

## PAPER

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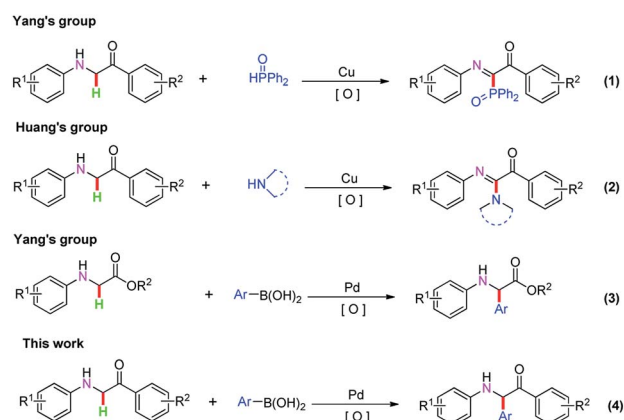
Palladium-catalyzed oxidative cross-coupling for the synthesis of  $\alpha$ -amino ketones†Xiao-Hong Wei,<sup>ID</sup>\* Zhen-Hua Li,<sup>ID</sup>\* Lian-Biao Zhao, Ping Zhang,  
Han-Cheng Zhou<sup>ID</sup> and Yan-Bin Wang

A novel oxidative cross-coupling reaction for the synthesis of  $\alpha$ -aryl  $\alpha$ -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  $\alpha$ -aminocarbonyl compounds and arylation. The mild reaction has a broad reaction scope and gives desired  $\alpha$ -aryl  $\alpha$ -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.<sup>1</sup>  $\alpha$ -Amino carbonyl compounds have important roles in natural products and are the key structural units of natural products.<sup>2</sup> These compounds have also been used in organic chemistry to synthesize biological activities, therapeutic agents, quinazolines, imidazoles, pyrazines, indoles, and pyrroles.<sup>3</sup> Therefore, the direct oxidative C–H functionalization has gained significant attention for the synthesis of a series of  $\alpha$ -amino carbonyl compounds.<sup>2i,2j,4</sup> For example, Li's group employed an oxidative coupling reaction to synthesize  $\alpha$ -amino carbonyl compounds from *N*-glycine derivatives by direct C–C bond formation under the catalysis of copper salts.<sup>5</sup> 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.<sup>4a,4d,4p,4t,6</sup> In 2013, Yang's group described a novel protocol for a copper-catalyzed oxidative phosphorylation reaction by using  $\alpha$ -amino carbonyls and diphenylphosphine ((1), Scheme 1).<sup>7</sup> Huang's group disclosed a general and efficient method for C–N oxidative cross-coupling through direct  $C_{sp^3}$ –H bond functionalization of  $\alpha$ -aminocarbonyl compounds with amines under the catalysis of copper salts ((2), Scheme 1).<sup>6a</sup> 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).<sup>4p</sup> Furthermore, transition metal-catalyzed direct C–H functionalization by an oxidative cross-coupling reaction has been reported in the past few years.<sup>8</sup> Although significant advances have been made along

these lines, the development of efficient synthetic methodologies for the synthesis of  $\alpha$ -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  $\alpha$ -amino ketone compounds by palladium-catalyzed direct C–H oxidation and arylation reactions ((4), Scheme 1).

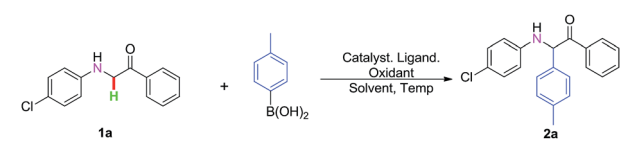
In an initial study, we chose 2-((4-chlorophenyl)amino)-1-phenylethanone **1a** and *para*-methylphenyl boric acid as the model substrate to evaluate different oxidants in the presence of 10 mol%  $Pd(OAc)_2$  with 2,2-bipyridine as a ligand in TFE at 60 °C (Table 1, entries 1–8). To our delight, the desired product **2a** was obtained in 14% yield by using 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetra-fluoroborate ( $T^+BF_4^-$ )<sup>4p</sup> 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**<sub>3</sub> as a ligand (Table 1,




Scheme 1 Transition metal-catalyzed reaction for the synthesis of  $\alpha$ -aminocarbonyl compounds.


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
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra06108h


Table 1 Optimization of the reaction conditions<sup>a,b</sup>



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












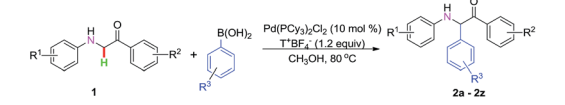


<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), *para*-methoxyphenyl boric acid (1.2 equiv.), catalyst (10 mol%), ligand (10 mol%) and oxidant (1.2 equiv.) was stirred in solvent (1 mL) at 60 °C under Ar for 20 h. <sup>b</sup> Yield of the isolated product. <sup>c</sup> 100 °C. <sup>d</sup> 80 °C.

entries 9–15). Then, different solvents were screened; using CH<sub>3</sub>OH 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<sub>3</sub>)<sub>2</sub>, Pd(TFA)<sub>2</sub>, PdCl<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>, and Pd(acac)<sub>2</sub>, while the reactivity of Pd(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> 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<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> or T<sup>+</sup>BF<sub>4</sub><sup>-</sup> (Table 1, entries 38 and 39).

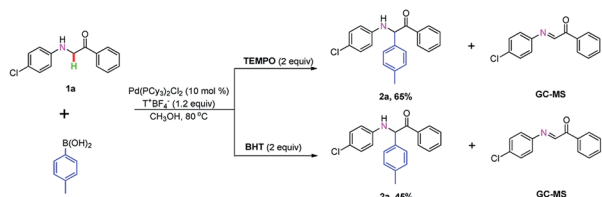
With the optimal reaction conditions in hand (Table 1, entry 37), we explored the C–H oxidative cross-coupling reaction of 2-((4-chlorophenyl)amino)-1-phenylethanone **1a** with arylboronic acids, as shown in Table 2. We first surveyed different substituents of arylboronic acids with electron-donating 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<sup>a,b</sup>


Entry	Product	Yield (%)
<b>2a</b>	R <sup>3</sup> = Me	86%
<b>2b</b>	R <sup>3</sup> = Et	80%
<b>2c</b>	R <sup>3</sup> = <i>i</i> -Pr	83%
<b>2d</b>	R <sup>3</sup> = MeO	83%
<b>2e</b>	<i>ortho</i> -Me	45%
<b>2f</b>	<i>ortho</i> -Me	Trace
<b>2g</b>	<i>ortho</i> -Me	69%
<b>2h</b>	R <sup>3</sup> = F	80%
<b>2i</b>	R <sup>3</sup> = Cl	51%, 45% <sup>c</sup>
<b>2j</b>	R <sup>3</sup> = Br	73%
<b>2k</b>	R <sup>3</sup> = I	77%
<b>2l</b>	R <sup>3</sup> = F	66%
<b>2m</b>	R <sup>3</sup> = Cl	64%
<b>2n</b>	R <sup>3</sup> = Br	60%
<b>2o</b>	R <sup>3</sup> = I	30%
<b>2p</b>	R <sup>3</sup> = Me	60%
<b>2q</b>	R <sup>3</sup> = Et	42%
<b>2r</b>	R <sup>3</sup> = <i>i</i> -Pr	50%
<b>2s</b>	R <sup>3</sup> = MeO	30%

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), *para*-methoxyphenyl boric acid (1.2 equiv.), Pd(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%), and 2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate (T<sup>+</sup>BF<sub>4</sub><sup>-</sup>) (1.2 equiv.) was stirred in CH<sub>3</sub>OH (1 mL) at 80 °C under Ar for 20 h. <sup>b</sup> Yield of the isolated product. <sup>c</sup> Potassium phenyltrifluoroborate as arylated reagents.



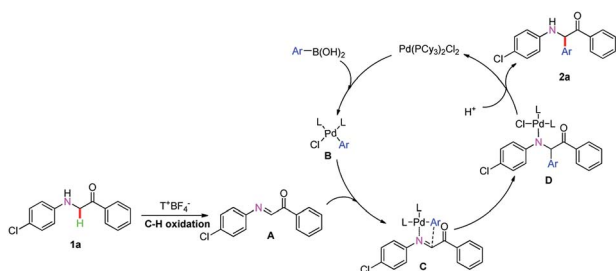


Scheme 2 Radical-trapping experiment.

**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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -imino intermediate **A** was detected by GC-MS (see ESI†). Based on the observed experimental results and pioneering reports,<sup>4p,9</sup> we have described a plausible mechanistic pathway in Scheme 3. Initially, the arylpalladium intermediate **B** was produced *via* a transmetalation reaction of Pd(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with aryl boric acid, which attacks the  $\alpha$ -imino intermediate **A** obtained by the *in situ* oxidation of **1a** by T<sup>+</sup>BF<sub>4</sub><sup>−</sup> 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<sup>+</sup>. 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  $\alpha$ -aryl  $\alpha$ -amino ketone compounds *via* Pd(II)-catalyzed oxidative coupling of  $\alpha$ -aminocarbonyl compounds with arylboric acids. This reaction occurs *via* direct C–H oxidation and arylation reactions. The coupling of  $\alpha$ -aminocarbonyl compounds gave functionalized  $\alpha$ -aryl  $\alpha$ -amino ketone compounds in moderate to excellent yields.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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