

Allylic Amination of Alkenes with Iminothianthrenes to Afford Alkyl Allylamines

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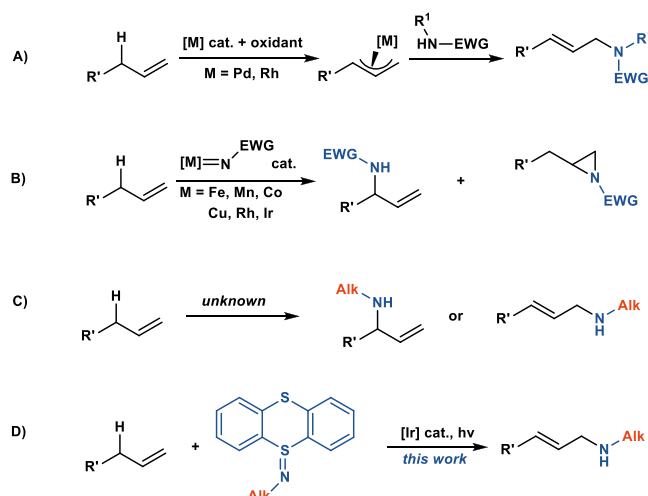
Supporting Information

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 allylamine 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 allylamine derivatives that are not directly accessible by other C–H functionalization reactions.

Several protocols for allylamine synthesis are available, for example by S_N2 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).⁹ The White^{9c,d} and Liu^{9e} groups independently reported palladium-catalyzed allylic C–H amination with sulfonylcarbamates. The scope of the nitro-

Scheme 1. Reaction Development^a



^a(A) Allylic C–H amination via π -allylmetal species. (B) Allylic C–H amination via metal–nitrenoid species. (C) Allylic C–H amination with alkylamines is unknown to date. (D) Our approach to allylic C–H amination with alkylamines. EWG = electron-withdrawing group; Alk = alkyl.

gen-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. Alkylamines 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

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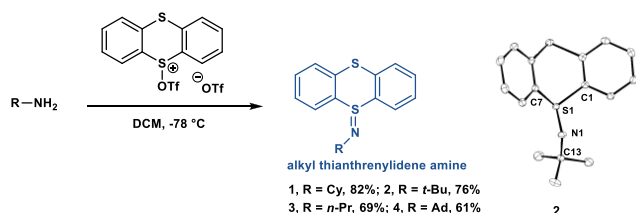
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limited to sulfonyl and carbamate groups because such compounds can be converted to nitrene(oid)s and not undergo Curtius rearrangement.^{10d–f} Dioxazolones were used as nitrene precursors by the Chang group to establish an intramolecular C–H amidation reaction, in which a well-designed iridium catalyst is essential for suppression of the competing Curtius rearrangement.¹¹ Alternatively, azides^{10g,h} are used as nitrene sources in C–H amination 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 amination reactions with alkyl azides catalyzed by iron complexes¹² and also showed a case of intermolecular amination with adamantyl azide.¹³ Alkylamines are used infrequently for metal–nitrenoid-mediated C–H amination, likely because of the strong metal–ligand multiple bonding that reduces the reactivity toward C–H amination in most cases.¹⁴ Furthermore, aziridination is often a competing pathway to allylic C–H amination 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 amination employ (sulfon)amide and carbamate-based nitrogen nucleophiles (Scheme 1C). Herein we report an allylic amination reaction that can afford alkyl allylamines and introduce thianthrene-based aminating reagents that can provide allylamines directly from olefins (Scheme 1D).

We developed a one-pot procedure for the synthesis of alkyl thianthrenylidene amines (iminothianthrenes).¹⁶ Primary alkylamines smoothly react with thianthrene-S-oxide activated by triflic anhydride to produce the iminothianthrenes (Scheme 2). Both bulky and linear amine-based iminothianthrenes (1–

Scheme 2. Synthesis of Alkyl Thianthrenylidene Amine and X-ray Crystal Structure of 2 (H Atoms Have Been Omitted for Clarity)^a



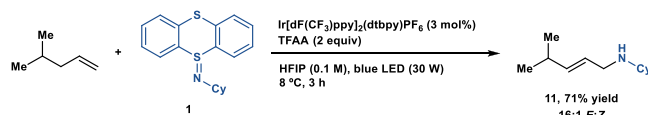
^aSelected bond distances (Å) and angles (deg): S(1)–N(1) 1.579(2), N(1)–C(13) 1.492(3); C(7)–S(1)–C(1) 96.03(12), C(13)–N(1)–S(1) 114.78(17).

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 sp²-hybridized nitrogen atom.¹⁷

Allylic C–H amination of 4-methylpent-1-ene was achieved using cyclohexylamine-derived iminothianthrene 1 as amination reagent under photocatalysis with an iridium photocatalyst ($E^\circ(\text{Ir}^{\text{III}*}/\text{Ir}^{\text{II}}) = 1.21 \text{ V vs SCE}$ and $E^\circ(\text{Ir}^{\text{III}*}/\text{Ir}^{\text{IV}}) = -0.89 \text{ V vs SCE}$),^{18a} providing allylamine 11 in 71% yield ($E:Z = 16:1$) together with thianthrene as the major byproduct (86%)

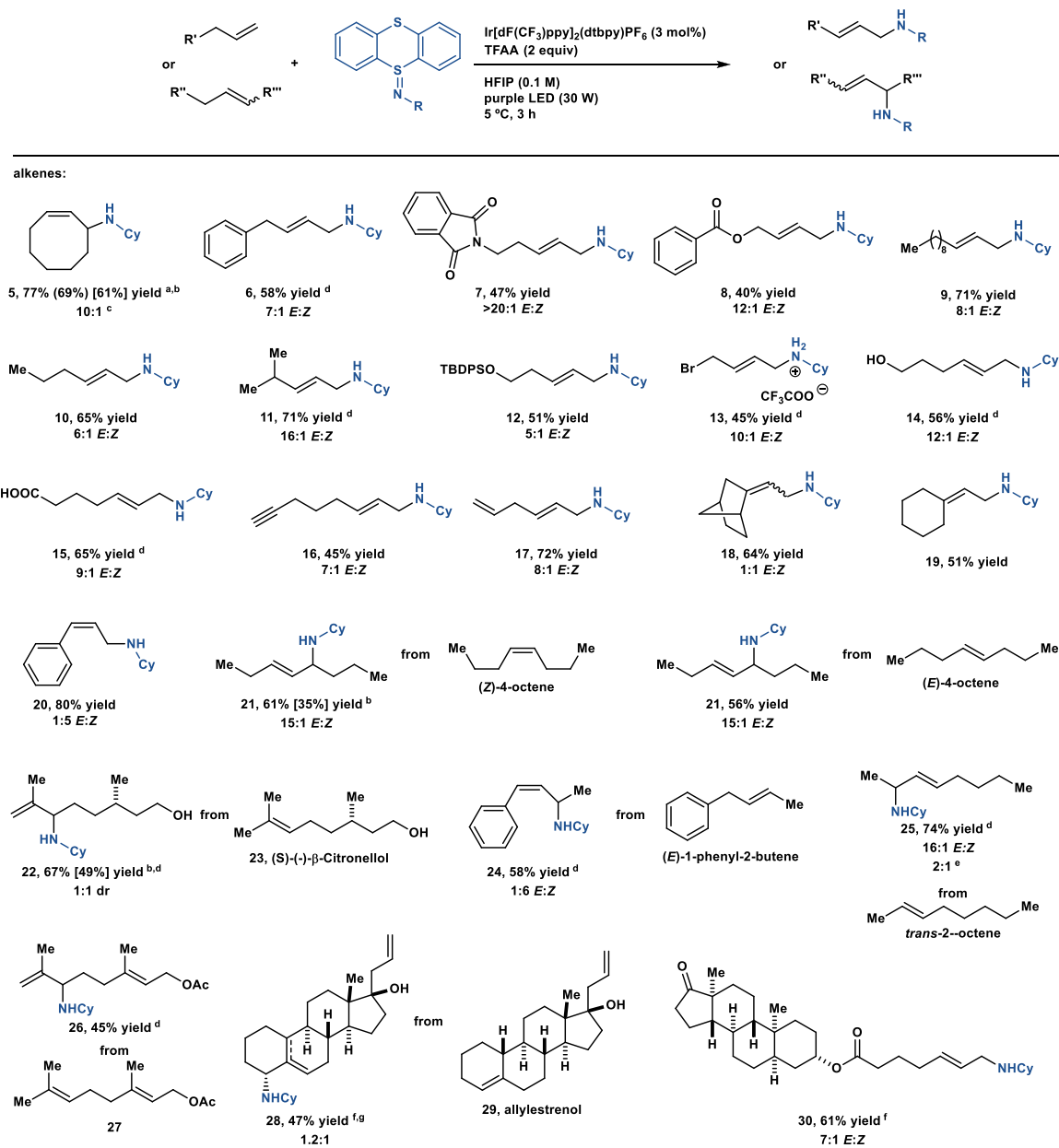
(Scheme 3). Both light and photocatalyst are required for a productive transformation. More reductive photocatalysts,

Scheme 3. Allylic C–H Amination by Iminothianthrenes

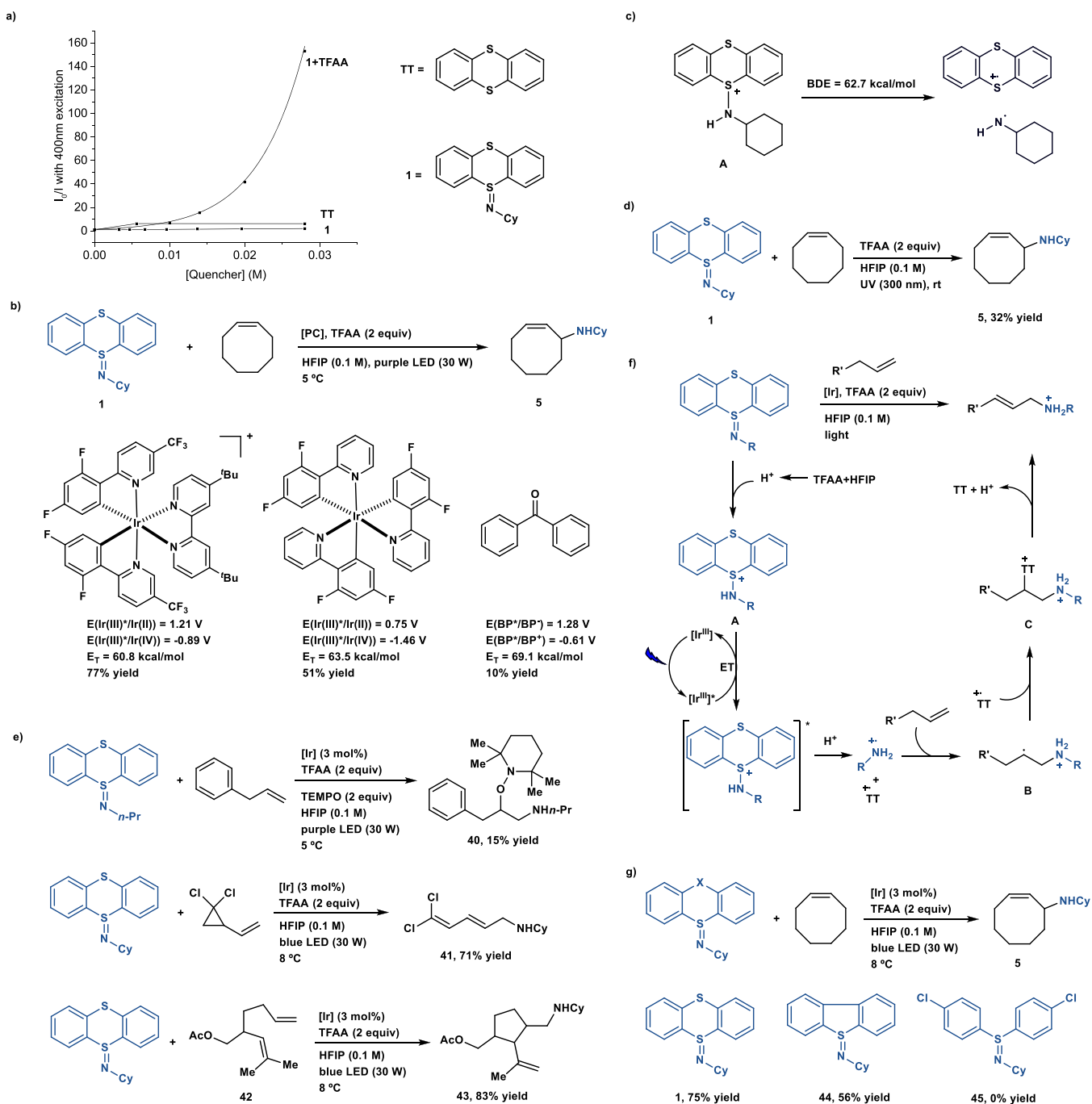


such as $\text{Ir}(\text{ppy})_3$ ($E^\circ(\text{Ir}^{\text{III}*}/\text{Ir}^{\text{IV}}) = -1.73 \text{ V vs SCE}$),^{18b} or more oxidative photocatalysts, such as Mes-Acr^+ ($E^\circ(\text{M}^*/\text{M}^-) = 2.15 \text{ V vs SCE}$),^{18c} failed to provide the amination product (Table S4). Oxidizing photocatalysts, including the one we employ, may oxidize the alkylamine products.¹⁹ To prevent deleterious product oxidation, we attempted to protonate the alkylamines 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 amination of the products was not observed, presumably because of protonation of the products (Table S9).

When terminal alkenes are used, linear amination products with *trans*-olefins are obtained selectively (6–17, 30) (Scheme 4). We also observed chemoselectivity in favor of allylic amination; the allylic C–H amination 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_N2' 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 unsaturated 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). Alkylamines with trisubstituted olefins are accessible as well (18, 19). The olefin geometry in internal alkenes is irrelevant for the stereochemical outcome of the product allylamine; both *cis*- and *trans*-4-octene 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-octene, which produces both constitutional isomers (25) in a ratio of 2:1. When allylarenes 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^h

^aFrom *cis*-cyclooctene. Isolated yield with the 1 mmol-scale yield in parentheses. ^bIsolated yield with 1.0 equiv of alkene in square brackets. ^cRatio of product to homoallyl isomer that was only observed for this substrate (Figures S1 and S15). ^d30 W blue LED (8 °C) instead of purple LED. ^eRatio of regioselectivity. ^f1.2 equiv of alkene was used. ^gHFIP (0.025 M). ^hGeneral conditions except where otherwise noted: iminothianthrene (0.1 mmol), alkene (0.15 mmol, 1.5 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (3 mol %), TFAA (2 equiv), HFIP (0.1 M), purple LED (30 W), 5 °C. TFAA = trifluoroacetic anhydride; HFIP = hexafluoroisopropanol.

Scheme 5. Mechanistic Investigations^a

^a(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.

the initially formed *trans*-styrene (Figure S16 and S17).²¹ 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, according to evidence from photoquenching, cyclic voltammetry, analysis of other energy transfer catalysts, and irradiation with UV light as well as computation (Scheme 5; see the Supporting Information for details).²² The excited iridium photocatalyst is effectively quenched by protonated iminothianthrene, as observed from Stern–Volmer quenching

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.²³ We measured the redox potential of protonated **1** (**A**) ($E_{\text{ox}} = 2.0$ V vs Ag/AgCl, $E_{\text{red}} = -1.4$ 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.²² The triplet excited state of the iridium catalyst has an energy of 61 kcal/mol and is long-lived (2.3 μs).^{18a} We attempted to compute the first excited triplet state energy of **A** (Scheme 5c; for details, see Figure S24). However, no-barrier fragmentation of the N–S bond was observed, which is consistent with radical formation but prevented us from obtaining the triplet energy of **A** to compare with the iridium catalyst triplet energy. Instead, we computed the ground-state bond dissociation energy of the N–S bond to be 63 kcal/mol, which attests to a relatively weak single bond that may be readily cleaved homolytically by an appropriate sensitizer. In support of the weak N–S bond in **A**, we observed a productive reaction in the absence of photosensitizer when UV light (300 nm) was employed (Scheme 5d; for the UV–vis spectrum of **A**, see Figure S14). All of the data are consistent with energy transfer catalysis for the reaction mechanism, as shown in Scheme 5f.²⁴ Typically, nitrogen-centered radicals favor hydrogen atom abstraction as opposed to addition to π systems.²⁵ Increasing their electrophilicity by protonation can lead to a switch in selectivity in favor of addition chemistry.^{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,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**,²⁷ although single-electron oxidation of the carbon radical by the thianthrene 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.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 thianthrene radical cation is key to the unusual observed reactivity, which enables the generation of alkyl allylamines directly. Other iminosulfides did not provide the product as well or at all (Scheme 5g).

In conclusion, a novel photocatalyzed allylic C–H amination reaction with allylamines 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 allylamines form stronger bonds with transition metal centers.

■ ASSOCIATED CONTENT

SI 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)

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Notes

The authors declare no competing financial interest.

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