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Direct C–H bond arylation of 2-hydroxybenzaldehydes with arylboronic acids via ligand-free palladium catalysis

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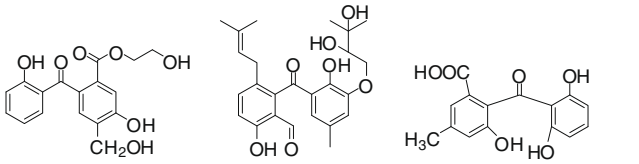
ABSTRACT

A mild and efficient ligand-free palladium-catalyzed direct C–H bond arylation reaction was developed to afford 2-hydroxybenzophenones in good to excellent yields from easily available 2-hydroxybenzaldehydes and arylboronic acids. The given reaction provided one of the easiest pathways for accessing 2-hydroxybenzophenones, and a variety of functional groups could be tolerated in this process.

Aryl ketone template is generally recognized as a privileged structure in medicinal chemistry, as exemplified by the marketing drugs such as Tricor, and important framework in organic transformations.[1] The prevalence of *ortho*-hydroxyl-substituted diaryl ketones in a large number of biologically active compounds,[2] natural products,[3] and cosmetics,[4] has resulted in a continued demand for the development of general and flexible synthetic methods of this structural moiety (Scheme 1). Therefore, many useful methods for their preparation have been developed, including transformation from *ortho*-functionalized diaryl ketones[5] or chromones,[6] acylation of benzoquinone[7] or related arenes,[8] Fries-type rearrangement,[9] addition of lithium or magnesium reagents to carboxylic derivatives,[10] and coupling reactions of nitriles with boronic acids.[11] Although these methods are effective for the synthesis of 2-hydroxybenzophenones, some of the reactions suffer from lacking atom economy,[6] incompatible with substrate scopes,[7] handling hazardous substances[8a] and harsh reaction conditions,[10], and inconvenient operation.[8a,10]

Recently, direct C–H bond arylation of aldehydes and their derivatives to give aryl ketones in a green way has attracted lot of attentions.[12] In this context, diaryl ketones have been achieved from aldehydes and organoboronic reagents[13] or aryl halides,[14] as well as obtained by arylation of *N*-*tert*-butyl-hydrazones,[15] *N*-pyrazyl[16] or pyridinyl[17] aldimines followed by hydrolysis. However, the existence of an *ortho*-hydroxyl group in aryl ketones led to main impediment in some transformations.[13g] Only few examples have been documented in the literatures involving the metal-catalyzed coupling reactions from 2-hydroxyarylaldehydes with hypervalent iodonium salts,[13a,b] boronic acids,[13c,e] or aryl halides[18] via the cleavage of the formyl C–H bond and gave 2-hydroxybenzophenones in low to moderate yields. In a program aiming at developing novel approaches for the efficient construction of heterocycles and the evaluation on their biological properties,[19] we herein reported an efficient direct aldehyde C–H bond arylation reaction via ligand-free palladium catalysis in good to high yields.



Scheme 1. Bioactive products with 2-hydroxybenzophenone moiety.

Initial study was performed by examining salicylaldehyde and phenylboronic acid in the presence of $Pd(OAc)_2$, $CuCl_2$, and Na_2CO_3 in DMF under oxygen atmosphere and the reaction afforded the product **3a** in 67% yield (Table 1, entry 1). Among various palladium sources screened (entries 1–5), $PdCl_2(PhCN)_2$ was found to give the best result (entry 5) and no product could be detected in the absence of palladium catalyst (entry 6). When the reactions were conducted with excess or without $CuCl_2$, **3a** was given in decreased yields (entries 7 and 8). A variety of organic and inorganic

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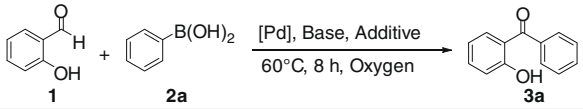
Table 1
Optimization of reaction conditions[a]



Entry	Pd source	Additive	Base	Yield[b] (%)
1	$Pd(OAc)_2$	$CuCl_2$	Na_2CO_3	67
2	$PdCl_2$	$CuCl_2$	Na_2CO_3	63
3	$PdCl_2(CH_3CN)_2$	$CuCl_2$	Na_2CO_3	65
4	$PdCl_2(PPh_3)_2$	$CuCl_2$	Na_2CO_3	54
5	$PdCl_2(PhCN)_2$	$CuCl_2$	Na_2CO_3	72
6	/	$CuCl_2$	Na_2CO_3	0
7	$PdCl_2(PhCN)_2$	$CuCl_2$	Na_2CO_3	40[c]
8	$PdCl_2(PhCN)_2$	/	Na_2CO_3	60
9	$PdCl_2(PhCN)_2$	$CuCl_2$	Et_3N	0
10	$PdCl_2(PhCN)_2$	$CuCl_2$	LiOAc	46
11	$PdCl_2(PhCN)_2$	$CuCl_2$	NaOAc	33
12	$PdCl_2(PhCN)_2$	$CuCl_2$	KOAc	17
13	$PdCl_2(PhCN)_2$	$CuCl_2$	CsOAc	43
14	$PdCl_2(PhCN)_2$	$CuCl_2$	K_3PO_4	46
15	$PdCl_2(PhCN)_2$	$CuCl_2$	K_2CO_3	56[d]
16	$PdCl_2(PhCN)_2$	$CuCl_2$	Cs_2CO_3	58
17	$PdCl_2(PhCN)_2$	$CuCl_2$	LiOH	67
18	$PdCl_2(PhCN)_2$	$CuCl_2$	NaOH	57
19	$PdCl_2(PhCN)_2$	$CuCl_2$	$NaHCO_3$	76
20	$PdCl_2(PhCN)_2$	$CuCl_2$	$NaHCO_3$	62[d]
21	**$PdCl_2(PhCN)_2$**	**$CuCl_2$**	**$NaHCO_3$**	**85[e]**
22	$PdCl_2(PhCN)_2$	$CuBr_2$	$NaHCO_3$	39
23	$PdCl_2(PhCN)_2$	$Cu(OAc)_2$	$NaHCO_3$	47
24	$PdCl_2(PhCN)_2$	$Cu(OTFA)_2$	$NaHCO_3$	47
25	$PdCl_2(PhCN)_2$	BQ	$NaHCO_3$	< 5

[a] The reaction was performed with salicylaldehyde (1.0 equiv), phenylboronic acid (1.2 equiv), palladium catalyst (5 mol %), additive (10 mol %), and base (2.0 equiv) in DMF (1 mL) for 8 h under 1 atm of O_2 on a 0.3 mmol scale. Cu(OTFA)$_2$ = cupric trifluoroacetate, BQ = *p*-benzoquinone.
[b] Isolated yields.
[c] Reaction was run under N_2 with 2.0 equiv of $CuCl_2$.
[d] Reaction was run under air.
[e] 1.7 equiv of **2a** was used.

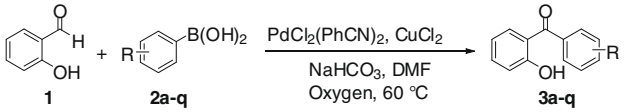
bases were tested (entries 9–19), and 76% yield of **3a** could be afforded using $NaHCO_3$ as the base (entry 19), while diminished yield was obtained under aerobic condition (entry 20). The best condition could be achieved when the amount of phenylboronic acid was increased to 1.7 equiv (entry 21). Further screening concerning oxidants which are frequently used in the palladium-catalyzed reactions gave less effective results (entries 22–25).

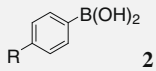
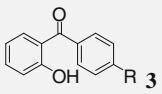
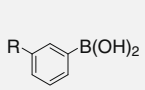
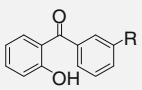
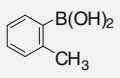
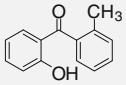
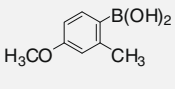
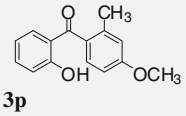
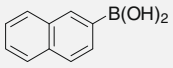
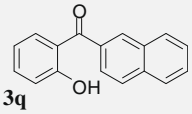
With the optimized conditions in hand, we next investigated the scope of the reaction using various arylboronic acids (Table 2). The reactions proceeded smoothly in the presence of a variety of functional groups, including benzoxyl, formyl, nitro, trifluoromethyl, and ethoxycarbonyl groups (entries 2–16). The electron-rich arylboronic acids which are usually active substrates in Suzuki reaction showed no better results than those reagents with electron-withdrawing groups (entries 3 and 4, 10 and 11). Generally, arylboronic acids with electron-deficient properties are prone to undergo homocoupling and protodeboronation side reactions. However in our case, the electron-deficient substrates could react smoothly with salicylaldehyde to give corresponding products **3e–i** (entries 5–9) and **3l–n** (entries 12–14) in good to excellent yields, respectively. It should be noted that, active formyl group attached to the boronic acid remained intact under the reaction condition (entry 14). Substrates with *ortho*-substitution gave comparatively lower yields, which may be due to the steric hindrance (entries 15 and 16). This reaction was not limited to simple aromatic boronic acids, the 2-naphthylboronic acid was also proved to be a good partner in this procedure and gave **3q** in 65% yield (entry 17).

To further explore the generality of this novel procedure, we examined the reaction using a wide range of 2-hydroxy-benzaldehydes with phenylboronic acid, and the results are summarized in Table 3. The presence of an alkyl or phenyl substituent on the hydroxybenzaldehyde appeared to be more beneficial for the reaction (entries 1–3 and 8–9). No significant electronic effects were observed concerning the substituents on hydroxybenzaldehyde (entries 1, 4, and 7), and the substrates containing multiple-bond functional groups, such as azoic and alkenyl moiety, could be tolerated in this procedure (entries 5 and 6). Substrate **1i** with a morpholino-methyl group on the *ortho* position of the hydroxyl group could also proceed well (entry 9), although longer reaction time was needed to complete the reaction. The naphthalene containing aldehyde **1j** could run smoothly in the reaction (entry 10) and the substrate **1k** with duel formyl groups gave corresponding double arylated product **4k** in 68% yield (entry 11). When 2-formylphenyl acetate **1l** was subjected to the reaction using K_2CO_3 as a base, deacylated product **3a** was produced instead in 55% yield (entry 12).

A tentative mechanism for the palladium-catalyzed direct C–H bond arylation reaction is proposed in Scheme 2.[13f,20] Complexa-

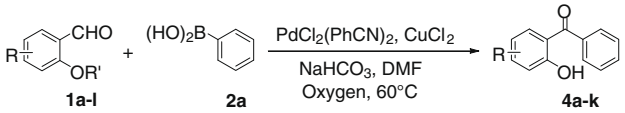
Table 2
Direct C–H arylation of salicylaldehyde with arylboronic acids[a]

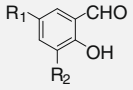
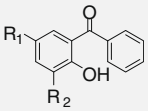
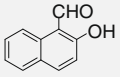
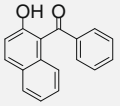
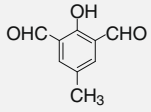
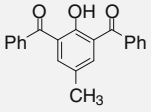
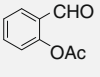
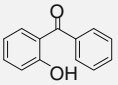


Entry	Arylboronic acids	Products	Time (h)	Yield[b] (%)
	 **2**	 **3**		
1	**2a**: R = H	**3a**: R = H	8	85[c]
2	**2b**: R = CH_3	**3b**: R = CH_3	11	86[c]
3	**2c**: R = OCH_3	**3c**: R = OCH_3	11	75
4	**2d**: R = OBn	**3d**: R = OBn	17	74[c]
5	**2e**: R = F	**3e**: R = F	8	96
6	**2f**: R = Cl	**3f**: R = Cl	7	77
7	**2g**: R = CF_3	**3g**: R = CF_3	7	80
8	**2h**: R = $COOC_2H_5$	**3h**: R = $COOC_2H_5$	7	74
9	**2i**: R = OTs	**3i**: R = OTs	14	92
				
10	**2j**: R = CH_3	**3j**: R = CH_3	8	70
11	**2k**: R = OCH_3	**3k**: R = OCH_3	10	66
12	**2l**: R = F	**3l**: R = F	7	86[c]
13	**2m**: R = NO_2	**3m**: R = NO_2	7	76[c]
14	**2n**: R = CHO	**3n**: R = CHO	8	68
15	 **2o**	 **3o**	10	63
16	 **2p**	 **3p**	11	66
17	 **2q**	 **3q**	9	65[c]

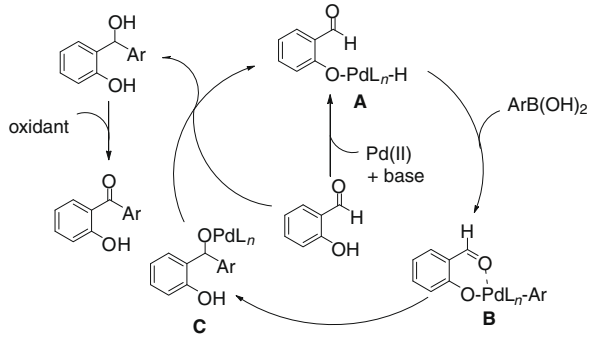
[a] The reactions were performed with salicylaldehyde (1.0 equiv), arylboronic acid (1.7 equiv), $PdCl_2(PhCN)_2$ (5 mol %), $CuCl_2$ (10 mol %), $NaHCO_3$ (2.0–3.0 equiv), and DMF (2 mL) under 1 atm O_2 on a 0.5 mmol scale.
[b] Isolated yields.
[c] 2.0 equiv of $NaHCO_3$ was used.

Table 3
Direct arylation of *o*-hydroxybenzaldehydes with phenylboronic acid[a]



Entry	Hydroxyaldehydes	Products	Time (h)	Yield[b] (%)
				
1	**1a**: $R_1 = NO_2$, $R_2 = H$	**4a**: $R_1 = NO_2$, $R_2 = H$	9	87[c]
2	**1b**: R_1 = *sec*-Bu, $R_2 = H$	**4b**: R_1 = *sec*-Bu, $R_2 = H$	8	90
3	**1c**: R_1 = Ph, $R_2 = H$	**4a**: R_1 = Ph, $R_2 = H$	8	80
4	**1d**: $R_1 = OCH_3$, $R_2 = H$	**4d**: $R_1 = OCH_3$, $R_2 = H$	12	79
5	**1e**: $R_1 = N_2$-*p*-$C_6H_4CH_3$, $R_2 = H$	**4e**: $R_1 = N_2$-*p*-$C_6H_4CH_3$, $R_2 = H$	25	74
6	**1f**: R_1 = CH=CHPh, $R_2 = H$	**4f**: R_1 = CH=CHPh, $R_2 = H$	13	54
7	**1g**: $R_1 = H$, $R_2 = OCH_3$	**4g**: $R_1 = H$, $R_2 = OCH_3$	11	78
8	**1h**: R_1 = Ph, R_2 = Ph	**4h**: R_1 = Ph, R_2 = Ph	9	92
9	**1i**: R_1 = *tert*-Bu, R_2 = 	**4i**: R_1 = *tert*-Bu, R_2 = 	16	82[c]
10	 **1j**	 **4j**	11	82
11	 **1k**	 **4k**	16	68[d]
12	 **1l**	 **3a**	9	55[e]

[a] The reactions were performed with hydroxybenzaldehyde (1.0 equiv), phenylboronic acid (1.7 equiv), $PdCl_2(PhCN)_2$ (5 mol %), $CuCl_2$ (10 mol %), and $NaHCO_3$ (3.0 equiv) in DMF (2 mL) under 1 atm O_2 on a 0.5 mmol scale.
[b] Isolated yields.
[c] Reaction was run at 80 °C with 2.0 equiv of phenylboronic acid.
[d] With phenylboronic acid (4.0 equiv), $PdCl_2(PhCN)_2$ (10 mol %), $CuCl_2$ (20 mol %) and $NaHCO_3$ (5.0 equiv).
[e] K_2CO_3 was used as a base.



Scheme 2. Plausible mechanism for the direct arylation of 2-hydroxy-benzaldehydes with arylboronic acids.

tion of the palladium catalyst with salicylaldehyde affords palladium(II) hydride **A**. The formed palladium complex subsequently reacts with arylboronic acid to give intermediate **B** via a transmetallation process. Addition of the carbon–palladium bond to the carbonyl group gives diarylmethoxypalladium intermediate **C**, which then yields 2-hydroxybenzophenone and also regenerates the palladium catalyst **A** in the presence of salicylaldehyde and oxidant. Currently, we cannot rule out the mechanistic possibility involving the five-membered palladacycle intermediate which was formed through chelation-assisted aldehyde C–H bond activation procedure.[21–23]

In summary, we have developed a mild and efficient ligand-free palladium-catalyzed arylation of 2-hydroxy-benzaldehydes with organoboronic acids in good to high yields. The given reaction provided one of the easiest pathways for accessing 2-hydroxybenzophenones. This new reaction involves formal aldehyde C–H bond arylation and a variety of functional groups could be tolerated in this process. The scope, mechanism, and synthetic applications of this catalytic reaction are under investigation in our laboratory.

Acknowledgments

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Supplementary data

Supplementary data (data and copies of the ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra for all compounds, and representative experimental procedures) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.166.

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