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# A catechol-catalyzed photocatalytic carbonylative four-component reaction of alkylboronic acids with aldehydes and amines†

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Carbonylation reactions employing CO as an easily accessible C1 source have emerged as one of the most powerful tools for constructing carbonyl-containing compounds from readily available starting materials. Despite the impressive achievements on carbonylative transformations, a fundamental limitation of these approaches lies in their reliance on transition

metal catalysis or a stoichiometric amount of activating reagents. Herein, we report the first photo-induced catechol-catalyzed four-component carbonylation reaction of alkylboronic acids with aldehydes and amines. A range of valuable substituted  $\alpha$ -amino ketones was produced in moderate to good yields.

## Green foundation

1. The first catechol-catalyzed photo-induced four-component carbonylation reaction.
2. Organocatalysts avoid the use of transition metal catalysts and photocatalysis makes use of the advantages of light.
3. Four-component carbonylation reaction of alkylboronic acids with aldehydes and amines for the direct synthesis of  $\alpha$ -aminoketones.

## Introduction

$\alpha$ -Amino ketones hold an important position in organic synthesis; they are not only key structural units of many natural products, bioactive molecules, and pharmaceuticals, but also serve as versatile synthetic intermediates, demonstrating good reactivity and diversity.<sup>1</sup> In 1850, Strecker's pioneering work laid an important foundation for the synthesis of  $\alpha$ -amino ketones.<sup>2</sup> Since then, various excellent methods for the synthesis of  $\alpha$ -amino ketones have been developed, such as using photocatalysis<sup>3</sup> or metal-free systems,<sup>4</sup> which have greatly improved the efficiency and selectivity of the synthesis. Despite these significant achievements, the quest for greener and more efficient methods for their synthesis remains a continuous pursuit. Carbonylation reactions<sup>5</sup> are a class of impor-

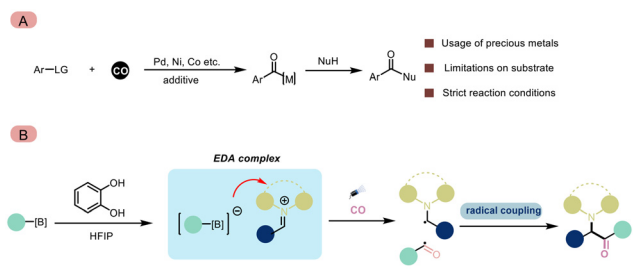
tant transformations for the synthesis of carbonyl-containing compounds, while increasing the carbon chain of the parent organic molecules. These reactions are widely used in the synthesis of various pharmaceutical intermediates, natural products, and functional materials, and hence play an important role in synthetic and medicinal chemistry.<sup>6</sup> Traditional carbonylation reactions are typically catalyzed by noble transition metals such as palladium<sup>7</sup> and rhodium,<sup>8</sup> with ligands modulating the catalyst's activity to enable efficient CO adsorption to yield a series of carbonylated compounds (Fig. 1A). In recent years, carbonylation reactions catalyzed by base metals such as nickel,<sup>9</sup> copper,<sup>10</sup> cobalt,<sup>11</sup> and manganese<sup>12</sup> have also made significant breakthroughs. Despite the obvious advantages of transition metal-catalyzed carbonylation reactions in synthesizing complex organic molecules, there are also some limitations, such as the high toxicity and cost of metal catalysts, sensitivity to air and moisture, and several others. The development of photocatalytic carbonylation offers the potential for sustainable carbonylative transformations.<sup>13</sup> However, in most of the cases, the need for precious metal photosensitizers counteracted the advantages somehow. To overcome these limitations, research on developing milder and greener<sup>14</sup> carbonylation procedures remains a constant goal for synthetic chemists.

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**Fig. 1** (A) Traditional carbonylation reactions and (B) catechol-catalysed carbonylation of alkyl boronic acid (this work).

Catalysts, which are capable of modulating the rates of chemical reactions, are ubiquitous in organic synthesis. Metal catalysts have traditionally been the mainstay in this field,<sup>15</sup> leveraging their pronounced catalytic activity to facilitate a vast array of transformations. As awareness of environmental sustainability continues to grow, non-metal catalysts have increasingly attracted the attention of chemists. These non-metal catalysts, typically composed of organic molecules containing oxygen, nitrogen, phosphorus, and other atoms, are more and more popular for their environmentally friendly attributes. In recent years, non-metal framework catalysts have made significant progress in enhancing the reaction efficiency. In asymmetric synthesis, nitrogen-containing catalysts are more commonly utilized as they exploit intermolecular hydrogen bonds formed by nitrogen–hydrogen atoms to elucidate the stereochemistry of the reaction.<sup>16</sup> Phosphorus-containing catalysts such as triphenylphosphine and chiral phosphoric acids either increase the electron density of the substrate to boost the efficiency of electrophilic reactions or control the chirality of the products through phosphorus–hydrogen bonding.<sup>17</sup> Oxygen-containing catalysts currently function as oxidants in a variety of nucleophilic reactions<sup>18</sup> and can also serve as radical initiators in radical reactions.<sup>19</sup> Phenolic compounds can also facilitate reactions through the formation of hydrogen bonds. Catechol, as an oxygen-containing organic compound, exhibits unique catalytic properties in chemical reactions. It can directly form intermediates with substrates that contain carbon–oxygen bonds<sup>20</sup> or silicon–oxygen bonds<sup>21</sup> to promote the progress of the reaction. It can also act as an activator to enhance the activity of metal catalysts such as palladium and copper to carry out the reaction. However, the example of catechol directly serving as a catalyst has not been reported so far. Organic photothermal molecules represent another category of non-metal catalysis, among which those with donor–acceptor (D–A) structures have been most extensively studied.<sup>22</sup> Through appropriate structural modifications, the twisted intramolecular charge transfer (TICT) effect can be enhanced, more effectively promoting the photothermal conversion process. For example, Qin's group<sup>23</sup> utilized catechol-derived intermediates to form EDA complexes with substrates, facilitating single-electron transfer to enabling the Mannich reaction of alkylboronic acids, yielding a series of sp<sup>3</sup> carbon-containing amine compounds.

In response to the call for green chemistry, carbonylation research has gradually shifted towards greener and more efficient directions in recent years, evolving from traditional precious metal catalysis to base metal catalysis and even non-metal catalysis. During this period, carbonylation reactions promoted by EDA (Electron Donor–Acceptor) complexes formed from specially structured organic photothermal molecules have been developed. In 2023, Chen's group<sup>24</sup> reported a visible-light-induced radical relay five-component radical diaminocarbonylation reaction of unactivated alkenes, where the EDA complex generated from Umemoto's reagent and amines under light irradiation yielded two radicals that subsequently underwent carbonylation and radical coupling to afford the desired products. Wu's group also reported several non-metal-catalyzed carbonylation reactions that were catalyzed by phosphines<sup>25</sup> and amines.<sup>26</sup> Although these excellent methods have enriched the content of carbonylation, the presence of some additional additives, such as bases, is still indispensable in these transformations. The pursuit of simpler and more efficient carbonylation methods remains our constant goal. In order to fill the gap where carbonylation of boronic acids was previously limited on catalyzed by metals, herein, we report a catechol-catalyzed carbonylation reaction induced by visible light using alkylboronic acids, aldehydes, and amines as the starting materials, which proceeds under a carbon monoxide atmosphere (Fig. 1B). In our design, the alkylboronic acid serves as the initial reactant, forming a boronate *in situ* with catechol. Meanwhile, the iminium ion generated from the condensation of aldehydes and amines then forms an EDA complex with the boronate, which undergoes single-electron transfer under light irradiation to generate two carbon radicals. These radicals subsequently undergo radical carbonylation and radical cross-coupling to yield the desired product. This method has the advantages of mild conditions and no need for additional additives. Using catechol as the catalyst and under light irradiation, a series of valuable  $\alpha$ -amino ketones was generated effectively and the scale up experiment proved the practicability of this protocol.

**Table 1** Screening of reaction conditions<sup>a</sup>

| Entry | Modifications                 | Yield (%)            |
|-------|-------------------------------|----------------------|
| 1     | None                          | 99 (90) <sup>b</sup> |
| 2     | 1 mL HFIP                     | 54                   |
| 3     | 390 nm instead of 456 nm      | 85                   |
| 4     | 365 nm instead of 456 nm      | 62                   |
| 5     | W/o light                     | 13                   |
| 6     | Catechol (30 mol%)            | 92                   |
| 7     | W/o catechol                  | 0                    |
| 8     | Air instead of N <sub>2</sub> | 59                   |
| 9     | nBuBpin instead of 3a         | 0                    |

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), **3a** (0.15 mmol), CO (60 bar), catechol (50 mol%), and HFIP (2 mL). The yield was determined by GC-FID analysis using dodecane as an internal standard.

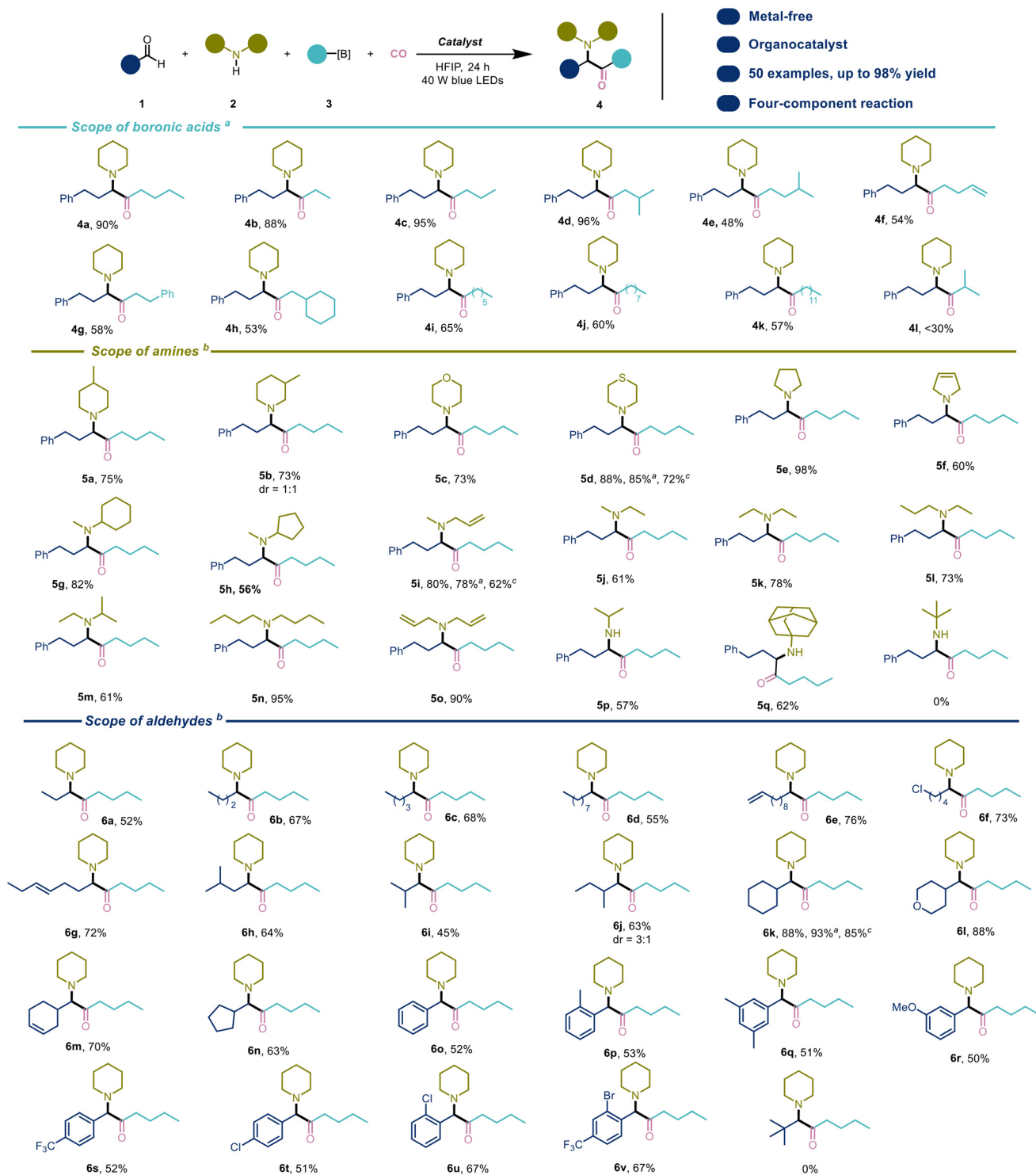
<sup>b</sup> Isolated yield.



## Results and discussion

At the start of our investigation, we selected phenylpropanal **1a**, piperidine **2a**, and *n*-butyl boronic acid **3a** as the substrates, and catechol as the catalyst under carbon monoxide

pressure to establish the catalytic system. Initially, we explored various solvents, including protic and aprotic solvents and polar and nonpolar solvents, yet none could yield the desired product except for hexafluoroisopropanol (HFIP), which afforded the desired product **4a** in 68% yield (for details, see



**Fig. 2** Substrate scope of the reaction. Standard conditions: **1** (0.1 mmol), **2** (0.1 mmol), **3** (0.15 mmol), HFIP (2 mL), CO (60 bar), rt, blue LEDs, 24 h, and isolated yield. <sup>a</sup> Catechol (50 mol%), <sup>b</sup> catechol (1.5 equiv.) and <sup>c</sup> catechol (30 mol%).

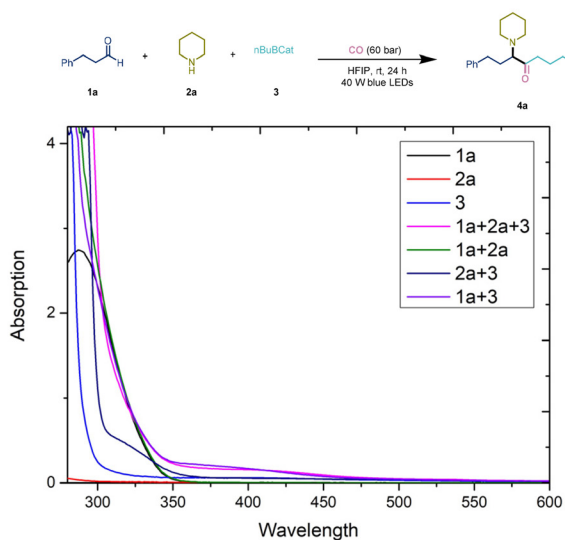


the ESI<sup>+</sup>). We speculate that HFIP not only serves as a solvent but also participates in the reaction, rendering its presence indispensable.<sup>27</sup> Subsequently, we adjusted the stoichiometric ratios of the three components. An optimized ratio of **1a** : **2a** : **3a** at 1 : 1 : 1.5 enhanced the yield to 75%. We further explored the catalytic effects of different groups on catechol. Both electron-withdrawing and electron-donating groups were tested, but unfortunately, none surpassed the catalytic efficacy of unsubstituted catechol. Adjusting the carbon monoxide pressure revealed its significant impact on the reaction. Increasing the pressure from 20 bar to 60 bar increased the yield from 48% to 74%. We also investigated the reaction concentration, finding that a 2 mL volume of HFIP increased the yield to 99% in GC (gas chromatography), with an isolated yield of 90% (Table 1, entry 1). In contrast, reducing the HFIP volume to 1 mL resulted in a reduced 54% yield of **4a** (Table 1, entry 2). The yield of the target product was reduced when shifting the blue light wavelength from 456 nm to 390 nm or 365 nm (Table 1, entries 3 and 4). In the absence of light irradiation, only 13% of the desired **4a** was detected (Table 1, entry 5). Reducing the amount of catechol to 30 mol% can still achieve a GC yield of 92% of the targeted product (Table 1, entry 6). The reaction failed in the absence of catechol (Table 1, entry 7), and a decreased yield was obtained when performing the reaction in air (Table 1, entry 8). No desired product could be detected when using nBuBpin as the reaction partner (Table 1, entry 9).

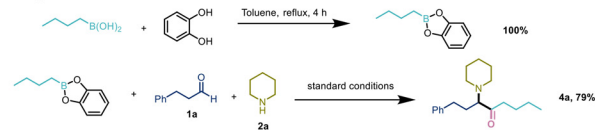
With the optimal reaction conditions established, we initiated an exploration of the substrate scope of the reaction (Fig. 2). A range of boronic acids was tested at the first stage. Primary alkylboronic acids exhibited favourable reactivity, achieving moderate to excellent yields of the desired products. For linear boronic acids, reactivity diminished progressively with increasing chain length (**4i**–**4k**). Primary boronic acids

with branched chains or those bearing alkenyl or aryl groups along the chain also demonstrated satisfactory reactivity (**4f** and **4g**). In comparison, secondary boronic acids showed a significant decrease in reactivity. Isopropyl boronic acid, for instance, yielded the corresponding product with less than 30% yield (**4l**). Tertiary boronic acids were also tested but entirely unreactive, likely due to their steric hindrance impeding CO insertion. Aromatic boronic acids were found to be unsuitable for this transformation and no desired product could be detected under the standard conditions. Subsequently, we examined the reactivity of various amines. Piperidine derivatives with methyl groups at different positions afforded the desired products **5a** and **5b** in 75% and 73% yields, respectively. Replacing piperidine with morpholine (**5c**) or thiomorpholine (**5d**) also resulted in high yields of the corresponding products. Notably, linear secondary amines, including both symmetric and asymmetric ones, exhibited excellent reactivity. Dibutylamine (**5n**) produced the corresponding product with an impressive yield of 95%, while asymmetric *N*-methylcyclohexylamine (**5g**) yielded the target product in 82% yield. Additionally, primary amines such as isopropylamine (**5p**) and adamantylamine (**5q**) underwent conversion with moderate to good yields. However, the reaction failed when aniline was tested. Lastly, we tested the reactivity of aldehydes bearing different substituents. Both aliphatic and aromatic aldehydes were compatible in this reaction. Short-chain aldehydes like propionaldehyde (**6a**) or long-chain aldehydes like nonanal (**6d**), as well as aldehydes with double bonds (**6e** and **6g**) or halogen groups (**6f**) on the chain, delivered the corresponding products with moderate to good yields (52–76%). Esters of cyclohexanone also exhibited moderate to good reactivity (**6k**–**6n**). For aromatic aldehydes (**6o**–**6v**), products were obtained regardless of whether the benzene ring was substituted with electron-withdrawing groups (–Cl,

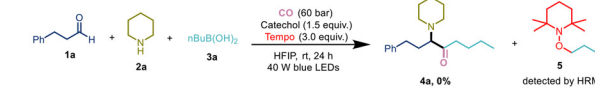
A. UV absorption spectrum



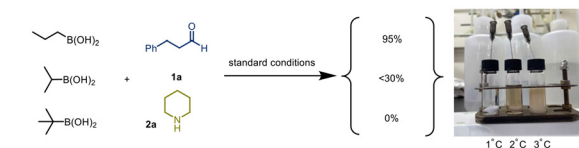
B. Synthesis of nBuBcat



C. Radical capture experiment



D. Comparison of the reactivity of alkylboronic acids



E. Scale-up experiment

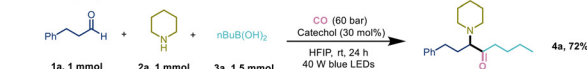


Fig. 3 Mechanistic studies and scale-up experiment.



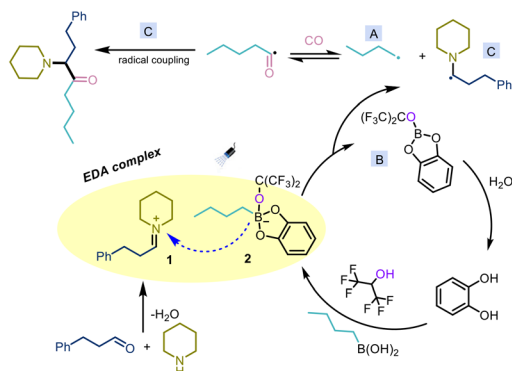


Fig. 4 Proposed reaction pathway.

–Br, and –CF<sub>3</sub>) or electron-donating groups (–Me and –OMe). However, the reaction failed with pivaldehyde. Higher loading of catechol was needed in some cases to make sure the concentration of the reactive intermediate generated *in situ* due to the decreased reactivity of the substrates.

To obtain insight into the reaction pathway, a series of control experiments was conducted (Fig. 3). The appearance of a new absorption band in the UV spectrum of a mixture of **1a**, **2a**, and **3** suggested the formation of an EDA complex (Fig. 3A).<sup>28</sup> The reaction of separately prepared *n*-butyl boronate with aldehydes and amines afforded the desired product in 79% yield (Fig. 3B). The addition of three equivalents of TEMPO (2,2,6,6-tetramethylpiperidinyloxy) completely inhibited the reaction, and the detection of **5** by HRMS indicated a radical pathway (Fig. 3C). The reactivity differences among primary, secondary, and tertiary alkyl boronic acids were further compared and confirmed (Fig. 3D). A scale-up reaction of our model system was carried out as well, and 75% of the desired **4a** was isolated (Fig. 3E).

Based on our results and understanding, we propose a plausible reaction mechanism (Fig. 4). Initially, *n*-butyl boronic acid reacts with catechol to form *n*-butyl boronate, while the aldehyde and amine react to form an iminium ion. In the presence of the solvent HFIP, these two species form an EDA complex. Subsequent photoirradiation generates two radicals, **A** and **C**, and another molecule **B**, which hydrolyzes to regenerate catechol. Radical **A**, after CO insertion, couples with radical **C** to yield the desired product. It is worth mentioning that the high pressure of CO was needed to drive the acyl radical generation, which is reversible. The direct reaction between intermediates **A** and **C** was the main side-reaction named the non-carbonylation reaction.

## Conclusions

In summary, we have developed a novel photocatalytic four-component carbonylative reaction of alkylboronic acids with aldehydes and amines catalyzed by catechol. Through radical intermediates, various substituted  $\alpha$ -amino ketones were produced with moderate to excellent yields. The reaction proceeds

under mild conditions, exhibits strong functional group tolerance, and offers a new and efficient route for the synthesis of  $\alpha$ -amino ketones.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the ESI.†

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