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Palladium-catalyzed non-directed C−H benzoxylation of simple arenes with iodobenzene dibenzoates

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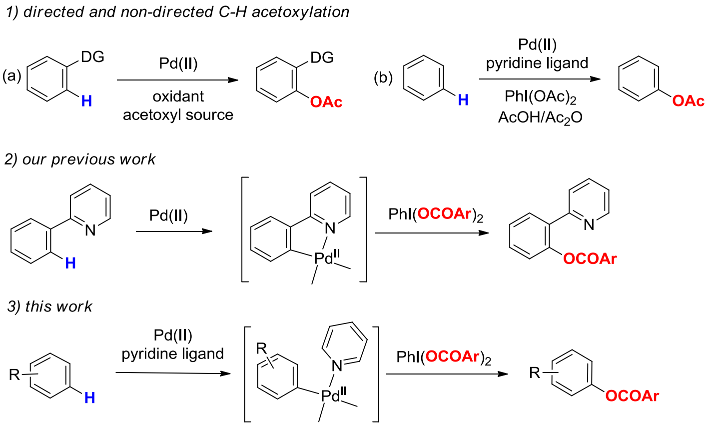
ABSTRACT

A palladium-catalyzed non-directed C–H benzoxylation of simple arenes with iodobenzene dibenzoates as both benzoxylate source and oxidant has been developed. The catalytic system was greatly promoted by a pyridine ligand. Good functional groups tolerance was showed in both hypervalent iodine reagents and arene substrates, which can be used for synthesis of aryl benzoates through simple aromatic compounds.

1. Introduction

During the past decade, transition-metal-catalyzed C–H bond functionalization has emerged as a powerful tool for organic synthesis. Significant progress have been approached in the development of transition-metal-catalyzed directing group-assisted *ortho*-functionalization of aromatic C–H bond.[1] Various directing groups were developed and employed in the vast majority of C–H bond functionalizations for promoting both the reactivity and selectivity.[2] However, it also became a main limitation of these methods as normally additional introduction and removal procedures of the directing groups were necessary. The development of transition-metal-catalyzed non-directed C–H bond functionalization, which avoids prefunctionalization of substrates and shows great atom economy, is highly desired.[3]

Among the C–H bond functionalizations, C–O bond formation especially acyloxylation has attracted considerable attention as the important role of ester functionality in natural products, pharmaceuticals, and functional materials.[4] In recent years, significant efforts have been made towards the transition-metal-catalyzed aromatic C–H acetoxylation with different directing groups (Scheme 1, (1a)).[5] However, the direct C–H acetoxylation of simple arenes still remained as a challenge. In 1996, a pioneering work by Crabtree showed the palladium-catalyzed C–H acetoxylation of arenes with $PhI(OAc)_2$ as oxidant although both the reactivity and selectivity was far from satisfying.[6] Until recently, Sanford discovered that pyridine ligand can promote the palladium-catalyzed C–H acetoxylation of arenes which could achieve high reactivity and controlling of the site-selectivity (Scheme 1, (1b)).[7–9] Nevertheless, most of previous research on C–H bond acyloxylation is focus on acetoxylation, the benzoxylation of C–H bond is less developed, although aryl benzoates are also important structures which can be found in



Scheme 1. Transition-metal-catalyzed C−H acyloxylation

[†] These authors contributed equally

∗ Corresponding author. Tel.: +86 27 59750460; fax: +86 27 59750482; E-mail:dongli@mail.hbut.edu.cn many natural products.[10] A number of methods were reported recently for transition-metal catalyzed directing group-assissted *ortho*-C–H benzoxylation with various benzoxy surrogates and external oxidants.[11] An only example of non-directed C–H benzoxylation of simple arenes was reported by Liu in 2015 under palladium catalysis with benzoic acids and iodosobenzene as oxidant however long reaction time was neccessay and only electron rich arenes can be employed.[12]

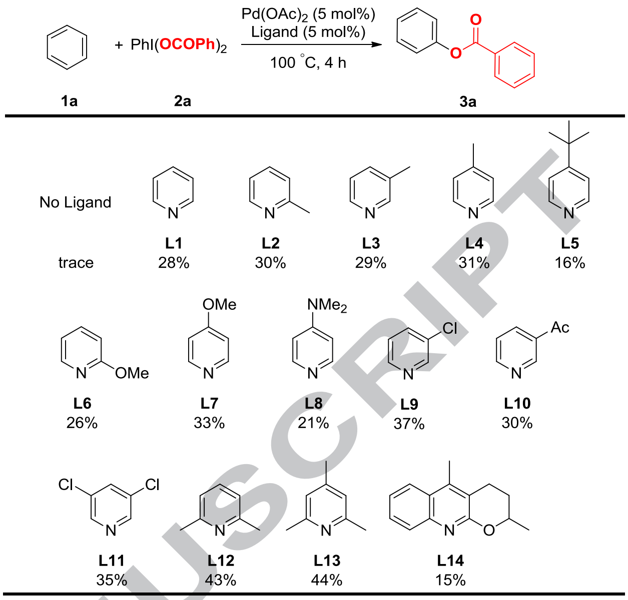
In 2015 our group reported a facile and efficient palladium-catalyzed *ortho*-benzoxylation of 2-arylpyridines with iodobenzene dibenzoates as both benzoxylate source and oxidant (Scheme 1, (2)).[13] The use of iodobenzene dibenzoates avoided employment of independent acyloxylate source and oxidant. It also demonstrated prior reactivity to acetoxylation under the standard conditions. Inspired by this work and previous study,[7] we envisioned pyridine could also act as independent ligand to promote the palladium-catalyzed C–H benzoxylation of simple arenes (Scheme 1, (3)). The behavior of iodobenzene dibenzoates in this reaction comparing with acetoxylation was also worth to be studied.

2. Results and discussion

In initial study, the reaction between benzene (**1a**) and iodobenzene dibenzoate (**2a**) with $Pd(OAc)_2$ under 100 °C showed poor reactivity (Table 1). However, when pyridine (**L1**) was added as the ligand, 28% yield of benzoxylation product **3a** was detected. We subsequently examined various commercial available pyridine derivatives as shown in Table 1 (**L2**–**L13**). Most mono-substituted pyridines which possessed a methyl-, methoxyl-, *N*,*N*-dimethylamino-, chloro- or acetyl group provided comparable product yield (26–37%), among which the 4-chloropyridine (**L9**) gave the best result. However the use of a steric bulky ligand 4-*tert*-butylpyridine (**L5**) lead to a decreased yield. No significant electronic effect was observed through these results however steric factor might be more effective. Muti-substituted pyridines were also investigated. To our delight, although 3,5-dichloropyridine (**L11**) didn't generate better result, 2,4-dimethylpyridine (**L12**) and 2,4,6-trimethylpyridine (**L13**) improved the product yield to 43% and 44% respectively. Another special pyridine analog ligand **L14** which has shown particular efficiency in various Pd-catalyzed C–H functionalization[14] was also examined but unfortunately it was not suitable in this reaction.

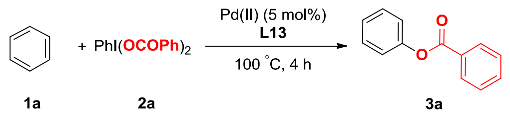
Further optimization was carried out by using 2,4,6-trimethylpyridine (**L13**) as the ligand (Table 2). Other Pd(II) catalysts were subsequently examined. Although $PdCl_2$ and $Pd_2(dba)_3$ didn't provide better result than $Pd(OAc)_2$ (Table 2, entries 1 and 2), 53% product was generated when $Pd(OCOCF_3)_2$ was used (entry 3). Effect of concentration was checked by altering the amount of benzene. Diluted reaction resulted in a slightly lower product yield (entry 4) however more concentrated condition was not favorable which lead to a great yield decreasing (entry 5). The Pd/ligand ratio was also investigated. Changing the ratio from 1:1 to 1.5:1 or 1:1.5 resulted in lower product yields. Further alteration such as Pd/ligand 2:1 drastically decreased the reactivity while the 1:2 combination even resulted in almost no reaction (entries 6–9). The 1:1 Pd/ligand ratio was necessary for high efficiency because it would generate a coordinatively unsaturated Pd-pyridine species which is essential for the subsequently C–H bond activation. This outcome was coincident with Sanford's previous study.[7] Finally, we found further improvement could be achieved by increasing the catalyst loading to 10 or 15 mol%, which provide 58 and 60% yield of product respectively (entries 10 and 11).

Table 1. Ligand Screening[a, b]



[a]Reaction conditions: $Pd(OAc)_2$ (5 mol%), ligand (5 mol%), iodobenzene dibenzoate (**2a**) (0.5 mmol) in benzene (**1a**) (1.0 mL) stirring at 100 ºC for 4 h. [b]GC yield by using $PhNO_2$ as an internal standard.

Table 2. Optimization of the reaction conditions[a]



Entry	Pd(II)	Pd/ Ligand	Benzene (mL)	Yield (%)[b]
1	$PdCl_2$	1/1	1	29
2	$Pd_2(dba)_3$	1/1	1	19
3	$Pd(OCOCF_3)_2$	1/1	1	53
4	$Pd(OCOCF_3)_2$	1/1	2	50
5	$Pd(OCOCF_3)_2$	1/1	0.5	13
6	$Pd(OCOCF_3)_2$	1.5/1	1	48
7	$Pd(OCOCF_3)_2$	1/1.5	1	40
8	$Pd(OCOCF_3)_2$	2/1	1	14
9	$Pd(OCOCF_3)_2$	1/2	1	<5
10[c]	$Pd(OCOCF_3)_2$	1/1	1	58
11[d]	$Pd(OCOCF_3)_2$	1/1	1	60

[a]Reaction conditions: Pd(II) (5 mol%), **L13**, iodobenzene dibenzoate (**2a**) (0.5 mmol) in benzene (**1a**) stirring at 100 ºC for 4 h. [b]GC yield by using $PhNO_2$ as an internal standard. [c]With 10 mol% $Pd(OCOCF_3)_2$. [d]With 15 mol% $Pd(OCOCF_3)_2$.

A preliminary kinetic study was carried out for illustrate the reaction rate as shown in Figure 1. With 5 mol% $Pd(OCOCF_3)_2$/**L13**, the reaction proceeded relatively fast during the first 2 hours and almost completed after 4 hours. Compare with the previous acetoxylation with same catalyst loading,[7] it demonstrated similar reaction rate however reached the equilibrium at a lower product yield.

The benzoxylation of benzene (**1a**) with various iodobenzene dibenzoate derivatives (**2**) were investigated under the optimized conditions as shown in Table 3. Both electron-donating functional groups such as OMe and Me and electron-withdrawing functional groups such as F, Cl, Br and NO_2 was tolerated on the benzoyl ring, affording the corresponding benzoxylation products in moderate to good yields.

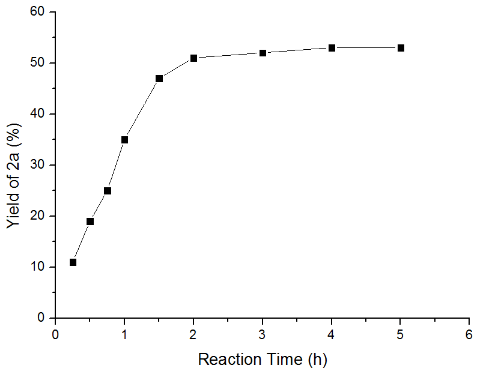
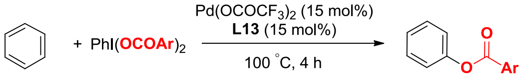
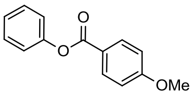
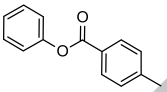
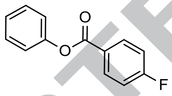
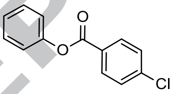
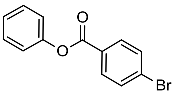
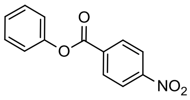


Figure 1. Plot of reaction rate of bezene benzoxylation. Reaction conditions: $Pd(OCOCF_3)_2$ (5 mol%), **L13** (5 mol%), iodobenzene dibenzoate (**2a**) (0.5 mmol) in benzene (**1a**) (1.0 mL) stirring at 100 ºC for 4 h. Yields determined by GC.

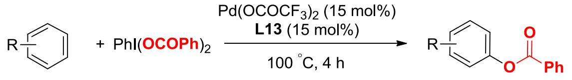
Table 3. The palladium-catalyzed benzoxylation of bezene[a]

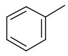
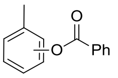
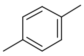
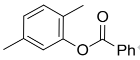
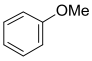
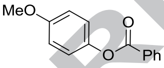
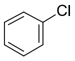
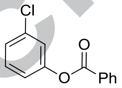
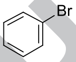
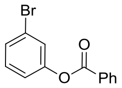
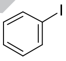
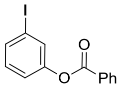
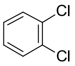
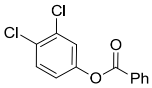
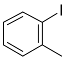
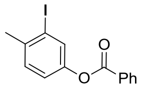
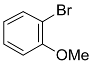
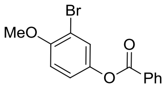


Entry	Ar	Product	Yield (%)[b]
1	4-OMe-C_6H_4 (**2b**)	 (**3b**)	68
2	4-CH_3-C_6H_4 (**2c**)	 (**3c**)	46
3	4-F-C_6H_4 (**2d**)	 (**3d**)	73
4	4-Cl-C_6H_4 (**2e**)	 (**3e**)	52
5	4-Br-C_6H_4 (**2f**)	 (**3f**)	41
6	4-NO_2-C_6H_4 (**2g**)	 (**3g**)	55

[a]Reaction conditions: $Pd(OCOCF_3)_2$ (5 mol%), **L13** (5 mol%), **2** (0.5 mmol) in **1a** (1.0 mL) stirring at 100 ºC for 4 h. [b]GC yield by using $PhNO_2$ as an internal standard.

Table 3. The palladium-catalyzed benzoxylation of arenes[a]



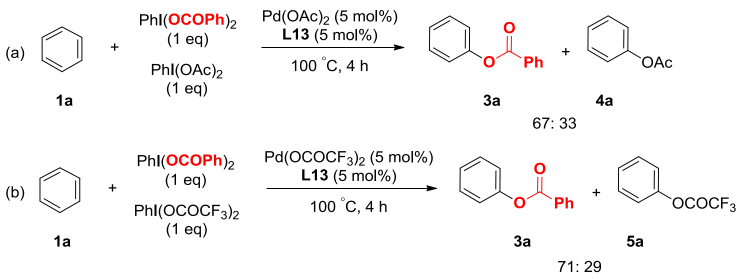
Entry	Substrate	Product	Yield (%)[b]
1	 (**1b**)	 (**3h**)	60 (*o*/*p*=52:48)
2	 (**1c**)	 (**3i**)	40
3	 (**1d**)	 (**3j**)	32
4	 (**1e**)	 (**3k**)	50
5	 (**1f**)	 (**3l**)	68
6	 (**1g**)	 (**3m**)	56
7	 (**1h**)	 (**3n**)	46
8	 (**1i**)	 (**3o**)	43
9	 (**1j**)	 (**3p**)	33

[a]Reaction conditions: $Pd(OCOCF_3)_2$ (5 mol%), **L13** (5 mol%), iodobenzene dibenzoate (**2a**) (0.5 mmol) in **1** (1.0 mL) stirring at 100 ºC for 4 h. [b]GC yield by using $PhNO_2$ as an internal standard.

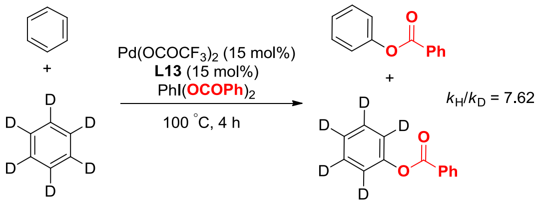
This method can also be applied for benzoxylation of other arenes (**1**) as shown in Table 4. Various electron-rich or electron-deficient arenes can be benzoxylated under the standard conditions. Generally, the electron-deficient arenes such as chlorobenzene (**1e**), bromobenzene (**1f**), iodobenzene (**1g**) and dichlorobenzene (**1h**) gave higher yields (46–68%) than electron-rich arenes such as toluene (**1b**), *p*-xylene (**1c**) and anisole (**1d**) (32–60%). The reaction of toluene gave a nearly 1:1 ratio mixture *ortho*- and *para*-benzoxylation product (entry 1). However, anisole reacted to generate mainly *para*-benzoxylation product in lower yield (entry 3). The reaction of electron-deficient arenes showed better site-selectivity, providing the *meta*-benzoxylation product in moderate to good yields (entries 4–7). Other disubstituted arenes with different type of substituents such as 2-methyl-iodobenzene (**1i**) and 2-methoxyl-bromobenze (**1j**) were also applicable for the C–H benzoxylation and gave the desired products in lower yield but good site-selectivity (entries 8 and 9).

The reaction mechanism was subsequently investigated through intermolecular KIE study (Scheme 2). By using 1:1 ratio of benzene and d_6-benzene as the substrates, the KIE was determined to be 7.62, which implied that the C−H bond activation was involved in the rate-determining step (RDS).

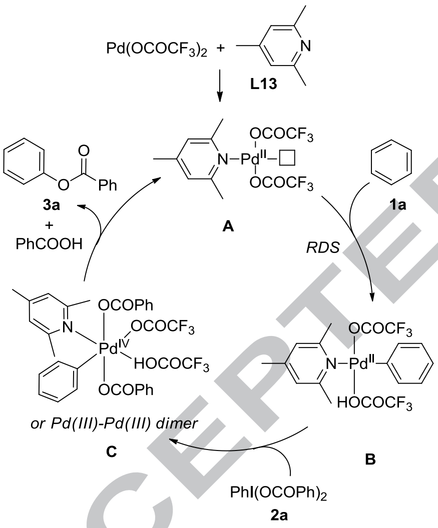
Based on the above study and previous reports,[7, 8, 13] a plausible mechanism for the pyridine ligand-assisted palladium-catalyzed non-directed C−H benzoxylation of arenes with



Scheme 4. Control experiments



Scheme 2. Intermolecular KIE study



Scheme 3. Proposed mechanism of the Pd-catalyzed C−H benzoxylation of benzene

iodobenzene dibenzoate (**2a**) was proposed in Scheme 3. Initially, the pyridine interacted with Pd(OCOCF$_3$)$_2$ to form a pyridine-ligated Pd(II) species **A**, which was coordinated unsaturated and subsquently activated the benzene C–H bond to form a σ-aryl Pd(II) complex **B**. Then complex **B** was oxidized by iodobenzene dibenzoate (**2a**) to generate an Pd(IV) benzoate complex **C** (or bimetallic Pd(III)-Pd(III) complex).[15] Finally, reductive elimination of intermediate **C** afforded the benzoxylation product **3a** rather than acetoxylation and regenerated the palladium(II) species.

Finally, some control experiments were carried out to illustrate the reaction mechanism. The pyridine-assisted Pd(OAc)$_2$ catalyzed reaction of benzene with same equivalent PhI(OCOPh)$_2$ and PhI(OAc)$_2$ generated the benzoxylation and acetoxylation product in a 67:33 ratio (Scheme 4a). While the Pd(OCOCF$_3$)$_2$ catalyzed reaction of benzene with same equivalent PhI(OCOPh)$_2$ and PhI(OCOCF$_3$)$_2$ generated the benzoxylation and acetoxylation product in a slightly higher ratio 71:29 (Scheme 4b). These results proved that in the reductive elimination step benzoxylation was more favored than acetoxylation. Moreover, it also explained why Pd(OCOCF$_3$)$_2$ was slightly more efficient than Pd(OAc)$_2$ in this method.

3. Conclusions

In conclusion, we have developed a palladium-catalyzed non-directed C–H benzoxylation of simple arenes using iodobenzene dibenzoates as both benzoxylate source and oxidant which made the protocol simple and facile. Pyridine ligand-assisting strategy was used which greatly promoted the reactivity. Good functional groups tolerance was showed in both hypervalent iodine and arene substrates. It would provide a new methodology for synthesis of aryl benzoates through simple aromatic compounds. Preliminary mechanistic study was also carried out and a plausible mechanism was proposed.

Acknowledgments

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Supplementary Material

Supplementary data associated with this article can be found, in the online version, at doi:

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Graphical Abstract

Palladium-catalyzed non-directed C−H benzoxylation of simple arenes with iodobenzene dibenzoates

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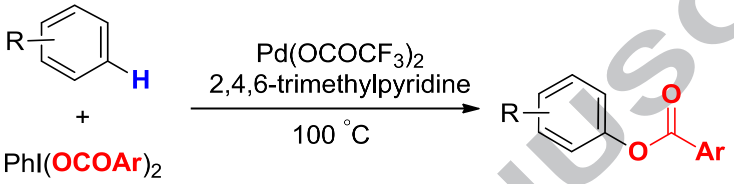

Highlights

- ► A palladium-catalyzed non-directed C–H benzoxylation of simple arenes is developed.
- ► Hypervalent iodine reagent iobenzene dibenzoates was used as both benzoxylate source and oxidant.
- ► Pyridine ligand-assisting strategy was used which greatly promoted the reactivity
- ► Good functional groups tolerance was showed in both hypervalent iodine and arene substrates.