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Facile synthesis of 1,2-aminoalcohols *via* α-C–H aminoalkylation of alcohols by photoinduced hydrogen-atom transfer catalysis†

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1,2-Aminoalcohols are common motifs found in a wide range of natural products and pharmaceutical compounds. Here we report a photocatalytic method for the direct conversion of readily available aliphatic alcohols into synthetically valuable 1,2-aminoalcohols. A dual catalytic system consisting of an acridinium photoredox catalyst and a cationic hydrogen-atom transfer (HAT) catalyst based on 1,4-diazabicyclo[2.2.2]octane (DABCO) enables an efficient and site-selective HAT from the α-C–H bonds of unprotected primary and secondary alcohols. The subsequent radical addition to a newly designed chiral *N*-sulfinyl α-iminoester afforded various 1,2-aminoalcohols, including enantiomerically enriched ones, under mild photochemical conditions with high atom and step economy.

1 Introduction

1,2-Aminoalcohols are a ubiquitous structural motif found in a diverse array of natural products, agrochemicals, and pharmaceuticals (Fig. 1a).[1] They also play a pivotal role in organic synthesis as privileged ligands and catalysts.[2] Therefore, the development of efficient methods for the preparation of these motifs, particularly in a stereoselective manner, is undoubtedly an important area of chemical research. While various approaches, including the oxyamination of alkenes,[3a–c] ring-opening of epoxides,[3d] reductive cross-coupling of carbonyls with imines,[3e] and others,[3f–m] have been reported to date, most of them suffer from intrinsic drawbacks. These include the necessity for noble metals and/or toxic chemicals, as well as multi-step synthesis for the preparation of specific substrates. Given the abundance and wide availability of aliphatic alcohols as feedstock chemicals, the direct conversion of primary or secondary alcohols into synthetically valuable 1,2-aminoalcohols would be an ideal approach. However, such methods are currently limited to a few reports where primary alcohols are the only applicable substrates.[4]

Hydrogen-atom transfer (HAT) is a powerful strategy to functionalize C(sp^3)–H bonds *via* the generation of carbon-centred radicals.[5] The recent development of photoinduced HAT catalytic systems, most of which are enabled by the combination with a photoredox catalyst (PC), has offered a unique opportunity to manipulate the C(sp^3)–H bonds of a wide range of substrates under mild conditions in high atom and step economy.[6] Imine derivatives are attractive acceptors for the carbon-centred radicals generated by the HAT process, providing structurally diverse amine derivatives. Indeed, photochemical methods for C–H aminoalkylation of a variety of substrates with different HAT catalysts have been reported in recent years (Fig. 1b).[7] Surprisingly, however, the use of alcohols as substrates for radical addition to imines *via* the HAT process has not been included in these reports, although site-selective HAT from the α-C–H bond of aliphatic alcohols has been achieved in several other C–H functionalization reactions.[8] Herein, we addressed this underexplored area by using a cationic HAT catalyst based on 1,4-diazabicyclo[2.2.2]octane (DABCO), which was recently developed by our group (Fig. 1c).[9] We envisioned that the highly electrophilic dicationic aminium radical **I** would be suitable for selective HAT from a strong but hydridic α-C–H bond of an alcohol with the aid of a favourable polar effect.[10] Meanwhile, imine derivatives were investigated in detail to identify an appropriate structure as an acceptor for the carbon-centred radical generated *in situ* from the alcohol substrate.

Based on our previous research,[9] the proposed mechanism for the present PC/HAT dual catalytic system is outlined in Fig. 2. Upon irradiation with visible light, the organophotoredox catalyst 9-mesityl-10-methylacridinium perchlorate (**Mes-Acr+**) transitions to a long-lived excited state (**Mes-Acr+***) with a high oxidation potential (E_{red}[**Mes-Acr+***/**Mes-Acr$^•$**] of 2.06 V *vs.* saturated calomel electrode (SCE) in MeCN),[11] which oxidizes the HAT catalyst (**DABCO+**) *via* single-electron transfer (SET) to generate the dicationic aminium radical **I**. The subsequent HAT process between the alcohol and **I** furnishes the corresponding

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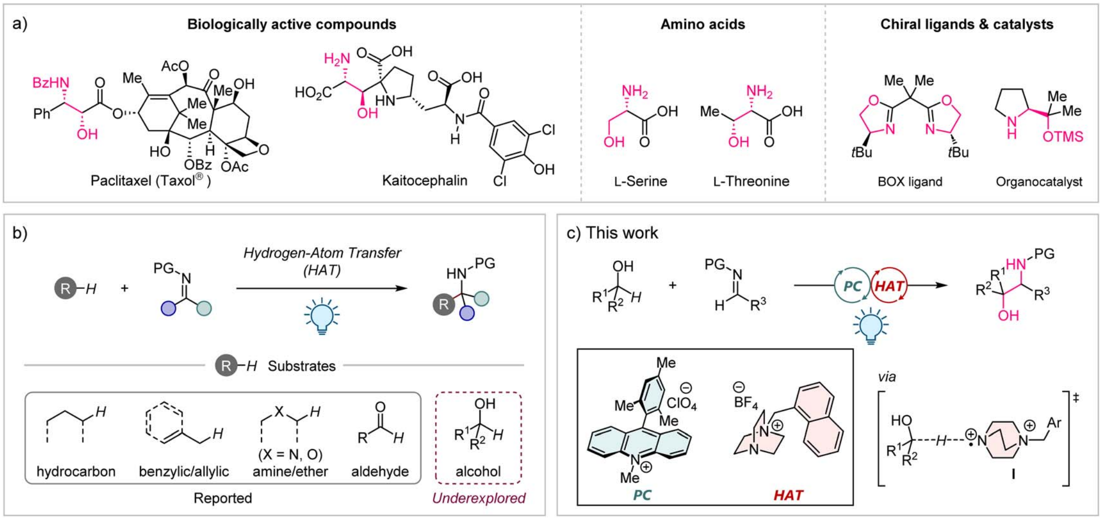


Fig. 1 (a) 1,2-Aminoalcohol as a ubiquitous structural motif. (b) C–H Aminoalkylation *via* HAT process. (c) Synthesis of 1,2-aminoalcohols from alcohols and imines by PC/HAT dual catalysis.

α-hydroxy carbon-centred radical **II**, which undergoes the radical addition to imine **1** to give the nitrogen-centred radical **IV**. The catalytic cycle would be closed by the single-electron reduction of **IV** by acridine radical **Mes-Acr**$^{\bullet}$ and the subsequent proton transfer, affording the desired 1,2-aminoalcohol.

2 Results and discussion

We commenced our investigation by screening imine derivatives as acceptors for the α-hydroxy carbon-centred radical generated *in situ* from ethanol (Fig. 3). Imine derivatives from *p*-chlorobenzaldehyde, including *N*-Boc imine **1a**, *N*-tosyl imine **1b**, and *N*-tosylhydrazone **1c**, provided none of the corresponding products. A more electrophilic *N*-tosylhydrazone derived from ethyl glyoxylate (**1d**) gave a detectable amount of the expected 1,2-aminoalcohol product, and the further introduction of an electron-withdrawing trifluoromethyl group at the sp^2 carbon of the hydrazone moiety (**1e**) significantly increased the yield. These trends indicate that the highly electrophilic

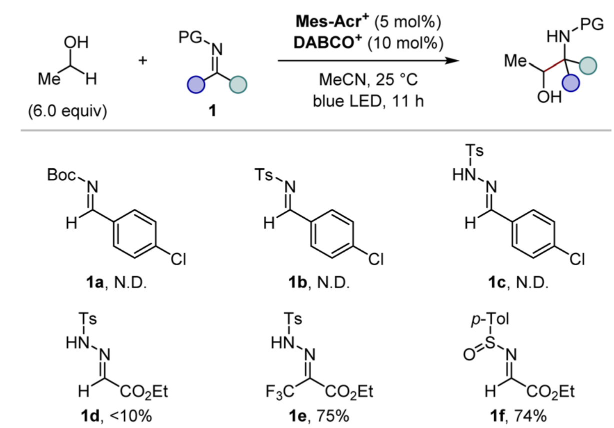


Fig. 3 Screening of imine derivatives. Yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. *Syn*/*anti* selectivity of the 1,2-aminoalcohol moiety was <1.6 : 1 in all cases. N.D. = Not Detected.

character at the imine moiety is crucial to achieve sufficient reactivity. Given the good balance between electrophilicity and chemical stability, applicability to asymmetric synthesis, and ease of deprotection, we focused on *N*-sulfinyl α-iminoesters as the imine partners. Gratifyingly, the reaction of ethyl (*E*)-*N*-(*p*-toluenesulfinyl)iminoacetate (**1f**) with ethanol gave the 1,2-aminoalcohol product in a good yield. We then moved on further investigations of the substituent of the sulfinyl moiety (Fig. 4). Since Ellman's *tert*-butyl-substituted *N*-sulfinyl imine is known to be incompatible with radical-mediated conditions, we focused on aryl-substituted *N*-sulfinyl derivatives.[12] Although *para*- or *ortho*-monosubstituted phenyl groups (**1f–h**) gave good yields of 1,2-aminoalcohol products, the stereochemistry of the α-carbon relative to the chiral sulfur centre in the sulfinyl moiety was not well controlled (<3 : 1 dr, Fig. 4, entries 1–3). On the other hand, the sterically more hindered mesityl group (**1i**)

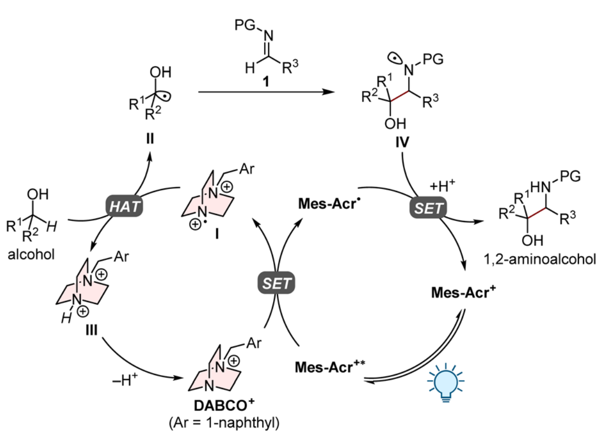
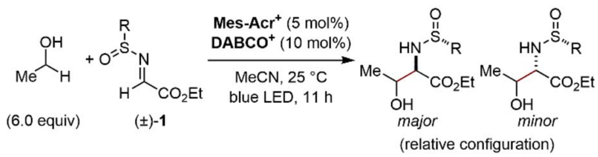


Fig. 2 Proposed catalytic cycle.



entry	R	yield (%)	major : minor
1	(1f)	74	<3 : 1
2	(1g)	70	1.9 : 1
3	(1h)	85	1.4 : 1
4	(1i)	34	>19 : 1
5	(1j)	93	7.3 : 1
6	(1k)	70	>19 : 1
7[a]	(1k)	83	>19 : 1

Fig. 4 Screening of *N*-sulfinyl α-iminoesters. Yields and ratios of isomers were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. *Syn*/*anti* selectivity of the 1,2-aminoalcohol moiety was <1.3 : 1 in all cases. [a]The reaction was run for 6 h using 3 equiv. of EtOH.

showed high diastereoselectivity at the α-carbon, albeit with a lower yield (Fig. 4, entry 4). Thus, we expected that the introduction of electron-withdrawing groups at the two *ortho*-positions of the phenyl ring would facilitate the transfer of chirality from the sulfur centre to the α-carbon while maintaining the high electrophilicity at the imine carbon, thereby delivering both high reactivity and diastereoselectivity. Indeed, the *ortho*-difluorophenyl group (**1j**) efficiently produced the product with an increased diastereoselectivity (Fig. 4, entry 5). Finally, the slightly bulkier *ortho*-dichlorophenyl group (**1k**) was found to be the optimal substituent of the sulfinyl moiety, affording the desired 1,2-aminoalcohol in a good yield with a high diastereoselectivity at the α-carbon (Fig. 4, entry 6). Although the *syn*/*anti* selectivity of the 1,2-aminoalcohol moiety was not controlled even after the optimization of reaction conditions (<1.3 : 1 in all cases), it was found that both the equivalents of ethanol and the reaction time could be reduced (Fig. 4, entry 7). Notably, other HAT catalysts, including those used in the reported conditions for radical addition to imine derivatives,[7] did not provide the desired radical adduct from ethanol and (±)-**1k** (See the ESI for details†). These results demonstrate an advantage of our photocatalytic system where the exceptionally electrophilic aminium radical **I** is responsible for an efficient HAT process from the α-C–H bond of the alcohol.

With the optimal *N*-sulfinyl α-iminoester in hand, the scope of primary and secondary alcohols was evaluated (Fig. 5). The relative stereochemistry between the α-carbon and the sulfur centre in the 1,2-aminoalcohol products was fully controlled in all cases (>19 : 1 dr). A series of (deuterated) methanol and primary alcohols with varying degrees of steric bulk were good substrates for hydrogen-atom abstraction by the cationic DABCO-based HAT catalyst, affording the corresponding products in moderate to high yields (**2k** and **3–9**). Alcohols bearing several functional groups, such as acetoxy (**10**), siloxy (**11**), chloro (**12**), *para*-substituted benzoyloxy (**13–16**), and phthaloyl groups (**17**), were well tolerated. Of note, these reactions occurred selectively at the α-C–H bond to the hydroxy group. Moreover, despite the increased steric hindrance, both acyclic (**18**, **19**, and **23–25**) and cyclic (**20–22**) secondary alcohols successfully afforded bulky 1,2-aminoalcohols. It was also possible to switch the ester group in the *N*-sulfinyl α-iminoester from ethyl to benzyl (**26** and **27**), suggesting the utility of our method for the synthesis of amino acids by the subsequent removal of the benzyl protecting groups. In addition to alcohols, the reactivity of other substrates was briefly examined. Cyclohexane, a representative of hydrocarbons containing stronger C–H bonds than the α-C–H bond of alcohols, afforded the α-monoalkylated amino acid derivative **28** in a good yield. The etheric substrates THF and 2,2-dimethyl-1,3-dioxolane were also suitable substrates, furnishing the corresponding products **29** and **30**, respectively, in high yields.

Having established our protocol for the facile construction of 1,2-aminoalcohols, an asymmetric synthesis was conducted by using optically active *N*-sulfinyl α-iminoesters (Fig. 6). Both enantiomers of **1k** were prepared according to Senanayake's method (see the ESI†).[13] The α-C–H aminoalkylation of cyclopentanol with (*R*)-**1k** under optimal conditions, followed by the deprotection of the sulfinyl moiety and *N*-benzoylation, afforded the enantiomerically enriched 1,2-aminoalcohol (*R*)-**31** with 98% *ee*. We then demonstrated the synthesis of all possible isomers of threonine and allothreonine derivatives. The use of ethanol and (*S*)-**1k** in this protocol provided a mixture of (2*S*,3*S*)-**32** and (2*S*,3*R*)-**32** as derivatives of L-allothreonine and L-threonine, respectively. Similarly, the reaction of ethanol with (*R*)-**1k** gave a mixture of (2*R*,3*S*)-**32** and (2*R*,3*R*)-**32**, which are derivatives of D-threonine and D-allothreonine, respectively. These results indicate that the present method can be used for rapid access to the desired stereoisomers of chiral 1,2-aminoalcohols starting from an aliphatic alcohol.

We performed analytical studies to better understand the reaction mechanism (Fig. 7). Stern–Volmer fluorescence quenching studies revealed that **DABCO$^+$** quenches the excited state of photocatalyst **Mes-Acr^{+}***, whereas quenching by (±)-**1k** is negligible (Fig. 7a). The reduction potential of (±)-**1k** was −1.2 V *vs.* SCE according to the cyclic voltammetry measurement, indicating that the single-electron reduction of (±)-**1k** by acridine radical **Mes-Acr$^{\bullet}$** ($E_{1/2}$[**Mes-Acr$^+$/Mes-Acr$^{\bullet}$**] = −0.57 V *vs.* SCE) would not be favoured (Fig. 7b).[11] Therefore, a radical–radical coupling between an α-hydroxy radical and an α-amino radical generated *in situ* from the alcohol and *N*-sulfinyl α-iminoester, respectively, would be unlikely. On the other hand, the efficient diastereocontrol at the α-carbon relative to the sulfur centre supports the radical addition pathway to the s-*cis* form of

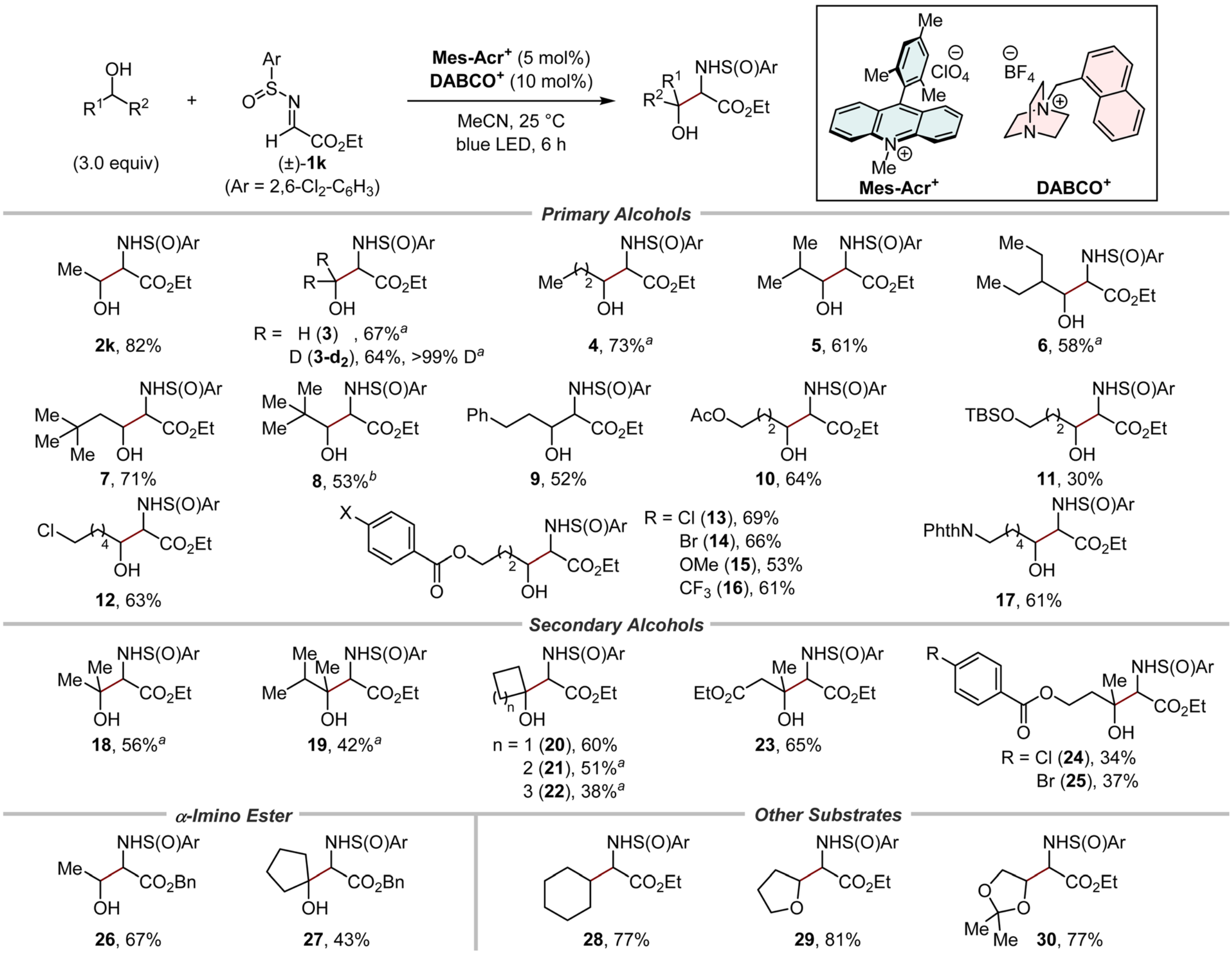


Fig. 5 Substrate scope. Combined yields of isolated products were shown. Unless otherwise noted, *syn*/*anti* selectivity of the 1,2-aminoalcohol moiety was <1.8 : 1 (see the ESI for details†). [a] 6.0 Equivalents of alcohols were used. [b] *Syn*/*anti* selectivity was 2.6 : 1.

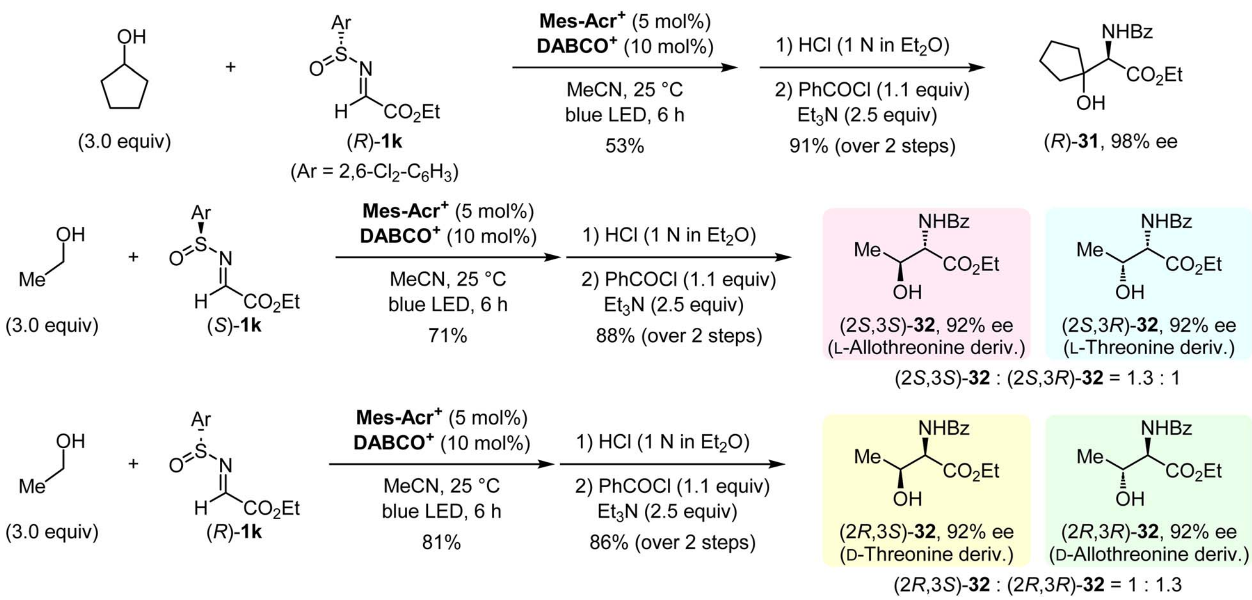


Fig. 6 Asymmetric synthesis of 1,2-aminoalcohols.

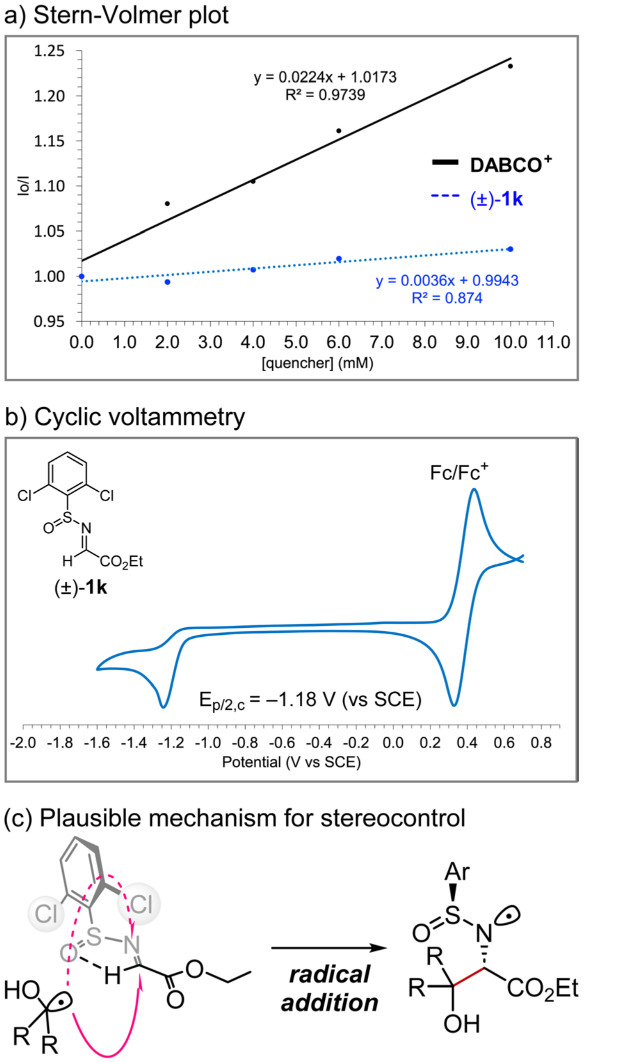


Fig. 7 Mechanistic studies.

the *N*-sulfinyl α-iminoester, which is conformationally locked due to internal hydrogen bonding, as described by Kärkäs *et al.* (Fig. 7c).[12b] Overall, these results are consistent with the proposed mechanism shown in Fig. 2.

3 Conclusions

In summary, we have developed a straightforward method for the synthesis of 1,2-aminoalcohols from readily available alcohols and imine derivatives. A dual photocatalytic system consisting of an acridinium organophotoredox catalyst and a cationic DABCO-based catalyst enabled an efficient and site-selective HAT from the α-C–H bond of various primary and secondary alcohols. In addition, a newly designed *N*-sulfinyl α-iminoester **1k** was found to be a suitable imine acceptor for the *in situ*-generated α-hydroxy carbon-centred radical, which successfully expanded the scope of C–H aminoalkylation *via* a photoinduced HAT process. The asymmetric synthesis of 1,2-aminoalcohols was also achieved by using an enantiomerically enriched *N*-sulfinyl α-iminoester.

Author contributions

A. M. conceptualized the research. A. M. and J. C. performed the experiments and prepared the manuscript. K. M. supervised the project and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

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