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Palladium-catalyzed oxidative cross-coupling for the synthesis of α -amino ketones†

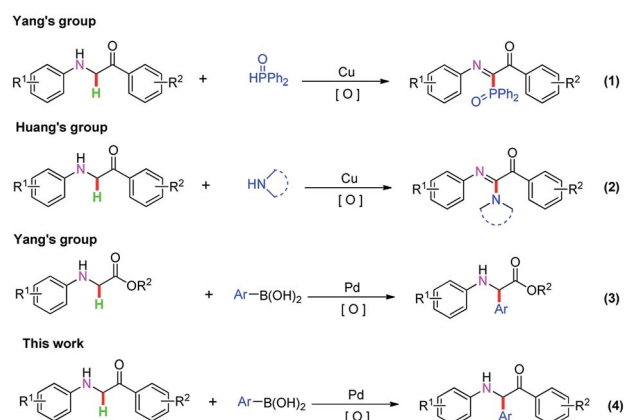
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A novel oxidative cross-coupling reaction for the synthesis of α -aryl α -amino ketones in the presence of palladium catalysts using $T^+BF_4^-$ as an oxidant has been developed. This transformation was achieved by direct C–H oxidation of α -aminocarbonyl compounds and arylation. The mild reaction has a broad reaction scope and gives desired α -aryl α -amino ketones in moderate to excellent yields.

Transition metal-catalyzed oxidative coupling reactions involving the formation of C–C bonds from C–H bonds have attracted considerable attention, indicating excellent atom economy and environmental friendliness.¹ α -Amino carbonyl compounds have important roles in natural products and are the key structural units of natural products.² These compounds have also been used in organic chemistry to synthesize biological activities, therapeutic agents, quinazolines, imidazoles, pyrazines, indoles, and pyrroles.³ Therefore, the direct oxidative C–H functionalization has gained significant attention for the synthesis of a series of α -amino carbonyl compounds.^{2i,2j,4} For example, Li's group employed an oxidative coupling reaction to synthesize α -amino carbonyl compounds from *N*-glycine derivatives by direct C–C bond formation under the catalysis of copper salts.⁵ Subsequently, stoichiometric amounts of chemical oxidants, such as DTBP, DDQ, TBHP, and 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetra-fluoroborate ($T^+BF_4^-$), have been applied to these reactions.^{4a,4d,4p,4t,6} In 2013, Yang's group described a novel protocol for a copper-catalyzed oxidative phosphonation reaction by using α -aminocarbonyls and diphenylphosphine ((1), Scheme 1).⁷ Huang's group disclosed a general and efficient method for C–N oxidative cross-coupling through direct C_{sp^3} -H bond functionalization of α -aminocarbonyl compounds with amines under the catalysis of copper salts ((2), Scheme 1).^{6h} In 2015, Yang's group developed a highly efficient route to synthesize chiral arylglycine derivatives *via* a palladium-catalyzed enantioselective direct C–H oxidation arylation reaction ((3), Scheme 1).^{4p} Furthermore, transition metal-catalyzed direct C–H functionalization by an oxidative cross-coupling reaction has been reported in the past few years.⁸ Although significant advances have been made along

these lines, the development of efficient synthetic methodologies for the synthesis of α -aminocarbonyl compounds *via* palladium-catalyzed oxidative cross-coupling still remains a challenging topic. Based on these considerable progresses, in this paper, we describe a highly efficient C–H oxidative cross-coupling reaction strategy for the synthesis of α -amino ketone compounds by palladium-catalyzed direct C–H oxidation and arylation reactions ((4), Scheme 1).

In an initial study, we chose 2-((4-chlorophenyl)amino)-1-phenylethanone **1a** and *para*-methylphenyl boric acid as the model substrate to evaluate different oxidants in the presence of 10 mol% $Pd(OAc)_2$ with 2,2-bipyridine as a ligand in TFE at 60 °C (Table 1, entries 1–8). To our delight, the desired product **2a** was obtained in 14% yield by using 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetra-fluoroborate ($T^+BF_4^-$)^{4p} as an oxidant (Table 1, entry 8). Based on these results, various ligands were used to carry out the reaction in the presence of 10 mol% $Pd(OAc)_2$. As expected, the best result of 29% yield was obtained by employing L_3 as a ligand (Table 1,

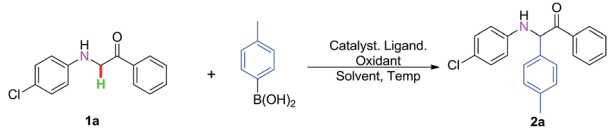


Scheme 1 Transition metal-catalyzed reaction for the synthesis of α -aminocarbonyl compounds.

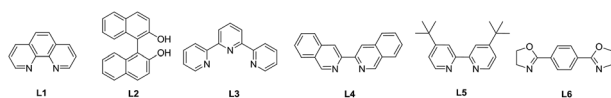
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Table 1 Optimization of the reaction conditions^{a,b}


Entry	Catalyst	Ligand	Oxidant	Solvent	Yield ^b
1	Pd(OAc) ₂	bpy	BQ	TFE	10%
2	Pd(OAc) ₂	bpy	Ag ₂ CO ₃	TFE	13%
3	Pd(OAc) ₂	bpy	K ₂ S ₂ O ₈	TFE	Trace
4	Pd(OAc) ₂	bpy	Air	TFE	8%
5	Pd(OAc) ₂	bpy	PhI(OAc) ₂	TFE	Trace
6	Pd(OAc) ₂	bpy	Ph ₃ CBF ₄	TFE	NR
7	Pd(OAc) ₂	bpy	C ₇ H ₇ BF ₄	TFE	Trace
8	Pd(OAc) ₂	bpy	T ⁺ BF ₄ ⁻	TFE	14%
9	Pd(OAc) ₂	L ₁	T ⁺ BF ₄ ⁻	TFE	24%
10	Pd(OAc) ₂	L ₂	T ⁺ BF ₄ ⁻	TFE	13%
11	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	TFE	29%
12	Pd(OAc) ₂	L ₄	T ⁺ BF ₄ ⁻	TFE	15%
13	Pd(OAc) ₂	L ₅	T ⁺ BF ₄ ⁻	TFE	20%
14	Pd(OAc) ₂	L ₆	T ⁺ BF ₄ ⁻	TFE	12%
15	Pd(OAc) ₂	PPh ₃	T ⁺ BF ₄ ⁻	TFE	16%
16	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DCE	21%
17	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	THF	31%
18	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	TOL	Trace
19	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ NO ₂	16
20	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DCM	18%
21	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	C ₂ H ₅ OH	37%
22	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DME	40%
23	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	DMF	8%
24	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	Dioxane	32%
25	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	47%
26 ^c	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	23%
27 ^d	Pd(OAc) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	71%
28 ^d	Pd(NO ₃) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	56%
29 ^d	Pd(TFA) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	43%
30 ^d	PdCl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	67%
31 ^d	Pd(PPh ₃) ₂ Cl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	60%
32 ^d	Pd(PPh ₃) ₄	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	38%
33 ^d	Pd(CH ₃ CN) ₂ Cl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	74%
34 ^d	Pd(acac) ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	58%
35 ^d	Pd(PhCN) ₂ Cl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	63%
36 ^d	Pd(cod)Cl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	66%
37 ^d	Pd(PCy₃)₂Cl₂	L ₃	T⁺BF₄⁻	CH₃OH	86%
38 ^d	Pd(PCy ₃) ₂ Cl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	Trace
39 ^d	Pd(PCy ₃) ₂ Cl ₂	L ₃	T ⁺ BF ₄ ⁻	CH ₃ OH	No

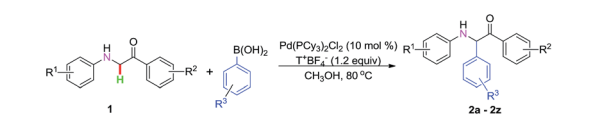


^a Reaction conditions: **1a** (0.1 mmol), *para*-methoxyphenyl boric acid (1.2 equiv.), catalyst (10 mol%), ligand (10 mol%) and oxidant (1.2 equiv.) was stirred in solvent (1 mL) at 60 °C under Ar for 20 h. ^b Yield of the isolated product. ^c 100 °C. ^d 80 °C.

entries 9–15). Then, different solvents were screened; using CH₃OH as the solvent with the set reaction conditions gave comparable results (entry 25), but others gave lower yields (Table 1, entries 16–25). When the temperature was increased to 80 °C, the yield of **2a** reached 71% (Table 1, entries 26 and 27).

To our delight, the reaction could occur in the presence of 10 mol% of catalysts such as Pd(NO₃)₂, Pd(TFA)₂, PdCl₂, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, Pd(CH₃CN)₂Cl₂, and Pd(acac)₂, while the reactivity of Pd(PCy₃)₂Cl₂ was better than others, affording the desired product **2a** in 86% yield (Table 1, entries 28–37). Furthermore, control experiments showed that no or trace amounts of the desired product was obtained in the absence of Pd(PCy₃)₂Cl₂ or T⁺BF₄⁻ (Table 1, entries 38 and 39).

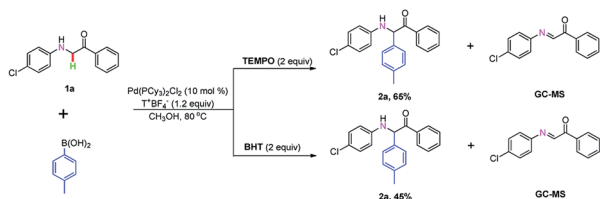
With the optimal reaction conditions in hand (Table 1, entry 37), we explored the C–H oxidative cross-coupling reaction of 2-(4-chlorophenyl)amino-1-phenylethanone **1a** with arylboronic acids, as shown in Table 2. We first surveyed different substituents of arylboronic acids with electron-donating groups, such as methyl, ethyl, isopropyl and methoxy, and found that they gave the desired product in 80–86% yields (Table 2, entries **2a–2d**). Meanwhile, the steric effect was examined using the *meta*- and *ortho*-methyl phenylboronic acids under identical conditions (Table 2, entries **2e** and **2f**). However, the steric effect in this transformation was very significant; only trace amounts of the product was obtained when *ortho*-methyl phenylboronic acids were introduced for the optimization of reaction conditions (Table 2, entry **2f**). When arylboronic acids with different electron-donating or electron-withdrawing groups afforded the desired products in excellent to moderate yields (Table 2, entries **2g–**

Table 2 Reaction conditions screening^{a,b}


2a , R ³ = Me, 86%	2e , 45%	2f , trace	2g , 69%
2b , R ³ = Et, 80%	2h , 80%	2i , 51%, 45% ^c	2n , 73%
2c , R ³ = Pr, 83%	2j , R ³ = F, 47%	2k , R ³ = Cl, 28%	2o , 77%
2d , R ³ = MeO, 83%	2l , R ³ = Br, 23%	2m , R ³ = I, 31%	2p , 66%
2r , R ² = F, 68%	2s , R ² = Br, 88%	2t , 64%	2u , 60%
2v , 30%	2w , 60%	2x , 42%	2y , 50%
2z , 30%			

^a Reaction conditions: **1a** (0.1 mmol), *para*-methoxyphenyl boric acid (1.2 equiv.), Pd(PCy₃)₂Cl₂ (10 mol%), and 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetra-fluoroborate (T⁺BF₄⁻) (1.2 equiv.) was stirred in CH₃OH (1 mL) at 80 °C under Ar for 20 h. ^b Yield of the isolated product. ^c Potassium phenyltrifluoroborate as arylated reagents.



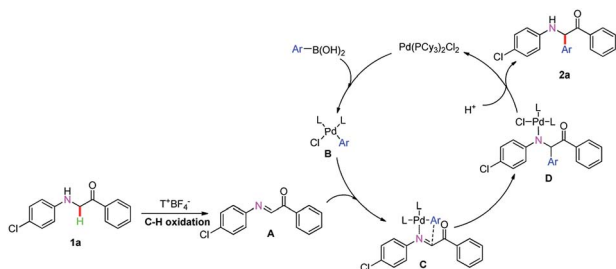


Scheme 2 Radical-trapping experiment.

2m). Moreover, in order to further expand the substrate scope, we selected potassium phenyltrifluoroborate as the arylated reagent under the optimized reaction conditions; the corresponding α -alkylation product **2i** was obtained in 45% yield (Table 2, entry **2i**).

Furthermore, the naphthalen-1-ylboronic acid and benzo [1,3]dioxol-5-ylboronic acid could also afford α -aminocarbonyl compounds **2n** and **2o** in 73–77% yields (Table 2, entries **2n** and **2o**). Of particular note is the heterocyclic boronic acid, which was also compatible for the reaction (Table 2, entries **2p** and **2q**). Moreover, the introduction of various electron-withdrawing or electron-donating substituents on the aniline moiety gave the corresponding α -aminocarbonyl compounds in 30–88% yields (Table 2, entries **2r–2x**); the electronic effect and the steric effect in this transformation was very notable (Table 2, entries **2t–2v**). Next, different substituent groups of α -carbonyl compounds bearing different functional groups were additionally examined and the corresponding products were generated in moderate yields (Table 2, entries **2y** and **2z**).

To investigate the mechanism of this transformation, experiments were carried out. The desired product was obtained in the range of 86% to 65% and 86% to 45% yield when 2.0 equivalents of radical-trapping reagents 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were used, respectively, under standardized reaction conditions (Scheme 2). To our delight, the key α -imino intermediate **A** was detected by GC-MS (see ESI[†]). Based on the observed experimental results and pioneering reports,^{4p,9} we have described a plausible mechanistic pathway in Scheme 3. Initially, the arylpalladium intermediate **B** was produced *via* a transmetalation reaction of Pd(PCy₃)₂Cl₂ with aryl boric acid, which attacks the α -imino intermediate **A** obtained by the *in situ* oxidation of **1a** by T⁺BF₄⁻ to form the complex **C**. Then, an aryl group was added to the imine to generate intermediate **D**.



Scheme 3 Proposed mechanism.

Finally, the product **2a** was obtained upon dissociation in the presence of H⁺. At the same time, the palladium catalyst was regenerated and synchronized into the next catalytic cycle (Scheme 3).

In summary, we have achieved a novel pattern for the synthesis of α -aryl α -amino ketone compounds *via* Pd(II)-catalyzed oxidative coupling of α -aminocarbonyl compounds with arylboric acids. This reaction occurs *via* direct C–H oxidation and arylation reactions. The coupling of α -aminocarbonyl compounds gave functionalized α -aryl α -amino ketone compounds in moderate to excellent yields.

Conflicts of interest

There are no conflicts to declare.

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