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Ambient-Temperature Ortho C−H Arylation of Benzoic Acids with Aryl Iodides with Ligand-Supported Palladium Catalyst

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Supporting Information

ABSTRACT: The ambient-temperature ortho C−H arylation of electron-deficient benzoic acids with aryl iodides has been achieved by using an Ac-Ile-OH-supported Pd catalyst. A wide range of unactivated benzoic acids could cross-couple an array of aryl iodides in moderate to excellent yields. The choice of HFIP as a solvent is crucial to realizing the mild C−H arylation, and the beneficial effect of the ligand on the reaction likely stems from the accelerated C−H activation process and the improved catalyst lifetime.

Over 20 years of efforts has led to great progress in the development of metal-catalyzed direct C−H functionalization.[1] As a result of the high dissociation energies of the breaking C−H bonds, the vast majority of these established reactions occur at high temperatures (often above 100 °C). As is well-known, mild reaction conditions such as ambient-temperature reactions are very beneficial to reaction selectivity control and functional group tolerance. In the context of mild C−H functionalization reactions,[1c,2−6] Fujiwara and co-workers reported the first example of mild C−H functionalization reactions in 1995.[2] Since this pioneering work, several elegant studies demonstrated that the in situ generation of electron-deficient metal−catalyst intermediates by using an acid as a solvent or an additive[3] or by abstracting anionic ligand from a metal−catalyst precursor[4a−g,i,l] was an effective strategy to achieve mild C−H functionalization reactions. The C−H transformations involving oxidation of the metal−catalyst to high-oxidation-state intermediates were shown to allow C−H functionalization to occur under mild conditions.[5] In these transformations, the high-oxidation-state metal−catalyst intermediates favor the C−H bond metalation step and also the subsequent reductive elimination step of new bond formations,[5b,d] especially when the reductive elimination has difficulty in proceeding. Despite the significant advances, mild C−H functionalization reactions are mainly limited to specific substrates, including electron-rich aromatic heterocycles,[3b,e,f,5d,e] arenes bearing electron-donating substituents[3a,c,d,g−i,4e,5f] and arenes containing an acidic C−H bond[6] such as pyridine *N*-oxides and their analogues,[6a,b,e] and polyfluoroarenes.[6c] The achievement of mild C−H functionalization of electronically unbiased substituted arenes remains a challenge.[7] Herein, we report a ligand-supported palladium-catalyst system[8] that enables ortho C−H arylation of electron-deficient benzoic acids with aryl iodides as arylating reagents at ambient temperature in high yield and selectivity.

Owing to the inherent electron deficiency of the benzene ring of benzoic acids, activation of aromatic C−H bonds of benzoic acids is difficult at ambient temperature. To date, no example of mild C−H functionalization of benzoic acids has been reported. In fact, in view of the ready availability and great diversity of substituted benzoic acids, metal-catalyzed transformations of benzoic acids have been investigated intensely.[9−12] Yu and co-workers demonstrated that Pd-catalyzed cross-coupling of benzoic acids with organic boron reagents led to ortho C−H arylation[10a] and alkylation.[8c] Satoh and Miura achieved a series of carboxyl-directed C−H functionalization reactions of benzoic acids with various coupling partners using Pd,[11a] Rh,[11b] Ru and Ir[11c] catalysts. Daugulis[10b] and Larrosa[10d,c] independently developed the Pd-catalyzed ortho arylation of benzoic acid with aryl iodides that necessitated elevated temperatures, which led to a decrease in reaction selectivity, forming a mixture of monosubstituted and disubstituted products or protodecarboxylation side products.

The investigation of the ambient-temperature ortho C−H arylation of benzoic acids stemmed from our continuing interest in the reactivity of benzoic acids.[12] When treating benzoic acid (**1a**) with 2 equiv of 4-iodoanisole (**2a**) in the presence of 1 equiv of Ag_2CO_3 and 1 equiv of Li_2CO_3 in 1 mL of hexafluoroisopropayl alcohol (HFIP)[13] for 24 h, we were surprised to find that the ortho arylation of benzoic acid could occur at ambient temperature (30 °C), albeit in a moderate yield (entry 1, Table 1). Using other bases in place of Li_2CO_3 improved the yields (entries 2−6). Among the bases used, Cs_2CO_3 gave the best result (entry 4). Interestingly, the positive effect of alkali-metal carbonates as bases on the yields increased with an increase in cation radius (entries 1−4), which might result from the difference in solubility or in the interaction of metal ions with benzoate substrate among those tested bases.[14] Prolonging the reaction time up to 36 h had no effect on the yield (entry 7), indicating that the catalyst lost its activity after 24 h. Inspired by Yu's pioneering work on ligand-accelerated C−H activation reactions,[8] we screened a variety of monoprotected amino acid

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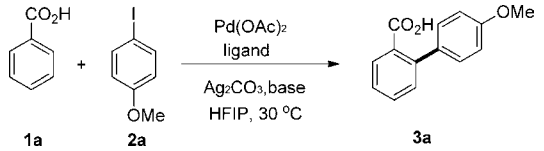
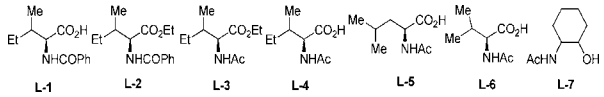
Table 1. Optimization of Pd-Catalyzed Ortho Arylation of Benzoic Acid[a]



1a 2a 3a

entry	ligand	base (amt (equiv))	time (h)	yield (%)[b]
1		Li_2CO_3 (1.0)	24	31
2		Na_2CO_3 (1.0)	24	33
3		K_2CO_3 (1.0)	24	37
4		Cs_2CO_3 (1.0)	24	44
5		Na_3PO_4 (0.5)	24	33
6		PivOCs (2.0)	24	43
7		Cs_2CO_3 (1.0)	36	45
8	**L-1**	Cs_2CO_3 (1.0)	24	65
9	**L-2**	Cs_2CO_3 (1.0)	24	48
10	**L-3**	Cs_2CO_3 (1.0)	24	55
11	**L-4**	Cs_2CO_3 (1.0)	24	71
12	**L-5**	Cs_2CO_3 (1.0)	24	62
13	**L-6**	Cs_2CO_3 (1.0)	24	56
14	**L-7**	Cs_2CO_3 (1.0)	24	51
15	**L-4**	Cs_2CO_3 (1.0)	36	95
16[c]	**L-4**	Cs_2CO_3 (1.0)	36	93
17[d]	***L-4***	***Cs_2CO_3 (0.5)***	***36***	***93***

[a]Reaction conditions unless specified otherwise: **1a** (0.20 mmol, 1 equiv), **2a** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol %), ligand (10 mol %), Ag_2CO_3 (1.0 equiv), HFIP (1.0 mL), 30 °C. Ligands:

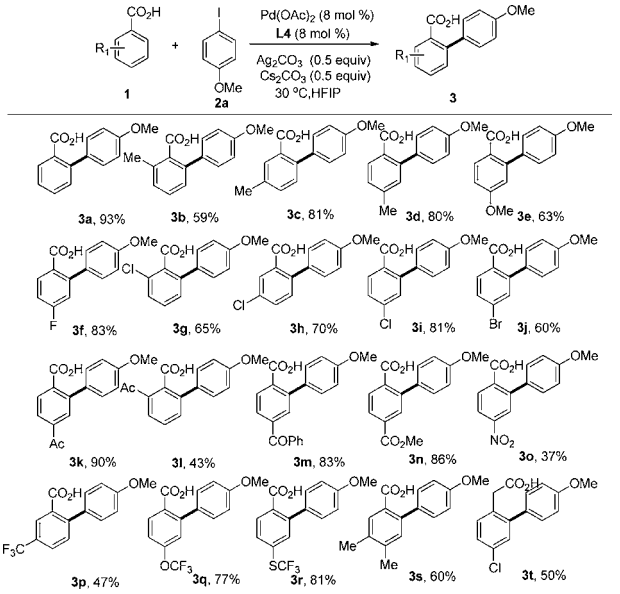


[b]Isolated yields are shown. [c]Reaction conditions: $Pd(OAc)_2$ (8 mol %), ligand (8 mol %). [d]Reaction conditions: $Pd(OAc)_2$ (8 mol %), ligand (8 mol %), Ag_2CO_3 (0.5 equiv).

ligands (MPAAs) and their analogues in the model reaction to improve the reaction yield. Gratifyingly, the use of MPAA as a ligand indeed gave increased yields (entries 8−14), and Ac-Ile-OH (**L-4**) exhibited the best performance (entry 11). Furthermore, the prolonged reaction afforded an excellent yield using 8 mol % of $Pd(OAc)_2$ and 8 mol % of **L-4** as a catalyst system (entry 16). Both Ag_2CO_3 and Cs_2CO_3 could be reduced to 0.5 equiv without compromise in yield (entry 17). The choice of HFIP as a solvent is essential to achieve this high-yielding ambient-temperature reaction, since other solvents such as AcOH, H_2O, and DMF were ineffective (see entries 17−22 in Table 1 of the Supporting Information).

The established reaction conditions were applicable to a variety of substituted benzoic acids and gave the corresponding products in moderate to excellent yield (Scheme 1). As expected, the benzoic acids containing electron-donating groups such as methyl and methoxy substituents on the ortho, meta, or para positions of the aryl moiety efficiently cross-coupled the 4-iodoanisole, producing the desired products in good to excellent yields (**3b−e**). To our delight, benzoic acids bearing electron-withdrawing groups could smoothly undergo ambient-temperature C−H arylation. These electron-withdrawing groups included halides (**3f−j**), ketones (**3k−m**), esters (**3n**), trifluoromethyl (**3p**), and even nitro (**3o**). The compatibility of halides in this reaction provided a handle for the further elaboration of ortho-arylation products. Although ketones and

Scheme 1. Scope of Benzoic Acids[a]



[a]Yields of isolated products are reported.

esters were capable of serving as directing groups for C−H functionalization under relatively mild conditions,[15] a carboxyl group overrode both esters and ketones in making the C−H arylation reaction occur exclusively at the position ortho to the carboxyl group. In addition to the electronic effect of substituents on the reaction, substituent positions were also observed to have an effect on the reaction yields, as exemplified by positional isomers of methyl-substituted benzoic acid (**3b−d**) and acetyl-substituted benzoic acid (**3k,l**). In these two sets of positional isomers, the ortho-substituted benzoic acids gave lower yields in comparison to their meta and para isomers, which might be attributed to the steric congestion from ortho substituents that influenced carboxyl-directed C−H palladation. Notably, phenylacetic acid (**1t**) could also undergo ortho arylation under mild conditions. In the process of exploring the scope of benzoic acids, we have observed that benzoic acids bearing an aryl substituent at the ortho position did not undergo ortho arylation under standard conditions, which would be the reason our reaction produced a monosubstituted product.

Next, the scope of aryl iodides was further investigated using the optimized reaction conditions (Scheme 2). Iodobenzene proved to be a highly reactive coupling partner and smoothly coupled carboxylic acids in an excellent yield (**4a**). Iodobenzenes bearing a variety of electron-donating groups such as methyl, isopropyl, and *tert*-butyl could also give excellent yields (**4b−f**). To our delight, the disubstituted iodobenzenes afforded the products in high yields (**4l−o**). The reactions of iodobenzenes bearing electron-withdrawing groups such as F, Cl, and CO_2Me required elevated temperature (50 °C) and an MPAA amount of 16 mol %, giving the corresponding products in moderate yields (**4g−j**). Unfortunately, ortho-substituted iodobenzenes gave no desired products and iodobenzenes bearing strongly electron withdrawing groups such as CF_3 and NO_2 only afforded low yields. Unlike the case for Pd-catalyzed traditional cross-coupling, electron-deficient aryl iodides showed a low reactivity in the C−H arylation reaction of benzoic acids, suggesting that our reaction may not involve the oxidative addition of aryl iodides to Pd species.

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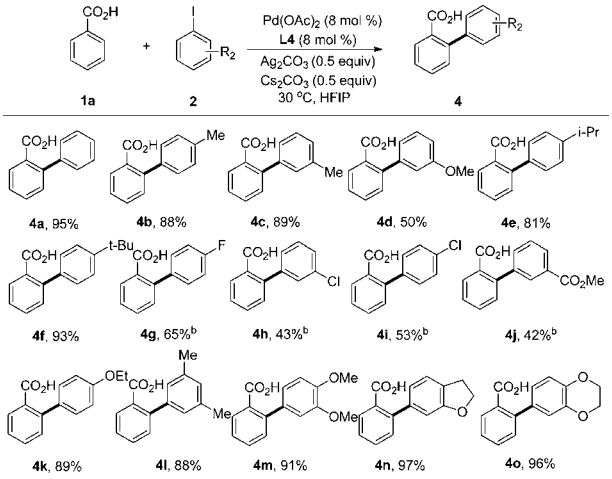
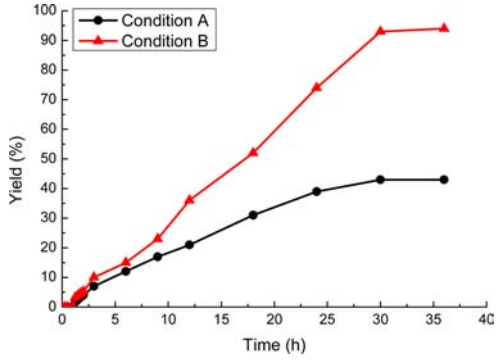
Scheme 2. Scope of Iodobenzenes[a]



[a]Yields of isolated products are reported. [b]Reaction conditions: ligand (16 mol %), Ag_2CO_3 (1.0 equiv), carried out at 50 °C.

To understand the origin of the efficiency-enhancement effect of the ligand MPAA, we investigated the kinetics of the arylation of benzoic acid in both the absence and presence of MPAA (Scheme 3). In the absence of MPAA (conditions A), the

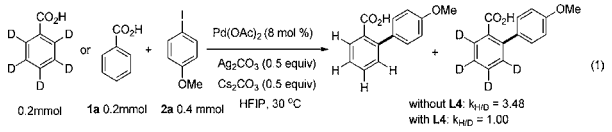
Scheme 3. Formation of Arylation Product 3a versus Reaction Time without Ligand L-4 (Conditions A) and with Ligand L-4 (Conditions B)



arylation product was no longer formed, with starting materials left after the reaction was conducted for 24 h (the black line), indicating that the Pd catalyst likely decomposed after 24 h. In contrast, with the aid of MPAA ligand (conditions B), the reaction is much faster than that without MPAA, and formation of the arylation product continued up to 95% (NMR yield) after 24 h (shown by the red line). As such, the efficiency enhancement of the ligand MPAA likely stemmed from both the accelerated reaction and the improved catalyst lifetime, consistent with a previous report by Yu and co-workers.[8a]

We measured the initial rates of the ortho-arylation reactions of benzoic acid and its deuterated analogues in both the presence and absence of the ligand **L-4** (see the Supporting Information for details) to obtain the primary kinetic isotope effect (KIE) (Scheme 4). In the absence of the ligand **L-4**, a KIE value of 3.48 was obtained by calculating the relative ratio of these independently measured initial rates, indicating that ortho C−H bond cleavage is the rate-limiting step. However, a KIE value of 1.00 was obtained in the presence of ligand **L-4**, suggesting that

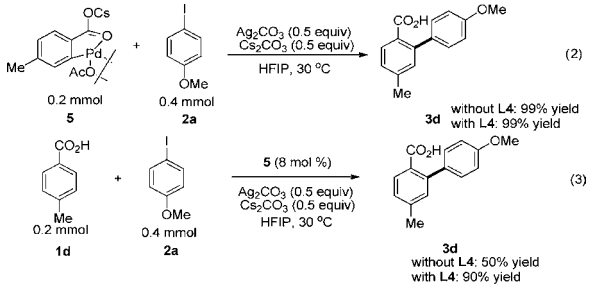
Scheme 4. KIE Measurements for the Ortho Arylation of Benzoic Acid



C−H cleavage was no longer the rate-determinating step as a result of ligand acceleration.[8a]

To investigate whether this C−H arylation of benzoic acid proceeds via a Pd-promoted C−H cleavage to form the cyclopalladated intermediate **5** (Scheme 5), we synthesized

Scheme 5. Reaction of Complex 5 and Its Catalytic Reactivity



and characterized **5** using a literature method.[16] Complex **5** reacted with **2a** in HFIP in the presence of 0.5 equiv of Ag_2CO_3 and 0.5 equiv of Cs_2CO_3 to quantitatively generate **3d** (eq 2, Scheme 5). Complexes could also serve as catalysts in place of $Pd(OAc)_2$ to effect the reaction of **1d** with **2a** in a high yield (eq 3, Scheme 5). These results implied that the cyclopalladated intermediate **5** is involved in the catalytic cycle of the current C−H arylation reaction.

In conclusion, we have developed the first the Pd-catalyzed method that enables ortho C−H arylation of the unactivated electron-deficient benzoic acids to occur at ambient temperature. This protocol exhibits a wide substrate scope and provides the arylation products in moderate to excellent yields. The use of HFIP as a solvent is the key to achieving mild C−H fuctionalization, and cesium carbonate as a base plays an important role in the improvement of the product yields. The mechanistic studies revealed that the efficiency-enhancement effect of the ligand resulted from the acceleration of the C−H activation process and the improvement in catalyst lifetime. Our ongoing work is to apply mild C−H functionalization to diverse reactions for the control of reaction selectivities.

■ ASSOCIATED CONTENT

Supporting Information

Text, a table, and figures giving experimental procedures and characterization data for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01398.

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Notes

The authors declare no competing financial interest.

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(7) To date, only a handful of benzenes bearing electron-withdrawing groups have been reported to undergo ambient-temperature C−H functionalization. For *N*-alkoxy benzamide, see refs 4a−e,g, for benzenes bearing ester or ketone groups, see refs 4k−m, and for benzenes bearing other electron-withdrawing groups, see refs 3j and 4j.

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