

Rh(I)-Catalyzed Carbon–Carbon Double-Bond Formation by Coupling of (Quinolin-8-yl)methanone with Arylaldehyde Tosylhydrazone

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Abstract: An alternative method for the direct arylvinylation of (quinolin-8-yl)methanone with substituted *N'*-benzylidene-4-methylbenzenesulfonohydrazide is described. The desired 3-aryl-1-(quinolin-8-yl)prop-2-en-1-one products are obtained in high yields through the catalytic reaction of (quinolin-8-yl)methanone and *N'*-arylidene-4-methylbenzenesulfonohydrazide (2 equiv) with [Rh(PPh₃)₃Cl] (10 mol%), Ag₂O (0.5 equiv), and Cs₂CO₃ (2 equiv) at 130 °C for 48 hours. Two plausible mechanisms involving C–H activation and migratory insertion of the carbene into the rhodium–carbon bond were proposed to explain the formation of the product.

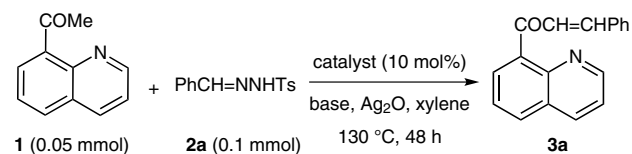
Key words: quinolinone, rhodium complex, hydrazones, C–C coupling, double-bond formation

Carbon–carbon double-bond formation is one of the most fundamental transformations in synthetic organic chemistry, and many methods have been developed for the construction of such bonds.¹ Among these methods, aldol condensation is the most applicable and efficient choice when constructing α,β -unsaturated aldehydes or ketones.^{1a,b} However, aldol condensation reactions usually proceed in the presence of strong bases, which requires the substrates to be insensitive to such conditions. The development of transition-metal-catalyzed cross-coupling reactions has drawn considerable attention because these kinds of reactions are indispensable tools for carbon–carbon bond formation in modern synthetic organic chemistry.² For example, the Heck reaction paved the way for the use of aryl or alkyl halides and olefinic compounds as key building blocks in the construction of new olefin compounds in high yields under mild reaction conditions.³ In the past decade, many research groups have developed coupling reactions through direct C–H bond activations. Compared with the traditional Heck reaction, these newly developed processes are more efficient in terms of the overall chemical transformation.⁴

On the other hand, diazo compounds react with organic halides,⁵ arylboronic acids,⁶ and terminal alkynes⁷ to enable compounds bearing carbon–carbon double bonds to undergo oxidative coupling reactions. The diazo compounds are ideal for the generation of carbon–carbon double bonds through coupling reactions because these substrates can be generated in situ from *N*-tosylhydrazones under basic conditions.⁸ Moreover, *N*-tosylhydra-

zones are easily derived from the corresponding aldehydes or ketones.⁹ In our previous study, we demonstrated that the reaction of (quinolin-8-yl)methanone with arylboronic acids produces aryl(quinolin-8-yl)methanone products through rhodium-chelation-assisted carbon–carbon bond activation.¹⁰ According to the above aspects, we propose that the reaction of (quinolin-8-yl)methanone with diazo substrates would yield a product in which the fragment of diazo is inserted between the C(O)–CH₃ bond. However, the experimental results show that the carbon–carbon double bond forms through an analogous mechanistic pathway involving C–H activation of the CH₃ group¹¹ and a rhodium carbene intermediate. We thus optimized the reaction conditions to establish an efficient method for the direct arylvinylation of (quinolin-8-yl)methanone with *N'*-arylidene-4-methylbenzenesulfonohydrazide. We report the results here.

Initially, (quinolin-8-yl)methanone (**1**) and *N'*-benzylidene-4-methylbenzenesulfonohydrazide (**2a**) were selected as cross-coupling partners to optimize the reaction conditions (Scheme 1).



Scheme 1 Cross-coupling of (quinolin-8-yl)methanone (**1**) and **2a**

The catalyst activities of a range of transition metals under the action of various bases were examined, and the results are summarized in Table 1. Rhodium complexes coordinate with directing groups, so they were considered first; initial results (entries 1–3) demonstrated that rhodium complexes exhibited low catalytic activity in the presence of Ag₂O under nitrogen at 130 °C without base. The product yields of the reactions varied according to the base used (Table 1, entry 6 and 10–16). The results show that Cs₂CO₃ was the best choice, and the reaction yielded the product in high yield (75%) after 48 hours in the presence of two equivalents of this base; increasing the amount of Cs₂CO₃ to 4.0 equiv did not lead to higher yield (Table 1, entries 6–8). Although other compounds such as K₂CO₃, K₃PO₄, *t*-BuOLi, *t*-BuOK, and MeONa are typically used as base in cross-coupling reactions, use of these additives in this system gave the desired product in less than 50% yield. When other rhodium complexes, such as

RhCl₃·3H₂O or [Rh₂(cod)₂Cl₂], were used as the catalyst, the reaction gave lower yield (Table 1, entries 4 and 5). Palladium complexes of Pd(OAc)₂, [Pd₂(dba)₃], and [Pd(PPh₃)₄] failed to generate the carbon–carbon double bond under the same conditions (Table 1, entries 17–19). Ru complexes such as RuCl₃·3H₂O, [Ru(PPh₃)₃Cl] or [Ru(cod)Cl₂] displayed lower catalytic activity (entries 20–22). In addition, the desired product was not obtained without a catalyst (Table 1, entry 9). Thus, [Rh(PPh₃)₃Cl] (10 mol%) and Cs₂CO₃ (2 equiv) were selected as the best catalyst and base, respectively.

Table 1 Optimization of the Catalyst and Base for Cross-Coupling of **1** and **2a**^a

Entry	Catalyst	Base (mmol)	Yield (%) ^b
1	RhCl ₃ ·3H ₂ O	–	0
2	Rh ₂ (cod) ₂ Cl ₂	–	<5
3	Rh(PPh ₃) ₃ Cl	–	<10
4	RhCl ₃ ·3H ₂ O	Cs ₂ CO ₃ (0.1)	25
5	Rh ₂ (cod) ₂ Cl ₂	Cs ₂ CO ₃ (0.1)	56
6	Rh(PPh ₃) ₃ Cl	Cs ₂ CO ₃ (0.1)	75
7	Rh(PPh ₃) ₃ Cl	Cs ₂ CO ₃ (0.05)	52
8	Rh(PPh ₃) ₃ Cl	Cs ₂ CO ₃ (0.2)	75
9	–	Cs ₂ CO ₃ (0.1)	0
10	Rh(PPh ₃) ₃ Cl	NaHCO ₃ (0.1)	32
11	Rh(PPh ₃) ₃ Cl	K ₂ CO ₃ (0.1)	47
12	Rh(PPh ₃) ₃ Cl	K ₃ PO ₄ (0.1)	<10
13	Rh(PPh ₃) ₃ Cl	NaOH (0.1)	35
14	Rh(PPh ₃) ₃ Cl	MeONa (0.1)	10
15	Rh(PPh ₃) ₃ Cl	<i>t</i> -BuOK (0.1)	<10
16	Rh(PPh ₃) ₃ Cl	<i>t</i> -BuOLi (0.1)	0
17	Pd(OAc) ₂	Cs ₂ CO ₃ (0.1)	0
18	Pd ₂ (dba) ₃	Cs ₂ CO ₃ (0.1)	0
19	Pd(PPh ₃) ₄	Cs ₂ CO ₃ (0.1)	0
20	RuCl ₃ ·3H ₂ O	Cs ₂ CO ₃ (0.1)	19
21	Ru(PPh ₃) ₃ Cl	Cs ₂ CO ₃ (0.1)	23
22	Ru(cod)Cl ₂	Cs ₂ CO ₃ (0.1)	48

^a Reaction conditions: **1** (0.05 mmol), **2a** (0.10 mmol), Ag₂O (0.025 mmol), catalyst (10.0 mol%), base (0.05 mmol or 0.1 mmol or 0.2 mmol), *o*-xylene (1.0 mL), 130 °C.

^b Isolated yield.

Further study revealed that the oxidant also plays an important role in achieving high yield. The corresponding yields using different oxidants are listed in Table 2. When copper salts were used as the oxidants, a low yield of **3a** was obtained (Table 2, entries 2–4). Silver salts, such as

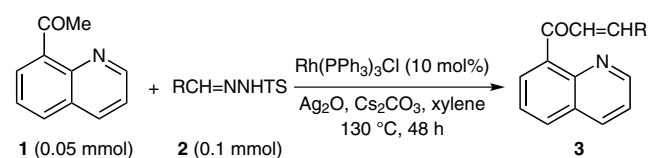
Ag₂CO₃ and AgSO₃CF₃, were also tested for the coupling reaction, but failed to produce higher yields than use of Ag₂O under similar reaction conditions (Table 2, entries 5–7). Oxidants K₂S₂O₈ and (NH₄)₂S₂O₈ were effective for the cross-coupling reactions of **1** and **2a** and the desired products were obtained with yields of 67 and 65%, respectively (Table 2, entries 8 and 9), however, the use of benzoic peroxyanhydride as oxidant prevented the reaction (Table 2, entry 10). Finally, 1,4-benzoquinone and tetrachlorobenzoquinone were also tested in an attempt to enhance the reaction, however, the product yields of 70 and 72%, respectively, were lower than those obtained when Ag₂O was used as oxidant (Table 2, entries 11 and 12). Thus, use of [(PPh₃)₃RhCl] as catalyst in combination with Cs₂CO₃ (2.0 equiv) and Ag₂O was selected as the optimal catalytic system for the transformation (Scheme 2).

Table 2 Optimization of the Oxidant for Cross-Coupling of **1** and **2a**

Entry	Oxidant	Yield (%) ^b
1	–	0
2	CuCl ₂	10
3	CuBr ₂	8
4	Cu(OAc) ₂	12
5	Ag ₂ O	75
6	Ag ₂ CO ₃	52
7	AgSO ₃ CF ₃	38
8	K ₂ S ₂ O ₈	67
9	(NH ₄) ₂ S ₂ O ₈	65
10	(PhCO) ₂ O ₂	0
11	1,4-benzoquinone	70
12	tetrachlorobenzoquinone	72

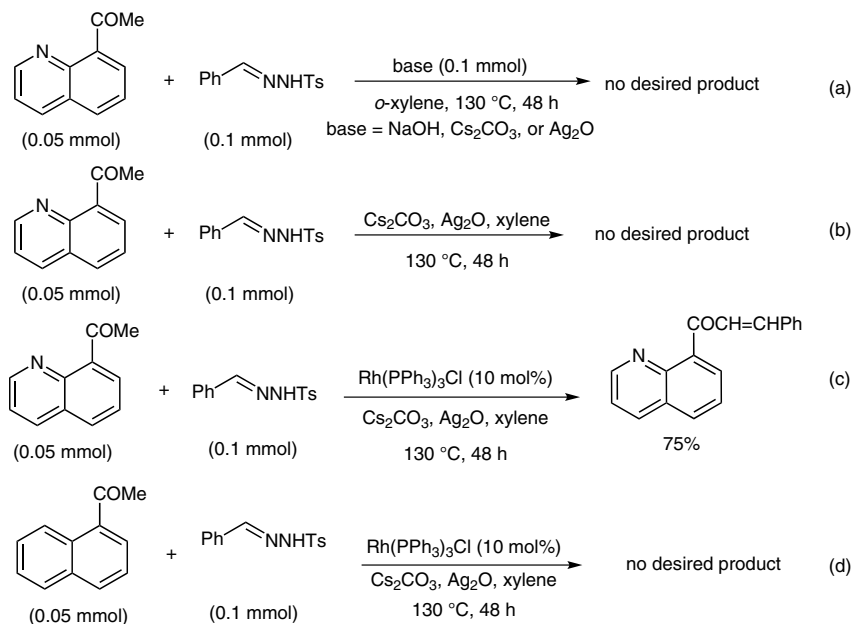
^a Reaction conditions: **1** (0.05 mmol), **2a** (0.1 mmol), [Rh(PPh₃)₃Cl] (10.0 mol%), Cs₂CO₃ (0.1 mmol), oxidant (0.025 mmol).

^b Isolated yield based on the amount of **1**.



Scheme 2 Reaction of **1** and arylaldehyde tosylhydrazones **2**

Benzaldehyde tosylhydrazones with a range of substituents were tested in the current transformations; the results are shown in Table 3. Benzaldehyde tosylhydrazones bearing an electron-donating group (Me, *i*-PrO, MeO or Ph) at the *para*-position showed good reactivity with **1** to produce the desired products in 73 to 78% yield (Table 3, entries 2–4 and 12). Tosylhydrazone of 1-naphthaldehyde



Scheme 3 Mechanism study

also showed good reactivity with **1**, and the desired product was obtained at 71% yield (Table 3, entry 13). Substitution of benzaldehyde tosylhydrazones at the *para*-

position by an electron-withdrawing group, such as -Cl, -Br or -I, resulted in a slight decrease in product yield (70–74%). However, when a substituent such as -Me, -Cl, -Br

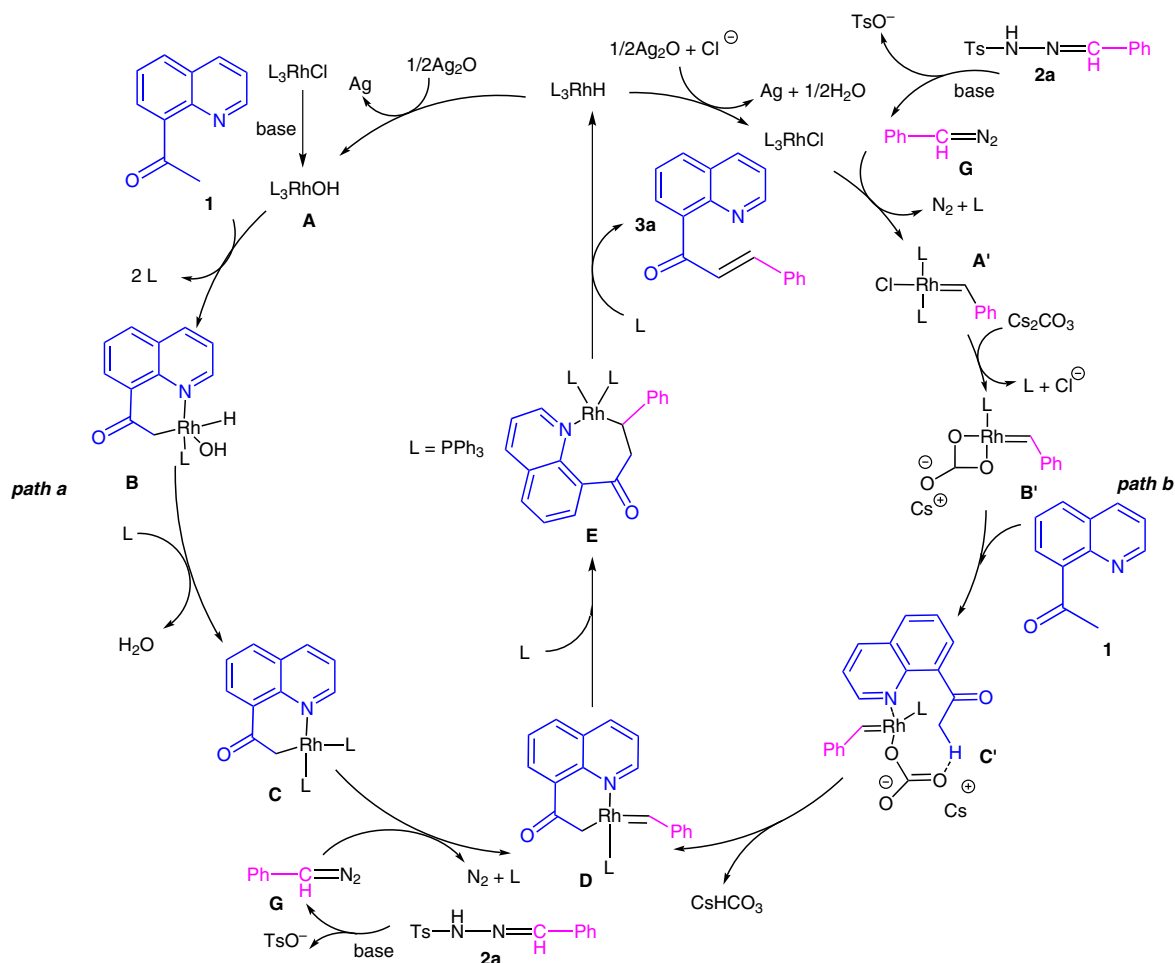
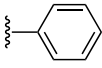
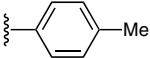
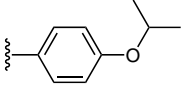
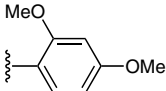
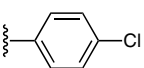
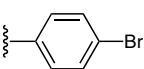
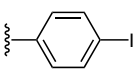
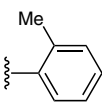
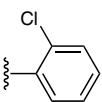
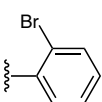
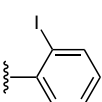
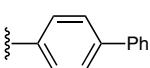
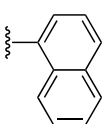
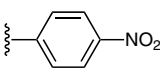
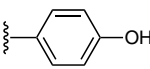
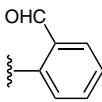
Scheme 4 Two plausible catalytic mechanisms for the cross-coupling reaction of **1** with benzaldehyde tosylhydrazone

Table 3 Reaction of **1** and Arylaldehyde Tosylhydrazones **2** Catalyzed by $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]^{\text{a}}$

Entry	2/3	R	Yield (%) ^b
1	a		75
2	b		76
3	c		78
4	d		75
5	e		70
6	f		73
7	g		74
8	h		68
9	i		66
10	j		65
11	k		63
12	l		73
13	m		71
14	n		0
15	o		0
16	p		0

^a Reaction conditions: **1** (0.05 mmol), **2** (0.10 mmol), Ag_2O (0.025 mmol), $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (10.0 mol%), Cs_2CO_3 (0.1 mmol), xylene (1.0 mL), 130 °C.

^b Isolated yield based on the amount of **1**.

or -I, was present at the *ortho*-position of the benzaldehyde tosylhydrazones, the product yield decreased significantly (Table 3, entries 8–11), indicating that the steric effect of arylaldehyde tosylhydrazone is an important factor for controlling reactivity. Halide substituents on the phenyl ring of the benzaldehyde tosylhydrazones were tolerated in the current transformation, which allowed further modification of these products. When a strong electron-withdrawing group substituted in the benzaldehyde tosylhydrazone, such as $-\text{NO}_2$ or $-\text{CHO}$ existed, the coupling reaction was completely shut down (Table 3, entries 14 and 16). This result suggests that the coupling reaction with **1** was affected significantly by the electron density of the arylaldehyde tosylhydrazone. That is, the higher the electron density on the phenyl ring of the arylaldehyde tosylhydrazones, the greater is the reactivity in the coupling reaction. Benzaldehyde tosylhydrazones bearing a hydroxyl group at the *para* position also prevented reaction with **1** because the hydroxyl group readily reacts with the base to yield insoluble salt.

No target product was observed when the reaction was conducted in the presence of Cs_2CO_3 , NaOH or Ag_2O , which are typical reaction conditions for aldol condensation (Scheme 3, a). The combination of Cs_2CO_3 and Ag_2O also gave no product (Scheme 3, b). The reaction occurred only when the rhodium complex was added in the presence of Ag_2O (0.5 equiv) and Cs_2CO_3 (2.0 equiv), indicating the importance of the rhodium complex in promoting the reaction (Scheme 3, c). When 1-(naphthalen-1-yl)ethanone was used as the substrate to replace (quinolin-8-yl)methanone, the reaction did not proceed in the presence of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (10 mol%), Ag_2O (0.5 equiv), and Cs_2CO_3 (2 equiv) at 130 °C for 48 hours, indicating that the nitrogen atom in the substrate may play an important role in directing the rhodium metal center close to the C–H bonds of the methyl group (Scheme 3, d). On the basis of this evidence we therefore conclude that the aldol condensation mechanism can be completely excluded.

Based on the above experiments, two plausible catalytic mechanisms based on C–H activation processes are proposed (Scheme 4). First, the chloride anion in $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ is replaced by a hydroxide anion through the treatment of base to form complex **A** (Scheme 4, path a). After ligand exchange reaction of **1** with complex **A**, the rhodium metal center moves close to the C–H bond of the Me group through coordination of the nitrogen atom of **1**. The oxidative addition of the C–H bond to the Rh(I) metal center in **A** then leads to the formation of Rh(III) complex **B** after removal of two phosphine ligands. A recent literature report also indicated that the *ortho*-C–H activation of 8-acylquinolines can be selectively achieved by the appropriate choice of catalysts and solvents.¹¹ Rh(III) complex **B** is unstable and subsequently loses a molecule of H_2O in the presence of PPh_3 ligand to yield Rh(I) complex **C**. Reaction of diazo compound **G**, generated in situ by treatment of benzaldehyde tosylhydrazone **2a** with base, with Rh(I) complex **C** produces rhodium carbene intermediate **D**. Similar reactions have been re-

ported in many previous cases.¹² Migration and insertion of the benzylidene group to the Rh–C bond produces intermediate **E**, and β -hydride elimination affords the product **3a** and generates the Rh–H compound. Catalyst **A** is finally regenerated from the latter species in the presence of Ag₂O, which enters the next cycle.

According to some literature reports,¹³ the important intermediate **D** can also be generated through the following four steps (Scheme 4, path b): First, a phosphine ligand of [Rh(PPh₃)₃Cl] may be replaced by diazo benzyl carbene to produce rhodium carbene intermediate **A'**. The chloride anion then exchanges with the carbonate ion of Cs₂CO₃, leading to the formation of complex **B'** after releasing a phosphine ligand. Further ligand exchange of **B'** with **1** gives complex **C'**, in which the rhodium metal is directed close to the C–H bond of the methyl group of **1**. The C–H activation then takes place, which is assisted by the oxygen atom of the carbonate anion, producing rhodium carbene intermediate **D** after loss of CsHCO₃.

To further investigate the reaction mechanism, more experiments were conducted in an attempt to trap some important intermediates generated during the reaction process as direct evidence. Thus, the stoichiometric reaction of [Rh(PPh₃)₃Cl] with **1** and **2a** under similar reaction conditions was conducted, but failed to reveal any mechanistic information. In this case, the desired product was obtained in high yield, with no key intermediate being observed either during or after the reaction by NMR or TLC analysis, indicating that the key intermediates may be formed in very low concentration that could not be observed by using conventional tools. In many cases, these rhodium carbene species are not stable and are difficult to detect by traditional methods.¹⁴ Although the isolation of the key intermediates was unsuccessful, the indirect evidence mentioned above do provide some hints for the C–H activation mechanism we proposed.

In conclusion, an alternative method for the direct arylvinylation of (quinolin-8-yl)methanone with substituted *N*-benzylidene-4-methylbenzenesulfonylhydrazide is described.¹⁵ The desired 3-aryl-1-(quinolin-8-yl)prop-2-en-1-one products are obtained in high yields through the catalytic reaction with [Rh(PPh₃)₃Cl] in the presence of Ag₂O and Cs₂CO₃ at 130 °C for 48 hours. Two plausible mechanisms involving the C–H activation and migratory insertion of the carbene into the rhodium–carbon bond were proposed to explain the formation of the products. Further efforts to expand the scope of this reaction are underway in our laboratories.

Acknowledgment

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- (15) **Synthesis of 3-Phenyl-1-(quinolin-8-yl)prop-2-en-1-one (Scheme 2 and Table 3, Entry 1); Typical Procedure:** A mixture of (quinolin-8-yl)methanone (85.5 mg, 0.5 mmol), *N'*-benzylidene-4-methylbenzenesulfonohydrazide (548.6 mg, 1.0 mmol), Ag₂O (58.0 mg, 0.25 mmol), Cs₂CO₃ (232 mg, 1.0 mmol), and [Rh(PPh₃)₃Cl] (46.65 mg, 0.05 mmol) under nitrogen in a screw-capped thick-walled Pyrex tube was heated at 130 °C with stirring. After heating for 48 h, the reaction mixture was cooled and directly purified by column chromatography on silica gel (hexane–EtOAc, 20:1) to afford 3-phenyl-1-(quinolin-8-yl)prop-2-en-1-one (75% yield).

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