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

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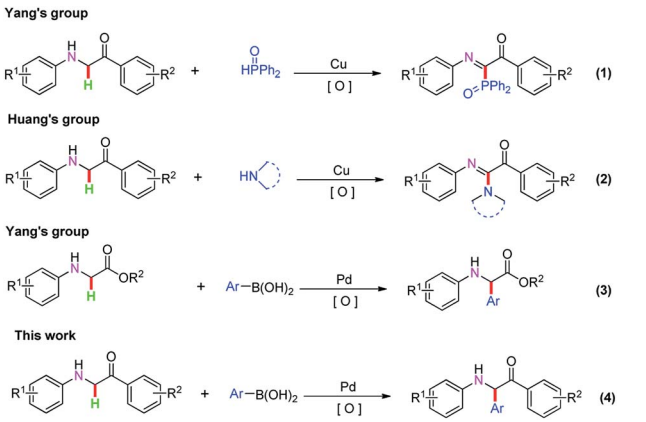
A novel oxidative cross-coupling reaction for the synthesis of α-aryl α-amino ketones in the presence of palladium catalysts using $T^+BF_4^-$ as an oxidant has been developed. This transformation was achieved by direct C–H oxidation of α-aminocarbonyl compounds and arylation. The mild reaction has a 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 activites, 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-amino-carbonyls 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 synthetize 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 $\mathbf{L_3}$ as a ligand (Table 1,



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

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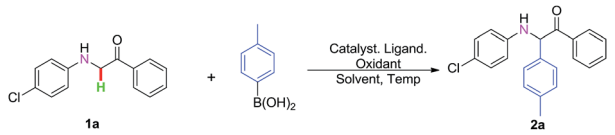
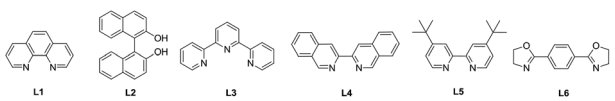
Table 1 Optimization of the reaction conditions[a,b]



Entry	Catalyst	Ligand	Oxidant	Solvent	Yield[b]
1	$Pd(OAc)_2$	bpy	BQ	TFE	10%
2	$Pd(OAc)_2$	bpy	Ag_2CO_3	TFE	13%
3	$Pd(OAc)_2$	bpy	$K_2S_2O_8$	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_3CBF_4	TFE	NR
7	$Pd(OAc)_2$	bpy	$C_7H_7BF_4$	TFE	Trace
8	$Pd(OAc)_2$	bpy	$T^+BF_4^-$	TFE	14%
9	$Pd(OAc)_2$	$\mathbf{L_1}$	$T^+BF_4^-$	TFE	24%
10	$Pd(OAc)_2$	$\mathbf{L_2}$	$T^+BF_4^-$	TFE	13%
11	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	TFE	29%
12	$Pd(OAc)_2$	$\mathbf{L_4}$	$T^+BF_4^-$	TFE	15%
13	$Pd(OAc)_2$	$\mathbf{L_5}$	$T^+BF_4^-$	TFE	20%
14	$Pd(OAc)_2$	$\mathbf{L_6}$	$T^+BF_4^-$	TFE	12%
15	$Pd(OAc)_2$	PPh_3	$T^+BF_4^-$	TFE	16%
16	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	DCE	21%
17	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	THF	31%
18	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	TOL	Trace
19	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	CH_3NO_2	16
20	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	DCM	18%
21	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	C_2H_5OH	37%
22	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	DME	40%
23	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	DMF	8%
24	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	Dioxane	32%
25	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	CH_3OH	47%
26[c]	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	CH_3OH	23%
27[d]	$Pd(OAc)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	CH_3OH	71%
28[d]	$Pd(NO_3)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	CH_3OH	56%
29[d]	$Pd(TFA)_2$	$\mathbf{L_3}$	$T^+BF_4^-$	CH_3OH	43%
30[d]	$PdCl_2$	$\mathbf{L_3}$	$T^+BF_4^-$	CH_3OH	67%
31[d]	$Pd(PPh_3)_2Cl_2$		$T^+BF_4^-$	CH_3OH	60%
32[d]	$Pd(PPh_3)_4$		$T^+BF_4^-$	CH_3OH	38%
33[d]	$Pd(CH_3CN)_2Cl_2$		$T^+BF_4^-$	CH_3OH	74%
34[d]	$Pd(acac)_2$		$T^+BF_4^-$	CH_3OH	58%
35[d]	$Pd(PhCN)_2Cl_2$		$T^+BF_4^-$	CH_3OH	63%
36[d]	$Pd(cod)Cl_2$		$T^+BF_4^-$	CH_3OH	66%
37[d]	$\mathbf{Pd(PCy_3)_2Cl_2}$		$\mathbf{T^+BF_4^-}$	$\mathbf{CH_3OH}$	**86%**
38[d]	$Pd(PCy_3)_2Cl_2$			CH_3OH	Trace
39[d]			$T^+BF_4^-$	CH_3OH	No



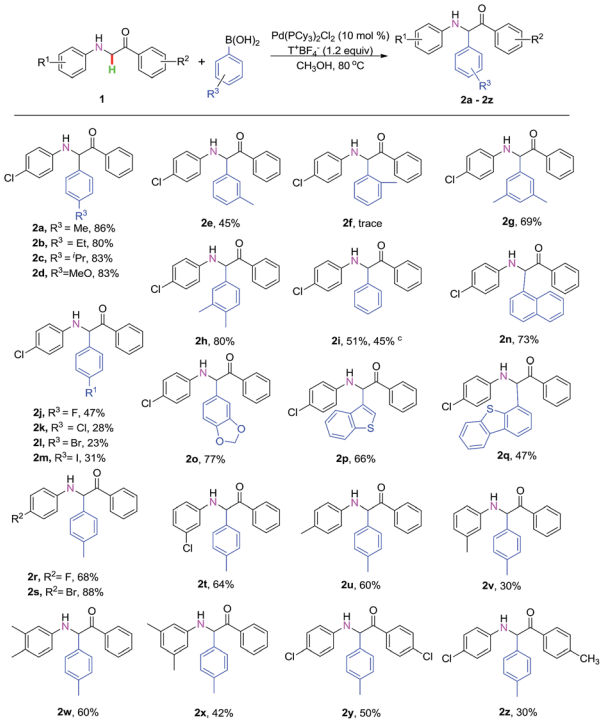
[a] Reaction conditions: 1a (0.1 mmol), *para*-methyphenyl boric acid (1.2 equiv.), catalyst (10 mol%), ligand (10 mol%) and oxidant (1.2 equiv.) was stirred in solvent (1 mL) at 60 °C under Ar for 20 h. [b] Yield of the isolated product. [c] 100 °C. [d] 80 °C.

entries 9–15). Then, different solvents were screened; using CH_3OH 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).

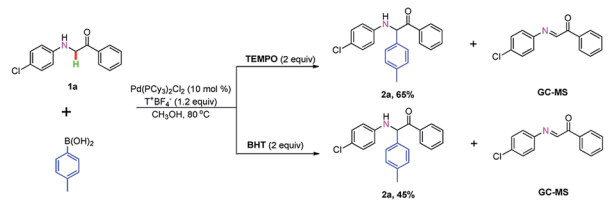
To our delight, the reaction could occur in the presence of 10 mol% of catalysts such as $Pd(NO_3)_2$, $Pd(TFA)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, $Pd(CH_3CN)_2Cl_2$, and $Pd(acac)_2$, while the reactivity of $Pd(PCy_3)_2Cl_2$ was better than others, affording the desired product **2a** 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 $Pd(PCy_3)_2Cl_2$ or $T^+BF_4^-$ (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 arylboric acids, as shown in Table 2. We first surveyed different substituents of arylboric 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 phenylboric 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 phenylboric acids were introduced for the optimization of reaction conditions (Table 2, entry **2f**). When arylboric 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]



[a] Reaction conditions: **1a** (0.1 mmol), *para*-methyphenyl boric acid (1.2 equiv.), $Pd(PCy_3)_2Cl_2$ (10 mol%), and 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetra-fluoroborate ($T^+BF_4^-$) (1.2 equiv.) was stirred in CH_3OH (1 mL) at 80 °C under Ar for 20 h. [b] Yield of the isolated product. [c] Potassium phenyltrifluoroborate as arylated reagents.

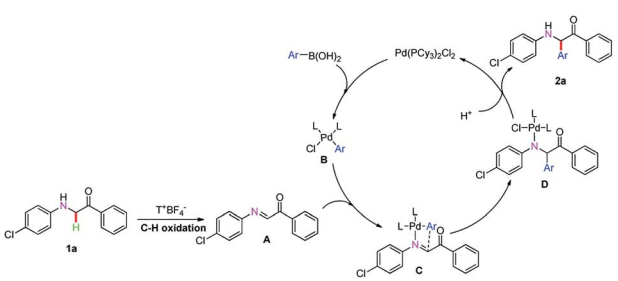


Scheme 2 Radical-trapping experiment.

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 moeity 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 transmetallation reaction of $Pd(PCy_3)_2Cl_2$ with aryl boric acid, which attacks the α-imino intermediate **A** obtained by the *in situ* oxidation of **1a** by $T^+BF_4^-$ 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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