is not critical (entry 7), but was found to be beneficial to reduce side reactions involving reduction of the ANP intermediate.[24] Among all the phosphine ligands tested, the more-electron-deficient tri(2-furyl)phosphine gave the optimal results (entry 9).[17b] Use of potassium carbonate as a base dramatically decreased the yield (entry 10). Addition of acetonitrile as a minor cosolvent was expected to assist de-chelation of the ketone carbonyl from the palladium intermediate; in pure THF the yield was lower[25] (entry 11). Finally, the reaction can still proceed at 60 °C albeit requiring a longer reaction time (entry 12).

The scope of the aryl iodides was examined first (Table 2). Gratifyingly, aryl iodides with various electron properties reacted well to afford the *meta*-substituted aryl ketones.[26] When electron-deficient aryl iodides were used, additional benzoyl anhydride and a lower reaction temperature were required to prevent homodimerization.[12b] Moreover, reactions with these substrates gave higher yields in the absence of

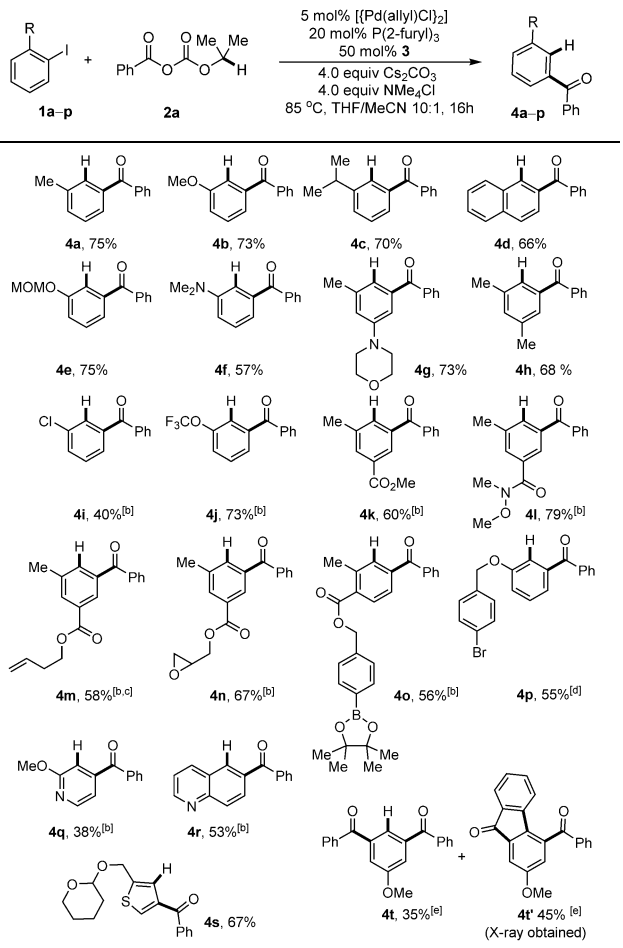
Table 1: Control experiments for *ortho* acylation.



Entry	Change from the stanard reaction conditions	Yield [%][a]
1	none	76
2	no [{Pd(allyl)Cl}$_2$]	0
3	no P(2-furyl)$_3$	0
4	no **3**	0
5	norbornene instead of **3**	73
6	no Cs_2CO_3	0
7	no NMe_4Cl	60
8	$Pd(OAc)_2$ instead of [{Pd(allyl)Cl}$_2$]	69
9	PPh_3 instead of P(2-furyl)$_3$	28
10	K_2CO_3 instead of Cs_2CO_3	12
11	Pure THF as solvent	63
12	60 °C[b]	56

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [b] Run for 40 h. THF = tetrahydrofuran.

Table 2: Substrate scope with different aryl iodides.[a]

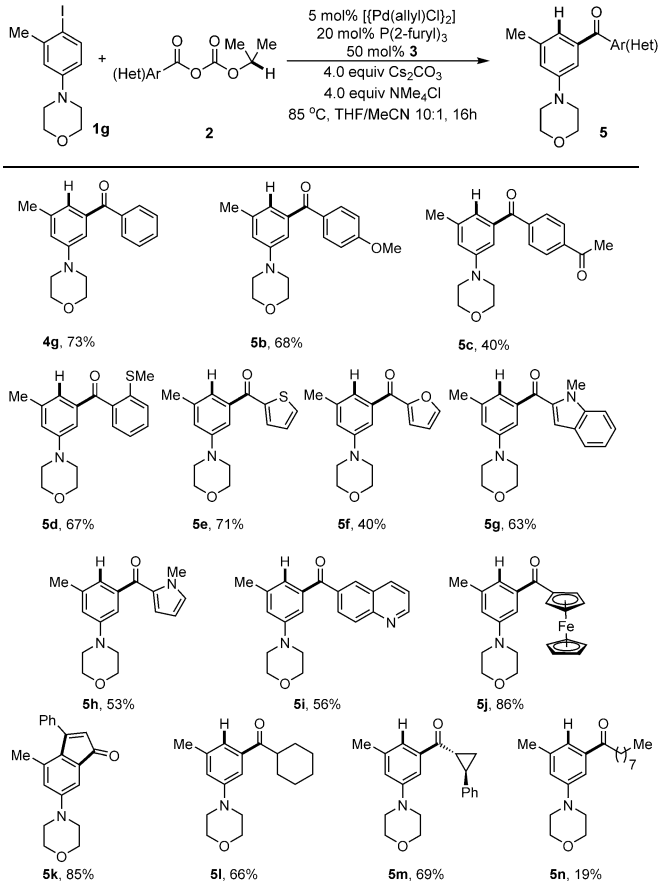


[a] All yields are those for isolated products. [b] 70 °C for 20 h without CH_3CN and NMe_4Cl; 1.5 equiv of **2a** and 2.0 equiv of Bz_2O were used. [c] 1.0 equiv of NBE* **3** was used. [d] 2.0 equiv of Bz_2O and 1.05 equiv of $ClCO_2iPr$ were used instead of **2a** and NMe_4Cl. [e] 1.5 equiv of **2a** and 2.0 equiv of Bz_2O were used. MOM = methoxymethyl.

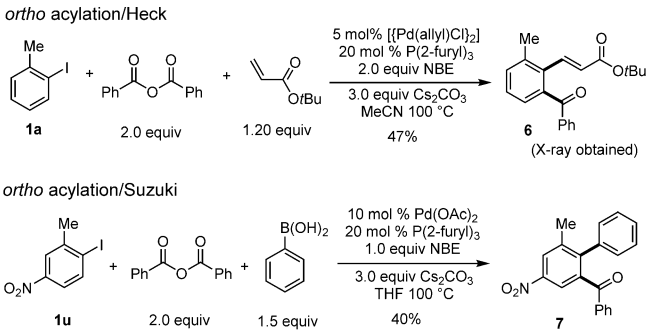
acetonitrile. Excellent functional-group tolerance was observed: methyl, benzyl, and trifluoromethyl ethers, MOM-protected phenols, tertiary amines, THP-protected alcohols, esters aryl chlorides and bromides, Weinreb amides, terminal olefins, epoxides, and arylboronic acid pinacol esters were all tolerated. Furthermore, heteroaryl iodides such as pyridine, thiophene, and quinoline derivatives (**4q–s**), were also suitable substrates, thus implying a good potential for pharmaceutical applications. For non-*ortho*-substituted aryl iodides (e.g **4t**), double *ortho* acylation was predominant, thus giving 1,3-diacylated arenes. Interestingly, a tandem cyclization product (**4t′**) was also isolated in this case, thus giving a 9-fluorenone derivative.

Next, the scope of anhydrides was explored (Table 3). A variety of isopropyl carbonate anhydrides were prepared rapidly in a single step from the corresponding carboxylic acids and commercially available isopropyl chloroformate. Both electron-rich and electron-deficient aryl anhydrides worked under the standard reaction conditions. Enolizable methyl ketones and *ortho* thioethers are compatible. Anhydrides derived from heteroarenes, such as thiophene, furan, *N*-methyl indole, pyrrole, quinoline, and ferrocene, all successfully coupled in moderate to good yields. Surprisingly, the alkenyl anhydride preferred to give a cyclized product (**5k**), although the reason is unclear. The alkyl carboxylic acid derivatives also afforded the desired acylation products **5l–n**.

Table 3: Substrate scope with carbonate anhydrides.[a]



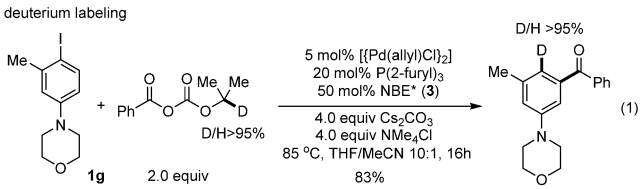
[a] All yields are those for isolated products.



Scheme 2. Coupling with *ipso* functionalization.

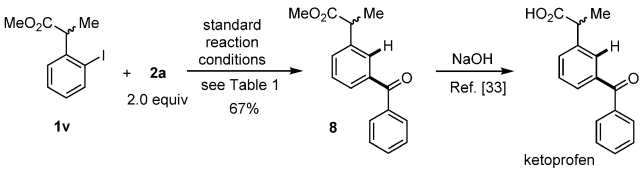
To further explore the reaction scope, we found that functional groups other than hydrogen can also be introduced at the *ipso* position, and is analogous to the standard Pd/NBE catalysis (Scheme 2). Preliminary studies indicated that the *ortho*-acylation reaction can be coupled with either a Heck or Suzuki reaction to install a vinyl or aryl group, respectively, in a position vicinal to the acyl group.[27] Note that, while the aryl-B(pin) moiety is intact under the reaction conditions (Table 2, **4o**), aryl boric acids can be effectively coupled.[17a,28]

To gain mechanistic insights of this reaction, a deuterium-labeling study was performed [Eq. (1)]. When the monodeuterated **2a** was synthesized and tested under the standard reaction conditions, more than 95% deuterium was incorporated at the *ipso*-position, and thus strongly supports the proposed hydride-transfer pathway (Figure 1). Notably, the monodeuterated product is difficult to access by classical C–H activation.



Finally, the synthetic utility of this method is demonstrated in the concise synthesis of ketoprofen (sold in a racemic form),[29] which is a nonsteroidal anti-inflammatory drug for relieving arthritis-related inflammatory pains or severe toothaches. Starting with readily available iodoarene **1v**,[30] reductive *ortho* acylation followed by hydrolysis[31] offered a distinct and efficient strategy to access ketoprofen (Scheme 3).

In summary, we have developed a reductive *ortho*-acylation method for a wide range of aryl iodides using Pd/NBE catalysis. This transformation introduces an acyl group and a hydrogen atom at the *ortho*- and *ipso*-positions, respectively, and is enabled by a bifunctional carbonate anhydride. Broad functional-group tolerance was observed, and various heterocycles were found to be suitable. We expect this mode of reactivity could potentially be generalized, thus allowing other related *ortho* functionalizations or *ortho*/*ipso*



Scheme 3. A synthetic application.

difunctionalization. Efforts towards expanding the reaction scope and detailed mechanistic studies to understand the C–C bond-formation step are underway.

Acknowledgements

We thank the CPRIT, Frasche Foundation, and Welch Foundation (F-1781) for funding. G.D. is a Searle Scholar and Sloan Fellow. Dr. Michael Young is acknowledged for X-ray crystallography and proofreading the manuscript. We thank Lin Deng for checking experiments. Johnson Matthey is thanked for a donation of palladium salts.

Keywords: acylation · arenes · C–H activation · heterocycles · palladium

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12664–12668
Angew. Chem. **2015**, *127*, 12855–12859

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Received: July 11, 2015
Published online: September 1, 2015

