Allylic Amination of Alkenes with Iminothianthrenes to Afford Alkyl Allylamines

Qiang Cheng, Junting Chen, Songyun Lin, and Tobias Ritter*

Cite This: J. Am. Chem. Soc. 2020, 142, 17287−17293

ABSTRACT: Allylic C−H amination is currently accomplished with (sulfon)amides or carbamates. Here we show the first allylic amination that can directly afford alkyl allylamines, enabled by the reactivity of thianthrene-based nitrogen sources that can be prepared from primary amines in a single step.

To date, allylic C−H amination can access synthetically valuable allylamines from olefins, derivatized as for example sulfonamides, carbamates, carboxamides, or N-heteroarenes.1 Especially transition metal catalysis that proceeds via π-allyl or nitrenoid intermediates has resulted in a large and powerful toolbox for synthetic chemists to build allyamine derivatives.1b While the synthetic utility of such methods is undisputed, most of them share a specific limitation with respect to the requirements of the nitrogen source: on the basis of the properties of the transition metal intermediates, none of the reported reactions is currently known to directly furnish alkyl allylamines as opposed to their derivatives in which electron density at the nitrogen is mitigated by appropriate substitution, most commonly as (sulfon)amides or carbamates.2 Here we present the first allylic C−H amination reaction that can directly furnish alkyl allylamines, enabled by thianthrenylideneamines. The thianthrene-based aminating reagents can be prepared from primary amines in a single step and react with olefins under photoirradiation with an appropriate photocatalyst. We propose that carbon−nitrogen bond formation proceeds through olefin addition to N-centered radicals (NCRs) generated from energy transfer between the photocatalyst and thianthrene-based aminating reagents under irradiation with light. The process differs conceptually from all other known olefin amination reactions enabled by iminothianthrene reactivity. Both terminal and internal olefins can be converted. The unusual approach provides access to desirable allylamines that are not directly accessible by other C−H functionalization reactions.

Several protocols for allylamine synthesis are available, for example by S$_2$2 or other allylic alkylation reactions, such as the Tsuji−Trost reaction.3 Other useful methods include the Overman rearrangement,4 alkenylation of imines,5 reductive amination of enals or enones,6 and hydroamination of allenes or dienes.7 Direct conversion of allylic C−H bonds to C−N bonds is scarcer.1 Currently, two major strategies are available for direct allylic C−H amination.8 Reactions can proceed through π-allylmetal species followed by attack with N-nucleophiles (Scheme 1A).8 The White9c,d and Liu9e groups independently reported palladium-catalyzed allylic C−H amination with sulfonylcarbamates. The scope of the nitrogen-based nucleophiles was further expanded to N-heteroarenes,9f,g sulfonamides,9h,i and carboxamides.9j Key to the success of C−H activation is the coordination of the alkenyl group to the transition metal for subsequent intramolecular C−H insertion. Allylamines compete with the alkene for metal coordination sites, therefore leading to low reactivity of allylic C−H activation.9h The other option proceeds through C−H insertion of metal−nitrenoid species (Scheme 1B).10 The nitrogen substituents for nitrenoid formation are generally...
limited to sulfonyl and carbamate groups because such compounds can be converted to nitrene(oid)s and not undergo Curtius rearrangement.\(^{3d-11}\) Dioxazolones were used as nitrene precursors by the Chang group to establish an intramolecular C–H amiation reaction, in which a well-designed iridium catalyst is essential for suppression of the competing Curtius rearrangement.\(^{11}\) Alternatively, azides\(^{12g,h}\) are used as nitrene sources in C–H amiation reactions, which allows expansion of the substituent scope on nitrogen to include phenyl and even alkyl groups. The Betley group reported the synthesis of N-heterocycles via intramolecular allylic C–H amiation reactions with alkyl azides catalyzed by iridium complexes\(^{12}\) and also showed a case of intermolecular amiation with adamantyl azide.\(^{13}\) Alkylamines are used infrequently for metal–nitrenoid-mediated C–H amiation, likely because of the strong metal–ligand multiple bonding that reduces the reactivity toward C–H amiation in most cases.\(^{14}\) Furthermore, aziridination is often a competing pathway to allylic C–H amiation in most reactions of transition-metal-catalyzed nitrene transfer with alkenes (Scheme 1B).\(^{15}\) Taken together, all currently known general methods for direct intermolecular allylic amication employ (sulfon)amide and carbamate-based nitrogen nucleophiles (Scheme 1C). Herein we report an allylic amiation reaction that can afford alkyl allylamines and introduce thianthrene-based amating reagents that can provide allylamines directly from olefins (Scheme 1D).

We developed a one-pot procedure for the synthesis of allyl thianthrenylidene amines (iminothianthrenes).\(^{16}\) Primary alkylamines smoothly react with thianthrene-S-oxide activated by triflic acid to produce the iminothianthrenes (Scheme 2). Both bulky and linear amine-based iminothianthrenes (1–4) are readily accessible and stable toward column chromatography on silica gel in air as well as insensitive to moisture. They can be stored in ambient atmosphere at room temperature without detectable decomposition for at least 1 year. Iminothianthrene 2 was characterized by single-crystal X-ray analysis. The sulfur–nitrogen bond distance and the related carbon–nitrogen–sulfur bond angle (see the Scheme 2 footnote) indicate a S=N double bond with an sp\(^2\)-hybridized nitrogen atom.\(^{17}\)

Allylic C–H amination of 4-methylpent-1-ene was achieved using cyclohexylamine-derived iminothianthrene 1 as amiation reagent under photocatalysis with an iridium photocatalyst (\(E^o(\text{Ir}^{III}/\text{Ir}^{IV}) = 1.21\) V vs SCE and \(E^o(\text{Ir}^{III}/\text{Ir}^{IV}) = -0.89\) V vs SCE),\(^{18}\) providing allylamine 11 in 71% yield (\(E,E = 16:1\)) together with thianthrene as the major byproduct (86%) (Scheme 3). Both light and photocatalyst are required for a productive transformation. More reductive photocatalysts, such as Ir(ppy)\(_3\) (\(E^°(\text{Ir}^{III}/\text{Ir}^{IV}) = -1.73\) V vs SCE),\(^{18b}\) or more oxidative photocatalysts, such as Mes-Acr' (\(E^°(\text{Mes}^-/\text{Mes}^+) = 2.15\) V vs SCE),\(^{18c}\) failed to provide the amiation product (Table S4). Oxidizing photocatalysts, including the one we employ, may oxidize the allylamines.\(^{19}\) To prevent deleterious product oxidation, we attempted to protonate the allylamines in situ. Addition of acids improved the reaction (Tables S2 and S5), and especially the combination of hexafluoroisopropanol (HFIP) with trifluoroacetic anhydride (TFAA) increased the product yield (Table S5). We established that the anhydride does not function as an acylating reagent to provide amides and that acetamides are not formed but instead that the anhydride provides protic acid through reaction with the protic solvent HFIP and functions as a water scavenger (Table S7 and Figures S18–S21). Aprotic solvents such as acetonitrile did not result in product formation (Tables S1 and S6). A lower reaction temperature improves the yield by slowing the side reactions that involve undesired S–N bond cleavage to afford primary amines (Tables S3 and S8). Excess iminothianthrene leads to deep-purple solutions and may interfere with light absorption, which has the potential to decrease the reaction yield (Table S3). A second amiation of the products was not observed, presumably because of protonation of the products (Table S9).

When terminal alkynes are used, linear amiation products with trans-olefins are obtained selectively (6–17, 30) (Scheme 4). We also observed chemoselectivity in favor of allylic amiation; the allylic C–H amiation occurred selectively in the presence of benzylic C–H bonds (6, 20), and branching at the allylic position increased the trans selectivity (9–11). The reaction conditions are mild, as illustrated by the synthesis of allyl bromide 13, which is prone to aziridine formation by intramolecular S\(_2\)2\(^{-}\) displacement of the formed allylamine product.\(^{20}\) The reaction is tolerant of functional groups including imides (7), esters (8, 26, 30), oxysilanes (12), alcohols (14, 22, 28), carboxylic acids (15), and ketones (30). Additionally, other unsubstituted groups such as arenes (6, 20) and alkynes (16) are tolerated and do not react. For substrates with more than one olefin (17, 27, 29), only monoamination is observed, which occurs selectively at the more electron-rich olefin (26, 28). Allylamines with trisubstituted olefins are accessible as well (18, 19). The olefin geometry in internal alkynes is irrelevant for the stereochemoal outcome of the product allylamine; both cis- and trans-4-ocetne afforded the same product selectivity (21). The regioselectivity can be high for 1,2-disubstituted olefins in which the substituents are sufficiently different (24) but is lower when they are not, such as in trans-2-ocetne, which produces both constitutional isomers (25) in a ratio of 2:1. When allylamines were used as substrates, the corresponding allylamines with a cis-olefin were obtained as the major products (20, 24), as opposed to the trans isomers for all of the other aliphatic compounds, which is explained by a known photocatalytic isomerization of
Scheme 4. Substrate Scope

From *cis*-cyclooctene. Isolated yield with the 1 mmol-scale yield in parentheses.

Isolated yield with 1.0 equiv of alkene in square brackets.

Ratio of product to homoallyl isomer that was only observed for this substrate (Figures S1 and S15).

30 W blue LED ($8^\circ$C) instead of purple LED.

Ratio of regioselectivity.

1.2 equiv of alkene was used.

HFIP (0.025 M).

General conditions except where otherwise noted: iminothianthrene (0.1 mmol), alkene (0.15 mmol, 1.5 equiv), Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$ (3 mol %), TFAA (2 equiv), HFIP (0.1 M), purple LED (30 W), 5 $^\circ$C.

TFAA = trifluoroacetic anhydride; HFIP = hexafluoroisopropanol.

---

"From *cis*-cyclooctene. Isolated yield with the 1 mmol-scale yield in parentheses. $^a$Isolated yield with 1.0 equiv of alkene in square brackets. $^b$Ratio of product to homoallyl isomer that was only observed for this substrate (Figures S1 and S15). $^c$30 W blue LED ($8^\circ$C) instead of purple LED. $^d$Ratio of regioselectivity. $^e$1.2 equiv of alkene was used. $^f$HFIP (0.025 M). $^g$General conditions except where otherwise noted: iminothianthrene (0.1 mmol), alkene (0.15 mmol, 1.5 equiv), Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$ (3 mol %), TFAA (2 equiv), HFIP (0.1 M), purple LED (30 W), 5 $^\circ$C. TFAA = trifluoroacetic anhydride; HFIP = hexafluoroisopropanol.
the initially formed trans-styrene (Figure S16 and S17). The conjugated dienes, allyl alcohols, and allylamines are unreactive substrates (Table S9).

Several thianthrene-based amination reagents made from different primary amines were evaluated in the photocatalyzed amination reaction. Both sterically crowded and linear alkylamine-based reagents (1−4) participate smoothly in the allylic C−H amination reaction (31−35). Amino alcohols are tolerated (37), while unprotected amino acids cannot be used to make the corresponding iminothianthrene reagents (Table S9).

We propose that the photocatalyst in the reaction functions as an energy transfer catalyst, as opposed to a photoredox catalyst, based on evidence from photoquenching, cyclic voltammetry, analysis of other energy transfer catalysts, and irradiation with UV light, as well as computational studies (Scheme 5; see the Supporting Information for details). The excited iridium photocatalyst is efficiently quenched by protonated iminothianthrene, as observed from Stern−Volmer quenching experiments (Scheme 5a).

Scheme 5. Mechanistic Investigations

(a) Stern−Volmer quenching experiments. (b) Reaction with other photosensitizers with higher triplet energy. (c) DFT studies of the bond dissociation energy (BDE) of A. (d) Reaction under UV light without photosensitizers. (e) Radical trap reaction with TEMPO and radical clock reactions. (f) Proposed mechanism. (g) Reactivity comparison of 1 with other iminosulfides. ET = energy transfer; TT = thianthrene; TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl.

Conjugated dienes, allyl alcohols, and allylamines are unreactive substrates (Table S9). We propose that the photocatalyst in the reaction functions as an energy transfer catalyst, as opposed to a photoredox catalyst, according to evidence from photoquenching, cyclic voltammetry, analysis of other energy transfer catalysts, and irradiation with UV light as well as computation (Scheme S5; see the Supporting Information for details). The excited iridium photocatalyst is effectively quenched by protonated iminothianthrene, as observed from Stern−Volmer quenching experiments (Scheme 5a).
experiments (Scheme 5a). Precomplexation in the ground state of the quencher and photocatalyst can lead to static quenching in addition to dynamic quenching, which may rationalize the observed nonlinear behavior.\textsuperscript{23} We measured the redox potential of protonated 1 (A) ($E_{\text{red}} = 2.0 \text{ V vs Ag/AgCl}$, $E_{\text{ox}} = -1.4 \text{ V vs Ag/AgCl}$; Figure S12), and no correlation between the product yield and redox potentials of photocatalysts was observed (Table S4). Instead, the amination reactivity is correlated to the energy of the first triplet excited state of the photocatalyst, as shown in Scheme 5b for two catalysts with higher triplet energy.\textsuperscript{22} The triplet excited state of the iridium catalyst has an energy of 61 kcal/mol and is computed the ground-state bond dissociation energy of the nitrogen-centered radicals favor hydrogen atom abstraction as opposed to addition to π systems.\textsuperscript{25a} Increasing their electrophilicity by protonation can lead to a switch in selectivity in favor of addition chemistry.\textsuperscript{25a} In our case, either protonation with an acid additive or strong hydrogen bonding with HFIP results in a (partial) cationic charge on the nitrogen radical,\textsuperscript{26} which subsequently adds to the olefin regioselectively to generate radical B. Radical–radical cross-coupling between transient carbon radical B and persistent thianthrenium radical cation may form C,\textsuperscript{27} although single-electron oxidation of the carbon radical by the thianthren radical cation cannot be excluded with our data. Subsequent elimination from C or deprotonation from the carbocation resulting from oxidation would form the allylamine product.\textsuperscript{28} Consistent with this mechanism are the observation of the TEMPO adduct 40 as well as the products 41 and 43 formed from the corresponding radical clock substrates, respectively (Scheme 5e). We hypothesize that the persistence of the thianthren radical cation is key to the unusual observed reactivity, which enables the generation of alkyl alkylamines directly. Other iminoureas did not provide the product as well as at all (Scheme 5g).

In conclusion, a novel photocatalyzed allylic C–H amination reaction with alkylamines has been established. Such reaction has not yet been achieved by either transition-metal-catalyzed allylic C–H activation or nitrene transfer reaction, as basic alkylamines form stronger bonds with transition metal centers.

## ASSOCIATED CONTENT

\section*{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08248.

Experimental procedures, characterization data, and crystallographic data (PDF)

Crystallographic data for 2 (CIF)
Kawana, A.; Mukaiyama, T. A Convenient Method for the Synthesis of β,γ-Unsaturated Amines from Alkenes via α,β-Unsaturated Diphenylsulfonylum Salts. *Chem. Lett.* 2003, 32, 626−627.

(7) Brice, J. L.; Harang, J. E.; Timokhin, V. I.; Anastasi, N. R.; Stahl, S. S. Aerobic Oxidative Amination of Unactivated Alkenes Catalyzed by Palladium. *J. Am. Chem. Soc.* 2005, 127, 2868−2869.

(8) Srivastava, R. S.; Khan, M. A.; Nicholls, K. M. Nitrosoarenes−Cu(I) Complexes Are Intermediates in Copper-Catalyzed Allylic Amination. *J. Am. Chem. Soc.* 2005, 127, 7278−7279.

(9) Clark, J. S.; Roche, C. Tuneable Asymmetric Copper-Catalysed Allylic Amination and Oxidation Reactions. *Chem. Commun.* 2005, 5175−5177.

(10) Pelletier, G.; Powell, D. A. Copper-Catalysed Amination of Allylic and Benzylic C−H Bonds. *Org. Lett.* 2006, 8, 6031−6034.

(11) Souto, J. A.; Zian, D.; Muniz, K. Iodine(III)-Mediated Intermolecular Allylic Amination under Metal-Free Conditions. *J. Am. Chem. Soc.* 2012, 134, 7242−7245.

(12) Bao, H.; Tambar, U. K. Catalytic Enantioselective Allylic Amination of Unactivated Terminal Olefins via an Ene Reaction/[3,3]-Rearrangement. *J. Am. Chem. Soc.* 2012, 134, 18495−18498.

(13) Brenner, J.; Depken, C.; Weber, T.; Breder, A. Direct Oxidative Allylic and Vinylic Amination of Alkenes through Selenium Catalysis. *Angew. Chem., Int. Ed.* 2013, 52, 8952−8956.

(14) Zhang, X.; Wang, M.; Li, P.; Wang, L. n-BuNI/TBHP-Catalyzed Direct Amination of Allylic and Benzylic C(sp)3−H with Anilines under Metal-Free Conditions. *Chem. Commun.* 2014, 50, 8006−8009.

(15) Kong, C.; Jana, N.; Jones, C.; Driver, T. G. Control of the Chemoselectivity of Nitrene Chemistry in Organic Synthesis: Still in Its Infancy? *Nat. Chem.* 2018, 10, 333−340.

(16) Selected recent reviews: (a) Dequirez, G.; Pons, V.; Dauban, P. Transition Metal-Catalyzed Iodine(III)-Mediated Nitrene Transfer Reactions: Efficient Tools for Challenging Syntheses. *Chem. Commun.* 2017, 53, 493−508. (f) Shimabayashi, T.; Sasakura, K.; Eguchi, A.; Okamoto, K.; Ohe, K. Recent Progress on Cyclic Nitrenoid Precursors in Transition-Metal-Catalyzed Nitrene-Transfer Reactions. *Chem. - Eur. J.* 2019, 25, 3156−3180. (g) Scrivin, E. F. V.; Turnbull, K. Azaides: Their Preparation and Synthetic Uses. *Chem. Rev.* 1998, 88, 297−368.

(17) Selected recent examples: (a) Iovan, D. A.; Wilding, M. J. T.; Baek, Y.; Hennessy, E. T.; Betley, T. A. Diairetoselective C−H Bond Amination for Disubstituted Pyrrolidines. *Angew. Chem., Int. Ed.* 2017, 56, 15599−15602.

(18) Hennessy, E. T.; Liu, R. A.; Duncan, R. A.; Betley, T. A. Iron-Mediated Intermolecular N-Group Transfer Chemistry with Olefinic Substrates. *Chem. Sci.* 2014, 5, 1526−1532.

(19) Bir, Y.; Hennessy, E. T.; Betley, T. A. Direct Manipulation of Metal Imido Geometry: Key Principles to Enhance C−H Amination Efficacy. *J. Am. Chem. Soc.* 2019, 141, 16944−16953.

(20) Alderson, J. M.; Corbin, J. R.; Schomaker, J. M. Tunable, Chemo- and Site-SelectIVE Nitrene Transfer Reactions through the Rational Design of Silver(I) Catalysts. *Acc. Chem. Res.* 2017, 50, 2147−2158.

(21) Kim, K.; Shine, H. J. Ion Radicals. XXX. Reactions of Thiannethrene Cation Radical Perchlorate with Amino Compounds. *J. Org. Chem.* 1974, 39, 2537−2539.

(22) Hennessy, E. T.; Kim, K. Cation radicals. XXVII. Sulfinilide Derivatives from Reaction of Thianthrene Cation Radical Peroxide with Amino Compounds. *J. Am. Chem. Soc.* 2008, 130, 3316−3318.

(23) Liu, G.; Yin, G.; Wu, L. Palladium-Catalysed Intermolecular Aerobic Oxidative Amination of Terminal Alkenes: Efficient Synthesis of Linear Allylamines Derivatives. *Angew. Chem., Int. Ed.* 2008, 47, 4733−4736.

(24) Iovan, D. A.; Wilding, M. J. T.; Baek, Y.; Hennessy, E. T.; Betley, T. A. Direct Manipulation of Metal Imido Geometry: Key Principles to Enhance C−H Amination Efficacy. *J. Am. Chem. Soc.* 2019, 141, 16944−16953.

(25) Alderson, J. M.; Corbin, J. R.; Schomaker, J. M. Tunable, Chemo- and Site-Selective Nitrene Transfer Reactions through the Rational Design of Silver(I) Catalysts. *Acc. Chem. Res.* 2017, 50, 2147−2158.

(26) Gilchrist, T. L.; Moody, C. J. The Chemistry of Sulfinilides. *Chem. Rev.* 1977, 77, 409−443.

(27) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohr, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. Single-Layer Electro-luminescent Devices and Photoinduced Hydrogen Production from an Ionic Iridium(III) Complex. *Chem. Mater.* 2005, 17, 5712−5719.

(28) Flamigni, L.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. Photochemistry and Photophysics of Coordination Compounds: Iridium. *Top. Curr. Chem.* 2007, 281, 143−204.

(29) Romero, N. A.; Nicewicz, D. A. Organic Photoelectrode Catalysis. *Chem. Rev.* 2016, 116, 10075−10166.

(30) Beatty, J. W.; Stephenson, C. R. J. Amine Functionalization via Oxidative Photoelectro Catalysis: Methodology Development and Complex Molecule Synthesis. *Acc. Chem. Res.* 2015, 48, 1474−1484.
(20) Hortmann, A. G.; Koo, J. A New Route to 2-Vinylaziridines and an Unusual Intramolecular Analog of the S$_2^t$ Reaction Leading to Aziridine Ring Formation. J. Org. Chem. 1974, 39, 3781–3783.

(21) (a) Molloy, J. J.; Morack, T.; Gilmour, R. Positional and Geometrical Isomerisation of Alkenes: The Pinnacle of Atom Economy. Angew. Chem., Int. Ed. 2019, 58, 13654–13664. (b) Singh, K.; Staig, S. J.; Weaver, J. D. Facile Synthesis of Z-Alkenes via Uphill Catalysis. J. Am. Chem. Soc. 2014, 136, 5275–5278.

(22) (a) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy Transfer Catalysis Mediated by Visible Light: Principles, Applications, Directions. Chem. Soc. Rev. 2018, 47, 7190–7202. (b) Zhou, Q.-Q.; Zou, Y.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible-Light-Induced Organic Photochemical Reactions through Energy-Transfer Pathways. Angew. Chem., Int. Ed. 2019, 58, 1586–1604.

(23) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: a Roadmap for Catalyst Design. Chem. Soc. Rev. 2016, 45, 5803–5820.

(24) (a) Teders, M.; Henkel, C.; Anhäuser, L.; Strieth-Kalthoff, F.; Gomez-Suarez, A.; Kleinmans, R.; Kaht, A.; Rentmeister, A.; Guldi, D.; Glorius, F. The Energy-Transfer-Enabled Biocompatible Disulfide–Ene Reaction. Nat. Chem. 2018, 10, 981–988. (b) Patra, T.; Mukherjee, S.; Ma, J.; Strieth-Kalthoff, F.; Glorius, F. Visible-Light-Induced Aryl and Alkyl Decarboxylative Functionalization Reactions. Angew. Chem., Int. Ed. 2019, 58, 10514–10520.

(25) (a) Chow, Y. L.; Danen, W. C.; Nielsen, S. F.; Rosenblatt, D. H. Nonaromatic Aminium Radicals. Chem. Rev. 1978, 78, 243–274. (b) Zard, S. Z. Recent Progress in the Generation and Use of Nitrogen-Centred Radicals. Chem. Soc. Rev. 2008, 37, 1603–1618. (c) Xiong, T.; Zhang, Q. New Amination Strategies Based on Nitrogen-Centered Radical Chemistry. Chem. Soc. Rev. 2016, 45, 3069–3087. (d) Zhao, Y.; Xia, W. Recent Advances in Radical-Based C–N Bond Formation via Photo/Electrochemistry. Chem. Soc. Rev. 2018, 47, 2591–2608. (e) Kärkiä, M. D. Photochemical Generation of Nitrogen-Centered Amidyl, Hydrazonyl, and Imidyl Radicals: Methodology Developments and Catalytic Applications. ACS Catal. 2017, 7, 4999–5022. (f) Jiang, H.; Studer, Å. Chemistry with N-Centered Radicals Generated by Single-Electron Transfer-Oxidation Using Photoredox Catalysis. CCS Chem. 2019, 1, 38–49.

(26) (a) Colomier, I.; Chamberlain, A. E. R.; Haughey, M. B.; Donohoe, T. J. Hexafluoroisopropanol as a Highly Versatile Solvent. Nat. Rev. Chem. 2017, 1, 0088. (b) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. Redox and Acidity Properties of 4-Substituted Aniline Radical Cations in Water. J. Am. Chem. Soc. 1994, 116, 1423–1427.

(27) Fischer, H. The Persistent Radical Effect: a Principle for Selective Radical Reactions and Living Radical Polymerizations. Chem. Rev. 2001, 101, 3581–3610.

(28) Lochynski, S.; Boduszek, B.; Shine, H. J. Oxidation of Organotins (R$_5$Sn, R$_5$SnMe$_6$, and R$_3$SnSnR$_3$) by the Thianthrene Cation Radical. J. Org. Chem. 1991, 56, 914–920.