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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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As featured in:



See Isao Kadota, Kenta Tanaka *et al.*, *Chem. Commun.*, 2025, **61**, 17364.


 Cite this: *Chem. Commun.*, 2025, 61, 17364

 Received 14th June 2025,  
 Accepted 3rd October 2025

DOI: 10.1039/d5cc03371c

rsc.li/chemcomm

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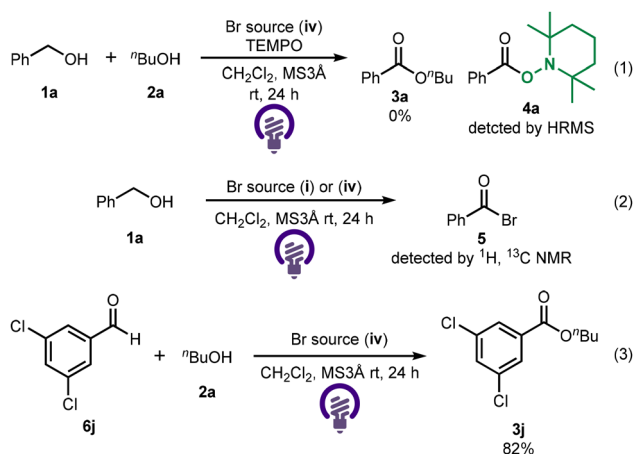
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Table 2 Scope of the alcohols suitable for this photochemical esterification<sup>a</sup>

<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.

This work was supported by Wesco Scientific Promotion Foundation and JSPS KAKENHI Grants JP25K18038. We appreciate the assistance of the Division of Instrumental Analysis at Okayama University with NMR spectroscopy and high-resolution mass spectrometry.

## 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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