

Activation of alcohols as sulfonium salts in the photocatalytic hetero-difunctionalization of alkenes

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Huaibo Zhao¹, Dario Filippini², Yiding Chen², Albert Gallego-Gamo¹, Louise S. Natrajan¹, Loïc R. E. Pantaine², Ciro Romano¹ & David J. Procter¹✉

Motifs related to 1,2-diols and 1,2-amino alcohols are found widely in bioactive natural products, drugs and agrochemicals. These highly sought-after substructures would ideally be constructed by the direct addition of alcohols to the C=C bond of alkenes, both common substrate classes in chemical synthesis. However, their direct union is only possible if one of the pair can be rendered electron-deficient through derivatization; such approaches typically require stoichiometric amounts of strong oxidants and often lack generality. Here we describe a straightforward process in which both simple and complex alcohols can be converted under photocatalytic conditions to the corresponding alkoxy radicals—via the formation of alkoxy sulfonium salts—that react with alkenes en route to 1,2-diol and 1,2-amino-alcohol derivatives. The method can be easily adapted from laboratory to industrial, kilogram scale using a photoflow system. Spectroscopic analysis and control experiments have been used to probe the underpinning mechanism.

The widespread presence of 1,2-diol and 1,2-amino-alcohol motifs in molecules of societal importance—including bioactive natural products (for example, paclitaxel and adrenaline), drugs (for example, labetalol and dapagliflozin) and agrochemicals (for example, metolachlor)^{1–4} (Fig. 1a)—continues to spur efforts to develop new methods for their construction. The highly sought-after installation of two heteroatom-containing groups across an alkene C=C bond would ideally be triggered by the direct reaction of alkenes with alcohols (or other heteroatom containing nucleophiles)—both common classes of feedstock. However, owing to the electron-rich nature of both alcohols and alkenes, their direct union is only possible if one of the reactants can be rendered electron-deficient through derivatization—for example, using epoxides/halonium ions formed from the alkene partners^{5–10}. These approaches typically require the use of stoichiometric amounts of strong oxidants and, thus, often lack generality, owing to functional group incompatibility, and lead to longer synthetic routes that involve

protecting group manipulation (Fig. 1b). Alternative approaches involve the use of transition metal reagents and catalysts to activate alkenes towards nucleophile addition or to activate partners towards addition across alkene C=C bonds followed by trapping of organometallic intermediates with electrophilic alcohol derivatives^{11–17}.

With the advent of photocatalysis, new methods for the hetero-difunctionalization of alkenes have emerged^{18–30} (Fig. 1c). Of note, the oxidation of alkenes to the corresponding radical cations under photocatalytic conditions prompts the addition of heteroatom nucleophiles. This approach, however, is mostly limited to particularly electron-rich alkenes, and internal nucleophiles are typically required^{31–34}. An alternative radical approach exploiting polarity reversal involves the generation of electrophilic alkoxy radicals and their engagement with the electron-rich highest occupied molecular orbital of alkene partners^{35,36}. Unfortunately, this approach is limited by the forcing conditions required for the generation of alkoxy radicals and their high reactivity,

¹Department of Chemistry, University of Manchester, Manchester, UK. ²Process and Analytical Chemistry, Pharmaron UK Ltd., Hoddesdon, UK.✉e-mail: david.j.procter@manchester.ac.uk

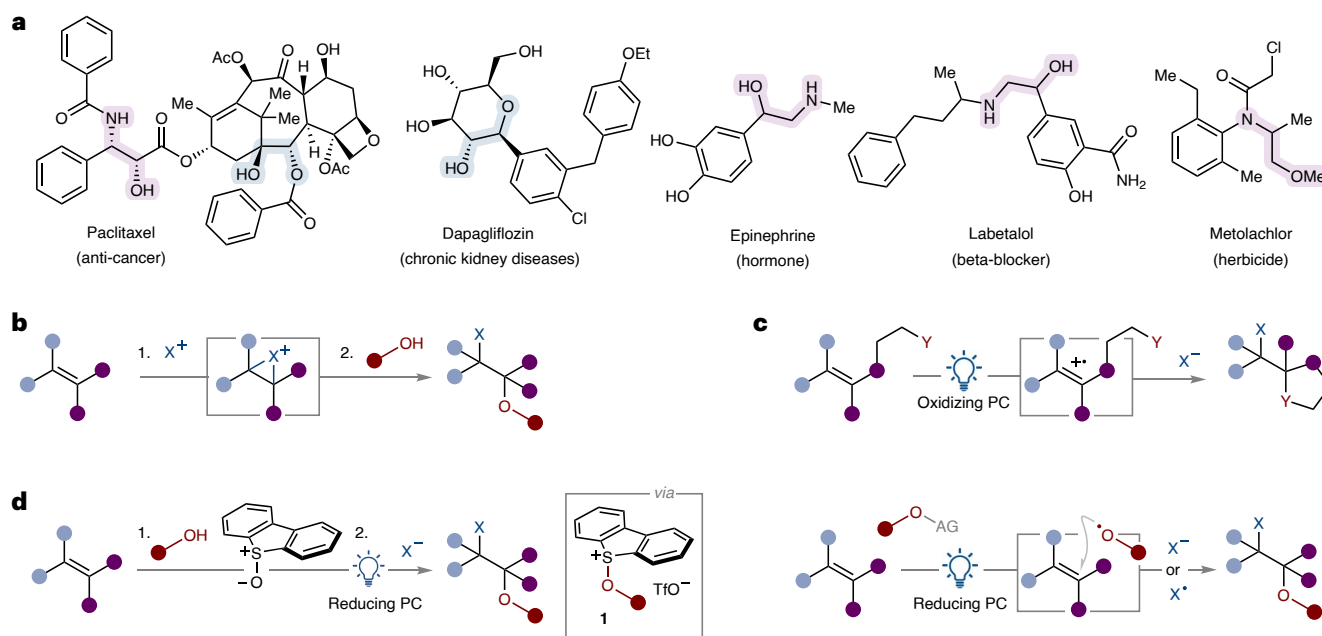


Fig. 1 | The importance of 1,2-diol and 1,2-amino-alcohol motifs and approaches for their construction. a, Selected natural products, pharmaceuticals and agrochemicals containing 1,2-diols or 1,2-amino-alcohol motifs. **b**, General approaches to achieve the hetero-difunctionalization of alkenes use polar chemistry, involve strong oxidants and show low functional group tolerance. **c**, General approaches to achieve the hetero-difunctionalization of alkenes using radical chemistry can have limited scope. Alkoxy radical

approaches involve precursors that are not formed directly from alcohols. **d**, Our approach towards the photocatalytic hetero-difunctionalization of alkenes uses readily accessible, yet little-explored, alkoxy sulfonium salts as bench-stable alkoxy radical precursors formed from both simple and complex alcohols. Ac, acetyl; AG, activating group; Et, ethyl; Me, methyl; PC, photocatalyst; Tf, trifluoromethanesulfonyl.

which result in side-reactions (for example, intra- and intermolecular hydrogen atom transfer (HAT) and fragmentation). Photocatalysis provides more user-friendly approaches to alkoxy radicals from a range of stable precursors^{37–49}. Elegant photocatalytic methods for the direct generation of alkoxy radicals from alcohols, under mild and generally applicable conditions, exploit proton-coupled electron transfer⁴⁹ and ligand-to-metal charge transfer⁵⁰; alkene functionalization using alkoxy radicals generated using these approaches currently leads to mono-functionalized products of hydroetherification rather than difunctionalized products. For alkene difunctionalization, alkoxy radicals are not typically prepared from alcohols and instead arise from alkyl (pseudo)halides by nucleophilic substitution in multi-step syntheses, thus they are subject to a limited palette of structural variability that reflects the requirements of S_N2 or S_N1 reactions. A more convenient approach involves the direct utilization of alcohol feedstocks that are converted in situ to the corresponding alkoxy radicals by photocatalysed proton-coupled electron transfer before alkene addition³⁶. This approach requires the combination of a base with an oxidizing photocatalyst. As the reduced photocatalyst must be oxidized in a later step to close the photocatalytic cycle, after the addition of the alkoxy radical to the alkene, hetero-difunctionalization of alkenes by two nucleophile partners using this approach has not been described.

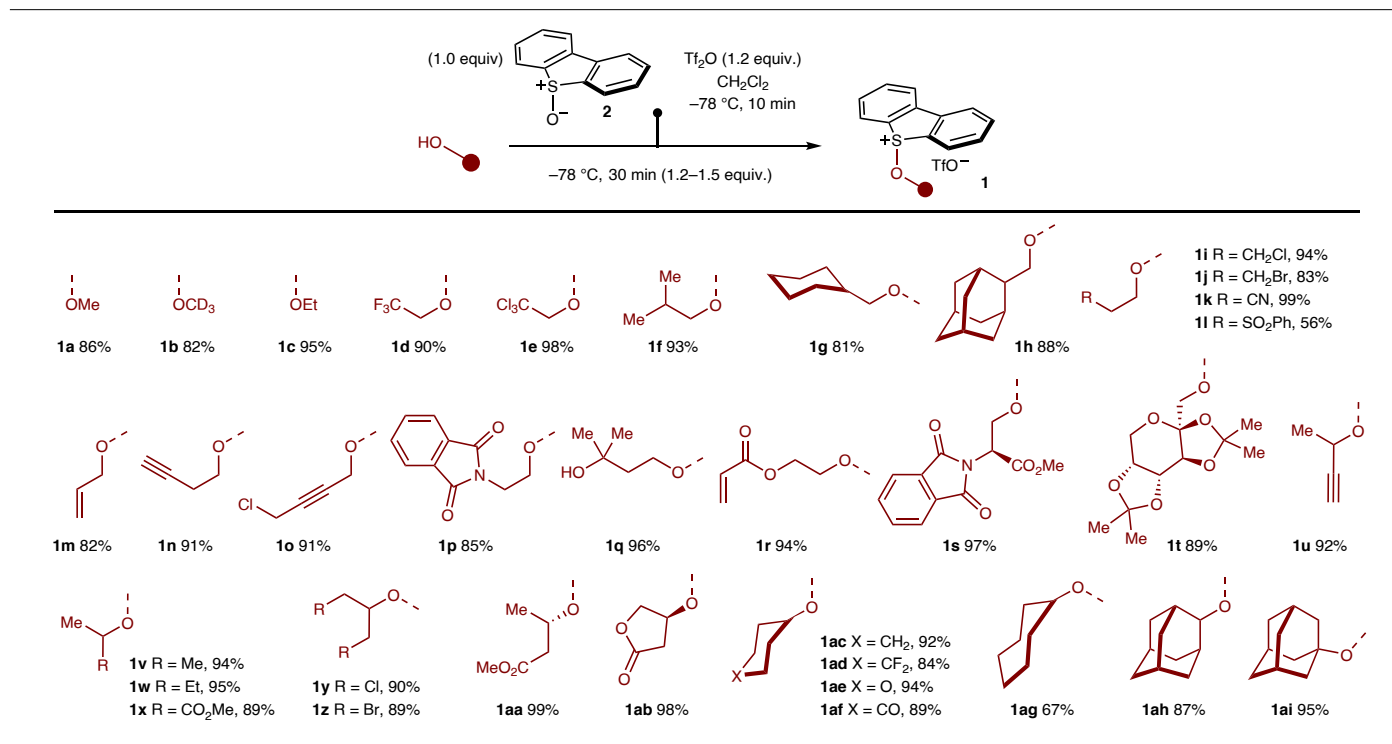
Our interest in the activation of substrates using sulfoxides in Pummerer-type processes, and the application of the resulting sulfonium salts in photochemistry^{51–57}, led us to consider alkoxy sulfonium salts (for example, **1**)^{58–66} as readily accessible, stable precursors of alkoxy radicals, which can be formed directly from a range of both simple and complex alcohols and that can be activated under mild reducing photocatalytic conditions (Fig. 1d). Upon addition of the resulting alkoxy radicals to an alkene, the resulting carbon radicals can close the photocatalytic cycle by reducing the oxidized form of the photocatalyst, setting the stage for the addition of a second nucleophile. By judicious choice of the nucleophile, for example, water, alcohol or

nitrile, products of alkene 1,2-alkoxy-hydroxylation, 1,2-dialkoxylation and 1,2-alkoxy-amidation can be accessed, respectively. Of note, the strategy enables the direct use of alcohols as alkoxy radical precursors, after straightforward activation as alkoxy sulfonium salts, which can either be isolated and characterized or used in convenient telescoped processes for alkene difunctionalization. Given the low redox potential of alkoxy sulfonium salts (E_p of -0.14 eV versus Ag/AgCl), the use of strong reductants (or oxidants) is avoided, and alcohol and alkene partners bearing a range of functional groups can be engaged. Importantly, both the synthesis of alkoxy sulfonium salts and the photocatalytic alkene hetero-difunctionalization are amenable to being scaled-up; the process has been carried out on a kilogram scale in an industrial setting using a photoflow approach.

Results and discussion

Synthesis of alkoxy sulfonium salts

Using commercial dibenzothiophene *S*-oxide **2** and adapting straightforward conditions used widely for the synthesis of more common aryl sulfonium salts⁵⁴, we have developed a robust protocol for the preparation of alkoxy sulfonium salts from a range of alcohols (Table 1). The alkoxy sulfonium salts were readily isolated and characterized, and the process was amenable to larger scale; 3.15 g of salt **1a** was prepared in 86% yield. Furthermore, **1a** was prepared on a 1-kg scale in an industrial setting (see ‘Large-scale, continuous 1,2-alkoxy-hydroxylation under photoflow conditions’ section). A range of alkoxy sulfonium salts—derived from primary and secondary alcohols—were prepared in high yield, although only a few tertiary alcohols could be engaged (for example, the formation of **1ai**), thus this is an area for future refinement of the approach. Crucially, products of alcohol oxidation were not observed⁶⁷. The process embraced both inexpensive, simple feedstock alcohols (**1a–h**)—including a deuterated alcohol (**1b**)—and complex alcohols derived from an amino acid (**1s**) and a sugar (**1t**), or alcohols from the chiral pool (**1aa** and **1ab**). The mild reaction conditions allowed the

Table 1 | Alkoxy sulfonium salts prepared from alcohols

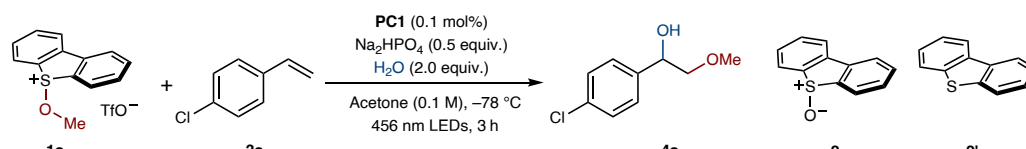
Ti_2O , trifluoromethanesulfonic anhydride.

presence of a number of important functional groups in the alcohol substrates to be tolerated, for example, halide (**1d,e,i,j,o,y,z** and **ad**), nitrile (**1k**), ester (**1s,x,aa,ab**), sulfone (**1l**), alkene (**1m**), alkyne (**1n,o,u**), tertiary alcohol (**1q**), acrylate (**1r**) and phthalimido (**1p,s**) motifs were compatible with alkoxy sulfonium salt synthesis, while a cyclic ketal delivered a sulfonium salt bearing the corresponding ketone functionality (**1af**). Crucially, enantiomerically pure alcohols, with the stereochemistry residing at (**1aa,ab**), or remote from the hydroxyl group (**1s,t**), gave alkoxy sulfonium salts with no loss of stereochemical integrity (Fig. 2).

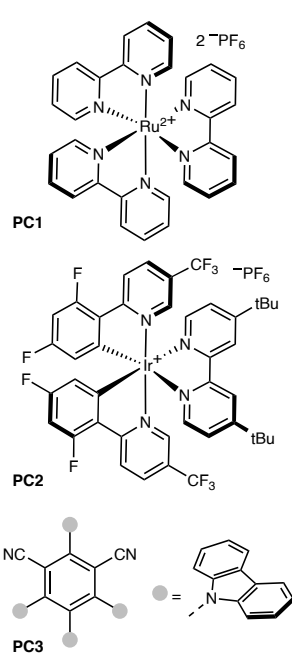
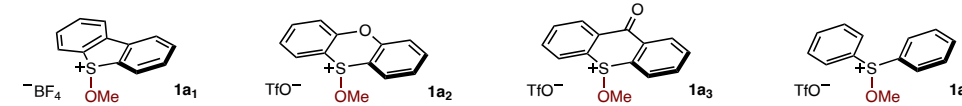
Photocatalytic 1,2-alkoxy-hydroxylation of alkenes

With alkoxy sulfonium salts in hand, we optimized the photocatalytic selective construction of two C–O bonds across an alkene (Table 2). Using alkoxy sulfonium salt **1a** and 4-chlorostyrene **3a**, we arrived at the optimized conditions highlighted in entry 1; **4a** was obtained in 83% yield when using the photocatalyst **PCl** (0.1 mol%) in acetone, in the presence of water (2.0 equiv.) and Na_2HPO_4 (50 mol%), under light irradiation at 456 nm. The formation of **2**—probably by hydrolysis of **1a**—and **2'**—by direct homolysis of **1a**—were minimized by reducing the reaction temperature and using a photocatalyst. At higher reaction temperatures, in the presence of more alkoxy sulfonium salt, the formation of the aryl ketone product arising from oxidation of **4a** was observed. We ascribe this to HAT from the benzylic position of **4a** by the alkoxy radical. Under our optimized conditions, only traces of aryl ketone byproduct are observed (Supplementary Table S1). The reaction is only marginally sensitive to the reaction temperature (entry 2) and the presence of a base (entry 3)—aspects that we later exploited in the development of a photoflow process. In contrast, the reaction shuts down in solvents other than acetone (entry 4). Using alternative alkoxy sulfonium salts, conveniently derived from other sulfoxides (entry 5), or photocatalysts (entry 7), gave lower yields of product. Addition of water was not essential—probably owing to adventitious water in the acetone solvent—and higher loadings of water did not improve the yield (entry 6). A low yield of **4a** was obtained in the absence of a photocatalyst (entry 9), and no product was observed without light (entry 10).

We next assessed the scope of the photocatalysed alkoxy-hydroxylation of alkenes using methoxy sulfonium salt **1a** and varying the alkene partner (Table 3). Styrene derivatives with electron-withdrawing and electron-donating groups at the *para*- (**4a–m,z** and **4aa–ac**), *meta*- (**4n–t**) and *ortho*-positions (**4u–y**) were effective substrates. Products with polyfunctionalized aromatic rings were obtained in good to high yields regardless of the position and electronic properties of the substituents (**4ad–ah**). The benzocyclobutane motif (**4ai**) and both 1- and 2-substituted naphthyl-units were also tolerated (**4aj** and **4ak**). Engaging heteroaryl-containing substrates in photocatalysis often proves challenging owing to the sensitivity of heteroaromatic motifs to light. Pleasingly, the use of heteroaryl-containing alkenes delivers the corresponding medicinally relevant products (**4al–aq**), albeit in lower yields. The protocol extends to more challenging polysubstituted alkenes (**4ar–be**), for example, compound **4ar** was obtained in 83% yield despite the presence of weak allylic C–H bonds, which could be prone to competing HAT by the alkoxy radical intermediate. Other 1,2-disubstituted alkenes could be effectively engaged, including those bearing primary alkyl bromide (**4as**), ester (**4at**), ketone (**4au**), tertiary alkyl hydroxyl (**4ay**) and nitrile (**4az**) motifs. Cyclic 1,2-disubstituted alkenes afforded the corresponding products **4aw** and **4ax** in good yields. The process also proved effective for the 1,2-hydroxy-alkoxy functionalization of trisubstituted alkenes (**4av**). The formation of **4ay** as a single diastereoisomer may be rationalized by invoking the interaction of the pendant hydroxyl group with one face of the intermediate benzylic carbocation (Fig. 3b), with subsequent nucleophilic attack by water on the opposite face⁶⁸. Interestingly, **4bc** was obtained in a moderate yield with no sign of radical ring-opening of the cyclopropyl substituent. This suggests a rapid oxidation of the intermediate benzyl radical to the corresponding carbocation in the catalytic cycle⁶⁹. Finally, the benzazepine motif present in arginine vasopressin receptor antagonists⁷⁰ can be conveniently decorated; **4be** was prepared in good yield and its structure confirmed by X-ray crystallographic analysis. Overall, this method tolerates various substitution patterns and functional

Table 2 | Optimization of the 1,2-alkoxy-hydroxylation of alkenes using alkoxy sulfonium salts


Entry	Deviation from standard conditions	4a (%)
1	None	83, (80)
2	At -30 °C, -20 °C, or 0 °C	68, 62, 52
3	NaH ₂ PO ₄ ·2H ₂ O or 2-Cl-pyridine as base	75, 80
4	CH ₂ Cl ₂ , MeOH, DMF	5, -, -
5	Using sulfonium salt 1a ₁₋₄	16–83
6	H ₂ O (5.0 equiv.) or no H ₂ O	73, 70
7	Using PC2-3	30, 24
8	No base	71
9	No PC1	15
10	No light	NR

General reaction conditions involved **1a** (0.1 mmol), **3a** (0.2 mmol), **PC1** (0.1 mol%), Na₂HPO₄ (0.5 equiv.) and H₂O (2.0 equiv.) dissolved in acetone (0.1 M) under irradiation by blue light-emitting diodes (LEDs; λ_{max} centred at 456 nm) at -78 °C for 3 h. Yields were determined by ¹H NMR spectroscopy using mesitylene as an internal standard. Isolated yields are reported in parentheses. DMF, *N,N*-dimethylformamide; NR, no reaction; tBu, *tert*-butyl.

groups, highlighting its wide applicability. The process is, however, currently specific for styrene-type alkenes, and no product formation was observed when alkyl substituted alkenes were employed; this may be because of parasitic HAT from allylic C–H bonds outcompeting the addition of the alkoxy radical to the C=C bond.

We next explored the scope of the photocatalytic process with respect to the alkoxy sulfonium salt using alkene **3a** (Fig. 2a). The reaction tolerated wide variation in the activated alcohol partner. Derivatives of simple alcohols, such as deuterated methanol (**4bf**) and ethanol (**4bg**), or more functionalized β-substituted derivatives (**4bh–bx**) were well-tolerated in the alkene difunctionalization. The reaction is not limited to primary alcohols; secondary (**4by–cl**) and tertiary alcohol derivatives (**4cm**) were also viable substrates. Importantly, products were obtained in good-to-high yield throughout, despite the known propensity of β-branched alkoxy radicals to undergo fragmentation⁷¹. A range of functional groups in the alcohol-derived partner were tolerated: for example, primary halides (**4bn,bo,bu,cc,cd**), nitriles (**4bm**), sulfones (**4bp**), phthalimides (**4bq**) and protected amino acid (**4bx**), hydroxyls (**4br**), ketones (**4cj**), α,β-unsaturated esters (**4bs**), alkenes (**4bt**), alkynes (**4bu,bv,cb**), esters (**4bx,ca,ce**), lactones (**4cf**) and ketals (in protected sugar **4bw**).

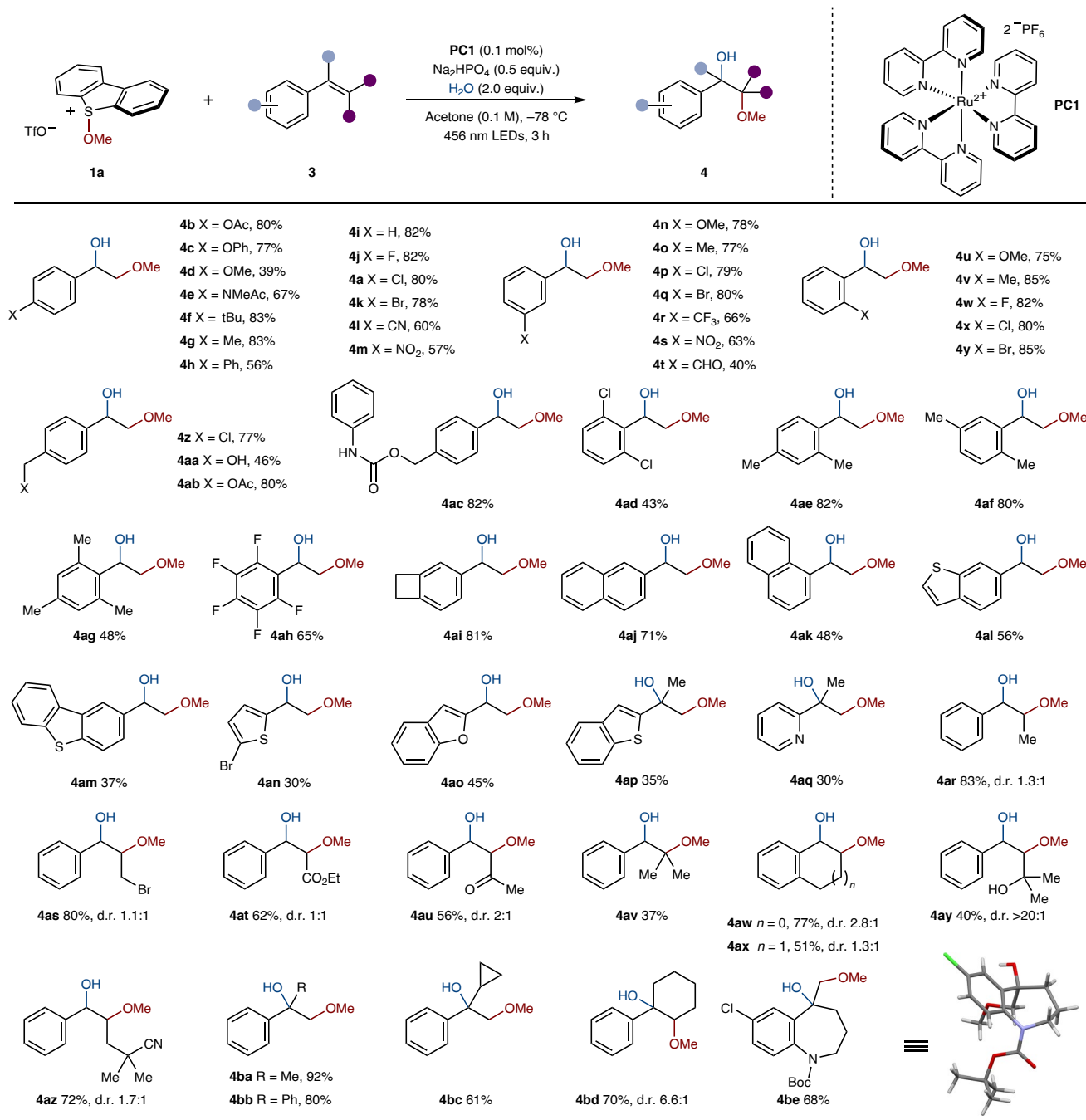
Photocatalysed 1,2-dialkoxylation and 1,2-alkoxy-amidation of alkenes

By varying the nucleophile used to quench the carbocation intermediate, we expanded our approach to other 1,2-difunctionalization reactions. Pleasingly, minimal tuning of the reaction conditions delivered an alkene dialkoxylation procedure. The synthesis of unsymmetrical 1,2-diethers—with different alkyl groups on the two oxygen atoms—from diols, is non-trivial owing to the similar reactivity of the two hydroxy groups and the need for efficient and toxic alkylating agents⁷² (Fig. 2b, left). Using methoxy sulfonium salt **1a** and alkene **3a**, with a range of alcohol nucleophile partners, allowed selective access to several 1,2-diethers. Careful drying of the alcohol nucleophile ensured the formation of only traces of the 1,2-alkoxy-hydroxylation products.

The alcohols used ranged from feedstock alcohols—such as methanol (**5a**), benzyl alcohol (**5e**), cyclobutanol (**5g**), *tert*-butanol (**5h**) and 2-methoxyethanol (**5d**), through alcohols containing functionality—such as bromoethanol (**5b**) and 2-(trimethylsilyl)ethanol (**5c**)—to complex alcohols such as a protected serine (**5f**). Highlighting the generality of this platform, the use of inexpensive nitriles as co-solvents resulted in the 1,2-alkoxy-amidation of alkene **3a** using alkoxy sulfonium salt **1a**^{21,73}; amides **6a–h** were isolated in moderate yields alongside traces of the 1,2-alkoxy-hydroxylation products. Finally, an analogue of the paclitaxel side chain **6i** (Fig. 1a) was prepared from ethyl cinnamate when using benzonitrile as co-solvent (Fig. 2b, right).

Large-scale, continuous 1,2-alkoxy-hydroxylation under photoflow conditions

Given the potential impact of developing a process that can be applied on industrial scale, the reaction was adapted from a batch process to an easily scaled photoflow process—a flow chemistry setting under light irradiation. We selected the reaction between methoxy sulfonium salt **1a** and styrene **3a** as a model system. Firstly, the synthesis of methoxy sulfonium salt **1a** was optimized for a 1-kg scale (Supplementary Information). Secondly, a rapid optimization campaign was performed taking into consideration key aspects of the method to make it compatible with the process chemistry flow reactor used and fulfilling requirements for its use in the pharmaceutical industry (Fig. 3a). Switching from an inorganic to an organic base removed any solubility concerns and ensured reaction homogeneity, while a 5-min residence time was found sufficient to achieve a good conversion and an excellent yield. The reaction temperature was raised from -30 °C to 0 °C, thus avoiding cryogenic conditions and unnecessary light diffraction from frost build-up on the reactor surface. As a stability study on the starting mixture indicated a slow decay of **1a** in the reaction mixture over 24 h, a two-feed system was established that consisted of two equal volume solutions of **1a** in acetone and styrene **3a** with photocatalyst, base and water, respectively. Both streams were mixed at the same flow rate and

Table 3 | Alkene scope in the photocatalytic 1,2-alkoxy-hydroxylation of alkenes

Boc, *tert*-butoxycarbonyl; d.r., diastereoisomeric ratio; Ph, phenyl.

cooled to $0\text{ }^\circ\text{C}$, allowing for fresh mixing and pre-cooling of the active reagents before irradiation. Process safety experiments (differential scanning calorimetry, and accelerating rate calorimetry) for starting mixtures did not reveal safety concerns (Supplementary Information). With these minor modifications to the standard conditions, we achieved good yields of **4a** in the gram-scale photoflow reactor. The reaction was then scaled up to the kilogram-scale photoflow reactor, starting with 1.0 kg of **1a**, and obtaining **4a** in a 64% yield over 3.5 h.

Mechanistic studies and the proposed catalytic cycle

Building on previous studies on the photochemistry of sulfonium salts by our team^{51–57} and by others^{74–76}, we propose the catalytic cycle set out

in Fig. 3b. Photoexcitation of **PC1** ($E^{*II/1}$ of -0.81 eV versus saturated calomel electrode (SCE))⁷⁷ under blue light triggers single electron transfer (SET) reduction of the alkoxy sulfonium salts **1** with the generation of alkoxy radicals **I**. The highly reactive alkoxy radicals add to the alkenes, generating benzylic radicals **II**, which are oxidized to the corresponding carbocations **III** ($E_{1/2}$ of $+0.74\text{ eV}$ versus SCE)⁷⁸ by **PC1**⁺ ($E_{1/2}^{III/II}$ of $+1.29\text{ eV}$ versus SCE)⁷⁷, closing the photocatalytic cycle (path a). Interception of the carbocation intermediates **III** by a nucleophile—water, alcohol or nitrile—furnishes the products of alkene 1,2-difunctionalization **4–6**. Mechanistic studies were conducted to probe the proposed catalytic cycle (Fig. 3c,d). Stern–Volmer fluorescence quenching studies revealed that the alkoxy sulfonium salt (for example, **1a**) is the only quencher of the

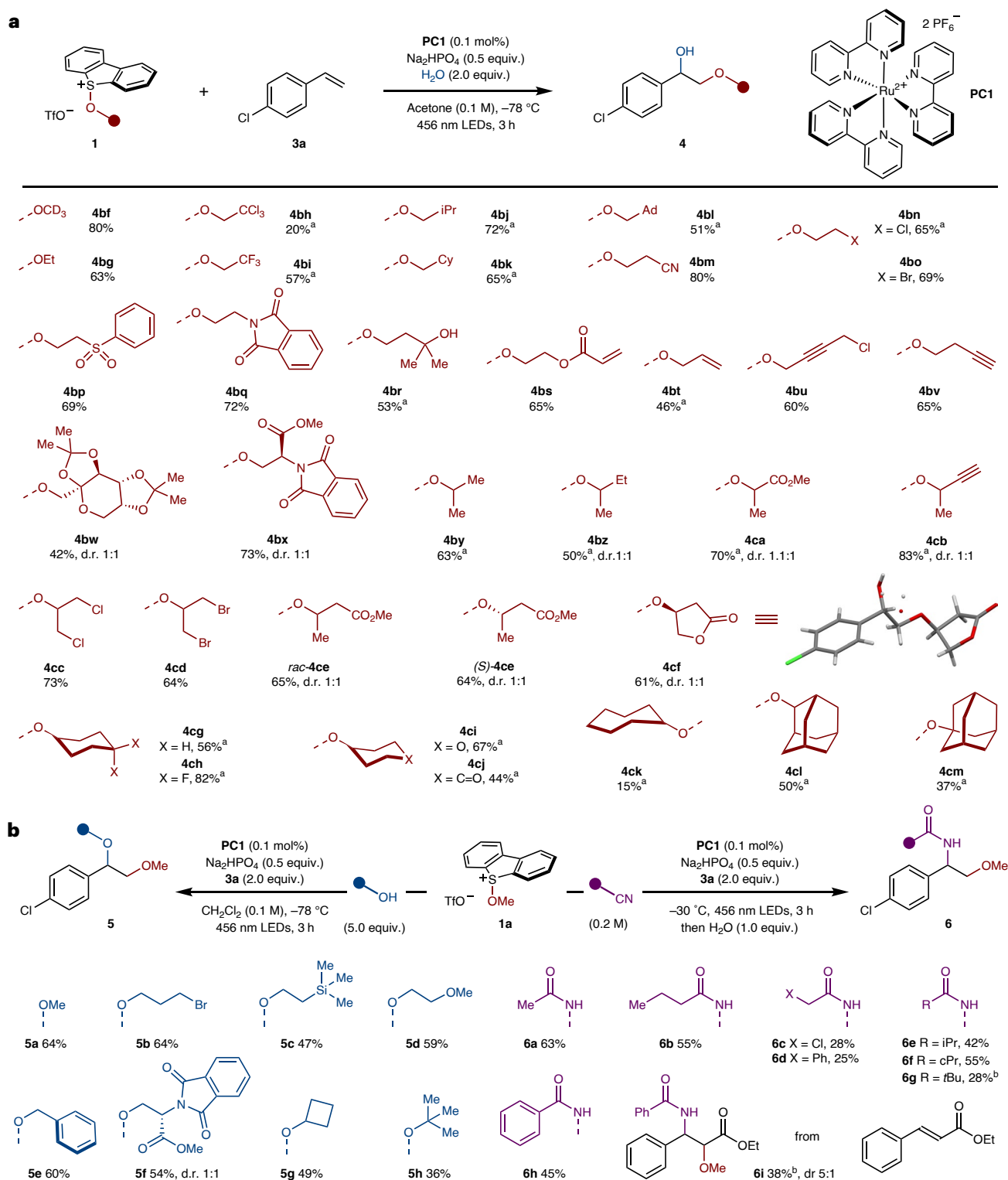


Fig. 2 | Alkoxy sulfonium salts in the photocatalytic difunctionalization of alkenes. a, The alkoxy sulfonium salt scope in the photocatalysed 1,2-alkoxyhydroxylation of alkenes. **b**, The substrate scope for the photocatalytic

1,2-dialkoxylation (left) and the 1,2-alkoxy-amidation (right) of alkenes.^aHere, 5.0 equiv. **3a** was used. ^bReaction run at 0°C . Ad, 1-adamantyl; iPr, cyclopropyl; Cy, cyclohexyl; iPr, isopropyl.

excited state of **PC1**, supporting the SET reduction of the salt in the first step of the reaction. Cyclic voltammetry studies on **1a** found a more positive reduction potential (E_p of -0.14 eV versus Ag/AgCl) than the photoexcited **PC1**, further supporting the proposed SET process. Addition of alkoxy radical **I** to the alkene was supported by a radical trapping experiment conducted under the standard reaction conditions in the

presence of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl. The 2,2,6,6-tetramethylpiperidine-1-oxyl-adduct **7**, resulting from interception of radical intermediates **II**, was detected by high-resolution mass spectrometry (HR-MS). The involvement of alkoxy radicals is also supported by the results obtained using sulfonium salt **1aj**, bearing a β -branched alkoxy motif; the introduction of 4-methyl-quinoline **8**,

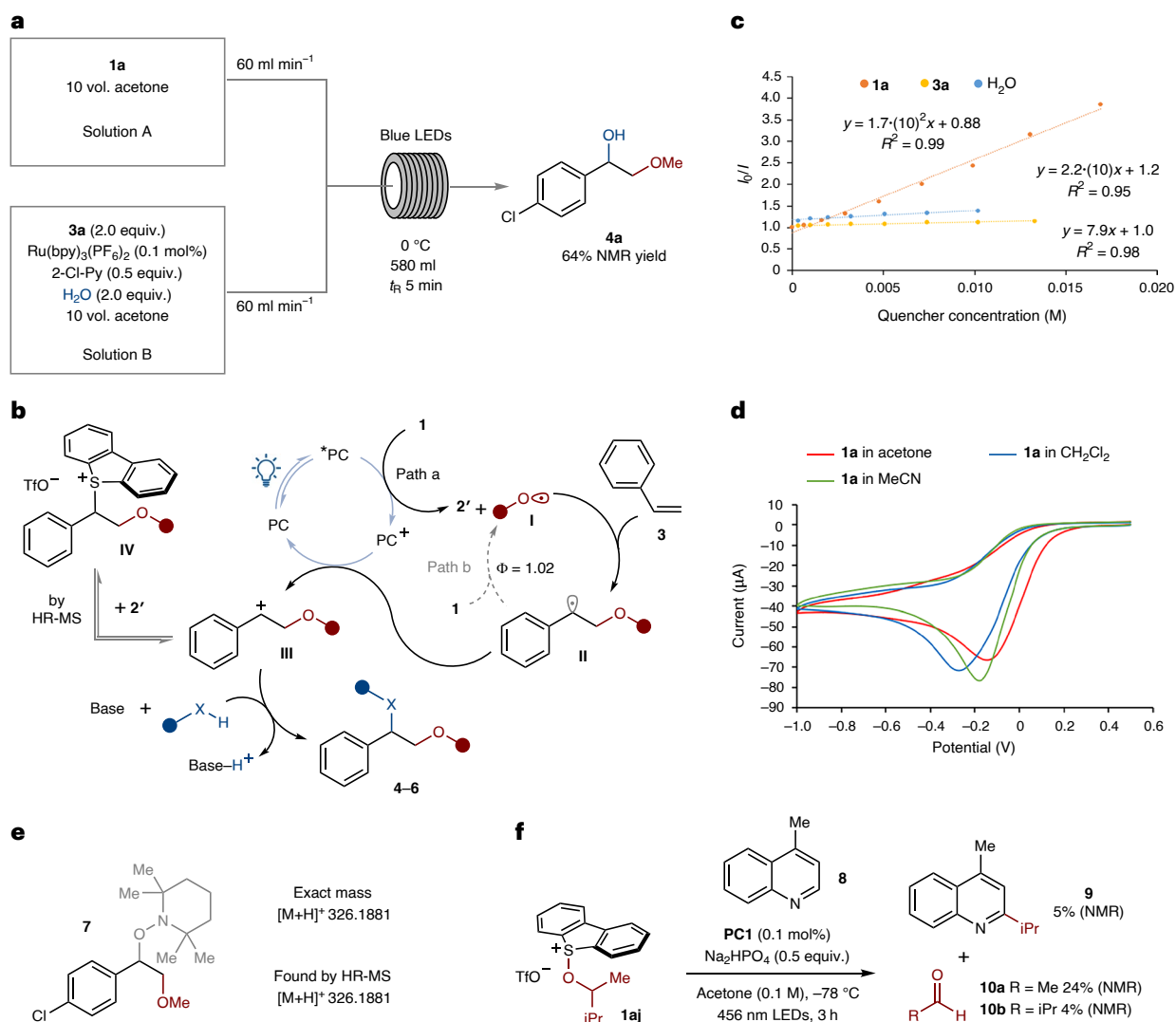


Fig. 3 | Reaction scale-up under photoflow conditions, proposed mechanism of alkene 1,2-alkoxy-hydroxylation and mechanistic studies supporting the proposed catalytic cycle. a, The optimized photocatalytic 1,2-alkoxy-hydroxylation of alkenes for a photoflow reactor. **b**, The proposed catalytic

cycle. **c**, Stern–Volmer fluorescence quenching studies. **d**, Cyclic voltammetry studies. **e**, A radical intermediate trapping experiment. **f**, A control experiment supporting the formation of an alkoxy radical intermediate. bpy, 2,2'-bipyridine; Py, pyridine; t_R, retention time.

under otherwise standard reaction conditions, gave Minisci-type coupling product **9** and aldehydes **10a,b** arising from radicals formed by β -scission of the alkoxy radical species⁷¹. The intermediacy of benzylic carbocations **III** is also corroborated by the detection by HR-MS of a sulfonium salt corresponding to **IV** formed by reaction of **III** with dibenzothiophene **2'** liberated in the early stages of the catalytic cycle. A quantum yield (Φ) of 1.02 was measured for the coupling of **1a** and **3a** to give **4a**, thus suggesting the involvement—at least partially—of a radical-chain mechanism, in which **II** reduces the starting alkoxy sulfonium salt **1a** (Fig. 3b, path b).

Conclusions

Convenient activation of both simple and complex alcohols as alkoxy sulfonium salts provides a platform for alkoxy radical generation from alcohols under mild photocatalytic conditions. Crucially, our alcohol activation involves addition of the alcohol hydroxyl group to the sulfur of a commercial sulfoxide in an interrupted Pummerer-type process, rather than displacement of alkyl halides by O-containing activating agents in S_N1 and S_N2 processes. Thus, alcohol activation is more general in that greater structural variation and functionality is tolerated in the alkoxy radical precursors. We have applied the approach in an efficient,

modular photocatalytic difunctionalization of alkenes, using alcohols activated directly as alkoxy sulfonium salts, that delivers 1,2-hydroxy ethers, symmetrical and unsymmetrical 1,2-diethers and 1,2-amido ethers. The mild nature of the process results in good functional group tolerance and scope, and the method can be easily adapted from laboratory to industrial scale using a photoflow system; a product of alkene difunctionalization was obtained in 3.5 h from a 1-kg scale process. Preliminary mechanistic studies suggest a photocatalytic cycle involving reduction of the alkoxy sulfonium salts to give alkoxy radicals that undergo intermolecular addition to alkenes. Subsequent oxidation of the carbon-centred radical adducts regenerates the photocatalyst and closes the catalytic cycle. We believe that straightforward activation of alcohols for use in photochemistry, through alkoxy sulfonium salt formation, will facilitate future developments in chemical synthesis.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41557-025-02003-7>.

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Methods

General procedure for the photocatalytic

1,2-alkoxy-hydroxylation of alkenes

A dry tube equipped with a stirring bar was charged with alkoxy sulfonium salt (0.10 mmol, 1.0 equiv.), Na_2HPO_4 (7 mg, 0.05 mmol, 0.5 equiv.) and alkene (if solid) (0.20 mmol, 2.0 equiv.). The tube was capped with an aluminium crimp seal with septum (polytetrafluoroethylene (PTFE)/butyl), then evacuated under high vacuum and backfilled with N_2 (three times). Degassed $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ in an acetone stock solution (1.0 ml, 0.1 mol%), and alkene (if liquid) (0.20 mmol, 2.0 equiv.) and H_2O (4 μl , 0.20 mmol, 2.0 equiv.) were sequentially added. The vial was purged with a stream of N_2 and the lid sealed with parafilm and placed approximately 5 cm from blue LEDs. The blue LEDs were switched on and the mixture was stirred under irradiation at -78°C for 3 h. The tube was allowed to warm to room temperature and was opened, and the reaction mixture was concentrated and purified by column chromatography on silica gel, eluting with hexane–ethyl acetate.

General procedure for the photocatalytic 1,2-dialkoxylation of alkenes

A dry tube equipped with a stirring bar was charged with alkoxy sulfonium salt (0.10 mmol, 1.0 equiv.), Na_2HPO_4 (7 mg, 0.05 mmol, 0.5 equiv.) and alkene (if solid) (0.20 mmol, 2.0 equiv.). The tube was capped with an aluminium crimp seal with septum (PTFE/butyl), then evacuated under high vacuum and backfilled with N_2 (three times). Degassed $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ in a CH_2Cl_2 stock solution (1.0 ml, 0.1 mol%), and alkene (if liquid) (0.20 mmol, 2.0 equiv.) and alcohol (0.50 mmol, 5.0 equiv.) were sequentially added. The vial was purged with a stream of N_2 and the lid sealed with parafilm and placed approximately 5 cm from blue LEDs. The blue LEDs were switched on and the mixture was stirred under irradiation at -78°C for 3 h. The tube was allowed to warm to room temperature and was opened, and the reaction mixture was concentrated and purified by column chromatography on silica gel, eluting with hexane–ethyl acetate.

General procedure for the photocatalytic 1,2-alkoxy-amidation of alkenes

A dry tube equipped with a stirring bar was charged with alkoxy sulfonium salt (0.10 mmol, 1.0 equiv.), Na_2HPO_4 (7 mg, 0.05 mmol, 0.5 equiv.) and alkene (if solid) (0.20 mmol, 2.0 equiv.). The tube was capped with an aluminium crimp seal with septum (PTFE/butyl), then evacuated under high vacuum and backfilled with N_2 (three times). Degassed $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ in an alkylnitrile stock solution (0.5 ml, 0.1 mol%), and alkene (if liquid) (0.20 mmol, 2.0 equiv.) and H_2O (2 μl , 0.10 mmol, 1.0 equiv.) were sequentially added. The vial was purged with a stream of N_2 and the lid sealed with parafilm and placed approximately 5 cm from blue LEDs. The blue LEDs were switched on and the mixture was stirred under irradiation at -30°C for 3 h. The tube was allowed to warm to room temperature and was opened, and the reaction mixture was concentrated and purified by column chromatography on silica gel, eluting with hexane–ethyl acetate.

Data availability

All data are provided in the main text or Supplementary Information, including experimental procedures, copies of NMR spectra and X-ray structure reports. Structural parameters are available from the Cambridge Crystallographic Data Centre (CCDC) under reference numbers 2432415 (**4be**) and 2432693 (**4cf**).

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Author contributions

D.J.P., C.R. and H.Z. conceived the project. H.Z. executed the chemical synthesis and mechanistic studies with assistance from A.G.-G. H.Z. carried out the spectroscopic studies with oversight from L.S.N. D.J.P. and C.R. oversaw the research. D.F., Y.C. undertook the scale-up work and photoflow chemistry with oversight from L.R.E.P. C.R., D.J.P. and H.Z. composed the manuscript. H.Z. compiled the supplementary materials, and D.J.P. and C.R. provided editorial feedback and oversight.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to David J. Procter.

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