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Redox-Neutral C(sp³)—H Alkenylation via Photocatalyzed Tandem Hydrogen Atom Transfer and Downstream Oxidative Radical Polar CrossoverMattia Lepori¹  | Luigi Dolcini¹  | Alexander Bell²  | Wolfgang Haumer²  | Joshua P. Barham^{1,2} ¹Fakultät für Chemie und Pharmazie, Universität Regensburg, Regensburg, Germany | ²Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow, UK**Correspondence:** Joshua P. Barham (Joshua-Philip.Barham@chemie.uni-regensburg.de; joshua.p.barham@strath.ac.uk)**Received:** 15 June 2026 | **Revised:** 8 August 2026 | **Accepted:** 10 September 2026**Keywords:** alkenylation | hydrogen atom transfer | photoredox catalysis | radical polar crossover | redox-neutral

ABSTRACT

Herein, we present a photocatalytic route that exploits a redox-neutral tandem hydrogen atom transfer (HAT) and oxidative radical polar crossover (RPC) manifold. This method enables the efficient synthesis of valuable allylic amides and ethers through the valorization of three classes of ubiquitous feedstock chemicals: carboxylic acids as precursors to hydrogen atom abstractors, amides or ethers as C(sp³)—H donors, and olefins as radical acceptors. The protocol operates under mild conditions, exhibits broad functional group tolerance, and is readily scalable. The redox-neutral nature of this transformation mechanistically distinguishes it from traditional net-oxidative approaches associated with exogenous stoichiometric oxidants. Crucially, it allows HAT substrates bearing “hydridic” C—H bonds (e.g., α - to heteroatom: X—CHR¹R²) to be engaged in Giese-type addition reactions and subsequent oxidative RPC/nucleophilic trapping, where traditional net-oxidative approaches inevitably result in Shono-type further oxidation of the HAT-derived radical (e.g., α - to heteroatom: X⁺=CR¹R²) and nucleophilic interception prior to intermolecular radical addition.

1 | Introduction

The direct functionalization of abundant and readily available feedstock chemicals represents a powerful strategy for the rapid construction of value-added molecular scaffolds. In this context, catalytic hydrogen atom transfer (HAT) has emerged as a compelling cost- and step-economical approach to generate radical intermediates from otherwise inert C—H bonds [1–3]. Such activations are classically achieved under thermal conditions, typically mediated by transition metal catalysts [4–7] or—more prominently in recent years—via photocatalysis [8–14]. Interception of the resulting nucleophilic C-centered radical by ubiquitous olefins enables efficient C—C formation, giving rise to metastable alkyl radical intermediates, often benzylic radicals when vinylarenes are employed as acceptors. Subsequent oxidative radical polar crossover (RPC) furnishes the corresponding carbocation species [15–17], leading to downstream

bond formation via polar chemistry within a three-component olefin difunctionalization manifold [18–22] or deprotonation at the β -position in Heck-type processes [22–24]. This oxidation step is typically accomplished either by (i) the use of exogenous stoichiometric oxidants (e.g., TBHP, Na₂S₂O₈) [25–27] or (ii) electrochemical anodic oxidation (Figure 1A) [28, 29]. While the former approach suffers from the generation of considerable chemical waste, the latter has been reported to be ineffective for substrates bearing activated “hydridic” C—H bonds, such as amides or ethers. In these cases, the α - to heteroatom radicals are rapidly oxidized at the anode in a Shono-type oxidation to the corresponding carbocations (e.g., oxocarbenium for ethers) [30], which are then trapped by nucleophiles [31–34].

In light of the limitations associated with net-oxidative processes, we questioned whether a redox-neutral strategy could be devised

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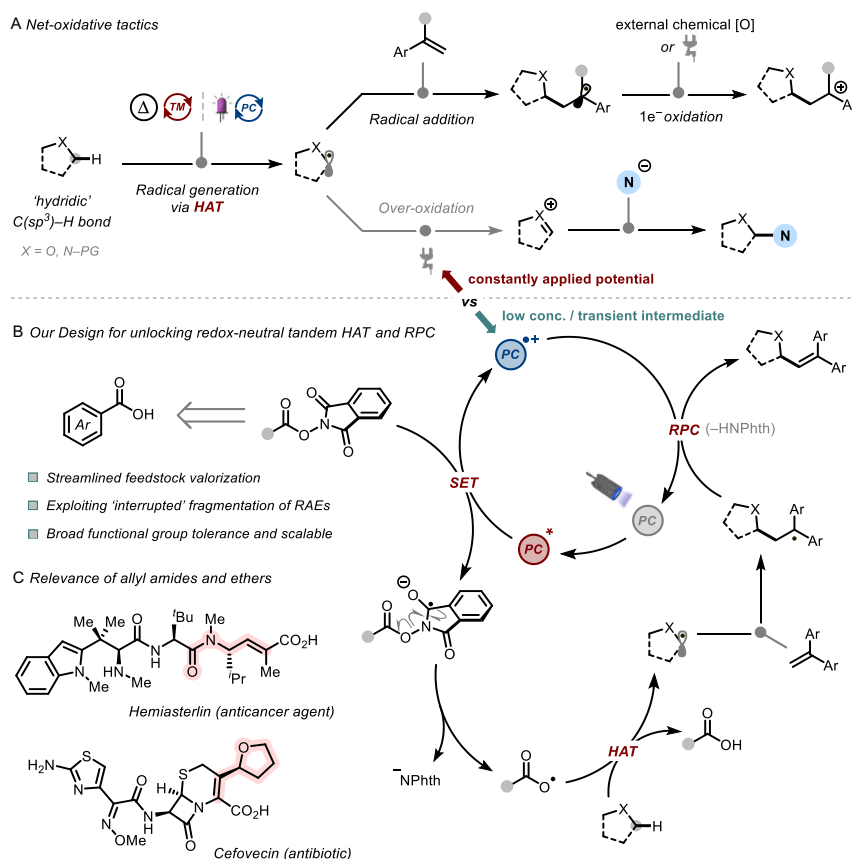


FIGURE 1 | (A) Canonical net-oxidative radical tactics for tandem HAT and oxidative RPC. (B) Our approach: photocatalyzed redox-neutral $C(sp^3)$ -H alkenylation harnessing benzoyloxy radical as hydrogen atom abstractor. (C) Active pharmaceutical ingredients containing allyl amides or ethers.

to unlock a tandem photocatalytic HAT and (downstream) oxidative RPC sequence [35–40]. Inspired by our previous disclosures involving (i) tandem reductive single electron transfer (SET) activations of *N*-hydroxyphthalimide (NHPI) redox-active esters (RAEs) and downstream oxidative RPC Heck-type alkenylations [22] and (ii) intermediacy of benzoyloxy radicals derived from reductive SET cleavage of N–O bonds [41], we were drawn to benzoyloxy radicals as competent HAT agents [42–45]. These can be easily generated via SET reduction of bench-stable and readily-accessible carboxylic acid-derived NHPI RAEs [46–48]. While alkyl RAEs typically undergo entropically-driven decarboxylative cleavage to release C-centered radicals along with the phthalimide anion (^-NPhth), aromatic carboxylic acid-derived analogs exhibit a distinct reactivity profile. In these systems, benzoyloxy radicals are formed through an “interrupted” fragmentation pathway [49], as decarboxylation leading to the generation of an aryl radical is kinetically disfavored (Figure 1B) [50–53]. Once generated, the O-centered electrophilic radical (BDE O–H = 111 kcal mol^{−1} for PhCO₂H) [9] could trigger the hydrogen abstraction from amides and ethers (BDE $C(sp^3)$ -H α - to N/O $\approx$ 90 kcal mol^{−1}) [10, 54], affording the α -amido or α -oxy radical. After Giese-type addition to the olefin, the ensuing RPC step is mediated by the oxidized form of the photocatalyst generated in the initial SET step, thereby furnishing the desired carbocation intermediate while closing the photocatalytic cycle. Herein, we report the successful realization of this design, leveraging a redox-neutral manifold for the streamlined synthesis of allylic amides and ethers; structural motifs widely encountered in pharmaceuticals (Figure 1C) [55–57].

2 | Results and Discussion

Our experimental investigation commenced with the optimization of the photocatalytic $C(sp^3)$ -H alkenylation reaction (for further details, see Section 5, Supporting Information). The desired product **4** was obtained in 42% yield when a solution of pentafluorobenzoic acid-derived NHPI ester **1a** (1.2 equiv.)—serving as a benzoyloxy radical precursor—1,1-diphenylethylene **2a** (1.0 equiv.) as a radical acceptor, 2,4,5,6-tetrakis(9*H*-carbazol-9-yl)isophthalonitrile (**4-CzIPN**, 5 mol%) as a photocatalyst, and trifluoroacetic acid (TFA, 10 equiv.) in *N,N*-dimethylacetamide (**3a**, 0.1 M)—acting as both C–H donor and solvent—was irradiated with blue LEDs (40 W, 427 nm Kessil lamp) for 16 h (Table 1, Entry 1). Noteworthy is the underperformance of the more expensive organophotocatalyst **3DPAFIPN** (Entry 2). TFA (10 equiv.) could be replaced with a sub-stoichiometric loading of milder Lewis acid Zn(OTf)₂ (0.5 equiv.) without a loss of efficiency (Entry 3). Various NHPI esters were evaluated, with **1a** outperforming benzoic acid and trifluoroacetic acid derivatives (**1b** and **1c**, Entry 4). Increasing the amount of **2a** to 2.0 equiv. improved the yield of **4** to 59% (Entry 5). Gratifyingly, the amount of **3a** could be halved by using acetonitrile as a co-solvent, affording alkenylation product **4** in a 65% yield when the irradiation time was extended to 40 h (Entry 6). TFA plays a major role in promoting the initial reduction of **1a** (vide infra) [58–60], as omission of the former resulted in a poor yield of **4** (Entry 7). A control experiment designed to probe the formation of a donor–acceptor complex [22, 61–63] between **1a** and **2a** led to lower yields, underscoring

TABLE 1 | Optimization of photocatalytic C(sp³)-H alkenylation conditions.

Entry	Deviation(s)	Yield of 4 (%) ^[a]
1	none	42
2	3DPAFIPN (5 mol%) instead of 4-CzIPN	29
3	Zn(OTf) ₂ (0.5 equiv.) instead of TFA	44
4	1b or 1c instead of 1a	32 / 25
5	1a:2a ratio = 1:2 instead of 1.2:1	59
6	3a:MeCN (1:1) as reaction solvent (0.1 M); 40 h irradiation ^[b]	65
7	no TFA	12
8	no 4-CzIPN	25
9	no light	n.d.

4-CzIPN **3DPAFIPN**

1b **1c**

Abbreviation: n.d. = not detected.

^aYields were determined by ¹H NMR using 1,1,2-trichloroethylene (1.0 equiv.) as an internal standard. Reactions performed on a 0.1 mmol scale.^b**1a** (1.0 equiv.) and **2a** (2.0 equiv.). For further details, see the Supporting Information.

the pivotal role of the photocatalyst in inducing the reaction and securing higher yields of **4** (Entry 8). Finally, no product formation was observed in the absence of light (Entry 9).

With the optimized conditions in hand, we next assessed the generality of the alkenylation protocol and found that a variety of readily-available C-H donors could be efficiently engaged and coupled with **2a** (Figure 2). Initial efforts focused on the variation of the acyl group in *N,N*-dimethylamides, affording the

desired products in moderate to good yields (**4–6**). Importantly, the reaction with **3a** was readily scalable up to a 3 mmol scale with only a marginal decrease in yield (for further details, see Section 9, Supporting Information). The diminished efficiency observed for conversion of *N,N*-dimethylbutanamide to **7** is likely due to the presence of additional C(sp³)-H bonds in the extended alkyl chain. These C(sp³)-H bonds are far enough away from the inductively withdrawing C=O group to react competitively, which likely promotes side reactions. *N,N*-Dimethylformamide (DMF) and

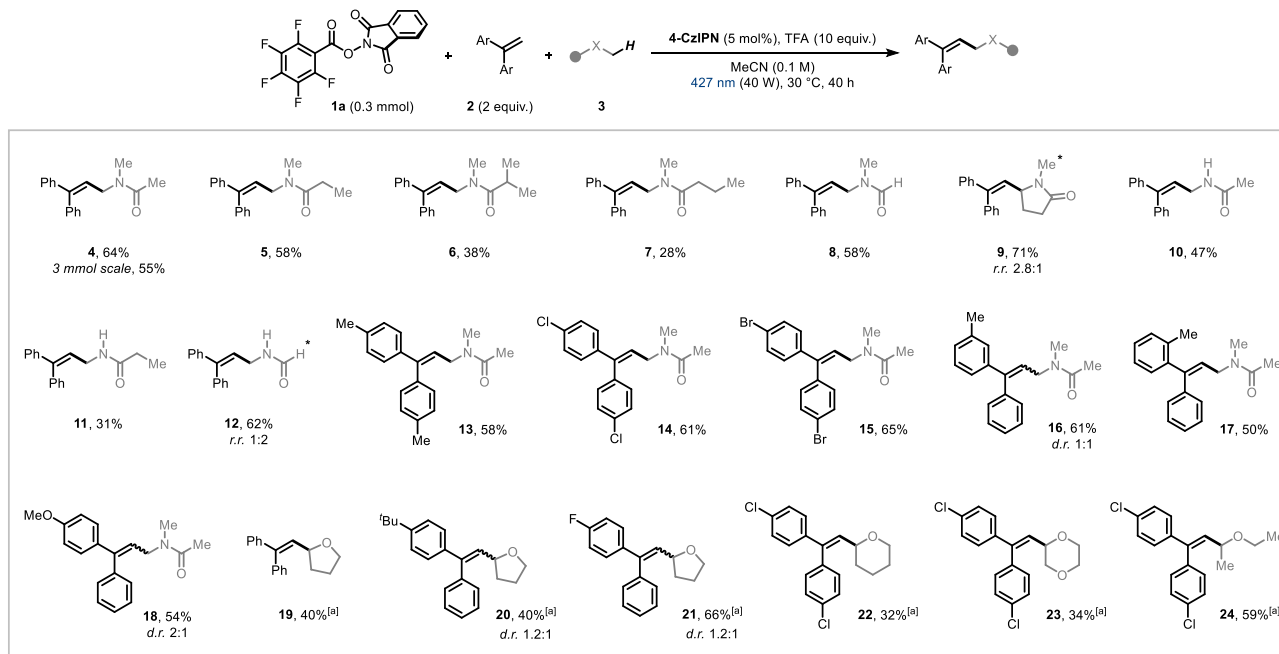


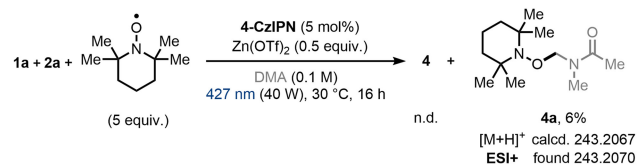
FIGURE 2 | Scope of the photocatalytic redox-neutral C(sp³)-H alkenylation. Reaction conditions: redox-active ester **1a** (0.3 mmol, 1.0 equiv.), 1,1-diarylolefin **2** (0.6 mmol, 2.0 equiv.), **4-CzIPN** (5 mol%), and C-H donor **3** (1.5 mL) in anhydrous MeCN (1.5 mL). Alternative HAT site to give another regioisomer is denoted with an asterisk. ^aEther used as the reaction solvent (0.1 M); 16 h irradiation time. For further details, see the Supporting Information. Isolated yields are reported.

N-methylpyrrolidone (NMP) afforded the corresponding alkenylated products in good to very good yields (**8–9**). Particularly notable was the formation of **8**, which confirmed that HAT at the C(sp³)–H bond α - to *N* in DMF predominates over HAT at the aldehydic C(sp²)–H bond. This demonstrates the complementarity of our approach to a previous report involving photogenerated iodanyl radicals [36], where the latter reactivity afforded positional regioisomers under otherwise similar conditions.

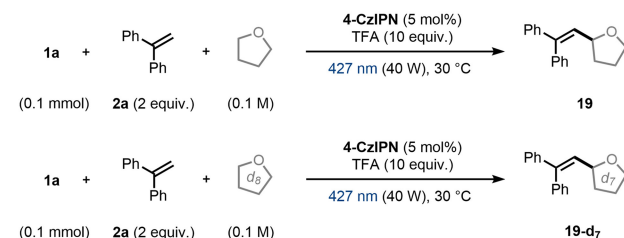
N-Methyl-substituted alkyl amides were also viable reactants under optimized conditions (**10–11**), albeit in lower yields than their dialkylated congeners (i.e., **4** and **5**). This could be due to a stabilizing/deactivating interaction between the N–H moiety and the benzoyloxy radical. When *N*-methylformamide was employed, a mixture of the corresponding allyl amide (from the α -amido radical) and its regioisomeric α,β -unsaturated carbonyl compound (from the acyl radical) was obtained (**12**) [64, 65]. Next, we extended the scope to different radical acceptors, successfully coupling **3a** with symmetric *para*-disubstituted 1,1-diarylolefins bearing electron-donating (Me) and -withdrawing (Cl and Br) substituents (**13–15**). Pleasingly, *meta*-, *ortho*-, and *para*-monosubstituted asymmetric acceptors also afforded the desired products in synthetically useful yields (**16–18**). Radical acceptors other than 1,1-diarylolefins were found to be unreactive under the optimized conditions (see Section 11, Supporting Information). Finally, the method was also extended to ethers, enabling the functionalization of tetrahydrofuran (**19–21**) as well as other cyclic (tetrahydropyran and 1,4-dioxane) and acyclic (diethyl ether) analogs (**22–24**).

In order to gain mechanistic insights into the developed alkenylation process, we conducted a series of additional experiments. The involvement of radical species was confirmed by a radical trapping experiment using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO): adduct **4a** was detected in both the ¹H NMR and HRMS of the crude reaction mixture, while the formation of the desired product **4** was completely inhibited (Figure 3A) [66]. Corroborating an initial reductive SET event within the catalytic cycle (vide supra, Figure 1B), the presence of TFA in the cyclic voltammetry experiments induced a clear positive shift in the reduction potential of **1a** (from –1.22 to –1.14 V vs SCE). This observation demonstrates LUMO lowering upon Brønsted acid activation of **1a** [58–60, 67], with the resulting reduction potential matching the excited-state half potential of *4-CzIPN (*E_{1/2} = –1.18 V vs SCE) [68], thereby enabling productive reactivity (for further details, see Section 8.5, Supporting Information). The observed kinetic isotope effect (KIE) value of 1.7 suggests that HAT may be involved in the rate-determining step (Figure 3B) [69]. Quantum yield measurements revealed that the reaction is photocatalytic in nature and that a radical chain is either absent or inefficient (Φ = 0.011, see Section 8.1, Supporting Information) [70]. Finally, we designed a reaction to probe the benzoyloxy radical as the indirect HAT abstractor in our system [71]. In particular, when the 2-methylbenzoic acid-derived NHPI ester (**1e**) was subjected to the reaction with **2a** in the presence of 4-CzIPN in acetonitrile, lactone **25** was obtained in a 25% yield (Figure 3C). This result strongly points to (i) the formation of a benzylic radical via a favorable intramolecular 1,5-HAT from the benzoyloxy radical generated upon SET reduction and “interrupted” fragmentation [72] and (ii) an oxidative RPC step following Giese-type addition, leading to a diphenylalkyl carbocation that undergoes swift lactonization.

A Radical trapping and inhibition experiment



B Parallel kinetic isotopic effect $k_H/k_D = 1.7$



C Probing benzoyloxy radical as HAT abstractor

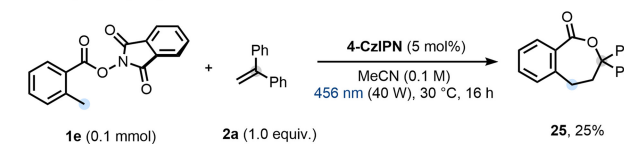


FIGURE 3 | (A) Radical trapping and inhibition experiment. (B) Kinetic isotope effect. (C) Probing benzoyloxy radical as a hydrogen atom abstractor. Yields were determined by ¹H NMR using 1,1,2-trichloroethylene as an internal standard.

3 | Conclusion

In summary, we have developed an operationally simple and modular C(sp³)–H alkenylation protocol that utilizes only abundant and cost-effective feedstock chemicals: carboxylic acids, amides, ethers, and olefins. The transformation proceeds through a tandem photocatalytic redox-neutral cascade, initiated by the generation of a benzoyloxy radical via reductive single-electron transfer of the pentafluorobenzoic acid-derived NHPI ester. The electrophilic radical triggers hydrogen atom transfer from amides or ethers, affording nucleophilic α -amido or α -oxy radicals. Subsequent addition of these radicals to 1,1-diarylolefins generates a benzylic radical intermediate, which undergoes (downstream) oxidative radical polar crossover and deprotonation to furnish valuable allylic amides and ethers. Importantly, the carboxylic acid byproduct can be readily recycled for the preparation of fresh NHPI ester, highlighting the sustainability of the process. This work expands the toolbox of methodologies combining HAT and RPC, which were previously limited to (i) the use of stoichiometric external oxidants or (ii) to “unactivated” C–H substrates (e.g., cyclohexane) to avoid undesired fast Shono-type oxidation of the incipient C-centered radicals.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Detailed experimental procedures, molecular characterization, and descriptions of all setups used in this study are available in the Supporting Information.

References

1. J. F. Hartwig and M. A. Larsen, "Undirected, Homogeneous C–H Bond Functionalization: Challenges and Opportunities," *ACS Central Science* 2 (2016): 281–292, <https://doi.org/10.1021/acscentsci.6b00032>.
2. L. Capaldo and D. Ravelli, "Hydrogen Atom Transfer (HAT): A Versatile Strategy for Substrate Activation in Photocatalyzed Organic Synthesis," *European Journal of Organic Chemistry* 2017 (2017): 2056–2071, <https://doi.org/10.1002/ejoc.v2017.15>.
3. J. Kaur and J. P. Barham, "Site-Selective C(sp³)–H Functionalizations Mediated by Hydrogen Atom Transfer Reactions via α -Amino/ α -Amido Radicals," *Synthesis* 54 (2022): 1461–1477, <https://doi.org/10.1055/a-1677-6619>.
4. M. S. Chen and M. C. White, "A Predictably Selective Aliphatic C–H Oxidation Reaction for Complex Molecule Synthesis," *Science* 318 (2007): 783–787, <https://doi.org/10.1126/science.1148597>.
5. W. Liu and J. T. Groves, "Manganese Catalyzed C–H Halogenation," *Accounts of Chemical Research* 48 (2015): 1727–1735, <https://doi.org/10.1021/acs.accounts.5b00062>.
6. Q. Michaudel, D. Thevenet, and P. S. Baran, "Intermolecular Ritter-Type C–H Amination of Unactivated sp³ Carbons," *Journal of the American Chemical Society* 134 (2012): 2547–2550, <https://doi.org/10.1021/ja212020b>.
7. K. M. Das, A. Pal, T. L. Surya, L. Roy, and A. Thakur, "Cu(II) Promoted C(sp³)–H Activation in Unactivated Cycloalkanes: Oxo-Alkylation of Styrenes to Synthesize β -Disubstituted Ketones," *Chemistry – A European Journal* 30 (2024): e202303776, <https://doi.org/10.1002/chem.202303776>.
8. L. Capaldo, L. L. Quadri, and D. Ravelli, "Photocatalytic Hydrogen Atom Transfer: The Philosopher's Stone for Late-Stage Functionalization?," *Green Chemistry* 22 (2020): 3376–3396, <https://doi.org/10.1039/D0GC01035A>.
9. H. Cao, X. Tang, H. Tang, Y. Yuan, and J. Wu, "Photoinduced Intermolecular Hydrogen Atom Transfer Reactions in Organic Synthesis," *Chem Catalysis* 1 (2021): 523–598, <https://doi.org/10.1016/j.checat.2021.04.008>.
10. L. Capaldo, D. Ravelli, and M. Fagnoni, "Direct Photocatalyzed Hydrogen Atom Transfer (HAT) for Aliphatic C–H Bonds Elaboration,"

Chemical Reviews 122 (2022): 1875–1924, <https://doi.org/10.1021/acs.chemrev.1c00263>.

11. L. Chang, S. Wang, Q. An, et al., "Resurgence and Advancement of Photochemical Hydrogen Atom Transfer Processes in Selective Alkane functionalizations," *Chemical Science* 14 (2023): 6841–6859, <https://doi.org/10.1039/d3sc01118f>.
12. F. S. Meger and J. A. Murphy, "Recent Advances in C–H Functionalisation Through Indirect Hydrogen Atom Transfer," *Molecules* 28 (2023): 6127, <https://doi.org/10.3390/molecules28166127>.
13. B. Feng, M. Lepori, M. Domański, et al., "Neutral Photogenerated N-Centred Radicals as a General, Catalytic Direct Hydrogen Atom Transfer Platform for Aliphatic C–H Functionalization," *Nature Catalysis* 9 (2026): 676–688, <https://doi.org/10.1038/s41929-026-01539-2>.
14. J. Kaur, L. Dolcini, D. Corsi, I. Daga, and J. P. Barham, "Two Reactivities for the Price of One Cycle: Sulfonamides as Dual Photoinduced Electron Transfer/Hydrogen Atom Transfer Catalysts," *ACS Catalysis* 16 (2026): 18892–18900, <https://doi.org/10.1021/acscatal.6c02004>.
15. J. A. Murphy, "The Radical Polar Crossover Reaction," in *Radicals Organic Synthesis*, ed. P. Renaud and M. P. Sibi (Wiley-VCH Verlag GmbH, 2001), ch. 2.7, 298–315.
16. R. J. Wiles and G. A. Molander, "Photoredox-Mediated Net-Neutral Radical/Polar Crossover Reactions," *Israel Journal of Chemistry* 60 (2020): 281–293, <https://doi.org/10.1002/ijch.201900166>.
17. M. Lepori, I. Dey, C. Pratley, and J. P. Barham, "Merging New and Old Concepts: Tandem Oxidative Radical-Polar Crossover Ritter Amidation via Multicomponent Photo- and Electrochemical Processes," *European Journal of Organic Chemistry* 27 (2024): e202400840, <https://doi.org/10.1002/ejoc.202400840>.
18. S. Gupta, A. Kundu, S. Ghosh, A. Chakraborty, and A. Hajra, "Visible Light-Induced Organophotoredox-Catalyzed Difunctionalization of Alkenes and Alkynes," *Green Chemistry* 25 (2023): 8459–8493, <https://doi.org/10.1039/D3GC03291D>.
19. Z.-L. Zhou, Y. Zhang, P.-Z. Cui, and J.-H. Li, "Photo-/Electrocatalytic Difunctionalization of Alkenes Enabled by C–H Radical Functionalization," *Chemistry – A European Journal* 30 (2024): e202402458, <https://doi.org/10.1002/chem.v30.62>.
20. G.-M. Cao, S.-S. Yan, L. Song, et al., "Navigating the Functionalization of Unactivated Alkenes via Visible Light Photocatalysis," *Chemical Society Reviews* 54 (2025): 6726–6806, <https://doi.org/10.1039/D5CS00181A>.
21. Y. Wang, Z.-P. Bao, X.-D. Mao, M. Hou, and X.-F. Wu, "Intermolecular 1,2-Difunctionalization of Alkenes," *Chemical Society Reviews* 54 (2025): 9530–9573, <https://doi.org/10.1039/D5CS00670H>.
22. M. Lepori, C. Pratley, I. Dey, V. Butera, V. Roider, and J. P. Barham, "Photocatalysis Enables Chemodivergent Radical Polar Crossover: Ritter-Type Amidation vs Heck-Type Olefin Carbonylfunctionalizations," *Chemistry – A European Journal* 31 (2025): e202500666, <https://doi.org/10.1002/chem.202500666>.
23. Z.-H. Xia, C.-L. Zhang, Z.-H. Gao, and S. Ye, "Switchable Decarboxylative Heck-Type Reaction and Oxo-Alkylation of Styrenes With *N*-Hydroxyphthalimide Esters Under Photocatalysis," *Organic Letters* 20 (2018): 3496–3499, <https://doi.org/10.1021/acs.orglett.8b01268>.
24. N. Kato, T. Nanjo, and Y. Takemoto, "A Pyridine-Based Donor–Acceptor Molecule: A Highly Reactive Organophotocatalyst That Enables the Reductive Cleavage of C–Br Bonds Through Halogen Bonding," *ACS Catalysis* 12 (2022): 7843–7849, <https://doi.org/10.1021/acscatal.2c02067>.
25. T. Wan, L. Capaldo, G. Laudadio, et al., "Decatungstate-Mediated C(sp³)–H Heteroarylation via Radical-Polar Crossover in Batch and Flow," *Angewandte Chemie, International Edition* 60 (2021): 17893–17897, <https://doi.org/10.1002/anie.202104682>.
26. C. Dai, F. Meschini, J. M. R. Narayanam, and C. R. J. Stephenson, "Friedel–Crafts Amidoalkylation via Thermolysis and Oxidative

- Photocatalysis," *Journal of Organic Chemistry* 77 (2012): 4425–4431, <https://doi.org/10.1021/jo300162c>.
27. C. Huang, Y.-S. Qin, C.-L. Wang, et al., "Visible Light-Induced C(sp³)-H Azolation of Ethers via Radical-Polar Crossover," *Chemical Communications* 60 (2024): 2669–2672, <https://doi.org/10.1039/D3CC06210D>.
 28. S. Zhang and M. Findlater, "Electrochemically Driven Hydrogen Atom Transfer Catalysis: A Tool for C(sp³)/Si-H Functionalization and Hydrofunctionalization of Alkenes," *ACS Catalysis* 13 (2023): 8731–8751, <https://doi.org/10.1021/acscatal.3c01221>.
 29. S. Schmid, S. Wu, I. Dey, M. Domański, X. Tian, and J. P. Barham, "Photoelectrochemical Heterodifunctionalization of Olefins: Carboamidation Using Unactivated Hydrocarbons," *ACS Catalysis* 14 (2024): 9648–9654, <https://doi.org/10.1021/acscatal.4c02320>.
 30. S. Su, Y. Guo, and J. Derosa, "Recent Developments in Shono-Type Oxidation: Strategies for Modular α -C(sp³)-H Functionalization," *ACS Electrochemistry* 2 (2026): 14–24, <https://doi.org/10.1021/acselectrochem.5c00443>.
 31. Z. Wang, K. Niu, Y. Liu, H. Song, and Q. Wang, "Electrochemical α -C(sp³)-H/O-H Cross-Coupling of Isochromans and Alcohols Assisted by Benzoic Acid," *Chemical Communications* 58 (2022): 10949–10952, <https://doi.org/10.1039/D2CC03883H>.
 32. Z.-R. Xu, Q.-R. Zhu, P.-Z. Zhang, H. Gao, and P.-L. Wang, "t-BuOK-Induced, NH₃·MeOH-Promoted Electrochemical C(sp³)-H Amination of Saturated Heterocycles With Sulfoximines," *Organic Letters* 27 (2025): 7785–7791, <https://doi.org/10.1021/acs.orglett.5c02042>.
 33. D. I. Ioannou, L. Capaldo, J. Sanramat, J. N. H. Reek, and T. Noël, "Accelerated Electrophotocatalytic C(sp³)-H Heteroarylation Enabled by an Efficient Continuous-Flow Reactor," *Angewandte Chemie, International Edition* 62 (2023): e202315881, <https://doi.org/10.1002/anie.202315881>.
 34. D. I. Ioannou, E. Bombonato, J. Sanramat, J. N. H. Reek, and T. Noël, "Oxidant-Free Amidation of Aldehydes Enabled by Electrophotocatalysis," *Chemistry – A European Journal* 31 (2025): e02237, <https://doi.org/10.1002/chem.202502237>.
 35. G. Pandey and R. Laha, "Visible-Light-Catalyzed Direct Benzylic C(sp³)-H Amination Reaction by Cross-Dehydrogenative Coupling," *Angewandte Chemie, International Edition* 54 (2015): 14875–14879, <https://doi.org/10.1002/anie.201506990>.
 36. M. Lu, Z. Lin, S. Chen, H. Chen, M. Huang, and S. Cai, "Visible-Light-Enabled Oxidative Coupling of Alkenes With Dialkylformamides to Access Unsaturated Amides," *Organic Letters* 21 (2019): 9929–9933, <https://doi.org/10.1021/acs.orglett.9b03870>.
 37. K. Zhang, L. Qiao, J. Xie, et al., "Visible-Light-Induced C(sp²)-C(sp³) Coupling Reaction for the Regioselective Synthesis of 3-Functionalized Coumarins," *Journal of Organic Chemistry* 86 (2021): 9552–9562, <https://doi.org/10.1021/acs.joc.1c00848>.
 38. Y. Zhang, N. A. Fitzpatrick, M. Das, et al., "A Photoredox-Catalyzed Approach for Formal Hydride Abstraction to Enable C–H Functionalization With Nucleophilic Partners (F, C, O, N, and Br/Cl)," *Chem Catalysis* 2 (2022): 292–308, <https://doi.org/10.1016/j.checat.2021.12.010>.
 39. M. Das, L. Zamani, C. Bratcher, and P. Z. Musacchio, "Azolation of Benzylic C–H Bonds via Photoredox-Catalyzed Carbocation Generation," *Journal of the American Chemical Society* 145 (2023): 3861–3868, <https://doi.org/10.1021/jacs.2c12850>.
 40. T. Hao, J. Shen, Y. Wei, and M. Shi, "Alkene Difunctionalization Enabled by Photocatalytic Hydrogen Atom Transfer From Haloalkane α -C(sp³)-H Bonds," *Chem Catalysis* 3 (2023): 100807, <https://doi.org/10.1016/j.checat.2023.100807>.
 41. J. Schütte, D. Corsi, W. Haumer, S. Schmid, J. Žurauskas, and J. P. Barham, "A Hydrazine-Free Photoredox Catalytic Synthesis of Azines by Reductive Activation of Readily Available Oxime Esters," *Green Chemistry* 26 (2024): 6446–6453, <https://doi.org/10.1039/D4GC00804A>.
 42. S. Mukherjee, B. Maji, A. Tlahuext-Aca, and F. Glorius, "Visible-Light-Promoted Activation of Unactivated C(sp³)-H Bonds and Their Selective Trifluoromethylthiolation," *Journal of the American Chemical Society* 138 (2016): 16200–16203, <https://doi.org/10.1021/jacs.6b09970>.
 43. S. Mukherjee, R. A. Garza-Sanchez, A. Tlahuext-Aca, and F. Glorius, "Alkynylation of C(O)-H Bonds Enabled by Photoredox-Mediated Hydrogen-Atom Transfer," *Angewandte Chemie, International Edition* 56 (2017): 14723–14726, <https://doi.org/10.1002/anie.201708037>.
 44. S. Mukherjee, T. Patra, and F. Glorius, "Cooperative Catalysis: A Strategy to Synthesize Trifluoromethyl-Thioesters From Aldehydes," *ACS Catalysis* 8 (2018): 5842–5846, <https://doi.org/10.1021/acscatal.8b01519>.
 45. M. Hirose, H. Sakaguchi, R. Hashimoto, et al., "Benzoic Acid Serves as Precursor of Catalytic HAT Reagent in a Two-Molecule Photoredox System," *Chemistry – A European Journal* 30 (2024): e202402285, <https://doi.org/10.1002/chem.202402285>.
 46. S. Murarka, "N-(Acyloxy)phthalimides as Redox-Active Esters in Cross-Coupling Reactions," *Advanced Synthesis & Catalysis* 360 (2018): 1735–1753, <https://advanced.onlinelibrary.wiley.com/doi/full/10.1002/adsc.201701615>.
 47. S. K. Parida, T. Mandal, S. Das, S. K. Hota, S. De Sarkar, and S. Murarka, "Single Electron Transfer-Induced Redox Processes Involving N-(Acyloxy)phthalimides," *ACS Catalysis* 11 (2021): 1640–1683, <https://doi.org/10.1021/acscatal.0c04756>.
 48. C. R. Azpilcueta-Nicolas and J.-P. Lumb, "Mechanisms for Radical Reactions Initiating From N-Hydroxyphthalimide Esters," *Beilstein Journal of Organic Chemistry* 20 (2024): 346–378, <https://doi.org/10.3762/bjoc.20.35>.
 49. M. Zheng, K. Gao, H. Qin, G. Li, and H. Lu, "Metal-to-Ligand Ratio-Dependent Chemodivergent Asymmetric Synthesis," *Angewandte Chemie, International Edition* 60 (2021): 22892–22899, <https://doi.org/10.1002/anie.202108617>.
 50. X.-Q. Hu, Z.-K. Liu, Y.-X. Hou, and Y. Gao, "Single Electron Activation of Aryl Carboxylic Acids," *iScience* 23 (2020): 101266, <https://doi.org/10.1016/j.isci.2020.101266>.
 51. L. J. Allen, P. J. Cabrera, M. Lee, and M. S. Sanford, "N-Acyloxyphthalimides as Nitrogen Radical Precursors in the Visible Light Photocatalyzed Room Temperature C–H Amination of Arenes and Heteroarenes," *Journal of the American Chemical Society* 136 (2014): 5607–5610, <https://doi.org/10.1021/ja501906x>.
 52. X. Zhao, B. Li, J. Xu, Q. Tang, Z. Cai, and X. Jiang, "Visible-Light-Driven Redox Neutral Direct C–H Amination of Glycine Derivatives and Peptides With N-Acyloxyphthalimides," *Chemistry – A European Journal* 27 (2021): 12540–12544, <https://doi.org/10.1002/chem.202101982>.
 53. Y. Toda, T. Kobayashi, F. Hirai, et al., "Visible-Light-Driven C–H Imidation of Arenes and Heteroarenes by a Phosphonium Ylide Organophotoredox Catalyst: Application to C–H Functionalization of Alkenes," *Journal of Organic Chemistry* 88 (2023): 9574–9578, <https://doi.org/10.1021/acs.joc.3c00988>.
 54. S. Angioni, D. Ravelli, D. Emma, D. Dondi, M. Fagnoni, and A. Albini, "Tetrabutylammonium Decatungstate (Chemo)selective Photocatalyzed, Radical C–H Functionalization in Amides," *Advanced Synthesis & Catalysis* 350 (2008): 2209–2214, <https://doi.org/10.1002/adsc.200800378>.
 55. H. Yan, L. Lu, G. Rong, et al., "Functionalization of Amides via Copper-Catalyzed Oxyalkylation of Vinylarenes and Decarboxylative Alkenylation of sp³ C–H," *Journal of Organic Chemistry* 79 (2014): 7103–7111, <https://doi.org/10.1021/jo501274f>.
 56. A. C. Olson, L. E. Overman, H. F. Sneddon, and J. W. Ziller, "Catalytic Asymmetric Synthesis of Branched Chiral Allylic Phenyl Ethers From (E)-Allylic Alcohols," *Advanced Synthesis & Catalysis* 351 (2009): 3186–3192, <https://doi.org/10.1002/adsc.200900678>.

57. H. Zhao, J. Brånalt, M. Perry, and C. Tyrchan, "The Role of Allylic Strain for Conformational Control in Medicinal Chemistry," *Journal of Medicinal Chemistry* 66 (2023): 7730–7755, <https://doi.org/10.1021/acs.jmedchem.3c00446>.
58. Z. Yan, B. Sun, X. Zhang, et al., "Construction of C(sp²)–C(sp³) Bond Between Quinoxalin-2(1H)-ones and N-Hydroxyphthalimide Esters via Photocatalytic Decarboxylative Coupling," *Chemistry – An Asian Journal* 14 (2019): 3344–3349, <https://doi.org/10.1002/asia.201900904>.
59. P. R. D. Murray, I. N.-M. Leibler, S. M. Hell, E. Villalona, A. G. Doyle, and R. R. Knowles, "Radical Redox Annulations: A General Light-Driven Method for the Synthesis of Saturated Heterocycles," *ACS Catalysis* 12 (2022): 13732–13740, <https://doi.org/10.1021/acscatal.2c04316>.
60. A. Tlahuext-Aca, R. A. Garza-Sanchez, and F. Glorius, "Multicomponent Oxyalkylation of Styrenes Enabled by Hydrogen-Bond-Assisted Photoinduced Electron Transfer," *Angewandte Chemie, International Edition* 56 (2017): 3708–3711, <https://doi.org/10.1002/anie.201700049>.
61. M.-C. Fu, R. Shang, B. Zhao, B. Wang, and Y. Fu, "Photocatalytic Decarboxylative Alkylations Mediated by Triphenylphosphine and Sodium Iodide," *Science* 363 (2019): 1429–1434, <https://doi.org/10.1126/science.aav3200>.
62. C. Zheng, G.-Z. Wang, and R. Shang, "Catalyst-Free Decarboxylation and Decarboxylative Giese Additions of Alkyl Carboxylates Through Photoactivation of Electron Donor-Acceptor Complex," *Advanced Synthesis & Catalysis* 361 (2019): 4500–4505, <https://advanced.onlinelibrary.wiley.com/doi/10.1002/adsc.201900803>.
63. G. E. M. Crisenza, D. Mazzarella, and P. Melchiorre, "Synthetic Methods Driven by the Photoactivity of Electron Donor–Acceptor Complexes," *Journal of the American Chemical Society* 142 (2020): 5461–5476, <https://doi.org/10.1021/jacs.0c01416>.
64. S. Bonciolini, M. Di Filippo, and M. Baumann, "A Scalable Continuous Photochemical Process for the Generation of Aminopropylsulfones," *Organic & Biomolecular Chemistry* 18 (2020): 9428–9432, <https://doi.org/10.1039/D0OB01801E>.
65. M. Lepori, D. I. Ioannou, J. P. Barham, and T. Noël, "Photocatalyzed Hydrogen Atom Transfer Enables Multicomponent Olefin Oxo-Amidomethylation Under Aerobic Conditions," *Chemical Science* 16 (2025): 22944–22951, <https://doi.org/10.1039/D5SC06277B>.
66. L. Buzzetti, G. E. M. Crisenza, and P. Melchiorre, "Mechanistic Studies in Photocatalysis," *Angewandte Chemie, International Edition* 58 (2019): 3730–3747, <https://doi.org/10.1002/anie.201809984>.
67. X. Wang, Y.-F. Han, X.-H. Ouyang, R.-J. Song, and J.-H. Li, "The Photoredox Alkylarylation of Styrenes With Alkyl N-Hydroxyphthalimide Esters and Arenes Involving C–H Functionalization," *Chemical Communications* 55 (2019): 14637–14640, <https://doi.org/10.1039/C9CC07494E>.
68. E. Speckmeier, T. G. Fischer, and K. Zeitler, "A Toolbox Approach to Construct Broadly Applicable Metal-Free Catalysts for Photoredox Chemistry: Deliberate Tuning of Redox Potentials and Importance of Halogens in Donor–Acceptor Cyanoarenes," *Journal of the American Chemical Society* 140 (2018): 15353–15365, <https://doi.org/10.1021/jacs.8b08933>.
69. E. M. Simmons and J. F. Hartwig, "On the Interpretation of Deuterium Kinetic Isotope Effects in C–H Bond Functionalizations by Transition-Metal Complexes," *Angewandte Chemie, International Edition* 51 (2012): 3066–3072, <https://doi.org/10.1002/anie.v51.13>.
70. M. A. Cismesia and T. P. Yoon, "Characterizing Chain Processes in Visible Light Photoredox Catalysis," *Chemical Science* 6 (2015): 5426–5434, <https://doi.org/10.1039/C5SC02185E>.
71. K. Yamashita, H. Sano, Y. Goto, H. Hayashi, and Y. Hamashima, "Direct Generation of Carboxyl Radicals From Carboxylic Acids Catalyzed by Photoactivated Ketones," *Journal of the American Chemical Society* 147 (2025): 29711–29721, <https://doi.org/10.1021/jacs.5c04571>.
72. W. Guo, Q. Wang, and J. Zhu, "Visible Light Photoredox-Catalysed Remote C–H Functionalisation Enabled by 1,5-Hydrogen Atom Transfer (1,5-HAT)," *Chemical Society Reviews* 50 (2021): 7359–7377, <https://doi.org/10.1039/D0CS00774A>.

Supporting Information

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