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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  $\text{CH}_2\text{Cl}_2$  (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  $\text{CH}_2\text{Cl}_2$  (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  $\text{CH}_2\text{Cl}_2$  (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>.

## Notes and references

- (a) J. Oreta and J. Nishikido, *Esterification: Methods, Reactions, and Applications*, Wiley-VCH, Weinheim, 2nd edn, 2010; (b) S. Tang, J. Yuan, C. Liu and A. Lei, *Dalton Trans.*, 2014, **43**, 13460–13470; (c) S. Gaspa, A. Porcheddu and L. De Luca, *Tetrahedron Lett.*, 2016, **57**, 3433–3440; (d) K. Ekoue-Kovi and C. Wolf, *Chem. Eur. J.*, 2008, **14**, 6302–6315; (e) L. Ding, P. Su, Y. Shi, H. Huang, L. Zhu, H. Zhang and B. Wang, *Ind. Eng. Chem. Res.*, 2024, **63**, 18667–18698; (f) J. Li, D. Zhu, D. J. Young, Y. Wang and H. Li, *Eur. J. Org. Chem.*, 2025, **28**, e202401398.
- (a) C. Liu, J. Wang, L. Meng, Y. Deng, Y. Li and A. Lei, *Angew. Chem., Int. Ed.*, 2011, **50**, 5144–5148; (b) D. Srimani, E. Balaraman, B. Gnanaprakasam, Y. Ben-David and D. Milstein, *Adv. Synth. Catal.*, 2012, **354**, 2403–2406; (c) J. Cheng, M. Zhu, C. Wang, J. Li, X. Jiang, Y. Wei, W. Tang, D. Xue and J. Xiao, *Chem. Sci.*, 2016, **7**, 4428–4434; (d) Y. Yu, J. Lin, A. Qin, H. Wang, J. Wang, W. Wang, G. Wu, Q. Zhang, H. Qian and S. Ma, *Org. Lett.*, 2024, **26**, 3469–3474; (e) R. Ray, R. D. Jana, M. Bhadra, D. Maiti and G. K. Lahiri, *Chem. Eur. J.*, 2014, **20**, 15618–15624; (f) S. Samanta, V. Pappula, M. Dinda and S. Adimurthy, *Org. Biomol. Chem.*, 2014, **12**, 9453–9456; (g) S. Gaspa, A. Porcheddu and L. De Luca, *Adv. Synth. Catal.*, 2016, **358**, 154–158.
- T. Nobuta, A. Fujiya, S. Hirashima, N. Tada, T. Miura and A. Itoh, *Tetrahedron Lett.*, 2012, **53**, 5306–5308.
- A. Dellisanti, E. Chessa, A. Porcheddu, M. Carraro, L. Pisano, L. De Luca and S. Gaspa, *Molecules*, 2024, **29**, 570.
- H. Yi, X. Hu, C. Bian and A. Lei, *ChemSusChem*, 2017, **10**, 79–82.
- Our recent reports see; (a) H. Ando, S. Kodaki, H. Takamura, I. Kadota and K. Tanaka, *Org. Biomol. Chem.*, 2024, **22**, 9032–9035; (b) H. Ando, H. Takamura, I. Kadota and K. Tanaka, *Chem. Commun.*, 2024, **60**, 4765–4768; (c) S. Nohara, S. Iwai, N. Yamaguchi, Y. Asada, Y. Kamiyama, Y. Tanaka, K. Tanaka and Y. Hoshino, *Synlett*, 2023, 2525–2529; (d) K. Tanaka, M. Kishimoto, Y. Tanaka, Y. Kamiyama, Y. Asada, M. Sukekawa, N. Ohtsuka, T. Suzuki, N. Momiyama, K. Honda and Y. Hoshino, *J. Org. Chem.*, 2022, **87**, 3319–3328; (e) M. R. El-kholany, T. Senoo, A. Mizutani, H. Takamura, T. Suzuki, I. Kadota and K. Tanaka, *Org. Lett.*, 2025, **27**, 4870–4874.
- (a) M. Leloire, C. Walshe, P. Devaux, R. Giovine, S. Duval, T. Bousquet, S. Chibani, J. Paul, A. Moissette, H. Vezin, P. Nerisson, L. Cantrel, C. Volkringer and T. Loiseau, *Chem. Eur. J.*, 2022, **28**, e202104437; (b) S. Zhao, J. Zhang, X. Wang, L. Wang, J. Wang and C. Pang, *ACS Appl. Polym. Mater.*, 2023, **5**, 2408–2416; (c) O. Plietzsch, A. Schade, A. Hafner, J. Huuskonen, K. Rissanen, M. Nieger, T. Muller and S. Bräse, *Eur. J. Org. Chem.*, 2013, **2013**, 283–299.
- (a) S. Huo, X. Deng, N. Yang, M. Qin, X. Zhang, X. Yao, C. An, P. Zhou and X. Lu, *Chem. Eng. J.*, 2024, **481**, 148562; (b) B. H. Wilson, H. S. Scott, O. T. Qazvini, S. G. Telfer, C. Mathonière, R. Clérac and P. E. Kruger, *Chem. Commun.*, 2018, **54**, 13391–13394; (c) D. De, V. Sharma, B. C. Sahu, R. K. Sahu and T. Maharana, *Polyhedron*, 2023, **230**, 116240; (d) G. R. M. O'Donohue, S. Chow, S. D. Houston, T. T. L. Nguyen, G. Paul Savage, H. E. Smyth and C. M. Williams, *Chem. Eur. J.*, 2025, **31**, e202404716.
- (a) P. Bosch, F. Del Monte, J. L. Mateo and R. S. Davidson, *J. Photochem. Photobiol., A*, 1993, **73**, 197–204; (b) I. Saito, T. Sakurai, T. Kurimoto and M. Takayama, *Tetrahedron Lett.*, 1994, **35**, 4797–4800; (c) Y.-B. Wang, F. Chen, M. Li, Q. Bu, Z. Du, J. Liu, B. Dai and N. Liu, *Green Chem.*, 2023, **25**, 1191–1200; (d) X. Li, J. Fan, D. Cui, H. Yan, S. Shan, Y. Lu, X. Cheng and T. Loh, *Eur. J. Org. Chem.*, 2022, e202200340.
- C. S. Colley, D. C. Grills, N. A. Besley, S. Jockusch, P. Matousek, A. W. Parker, M. Towrie, N. J. Turro, P. M. W. Gill and M. W. George, *J. Am. Chem. Soc.*, 2002, **124**, 14952–14958.
- (a) S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.*, 2003, **36**, 255–263; (b) E. T. Denisov and V. E. Tumanov, *Russ. Chem. Rev.*, 2005, **74**, 825–858.
- (a) N. Gong, Z. Zhao, D. James Young, X. Cao, Z. Ren and H. Li, *Chem. Eur. J.*, 2025, **31**, e202404225; (b) Z. Zhao, W. Li, Q. Shan, D. J. Young, Z.-G. Ren and H.-X. Li, *J. Org. Chem.*, 2025, **90**, 1616–1627; (c) S. Kang, M. T. La and H.-K. Kim, *Tetrahedron Lett.*, 2018, **59**, 3541–3546; (d) Y.-D. Kwon, M. T. La and H.-K. Kim, *New J. Chem.*, 2018, **42**, 10833–10841.

