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The direct photochemical cross-esterification of alcohols *via* site-selective C-H bromination

The direct photochemical cross-esterification of alcohols proceeds *via* the *in situ* generation of acyl bromides. The C-H bond of a benzyl alcohol is selectively activated by a bromo source under light irradiation, enabling the cross-esterification to afford the functionalized esters.

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**We have developed a direct photochemical cross-esterification of alcohols that proceeds *via* the *in situ* generation of acyl bromides. The C–H bond of a benzyl alcohol is selectively activated by a bromo source under light irradiation, enabling the cross-esterification to afford a variety of functionalized esters.**

Esters represent an important structural motif found in a wide variety of bioactive compounds and functional materials. While conventional esterification reactions typically use carboxylic acids or aldehydes as substrates,<sup>1</sup> the direct oxidative esterification of alcohols has been developed as an alternative method. The esterification of alcohols typically employs transition-metal catalysts or stoichiometric oxidants (Scheme 1(a)).<sup>2</sup> Meanwhile, photochemical transformations have gained significant attention in recent years due to their potential in sustainable energy-conversion systems, and several methods for the photochemical esterification of alcohols have been developed. In 2012, Itoh and co-workers have reported the cross-esterification of benzyl alcohol with aliphatic alcohols such as methanol as the solvent in the presence of CBr<sub>4</sub> under an oxygen atmosphere and irradiation from a household lamp (Scheme 1(b)).<sup>3</sup> More recently, in 2024, the one-pot, two-step esterification of benzyl alcohol with alcohols using trichloroisocyanuric acid (TCCA), a stoichiometric amount of triethylamine, and a catalytic amount of 4-dimethylaminopyridine (DMAP) under blue-light irradiation has been reported (Scheme 1(c)).<sup>4,5</sup> While these reactions represent useful methods that use alcohols as substrates, there are still only a few examples of the photochemical esterification of alcohols. Therefore, the development of more efficient approaches to photochemical esterification reactions remains highly desirable.

## The direct photochemical cross-esterification of alcohols *via* site-selective C–H bromination

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Recently, we have developed the photochemical esterification of aldehydes with alcohols *via* C–H bromination.<sup>6</sup> Given that bromo sources such as bromotrichloromethane (BrCCl<sub>3</sub>) effectively activate the C–H bonds of aldehydes, we hypothesized that they could also potentially activate the C–H bonds of benzyl alcohols, thus enabling the application of bromo sources in cross-esterification reactions. Here, we report the direct photochemical cross-esterification of alcohols *via* site-selective C–H bromination (Scheme 1; This work).



**Scheme 1** Examples of photochemical cross-esterification reactions of alcohols.

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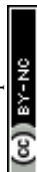


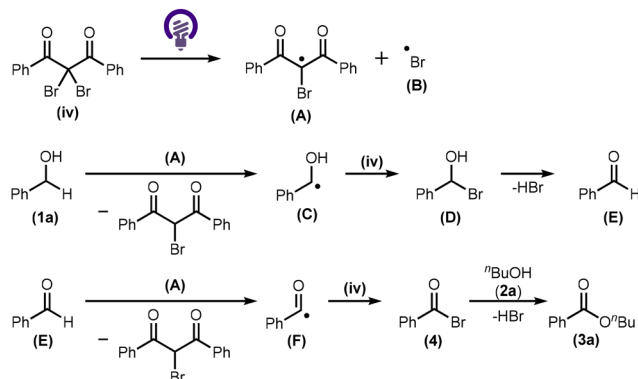


Table 2 Scope of the alcohols suitable for this photochemical esterification<sup>a</sup>

<sup>a</sup> All reactions were carried out using **1** (0.4 mmol), **2** (0.8 mmol), a Br source (**iv**) (2.4 mmol), and MS3A (100 mg) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) at room temperature under an argon atmosphere and LED irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ , 18 W) for 24 h. <sup>b</sup> The reaction was carried out using **1** (0.4 mmol), **2** (1.6 mmol), a Br source (**iv**) (2.4 mmol), and MS3A (100 mg) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) at room temperature under an argon atmosphere and LED irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ , 18 W) for 72 h. <sup>c</sup> The reaction was carried out using **1** (0.4 mmol), **2** (0.8 mmol), a Br source (**iv**) (2.4 mmol), and MS3A (100 mg) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) at room temperature under an argon atmosphere and LED irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ , 18 W) for 48 h.



Scheme 2 Mechanistic aspects of the photochemical cross-esterification of alcohols.



Scheme 3 Proposed reaction mechanism.



In summary, we have developed a method for the direct photochemical esterification of alcohols. The reaction affords the corresponding esters without the requirement for any additives such as bases, and bypasses the need for a sequential one-pot, two-step protocol. Various benzyl alcohols bearing electron-donating or electron-withdrawing substituents, as well as  $\pi$ -conjugated functionalities, were well tolerated in the reaction. Notably, this method is applicable to the synthesis of multi-substituted esters, which are commonly found in functional materials and are typically prepared *via* the Fischer esterification, which often proceeds under much harsher reaction conditions. The present reaction enables the synthesis of a wide range of functionalized esters from alcohols, making it a valuable tool for producing bioactive compounds and functional materials.

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## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cc03371c>.

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