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Catalytic Reductive Cross-Coupling between Aromatic Aldehydes and Arylnitriles

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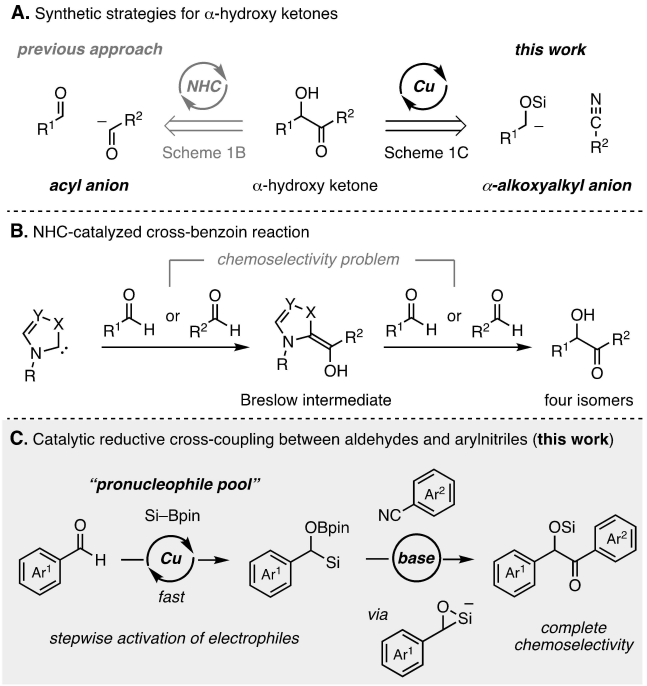
Abstract: A reductive cross-coupling reaction between aromatic aldehydes and arylnitriles using a copper catalyst and a silylboronate as a reductant is reported. This protocol represents an unprecedented approach to the chemoselective synthesis of α-hydroxy ketones by electrophile–electrophile cross-coupling.

α-Hydroxy ketones are important scaffolds found in pharmaceuticals and agrochemicals, as well as versatile and attractive synthetic intermediates.[1] They can be easily transformed into 1,2-diols or β-amino alcohols by reductive functionalization,[2] and to azoles and pyrroles by dehydrative cyclization.[3] Therefore, many synthetic methodologies have been reported to date.[4] Among them, the most simple and straightforward approach is the addition of an *acyl anion* to an aldehyde, which is well-known as a benzoin condensation reaction (Scheme 1A, left).[5] In this context, significant progress in N-heterocyclic carbene (NHC) catalysis has been made.[6] The NHC enables the catalytic conversion of an aldehyde to the corresponding acyl anion equivalent (Breslow intermediate), which undergoes nucleophilic addition to another aldehyde. However, NHC catalysts suffer from chemoselectivity issues. As shown in Scheme 1B, the NHC must distinguish between two electrophiles at two stages: in *the formation of the Breslow intermediate* and in its *subsequent nucleophilic attack* to obtain the desired α-hydroxy ketone out of the four possible isomers. To achieve high chemoselectivity, specific substrate design[7] and equivalent control[8] are required. To avoid this chemoselectivity problem, a completely different synthetic approach must be developed.

Previously, we reported reductive umpolung using a copper catalyst and a silylboronate to convert an aldehyde to a nucleophilic α-silyloxyalkylcopper(I) species.[9] The α-silyloxyalkylcopper(I) species, generated via addition of the silylcopper(I) species to an aldehyde followed by [1,2]-Brook rearrangement, could react with various electrophiles to afford a series of alcohol derivatives that are difficult to synthesize by classical methods using aldehydes as electrophiles. For example, our protocol enabled cross-pinacol coupling between aldehydes and ketones or imines to produce 1,2-diol or 1,2-amino alcohol derivatives, respectively.[9c,d] The catalytically-generated α-silyloxyalkylcopper(I) species from the aldehyde preferentially reacted with the less electrophilic ketone or imine over the aldehyde. While investigating the origin of the chemoselectivity, we discovered extremely fast consumption of the aldehyde before injection of the ketone or imine, which implied the intermediacy of an *O*-borylated α-silyl alcohol (see Supporting Information). This observation and Kleeberg's and Oestreich's report[10] indicated that reductive umpolung by copper catalysis preactivated the aldehyde, then the obtained *O*-borylated α-silyl alcohol adduct acted as a pronucleophile pool for the subsequent reaction with the electrophile in a one-pot manner. Thus, we speculated whether this tandem reaction system could provide a solution to the chemoselective synthesis of α-hydroxy ketones through the reaction between the α-silyloxyalkyl anion and an acyl cation synthon (Scheme 1C).



Scheme 1. Synthetic approaches to α-hydroxy ketones.

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Herein, we report a reductive cross-coupling reaction between aromatic aldehydes and arylnitriles, producing α-hydroxy ketones using a copper catalyst and a silylboronate as a reductant. This protocol allowed the assembly of inexpensive and readily available aldehydes and nitriles into highly valuable α-hydroxy ketones with complete chemoselectivity. This tandem reaction system is a unique approach to the intrinsic chemoselectivity issue of electrophile-electrophile cross-couplings.[11]

Initially, we evaluated the catalytic reductive cross-coupling between aldehydes and various acyl cation synthons. When reactive carboxylic acid derivatives such as acyl halides were used as the coupling partner, the desired α-hydroxy ketones were obtained in moderate yields with significant formation of *O*-acylated products (data not shown). To shut down the pathway to such byproducts, we turned our attention to arylnitriles, which possess lower reactivity than carboxylic acid derivatives. After a quick screening, we found that the reductive cross-coupling reaction of *p*-anisaldehyde (**1a**) (0.3 mmol) and benzonitrile (**2a**) (0.2 mmol) proceeded with a catalytic amount of copper(I) 2-thiophenecarboxylate (CuTc) (10 mol%) and 1,3-bis(2,4,6-trimethylphenyl) imidazolinium chloride (SIMes·HCl) (10 mol%) in the presence of (triethylsilyl)boronic acid pinacol ester [$Et_3SiB(pin)$][12] (0.3 mmol) and NaOtBu (0.22 mmol) in toluene at 80 °C for 3 h. The α-hydroxy ketone **3aa** was afforded in 69% isolated yield after desilylation by acidic workup with 10% HCl aqueous solution (Table 1, entry 1).

The substituent on the Si atom of the silylboronates was important to secure the high yield (Table 1, entries 2–5). The use of $PhMe_2SiB(pin)$, which exhibited high performance in our previous copper-catalyzed reductive umpolung, resulted in low yield (entry 2).[9c,d] When other trialkylsilylboronates including $^nBu_3SiB(pin)$, $Me_3SiB(pin)$ and $^tBuMe_2SiB(pin)$ were used, the product yield diminished drastically (entries 3–5).

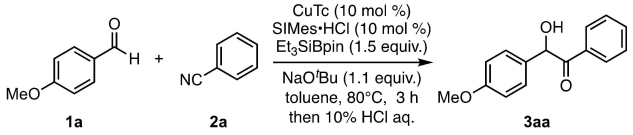
The steric environment of the NHC ligands also had an impact on the catalytic reactivity (entries 6–9). The reaction using IMes·HCl having a similar steric bulkiness to SIMes·HCl resulted in comparable reactivity (entry 6). On the other hand, bulkier SIPr and IPr did not produce **3aa** at all (entries 7 and 8). SICy possessing less bulkiness than SIMes in the view of $\%V_{bur}$[13] slightly decreased the product yield (entry 9).

The choice of Cu(I) source was significant for this reaction (Table 1, entries 10–12). The reaction proceeded less effectively when CuTc was replaced with copper chloride, bromide or iodide. The nature and quantity of alkoxide bases were also important (entries 13–17). The use of other alkali metal-based tertiary butoxide bases, LiO^tBu and KO^tBu, resulted in low and moderate product yields, respectively (entries 13 and 14). A smaller and weaker alkoxide base, NaOMe, drastically reduced the product yield (entry 15). Decreasing the amount of NaO^tBu resulted in low conversion (entries 16 and 17).

With the optimal conditions in hand, the scope of aldehydes in the reductive cross-coupling using benzonitrile (**2a**) was explored (Table 2, top). The products were isolated as the corresponding silyl ether forms. The reactions with *p*-, *m*-, and *o*-tolualdehyde gave the corresponding α-silyloxy ketone products in moderate to high yields (**4ba**–**4da**). Electron-donating groups such as *tert*-butyl, methoxy, methylthio, and dimethylamino substituents were tolerated at the *para*-position of the aromatic ring of the aldehydes (**4aa** and **4ea**–**4ga**). 3-Anisaldehyde and piperonal were also suitable substrates (**4ha** and **4ia**). Mono- and di-fluoro substituted aromatic aldehydes were also adoptable (**4ja** and **4ka**). Furthermore, heteroaromatic fragments such as thiophene and furan were incorporated into the α-position of the α-hydroxy ketone derivatives (**4la**–**4na**). 2-Naphthaldehyde was also a suitable substrate (**4oa**). The reactions with aliphatic aldehydes did not give the desired products at all (data not shown).

The scope of the arylnitriles as a coupling partner for benzaldehyde (**1p**) is shown in the bottom of Table 2. Neither electron-rich nor electron-deficient groups at the *para*-positions in the aromatic ring affected the reactivity (**4pb**–**4ph**). A methoxy group was also tolerated at the *meta*-position (**4pi**). Piperonylonitrile and 2-naphthonitrile participated in the reaction (**4pj** and **4pk**). Heteroaromatic rings such as indole, thiophene, pyridine and furan could be introduced to the acyl fragment of the product (**4pl**–**4po**). Antipsychotic drugs containing cyano groups, Citalopram and Cyamemazine, were efficiently functionalized (**4pp** and **4pq**). The reactions with aliphatic nitriles resulted in no product formation due to the lower reactivity than aromatic ones (data not shown). Notably, other isomers of α-hydroxy ketones were not observed at all

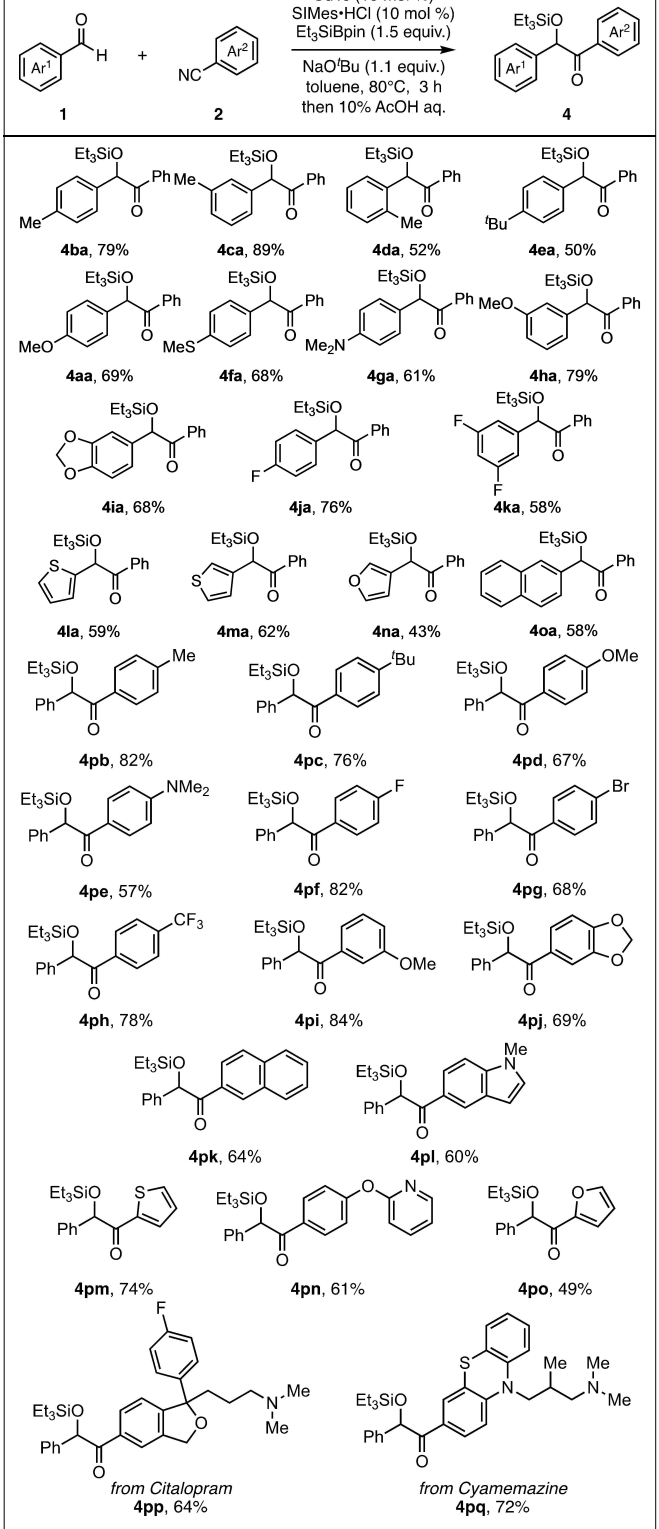
Table 1. Screening of reaction conditions.[a]



entry	change from standard conditions	yield (%) of **3aa**[b]
1	None	67 (69)
2[c]	$PhMe_2SiBpin$ instead of $Et_3SiBpin$	20
3[c]	$^nBu_3SiBpin$ instead of $Et_3SiBpin$	9
4[c]	$Me_3SiBpin$ instead of $Et_3SiBpin$	15
5[c]	$^tBuMe_2SiBpin$ instead of $Et_3SiBpin$	0
6	IMes·HCl instead of SIMes·HCl	63
7	SIPr·HCl instead of SIMes·HCl	0
8	IPr·HCl instead of SIMes·HCl	0
9	SICy·HCl instead of SIMes·HCl	30
10	CuCl instead of CuTc	50
11	CuBr instead of CuTc	51
12	CuI instead of CuTc	50
13	LiO^tBu instead of NaO^tBu	2
14	KO^tBu instead of NaO^tBu	45
15	NaOMe instead of NaO^tBu	8
16	NaO^tBu (20 mol%) instead of 1.1 equiv.	0
17	NaO^tBu (50 mol%) instead of 1.1 equiv.	32

[a] Reaction was carried out with **1a** (0.3 mmol), **2a** (0.2 mmol), $Et_3SiBpin$ (0.3 mmol), CuTc (10 mol%), SIMes·HCl (10 mol%), and base (0.22 mmol) in toluene (0.5 mL) at 80 °C for 3 h. [b] ^1H NMR yield based on **2a**. Yield of the isolated product is in parentheses. [c] Reaction was carried out with **1a** (0.3 mmol), **2a** (0.2 mmol), $R_3SiBpin$ (0.3 mmol), CuCl (10 mol%), SIMes·HCl (10 mol%), and NaO^tBu (0.22 mmol) in toluene (1.0 mL) at 80 °C for 3 h. IMes·HCl, 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride. SIPr·HCl, 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride. IPr·HCl, 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride. SICy·HCl, 1,3-dicyclohexylimidazolinium chloride.

Table 2. Substrate scope.[a]



[a] Reactions were carried out with **1** (0.3 mmol), **2** (0.2 mmol), $Et_3SiBpin$ (0.3 mmol), CuTc (10 mol%), SIMes·HCl (10 mol%), and NaO*t*Bu (0.22 mmol) in toluene (0.5 mL) at 80 °C for 3 h.

during the investigation of the reaction scope of aldehydes and arylnitriles.

To gain mechanistic insight into this reductive cross-coupling, several experiments were carried out (Figure 1). First, we monitored the silylation of **1p** under the optimal reaction conditions but excluding the arylnitrile and using only one equivalent of NaO^{t}Bu to correspond to the initiation sequence of the catalytic reaction (Figure 1A, top). After stirring the reaction mixture for 10 min and then passing it through a plug of silica gel, α-silyl alcohol **5a**, *O*-borylated α-silyl alcohol **5b**[14] and silylbenzylether **5c** were obtained in 43%, 22% and 17% yields, respectively, with recovery of a small amount of **1p** (5%). This result supported the intermediacy of the *O*-borylated α-silyl alcohol under the optimal conditions. We also evaluated the effect of other NHC ligands on the silylation of **1p** (Figure 1A, bottom). The reaction with IMes showed comparable reactivity as SIMes. On the other hand, IPr and SIPr did not give any silylated products. This result was consistent with Kleeberg's and Oestreich's report,[10] wherein the addition of an IPr-ligated-silylcopper(I) complex to the aldehyde was slow. The

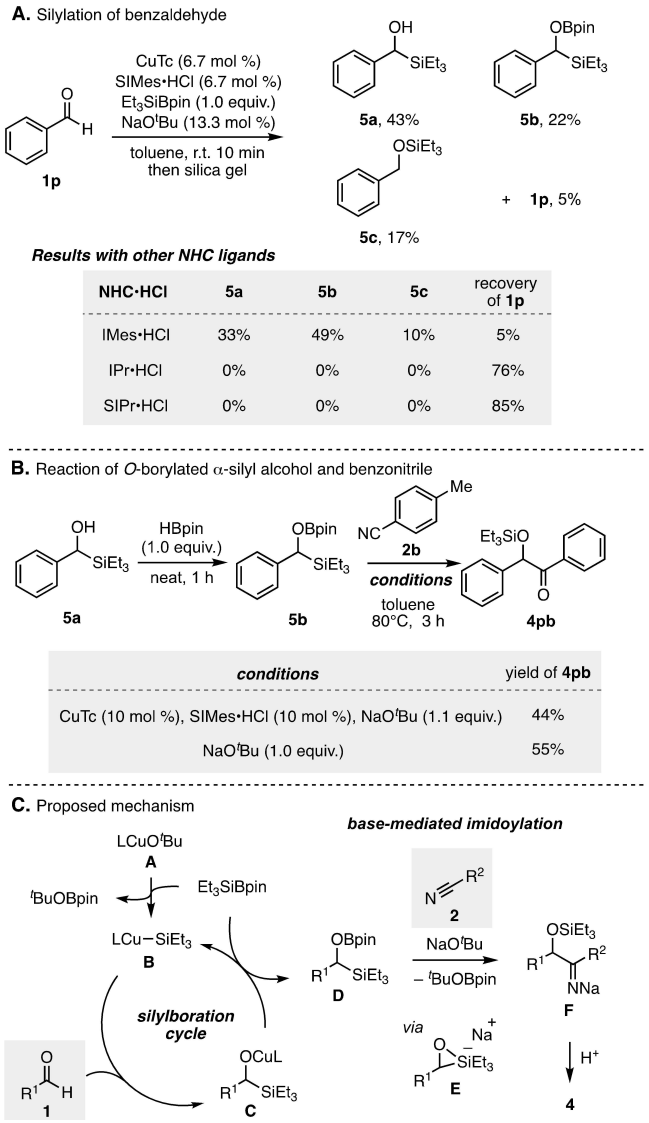


Figure 1. Mechanistic studies.

moderate steric bulkiness of the mesityl group would make the corresponding catalytic process extremely fast. These contrasting results between (S)IMes and (S)IPr ligands were reflected in the reactivity of the reductive cross-coupling (Table 1, entries 1 and 6 vs. entries 7 and 8).

Subsequently, to confirm whether the copper complex is essential or not in the reaction of the *O*-borylated silyl alcohol and benzonitrile, stoichiometric reactions between *O*-borylated silyl alcohol **5b** and *p*-tolunitrile (**2b**) were examined (Figure 1B). The *O*-borylated α-silyl alcohol **5b** was prepared by the reaction between **5a** and pinacolborane and used in a one-pot manner.[15] We found that the desired acylated product **4pb** was obtained without a copper catalyst. Therefore, the imidoylation step is promoted by NaO^{t}Bu alone.[16]

On the basis of these mechanistic studies and our previous studies,[9] a possible pathway for this reductive cross-coupling is outlined in Figure 1C. First, transmetalation between NHC-ligated copper(I) tertiary butoxide (**A**) and a silylboronate occurs to form the silylcopper(I) complex (**B**) and ^{t}BuOBpin. The catalytic cycle for silylboration of aldehyde (**1**) begins with the 1,2-addition of **B** across the carbonyl moiety of **1** producing a copper(I) α-silylalkoxide (**C**).[17] The transmetalation of **C** and a silylboronate regenerates **B** and produces *O*-borylated α-silyl alcohol (**D**) as a pronucleophile in the subsequent imidoylation. Next, a stoichiometric amount of NaO^{t}Bu converts **D** to the three-membered silicate intermediate (**E**),[16] which reacts with arylnitrile **2** to give the corresponding α-imidate alcohol (**F**). Finally, **F** is hydrolyzed to **4**.

To demonstrate the synthetic utility of this reductive cross-coupling, the obtained α-hydroxy ketones were derivatized to valuable scaffolds (Figure 2). α-Silyloxy ketone **4ja** was easily converted to *O*-silylated 1,2-amino alcohol **6ja** by reductive amination[18] with complete diastereoselectivity (Figure 2A). When the α-hydroxy ketone **3pb** was subjected to Rengarajan's conditions[19] for *in situ* formed acetal-assisted 1,2-aryl migration, the corresponding diarylacetate **7pb** was obtained in 91% yield (Figure 2B). Furthermore, fully arylated heteroarenes with different aryl groups could be synthesized (Figure 2C). Acylation of **3pd** with aroyl chloride followed by dehydrative cyclization in the presence of a NH_3 source resulted in the formation of triaryloxazole **8pd** (Figure 2C, top).[20] **3pd** reacted with **9a** to afford the tetraaryl-substituted pyrrole **10pd** with high regioselectivity (Figure 2C, bottom).[21]

In summary, we have developed a reductive cross-coupling reaction between aromatic aldehydes and arylnitriles using a copper catalyst and a silylboronate as a reductant. This protocol provides an unprecedented synthetic approach to α-hydroxy ketones with complete chemoselectivity. Attempts to extend this reaction to an asymmetric version with chiral NHC ligands with efficient enantioselectivity has not yet been achieved. Improvements to ligand design and applications of this tandem reaction system to other transformations are ongoing in our laboratory.

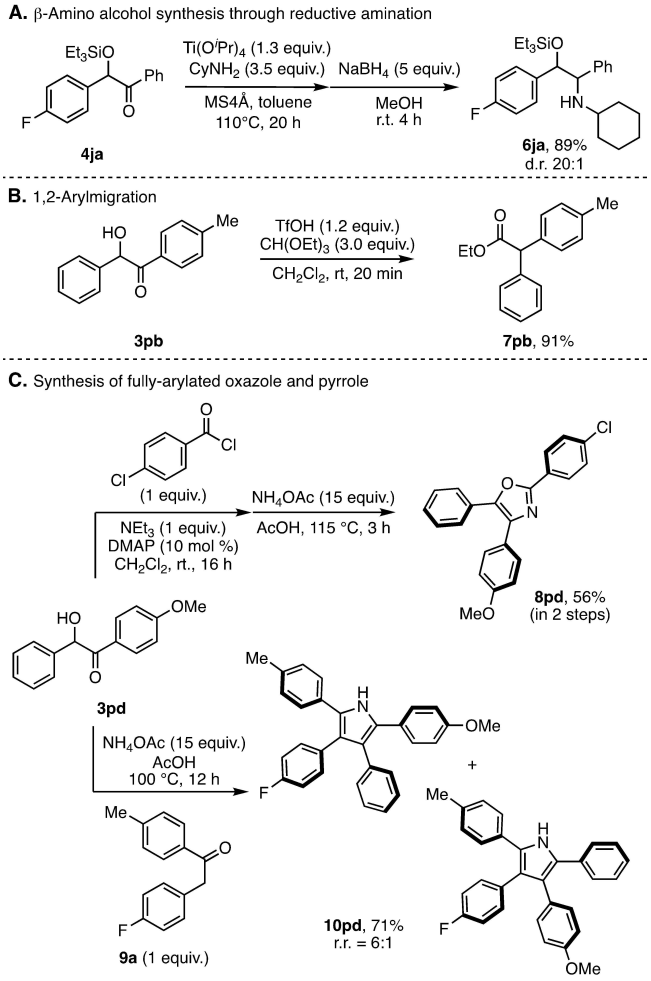


Figure 2. Product derivatizations.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Aldehyde · arylnitrile · copper · α-hydroxy ketone · reductive cross-coupling

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