UNIVERSITY OF AMSTERDAM

UvA-DARE (Digital Academic Repository)

Photocatalytic generation of ligated boryl radicals from tertiary amine-borane complexes

An emerging tool in organic synthesis

Capaldo, L.; Noël, T.; Ravelli, D.

DOI
10.1016/j.checat.2022.03.005

Publication date
2022

Document Version
Final published version

Published in
Chem Catalysis

License
CC BY-NC-ND

Link to publication

Citation for published version (APA):
Capaldo, L., Noël, T., & Ravelli, D. (2022). Photocatalytic generation of ligated boryl radicals from tertiary amine-borane complexes: An emerging tool in organic synthesis. *Chem Catalysis*, *2*(5), 957-966. https://doi.org/10.1016/j.checat.2022.03.005

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, P.O. Box 19185, 1000 GD Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (https://dare.uva.nl)

Download date:16 Sep 2026

Chem Catalysis

CellPress

Perspective

Photocatalytic generation of ligated boryl radicals from tertiary amine-borane complexes: An emerging tool in organic synthesis

Luca Capaldo,[1] Timothy Noël,[1] and Davide Ravelli[2,*]

SUMMARY

Photocatalysis has recently given impetus to the use of ligated boryl radicals (LBRs) in synthesis, thanks to the mild conditions required for their generation based on the use of visible light. LBRs are B-centered radicals wherein the boron atom is coordinated with a suitable Lewis base (e.g., amine, phosphine, or *N*-heterocyclic carbene [NHC]) and can be conveniently accessed from the corresponding ligated boranes through the cleavage of a B–H bond. While NHC-boranes featuring a rather labile B–H bond are routinely used in photocatalytic strategies, this perspective highlights the recent adoption of more challenging tertiary amine-boranes, which unlocked unprecedented reaction manifolds. The highlighted applications include the Minisci-type borylation of azines and the implementation of polarity-reversal catalysis for the generation of electrophilic C-centered radicals via hydrogen-atom transfer (HAT). The possibility to devise an analogous strategy based on halogen-atom transfer (XAT) is also discussed.

INTRODUCTION

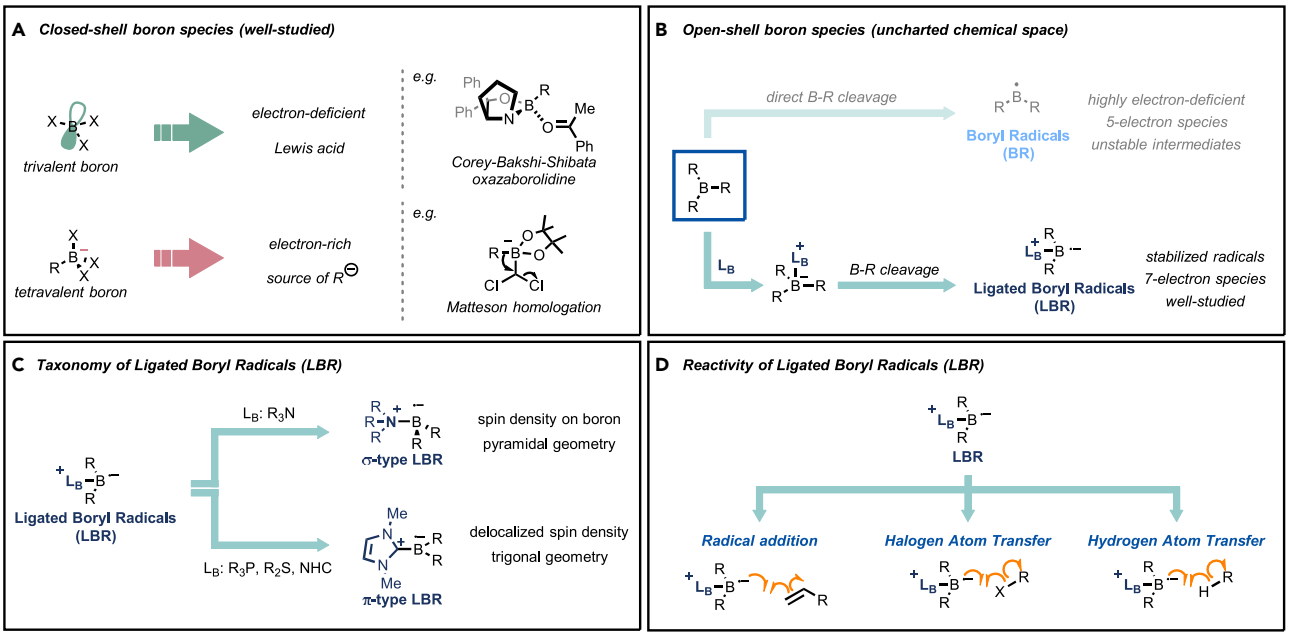
Radical species featuring an unpaired number of electrons play a key role in an impressive number of processes spanning from biology to chemistry,[1] and their importance in synthetic endeavors has increased steadily in recent years.[2,3] Concerning the applications in preparative organic chemistry, the most-studied derivatives include carbon- and nitrogen-based radicals, as well as chalcogen-based radicals (mainly oxygen- and sulfur-centered) and halogen atoms, while boron-based congeners have long remained in the background.[4,5]

B-based closed-shell species are known for their capability to act as Lewis acids (e.g., BX_3, X = halogen atom or organic substituent) due to the empty *p* orbital on the boron atom.[6,7] This reactivity has been widely investigated to promote an array of different transformations both in symmetric and asymmetric variants, with one prominent example being the use of oxazaborolidine derivatives in the Corey-Bakshi-Shibata reduction (Scheme 1A).[8] However, when a fourth substituent is attached to the B atom, a negatively charged molecular assembly is obtained, which can be conveniently used as a source of nucleophilic groups. A prime example of this concept can be found in the class of boron homologations (e.g., Matteson and Zweifel reactions),[9] involving the migration of a group from boron to an adjacent sp^2- or sp^3-hybridized carbon (Scheme 1A). Other examples pertain to the chemistry of alkali borohydrides ($NaBH_4$ and $LiBH_4$), which are routinely used for hydride transfer to carbonyl compounds (hydridic reduction), or organotrifluoroborates (RBF_3K), which can be employed as a source of nucleophilic alkyl groups in different synthetic transformations, including cross-coupling reactions.[10]

The bigger picture

Challenges and opportunities

- Photocatalysis is nowadays considered the elective tool for organoradicals generation in synthetic endeavors. Nevertheless, B-centered radicals have been adopted only sparsely, in stark contrast to their congeners of the 14–17th groups.
- NHC-boranes are typically exploited as a source of ligated boryl radicals (LBRs); however, their use is mainly restricted to radical additions onto unsaturated compounds (arenes, alkenes, and imines). Recently, the adoption of tertiary amine-borane complexes in the same role has unlocked new transformations.
- Two recent reports have capitalized on the peculiar features of LBRs generated from tertiary amine-borane complexes for the borylation of azines and as catalysts to trigger a hydrogen-atom transfer from a protic C–H bond.



Scheme 1. Boron species and their chemical reactivities

(A) Classical trivalent and tetravalent boron species and their polar reactivity.

(B) Open-shell boron species: boryl radicals (BRs) and ligated boryl radicals (LBRs).

(C) Taxonomy of LBRs.

(D) Typical reactivity of LBRs.

L_B, Lewis base.

(LIGATED) BORYL RADICALS

Despite this firmly established knowledge in polar chemistry of boron compounds, the use of boron-based open-shell species is currently underdeveloped.[4,5] Conceptually, a neutral boron-centered radical can be accessed through homolytic cleavage of a bond-at-boron in a trivalent boron derivative (with a general formula R_3B). This would lead to the formation of a highly electron-deficient and unstable intermediate ($R_2B^{\bullet}$), wherein the boron atom features only 5 electrons in its external valence shell (Scheme 1B). Things change dramatically, however, if the B center is coordinated with a suitable Lewis base (L_B). This leads to the so-called ligated boryl radicals (LBRs)[11–20] (general formula: L_B^{+} - $R_2B^{\bullet-}$), wherein the boron atom shares 7 electrons in its valence shell, showing a comparable behavior with respect to well-known C-, N- and O-/S-centered radicals and halogen atoms (Scheme 1B). (Overall, LBRs are neutral species; however, we explicitly indicate the presence of +/- formal charges on L_B and B, respectively. As a matter of fact, the L_B-B interaction involves a coordination (dative) bond, showing "significant polarity, lesser strength, and greater length" compared with covalent bonds, according to the IUPAC Gold Book[21] . On the other hand, some authors prefer to indicate this kind of interaction with a dative bond, with no charge separation.) Indeed, LBRs are characterized by a superior stability with respect to the corresponding non-ligated derivatives and have been detected by spectroscopic means,[11–14,18–20] while their properties have been the subject of extensive computational studies.[19,22] Notably, according to the nature of the L_B interacting with the boron atom, two different classes of LBRs can be described. First, when the L_B is a tertiary amine, a σ-type LBR results, with the spin density mainly localized at the boron center, which exhibits a pyramidal geometry.[11,13] However, when a primary or secondary amine functions as L_B, an aminyl-borane radical is ultimately formed as a result of its superior stability with respect to the LBR (the isomeric

[1]Flow Chemistry Group, Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands

[2]PhotoGreen Lab, Department of Chemistry, University of Pavia, viale Taramelli 12, 27100 Pavia, Italy

*Correspondence: davide.ravelli@unipv.it

https://doi.org/10.1016/j.checat.2022.03.005

amine-boryl).[23,24] Second, when *N*-heterocyclic carbenes (NHCs)[17,19,25] (or phosphines[12] or sulfides[26]) are employed as L_B, the spin density is delocalized over the entire carbene ligand, and a π-type radical results, wherein the boron atom assumes a trigonal planar geometry (Scheme 1C). Notably, depending on their steric and electronic properties, the substituents at boron (e.g., aromatic rings) can likewise have a role in this π delocalization.[27]

The chemistry of LBRs

Apart from a notable exception,[28] LBRs are nucleophilic radicals, and this feature heavily affects their reactivity.[29] Indeed, they show a chameleonic reactivity, depending on the reaction partners, as demonstrated by extensive kinetic studies.[30] They are prone to add to multiple C–C bonds (e.g., in alkenes, alkynes, and carbonyls),[31] as well as to nitriles and isocyanides,[13,32] leading to the formation of a new B–C bond. Alternatively, LBRs can also trigger halogen-atom transfer (XAT) from alkyl halides,[33] enabling access to the corresponding alkyl radicals.[12,34] Finally, LBRs can act as hydrogen abstractors, thus triggering a hydrogen-atom transfer (HAT) from protic positions (e.g., α to a carbonyl/carboxyl moiety), owing to their nucleophilic character.[35–40] The capacity of LBRs to abstract a hydrogen atom is largely dictated by the strength of the B–H bond formed, which in turn depends on the type of L_B interacting with the boron center. Thus, tertiary amine-boranes share a strong B–H bond, and the corresponding LBRs behave as potent H abstractors, while NHC- and phosphine-ligated boranes possess a more labile B–H bond, making the corresponding LBRs less suitable for this role.[41,42]

LBRs UNDER A NEW LIGHT

In terms of synthetic applications, LBRs have been mainly exploited in thermally initiated radical borylations adopting NHC-boranes as substrates.[31,43,44] In addition, ligated boranes have been sparsely used as reducing agents in radical chain processes,[18,25,45,46] as valid substitutes for classic Sn-/Si-based derivatives,[47] or as promoters for radical polymerizations.[48–50]

Quite recently, the generation of LBRs in synthetic endeavors has been experiencing a renewed interest from the chemical community, which can be mainly attributed to the rising interest in photocatalysis. Photocatalysis has provided synthesis practitioners with a robust and versatile toolbox for the generation of organoradicals under extremely mild conditions (i.e., room temperature catalysis, visible light). This powerful methodology is based on the use of a catalyst (termed "photocatalyst" [PC]) deputed for light absorption and for the ensuing activation of the target substrate, mostly via a single-electron transfer (SET)[51,52] or a HAT[53,54] step. Routinely employed PCs include Ru- and Ir-based polypyridyl complexes, whose redox properties can be finely tuned by judicious choice of the ligands around the metal center and their electronic properties. Alternatively, a cheaper and more eco-friendly alternative to metal-based PCs is represented by photoorganocatalysts[55,56] and heterogeneous semiconductor-based PCs.[57,58]

Despite that activation of stable boron species with visible light through photocatalysis has been long known,[59] the photocatalytic generation of LBRs has undergone an impressive development in the last 5 years. This has provided a number of elegant synthetic contributions based on the use of easily activatable NHC-boranes. As recently reviewed,[15,31,43,60,61] alkenes, imines, and substituted (hetero)aromatics are competent reaction partners and have been conveniently adopted toward the formation B–C(sp^3/sp^2) bonds via LBRs.

SYNTHETIC APPLICATIONS OF LBRs FROM TERTIARY AMINE-BORANES

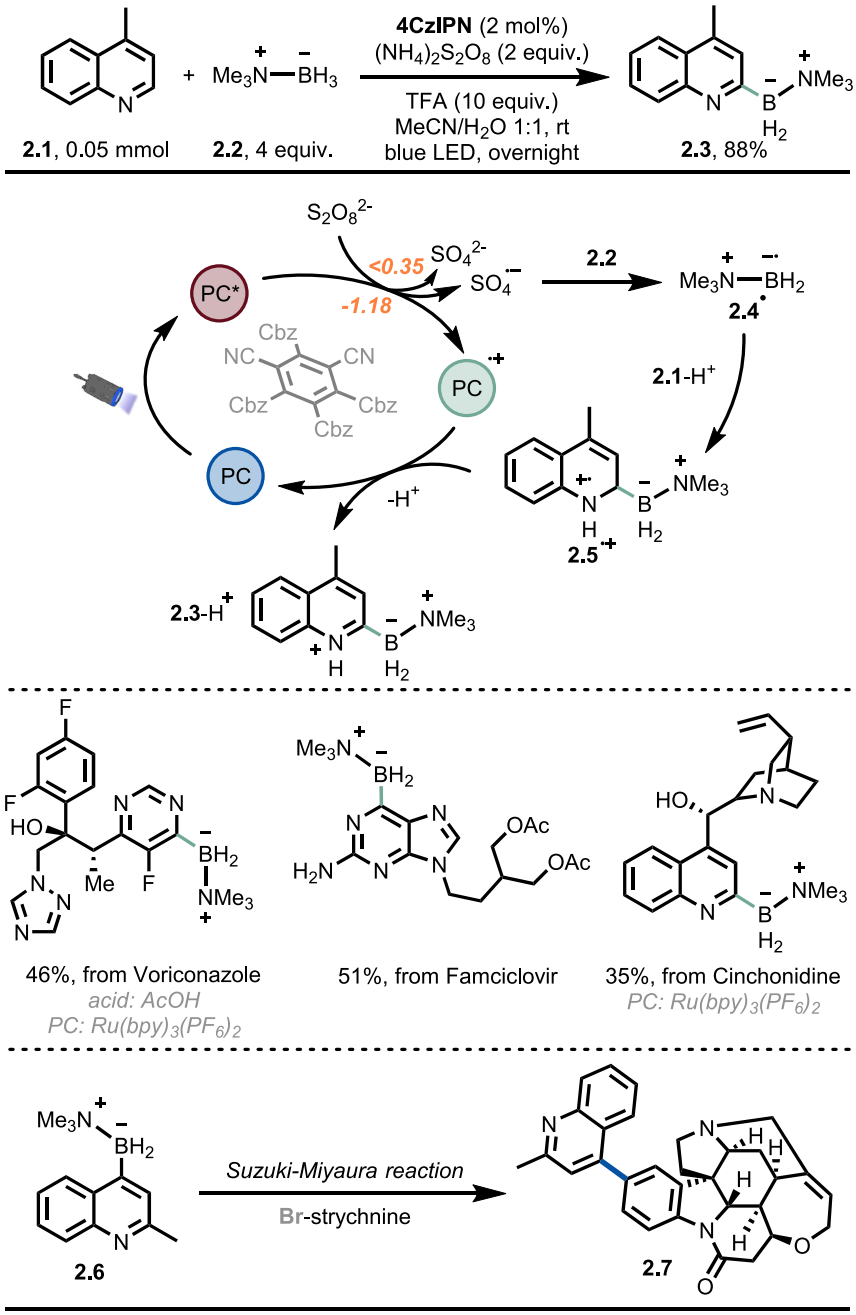
In stark contrast to NHC-boryl radicals, tertiary amine-boryl radicals have been under the spotlight only very recently. As mentioned, they show a more pronounced nucleophilicity[29] compared with NHC-boryl radicals as well as a stronger B–H bond.[41,42] Thanks to these features, two new reactivity modes could be unlocked: (1) a Minisci-type borylation of heteroaromatics and (2) polarity-reversal catalysis for the activation of electrophilic C–H bonds via HAT. In this perspective, we aim to highlight such recent breakthroughs.

Minisci-type borylation of azines

Traditionally, (protonated) azines have been reported to work as competent radical traps for C-centered radicals generated via either thermal or photocatalytic methods according to a Minisci-type transformation.[62] Due to their intrinsic electron-poor properties, these heterocyclic derivatives are ideal substrates to trap nucleophilic LBRs. Thus, the radical borylation of azines with tertiary amine-borane complexes has been reported (Scheme 2).[63,64] It is important to stress that the authors attempted the same reaction with other LBR precursors such as $Ph_3P^+–BH_3^-$ and $NHC^+–BH_3^-$; however, the product was not formed in either case. To explain this result, the authors invoked the importance of the Me_3N group to confer a highly nucleophilic character to the σ-boryl radical.

When a CH_3CN/H_2O solution of lepidine (**2.1**) and borane trimethylamine complex (**2.2**, 4 equiv) was irradiated in the presence of **4CzIPN** (2,4,5,6-Tetrakis(9H-carbazol-9-yl)isophthalonitrile; 2 mol %) as a PC and ammonium persulfate as a sacrificial oxidant, the desired borylation occurred smoothly at the 2 position of **2.1** to afford **2.3** in 88% yield on a 0.05 mmol scale. Notably, the reaction could be performed on a gram scale and afforded 1.65 g of **2.3**, corresponding to a 77% yield of the isolated product. In some cases, the reaction performed well (65% nuclear magnetic resonance [NMR] yield) in the absence of the PC due to a radical chain process triggered by photodecomposition of persulfate. However, the addition of a PC gave the most reliable reaction performance across a wide variety of substrates.

Concerning the mechanism, the reaction initiated with the oxidative quenching of the excited state of **4CzIPN** (generated upon blue light irradiation; $E_{1/2}$[**4CzIPN**$^{\bullet+}$/**4CzIPN***] = -1.18 V versus saturated calomel electrode [SCE])[65] by the persulfate anion to form a sulfate radical anion ($SO_4^{\bullet-}$) upon decomposition (the redox potential of the $S_2O_8^{2-}/SO4^{\bullet-}$ redox couple has been estimated to be $\leq$0.35 V versus SCE in aqueous solution).[66] Next, $SO_4^{\bullet-}$ was in turn responsible for the cleavage of the strong B–H bond (~101 kcal mol^{-1}) in **2.2** via a HAT step, affording the corresponding LBR **2.4**$^{\bullet}$. Finally, the latter intermediate was trapped by protonated lepidine (**2.1**-H$^+$), and the resulting adduct closed the photocatalytic cycle to recover **4CzIPN** and also yielded (protonated) **2.3** (Scheme 2). This methodology could also be used to enable the radical borylation of biologically relevant compounds, such as Voriconazole, Cinchonidine, and Famciclovir. $(Ru(bpy)_3(PF_6)_2$ was used as the PC for the first two compounds (bpy, 2,2′-bipyridine). It is important to mention that the obtained borylated products are bench-stable compounds and that the B–C(sp^2) bond can be readily converted to C–O via oxidation or to C–C/C–heteroatom bonds via transition-metal-catalyzed transformations, such as Suzuki-Miyaura or Chan-Lam coupling reactions (see, e.g., the conversion of **2.6** to **2.7** in Scheme 2).[63]



Scheme 2. Photocatalyzed radical borylation of azines

Numbers in orange are the redox potentials (versus SCE) of the relevant redox couples.

Functionalization of protic C–H bonds

Very recently, LBRs have been adopted to address a long-standing challenge in the field of photocatalytic HAT,[53] namely the cleavage of protic C–H bonds. In the conventional approach, light is exploited by the PC to cleave a C–H bond, either directly or indirectly,[67] and ultimately forms a C-centered radical. Despite the variety of methodologies reported so far based on this manifold, the polarity of the crucial HAT step remains limited by the fact that most common H-abstracting species are

electrophilic in nature and abstract preferentially hydridic hydrogens, in turn delivering nucleophilic organoradicals.[53,68] On the contrary, the activation of protic C−H bonds (for the generation of electrophilic radicals) is polarity mismatched and, thus, kinetically disfavored. This has limited the potential of HAT over the years with respect, for example, to photoredox catalytic manifolds, wherein electrophilic radicals can be readily generated via SET.[69]

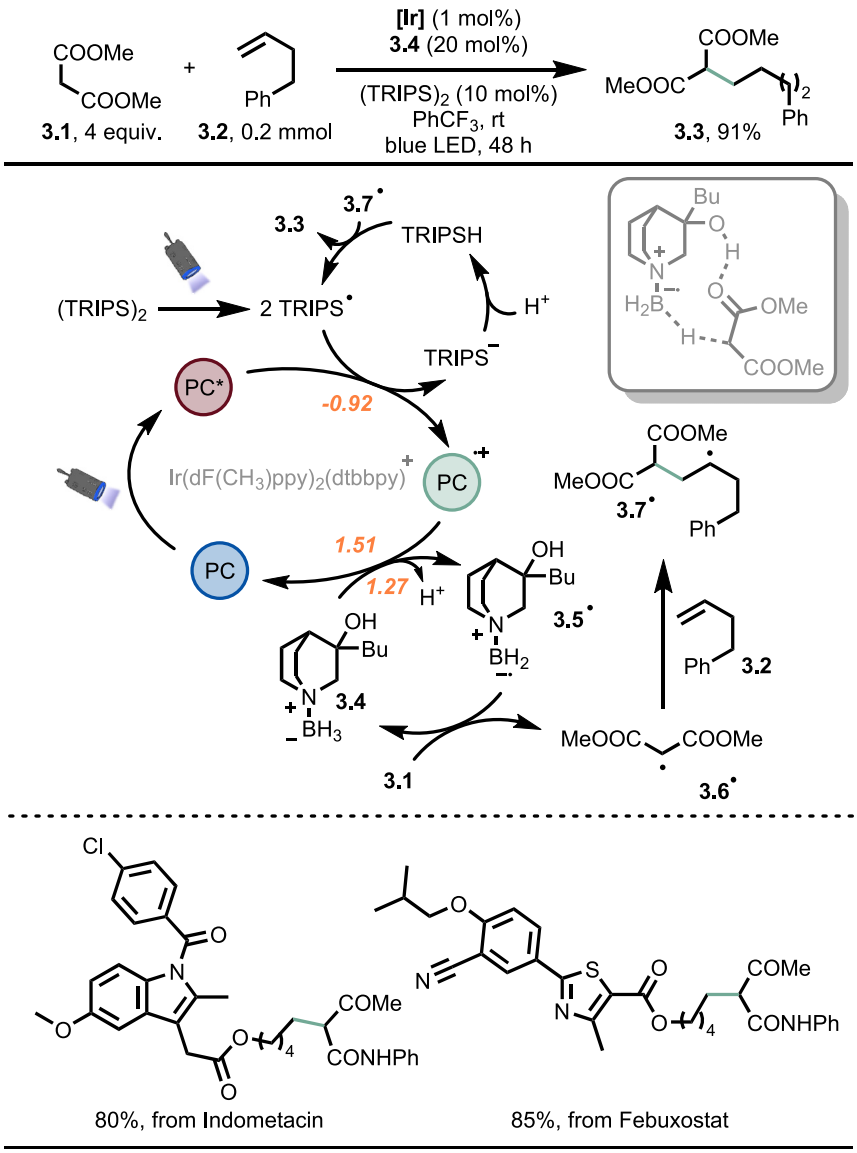
Back in the 90s, Roberts introduced the concept of polarity-reversal catalysis (PRC),[35,70] wherein the selective abstraction of a hydrogen atom from protic C−H bonds by an electrophilic radical was demonstrated, owing to the use of ligated boranes as catalysts. In other words, it was shown that the latter compounds could be used as co-catalysts to tweak the intrinsic philicity of HAT,[68,70] although only a handful of preparative examples have been reported.[71–73]

Very recently, this concept was exploited to enable a photocatalytic PRC strategy for the hydroalkylation of unactivated olefins (Scheme 3).[74] Thus, the irradiation with blue light of dimethyl malonate **3.1** (4 equiv) and olefin **3.2** (0.2 mmol) in the presence of an Ir-based PC (1 mol %), 2,4,6-triisopropylbenzene disulfide $(TRIPS)_2$, and the quinuclidine borane complex **3.4** led to the desired reactivity (91% yield of the isolated **3.3**). Interestingly, when 2,4,6-triisopropylbenzene thiol TRIPSH (10 mol %) was used as a terminal H donor and an NHC-borane as co-catalyst, only thiol-ene reaction byproducts were observed.

As for the proposed mechanism, light absorption by $(TRIPS)_2$ led to the production of a couple of thiyl radicals that were responsible for the oxidative quenching of the excited state of the PC ($E_{1/2}[Ir^{IV}/Ir^{III}*]$ = -0.92 V versus SCE in MeCN; for comparison, $E[PhS^{\bullet}/PhS^{-}]$ = +0.16 V versus SCE). Next, the highly oxidizing Ir^{IV} species ($E_{1/2}[Ir^{IV}/Ir^{III}]$ = +1.51 V versus SCE) delivered a nucleophilic LBR (**3.5**$^{\bullet}$) from **3.4** either via an electron transfer/proton transfer (ET/PT) sequence ($E_{p/2}$ (**3.4**) = +1.27 V versus SCE) or a proton-coupled ET (PCET) process. At this stage, LBR **3.5**$^{\bullet}$ cleaved the protic C−H bond in **3.1** to afford the corresponding electrophilic alkyl radical **3.6**$^{\bullet}$, which was in turn trapped by **3.2**. The resulting radical adduct **3.7**$^{\bullet}$ was finally quenched by TRIPSH generated during the reaction (Scheme 3). Remarkably, the authors tested several tertiary amine-boranes similar to **3.4**, but all of them gave lower yields. From NMR titration and density functional theory (DFT) calculations, they were able to prove that **3.1** and **3.4** interact via H bonding, which results in the formation of the expected LBR via an oxidative PCET pathway with Ir^{IV}, where the ester group of the malonate is acting as the base. Furthermore, such H bonding favors the key HAT event, confirming the importance of the hydroxyl moiety in **3.4** (see inset in Scheme 3). Finally, it is also important to stress that the reaction occurred under very mild conditions, and a wide variety of functional groups was tolerated, as shown in the case of Indomethacin (NSAID) and Febuxostat (drug for the treatment of gout).[74]

CONCLUSIONS AND OUTLOOK

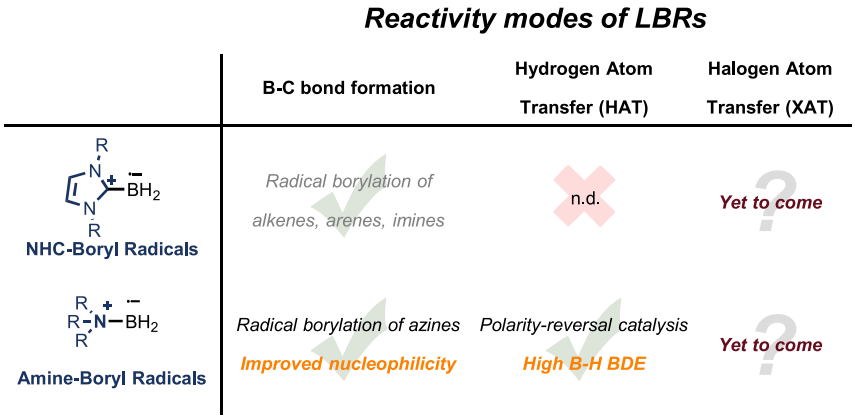
As shown in the present contribution, tertiary amine-borane complexes have enabled to significantly push the boundaries of synthetic applications of photocatalytically generated LBRs (Scheme 4). In the first highlighted example, the strong nucleophilic character of said radicals was used to unlock a Minisci-type radical borylation of azines, which allowed for the direct installation of highly versatile boron-based handles for late-stage diversification campaigns.[63] In the second example, the authors took advantage of the high bond dissociation energy (BDE) of the



Scheme 3. Hydroalkylation of unactivated olefins via polarity-reversal catalysis (PRC)
Numbers in orange are the redox potentials (versus SCE) of the relevant redox couples.

B–H bond in tertiary amine-borane complexes to eventually reach a long-standing goal in photocatalysis via HAT: the cleavage of protic, aliphatic C(sp^3)–H bonds.[74] Another intriguing opportunity offered by LBRs deriving from amine-borane complexes is the possibility to devise tailor-made HAT catalysts by simply choosing a suitable, commercially available amine to be reacted with the appropriate boron-based reagent. Moreover, as shown in the hydroalkylation of unactivated olefins (Scheme 3), weak interactions can play a decisive role in establishing this chemistry: indeed, one can imagine exploiting these forces to reach high levels of selectivity in the designed synthetic application.

Remarkably, as mentioned in the introduction, LBRs can also be used as XAT agents.[12,34,45] Accordingly, it is foreseen that, thanks to the operationally simple conditions offered by photocatalysis and the recent surge of interest in this



Scheme 4. Synthetic applications of LBRs in photocatalytic manifolds

methodology,[33] synthetic applications based on amine-boryl radical-mediated XAT are expected to emerge in the near future.

The successful merger of the photocatalytic activation manifold with the chemistry of boryl radicals is yet another demonstration of the versatility of photocatalysis as a radical generation methodology[2,75] that offers unparalleled mild conditions and enables the full exploitation of the chemistry of the generated intermediates, further fostering the importance of radical-based methodologies in synthetic endeavors.

ACKNOWLEDGMENTS

L.C. acknowledges European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement no. 101023615 (project name: HAT-TRICK).

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. C. Chatgilialoglu, and A. Studer, eds. (2012). Encyclopedia of Radicals in Chemistry, Biology and Materials (John Wiley & Sons, Ltd).
2. Galliher, M.S., Roldan, B.J., and Stephenson, C.R.J. (2021). Evolution towards green radical generation in total synthesis. Chem. Soc. Rev. *50*, 10044–10057.
3. Yan, M., Lo, J.C., Edwards, J.T., and Baran, P.S. (2016). Radicals: reactive intermediates with translational potential. J. Am. Chem. Soc. *138*, 12692–12714.
4. Renaud, P. (2012). Boron in radical chemistry. In Encyclopedia of Radicals in Chemistry, Biology and Materials, C. Chatgilialoglu and A. Studer, eds. (John Wiley & Sons, Ltd).
5. Su, Y., and Kinjo, R. (2017). Boron-containing radical species. Coord. Chem. Rev. *352*, 346–378.
6. Lawson, J.R., and Melen, R.L. (2017). Recent developments and applications of Lewis acidic boron reagents. In Organometallic Chemistry, *vol 41*Organometallic Chemistry (The Royal Society of Chemistry), pp. 1–27.
7. Sivaev, I.B., and Bregadze, V.I. (2014). Lewis acidity of boron compounds. Coord. Chem. Rev. *270–271*, 75–88.
8. Corey, E.J., Shibata, S., and Bakshi, R.K. (1988). An efficient and catalytically enantioselective route to (S)-(-)-phenyloxirane. J. Org. Chem. *53*, 2861–2863.
9. Wang, H., Jing, C., Noble, A., and Aggarwal, V.K. (2020). Stereospecific 1,2-migrations of boronate complexes induced by electrophiles. Angew. Chem. Int. Ed. *59*, 16859–16872.
10. Darses, S., and Genet, J.-P. (2008). Potassium organotrifluoroborates: new perspectives in organic synthesis. Chem. Rev. *108*, 288–325.
11. Baban, J.A., and Roberts, B.P. (1983). An e.s.r. study of amine-boryl radicals (R_3N–$BH_2^{\bullet}$) in solution. J. Chem. Soc. Chem. Commun. 1224–1226.
12. Baban, J.A., and Roberts, B.P. (1984). An electron spin resonance study of phosphine-boryl radicals; their structures and reactions with alkyl halides. J. Chem. Soc. Perkin Trans. *2*, 1717–1722.

13. Baban, J.A., Marti, V.P.J., and Roberts, B.P. (1985). Ligated boryl radicals. Part 2. Electron spin resonance studies of trialkylamin–boryl radicals. J. Chem. Soc. Perkin Trans. *2*, 1723–1733.

14. Baban, J.A., Marti, V.P.J., and Roberts, B.P. (1985). Spin-trapping of ligated boryl radicals. Tetrahedron Lett. *26*, 1349–1352.

15. Taniguchi, T. (2021). Advances in chemistry of *N*-heterocyclic carbene boryl radicals. Chem. Soc. Rev. *50*, 8995–9021.

16. Martin, C.D., Soleilhavoup, M., and Bertrand, G. (2013). Carbene-stabilized main group radicals and radical ions. Chem. Sci. *4*, 3020–3030.

17. Curran, D.P., Solovyev, A., Makhlouf Brahmi, M., Fensterbank, L., Malacria, M., and Lacôte, E. (2011). Synthesis and reactions of N-heterocyclic carbene boranes. Angew. Chem. Int. Ed. *50*, 10294–10317.

18. Ueng, S.-H., Makhlouf Brahmi, M., Derat, E., Fensterbank, L., Lacôte, E., Malacria, M., and Curran, D.P. (2008). Complexes of borane and N-heterocyclic carbenes: a new class of radical hydrogen atom donor. J. Am. Chem. Soc. *130*, 10082–10083.

19. Ueng, S.-H., Solovyev, A., Yuan, X., Geib, S.J., Fensterbank, L., Lacôte, E., Malacria, M., Newcomb, M., Walton, J.C., and Curran, D.P. (2009). *N*-heterocyclic carbene boryl radicals: a new class of boron-centered radical. J. Am. Chem. Soc. *131*, 11256–11262.

20. Walton, J.C., Brahmi, M.M., Fensterbank, L., Lacôte, E., Malacria, M., Chu, Q., Ueng, S.-H., Solovyev, A., and Curran, D.P. (2010). EPR studies of the generation, structure, and reactivity of *N*-heterocyclic carbene borane radicals. J. Am. Chem. Soc. *132*, 2350–2358.

21. IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997)

22. Hioe, J., Karton, A., Martin, J.M.L., and Zipse, H. (2010). Borane-lewis base complexes as homolytic hydrogen atom donors. Chem. Eur. J. *16*, 6861–6865.

23. Green, I.G., and Roberts, B.P. (1986). Homolytic reactions of ligated boranes. Part 3. Electron spin resonance studies of radicals derived from dialkylamine–boranes. J. Chem. Soc. Perkin Trans. *2*, 1597–1606.

24. Kirwan, J.N., and Roberts, B.P. (1989). Homolytic reactions of ligated boranes. Part 11. Electron spin resonance studies of radicals derived from primary amine–boranes. J. Chem. Soc. Perkin Trans. *2*, 539–550.

25. Walton, J.C. (2009). Linking borane with N-heterocyclic carbenes: effective hydrogen-atom donors for radical reactions. Angew. Chem. Int. Ed. *48*, 1726–1728.

26. Baban, J.A., and Roberts, B.P. (1987). Homolytic reactions of ligated boranes. Part 6. Electron spin resonance studies of dialkyl sulphide-boryl radicals. J. Chem. Soc. Perkin Trans. *2*, 497–505.

27. Paul, V., and Roberts, B.P. (1988). Homolytic reactions of ligated boranes. Part 10. Electron spin resonance studies of radicals derived from ligated arylboranes. J. Chem. Soc. Perkin Trans. *2*, 1895–1901.

28. Subervie, D., Graff, B., Nerkar, S., Curran, D.P., Lalevée, J., and Lacôte, E. (2018). Difluorination at boron leads to the first electrophilic ligated boryl radical (NHC-$BF_2^{\bullet}$). Angew. Chem. Int. Ed. *57*, 10251–10256.

29. Wu, C., Hou, X., Zheng, Y., Li, P., and Lu, D. (2017). Electrophilicity and nucleophilicity of boryl radicals. J. Org. Chem. *82*, 2898–2905.

30. Sheeller, B., and Ingold, K.U. (2001). Absolute rate constants for some reactions of the triethylamine-boryl radical and the borane radical anion. J. Chem. Soc. Perkin Trans. *2*, 480–486.

31. Taniguchi, T. (2019). Boryl radical addition to multiple bonds in organic synthesis. Eur. J. Org. Chem. *2019*, 6308–6319.

32. Diart, V., and Roberts, B.P. (1992). EPR studies of the additon of 1,1-bis(alkoxycarbonyl)alkyl radicals and tris(ethoxycarbonyl)methyl radicals to alkenes and to alkyl isocyanides. J. Chem. Soc. Perkin Trans. *2*, 1761–1768.

33. Juliá, F., Constantin, T., and Leonori, D. (2022). Applications of halogen-atom transfer (XAT) for the generation of carbon radicals in synthetic photochemistry and photocatalysis. Chem. Rev. *122*, 2292–2352.

34. Roberts, B.P., and Steel, A.J. (1994). The effects of β-alkoxy substituents on radical reactions: halogen-atom abstraction from alkyl chlorides. J. Chem. Soc. Perkin Trans. *2*, 2411–2422.

35. Paul, V., and Roberts, B.P. (1987). Polarity reversal catalysis of hydrogen atom abstraction reactions. J. Chem. Soc. Chem. Commun. 1322–1324.

36. Paul, V., Roberts, B.P., and Willis, C.R. (1989). Homolytic reactions of ligated boranes. Part 12. Amine–alkylboranes as polarity reversal catalysts for hydrogen-atom abstraction by *t*-butoxyl radicals. J. Chem. Soc. Perkin Trans. *2*, 1953–1961.

37. Kaushal, P., Mok, P.L.H., and Roberts, B.P. (1990). Homolytic reactions of ligated boranes. Part 15. Comparative studies of amine–boranes as donor polarity reversal catalysts for hydrogen-atom abstraction. J. Chem. Soc. Perkin Trans. *2*, 1663–1670.

38. Mok, P.L.H., and Roberts, B.P. (1991). Enantioselective α-hydrogen-atom abstraction from an ester by an optically active amine-boryl radical. J. Chem. Soc. Chem. Commun. 150–152.

39. Mok, P.L.H., and Roberts, B.P. (1992). Enantioselective hydrogen-atom abstraction by optically active amine-boryl radicals: an ESR spectroscopic study. Tetrahedron Lett. *33*, 7249–7252.

40. Mok, P.L.H., Roberts, B.P., and McKetty, P.T. (1993). Homolytic reactions of ligated boranes. Part 16. Enantioselective hydrogen-atom abstraction by chiral amine-boryl radicals: catalytic kinetic resolution of esters and of camphor. J. Chem. Soc. Perkin Trans. *2*, 665–674.

41. Rablen, P.R. (1997). Large effect on borane bond dissociation energies resulting from coordination by Lewis bases. J. Am. Chem. Soc. *119*, 8350–8360.

42. Rablen, P.R., and Hartwig, J.F. (1996). Accurate borane sequential bond dissociation energies by high-level ab initio computational methods. J. Am. Chem. Soc. *118*, 4648–4653.

43. Jin, J., Xia, H., Zhang, F., and Wang, Y. (2020). Lewis-base boryl radicals enabled borylation, radical catalysis and reduction reactions. Chin. J. Org. Chem. *40*, 2185–2194.

44. Friese, F.W., and Studer, A. (2019). New avenues for C–B bond formation via radical intermediates. Chem. Sci. *10*, 8503–8518.

45. Baban, J.A., and Roberts, B.P. (1988). Homolytic reactions of ligated boranes. Part 9. Overall addition of alkanes to electron-deficient alkenes by a radical chain mechanism. J. Chem. Soc. Perkin Trans. *2*, 1195–1200.

46. Barton, D.H.R., and Jacob, M. (1998). Phosphine-boranes as selective reagents for the radical deoxygenation of a hindered secondary alcohol. Tetrahedron Lett. *39*, 1331–1334.

47. Lucarini, M., Pedulli, G.F., and Valgimigli, L. (1996). Homolytic reactivity of ligated boranes toward alkyl, alkoxyl, and peroxyl radicals. J. Org. Chem. *61*, 1161–1164.

48. Lalevée, J., Tehfe, M.A., Allonas, X., and Fouassier, J.P. (2008). Boryl radicals as a new photoinitiating species: a way to reduce the oxygen inhibition. Macromolecules *41*, 9057–9062.

49. Telitel, S., Schweizer, S., Morlet-Savary, F., Graff, B., Tschamber, T., Blanchard, N., Fouassier, J.P., Lelli, M., Lacôte, E., and Lalevée, J. (2013). Soft photopolymerizations initiated by dye-sensitized formation of NHC-boryl radicals under visible light. Macromolecules *46*, 43–48.

50. Lalevée, J., Telitel, S., Tehfe, M.A., Fouassier, J.P., Curran, D.P., and Lacôte, E. (2012). *N*-heterocyclic carbene boranes accelerate type I radical photopolymerizations and overcome oxygen inhibition. Angew. Chem. Int. Ed. *51*, 5958–5961.

51. Bell, J.D., and Murphy, J.A. (2021). Recent advances in visible light-activated radical coupling reactions triggered by (i) ruthenium, (ii) iridium and (iii) organic photoredox agents. Chem. Soc. Rev. *50*, 9540–9685.

52. McAtee, R.C., McClain, E.J., and Stephenson, C.R.J. (2019). Illuminating photoredox catalysis. Trends Chem. *1*, 111–125.

53. Capaldo, L., Ravelli, D., and Fagnoni, M. (2022). Direct photocatalyzed hydrogen atom transfer (HAT) for aliphatic C–H bonds elaboration. Chem. Rev. *122*, 1875–1924.

54. Cao, H., Tang, X., Tang, H., Yuan, Y., and Wu, J. (2021). Photoinduced intermolecular hydrogen atom transfer reactions in organic synthesis. Chem. Catal. *1*, 523–598.

55. Ravelli, D., Fagnoni, M., and Albini, A. (2013). Photoorganocatalysis. What for? Chem. Soc. Rev. *42*, 97–113.

56. Romero, N.A., and Nicewicz, D.A. (2016). Organic photoredox catalysis. Chem. Rev. *116*, 10075–10166.

57. Riente, P., and Noël, T. (2019). Application of metal oxide semiconductors in light-driven organic transformations. Catal. Sci. Technol. *9*, 5186–5232.

58. Savateev, A., Ghosh, I., König, B., and Antonietti, M. (2018). Photoredox catalytic organic transformations using heterogeneous carbon nitrides. Angew. Chem. Int. Ed. *57*, 15936–15947.

59. Duret, G., Quinlan, R., Bisseret, P., and Blanchard, N. (2015). Boron chemistry in a new light. Chem. Sci. *6*, 5366–5382.

60. Tian, Y.-M., Guo, X.-N., Braunschweig, H., Radius, U., and Marder, T.B. (2021). Photoinduced borylation for the synthesis of organoboron compounds. Chem. Rev. *121*, 3561–3597.

61. Lai, D., Ghosh, S., and Hajra, A. (2021). Light-induced borylation: developments and mechanistic insights. Org. Biomol. Chem. *19*, 4397–4428.

62. Proctor, R.S.J., and Phipps, R.J. (2019). Recent advances in minisci-type reactions. Angew. Chem. Int. Ed. *58*, 13666–13699.

63. Kim, J.H., Constantin, T., Simonetti, M., Llaveria, J., Sheikh, N.S., and Leonori, D. (2021). A radical approach for the selective C–H borylation of azines. Nature *595*, 677–683.

64. Yang, S., and Ye, J. (2021). Borylation of azines via a Minisci-type reaction. Chem *7*, 1703–1705.

65. Speckmeier, E., Fischer, T.G., and Zeitler, K. (2018). 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. J. Am. Chem. Soc. *140*, 15353–15365.

66. Memming, R. (1969). Mechanism of the electrochemical reduction of persulfates and hydrogen peroxide. J. Electrochem. Soc. *116*, 785–790.

67. Capaldo, L., and Ravelli, D. (2017). Hydrogen atom transfer (HAT): a versatile strategy for substrate activation in photocatalyzed organic synthesis. Eur. J. Org. Chem. *2017*, 2056–2071.

68. Parsaee, F., Senarathna, M.C., Kannangara, P.B., Alexander, S.N., Arche, P.D.E., and Welin, E.R. (2021). Radical philicity and its role in selective organic transformations. Nat. Rev. Chem. *5*, 486–499.

69. Lenardon, G.V.A., Nicchio, L., and Fagnoni, M. (2021). Photogenerated electrophilic radicals for the umpolung of enolate chemistry. J. Photochem. Photobiol. C Photochem. Rev. *46*, 100387.

70. Roberts, B.P. (1999). Polarity-reversal catalysis of hydrogen-atom abstraction reactions: concepts and applications in organic chemistry. Chem. Soc. Rev. *28*, 25–35.

71. Hai-Shan, D., and Roberts, B.P. (1992). Amine-boranes as polarity reversal catalysts for radical chain 2,3-epoxypropanation reactions of esters. Tetrahedron Lett. *33*, 4621–4624.

72. Hai-Shan, D., and Roberts, B.P. (1992). Radical chain addition to vinyl epoxides catalysed by amine-boranes: synthesis of allylic alcohols. Tetrahedron Lett. *33*, 6169–6172.

73. Dang, H.-S., and Roberts, B.P. (1993). Homolytic reactions of ligated boranes. Part 17. Amine–Boranes as polarity reversal catalysts for radical chain reactions of esters with vinylic epoxides and with allylic tert-butyl peroxides. J. Chem. Soc. Perkin Trans. 1 *8*, 891–898.

74. Lei, G., Xu, M., Chang, R., Funes-Ardoiz, I., and Ye, J. (2021). Hydroalkylation of unactivated olefins via visible-light-driven dual hydrogen atom transfer catalysis. J. Am. Chem. Soc. *143*, 11251–11261.

75. Crespi, S., and Fagnoni, M. (2020). Generation of alkyl radicals: from the tyranny of tin to the photon democracy. Chem. Rev. *120*, 9790–9833.