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Visible-light excitation of iminium ions enables the enantioselective catalytic β-alkylation of enals

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Chiral iminium ions—generated upon condensation of α,β-unsaturated aldehydes and amine catalysts—are used extensively by chemists to make chiral molecules in enantioenriched form. In contrast, their potential to absorb light and promote stereocontrolled photochemical processes remains unexplored. This is despite the fact that visible-light absorption by iminium ions is a naturally occurring event that triggers the mechanism of vision in higher organisms. Herein we demonstrate that the direct excitation of chiral iminium ions can unlock unconventional reaction pathways, enabling enantioselective catalytic photochemical β-alkylations of enals that cannot be realized via thermal activation. The chemistry uses readily available alkyl silanes, which are recalcitrant to classical conjugate additions, and occurs under illumination by visible-light-emitting diodes. Crucial to success was the design of a chiral amine catalyst with well-tailored electronic properties that can generate a photo-active iminium ion while providing the source of stereochemical induction. This strategy is expected to offer new opportunities for reaction design in the field of enantioselective catalytic photochemistry.

Enantioselective organocatalysis has emerged in recent years as a powerful technology in the realm of chiral molecule synthesis[1]. This strategy uses chiral small organic molecules as catalysts to trigger and control a chemical reaction via generic mechanisms of substrate activation and induction[2]. One such mode of activation exploits the capacity of secondary amines of type **1** to reversibly condense with enals **2** to form iminium ion intermediates **I** (Fig. 1a). Electronic redistribution within **I**, by lowering the energy of the lowest unoccupied molecular orbital (LUMO), facilitates conjugate additions of nucleophiles to the β-carbon atom[3]. Over the past 15 years, the ground-state reactivity of electron-poor iminium ions has found a myriad of applications in the stereoselective β-functionalization of enals **1**, effectively complementing established metal-based asymmetric strategies for conjugate additions to unsaturated carbonyl compounds[4].

Iminium ions also play a crucial role in biological systems. Nature uses the capacity of these ions for absorbing visible light to trigger the primary photochemical event underlying visual transduction[5,6]. The mechanism of vision in vertebrates is initiated by light excitation of the iminium ion formed upon condensation of 11-*cis*-retinal with the ε-amino group of a lysine residue within opsins (Fig. 1b). Crucially, 11-*cis*-retinal undergoes a bathochromic absorption shift from the ultraviolet (~370 nm) to the visible region (>400 nm) upon formation of the iminium ion[7]. Although the photoexcitation of iminium ions is a well-established biochemical process, it is largely underused by the organic chemistry community. The photoactivity of preformed cyclic non-conjugated iminium ions was exploited in chemical synthesis during the 1980s[8–11]. However, to the best of our knowledge, this light-driven strategy remains unexplored in the realm of enantioselective catalysis.

We recently questioned whether the synthetic potential of iminium ion catalysis could be expanded from the established ground-state domain into the seemingly distinct fields of excited-state reactivity[12] and asymmetric photochemistry[13]. We were motivated by our recent studies demonstrating that chiral enamines[14–16], key intermediates in thermal organocatalytic enantioselective processes[17], could directly participate in the photoexcitation of substrates while inducing the stereocontrolled formation of chiral products (Fig. 1c). Specifically, we showed that electron-rich enamines, which are primarily understood as nucleophiles in their ground state, could become strong reductants upon light excitation and trigger the formation of radicals through the SET reduction of electron-poor organic halides. At the same time, the ground-state chiral enamines provided effective stereochemical control over the enantioselective radical trapping process. That strategy, where stereoinduction and photoactivation merged in a sole chiral organocatalytic intermediate, enabled light-driven enantioselective transformations that could not be realized using the thermal reactivity of enamines. For the present study, we thus surmised that using light excitation to bring the electron-poor iminium ion **I** to an electronically excited state **I*** could provide further opportunities for reaction inventions. Since an excited state possesses much higher electronic affinity (that is, it is a better electron acceptor) than the ground state[18], we hypothesized that the photoexcited iminium ion **I*** could function as a strong oxidant, affording reactive open-shell intermediates upon SET oxidation of electron-rich substrates of type **3** (Fig. 1d). If successful, this strategy would complement the photochemical activity of enamines by using a completely different series of radical precursors. In addition, it would unlock unique reaction manifolds that are unavailable to conventional ground-state iminium ion chemistry. Herein, we document how this ideal was translated to experimental reality, demonstrating that visible-light excitation of catalytically generated chiral iminium ions **I** enables highly stereoselective β-alkylations of enals **2** that cannot be realized via thermal activation. More specifically, non-nucleophilic and readily available organic trimethylsilane reagents **3**, which are recalcitrant to classical conjugate addition manifolds, have been successfully used as coupling partners for photochemical enal functionalizations.

Results and discussion

Design plan. Figure 2 presents a detailed description of our proposed mechanism for the photochemical β-alkylation of enals

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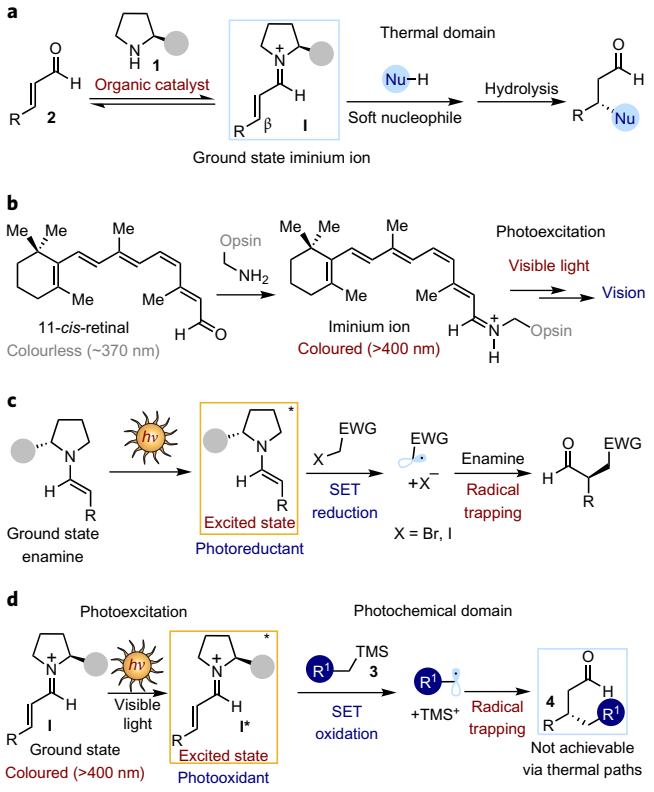


Figure 1 | Reactivities of iminium ions in biological systems and enantioselective catalytic synthesis. a, Established ground-state reactivity of chiral iminium ions **I** as electrophiles in enantioselective conjugate additions. **b**, In biological systems, the visible-light excitation of the iminium ion—formed upon condensation of 11-*cis*-retinal with a lysine residue of opsins—is the primary photochemical event of vision. **c**, Our previous studies demonstrated that chiral enamines, which are primarily understood as nucleophiles in their ground state, can become potent single-electron reductants upon light excitation and trigger the generation of radicals through the SET reduction of electron-poor organic halides, thus promoting enantioselective α-alkylation of aldehydes. **d**, Proposed strategy to unlock reaction manifolds unavailable to conventional ground-state iminium ion chemistry: enantioselective β-alkylation of enals with non-nucleophilic alkyl silanes **3** driven by the visible-light excitation of iminium ions **I**, which act as chiral photo-oxidants to afford reactive open-shell intermediates upon SET oxidation of **3**. TMS, trimethylsilyl; EWG, electron-withdrawing group; SET, single-electron transfer. The filled grey circles represent a bulky substituent on the chiral amine catalyst.

2 with alkyl silanes **3**, enabled by iminium ion excitation. We anticipated that, in analogy with the biological mechanism of vision (Fig. 1b), the condensation of a chiral secondary amine catalyst **1** with enal **2** would convert an achromatic substrate into a coloured iminium ion **I**. Visible-light excitation (>400 nm) would then provide an electronically excited state **I*** through a π–π* transition, which could function as a strong oxidant in single-electron transfer (SET) processes. Specifically, we hoped that an SET from the electron-rich alkyl trimethylsilane **3** to the photo-excited iminium ion **I*** would occur to furnish the 5π-electron β-enaminyl radical intermediate **II** along with the silyl radical cation **III**. Mechanistically, the choice of organic silanes **3** as redox partners is motivated by (i) their relatively low oxidation potential (E_{ox}), which facilitates their SET oxidation[19]; and (ii) the tendency of the resulting **III** to undergo rapid desilylation in the presence of weak nucleophiles, including solvents such as acetonitrile (CH_3CN) (ref. 20). Such irreversible fragmentation of the carbon–silicon bond in **III** is critical because, by hampering an unproductive back-electron transfer (BET), it would trigger the generation of neutral radical intermediates **IV** along with a formal trimethylsilyl cation (TMS^+). At this juncture, we presumed that a stereocontrolled intermolecular coupling of the chiral β-enaminyl radical **II** with **IV** would form a new C–C bond while forging the stereogenic centre. The resulting enamine intermediate **V**, upon hydrolysis, would regenerate the catalyst **1** while liberating the β-functionalized aldehyde **4**.

From the outset, we recognized the choice of the chiral secondary amine **1** as key to realizing our design plan. Indeed, the electronic properties of catalyst **1** must be adequately tuned to chemically enable four critical steps, including (i) the generation of an iminium ion **I** that can absorb visible light to reach an excited state **I***, and (ii) the effective SET reduction of **I*** from the silane **3**. The last step requires the catalyst to confer a high oxidizing capability to the excited iminium ion **I***, because the thermodynamic facility of photoinduced SET is determined by the difference between the donor oxidation potential (E_{ox} ($\mathbf{3}^{\bullet+}/\mathbf{3}$)) and the acceptor excited state reduction potential (E_{red}^* ($\mathbf{I}^*/\mathbf{I}^{\bullet-}$)). At the same time, since a secondary amine may be prone to SET oxidation[21], catalyst **1** should (iii) not be electron-rich enough to outcompete **3** as a redox donor in the reduction of **I*** — that is, E_{ox} ($\mathbf{I}^{\bullet+}/\mathbf{1}$) should be higher than E_{ox} ($\mathbf{3}^{\bullet+}/\mathbf{3}$). Finally, the chiral catalyst should (iv) enforce high levels of enantiocontrol in the coupling of the planar 5π-electron β-enaminyl radical **II** with alkyl radicals **IV**. With respect to this C–C bond-forming event, it was recently demonstrated that β-enaminyl radicals of type **II**,

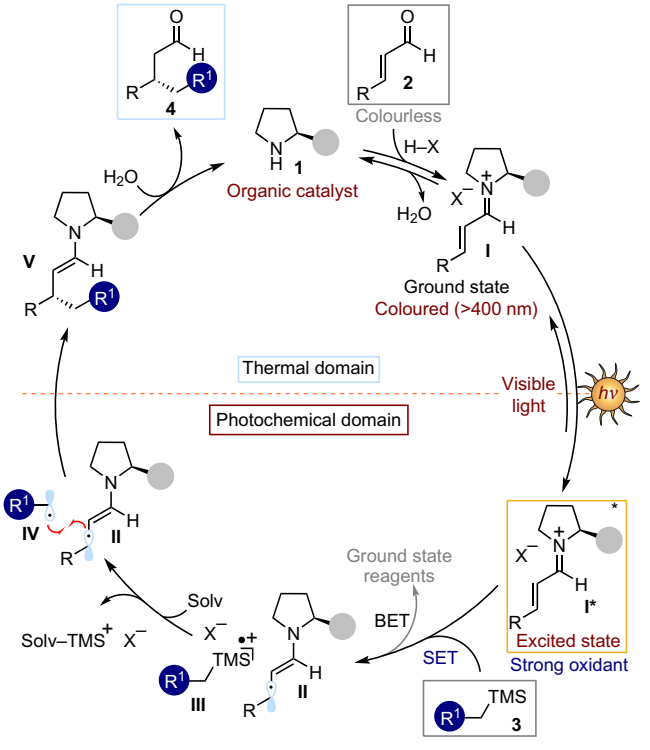
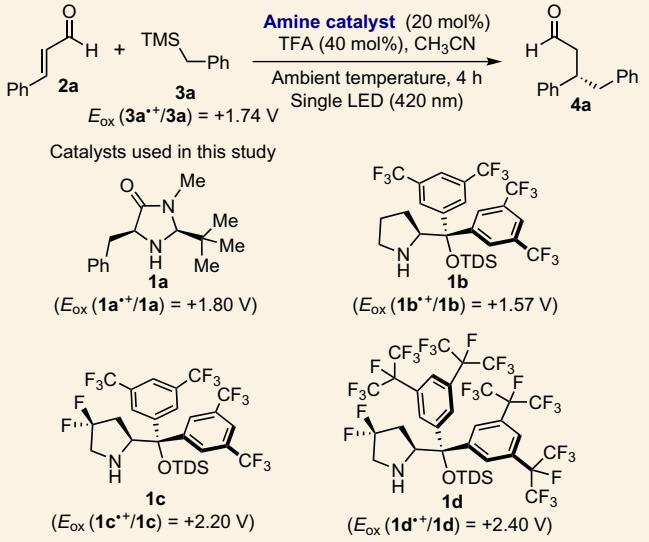


Figure 2 | Design plan and mechanistic proposal: exploiting the direct photoexcitation of transiently generated chiral iminium ions I to enable stereocontrolled photochemical processes. Central to this study is the high oxidizing capability of the excited iminium ion **I*** that can drive, by SET oxidation of **3**, the formation of alkyl radicals **IV** and the chiral β-enaminyl radical intermediate **II**, which are primed for the ensuing enantiocontrolled radical coupling reaction. H–X, organic acid; TMS, trimethylsilyl; SET, single-electron transfer; BET, back-electron transfer. The filled grey circles represent a bulky substituent on the chiral amine catalyst; Solv, nucleophilic solvent, such as CH_3CN or water.

Table 1 | The model reaction and the chiral catalysts evaluated.



Entry	Catalyst	Light	3a yield (%)	e.e. (%)
1	1a	On	79	30
2	None	On	0	-
3	1a	Off	0	-
4	1b	On	28	76
5	1c	On	83	85
6	1d	On	87	88

E_{ox} for catalysts 1 measured by cyclic voltammetry versus Ag/Ag^+ in CH_3CN.

generated via a completely different approach[22,23], are generally prone to radical–radical coupling mechanisms, albeit not through stereocontrolled manifolds.

Photochemical enantioselective β-benzylation of cinnamaldehyde. We tested the feasibility of our photochemical strategy by exploring the reaction between cinnamaldehyde **2a** and benzyl trimethylsilane **3a** (Table 1). The choice of **3a** was motivated by its established tendency toward a SET oxidation–desilylation sequence to afford a benzyl radical[24], which is facilitated by the presence of the trimethylsilyl (TMS) electroauxiliary group[19] and the relatively low oxidation potential (E_{ox} (**3a**$^{\bullet+}$/**3a**) = +1.74 V versus Ag/Ag^+ in CH_3CN). We confirmed that the condensation of the colourless **2a** with the commercially available imidazolidinone catalyst **1a** (ref. 3) generated an iminium ion **Ia** absorbing until 440 nm (blue line, Fig. 3a). With the aim of selectively exciting the transient chiral iminium ion **Ia**, we conducted the explorative experiments detailed in Table 1 in CH_3CN under irradiation by a single high-power visible-light-emitting diode (LED, λ_{max} = 420 nm). Gratifyingly, 20 mol% of catalyst **1a** provided the desired β-benzylated aldehyde product **4a** with a chemical yield as high as 79% after 4 h, albeit with a low level of enantiomeric excess (e.e. entry 1, Table 1). No product formation was detected in the absence of catalyst **1a** or light (entries 2 and 3), demonstrating that both components are needed for this photochemical protocol. The inhibition of the reactivity was also observed under an aerobic atmosphere and in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 1 equiv.), the latter experiment being indicative of a radical mechanism.

To unambiguously establish the implication of the iminium ion within the photochemical regime, we investigated the photophysical behaviour of preformed **Ia**. The reduction potential of the excited iminium ion (E_{red}* (**Ia***/**Ia**$^{\bullet-}$)), which was estimated as +2.3 V (versus Ag/Ag^+ in CH_3CN) on the basis of electrochemical and spectroscopic measurements (details in Supplementary Section F4), establishes the thermodynamic feasibility of the SET oxidation of **3a**. In addition, we recorded the emission spectrum of **Ia** upon excitation at 400 nm (red dotted line in Fig. 3a). A series of Stern–Volmer studies, detailed in Supplementary Fig. 29, revealed that benzylsilane **3a** effectively quenched the excited state of **Ia**, in consonance with the SET mechanism triggered by the iminium ion-photoactivity proposed in Fig. 2.

Catalyst optimization. We then focused on identifying a chiral amine catalyst that could enforce a high level of stereocontrol. The diarylprolinol silylether **1b**, generally used in stereoselective iminium ion-catalysed thermal reactions[25], provided greatly improved enantioinduction but at the expense of reactivity (28% yield, 76% e.e., entry 4, Table 1). The poor catalytic activity of **1b** was rationalized on the basis of its electron-rich nature, which imparted an oxidation potential (E_{ox} (**1b**$^{\bullet+}$/**1b**)) of +1.57 V versus Ag/Ag^+ in CH_3CN, a slightly lower value than the E_{ox} of benzyl silane **3a**. This situation makes catalyst **1b** prone to a SET oxidation from the photoexcited iminium ion (E_{red}* (**Ib***/**Ib**$^{\bullet-}$) = +2.3 V versus Ag/Ag^+ in CH_3CN), an event which would trigger the formation of an unstable and highly reactive amine radical cation[26], resulting in an undesired catalyst degradation path. This scenario was confirmed by NMR analysis, which revealed that the overall amount of amine **1b** constantly decreased during the reaction (see Supplementary Section F1). These observations prompted us to modify the electronic properties of the diarylprolinol catalyst **1b** in order to enhance stability towards oxidation by attenuating its electron-donor ability. The incorporation of electron-withdrawing fluorine atoms is widely used in medicinal chemistry to lower the susceptibility of nearby moieties to enzymatic oxidation[27]. In addition, it is known that fluorine introduction strongly reduces amine basicity[28]. These considerations provided a rationale for the higher oxidation potential measured for the *gem*-difluorinated catalyst **1c** (E_{ox} (**1c**$^{\bullet+}$/**1c**) = +2.20 V versus Ag/Ag^+ in CH_3CN), and its excellent catalytic activity in the photochemical reaction (entry 5, Table 1, product **4a** formed in 83% yield and 85% e.e.). To better investigate the effect of amine **1c**, we synthesized tetrafluoroborate salts of the iminium ion **Ic**, generated upon condensation with substrate **2a**, which were characterized by X-ray single-crystal analysis (Fig. 3a). Interestingly, the *gem*-difluorine atoms induce a strong conformational control over the pyrrolidine ring, as triggered by stereoelectronic effects and charge-dipole interactions[29], which has no counterpart in the structure of iminium ion **Ib**, thus providing a possible rationale for the increased level of stereoselectivity. A final cycle of catalyst optimization established amine **1d**, possessing bulkier perfluoro-isopropyl groups on the arene scaffold, as suitable for improving enantiocontrol while preserving the catalytic activity (entry 6, Table 1).

Importantly, this photochemical process furnishes the enantioenriched β-benzylated aldehyde **4a**, a synthetically useful chiral compound that cannot be easily accessed by other direct stereoselective methods. In the polar domain, the intrinsic instability of benzyl-metallic derivatives[30], along with the competing 1,2-addition manifold, generally complicates the development of metal-catalysed conjugate additions. This is why, to our knowledge, no catalytic asymmetric conjugate additions of benzyl-metallic reagents to enals have been reported, aside from non stereoselective[31] or indirect variants[32]. In addition, thermal enantioselective iminium ion chemistry has been successful for only a specific class of highly activated nitro-toluene substrates[33,34]. In the realm of open-shell reactivity, it is well-known that the large resonance stabilization of benzyl radicals makes their addition to electron-poor olefins difficult[35,36], a situation which generally favours the formation of dimeric bibenzyl derivatives instead. This is why successful strategies for benzyl radical addition to electron-poor alkenes, aside from a recently reported exception[37], have largely relied upon SET

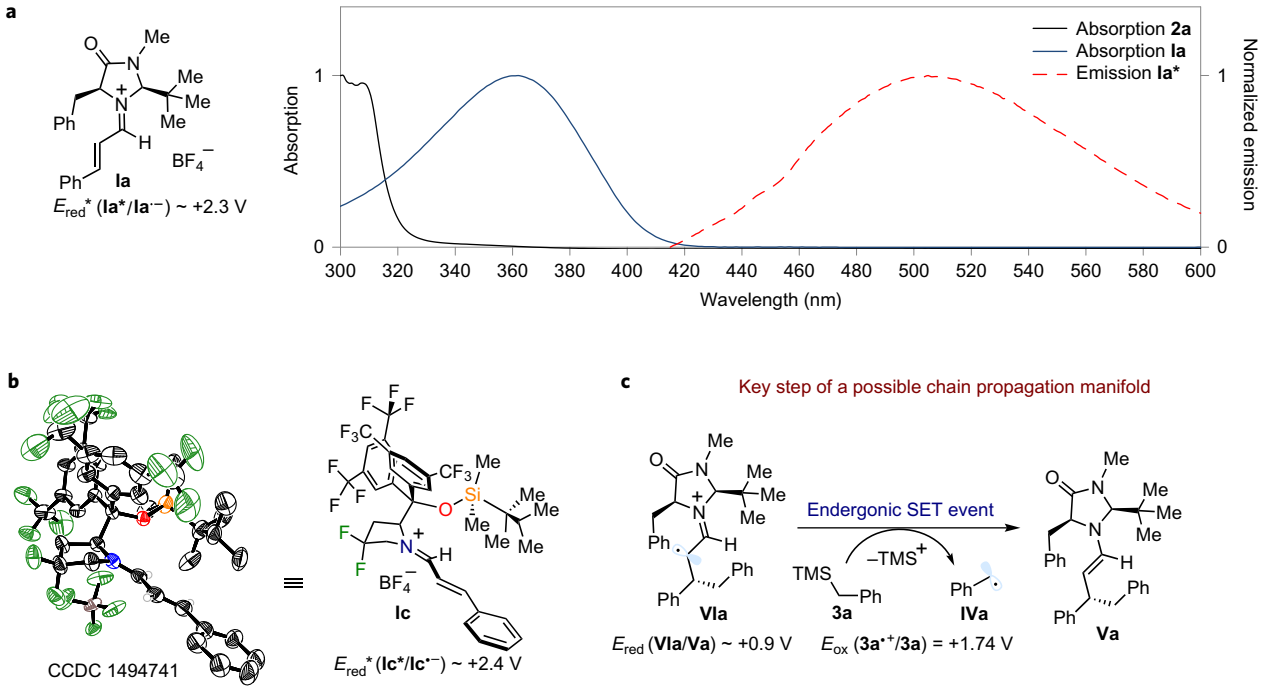


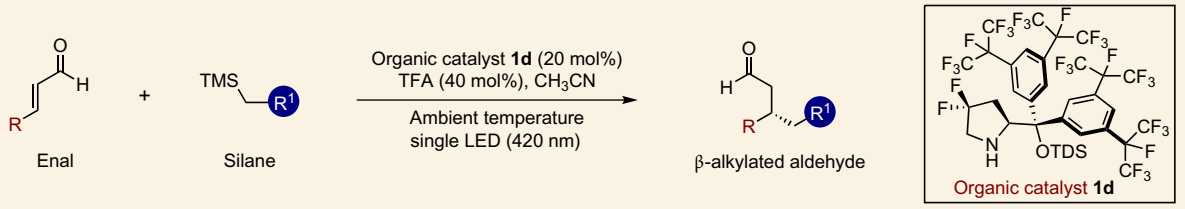
Figure 3 | Photophysical and structural characterization of iminium ions and mechanistic investigations. a, Absorption of cinnamaldehyde **2a** (black line) and the preformed iminium ion **Ia** (blue line), and emission of **Ia*** (excitation at 400 nm, red dotted line) in CH_3CN. **b**, X-ray crystal structure of the iminium ion **Ic**. E_{red}^* versus Ag/Ag^+ in CH_3CN for the excited iminium ions **I*** estimated on the basis of electrochemical and spectroscopic measurements. **c**, Assessing the feasibility of a radical chain propagation mechanism: the photochemical activity of the excited iminium ion **I** would serve as an initiation event, generating the benzyl radical **IVa**, which could be trapped by a ground-state iminium ion **I**. The endergonicity of the SET between **3a** and the α-iminyl radical cation **VI**, which would be essential to sustain a chain propagation manifold by regenerating **IVa**, means that this process is thermodynamically disfavoured. E_{red} (**VIa**/**Va**) measured by cyclic voltammetry versus Ag/Ag^+ in CH_3CN of an analogue of enamine **Va**, see Supplementary Fig. 1 for details and a comprehensive picture of this mechanism. TFA, trifluoroacetic acid; TDS, thexyl-dimethylsilyl; TMS, trimethylsilyl.

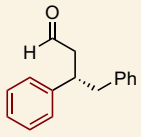
reduction of the acceptor to form an alkene radical anion, which is a much better trap for benzyl radicals[9,10,38]. As depicted in Fig. 2, our strategy is based upon a similar mechanistic pattern, the coupling between the β-enaminyl radical **II** and the benzyl radical **IVa** providing the desired adduct **4a**. A variety of data are consistent with this radical–radical combination mechanism. First, we did not observe the formation of bibenzyl. In addition, we measured the quantum yield of the process catalysed by amine **Ic**, which was found to be 0.05 ($\lambda = 400$ nm in CH_3CN). Although these data do not completely rule out a radical-chain process triggered by the conjugate addition of benzyl radical **IVa** to the ground-state iminium ion **I**, a chain propagation mechanism is unlikely for several reasons: (i) the already-mentioned poor nucleophilicity of benzyl radicals[35], (ii) the low tendency of iminium ions to trap radicals[39], and (iii) the endergonic SET between the benzyl silane **3a** and the α-iminyl radical cation **VI** (Fig. 3c), which would ensue from the radical addition to **I**. The last SET process, which would be essential for a chain propagation manifold by regenerating the benzyl radical **IVa**, is highly disfavoured when considering the redox potentials of the intermediates.

Scope of enantioselective photochemical β-alkylations of enals. Adopting the optimized conditions described in Table 1, entry 6, we then demonstrated the generality of the photochemical β-benzylation process by evaluating a variety of enals **2** and benzyl trimethylsilanes **3**. The results are reported in Table 2. Different substitution patterns at the aromatic moiety of **2** were well tolerated, regardless of their electronic and steric properties and position on the phenyl ring (products **4a–i**). The method is synthetically useful, with a good efficiency maintained when running the reaction on a 1 mmol scale (product **4a**). One limitation of the system is that the presence of a β-alkyl fragment in **2** completely inhibits the reaction (**4j**). Experiments to probe the scope of the benzyl silane component **3** revealed that a wide range of substituents are tolerated on the aryl ring (adducts **4k–q**). The presence of a *gem*-dimethyl substituent at the benzylic position provides the corresponding product **4r** bearing a quaternary carbon, while monosubstituted benzyl silanes afford compounds **4s**,**t**, having two vicinal stereogenic centres, with high enantiomeric purity, albeit with a poor diastereomeric ratio. Notably, heteroaryl frameworks can also be included in the product, as shown for the indolyl- and benzothienyl-substituted adducts **4u** and **4v**, respectively.

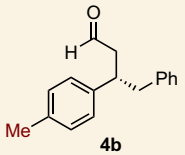
We then wondered if the photoexcitation of iminium ions could provide a widely applicable mechanism of substrate activation suitable for a broad range of stereocontrolled enal β-functionalizations. On the basis of our mechanistic proposal, the simple use of well-established physical properties should permit the predictable and rational identification of competent substrates. In theory, any organic silane possessing an appropriate oxidation potential (that is, E_{ox} lower than **3a**) should have the capability to serve as a viable coupling partner. Following this reasoning, we found that α-silyl thioethers, α-silyl amines, and α-silyl ethers could productively engage in the photochemical asymmetric process. This is because the silyl group at the α-position of the heteroatom imparts an adequately low oxidation potential to these substrates through $\sigma \rightarrow n$ orbital interactions[19]. As a result, chiral aldehydes **5a–h** bearing a methylene-heteroatom fragment at the β-position could be synthesized with moderate-to-high stereoselectivity (products depicted in the last row of Table 2). Crystals from a derivative of compound **5a** were suitable for X-ray analysis, which secured the absolute configuration of the products.

Table 2 | Substrate scope for the photochemical β-alkylation of enals.

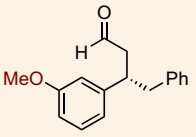




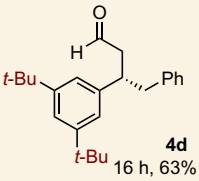
4a
16 h (48 h)*
87% (73%)* yield
88% (88%)* e.e.



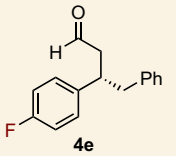
4b
16 h, 74% yield
78% e.e.



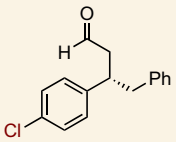
4c
48 h, 62% yield
82% e.e.



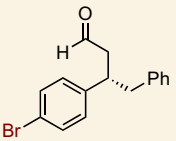
4d
16 h, 63% yield
68% e.e.



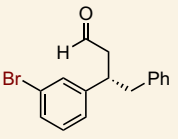
4e
16 h, 76% yield
85% e.e.



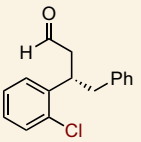
4f
16 h, 75% yield
86% e.e.



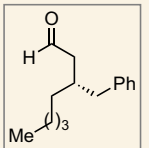
4g
16 h, 74% yield
84% e.e.



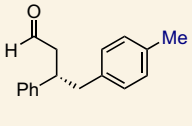
4h
16 h, 73% yield
86% e.e.



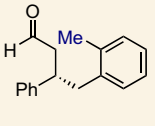
4i
16 h, 75% yield
88% e.e.



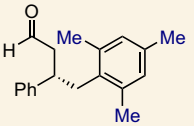
4j
Not detected



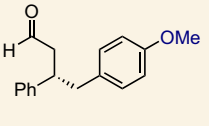
4k
16 h, 90% yield
91% e.e.



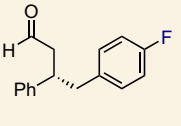
4l
16 h, 85% yield
90% e.e.



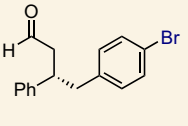
4m
16 h, 93% yield
93% e.e.



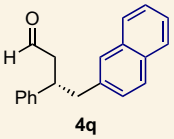
4n
16 h, 77% yield
92% e.e.



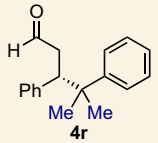
4o
16 h, 80% yield
85% e.e.



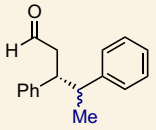
4p
16 h, 66% yield
78% e.e.



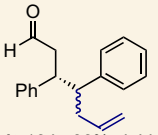
4q
16 h, 77% yield
91% e.e.



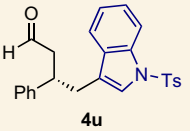
4r
16 h, 46% yield
71% e.e.



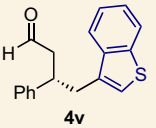
4s 16 h, 92% yield
1.2:1 d.r.; 92% e.e.$_{major}$
92% e.e.$_{minor}$



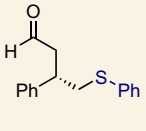
4t 16 h, 66% yield
1.5:1 d.r.; 92% e.e.$_{major}$
90% e.e.$_{minor}$



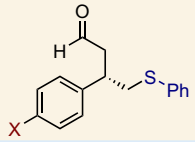
4u
56 h, 52% yield
94% e.e.



4v
48 h, 55% yield
87% e.e.†

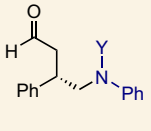


5a 24 h,
73% yield
90% e.e.‡



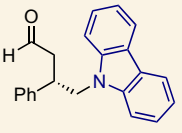
X = MeO: **5b**
24 h, 81% yield
79% e.e.#

X = CF_3: **5c**
48 h, 43% yield
81% e.e.#

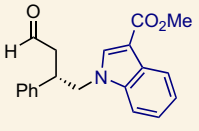


Y = Ph: **5d**
24 h, 58% yield
75% e.e.‡

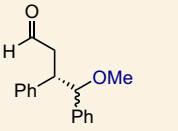
Y = BOC: **5e**
24 h, 63% yield
71% e.e.



5f
16 h, 82% yield
81% e.e.



5g
48 h, 64% yield
92% e.e.‡



5h 24 h, 56% yield†
1.9:1 d.r.; 68% e.e.$_{major}$
61% e.e.$_{minor}$

Survey of the α,β-unsaturated aldehydes (products 4a–j), the benzylsilane derivatives (products 4k–v), and the α-silyl thioethers (products 5a–c), α-silyl amines (products 5d–g), and α-silyl ethers (product 5h) that can participate in the reaction. Reactions performed on a 0.1 mmol scale using 3 equiv. of enals; the excess of enal secured a more effective iminium ion formation. Reaction time, yields and enantiomeric excesses of the isolated products are indicated below each entry (average of two runs per substrate). Generally, full consumption of the limiting silane substrate was observed at the end of the reaction. *Performed on a 1 mmol scale. †Using catalyst 1c. ‡Using catalyst **1b** in a 3:1 CH_3CN/H_2O solvent mixture. #Using catalyst 1c in a 3:1 CH_3CN/H_2O solvent mixture. TFA, trifluoroacetic acid; TDS, thexyl-dimethylsilyl; Ts, 4-toluenesulfonyl; BOC, *tert*-butyloxycarbonyl; TMS, trimethylsilyl.

Conclusions

In summary, we have developed a new and simple strategy to control the stereochemical outcome of catalytic photochemical reactions driven by visible light. Specifically, our studies demonstrate that chiral iminium ions, key intermediates in thermal enantioselective organocatalytic processes, can unlock previously inaccessible reactivities when reaching an excited state upon visible-light absorption, while inducing effective stereochemical control over the ensuing C–C bond-forming event. These findings are expected to open new avenues for reaction design in the field of enantioselective photochemical processes.

Data availability. X-ray crystallographic data for amine 1c, iminium ion **Ic**, and a derivative of compound 5a are freely available from the Cambridge Crystallographic Data Centre, accession numbers CCDC 1494740, 1494741, and 1494742, respectively.

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Author contributions

M.S. was involved in the discovery and initial development of the light-driven reactions. C.V. and Y.P.R. designed and synthesized the catalysts. C.V., Y.P.R. and L.B. performed the experiments. All of the authors analysed the data and designed the experiments. P.M directed the project and wrote the manuscript with contributions from all of the authors.

Additional information

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Competing financial interests

The authors declare no competing financial interests.